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# Sc(OTf)$_3$-Catalyzed Oligomerization of Indole: One-Pot Synthesis of 2-[2,2-Bis(indol-3-yl)ethyl]anilines and 3-(Indolin-2-yl)indoles

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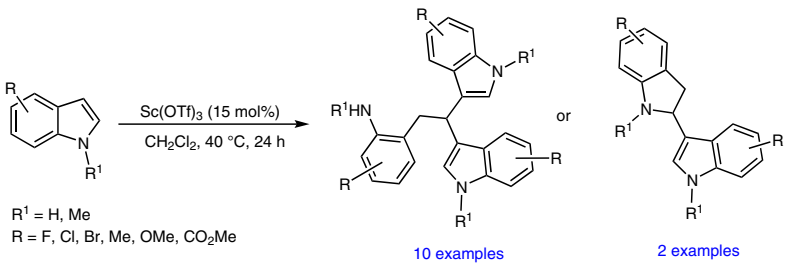


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**Abstract** Oligomerization of substituted indoles and *N*-methylindoles was investigated in the presence of catalytic amounts of scandium triflate in dichloromethane. Two types of indole oligomer, 2-[2,2-bis(indol-3-yl)ethyl]anilines and 3-(indolin-2-yl)indoles were obtained based on the substituent on indole ring. This study constitutes the first example of Sc(OTf)$_3$-catalyzed oligomerization of indoles and gave good yield of 2-[2,2-bis(indol-3-yl)ethyl]anilines and 3-(indolin-2-yl)indoles.

**Key words** oligomerization, scandium triflate, bis(indolyl)methanes, indole, dimer, trimer

Indole is a ubiquitous heterocycle that is found in natural products, pharmaceuticals, agrochemicals and other synthetic organic compounds.[1] Given their diverse biological properties, structural modification of the indole nucleus has attracted the attention of many synthetic organic chemists in recent years. A large number of naturally isolated alkaloids with a dimeric indole scaffold and synthetically prepared bis(indolyl) compounds have been found to exhibit a wide range of biological activities, including antibiotic, antitumor, antiviral, diuretic, and anticancer action (Figure 1).[2] Thus, several methods have been developed for their synthesis using different catalysts.[3]

On the other hand, indole itself polymerizes to polyindole (dimer or trimer) under acidic conditions (Scheme 1).[4] Geller[5] reported the first acid-catalyzed self-addition product of indole as a trimer, which was further studied by Smith[6] and it was found to have the structure of indole-3,3′-trimer **2**. Later, the Ishii group reported a new indole-2,3′-trimer **3** formed by the self-addition of indole in the

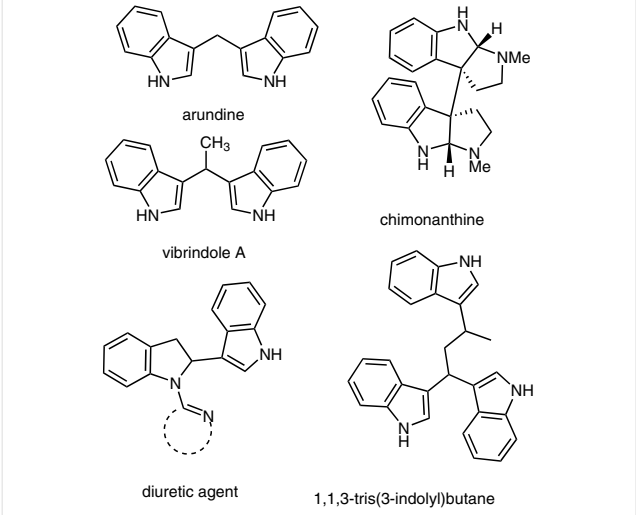
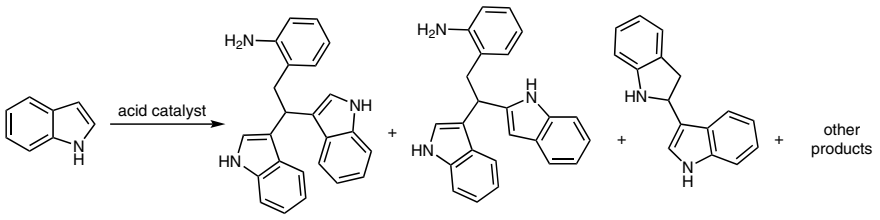



**Figure 1** Structures of some bioactive indole dimers and trimers

presence of *p*-toluenesulfonic acid (*p*-TSA) in benzene at reflux.[7] When indole was treated with 98% formic acid, indole trimer **2** and dimer **4** were obtained in 30 and 32% yields, respectively.[8] A mixture of indole trimers **2** and **3** and dimer **4** and was obtained by the reaction of 3-bromoindole and indole in the presence of trifluoroacetic acid (TFA) in dichloromethane at room temperature.[9] These reactions were catalyzed by Brønsted acids and required a stoichiometric amount of catalyst. Pal et al. reported InCl$_3$-mediated oligomerization of indole in which indole 3,3′-trimer **2** was obtained in 46% yield along with unexpected 3-acetylindole.[10] Thus, indole oligomerization is sensitive to the substituent on the indole ring, acid concentration, temperature, and the nature of both the solvent and the acid.




| | 2 | 3 | 4 | |
|---|---|---|---|---|
| $CF_3CO_2H/CH_2Cl_2$[6] | 8% | 2% | 6% | - |
| *p*-TSA[7] | - | 39% | - | - |
| $HCH_2Cl_2H$[8] | 30% | - | 32% | - |
| $InCl_3$[10] | 46% | - | - | 40% |

**Scheme 1** Acid-catalyzed oligomerization of indole

Over the past decade, rare-earth triflates have drawn the attention of chemists as water-compatible, environment friendly, noncorrosive and reusable Lewis acids for a variety of organic transformations.[11] Among these metal triflates, $Sc(OTf)_3$ shows high catalytic activities even compared with lanthanide triflate in some cases.[12] The unique properties of $Sc(OTf)_3$ and differential behavior of indole with different acids prompted us to investigate indole oligomerization using $Sc(OTf)_3$.

To evaluate metal triflate catalyzed oligomerization of indole, unsubstituted indole (**1a**) was chosen as a model substrate. Reaction of **1a** with $Sc(OTf)_3$ (10 mol%) at 40 °C in $CH_2Cl_2$ after 24 hours resulted in formation of a new product along with unreacted **1a**. The product was isolated by column chromatography and characterized by NMR and mass analysis. The spectral data were consistent with the reported data for **2a**.[13] Bisai et al. also observed formation of indole-3,3′-trimer **2a** during his work on Friedel–Crafts alkylations of 3-hydroxy-3-methyl-2-oxindole with indole (**1a**) in the presence of $In(OTf)_3$.[14]

To increase the yield of the product **2a**, we further screened solvents using $Sc(OTf)_3$ (10 mol%) as catalyst (Table 1, entry 1–5). Nonpolar solvents gave better yield as compared with polar solvents and the best yield was obtained in $CH_2Cl_2$ (60%). In acetonitrile and 1,4-dioxane the yield of **2a** was poor and 3-(indolin-2-yl)-1*H*-indole **4a** (<5%) was also obtained along with **2a**. Thus, we selected $CH_2Cl_2$ as the solvent of choice for further study.

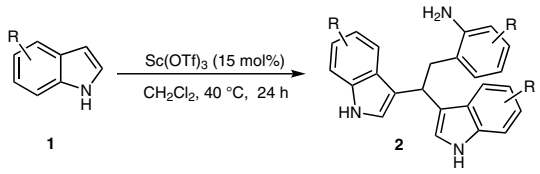
We then studied the effect of different metal triflates such as $Sc(OTf)_3$, $Bi(OTf)_3$, AgOTf, $Ce(OTf)_3$, $In(OTf)_3$, $Eu(OTf)_3$, and $La(OTf)_3$, as catalysts in $CH_2Cl_2$ (Table 1, en-

**Table 1** Optimization of Reaction Conditions for Formation of **2a**[a]

| Entry | Catalyst (mol%) | Solvent | Yield (%)[b] | |
|---|---|---|---|---|
| | | | **2a** | **3a** |
| 1 | $Sc(OTf)_3$ (10) | $CH_2Cl_2$ | 60 | 0 |
| 2 | $Sc(OTf)_3$ (10) | DCE | 48 | 0 |
| 3 | $Sc(OTf)_3$ (10) | $CHCl_3$ | 27 | 0 |
| 4 | $Sc(OTf)_3$ (10) | toluene | 19 | <5[c] |
| 5 | $Sc(OTf)_3$ (10) | MeCN | 10 | <5[c] |
| 6 | $Sc(OTf)_3$ (5) | $CH_2Cl_2$ | 49 | 0 |
| 7 | $Sc(OTf)_3$ (15) | $CH_2Cl_2$ | 66 | 0 |
| 8 | $Bi(OTf)_3$ (10) | $CH_2Cl_2$ | 32 | 0 |
| 9 | AgOTf (10) | $CH_2Cl_2$ | 18 | <5[c] |
| 10 | $Ce(OTf)_3$ (10) | $CH_2Cl_2$ | 12 | <5[c] |
| 11 | $In(OTf)_3$ (10) | $CH_2Cl_2$ | 55 | 0 |
| 12 | $Eu(OTf)_3$ (10) | $CH_2Cl_2$ | 16 | <5[c] |
| 13 | $La(OTf)_3$ (10) | $CH_2Cl_2$ | 14 | <5[c] |

[a] General reaction conditions: Indole **1a** (1.0 mmol), $M(OTf)_n$ (*x* mol%), solvent (5 mL), 40 °C, 24 h.
[b] Isolated yield after column chromatography.
[c] Based on TLC, product was not isolated.

**Table 2** Trimerization of Substituted Indoles Using $Sc(OTf)_3$[a]




| Entry | R | Yield (%)[b] | Entry | R | Yield (%)[b] |
|---|---|---|---|---|---|
| **a** | H | 66 | **f** | 6-$CO_2Me$ | 45 |
| **b** | 5-Cl | 54 | **g** | 5-CN | – |
| **c** | 5-Br | 52 | **h** | 5-OMe | 76 |
| **d** | 5-F | 51 | **i** | 5-Me | 74 |
| **e** | 6-Cl | 52 | | | |

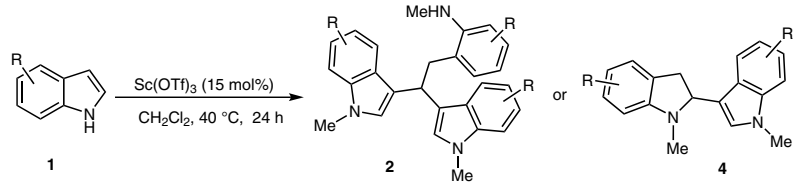
[a] General reaction conditions: indole **1a** (1.0 mmol), $Sc(OTf)_3$ (15 mol%), $CH_2Cl_2$ (5 mL), 40 °C, 24 h.
[b] Isolated yield after column chromatography.

tries 1 and 8–13). Among the metal triflates screened, $In(OTf)_3$ and $Sc(OTf)_3$ gave **2a** in 55 and 60% isolated yield, respectively. After performing solvent and catalyst study, we standardized catalyst loading, reaction time and temperature. The yield of **2a** increased from 49 to 66% on increasing $Sc(OTf)_3$ loading from 5 to 15 mol% (entries 6 and 7). Further increase in catalyst loading did not improve the yield but resulted in sluggish reaction with a mixture of products **2a** and **4a**. Increasing the reaction time from 24 to 72 hours did not result in an increase in yield. Increasing reaction temperature from 40 to 80 °C resulted in the disappearance of **2a**. Thus, $Sc(OTf)_3$ (15 mol%) in dichloromethane was selected as the reaction conditions to study the oligomerization of indoles.

Substituted indoles **1a–i** were treated with $Sc(OTf)_3$ (15 mol%) in dichloromethane at 40 °C for 24 hours and the products formed were analyzed. The results are shown in Table 2. It was observed that indoles with electron-withdrawing groups at C-5 and C-6 positions (**1b–f**) afforded lower yields of the corresponding indole 3,3′-trimer (**2b–f**), compared with indoles with electron-donating groups. Indole derivatives with strong electron-withdrawing groups such as a cyano group at the C-5 position (**1g**) did not react under these conditions. Azaindole and 3-substituted indoles also did not undergo oligomerization under these conditions.

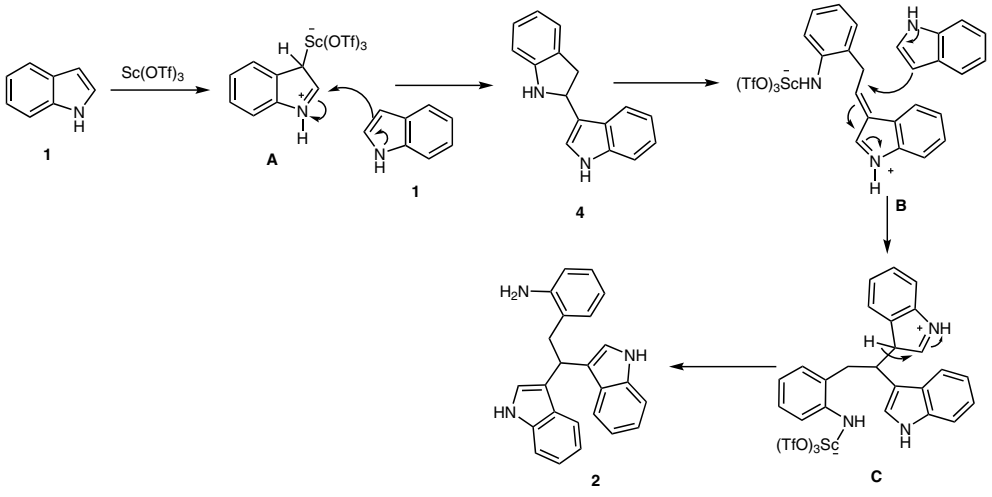
We then turned our attention towards the 1-methylindole derivatives (Table 3). *N*-Methylindole (**1j**) and 5-bromo-*N*-methylindole (**1k**), on treatment with $Sc(OTf)_3$ under the optimized reaction conditions, gave the corresponding

**Table 3** Oligomerization of *N*-Methylindoles using $Sc(OTf)_3$[a]




| Entry | R | Yield (%)[b] | |
|---|---|---|---|
| | | **2** | **4** |
| **j** | H | 54 | 0 |
| **k** | 5-Br | 50 | 0 |
| **l** | 5-Me | 0 | 56 |
| **m** | 5-OMe | 0 | 58 |

[a] General reaction conditions: Indole **1a** (1.0 mmol), $Sc(OTf)_3$ (15 mol%), $CH_2Cl_2$ (5 mL), 40 °C, 24 h.
[b] Isolated yield after column chromatography.




**Scheme 2** Proposed mechanism for the formation of indole dimer **4** and trimers **2**

indole-3,3′-trimers **2j** and **2k** in 54 and 50% yields, respectively. However, 5-methyl-*N*-methylindole (**1l**) and 5-methoxy-*N*-methylindole (**1m**) afforded the corresponding indole-2,3′-dimers **4l** and **4m** instead of indole-3,3′-trimers, in 56 and 58% yields, respectively.

Dimer **4** is possibly formed through generation of indolinium cation **A** by coordination of $Sc(OTf)_3$ at the C-3 position followed by nucleophilic attack by a second indole at the electrophilic C-2 position of **A** (Scheme 2). This pathway is consistent with previous reports[14,15] and with the substituent effect observed on the yield. Lower yields were obtained from indoles with electron-withdrawing groups compared with indoles with electron-donating groups. Dimer **4** was then converted into intermediate **B**, which acts as a Michael acceptor to react with a third molecule of indole **1** to furnish the indole-3,3′-trimer **2**.

In conclusion, we have described oligomerization of indole catalyzed by scandium triflate, a water-compatible, reusable Lewis acid, in dichloromethane. The product formation is found to be dependent on the substituent present on the indole ring. This is the first report on the oligomerization of indole using metal triflate, and provides a one-pot method for the preparation of 2-[2,2-bis(indol-3-yl)ethyl]anilines and 3-(indolin-2-yl)indoles.

Indoles and metal triflates were purchased from Sigma–Aldrich, India. Melting points were determined by the open capillary tube method with a melting point apparatus (EZ-Melt) and are uncorrected. IR spectra were recorded with an FTIR spectrometer and the values are expressed in $cm^{-1}$. The $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker (300 and 400 MHz) NMR spectrometer. High-resolution mass spectra (HRMS) were obtained with a quadrupole time of flight (qTOF) mass spectrometer. Thin-layer chromatography (TLC) was performed on pre-coated alumina sheets and detected under UV light. Silica gel (100–200 mesh) was used for column chromatography.

### Oligomerization of Indole; General Procedure

A mixture of indole **1a–n** (1.0 mmol), dichloromethane (5.0 mL) and $Sc(OTf)_3$ (74 mg, 15 mol%) in a round-bottom flask of 10 mL was stirred for 24 h at reflux. The progress of the reaction was monitored by TLC (EtOAc–hexane, 6:4 v/v). After completion of the reaction, the mixture was diluted with water (5 mL) and extracted with dichloromethane (2 × 10 mL). The combined organic phases were dried over anhydrous $Na_2SO_4$ and evaporated under vacuum. The residue was purified by column chromatography on silica gel (100–200 mesh) to afford the pure product **2** or **4**.

### 2-[2,2-Di(1*H*-indol-3-yl)ethyl]aniline (2a)

Yield: 66% (77 mg); brown solid; mp 169–170 °C (lit.[9,16] 167–169 °C).

FTIR (KBr): 3433, 3333, 3209, 3055, 2932, 1620, 1450, 1250, 802, 748 $cm^{-1}$.

$^1H$ NMR (300 MHz, DMSO-$d_6$): δ = 10.68 (s, 2 H), 7.52 (d, *J* = 7.9 Hz, 2 H), 7.30–7.22 (m, 4 H), 6.97 (t, *J* = 7.1 Hz, 2 H), 6.90–6.73 (m, 4 H), 6.56 (d, *J* = 6.9 Hz, 1 H), 6.33 (t, *J* = 6.8 Hz, 1 H), 4.85 (t, *J* = 7.5 Hz, 1 H), 4.67 (s, 2 H), 3.35 (d, *J* = 6.4 Hz, 2 H).

$^{13}C$ NMR (75 MHz, DMSO-$d_6$): δ = 146.7, 136.9, 129.6, 127.1, 126.5, 125.1, 122.7, 120.9, 119.5, 119.1, 118.3, 116.6, 115.1, 111.7, 36.3, 32.9.

ESI-TOF: *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{22}N_3^+$: 352.1808; found: 352.1861.

### 2-[2,2-Bis(5-chloro-1*H*-indol-3-yl)ethyl]-4-chloroaniline (2b)

Yield: 54% (82 mg); brown solid; mp 104–106 °C.

FTIR (KBr): 3441, 2932, 1620, 1458, 1273, 1095, 802, 741 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 11.00 (s, 2 H), 7.48 (dd, *J* = 17.9, 1.9 Hz, 2 H), 7.31 (d, *J* = 8.6 Hz, 2 H), 6.98 (dd, *J* = 8.6, 1.9 Hz, 2 H), 6.90 (d, *J* = 2.3 Hz, 1 H), 6.82 (dd, *J* = 8.5, 2.4 Hz, 1 H), 6.59 (d, *J* = 8.5 Hz, 1 H), 5.05 (s, 2 H), 4.87 (t, *J* = 7.6 Hz, 1 H), 3.31 (d, *J* = 7.6 Hz, 2 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 145.9, 135.3, 129.2, 128.1, 126.5, 126.3, 124.7, 123.1, 121.1, 119.6, 118.7, 118.4, 116.4, 113.3, 35.7, 32.1.

ESI-TOF: *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{19}Cl_3N_3^+$: 454.0639; found: 454.0642.

### 2-[2,2-Bis(5-bromo-1*H*-indol-3-yl)ethyl]-4-bromoaniline (2c)

Yield: 52% (102 mg); brown solid; mp 194–196 °C.

FTIR (KBr): 3441, 2924, 1497, 1450, 1242, 1080, 795, 733 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 11.02 (s, 2 H), 7.64 (d, *J* = 1.2 Hz, 2 H), 7.44 (d, *J* = 2.0 Hz, 2 H), 7.26 (d, *J* = 8.6 Hz, 1 H), 7.09 (dd, *J* = 8.6, 1.7 Hz, 1 H), 7.02 (d, *J* = 2.0 Hz, 1 H), 6.93 (dd, *J* = 8.5, 2.1 Hz, 1 H), 6.54 (d, *J* = 8.5 Hz, 1 H), 5.07 (s, 1 H), 4.86 (t, *J* = 7.6 Hz, 1 H), 3.29 (d, *J* = 7.6 Hz, 2 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 146.3, 135.5, 132.0, 129.2, 128.8, 127.0, 124.6, 123.6, 121.7, 118.4, 116.9, 113.8, 111.2, 107.2, 35.8, 32.1.

ESI-TOF: *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{19}Br_3N_3^+$: 585.9124; found: 585.9132.

### 2-[2,2-Bis(5-fluoro-1*H*-indol-3-yl)ethyl]-4-fluoroaniline (2d)

Yield: 51% (69 mg); brown solid; mp 164–166 °C.

FTIR (KBr): 3464, 2924, 1628, 1489, 1265, 1026, 856, 741 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 10.86 (s, 2 H), 7.45 (d, *J* = 1.8 Hz, 2 H), 7.26 (dd, *J* = 8.7, 4.5 Hz, 3 H), 7.22 (d, *J* = 2.1 Hz, 1 H), 6.82 (td, *J* = 9.2, 2.3 Hz, 2 H), 6.69 (dd, *J* = 10.3, 2.6 Hz, 1 H), 6.62 (td, *J* = 8.5, 2.8 Hz, 1 H), 6.56 (dd, *J* = 8.5, 5.4 Hz, 1 H), 4.81 (t, *J* = 7.6 Hz, 1 H), 4.72 (s, 2 H), 3.32 (d, *J* = 7.7 Hz, 2 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 156.7 (d, *J* = 230.2 Hz), 153.6, 143.2, 133.5, 127.2 (d, *J* = 9.7 Hz), 126.5 (d, *J* = 6.5 Hz), 124.9, 118.8 (d, *J* = 4.6 Hz), 115.9, 115.6 (d, *J* = 9.1 Hz), 112.8 (s), 112.5 (d, *J* = 9.8 Hz), 109.1 (d, *J* = 26.0 Hz), 104.1 (d, *J* = 23.1 Hz), 35.7, 32.3.

ESI-TOF: *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{19}F_3N_3^+$: 406.1526; found: 406.1524.

### 2-[2,2-Bis(6-chloro-1*H*-indol-3-yl)ethyl]-5-chloroaniline (2e)

Yield: 52% (79 mg); brown solid; mp 232–234 °C.

FT-IR (KBr): 3441, 3387, 3063, 2924, 1620, 1450, 1095, 849, 802 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 10.91 (s, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.32 (s, 4 H), 6.85 (d, *J* = 8.1 Hz, 2 H), 6.73 (d, *J* = 8.0 Hz, 1 H), 6.61 (s, 1 H), 6.29 (d, *J* = 7.2 Hz, 1 H), 5.14 (s, 2 H), 4.80 (t, *J* = 7.3 Hz, 1 H), 3.31 (d, *J* = 7.3 Hz, 2 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 148.5, 137.2, 131.2, 130.9, 125.9, 125.8, 123.9, 123.3, 120.8, 118.9, 118.7, 115.6, 114.0, 111.4, 35.6, 32.4.

ESI-TOF: *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{19}Cl_3N_3^+$: 454.0639; found: 454.0640.

**Dimethyl 3,3′-{2-[2-Amino-4-(methoxycarbonyl)phenyl]ethane-1,1-diyl}bis(1*H*-indole-6-carboxylate) (2f)**

Yield: 45% (79 mg); brown solid; mp 213–214 °C.

FTIR (KBr): 3364, 3286, 2924, 1697, 1620, 1435, 1296, 1250, 825, 771 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 11.22 (s, 2 H), 7.96 (s, 2 H), 7.57 (d, *J* = 7.7 Hz, 4 H), 7.47 (d, *J* = 8.5 Hz, 2 H), 7.23 (s, 1 H), 6.89 (q, *J* = 7.8 Hz, 2 H), 5.18 (s, 2 H), 4.98 (t, *J* = 7.6 Hz, 1 H), 3.81 (s, 6 H), 3.74 (s, 3 H), 3.43 (d, *J* = 7.6 Hz, 2 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 167.7, 167.2, 147.2, 136.0, 130.5, 130.0, 129.9, 128.1, 127.0, 122.1, 119.3, 119.2, 119.1, 117.1, 115.5, 113.8, 55.4, 52.2, 36.4, 32.1.

ESI-TOF: *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{28}N_3O_6^+$: 526.1973; found: 526.1970.

**2-[2,2-Bis(5-methoxy-1*H*-indol-3-yl)ethyl]-4-methoxyaniline (2h)**

Yield: 76% (112 mg); brown solid; mp 119–120 °C [Lit.[10] 117–119 °C].

FTIR (KBr): 3450, 3418, 3050, 2924, 1620, 1428, 795, 741 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 10.57 (s, 2 H), 7.25 (d, *J* = 2.3 Hz, 2 H), 7.19 (s, 1 H), 7.16 (s, 1 H), 7.02 (d, *J* = 2.4 Hz, 2 H), 6.66 (d, *J* = 2.4 Hz, 1 H), 6.64 (d, *J* = 2.4 Hz, 1 H), 6.52 (t, *J* = 5.3 Hz, 2 H), 6.42 (dd, *J* = 8.5, 2.9 Hz, 1 H), 4.75 (t, *J* = 7.5 Hz, 1 H), 4.38 (s, 2 H), 3.67 (s, 6 H), 3.42 (s, 3 H), 3.32 (d, *J* = 7.5 Hz, 2 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 152.9, 151.2, 140.4, 132.1, 127.5, 127.0, 123.5, 118.9, 116.1, 116.0, 112.2, 111.9, 110.8, 101.8, 55.7, 55.3, 36.5, 32.9.

ESI-TOF: *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{28}N_3O_3^+$: 442.2125; found: 442.2129.

**2-[2,2-Bis(5-methyl-1*H*-indol-3-yl)ethyl]-4-methylaniline (2i)**

Yield: 74% (97 mg); brown solid; mp 178–179 °C.

FTIR (KBr): 3464, 3418, 3055, 2924, 1628, 1420, 795, 741 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 10.57 (s, 2 H), 7.30 (s, 2 H), 7.17 (d, *J* = 7.0 Hz, 4 H), 6.82 (d, *J* = 7.8 Hz, 3 H), 6.62 (d, *J* = 7.5 Hz, 1 H), 6.48 (d, *J* = 7.6 Hz, 1 H), 4.78 (t, *J* = 6.2 Hz, 1 H), 4.46 (s, 2 H), 3.26 (d, *J* = 6.7 Hz, 2 H), 2.30 (s, 6 H), 2.00 (s, 3 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 144.2, 135.3, 130.2, 127.4, 127.0, 126.5, 125.5, 124.8, 122.8, 122.6, 119.1, 118.7, 115.4, 111.4, 36.5, 33.3, 21.8, 20.8.

ESI-TOF: *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{28}N_3^+$: 394.2278; found: 394.2282.

**2-[2,2-Bis(1-methyl-1*H*-indol-3-yl)ethyl]-*N*-methylaniline (2j)**

Yield: 54% (71 mg); colorless solid; mp 135–136 °C [Lit.[10] 135–137 °C].

FTIR (KBr): 3433, 3055, 2924, 1605, 1512, 1474, 1065, 820, 741 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 7.53 (d, *J* = 7.9 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.22 (s, 2 H), 7.07 (t, *J* = 7.5 Hz, 2 H), 6.92 (dt, *J* = 17.9, 5.4 Hz, 4 H), 6.44 (d, *J* = 8.0 Hz, 1 H), 6.36 (t, *J* = 7.3 Hz, 1 H), 4.95–4.89 (m, 1 H), 4.87 (d, *J* = 7.4 Hz, 1 H), 3.69 (s, 6 H), 3.34 (d, *J* = 7.4 Hz, 2 H), 2.63 (d, *J* = 4.6 Hz, 3 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 148.0, 137.2, 128.9, 127.4, 127.1, 127.0, 125.1, 121.2, 119.6, 118.6, 118.5, 115.9, 109.9, 109.3, 36.4, 32.7, 32.2, 30.8.

ESI-TOF: *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{28}N_3^+$: 394.2278; found: 394.2274.

**2-[2,2-Bis(5-bromo-1-methyl-1*H*-indol-3-yl)ethyl]-4-bromo-*N*-methylaniline (2k)**

Yield: 50% (105 mg); white solid; mp 220–221 °C.

FTIR (KBr): 3441, 2924, 1504, 1474, 1288, 1049, 795, 733 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 7.63 (d, *J* = 1.8 Hz, 2 H), 7.34 (s, 1 H), 7.32 (s, 1 H), 7.29 (s, 2 H), 7.19 (d, *J* = 1.9 Hz, 1 H), 7.17 (d, *J* = 1.9 Hz, 1 H), 7.06 (dd, *J* = 8.6, 2.4 Hz, 1 H), 6.95 (d, *J* = 2.4 Hz, 1 H), 6.36 (d, *J* = 8.7 Hz, 1 H), 5.25 (d, *J* = 4.9 Hz, 1 H), 4.87 (t, *J* = 7.6 Hz, 1 H), 3.71 (s, 6 H), 3.23 (d, *J* = 7.6 Hz, 2 H), 2.64 (d, *J* = 4.8 Hz, 3 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 147.2, 135.9, 131.5, 129.5, 129.0, 128.8, 127.2, 123.8, 121.8, 117.8, 112.1, 111.5, 111.2, 106.9, 36.3, 33.0, 31.3, 30.7.

ESI-TOF: *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{25}Br_3N_3^+$: 627.9593; found: 627.9598.

**3-(1,5-Dimethylindolin-2-yl)-1,5-dimethyl-1*H*-indole (4l)**

Yield: 56% (81 mg); white solid; mp 142–144 °C.

FTIR (KBr): 3047, 2908, 2854, 1612, 1489, 1327, 1265, 795 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 7.31 (d, *J* = 12.6 Hz, 3 H), 6.98 (d, *J* = 8.1 Hz, 1 H), 6.88 (d, *J* = 9.5 Hz, 2 H), 6.46 (d, *J* = 7.6 Hz, 1 H), 4.48–4.37 (m, 1 H), 3.74 (s, 3 H), 3.36 (s, 3 H), 3.18 (dd, *J* = 15.3, 8.6 Hz, 1 H), 3.10–2.93 (m, 1 H), 2.33 (s, 3 H), 2.22 (s, 3 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 151.6, 136.2, 129.5, 128.7, 127.9, 127.4, 127.0, 126.6, 125.2, 123.3, 119.6, 113.6, 110.1, 107.7, 65.3, 37.4, 34.9, 32.8, 21.7, 21.0.

ESI-TOF: *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{23}N_2^+$: 291.1856; found: 291.1860.

**5-Methoxy-3-(5-methoxy-1-methylindolin-2-yl)-1-methyl-1*H*-indole (4m)**

Yield: 58% (94 mg); white solid; mp 104–105 °C.

FTIR (KBr): 2947, 2831, 1620, 1490, 1242, 1026, 802 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 7.31 (d, *J* = 9.9 Hz, 2 H), 6.97 (d, *J* = 2.2 Hz, 1 H), 6.83–6.74 (m, 2 H), 6.66 (dd, *J* = 8.3, 2.0 Hz, 1 H), 6.48 (d, *J* = 8.4 Hz, 1 H), 4.48–4.38 (m, 1 H), 3.73 (s, 3 H), 3.68 (s, 3 H), 3.67 (s, 3 H), 3.37 (s, 3 H), 3.23 (dd, *J* = 15.5, 8.4 Hz, 1 H), 2.98 (dd, *J* = 15.1, 11.2 Hz, 1 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 153.5, 153.0, 148.0, 132.9, 130.9, 129.0, 127.2, 113.8, 112.2, 111.7, 111.5, 111.0, 108.0, 102.0, 65.3, 55.9, 55.8, 37.5, 35.3, 33.0.

ESI-TOF: *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{23}N_2O_2^+$: 323.1754; found: 323.1758.

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## Supporting Information

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