# Supporting Information 2

Dihydroindeno[1,2-b]pyrroles: New Al\(^{3+}\) selective off-on chemosensors for bio-imaging in living HepG2 cell

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Experimental Section

General information of materials and instruments:
All commercially available chemicals were purchased from Aldrich, USA or Spectrochem, India, and used without further purification. All solvents were used as received. All the reactions were performed in a round-bottomed flask with magnetic stir bar at room temperature (25-30°C) without taking precautions to exclude air and moisture. The progress of the reaction was checked by glass sheets pre-coated TLC with silica gel (with binder, 300 mesh, Spectrochem) and column chromatography was performed using silica gel (60-120 mesh). \(^1\)H/\(^{13}\)C NMR spectra were recorded in a 300 MHz Bruker instrument using CDCl\(_3\), DMSO-d\(_6\) solvent with TMS as reference. HRMS with an ESI resource were acquired using a Waters XEVO-G2S Q TOF mass spectrometer. 2400 Series II CHNS Analyzer, Perkin Elmer USA was used for elemental analyses. Melting points were recorded with an open capillary on an electrical melting point apparatus. IR experiment was performed using KBr pellets on Perkin Elmer RX-1 FTIR spectrophotometer and the single crystal structure of the synthesized compounds were confirmed by an X-ray crystallography experiment on a Bruker SMART diffractometer.

General procedure for synthesis of Novel Dihydroindeno[1,2-b]pyrroles derivatives:
A mixture of ninhydrin (1 mmol), acetylenedicarboxylates (1 mmol) and amines (1 mmol) were taken in PEG/H\(_2\)O in 1:3 (v/v) ratio (5 mL) and stirred for 2 hour at room temperature (25-30°C). The completion of the reaction indicated by thin layer chromatography (TLC) using aluminium plates coated with silica gel (Merck). After the completion of the reaction, the mixture was diluted with ethyl acetate. As a result bilayer formations take place and the organic crude product was separated from the PEG-H\(_2\)O system and comes into organic layer. The lower part (contain PEG-H\(_2\)O) of the bilayer was separated using separating funnel and it is reused for the next cycle as solvent system. Other part of the solution was evaporated in a rotary evaporator. Finally, the crude residue was subjected to column chromatography to afford the desired product as solid using 20 % ethyl acetate in petroleum ether (60-80 °C) as eluant. Some of the synthesised compounds have been purified by preparative TLC rather than the column chromatography, as it increases the green impact of the methodology. All the obtained products were characterized by IR, \(^1\)H/\(^{13}\)C NMR, melting point measurements, CHN. HRMS of some compounds are given.
Table 3. Structures of synthesized dihydroindeno[1,2-\textit{b}]pyrroles 6(a-j)\textsuperscript{a}

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<tr>
<td>NO\textsubscript{2}</td>
<td>MeO\textsubscript{2}C</td>
<td>6j</td>
<td>78 %</td>
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\textsuperscript{a}Reactions conditions: The reaction was conducted with ninhydrin (1 mmol) and dimethylacetylenedicarboxylate (1 mmol) with different amines (1 mmol) under the optimized condition.
Spectroscopic and Analytical characterization of compounds 4a-4n:

**Diethyl 3a,8b-dihydroxy-4-oxo-1-phenyl-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (4a):** Yield 90 % (381 mg); white solid; Mp: 130°C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.56; IR (νmax, KBr, cm⁻¹): 3393, 2980, 1723, 1667, 1574, 1495, 1264, 1023, 761; ¹H NMR (300 MHz, CDCl₃) δH: 7.89-7.86 (m, 1H, Ar-H), 7.49-7.47 (m, 2H, ArH), 7.39-7.34 (m, 3H, ArH), 7.30-7.29 (m, 1H, ArH), 6.80-6.77 (m, 1H, ArH), 5.15 (broad-s, 2H, OH), 4.18 (q, J=7.1 Hz, 2H, OCH₂), 4.07 (q, J=7.2 Hz, 2H, OCH₂) 1.24 (t, J=7.1 Hz, 3H, CH₃), 1.00 (t, J=7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δC:197.2, 163.8, 161.3, 151.1, 147.1, 135.9, 135.5, 135.1, 130.5, 129.4, 129.1, 129.0, 128.9, 128.6, 125.0, 124.6, 97.8, 95.6, 83.5, 62.3, 60.2, 22.6, 14.3, 13.6; Anal. calcd. for C₂₃H₂₁NO₇; C: 65.24; H: 5.00; N: 3.31. Found: C: 65.32 H: 5.05; N: 3.32%.

**Diethyl 3a,8b-dihydroxy-4-oxo-1-m-tolyl-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (4b):** Yield 91% (398 mg); white solid; Mp:168°C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.54; IR (νmax, KBr, cm⁻¹): 3487, 3329, 2897, 1758, 1734, 1516, 1445,1128,956; ¹H NMR (300 MHz, CDCl₃) δH: 7.81-7.79 (m, 1H, Ar-H), 7.43-7.40 (m, 2H, ArH), 6.99-6.96 (m, 1H, ArH), 6.76-6.73(m, 1H, ArH), 5.03 (broad-s, 2H, OH),4.17-3.98(m, 4H, OCH₂), 2.26(s, 3H, Ar-CH₃), 1.17(t, J=7.2 Hz, 3H, CH₃), 0.95(t, J=6.9 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δC:197.3, 163.9, 161.3, 151.2, 147.1, 139.0, 135.9, 135.4, 130.4, 129.3,129.2, 128.8, 125.8,125.0, 124.6, 97.7, 95.6, 95.5, 83.6, 83.5, 62.2, 60.2, 21.3, 14.3, 13.6; Anal. calcd. for C₂₄H₂₃NO₇; C: 65.90; H: 5.30; N: 3.20. Found: C: 65.96 H: 5.32; N: 3.21%.

**Diethyl 3a,8b-dihydroxy-4-oxo-1-p-tolyl-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (4c):** Yield 93% (407 mg); white solid; Mp:168-170 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.50; IR (νmax, KBr, cm⁻¹): 3479, 3325, 2981, 1751, 1721, 1514, 1439,1028,963; ¹H NMR (300 MHz, CDCl₃) δH: 7.90-7.87 (m, 1H, Ar-H), 7.51-7.48 (m, 2H, ArH), 7.17-7.14 (m, 4H, ArH), 6.86-6.83 (m, 1H, ArH), 5.07 (broad-s, 2H, OH),4.28-4.20(m, 2H, OCH₂),4.18-4.05(m, 2H, OCH₂), 2.39(s, 3H, Ar-CH₃), 1.25(t, J=7.2 Hz, 3H, CH₃), 1.04(t, J=7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δC:197.2, 163.8, 161.2, 151.3, 147.1, 138.6, 135.4, 135.1, 133.0, 130.4, 129.6, 128.7, 125.0, 124.5, 97.3, 95.4, 83.4, 62.2, 60.1, 21.1, 14.2, 13.5; Anal. calcd. for C₂₄H₂₃NO₇; C: 65.90; H: 5.30; N: 3.20. Found: C: 65.98 H: 5.35; N: 3.22%. 

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**Supporting Information**
Diethyl 3a,8b-dihydroxy-1-(4-isopropylphenyl)-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (4d): Yield 92 % (428 mg); white solid; Mp: 186-188 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.59; IR (νmax, KBr, cm⁻¹): 3443, 3378, 1726, 1676, 1498, 1267, 1218, 1128, 762; ¹H NMR (300 MHz, CDCl₃) δH: 7.92-7.90 (m, 1H, Ar-H), 7.56-7.51 (m, 2H, ArH), 7.28-7.18 (m, 4H, ArH), 4.93 (s, 1H, OH), 4.78 (s, 1H, OH), 4.29-4.19 (m, 2H, OCH₂), 4.17-4.08 (m, 2H, OCH₂), 2.99-2.94 (m, 1H, CH), 1.30-1.26 (m, 9H, CH₃), 1.00 (t, J=7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δC:197.1, 163.8, 161.2, 151.4, 149.6, 147.2, 135.5, 135.2, 133.2, 130.4, 128.9, 126.9, 124.9, 124.2, 97.2, 95.4, 83.4, 62.2, 60.2, 33.8, 23.9, 23.4, 14.3, 13.5; Anal. calcd. for C₂₆H₂₇NO₇: C: 67.09; H: 5.85; N: 3.01. Found: C: 67.18 H: 5.90; N: 3.01%.

Diethyl 1-(4-tert-butylphenyl)-3a,8b-dihydroxy-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (4e): Yield 91 % (436 mg); white solid; Mp: 176°C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.60; IR (νmax, KBr, cm⁻¹): 3392, 3180, 1728, 1695, 1492, 1269, 1218, 1138, 763; ¹H NMR (300 MHz, CDCl₃) δH: 7.94-7.71 (m, 1H, Ar-H), 7.58-7.53 (m, 2H, ArH), 7.44-7.41 (m, 2H, ArH), 7.24-7.21 (m, 2H, ArH), 6.90-6.87 (m, 1H, ArH), 4.85 (broad-s, 2H, OH), 4.29-4.20 (m, 2H, OCH₂), 1.37 (s, 9H, CH₃), 1.29 (t, J=3.6 Hz, 3H, CH₃), 1.00 (t, J=7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δC:197.1, 163.9, 161.2, 151.9, 151.4, 147.2, 135.6, 135.2, 133.0, 130.4, 128.6, 125.9, 125.8, 125.0, 124.7, 97.2, 95.4, 83.4, 62.2, 60.2, 34.7, 31.3, 31.1, 14.3, 13.6, 13.5; Anal. calcd. for C₂₇H₃₀NO₇: C: 67.63; H: 6.10; N: 2.92. Found: C: 67.69 H: 6.14; N: 2.93%.

Diethyl 1-(3,4-dimethylphenyl)-3a,8b-dihydroxy-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (4f): Yield 95 % (429 mg); white solid; Mp: 172 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.52; IR (νmax, KBr, cm⁻¹): 3392, 3175, 1729, 1698, 1628, 1468, 1224, 1134, 765; ¹H NMR (300 MHz, CDCl₃) δH: 7.87-7.84 (m, 1H, Ar-H), 7.50-7.46 (m, 2H, ArH), 7.09 (d, J=8.1Hz, 2H, ArH), 6.96-6.93 (m, 1H, ArH), 4.23-4.05 (m, 4H, OCH₂), 2.24 (d, J=15.3Hz, 6H, Ar-CH₃), 1.23 (t, J=7.2Hz, 3H, CH₃), 1.03 (t, J=7.2Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δC:197.2, 163.8, 161.2, 151.3, 147.1, 137.3, 137.1, 135.3, 135.0, 133.2, 130.3, 129.6, 126.0, 125.0, 124.4, 97.1, 95.4, 83.4, 62.1, 59.9, 19.6, 19.4, 14.2, 13.5; Anal. calcd. for C₂₅H₂₅NO₇: C: 66.51; H: 5.58; N: 3.10. Found: C: 66.45 H: 5.54; N: 3.09%; HRMS (ESI) calcd for C₂₅H₂₅NO₇: 474.1529 (M+Na⁺); found: 474.1542
Diethyl 3a,8b-dihydroxy-1-(4-methoxyphenyl)-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (4g): Yield 97 % (440 mg); white solid; Mp: 136 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.51; IR (νmax, KBr, cm⁻¹): 3417, 2981, 1728, 1513, 1445, 1293, 1250, 1161, 770; ¹H NMR (300 MHz, CDCl₃) δH: 7.59-7.56 (m, 1H, Ar-H), 7.25-7.17 (m, 2H, ArH), 7.03-6.90 (m, 2H, ArH), 6.62-6.59 (m, 3H, ArH), 5.18 (broad-s, 2H, OH), 3.96-3.75 (m, 4H, OCH₂), 2.39 (s, 3H, Ar-CH₃), 3.54 (s, 3H, OMe), 0.93 (t, J=7.2 Hz, 3H, CH₃), 0.74 (t, J=7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δC: 197.2, 163.7, 161.2, 159.5, 151.4, 147.0, 135.2, 135.0, 130.5, 130.2, 127.8, 124.9, 124.3, 113.9, 96.7, 95.4, 83.4, 62.0, 59.9, 55.2, 14.0, 13.4; Anal. calcd. for C₂₄H₂₃NO₈; C: 63.57; H: 5.11; N: 3.09. Found: C: 63.65 H: 5.20; N: 3.11%

Diethyl 1-(4-chlorophenyl)-3a,8b-dihydroxy-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (4h): Yield 87 % (398 mg); white solid; Mp: 176 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.49; IR (νmax, KBr, cm⁻¹): 3424, 2953, 1722, 1576, 1444, 1276, 1162, 776; ¹H NMR (300 MHz, CDCl₃) δH: 7.75 (t, J=3.6Hz, 1H, Ar-H), 7.25-7.13 (m, 4H, ArH), 6.73-6.70 (m, 1H, ArH), 5.39-5.26 (broad-s, 2H, OH), 4.10-3.94 (m, 4H, OCH₂), 1.10 (t, J=7.2 Hz, 3H, CH₃), 0.93 (t, J=7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δC: 196.7, 163.3, 160.9, 150.3, 146.6, 135.3, 134.7, 134.2, 134.1, 130.2, 129.9, 128.9, 124.4, 98.1, 95.4, 83.2, 62.1, 60.0, 13.9, 13.3; Anal. calcd. for C₂₃H₂₀ClNO₇; C: 60.33; H: 4.40; N: 3.06. Found: C: 60.41 H: 4.43; N: 3.07%

Diethyl 1-(4-bromophenyl)-3a,8b-dihydroxy-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (4i): Yield 89% (447 mg); white solid; Mp: 176-178 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.50; IR (νmax, KBr, cm⁻¹): 3414, 3178, 1999, 1734, 1695, 1495, 1293, 1126, 760; ¹H NMR (300 MHz, CDCl₃) δH: 7.92-7.89 (m, 1H, Ar-H), 7.55-7.53 (m, 4H, ArH), 7.28-7.19 (m, 2H, ArH), 6.87-6.83 (m, 1H, ArH), 4.99 (broad-s, 2H, OH), 4.28-4.09 (m, 4H, OCH₂), 1.28 (t, J=7.2 Hz, 3H, CH₃), 1.10 (t, J=7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δC: 196.9, 163.6, 161.0, 150.5, 146.9, 135.7, 135.1, 135.0, 132.3, 130.6, 130.2, 124.8, 124.7, 122.5, 98.6, 95.5, 83.3, 62.5, 60.4, 14.2, 13.7; Anal. calcd. for C₂₃H₂₀BrNO₇; C: 54.99; H: 4.01; N: 2.79. Found: C: 54.96 H: 4.00; N: 2.78%; HRMS (ESI) calcd for C₂₃H₂₀BrNO₇: 524.0321 (M+Na⁺); found: 524.0319.

3-(2,3-bis(ethoxycarbonyl)-3a,8b-dihydroxy-4-oxo-3a,4-dihydroindeno[1,2-b]pyrrol-1(8bH)-yl)benzoic acid (4j): Yield 83 % (388 mg); white solid; Mp: 188 °C (EtOH); Rf [40
% EtOAc / petroleum ether (60-80°C): 0.46; IR (νmax, KBr, cm−1): 3393, 3168, 1738, 1696, 1495, 1298, 1217, 1123, 762; 1H NMR (300 MHz, DMSO-d6) δH: 13.27(broad-s, 1H, COOH), 7.99 (d, J=7.5Hz, 1H, Ar-H), 7.82 (d, J=6.0Hz, 1H, Ar-H), 7.74 (s, 1H, Ar-H), 7.69(s, 1H, Ar-H), 7.61-7.53(m, 3H, Ar-H), 6.68(d, J=7.8Hz, 1H, OH), 6.42(s, 1H, OH), 4.07-3.95(m, 4H, OCH2), 1.17 (t, J=6.9Hz, 3H, CH3), 0.96 (t, J=7.1Hz, 3H, CH3); 13C NMR (75 MHz, DMSO-d6) δC: 197.1, 166.6, 162.6, 161.5, 149.9, 136.7, 135.5, 135.0, 132.7, 131.7, 130.5, 129.5, 128.8, 125.0, 123.6, 99.9, 96.5, 84.3, 61.9, 59.1, 14.3, 13.3; Anal. calcd. for C24H21NO9; C: 61.67; H: 4.53; N: 3.00. Found: C: 61.73 H: 4.58; N: 3.02% HRMS (ESI) calcd for C24H21NO9: 490.1114 (M+Na)+; found: 490.1117

4-(2,3-bis(ethoxycarbonyl)-3a,8b-dihydroxy-4-oxo-3a,4-dihydroindeno[1,2-b]pyrrol-1(8bH)-yl)benzoic acid (4k): Yield 80% (374 mg); pale yellow solid; Mp: 206-208°C (EtOH); Rf [40% EtOAc / petroleum ether (60-80°C)]: 0.44; IR (νmax, KBr, cm−1): 3505, 3206, 1574, 1553, 1576, 1432, 1257, 771; 1H NMR (300 MHz, DMSO-d6) δH: 8.03-7.90 (m, 2H, Ar-H), 7.81-7.73 (m, 2H, Ar-H), 7.60 (t, J=2.4Hz, 2H, Ar-H), 7.35 (q, J=4.2Hz, 2H, Ar-H), 6.72(s, 1H, OH), 6.45(s, 1H, OH), 4.07-3.97(m, 4H, OCH2), 1.20-1.14 (m, 3H, CH3), 1.03-1.00 (m, 3H, CH3); 13C NMR (75 MHz, DMSO-d6) δC: 197.1, 166.9, 162.6, 161.5, 149.5, 146.8, 140.9, 135.4, 135.7, 134.9, 130.8, 130.3, 129.9, 127.7, 123.6, 101.1, 96.9, 84.5, 62.1, 59.3, 14.3, 13.5; Anal. calcd. for C24H21NO9; C: 61.67; H: 4.53; N: 3.00. Found: C: 61.72 H: 4.57; N: 3.03%; HRMS (ESI) calcd for C24H21NO9: 490.1114 (M+Na)+; found: 490.1135

Diethyl 3a,8b-dihydroxy-1-(3-nitrophenyl)-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (4l): Yield 81% (379 mg); pale yellow solid; Mp: 204°C (EtOH); Rf [40% EtOAc / petroleum ether (60-80°C)]: 0.47; IR (νmax, KBr, cm−1): 3413, 3176, 1738, 1692, 1492, 1293, 1219, 1126, 763; 1H NMR (300MHz, DMSO-d6) δH: 8.33 (d, J=8.1Hz, 1H, Ar-H), 8.21(s, 1H, Ar-H) 7.87-7.77 (m, 3H, Ar-H), 7.64 (d, J=5.4Hz, 3H, Ar-H), 6.84-6.82 (s, 1H, OH), 6.65(s,1H,OH), 4.08-4.07(m, 4H, OCH2), 1.19(t, J=6.8Hz, 3H, CH3), 1.01 (t, J=6.8Hz, 3H, CH3); 13C NMR (75 MHz, DMSO-d6) δC: 196.9, 162.5, 161.4, 149.1, 148.4, 146.6, 137.7, 135.8, 134.9, 134.6, 130.9, 130.7, 124.9, 123.6, 122.8, 122.7, 101.4, 96.9, 84.4, 62.2, 59.3, 14.2, 13.4; Anal. calcd. for C23H20N2O9; C: 58.97; H: 4.30; N: 5.98. Found: C: 58.91; H: 4.28; N: 5.97%;
Diethyl 3a,8b-dihydroxy-1-(4-nitrophenyl)-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (4m): Yield 76 % (356 mg); pale yellow solid; Mp: 206 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.46; IR (ν_max, KBr, cm⁻¹): 3473, 3187, 1734, 1696, 1467, 1283, 1205, 1145, 761; ¹H NMR (300 MHz, CDCl₃) δ_H: 8.28 (d, J=9.6Hz, 2H, Ar-H), 7.94-7.91 (m, 1H, ArH), 7.60-7.51 (m, 4H, ArH), 6.82 (d, J=6.6Hz, 1H, ArH), 5.13(s, 2H, OH), 4.27-4.12(m, 4H, OCH₂), 1.30 (t, J=7.2Hz, 3H, CH₃), 1.15 (t, J=7.2Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ_C:196.4, 163.3, 160.9, 149.3, 146.8, 146.7, 142.9, 136.0, 134.9, 130.9, 127.7, 125.0, 124.7, 124.3, 101.4, 96.2, 83.4, 62.9, 60.7, 14.2, 13.7; Anal. calcd. for C_{23}H_{20}N_{2}O_{9}; C : 58.97; H: 4.30; N: 5.98. Found: C: 58.90; H: 4.27; N: 5.96%; HRMS (ESI) calcd for C_{23}H_{20}N_{2}O_{9}: 491.1066 (M+Na⁺); found: 491.1106

Diethyl 1-benzyl-3a,8b-dihydroxy-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (4n): Yield 80 % (350 mg); white solid; Mp: 124 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.58; IR (ν_max, KBr, cm⁻¹): 3468, 3182, 1738, 1694, 1465, 1278, 1215, 1128, 764; ¹H NMR (300 MHz, CDCl₃) δ_H: 7.90 (d, J=8.1Hz, 1H, Ar-H), 7.67 (t, J=7.4Hz, 1H, ArH), 7.59-7.55 (m, 2H, ArH), 7.28-7.27 (m, 3H, ArH), 7.21-7.19 (m, 2H, ArH) 4.96(d, J=15.9Hz ,1H, OH), 4.79(d, J=15.9Hz ,2H,Ar-CH₂), 4.62(s, 1H, OH), 4.21-4.12(m, 2H, OCH₂), 3.93-3.86(m, 2H, OCH₂) 1.23 (t, J=7.2Hz, 3H, CH₃), 0.97 (t, J=7.2Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ_C:197.0, 163.7, 161.7, 150.8, 147.5, 136.6, 136.0, 135.2, 130.6, 128.5, 128.3, 127.8, 127.7, 124.7, 124.4, 96.4, 95.1, 83.7, 62.3, 60.0, 46.6, 14.3, 13.3; Anal. calcd. for C_{24}H_{23}NO_{7}; C: 65.90; H: 5.30; N: 3.20. Found: C: 65.85; H: 5.26; N: 3.18%.
Spectroscopic and Analytical characterization of compounds (6a-6j & A)

Dimethyl 3a,8b-dihydroxy-4-oxo-1-p-tolyl-1,3a,4,8b-tetrahydroindo[1,2-b]pyrrole-2,3-dicarboxylate (6a): Yield 90 % (368 mg); white solid; Mp: 168 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.51; IR (νmax, KBr, cm⁻¹): 3475, 3328, 2978, 1754, 1720, 1509, 1436,1028,962; ¹H NMR (300 MHz, CDCl3) δH: 7.92-7.88 (m, 1H, Ar-H), 7.53-7.50 (m, 2H, ArH), 7.21-7.14 (m, 4H, ArH) , 6.84-6.81 (m, 1H, ArH), 5.30(broad-s, 2H, OH), 3.77(s, 3H, OMe), 3.65(s, 3H, OMe), 2.41(s, 3H, Ar-CH3), ; ¹³C NMR (75 MHz, CDCl₃) δC: 197.2, 164.3, 161.8, 151.5, 147.0, 138.6, 135.5, 135.1, 133.1, 130.4, 129.7, 128.4, 125.0, 124.5, 97.7, 95.6, 83.4, 52.9, 51.4, 21.1.; Anal. calcd. for C₂₂H₁₉NO₇; C: 64.54; H: 4.68; N: 3.42. Found: C: 64.59H: 5.38; N: 3.24%;

Dimethyl 3a,8b-dihydroxy-1-(4-isopropylphenyl)-4-oxo-1,3a,4,8b-tetrahydroindo[1,2-b]pyrrole-2,3-dicarboxylate (6b): Yield 91 % (398 mg); grey solid; Mp: 184 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.56; IR (νmax, KBr, cm⁻¹): 3477, 3334, 2978, 1754, 1726, 1524, 1445,1027,961; ¹H NMR (300 MHz, CDCl₃) δH: 7.93-7.90 (m, 1H, Ar-H), 7.57-7.52 (m, 2H, ArH), 7.28-7.19 (m, 4H, ArH) , 6.84-6.81 (m, 1H, ArH), 4.70(broad-s, 2H, OH), 3.79(s, 3H, OMe), 3.67(s, 3H, OMe), 3.00-2.96(m,1H,CH), 1.30 (d, J=6.9 Hz, 6H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δC: 197.1, 164.2, 161.8, 151.6, 149.6, 147.0, 135.6, 135.1, 133.2, 130.5, 128.4, 127.2, 125.0, 124.6, 97.5, 95.5, 83.3, 53.3, 51.5, 33.8, 23.9, 23.8, 14.3, 13.5; Anal. calcd. for C₂₄H₂₃NO₇; C: 65.90; H: 5.30; N: 3.20. Found: C: 65.98H: 5.34; N: 3.21%; HRMS (ESI) calcd for C₂₄H₂₃NO₇: 460.1372 (M+Na)⁺; found: 460.1377

Dimethyl 1-(4-tert-butylphenyl)-3a,8b-dihydroxy-4-oxo-1,3a,4,8b-tetrahydroindo[1,2-b]pyrrole-2,3-dicarboxylate (6c): Yield 94 % (424 mg); white solid; Mp: 172 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.58; IR (νmax, KBr, cm⁻¹): 3393, 3178, 1736, 1696, 1495, 1296, 1225, 1132, 764; ¹H NMR (300 MHz, CDCl₃) δH: 7.92-7.89 (m, 1H, Ar-H), 7.55-7.51(m, 2H, ArH), 7.40(d, J=8.4Hz, 2H, ArH), 7.21 (d, J=8.4Hz, 2H, ArH) , 6.84-6.81 (m, 1H, ArH), 4.88(broad-s, 2H, OH), 3.77(s, 3H, OMe), 3.66(s, 3H, OMe), 1.36(s, 9H, Me); ¹³C NMR (75 MHz, CDCl₃) δC: 197.1, 164.3, 161.8, 151.9,151.6, 147.0, 135.6, 135.1, 132.9, 130.5, 128.1, 126.0, 125.0, 124.6, 97.5, 95.6, 83.4, 53.0, 51.5, 34.7, 31.3.; Anal. calcd. for C₂₅H₂₅NO₇; C: 66.51; H: 5.58; N: 3.10. Found: C: 66.47H: 5.55; N: 3.09%; HRMS (ESI) calcd for C₂₅H₂₅NO₇: 474.1529 (M+Na)⁺; found: 474.1587
Dimethyl 3a,8b-dihydroxy-1-(4-methoxyphenyl)-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (6d): Yield 95 % (404 mg); pale yellow solid; Mp: 134 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.54; IR (ν max, KBr, cm⁻¹): 3421, 2982, 1725, 1526, 1455, 1296, 1245, 1168, 772; ¹H NMR (300 MHz, CDCl₃) δH: 7.78-7.75 (m, 1H, Ar-H), 7.40 (t, J=4.4Hz, 2H, ArH), 7.08(d, J=9.0Hz, 2H, ArH), 6.80-6.70(m, 3H, ArH), 4.85(broad-s, 2H, OH), 3.73(m, 3H, OCH₃), 3.62(s, 3H, OMe), 3.52(s, 3H, Ar-OMe); ¹³C NMR (75 MHz, CDCl₃) δC:197.2, 164.3, 161.8, 159.6, 151.7, 147.0, 135.6, 135.1, 130.4, 130.2, 128.0, 125.0, 124.6, 114.2, 97.1, 95.5, 83.3, 55.4, 55.9, 51.9; Anal. calcd. for C₂₂H₁₉NO₈: C: 62.12; H: 4.50; N: 3.29. Found: C: 62.18; H: 4.53; N: 3.30%

Dimethyl 1-(4-chlorophenyl)-3a,8b-dihydroxy-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (6e): Yield 86 % (370 mg); white solid; Mp: 172 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.50; IR (ν max, KBr, cm⁻¹): 3420, 2952, 1721, 1569, 1441, 1271, 1161, 775; ¹H NMR (300 MHz, CDCl₃) δH: 7.89 (t, J=3.9Hz, 1H, Ar-H), 7.54 (t, J=3.9Hz, 2H, ArH), 7.38 (d, J=8.1Hz, 2H, ArH), 7.26(d, J=8.7Hz, 2H, ArH), 6.84-6.81 (m, 1H, ArH), 5.17(broad-s, 2H, OH), 3.74(s, 3H, OMe), 3.66(s, 3H, OMe); ¹³C NMR (75 MHz, CDCl₃) δC:197.0, 164.0, 161.6, 150.9, 146.8, 135.8, 135.0, 134.5, 130.6, 129.7, 129.4, 124.7, 98.7, 95.8, 83.4, 53.4, 51.1, 51.5; Anal. calcd. for C₂₁H₁₆ClNO₇: C: 58.68; H: 3.75; N: 3.26. Found: C: 58.75 H: 3.79; N: 3.28%

Dimethyl 1-(2-bromophenyl)-3a,8b-dihydroxy-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (6f): Yield 88 % (417 mg); white solid; Mp: 152 °C (EtOH); Rf [40 % EtOAc / petroleum ether (60-80°C)]: 0.50; IR (ν max, KBr, cm⁻¹): 3397, 2941, 1734, 1570, 1445, 1279, 1173, 771; ¹H NMR (300 MHz, CDCl₃) δH: 7.90-7.89 (m, 1H, Ar-H), 7.82-7.67(m, 1H, ArH), 7.64-7.46 (m, 4H, ArH), 7.42-7.28(m, 1H, ArH), 6.87-6.84 (m, 1H, ArH), 5.36(s, 1H, OH), 5.00 (s, 1H, OH), 3.80(s, 3H, OMe), 3.63 (s, 3H, OMe); ¹³C NMR (75 MHz, CDCl₃) δC: 196.8, 196.5, 164.0, 163.7, 160.8, 150.7, 150.1, 148.7, 146.8, 135.7, 135.5, 135.2, 134.7, 134.1, 133.8, 133.4, 133.2, 133.1, 130.9, 130.5, 130.4, 130.0, 127.9, 127.5, 127.2, 125.3, 124.7, 124.4, 98.1, 96.7, 95.7, 83.1, 82.9, 52.5, 52.4, 51.3, 51.2; Anal. calcd. for C₂₁H₁₆BrNO₇: C: 53.18; H: 3.40; N: 2.95. Found: C: 53.26; H: 3.45; N: 2.97%; HRMS (ESI) calcd for C₂₁H₁₆BrNO₇: 496.0008 (M+Na)⁺; found: 498.0005

3-(3a,8b-dihydroxy-2,3-bis(methoxycarbonyl)-4-oxo-3a,4-dihydroindeno[1,2-b]pyrrole-1(8bH)-yl)benzoic acid (6g): Yield 82 % (360 mg); white solid; Mp: 186°C (EtOH); Rf [40
% EtOAc / petroleum ether (60-80°C): 0.43; IR (ν_max, KBr, cm⁻¹): 3395, 3167, 1734, 1698, 1496, 1297, 1218, 1121, 763; ¹H NMR (300 MHz, DMSO-d₆) δ_H: 13.25(broad-s, 1H, COOH), 8.01-7.99 (m, 2H, ArH), 7.81 (s, 3H, ArH), 7.61(s, 3H,Ar-H), 7.51(s, 1H, ArH), 6.69 (s, 1H, OH), 6.50(s, 1H, OH), 3.62(s, 3H, OCH₃), 3.57(s, 3H, OCH₃); ¹³C NMR (75 MHz, DMSO-d₆) δ_C: 197.5, 167.0, 163.8, 150.5, 147.1, 137.1, 136.0, 135.3, 132.6, 132.2, 131.1, 130.0, 129.5, 129.2, 129.1, 125.3, 124.0, 100.7, 97.1, 84.6, 53.2, 51.3; Anal. calcd. for C₂₂H₁₇NO₉; C: 60.14; H: 3.90; N: 3.19. Found: C: 60.21; H: 3.94; N: 3.22%; HRMS (ESI) calc'd for C₂₂H₁₇NO₉: 462.0801 (M+ Na⁺); found: 462.0844.

4-(3a,8b-dihydroxy-2,3-bis(methoxycarbonyl)-4-oxo-3a,4-dihydroindeno[1,2-b]pyrrol-1(8bH)-yl)benzoic acid (6h): Yield 80 % (351 mg); white solid; Mp: 204 °C (EtOH); Rᶠ [40 % EtOAc / petroleum ether (60-80°C)]: 0.44; IR (ν_max, KBr, cm⁻¹): 3503, 3207, 1753, 1591, 1575, 1434, 1257, 772; ¹H NMR (300 MHz, DMSO-d₆) δ_H: 13.13-13.10(broad-s, 1H, COOH), 8.02 (d, J=7.8Hz, 2H, Ar-H), 7.80 (s, 1H, ArH), 7.61-7.60 (m, 3H, ArH), 7.36(d, J=7.8Hz, 2H, Ar-H), 6.73-6.71(s,1H,OH), 6.52(s, 1H, OH), 3.62-3.60(s, 6H, OCH₃); ¹³C NMR (75 MHz, DMSO-d₆) δ_C: 197.0, 166.8, 163.4, 162.1, 149.6, 146.7, 140.9, 135.7, 134.8, 130.7, 130.3, 129.8, 127.2, 124.9, 123.5, 101.4, 97.0, 84.4, 52.9, 51.0; Anal. calcd. for C₂₂H₁₇NO₉; C: 60.20; H: 3.93; N: 3.21%

Dimethyl 3a,8b-dihydroxy-1-(3-nitrophenyl)-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (6i): Yield 81 % (357 mg); white solid; Mp: 202 °C (EtOH); Rᶠ [40 % EtOAc / petroleum ether (60-80°C)]: 0.47; IR (ν_max, KBr, cm⁻¹): 3438, 1767, 1724, 1576, 1492, 1339, 1277, 1172, 779; ¹H NMR (300 MHz, CDCl₃) δ_H: 8.27-8.24 (m,2H, Ar-H), 7.95-7.92(m, 1H, Ar-H), 7.78-7.75 (m, 1H, ArH), 7.66-7.54 (m, 3H, ArH), 6.82-6.79 (m, 1H, Ar-H), 5.19(s, 1H, OH), 5.04(s, 1H, OH), 3.79(s, 3H, OCH₃), 3.72(s, 3H, OCH₃); ¹³C NMR (75 MHz, CDCl₃) δ_C: 196.5, 163.8, 161.5, 149.9, 148.6, 146.7, 137.7, 136.1, 135.0, 133.8, 131.0, 130.2, 125.1, 124.3, 123.0, 122.7, 100.6, 96.1, 83.4, 53.3, 51.8; Anal. calcd. for C₂₁H₁₆N₂O₉; C: 57.28; H: 3.66; N: 6.36. Found: C: 57.35; H: 3.68; N: 6.37%; HRMS (ESI) calc'd for C₂₁H₁₆N₂O₉: 463.0753 (M+ Na⁺); found: 463.0773

Dimethyl 3a,8b-dihydroxy-1-(4-nitrophenyl)-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-2,3-dicarboxylate (6j): Yield 78 % (344 mg); yellow solid; Mp: 198 °C (EtOH); Rᶠ [40 % EtOAc / petroleum ether (60-80°C)]: 0.46; IR (ν_max, KBr, cm⁻¹): 3432, 1756, 1726, 1576, 1498, 1344, 1275, 1164, 778; ¹H NMR (300MHz, CDCl₃) δ_H: 8.28 (d, J=8.7Hz, 2H,
Ar-H), 7.92-7.90(m, 1H, Ar-H), 7.59-7.54 (m, 4H, ArH), 6.84-6.82 (m, 1H, ArH) , 5.35(s, 1H, OH), 5.18(s, 1H, OH), 3.78(s, 3H, OCH 3), 3.72(s, 3H, OCH 3); 13C NMR (75 MHz, CDCl 3 ) δC:196.4, 163.7, 161.5,149.9, 146.7, 142.8, 136.1, 134.8, 130.9, 127.5, 125.0, 124.7, 124.6,124.3, 101.6, 96.4, 83.4, 53.4, 51.8; Anal. calcd. for C21H16N2O9; C: 57.28; H: 3.66; N: 6.36. Found: C: 57.37; H: 3.69; N: 6.38%; HRMS (ESI) calcd for C21H16N2O9: 463.0753 (M+Na)+; found: 463.0786

Diethyl 2-(phenylamino)fumarate (Intermediate A):

1H NMR (300MHz, CDCl 3 ) δH: 9.75(s ,1H, NH-Ar), 8.00 (d, J=8.2Hz, 2H, Ar-H), 6.88 (d, J=8.7Hz, 2H, Ar-H), 5.57 (s, 1H, -CH), 4.24-4.16(m, 4H, OCH 2), 1.29 (t, J=7.1Hz, 3H, CH 3), 1.15 (t, J=7.1Hz, 3H, CH 3); 13C NMR (75 MHz, CDCl 3 ) δC:170.8, 169.1, 164.0, 146.4, 145.3, 132.4, 131.5, 123.9, 119.2, 113.8, 97.7, 62.4, 60.4, 14.3, 13.7; HRMS (ESI) calcd for C15H17NO6: 308.1125 (M+H)+; found: 308.1122.
Copy of $^1$H and $^{13}$C NMR spectra of synthesized compounds (4a-4n):

$^1$H NMR of compound 4a

$^{13}$C NMR of compound 4a
$^1$H NMR of compound 4b

$^{13}$C NMR of compound 4b
**Supporting Information**

**1H NMR of compound 4c**

![1H NMR of compound 4c](image)

**13C NMR of compound 4c**

![13C NMR of compound 4c](image)
$^1$H NMR of compound 4d

$^{13}$C NMR of compound 4d
$^1$H NMR of compound 4e

$^{13}$C NMR of compound 4e
\(^1\)H NMR of compound 4f

\(^{13}\)C NMR of compound 4f
$^{1}$H NMR of compound 4g

$^{13}$C NMR of compound 4g
$\text{^1H NMR of compound 4h}$

$\text{^{13}C NMR of compound 4h}$
$^{1}H$ NMR of compound 4i

$^{13}C$ NMR of compound 4i
\( ^1H \text{ NMR of compound 4j} \)

\( ^{13}C \text{ NMR of compound 4j} \)
$^{1}$H NMR of compound 4k

$^{13}$C NMR of compound 4k
$^1$H NMR of compound 41

$^{13}$C NMR of compound 41
$^1$H NMR of compound 4m

$^{13}$C NMR of compound 4m
$^1$H NMR of compound 4n

$^{13}$C NMR of compound 4n
Copy of $^1$H and $^{13}$C NMR spectra of synthesized compounds (6a-6j):

$^1$H NMR of compound 6a

$^{13}$C NMR of compound 6a
$^1$H NMR of compound 6b

$^{13}$C NMR of compound 6b
$^1$H NMR of compound 6c

$^{13}$C NMR of compound 6c
$^1$H NMR of compound 6d

$^{13}$C NMR of compound 6d
$^1$H NMR of compound 6e

$^{13}$C NMR of compound 6e
$^1$H NMR of compound 6f

$^{13}$C NMR of compound 6f
$^1$H NMR of compound 6g

$^{13}$C NMR of compound 6g
$^1$H NMR of compound 6h

$^{13}$C NMR of compound 6h
$^1$H NMR of compound 6i

$^{13}$C NMR of compound 6i
\[ \text{\textsuperscript{1}H NMR of compound 6j} \]

\[ \text{\textsuperscript{13}C NMR of compound 6j} \]
Copy of $^1$H and $^{13}$C NMR spectra of Intermediate A:

$^1$H NMR of Intermediate A

$^{13}$C NMR of Intermediate A