Efficient Ru^{III}-catalyzed condensation of indoles and aldehydes or ketones

Khalil Tabatabaeian, Manouchehr Mamaghani, Nosratollah Mahmoodi, and Alireza Khorshidi

Abstract: Synthesis of bis(indolyl)methanes through condensation of indoles and various aldehydes or ketones, using Ru^{III} as catalyst, is reported. It was found that the catalytic system involving Ru^{III} affords the products smoothly under very mild conditions in good to high yields.

Key words: aldehydes, ketones, bis(indolyl)methanes, indoles, ruthenium.

Résumé : Utilisant du Ru(III) comme catalyseur, on a réalisé la synthèse de bis(indolyl)méthanes par le biais de la condensation d'indoles et de divers aldéhydes ou cétones. On a trouvé que le système catalytique impliquant du Ru(III) permet d'obtenir facilement les produits dans des conditions douces et avec des rendements allant de bon à élevés.

Mots clés : aldéhydes, cétones, bis(indolyl)méthanes, indoles, ruthénium.

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Introduction

Transition metal-catalyzed C–H bond activation has received considerable attention in synthetic organic chemistry since the cleavage of an unreactive C–H bond and subsequent addition of the C–H unit into unsaturated substrates could lead to the formation of a new C–C bond (1). The formation of a C–C bond is one of the most fundamental projects in organic chemistry. Much effort has naturally been devoted to developing more convenient and efficient strategies for the formation of C–C bonds. During the last two decades, many successful applications of catalytic C–H bond activation directed toward the construction of C–C bonds have been reported in synthetic communities (2).

The development of new efficient synthetic methods leading to indole derivatives continues to receive much attention in organic synthesis because of their biological activities (3). Various indole derivatives occur in many pharmacologically and biologically active compounds (4). Among of them, bis(indolyl)methanes possess a wide range of biological activity and their synthesis has received a considerable amount of interest (5, 6). Generally, bis(indolyl)methanes are prepared by the condensation of indoles with various aldehydes or ketones in the presence of either protic (7) or Lewis acids (8–10). On the other hand, Ru^{III} salts are well-known to catalyze many organic transformations, including aldol and Michael reactions (11), oxidation reactions of alkanes (12), oxidative cyanation of amines (13), and many others (14). We found that Ruthenium (III) chloride hydrate is a very effective catalyst for the double addition of indoles to aldehydes or ketones, yielding bis(indolyl) derivatives in high yields. The ruthenium catalyst was used in low concentrations (as low as 1.2 mol%) and a relatively easy work-up affords catalytic formation of a carbon–carbon bond under mild reaction conditions. To the best of our knowledge, this is the first report on the use of Ru^{III} salts as catalyst for the condensation of indoles with various aldehydes or ketones.

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Results and discussion

Typical results of the ruthenium-catalyzed condensation of indoles and aldehydes or ketones are shown in Tables 1 and 2 and they indicate the scope of the reaction. Treatment of benzaldehyde (1.2 mmol) with indole (2 mmol) in the presence of $RuCl_3 \cdot nH_2O$ catalyst (1.2 mol%) in methanol (2 mL) at RT for 27 min gave the corresponding 3,3′-bis(indolyl)phenylmethane in 92% yield (product 1a). No attempts were made to characterize byproducts since they are formed in trace amounts (using GLC analysis). The reaction can be used for substituted aromatic aldehydes with either electron-donating or electron-withdrawing groups (Table 1, entries b–e). Furthermore, the reaction of indole with aliphatic aldehydes furnished high yields of the corresponding product class (Table 1, entries f and g).

Encouraged by these results, we studied the condensation reaction between indole and some ketones. The method is highly chemoselective, as ketones do not participate in the reaction in ambient conditions. This selectivity might be useful in the reaction of multifunctional carbonyl compounds with indole since they have both aldehyde and ketone functionalities. However, the method is still effective enough to afford the condensation products of indole and ketones through reflux of the reaction mixture (Table 1, entries h–l) in good yields.

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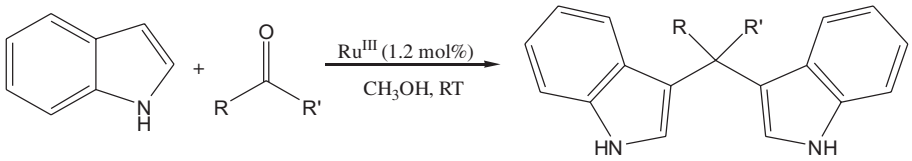
Table 1. Ru^{III}-catalyzed condensation of indole and aldehydes or ketones.



Entry	R	R′	Product	Time (min)	Yield (%)[a]
a	C_6H_5	H	**1a**	27	92[c]
b	4-pr^i-C_6H_4	H	**1b**	25	93
c	4-OHC_6H_4	H	**1c**	30	82[d]
d	2-ClC_6H_4	H	**1d**	30	88[c]
e	3-$NO_2C_6H_4$	H	**1e**	30	85[e]
f	CH_3	H	**1f**	30	73
g	$CH_3(CH_2)_3$	H	**1g**	30	87
h	C_6H_5	CH_3	**1h**	180[b]	68[d]
i	4-$CH_3OC_6H_4$	CH_3	**1i**	60[b]	72
j	3,4-$(CH_3O)_2C_6H_3$	CH_3	**1j**	120[b]	77
k	4-$NO_2C_6H_4$	CH_3	**1k**	120[b]	73
l	C_6H_5	C_6H_5	**1l**	180[b]	51

Note: All products were characterized by ^1H NMR, ^{13}C NMR, and IR data.
[a]Isolated yields.
[b]Reflux.
[cde]Identified by comparison with authentic samples (15, 16, 8).

With regard to the indole moiety, the present protocol is noteworthy because substituted indoles underwent smooth reactions with aromatic aldehydes giving excellent yields of products (Table 2). For example, treatment of 1-, 2-, and 5-substituted indoles with various aromatic aldehydes gave corresponding products **2a**–**2f**, most of them insoluble in the reaction media (solvent methanol) and this makes the work-up even easier (see Experimental section). Also, the reaction times for 1- and 2-substituted indoles are much less than those of unsubstituted substrates.

The reaction of indole and benzaldehyde was taken as a representative example and the progress of the reaction was monitored by GLC technique. To examine the influence of the catalyst concentration, we also carried out the reaction of benzaldehyde and indole in different catalyst concentrations. Due to the decomposition of the products under chromatographic conditions, decrease in the corresponding aldehyde peak areas was selected as a measure of reaction coordinate. Also, the peak of methanol was used as internal standard. The results are summarized in Table 3.

These results reveal that the Ru^{III} system is at least four times more effective than the previously reported catalytic system using Fe^{III} in ionic liquids (15) in terms of utilized catalyst concentration (1.2% vs. 5%). Also, the catalytic activity is nearly ten times greater in terms of reaction time (3 min vs. 30 min in ~5 mol% of catalyst).

Conclusion

In brief, we have developed a convenient method for the synthesis of bis(indolyl)methanes using the condensation reaction of indoles and aldehydes or ketones in the presence of $RuCl_3 \cdot nH_2O$ as efficient catalyst. With regard to the previous works, the present protocol has several advantages. As the reaction solvent, methanol has lower toxicity in contrast to CH_3CN (8–10). In the reaction of substituted indoles with aromatic aldehydes, the products are mainly insoluble in methanol, therefore simple filtration of the reaction mixture and rinsing with methanol provides completely pure products. The unique feature of the reaction is selectivity between ketones and aldehydes at ambient temperature while the other methods catalyze the reaction of both aldehydes and ketones at room temperature (8–10) or only catalyze the reaction of aldehydes (15). Further manipulation of this reaction is underway.

Experimental

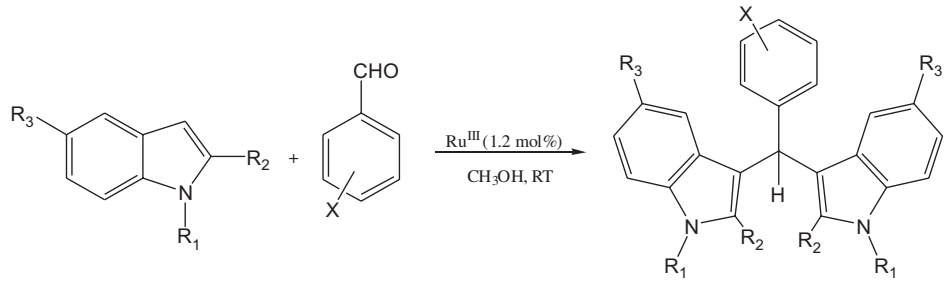
General

IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer. ^1H NMR spectra were obtained on a Bruker DRX-500 Avance and ^{13}C NMR spectra were obtained on a Bruker DRX-125 Avance. Chemical shifts of ^1H and ^{13}C NMR spectra were expressed in parts per million downfield from tetramethylsilane. Analytical GLC evaluations of product mixtures were carried out on a Varian CP-3800 chromatograph (using a split/splitless injector, CP Sil 8CB column, FID assembly). Melting points were measured on a BÜCHI Melting Point B-540 and are uncorrected. Elemental analyses were made with a Carlo-Erba EA1110 CNNO-S analyzer and agreed with the calculated values.

Materials

HPLC grade methanol was used as solvent and all other materials were purchased from Merck and used without further purification.

Table 2. Ru^{III}-catalyzed condensation of substituted indoles and aldehydes.



Entry	R_1	R_2	R_3	X	Product	Time (min)	Yield (%)[a]
a	CH_3	H	H	H	**2a**	5	98
b	CH_3	H	H	4-pr^i-C_6H_4	**2b**	3	98
c	CH_3	H	H	3-(CH_3O)-4-$(HO)C_6H_3$	**2c**	10	95
d	H	CH_3	H	H	**2d**	3	98[b]
e	H	CH_3	H	4-pr^i-C_6H_4	**2e**	10	96
f	H	H	Br	H	**2f**	30	75

Note: All products were characterized by ^1H NMR, ^{13}C NMR, and IR data.
[a]Isolated yields.
[b]Identified by comparison with authentic samples (17).

Table 3. $RuCl_3 \cdot nH_2O$-catalyzed condensation of benzaldehyde and indole in different catalyst concentrations.

Entry	Reaction time (min)	Aldehyde consumption (%)	Catalyst concentration (mol% Ru/aldehyde)
1	27	98	1.2
2	3	91.6	1.9
3	15	97.8	1.9
4	27	97.8	1.9
5	3	96.7	3.8
6	15	97.2	3.8
7	27	97.6	3.8
8	3	98	5.6
9	15	98.3	5.6
10	27	98.3	5.6

Ruthenium-catalyzed condensation of benzaldehyde and indole

A 20 mL flask equipped with a magnetic stirring bar was charged with methanol (2 mL), benzaldehyde (127.4 mg, 1.2 mmol), and indole (234.4 mg, 2 mmol). $RuCl_3 \cdot nH_2O$ (3 mg, 0.014 mmol) was added into the flask and the reaction mixture was stirred at RT. After 0.5 h, the reaction mixture was purified by preparative TLC (petroleum ether – ethyl acetate, 10:4) providing a pure product (296 mg, 92%). The same procedure was also used for the other products listed in Tables 1 and 2. In the case of entries a–e in Table 2, simple filtration of the reaction mixture and treatment with methanol provided pure products.

3,3-Bis(indolyl)-4-isopropylphenylmethane (1b)

Solid, mp 153 to 154 °C. IR (KBr, cm^{-1}) υ: 422, 468, 497, 586, 599, 744, 752, 792, 1010, 1089, 1215, 1338, 1417, 1456, 1510, 2867, 2962, 3051, 3421 (NH). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, ppm) δ: 1.29 (d, 6H, J = 7.00 Hz, $(CH_3)_2CH$), 2.93 (sept, J = 7.00 Hz, -$CH(CH_3)_2$), 5.91 (s, 1H, Ar-CH), 6.7 (s, 2H), 7.06 (t, J = 7.5 Hz, 2H), 7.18 (d, J = 8.00 Hz, 2H), 7.21 (t, J = 7.5 Hz, 2H), 7.3 (d, J = 7.3 Hz, 2H), 7.39 (d, J = 8.00 Hz, 2H), 7.46 (d, J = 7.9 Hz, 2H), 7.91 (br, s, 2H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm) δ: 24.51, 34.11, 40.2, 111.46, 119.6, 120.42, 120.44, 122.3, 124.0, 126.66, 127.6, 128.98, 137.12, 141.7, 146.92. Anal. calcd. for $C_{26}H_{24}N_2$: C 85.68, H 6.64, N 7.69; found: C 85.74, H 6.67, N 7.65.

3,3′-Bis(indolyl)methylmethane (1f)

Solid, mp 157–159 °C. IR (KBr, cm^{-1}) υ: 424, 499, 578, 740, 756, 815, 1018, 1097, 1220, 1334, 1421, 1456, 2837, 2925, 2956, 3417 (NH). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, ppm) δ: 1.87 (d, J = 7.06 Hz, 3H), 4.74 (q, J = 6.96 Hz, 1H), 6.96 (d, J= 2.06 Hz, 2H), 7.10 (t, J = 7.53 Hz, 2H), 7.23 (t, J = 7.30 Hz, 2H), 7.39 (d, J = 8.15 Hz, 2H), 7.64 (d, J = 7.92 Hz, 2H), 7.89 (br, s, 2H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm) δ: 22.17, 28.62, 111.50, 119.46, 120.18, 121.64, 122.13, 122.22, 127.36, 137.09. Anal. calcd. for $C_{18}H_{16}N_2$: C 83.04, H 6.19, N 10.76; found: C 83.11, H 6.24, N 10.78.

3,3′-Bis(indolyl)butylmethane (1g)

Viscous liquid. IR (KBr, cm^{-1}) υ: 424, 487, 582, 740, 800, 929, 1010, 1093, 1218, 1244, 1336, 1417, 1456, 2856, 2927, 2954, 3055, 3415 (NH). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, ppm) δ: 0.97 (t, J = 6.95 Hz, 3H), 1.44–1.49 (m, 4H), 2.27–2.33 (m, 2H), 4.55 (t, J = 7.40 Hz, 1H), 6.98 (d, J = 2.08 Hz, 2H), 7.14 (t, J = 7.43 Hz, 2H), 7.24 (t, J = 7.35 Hz, 2H), 7.36 (d, J = 8.12 Hz, 2H), 7.70 (d, J = 7.90 Hz, 2H), 7.84 (br, s, 2H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm) δ: 14.64, 23.33, 31.03, 34.42, 36.09, 111.59, 119.44, 120.14, 120.97, 121.93, 122.16, 127.63, 137.02. Anal. calcd. for $C_{21}H_{22}N_2$: C 83.40, H 7.33, N 9.26; found: C 83.43, H 7.36, N 9.25.

3,3′-Bis(indolyl)methyl-4-methoxyphenylmethane (1i)

Solid, mp 225–227 °C. IR (KBr, cm^{-1}) υ: 428, 457, 588, 613, 742, 783, 823, 844, 1004, 1026, 1080, 1097, 1178, 1244, 1290, 1336, 1369, 1411, 1456, 1508, 1604, 2831, 2935, 2977, 3058, 3413 (NH). ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 25 °C, ppm) δ: 2.05 (s, 3H), 3.52 (s, 3H), 6.42 (d, *J* = 2.35 Hz, 2H), 6.50 (d, *J* = 8.76 Hz, 2H), 6.58 (t, *J* = 7.82 Hz, 2H), 6.80 (t, *J* = 7.75 Hz, 2H), 7.00 (d, *J* = 8.00 Hz, 2H), 7.05 (d, *J* = 8.76 Hz, 2H), 7.10 (d, *J* = 8.12 Hz, 2H), 9.58 (br, s, 2H, NH). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, 25 °C, ppm) δ: 29.30, 43.19, 55.32, 111.67, 113.05, 118.36, 120.96, 121.94, 123.89, 124.22, 126.64, 129.28, 137.60, 140.97, 157.52. Anal. calcd. for $C_{25}H_{22}N_2O$: C 81.94, H 6.05, N 7.64; found: C 81.87, H 6.11, N 7.66.

3,3′-Bis(indolyl)methyl-3,4-dimethoxyphenylmethane (1j)

Solid, mp 218–220 °C. IR (KBr, cm^{-1}) υ: 424, 478, 547, 580, 605, 655, 738, 746, 763, 783, 817, 873, 1004, 1022, 1095, 1110, 1139, 1228, 1245, 1253, 1334, 1409, 1444, 1460, 1506, 1593, 2839, 2933, 2960, 3355, 3413. ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 25 °C, ppm) δ: 1.75 (s, 3H), 3.09 (s, 3H), 3.29 (s, 3H), 6.17 (d, *J* = 2.40 Hz, 2H), 6.22 (d, *J* = 8.48 Hz, 1H), 6.27 (t, *J* = 7.5 Hz, 2H), 6.35 (dd, *J* = 8.50 Hz, *J* = 2.11 Hz, 1H), 6.44–6.50 (m, 3H), 6.69 (d, *J* = 8.03 Hz, 2H), 6.81 (d, *J* = 8.11 Hz, 2H), 9.78 (br, s, 2H, NH). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, 25 °C, ppm) δ: 29.22, 43.19, 55.69, 55.72, 110.51, 111.52, 112.39, 118.02, 120.32, 120.63, 121.57, 123.55, 123.59, 126.37, 137.35, 141.36, 146.72, 147.83. Anal. calcd. for $C_{26}H_{24}N_2O_2$: C 78.76, H 6.10, N 7.07; found: C 78.81, H 6.11, N 7.10.

3,3′-Bis(indolyl)methyl-4-nitrophenylmethane (1k)

Solid, mp 250 to 251 °C. IR (KBr, cm^{-1}) υ: 422, 457, 551, 582, 636, 700, 744, 770, 808, 862, 1008, 1107, 1245, 1338, 1409, 1458, 1504, 1591, 2923, 2981, 3045, 3409 (NH). ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 25 °C, ppm) δ: 2.04 (s, 3H), 6.42 (d, *J* = 2.42 Hz, 2H), 6.54 (t, *J* = 7.60 Hz, 2H), 6.76 (t, *J* = 7.60 Hz, 2H), 6.87 (d, *J* = 8.07 Hz, 2H), 7.07 (d, *J* = 8.17 Hz, 2H), 7.28 (d, *J* = 8.94 Hz, 2H), 7.75 (d, *J* = 8.87 Hz, 2H), 9.98 (br, s, 2H, NH). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, 25 °C, ppm) δ: 29.16, 44.25, 111.91, 118.64, 121.22, 121.37, 122.24, 123.02, 124.01, 126.16, 129.32, 137.59, 145.99, 156.70. Anal. calcd. for $C_{24}H_{19}N_3O_2$: C 75.57, H 5.02, N 11.02; found: C 75.52, H 5.05, N 11.06.

3,3′-Bis(indolyl)diphenylmethane (1l)

Solid. IR (KBr, cm^{-1}) υ: 426, 487, 580, 607, 624, 702, 742, 815, 1012, 1033, 1101, 1242, 1336, 1373, 1413, 1456, 1485, 1606, 1720, 2850, 2920, 3053, 3407 (NH). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm) δ: 6.80–6.85 (m, 4H), 6.87 (d, *J* = 2.47 Hz, 2H), 7.10–7.15 (m, 3H), 7.20–7.27 (m, 5H), 7.34–7.37 (m, 6H), 7.95 (br, s, 2H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm) δ: 54.65, 111.61, 112.30, 119.48, 120.05, 121.96, 122.96, 126.39, 127.89, 128.16, 130.56, 137.26, 146.39. Anal. calcd. for $C_{29}H_{22}N_2$: C 87.41, H 5.56, N 7.03; found: C 87.44, H 5.60, N 6.99.

3,3′-Bis(1-methyl-indolyl)phenylmethane (2a)

Solid, mp 199–201 °C. IR (KBr, cm^{-1}) υ: 428, 518, 572, 702, 742, 769, 800, 1010, 1118, 1130, 1150, 1199, 1224, 1238, 1328, 1369, 1425, 1475, 2933, 3020, 3053. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm) δ: 3.73 (s, 6H), 5.95 (s, 1H), 6.59 (s, 2H), 7.06 (t, *J* = 7.72 Hz, 2H), 7.21–7.28 (m, 3H), 7.31–7.37 (m, 4H), 7.41 (d, *J* = 5.32 Hz, 2H), 7.44 (d, *J* = 7.90 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm) δ: 33.11, 40.52, 109.48, 118.70, 119.07, 120.48, 121.85, 126.45, 127.90, 128.63, 128.70, 129.13, 137.85, 144.89. Anal. calcd. for $C_{25}H_{22}N_2$: C 85.68, H 6.33, N 7.99; found: C 85.69, H 6.33, N 8.01.

3,3′-Bis(1-methyl-indolyl)-4-isopropylphenylmethane (2b)

Solid, mp 147–149 °C. IR (KBr, cm^{-1}) υ: 426, 567, 595, 676, 738, 767, 804, 860, 1010, 1105, 1153, 1222, 1261, 1326, 1369, 1421, 1465, 1510, 1548, 1612, 2871, 2925, 2958, 3049. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm) δ: 1.30 (d, *J* = 6.90 Hz, 6H), 2.95 (sep, *J* = 6.90 Hz, 1H), 3.74 (s, 6H), 5.92 (s, 1H), 6.62 (s, 2H), 7.06 (t, *J* = 7.20 Hz, 2H), 7.18 (d, *J* = 7.90 Hz, 2H), 7.26 (t, *J* = 8.00 Hz, 2H), 7.31–7.35 (m, 4H), 7.46 (d, *J* = 7.90 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm) δ: 24.50, 33.11, 34.09, 40.09, 109.45, 118.97, 118.99, 120.54, 121.78, 126.63, 127.97, 128.61, 128.90, 137.84, 142.12, 146.76. Anal. calcd. for $C_{28}H_{28}N_2$: C 85.67, H 7.19, N 7.14; found: C 85.70, H 7.20, N 7.15.

3,3′-Bis(1-methyl-indolyl)-3-methoxy-4-hydroxyphenylmethane (2c)

Solid, mp 147–149 °C. IR (KBr, cm^{-1}) υ: 426, 505, 690, 738, 779, 804, 869, 1010, 1026, 1116, 1199, 1220, 1251, 1267, 1326, 1369, 1427, 1508, 1612, 2935, 3490. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm) δ: 3.74 (s, 6H), 3.84 (s, 3H), 5.56 (s, 1H), 5.88 (s, 1H), 6.59 (s, 2H), 6.86 (d, *J* = 8.14 Hz, 1H), 6.89 (d, *J* = 8.14 Hz, 1H), 6.96 (s, 1H), 7.07 (t, *J* = 7.35 Hz, 2H), 7.27 (t, *J* = 7.21 Hz, 2H), 7.36 (d, *J* = 8.12 Hz, 2H), 7.46 (d, *J* = 7.85 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm) δ: 33.13, 40.22, 56.35, 109.50, 111.86, 114.41, 118.94, 119.05, 120.51, 121.68, 121.84, 127.88, 128.68, 136.99, 137.85, 144.20, 146.75. Anal. calcd. for $C_{26}H_{24}N_2O_2$: C 78.76, H 6.10, N 7.07; found: C 78.81, H 6.15, N 7.10.

3,3′-Bis(2-methyl-indolyl)-4-isopropylphenylmethane (2e)

Solid, mp 224–226 °C. IR (KBr, cm^{-1}) υ: 451, 493, 582, 599, 740, 784, 833, 1016, 1220, 1244, 1299, 1342, 1423, 1458, 1510, 2920, 2956, 3049, 3396 (NH), 3438. ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 25 °C, ppm) δ: 0.94 (d, *J* = 6.90 Hz, 6H), 1.78 (s, 6H), 2.59 (sep, *J* = 6.90 Hz, 1H), 5.63 (s, 1H), 6.44 (t, *J* = 8.04 Hz, 2H), 6.62–6.65 (m, 4H), 6.77 (d, *J* = 8.12 Hz, 2H), 6.86 (d, *J* = 8.04 Hz, 2H), 6.93 (d, *J* = 8.05 Hz, 2H), 9.50 (br, s, 2H, NH). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, 25 °C, ppm) δ: 12.51, 24.36, 33.72, 38.93, 110.44, 113.13, 118.36, 119.16, 119.96, 126.04, 128.99, 129.03, 132.41, 135.49, 141.68, 146.35. Anal. calcd. for $C_{28}H_{28}N_2$: C 85.67, H 7.19, N 7.14; found: C 85.69, H 7.17, N 7.14.

3,3′-Bis(5-bromo-indolyl)phenylmethane (2f)

Solid, mp 246–248 °C. IR (KBr, cm^{-1}) υ: 420, 487, 584, 609, 659, 703, 732, 750, 771, 800, 858, 871, 881, 979, 1099, 1217, 1334, 1417, 1442, 1460, 1560, 1596, 3417 (NH). ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 25 °C, ppm) δ: 5.14 (s, 1H), 6.11 (d, *J* = 1.94 Hz, 2H), 6.52 (dd, *J* = 8.57, *J* = 10.73 Hz, 2H), 6.59 (t, *J* = 7.00 Hz, 1H), 6.65–6.71 (m, 6H), 6.75 (d, *J* = 1.40 Hz, 2H), 10.13 (br, s, 2H, NH). ^{13}C NMR

(125 MHz, $(CD_3)_2SO$, 25 °C, ppm) δ: 39.75, 111.35, 113.31, 117.72, 121.43, 123.68, 125.33, 126.19, 128.22, 128.39, 128.47, 135.56, 143.94. Anal. calcd. for $C_{23}H_{16}Br_2N_2$: C 57.53, H 3.36, N 5.83; found: C 57.46, H 3.31, N 5.85.

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