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Synthesis of isoquinolines,quinoline and indolizine using multicomponent

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Abstract: Isoquinoline reacts smoothly with ethyl bromopyruvate in the presence of dialkyl acetylenedicarboxylates or diaryloylacetylene to produceisoquinoline derivatives in good yields. Quinoline and pyridine react with ethyl bromopyruvate in the presence of dimethyl acetylenedicarboxylate to produce quinolines and indolizine derivatives.

Keywords: Quinoline; Indolizine; MulticomponentReaction;Isoquinoline

Introduction

The development of simple synthetic routes for widely used organic compounds from readily available reagents is one of the major tasks in organic synthesis [1]. Bridgehead nitrogen heterocycles are of interest because they constitute an important class of natural products, many of which exhibit useful biological activity [2, 3]. The reaction of nucleophiles, nitrogen-containing heterocycles in particular, with activated acetylenes has been the subject of significant research over the last several decades [4]. The earliest work in this area appears to be that of Diels and Alder, who in 1932 showed that pyridine reacts smoothly with dimethyl acetylenedicarboxylate (DMAD) to form an adduct of unknown structure [5]. Decades later, the structure of the adduct was established as the 4*H*-quinolizine by the systematic and elaborate investigations of Acheson and co-workers [6]. The intermediacy of 1,4-dipolar species was established by its intramolecular trapping with carbonyl groups by Winterfeldt [7]. Reports of intermolecular trapping of the 1,4-dipole with carbon dioxide and phenyl isocyanate, respectively, by Acheson and Plunkett and Huisgen et al. are also noteworthy [8,9]. As part of our current studies on the development of new routes in heterocyclic synthesis,[10] in this paper, we wish to report a simple synthesis of functionalized pyrrolo[2,1-*a*]isoquinolines, pyrrolo[1,2-*a*]quinoline and indolizine. The reaction of isoquinoline (**1**) and dimethyl acetylenedicarboxylate (**2a**) in the presence of ethyl bromopyruvate (**3**) proceeds smoothly in dichloromethane at ambient temperature to produce dimethyl 1-(2-ethoxy-2-oxoacetyl)pyrrolo[2,1-*a*]isoquinoline-2,3-dicarboxylates (**4a**) in 91-94% yields (Scheme 1).

Isoquinoline reacts with the electron-deficient compound (**2**) in the presence of ethyl bromopyruvate in CH_2Cl_2 at room temprature. The products were separated by column and characterized on the basis of their elemental analyses and their IR, ^{1}H NMR and ^{13}C NMR spectra. The mass spectrum of **4a** displayed the molecular ion (M^+) peak at m/z = 383, which is consistent with the 1:1:1 adduct of isoquinoline, dimethyl acetylenedicarboxylate (DMAD) and ethyl bromopyruvate. The ^{1}H NMR spectrum of

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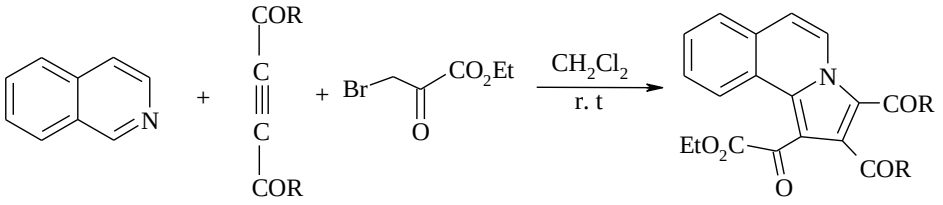
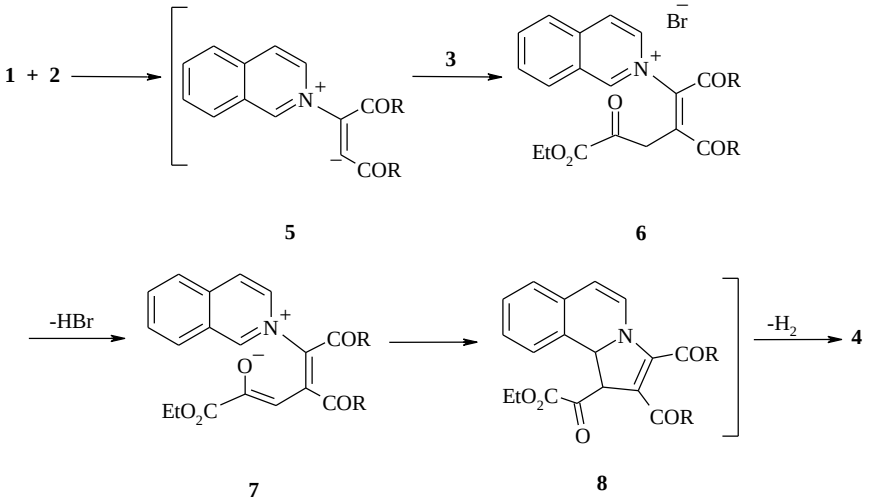
4aexhibited two methoxy group (δ= 3.90 and 3.99), a methyl (δ = 1.38, t, $^3J_{HH}$ = 7.1 Hz) and a methylene (δ = 4.36 ppm) group, along with multiplets at δ = 7.54-9.31 for the isoquinoline moiety. The proton-decoupled ^{13}C NMR spectrum of **4a** showed 20 distinct resonances in agreement with the proposed structure.



1 **2** **3**

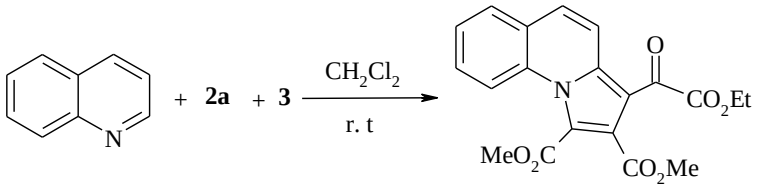
2, 4	R	Yield of **4**
a	OMe	91
b	OEt	94
c	O-*i*-pro	91
d	O^{t}Bt	92
e	C_6H_5	93
f	4-CH_3-C_6H_4	93

Although we have not established the mechanism of the reaction between isoquinoline and activated acetylenes in the presence of ethyl bromopyruvate in an experimental manner, a possible explanation is proposed in Scheme 2. The first step may involve addition of isoquinoline to the acetylenic ester and formation of the 1:1 adduct **5**. Subsequent nucleophilic attack of **5** to ethyl bromopyruvate yields the 1:1:1 adduct **6**, which is converted to **4** by elimination of hydrogen.

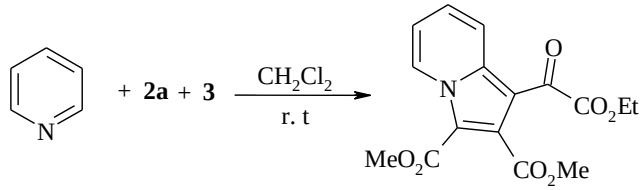


5 **6** **7** **8**

Reaction of quinoline **9** and pyridin **11** with dimethyl acetylenedicarboxylates in the presence of ethyl bromopyruvate proceeds smoothly in dichloromethane at ambient temperature to produce dimethyl 3-(2-ethoxy-2-oxoacetyl)pyrrolo[1,2-*a*]quinoline-1,2-dicarboxylates **(10)** and dimethyl 1-(2-ethoxy-2-oxoacetyl)-2,3-indolizine dicarboxylates**(12)** in 90-93% yields (Scheme 4).



9 **10**



11 **12**

Scheme 3

The ^{1}HNMR spectrum of **10**exhibited two singlets readily recognized as arising from two methoxy δ= 3.91 and 3.95, a triplet at δ = 1.39 ($^3J_{HH}$ = 7.1 Hz) for methyl of esterand a quartet atδ = 4.30 ppm for OCH_2, along with multiplets at δ = 7.50-8.21 for the quinoline moieties.The proton-decoupled ^{13}C NMR spectrum of **10** showed 20 distinct resonances in agreement with the proposed structure.

In conclusion we have uncovered a novel reaction of isoquinoline, quinoline and pyridine with activated acetylene in the presence of ethyl bromopyruvate to afford dialkyl 1-(2-ethoxy-2-oxoacetyl)pyrrolo[2,1-*a*]isoquinoline-2,3-dicarboxylates, ethyl 2-[2,3-diarylpyrrolo[2,1-*a*]isoquinoline-1-yl]-2-oxoacetates, dimethyl 3-(2-ethoxy-2-oxoacetyl)pyrrolo[1,2-*a*]quinoline-1,2-dicarboxylates and dimethyl 1-(2-ethoxy-2-oxoacetyl)-2,3-indolizine dicarboxylates. The present method has the advantages that not only are the reaction performed under neutral conditions, but also the substances can be mixed without any activation or modification. The simplicity of the present procedure makes it an interesting alternative to other approaches.[3] The procedure described here provides an acceptable one-pot method for the preparation of functionalized pyrrolo [2,1-*a*]isoquinolines, pyrrolo[1,2-*a*]quinoline and indolizine

Experimental

Dibenzoylacetylene and 4,4'-dimethylphenoylacetylen was prepared by a known procedure.[11, 12] Other chemicals used in this work were purchased from Fluka and used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. NMR spectra were recorded with a Bruker DRX-500 AVANCE instrument (500.1 MHz for ^{1}H and 125.7 MHz for ^{13}C) with $CDCl_3$ as solvent. Chemical shifts are given in ppm (δ) relative to internal TMS, and coupling constant (J) are reported in Hertz (Hz). Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. These results agreed favorably with the calculated values. Mass spectra were recorded with a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were measured with a Shimadzu IR-460 spectrometer.

The typical procedure for the synthesis of dimethyl 1-(2-ethoxy-2-oxoacetyl)pyrrolo[2,1-a]isoquinoline-2,3-dicarboxylate (4a):

To a stirred solution of 0.28 g DMAD (2 mmol) and 0.39 g ethyl bromopyruvate (2 mmol) in 10 mL CH_2Cl_2 was added 0.26 g isoquinoline (2 mmol) at room temperature. The reaction mixture was then stirred for 24 h. The solvent was removed under reduced pressure and the viscous residue was purified by column chromatography (Merck 230-400 mesh) using *n*-hexane-EtOAc (4:1) as eluent to give **4a**.
pale yellow crystals, yield: 0.70 g (91%),m.p. 102-104°C. IR (KBr): ν = 1729, 1713, 1700 and 1632 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.38 (3 H, t, $^3J_{HH}$ = 7.2 Hz, CH_3), 3.90 (3 H, s, OCH_3), 3.99 (3 H, s, OCH_3), 4.36 (2 H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2), 7.54 (1 H, d, $^3J_{HH}$ = 7.6 Hz, CH), 7.69 (1 H, t, $^3J_{HH}$ = 7.2 Hz,CH), 7.73 (1 H, t, $^3J_{HH}$ = 7.2 Hz, CH), 7.93 (1 H, d, $^3J_{HH}$ = 7.5 Hz, CH), 8.69 (1 H, d, $^3J_{HH}$ = 7.5 Hz, CH), 9.31 (1 H, d, $^3J_{HH}$ = 7.6 Hz, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$):δ= 14.1 (CH_3), 53.0 (OCH_3), 53.1 (OCH_3), 63.1 (OCH_2), 112.5 (C), 117.9 (CH), 119.9 (C), 124.4 (C), 124.9 (CH), 126.1 (CH), 128.4(CH), 129.5 (CH), 129.9 (C), 130.7 (CH), 131.0 (C), 133.8 (C), 163.7 (C=O), 164.7 (C=O), 166.1 (C=O), 177.4 (C=O) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 383 (M^+, 20), 324 (18), 310 (100), 167 (46), 149 (84), 129 (100), 59 (100).
Anal. Calcd for $C_{20}H_{17}NO_7$ (383.4): C, 62.66; H, 4.47; N, 3.65. Found: C, 62.62; H, 4.48; N, 3.76 %.

Diethyl 1-(2-ethoxy-2-oxoacetyl)pyrrolo[2,1-a]isoquinoline-2,3-dicarboxylates (4b):

Yellow powder, yield: 0.78 g (94%), m.p. 140-142 °C. IR (KBr): ν =1722, 1715, 1710 and 1630 (C=O) cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.37 (3 H, t, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.38 (3 H, t, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.41 (3 H, t, $^3J_{HH}$ = 7.2 Hz, CH_3), 4.35 (2 H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2), 4.36 (2 H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2), 4.48 (2 H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2), 7.49 (1 H, d, $^3J_{HH}$ = 7.6 Hz, CH), 7.65 (1 H, t, $^3J_{HH}$ = 7.3 Hz,CH), 7.68 (1 H, t, $^3J_{HH}$ = 7.3 Hz,CH), 7.88 (1 H, d, $^3J_{HH}$ = 7.5 Hz, CH), 8.65 (1 H, d, $^3J_{HH}$ = 7.5 Hz, CH), 9.27 (1 H, d, $^3J_{HH}$ = 7.6 Hz, CH) ppm.^{13}C NMR (125.7 MHz, $CDCl_3$):*δ* = 14.1 (CH_3), 14.2 (CH_3), 14.3 (CH_3), 62.5 (OCH_2), 62.7 (OCH_2), 63.0 (OCH_2), 112.9 (C), 117.8 (CH), 119.9 (C), 124.4 (C), 124.9 (CH), 125.1 (CH), 128.4 (CH), 129.4 (CH), 129.9 (C), 130.5 (CH), 131.0 (C), 133.6 (C), 163.7 (C=O), 164.3 (C=O), 165.7 (C=O), 177.4 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 411 (M^+, 44), 338 (100), 264 (78), 164 (32).
Anal. Calcd for $C_{22}H_{21}NO_7$ (411.408): C, 64.23; H, 5.14; N, 3.40. Found: C, 64.20; H, 5.10; N, 3.40 %.

Di(iso-propyl) 1-(2-ethoxy-2-oxoacetyl)pyrrolo[2,1-a]isoquinoline-2,3-dicarboxylates (4c):

Yellow powder,yield: 0.80 g (91%),m.p. 138-140 °C. IR (KBr): ν =1739, 1714, 1710 and 1620 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.23 (3 H, t, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.38 (6 H, d, $^3J_{HH}$ = 6.8 Hz, 2 CH_3), 1.44 (6 H, d, $^3J_{HH}$ = 6.8 Hz, 2 CH_3), 4.36 (2 H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2), 5.18 (1 H, m, CH), 5.36 (1 H, m, CH), 7.19 (1 H, d, $^3J_{HH}$ = 7.7 Hz, CH), 7.54 (1 H, t, $^3J_{HH}$ = 7.4 Hz, CH), 7.59 (1 H, t, $^3J_{HH}$ = 7.4 Hz, CH), 7.70 (1 H, d, $^3J_{HH}$ = 7.5 Hz, CH), 8.44 (1 H, d, $^3J_{HH}$ = 7.5 Hz, CH), 9.23 (1 H, d, $^3J_{HH}$ = 7.7 Hz, CH) ppm.^{13}C NMR (125.7 MHz, $CDCl_3$):*δ*= 13.9 (CH_3), 21.7 (2 CH_3), 21.8 (2 CH_3), 62.5 (O CH_2), 69.9 (*C*HMe_2), 70.2 (*C*HMe_2), 113.0 (C), 116.9 (CH), 119.4 (C), 123.9 (C), 124.2 (CH), 125.0 (CH), 127.3 (CH), 128.3 (CH), 128.7 (C), 129.5 (CH), 129.9 (C), 132.5 (C), 163.1 (C=O), 163.2 (C=O), 165.0 (C=O), 176.7 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 439 (M^+, 5), 257 (36), 215 (64), 173 (100), 141 (98), 58 (68). Anal. Calcd for $C_{24}H_{25}NO_7$ (439.5): C, 65.59; H, 5.73; N, 3.19. Found: C, 65.60; H, 5.70; N, 3.20 %.

Di(tert-butyl)1-(2-ethoxy-2-oxoacetyl)pyrrolo[2,1-a]isoquinoline-2,3-dicarboxylates (4d):

Pale yellow cristal,yield: 0.86 g (92%),m.p. 193-195 °C. IR (KBr): ν = 1736, 1715, 1714 and 1615(C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.38 (3 H, t, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.59 (9 H, s, 3 CH_3), 1.71 (9 H, s, 3 CH_3), 4.39 (2 H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2), 7.50 (1 H, d, $^3J_{HH}$ = 7.7 Hz, CH), 7.71 (1 H, d, $^3J_{HH}$ = 7.2 Hz,CH), 7.73 (1 H, t, $^3J_{HH}$ = 7.2 Hz, CH), 7.93 (1 H, t, $^3J_{HH}$ = 7.5 Hz, CH), 8.55 (1 H, d, $^3J_{HH}$ = 7.5 Hz, 1 CH), 9.21 (1 H, d, $^3J_{HH}$ = 7.7 Hz, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$):*δ*= 14.2 (CH_3), 28.3 (3 CH_3), 28.4 (3 CH_3), 62.9 (OCH_2), 83.4 (*C*Me_3), 84.0 (*C*Me_3), 114.9 (C), 117.3 (CH), 119.8 (C), 124.6 (C), 124.9 (CH), 125.6 (CH), 128.5 (CH), 129.1 (CH), 130.2 (C), 130.3 (CH), 131.8 (C), 132.4 (C), 163.5 (C=O), 163.8 (C=O), 165.0 (C=O), 177.3 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 467 (M^+, 38), 356 (52), 265 (58), 264 (100), 58 (38). Anal. Calcd for $C_{26}H_{29}NO_7$ (467.5): C, 66.80; H, 6.25; N, 3.00. Found: C, 66.80; H, 6.30; N, 3.00 %.

Ethyl 2-[2,3-dibenzoyl pyrrolo[2,1-a]isoquinoline-1-yl]-2-oxoacetate (4e):

Yellow powder,yield: 0.88 g (93%),m.p. 190-192 °C. IR (KBr):ν =1741, 1714, 1690 and 1631 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 0.97 (3 H, t, $^3J_{HH}$ = 7.2 Hz, CH_3), 3.85 (2 H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2), 7.31 (1 H, d, $^3J_{HH}$ = 7.6 Hz, CH), 7.34 (4 H, m, 4 CH of C_6H_5), 7.50 (1 H, d, $^3J_{HH}$ = 7.2 Hz, CH of C_6H_5), 7.54 (1 H, t, $^3J_{HH}$ = 7.2 Hz,CH), 7.56 (1 H, t, $^3J_{HH}$ = 7.2 Hz, CH), 7.64 (4 H, m, 4 CH of C_6H_5), 7.67 (1 H, d, $^3J_{HH}$ = 7.2 Hz, CH of C_6H_5), 8.0 (1 H, t, $^3J_{HH}$ = 7.9 Hz, CH), 8.06 (1 H, d, $^3J_{HH}$ = 7.9 Hz, CH), 9.58 (1 H, d, $^3J_{HH}$ = 7.6 Hz, CH) ppm.^{13}C NMR (125.7 MHz, $CDCl_3$):*δ* = 13.6 (CH_3), 62.8 (OCH_2), 117.8 (CH), 120.2 (C), 120.7 (C), 124.5 (C), 125.5 (CH), 126.3 (CH), 128.1 (CH), 129.1 (2 CH), 129.2 (CH), 129.4 (2 CH), 130.4 (2 CH), 130.5 (C), 130.7 (2 CH), 131.4 (CH), 134.2 (CH), 134.3 (C), 134.5 (CH), 137.6 (C), 138.9 (C), 139.3 (C), 163.7 (C=O), 177.2 (C=O), 192.2 (C=O), 193.8 (C=O) ppm.MS (EI, 70 eV): *m*/*z* (%) = 475 (M^+, 48), 402 (100), 324 (86), 105 (100), 77 (100). Anal. Calcd for $C_{30}H_{21}NO_5$ (475.8): C, 75.78; H, 4.45; N, 2.95. Found: C, 75.80; H, 4.40; N, 2.30 %.

Ethyl 2-[2,3-bis(4-methylbenzoyl)pyrrolo[2,1-a]isoquinoline-1-yl]-2-oxoacetate (4f):

Yellow crystals,yield: 0.94 g (93%),m.p. 181-183 °C. IR (KBr): ν =1725, 1716, 1669 and 1600 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.07 (3 H, t, $^3J_{HH}$ = 7.2 Hz, CH_3), 2.33 (3 H, s, Me), 2.35 (3 H, s,

Me), 3.98 (2 H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2), 7.07(1 H, d, $^3J_{HH}$ = 7.5 Hz, CH), 7.26 (1 H, t, $^3J_{HH}$ = 7.3 Hz, CH), 7.37 (1 H, t, $^3J_{HH}$ = 7.3 Hz, CH), 7.42 (2 H, d, $^3J_{HH}$ = 7.3 Hz, 2 CH), 7.46 (1 H, d, $^3J_{HH}$ = 7.3 Hz, CH), 7.61 (2 H, d, $^3J_{HH}$ = 7.6 Hz, 2 CH), 7.79 (2 H, d, $^3J_{HH}$ = 7.5 Hz, 2 CH), 8.01 (2 H, t, $^3J_{HH}$ = 7.9 Hz, 2 CH), 8.21 (1 H, d, $^3J_{HH}$ = 7.9 Hz, CH), 9.60 (1 H, d, $^3J_{HH}$ = 7.5 Hz, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$):δ = 14.1 (CH_3), 21.7 (CH_3 of Ar), 21.8 (CH_3 of Ar), 62.5 (OCH_2), 116.9 (C), 119.2 (CH), 123.9 (C), 124.7 (C), 125.6 (CH), 127.4 (CH), 128.5 (2 CH), 128.9 (CH), 129.1 (CH), 129.6 (C), 129.9 (CH), 130.2 (2 CH), 130.4 (C), 133.7 (2 CH), 135.5 (2 CH), 136.0 (C), 137.3 (C_{ipso}), 144.5 (C_{ipso}), 144.8 (C_{ipso}), 145.6 (C_{ipso}), 163.2 (C=O), 176.4 (C=O), 191.8 (C=O), 193.5 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = Anal. Calcd for $C_{32}H_{25}NO_5$ (503.6): C, 76.33; H, 5.00; N, 2.78. Found: C, 76.30; H, 5.00; N, 2.70 %.

Dimethyl 3-(2-ethoxy-2-oxoacetyl)pyrrolo[1,2-a]quinoline-1,2-dicarboxylate(10):

Yellow powder, yield: 0.70 g (91%),m.p. 105-107°C.

IR (KBr): ν = 1719, 1712, 1710 and 1635 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.39 (3 H, t, $^3J_{HH}$ = 7.2 Hz, CH_3),3.91 (3 H, s, OCH_3), 3.95 (3 H, s, OCH_3), 4.30 (2 H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2),7.50 (1 H, d, $^3J_{HH}$ = 7.5 Hz, CH),7.56 (1 H, t, $^3J_{HH}$ = 7.2 Hz,CH),7.60 (1 H, t, $^3J_{HH}$ = 7.2 Hz, CH),7.79 (1 H, d, $^3J_{HH}$ = 7.7 Hz, CH),8.15 (1 H, d, $^3J_{HH}$ = 7.2 Hz, CH), 8.21 (1 H, d, $^3J_{HH}$ = 7.7 Hz, CH) ppm.^{13}C NMR (125.7 MHz, $CDCl_3$):δ= 13.7 (CH_3), 51.9 (OCH_3), 52.8 (OCH_3), 63.0 (OCH_2),117.0 (C), 117.6 (CH), 119.7 (CH), 124.2 (C), 125.4 (CH), 126.3 (C), 128.8 (CH), 129.2 (CH), 129.5 (C), 129.8 (CH), 132.4 (C), 132.8 (C), 163.0 (C=O), 163.7 (C=O), 165.1 (C=O), 175.2 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 383 (M^+, 20), 324 (18), 310 (100), 167 (46), 149 (84), 129 (100), 59 (100). Anal. Calcd for $C_{20}H_{17}NO_7$ (383.4): C, 62.66; H, 4.47; N, 3.65. Found: C, 62.70; H, 4.50; N, 3.65 %.

Dimethyl 1-(2-ethoxy-2-oxoacetyl)-2,3-indolizinedicarboxylate (12):

Yellow crystal, yield: 0.61 g (90%),m.p. 98-100°C.

IR (KBr): ν = 1725, 1716, 1711 and 1642 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.40 (3 H, t, $^3J_{HH}$ = 7.2 Hz, CH_3),3.90 (3 H, s, OCH_3), 3.93 (3 H, s, OCH_3),4.36 (2 H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2), 7.14 (1 H, t, $^3J_{HH}$ = 7.2 Hz,CH), 7.47 (1 H, t, $^3J_{HH}$ = 7.2 Hz, CH), 8.47 (1 H, d, $^3J_{HH}$ = 7.3 Hz, CH), 9.51 (1 H, d, $^3J_{HH}$ = 7.2 Hz, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$):δ= 14.0 (CH_3), 52.2 (OCH_3), 52.7 (OCH_3), 62.3 (OCH_2),113.8 (C), 116.9 (CH), 120.1 (C),120.4 (CH),128.3 (CH), 129.4 (C), 130.2 (CH), 139.2 (C), 162.8 (C=O), 163.5 (C=O), 165.2 (C=O), 175.2 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = Anal. Calcd for $C_{16}H_{15}NO_7$ (333.3): C, 57.66; H, 4.54; N, 4.20. Found: C, 57.60; H, 4.50; N, 4.20 %.

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