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Full-length paper

A simple approach to the synthesis of highly functionalized pyrrole derivatives

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Summary

The reaction of dibenzoylacetylene and enaminocarbonyl compounds leads to 3-alkylidene-2,3-dihydro-1*H*-pyrrol-2-ol derivatives in nearly quantitative yields. The reaction of this heterocyclic system with alcohols in the presence of a catalytic amount of HCl produces highly functionalized pyrroles in good yields.

Introduction

Simple nitrogen-containing heterocycles receive a considerable attention in the literature, as a consequence of their exciting biological properties and their role as pharmacophores of historical importance [1]. Of these heterocycles, the synthesis, reactions, and biological activities of pyrrole-containing molecules stands as an area of research in heteroaromatic chemistry and this structural motif appears in a large number of pharmaceutical agents and natural products [2]. Accordingly, many strategies have been developed for the preparation of pyrroles [2–9]. Enaminones are employed in several new preparations of the pyrrole derivatives. For example, the conjugate addition of alkyl 3-aminocrotonates to (*E*)-1,2-dibenzoylethylene results in the formation of polysubstituted pyrroles [10]. We wish to report an efficient route to polysubstituted pyrroles using dibenzoylacetylene (**1**) and enaminones **2**, derived from pentane-2,4-dione or methyl acetoacetate, followed by treatment of the addition product with various alcohols under acidic conditions.

The reaction of **1** with **2**, at ambient temperature in CH_2Cl_2, leads to 2-(2-hydroxy-5-methyl-2-phenyl-1,2-dihydro-pyrrol-3-ylidene)-1-phenyl-ethanone derivatives **3** in nearly quantitative yields (Scheme 1).

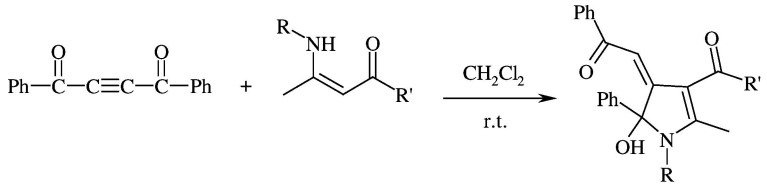
An alcohol (CH_3OH or C_2H_5OH):CH_2Cl_2 (1:20) solution of **3a–3d** in the presence of a catalytic amount of concentrated HCl was stirred at room temperature for 12 h to produce the pyrrole derivatives **4** and/or **5** (Scheme 2).

The structures of compounds **3–5** were deduced from their elemental analyses and their IR, ^{1}H NMR and ^{13}C NMR spectroscopic data. For example, the ^{1}H NMR spectrum of **3a** exhibited four singlets identified as methyl ($\delta = 2.41$ and 2.44), NH ($\delta = 8.15$), and olefinic ($\delta = 6.82$) protons along with multiplets ($\delta = 7.32$–7.84) for the aromatic protons. The OH proton resonance at $\delta = 8.64$ disappeared after addition of D_2O to the $CDCl_3$ solution of **3a**. The ^{1}H decoupled ^{13}C NMR spectrum of **3a** showed 17 distinct resonances in agreement with the proposed structure. The ^{1}H NMR spectrum of **4a** exhibited five singlets identified as methyl ($\delta = 2.37$ and 2.42), methoxy ($\delta = 3.45$), methine ($\delta = 6.51$), and NH ($\delta = 9.53$) protons along with multiplets ($\delta = 7.10$–7.69) for the aromatic protons. The mass spectra of compound **3–5** displayed molecular ion peaks at appropriate m/z values.

The mechanism proposed for the reaction between dibenzoylacetylene **1** and enaminone **2** (see Scheme 3) is the same as the one suggested by Kaupp and co-workers [10] except for the last step as there is no possibility of elimination of water. It is reasonable to assume that **3** results from initial addition of enaminone **2** to the acetylenic ketone and subsequent cyclization of the iminoketone intermediate **7** to yield **3**.

Protonation of compound **3** in acidic alcohol solutions can lead to two intermediates **9** and **11** (see Scheme 4). The subsequent attack of the alcohol on **9** or **11** leads to polysubstituted pyrroles **4** or **5**, respectively.

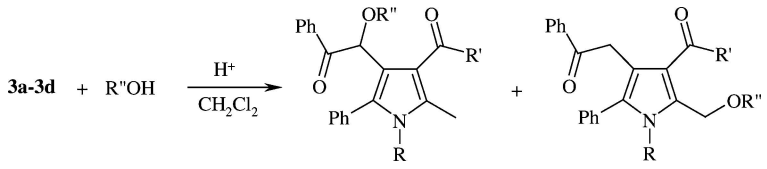
When R = hydrogen, as for **3a**, the reaction proceeds through intermediate **9** and leads to **4**. When R = Ph or $PhCH_2$ and $R' = CH_3$, only pyrrole derivative **5** is obtained. However, when R = $PhCH_2$ and $R' = OCH_3$ both **4f** and **5f** are obtained. It seems that greater electron-withdrawing ability of the R-CO group increases the acidity of the methyl



1 **2** **3**

2,3	R	R'	Yield (%) of **3**
a	H	CH_3	99
b	Ph	CH_3	99
c	$PhCH_2$	CH_3	98
d	$PhCH_2$	OCH_3	98

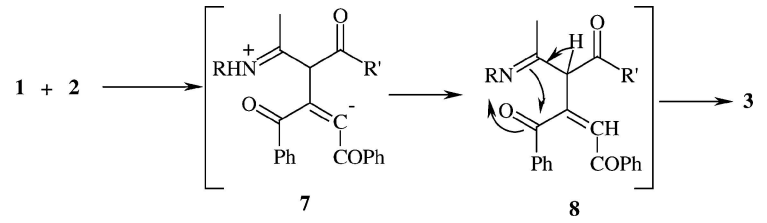
Scheme 1.



4 **5**

4,5	R	R'	R"	Yield (%) of **4**	Yield (%) of **5**
a	H	CH_3	CH_3	77	-
b	H	CH_3	C_2H_5	67	-
c	Ph	CH_3	CH_3	-	80
d	$PhCH_2$	CH_3	CH_3	-	84
e	$PhCH_2$	CH_3	C_2H_5	-	70
f	$PhCH_2$	OCH_3	CH_3	51	34

Scheme 2.



7 **8**

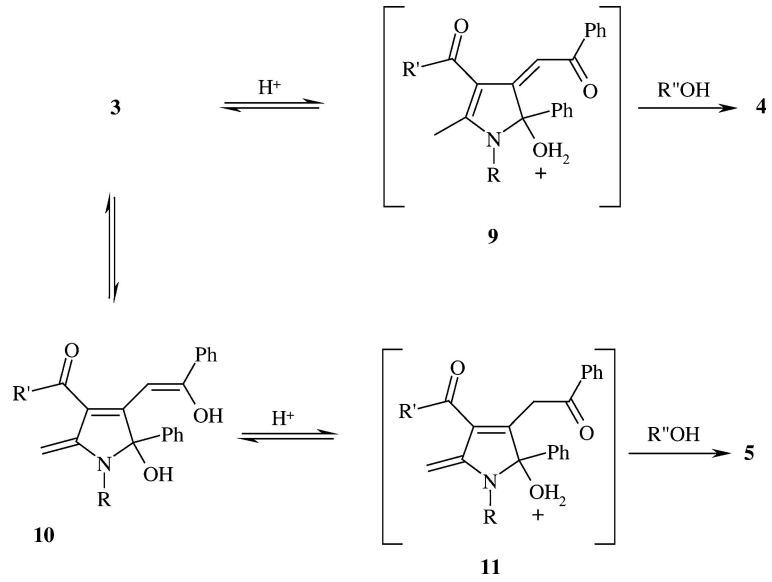
Scheme 3.

protons and facilitates enolization of compound **3**, which leads to product **5** *via* intermediate **10**. When the reaction was carried out in CH_2Cl_2:CH_3OH (20:1), **4f** and **5f** were produced in 51 and 34% yield, respectively. However, the **4f**:**5f** ratio depends on CH_2Cl_2:CH_3OH ratio. In absolute methanol, **4f** and **5f** were produced in 60 and 35% yields, respectively.

The presented reactions of enaminones with dibenzoylacetylene provide a simple entry into the synthesis of polyfunctionalised pyrrole derivatives of potential synthetic interest. The simplicity of the present procedure makes it an interesting alternative to complex multistep approaches [2–9].

Materials and methods

Melting points were measured with an Electrothermal 9100 apparatus. Elemental analyses (C, H, N) were performed using a Heraeus CHN-O-Rapid analyzer; the results agreed favorably with the calculated values. IR spectra were measured with a Shimadzu IR-460 spectrometer. ^1H and ^{13}C NMR spectra were measured with a Bruker DRX-500 AVANCE instrument with $CDCl_3$ as solvent at 500.1 and 125.7 MHz. Mass spectra were recorded with a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. Dibenzoylacetylene [11, 12] and enaminones [13, 14] were prepared by known methods.



Scheme 4.

Preparation of 2-(4-Acetyl-1-benzyl-2-hydroxy-5-methyl-2-phenyl-1,2-dihydro-pyrrol-3-ylidene)-1-phenyl-1-ethanone (3a)

Typical procedure

To a stirred solution of 0.47 g dibenzoylacetylene (2 mmol) in 20 mL CH_2Cl_2 was added a mixture of 0.20 g methyl 3-amino-but-2-enoate (2 mmol) in 5 mL CH_2Cl_2 at room temperature. The reaction mixture was then stirred for 12 h. The solvent was removed under reduced pressure, and the residue was washed with diethyl ether. The product was obtained as yellow powder; yield 0.66 g (99%), mp 161–162 °C.

IR (KBr): 3370 (OH), 3130 (NH), 1609 (C=O) cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 8.64 (s, 1H, OH), 8.15 (s, 1 H, NH), 7.32–7.84 (m, 10 H, 2 Ph), 6.85 (s, 1 H, =CH), 2.41 and 2.44 (2s, 6 H, 2 CH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 192.15 and 192.46 (2 C=O), 168.05, 165.59, 140.74, and 138.87 (4 C), 132.54, 128.52, 128.49, 128.36, 128.31, and 124.93 (10 CH), 111.09 (C), 110.68 (CH), 92.28 (HO–C), 31.36 and 18.03 (2 CH_3).

MS (EI, 70 eV): m/z(%) = 333 (M^+, 4), 228 (11), 105 (100).

Anal. Calcd. for $C_{21}H_{19}NO_3$(333.1): C, 75.66; H, 5.74; N, 4.20. Found: C, 75.6; H, 5.8; N, 4.2%.

2-(4-Acetyl-2-hydroxy-5-methyl-1,2-diphenyl-1,2-dihydro-3H-pyrrol-3-ylidene)-1-phenyl-1-ethanone (3b)

Yellow powder; yield 0.82 g (99%), mp 171–172 °C.

IR (KBr): 3400 (OH), 1614 (C=O) cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 8.68 (s, 1H, OH), 7.89 (s, 1 H, = CH), 7.82 (d, 2H, $^3J_{HH}$ = 7.5 Hz, 2CH), 6.80–7.45 (m, 13 H, 13 CH), 2.54 and 2.27 (2s, 6 H, 2 CH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 191.92 and 192.34 (2 C=O), 169.17, 166.20, 139.49, 139.18, and 128.38 (5 C), 134.77, 132.25, 129.83, 128.94, 128.88, 128.36, 128.27, 127.50, and 125.75 (15 CH), 112.04 (C), 109.19 (CH), 96.80 (HO–C), 31.90 and 16.98 (2 CH_3).

MS (EI, 70 eV): m/z(%) = 409 (M^+, 2), 304 (5), 105 (100).

Anal. Calcd. for $C_{27}H_{23}NO_3$ (409.2): C, 79.20; H, 5.66; N, 3.42. Found: C, 79.3; H, 5.6; N, 3.4%.

2-(4-Acetyl-1-benzyl-2-hydroxy-5-methyl-2-phenyl-1,2-dihydro-3H-pyrrol-3-ylidene)-1-phenyl-1-ethanone (3c)

Yellow powder; yield 0.83 g (98%), mp 163–165 °C.

IR (KBr: 3376 (OH), 1613 (C=O) cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 9.22 (s, 1H, OH), 7.81 (d, 2 H, $^3J_{HH}$ = 7.9 Hz, 2 CH), 7.71 (s, 1 H, =CH), 7.61 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, 2 CH), 7.24–7.45 (m, 9 H, 9 CH), 7.20 (d, 2 H, $^3J_{HH}$ = 7.3 Hz, 2 CH), 4.40 (AB quartet, 2 H, CH_2), 2.49 and 2.31 (2s, 6 H, 2 CH_3), ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 191.67 and 192.03 (2 C=O), 170.88, 166.90, 139.56, 139.33, and 128.70 (5 C), 136.41, 132.21, 128.72, 128.29, 128.07, 127.50, 126.78, and 125.74 (15 CH), 111.79 (C), 108.09 (CH), 96.07 (HO–C), 46.29 (CH_2), 31.89 and 16.22 (2 CH_3).

MS (EI, 70 eV): m/z(%) = 423 (M^+, 3), 318 (7), 91 (100).

Anal. Calcd. for $C_{28}H_{25}NO_3$ (423.2): C, 79.41; H, 5.95; N, 3.31. Found: C, 79.4; H, 5.9; N, 3.2%.

Methyl 1-benzyl-2-hydroxy-5-methyl-3-[(Z)-2-oxo-2-phenylethylidene]-2-phenyl-1,2-dihydro-3H-pyrrol-4-carboxylate (3d)

Yellow powder; yield 0.86 g (98%), mp 145–147 °C.

IR (KBr): 3380 (OH), 1668 (C=O) cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 9.18 (s,1H, OH), 7.81 (d, 2 H, $^3J_{HH}$ = 7.9 Hz, 2 CH), 7.74 (s, 1 H, = CH), 7.61 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, 2 CH), 7.20–7.44 (m, 9 H,

9 CH)2.43 (s, 3 H, CH_3), 7.10 (d, 2 H, $^3J_{HH}$ = 7.3 Hz, 2 CH), 4.47 (AB quartet, 2 H, NCH_2), 3.83 (s, 3 H, OCH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 191.67 and 192.03 (2 C=O), 170.88, 166.90, 139.56, 139.33, and 128.70 (5 C), 136.41, 132.21, 128.72, 128.32, 128.30, 128.07, 127.50, 126.78, and 125.74 (15 CH), 111.78 (C), 108.09 (CH), 96.32 (HO–C), 52.31 (OCH_3), 46.27 (NCH_2), 16.22 (CH_3).

MS (EI, 70 eV): m/z(%) = 439 (M^+, 2), 334 (6), 105 (65), 91 (100).

Anal. Calcd. for $C_{28}H_{25}NO_4$ (439.2): C, 76.52; H, 5.73; N, 3.19. Found: C, 76.4; H, 5.7; N, 3.1%.

The general procedure for preparation of **4a**–**4f** and **5c–5f** is as follows (exemplified by **4a**): To a stirred solution of 0.67 g **3a** (2 mmol) and 1 mL methanol in 20 mL CH_2Cl_2 was added one drop of concentrated hydrochloric acid solution at room temperature. The reaction mixture was then allowed to stand for 12 h. The solvent was removed under reduced pressure, and the residue was separated by silica gel (Merck 230–400 mesh) column chromatography using *n*-Hexane-EtOAc mixture as eluent.

2-(4-Acetyl-5-methyl-2-phenyl-1H-pyrrol-3-yl)-2-methoxy-1-phenyl-1-ethanone (4a)

White powder; yield 0.53 g (77%), mp 123–125 °C.

IR (KBr): 3185 (NH), 1684, and 1593 (C=O) cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 9.53 (s, 1 H, NH), 7.10–7.69 (m, 10 H, 2 Ph), 6.51 (s, 1 H, O–CH), 3.45 (s, 3 H, O CH_3), 2.42 and 2.37 (2s, 6H, 2 CH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 195.90 and 197.29 (2 C=O), 136.41 (CH), 135.76 (C), 132.09 (CH), 131.90 and 130.71 (2 C), 128.25 (C), 128.45, 128.59, and 129.04 (6 CH), 128.22 (2 CH), 116.09 and 120.73 (2 C), 78.44 (O–CH), 57.21 (OCH_3), 15.27 and 30.95 (2 CH_3).

MS (EI, 70 eV): m/z(%) = 347 (M^+, 1), 316 (4), 242 (100), 105 (16).

Anal. Calcd. for $C_{22}H_{21}NO_3$ (347.2): C, 76.06; H, 6.09; N, 4.03. Found: C, 76.0; H, 6.1; N, 4.1%.

2-(4-Acetyl-5-methyl-2-phenyl-1H-pyrrol-3-yl)-2-ethoxy-1-phenyl-1-ethanone (4b)

White powder; yield 0.49 g (67%), mp 77–79 °C.

IR (KBr): 3180 (NH), 1690, and 1595 (C=O) cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 9.32 (s, 1 H, NH), 7.10–7.75 (m, 10 H, 2 Ph), 6.45 (s, 1 H, OCH), 3.62 (q, 2 H, $^3J_{HH}$ = 7.5 Hz, CH_2), 2.48 and 2.42 (2s, 6 H, 2 CH_3), 1.15 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, CH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 196.37 and 197.79 (2 C=O), 136.34 (CH), 135.55 (C), 132.13 (CH), 131.19 and 131.15 (2 C), 129.22, 128.42, and 128.30 (6 CH), 128.15 (C), 128.05 (2 CH), 121.27 and 116.80 (2 C), 77.2 (OCH), 65.13 (OCH_2), 30.41, 15.30, and 14.82 (3 CH_3), MS (EI, 70 eV): m/z(%) = 361 ($M^{+\cdot}$, 3), 316 (50), 256 (100), 105 (73).

Anal. Calcd. for $C_{23}H_{23}NO_3$ (361.4): C, 76.43; H, 6.41; N, 3.88. Found: C, 76.4; H, 6.3; N, 3.7%.

Methyl 1-benzyl-4-(1-methoxy-2-oxo-2-phenylethyl)-2-methyl-5-phenyl-1H-pyrrole-3-carboxylate (4f)

White powder; yield 0.46 g (51%), mp 133–135 °C.

IR (KBr): 1680 (C=O) cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 7.52 (d, 2 H, $^3J_{HH}$ = 7.4 Hz, 2 CH), 7.43–6.66 (m, 13 H, 13 CH), 6.11 (s, 1 H, CH), 4.84 (AB quartet, 2 H, CH_2), 3.83 and 3.52 (2s, 6 H, 2 CH_3), 2.41 (s, 3 H, CH_3), ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 196.58 (C=O), 166.05 (C=O, ester), 137.21 (CH), 136.35 and 137.06 (2 C), 134.73 and 131.97 (3 CH), 130.04 (C), 128.79 (CH), 127.74 (C), 128.70, 128.43, 127.75, and 127.26 (8 CH), 125.39 (C), 125.38 (2 CH), 117.73 and 110.54 (2 C), 79.02 (CH–O), 57.65 and 50.69 (2 CH_3), 47.52 (CH_2), 12.21 (CH_3).

MS (EI, 70 eV): m/z(%) = 453 (M^+, 4), 422 (9), 348 (25), 105 (28), 91 (100).

Anal. Calcd. for $C_{29}H_{27}NO_4$(453.2): C, 76.80; H, 6.00; N, 3.09. Found: C, 76.8; H, 5.9; N, 3.1%.

2-[4-Acetyl-5-(methoxymethyl)-1,2-diphenyl-1H-pyrrol-3-yl]-1-phenyl-1-ethanone (5c)

White powder; yield 0.68 g (80%), mp 153–155 °C.

IR (KBr): 1670, 1633 (C=O) cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 7.10–8.32 (m, 15 H, 3 Ph), 4.28 and 4.25 (2s, 4 H, 2 CH_2), 3.38 (s, 3 H, OCH_3), 2.61 (s, 3 H, CH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 195.64 and 198.90 (2 C=O), 137.61 (CH), 137.21, 135.27, and 133.83 (3 C), 132.61 (CH), 130.90 (C), 130.51, 128.71, 128.59, 128.46, and 128.21 (10 CH), 128.18 (C), 128.04 (2 CH), 127.54 (CH), 123.75 and 116.86 (2 C), 64.37 (CH_2), 58.10 (OCH_3), 36.84 (CH_2), 29.74 (CH_3).

MS (EI, 70 eV): m/z(%) = 423 (M^+, 5), 392 (8), 318 (13), 105 (100).

Anal. Calcd. for $C_{28}H_{25}NO_3$ (423.2): C, 79.41; H, 5.95; N, 3.31. Found: C, 79.3; H, 6.0; N, 3.2%.

2-[4-Acetyl-1-benzyl-5-(methoxymethyl)-2-phenyl-1H-pyrrol-3-yl]-1-phenyl-1-ethanone (5d)

White powder; yield 0.74 g (84%); mp 150–152°C.

IR (KBr): 1673, 1633 (C=O) cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 7.99 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, 2CH), 7.52–7.21 (m, 11 H, 11 CH), 6.91 (d, 2 H, $^3J_{HH}$ = 7.7 Hz, 2CH), 5.17, 4.55, and 4.25 (3s, 6 H, 3 CH_2), 3.35 and 2.51 (2s, 6 H, 2 CH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 195.31 and 198.53 (2 C=O), 137.80 (CH), 137.48, 135.54, and 132.74 (3 C), 132.60 and 130.82 (3 CH), 130.75 (C), 128.75 (2 CH), 128.52 (C), 128.47 128.43, and 128.13 (6 CH), 127.30 (CH), 125.70 (2 CH), 123.80 and 116.16 (2 C), 64.20 (CH_2), 58.19 (OCH_3), 48.13 and 36.64 (2 CH_2), 30.29 (CH_3).

MS (EI, 70 eV): m/z(%) = 437 (M^+, 3), 406 (9), 105 (29), 91 (100).

Anal. Calcd. for $C_{29}H_{27}NO_3$ (437.2): C, 79.61; H, 6.22; N, 3.20. Found: C, 79.7; H 6.2; N, 3.1%.

2-[4-Acetyl-1-benzyl-5-(ethoxymethyl)-2-phenyl-1H-pyrrol-3-yl]-1-phenyl-1-ethanone (5e)

White powder; yield 0.63 g (70%), mp 134–135 °C.

IR (KBr): 1675, 1636 (C=O) cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 7.98$ (d, 2 H, $^3J_{HH} =$ 7.5 Hz, 2CH), 7.59–7.17 (m, 11 H, 11 CH), 6.92 (d, 2 H, $^3J_{HH}$ 7.3 Hz, 2CH), 5.15, 4.57, and 4.22 (3s, 6 H, 3 CH_2), 3.48 (q, 2 H, $^3J_{HH} = 7.0$ Hz, OCH_2), 2.49 (s, 3 H, CH_3), 1.17 (t, 3 H, $^3J_{HH} = 7.0$ Hz, CH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 195.34$ and 198.60 (2 C=O), 137.84 (CH), 137.50, 135.46, and 132.51 (3 C), 132.99 and 130.82 (3 CH), 130.12 (C), 128.83 (2 CH), 128.70 (C), 128.43, 128.40, and 128.12 (6 CH), 127.23 (CH), 125.71 (2 CH), 123.62 and 116.20 (2 C), 66.05 and 62.37 (2 OCH_2), 48.14 (N–CH_2), 36.62 (CH_2CO), 30.23 (CH_3), 15.06 (Me).

MS (EI, 70 eV): $m/z(\%) = 451$ (M^+, 3), 406 (45), 346 (70), 105 (30), 91 (100).

Anal. Calcd. for $C_{30}H_{29}NO_3$(451.6): C, 79.80; H, 6.47; N, 3.10. Found: C, 79.8; H, 6.5; N, 3.0 %.

Methyl 1-benzyl-2-(methoxymethyl)-4-(2-oxo-2-phenylethyl)-5-phenyl-1H-pyrrole-3-carboxylate (5f)

White powder; yield 0.31 g (34%), mp 147–148 °C.

IR (KBr): 1693 (C=O) cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 6.80$–8.18 (m, 15 H, 3 Ph), 5.27, 4.82, and 4.33 (3 s, 6 H, 3 CH_2), 3.59 and 3.35 (2 s, 6 H, 2 OCH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 198.39$ (C=O), 165.32 (C=O, ester), 137.76 (CH), 137.27 and 135.23 (2 C), 134.39 (CH), 130.65 and 134.29 (2 C), 130.63, 128.52, 128.43, and 128.26 (8 CH), 128.12 (C), 127.82, 126.96, and 125.54 (5 CH), 116.17 and 113.36 (2 C), 63.40 (CH_2), 57.54 and 50.41 (2 CH3), 47.93 and 34.40 (2 CH_2).

MS (EI, 70 eV): $m/z(\%) = 453$ (M^+, 2), 422 (10), 348 (22), 105 (28), 91 (100).

Anal. Calcd. for $C_{29}H_{27}NO_4$ (453.2): C, 76.80; H, 6.00; N, 3.09. Found: C, 76.7; H, 5.9; N, 3.1%.

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