# Supporting Information 

Halogen Bond-Catalyzed Friedel-Crafts Reactions of Aldehydes and Ketones Using a Bidentate Halogen Bond Donor Catalyst: Synthesis of Symmetrical Bis(indolyl)methanes

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## 1. General information

Reagents were purchased from the Acros, Aldrich, or Lancaster chemical companies, and were used as received. Reactions were monitored by thin-layer chromatography (TLC) analysis using $\mathrm{GF}_{254}$ silica gel coated plates. Chromatography was performed using silica gel (230-400 mesh, Merck). NMR spectra were recorded on a Bruker DRX-400/DRX-500 spectrometer operating at $400 / 500 \mathrm{MHz}$ for ${ }^{1} \mathrm{H}$ analysis, $100 / 125 \mathrm{MHz}$ for ${ }^{13} \mathrm{C}$ analysis and 376 MHz for ${ }^{19} \mathrm{~F}$ analysis. Chemical shift data is expressed in ppm with reference to TMS. High-resolution EI-MS/ESI-MS data was recorded on a Bruker APEX IV mass spectrometer.

## 2. Synthesis of 4, 4-BF 4,9 and 10

## A. 1,3-Bis(1H-benzo[d]2midazole-1-yl)benzene (5) ${ }^{1}$



Under an Ar atmosphere, 1,3-dibromobenzene ( $1.5 \mathrm{~mL}, 12 \mathrm{mmol}, 1.0$ equiv), benzimidazole ( $3.5 \mathrm{~g}, 30 \mathrm{mmol}, 2.5$ equiv), $\mathrm{CuO}\left(0.31 \mathrm{~g}, 4 \mathrm{mmol}, 0.3\right.$ equiv), $\mathrm{K}_{2} \mathrm{CO}_{3}$ ( 4.1 $\mathrm{g}, 30 \mathrm{mmol}, 2.5$ equiv) and dry DMSO ( 60 mL ) were combined and stirred at $150{ }^{\circ} \mathrm{C}$ for 48 h . The reaction mixture was then cooled to room temperature, diluted with ethyl acetate ( 150 mL ) and filtered through a short plug of celite. The filtrate was washed with water ( $2 \times 100 \mathrm{~mL}$ ) and brine ( 100 mL ). The organic layer was dried with anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated. The crude product was purified by silica gel chromatography using dichloromethane:methanol (20:1) as the eluent to afford 5 as a white solid ( $2.35 \mathrm{~g}, 63 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.15(\mathrm{~s}, 2 \mathrm{H}), 7.84-7.87$ (m, 2H), 7.75-7.79(m, 1H) 7.68-7.69 (t, J = 2.0 Hz, 1 H), 7.57-7.61 (m, 4H), 7.32-7.34 (m, $4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=144.1,142.0,138.0,133.3,131.8,124.2,123.3$, 123.1, 120.9, 119.1, 110.2. $\mathrm{M} / \mathrm{S}(\mathrm{ESI})$ for $\mathrm{C}_{20} \mathrm{H}_{14} \mathrm{~N}_{4}(\mathrm{M}+\mathrm{H})$ : calculated 311.1291, found 311.1283.

## B. 1,3-Bis(2-iodo-1 H-benzo[d]3midazole-1-yl)benzene (6) ${ }^{2}$



Under an Ar atmosphere, LDA (Lithium diisopropylamide) ( $1.9 \mathrm{~mL}, 1.0 \mathrm{M}$ in hexane, 10.8 mmol, 2.4 equiv) were added to a solution of dry $\operatorname{THF}(10 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$. The solution was then cooled to $-78^{\circ} \mathrm{C}$ and 5 ( $1.4 \mathrm{~g}, 4.5 \mathrm{mmol}, 1.0$ equiv) in dry THF ( 120 mL ) was added dropwise. The reaction mixture was stirred for 2 h and then a solution of iodine ( 2.74 g , $10.8 \mathrm{mmol}, 2.4$ equiv) in dry THF ( 23 mL ) was added dropwise. The resulting reaction mixture was gradually warmed to room temperature and stirred for 24 h more. The solvent was then removed, and the residue was dissolved in dichloromethane ( 300 mL ) and washed with a saturated $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ solution ( 200 mL ). The separated aqueous layer was extracted with additional dichloromethane ( 300 mL ) and the combined organic layers were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated. The crude product was purified by silica gel chromatography using dichloromethane:ethyl acetate (10:1) as the eluent to afford 6 as a yellow solid $\left(2.1 \mathrm{~g}, 3.8 \mathrm{mmol}, 83 \%\right.$ yield). ${ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta=7.84-7.87(\mathrm{t}, \mathrm{J}=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.79-7.81(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.66-7.68(\mathrm{dd}, J=$ $2.0 \mathrm{~Hz}, 2.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), $7.52(\mathrm{t}, \mathrm{J}=2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.23-7.31(\mathrm{~m}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta=145.6,138.1,137.4,131.3,129.5,128.4,124.2,123.3,119.7,110.1,102.9$. $\mathrm{M} / \mathrm{S}(\mathrm{ESI})$ for $\mathrm{C}_{20} \mathrm{H}_{12} \mathrm{l}_{2} \mathrm{~N}_{4}(\mathrm{M}+\mathrm{H})$ : calculated 562.9224, found 562.9200.

## C. Catalyst 4



Under an Ar atmosphere, $6(0.42 \mathrm{~g}, 0.75 \mathrm{mmol}, 1.0$ equiv) was dissolved in dichloromethane ( 25 mL ). Methyl triflate ( $3.0 \mathrm{mmol}, 4.0$ equiv) was then added dropwise and the solution was stirred at room temperature for 24 h . The solvent was removed, and the residue was dissolved in acetonitrile ( 2 mL ). Catalyst 4 was precipitated as a white solid ( $0.57 \mathrm{~g}, 85 \%$ ) by the addition of diethyl ether ( 25 mL ). ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=8.13-8.18(\mathrm{q}, \mathrm{J}=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.96-8.03(\mathrm{~m}, 4 \mathrm{H}), 7.84(\mathrm{~s}, 1 \mathrm{H}), 7.63-7.74$ ( $\mathrm{m}, 4 \mathrm{H}$ ), $7.54-7.58(\mathrm{t}, \mathrm{J}=10.0 \mathrm{~Hz}, 2 \mathrm{H}), 4.18(\mathrm{~s}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=$ $137.3,135.9,135.0,134.4,132.5,129.5,128.7,128.3,123.2,120.6,115.7,114.5,114.4$, 114.2, 114.0, 37.9. $\mathrm{M} / \mathrm{S}$ (ESI) for $\mathrm{C}_{24} \mathrm{H}_{18} \mathrm{~F}_{6} \mathrm{I}_{2} \mathrm{~N}_{4} \mathrm{O}_{6} \mathrm{~S}_{2}(\mathrm{M}+\mathrm{H})$ : calculated 890.8734, found 890.7513 .

## D. Catalyst 4- $\mathrm{BF}_{4}$



Under an Ar atmosphere, $6(0.09 \mathrm{~g}, 0.16 \mathrm{mmol}, 1.0$ equiv) was dissolved in dichloromethane ( 6.5 mL ). Trimethyloxonium tetrafluoroborate ( $0.06 \mathrm{~g}, 0.42 \mathrm{mmol}$ ) was then added and the solution was stirred at room temperature for 24 h and the reaction was quenched with MeOH ( 10.0 mL ). The solvent was removed, and the residue was dissolved in $\mathrm{MeOH}(3 \mathrm{~mL})$. Catalyst $4-\mathrm{BF}_{4}$ was precipitated as a white solid ( 0.10 g , $83 \%)$ by the addition of diethyl ether ( 25 mL ). ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right): \delta=8.13-8.16$ (m, 1H), 7.95-8.03 (m, 4H), $7.83(\mathrm{~s}, 1 \mathrm{H}), 7.70-7.72(\mathrm{~m}, 2 \mathrm{H}), 7.63-7.67(\mathrm{t}, \mathrm{J}=7.8 \mathrm{~Hz}$, $2 \mathrm{H}), 7.54-7.60(\mathrm{~m}, 2 \mathrm{H}), 4.18(\mathrm{~s}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=137.2$, 135.0, $134.4,132.5,128.8,128.4,114.9,114.5,114.4,114.2,114.0,37.9 .{ }^{19} \mathrm{~F}$ NMR (376 MHz, $\mathrm{CD}_{3} \mathrm{CN}$ ): -151.72, -151.77. $\mathrm{M} / \mathrm{S}$ (ESI) for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{~B}_{2} \mathrm{~F}_{8} \mathrm{l}_{2} \mathrm{~N}_{4}$ (M-OTf): calculated 679.0181, found 678.9630.

## E. Compound 9



Under an Ar atmosphere, 5 ( $0.23 \mathrm{~g}, 0.75 \mathrm{mmol}, 1.0$ equiv) was dissolved in dichloromethane ( 25 mL ). Methyl triflate ( $3.0 \mathrm{mmol}, 4.0$ equiv) was then added dropwise and the solution was stirred at room temperature for 24 h . The solvent was removed, and the residue was dissolved in acetonitrile ( 2 mL ). Compound 9 was precipitated as a white solid ( $0.43 \mathrm{~g}, 90 \%$ ) by the addition of diethyl ether ( 25 mL ). ${ }^{1} \mathrm{H} \mathrm{NMR}(500 \mathrm{MHz}$, $\left.\mathrm{CD}_{3} \mathrm{CN}\right): \delta=9.53(\mathrm{~s}, 2 \mathrm{H}), 8.04-8.10(\mathrm{~m}, 4 \mathrm{H}), 7.92-8.01(\mathrm{~m}, 2 \mathrm{H}), 7.90-7.92(\mathrm{~m}, 2 \mathrm{H}), 7.76-$ $7.82(\mathrm{~m}, 4 \mathrm{H}), 4.21(\mathrm{~s}, 6 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right): \delta=143.2,135.7,133.8,133.3$, 132.5, 129.1, 128.7, 128.5, 123.5, 123.3, 120.7, 114.8, 114.5, 34.7. M/S (ESI) for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{~F}_{6} \mathrm{~N}_{4} \mathrm{O}_{6} \mathrm{~S}_{2}$ (M-OTf): calculated 489.1203, found 489.1187.

## F. 1-Phenyl-1 H-benzo[d]imidazole (SI-1) ${ }^{1}$


$\mathrm{SI}-1$
Under an Ar atmosphere, bromobenzene ( $1.3 \mathrm{~mL}, 12 \mathrm{mmol}, 1.0$ equiv), benzimidazole ( $3.5 \mathrm{~g}, 30 \mathrm{mmol}, 2.4$ equiv), $\mathrm{CuO}\left(0.31 \mathrm{~g}, 4 \mathrm{mmol}, 0.3\right.$ equiv), $\mathrm{K}_{2} \mathrm{CO}_{3}(4.1 \mathrm{~g}, 30 \mathrm{mmol}$, 2.5 equiv) and dry DMSO ( 60 mL ) were combined and were stirred at $150^{\circ} \mathrm{C}$ for 48 h . The reaction mixture was then cooled to room temperature, diluted with ethyl acetate $(150 \mathrm{~mL})$ and filtered through a short plug of celite. The filtrate was washed with water (2 $\times 100 \mathrm{~mL}$ ) and brine ( 100 mL ). The organic layer was dried with anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, concentrated. The crude product was purified by silica gel chromatography using methanol:dichloromethane ( $30: 1$ ) to afford $\mathbf{S I - 1}$ as a pale yellow oil ( $1.86 \mathrm{~g}, 80 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.27-8.29(\mathrm{~d}, J=9.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.87-7.89(\mathrm{q}, J=3.0 \mathrm{~Hz}, 1 \mathrm{H})$, $7.52-7.60(\mathrm{~m}, 5 \mathrm{H}), 7.47-7.50(\mathrm{t}, \mathrm{J}=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.34-7.39(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta=143.5,143.0,136.2,133.6,130.2,128.4,124.3,124.1,123.3,120.4,110.8$. $\mathrm{M} / \mathrm{S}(\mathrm{ESI})$ for $\mathrm{C}_{13} \mathrm{H}_{10} \mathrm{~N}_{2} \mathrm{O}(\mathrm{M}+\mathrm{H})$ : calculated 195.0917, found 195.0912 .

## G. 2-lodo-1-phenyl-1H-benzo[d]imidazole (SI-2) ${ }^{2}$



Under an Ar atmosphere, $n$ - $\mathrm{BuLi}(2.3 \mathrm{~mL}, 2.4 \mathrm{M}$ in hexane, $5.4 \mathrm{mmol}, 1.2$ equiv) was added dropwise to a solution of $0.8 \mathrm{~mL}(\operatorname{Pr})_{2} \mathrm{NH}(0.8 \mathrm{~mL}, 5.8 \mathrm{mmol}, 1.3$ equiv) in dry THF ( 10 mL ) at $0^{\circ} \mathrm{C}$. After stirring for 15 min , the solution was cooled to $-78{ }^{\circ} \mathrm{C}$ and $\mathbf{S I - 1}$ $(0.87 \mathrm{~g}, 4.5 \mathrm{mmol}, 1.0$ equiv) in dry THF ( 60 mL ) was added dropwise. The reaction mixture was stirred for 2 h and then a solution of iodine ( $1.37 \mathrm{~g}, 5.4 \mathrm{mmol}, 1.2$ equiv) in dry THF ( 12 mL ) was added dropwise. The resulting reaction mixture was gradually warmed to room temperature and stirred 24 h more. The solvent was then removed, and the residue was dissolved in dichloromethane ( 150 mL ) and washed with saturated $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ solution ( 100 mL ). The separated aqueous layer was extracted with additional dichloromethane ( 150 mL ) and the combined organic layers obtained were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated. The crude product was purified by silica gel chromatography using dichloromethane:ethyl acetate (5:1) as the eluent to afford $\mathbf{S I - 2}$ as a yellow solid ( $0.43 \mathrm{~g}, 1.35 \mathrm{mmol}, 30 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.78-7.80$ (d, $J=8.5 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.56-7.62 (m, 3H), 7.39-7.41 (m, 2H), 7.24-7.27 (m, 1H), 7.18-7.21 (t, $J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.13-7.14(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=145.5$, 137.6, 136.7, 129.9, 129.7, 128.3, 123.7, 122.8, 119.3, 110.4, 103.6. M/S (ESI) for $\mathrm{C}_{13} \mathrm{H}_{9} \mathrm{~N}_{2}(\mathrm{M}+\mathrm{H})$ : calculated 321.9961, found 321.9905.

## H. Catalyst 10



Under an Ar atmosphere, SI-2 ( $0.24 \mathrm{~g}, 0.75 \mathrm{mmol}, 1.0$ equiv) was dissolved in dichloromethane ( 25 mL ). Methyl triflate ( $3.0 \mathrm{mmol}, 4.0$ equiv) was then added dropwise and the solution was stirred at room temperature for 24 h . The solvent was removed, and the residue was dissolved in acetonitrile ( 2 mL ). Catalyst 10 was precipitated as a white solid $\left(0.31 \mathrm{~g}, 85 \%\right.$ yield) by addition of diethyl ether ( 25 mL ). ${ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz}$, $\mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=7.93-7.95(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.75-7.82(\mathrm{~m}, 3 \mathrm{H}), 7.68-7.70(\mathrm{t}, J=4.0 \mathrm{~Hz}$, $1 \mathrm{H}), 7.55-7.60(\mathrm{~m}, 3 \mathrm{H}), 7.37-7.39(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.15(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CD}_{3} \mathrm{CN}\right): \delta=135.9,135.7,135.0,132.8,131.7,128.8,128.7,128.5,128.2,123.4,120.8$, 114.9, 114.9, 37.8. M/S (ESI) for $\mathrm{C}_{15} \mathrm{H}_{12} \mathrm{~F}_{3} \mathrm{IN}_{2} \mathrm{O}_{3} \mathrm{~S}$ (M-OTf): calculated 335.0040, found 335.0028 .

## References:

1. (a) Zhang, H.; Cai, Q.; Ma, D. J. Org. Chem. 2005, 70, 5164. (b) Ganta, S.; Chand, D. K. Dalton Trans. 2015, 44, 15181.
2. Jungbauer, S. H.; Huber, S. M. J. Am. Chem. Soc. 2015, 137, 12110.

## 3. General procedure for Friedel-Crafts reactions



Indole $7(4.0 \mathrm{mmol})$, and $4(8.9 \mathrm{mg}, 0.01 \mathrm{mmol})$ were added to a 1-dram vial equipped with a stirring bar. Acetonitrile ( 2 mL ) was added followed by the aldehyde or ketone 8 $(1.0 \mathrm{mmol})$. The reaction was stirred and heated to $70^{\circ} \mathrm{C}$. The progress of the reaction was monitored by TLC. When the reaction was determined to be complete, the solvent was removed and the crude product was purified by silica gel chromatography to afford product 1.
4. Figure SI-1. Structures of indoles 7a-f and aldehydes and ketones 8a-w

7a

7b

7c

7d

$7 e$

7f

8a

8b

8g

8h

8c

8d

8 e

$8 f$

8j

8k

81



$8 t$


8u


8p

8q

$8 v$

8w



8s



80
5. Figure SI-2. NMR experiments
A. ${ }^{13} \mathrm{C}$ NMR shift of $\mathrm{C}=\mathrm{O}$ carbon of $\mathbf{8 a}$


8a


4

Molar ratio (8a to 4) Only 8a
$\left.\begin{array}{c}\text { Molar ratio (8a to 4) } \\ \text { Only 8a } \\ 50: 1 \\ 30: 1 \\ 20: 1 \\ 10: 1\end{array}\right]$
B. ${ }^{13} \mathrm{C}$ NMR shift of $\mathrm{C}=\mathrm{I}$ carbon on catalyst



Molar ratio (8a to 4)
4

$$
-
$$

50:1
30:1

C. ${ }^{1} \mathrm{H}$ NMR study of catalyst 4 when heated at $70^{\circ} \mathrm{C}$
Heated for 72 h

## 6. Characterization data for bis(indolyl)methanes 1a-1ab

## 3,3'-(Phenylmethylene)bis(1 H-indole) (1a) ${ }^{1}$



The reaction between 7a and 8a required 3 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate (4:1) as the eluent to afford 1a as a red solid ( $302 \mathrm{mg}, 94 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.89(\mathrm{~s}, 2 \mathrm{H}), 7.38-7.39(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.33-7.35(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 4 \mathrm{H}), 7.25-7.28$ (m, 2H), 7.18-7.22 (m, 1H), 7.14-7.18 (m, 2H), 6.98-7.01 (m, 2H), 6.64 (dd, J = 0.5 Hz, $1.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.88(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=144.1,136.8,128.9,128.3$, 127.2, 126.3, 123.7, 122.1, 120.1, 119.9, 119.4, 111.2, 40.3. M/S (ESI) for $\mathrm{C}_{23} \mathrm{H}_{18} \mathrm{~N}_{2}(\mathrm{M}-$ H): calculated 321.1386 found 321.1383.

## 3,3'-(p-Tolylmethylene)bis( 1 H -indole) (1b) ${ }^{1}$



The reaction between $\mathbf{7 a}$ and $\mathbf{8 b}$ required 11 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $4: 1$ ) as the eluent to afford $\mathbf{1 b}$ as a red solid ( $319 \mathrm{mg}, 95 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.69(\mathrm{~s}, 2 \mathrm{H}), 7.36-7.38(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~s}, 2 \mathrm{H})$, 7.19-7.21 (t, $J=4.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.12-7.15(\mathrm{~m}, 2 \mathrm{H}), 7.05-7.06(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.96-6.99$ (m, 2H), 6.54-6.55 (d, J = $1.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), $5.81(\mathrm{~s}, 1 \mathrm{H}), 2.30(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta=141.1,136.8,135.6,129.0,128.7,127.2,123.7,122.0,120.1,120.0,119.3$, 111.2, 39.9, 21.2. M/S (ESI) for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{~N}_{2}(\mathrm{M}-\mathrm{H})$ : calculated 335.1543 , found 335.1530.


## 3,3'-( $m$-Tolylmethylene)bis( 1 H -indole) (1c) ${ }^{1}$

The reaction between $\mathbf{7 a}$ and $\mathbf{8 c}$ required 12 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $4: 1$ ) as the eluent to afford $1 \mathbf{c}$ as a red solid ( $329 \mathrm{mg}, 98 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.76$ (s, 2H), 7.37-7.39 (d, J=8.0 Hz, 2H), 7.28-7.30 (d, J=8.0 Hz, 2H), 7.10-7.16 (m, 5H), 6.977.01 (m, 3H), 6.57-6.58 (dd, $J=1.0 \mathrm{~Hz}, 1.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), $5.82(\mathrm{~s}, 1 \mathrm{H}), 2.27(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=144.1,137.8,136.8,129.6,128.2,127.2,127.0,125.9,123.7$, 122.0, 120.1, 119.9, 119.3, 111.1, 40.2, 21.7. M/S (ESI) for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{~N}_{2}(\mathrm{M}-\mathrm{H})$ : calculated 335.1543 , found 335.1527 .


## 3,3'-(o-Tolylmethylene)bis( 1 H -indole) (1d) ${ }^{1}$

The reaction between 7a and 8d required 20 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate (4:1) as the eluent to afford 1d as a red solid ( $326 \mathrm{mg}, 97 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $=7.72$ (s, 2H), 7.33-7.34 (d, J= $8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.29-7.30(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.18-7.21(\mathrm{t}, \mathrm{J}$ $=6.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.10-7.16(\mathrm{~m}, 3 \mathrm{H}), 7.06-7.07(\mathrm{~m}, 1 \mathrm{H}), 6.97-7.02(\mathrm{~m}, 3 \mathrm{H}), 6.46-6.47$ (dd, J $=0.5 \mathrm{~Hz}, 1.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.00(\mathrm{~s}, 1 \mathrm{H}) 2.36(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=142.2$, 136.8, 136.2, 130.3, 128.5, 127.3, 126.2, 125.9, 124.0, 122.0, 119.9, 119.3, 119.2, 111.2, 36.3, 19.7. M/S (ESI) for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{~N}_{2}(\mathrm{M}-\mathrm{H})$ : calculated 335.1543, found 335.1529.


3,3'-((2,6-Dimethylphenyl)methylene)bis(1 H-indole) (1e)
The reaction between $7 \mathbf{a}$ and $8 \mathbf{e}$ required 72 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $1: 1$ ) as the eluent to afford $\mathbf{1 e}$ as a red solid ( $35 \mathrm{mg}, 10 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.90(\mathrm{~s}, 2 \mathrm{H})$, 7.36-7.38 (d, $J=8.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.27-7.29 (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.17-7.20(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H})$, 7.08-7.11 (t, $J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.98-7.02$ (m, 4H), 6.65 (s, 2H), 6.27 (s, 1H), 2.19 (s, 6H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=139.8,137.4,136.8,129.5,127.6,126.3,123.7,122.0$, 120.1, 119.3, 117.7, 111.1, 36.2, 21.5. M/S (EI) for $\mathrm{C}_{25} \mathrm{H}_{22} \mathrm{~N}_{2}$ : calculated 350.1783, found 350.1778 .


3,3'-((4-Methoxyphenyl)methylene)bis( $\mathbf{1 H}$-indole) ( 1 f$)^{1}$
The reaction between 7a and 8f required 9 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $3: 1$ ) as the eluent to afford 1 f as orange foam ( $327 \mathrm{mg}, 93 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.87$ (s, 2H), 7.38-7.39 (d, J=8.0 Hz, 2H), 7.33-7.35 (d, J=8.0 Hz, $2 \mathrm{H}), 7.23-7.25(\mathrm{t}, J=4.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.14-7.17(\mathrm{~m}, 2 \mathrm{H}), 6.98-7.01(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.80-$ $6.83(\mathrm{~m}, 2 \mathrm{H}), 6.63-6.64(\mathrm{dd}, \mathrm{J}=0.5 \mathrm{~Hz}, 1.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.83(\mathrm{~s}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=158.0,136.9,136.4,129.7,127.2,123.7,122.0,120.2,120.1$, 119.3, 113.7, 111.1, 55.4, 39.5. M/S(ESI) for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}(\mathrm{M}-\mathrm{H})$ : calculated 351.1492, found 351.1481.


## 3,3'-((4-((Tert-butyldimethylsilyl)oxy)phenyl)methylene)bis( $1 H$-indole) ( 1 g$)^{2}$

The reaction between 7 a and 8 g required 5 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $5: 1$ ) as the eluent to $\mathbf{1 g}$ as a red solid. ( $371 \mathrm{mg}, 82 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.83$ (s, 2H), 7.39-7.41 (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.33-7.35 (d, $J=8.0 \mathrm{~Hz} 2 \mathrm{H}$ ), 7.16-7.23 (m, 4H), 7.007.03 (t, J = 7.5 Hz, 2H), 6.77-6.79 (d, J = $8.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), 6.60 (s, 2H), 5.84 (s, 1H), 1.00 (s, 9 H ), 0.20 (s, 6H). ${ }^{13} \mathrm{C}$ NMR (125MHz, $\mathrm{CDCl}_{3}$ ): $\delta=154.0,136.9,136.8,129.7,127.2$, 123.7, 122.0, 120.2, 120.1, 119.8, 119.3, 111.1, 39.5, 25.8, 18.3, -4.3. M/S (EI) for $\mathrm{C}_{29} \mathrm{H}_{32} \mathrm{~N}_{2} \mathrm{OSi}$ : calculated 452.2284, found 452.2279.


## 3,3'-((4-(Allyloxy)phenyl)methylene)bis(1 H-indole) (1h) ${ }^{3}$

The reaction between 7 a and 8 h required 12 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $5: 1$ ) as the eluent to afford 1 h as a red solid ( $333 \mathrm{mg}, 88 \%$ yield). ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ): $\delta=7.89(\mathrm{~s}, 2 \mathrm{H}), 7.39-7.40(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.33-7.35(\mathrm{~d}$, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.23-7.26(\mathrm{~m}, 2 \mathrm{H}), 7.15-7.18(\mathrm{~m}, 2 \mathrm{H}), 7.00-7.03(\mathrm{~m}, 2 \mathrm{H}), 6.83-6.85(\mathrm{~m}$, 2H), 6.62 (s, 2H), 6.04-6.09 (m, 1H), 5.84 (s, 1H), 5.39-5.43 (m, 1H), 5.27-5.29 (dd, J = $1.0 \mathrm{~Hz}, 1.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.50-4.51(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=157.1,136.8$, 136.6, 133.7, 129.7, 127.2, 123.7, 122.0, 120.1, 119.3, 117.7, 114.5, 111.2, 69.0, 39.5. $\mathrm{M} / \mathrm{S}(\mathrm{EI})$ for $\mathrm{C}_{26} \mathrm{H}_{22} \mathrm{~N}_{2} \mathrm{O}$ : calculated 378.1732, found 378.1727.


## 4-(Di(1 H-indol-3-yl)methyl)phenyl acetate (1i) ${ }^{4}$

The reaction between 7 a and 8 i required 48 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $4: 1$ ) as the eluent to afford $\mathbf{1 i}$ as a red solid ( $350 \mathrm{mg}, 92 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.59$ (s, 2H), 7.30-7.32 (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.17-7.20 (t, $J=7.3 \mathrm{~Hz}$, $4 \mathrm{H}), 7.09-7.12(\mathrm{t}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.94-6.97(\mathrm{~m}, J=3.8 \mathrm{~Hz}, 2 \mathrm{H})$, 6.89-6.90 (d, J = $8.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), $6.25(\mathrm{~s}, 2 \mathrm{H}), 5.76(\mathrm{~s}, 1 \mathrm{H}), 2.23(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta=170.1,148.9,141.8,136.7,129.7,127.0,124.0,121.9,121.2,119.8,119.2$, 119.2, 111.3, 39.5, 21.3. M/S (EI) for $\mathrm{C}_{25} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{2}$ : calculated 380.1525, found 380.1512.


3,3'-((4-(Trifluoromethyl)phenyl)methylene)bis(1 H-indole) $(1 \mathrm{j})^{1}$
The reaction between $\mathbf{7 a}$ and $\mathbf{8 j}$ required 1.5 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $4: 1$ ) as the eluent to afford $\mathbf{1 j}$ as a red solid. ( $371 \mathrm{mg}, 95 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.94$ (s, 2H), 7.50-7.52 (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.42-7.44 (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.33-7.35 (m, 4H), 7.16-7.19 (m, 2H), 6.99-7.02 (m, 2H), 6.61-6.62 (t, J = 1.0 Hz, 2H), $5.93(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=148.3,136.8,129.1,128.7,128.5,127.0,125.6,125.4$, 125.3, 125.3, 123.8, 123.5, 122.3, 119.9, 119.6, 118.9, 111.3, 40.2. M/S (ESI) for $\mathrm{C}_{24} \mathrm{H}_{17} \mathrm{~F}_{3} \mathrm{~N}_{2}(\mathrm{M}-\mathrm{H})$ : calculated 389.1260, found 389.1242.


3,3'-((4-Nitrophenyl)methylene)bis( 1 H -indole) ( $\mathbf{1 k})^{4}$
The reaction between $\mathbf{7 a}$ and $\mathbf{8 k}$ required 12 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $2: 1$ ) as the eluent to afford $\mathbf{1 k}$ as an orange solid ( $338 \mathrm{mg}, 92 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , Acetone$\mathrm{d}_{6}$ ): $\delta=10.14(\mathrm{~s}, 2 \mathrm{H}), 8.14-8.16(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.63-7.64(\mathrm{~d}$, $J=8 \mathrm{~Hz}, 2 \mathrm{H}$ ), $7.42-7.44(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.36-7.38(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.09-7.12(\mathrm{t}, J$ $=6.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.94-6.95(\mathrm{t}, J=3.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.90-6.92(\mathrm{~d}, J=13.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.10(\mathrm{~s}, 1 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( 125 MHz , Acetone $-\mathrm{d}_{6}$ ): $\delta=153.9,147.3,138.1,130.5,127.8,124.8,124.1$, 122.4, 120.0, 119.6, 118.4, 112.3, 41.0. M/S (EI) for $\mathrm{C}_{25} \mathrm{H}_{17} \mathrm{~N}_{3} \mathrm{O}_{2}$ : calculated 367.1321, found 367.1318.


## 3,3'-((4-Chlorophenyl)methylene)bis(1 H-indole) (1I) ${ }^{1}$

The reaction between $\mathbf{7 a}$ and $8 \mathbf{l}$ required 1.5 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate (4:1) as the eluent to afford 11 as a red foam ( $328 \mathrm{mg}, 92 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.91$ (s, 2H), 7.35-7.36 (m, 4H), 7.25-7.27 (m, 2H), 7.22-7.25 (m, 2H), 7.16-7.19 (m, 2H), 6.99-7.03 (t, $J=9.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.63-6.64(\mathrm{dd}, J=0.5 \mathrm{~Hz}, 1.0 \mathrm{~Hz}, 2 \mathrm{H})$, 5.85 (s, 1H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=142.7,136.8,131.9,130.2,128.5,127.0$, 123.7, 122.2, 120.0, 119.5, 119.4, 111.2, 39.8. $\mathrm{M} / \mathrm{S}(\mathrm{ESI})$ for $\mathrm{C}_{23} \mathrm{H}_{17} \mathrm{ClN}_{2}(\mathrm{M}+\mathrm{H})$ : calculated 357.1153 , found 357.0955 .

## 3,3'-((4-lodophenyl)methylene)bis(1 H-indole) (1m) ${ }^{5}$



The reaction between 7 a and 8 m required 2.5 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate (4:1) as the eluent to afford $\mathbf{1 m}$ as a red foam ( $416 \mathrm{mg}, 93 \%$ yield). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ): $\delta=$ 7.86 (s, 2H), 7.59-7.60 (d, J = $8.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.34-7.39 (m, 4H), 7.18-7.21 (t, $J=7.8 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.08-7.10 (d, $J=8.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.02-7.05 (m, 2H), 6.60-6.62 (t, J = 6.3 Hz, 2H), $5.83(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=143.9,137.4,136.8$, 131.0, 127.0, 123.8, 122.2, 119.9, 119.5, 119.1, 111.3, 91.6, 39.9. M/S (EI) for $\mathrm{C}_{23} \mathrm{H}_{17} \mathrm{IN}_{2}$ : calculated 448.0436, found 448.0439.


## Arsindoline A (1n) ${ }^{6}$

The reaction between $\mathbf{7 a}$ and $\mathbf{8 n}$ required 18 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $2: 1$ ) as the eluent to afford $1 \mathbf{n}$ as a red solid ( $280 \mathrm{mg}, 75 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.73-$ $8.74(\mathrm{~d}, J=3.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.14-8.15(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 8.04-8.06(\mathrm{~d}, J=10.0 \mathrm{~Hz}, 2 \mathrm{H})$, $7.65-7.68(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.41-7.44(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.36-7.38(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 4 \mathrm{H})$, $7.18-7.21(\mathrm{t}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.15(\mathrm{~d}, J=4.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.00-7.03(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.65$ (s, 1H), $6.56(\mathrm{~s}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=150.6,149.7,148.7,136.9,130.2$, 129.1, 127.5, 126.9, 126.7, 124.5, 124.3, 122.4, 121.1, 119.7, 117.9, 111.4, 35.7. M/S (ESI) for $\mathrm{C}_{26} \mathrm{H}_{19} \mathrm{~N}_{3}(\mathrm{M}+\mathrm{H})$ : calculated 374.1652, found 374.1642.

## 3,3'-(2-Methylpropylidene)bis(1 H-indole) (10) ${ }^{1}$



The reaction between 7 a and 80 required 11 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate (5:1) as the eluent to afford 10 as a white foam ( $231 \mathrm{mg}, 80 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.60-6.62(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.48 (s, 2H), 7.07-7.19 (m, 4H), 7.01-7.04 (t, $J=7.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 6.82-6.83 (d, J = 8.0 Hz, $2 \mathrm{H}), 4.18-4.19(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.53-2.62(\mathrm{~m}, 1 \mathrm{H}), 0.95-0.97(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (125 MHz, $\mathrm{CDCl}_{3}$ ): $\delta=136.3,127.7,121.8,121.7,119.7,119.7,119.0,111.2,41.2$, 33.0, 21.9. $\mathrm{M} / \mathrm{S}(\mathrm{ESI})$ for $\mathrm{C}_{20} \mathrm{H}_{20} \mathrm{~N}_{2}(\mathrm{M}+\mathrm{H})$ : calculated 289.1699, found 289.1685.

## 3,3'-(3-Phenylpropane-1,1-diyl)bis(1 H-indole) (1p) ${ }^{4}$



The reaction between 7 a and 8 p required 30 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $3: 1$ ) as the eluent to afford $\mathbf{1 p}$ as a red foam ( $273 \mathrm{mg}, 78 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=9.06$ (s, 2H), 7.44-7.46 (dd, $J=1.0 \mathrm{~Hz}, 1.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.34-7.36 (m, 2H), 7.25-7.28 (t, J = 7.5 $\mathrm{Hz}, 2 \mathrm{H}), 7.16-7.19$ (m, 5H), 7.04-7.07 (m, 2H), 6.89-6.93 (m, 2H), 4.45 (s, 1H), 2.65-2.67 (d, $J=8.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), 2.51-2.53 (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (125 MHz, $\mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=$ 143.9, 137.8, 129.5, 129.3, 127.9, 126.6, 122.9, 122.2, 120.2, 120.1, 119.4, 112.3, 38.0, 35.2, 34.4. $\mathrm{M} / \mathrm{S}(\mathrm{ESI})$ for $\mathrm{C}_{25} \mathrm{H}_{22} \mathrm{~N}_{2}(\mathrm{M}+\mathrm{H})$ : calculated 351.1856, found 351.1824.


## Ethyl 2,2-di(1H-indol-3-yl)acetate (1q) ${ }^{7}$

The reaction between 7 a and $\mathbf{8 q}$ required 0.5 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $6: 1$ ) as the eluent to afford $1 \mathbf{q}$ as a red solid. ( $270 \mathrm{mg}, 85 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{Cl}$ ): $\delta=8.00(\mathrm{~s}, 2 \mathrm{H}), 7.61-7.63(\mathrm{t}, \mathrm{J}=$ $3.8 \mathrm{~Hz}, 2 \mathrm{H}$ ), $7.28-7.30(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.15-7.18(\mathrm{~m}, 2 \mathrm{H}), 7.06-7.09(\mathrm{~m}, 2 \mathrm{H}), 7.00(\mathrm{~d}$, $J=2.5 \mathrm{~Hz}, 2 \mathrm{H}), 5.49(\mathrm{~s}, 1 \mathrm{H}), 4.18-4.23(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 1.23-1.26(\mathrm{t}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{Cl}$ ): $\delta=173.7,136.5,126.8,123.5,122.2,119.7,119.4,113.7$, 111.4, 61.3, 40.8, 14.4. $\mathrm{M} / \mathrm{S}(\mathrm{ESI})$ for $\mathrm{C}_{28} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{2}(\mathrm{M}+\mathrm{H})$ : calculated 319.1441, found 319.1428.


## Ethyl 2,2-di(1 H-indol-3-yl)propanoate (1r) ${ }^{8}$

The reaction between 7 a and 8 r required 2 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $5: 1$ ) as the eluent to afford 1 r as a white solid ( $242 \mathrm{mg}, 73 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.98$ (s, 2H), 7.52-7.54 (dd, J $=0.5 \mathrm{~Hz}, 0.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.34-7.36 (d, J = $8.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.14-7.17 (m, 2H), 7.00-7.02 (m, $2 \mathrm{H}), 6.96(\mathrm{~d}, J=2.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.14-4.18(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.12(\mathrm{~s}, 3 \mathrm{H}), 1.10-1.13(\mathrm{t}, J=$ $7.3 \mathrm{~Hz}, 3 \mathrm{H}$ ). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=175.6,136.9,126.2,123.1,121.8,121.7$, 119.3, 119.2, 111.4, 61.3, 46.5, 26.0, 14.3. M/S (ESI) for $\mathrm{C}_{21} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{2}(\mathrm{M}+\mathrm{Na})$ : calculated 355.1417 , found 355.1400 .


## Trisindoline (1s) ${ }^{6}$

The reaction between $\mathbf{7 a}$ and $8 \mathbf{s}$ required 12 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate (1:1) as the eluent to afford 1 s as a white solid ( $335 \mathrm{mg}, 92 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{DMSO}-\mathrm{d}_{6}$ ): $\delta=$ $10.95(\mathrm{~d}, J=1.5 \mathrm{~Hz}, 2 \mathrm{H}), 10.59(\mathrm{~s}, 1 \mathrm{H}), 7.34-7.36(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.21-7.24(\mathrm{t}, J=$ $7.0 \mathrm{~Hz}, 4 \mathrm{H}$ ), 6.98-7.03 (m, 3H), 6.91-6.94 (m, 1H) 6.84-6.85 (d, J = $2.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), 6.786.81 ( $\mathrm{m}, 2 \mathrm{H}$ ). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, ~ D M S O-\mathrm{d}_{6}$ ): $\delta=178.7,141.3,136.9,134.6,127.8$, 125.7, 124.9, 124.3, 121.4, 120.9, 120.8, 118.2, 114.3, 111.6, 109.6, 52.6. M/S (ESI) for $\mathrm{C}_{24} \mathrm{H}_{17} \mathrm{~N}_{3} \mathrm{O}(\mathrm{M}+\mathrm{H})$ : calculated 364.1444, found 364.1430.


## 3,3-Di(1H-indol-3-yl)-7-chloroindolin-2-one (1t) ${ }^{9}$

The reaction between $\mathbf{7 a}$ and $8 \mathbf{t}$ required 15 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate (1:1) as the eluent to afford 1t as an off white solid ( $310 \mathrm{mg}, 78 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , DMSO-d6): $\delta=11.04(\mathrm{~s}, 1 \mathrm{H}), 11.02(\mathrm{~s}, 2 \mathrm{H}) 7.36-7.37(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H})$, 7.30-7.32 (d, $J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.18-7.22(\mathrm{~m}, 3 \mathrm{H}), 7.01-7.04(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.94-6.97$ (t, $J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.86(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.80-6.83(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , DMSO-d6): $\delta=178.6,139.0,137.0,136.3,127.9,125.5,124.4,123.5,122.9$, $121.1,120.6,118.4,113.8,113.6,111.7,53.5 . \mathrm{M} / \mathrm{S}(\mathrm{ESI})$ for $\mathrm{C}_{24} \mathrm{H}_{16} \mathrm{CIN}_{3} \mathrm{O}(\mathrm{M}+\mathrm{H})$ : calculated 398.1055, found 398.1036.


## 3,3'-(Cyclohexane-1,1-diyl)bis(1 $\boldsymbol{H}$-indole) (1u) ${ }^{10}$

The reaction between $7 \mathbf{a}$ and $8 \mathbf{u}$ required 15 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate (5:1) as the eluent to afford $\mathbf{1 u}$ as a yellow solid. ( $260 \mathrm{mg}, 83 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=9.08$ (s, 2H), 7.34 (dd, J = $0.5 \mathrm{~Hz}, 2.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.28-7.31(\mathrm{~m}, 4 \mathrm{H}), 6.91-6.94(\mathrm{~m}, 2 \mathrm{H}), 6.70-6.74(\mathrm{~m}, 2 \mathrm{H})$, $2.46-2.48(\mathrm{t}, J=5.8 \mathrm{~Hz}, 4 \mathrm{H}), 1.62-1.67(\mathrm{~m}, 4 \mathrm{H}), 1.57-1.58(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CD}_{3} \mathrm{CN}\right): \delta=138.2,127.3,123.9,123.2,121.7,121.7,118.9,112.2,39.8,37.9,27.6$, 23.8. $\mathrm{M} / \mathrm{S}$ (EI) for $\mathrm{C}_{22} \mathrm{H}_{22} \mathrm{~N}_{2}$ : calculated 314.1783, found 314.1774.


3,3'-(Phenylmethylene)bis(6-bromo-1H-indole) (1v) ${ }^{11}$ The reaction between $\mathbf{7 b}$ and $8 \mathbf{a}$ equired 31 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $3: 1$ ) as the eluent to afford 1 v as a red solid. ( $421 \mathrm{mg}, 88 \%$ yield). ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right): \delta=9.18(\mathrm{~s}, 2 \mathrm{H}), 7.57-7.58(\mathrm{~d}, J=1.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.28-7.33$ (m, 4H), 7.17-7.22 (m, 3H), 7.02-7.04 (dd, $J=1.5 \mathrm{~Hz}, 1.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), 6.75 (t, $J=1.0 \mathrm{~Hz}$, $2 \mathrm{H}), 5.84(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=145.3,138.7,129.4,129.3,127.2$, 126.9, 125.6, 122.7, 121.8, 119.9, 115.5, 115.2, 40.7. M/S (ESI) for $\mathrm{C}_{23} \mathrm{H}_{16} \mathrm{Br}_{2} \mathrm{~N}_{2}(\mathrm{M}+\mathrm{H})$ : calculated 478.9753, found 478.9547.


3,3'-(Phenylmethylene)bis(6-methyl-1 H-indole) (1w) ${ }^{12}$
The reaction between 7c and 8a required 6 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $3: 1$ ) as the eluent to afford $\mathbf{1 w}$ as a red solid ( $336 \mathrm{mg}, 96 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta=7.60(\mathrm{~s}, 2 \mathrm{H}) .7 .33-7.39(\mathrm{~m}, 2 \mathrm{H}), 7.30-7.33(\mathrm{~m}, 4 \mathrm{H}), 7.24-7.27(\mathrm{~m}, 1 \mathrm{H}), 7.11$ (s, 2H), 6.89-6.91 (m, 2H), 6.51 (s, 2H), $5.87(\mathrm{~s}, 1 \mathrm{H}), 2.49-2.50(\mathrm{~d}, \mathrm{~J}=3.0 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=144.3,137.2,131.7,128.8,128.3,126.1,125.1,123.1$, 121.0, 119.7, 119.6, 111.2, 40.3, 21.8. $\mathrm{M} / \mathrm{S}$ (ESI) for $\mathrm{C}_{25} \mathrm{H}_{22} \mathrm{~N}_{2}(\mathrm{M}-\mathrm{H})$ : calculated 349.1699 , found 349.1681 .


## 3,3'-(Phenylmethylene)bis(5-bromo-1 H-indole) (1x) ${ }^{11}$

The reaction between 7d and 8a required 24 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $3: 1$ ) as the eluent to afford $1 x$ as a red solid. ( $440 \mathrm{mg}, 92 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=$ 9.25 (s, 2H), 7.41 (d, $J=2.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), $7.29-7.35(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 6 \mathrm{H}), 7.22-7.25(\mathrm{~m}, 1 \mathrm{H})$, 7.19-7.21 (dd, J = $1.5 \mathrm{~Hz}, 2.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), $6.79(\mathrm{t}, J=1.3 \mathrm{~Hz}, 2 \mathrm{H}), 5.82(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=145.1,136.6,129.6,129.4,129.3,127.3,126.2,125.1,122.6$, 119.3, 114.3, 112.5, 40.5. M/S (ESI) for $\mathrm{C}_{23} \mathrm{H}_{16} \mathrm{Br}_{2} \mathrm{~N}_{2}(\mathrm{M}+\mathrm{H})$ : calculated 478.9753, found 478.9548.


## 3,3'-(Phenylmethylene)bis(5-iodo-1 H-indole) (1y) ${ }^{13}$

The reaction between 7 e and 8 a required 22 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $3: 1$ ) as the eluent to afford 1 y as a red solid. ( $527 \mathrm{mg}, 92 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=$ 7.97 (s, 2H), 7.68 (s, 2H), 7.41-7.44 (dd, J = $1.2 \mathrm{~Hz}, 1.2 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.24-7.32 (m, 5H), 7.14-7.16 (d, $J=8.8 \mathrm{~Hz}, 2 \mathrm{H}$ ), $6.60(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.74(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta=143.2,136.0,130.6,129.6,128.7,128.7,128.6,126.7,124.5,119.0,113.3$, 83.1, 40.0. $\mathrm{M} / \mathrm{S}(\mathrm{El})$ for $\mathrm{C}_{23} \mathrm{H}_{16} \mathrm{I}_{2} \mathrm{~N}_{2}$ : calculated 573.9403, found 573.9419.


3,3'-(Phenylmethylene)bis(1-methyl-1H-indole) (1z) ${ }^{12}$
The reaction between 7 f and 8 a required 15 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate ( $8: 1$ ) as the eluent to afford $\mathbf{1 z}$ as a pink solid ( $308 \mathrm{mg}, 88 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.37-$
$7.39(\mathrm{~m}, 2 \mathrm{H}), 7.29-7.35(\mathrm{~m}, 2 \mathrm{H}), 7.24-7.28(\mathrm{~m}, 4 \mathrm{H}), 7.18-7.22(\mathrm{~m}, 3 \mathrm{H}), 6.97-7.00(\mathrm{~m}, 2 \mathrm{H})$, $6.52(\mathrm{~d}, \mathrm{~J}=0.5 \mathrm{~Hz}, 2 \mathrm{H}), 5.88(\mathrm{~s}, 1 \mathrm{H}), 3.67(\mathrm{~s}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (125MHz, $\left.\mathrm{CDCl}_{3}\right): \delta=144.6$, 137.5, 128.8, 128.4, 128.3, 127.6, 126.1, 121.5, 120.2, 118.8, 118.4, 109.2, 40.2, 32.8. $\mathrm{M} / \mathrm{S}(\mathrm{ESI})$ for $\mathrm{C}_{25} \mathrm{H}_{22} \mathrm{~N}_{2}(\mathrm{M}+\mathrm{H})$ : calculated 351.1856, found 351.1839.

## Arundine (1aa) ${ }^{6}$



The reaction was performed according to the general procedure using $7 \mathrm{a}(117 \mathrm{mg}, 1.0 \mathrm{mmol}), 4(8.9 \mathrm{mg}, 0.01 \mathrm{mmol})$ and $8 \mathbf{v}$ ( $35-40 \mathrm{wt}$. \% in $\mathrm{H}_{2} \mathrm{O}$ ) ( 4.0 mmol ) at room temperature. The reaction time was 30 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate (6:1) as the eluent to afford 1aa as a brown solid ( $153 \mathrm{mg}, 62 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.86$ (s, 2H), 7.62-7.63 (d, J = 8.0 Hz, 2H), 7.34-7.35 (d, J = 8.0 Hz, 2H), 7.17-7.20 (t, J = 14.5 Hz, 2H), 7.07-7.10 (t, J = $7.3 \mathrm{~Hz}, 2 \mathrm{H}$ ), 6.92 (s, 2H), 4.24 (s, 2H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=136.6,127.7$, 122.3, 122.0, 119.4, 119.3, 115.8, 111.2, 21.3. $\mathrm{M} / \mathrm{S}(\mathrm{ESI})$ for $\mathrm{C}_{17} \mathrm{H}_{14} \mathrm{~N}_{2}(\mathrm{M}+\mathrm{H})$ : calculated 247.1230, found 247.1228.


Vibrindole A (1ab) ${ }^{6}$
The reaction was performed according to the general procedure using 7 a ( $117 \mathrm{mg}, 1.0 \mathrm{mmol}$ ), $4(8.9 \mathrm{mg}, 0.01 \mathrm{mmol})$ and $8 \mathbf{w}$ ( 50 wt . \% in EtOH ) $(4.0 \mathrm{mmol})$ at room temperature. The reaction time was 58 h and product purification by silica gel chromatography was carried out using hexane:ethyl acetate (6:1) as the eluent to afford $\mathbf{1 a b}$ as a white solid ( $195 \mathrm{mg}, 75 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.84(\mathrm{~s}, 2 \mathrm{H}), 7.56-7.58(\mathrm{t}, J=4.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.33-7.34(\mathrm{~d}, J=8.0$ $\mathrm{Hz}, 2 \mathrm{H}), 7.14-7.17(\mathrm{~m}, 2 \mathrm{H}), 7.02-7.05(\mathrm{~m}, 2 \mathrm{H}), 6.91(\mathrm{t}, J=1.3 \mathrm{~Hz}, 2 \mathrm{H}), 4.65-4.70(\mathrm{q}, J=$ $7.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.80-1.81(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=136.8,127.1$, 121.9, 121.8, 121.3, 119.9, 119.2, 111.2, 28.3, 21.9. M/S (ESI) for $\mathrm{C}_{18} \mathrm{H}_{16} \mathrm{~N}_{2}(\mathrm{M}+\mathrm{H})$ : calculated 261.1386, found 261.1375 .

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## 7. NMR spectra















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