# Synthesis of New *N*-alkyl-5-formyl-2-methylpyrrole Derivatives from Glucosamine

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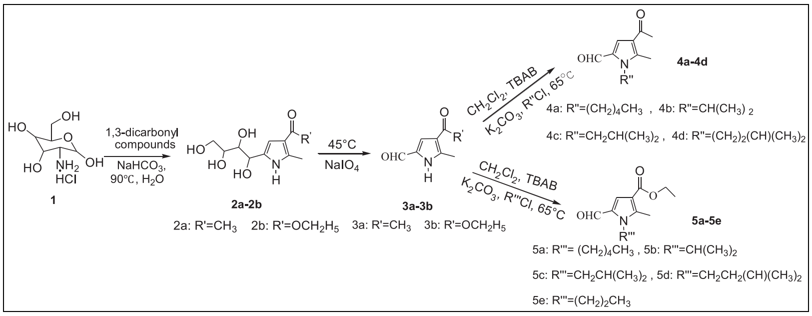

Glucosamine hydrochloride **1** was treated with 1,3-dicarbonyl compounds to obtain 2-methyl-5-(1,2,3,4-tetrahydroxy-butyl) pyrrole **2a** and **2b**, respectively. Under the role of $NaIO_4$, **2a** and **2b** were successfully transformed into the related 5-formal pyrrole derivative **3a** and **3b**, respectively. Compounds **4a**–**4d** and **5a**–**5e** were obtained by reacting **3a** and **3b** with chlorinated hydrocarbons by alkylation reactions, respectively. The structures of all new products were confirmed by IR, NMR, and HRMS spectra.

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## INTRODUCTION

The special structure and the biological activity made the pyrrole derivatives widely applicated in the food, material, medicine, and perfume industry [1–5]. Recently, the synthesis of new pyrrole derivatives has especially gained popularity because these flavor precursors, having pyrrole derivatives with potent perfume properties, in the course of processing and storage, could avoid the volatility of flavoring substances under the condition of heat cracking, those formed aldehyde, ester compounds, ketone are the pyrolysis products of the tobacco composition [6].

In our previous work, three *N*-(2, 5-dimethylpyrrole) glycine esters were synthesized [7], among them *N*-(2,5-dimethylpyrrole) glycine benzyl ester, produced to enhance the aroma quality and volume of aroma, reduce irritancy, and improve the aftertaste. In order to develop some new pyrrole derivatives with potent perfume properties, here, we report the synthesis of a series of *N*-Alkyl-5-formyl-2-methylpyrrole derivatives.

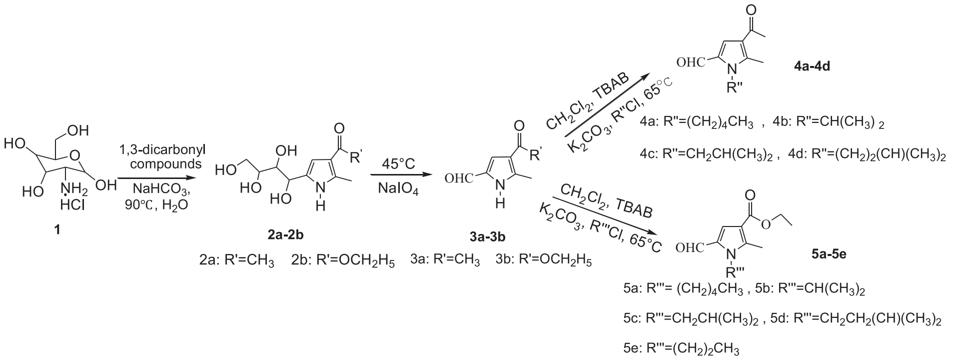
## RESULTS AND DISCUSSION

The $^1$H NMR spectrum of **2a** revealed the presence of two methyl signals at δ 2.32 and 2.36 ppm, and the signal at δ 6.45 ppm was assigned to the double bond C. Its $^{13}$C NMR signal at δ 199.9 ppm indicated that there was a carbonyl group, meanwhile the $^{13}$C NMR spectrum showed the presence of four double bond C signals at δ 108.0, 119.8, 130.5, and 137.9 ppm, which indicated compound **2a** to form a pyrrole ring. The $^{13}$C NMR signals at δ 73.8, 71.2, 66.3, and 62.4 ppm were assigned to four C─O bonds, and the HRMS of **2a** exhibited molecular ions $[M + H]^+$ at *m/z* 244.1188, these data indicated that **2a** was a pyrrole derivative including one tetrahydroxy group [8]. $^{13}$C NMR signal of **2b** at δ 168.3 ppm indicated that there was an ester carbonyl group, and the HRMS of **2b** exhibited molecular ions $[M + Na]^+$ at *m/z* 296.1118. So compound **2b** is the target product.

The $^{13}$C NMR spectrum of **3a** showed two methyl signals at δ 14.3 and 28.2 ppm and two carbonyl signals at δ 179.1 and 194.4 ppm. The $^{13}$C NMR revealed pyrrole ring at δ 123.5, 123.8, 130.1, and 143.6 ppm. The $^{13}$C NMR spectrum of **3b** showed two methyl signals at δ 13.6 and 14.5 ppm, two carbonyl signals at δ 164.3 and 179.0 ppm, and one methylene signal at δ 60.0 ppm. The $^{13}$C NMR revealed pyrrole ring at δ 115.4, 123.7, 130.5, and 143.2 ppm. So compounds **3a** and **3b** are objective products [9].

The $^{13}$C NMR of compounds **4a**, **4b**, **4c**, and **4d** showed N─$\underline{C}$ signals at δ 45.1, 47.7, 51.7, and 43.8 ppm, respectively. The $^{13}$C NMR spectra of **5a**–**5e** showed the N─$\underline{C}$ signals at δ 45.4, 48.9, 52.0, 44.0, and 46.8 ppm, respectively. Compounds **4a**–**4d** and **5a**–**5e** are target products [10].

**Scheme 1.** Synthesis of N-alkyl-5-formyl-2-methylpyrrole derivatives.



## CONCLUSION

The structures of all the new pyrrole derivatives (**4a**, **4b**, **4c**, **4d**, **5a**, **5b**, **5c**, **5d**, and **5e**) were in agreement with infrared, NMR, and HRMS spectra. These compounds could be useful in the chemical and perfume–chemical fields. Further studies on these pyrrole derivatives are now in progress.

## EXPERIMENTAL

In the presence of $NaHCO_3$, the reaction of glucosamine hydrochloride **1** with acetyl acetone (1.2 eq) in $H_2O$ at 90°C for 8 h afforded 2-methyl-5-(1,2,3,4-tetrahydroxy-butyl) pyrrole **2a** in 86% yield. Similarly, treatment of **1** with ethyl acetoacetate (1.2 eq) gave a 2-acetyl-5-(1,2,3,4-tetrahydroxy-butyl) pyrrole **2b** in 81%. Oxidation of **2a** and **2b** with $NaIO_4$ in methanol at 45°C for 3 h gave 5-formyl-2-methyl pyrrole derivative **3a** in 80% yield and **3b** in 90% yield, respectively. In the presence of tetrabutylammonium bromide, compound **3a** was treated with R''-Cl (1.0 eq) in $CH_2Cl_2$ at 65°C for 10 h, then the mixture was evaporated in vacuum to dryness, treated with water to remove the $K_2CO_3$, followed by extraction with EtOAC, affording **4a** in 81% yield, **4b** in 81% yield, **4c** in 84% yield, and **4d** in 81% yield. The reaction of compound **3b** with R'''-Cl (1.0 eq) in $CH_2Cl_2$ at 65°C for 10 h gave **5a** in 78% yield, **5b** in 75% yield, **5c** in 82% yield, **5d** in 78% yield, and **5e** in 80% yield (Scheme 1).

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[10] Compound **2a**; yield 86%; $^1H$ NMR (400.1MHz, $D_2O$): δ 6.45 (s, 1H, H-4), 4.70 (s, 1H, H-3′), 3.65 (m, 2H, H-1′, H-4′), 3.58 (d, *J*=2.9Hz, 1H, H-3′), 3.47–3.57 (dd, *J*=6.5Hz, 1H, H-2′), 2.36 (s, 3H, $=-CH_3$), 2.32 (s, 3H, $CO\underline{CH_3}$); $^{13}C$ NMR (100.6MHz, $D_2O$): δ 199.9 (C=O), 137.9 (C-2), 130.5 (C-5), 119.8 (C-3), 108.0 ($\underline{CH}=C$), 73.8 (C-1′), 71.2 (C-2′), 66.3 (C-3′), 62.4 (C-4′), 27.5 ($=-CH_3$), 13.1 ($CO\underline{CH_3}$); HRMS: Calcd. For $C_{11}H_{17}NO_5$ $[M + H]^+$ 244.1185, found $[M + H]^+$ 244.1188; Compound **2b**: yield 81%, mp 153–154°C; $^1H$ NMR (400 MHz, $D_2O$): δ 1.21 (t, 3H, *J*=7.1Hz, $OCH_2\underline{CH_3}$), 2.34 (S, 3H, $=-CH_3$), 3.47 (dd, 1H, *J*=7.70Hz, *J*=4.9Hz, OH), 3.58 (m, 1H, H-2′), 3.64 (m, 2H, H-l', H-4′), 4.15 (q, 2H, *J*=7.1 Hz, $O\underline{CH_2}CH_3$), 4.72 (m, 2H, H-3′, OH), 6.36 (s, 1H, H-4); $^{13}C$ NMR (100MHz, $D_2O$): δ 12.1 ($OCH_2\underline{CH_3}$), 13.6($=-CH_3$), 60.7 ($O\underline{CH_2}CH_3$), 62.4 (C-4′), 66.4 (C-3′), 71.3 (C-2′), 74.0 (C-1′), 107.1 (C-4), 110.0 (C-3), 130.3 (C-5), 137.5 (C-2), 168.3(C=O); IR (KBr), *v*: 2932, 1702, 1224, 1090$cm^{-1}$; HRMS: Calcd for $C_{12}H_{19}NO_6$ $[M + Na]^+$ 296.1110, found $[M + Na]^+$ 296.1118; Compound **3a**, 80%, mp 144–145°C; $^1H$ NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H, $CH_3$), 2.68 (s, 3H, $=-CH_3$), 7.32–7.33 (d, *J*=2.44MHz, 1H, =CH), 9.46 (s, 1H, O=CH), 10.80 (s, 1H, NH); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 14.3 ($=-CH_3$), 28.2 ($CO\underline{CH_3}$), 123.5 (C-3), 123.8 (C-4), 130.1 (C-2); 143.6 (C-5), 179.1 (HC=O), 194.4($\underline{C}OCH_3$); HRMS: Calcd for $C_8H_9NO_2$ $[M + H]^+$ 152.0670, found $[M + H]^+$ 152.0668; Compound **3b**; yield 90%, mp 133–134°C; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.35 (t, *J*=7.1Hz, 3H, $OCH_2\underline{CH_3}$), 2.62 (s, 3H,$=-CH_3$), 4.30 (q, *J*=7.1Hz, 2H, $O\underline{CH_2}CH_3$), 7.36 (s, =CH), 9.43 (s, 1H, O=CH), 10.16 (s, 1H, NH); $^{13}C$ NMR (100 MHz, $CDCl_3$), δ: 13.6 ($=-CH_3$), 14.5 ($OCH_2\underline{CH_3}$), 60.0 ($O\underline{CH_2}CH_3$), 115.4 (C-4), 123.7 (C-3), 130.5 (C-2), 143.2 (C-5), 164.3 ($O\underline{C}=O$), 179.0 (HC=O); IR (KBr), *v*: 3400, 2970, 1709, 1670, 1544, 1128$cm^{-1}$; HRMS: Calcd for $C_9H_{11}NO_3$ $[M + H]^+$ 182.0817, found $[M + H]^+$ 182.0817; Compound **4a:** yield 81%; $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J*=7.4Hz, 3H, $CH_2CH_2\underline{CH_3}$), 1.34 (m, 4H, $CH_2CH_2\underline{CH_2CH_2}CH_3$), 1.66 (m, 2H, $CH_2\underline{CH_2}CH_2CH_2CH_3$), 2.45 (s, 3H, $COCH_3$), 2.61 (s, 3H, $=-CH_3$), 4.31 (m, 2H, $N-CH_2$), 7.28 (s, 1H, C=CH), 9.49 (s, 1H, O=CH); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 11.4 ($=-CH_3$), 13.9 ($CH_2CH_2CH_2CH_2\underline{CH_3}$), 22.9 ($CH_2CH_2CH_2\underline{CH_2}CH_3$),

28.3 ($\mathrm{CO\underline{CH_3}}$), 28.7 ($\mathrm{CH_2CH_2\underline{CH_2}CH_2CH_3}$), 30.3 ($\mathrm{CH_2\underline{CH_2}CH_2CH_2CH_3}$), 45.1 ($\mathrm{NCH_2}$), 122.4 (C-4), 126.6 (C-5), 130.1 (C-3), 143.8 (C-2), 178.8 (HC═O), 194.2 (O═$\mathrm{\underline{C}CH_3}$), IR (KBr), *v*: 2958, 1659, 1536, 1482, 1430, 1351cm$^{-1}$; HRMS: Calcd for $\mathrm{C_{13}H_{19}NO_2}$ [M + H]$^+$ 222.1494, found [M + H]$^+$ 222.1500; Compound **4b**: yield 81%; $^1$H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 1.55 (d, *J*=7.0Hz, 6H, $\mathrm{CH\underline{(CH_3)_2}}$), 2.45 (s, 3H, $\mathrm{COCH_3}$), 2.70 (s, 3H, ═—$\mathrm{CH_3}$), 5.17 (m, 1H, N—CH), 7.32 (s, 1H, C═CH), 9.47 (s, 1H, O═CH); $^{13}$C NMR (100MHz, $\mathrm{CDCl_3}$): δ 20.0 (═—$\mathrm{CH_3}$), 27.4 ($\mathrm{CO\underline{CH_3}}$), 47.7 (NCH), 121.4 (C-4), 128.3 (C-5), 129.5 (C-3), 143.3 (C-2), 177.1 (HC═O), 193.3(O═C); IR (KBr), *v*: 2977, 1657, 1531, 1481, 1432, 1376cm$^{-1}$; HRMS: Calcd for $\mathrm{C_{11}H_{15}NO_2}$ [M + H]$^+$ 194.1181, found [M + H]$^+$ 194.1189; Compound **4c**: yield 84%; $^1$H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 0.90 (d, *J*=6.8Hz, 6H, $\mathrm{CH\underline{(CH_3)_2}}$), 2.06 (m, CH, $\mathrm{\underline{CH}(CH_3)_2}$), 2.46 (s, 3H, $\mathrm{COCH_3}$), 2.60 (s, 3H, ═—$\mathrm{CH_3}$), 4.15 (m, 2H, N—$\mathrm{CH_2}$), 7.29 (s, 1H, C═CH), 9.48 (s, 1H, O═CH); $^{13}$C NMR (100MHz, $\mathrm{CDCl_3}$): δ 12.1 (═—$\mathrm{CH_3}$), 19.6 ($\mathrm{\underline{CH}(CH_3)_2}$), 28.3 ($\mathrm{CO\underline{CH_3}}$), 29.9 ($\mathrm{CH\underline{(CH_3)_2}}$), 51.7 ($\mathrm{NCH_2}$), 122.4 (C-4), 126.9 (C-5), 130.6 (C-3), 144.4 (C-2), 178.9 (HC═O), 194.3 (O═C); IR (KBr), *v*: 2961, 1659, 1532, 1481, 1428, 1389, 1349cm$^{-1}$; HRMS: Calcd for $\mathrm{C_{12}H_{17}NO_2}$ [M + H]$^+$ 208.1338, found [M + H]$^+$ 208.1347; Compound **4d**: yield 81%; $^1$H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 0.97 (t, *J*=6.6Hz, 6H, $\mathrm{CH_2CH_2CH\underline{(CH_3)_2}}$), 1.55 (t, *J*=7.1Hz, 1H, $\mathrm{CH_2CH_2\underline{CH}(CH_3)_2}$), 1.71 (m, 2H, $\mathrm{CH_2\underline{CH_2}CH(CH_3)_2}$), 2.45 (s, 3H, $\mathrm{COCH_3}$), 2.60 (s, 3H, ═—$\mathrm{CH_3}$), 4.33 (m, 2H, N—$\mathrm{CH_2}$), 7.26 (s, 1H, C═CH), 9.49 (s, 1H, O═CH); $^{13}$C NMR (100MHz, $\mathrm{CDCl_3}$): δ 11.3 (═—$\mathrm{CH_3}$), 22.4 ($\mathrm{CH_2CH_2CH\underline{(CH_3)_2}}$), 26.2 ($\mathrm{CH_2CH_2\underline{CH}(CH_3)_2}$), 28.3 ($\mathrm{CO\underline{CH_3}}$), 39.3 ($\mathrm{CH_2\underline{CH_2}CH(CH_3)_2}$), 43.8 ($\mathrm{NCH_2}$), 122.4 (C-4), 126.5 (C-5), 130.1 (C-3), 143.8 (C-2), 178.8 (HC═O), 194.2(O═C), IR (KBr), *v*: 2955, 1677, 1656, 1537, 1478, 1389cm$^{-1}$; HRMS: Calcd for $\mathrm{C_{13}H_{19}NO_2}$ [M + H]$^+$ 222.1494, found [M + H]$^+$ 222.1511; Compound **5a:** yield 78%; $^1$H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 0.90 (d, *J*=7.0Hz, 3H, $\mathrm{NCH_2CH_2CH_2CH_2\underline{CH_3}}$), 1.35 (m, 4H, $\mathrm{NCH_2\underline{CH_2CH_2}}$; 3H, $\mathrm{OCH_2\underline{CH_3}}$),1.65 (m, 2H, $\mathrm{N\underline{CH_2}CH_2}$), 2.59 (s, 3H, ═—$\mathrm{CH_3}$), 4.30 (m, 4H, $\mathrm{OCH_2}$;$\mathrm{NCH_2}$), 7.32 (s, 1H, C═CH), 9.46 (s, 1H, O═CH); $^{13}$C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 11.0 (═—$\mathrm{CH_3}$), 13.9 ($\mathrm{CH_2CH_2CH_2CH_2\underline{CH_3}}$), 14.4 ($\mathrm{OCH_2\underline{CH_3}}$), 22.3 ($\mathrm{CH_2CH_2\underline{CH_2}CH_3}$), 28.7 ($\mathrm{\underline{CH_2}CH_2CH_3}$), 30.3 ($\mathrm{NCH_2\underline{CH_2}}$), 45.4 ($\mathrm{NCH_2}$), 59.9 ($\mathrm{OCH_2}$), 114.3 (C-4), 126.6 (C-3), 130.3 (C-2), 144.1 (C-5), 164.2 (O═C—O), 179.0(HC═O); IR (KBr), *v*: 3404.9, 2959, 1713, 1668, 1548, 1480, 1216cm$^{-1}$; HRMS: Calcd for $\mathrm{C_{14}H_{21}NO_3}$ [M + H]$^+$ 252.1600, found [M + H]$^+$ 252.1597; Compound **5b**: yield 75%; $^1$H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 1.35 (t, *J*=7.1Hz, 3H, $\mathrm{OCH_2\underline{CH_3}}$), 1.54 (d, *J*=7.0Hz, 6H, $\mathrm{CH\underline{(CH_3)_2}}$), 2.68 (s, 3H, ═—$\mathrm{CH_3}$), 4.29 (q, 2H, *J*=7.1Hz, $\mathrm{O\underline{CH_2}CH_3}$), 5.14 (s, 1H, N—CH), 7.38 (s, 1H, C═CH), 9.41 (s, 1H, HC═O); $^{13}$C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 14.4 ($\mathrm{OCH_2\underline{CH_3}}$), 14.4 (═—$\mathrm{\underline{CH_3}}$) 21.0 ($\mathrm{CH\underline{(CH_3)_2}}$), 48.9 (NCH), 59.9 ($\mathrm{O\underline{CH_2}CH_3}$), 114.4 (C-4), 128.8 (C-3), 130.8 (C-2), 144.5 (C-5), 164.2 (O═C—O), 178.3(HC═O); IR (KBr), *v*: 3408, 2977, 1709, 1674, 1546, 1130 cm$^{-1}$; HRMS: Calcd for $\mathrm{C_{12}H_{17}NO_3}$ [M + H]$^+$ 224.1287, found [M + H]$^+$ 224.1287; Compound **5c**: yield 82%;$^1$H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 0.89 (d, *J*=6.8Hz, 6H, $\mathrm{CH\underline{(CH_3)_2}}$), 1.36 (t, *J*=7.1Hz, 3H, $\mathrm{OCH_2\underline{CH_3}}$), 2.05 (m, 1H, $\mathrm{\underline{CH}(CH_3)_2}$), 2.58 (s, 3H, ═—$\mathrm{CH_3}$), 4.14 (d, *J*=7.2Hz, 2H, N—$\mathrm{CH_2}$), 4.30 (q, *J*=7.1Hz 2H,O—$\mathrm{\underline{CH_2}CH_3}$), 7.35 (s, 1H, C═CH), 9.45 (s, 1H, HC═O);$^{13}$C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 11.6 (═—$\mathrm{CH_3}$), 14.4 ($\mathrm{OCH_2\underline{CH_3}}$), 19.6 ($\mathrm{CH\underline{(CH_3)_2}}$), 29.9 ($\mathrm{\underline{CH}(CH_3)_2}$), 52.0 ($\mathrm{NCH_2}$), 59.9 (O—$\mathrm{\underline{CH_2}CH_3}$), 114.3 (C-4), 126.9 (C-3), 130.8 (C-2), 144.6 (C-5), 164.3 (O═C—O), 179.0 (HC═O); IR (KBr), *v*: 3317, 2963, 1710, 1667, 1548, 1065cm$^{-1}$; HRMS: Calcd for $\mathrm{C_{13}H_{19}NO_3}$ [M + H]$^+$ 238.1443, found [M + H]$^+$ 238.1441; Compound **5d**: yield 78%; $^1$H NMR (400MHz, $\mathrm{CDCl_3}$): δ 0.98 (d, *J*=6.6Hz, 6H, $\mathrm{CH\underline{(CH_3)_2}}$), 1.35 (t, *J*=7.1Hz, 3H, $\mathrm{OCH_2\underline{CH_3}}$), 1.55 (m, 2H, $\mathrm{NCH_2\underline{CH_2}}$), 1.70 (m, 1H, $\mathrm{\underline{CH}(CH_3)_2}$), 2.59 (s, 3H, ═—$\mathrm{CH_3}$), 4.31 (m, 4H, O—$\mathrm{\underline{CH_2}CH_3}$, N—$\mathrm{CH_2}$), 7.32 (s, 1H, C═CH), 9.46 (s, 1H, O═CH); $^{13}$C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 10.8 (═—$\mathrm{CH_3}$), 14.4 ($\mathrm{OCH_2\underline{CH_3}}$), 22.4 ($\mathrm{CH\underline{(CH_3)_2}}$), 26.2 ($\mathrm{NCH_2\underline{CH_2}}$), 39.4 ($\mathrm{NCH_2\underline{CH_2}}$), 44.0 ($\mathrm{NCH_2}$), 59.9 (O—$\mathrm{\underline{CH_2}CH_3}$), 114.3 (C-4), 126.6 (C-3), 130.3 (C-2), 143.9 (C-5), 164.2 (O═C—O), 179.0 (HC═O); IR (KBr), *v*: 2959, 1709, 1667, 1547, 1191cm$^{-1}$; HRMS: Calcd for $\mathrm{C_{14}H_{21}NO_3}$ [M + H]$^+$ 252.1600, found [M + H]$^+$ 252.1597; Compound **5e**: yield 80%, $^1$H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 0.93 (t, *J*=7.4Hz, 3H, $\mathrm{CH_2CH_2\underline{CH_3}}$), 1.36 (t, *J*=7.1Hz, 3H, $\mathrm{OCH_2\underline{CH_3}}$), 1.70 (m, 2H, $\mathrm{CH_2\underline{CH_2}CH_3}$), 2.59 (s, 3H, ═—$\mathrm{CH_3}$), 4.29 (m, 4H, N—$\mathrm{CH_2}$; O—$\mathrm{\underline{CH_2}CH_3}$), 7.33(s, 1H, C═CH), 9.46(s, 1H, O═CH); $^{13}$C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 10.9 (═—$\mathrm{CH_3}$), 13.7 ($\mathrm{CH_2CH_2\underline{CH_3}}$), 14.4 ($\mathrm{OCH_2\underline{CH_3}}$), 23.9 ($\mathrm{CH_2\underline{CH_2}CH_3}$), 46.8 ($\mathrm{NCH_2}$), 59.9 (O—$\mathrm{\underline{CH_2}CH_3}$), 114.3 (C-4), 126.7 (C-3), 130.5 (C-2), 144.2 (C-5), 164.3 (O═C—O), 179.0 (HC═O); IR (KBr), *v*: 2971, 1709, 1667, 1546, 1480, 1386, 1247, 1192cm$^{-1}$; HRMS: Calcd for $\mathrm{C_{12}H_{17}NO_3}$ [M + H]$^+$ 224.1287, found [M + H]$^+$ 223.1281.