Supporting Information

Synthesis of a Novel Type of 2,3′-BIMs via Platinum-Catalysed Reaction of Indolylallenenes with Indoles

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1. General experiment details

All reagents were purchased from commercial sources and used without further purification, unless stated otherwise. All reactions were carried out under nitrogen atmosphere and in the absence of moisture, unless stated otherwise. Reactions using microwave irradiation were carried out in Biotage Initiator+ Microwave system. Reactions were monitored using Thin Layer Chromatography (TLC) using 0.2 mm thick silica gel plates 60F-254 (5735 Merck) with a mobile phase of hexane and ethyl acetate, with visualization by illumination by uv light $\lambda = 254$ nm or staining with either potassium permanganate or phosphomolybdic acid solution.

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker (500 MHz) spectrometer with CDCl$_3$ solvent. Chemical shifts ($\delta$) are given in parts per million (ppm) and coupling constants values ($J$) are given in Hertz (Hz), and are approximated to the nearest 0.1 Hz. $^{13}$C NMR was recorded using broad-band proton decoupling. Abbreviations used in NMR analyses are as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, dq = doublet of quartets, qd = quartet of doublets and m = multiplet. HRMS were performed by EPSRC National Mass Spectrometry Service Centre, Swansea.
2. Optimisation

Screening of solvent, time, temperature, concentration and equivalents of platinum, indole and methanol were carried out for the reaction of 3-methyl-N-(2,3-butadienyl)indole 1\textsubscript{a} with external indole 2\textsubscript{a} to optimise the conditions for selective formation of BIM 3\textsubscript{aa}. These reactions were carried out at the Novartis laboratories using LCMS ELSD (Evaporative Light Scattering Detector) traces for detecting the different components of the reactions.

Reported reactions by Muñoz et al.\textsuperscript{1} were carried out at 70°C using thermal heating in an oil bath. However, it was established that using microwave irradiation decreased the reaction time dramatically from 20 hours to 1-2 hours as well as increasing both the selectivity and yield of product 3\textsubscript{aa}. Microwave irradiation was therefore used for all further screening and extensive screening of solvent and temperature was carried out with THF, 1,4-Dioxane, CPME (cyclopentylmethyl ether) and 2-methyl THF (Table 2.1). We found that 1,4-dioxane at 130°C under microwave irradiation for 1 hour gave 71 % yield (61% isolated) to desired compound 3\textsubscript{aa}. For practical experimental reasons, concentration of 0.2M was preferred due to the limitation of minimum solvent required for microwave experiments.

![Diagram](image.png)

Table 2.1. Screening of conditions for the intra-intermolecular reaction of indole 2\textsubscript{a} and 3-methyl-N-(2,3-butadienyl)indole 1\textsubscript{a}.

| Entry | Solvent    | Concentration | Temp (°C) | Time (min) | % 4\textsubscript{a}/4\textsubscript{a'} | % 3\textsubscript{aa}\textsuperscript{a} |
|-------|------------|---------------|-----------|------------|-----------------------------------------|---------------------------------|
| 1     | THF        | 0.2M          | 100       | 180        | 0                                       | 33                              |
| 2     | THF        | 0.2M          | 130       | 30         | 0                                       | 37                              |
| 3     | 1,4-Dioxane| 0.2M          | 130       | 60         | 5 (0.3:1)                               | 61                              |
| 4     | 1,4-Dioxane| 0.1M          | 120       | 60         | 12 (1:1.3)                              | 58                              |
| 5     | 1,4-Dioxane| 0.4M          | 120       | 60         | 0                                       | 68                              |
| 6     | 1,4-Dioxane| 0.2M          | 150       | 15         | 0                                       | 47                              |
| 7     | CPME       | 0.2M          | 180       | 20         | 5                                       | 39                              |
| 8     | 2-Methyl THF| 0.2M         | 150       | 15         | 0                                       | 5                               |

\textsuperscript{a) Isolated product.}

\textsuperscript{1} M. P. Muñoz, M. de la Torre and M. A. Sierra, Chem. Eur. J. 2012, 18, 4499-4504.
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Variations in equivalents of platinum, indole and methanol were then explored. We found that although results were slightly better with PtCl₂ 10 mol %, similar reactivity was achieved when 5 mol % was used, so this was chosen as the optimized conditions. Table 2.2 shows the results when different amounts of methanol were used, with the best results achieved with 3 or more equivalents as already reported (entries 3-5).

Table 2.2. Screening eqs of MeOH for the intra-intermolecular reaction of indole 2a and 3-methyl-N-(2,3-butadienyl)indole 1a.

| Entry | Equivalents of MeOH | % conversion to 3aa¹ |
|-------|---------------------|----------------------|
| 1     | 1                   | 92                   |
| 2     | 2.5                 | 95                   |
| 3     | 3                   | 100                  |
| 4     | 3.5                 | 100                  |
| 5     | 4                   | 100                  |

¹) Measured by LCMS ELDS.

The equivalent of indole to allene was also investigated and Table 2.3 shows that using 3 or 4 equivalents gives the best conversion to product 3aa.

Table 2.3. Screening eqs of indole 2a for the intra-intermolecular reaction of indole 2a and 3-methyl-N-(2,3-butadienyl)indole 1a.

| Entry | Equivalents of indole 2a | % conversion to 3aa² |
|-------|--------------------------|----------------------|
| 1     | 1                        | 100⁰                 |
| 2     | 1.5                      | 91                   |
| 3     | 2                        | 91                   |
| 4     | 2.5                      | 90                   |

⁰) Measured by LCMS ELDS.
After this screening we chose the optimised conditions as: microwave irradiation at 130°C for 1 hour with 5 mol % PtCl₂, 3 eqs indole, 3 eqs of methanol and 1,4-dioxane (0.2 M). These newly optimised conditions were able to give an isolated yield of 61 % for compound 3aa. It is important to state that the reaction requires dry 1,4-dioxane as the solvent as reactions carried out with wet 1,4-dioxane under optimised conditions resulted mainly in the formation of the cyclised products 4a/4a’ (Table 2.4).

| Entry | Dioxane | % yield of 4a/4a’ | % yield of 3aa |
|-------|---------|------------------|---------------|
| 1     | Wet     | 58 % (not isolated) | 0             |
| 2     | Dry     | 5                | 61            |

3. General procedure for platinum-catalysed reaction of indolyl allene with external nucleophile under optimised conditions

PtCl₂ (5 mol %) and the appropriate nucleophile (3 eqs) were added to a microwave vial, capped and flushed with N₂ atmosphere. The solids were dissolved in dry 1,4-dioxane and the appropriate indolylallene (1 eq) dissolved in dry 1,4-dioxane (0.2 M) was added. Dry methanol (3 eqs) was added and the vial was heated under microwave irradiation at 130°C for 1 hour, or the appropriated time indicated for each particular compound. The resulting reaction mixture was filtered through Celite and washed with DCM and compounds purified via column chromatography in silica gel with Pet/EtOAc.
4. Characterisation of products

2,3’-BIM 3aa and cycles 4a/4a’:

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Cycles 4a and 4a’: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.48 – 7.42 (m, 2H, H-\(7+7'\)), 7.21 – 6.92 (m, 6H, H-\(4-6\) and H-\(4'-6'\)), 6.59 (dt, \(J = 9.9\), 1.8 Hz, 1H, H-13\'), 6.04 – 5.93 (m, 2H, H-11 and H-12), 5.92 – 5.86 (m, 1H, H-12'), 4.53 (ddd, \(J = 6.7\), 4.4, 2.7 Hz, 2H, H-10), 3.98 (t, \(J = 6.9\) Hz, 2H, H-10'), 3.47 – 3.41 (m, 2H, H-13), 2.58 – 2.52 (m, 2H, H-11'), 2.24 (s, 3H, H-14'), 2.19 (s, 3H, H-14). \(^1\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 136.74 (C-9'), 135.3 (C-9), 131.6 (C-2'), 129.2 (C-2), 129.2 (C-8'), 128.5 (C-8), 122.9 (CH, C-12'), 122.1 (CH, C-11 or 12), 121.9 (CH, C-4-6 or C-4'-6'), 120.5 (CH, C-11 or 12), 120.3 (CH, C-4-6 or C-4'-6'), 119.2 (CH, C-4-6 or C-4'-6'), 118.9 (CH, C-4-6 or C-4'-6'), 118.8 (CH, C-7 or C-7'), 118.5 (CH, C-13'), 117.8 (CH, C-7 or C-7'), 108.5 (CH, C-4-6 and C-4'-6'), 108.4 (CH, C-4-6 and C-4'-6'), 107.5 (C-3'), 104.5 (C-3) 41.8 (CH\(_2\), C-10), 39.8 (CH\(_2\), C-10'), 24.4 (CH\(_2\), C-11'), 22.8 (CH\(_2\), C-13), 8.3 (CH\(_3\), C-14), 8.1 (CH\(_3\), C-14'). Spectra consistent with previously published data.\(^1\)

2,3’-BIM 3aa: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.81 (s, 1H, H-17), 7.66 (d, \(J = 7.9\) Hz, 1H, H-4), 7.57 (d, \(J = 7.8\) Hz, 1H, H-7), 7.36 (t, \(J = 7.4\) Hz, 2H, H-5 + H-6), 7.23 (m, 2H, H-19 + H-20), 7.16 (t, \(J = 7.5\) Hz, 2H, H-18 + H-21), 6.52 (s, 1H, H-16), 4.81 (t, \(J = 4.3\) Hz, 1H, H-13), 4.34 – 4.25 (m, 1H, H-10), 3.94 (td, \(J = 11.1\), 4.8 Hz, 1H, H-10), 2.44 – 2.35 (m, 1H, H-12), 2.24 – 2.15 (m, 1H, H-12), 2.15 – 2.06 (m, 1H, H-11), 2.03 (s, 3H, H-14), 1.97 – 1.88 (m, 1H, H-11). \(^1\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 136.70 (C-2), 135.88 (C-9), 134.87 (C-23), 128.74 (C-8), 126.22 (C-22), 123.28 (CH, C-16), 121.94 (CH, C-19/20), 120.29 (CH, C-19/20), 119.34 (CH, C-18/21), 118.98 (CH, C-4), 118.78 (C-3), 118.05 (CH, C-7), 111.36 (CH, C-5/6), 108.65 (CH, C-5/6), 105.96 (C-15), 42.58 (CH\(_2\), C-10), 30.42 (CH, C-13), 28.17 (CH\(_2\), C-12), 19.56 (CH\(_2\), C-11), 8.36 (CH\(_3\), C-14). Spectra consistent with previously published data.\(^1\) M.P. 151-158°C.
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2,3’-BIM 3ba

Synthesised using the general procedure from 5-methoxy-1-(2,3-butadien-1-yl)-3-methyl-1H-indole (60 mg, 0.28 mmol), dry methanol (34 µl, 0.84 mmol), indole (98 mg, 0.84 mmol), PtCl₂ (3.7 mg, 0.014 mmol) in 1.4 mL of dry 1,4-dioxane. Obtained by column chromatography, Pet/EtOAc (20:1), 44.1 mg, 0.13 mmol, 48 % of compound 3ba as a fluorescent yellow solid.

\(^1\)H NMR (500 MHz, CDCl₃) δ 7.88 (s, 1H, H-19), 7.63 (d, J = 8.2 Hz, 1H, H-7), 7.37 (d, J = 8.2 Hz, 1H, H-20), 7.23-7.19 (m, 2H, H-21+22), 7.16-7.11 (m, 1H, H-6), 6.98 (d, J = 2.4 Hz, 1H, H-4), 6.85 (dd, J = 8.2, 2.4 Hz, 1H, H-23), 6.56 (d, J = 1.6 Hz, 1H, H-18), 4.77 (t, J = 4.3 Hz, 1H, H-13), 4.26-4.2 (m, 1H, H-10), 3.91-3.86 (m, 1H, H-10), 3.88 (s, 3H, H-15), 2.35 – 2.32 (m, 1H, H-12), 2.20 – 2.12 (m, 1H, H-12), 2.11-2.05 (m, 1H, H-11), 1.97 (s, 3H, H-16), 1.93-1.86 (m, 1H, H-11).

\(^13\)C NMR (126 MHz, CDCl₃) δ 153.96 (C-5), 136.69 (C-2), 135.63 (C-9), 131.27 (C-8), 128.93 (C-25), 126.22 (C-24), 123.23 (CH, C-18), 121.94 (CH, C-21/22), 119.33 (CH, C-6), 118.97 (CH, C-7), 118.85 (C-3), 111.31 (CH, C-20), 110.10 (CH, C-23), 109.26 (CH, C-21/22), 105.58 (C-17), 100.31 (CH, C-4), 56.08 (CH₃, OMe, C-15), 42.61 (CH₂, C-10), 30.40 (CH₂, C-13), 28.07 (CH₂, C-12), 19.55 (CH₂, C-11), 8.38 (CH₃-C-16). \(\nu_{max}/cm^{-1}:\) 3410 (s, NH), 3053, 2942 (m, CH). M.P. 189-192°C.

2,3’-BIM 3ca

Synthesised using the general procedure from 5-methyl-1-(2,3-butadien-1-yl)-3-methyl-1H-indole (45 mg, 0.23 mmol), dry methanol (3.1 µl, 0.68 mmol), indole (80 mg, 0.68 mmol), PtCl₂ (3 mg, 0.011 mmol) in 1.4 mL of dry 1,4-dioxane (0.2 M). Obtained by column chromatography, Pet/Et₂O (20:1) 15.1 mg, 0.05 mmol, 21 % of compound 3ca as a yellow oil.

\(^1\)H NMR (500 MHz, CDCl₃) δ 7.85 (s, 1H, H-18), 7.64 (d, J = 8.1 Hz, 1H, H-Ar), 7.36 (d, J = 8.1 Hz, 1H, H-Ar), 7.32 (d, J = 0.7 Hz, 1H, H-Ar), 7.24 – 7.18 (m, 2H, H-Ar), 7.16 – 7.11 (m, 1H, H-Ar), 7.02 (dd, J = 8.1, 1.4 Hz, 1H, H-Ar), 6.53 (dd, J = 2.3, 0.7 Hz, 1H, H-17), 4.78 (t, J = 4.3 Hz, 1H, H-13), 4.25 (dd, J = 11.2, 4.9, 3.5 Hz, 1H, H-10), 3.89 (dd, J = 11.2, 4.9 Hz, 1H, H-10), 2.49 (s, 3H, H-14), 2.39 – 2.33 (m, 1H, H-12), 2.21 – 2.12 (m, 1H, H-12), 2.11 – 2.01 (m, 1H, H-11), 1.98 (s, 3H, H-15), 1.92 – 1.85 (m, 1H, H-11). \(^13\)C NMR (126 MHz, CDCl₃) δ 136.69 (C-2), 134.9 (C-9), 134.3 (C-24), 128.9 (C-5), 128.1 (C-8), 126.2 (C-23), 123.3 (CH, C-17), 121.9 (CH Ar), 121.8 (CH Ar), 119.8 (C-3), 119.3 (CH Ar), 118.9 (CH Ar), 117.8 (CH Ar), 111.3 (CH Ar), 108.3 (CH Ar), 105.4 (C-16), 42.6 (CH₂, C-10), 30.4 (CH, C-13), 28.1 (CH₂, C-12), 21.6 (CH₃, C-14), 19.6 (CH₂, C-11), 8.3 (CH₃, C-15). HRMS (FTMS + p NSI) ((DCM) / MeOH + NH₄OAc): Calculated for C₂₂H₂₂N [M+H]: 315.1856 found: 315.1858.
Supporting Information

2,3'-BIM 3da and cycles 4d:4d'

Cycle 4d  
Cycle 4d'

Synthesised using the general procedure from 5-bromo-1-(2,3-butadien-1-yl)-3-methyl-1H-indole (100 mg, 0.38 mmol), PtCl₂ (5 mg, 0.02 mmol), indole (133 mg, 1.14 mmol) and dry methanol (50 µl, 1.14 mmol) in 1.9 mL of dry 1,4-dioxane. Obtained by column chromatography, Pet:EtOAc, (15:1), 30 mg, 0.08 mmol, 20 % of compound 3da as a brown oil and 53 mg, 0.2 mmol, 53 % of compounds 4d:4d' as an inseparable mixture (1:0.95).

Cycles 4d:4d': ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, J = 1.7 Hz, 1H, H-4'), 7.53 (d, J = 1.8 Hz, 1H, H-4'), 7.21 – 7.11 (m, 2H, H-6 and H-7), 7.00 (m, 2H, H-6' and H-7'), 6.56 (d, J = 9.9 Hz, 1H, H-12), 6.02 - 5.95 (m, 1H, H-11), 5.92 (m, 2H, H-13' and H-12'), 4.46 (s, 2H, H-11'), 3.97 – 3.88 (m, 2H, H-13), 3.40 (s, 2H, H-10'), 2.59 – 2.47 (m, 2H, H-10), 2.17 (s, 3H, H-15), 2.12 (s, 3H, H-15'). ¹³C NMR (126 MHz, CDCl₃) δ 135.36 (C-9 or 9'), 133.99 (C-9 or 9'), 132.57 (C-2 or 2'), 130.85 (C-2 or 2'), 130.66 (C-8 or 8'), 130.18 (C-8 or 8'), 124.57 (CH, C-4'), 123.76 (CH, C-4'), 122.89 (CH, C-6), 121.90 (CH, C-7), 121.36 (CH, C-6'), 120.39 (CH, C-7'), 120.29 (CH, C-12), 118.24 (CH, C-11), 112.52 (C-5 or 5'), 112.00 (C-5 or 5'), 109.89 (CH, C-13'), 107.02 (C-3 or 3'), 104.01 (C-3 or 3'), 41.83 (CH₂, C-11), 38.86 (CH₂, C-13), 30.95 (CH, C-12'), 24.31 (CH₃, C-10'), 22.80 (CH₃, C-10), 8.19 (CH₃, H-15), 8.04 (CH₃, H-15'). fmax/cm⁻¹: 2967 (m, =C-H), 2924 (s, C-H), 2857 (m, C-H), 1699 (m, C=C), 1459 (m, C-C in ring) 1351 (w, Ar-H), 1204 (w, C-N).

2,3'-BIM 3da: ¹H NMR (500 MHz, CDCl₃) δ 7.97 (s, 1H, H-18), 7.65 - 7.60 (d, J = 1.8 Hz, 1H, H-7), 7.57 (d, J = 8.0 Hz, 1H, H-4), 7.39 - 7.32 (m, 1H, H-6), 7.23 - 7.14 (m, 4H, H-22, H-20, H-19 and H-21), 6.51 - 6.48 (m, 1H, H-17), 4.75 (t, J = 4.4 Hz, 1H, H-13), 4.26 - 4.17 (m, 1H, H-10), 3.88 (td, J = 11.1, 4.9 Hz, 1H, H-10), 2.38 - 2.31 (m, 2H, H-11 and H-12), 2.03 (s, 3H, H-15), 1.92 (d, J = 9.4 Hz, 2H, H-12 and H-11). ¹³C NMR (126 MHz, CDCl₃) δ 136.70 (C-9), 132.61 (C-2), 134.48 (C-12), 126.12 (C-23), 123.00 (CH, C-17), 122.92 (CH, C-22/21/20/19), 122.06 (CH, C-22/21/20/19), 120.63 (CH, C-4), 119.43 (CH, C-7), 118.91 (CH, C-22/21/20/19), 118.45 (C-5), 112.31 (C-3), 111.38 (CH, C-6), 110.04 (CH, C-22/21/20/19), 105.81 (C-16), 42.65 (CH₂), 30.45 (CH, C-13), 28.00 (CH₂, C-11), 19.45 (CH₂, C-12), 8.24 (CH₃, C-15). fmax/cm⁻¹: 3383 (m, br, N-H), 2957 (m, =C-H), 2924 (s, C-H), 2854 (m, C-H), 1713 (s, C=C), 1461 (s, Ar-H), 1366 (m, C-N). HRMS (FTMS + p NSI) ((MeOH)/ MeOH + NH₄OAc): Calc. for C₂₁H₁₉BrN₂ (M⁺H): 379.0804. Found: 379.0807. Calc. for C₂₁H₁₉BrN₂ [M+H]⁺: 381.0784. Found: 381.0786.
Supporting Information

Cycles 4e:4e’:

Cycle 4e

Cycle 4e’

Synthesised using the general procedure from 5-cyano-1-(2,3-butadien-1-yl)-3-methyl-1H-indole (70 mg, 0.34 mmol), dry methanol (42 µl, 1.02 mmol), indole (119 mg, 1.02 mmol), PtCl₂ (4.5 mg, 0.02 mmol) in 2.5 mL of dry 1,4-dioxane (0.14 M). Obtained by column chromatography, Pet/EtOAc (10:1), 32.9 mg, 0.16 mmol, 47 % of compounds 4e:4e’ as an inseparable mixture (0.78:1) as a brown oil.

1H NMR (500 MHz, CDCl₃) δ 7.92-7.85 (m, 2H; H-4 and H-4’), 7.46-7.41 (m, 2H; H-6 and H-6’), 7.33 (d, J = 8.5 Hz, 1H; H-7 and 7’), 7.27 (d, J = 8.5 Hz, 1H, H-7 and 7’), 6.73-6.69 (m, 1H; H-13’), 6.13-6.09 (m, 1H, H-11+12’ and H-12’), 4.69-4.64 (m, 2H, H-10), 4.13 (t, J = 7.0 Hz, 2H, H-10’), 3.56 (m, 2H; H-13), 2.70 (ddd, J = 9.7, 6.7, 3.3 Hz, 2H, H-11’), 2.34 (s, 3H, H-16’), 2.29 (s, 3H, H-16). 13C NMR (126 MHz, CDCl₃) δ 124.95 (CH, C-6/6’), 124.73 (CH, CH=C, C-11/12/12’), 124.19 (CH, C-4/4’), 123.33 (CH, C-6/6’), 123.33 (CH, C-4/4’), 121.92 (CH, CH=C, C-11/12/12’), 120.41 (CH, CH=C, C-11/12/12’), 118.08 (CH, CH=C, C-13’), 109.20 (CH, C-7/7’), 109.01 (CH, C-7/7’), 41.96 (CH₃, C-10), 39.89 (CH₃, C-10’), 24.16 (CH₂, C-11’), 22.78 (CH₂, C-13), 14.22, 8.14 (CH₃, C-16), 7.97 (CH₃, C-16’). Some quaternary carbons not detected. HRMS (ASAP) Solid: Calculated for C₁₄H₁₃N₂ [M+H]⁺: 209.1082. Found: 209.1079.

Cycles 4f:4f’:

Cycle 4f

Cycle 4f’

Synthesised using the general procedure from 5-chloro-1-(2,3-butadien-1-yl)-3-methyl-1H-indole (100 mg, 0.46 mmol), dry methanol (56 µl, 1.38 mmol), indole (161 mg, 1.38 mmol), PtCl₂ (6.1 mg, 0.023 mmol) in 3 mL of dry 1,4-dioxane (0.15 M). Obtained by column chromatography, Pet/EtOAc (20:1) 35.2 mg, 0.16 mmol, 35 % compounds 4f:4f’ as an inseparable mixture (0.8:1) as a brown oil.

1H NMR (500 MHz, CDCl₃) δ 7.42 (d, J = 2.0 Hz, 2H, H-7 and 7’), 7.39 (t, J = 1.3 Hz, 2H, H-4 and 4’), 7.04 (d, J = 1.3 Hz, 2H, H-6 and 6’), 6.59 – 6.56 (m, 1H, H-13’), 6.04 – 5.90 (m, 3H, H-11 and 12 and H-12’), 4.53 – 4.48 (m, 2H, H-10), 3.96 (t, J = 6.9 Hz, 2H, H-10’), 3.45 – 3.41 (m, 2H, H-13), 2.59 – 2.54 (m, 2H, H-11’), 2.19 (s, 3H, H-15), 2.14 (s, 3H, H-15’). 13C NMR (126 MHz, CDCl₃) δ 135.1 (C-9 or 9’), 132.7 (C-2 or 2’), 130.8 (C-5 or 5’), 130.2 (C-5 or 5’), 124.9 (C-8 or 8’), 124.5 (C-8 or 8’), 123.69 (CH, C-12’), 122.03 (CH, C-6 or 6’), 121.89 (CH, C-11 or 12), 120.41 (CH, C-11 or 12), 118.37 (CH, C-13’ and 7 or 7’), 117.35 (CH, C-4 or 4’), 109.41 (CH, C-7 or 7’), 109.33 (CH, C-6 or 6’), 107.10 (C-3 or 3’), 41.85 (CH₃, C-10), 39.89 (CH₂, C-10’), 24.33 (CH₃, C-11’), 22.83 (CH₂, C-13), 8.19 (CH₃, C-15), 8.04 (CH₃, C-15’). v_max cm⁻¹: 2967 (m, =C-H), 2924 (s, C-H), 2857 (m, C-H), 1699 (m, C=C), 1459 (m, C=C in ring) 1351 (w, Ar-H), 1204 (w, C-N). HRMS (ASAP) Solid: Calculated for C₁₃H₁₂ClN [M+H]⁺: 218.0739. Found: 218.0737.
Supporting Information

2,3’-BIM 3ab

Synthesised following a modification of the general procedure: from indole 1a (40 mg, 0.21 mmol), dry methanol (17 µl, 0.65 mmol), 5-methoxy indole (96 mg, 0.65 mmol), PtCl₂ (5.8 mg, 0.02 mmol) in 0.5 mL of dry 1,4-dioxane. Obtained after 3h of irradiation under microwave conditions at 130 °C (3ab, 58%).

2,3’-BIM 3ab: ¹H NMR (500 MHz, CDCl₃) δ 7.58 (s, 1H; H-17), 7.45 (d, J = 7.9 Hz, 1H; H-7), 7.22 (d, J = 7.9 Hz, 1H; H-4), 7.13 – 7.08 (m, 2H; H-5 & H-18), 7.07 – 7.01 (m, 1H; H-6), 6.89 (d, J = 2.4 Hz, 1H; H-21), 6.76 (dd, J = 8.6, 2.4 Hz, 1H; H-19), 6.35 (d, J = 2.3 Hz, 1H; H-16), 4.67 – 4.61 (m, 1H; H-13), 4.16 (dd, J = 11.2, 5.0, 3.2 Hz, 1H; H-10), 3.79 (td, J = 11.2, 5.0 Hz, 1H; H-10), 3.72 (s, 3H; H-22), 2.27–1.95 (m, 3H; 2H-12 & H-11), 1.92 (s, 3H; H-14), 1.85 – 1.73 (m, 1H; H-11). ¹³C NMR (126 MHz, CDCl₃) δ 154.19 (C-4), 136.19 (C-20), 136.19 (C-9), 135.20 (C-24), 132.13 (C), 129.05 (C-8), 126.93 (C-23), 124.42 (CH, C-16), 120.63 (CH, C-5), 119.30 (CH, C-6), 118.71 (C-3), 118.37 (CH, H-7), 112.18 (CH, C-18), 112.18 (CH, C-19), 108.98 (CH, C-4), 106.28 (C-15), 101.31 (CH, C-21), 56.29 (CH₃, C-22), 42.88 (N-CH₂, C-10), 30.62 (CH, C-13), 28.38 (CH₂, C-12), 19.80 (CH₂, C-11), 8.69 (CH₃, C-14). HRMS (FTMS + p NSI) (DCM/ MeOH + NH₄OAc): Calc. for C₂₂H₂₂N₂O [M+H]⁺: 331.1805: Found: 331.1805.

2,3’-BIM 3ac

Synthesised following a modification of the general procedure: from indole 1a (40 mg, 0.21 mmol), dry methanol (17 µl, 0.65 mmol), 2-methylindole (86 mg, 0.65 mmol), PtCl₂ (5.8 mg, 0.02 mmol) in 0.5 mL of dry 1,4-dioxane. Obtained after 3h of irradiation under microwave conditions at 130 °C (3ac, 57%).

2,3’-BIM 3ac: ¹H NMR (500 MHz, CDCl₃) δ 7.69 (s, 1H; H-17), 7.49 (d, J = 8.0 Hz, 1H; H-7), 7.36 (d, J = 8.0 Hz, 1H; H-4), 7.27 (d, J = 8.0 Hz, 1H; H-19), 7.20 (ddd, J = 8.0, 7.1, 1.2 Hz, 1H; H-5), 7.17 – 7.06 (m, 3H; H-22, H-6, H-20), 6.95 (t, J = 7.4 Hz, 1H; H-21), 4.67 (t, J = 5.8 Hz, 1H; H-13), 4.28 – 4.11 (m, 2H; H-10), 2.23 – 1.95 (m, 7H; H-14, H-12, H-11), 1.83 (s, 3H, H-17). ¹³C NMR (126 MHz, CDCl₃) δ 135.49 (C-16), 135.08 (C-2), 134.12 (C-8), 131.06 (C-24), 128.77 (C-15), 127.97 (C-8), 120.88 (C-23), 120.21 (CH, C-5), 119.19 (CH, C-21), 118.83 (CH, C-6), 118.33 (CH, C-22), 117.99 (CH, C-7), 113.70 (C-3), 110.13 (CH, C-19), 108.52 (CH, C-4), 42.57 (N-CH₂, C-10), 30.83 (CH, C-13), 29.71 (CH₂, C-11), 21.61 (CH₂, C-12), 11.77 (CH₃, C-14), 8.16 (CH₃, C-17). HRMS (FTMS + p NSI) (DCM/ MeOH + NH₄OAc): Calc. for C₂₂H₂₂N₂O [M+H]⁺: 315.1783. Found: 315.1856.
Supporting Information

2,3'-BIM 3ad

Synthesised using the general procedure from 1-(2,3-butadien-1-yl)-3-methyl-1H-indole (100 mg, 0.55 mmol), PtCl₂ (7.2 mg, 0.028 mmol), 2-phenyl-1H-indole (319 mg, 1.65 mmol), dry methanol (67 µL, 1.65 mmol) and 2.75 mL (0.2 M) of dry 1,4-dioxane. Obtained by column chromatography, Pet:EtOAc, (20:1), 77 mg, 0.21 mmol, 35% of compound 3ad as a red/brown oil.

¹H NMR (500 MHz, CDCl₃) δ 7.84 (s, 1H, H-17), 7.45 (d, J = 7.9 Hz, 2H, Ar), 7.37 (d, J = 7.3 Hz, 2H, Ar), 7.13 (d, J = 7.3 Hz, 2H, Ar), 7.06 (s, 1H, Ar), 7.03 – 7.00 (m, 2H, Ar), 6.90 – 6.86 (m, 1H, Ar), 6.81 (d, J = 7.8 Hz, 1H, Ar), 6.70 – 6.65 (m, 1H, Ar), 4.54 (dd, J = 9.2, 5.8 Hz, 1H, H-13), 4.11 (dd, J = 10.2, 5.3 Hz, 1H, H-10), 3.91 (td, J = 11.0, 4.3 Hz, 1H, H-10), 2.13 – 1.99 (m, 3H, H-12 + H-11), 1.91 – 1.80 (m, 1H, H-11), 1.50 (s, 3H, H-14).

¹³C NMR (126 MHz, CDCl₃) δ 137.91, 136.85, 135.52, 134.49, 129.29, 129.06, 128.91, 127.74, 125.19, 122.38, 122.11, 120.69, 120.30, 119.57, 115.62, 110.93, 108.42, 106.78, 42.52 (CH₂, C-10), 32.22 (CH, C-13), 30.54 (CH₂, C-11/12), 23.09 (CH₂, C-11/12), 8.36 (CH₃, C-14).

HRMS (FTMS) Calculated for C₂₇H₂₅N₂H [M+1]⁺: 377.2012. Found: 377.2011.

2,3'-BIM 3ai

Synthesised following a modification of the general procedure: from indole 1a (40 mg, 0.21 mmol), dry methanol (17 µL, 0.65 mmol), N-methylindole (86 mg, 0.65 mmol), PtCl₂ (5.8 mg, 0.02 mmol) in 0.5 mL of dry 1,4-dioxane. Obtained after 3h of irradiation under microwave conditions at 130 °C, (3ai, 61%).

2,3' BIM 3ah: ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, J = 7.9 Hz, 1H, H-4), 7.47 (d, J = 7.7 Hz, 1H, H-18), 7.24 (dd, J = 14.9, 8.1 Hz, 2H, H-7+H-21), 7.17 – 7.09 (m, 2H, H-5+H-19), 7.08 – 7.03 (m, 2H, H-6+H-20), 6.30 (s, 1H, H-16), 4.72 (t, J = 4.1 Hz, 1H, H-13), 4.21 (dd, J = 11.2, 4.9, 3.1 Hz, 1H, H-10), 3.82 (td, J = 11.2, 4.8 Hz, 1H, H-10), 3.56 (s, 3H, H-17), 2.32 – 2.26 (m, 1H, H-12), 2.12 – 2.06 (m, 1H, H-12), 2.06 – 1.98 (m, 1H, H-11), 1.95 (s, 3H, H-14), 1.84 – 1.78 (m, 1H, H-11).

¹³C NMR (126 MHz, CDCl₃) δ 137.4 (C-2), 135.9 (C-9), 135.07 (C-23), 128.7 (C-8), 128.12 (CH, C-16), 126.6 (C-22), 121.4 (CH, C-6/20), 120.2 (CH, C-6/20), 119.0 (CH, C-4), 118.9 (CH, C-5/19), 118.7 (CH, C-5/19), 118.0 (CH, C-18), 117.1 (C-3), 109.4 (CH, C-7/21), 108.7 (CH, C-7/21), 105.9 (C-15), 42.6 (CH₂, C-10), 32.6 (CH₃, C-17), 30.2 (CH, C-13), 28.2 (CH₂, C-12), 19.4 (CH₂, C-11), 8.4 (CH₃, C-14). νmax/cm⁻¹: 3410 (s, NH), 3053, 2942 – 2830 (m, C-H), 1618 – 1578
Supporting Information

(w, C=C), 1484 (s, C-H methyl), 1456 (m, C-C in ring), 1227 (s, C-N). HRMS (FTMS + p NSI) (DCM / MeOH + NH₄OAc): Calc. for C₂₂H₂₂N₂ [M+H]+: 315.4320; Found: 315.4220.

2,3’-BIM 3aj

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H
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N    N
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/   MeO
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Synthesised following a modification of the general procedure: from indole 1a (70 mg, 0.38 mmol), dry methanol (48 µl, 1.14 mmol), 4-methoxyindole (168 mg, 1.14 mmol), PtCl₂ (10.2 mg, 0.04 mmol) in 1 mL of dry 1,4-dioxane. Obtained after 3h of irradiation under microwave conditions at 130 °C, and isolated by column chromatography, Pet/EtOAc/DCM, (8:1:1), 78 mg, 62 % of compound 3aj as a pale green thick oil.

¹H NMR (500 MHz, CDCl₃) δ 7.80 (s, 1H, NH), 7.54 (d, J = 7.7 Hz, 1H, Ar), 7.31 (d, J = 7.3 Hz, 1H, Ar), 7.17 (m, 1H, Ar), 7.11 (m, 2H, Ar), 6.96 (d, J = 6.9 Hz, 1H, Ar), 6.56 (d, J = 7.3 Hz, 1H, Ar), 6.27 (s, 1H, Ar), 5.06 (m, 1H), 4.27 (m, 1H), 3.91 (s, 3H, OMe), 3.87 (m, 1H), 2.40 (m, 1H), 2.18 (m, 2H), 2.05 (s, 3H, Me), 1.85 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 154.8, 138.3 (1C, Ar), 136.2 (1CH, Ar), 135.8 (1C, Ar), 135.1 (1C, Ar), 132.8 (1C, Ar), 126.8 (1C, Ar), 121.8 (1CH, Ar), 120.3 (1CH, Ar), 118.9 (1CH, Ar), 118.0 (1CH, Ar), 116.5 (1C, Ar), 106.5 (1CH, Ar), 105.5 (1CH, Ar), 104.5 (1CH, Ar), 99.5 (1CH, Ar), 55.2 (1C, OMe), 42.7 (1C, CHH), 31.0 (1C, CH), 28.8 (1C, CHH), 16.7 (1C, CHH), 6.42 (1C, Me). HRMS (FTMS) Calculated for C₂₂H₂₃N₂O [M]+: 331.1805. Found: 331.1801.

2,3’-BIM 3ak

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N
/   \   /
N    N
/ \   /  \
/   MeO
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Synthesised following a modification of the general procedure: from indole 1a (70 mg, 0.38 mmol), dry methanol (48 µl, 1.14 mmol), N-methyl-5-methoxyindole (161 mg, 1.14 mmol), PtCl₂ (10.2 mg, 0.04 mmol) in 1 mL of dry 1,4-dioxane. Obtained after 3h of irradiation under microwave conditions at 130 °C, and isolated by column chromatography, Pet/EtOAc/DCM, (8:1:1), 106 mg as a non-separable mixture of compound 3ak (59%) and indole 2j (starting material recovered 28 mg, 15%) as an orange thick oil.

¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, J = 7.5 Hz, 1H, Ar), 7.46 (d, J = 7.5 Hz, 1H, Ar), 7.25 (m, 2H, Ar), 7.05 (m, 2H, Ar), 6.88 (s, 1H, Ar), 6.27 (s, 1H, Ar), 4.76 (m, 1H), 4.31 (m, 1H), 3.91 (m, 1H), 3.84 (s, 3H, OMe), 3.61 (s, 3H, Me), 2.35 (m, 1H), 2.34 (s, 3H, Me), 2.41 (m, 1H), 1.90 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 153.6 (1C, Ar), 153.8 (1C, Ar), 151.5 (1C, Ar), 132.8 (1C, Ar), 126.8 (1C, Ar), 121.8 (1CH, Ar), 120.3 (1CH, Ar), 118.9 (1CH, Ar), 118.0 (1CH, Ar), 116.5 (1C, Ar), 111.4 (1CH, Ar), 110.9 (1C, Ar), 110.1 (1CH, Ar), 106.5 (1CH, Ar), 105.9 (1C, Ar), 101.1 (1CH, Ar), 56.0 (1C, OMe), 42.6 (1C, CHH), 30.2 (1C, CH), 28.1 (1C, CHH), 19.3 (1C, CHH), 8.3 (1C, Me). HRMS (FTMS) Calculated for C₂₃H₂₅N₂O [M]+: 345.1961. Found: 345.1959.
Supporting Information

2,3'-BIM 3a

![Chemical Structure](image)

Synthesised following a modification of the general procedure: from indole 1a (70 mg, 0.38 mmol), dry methanol (48 µl, 1.14 mmol), N-methyl-4-methoxyindole (184 mg, 1.14 mmol), PtCl₂ (10.2 mg, 0.04 mmol) in 1 mL of dry 1,4-dioxane. Obtained after 3h of irradiation under microwave conditions at 130°C, and isolated by column chromatography, Pet/EtOAc/DCM, (20:1:1), 79 mg, 60% of compound 3a as a bright yellow thick oil.

\(^1\)H NMR (500 MHz, CDCl₃) δ 7.47 (d, J = 7.5 Hz, 1H, Ar), 7.24 (d, J = 7.3 Hz, 1H, Ar), 7.06 (m, 3H, Ar), 6.82 (d, J = 6.8 Hz, 1H, Ar), 6.47 (d, J = 6.5 Hz, 1H, Ar), 6.04 (s, 1H, Ar), 4.96 (m, 1H), 4.20 (m, 1H), 3.89 (s, 3H, OMe), 3.78 (m, 1H), 3.48 (s, 3H), 2.30 (m, 1H), 2.04 (m, 1H), 2.01 (s, 3H, Me), 1.76 (m, 1H), 1.50 (br s, 1H).

\(^13\)C NMR (126 MHz, CDCl₃) δ 154.8 (1C, Ar), 139.0 (1C, Ar), 136.4 (1C, Ar), 135.8 (1C, Ar), 128.8 (1C, Ar), 126.9 (1CH, Ar), 122.2 (1CH, Ar), 119.9 (1CH, Ar), 118.8 (1CH, Ar), 118.1 (1C, Ar), 117.9 (1CH, Ar), 116.7 (1C, Ar), 106.6 (1CH, Ar), 105.5 (1C, Ar), 102.6 (1CH, Ar), 99.3 (1CH, Ar), 55.3 (1C, OMe), 42.7 (1C, CHH), 32.8 (1C, CH), 30.8 (1C, Me), 28.8 (1C, CHH), 18.5 (1C, CHH), 6.45 (1C, Me).

HRMS (FTMS) Calculated for C₂₃H₂₅N₂O [M]⁺: 345.1961. Found: 345.1961.

2,3'-BIM 3am

![Chemical Structure](image)

Synthesised following a modification of the general procedure: from indole 1a (70 mg, 0.38 mmol), dry methanol (48 µl, 1.14 mmol), N-ethylindole (146 mg, 1.14 mmol), PtCl₂ (10.2 mg, 0.04 mmol) in 1 mL of dry 1,4-dioxane. Obtained after 3h of irradiation under microwave conditions at 130°C, and isolated by column chromatography, Pet/EtOAc/DCM, (16:1:1), 77 mg, 63% of compound 3am as a bright orange thick oil. 1% of cyclic intermediate 4a and 0.3% of intermediate 4a' were detected on the reaction mixture NMR, although not isolated after column chromatography.

\(^1\)H NMR (500 MHz, CDCl₃) δ 7.66 (d, J = 7.5 Hz, 1H, Ar), 7.57 (d, J = 7.3 Hz, 1H, Ar), 7.35 (m, 2H, Ar), 7.23 (m, 2H, Ar), 7.14 (m, 2H, Ar), 6.46 (s, 1H, Ar), 4.81 (m, 1H), 4.30 (m, 1H), 4.03 (q, J = 7.2 Hz, CH₂), 3.91 (m, 1H), 2.37 (m, 1H), 2.11 (m, 2H), 2.03 (s, 3H, Me), 1.91 (m, 1H), 1.34 (t, J = 7.2 Hz, Me).

\(^13\)C NMR (126 MHz, CDCl₃) δ 136.4 (1C, Ar), 135.8 (1C, Ar), 135.1 (1C, Ar), 128.7 (1C, Ar), 126.7 (1C, Ar), 126.4 (1CH, Ar), 121.3 (1CH, Ar), 120.2 (1CH, Ar), 119.3 (1CH, Ar), 118.9 (1CH, Ar), 118.6 (1CH, Ar), 118.0 (1CH, Ar), 117.2 (1CH, Ar), 109.5 (1CH, Ar), 108.6 (1CH, Ar), 105.9 (1C, Ar), 42.8 (1C, CHH), 40.7 (1C, CHH), 30.4 (1C, CH), 28.3 (1C, CHH), 19.5 (1C, CHH), 15.5 (1C, Me), 8.3 (1C, Me).

HRMS (FTMS) Calculated for C₂₃H₂₅N₂ [M]⁺: 329.2018. Found: 329.2018.
Supporting Information

2,3’-BIM 3bb:

Synthesised using the general procedure from 5-methoxy-3-methyl indolyl allene (71 mg, 0.33 mmol), dry methanol (36 µl, 0.89 mmol), 5-methoxy-1H-indole (132 mg, 0.89 mmol) and PtCl₂ (4.4 mg, 0.016 mmol) in 1.7 mL of dry 1,4-dioxane. Obtained by column chromatography Pet/EtOAc, (20:1), 43.6 mg, 0.12 mmol, 40 % of compound 3bb as an orange/brown solid.

¹H NMR (500 MHz, CDCl₃) δ 7.78 (s, 1H, H-19), 7.22 (m, 2H, H-7 + H-20), 6.98 (t, J = 2 Hz, 2H, H-4 + H-23), 6.85 (m, 2H, H-6 + H-21), 6.54 (d, J = 2 Hz, 1H, H-18), 4.73 (t, J = 4.3 Hz, 1H, H-13), 4.24 (ddd, J = 11.0, 4.9, 3.1 Hz, 1H, H-10), 3.87 (m, 4H, H-10 + H-15), 3.82 (s, 3H, H-27), 2.32 (m, 1H, H-12), 2.11-2.05 (m, 2H, H-12 + H-11), 1.99 (s, 3H, H-16), 1.90 (m, 1H, H-11). ¹³C NMR (126 MHz, CDCl₃) δ 153.90 (C-5 and C-22), 124.02 (CH, C-18), 111.94 (CH, C-7 or C-20), 111.90 (CH, C-6 or C-21), 118.97 (CH, C-4), 111.31 (CH, C-7), 110.13 (CH, C-6 or C-21), 109.24 (CH, C-7 or C-20), 100.97 (CH, C-23 or C-4), 56.08 (CH₃, C-15), 55.93 (CH₃, C-27), 42.59 (CH₂, C-10), 30.29 (CH, C-13), 27.96 (CH₂, C-12), 19.47 (CH₂, C-11), 8.37 (CH₃ – C-16). Some quaternary carbons not detected. v_max/cm⁻¹: 3410 (s, NH), 3053, 2942 / MeOH + NH₃OAc: Calc. for C₂₃H₂₃N₂O₂ [M+H]⁺: 360.1910: Found: 361.1911. M.P. = 180-182°C.

2,3’BIM 3ga:

Synthesised using the general procedure from 1-(2,3-butadien-1-yl)-3-ethyl-1H-indole (109.3 mg, 0.55 mmol), PtCl₂ (7.4 mg, 0.03 mmol), indole (194.7 mg, 1.66 mmol), methanol (0.074 mL, 1.66 mmol) and 2.77 mL of dry 1,4-dioxane. Obtained by column chromatography, Pet/EtOAc, (20:1), 71.7 mg, 0.23 mmol, 41 % of compound 3ga as a brown oil.

¹H NMR (500 MHz, CDCl₃) δ 7.91 (s, 1H, H16), 7.67 (d, J = 7.8 Hz, 1H, H-4), 7.62 (d, J = 7.8 Hz, 1H, H-7), 7.41 (d, J = 8.1 Hz, 1H, H-17), 7.37 (d, J = 8.1 Hz, 1H, H-20), 7.27 – 7.20 (m, 2H, H-5+H-6), 7.19 – 7.13 (m, 2H, H-18 + H-19), 6.60 (dd, J = 2.3, 0.7 Hz, 1H, H-15), 4.86 (t, J = 3.7 Hz, 1H, H-13), 4.33 (ddd, J = 11.2, 5.0, 2.9 Hz, 1H, H-10), 3.94 (ddd, J = 11.2, 4.8 Hz, 1H, H-10), 2.55 (q, J = 7.5 Hz, 2H, H-23), 2.44 – 2.38 (m, 1H, H-12), 2.24 – 2.15 (m, 1H, H-12), 2.15 – 2.07 (m, 1H, H-11), 1.97 – 1.89 (m, 1H, H-11), 1.06 (t, J = 7.5 Hz, 3H, H-24). ¹³C NMR (126 MHz, CDCl₃) δ 136.09 (C-22), 134.37 (C-2), 123.39 (CH, C-15), 121.93 (CH, C-5/C-6), 120.20 (CH, C-5/C-6), 119.37 (CH, C-18/C-19), 118.97 (CH, C-18/C-19), 118.88 (CH, C-4), 118.41 (CH, C-7), 111.33 (CH, C-17), 108.76 (CH, C-20), 42.58 (N-CH₂, C-10), 30.21 (CH, C-13), 28.04 (CH₂, C-11), 19.30 (CH₂, C-12), 17.27 (CH₂, C-23), 14.94 (CH₂, C-24). Some quaternary carbons not detected.
Synthesised using the general procedure from 1-(2,3-butadien-1-yl)-3-isopropyl-1H-indole (167.1 mg, 0.791 mmol), PtCl₂ (10.52 mg, 0.040 mmol), indole (278 mg, 2.372 mmol), methanol (0.096 mL, 2.372 mmol) and 3.95 mL of dry 1,4-dioxane. Obtained by ISCO column chromatography using 2 x 12g silica gel Redisep columns eluting with a gradient of i-

Supporting Information

HRMS (FTMS + p APCI, ASAP) (MeOH) Calc. for C₂₂H₂₃N₂ [M-H]⁺: 313.1699. Found: 313.1699.
Calc. for C₂₂H₂₃N₂ [M+H]⁺: 315.1856. Found: 315.1856.

2,3'BIM 3ha and cycle 4h':

Cycle 4h': ¹H NMR (500 MHz, CDCl₃) δ 7.60 (d, J = 8.0 Hz, 1H, H-4), 7.14 (d, J = 8.2 Hz, 1H, H-7), 7.08 (dd, J = 8.0, 7.0, 1.1 Hz, 1H, H-5), 6.95 (dd, J = 8.2, 7.0, 1.1 Hz, 1H, H-6), 6.64 (dt, J = 10.0, 1.8 Hz, 1H, H-13), 5.87 (dt, J = 10.0, 4.5 Hz, 1H, H-12), 3.97 (t, J = 6.9 Hz, 2H, H-10), 3.21 (heptet, J = 7.1 Hz, 1H, H-14), 2.56 – 2.50 (m, 2H, H-11), 1.35 (d, J = 7.1 Hz, 6H, H-18), 6.95 (ddd, J = 7.0, 2.5, 1.75 Hz, 1H, H-24), 1.07 (d, J = 7.0 Hz, 3H, H-24). ¹³C NMR (126 MHz, CDCl₃) δ 130.13 (C-2), 122.94 (CH, C-12), 121.69 (CH, C-5), 120.29 (CH, C-4), 118.96 (CH, C-6), 118.66 (CH, C-13), 108.67 (CH, C-7), 39.71 (CH₂, C-10), 25.64 (CH, C-14), 24.29 (CH₂, C-11), 23.59 (CH₃, C-15). Some quaternary carbons not detected. HRMS (FTMS + p APCI) (DCM): Calc. for C₅₉H₆₆N [M-H]⁺: 210.1277. Found: 210.1280.

2,3'-BIM 3ha: ¹H NMR (500 MHz, CDCl₃) δ 7.76 (s, 1H, H-16), 7.66 (d, J = 7.9 Hz, 1H, H-4), 7.58 (d, J = 7.8 Hz, 1H, H-7), 7.29 (d, J = 8.1 Hz, 1H, H-17), 7.25 (d, J = 8.1 Hz, 1H, H-20), 7.16 – 7.12 (m, 1H, H-5), 7.12 – 7.09 (m, 1H, H-6), 7.09 – 7.06 (m, 1H, H-18), 7.04 – 7.00 (m, 1H, H-19), 6.43 (dd, J = 2.3, 0.8 Hz, 1H, H-15), 4.79 (dd, J = 5.0, 2.7 Hz, 1H, H-13), 4.22 (dd, J = 11.5, 5.4, 1.5 Hz, 1H, H-10), 3.78 (td, J = 11.5, 4.9 Hz, 1H, H-10), 2.88 (heptet, J = 7.1 Hz, 1H, H-23), 2.33 – 2.27 (m, 1H, H-12), 2.09 – 2.03 (m, 1H, H-12), 2.02 – 1.91 (m, 1H, H-11), 1.82 – 1.75 (m, 1H, H-11), 1.25 (d, J = 7.1 Hz, 3H, H-24), 1.07 (d, J = 7.0 Hz, 3H, H-24). ¹³C NMR (126 MHz, CDCl₃) δ 136.67 (C-9), 136.53 (C-22), 133.51 (C-2), 126.50 (C-8), 126.11 (C-8), 123.55 (CH, C-15), 121.94 (CH, C-5), 120.09 (CH, C-4), 119.96 (CH, C-6), 119.49 (C-3), 119.38 (CH, C-18), 118.90 (CH, C-7), 118.62 (CH, C-19), 116.49 (C-14), 111.35 (CH, C-17), 108.97 (CH, C-20), 42.53 (CH₂, C-10), 30.11 (CH₂, C-13), 27.77 (CH₂, C-11), 25.57 (CH, C-23), 23.33 (CH₃, C-24), 22.33 (CH₃, C-24), 18.88 (CH₂, C-12). HRMS (FTMS + p NSI) ((MeOH) / MeOH + NH₄OAc): Calc. for C₃₃H₃₅N₂ [M+H]⁺: 329.2012. Found: 329.2016.
Supporting Information

Synthesised using the general procedure from 1-(2,3-butadien-1-yl)-3-(2-methyl-2-propanyl)-1H-indole (60 mg, 0.26 mmol), PtCl₂ (3.5 mg, 0.013 mmol), indole (91 mg, 0.78 mmol), methanol (0.030 mL, 0.78 mmol) and 1.3 mL of dry 1,4-dioxane. Obtained column chromatography eluting, Petroleum ether/DCM/AcOEt 14:1:1, 14 mg, 0.062 mmol, 25 % of compound 4i′ as a bright yellow oil and 15 mg, 0.044 mmol, 19 % of compound 3ja as a dark yellow oil.

**Cycle 4i′; ¹H NMR** (500 MHz, CDCl₃) δ = 7.78 (dd, J=8.2, 1.1, 1H), 7.15 (d, J=8.2, 1H), 7.08 (ddd, J=8.2, 7.0, 1.1, 1H), 7.01 – 6.92 (m, 2H), 5.88 (dt, J=10.4, 4.5, 1H), 3.97 (t, J=6.9, 2H), 2.49 (tdd, J=6.7, 4.5, 1.8, 2H), 1.49 (s, 9H). **¹³C NMR** (126 MHz, CDCl₃) δ = 137.13, 129.95, 127.33, 123.43, 122.38, 121.71, 121.62, 118.54, 108.73, 100.10, 39.91, 34.20, 32.57, 24.04. **HRMS** (FTMS + p APCI, ASAP) (MeOH) Calc. for C₁₆H₁₅N [M+H]+: 226.1590. Found: 226.1586.

**2,3′-BIM 3ja; ¹H NMR** (500 MHz, CDCl₃) δ = 7.89 (dt, J=8.1, 0.9, 1H), 7.65 (d, J=7.7, 1H), 7.36 (dt, J=8.1, 0.9, 1H), 7.31 (dt, J=8.2, 0.9, 1H), 7.24 – 7.14 (m, 3H), 7.10 (ddd, J=8.2, 7.0, 1.2, 1H), 6.38 (dd, J=2.4, 1.0, 1H), 5.37 – 5.08 (m, 0H), 4.35 (dd, J=11.7, 6.0, 1H), 3.83 (ddd, J=12.5, 11.6, 5.3, 1H), 2.43 – 2.35 (m, 1H), 2.13 (tdd, J=13.0, 4.6, 2.6, 1H), 2.01 (dddt, J=16.3, 13.3, 8.8, 2.6, 1H), 1.84 – 1.72 (m, 1H), 1.40 (s, 9H). **¹³C NMR** (126 MHz, CDCl₃) δ = 136.98 (C), 136.78 (C), 133.56 (C), 127.29 (C), 125.79 (C), 124.29 (C), 122.05 (CH), 121.97 (CH), 121.00 (C), 120.24 (CH), 119.49 (CH), 118.93 (CH), 118.57 (CH), 118.30 (C), 111.41 (CH), 109.03 (CH), 43.07 (CH₂), 33.93 (C), 31.79 (CH), 31.46 (3 × CH₃), 27.53 (CH₂); 18.18 (CH₃). **HRMS** (FTMS + p APCI, ASAP) (MeOH) Calc. for C₂₆H₂₇N₂ [M-H]−: 341.2013. Found: 343.2008. Calc. for C₂₆H₂₇N₂ [M+H]+: 343.2169. Found: 343.2167.

**2,3′-BIM 3ja**

Synthesised using the general procedure from 1-(2,3-butadien-1-yl)-3-phenyl-1H-indole (233 mg, 0.950 mmol), PtCl₂ (13 mg, 0.047 mmol), indole (334 mg, 2.85 mmol), methanol (0.115 mL, 2.85 mmol) and 4.75 mL of dry 1,4-dioxane. Obtained by ISCO column chromatography using an 12g silica gel Redisep column eluting with a gradient of i-hexane to 2.5% ethyl acetate using the instrument’s default settings to yield traces (<5%) of compounds 4j and 4j′ as an inseparable mixture (1:1) as a brown oil and 39.1 mg, 0.108 mmol, 11 % of compound 3ja as a brown oil.

**2,3′-BIM 3ja; ¹H NMR** (500 MHz, CDCl₃) δ 7.93 (s,1H, H-16), 7.82 (d, J = 7.8 Hz, 1H, H-17), 7.62 (d, J = 8.2 Hz, 1H, H-20), 7.42 – 7.38 (m, 4H, H-25), 7.31 – 7.28 (m, 1H, H-26), 7.27 – 7.20 (m, 4H, H-4+H-7), 7.18 – 7.12 (m, 2H, H-18 + H-19), 6.63 (d, J = 1.6 Hz, 1H, H-15), 4.92 (t, J = 3.7 Hz, 1H, H-13), 4.45 (ddd, J = 11.6, 5.8, 1.9 Hz, 1H, H-10), 3.98 (td, J = 11.6, 5.5 Hz, 1H, H-10), 2.47 – 2.41 (m, 1H, H-12), 2.24 – 2.17 (m, 1H, H-12), 2.17 – 2.09 (m, 1H, H-11), 1.99 – 1.92 (m, 1H, H-11). **¹³C NMR** (126 MHz, CDCl₃) δ 136.79 (C-9), 136.69 (C-22), 136.26 (C-2), 135.40 (C-23), 128.77 (C-Ar), 128.28 (C-Ar), 127.41 (C-Ar), 125.67 (C-Ar), 125.29 (C-Ar), 123.29 (C-Ar), 123.97 (CH, CH=C, C-15), 121.98 (C-Ar), 121.07 (C-Ar), 120.20 (C-Ar), 119.73 (C-Ar), 119.40 (C-Ar), 119.34 (CH, C-17), 119.10 (CH, C-20), 112.41 (C-26), 111.30 (CH, C-25), 109.20, (CH, C-
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24), 42.88 (N-CH₃, C-10), 30.69 (CH, C-13), 27.38 (CH₂, C-11), 18.44 (CH₂, C-12). HRMS (FTMS + p NSI) ([DCM] / MeOH + NH₄OAc): Calc. for C₁₉H₁₉N₂ [M+H]⁺ 363.1856; Found: 363.1857.

Trisindole 5ka

& Allyl indole 6ka

Synthesised using the general procedure from 1-(2,3-butadien-1-yl)-3-carbonitrile-1H-indole (140.2 mg, 0.722 mmol), PtCl₂ (9.60 mg, 0.036 mmol), indole (254 mg, 2.165 mmol), methanol (0.088 mL, 2.165 mmol) and 3.61 mL of dry 1,4-dioxane. Obtained by ISCO column chromatography using a 12g silica gel Redisep column eluting with a gradient of i-hexane to 40% ethyl acetate using the instrument’s default settings to yield 33 mg, 0.106 mmol, 15 % of compound 6ka as a brown oil and 128 mg, 0.0299 mmol, 41 % of compound 5ka as a brown oil.

Trisindole 5ka: ¹H NMR (500 MHz, CDCl₃) δ 7.85 (s, 2H, H-16), 7.67 – 7.63 (m, 1H, H-2), 7.42 (d, J = 8.0 Hz, 2H, H-17), 7.23 (d, J = 8.1 Hz, 2H, H-20), 7.19 – 7.12 (m, 2H, H-4 + H-7), 7.09 – 7.04 (m, 2H, H-18), 6.97 – 6.91 (m, 2H, H-19), 6.77 (d, J = 2.2 Hz, 2H, H-15), 4.38 (t, J = 7.5 Hz, 1H, H-13), 3.98 (t, J = 7.1 Hz, 2H, H-10), 2.13 (dt, J = 15.4, 7.6 Hz, 2H, H-12), 1.87 (dt, J = 15.7, 7.4 Hz, 2H, H-11). ¹³C NMR (126 MHz, CDCl₃) δ 136.60 (C-9), 135.36 (C-22), 134.70, 127.91 (C-8), 126.81 (C-21), 123.69 (CH, C-4 + C-7), 122.03 (CH, C-4 and C-7 and C-18), 121.45 (CH, CH=C, C-15), 119.91 (CH, C-2), 119.28 (CH, C-17), 119.25 (CH, C-19), 111.30 (CH, C-20), 110.62 (CH, C-4 + C-7), 47.19 (N-CH₃, C-10), 33.77 (CH, C-13), 32.59 (CH₂, C-12), 28.41 (CH₂, C-11). Quaternary carbons detected. HRMS (FTMS + p NSI) ([MeOH] / MeOH + NH₄OAc): Calc. for C₁₉H₁₉N₂ [M+H]⁺: 429.2074. Found: 429.2080.

Allyl indole 6ka: ¹H NMR (500 MHz, CDCl₃) δ 7.93 (s, 1H, H-16), 7.69 (m, 1H, H-4), 7.52 (s, 1H, H-2), 7.45 (dd, J = 7.9, 0.9 Hz, 1H, H-7), 7.35 – 7.28 (m, 2H, H-17 + H-20), 7.23 (dd, J = 14.2, 7.1, 1.3 Hz, 2H, H-5 + H-6), 7.13 (dd, J = 8.2, 7.1, 1.1 Hz, 1H, H-18), 7.04 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H, H-19), 6.87 (d, J = 2.3 Hz, 1H, H-15), 5.91 (dt, J = 15.4, 6.2, 1.4 Hz, 1H, H-12), 5.65 (dt, J = 15.4, 6.1, 1.6 Hz, 1H, H-11), 4.65 (dd, J = 6.2, 1.2 Hz, 2H, H-10), 3.47 (d, J = 6.1, 1.2 Hz, 2H, H-13). ¹³C NMR (126 MHz, CDCl₃) δ 135.05 (CH, CH=C, C-11), 134.46 (CH, C-2), 123.96 (CH, CH=C, C-12), 123.77 (CH, C-5/C-6), 122.20 (CH, C-5/C-6), 122.24 (CH, C-18), 121.75 (CH, CH=C, C-15), 119.91 (CH, C-4), 119.46 (CH, C-19), 119.16 (CH, C-17), 119.19 (CH, C-20), 110.90 (CH, C-7), 48.77 (CH₂, C-10), 28.05 (CH₂, CH₂, C-13). Quaternary carbons not detected. HRMS (FTMS + p NSI) ([DCM] / MeOH + NH₄OAc): Calc. for C₁₉H₁₉N₂ [M+H]⁺: 312.1495. Found: 312.1498.
Supporting Information

**Trisindole 5la**

![Diagram of trisindole 5la]

Synthesised using the general procedure from 1-(2,3-butadien-1-yl)-3-carboxylate-1H-indole (210.1 mg, 0.924 mmol), PtCl₂ (12 mg, 0.046 mmol), indole (325 mg, 2.77 mmol), methanol (0.112 mL, 2.77 mmol) and 4.75 mL of dry 1,4-dioxane. Obtained by ISCO column chromatography using a 12g silica gel Redisep column eluting with a gradient of i-hexane to 100% ethyl acetate using the instrument’s default settings to yield 39.7 mg.

**Trisindole 5la**: ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, J = 4.9, 3.8 Hz, 1H, H-4), 7.81 (s, 2H, H-16), 7.63 (s, 1H, H-2), 7.41 (d, J = 8.0 Hz, 2H, H-17), 7.19 (d, J = 8.1 Hz, 2H, H-20), 7.16 – 7.14 (m, 1H, H-7), 7.12 – 7.10 (m, 2H, H-5 + H-6), 7.07 – 7.03 (m, 2H, H-19), 6.94 – 6.90 (m, 2H, H-18), 6.69 (d, J = 2.2 Hz, 2H, H-15), 4.35 (t, J = 7.5 Hz, 1H, H-13), 3.97 (t, J = 7.1 Hz, 2H, H-10), 3.81 (s, 3H, H-25), 2.10 (m, 2H, H-12), 1.86 (m, 2H, H-11). ¹³C NMR (126 MHz, CDCl₃) δ 165.7 (C-23), 136.59 (C-9), 136.54 (C-21), 134.38 (CH, C-2), 126.87 (C-8), 126.71 (C-22), 122.67 (CH, C-4), 121.91 (CH, C-19), 121.84 (CH, C-7), 121.74 (CH, C-5 or C-6), 121.52 (CH, C-15), 119.39 (CH, C-17), 119.18 (CH, C-18), 111.25 (CH, C-20), 110.15 (CH, C-5 or C-6), 106.76 (C-3), 51.02 (CH₃, C-25), 46.99 (CH₃, C-10), 33.72 (CH₂, C-13), 32.65 (CH₂, C-12), 28.38 (CH₂, C-11). HRMS (FTMS + p NSI) [(MeOH) / MeOH + NH₄OAc]: Calc. for C₃₀H₂₀N₂O₄Na [M+Na]^+: 484.1995. Found: 484.1989.

**Allyl indole 6la**

![Diagram of allyl indole 6la]

Synthesised using the general procedure from 1-(2,3-butadien-1-yl)-3-carboxylate-1H-indole (210.1 mg, 0.924 mmol), PtCl₂ (12 mg, 0.046 mmol), indole (325 mg, 2.77 mmol), methanol (0.112 mL, 2.77 mmol) and 4.75 mL of dry 1,4-dioxane. Obtained by ISCO column chromatography using a 12g silica gel Redisep column eluting with a gradient of i-hexane to 100% ethyl acetate using the instrument’s default settings to yield 39.7 mg, 0.115 mmol, 13% of compound 6la as a brown oil and 136.9 mg, 0.297 mmol, 32% of compound 5la as a brown oil.

**Allyl indole 6la**: ¹H NMR (500 MHz, CDCl₃) δ 8.10 (m, 1H, H-4), 7.96 (s, 1H, H-16), 7.74 (s, 1H, H-2), 7.45 (m, 1H, H-17), 7.28 (m, 1H, H-7), 7.26 (d, J = 8.1 Hz, 1H, H-20), 7.20 – 7.17 (m, 2H, H-5 + H-6), 7.13 – 7.08 (m, 1H, H-19), 7.04 – 6.99 (m, 1H, H-18), 6.82 (d, J = 2.2 Hz, 1H, H-15), 5.86 (ddt, J = 15.3, 6.3, 1.2 Hz, 1H, H-12), 5.64 (ddt, J = 15.2, 6.1, 1.5 Hz, 1H, H-11), 4.61 (dd, J = 6.1, 1.0 Hz, 2H, H-10), 3.43 (dd, J = 6.4, 2H, H-13), 3.82 (s, 3H, H-25). ¹³C NMR (126 MHz, CDCl₃) δ 165.6 (C-23), 136.6 (C-9), 136.4 (C-21), 134.3 (CH, C-11), 134.15 (CH, C-2), 127.2 (C-8), 126.8 (C-22), 124.5 (CH, C-12), 122.7 (CH, C-5 or C-6), 122.1 (CH, C-19), 121.9 (CH, C-5 or C-6), 121.9 (CH, CHC, C-15), 121.7 (CH, C-4), 119.4 (CH, C-18), 118.9 (CH, C-17), 113.7 (C-14), 111.22 (CH, C-20), 110.3 (CH, C-7), 107.1 (C-3), 51.0 (CH₃, C-25), 48.7 (N-CH₂ C-10), 28.2 (CH₂, C-13). HRMS (FTMS + p NSI) [(MeOH) / MeOH + NH₄OAc]: Calc. for C₂₂H₂₁N₂O₃ [M+H]^+: 345.1598. Found: 345.1601.
Supporting Information

Trisindole 5ma

Allyl indole 6ma

Synthesised using the general procedure from 1-(2,3-butadien-1-yl)-3-formyl-1H-indole (44.5 mg, 0.226 mmol), PtCl₂ (3.00 mg, 0.011 mmol), indole (79 mg, 0.677 mmol), methanol (0.027 mL, 0.677 mmol) and 1.1 mL of dry 1,4-dioxane. Obtained by ISCO column chromatography using a 12g silica gel Redisep columns eluting with a gradient of i-hexane to 40% ethyl acetate using the instrument’s default settings to yield 3.6 mg, 0.011 mmol, 5% of compound 6ma as a brown oil and 4.6 mg, 0.011 mmol, 5% of compound 5ma as a brown oil.

Trisindole 5ma: ¹H NMR (500 MHz, CDCl₃) δ 9.95 (s, 1H, H-24), 8.33 (d, J = 6.9, 1.3 Hz, 1H, H-4), 7.94 (s, 2H, H-16), 7.58 (s, 1H, H-2), 7.55 (d, J = 7.9 Hz, 1H, H-17), 7.37 (d, J = 8.2 Hz, 1H, H-20), 7.35 – 7.30 (m, 2H, H-5+H-6), 7.27 (dd, J = 8.4, 6.9 Hz, 1H, H-7), 7.20 (ddd, J = 8.1, 7.0 Hz, 2H, H-19), 7.06 (ddd, J = 8.0, 7.1, 0.9 Hz, 2H, H-18), 6.92 (d, J = 2.2 Hz, 2H, H-15), 4.54 (t, J = 7.5 Hz, 1H, H-13), 4.19 (t, J = 7.1 Hz, 2H, H-10), 2.31 (m, 2H, H-12), 2.09 (m, 2H, H-11). ¹³C NMR (126 MHz, CDCl₃) 138.35 (CH), 123.72 (CH), 123.01 (CH), 122.18 (CH), 122.10 (CH), 121.47 (CH), 119.42 (CH), 119.34 (CH), 110.07 (CH), 47.44 (CH₂), 33.94 (CH₂), 28.50 (CH₂). Quaternary carbons not detected.

HRMS (FTMS + p NSI) (MeOH)/(MeOH + NH₄OAc): Calc. for C₁₃H₁₂N₂O [M+H]+: 332.2070. Found: 332.2070

Allyl indole 6ma: ¹H NMR (500 MHz, CDCl₃) δ 10.0 (s, 1H, H-24), 8.34 (dd, J = 5.9, 3.0 Hz, 1H, H-4), 8.04 (s, 1H, H-16), 7.74 (s, 1H, H-2), 7.58 (d, J = 7.9 Hz, 1H, H-17), 7.44 – 7.38 (m, 2H, H-7 + H-20), 7.35 (dd, J = 6.2, 3.0 Hz, 2H, H-5 + H-6), 7.24 (t, J = 7.5 Hz, 1H, H-19), 7.14 (t, J = 7.5 Hz, 1H, H-18), 6.99 (d, J = 1.5 Hz, 1H, H-15), 6.05 (dt, J = 13.8, 6.2 Hz, 1H, H-11), 5.80 (dt, J = 13.8, 6.2 Hz, 1H, H-12), 4.78 (d, J = 6.2 Hz, 2H, H-10), 3.59 (d, J = 6.2 Hz, 2H, H-13). ¹³C NMR (126 MHz, CDCl₃) 184.59 (C-23), 140.19, 138.06 (CH, C-2), 135.11 (CH, C-11), 124 (CH, C-5/C-6), 123.95 (CH, C-12), 122.97 (CH, C-5 or C-6), 122.26 (CH, C-4), 121.82 (CH, C-19), 121.79 (CH, C-15), 119.48 (CH, C-18), 119.23 (C-3), 118.91 (CH, C-17), 111.25 (CH, C-7 or C-20), 110.32 (CH, C-7 or C-20), 48.87 (CH₂, N=CH₂ C-10), 28.22 (CH₂, C-13), 27.97. Quaternary carbons not detected. HRMS (FTMS + p NSI) ((MeOH)/MeOH + NH₄OAc): Calc. for C₁₃H₁₂N₂O₂Na [M+Na]+: 337.1311. Found: 337.1315.
Supporting Information

**Trisindole 5na**

![Trisindole 5na structure]

**Allyl indole 6na**

![Allyl indole 6na structure]

Synthesised using the general procedure from 1-(2,3-butadien-1-yl)-3-ethanoate-1H-indole (213.3 mg, 1.010 mmol), PtCl₄ (13 mg, 0.05 mmol), indole (335 mg, 3.03 mmol), methanol (0.123 mL, 3.03 mmol) and 4.75 mL of dry 1,4-dioxane. Obtained by ISCO column chromatography using a 12g silica gel RediSep column eluting with a gradient of i-hexane to 100 % ethyl acetate using the instrument’s default settings to yield 36.4 mg, 0.111 mmol, 11 % of compound 6na as a brown oil and 103.4 mg, 0.232 mmol, 23 % of compound 5na as a brown oil.

**Trisindole 5na**: ¹H NMR (500 MHz, CDCl₃) δ 8.41 (m, 1H, H-4), 7.94 (s, 1H, H-16), 7.63 (s, 1H, H-2), 7.55 (d, J = 8.1 Hz, 2H, H-17), 7.37 (d, J = 8.1 Hz, 2H, H-20), 7.32 (dd, J = 5.9, 2.1 Hz, 1H, H-7), 7.28 – 7.25 (m, 2H, H-5 + H-6), 7.22 – 7.17 (m, 2H, H-19), 7.09 – 7.04 (m, 2H, H-18), 6.90 (d, J = 2.2 Hz, 2H, H-15), 4.53 (t, J = 7.5 Hz, 1H, H-13), 4.17 (t, J = 7.1 Hz, 2H, H-10), 2.49 (s, 3H, H-24), 2.30 (m, 2H, H-12), 2.12 – 2.04 (m, 2H, H-11). ¹³C NMR (126 MHz, CDCl₃) δ 193.2 (C-23), 136.84 (C-9), 136.61 (C-21), 134.99 (CH, C-2), 126.85 (C-8), 126.37 (C-22), 122.61 (CH, C-4), 121.95 (CH, C-19), 121.54 (CH, C-15), 119.37 (CH, C-17), 119.20 (CH, C-18), 111.30 (CH, C-20), 109.98 (CH, C-7), 47.04 (N-CH₂, C-10), 33.78 (CH₂, C-13), 32.67 (CH₂, C-12), 28.41 (CH₂, C-11), 27.63 (CH₃, C-24). HRMS (FTMS + p NSI) ((MeOH) / MeOH + NH₄OAc): Calc. for C₁₂H₁₂N₂O [M+H]⁺: 329.1648. Found: 329.1652.

**Allyl indole 6na**: ¹H NMR (500 MHz, CDCl₃) δ 8.30 (m, 1H, H-4), 7.96 (s, 1H, H-16), 7.64 (s, 1H, H-2), 7.47 (m, 1H, H-17), 7.29 (m, 1H, H-6 + H-7), 7.23 – 7.19 (m, 2H, H-5+ H-20), 7.15 – 7.10 (m, 1H, H-19), 7.03 (ddd, J = 7.9, 7.1, 0.9 Hz, 1H, H-18), 6.87 (d, J = 2.2 Hz, 1H, H-15), 5.92 (dt, J = 15.3, 6.3, 1.3 Hz, 1H, H-12), 5.69 (ddt, J = 15.3, 6.1, 1.5 Hz, 1H, H-11), 4.65 (dd, J = 6.1, Hz, 2H, H-10), 3.47 (d, J = 6.3 Hz, 2H, H-13), 2.41 (s, 3H, H-24). ¹³C NMR (126 MHz, CDCl₃) δ 193.15 (C-23), 136.89 (C-9), 136.45 (C-21), 134.70 (CH, C-12), 134.60 (CH, C-2), 127.22 (C-8), 126.47 (C-22), 124.32 (CH, C-11), 122.63 (CH, C-5 + C-20), 122.59 (CH, C-4), 122.20 (CH, C-19), 121.84 (CH, CH=C, C-15), 119.46 (CH, C-18), 118.89 (CH, C-17), 117.14 (C-3), 113.63 (C-14), 111.26 (CH, C-6 or C-7), 110.09 (CH, C-6 or C-7), 48.70 (N-CH₂, C-10), 28.22 (CH₃, C-13), 27.62 (CH₃, C-24). HRMS (FTMS + p NSI) ((MeOH) / MeOH + NH₄OAc): Calc. for C₃₀H₂₆N₂O [M+H]⁺: 446.2227. Found: 446.2226.
Supporting Information

Trisindole 5oa

Synthesised using the general procedure from 3-cyanoindolyl allene (50 mg, 0.28 mmol), PtCl₂ (3.7 mg, 0.014 mmol), indole (98 mg, 0.84 mmol) and dry methanol (22 μl, 0.84 mmol) in 2 mL of dry 1,4-dioxane (0.15 M). Obtained by column chromatography, Pet/EtOAc (50:1) 47.2 mg, 0.11 mmol, 41 % of product 6oa as brown/orange liquid and 22.7 mg, 0.076 mmol, 27 % of product 5oa as an orange/brown solid.

**Trisindole 5oa:** ¹H NMR (500 MHz, Acetone) δ 10.06 (s, 2H, H-15), 8.00 (s, 1H, H-2), 7.69 – 7.65 (m, 1H, H-7), 7.49 (d, J = 8.0 Hz, 2H, H-16), 7.40 (dd, J = 7.0, 1.0 Hz, 1H, H-4), 7.37 (d, J = 8.1 Hz, 2H, H-19), 7.32 (d, J = 1.5 Hz, 2H, H-14), 7.29 – 7.22 (m, 2H, H-6 and H-5), 7.07 – 7.01 (m, 2H, H-18), 6.90 (ddd, J = 8.0, 7.1, 1.0 Hz, 2H, H-17), 4.56 (t, J = 7.6 Hz, 1H, H-12), 4.46 – 4.37 (m, 2H, H-10), 2.88 (q, J = 7.6 Hz, 2H, H-11). ¹³C NMR (126 MHz, CDCl₃) δ 136.82 (C), 135.42 (C), 135.12 (2CH, C-16), 128.17 (C), 126.63 (C), 123.82 (CH, C-4), 122.39 (2CH, C-18), 122.23 (CH, C-6), 121.76 (2CH, C-14), 120.13 (CH, C-7), 119.64 (2CH, C-17), 119.37 (CH, C-2), 118.50 (C), 116.08 (C), 111.48 (2CH, C-19), 110.85 (CH, C-4), 85.68 (C), 46.19 (CH₂, C-10), 35.38 (CH₂, C-11), 31.73 (CH, C-12). HRMS: Calculated for C_{28}H_{22}N₄[M+H]: 415.1918 Found: 415.1917.

Allyl indole 6oa: ¹H NMR (500 MHz, CDCl₃) δ 8.06 (s, 1H, H-15), 7.81 (s, 1H, H-2), 7.75 (d, J = 7.5 Hz, 1H, H-7), 7.64 (d, J = 8.0 Hz, 1H, H-4), 7.46 – 7.40 (m, 2H, H-19 and H-16), 7.36 – 7.32 (m, 1H, H-17), 7.32 – 7.29 (m, 1H, H-6), 7.26 – 7.22 (m, 1H, H-18), 7.15 (ddd, J = 8.0, 7.3, 1.0 Hz, 1H, H-5), 7.10 (d, J = 2.3 Hz, 1H, H-14), 7.03 (dt, J = 3.1, 1.6 Hz, 1H, H-10), 6.26 – 6.20 (m, 1H, H-11), 3.75 (ddd, J = 6.6, 1.6, 1.0 Hz, 2H, H-12). ¹³C NMR (126 MHz, CDCl₃) δ 136.66 (C), 134.92 (C), 131.69 (CH, C-2), 127.83 (C), 127.23 (C), 124.62 (CH, C-17), 123.78 (CH, C-10), 122.95 (CH, C-6), 122.55 (CH, C-18), 122.18 (CH, C-14), 120.95 (CH, C-11), 120.13 (CH, C-7), 119.82 (CH, C-5), 118.96 (CH, C-4), 115.63 (C), 113.32 (C), 111.54 (CH, C-19), 110.91 (CH, C-16), 88.23 (C), 26.16 (CH₂, C-12). HRMS (FTMS + p NSI) (DCM/ MeOH + NH₄OAc): Calc. for C_{29}H_{19}N₅ [M+H]: 298.1341 Found: 298.1339.

Cycle 4p

Synthesised using the general procedure from 1-(hexa-4,5-dien-1-yl)-3-methyl-1H-indole 1p (330 mg, 1.5 mmol), platinum (II) chloride (20 mg, 0.075), indole (550 mg, 4.7 mmol), dry methanol (190 μL, 4.7 mmol) and 10 mL (0.15 M) of dry 1,4-dioxane. Obtained by column chromatography eluting with a gradient of 0-10% ethyl acetate in hexane, 165 mg, 0.78 mmol, 52 % of compounds 4p and 4p as an inseparable mixture (1:0.1) as a brown oil.
Supporting Information

**Cycle 4p**: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 7.57 (dt, $J = 7.8$, 0.9, 1H), 7.29 – 7.18 (m, 2H), 7.09 (dd, $J = 8.0$, 6.6, 1.4, 1H), 5.77 (tt, $J = 4.8$, 1.4 Hz 1H), 4.04 (t, $J = 7.0$, 2H), 2.67 (m, 2H), 2.59 – 2.52 (m, 2H), 2.51 (s, 3H), 1.23 (t, $J = 7.0$, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 136.04 (C), 135.50 (C), 131.83 (C), 129.56 (C), 122.02 (CH), 119.29 (CH), 118.87 (CH), 118.71 (CH), 108.44 (CH), 106.71 (C), 39.92 (CH$_2$), 26.79 (CH$_3$), 24.45 (CH$_3$), 13.87 (CH$_3$), 10.35 (CH$_3$). HRMS (FTMS + p APCI, ASAP) (MeOH) Calc. for C$_{12}$H$_{18}$N [M+H]$^+$: 212.1434. Found: 212.1429.

**Compound 3an**

![Diagram of Compound 3an](image)

Synthesised using the general procedure from 3-methyl indolyl allene (100 mg, 0.55 mmol), PtCl$_2$ (7.3 mg, 0.0275 mmol), pyrrole (111 mg, 1.65 mmol) and dry methanol (67 $\mu$L, 1.65 mmol) in 2.75 mL of dry 1,4-dioxane. Obtained by column chromatography, Pet/EtOAc, 20:1, 89.8 mg, 0.36 mmol, 65% of compound 3an as a brown solid compound.

$^3$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.77 (bs, 1H, H-18), 7.59 (d, $J = 7.8$ Hz, 1H, H-4), 7.32 (d, $J = 8.1$ Hz, 1H, H-7), 7.24 (m, 1H, H-6), 7.18 (m, 1H, H-5), 6.58 (dd, $J = 4.0$, 2.5 Hz, 1H, H-17), 6.22 (dd, $J = 5.8$, 2.7 Hz, 1H, H-16), 6.04 (bs, 1H, H-15), 4.55 (t, $J = 4.5$ Hz, 1H, H-13), 4.20 (dt, $J = 11.2$, 4.7 Hz, 1H, H-10), 3.91 (m, 1H, H-10), 2.26 (m, 1H, H-12), 2.18 (m, 1H, H-12), 2.14 (s, 3H, H-19), 2.08 (m, 1H, H-11), 2.00 (m, 1H, H-11). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 136.2 (C-3), 133.5 (C-2), 132.9 (C-4), 128.6 (C-9), 121.0 (CH, Ar, C-6), 119.3 (CH, Ar, C-5), 118.3 (CH, Ar, C-4), 116.0 (CH, CH=C, C-17), 108.9 (CH, Ar, C-7), 108.8 (CH, Ar, C-16), 104.7 (CH, CH=C, C-15), 42.5 (CH$_2$, C-10), 32.2 (CH, C-13), 29.5 (CH$_2$, C-12), 20.0 (CH$_2$, C-11), 8.25 (CH$_3$, C-19). $\nu_{max}$/cm$^{-1}$: 3407 (m, br, N-H), 2930 (s, C-H), 2860 (m, C-H), 1695, 1667, 1462, 1360 (m, C-N), 739. HRMS (FTMS + p NSI) (DCM/MeOH + NH$_4$OAc): Calculated for C$_{17}$H$_{18}$N$_2$ [M+H]$^+$: 251.1545. Found: 251.1543.

**Dimers**

In reactions with external indoles (entries 8, 10, 11 and 12, Table 1) and in the reaction with the ethyl derivative in C3 of the indolylallene (entry 2, Table 2), small amounts (3-10 %) of a dimer were isolated (see tables 1 and 2 in main manuscript). The structure of the dimers was confirmed by HRMS and tentatively assigned by NMR analysis ($^1$H, $^{13}$C, COSY, HSQC and HMBC)

**Dimer 7a**

![Diagram of Dimer 7a](image)

$^3$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.58 – 7.50 (m, 2H) 8H 7.30 – 7.04 (m, 6H), 6.65 (s, 1H, H-13), 4.18 – 3.92 (m, 4H, H-10 and H-18), 2.83 – 2.41 (m, 4H, H-11 and H-17), 2.32 (s, 3H, H-22), 2.20 (s, 3H, H-14), 1.69 (s, 3H, H-16). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 144.96 (C$_3$), 138.98 (C$_3$), 136.39 (C$_8$), 133.44 (C$_9$), 132.19 (C$_{10}$), 131.77 (C$_{10}$), 129.58 (C$_{11}$), 121.95 (C-AR), 120.67 (C-AR), 119.03 (C-AR), 118.84 (C-AR), 118.77 (C-AR), 118.74 (C-AR), 112.82 (C-13), 109.45 (C-AR), 108.52 (C-AR), 107.37
Supporting Information

(Cₙ), 101.45 (Cₙ), 46.98 (Cₙ), 42.36(C-11, C-17, C-10 or C-18), 40.60 (C-10 or C-18), 26.31 (C-11 or C-17), 23.87 (C-16), 8.42 (C-22), 8.31 (C-14).

HRMS ASAP (Solid): Calc. for C₂₆H₂₇N₂ [M+H]⁺: 367.2096. Found: 367.2174.

Dimer 7g

\[ \begin{align*}
\text{Et} & \quad \text{N} \quad \text{Et} \\
\text{N} & \quad \text{Me} \quad \text{N} \\
\text{Me} & \quad \text{Me} \\
\end{align*} \]

\[^{1}H\text{ NMR (500 MHz, CDCl}_3\delta = 7.59 \ (d, J=7.9, 1H), 7.56 \ (d, J=7.9, 1H), 7.24 \text{–} 7.13 \ (m, 4H), 7.09 \ (t, J=7.5, 1H), 7.05 \ (t, J=7.4, 1H), 6.64 \ (s, 1H), 4.24 \text{–} 4.02 \ (m, 3H), 4.01 \text{–} 3.82 \ (m, 1H), 2.78 \ (q, J=7.3, 2H), 2.69 \ (q, J=7.3, 2H), 2.77 \text{–} 2.54 \ (m, 2H), 2.54 \text{–} 2.31 \ (m, 2H), 1.70 \ (s, 3H), 1.25 \ (t, J=7.3, 3H), 1.23 \ (t, J=7.3, 3H).\]

\[^{13}C\text{ NMR (126 MHz, CDCl}_3\delta = 144.40, 139.19, 136.49, 132.51, 132.42, 131.49, 128.61, 121.86, 120.64, 119.30, 119.06, 119.01, 118.69, 114.31, 112.75, 109.59, 108.66, 108.58, 47.18, 42.53, 42.30, 40.51, 26.17, 24.44, 22.85, 17.28, 16.17, 15.81.\]

HRMS ASAP (Solid): Calc. for C₂₈H₃₁N₂ [M+H]⁺: 395.2487. Found: 395.479.

5. 6-Endo Cyclisation Products as Intermediates in the formation of 2,3’-BIMs and deuterium labelling studies

5.1. Synthesis of 4a with gold catalysis

[Bis(trifluoromethanesulfonyl)imidate[(triphenylphosphine)gold(I)] (22 mg, 0.0275 mmol) and 1-(2, 3-butadien-1-yl)-3-methyl-1H-indole (100 mg, 0.55 mmol) were added to a microwave vial, capped and flushed with N₂. The solids were dissolved in 14 mL toluene (0.04 M) and stirred at rt for 1 hour. The resulting reaction mixture was filtered through celite and washed with DCM. Compound 4a was isolated after concentration in vacuum, 98 mg, 0.54 mmol, 98 % as a brown oil.

**Cycle 4a:** \[^{1}H\text{ NMR (500 MHz, CDCl}_3\delta = 7.48 \text{–} 7.42 \ (m, 2H, H-7), 7.21 \text{–} 7.19 \ (m, 1H, H-4), 7.12 \text{–} 7.02 \ (m, 2H, H-5 \text{+} H-6), 6.05 \text{–} 5.94 \ (m, 2H, H-11 \text{+} H-12), 4.57 \text{–} 4.52 \ (m, 2H, H-10), 3.48 \text{–} 3.42 \ (m, 2H, H-13), 2.19 \ (s, 3H, H-14).\]

\[^{13}C\text{ NMR (126 MHz, CDCl}_3\delta = 122.08 \ (C-12), 120.52 \ (C-11), 120.24 \ (C-Ar), 119.14 \ (C-Ar), 117.74 \ (C-Ar), 108.48 \ (C-Ar), 41.82 \ (C-10), 22.81 \ (C-13), 8.28 \ (C-14).\]

Spectra consistent with previously published data.

2 J. Barluenga, M. Piedratig, A. Ballesteros, A. L. S. Sobrino and J. M. Gonzalez, Chem. Eur. J. 2010, 16, 11827-18831.
5.2 Synthesis of deuterated indoles and indolyl allenes

5.2.a. Synthesis of 1-(2,3-butadien-1-yl)-3-methyl-2-deutero-1H-indole (1a) from 3-methyl-1H-indole (11)³

Sodium hydroxide (267 mg, 6.7 mmol) was dissolved in DCM (15 mL, 0.25 M) under N₂. 3-Methylindole 9 (500 mg, 3.82 mmol) was added and the reaction mixture was stirred for 30 minutes. A solution of p-toluene sulfonfyl chloride (798 mg, 4.2 mmol) was added and the reaction mixture was stirred for 30 minutes. The reaction was stopped and filtered, the filtrate was evaporated under pressure to give 634.9 mg, 2.8 mmol, 75% of compound 10 as a white solid. Compound 10: ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, J = 8.2 Hz, 1H, H-4), 7.74 (d, J = 8.2 Hz, 2H, H-12), 7.45 (d, J = 7.3 Hz, 1H, H-7), 7.31 (m, 2H, H-2 + H-6), 7.23 (td, J = 7.5, 1.1 Hz, 1H, H-5), 7.19 (dd, J = 8.2, 1.0 Hz, 2H, H-11), 2.33 (s, 3H, H-13), 2.24 (d, J = 1.2 Hz, 3H, H-14). ¹³C NMR (126 MHz, CDCl₃) δ 144.76 (C-10), 135.57 (C-9), 131.91 (C-8), 129.8 (CH, C-11), 126.7 (CH, C-12), 124.5 (CH, C-2), 123.0 (CH, C-5), 122.9 (CH, C-6), 119.3 (CH, C-4), 118.71 (C-3), 113.8 (CH, C-7), 21.7 (CH₃, C-14), 9.8 (CH₃, C-15).

3-Methyl-1-tosyl-1H-indole 10 (811.7 mg, 2.8 mmol) was dissolved in 11.4 mL of dry THF under N₂ and cooled to -78°C. n-Butyl lithium (2.25 ml, 5.64 mmol) was added dropwise to the solution and the reaction mixture was stirred at rt for 2 hours. The reaction was re-cooled to -78°C, quenched with D₂O and warmed to room temperature. The solid precipitate was filtered off and the filtrate evaporated under pressure to give 634.9 mg, 2.2 mmol, 78% of compound 11 as a yellow solid with ~90% D incorporation. Compound 11: ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, J = 8.2 Hz, 1H, H-4), 7.74 (d, J = 8.2 Hz, 2H, H-12), 7.45 (d, J = 7.3 Hz, 1H, H-7), 7.31 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H, H-6), 7.23 (td, J = 7.5, 1.1 Hz, 1H, H-5), 7.21 – 7.17 (m, 2H, H-11), 2.33 (s, 3H, H-13), 2.24 (d, J = 1.2 Hz, 3H, H-14).

³ A. R. Katritzky and K. Akutagawa, Tetrahedron Lett. 1985, 26, 5935-5938.
1-Phenylsulphonyl-[2-2H]-3-methylindole 11 (634.9 mg, 2.2 mmol) was added to a round bottomed flask. Methanol (8.5 mL) was added followed by 2.3 mL of a 2M NaOH solution and the mixture was heated at reflux under nitrogen overnight. The reaction did not go to completion, but deprotection was observed by NMR to be around 50 %. The reaction mixture was cooled down, poured into water (10 mL) and extracted with Et₂O. The organic layer was dried with MgSO₄, filtered and concentrated in vacuum to give 12 96.9 mg, 0.7 mmol, 45 % as a pale yellow solid with 85 % deuterium incorporation. This compound was used in the next step without further purification. Compound 12: ¹H NMR (500 MHz, CDCl₃) δ 7.90 (s, 1H, H-1), 7.62 (dd, J = 7.9, 0.6 Hz, 1H, H-4), 7.39 (d, J = 8.1 Hz, 1H, H-7), 7.23 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H, H-6), 7.16 (td, J = 7.6, 1.0 Hz, 1H, H-5), 7.01 (d, J = 1.0 Hz, 0.15H, H-2, H'), 2.38 (s, 3H, H-10). ¹³C NMR (126 MHz, CDCl₃) δ 121.88 (CH, C-6), 119.12 (CH, C-5), 118.84 (CH, C-4), 110.93 (CH, C-7), 9.66 (CH₃, C-10). Some quaternary carbons not detected.
Sodium hydride (41 mg, 1.03 mmol) added to round bottomed flask under N₂ and dissolved in 11 mL THF. The reaction was cooled to 0°C and a solution of 2-deutero-3-methyl-1H-indole 12 (271.4 mg 0.65 mmol) in THF was added and stirred for 30 minutes at 0°C. Propargyl bromide (145 mg, 0.98 mmol) was slowly added and the reaction warmed to room temperature, after 2 hours the reaction was quenched with NaHCO₃ and worked up with Et₂O and water. Obtained after column chromatography, Hex:EtOAc, 20:1 to give compound 13, 53 mg, 0.3 mmol, 48% as a yellow oil with 88% deuterium incorporation at position 2. Compound 13: ¹H NMR (500 MHz, CDCl₃) δ 7.60-7.57 (m, 1H, H-4), 7.36 (d, J = 8.2 Hz, 1H, H-7), 7.25 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H, H-6), 7.13 (ddd, J = 7.9, 7.1, 1.0 Hz, 1H, H-5), 6.98 (d, J = 1.0 Hz, 0.12 H, H-2, H²), 4.83 (d, J = 2.5 Hz, 2H, H-10), 2.37 (t, J = 2.5 Hz, 1H, H-12), 2.34 (s, 3H, H-13). ¹³C NMR (126 MHz, CDCl₃) δ 121.82 (CH, C-5), 119.19 (CH, C-6 and C-7), 109.12 (CH, C-4), 73.10 (CH, C-12), 35.46 (CH₃, C-10), 9.55 (CH₃, C-13). Some quaternary carbons not detected.

Paraformaldehyde (33 mg, 1.09 mmol), CuBr (19 mg, 0.132 mmol) and 3-methyl-1-(2-propynyl)-1H-indole (74 mg, 0.44 mmol) were added to a microwave vial, sealed, flushed with N₂ and dissolved in 2.2 mL dioxane. iPr₂NH (123 µl, 0.88 mmol) was added drop wise and the reaction was heated at 150°C using microwave irradiation for 10 minutes. The reaction was filtered through celite, washed with DCM and concentrated in vacuum. Obtained after column chromatography using Pet Ether/EtOAc, 70:1, to give compound d-1a, 55.1 mg, 0.3 mmol, 68% as a yellow oil with 88% deuterium incorporation. Compound d-1a: ¹H NMR (500 MHz,
Supporting Information

CDCl$_3$ δ 7.57 (d, $J = 7.9$ Hz, 1H, H-$\text{d-4}$), 7.32 (d, $J = 8.2$ Hz, 1H, H-$\text{d-7}$), 7.21 (t, $J = 7.6$ Hz, 1H, H-$\text{d-6}$), 7.11 (t, $J = 7.4$ Hz, 1H, H-$\text{d-5}$), 6.90 (s, 0.12 H, H-$\text{d-2}$), 5.33 – 5.27 (m, 1H, H-$\text{d-11}$), 4.84 (dt, $J = 6.6$, 2.5 Hz, 2H, H-$\text{d-13}$), 4.68 (dt, $J = 6.6$, 2.6 Hz, 2H, H-$\text{d-10}$), 2.33 (d, $J = 2.2$ Hz, 3H, H-$\text{d-4}$). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 121.47 (CH, C-$\text{d-5}$), 4.68 (dt, $J = 6.8$ Hz, 2H, H-$\text{d-2}$), 5.27 (m, 1H, H-$\text{d-11}$), 119.04 (CH, C-$\text{d-5}$), 118.74 (CH, C-$\text{d-4}$), 109.43 (CH, C-$\text{d-7}$), 87.59 (CH, CH=C=C, C-$\text{d-11}$), 67.11 (CH$_2$, CH$_2$=C=C, C-$\text{d-13}$), 45.14 (N-CH$_2$, C-$\text{d-10}$), 9.57 (CH$_3$, C-$\text{d-14}$). Some quaternary carbons not detected.

5.2.b. Synthesis of deuterated indolyl allene $\text{d-2-1a}$:

Deuterated paraformaldehyde (98 % D, 280 mg, 8.75 mmol), CuBr (150 mg, 1.05 mmol) and 3-methyl-1-(2-propyn-1-yl)-1H-indole (592 mg, 3.5 mmol) were added to a microwave vial, sealed and flushed with N$_2$. iPr$_2$NH (2 eqs) was added drop wise and the reaction was heated at 150°C using microwave irradiation for 10 minutes. The reaction was filtered through celite, washed with DCM and concentrated in vacuum. Compound 59 was obtained after column chromatography, Pet Ether/EtOAc, 20:1, 462.4 mg, 2.5 mmol, 71 % as a yellow oil with >95 % D incorporation. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.57 (d, $J = 7.9$ Hz, 1H, H-$\text{d-4}$), 7.32 (d, $J = 8.2$ Hz, 1H, H-$\text{d-7}$), 7.21 (t, $J = 7.6$ Hz, 1H, H-$\text{d-6}$), 7.11 (t, $J = 7.4$ Hz, 1H, H-$\text{d-5}$), 6.90 (s, 1H, H-$\text{d-2}$), 5.29 (t, $J = 6.8$ Hz, 1H, H-$\text{d-11}$), 4.68 (d, $J = 6.8$ Hz, 2H, H-$\text{d-10}$), 2.24 (s, 3H, H-$\text{d-14}$).
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5.2.c. Synthesis of 1-methyl-(3-²H)-1H-indole, d-2i:

All glassware for this experiment was prewashed with deuterium oxide and dried to minimize proton exchange during the reaction.

To a pre-washed round bottomed flask was added 1-methylindole (1220 mg, 9.3 mmol), 2.5 mL D₂O was added, the reaction mixture was heated to 80°C and left for 18 hours. The reaction mixture was worked up with DCM and D₂O. Product obtained after concentrating in vacuum, to yield 1093 mg, 8.27 mmol, 89 % of compound d-2i with 90 % D incorporation. ¹H NMR (500 MHz, CDCl₃) δ 7.71 – 7.67 (m, 1H, H-4), 7.38 (d, J = 8.2 Hz, 1H, H-7), 7.30 – 7.26 (m, 1H, H-5), 7.17 (m, 1H, H-6), 7.10 (s, 1H, H-2), 6.55 (d, J = 3.1 Hz, 0.1H, H²-3), 3.85 (s, 3H, H-10). ¹³C NMR (126 MHz, CDCl₃) δ 136.7 (C-9), 128.8 (C-8), 128.5 (CH, C-2), 121.5 (CH, C-5), 120.9 (CH, C-4), 119.3 (CH, C-6), 109.2 (CH, C-7), 32.8 (CH₃, C-10).
Supporting Information

5.3. Reaction profile of 1a with d-2i monitored by $^1$H NMR

Platinum-catalysed reaction was carried out under optimal conditions and microwave irradiation with the previously isolated 6-endo cycle 4a and external N-methyl indole d-2i with deuterium incorporated into position 3 of the indole (Figure 5.3.1) using dimethylsulfone as internal reference. Samples of the reaction mixture were taken every 10 minutes over a 90-minute period and the progress of the reaction was analysed by $^1$H NMR of the crude using the signals corresponding to the protons in position $a$ of the three compounds: 4 ppm (CH$_2$, 4a), 4.5 ppm (CH$_2$, 4a') and 4.18 ppm (CH diastereotopic, 3ai) to measure the integrals/concentrations of products 4a, 4a' and 3ai over time using the signal of the dimethylsulfone as reference.

![Figure 5.3.1. Platinum-catalysed reaction of cycle 4a with deuterated N-methyl indole d-2i and $^1$H-NMR profile of the reaction highlighting consumption of 4a and formation of 4a' and 3ai over 90 minutes.](image)

The plot the concentration of the products over time (Figure 5.3.2) shows that the non-conjugated cycle 4a isomerizes to the conjugated cycle 4a' within the first 20 minutes. Also noted is that as soon as isomerisation to cycle 4a' begins, so does the formation of compound 3ai, although at a slower rate. At 20 minutes, concentration of cycle 4a' starts to decrease as the concentration of 3ai continues to increase and once both of the cycles are consumed the reaction is complete.
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Figure 5.3.2. Reaction profile showing the consumption of cycle 4a, formation and consumption of cycle 4a' with subsequent formation of 2,3'-BIM 3ai.

The reaction was carried out with deuterated N-methyl indole d-2i, with 90 % deuterium incorporation at the beginning of the reaction. After 5 minutes we observed a loss of deuterium in position 3. Overall we observe a deuterium loss in the external indole of 41 % from position 3 and analysis of the NMRs shows that deuterium is incorporated into cycle 4a' at position d within the first 10 minutes. Analysis also shows that deuterium is incorporated into position d of compound 3ai after 10 minutes with around 31 % deuterium incorporated in the final compound.

5.4. Experiments with deuterated intermediates

5.4.a. 3-Methyl-N-(2,3-butadienyl)indole d2-1a was reacted using gold catalysis to form the non-conjugated cycle d2-4a in an 82 % yield, with 90 % deuterium incorporation at position d (Figure 5.4.1).

Figure 5.4.a. Au-catalysed cyclisation of deuterated 3-methyl-N-(2,3-butadienyl) indole d2-1a with retention of deuterium.
5.4.b. Cycle $d_2$-4a was reacted under platinum conditions without the external indole. Successful isomerisation occurred with >99 % conversion to cycle $d_2$-4a' with an 82 % yield. Analysis of the $^1$H NMR identified that deuterium was incorporated into positions c and d in 26 and 40 % respectively (Figure 5.4.b). Some deuterium loss is observed in the process (~20%).

Figure 5.4.b. Pt catalysed isomerisation of cycle $d_2$-4a to cycle $d_2$-4a'.

5.4.c. When cycle $d_2$-4a was subject to optimized conditions in the presence of external indole 2i, only traces of the desired 2,3'-BIM were identified in the crude $^1$H NMR and only cycles $d_2$-4a and $d_2$-4a' were isolated from the reaction mixture in a 75 % yield in a mixture with a ratio of 1:0.7 ($d_2$-4a: $d_2$-4a') and that cycle $d_2$-4a had 29 % deuterium incorporation at position d and cycle $d_2$-4a' had deuterium in the expected c and d positions with 6 and 30 % respectively. Also noted from the crude NMR is the incorporation of 12 % deuterium into position 3 of the external indole 2i (Scheme 5.4.c).
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When cycle $d_2$-$4a'$ obtained from the reaction in Figure 5.4.b was subject to the platinum conditions with the external indole $2i$, cycle $d_2$-$4a'$ and product $3ai$ were isolated in 44 and 38 % yields respectively. Analysis of cycle $d_2$-$4a'$ shows deuterium retention in position $d$ and partial loss in $c$, whereas analysis of compound $3ai$ by both $^1$H NMR and HSQC NMR indicated that no deuterium was incorporated into the final compound (Scheme 5.4.d).

Scheme 5.4.e. Au-catalysed cyclisation of 3-methyl-2-deuterio-1-(2,3-butadien-1-yl) indole $d$-$1a$.

5.4.f. Isomerisation of cycle $d$-$4a$ was carried out under platinum conditions with no external indole, however 100 % conversion was not achieved and cycles $d$-$4a$ and $d$-$4a'$
were obtained in a ratio of 1:5 (Scheme 5.4.f). The crude $^1$H NMR shows deuterium incorporation of both cycles at position c, with cycle $d$-4a containing 8 % and cycle $d$-4a$'$ containing 16 %.

![Scheme 5.4.f.](image)

5.4.g. The mixture two deuterated cycles obtained in the reaction shown in Scheme 5.4.f. was reacted with external indole 2i using standard platinum conditions, this resulted in the formation of the 2,3'-BIM $d_n$-3ai and cycle $d$-4a$'$ (Scheme 5.4.g). Analysis of the crude $^1$H NMR showed a ratio of 1:2 ($d$-4a$'$:$d_n$-3ai) and deuterium incorporation was found ~8 % deuterium was incorporated at position c$''$ of $d$-4a$'$ and only 8 % was observed at position d of compound $d_n$-3ai.

![Scheme 5.4.g.](image)

6. Further Labelling Experiments

6.1. Deuteration experiments

Reactions were carried out using deuterated and undeuterated starting materials 1a, $d_2$-1a, $d$-1a, 2i, $d$-2i or a combination of them in the absence and presence of methanol, either CH$_3$OH or CD$_3$OD (Table 6.1). The ratio of the three products and the deuterium incorporation in the different positions observed for all the compounds are indicated for each reaction. The deuterium incorporation was analysed by measuring the integrals of the different signals of all the products in the $^1$H NMR of the crude and by analysis of the $^1$H NMR and the HSQC of the purified compounds when possible.

Representative analysis of a pure sample of 2,3'BIM $d_n$-3ai obtained in the reaction in entry 1 in Table 6.1 is shown below: Analysis of the $^1$H NMR of the purified $d_n$-3ai in figure 6.1a shows deuteration incorporation in positions b to d, this was established by comparing the spectrum of the deuterated product with the non-deuterated example, analysing the disappearance of signals or change in multiplicity on those positions and measuring the integrals in relationship to the signal of the proton at 6.25 ppm corresponding to one proton on the C2 position on the N-methyl indole. Position a is unaffected in the reaction, whereas positions b to d have significantly lower integrals which supports deuteration incorporation. Interestingly, both diastereotopic positions of methylenes b and c showed some degree of deuteration incorporation. These are also supported by analysis of the HSQC (Figure 6.1b) where we observe a mixture of CH$_2$ (blue spots) and CHD (red spots, shifted to the top right of the blue signals due to the isotope effect), the intensity of these two signals are in proportion to the calculated % D incorporation.
Supporting Information

Figure 6.1a. $^1$H NMR highlighting deuterium incorporation in compound d₃⁻3ai from reaction shown in entry 1 Table 6.1.

Figure 22. HSQC NMR for compound d₃⁻3ai, showing clearly the deuterium incorporation at positions b and c.
## Supporting Information

### Table 6.1. Summary of deuteration experiments

| Entry | \(d\)-Starting material | MeOH source | \(d\)-4a : \(d\)-4a' | \(d\)-3ai | %D in recovered indole |
|-------|--------------------------|-------------|-----------------|-----------------|-------------------------|
| 1     | ![Image](image1.png)    | MeOH (3 eq) | Traces          | ![Image](image2.png) | 31% yield; 62 (28% loss) |
| 2     | ![Image](image3.png)    | CD\(_3\)OD (3 eq) | 3% yield | ![Image](image4.png) | 19% yield; 55 (35% loss) |
| 3     | ![Image](image5.png)    | --          | 7% yield | ![Image](image6.png) | 4% yield; 27 (63% loss)  |
| 4     | ![Image](image7.png)    | MeOH (3 eq) | 12% | ![Image](image8.png) | 31%; 24 (gain) |
| 5     | ![Image](image9.png)    | CD\(_3\)OD (3 eq) | 1 : 1\(^a\) | ![Image](image10.png) | 42 (gain) |

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\(a\). Ratio of products in the \(^1\)H NMR of the crude. \(b\). Measured in the \(^1\)H NMR of the crude. \(c\). Not accurate due to overlap of the signals. \(d\). Not formed in the reaction.
| Entry | d-Starting material | MeOH source | $d_{-}4a : d_{-}4a'$ | $d_{-}3ai$ | %D in recovered indole |
|-------|---------------------|-------------|---------------------|-----------|----------------------|
| 6     | ![Image](image)     | --          | 1.6 : 1<sup>a</sup> | --        | 20 (gain)            |
| 7     | ![Image](image)     | MeOH (3 eq) | 1.5 : 1<sup>a</sup> | --        | 42 (48% loss)        |
| 8     | ![Image](image)     | CD$_3$OD (3 eq) | 1.6 : 1<sup>a</sup> | --        | 59 (31% loss)        |
| 9     | ![Image](image)     | --          | 1.2 : 1<sup>a</sup> | --        | 31 (59% loss)        |

a. Ratio of products in the $^1$H NMR of the crude. b. Measured in the $^1$H NMR of the crude. c. Not accurate due to overlap of the signals. d. Not formed in the reaction.
Supporting Information

| Entry | d-Starting material | MeOH source | $d_n$-4a:$d_n$-4a' | $d_n$-3ai | %D in recovered indole |
|-------|---------------------|-------------|-------------------|-----------|-----------------------|
| 10    | ![D]-MeOH (88%D)    | MeOH (3 eq) | 1 : 2.4 : 1.4     | (CH), b: 0%D<sup>b</sup> (CH), c: 0%D<sup>b</sup> (CH)<sub>2</sub>, d: 15%D<sup>b</sup> | (CH), b: 30%D<sup>b</sup> (CH), c: 16%D<sup>b</sup> (CH), d: 21%D<sup>b</sup> | (CH)<sub>2</sub>, b: 0-50%D<sup>c</sup> (CH), c: 0-50%D<sup>c</sup> (CH), d: 30%D |
| 11    | ![D]-MeOH (88%D)    | CD<sub>3</sub>OD (3 eq) | 0.2 : 1 : 0.4 | (CH), b: 42%D<sup>b</sup> (CH), c: 73%D<sup>b</sup> (CH)<sub>2</sub>, d: 89%D<sup>b</sup> | (CH)<sub>2</sub>, b: 33%D (CH), c: 62%D (CH), d: 47%D | (CH)<sub>2</sub>, b: 0-50%D<sup>c</sup> (CH), c: 0-50%D<sup>c</sup> (CH), d: 29%D |
| 12    | ![D]-MeOH (88%D)    | --          | 0.3 : 1 : 0.4     | (CH), b': 20%D (CH), c': 10%D (CH)<sub>2</sub>, d': 0-50%D<sup>c</sup> | (CH)<sub>2</sub>, b': 11%D (CH), c': 33%D (CH), d': 16%D | (CH)<sub>2</sub>, b: 0-50%D<sup>c</sup> (CH), c: 0-50%D<sup>c</sup> (CH), d: 10%D |

a. Ratio of products in the <sup>1</sup>H NMR of the crude. b. Measured in the <sup>1</sup>H NMR of the crude. c. Not accurate due to overlap of the signals. d. Not formed in the reaction.
6.2. $^{13}$C-Labeling experiments

6.2.a. Synthesis of $^{13}$C-1a

$^{13}$C-labelled 3-methyl-N-(2,3-butadienyl)indole $^{13}$C-1a, with the $^{13}$C in the terminal carbon of the allene, was synthesized by standard Crabbé homologation using $^{13}$C-paraformaldehyde.

$^{13}$C Paraformaldehyde (99 % atom) (229 mg, 7.38 mmol), CuBr (127 mg, 0.885 mmol) and 3-methyl-1-(2-propyn-1-yl)-1H-indole (500 mg, 2.95 mmol) were added to a microwave vial, sealed, flushed with N$_2$ and dissolved in 14.75 mL dioxane. iPr$_2$NH (827 µl, 5.9 mmol) was added drop wise and the reaction was heated at 150°C for 10 minutes. The reaction was filtered through Celite, washed with DCM and concentrated in vacuum. $^{13}$C-1a was obtained after column chromatography using Pet Ether/EtOAc, 30:1, 428.7 mg, 2.32 mmol, 79 % as a yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.59 (dt, $J = 7.9$, 1.0 Hz, 1H, H-4), 7.34 (dt, $J = 8.2$, 0.9, Hz, 1H, H-7), 7.23 (ddd, $J = 8.2$, 7.0, 1.2Hz, 1H, H-5), 7.13 (ddd, $J = 7.9$, 7.0, 1.0 Hz, H-6), 6.91 (d, $J = 1.0$ Hz, 1H, H-2), 5.39 – 5.18 (m, 1H, H-11), 4.87 (ddt, $J_{C-H} = 168.73$ Hz, $J_{H-H} = 6.6$, 2.7 Hz, 2H, H-13), 4.70 – 4.68 (m, 2H, H-10), 2.35 (d, $J = 1.0$ Hz, 3H, H-14). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 76.92 ($^{13}$CH$_3$, C-13).
Supporting Information

$^{13}$C NMR (126 MHz, CDCl$_3$)

6.2.b. Reaction profile of $^{13}$C-1a with indole $d$-2i

$^{13}$C-labelled 3-methyl-$N$-(2,3-butadienyl)indole $^{13}$C-1a was reacted with deuterated $N$-methyl indole $d$-2i using mw irradiation in the presence of deuterated methanol under normal optimised conditions using dimethylsulfone as the internal standard (Scheme 6.2.b).

![Scheme 6.2.b.](attachment:image)

Scheme 6.2.b. Platinum-catalysed reaction of $^{13}$C-labelled 3-methyl-$N$-(2,3-butadienyl)indole $^{13}$C-1a with deuterated $N$-methyl indole $d$-2i in the presence of deuterated methanol.

The reaction was monitored by $^1$H NMR and $^{13}$C NMR over a 90-minute period, with samples taken every 10 minutes and the progress of the reaction was analysed by $^1$H NMR of the crude using the signals corresponding to the protons in position α of the three compounds: 4 ppm (CH$_2$, 4a), 4.5 ppm (CH$_2$, 4a') and 4.18 ppm (CH diastereotopic, 3ai) to measure the integrals/concentrations of products 4a, 4a' and 3ai over time using the signal of the dimethylsulfone as reference. Analysis of the $^1$H NMR spectra of the crude of the samples showed very fast reaction of the allenyl indole 1a to form cycle 4a and isomerization of cycle 4a to 4a' as seen before. However, in this case full conversion of
Supporting Information

cycle 4a’ to the BIM 3ai was not observed probably due to a kinetic isotope effect on the 13C-analogues (Figure 6.2.b.1, compare with graph in Figure 5.3.2).

Figure 6.2.b.1. Reaction profile showing the reaction progress for the $^{13}$C labelled reaction in scheme 6.2.b.

Analysis of the $^{13}$C NMR spectra showed high deuterium incorporation in the labeled carbon in all compounds from early stages of the reaction (Figure 6.2.b.2).
6.3. Reaction of 3ai in the presence of PtCl\(_2\) and CD\(_3\)OD

The isolated non-labeled 2,3'-BIM 3ai was reacted under platinum conditions in the presence of deuterated methanol to determine if deuterium incorporation can occur further at position \(d\) in an out-of-cycle process (Scheme 6.3). The \(^1\)H NMR after 1 hour shows 42 % deuterium incorporation at position \(d\) only (Figure 6.3).

Scheme 6.3. Platinum-catalysed reaction to highlight deuterium exchange at position \(d\) of compound 3ai in the presence of deuterated methanol.

Figure 6.3a. \(^1\)H NMR spectra of 3ai before the reaction shown in scheme 6.3.

Figure 6.3b. \(^1\)H NMR spectra of 3ai after the reaction shown in scheme 6.3.
Supporting Information

7. NMR spectra

**Cycle 4a**

![Cycle 4a and its NMR spectra](image)

**Cycle 4a**

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

**Cycle 4a’**

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

2,3'-BIM 3aa

\[
\begin{align*}
\text{H NMR (500 MHz, CDCl}_3, 25^\circ \text{C, TMS)}
\end{align*}
\]

\[
\begin{align*}
\text{\underline{\text{C NMR (126 MHz, CDCl}_3, 25^\circ \text{C)}}}
\end{align*}
\]
Supporting Information

2,3′-BIM 3ba

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

2,3-BIM 3ca

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (CDCl$_3$)

2D HSQC (CDCl$_3$)
Supporting Information

2,3'-BIM 3da

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

Cycles 4d:4d' (1:0.95)

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

Cycles 4e:4e' (0.78:1)

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

Cycles 4f:4f' (0.8:1)

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

2,3'-BIM 3ab

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)

2D gCOSY (CDCl$_3$)
Supporting Information

2D HSQC (CDCl₃)
Supporting Information

2,3'-BIM 3ac

$^1$H NMR (500 MHz, CDCl$_3$, 25$^\circ$C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25$^\circ$C)
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

2,3’-BIM 3ad

\[\text{H NMR (500 MHz, CDCl}_3, \text{ 25°C, TMS)}\]

\[\text{\textsuperscript{13}C NMR (126 MHz, CDCl}_3, \text{ 25°C)}\]

\[\text{\textsuperscript{13}C NMR (126 MHz, CDCl}_3, \text{ 25°C)}\]
Supporting Information

2D gCOSY (CDCl₃)

NOESY
Supporting Information

2,3'-BIM 3ai

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

2,3'-BIM 3aj

![Chemical structure of 2,3'-BIM 3aj](image)

![NMR spectra of 2,3'-BIM 3aj](image)
Supporting Information

2,3’-BIM 3ak

![Chemical structure of 2,3’-BIM 3ak](image)

![NMR spectra of 2,3’-BIM 3ak](image)
Supporting Information

2,3'-BIM 3al

![Chemical Structure Image]
Supporting Information

2,3'-BIM 3am
Supporting Information

2,3'-BIM 3bb

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

2,3'-BIM 3ga

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D HSQC (CDCl$_3$)
Supporting Information

Cycle 4h′

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D HSQC (CDCl₃)
Supporting Information

2,3'-BIM 3ha

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D HSQC (CDCl₃)
Supporting Information

Cycle 4r'

\[ \text{\textsuperscript{1}H NMR (500 MHz, CDCl}_3, 25^\circ\text{C, TMS)}] \]

\[ \text{\textsuperscript{13}C NMR (126 MHz, CDCl}_3, 25^\circ\text{C)}] \]
Supporting Information

2,3'-BIM 3ia

\[
\text{H NMR (500 MHz, CDCl}_3, \text{25}^\circ\text{C, TMS)}
\]

\[
\text{C NMR (126 MHz, CDCl}_3, \text{25}^\circ\text{C)}
\]
Supporting Information

2D HSQC (CDCl₃)
Supporting Information

2,3'-BIM 3ja

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D HSQC (CDCl₃)
Supporting Information

Trisindole 5ka

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D HSQC (CDCl₃)
Supporting Information

Allyl indole 6ka

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D HSQC (CDCl₃)
Supporting Information

Trisindole 5la

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D HSQC (CDCl$_3$)
Supporting Information

Allyl indole 6la

$^1$H NMR (500 MHz, CDCl$_3$, 25$^\circ$C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25$^\circ$C)
Supporting Information

2D HSQC (CDCl₃)
Supporting Information

Trisindole 5ma

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

2D HSQC (CDCl$_3$)
Supporting Information

Allyl indole 6ma

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D HSQC (CDCl₃)
Supporting Information

Trisindole 5Na

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D HSQC (CDCl₃)
Supporting Information

 Allyl indole 6na

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D HSQC (CDCl$_3$)
Supporting Information

Trisindole 5oa

$^1$H NMR (500 MHz, acetone-$d_6$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (acetone-\textit{d}_6)

2D HSQC (CDCl$_3$)
Supporting Information

Allyl indole 6oa

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

Cycles 4p' and 4p (traces)

\[ \text{Me} \quad \text{Me} \]

\[ \text{H NMR (500 MHz, CDCl}_3, 25^\circ\text{C, TMS)} \]

\[ \text{Me} \quad \text{Me} \]

\[ \text{C NMR (126 MHz, CDCl}_3, 25^\circ\text{C)} \]

\[ \text{Me} \quad \text{Me} \]

\[ \text{NMR spectra for 1H and 13C showing characteristic resonances for the molecules.} \]
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

Dimer 7a

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25°C)
Supporting Information

2D gCOSY (CDCl₃)

2D HSQC (CDCl₃)
Supporting Information

2D HMBC (CDCl₃)
Supporting Information

Dimer 7g

\[
\begin{align*}
\text{H NMR (500 MHz, CDCl}_3, 25^\circ\text{C, TMS)}
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (126 MHz, CDCl}_3, 25^\circ\text{C)}
\end{align*}
\]
Supporting Information

**Compound 3an**

$^1$H NMR (500 MHz, CDCl$_3$, 25$^\circ$C, TMS)

$^{13}$C NMR (126 MHz, CDCl$_3$, 25$^\circ$C)
Supporting Information

2D gCOSY (CDCl$_3$)

2D HSQC (CDCl$_3$)
Supporting Information

2D HMBC (CDCl₃)