SOME ACID-CATALYSED REACTIONS OF INDOL-3-YL AND INDOL-2-YL DISUBSTITUTED METHANOLS

Mardi SANTOSO[1], Naresh KUMAR[2] and David StClair BLACK[3,*]

School of Chemistry, The University of New South Wales, UNSW Sydney, NSW 2052, Australia; e-mail: [1] msantoso@its.ac.id, [2] n.kumar@unsw.edu.au, [3] d.black@unsw.edu.au

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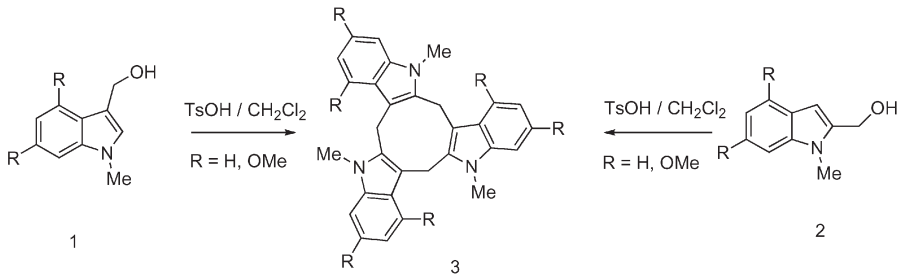
Dedicated to Dr. Alfred Bader on the occasion of his 85th birthday.

1-Substituted indol-3-yl and indol-2-yl disubstituted methanols do not undergo acid-catalysed trimerisation to yield indolocyclotriveratrylenes, unlike the related primary 1-substituted indol-3-yl- and -2-ylmethanols. The 1-substituted indol-3-ylmethanols **10** and **11** gave diindol-3-ylmethanes **12** and **13**, respectively, on treatment with *p*-toluenesulfonic acid in dichloromethane. In contrast, the indol-2-ylmethanols **22** and **23** gave the reduced indolo[3,2-*b*]carbazoles **24** and **25**, respectively, on treatment with boron trifluoride etherate in benzene. An X-ray crystal structure of compound **24** is described.

Keywords: Indoles; Diindol-3-ylmethanes; Indolocarbazoles; Acid-catalysed addition reactions; Isatins; Ketone reduction.

Simple *N*-substituted indole-3- or indole-2-methanols **1** and **2** have been shown to undergo acid-catalysed cyclotrimerisation reactions, usually involving *p*-toluenesulfonic acid in dichloromethane, to form "indolocyclotriveratrylenes" or [2,3;2,3;2,3]calix[3]indoles **3** in yields approximating 40% [1] (Scheme 1).



SCHEME 1

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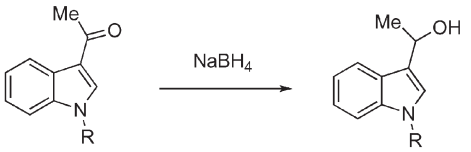
It is assumed that these reactions proceed through the intermediacy of primary benzylic cations. It was consequently of interest to study similar reactions that would involve secondary benzylic cation intermediates, which could arise from similar acid-catalysed reactions of indole-3- or -2-methanols. The introduction of an additional substituent on the carbon atom bearing the hydroxy group gives an enormous scope of possibilities. We have investigated a small variety of such substituents and the results of our experiments are described herein.

One way in which such secondary benzylic cations can be generated is through acid-catalysed additions of aldehydes to indoles. We have previously investigated the reactions of the activated parent 4,6-dimethoxyindole with aromatic aldehydes under the influence of phosphoryl chloride as the acid catalyst[2]. In this study, cyclodimerisation occurred smoothly to give indolo[3,2-*b*]carbazoles, via the intermediacy of reduced derivatives which were readily oxidised under the reaction conditions. Similar reduced indolo[3,2-*b*]carbazoles have been formed by reaction of diindol-3-ylmethanes with aldehydes and ketones[3,4]. In all these cases, the indole compounds were unsubstituted at nitrogen. As the formation of indolocyclotriveratrylenes usually requires the presence of a substituent at the indole nitrogen atom, it was decided to make this an essential part of the study involving secondary methanol derivatives.

RESULTS AND DISCUSSION

Preparation and Acid-Catalysed Reactions of Indol-3-yl Disubstituted Methanols

All the disubstituted methanol derivatives were generated by the reduction of related ketones using sodium borohydride in ethanol. Reduction of 3-acetyl-1-benzylindole[5] (**4**) gave the new methanol compound **6** in 96% yield (Scheme 2). Most indolemethanol compounds are quite sensitive, and



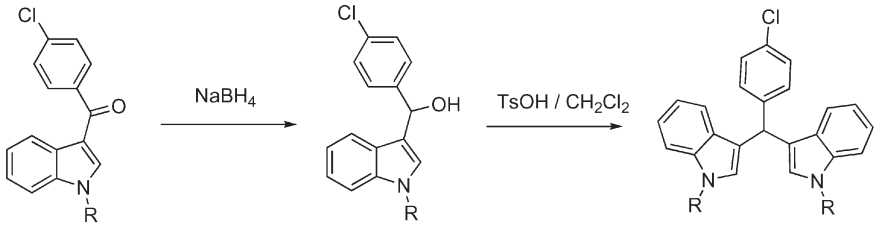
4: R = CH_2Ph **6**: R = CH_2Ph, 96 %

5: R = H **7**: R = H, 0 %

SCHEME 2

therefore difficult to obtain fully pure. For instance, the related *N*-methyl derivative of compound **7**, formed by reduction of the *N*-methyl derivative of compound **5**, has been reported to be unstable and to undergo polymerisation[6]. Although the methanol **6** could be obtained pure, on treatment with *p*-toluenesulfonic acid or hydrochloric acid in dichloromethane, it gave complex reaction mixtures which could not be separated.

It was hoped that more stable methanols could be formed from 3-benzoylindoles, so the *N*-methyl- and *N*-allylindoles, **8** and **9**, respectively, were reduced to the methanols **10** and **11**, respectively, in very high yields. Compound **10** was fully characterised, but compound **11** could not be obtained analytically pure. Treatment of methanols **10** and **11** with *p*-toluenesulfonic acid gave the diindol-3-ylmethanes **12** and **13**, respectively, in good yields, accompanied by 4-chlorobenzaldehyde as a by-product (Scheme 3).



8: R = Me

9: R = $CH_2CH{=}CH_2$

10: R = Me, 99 %

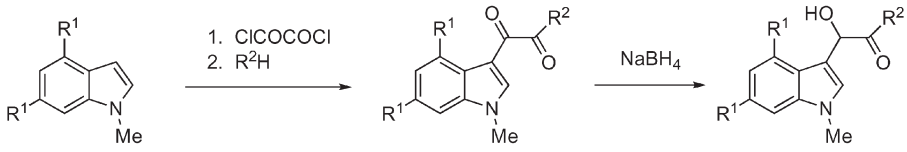
11: R = $CH_2CH{=}CH_2$, 94 %

12: R = Me, 71 %

13: R = $CH_2CH{=}CH_2$, 68 %

SCHEME 3

Indoles react readily at C3 with oxalyl chloride. Consequently, 1-methylindole was converted into the glyoxylic amide **14**, by quenching the intermediate glyoxyloyl chloride with 3,5-dimethoxyaniline. The related 4,6-dimethoxyindole was similarly converted into the glyoxylic amide **15**, quenching this time with pyrrolidine. Reaction of 4,6-dimethoxyindole with oxalyl chloride has been reported[7] to give the indole-7-glyoxyloyl chloride, but in our hands, a mixture of 3- and 7-isomers was formed and the resulting amides could be separated by chromatography. Reduction of the keto-amides **14** and **15** gave high yields of the respective alcohols **16** and **17** (Scheme 4), but these could not be obtained pure, and on direct treatment with acid gave complex reaction mixtures. It is perhaps not surprising that these alcohols are sensitive to acid, as the resulting benzylic cations would be destabilised by the adjacent carbonyl groups.



14: R^1 = H, R^2 = 3,5-$(MeO)_2C_6H_3NH$, 66 % **16**: R^1 = H, R^2 = 3,5-$(MeO)_2C_6H_3NH$, 97 %

15: R^1 = OMe, R^2 = pyrrolidin-1-yl, 27 % **17**: R^1 = OMe, R^2 = pyrrolidin-1-yl, 92 %

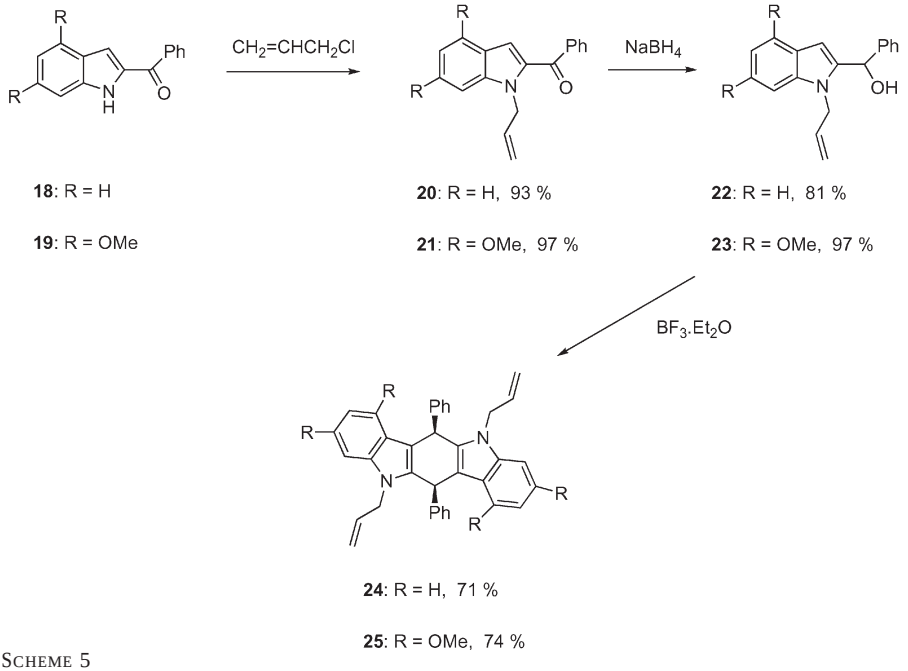
SCHEME 4

Preparation and Acid-Catalysed Reactions of Indol-2-yl Disubstituted Methanols

The required indol-2-ylmethanols can be prepared by reduction of 2-acylindoles. The synthetic route developed[8] from *N*-phenacylisatins was used to prepare the known 2-benzoylindole[9] **18** and 2-benzoyl-4,6-dimethoxyindole[8,10,11] **19**. These were *N*-alkylated with allyl chloride and sodium iodide to give compounds **20** and **21**, respectively, in very high yields. Reduction of the products with sodium borohydride afforded the previously unreported methanols **22** and **23**, the former but not the latter being fully characterised. In these cases the standard conditions of *p*-toluenesulfonic acid in dichloromethane gave a product mixture, but treatment of the two methanols **22** and **23** with boron trifluoride etherate in benzene gave good yields of the reduced indolocarbazoles **24** and **25**, respectively (Scheme 5).

The "dimeric" structure of compound **24** was clear from the mass spectroscopic data which showed a molecular ion at *m/z* 490. The detailed structure was established by NMR spectroscopy and X-ray crystallography. The ^{1}H NMR spectrum showed a single methine proton resonance at δ 5.75 ppm, consistent with the dihydroindolo[3,2-*b*]carbazole structure, and also ruling out the alternative dihydroindolo[2,3-*b*]carbazole structure, which would show two different methine protons. The X-ray crystal structure showed that the dihydroindolocarbazole framework is essentially planar, and that the two phenyl substituents are *syn* to each other (Fig. 1). Similarly, compound **25** showed a molecular ion at *m/z* 610, and the ^{1}H NMR spectrum displayed a single methine proton resonance at δ 5.84 ppm.

Earlier investigations have shown that the heating in ethanol of 2-(1-hydroxyethyl)-1-methylindole with Amberlite IR-120 ion exchange resin gave a 55% yield of crude 5,6,11,12-tetramethyl-6,12-dihydroindolo[3,2-*b*]-



18: R = H

19: R = OMe

20: R = H, 93 %

21: R = OMe, 97 %

22: R = H, 81 %

23: R = OMe, 97 %

24: R = H, 71 %

25: R = OMe, 74 %

SCHEME 5

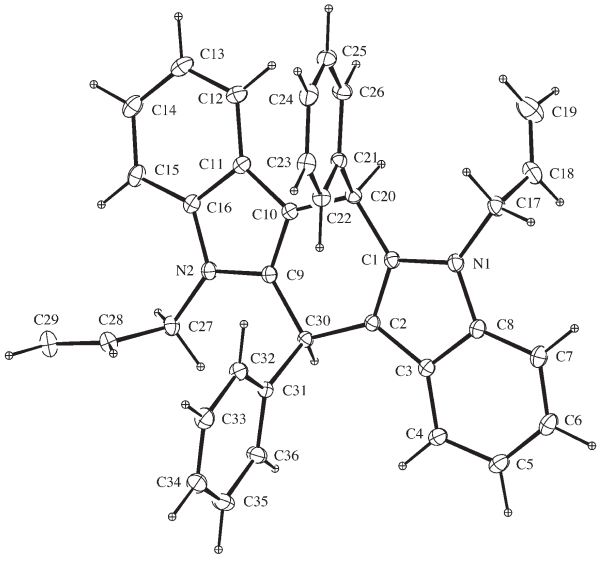


FIG. 1

ORTEP diagram of structure **24**. Hydrogen atoms and the solvent molecule are ommited for clarity

carbazole[12]. Further related indolocarbazole structures can be formed in acid-catalysed reactions of similar substrates in which the hydroxy group is replaced by a benzimidazol-1-yl group[13].

CONCLUSION

Acid-catalysed reactions of indol-3- and indol-2-yl disubstituted methanols do not yield indolocyclotriveratrylenes. The 3-methanols **10** and **11** gave diindol-3-ylmethanes **12** and **13**, respectively, while the 2-methanols **22** and **23** gave the reduced indolo[3,2-*b*]carbazoles **24** and **25**, respectively.

EXPERIMENTAL

Melting points were measured using a Mel-Temp melting point apparatus, and are uncorrected. Microanalyses were performed by the Microanalytical Unit, Research School of Chemistry, The Australian National University. ^{1}H and ^{13}C NMR spectra (δ, ppm; *J*, Hz) were obtained on a Bruker AC300F (300 MHz) spectrometer. Mass spectra were recorded on either an AEI MS 12 (EI) or a Finnegan MAT (MALDI) spectrometer. IR spectra (ν, cm^{-1}) were recorded with a Perkin–Elmer 298 IR spectrometer. UV-Vis spectra were recorded using a Hitachi U-3200 spectrometer. Column chromatography was carried out using Merck 70–230 mesh silica gel, whilst preparative thin layer chromatography was performed using Merck silica gel 7730 60GF$_{254}$. Flash chromatography[14] was carried out using Merck 60H silica gel.

1-(1-Benzylindol-3-yl)ethanol (**6**)

A mixture of 3-acetyl-1-benzylindole[5] (**4**) (0.76 g, 3.05 mmol) and sodium borohydride (0.60 g, 15.86 mmol) in absolute ethanol was heated under reflux for 2 h. After cooling, a small amount of 10% sodium hydroxide was added and the solvent was evaporated under reduced pressure. Water was added and the resulting white precipitate was filtered off, washed with water and dried to afford the alcohol **6** as a yellowish solid (0.74 g, 96%), m.p. 76–77 °C. IR (Nujol): 3350, 1610, 1550, 1460, 1380, 1340, 1300, 1260, 1180, 1130, 1080, 1040, 990, 880, 820, 790, 770, 740, 700. UV (MeOH (ε)): 222 (35,500), 285 (6,500). ^{1}H NMR (300 MHz, $CDCl_3$): 1.70 d, 3 H, *J* = 6.2 (Me); 1.98 d, 1 H, *J* = 4.6 (OH); 5.28 s, 3 H (CH_2 and C**H**OH); 7.10–7.31 m, 9 H (ArH); 7.82 m, 1 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 23.77, Me; 49.98, CH_2; 64.10, CHOH; 109.85, 119.44, 119.79, 122.06, 124.74, 126.86, 127.64, 128.74, ArCH; 120.32, 126.41, 136.99, 137.34, ArC. MS (EI), *m/z* (%): 252 (5), 251 (25) [$M^{\bullet+}$], 236 (40), 91 (100). For $C_{17}H_{17}NO{\cdot}0.25H_2O$ calculated: 79.8% C, 6.9% H, 5.5% N; found: 79.6% C, 6.8% H, 5.4% N.

3-(4-Chlorobenzoyl)-1-methylindole (**8**)

Method A: 3-(4-Chlorobenzoyl)indole (0.12 g, 0.47 mmol) and freshly crushed potassium hydroxide (0.11 g, 1.96 mmol) in dry dimethyl sulfoxide (25 ml) were stirred at room temperature for 1 h. Iodomethane (0.02 ml, 0.32 mmol) was added and the mixture was stirred for an additional 1 h. Water was added and the resulting white precipitate was filtered off, washed with water and dried (0.11 g, 85%), m. p. 144–145 °C. IR (Nujol): 1610, 1580, 1505,

1450, 1365, 1260, 1225, 1150, 1120, 1080, 1060, 1030, 1000, 965, 870, 840, 770, 745, 720, 690. UV (MeOH (ε)): 254 (21,600), 322 (19,400). ^{1}H NMR (300 MHz, $CDCl_3$): 3.85 s, 3 H, Me; 7.33–7.78 m, 7 H, ArH; 7.51 s, 1 H (H2); 8.36–8.42 m, 1 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 33.62, Me; 109.69, 122.72, 122.87, 123.83, 128.57, 130.11, 137.61, ArCH; 115.49, 127.14, 137.31 (2×), 139.27, ArC; 189.39, CO. MS (EI), *m/z* (%): 271 (10) [$M^{\bullet+}$, ^{37}Cl], 269 (30) [$M^{\bullet+}$, ^{35}Cl], 158 (100), 77 (100).

Method B: 4-Chloro-*N*,*N*-dimethylbenzamide (1.44 g, 7.84 mmol) was stirred and warmed at 60 °C, phosphoryl chloride (0.88 ml, 9.44 mmol) was added and the mixture was stirred for 5 min. 1-Methylindole (1.03 g, 7.85 mmol) was added and the mixture was heated at 80 °C for 2 h. Aqueous sodium hydroxide (10%) was added to the mixture and the product was extracted with dichloromethane. The combined extract was washed with brine, dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified using column chromatography with dichloromethane eluent to yield the ketone **8** as a white solid (1.41 g, 67%).

1-Allyl-3-(4-chlorobenzoyl)indole (**9**)

4-Chloro-*N*,*N*-dimethylbenzamide (1.55 g, 8.44 mmol) was stirred and warmed at 60 °C, phosphoryl chloride (0.88 ml, 9.44 mmol) was added and the mixture was stirred for 5 min. 1-Allylindole (1.27 g, 8.08 mmmol) was added and the mixture was heated at 80 °C for 2 h. Aqueous sodium hydroxide (10%) was added to the cooled mixture and the product was extracted with dichloromethane. The combined extract was washed with brine, dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified using column chromatography with dichloromethane eluent to yield the ketone **9** as a white solid (1.53 g, 67%), m.p. 126–127 °C. IR (Nujol): 1610, 1580, 1455, 1370, 1190, 1170, 1080, 1000, 935, 870, 840, 765, 740. UV (MeOH (ε)): 254 (33,500), 321 (27,600). ^{1}H NMR (300 MHz, $CDCl_3$): 4.76 d, 2 H, J = 5.6 (H1′); 5.17 d, 1 H, J = 16.9 (H3′); 5.29 d, 1 H, J = 10.81 (H3′); 5.93–6.06 m, 1 H (H2′); 7.31–7.77 m, 8 H (ArH); 8.38–8.41 m, 1 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 49.45, C1′; 118.74, C3′; 134.90, C2′; 110.14, 122.70, 122.86, 123.79, 128.54, 130.08, 136.90, ArCH; 115.70, 127.23, 136.97, 137.30, 139.13, ArC; 189.40, CO. MS (EI), *m/z* (%): 297 (5) [$M^{\bullet+}$, ^{37}Cl], 295 (10) [$M^{\bullet+}$, ^{35}Cl], 184 (30), 41 (100). For $C_{18}H_{14}ClNO{\cdot}0.25H_2O$ calculated: 72.0% C, 4.9% H, 4.7% N; found: 72.3% C, 4.8% H, 4.6% N.

(4-Chlorophenyl)(1-methylindol-3-yl)methanol (**10**)

3-(4-Chlorobenzoyl)-1-methylindole (**8**) 0.70 g, 2.60 mmol) was dissolved in tetrahydrofuran (50 ml), sodium borohydride (2.46 g, 0.065 mol) was added and followed by addition of absolute ethanol (20 ml). The mixture was heated under reflux for 2 h and, after cooling, the solvent was evaporated under reduced pressure to dryness. The residue was suspended in aqueous sodium hydroxide (10%) and the resulting white precipitate was filtered off, washed with water and dried to afford the alcohol as a white solid (0.70 g, 99%), m.p. 109–110 °C. IR (Nujol): 3300, 1580, 1540, 1450, 1370, 1320, 1300, 1230, 1190, 1140, 1120, 1080, 1050, 1010, 980, 810, 730. UV (MeOH, (ε)): 223 (58,800), 285 (7,400). ^{1}H NMR (300 MHz, $CDCl_3$): 3.73 s, 3 H (Me); 6.11 d, 1 H, J = 4.1 (C**H**OH); 6.79 s, 1 H (H2); 7.11 m, 1 H (ArH); 7.23–7.34 m, 4 H (ArH); 7.44 m, 2 H (ArH); 7.57 m, 1 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 32.73, CH_3; 69.44, CHOH; 109.47, 119.57, 119.59, 122.14, 127.44, 127.83, 128.36, ArCH; 117.93, 126.12, 132.94, 137.44, 142.22, ArC. MS (EI), *m/z* (%): 273 (20) [$M^{\bullet+}$,

^{37}Cl], 272 (10) [M$^{\bullet+}$, ^{35}Cl], 271 (65) [M$^{\bullet+}$, ^{35}Cl], 254 (55), 160 (35), 139 (25), 132 (100), 130 (20), 117 (35), 77 (30). For $C_{16}H_{14}ClNO \cdot 0.33H_2O$ calculated: 69.2% C, 5.3% H, 5.0% N; found: 69.2% C, 5.3% H, 5.0% N.

(1-Allylindol-3-yl)(4-chlorophenyl)methanol (**11**)

1-Allyl-3-(4-chlorobenzoyl)indole (**9**) (0.35 g, 1.18 mmol) was dissolved in tetrahydrofuran (30 ml), sodium borohydride (0.35 g, 9.25 mmol) was added and followed by addition of absolute ethanol (20 ml). The mixture was refluxed for 2 h and, after cooling, the solvent was evaporated under reduced pressure to dryness. The residue was suspended in aqueous sodium hydroxide (10%) and the product was extracted several times with dichloromethane. The combined extracts were dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure to give the title alcohol as a yellowish oil (0.33 g, 94%). IR (neat): 3340, 3060, 2920, 2860, 1460, 1265, 1180, 1090, 1040, 1020, 925, 800, 745. UV (CH_2Cl_2 (ε)): 229 (132,000), 273 (26,800). ^{1}H NMR (300 MHz, $CDCl_3$): 4.67 d, 2 H, *J* = 5.6 (H1′); 5.11 d, 1 H, *J* = 16.9 (H3′); 5.21 d, 1 H, *J* = 10.2 (H3′); 5.91–6.04 m, 1 H (H2′); 6.13 s, 1 H (C**H**OH); 6.87 s, 1 H (H2); 7.10 and 7.23 2 m (H6 and H5); 7.30–7.34 m, 3 H (ArH); 7.44 m, 2 H (ArH); 7.57 m, 1 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 48.91, C1′; 69.59, CHOH; 117.58, C3′; 133.20, C2′; 109.90, 119.72, 119.75, 122.20, 126.38, 127.90, 128.42, ArCH; 118.34, 126.34, 133.00, 136.92, 142.18, ArC. MS (EI), *m/z* (%): 299 (20) [M$^{\bullet+}$, ^{37}Cl], 297 (55) [M$^{\bullet+}$, ^{35}Cl], 282 (20), 280 (55), 186 (35), 184 (50), 158 (65), 156 (30), 139 (75), 130 (45), 117 (45), 111 (50), 111 (50), 41 (100).

(4-Chlorophenyl)bis(1-methylindol-3-yl)methane (**12**)

(4-Chlorophenyl)(1-methylindol-3-yl)methanol (**10**) (0.20 g, 0.74 mmol) in dichloromethane was treated with a small amount of *p*-toluenesulfonic acid monohydrate, and stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the crude product was purified using column chromatography with dichloromethane/light petroleum (1:1) eluent to afford the product as a white solid (0.10 g, 71%), m.p. 204–205 °C. IR (Nujol): 1640, 1600, 1580, 1460, 1420, 1380, 1320, 1220, 1200, 1150, 1120, 1080, 1010, 920, 860, 830, 800, 730, 700. UV (CH_2Cl_2 (ε)): 231 (66,600), 293 (16,300). ^{1}H NMR (300 MHz, $CDCl_3$): 3.71 s, 6 H, Me; 5.91 s, 1 H (CH bridging); 6.56 s, 2 H (H2); 7.05 m, 2 H (ArH); 7.23–7.35 m, 8 H (ArH); 7.41 m, 2 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 32.66, Me; 39.55, CH bridging; 109.15, 118.78, 119.93, 121.59, 128.32 (2×), 130.06, ArCH; 117.77, 127.30, 131.68, 137.45, 143.04, ArC. MS (EI), *m/z* (%): 386 (30) [M$^{\bullet+}$, ^{37}Cl], 384 (95) [M$^{\bullet+}$, ^{35}Cl], 383 (30), 274 (20), 273 (100), 257 (20), 253 (30). For $C_{25}H_{21}ClN_2$ calculated: 78.0% C, 5.5% H, 7.3% N; found: 77.7% C, 5.7% H, 7.1% N.

Bis(1-allylindol-3-yl)(4-chlorophenyl)methane (**13**)

(1-Allylindol-3-yl)(4-chlorophenyl)methanol (**11**) (0.42 g, 1.41 mmol) in dichloromethane was treated with a small amount of *p*-toluenesulfonic acid monohydrate or hydrochloric acid, and stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (dichloromethane/light petroleum, 1:1) to afford the product as a white solid (0.21 g, 68%), m.p. 297–299 °C. IR (Nujol): 3040, 1455, 1365, 1335, 1190, 1150, 1080, 1010, 990, 920, 860, 740. UV (CH_2Cl_2 (ε)): 230 (48,100), 293 (11,000). ^{1}H NMR (300 MHz, $CDCl_3$): 4.65 m, 4 H (H1′); 5.06 m, 2 H

(H3′); 5.18 m, 2 H (H3′); 5.90–6.01 m, 3 H (H2′ and CH bridging); 6.60 s, 2 H (H2); 7.03 m, 2 H (ArH); 7.19–7.41 m, 10 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 39.66, CH bridging; 48.73, C1′; 116.93, C3′; 130.10, C2′; 109.61, 118.97, 120.04, 121.63, 127.35, 128.37, 133.65, ArCH; 118.09, 127.57, 131.71, 136.90, 142.91, ArC. MS (ES), *m/z* (%): 439 (30) [$M^{\bullet+}$, ^{37}Cl], 437 (90) [$M^{\bullet+}$, ^{35}Cl], 435 (100), 280 (25).

N-(3,5-Dimethoxyphenyl)-1-methylindol-3-ylglyoxylamide (**14**)

1-Methylindole (1.99 g, 15.17 mmol) in anhydrous ether (35 ml) was cooled in ice, and treated dropwise while stirring with a solution of oxalyl chloride (1.46 ml, 16.74 mmol) in anhydrous ether (5 ml). After stirring in ice for 1 h, the glyoxyloyl chloride was collected by filtration. It was dissolved in anhydrous ether (50 ml) and treated dropwise with a solution of 3,5-dimethoxyaniline (2.61 g, 17.04 mmol) in anhydrous ether (50 ml) with ice cooling. It was stirred in ice for additional 1 h, and the resulting precipitate was filtered off, washed with water and dried to afford the keto-amide as a yellowish solid (3.39 g, 66%), m.p. 165–166 °C. IR (Nujol): 3340, 1690, 1600, 1460, 1370, 1290, 1260, 1200, 1120, 1080, 1050, 1010, 980, 940, 850, 820, 790, 770, 750, 680. UV (MeOH (ε)): 263 (5,400), 276 (4,800), 338 (9,500). ^{1}H NMR (300 MHz, $CDCl_3$): 3.81 s, 6 H (OMe); 3.86 s, 3 H (Me); 6.30 t, 1 H (ArH); 6.96 d, 2 H (ArH); 7.36–7.38 m, 3 H (ArH); 8.43–8.46 m, 1 H (ArH); 9.00 s, 1 H (H2); 9.35 bs, 1 H (NH). ^{13}C NMR (75 MHz, $CDCl_3$): 33.73, Me; 55.43, OMe; 97.56, 98.18, 109.97, 122.66, 123.61, 124.03, 142.24, ArCH; 111.65, 127.74, 137.08, 138.69, 160.19, 161.20, 179.46, ArC. MS (EI), *m/z* (%): 338 (5) [$M^{\bullet+}$], 158 (100). For $C_{19}H_{17}N_2O_4$ calculated: 67.4% C, 5.4% H, 8.3% N; found: 67.4% C, 5.5% H, 8.3% N.

1-(4,6-Dimethoxy-1-methylindol-3-ylglyoxyloyl)pyrrolidine (**15**)

4,6-Dimethoxyindole (0.59 g, 3.33 mmol) in anhydrous ether (25 ml) was cooled in ice, and treated dropwise while stirring with a solution of oxalyl chloride (0.32 ml, 3.78 mmol) in anhydrous ether (5 ml). After stirring in ice for 1 h, the resulting yellow precipitate was filtered off to yield crude material which was suspended in anhydrous ether (20 ml), and treated dropwise while stirring with a solution of pyrrolidine (0.31 ml, 3.71 mmol) in anhydrous ether (5 ml) with ice cooling. After stirring in ice for 1 h, the resulting precipitate was filtered off and purified using flash chromatography with ethyl acetate to afford (4,6-dimethoxyindol-3-ylglyoxyloyl)pyrrolidine as an orange solid (0.27 g, 27%), m.p. 169–170 °C. IR (Nujol): 3330, 1590, 1450, 1370, 1270, 1210, 1140, 1030, 840, 800, 780. UV (MeOH (ε)): 253 (16,800), 348 (32,200). ^{1}H NMR (300 MHz, $CDCl_3$): 1.89–1.91 m, 4 H (CH_2); 3.57–3.65 m, 4 H (CH_2); 3.77 and 3.86 2 s, 6 H (OMe); 6.11 d, 1 H, J = 1.5 (H5); 6.39 d, 1 H, J = 1.5 (H7); 7.47 s, 1 H (H2); 9.87 bs, 1 H (NH). ^{13}C NMR (75 MHz, $CDCl_3$): 23.86, 26.07, 45.84, 47.26, CH_2; 55.33 and 55.51, OMe; 86.12, C5; 93.17, C7; 113.07, C2; 114.69, 130.69, 140.79, 155.75, 162.03, 164.15, 180.38, ArC. MS (EI), *m/z* (%): 302 (25) [$M^{\bullet+}$], 204 (100), 176 (25), 149 (40). For $C_{16}H_{18}N_2O_4$ calculated: 63.6% C, 6.0% H, 9.3% N; found: 63.4% C, 6.1% H, 9.0% N.

(4,6-Dimethoxyindol-3-ylglyoxyloyl)pyrrolidine (0.21 g, 0.69 mmol) and freshly crushed potassium hydroxide (0.15 g, 2.67 mmol) in dry dimethyl sulfoxide (15 ml) were stirred at room temperature for 1 h. Iodomethane (0.09 ml, 1.45 mmol) was added and the mixture was stirred for an additional 1 h. Water was added and the product was extracted with dichloromethane several times. The combined extracts were washed with brine several times, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The crude

product was purified using column chromatography with ethyl acetate/light petroleum (1:1) eluent to afford the keto-amide **15** as a yellow solid (0.18 g, 82 %), m.p. 180–181 °C. IR (Nujol): 1620, 1585, 1460, 1380, 1350, 1320, 1260, 1210, 1150, 1070, 1040, 820, 760, 720. UV (MeOH (ε)): 251 (18,100), 341 (34,400). ^{1}H NMR (300 MHz, $CDCl_3$): 1.90–1.98 m, 4 H (CH_2); 3.49 t, 2 H (CH_2); 3.63 t, 2 H (CH_2); 3.89 s, 6 H (OMe); 4.05 s, 3 H (Me); 6.16 d, 1 H, *J* = 1.6 (H5); 6.30 d, 1 H, *J* = 1.6 (H7); 7.37 s, 2 H (H2). ^{13}C NMR (75 MHz, $CDCl_3$): 24.14, 25.97, 45.35, 47.01, CH_2; 32.34, Me; 55.47 and 55.67, OMe; 84.08, C5; 93.16, C7; 115.48, C2; 113.35, 129.92, 143.42, 155.86, 162.16, 165.27, 183.10, ArC. MS (EI), *m/z* (%): 316 (20) [$M^{\bullet+}$], 218 (100), 149 (85), 137 (20), 121 (20). For $C_{17}H_{20}N_2O_4$ calculated: 64.5% C, 6.4% H, 8.9% N; found: 64.7% C, 6.5% H, 8.8% N.

N-(3,5-Dimethoxyphenyl)-2-hydroxy-2-(1-methylindol-3-yl)acetamide (**16**)

N-(3,5-Dimethoxyphenyl)-1-methylindol-3-ylglyoxylamide (**14**) (0.87g, 2.57 mmol) was dissolved in tetrahydrofuran (40 ml), and sodium borohydride (0.49 g, 12.95 mmol) and absolute ethanol (20 ml) were added. The mixture was stirred at room temperature for 2.5 h, and the colourless solution was evaporated to dryness. The residue was suspended in aqueous sodium hydroxide (10%) and the resulting white precipitate was filtered off, washed with water and dried to yield the alcohol **16** (0.84 g, 97%), m.p. 63–64 °C. IR (Nujol): 3350, 1660, 1600, 1530, 1460, 1380, 1340, 1260, 1200, 1150, 1080, 1010, 820, 740. UV (CH_2Cl_2 (ε)): 229 (33,000), 253 (11,500). ^{1}H NMR (300 MHz, $CDCl_3$): 3.68 s, 3 H (Me); 3.73 s, 6 H (OMe); 5.35 s, 1 H (C**H**OH); 6.23 t, 1 H (ArH); 6.78 m, 2 H (ArH); 7.07–7.30 m, 4 H (ArH); 7.65 m, 1 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 32.87, Me; 55.43, OMe; 68.72, CHOH; 97.10, 98.08, 109.74, 119.27, 120.18, 122.46, 128.63, ArCH; 112.30, 125.88, 137.47, 139.06, 161.13, ArC; 170.71, CO. MS (EI), *m/z* (%): 340 (5) [$M^{\bullet+}$], 160 (95), 153 (100), 152 (20), 132 (35), 124 (65), 117 (35).

1-[2-(4,6-Dimethoxy-1-methylindol-3-yl)-2-hydroxyacetyl]pyrrolidine (**17**)

1-(4,6-Dimethoxy-1-methylindol-3-ylglyoxyloyl)pyrrolidine (**15**) (0.12 g, 0.38 mmol) and sodium borohydride (0.36 g, 9.52 mmol) in absolute ethanol (45 ml) was stirred for 3 h. A small amount of 10% sodium hydroxide was added and the solvent was evaporated. The white precipitate was filtered off, washed with water and dried to afford the title compound as a white solid (0.11 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$ + [$(CD_3)_2SO$]): 1.52–1.58 m, 4 H (CH_2); 2.71–3.35 m, 4 H (CH_2); 3.43 s, 3 H (Me); 3.56, 3.58 2 s, 6 H (OMe); 4.34 d, 1 H, *J* = 5.6 (C**H**OH); 5.01 d, 1 H, *J* = 5.6 (CHO**H**); 5.89 d, 1 H (H5); 6.02 s, 1 H (H2); 6.09 d, 1 H (H7). ^{13}C NMR (75 MHz, $CDCl_3$ + [$(CD_3)_2SO$]): 23.14, 25.17, 45.32, 45.99, CH_2; 29.84, Me; 54.58 and 54.98, OMe; 65.31, CHOH; 84.62, C5; 90.90, C7; 98.32, C2; 111.20, 132.85, 138.78, ArC; 153.01 and 157.14, C-OMe; 168.60, CO.

2-Benzoylindole (**18**)

A solution of sodium hydroxide (1.29 g, 32.25 mmol) in methanol (75 ml) was added to isatin (4.65 g, 0.032 mol) and the mixture was refluxed for 1 h. After cooling, the methanol was evaporated, and the residue was suspended in dry dimethylformamide (30 ml). A solution of phenacyl bromide (6.47 g, 0.033 mol) in dry dimethylformamide (20 ml) was added and the mixture was heated at 100 °C for 16 h. It was cooled and then poured into a mixture of ice and 10% hydrochloric acid (40 ml). The resulting precipitate was filtered off,

washed with water, dried, suspended in 20% aqueous sodium hydroxide solution (100 ml) and refluxed for 12 h. After cooling, the mixture was diluted with water and the product was extracted with dichloromethane. The combined extract was dried over anhydrous magnesium sulfate, evaporated under reduced pressure and recrystallized from dichloromethane/light petroleum to afford the title compound as a white solid (3.13 g, 44%), m.p. 147–148 °C (lit.[9] gives 149–150 °C). ^{1}H NMR (300 MHz, $CDCl_3$): 7.15–7.20 m, 2 H (ArH); 7.36–7.41 m, 1 H (ArH); 7.47–7.66 m, 4 H (ArH); 7.73 m, 1 H (ArH); 7.99 m, 2 H (ArH); 9.28 bs, 1 H (NH). ^{13}C NMR (75 MHz, $CDCl_3$): 112.30, 112.97, 120.93, 123.13, 126.44, 128.40, 129.22 and 132.29, ArCH; 127.63, 134.30, 137.32, 138.01, ArC; 187.35, CO.

1-Allyl-2-benzoylindole (**20**)

2-Benzoylindole **18** (0.84 g, 3.80 mmol) and freshly crushed potassium hydroxide (0.85 g, 0.015 mol) in dry dimethyl sulfoxide (15 ml) were stirred for 1 h. Allyl chloride (0.62 ml, 7.61 mmol) and sodium iodide (1.14 g, 7.61 mmol) were added and the mixture was stirred for 1 h. Water was added and the mixture was extracted with dichloromethane. The combined extract was washed with brine, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The crude product was purified using flash chromatography with chloroform/light petroleum (1:1) eluent to afford the ketone **20** as a yellowish solid (0.93 g, 93%), m.p. 66–67 °C. IR (Nujol): 3060, 1640, 1520, 1460, 1380, 1340, 1270, 1210, 1170, 1140, 1000, 930, 825, 800, 745, 730, 705, 690. UV (CH_2Cl_2 (ε)): 227 (30,800), 250 (24,200), 319 (33,500). ^{1}H NMR (300 MHz, $CDCl_3$): 5.03 m, 1 H (H3′); 5.16 m, 1 H (H3′); 5.28 m, 2 H (H1′); 6.04–6.17 m, 1 H (H2′); 7.06 s, 1 H (H3); 7.20 m, 1 H (ArH); 7.38–7.64 m, 5 H (ArH); 7.71 m, 1 H (ArH); 7.94 m, 2 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 46.98, C1′; 116.12, C3′; 134.03, C2′; 110.72, 115.29, 120.85, 122.96, 125.91, 128.10, 129.62, 132.07, ArCH; 128.55, 134.38, 139.30,139.74, ArC; 188.36, CO. MS (EI), *m/z* (%): 261 (25) [$M^{\bullet+}$], 105 (40), 78 (35), 77 (100), 41 (68). For $C_{18}H_{15}NO$ calculated: 82.7% C, 5.8% H, 5.4% N; found: 82.3% C, 5.9% H, 5.2% N.

1-Allyl-2-benzoyl-4,6-dimethoxyindole (**21**)

2-Benzoyl-4,6-dimethoxyindole[10] (**19**) (0.56 g, 1.99 mmol) and freshly crushed potassium hydroxide (0.45 g, 8.02 mmol) in dry dimethyl sulfoxide (10 ml) were stirred for 1 h. Allyl chloride (0.33 ml, 4.05 mmol) and sodium iodide (1.19 g, 7.94 mmol) were added and the mixture was stirred for an additional 1 h. Water was added and the precipitate was filtered off, washed with water and dried to afford the ketone **21** as a yellow solid (0.62 g, 97%), m.p. 112 °C. IR (Nujol): 1600, 1580, 1445, 1370, 1270, 1240, 1200, 1180, 1150, 1110, 1080, 990, 925, 910, 890, 800, 730, 715, 690. UV (MeOH (ε)): 255 (18,500), 350 (20,900). ^{1}H NMR (300 MHz, $(CD_3)_2SO$): 3.83 s, 6 H, OMe; 4.87 m, 1 H (H3′); 5.06 m, 1 H (H3′); 5.21 m, 2 H (H1′); 5.96–6.05 m, 1 H (H2′); 6.26, 6.63, 6.86 3 s, 3 H (H5, H3, H7); 7.51–7.66 m, 3 H (ArH); 7.78 m, 2 H (ArH). ^{13}C NMR (300 MHz, $(CD_3)_2SO$): 46.79, C1′; 115.92, C3′; 134.87, C2′; 55.59 and 55.89, OMe; 85.80, C5; 93.24, C7; 113.48, C3; 128.59, 129.29, 132.20, ArCH; 111.92, 132.20, 139.45, 141.91, ArC; 155.07 and 161.09, C-OMe; 186.60, CO. MS (EI), *m/z* (%): 322 (25) [$M^{\bullet+}$ + 1], 321 (100) [$M^{\bullet+}$], 244 (20), 105 (90), 77 (90), 41 (75). For $C_{20}H_{19}NO_3$ calculated: 74.7% C, 6.0% H, 4.4% N; found: 74.6% C, 5.9% H, 4.6% N.

(1-Allylindol-3-yl)phenylmethanol (**22**)

1-Allyl-2-benzoylindole (**20**) (0.93 g, 3.56 mmol) and sodium borohydride (0.72 g, 19.03 mmol) in absolute ethanol (40 ml) were stirred for 1 h. The mixture was evaporated under reduced pressure to dryness, the residue was suspended in aqueous sodium hydroxide (10%) and the resulting precipitate was filtered off, washed with water and dried to yield the alcohol **22** as a white solid (0.76 g, 81%), m. p. 94–95 °C. IR (Nujol): 3400, 1450, 1400, 1370, 1310, 1260, 1200, 1160, 1130, 985, 920, 840, 790, 740, 730, 710. UV (MeOH (ε)): 224 (36,500), 277 (8,200). ^{1}H NMR (300 MHz, $CDCl_3$): 4.69–4.87 m, 2 H (H1′); 4.92 m, 1 H (H3′); 5.13 m, 1 H (H3′); 5.81–5.93 m, 1 H (H2′); 6.01 d, 1 H, *J* = 4.9 (C**H**OH); 6.32 s, 1 H (H3); 7.18 m, 1 H (ArH); 7.25–7.49 m, 7 H (ArH); 7.63 m, 1 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 45.97, C1′; 116.11, C3′; 133.62, C2′; 69.65, CHOH; 102.07, 109.67, 119.66, 120.83, 121.93, 126.60, 127.82, 128.35, ArCH; 127.14, 137.61, 141.05, 141.21, ArC. MS (EI), *m/z* (%): 266 (20) [$M^{\bullet+}$ + 1], 263 (100) [$M^{\bullet+}$], 246 (30), 221 (20), 204 (55), 186 (20), 168 (40), 158 (70), 156 (50), 144 (35), 130 (40), 117 (50), 105 (85), 77 (60), 41 (45). For $C_{18}H_{17}NO{\cdot}0.5H_2O$ calculated: 79.4% C, 6.7% H, 5.1% N; found: 79.2% C, 6.5% H, 5.1% N.

(1-Allyl-4,6-dimethoxyindol-2-yl)phenylmethanol (**23**)

A mixture of 1-allyl-2-benzoyl-4,6-dimethoxyindole (**21**) (0.38 g, 1.18 mmol) and sodium borohydride (0.22 g, 5.82 mmol) in absolute ethanol (50 ml) was stirred for 1 h. The mixture was evaporated to dryness and the residue was suspended in aqueous sodium hydroxide (5%). The resulting precipitate was filtered off, washed with water and dried to afford the title alcohol as a white solid (0.37 g, 97%), m. p. 119–120 °C. IR (Nujol): 3420, 1650, 1640, 1595, 1450, 1375, 1250, 1205, 1160, 1140, 1085, 1040, 980, 910, 790, 765, 740, 720, 695. UV (MeOH (ε)): 226 (13,800), 276 (4,300). ^{1}H NMR (300 MHz, $CDCl_3$): 3.83 and 3.87 2 s, 6 H (OMe); 4.62–4.81 m, 2 H (H3′); 4.86 m, 1 H (H1′); 5.09 m, 1 H (H1′); 5.78–5.95 m, 1 H (H2′); 5.94 d, 1 H, *J* = 4.9 (C**H**OH); 6.20 d, 1 H, *J* = 1.7 (H5); 6.23 s, 1 H (H3); 6.33 d, 1 H, *J* = 1.7 (H7); 7.26–7.44 m, 5 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 46.17, C1′; 116.00, C3′; 133.60, C2′; 55.22 and 55.62, OMe; 85.74, C5; 91.47, C7; 99.60, C3; 126.49, 127.65, 128.28, ArCH; 112.08, 138.43, 139.07, 141.39, ArC; 153.74 and 157.65, C-OMe. MS (EI), *m/z* (%): 323 (60) [$M^{\bullet+}$], 306 (20), 105 (100), 77 (40), 41 (55).

5,11-Diallyl-6,12-diphenyl-6,12-dihydro-5*H*,11*H*-indolo[3,2-*b*]carbazole (**24**)

(1-Allylindol-3-yl)phenylmethanol (**22**) (0.06 g, 0.23 mmol) in benzene was treated with a catalytic amount of boron trifluoride diethyl etherate and stirred for 30 min. The solution was evaporated and the crude product was purified using flash chromatography with dichloromethane eluent to yield the compound **24** as a white solid (0.04 g, 71%), m.p. 308–309 °C. IR (Nujol): 1450, 1370, 1160, 1010, 990, 915, 860, 800, 770, 730, 720, 700. UV (CH_2Cl_2 (ε)): 234 (56,100), 287 (17,500), 294 sh (16,400). ^{1}H NMR (300 MHz, $CDCl_3$): 4.41–4.74 m, 4 H (H1′); 4.79 m, 2 H (H3′); 4.96 m, 2 H (H3′); 5.35–5.47 m, 2 H (H2′); 5.76 s, 2 H (CH bridging); 6.97 m, 2 H (ArH); 7.06–7.29 m, 10 H (ArH); 7.36 m, 4 H (ArH); 7.47 m, 2 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 40.03, CH bridging; 45.96, C1′; 115.89, C3′; 133.10, C2′; 109.35, 118.99, 119.08, 121.18, 126.55, 128.57, 128.85, ArCH; 112.07, 125.74, 135.75, 137.63, 143.65, ArC. MS (EI), *m/z* (%): 491 (35) [$M^{\bullet+}$ + 1], 490 (100) [$M^{\bullet+}$], 449 (30), 413 (70), 372 (25), 331 (75). For $C_{36}H_{30}N_2{\cdot}0.5CH_2Cl_2$ calculated: 82.2% C, 5.9% H, 5.3% N;

found: 82.2% C, 5.8% H, 5.2% N. Crystals for a single crystal X-ray determination were obtained by recrystallization from dichloromethane/light petroleum.

5,11-Diallyl-1,3,7,9-tetramethoxy-6,12-diphenyl-6,12-dihydro-5*H*,11*H*-indolo[3,2-*b*]carbazole (**25**)

(1-Allyl-4,6-dimethoxyindol-2-yl)phenylmethanol (**23**) (0.10 g, 0.31 mmol) in benzene was treated with a catalytic amount of boron trifluoride diethyl etherate and stirred for 1 h. The solvent was evaporated and the crude product was purified using flash chromatography with dichloromethane eluent to afford the compound **25** as a white solid (0.07 g, 74%), m.p. 118–119 °C. IR (Nujol): 1600, 1580, 1450, 1375, 1250, 1200, 1150, 1050, 920, 800, 700. UV (CH_2Cl_2 (ε)): 234 (93,800), 281 (30,500), 344 (4,400). ^{1}H NMR (300 MHz, $CDCl_3$): 3.81 and 3.94 2 s, 12 H (OMe); 4.58 d, 4 H (H1′); 4.85 m, 2 H (H3′); 4.98 m, 2 H (H3′); 5.50–5.61 m, 2 H (H2′); 5.84 s, 2 H (CH bridging); 6.22 d, 2 H, *J* = 1.8 (H5); 6.30 d, 2 H, *J* = 1.8 (H7); 7.09–7.27 m, 6 H (ArH); 7.45 m, 4 H (ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 39.44, CH bridging; 45.89, C1′; 116.19, C3′; 133.12, C2′; 54.63 and 55.67, OMe; 85.99, C5; 91.25, C7; 125.96, 127.70, 129.58, ArCH; 112.61, 127.45, 135.34, 138.58, 144.48, ArC; 154.09 and 156.77, C-OMe. MS (EI), *m/z* (%): 610 (25) [$M^{\bullet+}$], 533 (30), 305 (35), 91 (85), 77 (70), 41 (100). For $C_{40}H_{38}N_2O_4$ calculated: 78.7% C, 6.3% H, 4.6% N; found: 78.7% C, 6.4% H, 4.5% N.

Crystallographic Study on Compound **24**

Crystal data. $C_{36}H_{30}N_2 \cdot (CH_2Cl_2)_{0.5}$, M = 533.1, triclinic, space group $P\bar{1}$, a = 10.830(5) Å, b = 11.408(4) Å, c = 12.847(5) Å, α = 66.88(3)°, β = 80.77(3)°, γ = 76.53(3)°, V = 1415(1) Å^3, D_C = 1.25 g cm^{-3}, Z = 2, μ_{Cu} = 13.92 cm^{-1}. Crystal size 0.21 × 0.24 × 0.24 mm, $2\theta_{max}$ = 140°, minimum and maximum transmission factors 0.72 and 0.79. The number of reflections was 4272 considered observed out of 5371 unique data. Final residuals R, R_w were 0.052, 0.070 for the observed data.

Structure determination. Reflection data were measured with an Enraf–Nonius CAD-4 diffractometer in θ/2θ scan mode using graphite monochromatized copper radiation (λ = 1.54184 Å). Data were corrected for absorption using the analytical method of De Meulenaer and Tompa[15]. Reflections with $I > 3\sigma(I)$ were considered observed. The structure was determined by direct phasing and Fourier methods. The solvent molecule with occupancy 0.5 was disordered about a centre of symmetry, and was refined as a rigid body with idealised geometry. Hydrogen atoms were included in calculated positions and were assigned thermal parameters equal to those of the atom to which they were bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full-matrix least-squares. Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography[16]. Structure solutions were by SIR92 [17] and refinement used RAELS [18]. ORTEP-II [19] running on Power MacIntosh was used for the structural diagrams, and a DEC Alpha-AXP Workstation was used for calculations.

CCDC 721778 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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