Efficient Synthesis of Functionalized 2,5-Dihydropyrrole Derivatives by Ph_3P-Promoted Condensation between Acetylene Esters and α-Arylamino Ketones

Mohammad Anary-Abbasinejad,* Ehsanorreza Poorhassan, Alireza Hassanabadi

Department of Chemistry, Islamic Azad University, Yazd Branch, PO Box 89195-155, Yazd, Iran
Fax +98(351)8211109; E-mail: mohammadanary@yahoo.com

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Abstract: A new and efficient one-pot synthesis of polysubstituted 2,5-dihydropyrrole derivatives by reaction between dialkyl acetylenedicarboxylates and β-aminoketones promoted by triphenylphosphine, is described. The prepared 2,5-dihydropyrroles can be easily oxidized to the corresponding pyrrole derivatives by chromium trioxide.

Key words: 2,5-dihydropyrroles, dialkyl acetylenedicarboxylates, β-aminoketones, triphenylphosphine, intramolecular Wittig reaction

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] 2,5-Dihydropyrroles are important compounds which exhibit a wide range of biological activities and are useful intermediates in synthesizing natural products. Some 2,4-bisaryl-2,5-dihydropyrrole derivatives have been recently studied as novel, water-soluble KSP inhibitors.[2] 2,5-Bisaryl-2,5-dihydropyrrole derivatives are part of an important class of photochromic compounds and often exhibit excellent photochromic properties, thermal and photochemical stability and very good fatigue resistance for photochemical reversibility.[3] In addition, their herbicidal,[4] pesticidal,[5] and anti-tumor[6] activities increasingly necessitate new research in order to simplify the synthesis of these materials. Despite their wide application range, available routes for the synthesis of 2,5-dihydropyrroles are limited. Previous syntheses of 2,5-dihydropyrroles utilized the Birch-reduction of electron-deficient pyrroles,[7] ring-closing metathesis (RCM) reactions,[8] 1,3-dipolar cycloaddition of azomethine ylides to 2-(*p*-tolylsulfinile)acrylate,[9] and $TiCl_4$/Zn promoted reductive cyclization of *N*,*N*-bis(2-aryl-2-oxoethyl)anilines.[3] Intramolecular Wittig reaction of the intermediates generated by the three-component addition reaction of activated acetylenes, triphenylphosphine and 2-amino carbonyl compounds has been recently used for the synthesis of five-membered nitrogen heterocycles.[10–12] In a continuation of our work on the reaction between trivalent phosphorus nucleophiles and electron-deficient acetylenic compounds in the presence of organic N-H acidic compounds,[13–15] here we wish to report an efficient, simple and one-pot synthetic method for some N-substituted 2,5-dihydropyrrole derivatives through the reaction of dialkyl acetylenedicarboxylates, α-arylaminoketones and triphenylphosphine.

Thus, reaction between dimethyl acetylenedicarboxylate (**2**; DMAD), 1-(4-bromophenyl)-2-(4-methoxyphenylamino)ethanone (**1a**) and triphenylphosphine in dichloromethane at room temperature after 24 hours, afforded dimethyl 4-(4-bromophenyl)-1-(4-methoxyphenyl)-2,4-dihydro-1*H*-pyrrole-2,3-dicarboxylate (**3a**) in 90% yield.[16] Under similar conditions, different 2,5-dihydropyrrole derivatives were obtained using different derivatives of acetylene diesters and α-aminoketones (Table 1).

The structures of compounds **3a**–**h** were deduced from their elemental analyses and their IR, ^{1}H, and ^{13}C NMR spectra. The mass spectra of these 2,5-dihydropyrroles were fairly similar and displayed molecular ion peaks. The 500 MHz ^{1}H NMR spectrum of compound **3a** exhibited three sharp signals at δ = 3.70, 3.73 and 3.75 ppm arising from the three methoxy groups. The 2,5-dihydropyrrole ring displayed an ABX pattern for the 2-CH and the 5-CH_2 spin system, with the geminal methylene protons resonating as two double doublets at δ = 4.50 ($J_{H–H}$ = 15.7 Hz, $J_{H–H}$ = 2.3 Hz) and 4.72 ($J_{H–H}$ = 15.7 Hz, $J_{H–H}$ = 6.5 Hz) and the methine proton as a double doublet at δ = 5.39 ($J_{H–H}$ = 6.5 Hz, $J_{H–H}$ = 2.3 Hz). Aromatic protons showed two para-substituted phenyl ring patterns; four 2 H doublets were observed at δ = 6.63 ($J_{H–H}$ = 8.9 Hz), 6.85 ($J_{H–H}$ = 8.9 Hz), 7.35 ($J_{H–H}$ = 8.4 Hz), and 7.55 ($J_{H–H}$ = 8.4 Hz). In agreement with the proposed structure, the ^{13}C NMR spectrum of compound **3a** showed sixteen distinct resonances. The structural assignments made on the basis of the NMR spectra of compound **3a** were also supported by its IR spectrum; the ester carbonyl groups exhibited strong absorption bands at 1740 and 1699 cm^{-1}.

A plausible mechanism for formation of compounds **3** is illustrated in Scheme 1. On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[17–22] it is reasonable to assume that 2,5-dihydropyrrole **3** resulted from the initial addition of triphenylphosphine to the acetylene diester and subsequent protonation of the 1:1 adduct by α-aminoketones. Then, the positively charged ion intermediate **4** is attacked by the conjugate anion of α-aminoketones **5** to form the phosphorane **6**, which is converted into product **3** through an intramolecular Wittig reaction.

To examine the ease of oxidation of the prepared 2,5-dihydropyrrole derivatives to the corresponding pyrroles, we carried out the reaction of a selection of substrates with

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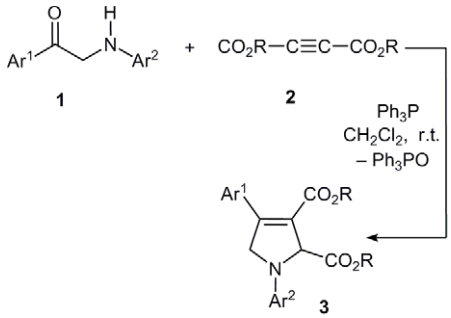
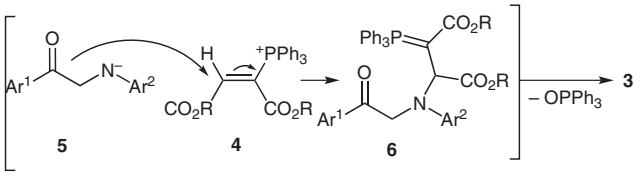
Table 1 Reaction between Dialkyl Acetylenedicarboxylate and α-Aminoketones in the Presence of Triphenylphosphine



Product	Ar^1	Ar^2	R	Yield of **3** (%)[a]
3a	4-BrC_6H_4	4-$MeOC_6H_4$	Me	95
3b	4-BrC_6H_4	4-$MeOC_6H_4$	Et	95
3c	4-ClC_6H_4	4-$MeOC_6H_4$	Me	90
3d	4-ClC_6H_4	4-$MeOC_6H_4$	Et	95
3e	4-BrC_6H_4	4-$MeOC_6H_4$	*t*-Bu	94
3f	Ph	4-$MeOC_6H_4$	Me	90
3g	Ph	4-$MeOC_6H_4$	Me	89
3h	Ph	4-ClC_6H_4	Me	90

[a] Isolated yield.

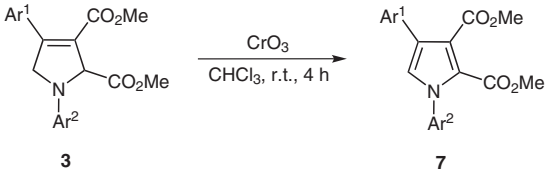


Scheme 1 Suggested mechanism for formation of compound **3**

chromium trioxide. Thus, treatment of dimethyl 4-phenyl-1-(4-methoxyphenyl)-2,4-dihydro-1*H*-pyrrole-2,3-dicarboxylate (**3f**) with chromium trioxide in chloroform at room temperature for five hours, and separation by column chromatography, led to dimethyl 4-phenyl-1-(4-methoxyphenyl)pyrrole-2,3-dicarboxylate (**7a**) in 83% yield.[23] Under similar conditions, pyrrole derivatives **7b** and **7c** were obtained, respectively, from the oxidation of 2,5-dihydropyrrole derivatives **3g** and **3a**, in good yields (Table 2). The ^{1}H NMR spectrum of compound **7a** exhibited three sharp signals at δ = 3.76, 3.86 and 3.88 ppm arising from three methoxyl groups. A singlet (1 H) was observed at δ = 7.10 ppm, arising from the CH of the pyrrole ring. Aromatic protons resonated between δ = 6.98 and 7.30 ppm.

In conclusion, we have defined a new, efficient, simple, and one-pot approach to some polysubstituted 2,5-dihydropyrrole derivatives through a reaction between dialkyl acetylenedicarboxylates and β-aminoketones promoted by triphenylphosphine. Furthermore, the prepared 2,5-dihydropyrroles can be easily oxidized to the corresponding pyrrole derivatives by chromium trioxide. Advantages of the reported method are that the reactions can be performed under neutral conditions and that the readily available starting materials can be mixed without any further purification or activation.

Table 2 Oxidation of 2,5-Dihydropyrrole Derivatives to the Corresponding Pyrroles by CrO_3



Product	Ar^1	Ar^2	Yield of **7** (%)[a]
7a	Ph	4-$MeOC_6H_4$	83
7b	Ph	4-MeC_6H_4	85
7c	4-BrC_6H_4	4-$MeOC_6H_4$	80

[a] Isolated yield.

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(16) General procedure for the preparation of compounds **3a–h**: To a magnetically stirred solution of β-aminoketone (1 mmol)

and triphenylphosphine (0.28 g, 1 mmol) in CH_2Cl_2 (10 mL), was added dropwise a mixture of dialkyl acetylenedicarboxylate (1 mmol) in CH_2Cl_2 (5 mL) at room temperature. The reaction mixture was stirred for 24 h, then the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexane–EtOAc). The solvent was removed under reduced pressure to afford the product.

3a: White powder; mp 110–112 °C; IR (KBr): 1740, 1699 (ester) cm^{-1}; Anal. Calcd for $C_{21}H_{20}BrNO_5$: C, 56.52; H, 4.52; N, 3.14. Found: C, 56.51; H, 4.33; N, 3.17; MS: *m/z* (%) = 445 (4); ^1H NMR (500 MHz, $CDCl_3$): δ = 3.70, 3.73 and 3.75 (9 H, 3 × s, 3 × OCH_3), 4.50 (1 H, dd, *J* = 15.7 Hz, *J* = 2.3 Hz, HC*H*), 4.72 (1 H, dd, *J* = 15.7 Hz, *J* = 6.5 Hz, HC*H*), 5.39 (1 H, dd, *J* = 6.5 Hz, *J* = 2.3 Hz, CH), 6.63 and 6.85 (4 H, 2 × d, *J* = 8.9 Hz, ArH), 7.35 and 7.55 (4 H, 2 × d, *J* = 8.4 Hz, ArH); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 52.3, 52.9 and 56.2 (3 × OCH_3), 61.3 (CH_2), 70.3 (CH), 113.1, 115.6, 124.2, 125.3, 130.2, 131.8, 131.9, 140.1, 151.2 and 152.6 (aromatic and olefinic carbons), 163.5 and 172.1 (2 × CO ester). **3b**: Viscose oil; IR (neat): 1726 (ester) cm^{-1}; Anal. Calcd for $C_{23}H_{24}BrNO_5$: C, 58.24; H, 5.10; N, 2.95. Found: C, 58.10; H, 5.29; N, 2.78; MS: *m/z* (%) = 473 (11); ^1H NMR (500 MHz, $CDCl_3$): δ = 1.20 (6 H, m, 2 × CH_3), 3.73 (3 H, s, OCH_3), 4.14 (4 H, m, 2 × OCH_2), 4.77 (1 H, dd, *J* = 15.6 Hz, *J* = 2.3 Hz, HCH), 4.71 (1 H, dd, *J* = 15.6 Hz, *J* = 6.5 Hz, HC*H*), 5.38 (1 H, dd, *J* = 6.5 Hz, *J* = 2.3 Hz, CH), 6.66 and 6.85 (4 H, 2 × d, *J* = 9.0 Hz, 4 H, ArH), 7.36 and 7.52 (4 H, 2 × d, *J* = 8.5 Hz, ArH); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 23.2 and 24.2 (2 × CH_3), 55.9 (OCH_3), 61.2, 61.3 and 61.7 (3 × OCH_2), 70.4 (CH), 113.2, 115.5, 124.0, 126.2, 129.9, 130.3, 132.0, 140.1, 150.8 and 152.6 (aromatic and olefinic carbons), 162.9 and 171.7 (2 × CO ester). **3c**: White powder; mp 114–116 °C; IR (KBr): 1735, 1709 (ester) cm^{-1}; Anal. Calcd for $C_{21}H_{20}ClNO_5$: C, 62.77; H, 5.02; N, 3.49. Found: C, 62.91; H, 5.17; N, 3.33; MS: *m/z* (%) = 401 (27); ^1H NMR (500 MHz, $CDCl_3$): δ = 3.51, 3.54 and 3.57 (9 H, 3 × s, 3 × OCH_3), 4.33 (1 H, dd, *J* = 15.6 Hz, *J* = 2.4 Hz, HC*H*), 4.53 (1 H, dd, *J* = 15.6 Hz, *J* = 6.4 Hz, HCH), 5.21 (1 H, dd, *J* = 6.4 Hz, *J* = 2.4 Hz, CH), 6.45 and 6.68 (4 H, 2 × d, *J* = 8.8 Hz, ArH), 7.18–7.25 (4 H, m, C_6H_4Cl); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 51.8, 52.4 and 52.7 (3 × OCH_3), 60.9 (CH_2), 69.9 (CH), 112.7, 115.2, 124.8, 128.5, 129.6, 131.0, 135.5, 139.8, 150.8 and 152.2 (aromatic and olefinic carbons), 163.1 and 173.7 (2 × CO ester). **3d**: Viscose oil; IR (neat): 1730, 1710 (2 × CO ester) cm^{-1}; Anal. Calcd for $C_{23}H_{24}ClNO_5$: C, 64.26; H, 5.63; N, 3.26. Found: C, 64.20; H, 5.54; N, 3.37; MS: *m/z* (%) = 429 (25); ^1H NMR (500 MHz, $CDCl_3$): δ = 1.01, 1.04 (6 H, 2 × t, *J* = 7.4 Hz, 2 × CH_3), 3.51 (4 H, m, 2 × OCH_2), 3.57 (3 H, s, OCH_3), 4.32 (1 H, dd, *J* = 15.6 Hz, *J* = 2.4 Hz, HC*H*), 4.53 (1 H, dd, *J* = 15.6 Hz, *J* = 6.4 Hz, HC*H*), 5.20 (1 H, dd, *J* = 6.4 Hz, *J* = 2.4 Hz, CH), 6.45 and 6.67 (4 H, 2 × d, *J* = 8.8 Hz, $C_6H_4OCH_3$), 7.18–7.26 (4 H, m, C_6H_4Cl); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.1 and 14.2 (2 × CH_3), 55.4 (OCH_3), 60.8, 60.9 and 61.3 (3 × CH_2), 68.2 (CH), 112.8, 114.2, 115.1, 122.6, 125.3, 128.4, 129.7, 131.2, 135.3, 139.7, 150.4 and 152.1 (aromatic and olefinic carbons), 162.6 and 171.5 (2 × CO ester). **3e**: Viscose oil; IR (neat): 1734, 1715 (2 × CO ester) cm^{-1}; Anal. Calcd for $C_{27}H_{32}ClNO_5$: C, 66.73; H, 6.64; N, 2.88. Found: C, 66.91; H, 6.61; N, 2.73. MS: *m/z* (%) = 485 (9); ^1H NMR (500 MHz, $CDCl_3$): δ = 1.19 and 1.21 (18 H, 2 × s, 6 × CH_3), 4.25 (1 H, dd, *J* = 15.6 Hz, *J* = 2.4 Hz, HC*H*), 4.45 (1 H, dd, *J* = 15.6 Hz, *J* = 6.4 Hz, HC*H*), 5.05 (1 H, dd, *J* = 6.4 Hz, *J* = 2.4 Hz, CH), 6.45 and 6.66 (4 H, 2 × d, *J* = 9.0 Hz, $C_6H_4OCH_3$), 7.00–7.20 (4 H, m, C_6H_4Cl); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 27.9 and 29.8 (6 × CH_3), 55.6, 55.7 (2 × OCH_3), 60.7 (CH_2), 71.1 (CH), 81.4 and 81.8 (2 × OC), 112.9, 115.0, 124.5, 127.2, 128.6, 129.5, 131.4, 134.9, 139.9, 147.8 and 151.9 (aromatic and olefinic carbons), 161.9 and 171.8 (2 × CO ester). **3f**: Viscose oil; IR (KBr): 1733, 1711 (ester) cm^{-1}; Anal. Calcd for $C_{21}H_{21}NO_5$: C, 68.65; H, 5.76; N, 3.81. Found: C, 68.88; H, 5.66; N, 3.94. MS: *m/z* (%) = 367 (23). ^1H NMR (500 MHz, $CDCl_3$): δ = 3.50, 3.57 and 3.59 (9 H, 3 × s, 3 × OCH_3), 4.36 (1 H, dd, *J* = 15.6 Hz, *J* = 2.4 Hz, HC*H*), 4.58 (1 H, dd, *J* = 15.6 Hz, *J* = 6.4 Hz, HCH), 5.23 (1 H, dd, *J* = 6.4 Hz, *J* = 2.4 Hz, CH), 6.48 and 6.62 (4 H, 2 × d, *J* = 8.8 Hz, ArH), 7.23–7.55 (5 H, m, C_6H_5); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 51.2, 52.4 and 52.7 (3 × OCH_3), 60.8 (CH_2), 69.9 (CH), 113.7, 115.8, 124.3, 124.9, 128.5, 129.1, 131.0, 139.8, 150.7 and 151.9 (aromatic and olefinic carbons), 163.1 and 173.7 (2 × CO ester). **3g**: Viscose oil; IR (neat): 1735, 1707 (ester) cm^{-1}; Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99. Found: C, 71.70; H, 5.78; N, 3.72; MS: *m/z* (%) = 351 (31); ^1H NMR (500 MHz, $CDCl_3$): δ = 2.33 (3 H, s, CH_3), 3.66 and 3.71 (6 H, 2 × s, 2 × OCH_3), 4.57 (1 H, dd, *J* = 15.8 Hz, *J* = 2.3 Hz, HC*H*), 4.76 (1 H, dd, *J* = 15.8 Hz, *J* = 6.4 Hz, HC*H*), 5.45 (1 H, dd, *J* = 6.4 Hz, *J* = 2.3 Hz, CH), 7.23–7.59 (9 H, m, ArH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 21.6 (CH_3), 52.2, 52.9 (2 × OCH_3), 61.0 (CH_2), 70.0 (CH), 112.2, 124.5, 127.2, 128.5, 128.6, 128.9, 129.9, 130.5, 143.5, 152.3 (aromatic and olefinic carbons), 164.3, 172.4 (2 × CO ester). **3h**: Viscose oil; IR (neat): 1732, 1695 (ester) cm^{-1}; Anal. Calcd for $C_{20}H_{18}ClNO_4$: C, 64.61; H, 4.88; N, 3.77. Found: C, 64.79; H, 4.80; N, 3.90; MS: *m/z* (%) = 371 (27); ^1H NMR (500 MHz, $CDCl_3$): δ = 3.69 and 3.74 (6 H, 2 × s, 2 × OCH_3), 4.55 (1 H, dd, *J* = 15.7 Hz, *J* = 2.0 Hz, HC*H*), 4.75 (1 H, dd, *J* = 15.7 Hz, *J* = 6.2 Hz, HC*H*), 5.41 (1 H, dd, *J* = 6.2 Hz, *J* = 2.0 Hz, CH), 6.61 and 7.2 (4 H, 2 × d, *J* = 8.9 Hz, C_6H_4Cl), 7.40–7.48 (5 H, m, C_6H_5); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 52.2 and 53.0 (2 × OCH_3), 60.9 (CH_2), 70.0 (CH), 113.3, 115.7, 123.1, 124.4, 128.5, 128.6, 129.8, 130.0, 144.2 and 151.0 (aromatic and olefinic carbons), 163.5 and 171.7 (2 × CO ester).

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(23) General procedure for the preparation of compounds **7a–c**: To a magnetically stirred solution of dihydropyrrole derivative **3** (1 mmol) in $CHCl_3$ (10 mL), was added CrO_3 (1 mmol) at room temperature. The reaction mixture was stirred for 4 h, then the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexane–EtOAc). The solvent was removed under reduced pressure to afford the product.
7a: White powder; mp 123–125 °C; IR (KBr): 1740, 1707 (ester) cm^{-1}; Anal. Calcd for $C_{21}H_{19}NO_5$: C, 69.03; H, 5.24; N, 3.83. Found: C, 69.31; H, 5.19; N, 3.89; MS: *m/z* (%) = 365 (34); ^1H NMR (500 MHz, $CDCl_3$): δ = 3.76, 3.86, 3.88 (9 H, 3 × s, 3 × OCH_3), 6.98 and 7.30 (4 H, 2 × d, *J* = 9.0 Hz, ArH), 7.10 (1 H, s, CH of pyrrole), 7.28–7.45 (5 H, C_6H_5); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 52.3, 55.9 and 56.2 (3 × OCH_3), 114.4, 121.9, 123.8, 125.0, 126.7, 127.5, 127.8, 128.1, 129.9, 132.8, 133.7 and 159.9 (aromatic and olefinic carbons), 160.9 and 167.2 (2 × CO ester). **7b**: Viscose oil; IR

(KBr): 1740, 1707 (ester) cm^{-1}; Anal. Calcd for $C_{21}H_{19}NO_4$: C, 72.19; H, 5.48; N, 4.01. Found: C, 72.40; H, 5.29; N, 4.09; MS: *m*/*z* (%) = 349 (19); ^1H NMR (500 MHz, $CDCl_3$): δ = 2.42, 3.73, 3.85 (9 H, 3 × s, 3 × CH_3), 6.64 and 7.10 (4 H, 2 × d, *J* = 8.4 Hz, $C_6H_4CH_3$), 6.99 (1 H, s, CH of pyrrole), 7.23–7.59 (5 H, m, C_6H_5); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.7, 52.4 and 52.8 (3 × CH_3), 121.9, 123.7, 125.1, 126.3, 126.4, 127.6, 128.1, 129.0, 130.0, 133.0, 133.6, 137.4 (aromatic and olefinic carbons), 160.9, 167.2 (2 × CO ester).
7c: Viscose oil; IR (neat): 1712, 1743 (ester) cm^{-1}; Anal. Calcd for $C_{21}H_{18}BrNO_5$: C, 56.77; H, 4.08; N, 3.15. Found: C, 56.90; H, 4.22; N, 3.39; MS: *m*/*z* (%) = 443 (24); ^1H NMR (500 MHz, $CDCl_3$): δ = 3.77, 3.83, 3.81 (9 H, 3 × s, 3 × OCH_3), 6.99 and 7.29 (4 H, 2 × d, *J* = 9.1 Hz, ArH), 7.15 (1 H, s, CH of pyrrole), 7.47 and 7.63 (4 H, 2 × d, *J* = 8.3 Hz, ArH); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 52.3, 56.1 and 56.4 (3 × OCH_3), 113.1, 121.9, 123.8, 125.7, 126.7, 127.8, 130.2, 131.0, 131.7, 132.8, 133.6, 159.2 (aromatic and olefinic carbons), 160.8, 167.2 (2 × CO ester).