Design, Characterization and Catalytic evaluation of Halometallic Ionic Liquid Incorporated Nd2O3 nanoparticles ([smim][FeCl4]-@Nd2O3) for the Synthesis of N-aryl Indeno Pyrrole derivatives

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General Experimental details

All the chemicals used were of analytical grade and used without further purification. $NdCl_3$ (CDH, India, 98%), NaOH (Alfa Aesar, China, 99%), Dimedone, indanedione and aromatic amines (CDH, India, 98%). Melting points of the synthesized compounds were taken in a Stuart SMP30 instrument and are uncorrected. The IR spectra were recorded on Perkin Elmer RXI spectrometer using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance III 400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard and $DMSOd_6/CDCl_3$ as solvent. ESI-MS was recorded on a Quattro II (ESI) spectrometer. Elemental analyses (C, H and N) were conducted using the Elemental vario EL III elemental analyser. TGA data were obtained with a DSC-60 Shimadzu instrument. TG Analysis was performed in the temperature range 0–750°C at a constant heating rate of 20°C min^{-1} in a nitrogen atmosphere. X-ray diffractograms (XRD) of the catalyst were recorded on a Shimadzu 6100 X-ray diffractometer using Cu Kalfa radiation (λ = 1.54Å) in the range of 2θ = 10–80°, with a scan rate of 8°/min. SEM-EDX characterization of the catalyst was performed on a JEOL JSM-6510 scanning electron microscope equipped with an energy-dispersive X-ray spectrometer operating at 20 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed on spectrometer (Model no. PHI 5000 Versa Prob II, FEI Inc.) with Auger Electron Spectroscopy (AES) module and C60 sputter gun using Kα A1 X-ray source. Origin software was used for fitting analysis using Gaussian function. with Shirely background subtraction. The high resolution spectra was measured with pass energies of 23.5 eV and 0.025eV step. TEM analysis was performed on JEM-2100 F Model (ACC. Voltage: 200 kV) electron microscope.

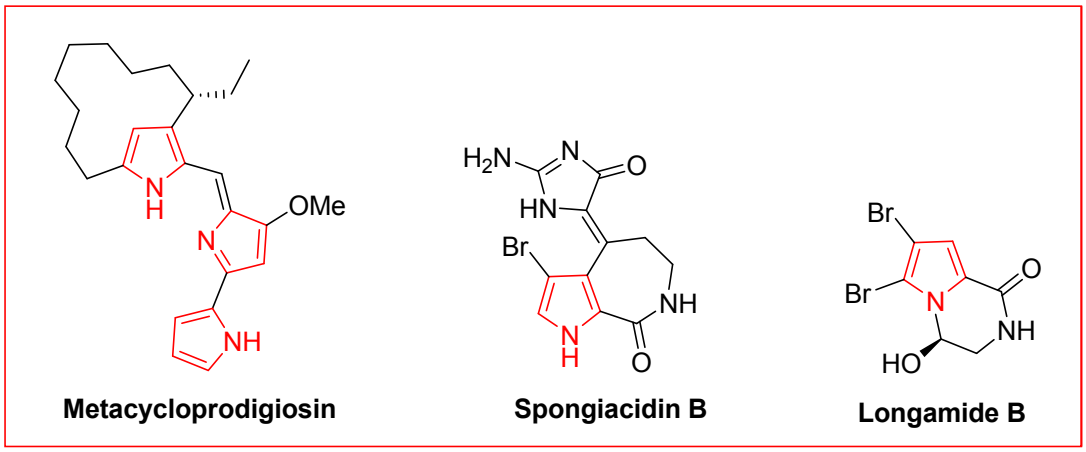

Figure S1: Structures of some biologically active pyrrole fused organic moieties

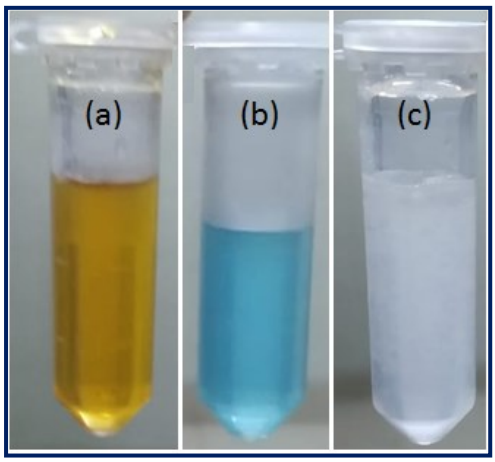

Figure S2: Photographs of (a) IL-1, (b) IL-2 and (c) IL-3

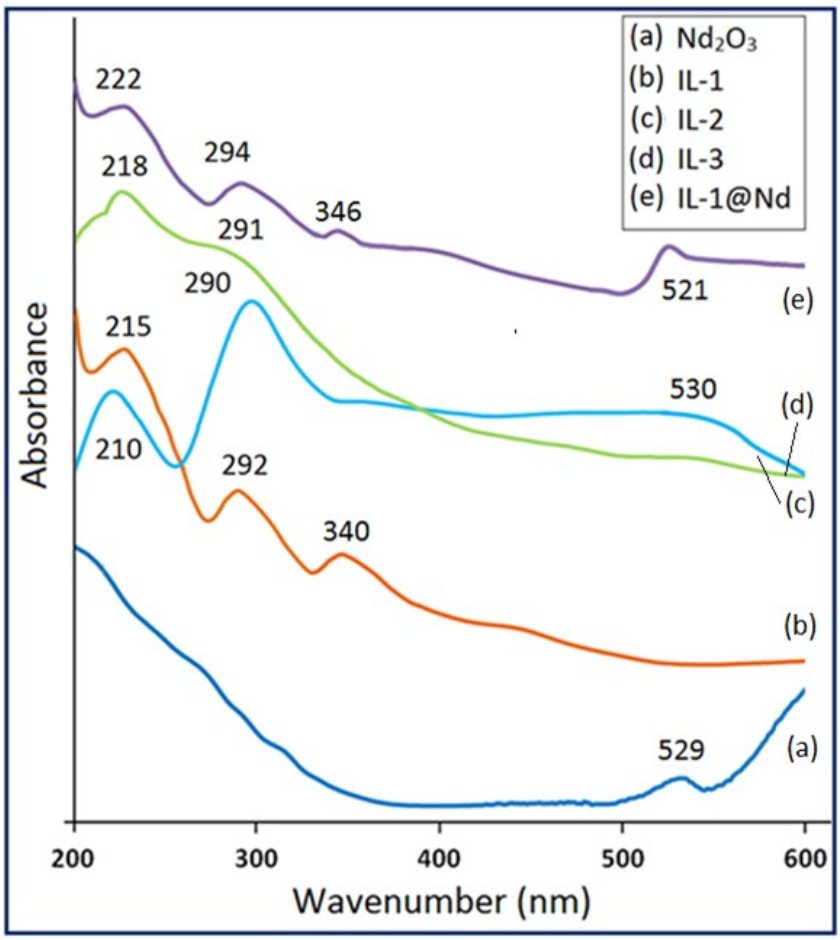

Figure S3: UV-Vis DRS of (a) Nd_2O_3 NPs (b) IL-1 (c) IL-2 (d) IL-3 and (e) IL-1@Nd

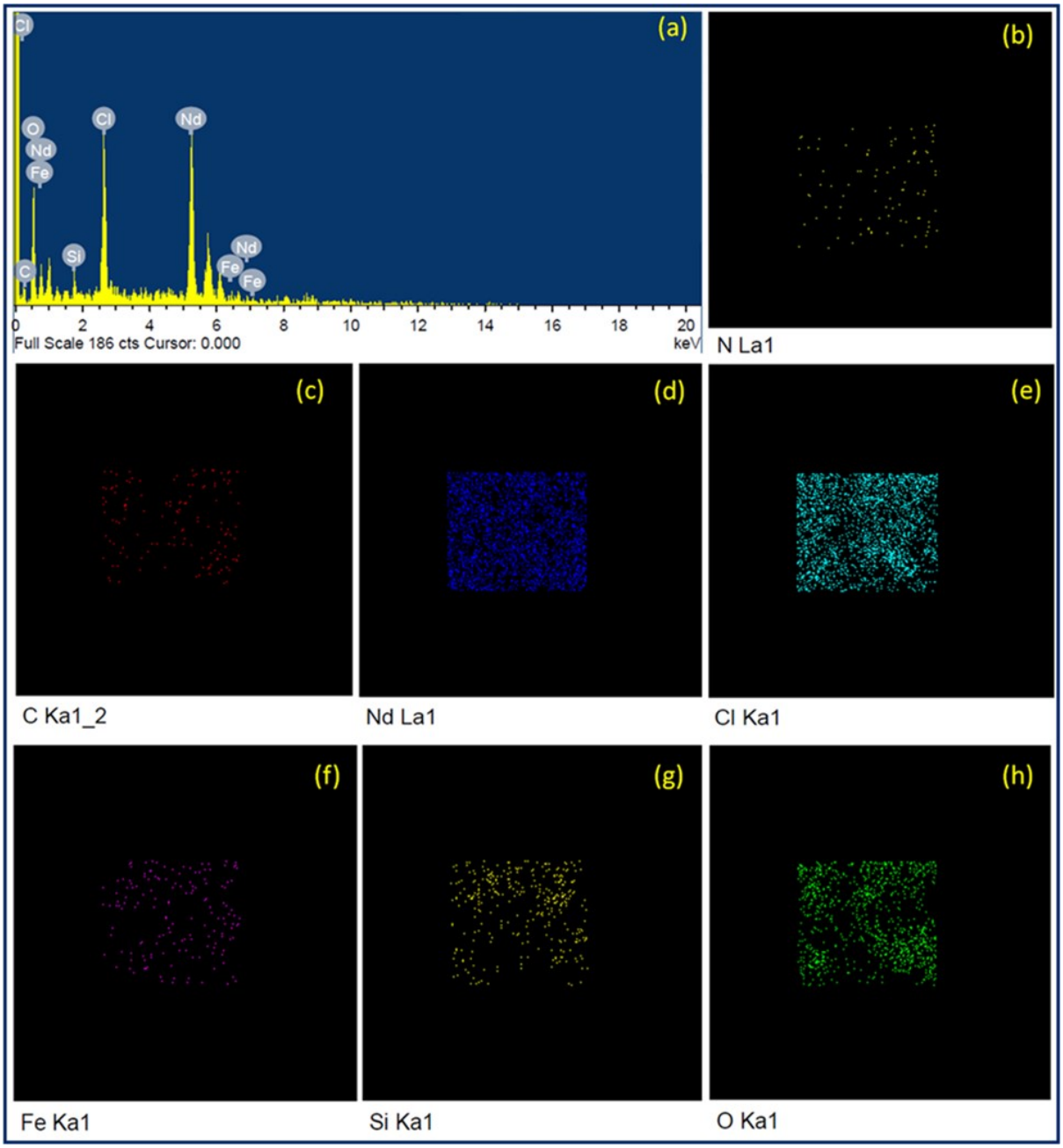

Figure S4: (a) EDX spectrum of IL-1@Nd; Elemental mapping image of (b) Nitrogen (c) Carbon (d) Neodymium (e) Chlorine (f) Iron (g) Silicon and (h) Oxygen

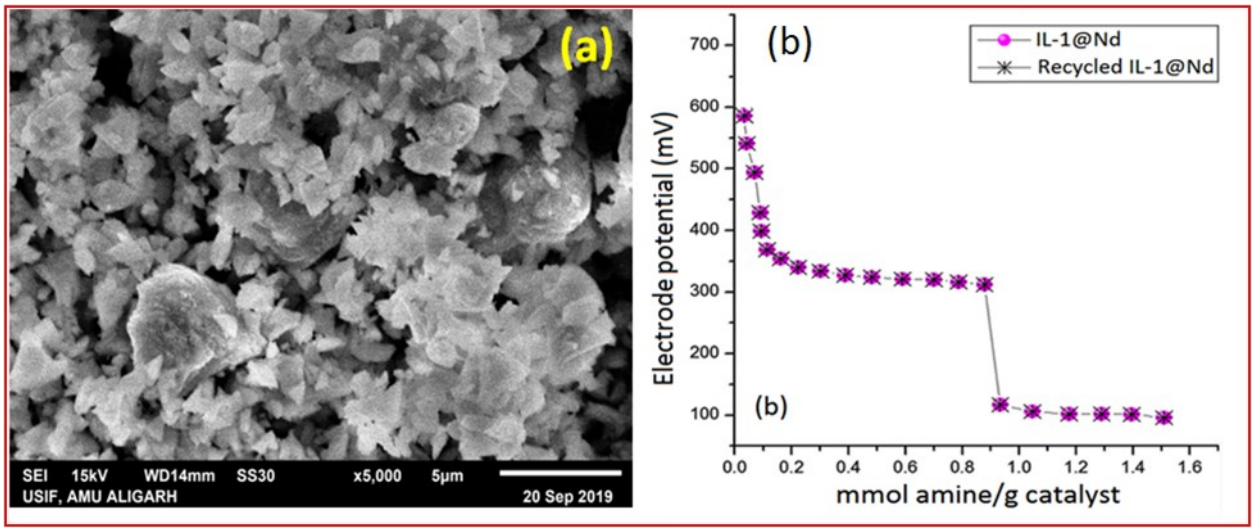

Figure S5: (a) SEM image of recycled IL-1@Nd (b) Comparison of acidic sites of fresh and recycled IL-1@Nd by potentiometric titration

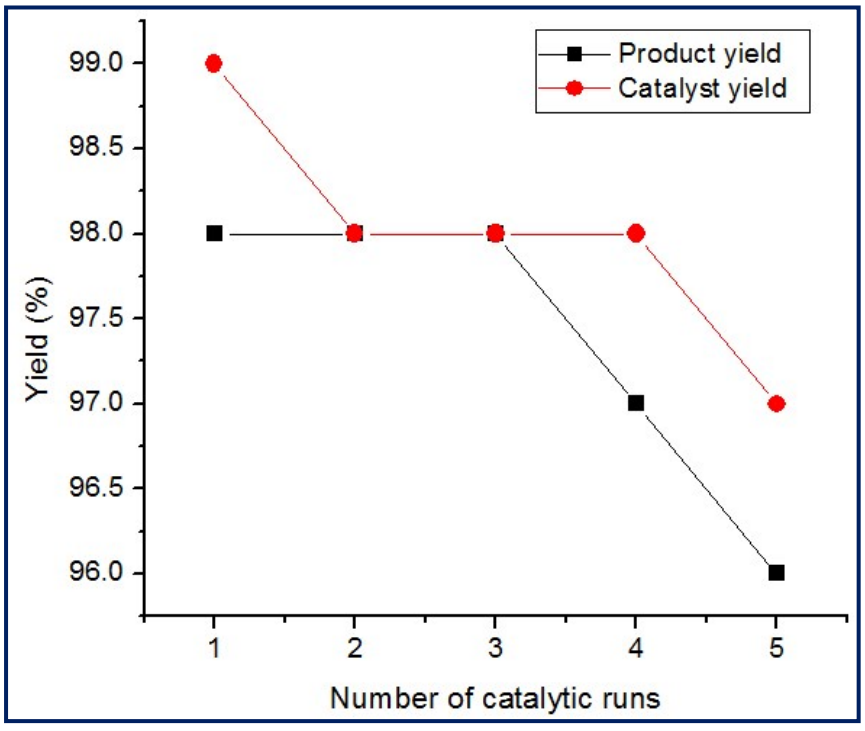

Figure S6: Recycling data of catalyst

Table S1: Effect of solvent on model reaction[a]

Entry	Solvent	Time[b]	Yield[c] (%)
1	Hexane	40 min	74
2	MeCN	28min	82

3	THF	35 min	78
4	DMSO	30min	86
5	MeOH	28 min	90
6	EtOH	25 min	92
7	No solvent	5 min	98

[a]*Reaction conditions*: Dimedone **1a** (2 mmol), 4-chloroaniline **2a** (2 mmol), ninhydrin **3** (2 mmol), IL-1@Nd (80 mg), Solvents/no solvent, T = 80˚C. [b]Reaction progress monitored by TLC. [c]Isolated yield.

Table S2: Effect of temperature on model reaction[a]

Entry	**Temperature**	**Time[b]**	**Yield[c] (%)**
1	25˚C	1h	78
2	40˚C	50 min	82
3	60˚C	22 min	88
4	80˚C	5 min	98
5	100˚C	5 min	98

[a]*Reaction conditions*: Dimedone **1a** (2 mmol), 4-chloroaniline **2a** (2 mmol), ninhydrin **3** (2 mmol), IL-1@Nd (80 mg), Solvent-free. [b]Reaction progress monitored by TLC. [c]Isolated yield.

Table S3: Effect of Loading of IL-1 on model reaction[a]

Entry	**Loading of IL-1 on Nd_2O_3 (v/w)**	**Time[b]**	**Yield[c] (%)**
17	5%	50 min	70
18	10%	40 min	76
19	15%	20 min	80
20	20%	5min	98
21	25%	5 min	98

[a]*Reaction conditions*: Dimedone **1a** (2 mmol), 4-chloroaniline **2a** (2 mmol), ninhydrin **3** (2 mmol), IL-1@Nd (80 mg), Solvent-free, T = 80˚C. [b]Reaction progress monitored by TLC. [c]Isolated yield.

Table S4: Effect of catalyst amount on model reaction[a]

Entry	**Amount of catalyst**	**Time[b]**	**Yield[c] (%)**

1	10 mg	35 min	82
2	20 mg	28 min	86
3	30 mg	19 min	90
4	40 mg	12 min	92
5	50 mg	5 min	98

[a]*Reaction conditions*: Dimedone **1a** (2 mmol), 4-chloroaniline **2a** (2 mmol), ninhydrin **3** (2 mmol), IL-1@Nd, Solvent-free, T = 80˚C. [b]Reaction progress monitored by TLC. [c]Isolated yield.

Table S5: Green matrix calculation for synthesized compounds (**4a-l**)

Compound	%Yield	%AE[a]	%CE[b]	%RME[c]	%OE[d]	PMI[e]	SI[f]	E-factor
4a	87	84.21	94.73	73.46	87.24	5.69	4.23	4.69
4b	94	85.39	94.73	80.22	93.95	4.89	3.57	3.89
4c	92	86.69	94.73	79.90	92.17	4.61	3.28	3.61
4d	94	85.74	94.73	80.63	94.05	4.79	3.47	3.79
4e	90	84.79	94.73	76.49	90.22	5.31	3.91	4.31
4f	93	85.39	94.73	79.34	92.92	4.97	3.61	3.97
4g	91	85.90	95.65	78.39	91.26	4.79	3.46	3.79
4h	89	84.44	94.73	75.43	89.33	5.36	3.97	4.36
4i	94	84.73	95.00	79.88	94.28	4.99	3.68	3.99
4j	88	85.27	95.00	74.97	87.93	5.27	3.85	4.27

a = percent atom economy, b = percent carbon efficiency, c = percent reaction mass efficiency, d = percent overall efficiency, e = process mass intensity, f = solvent intensity

Catalyst amount was not used in the calculations because of its reusability. [48]

Calculations up to the crude product in all cases.

Spectral data of compounds

4b,9b-dihydroxy-7,7-dimethyl-5-(naphthalen-1-yl)-4b,5,7,8-tetrahydroindeno[1,2-b]indole-9,10(6H,9bH)-dione **(4f)**

Greenish yellow solid; m.p.: 186-188°C; IR (KBr) (*v*max, cm^{-1}): 3412, 3076, 2843, 1713, 1690.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.90, 0.96 (s, 6H, 2xCH_3), 1.88 (s, 2H, CH_2), 2.29 (s, 2H, CH_2), 5.11 (s, 1H, OH), 5.95 (s, 1H, OH), 6.49-8.07 (m, 11H, ArH). ^{13}C NMR (100 MHz): δ 26.56, 35.39, 44.91, 49.73, 80.98, 100.14, 105.64, 112.94, 116.27, 121.21, 122.58, 122.90, 124.20, 128.64,132.37, 134.57, 146.90, 147.57, 152.25, 153.46, 158.52, 160.01, 167.53, 190.76, 195.52. ESI-MS (m/z) 425.16 (M^++1). Anal. Calcd ($C_{27}H_{23}NO_4$): C, 76.22; H, 5.45; N, 3.29.Anal. Found ($C_{27}H_{23}NO_4$): C, 76.22; H, 5.45; N, 3.29.

5-(4-chlorophenyl)-4b,10b-dihydroxy-4bH-diindeno[1,2-b:2',1'-d]pyrrole-10,11(5H,10bH)-dione **(4g)**

White solid; m.p.: 210-212 °C; IR (KBr) (*v*max, cm^{-1}): 3426, 3081, 1720, 1694.

^{1}H NMR (DMSO-d_6, 400 MHz): 5.29 (s, 1H, OH), 5.48 (s, 1H, OH), 6.36-7.62 (m, 12H, ArH) .

^{13}C NMR (100 MHz): δ 83.06, 99.08, 102.81, 113.48, 113.67, 114.20, 117.05, 123.95, 125.05, 127.03, 127.53, 127.79, 128.42, 131.66, 133.72, 140.01, 146.34, 153.09, 154.10, 159.65, 161.26, 164.96, 189.01, 194.49.

ESI-MS (m/z) 415.06 (M^{+}+1). Anal.Calcd ($C_{24}H_{14}ClNO_4$): C, 69.32; H, 3.39; Cl, 8.53; N, 3.37. Anal. Found ($C_{24}H_{14}ClNO_4$): C, 69.32; H, 3.39; Cl, 8.53; N, 3.37.

5-(4-bromophenyl)-4b,10b-dihydroxy-4bH-diindeno[1,2-b:2',1'-d]pyrrole-10,11(5H,10bH)-dione **(4h)**

White solid; m.p.: 224-226°C; IR (KBr) (*v*max, cm^{-1}): 3418, 3069, 1718, 1698.^{1}H NMR (DMSO-d_6, 400 MHz): δ5.05 (s, 1H, OH), 5.64 (s, 1H, OH), 6.73-7.56 (m, 12H, ArH). ^{13}C NMR (100 MHz): δ 82.73, 104.50, 108.92, 113.21, 117.03, 119.31, 122.30, 124.41, 125.03, 126.05,127.84, 128.89, 132.35, 138.28, 141.00, 144.70,149.30,152.66, 153.36, 158.27, 160.78, 168.88, 190.36, 195.20. ESI-MS (m/z) 459.01 (M^{+}+1). Anal.Calcd ($C_{24}H_{14}BrNO_4$): C, 62.64; H, 3.07; Br, 17.35; N, 3.04.Anal. Found ($C_{24}H_{14}BrNO_4$): C, 62.63; H, 3.07; Br, 17.36; N, 3.04.

4b,10b-dihydroxy-5-(4-methoxyphenyl)-4bH-diindeno[1,2-b:2',1'-d]pyrrole-10,11(5H,10bH)-dione **(4i)**

Yellow solid; m.p.: 198-200°C; IR (KBr) (*v*max, cm^{-1}): 3421, 3057, 1724, 1689. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 3.90 (s, 3H, OCH_3), 5.34 (s, 1H, OH), 5.66 (s, 1H, OH), 7.25-8.22 (m, 12H, ArH). ^{13}C NMR (100 MHz): 82.89, 101.64, 105.91, 112.43, 115.28, 120.57, 127.30, 127.32, 128.90, 130.24, 132.00, 133.82, 136.86, 141.40, 144.86, 149.54, 152.56, 155.68, 159.38, 163.14, 165.21, 189.18, 194.02. ESI-MS (m/z) 411.11 (M^{+}+1). Anal.Calcd ($C_{25}H_{17}NO_5$): C, 72.99; H, 4.15; N, 3.40. Anal. Found ($C_{25}H_{17}NO_5$): C, 72.99; H, 4.16; N, 3.41.

4b,10b-dihydroxy-5-(4-nitrophenyl)-4bH-diindeno[1,2-b:2',1'-d]pyrrole-10,11(5H,10bH)-dione **(4j)**

Yellow solid; m.p.: 204-206 °C; IR (KBr) (*v*max, cm^{-1}): 3427, 3066, 1731, 1693. ^{1}H NMR (DMSO-d_6, 400 MHz): 5.38 (s, 1H, OH), 5.74 (s, 1H, OH), 6.38-8.22 (m, 12H, ArH) .^{13}C

NMR (100 MHz): δ 82.69, 105.21, 110.78, 114.31, 121.51, 122.91, 124.60, 127.65, 128.72, 129.70, 132.50, 136.50, 139.69, 142.15, 146.82, 148.85, 151.32, 156.56, 158.29, 159.68, 162.93, 190.63, 199.81. ESI-MS (m/z) 426.09 (M^++1). Anal.Calcd ($C_{24}H_{14}N_2O_6$): C, 67.61; H, 3.31; N, 6.57. Anal. Found ($C_{24}H_{14}N_2O_6$): C, 67.61; H, 3.31; N, 6.57.

4b,10b-dihydroxy-5-(3-nitrophenyl)-4bH-diindeno[1,2-b:2',1'-d]pyrrole-10,11(5H,10bH)-dione **(4k)**

White solid; m.p.: 230-232°C; IR (KBr) (*v*max, cm^{-1}): 3417, 3071, 1722, 1696. ^1H NMR (DMSO-d_6, 400 MHz): 5.28 (s, 1H, OH), 5.68 (s, 1H, OH), 7.00-8.33 (m, 12H, ArH). ^{13}C NMR (100 MHz): δ 82.63, 11.50, 115.42, 119.53, 121.16, 123.42, 125.60, 125.82, 128.19, 128.77, 129.74, 131.93, 134.63, 135.75, 137.83, 139.27, 141.42, 146.08, 147.82, 149.21, 150.04, 154.15, 157.86, 160.94, 192.28, 198.66. ESI-MS (m/z) 426.09 (M^++1). Anal.Calcd ($C_{24}H_{14}N_2O_6$): C, 67.61; H, 3.32; N, 6.57. Anal. Found ($C_{24}H_{14}N_2O_6$): C, 67.60; H, 3.31; N, 6.57.

5-(2-chlorophenyl)-4b,10b-dihydroxy-4bH-diindeno[1,2-b:2',1'-d]pyrrole-10,11(5H,10bH)-dione **(4l)**

Yellow solid; m.p.: 242-244°C; IR (KBr) (*v*max, cm^{-1}): 3381, 2961, 1711, 1657. ^1H NMR (DMSO-d_6, 400 MHz): 5.25 (s, 1H, OH), 5.60 (s, 1H, OH), 6.73-7.55 (m, 12H, ArH). ^{13}C NMR (100 MHz): δ 84.83, 114.31, 116.44, 118.91, 120.70, 124.14, 125.94, 128.42, 129.81, 134.04, 135.77, 140.36, 143.89, 145.28, 147.40, 149.53, 154.03, 155.84, 158.95, 163.54, 165.33, 168.13, 193.44, 200. ESI-MS (m/z) 415.82 (M^++1). Anal.Calcd ($C_{24}H_{14}ClNO_4$): C, 69.31; H, 3.39; Cl, 8.53; N, 3.37. Anal. Found ($C_{24}H_{14}ClNO_4$): C, 69.32; H, 3.38; Cl, 8.53; N, 3.36.