Supporting Information
for DOI: 10.1055/s-0037-1609655
© Georg Thieme Verlag KG Stuttgart · New York 2018
Table of Contents

1. General information ............................................................... S2
2. General procedure for synthesis ............................................ S2
3. Copies of $^1$H and $^{13}$C NMR-spectra ................................... S9-S26
General information

All reagents were commercial products without further purification, unless otherwise stated. Analytical thin layer chromatography (TLC) was performed using Merck silica gel GF254 plates. Melting points were measured on an X-4 melting point apparatus. $^1$HNMR spectra were recorded on a 400 MHz instrument (Bruker Avance 400 Spectrometer). Chemical shifts (δ) are given in ppm relative to TMS as the internal reference, with coupling constants (J) in Hz. $^{13}$C NMR spectra were recorded at 100 MHz. Chemical shift were reported in ppm with the internal chloroform signal at 77.0 ppm or DMSO-$d_6$ signal at 39.6 ppm as a standard. HRMS (ESI) was measured with a Bruker Daltonics APEXII instrument.

General procedure for synthesis

**Synthesis and property of the solid acid catalyst**

In the typical procedure, 10 g furaldehyde, 5 g hydroxyethylsulfonic acid and 80 mL deionized water was carefully added to 100 mL Teflon-lined stainless steel autoclaves, which were heated in an oven at 200 °C for 5 h. The resulting solid was filtered and washed with water and methanol, and dried in a vacuum oven at 110 °C for 5 h. The acidity of the solid acid was 2.4 mmol/g. The acid strength of it was determined by thermodesorption of chemisorbed ammonia (NH$_3$-TPD). The solid acid had great acid strength in which ammonia was desorbed at 400 to 600 °C.

The scanning electron microscopy (SEM) images of the carbonaceous material show that the resulting particles grow in size with the reaction time with a diameter of 5-10 μm as depicted in figure 3(a, b). The figure shows the morphologies of the materials, micrometer sized, microporous carbon spheres and there were many micro-sized carbon spheres attached to the surface of the big carbon spheres to form the strawberry-like structure (figure a). The carbonaceous obtained from the single furaldehyde formed the carbon spheres with smooth surface (figure c).
Synthesis of 5a,10a-dihydroxy-3-methyl-2,5-disubstituted-2,5,5a,10a-tetrahydroindeno [2′,1′:4,5]pyrrolo[3,2-c]pyridine-1,10-diones 5.

A mixture of 4-hydroxy-6-methyl-2H-pyran-2-one (1, 0.5 mmol), amines (2, 1.0 mmol), and solid acid (10 mg) were submitted in water (3.0 mL) in sealed tube. The mixture was heated at 80 °C until TLC revealed that conversion of starting material was complete about 2 h. Then, 2,2-dihydroxy-1H-indene-1,3(2H)-dione (4, 0.5 mmol) was added and heated at same reaction temperature for another 4 h. The reaction mixture was cooled to room temperature. The solid was filtered and wash with water. The crude product and solid acid were submitted to hot 95% EtOH. The catalyst was filtered, and the pure product 5 was obtained from mother liquid.

Synthesis of 5a,10a-dihydroxy-3-methyl-5-aryl-5a,10a-dihydro-1H-indeno[1,2-b]pyrano[3,4-d]pyrrole-1,10(5H)-diones 7.

A mixture of 4-hydroxy-6-methyl-2H-pyran-2-one (1, 0.5 mmol), amines (2, 0.5 mmol), and solid acid (10 mg) were submitted in water (3.0 mL) in sealed tube. The mixture was stirred at room temperature until TLC revealed that conversion of starting material was complete about 12 h. Then, 2,2-dihydroxy-1H-indene-1,3(2H)-dione (4, 0.5 mmol) was added and heated at 80 °C for another 4 h. The reaction mixture was cooled to room temperature. The solid was filtered and wash with water. The crude product and solid acid were submitted to hot 95% EtOH. The catalyst was filtered, and the pure product 7 was obtained from mother liquid.


Compound 5a (1.0 mmol) and HOAc (0.5 mL) were submitted in EtOH (3.0 mL). The mixture was heated at 80 °C until TLC revealed that conversion of starting material was complete about 3 h. The reaction mixture was cooled to room temperature and diluted with cooling water (30 mL). Then, the resulted solid was filtered and wash with water and
subsequently dried and recrystallized from EtOH (95%) to give pure product.

5a,10a-dihydroxy-3-methyl-2,5-diphenyl-2,5,5a,10a-tetrahydroindeno[2',1':4,5]pyrrolo[3,2-c]
pyridine-1,10-dione (5a)

Yield: 177.0 mg (81%); yellow crystal; mp: 238-240 °C. 1H NMR (400 MHz, CDCl3): \( \delta = \\
7.85-7.86 \text{ (m, 1H, ArH)}, 7.79-7.52 \text{ (m, 10H, ArH)}, 7.20-7.23 \text{ (m, 1H, ArH)}, 7.11-7.14 \text{ (m, 1H, ArH)}, 6.78 \text{ (dd, } J = 5.6, 2.8 \text{ Hz, 1H, ArH)}, 6.41 \text{ (br, s, 1H, OH)}, 5.63 \text{ (s, 1H, CH)}, 5.36 \text{ (s, 1H, OH)}, 1.83 \text{ (s, 3H, CH3)}. 13C NMR (100 MHz, CDCl3): \( \delta = \\
197.3, 161.2, 155.9, 150.7, 147.7, 138.3 \text{ (2C)}, 136.9, 135.2 \text{ (2C)}, 135.0, 129.9, 129.4, 128.8, 128.7, 128.5, 128.4, 127.8 \text{ (2C)}, 124.9, 124.5, 100.2, 96.2, 93.4, 82.7, 77.3, 22.5. IR (KBr, \( \nu \), cm\(^{-1}\)): 3403, 1721, 1638, 1487, 1454, 1357, 1197, 1021, 943, 870, 772. HRMS (ESI): \( m/z \ [M + H]^+ \) calcd for C27H21N2O4+: 437.1496; found: 437.1495.

5a,10a-dihydroxy-3-methyl-2,5-di-p-tolyl-2,5,5a,10a-tetrahydroindeno[2',1':4,5]pyrrolo[3,2-c]
pyridine-1,10-dione (5b)

Yield: 174.4 mg (75%); yellow crystal; mp: 246-248 °C. 1H NMR (400 MHz, CDCl3): \( \delta = \\
7.87 \text{ (dd, } J = 7.2, 3.2 \text{ Hz, 1H, ArH)}, 7.45-7.51 \text{ (m, 2H, ArH)}, 7.23-7.31 \text{ (m, 6H, ArH)}, 7.07-7.09 \text{ (m, 1H, ArH)}, 6.98-7.01 \text{ (m, 1H, ArH)}, 6.83-6.85 \text{ (m, 1H, ArH)}, 6.56 \text{ (br, s, 1H, OH)}, 5.59 \text{ (s, 1H, CH)}, 5.10 \text{ (s, 1H, OH)}, 2.47 \text{ (s, 3H, CH3)}, 2.39 \text{ (s, 3H, CH3)}, 1.83 \text{ (s, 3H, CH3)}. 13C NMR (100 MHz, CDCl3): \( \delta = \\
197.4, 161.3, 156.1, 150.9, 147.8, 138.4 \text{ (2C)}, 137.8, 135.6, 135.2 \text{ (2C)}, 135.0, 134.0, 130.1, 129.9, 128.6 \text{ (2C)}, 128.4, 128.0 \text{ (2C)}, 125.0, 124.5, 99.9, 95.9, 93.3, 82.5, 22.4, 21.3, 21.2. IR (KBr, \( \nu \), cm\(^{-1}\)): 3402, 1721, 1636, 1487, 1450, 1357, 1198, 1149, 1022, 941, 871, 766. HRMS (ESI): \( m/z \ [M + H]^+ \) calcd for C29H25N2O4+: 465.1809; found: 465.1811.

2,5-bis(2,4-dimethylphenyl)-5a,10a-dihydroxy-3-methyl-2,5,5a,10a-tetrahydroindeno[2',1':4,5]pyrrolo[3,2-c]
pyridine-1,10-dione (5c)

Yield: 182.4 mg (74%); green crystal; mp: 212-214 °C. 1H NMR (400 MHz, CDCl3): \( \delta = \\
7.87 \text{ (dd, } J = 6.4, 2.8 \text{ Hz, 1H, ArH)}, 7.56 \text{ (d, } J = 8.0 \text{ Hz, 1H, ArH)}, 7.46-7.50 \text{ (m, 2H, ArH)}, 7.17 \text{ (d, } J = 7.6 \text{ Hz, 1H, ArH}), 7.03-7.11 \text{ (m, 3H, ArH)}, 6.88-6.97 \text{ (m, 1H, ArH)}, 6.86-6.87 \text{ (m, 1H, ArH)}, 5.25 \text{ (br, s, 1H, OH)}, 5.24 \text{ (s, 1H, CH)}, 2.42 \text{ (s, 3H, CH3)}, 2.34 \text{ (s, 3H, CH3)}, 2.06 \text{ (s, 3H, CH3)}, 1.75 \text{ (s, 3H, CH3)}, 1.31 \text{ (s, 3H, CH3)}. 13C NMR (100 MHz, CDCl3): \( \delta = \\
197.7, 160.7, 156.1, 150.7, 148.6, 138.6 \text{ (2C)}, 137.3, 135.6, 135.3 \text{ (2C)}, 135.0, 134.9, 131.7, 131.6, 131.5, 131.1, 129.8, 128.0 \text{ (2C)}, 127.7, 124.6, 99.0, 95.9, 93.1, 82.4, 21.9, 21.2, 21.1, 18.1, 17.7. IR (KBr, \( \nu \), cm\(^{-1}\)): 3400, 1720,
2,5-bis(4-fluorophenyl)-5a,10a-dihydroxy-3-methyl-2,5,5a,10a-tetrahydroindeno[2',1':4,5]pyrrolo[3,2-c]pyridine-1,10-dione (5d)

Yield: 196.1 mg (83%); yellow crystal; mp: 210-212 °C. 1H NMR (400 MHz, DMSO-d6): $\delta = 7.60$ (dd, $J = 7.6, 1.2$ Hz, 1H, ArH), 7.51-7.57 (m, 2H, ArH), 7.30-7.41 (m, 6H, ArH), 7.22-7.28 (m, 3H, ArH), 6.68 (d, $J = 7.6$ Hz, 1H, ArH), 6.18 (s, 1H, OH), 5.55 (s, 1H, CH), 3.41 (s, 3H, OMe), 1.75 (s, 3H, CH3). 13C NMR (100 MHz, DMSO-d6): $\delta = 197.6, 161.9$ ($J_{CF1} = 243.0$ Hz), 161.6 ($J'_{CF1} = 243.0$ Hz), 159.5, 155.0, 151.1, 147.8, 135.5, 135.3 (2C), 133.5, 131.6 (2C), 131.5 ($J_{CF3} = 9.0$ Hz), 131.4 ($J'_{CF3} = 9.0$ Hz), 130.5 (2C), 125.4 (2C), 123.7, 116.6 ($J_{CF2} = 22.8$ Hz), 116.4 ($J'_{CF2} = 29.4$ Hz), 99.9, 96.6, 92.2, 84.0, 22.3. IR (KBr, $\nu$, cm$^{-1}$): 3402, 1720, 1639, 1487, 1452, 1355, 1149, 1053, 944, 871, 771. HRMS (ESI): $m/z [M + H]^+$ calcd for C27H19F2N2O4+: 473.1307; found: 473.1310.

2,5-bis(4-chlorophenyl)-5a,10a-dihydroxy-3-methyl-2,5,5a,10a-tetrahydroindeno[2',1':4,5]pyrrolo[3,2-c]pyridine-1,10-dione (5e)

Yield: 219.5 mg (87%); yellow crystal; mp: 265-266 °C. 1H NMR (400 MHz, DMSO-d6): $\delta = 7.73$ (d, $J = 7.2$ Hz, 1H, ArH), 7.50-7.61 (m, 6H, ArH), 7.36 (d, $J = 8.4$ Hz, 2H, ArH), 7.18-7.24 (m, 3H, ArH), 6.70 (d, $J = 7.2$ Hz, 1H, ArH), 6.22 (s, 1H, OH), 5.63 (s, 1H, CH), 1.76 (s, 3H, CH3). 13C NMR (100 MHz, DMSO-d6): $\delta = 197.4, 159.4, 154.7, 150.9, 147.7, 138.1$ (2C), 136.4, 135.6, 135.2 (2C), 133.2, 132.3, 131.4, 131.2, 130.8, 130.6, 129.8, 129.6, 125.3 (2C), 123.7, 100.3, 96.8, 92.4, 84.0, 22.2. IR (KBr, $\nu$, cm$^{-1}$): 3401, 1721, 1638, 1487, 1451, 1355, 1149, 1023, 940, 870, 767. HRMS (ESI): $m/z [M + H]^+$ calcd for C27H19Cl2N2O4+: 505.0716; found: 505.0706.

2,5-bis(4-bromophenyl)-5a,10a-dihydroxy-3-methyl-2,5,5a,10a-tetrahydroindeno[2',1':4,5]pyrrolo[3,2-c]pyridine-1,10-dione (5f)

Yield: 249.1 mg (84%); white crystal; mp: 279-280 °C. 1H NMR (400 MHz, DMSO-d6): $\delta = 7.73$ (d, $J = 8.8$ Hz, 3H, ArH), 7.57-7.70 (m, 3H, ArH), 7.30-7.41 (m, 6H, ArH), 7.31 (d, $J = 8.8$ Hz, 2H, ArH), 7.12-7.16 (m, 2H, ArH), 6.71 (d, $J = 7.6$ Hz, 1H, ArH), 6.23 (s, 1H, OH), 5.64 (s, 1H, CH), 1.76 (s, 3H, CH3). 13C NMR (100 MHz, DMSO-d6): $\delta = 197.4, 159.3, 154.7, 150.8, 147.7, 138.5$ (2C), 136.8, 135.6, 135.2 (2C), 132.8, 132.6, 131.8, 131.5, 131.1, 130.6, 125.3 (2C), 123.7, 100.3, 96.8, 92.4, 84.0, 22.2. IR (KBr, $\nu$, cm$^{-1}$): 3401, 1721, 1638, 1487, 1451, 1355, 1149, 1023, 940, 870, 767. HRMS (ESI): $m/z [M + H]^+$ calcd for C27H19Br2N2O4+: 527.0822; found: 527.0821.
123.7, 121.7, 120.8, 100.4, 96.8, 92.4, 84.0, 22.3. IR (KBr, ν, cm⁻¹): 3400, 1722, 1637, 1488, 1451, 1356, 1194, 1151, 1028, 942, 870, 770. HRMS (ESI): m/z [M + H]⁺ calcd for C₂₇H₁₉Br₂N₂O₄⁺: 592.9706; found: 592.9708.

5a,10a-dihydroxy-3-methyl-2,5-bis(4-(trifluoromethyl)phenyl)-2,5,5a,10a-tetrahydroindeno[2',1':4,5]pyrrolo[3,2-c]pyridine-1,10-dione (5g)

Yield: 229.2 mg (80%); yellow solid; mp: 251-252 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 7.87-7.93 (m, 4H, ArH), 7.73-7.76 (m, 1H, ArH), 7.54-7.63 (m, 4H, ArH), 7.43-7.49 (m, 3H, ArH), 6.70 (d, J = 8.8 Hz, 1H, ArH), 6.32 (s, 1H, OH), 5.79 (s, 1H, CH), 1.78 (s, 3H, CH₃). ¹³C NMR (100 MHz, DMSO-d₆): δ = 197.3, 159.3, 154.5, 150.6, 147.6 (2C), 142.9 (2C), 141.6 (2C), 135.7 (2C), 135.2 (2C), 130.6 (JCF₁ = 26.0 Hz) (2C), 126.8 (J'CF₁ = 26.0 Hz), 125.1 (3C), 123.8 (2C), 101.2, 97.3, 92.8, 84.1, 22.1. IR (KBr, ν, cm⁻¹): 3405, 1721, 1639, 1487, 1452, 1452, 1358, 1195, 1149, 1029, 945, 877, 775. HRMS (ESI): m/z [M + H]⁺ calcd for C₂₉H₁₉F₆N₂O₄+: 573.1244; found: 573.1241.

2,5-bis(2-fluorophenyl)-5a,10a-dihydroxy-3-methyl-2,5,5a,10a-tetrahydroindeno[2',1':4,5]pyrrolo[3,2-c]pyridine-1,10-dione (5h)

Yield: 165.5 mg (70%); white crystal; mp: 220-222 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.80-7.84 (m, 2H, ArH), 7.48-7.56 (m, 3H, ArH), 7.34-7.38 (m, 2H, ArH), 7.14-7.20 (m, 4H, ArH), 6.85 (d, J = 6.4 Hz, 1H, ArH), 5.44 (s, 1H, CH), 5.36 (br, s, 1H, OH), 1.88 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ = 196.9, 159.1 (JCF₁ = 249.9 Hz), 158.0 (J'CF₁ = 248.6 Hz), 156.0, 147.9, 135.5, 134.8, 132.1, 131.5 (JCF₁ = 9.0 Hz), 131.4 (J'CF₁ = 9.0 Hz), 130.9, 130.7, 130.6, 130.2, 125.8, 125.3, 124.8, 124.6, 123.8, 116.6 (JCF₂ = 19.9 Hz), 116.2 (J'CF₂ = 19.3 Hz), 99.8, 96.0, 93.7, 82.4, 82.3, 21.6. IR (KBr, ν, cm⁻¹): 3401, 1720, 1637, 1489, 1452, 1357, 1195, 1149, 1029, 941, 871, 767. HRMS (ESI): m/z [M + H]⁺ calcd for C₂₀H₁₀F₂N₂O₄⁺: 473.1307; found: 473.1312.

2,5-bis(3-chlorophenyl)-5a,10a-dihydroxy-3-methyl-2,5,5a,10a-tetrahydroindeno[2',1':4,5]pyrrolo[3,2-c]pyridine-1,10-dione (5i)

Yield: 181.5 mg (72%); white crystal; mp: 247-248 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 7.74 (d, J = 7.2 Hz, 1H, ArH), 7.49-7.61 (m, 7H, ArH), 7.36 (s, 1H, OH), 7.29 (d, J = 6.0 Hz, 1H, ArH), 7.15-7.21 (m, 2H, ArH), 6.67-6.70 (m, 2H, ArH), 6.25 (d, J = 4.0 Hz, 1H, OH), 5.65 (s, 1H, CH),
3.41 (s, 3H, OMe), 1.79 (s, 3H, CH₃). ¹³C NMR (100 MHz, DMSO-d₆): δ = 197.4, 159.3, 154.6, 150.9, 147.6, 140.6, 139.0, 135.6, 135.2, 133.9, 133.6, 131.3, 131.1, 130.7, 129.6, 129.4, 128.8, 128.4, 128.0, 127.8, 125.2, 123.7, 100.5, 97.0, 92.3, 84.0, 22.2. IR (KBr, ν, cm⁻¹): 3402, 1721, 1638, 1487, 1452, 1357, 1195, 1149, 1029, 941, 872, 768. HRMS (ESI): m/z [M + H]⁺ calcd for C₂₇H₁₉Cl₂N₂O₄⁺: 505.0716; found: 505.0706.

2,5-dibenzyl-5a,10a-dihydroxy-3-methyl-2,5,5a,10a-tetrahydroindeno[2',1':4,5]pyrrolo[3,2-c]pyridine-1,10-dione (5j)

Yield: 186.7 mg (83%); yellow solid; mp: 244-246 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 7.73 (t, J = 7.2 Hz, 2H, ArH), 7.66 (t, J = 7.6 Hz, 1H, ArH), 7.54 (t, J = 7.2 Hz, 1H, ArH), 7.26-7.28 (m, 6H, ArH), 7.18-7.23 (m, 2H, ArH), 7.07 (d, J = 7.2 Hz, 2H, ArH), 6.83 (s, 1H, OH), 6.05 (s, 1H, OH), 5.42 (s, 1H, CH), 5.23 (d, J = 16.0 Hz, 1H, CH₂), 4.97-5.07 (m, 2H, CH₂), 4.72 (t, J = 17.2 Hz, 1H, CH₂), 1.99 (s, 3H, CH₃). ¹³C NMR (100 MHz, DMSO-d₆): δ = 197.8, 159.1, 154.9, 151.0, 148.9 (2C), 138.9, 138.5, 135.8 (2C), 130.4, 128.9 (2C), 128.7, 127.6 (2C), 127.3, 126.8, 125.4 (2C), 123.4 (2C), 98.7, 95.6, 92.4, 84.2, 45.3, 45.1, 21.3. IR (KBr, ν, cm⁻¹): 3400, 1721, 1637, 1487, 1451, 1357, 1194, 1149, 1028, 941, 870, 769. HRMS (ESI): m/z [M + H]⁺ calcd for C₂₉H₂₅N₂O₄⁺: 465.1809; found: 465.1802.

2,5-dibutyl-5a,10a-dihydroxy-3-methyl-2,5,5a,10a-tetrahydroindeno[2',1':4,5]pyrrolo[3,2-c]pyridine-1,10-dione (5k)

Yield: 160.7 mg (81%); brown crystal; mp: 232-234 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 7.88 (d, J = 7.6 Hz, 1H, ArH), 7.76 (t, J = 7.2 Hz, 1H, ArH), 7.66 (d, J = 7.6 Hz, 1H, ArH), 7.53 (t, J = 7.6 Hz, 1H, ArH), 6.43 (s, 1H, OH), 5.77 (br, s, 1H, OH), 5.69 (s, 1H, CH), 3.61-3.80 (m, 3H, CH₂), 3.39-3.41 (m, 1H, CH₂), 2.26 (s, 3H, CH₃), 1.49-1.64 (m, 2H, CH₂), 1.26-1.45 (m, 6H, CH₂), 0.92-0.96 (m, 6H, CH₃). ¹³C NMR (100 MHz, DMSO-d₆): δ = 197.8, 158.8, 154.3, 150.6, 149.1, 135.8, 135.3, 130.2 (2C), 125.1, 123.4, 98.1, 95.4, 91.7, 84.1, 42.6, 41.4, 32.1, 31.1, 21.0, 20.2, 14.3, 14.1. IR (KBr, ν, cm⁻¹): 3398, 1718, 1635, 1484, 1357, 1194, 1020, 947, 870, 766. HRMS (ESI): m/z [M + H]⁺ calcd for C₂₃H₂₉N₂O₄⁺: 397.2122; found: 397.2120.

5a,10a-dihydroxy-3-methyl-2,5-dipropyl-2,5,5a,10a-tetrahydroindeno[2',1':4,5]pyrrolo[3,2-c]pyridine-1,10-dione (5l)
Yield: 147.6 mg (80%); yellow crystal; mp: 228-230 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.89$ (d, $J = 7.6$ Hz, 1H, ArH), 7.75 (t, $J = 7.6$ Hz, 1H, ArH), 7.66 (d, $J = 7.6$ Hz, 1H, ArH), 7.52 (t, $J = 7.6$ Hz, 1H, ArH), 6.44 (s, 1H, OH), 5.79 (br, s, 1H, OH), 5.71 (s, 1H, CH), 3.57-3.75 (m, 3H, CH$_2$), 3.36-3.38 (m, 1H, CH$_2$), 2.25 (s, 3H, CH$_3$), 1.51-1.70 (m, 2H, CH$_2$), 1.44-1.48 (m, 2H, CH$_2$), 0.95 (t, $J = 7.6$ Hz, 3H, CH$_3$), 0.93 (t, $J = 7.6$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 197.8$, 158.9, 154.3, 150.6, 149.2, 135.9, 135.3, 130.2, 125.1, 123.4, 98.1, 95.4, 91.7, 84.1, 44.4, 43.3, 23.2, 22.3, 21.0, 11.8, 11.7. IR (KBr, $\nu$, cm$^{-1}$): 3395, 1720, 1637, 1488, 1451, 1191, 1151, 1026, 941, 873, 769. HRMS (ESI): $m/z$ [M + H$^+$] calcd for C$_{21}$H$_{25}$N$_2$O$_4$+: 369.1809; found: 369.1813.

5a,10a-dihydroxy-5-(4-methoxyphenyl)-3-methyl-5a,10a-dihydro-1H-indeno[1,2-b]pyrano[3,4-d]pyrrole-1,10(5H)-dione (7a)

Yield: 147.2 mg (75%); gray solid; mp: 286-288 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.60$ (d, $J = 7.2$ Hz, 1H, ArH), 7.53-7.63 (m, 2H, ArH), 7.38 (s, 1H, OH), 7.20 (d, $J = 8.0$ Hz, 2H, ArH), 7.07 (d, $J = 8.8$ Hz, 2H, ArH), 6.73 (d, $J = 7.6$ Hz, 1H, ArH), 6.36 (s, 1H, OH), 5.59 (s, 1H, CH), 3.83 (s, 3H, OMe), 2.06 (s, 3H, CH$_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 197.4$, 167.4, 159.4, 158.5, 158.2, 147.7, 135.7 (2C), 135.0, 130.8, 128.4 (2C), 125.6 (2C), 123.8, 114.9, 97.1, 93.1, 91.4, 83.1, 55.8, 20.4. IR (KBr, $\nu$, cm$^{-1}$): 3401, 1720, 1637, 1488, 1451, 1356, 1149, 1028, 875, 758. HRMS (ESI): $m/z$ [M + H$^+$] calcd for C$_{22}$H$_{18}$NO$_6$+: 392.1129; found: 392.1131.

5-(4-fluorophenyl)-5a,10a-dihydroxy-3-methyl-5a,10a-dihydro-1H-indeno[1,2-b]pyrano[3,4-d]pyrrole-1,10(5H)-dione (7b)

Yield: 134.9 mg (71%); white solid; mp: 294-296 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.76$ (d, $J = 7.6$ Hz, 1H, ArH), 7.54-7.63 (m, 2H, ArH), 7.51 (s, 1H, OH), 7.34-7.40 (m, 4H, ArH), 6.70 (d, $J = 7.6$ Hz, 1H, ArH), 6.43 (s, 1H, OH), 5.65 (s, 1H, CH), 2.07 (s, 3H, CH$_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 197.3$, 167.6, 162.5, 160.8, 159.2 ($J_{CF1} = 228.0$ Hz), 158.5, 157.9, 147.5, 135.8 (2C), 132.3, 131.6 ($J_{CF2} = 9.0$ Hz), 130.9, 125.4 (2C), 123.9, 116.7 ($J_{CF3} = 22.0$ Hz), 97.2, 93.1, 83.1, 20.4. IR (KBr, $\nu$, cm$^{-1}$): 3402, 1721, 1634, 1487, 1452, 1357, 1195, 946, 875, 766. HRMS (ESI): $m/z$ [M + H$^+$] calcd for C$_{21}$H$_{15}$FNO$_5$+: 380.0933; found: 380.0933.
Yield: 128.5 mg (65%); white solid; mp: 285-286 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.76$ (d, $J = 7.6$ Hz, 1H, ArH), 7.54-7.63 (m, 5H, ArH+OH), 7.32 (d, $J = 8.4$ Hz, 2H, ArH), 6.71 (d, $J = 7.6$ Hz, 1H, ArH), 6.44 (s, 1H, OH), 5.71 (s, 1H, CH), 2.07 (s, 3H, CH$_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 197.2$, 167.6, 158.5, 157.7, 147.4, 135.9 (2C), 135.2, 135.0, 133.2, 131.0, 130.9, 129.9, 125.3 (2C), 123.9, 97.4, 93.2, 92.3, 83.1, 20.4. IR (KBr, $\nu$, cm$^{-1}$): 3400, 1720, 1638, 1487, 1452, 1191, 1149, 1025, 940, 870, 767. HRMS (ESI): $m/z$ [M + H]$^+$ calcd for C$_{21}$H$_{15}$ClNO$_5^+$: 396.0633; found: 396.0635.

5-(4-bromophenyl)-5a,10a-dihydroxy-3-methyl-5a,10a-dihydro-1H-indeno[1,2-b]pyrano[3,4-d]pyrrole-1,10(5H)-dione (7d)

Yield: 156.2 mg (71%); light yellow solid; mp: 275-276 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.72$-7.77 (m, 3H, ArH), 7.62 (t, $J = 6.8$ Hz, 1H, ArH), 7.56 (t, $J = 6.8$ Hz, 2H, ArH+OH), 7.25 (d, $J = 8.4$ Hz, 2H, ArH), 6.71 (t, $J = 7.6$ Hz, 1H, ArH), 6.46 (br, s, 1H, OH), 5.72 (s, 1H, CH), 2.07 (s, 3H, CH$_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 197.2$, 167.6, 158.5, 157.6, 147.4, 135.9 (2C), 135.6, 134.9, 132.9, 131.3, 130.9, 125.3 (2C), 123.9, 121.7, 97.4, 93.2, 92.4, 83.1, 20.4. IR (KBr, $\nu$, cm$^{-1}$): 3400, 1721, 1636, 1487, 1452, 1357, 1151, 1028, 940, 867, 769. HRMS (ESI): $m/z$ [M + H]$^+$ calcd for C$_{21}$H$_{15}$BrNO$_5^+$: 440.0128; found: 440.0130.

3-methyl-2,5-diphenyl-2,5-dihydroindeno[2',1':4,5]pyrrolo[3,2-c]pyridine-1,10-dione (8a)

Yield: 117.5 mg (73%); yellow solid; mp: 289-290 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.81$ (d, $J = 6.8$ Hz, 1H, ArH), 7.62 (d, $J = 6.8$ Hz, 1H, ArH), 7.42-7.52 (m, 5H, ArH), 7.22-7.31 (m, 7H, ArH), 5.82 (s, 1H, CH), 2.01 (s, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 186.2$, 169.3, 167.8, 158.7, 157.3, 142.6, 137.3, 134.7, 134.4, 131.1 (2C), 130.0, 129.9, 129.7, 129.3, 129.0 (2C), 128.4, 128.0, 127.9, 127.7, 126.0, 122.4, 99.7, 95.7, 93.0, 23.5. IR (KBr, $\nu$, cm$^{-1}$): 3069, 1760, 1689, 1482, 1428, 1211, 739. HRMS (ESI): $m/z$ [M + H]$^+$ calcd for C$_{27}$H$_{19}$N$_2$O$_2^+$: 403.1441; found: 403.1437.

Reference

Copies of $^1$H and $^{13}$C NMR-spectra