

A New Approach to the Synthesis of 1,2,3,5-Tetrasubstituted Pyrroles

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ABSTRACT: 2-Propargyl-1,3-dicarbonyl derivatives, namely the corresponding cumulenenes and diethoxyphosphoryloxy containing substances in the reactions with primary amines, are converted into the corresponding 1,2,3,5-tetrasubstituted pyrroles.

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INTRODUCTION

Pyrroles are very important compounds as they occur in a large number of the natural products and display a variety of biological activities [1]. The pyrrole alkaloids of the prodigiosin family make up an unusual group in the chemistry of the natural products [2a]; prodigiosin and its derivatives showed high cytotoxic and/or anticancer activity [2b–e]. The tetrasubstituted pyrrole derivatives displayed antiproliferative activity against human promyelocytic leukemia cell line HL60 [3a], antiviral [3b], and anti-inflammatory activities [3c].

During the last two decades, a few publications on the synthesis of 1,2,3,5-tetrasubstituted pyrrole derivatives have been reported. Thus, Mansour and Sauve synthesized the 1,2,3,5-tetrasubstituted pyr-

rolecarboxylates from ethyl bromopyruvate and aminoacetic thioamides via a cyclocondensation reaction [4]. Brandsma et al. described highly efficient one-pot synthesis of the 1,2,3,5-tetrasubstituted pyrroles starting from the alkyl isothiocyanates and the 2-alkynyl amines or the 2-alkynyl ethers [5]. The 1,2,3,5-tetrasubstituted pyrroles can also be synthesized in good yields in a one-pot, three-step, four-component process by a coupling-isomerization-Stetter reaction-Paal-Knorr sequence of an electron-poor (hetero)aryl halide, a terminal propargyl alcohol, an aldehyde, and a primary amine [6]. Arcadi et al. described a synthesis of the chiral 1,2,3,5-substituted pyrrole derivatives via gold catalyzed amination/annulation reactions of the 2-propynyl-1,3-dicarbonyl compounds [7]. The 2-(2-bromoallyl)-1,3-dicarbonyl compounds were converted into the β -enamino, β -hydrazino esters and ketones, followed by a base-promoted cyclization, leading to the formation of the corresponding 1,2,3,5-tetrasubstituted pyrroles [8].

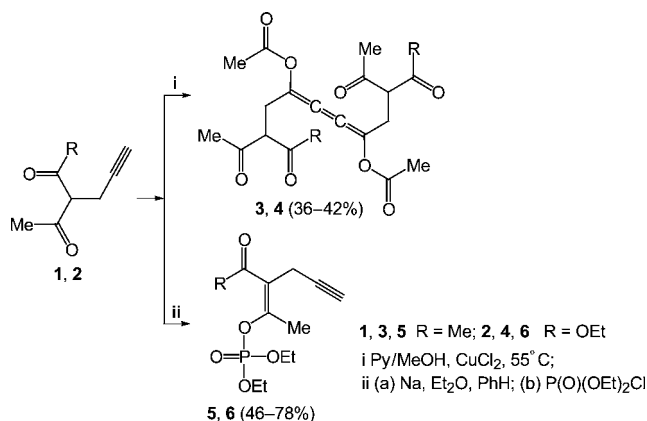
In our previous work on the pyrrole chemistry [9], we have described a synthesis of the substituted pyrroles and dipyrroles in high yields using a new synthetic method under the mild conditions in the Glaser coupling reaction.

RESULTS AND DISCUSSION

We had earlier shown that in the Glaser reaction, the α -propargyl-substituted β -dicarbonyl compounds 1

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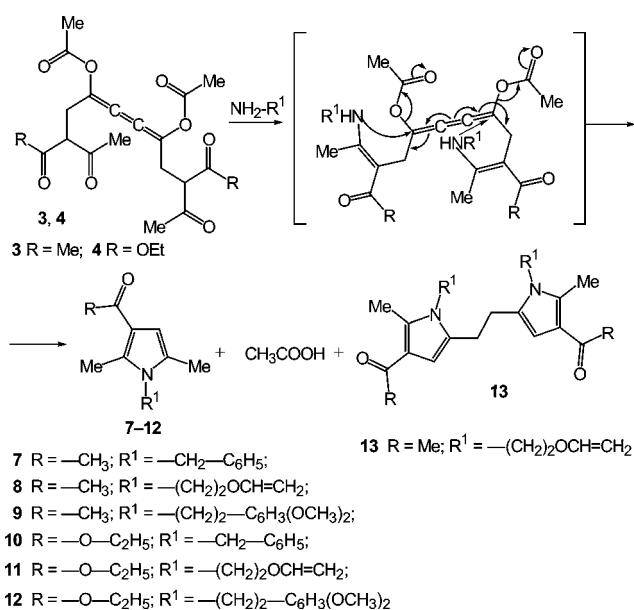
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SCHEME 1

and **2** gave polyfunctional-substituted cumulenes **3** and **4** in a pyridine–methanol solution in the presence of cupric chloride [9], and with the diethylphosphoric acid chloride the same **1** and **2** gave enolphosphates **5** and **6** [10] (Scheme 1).

Now we have found that the *N*-substituted 2,5-dimethyl-3-acetyl (ethoxy carbonyl) pyrroles **7–12** are formed in a good yield by refluxing of the cumulenes **3** and **4** with primary amines (benzylamine, 2-vinylxyethylamine, homoveratrylamine) in benzene or in methylene chloride in the presence of the 4 Å molecular sieves (Scheme 2). The *N*-benzylpyrroles **7** and **10** were also obtained by refluxing of the cumulenes **3** and **4** with the benzylamine in a benzene medium in an apparatus equipped with a Dean–Stark trap under an argon atmosphere.



SCHEME 2

The pyrroles **7–12** have been isolated by column chromatography on silica gel. Some degradation and resinification observed in this process lead to decrease in their yields. It has to store the pyrroles **7–12** at a reduced temperature and in an inert atmosphere because they will quickly resinificate at the room temperature. The data of an elemental analysis (Table 1), the IR (Table 2), ¹H NMR (Table 3), and ¹³C NMR (Table 4) spectra corroborate a composition and a structure of the pyrroles **7–12**. The intensive bands at 1360–1448 cm⁻¹ characteristic for the valency oscillations of a pyrrole ring, the bands at 1524–1656 m⁻¹ from a O=C—C=C—N conjugate system for the 3-acetylsubstituted pyrroles **7–9** and at 1520–1728 cm⁻¹ for the 3-carboethoxy pyrroles **10–12** are in the IR spectra. There are the characteristic bands for the functional groups of the *N*-substituents in the spectra also (Table 2).

In the pyrroles **7–9** ¹H NMR spectra, three singlets are presented from three methyl groups at 2.01–2.54 ppm (Table 3). In the pyrroles **10–12** ¹H NMR spectra, two singlets are appeared from two methyl groups directly bounded with a pyrrole ring at 2.09–2.50 ppm and the resonance signals from the ethoxyl radical: a quartet at 4.1–4.2 ppm and a triplet at 1.2–1.3 ppm. A singlet at 6.1–6.3 ppm from one proton gave the proof of one hydrogen atom present in a pyrrole's ring. The characteristic signals for the *N*-substituents are also observed in the ¹H NMR spectra of pyrroles **7–12** (Table 3).

In the ¹³C NMR spectra of the pyrroles **7–12**, the four signals are appeared in a characteristic area 107–136 ppm (Table 4). In the monoresonance spectra, it looks as three singlets and one doublet signals. The presence of three methyl groups is corroborated by three quadruplets at 11.5, 12.0, and 28.5 ppm in the monoresonance spectra.

The formation of the dipyrrole **13** was registered only in the reactions of cumulene **3** with 2-vinylxyethylamine at room temperature in 5% yield, as it was shown by a chromatomass-spectrometry method (the mass spectrum of dipyrrole **13**, *m/z*: M⁺ 412(1), 343(1), 222(1), 221(1), 220(1), 219(1), 208(3), 207(20), 206(8), 193(6), 192(40), 179(9), 178(11), 165(5), 164(20), 163(4), 162(2), 152(3), 151(8), 150(7), 149(20), 138(4), 137(12), 136(16), 135(5), 134(6), 122(21), 121(28), 120(20), 108(20), 107(10), 95(9), 94(10), 93(9), 80(5), 79(8), 77(12), 70(22), 57(10), 56(30), 55(13), 45(30), 44(38), 43(100), 42(50), 41(30), 40(15), 39(15)).

We found that the diethoxyphosphoryloxy derivatives of the β-dicarbonyl compounds, namely the 2-acetyl-1-methylpent-1-en-4-ynyl diethyl ester of the phosphoric acid **5** and the ethyl-2-[1-(diethoxyphosphoryloxy)ethylenedene]pent-4-ynoate

TABLE 1 Physical, Chemical Characteristics and Analytical Data for Pyrroles 7–12

	Molecular Formula	Found, Calculated (%)			R_f^a	M.p. (°C) (Solvent)	Yield (%)	
		C	H	N			A ^b	B ^b
7	C ₁₅ H ₁₇ NO	79.10, 79.26	7.60, 7.54	–	0.8	–	89	70
8	C ₁₂ H ₁₇ NO ₂	69.74, 69.54	8.31, 8.27	–	0.6	63–65 (hexane)	73	65
9	C ₁₈ H ₂₃ NO ₃	71.66, 71.73	7.57, 7.69	–	0.5	–	50	69
10	C ₁₆ H ₁₉ NO ₂	74.58, 74.68	7.25, 7.44	5.51, 5.44	0.6	41–42 (hexane)	75	74
11	C ₁₃ H ₁₉ NO ₃	66.07, 65.80	8.20, 8.07	5.98, 5.90	0.7	–	35	82
12	C ₁₉ H ₂₅ NO ₄	69.02, 68.86	7.72, 7.60	–	0.6	–	75	61

^aSilufol, Ph-H:Me₂CO = 5:1.

^bA: yields of pyrroles obtained from cumulenes; B: yields of pyrroles obtained from enolphosphates.

TABLE 2 IR Data for Pyrroles 7–12, ν (cm⁻¹)

7	1656 (N=C=C=O), 1312, 1416, 1472, 1541 (pyrrole), 696, 728 (Ph)
8	1652 (N=C=C=O), 1364, 1384, 1420, 1524, 1548, 1576 (pyrrole), 1008, 1200 (C–O–C)
9	1652 (N=C=C=O), 1364, 1384, 1420, 1524, 1548, 1576 (pyrrole), 690, 724 (Ph)
10	1728 (O=C=O), 1376, 1400, 1448, 1520, 1560 (pyrrole), 688, 720, 1608 (Ph)
11	1728 (O=C=O), 1632 (C=C), 1360, 1392, 1448, 1520 (pyrrole)
12	1728 (O=C=O), 1376, 1400, 1448, 1526, 1548 (pyrrole), 694, 734, 1600 (Ph)

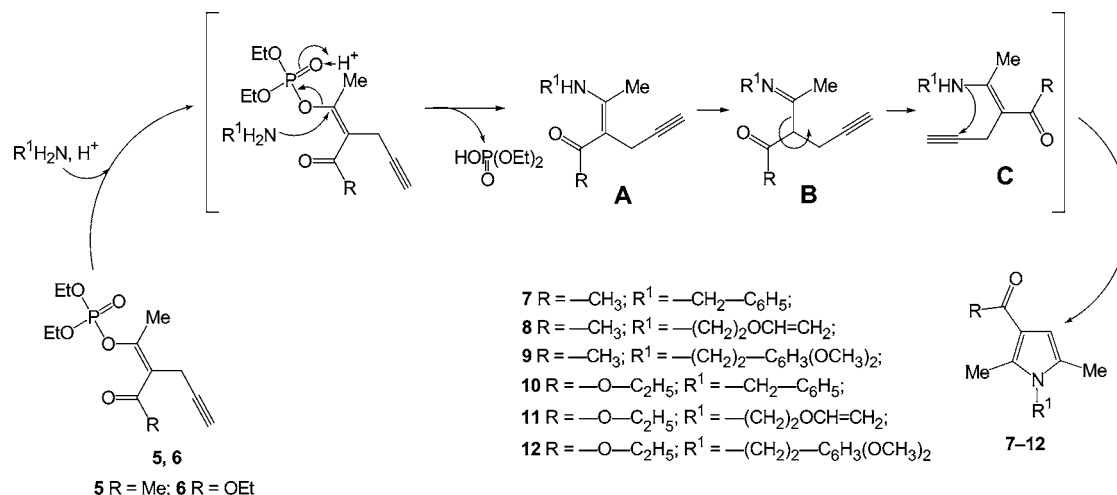
TABLE 3 ¹H NMR Data for Pyrroles 7–12, δ (ppm) and J (Hz)

7	2.12 (3H, s, Pyr-CH ₃), 2.39 (3H, s, Pyr-CH ₃), 2.47 (3H, s, C(O)CH ₃), 5.02 (2H, s, N-CH ₂ -Ph); 6.28 (1H, brs, Pyr-H), 6.82–7.30 (5H, m, Ph)
8	2.22 (3H, s, Pyr-CH ₃), 2.33 (3H, s, Pyr-CH ₃), 2.54 (3H, s, C(O)CH ₃); 3.82 (2H, t, $J=6.0$, N-CH ₂ -CH ₂ -O), 4.05 (2H, t, $J=6.0$, N-CH ₂ -CH ₂ -O); 4.00 (1H, dd, $J=2.4, 6.9$, CH=CH ₂ , <i>cis</i>); 4.13 (1H, dd, $J=2.7, 14.1$, CH=CH ₂ , <i>trans</i>), 6.19 (1H, brs, Pyr-H); 6.36 (1H, dd, $J=6.9, 4.4$, O-CH-CH ₂)
9	2.00 (3H, s, Pyr-CH ₃), 2.34 (3H, s, Pyr-CH ₃), 2.44 (3H, s, C(O)CH ₃); 2.82 (2H, t, $J=7.2$, N-CH ₂ -CH ₂ -Ar), 3.95 (2H, t, $J=7.2$, N-CH ₂ -CH ₂ -Ar), 3.75 (3H, s, OCH ₃); 3.84 (3H, s, OCH ₃), 6.16 (1H, brs, Pyr-H), 6.34 (1H, d, $J=2.1$, Ar-H), 6.61 (1H, dd, $J=2.1, 8.1$, Ar-H); 6.76 (1H, d, $J=8.1$, Ar-H)
10	1.32 (3H, t, $J=7.2$, OCH ₂ -CH ₃), 2.09 (3H, s, Pyr-CH ₃), 2.43 (3H, s, Pyr-CH ₃); 4.21 (2H, q, $J=7.2$, OCH ₂ -CH ₃), 4.95 (2H, s, N-CH ₂ -Ph), 6.33 (1H, brs, Pyr-H); 6.86 (2H, d, $J=6.3$, 2Ph-H), 7.22–7.31 (3H, m, 3Ph-H)
11	1.30 (3H, t, $J=7.2$, OCH ₂ -CH ₃), 2.20 (3H, s, Pyr-CH ₃), 2.53 (3H, s, Pyr-CH ₃); 3.80 (2H, t, $J=6.0$, N-CH ₂ -CH ₂ -O), 4.04 (2H, t, $J=6.0$, N-CH ₂ -CH ₂ -O); 4.01 (1H, dd, $J=2.4, 6.9$, CH=CH ₂ , <i>cis</i>), 4.13 (1H, dd, $J=2.4, 14.4$, CH=CH ₂ , <i>trans</i>); 4.22 (2H, q, $J=7.2$, O-CH ₂ -CH ₃), 6.25 (1H, brs, Pyr-H), 6.36 (1H, dd, $J=6.9, 14.4$, CH=CH ₂)
12	1.23 (3H, t, $J=7.2$, OCH ₂ -CH ₃), 1.93 (3H, s, Pyr-CH ₃), 2.16 (3H, s, Pyr-CH ₃); 2.77 (2H, t, $J=6.9$, N-CH ₂ -CH ₂ -Ph), 3.40 (2H, q, $J=6.9$, N-CH ₂ -CH ₂ -Ph), 3.87 (3H, s, OCH ₃); 3.89 (3H, s, OCH ₃), 4.06 (2H, q, $J=7.5$, OCH ₂ -CH ₃), 6.22 (1H, s, Pyr-H), 6.71–6.84 (3H, m, Ar-H)

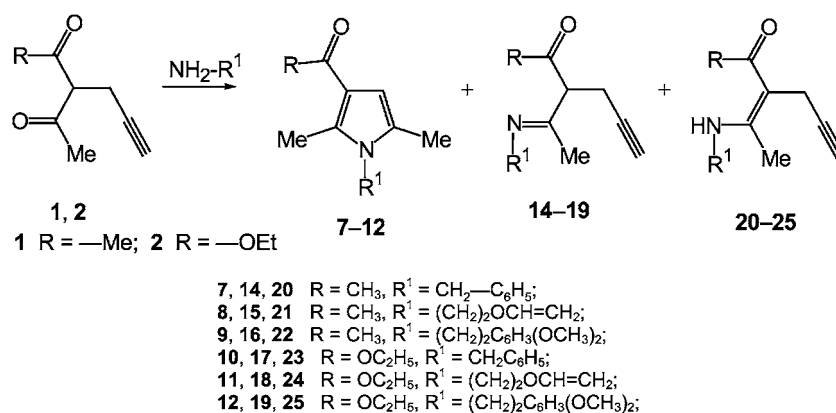
6, gave the same pyrroles 7–12 by refluxing in the benzene with primary amines in the presence of the 4 Å molecular sieves and the catalytic amounts of the *p*-toluenesulfonic acid. Probably, a reaction may proceed through the following stages: a proton of a catalyst and an amine attack the phosphoryl derivative 5 (or 6), and an amine substitutes a diethoxyphosphoryloxy group giving the intermediate enamine A. Simultaneously, a proton—a catalyst of a process—is regenerated. The enamine A through the imine B passes in the enamine C, which by an intramolecular attack of a nitrogen atom on a carbon–carbon triple bond is cyclized into the

pyrroles 3–12 (Scheme 3). It is worthnoting that the diethoxyphosphoryl derivatives 5 and 6 are rather stable when heated in the aprotic solvents in the presence of a catalytic amount of *p*-toluenesulfonic acid and in the absence of the nucleophiles and not transformed for 20 h.

The reactions of 3-acetylhex-5-yn-2-one 1 and ethyl-2-acetylpent-4-ynoate 2 with the same primary amines in the similar conditions (namely under refluxing in benzene at 8 h in the presence of the 4 Å molecular sieves and *p*-toluenesulfonic acid) give only the mixtures of imines 14–19, enamines 20–25, and pyrroles 7–12 having a very small content of



SCHEME 3



SCHEME 4

the pyrroles **7–12** as it was established by an analysis for the spectral data of the reaction mixtures (Scheme 4).

CONCLUSION

It has been established that tetrasubstituted cumulenes **3** and **4** gave 1,2,3,5-tetrasubstituted pyrroles **7–12** in good and high yields in the reactions with primary amines. This process is accompanied by the splitting off a central double bond for a cumulene's system. It has been found that the same pyrroles **7–12** can be obtained in the mild conditions in high yields in the reactions of enolphosphates **5** and **6** with primary amines.

EXPERIMENTAL

The 2-propargyl-1,3-dicarbonyl compounds **1** and **2** were synthesized by a routine method and their

physical characteristics were similar to those described in the literature [11]. The IR spectra were recorded on a Specord M-80 spectrometer for the solutions in CCl₄. The ¹H and ¹³C NMR spectra were measured on a Mercury-300 spectrometer (300 MHz for ¹H, 75.457 MHz for ¹³C), using HMDS as an internal standard. The mass spectra were measured on an HP 5972 instrument under the standard conditions (EI, 70 eV). A reaction course and a purity of the compounds were monitored by TLC on Silufol UV-254 plates in a benzene:acetone (5:1 or 10:1) mixture using Chromatocop instrument or I₂ for visualization.

General Procedures for the Synthesis of 1,2,3,5-Tetrasubstituted Pyrroles

Synthesis from Cumulenes. A mixture of **3** or **4** (0.001 mol), fresh distilled primary amine (0.002 mol), and the 4 Å molecular sieves (1 g) in

TABLE 4 ^{13}C NMR (Monoresonance) Data for Pyrroles 7–12, δ (ppm) and J (Hz)

7	11.4 (q, $J = 129$, Pyr-CH ₃), 11.8 (q, $J = 128$, Pyr-CH ₃), 28.2 (q, $J = 125$, C(O)CH ₃); 46.3 (t, $J = 138$, N-CH ₂ -Ph), 108.1 (d, $J = 170$, Pyr-CH), 119.9 (s, Pyr-C-C(O)), 127.5 (s, Pyr-C-CH ₃); 134.8 (s, Pyr-C-CH ₃), 125.2 (d, $J = 156$, Ph), 127.1 (d, $J = 161$, Ph), 128.6 (d, $J = 160$, Ph); 136.4 (s, Ph), 194.8 (s, C=O)
8	11.6 (q, $J = 129$, Pyr-CH ₃), 12.1 (q, $J = 127$, Pyr-CH ₃), 28.3 (q, $J = 127$, C(O)CH ₃); 42.2 (t, $J = 138$, N-CH ₂ -CH ₂ -O), 66.1 (t, $J = 139$, N-CH ₂ -CH ₂ -O), 87.0 (t, $J = 159$, OCH=CH ₂); 108.1 (d, $J = 170$, Pyr-C-H), 119.9 (s, Pyr-C-C(O)), 127.5 (s, Pyr-C-CH ₃), 134.7 (s, Pyr-C-CH ₃); 150.8 (d, $J = 183$, OCH=CH ₂), 195.7 (s, C=O)
9	11.8 (q, $J = 129$, Pyr-CH ₃), 12.1 (q, $J = 127$, Pyr-CH ₃), 28.5 (q, $J = 127$, C(O)CH ₃); 36.3 (t, $J = 125$, N-CH ₂ -CH ₂ -Ar), 45.1 (t, $J = 142$, N-CH ₂ -CH ₂ -Ar); 55.8 (qd, q, $J = 144$, d, $J = 10$, 2OCH ₃), 108.1 (d, $J = 170$, Pyr-CH), 119.9 (s, Pyr-C-C(O)); 127.4 (s, Pyr-C-CH ₃), 130.2 (s, Pyr-C-CH ₃), 11.3 (d, $J = 154$, Ar-CH), 112.0 (d, $J = 154$, Ar-CH); 120.8 (d, $J = 154$, Ar-CH), 134.6 (s, Ar-C-C-), 148.0 (s, Ar-C-O), 149.0 (s, Ar-C-O), 194.9 (s, C=O)
10 ^a	10.9 (q, $J = 105$, Pyr-CH ₃), 11.7 (q, $J = 106$, Pyr-CH ₃), 14.2 (q, $J = 107$, OCH ₂ -CH ₃); 46.4 (t, $J = 103$, OCH ₂ Ph), 58.8 (t, $J = 115$, OCH ₂ -CH ₃), 107.4 (d, $J = 121$, Pyr-C-H); 110.8 (s, Pyr-C-C(O)), 125.2 (d, $J = 104$, 2C-Ph), 127.0 (d, $J = 103$, Ph), 127.9 (s, Pyr-C-CH ₃); 128.5 (d, $J = 104$, 2C-Ph), 135.1 (s, Pyr-C-CH ₃), 136.7 (s, Ph), 165.3 (brs, O-C=O)
11	11.4 (q, $J = 129$, Pyr-CH ₃), 12.3 (q, $J = 127$, Pyr-CH ₃), 14.5 (q, $J = 126$, OCH ₂ -CH ₃); 42.6 (t, $J = 137$, N-CH ₂ CH ₂ -O), 59.1 (t, $J = 147$, OCH ₂ -CH ₃), 66.5 (t, $J = 141$, N-CH ₂ CH ₂ O); 87.2 (t, $J = 157$, OCH=CH ₂), 107.7 (d, $J = 173$, Pyr-CH), 111.1 (s, Pyr-C(O)), 127.8 (s, Pyr-C-CH ₃); 135.4 (s, Pyr-C-CH ₃), 151.2 (d, $J = 183$, OCH=CH ₂), 165.6 (s, O-C=O)
12	14.0 (q, $J = 129$, Pyr-CH ₃), 14.1 (q, $J = 127$, Pyr-CH ₃), 16.7 (q, $J = 134$, OCH ₂ -CH ₃); 36.8 (t, $J = 125$, N-CH ₂ CH ₂ -Ar), 44.9 (t, $J = 142$, N-CH ₂ CH ₂ -Ar); 55.6 (qd, q, $J = 144$, d, $J = 10$, 2OCH ₃), 58.5 (t, $J = 147$, OCH ₂ CH ₃), 110.4 (d, $J = 172$, Pyr-CH); 112.5 (d, $J = 154$, Ar), 119.5 (s, Pyr-C-C(O)), 121.2 (d, $J = 154$, Ar), 130.7 (s, Pyr-C-CH ₃); 131.2 (s, Pyr-C-CH ₃), 134.7 (s, Ar), 147.6 (s, Ar), 148.8 (s, Ar), 161.7 (s, O-C=O)

^aSpectrum was recorded under partial quench of the resonance with protons.

benzene or methylene chloride (10–20 mL) was refluxed 1–6 h till a full conversion of **3** or **4** was gained according the thin-layer chromatography data. Then a reaction mixture was cooled to room temperature, and acetic acid was added up to a neutral reaction. The molecular sieves were filtered off and the solution was concentrated. The pyrroles **7–12** were purified by column chromatography on silica gel with an elution by benzene and then by benzene–acetone in different ratios (20:1, 10:1, 5:1, 2:1, 1:1).

Synthesis from Enolphosphates. A mixture of **5** or **6** (0.0012 mol), fresh distilled primary amine (0.001 mol), the 4 Å molecular sieves (3 g), and *p*-toluenesulfonic acid (0.01 g) in 15 mL benzene was refluxed 1–3 h till a full conversion of an amine was gained according the thin-layer chromatography data. Then the reaction mixture was cooled to room temperature. The molecular sieves were filtered off and the solution was concentrated. The pyrroles **7–12** were purified by column chromatography on silica gel with an elution by benzene and then by benzene–acetone in different ratios (20:1, 10:1, 5:1, 2:1, 1:1).

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