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One-pot three-component reaction of ninhydrin, 1,3-dicarbonyl compounds, and primary amines to afford indeno[1,2-*b*]pyrrol-4(1*H*)-ones

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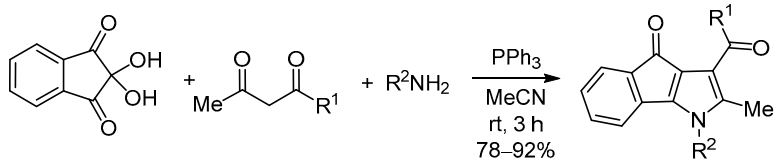


R^1 = Me, OEt; R^2 = Me, Et, *n*-Pr, Ph, Bn, 4-$MeOC_6H_4CH_2$, 4-$MeOC_6H_4$

A convenient one-pot three-component synthesis of indeno[1,2-*b*]pyrrol-4(1*H*)-ones has been developed. The reaction of ninhydrin, 1,3-dicarbonyl compounds, and primary amines in the presence of PPh_3 in MeCN at room temperature produces the respective indeno-[1,2-*b*]pyrrol-4(1*H*)-ones in high yields. The synthesized pyrrole derivatives have been used in the Diels–Alder reaction with dialkyl acetylenedicarboxylates in MeCN under reflux conditions to obtain indeno[1,2-*b*]pyrano[3,4-*d*]pyrroles in high yields.

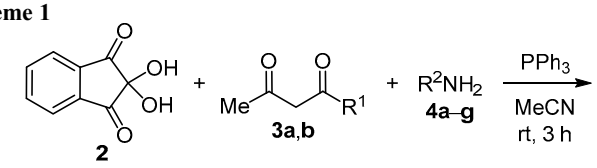
Keywords: dialkyl acetylenedicarboxylate, 1,3-dicarbonyl compound, ninhydrin, primary amine, pyrrole, Diels–Alder reaction, three-component reaction.

Pyrrole and its derivatives are highly important compounds because of the broad range of its biological activities. They have been employed as antibacterial,[1] antitumor,[2] anti-inflammatory,[3] and antifungal agents.[4] Pyrrole core has been also incorporated in a cholesterol-lowering drug atorvastatin.[5] In addition, several pyrroles display significant antioxidative properties[6] or have been successfully exploited as intermediates in the synthesis of numerous natural products, agrochemicals, flavorings, dyes, and functional materials.[7] Pyrrole derivatives have been used as chemosensors in production of lasers and image recognition.[8] Polysubstituted pyrroles have been used as antibacterial,[9] inotropic,[10] antitumor,[11] anti-inflammatory,[3] and antifungal agents[12] and antioxidants.[6b] Finally, indeno[1,2-*b*]-pyrroles exhibit a wide range of biological activities.[13]

According to the aforementioned, pyrrole is one of the most broadly available heterocyclic motif in bioactive natural products, drugs, and materials. For this reason, synthesis and application of substituted pyrroles have attracted increased attention.[14] Conventionally used procedures for preparation of functionalized pyrroles involve the Paal–Knorr, Hantzsch, and Knorr reactions. Recently, advanced synthetic strategies for obtaining substituted pyrroles have been developed. These methods include ring opening cyclization,[15] multicomponent reactions,[16] cycloaddition,[17] oxidative coupling reactions,[18] isocyanide-based reactions,[19] rearrangement reactions,[20] hydroamination/cyclizations,[21] and aza-Wittig reactions.[22] Although these divergent synthetic approaches are useful, many of them require utilization of catalysts, elevated temperatures, and relatively complex substrates.[14f,23] Therefore, the development of efficient procedures for the synthesis of functionalized pyrroles using structurally simple and readily available starting materials is still an important subject of interest.[24]

Previously, a reaction of ninhydrin, 1,3-dicarbonyl compounds, and primary amines was investigated and dihydroxypyrroles were obtained at room temperature without exploitation of any catalyst.[25] Herein, we report a synthesis of indeno[1,2-*b*]pyrrol-4(1*H*)-ones under mild and catalyst-free conditions using ninhydrin, 1,3-dicarbonyl compounds, primary amines, and PPh_3.

Scheme 1



	R^1	R^2	Yield, %
1a	Me	Me	92
1b	Me	Et	90
1c	Me	Ph	78
1d	Me	Bn	85
1e	Me	4-$MeOC_6H_4CH_2$	87
1f	OEt	*n*-Pr	87
1g	OEt	4-$MeOC_6H_4$	80

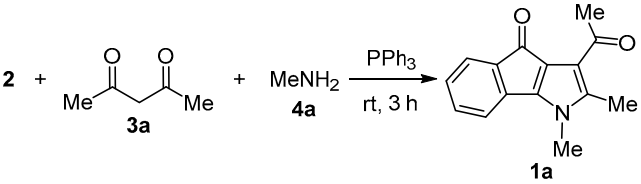
Functionalized pyrroles **1a**–**g** were obtained in high yields *via* the reaction of ninhydrin (**2**), 1,3-dicarbonyl compounds **3a**,**b**, primary amines **4a**–**g**, and PPh_3 in MeCN at room temperature (Scheme 1). The simplicity of the demonstrated method suggests that it may be an interesting alternative to the complex multistep approaches. The synthesis was performed without any catalyst. However, PPh_3 played a crucial role in this reaction. Without PPh_3, the respective dihydroxypyrroles[25] were generated, whereas addition of PPh_3 to the reaction mixture promoted the formation of indeno[1,2-*b*]pyrrol-4(1*H*)-ones[13] and subsequent elimination of triphenylphosphine oxide.

To provide the most suitable reaction conditions, effect of different solvents and temperatures on formation of pyrrole derivative **1a** was examined. Solvents, such as MeCN, DMF, H_2O, PhMe, and Et_2O, and solvent-free conditions were tested. Among them, MeCN provided the highest yield of product **1a** (Table 1, entry 8). The most favorable temperature for this chemical transformation was room temperature. Increase in the temperature did not change the yield of indeno[1,2-*b*]pyrrol-4(1*H*)-one **1a**. Therefore, the highest yield (92%) of product **1a** was obtained when the reaction was performed in MeCN at room temperature.

The structures of compounds **1a**–**g** were assigned by IR, ^1H and ^{13}C NMR spectroscopic and mass spectral data. For example, three singlets of methyl group protons at 2.52, 2.83, and 3.54 ppm along with signals of aromatic moiety were observed in the ^1H NMR spectrum of product **1a**. The ^{13}C NMR spectrum of indeno[1,2-*b*]pyrrol-4(1*H*)-one **1a**, containing signals of two carbonyl groups at 188.3 and 191.2 ppm, was in agreement with the proposed structure. Furthermore, a peak of molecular ion with *m*/*z* 239 was observed in the mass spectrum of compound **1a**. Product **1c** has been described previously.[26]

A plausible mechanism for the formation of compounds **1a**–**g** has been proposed on an example of pyrrole **1a**

Table 1. Optimization of solvent for the synthesis of indeno[1,2-*b*]pyrrol-4(1*H*)-one **1a***



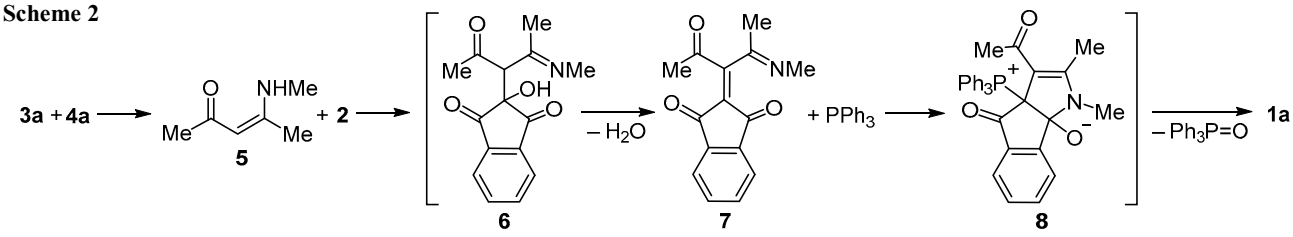
Entry	Solvent	Yield, %	Entry	Solvent	Yield, %
1	CH_2Cl_2	67	6	H_2O	–**
2	$CHCl_3$	72	7	–	45
3	DMF	58	8	MeCN	92
4	PhMe	78	9	EtOH	38
5	Et_2O	–**	10	THF	54

* Reaction conditions: ninhydrin (**2**) (356 mg, 2 mmol), pentane-2,4-dione (**3a**) (200 mg, 2 mmol), methylamine (**4a**) solution in THF (2 M, 0.1 ml, 2 mmol), PPh_3 (524 mg, 2 mmol), MeCN (7 ml), rt, 3 h.
** The reaction did not proceed.

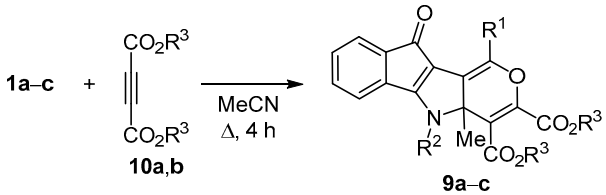
(Scheme 2). Enaminone **5**, produced in initial reaction of pentane-2,4-dione (**3a**) and methylamine (**4a**), as a nucleophile attacks ninhydrin (**2**) and generates intermediate **6**. Adduct **6** is then converted into compound **7** by elimination of H_2O, and intermediate **7** further reacts with PPh_3 to produce zwitterion **8**. Finally, elimination of triphenylphosphine oxide leads to the formation of product **1a**.

The obtained indeno[1,2-*b*]pyrrol-4(1*H*)-ones **1a**–**c** were further used in synthesis of other pyrrole derivatives **9a**–**c**. The Diels–Alder reaction of compounds **1a**–**c** and dialkyl acetylenedicarboxylates **10a**,**b** in MeCN under reflux conditions furnished the respective indeno[1,2-*b*]pyrano-[3,4-*d*]pyrroles **9a**–**c** in high yields (Scheme 3). Two slightly different procedures were tested for the synthesis of products **9a**–**c**. In the first one, compounds **1a**–**c** were not isolated and dialkyl acetylenedicarboxylates **10a**,**b**

Scheme 2



Scheme 3



	R^1	R^2	R^3	Yield, %
9a	Me	Me	Me	83
9b	Me	Et	Me	80
9c	Me	Ph	Et	75

were added directly to the initial reaction mixture which was then refluxed for 4 h. In the second procedure, indeno-[1,2-*b*]pyrrol-4(1*H*)-ones **1a**–**c** were separated from the starting mixture and further exploited in the reaction with activated acetylenic compounds **10a**,**b**, performed in MeCN under reflux conditions for 4 h. Both of the tested methods ensured the formation of products **9a**–**c**. However, the yields of indeno[1,2-*b*]pyrano[3,4-*d*]pyrroles **9a**–**c**, obtained in a one-pot synthesis, were lower than those achieved in the second procedure.

The structures of compounds **9a**–**c** were confirmed by IR, ^{1}H and ^{13}C NMR spectroscopic and mass spectral data. For example, three singlets of methyl group protons at 1.56, 2.35, and 3.12 ppm, two singlets of carbomethoxy group protons at 3.75 and 3.83 ppm, and signals of aromatic moiety were observed in ^{1}H NMR spectrum of indeno[1,2-*b*]pyrano[3,4-*d*]pyrrole **9a**. The ^{13}C NMR spectrum of compound **9a**, containing signals of three carbonyl groups at 161.3, 165.3, and 188.4 ppm was in agreement with the proposed structure. In addition, a peak of molecular ion with *m*/*z* 381 was present in the mass spectrum of product **9a**.

In summary, a reaction of ninhydrin, 1,3-dicarbonyl compounds, primary amines, and PPh_3 in MeCN at room temperature has been studied and indeno[1,2-*b*]pyrrol-4(1*H*)-ones have been obtained in high yields. These compounds have been used in the Diels–Alder reaction with dialkyl acetylenedicarboxylates to produce the respective indeno[1,2-*b*]pyrano[3,4-*d*]pyrroles in high yields. The advantages of the developed synthetic procedures are mild and clean reaction conditions, short reaction times, and high yields of the products. Moreover, the reactions proceed smoothly without exploitation of a catalyst and without activation or modification of the starting materials prior to the synthesis.

Experimental

IR spectra were acquired on a Shimadzu IR-460 spectrometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker FT-500 spectrometer (500 and 126 MHz, respectively) in $CDCl_3$ solutions, and TMS was applied as internal standard. Mass spectra were obtained on a Finnigan-MAT 8430 spectrometer using EI method (70 eV). Elemental analyses were performed on a PerkinElmer model 240-C instrument. Melting points were determined on an Electrothermal 9100 apparatus. The reaction progress was monitored by TLC on Silica gel 60G F254 glass plates, visualization under UV light.

All reagents were purchased from Fluka and employed without further purification. Methylamine (**4a**) and ethylamine (**4b**) were applied as 2 M solutions in THF.

Synthesis of indeno[1,2-*b*]pyrrol-4(1*H*)-ones 1a–g (General method). A solution of 1,3-dicarbonyl compound **3a**,**b** (2 mmol) and primary amine **4a**–**g** (2 mmol) in MeCN (5 ml) was prepared and stirred at room temperature for 30 min. Ninhydrin (**2**) (356 mg, 2 mmol) was added and the reaction mixture was stirred at room temperature for 15 min. Subsequently, a solution of PPh_3 (524 mg, 2 mmol) in MeCN (2 ml) was slowly added to the mixture, and the reaction progress was monitored by TLC (eluent hexane–EtOAc, 5:1). After completion of the reaction (3 h), MeCN was evaporated and the residue was purified by column chromatography (silica gel, eluent hexane–EtOAc, 5:1).

3-Acetyl-1,2-dimethylindeno[1,2-*b*]pyrrol-4(1*H*)-one (1a). Yield 440 mg (92%), pale-yellow powder, mp 138–140°C. R_f 0.87. IR spectrum, ν, cm^{-1}: 1727, 1725, 1694, 1584, 1487, 1357. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.52 (3H, s, 2-CH_3); 2.83 (3H, s, C(O)CH_3); 3.54 (3H, s, NCH_3); 7.53 (1H, d, ^3J = 7.6, H Ar); 7.58 (1H, d, ^3J = 7.5, H Ar); 7.63 (1H, t, ^3J = 7.6, H Ar); 7.74 (1H, t, ^3J = 7.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 14.2 (CH_3); 31.3 (CH_3); 36.3 (CH_3); 109.2 (C); 120.8 (C Ar); 124.8 (C Ar); 125.2 (C); 128.6 (C Ar); 132.2 (C); 135.3 (C Ar); 142.6 (C); 148.2 (C); 148.7 (C); 188.3 (C=O); 191.2 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 239 $[M]^+$ (15), 196 $[M–C_2H_3O]^+$ (84), 43 $[CH_3C{\equiv}O]^+$ (100). Found, %: C 75.43; H 5.62; N 5.97. $C_{15}H_{13}NO_2$. Calculated, %: C 75.30; H 5.48; N 5.85.

3-Acetyl-1-ethyl-2-methylindeno[1,2-*b*]pyrrol-4(1*H*)-one (1b). Yield 456 mg (90%), pale-yellow powder, mp 145–147°C. IR spectrum, ν, cm^{-1}: 1732, 1728, 1687, 1589, 1462, 1373. R_f 0.52. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 (3H, t, ^3J = 7.4, NCH$_2$C$\underline{H}_3$); 2.53 (3H, s, 2-CH_3); 2.95 (3H, s, C(O)CH_3); 4.25 (2H, q, ^3J = 7.4, NC$\underline{H}_2$CH$_3$); 7.45 (1H, d, ^3J = 7.6, H Ar); 7.54 (1H, t, ^3J = 7.5, H Ar); 7.72 (1H, d, ^3J = 7.6, H Ar); 7.83 (1H, t, ^3J = 7.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 14.3 (CH_3); 16.2 (CH_3); 31.5 (CH_3); 43.2 ($\underline{C}H_2CH_3$); 109.3 (C); 121.2 (C Ar); 125.2 (C Ar); 125.5 (C); 128.7 (C Ar); 132.4 (C); 134.8 (C Ar); 142.7 (C); 147.6 (C); 148.3 (C); 187.6 (C=O); 192.3 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 253 $[M]^+$ (15), 210 $[M–C_2H_3O]^+$ (78), 43 $[CH_3C{\equiv}O]^+$ (100). Found, %: C 75.96; H 6.12; N 5.68. $C_{16}H_{15}NO_2$. Calculated, %: C 75.87; H 5.97; N 5.53.

3-Acetyl-2-methyl-1-phenylindeno[1,2-*b*]pyrrol-4(1*H*)-one (1c).[26] Yield 470 mg (78%), pale-yellow powder, mp 163–165°C. IR spectrum, ν, cm^{-1}: 1730, 1727, 1696, 1564, 1487, 1378. R_f 0.38. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.52 (3H, s, 2-CH_3); 2.83 (3H, s, C(O)CH_3); 7.04 (1H, d, ^3J = 7.6, H Ar); 7.18 (1H, t, ^3J = 7.5, H Ar); 7.28 (2H, t, ^3J = 7.5, H Ar); 7.36 (2H, d, ^3J = 7.6, H Ar); 7.58 (1H, t, ^3J = 7.6, H Ar); 7.65 (1H, d, ^3J = 7.6, H Ar); 7.76 (1H, t, ^3J = 7.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 15.2 (CH_3); 31.4 (CH_3); 113.8 (C); 120.4 (C Ar); 122.8 (2C Ar); 124.6 (C Ar); 125.7 (C Ar); 128.3 (C Ar); 129.4 (2C Ar); 131.7 (C); 135.4 (C Ar); 142.5 (C); 145.6 (C); 147.2 (C); 147.8 (C); 188.2 (C=O); 192.5 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 301 $[M]^+$ (15), 258 $[M–C_2H_3O]^+$ (64), 77 $[C_6H_5]^+$ (68), 43 $[CH_3C{\equiv}O]^+$ (100). Found, %: C 79.85; H 5.18; N 4.78. $C_{20}H_{15}NO_2$. Calculated, %: C 79.72; H 5.02; N 4.65.

3-Acetyl-1-benzyl-2-methylindeno[1,2-*b*]pyrrol-4(1*H*)-one (1d). Yield 536 mg (85%), pale-yellow powder, mp 175–177°C. IR spectrum, ν, cm^{-1}: 1735, 1728, 1697, 1585, 1489, 1374. R_f 0.29. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.12 (2H, s, NCH_2); 2.52 (3H, s, 2-CH_3); 2.83 (3H, s, C(O)CH_3); 7.12 (1H, d, ^3J = 7.6, H Ar); 7.23 (1H, t, ^3J = 7.5, H Ar); 7.32 (2H, t, ^3J = 7.5, H Ar); 7.43 (2H, d, ^3J = 7.6, H Ar); 7.64 (1H, t, ^3J = 7.6, H Ar); 7.73 (1H, d, ^3J = 7.6, H Ar); 7.85 (1H, t, ^3J = 7.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 14.5 (CH_3); 31.6 (CH_3); 47.3 (CH_2); 109.2 (C); 120.5 (C Ar); 124.3 (C Ar); 124.8 (C); 128.5 (C Ar); 129.2 (2C Ar); 129.8 (2C Ar); 130.7 (C Ar); 132.3 (C); 135.2

(C Ar); 135.8 (C); 143.2 (C); 147.3 (C); 147.6 (C); 188.4 (C=O); 193.6 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 315 $[M]^+$ (10), 272 $[M–C_2H_3O]^+$ (68), 91 $[C_7H_7]^+$ (88), 43 $[CH_3C{\equiv}O]^+$ (100). Found, %: C 80.12; H 5.58; N 4.62. $C_{21}H_{17}NO_2$. Calculated, %: C 79.98; H 5.43; N 4.44.

3-Acetyl-1-(4-methoxybenzyl)-2-methylindeno[1,2-*b*]-pyrrol-4(1*H*)-one (1e). Yield 601 mg (87%), yellow powder, mp 181–183°C. IR spectrum, ν, cm^{-1}: 1729, 1725, 1696, 1578, 1487, 1375. R_f 0.25. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.15 (2H, s, NCH_2); 2.54 (3H, s, 2-CH_3); 2.85 (3H, s, $C(O)CH_3$); 3.78 (3H, s, OCH_3); 7.15 (2H, d, ^3J = 7.8, H Ar); 7.25 (2H, d, ^3J = 7.8, H Ar); 7.52 (1H, d, ^3J = 7.6, H Ar); 7.63 (1H, t, ^3J = 7.6, H Ar); 7.72 (1H, d, ^3J = 7.6, H Ar); 7.85 (1H, t, ^3J = 7.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 14.6 (CH_3); 31.4 (CH_3); 46.7 (CH_2); 55.6 (OCH_3); 108.7 (C); 113.2 (2C Ar); 120.7 (C Ar); 124.5 (C Ar); 125.2 (C); 128.6 (C Ar); 131.2 (C); 132.4 (C); 133.4 (2C Ar); 135.2 (C Ar); 143.3 (C); 147.2 (C); 148.3 (C); 158.6 (C); 187.6 (C=O); 193.5 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 345 $[M]^+$ (10), 302 $[M–C_2H_3O]^+$ (56), 91 $[C_7H_7]^+$ (86), 43 $[CH_3C{\equiv}O]^+$ (100). Found, %: C 76.63; H 5.65; N 4.22. $C_{22}H_{19}NO_3$. Calculated, %: C 76.50; H 5.54; N 4.06.

Ethyl 2-methyl-4-oxo-1-propyl-1,4-dihydroindeno-[1,2-*b*]pyrrole-3-carboxylate (1f). Yield 517 mg (87%), yellow powder, mp 145–147°C. IR spectrum, ν, cm^{-1}: 1745, 1728, 1725, 1685, 1574, 1468, 1376. R_f 0.32. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.12 (3H, t, ^3J = 7.4, $N(CH_2)_2C\underline{H}_3$); 1.38 (3H, t, ^3J = 7.4, $CO_2CH_2C\underline{H}_3$); 1.65–1.73 (2H, m, $NCH_2C\underline{H}_2CH_3$); 2.92 (3H, s, 2-$CH_3$); 4.26 (2H, q, ^3J = 7.4, $CO_2C\underline{H}_2CH_3$); 4.93 (2H, t, ^3J = 7.3, $NC\underline{H}_2CH_2CH_3$); 7.56 (1H, d, ^3J = 7.6, H Ar); 7.64 (1H, d, ^3J = 7.5, H Ar); 7.73 (1H, t, ^3J = 7.6, H Ar); 7.82 (1H, t, ^3J = 7.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 11.3 (CH_3); 14.2 (CH_3); 15.6 (CH_3); 26.3 (CH_2); 52.4 (CH_2); 61.3 ($CO_2\underline{C}H_2$); 101.2 (C); 109.4 (C); 121.4 (C Ar); 124.6 (C Ar); 127.2 (C Ar); 131.2 (C); 133.6 (C Ar); 142.2 (C); 146.4 (C); 149.2 (C); 167.3 (C=O); 188.3 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 297 $[M]^+$ (10), 252 $[M–C_2H_5O]^+$ (86), 45 $[C_2H_5O]^+$ (100). Found, %: C 72.83; H 6.58; N 4.82. $C_{18}H_{19}NO_3$. Calculated, %: C 72.71; H 6.44; N 4.71.

Ethyl 1-(4-methoxyphenyl)-2-methyl-4-oxo-1,4-dihydro-indeno[1,2-*b*]pyrrole-3-carboxylate (1g). Yield 578 mg (80%), yellow powder, mp 168–170°C. IR spectrum, ν, cm^{-1}: 1747, 1725, 1697, 1578, 1464, 1386. R_f 0.27. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.35 (3H, t, ^3J = 7.4, $CO_2CH_2C\underline{H}_3$); 2.83 (3H, s, 2-CH_3); 3.85 (3H, s, OCH_3); 4.26 (2H, q, ^3J = 7.4, $CO_2C\underline{H}_2CH_3$); 6.95 (2H, d, ^3J = 7.6, H Ar); 7.06 (1H, d, ^3J = 7.6, H Ar); 7.22 (2H, d, ^3J = 7.6, H Ar); 7.52 (1H, t, ^3J = 7.6, H Ar); 7.63 (1H, d, ^3J = 7.6, H Ar); 7.75 (1H, t, ^3J = 7.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 14.2 (CH_3); 15.6 (CH_3); 55.6 (OCH_3); 61.7 ($CO_2\underline{C}H_2$); 106.6 (C); 113.7 (2C Ar); 116.3 (C); 120.5 (C Ar); 125.3 (2C Ar); 125.8 (C Ar); 127.6 (C Ar); 131.3 (C); 134.5 (C Ar); 139.2 (C); 141.2 (C); 144.3 (C); 147.6 (C); 158.6 (C); 164.3 (C=O); 187.6 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 361 $[M]^+$ (10), 316 $[M–C_2H_5O]^+$ (68), 45 $[C_2H_5O]^+$ (100). Found, %: C 73.26; H 5.42; N 3.96. $C_{22}H_{19}NO_4$. Calculated, %: C 73.12; H 5.30; N 3.88.

Synthesis of indeno[1,2-*b*]pyrano[3,4-*d*]pyrroles 9a–c (General method). Dialkyl acetylenedicarboxylate **10a**,**b** (2 mmol) was added to a stirred solution of indeno[1,2-*b*]-pyrrol-4(1*H*)-one **1a–c** (2 mmol) in MeCN (6 ml). The mixture was refluxed, and the reaction progress was monitored by TLC (eluent hexane–EtOAc, 7:1). After completion of the reaction (4 h), the mixture was cooled down and MeCN was evaporated. The residue was purified by column chromatography (silica gel, eluent hexane–EtOAc, 7:1).

Dimethyl 1,4a,5-trimethyl-10-oxo-4a,5-dihydro-10*H*-indeno[1,2-*b*]pyrano[3,4-*d*]pyrrole-3,4-dicarboxylate (9a). Yield 0.63 g (83%), pale-yellow powder, mp 172–174°C. IR spectrum, ν, cm^{-1}: 1743, 1727, 1695, 1587, 1465, 1325. R_f 0.65. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.56 (3H, s, 4a-CH_3); 2.35 (3H, s, 1-CH_3); 3.12 (3H, s, NCH_3); 3.75 (3H, s, CO_2CH_3); 3.83 (3H, s, CO_2CH_3); 7.54 (1H, t, ^3J = 7.6, H Ar); 7.64 (1H, t, ^3J = 7.5, H Ar); 7.78 (1H, d, ^3J = 7.6, H Ar); 7.92 (1H, d, ^3J = 7.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 13.5 (CH_3); 18.2 (CH_3); 34.2 (CH_3); 51.2 ($CO_2\underline{C}H_3$); 52.4 ($CO_2\underline{C}H_3$); 71.2 (C); 105.3 (C); 115.2 (C); 116.4 (C); 121.6 (C Ar); 124.3 (C Ar); 127.2 (C Ar); 131.2 (C); 133.4 (C Ar); 138.6 (C); 141.6 (C); 144.7 (C); 154.2 (C); 161.3 (C=O); 165.3 (C=O); 188.4 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 381 $[M]^+$ (10), 350 $[M–CH_3O]^+$ (68), 31 $[CH_3O]^+$ (100). Found, %: C 66.28; H 5.16; N 3.78. $C_{21}H_{19}NO_6$. Calculated, %: C 66.14; H 5.02; N 3.67.

Dimethyl 5-ethyl-1,4a-dimethyl-10-oxo-4a,5-dihydro-10*H*-indeno[1,2-*b*]pyrano[3,4-*d*]pyrrole-3,4-dicarboxylate (9b). Yield 0.63 g (80%), pale-yellow powder, mp 183–185°C. IR spectrum, ν, cm^{-1}: 1745, 1729, 1698, 1586, 1478, 1373. R_f 0.43. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.15 (3H, t, ^3J = 7.4, $NCH_2C\underline{H}_3$); 1.56 (3H, s, 4a-CH_3); 2.37 (3H, s, 1-CH_3); 3.75 (3H, s, CO_2CH_3); 3.87 (3H, s, CO_2CH_3); 4.25–4.38 (2H, m, $NC\underline{H}_2CH_3$); 7.56 (1H, t, ^3J = 7.8, H Ar); 7.68 (1H, t, ^3J = 7.8, H Ar); 7.82 (1H, d, ^3J = 7.7, H Ar); 7.95 (1H, d, ^3J = 7.8, H Ar). ^{13}C NMR spectrum, δ, ppm: 13.4 (CH_3); 13.8 (CH_3); 19.2 (CH_3); 43.2 (CH_2); 51.4 ($CO_2\underline{C}H_3$); 52.6 ($CO_2\underline{C}H_3$); 68.2 (C); 105.4 (C); 115.6 (C); 117.2 (C); 121.2 (C Ar); 124.5 (C Ar); 127.6 (C Ar); 130.8 (C); 133.2 (C Ar); 137.2 (C); 142.3 (C); 144.5 (C); 154.3 (C); 162.4 (C=O); 166.7 (C=O); 188.5 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 395 $[M]^+$ (15), 364 $[M–CH_3O]^+$ (78), 31 $[C_2H_5O]^+$ (100). Found, %: C 66.94; H 5.47; N 3.67. $C_{22}H_{21}NO_6$. Calculated, %: C 66.83; H 5.35; N 3.54.

Diethyl 1,4a-dimethyl-10-oxo-5-phenyl-4a,5-dihydro-10*H*-indeno[1,2-*b*]pyrano[3,4-*d*]pyrrole-3,4-dicarboxylate (9c). Yield 0.71 g (75%), pale-yellow powder, mp 196–198°C. IR spectrum, ν, cm^{-1}: 1746, 1728, 1694, 1587, 1476, 1375. R_f 0.37. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.14 (3H, t, ^3J = 7.4, $CO_2CH_2C\underline{H}_3$); 1.18 (3H, t, ^3J = 7.4, $CO_2CH_2C\underline{H}_3$); 1.68 (3H, s, 4a-CH_3); 2.38 (3H, s, 1-CH_3); 4.23 (2H, q, ^3J = 7.4, $CO_2C\underline{H}_2CH_3$); 4.34 (2H, q, ^3J = 7.4, $CO_2C\underline{H}_2CH_3$); 7.06 (2H, d, ^3J = 7.6, H Ar); 7.12 (1H, t, ^3J = 7.6, H Ar); 7.34 (2H, t, ^3J = 7.6, H Ar); 7.63 (1H, t, ^3J = 7.8, H Ar); 7.72 (1H, t, ^3J = 7.8, H Ar); 7.85 (1H, d, ^3J = 7.5, H Ar); 7.93 (1H, d, ^3J = 7.8, H Ar). ^{13}C NMR spectrum, δ, ppm: 13.2 (CH_3); 13.6 (CH_3); 14.3 (CH_3); 19.4 (CH_3); 61.2 (CH_2); 62.4 (CH_2); 68.6 (C); 109.2 (C); 114.3 (C); 115.6 (C); 121.3 (C Ar); 124.2 (C Ar); 124.8 (C Ar); 126.3 (2C Ar); 127.2 (C Ar); 128.6 (2C Ar); 130.6 (C); 133.4 (C Ar); 138.4 (C); 141.5 (C); 143.4 (C); 145.2 (C); 153.4

(C); 163.6 (C=O); 167.2 (C=O); 187.6 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 471 $[M]^+$ (10), 426 $[M–C_2H_5O]^+$ (62), 45 $[C_2H_5O]^+$ (100). Found, %: C 71.45; H 5.47; N 3.14. $C_{28}H_{25}NO_6$. Calculated, %: C 71.33; H 5.34; N 2.97.

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