Supporting Information

Synthesis of Annulated Bis-indoles through Au(I)/Brønsted Acid-Catalyzed Reactions of \((1H\text{-indol-3-yl})(aryl)\text{methanols with 2-}(\text{arylethynyl})\text{-}1H\text{-indoles}\)

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1. Experimental Section

1.1 General Information:

Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in desiccators. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining KMnO₄ or anisaldehyde and charring on a hot plate. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in petroleum ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump. Melting points are uncorrected and recorded using digital Melting Point Apparatus. The ¹H NMR spectra and ¹³C NMR spectra were recorded on 200/400/500 MHz spectrometers in appropriate solvents using TMS as an internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ¹H NMR signals are designated as s (singlet), brs (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet) etc. HRMS (ESI) data were recorded using quadrupole analyser. The gold catalysts Ph₃PAuCl was prepared according to literature known procedures.¹ The chiral Brønsted acid catalyst BH¹ was prepared by following literature known procedures.²
1.2. Synthesis of (1H-indol-3-yl)(aryl)methanols 1:

Preparation method for 1a, 1b, 1d, 1g, 1j and 1k (1H-indol-3-yl)(aryl)methanols were known in the literature.\textsuperscript{3} Other substrates such as 1c, 1e, 1f, 1h, 1i, 1l and 1m were prepared according to following representative procedure.

**Representative procedure:** A 50 mL round-bottomed flask was charged with indole 8a (1g, 8.54 mmol), benzaldehyde 9a (300 mg, 2.85 mmol) and tetramethylguanidine (65 mg, 0.57 mmol). Then the water (3 mL) was added and the resultant mixture was stirred for 24 h. Water (20 mL) was introduced in the flask and the reaction mixture was extracted with EtOAc (20 mL x 3). The combined organic phase was dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography using EtOAc:petroleum ether (3:7) as eluent to give (1H-indol-3-yl)(phenyl)methanol 1a.

![Synthesis of (1H-indol-3-yl)(aryl)methanols 1](image)

1.3. Synthesis of aryl(1H-pyrrol-2-yl)methanol 4:

**Representative procedure:** To a 50 mL round-bottom flask, N-methyl-1H-pyrrole-2-carbaldehyde 10a (220 mg, 2 mmol) and 10 mL dry THF was charged under N\textsubscript{2}. The phenyl magnesium bromide (3 mmol) (3 mL, 1 M solution in THF) was added and the mixture was continued to stir at room temperature for 1 h. After completion of reaction, the mixture was quenched by adding sat. NH\textsubscript{4}Cl solution. The product was extracted with EtOAc (20 mL x 3)
and the combined extracts were dried over Na₂SO₄, filtered, and concentrated in vacuum. The crude phenyl(1H-pyrrol-2-yl)methanol 4a obtained was used without further purification.

1.4. Synthesis of 2-(arylethynyl)-1H-indoles 2:

Preparation methods for 2a-k alkynyl indoles were known in the literature, while, 2l and 2m were prepared according to following procedure in two steps from ortho-gem-dibromovinylaniline 11a.

Representative procedure: To a 50 mL round-bottom flask, ortho-gem-dibromovinylaniline 11a (275 mg, 1 mmol), phenylacetylene 12a (153 mg, 1.5 mmol), PPh₃ (30 mg, 0.11 mmol), iPr₂NH (350 μL, 2.5 mmol) and 10 mL dry toluene was charged under N₂. Finally, 10% Pd/C (52 mg, 0.02 mmol) and CuI (9.6 mg, 0.05 mmol) were added. The resulting mixture was heated at 100 °C for 1 h. The mixture was diluted with EtOAc (30 mL), washed with H₂O (20 mL), brine (15 mL) and dried over Na₂SO₄. The crude material after removal of solvent was purified by chromatography using EtOAc:petroleum ether (1:9) to give 2-(phenylethynyl)-1H-indole 2a.
Representative procedure for the synthesis of 2k: To a 50 mL round-bottom flask, 2a (217 mg, 1 mmol) and dry DMF 10 mL were added under N₂. The mixture was cooled to 0 °C and NaH (58 mg, 1.5 mmol) followed by benzyl bromide (255 mg, 1.5 mmol), were added. The mixture was heated to room temperature and stirred for 2 h, the mixture was quenched by adding sat. NH₄Cl solution. The crude product was extracted with EtOAc (20 mL x 3). The combined extracts were dried over Na₂SO₄, concentrated in vacuum and purified by column chromatography using EtOAc:petroleum ether (1:9) to give 1-benzyl-2-(phenylethynyl)-indole 2k.

1.5. Synthesis of annulated bis-indoles 3:

Representative procedure: To a oven-dried screw-capped vial equipped with magnetic stir bar, were added (1H-indol-3-yl)(phenyl)methanol 1a (25 mg, 0.115 mmol), 2-(phenylethynyl)-1H-indole 2a (26 mg, 0.115 mmol), Ph₃PAuCl (2.9 mg, 0.0058 mmol), AgOTf (1.5 mg, 0.0058 mmol), BH (4 mg, 0.0115 mmol) in one portion, was dissolved in DCE (2 mL) under nitrogen. The solution was heated to 80 °C for 8 h. The solvent was removed to obtain the residue which was purified by silica gel column chromatography using EtOAc:petroleum ether (2:8) as an eluent to afford product 3a.

Synthesis of enantioenriched 3a: To a oven-dried screw-capped vial equipped with magnetic stir bar, were added (1H-indol-3-yl)(phenyl)methanol 1a (25 mg, 0.115 mmol), 2-(phenylethynyl)-1H-indole 2a (26 mg, 0.115 mmol), Ph₃PAuMe (2.74 mg, 0.0058 mmol), BH* (8 mg, 0.0115 mmol) in one portion, was dissolved in DCE (2 mL) under nitrogen. The solution was stirred at 0 °C for 12 h then heated to 80 °C for 4 h, the solvent was removed to
obtain the residue which was purified by silica gel column chromatography using EtOAc:petroleum ether (2:8) as an eluent to afford enantio-pure 3a.

**Synthesis of 3a from phenyl (1H-pyrrol-2-yl)methanol 1a with 2-(phenylbuta-1,3-diyn-1-yl)aniline 7:**

To a oven-dried screw-capped vial equipped with magnetic stir bar, were added 2-(phenylbuta-1,3-diyn-1-yl)aniline 7 (25 mg, 0.115 mmol), (1H-indol-3-yl)(phenyl)methanols 1a (26 mg, 0.115 mmol), PdCl$_2$ (1.1 mg, 0.0058 mmol), BH (4 mg, 0.0115 mmol) followed by DCE (2 mL) under nitrogen atmosphere. The solution was heated to 80 °C for 12 h. The reaction mixture was brought to room temperature. The flask was charged with Ph$_3$PAuCl (2.9 mg, 0.0058 mmol) and AgOTf (1.5 mg, 0.0058 mmol) and the reaction mixture was again heated to 80 °C for 8 h. The solvent was removed to obtain the residue which was purified by silica gel column chromatography using EtOAc:petroleum ether (2:8) as an eluent to afford product 3a.

1.6. **Synthesis of annulated pyrrole 5:**

**Representative procedure:** To a oven-dried screw-capped vial equipped with magnetic stir bar, were added (1-methyl-1H-pyrrol-2-yl)(phenyl)methanol 4a (21 mg, 0.115 mmol), 2-(phenylethynyl)-1H-indoles 2a (26 mg, 0.115 mmol), Ph$_3$PAuCl (2.9 mg, 0.0058 mmol), AgOTf (1.5 mg, 0.0058 mmol) and BH (4 mg, 0.0115 mmol) followed by DCE (2 mL) under nitrogen atmosphere. The solution was heated to 80 °C. After 8 h, the solvent was removed to obtain the residue which was purified by silica gel column chromatography using EtOAc:petroleum ether (2:8) as an eluent to afford product 5a.

1.7. **Synthesis of 3-((1H-indol-3-yl)(phenyl)methyl)-2-(phenylethynyl)-1H-indole 6:**

To a oven-dried screw-capped vial equipped with magnetic stir bar, were added (1H-indol-3-yl)(phenyl)methanol 1a (25 mg, 0.115 mmol), 2-(phenylethynyl)-1H-indole 2a (26 mg,
0.115 mmol), BH (4 mg, 0.0115 mmol) and DCE (2 mL) under nitrogen. The reaction mixture was stirred at room temperature for 12 h. The solvent was removed to obtain the residue which was purified by silica gel column chromatography using EtOAc:petroleum ether (1:9) as an eluent to afford product 6.

2. Analytical data

*Anthracen-9-yl(1H-indol-3-yl)methanol* (1e): white solid, 1.44 g, 62% yield; mp = 214 °C; $R_f = 0.25$ (petroleum ether/EtOAc = 75/25); $^1$H NMR (200 MHz, CDCl$_3$) $\delta = 8.63$ - 8.56 (m, 2 H), 8.49 (s, 1 H), 8.02 - 7.99 (m, 2 H), 7.99 - 7.91 (m, 1 H), 7.88 - 7.79 (m, 1 H), 7.74 - 7.70 (m, 1 H), 7.46 - 7.30 (m, 6 H), 7.25 - 7.10 (m, 2 H), 6.56 (s, 1 H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta = 136.6$, 133.9, 131.7, 129.7, 129.1, 128.7, 128.4, 128.2, 126.5, 125.4, 125.3, 124.8, 123.5, 123.4, 122.2, 119.9, 118.5, 111.1, 66.8; HRMS (ESI) calcd for C$_{23}$H$_{17}$NO (M$^+$ + H) 324.1382, found 324.1383.

*(2-Bromo-5-fluorophenyl)(1H-indol-3-yl)methanol* (1e): yellow solid, 1.6 g, 59% yield; mp = 168 °C; $R_f = 0.32$ (petroleum ether/EtOAc = 75/25); $^1$H NMR (200 MHz, CDCl$_3$:DMSO d$_6$, 4:1 ratio) $\delta = 10.33$ (s, 1 H), 7.66 - 7.61 (m, 1 H), 7.54 (dd, $J = 2$, 8 Hz, 1 H), 7.36 (dd, $J = 6$, 8 Hz, 1 H), 7.26 - 7.23 (m, 1 H), 7.04 - 6.90 (m, 2 H), 6.95 - 6.79 (m, 1 H), 6.76 - 6.72 (m, 1 H), 6.19 (s, 1 H), 5.45 (s, 1 H); $^{13}$C NMR (50 MHz, CDCl$_3$:DMSO d$_6$, 4:1 ratio) $\delta = 163.9$-159.0(d, $J = 245.5$ Hz), 146.3-146.2 (d, $J = 6.6$ Hz), 136.2, 133.0-132.9 (d, $J = 7.68$ Hz), 125.6, 123.0, 120.9, 118.6, 118.4, 116.7, 115.6, 115.3, 115.1, 114.8, 114.6, 111.0, 67.7; HRMS (ESI) calcd for C$_{15}$H$_{11}$BrFNO (M$^+$ + H) 320.0008, found 320.0010.

*(2-Bromo-4-methylphenyl)(1H-indol-3-yl)methanol* (1f): white solid, 1.40 g, 52% yield; mp = 159 °C; $R_f = 0.23$ (petroleum ether/EtOAc = 75/25); $^1$H NMR (200 MHz, CDCl$_3$) $\delta = 8.01$ (s, 1 H), 7.63 - 7.58 (m, 1 H), 7.51 (d, $J = 8$ Hz, 1 H), 7.31 - 7.23 (m, 2 H), 7.18 - 7.01 (m, 3 H), 7.05 (d, $J = 8$ Hz, 2 H), 6.93 - 6.89 (m, 2 H), 6.75 - 6.63 (m, 1 H), 6.12 (s, 1 H), 2.41 (s, 3 H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta = 137.9$-133.4 (d, $J = 234.3$ Hz), 130.7, 125.8, 123.0, 122.7, 121.5, 116.2, 114.9, 114.6, 113.9, 113.3, 112.7, 112.1, 111.7, 68.3; HRMS (ESI) calcd for C$_{23}$H$_{17}$NO (M$^+$ + H) 324.1382, found 324.1383.
6.82 - 6.77 (m, 2 H), 6.38 (s, 1 H), 2.25 (s, 3 H); $^{13}$C NMR (50 MHz, CDCl$_3$) δ = 139.2, 139.0, 136.4, 133.1, 128.3, 128.0, 125.8, 123.1, 122.4, 122.2, 119.7, 119.5, 117.9, 111.2, 69.2, 20.6; HRMS (ESI) calcd for C$_{16}$H$_{14}$BrNO (M$^+$ + H) 316.0256, found 316.0259.

$(1H$-indol-3-yl)(thiophen-2-yl)methanol (II): white solid, 1.08 g, 55% yield; mp = 187 °C; $R_f$ = 0.2 (petroleum ether/EtOAc = 75/25); $^1$H NMR (200 MHz, CDCl$_3$) δ = 10.07 (s, 1 H), 7.83 - 7.80 (m, 3 H), 7.72 - 7.69 (m, 1 H), 7.49 - 7.42 (m, 2 H), 7.38 - 7.33 (m, 1 H), 7.28 - 7.25 (m, 2 H), 6.52 - 6.44 (s, 1 H); $^{13}$C NMR (50 MHz, CDCl$_3$) δ = 150.4, 140.4, 137.2, 136.3, 133.5, 131.9, 131.7, 128.9, 128.3, 127.5, 127.1, 126.4, 123.38, 123.2, 123.2 122.7, 120.0, 119.9, 118.7, 118.3, 117.5, 110.6, 110.6, 32.4; HRMS (ESI) calcd for C$_{13}$H$_{11}$NOS (M$^+$ + H) 230.0639, found 230.0634.

*Methyl 3-(hydroxy(phenyl)methyl)-1H-indole-6-carboxylate (II):* white solid, 1.44 g, 60% yield; mp = 158 °C; $R_f$ = 0.27 (petroleum ether/EtOAc = 80/20); $^1$H NMR (500 MHz, DMSO d$_6$) δ = 11.32 (s, 1 H), 8.03 (s, 1 H), 7.58 (m, 2 H), 7.46 (d, $J$ = 8.0 Hz, 2 H), 7.41 - 7.38 (m, 1 H), 7.31 (m, 3 H), 7.21(m, 1 H), 6.0 (s, 1 H), 5.71 (s, 3H); $^{13}$C NMR (125 MHz, DMSO d$_6$) δ = 167.2, 145.5, 135.8, 129.1, 127.9, 126.7, 126.6, 126.2, 122.0, 120.3, 119.3, 119.0, 113.4, 68.6, 51.7; HRMS (ESI) calcd for C$_{17}$H$_{15}$NO$_3$ (M$^+$ + H) 281.1047, found 281.1046.

*(7-(Benzyloxy)-1H-indol-3-yl)(phenyl)methanol (1m):* gray solid, 1.46 g, 54% yield; mp = 118 °C; $R_f$ = 0.34 (petroleum ether/EtOAc = 70/30); $^1$H NMR (200 MHz, DMSO d$_6$) δ = 11.00 (s, 1 H), 7.56 - 7.51 (m, 2 H), 7.44 - 7.38 (m, 3 H), 7.36 - 7.19 (m, 5 H), 7.11 - 6.98 (m, 2 H), 6.80 - 6.75 (m, 1 H), 6.71 (s, 1 H), 5.94 - 5.87 (m, 1 H), 5.59 (d, $J$ = 4 Hz, 1 H), 5.24 (s, 2 H); $^{13}$C NMR (50 MHz, DMSO d$_6$) δ = 145.8, 144.9, 137.4, 128.3, 127.7, 127.6, 127.4, 127.3, 126.7, 126.3, 126.3, 122.3, 120.2, 118.8, 112.6, 102.8, 69.0, 68.8; HRMS (ESI) calcd for C$_{22}$H$_{19}$NO$_2$ (M$^+$ + H) 330.1415, found 330.1419.
1-benzyl-2-(phenylethynyl)-1H-indole (2l): white solid, 257 mg, 84% yield; mp = 153 °C; R_f = 0.70 (petroleum ether/EtOAc = 95/05); ¹H NMR (200 MHz, CDCl₃) δ = 7.62 (d, J = 7 Hz, 1 H), 7.48 - 7.45 (m, 2 H), 7.36 - 7.32 (m, 4 H), 7.24 - 7.18 (m, 6 H), 7.21 - 7.11 (m, 1 H), 6.93 (s, 1 H), 5.52 (s, 2 H); ¹³C NMR (50 MHz, CDCl₃) δ = 137.6, 136.8, 132.5, 131.4, 128.6, 128.5, 128.4, 127.8, 127.5, 127.4, 126.8, 123.2, 122.6, 121.9, 121.0, 120.2, 110.0, 108.0, 95.4, 81.1, 48.0; HRMS (ESI) calcd for C₂₃H₁₇N (M⁺ + H) 308.1361, found 308.1360.

1-allyl-2-(phenylethynyl)-1H-indole (2m): brown liquid, 175 mg, 68% yield; R_f = 0.72 (petroleum ether/EtOAc = 95/05); ¹H NMR (200 MHz, CDCl₃) δ = 7.48 - 7.40 (m, 4 H), 7.45 - 7.27 (m, 2 H), 7.28 - 7.19 (m, 2 H), 7.16 - 6.04 (s, 1 H), 6.79 (s, 1 H), 6.06 - 5.80 (m, 1 H), 5.12 - 4.98 (m, 2 H), 4.86 (d, J = 6 Hz, 2 H); ¹³C NMR (50 MHz, CDCl₃) δ = 136.7, 133.2, 132.4, 131.4, 129.2, 128.5, 128.4, 127.4, 123.0, 122.7, 121.0, 120.1, 116.8, 109.8, 107.8, 95.1, 80.9, 46.7; HRMS (ESI) calcd for C₁₉H₁₅N (M⁺ + H) 258.1204, found 258.1210.

6,13-Diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3a): yellow solid, 44.6 mg, 92% yield; mp = 207 °C; R_f = 0.5 (petroleum ether/EtOAc = 90/10); ¹H NMR (200 MHz, CDCl₃:DMSO d₆, 4:1 ratio) δ = 10.54 (s, 1 H), 9.61 (s, 1 H), 7.80 (d, J = 8 Hz, 2 H), 7.65 - 7.48 (m, 3 H), 7.52 (d, J = 7.9 Hz, 3 H), 7.31 (d, J = 6 Hz, 5 H), 7.07 - 6.99 (m, 5 H), 6.87 (s, 1 H), 6.18 (s, 1 H); ¹³C NMR (50 MHz, CDCl₃:DMSO d₆, 4:1 ratio) δ = 145.9, 140.6, 136.9, 136.5, 132.7, 131.5, 131.5, 128.3, 128.1, 127.5, 127.4, 127.1, 126.8, 126.4, 125.2, 122.2, 121.9, 119.2, 118.7, 117.5, 117.3, 116.7, 116.3, 111.0, 110.4, 36.8; HRMS (ESI) calcd for C₃₁H₂₂N₂ (M⁺ + H) 423.1785, found 423.1786; HPLC conditions: Chiralpak IA, 70:30 n-hexane/IPA, flow rate 1 mL/min; λ = 254 nm; t_major = 12.34 min, t_minor = 25.63 min.

13-(Naphthalen-1-yl)-6-phenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3b): yellow solid, 47 mg, 88% yield; mp = 192 °C; R_f = 0.52 (petroleum ether/EtOAc = 90/10); ¹H NMR (500 MHz, CDCl₃+DMSO d₆) δ = 10.61 (s, 1 H), 9.87 (s, 1 H), 8.33 (d, J = 7 Hz, 1 H),
7.67 (d, \( J = 7.0 \) Hz, 1 H), 7.67 (d, \( J = 8 \) Hz, 1 H), 7.48 - 7.41 (m, 3 H), 7.35 (d, \( J = 8 \) Hz, 3 H), 7.26 (m, 8 H), 7.05 (t, \( J = 7 \) Hz, 2 H), 6.82 - 6.75 (m, 3 H), 6.68 (s, 1 H); \(^{13}\text{C} \text{NMR} (125 \text{ MHz, CDCl}_3 + \text{DMSO d}_6) \ \delta = 145.4, 140.0, 136.3, 130.9, 127.7, 127.0, 126.8, 125.9, 124.7, 118.6, 118.1, 118.1, 116.7, 110.4, 109.9, 36.2.; \text{HRMS} \ (\text{ESI}) \text{ calcd for } \text{C}_{35}\text{H}_{24}\text{N}_2 \text{ (M}^+ \text{+ H) 473.1939, found 473.1940.}

\text{13-} \text{(Anthracen-9-yl)-6-phenyl-8,13-dihydro-5H-cyclohept[1,2-b:5,4-b']bisindole \ (3c):}
\text{yellowish solid, 49.8 mg, 83\% yield; mp = 183 °C; } \text{R}_f = 0.6 \text{ (petroleum ether/EtOAc = 85/15); \text{H} NMR (500 MHz, CDCl}_3 + \text{DMSO d}_6) \ \delta = 10.56 (s, 1 H), 9.63 (s, 1 H), 7.83 (d, \( J = 6.5 \) Hz, 2 H), 7.67 - 7.62 (m, 5 H), 7.53 - 7.51 (m, 2 H), 7.45 - 7.43 (m, 2 H), 7.39 (d, \( J = 6.5 \) Hz, 1 H), 7.29 (m, 5 H), 7.05 - 7.04 (m, 4 H), 6.95 - 6.91 (m, 1 H), 6.87 (s, 1 H), 6.19 (s, 1 H); \text{C NMR (125 MHz, CDCl}_3 + \text{DMSO d}_6) \ \delta = 145.9, 131.7, 128.2, 128.1, 127.5, 127.3, 126.5, 125.2, 121.9, 119.1, 118.6, 117.5, 111.1, 110.4, 36.8.; \text{HRMS} \ (\text{ESI}) \text{ calcd for } \text{C}_{39}\text{H}_{26}\text{N}_2 \text{ (M}^+ \text{+ H) 523.2096, found 523.2098.}

\text{13-} \text{(3-Fluorophenyl)-6-phenyl-8,13-dihydro-5H-cyclohept[1,2-b:5,4-b']bisindole \ (3d): yellow}
\text{solid, 47.5 mg, 94\% yield; mp = 160 °C; } \text{R}_f = 0.57 \text{ (petroleum ether/EtOAc = 90/10); \text{H} NMR (500 MHz, DMSO d}_6) \ \delta = 11.22 (s, 1 H), 10.53 (s, 1 H), 8.07 (dd, \( J = 2, 7.4 \) Hz, 2 H), 7.56 (d, \( J = 2 \) Hz, 4 H), 7.50 - 7.45 (m, 1 H), 7.41 - 7.35 (m, 2 H), 7.24 (d, \( J = 7.4 \) Hz, 1 H), 7.19 - 7.07 (m, 6 H), 6.95 (s, 1 H), 6.87 - 6.80 (m, 1 H), 6.38 (s, 1 H); \text{C NMR (125 MHz, DMSO d}_6) \ \delta = 163.5-161.5(d, \( J = 243.17 \) Hz), 150.1-150.0 (d, \( J = 5.72 \) Hz), 141.2, 137.5-137.4 (d, \( J = 12.4 \) Hz), 133.6, 132.6, 132.3, 130.4-130.4 (d, \( J = 7.6 \) Hz), 129.3, 128.8, 128.4, 127.6, 127.4, 123.4, 123.0 (d, \( J = 7.6 \) Hz), 119.9, 119.5, 119.5, 118.9, 118.7, 117.1, 116.7, 113.9, 113.7, 113.0, 112.8, 112.1, 111.4, 36.8; \text{HRMS} \ (\text{ESI}) \text{ calcd for } \text{C}_{31}\text{H}_{21}\text{FN}_2 \text{ (M}^+ \text{+ H) 441.1689, found 441.1690.}
13-(2-Bromo-5-fluorophenyl)-6-phenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole

(3e): brown solid, 57 mg, 96% yield; mp = 159 °C; \( R_f = 0.59 \) (petroleum ether/EtOAc = 80/20);
\(^1\)H NMR (500 MHz, DMSO \( d_6 \)) \( \delta = 11.37 \, (s, \, 1 \, H) \), 10.60 \, (s, \, 1 \, H) \), 8.15 \, (d, \, \( J = 8.0 \) Hz, \, 1 \, H) \), 8.11 \, (d, \, \( J = 8.0 \) Hz, \, 1 \, H) \), 7.63 - 7.59 \, (m, \, 4 \, H) \), 7.57 - 7.51 \, (m, \, 3 \, H) \), 7.38 \, (t, \, \( J = 8.0 \) Hz, \, 2 \, H) \), 7.21 - 7.13 \, (m, \, 2 \, H) \), 7.13 - 7.08 \, (m, \, 2 \, H) \), 7.07 \, (s, \, 1 \, H) \), 6.89 \, (m, \, 1 \, H) \), 6.65 \, (s, \, 1 \, H) \); \(^13\)C NMR (125 MHz, DMSO \( d_6 \)) \( \delta = 162.7-160.8 \, (d, \, \( J = 244.4 \) Hz) \), 149.8-149.8 \, (d, \, \( J = 6.68 \) Hz) \), 140.5, 136.9-136.7 \, (d, \, \( J = 18.12 \) Hz) \), 133.4-131.9, 131.5, 129.0, 128.3, 128.1, 126.9, 126.7, 122.8 - 122.8 \, (d, \, \( J = 3.82 \) Hz) \), 119.7, 119.2, 118.7, 118.5, 117.2, 117.0, 116.8, 116.3, 116.1, 115.9, 113.8, 111.8, 111.0, 37.8.; HRMS (ESI) calcd for C\(_{31}\)H\(_{20}\)FBrN\(_2\) (M\(^+\) + H) 519.0704, found 519.0710.

13-(2-bromo-4-methylphenyl)-6-phenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole

(3f): gray solid, 53.2 mg, 90% yield; mp = 173 °C; \( R_f = 0.54 \) (petroleum ether/EtOAc = 90/10);
\(^1\)H NMR (500 MHz, CDCl\(_3\):DMSO \( d_6 \), 4:1 ratio) \( \delta = 10.60 \, (s, \, 1 \, H) \), 9.69 \, (s, \, 1 \, H) \), 7.87 - 7.77 \, (m, \, 3 \, H) \), 7.44 \, (d, \, \( J = 8.0 \) Hz, \, 3 \, H) \), 7.32 \, (d, \, \( J = 2 \) Hz, \, 2 \, H) \), 7.29 - 7.23 \, (m, \, 3 \, H) \), 7.10 - 7.05 \, (m, \, 2 \, H) \), 7.05 - 6.96 \, (m, \, 3 \, H) \), 6.86 \, (s, \, 1 \, H) \), 6.18 \, (s, \, 1 \, H) \), 2.40 \, (s, \, 3 \, H) \); \(^13\)C NMR (125 MHz, CDCl\(_3\):DMSO \( d_6 \), 4:1 ratio) \( \delta = 146.0, 137.6, 136.9, 136.8, 136.4, 132.6, 131.8, 128.8, 128.0, 127.5, 126.4, 125.2, 118.6, 117.4, 111.0, 36.7, 20.7.; HRMS (ESI) calcd for C\(_{32}\)H\(_{23}\)BrN\(_2\) (M\(^+\) + H) 515.1045, found 515.1046.

13-(3-Methoxyphenyl)-6-phenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole

(3g): yellow solid, 45.7 mg, 88% yield; mp = 124 °C; \( R_f = 0.56 \) (petroleum ether/EtOAc = 85/15);
\(^1\)H NMR (500 MHz, CDCl\(_3\):DMSO \( d_6 \), 4:1 ratio) \( \delta = 10.58 \, (s, \, 1 \, H) \), 9.41 \, (s, \, 1 \, H) \), 8.28 - 8.21 \, (m, \, 2 \, H) \), 7.93 \, (d, \, \( J = 6 \) Hz, \, 2 \, H) \), 7.83 \, (t, \, \( J = 8 \) Hz, \, 3 \, H) \), 7.77 \, (d, \, \( J = 7 \) Hz, \, 1 \, H) \), 7.67 \, (d, \, \( J = 8 \) Hz, \, 2 \, H) \), 7.64 \, (d, \, \( J = 7 \) Hz, \, 1 \, H) \), 7.47 \, (d, \, \( J = 7.0 \) Hz, \, 3 \, H) \), 7.51 \, (d, \, \( J = 4 \) Hz, \, 2 \, H) \), 7.35 - 7.33 \, (m, \, 1 \, H) \), 6.89 \, (s, \, 1 \, H) \), 6.59 \, (s, \, 1 \, H) \), 3.94 \, (s, \, 3 \, H) \); \(^13\)C NMR (125 MHz, CDCl\(_3\):DMSO \( d_6 \), 4:1 ratio)
δ = 158.8, 147.4, 140.4, 137.0, 136.3, 132.6, 131.7, 131.4, 128.4, 128.3, 128.2, 128.1, 127.5, 127.2, 126.9, 123.4, 122.3, 122.0, 120.7, 119.1, 118.9, 118.7, 118.0, 117.6, 117.5, 116.7, 116.2, 112.6, 110.8, 110.7, 110.4, 110.2, 54.3, 36.9.; HRMS (ESI) calcd for C_{32}H_{24}N_{2}O (M^+ + H) 453.1966, found 453.1961.

6-Phenyl-13-(furyl-2-yl)-8,13-dihydro-5I-cyclohepta[1,2-b:5,4-b']bisindole (3h): brown solid, 45 mg, 95% yield; mp = 139 °C; R_f = 0.55 (petroleum ether/EtOAc = 90/10); ^1H NMR (500 MHz, DMSO d_6) δ = 11.11 (s, 1 H), 10.46 (s, 1 H), 7.89 (d, J = 7.6 Hz, 1 H), 7.95 (d, J = 7.6 Hz, 1 H), 7.57 - 7.49 (m, 4 H), 7.49 - 7.38 (m, 2 H), 7.36 - 7.30 (m, 3 H), 7.16 - 7.11 (m, 1 H), 7.10 - 7.07 (m, 2 H), 6.86 (s, 1 H), 6.78 (d, J = 2 Hz, 1 H), 6.69 (dd, J = 2, 8 Hz, 1 H), 6.52 (s, 1 H); ^13C NMR (125 MHz, DMSO d_6) δ = 150.7, 140.4, 136.6, 136.5, 132.9, 131.6, 131.5, 130.6, 128.4, 128.5, 128.0, 127.6, 126.4, 126.1, 125.8, 124.8, 123.2, 123.1, 122.1, 118.9, 118.7, 118.6, 118.0, 117.7, 116.6, 116.5, 111.3, 110.5, 31.4.; HRMS (ESI) calcd for C_{29}H_{20}N_{2}O (M^+ + H) 413.1576, found 413.1578.

6-Phenyl-13-(thiophen-2-yl)-8,13-dihydro-5I-cyclohepta[1,2-b:5,4-b']bisindole (3i): dark brown solid, 47.2 mg, 96% yield; mp = 148 °C; R_f = 0.43 (petroleum ether/EtOAc = 90/10); ^1H NMR (200 MHz, DMSO d_6) δ = 11.19 (s, 1 H), 10.55 (s, 1 H), 8.08 (t, J = 8 Hz, 2 H), 7.57 (d, J = 2 Hz, 3 H), 7.52 - 7.41 (m, 3 H), 7.41 - 7.23 (m, 2 H), 7.13 - 7.05 (m, 4 H), 6.93 (s, 1 H), 6.82 (d, J = 2 Hz, 1 H), 6.73 (dd, J = 2, 8 Hz, 1 H), 6.60 (s, 1 H); ^13C NMR (50 MHz, DMSO d_6) δ = 151.1, 140.8, 136.9, 136.8, 133.2, 131.9, 128.8, 128.3, 126.4, 126.1, 123.6, 122.5, 118.9, 116.9, 111.6, 31.8.; HRMS (ESI) calcd for C_{29}H_{20}N_{2}S (M^+ + H) 429.1347, found 429.1348.

2-Nitro-6,13-diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3j): yellow solid, 43 mg, 80% yield; mp = 149 °C; R_f = 0.46 (petroleum ether/EtOAc = 90/10); ^1H NMR (200 MHz, DMSO d_6) δ = 11.27 (s, 1 H), 11.24 (s, 1 H), 9.14 (d, J = 2 Hz, 1 H), 8.23 (d, J = 7.6 Hz,
1H, 8.02 (dd, J = 2, 8 Hz, 1 H), 7.57 - 7.50 (m, 5 H), 7.43 - 7.33 (m, 5 H), 7.13 (t, J = 7.6 Hz, 4 H), 7.05 (s, 1 H), 6.55 (s, 1 H); 13C NMR (50 MHz, DMSO d6) δ = 163.1, 161.1, 140.9, 137.2, 133.7, 132.2, 131.9, 129.3, 128.6, 128.5, 123.1, 120.1, 119.5, 119.0, 118.8, 112.1, 111.4; HRMS (ESI) calcd for C31H21N3O2 (M+ + H) 468.1634, found 468.1635.

6,13-Diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole-1-carbonitrile (3k): yellowish solid, 42 mg, 82% yield; mp = 138 °C; Rf = 0.67 (petroleum ether/EtOAc = 80/20); 1H NMR (400 MHz, DMSO d6) δ = 11.31 (s, 1 H), 11.27 (s, 1 H), 7.83 (d, J = 7.3 Hz, 1 H), 7.71 (d, J = 7.8 Hz, 1 H), 7.59 (d, J = 7.3 Hz, 2 H), 7.54 (br. s., 4 H), 7.50 - 7.46 (m, 1 H), 7.42 (d, J = 7.8 Hz, 1 H), 7.26 - 7.23 (m, 3 H), 7.16 - 7.12 (m, 3 H), 7.10 (s, 1 H), 7.04 (d, J = 6.8 Hz, 1 H), 6.96 (s, 1 H); 13C NMR (100 MHz, DMSO d6) δ = 145.1, 140.2, 137.3, 137.0, 135.8, 133.7, 132.5, 131.8, 129.6, 129.5, 129.0, 128.7, 128.2, 128.1, 126.9, 126.6, 126.6, 125.9, 124.9, 122.7, 121.9, 121.5, 119.8, 119.5, 117.6, 117.1, 115.9, 111.4, 99.3, 34.5; HRMS (ESI) calcd for C32H21N3 (M+ + H) 448.1735, found 448.1736.

Methyl 6,13-diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole-3-carboxylate (3l): gray solid, 53 mg, 96% yield; mp = 153 °C; Rf = 0.51 (petroleum ether/EtOAc = 90/10); 1H NMR (200 MHz, CDCl3:DMSO d6, 4:1 ratio) δ = 10.64 (s, 1 H), 10.24 (s, 1 H), 8.02 (d, J = 7.8 Hz, 2 H), 7.50 (d, J = 8 Hz, 2 H), 7.40 (s, 6 H), 7.07 (d, J = 2.4 Hz, 3 H), 7.06 - 6.99 (m, 3 H), 6.94 (d, J = 8 Hz, 1 H), 6.88 (s, 1 H), 6.18 (s, 1 H), 2.81 (s, 3 H); 13C NMR (50 MHz, CDCl3:DMSO d6, 4:1 ratio) δ = 166.7, 145.1, 135.2, 131.1, 127.8, 127.7, 127.2, 127.0, 125.9, 124.9, 120.2, 119.0, 118.3, 116.4, 113.0, 110.1, 50.7, 38.4; HRMS (ESI) calcd for C33H24N2O2 (M+ + H) 481.1838, found 481.1840.

4-(Benzyloxy)-6,13-diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3m): yellow solid, 55.9 mg, 92% yield; mp = 131 °C; Rf = 0.46 (petroleum ether/EtOAc = 90/10); 1H NMR (400 MHz, DMSO d6) δ = 11.17 (s, 1 H), 10.18 (s, 1 H), 8.03 (d, J = 7.9 Hz, 1 H), 7.56 (d, J =
7.9 Hz, 1 H), 7.54 (t, \( J = 6.4 \) Hz, 3 H), 7.46 (d, \( J = 7.3 \) Hz, 3 H), 7.32 (d, \( J = 5.5 \) Hz, 5 H), 7.27 (d, \( J = 7.3 \) Hz, 2 H), 7.16 (d, \( J = 7.3 \) Hz, 1 H), 7.10 (d, \( J = 7.9 \) Hz, 3 H), 7.04 - 6.97 (m, 2 H), 6.95 (s, 1 H), 6.76 (d, \( J = 7.9 \) Hz, 1 H), 6.26 (s, 1 H), 5.24 (d, \( J = 4.9 \) Hz, 2 H); \(^{13}\)C NMR (100 MHz, DMSO \( d_6 \)) \( \delta = 146.2, 144.8, 141.1, 137.3, 137.0, 133.3, 132.0, 132.0, 128.9, 128.6, 128.3, 128.2, 128.0, 127.6, 127.6, 127.4, 127.2, 126.7, 125.6, 122.3, 119.5, 118.9, 118.8, 118.4, 117.3, 111.1, 110.9, 104.8, 69.1, 36.5.; HRMS (ESI) calcd for C\(_{38}\)H\(_{28}\)N\(_2\)O (M\(^+\) + H) 529.2202, found 529.2203.

5-Methyl-7,13-diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3n): gray solid, 44.6 mg, 89% yield; mp = 155 °C; \( R_f = 0.58 \) (petroleum ether/EtOAc = 90/10); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 8.02 - 7.96 \) (m, 2 H), 7.85 (s, 1 H), 7.62 (d, \( J = 7.0 \) Hz, 2 H), 7.54 - 7.50 (m, 2 H), 7.49 - 7.45 (m, 1 H), 7.34 - 7.28 (m, 4 H), 7.25 - 7.20 (m, 4 H), 7.15 (t, \( J = 7 \) Hz, 2 H), 7.05 (t, \( J = 7 \) Hz, 1 H), 6.96 (s, 1 H), 6.40 (s, 1 H), 3.86 (s, 3 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta = 145.2, 140.9, 138.7, 136.7, 133.5, 132.9, 131.7, 128.9, 128.3, 128.0, 127.6, 126.9, 126.8, 125.7, 123.3, 122.8, 119.8, 119.5, 118.5, 118.3, 117.7, 117.2, 110.6, 108.9, 36.4, 29.9.; HRMS (ESI) calcd for C\(_{32}\)H\(_{24}\)N\(_2\) (M\(^+\) + H) 437.1939, found 437.1941.

5-Benzyl-7,13-diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3o): gray solid, 50 mg, 85% yield; mp = 143 °C; \( R_f = 0.62 \) (petroleum ether/EtOAc = 85/15); \(^1\)H NMR (500 MHz, CDCl\(_3\):DMSO d\(_6\), 4:1 ratio) \( \delta = 10.43 \) (s, 1 H), 8.07 (d, \( J = 7.6 \) Hz, 1 H), 8.00 (d, \( J = 8.0 \) Hz, 1 H), 7.47 (d, \( J = 8 \) Hz, 1 H), 7.43 (d, \( J = 7 \) Hz, 2 H), 7.41 - 7.37 (m, 3 H), 7.32 (d, \( J = 8.0 \) Hz, 1 H), 7.39 (d, \( J = 7 \) Hz, 2 H), 7.28 (d, \( J = 7.6 \) Hz, 2 H), 7.25 - 7.18 (m, 2 H), 7.17 - 7.12 (m, 2 H), 7.10 - 7.07 (m, 5 H), 6.99 (d, \( J = 7 \) Hz, 1 H), 6.92 (s, 1 H), 6.32 (s, 1 H), 5.63 (s, 2 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\):DMSO d\(_6\), 4:1 ratio) \( \delta = 145.7, 140.8, 138.3, 137.9, 137.0, 133.8, 132.3, 131.3, 128.4, 128.4, 128.3, 127.7, 126.9, 126.5, 126.6, 126.3, 126.1, 125.5, 122.6, 122.3,
5-Allyl-7,13-diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3p): yellow solid, 46.75 mg, 88% yield; mp = 152 °C (decomposition); $R_f$ = 0.54 (petroleum ether/EtOAc = 90/10); $^1$H NMR (500 MHz, CDCl$_3$:DMSO d$_6$, 4:1 ratio) δ = 10.48 (s, 1 H), 8.04 (d, $J$ = 7.6 Hz, 1 H), 7.99 (d, $J$ = 8 Hz, 1 H), 7.57 - 7.54 (m, 2 H), 7.49 (t, $J$ = 7.4 Hz, 2 H), 7.45 - 7.41 (m, 1 H), 7.39 (d, $J$ = 8 Hz, 1 H), 7.34 (d, $J$ = 8 Hz, 1 H), 7.28 (d, $J$ = 7.6 Hz, 3 H), 7.19 (t, $J$ = 7.4 Hz, 1 H), 7.12 - 7.07 (m, 6 H), 6.98 (t, $J$ = 7.2 Hz, 1 H), 6.91 (s, 1 H), 6.30 (s, 1 H), 6.00 (dt, $J$ = 6, 11.1 Hz, 1 H), 5.11 (d, $J$ = 10.3 Hz, 1 H), 5.05 - 4.95 (m, 2 H), 4.87 (d, $J$ = 17.2 Hz, 1 H); $^{13}$C NMR (125 MHz, CDCl$_3$:DMSO d$_6$, 4:1 ratio) δ = 144.0, 139.1, 135.7, 135.3, 132.3, 132.1, 130.4, 129.7, 126.8, 126.7, 126.0, 124.8, 124.8, 124.5, 123.7, 120.7, 120.6, 117.4, 117.0, 116.4, 116.0, 115.9, 115.9, 115.1, 114.0, 109.7, 107.5, 43.0, 34.1.; HRMS (ESI) calcd for C$_{34}$H$_{26}$N$_2$ (M$^+$ + H) 463.2159, found 463.2166.

6-(4-Chlorophenyl)-13-phenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3q): gray solid, 48.72 mg, 93% yield; mp = 144 °C; $R_f$ = 0.55 (petroleum ether/EtOAc = 90/10); $^1$H NMR (400 MHz, DMSO d$_6$) δ = 11.71 (s, 1 H), 10.89 (s, 1 H), 8.61 (d, $J$ = 4 Hz, 1 H), 7.80 (t, $J$ = 7.6 Hz, 1 H), 7.49 (d, $J$ = 7.9 Hz, 1 H), 7.42 - 7.32 (m, 5 H), 7.32 - 7.25 (m, 3 H), 7.20 - 7.17 (m, 2 H), 7.13 (t, $J$ = 7.6 Hz, 1 H), 7.03 (t, $J$ = 7.3 Hz, 1 H), 6.93 - 6.84 (m, 2 H), 6.84 (br., s., 1 H), 6.12 (s, 1 H); $^{13}$C NMR (100 MHz, DMSO d$_6$) δ = 162.2, 160.3, 149.3, 149.3, 140.0, 136.4, 136.3, 133.4, 133.4, 132.8, 131.5, 131.1, 128.5, 127.8, 127.7, 126.4, 126.2, 122.3, 122.3, 119.2, 118.7, 118.2, 118.0, 116.7, 116.5, 116.3, 115.8, 115.6, 115.4, 113.3, 111.3, 110.5, 37.2.; HRMS (ESI) calcd for C$_{34}$H$_{28}$ClN$_2$ (M$^+$ + H) 475.1442, found 475.1450.

4-(13-Phenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindol-6-yl)benzonitrile (3r): gray solid, 48.83 mg, 95% yield; mp = 143 °C; $R_f$ = 0.55 (petroleum ether/EtOAc = 90/10); $^1$H
NMR (200 MHz, DMSO d$_6$) $\delta$ = 11.31 (s, 1 H), 11.27 (s, 1 H), 7.83 (dd, $J = 3$, 8.1 Hz, 1 H), 7.71 (d, $J = 8.1$ Hz, 1 H), 7.60 - 7.55 (m, 4 H), 7.54 (s, 3 H), 7.44 - 7.40 (m, 1 H), 7.32 - 7.25 (m, 3 H), 7.24 - 7.15 (m, 3 H), 7.14 - 7.09 (m, 1 H), 7.1 - 7.02 (s, 1 H), 6.96 (s, 1 H); $^{13}$C NMR (50 MHz, DMSO d$_6$) $\delta$ = 144.3, 139.3, 136.4, 136.1, 135.0, 131.6, 130.9, 128.1, 127.3, 126.0, 125.7, 125.0, 118.6, 116.8, 33.6; HRMS (ESI) calcd for C$_{32}$H$_{21}$N$_3$ (M$^+$+ H) 448.1735, found 448.1737.

13-Phenyl-6-(p-tolyl)-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3s): yellow solid, 40.1 mg, 80% yield; mp = 162 °C; $R_f$ = 0.53 (petroleum ether/EtOAc = 90/10); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 7.97 (s, 1 H), 7.87 (s, 1 H), 7.5 (d, $J = 7.2$ Hz, 2 H), 7.37 (d, $J = 7.2$ Hz, 2 H), 7.33 (d, $J = 7.6$ Hz, 3 H), 7.24 (m, 6 H), 7.15 (t, $J = 7.2$ Hz, 2 H), 7.06 (t, $J = 7.2$ Hz, 2 H), 6.77 (s, 1 H), 6.37 (s, 1 H), 2.49 (s, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ = 145.6, 138.2, 137.6, 137.3, 136.4, 133.4, 131.9, 131.9, 129.5, 128.7, 128.2, 128.1, 127.7, 127.0, 125.8, 123.2, 123.0, 121.9, 119.8, 119.7, 118.5, 118.4, 118.37, 117.7, 117.5, 110.6, 110.5, 36.97, 21.24; HRMS (ESI) calcd for C$_{32}$H$_{24}$N$_2$ (M$^+$+ H) 437.1995, found 437.1998.

6-(4-Methoxyphenyl)-13-phenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3t): yellow solid, 39.72 mg, 82% yield; mp = 147 °C; $R_f$ = 0.57 (petroleum ether/EtOAc = 90/10); $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ = 8.02 - 7.97 (m, 2 H), 7.86 (s, 1 H), 7.63 (d, $J = 7.0$ Hz, 2 H), 7.54 - 7.51 (dd, $J = 2$, 7.5 Hz, 2 H), 7.51 - 7.47 (m, 1 H), 7.32 - 7.29 (m, 4 H), 7.25 - 7.21 (m, 4 H), 7.15 (t, $J = 7.5$ Hz, 2 H), 7.06 (t, $J = 7.5$ Hz, 1 H), 6.96 (s, 1 H), 6.40 (s, 1 H), 3.86 (s, 3 H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ = 145.2, 140.9, 138.7, 136.7, 133.5, 132.9, 131.7, 128.9, 128.3, 128.0, 127.6, 126.9, 126.8, 125.7, 123.3, 122.8, 119.8, 119.5, 118.5, 118.4, 118.3, 117.7, 117.1, 110.6, 108.9, 36.3, 29.7; HRMS (ESI) calcd for C$_{32}$H$_{24}$ON$_2$ (M$^+$+ H) 453.1939, found 453.1950.
13-Phenyl-6-(pyridin-2-yl)-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3u): dark brown solid, 38.9 mg, 80% yield; mp = 190 °C (decomposition); $R_f$ = 0.38 (petroleum ether/EtOAc = 85/15); $^1$H NMR (200 MHz, CDCl$_3$:DMSO d$_6$, 4:1 ratio) $\delta$ = 11.72 (s, 1 H), 10.89 (s, 1 H), 8.61 (d, $J$ = 4 Hz, 1 H), 7.90 - 7.76 (m, 2 H), 7.50 (d, $J$ = 7.8 Hz, 1 H), 7.43 - 7.33 (m, 5 H), 7.31 - 7.23 (m, 3 H), 7.21 (d, $J$ = 8 Hz, 2 H), 7.17 - 7.08 (m, 1 H), 7.03 (t, $J$ = 7.8 Hz, 1 H), 6.94 - 6.87 (m, 1 H), 6.84 (s, 1 H), 6.12 (s, 1 H); $^{13}$C NMR (50 MHz, CDCl$_3$:DMSO d$_6$, 4:1 ratio) $\delta$ = 145.4, 140.0, 136.3, 136.0, 132.2, 131.3, 130.9, 127.7, 127.6, 127.0, 126.8, 126.5, 126.2, 125.9, 124.7, 121.6, 121.4, 118.6, 118.2, 117.0, 116.8, 116.1, 115.7, 110.4, 109.9, 36.2.; HRMS (ESI) calcd for C$_{30}$H$_{21}$N$_3$ (M$^+$ + H) 424.1735, found 424.1736.

2-Fluoro-7,13-diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3v): yellow solid, 41 mg, 81% yield; mp = 167 °C; $R_f$ = 0.54 (petroleum ether/EtOAc = 85/15); $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ = 8.03 (s, 1 H), 7.94 (dd, $J$ = 7.6, 7.2 Hz, 2 H), 7.86 (s, 1 H), 7.59 (d, $J$ = 6.9 Hz, 2 H), 7.55 - 7.45 (m, 3 H), 7.36 (d, $J$ = 7.2 Hz, 1 H), 7.30 - 7.21 (m, 5 H), 7.17 - 7.06 (m, 2 H), 7.01 (d, $J$ = 8.2 Hz, 1 H), 6.81 (s, 1 H), 6.75 (t, $J$ = 7.6 Hz, 1 H), 6.36 (s, 1 H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ = 163.8-161.8 (d, $J$ = 247 Hz), 148.2-148.1 (d, $J$ = 5.72 Hz), 140.3, 137.4, 136.4, 133.5, 131.8-131.8 (d, $J$ = 4.77 Hz), 129.4-129.4 (d, $J$ = 7.63 Hz), 129.0, 128.8, 128.4, 127.9, 127.5, 123.4, 123.3, 122.5-122.6 (d, $J$ = 1.91 Hz), 120.1, 120.0, 118.7, 118.3, 117.3, 116.9, 114.0, 113.9, 112.8, 112.7, 110.7, 110.6, 36.6.; HRMS (ESI) calcd for C$_{31}$H$_{21}$FN$_2$ (M$^+$ + H) 441.1689, found 441.1690.

3-Methyl-7,13-diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3w): gray solid, 41.62 mg, 83% yield; mp = 154 °C; $R_f$ = 0.6 (petroleum ether/EtOAc = 80/20); $^1$H NMR (200 MHz, CDCl$_3$:DMSO d$_6$, 4:1 ratio) $\delta$ = 10.73 (s, 1 H), 9.87 (s, 1 H), 7.83 (d, $J$ = 7 Hz, 2 H), 7.46 (d, $J$ = 8 Hz, 2 H), 7.30 (m, 6 H), 7.08 (d, $J$ = 2 Hz, 3 H), 7.06 - 6.99 (m, 3 H), 6.96 (d, $J$ = 7 Hz, 1 H), 6.88 (s, 1 H), 6.19 (s, 1 H), 2.41 (s, 3 H); $^{13}$C NMR (50 MHz, CDCl$_3$:DMSO d$_6$, 4:1 ratio) $\delta$ = 148.0, 140.0, 136.4, 136.3, 132.2, 131.3, 130.9, 129.0, 128.8, 128.4, 127.9, 127.5, 123.4, 123.3, 122.5-122.6 (d, $J$ = 1.91 Hz), 120.1, 120.0, 118.7, 118.3, 117.3, 116.9, 114.0, 113.9, 112.8, 112.7, 110.7, 110.6, 36.6.; HRMS (ESI) calcd for C$_{31}$H$_{21}$FN$_2$ (M$^+$ + H) 441.1689, found 441.1690.
ratio) $\delta = 145.2, 140.8, 138.7, 136.7, 133.0, 131.7, 128.9, 128.3, 128.0, 127.6, 127.19, 126.8, 125.8, 123.3, 122.8, 119.8, 119.5, 118.5, 118.4, 118.3, 117.7, 117.2, 110.2, 39.8, 19.8;

HRMS (ESI) calcd for C$_{32}$H$_{24}$N$_2$ (M$^+$ + H) 437.1939, found 437.1940.

2-Methoxy-7,13-diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (3x): yellow solid, 40.5 mg, 78% yield; mp = 168 °C; $R_f$ = 0.53 (petroleum ether/EtOAc = 90/10); $^1$H NMR (200 MHz, CDCl$_3$) $\delta =$ 8.03 (s, 1 H), 7.95 - 7.90 (m, 2 H), 7.83 (s, 1 H), 7.55 - 7.43 (m, 6 H), 7.25 - 7.16 (m, 5 H), 7.19 - 6.96 (m, 3 H), 6.94 (s, 1 H), 6.76 (s, 1 H), 6.66 - 6.55 (m, 1 H), 6.32 (s, 1 H), 3.63 (s, 3 H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta =$ 159.4, 147.3, 140.4, 137.3, 131.7, 129.0, 128.9, 128.8, 128.2, 123.2, 123.0, 119.8, 119.5, 118.4, 113.2, 110.8, 110.5, 54.9, 37.1; HRMS (ESI) calcd for C$_{32}$H$_{24}$ON$_2$ (M$^+$ + H) 453.1889, found 453.1890.

1-Methyl-4,11-diphenyl-6,11-dihydro-1H-pyrrolo[2',3':4,5]cyclohepta[1,2-b]indole (5a): brown solid, 27.5 mg, 62% yield; mp = 152 °C; $R_f$ = 0.64 (petroleum ether/EtOAc = 90/10); $^1$H NMR (200 MHz, CDCl$_3$:DMSO d$_6$, 4:1 ratio) $\delta =$ 10.45 (s, 1 H), 7.74 - 7.72 (m, 1 H), 7.56 - 7.48 (m, 2 H), 7.34 (dd, $J = 2$, 7 Hz, 2 H), 7.26 - 7.22 (dd, $J = 2$, 7.1 Hz, 2 H), 7.18 (m, 2 H), 7.11 (m, 2 H), 7.00 (m, 3 H), 6.53 (d, $J = 4$ Hz, 1 H), 6.51 (s, 1 H), 5.85 (s, 1 H), 5.80 (d, $J = 4$ Hz, 1 H), 3.71 (s, 3 H); $^{13}$C NMR (50 MHz, CDCl$_3$:DMSO d$_6$, 4:1 ratio) $\delta =$ 143.9, 142.4, 136.6, 135.7, 127.3, 127.1, 126.8, 126.4, 125.9, 125.6, 124.9, 117.8, 116.1, 112.6, 111.9, 109.6, 33.1, 28.3; HRMS (ESI) calcd for C$_{28}$H$_{22}$N$_2$ (M$^+$ + H) 387.1858, found 387.1856.

1-Methyl-2-(2-nitrophenyl)-4,11-diphenyl-6,11-dihydro-1H-pyrrolo[2',3':4,5]cyclohepta[1,2-b]indole (5b): yellow solid, 39.5 mg, 68% yield; mp = 138 °C (decomposition); $R_f$ = 0.54 (petroleum ether/EtOAc = 90/10); $^1$H NMR (200 MHz, CDCl$_3$:DMSO d$_6$, 4:1 ratio) $\delta =$ 10.86 (s, 1 H), 7.91 - 7.87 (t, $J = 6.0$ Hz, 2 H), 7.64 (t, $J = 6.0$ Hz, 1 H), 7.57 - 7.54 (m, 1 H), 7.53 - 7.47 (m, 3 H), 7.40 - 7.34 (m, 2 H), 7.32 - 7.27 (m, 2 H), 7.23 (d, $J = 8.0$ Hz, 2 H), 7.17 - 7.11 (d, $J = 8.0$ Hz, 2 H), 7.10 - 6.99 (m, 3 H), 6.60 (s, 1 H), 6.04 (s, 1 H), 5.85 (s, 1 H), 3.53 (s, 3
H; $^{13}$C NMR (50 MHz, CDCl$_3$:DMSO d$_6$, 4:1 ratio) $\delta$ = 147.8, 142.9, 141.5, 135.3, 135.1, 131.7, 131.6, 131.4, 131.0, 127.6, 126.7, 126.6, 126.4, 125.9, 125.8, 125.5, 125.3, 125.1, 124.4, 122.2, 120.1, 118.0, 117.3, 115.9, 112.7, 111.5, 109.1, 108.4, 36.6, 30.1.; HRMS (ESI) calcd for C$_{34}$H$_{25}$N$_3$O$_2$ (M$^{+}$+ H) 508.1947, found 508.1946.

3-((1H-indol-3-yl)(phenyl)methyl)-2-(phenylethynyl)-1H-indole (6): yellowish solid, 41 mg, 84% yield; mp = 175 °C (decomposition); $R_f$ = 0.63 (petroleum ether/EtOAc = 85/15); $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ = 8.1 - 8.05 (s, 1 H), 7.88 s, 1 H), 7.45 - 7.36 (m, 4 H), 7.35 (td, $J$ = 2, 2.8 Hz, 2 H), 7.30 - 7.28 (m, 4 H), 7.24 (dd, $J$ = 2, 2.8 Hz, 2 H), 7.23 - 7.16 (m, 2 H), 7.16 - 7.08 (m, 2 H), 7.03 - 6.91 (m, 2 H), 6.93 (d, $J$ = 2 Hz, 1 H), 6.16 - 6.11 (s, 1 H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ = 143.3, 136.2, 131.3, 128.8, 128.3, 128.0, 126.0, 123.8, 121.8, 120.7, 119.8, 119.2, 117.0, 110.9, 110.8, 95.6, 81.3, 40.2; HRMS (ESI) calcd for C$_{31}$H$_{22}$N$_2$ (M$^{+}$+ H) 423.1870, found 423.1875.
3. Spectral data

\[1^1H\text{ NMR, CDCl}_3, 200\text{ MHz}\]

\[1^1C\text{ NMR, CDCl}_3, 50\text{ MHz}\]
$^1$H NMR, CDCl$_3$:DMSO d$_6$ (4:1), 200 MHz

$^{13}$C NMR, CDCl$_3$:DMSO d$_6$ (4:1), 50 MHz
$^1$H NMR, CDCl$_3$, 200 MHz

$^{13}$C NMR, CDCl$_3$, 50 MHz
$^1$H NMR, CDCl$_3$, 200 MHz

$^{13}$C NMR, CDCl$_3$, 50 MHz
$^1$H NMR, DMSO $d_6$, 200 MHz

$^{13}$C NMR, DMSO $d_6$, 50 MHz
\[\text{CHLOROFORM-d}\]

\[^1\text{H NMR, CDCl}_3, 200 \text{ MHz}\]

\[^{13}\text{C NMR, CDCl}_3, 50 \text{ MHz}\]
$\text{CHLOROFORM-d}$

$^1\text{H NMR, CDCl}_3$, 200 MHz

$^{13}\text{C NMR, CDCl}_3$, 50 MHz

$\text{NMR, CDCl}_3$, 200 MHz

$\text{NMR, CDCl}_3$, 50 MHz
$^1$H NMR, CDCl$_3$-DMSO d$_6$ (4:1), 200 MHz

$^{13}$C NMR, CDCl$_3$-DMSO d$_6$ (4:1), 50 MHz
$^1$H NMR, CDCl$_3$:DMSO d$_6$ (4:1), 500 MHz

$^1$H NMR, CDCl$_3$:DMSO d$_6$ (4:1), 125 MHz
$^1$H NMR, CDCl$_3$:DMSO d$_6$ (4:1), 500 MHz

$^{13}$C NMR, CDCl$_3$:DMSO d$_6$ (4:1), 125 MHz
$^1$H NMR, DMSO $d_6$, 500 MHz

$^{13}$C NMR, DMSO $d_6$, 125 MHz
$^1$H NMR, DMSO $d_6$, 500 MHz

$^{13}$C NMR, DMSO $d_6$, 125 MHz
$^1$H NMR, CDCl$_3$:DMSO d$_6$ (4:1), 200 MHz

$^{13}$C NMR, CDCl$_3$:DMSO d$_6$ (4:1), 50 MHz
$^1$H NMR, CDCl$_3$:DMSO-d$_6$ (4:1), 500 MHz

$^{13}$C NMR, CDCl$_3$:DMSO-d$_6$ (4:1), 125 MHz
$^1$H NMR, DMSO $d_6$, 500 MHz

$^{13}$C NMR, DMSO $d_6$, 125 MHz
\[\text{HNMR, DMSO } d_6, 200 \text{ MHz}\]

\[\text{^13C NMR, DMSO } d_6, 50 \text{ MHz}\]
**1H NMR, DMSO d$_6$, 400 MHz**

**13C NMR, DMSO d$_6$, 100 MHz**

NH

NH

NC

NC

DMSO d$_6$
$^1$H NMR, CDCl$_3$:DMSO d$_6$ (4:1), 400 MHz

$^{13}$C NMR, CDCl$_3$:DMSO d$_6$ (4:1), 100 MHz
$^{1}$H NMR, CDCl$_3$, 500 MHz

$^{13}$C NMR, CDCl$_3$, 125 MHz
$^1$H NMR, CDCl$_3$:DMSO d$_6$ (4:1), 500 MHz

$^{13}$C NMR, CDCl$_3$:DMSO d$_6$ (4:1), 125 MHz
$^1$H NMR, CDCl$_3$/DMSO d$_6$ (4:1), 500 MHz

$^1^3$C NMR, CDCl$_3$/DMSO d$_6$ (4:1), 125 MHz
$^1$H NMR, DMSO $d_6$, 200 MHz

$^{13}$C NMR, DMSO $d_6$, 50 MHz

DMSO

DMSO-d$_6$

Water
$^1$H NMR, CDCl$_3$, 200 MHz

$^{13}$C NMR, CDCl$_3$, 50 MHz
$^1$H NMR, CDCl$_3$:DMSO d$_6$ (4:1), 200 MHz

$^{13}$C NMR, CDCl$_3$:DMSO d$_6$ (4:1), 50 MHz
$^1$H NMR, CDCl$_3$, 500 MHz

$^{13}$C NMR, CDCl$_3$, 125 MHz
$^1$H NMR, CDCl$_3$-DMSO d$_6$ (4:1), 200 MHz

$^{13}$C NMR, CDCl$_3$-DMSO d$_6$ (4:1), 50 MHz
\[ ^1H \text{ NMR, CDCl}_3, 200 \text{ MHz} \]

\[ ^{13}C \text{ NMR, CDCl}_3, 50 \text{ MHz} \]
$^1$H NMR, CDCl$_3$:DMSO d$_6$ (4:1), 200 MHz

$^{13}$C NMR, CDCl$_3$:DMSO d$_6$ (4:1), 50 MHz
$^1$H NMR, CDCl$_3$:DMSO $d_6$ (4:1), 500 MHz

$^{13}$C NMR, CDCl$_3$:DMSO $d_6$ (4:1), 125 MHz
4. 2D NMR spectrum for 5a

$^{1}$$H$$-^{1}$$H$ COSY spectrum for 5a

$^{1}$$H$ NMR, CDCl$_3$:DMSO $d_6$ (4:1), 400 MHz
NOESY spectrum for 5a

Enlarged NOESY spectrum for 5a
HSQC spectrum for 5a

HMBC spectrum for 5a
5. HPLC Analysis of 3a

![HPLC Analysis Diagram]

### VWD: Signal A, 254 nm Results

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### VWD: Signal A, 254 nm Results

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6. ORTEP diagram for “3n” (CCDC No. 1503514):

![ORTEP diagram](image)