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Research Article

Complete Assignment of ^{1}H and ^{13}C NMR Spectra of 1,2,4-Trisubstituted Pyrroles

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1,2,4-Trisubstituted pyrroles were synthesized with an original one-pot domino allylic amination/palladium-catalysed Sonogashira cross-coupling and heterocyclisation process. ^{1}H and ^{13}C NMR spectra were assigned for twelve new compounds containing different substituents in positions 1 and 2, and a carboxylic acid or ester group in position 4. Each assignment was based on the combination of one, and two-dimensional experiments (APT, COSY, HMBC).

1. Introduction

Pyrroles are key structural motifs in various classes of natural products [1, 2], synthetic pharmaceuticals, and electrical conducting polymers [3–6] and are also valuable synthetic intermediates [7, 8]. In addition to a number of traditionally employed approaches, such as Paal-Knorr synthesis [9–15], several transition metal-catalyzed methods [16–21] and catalytic multicomponent coupling approaches [22–24] have recently emerged for the synthesis of pyrroles. Nevertheless, and despite recent advances in domino reactions [25–28], there is still a need for very flexible and general approaches with wide functional group tolerance.

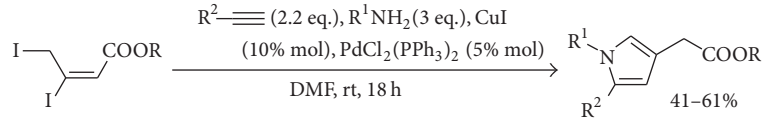
In continuation of our interest in the design of new reactions for the synthesis of lactones and lactams through tandem C–C bond formation/heterocyclisation [29–32], we recently reported an efficient novel one-pot domino allylic amination/palladium-catalysed Sonogashira cross-coupling and heterocyclisation process that allows the direct synthesis of 1,2,4-trisubstituted pyrroles (Scheme 1) starting from readily available (E)-3,4-diiodobut-2-enoic acid [33]. Good yields of the new pyrroles were obtained and a series of 1,2,4-trisubstituted pyrroles was prepared.

We describe here the spectral assignment containing a subjective analysis of the chemical shifts for these pyrroles. We report the complete assignment of each of their ^{1}H and ^{13}C NMR spectra.

2. Experimental

2.1. Compounds. Pyrroles **1a–f**, **2a-b**, **3**, **4**, and **5a-b** were prepared and purified according to the previously described method of synthesis [33].

2.2. Spectra. All NMR spectra were recorded in $CDCl_3$ at room temperature on either a Bruker AC-200 or a Bruker Avance-300 instrument using 5 mm sample tubes. All samples were freshly dissolved in $CDCl_3$ (0.6 mL). Chemical shifts (δ) in ppm are reported as quoted relative to the residual signals of chloroform (^{1}H, 7.26 ppm; ^{13}C, 77.16 ppm). Multiplicities are described as: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), and m (multiplet); coupling constants (J) are reported in Hertz (Hz). ^{13}C NMR spectra were recorded with total proton decoupling.



Scheme 1: One-pot synthesis of 1,2,4-trisubstituted pyrroles.

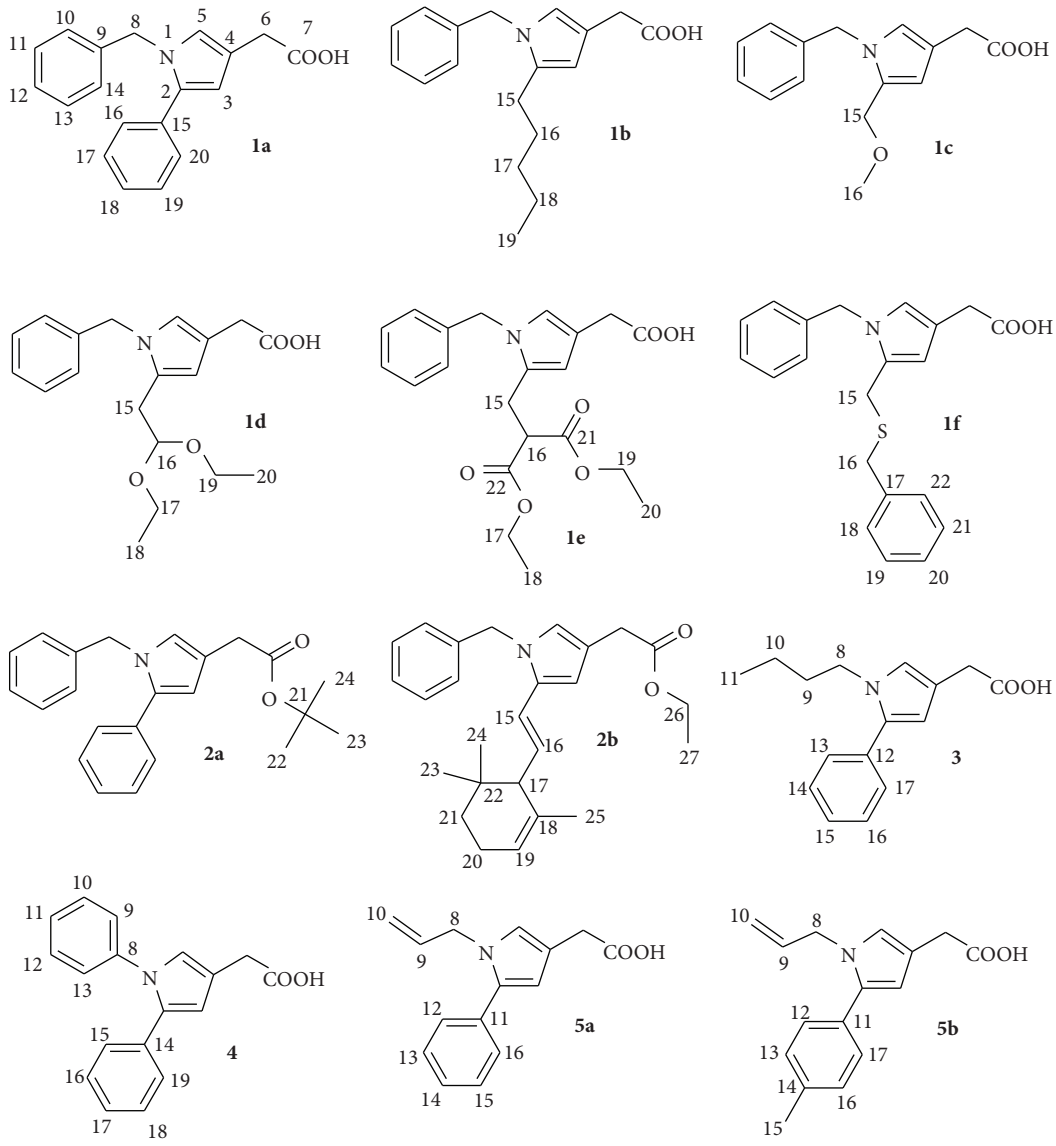


Figure 1: Structure of 1,2,4-trisubstituted pyrroles with numbering.

The complete assignment of each ^{1}H and ^{13}C NMR chemical shift for these pyrroles was achieved by 1D and 2D NMR techniques, including APT experiments, ^{1}H–^{1}H COSY, ^{1}H–^{13}C Hetcor exp, and HMBC spectra.

^{1}H NMR spectra were recorded at a proton frequency of 300.13 MHz with a spectral width of 4 kHz with 32 K data points, using a 90° pulse and repetition time of 3 s. The ^{13}C NMR spectra were obtained with a pulse angle

Table 1: ^{1}H NMR chemical shift assignments (ppm) for pyrroles **1a–f, 2a-b, 3a-b, 4**, and **5a-b** in $CDCl_3$.

H	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**2a**	**2b**	**3**	**4**	**5a**	**5b**
H-3	6.25 (d, *1.9*)	6.01 (brs)	6.15 (brs)	6.03 (d, *1.9*)	5.94 (brs)	6.19 (d, *1.3*)	6.27 (d, *1.9*)	6.28 (d, *1.7*)	6.17 (d, *1.9*)	6.44 (d, *1.9*)	6.21 (d, *1.9*)	6.19 (brs)
H-5	6.70 (d, *1.9*)	6.62 (brs)	6.63 (brs)	6.56 (d, *1.9*)	6.57 (brs)	6.71 (d, *1.3*)	6.71 (d, *1.9*)	6.60 (d, *1.7*)	6.76 (d, *1.9*)	6.93 (d, *1.9*)	6.73 (d, *1.9*)	6.72 (brs)
H-6	3.59 (s)	3.58 (s)	3.49 (s)	3.51 (s)	3.47 (s)	3.58 (s)	3.47 (s)	3.47 (s)	3.10 (s)	3.64 (s)	3.59 (s)	3.59 (s)
H-7	—	10.20 (bs)	—	—	10.25 (brs)	10.35 (brs)	—	—	—	—	—	9.90 (bs)
H-8	5.11 (s)	5.05 (s)	5.10 (s)	5.08 (s)	5.04 (s)	5.16 (s)	5.13 (s)	5.06 (s)	3.92 (t, *7.2*)	—	4.51 (dt, *5.1*, *1.6*)	4.50 (dt, *5.2*, *1.6*)
H-9	—	—	—	—	—	—	—	—	1.66–1.69 (m)	7.11–7.48 (m, 10Har)	5.98 (ddt, *17.0*, *10.3*, *5.1*)	5.97 (ddt, *16.9*, *10.4*, *5.1*)
H-10	7.03–7.06 (m, 2Har)	7.07–7.10 (m, 2Har)	7.07–7.10 (m, 2Har)	7.01–7.03 (m, 2Har)	7.01–7.04 (m, 2Har)	7.10–7.13 (m, 2Har)	7.04–7.07 (m, 2Har)	7.04–7.09 (m, 2Har)	1.21–1.32 (m)	7.11–7.48 (m, 10Har)	5.09 (dd, H10′, *17.0*, *1.4*) 5.22 (dd, *10.3*, *1.4*)	5.10 (bd, H10′, *16.9*) 5.20 (dd, *10.4*)
H-11	7.27–7.35 (m, 8Har)	7.31–7.44 (m, 3Har)	7.27–7.33 (m, 3Har)	7.24–7.37 (m, 3Har)	7.26–7.36 (m, 3Har)	7.37–7.41 (m, 8Har)	7.23–7.37 (m, 8Har)	7.24–7.35 (m, 3Har)	0.87 (t, *7.2*)	7.11–7.48 (m, 10Har)	—	—
H-12	7.27–7.35 (m, 8Har)	7.31–7.44 (m, 3Har)	7.27–7.33 (m, 3Har)	7.24–7.37 (m, 3Har)	7.26–7.36 (m, 3Har)	7.37–7.41 (m, 8Har)	7.23–7.37 (m, 8Har)	7.24–7.35 (m, 3Har)	—	7.11–7.48 (m, 10Har)	7.27–7.41 (m, 5Har)	7.32 (d, *7.9*)
H-13	7.27–7.35 (m, 8Har)	7.31–7.44 (m, 3Har)	7.27–7.33 (m, 3Har)	7.24–7.37 (m, 3Har)	7.26–7.36 (m, 3Har)	7.37–7.41 (m, 8Har)	7.23–7.37 (m, 8Har)	7.24–7.35 (m, 3Har)	7.30–7.43 (m, 5Har)	7.11–7.48 (m, 10Har)	7.27–7.41 (m, 5Har)	7.22 (d, *7.9*)
H-14	7.03–7.06 (m, 2Har)	7.07–7.10 (m, 2Har)	7.07–7.10 (m, 2Har)	7.01–7.03 (m, 2Har)	7.01–7.04 (m, 2Har)	7.10–7.13 (m, 2Har)	7.04–7.07 (m, 2Har)	7.04–7.09 (m, 2Har)	7.30–7.43 (m, 5Har)	—	7.27–7.41 (m, 5Har)	—
H-15	—	2.50 (t, *7.3*)	4.28 (s)	2.79 (d, *5.5*)	3.09 (d, *7.7*)	3.75 (s)	—	6.10 (d, *15.6*)	7.30–7.43 (m, 5Har)	7.11–7.48 (m, 10Har)	7.27–7.41 (m, 5Har)	2.40 (s)
H-16	7.27–7.35 (m, 8Har)	1.55–1.58 (m, 2H)	3.36 (s)	4.53 (t, *5.5*)	3.56 (t, *7.7*)	3.63 (s)	7.23–7.37 (m, 8Har)	5.75 (d, *15.6*)	7.30–7.43 (m, 5Har)	7.11–7.48 (m, 10Har)	7.27–7.41 (m, 5Har)	7.22 (d, *7.9*)
H-17	7.27–7.35 (m, 8Har)	1.25–1.30 (m, 2H)	—	3.37–3.66 (m, 4H)	4.17 (q, 4H, *7.2*)	—	7.23–7.37 (m, 8Har)	1.93–2.08 (m, 3H)	7.30–7.43 (m, 5Har)	7.11–7.48 (m, 10Har)	—	7.32 (d, *7.9*)
H-18	7.27–7.35 (m, 8Har)	1.25–1.30 (m, 2H)	—	1.16 (t, 6H, *7.1*)	1.23 (t, 6H, *7.2*)	7.37–7.41 (m, 8Har)	7.23–7.37 (m, 8Har)	—	—	7.11–7.48 (m, 10Har)	—	—
H-19	7.27–7.35 (m, 8Har)	1.22 (t, 3H)	—	3.37–3.66 (m, 4H)	4.17 (q, 4H, *7.2*)	7.37–7.41 (m, 8Har)	7.23–7.37 (m, 8Har)	5.37-5.38 (m)	—	7.11–7.48 (m, 10Har)	—	
H-20	7.27–7.35 (m, 8Har)	—	—	1.16 (t, 6H, *7.1*)	1.23 (t, 6H, *7.2*)	7.37–7.41 (m, 8Har)	7.23–7.37 (m, 8Har)	1.93–2.08 (m, 3H)	—	—	—	—

Table 1: Continued.

H	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**2a**	**2b**	**3**	**4**	**5a**	**5b**
H-21	—	—	—	—	—	7.37–7.41 (m, 8Har)	—	1.55–1.67 (m)	—	—	—	—
H-22	—	—	—	—	—	7.37–7.41 (m, 8Har)	1.51 (s)	—	—	—	—	—
H-23	—	—	—	—	—	—	1.51 (s)	0.76 (s)	—	—	—	—
H-24	—	—	—	—	—	—	1.51 (s)	0.86 (s)	—	—	—	—
H-25	—	—	—	—	—	—	—	1.48 (d, *1.7*)	—	—	—	—
H-26	—	—	—	—	—	—	—	4.17 (q, *7.1*)	—	—	—	—
H-27	—	—	—	—	—	—	—	1.28 (t, *7.1*)	—	—	—	—

Table 2: ^{13}C NMR chemical shift assignments (ppm) for pyrroles **1a–f, 2a-b, 3a-b, 4**, and **5a-b** in $CDCl_3$.

H	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**2a**	**2b**	**3**	**4**	**5a**	**5b**
C-2	133.4	134.6	138.7	129.0	129.6	128.1	133.6	132.5	133.7	133.1	133.4	134.6
C-3	110.3	107.4	112.1	109.5	108.6	111.5	110.2	107.1	110.1	112.1	110.0	109.1
C-4	115.6	114.3	114.5	114.4	114.4	114.2	116.9	115.9	114.4	116.3	115.2	114.7
C-5	122.6	120.1	122.6	120.6	121.0	122.2	122.0	120.3	121.5	123.7	121.7	120.9
C-6	31.3	33.6	33.4	33.5	33.3	33.5	34.8	33.5	33.8	33.2	33.4	32.9
C-7	178.8	179.4	178.7	179.0	178.9	179.2	172.2	178.9	178.7	178.3	179.2	178.2
C-8	51.1	50.6	50.9	50.9	50.7	50.8	51.0	51.0	47.8	134.4	49.9	49.3
C-9	139.1	138.9	138.7	138.9	138.3	138.5	139.3	138.6	32.6	126.1	135.2	134.7
C-10	129.3	129.2	129.2	129.1	129.2	129.3	129.2	129.1	20.8	128.5	117.6	116.9
C-11	127.0	126.9	127.3	127.0	126.9	127.3	126.9	126.9	14.2	126.8	133.4	130.0
C-12	127.5	127.8	127.9	127.7	127.9	127.5	127.3	127.7	135.8	128.5	128.8	128.6
C-13	127.0	126.9	127.3	127.0	126.9	127.3	126.9	126.9	129.0	126.1	129.2	128.9
C-14	129.3	129.2	129.2	129.1	129.2	129.3	129.2	129.1	129.6	140.7	127.4	136.6
C-15	135.6	32.1	66.3	32.1	25.8	27.4	135.3	121.3	127.5	128.7	129.2	21.1
C-16	128.9	26.7	57.5	103.5	52.0	36.0	128.8	130.9	129.6	129.4	128.8	128.9
C-17	129.1	28.8		62.6	62.0	138.9	129.1	55.3	129.0	127.0		128.6
C-18	127.8	23.0		15.6	14.4	129.6	127.7	134.5		129.4		
C-19	129.1	14.5		62.6	62.0	129.0	129.1	121.1		128.7		
C-20	128.9			15.6	14.4	128.0	128.8	23.5				
C-21					169.2	129.0	80.7	31.9				
C-22					169.2	129.6	28.6	32.9				
C-23							28.6	27.9				
C-24							28.6	27.3				
C-25								23.2				
C-26								61.0				
C-27								14.6				

of 90°, an acquisition time of 1.3 s and a sweep width of 220 ppm. The pulse repetition time was 3 s. Exponential multiplication was applied before the Fourier transformation in both cases.

A typical proton-proton Cosy experiment at 200 MHz was performed at a spectral width of 2000 Hz in the F_2 domain and 2000 Hz in the F_1 domain. Spectra were acquired with 1 K data points in F_2 with eight transients, two dummy scans and 256 experiments.

A typical carbon-proton correlated 2D spectrum at 50 MHz (or 75 MHz) was acquired with a spectral width of 14000 Hz in the F_2 domain and 1000 Hz (2000 Hz) in the F_1 domain. Spectra were acquired with 1 K data points in F_2 and 256 W in F_1 with 64 transients (two dummy scans) over 128 experiments. The delay between scans was 2 s.

The APT experiment was run with 90° and 180° pulse widths of 21 and 42 μs in the 10 mm probe and 35 and 70 μs in the 12 mm probe, respectively. A 7.1 ms delay corresponding to $1/J(\mathrm{CH})$ provided positive signals for quaternary (C) and methylene (CH_2) resonance and negative intensities for methine (CH) and methyl (CH_3) resonance.

The long-range ^{1}H–^{13}C correlation (HMBC) spectra were obtained using the following sequence: spectra resulted from a 256 × 2048 data matrix with 16 scans per t_1 increment. Spectral widths of 3.5 kHz in f_2 and 16.7 kHz in f_1 were used. The acquisition time was 0.30 s, the delays were set at 3.45 ms ($1/^2J(\mathrm{C,H})$) and 65 ms (corresponding to an average $1/^nJ(\mathrm{C,H})$ of 7.7 Hz) and the recycle time was 1.44 s. Fourier transformation was performed on a 2 K × 1 K data matrix.

3. Results and Discussion

The structures and numbering schemes for 1,2,4-trisubstituted pyrroles **1a–f**, **2a-b**, **3**, **4**, and **5a-b** are shown in Figure 1. The ^{1}H and ^{13}C assignments for each pyrrole are given in Tables 1 and 2, respectively. The twelve pyrroles are systematically related to each other by changes occurring with the R^1, R^2, or R substituents. As shown in Figure 1, there were four different substituents R^1 (benzyl, butyl, phenyl, or allyl: series **1** and **2**, **3**, **4**, and **5**, resp.), two types of substituent R (H or alkyl) which led to two types of function (carboxylic acid or ester, series **1**, **3**, **4**, and **5** or **2**, resp.). The nature of substituent R^2 in position 2 varied greatly: phenyl, pentyl, ether, diester, thiol, and even β-ionone, which led to pyrrole retinoid **2b**.

The carbon type (C, CH, CH_2, CH_3) was determined using an APT experiment. Assignment of each protonated carbon was performed by 2D heteronuclear-correlated experiments using delay values that corresponded to $^1J(\mathrm{CH})$.

The 1,2,4-trisubstituted pyrrole structure was determined through the H-3 and H-5 signal appearing as a doublet with $^4J_{H\text{-}H}$ coupling ($^4J_{H\text{-}3\text{–}H\text{-}5}$ = 1.3 to 1.9 Hz) that confirmed the substitution position (Table 1).

H-6 and H-8 appearing as singlets and the nonprotonated carbons C-2 and C-4 were assigned using delays in the 2D experiment to emphasize the long range coupling (HMBC), with either ^2J(C,H) or ^3J(C,H) between the carbons and protons.

Attribution of the aromatic carbon for compounds **1a–f** and **2a-b** was performed through protons H-10 and H-14 appearing as a doublet which, using the 2D heteronuclear-correlated experiments with delay values that corresponded to ^1J(CH), correlated with the upfield methine aromatic carbon resonance (C-10) and (C-14).

For all phenyl substituents the aromatic carbons were attributed using delays in the 2D experiment to emphasize the long range coupling (HMBC), with either ^2J(C,H) or ^3J(C,H) between the carbons and protons.

Assignment of protons and carbons of saturated chains was determined using the multiplicity of the proton signals, their coupling constant, a typical proton-proton Cosy experiment and heteronuclear-correlated experiments using delay values that corresponded to ^1J(CH).

Protons of the allyl group in compound **5a** were assigned using the multiplicity of the proton signals H-8 (dt), H-9 (ddt), H-10 (dd), and H-10′ (dd), and (C-8), (C-9), and (C-10) resonance was correlated with their respective protons by ^1J(C,H) coupling.

Concerning compound **2b**, the nonprotonated carbons C-18 and C-22 were assigned using delays in the 2D experiment to emphasize the long range coupling (HMBC), with either ^2J(C,H) or ^3J(C,H) between the carbons and protons.

Using the 2D heteronuclear-correlated experiment, we determined that the downfield methyl proton resonance (H-23) correlated with the upfield methyl carbon resonance (C-23). Carbonyl carbons of **1a–f, 3, 4**, and **5a-b** appeared at 178–180 ppm and those of the C-6 of esters **2a** and **2b** at 172.2 and 178.9 ppm, respectively (Table 2).

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