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Oxidative free radical reactions of enamino esters

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Abstract—Oxidative free radical reactions of enamino esters are described. Electrophilic carbon-centered radicals produced by the cerium(IV) ammonium nitrate (CAN) oxidation of β-dicarbonyl compounds undergo efficient addition to the C–C double bond of enamino esters. This CAN mediated free radical reaction between enamino esters and β-dicarbonyl compounds provides a novel method for the synthesis of highly substituted pyrroles. The direct CAN oxidation of β-enaminocinnamates gave the dimerization products effectively.

1. Introduction

Free radical reactions have become increasingly important in organic synthesis in the last two decades.[1] The oxidative addition of an electrophilic carbon-centered radicals to alkenes mediated by metal salts has received considerable attention in the organic synthesis for the construction of carbon–carbon bonds. Among these, manganese(III) acetate and cerium(IV) ammonium nitrate (CAN) have been used most efficiently.[1d–f,2,3] These reactions can be performed intermolecularly and intramolecularly. Pyrroles are important substructures of pharmaceutically important compounds and also of numerous natural products.[4] Accordingly, substantial attention has been paid to develop efficient methods for the synthesis of pyrroles.[5] We describe here a novel method for the synthesis of highly substituted pyrroles via the oxidative free radical reactions of enamino esters.

2. Results and discussion

The CAN mediated reaction between β-aminocinnamate **1** and β-dicarbonyl compound **2** was first examined (Eq. 1). When β-anilinocinnamate **1a** was treated with ethyl acetoacetate (**2a**) and CAN in methanol at room temperature, **3a** was obtained in 54% yield (Table 1, entry 1). A plausible mechanism for this reaction is shown in Scheme 1. Initiation occurs with CAN oxidation of **2a** to produce radical **5a**. This radical intermediate **5a** undergoes intermolecular addition followed by oxidation to give **7a**, which undergoes condensation reaction to produce **3a** (path a). There is no trace of another expected product **10a** can be detected, which is presumably derived from the intramolecular cyclization followed by retro Claisen condensation and oxidation of radical intermediate **8a** (path b). This high selectivity for the formation of pyrrole **3a** can be ascribed to the strong oxaphilicity of cerium salt and it enhances the condensation rate of **7a**.[6] With other β-keto esters (R^2=OR), in addition to the desired major product **3**, a competitive oxidative dimerization product **4** was also obtained (entries 2–4). The ratios of **3/4** decrease as the size of substituents (R^1) on β-keto esters increases. This is presumably due to the steric effect exerted by R^1 group—the addition rate (**1→6**) was retarded by the larger R^1 and the oxidative dimerization of **1a** occurred. With 1,3-diones, the reaction of **1a** resulted in the formation of **3** and **4** (entries 5 and 6). The scope of this reaction was explored using a variety of β-aminocinnamate **1** and the results were also shown in Table 1. In all cases, β-aminocinnamate **1** was smoothly converted to the corresponding pyrrole **3** as the major (only) product (entries 7–13). In addition, when β-anilinocrotonate **11** was treated with ethyl acetoacetate (**2a**) and CAN under similar reaction conditions, no desired

Table 1. Free radical reactions of β-aminocinnamate **1**

Entry	Cinnamate	β-Dicarbonyl compound	Product (yield (%))	
1	**1a**	**2a**: R^1=Me, R^2=OEt	**3a** (54)	**4a** (0)
2	**1a**	**2b**: R^1=Et, R^2=OMe	**3b** (51)	**4a** (trace)
3	**1a**	**2c**: R^1=Pr, R^2=OEt	**3c** (44)	**4a** (9)
4	**1a**	**2d**: R^1=^{i}Pr, R^2=OEt	**3d** (29)	**4a** (12)
5	**1a**	**2e**: R^1=Me, R^2=Me	**3e** (36)	**4a** (10)
6	**1a**	**2f**: R^1=Et, R^2=Et	**3f** (35)	**4a** (14)
7	**1b**	**2a**: R^1=Me, R^2=OEt	**3g** (54)	**4b** (0)
8	**1b**	**2f**: R^1=Et, R^2=Et	**3h** (33)	**4b** (18)
9	**1c**	**2a**: R^1=Me, R^2=OEt	**3i** (54)	**4c** (0)
10	**1c**	**2f**: R^1=Et, R^2=Et	**3j** (37)	**4c** (16)
11	**1d**	**2a**: R^1=Me, R^2=OEt	**3k** (45)	**4d** (0)
12	**1e**	**2a**: R^1=Me, R^2=OEt	**3l** (53)	**4e** (0)
13	**1e**	**2f**: R^1=Et, R^2=Et	**3m** (39)	**4e** (9)

Keywords: Cerium(IV) ammonium nitrate; Oxidative; Free radical; Enamino esters.
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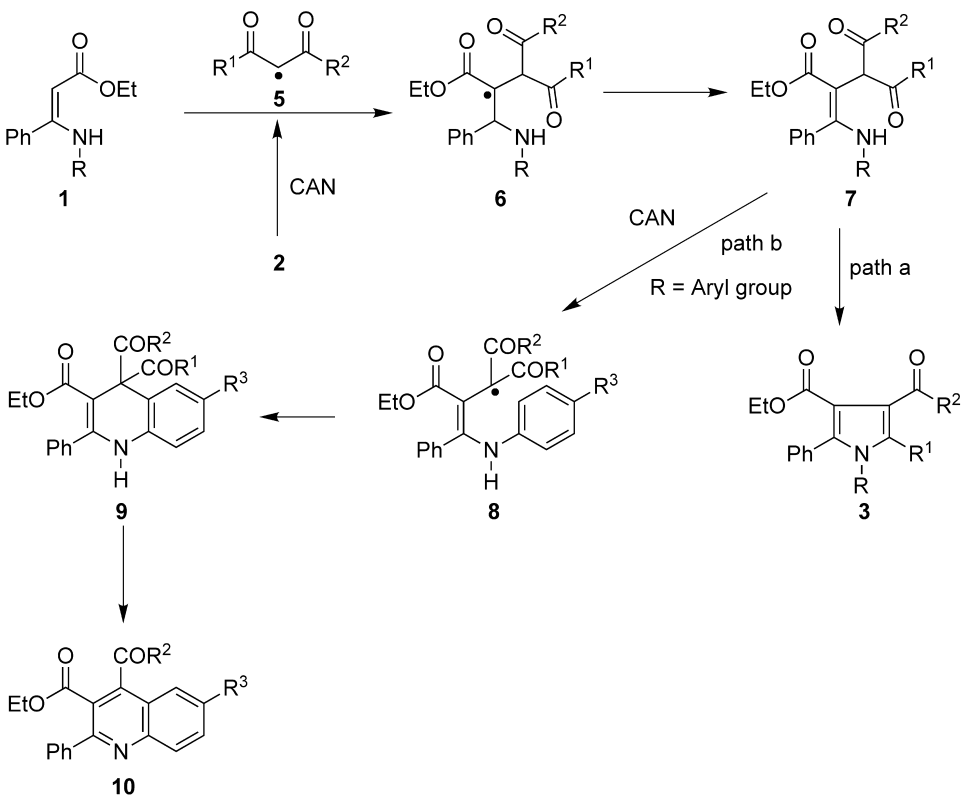
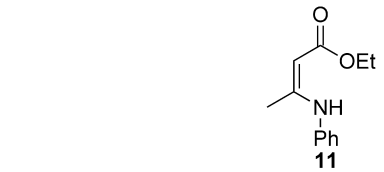
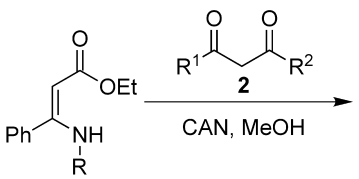


Scheme 1.

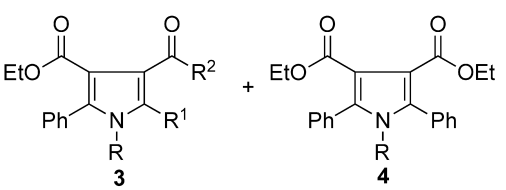
product could be found. It is probably due to the CAN liability of **11**.



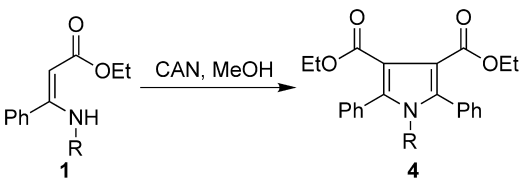


1a: R = p-chlorophenyl
1b: R = p-bromophenyl
1c: R = p-ethoxycarbonylphenyl
1d: R = phenyl
1e: R = cyanomethyl

(1)



The preparation of highly substituted C_2-symmetric pyrroles by the oxidative dimerization of enamino esters has been reported.[7] On the basis of the generation of **4** in above reaction, we expected that the direct oxidation of **1** would produce **4** effectively. Indeed, the formation of **4a** (48%) was achieved by the reaction of **1a** with CAN in methanol at room temperature (Eq. 2). Results of the CAN mediated oxidative dimerization of **1** are summarized in Table 2. While β-anilinocinnamates **1a**–**1d** were converted to the corresponding dimerization products in fair yields (entries 1–4), the dimerization of β-alkylaminocinnamate **1e** was less productive (entry 5).



(2)

Table 2. Oxidative dimerizations of β-aminocinnamate **1**

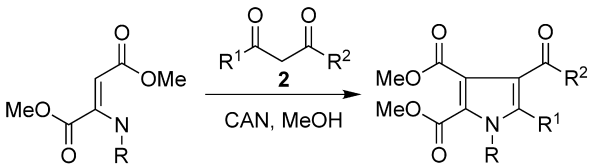
Entry	Cinnamate	Product (yield (%))
1	**1a**	**4a** (48)
2	**1b**	**4b** (46)
3	**1c**	**4c** (56)
4	**1d**	**4d** (58)
5	**1e**	**4e** (22)

We next study this oxidative free radical reaction with 2-aminofumarate **12** (Eq. 3). The reaction of 2-anilinofumarate **12a** with ethyl acetoacetate (**2a**) and CAN in methanol at room temperature afforded **13a** in 60% yield (Table 3, entry 1). Pyrrole **13a** was formed presumably via a similar route shown in Scheme 1. The results of this reaction with a variety of β-dicarbonyl compounds are summarized in Table 3. In contrast to **1**, pyrrole **13** was obtained as the only product and no dimerization product **14**[8] could be

Table 3. Free radical reactions of 2-aminofumarate **12**

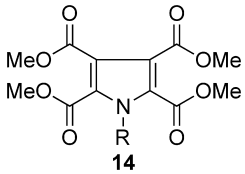
Entry	Fumarate	β-Dicarbonyl compound	Product (yield (%))
1	**12a**	**2a**: R^1=Me, R^2=OEt	**13a** (60)
2	**12a**	**2b**: R^1=Et, R^2=OMe	**13b** (65)
3	**12a**	**2c**: R^1=Me, R^2=Me	**13c** (41)
4	**12a**	**2d**: R^1=Et, R^2=Et	**13d** (61)
5	**12b**	**2a**: R^1=Me, R^2=OEt	**13e** (69)
7	**12b**	**2c**: R^1=Me, R^2=Me	**13f** (33)
8	**12b**	**2d**: R^1=Et, R^2=Et	**13g** (62)
9	**12c**	**2a**: R^1=Me, R^2=OEt	**13h** (67)
10	**12c**	**2b**: R^1=Et, R^2=OMe	**13i** (61)
11	**12c**	**2c**: R^1=Me, R^2=Me	**13j** (41)
12	**12c**	**2d**: R^1=Et, R^2=Et	**13k** (53)
13	**12d**	**2a**: R^1=Me, R^2=OEt	**13l** (57)
14	**12d**	**2c**: R^1=Me, R^2=Me	**13m** (32)
15	**12e**	**2a**: R^1=Me, R^2=OEt	**13n** (68)
16	**12e**	**2b**: R^1=Et, R^2=OMe	**13o** (70)
17	**12e**	**2c**: R^1=Me, R^2=Me	**13p** (40)

found. We speculate that it may be due to some unknown effects of the additional methoxycarbonyl group of **12**. For unknown reason, the reaction yield was rather poor when this reaction was performed with 2,4-pentanedione (**2c**) (entries 3, 7, 11, 14 and 17).



(3)

12a: R = p-ethoxycarbonylphenyl
12b: R = p-cyanophenyl
12c: R = p-bromophenyl
12d: R = benzyl
12e: R = methoxycarbonylmethyl



In conclusion, radical **5** generated from the CAN oxidation of β-dicarbonyl compounds undergoes efficient addition to the C–C double bond of enamino esters. This free radical reaction provides a novel method for the synthesis of highly substituted pyrroles from readily available enamino esters and β-dicarbonyl compounds. The dimerization product **4** can also be synthesized effectively by the direct CAN oxidation of β-aminocinnamates.

3. Experimental

3.1. General considerations

Melting points are uncorrected. Infrared spectra were taken with a Hitachi 260-30 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 or AVANCE-300 spectrometer. Chemical shifts are reported in ppm relative to TMS as internal reference. Elemental analyses were performed with Heraeus CHN-Rapid Analyzer. Analytical thin-layer chromatography was performed with precoated silica gel 60 F-254 plates (0.25 mm thick) from EM Laboratories and visualized by UV. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (70–230 mesh). The starting enamino esters **1**[7b,9b] and **12**[7a,9a] were synthesized according to literature procedures.

3.2. Typical experimental procedure for the reaction between β-aminocinnamate 1 and β-dicarbonyl compounds

A solution of 134 mg (0.44 mmol) of **1a**, 349 mg (2.68 mmol) of ethyl acetoacetate, 223 mg (2.65 mmol) of sodium bicarbonate and 729 mg (1.33 mmol) of CAN in 10 mL of methanol was stirred at room temperature for 10 min. The reaction mixture was diluted with 100 mL of ethyl acetate, washed with 50 mL of saturated aqueous sodium bisulfite, three 50 mL portions of water, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed over 15 g of silica gel (eluted with 1:8 ethyl acetate–hexane) followed by recrystallization (hexane–ethyl acetate) to give 99 mg (54%) of **3a**.

3.3. Typical experimental procedure for the oxidative dimerization reaction of β-aminocinnamate 1

A solution of 135 mg (0.44 mmol) of **1a**, 145 mg (1.72 mmol) of sodium bicarbonate and 541 mg (0.98 mmol) of CAN in 10 mL of methanol was stirred at room temperature for 10 min. The reaction mixture was diluted with 100 mL of ethyl acetate, washed with 50 mL of saturated aqueous sodium bisulfite, three 50 mL portions of water, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed over 15 g of silica gel (eluted with 1:7 ethyl acetate–hexane) followed by recrystallization (hexane–ethyl acetate) to give 52 mg (48%) of **4a**.

3.4. Typical experimental procedure for the reaction between 2-aminofumarate 12 and β-dicarbonyl compounds

A solution of 122 mg (0.40 mmol) of **12a**, 218 mg (1.68 mmol) of ethyl acetoacetate and 430 mg (0.79 mmol) of CAN in 10 mL of methanol was stirred at room temperature for 15 min. The reaction mixture was diluted with 100 mL of ethyl acetate, washed with 50 mL of saturated aqueous sodium bisulfite, three 50 mL portions of water, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed over 15 g of silica gel (eluted with 1:3.5 ethyl acetate–hexane) followed by recrystallization (hexane–ethyl acetate) to give 100 mg (60%) of **13a**

3.4.1. 1-(*p*-Chlorophenyl)-3,4-diethoxycarbonyl-2-methyl-5-phenylpyrrole 3a. Colorless crystals; mp 112–113 °C; IR($CHCl_3$) 2990, 1705, 1535, 1495, 1430 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, J=7.1 Hz, 3H, CH_3), 1.35 (t, J=7.1 Hz, 3H, CH_3), 2.31 (s, 3H, CH_3), 4.17 (q, J=7.1 Hz, 2H, OCH_2), 4.32 (q, J=7.1 Hz, 2H, OCH_2), 6.99 (d, J=8.6 Hz, 2H, ArH), 7.09–7.22 (m, 5H, ArH), 7.30 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 12.2

(q), 13.9 (q), 14.2 (q), 60.2 (t), 60.7 (t), 112.4 (s), 116.1 (s), 127.8 (d), 127.9 (d), 129.4 (d), 129.7 (d), 130.1 (s), 130.3 (d), 134.4 (s), 134.5 (s), 135.5 (s), 136.0 (s), 164.7 (s), 165.8 (s). Anal. calcd for $C_{23}H_{22}ClNO_4$: C, 67.07; H, 5.38; N,3.40. Found: C, 67.04; H, 5.36; N, 3.38.

3.4.2. 1-(*p*-Chlorophenyl)-3-ethoxycarbonyl-2-ethyl-4-methoxycarbonyl-5-phenylpyrrole 3b. Colorless crystals; mp 121–122 °C; IR($CHCl_3$) 2990, 1710, 1495, 1440, 1295 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.02 (t, J=7.4 Hz, 3H, CH_3), 1.15 (t, J=7.1 Hz, 3H, CH_3), 2.74 (q, J=7.4 Hz, 2H, CH_2), 3.85 (s, 3H, OCH_3), 4.17 (q, J=7.1 Hz, 2H, OCH_2), 7.03 (d, J=8.6 Hz, 2H, ArH), 7.09–7.14 (m, 2H, ArH), 7.15–7.21 (m, 3H, ArH), 7.30 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0 (q), 14.3 (q), 19.0 (t), 51.3 (q), 60.7 (t), 111.4 (s), 116.1 (s), 127.8 (d), 127.9 (d), 129.3 (d), 129.9 (d), 130.1 (s), 130.4 (d), 134.6 (s), 134.7 (s), 135.4 (s), 142.0 (s), 165.0 (s), 165.8 (s). Anal. calcd for $C_{23}H_{22}ClNO_4$: C, 67.07; H, 5.38; N, 3.40. Found: C, 67.18; H, 5.46; N, 3.35.

3.4.3. 1-(*p*-Chlorophenyl)-3,4-diethoxycarbonyl-2-phenyl-5-propylpyrrole 3c. Colorless crystals; mp 92–93 °C; IR($CHCl_3$) 2975, 1705, 1495, 1435, 1280, 1195 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J=7.6 Hz, 3H, CH_3), 1.14 (t, J=7.1 Hz, 3H, CH_3), 1.35 (t, J=7.1 Hz, 3H, CH_3), 1.43 (sextet, J=7.6 Hz, 2H, CH_2), 2.66–2.72 (m, 2H, CH_2), 4.17 (q, J=7.1 Hz, 2H, OCH_2), 4.32 (q, J=7.1 Hz, 2H, OCH_2), 7.01 (d, J=8.6 Hz, 2H, ArH), 7.09–7.13 (m, 2H, ArH), 7.15–7.20 (m, 3H, ArH), 7.29 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.9 (q), 14.0 (q), 14.2 (q), 23.2 (t), 27.5 (t), 60.1 (t), 60.7 (t), 112.1 (s), 116.3 (s), 127.7 (d), 127.9 (d), 129.2 (d), 130.0 (d), 130.1 (s), 130.4 (d), 134.5 (s), 135.5 (s), 140.5 (s), 164.5 (s), 165.9 (s). Anal. calcd for $C_{25}H_{26}ClNO_4$: C, 68.25; H, 5.96; N, 3.18. Found: C, 68.24; H, 6.02; N, 3.20.

3.4.4. 1-(*p*-Chlorophenyl)-3,4-diethoxycarbonyl-2-isopropyl-5-phenylpyrrole 3d. Colorless needles; mp 154–155 °C; IR($CHCl_3$) 2985, 1715, 1495, 1270, 1190 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 (t, J=7.2 Hz, 3H, CH_3), 1.25 (d, J=7.1 Hz, 6H, CH_3), 1.38 (t, J=7.1 Hz, 3H, CH_3), 2.87 (septet, J=7.1 Hz, 1H, CH), 4.11 (q, J=7.2 Hz, 2H, OCH_2), 4.36 (q, J=7.1 Hz, 2H, OCH_2), 7.00 (d, J=8.6 Hz, 2H, ArH), 7.09–7.13 (m, 2H, ArH), 7.14–7.21 (m, 3H, ArH), 7.27 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.9 (q), 14.2 (q), 21.5 (q), 26.6 (d), 60.3 (t), 60.8 (t), 113.1 (s), 114.8 (s), 127.5 (d), 128.0 (d), 129.2 (d), 130.3 (d), 130.5 (s), 130.8 (d), 134.6 (s), 135.78 (s), 135.81 (s), 141.9 (s), 164.8 (s), 166.2 (s). Anal. calcd for $C_{25}H_{26}ClNO_4$: C, 68.25; H, 5.96; N, 3.18. Found: C, 68.27; H, 6.01; N, 3.21.

3.4.5. 3-Acetyl-1-(*p*-chlorophenyl)-4-ethoxycarbonyl-2-methyl-5-phenylpyrrole 3e. Colorless crystals; mp 127–128 °C; IR($CHCl_3$) 3010, 1705, 1660, 1495, 1415 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (t, J=7.1 Hz, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 4.13 (q, J=7.1 Hz, 2H, OCH_2), 6.98 (q, J=8.6 Hz, 2H, ArH), 7.10–7.15 (m, 2H, ArH), 7.16–7.25 (m, 3H, ArH), 7.29 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4 (q), 13.8 (q), 31.0 (q), 60.6 (t), 114.4 (s), 123.1 (s), 127.6 (d), 128.1 (d), 129.4 (d), 129.7 (d), 130.5 (s), 130.8 (d), 134.2 (s), 134.6 (s), 135.3 (s), 136.9 (s), 165.2 (s), 197.7 (s). Anal. calcd for $C_{22}H_{20}ClNO_3$: C, 69.20; H, 5.28; N, 3.67. Found: C, 69.20; H, 5.30; N, 3.62.

3.4.6. 1-(*p*-Chlorophenyl)-3-ethoxycarbonyl-5-ethyl-2-phenyl-4-propionylpyrrole 3f. Colorless needles; mp 123–124 °C; IR($CHCl_3$) 2985, 1700, 1495, 1420, 1170 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J=7.4 Hz, 3H, CH_3), 1.05 (t, J=7.1 Hz, 3H, CH_3), 1.20 (t, J=7.3 Hz, 3H, CH_3), 2.59 (q, J=7.4 Hz, 2H, CH_2), 2.84 (q, J=7.3 Hz, 2H, CH_2), 4.10 (q, J=7.1 Hz, 2H, OCH_2), 7.02 (d, J=8.5 Hz, 2H, ArH), 7.09–7.13 (m, 2H, ArH), 7.15–7.22 (m, 3H, ArH), 7.28 (d, J=8.5 Hz (2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 8.6 (q), 13.8 (q), 14.6 (q), 18.8 (t), 36.5 (t), 60.3 (t), 113.7 (s), 112.6 (s), 127.5 (d), 128.0 (d), 129.2 (d), 130.0 (d), 130.7 (s), 130.9 (d), 134.6 (s), 135.4 (s), 137.1 (s), 138.8 (s), 165.1 (s), 201.8 (s). Anal. calcd for $C_{24}H_{24}ClNO_3$: C, 70.32; H, 5.90; N, 3.42. Found: C, 70.27; H, 5.90; N, 3.36.

3.4.7. 1-(*p*-Bromophenyl)-3,4-diethoxycarbonyl-2-methyl-5-phenylpyrrole 3g. Colorless crystals; mp 109–110 °C; IR($CHCl_3$) 2990, 1705, 1495, 1425, 1280 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, J=7.1 Hz, 3H, CH_3), 1.35 (t, J=7.1 Hz, 3H, CH_3), 2.31 (s, 3H, CH_3), 4.17 (q, J=7.1 Hz, 2H, OCH_2), 4.32 (q, J=7.1 Hz, 2H, OCH_2), 6.92 (d, J=8.5 Hz, 2H, ArH) (7.08–7.23 (m, 5H, ArH), 7.45 (d, J=8.5 Hz(2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.2 (q), 14.0 (q), 14.3 (q), 60.2 (t), 60.7 (t), 112.4 (s), 116.2 (s), 122.5 (s), 127.8 (d), 128.0 (d), 130.0 (d), 130.1 (s), 130.4 (d), 132.4 (d), 134.5 (s), 135.97 (s), 136.00 (s), 164.7 (s), 165.8 (s). Anal. calcd for $C_{23}H_{22}BrNO_4$: C, 60.54; H, 4.86; N, 3.07. Found: C, 60.62; H, 4.96; N, 3.08.

3.4.8. 1-(*p*-Bromophenyl)-3-ethoxycarbonyl-5-ethyl-2-phenyl-4-propionylpyrrole 3h. Colorless needles; mp 131–132 °C; IR($CHCl_3$) 2985, 1695, 1490, 1420, 1170, 1125 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J=7.4 Hz, 3H, CH_3), 1.05 (t, J=7.1 Hz, 3H, CH_3), 1.20 (t, J=7.3 Hz, 3H, CH_3), 2.59 (q, J=7.4 Hz, 2H, CH_2), 2.84 (q, J=7.3 Hz, 2H, CH_2), 4.10 (q, J=7.1 Hz, 2H, OCH_2), 6.96 (d, J=8.6 Hz, 2H, ArH), 7.09–7.13 (m, 2H, ArH), 7.16–7.23 (m, 3H, ArH), 7.43 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 8.6 (q), 13.8 (q), 14.7 (q), 18.8 (t), 36.5 (t), 60.4 (t), 113.7 (s), 122.57 (s), 122.63 (s), 127.6 (d), 128.1 (d), 130.2 (d), 130.6 (s), 130.8 (d), 132.2 (d), 135.9 (s), 137.1 (s), 138.8 (s), 165.1 (s), 201.9 (s). Anal. calcd for $C_{24}H_{24}BrNO_3$: C, 63.44; H, 5.32; N, 3.08. Found: C, 63.45; H, 5.37; N, 3.12.

3.4.9. 3,4-Diethoxycarbonyl-1-(*p*-ethoxycarbonylphenyl)-2-methyl-5-phenylpyrrole 3i. Colorless crystals; mp 117–118 °C; IR($CHCl_3$) 2990, 1715, 1485, 1270, 1190 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, J=7.1 Hz, 3H, CH_3), 1.35 (t, J=7.1 Hz, 3H, CH_3), 1.37 (t, J=7.1 Hz, 3H, CH_3), 2.23 (s, 3H, CH_3), 4.18 (q, J=7.1 Hz, 2H, OCH_2), 4.33 (q, J=7.1 Hz, 2H, OCH_2), 4.36 (q, J=7.1 Hz, 2H, OCH_2), 7.09–7.20 (m, 7H, ArH), 8.01 (d, J=8.5 Hz (2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.2 (q), 14.0 (q), 14.2 (q), 14.3 (q), 60.2 (t), 60.7 (t), 61.3 (t), 112.7 (s), 116.4 (s), 127.8 (d), 128.0 (d), 128.5 (d), 130.0 (s), 130.36 (d), 130.41 (d), 134.4 (s), 135.9 (s), 140.9 (s), 164.7 (s), 165.5 (s), 165.7 (s). Anal. calcd for $C_{26}H_{27}NO_6$: C, 69.47; H, 6.05; N, 3.12. Found: C, 69.45; H, 6.05; N, 3.04.

3.4.10. 3-Ethoxycarbonyl-1-(*p*-ethoxycarbonylphenyl)-5-ethyl-2-phenyl-4-propionylpyrrole 3j. Colorless needles; mp 111–112 °C; IR($CHCl_3$) 2990, 1715, 1485, 1415, 1280 cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$) δ 0.95 (t, J=7.4 Hz, 3H, CH_3), 1.06 (t, J=7.1 Hz, 3H, CH_3), 1.21 (t, J=7.3 Hz, 3H, CH_3), 1.38 (t, J=7.1 Hz, 3H, CH_3), 2.60 (q, J=7.4 Hz, 2H, CH_2), 2.85 (q, J=7.3 Hz, 2H, CH_2, 4.11 (q, J=7.1 Hz, 2H, OCH_2), 4.36 (q, J=7.1 Hz, 2H, OCH_2), 7.09–7.23 (m, 7H, ArH), 7.99 (d, J=8.5 Hz (2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 8.6 (q), 13.8 (q), 14.2 (q), 14.6 (q), 18.9 (t), 36.6 (t), 60.4 (t), 61.4 (t), 113.8 (s), 122.8 (s), 127.6 (d), 128.1 (d), 128.7 (d), 130.3 (d), 130.6 (s), 130.9 (d), 137.1 (s), 138.7 (s), 140.8 (s), 165.1 (s), 165.5 (s), 201.9 (s). Anal. calcd for $C_{27}H_{29}NO_5$: C, 72.46; H, 6.53; N, 3.13. Found: C, 72.42; H, 6.55; N, 3.06.

3.4.11. 3,4-Diethoxycarbonyl-2-methyl-1,5-diphenylpyrrole 3k. Colorless crystals; mp 94–95 °C; IR($CHCl_3$) 2990, 1705, 1495, 1425, 1280 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, J=7.1 Hz, 3H, CH_3), 1.35 (t, J=7.1 Hz, 3H, CH_3), 2.32 (s, 3H, CH_3), 4.18 (q, J=7.1 Hz, 2H, OCH_2), 4.32 (q, J=7.1 Hz, 2H, OCH_2), 7.02–7.08 (m, 2H, ArH), 7.14 (s, 5H, ArH), 7.28–7.35 (m, 3H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.2 (q), 13.9 (q), 14.2 (q), 60.0 (t), 60.6 (t), 112.0 (s), 115.9 (s), 127.6 (d), 127.7 (d), 128.41 (d), 128.43 (d), 129.0 (d), 130.3 (d), 134.5 (s), 136.2 (s), 136.9 (s), 164.8 (s), 166.0 (s). Anal. calcd for $C_{23}H_{23}NO_4$: C, 73.19; H, 6.14; N, 3.71. Found: C, 73.14; H, 6.13; N, 3.71.

3.4.12. 1-Cyanomethyl-3,4-diethoxycarbonyl-2-methyl-5-phenylpyrrole 3l. Colorless crystals; mp 79–80 °C; IR($CHCl_3$) 2990, 1710, 1445, 1425, 1300, 1240, 1185 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.09 (t, J=7.1 Hz, 3H, CH_3), 1.34 (t, J=7.1 Hz, 3H, CH_3), 2.61 (s, 3H, CH_3), 4.10 (q, J=7.1 Hz, 2H, OCH_2), 4.30 (q, J=7.1 Hz, 2H, OCH_2), 4.55 (s, H, NCH_2), 7.36–7.42 (m, 2H, ArH), 7.44–7.50 (m, 3H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 11.0 (q), 13.8 (q), 14.2 (q), 32.5 (t), 60.4 (t), 60.6 (t), 113.5 (s), 113.9 (s), 116.3 (s), 128.8 (d), 129.0 (s), 129.5 (d), 130.4 (d), 134.4 (s), 134.7 (s), 164.3 (s), 164.7 (s). Anal. calcd for $C_{19}H_{20}N_2O_4$: C, 67.05; H, 5.92; N, 8.23. Found: C, 66.99; H, 5.93; N, 8.22.

3.4.13. 1-Cyanomethyl-3-ethoxycarbonyl-5-ethyl-2-phenyl-4-propionylpyrrole 3m. Colorless needles; mp 84–85 °C; IR($CHCl_3$) 2990, 1700, 1485, 1430, 1285, 1155 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (t, J=7.2 Hz, 3H, CH_3), 1.17 (t, J=7.3 Hz, 3H, CH_3), 1.30 (t, J=7.5 Hz, 3H, CH_3), 2.79 (q, J=7.3 Hz, 2H, CH_2), 2.81 (q, J=7.5 Hz, 2H, CH_2), 4.05 (q, J=7.2 Hz, 2H, OCH_2), 4.53 (s, 2H, NCH_2), 7.36–7.41 (m, 2H, ArH), 7.46–7.52 (m, 3H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 8.5 (q), 13.6 (q), 14.5 (q), 18.5 (t), 32.1 (t), 36.7 (t), 60.3 (t), 114.0 (s), 114.3 (s), 123.6 (s), 128.6 (d), 129.5 (d), 129.7 (s), 130.6 (d), 136.8 (s), 136.9 (s), 164.1 (s), 202.0 (s). Anal. calcd for $C_{20}H_{22}N_2O_3$: C, 70.99; H, 6.55; N, 8.28. Found: C, 70.93; H, 6.58; N, 8.32.

3.4.14. 1-(*p*-Chlorophenyl)-3,4-diethoxycarbonyl-2,5-diphenylpyrrole 4a. Colorless crystals; mp 174–175 °C; IR($CHCl_3$) 2990, 1715, 1490, 1375, 1280 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, J=7.1 Hz, 6H, CH_3), 4.19 (q, J=7.1 Hz, 4H, OCH_2), 6.76 (d, J=8.5 Hz, 2H, ArH), 7.05 (d, J=8.5 Hz, 2H, ArH), 7.14–7.27 (m, 10H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$), δ 13.9 (q), 60.0 (t), 115.4 (s), 127.7 (d), 128.2 (d), 128.8 (d), 129.9 (d), 130.2 (s), 130.8 (d), 133.7 (s), 135.5 (s), 136.4 (s), 164.8 (s). Anal. calcd for $C_{28}H_{24}ClNO_4$: C, 70.98; H, 5.10; N, 2.96. Found: C, 70.95; H, 5.18; N, 3.04.

3.4.15. 1-(*p*-Bromophenyl)-3,4-diethoxycarbonyl-2,5-diphenylpyrrole 4b. Colorless crystals; mp 165–166 °C; IR($CHCl_3$) 2990, 1715, 1490, 1375, 1275 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, J=7.1 Hz, 6H, CH_3), 4.18 (q, J=7.1 Hz, 4H, OCH_2), 6.70 (d, J=8.3 Hz, 2H, ArH), 7.31–7.14 (m, 12H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$), δ 13.9 (q), 60.6 (t), 115.5 (s), 121.8 (s), 127.8 (d), 128.2 (d), 130.2 (d), 130.8 (d), 131.8 (d), 136.1 (s), 136.4 (s), 164.8 (s). Anal. calcd for $C_{28}H_{24}BrNO_4$: C, 64.87; H, 4.67; N, 2.70. Found: C, 64.98; H, 4.71; N, 2.73.

3.4.16. 3,4-Diethoxycarbonyl-1-(*p*-ethoxycarbonylphenyl)-2,5-diphenylpyrrole 4c. Colorless crystals; mp 183–184 °C; IR($CHCl_3$) 2990, 1715, 1485, 1275, 1190 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), 1.16 (t, J=7.1 Hz, 6H, CH_3), 1.33 (t, J=7.1 Hz, 3H, CH_3), 4.19 (q, J=7.1 Hz, 4H, OCH_2), 4.29 (q, J=7.1 Hz, 2H, OCH_2), 6.89 (d, J=8.6 Hz, 2H, ArH), 7.15–7.25 (m, 10H, ArH), 7.76 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.9 (q), 14.2 (q), 60.6 (t), 61.2 (t), 115.7 (s), 127.7 (d), 128.3 (d), 128.7 (d), 129.6 (s), 129.8 (d), 130.1 (s), 130.8 (d), 136.4 (s), 140.9 (s), 164.8 (s), 165.5 (s). Anal. calcd for $C_{31}H_{29}NO_6$: C, 72.78; H, 5.71; N, 2.74. Found: C, 72.80; H, 5.80; N, 2.82.

3.4.17. 3,4-Diethoxycarbonyl-1,2,5-triphenylpyrrole 4d. Colorless crystals; mp 139–140 °C; IR($CHCl_3$) 2990, 1715, 1485, 1270, 1190 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, J=7.1 Hz, 6H, CH_3), 4.19 (q, J=7.1 Hz, 4H, OCH_2), 6.81–6.86 (m, 2H ArH), 7.04–7.11 (m, 3H, ArH), 7.16–7.24 (m, 10H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.9 (q), 60.5 (t), 115.1 (s), 127.5 (d), 127.8 (d), 128.0 (d), 128.5 (d), 128.8 (d), 130.5 (s), 130.8 (d), 136.6 (s), 137.0 (s), 165.0 (s). Anal. calcd for $C_{28}H_{25}NO_4$: C, 76.52; H, 5.93; N, 3.19. Found: C, 76.45; H, 5.80; N, 3.17.

3.4.18. 1-Cyanomethyl-3,4-diethoxycarbonyl-2,5-phenylpyrrole 4e. Colorless needles; mp 155–156 °C; IR($CHCl_3$) 2990, 1725, 1485, 1445, 1310 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 (t, J=7.1 Hz, 6H, CH_3), 4.13 (q, J=7.1 Hz, 4H, OCH_2), 4.37 (s, 2H, NCH_2), 7.52 (s, 10H, ArH), ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8 (q), 33.6 (t), 60.6 (t), 114.7 (s), 116.0 (s), 128.8 (d), 129.2 (s), 129.7 (d), 130.6 (d), 136.6 (s), 164.1 (s). Anal. calcd for $C_{24}H_{22}N_2O_4$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.51; H, 5.52; N, 6.96.

3.4.19. 3-Ethoxycarbonyl-1-(*p*-ethoxycarbonylphenyl)-4,5-dimethoxycarbonyl-2-methylpyrrole 13a. Colorless needles; mp 141–142 °C; IR($CHCl_3$) 2990, 1715, 1610, 1510, 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, J=7.1 Hz, 3H, CH_3), 1.42 (t, J=7.1 Hz, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.64 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 4.30 (q, J=7.1 Hz, 2H, OCH_2), 4.42 (q, J=7.1 Hz, 2H, OCH_2), 7.28 (d, J=8.2 Hz, 2H, ArH), 8.20 (d, J=8.2 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.2 (q), 14.1 (q), 14.2 (q),

51.7 (q), 52.6 (q), 60.4 (t), 61.3 (t), 111.7 (s), 120.2 (s), 125.9 (s), 127.7 (d), 130.5 (d), 131.3 (s), 141.1 (s), 141.6 (s), 159.1 (s), 163.0 (s), 165.4 (s), 166.4 (s). Anal. calcd for $C_{21}H_{23}NO_8$: C, 60.43; H, 5.55; N, 3.36; Fond: C, 60.39; H, 5.60; N, 3.30.

3.4.20. 1-(*p*-Ethoxycarbonylphenyl)-2-ethyl-3,4,5-trimethoxycarbonylpyrrole 13b. Colorless needles; mp 97–98 °C; IR($CHCl_3$) 2990, 1715, 1510, 1465, 1275 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (t, J=7.4 Hz, 3H, CH_3), 1.42 (t, J=7.1 Hz, 3H, CH_3), 2.69 (q, J=7.4 Hz, 2H, CH_2), 3.63 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 4.42 (q, J=7.1 Hz, 2H, OCH_2), 7.31 (d, J=8.4 Hz, 2H, ArH), 8.20 (d, J=8.4 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8 (q), 14.3 (q), 19.1 (t), 51.6 (q), 51.8 (q), 52.8 (q), 61.3 (t), 110.9 (s), 120.2 (s), 126.1 (s), 127.9 (d), 130.4 (d), 131.4 (s), 141.0 (s), 147.4 (s), 159.1 (s), 163.2 (s), 165.4 (s), 166.6 (s). Anal. calcd for $C_{21}H_{23}NO_8$: C, 60.43; N, 3.36; H, 5.55. Found: C, 60.42; N, 3.34; H, 5.61.

3.4.21. 3-Acetyl-1-(*p*-ethoxycarbonylphenyl)-4,5-dimethoxycarbonyl-2-methylpyrrole 13c. Colorless crystals; mp 129–130 °C; IR($CHCl_3$) 3010, 1720, 1670, 1445, 1275 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.42 (t, J=7.1 Hz, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.64 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 4.42 (q, J=7.1 Hz, 2H, OCH_2), 7.28 (d, J=8.2 Hz, 2H, ArH), 8.20 (d, J=8.2 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.0 (q), 14.3 (q), 29.6 (q), 51.9 (q), 52.9 (q), 61.4 (t), 120.85 (s), 120.93 (s), 125.0 (s), 127.8 (d), 130.6 (d), 131.4 (s), 140.6 (s), 141.0 (s), 159.3 (s), 165.4 (s), 167.0 (s), 193.2 (s). Anal. calcd for $C_{20}H_{21}NO_7$: C, 62.01; H, 5.46; N, 3.62. Found: C, 61.90; H, 5.42; N, 3.57.

3.4.22. 1-(*p*-Ethoxycarbonylphenyl)-2-ethyl-4,5-dimethoxycarbonyl-3-propionylpyrrole 13d. Colorless needles; mp 104–105 °C; IR($CHCl_3$) 2990, 1720, 1670, 1495, 1460 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, J=7.4 Hz, 3H, CH_3), 1.16 (t, J=7.1 Hz, 3H, CH_3), 1.42 (t, J=7.1 Hz, 3H, CH_3), 2.66 (q, J=7.4 Hz, 2H, CH_2), 2.76 (q, J=7.1 Hz, 2H, CH_2), 3.62 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 4.42 (q, J=7.1 Hz, 2H, OCH_2), 7.31 (d, J=8.2 Hz, 2H, ArH), 8.20 (d, J=8.2 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 7.8 (q), 13.8 (q), 14.2 (q), 19.5 (t), 34.1 (t), 51.8 (q), 52.9 (q), 61.3 (t), 119.9 (s), 120.8 (s), 124.6 (s), 127.9 (d), 130.3 (d), 131.4 (s), 140.9 (s), 146.1 (s), 159.3 (s), 165.4 (s), 167.3 (s), 196.1 (s). Anal. calcd for $C_{22}H_{25}NO_7$: C, 63.60; N, 3.37; H, 6.07. Found: C, 63.46; N, 3.35; H, 6.07.

3.4.23. 1-(*p*-Cyanophenyl)-3-ethoxycarbonyl-4,5-dimethoxycarbonyl-2-methylpyrrole 13e. Colorless crystals; mp 156–157 °C; IR($CHCl_3$) 3010, 2235, 1715, 1510, 1445, 1280 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, J=7.1 Hz, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.66 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 4.30 (q, J=7.1 Hz, 2H, OCH_2), 7.34 (d, J=8.4 Hz, 2H, ArH), 7.83 (d, J=8.4 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.2 (q), 14.1 (q), 51.9 (q), 52.7 (q), 60.5 (t), 112.2 (s), 113.5 (s), 117.6 (s), 120.2 (s), 126.2 (s), 128.8 (d), 133.1 (d), 141.2 (s), 141.5 (s), 159.1 (s), 162.8 (s), 166.1 (s). Anal. calcd for $C_{19}H_{18}N_2O_6$: C, 61.62; N, 7.56; H, 4.90. Found: C, 61.64; N, 7.54; H, 5.01.

3.4.24. 3-Acetyl-1-(*p*-cyanophenyl)-4,5-dimethoxycarbonyl-2-methylpyrrole 13f. Colorless crystals; mp 200–201 °C; IR($CHCl_3$) 3010, 2955, 2235, 1720, 1670, 1495, 1445 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.66 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 7.35 (d, J=8.4 Hz, 2H, ArH), 7.83 (d, J=8.4 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.0 (q), 29.5 (q), 52.0 (q), 53.0 (q), 113.6 (s), 117.6 (s), 120.7 (s), 121.2 (s), 125.2 (s), 128.9 (d), 133.2 (d), 140.5 (s), 141.1 (s), 159.2 (s), 166.8 (s), 193.1 (s). Anal. calcd for $C_{18}H_{16}N_2O_5$: C, 63.52; N, 8.23; H, 4.74. Found: C, 63.44; N, 8.11; H, 4.70.

3.4.25. 1-(*p*-Cyanophenyl)-2-ethyl-4,5-dimethoxycarbonyl-3-propionylpyrrole 13g. Colorless needles; mp 117–118 °C; IR($CHCl_3$) 2990, 2235, 1720, 1670, 1495, 1445 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, J=7.4 Hz, 3H, CH_3), 1.16 (t, J=7.1 Hz, 3H, CH_3), 2.65 (q, J=7.4 Hz, 2H, CH_2), 2.75 (q, J=7.1 Hz, 2H, CH_2), 3.65 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 7.37 (d, J=8.2 Hz, 2H, ArH), 7.83 (d, J=8.2, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) (7.8 (q), 13.8 (q), 19.5 (t), 34.2 (t), 52.0 (q), 53.0 (q), 113.6 (s), 117.6 (s), 120.1 (s), 120.6 (s), 124.9 (s), 129.0 (d), 133.0 (d), 141.0 (s), 146.1 (s), 159.2 (s), 167.1 (s), 196.0 (s). Anal. calcd for $C_{20}H_{20}N_2O_5$: C, 65.21; N, 7.60; H, 5.47. Found: C, 65.26; N, 7.50; H, 5.52.

3.4.26. 1-(*p*-Bromophenyl)-3-ethoxycarbonyl-4,5-dimethoxycarbonyl-2-methylpyrrole 13h. Colorless crystals; mp 151–152 °C; IR($CHCl_3$) 3005, 2955, 1710, 1510, 1495, 1445 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, J=7.1 Hz, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.66 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 4.29 (q, J=7.1 Hz, 2H, OCH_2), 7.07 (d, J=8.6 Hz, 2H, ArH), 7.63 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.2 (q), 14.1 (q), 51.8 (q), 52.6 (q), 60.4 (t), 111.6 (s), 120.2 (s), 123.3 (s), 125.8 (s), 129.2 (d), 132.4 (d), 136.3 (s), 141.8 (s), 159.1 (s), 163.0 (s), 166.4 (s). Anal. calcd for $C_{18}H_{18}BrNO_6$: C, 50.96; H, 4.28; N, 3.30. Found: C, 50.97; H, 4.30; N, 3.30.

3.4.27. 1-(*p*-Bromophenyl)-2-ethyl-3,4,5-trimethoxycarbonylpyrrole 13i. Colorless crystals; mp 122–123 °C; IR($CHCl_3$) 3010, 2955, 1715, 1510, 1495, 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, J=7.4 Hz, 3H, CH_3), 2.69 (q, J=7.4 Hz, 2H, CH_2), 3.65 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 7.10 (d, J=8.4 Hz, 2H, ArH), 7.63 (d, J=8.4 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.9 (q), 19.0 (t), 51.6 (q), 51.9 (q), 52.8 (q), 110.8 (s), 120.1 (s), 123.5 (s), 126.0 (s), 129.4 (d), 132.4 (d), 136.1 (s), 147.6 (s), 159.2 (s), 163.2 (s), 166.6 (s). Anal. calcd for $C_{18}H_{18}BrNO_6$: C, 50.96; H, 4.28; N, 3.30; Found: C, 50.96; H, 4.34; N, 3.29.

3.4.28. 3-Acetyl-1-(*p*-bromophenyl)-4,5-dimethoxycarbonyl-2-methylpyrrole 13j. Colorless crystals; mp 176–177 °C; IR($CHCl_3$) 3010, 2955, 1725, 1670, 1495, 1445 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.66 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 7.08 (d, J=8.6 Hz, 2H, ArH), 7.64 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.1 (q), 29.6 (q), 51.9 (q), 52.9 (q), 120.8 (s), 123.5 (s), 124.9 (s), 129.3 (d), 132.5 (d), 136.2 (s), 140.8 (s), 159.3 (s), 167.1 (s), 193.2 (s). Anal. calcd for $C_{17}H_{16}BrNO_5$: C, 51.79; H, 4.09; N, 3.55. Found: C, 51.75; H, 4.09; N, 3.51.

3.4.29. 1-(*p*-Bromophenyl)-2-ethyl-4,5-dimethoxycarbonyl-3-propionylpyrrole 13k. Colorless crystals; mp 91–92 °C; IR($CHCl_3$) 2985, 2955, 1725, 1670, 1495, 1460 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, J=7.4 Hz, 3H, CH_3), 1.16 (t, J=7.1 Hz, 3H, CH_3), 2.66 (q, J=7.4 Hz, 2H, CH_2), 2.75 (q, J=7.1 Hz, 2H, CH_2), 3.65 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 7.10 (d, J=8.5 Hz, 2H, ArH), 7.63 (d, J=8.5 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 7.8 (q), 13.9 (q), 19.5 (t), 34.2 (t), 51.9 (q), 52.9 (q), 119.8 (s), 120.8 (s), 123.5 (s), 124.6 (s), 129.5 (d), 132.4 (d), 136.1 (s), 146.4 (s), 159.4 (s), 167.4 (s), 196.2 (s). Anal. calcd for $C_{19}H_{20}BrNO_5$: C, 54.04; H, 4.77; N, 3.32. Found: C, 54.06, H, 4.83; N, 3.33.

3.4.30. 1-Benzyl-3-ethoxycarbonyl-4,5-dimethoxycarbonyl-2-methylpyrrole 13l. Colorless crystals; mp 111–112 °C; IR($CHCl_3$) 3010, 2955, 1705, 1470, 1445 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, J=7.1 Hz, 3H, CH_3), 2.50 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 4.26 (q, J=7.1 Hz, 2H, OCH_2), 5.63 (s, 2H, NCH_2), 6.93–6.99 (m, 2H, ArH), 7.21–7.33 (m, 3H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 11.3 (q), 14.1 (q), 48.4 (t), 51.8 (q), 52.4 (q), 60.2 (t), 111.3 (s), 118.9 (s), 125.8 (d), 126.2 (s), 127.4 (d), 128.8 (d), 136.2 (s), 141.6 (s), 160.0 (s), 163.2 (s), 166.8 (s). Anal. calcd for $C_{19}H_{21}NO_6$: C, 63.50; N, 3.90; H, 5.89. Found: C, 63.41; N, 3.85; H, 5.95.

3.4.31. 3-Acetyl-1-benzyl-4,5-dimethoxycarbonyl-2-methylpyrrole 13m. Colorless crystals; mp 138–139 °C; IR($CHCl_3$) 3010, 1715, 1665, 1505, 1445 cm^{-1}; ^1H (400 MHz, $CDCl_3$) δ 2.39 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 3.76 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 5.63 (s,2H, NCH_2), 6.94–6.99 (m, 2H, ArH), 7.22–7.34 (m, 3H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.0 (q), 29.5 (q), 48.3 (t), 51.9 (q), 52.7 (q), 119.5 (s), 120.6 (s), 125.1 (s), 125.8 (d), 127.5 (d), 128.8 (d), 136.1 (s), 140.6 (s), 160.1 (s), 167.5 (s), 193.4 (s). Anal. calcd for $C_{18}H_{19}NO_5$: C, 65.64; N, 4.25; H, 5.81. Found: C, 65.68; N, 4.18; H, 5.88.

3.4.32. 3-Ethoxycarbonyl-4,5-dimethoxycarbonyl-1-methoxycarbonylmethyl-2-methylpyrrole 13n. Colorless crystals; mp 121–122 °C; IR($CHCl_3$) 3005, 2960, 1745, 1715, 1515 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, J=7.1 Hz, 3H, CH_3), 2.52 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 4.26 (q, J=7.1 Hz, 2H, OCH_2), 5.08 (s, 2H, NCH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) (11.0 (q), 14.1 (q), 46.5 (t), 51.9 (q), 52.4 (q), 52.7 (q), 60.3 (t), 112.2 (s), 118.8 (s), 126.0 (s), 141.5 (s), 160.2 (s), 163.0 (s), 166.5 (s), 167.8 (s). Anal. calcd for $C_{15}H_{19}NO_8$: C, 52.78; N, 4.10; H, 5.61. Found: C, 52.77; N, 4.07; H, 5.68.

3.4.33. 2-Ethyl-3,4,5-trimethoxycarbonyl-1-methoxycarbonylmethylpyrrole 13o. Colorless crystals; mp 113–114 °C; IR($CHCl_3$) 3010, 2960, 1745, 1710, 1605 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.15 (t, J=7.5 Hz, 3H, CH_3), 2.96 (q, J=7.5 Hz, 2H, CH_2), 3.78 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 5.05 (s, 2H, NCH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.2 (q), 18.4 (t), 46.5 (t), 51.5 (q), 51.9 (q), 52.5 (q), 52.7 (q), 110.5 (s), 118.9 (s), 126.1 (s), 146.8 (s), 160.2 (s), 163.2 (s), 166.6 (s), 168.0 (s). Anal. calcd for $C_{15}H_{19}NO_8$: C, 52.78; N, 4.10; H, 5.61. Found: C, 52.81; N, 4.06; H, 5.64.

3.4.34. 3-Acetyl-4,5-dimethoxycarbonyl-1-methoxycarbonylmethyl-2-methylpyrrole 13p. Colorless crystals; mp 101–102 °C; IR($CHCl_3$) 3010, 2955, 1740, 1715, 1670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 5.09 (s, 2H, NCH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) (11.8 (q), 29.5 (q), 46.4 (t), 52.0 (q), 52.8 (q), 119.2 (s), 120.5 (s), 125.1 (s), 140.6 (s), 160.3 (s), 167.2 (s), 167.8 (s), 193.3 (s). Anal. calcd for $C_{14}H_{17}NO_7$: C, 54.02; N, 4.50; H, 5.50. Found: C, 54.04; N, 4.47; H, 5.57.

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