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Introducing tetramethylurea as a new methylene precursor: Microwave-assisted $RuCl_3$-catalyzed cross dehydrogenative coupling approach to bis(indolyl)methanes

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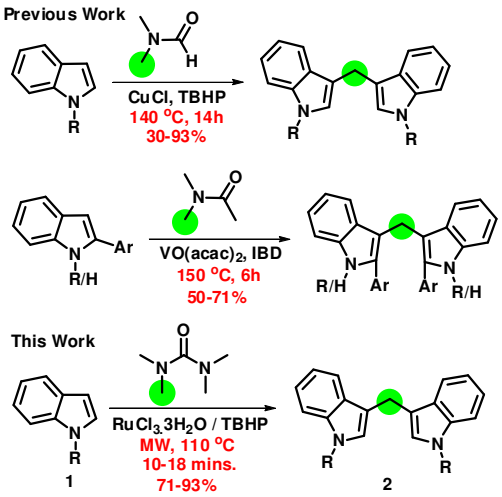
Here we report a microwave assisted Ru(III)/TBHP-mediated reaction of indoles with tetramethylurea (TMU) synthesizing symmetrical as well as unsymmetrical bis(indolyl)methanes, where TMU acts as a methylenating agent. This is the first report where TMU is used as methylene source. Moreover, The synthesis of unsymmetrical bis(indolyl)methanes by using carbon precursor is also reported here for the first time. Various substituted indoles are used for the reaction. The reaction is high yielding and takes much shorter time to accomplish compared to existing methods.

Introduction

Functionalization of amines *via* C-H activation has recently attracted much attention in organic chemistry and the fine chemical industry as functionalized amines are highly useful intermediates for the synthesis of many pharmaceuticals and functional materials.[1] Direct introduction of a substituent/functional group at the α-position of tertiary amines has usually been achieved by using transition metal catalysts with an oxidant to generate the iminium ion, which subsequently reacts with various C/N/O/S nucleophiles.[2] When such reactions are carried out under microwave irradiation, it becomes more interesting as the technique offers simple, clean, fast, efficient, and economic way for the synthesis of many organic molecules compared to conventional thermal methods. Therefore, this generates the momentum for many chemists to switch from conventional heating to microwave assisted technique.[3]

Bis(heterocycle)methanes have attracted much attention of organic chemists in recent years due to their broad spectrum of biological activities. For example, bis(indolyl)methanes (BIM) and its derivatives are available as dietary supplements, which increases the 2-hydroxylation of estrogen metabolites, that helps to reduce the risk of breast and prostate cancer.[4] It is also used to treat recurrent respiratory papillomatosis, a rare respiratory disease with tumors in the upper respiratory tracts.[5] In addition, due to its innate immune modulating properties, BIM is also under investigation as a treatment for a variety of viral and bacterial infections.[6] Although numerous reports are available for the synthesis of substituted BIMs, however, BIMs having methylene bridge is difficult to synthesize by usual coupling of indoles with formaldehyde.[7] They are synthesized by the acid catalyzed dimerization of indole-3-carbinol, which itself is very difficult to prepare because of its high instability.[8] Jaisankar[9a] and Li et al.[9b] synthesized them by using hexamethylenetetramine and tetramethylethylenediamine as methylene precursors. These methods either require high catalyst loading[9b] or longer reaction time.[9a]



Scheme1. Reaction of indoles with different carbon precursors

Results and discussion

N,N-Dimethylformamide (DMF)[10] and dimethylsulfoxide (DMSO)[11] are well known polar aprotic solvents, have already proven to be a multipurpose reagents used for the

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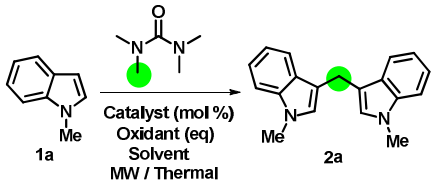
Table 1. Optimization of the reaction[a]



Entry	Catalyst (mol %)	Oxidant (eq.)	Solvent	Temp. (°C) MW (Thermal)	Time (mins.) MW (Thermal)	Yield (%)[c] MW (Thermal)
1	$Cu(OAc)_2.H_2O$ (10)	TBHP (2)	---	110 (130)	15 (120)	60 (56)
2	CuBr (10)	TBHP (2)	---	110 (130)	20 (180)	40 (32)
3	$FeCl_3.6H_2O$ (10)	TBHP (2)	---	110 (130)	20 (180)	none
4	$AgNO_3$ (10)	TBHP (2)	---	110 (130)	20 (180)	none
5	$RuCl_3.3H_2O$ (10)	TBHP (2)	---	110 (130)	10 (90)	85 (77)
6	I_2 (10)	TBHP (2)	---	110 (130)	20 (180)	48 (42)
7	TBAI (10)	TBHP (2)	---	110 (130)	20 (180)	50 (46)
8	$RuCl_3.3H_2O$ (10)	TBHP (2)[b]	---	110 (130)	10 (90)	72 (65)
9	$RuCl_3.3H_2O$ (10)	TBHP (1)	---	110 (130)	10 (90)	68 (60)
10	$RuCl_3.3H_2O$ (10)	TBHP (3)	---	110 (130)	10 (90)	82 (71)
11	**$RuCl_3.3H_2O$ (5)**	**TBHP (2)**	**---**	**110 (130)**	**10 (90)**	**85 (76)**
12	$RuCl_3.3H_2O$ (3)	TBHP (2)	---	110 (130)	10 (90)	72 (64)
13	$RuCl_3.3H_2O$ (10)	TBHP (2)	Toluene	110 (reflux)	15 (120)	61 (52)
14	$RuCl_3.3H_2O$ (10)	TBHP (2)	CH_3CN	110 (reflux)	20 (180)	42 (40)
15	$RuCl_3.3H_2O$ (10)	TBHP (2)	EtOH	110 (reflux)	15 (180)	38 (25)
16	$RuCl_3.3H_2O$ (10)	TBHP (2)	H_2O	110 (reflux)	15 (120)	49 (36)
17	$RuCl_3.3H_2O$ (10)	H_2O_2 (2)	---	110 (130)	15 (90)	66 (63)
18	$RuCl_3.3H_2O$ (10)	DTBP (2)	---	110 (130)	20 (180)	trace (n.r.)[d]
19	$RuCl_3.3H_2O$ (10)	$K_2S_2O_8$ (2)	---	110 (130)	20 (180)	trace (n.r.)
20	$RuCl_3.3H_2O$ (10)	air	---	110 (130)	20 (180)	n.r. (n.r.)
21[e]	$RuCl_3.3H_2O$ (100)	---	---	110 (130)	20 (180)	n.r. (n.r.)

[a] Unless otherwise mentioned, all the reactions were performed by using **1a** (1.0 mmol, 131 mg) and TMU (2.0 mmol, 232 mg). TBHP (5.5M in decane) was used. [b] TBHP (70 % in water) was used. [c] Products were purified by column chromatography by using silica gel (100-200 mesh) and yields are for the isolated products. [d] n.r.: no reaction. [e] The reaction was performed on 0.5 mmol scale.

introduction of diverse units including -CH_2 and -CH_3. N,N-Dimethylacetamide (DMA) is another aprotic solvent used for the similar purpose.[12] Recently, DMF and DMA were used as a methylene source for the synthesis of 3,3-bis(indolyl)methane (BIM) in presence of transition metal catalysts (Scheme 1).[13] Although the methods give moderate yield, but require long reaction time, high temperature or only 2-aryl substituted indole as substrate and, therefore, developing a method with shorter reaction time and better substrate compatibility is in demand. Tetramethylurea (TMU) is also an aprotic solvent used in organic synthesis. It is widely obtained as a byproduct in pharmaceutical industry from the amide coupling reaction when benzotriazolyluronium salts (e.g. HBTU, HATU) are used as coupling agents.[14] In continuation of our work on the α-C-H functionalization of tertiary amine,[15] here we disclose TMU as a new methylene precursor for the synthesis of BIMs catalyzed by $RuCl_3.3H_2O$ under microwave irradiation (Scheme 1). To the best of our knowledge, this is the first report of the application of TMU as a methylene precursor.

We considered the conversion of **1a** into **2a** as the model reaction for the optimization of the reaction condition.

Different catalysts and oxidants were screened for the reaction. We compared the yield of the reaction in both the microwave and thermal condition, but obtained better yield in shorter time by using the former technique (Table 1). We then established that $RuCl_3.3H_2O$ (5 mol %) and *tert*-butyl hydroperoxide (TBHP in decane, 2 eq) in TMU (2 eq) at 110 ˚C under microwave irradiation were the optimized conditions for the reaction (entry 11, Table 1). Screening of other oxidants such as H_2O_2 gave us 61 % yield, whereas DTBP and $K_2S_2O_8$ produced only traces of product (entries 17-19, Table 1). However, no reaction took place when air was used as the oxidant (entry 20, Table 1). We then checked the reaction with different amount of TBHP and found that both the decrease and increase of the loading of TBHP result in decrease in the yield (entry 9 and 10, Table 1). On the other hand, decreasing the amount of $RuCl_3.3H_2O$ from 5 to 3 mol % decreases the yield (entry 12, Table 1). However, no effect was observed on the yield with increased catalyst loading (entry 5, Table 1). Use of other catalysts such as Cu(II), Cu(I), Fe(III), Ag(I) and molecular I_2 provided lower yield. A variety of solvents was also checked, but none of them produced good yield.

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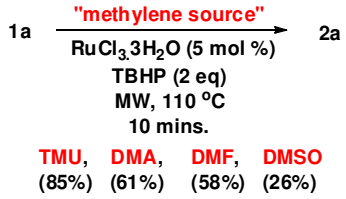
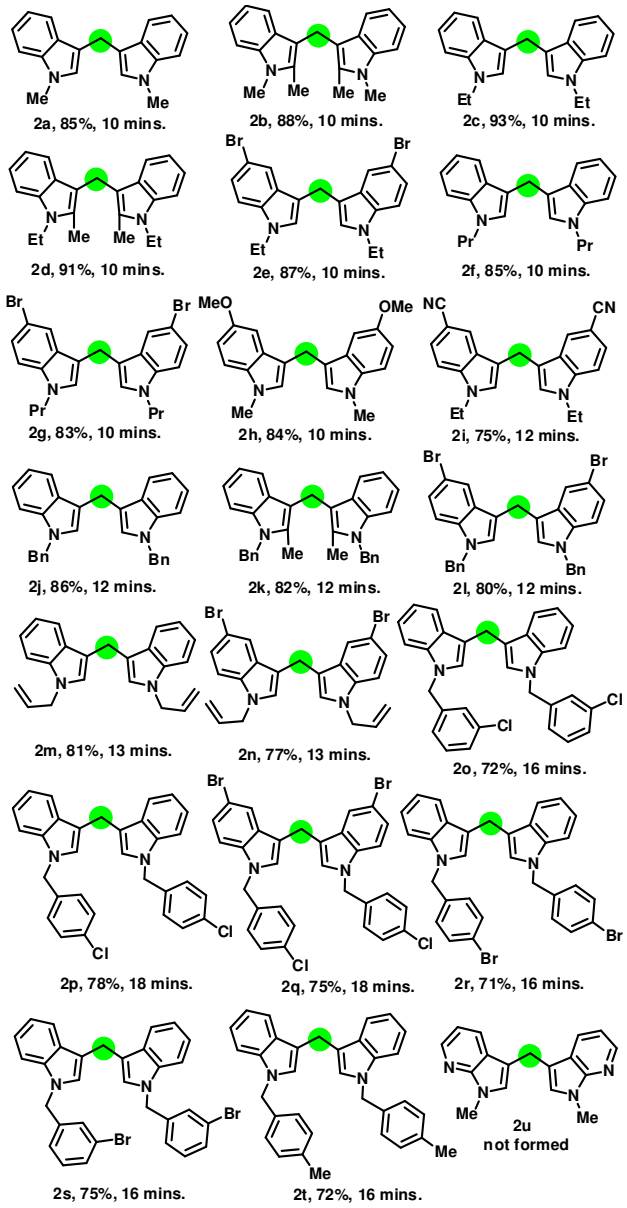


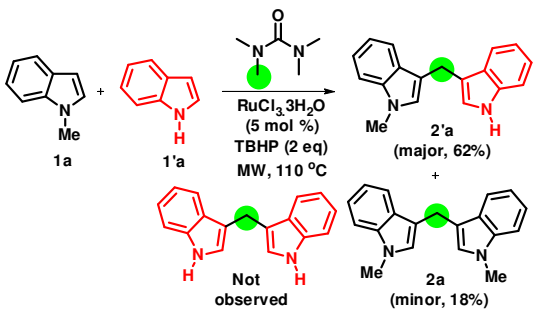
Scheme 2. Comparison of yield of BIM with different methylene precursors



Scheme 3. Substrate scope for the synthesis of BIMs (**2**). Reaction conditions: 1 (1.0 mmol), TMU (2.0 mmol, 232 mg), $RuCl_3.3H_2O$ (5 mol %, 13 mg), TBHP (5.5M in decane, 2.0 mmol, 364 mg) at 110 °C under microwave irradiation. Products were purified by column chromatography using silica gel (100-200 mesh) and yields are for the isolated products.

(Table 1). When DMF, DMA and DMSO were used as methylene precursors, they produced lower yield of the product compared to TMU under optimized condition (Scheme 2).

Having identified the optimized conditions, we next investigated the substrate scope for the synthesis of BIMs (Scheme 3). We used a variety of N-substituted indoles and to our delight, the resultant BIMs were obtained in good to excellent yield. N-alkylindole produced higher yield than N-benzyl/allylindole. The yield of the product was not affected when electron-donating group is present on the phenyl ring of indole (e.g., **2h** Scheme 3). On the other hand, presence of electron-withdrawing group produced comparatively lower yield (e.g., **2c** Vs **2i**, Scheme 3). When 7-aza-1-methylindole was used, we did not obtain any product (**2u**, Scheme 3). The reason we believe is that the nitrogen atom on the phenyl ring of indole may coordinate to the metal catalyst which prevents the reaction. N-H indoles did not react in this condition. However, when 1:1 mixture of N-methylindole (**1a**) and N-H indole (**1'a**) was used under the optimized condition, we obtained unsymmetrical BIM (**2'a**) as the major product along with symmetrical BIM (**2a**) as minor (Scheme 4). As the synthesis of unsymmetrical BIMs was difficult by other



Scheme 4. Cross reaction between two different indoles

methods,[16] we were interested to investigate the substrate scope for their synthesis. To our delight, compounds **2'** which contain a wide range of substituents could be obtained in moderate yields as summarized in scheme 5. The products of these reactions were characterized by NMR spectroscopy as well as X-ray crystallography (single crystal X-ray structure of **2b** and **2'a**, Figure 1).[17]

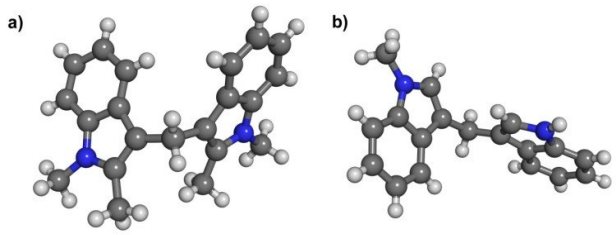


Figure 1. X-ray structure of compound **2b** and **2'a**

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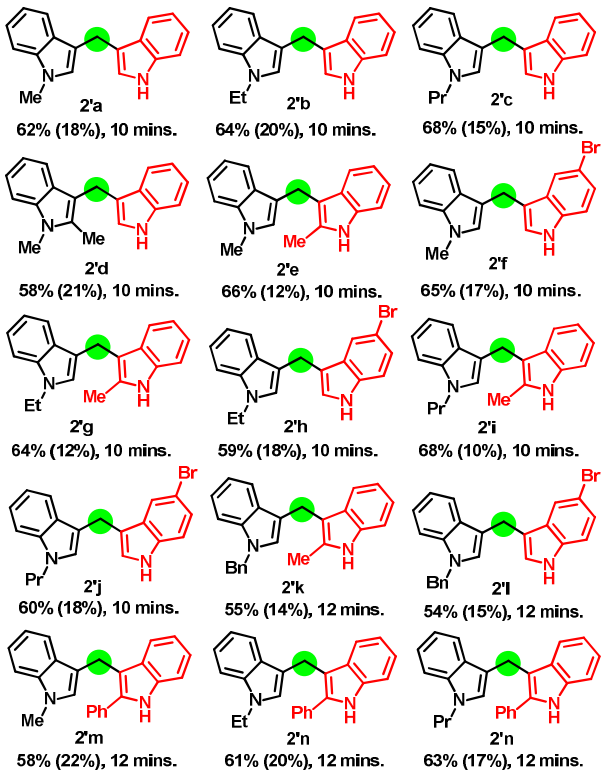
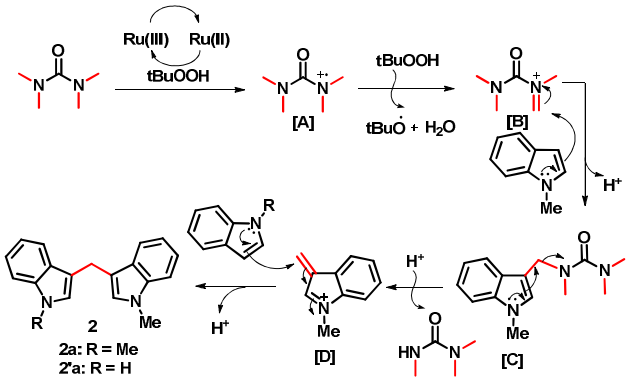
To find out the reaction mechanism, we carried out the model reaction in presence of radical scavengers such as BHT, TEMPO under the optimized reaction condition to check the possibility of radical route. We noticed a substantial inhibition of the formation of **2a** by both the radical scavengers and obtained 11 % of **2a** in case of BHT, whereas TEMPO produced only 7 % of **2a**. Therefore, we believe that the formation of BIMs involved free radical route. We also noticed that use of stoichiometric amount of catalyst in absence of TBHP produced no product, which confirms that TBHP acts more than as an oxidant. We, therefore, propose a tentative mechanism for the formation of **2** on the basis of our experiments and relevant reports (Scheme 6).[1a, 13a] First, Ru(III) removes an electron from the nitrogen of TMU, which generates a radical cation [**A**]. In presence of TBHP, [**A**] gets converted to iminium ion [**B**]. This ion is then attacked by N-substituted indole (**1a**) generating [**C**], which subsequently eliminates a molecule of trimethylurea to produce alkylideneindoleninium ion [**D**]. This ion either can be attacked by another N-substituted indole (**1a**) or NH-indole (**1'a**, if cross reaction is performed) furnishing **2a** or **2'a** respectively.



Scheme 5. Substrate scope for the synthesis of unsymmetrical BIMs (2'). Reaction conditions: 1 (0.5 mmol), 1' (0.5 mmol), TMU (2.0 mmol, 232 mg), $RuCl_3.3H_2O$ (5 mol %, 13 mg), TBHP (5.5M in decane, 2.0 mmol, 364 mg) at 110 °C under microwave irradiation. Products were purified by column chromatography using silica gel (100-200 mesh) and yields are for the isolated products. The yields shown in the parenthesis are the amount of corresponding symmetrical BIMs of N-alkylindoles.



Scheme 6. Tentative mechanism proposed for the reaction

Conclusions

In conclusion, we have developed a microwave assisted $RuCl_3.3H_2O$/TBHP mediated reaction of indoles with tetramethylurea, which produced 3,3-bis(indolyl)methanes in good to excellent yield with relatively shorter reaction time. Moreover, unsymmetrical bis(indolyl)methanes can also be synthesized in moderate yield by this method. The methylene carbon of the product molecule is delivered by TMU. This is the first report of TMU as a methylenating agent. Since a large amount of TMU is obtained as industrial byproduct, their use as the methylenating agent in the reaction made the methodology more useful.

Experimental

General information

All the commercially available reagents were used as received. Melting points were determined in open capillary tubes with a Buchi-540 micro melting point apparatus and were uncorrected. I.R. spectra were recorded on a Perkin-Elmer system 2000 FT-IR spectrometer. Mass spectra (ESI-HRMS) were recorded on Agilent Accurate-Mass Q-TOF LC/MS 6520. NMR spectra were recorded on a Bruker Avance DPX-300 and -500 NMR spectrometer with TMS as the internal standard at room temperature. Chemical shifts (δ) are quoted in ppm and coupling constants (*J*) are measured in Hertz (Hz). All the experiments were monitored by thin layer chromatography (TLC) on pre-coated silica gel plates (Merck) and visualized under UV lamp at 254 nm for UV active materials. Further visualization was achieved by staining $KMnO_4$ warming in a hot air oven or by iodine vapor. Column chromatography was performed on silica gel (100-200 mesh, Merck) using ethyl acetate/hexane as eluent.

Microwave instrumentation

All microwave reactions were carried out in a Synthos 3000 (Anton Paar) microwave reactor. The multitude microwave has a twin magnetron (2.45 GHz) with maximum output power of 1400 W. The

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output power can be controlled in unpulsed control mode over whole power which is adjustable in 1 W increment. A 68xxx series microprocessor system control is used to measure power, pressure, time and temperature during the reaction. The temperature and pressure were monitored throughout the reaction by an infrared detector. The temperature can be measured from 0 to 280 °C with uncertainty ±1%. The pressure can be measured from 0 to 86 bar with uncertainty ±0.2 bar. The MW power is initially set at 600 W but during the course of the reaction, once the set temperature is reached, the reactor automatically adjusts the power by lowering it.

Representative procedure for the synthesis of 2a

N-methylindole (1 mmol, 131 mg), TMU (2 mmol, 232 mg), $RuCl_3.3H_2O$ (5 mol %, 13 mg) and TBHP (5.5 M in decane, 2 mmol, 364 mg) were irradiated in a closed vessel inside a microwave reactor at 110 ˚C for specified time. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature and poured into water (10 mL). Then extracted with ethyl acetate (2 x 10 mL) and dried over anhydrous Na_2SO_4. Removed the solvent under reduced pressure and purified the crude product by column chromatography (silica gel, 100-200 mesh; ethyl acetate/hexane as eluent) to obtain the desired product **2a**.

The representative procedure for the synthesis of 2'a

The procedure is same as above except in place of N-methylindole, a mixture of N-methylindole (0.5 mmol) and NH-indole (0.5 mmol) were taken.

Bis(1-methyl-1H-indol-3-yl)methane (2a)[18]

Low melting red solid; Yield 85 %, 233 mg; IR ($CHCl_3$): 3080, 2913, 1644, 1396, 1218, 1052 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.23-7.20 (m, 2H), 7.10-7.07 (m, 2H), 6.79 (s, 2H), 4.22 (s, 2H), 3.70 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.1, 127.9, 126.9, 121.4, 119.3, 118.5, 114.3, 109.1, 32.6, 20.9; HRMS (ESI) exact mass calculated for $C_{19}H_{18}N_2$ $[M + H]^+$: 275.1548; found: 275.1553.

Bis(1,2-dimethyl-1H-indol-3-yl)methane (2b)

Light red solid; Yield 88 %, 266 mg; Mp = 111-113 °C; IR (KBr): 3102, 2926, 1622, 1376, 1210, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.22-7.19 (m, 2H), 7.10-7.07 (m, 2H), 6.97-6.94 (m, 2H), 4.14 (s, 2H), 3.61 (s, 6H), 2.36 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.5, 133.1, 132.6, 128.5, 128.3, 128.0, 120.2, 118.5, 118.4, 110.3, 108.3, 29.4, 19.9, 10.4; HRMS (ESI) exact mass calculated for $C_{21}H_{22}N_2$ $[M + H]^+$: 303.1861; found: 303.1856.

Bis(1-ethyl-1H-indol-3-yl)methane (2c)[18a]

Red gummy solid; Yield 93 %, 281 mg; IR ($CHCl_3$): 3087, 2933, 1621, 1377, 1216, 1061, 744 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.63-7.61 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.22-7.19 (m, 2H), 7.09-7.06 (m, 2H), 6.86 (s, 2H), 4.23 (s, 2H), 4.09 (q, *J* = 7.2 Hz, 4H), 1.40 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.1, 128.1, 125.3, 121.2, 119.4, 118.5, 114.3, 109.1, 40.7, 21.1, 15.5; HRMS (ESI) exact mass calculated for $C_{21}H_{22}N_2$ $[M + H]^+$: 303.1861; found: 303.1867.

Bis(1-ethyl-2-methyl-1H-indol-3-yl)methane (2d)[18a]

Brown solid; Yield 91 %, 300 mg; Mp = 98-100 °C; IR (KBr): 3082, 2917, 2856, 1622, 1385, 1210, 1066, 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 7.0 Hz, 2H), 6.96-6.93 (m, 2H), 4.14 (s, 2H), 4.11 (q, *J* = 7.2 Hz, 4H), 2.35 (s, 6H), 1.30 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.4, 131.9, 128.3, 120.1, 118.5, 118.4, 110.4, 108.3, 37.6, 19.9, 15.4, 10.2; HRMS (ESI) exact mass calculated for $C_{23}H_{26}N_2$ $[M + H]^+$: 331.2174; found: 331.2179.

Bis(5-bromo-1-ethyl-1H-indol-3-yl)methane (2e)

White solid; Yield 87 %, 400 mg; Mp = 141-142 °C; IR (KBr): 3069, 2856, 1626, 1465, 1391, 1218, 988, 744 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, *J* = 1.8 Hz, 2H), 7.28 (d, *J* = 1.8 Hz, 1H), 7.26 (d, *J* = 1.8 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.85 (s, 2H), 4.11 (s, 2H), 4.07 (q, *J* = 7.3 Hz, 4H), 1.40 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.9, 129.6, 126.4, 124.1, 121.9, 113.5, 112.0, 110.7, 41.0, 20.9, 15.5; HRMS (ESI) exact mass calculated for $C_{21}H_{20}Br_2N_2$ $[M + H]^+$: 459.0071; found: 459.0066.

Bis(1-propyl-1H-indol-3-yl)methane (2f)

Brown gummy solid; Yield 85 %, 280 mg; IR ($CHCl_3$): 3077, 2913, 1640, 1394, 1212, 1118, 1054, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.21-7.17 (m, 2H), 7.07-7.04 (m, 2H), 6.83 (s, 2H), 4.22 (s, 2H), 3.98 (t, *J* = 7.2 Hz, 4H), 1.83-1.76 (m, 4H), 0.88 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.4, 128.0, 126.1, 121.1, 119.4, 118.4, 114.0, 109.2, 47.8, 23.6, 21.1, 11.5; HRMS (ESI) exact mass calculated for $C_{23}H_{26}N_2$ $[M + H]^+$: 331.2174; found: 331.2180.

Bis(5-bromo-1-propyl-1H-indol-3-yl)methane (2g)

White solid; Yield 83 %, 405 mg; Mp = 124-126 °C; IR (KBr): 3054, 2858, 1630, 1462, 1364, 1204, 1012, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J* = 1.5 Hz, 2H), 7.26-7.24 (m, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.84 (s, 2H), 4.11 (s, 2H), 3.99 (t, *J* = 7.0 Hz, 4H), 1.84-1.77 (m, 4H), 0.89 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.2, 129.5, 127.2, 124.1, 121.9, 113.2, 111.9, 110.8, 48.0, 23.5, 21.0, 11.5; HRMS (ESI) exact mass calculated for $C_{23}H_{24}Br_2N_2$ $[M + H]^+$: 487.0384; found: 487.0379.

Bis(5-methoxy-1-methyl-1H-indol-3-yl)methane (2h)[18b]

White solid; Yield 84 %, 281 mg; Mp = 134-136 °C; IR (KBr): 3051, 2853, 1630, 1466, 1361, 1188, 1056, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.21 (d, *J* = 6.6 Hz, 2H), 7.05 (d, *J* = 1.8 Hz, 2H), 6.88 (d, *J* = 6.2 Hz, 2H), 6.77 (s, 2H), 4.14 (s, 2H), 3.81 (s, 6H), 3.66 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.8, 132.8, 128.2, 127.6, 113.8, 111.6, 109.8, 101.2, 56.2, 32.7, 20.8; HRMS (ESI) exact mass calculated for $C_{21}H_{22}N_2O_2$ $[M + H]^+$: 335.1760; found: 335.1766.

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3,3'-Methylenebis(1-ethyl-1H-indole-5-carbonitrile) (2i)[18a]

Brown solid; Yield 75 %, 264 mg; Mp = 139-141 °C; IR (KBr): 3056, 2842, 2226, 1621, 1442, 1364, 1201, 1011, 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 1.8 Hz, 2H), 7.43 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 6.99 (s, 2H), 4.22 (s, 2H), 4.16 (q, *J* = 7.3 Hz, 4H), 1.45 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.8, 127.4, 127.2, 124.9, 124.4, 120.9, 114.6, 110.0, 101.6, 41.1, 21.0, 15.3; HRMS (ESI) exact mass calculated for $C_{23}H_{20}N_4$ $[M + H]^+$: 353.1766; found: 353.1761.

Bis(1-benzyl-1H-indol-3-yl)methane (2j)[18]

Off white solid; Yield 86 %, 366 mg; Mp = 131-132 °C; IR (KBr): 3109, 3052, 2856, 1620, 1369, 1216, 1035, 742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.26-7.23 (m, 10H), 7.17-7.14 (m, 2H), 7.08 (d, *J* = 7.2 Hz, 4H), 6.92 (s, 2H), 5.25 (s, 4H), 4.26 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.9, 136.8, 128.6, 128.2, 127.4, 126.6, 126.5, 121.6, 119.5, 118.8, 114.8, 109.6, 49.8, 21.2; HRMS (ESI) exact mass calculated for $C_{31}H_{26}N_2$ $[M + H]^+$: 427.2174; found: 427.2180.

Bis(1-benzyl-2-methyl-1H-indol-3-yl)methane (2k)

White solid; Yield 82 %, 372 mg; Mp = 129-131 °C; IR (KBr): 3104, 3056, 2849, 1622, 1366, 1201, 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.27-7.16 (m, 7H), 7.08-7.03 (m, 3H), 6.97-6.94 (m, 2H), 6.90-6.89 (m, 4H), 5.32 (s, 4H), 4.21 (s, 2H), 2.36 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1, 136.3, 132.4, 128.6, 128.5, 128.1 (2C), 127.0, 125.7, 120.5, 118.7, 118.5, 111.0, 108.7, 46.2, 20.1, 10.5; HRMS (ESI) exact mass calculated for $C_{33}H_{30}N_2$ $[M + H]^+$: 455.2487; found: 455.2491.

Bis(1-benzyl-5-bromo-1H-indol-3-yl)methane (2l)

White shining solid; Yield 80 %, 467 mg; Mp = 174-176 °C; IR (KBr): 3114, 2855, 1612, 1468, 1354, 1192, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 1.7 Hz, 2H), 7.31-7.28 (m, 4H), 7.26-7.24 (m, 2H), 7.22-7.20 (m, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 7.06-7.04 (m, 4H), 6.92 (s, 2H), 5.23 (s, 4H), 4.14 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.2, 135.5, 129.7, 128.8, 127.7, 127.6, 126.5, 124.5, 122.0, 113.8, 112.3, 111.2, 50.1, 21.2; HRMS (ESI) exact mass calculated for $C_{31}H_{24}Br_2N_2$ $[M + H]^+$: 583.0384; found: 583.0389.

Bis(1-allyl-1H-indol-3-yl)methane (2m)

Brown gummy solid; Yield 81 %, 264 mg; IR ($CHCl_3$): 3084, 2950, 2831, 1631, 1368, 1216, 1019, 744 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.21-7.18 (m, 2H), 7.09-7.06 (m, 2H), 6.85 (s, 2H), 5.99-5.91 (m, 2H), 5.16-5.14 (m, 2H), 5.08-5.04 (m, 2H), 4.66-4.64 (m, 4H), 4.23 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.3, 136.5, 133.7, 126.0, 121.4, 119.4, 118.7, 116.9, 114.5, 114.1, 109.5, 48.6, 22.7; HRMS (ESI) exact mass calculated for $C_{23}H_{22}N_2$ $[M + H]^+$: 327.1861; found: 327.1856.

Bis(1-allyl-5-bromo-1H-indol-3-yl)methane (2n)

Red gummy solid; Yield 77 %, 373 mg; IR ($CHCl_3$): 3081, 2958, 1630, 1467, 1361, 1214, 1012, 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 1.8 Hz, 2H), 7.27-7.25 (m, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.85 (s, 2H), 5.98-5.90 (m, 2H), 5.19-5.17 (m, 2H), 5.02-4.99 (m, 2H), 4.65-4.64 (m, 4H), 4.12 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.1, 133.1, 129.4, 127.2, 124.2, 121.8, 117.1, 113.4, 112.1, 111.1, 48.7, 20.9; HRMS (ESI) exact mass calculated for $C_{23}H_{20}Br_2N_2$ $[M + H]^+$: 483.0071; found: 483.0068.

Bis(1-(3-chlorobenzyl)-1H-indol-3-yl)methane (2o)

Brownish gummy solid; Yield 72 %, 356 mg; IR (KBr): 3074, 2831, 1624, 1471, 1359, 1213, 1146, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.23-7.16 (m, 8H), 7.12-7.09 (m, 2H), 7.07 (m, 2H), 6.94-6.91 (m, 4H), 5.22 (s, 4H), 4.28 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 136.5, 134.4, 129.9, 128.1, 127.6, 126.5, 126.4, 124.6, 121.8, 119.5, 119.0, 114.8, 109.4, 49.2, 21.2; HRMS (ESI) exact mass calculated for $C_{31}H_{24}Cl_2N_2$ $[M + H]^+$: 495.1395; found: 495.1390.

Bis(1-(4-chlorobenzyl)-1H-indol-3-yl)methane (2p)

Reddish solid; Yield 78 %, 386 mg; Mp = 121-123 °C; IR (KBr): 3074, 2856, 1590, 1472, 1364, 1184, 1092, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.23-7.20 (m, 5H), 7.19-7.14 (m, 3H), 7.09-7.06 (m, 2H), 6.99-6.98 (m, 4H), 6.88 (s, 2H), 5.20 (s, 4H), 4.25 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7, 136.3, 133.2, 128.8, 128.2, 128.0, 127.8, 126.3, 121.8, 119.5, 119.0, 115.0, 109.5, 49.2, 21.2; HRMS (ESI) exact mass calculated for $C_{31}H_{24}Cl_2N_2$ $[M + H]^+$: 495.1395; found: 495.1398.

Bis(5-bromo-1-(4-chlorobenzyl)-1H-indol-3-yl)methane (2q)

Brownish solid; Yield 75 %, 490 mg; Mp = 186-188 °C; IR (KBr): 3087, 2962, 2837, 1634, 1468, 1374, 1184, 1147, 1093, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 1.7 Hz, 2H), 7.26-7.24 (m, 4H), 7.22-7.20 (m, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.96-6.94 (m, 4H), 6.91 (s, 2H), 5.18 (s, 4H), 4.13 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.6, 135.2, 133.3, 129.6, 128.9, 127.7, 127.4, 124.6, 122.0, 113.7, 112.3, 111.1, 49.3, 21.2; HRMS (ESI) exact mass calculated for $C_{31}H_{22}Br_2Cl_2N_2$ $[M + H]^+$: 650.9605; found: 650.9609.

Bis(1-(4-bromobenzyl)-1H-indol-3-yl)methane (2r)

Brown solid; Yield 71 %, 415 mg; Mp = 149-151 °C; IR (KBr): 3037, 2911, 2851, 1630, 1476, 1365, 1211, 1134, 1022, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.39-7.35 (m, 4H), 7.20-7.13 (m, 4H), 7.09-7.05 (m, 2H), 6.91 (d, *J* = 8.2 Hz, 4H), 6.86 (s, 2H), 5.17 (s, 4H), 4.24 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.8, 136.7, 131.8, 128.3, 128.2, 126.3, 121.8, 121.3, 119.5, 119.0, 115.0, 109.5, 49.2, 21.2; HRMS (ESI) exact mass calculated for $C_{31}H_{24}Br_2N_2$ $[M + H]^+$: 583.0384; found: 583.0389.

Bis(1-(3-bromobenzyl)-1H-indol-3-yl)methane (2s)

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Off white solid; Yield 75 %, 438 mg; Mp = 104-106 ^{o}C; IR (KBr): 3061, 2936, 2854, 1620, 1472, 1368, 1201, 1172, 1016, 744 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.21-7.15 (m, 6H), 7.13-7.08 (m, 4H), 6.97-6.95 (m, 2H), 6.88 (s, 2H), 5.20 (s, 4H), 4.26 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.2, 136.7, 130.6, 130.3, 129.6, 128.2, 126.3, 125.2, 122.8, 121.9, 119.5, 119.1, 115.1, 109.4, 49.2, 21.2; HRMS (ESI) exact mass calculated for $C_{31}H_{24}Br_2N_2$ [M + H]$^{+}$: 583.0384; found: 583.0378.

Bis(1-(4-methylbenzyl)-1H-indol-3-yl)methane (2t)

Brownish solid; Yield 72 %, 327 mg; Mp = 99-101 ^{o}C; IR ($CHCl_3$): 3074, 2932, 2837, 1622, 1462, 1360, 1221, 1002, 743 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.25-7.18 (m, 3H), 7.15-7.11 (m, 2H), 7.10-7.04 (m, 6H), 6.97-6.95 (m, 3H), 6.88 (s, 2H), 5.18 (s, 4H), 4.24 (s, 2H), 2.29 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.0, 136.8, 134.8, 129.3 (2C), 126.7, 126.4 (2C), 121.5, 120.2, 119.4, 118.7, 114.7, 109.6, 49.6, 21.2, 21.0; HRMS (ESI) exact mass calculated for $C_{33}H_{30}N_2$ [M - H]$^{+}$: 453.2331; found: 453.2337.

3-((1H-indol-3-yl)methyl)-1-methyl-1H-indole (2'a)

White solid; Yield 62 %, 161 mg; Mp = 181-182 ^{o}C; IR (KBr): 3408, 3045, 2929, 1615, 1456, 1325, 1085, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (bs, 1H), 7.63-7.60 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.23-7.16 (m, 2H), 7.10-7.06 (m, 2H), 6.89 (m, 1H), 6.76 (s, 1H), 4.22 (s, 2H), 3.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.1, 136.4, 127.9, 127.5, 127.0, 122.1, 121.8, 121.4, 119.2 (2C), 119.1, 118.5, 115.8, 114.1, 111.0, 109.1, 32.5, 21.0; HRMS (ESI) exact mass calculated for $C_{18}H_{16}N_2$ [M + H]$^{+}$: 261.1392; found: 261.1385.

3-((1H-indol-3-yl)methyl)-1-ethyl-1H-indole (2'b)

Brownish solid; Yield 64 %, 175 mg; Mp = 184-186 ^{o}C; IR (KBr): 3411, 3058, 2917, 1614, 1336, 1092, 744 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (bs, 1H), 7.62-7.59 (m, 2H), 7.31-7.29 (m, 2H), 7.21-7.15 (m, 2H), 7.10-7.05 (m, 2H), 6.86 (s, 1H), 6.82 (s, 1H), 4.22 (s, 2H), 4.04 (q, *J* = 7.3 Hz, 2H), 1.36 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.4, 136.1, 128.0, 127.5, 125.2, 122.2, 121.8, 121.2, 119.4, 119.2, 119.1, 118.5, 115.8, 114.1, 111.0, 109.2, 40.7, 21.1, 15.5; HRMS (ESI) exact mass calculated for $C_{19}H_{18}N_2$ [M + H]$^{+}$: 275.1548; found: 275.1554.

3-((1H-indol-3-yl)methyl)-1-propyl-1H-indole (2'c)

Light red solid; Yield 68 %, 196 mg; Mp = 191-193 ^{o}C; IR (KBr): 3408, 3048, 2913, 1614, 1461, 1375, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (bs, 1H), 7.63-7.60 (m, 2H), 7.36-7.30 (m, 2H), 7.21-7.17 (m, 2H), 7.10-7.05 (m, 2H), 6.93-6.92 (m, 1H), 6.85 (s, 1H), 4.23 (s, 2H), 3.99 (t, *J* = 7.0 Hz, 2H), 1.84-1.77 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.4 (2C), 128.0, 127.6, 126.1, 122.2, 121.8, 121.2, 119.3, 119.2, 119.1, 118.4, 115.9, 113.8, 111.0, 109.3, 47.8, 23.6, 21.1, 11.5; HRMS (ESI) exact mass calculated for $C_{20}H_{20}N_2$ [M + H]$^{+}$: 289.1705; found: 289.1701.

3-((1H-indol-3-yl)methyl)-1,2-dimethyl-1H-indole (2'd)

White solid; Yield 58 %, 159 mg; Mp = 176-178 ^{o}C (dec); IR (KBr): 3417, 3056, 2927, 1661, 1396, 1210, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68-7.66 (m, 2H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.27-7.24 (m, 2H), 7.18-7.09 (m, 3H), 7.02-6.99 (m, 1H), 6.62 (m, 1H), 4.17 (s, 2H), 3.65 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.6, 136.4, 132.2, 128.0, 127.3, 122.0, 121.8, 120.4, 119.1, 118.8, 118.6, 118.5, 116.4, 110.0, 109.5, 108.4, 29.5, 20.2, 10.3; HRMS (ESI) exact mass calculated for $C_{19}H_{18}N_2$ [M + H]$^{+}$: 275.1548; found: 275.1543.

2-Methyl-3-((1-methyl-1H-indol-3-yl)methyl)-1H-indole (2'e)

Off-white solid; Yield 66 %, 181 mg; Mp = 201-203 ^{o}C; IR (KBr): 3402, 3055, 2926, 2856, 1682, 1470, 1327, 1013, 742 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (bs, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.31-7.22 (m, 3H), 7.17-7.11 (m, 2H), 7.08-7.03 (m, 1H), 6.58 (s, 1H), 4.18 (s, 2H), 3.65 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.2, 137.1, 135.3, 127.7, 126.8, 125.0, 121.3, 120.8, 119.0, 118.9, 118.6, 118.5, 114.6, 112.2, 110.0, 109.0, 32.5, 19.7, 11.7; HRMS (ESI) exact mass calculated for $C_{19}H_{18}N_2$ [M + H]$^{+}$: 275.1548; found: 275.1553.

5-Bromo-3-((1-methyl-1H-indol-3-yl)methyl)-1H-indole (2'f)

Brown solid; Yield 65 %, 220 mg; Mp = 211-213 ^{o}C; IR ($CHCl_3$): 3413, 3035, 2923, 1624, 1461, 1376, 1211, 1089, 744 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (bs, 1H), 7.75 (d, *J* = 1.8 Hz, 1H), 7.58-7.56 (m, 1H), 7.30-7.28 (m, 1H), 7.25-7.19 (m, 3H), 7.09-7.06 (m, 1H), 6.92 (m, 1H), 6.76 (s, 1H), 4.17 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.2, 135.0, 129.3, 127.7, 126.9, 124.7, 123.4, 121.8, 121.5, 119.2, 118.6, 115.6, 113.5, 112.5, 109.2, 32.6, 21.0; HRMS (ESI) exact mass calculated for $C_{18}H_{15}BrN_2$ [M + H]$^{+}$: 339.0497; found: 339.0499.

1-Ethyl-3-((2-methyl-1H-indol-3-yl)methyl)-1H-indole (2'g)

Gummy solid; Yield 64 %, 184 mg; IR ($CHCl_3$): 3401, 3081, 2922, 1641, 1470, 1377, 1216, 1042, 743 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (bs, 1H), 7.68-7.66 (m, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.30-7.27 (m, 2H), 7.21-7.18 (m, 1H), 7.12-7.08 (m, 2H), 7.03-7.00 (m, 1H), 6.62 (s, 1H), 4.15 (s, 2H), 4.01 (q, *J* = 7.3 Hz, 2H), 2.38 (s, 3H), 1.33 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.1, 136.1, 135.2, 129.0, 127.9, 125.1, 121.2, 120.7, 119.0 (2C), 118.6, 118.4, 114.6, 110.5, 110.0, 109.1, 40.7, 19.8, 15.5, 11.8; HRMS (ESI) exact mass calculated for $C_{20}H_{20}N_2$ [M + H]$^{+}$: 289.1705; found: 289.1702.

5-Bromo-3-((1-ethyl-1H-indol-3-yl)methyl)-1H-indole (2'h)

White solid; Yield 59 %, 208 mg; Mp = 197-199 ^{o}C; IR (KBr): 3417, 3058, 2911, 1617, 1460, 1375, 1210, 1092, 744 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (bs, 1H), 7.74 (d, *J* = 1.0 Hz, 1H), 7.58-7.56 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.26-7.24 (m, 1H), 7.22-7.19 (m, 2H), 7.08-7.05 (m, 1H), 6.91 (d, *J* = 1.2 Hz, 1H), 6.84 (s, 1H), 4.17 (d, *J* = 1.0 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.2, 135.0, 129.3, 127.9, 125.2, 124.7, 123.4, 121.8, 121.3, 119.3,

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118.6, 115.6, 113.5, 112.4, 109.2, 40.7, 21.0, 15.5; HRMS (ESI) exact mass calculated for $C_{19}H_{17}BrN_2$ $[M + H]^+$: 353.0653; found: 353.0647.

2-Methyl-3-((1-propyl-1H-indol-3-yl)methyl)-1H-indole (2'i)

White solid; Yield 68 %, 205 mg; Mp = 177-179 ^oC; IR ($CHCl_3$): 3405, 3054, 2927, 1615, 1464, 1366, 1156, 740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.84 (bs, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.33-7.20 (m, 3H), 7.15-7.02 (m, 3H), 6.66 (s, 1H), 4.19 (s, 2H), 3.95 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.81-1.74 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.1, 136.4, 135.2, 129.0, 128.8, 125.9, 125.0, 121.1, 120.7, 119.0 (2C), 118.6, 118.4, 114.3, 110.0, 109.3, 47.8, 23.5, 19.9, 11.5; HRMS (ESI) exact mass calculated for $C_{21}H_{22}N_2$ $[M + H]^+$: 303.1861; found: 303.1864.

5-Bromo-3-((1-propyl-1H-indol-3-yl)methyl)-1H-indole (2'j)

Pale yellow solid; Yield 60 %, 220 mg; Mp = 188-190 ^oC (dec); IR ($CHCl_3$): 3410, 3058, 2919, 1624, 1473, 1359, 1201, 1081, 742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.90 (bs, 1H), 7.74 (m, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.26-7.25 (m, 1H), 7.21-7.18 (m, 2H), 7.08-7.05 (m, 1H), 6.92 (m, 1H), 6.84 (s, 1H), 4.17 (s, 2H), 4.00 (t, *J* = 7.0 Hz, 2H), 1.85-1.78 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.5, 135.0, 129.3, 127.8, 126.1, 125.3, 124.6, 123.4, 121.9, 121.3, 119.3, 118.5, 115.6, 113.2, 112.4, 109.4, 47.8, 23.5, 21.1, 11.5; HRMS (ESI) exact mass calculated for $C_{20}H_{19}BrN_2$ $[M + H]^+$: 367.0810; found: 367.0815.

1-Benzyl-3-((2-methyl-1H-indol-3-yl)methyl)-1H-indole (2'k)

White solid; Yield 55 %, 193 mg; Mp = 222-224 ^oC; IR ($CHCl_3$): 3405, 3056, 2924, 1619, 1465, 1332, 1172, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (bs, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.26-7.06 (m, 8H), 7.01-6.96 (m, 3H), 6.70 (s, 1H), 5.16 (s, 2H), 4.17 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.4, 136.7, 135.2, 128.7, 128.5, 128.1, 127.5, 126.5, 126.4, 124.9, 121.8, 121.5, 120.7, 119.5, 119.0, 118.8, 118.6, 115.2, 112.2, 110.0, 109.8, 109.6, 49.7, 19.9, 11.8; HRMS (ESI) exact mass calculated for $C_{25}H_{22}N_2$ $[M + H]^+$: 351.1861; found: 351.1866.

1-Benzyl-3-((5-bromo-1H-indol-3-yl)methyl)-1H-indole (2'l)

White solid; Yield 54 %, 224 mg; Mp = 210-212 ^oC; IR ($CHCl_3$): 3420, 3030, 2925, 1614, 1464, 1333, 1092, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.90 (bs, 1H), 7.72 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.27-7.23 (m, 5H), 7.18-7.17 (m, 2H), 7.07 (d, *J* = 7.0 Hz, 3H), 6.92 (s, 1H), 6.87 (s, 1H), 5.23 (s, 2H), 4.18 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.7, 136.8, 135.0, 129.2, 128.7, 128.0, 127.4, 126.6, 126.4, 124.7, 123.4, 121.8, 121.7, 119.3, 118.9, 115.3, 114.1, 112.5, 112.4, 109.7, 49.8, 21.2; HRMS (ESI) exact mass calculated for $C_{24}H_{19}BrN_2$ $[M + H]^+$: 415.0810; found: 415.0812.

1-Methyl-3-((2-phenyl-1H-indol-3-yl)methyl)-1H-indole (2'm)

White solid; Yield 58 %, 195 mg; Mp = 161-163 ^oC; IR (KBr): 3407, 3046, 2927, 1603, 1458, 1330, 1236, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.03 (bs, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.48-7.44 (m, 3H), 7.33-7.29 (m, 3H), 7.25-7.16 (m, 3H), 7.15-7.12 (m, 1H), 7.08-7.05 (m, 1H), 7.01-6.98 (m, 1H), 6.47 (s, 1H), 4.25 (d, *J* = 0.9 Hz, 2H), 3.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.2, 136.0, 134.7, 132.9, 129.6, 128.9, 127.7, 127.6, 127.2, 122.3, 121.4, 119.7, 119.6, 119.0, 118.5, 114.6, 111.5, 110.7, 109.1, 32.6, 20.6; HRMS (ESI) exact mass calculated for $C_{24}H_{20}N_2$ $[M + H]^+$: 337.1705; found: 337.1703.

1-Ethyl-3-((2-phenyl-1H-indol-3-yl)methyl)-1H-indole (2'n)

White solid; Yield 61 %, 214 mg; Mp = 167-169 ^oC; IR (KBr): 3402, 3048, 2923, 1608, 1456, 1336, 1228, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.10 (bs, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.55-7.52 (m, 3H), 7.40-7.36 (m, 3H), 7.32-7.28 (m, 2H), 7.25-7.19 (m, 2H), 7.14-7.11 (m, 1H), 7.08-7.05 (m, 1H), 6.61 (s, 1H), 4.32 (d, *J* = 1.2 Hz, 2H), 3.98 (q, *J* = 7.3 Hz, 2H), 1.29 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.2, 136.0, 134.7, 132.9, 129.7, 128.9, 127.8, 127.6, 127.5, 125.5, 122.2, 121.3, 119.8, 119.6, 119.1, 118.5, 114.6, 111.6, 110.7, 109.2, 40.7, 20.6, 15.5; HRMS (ESI) exact mass calculated for $C_{25}H_{22}N_2$ $[M + H]^+$: 351.1861; found: 351.1865.

2-phenyl-3-((1-propyl-1H-indol-3-yl)methyl)-1H-indole (2'o)

White solid; Yield 63 %, 229 mg; Mp = 185-187 ^oC; IR (KBr): 3407, 3043, 2921, 2855, 1611, 1447, 1330, 1221, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.19 (bs, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.62-7.60 (m, 3H), 7.46-7.37 (m, 5H), 7.32-7.11 (m, 4H), 6.67 (s, 1H), 4.40 (s, 2H), 3.95 (t, *J* = 7.2 Hz, 2H), 1.83-1.71 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.5, 136.0, 134.7, 132.9, 129.7, 129.0, 128.9, 127.8, 127.6, 127.5, 126.3, 122.2, 121.2, 119.7, 119.5, 119.1, 118.4, 114.3, 111.5, 110.7, 109.3, 47.7, 23.4, 20.6, 11.4; HRMS (ESI) exact mass calculated for $C_{26}H_{24}N_2$ $[M + H]^+$: 365.2018; found: 365.2024.

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