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# Complete assignment of NMR data of 22 phenyl-1*H*-pyrazoles' derivatives

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**Complete assignment of $^{1}$H and $^{13}$C NMR chemical shifts and *J*($^{1}$H/$^{1}$H and $^{1}$H/$^{19}$F) coupling constants for 22 1-phenyl-1*H*-pyrazoles' derivates were performed using the concerted application of $^{1}$H 1D and $^{1}$H, $^{13}$C 2D gs-HSQC and gs-HMBC experiments. All 1-phenyl-1*H*-pyrazoles' derivatives were synthesized as described by Finar and co-workers. The formylated 1-phenyl-1*H*-pyrazoles' derivatives were performed under Duff's conditions.** 

**Keywords:** NMR; $^{1}$H NMR; $^{13}$C NMR; 2D NMR; 1-phenyl-1*H*-pyrazoles

## Introduction

Simple nitrogen-containing heterocycles are compounds which receive a lot of attention as a consequence of their extensive properties. This structural motif appears as a component in a large number of products either as a bioactive agent in the pharmaceutical and herbicidal area[1–4] or in the dyestuff industry.[5] Among these heterocycles, pyrazoles' derivates have demonstrated promising properties for developing drugs for the treatment of neurological disorders, diabetes, as an anti-inflammatory, analgesic and antipyretic.[6–9]

Recently, the synthesis and pharmacological evaluation of new derivates of *N*-phenylpiperazine were described as multi-target compounds potentially useful for the treatment of schizophrenia.[10] The synthetic route planned to achieve these compounds explored 1-phenyl-1*H*-pyrazoles' derivates as intermediary. The 1-phenyl-1*H*-pyrazole derivates were synthesized through the classical method described by Finar and Godfrey.[6] On the other hand, chemoselective and regiospecific formylations of 1-phenyl-1*H*-pyrazoles' derivatives were performed under Duff's conditions.[11–13]

In this paper, we present a detailed compilation of NMR spectroscopic data for 22 phenyl-1H-pyrazoles' derivatives. In addition to chemical shift analyses, our data carefully highlight the signal's multiplicities by measuring as many coupling constant as possible, providing clues for reference purposes for synthetic researchers. Currently, data clarifying *J*-coupling are limited and, in most cases, the information is simplistic, especially for aromatic compounds with nucleus magnetically nonequivalent. In fact, to eliminate doubts regarding multiplicities and constants values and to confirm our data, computational simulator was used.

## Experimental

All 1-phenyl-1H-pyrazoles' derivates were synthesized as described by Finar and Godfrey[6] (Scheme 1). The $^{1}$H, $^{13}$C NMR measurements were done using a Bruker Avance III 500 instrument (operating at 500.13 MHz for $^{1}$H) equipped with a 5-mm tuneable multinuclear triple resonance probehead equipped with z gradient. To acquire $^{1}$H and $^{13}$C experiments, samples containing 20 mg of substances (Fig. 1) typically in $CDCl_3$ (or DMSO-$d_6$) and 1% tetramethylsilane as internal standard were used. Following 1D and 2D pulse sequences from the Bruker User Library were used for the NMR experiments:

*$^{1}$H 1D (500.13 MHz):* $\pi/2$ pulse for $^{1}$H 9.9 μs, spectral width 7500 Hz, acquisition time 4.37 s, relaxation delay 1.0 s and the 16 transient free-induction decay were collected with 64K data points.

*HSQC (500.13/125.76 MHz)*: 2D $^{1}$H/$^{13}$C correlation via double inept transfer, using the phase-sensitive Echo/Antiecho-TPPI gradient selection, with decoupling during acquisition, using trim pulses in inept transfer: $\pi/2$ pulse for $^{1}$H 9.9 μs, spectral width in *F*2 7.5 kHz, acquisition time 0.27 s, relaxation delay 1.0 s, 16 transients per increment, 256 complex data points in *F*1, spectral width in *F*1 21 kHz and linear prediction in *F*1 up to 1 K complex data points.

*HMBC (500.13/125.76 MHz)*: 2D $^{1}$H/$^{13}$C correlation via heteronuclear zero and double quantum coherence, optimized for long-range couplings, no decoupling during acquisition, using gradient pulses for selection: $\pi/2$ pulse for $^{1}$H 9.9 μs, spectral width in *F*2 7.5 kHz, acquisition time 0.27 s, relaxation delay 1.0 s, 32 transients per increment, 256 complex data points in *F*1, spectral width in *F*1 28 kHz, linear prediction in *F*1 up to 1 K real data points.

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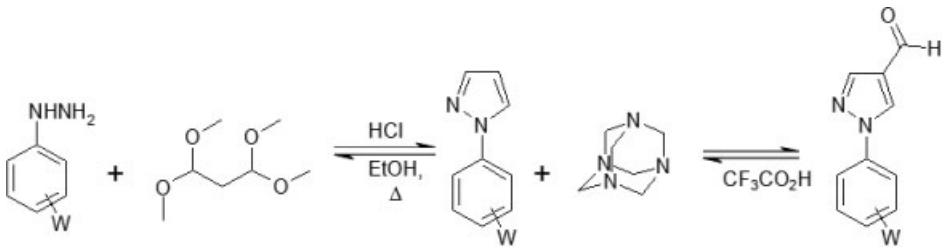
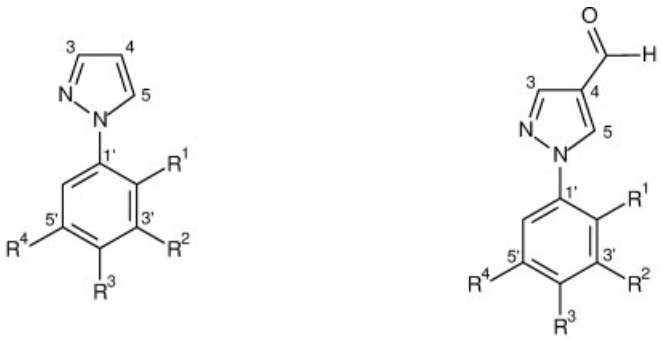



**Scheme 1.** Synthetic route to the studied compounds.




| Compound | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Compound | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | H | H | H | H | 9 | H | H | H | H |
| 2 | H | H | Me | H | 10 | H | H | Me | H |
| 3 | Me | H | H | Me | 11 | Me | H | H | Me |
| 4 | H | H | $NO_2$ | H | 12 | H | H | $NO_2$ | H |
| 5 | H | $NO_2$ | H | H | 13 | H | $NO_2$ | H | H |
| 6 | H | Cl | H | H | 14 | H | Cl | H | H |
| 7 | H | F | H | H | 15 | H | H | Cl | H |
| 8 | F | H | F | H | 16 | H | F | H | H |
| | | | | | 17 | H | H | F | H |
| | | | | | 18 | F | H | F | H |
| | | | | | 19 | $CF_3$ | H | H | H |
| | | | | | 20 | Br | H | H | H |
| | | | | | 21 | H | Br | H | H |
| | | | | | 22 | H | H | Br | H |

**Figure 1.** Structures of the studied compounds.

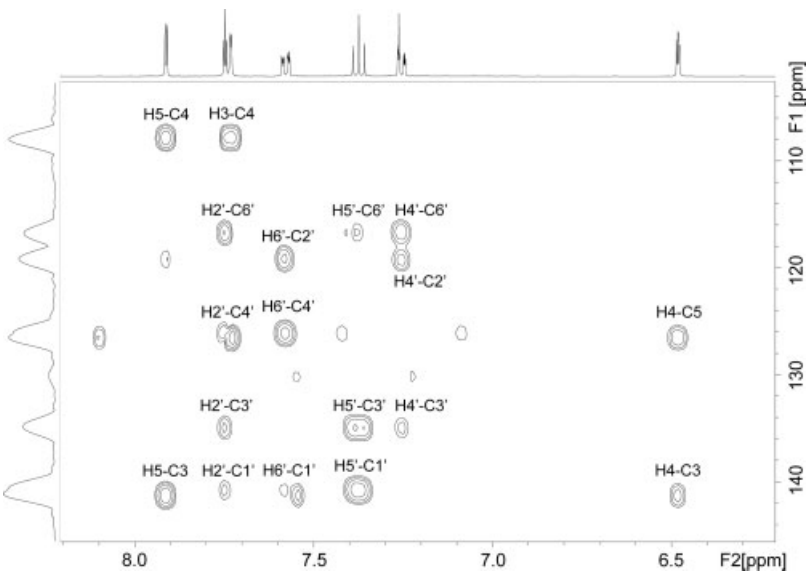



**Figure 2.** HMBC cross-peaks of the compound 1-(3-chlorophenyl)-1*H*-pyrazole (**6**). $^1$J couplings was not assigned.

Magnetic Resonance in Chemistry

**Table 1.** $^{1}$H NMR chemical shifts of 1-phenyl-1*H*-pyrazoles derivates in $CDCl_3$

| | Compound ($\delta$ of $^{1}$H (*J*, Hz)) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Positions | 1 | 2 | 3 | 4 | 5 | 6 | 7[a] | 8[a] |
| 3 | 7.73 (dd, 1.9, 0.5) | 7.70 (dd, 1.7, 0.5) | 7.71 (dd, 1.9, 0.6) | 7.81 (dd, 1.6; 0.5) | 7.78 (d, 1.7) | 7.73 (d, 1.8) | 7.73 (d, 1.7) | 7.74 (dd, 1.9, 0.6) |
| 4 | 6.47 (dd, 2.4, 1.9) | 6.44 (dd, 2.4, 1.7) | 6.43 (dd, 2.3, 1.9) | 6.57 (dd, 1.6, 2.6) | 6.54 (dd, 1.7, 2.6) | 6.48 (dd, 1.8, 2.5) | 6.48 (dd, 2.2, 1.7) | 6.49 (dd, 1.9, 2.5) |
| 5 | 7.93 (dd, 2.4, 0.5) | 7.87 (dd, 2.4, 0.5) | 7.59 (dd, 2.3, 0.6) | 8.05 (d, 2.6, 0.5) | 8.03 (d, 2.6) | 7.91 (d, 2.5) | 7.92 (d, 2.2) | 7.93 (td, 2.5, 0.6) |
| 2′ | 7.69 (dddd, 7.5, 2.2, 1.6, 0.7) | 7.56 (dd, 9.1, 2.6) | – | 7.90 (dd, 10.0, 2.9) | 8.56 (t, 2.2) | 7.75 (t, 2.1) | 7.47 (ddd, 7.9, 2.2, 1.1) | – |
| 3′ | 7.45 (dddd, 7.5, 7.4, 1.9, 0.9) | 7.23 (ddq, 9.1, 1.9, 0.6) | 7.19 (d, 7.8) | 8.35 (dd, 10.0, 1.9) | – | – | – | 6.99 (dddd, 13.7, 5.4, 2.7, 0.6) |
| 4′ | 7.29 (tdd, 7.4, 1.6, 1.2) | – | 7.12 (dd, 7.8, 1.4) | – | 8.13 (ddd, 8.1, 2.2, 0.9) | 7.26 (ddd, 8.0, 2.1, 0.9) | 6.98 (tdd, 8.1, 2.2, 1.1) | – |
| 5′ | 7.45 (ddd, 7.4, 7.2, 1.9, 0.7) | 7.23 (ddq, 8.5, 1.9, 0.6) | – | 8.35 (dd, 9.3, 1.9) | 7.64 (t, 8.1) | 7.37 (t, 8.0) | 7.40 (td, 8.1, 6.0) | 7.00 (dddd, 9.4, 7.9, 2.7, 1.4) |
| 6′ | 7.69 (ddd, 7.2, 2.2, 1.2, 0.9) | 7.56 (dd, 8.5, 2.6) | 7.16 (d, 1.4) | 7.90 (ddd, 9.3, 2.9) | 8.09 (ddd, 8.1, 2.2, 0.9) | 7.58 (ddd, 8.0, 2.1, 0.9) | 7.48 (dt, 8.1, 2.2) | 7.85 (dddd, 9.4, 8.9, 5.4, 0.6) |
| 2′-Me | | – | 2.19 (s) | – | – | – | – | – |
| 4′-Me | | 2.37 (t, 0.6) | – | – | – | – | – | – |
| 5′-Me | | – | 2.35 (s) | – | – | – | – | – |
| Positions | 9 | 10 | 11 | 12 | 13[b] | 14 | 15 | 16[a] |
| 3 | 8.17 (d, 0.5) | 8.14 (d, 0.6) | 8.16 (d, 0.6) | 8.23 (d, 0.5) | 8.34 (d, 0.5) | 8.18 (d, 0.5) | 8.17 (d, 0.5) | 8.17 (d, 0.5) |
| 5 | 8.44 (d, 0.5) | 8.39 (d, 0.6) | 8.12 (d, 0.6) | 8.63 (d, 0.5) | 9.46 (d, 0.5) | 8.45 (d, 0.5) | 8.42 (d, 0.5) | 8.46 (d, 0.5) |
| 2′ | 7.73 (ddd, 7.4, 2.1, 1.2) | 7.59 (ddq, 9.0, 2.4, 0.3) | | 7.98 (dd, 10.0, 2.9) | 8.71 (t, 2.2) | 7.79 (t, 2.1) | 7.68 (dd, 9.8, 2.2) | 7.53 (dddd, 10.3, 2.4, 1.9, 0.7) |
| 3′ | 7.51 (dddd, 7.4, 7.0, 2.0, 1.9) | 7.29 (ddq, 9.0, 1.9, 0.7) | 7.23 (d, 7.8) | 8.40 (dd, 10.0, 2.1) | – | – | 7.48 (dd, 9.8, 2.9) | – |
| 4′ | 7.39 (tt, 7.0, 1.2) | – | 7.19 (dd, 7.8, 1.5) | – | 8.23 (ddd, 8.2, 2.2, 0.9) | 7.37 (ddd, 8.1, 2.1, 1.0) | – | 7.10 (dddd, 8.1, 7.9, 2.4, 1.5) |

**Table 1.** (*Continued*).

| Positions | 9 | 10 | 11 | 12 | 13[b] | 14 | 15 | 16[a] |
|---|---|---|---|---|---|---|---|---|
| 5′ | 7.51 (ddd, 8.2, 7.0, 1.9) | 7.29 (ddq, 8.7, 1.9, 0.7) | – | 8.40 (dd, 9.1, 2.1) | 7.84 (t, 8.2) | 7.44 (t, 8.1) | 7.48 (dd, 9.0, 2.9) | 7.48 (dddd, 8.1, 7.4, 5.4, 0.7) |
| 6′ | 7.73 (dddd, 8.2, 2.1, 2.0, 1.2) | 7.59 (ddq, 8.7, 2.4, 0.3) | 7.16 (d, 1.5) | 7.98 (dd, 9.1, 2.9) | 8.39 (ddd, 8.2, 2.2, 0.9) | 7.61 (ddd, 8.1, 2.1, 1.0) | 7.68 (dd, 9.0, 2.2) | 7.51 (ddd, 7.4, 1.9, 1.5) |
| CHO | 9.97 (s) | 9.95 (s) | 9.96 (s) | 10.02 (s) | 9.94 (s) | 9.97 (s) | 9.97 (s) | 9.98 (s) |
| 2′-Me | – | | 2.21 (s) | – | – | – | – | – |
| 4′-Me | – | 2.41 (tt, 0.3, 0.7) | – | – | – | – | – | – |
| 5′-Me | – | – | 2.37 (s) | – | – | – | – | – |

| Positions | 17[a] | 18[a,b] | 19[a] | 20 | 21 | 22 |
|---|---|---|---|---|---|---|
| 3 | 8.16 (d, 0.5) | 8.30 (d, 0.4) | 8.19 (d, 0.5) | 8.19 (d, 0.5) | 8.17 (d, 0.5) | 8.17 (d, 0.5) |
| 5 | 8.40 (d, 0.5) | 8.91 (dd, 2.16, 0.4) | 8.21 (qui, 0.5) | 8.34 (d, 0.5) | 8.43 (d, 0.5) | 8.43 (d, 0.5) |
| 2′ | 7.70 (ddd, 9.3, 4.6, 3.4) | – | – | – | 7.94 (t, 2.0) | 7.64 (dd, 9.3, 3.4) |
| 3′ | 7.21 (ddd, 9.3, 8.3, 3.4) | 7.62 (ddd, 11.6, 9.0, 2.8) | 7.57 (dddq, 7.7, 1.5, 0.5, 0.6) | 7.74 (dd, 8.0, 1.3) | – | 7.62 (dd, 9.3, 2.3) |
| 4′ | – | – | 7.66 (tdq, 7.7, 1.5, 0.8) | 7.36 (ddd, 8.0, 7.5, 1.7) | 7.52 (ddd, 8.1, 2.0, 0.9) | – |
| 5′ | 7.21 (ddd, 9.3, 10.3, 3.4) | 7.31 (dddd, 9.0, 8.1, 2.8, 1.5) | 7.74 (tdq, 7.7, 1.5, 0.5) | 7.47 (td, 7.5, 1.3) | 7.38 (t, 8.1) | 7.62 (dd, 8.3, 2.3) |
| 6′ | 7.70 (ddd, 10.3, 4.6, 3.4) | 7.88 (td, 9.0, 6.0) | 7.86 (ddqui, 7.7, 1.5, 0.5) | 7.54 (dd 7.5, 1.7) | 7.66 (ddd, 8.1, 2.0, 0.9) | 7.64 (dd, 8.3, 3.4) |
| CHO | 9.97 (s) | 9.92 (s) | 9.98 (s) | 9.99 (s) | 9.97 (s) | 9.97 (s) |

[a] H–F coupling constants are also included.
[b] Spectra in DMSO-$d_6$.

**Table 2.** $^{13}C$ NMR chemical shifts (ppm) for 1-phenyl-1*H*-pyrazoles derivates in $CDCl_3$

| | Position ($\delta$ of $^{13}C$) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compounds | 3 | 4 | 5 | 1′ | 2′ | 3′ | 4′ | 5′ | 6′ | CHO | $CF_3$ | Me (2′) | Me (4′) | Me (5′) |
| 1 | 141.1 | 107.7 | 126.6 | 140.1 | 119.2 | 129.3 | 126.4 | 129.3 | 119.2 | – | – | – | – | – |
| 2 | 140.8 | 107.2 | 126.8 | 138.0 | 119.3 | 129.8 | 136.2 | 129.8 | 119.3 | – | – | – | 20.8 | – |
| 3 | 139.7 | 105.8 | 130.2 | 139.2 | 130.3 | 130.8 | 128.8 | 136.4 | 126.5 | – | – | 17.4 | – | 20.5 |
| 4 | 142.7 | 109.2 | 126.9 | 144.3 | 118.5 | 125.4 | 145.3 | 125.4 | 118.5 | – | – | – | – | – |
| 5 | 142.3 | 108.8 | 126.8 | 141.0 | 113.5 | 148.9 | 120.6 | 130.3 | 124.3 | – | – | – | – | – |
| 6 | 141.3 | 107.8 | 126.5 | 140.7 | 119.2 | 134.9 | 126.2 | 130.1 | 116.7 | – | – | – | – | – |
| 7 | 141.6 | 107.9 | 126.7 | 141.4 | 114.2 | 163.3 | 112.9 | 130.6 | 106.6 | – | – | – | – | – |
| 8 | 140.7 | 107.4 | 130.5 | 124.6 | 153.6 | 105.0 | 160.7 | 111.9 | 125.5 | – | – | – | – | – |
| 9 | 141.7 | 125.6 | 130.0 | 139.0 | 119.8 | 129.8 | 127.9 | 129.8 | 119.8 | 184.2 | – | – | – | – |
| 10 | 141.8 | 125.6 | 130.1 | 136.9 | 119.9 | 130.3 | 138.4 | 130.3 | 119.9 | 184.2 | – | – | 21.1 | – |
| 11 | 140.8 | 124.6 | 133.9 | 138.5 | 130.2 | 131.0 | 130.3 | 136.8 | 126.4 | 184.2 | – | 17.3 | – | 20.6 |
| 12 | 142.6 | 126.9 | 130.6 | 143.5 | 119.7 | 125.6 | 146.8 | 125.6 | 119.7 | 183.7 | – | – | – | – |
| 13[a] | 141.5 | 125.8 | 133.0 | 139.6 | 113.5 | 148.4 | 121.6 | 130.9 | 124.6 | 184.9 | – | – | – | – |
| 14 | 141.7 | 125.7 | 129.8 | 139.9 | 120.0 | 135.6 | 127.7 | 130.4 | 117.3 | 183.9 | – | – | – | – |
| 15 | 141.9 | 125.7 | 129.9 | 137.6 | 120.8 | 129.7 | 133.7 | 129.7 | 120.8 | 183.9 | – | – | – | – |
| 16 | 141.7 | 125.8 | 130.2 | 140.3 | 107.6 | 163.0 | 114.8 | 131.0 | 115.0 | 184.0 | – | – | – | – |
| 17 | 141.7 | 125.6 | 130.0 | 135.3 | 121.6 | 116.5 | 161.8 | 116.5 | 121.6 | 184.0 | – | – | – | – |
| 18[a] | 140.6 | 125.2 | 136.2 | 124.0 | 154.2 | 105.2 | 161.4 | 112.2 | 126.8 | 183.9 | – | – | – | – |
| 19 | 141.5 | 125.0 | 135.5 | 133.7 | 122.2 | 129.1 | 130.1 | 133.3 | 127.3 | 183.8 | 126.7 | – | – | – |
| 20 | 141.2 | 125.0 | 135.1 | 138.9 | 118.3 | 134.2 | 130.9 | 128.6 | 128.3 | 184.2 | – | – | – | – |
| 21 | 142.0 | 125.9 | 130.1 | 139.9 | 123.2 | 122.7 | 131.1 | 131.2 | 118.1 | 183.8 | – | – | – | – |
| 22 | 142.0 | 125.9 | 130.0 | 138.1 | 121.3 | 133.0 | 121.6 | 133.0 | 121.3 | 183.8 | – | – | – | – |

[a] Spectra in DMSO-$d_6$.

## Results and Discussion

The 1-phenyl-1*H*-pyrazoles' derivates were synthesized with fluorine, bromide, chlorine, nitro or methyl groups, mono- or di-substituted in the *ortho*-, *meta*- and *para*-positions (Fig. 1). The structures of the molecules were investigated and confirmed by NMR spectroscopy, combining the $^1H$, HSQC and HMBC correlation spectra, as shown in an example of Fig. 2. $^1H$ and $^{13}C$ chemical shifts, together with *J*-coupling constants ($^1H/^1H$ and $^1H/^{19}F$), for all 1-phenyl-1*H*-pyrazoles' derivates were assigned and are summarized in Tables 1 and 2.

A careful analysis was undertaken of the expansions of multiple signals from the $^1H$ NMR spectra, measuring as many coupling constants as possible and clarifying the multiplicities. Doubts concerning multiplicities and *J*-coupling constants values were eliminated using spectral simulations with the software first-order multiplet simulator/checker (FOMSC3)[14] which calculates and plots NMR first-order multiplets starting from information about coupling constants values. The similarity observed from the comparison between the experimental and simulated spectra, as shown in Fig. 3, served as the basis for confirmation of $^1H/^1H$ and $^1H/^{19}F$ *J*-coupling constants and strongly suggests that the coupling constant values and the multiplicities shown in Table 1 are correct. The displaying of coupling patterns was valuable for the assignment of proton signals since the coupling patterns of aromatic protons differ greatly depending on the number of protons involved in the spin system. In particular, the *para*-substituted aromatic systems presented a typical pattern splitting. As known, these protons are chemically equivalent, but magnetically nonequivalent; therefore, they have the same chemical shift, but different couplings constants, showing an AA′BB′ splinting system. As a result of this effect, the intensity of the signal did not fit the rules of the intensity for first-order systems.

As expected, noticeable differences in $^1H$ and $^{13}C$ chemical shift values were observed in the pyrazole ring of carbaldehyde compounds because of CHO anisotropic effects. Once this group deshields the nucleus of $^1H$ in positions 3 and 5, the chemical shift values change from an average of 7.7 to 8.2 ppm. A similar effect is also observed with carbon in position 4 which is deshielded by approximately 20 ppm.

In the phenyl ring, the chemical shift values were mainly dependent on the substituent pattern. In the $^{13}C$ NMR data, differences were more pronounced in the atoms directly attached to the substituent group. The most pronounced effect is observed in aromatic carbons directly attached to the fluorine deshielded by approximately 33 ppm, followed by carbons directly attached to the $NO_2$ group deshielded approximately by 19 ppm, carbons attached to the $CH_3$ group deshielded by 7–10 ppm, and those attached to chlorine that were deshield by 5 ppm. Finally, the carbons attached to bromide were shielded by 7 ppm.

In the $^1H$ spectra, no significant differences were detected in halides, and the greatest effect is observed in the $NO_2$ group which increases the chemical shift values in the range of 0.9 ppm in *ortho* position, 0.3 ppm in *meta* position and 0.6 ppm in *para* position. All chemical shifts were compared with the parent compound.

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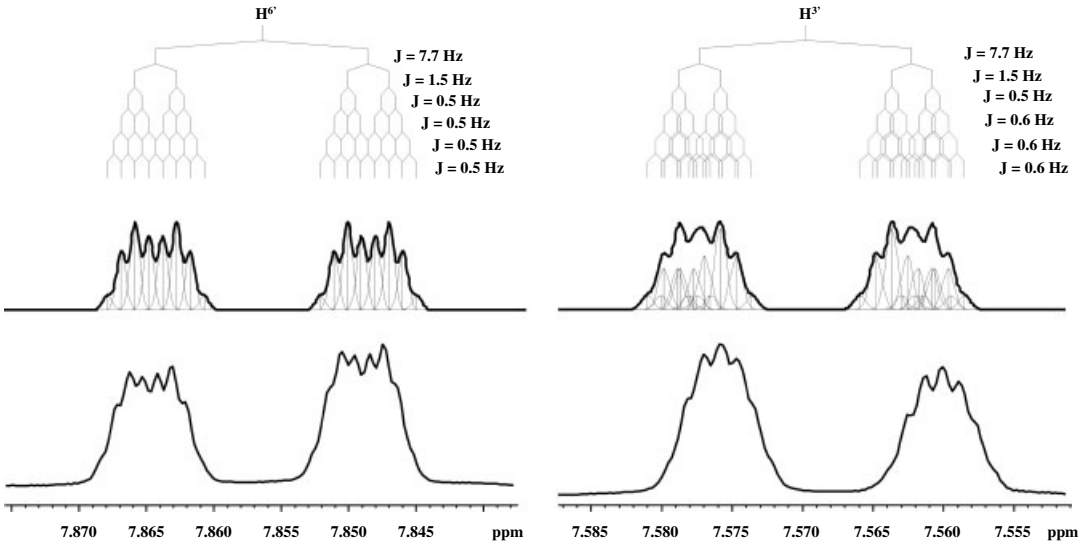


**Figure 3.** Comparison between the experimental (lower panel) and simulated spectra by FOMSC3 (upper panel) of 6′ (left) and 3′ (right) $^{1}$H from 1-(2-trifluoromethyl)-1*H*-pyrazole-4-carbaldehyde (**19**).

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