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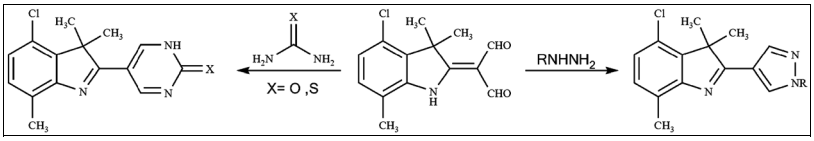

4-Chloro-2,3,3,7-tetramethyl-3*H*-indole (an indolenine) was produced by the reaction of 5-chloro-2-methylphenylhydrazine hydrochloride with 3-methylbutan-2-one via Fischer reaction. Exposure of the indolenine to the Vilsmeier reagent at 50°C produced a β-diformyl compound, 2-(4-chloro-1,3-dihydro-3,3,7-trimethyl-2*H*-indol-2-ylidene)propanedial. This dialdehyde was reacted with arylhydrazines, acetamidinium chloride, urea, thiourea, guanidinium chloride, and cyanoacetamide to give various 5-membered and 6-membered heterocyclic products, each carrying a 4-chloro-3,3,7-trimethyl-3*H*-indol-2-yl unit as a substituent, in excellent yields.

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INTRODUCTION

In 1925 Fischer, Müller, and Vilsmeier [1] published a paper describing the reaction between phosphoryl chloride and *N*-methylacetanilide, giving a number of products, including the quinolinium salt **1** and the salt **2** (Scheme 1).

The probable course of the reaction was given in a paper by Vilsmeier and Haack [2] who made the important discovery that the reagent obtained from *N*-methylformanilide and phosphoryl chloride, represented as the salt **3**, would react with *N*,*N*-dimethylaniline, giving 4-(*N*,*N*-dimethylamino) benzaldehyde **4** after a final hydrolytic step (Scheme 2). It was later shown that the actual electrophilic species is the *N*,*N*-dimethyl chloromethyleneiminium cation [3].

In 1959, Fritz [4] reported the *N*-formylation of a 3,3-disubstituted 3*H*-indole (indolenine) using the Vilsmeier reagent from DMF and $POCl_3$ giving an enamide, **6**. Further reaction of **6** with the Vilsmeier reagent and hydrolysis produced **8**. Formation of this product probably involves the intermediacy of **7**, from which the *N*-formyl group is hydrolytically removed during work-up. The *N*-methyl enamine **9** was directly C-formylated, producing **10** [4] (Scheme 3).

We have shown previously that the reaction of 2,3,3-trimethyl-3*H*-indoles with the Vilsmeier reagent, producing aminomethylene malondialdehydes, for example, **11**, is a general process, by demonstrating the transformation using variously substituted 2,3,3-trimethyl-3*H*-indoles [5–7]. Additionally, we have described a simple and straightforward preparation of 4-(2,3,3-trimethyl-3*H*-indol-2-yl)-substituted pyrazoles by condensation of these aminomethylene malondialdehydes with hydrazine and arylhydrazines [5,7] (Scheme 4). Recently, other workers used the original aminomethylene malondialdehyde **11** [5] in a similar way, in reactions with hydrazides giving 4-(2,3,3-trimethyl-3*H*-indol-2-yl)-substituted *N*-acyl- and *N*-thioacylpyrazoles [8].

We have now extended our studies of aminomethylene malondialdehydes and demonstrated the synthesis of various heterocycles by condensations with various reactants, producing both 5-membered and 6-membered heterocycles.

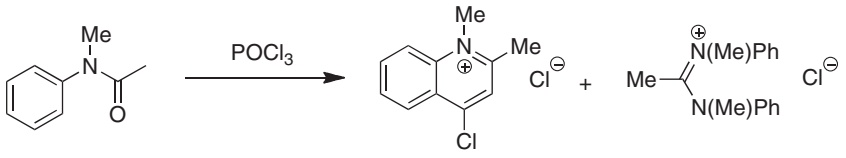
RESULTS AND DISCUSSION

Diazotisation of 5-chloro-2-methylbenzenamine, then reduction of the diazonium salt with tin(II) chloride, produced the corresponding hydrazinium chloride **13**. Reaction of 5-chloro-2-methylphenylhydrazine hydrochloride **13** with isopropyl methyl ketone in a Fischer reaction produced the 4-chloro-2,3,3,7-tetramethyl-3*H*-indole **14** in good yield. The structure of the indolenine was evident from its molecular formula, a six-hydrogen singlet signal for the geminal methyl groups at δ 1.44 and a singlet signal for the imine methyl group resonating at δ 2.52.

The indolenine **14** was reacted with the Vilsmeier reagent to produce a diformyl compound (2-(4-chloro-1,3-dihydro-3,3,7-trimethyl-2*H*-indol-2-ylidene)propanedial, **15**) in good yield (Scheme 5). The structure of this compound rests on the observation of two one-hydrogen singlets at δ 9.79 and 9.81 ppm corresponding to the two different aldehyde protons and a one-hydrogen signal for the *N*-hydrogen appearing at δ 13.77.

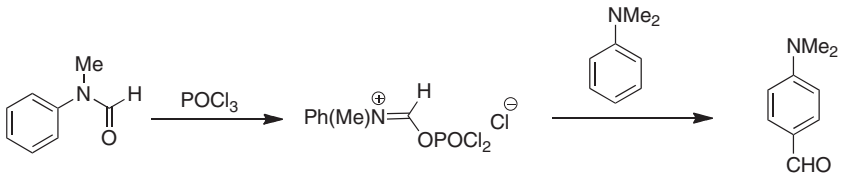
1,3-Dialdehydes represent interesting building blocks for the synthesis of various heterocyclic ring systems, which often show high biological activities [9,10]. As in our previous work [5,7], the reaction of monosubstituted hydrazines with aminomethylene malondialdehyde **15** resulted in the

Scheme 1



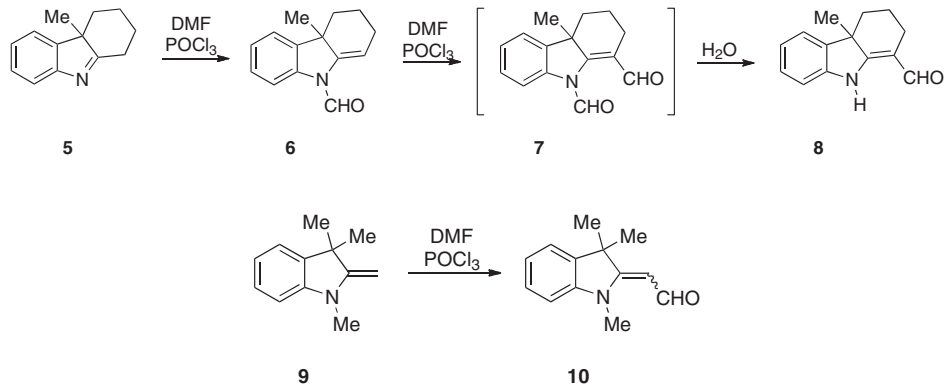
1 **2**

Scheme 2



3 **4**

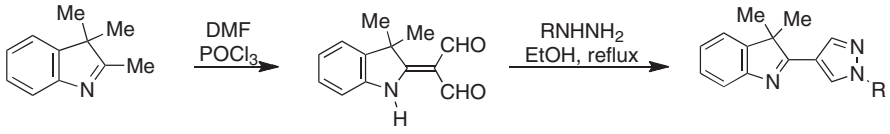
Scheme 3



5 **6** **7** **8**

9 **10**

Scheme 4



11 **12**

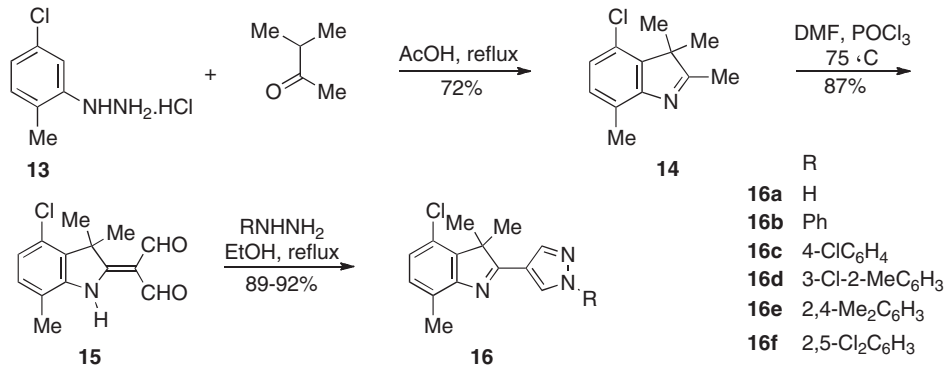
efficient formation of pyrazoles **13a–f**, with migration of the double bond to reform the imine unit (Scheme 5).

In extension of this work, we also examined the reactions of acetamidinium chloride, urea, thiourea, guanidinium chloride, and 2-cyanoacetamide with aminomethylene malondialdehyde **15**.

Reaction of 1,3-dialdehyde **15** with acetamidinium chloride [11] produced a new heterocyclic compound **17** (Scheme 6). The evidence for the formation of the pyrimidine ring and again the migration of the double bond back to give an imine, rests on a signal at δ 9.38 for the additional methyl group and a two-hydrogen singlet for the aromatic pyrimidine ring protons. There were three singlets, at δ 1.73 ppm, δ 2.62, and δ 2.87 ppm, for the geminal methyl groups, the benzene methyl and the pyrimidine methyl, respectively.

Condensations of 1,3-dialdehyde **15** with urea and thiourea gave the corresponding six-membered heterocyclic compounds **18a** and **18b** (Scheme 7). The structures of these new compounds rest on the presence of N–H stretching absorptions at 3140 cm^{-1} for **18a** and 3145 cm^{-1} for **18b** and singlets at δ 8.97 and δ 9.43 ppm for the pyridine ring protons of **18a** and **18b**.

Scheme 5



The reaction of 1,3-dialdehyde **15** with guanidinium chloride produced the product of further reaction of the expected aminopyrimidine, namely a product in which the first-formed aminopyrimidine had condensed with a further mol equivalent of the dialdehyde. We speculate that this product is one of the possible structural isomers in which the amino group has reacted with one or other of the aldehyde groups of **15** and hence have either the *Z* or *E* structures **19a/19b** shown in Scheme 8. Without further evidence, it is not possible at this stage to distinguish these.

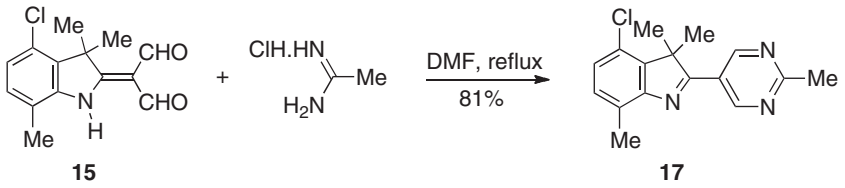
Finally, we studied the reaction of dialdehyde **15** with cyanoacetamide and obtained 5-(4-chloro-3,3,7-trimethyl-3*H*-indol-2-yl)-2-oxo-1,2-dihydropyridine-3-carbonitrile **20**. The pyridone was obtained pure in better than 80% yield with no evidence of any other product being formed (Scheme 9).

Compound **20** was fully identified by ^{1}H NMR spectroscopy and by other techniques. IR absorptions at 3167 and 1663 cm^{-1} were evidence for the presence of N–H and C═O bonds, respectively, further confirmed by an ^{1}H NMR one-hydrogen signal for the *N*-hydrogen appearing at δ 13.06. The cyano group was represented by an IR peak at 2231 cm^{-1}. The pyridone ring protons resonated as singlets at δ 8.44 and 8.81.

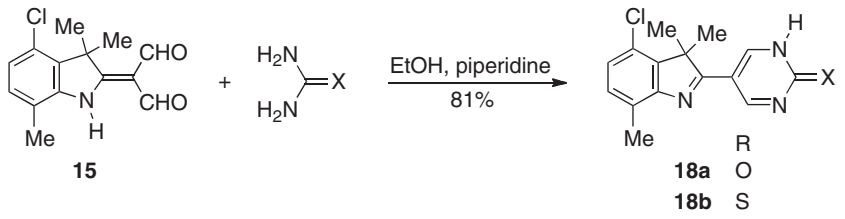
CONCLUSIONS

We have shown that 4-chloro-2,3,3,7-tetramethyl-3*H*-indole can be produced by the reaction of 5-chloro-2-methylphenylhydrazine hydrochloride with 3-methylbutan-2-one. Exposure of this compound to the Vilsmeier reagent produced 2-(4-chloro-1,3-dihydro-3,3,7-trimethyl-2*H*-indol-2-ylidene)propanedial. This dialdehyde was shown to react with arylhydrazines, acetamidinium chloride, urea, thiourea, guanidinium chloride, and cyanoacetamide to give various 5-membered and 6-membered heterocyclic products, each carrying a 4-chloro-3,3,7-trimethyl-3*H*-indol-2-yl unit as a substituent. We suggest that these intriguing and novel scaffolds could provide the basis for the development of libraries for biological evaluation.

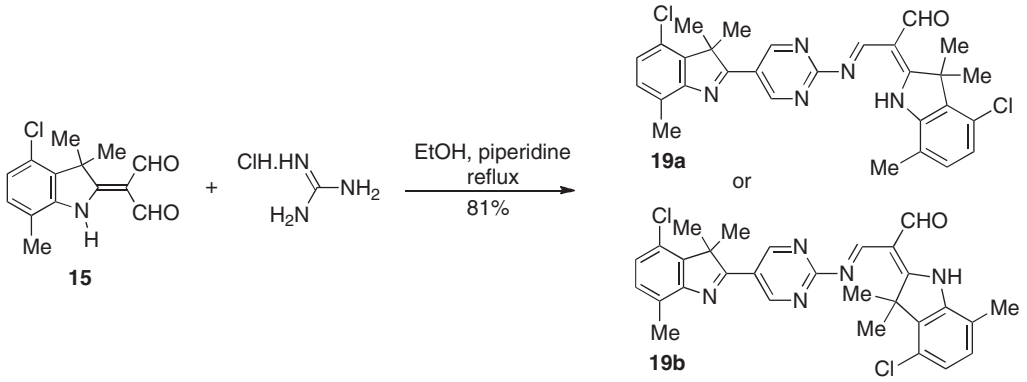
Scheme 6



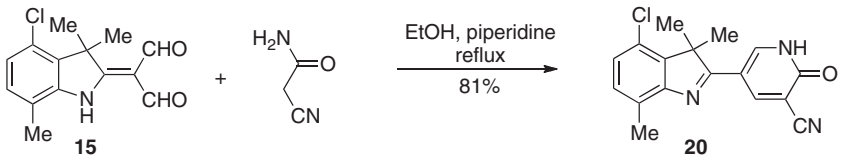
Scheme 7



Scheme 8



Scheme 9



EXPERIMENTAL

The chemicals used in this work were obtained from Fluka and Merck and were used without purification. Melting points were measured on an electrothermal IA9200 apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Avance AQS 300 MHz spectrometer (Brucker, Karlsruhe, Germany) at 300 and 75 MHz, respectively. Chemical shifts δ are in parts per million (ppm) measured in $CDCl_3$ and DMSO-d_6 as solvents and relative to TMS as the internal standard. IR spectra were obtained on a Nexus 670 FT-IR instrument (Thermonicolet, USA). High resolution mass spectra were recorded on an Agilent Technology (HP, Santa Clara, CA) MS Model: 5973 Network Mass, selective Detector Ion source: Electron Impact (EI) 70 eV, ion source temperature: 230°C Analyzer: quadrupole, and relative abundances of fragments are quoted in parentheses after the *m/z* values. Elemental analyses were performed with Heraeus (Germany) CHN-O rapid analyzer.

4-Chloro-2,3,3,7-tetramethyl-3*H*-indole (14). A mixture of arylhydrazine hydrochloride hydrazine **13** (5 g, 25 mmol) and isopropyl methyl ketone (3.25 mL, 30 mmol) was heated at reflux in acetic acid (30 mL) overnight and then cooled, diluted with H_2O (50 mL), and neutralized with solid Na_2CO_3, the aqueous solution was extracted with EtOAc (3 × 30 mL). The combined organic layers were dried over Na_2SO_4 and solvent was evaporated to give **14** (4.4 g, 85%) as a viscous oil; FT-IR (KBr) ν_{max}/cm^{-1}: 3036, 2967, 2928, 2869, 1580, 1474, 1458, 1377, 923; ^{1}H NMR ($CDCl_3$): δ 1.44 (s, 6H), 2.28 (s, 3H), 2.52 (s, 3H), 6.99 (d, *J* = 8.7 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 15.24, 16.52, 19.86, 55.90, 125.68, 126.59, 128.15, 130.25, 140.73, 153.67, 187.84; MS (EI) *m/z* 207 (M^+), 206, 192(100),178, 166; Found: M^+ 207.0814, $C_{12}H_{14}^{35}ClN$ requires M 207.0815.

2-(4-Chloro-1,3-dihydro-3,3,7-trimethyl 2*H*-indol-2-ylidene) propanedial (15). To DMF (10 mL) cooled in an ice bath was added dropwise $POCl_3$ (6 mL, 66 mmol) with stirring over a period of 2 h at below 25°C. After addition was completed, a solution of the trimethylindolenine **14** (2.6 g, 12.6 mmol) in DMF (10 mL) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 50°C for 2 h. The resulting solution was added to ice-cooled water, and the pH was adjusted to 8.0 by the addition of aq. NaOH (35%) and the mixture was extracted with EtOAc (3 × 30 mL). The organic layer was washed with hot water and dried over Na_2SO_4. The solvent was evaporated and the resulting product was purified by crystallization from boiling aq. ethanol, to give **15** (2.9 g, 87%); mp 150–151°C; FT-IR (KBr) ν_{max}/cm^{-1}: 3055, 2980, 2925, 2873, 2761, 1626, 1604, 1520, 1469, 1236, 1161, 774; ^{1}H NMR ($CDCl_3$): δ 1.92 (s, 6H), 2.40 (s, 3H), 7.06 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 9.79 (s, 1H), 9.81 (s, 1H), 13.77 (bs, 1H); ^{13}C NMR ($CDCl_3$): δ 15.91, 19.69, 53.39, 109.11, 120.86, 126.79, 127.40, 130.86, 135,33, 140.00, 179.29, 187.52, 192.81; MS (EI) *m/z* 263 (M^+), 236, 220(100), 192, 157; Found: M^+ 263.0717, $C_{14}H_{14}^{35}ClNO_2$ requires M 263.0713.

General procedure for synthesis of (16a–f). A mixture of 2-(4-chloro-1,3-dihydro-3,3,7-trimethyl-2*H*-indol-2-ylidene)propanedial **15** (1.1 mmol) and hydrazine hydrate (80% w/w) or aryl hydrazine hydrochloride (1.11 mmol) in absolute EtOH (5 mL) was heated with stirring at reflux. After complete conversion (TLC), the reaction mixture was cooled and concentrated; the resulting crystals were collected by filtration and recrystallized from EtOH to give the corresponding pyrazoles.

4-Chloro-3,3,7-trimethyl-2-(1H-pyrazol-4-yl)-3H-indole (16a). (Yield 90%); mp 259–260°C; FT-IR (KBr) ν_{max}/cm^{-1}; 3166, 2971, 2932, 1569, 1458, 951, 731; ^{1}H NMR ($CDCl_3$): δ 1.69 (s, 6H), 2.60 (s, 3H), 7.06 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 8.37 (s, 2H), 9.50–10.50 (bs, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 16.66, 21.38, 55.48, 115.27, 126.06, 126.26, 128.50, 130.59, 134.74, 140.84, 153.02, 178.57; MS (EI): *m/z* 259 (M^+), 115, 93 (100), 66; Found: M^+ 259.0875, $C_{14}H_{14}^{35}ClN_3$ requires M 259.0876.

4-Chloro-3,3,7-trimethyl-2-(1-phenyl-1H-pyrazol-4-yl)-3H-indole (16b). (Yield 92%); mp 141–142°C; FT-IR (KBr)

ν_{max}/cm^{-1}: 3055, 2971, 2932, 2873, 1557, 1500, 950, 753, 686; ^1H NMR ($CDCl_3$): δ 1.71 (s, 6H), 2.61 (s, 3H), 7.05 (d, $J = 8.1$ Hz, 1H), 7.11 (d, $J = 8.1$ Hz, 1H), 7.37 (t, $J = 8.1$ Hz, 1H), 7.52 (t, $J = 8.1$ Hz, 2H), 7.80 (d, $J = 8.1$ Hz, 2H), 8.33 (s, 1H), 8.61 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 16.58, 21.34, 55.51, 117.68, 119.54, 125.99, 126.21, 127.37, 127.50, 128.74, 129.61, 130.54, 139.50, 140.85, 141.04, 177.88; MS (EI): *m/z* 335 (M^+), 115, 77 (100), 51; Found: M^+ 335.1186, $C_{20}H_{18}^{35}ClN_3$ requires M 335.1189.

4-Chloro-2-(1-(4-chlorophenyl)-1H-pyrazol-4-yl)-3,3,7-trimethyl-3H-indole (16c). (Yield 89%); mp 181–183°C; FT-IR (KBr) ν_{max}/cm^{-1}: 3065, 2971, 2930, 1577, 1499, 1457, 1228, 951, 831; ^1H NMR ($CDCl_3$): δ 1.91 (s, 6H), 2.91 (s, 3H), 7.23 (d, $J = 8.1$ Hz, 1H), 7.27 (d, $J = 8.1$ Hz, 1H), 7.50 (d, $J = 8.7$ Hz, 2H), 7.91 (d, $J = 8.7$ Hz, 2H), 8.44 (s, 1H), 11.28 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 18.61, 22.46, 54.28, 111.07, 121.03, 126.88, 127.35, 129.21, 130.06, 132.62, 134.57, 136.08, 136.66, 137.14, 142.22, 179.43; MS (EI): *m/z* 369 (M^+), 191, 154, 128, 111, 75; Found: M^+ 369.0801, $C_{20}H_{17}^{35}Cl_2N_3$ requires M 369.0800.

4-Chloro-2-(1-(3-chloro-2-methylphenyl)-1H-pyrazol-4-yl)-3,3,7-trimethyl-3H-indole (16d). (Yield 90%); mp 185–187°C; FT-IR (KBr) ν_{max}/cm^{-1}: 3060, 2971, 2927, 1561, 1496, 1453, 955, 840; ^1H NMR ($CDCl_3$): δ 1.71 (s, 6H), 2.31 (s, 3H), 2.61 (s, 3H), 7.08 (d, $J = 8.1$ Hz, 1H), 7.10 (d, $J = 8.1$ Hz, 1H), 7.29–7.35 (m, 3H), 7.44 (s, 1H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 16.49, 17.80, 21.34, 55.51, 117.06, 126.09, 126.19, 126.49, 128.78, 129.02, 130.50, 131.07, 132.01, 132.12, 132.55, 139.94, 140.56, 141.00,177.77; Found: M^+ 383.0958, $C_{21}H_{19}^{35}Cl_2N_3$ requires M 383.0956.

4-Chloro-2-(1-(2,4-dimethylphenyl)-1H-pyrazol-4-yl)-3,3,7-trimethyl-3H-indole (16e). (Yield 91%); mp 188–190°C; FT-IR (KBr) ν_{max}/cm^{-1}: 3066, 2973, 2925, 1634, 1566, 1489, 1313, 1233, 733; ^1H NMR ($CDCl_3$): δ 1.69 (s, 9H), 2.30 (s, 3H), 2.58 (s, 3H), 7.05 (d, $J = 7.5$ Hz, 1H), 7.10 (d, $J = 7.5$ Hz, 1H), 7.30 (d, $J = 7.8$ Hz, 1H), 7.36 (d, $J = 7.8$ Hz,1H), 7.44 (s, 1H), 8.28 (s, 1H), 8.34 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 16.45, 17.80, 21.30, 55.56, 117.20, 125.89, 126.12, 126.18, 128.83, 129.00, 130.45, 131.02, 132.00, 132.15, 132.54, 139.98, 140.51, 141.15, 154.02, 177.76; Found: M^+ 363.1502, $C_{22}H_{22}^{35}ClN_3$ requires M 363.1502.

4-Chloro-2-(1-(2,5-dichlorophenyl)-1H-pyrazol-4-yl)-3,3,7-trimethyl-3H-indole (16f). (Yield 89%); mp 161–162°C; FT-IR (KBr) ν_{max}/cm^{-1}: 3065,2959, 2870, 2577, 2530, 1617, 1581, 1520, 1471, 1349, 1226, 1144; ^1H NMR ($CDCl_3$): δ 1.69 (s, 6H), 2.59 (s, 3H), 7.05 (d, $J = 8.1$ Hz, 1H), 7.01 (d, $J = 8.1$ Hz), 7.37 (d, $J = 8.7$ Hz, 1H), 7.51 (d, $J = 8.7$ Hz, 1H), 7.73 (s, 1H), 8.39 (s, 1H), 8.55 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 16.54, 21.30, 55.52, 117.28, 126.20, 127.66, 128.42, 128.94, 129.56, 130.55, 131.69, 133.64, 138.18, 141.05, 141.33, 177.42; MS (EI): *m/z* 403 (M^+) 271, 255, 220, 182, 162; Found: M^+ 403.0409, $C_{20}H_{16}^{35}Cl_3N_3$ requires M 403.0410.

4-Chloro-3,3,7-trimethyl-2-(2-methylpyrimidin-5-yl)-3*H*-indole (17). A mixture of 2-(4-chloro-1,3-dihydro-3,3,7-trimethyl-2*H*-indol-2-ylidene)propanedial **15** (0.2 g, 0.76 mmol) and acetamidine hydrochloride (0.078 g, 0.83 mmol) in DMF (10 mL) was heated at reflux for 3 days. After complete conversion (TLC), the reaction mixture was allowed to cool overnight. Filtration furnished compound **17** (0.18 g, 83%). Recrystallization from DMF gave pure product, mp 144–146°C; FT-IR (KBr) ν_{max}/cm^{-1}: 3055, 2979, 2926, 1582, 1552, 1450, 1374, 991, 802; ^1H NMR ($CDCl_3$): δ 1.73 (s, 6H), 2.62 (s, 3H), 2.87 (s, 3H), 7.13 (d, $J = 8.1$ Hz, 1H), 7.20 (d, $J = 8.1$ Hz, 1H),9.38 (s, 2H); ^{13}C NMR ($CDCl_3$): 16.35, 20.46, 25.92, 56.02, 124.03, 126.15, 127.38, 130.21, 130.64, 141.72, 156.16, 168.98, 177.94; MS (EI): *m/z* 285 (M^+), 270, 229, 192, 166, 115; Found: M^+ 285.1030, $C_{16}H_{16}^{35}ClN_3$ requires M 285.1033.

General procedure for synthesis of (18a,b, 19, 20). Urea, thiourea, or cyanoacetamide (0.626 mmol) was dissolved in hot EtOH (8 mL, 95%) then dialdehyde **15** (0.57 mmol) and piperidine (0.11 g, 0.12 mL, and 1.25 mmol) were added with stirring and the mixture was heated at reflux for 24 h. The mixture was cooled, filtered, and the precipitate washed with aqueous ethanol.

5-(4-Chloro-3,3,7-trimethyl-3H-indol-2-yl)pyrimidin-2(1H)-one (18a). (Yield 79%); mp 300°C (dec); FT-IR (KBr) ν_{max}/cm^{-1}: 3140, 3024, 2922, 2855, 1727, 1669, 1553, 1461, 1237; ^1H NMR (DMSO-d_6): δ 1.54 (s, 6H), 2.45 (s, 3H), 7.08 (d, $J = 8.1$ Hz, 1H), 7.15 (d, $J = 8.1$ Hz, 1H), 8.97 (s, 2H), 12.51 (bs, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 16.49, 20.58, 55.38, 101.28, 109.44, 125.52, 126.51, 129.06, 131.15, 141.73, 153.28, 155.95, 178.09; Found: M^+ 287.0824, $C_{15}H_{14}^{35}ClN_3O$ requires M 287.0825.

5-(4-Chloro-3,3,7-trimethyl-3H-indol-2-yl)pyrimidine-2(1H)-thione (18b). (Yield 81%); mp 286–287°C (dec); FT-IR (KBr) ν_{max}/cm^{-1}: 3145, 2977, 2924, 2632, 2548, 1627, 1460, 1240, 982, 788; ^1H NMR (DMSO-d_6): δ 1.58 (s, 6H), 2.48 (s, 3H), 7.13 (d, $J = 8.1$ Hz, 1H), 7.20 (d, $J = 8.1$ Hz, 1H), 9.43 (s, 2H), 13.14 (bs, 1H, NH); *Anal*. Calcd. for $C_{15}H_{14}^{35}ClN_3S$: C, 59.30; H, 4.64; N, 13.83% Found: C, 59.16; H, 4.59; N, 13.77%.

3-((5-(4-Chloro-3,3,7-trimethyl-3H-indol-2-yl)pyrimidin-2-yl)imino)-2-(4-chloro-1,3-dihydro-3,3,7-trimethyl-2H-indol-2-ylidene)propanal (19a and 19b). To a solution of guanidine hydrochloride (0.06 g, 0.63 mmol) in hot EtOH (8 mL, 95%), dialdehyde **11** (0.33 g, 1.25 mmol) and piperidine (0.05 g, 0.63 mmol) were added with stirring, then the mixture was heated at reflux for 24 h. The mixture was cooled and filtered and the precipitate was washed with ethanol (95%) to give **19a** or **19b** (0.51 g, 77%); mp 248–249°C; FT-IR (KBr) ν_{max}/cm^{-1}: 3160, 2975, 2929, 2869, 1678, 1618, 1569, 1461, 1294, 1183; ^1H NMR ($CDCl_3$): δ 1.75 (s, 6H), 1.82 (s, 6H), 2.61 (s, 3H), 2.64 (s, 3H), 7.08–7.16 (m, 4H), 8.94 (s, 1H, H-C═N, due to isomer **19a** or **19b**), 9.37 (s, 2H, pyrimidine ring protons), 9.63 (s, 1H, CHO), 14.40 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 16.36, 16.62, 18.30, 20.64, 55.81, 57.25, 111.88, 122.66, 126.13, 126.22, 126.78, 127.23, 127.84, 130.04, 130.66, 140.80, 141.68, 151.34, 153.49, 153.49, 157.54, 158.27, 177.46, 182.70, 188.67; Found: M^+ 531.1593, $C_{29}H_{27}^{35}Cl_2N_5O$ requires M 531.1593.

5-(4-Chloro-3,3,7-trimethyl-3H-indol-2-yl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (20). (Yield 81%); mp 300°C (dec.); FT-IR (KBr) ν_{max}/cm^{-1}: 3167, 3085, 2995, 2923, 2231, 1663, 1552, 1551, 1455, 1226; ^1H NMR (DMSO-d_6): δ 1.56 (s, 6H), 2.46 (s, 3H), 7.10 (d, $J = 7.8$, 1H), 7.18 (d, $J = 7.8$, 1H), 8.44 (s, 1H), 8.81 (s, 1H), 13.06 (bs, 1H); ^{13}C NMR (DMSO-d_6): δ 16.46, 20.56, 55.27, 104.90, 111.32, 116.16, 125.48, 126.71, 129.21, 131.15, 141.97, 142.69, 147.98, 152.94, 159.92, 178.03; Found: M^+ 311.0821, $C_{17}H_{14}^{35}ClN_3O$ requires M 311.0825.

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