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# SYMTHESIS OF BIS(INDOLYL)METHANE DERIVATIVES BY ACID-CATALYZED REACTIONS OF INDOLES WITH VINYL ETHERS

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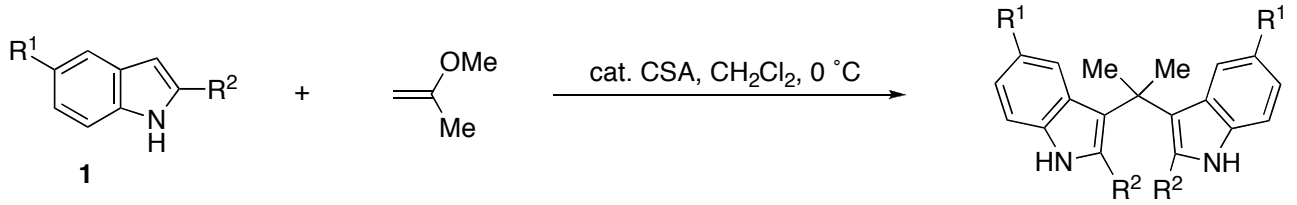
**Abstract** - 2,2-Bis(indol-3-yl)propane derivatives have been synthesized by the reaction of 3-nonsubstituted indoles with 2-methoxypropene in dichloromethane in the presence of a catalytic amount of (±)-camphor-10-sulfonic acid. The similar treatment of 3-substituted indoles with 2-methoxypropene under the same conditions has resulted in the formation of 2,2-bis(indol-2-yl)propanes. The reaction of 3-substituted indoles with ethoxyethene has afforded bis(indol-1-yl)ethanes. Subsequently, 3-substituted indoles have proved to react with excess vinyl ethers under the same conditions to afford the corresponding 1-(1-alkoxyalkyl)indoles.

## INTRODUCTION

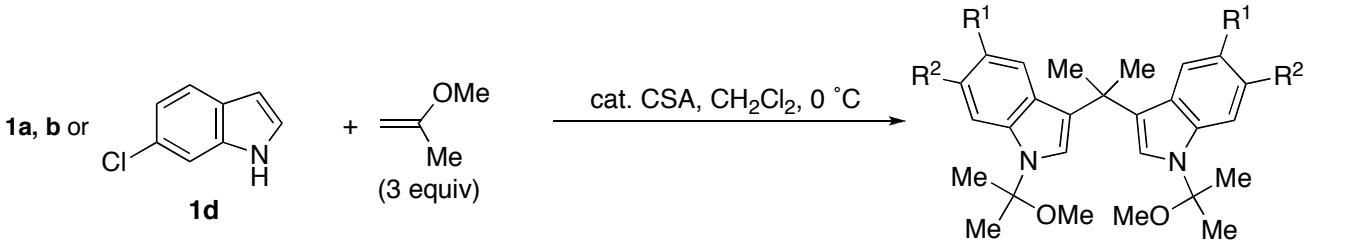
There has been substantial interest in bis(indol-3-yl)methane and its derivatives, because some of them have been reported to display a range of biological properties.[1] These derivatives have been reported to be useful as highly selective colorimetric and ratiometric fluorescent molecular chemosensors for $Cu^{2+}$ cations.[2] Moreover, an elaboration of these derivatives to more complex molecules has been reported.[3] Bis(indol-3-yl)methane derivatives have been synthesized by acid-catalyzed condensation of indoles with carbonyl compounds.[4] Recently, a wide variety of catalysts have been reported to be useful for this condensation reaction.[5] A one-pot preparation from 2-alkynylanilines using iron-palladium[6a] or gold[6b] catalysis systems has recently reported. In this paper we wish to demonstrate the results of our investigation on the reactions of indoles with vinyl ethers in the presence of a catalytic amount of an acid, which offer facile synthetic procedures for bis(indol-3-yl)methane, bis(indol-2-yl)methane,[7] and bis(indol-1-yl)methane derivatives.[8] We also present a synthesis of 3-substituted 1-(1- alkoxyalkyl)indoles from 3-substituted indoles and vinyl ethers.

## RESULTS AND DISCUSSION

Bis(indol-3-yl)propanes (**2a-c**) were prepared from the respective 3-nonsubstituted indoles (**1a-c**) and 2-methoxypropene as shown in Scheme 1. It was found that when **1a-c** were treated with 2-methoxypropene in the presence of a catalytic amount of (±)-camphor-10-sulfonic acid in dichloromethane at 0 ˚C, two to one condensation took place to lead to the desired products (**2a-c**) in the yields listed in Scheme 1. While condensation using indole (**1a**) and 5-bromoindole (**1b**) proceeded cleanly to give the corresponding bis(indol-3-yl)propanes (**2a** and **2b**) in fair-to-good yields, the reaction using 2-methylindole (**1c**) gave a somewhat complicated mixture of products and the desired product (**2c**) was isolated in only low-to-moderate yield. This is probably attributable to the steric encumbrance due to the 2-methyl group. It should be noted that the reactions of indole (**1a**) with ethoxyethene or 1*H*-2,3-dihydropyran under the same conditions as described above resulted in the formation of intractable mixtures of products.




**Scheme 1**

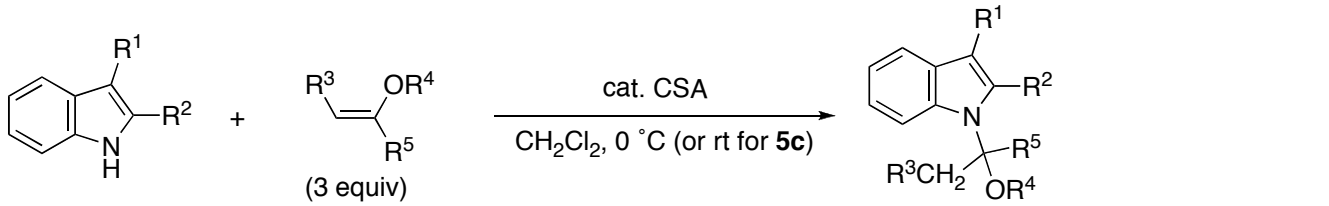



**Scheme 2**

We anticipated that the use of excess 2-methoxypropene would be expected to afford 2,2-bis[1-(1-methoxy-1-methylethyl)indol-3-yl]propanes (**3**) by condensation of 3-nonsubstituted indoles with 2-methoxypropene accompanying *N*,*N*'-bis(1-methoxy-1-methylethylation), and the reactions were conducted as shown in Scheme 2. Thus, the mixture of 2,3-nonsubstituted indoles (**1a**, **1b**, and **1d**) and 3

molar amounts of 3-methoxypropene in dichloromethane was treated with a catalytic amount of (±)-camphor-10-sulfonic acid at 0 ˚C to result in the formation of **3** in good yields. In the case of using 2-methylindole (**1c**), *N*-(1-methoxy-1-methylethylation) did not occur. This is again presumed to be ascribed to the steric encumbrance due to the 2-methyl group.

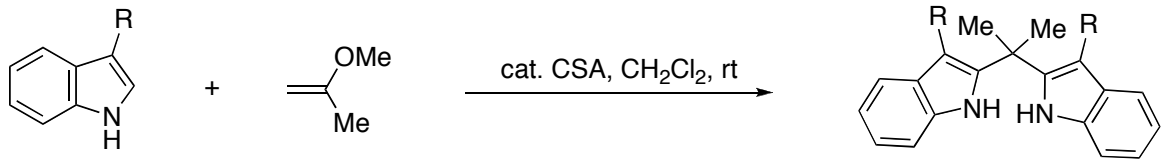
Subsequently, the possibility of the preparation of *N*-(1-alkoxyalkylation) of 3-substituted indoles was examined. We found that the reactions of 3-substituted indoles (**4a-c**) with 3 molar amounts of vinyl ethers, such as 2-methoxypropene, 1*H*-2,3-dihydropyran, 2,3-dihydrofuran, and ethoxyethene, in the presence of a catalytic amount of (±)-camphor-10-sulfonic acid in dichloromethane under conditions indicated in Scheme 3 led to the formation of 1-(2-methoxypropyl)- (**5a**), 1-(tetrahydropyan-2-yl)- (**5b**), 1-(tetrahydrofuran-2-yl)- (**5c**), and 1-(1-ethoxylethyl)-indole derivatives (**5d**), respectively, in moderate-to-fair yields. While the reactions of 3-methylindole (**4a**) with 2-methoxypropene and 1*H*-2,3-dihydropyran producing **5a** and **5b** proceeded smoothly, the reaction of methyl indole-3-carboxylate (**4b**) with 2,3-dihydrofuran producing **5c** required an elevated reaction temperature (room temperature) and a prolonged reaction time (6 d) and that of 2,3-dimethylindole (**4c**) with ethoxyethene producing **5d** required a prolonged reaction time (10 h). These are possibly due to the lower reactivity of **4b** and the steric encumbrance around the reaction center for **4c**.




**4a** $R^1$ = Me, $R^2$ = H
**4b** $R^1$ = $CO_2$Me, $R^2$ = H
**4c** $R^1$ = $R^2$ = Me

**5a** $R^1$ = $R^4$ = $R^5$ = Me, $R^2$ = $R^3$ = H 54%
**5b** $R^1$ = Me, $R^3$-$R^4$ = $(CH_2)_3$, $R^2$ = $R^5$ = H 62%
**5c** $R^1$ = $CO_2$Me, $R^3$-$R^4$ = $(CH_2)_2$, $R^2$ = $R^5$ = H 45%
**5d** $R^1$ = $R^2$ = Me, $R^3$ = $R^5$ = H, $R^4$ = Et 56%

**Scheme 3**




**4a** R = Me
**4d** R = Et

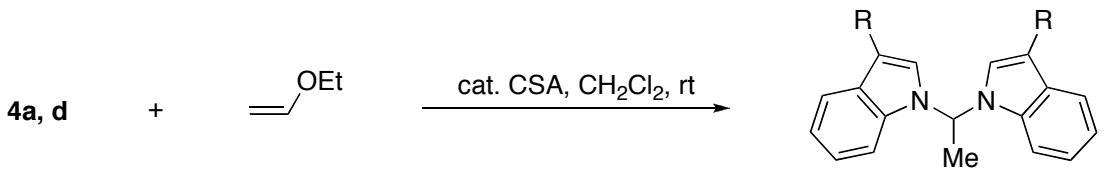
**6a** 42%
**6d** 34%

**Scheme 4**

Scheme 4 shows that 2,2-bis(indol-2-yl)propanes (**6**) could be prepared by the treatment of 3-substituted indoles (**4a**) and (**4d**) with 2-methoxypropene in the presence of a catalytic amount of (±)-camphor-10-

sulfonic acid in dichloromethane at room temperature, though the yields are low-to-moderate.

On the other hand, treatment of 3-substituted indoles (**4a**) and (**4d**) with ethoxyethene under conditions similar to those described for the preparation of **6** resulted in the formation of 1,1-bis(indol-1-yl)ethanes **7** in moderate yields, as shown in Scheme 5. Reason for the differences between the results using 2-methoxypropene and ethoxyethene can not be clarified.




**7a** R = Me 62%
**7d** R = Et 52%

**Scheme 5**

In conclusion, we have demonstrated that the reactions of indoles with vinyl ethers, such as 2-methoxypropene and ethoxyethene, provide a new method for the construction of three types of bis(indolyl)methane structures. Studies are now in progress to investigate details of the reactions of indoles with vinyl ethers and related compounds.

## EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were determined with a Shimadzu FTIR-8300 spectrophotometer. The $^1$H NMR spectra were determined in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz. The $^{13}$C NMR spectra were determined in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low- and high-resolution MS spectra (EI, 70 eV) were measured by a JEOL JMS AX505 HA spectrometer. TLC was carried out on a Merck Kieselgel 60 $PF_{254}$. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

**Starting Materials.** All chemicals used in this study were commercially available.

**1-Isocyano-2-propylbenzene.** This compound was by treating 2-(lithiomethyl)phenyl isocyanide, generated according to the procedure reported by Ito et al.,[9] with iodoethane in diglyme at –78 °C in 86% yield; a colorless liquid; bp 60–63 °C/1.45 mmHg; IR (neat) 2122 cm$^{-1}$; $^1$H NMR δ 0.99 (t, $J$ = 7.3 Hz, 3H), 1.69 (sext, $J$ = 7.3 Hz, 2H), 2.74 (t, $J$ = 7.3 Hz, 2H), 7.21 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 1H), 7.26 (d, $J$ = 7.8 Hz, 1H), 7.32 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 1H), 7.34 (d, $J$ = 7.8 Hz, 1H). MS $m/z$ 145 ($M^+$, 100). HR-MS Calcd for $C_{10}H_{11}N$: M, 145.0891. Found: $m/z$ 145.0905.

**3-Ethylindole (4d).** This compound was prepared by treating the above isocyanide with lithium 2,2,6,6-tetrapiperidide in diglyme at –78 ˚C, followed by rising the reaction temperature to room temperature, according to the procedure reported by Ito et al.[9] in 70% yield; a light brown solid; mp 36–37 ˚C (pentane) (lit.,[10] 37 ˚C); IR (KBr) 3055, 1618 $cm^{-1}$; $^1H$ NMR δ 1.34 (t, *J* = 7.3 Hz, 3H), 2.79 (qd, *J* = 7.3, 0.9 Hz, 2H), 6.98 (t, *J* = 0.9 Hz, 1H), 7.11 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1H), 7.19 (dd, *J* = 7.8, 7.3 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.89 (br s, 1H).

**Typical Procedure for the Preparation of 2,2-Bis(indol-3-yl)propanes (2). 3-[1-(Indol-3-yl)-1-methylethyl]indole (2a).** To a stirred solution of indole (**1a**) (0.12 g, 1.0 mmol) and 2-methoxypropene (72 mg, 1.0 mmol) in $CH_2Cl_2$ (3 mL) at 0 ˚C was added (±)-camphor-10-sulfonic acid (12 mg, 0.050 mmol). After stirring had been continued for 30 min, saturated aqueous $NaHCO_3$ (10 mL) and $CH_2Cl_2$ (10 mL) were added. The layers were separated, and the aqueous layer was extracted with $CH_2Cl_2$ three times (5 mL each). The combined extracts were washed with brine and dried over anhydrous $Na_2SO_4$. After evaporation of the solvent, the residue was purified by preparative TLC on silica gel (1:3 THF–hexane) to give **2a** (98 mg, 73%); a white solid; mp 171–174 ˚C (hexane–$Et_2O$) (lit.,[11] 175 ˚C ); IR (KBr) 3408, 3391, 1624 $cm^{-1}$. The $^1H$ NMR data for this product were identical to those reported previously.[11]

**5-Bromo-3-[1-(5-bromoindol-3-yl)-1-methylethyl]indole (2b):** mp 163–165 ˚C (lit.,[12] 165–166 ˚C). The spectral data (IR and $^1H$ NMR) were identical to those reported previously.[12]

**2-Methyl-3-[1-methyl-1-(2-methylindol-3-yl)ethyl]indole (2c):** mp 195–196 ˚C (hexane–$CH_2Cl_2$) (lit.,[13] 197 ˚C); IR (KBr) 3385 $cm^{-1}$; $^1H$ NMR δ 2.03 (s, 6H), 2.22 (s, 6H), 6.88 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 2H), 7.02 (ddd, *J* = 8.2, 7.3, 0.9 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.60 (br s, 2H).

**Typical Procedure for the Preparation of *N,N'*-Bismethoxyalkylated 2,2-Bis(indol-3-yl)propanes (3). 1-(1-Methoxy-1-methylethyl)-3-{1-[1-(1-methoxy-1-methylethyl)indol-3-yl]-1-methylethyl}indole (3a).** To a stirred solution of indole (**1a**) (0.12 g, 1.0 mmol) and 2-methoxypropene (0.22 g, 3.0 mmol) in $CH_2Cl_2$ (3 mL) at 0 ˚C was added (±)-camphor-10-sulfonic acid (12 mg, 0.050 mmol). After 10 min, the resulting mixture was worked up in a manner similar to that for the preparation of **2a**. The residual solid was recrystallized from hexane–$CH_2Cl_2$ to give **3a** (0.13 g, 60%); colorless needles; mp 173–176 ˚C; IR (KBr) 1609 $cm^{-1}$; $^1H$ NMR δ 1.84 (s, 12H), 1.88 (s, 6H), 3.05 (s, 6H), 6.82 (dd, *J* = 7.8, 7.3 Hz, 2H), 7.02 (s, 2H), 7.03 (dd, *J* = 7.8, 7.3 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 2H); $^{13}C$ NMR δ 26.53, 29.92, 34.71, 49.42, 88.66, 113.95, 118.42, 120.94, 121.01, 121.74, 123.94, 128.29, 136.45; MS *m/z* 418 ($M^+$, 13), 354 (32), 339 (100). Anal. Calcd for $C_{27}H_{34}N_2O_2$: C, 77.48; H, 8.19; N, 6.69. Found: C, 77.37; H, 8.24; N, 6.60.

**5-Bromo-3-{1-[5-bromo-1-(1-methoxy-1-methylethyl)indol-3-yl]-1-methylethyl}-1-(1-methoxy-1-methylethyl)indole (3b):** colorless needles; mp 202–203 ˚C (hexane–$CH_2Cl_2$); IR (KBr) 1597 $cm^{-1}$; $^1H$ NMR δ 1.83 (s, 6H), 1.86 (s, 12H), 3.05 (s, 6H), 7.07 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.23 (d, *J* = 1.8 Hz, 2H), 7.26 (s, 2H), 7.62 (d, *J* = 8.7 Hz, 2H); MS *m/z* 574 ($M^+$, 7.2), 510 (27), 495 (100). Anal. Calcd for $C_{27}H_{32}Br_2N_2O_2$:

C, 56.26; H, 5.60; N, 4.86. Found: C, 56.13; H, 5.63; N, 4.84.

**6-Chloro-3-{1-[6-chloro-1-(1-methoxy-1-methylethyl)indol-3-yl]-1-methylethyl}-1-(1-methoxy-1-methylethyl)indole (3d):** colorless needles; mp 240–245 °C (hexane–$CH_2Cl_2$); IR (KBr) 1603 $cm^{-1}$; $^1H$ NMR δ 1.82 (s, 18H), 3.06 (s, 6H), 6.76 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.01 (s, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 1.8 Hz, 2H); MS *m/z* 486 ($M^+$, 10), 342 (42), 73 (100). Anal. Calcd for $C_{27}H_{32}Cl_2N_2O_2$: C, 66.53; H, 6.62; N, 5.75. Found: C, 66.31; H, 6.50; N, 5.90.

**Typical Procedure for the Preparation of *N*-Alkoxyalkylated Indoles (5). 1-(1-Methoxy-1-methylethyl)-3-methylindole (5a).** To a stirred solution of 3-methylindole (**4a**) (0.13 g, 1.0 mmol) and 2-methoxypropene (0.22 g, 3.0 mmol) in $CH_2Cl_2$ (3 mL) at 0 °C was added (±)-camphor-10-sulfonic acid (12 mg, 0.050 mmol). After 30 min, the resulting mixture was worked up as described above. The residue was subjected to column chromatography on neutral alumina to give **5a** (0.11 g, 54%); a pale-yellow oil; $R_f$ 0.35 (hexane); IR (neat) 1610 $cm^{-1}$; $^1H$ NMR δ 1.80 (s, 6H), 2.31 (d, *J* = 0.9 Hz, 3H), 3.04 (s, 3H), 6.91 (s, 1H), 7.12 (ddd, *J* = 7.8, 7.3, 0.9 Hz, 1H), 7.18 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H); MS *m/z* 203 ($M^+$, 9.0) and 149 (100). Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.79; H, 8.53; N, 6.76.

**3-Methyl-1-(tetrahydropyran-2-yl)-3-methylindole (5b):** a pale-yellow oil; $R_f$ 0.35 (1:19 $Et_2O$–hexane); IR (neat) 1614 $cm^{-1}$; $^1H$ NMR δ 1.61–1.80 (m, 3H), 1.99–2.18 (m, 3H), 2.31 (d, *J* = 0.9 Hz, 3H), 3.73 (td, *J* = 11.5, 2.3 Hz, 1H), 4.09 (dt, *J* = 11.5, 1.8 Hz, 1H), 5.45 (dd, *J* = 10.1, 2.3 Hz, 1H), 7.08 (s, 1H), 7.12 (dd, *J* = 7.8, 7.3 Hz, 1H), 7.21 (dd, *J* = 7.8, 7.3 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H); MS *m/z* 216 [$(M+1)^+$, 42], 131 (100). Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.08; H, 8.12; N, 6.38.

**Methyl 1-(Tetrahydrofuran-2-yl)indole-3-carboxylate (5c):** for 6 d at rt; a pale-yellow oil; $R_f$ 0.21 (1:2 $CH_2Cl_2$–hexane); IR (neat) 1695, 1614 $cm^{-1}$; $^1H$ NMR δ 2.12–2.17 (m, 2H), 2.38–2.49 (m, 2H), 3.91 (s, 3H), 4.05 (dt, *J* = 8.2, 7.3 Hz, 1H), 4.21 (ddd, 8.2, 6.4, 1.8 Hz, 1H), 6.24 (dd, *J* = 6.6, 3.2 Hz, 1H), 7.28 (t, *J* = 6.5 Hz, 1H), 7.30 (t, *J* = 6.5 Hz, 1H), 7.45 (dd, *J* = 6.5, 2.7 Hz, 1H), 7.95 (s, 1H), 8.17 (dd, *J* = 6.5, 2.7 Hz, 1H); $^{13}C$ NMR δ 24.21, 32.08, 51.01, 69.00, 86.29, 107.57, 110.51, 121.76, 122.19, 122.90, 127.09, 130.66, 135.62, 165.54; MS *m/z* 245 ($M^+$, 40), 175 (100). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.41; H, 6.31; N, 5.60.

**1-(1-Ethoxyethyl)-2,3-dimethylindole (5d):** for 10 h at 0 °C; a pale-yellow oil; $R_f$ 0.54 (1:19 $Et_2O$–hexane); IR (neat) 1614 $cm^{-1}$; $^1H$ NMR δ 1.15 (t, *J* = 7.3 Hz, 3H), 1.69 (d, *J* = 6.0 Hz, 3H), 2.23 (s, 3H), 2.40 (s, 3H), 3.24–3.38 (m, 2H), 5.67 (q, *J* = 6.0 Hz, 1H), 7.08 (td, *J* = 7.3, 1.4 Hz, 1H), 7.12 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1H), 7.47 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H); MS *m/z* 217 ($M^+$, 3.2), 172 (100). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.30; H, 8.90; N, 6.50.

**Typical Procedure for the Preparation of 2,2-Bis(indol-2-yl)propanes (6). 3-Methyl-2-[1-methyl-1-(3-methylindol-2-yl)ethyl]indole (6a).** To a stirred solution of 3-methylindole (**4a**) (0.13 g, 1.0 mmol)

and 2-methoxypropene (72 mg, 1.0 mmol) in $CH_2Cl_2$ (3 mL) at rt was added (±)-camphor-10-sulfonic acid (12 mg, 0.050 mmol). After stirring overnight, the resulting mixture was worked up as described above. The resulting residue was purified by preparative TLC on silica gel to give **6** (64 mg, 42%); a yellow viscous oil; $R_f$ 0.17 (1:9 THF–hexane); IR (neat) 3439, 1615 $cm^{-1}$; $^1H$ NMR δ 1.91 (s, 6H), 2.11 (s, 6H), 7.11 (ddd, *J* = 7.8, 7.3, 0.9 Hz, 2H), 7.16 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.89 (br s, 2H); $^{13}C$ NMR δ 9.40, 28.11, 37.41, 106.94, 110.51, 118.12, 119.19, 121.42, 130.18, 134.06, 139.02; MS *m/z* 302 ($M^+$, 100). Anal. Calcd for $C_{21}H_{22}N_2$: C, 83.40; H, 7.33; N, 9.26. Found: C, 83.55; H, 7.96; N, 8.25.

**3-Ethyl-2-[1-(3-ethylindol-2-yl)-1-methylethyl]indole (6d):** a yellow viscous oil; $R_f$ 0.22 (1:4 $Et_2O$–hexane); IR (neat) 3420, 1615 $cm^{-1}$; $^1H$ NMR δ 1.15 (t, *J* = 7.3 Hz, 6H), 1.93 (s, 6H), 2.62 (q, *J* = 7.3 Hz, 4H), 7.10 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 2H), 7.15 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.83 (br s, 2H); MS *m/z* 330 ($M^+$, 100). Anal. Calcd for $C_{23}H_{26}N_2$: C, 83.59; H, 7.93; N, 8.48. Found: C, 83.11; H, 7.50; N, 9.29.

**Typical Procedure for the Preparation of 1,1-Bis(indol-1-yl)ethanes (7). 3-Methyl-1-[1-(3-methylindol-1-yl)ethyl]indole (7a).** To a stirred solution of 3-methylindole (**4a)** (0.13 g, 1.0 mmol) and ethyl vinyl ether (72 mg, 1.0 mmol) in $CH_2Cl_2$ (3 mL) at rt was added (±)-camphor-10-sulfonic acid (12 mg, 0.050 mmol). After 10 min, the resulting mixture was worked up as described above. The resulting residue was purified by preparative TLC on silica gel to give **7a** (89 mg, 62%); a yellow viscous oil; $R_f$ 0.31 (1:19 $Et_2O$–hexane); IR (neat) 1614 $cm^{-1}$; $^1H$ NMR δ 2.08 (d, *J* = 6.9 Hz, 3H), 2.29 (d, *J* = 0.9 Hz, 6H), 6.82 (q, *J* = 6.9 Hz, 1H), 6.97 (s, 2H), 7.11 (ddd, *J* = 7.8, 7.3, 0.9 Hz, 2H), 7.16 (ddd, *J* = 7.8, 7.3, 0.9 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H); $^{13}C$ NMR δ 9.74, 20.87, 62.10, 109.22, 111.98, 119.21, 119.48, 121.80, 122.13, 129.29, 135.78; MS *m/z* 288 ($M^+$, 18), 158 (100). Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.15; H, 6.99; N, 9.64.

**3-Ethyl-1-[1-(3-ethylindol-1-yl)ethyl]indole (7d):** a yellow viscous oil; $R_f$ 0.50 (1:19 $Et_2O$–hexane); IR (neat) 1611 $cm^{-1}$; $^1H$ NMR δ 1.30 (t, *J* = 7.3 Hz, 6H), 2.08 (d, *J* = 6.9 Hz, 3H), 2.75 (qd, *J* = 7.3, 0.9 Hz, 4H), 6.81 (q, *J* = 6.9 Hz, 1H), 6.97 (s, 2H), 7.10 (dd, *J* = 7.8, 7.3 Hz, 2H), 7.16 (dd, *J* = 7.8, 7.3 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H); MS *m/z* (%) 316 ($M^+$, 14), 172 (100). Anal. Calcd for $C_{22}H_{24}N_2$: C, 83.50; H, 7.64; N, 8.85. Found: C, 83.40; H, 7.72; N, 8.79.

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