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A multicomponent one-pot synthesis of thiazole derivatives under solvent free conditions using Fe_3O_4/ZnO nanocatalyst

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Abstract: An efficient and convenient procedure has been developed for the synthesis of thiazole derivatives by one-pot condensation reaction of isothiocyanates, thiourea and ethyl bromopyruvate under environmentally solvent free conditions. The ability of some synthesized compounds to scavenge the DPPH radical was measured and the results proved this observation. Moreover, the antimicrobial activity of some synthesized compounds proved by employing the disk diffusion test on Gram-positive and Gram-negative bacteria. The obtained results of disk diffusion test showed that compound **4a-4d** prevented the bacterial growth.

Keywords: 1,3-Thiazole, Isothiocyanate, Ethyl bromopyruvate, Tetramethyl thiourea, Ammonium thiocyanate, Fe3O4/ZnO nanoparticles, Multi-component reaction.

Introduction

Multicomponent reactions (MCRs), with three or more reactants join in a one-pot procedure to afford a single product [1-3]. They are economically and environmentally useful because multi-step synthesis produce large amounts of trash frequently because of complex isolation actions frequently involving comfortable, toxic, and hazardous solvents after each step [4-7]. MCRs are absolutely suited for combinatorial library synthesis and increased utilize in the finding procedure for new drugs and agrochemicals [8]. They supply a dominant tool toward the one-pot synthesis of diverse and complex compounds as well as small and drug-like heterocycles [9]. Green chemistry move towards hold out significant potential not only for reduction of byproducts, waste produced, and lowering of energy but also in the expansion of new methodologies toward before exclusive materials, using existing technologies [10].

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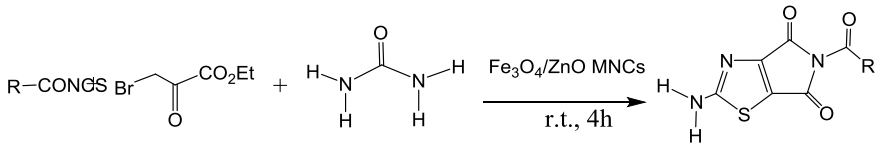
Between existing part of chemistry, medicinal and pharmaceutical chemistry are possibly developed for greening [11]. Thiazoles occupy a prominent position among heterocycles. In nature, the thiazolium ring is the chemically active center in the coenzyme derived from vitamin B1 (thiamin). A large number of thiazoles obtained from microbial and marine origins exhibit important biological effects such as antitumor, antifungal, antibiotic, and antiviral activities [12]. Synthetic thiazoles have also been shown to exhibit a wide variety of biological activity [13], while others have found application as liquid crystals [14] and cosmetic sunscreens [15]. The classical method for the synthesis of thiazoles is the Hantzsch process, in which a □-haloketone is condensed with a thioamide [16]. This method gives excellent yields for simple thiazoles. This method gives excellent yields for simple thiazoles; however, for some substituted examples low yields have been reported as a result of

dehalogenation of the haloketone during the reaction [15, 17]. As part of our current studies on the development of new routes in heterocyclic synthesis [18-21], we report an efficient synthetic route to functionalized thiazoles. It can refer to the formation of nanoparticle structures which capped by organic materials from living organisms or plants. This method is a cheap, bio friendly, safe and green procedure. These plants extract show some phytochemicals properties that play in both decreasing capping and stabilization agent. Recently, nanoparticles have become the subject of important research, since they have shown to be potential in many applications. Commonly, several various chemical and physical methods have been applied so far for the preparation Fe_3O_4/ZnO MNPs. The Fe_3O_4 encapsulated with ZnO nanoparticles gives better results in biomedicine because ZnO is biocompatible (non-toxic) and easy to penetrate cells.[30] Gordon et al. in 2011 synthesized Fe_3O_4/ZnO MNPs and studied its antimicro-bial activity. Li et al. in 2016 prepared Fe_3O_4/ZnO MNPs used as a nanoprobe for fluorescent chemosensor. Roeinfard et al. in 2017 synthesized Fe_3O_4/ZnO MNPs sol-gel method and investigated its cytotoxicity against breast cancer cells.Diverse physical and chemical methods are employed for the preparation of Fe_3O_4 and Fe_3O_4/ZnO MNPs such as co-precipitation, hydrothermal, microemulsion and biosynthesis. Also, compounds that have the antioxidant activity due to their redox properties and chemical structure have chief roles such as middle metals chelators and filling singlet and triplet oxygen molecules with the negative effect of free radicals. Many diseases such as cardiovascular, inflammatory bowel syndrome, cancer, ageing, atherosclerosis, and Alzheimer's disease could be prevented or decreased by employing these compounds. At present, bacteria that are resistant to drugs have generated considerable problems in the performance of many communicable diseases. Therefore, discovering new ways to extirpate these pathogens are important. For this reason, recent studies have focused on the study of the antibacterial effects of new synthesized compounds.

Results and discussion

The reaction of isothiocyanate **1**, ethyl bromopyruvate **2** and thiourea **3** produced 1,3-thiazole derivatives **4** in 78-90% yields (Scheme **1**).



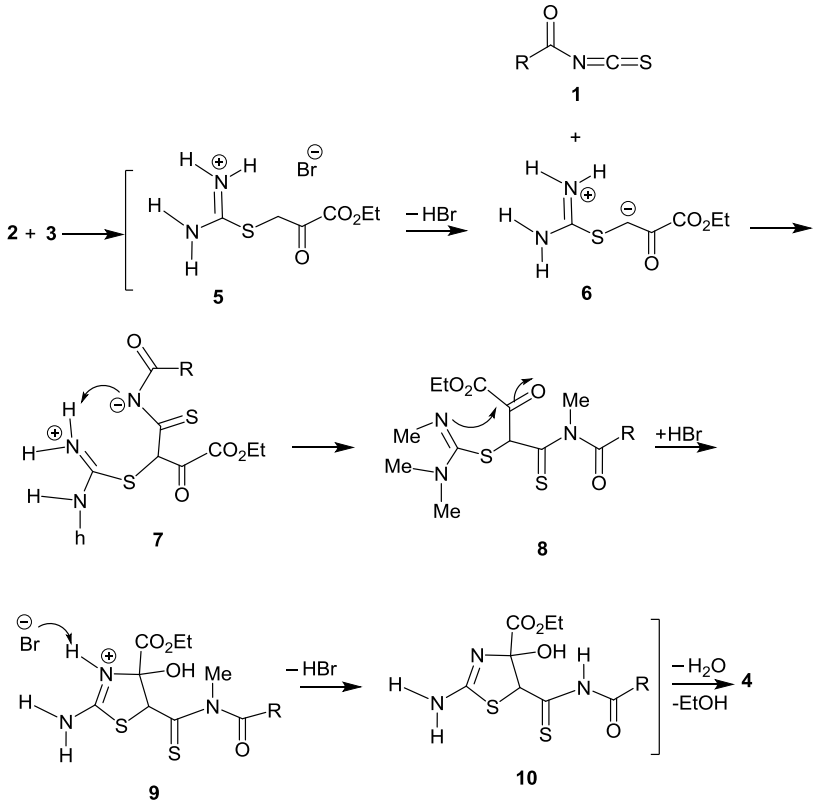
1 **2** **3** **4**

1, 4	R	Yield/ % of 4
a	Ph	90
b	*p*-Me-C_6H_4	85
c	*p*-NO_2-C_6H_4	83
d	*p*-Br-C_6H_4	78
e	*p*-Cl-C_6H_4	82

Scheme 1. Synthesis of thiazole derivatives **4**.

The structures of compounds **4a**–**4e** were apparent from their mass spectra, which displayed in each case, the molecular ion peak at the appropriate *m/z* values. The ^{1}H and ^{13}C-NMR spectroscopic data, as well as IR spectra, are in agreement with the proposed structures. For example, the ^{1}H-NMR spectrum of **5a** exhibited one triplet at 1.32 (J = 7.2) from methyl proton, three singlet for NMe groups at 3.27, 3.32 and 3.46 and one quartet at 4.23 (J = 7.2) for OCH_2 moiety. The carbonyl and thionyl groups resonances in the ^{13}C-NMR spectra of **4a** appear at 167.1 (C=O), 177.4 (C=O) and 208.2 (C=O) ppm. The mass spectrum of **4a** displayed the molecular ion peak at *m/z* = 377. Mechanistically, it is conceivable that the reaction

involves the initial formation of intermediate **5** between **2** and **3**, which elimination of HBr of **5** generate **6**. This intermediate undergoes a nucleophilic attack to **1** to produce **7.** Finally, water elimination from **10** produces **4** (Scheme **2**).



Scheme 2. Proposed mechanism for the formation of **4**.

The shape of Fe_3O_4-MNPs (Figure **1a**), ZnO-NPs (Figure **1b**) and Fe_3O_4/ZnO-MCNPs (Figure **1c**) was confirmed by giving SEM image.

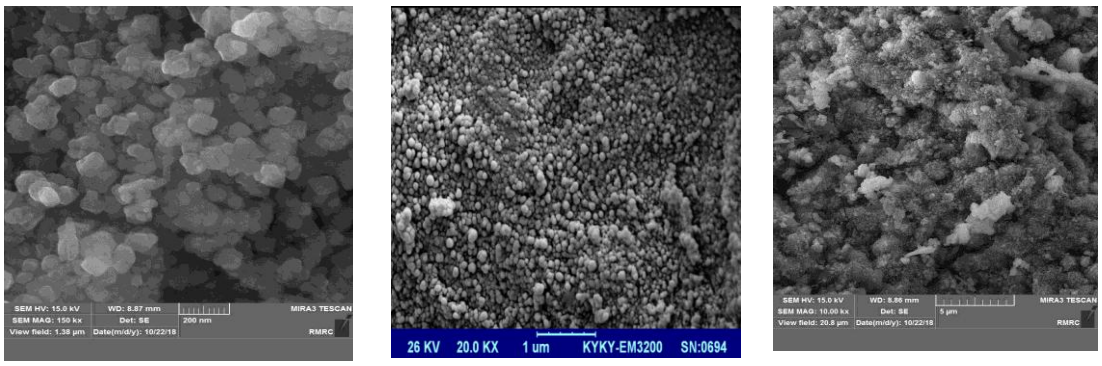


Figure 1. 1a.SEM image of ZnO-NPs; **1b.** Fe_3O_4-MCNPs **1c.** Fe_3O_4/ZnO MCNPs.

The XRD pattern of the Fe_3O_4-MCNPs (Figure **2b**), ZnO-NPs (Figure **2a**) and Fe_3O_4/ZnO-MCNPs (Figure **2c**) confirmed the nanoscale of catalyst. The average crystal size for Fe_3O_4/ZnO MCNPs is about 45 nm. For

the prepared Fe_3O_4 nanoparticles the diffraction peaks appear at ~ 30.3◦, 35.5◦, 43.2◦, 57.2◦and 62.7◦which are indexed to (220), (311), (400), (511) and (440) planes. It was confirmed to cubic inverse spinel structure compared well with the JCPDS card no. 19–0629. For Fe_3O_4/ZnO MNPs, the diffraction peaks indexed as (100), (002), (101), (102), (110), (103), (112) and (202) planes which correspond to the hexagonal crystal structure of ZnO nanoparticles and are well matched with JCPDS card no. 36–1451. EDX spectrum of Bio-Fe_3O_4/ZnO MCNPs for the sample indicates the clear presence of Fe, O and Fe, Zn, O compo-nents in Figure **5**. There is no impurity peak is observed in the EDX spectra and this confirms that the prepared samples are pure form and also shows the uniform distribution of constituent elements.

To obtain a clear size, shape and structural image of the nanoparticles the sample was analyzed using transmission electron microscopy (Figure **6**). Transmission electron microscope image reveals the size of the synthesized Fe_3O_4/ZnO-MCNPs to be less than 40 nm.

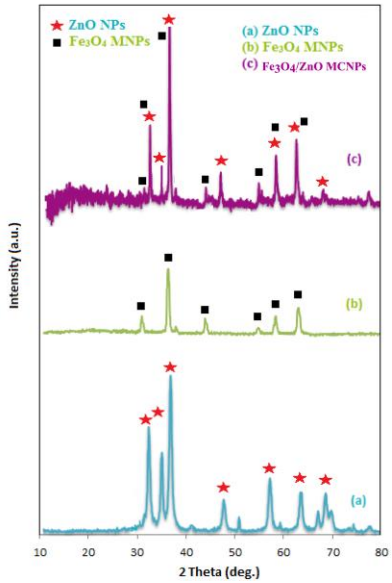


Figure 2. XRD spectra of a) ZnO-NPs; b) Fe_3O_4 MNPs; c) Fe_3O_4/ZnO MCNPs.

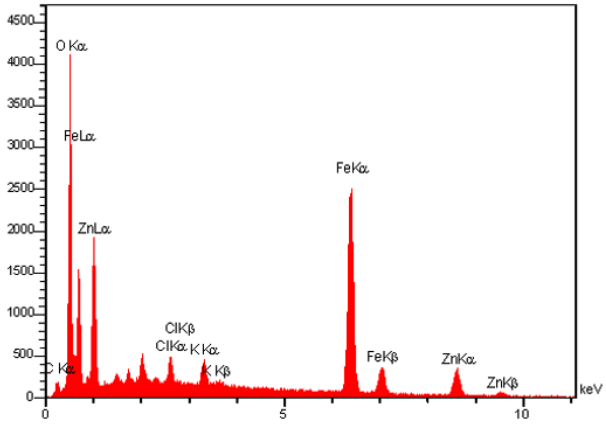


Figure 3. EDX spectra of Bio-Fe_3O_4/ZnO MCNPs.

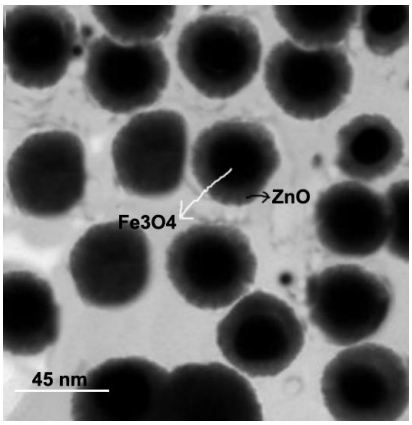


Figure 4. TEM image of the green Fe_3O_4/ZnO-MCNPs.

Study of antioxidant activity employing Diphenyl-2-picrylhydrazyl (DPPH):

For determination of antioxidant activity of some synthesized compounds and their antioxidant property in foods and biological systems [58, 59] as well as power of compounds to take free radicals, diphenyl-2-picrylhydrazyl (DPPH) radical trapping experiment is widely used. In this experiment, the DPPH radical takes the hydrogen atom (or one electron) of synthesized compounds **4a-4d** and gives an evaluation of antioxidant activity basis of free radical trapping. The absorption of DPPH radical was observed area 517 nm but when DPPH radical is reduced by an antioxidant or a radical species its absorption decreases. As shown from the results, free radical trapping activity of compounds **4a-4d** is weaker than to BHT and TBHQ. Therefore, concentration and structure were key factor on the DPPH trapping activity (P<0.05) (Figure **7**). Normally, the DPPH scavenging ability of these compounds was attained TBHQ>BHT>**4b**>**4c**>**4a**>**4d** respectively. The free radical trapping power had been enhanced from 200 to 1000 ppm. So, by rising concentration in all samples, the free radical activity was raised. For instance, compound **4f** with a concentration of 1000 ppm had 91.76% inhibition while a concentration of 200 ppm of compound **4f** was exhibited 47.93% free radical inhibition.

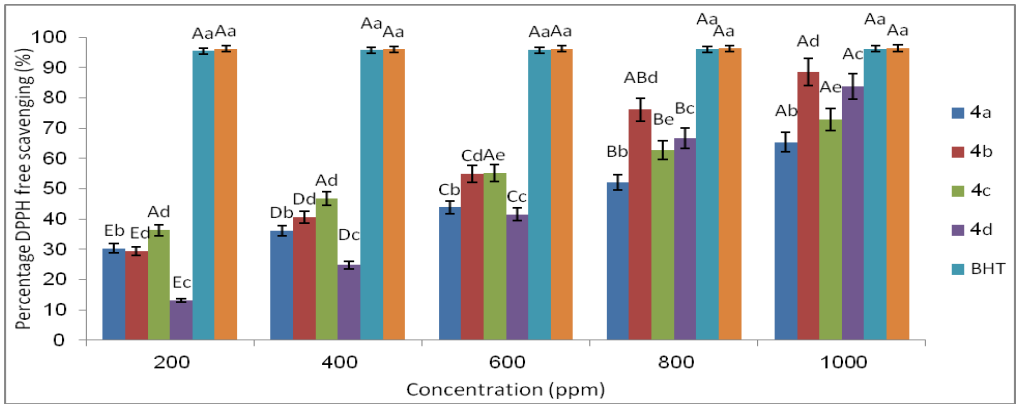


Figure 5. Radical trapping activity (RSA) of compounds **4a-4d**

Ferric ions (Fe^{3+}) reducing potential (FRAP):

Reducing power of the synthesized compounds was determined by calculating of the exchange amount of Fe^{3+}/ferricyanide complex to the Fe^{2+}/ferrous form at 700 nm.[55] The reducing power of compounds **4a-4d** compared with synthetic antioxidants (BHT and TBHQ) are showed in Figure **2**. The bigger reducing power means higher absorbance of the compounds. The reducing activity order of compounds **4a-4d** was

as following: TBHQ>BHT>**4b**>**4c**>**4a**>**4d** (Figure **8**). In all them, the increasing concentration was enhanced ferric ions reducing power. Compounds **5f** show very good reducing activity compared to standards (BHT and TBHQ).

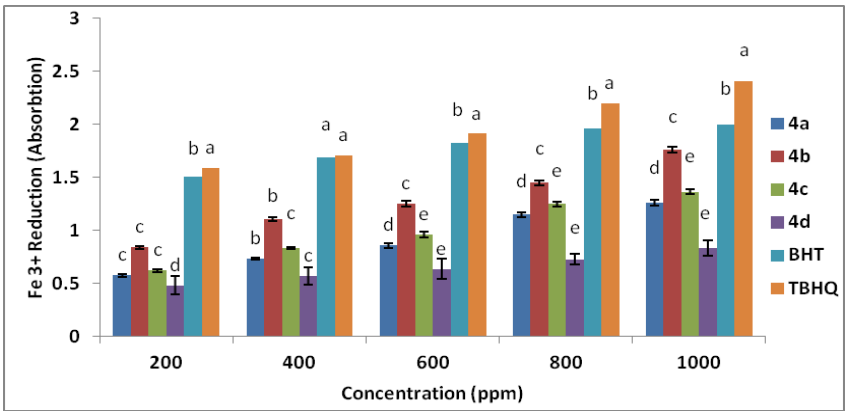


Figure 6. Ferric ions (Fe^{3+}) reducing antioxidant power (FRAP) of compounds **4a-4d**.

Analysis of the antibacterial activity of synthesized compounds:

Also, a comparison between the activity of our synthesized compounds with Streptomycin and Gentamicin as standard drug was discussed. The results of the antimicrobial activity of some synthezized compounds on bacterial species are shown in Table **1**. The present study indicated that the type of bacteria and concentration of compounds are effective on the diameter of the inhibition zone. It is apparent from the data listed in Table **3**, the synthesized compounds **4b, 4d, 4f** and **4h** are active against Gram positive and Gram negative bacteria So that the inhibition zone diameter of compounds has the maximum effect on *Escherichia coli*.

Table 1. The antibacterial activity of the tested compounds.

Compounds	***Staphylococcus aureus* (+)**	***Bacillus subtilis* (+)**	***Bacillus cereus* (+)**	***Pseudomonas aurignosa* (-)**	***Escherichia coli*(-)**	***Klebsiella pneumoniae* (-)**
4a	8	6	10	--	9	---
4b	18	19	19	17	22	19
4c	19	19	21	18	23	16
4d	---	5	8	---	12	3
4e	16	18	20	16	22	19
Streptomycin	16	24	24	19	25	23
Gentamicin	19	22	23	18	24	21

Conclusion

In conclusion, we have described a convenient route to functionalized 1,3-thiazoles from isothiocyanate, thiourea and ethyl bromopyruvate. The advantage of the present procedure is that the reaction is performed in water and the starting material can be used without

any activation or modification. The simplicity of the present procedure makes it an interesting alternative to other approaches. The procedure described here provides an acceptable one-pot method for the preparation of functionalized thiazols.

Experimental

All materials and solvents that are employed in this research are purchased from Fluka (Buchs, Switzerland) and employed with any purification. An Electrothermal 9100 apparatus and Shimadzu IR-460 spectrometer are used for measuring melting points and IR spectra respectively. For giving the ^{1}H, and ^{13}C-NMR spectra, a BRUKER DRX-400 AVANCE spectrometer at 400.1 and 100 MHz, respectively was employed. A FINNIGAN-MAT 8430 spectrometer with an ionization potential of 70 eV was used for recording mass spectra. The morphology of bio-ZnO NPs and bio-Fe_3O_4/ZnO MCNPs was characterized by scanning electron microscopy (SEM) using a Holland Philips XL30 microscope. Crystalline structure of bio-ZnO NPs and bio-Fe_3O_4/ZnO MNPs was characterized by X-ray diffraction (XRD) analysis at room temperature using a Holland Philips Xpert X-ray powder diffractometer, with CuK_α radiation (λ=0.15406 nm), with 2θ ranging from 20 to 80°. The average crystallite size was calculated using Scherrer's formula; $D= 0.9\lambda/\beta \cos\theta$, where D is the diameter of the nanoparticles, λ (CuK_α) =1.5406 Å and β is the full-width at half-maximum of the diffraction lines.

Preparation of Bio-Fe_3O_4/ZnO MNPs:

Dried *Petasites hybridus* rhizome (10 g) was poured in 100 mL water in two-neck round bottom flask (250 mL) under reflux condition. After 2 h, the mixture was filtered and water extract was applied for preparation of Fe_3O_4/ZnO-MNPs as following. $Zn(OAC)_2$ (1.5 g) and $FeCl_2.4H_2O$ (1.5 g) was solved in deionized water (10 mL). Then, *Petasites hybridus* rhizome water extract (30 mL) was added to previous mixture gently at 85 ^{o}C in round bottom flask for 8h. Then it was cooled to room temperature, sonicated for 10 min and were centrifuged at 7000 rpm for about 10 min for removing the unwanted organic matters and then were filtered. The precipitate was collected by filtration and washed with distilled water and ethanol (96%) for several times. The samples were then heated at 500 °C for 1 h. Bio-Fe_3O_4/ZnO MCNPs was dried in the air at room temprature during 24 h.

General procedure for preparation of compounds 4:

To a stirred solution of 0.15 g of ammonium thiocyanate (2 mmol) in 15 mL of acetone was added acid chloride (2 mmol), and the mixture was refluxed for 5 min. Then, a solution of 0.39 g of **3** (2 mmol) in acetone (10 mL) was added gently. Finally, 0.26 g of **4** (2 mmol) was added slowly at room temperature. The reaction mixture was then stirred for 12 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO_2; hexane/AcOEt 10:1) to afford the pure title compounds.

Ethyl 5-{[benzoyl(methylamino)]carbothioyl}-2-(dimethylamino)-1,3-thiazole-4-carboxylates (5a):

Yield: 0.68 g (90%). Orange powder, mp 122-124 °C. IR (KBr): 17210; 1653; 1510; 1372; 1124. ^{1}H-NMR: 1.32 (*t*, ^{3}J = 7.2, Me); 3.27 (*s*, Me); 3.32 (*s*, Me); 3.46 (*s*, Me); 4.23 (*q*, ^{3}J = 7.2, OCH_2); 7.43 (*t*, ^{3}J = 7.2, 2 CH); 7.53 (*t*, ^{3}J = 7.5, CH); 7.80 (*d*, ^{3}J = 7.5, 2 CH). ^{13}C-NMR: 14.1 (Me); 36.4 (Me); 36.9 (Me); 38.7 (Me); 62.2 (OCH_2); 128.4 (2 CH); 128.6 (2 CH); 129.5 (C); 130.1 (CH); 133.5 (C); 153.9 (C); 158.2 (C); 167.1 (C=O); 177.4 (C=O); 208.2 (C=S). EI-MS: 377 ($M^{+\bullet}$, 15), 272 (60), 243 (62), 223 (45), 134 (54), 105 (100), 45 (64). Anal. calc. for $C_{17}H_{19}N_3O_3S_2$ (377.74): C 54.09, H 5.07, N 11.13; found: C 54.10, H 5.05, N 11.10.

Ethyl 5-{[4-methylbenzoyl (methylamino)] carbothioyl}-2-(dimethylamino)-1,3-thiazole-4-carboxylates (5b):

Yield: 0.66 g (85%). Yellow powder, mp 130-132 °C, IR (KBr): 1720; 1655; 1512; 1369; 1022. ^{1}H-NMR: 1.41 (*t*, *J* = 7.2, Me); 2.42 (*s*, Me); 3.13 (*s*, Me); 3.26 (*s*, Me); 3.53 (*s*, Me); 4.42 (*q*, *J* = 7.2, OCH_2); 7.30 (*d*, *J* = 7.8, 2 CH); 7.52 (*d*, *J* = 7.8, 2 CH). ^{13}C-NMR: 13.9 (Me); 22.9 (Me); 36.4 (Me); 38.8 (Me); 43.1 (Me); 62.2 (OCH_2); 129.1 (2 CH); 129.5 (C); 130.1 (2 CH); 130.8 (C); 144.3 (C); 153.9 (C); 160.2 (C); 167.7 (C=O); 177.4 (C=O; 208.7 (C=S). EI-MS: 391 ($M^{+\bullet}$, 5), 272 (36), 243 (85), 192 (58), 148 (76), 119 (100), 45 (48). Anal. calc. for $C_{18}H_{21}N_3O_3S_2$ (391.50): C 55.22, H 5.41, N 10.73; found: C 55.20, H 5.40, N 10.70.

Ethyl 5-{[4-nitrobenzoyl(methylamino)]carbothioyl}-2-(dimethylamino)-1,3-thiazole-4-carboxylates (5c):

Yield: 0.70 g (83%). Red powder, mp 155-157 °C. IR (KBr): 1715; 1679; 1599; 1369; 1176; 1116. ^{1}H-NMR: 1.39 (*t*, *J* = 7.2, Me); 3.13 (*s*, Me); 3.28 (*s*, Me); 3.51 (*s*, Me); 4.43 (*q*, *J* = 7.2, OCH_2); 8.03 (*d*, *J* = 8.1, 2 CH); 8.32 (*d*, *J* = 8.1, 2 CH). ^{13}C-NMR: 14.0 (Me);

35.9 (Me); 37.0 (Me); 38.8 (Me); 62.2 (OCH_2); 123.6 (C); 123.8 (2 CH); 129.3 (2 CH); 131.1 (C); 137.9 (C); 150.3 (C); 153.9 (C); 167.4 (C=O); 177.4 (C=O); 208.3 (C=S). EI-MS: 422 ($M^{+\bullet}$, 10), 272 (66), 223 (45), 199 (62), 179 (64), 150 (100);, 45 (84). Anal. calc. for $C_{17}H_{18}N_4O_5S_2$ (422.47): C 48.33, H 4.29, N 13.26; found: C 48.30, H 4.30, N 13.25.

Ethyl 5-{[4-bromobenzoyl(methylamino)]carbothioyl}-2-(dimethylamino)-1,3-thiazole-4-carboxylates (5d):

Yield: 0.71 g (78%). Red powder, mp 152-154 °C. IR (KBr): 1762; 1724; 1664; 1579; 1369; 1101. ^{1}H-NMR: 1.42 (*t*, *J* = 7.2, Me); 3.05 (*s*, Me); 3.14 (*s*, Me); 3.47 (*s*, Me); 4.38 (*q*, *J* = 7.2, OCH_2); 7.59 (*d*, *J* = 7.8, 2 CH); 7.69 (*d*, *J* = 7.8, 2 CH). ^{13}C-NMR: 14.0 (Me); 36.4 (Me); 36.9 (Me); 38.8 (Me); 62.2 (OCH_2); 127.9 (C); 128.9 (2 CH); 129.1 (C); 129.4 (2 CH); 132.9 (C); 150.3 (C); 153.9 (C); 167.7 (C=O); 177.4 (C=O); 208.2 (C=S). EI-MS: 456 ($M^{+\bullet}$, 10), 454 (5), 272 (44), 257 (36), 243 (60), 213 (65), 184 (100), 45 (84). Anal. calc. for $C_{17}H_{18}BrN_3O_3S_2$ (456.37): C 44.74, H 3.98, N 9.21; found: C 44.70, H 3.95, N 9.20.

Ethyl 5-{[4-chlorobenzoyl(methylamino)]carbothioyl}-2-(dimethylamino)-1,3-thiazole-4-carboxylates (5e):

Yield: 0.67 g (82%). Yellow powder, mp 165-167 °C. IR (KBr): 1759; 1721; 1665; 1584; 1354; 1027. ^{1}H-NMR: 1.42 (*t*, *J* = 7.2, Me); 3.05 (*s*, Me); 3.14 (*s*, Me); 3.47 (*s*, Me); 4.38 (*q*, *J* = 7.2, OCH_2); 7.59 (*d*, *J* = 7.5, 2 CH); 7.69 (*d*, *J* = 7.5, 2 CH). ^{13}C-NMR: 14.3 (Me); 35.7 (Me); 37.0 (Me); 38.8 (Me); 62.4 (OCH_2); 128.4 (2 CH); 129.2 (C); 130.1 (2 CH); 132.5 (C); 136.4 (C); 150.4 (C); 154.0 (C); 168.2 (C=O); 177.5 (C=O); 208.4 (C=S). EI-MS: 411 ($M^{+\bullet}$, 15), 243 (34), 212 (80), 199 (46), 168 (86), 139 (100), 45 (36). Anal. calc. for $C_{17}H_{18}ClN_3O_3S_2$ (411.92): C 49.57, H 4.40, N 10.20; found: C 49.55, H 4.40, N 10.21.

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