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Versatile and green synthesis, spectroscopic characterizations, crystal structure and DFT calculations of 1,2,3–triazole–based sulfonamides

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ABSTRACT

A green, and practically reliable method for the synthesis of novel 1,2,3–triazole-based sulfonamides via copper (I)–catalyzed azide–alkyne [3 + 2] cycloaddition reaction was reported. The desired products were characterized by CHN analysis, FT-IR, ^{1}H and ^{13}C NMR, ESI-MS spectroscopy, single crystal X-ray diffraction and density functional theory (DFT) geometry optimization and molecular orbital calculations. Mild and green reaction conditions, atom-economic and high yields (61–91%) make this protocol an attractive option for the synthesis of 1,2,3–triazoles bearing sulfonamide moiety. Geometrical structures, vibrational frequencies, ^{1}H and ^{13}C chemical shift values, Mulliken charge distribution and electrophilicity index (HOMO-LUMO analysis) of the characterized structure of **3f** in the ground state have been calculated with the aid of DFT studies. The calculated chemical shifts (NMR) and vibrational frequencies (FT-IR) are in compliance with the experimental findings. The aim of the DFT study was to make a reasonable assignment of vibrational bands and chemical shifts.

1. Introduction

Sulfonamides are organic sulfur compounds which have attracted great attention for their interesting pharmacological activity [1–3]. On the other hand, 1,2,3–triazoles have aroused high favor in medicine for their diverse pharmacological and biological activities such as, β–lactamase inhibitors, anticancer, antifungal, antiviral and anti–HIV activities [4,5]. The synthesis of 1,2,3–triazoles strongly relies on copper (I)–catalyzed azide–alkyne [3 + 2] Huisgen cycloaddition reaction (CuAAC reaction). The potential of this reaction type is very high, because alkyne and azide moieties can be incorporated into a broad range of compounds. To date, CuAAC reaction is the best and the most popular 'click' reaction, due to high reliability and its wide range of applications in chemistry and biochemistry [6]. However hundreds of scientific papers describing the synthetic potencies of CuAAC have been published. Nevertheless, relatively few examples in which this robust method is applied to triazoles containing sulfonamide moiety exist [7–9]. It is interesting to note that triazoles containing sulfonamide moiety are known to have some biological and pharmaceutical properties, such as aromatase inhibition, thrombin inhibition, antitumor, antibacterial and antifungal activities [10–12]. Prompted by these facts, in this study 1,2,3–triazole group has been coupled with sulfonamide moiety using CuAAC reaction to synthesis of a new class of 1,2,3–triazole-based sulfonamides (Scheme 1).

2. Experimental

2.1. General information

All the chemicals required for the synthesis of the 1,2,3–triazole–based sulfonamides **3** were purchased from Sigma-Aldrich (St. Louis, MO, USA), Fluka (Neu-Ulm, Germany) and Merck (Darmstadt, Germany) companies and were used as received. The all synthesized compounds **3** gave satisfactory spectroscopic data. A Bruker (DRX-400 Avance) NMR was used to record the ^{1}H NMR and ^{13}C NMR spectra. All NMR spectra were determined in $CDCl_3$ at ambient temperature. LC-MS analysis was performed on an Agilent 1200 LC system (Agilent, Waldbronn, Germany). All the reactions are monitored by thin layer chromatography (TLC) carried out on silica gel with UV light and iodine, as detecting agents.

2.2. Computational details

All geometry optimizations and frequency calculations of all species were carried out using the Gaussian 03 program [13].

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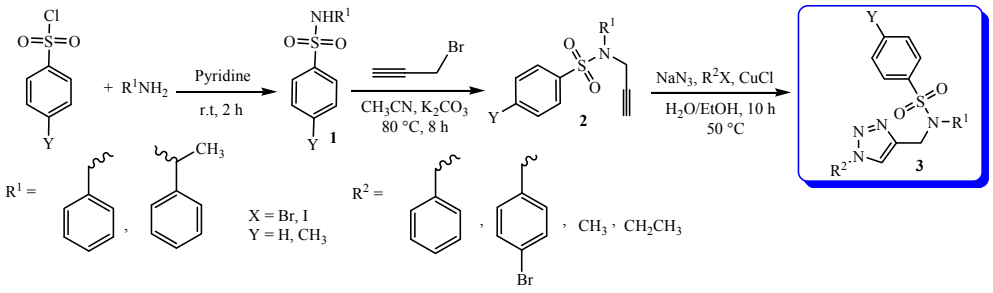


Scheme 1. The general method for synthesis of 1,2,3–triazole–based sulfonamides **3**.

Density Functional Theory with the Becke three parameters hybrid functional (DFT-B3LYP) calculations were performed with a 6-31 ++G (d, p) basis set for all atoms. Vibrational frequencies were calculated at the same level to ensure that each stationary point is a real minimum. Harmonic-oscillator approximation was also used for the thermodynamic partition functions. After geometry optimization and frequency calculations, zero-point energies (ZPEs) and thermal corrections are obtained at 298 K.

2.3. General procedure for the synthesis of 1,2,3–triazole–based sulfonamides **3**

To a suspension of CuCl (0.1 mmol) in H_2O/EtOH (5 mL, 1:1), were added sodium azide (1 mmol) and alkyl halide (1 mmol), and the resulting mixture was stirred at room temperature for 1 h. *N*-propargyl sulfonamides **2** (1 mmol) was added to the reaction mixture and the mixture was stirred at 50 °C for 9 h [14]. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was recovered by filtration. Water (5 mL) was added to the reaction mixture and extracted with EtOAc (3 × 10 mL) and dried over Na_2SO_4. The crude was concentrated under vacuum and was purified by preparative TLC (eluent: petroleum ether/ethyl acetate 3:1) to afford the desired products **3**.

2.4. Spectroscopic data of the products ***3a-k***

3a: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 4.34 (s, 2H), 4.39 (s, 2H), 5.37 (s, 2H), 7.15–7.66 (m, 15H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.51, 42.21, 51.17, 54.03, 123.12, 127.22, 127.68, 128.04, 128.41, 128.70, 129.08, 129.65, 134.41, 135.82, 136.89, 143.41, 143.71 ppm. Anal. Calcd for $C_{24}H_{24}N_4O_2S$: C, 66.64; H, 5.59; N, 12.95. Found: C, 66.57; H, 5.64. N, 13.04; **3b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 4.36 (s, 2H), 4.43 (s, 2H), 5.36 (s, 2H), 7.08 (d, J = 8 Hz, 2H), 7.23 (m, 5H), 7.26–7.28 (m, 3H), 7.52 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.59, 42.39, 51.44, 53.43, 123.29, 127.28, 127.76, 128.47, 128.74, 129.71, 129.75, 132.30, 133.43, 135.82, 136.74, 143.59, 144.09. MS (ESI): 511 and 513 $[M+H]^+$. Anal. Calcd for $C_{24}H_{23}BrN_4O_2S$: C, 56.36; H, 4.53; N, 10.95. Found: C, 56.27; H, 4.66. N, 11.09; **3c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3H), 3.97 (s, 3H), 4.38 (s, 2H), 4.43 (s, 2H), 7.21–7.29 (m, 6H), 7.32 (d, J = 8 Hz, 2H), 7.73 (d, J = 8 Hz, 2H) . ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.56, 36.57, 42.15, 51.07, 124.37, 127.34, 127.72, 128.48, 128.76, 129.73, 135.91, 136.94, 143.57. MS (ESI): 357 $[M+H]^+$. Anal. Calcd for $C_{18}H_{20}N_4O_2S$: C, 60.65; H, 5.66; N, 15.72. Found: C, 60.80; H, 5.53. N, 15.86; **3d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 (t, J = 7.2 Hz, 3H), 2.42 (s, 3H), 4.28 (q, J = 7.6 Hz, 2H), 4.40 (s, 2H), 4.44 (s, 2H), 7.24–7.28 (m, 6H), 7.32 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.34, 21.55, 42.31, 45.22, 51.21, 122.62, 127.30, 127.72, 128.47, 128.76, 129.73, 136.01, 137.03, 143.25, 143.51. MS (ESI): 371 $[M+H]^+$. Anal. Calcd for $C_{19}H_{22}N_4O_2S$: C, 61.60; H, 5.99; N, 15.12. Found: C, 61.71; H, 5.83. N, 15.23; **3e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (d, J = 7.2 Hz, 3H), 2.45 (s, 3H), 4.40 (br s, 2H), 5.22 (q, J = 7.2 Hz, 1H), 5.38 (s, 2H), 7.16–7.22 (m, 8H), 7.27 (d, J = 8 Hz, 2H), 7.37–7.41 (m, 3H), 7.68 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.99, 21.57, 39.13, 54.02, 55.94, 123.51, 127.1, 127.61, 127.74, 128.05, 128.26, 128.68, 129.05, 129.75, 134.63, 137.82, 139.55, 143.39, 146.1. Anal. Calcd for $C_{25}H_{26}N_4O_2S$: C 67.24, H 5.87, N 12.55, Found: C 67.17, H 5.96, N 12.48; **3f**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (d, J = 7.2 Hz, 3H), 2.45 (s, 3H), 4.40 (br s, 2H), 5.23 (q, J = 7.2 Hz, 1H), 5.33 (s, 2H), 7.07 (d, J = 8.4 Hz, 2H), 7.14–7.24 (m, 6H), 7.27 (d, J = 7.6 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.91, 21.59, 39.05, 53.33, 55.92, 122.83, 127.09, 127.62, 127.74, 128.26, 129.68, 129.79, 132.20, 133.65, 137.69, 139.52, 143.49; FT-IR (KBr): 2957, 2930, 1727, 1380, 1155, 813; Anal. Calcd for $C_{25}H_{25}BrN_4O_2S$: C 57.14, H 4.80, N 10.66, Found: C 57.21, H 4.72, N 10.75; **3g**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (d, J = 6.8 Hz, 3H), 2.46 (s, 3H), 3.93 (s, 3H), 4.41 (br s, 2H), 5.23 (q, J = 7.2 Hz, 1H), 7.16–7.23 (m, 5H), 7.31–7.33 (m, 3H), 7.72 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.10, 21.58, 36.63, 39.14, 55.95, 124.76, 127.15, 127.57, 127.76, 128.27, 129.81, 137.69, 139.64, 143.51, 145.89. MS (ESI): 371 $[M+H]^+$. Anal. Calcd for $C_{19}H_{22}N_4O_2S$: C, 61.60; H, 5.99; N, 15.12. Found: C, 61.74; H, 6.09. N, 15.27; **3h**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40–1.46 (m, 6H), 2.45 (s, 3H), 4.26 (q, J = 7.2 Hz, 2H), 4.42 (br s, 2H), 5.25 (q, J = 6.8 Hz, 1H), 7.20 (m, 5H), 7.27 (s, 1H), 7.32 (d, J = 8 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.38, 16.95, 21.56, 39.13, 45.22, 55.90, 122.96, 127.09, 127.60, 127.76, 128.27, 129.79, 137.80, 139.69, 143.45, 145.50. MS (ESI): 385 $[M+H]^+$. Anal. Calcd for $C_{20}H_{24}N_4O_2S$: C, 62.48; H, 6.29; N, 14.57. Found: C, 62.35; H, 6.38. N, 14.64; **3i**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (d, J = 6.8 Hz, 3H), 4.42 (br s, 2H), 5.26 (q, J = 6.8 Hz, 1H), 5.36–5.44 (m, 2H), 7.16–7.21 (m, 8H), 7.39–7.50 (m, 5H), 7.58 (t, J = 7.9 Hz, 1H), 7.81 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.15, 39.01, 54.30, 56.08, 127.07, 127.68, 127.75, 128.11, 128.31, 128.74, 129.06, 129.17, 132.64, 134.55, 139.39, 140.75. Anal. Calcd for $C_{24}H_{24}N_4O_2S$: C 66.64, H 5.59, N 12.95, Found: C 66.73, H 5.50, N 12.87; **3k**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (d, J = 6.8 Hz, 3H), 4.42 (br s, 2H), 5.25 (q, J = 6.8 Hz, 1H), 5.35 (br s, 2H), 7.07 (d, J = 8 Hz, 2H), 7.16–7.20 (m, 5H), 7.49–7.63 (m, 5H), 7.83 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.15, 39.18, 53.33, 56.09, 122.88, 127.04, 127.69, 127.73, 128.30 (2C), 129.19, 129.69, 132.20, 132.68, 133.67, 139.40, 140.71. Anal. Calcd for $C_{24}H_{23}BrN_4O_2S$: C 56.36, H 4.53, N 10.95, Found: C 56.45, H 4.61, N 11.07.

3. Results and discussion

3.1. Synthesis 1,2,3–triazole–based sulfonamides **3**

The starting alkyne bearing sulfonamide **2** are readily prepared in house [14]. Treatment of *para*-toluene sulfonyl chloride with amine in pyridine at room temperature for 2 h gave the

corresponding sulfonamide in excellent yields (>85%). The *N*-propargylsulfonamides **2** were then prepared in high yield (>78%) by the treatment of the synthesized sulfonamide with propargyl-bromide in the presence of K_2CO_3 in refluxing acetonitrile for 8 h. The [3 + 2] cycloaddition reaction of **2** with alkyl azide (R^2N_3) in the presence of CuCl (10 mol %) led to the desired 1,2,3–triazole–based sulfonamides **3** in high yield after 10 h at 50 °C H_2O/EtOH.

Preliminary investigation of the model reaction (benzyl bromide, sodium azide and *N*-propargyl sulfonamide 2-(*N*-benzyl-*N*-tosylprop-2-yn-1-amine)) showed that the cycloaddition reaction did not proceed in the absence of catalyst after 8 h, while good results were obtained in the presence of CuCl after 10 h. In the mixed solvent EtOH/H_2O the corresponding triazole **3a** was obtained in excellent yield. Furthermore, the effect of temperature was also examined by carrying out the model reaction in the presence of CuCl (10 mol%) at room temperature (25 °C) and 50 °C. It was observed that the yield was increased as the reaction temperature was raised to 50 °C. In order to prove the applicability of the optimized reaction condition for the synthesis of various 1,2,3-triazoles bearing sulfonamide group, we examined various combination of substrates. All the reactions efficiently proceed to give the corresponding 1,2,3-triazole derivatives in good yields (Scheme 2).

3.2. Structural characterization of 1,2,3–triazole–based sulfonamides **3**

The structure of the products were confirmed by CHN, ^{1}H NMR, ^{13}C NMR and FT-IR analysis. The ^{1}H NMR and ^{13}C NMR spectra of the products clearly indicated the formation of the desired products **3**. The ^{1}H NMR spectrum of **3f** consisted of a doublet line at δ = 1.38 ppm to the methyl group, five benzylic protons at δ = 4.40–5.33 ppm and 13 protons for aromatic rings and one heterocycle proton at δ = 7.07–7.69 ppm. The ^{1}H–decoupled ^{13}C NMR spectrum of **3f** showed 18 resonances.

Unambiguous evidence for the structure of **3f** was obtained from a single-crystal X-ray analysis. Röntgen crystal structure of **3f** is shown in Fig. 1. X-ray diffraction intensity data for a single-crystal of **3f** (0.40 × mm 0.13 mm × 0.10 mm) were collected at 293 K on a crystal diffractometer STOE-IPDS 2T equipped with graphite monochromated MoKα radiation (k = 0.71073 Å). Crystallographic data for the structural analysis have been deposited to Cambridge Crystallographic Data Centre, with CCDC reference number 1456414. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data–request/cif. A summary of crystal data and data collection parameters are presented in Table 1.

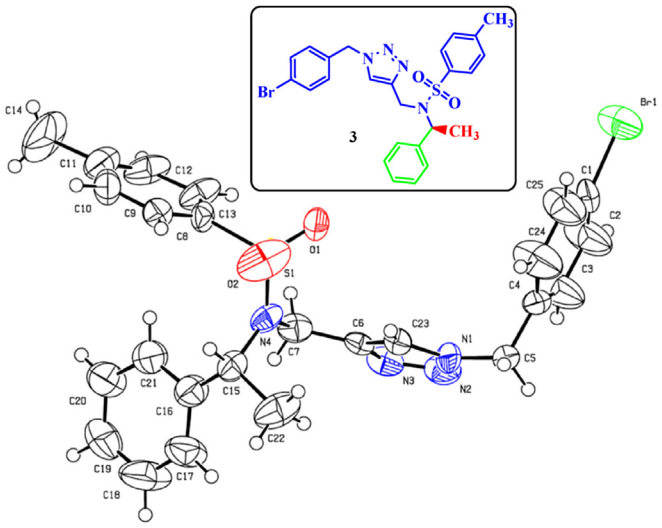
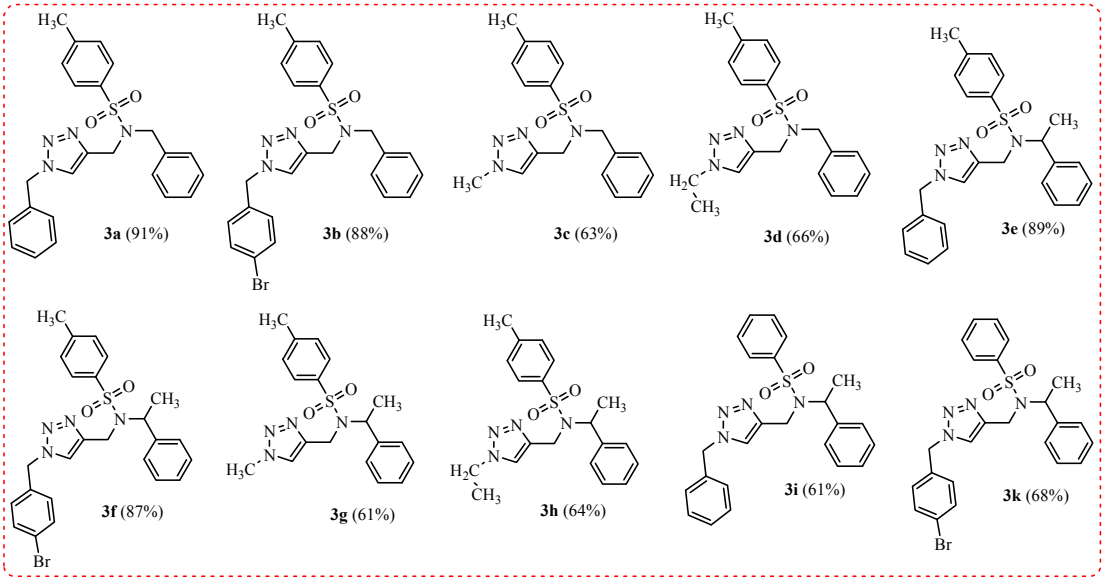


Fig. 1. Röntgen crystal structure of **3f**.

Table 1
Crystallographic data of 1,2,3–triazole–based sulfonamide **3f**.

Empirical formula	$C_{25}H_{25}BrN_4O_2S$	a(Å)	5.8743 (12)
Formula weight (gmol^{-1})	525.45	b(Å)	14.560 (3)
T(K)	293	c(Å)	28.662 (6)
Mu (MoKα) [/mm]	1.791	V (Å^3)	2451.5 (9)
Crystal system	Orthorhombic	Z	4
Space group	$P2_12_12_1$	Dcalc (g cm^{-3})	1.424



Scheme 2. The synthesized structures of a variety of 1,2,3–triazole–based sulfonamides **3a-k**.

3.3. Theoretical studies on 1,2,3–triazole–based sulfonamide **3f**

Quantum calculation chemistry has been quite successful in providing theoretical background of popular qualitative chemical concepts [15]. Quantum chemical calculations help chemist to calculate the structural and physicochemical properties of the molecule. With the encouraging experimental data of 1,2,3–triazole–based sulfonamides **3**, our attention was focused on calculations for investigation of physicochemical properties of **3f** such as structural data, NMR data, FT-IR frequencies, Mulliken charge distribution and electrophilicity index.

3.3.1. Benchmarking of methods

As one of our goals is to find an accurate method that is computationally efficient, we have focused on two methods HF and DFT with different basis sets. The representative structural parameters for **3f** via X-ray diffraction are: C1-Br1 1.887 Å, C15-C22 1.581 Å, C8-S1 1.787 Å, N1-N2 1.352 Å and N4-S1 1.634 Å, N4C15C22 107.2°, N4C7C6 115.3°, N1C5C4 112.0°, Br1C1C2 120.2° and Br1C1C25 120.5°. These structural data can help to find the optimal method for calculations. The correlation coefficient for the bond lengths and bond angles along error in data for HF and DFT with different basis sets for **3f** are available in supporting information (Table S1, and Fig. 26S). Calculations show that B3LYP with basis set 6-31++G (d, p) gave satisfactory results and structural parameters have good agreement with experimental data (Table 2). The optimized geometric parameters in Table 2 are in good agreement with the X-ray experimental results. The differences between the two values are within normal ranges.

The experimental N1-N2, and C8-S1 distances of 1.352 and 1.787 are very accurately regenerated by B3LYP/6-31++G (d, p) with values of 1.351 and 1.798 Å, respectively for **3f**. On the other hand BrlC1C2 bond angle of 120.20°, is well represented by this computational method, 119.48°. Thus, the highest level of theory used here, B3LYP/6-31++G (d, p), produces calculated bond lengths and bond angles that are in good agreement with the experimental values (Fig. 2).

3.3.2. Calculation of electrophilicity index of **3f** (HOMO-LUMO analysis)

Many of the organic reactions can be described in terms of the electrophilic and nucleophilic reactions. Electrophilicity is relative reactivity of a molecule that is sufficient to describe the reactivity of compounds [16]. Based on the work of Parr et al. the electrophilicity index is calculated according to the equation [17,18].

Table 2
Computed structural parameters and error percent with respect to experimental data for the B3LYP/6-31++G (d, p) of **3f**.

Geometrical parameters	Experimental	Theoretical	Error in data
Bond lengths (Å)			
C1-Br1	1.8870	1.9020	0.7042
C15-C22	1.5810	1.5360	−2.8495
C8-S1	1.7870	1.7982	0.6267
N1-N2	1.3520	1.3512	−0.0607
N4-S1	1.6340	1.6981	3.9217
Bond angles (°)			
N4-C15-C22	107.20	112.7502	5.1774
N4-C7-C6	115.30	114.7572	−0.4708
N1-C5-C4	112.00	113.8292	1.6332
Br1-C1-C2	120.20	119.4826	−0.5968
Br1-C1-C25	120.50	119.5368	−0.7993

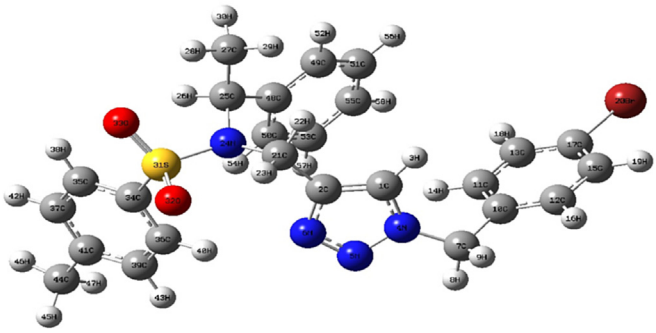


Fig. 2. Optimized geometry for the B3LYP/631++G (d, p) of **3f**.

$$\omega = \mu^2 / 2\eta$$

where μ and η are the chemical potential and chemical hardness, respectively given by:

$$\mu = (E_{LUMO} + E_{HOMO})/2 \quad \text{and} \quad \eta = (E_{LUMO} - E_{HOMO})/2$$

E_{LUMO} is the energy of the lowest unoccupied molecular orbital and E_{HOMO} is the energy of the highest occupied molecular orbital. HOMO and LUMO as main orbitals are responsible for reactivity of compounds [19]. The HOMO (π donor) represents the ability to give an electron and the LUMO (π acceptor) represents the ability to obtain an electron. The HOMO and LUMO energy calculated by B3LYP/6-31++G (d, p) for **3f** is shown in Fig. 3. The HOMO orbital is mainly located on the aryl ring bearing bromine atom, while the LUMO orbital is localized on the sulfonamide moiety as well as the aryl ring bearing methyl group.

3.3.3. FT-IR spectrum study of **3f**

A main important goal of this part is to assign the experimental frequencies to the computed vibrational modes of **3f** properly. The experimental and the calculated infrared spectra of **3f** by the DFT method at the B3LYP/6-31++G (d, p) level are shown in Fig. 4. The

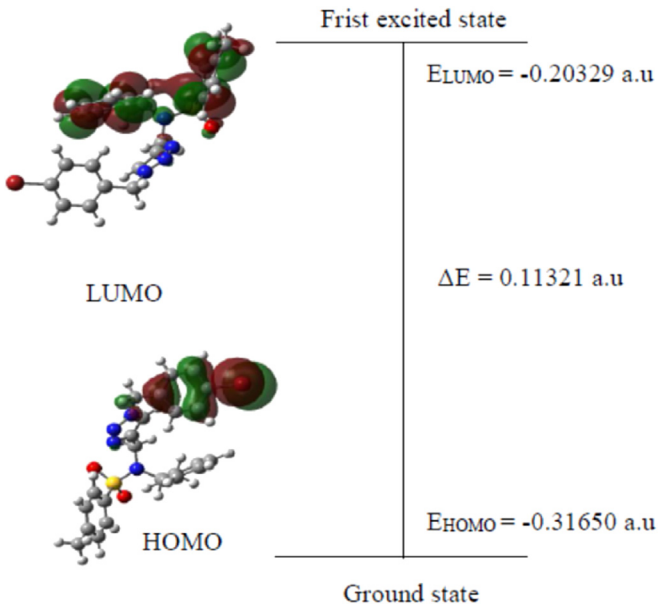


Fig. 3. The HOMO and LUMO gap for **3f**.

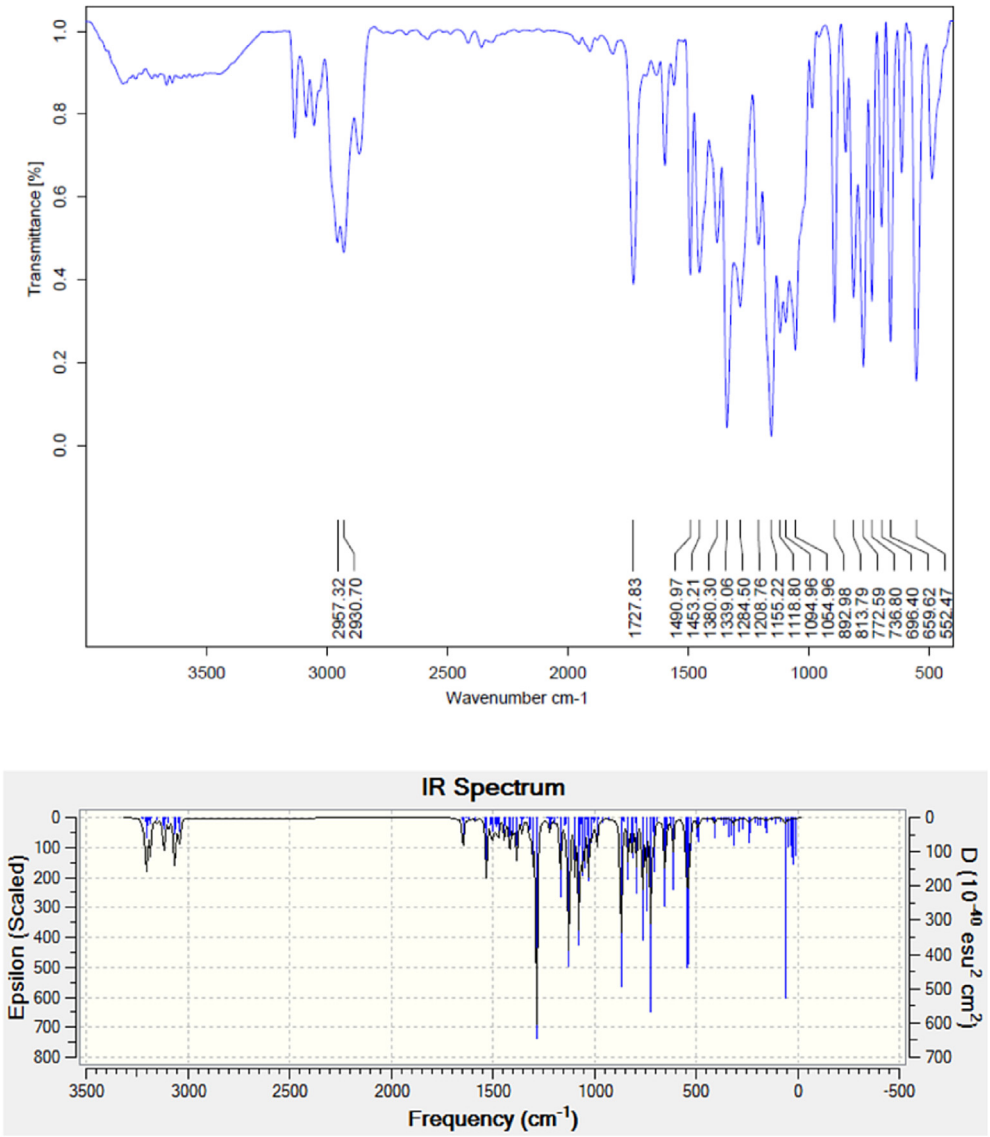


Fig. 4. Experimental (top) and calculated (down) FT-IR spectra of **3f**.

vibrational band assignments have been made by using GaussView molecular visualization program [20]. It should be noted that the scaling factors 0.98 and 0.99 for below 1800 cm^{-1} and above 1800 cm^{-1} were applied for calculated frequencies, respectively. In general, there was a good agreement between experimental and calculated frequencies. The aromatic C—H stretching vibrations are presented in the region 3225–3112 cm^{-1}. In obtained experimental IR spectrum, due to the low dipole moment changes in aromatic rings, the intensities of aromatic C—H bond stretching are weak and it is hard to assign the peaks to each aromatic ring separately. Aliphatic CH, CH_2 and CH_3 asymmetric and symmetric calculated stretching vibrations mainly are observed in the region 2976-3087 cm^{-1} and its experimental counterpart appear in the region 2930-2957 cm^{-1}.

For aromatic rings, the bands are observed at 1530, 1490 and 1453 cm^{-1} are assigned to the C—H in-plane rocking vibrations of aromatic rings. The calculated values of this mode were somewhat shifted to the lower frequencies appearing at 1513, 1467 and 1421 cm^{-1}. Triazole ring C—C stretching band for the titled compound in calculated IR spectrum appears at 1569 cm^{-1}. Strong asymmetric and symmetric S=O stretching band for sulfonamide group were observed at 1339 and 1155 cm^{-1} and their calculated counterparts appear at 1270 and 1067 cm^{-1}, respectively.

3.3.4. *NMR spectral studies of **3f***

The NMR computations were performed using the gauge-independent atomic orbital (GIAO) method [16]. Chemical shifts were reported in parts per million relative to tetramethylsilane (TMS) for ^1H NMR and ^{13}C NMR spectra. Relative chemical shifts were calculated by using the corresponding TMS shielding calculated at the same theoretical level as the reference. Computed B3LYP/6-311++G (d, p) ^1H and ^{13}C chemical shifts for **3f** are listed in supporting information (Table 2S). Computed and experimental aliphatic ^1H and ^{13}C chemical shifts of **3f** is presented at Table 3. According to the comparison between experimental and calculated data, the calculated ^1H and ^{13}C chemical shifts are in acceptable agreement with the experimental results.

The most deviation is observed in the ^{13}C chemical shift of carbon-27 of **3f**, 16.91 ppm, whereas it was calculated as 13.58 ppm.

Table 3
Computed B3LYP/6-31++G (d, p) and experimental aliphatic ^{1}H and ^{13}C chemical shifts of **3f**.

Atom[a]	Theoretical chemical shift/ppm	Experimental chemical shift/ppm	$\lvert\delta_{exp}-\delta_{B3LYP}\rvert$
H8	5.72	5.33	0.39
H22	3.76	4.40	0.64
H26	4.64	5.23	0.59
H30	1.23	1.38	0.15
H47	2.52	2.45	0.07
C7	54.68	53.33	1.35
C21	35.91	39.05	3.14
C25	56.49	55.92	0.57
C27	13.58	16.91	3.33
C44	21.30	21.59	0.29

[a] For numbering of atoms refer Fig. 2.

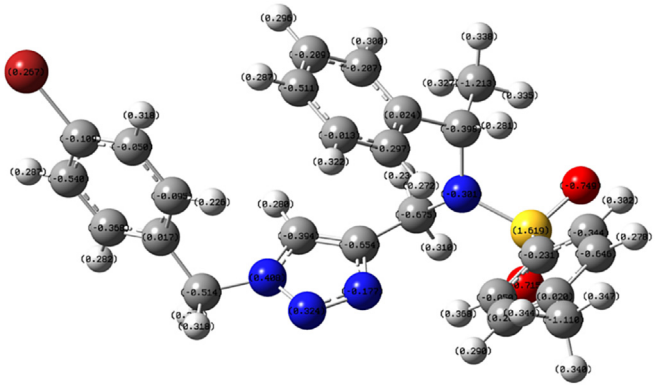


Fig. 5. The Mulliken charge distribution for **3f**.

3.3.5. *Mulliken analysis of **3f***

Atomic charge in molecules has been used to describe the processes of electronegativity equalization and charge transfer in chemical reactions. Mulliken atomic charge affect electronic structure, dipole moment, and molecular polarizability [21]. The Mulliken charge distribution structure of **3f** is shown in Fig. 5. All the hydrogen atoms exhibit a net positive charge in Mulliken analysis. These magnitudes are changing between 0.226 and 0.368 in Mulliken analysis. The oxygen and nitrogen atoms on sulfonamide moiety in **3f** exhibit a negative charge and sulfur atom a positive charge.

4. Conclusions

In summary, we have developed a convenient and green 1,3-dipolar cycloaddition reaction involving *N*-propargyl sulfonamides and alkyl azides in the mixed solvent EtOH/H_2O, which affords 10 novel analogues of 1,2,3-triazole-based sulfonamides as fine chemicals in good yields (61–91%). The structure of the synthesized compounds were fully determined by X-ray, NMR, CHN and ESI-MS analysis. The optimized bond lengths, bond angles, calculated frequencies and chemical shifts (NMR) for **3f** showed the agreement with the experimental results. HOMO-LUMO analysis pointed that the HOMO orbital is mainly located on the aryl ring bearing bromine atom, while the LUMO orbital is localized on the sulfonamide moiety as well as the aryl ring bearing methyl group.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2016.11.027.

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