Article

An Efficient Synthesis and DFT-Assisted Calculations of New 1, 2, 3-Triazole Derivatives

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Abstract

Under a facial 1, 3 dipolar cycloaddition reaction, three new derivatives of 1, 2, 3-triazole (**5a-c**) were synthesized from azides-based anilinesulfonamide derivatives (**3a-c**) and pentane-2, 4-dione (**4**) in the presence of K_2CO_3 as a mild catalyst. The chemical structures of the synthesized 1, 2, 3-triazole (**5a-c**) were elucidated using different analytical techniques including ^{1}H and ^{13}C-NMR, FT-IR, and Mass spectra. Gaussian 09 program using the functional (B3LYP/6-31G(d,p)) has been undertaken to identify the optimal geometries of the synthesized 2, 3-triazole (**5a-c**). The geometrical optimizations for these derivatives are conducted to DFT-assisted calculations at the same level of B3LYP/6-31G(d,p). DFT-assisted calculations were carried out to identify several important parameters including chemical hardness (η), electronic chemical potential (μ), electrophilicity (ω), and energy gap (ΔE_{gap}) for both molecular orbitals (LUMO and HOMO). These parameters are used as efficient descriptors for evaluating the interactions for the selected molecules and their reactivity. The results revealed that the triazole derivative (**5c**) is found to be more reactive than the other derivatives (**5a** and **5b**).

Keywords: 1, 2, 3-Triazole, 1, 3 Dipolar cycloaddition, Azid, DFT studies.

1. Introduction

The organic compounds involving heteroatoms such as N, O, and S have been extensively investigated to discover their potential biological activities [1]. Among of these compounds, heterocyclic compounds which are found to offer a broad spectrum of pharmaceutical applications [2]. The biological activity of these compounds are attributed from the presence of one or more electron pair in heteroatoms [3]. The electron pair is found to be interacted with the active sites of the surface of proteins or enzymes *via* an electron donation mechanism [4]. Thus, an electron rich bond acts to facilitate the connection with the selected organism and release the biological effects. Furthermore, the reactivity of these heterocyclic compounds is recognized to be highly influenced by their chemical structure nature, concentration, and their ability to donate and accept the electrons [5]. Thus, the development of the chemical structures of these heterocyclic by modification or functionalization methods is of growing interest in the field of heterocyclic chemistry.

1, 2, 3-Triazole molecule and its derivatives have emerged as an important moiety which have introduced a long scope of fascinating applications in agriculture, medicine, pharmacological industry, and etc. [6-8]. These compounds are reported to show a broad spectrum of biological activities. A modification or functionalization of 1, 2, 3-triazole uncle with a different reactive moiety such as sulfonamide in order to enhance biochemical properties and rise new added applications has become a challenging for the researchers. Several articles have been recently addressed some works that show the pharmacological activities given by arylsulfonyl-triazole systems [9]. These systems are developed with the essential target focuses on enhancement their biological activities. For these systems, the enhancement of the biological activities have been pursued by employing arylsulfonyl-triazole structures due to these systems contain a pharmacological moiety [10]. Thus, the arylsulfonyl-triazole systems are conducted for utilizing as important bioactive structure for developing and releasing highly potential biological activities [11]. It is very needed to design and develop of chemical structures of 1, 2, 3-triazole derivatives. As a part of our interest in view of biological activity, we herein report the efficient synthesis of novel 1, 2, 3-triazole derivatives (**5a-c**) (Scheme 1) and study their theoretical structures and reactivity using DFT-assisted calculations.

2. Chemicals and Methods

Solvents and required chemicals were purchased from Sigma-Aldrich. All chemicals used in this work, were at least of ACS grade, solvents were order in highly analytical grade. Analytical properties to monitor the progress of the reactions were carried out by using TLC plates precoated with a silica gel 60 UV 254. UV light was employed to visualize the obtained compounds. FT-IR spectra were collected on Shimadzu FTIR-8300 infrared spectrophotometer (Iraq, University of Basrah) and the absorbance were acquired between 4000-400 cm^{-1}. At room temperature, ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Anovo AV-400 spectrometer (Iraq, University of Basrah) in DMSO-d_6 as solvent associated with a common signal of ^{1}H spectra at δ 2.50 ppm and 3.40 ppm for its water molecule as well as other signal of ^{13}C spectra at δ 49.5 ppm. Decoupling values (*J*) for integrated protons are given in Hz. a Gallenkamp melting device are employed to determine melting points depends on capillary tubes.

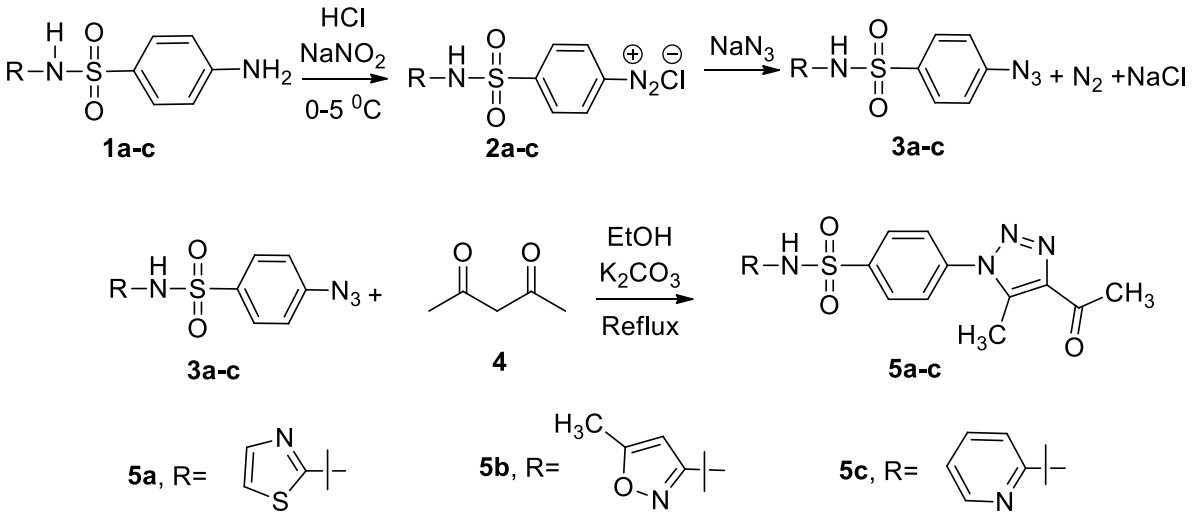
2.1. General synthesis of azides-derived aniline sulfonamide derivatives (3a-c).

All azides derivatives were prepared according to methods in the references [12, 13]. To a cooled solution of the selected aniline sulfonamide derivatives (**1a-c**) (0.02 mol), concentration hydrochloric acid (5.0 mL) and water (20 mL), sodium nitrite ($NaNO_2$) (0.022 mol) in water (5.0 mL) was gradually added at 0-5 °C. After stirring process for 20 min, water (5 mL) was added to above stirred mixture till the diazanium salts (**2a-c**) are constructed. To freshly formed diazanium salt, sodium azid (NaN_3) (0.025 mol) dissolved in distilled water (5.0 mL) was slowly added under keeping stirring process at 0 °C until a white solid is formed. The produced precipitate was collected, separated, dried, and conducted to recrystallization step using the appropriate solvents to afford colorless needle crystals (**3a-c**).

2.2. General synthesis of new 1, 2, 3-triazole derivatives (5a-c) [12].

To a solution of pentane-2, 4-dione (**4**) (2.0 mmol) and K_2CO_3 (1.0 gm, 6 mmol) in EtOH (50 mL) in a round-bottomed flask (50 mL) connected to a reflux condenser, the prepared azide derivatives (**3a-c**) were gradually added. The above content was heated to reflux for until the starting materials were consumed under an appropriate time as indicated by TLC (ethyl acetate/petroleum ether, 8: 2). After the reactants were consumed, the residual mixture was left to cool and treated with a solution of hydrochloric acid (10%) until the neutral state was acquired. To above neutral mixture, a mixture solution of DCM and water (1:1, 40 mL) was added. The extracted organic

layers were collected, wished with a brine solution, dried over anhydrous Na_2SO_4 or $MgSO_4$, and filtered. The collected precipitate was conducted to recrystallization step from a mixture of EtOH and hexane (1: 1) and the product was filtered and undergone to elucidate the analytical properties.



Scheme 1. Synthetic pathway of 1, 2, 3-triazole derivatives (5a-c).

4-(5-Methyl-4-acetyl-*1H*-1, 2, 3-triazol-1-yl)-*N*-(thiazol-2-yl)benzenesulfonamide (5a)

Yield (85%), yellow solid, m.p. 247–248 °C, FT-IR (ν, cm^{-1}): 3143, 3101 (C-H, Ar), 2900 (C-H, CH_3), 1681 (C=O), 1571 (C=C), 1419 (C-N). ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm): 2.55 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 6.66 (d, 1H, J= 1.8 Hz, thiazole ring), 7.31 (d, 2H, J= 2.1 Hz, CH-Ar), 7.32 (d, 1H, J= 1.8 Hz, thiazole ring), 7.83 (d, 2H, J= 2.0 Hz, CH-Ar), 12.86 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm): 10.2 (CH_3), 19.3 (CH_3), 119.7 (CH, thiazole), 122.7 (CH, thiazole), 127.4 (CH, Ar), 128.9 (CH, Ar), 136.2 (C, triazol), 137.5 (C, Ar), 139.8 (C, triazol), 142.2 (C, Ar), 144.2 (C, thiazole), 194.8 (C=O). EI-MS: *m/z* 363 $[M]^+$ observed for $C_{14}H_{13}N_5O_3S_2$.

4-(4-Acetyl-5-methyl-*1H*-1, 2, 3-triazol-1-yl)-*N*-(5-methylisoxazol-3-yl)benzenesulfonamide (5b)

Yield (80%), colorless solid, m.p. 214–216 °C, FT-IR (ν, cm^{-1}): 3103 (C-H, Ar), 2904, 2892 (C-H, CH_3), 1687 (C=O), 1557 (C=C), 1421 (C-N). ^{1}H NMR (DMSO-*d6*, 400 MHz) δ (ppm): 2.03 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.59 (s, 3H, CH3), 6.84 (s, 1H,

isoxazole ring), 7.30 (d, 2H, *J*= 2.3 Hz, CH-Ar), 7.88 (d, 2H, *J*= 2.2 Hz, CH-Ar), 8.31 (s, 1H, NH). ^{13}C NMR (DMSO-*d6*, 100 MHz) δ (ppm): 9.9 (CH_3), 10.2 (CH_3), 20.2 (CH_3), 100.8 (CH, isoxazole), 119.9 (C, isoxazole), 126.4 (CH, Ar), 129.2 (CH, Ar), 137.2 (C, Ar), 138.8 (C, triazol), 138.8 (C, Ar), 143.2 (C, triazol), 149.9 (C, isoxazole), 193.9 (C=O). EI-MS: *m/z* 361 $[M]^+$ observed for $C_{15}H_{15}N_5O_4S$.

4-(4-Acetyl-5-methyl-*1H*-1, 2, 3-triazol-1-yl)-*N*-(pyridin-2-yl)benzenesulfonamide (5c)

Yield (80%), pink solid, m.p. 162–164 °C, FT-IR (ν, cm^{-1}): 3037 (C-H, Ar), 2870 (C-H, CH_3), 1687 (C=O), 1551 (C=C), 1422 (C-N). ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm): 2.54 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 6.66 (d, 1H, *J*= 1.8 Hz, CH-Ar), 7.26 (d, 2H, *J*= 1.9 Hz, CH-Ar), 7.86 (t, 2H, *J*= 2.1 Hz, CH-Ar), 7.97 (d, 1H, *J*= 1.8 Hz, CH-Ar), 8.09 (t, 1H, *J*= 1.6 Hz, CH-Ar), 8.11(d, 1H, *J*= 1.6 Hz, CH-Ar). ^{13}C NMR (DMSO-*d6*, 100 MHz) δ (ppm): 10.3 (CH_3), 28.3 (CH_3), 115.7 (CH, Ar), 119.7 (CH, Ar), 126.4 (CH, Ar), 128.3 (CH, Ar), 137.2 (CH, Ar), 141.2 (C, Ar), 142.3 (C, Ar), 143.2 (C, triazol), 143.5 (C, Ar), 144.2 (C, triazol), 193.8 (C=O). EI-MS: *m/z* 357 $[M]^+$ observed for $C_{16}H_{15}N_5O_3S$.

3. Results and Discussion

3.1. Chemistry

The conversion of aniline-sulfonamide derivatives to azide-sulfonamide derivatives offer a good route in organic chemistry towards the synthesis of aryl-, and heterocyclic-sulfonamide system bearing a triazole group with promising biological properties. Generally, the introduced methods to synthesize azide-sulfonamide derivatives focuses on using a diazotization step of an selected aniline-sulfonamide system that is treated with an aqueous acidic $NaNO_2$/HCl followed by an addition of stoichiometric [14]. Thus, we report the synthesis of new 1, 2, 3-triazole derivatives (**5a-c**) *via* a 1, 3-cycloaddition reaction. In the initial step, aniline-sulfonamide derivatives (**1a-c**) were treated with $NaNO_2$ and con. HCl at 0 ºC to give fresh diazonium salt (**2a-c)** solutions. In the second step, the fresh diazonium salt (**2a-c**) solutions were directly conducted to NaN_3 to obtain to the azide-sulfonamide derivatives (**3a-c**) according to the known mechanism as shown in **Fig 1**. In final step, the prepared azide-sulfonamide derivatives (**3a-c**) were directly conducted to a 1, 3-cycloaddition reaction under a K_2CO_3-catalyzed click reaction to obtain new 1, 2, 3-triazole derivatives (**5a-c**). After optimization in

terms of amount of catalysts, solvent, and reaction conditions, we found that 3 mmol (3 equivalent) of K_2CO_3 as a catalyst and EtOH as a solvent are the best optimal conditions to obtain the target derivatives under click synthesis (**5a-c**).

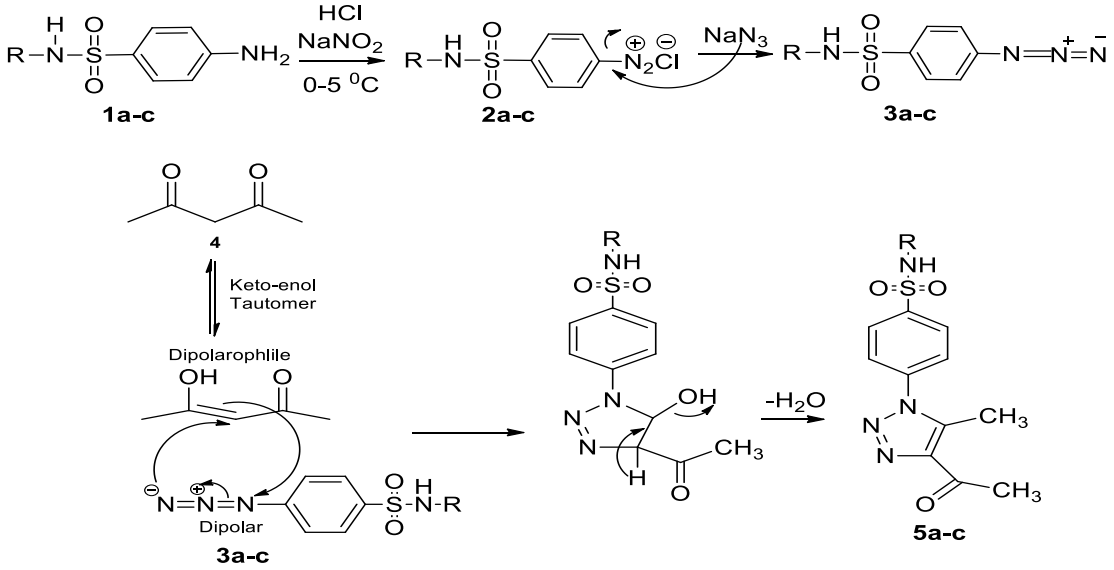


Fig. 1. A plausible mechanism towards 1, 2, 3-triazole derivatives synthesis (5a-c).

The identification of the synthesized triazole derivatives (**5a-c**) on terms of confirming their chemical structures was established using FT-IR and ^{1}H, ^{13}C NMR, and Mass spectra. The vibrational frequencies that are noted in the FT-IR spectra with the regions 3037–3143 cm^{-1} attributed to C-H aromatic stretching. C-H Aliphatic stretching appeared at the regions 2870–2904 cm^{-1}, while the strong bands of vibrational stretching at the regions 1681–1687 cm^{-1} were assigned to the carbon of C=O groups (**Figs. 2-4**). In the ^{1}H NMR spectra (**Figs. 5-7**), the synthesized 1, 2, 3-triazole derivatives (**5a-c**) showed singlet signals at chemical shifts δ 2.03–2.64 ppm corresponded to the methyl groups attached with the triazole uncle. Singlet to triplet singles at chemical shifts δ 6.68–8.11 ppm returned to the aromatic resonance of protons (Aromatic-CH). In addition, the chemical shifts for ^{13}C NMR spectra (**Figs. 8-10**) for the synthesized 1, 2, 3-triazole derivatives (**5a-c**) are observed at 9.9–28.3 ppm (carbons, CH_3), 100.8-119.7 (heterocyclic carbons), 126.4–138.7 ppm (aromatic carbons), 139.2–144.2 ppm (triazole carbons), and 193.8–194.8 ppm (carbonyl carbons). EI-Mass spectra for the synthesized derivatives show that the associated with the values of *m/z* (%) were identical with their drawn structures (**Figs. 11-13**).

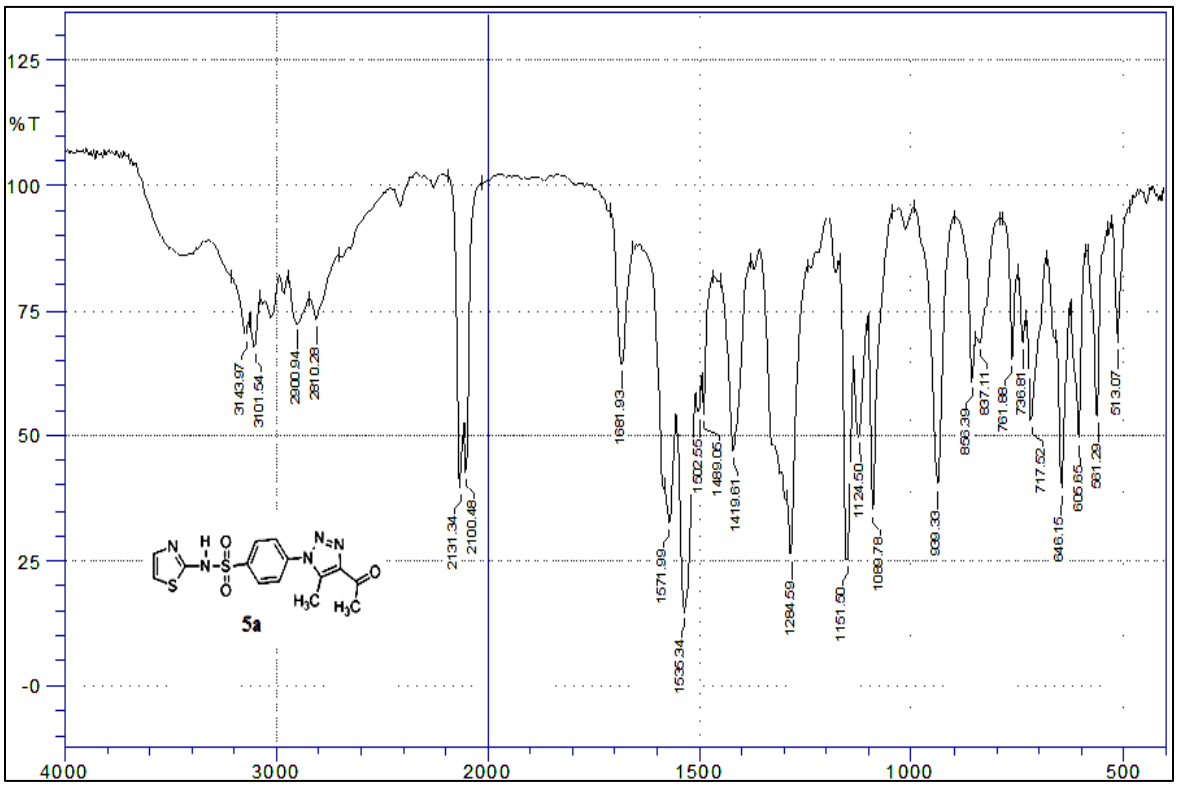


Fig. 2. FT-IR spectrum of derivative (5a)

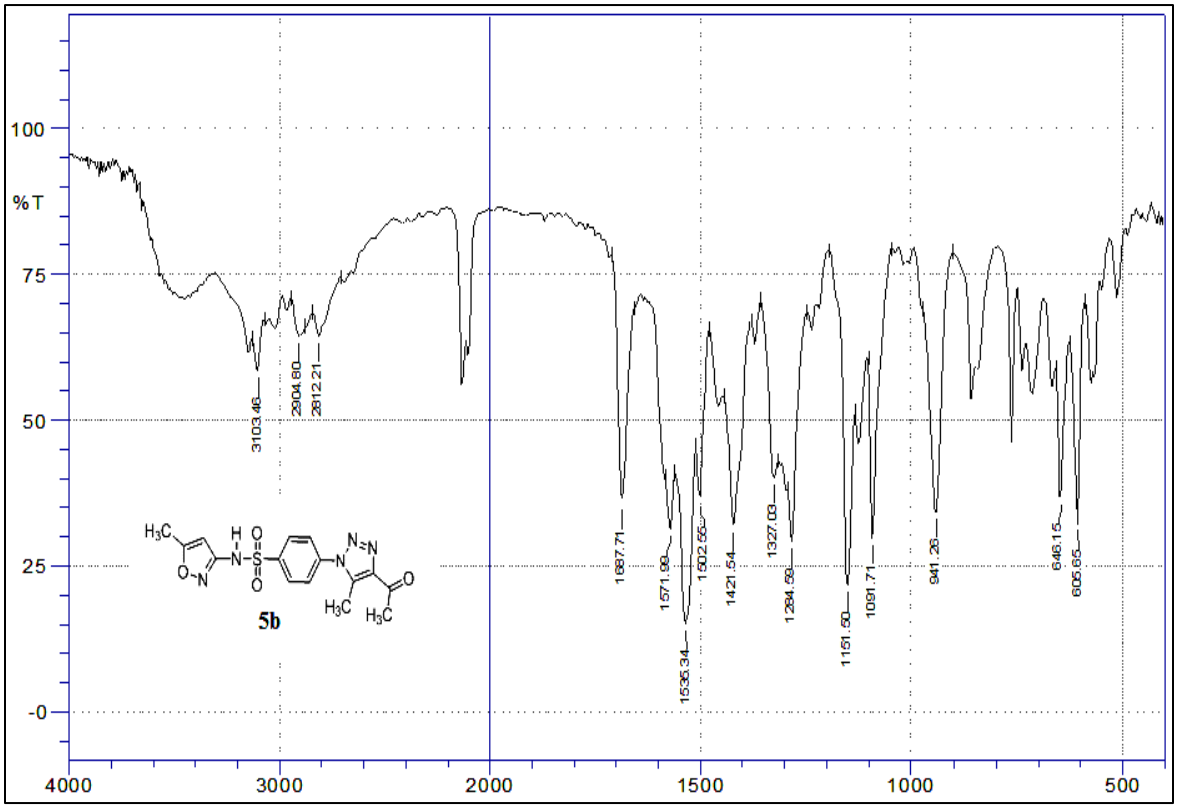


Fig. 3. FT-IR spectrum of derivative (5b).

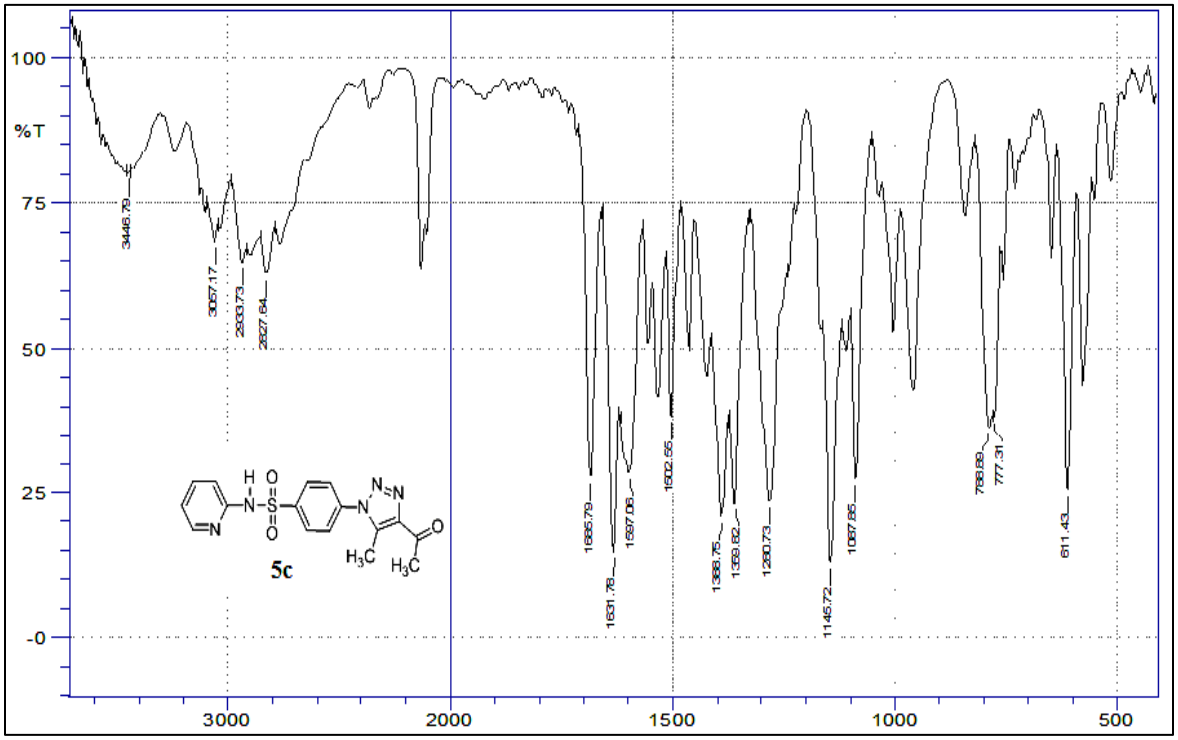


Fig. 4. FT-IR spectrum of derivative (5c).

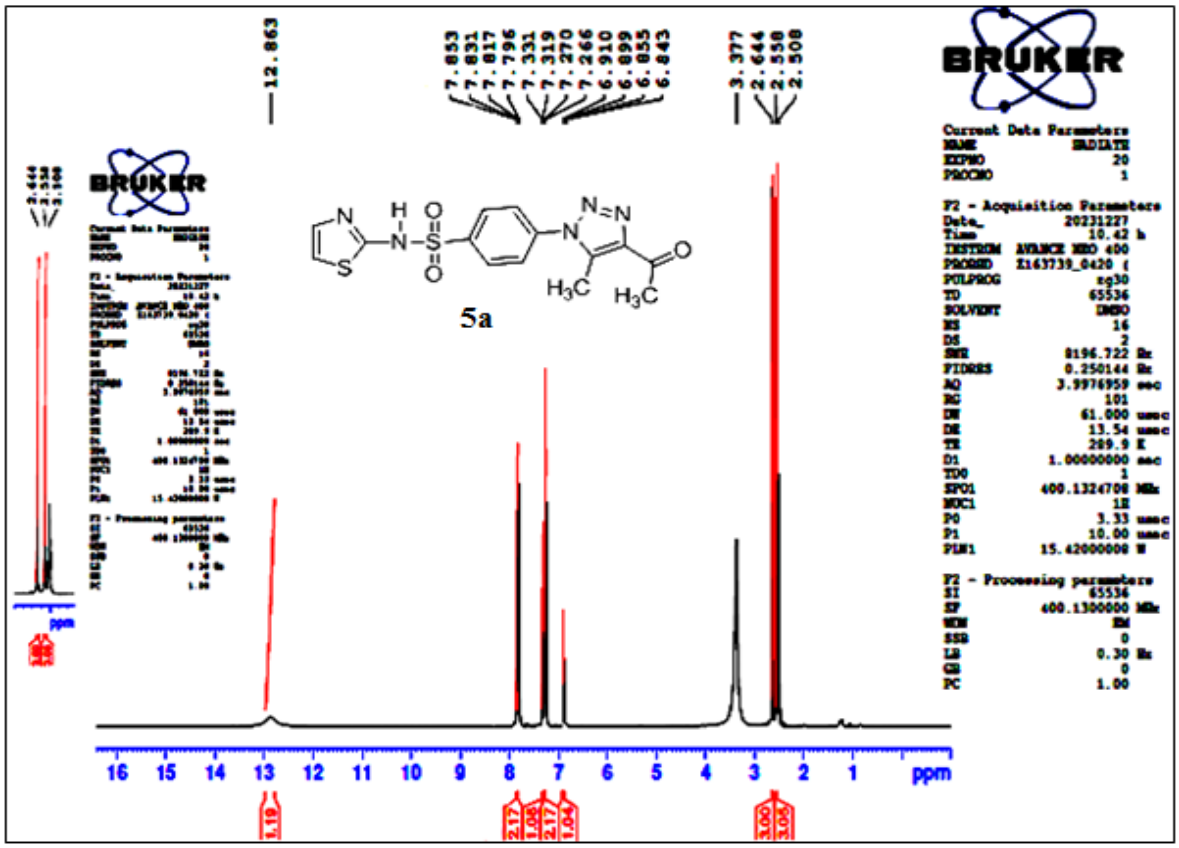


Fig. 5. ^{1}HNMR spectrum of derivative (5a).

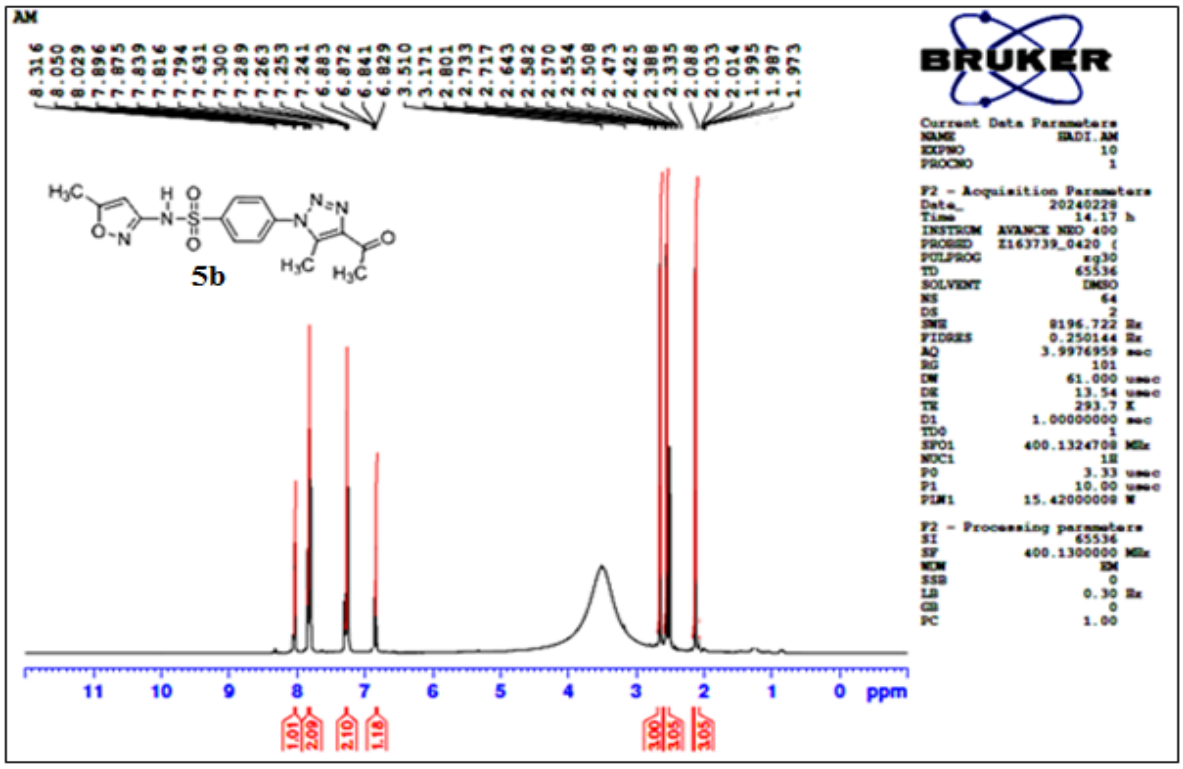


Fig. 6. ^{1}HNMR spectrum of derivative (5b).

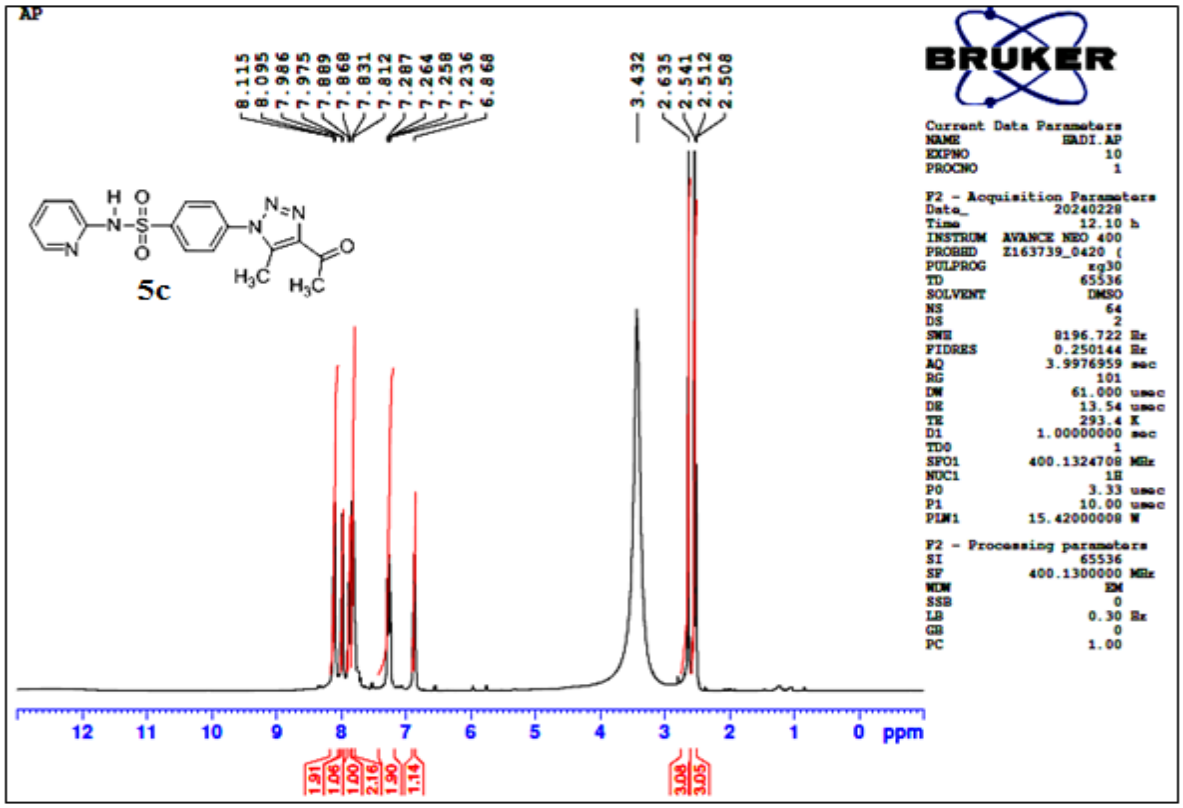


Fig. 7. ^{1}HNMR spectrum of derivative (5c).

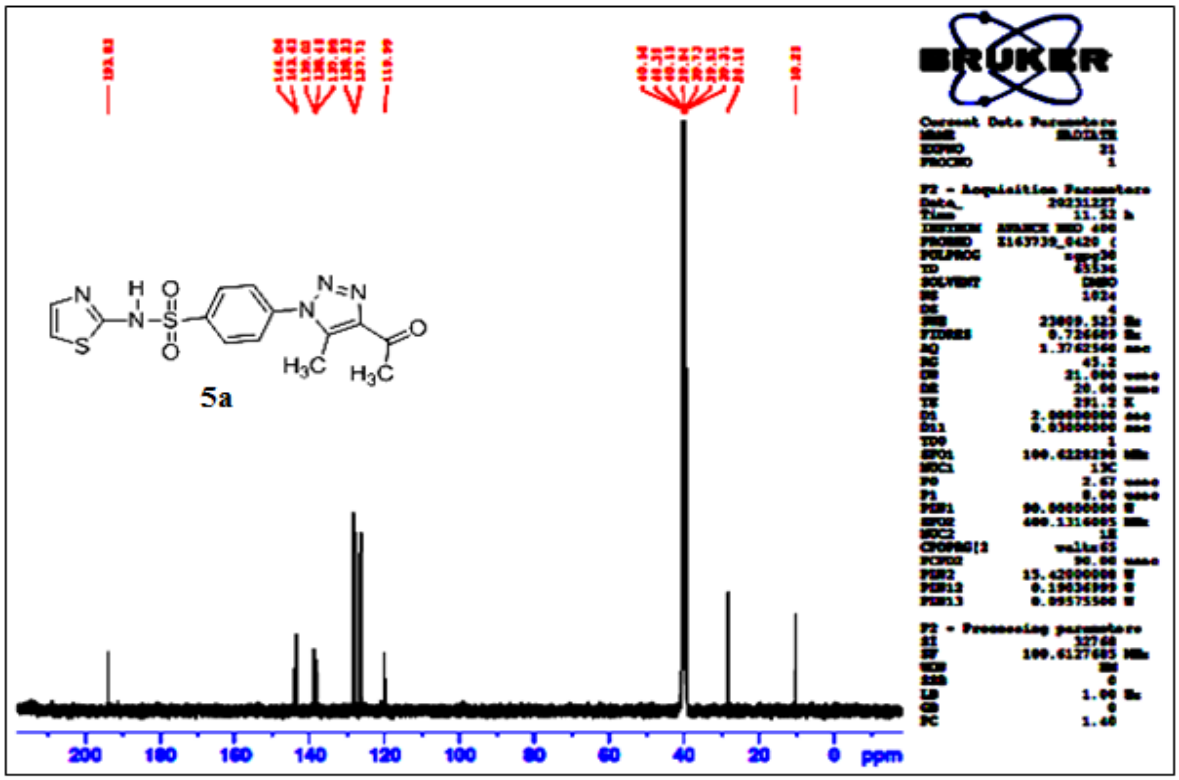


Fig. 8. ^{13}CNMR spectrum of derivative (5a).

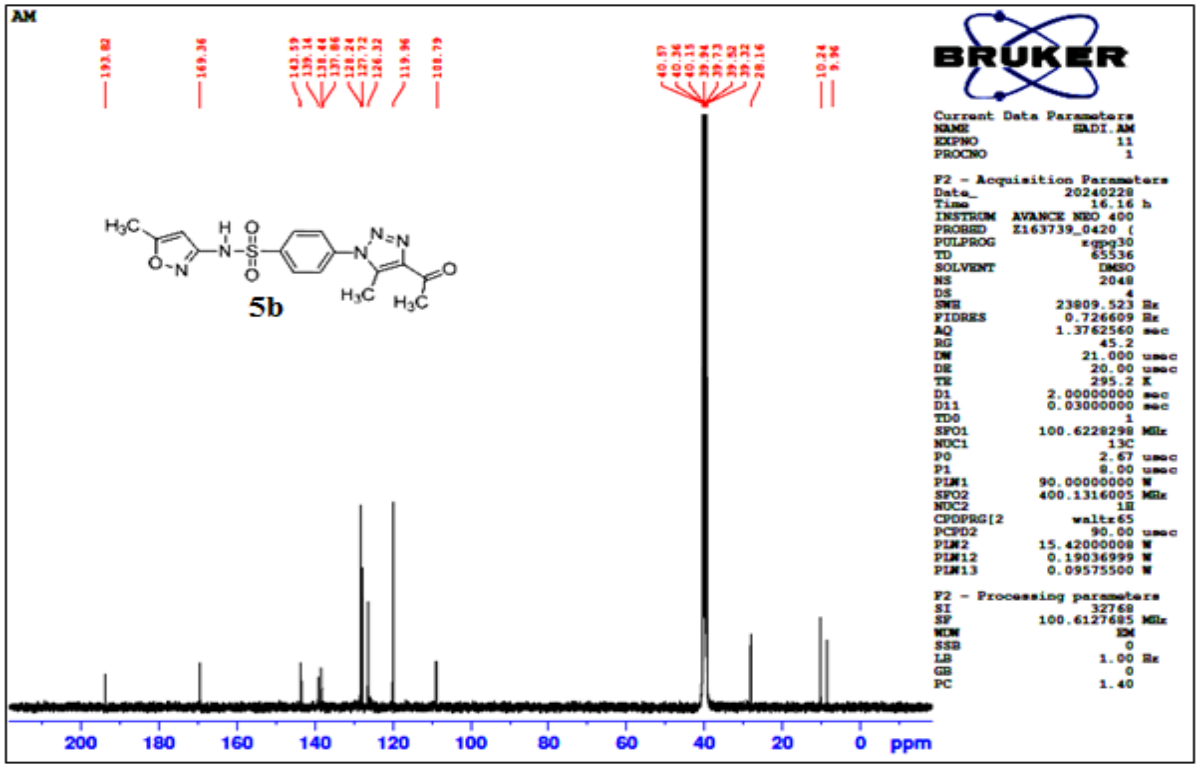


Fig. 9. ^{13}CNMR spectrum of derivative (5b).

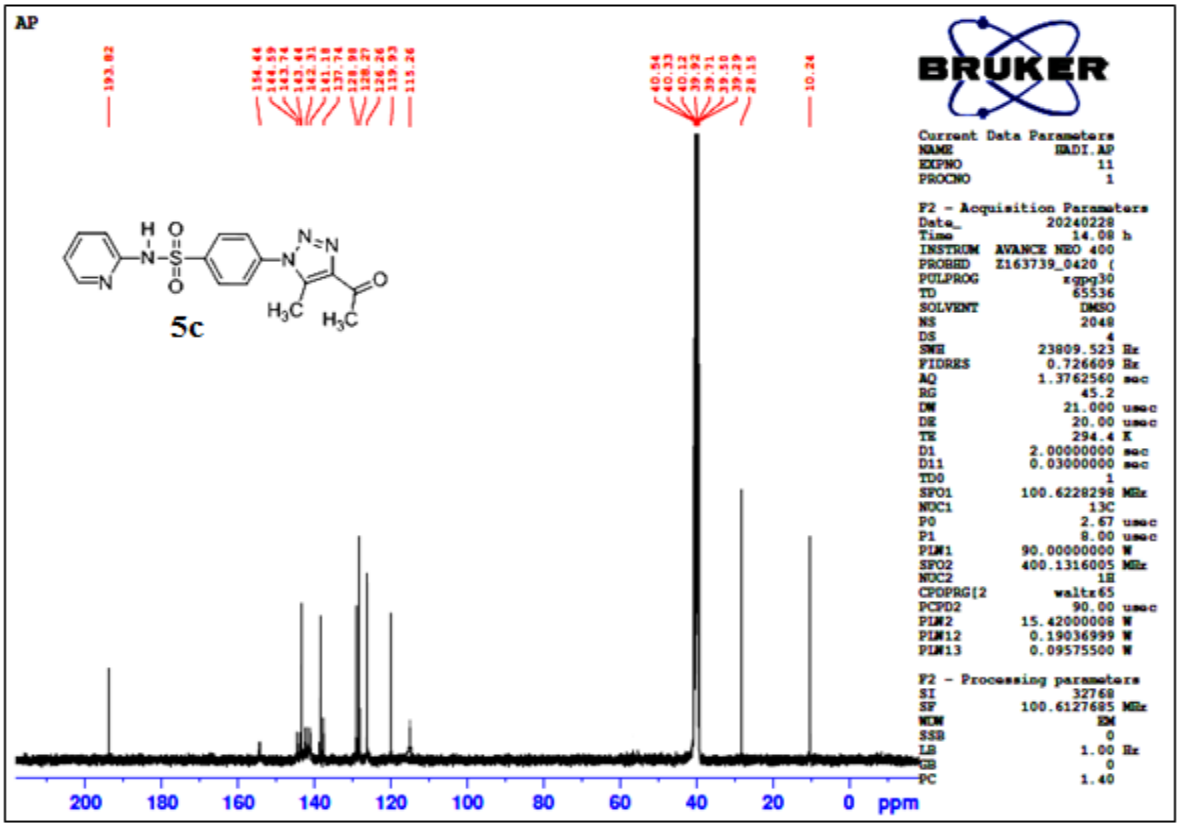


Fig. 10. ^{13}CNMR spectrum of derivative (5c).

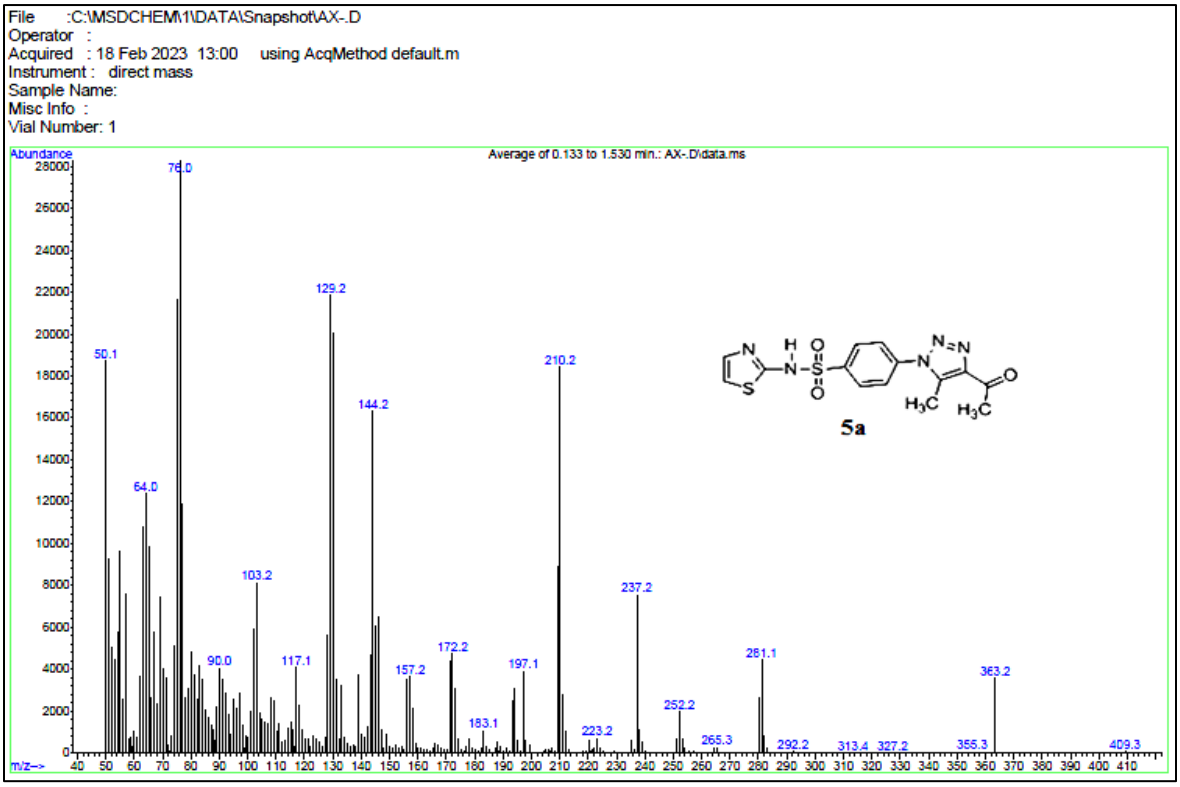


Fig. 11. EI-Mass spectrum of the derivative (5a) associated with *m/z* (%).

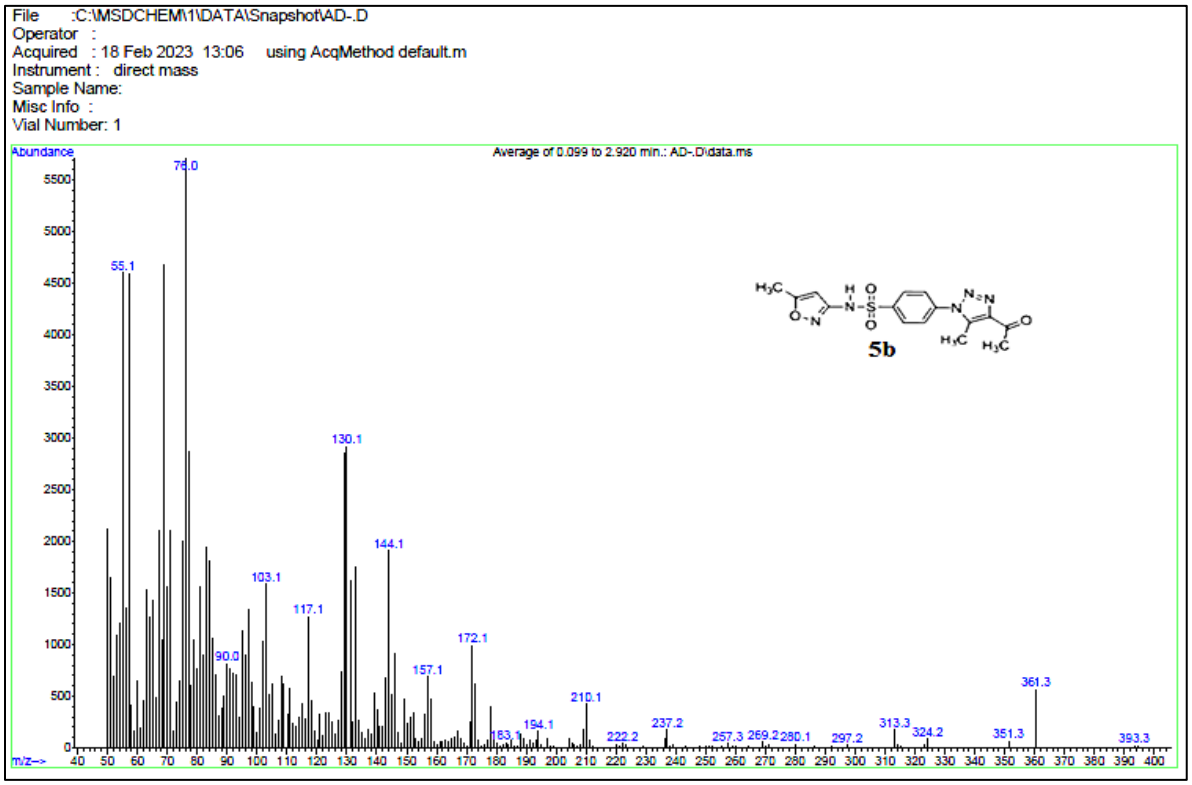


Fig. 12. EI-Mass spectrum of the derivative (5b) associated with *m/z* (%).

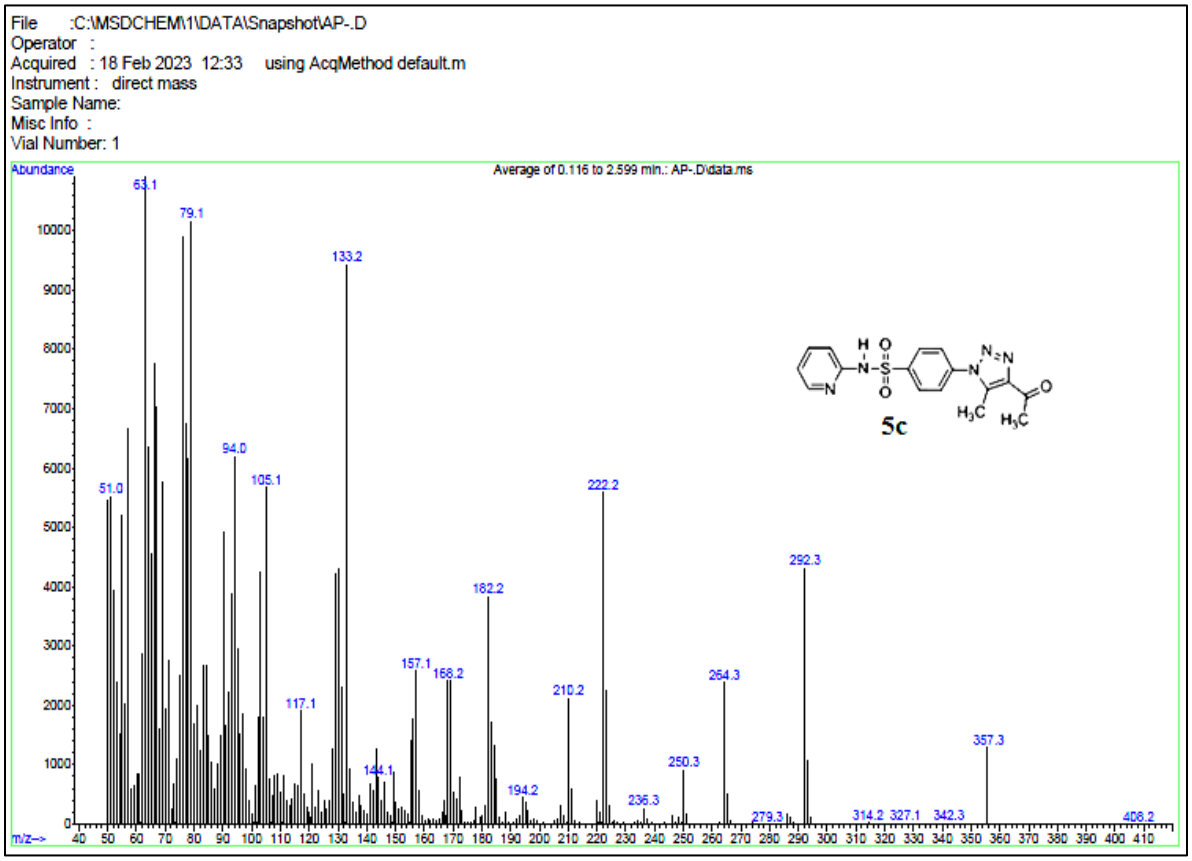


Fig. 13. EI-Mass spectrum of the derivative (5c) associated with *m/z* (%).

3.2. DFT-assisted calculations

Density functional theory (DFT)-supported calculations with the selected exchange-correlation (B3LYP) as exchange-correlation functional are emerged as good tools in the identification of molecular structures and in geometrical molecule parameters assessment as these parameters can help to realize potential reactivity of the molecules, Such parameters include hydrogen bonding, conjugation state, adequate stability, high charge mobility, vibrational frequencies, natural bond molecular orbitals, and etc. [15, 16].

Geometry optimization of the synthesized target derivatives (**5a-5c**) are acquired using DFT-assisted calculations at the B3LYP/6–31G(d) level [17, 18]. The vibrational frequencies analyses for the optimal geometry were calculated to confirm if the selected molecules are in a minimum local or high energy structure. All calculations were conducted to Gaussian 09 program to complete other theoretical calculations [19]. The optimal structures of the synthesized derivative (**5a-5c**) are configured in **Fig. 14**.

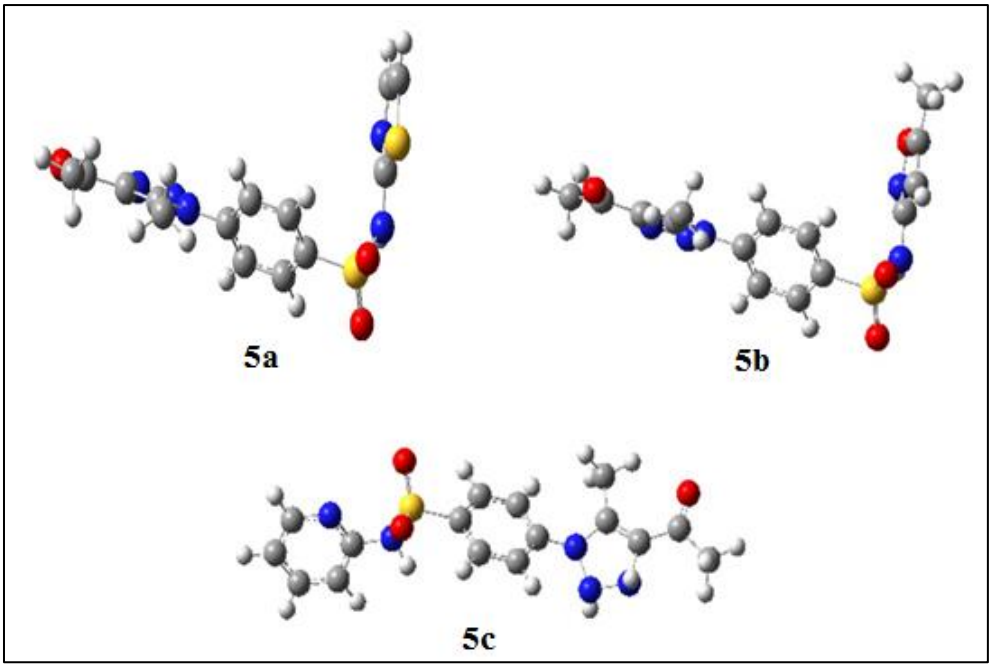


Fig. 14. Optimal geometries of LEC for the derivatives (5a-c) using DFT/B3LYP/6-31G(d) level.

The reactivity of 1, 2, 3-triazole derivatives (**5a-c**) has been extensively investigated through the identification of some theoretical DFT-parameters. These parameters were used to expound the reactivity of the selected molecules. Tow of important theoretical parameters are E_{HOMO} (Energy of Highest Occupied Molecular Orbital) and E_{LUMO} (Energy of Lowest Unoccupied Molecular Orbital) which are calculated and shown in **Fig. 15**. The other theoretical parameters include the electronic chemical potential (μ), chemical hardness (η), and electrophilicity (ω) are calculated for 1, 2, 3-triazole derivatives (**5a-c**) in order to assess their chemical and physical reactivity. The optimal structures of the derivatives (**5a-c**) is the basis to generate aforementioned theoretical reactivity parameters. These parameters are calculated according to Equations (1-4) [20, 21].

Energy gap (ΔE_{gap}):

$$\Delta E gap = (E_{LUMO} - E_{HOMO}) \dots\dots\dots (1)$$

Electronic chemical potential (μ):

$$\mu = {}^{1}/_{2}\,(E_{HOMO} + E_{LUMO}) \dots\dots\dots (2)$$

Chemical hardness (η):

$$\eta = {}^{1}/_{2}\,(E_{HOMO} - E_{LUMO}) \dots\dots\dots (3)$$

Electrophilicity power (ω): $\omega = \mu^2/2\eta$ ……(4)

Com.	HOMO	LUMO	(ΔE)	(η)	(μ)	(ω)

A soft or hard is possible property for the molecules and this property can be identified by calculation of chemical hardness. For the hard molecules, the expected chemical hardness is high than the soft molecules. In general, the molecules which possess lower chemical hardness will be become reactive [22]. The correlation of viability of a chemical species and the electronic chemical potential is essentially based on exchange electronic density with other analogues compounds. A molecule that shows high potential electronic density is characterized as a stronger electron acceptor. Electrophilicity power as a chemical reactivity index is represented to explain the molecules abilities to accept an electron [23].

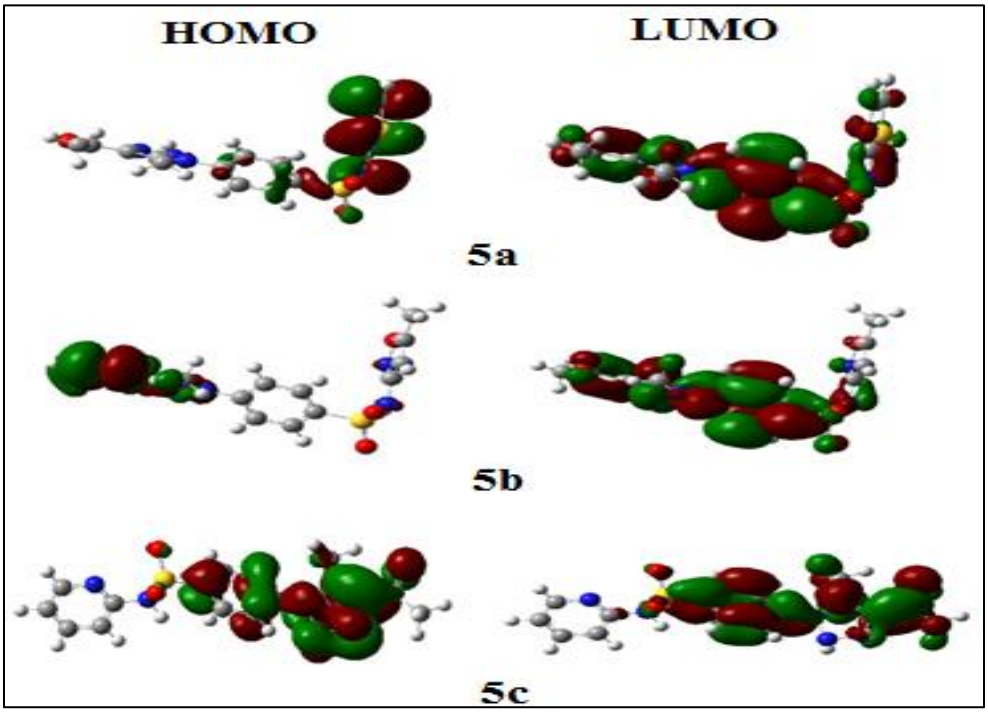


Fig. 15. HOMO and LUMO representations of the derivatives (5a-c) calculated with DFT/ B3LYB/6-31G (d) level.

Table 1. Reactivity parameters of the synthesized 1, 2, 3-triazole derivatives (5a-c) calculated with DFT/ B3LYB/6-31G (d) level.

5a	-6.571	-2.123	4.448	2.224	-4.347	4.24829
5b	-6.985	-2.050	4.935	2.4675	-4.5175	4.13532
5c	-5.609	-1.721	3.888	1.944	-3.665	3.45479

According to data shown in **Table 1**, the chemical hardness (η), electrophilicity power (ω) and energy gap (ΔE_{gap}) of the synthesized derivatives (**5a-c**), the derivative (**5c**) is found to be more reactive than the other derivatives (**5a** and **5b**).

On the other hand, the identification of potential electrostatic molecule (PEM) or the electrostatic potential surfaces (EPS) map is considered as very useful tool to understand the spread and locations of electrons density on the selected molecules [24]. PEM is a very useful for revealing the electrons density locations that appeared on specific atoms [25]. Therefore, it is important map to interpret the potential electrostatic state *via* the positive, negative and neutral of molecule atoms, as well as it helps to elucidate the size of the selected molecular and the shape. The region of maximum negative part is a favorable site for electrophilic attack whereas the region of maximum positive state is a favorable site for nucleophilic attack. The electrostatic potential surfaces (EPS) of the synthesized derivatives (**5a-c**) are shown in **Fig. 16**. It was observed that negative potential of the derivative (**5c**) refers to oxygen atoms while the positive potential the derivative (**5b**) refers to nitrogen atoms. The regions that have the maximum negative potential were noted over those atoms which are considered as favorable centers for electrophilic attack (major centers for offering electronic) due to they possess more negative charges, thus the derivative (**5c**) is ultimately having high reactivity than other derivatives.

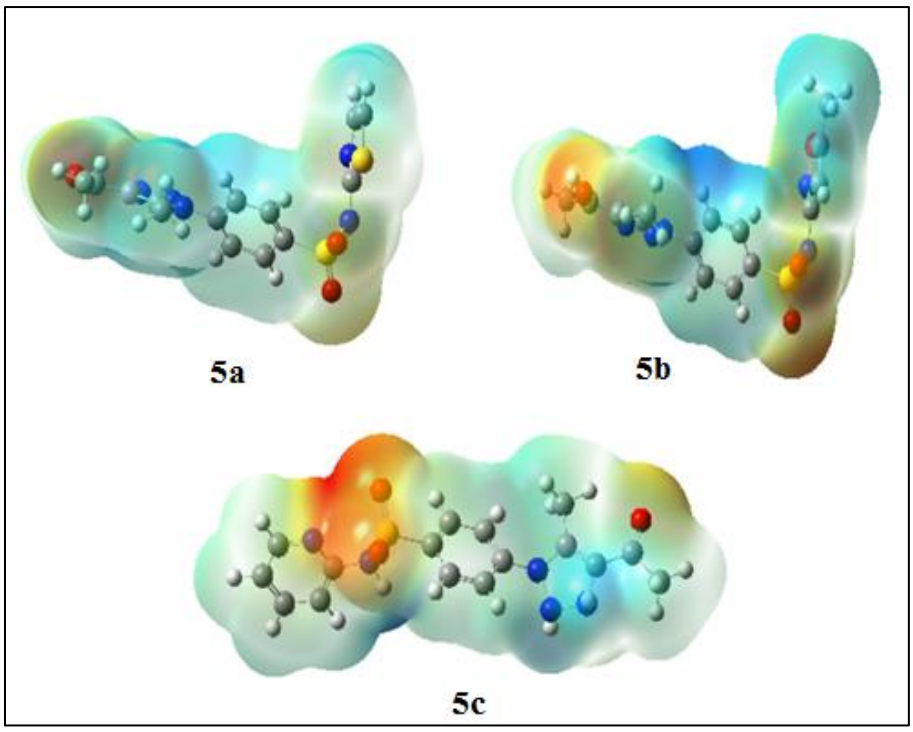


Fig. 16. PEM maps for the synthesized 1, 2, 3-triazole derivatives (5a-c).

Conclusions

This work introduces an efficient synthesis of three novel derivatives of 1, 2, 3-triazole (**5a-c**) were synthesized *via* a 1, 3 dipolar cycloaddition reaction that basis on azides-based anilinesulfonamide derivatives and pentane-2, 4-dione in the presence of K_2CO_3 as a mild catalyst. The identification of their chemical structural was confirmed by conducting with nuclear magnetic resonance ^{1}H, and ^{13}C NMR, FT-IR, and Mass spectroscopies. The optimal geometrical structures and other theoretical parameters for these derivative were acquired using DFT-assisted calculations at B3LYP/6–31G(d) level in order to improve their reactivates.

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