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Montmorillonite K-10 clay catalyzed solvent-free synthesis of bis-indolylindane-1,3-dione, 2-(1′,3′-dihydro-1*H*-[2,3′]biindolyl-2′-ylidene)-indan-1,3-dione and bisindolylindeno[1,2-*b*]quinoxaline under microwave irradiation

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ABSTRACT

An environmentally benign protocol has been described for the synthesis of novel 2-(1′,3′-dihydro-1*H*-[2,3′]biindolyl-2′-ylidene)-indan-1,3-diones/bis-indolylindane-1,3-diones from ninhydrin and 3-substituted/unsubstituted indoles. It uses montmorillonite K-10 as catalyst in a solvent-free condition under microwave irradiation. The method was also used for the synthesis of novel bisindolylindeno[1,2-*b*]quinoxaline derivatives.

1. Introduction

In recent years growing interest is being observed in the use of solid acidic catalysts in acid dependent organic syntheses.[1,2] This interest is likely to increase with demanding environmental legislation, public and corporate pressure, and drive toward clean technology. In this perspective, montmorillonite K-10 Clay (Mont. K-10), known to behave both as protic and Bronsted acid,[3] is a widely studied catalyst found useful in many organic reactions, viz., synthesis of γ-lactones,[4] synthesis of fused heterocycles,[5] Friedel–Crafts reaction,[6] synthesis of biomarkers,[7] oxidative demethylation of methylphenols to benzoquinones,[8] (2,5) intramolecular ene cyclization,[9] Michael addition,[10] Boc group removal from aromatic amines,[11] Diels–Alder reaction[12] and so on. It has also been used in many microwave reactions both in liquid phase as well as solvent-free conditions.[13–16]

Important pharmaceuticals often possess heterocyclic moieties as their building blocks.[17] The extensive use of heterocyclic compounds in the pharmaceutical industry is perhaps attributable to the availability of ample range of reactions that facilitate subtle structural modifications in heterocyclic compounds.[18–20] Since indole and its derivatives possess various biological activities,[21] development of new methodologies for the synthesis of indole derivatives, which will yield subsets of heterocycles having potentiality to serve as templates for new biologically active molecules, is of great importance.

In this context, we wish to describe a convenient and simple methodology for the synthesis of 2-(1′,3′-dihydro-1*H*-[2,3′]biindolyl-2′-ylidene)-indan-1,3-diones/bis-indolylindane-1,3-diones (by reacting ninhydrin with 3-substituted/unsubstituted indoles) and also bisindolylindeno[1,2-*b*]quinoxalines (from the reaction of ninhydrin, 1,2-phenylenediamine, and indole). The reactions were carried out using montmorillonite K-10 as solid acidic catalyst in solvent-free condition under microwave irradiation. The novelty of the methodology lies in its eco-friendly operation, formation of structurally unique molecules, short reaction time, and excellent yield.

2. Results and discussion

Initially, 1 mmol ninhydrin (**2**) and 2 mmol indole (**1a**) were added to the montmorillonite K-10 (0.5 g) in a mortar and mixed

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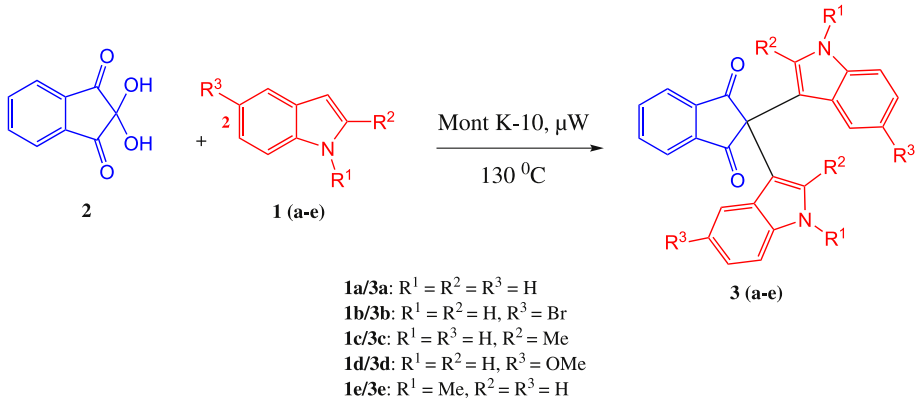
thoroughly. The resulting mixture was transferred into a beaker and exposed to microwave irradiation at 130 °C for 5 min to afford 2,2-bis-(1*H*-indol-3-yl)-indan-1,3-dione (**3a**) in excellent yield (Scheme 1).



1a/3a: $R^1 = R^2 = R^3 = H$
1b/3b: $R^1 = R^2 = H$, $R^3 = Br$
1c/3c: $R^1 = R^3 = H$, $R^2 = Me$
1d/3d: $R^1 = R^2 = H$, $R^3 = OMe$
1e/3e: $R^1 = Me$, $R^2 = R^3 = H$

Scheme 1. Montmorillonite K-10 catalyzed solvent-free synthesis of **3a**–**e**.

Thereafter, differently substituted indole derivatives (**1b**–**h**) were reacted with ninhydrin (**2**). Of these, 5-bromo (**1b**), 2-methyl (**1c**), 5-methoxy (**1d**), and 1-methyl (**1e**) indoles reacted smoothly to produce novel bis-indolylindane-1,3-diones (**3b**–**e**) in high yield (Table 1, entries 2–5). The characteristic quaternary carbon signal displayed at δ 59–60 in the ^{13}C NMR spectrum of the products (**3a**–**e**) clearly indicates the attachment of two indole moieties at C-2 of ninhydrin. Finally, single crystal X-ray crystallographic analysis of **3d** led to confirmation of the assumed structure (Fig. 1).

With 3-substituted indoles viz., 3-methylindole (**1f**), indole-3-acetic acid (**1g**), and indole-3-propionic acid (**1h**), the coupling with ninhydrin was smooth but yielded somewhat different products (**3f**–**h**) with high yield and selectivity (Table 1, entries 6–8). The spectroscopic data (HRMS and NMR) of **3f**–**h** strongly indicated the involvement of 2 mol of indole in the formation of the products. Though the spectral characteristics of **3g** were very close to those of **3f**, the data appeared to be inadequate for unambiguous determination of the structures. Eventually this was elucidated by single crystal X-ray analysis of **3f**. ORTEP representation of the molecular structure of **3f**, showing also the atomic numbering, is given in Figure 2. Thus, the complete structure of the compound was unequivocally established as 2-(3,3′-dimethyl-1′,3′-dihydro-1*H*-[2,3′]biindolyl-2′-ylidene)-indan-1,3-dione.

The structure of **3g** and **3h** could thereafter be determined from IR, NMR, and mass spectral correlations. In case of **3h**, the reaction had proceeded further as the –COOH group of one indole moiety was in close proximity to the nitrogen atom of the other indole unit to form a spiro fused six-membered lactam.

The plausible mechanism for the formation of 2-(1′,3′-dihydro-1*H*-[2,3′]biindolyl-2′-ylidene)-indan-1,3-dione derivatives (**3f**–**h**) is depicted in Scheme 2.

Ninhydrin is in equilibrium with indane-1,2,3-trione (**2a**). The electrophilic substitution at C-2 of indole, possibly via 1,2-migration after an initial attack at C-3 of indole,[22,23] produced carbocation intermediate **2b**, which was attacked by another indole moiety to form intermediate **2c**. Finally, intermediate **2c** after dehydration formed the 2-(1′,3′-dihydro-1*H*-[2,3′]biindolyl-2′-ylidene)-indan-

Table 1
Montmorillonite K-10 catalyzed solvent-free synthesis of **3a**–**h** and **5a**–**i**

Entry	Indole	Other substrate	Product[a]	Time[b] (min)	Yield[c] (%)
1	**1a**	**2**	**3a**	5	95
2	**1b**	**2**	**3b**	5	94
3	**1c**	**2**	**3c**	5	94
4	**1d**	**2**	**3d**	6	96
5	**1e**	**2**	**3e**	5	92
6	**1f**	**2**	**3f**	5	96
7	**1g**	**2**	**3g**	6	92
8	**1h**	**2**	**3h**	6	90
9	**1a**	**2**+**4a**	**5a**	5	94
10	**1b**	**2**+**4a**	**5b**	5	96
11	**1d**	**2**+**4a**	**5c**	5	92
12	**1e**	**2**+**4a**	**5d**	6	94
13	**1a**	**2**+**4b**	**5e**	6	95
14	**1c**	**2**+**4b**	**5f**	5	94
15	**1d**	**2**+**4b**	**5g**	6	92
16	**1e**	**2**+**4b**	**5h**	5	94
17	**1e**	**2**+**4c**	**5i**	6	92

[a] All the products were characterized by IR, NMR, and Mass spectroscopy.
[b] Extension of the reaction does not improve the products yield.
[c] Yield refers to pure products after crystallization.

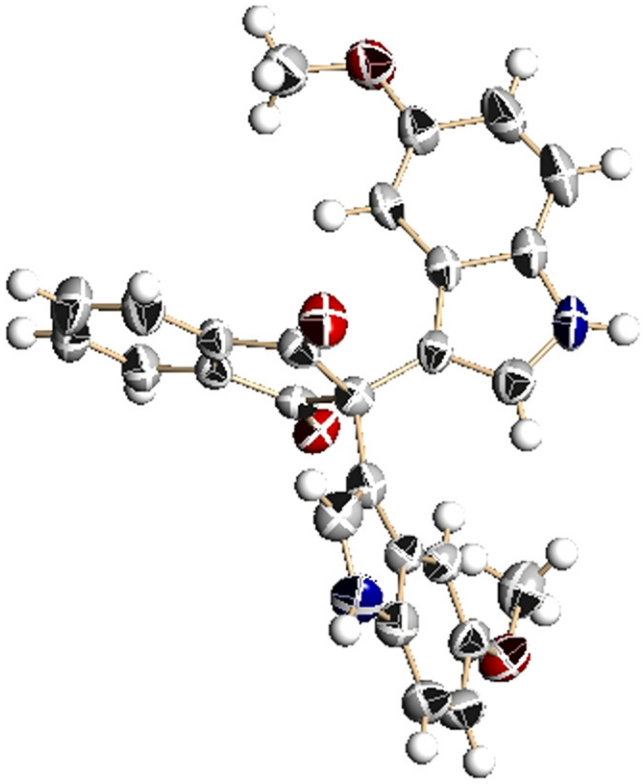


Figure 1. ORTEP representation of **3d**.

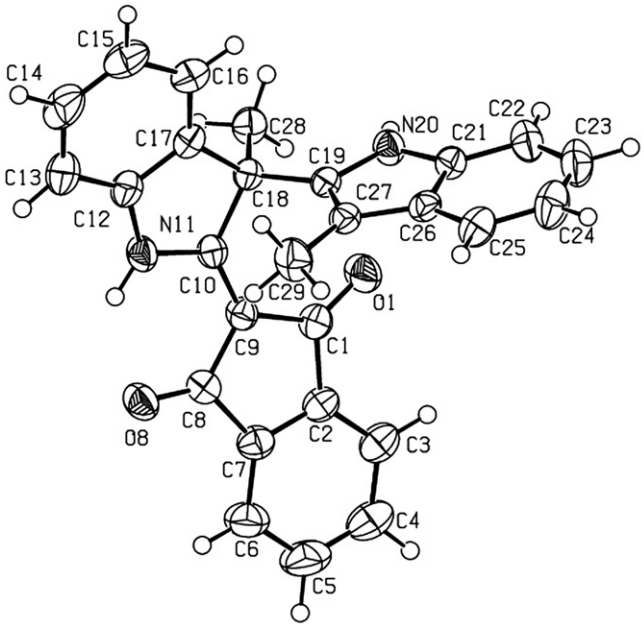


Figure 2. ORTEP representation of **3f**.

1,3-diones (**3f**–**h**). It was noted that in case of indoles having electron withdrawing groups at 3-position, viz., 3-cyanoindole, indole-3-carboxaldehyde, indole-3-carboxylic acid, failed to react as anticipated.

However, when the reaction was performed following the same protocol using 1 equiv of indoles (**1i** and **1j**), exclusively 2-hydroxy-2-(1*H*-indol-3-yl)-indan-1,3-dione (**3i**) and 2-hydroxy-2-(1*H*-indol-2-yl)-indan-1,3-dione (**3j**) derivatives were formed (Scheme 3) with excellent yields (95%), which appears similar to the earlier report.[24]

Next, we attempted to synthesize novel bisindolylindeno[1,2-*b*] quinoxalines from the reaction of ninhydrin (**2**) with 1,2-phenylenediamine (**4a**–**c**) and indole (**1a**–**e**) derivatives under the same reaction condition (Scheme 4).

In this case, initially the condensation of ninhydrin (**2**) and 1,2-phenylenediamine (**4a**–**c**) took place to produce the intermediate **A**, which reacted with 2 mol of indoles (**1a**–**e**) via the intermediate **A** to generate **5a**–**i** in high yield (Table 1, entries 9–17). All the structures were established by mass, ^{1}H and ^{13}C NMR spectral analysis. Single crystal X-ray crystallographic analysis of **5b** was also carried out for unambiguous determination of its structure (Fig. 3).

3. Conclusion

In summary, we have developed an eco-friendly methodology for the solvent-free synthesis of bis-indolylindane-1,3-dione, 2-(1′,3′-dihydro-1*H*-[2,3′]biindolyl-2′-ylidene)-indan-1,3-dione, and bisindolylindeno[1,2-*b*]quinoxaline using montmorillonite K-10 as solid catalyst under microwave irradiation. Bio-evaluation of the synthesized compounds is in progress in our laboratory.

4. Experimental section

4.1. General experimental

Melting points were determined with a capillary melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FTIR (model 410) in KBr pellets. ESI-MS (positive) was conducted using LC-ESI-Q-TOF micro Mass spectrometer (Indian Institute of Chemical Biology, Kolkata). The NMR spectra were taken on a BRUKER 300/600 DPX spectrometer operating at 300/600 MHz for ^{1}H and 75/150 MHz for ^{13}C, respectively, with tetramethylsilane (TMS) as an internal standard and the chemical shifts are reported in δ units. Microwave irradiation was performed by using a mono-mode Discover microwave reactor (CEM Corp., Matthews, NC, USA). Ninhydrin, montmorillonite K-10, *ortho*-phenylenediamine and indole derivatives were purchased from Aldrich Chemical Ltd (USA). Thin layer chromatography was performed on pre-coated silica gel 60 F_{254} aluminum sheets (E. Merck, Germany) using different solvent system.

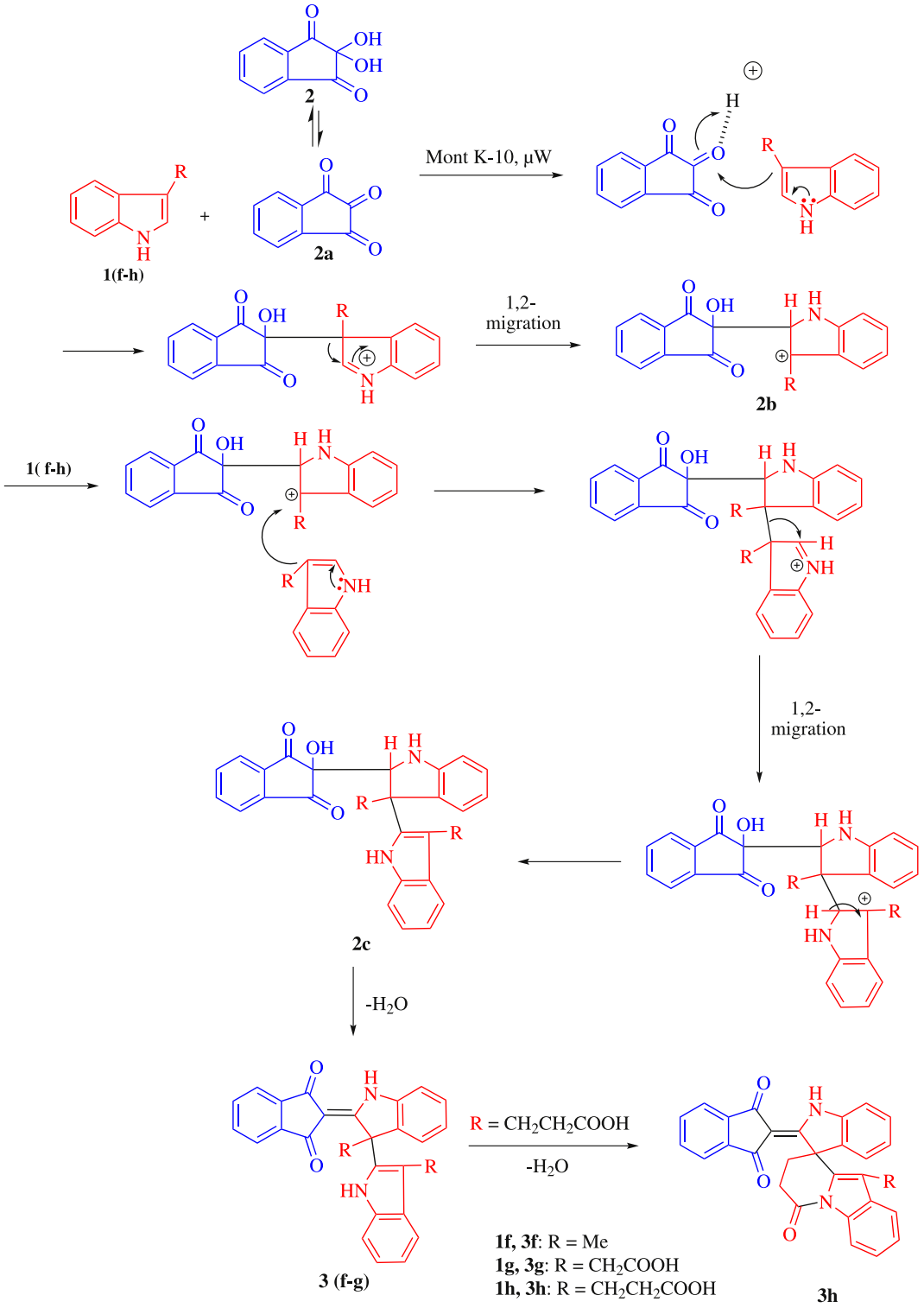
4.2. General reaction procedure for the synthesis of bis-indolylindane-1,3-dione, 2-(1′,3′-dihydro-1*H*-[2,3′]biindolyl-2′-ylidene)-indan-1,3-dione and bisindolylindeno[1,2-*b*] quinoxaline derivatives

Montmorillonite K-10 (0.5 g) was placed in a mortar followed by either 1 mmol ninhydrin (**2**) and 2 mmol indole derivative (**1a**–**h**) [for the synthesis **3a**–**h**] or 1 mmol ninhydrin (**2**), 1 mmol 1,2-phenylenediamine derivative (**4a**–**c**), and 2 mmol indole derivative (**1a**–**e**) [for the synthesis **5a**–**i**]. The reactants were mixed well for 5 min using a pestle. The homogenized mixture was placed in a beaker, preheated in a microwave oven for 2 min at 130 °C (250 W) and the heating was continued for 5–6 min to complete the reaction (monitored by TLC). The contents were cooled to room temperature and mixed thoroughly with 10 mL of acetone. The solid inorganic material was filtered off and the filtrate was evaporated to dryness. The residue was crystallized from chloroform/hexane or chloroform/methanol mixture to afford pure **3a**–**h** or **5a**–**i**. All the products were identified by spectroscopic analysis (IR, NMR, and MS). The recovered catalyst was washed by acetone (4×5 mL), activated by keeping in oven for 3 h at 120 °C, and directly used in the next experiment without any loss of activity.

*4.2.1. 2,2-Bis-(1H-indol-3-yl)-indan-1,3-dione (**3a**).* Yellow prisms (95% yield), mp 208–210 °C; R_f (ethyl acetate/petroleum ether 1:1) 0.28; IR (KBr, cm^{-1}) ν 3399, 1702, 1246, 747; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 6.84 (t, 2H, J=7.5 Hz), 6.96 (s, 2H), 7.05 (t, 2H, J=7.2 Hz), 7.20 (d, 2H, J=7.8 Hz), 7.38 (d, 2H, J=8.1 Hz), 8.09 (m, 4H), 11.17 (s, 2H, −NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 59.6 (C), 110.7 (2×CH), 112.2 (2×C), 119.2 (4×CH), 120.5 (2×CH), 121.7 (2×CH), 124.2 (2×CH), 125.9 (2×CH), 137.1 (2×C), 137.3 (2×C), 140.1 (2×C), 199.6 (2×CO); MS: (ESI-MS, positive mode) m/z 377 [M+H]$^{+}$, 399 [M+Na]$^{+}$. HRMS (ESI) m/z calcd for $C_{25}H_{16}N_2O_2Na$: 399.1109; found: 399.1096.

*4.2.2. 2,2-Bis-(5-bromo-1H-indol-3-yl)-indan-1,3-dione (**3b**).* Yellow prisms (94% yield), mp 104–106 °C; R_f (ethyl acetate/petroleum ether 1:1) 0.20; IR (KBr, cm^{-1}) ν 3445, 1702, 1457, 1239; ^{1}H NMR (pyridine-d_5, 300 MHz) δ 7.32 (s, 2H), 7.35 (m, 2H), 7.39 (m, 2H,), 7.41 (s, 2H), 7.65 (m, 1H), 7.74 (m, 1H), 8.09 (m, 1H), 8.29 (m, 1H), 12.70 (s, 2H, −NH); ^{13}C NMR (pyridine-d_5, 75 MHz) δ 60.0 (C), 111.4 (2×C), 113.1 (2×C), 114.1 (2×CH), 124.3 (2×CH), 125.0 (4×CH), 127.9 (2×CH), 128.6 (2×C), 136.7 (2×CH), 136.9 (2×C), 140.6 (2×C), 199.7 (2×CO); MS: (ESI-MS, positive mode) m/z 555 (M^{+}+Na, 30), 557 (M^{+}+2+Na, 100), 559 (M^{+}+4+Na, 35). HRMS (ESI) calcd for $C_{25}H_{14}Br_2N_2O_2Na$: 554.9320; found: 554.9313.

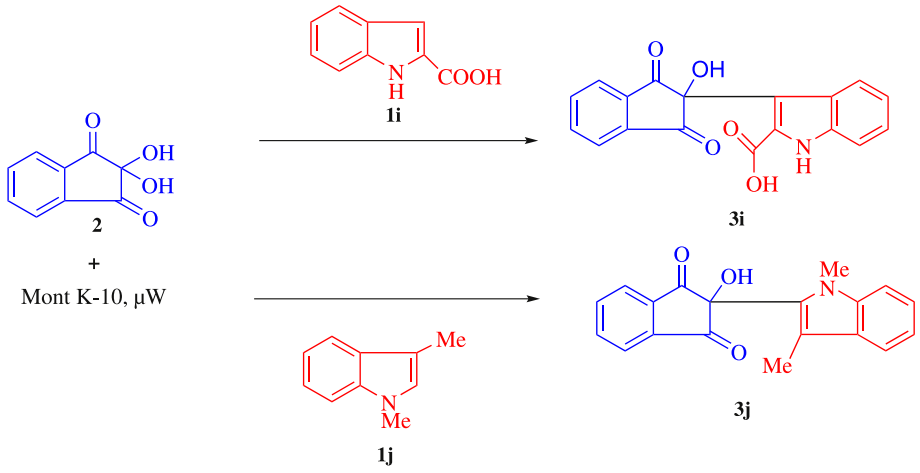
*4.2.3. 2,2-Bis-(2-methyl-1H-indol-3-yl)-indan-1,3-dione (**3c**).* Yellow needles (94% yield), mp 108–110 °C; R_f (ethyl acetate/petroleum ether 1:1) 0.24; IR (KBr, cm^{-1}) ν 3369, 1706, 1459, 1256, 738; ^{1}H NMR (pyridine-d_5, 300 MHz) δ 2.38 (s, 6H, 2×Me), 6.98 (m, 2H), 7.13 (m, 4H,), 7.33 (s, 2H), 7.48 (d, 1H, J=8.0 Hz), 7.75 (m, 2H), 8.21 (m, 1H), 12.14 (s, 2H, −NH); ^{13}C NMR (pyridine-d_5, 75 MHz) δ 13.9 (2×CH_3), 59.2 (C), 107.7 (2×C), 111.3 (2×CH), 119.5 (2×CH), 120.7



Scheme 2. Plausible mechanism for the formation of **3f**–**h**.

(2×CH), 121.0 (2×CH), 124.3 (CH), 128.7 (CH), 135.7 (2×C), 136.3 (2×CH), 136.5 (4×C), 142.6 (2×C), 199.6 (2×CO); MS: (ESI-MS, positive mode) *m*/*z* 427 $[M+Na]^+$. HRMS (ESI) *m*/*z* calcd for $C_{27}H_{20}N_2O_2Na$: 427.1422; found: 427.1416.

*4.2.4. 2,2-Bis-(5-methoxy-1H-indol-3-yl)-indan-1,3-dione (**3d**).* Yellow prisms (96% yield), mp 114–116 °C; R_f (ethyl acetate/petroleum ether 1:1) 0.22; IR (KBr, cm^{-1}) ν 3392, 1702, 1483, 1213; ^1H NMR (DMSO-d_6, 300 MHz) δ 3.36 (s, 3H), 3.51 (s, 3H), 6.65 (s, 2H), 6.73 (d, 2H, *J*=8.7 Hz), 6.94 (s, 2H), 7.28 (d, 2H, *J*=8.7 Hz), 8.10 (m, 4H), 11.01 (s, 2H, –NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 55.1 (2×CH_3), 59.2 (C), 102.7 (2×CH), 109.7 (2×C), 110.9 (2×CH), 112.5 (2×CH), 123.8 (2×CH), 126.0 (2×C), 126.3 (2×CH), 132.1 (2×C), 137.0 (2×CH), 139.8 (2×C), 152.9 (2×C), 199.4 (2×CO); MS: (ESI-MS, positive mode) *m*/*z* 459 $[M+Na]^+$. HRMS (ESI) calcd for $C_{27}H_{20}N_2O_4Na$: 459.1321; found: 459.1342.

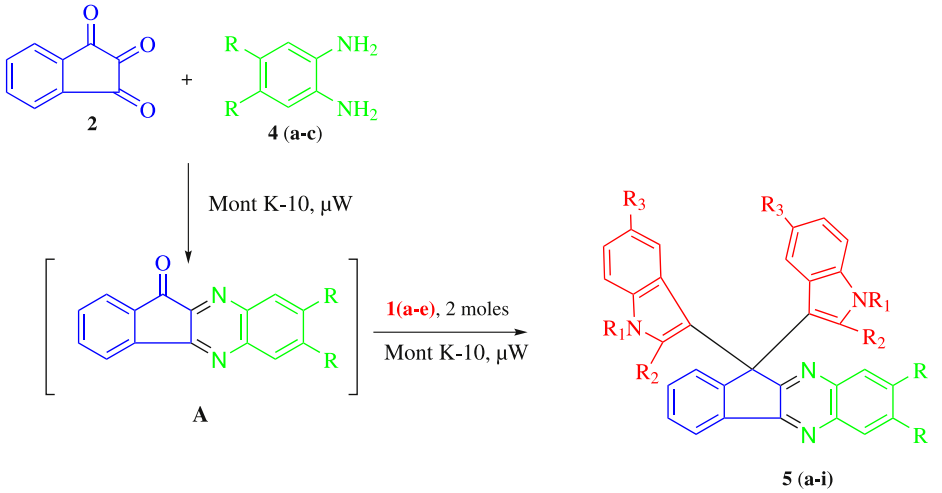


Scheme 3. Montmorillonite K-10 catalyzed condensation of ninhydrin with 1 equiv of indole derivative.

*4.2.5. 2,2-Bis-(1-methyl-1H-indol-3-yl)-indan-1,3-dione(**3e**).* Yellow prisms (92% yield), mp 232–234 °C; R_f (ethyl acetate/petroleum ether 1:2) 0.55; IR (KBr, cm^{-1}) ν 1710, 1256, 740; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.62 (s, 6H, CH_3), 6.87 (s, 2H), 6.97 (t, 2H, J=7.4 Hz), 7.15 (m, 2H), 7.23 (d, 2H, J=8.1 Hz), 7.43 (d, 2H, J=8.0 Hz), 7.82 (m, 2H), 8.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.7 (2×CH_3), 59.5 (C), 109.3 (2×CH), 110.1 (2×C), 119.4 (2×CH), 121.0 (2×CH), 121.8 (2×CH), 124.0 (2×CH), 126.1 (2×C), 129.6 (2×CH), 135.9 (2×CH), 137.5 (2×C), 140.4 (2×C), 199.6 (2×CO); MS: (ESI-MS, positive mode) m/z 405 $[M+H]^+$. HRMS (ESI) m/z calcd for $C_{27}H_{20}N_2O_2Na$: 427.1422; found: 427.1416.

*4.2.6. 2-(3,3′-Dimethyl-1′,3′-dihydro-1H-[2,3′]biindolyl-2′-ylidene)-indan-1,3-dione (**3f**).* Yellow prisms (96% yield), mp 284–286 °C; R_f (ethyl acetate/petroleum ether 1:2) 0.53; IR (KBr, cm^{-1}) ν 3321, 1642, 1563, 747; ^1H NMR (pyridine-d_5, 600 MHz) δ 1.92 (s, 3H), 2.55 (s, 3H), 7.15 (m, 2H), 7.23 (m, 1H), 7.29 (d, 1H, J=7.8), 7.33 (m, 1H), 7.40 (m, 1H), 7.46 (m, 2H), 7.57 (m, 3H), 7.83 (d, 1H, J=7.2 Hz), 12.32 (s, 1H, –NH), 12.95 (s, 1H, –NH); ^{13}C NMR (pyridine-d_5, 75 MHz) δ 9.8 (CH_3), 23.8 (CH_3), 55.4 (C), 104.3 (C), 108.5 (C), 113.1 (CH), 114.0 (CH), 119.8 (CH), 120.4 (CH), 122.8 (CH), 123.3 (CH), 125.1 (C), 126.4 (2×CH), 130.0 (2×CH), 134.6 (CH), 134.7 (C), 134.9 (CH), 137.7 (C), 140.2 (C), 141.5 (C), 142.1(C), 142.7 (C), 173.1 (C), 189.5 (CO), 194.9 (CO); MS: (ESI-MS, positive mode) m/z 405 $[M+H]^+$, 427 $[M+Na]^+$. HRMS (ESI) calcd for $C_{27}H_{20}N_2O_2Na$: 427.1422; found: 427.1414.

*4.2.7. [3′-Carboxymethyl-2′-(1,3-dioxo-indan-2-ylidene)-2′,3′-dihydro-1H,1′H-[2,3′]biindolyl-3-yl]-acetic acid (**3g**).* Yellow needles (92% yield), mp >300 °C; R_f (methanol/chloroform 1:4) 0.64; IR (KBr, cm^{-1}) ν 3377, 1713, 1552, 1221; ^1H NMR (DMSO-d_6, 300 MHz) δ 2.83 (m, 1H), 3.09 (m, 1H), 3.17 (s, 1H, COOH), 3.51 (m, 1H), 3.92 (m, 1H), 4.11 (s, 1H, COOH), 7.11 (m, 1H,), 7.27 (m, 1H), 7.42 (m, 4H), 7.52 (m, 1H), 7.63 (m, 4H), 8.10 (d, 1H, J=7.8 Hz), 12.01 (s, 1H, –NH), 12.35 (s, 1H, –NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 28.4 (CH_2), 47.6 (CH_2), 51.6 (C), 102.1 (C), 106.3 (C), 113.2 (CH), 113.3 (CH), 120.1 (CH), 121.1 (CH), 121.6 (CH), 123.1 (CH), 123.6 (CH), 123.9 (CH), 124.9 (CH), 129.2 (2×CH), 129.7 (C), 133.6 (CH), 134.2 (C), 134.7 (C), 139.4 (C), 139.6 (C), 140.1 (C), 141.5 (C), 165.5 (C), 169.2 (C), 170.6 (C), 188.0 (CO), 191.3 (CO). MS: (ESI-MS, positive mode) m/z 515 $[M+Na]^+$. HRMS (ESI) calcd for $C_{29}H_{20}N_2O_6Na$: 515.1219; found: 515.1219.



4a: R = H
4b: R = Me
4c: R = Cl

5a: R =R_1=R_2=R_3= H
5b: R =R_1=R_2= H, R_3= Br
5c: R =R_1=R_2= H, R_3=OMe
5d: R =R_2=R_3= H, R_1= Me
5e: R = Me, R_1=R_2=R_3= H
5f: R =R_2= Me, R_1=R_3= H
5g: R = Me, R_1=R_2=H, R_3= OMe
5h: R =R_1= Me, R_2=R_3=H
5i : R = Cl, R_1= Me, R_2=R_3= H

Scheme 4. Montmorillonite K-10 catalyzed solvent-free synthesis of **5a**–**i**.

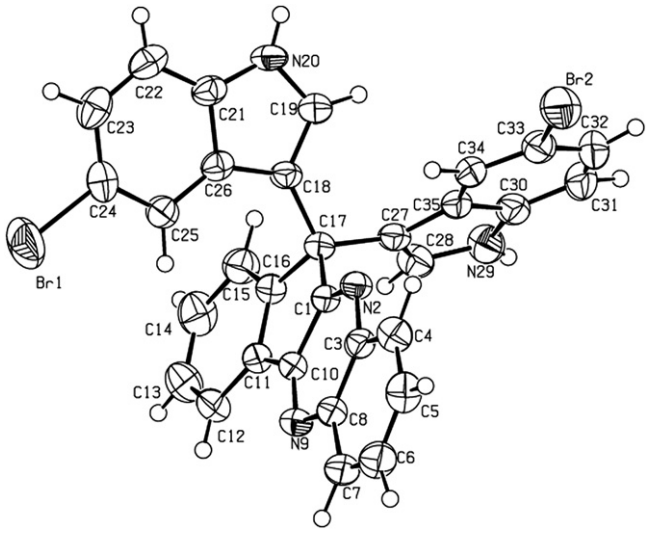


Figure 3. ORTEP representation of **5b**.

*4.2.8. Compound **3h**.* Green needles (90% yield), mp 290–292 °C; R_f (methanol/chloroform 1:9) 0.77; IR (KBr, cm^{-1}) ν 3253, 1701, 1562, 1216; ^1H NMR (DMSO-d_6, 300 MHz) δ 1.60 (m, 1H), 1.76 (m, 1H), 1.92 (1H, m), 2.27 (2H, m), 2.89 (1H, m), 3.20 (m, 2H), 7.10 (m, 1H), 7.22 (m, 1H), 7.38 (m, 3H), 7.51 (m, 2H), 7.70 (m, 4H), 8.53 (d, 1H, J=8.1 Hz), 11.93 (s, 1H, −NH), 12.50 (s, 1H, −NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 19.0 (CH_2), 30.4 (CH_2), 31.1 (CH_2), 32.4 (CH_2), 52.3 (C), 101.5 (C), 114.5 (CH), 115.8 (C), 116.6 (CH), 119.0 (CH), 121.5 (CH), 122.0 (CH), 123.9 (CH), 124.1 (CH), 125.0 (CH), 129.5 (2×CH), 129.8 (C), 132.2 (C), 134.3 (2×CH), 134.6 (C), 135.6 (C), 139.4 (C), 139.9 (C), 141.3 (C), 168.4 (C), 169.6 (C), 173.4 (C), 187.9 (CO), 191.9 (CO); MS: (ESI-MS, positive mode) m/z 503 $[M+H]^+$, 525 $[M+Na]^+$. HRMS (ESI) calcd for $C_{31}H_{22}N_2O_5Na$: 525.1426; found: 525.1405.

*4.2.9. 3-(2-Hydroxy-1,3-dioxo-indan-2-yl)-1H-indole-2-carboxylic acid (**3i**).* Green needles (90% yield), mp 274–276 °C; R_f (methanol/chloroform 1:4) 0.65; IR (KBr, cm^{-1}) ν 3421, 1456, 1104, 760; ^1H NMR (DMSO-d_6, 300 MHz) δ 6.38 (d, 1H, J=7.8 Hz), 6.64 (t, 1H, J=7.5 Hz), 6.99 (m, 1H), 7.37 (d, 1H, J=8.1 Hz), 8.10 (m, 5H), 11.18 (s, 1H), 13.68 (br s, 1H); ^{13}C NMR (pyridine-d_5, 75 MHz) δ 81.1 (C), 114.7 (2×CH), 119.5 (C), 122.0 (2×CH), 126.5 (2×CH), 126.6 (2×CH), 129.3 (C), 131.5 (C), 136.9 (C), 139.4 (C), 143.4 (C), 166.7 (C), 200.6 (2×CO); MS: (ESI-MS, positive mode) m/z 322 $[M+H]^+$. HRMS (ESI) m/z calcd for $C_{18}H_{11}NO_5Na$: 344.0535; found: 344.0535.

*4.2.10. 2-(1,3-Dimethyl-1H-indol-2-yl)-2-hydroxy-indan-1,3-dione (**3j**).* Yellow needles (92% yield), mp 185–188 °C; R_f (ethyl acetate/petroleum ether 1:2) 0.57; IR (KBr, cm^{-1}) ν 3365, 3054, 1710, 1254; ^1H NMR (DMSO-d_6, 300 MHz) δ 1.84 (s, 3H), 4.13 (s, 3H), 7.00 (m, 1H,), 7.18 (t, 1H, J=7.5 Hz), 7.31 (s, 1H), 7.41 (d, 2H, J=8.1 Hz), 8.10 (m, 4H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 9.80 (CH_3), 32.9 (CH_3), 77.4 (C), 108.6 (C), 109.3 (CH), 118.5 (CH), 118.9 (CH), 122.6 (CH), 124.1 (2×CH), 127.5 (C), 128.2 (C), 137.4 (2×CH), 137.5 (2×C), 140.1 (C), 197.4 (2×CO); MS: (ESI-MS, positive mode) m/z 306 $[M+H]^+$, 328 $[M+Na]^+$. HRMS (ESI) calcd for $C_{19}H_{15}NO_3Na$: 328.0950; found 328.0944.

*4.2.11. 11,11-Bis-(1H-indol-3-yl)-11H-indeno[1,2-b]quinoxaline (**5a**).* Yellow prisms (94% yield), mp 276–278 °C; R_f (ethyl acetate/petroleum ether 1:1) 0.25; IR (KBr, cm^{-1}) ν 3414, 1336, 750; ^1H NMR (DMSO-d_6, 300 MHz) δ 6.74 (t, 2H, J=7.5 Hz), 6.91 (s, 2H), 6.99 (t, 2H, J=7.5 Hz), 7.08 (d, 2H, J=7.8 Hz), 7.36 (d, 2H, J=8.1 Hz), 7.64 (m, 4H), 7.76 (m, 1H), 7.91 (d, 1H, J=8.1 Hz), 8.16 (d, 1H, J=8.1 Hz), 8.30 (d, 1H, J=8.9 Hz), 11.0 (s, 2H, −NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 53.1 (C), 111.7 (2×CH), 115.6 (2×C), 118.3 (2×CH), 120.8 (CH), 121.0 (CH), 122.1 (2×CH), 124.7 (2×CH), 125.8 (2×C), 126.4 (CH), 128.6 (CH), 128.8 (CH), 129.1 (CH), 129.2 (CH), 129.5 (CH), 131.9 (2×CH), 135.3 (C), 137.0 (C), 140.7 (C), 141.6 (C), 152.7 (2×C), 153.3 (C), 165.5 (C); MS: (ESI-MS, positive mode) m/z 449 $[M+H]^+$, 471 $[M+Na]^+$. HRMS (ESI) calcd for $C_{31}H_{20}N_4Na$: 471.1586; found 471.1586.

*4.2.12. 11,11-Bis-(5-bromo-1H-indol-3-yl)-11H-indeno[1,2-b]quinoxaline (**5b**).* Yellow prisms (96% yield), mp 274–276 °C; R_f (ethyl acetate/petroleum ether 1:1) 0.24; IR (KBr, cm^{-1}) ν 3421, 1456, 1104, 760; ^1H NMR (pyridine-d_5, 300 MHz) δ 7.17 (s, 2H), 7.29 (m, 2H), 7.48 (m, 6H), 7.89 (d, 1H, J=7.5 Hz), 8.11 (d, 1H, J=8.4 Hz), 8.16 (s, 2H), 8.27 (d, 1H, J=8.4 Hz), 8.52 (d, 1H, J=7.2 Hz), 12.47 (2H, −NH); ^{13}C NMR (pyridine-d_5, 75 MHz) δ 54.0 (C), 112.6 (2×C), 114.0 (2×CH), 116.8 (2×C), 122.9 (2×CH), 124.4 (CH), 124.7 (CH), 127.0 (CH), 127.1 (CH), 129.0 (2×C), 129.1 (CH), 129.2 (CH), 129.5 (CH), 129.7 (CH), 130.0 (2×CH), 132.2 (2×CH), 136.6 (C), 137.2 (C), 141.9 (C), 142.9 (C), 152.9 (2×C), 154.0 (C), 165.8 (C); MS: (ESI-MS, positive mode) m/z 627 (M^++Na, 40), 629 (M^++2+Na, 82), 631 (M^++4+Na, 45). HRMS (ESI) calcd for $C_{31}H_{18}Br_2N_4Na$: 626.9796; found 626.9796.

*4.2.13. 11,11-Bis-(5-methoxy-1H-indol-3-yl)-11H-indeno[1,2-b]quinoxaline (**5c**).* Brown needles (92% yield), mp 212–214 °C; R_f (ethyl acetate/petroleum ether 1:1) 0.22; IR (KBr, cm^{-1}) ν 3411, 1479, 1213, 762; ^1H NMR (DMSO-d_6, 300 MHz) δ 3.42 (s, 6H), 6.56 (s, 2H), 6.68 (m, 2H), 6.95 (m, 2H), 7.27 (d, 2H, J=8.8 Hz), 7.72 (m, 5H), 7.95 (d, 1H, J=7.9 Hz), 8.19 (m, 1H), 8.32 (m, 1H), 10.87 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 53.1 (C), 55.0 (2×CH_3), 103.1 (2×CH), 110.6 (2×CH), 112.2 (2×CH), 115.0 (2×C), 122.0 (2×CH), 125.5 (CH), 126.2 (2×C), 126.5 (CH), 128.7 (CH), 128.8 (CH), 129.2 (CH), 129.6 (CH), 132.0 (2×CH), 132.2 (C), 135.4 (2×C), 140.7 (C), 141.6 (C), 152.4 (2×C),152.7 (C),153.3 (C), 164.6 (C); MS: (ESI-MS, positive mode) m/z 509 $[M+H]^+$, 531 $[M+Na]^+$. HRMS (ESI) calcd for $C_{33}H_{24}N_4O_2Na$: 531.1797; found 531.1819.

*4.2.14. 11,11-Bis-(1-methyl-1H-indol-3-yl)-11H-indeno[1,2-b]quinoxaline (**5d**).* Green prisms (94% yield), mp 182–184 °C; R_f (ethyl acetate/petroleum ether 1:2) 0.66; IR (KBr, cm^{-1}) ν 3052, 1469, 744; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.62 (s, 6H, CH_3), 6.78 (s, 2H), 6.84 (t, 2H, J=7.5 Hz), 7.10 (t, 2H, J=7.2 Hz), 7.23 (m, 4H), 7.44 (t, 1H, J=7.2 Hz), 7.54 (m, 2H), 7.65 (m, 2H), 7.98 (d, 1H, J=8.1 Hz), 8.13 (d, 1H, J=8.4 Hz), 8.34 (d, 1H, J=7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.5 (CH_3), 32.7 (CH_3), 53.3 (C), 109.1 (2×CH), 115.7 (2×C), 118.7 (2×CH), 121.4 (2×CH), 122.0 (2×CH), 122.4 (2×CH), 126.4 (C), 126.6 (CH), 128.4 (CH), 128.7 (CH), 128.8 (CH), 129.0 (C), 129.9 (2×CH), 131.6 (C), 136.0 (C), 137.7 (2×CH), 141.7 (C), 142.2 (C), 152.9 (2×C), 153.7 (C), 165.4 (C); MS: (ESI-MS, positive mode) m/z 477 $[M+H]^+$, 499 $[M+Na]^+$. HRMS (ESI) calcd for $C_{33}H_{25}N_4$ $[M+H]^+$: 477.2079; found 477.2077.

*4.2.15. 11,11-Bis-(1H-indol-3-yl)-7,8-dimethyl-11H-indeno[1,2-b]quinoxaline (**5e**).* Yellow prisms (95% yield), mp 218–220 °C; R_f (ethyl acetate/petroleum ether 1:1) 0.30; IR (KBr, cm^{-1}) ν 3414, 1335, 747; ^1H NMR (DMSO-d_6, 300 MHz) δ 2.34 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 6.77 (m, 2H), 6.93 (s, 2H), 7.02 (t, 2H, J=7.2 Hz), 7.12 (d, 2H, J=7.8 Hz), 7.39 (d, 2H, J=7.8 Hz), 7.53 (m, 2H), 7.68 (d, 1H, J=9.6 Hz), 7.92 (s, 1H), 8.25 (d, 1H, J=6.6 Hz), 8.33 (s, 1H), 11.0 (s, 2H, −NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 19.6 (CH_3), 19.7 (CH_3), 53.1 (C), 111.7 (2×CH), 116.0 (2×CH), 118.3 (2×CH), 121.0 (CH), 121.8 (CH), 124.6 (2×CH), 125.9 (2×C), 126.3 (CH), 127.9 (CH), 128.4 (CH), 128.5 (CH), 131.4 (2×CH), 135.7 (C), 137.0 (C), 139.2 (C), 139.5 (C), 139.6 (2×C), 140.4 (2×C), 152.3 (2×C), 152.5 (C), 164.6 (C); MS: (ESI-MS, positive mode) m/z 477 $[M+H]^+$, 499 $[M+Na]^+$. HRMS (ESI) calcd for $C_{33}H_{24}N_4Na$: 499.1899, found 499.1882.

*4.2.16. 7,8-Dimethyl-11,11-bis-(2-methyl-1H-indol-3-yl)-11H-indeno [1,2-b]quinoxaline (**5f**).* Brown needles (94% yield), mp 204–206 °C; R_f (ethyl acetate/petroleum ether 1:1) 0.72; IR (KBr, cm^{-1}) ν 3403, 1455, 745; ^1H NMR (DMSO-d_6, 300 MHz) δ 1.68 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 6.46 (m, 2H), 6.60 (t, 1H, J=7.5 Hz), 6.85 (m, 2H), 7.20 (m, 2H), 7.48 (m, 1H), 7.58 (m, 1H), 7.63 (m, 2H), 7.91 (s, 1H), 8.17 (d, 1H, J=7.5 Hz), 8.32 (s, 1H), 10.85 (s, 1H, -NH), 10.92 (s, 1H, −NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 13.7 (CH_3), 13.8 (CH_3), 19.6 (CH_3), 19.8 (CH_3), 53.2 (C), 110.5 (2×CH), 110.9 (C), 111.8 (C), 117.9 (CH), 118.0 (CH), 119.5 (CH), 119.8 (CH), 121.6 (2×CH), 127.0 (CH), 127.8 (C), 127.9 (CH), 128.5 (2×CH), 131.4 (2×CH), 132.1 (C), 134.3 (C), 134.9 (C), 135.1 (C), 139.3 (C), 139.6 (C), 139.7 (C), 140.3 (2×C), 152.5 (2×C), 153.0 (C), 165.4 (C); MS: (ESI-MS, positive mode) m/z 505 $[M+H]^+$, 527 $[M+Na]^+$. HRMS (ESI) calcd for $C_{35}H_{28}N_4Na$: 527.2212; found 527.2198.

*4.2.17. 11,11-Bis-(5-methoxy-1H-indol-3-yl)-7,8-dimethyl-11H-indeno[1,2-b]quinoxaline (**5g**).* Brown needles (92% yield), mp 216–218 °C; R_f (ethyl acetate/petroleum ether 1:1) 0.25; IR (KBr, cm^{-1}) ν 3372, 1482, 1214, 796; ^1H NMR (DMSO-d_6, 300 MHz) δ 2.34 (s, 3H), 2.45 (s, 3H), 3.42 (s, 6H), 6.48 (s, 2H), 6.64 (d, 2H, J=8.4 Hz), 6.87 (s, 2H), 7.22 (d, 2H, J=8.7 Hz), 7.59 (m, 3H), 7.66 (s, 1H), 7.94 (s, 1H), 8.24 (m, 1H), 10.80 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 19.6 (CH_3), 19.7 (CH_3), 52.1 (C), 55.0 (2×CH_3), 103.2 (2×CH), 110.5 (2×CH), 112.1 (2×CH), 115.2 (2×C), 121.7 (2×CH), 125.4 (CH), 126.2 (2×C), 126.4 (CH), 127.9 (CH), 128.3 (CH), 128.5 (CH), 131.4 (CH), 132.2 (C), 135.7 (2×C), 139.3 (C), 139.5 (C), 140.4 (2×C), 152.3 (4×C), 164.6 (C); MS: (ESI-MS, positive mode) m/z 537 $[M+H]^+$, 559 $[M+Na]^+$. HRMS (ESI) calcd for $C_{35}H_{28}N_4O_2Na$: 559.2110; found 559.2128.

*4.2.18. 7,8-Dimethyl-11,11-bis-(1-methyl-1H-indol-3-yl)-11H-indeno [1,2-b]quinoxaline (**5h**).* Green needles (94% yield), mp 170–172 °C; R_f (ethyl acetate/petroleum ether 1:2) 0.72; IR (KBr, cm^{-1}) ν 3049, 1469, 740; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.38 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 3.65 (s, 6H, CH_3), 6.78 (s, 2H), 6.84 (m, 2H), 7.10 (m, 2H), 7.22 (m, 4H), 7.42 (m, 1H), 7.52 (m, 1H), 7.69 (d, 1H, J=7.5 Hz), 7.75 (s, 1H), 7.89 (s, 1H), 8.31 (d, 1H, J=7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.0 (CH_3), 20.2 (CH_3), 32.7 (2×CH_3), 53.3 (C), 109.1 (2×CH), 115.9 (2×C), 118.6 (2×CH), 121.3 (2×CH), 122.0 (CH), 122.1 (CH), 126.4 (2×CH), 126.6 (2×C), 128.0 (CH), 128.2 (CH), 128.8 (CH), 129.1 (CH), 131.1 (2×CH), 136.3 (C), 137.7 (C), 138.6 (C), 139.2 (C), 140.5 (C), 141.0 (C), 152.7 (2×C), 152.8 (C), 164.5 (C); MS: (ESI-MS, positive mode) m/z 505 $[M+H]^+$, 527 $[M+Na]^+$. HRMS (ESI) calcd for $C_{35}H_{28}N_4Na$: 527.2212; found 527.2224.

*4.2.19. 7,8-Dichloro-11,11-bis-(1-methyl-1H-indol-3-yl)-11H-indeno [1,2-b]quinoxaline (**5i**).* Green prisms (92% yield), mp 186–188 °C; R_f(ethyl acetate/petroleum ether 1:2) 0.68; IR (KBr, cm^{-1}) ν 3047, 1470, 742; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.66 (s, 6H, CH_3), 6.76 (s, 2H), 6.86 (m, 2H), 7.13 (m, 2H), 7.23 (m, 4H), 7.53 (m, 2H), 7.65 (1H, d, J=7.5 Hz), 8.08 (s, 1H), 8.23 (s, 1H), 8.30 (1H, d, J=7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.8 (2×CH_3), 53.4 (C), 109.3 (2×CH), 115.3 (2×C), 118.9 (2×CH), 121.6 (CH), 121.9 (CH), 122.7 (2×CH), 126.5 (2×C), 126.6 (2×CH), 128.6 (CH), 128.9 (CH), 129.4 (CH), 130.5 (CH), 132.2 (2×CH), 132.5 (C), 133.2 (C), 135.4 (C), 137.7 (C), 140.4 (C), 141.2 (C), 153.0 (2×C), 154.8 (C), 166.6 (C); MS: (ESI-MS, positive mode) m/z 545 $[M+H]^+$, 547 $[M+2+H]^+$, 549 $[M+4+H]^+$, 567 $[M+Na]^+$, 569 $[M+2+Na]^+$, 571 $[M+4+Na]^+$. HRMS (ESI) calcd for $C_{33}H_{22}Cl_2N_4Na$: 567.1119; found 567.1104.

4.3. X-ray experiments, structure determination, and refinements

*4.3.1. Crystal data for **3d**.* Single crystal data for compound **3d**: $C_{27}H_{20}N_2O_4$ 436.14, triclinic, space group P-1, unit cell parameters: a=10.4755(11) Å, b=11.2253(11) Å, c=11.3541(19) Å, α=115.209(8)°, β=107.583(8)°, γ=102.220(6)°; d_{calcd}=1.418 g cm^{-3}. Diffraction data were measured with Mo Kα (0.71073 Å) radiation at 296 K using Kappa Apex 2. The structure was solved by direct methods using the SHELXL-97 program. Refinements of F^2 were carried out against all reflection using SHELXL-97. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric position and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The final R-values were $R1$ 0.0382, and $wR2$ 0.1028.

*4.3.2. Crystal data for **3f**.* X-ray data collection for **3f** was carried out on a Huber four circle diffractometer (Mo Kα radiation, λ=0.7107 Å, graphite monochromator) equipped with a Bruker APEX CCD area detector. A total of 28,379 reflections ($2\theta \leq 54°$) were measured in three runs, each with 1150 frames in φ increments of 0.3°. Integration and merging with SAINT and XPREP.[25] Structure solution (SHELXS)[26] and refinement (SHELXL)[26] ran routinely. C, N, and O atoms were refined anisotropically, isotropic displacement parameters were assigned to the hydrogens, which were located from difference syntheses. The asymmetric unit consists of one molecule of the title compound, $C_{27}H_{20}N_2O_2$.

$C_{27}H_{20}N_2O_2$, M_r=404.45, yellow block shaped crystals were grown from chloroform/methanol. Dimensions of the specimen used for X-ray experiments 0.54×0.40×0.15 mm. Space group monoclinic $C2/c$. Lattice constants a=27.645(6) Å, b=7.886(2) Å, c=19.100(4) Å, β=91.82(3)°, cell volume V=4162.(2) $Å^3$, formula units/cell Z=8, X-ray density ρ_x=1.291 g cm^{-3}, $2\theta_{max}$=54°. Number of independent reflections were 4521, observed ($F_o > 4\sigma(F_o)$) 3989, linear absorption coeff. μ=8.2 cm^{-1}, R_{int}=0.030, R_σ=0.018. After convergence of refinements R_1=0.055, R_w=0.146, GoF=1.06.

*4.3.3. Crystal data for **5b**.* X-ray data collection for **5b** was carried out on a Huber four circle diffractometer (Mo Kα radiation, λ=0.7107 Å, graphite monochromator) equipped with a Bruker APEX CCD area detector. A total of 34,576 reflections ($2\theta \leq 54°$) were measured in three runs, each with 1150 frames in φ increments of 0.3°. Integration and merging with SAINT and XPREP.[25] Structure solution (SHELXS)[26] and refinement (SHELXL)[26] ran routinely. C, N, O, and Br atoms were refined anisotropically, isotropic displacement parameters were assigned to the hydrogens, which were located from difference syntheses. The asymmetric unit consists of one molecule of the title compound, $C_{31}H_{18}N_4Br_2$. Absorption correction was made with SADABS.

$C_{31}H_{18}N_4Br_2$, M_r=606.3, yellow block shaped crystals were grown from chloroform/hexane. Dimensions of the specimen used for X-ray experiments 0.50×0.46×0.40 mm. Space group monoclinic $C2/c$. Lattice constants a=21.996(5) Å, b=19.218(4) Å, c=14.002(3) Å, β=121.19(3)°, cell volume V=5063.(2) $Å^3$, formula units/cell Z=8, X-ray density ρ_x=1.591 g cm^{-3}, $2\theta_{max}$=54°. Number of independent reflections were 5491, observed ($F_o > 4\sigma(F_o)$) 4653, linear absorption coeff. μ=32.3 cm^{-1}, R_{int}=0.027, R_σ=0.019. After convergence of refinements R_1=0.050, R_w=0.121, GoF=1.08.

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Supplementary data

^1H and ^{13}C NMR spectra and crystallographic data of all compounds. Crystallographic data in CIF format are available free of charge via the internet. CCDC 752085/734164/734165 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). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.04.084. These data include MOL files and InChiKeys of the most important compounds described in this article.

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