SUPPORTING INFORMATION

A simple and efficient synthesis of highly substituted indeno[1,2-b]pyrrole and acenaphtho[1,2-b]pyrrole derivatives by tandem three-component reactions

Songlei Zhu 1†, Xiaodong Tang 1†, Ying Ma 1, Ren Wen 2, Lanqi Cen 1, Panwei Gong 1, and Jing Wang 1, *

1. Department of Chemistry, School of Pharmacy, Xuzhou Medical University, Xuzhou Jiangsu 221004, China;
2. Nanjing Hicin Pharmaceutical Co., Ltd, Nanjing, Jiangsu 210009, China

*To whom correspondence should be addressed.
E-mail: songleizhu@xzmc.edu.cn
Phone: 86-516-83262098

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1. Experimental

1.1. General

Melting points were recorded on an Electrothermal digital melting point apparatus and uncorrected. IR Spectra were recorded on a Nicolet FT-IR500 spectrophotometer using KBr optics. $^1$H NMR and $^{13}$C MNR spectra were recorded on a JMTC-400/54/SS spectrometer using DMSO-$d_6$ as solvent and TMS as internal standard. HRMS analyses were conducted on a Bruker micro-TOF-Q-MS analyzer. X-Ray diffraction data were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo-Kα radiation.

1.2. Typical experimental procedure

1.2.1 Typical experimental procedure for 4

A mixture of an equimolar amount of 1,3-dicarbonyl compound 2 (0.5 mmol) and tryptamine 3 (0.5 mmol) was stirred in ethanol at room temperature for 1h. Ninhydrin 1 (0.5 mmol) was then added to this solution and stirred at room temperature for 0.5-1h. Completion of the reaction was monitored with TLC, the mixture was poured into cold water, then filtered and washed with EtOH (95%). The precipitate was purified by recrystallization from EtOH to give the product 4.

1.2.2 Typical experimental procedure for 6

A mixture of an equimolar amount of 1,3-dicarbonyl compound 2 (0.5 mmol) and tryptamine 3 (0.5 mmol) was stirred in ethanol at room temperature for 1h. Acenaphthenequinone 5 (0.5 mmol) was then added to this solution and stirred at room temperature for 0.5-1h. Completion of the reaction was monitored with TLC, the mixture was poured into cold water, then filtered and washed with EtOH (95%). The precipitate was purified by recrystallization from EtOH to give the product 6.

1.2.3 Typical experimental procedure for 8

A mixture of an equimolar amount of 1,3-dicarbonyl compound 2 (0.5 mmol) and benzylamine 7 (0.5 mmol) were stirred in ethanol at room temperature for 2h. Ninhydrin 1 (0.5 mmol) was then added to this solution and stirred at room temperature for 0.5-1h. Completion of the reaction was monitored with TLC, the reaction mixture was poured into ice cold water. Then, the addition of brine solution
to the reaction mixture brought the precipitate. The precipitate was filtered, washed with water to give the product 8. The crystal for X-ray diffraction was developed by recrystallization from EtOH.

2. X-Ray crystallographic data

![Crystal structure of 6d with ethanol solvent](image)

**Figure 1.** The crystal structure of 6d with ethanol solvent

| Table 1. Crystallographic data of compound 6d (CCDC: 1866992) |
|---------------------------------------------------------------|
| Empirical formula                                            | C_{32}H_{36}N_{2}O_{5} |
| Formula weight                                               | 528.63                |
| Temperature                                                  | 298(2) K              |
| Wavelength                                                   | 0.71073 Å             |
| Crystal system, space group                                   | Triclinic, P-1        |
| a = 9.9141(9) Å                                             | alpha = 117.069(3) deg. |
| b = 12.5687(11) Å                                           | beta = 93.6000(10) deg. |
| c = 13.6349(12) Å                                           | gamma = 107.657(2) deg. |
| Volume                                                       | 1400.7(2) Å^3         |
| Z, Calculated density                                         | 2, 1.253 Mg/m^3       |
| Absorption coefficient                                       | 0.085 mm^{-1}         |
| F(000)                                                       | 564                   |
| Crystal size                                                 | 0.30 x 0.18 x 0.14 mm |
| Theta range for data collection                              | 2.35 to 25.02 deg.    |
| Limiting indices                                             | -11<=h<=11, -11<=k<=14, -16<=l<=15 |
| Reflections collected / unique                               | 6978 / 4822 [R(int) = 0.0878] |
| Data / restraints / parameters                               | 4822 / 0 / 378        |
| Goodness-of-fit on F^2                                        | 0.87                  |
| Final R indices [I>2sigma(I)]                                | R1 = 0.0941, wR2 = 0.2203 |
| R indices (all data)                                         | R1 = 0.2250, wR2 = 0.2842 |
Largest diff. peak and hole 0.483 and -0.279 e.A^-3

Figure 2. The crystal structure of 8f

Table 2. Crystallographic data of compound 8f (CCDC: 1866994)

| Property                                      | Value                                            |
|-----------------------------------------------|--------------------------------------------------|
| Empirical formula                             | C_{21}H_{19}NO_{4}                               |
| Formula weight                                | 349.37                                           |
| Temperature                                   | 298(2) K                                        |
| Wavelength                                    | 0.71073 Å                                       |
| Crystal system, space group                   | Monoclinic, P2(1)/n                              |
| a                                             | 8.1950(9) Å                                     |
| alpha                                         | 90 deg.                                         |
| b                                             | 16.7069(15) Å                                   |
| beta                                          | 102.369(2) deg.                                 |
| c                                             | 12.8179(12) Å                                   |
| gamma                                         | 90 deg.                                         |
| Volume                                        | 1714.2(3) Å                                     |
| Z, Calculated density                         | 4, 1.354 Mg/m^3                                  |
| Absorption coefficient                        | 0.094 mm^-1                                     |
| F(000)                                        | 736                                              |
| Crystal size                                  | 0.45 x 0.21 x 0.18 mm                           |
| Theta range for data collection               | 2.44 to 25.02 deg.                              |
| Limiting indices                              | -9<=h<=8, -19<=k<=18, -15<=l<=15                 |
| Reflections collected / unique                | 8456 / 3003 [R(int) = 0.0420]                    |
| Data / restraints / parameters                | 3003 / 0 / 235                                  |
| Goodness-of-fit on F^2                        | 1.017                                            |
| Final R indices [I>2sigma(I)]                 | R1 = 0.0465, wR2 = 0.1078                        |
|                                               | R1 = 0.0854, wR2 = 0.1269                       |
| Largest diff. peak and hole                   | 0.246 and -0.241 e.A^-3                         |
3. Characterization data of compounds

4a) methyl 1-((2-(1H-indol-3-yl)ethyl)-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate

Yellow solid; m.p.: 149-151°C; IR(\text{cm}^{-1}): 744, 1194, 1356, 1437, 1551, 1655, 1717, 3410; $^1$H NMR (400 MHz, DMSO-$d_6$; δ, ppm): 2.22 (s, 3H, CH$_3$), 2.92-3.00 (m, 1H, CH), 3.14-3.21 (m, 1H, CH), 3.55 (s, 3H, OCH$_3$), 3.72-3.80 (m, 1H, CH), 5.67 (s, 1H, OH), 6.77 (s, 1H, OH), 7.02 (t, $J$=8.0 Hz, 1H, ArH), 7.10 (t, $J$=8.0 Hz, 1H, ArH), 7.29 (s, 1H, ArH), 7.37 (d, $J$=8.0 Hz, 1H, ArH), 7.56 (t, $J$=8.0 Hz, 1H, ArH), 7.63 (d, $J$=8.0 Hz, 1H, ArH), 7.70-7.77 (m, 2H, ArH), 7.89 (d, $J$=8.0 Hz, 1H, ArH), 10.92 (s, 1H, NH); $^{13}$C NMR (100 MHz, DMSO-$d_6$; δ, ppm): 13.16, 27.45, 43.10, 50.15, 84.97, 94.74, 95.15, 111.74, 111.99, 118.86, 118.97, 121.56, 123.50, 123.72, 124.96, 127.62, 130.64, 135.51, 136.01, 136.73, 148.68, 160.53, 166.27, 198.83. HRMS calcd for C$_{24}$H$_{22}$N$_2$O$_5$ [M+H]$^+$: 418.1529, found: 418.1545.

4b) ethyl 1-((2-(1H-indol-3-yl)ethyl)-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate

Yellow solid; m.p.: 121-123°C; IR(\text{cm}^{-1}): 744, 1175, 1339, 1414, 1551, 1655, 1717, 3408; $^1$H NMR (400 MHz, DMSO-$d_6$; δ, ppm): 1.17 (t, $J$=8.0 Hz, 3H, CH$_3$), 2.19 (s, 3H, CH$_3$), 2.87-2.95 (m, 1H, CH), 3.09-3.17 (m, 1H, CH), 3.67-3.75 (m, 1H, CH), 3.91-4.06 (m, 3H, CH$_2$+CH), 5.55 (s, 1H, OH), 6.74 (s, 1H, OH), 6.99 (t, $J$=8.0 Hz, 1H, ArH), 7.06 (t, $J$=8.0 Hz, 1H, ArH), 7.26 (s, 1H, ArH), 7.33 (d, $J$=8.0 Hz, 1H, ArH), 7.53 (t, $J$=8.0 Hz, 1H, ArH), 7.59 (d, $J$=8.0 Hz, 1H, ArH), 7.67-7.74 (m, 2H, ArH), 7.86 (d, $J$=8.0 Hz, 1H, ArH), 10.89 (s, 1H, NH); $^{13}$C NMR (100 MHz, DMSO-$d_6$; δ, ppm): 13.18, 15.13, 27.47, 43.08, 58.28, 84.98, 94.83, 95.10, 111.76, 111.98, 118.86, 118.96, 121.56, 123.49, 123.69, 124.97, 127.62, 130.63, 135.54, 135.98, 136.73, 148.73, 160.18, 166.79, 198.75. HRMS calcd for C$_{25}$H$_{24}$N$_2$O$_5$ [M+H]$^+$: 432.1685, found: 432.1701.
4c) isopropyl 1-(2-(1H-indol-3-yl)ethyl)-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindenoc[1,2-b]pyrrole-3-carboxylate

Yellow soid; m.p.: 101-103°C; IR cm⁻¹: 743, 1107, 1175, 1416, 1553, 1647, 1718, 3412; ¹H NMR (400 MHz, DMSO-d₆; δ, ppm): 1.18 (t, J=8.0 Hz, 6H, 2CH₃), 2.20 (s, 3H, CH₃), 2.86-2.94 (m, 1H, CH), 3.10-3.16 (m, 1H, CH), 3.67-3.75 (m, 1H, CH), 3.92-4.00 (m, 1H, CH), 4.81-4.87 (m, 1H, CH), 5.42 (s, 1H, OH), 6.72 (s, 1H, OH), 6.98 (t, J=8.0 Hz, 1H, ArH), 7.06 (t, J=8.0 Hz, 1H, ArH), 7.26 (s, 1H, ArH), 7.34 (d, J=8.0 Hz, 1H, ArH), 7.53 (t, J=8.0 Hz, 1H, ArH), 7.59 (d, J=8.0 Hz, 1H, ArH), 7.67-7.74 (m, 2H, ArH), 7.86 (d, J=8.0 Hz, 1H, ArH), 10.88 (s, 1H, NH), 13C NMR (100 MHz, DMSO-d₆; δ, ppm): 13.22, 22.54, 27.50, 43.06, 65.28, 85.00, 95.04, 111.79, 111.98, 118.87, 118.96, 121.56, 123.50, 123.62, 124.96, 127.62, 130.62, 135.54, 135.95, 136.74, 148.83, 159.82, 163.35, 198.77. HRMS calcd for C₂₆H₂₆N₂O₅ [M+H]+: 446.1842, found: 446.1838.

4d) tert-butyl 1-(2-(1H-indol-3-yl)ethyl)-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindenoc[1,2-b]pyrrole-3-carboxylate

Yellow soid; m.p.: 110-112°C; IR cm⁻¹: 743, 1153, 1366, 1458, 1560, 1655, 1718, 3412; ¹H NMR (400 MHz, DMSO-d₆; δ, ppm): 1.41 (s, 9H, 3CH₃), 2.18 (s, 3H, CH₃), 2.85-2.92 (m, 1H, CH), 3.08-3.15 (m, 1H, CH), 3.66-3.74 (m, 1H, CH), 3.90-3.98 (m, 1H, CH), 5.28 (s, 1H, OH), 6.69 (s, 1H, OH), 6.99 (t, J=8.0 Hz, 1H, ArH), 7.06 (t, J=8.0 Hz, 1H, ArH), 7.25 (s, 1H, ArH), 7.34 (d, J=8.0 Hz, 1H, ArH), 7.53 (t, J=8.0 Hz, 1H, ArH), 7.59 (d, J=8.0 Hz, 1H, ArH), 7.68-7.74 (m, 2H, ArH), 7.85 (d, J=8.0 Hz, 1H, ArH), 10.88 (s, 1H, NH), 13C NMR (100 MHz, DMSO-d₆; δ, ppm): 13.12, 27.53, 28.95, 43.01, 78.24, 84.97, 94.93, 96.01, 111.81, 111.98, 118.87, 118.96, 121.56, 123.50, 123.62, 124.96, 127.62, 130.60, 135.54, 135.95, 136.74, 148.83, 159.82, 165.35, 198.77. HRMS calcd for C₂₇H₂₈N₂O₅ [M+H]+: 460.1998, found: 460.1969.

4e) benzyl 1-(2-(1H-indol-3-yl)ethyl)-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindenoc[1,2-b]pyrrole-3-carboxylate

Yellow soid; m.p.: 100-102°C; IR cm⁻¹: 743, 1157, 1340, 1412, 1547, 1655, 1718, 3423; ¹H NMR (400 MHz, DMSO-d₆; δ, ppm): 2.21 (s, 3H, CH₃), 2.89-2.96 (m, 1H, CH), 3.11-3.18 (m, 1H, CH), 3.70-3.78 (m, 1H, CH), 3.96-4.03 (m, 1H, CH), 5.28 (s, 1H, OH), 6.69 (s, 1H, OH), 5.08 (s, 2H, CH₂), 5.69 (s, 1H, OH), 6.80 (s, 1H, OH), 6.99 (t, J=8.0 Hz, 1H, ArH), 7.06 (t, J=8.0 Hz, 1H,
ArH), 7.22-7.26 (m, 2H, ArH), 7.31-7.35 (m, 3H, ArH), 7.46 (d, J=8.0 Hz, 1H, ArH), 7.54 (t, J=8.0 Hz, 1H, ArH), 7.60 (d, J=8.0 Hz, 1H, ArH), 7.69-7.75 (m, 2H, ArH), 7.87 (d, J=8.0 Hz, 1H, ArH), 10.89 (s, 1H, NH); 13C NMR (100 MHz, DMSO-d6; δ, ppm): 13.33, 27.42, 43.16, 63.97, 85.10, 94.57, 95.20, 111.74, 111.99, 118.87, 118.98, 121.57, 123.54, 123.71, 125.02, 127.63, 127.69, 128.65, 130.69, 135.60, 136.04, 136.74, 138.43, 148.66, 160.99, 166.58, 198.88.; HRMS calcd for C30H26N2O5 [M+H]+: 494.1842, found: 494.1853.

4f) 1-(2-(1H-indol-3-yl)ethyl)-3-acetyl-3a,8b-dihydroxy-2-methyl-3a,8b-dihydroindenof1,2-bpyrrol-4(1H)-one
Yellow solid; m.p.: 164-166°C; IR(cm⁻¹): 748, 1356, 1406, 1481, 1601, 1718, 3412; 1H NMR (400 MHz, DMSO-d6; δ, ppm): 2.26 (s, 3H, CH₃), 2.31 (s, 3H, CH₃), 2.85-2.89(m, 1H, CH), 3.10-3.15 (m, 1H, CH), 3.71-3.76 (m, 1H, CH), 3.91-3.96 (m, 1H, CH), 6.02 (s, 1H, OH), 6.89 (s, 1H, OH), 6.99 (t, J=8.0 Hz, 1H, ArH), 7.06 (t, J=8.0 Hz, 1H, ArH), 7.26 (s, 1H, ArH), 7.34 (d, J=8.0 Hz, 1H, ArH), 7.57 (t, J=8.0 Hz, 2H, ArH), 7.72-7.79 (m, 2H, ArH), 7.91 (d, J=8.0 Hz, 1H, ArH), 10.88 (s, 1H, NH); 13C NMR (100 MHz, DMSO-d6; δ, ppm): 13.92, 27.20, 30.08, 42.83, 85.36, 95.25, 106.97, 111.67, 112.02, 118.79, 119.02, 121.61, 123.65, 123.95, 125.16, 127.57, 130.77, 135.25, 136.45, 136.73, 149.34, 160.59, 193.57, 200.43.; HRMS calcd for C24H22N2O4 [M+H]+: 402.7580, found: 402.1596.

6a) methyl 7-(2-(1H-indol-3-yl)ethyl)-6b,9a-dihydroxy-8-methyl-6b,9a-dihydro-7H-acenaphtho[1,2-b]pyrrole-9-carboxylate
White solid; m.p.: 161-163°C; IR(cm⁻¹): 746, 787, 833, 1003, 1080, 1198, 1383, 1439, 1560, 1637, 3421; 1H NMR (400 MHz, DMSO-d6; δ, ppm): 2.19 (s, 3H, CH₃), 2.84-2.91 (m, 1H, CH), 3.06-3.13 (m, 1H, CH), 3.66 (s, 3H, CH₃), 3.70-3.76 (m, 2H, CH₂), 5.51 (s, 1H, OH), 6.49 (s, 1H, OH), 6.99 (t, J=8.0 Hz, 1H, ArH), 7.07 (t, J=8.0 Hz, 1H, ArH), 7.25 (s, 1H, ArH), 7.34 (d, J=8.0 Hz, 1H, ArH), 7.52-7.62 (m, 4H, ArH), 7.70 (d, J=8.0 Hz, 1H, ArH), 7.76-7.82 (m, 2H, ArH), 10.90 (s, 1H, NH); 13C NMR (100 MHz, DMSO-d6; δ, ppm): 13.05, 19.11, 27.00, 43.19, 50.08, 56.58, 87.65, 99.60, 100.90, 111.96, 112.03, 118.75, 118.86, 119.60, 121.57, 123.58, 123.85, 125.27, 127.62, 128.27, 129.10, 131.30, 136.45, 136.75, 142.28, 145.98, 160.48, 166.46. HRMS calcd for C27H22N2O4 [M+H]+: 440.1736, found: 440.1745.
6b) ethyl 7-(2-(1H-indol-3-yl)ethyl)-6b,9a-dihydroxy-8-methyl-6b,9a-dihydro-7H-acenaphtho[1,2-b] pyrrole-9-carboxylate

White solid; m.p.: 145-147°C; IR (cm⁻¹): 748, 785, 833, 1080, 1173, 1188, 1339, 1418, 1566, 1618, 3366; ¹H NMR (400 MHz, DMSO-d₆; δ, ppm): 1.28 (t, J=8.0 Hz, 3H, CH₃), 2.20 (s, 3H, CH₃), 2.83-2.90 (m, 1H, CH), 3.05-3.12 (m, 1H, CH), 3.67-3.78 (m, 2H, CH₂), 4.07-4.19 (m, 2H, CH₂), 5.47 (s, 1H, OH), 6.46 (s, 1H, OH), 6.99 (t, J=8.0 Hz, 1H, ArH), 7.06 (t, J=8.0 Hz, 1H, ArH), 7.25 (s, 1H, ArH), 7.34 (d, J=8.0 Hz, 1H, ArH), 7.52-7.61 (m, 4H, ArH), 7.70 (d, J=8.0 Hz, 1H, ArH), 7.77 (d, J=8.0 Hz, 1H, ArH), 7.83 (d, J=8.0 Hz, 1H, ArH), 10.89 (s, 1H, NH), ¹³C NMR (100 MHz, DMSO-d₆; δ, ppm): 13.13, 15.38, 27.01, 43.18, 58.28, 87.67, 99.72, 100.84, 111.96, 112.02, 118.75, 119.97, 119.56, 121.55, 123.56, 123.81, 125.24, 127.61, 128.26, 129.03, 131.28, 134.43, 136.73, 142.29, 145.96, 160.24, 166.02. HRMS calcd for C₂₈H₂₆N₂O₄ [M+H]⁺: 454.1893, found: 454.1931.

6c) isopropyl 7-(2-(1H-indol-3-yl)ethyl)-6b,9a-dihydroxy-8-methyl-6b,9a-dihydro-7H-acenaphtho[1,2-b] pyrrole-9-carboxylate

White solid; m.p.: 161-163°C; IR (cm⁻¹): 731, 785, 833, 997, 1080, 1107, 1175, 1400, 1568, 1605, 3325; ¹H NMR (400 MHz, DMSO-d₆; δ, ppm): 1.27 (dd, J₁=8.0 Hz, J₂=16.0 Hz, 6H, 2CH₃), 2.21 (s, 3H, CH₃), 2.81-2.89 (m, 1H, CH), 3.04-3.11 (m, 1H, CH), 3.69-3.74 (m, 2H, CH₂), 4.97-5.03 (m, 1H, CH), 5.42 (s, 1H, OH), 6.45 (s, 1H, OH), 6.99 (t, J=8.0 Hz, 1H, ArH), 7.06 (t, J=8.0 Hz, 1H, ArH), 7.25 (s, 1H, ArH), 7.34 (d, J=8.0 Hz, 1H, ArH), 7.52-7.61 (m, 4H, ArH), 7.70 (d, J=8.0 Hz, 1H, ArH), 7.77 (d, J=8.0 Hz, 1H, ArH), 7.90 (d, J=8.0 Hz, 1H, ArH), 10.89 (s, 1H, NH), ¹³C NMR (100 MHz, DMSO-d₆; δ, ppm): 13.22, 22.83, 22.91, 27.04, 43.17, 58.10, 87.69, 99.96, 100.80, 111.97, 112.02, 118.75, 119.52, 121.55, 121.77, 123.53, 123.80, 125.21, 127.60, 128.24, 128.99, 131.27, 136.43, 136.74, 142.29, 145.98, 159.94, 165.57. HRMS calcd for C₂₉H₂₈N₂O₄ [M+H]⁺: 468.2049, found: 468.2066.
6d) tert-butyl 7-(2-(1H-indol-3-yl)ethyl)-6b,9a-dihydroxy-8-methyl-6b,9a-dihydro-7H-acenaphtho[1,2-b]pyrrole-9-carboxylate

White solid; m.p.: 112-114°C; IR(cm⁻¹): 741, 785, 833, 1080, 1150, 1366, 1393, 1572, 1649, 3349; ¹H NMR (400 MHz, DMSO-d₆; δ, ppm): 1.50 (s, 9H, 3CH₃), 2.18 (s, 3H, CH₃), 2.81 (s, 1H, CH), 3.05 (s, 1H, CH), 3.68 (s, 2H, CH₂), 5.34 (s, 1H, OH), 6.42 (s, 1H, OH), 6.99 (t, J=8.0 Hz, 1H, ArH), 7.06 (t, J=8.0 Hz, 1H, ArH), 7.24 (s, 1H, ArH), 7.34 (d, J=8.0 Hz, 1H, ArH), 7.51-7.60 (m, 4H, ArH), 7.70 (d, J=8.0 Hz, 1H, ArH), 7.77 (d, J=8.0 Hz, 1H, ArH), 7.91 (d, J=8.0 Hz, 1H, ArH), 10.89 (s, 1H, NH); ¹³C NMR (100 MHz, DMSO-d₆; δ, ppm): 13.24, 19.10, 27.07, 29.19, 43.11, 56.56, 78.11, 87.72, 100.68, 100.99, 112.00, 118.74, 118.96, 119.45, 121.41, 121.54, 123.49, 123.78, 125.15, 125.79, 128.24, 129.07, 131.29, 136.41, 136.73, 142.34, 146.23, 159.12, 165.79. HRMS calcd for C₃₀H₃₀N₂O₄ [M+H]+: 482.2206, found: 482.2245.

6e) benzyl 7-(2-(1H-indol-3-yl)ethyl)-6b,9a-dihydroxy-8-methyl-6b,9a-dihydro-7H-acenaphtho[1,2-b]pyrrole-9-carboxylate

White solid; m.p.: 95-97°C; IR(cm⁻¹): 699, 743, 783, 833, 1080, 1167, 1190, 1346, 1416, 1456, 1560, 1649, 3416; ¹H NMR (400 MHz, DMSO-d₆; δ, ppm): 2.22 (s, 3H, CH₃), 2.87 (s, 1H, CH), 3.07 (s, 1H, CH), 3.75 (s, 2H, CH₂), 5.21 (s, 2H, CH₂), 5.56 (s, 1H, OH), 6.52 (s, 1H, OH), 6.99 (t, J=8.0 Hz, 1H, ArH), 7.06 (t, J=8.0 Hz, 1H, ArH), 7.26-7.36 (m, 5H, ArH), 7.41-7.47 (m, 3H, ArH), 7.54-7.62 (m, 3H, ArH), 7.68 (d, J=8.0 Hz, 1H, ArH), 7.78 (d, J=8.0 Hz, 2H, ArH), 10.90 (s, 1H, NH); ¹³C NMR (100 MHz, DMSO-d₆; δ, ppm): 13.22, 26.97, 43.26, 63.98, 87.73, 99.42, 100.92, 111.95, 112.02, 118.75, 118.98, 119.62, 121.55, 121.87, 123.56, 123.84, 125.29, 127.61, 127.97, 128.22, 128.83, 128.95, 131.27, 136.43, 136.75, 138.47, 142.19, 145.83, 160.85, 165.73. HRMS calcd for C₃₃H₂₈N₂O₄ [M+H]+: 516.2049, found: 516.2058.

8a) methyl 1-benzyl-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate

White solid; m.p.: 154-156°C; IR(cm⁻¹): 784, 823, 1101, 1296, 1427, 1562, 1635, 1721, 3398; ¹H NMR (400 MHz, DMSO-d₆; δ, ppm): 1.93 (s, 3H, CH₃), 3.50 (s, 3H, CH₃), 4.75 (d, J=16.0 Hz, 1H, CH), 5.12 (d, J=16.0 Hz, 1H, CH), 5.70 (s, 1H, OH), 6.79 (s, 1H, OH), 7.19-7.29 (m, 5H, ArH), 7.53 (t, J=8.0 Hz, 1H, ArH), 7.65-7.70(m, 2H, ArH), 7.77 (d, J=8.0 Hz, 1H, ArH); ¹³C NMR (100 MHz, DMSO-d₆; δ, ppm): 13.65, 45.38, 50.20, 85.04, 94.63, 95.59, 123.46, 125.27, 127.23, 127.37, 128.84, 130.65, 135.49, 135.86, 139.40, 148.54, 160.86, 166.19, 198.81. HRMS calcd for C₂₃H₁₉NO₅ [M+H]+: 365.1263, found: 365.1279.
8b) **ethyl 1-benzyl-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate**

Yellow solid; m.p.: 72-73°C; IR (cm$^{-1}$): 765, 852, 1091, 1216, 1437, 1545, 1629, 1743, 3421; $^1$H NMR (400 MHz, DMSO-d$_6$; δ, ppm): 1.15 (t, $J=8.0$ Hz, 3H, CH$_3$), 1.92 (s, 3H, CH$_3$), 3.90-4.05 (m, 2H, CH$_2$), 4.75 (d, $J=16.0$ Hz, 1H, CH), 5.10 (d, $J=16.0$ Hz, 1H, CH), 5.61 (s, 1H, OH), 6.78 (s, 1H, OH), 7.20-7.29 (m, 5H, ArH), 7.53 (t, $J=8.0$ Hz, 1H, ArH), 7.64-7.70 (m, 2H, ArH), 7.76 (d, $J=8.0$ Hz, 1H, ArH); $^{13}$C NMR (100 MHz, DMSO-d$_6$; δ, ppm): 13.67, 15.08, 45.36, 58.37, 85.07, 94.58, 95.67, 123.45, 125.27, 127.36, 128.83, 130.64, 135.52, 139.44, 148.56, 160.50, 165.70, 198.73. HRMS calcd for C$_{22}$H$_{21}$NO$_5$ [M+H]$^+$: 379.1420, found: 379.1438.

8c) **isopropyl 1-benzyl-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate**

Pale yellow solid; m.p.: 71-73°C; IR (cm$^{-1}$): 756, 918, 1096, 1285, 1408, 1533, 1667, 1715, 3426; $^1$H NMR (400 MHz, DMSO-d$_6$; δ, ppm): 1.15 (t, $J=8.0$ Hz, 6H, 2CH$_3$), 1.92 (s, 3H, CH$_3$), 4.73-4.84 (m, 2H, CH$_2$), 5.08 (d, $J=16.0$ Hz, 1H, CH), 5.50 (s, 1H, OH), 6.77 (s, 1H, OH), 7.19-7.28 (m, 5H, ArH), 7.52 (t, $J=8.0$ Hz, 1H, ArH), 7.64-7.70 (m, 2H, ArH), 7.76 (d, $J=8.0$ Hz, 1H, ArH); $^{13}$C NMR (100 MHz, DMSO-d$_6$; δ, ppm): 13.67, 22.59, 45.33, 65.40, 85.08, 94.54, 95.85, 123.44, 125.28, 127.23, 127.35, 128.83, 130.63, 135.52, 135.79, 139.46, 148.62, 160.16, 165.25, 198.74. HRMS calcd for C$_{23}$H$_{23}$NO$_5$ [M+H]$^+$: 393.1576, found: 393.1561.

8d) **tert-butyl 1-benzyl-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate**

Yellow solid; m.p.: 83-85°C; IR (cm$^{-1}$): 749, 925, 1163, 1276, 1418, 1556, 1638, 1729, 3398; $^1$H NMR (400 MHz, DMSO-d$_6$; δ, ppm): 1.38 (s, 9H, 3CH$_3$), 1.89 (s, 3H, CH$_3$), 4.74 (d, $J=16.0$ Hz, 1H, CH), 5.06 (d, $J=16.0$ Hz, 1H, CH), 5.37 (s, 1H, OH), 6.74 (s, 1H, OH), 7.18-7.28 (m, 5H, ArH), 7.52 (t, $J=8.0$ Hz, 1H, ArH), 7.65 (t, $J=8.0$ Hz, 1H, ArH), 7.70 (d, $J=8.0$ Hz, 1H, ArH), 7.72 (d, $J=8.0$ Hz, 1H, ArH); $^{13}$C NMR (100 MHz, DMSO-d$_6$; δ, ppm): 13.58, 28.89, 45.28, 78.36, 85.06, 94.46, 96.84, 123.44, 125.26, 127.21, 127.33, 128.82, 130.61, 135.54, 135.77, 139.53, 148.72, 159.64, 165.33, 198.92. HRMS calcd for C$_{24}$H$_{25}$NO$_5$ [M+H]$^+$: 407.1733, found: 407.1749.
8e) benzyl 1-benzyl-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindenof1,2-b]pyrrole-3-carboxylate

Yellow solid; m.p.: 70-71°C; IR(\text{cm}^{-1}): 732, 838, 1119, 1239, 1430, 1562, 1669, 1728, 3411; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm): 1.94 (s, 3H, CH$_3$), 4.77 (d, $J$=16.0 Hz, 1H, CH), 5.02-5.14 (m, 3H, CH$_2$CH), 5.75 (s, 1H, OH), 6.84 (s, 1H, OH), 7.20-7.33 (m, 8H, ArH), 7.45 (d, $J$=8.0 Hz, 1H, ArH), 7.54 (t, $J$=8.0 Hz, 1H, ArH), 7.65-7.73 (m, 2H, ArH), 7.77 (d, $J$=8.0 Hz, 1H, ArH); $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm): 13.81, 45.53, 64.07, 85.16, 94.69, 95.40, 123.50, 125.33, 127.24, 127.38, 127.71, 127.76, 128.64, 128.85, 130.70, 135.58, 135.87, 138.29, 139.31, 148.50, 161.33, 166.52, 198.87. HRMS calcd for C$_{27}$H$_{23}$NO$_5$ [M+H]$^+$: 441.1576, found: 441.1589.

8f) 3-acetyl-1-benzyl-3a,8b-dihydroxy-2-methyl-3a,8b-dihydroindenof1,2-b]pyrrol-4(1H)-one

White solid; m.p.: 175-177°C; IR(\text{cm}^{-1}): 756, 841, 1093, 1216, 1435, 1562, 1674, 1735, 3417; $^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm): 1.97 (s, 3H, CH$_3$), 2.31 (s, 3H, CH$_3$), 4.81 (d, $J$=16.0 Hz, 1H, CH), 5.05 (d, $J$=16.0 Hz, 1H, CH), 6.05 (s, 1H, OH), 6.96 (s, 1H, OH), 7.11 (d, $J$=8.0 Hz, 2H, ArH), 7.16-7.25 (m, 3H, ArH), 7.54 (t, $J$=8.0 Hz, 1H, ArH), 7.65 (t, $J$=8.0 Hz, 1H, ArH), 7.73-7.79 (m, 2H, ArH); $^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm): 14.32, 30.07, 45.21, 85.42, 94.79, 106.51, 123.88, 125.53, 127.05, 127.32, 128.81, 130.73, 135.23, 136.23, 139.04, 149.25, 160.80, 193.76, 200.46. HRMS calcd for C$_{21}$H$_{19}$NO$_4$ [M+H]$^+$: 349.1314, found: 349.1325.
4. Original $^1$HNMR and $^{13}$CNMR spectra

$^1$H for 4a

$^{13}$C for 4a
$^1$H for 4b

$^{13}$C for 4b
$^1$H for 4c

$^{13}$C for 4c
$^1$H for 4d

$^{13}$C for 4d
$^1$H for 4e

$^{13}$C for 4e
$^1$H for 6a

$^{13}$C for 6a
$^1$H for 6b

$^{13}$C for 6b
$^1$H for 6c

$^{13}$C for 6c
$^1$H for 6d

$^{13}$C for 6d
$^1\text{H for 6e}$

$^{13}\text{C for 6e}$
$^1\text{H for 8e}$

$^{13}\text{C for 8e}$
$^1$H for 8f

$^{13}$C for 8f