# Synthesis of Functionalized Tetrahydro-4-oxoindeno[1,2-*b*]pyrroles from Ninhydrin, Acetylenedicarboxylates, and Primary Amines

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A one-pot synthesis of dialkyl 1,3a,4,8b-tetrahydro-3a,8b-dihydroxy-1-alkyl-4-oxoindeno[1,2-*b*]pyrrole-2,3-dicarboxylates *via* three-component reaction from indan-1,2,3-trione hydrate (ninhydrin), primary amines, and dialkyl acetylenedicarboxylates is described.

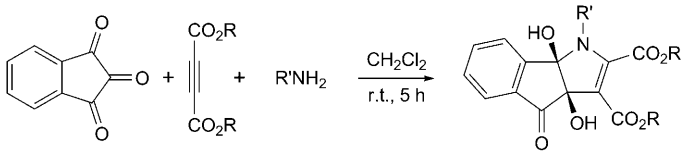
**Introduction.** – Multicomponent reactions (MCRs) have been frequently used by synthetic chemists as a facile means to generate molecular diversity from bifunctional substrates that react sequentially in an intramolecular fashion [1]. Five-membered, N-containing heterocycles are important building blocks of an extensive number of biologically active compounds [2]. Among them, pyrroles are heterocycles of great importance because of their presence in numerous natural products like heme, chlorophyll, vitamin $B_{12}$, and various cytochrome enzymes [3]. Some of the recently isolated pyrrole-containing marine natural products have been found to exhibit considerable cytotoxicity and to function as multidrug-resistant reversal agents [4]. Many of these biologically active compounds have emerged as chemotherapeutic agents. In addition, polysubstituted pyrroles are molecular frameworks with immense importance in material science [5]. They have been also employed as antioxidants, and antibacterial, ionotropic, antitumor, anti-inflammatory, and antifungal agents [6–11]. Moreover, they are a highly versatile class of intermediates in the synthesis of natural products as well as in heterocyclic chemistry [12].

**Results and Discussion.** – As part of our current studies on the development of new routes in heterocyclic synthesis [13–15], we report an efficient procedure for direct synthesis of tetrahydro-dihydroxy-indeno[1,2-*b*]pyrrole-2,3-dicarboxylates (**4**) from the reaction of ninhydrin (**1**) and acetylenedicarboxylates **2** in the presence of primary amines, **3**, at room temperature (*Scheme 1*).

Structures of compounds **4a**–**4k** were determined by IR, $^1$H- and $^{13}$C-NMR, and MS data. The $^1$H-NMR spectrum of **4a** exhibited four *singlet*s for MeO (3.55 and 3.78 ppm) and OH (4.99 and 5.41 ppm) H-atoms. Due to the presence of stereogenic centers in these products, the H-atoms of $CH_2$ group are diasterotopic, and exhibit *AB* systems. The CO group resonances in the $^{13}$C-NMR spectrum of **4a** appear at 162.1, 164.1, and 197.1 ppm. The mass spectrum of **4a** displayed the molecular-ion peak at *m*/*z* 409.

Although the mechanistic details of the reaction are not known, a plausible rationalization may be advanced to explain the product formation (*Scheme 2*).

*Scheme 1*



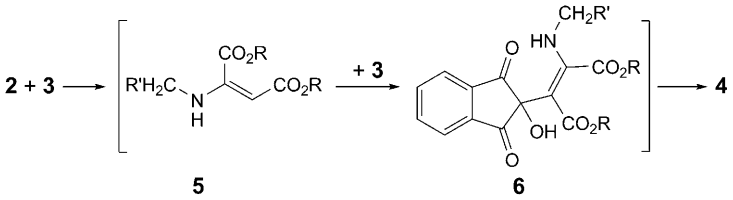

**1**

| R | R' |
|---|---|
| **2a** Me | **3a** Bn |
| **2b** Et | **3b** 4-Me–$C_6H_4CH_2$ |
| | **3c** 4-MeO–$C_6H_4CH_2$ |
| | **3d** 2-Cl–$C_6H_4CH_2$ |
| | **3e** Pr |
| | **3f** $^t$Bu |

| | R | R' | Yield [%] |
|---|---|---|---|
| **4a** | Me | Bn | 85 |
| **4b** | Me | 4-Me–$C_6H_4CH_2$ | 87 |
| **4c** | Me | 4-MeO–$C_6H_4CH_2$ | 90 |
| **4d** | Me | 2-Cl–$C_6H_4CH_2$ | 75 |
| **4e** | Et | Bn | 84 |
| **4f** | Et | 4-Me–$C_6H_4CH_2$ | 86 |
| **4g** | Et | 4-MeO–$C_6H_4CH_2$ | 89 |
| **4h** | Et | 2-Cl–$C_6H_4CH_2$ | 74 |
| **4i** | Me | Pr | 78 |
| **4j** | Me | $^t$Bu | 80 |
| **4k** | Et | $^t$Bu | 78 |

Presumably, the zwitterionic intermediate **5** formed from the reaction of **3** with activated acetylenes is attacked by ninhydrin to produce **6**. Intermediate **6** can undergo cyclization under the reaction conditions employed to produce **4**.

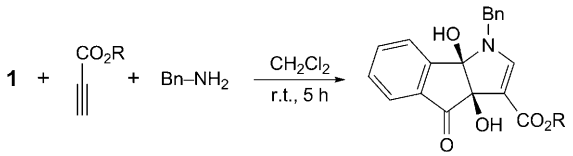
*Scheme 2*




**5** **6**

Under similar conditions, the reaction of ninhydrin **1** and alkyl prop-2-ynoates **7** in the presence of $BnNH_2$ (**3a**) led to tetrahydrooxoindeno[1,2-*b*]pyrrole-3-carboxylates **8** in good yields (*Scheme 3*).

*Scheme 3*




| R | 3a |
|---|---|
| **7a** Me | |
| **7b** Et | |

| | R | Yield [%] |
|---|---|---|
| **8a** | Me | 85 |
| **8b** | Et | 87 |

In conclusion, we have described a convenient route to functionalized tetrahydrooxoindeno[1,2-*b*]pyrroles from a three-component reaction of ninhydrin, acetyle-

nedicarboxylates, and primary alkylamines. The advantage of the presented procedure is that the reaction is performed by simple mixing of the starting materials.

## Experimental Part

*General*. Compounds **1**, **2**, and **3** were obtained from *Merck*, and used without further purification. M.p.: *Electrothermal 9100* apparatus; uncorrected. IR Spectra: *Shimadzu IR-460* spectrometer; in KBr; in $cm^{-1}$. $^1H$- and $^{13}C$-NMR spectra: *Bruker DRX-500 AVANCE* instrument, in $CDCl_3$ at 500.1 and 125.7 MHz, resp.; $\delta$ in ppm, $J$ in Hz. MS: *Finnigan-MAT-8430* mass spectrometer, at 70 eV; in *m/z*. Elemental analyses (C, H, N): *Heraeus CHN-O-Rapid* analyzer.

*General Procedure for the Preparation of Compounds* **4**. To a stirred soln. of **3a** (2 mmol) and **2a** (2 mmol) in $CH_2Cl_2$ (5 ml) was added a soln. of ninhydrin (**1**; 0.32 g, 2 mmol) in $CH_2Cl_2$ (5 ml) at r.t. After completion of the reaction (1–3 h) as indicated by TLC (hexane/AcOEt 8:1), the solvent was removed under reduced pressure to leave a residue that was purified by column chromatography (CC; $SiO_2$; hexane/AcOEt 8:1) to afford the pure products.

*Dimethyl 1-Benzyl-1,3a,4,8b-tetrahydro-3a,8b-dihydroxy-4-oxoindeno[1,2-*b*]pyrrole-2,3-dicarboxylate* (**4a**). Yield: 0.62 g (85%). Colorless crystals. M.p. 126–128°. IR: 3445 (br.), 1742, 1712, 1686, 1569, 1468, 1218, 1180. $^1H$-NMR: 3.55 (*s*, MeO); 3.78 (*s*, MeO); 4.90 (*d*, $^2J = 15.7$, CH); 4.99 (*s*, OH); 5.07 (*d*, $^2J = 15.7$, CH); 5.42 (*s*, OH); 7.33 (*d*, $^3J = 7.3$, 2 CH); 7.38–7.42 (*m*, 5 CH); 7.76 (*t*, $^3J = 7.5$, CH); 7.99 (*d*, $^3J = 8.1$, CH). $^{13}C$-NMR: 46.8 ($CH_2N$); 51.2 (MeO); 52.7 (MeO); 83.7 (C); 95.4 (C); 124.5 (CH); 124.7 (CH); 127.8 (CH); 128.1 (2 CH); 128.5 (2 CH); 130.6 (CH); 135.2 (C); 136.1 (CH); 136.5 (2 C); 147.4 (C); 151.1 (C); 162.2 (C=O); 164.2 (C=O); 197.1 (C=O). EI-MS: 409 (10), 346 (50), 300 (80), 105 (100), 76 (30). Anal. calc. for $C_{22}H_{19}NO_7$ (409.39): C 64.55, H 4.68, N 3.42; found: C 64.32, H 4.51, N 3.32.

*Dimethyl 1,3a,4,8b-Tetrahydro-3a,8b-dihydroxy-1-(4-methylbenzyl)-4-oxoindeno[1,2-*b*]pyrrole-2,3-dicarboxylate* (**4b**). Yield: 0.66 g (87%). White powder. M.p. 123–125°. IR: 3450 (br.), 1742, 1713, 1665, 1573, 1466, 1205, 1179. $^1H$-NMR: 2.32 (*s*, Me); 3.46 (*s*, MeO); 3.67 (*s*, MeO); 4.70 (*d*, $^2J = 15.0$, CH); 4.90 (*s*, $^2J = 15.0$, CH); 4.99 (*s*, OH); 5.29 (*s*, OH); 7.05 (*d*, $^3J = 7.8$, 2 CH); 7.13 (*d*, $^3J = 7.8$, 2 CH); 7.55 (*t*, $^3J = 7.5$, CH); 7.67 (*t*, $^3J = 7.5$, CH); 8.36 (*d*, $^3J = 8.0$, 2 CH). $^{13}C$-NMR: 21.1 (Me); 46.7 ($CH_2N$); 51.2 (MeO); 52.7 (MeO); 83.7 (C); 95.2 (C); 124.4 (CH); 124.7 (CH); 128.0 (2 CH); 129.2 (2 CH); 130.7 (CH); 131.8 (C); 133.4 (C); 135.2 (C); 136.1 (CH); 137.7 (C); 147.4 (C); 151.1 (C); 162.1 (C=O); 164.1 (C=O); 197.0 (C=O). EI-MS: 423 (15), 318 (65), 287 (54), 105 (100), 90 (84), 76 (42). Anal. calc. for $C_{23}H_{21}NO_7$ (423.42): C 65.24, H 5.00, N 3.31; found: C 65.12, H 4.87, N 3.24.

*Dimethyl 1,3a,4,8b-Tetrahydro-3a,8b-dihydroxy-1-(4-methoxybenzyl)-4-oxoindeno[1,2-*b*]pyrrole-2,3-dicarboxylate* (**4c**). Yield: 0.66 g (78%). Yellow powder. M.p. 127–129°. IR: 3445 (br.), 1742, 1712, 1662, 1569, 1468, 1240, 1180. $^1H$-NMR: 3.47 (*s*, MeO); 3.66 (*s*, MeO); 3.77 (*s*, MeO); 4.67 (*d*, $^2J =$ 15.5, CH); 4.87 (*d*, $^2J = 15.5$, CH); 4.92 (*s*, OH); 5.41 (*s*, OH); 7.05 (*d*, $^3J = 8.3$, 2 CH); 7.12 (*d*, $^3J = 8.3$, 2 CH); 7.55 (*t*, $^3J = 7.4$, CH); 7.67 (*t*, $^3J = 7.7$, CH); 8.36 (*d*, $^3J = 8.0$, 2 CH). $^{13}C$-NMR: 46.4 ($CH_2N$); 51.2 (MeO); 52.7 (MeO); 55.3 (MeO); 83.7 (C); 95.3 (C); 114.0 (2 CH); 124.5 (CH); 124.7 (CH); 128.4 (C); 129.5 (2 CH); 130.6 (CH); 135.2 (2C); 136.2 (CH); 147.4 (C); 151.1 (C); 159.4 (C); 162.2 (C=O); 164.2 (C=O); 197.1 (C=O). Anal. calc. for $C_{23}H_{21}NO_8$ (439.42): C 62.87, H 4.82, N 3.19; found: C 62.74, H 4.76, N 3.08.

*Dimethyl 1-(2-Chlorobenzyl)-1,3a,4,8b-tetrahydro-3a,8b-dihydroxy-4-oxoindeno[1,2-*b*]pyrrole-2,3-dicarboxylate* (**4d**). Yield: 0.66 g (82%). White powder. M.p. 130–132°. IR: 3430 (br.), 1725, 1720, 1687, 1545, 1432, 1254, 1100. $^1H$-NMR: 3.55 (*s*, MeO); 3.71 (*s*, MeO); 4.54 (*s*, OH); 4.68 (*s*, OH); 4.84 (*d*, $^2J = 15.6$, CH); 4.97 (*d*, $^2J = 15.6$, CH); 7.07 (*d*, $^3J = 8.3$, CH); 7.18 (*t*, $^3J = 8.3$, CH); 7.24 (*t*, $^3J = 7.5$, CH); 7.36 (*d*, $^3J = 7.5$, CH); 7.52–7.56 (*m*, 2 CH); 7.62 (*t*, $^3J = 7.8$, CH); 7.87 (*d*, $^3J = 7.5$, CH). $^{13}C$-NMR: 44.1 ($CH_2N$); 51.4 (MeO); 52.9 (MeO); 83.6 (C); 95.4 (C); 124.4 (CH); 124.7 (CH); 126.8 (CH); 128.9 (CH); 129.0 (CH); 129.4 (CH); 129.7 (C); 130.7 (CH); 132.6 (C); 134.2 (C); 135.1 (C); 136.2 (CH); 147.3 (C); 151.1 (C); 161.8 (C=O); 164.1 (C=O); 196.9 (C=O). Anal. calc. for $C_{22}H_{18}ClNO_7$ (443.84): C 59.54, H 4.09, N 3.16; found: C 59.45, H 4.00, N 3.10.

*Diethyl 1-Benzyl-1,3a,4,8b-tetrahydro-3a,8b-dihydroxy-4-oxoindeno[1,2-*b*]pyrrole-2,3-dicarboxylate* (**4e**). Yield: 0.64 g (80%). White powder. M.p. 128–130°. IR: 3435 (br.), 1749, 1714, 1666, 1559, 1474,

1195, 1159. $^1$H-NMR: 0.98 (*t*, $^3J$ = 7.2, Me); 1.23 (*t*, $^3J$ = 7.3, Me); 3.85–3.89 (*m*, ($CH_2O$); 4.16–4.19 (*m*, ($CH_2O$); 4.32 (*s*, OH); 4.59 (*s*, OH); 4.76 (*d*, $^2J$ = 15.8, CH); 4.93 (*d*, $^2J$ = 15.8, CH); 7.19–7.28 (*m*, 5 CH); 7.55 (*t*, $^3J$ = 7.8, 2 CH); 7.65 (*t*, $^3J$ = 7.5, CH); 7.89 (*d*, $^3J$ = 8.0, CH). $^{13}$C-NMR: 13.4 (Me); 14.3 (Me); 46.7 ($CH_2N$); 60.0 ($CH_2O$); 62.4 ($CH_2O$); 83.7 (C); 95.0 (C); 124.4 (CH); 124.8 (CH); 127.8 (CH); 127.9 (2 CH); 128.5 (2 CH); 130.6 (CH); 131.5 (C); 135.3 (C); 136.0 (CH); 136.7 (C); 147.5 (C); 150.8 (C); 161.7 (C=O); 163.7 (C=O); 196.9 (C=O). Anal. calc. for $C_{24}H_{23}NO_7$ (437.45): C 65.90, H 5.30, N 3.20; found: C 65.78, H 5.23, N 3.14.

*Diethyl 1,3a,4,8b-Tetrahydro-3a,8b-dihydroxy-1-(4-methylbenzyl)-4-oxoindeno[1,2-*b*]pyrrole-2,3-dicarboxylate* (**4f**). Yield: 0.66 g (75%). Yellow powder. M.p. 131–133°. IR: 3415 (br.), 1739, 1716, 1686, 1575, 1442, 1150, 1124. $^1$H-NMR: 0.98 (*d*, $^3J$ = 7.4, Me); 1.22 (*d*, $^3J$ = 7.4, Me); 2.32 (*s*, Me); 3.91–3.95 (*m*, $CH_2O$); 4.16–4.20 (*m*, $CH_2O$); 4.32 (*s*, OH); 4.59 (*s*, OH); 4.72 (*d*, $^2J$ = 15.9, CH); 4.90 (*d*, $^2J$ = 15.9, CH); 7.05–7.10 (*m*, 4 CH); 7.52 (*d*, $^3J$ = 7.7, 2 CH); 7.67 (*t*, $^3J$ = 6.6, CH); 7.89 (*t*, $^3J$ = 7.4, CH). $^{13}$C-NMR: 13.3 (Me); 14.3 (Me); 21.0 (Me); 46.5 ($CH_2N$); 60.0 ($CH_2O$); 62.4 ($CH_2O$); 83.7 (C); 95.0 (C); 124.4 (CH); 124.7 (CH); 127.9 (2 CH); 129.2 (2 CH); 129.7 (C); 130.6 (CH); 133.6 (C); 135.3 (C); 136.0 (CH); 137.6 (C); 147.6 (C); 150.8 (C); 161.7 (C=O); 163.7 (C=O); 197.0 (C=O). Anal. calc. for $C_{25}H_{25}NO_7$ (451.47): C 66.51, H 5.58, N 3.10; found: C 66.40, H 5.45, N 3.02.

*Diethyl 1,3a,4,8b-Tetrahydro-3a,8b-dihydroxy-1-(4-methoxybenzyl)-4-oxoindeno[1,2-*b*]pyrrole-2,3-dicarboxylate* (**4g**). Yield: 0.53 g (80%). Yellow crystals. M.p. 129–131°. IR: 3354 (br.), 1745, 1727, 1675, 1547, 1389, 1254, 1142. $^1$H-NMR: 0.95 (*t*, $^3J$ = 7.5, Me); 1.21 (*t*, $^3J$ = 7.4, Me); 3.75 (*s*, MeO); 4.12–4.16 (*m*, $CH_2O$); 4.22–4.25 (*m*, $CH_2O$); 4.25 (*d*, $^2J$ = 14.9, CH); 4.74 (*d*, $^2J$ = 14.9 CH); 4.65 (*s*, OH); 5.12 (*s*, OH); 7.12 (*d*, $^3J$ = 8.0, 2 CH); 7.27 (*d*, $^3J$ = 8.5, 2 CH); 7.62 (*t*, $^3J$ = 7.4, CH); 7.84 (*t*, $^3J$ = 7.7, CH); 8.54 (*d*, $^3J$ = 8.0, 2 CH). $^{13}$C-NMR: 14.0 (Me); 14.2 (Me); 47.8 ($CH_2N$); 52.3 (MeO); 62.0 ($CH_2O$); 62.7 ($CH_2O$); 83.6 (C); 97.2 (C); 113.1 (2 CH); 124.2 (CH); 124.9 (CH); 127.9 (C); 129.7 (2 CH); 131.0 (CH); 135.7 (2C); 136.7 (CH); 148.4 (C); 150.9 (C); 160.4 (C); 162.7 (C=O); 164.5 (C=O); 198.6 (C=O). Anal. calc. for $C_{25}H_{25}NO_8$ (467.47): C 64.23, H 5.39, N 3.00; found: C 64.14, H 5.28, N 2.95.

*Diethyl 1-(2-Chlorobenzyl)-1,3a,4,8b-tetrahydro-3a,8b-dihydroxy-4-oxoindeno[1,2-*b*]pyrrole-2,3-dicarboxylate* (**4h**). Yield: 0.69 g (74%). Pale yellow powder. M.p. 133–135°. IR: 3425 (br.), 1739, 1707, 1675, 1580, 1463, 1289, 1128. $^1$H-NMR: 0.90 (*t*, $^3J$ = 7.2, Me); 1.13 (*t*, $^3J$ = 7.3, Me); 4.05 (*q*, $^3J$ = 7.4, $CH_2O$); 4.10 (*q*, $^3J$ = 7.5, $CH_2O$); 4.90 (*d*, $^2J$ = 15.4, CH); 4.95 (*d*, $^2J$ = 15.4, CH); 5.00 (*s*, OH); 5.12 (*s*, OH); 6.98–7.02 (*m*, 2 CH); 7.08 (*t*, $^3J$ = 8.0, CH); 7.26 (*d*, $^3J$ = 8.2, CH); 7.41 (*t*, $^3J$ = 8.6, CH); 7.42–7.44 (*m*, 2 CH); 7.78 (*d*, $^3J$ = 8.5, CH). $^{13}$C-NMR: 14.1 (Me); 14.2 (Me); 44.0 ($CH_2N$); 59.9 ($CH_2O$); 60.4 ($CH_2O$); 83.9 (C); 95.5 (C); 124.4 (CH); 124.5 (C); 124.6 (CH); 126.7 (CH); 126.8 (C); 128.7 (CH); 129.0 (CH); 129.2 (CH); 130.6 (CH); 132.3 (C); 134.5 (C); 135.1 (C); 135.9 (CH); 147.4 (C); 161.9 (C=O); 163.7 (C=O); 197.1 (C=O). Anal. calc. for $C_{24}H_{22}ClNO_7$ (471.89): C 61.09, H 4.70, N 2.97; found: C 61.00, H 4.62, N 2.90.

*Dimethyl 1,3a,4,8b-Tetrahydro-3a,8b-dihydroxy-4-oxo-1-propylindeno[1,2-*b*]pyrrole-2,3-dicarboxylate* (**4i**). Yield: 0.56 g (78%). White powder. M.p. 125–127°. IR: 3398 (br.), 1728, 1720, 1654, 1526, 1395, 1257, 1112. $^1$H-NMR: 0.92 (*t*, $^3J$ = 7.2, Me); 1.69–1.72 (*m*, $CH_2$); 3.39–3.41 (*m*, CH); 3.62–3.64 (*m*, CH); 3.67 (*s*, MeO); 3.85 (*s*, MeO); 4.62 (*s*, OH); 4.84 (*s*, OH); 7.54 (*t*, $^3J$ = 7.8, CH); 7.75–7.78 (*m*, 2 CH); 7.84 (*d*, $^3J$ = 7.6, CH). $^{13}$C-NMR: 11.4 (Me); 24.4 ($CH_2$); 45.38 ($CH_2$); 51.2 (MeO); 53.0 (MeO); 83.6 (C); 95.4 (C); 124.0 (CH); 124.3 (C); 124.8 (CH); 130.6 (CH); 135.2 (C); 136.2 (CH); 147.5 (C); 151.5 (C); 162.5 (C=O); 164.3 (C=O); 197.1 (C=O). Anal. calc. for $C_{18}H_{19}NO_7$ (361.35): C 59.83, H 5.30, N 3.88; found: C 59.75, H 5.18, N 3.74.

*Dimethyl 1-(*tert*-Butyl)-1,3a,4,8b-tetrahydro-3a,8b-dihydroxy-4-oxoindeno[1,2-*b*]pyrrole-2,3-dicarboxylate* (**4j**). Yield: 0.60 g (80%). Pale yellow powder. M.p. 132–134°. IR: 3374 (br.), 1725, 1718, 1687, 1530, 1375, 1242, 1110. $^1$H-NMR: 1.48 (*s*, $^t$Bu); 3.68 (*s*, MeO); 3.82 (*s*, MeO); 4.85 (*s*, OH); 5.05 (*s*, OH); 7.23 (*t*, $^3J$ = 7.5, CH); 7.58–7.61 (*m*, 2 CH); 7.75 (*d*, $^3J$ = 7.5, CH). $^{13}$C-NMR: 28.7 ($Me_3$C); 51.4 (MeO); 52.8 (MeO); 56.0 ($Me_3C$); 93.8 (C); 95.6 (C); 124.2 (CH); 124.8 (C); 125.0 (CH); 131.2 (CH); 134.8 (C); 136.5 (CH); 148.2 (C); 152.4 (C); 162.4 (C=O); 164.3 (C=O); 195.7 (C=O). Anal. calc. for $C_{19}H_{21}NO_7$ (375.37): C 60.79, H 5.64, N 3.73; found: C 60.68, H 5.58, N 3.64.

*Diethyl 1-(*tert*-Butyl)-1,3a,4,8b-tetrahydro-3a,8b-dihydroxy-4-oxoindeno[1,2-*b*]pyrrole-2,3-dicarboxylate* (**4k**). Yield: 0.69 g (78%). Pale yellow powder. M.p. 137–139°. IR: 3435 (br.), 1737, 1710, 1664, 1578, 1460, 1279, 1125. $^1$H-NMR: 1.12 (*t*, $^3J$ = 7.2, Me); 1.18 (*t*, $^3J$ = 7.2, Me); 1.45 (*s*, $^t$Bu); 4.15 (*q*,

$^3J = 7.2$, $CH_2$); 4.18 (*q*, $^3J = 7.2$, $CH_2$); 4.98 (*s*, OH); 5.10 (*s*, OH); 7.20 (*t*, $^3J = 7.3$, CH); 7.60–7.63 (*m*, 2 CH); 7.72 (*d*, $^3J = 7.3$, CH). $^{13}$C-NMR: 14.0 (Me); 14.2 (Me); 28.7 ($Me_3C$); 57.2 ($Me_3C$); 60.4 ($CH_2O$); 61.3 ($CH_2O$); 85.4 (C); 96.2 (C); 123.8 (CH); 124.5 (C); 124.8 (CH); 130.8 (CH); 134.6 (C); 137.2 (CH); 148.5 (C); 151.6 (C); 161.9 (C=O); 165.7 (C=O); 196.7 (C=O). Anal. calc. for $C_{21}H_{25}NO_7$ (403.43): C 62.52, H 6.25, N 3.47; found: C 62.48, H 6.18, N 3.38.

*Methyl 1-Benzyl-1,3a,4,8b-tetrahydro-3a,8b-hydroxy-4-oxoindeno[1,2-*b*]pyrrole-3-carboxylate* (**8a**). Yield: 0.53 g (75%). White crystals. M.p. 125–127°. IR: 3444 (br.), 1757, 1725, 1675, 1558, 1450, 1227, 1154. $^1$H-NMR: 3.56 (*s*, MeO); 4.56 (*d*, $^2J = 13.8$, CH); 4.87 (*d*, $^2J = 13.8$, CH); 5.12 (*s*, OH); 5.42 (*s*, OH); 7.30 (*d*, $^3J = 7.5$, 2 CH); 7.32–7.43 (*m*, 5 CH); 7.60 (*s*, CH); 7.67 (*t*, $^3J = 7.5$, CH); 7.95 (*d*, $^3J = 7.8$, CH). $^{13}$C-NMR: 48.4 ($CH_2$); 51.5 (MeO); 85.4 (C); 98.7 (C); 124.0 (CH); 124.6 (CH); 126.5 (CH); 127.8 (2 CH); 128.0 (2 CH); 131.0 (CH); 135.7 (C); 136.8 (CH); 137.0 (2 C); 145.4 (C); 147.1 (CH); 167.4 (C=O); 195.4 (C=O). Anal. calc. for $C_{20}H_{17}NO_5$ (351.36): C 68.37, H 4.88, N 3.99; found: C 68.27, H 4.70, N 3.79.

*Ethyl 1-Benzyl-1,3a,4,8b-tetrahydro-3a,8b-hydroxy-4-oxooindeno[1,2-*b*]pyrrole-3-carboxylate* (**8b**). Yield: 0.64 g (87%). White powder. M.p. 127–129°. IR: 3445 (br.), 1748, 1732, 1684, 1562, 1457, 1220, 1153. $^1$H-NMR: 1.15 (*t*, $^3J = 7.3$, Me); 4.25 (*q*, $^3J = 7.2$, $CH_2O$); 4.68 (*d*, $^2J = 12.7$, CH); 4.83 (*d*, $^2J = 12.7$, CH); 5.15 (*s*, OH); 5.38 (*s*, OH); 7.34 (*d*, $^3J = 7.4$, 2 CH); 7.38–7.42 (*m*, 5 CH); 7.58 (*s*, CH); 7.62 (*t*, $^3J = 7.4$, CH); 7.82 (*d*, $^3J = 7.5$, CH). $^{13}$C-NMR: 14.5 (Me); 48.5 ($CH_2N$); 60.6 ($CH_2-O$); 86.7 (C); 98.3 (C); 123.8 (CH); 124.2 (CH); 125.8 (CH); 127.2 (2 CH); 128.4 (2 CH); 131.5 (CH); 136.4 (C); 137.3 (CH); 137.8 (2 C); 147.2 (C); 148.6 (CH); 165.4 (C=O); 196.7 (C=O). Anal. calc. for $C_{21}H_{19}NO_5$ (365.38): C 69.03, H 5.24, N 3.83; found: C 69.12, H 5.34, N 3.92.

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