

Synthesis of 2,2'-bis(1-(2-aryl)-1*H*-pyrazol-4-yl)-3,3,3',3'-tetramethyl-3*H*,3'*H*-5,5'-biindoles and 2,7-bis(1-(3-aryl)-1*H*-pyrazol-4-yl)-1,1,6,6-tetramethyl-1,6-dihydroindolo[7,6-*g*]indoles

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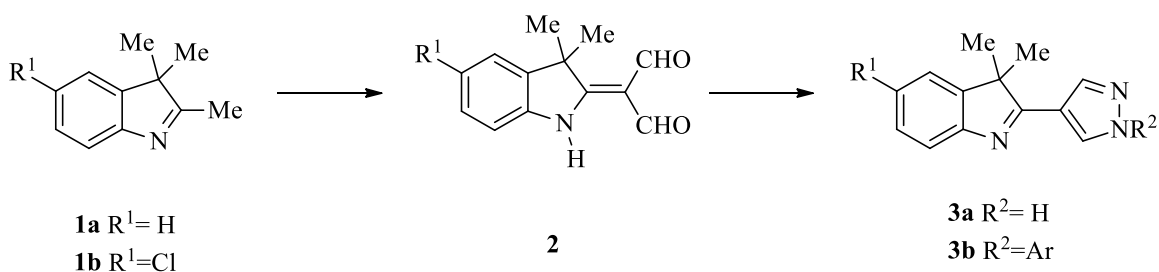
Abstract

2,2'-(Biphenyl-4,4'-diyl)bis(hydrazinium) chloride and 2,2'-(naphthalene-1,5-diyl)bis(hydrazinium) chloride were converted *via* Fischer syntheses with 3-methylbutan-2-one into bisindolenines, 2,2',3,3,3',3'-hexamethyl-3*H*,3'*H*-5,5'-biindole **10** and 2,3,3,7,8,8-hexamethyl-3*H*,8*H*-indolo[7,6-*g*]indole **14**, respectively. Exposure of the bisindolenines to the Vilsmeier reagent produced tetraformyl compounds **11** and **15**, which reacted with hydrazine and arylhydrazines to give the corresponding pyrazoles **12** and **16** in excellent yields.

Keywords: Arylhydrazines, bisindolenine, Fischer reaction, hydrazine, pyrazole, Vilsmeier reagent

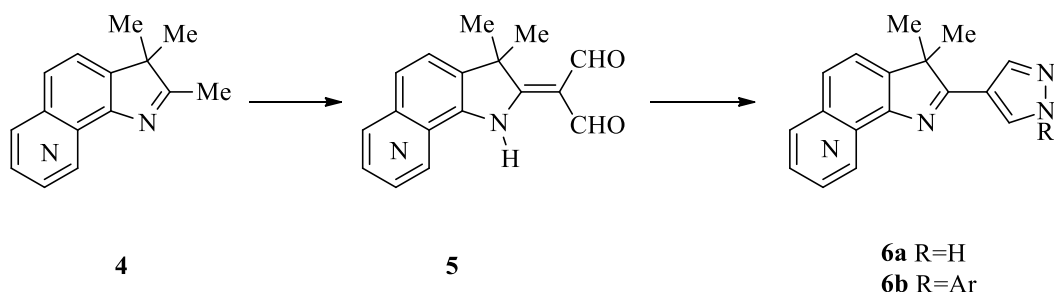
Introduction

We recently described the reaction of 2,3,3-trimethylindolenines (3*H*-indoles) **1** with the Vilsmeier reagent formed from dimethylformamide and phosphorus oxychloride to produce aminomethylene malondialdehydes **2** (Scheme 1).^{1,2} Additionally we showed that the pyridoindolenines 2,3,3-trimethyl-3*H*-pyrrolo[2,3-*f*]quinoline and 2,3,3-trimethyl-3*H*-pyrrolo[3,2-*h*]quinoline **4** behave similarly (Scheme 2).³



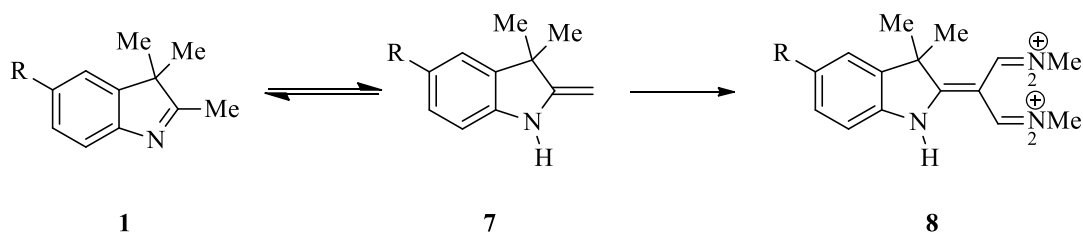
Scheme 1

The malondialdehydes **2,5** reacted with hydrazine or arylhydrazines to produce substituted pyrazoles **3,6**.^{1,3,4} We have now been able to show that the principles embodied in these transformations can be incorporated into bisindolenine systems, and thus have prepared several more complex pyrazoles.



Scheme 2

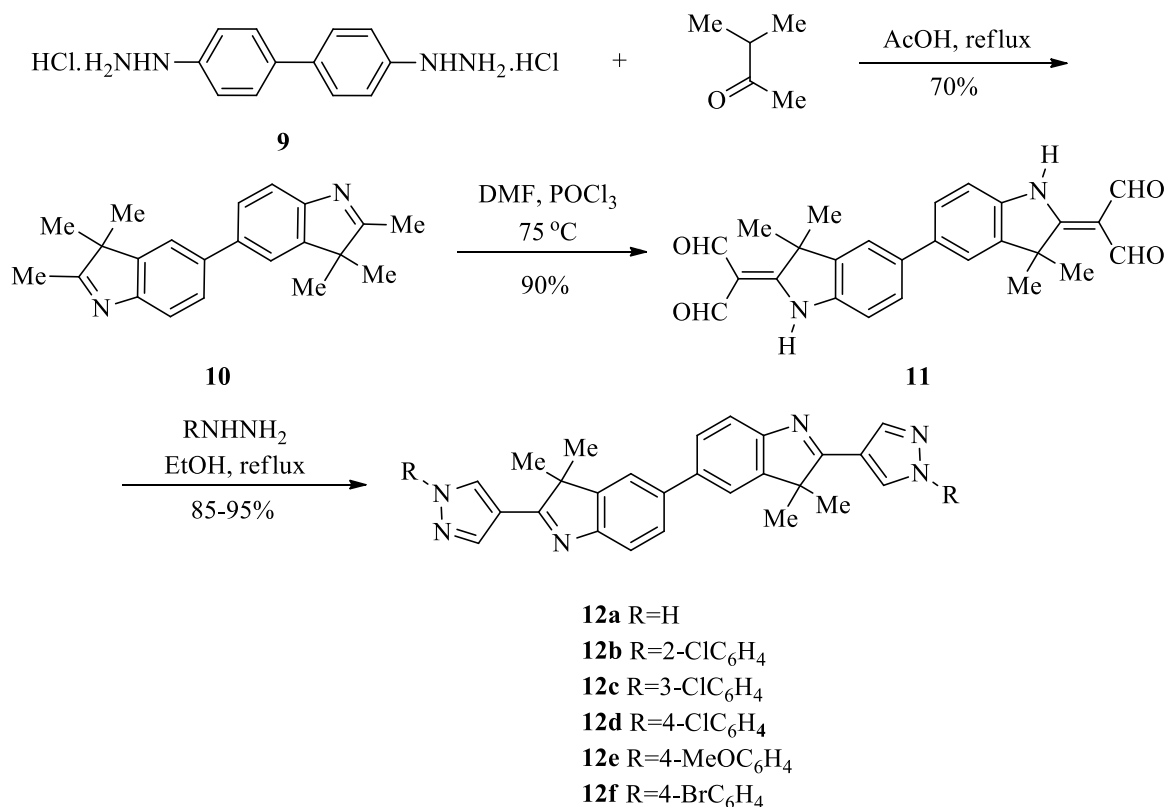
For the mechanism of formation of the aminomethylene malondialdehydes, we suggested that a small equilibrium concentration of an enamine tautomer **7** is successively C-substituted and thus, before hydrolysis during work-up, species **8** is present (Scheme 3). We propose that a comparable mechanism operates in the work described herein.



Scheme 3

Results and Discussion

Diazotisation of benzidine and naphthalene-1,5-diamine, then reduction of the diazonium salts with tin(II) chloride, produced the corresponding bis hydrazinium chlorides **9** and **13**.⁵ Reaction of 2,2'-(biphenyl-4,4'-diyl)bis(hydrazinium)chloride **9** with isopropyl methyl ketone in a Fischer reaction⁶ produced the bisindolenine 2,2',3,3',3',3'-hexamethyl-3*H*,3'*H*-5,5'-biindole **10** in good yield (Scheme 4).

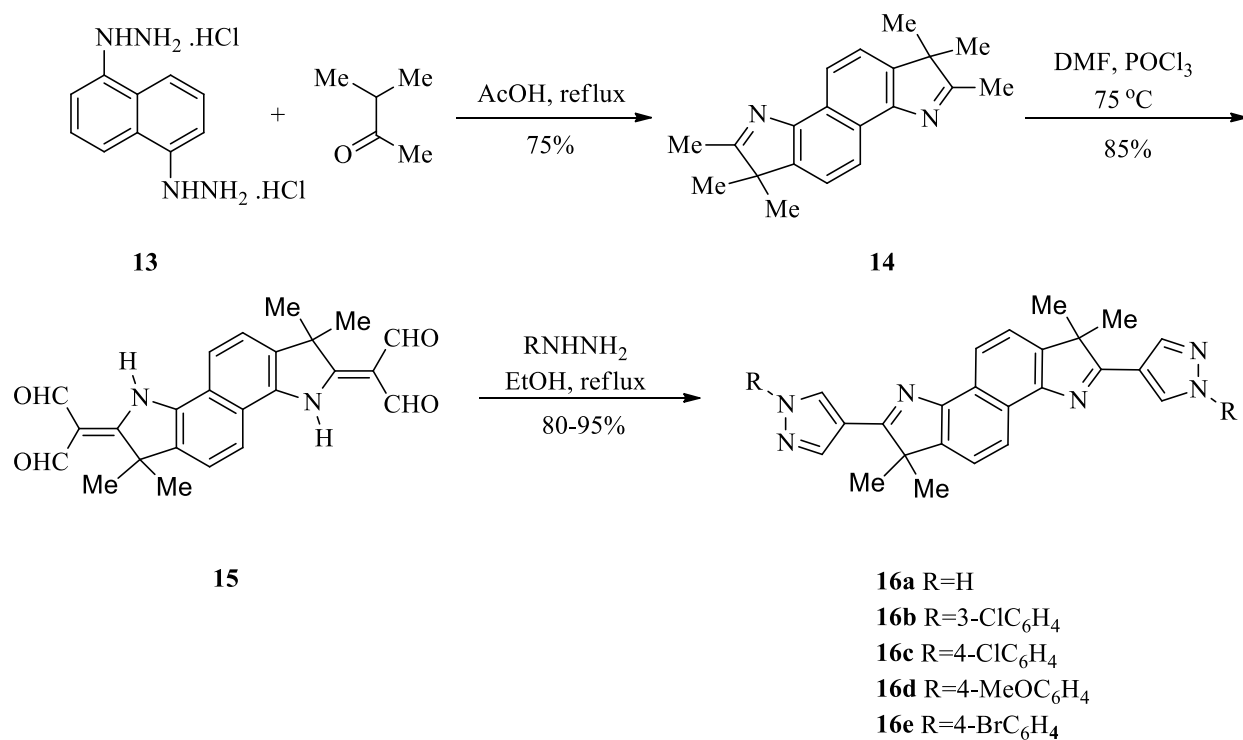


Scheme 4

Similarly, 2,2'-(naphthalene-1,5-diyl)bis(hydrazinium) chloride **13** reacted with isopropyl methyl ketone in hot acetic acid to give 2,3,3,7,8,8-hexamethyl-3*H*,8*H*-indolo[7,6-*g*]indole⁷ **14** (Scheme 5), which was used previously in the synthesis of photochromic compounds.⁸

The structure of the bisindolenine **10** was evident from its molecular formula, the twelve-hydrogen singlet for the geminal methyl groups, at δ 1.33 ppm, and a singlet signal for the imine methyl groups resonating at δ 2.30 ppm.

Each of the bisindolenines **10**, **14** was now reacted with the Vilsmeier reagent in yields of 90% and 85%, respectively, and tetraformyl compounds **11**, **15** were obtained (Schemes 4 and 5). The structures of the aminomethylene malondialdehydes rests on the observation of two two-hydrogen singlets at δ 9.79 and δ 9.83 for **11** and δ 9.83 and δ 9.87 for **15** corresponding to aldehyde protons. Absorptions at 3136 cm⁻¹ and 3130 cm⁻¹ for **11** and **15**, respectively, were evidence for the presence of N-H bonds, further confirmed by ¹H NMR two-hydrogen signals for the N-hydrogens appearing at δ 13.64 (**11**) and δ 14.35 (**15**), respectively. As in our previous work,^{1,3} the aminomethylene malondialdehydes reacted with hydrazine and various arylhydrazines to give pyrazoles, with migration of the double bond to reform the imine unit (Schemes 4 and 5). For pyrazoles **12a-f**, the newly formed five-membered heterocyclic ring protons resonated in the range δ 8.35-9.37 and for the pyrazoles **16a-e** in the range δ 8.50-9.38.



Scheme 5

Conclusions

We have been able to show that the principles embodied in transformations of simple indolenines *via* Vilsmeier formylations can be incorporated into more complex bisindolenine systems and thus have prepared several pyrazoles in excellent yields.

Experimental Section

General. Melting points were recorded on a Philip Harris C4954718 apparatus. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance AQS 300 MHz spectrometer, at 300 MHz and 75 MHz respectively. Chemical shifts δ are in parts per million (ppm) measured in CDCl₃ and DMSO-*d*₆ as solvents and relative to TMS as the internal standard. Infrared spectra were recorded on a Thermo Nicolet-Nexus 670 FT-IR instrument. High resolution mass spectra were recorded on an Agilent Technology (HP), 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.

2,2',3,3,3',3'-Hexamethyl-3H,3'H-5,5'-biindole (10). A mixture of 2,2'-(biphenyl-4,4'-diyl)bis(hydrazinium)chloride (8.29 g, 28.9 mmol) and isopropyl methyl ketone (6.52 mL, 60.60 mmol) was heated at reflux in acetic acid (50 mL) for 12 h and then cooled, diluted with water (50 mL), and neutralized with NaOH 2M, then extracted with ethyl acetate (4 × 100 mL). The organic layer was dried over Na₂SO₄. The solvent was evaporated and the resulting viscous oil crystallized from EtOH to give the 2,2',3,3,3',3'-hexamethyl-3H,3'H-5,5'-biindole **10**. (6.38 g, Yield 70%); mp 104-106 °C; FT-IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 2962, 2927, 1685, 1574, 1458, 1409; ¹H NMR (CDCl₃): δ 1.33 (s, 12H), 2.30 (s, 6H), 7.49 (s, 2H), 7.53 (d, $J = 8.1$ Hz, 2H), 7.59 (d, $J = 8.1$ Hz, 2H); ¹³C NMR (CDCl₃): δ 15.45, 23.18, 53.75, 119.95, 120.30, 126.81, 138.70, 146.32, 152.99, 188.21; MS (EI, 70 ev): m/z (%) 316 (M⁺, 100), 301 (32), 285 (10), 84 (82), 47 (20). Found: [M]⁺ 316.1939, C₂₂H₂₄N₂ requires [M]⁺ 316.1939.

2,2'-(3,3,3',3'-Tetramethyl-5,5'-biindoline-2,2'-diylidene)dimalonaldehyde (11). To *N,N*-dimethylformamide (2 mL) cooled in an ice bath was added dropwise phosphorus oxychloride (1.6 mL, 17.4 mmol) with stirring at below 5 °C. After this addition, a solution of **10** (2.9 mmol, 0.918 g) in DMF (2 mL) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 75 °C for 12 h. The resulting solution was added to ice-cooled water and made alkaline with NaOH (aq.) solution. The resulting precipitate was collected by filtration after 24 h, dried in air, recrystallized from ethanol, to give **11** (1.12 g, Yield 90%); mp 213-215 °C; FT-IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3136, 2967, 2926, 2765, 1677, 1601, 1520, 1473, 1202; ¹H NMR (CDCl₃): δ 1.82 (s, 12H), 7.50 (s, 2H), 7.55 (d, $J = 8.1$ Hz, 2H), 7.59 (d, $J = 8.1$ Hz, 2H), 9.79 (s, 2H), 9.83 (s, 2H), 13.64 (bs, 2H); ¹³C NMR (CDCl₃): δ 23.46, 51.49, 109.65, 112.96, 120.96, 127.40, 138.50, 138.95, 141.65, 179.37, 187.81, 192.59; MS (EI, 70 ev): m/z (%) 428 (M⁺, 15), 400 (13), 361 (52), 291 (24), 263 (38), 248 (36), 191 (30), 149 (38), 57 (100), 41 (51). Found: [M]⁺ 428.1737, C₂₆H₂₄N₂O₄ requires [M]⁺ 428.1736.

General procedure for synthesis of (12a-f)

A mixture of the tetraformyl compound **11** (0.117 mmol) and the hydrazine or aryl hydrazine (0.23 mmol) in absolute ethanol (5 mL) was heated with stirring at reflux for 6-8 h. After cooling and concentrating the solution, the resulting crystals were collected by filtration and recrystallized from EtOH to give the corresponding pyrazoles.

3,3,3',3'-Tetramethyl-2,2'-di(1H-pyrazol-4-yl)-3H,3'H-5,5'-biindole (12a). (0.044 g, Yield 90%); mp 218-220 °C; FT-IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3168, 2964, 1612, 1567, 1535, 1458; ¹H NMR (DMSO-*d*₆): δ 1.50 (s, 12H), 7.53 (d, $J = 7.8$ Hz, 2H), 7.62 (d, $J = 7.8$ Hz, 2H), 7.81 (s, 2H), 8.35 (s, 4H), 12.75 (bs, 2H); ¹³C NMR (DMSO-*d*₆): δ 24.71, 53.24, 115.28, 119.81, 120.41, 126.68, 127.70, 137.73, 147.78, 153.39, 179.45; MS (EI, 70 ev): m/z (%) 420 (M⁺, 63), 405 (24), 370 (17), 354 (13), 302 (100), 287 (47), 44 (18). Found: [M]⁺ 420.2062, C₂₆H₂₄N₆ requires [M]⁺ 420.2062.

2,2'-Bis[1-(2-chlorophenyl)-1H-pyrazol-4-yl]-3,3,3',3'-tetramethyl-3H,3'H-5,5'-biindole (12b). (0.067 g, Yield 89%); mp 155-157 °C; FT-IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 2967, 2927, 1612, 1576, 1527, 1492, 1459; ¹H NMR (DMSO-*d*₆): δ 1.59 (s, 12H), 7.56-7.76 (m, 12H), 7.91 (s, 2H), 8.51 (s,

2H), 9.04 (s, 2H); ^{13}C NMR (DMSO- d_6): δ 24.58, 53.44, 116.48, 119.84, 120.75, 126.99, 128.25, 128.77, 128.83, 128.87, 131.01, 133.82, 137.71, 138.26, 141.32, 147.60, 151.97, 178.78; MS (EI, 70 ev): m/z (%) 644 (1), 642 (6), 640 (M^+ , 10), 480 (28), 467 (29), 440 (26), 412 (100), 397 (32), 111 (10). Found: $[\text{M}]^+$ 640.1909, $\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{N}_6$ requires $[\text{M}]^+$ 640.1909.

2,2'-Bis[1-(3-chlorophenyl)-1H-pyrazol-4-yl]-3,3,3',3'-tetramethyl-3H,3'H-5,5'-biindole (12c). (0.064 g, Yield 85%); mp 153-155 °C; FT-IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2967, 2928, 1620, 1593, 1529, 1487, 1461, 1408; ^1H NMR (DMSO- d_6): δ 1.61 (s, 12H), 7.43 (d, $J = 7.8$ Hz, 2H), 7.57 (d, $J = 7.8$ Hz, 2H), 7.61 (t, $J = 7.8$ Hz, 2H), 7.70 (d, $J = 7.8$ Hz, 2H), 7.91 (s, 2H), 8.03 (d, $J = 7.8$ Hz, 2H), 8.2 (s, 2H), 8.48 (s, 2H), 9.33 (s, 2H); ^{13}C NMR (DMSO- d_6): δ 24.36, 53.46, 117.95, 118.31, 119.02, 120.23, 120.59, 126.88, 127.14, 128.76, 131.74, 134.56, 138.18, 140.75, 142, 148.05, 153.02, 178.52; MS (EI, 70 ev): m/z (%) 644 (1), 642 (6), 640 (M^+ , 10), 480 (35), 467 (30), 440 (25), 412 (100), 397 (30), 111 (18). Found: $[\text{M}]^+$ 640.1908, $\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{N}_6$ requires $[\text{M}]^+$ 640.1909.

2,2'-Bis[1-(4-chlorophenyl)-1H-pyrazol-4-yl]-3,3,3',3'-tetramethyl-3H,3'H-5,5'-biindole (12d). (0.071 g, Yield 95%); mp 222-225 °C; FT-IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2968, 2927, 1610, 1577, 1529, 1499, 1463; ^1H NMR (DMSO- d_6): δ 1.14 (s, 12H), 7.54-7.61 (m, 8H), 7.84 (s, 2H), 8.01 (d, $J = 8.7$ Hz, 4H), 8.40 (s, 2H), 9.21 (s, 2H), ^{13}C NMR (DMSO- d_6): δ 24.38, 53.44, 118.27, 120.21, 120.57, 121.05, 126.85, 128.57, 129.94, 131.57, 138.13, 138.47, 141.79, 148.04, 153.13, 178.56; MS (EI, 70 ev): m/z (%) 644 (1), 642 (6), 640 (M^+ , 10), 480 (28), 467 (43), 440 (27), 412 (100), 397 (44), 111 (13). Found: $[\text{M}]^+$ 640.1909, $\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{N}_6$ requires $[\text{M}]^+$ 640.1909.

2,2'-Bis[1-(4-methoxyphenyl)-1H-pyrazol-4-yl]-3,3,3',3'-tetramethyl-3H,3'H-5,5'-biindole (12e). (0.067 g, Yield 90%); mp 182-186 °C; FT-IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2963, 2928, 1610, 1560, 1514, 1459, 1250, 1172, 1034; ^1H NMR (DMSO- d_6): δ 1.64 (s, 12H), 3.82 (s, 6H), 7.11 (d, $J = 8.4$ Hz, 4H), 7.63 (d, $J = 7.8$ Hz, 2H), 7.73 (d, $J = 7.8$ Hz, 2H), 7.88 (s, 2H), 7.92 (d, $J = 8.4$ Hz, 4H), 8.39 (s, 2H), 9.12 (s, 2H); ^{13}C NMR (DMSO- d_6): δ 24.63, 53.41, 55.98, 115.11, 116.54, 119.39, 120.86, 121.21, 127.09, 129.17, 133.05, 138.31, 141.51, 147.35, 150.85, 158.84, 178.99; MS (EI, 70 ev): m/z (%) 632 (M^+ , 2), 476 (50), 463 (58), 436 (31), 408 (100), 393 (87), 204 (33), 77 (22), 57 (23), 43 (23). Found: $[\text{M}]^+$ 632.2898, $\text{C}_{40}\text{H}_{36}\text{N}_6\text{O}_2$ requires $[\text{M}]^+$ 632.2899.

2,2'-Bis[1-(4-bromophenyl)-1H-pyrazol-4-yl]-3,3,3',3'-tetramethyl-3H,3'H-5,5'-biindole (12f). (0.074 g, Yield 87%); mp 230-233 °C; FT-IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2969, 2927, 1611, 1577, 1529, 1495, 1463; ^1H NMR (DMSO- d_6): δ 1.63 (s, 12H), 7.64 (d, $J = 7.8$ Hz, 2H), 7.72 (d, $J = 7.8$ Hz, 2H), 7.76 (d, $J = 8.1$ Hz, 4H), 7.96 (s, 2H), 8.02 (d, $J = 8.1$ Hz, 4H), 8.57 (s, 2H), 9.37 (s, 2H); ^{13}C NMR (DMSO- d_6): δ 24.47, 53.46, 117.48, 119.73, 120.09, 120.81, 121.48, 127.06, 129.27, 132.90, 138.35, 138.74, 142.135, 147.60, 151.44, 178.71; MS (EI, 70 ev): m/z (%) 732 (2), 730 (4), 728 (M^+ , 2), 485 (54), 417 (54), 327 (23), 171 (100), 92 (43), 65 (57), 43 (35). Found: $[\text{M}]^+$ 728.0897, $[\text{M}+2]^+$ 730.0878, $\text{C}_{38}\text{H}_{30}\text{Br}_2\text{N}_6$ requires $[\text{M}]^+$ 728.0899, $[\text{M}+2]^+$ 730.0878.

2,2'-(1,1,6,6-Tetramethylindolo[7,6-g]indole-2,7(1H,3H,6H,8H)-diylidene)dimalonaldehyde (15). To *N,N*-dimethylformamide (3 mL) cooled in an ice bath was added dropwise phosphorus oxychloride (2.2 mL, 24 mmol) with stirring at below 5 °C. After this addition, a solution of **14** (1.16 g, 4 mmol) in DMF (2.5 mL) was added dropwise. The cooling bath was removed and the

reaction mixture was stirred at 75 °C for 12 h. The resulting solution was added to ice-cooled water and made alkaline with NaOH (aq.) solution. The resulting precipitate was collected by filtration after 24 h, dried in air, recrystallized from ethanol, to give **15**. (1.37 g, Yield 85%); mp 215-218 °C; FT-IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3130, 2924, 2854, 2766, 1679, 1614, 1592, 1516, 1308; ^1H NMR (CDCl_3): δ 1.86 (s, 12H), 7.63 (d, $J = 8.4$ Hz, 2H), 7.88 (d, $J = 8.4$ Hz, 2H), 9.83 (s, 2H), 9.87 (s, 2H), 14.35 (bs, 2H); ^{13}C NMR (CDCl_3): δ 22.87, 52.66, 110.20, 118.83, 120.50, 120.75, 135.48, 137.45, 179.94, 187.65, 192.73; MS (EI, 70 ev): m/z (%) 402 (M^+ , 68), 374 (43), 359 (80), 335 (32), 265 (57), 237 (46), 222 (100), 194 (39), 165 (30), 69 (36), 44 (98). Found: $[\text{M}]^+$ 402.1580, $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_4$ requires $[\text{M}]^+$ 402.1579.

General procedure for synthesis of (16a-e)

A mixture of the tetraformyl compound **15** (0.2 mmol) and the hydrazine or aryl hydrazines (0.4 mmol) in absolute ethanol (10 mL) was heated with stirring at reflux for 10-12 h. After cooling and concentrating the solution, the resulting crystals were collected by filtration and recrystallized from EtOH to give the corresponding pyrazoles.

1,1,6,6-Tetramethyl-2,7-di(1H-pyrazol-4-yl)-1,6-dihydroindolo[7,6-g]indole (16a). (0.063 g, Yield 80%); mp 220-221 °C; FT-IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3191, 2961, 2925, 2861, 1627, 1572, 1517; ^1H NMR ($\text{DMSO}-d_6$): δ 1.52 (s, 12H), 7.74 (d, $J = 8.1$ Hz, 2H), 8.38 (d, $J = 8.1$ Hz, 2H), 8.50 (s, 4H), 13.38 (bs, 2H); ^{13}C NMR ($\text{DMSO}-d_6$): δ 24.36, 54.37, 115.56, 120.02, 120.32, 127.01, 130.95, 142.56, 149.62, 179.68; MS (EI, 70 ev): m/z (%) 394 (M^+ , 100), 379 (46), 261 (32), 83 (23), 57 (42), 43 (66). Found: $[\text{M}]^+$ 394.1906, $\text{C}_{24}\text{H}_{22}\text{N}_6$ requires $[\text{M}]^+$ 394.1906.

2,7-Bis(1-(3-chlorophenyl)-1H-pyrazol-4-yl)-1,1,6,6-tetramethyl-1,6-dihydroindolo[7,6-g]indole (16b). (0.11 g, Yield 89%); mp 234-237 °C; FT-IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 2960, 2926, 2863, 1610, 1595, 1571, 1488, 1457; ^1H NMR ($\text{DMSO}-d_6$): δ 1.60 (s, 12H), 7.42 (d, $J = 7.8$ Hz, 2H), 7.57 (t, $J = 8.1$ Hz, 2H), 7.79 (d, $J = 8.1$ Hz, 2H), 8.03 (d, $J = 7.8$ Hz, 2H), 8.20 (s, 2H), 8.44 (d, $J = 8.1$ Hz, 2H), 8.54 (s, 2H), 9.33 (s, 2H); ^{13}C NMR ($\text{DMSO}-d_6$): δ 23.97, 54.58, 117.90, 118.60, 118.98, 120.23, 120.87, 127.07, 127.11, 128.45, 131.70, 134.54, 140.78, 141.89, 143.17, 149.33, 178.64; MS (EI, 70 ev): m/z (%) 618 (1), 616 (4), 614 (M^+ , 7), 482 (18), 441 (22), 394 (24), 371 (100), 356 (31), 152 (35), 127 (40), 57 (47), 43 (67). Found: $[\text{M}]^+$ 614.1754, $\text{C}_{36}\text{H}_{28}\text{Cl}_2\text{N}_6$ requires $[\text{M}]^+$ 614.1753.

2,7-Bis(1-(4-chlorophenyl)-1H-pyrazol-4-yl)-1,1,6,6-tetramethyl-1,6-dihydroindolo[7,6-g]indole (16c). (0.108 g, Yield 88%); mp 213-215 °C; FT-IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 2964, 2926, 2863, 1612, 1567, 1495, 949; ^1H NMR ($\text{DMSO}-d_6$): δ 1.63 (s, 12H), 7.64 (d, $J = 8.4$ Hz, 4H), 7.86 (d, $J = 8.1$ Hz, 2H), 8.10 (d, $J = 8.4$ Hz, 4H), 8.54 (d, $J = 8.1$ Hz, 2H), 8.64 (s, 2H), 9.38 (s, 2H); ^{13}C NMR ($\text{DMSO}-d_6$): δ 24.15, 54.57, 117.37, 120.63, 121.25, 121.50, 126.06, 129.54, 129.72, 130, 131.88, 138.31, 142.27, 143.08, 179.30; MS (EI, 70 ev): m/z (%) 618 (1), 616 (4), 614 (M^+ , 7), 394 (5), 371 (4), 279 (8), 167 (17), 149 (51), 127 (100), 84 (36), 71 (43), 57 (75), 43 (90). Found: $[\text{M}]^+$ 614.1751, $\text{C}_{36}\text{H}_{28}\text{Cl}_2\text{N}_6$ requires $[\text{M}]^+$ 614.1753.

2,7-Bis(1-(4-methoxyphenyl)-1H-pyrazol-4-yl)-1,1,6,6-tetramethyl-1,6-dihydroindolo[7,6-g]indole (16d). (0.115 g, Yield 95%); mp 223-225 °C; FT-IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 2971, 2930, 1612,

1578, 1515, 1255, 1175; ^1H NMR (DMSO- d_6): δ 1.64 (s, 12H), 3.82 (s, 6H), 7.12 (d, $J = 8.4$ Hz, 4H), 7.88 (d, $J = 8.7$ Hz, 2H), 7.95 (d, $J = 8.4$ Hz, 4H), 8.60 (d, $J = 8.7$ Hz, 2H), 8.65 (s, 2H), 9.33 (s, 2H); ^{13}C NMR (DMSO- d_6): δ 24.26, 54.51, 55.98, 115.11, 116.16, 116.82, 120.55, 121.21, 122.24, 126.24, 129.04, 133.09, 141.52, 142.91, 158.81, 179.45; MS (EI, 70 ev): m/z (%) 606 (M^+ , 100), 591 (30), 434 (9), 367 (16), 303 (20), 108 (16), 77 (14), 44 (16). Found: $[\text{M}]^+$ 606.2744, $\text{C}_{38}\text{H}_{34}\text{N}_6\text{O}_2$ requires $[\text{M}]^+$ 606.2743.

2,7-Bis(1-(4-bromophenyl)-1H-pyrazol-4-yl)-1,1,6,6-tetramethyl-1,6-dihydroindolo[7,6-g]indole (16e). (0.122 g, Yield 87%); mp 229-230 °C; FT-IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2969, 2927, 1619, 1573, 1524, 1494; ^1H NMR (DMSO- d_6): δ 1.62 (s, 12H), 7.77 (d, $J = 8.4$ Hz, 4H), 7.85 (d, $J = 8.1$ Hz, 2H), 8.05 (d, $J = 8.4$ Hz, 4H), 8.51 (d, $J = 8.1$ Hz, 2H), 8.61 (s, 2H), 9.36 (s, 2H); ^{13}C NMR (DMSO- d_6): δ 24.10, 54.58, 120.06, 120.54, 121.48, 126.48, 129.16, 132.21, 132.44, 132.63, 132.90, 138.77, 142.14, 143.12, 179.12; MS (EI, 70 ev): m/z (%) 706 (4), 704 (8), 702 (M^+ , 4), 614 (20), 524 (34), 484 (32), 458 (100), 441 (40), 229 (18), 171 (25), 65 (23), 43 (41). Found: $[\text{M}]^+$ 702.0744, $[\text{M}+2]^+$ 704.0721, $\text{C}_{36}\text{H}_{28}\text{Br}_2\text{N}_6$ requires $[\text{M}]^+$ 702.0742, $[\text{M}+2]^+$ 704.0722.

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