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Advanced Synthesis & Catalysis

Phosphine-Free Manganese(II)-Catalyst Enables Acceptorless Dehydrogenative Coupling of Alcohols with Indoles

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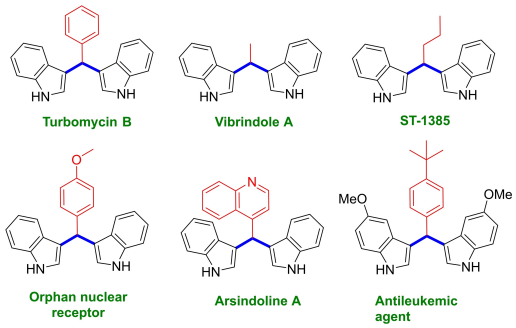
Abstract: Herein, an air-stable, molecularly defined NNN–Mn(II) pincer complex catalyzed acceptorless dehydrogenative coupling of alcohols with indoles is reported. A wide variety of symmetrical and unsymmetrical bis(indolyl)methane derivatives as well as some structurally important products such as Vibrindole A, Turbomycin B alkaloid, Antileukemic, and Anticancer agents were synthesized. Mechanistic studies illustrate the importance of the NH moiety in the complex and the crucial role of metal-ligand cooperation during catalysis.

Keywords: manganese; phosphine-free; acceptorless dehydrogenation; alcohol; indole

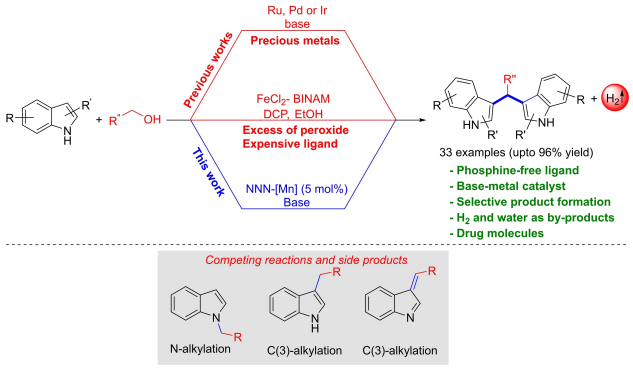
Transition-metal catalysis plays a vital role in the development of new sustainable and environmentally benign procedures for the green synthesis of a wide range of structurally important organic compounds, pharmaceuticals, and fine chemicals.[1] They have significantly revolutionized the key areas of organic synthesis by providing efficient and sustainable alternatives to the so-called conventional organic transformations.[2] The noble-metal (Ru, Rh, Pd, or Ir) based complexes have substantially dominated the field of homogenous catalysis over the past decades due to their generality, improved catalytic activity, and selectivity in most of the organic transformations.[3] Undoubtedly, the attainments of such precious metal complexes are enormous; however, because of the increasing demand, high cost, and limited availability of noble metal precursors; the development of synthetic procedures based on abundantly available, less toxic, and inexpensive first-row transition metal complexes is highly desirable.[4] There has been great interest in the past few years in the development of earth-abundant-metal based complexes as catalysts for various C–X (X = C, N, O) bond-forming reactions via the acceptorless dehydrogenative coupling (ADC) strategy, which were largely the arena of precious metal catalysis.[5] Of late, manganese-based pincer complexes have been effectively utilized for the acceptorless dehydrogenation (AD) and borrowing hydrogenation (BH) reactions.[6] Manganese is third only to iron and titanium among the transition elements in its abundance in Earth's crust plus it is essential in various life forms. Hence, molecularly-defined manganese complexes are the highly attractive candidates for the design of new catalytic transformations.

N-heterocycles are prevalent in natural products, pharmaceuticals, and materials science.[7] For instance, indole motifs play a vital role in many drug molecules, bioactive alkaloids, agrochemicals, and advanced organic materials.[8] Particularly, bis(indolyl)methane derivatives (BIMs) are of great significance in organic synthesis as well as in natural products and pharmaceutical industries.[9] Several bioactive natural products such as Vibrindole A, Arsindoline A, Turbomycin B, and Arundine contain BIM scaffold (Scheme 1).[9a,d]

Besides, BIMs are key units in a wide range of bioactive compounds with widespread biological and pharmacological activities, for example, they have anticancer, antifungal, antimicrobial, antibacterial, and antitumor activities.[9] Given the importance of BIMs, there is significant interest in the development of novel and efficient synthetic protocols for their preparation. Conventional methods for the synthesis of BIMs are



Scheme 1. Selected examples of pharmaceutically active compounds containing BIMs.[9a,d]



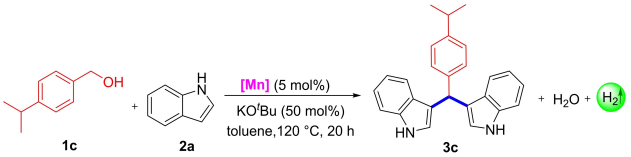
Scheme 2. Transition-metal catalyzed synthesis of BIMs.

largely based on the Friedel-craft alkylation of indoles with aldehydes or ketones in the presence of Lewis/Brønsted acids, and transition metals.[10] However, due to the use of stoichiometric amounts of acids, and easily oxidizable aldehyde precursors, these methods require significant modification in terms of atom-economy and sustainability. Therefore, the development of sustainable and green procedures for the efficient synthesis of BIMs is highly desirable. In this context, the ADC reaction can be considered as a highly atom-economical and environmentally benign approach in which the intermediates resulted from the initial dehydrogenation process participate in further reactions and liberates molecular hydrogen (and water) as the sole by-product. Furthermore, the possibility of using alcohol as an alkylating agent increases the interest for this sustainable reaction, since alcohols are easy to handle, inexpensive, and abundantly available by a variety of industrial processes or even from renewable resources such as lignocellulose biomass.[11] Utilizing alcohols as the alkylating agent, Yokoyama and Hikawa reported a palladium-catalyzed cascade process for the synthesis of BIMs.[12a] Of late, the research group of Sekar reported an iron(II) chloride-1,1'-binaphthyl-2,2'-diamine ($FeCl_2$-BINAM) complex catalyzed domino synthesis of BIMs directly from indoles and alcohols.[12b] In this protocol, an earth-abundant iron was used as the catalyst along with an expensive BINAM ligand and an excess of dicumyl peroxide (DCP) as an oxidant. Very recently, the research group of Srimani reported the ruthenium pincer complex catalyzed selective synthesis of C-3 alkylated indoles and BIMs directly from indoles and alcohols.[12c] Langer et al. also reported a copper-catalyzed alkylation of indoles with an excess of alcohols using air as an oxidant for the synthesis of BIMs (Scheme 2).[12d]

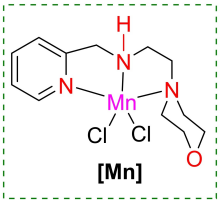
Despite notable contributions for the synthesis of BIMs from indoles and alcohols, an efficient and robust method based on earth-abundant transition-metal complexes remains scarce. Unlike previously reported precious catalytic systems, this is the first example of NNN–Mn(II) pincer complex catalyzed acceptorless dehydrogenative coupling of indoles and alcohols to access a diverse range of bis(indolyl) methane derivatives.

At the outset, we explored the reaction with 4-isopropylbenzyl alcohol (**1 c**) and unsubstituted indole **2 a** as the model substrates (Table 1). Thus, the reaction

Table 1. Optimization of the reaction conditions.[a,b]



Entry	Reaction condition	Yield of **3 c** (%)[b]
1	alcohol:indole (1:2)	65 (70)[c]
2	alcohol:indole (1:1)	96 (99)[c]
3	alcohol:indole (2:1)	96 (99)[c]
4	no catalyst	< 5%
5	no KO^{t}Bu	trace
6	$MnCl_2 \cdot 4H_2O$	20
7	[Mn] (3 mol%)	86 (90)[c]
8	30 mol% KO^{t}Bu	85
9	NaO^{t}Bu, Cs_2CO_3, K_2CO_3 as base	< 47%
10	*m*-xylene, n-octane, 1,4-dioxane, CH_3CN as solvent	< 61%



[a] Reaction conditions: alcohol **1 c** (0.5 mmol), indole **2 a** (0.5 mmol), catalyst **[Mn]** (5 mol%), KO^{t}Bu (50 mol%) and toluene solvent (1.0 mL) were heated at 120 °C (oil-bath temperature) for 20 h under Ar atm.

[b] Yield of the isolated product.

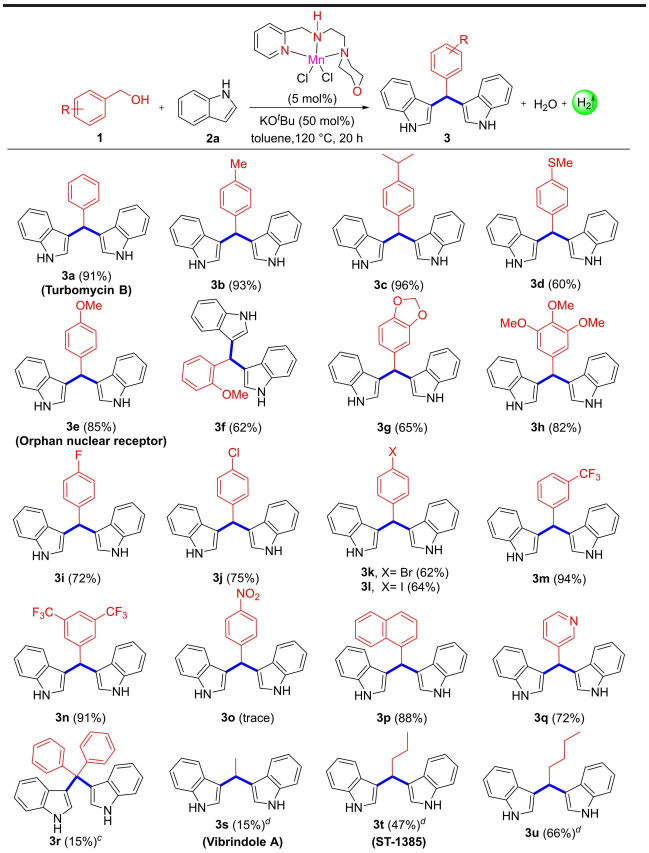
[c] GC conversion of indole using mesitylene as an internal standard.

of **1c** (0.5 mmol) and **2a** (1.0 mmol) in the presence of NNN–Mn(II) pincer complex, **[Mn]** (5 mol%) and KO^{t}Bu (50 mol%) in toluene solvent in a closed system at 120 °C (oil-bath temperature) for 20 h resulted in 65% yield of 3,3′-((4-isopropylphenyl) methylene)bis(1H-indole) (**3c**; Table 1, entry 1). Notably, with 0.5 mmol of indole (i.e. alcohol:indole = 1:1) and keeping the remaining conditions same, the reaction ensued in approximately complete conversion of starting indole **2a** with a selective formation of the product **3c** in 96% isolated yield (Table 1, entry 2).

When the reaction was performed using 2 eq. of alcohol with respect to indole, the starting indole was fully converted to the desired product (Table 1, entry 3). Gratifyingly, despite the possibility of forming the C3-benzylated and N-benzylated products, the product **3c** was obtained selectively in excellent yield. The starting material indole **2a** was recovered unchanged when a control experiment was conducted in the absence of a base, while in the absence of the catalyst system, only a trace amount of product formation (< 5%) was observed (Table 1, entries 4 and 5). By lowering the mol% of Mn-catalyst (3 mol%) and KO^{t}Bu (30 mol%), a reduced yield of product **3c** was observed under the standard reaction conditions (Table 1, entries 7–8). Next, changing the base from KO^{t}Bu to either of NaO^{t}Bu (47%), Cs_2CO_3 (trace), and K_2CO_3 (0%) resulted in lower yield of the desired product (Table 1, entry 9). A comparison of the Mn-(II)-catalyzed reaction in different solvents such as *m*-xylene, n-octane, 1,4-dioxane, CH_3CN showed that toluene was the best solvent (Table 1, entry 10). Notably, shifting the temperature from 120 °C in either an upward or downward direction resulted in a lower yield of the desired product. Accordingly, the optimal condition for the reaction is alcohol (0.5 mmol), indole (0.5 mmol), **[Mn]** (5 mol%) and KO^{t}Bu (0.25 mmol) in 1.0 mL of toluene solvent in a close system at 120 °C for 20 h.

With the optimal reaction conditions, next, we have investigated the scope and generality of the present NNN–Mn(II)-catalyzed dehydrogenative coupling of alcohols with indoles to access diverse BIMs (Table 2). Initially, the reaction of unsubstituted indole **2a** with benzyl alcohol (**1a**) selectively afforded 3,3′-(phenylmethylene)bis(1H-indole) product which acts as an antibiotic and natural product named Turbomycin B in 91% isolated yield.[9d] Notably, the reaction of indole with primary benzylic alcohols bearing an electron-donating substituent such as methyl, thiomethyl, isopropyl, and methoxy groups afforded the corresponding bis(indolyl)methane derivatives **3b–f** in 60–96% isolated yields. It is noteworthy that the product **3e** is an orphan nuclear receptor.[9a] Similarly, electronically deactivated benzylic alcohols, which are extremely poor substrates in Lewis- or Brønsted acid-catalyzed Friedel – Crafts reactions, bearing an electron-withdrawing group such as fluoro, chloro, bromo, iodo and trifluoromethyl groups were well tolerated and the desired products **3i–m** were obtained in 62 – 94% yields. Surprisingly, 4-nitrobenzyl alcohol (**1o**) failed to give the desired product. In addition, reaction with di- and tri-substituted benzyl alcohols (**1g**, **1h** and **1n**) worked well and provided the desired products in 65–91% yields. A polyaromatic compound, 1-naphthalenemethanol (**1p**) reacted smoothly under the optimized reaction conditions and provided the desired product **3p** in 88% yield. Interestingly, heteroaromatic alcohol such as 3-pyridinemethanol (**1q**) also reacted efficiently with **2a** to afford the product **3q** in 72% yield. When 1,1-diphenylmethanol was reacted with indole under the standard reaction conditions, only a trace amount of product was observed along with the complete conversion of a secondary alcohol to the corresponding ketone. Later,

Table 2. Synthesis of bis(indolyl)methanes: Scope of alcohols.[a,b]



[a] Reaction conditions: alcohol **1** (0.5 mmol), indole **2a** (0.5 mmol), catalyst **[Mn]** (5 mol%), KO^{t}Bu (50 mol%), and toluene solvent (1.0 mL) were heated at 120 °C (oil-bath temperature) for 20 h under Ar atm.
[b] Yield of the isolated product.
[c] The reaction was carried out for 48 h.
[d] The reaction performed with alcohol (3.0 eq.), **[Mn]** (10 mol%), and KO^{t}Bu (1.0 eq.) for 28 h.

under the modified reaction conditions (prolonged reaction time), the product **3r** was obtained in 15% isolated yield. Pleasingly, aliphatic alcohols such as ethanol, 1-butanol, and 1-pentanol were also reactive and afforded the desired products **3s–3u** in 15–66% yields, however, the reaction was performed with 10 mol% Mn-catalyst and 1.0 eq. of KO^{t}Bu. The product **3s** is a natural product known as Vibrindole A,[9a] which is used to treat fibromyalgia and bowel syndrome.

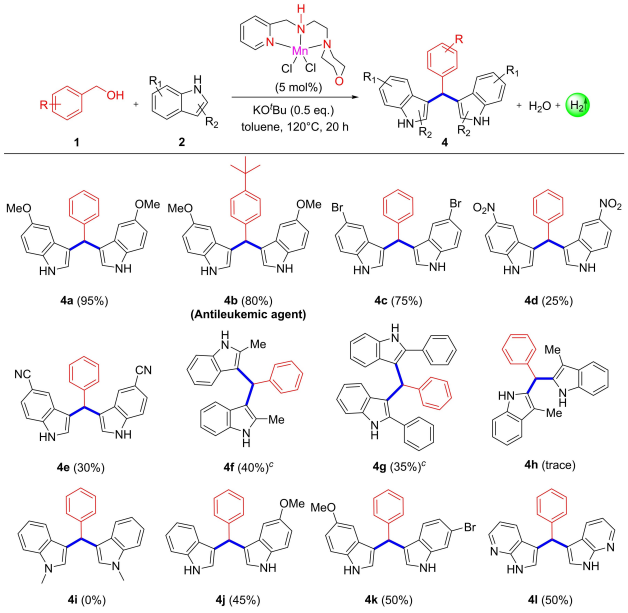
Next, we have explored the scope of indoles in the present Mn-catalyzed ADC reaction with alcohols (Table 3). Initially, we have explored the effect of substituents on the six as well as a five-membered ring of indole, and it was found that the nature along with the position of the substituents on indole has a considerable effect on the desired product yields. The reaction of benzyl alcohol and 4-tert-butylbenzyl alcohol with electron-rich indole such as 5-methoxyindole provided the corresponding products **4a** and **4b** in 95% and 80% yields, respectively. It is important to note that product **4b** acts as an Antileukemic agent.[9a] The electronically deactivated indoles bearing a mild electron-withdrawing substituent on the six-membered benzene ring of indole such as 5-bromo afforded the desired product **4c** in good yield while strong electron-withdrawing substituent such as 5-nitro and 5-cyano groups have remarkable effect on the reaction efficiency and the corresponding products **4d** and **4e** were obtained in 25% and 30% yields, respectively. Further, the effect of substituents on the pyrrole ring of indole was examined. The reaction of 2-methyl and 2-phenyl substituted indole with benzyl alcohol under the standard reaction conditions afforded a poor yield of the desired products. To our delight, with 1.0 eq. of base, the desired products **4f** and **4g** were isolated in 40% and 35% yields, respectively. Additionally, the reaction of 3-methylindole and N-methylindole with benzyl alcohol didn't lead to any product formation and only the unreacted starting indoles were recovered. The inert nature of N-methylindole suggests that the indole N–H bond is involved in a key interaction with the base. Next, we thought to examine the scope of our protocol with respect to a 1:1 mixture of different indoles to synthesize unsymmetrical bis(indolyl)methanes.

Delightfully, the reaction of indole and 5-methoxyindole with benzyl alcohol underwent the desired reaction with almost complete conversion of the starting indoles, and the desired unsymmetrical bis(indolyl)methane **4j** was obtained in 45% yield. Although the starting indole was fully consumed, the desired product yield was low due to the formation of symmetrical products with respect to indole and 5-methoxyindole. Further, the reaction of 5-methoxyindole and 6-bromoindole with benzyl alcohol also delivered the corresponding product **4k** in moderate yield. A heteroaromatic indole, 7-azaindole, provided the desired product **4l** in 50% isolated yield. To demonstrate the practical utility of the present phosphine-free Mn-catalysis, a large-scale reaction with benzyl alcohol (**1a**) and indole (**2a**) was performed, and the product **3a** was obtained in 87% yield which shows that the efficiency of the small-scale reaction remains upon scale-up (see ESI).

Having developed an efficient method to access substituted BIMs, the mechanism of this coupling reaction was investigated. Firstly, the progress of the reaction was monitored using gas chromatography (GC) to gain detailed information about the catalytic process (Figure 1). Monitoring the progress of the reaction indicated that around 0.8 equivalent of 4-methoxybenzyl alcohol was used during the reaction and the consumption of indole follows an exponential decay. The rate of product formation is faster as approximately 27.6% bis(indolyl)methane **3e** was observed just after the completion of 2 h. The intermediate 4-methoxybenzaldehyde was also detected in GC which was utilized in the reaction with indole.

Further, the reaction of 4-methoxybenzyl alcohol under the standard reaction conditions in the absence of indole provided the dehydrogenated product 4-methoxybenzaldehyde in 90% yield (Scheme 3a). The reaction failed to give the quantitative conversion of 4-

Table 3. Synthesis of bis(indolyl)methanes: Scope of indoles.[a,b]



[a] Reaction conditions: alcohol **1** (0.5 mmol), indole **2a** (0.5 mmol), catalyst **[Mn]** (5 mol%), KO^{t}Bu (50 mol%) and toluene solvent (1.0 mL) were heated at 120 °C (oil-bath temperature) for 20 h under Ar atm.
[b] Yield of the isolated product.
[c] The reaction was carried out with 1.0 eq. KO^{t}Bu.

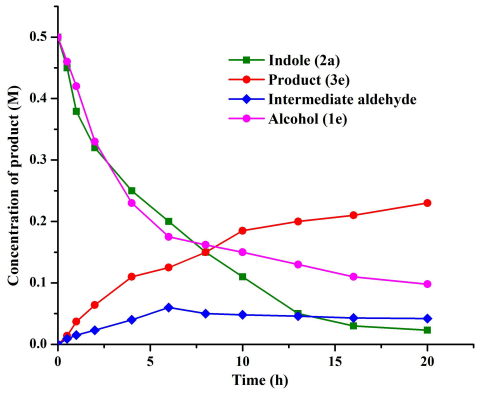
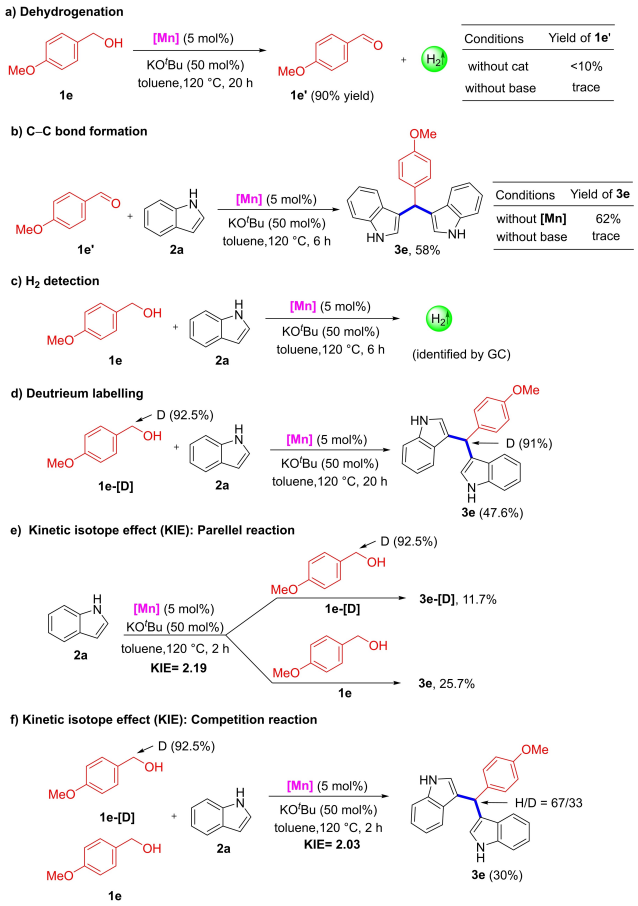


Figure 1. Kinetic profile of the NNN–Mn(II) pincer complex catalyzed ADC of **1 e** with indole (**2 a**).

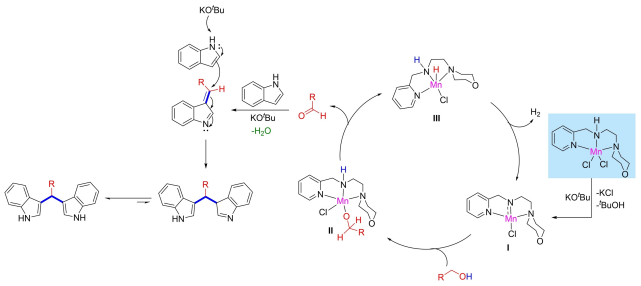


Scheme 3. Mechanistic experiments.

methoxybenzyl alcohol in the absence of a base or Mn-catalyst. Additionally, the condensation of indole with 4-methoxybenzaldehyde under the standard reaction conditions was found to be fast and a similar rate was observed when the reaction was performed with base alone (Scheme 3b). Hence, the manganese catalyst is playing a key role in the activation of alcohols to give the corresponding aldehydes or ketones while KO^{t}Bu catalyzes the condensation of indoles with aldehydes or ketones to give the alkylideneindolenine intermediates and further reaction with another indole moiety to provide the desired BIMs. Notably, the evolution of hydrogen gas during the reaction was qualitatively analyzed by gas chromatography, which suggests that the process proceeds via ADC strategy (Scheme 3c). Further, the reaction of indole with deuterium-labelled alcohol **1 e**-[D] was studied under the standard reaction conditions and the analysis of the product using ^{1}H NMR revealed 91% deuterium incorporation in the product (Scheme 3d). Next, we performed parallel and competitive experiments of **1 e** and **1 e-[D]** with indole to perceive the kinetic isotope effect (KIE) (Scheme 3e and 3 f). The K_H/K_D value obtained in parallel and competitive experiments were 2.19 and 2.03, respectively. The KIE values obtained are in close agreement with each other and provide very strong support that the dehydrogenation of the alcohol took place at or before the rate-determining step.

Based on the mechanistic studies and the previous literature reports,[13] a plausible mechanism for the acceptorless dehydrogenative coupling of alcohols with indoles catalyzed by an NNN–Mn (II) pincer complex is shown in Scheme 4. In the presence of a base, the precatalyst generates the coordinatively unsaturated reactive intermediate **I** followed by alcohol activation *via* metal-ligand cooperation (MLC) results in the formation of an alkoxy type intermediate **II**. At this point, the complex **II** undergoes *β*-hydride elimination of the alkoxide to yield the dehydrogenated product (aldehyde or ketone) with the formation of Mn–H species **III** which further releases a molecule of hydrogen to generate the active catalyst **I** and the cycle continues. Next, the *in situ* generated aldehyde or ketone undergoes a base-catalyzed condensation reaction with indole (**2 a**) to yield alkylideneindolenine intermediate which upon Michael-type nucleophilic addition of another indole molecule results in the formation of the BIM product.

In conclusion, we have reported an example of base metal-catalyzed alkylation of indoles using alcohols to



Scheme 4. Plausible mechanism.

access a diverse range of value-added bis(indolyl) methanes. An easy to handle, air- and moisture-stable earth-abundant manganese catalyst is used for this process. Mechanistic studies showed that the reaction proceeds *via* acceptorless dehydrogenation of alcohols followed by a catalyst-independent cascade process. The protocol is scalable and suitable in the preparation of important bioactive molecules.

Experimental Section

General Procedure for Synthesis of Bis(3-Indolyl) methanes

To an oven dried schlenk tube, indole (0.5 mmol, 1 eq.), alcohol (0.5 mmol, 1 eq.), **[Mn]** catalyst (5 mol%), KO^{t}Bu (0.25 mmol, 50 mol%) and toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 120 °C (oil-bath temperature) for 20 h. Then, the reaction was quenched with water (2 mL) and extracted with dichloromethane/ethyl acetate (3 × 4 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230–400 mesh size) using petroleum-ether/ethyl acetate as an eluting system to yield the desired bis(3-indolyl)methane product **3** or **4**.

3,3′-(Phenylmethylene)bis(1H-Indole) (3 a)

Red solid, 91% (73.3 mg) isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.86 (br s, 2 H), 7.42 (d, J = 8.1 Hz, 2 H), 7.35–7.38 (m, 4 H), 7.28–7.32 (m, 2H), 7.17–7.26 (m, 3 H), 7.01–7.05 (m, 2 H), 6.64 (dd, J = 2.4, 0.9 Hz, 2 H), 5.91 (s, 1 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 144.0, 136.6, 128.7, 128.2, 127.0, 126.1, 123.6, 121.9, 119.9, 119.6, 119.2, 111.0, 40.1. **HRMS** (ESI) m/z calcd for $C_{23}H_{17}N_2$ $(M-H)^+$: 321.1386, found: 321.1393.

3,3′-(*p*-Tolylmethylene)bis(1H-Indole) (3 b)

Red solid, 93% (78.2 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.89 (br s, 2 H), 7.41 (d, J = 7.9 Hz, 2 H), 7.36 (d, J = 8.1 Hz, 2 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.16–7.20 (m, 2 H), 7.10 (d, J = 7.8 Hz, 2 H), 7.00–7.04 (m, 2 H), 6.66 (dd, J = 2.4, 0.9 Hz, 2 H), 5.87 (s, 1 H), 2.34 (s, 3 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ ppm 141.0, 136.7, 135.5, 128.9, 128.5, 127.1, 123.5, 121.8, 119.9, 119.2, 111.0, 39.7, 21.1. **HRMS** (ESI) m/z calcd for $C_{24}H_{19}N_2$ $(M-H)^+$: 335.1543, found: 335.1548.

3,3′-((4-Isopropylphenyl)methylene)bis(1H-Indole) (3 c)

Red solid, 96% (87.4 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.88 (br s, 2 H), 7.41 (d, J = 8.0 Hz, 2 H), 7.34 (d, J = 8.1 Hz, 2 H), 7.25–7.27 (m, 2 H), 7.16 (t, J = 7.8 Hz, 2 H), 7.13 (d, J = 8.1 Hz, 2 H), 7.00 (t, J = 7.5 Hz, 2 H), 6.66 (d, J = 1.9 Hz, 2 H), 5.86 (s, 1 H), 2.88 (quint, J = 6.9 Hz, 1 H), 1.24 (d, J = 6.9 Hz, 6 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ ppm 146.4, 141.2, 136.6, 128.5, 127.1, 126.2, 123.5, 121.8, 120.0, 119.9, 119.1, 111.0, 39.7, 33.6, 24.0. **HRMS** (ESI) m/z calcd for $C_{26}H_{23}N_2$ $(M-H)^+$: 363.1856, found: 363.1862.

3,3′-((4-(Methylthio)phenyl)methylene)bis(1H-Indole) (3 d)

Red solid, 60% (55.2 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.85 (br s, 2 H), 7.39 (d, J = 8.0 Hz, 2 H), 7.34 (d, J = 8.4 Hz, 2 H), 7.26 (d, J = 8.4 Hz, 2 H), 7.16–7.18 (m, 4 H), 7.01 (t, J = 7.4 Hz, 2 H), 6.62 (br s, 2 H), 5.84 (s, 1 H), 2.46 (s, 3 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ ppm 141.1, 136.7, 135.5, 129.2, 127.0, 126.7, 123.6, 121.9, 119.9, 119.5, 119.2, 111.0, 39.6, 16.0. **HRMS** (ESI) m/z calcd for $C_{24}H_{19}N_2S$ $(M-H)^+$: 367.1263, found: 367.1270.

3,3′-((4-Methoxyphenyl)methylene)bis(1H-Indole) (3 e)

Orange solid, 85% (74.8 mg) isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.90 (br s, 2 H), 7.40 (d, J = 8.0 Hz, 2 H), 7.36 (d, J = 8.4 Hz, 2 H), 7.25–7.27 (m, 2 H), 7.18 (t, J = 7.6 Hz, 2 H), 7.01 (t, J = 7.6 Hz, 2 H), 6.82–6.84 (m, 2 H), 6.65 (d, J = 1.9 Hz, 2 H), 5.85 (s, 1 H), 3.79 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 157.9, 136.7, 136.2, 129.6, 127.0, 123.5, 121.9, 120.0, 119.2, 113.5, 111.0, 55.2, 39.3. **HRMS** (ESI) m/z calcd for $C_{24}H_{19}N_2O$ $(M-H)^+$: 351.1492, found: 351.1496.

3,3′-((2-Methoxyphenyl)methylene)bis(1H-Indole) (3 f)

Orange solid, 62% (54.6 mg) isolated yield. **^{1}H NMR** (500 MHz, DMSO-d6): δ ppm 10.78 (br s, 2 H), 7.35 (d, J = 8.2 Hz, 2 H), 7.24 (d, J = 7.8 Hz, 2 H), 7.13–7.19 (m, 2 H), 7.00–7.05 (m, 3 H), 6.86 (t, J = 7.6 Hz, 2 H), 6.81 (t, J = 7.3 Hz, 1 H), 6.74 (br s, 2 H), 6.23 (s, 1 H), 3.80 (s, 3 H). **^{13}C NMR** (126 MHz, DMSO-d6): δ ppm 156.3, 136.7, 132.7, 129.2, 127.1, 126.8, 123.6, 120.9, 120.1, 119.0, 118.2, 117.9, 111.5, 110.9, 55.6, 31.5. **HRMS** (ESI) m/z calcd for $C_{24}H_{19}N_2O$ $(M-H)^+$: 351.1492, found: 351.1496.

3,3′-(Benzo[d][1,3]dioxol-5-ylmethylene)bis(1H-Indole) (3 g)

Red solid, 65% (59.5 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.76 (br s, 2 H), 7.45 (d, J = 7.9 Hz, 2 H), 7.33 (d, J = 8.0 Hz, 2 H), 7.22 (t, J = 7.5 Hz, 2 H), 7.07 (t, J = 7.4 Hz, 2 H), 6.86–6.88 (m, 2 H), 6.77 (d, J = 8.1 Hz, 1 H), 6.59 (br s, 2 H), 5.92 (s, 2 H), 5.84 (s, 1 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ ppm 147.4, 145.7, 138.1, 136.6, 126.9, 123.5, 121.9, 121.5, 119.8, 119.6, 119.2, 111.0, 109.3, 107.9, 100.7, 39.8. **HRMS** (ESI) m/z calcd for $C_{24}H_{17}N_2O_2$ $(M-H)^+$: 365.1285, found: 365.1289.

3,3′-((3,4,5-Trimethoxyphenyl)methylene)bis(1H-Indole) (3 h)

Red solid, 82% (84.5 mg) isolated yield. **^{1}H NMR** (500 MHz, DMSO-d6): δ ppm 10.78 (br s, 2 H), 7.33–7.35 (m, 4 H), 7.03

(t, J=7.4 Hz, 2 H), 6.86–6.89 (m, 4 H), 6.72 (s, 2 H), 5.78 (s, 1 H), 3.65 (s, 6 H), 3.63 (s, 3 H). **^{13}C NMR** (126 MHz, DMSO-d6): δ ppm 152.5, 140.7, 136.5, 135.7, 126.6, 123.5, 120.8, 119.1, 118.1, 111.4, 105.8, 60.0, 55.8, 39.0. **HRMS** (ESI) m/z calcd for $C_{26}H_{23}O_3N_2$ $(M-H)^+$: 411.1703, found: 411.1708.

3,3′-((4-Fluorophenyl)methylene)bis(1H-Indole) (3 i)

Red solid, 72% (61.2 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.81 (br s, 2 H), 7.25–7.29 (m, 4 H), 7.18–7.23 (m, 2 H), 7.07–7.12 (m, 2 H), 6.84–6.95 (m, 4 H), 6.54 (dd, J= 2.4, 1.0 Hz, 2 H), 5.79 (s, 1 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ ppm 161.4 (d, J=244.1 Hz), 139.6 (d, J=2.9 Hz), 136.7, 130.0 (d, J=8.0 Hz), 126.9, 123.5, 122.0, 119.8, 119.5, 119.3, 114.9 (d, J=21.1 Hz), 111.1, 39.4. **HRMS** (ESI) m/z calcd for $C_{23}H_{16}FN_2$ $(M-H)^+$: 339.1292, found: 339.1296.

3,3′-((4-Chlorophenyl)methylene)bis(1H-Indole) (3 j)

Orange solid, 75% (66.8 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.86 (br s, 2 H), 7.28 (d, J=8.6 Hz, 4 H), 7.15–7.20 (m, 4 H), 7.10 (t, J=7.6 Hz, 2 H), 6.94 (t, J= 7.5 Hz, 2 H), 6.56 (br s, 2 H), 5.78 (s, 1 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ ppm 142.5, 136.7, 131.8, 130.0, 128.3, 126.9, 123.6, 122.1, 119.8, 119.3, 119.2, 111.1, 39.6. **HRMS** (ESI) m/z calcd for $C_{23}H_{16}ClN_2$ $(M-H)^+$: 355.0997, found: 355.1002.

3,3′-((4-Bromophenyl)methylene)bis(1H-Indole) (3 k)

Red solid, 62% (61.4 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.89 (br s, 2 H), 7.35–7.42 (m, 6 H), 7.18–7.24 (m, 4 H), 7.02–7.06 (m, 2 H), 6.62 (dd, J=2.3, 0.8 Hz, 2 H), 5.86 (s, 1 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ ppm 143.1, 136.6, 131.3, 130.4, 126.8, 123.6, 122.0, 119.9, 119.8, 119.3, 119.0, 111.1, 39.6. **LCMS** (ESI) m/z for $C_{23}H_{18}BrN_2$ $(M+H)^+$: 401.0.

3,3′-((4-Iodophenyl)methylene)bis(1H-Indole) (3 l)

Red solid, 64% (71.7 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.90 (br s, 2 H), 7.61 (d, J=8.4 Hz, 2 H), 7.36–7.39 (m, 4 H), 7.18–7.22 (m, 2 H), 7.11 (d, J=8.1 Hz, 2 H), 7.01–7.05 (m, 2 H), 6.64 (dd, J=2.4, 0.9 Hz, 2 H) 5.84 (s, 1 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ ppm 143.8, 137.3, 136.6, 130.8, 126.8, 123.6, 122.1, 119.8, 119.3, 119.0, 111.1, 91.4, 39.8. **LCMS** (ESI) m/z for $C_{23}H_{17}IN_2$ $(M)^+$: 448.0.

3,3′-((3-(Trifluoromethyl)phenyl)methylene)bis(1H-Indole) (3 m)

Pink solid, 94% (91.7 mg) isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.93 (br s, 2 H), 7.67 (s, 1 H), 7.52 (t, J= 7.8 Hz, 2 H), 7.37–7.41 (m, 5 H), 7.19–7.23 (m, 2 H), 7.03–7.07 (m, 2 H), 6.62 (br s, 2H), 5.97 (s, 1 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 145.0, 136.6, 132.0, 130.4 (q, J= 31.9 Hz), 128.7, 126.7, 125.4 (q, J=3.8 Hz), 124.3 (q, J= 272.2 Hz), 123.6, 123.1 (q, J=3.8 Hz), 122.1, 119.7, 119.4, 118.8, 111.1, 40.0. **HRMS** (ESI) m/z calcd for $C_{24}H_{16}F_3N_2$ $(M-H)^+$: 389.1260, found: 389.1267.

3,3′-((3,5-Bis(trifluoromethyl)phenyl)methylene)bis(1H-Indole) (3 n)

Red solid, 91% (104.2 mg) isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.96 (br s, 2 H), 7.85 (s, 2 H), 7.81 (s, 1 H), 7.39 (t, J=6.9 Hz, 4 H), 7.23–7.27 (m, 2 H), 7.08 (t, J= 7.6 Hz, 2 H), 6.62 (d, J=1.8 Hz, 2 H), 6.05 (s, 1 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 146.7, 136.7, 131.4 (q, J=33.2 Hz), 128.7, 126.5, 123.7, 123.4 (q, J=273.2 Hz), 122.4, 120.5 (apparent sept, J=3.4 Hz), 119.6, 119.4, 117.9, 111.3, 40.0. **HRMS** (ESI) m/z calcd for $C_{25}H_{15}F_6N_2$ $(M-H)^+$: 457.1134, found: 457.1142.

3,3′-(Naphthalen-1-ylmethylene)bis(1H-Indole) (3 p)

Red solid, 88% (81.9 mg) isolated yield. **^{1}H NMR** (400 MHz, DMSO-d6): δ ppm 10.86 (br s, 2 H), 8.29 (d, J=8.0 Hz, 1 H), 7.92 (d, J=7.6 Hz, 1 H), 7.77 (d, J=8.4 Hz, 1 H), 7.43–7.47 (m, 2 H), 7.39 (d, J=8.0 Hz, 2 H), 7.36 (d, J=7.6 Hz, 1 H), 7.31 (d, J=7.6 Hz, 3 H), 7.05 (t, J=7.4 Hz, 2 H), 6.86 (t, J= 7.4 Hz, 2 H), 6.78 (br s, 2 H), 6.68 (s, 1 H). **^{13}C NMR** (100.6 MHz, DMSO-d6): δ ppm 140.4, 136.7, 133.7, 131.4, 128.7, 126.7, 125.9, 125.6, 125.4, 124.4, 124.1, 121.0, 119.1, 118.4, 117.8, 111.6, 35.4. **HRMS** (ESI) m/z calcd for $C_{27}H_{19}N_2$ $(M-H)^+$: 371.1543, found: 371.1548.

3,3′-(Pyridin-3-ylmethylene)bis(1H-Indole) (3 q)

Pink solid, 72% (58.2 mg) isolated yield. **^{1}H NMR** (500 MHz, DMSO-d6): δ ppm 10.90 (br s, 2 H), 8.61 (s, 1 H), 8.39 (d, J= 3.8 Hz, 1 H), 7.70 (d, J=7.6 Hz, 1 H), 7.36 (d, J=8.0 Hz, 2 H), 7.28–7.30 (m, 3 H), 7.05 (t, J=7.4 Hz, 2 H), 6.87–6.89 (m, 4 H), 5.91 (s, 1 H). **^{13}C NMR** (126 MHz, DMSO-d6): δ ppm 149.6, 147.2, 140.3, 136.6, 135.7, 126.4, 123.7, 123.3, 121.1, 119.0, 118.4, 117.2, 111.6, 37.1. **HRMS** (ESI) m/z calcd for $C_{22}H_{18}N_3$ $(M+H)^+$: 324.1495, found: 324.1494.

Di(1H-Indol-3-yl)diphenylmethane (3 r)

Colourless solid, 15% (14.9 mg) isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.87 (br s, 2 H), 7.27–7.31 (m, 6 H), 7.17–7.22 (m, 6 H), 7.04–7.08 (m, 2 H), 6.74–6.80 (m, 6 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 145.9, 136.8, 130.1, 127.7, 127.4, 125.9, 124.9, 123.8, 122.5, 121.5, 119.0, 110.9, 53.8. **HRMS** (ESI) m/z calcd for $C_{29}H_{21}N_2$ $(M-H)^+$: 397.1699, found: 397.1763.

3,3′-(Ethane-1,1-diyl)bis(1H-Indole) (3 s)

White solid, 15% (10.0 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.89 (br s, 2 H), 7.60 (d, J=8.0 Hz, 2 H), 7.36 (d, J=8.1 Hz, 2 H), 7.16–7.20 (m, 2 H), 7.04–7.08 (m, 2 H), 6.93 (d, J=1.1 Hz, 2 H), 4.70 (q, J=7.1 Hz, 1 H), 1.83 (d, J= 7.1 Hz, 3 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ ppm 136.6, 126.9, 121.7, 121.6, 121.2, 119.7, 119.0, 111.0, 28.1, 21.7. **LCMS** (ESI) m/z for $C_{18}H_{17}N_2$ $(M+H)^+$: 261.0.

3,3′-(Butane-1,1-diyl)bis(1H-Indole) (3 t)

Brown solid, 47% (33.9 mg) isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.83 (br s, 2 H), 7.65 (d, J = 8.1 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.17–7.21 (m, 2 H), 7.06–7.10 (m, 2 H), 6.96 (d, J = 2.0 Hz, 2 H), 4.53 (t, J = 7.4 Hz, 1 H), 2.21–2.27 (m, 2 H), 1.45–1.50 (m, 2 H), 1.00 (t, J = 7.4 Hz, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 136.5, 127.1, 121.6, 121.4, 120.5, 119.6, 118.9, 111.0, 38.1, 33.6, 21.4, 14.2. **HRMS** (ESI) m/z calcd for $C_{20}H_{19}N_2$ $(M-H)^+$: 287.1543, found: 287.1547.

3,3′-(Pentane-1,1-diyl)bis(1H-Indole) (3 u)

Brown solid, 66% (49.9 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.68 (br s, 2 H), 7.51 (d, J = 8.1 Hz, 2 H), 7.19–7.21 (m, 2 H), 7.03–7.07 (m, 2 H), 6.93–6.97 (m, 2 H), 6.84 (d, J = 2.4 Hz, 2 H), 4.38 (t, J = 7.4 Hz, 1 H), 2.10–2.15 (m, 2 H), 1.26–1.33 (m, 4 H), 0.78 (t, J = 7.1 Hz, 3 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ ppm 136.5, 127.1, 121.7, 121.4, 120.5, 119.6, 118.9, 111.0, 35.6, 33.9, 30.5, 22.8, 14.1. **HRMS** (ESI) m/z calcd for $C_{21}H_{21}N_2$ $(M-H)^+$: 301.1699, found: 301.1705.

3,3′-(Phenylmethylene)bis(5-Methoxy-1H-Indole) (4 a)

Red solid, 95% (90.8 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$ + DMSO-d6): δ ppm 10.45 (br s, 2 H), 7.32 (d, J = 7.3 Hz, 2 H), 7.19–7.24 (m, 4 H), 7.13 (t, J = 7.3 Hz, 1 H), 6.64–6.72 (m, 6 H), 5.69 (s, 1 H), 3.59 (s, 6 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$ + DMSO-d6): δ ppm 152.6, 144.6, 131.7, 128.2, 127.7, 126.8, 125.5, 124.2, 117.5, 111.7, 110.4, 101.2, 55.1, 39.8. **HRMS** (ESI) m/z calcd for $C_{25}H_{21}O_2N_2$ $(M-H)^+$: 381.1598, found: 381.1603.

3,3′-((4-(Tert-Butyl)phenyl)methylene)bis (5-Methoxy-1H-Indole) (4 b)

Red solid, 80% (87.6 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.81 (br s, 2 H), 7.27–7.32 (m, 4 H), 7.23 (d, J = 8.5 Hz, 2 H), 6.82–6.85 (m, 4 H), 6.69 (br s, 2 H), 5.76 (s, 1 H), 3.70 (s, 6 H), 1.32 (s, 9 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ ppm 153.6, 148.7, 140.8, 131.8, 128.3, 127.6, 125.0, 124.3, 119.5, 111.8, 111.6, 102.0, 55.8, 39.8, 34.4, 31.4. **HRMS** (ESI) m/z calcd for $C_{29}H_{29}O_2N_2$ $(M-H)^+$: 437.2224, found: 437.2229.

3,3′-(Phenylmethylene)bis(5-Bromo-1H-Indole) (4 c)

Orange solid, 75% (89.6 mg) isolated yield. **^{1}H NMR** (400 MHz, DMSO-d6): δ ppm 11.07 (br s, 2 H), 7.43 (d, J = 2.0 Hz, 2 H), 7.33–7.35 (m, 4 H), 7.27–7.31 (m, 2 H), 7.17–7.21 (m, 1 H), 7.16 (dd, J = 8.6, 1.9 Hz, 2 H), 6.89 (d, J = 2.0 Hz, 2 H), 5.86 (s, 1 H). **^{13}C NMR** (100.6 MHz, DMSO-d6): δ ppm 144.3, 135.3, 128.4, 128.2, 126.1, 125.3, 123.5, 121.2, 117.7, 113.6, 110.9, 38.9. **HRMS** (ESI) m/z calcd for $C_{23}H_{15}Br_2N_2$ $(M-H)^+$: 476.9597, found: 476.9604.

3,3′-(Phenylmethylene)bis(5-Nitro-1H-Indole) (4 d)

Yellow solid, 25% (25.8 mg) isolated yield. **^{1}H NMR** (400 MHz, DMSO-d6): δ ppm 11.66 (br s, 2 H), 8.32 (d, J = 2.3 Hz, 2 H), 7.97 (dd, J = 9.0, 2.3 Hz, 2 H), 7.55 (d, J = 9.1 Hz, 2 H), 7.39–7.41 (m, 2 H), 7.30–7.34 (m, 2 H), 7.20–7.24 (m, 1 H), 7.14 (d, J = 1.8 Hz, 2 H), 6.20 (s, 1 H). **^{13}C NMR** (100.6 MHz, DMSO-d6): δ ppm 143.8, 140.2, 139.8, 128.5, 128.2, 127.6, 126.4, 125.8, 120.5, 116.6, 116.2, 112.1, 38.5. **HRMS** (ESI) m/z calcd for $C_{23}H_{15}O_4N_4$ $(M-H)^+$: 411.1088, found: 411.1103.

3,3′-(Phenylmethylene)bis(1H-Indole-5-Carbonitrile) (4 e)

Colourless solid, 30% (27.9 mg) isolated yield. **^{1}H NMR** (400 MHz, DMSO-d6): δ ppm 11.50 (br s, 2 H), 7.80 (br s, 2 H), 7.53–7.55 (m, 2 H), 7.37–7.41 (m, 4 H), 7.30 (t, J = 7.5 Hz, 2 H), 7.19–7.22 (m, 1 H), 7.14 (d, J = 1.9 Hz, 2 H), 6.03 (s, 1 H). **^{13}C NMR** (100.6 MHz, DMSO-d6): δ ppm 144.0, 138.2, 128.4, 128.2, 126.3, 126.2, 124.6, 123.8, 120.8, 118.8, 112.9, 100.4, 38.5. **HRMS** (ESI) m/z calcd for $C_{25}H_{15}N_4$ $(M-H)^+$: 371.1291, found: 371.1298.

3,3′-(Phenylmethylene)bis(2-Methyl-1H-Indole) (4 f)

Pink solid, 40% (35 mg) isolated yield. **^{1}H NMR** (500 MHz, DMSO-d6): δ ppm 10.76 (br s, 2 H), 7.18–7.27 (m, 7 H), 6.87–6.91 (m, 2 H), 6.81 (d, J = 7.8 Hz, 2 H), 6.65–6.69 (m, 2 H), 5.93 (s, 1 H), 2.07 (s, 6 H). **^{13}C NMR** (126 MHz, DMSO-d6): δ ppm 144.3, 135.1, 132.1, 128.7, 128.3, 127.9, 125.8, 119.5, 118.5, 117.9, 112.2, 110.3, 38.6, 11.9. **HRMS** (ESI) m/z calcd for $C_{25}H_{21}N_2$ $(M-H)^+$: 349.1699, found: 349.1704.

3,3′-(Phenylmethylene)bis(2-Phenyl-1H-Indole) (4 g)

Brown solid, 35% (41.5 mg) isolated yield. **^{1}H NMR** (400 MHz, DMSO-d6): δ ppm 11.33 (br s, 2 H), 7.38 (d, J = 8.1 Hz, 2 H), 7.29–7.32 (m, 4 H), 7.27 (d, J = 7.4 Hz, 2 H), 7.21–7.24 (m, 7 H), 7.16 (d, J = 7.1 Hz, 2 H), 6.99–7.03 (m, 2 H), 6.90 (d, J = 8.1 Hz, 2 H), 6.65–6.69 (m, 2 H), 5.98 (s, 1 H). **^{13}C NMR** (100.6 MHz, DMSO-d6): δ ppm 145.5, 136.3, 135.3, 132.8, 128.7, 128.3, 128.2, 128.0, 127.2, 126.0, 120.9, 120.8, 118.5, 114.2, 111.3, 38.9. **HRMS** (ESI) m/z calcd for $C_{35}H_{25}N_2$ $(M-H)^+$: 473.2012, found: 473.2019.

(R)-3-((1H-Indol-3-yl)(phenyl)methyl)-5-Methoxy-1H-Indole (4 j)

Red solid, 45% (39.6 mg) isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.87 (br s, 1 H), 7.77 (br s, 1 H), 7.41 (d, J = 8.0 Hz, 1 H), 7.37 (d, J = 7.3 Hz, 2 H), 7.35 (d, J = 8.4 Hz, 1 H), 7.30 (t, J = 7.8 Hz, 2 H), 7.22–7.25 (m, 2 H), 7.19 (t, J = 8.0 Hz, 1 H), 7.03 (t, J = 7.8 Hz, 1 H), 6.85–6.87 (m, 2 H), 6.64 (d, J = 1.5 Hz, 1 H), 6.61 (d, J = 1.9 Hz, 1 H), 5.85 (s, 1 H), 3.72 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 153.6, 144.0, 136.7, 131.8, 128.7, 128.2, 127.4, 127.0, 126.1, 124.4, 123.6, 121.8, 119.9, 119.5, 119.3, 119.1, 111.9, 111.7, 111.0, 101.8, 55.8, 40.2. **HRMS** (ESI) m/z calcd for $C_{24}H_{19}N_2O$ $(M-H)^+$: 351.1492, found: 351.1498.

(S)-6-Bromo-3-((5-Methoxy-1H-Indol-3-yl)(phenyl) methyl)-1H-Indole (4k)

Red solid, 50% (53.8 mg) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.88 (br s, 1 H), 7.83 (br s, 1 H), 7.47 (d, J= 1.5 Hz, 1 H), 7.28–7.35 (m, 4 H), 7.21–7.25 (m, 3 H), 7.10 (dd, J=8.4 Hz, 1.7 Hz, 1 H), 6.86 (dd, J=8.7 Hz, 2.4 Hz, 1 H), 6.82 (d, J=2.4 Hz, 1 H), 6.61–6.62 (m, 2 H), 5.80 (s, 1 H), 3.72 (s, 3 H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ ppm 153.7, 143.6, 137.4, 131.8, 128.6, 128.3, 127.3, 126.3, 125.9, 124.3, 124.2, 122.5, 121.2, 119.7, 119.0, 115.4, 113.9, 111.9, 111.8, 101.8, 55.8, 40.1. **HRMS** (ESI) m/z calcd for $C_{24}H_{18}BrN_2O$ $(M-H)^+$: 429.0597, found: 429.0603.

3,3′-(Phenylmethylene)bis(1H-Pyrrolo[2,3-*b*] pyridine) (4l)

Colourless solid, 50% (40.5 mg) isolated yield. **^{1}H NMR** (400 MHz, DMSO-d6): δ ppm 11.42 (br s, 2 H), 8.16 (d, J= 3.9 Hz, 2 H), 7.60 (dd, J=7.8, 1.3 Hz, 2 H), 7.36 (d, J= 7.3 Hz, 2 H), 7.28 (t, J=7.5 Hz, 2 H), 7.17–7.21 (m, 1 H), 6.98 (d, J=2.1 Hz, 2 H), 6.92 (dd, J=7.9, 4.6 Hz, 2 H), 5.86 (s, 1 H). **^{13}C NMR** (100.6 MHz, DMSO-d6): δ ppm 148.9, 144.1, 142.5, 128.3, 127.2, 126.2, 123.9, 118.8, 116.5, 114.9, 38.9. **HRMS** (ESI) m/z calcd for $C_{21}H_{17}N_4$ $(M+H)^+$: 325.1448, found: 325.1444.

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