Rapid microwave promoted heterocyclization of primary amines with triethyl orthoformate and sodium azide using zinc sulfide nanoparticles as recyclable catalyst

Hossein Naeimi, Fatemeh Kiani and Mohsen Moradian
Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, I.R. Iran

ABSTRACT
Microwave assisted synthesis of 1-substituted-1H-tetrazoles was developed using zinc sulfide nanoparticles as heterogeneous catalyst under solvent free conditions. The tetrazole derivatives were easily prepared through heterocyclization of primary amines with triethyl orthoformate and sodium azide in the presence of ZnS NPs. The experimental results were shown that a series of 1-substituted tetrazoles were synthesized under microwave irradiation by ZnS NPs as an effective and reusable heterogeneous catalyst in excellent yields. This protocol has advantages rather than other reported methods such as non-acidic catalyst, solvent free conditions and greener process as well as a solid recyclable catalyst. The catalyst was recovered and reused for several cycles with consistent activity.

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Tetrazoles; microwave irradiation; zinc sulfide nanoparticles; primary amines; cyclization

Introduction
Tetrazoles have a wide range of applications in a variety of chemistry, pharmaceuticals and material science areas such as medicinal chemistry (1-4), metal coordination chemistry (5, 6), information recording systems (7) and explosives and rocket propellants (8). In Figure 1, for example the cefazolin drug containing 1-substituted tetrazole ring is shown.

Although many 5-substituted tetrazoles are known and developed, the 1-substituted tetrazoles are rarely described and few their synthetic methods have been reported. The first reported work for the synthesis of 1-substituted 1H-tetrazoles via heterocyclization of primary amines with orthoformic acid and sodium azide has been reported by Kamiya and Saito using acetic acid as a catalyst (9). The aforesaid protocol during decades has been developed by chemists and attempted to approach greener, faster and high performance procedure that leads rapidly and smoothly to 1-substituted tetrazoles. On the basis of Kamiya method and widespread utility of these compounds, some methods for the preparation of 1-substituted tetrazoles were recently developed and reported (10-16). Recently, using the ytterbium (III) triflate (10), [HBIM] BF₄ (17), [bbim] Br (15), [PMIM (SO₃H)] OTf/TMSN₃ (11), FeCl₃ (18), and Fe₃O₄@silica sulfonic acid (19) as catalyst for heterocyclization of primary amines and triethyl orthoformate with sodium azide has been reported. The procedures have some drawbacks such as; acidic conditions, tedious workup, and they require use of toxic and volatile substances. It is notable that the combination of azide salt and Brønsted acid catalyst produced volatile and toxic gaseous HN₃. It is well known that molecules undergo excitation with electromagnetic radiation. This effect is utilized in microwave ovens to heat the chemical reaction mixtures. The scrutinized rate acceleration upon microwave irradiation is due to material–wave interactions leading to thermal and...
particular effects. The reaction mixture is heated from the inside since the microwave energy is transferred directly to the reagents. The solid catalysts absorb micro-wave irradiation, thus they can serve as an internal heat source for the reactions.

In the present work, we have attempted to develop a more facile and convenient route for the synthesis of 1-substituted 1H-tetrazoles through heterocyclization of primary amines, triethyl orthoformate and sodium azide with ZnS NPs as a heterogeneous catalyst under solvent free and microwave conditions.

Experimental

Materials

All commercially available reagents were used without further purification and purchased from the Merck Chemical Company in high purity. The used solvents were purified by standard procedure.

Apparatus

IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 IR spectrophotometer. The $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ on a Bruker DRX-400 spectrometer. XRD patterns were recorded by an XPERTPro (Philips) instrument with 1.54 Ångström wavelengths of X-ray beam and Cu anode material. Scanning electron microscope (SEM) of nanoparticles was performed on a FESEM Hitachi S4160. The microwave irradiations were carried out in microwave oven specially designed for the organic synthesis (Milestone LAVIS 1000 Basic Microwave). Transmission electron microscopy (TEM) was performed with a Jeol JEM-2100UHR, operated at 200 kV. The BET surface analysis was measured by Micrometrics BET analyzer. Melting points were obtained with a Yanagimoto micro melting point apparatus are uncorrected. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

General procedure for the synthesis of ZnS nanoparticles

In a general procedure, 0.01 mol of zinc nitrate hexahydrate was dissolved in 20 ml of propylene glycol under vigorous stirring at 90°C. Then, 10 ml of thioacetamide solution in propylene glycol (1 M) was previously prepared and added drop wise to the solution over 10 min. Afterward, the solution was exposed to irradiate at microwave oven followed a working cycle of 50 s. on and 100 s. off at 350 watts and temperature of 50°C. After completion of the reaction, the mixture was slowly cooled to room temperature. The precipitate was filtered and consecutively washed with deionized water (5 × 50 ml) and absolute ethanol (3 × 10 ml) and was dried under vacuum at room temperature for 7 h (20).

Typical procedure for the synthesis of tetrazole derivatives under microwave irradiation

A mixture of selected primary amine (1 mmol), triethyl orthoformate (1.2 mmol) and sodium azide (1 mmol) in the presence of 0.06 g ZnS NPs was irradiated in microwave oven at 600 watts and temperature of 60°C. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the mixture was diluted by 1:1 H$_2$O:ethylacetate (10 ml), stirred at ambient temperature (20 min) and centrifuged to separate the solid catalyst. The organic layer was separated, dried over sodium sulphate, and the solvent was distilled off under reduced pressure. In order to further purification, recrystallization of the product was performed at 3:1 EtOAc:MeOH to yield the desired products.

Typical procedure for the synthesis of tetrazole derivatives under conventional condition

ZnS NPs (0.06 g) was added to a mixture of amine (1 mmol), NaN$_3$ (2 mmol), triethyl orthoformate (1.2 mmol) and stirred at temperature of 110°C. After completion (as monitored by TLC), the reaction mixture was diluted with cold water (5 mL) and extracted with ethyl acetate (3 × 10 mL). The catalyst was removed by filtration and the combined organic layers were washed with brine and dried over anhydrous Na$_2$SO$_4$. After concentration, the product was recrystallised from EtOAc–MeOH to afford the pure product.

1-phenyl-1H-1,2,3,4-tetrazole. (Table 3, Entry 1) yellow solid. m.p = 63–65°C; IR (KBr)/ v (cm$^{-1}$): 3051 (C-H, sp$^2$ stretch Ar), 1677 (C=N), 1588, 1488 (C=C); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm = 7.07–7.34 (m, 5H, ArH), 8.20 (s, 1H tetrazole); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm = 119, 123, 129, 145, 148.
1-(4-Bromophenyl)-1H-1,2,3,4-tetrazole. (Table 3, Entry 3) White solid. m.p = 183–185°C; IR (KBr)/ v (cm⁻¹): 3151 (C-H, sp² stretch, Ar), 1659 (C=N), 1576, 1481 (C=C); ¹H NMR (400 MHz, CDCl₃) δ ppm = 6.92–6.94 (d, 2H, ArH), 7.40–7.42 (d, 2H, ArH), 8.09 (s, 1H tetrazole); ¹³C NMR (100 MHz, CDCl₃) δ ppm = 116.43, 120.76, 132.03, 143.99, 149.29.

1-(4-Methylphenyl)-1H-1,2,3,4-tetrazole. (Table 3, Entry 2) Light yellow solid. m.p = 93–94°C; IR (KBr)/ v (cm⁻¹): 3022 (C-H, sp³ stretch, Ar), 2918 (C-H, sp³ stretch), 1664 (C=C), 1607, 1506 (C=C); ¹H NMR (400 MHz, CDCl₃) δ ppm = 2.34 (s, 3H, Me), 6.94–6.96 (d, 2H, ArH), 7.11–7.13 (d, 2H, ArH), 8.17 (s, 1H tetrazole); ¹³C NMR (100 MHz, CDCl₃) δ ppm = 20.79, 119.08, 129.63, 130.72, 144.10, 147.78.

1-(3-Methylphenyl)-1H-1,2,3,4-tetrazole. (Table 3, Entry 4) White solid. m.p = 112–114°C; IR (KBr)/ v (cm⁻¹): 3066 (C-H, sp² stretch, Ar), 2920 (C-H, sp³ stretch), 1680 (C=C), 1598, 1483 (C=C); ¹H NMR (400 MHz, CDCl₃) δ ppm = 2.33 (s, 3H, Me), 6.86 (s, 1H, ArH), 6.89–6.91 (d, 2H, ArH), 7.18–7.22 (t, 1H, ArH), 8.21 (s, 1H tetrazole); ¹³C NMR (100 MHz, CDCl₃) δ ppm = 21.43, 115.93, 119.97, 124.06, 129.19, 139.26, 145.28, 149.23.

1-(2-Methylphenyl)-1H-1,2,3,4-tetrazole. (Table 3, Entry 5) White solid. m.p = 153–155°C; IR (KBr)/ v (cm⁻¹): 3015 (C-H, sp³ stretch, Ar), 2870 (C-H, sp³ stretch), 1664 (C=C), 1488, 1590 (C=C); ¹H NMR (400 MHz, CDCl₃) δ ppm = 2.33 (s, 3H, Me), 7.02–7.03 (d, 1H, ArH), 7.05–7.07 (d, 1H, ArH), 7.18–7.22 (t, 2H, ArH), 8.08 (s, 1H tetrazole); ¹³C NMR (100 MHz, CDCl₃) δ ppm = 17.94, 117.68, 123.43, 127.81, 130.72, 144.10, 147.78.

1-(4-(4-Bromophenyl)-1H-1,2,3,4-tetrazole. (Table 3, Entry 6) Yellow solid. m.p = 148–150°C; IR (KBr)/ v (cm⁻¹): 3075 (C-H, sp² stretch, Ar), 2995 (C-H, sp³ stretch), 1669 (C=C), 1499, 1585 (C=C); ¹H NMR (400 MHz, CDCl₃) δ ppm = 2.60 (s, 3H, Me), 7.13–7.15 (d, 2H, ArH), 7.95–7.97 (d, 2H, ArH), 8.30 (s, 1H tetrazole); ¹³C NMR (100 MHz, CDCl₃) δ ppm = 26, 113, 118, 130, 132, 147, 196.

1-(2,4-Dimethylphenyl)-1H-1,2,3,4-tetrazole. (Table 3, Entry 7) White solid. m.p = 133–135°C; IR (KBr)/ v (cm⁻¹): 3069 (C-H, sp² stretch, Ar), 2914 (C-H, sp³ stretch), 1663 (C=C), 1495, 1607 (C=C); ¹H NMR (400 MHz, CDCl₃) δ ppm = 2.29 (s, 3H, Me), 2.30 (s, 3H, Me), 6.94–6.96 (d, 1H, ArH), 6.98–7.00 (d, 1H, ArH), 7.02 (s, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃) δ ppm = 17, 20, 117, 127, 131, 132, 147, 159, 163.

1-(Naphthalene-1-yl)-1H-1,2,3,4-tetrazole. (Table 3, Entry 8) White solid. m.p = 181–183°C; IR (KBr)/ v (cm⁻¹): 3048 (C-H, sp³ stretch, Ar), 1658 (C=N), 1574, 1432 (C=C); ¹H NMR (400 MHz, CDCl₃) δ ppm = 7.23–8.27 (m, 7H, ArH), 8.36 (s, 1H tetrazole); ¹³C NMR (100 MHz, CDCl₃) δ ppm = 114, 122, 124, 125, 126, 126, 127, 128, 134, 149.

Results and discussion

Characterization of the ZnS nanocrystals

The microstructures of the synthesized zinc sulfide nanoparticles were confirmed by X-ray diffractometer (XRD), Diffuse Reflectance Spectroscopy (DRS), scanning electron microscope (SEM) and transmission electron microscope (TEM) techniques.

As revealed in Figure 2, there are three broad peaks in the XRD pattern of the synthesized ZnS nanoparticles. The diffraction peaks at 2θ values of 28.80, 48.70 and 57.00 corresponds to (111), (220) and (311) diffraction plans of cubic ZnS, respectively. According to the
Debye–Scherrer equation, the average particle sizes of the as-synthesized nano ZnS were calculated and the results show that nano ZnS was obtained with an average diameter of 17.8 nm.

As can be seen in Figure 3, the images of both scanning electron and transmission electron microscopes were confirmed the size of the nanoparticles as 24–28 nanometers.

UV–visible diffuse reflectance spectrum of ZnS nanoparticles in the wavelength range of 200–900 nm was shown in Figure 4. The band gap energy from UV-DRS was revealed the shift of band edge at shorter wavelength compared to bulk ZnS (337 nm) due to the particle size of nano ZnS. The amount of acid sites can be calculated by NH$_3$-TPD that in this study, the total acidity (mmol NH$_3$·g$_{\text{cat}}^{-1}$) of catalyst was obtained 0.32.

Catalytic activity of ZnS nanoparticles

Herein, an efficient microwave assisted synthesis of 1-substituted tetrazoles through one-pot [3+2] cycloaddition condensation reaction of sodium azide, primary amines and triethyl orthoformate with ZnS NPs is reported. In this synthetic method, the 1-substituted tetrazoles were obtained in high yields and convenient reaction times under solvent free conditions. The novelty of this method was included application of microwave in this synthesis and also using the green nano catalyst and safe process due to the usage of equal stoichiometric amounts of sodium azide. Consequently, the liberation of hydrazoic acid gas was avoided. Because of the stability and reusability of ZnS nanoparticles, they have attracted much interest in relation to the available methods by different catalysts. Additionally, this is the first report for the microwave promoted synthesis of 1-substituted-$1H$-tetrazole at solvent-free conditions.

In order to optimize the reaction conditions, typical reaction of aniline, triethyl orthoformate and sodium azide was chosen. Firstly, the reaction was carried out in the presence of various amounts of catalyst under solvent free conditions and at 600 watts of microwave oven. It was found that, in the presence of 0.06 g of

![Figure 2. The XRD pattern of zinc sulfide nanoparticles.](image)

![Figure 3. The SEM image (a) and TEM image (b) of ZnS nanoparticles.](image)

![Figure 4. UV–visible diffuse reflectance spectrum of ZnS nanoparticles.](image)
the catalyst, the reaction was completed after 20 min to afford the related products in 88% yield (Table 1). It is notable that in this protocol, the initial substrates were treated with only an equimolar amount of sodium azide for the reaction completion.

In order to investigate the optimization of the reaction temperature for the best yield of the desired product, the reaction was performed at microwave oven with various irradiation powers from 100 to 900 watts (Table 1, entries 1–6). It was observed that the desired product was produced only with 25% isolated yield at 100 watts power (Table 2, entry 1). On the other hand, the desired product was obtained in 88% yield at 600 watts power of irradiation (Table 2, entry 4). However, the higher power of microwave irradiation dose not produced desire product in higher yield, because of side reactions that occurred in high energy of irradiation (Table 2, entries 5 and 6). The side reactions in high energy power can be related to initial amine oxidation and also destructed of final products by thermolysis during reaction time (21, 22).

Also, for better understand of microwave in compared with the thermal conditions on the reaction yields and times, the sample reaction was performed in thermal conditions and the results were shown in Table 2. The results were indicated that the reaction under thermal condition was performed in higher reaction time and lower product yield than the reaction under microwave condition (Table 2, entries 7 and 8 vs. 4). The unique combination of zinc sulfide nanoparticles catalyst with microwave irradiation resulted in several useful features. Solid nanoparticles absorb microwave irradiation and convert them into heat, thus they can use as an internal heat source for the reaction. It is the most direct and selective heating that can provided for performing a reaction. The thermal effects largely result from a more efficient energy transfer to the reaction mixture which is known as dielectrically heating.

Microwave irradiation is used for a variety of organic syntheses due to short reaction times, easy workup and excellent yields. The scrutinized rate acceleration upon microwave irradiation is due to material–wave interactions leading to thermal and particular effects. The reaction mixture is heated from the inside since the microwave energy is transfered directly to the reagents. The solid catalysts absorb microwave

| Entry | Nano ZnS (g) | Time (min) | Yield (%)b |
|-------|-------------|------------|------------|
| 1     | –           | 120        | <2         |
| 2     | Bulk ZnS (0.1) | 60        | 11         |
| 3     | 0.02        | 40         | 43         |
| 4     | 0.04        | 40         | 58         |
| 5     | 0.05        | 30         | 74         |
| 6     | 0.06        | 20         | 88         |
| 7     | 0.07        | 20         | 88         |

aReaction conditions: aniline 1.0 mmol, triethyl orthoformate 1.2 mmol and sodium azide 1.0 mmol under 600 watts microwave irradiation at 60°C. bIsolated yields.

| Entry | Reaction conditions | Time (min) | Yield (%)b |
|-------|---------------------|------------|------------|
| 1     | Mw, 100 w           | 65         | 25         |
| 2     | Mw, 300 w           | 50         | 43         |
| 3     | Mw, 450 w           | 40         | 68         |
| 4     | Mw, 600 w           | 40         | 88         |
| 5     | Mw, 750 w           | 40         | 82         |
| 6     | Mw, 900 w           | 20         | 74         |
| 7     | Heat, 110°C         | 100        | 55         |
| 8     | Heat, 130°C         | 120        | 63         |

aReaction conditions: aniline 1.0 mmol, triethyl orthoformate 1.2 mmol, sodium azide 1.0 mmol and 0.06 g of ZnS NPs as catalyst. bIsolated yields.
Table 3. Synthesis of 1-substituted tetrazoles\(^a\).

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\begin{align*}
\text{Entry} & \quad \text{Amine} & \quad \text{Product} & \quad \begin{array}{c}
\text{Microwave condition} \\
\text{Time (min) / Yield (%)}\(^b\)
\end{array} & \quad \begin{array}{c}
\text{Thermal condition} \\
\text{Time (h) / Yield (%)}\(^b\)
\end{array} & \quad \text{Ref.} & \quad \text{TON} \\
1 & \text{NH}_2 & \text{NH}_2 & 20/88 & 4.5/78 & (24) & 14.66 \\
2 & \text{NHN}_{\text{H}} & \text{NHN}_{\text{H}} & 20/88 & 4.2/74 & (24) & 14.66 \\
3 & \text{BrN}_{\text{H}} & \text{BrN}_{\text{H}} & 22/85 & 4.5/79 & (25) & 14.10 \\
4 & \text{HOCN}_{\text{H}} & \text{HOCN}_{\text{H}} & 23/88 & 4.7/76 & (18) & 14.66 \\
5 & \text{NH}_{\text{H}} & \text{NH}_{\text{H}} & 25/84 & 4.5/64 & (25) & 14.00 \\
6 & \text{OCON}_{\text{H}} & \text{OCON}_{\text{H}} & 25/82 & 3.0/72 & (26) & 13.66 \\
7 & \text{CH}_{\text{H}} & \text{CH}_{\text{H}} & 25/80 & 4.5/63 & (24) & 13.30 \\
8 & \text{ClC}_{\text{H}} & \text{ClC}_{\text{H}} & 25/77 & 4.2/64 & (24) & 12.83 \\
9 & \text{ClN}_{\text{H}} & \text{ClN}_{\text{H}} & 23/79 & 4.5/68 & (25) & 13.10 \\
10 & \text{ClNH}_{\text{H}} & \text{ClNH}_{\text{H}} & 22/80 & 4.7/65 & (24) & 13.30 \\
11 & \text{ClNH}_{\text{H}} & \text{ClNH}_{\text{H}} & 28/78 & 5.5/61 & (24) & 13.00 \\
12 & \text{NH}_{\text{H}} & \text{NH}_{\text{H}} & 28/73 & 6.7/56 & (26) & 12.10 \\
13 & \text{CF}_{\text{H}} & \text{CF}_{\text{H}} & 23/87 & 4.8/76 & (25) & 14.50 \\
14 & \text{EON}_{\text{H}} & \text{EON}_{\text{H}} & 25/79 & 4.5/63 & (27) & 13.16 \\
\end{align*}
\]

\(^a\)Reaction conditions: a mixture of selected amine 1.0 mmol, triethyl orthoformate 1.2 mmol, sodium azide 1.0 mmol and ZnS NPs 0.06 g under 600 watt power of microwave irradiation at 60°C or thermal conditions were occurred. \(^b\)Isolated yields.
irradiation, thus they can serve as an internal heat source for the reactions (23). The efficiency of ZnS nanoparticles to promote this cyclization reaction was correlated to the activity of the catalyst surface. In order to determine the functional limitations of the reaction, a variety of primary aromatic amines were used to investigate the scope and generality of this process (Table 3). It was found that a wide range of aromatic amine derivatives containing electron withdrawing as well as electron donating groups produced corresponding tetrazoles in excellent yields (Table 3). Also, the resulted yields and times of the reaction under microwave conditions for all products was compared with the results related to thermal conditions in Table 3.

Due to the results from BET surface analysis, the specific surface area of the ZnS NPs (248 m²g⁻¹) is higher than the bulk material so there is increased catalytic activity and thereupon more catalytic reactions can occur at the same time. It is clear from the four sequences of steps that zinc sulfide could activate methoxy groups and facilitated sequential nucleophilic displacement by amine and azide anions.

In order to show the merit of this study, we compared the obtained results in the present work with the recently reported results. For this purpose, the reactions of 4-methyl aniline as substrate, triethyl orthoformate and sodium azide were chosen as a model reaction was carried out and investigated the yields and reaction times (Table 4). It is worth mentioning that this method is faster and simpler than the existing methods. The efficiency and generality of the ZnS NPs can be elucidated by comparison of the results in this protocol with the previously reported methods.

The possibility of recovering and recycling the catalyst from the reaction is one of the utmost important benefits for greener and commercial applicable processes. In order to study the recovery and reusability of catalyst, the reaction was carried out with aniline, triethyl orthoformate, and sodium azide as a model reaction under the optimized reaction conditions.

Table 4. Comparison of 1-substituted tetrazole synthesis by ZnS NPs with the literature reported methods.

| Entry | Catalyst          | Reaction conditions | Time (min): Yield (%) Ref. |
|-------|-------------------|---------------------|----------------------------|
| 1     | ZnS NPs           | Mw/ 600 w, 60°C     | 20: 88 [a]                 |
| 2     | Natrolite zeolite | 120°C               | 240: 83 (26)               |
| 3     | FeCl₃-SiO₂        | 130°C               | 135: 85 (18)               |
| 4     | FeCl₃-SiO₂        | Ultrasonic Ir./45°C | 135: 85 (18)               |
| 5     | IL [EtNH₃][NO₃]  | 50°C                | 45: 84 (11)                |
| 6     | IL [bbim]Br      | 30°C                | 80: 88 (15)                |
| 7     | Bentonite@Cu NPs | 120°C               | 180: 87 (28)               |
| 8     | IL [EtNH₃][NO₃]  | 100°C               | 45: 85 (11)                |

[a]This work.

After completion of the reaction, the mixture was diluted by 1:1 H₂O/EtOAc (10 ml), stirred at ambient temperature (20 min) and centrifuged to separate catalyst.

The solid catalyst was dried at 60°C under reduced pressure to obtain almost quantitatively of the crude ZnS nanoparticles. The reusability of catalyst was investigated and reused for seven times with a minimal loss of activity (Figure 5).

In order to investigate the crystallinity of nanoparticles catalyst after the reaction runs, the XRD pattern of reused catalyst was provided and indicated in Figure 6. It was founded that there are no changes in the crystallinity of the ZnS nanoparticles.

In accordance to the reported mechanism by P.N. Gaponik and co-workers (26) for the formation of 1-substituted tetrazoles, and reported works based on the catalytic activity of zinc sulfide nanoparticles as Lewis acid catalyst (29-32), a proposed reaction mechanism for present work was indicated in Scheme 1.
In this way, the triethyl orthoformate can be activated via coordination of oxygen to zinc atoms as acceptor of electron density at ZnS NPs, to eliminate the ethanol moiety followed by substitution of aniline molecule as a nucleophile. The intermediate A is formed and activated by the catalyst. Then, the A was treated with azide anion to remove an ethanol molecule for the formation of azidoimine B as intermediate. Finally, the target tetrazol was produced by intramolecular cyclization of B followed by regeneration of the catalyst.

Conclusions
In this research, an efficient and green method for the synthesis of 1-substituted 1H-tetrazoles was developed by microwave irradiation through heterocyclization reaction of aniline moieties, triethyl orthoformate and sodium azide with ZnS NPs. This novel protocol has significant advantages in competition with the previously reported methods such as; solvent free conditions, high yields, any side reactions, no elimination of HN₃ as a harmful and volatile gas, easy work-up and reusability of the catalyst.

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Notes on contributors
Hossein Naeimi was received his M.Sc. degree in 1991 from Shahid Beheshti University and Ph.D. degree in 1998 from Shiraz University. After working at Government College, he became Assistant Professor at University of Kashan and subsequently became Associate Professor in 2004 and Professor in 2008. His research interests include synthesis of organic compounds, heterocycles and nanocatalysts.

Fatemeh Kiani received her B.Sc. degree in Chemistry from the University of BuAliSina in 2008 and then her M.Sc. degree in organic chemistry from the Kashan university in 2012.

Mohsen Moradian received his B.Sc. degree in Chemistry from the University of Yazd, in 2002 and then his M.Sc. degree in Organic chemistry from University of Kashan in 2005. He received his Ph.D. degree in Organic Chemistry from the same University in 2013. He joined the Department of Organic Chemistry at the University of Kashan in 2013. His research interest includes the application of new methods and catalysts in organic synthesis.

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