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Synthesis of Some Indolylpyrroles and Indolylpyrrolylketones

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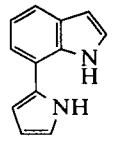
Abstract: The 2-(7-indolyl)pyrrole **12** has been synthesised from 4,6-dimethoxy-2,3-diphenylindole **4** *via* the 1,4-diketone **11**, generated from the 4-nitroketone **7**. Reaction of tosylmethylisocyanide with some α,β-unsaturated ketones also yielded the indolylpyrrole **15** and the indolylpyrrolylketones **13** and **17**. © 1997 Elsevier Science Ltd.

The 2-(7-indolyl)pyrrole ring system **1** is of interest because it presents the two pyrrole rings in the same relationship as exists in the porphyrins (and especially the benzoporphyrins). However, the structural fragment itself does not appear to have any known parallels in nature, nor have any examples of similar compounds been produced in the laboratory. We have therefore investigated possible synthetic routes to such compounds and in the course of this work have also generated some other types of indolylpyrroles. The synthetic approaches are based on the known reactivity of 4,6-dimethoxyindoles at C7 [1]. Several examples of indolylpyrroles have been reported in the literature. Treatment of 3-bromoindole with pyrrole or *N*-methylpyrrole in trifluoroacetic acid produced the corresponding 2-(2-indolyl)pyrroles **2** in excellent yield [2,3]. Various locked 2-(2-indolyl)pyrroles, such as compound **3,** have been formed through thermal rearrangement of isoxazolines, which in turn were prepared by 1,3-dipolar cycloaddition of dimethyl acetylenedicarboxylate to a β-carboline N-oxide [4-6].



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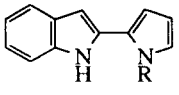
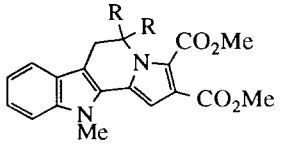


2 R = H,Me



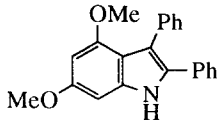
3 R = H,Me

The formation of a 2-(7-indolyl)pyrrole appeared to be possible by three fundamental approaches. These were (i) the direct introduction of a pyrrole ring at the indole C7 through palladium based coupling reactions, (ii) the suitable functionalisation of the indole C7 to allow subsequent construction of a pyrrole ring, and (iii) the Vilsmeier reaction of a pyrrolidinone derivative to give an intermediate pyrroline derivative, which could subsequently be converted into a pyrrole. The first approach has been used to produce 2-(2-pyrrolyl)pyrroles [7-9] and 2-(2-indolyl)indoles [10] and in general would seem to favour 2,2-coupling over 2,7-

coupling. Whilst this approach would be expected to succeed with indole **4**, it would not be generally applicable to indoles also unsubstituted at C2. The second approach is the subject of this paper and the third route will be dealt with in a following paper.

The Paal-Knorr route to pyrroles

This route requires the formation of indolyl-1,4-diketones, which can be generated potentially in various ways. Direct acylation using a 4-oxo-acid chloride such as levulinyl chloride or succinyl chloride and a range of Lewis acid catalysts was found to be unsuccessful, despite the fact that oxalyl chloride has been shown to react easily.[11] However, 4,6-dimethoxy-2,3-diphenylindole **4** readily undergoes Friedel-Crafts acylation with cinnamoyl chloride and stannic chloride to give the indolylpropenone **5**.[12] 2-Nitropropane has already been shown to undergo Michael addition to the chalcone **5**, [12] so nitromethane and nitroethane were used to generate the 4-nitroketones **6** and **7** respectively in 60% and 95% yield. Compound **7** contains two chiral centres and was shown by ^{1}H and ^{13}C NMR to be a mixture of diastereomers.



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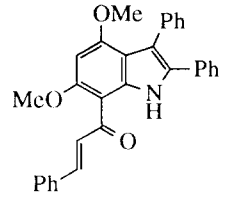

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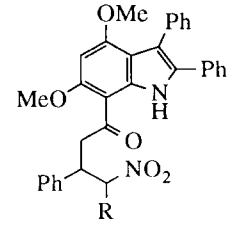
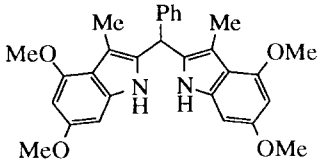


6 R = H

7 R = Me

As it was desired to prepare more complex combinations of indolylpyrroles, the acylation of the 2,2'-diindolylphenylmethane **8** with cinnamoyl chloride and stannic chloride was also investigated. Unfortunately considerable decomposition could not be avoided, and the desired bis-chalcone **9** could only be obtained in 26% yield, together with a trace of the simpler bis-chalcone **10**. The acid catalysed decomposition of the diindolylmethane **8** to 4,6-dimethoxy-3-methylindole has been observed in other reactions.[13] The chalcones **9** and **10** were not obtained in sufficient yield to warrant further elaboration.



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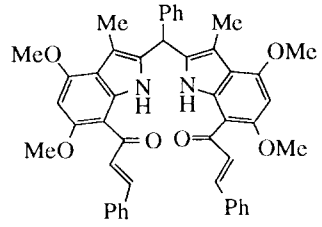

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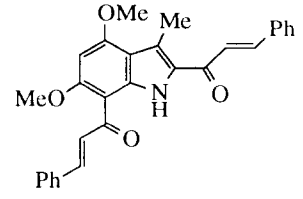

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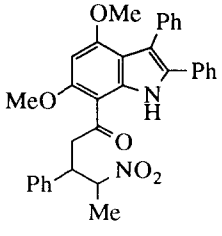
The oxidation of primary and secondary nitro groups to aldehydes and ketones was first accomplished by the treatment of its alkali metal salt with mineral acid,[14] and has since been effected by a range of other reagents. Both nitroketones were recovered unchanged after treatment with titanous ions in aqueous

tetrahydrofuran,[15] possibly because of poor solubility. Ozonolysis[16] could not be used because of oxidative decomposition of the indole ring, and use of the milder oxidising agent iodoxybenzene[17] was ineffective. However, treatment of the potassium nitronate salt of **7** with 27% hydrogen peroxide, according to the method of Olah,[18] gave the diketone **11** unreliably in yields up to 60% . Because of this lack of reliability, the preferred method[19] was the treatment of indole **7** in ethanolic sodium hydroxide with dilute hydrochloric acid: even so, the diketone **11** could only be obtained in the modest yield of 53%. Treatment of the diketone **11** with ammonium acetate gave the desired indolylpyrrole **12** in 70% yield. The ^{1}H NMR spectrum of **12** shows the single pyrrole ring proton as a broad singlet at 6.67 ppm, resulting from meta-coupling with the pyrrole NH, which was confirmed to be the more downfield of the two NH protons by a COSY experiment.



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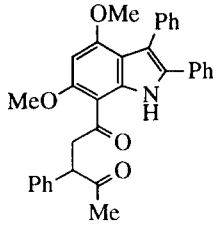

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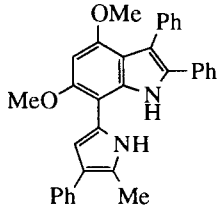

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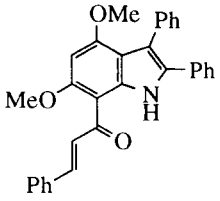
Other approaches from the nitroketone, including treatment with a combination of diphenylsulfide and tributylphosphine,[20] were unsuccessful. The Paal-Knorr route was not developed further, because it was overtaken by a superior outcome from the Vilsmeier approach.

The TosMIC route to pyrroles

α,β-Unsaturated ketones can be converted into pyrroles by treatment with tosylmethylisocyanide (tosmic),[21] and use of the propenone **5** and similar compounds could lead to the formation of related systems combining indole and pyrrole rings. These could prove useful in a comparative sense. Treatment of chalcone **5** with tosylmethylisocyanide gave the indolylpyrrolylketone **13** in moderate yield. The ^{1}H NMR spectrum in dimethylsulfoxide showed the two NH protons at 8.56 and 10.25 ppm, with the more upfield peak being assigned to the pyrrole NH on the basis of greater signal breadth, as well as the possibility of intramolecular hydrogen bonding of the indole NH to the adjacent carbonyl oxygen atom.



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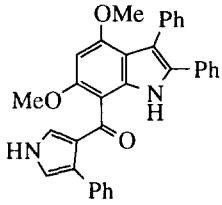

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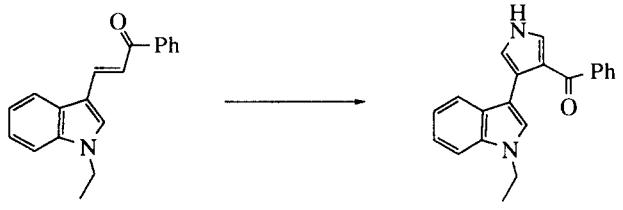
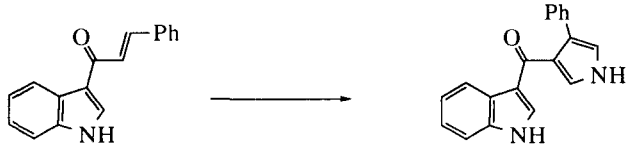
The directly linked indolylpyrrole **15** and the indolylpyrrolylketone **17** were similarly formed from the propenones **14** and **16** respectively. The spectroscopic characteristics of the ketone **17** reflected those

observed for compounds **13** and **15**, with the exception of a relatively large downfield shift in the resonance values of both NH protons (11.52 and 12.59 ppm).



14 **15**



16 **17**

EXPERIMENTAL

General Information

^{1}H n.m.r. spectra were recorded at 300 MHz with a Bruker CXP-300 or at 500 MHz with a Bruker AM-500 spectrometer, and refer to deuterochloroform solutions with chloroform (7.26 ppm) as an internal standard. Signals due to exchangeable protons (NH) were identified by exchange with deuterium oxide. The usual notational conventions are used. ^{13}C n.m.r. spectra were recorded at 125.77 MHz with a Brucker AM-500 spectrometer, and refer to deuterochloroform solutions with chloroform (77.0 ppm) as an internal standards. Low resolution mass spectra were obtained on an A.E.I. MS12 spectrometer at 70eV and 8000V accelerating potential at 210 °C ion source temperature. Infrared spectra were recorded with a Perkin Elmer 580B and refer to paraffin mulls or KBr disks of solids. Ultraviolet spectra were measured using a Hitachi UV-3200 spectrophotometer. Microanalyses were performed by Dr. H.P. Pham of the UNSW Microanalytical Unit.

1-(4',6'-Dimethoxy-2',3'-diphenylindol-7'-yl)-4-nitro-3-phenylbutan-1-one (6)

Nitromethane (0.13 g, 2.2 mmol) was added dropwise under nitrogen to a solution of dry methanol (15 mL) containing fresh sodium methoxide (0.12 mL, 2.2 mmol). After a further 5 min stirring, a solution of indole chalcone[12] **5** (0.5 g, 1.1 mmol) in methanol (25 mL) was added and the resulting solution was refluxed until the yellow colour had diminished substantially. The solution was then concentrated and acidified to pH 6. The pale yellow precipitate was filtered off and washed thoroughly with a 50/50 ethanol / water solution and

dried to give the nitroketone **6** (0.34 g, 60%) m.p. 196°C. (Found: C, 74.4; H, 5.6 ; N, 5.3. $C_{32}H_{28}N_2O_5$ requires C, 73.9; H, 5.4; N, 5.4%). ν_{max} 3380, 2940, 2850, 1621, 1594, 1551, 1466, 1380, 1326, 1289, 1265, 1239, 1226, 1167, 1140, 1084, 1033, 996, 796, 768, 705, 640 cm^{-1}. ^1H NMR δ ($CDCl_3$) 3.53, dd, H2; 3.85 and 4.06, 2s, OMe; 4.25, m, H3; 4.70 and 4.90, dd, H4; 6.20, s, H5'; 7.19-7.46, m, ArH; 11.17, bs, NH. ^{13}C NMR δ ($CDCl_3$) 40.0, C3'; 47.3, C2; 55.3 and 56.2, OMe; 80.2, C4; 87.1, CH; 103.92, 113.11, 114.27, 132.38, 133.18, 135.6, 138.8, 140.16, 160.11 and 160.89, ArC; 126.14, 127.12, 127.47, 127.55, 127.92, 128.44, 128.94 and 131.33, ArCH; 196.82, CO. Mass spectrum *m/z*: 521(M+1, 4%), 520(M, 12), 382(10), 356(10), 57(100).

1-(4',6'-Dimethoxy-2',3'-diphenylindol-7'-yl)-4-nitro-3-phenylpentan-1-one (7)

Nitroethane (0.38 g, 5 mmol) was added dropwise under nitrogen to a solution of absolute ethanol (15 mL) containing sodium ethoxide (0.5 mL, 6.4 mmol). After a further 5 min stirring, a solution of indole chalcone **5** (1.0 g, 2.2 mmol) in ethanol (25 mL) was added and the resulting solution was refluxed until the yellow colour had diminished substantially. The solution was then concentrated and acidified to pH 6. The pale yellow precipitate was filtered off and washed thoroughly with a (1:1) ethanol / water solution and dried to give the nitroketone **7** (1.12 g, 95%) m.p. 174.5-176 °C (Found: C, 72.9; H, 5.5; N, 5.1. $C_{33}H_{30}N_2O_5.1/2\ H_2O$ requires C, 72.9; H, 5.5; N, 5.2%). ν_{max} 3415, 2932, 1632, 1621, 1594, 1551, 1466, 1380, 1326, 1289, 1265, 1239, 1226, 1167, 1140, 1084, 1033, 996, 796, 768, 705, 640 cm^{-1}. ^1H NMR δ ($CDCl_3$) 1.48 and 1.49, 2d, Me; 3.45-3.68, m, H2; 4.04 and 4.06, 2s, OMe; 4.10, m, H3; 4.90-5.03, m, H4; 6.21, s, H5' ; 7.19-7.36, m, ArH; 10.97, bs, NH; ^{13}C NMR δ ($CDCl_3$) 16.82 and 17.30, Me; 45.03, C3; 45.34 and 46.92, C2; 45.85, C4; 55.26 and 56.27, OMe; 87.22, 87.48, 126.15, 126.17, 127.18, 127.22, 127.46, 127.98, 128.32, 128.46, 128.58, 128.74 and 131.34, ArCH; 103.93, 104.03, 113.0, 114.18, 132.32, 132.92, 135.66, 138.11, 138.21, 139.09, 139.34, 159.94, 159.93, 160.53 and 160.73, ArC; 196.71 and 198.04, CO. Mass spectrum *m/z* 536(M+2, 3%), 535(M+1, 16), 534(M, 41), 488(37), 487(100), 382(29), 357(29), 356(92).

2,2'-Di-(4,6-dimethoxy-3-methyl-7-(3-phenylprop-2-enoyl)indolyl)-phenylmethane (9) and 4,6-dimethoxy-3-methyl-2,7-di(3'-phenylprop-2'-enoyl)indole (10)

Cinnamoyl chloride (1.07 g, 6.45 mmol) was added to an ice cooled suspension of the diindolyl phenylmethane **8** (0.50 g, 1.1 mmol) in anhydrous benzene. Stannic chloride (1.0 mL, 8.85 mmol) diluted in benzene (10 mL) was then added dropwise to the solution. The dark brown solution which formed was maintained at 5°C with stirring overnight before being destroyed by the addition of cold water. The solution was then extracted with dichloromethane, dried and evaporated to yield a brown residue. Flash chromatography (dichloromethane / petroleum ether) gave two products (i) the desired product **9** as a yellow solid (210 mg, 26%) m.p. 273-275°C (Found: C, 76.2; H, 5.7; N, 3.7. $C_{47}H_{42}N_2O_6.1/2H_2O$ requires C, 76.3; H, 5.7; N, 3.8%) . λ_{max} 227nm(ε 16822), 294(12125). ν_{max} 3385, 2911, 1641, 1600, 1576, 1465, 1380, 1331, 1286, 1221, 1195, 1176, 994, 975, 798, 773, 756, 727, 704, 690, 568 cm^{-1}. ^1H NMR δ ($CDCl_3$) 2.28, s, Me; 3.98 and 4.04, 2s, OMe; 5.82, s, CH; 6.20, s, H5', 7.23-7.37, m, ArH; 7.59, d, J15.7Hz, C<u>H</u>=CHCO; 7.95, d, J15.7Hz, CH=C<u>H</u>CO; 10.49, bs, NH. Mass spectrum: *m/z*: 731(M+1, 5%), 730(M, 15), 640(8), 367(25), 312(10), 336(12), 31(100). (ii) compound **10** was isolated as an orange/yellow solid (93 mg, 9%) m.p. 200-202°C (Found: C, 76.6; H 5.4; N 2.8. $C_{29}H_{25}NO_4$. requires C 77.1; H 5.6; N 3.1%). λ_{max} 222nm(ε 22760), 310(21240), 376(26540). ν_{max} 3421, 2909, 1607, 1584, 1512, 1467, 1414, 1381, 1329, 1311, 1284, 1221, 1201, 1187, 1139, 1057, 991, 979, 863, 797, 772, 758, 725, 692, 567, 494cm^{-1}. ^1H NMR δ ($CDCl_3$) 2.86, s,

Me; 4.04 and 4.07, 2s, OMe; 6.18, s, H5'; 7.25-7.67, m, ArH; 7.81, d, J15.6Hz, CH=CHCO; 7.93, d, J15.7Hz, CH=CHCO; 11.35, bs, NH. Mass spectrum: *m/z* 453(M+2, 6%), 452(M+1, 37), 451(M, 100), 374(24).

1-(4',6'-Dimethoxy-2',3'-diphenylindol-7'-yl)-3-phenylpentan-1,4-dione (11)

Nitroketone **7** (1.3 g, 2.5 mmol) was dissolved in a saturated solution of ethanolic sodium hydroxide (120 mL). The solution was then added dropwise over a 2h period to a stirred solution of 3M hydrochloric acid (120 mL). The brown precipitate which formed was extracted with dichloromethane and evaporated to dryness. The residue was then flash chromatographed and the fraction eluted with dichloromethane to yield the indole diketone **11** as a yellow solid (0.67 g, 53%) m.p. 186-188°C. (Found: C, 78.7; H, 5.6; N, 2.7. $C_{33}H_{29}NO_4$ requires C 78.7; H, 5.8; N, 2.7%). ν_{max} 3422, 2910, 1723, 1618, 1590, 1553, 1465, 1381, 1226, 1209, 1160, 1135, 994, 804, 769, 725, 699 cm^{-1}. ^1H NMR δ ($CDCl_3$) 2.27, s, Me; 3.33, dd, J3.47Hz, 18.67Hz, 1H, H2; 3.78 and 3.97, 2s, OMe; 4.12, dd, J10.52Hz, 18.66Hz, 1H, H2; 4.46, dd, J3.43Hz, 10.52Hz, H3; 6.17, s, H5'; 7.21-7.36, m, ArH; 11.10, bs, NH. ^{13}C NMR δ ($CDCl_3$) 29.44, Me; 48.27, C2; 54.28, C3; 55.30 and 56.17, OMe; 87.27, 126.07, 127.06, 127.28, 127.41, 128.00, 128.40, 128.55, 128.98 and 131.43, ArCH; 103.95, 114.17, 132.58, 132.96, 135.78, 138.20, 138.76, 159.84 and 161.02 ArC; 198.12 and 208.15, CO. Mass spectrum: *m/z*: 504(M+1, 12%), 503(M, 35), 460(12), 356(39), 254(20).

2-(4',6'-Dimethoxy-2',3'-diphenylindol-7'-yl)-5-methyl-4-phenylpyrrole (12)

Ammonium acetate (2.0g, 26 mmol) was added to the indole diketone **11** (0.5 g, 1.0 mmol) dissolved in absolute ethanol (30 mL). The resulting mixture was then refluxed for 2h before being allowed to cool to room temperature. The solvent was removed, the residue dissolved in dichloromethane and washed with water (60 mL). Flash chromatography (dichloromethane/petroleum ether) gave the desired 2-(7-indolyl)pyrrole **12** as a cream solid (0.46g, 70%). m.p. 212-214°C. (Found: C, 81.3; H, 5.6; N, 5.7. $C_{33}H_{28}N_2O_2$ requires C 81.8; H, 5.8; N, 5.8%). ν_{max} 3443, 3423, 3405, 2910, 1604, 1504, 1467, 1380, 1258, 1137, 1092, 813, 790, 764, 746, 725, 699 cm^{-1}. λ_{max} 242nm(ε 34960), 317(21060). ^1H NMR δ ($CDCl_3$) 2.53, s, Me; 3.75 and 3.98, 2s, OMe; 6.39, s, H5'; 6.67, s, H3; 7.12-7.52, m, ArH; 8.73, bs, NH (indole); 9.17, bs, NH (pyrrole). ^{13}C NMR δ ($CDCl_3$) 12.9, Me; 55.5 and 57.1, OMe; 89.9, 106.2, 125.2, 125.9, 127.1, 127.4, 127.6, 128.0, 128.5, 128.6 and 131.5, ArCH; 98.4, 113.9, 115.1, 121.6, 123.8, 124.2, 132.8, 132.9, 135.2, 135.9, 137.0, 152.5 and 153.6, ArC. Mass spectrum: *m/z* 486(M+2, 6%), 485(M+1, 37), 484(M, 100), 470(30), 469(86).

3-(4,'6'-Dimethoxy-2',3'-diphenylindole-7'-carbonyl)-4-phenylpyrrole (13)

A solution containing the indole chalcone **5** (0.46 g, 1.0 mmol) and *p*-tosylmethylisocyanide (0.131g, 1.0 mmol) was added dropwise to a suspension of sodium hydride (25 mg, 60% dispersion in oil) in diethyl ether. The reaction mixture was then refluxed for 12h before being allowed to cool. Removal of the solvent gave a yellow solid which was flash chromatographed and eluted with dichloromethane to give the indolyl pyrrolyl ketone **13** as a cream solid (0.28 g, 55%) m.p. 106-108°C (dec.). (Found: C, 76.9; H, 5.2; N, 5.3. $C_{33}H_{26}N_2O_3.H_2O$ requires C, 76.8; H, 5.4; N, 5.4%). ν_{max} 3420, 3271, 3059, 2967, 1605, 1592, 1552, 1522, 1492, 1466, 1455, 1439, 1389, 1328, 1294, 1223, 1159, 1030, 995, 762, 702 cm^{-1}. ^1H NMR δ (d^6 DMSO) 3.63 and 4.70, 2s, OMe; 6.01, s, H5'; 6.85, t, H5; 7.21-7.48, m, ArH; 8.55, bs, NH (pyrrole); 10.25, bs, NH (indole). ^{13}C NMR δ (d^6 DMSO) 59.25 and 60.10, OMe; 93.27, 123.00, 129.44, 129.84, 130.85, 131.23, 131.40, 131.65, 131.93, 132.52 and 135.17, ArCH; 111.97, 116.60, 117.50, 127.71, 128.77, 132.47, 136.18, 137.10, 139.60, 139.75, 140.00, 158.90 and 159.50, ArC; 192.35, CO. Mass spectrum: *m/z* 500(M+2, 8%), 498(M, 100), 482(90), 355(35).

3-Benzoyl-4-(N-ethylindol-3'-yl)pyrrole (15)

A solution containing the indolechalcone **14** (1.0 g, 3.6 mmol) and *p*-tosylmethylisocyanide (0.7 g, 3.6 mmol) in tetrahydrofuran was added dropwise to a stirred suspension of sodium hydride (0.095 g, 4.0 mmol) in dry tetrahydrofuran. The solution was then refluxed for 4h whereupon a white precipitate formed. Upon cooling, the solid was filtered, washed with dichloromethane/petroleum ether (0°C) and dried to yield the pyrrole **15** as a white solid (0.39 g, 35%) m.p. 182-184°C. (Found: C, 79.1; H, 5.8; N, 8.8. $C_{21}H_{18}N_2O.1/4\ H_2O$ requires C, 79.2; H, 5.9; N, 8.7%). ν_{max} 3384, 3264, 3055, 2979, 1629, 1578, 1512, 1474, 1453, 1386, 1358, 1338, 1219, 1167, 1097 cm^{-1} ^1H NMR δ (d^6 DMSO) 1.45, t, Me; 4.15, q, CH_2; 7.01-7.85, m, ArH; 8.85, bs, NH; ^{13}C NMR δ (d^6 DMSO) 19.41, Me; 44.50, CH_2; 113.49, 122.29, 122.46 122.75, 123.76, 124.80, 131.70, 132.02, 132.83, 135.17, 139.44, 144.57, ArCH; 112.56, 121.92, 125.03, 130.96, 131.13, 131.53, ArC 194.40, CO. Mass spectrum: *m/z* 315(M+1, 40%), 314(M, 100), 299(20), 105(35).

3-(Indol-3'-carbonyl)-4-phenylpyrrole (17)

A solution of the indolechalcone **16** (1.0 g, 4.0 mmol) and *p*-tosylmethylisocyanide (0.78 g, 4.0 mmol) in tetrahydrofuran was added dropwise to a stirred suspension of sodium hydride (0.095 g, 4.0 mmol) in dry tetrahydrofuran. The solution was then refluxed for 4h to give a white precipitate. Upon cooling, the solid was filtered and dried to yield the indolyl pyrrolyl ketone **17** as a white solid (0.58 g, 50%) m.p. 162-164°C. ν_{max} 3403, 3258, 1603, 1572, 1547, 1523, 1492, 1455, 1431, 1398, 1242, 847, 757cm^{-1}. ^1H NMR δ (d^6 DMSO) 7.00-7.50, m, ArH; 7.95, d, H2'; 8.25, d, H2; 11.45 and 11.75, 2bs, NH. ^{13}C NMR δ (d^6 DMSO) 118.75, 121.41, 121.75, 122.82, 124.61, 125.46, 128.04, 134.34, 134.60, 136.05, 136.69 ArCH; 123.21, 112.17, 117.66, 124.65, 126.55, 128.15, ArC; 185.99, CO. Mass spectrum: *m/z* 287(M+1, 20%), 286(M, 95), 269(100), 144(60).

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