Ni@zeolite-Y nanoporous; a valuable and efficient nanocatalyst for the synthesis of N-benzimidazole-1,3-thiazolidinones

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ABSTRACT

In this project, Ni(II) ion stabilized on zeolite-Y (NNZ) was developed as a high efficient nanoporous catalyst for the synthesis of 3-benzimidazolyl-1,3-thiazolidin-4-one derivatives via condensation of 2-aminobenzimidazole, aromatic aldehydes and thioglycolic acid in ethanol under ambient conditions. Compared with conventional protocols, this methodology has promising features such as the use of inexpensive, stable, recyclable and safe catalyst, shorter reaction times and higher yields, nontoxic solvent and easy isolation of the products.

INTRODUCTION

By having nitrogen and sulfur atoms in a five-membered ring, 1,3-Thiazolidin-4-ones are belonging to heterocyclic compounds that can be found as a core structure in the natural and synthetic pharmaceutical, agricultural compounds and displaying a broad spectrum of biological activities (1, 2). Also, some important derivatives of thiazolidinone, such as Rosiglitazone and Pioglitazone, are known marketed drugs with hypoglycemic action to treat diabetes (Scheme 1) (3).

Nowadays, so many reports on the biological activity of thiazole derivatives in various fields have convinced researchers to introduce innovative new pathways to synthesize them (4). The main method for synthesis of thiazolidinone is condensation of corresponding starting materials by refluxing in high temperature and toxic solvents during multi-step reactions and work-ups (5, 6). Recently, the one-pot catalytic approaches have been reported for the synthesis of 1,3-thiazolidinones by various catalysts or reagents such as DCC (7), Bi(SCH2CO2)3H3 (8), Schiff base MCM-41/CuSO4 (9), Pd NPs (10), silica gel (11), Alum (12), DIPEA reagent (13), catalyst-free, H2O (14), HClO4-SiO2 (15), Fe3O4/SiO2/Salen/Mn (16), CoFe2O4@SiO2 (17), ammonium persulfate (18) and La(NO3)3 (19). However, all of these methodologies have some disadvantages including the use of toxic solvents, prolonged heating, tedious work-up, by-products and low yield.

Zeolites are valuable microporous aluminosilicates, which have been acting as molecular sieves, ion-exchangers and catalysts, and so far several reviews have been reported on their synthesis and application (20, 21). One of the significant properties of zeolites for catalytic applications is their ability to exchange cations without decomposing the crystalline structure (22). Also, the use of solid heterogeneous catalytic systems has provided some of the most attractive fields in organic transformations and chemical industries (23, 24). They have many advantages such as thermal stability, persistence in all organic solvents, low-cost handling, nontoxic and environmentally safe. In recent decades, development of solid acids as catalyst for variety of organic reactions has become a major area of research. One of the major problems of the homogeneous acid catalysts is the difficulty in separating the catalysts from the reaction mixture at the end of the process. Therefore, the use of catalysts on solid supports has received significant attention (23–26).

By considering these facts and as part of ongoing research on using the new nanocatalysts in the synthesis of heterocyclic compounds containing benzimidazole nucleus (23, 24), we decided to report the preparation, identification and application of Ni@zeolite-Y nanoporous as an effective nanocatalyst for the synthesis of 2-((1H-benzo[d]imidazol-2-ylamino)(aryl)-1,3-thiazolidin-4-ones, 4a–1 derived from raw materials including
2-aminobenzimidazole, aromatic aldehydes, and 2-mercaptoacetic acid under a mild and green three-component reaction (Scheme 2).

Results and discussion

Nano-nickel/zeolite-Y (NNZ) was prepared using a previously reported procedure (23, 24). In order to obtain the nano-size Ni@zeolite, ultrasonic irradiation was used. FT-IR spectra of zeolite and Ni-doped zeolite is depicted in Figure 1. The broad peak in 3418 cm\(^{-1}\) region is related to the O–H stretching of hydrogen-bonded internal silanol groups and hydroxyl stretching of water, while the peak at 1634 cm\(^{-1}\) corresponds to the O–H group bending mode of water. Besides, the peaks around 1017 to 722 cm\(^{-1}\) are attributed to the

Scheme 1. Some commercial drugs containing the thiazolidine and 2-aminobenzimidazole moieties.

Scheme 2. Synthetic method for compounds 4a–l.

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Figure 1. The FT-IR spectrum (a) zeolite-Y and (b) Ni@zeolite-Y nano-porous.
symmetric and asymmetric stretching vibrations of the Si–O–Si groups, respectively. The displacement of IR bands to lower frequencies (red-shift) in the Ni@zeolite-Y spectrum, as compared with zeolite-NaY, confirms the exchange of a number of Ni$^{2+}$ (heavier cation) with Na$^{+}$ ion (27). The comparison of these two IR spectra (bands at 575 and 578 cm$^{-1}$) also shows the structure of the final nanoporos product remains preserved (28).

Scanning electron microscopy (SEM) images of the Ni@zeolite-Y are shown in Figure 2. In Figure 2(a), SEM photograph indicated that the morphology of Ni@zeolite-Y crystals was obtained without the formation of separate amorphous mesoporous crystals. The image in Figure 2(b) showed that the particles are mainly about 10–47 nm. The layer structure of the zeolite is also shown in Figure 2(c). In Figure 2(e), the presence of all constituent elements (Ni, Na, Al, Si, and O) in Ni@zeolite-Y nanocomposite has been confirmed by energy dispersive X-ray (EDX) analysis.

Atomic absorption spectroscopy was performed to determine the concentration of Ni(II) ion loaded on zeolite which was 3.56 mmol/g (21%). Nitrogen adsorption/desorption isotherms of the zeolite-Y and Ni(II)@zeolite-Y samples are shown in Figure 3. The adsorption isotherms of the zeolite-Y exhibit the type I isotherm as defined by Brunauer (29), indicating the characteristic of a microporous structure. The N$_2$ isotherm of the Ni(II)@zeolite-Y shows type IV isotherms with a very small H$_1$ hysteresis loop in the range of 0.5–0.9 p/p$^0$ according to the IUPAC classification, indicating a mesoporous modified zeolite. Also, by the shape of its hysteresis, it can be seen that Ni(II)@zeolite-Y has cylindrical pores (30).

The values of the structural parameters obtained from the BET (Brunauer–Emmet–Teller) analysis are given in Table 1. $S_{BET}$ values correspond to the total area that includes the external surface of the particles and the internal surface described by pores. The $S_{BET}$ decreased from 619.66 m$^2$/g for parent zeolite-Y to 269.47 m$^2$/g for Ni(II)@zeolite-Y. Reduce surface area of the prepared nanocomposite indicated that the ion-exchange process occurred for the structural zeolite. Further, the data in this table reveals that the pore volume and maximum pore volume of Ni(II)/zeolite-Y decreased with cation exchange of nickel (II) ion inside the mesoporous of zeolite-Y.

In the next step, the catalytic potential of Ni(II)/zeolite-Y nonporous has been explored for the synthesis of thiazolidinone. The catalytic activity of modified zeolite-Y was examined on 4-nitrobenzaldehyde, 2-aminobenzimidazole and thioglycolic acid as an initial model reaction at room temperature in the presence of different amount of nanocatalyst and solvents. The results are summarized in Table 2. It can be found from the experimental results that the highest yield of the product was obtained with 10% w/w of NNZ in ethanol as reaction medium (Table 2, entry 2). It indicated that the yield of the reaction in the absence of nanocatalyst was negligible (Table 2, entry 9).

By extension of this method and employing various aromatic aldehydes under the optimized conditions, some 2-((1H-benzo[d]imidazol-2-ylamino)(aryl) 1,3-thiazolidin-4-one derivatives were synthesized via one-pot reaction. The results presented in Table 3. Based on these results, the nanocatalyst showed high activity for the preparation of various types of aryl aldehydes to afford the corresponding 1,3-thiazolidin-4-ones in excellent yields in short reaction times. Additionally, the work-up procedure was very simple, the amount of used catalyst is low and the time of the reaction is short in comparison to some previous methods. It should be noted that the yield of the corresponding product did not improve using aliphatic aldehydes such as formaldehyde, acetaldehyde, and propionaldehyde. This may suggest that donor-acceptor interactions between the π-electrons of the aromatic ring and empty d-orbital of surface nickel ions can improve this process for aromatic aldehydes.

Probable reaction mechanism for the preparation of the 1,3-thiazolidin-4-ones (4a–l) is proposed in Scheme 3. Firstly, nano-Ni@zeolite activates the carbonyl group of the aldehyde to form intermediate 2a–l, and then 2-aminobenzimidazole as a nucleophile attacks it to afford the intermediate 5 that is followed by catalytic oxidation to form the intermediate I. The Schiff base I is a stable structure with a high melting point that can be separated through a two-way route. In the second catalytic activating stage, the nucleophilic attack of thioglycolic acid takes place to produce the third intermediate II. Eventually, after the intermolecular nucleophilic attack and the loss of the second water molecule, cyclization of 1,3-thiazolidin-4-one rings 4a–l can be done.

Also, the recyclability of the NNZ catalyst was tested. For the first step, the model reaction was carried out under the optimized conditions. After the completion of the reaction, the nanocatalyst was separated with filtration. Then, the filtrated catalyst was refluxed in ethanol for 4 h and dried at oven to 100°C. The recycled nanocatalyst was reused five times without significant loss of catalytic activity. Furthermore, the Ni content of the recovered catalyst estimated by atomic absorption spectroscopy was 3.72 mmol/g (22%). Therefore, not the Ni leaking to the solution was observed.

The products of 4a–e and 4g–k have been reported in our previous work (19). The compounds 4f and 4l are new heterocycles and which their structures were
Figure 2. SEM image (a) and EDX spectrum (b) of Ni(II)@zeolite-Y nanoporous.
assigned using spectroscopic data. In the IR spectrum of compound 4l, two sharp bands at the region between 3478 and 1707 cm$^{-1}$ are related to vibrations of the NH and C = O groups, respectively. In the $^1$H-NMR spectra, two diastereotopic hydrogens that appear as a doublet with $J = 16.50–16.53$ Hz around 3.92–4.28 ppm are attributed to the methylene group of the thiazolidinone segment and the singlet signal at 12.45 ppm is referred to the resonance of NH proton of benzimidazole. The other signals observed at the expected region are consistent with their heterocyclic structures. In the mass spectrum of 4l, the molecular ion peak can be seen with an abundance of 100% and by considering the fragmentation pattern, cyclization mechanism at the last step of synthesis can be proved.

Furthermore, by considering literature reports on different synthesis pathway for preparation thiazolidin-4-one derivatives and comparing them with reaction conditions using recycled NNZ catalyst in Scheme 4, some evident advantages of earlier work such as short reaction time, no need to high temperature and toxic solvent, and good to excellent yield are undeniable.

### Experimental methods

#### General

All of the compounds were identified by their physical and spectroscopic data. IR spectra were recorded as KBr disc on a galaxy series FT-IR 5000 spectrometer. $^1$H-NMR and $^{13}$C-NMR spectra were recorded on Brucker spectrophotometer (300 MHz) in DMSO-$d_6$. The Mass spectra were recorded on an Agilent model: 5975C VL MSD with Triple-Axis detector spectrometer at 70 eV. To examine the shape, size and atom type of nanoparticles, FE-SEM and EDX image was acquired by using a MIRA III from TESCAN Company and Philips XL30. Nitrogen adsorption and desorption isotherms (BET analysis) were measured at 196°C by a Japan Belsorb II system after the samples were vacuum dried at 150°C overnight. Melting points were measured by using capillary tubes on an electrothermal digital apparatus and are uncorrected.

### Table 1. Porosimetry values for zeolite-Y and its functionalized.

| Material               | $S_{BET}$ $^{a}$ (m$^2$.g$^{-1}$) | $V_{BET}$ $^{b}$ (cm$^3$.g$^{-1}$) | $D_{BJH}$ $^{c}$ (nm) | $V_{BJH}$ $^{d}$ (cm$^3$.g$^{-1}$) | $D_{PS}$ $^{e}$ (nm) | $V_{APS}$ $^{d}$ (cm$^3$.g$^{-1}$) | $P$ $^{e}$ (nm) |
|------------------------|----------------------------------|----------------------------------|----------------------|----------------------------------|----------------------|----------------------------------|----------------|
| Zeolite -Y             | 619.66                           | 0.0667                           | 4.84                 | 0.3091                           | 9.6827               |                                  |                |
| Ni(II)/zeolite-Y       | 269.47                           | 0.0536                           | 5.13                 | 0.1189                           | 20.7506              |                                  |                |

$^{a}$Specific surface area.

$^{b}$Pore volume.

$^{c}$Pore size (calculated from the adsorption branch).

$^{d}$Maximum pore volume at p/p$^*$ = 0.174699824 (estimated using the Horvath–Kawazoe method).

$^{e}$Average particle size (estimated using the Temkin method).

### Table 2. Optimizing the model reaction conditions at room temperature.

| Entry | Catalyst loading (%W) | Solvent | Time (min) | Yield (%) $^a$ |
|-------|------------------------|---------|------------|----------------|
| 1     | 5                      | EtOH    | 30         | 85             |
| 2     | 10                     | EtOH    | 25         | 95             |
| 3     | 15                     | EtOH    | 30         | 83             |
| 5     | 20                     | EtOH    | 45         | 68             |
| 5     | 10                     | MeOH    | 35         | 73             |
| 5     | 10                     | CHCl$_3$ | 60        | 53             |
| 7     | 10                     | MeCN    | 60         | 57             |
| 8     | 10                     | Acetone | 35         | 87             |
| 9     | 10$^b$                 | EtOH    | 120        | trace          |
| 10    | –                      | EtOH    | 60         |                |

$^a$Isolated yield.

$^b$This reaction was carried out using non-metallic nano zeolite.

$^c$Reaction was continued under reflux conditions for 4 h.

Figure 3. $N_2$ adsorption/desorption isotherms of the zeolite-Y and Ni@zeolite-Y samples.
Table 3. Synthesis of compounds 4a–l in the presence of 10%, w/w nano-Ni@zeolite-Y in ethanol at room temperature.

| Entry | Ar-CHO | Product | Time (min) | M.p. (°C) | Yield (%)a |
|-------|--------|---------|------------|-----------|------------|
| 1     |        | ![Image](4a) | 30         | 209–210 (208–210)b | 85         |
| 2     |        | ![Image](4b) | 25         | 245–246 (245–246) | 90         |
| 3     |        | ![Image](4c) | 30         | 261 (260–261)     | 93         |
| 4     |        | ![Image](4d) | 25         | 147–148 (146–148) | 93         |
| 5     |        | ![Image](4e) | 25         | 208–210 (207–210) | 95         |
| 6     |        | ![Image](4f) | 25         | 181–182         | 93         |
| 7     |        | ![Image](4g) | 25         | 229–230 (229–230) | 92         |
| 8     |        | ![Image](4h) | 30         | 244–246 (244–246) | 94         |
| 9     |        | ![Image](4i) | 30         | 265–267 (263–266) | 81         |

(Continued)
Preparation of nano-Ni@zeolite-Y

2.0 g NaY zeolite in a 150-mL flask (obtained in our laboratory in accordance with the previously reported method), was added to an aqueous solution of NiCl₂·2H₂O (0.01 M, 100 mL) at room temperature. The mixture was stirred for 24 h and then it was filtered. The resulting precipitate was washed with water until the filtrate was colorless. The Ni@zeolite-Y (0.2 g) was handled with ultrasound for 1 h to provide nano-size particles. The nanocatalyst was then used without further purification.

General procedure for the synthesis of thiazolidinones

A mixture of 2-aminobenzimidazole (1.1 mmol), aromatic aldehyde (1 mmol) and thioglycolic acid (1.2 mmol) in 5 mL ethanol was prepared. The mixture was stirred for 5 min. Nano-Ni@zeolite-Y (10%W) as a catalyst then was added and the reaction mixture stirred magnetically at room temperature. The progress and completion of the reaction was monitored by TLC (n-hexane/ethyl acetate: 2:1 v/v) during appropriate time periods. After completion of the reaction, 5 ml ethanol was added and the catalyst was separated by simple filtration. Filtrate was added to 10 ml of cold water and the precipitate was filtered off and washed with cold ethanol–water mixture. For more purification, the product was recrystallized from ethanol–water mixture and air dried.

Spectroscopic data for the new compounds

3-(1H-benzo[d]imidazol-2-yl)-2-phenylthiazolidin-4-one (4a)

IR (KBr) (νmax): 3360 (NH), 1700 (C=O), 1532 (C=N), 1381, 1269 (C=C), 1117 (C–N), 655 (C–S–C) cm⁻¹; ¹H-NMR (300 MHz, DMSO-d₆) δH: 12.44 (1H, s, NH), 7.50 (1H, d, J = 7.50 Hz, H-Ar), 7.24 – 7.39 (6H, m, H-Ar), 7.06 – 7.11 (2H, m, H-Ar), 6.77 (1H, s, CH), 4.17 (1H, d, J = 16.56 Hz, SCH₂), 3.93 (1H, d, J = 16.53 Hz, SCH₂) ppm; ¹³C-NMR (75 MHz, DMSO-d₆) δC: 171.7, 144.4, 141.4, 134.4, 128.6, 127.9, 125.3, 121.6, 111.2, 61.5, 32.0 ppm; MS (m/z, %): 295.1 (M⁺, 40), 249.1 (31), 220.1 (44), 133.1 (100), 105.1 (69), 77.1 (40).

3-(1H-benzo[d]imidazol-2-yl)-2-(2-hydroxyphenyl)thiazolidin-4-one (4b)

IR (KBr) (νmax): 3553 (OH), 3329 (NH), 1705 (C=O), 1532 (C=N), 1456, 1363, 1274 (C=C), 1231 (C–N), 669 (C–S–C) cm⁻¹; ¹H-NMR (300 MHz, DMSO-d₆) δH: 12.43 (1H, s, NH), 10.11 (1H, s, OH), 7.51 (1H, d, J = 7.23 Hz, H-Ar), 7.37 (1H, d, J = 7.32 Hz, H-Ar), 7.06 – 7.13 (3H, m, H-Ar), 6.92 (1H, d, J = 7.59 Hz, H-Ar), 6.83 (1H, d, J = 8.01 Hz, H-
Scheme 3. Proposed mechanism for the synthesis of compounds 4a–l.

Scheme 4. Comparison of some different synthetic methods for preparation of thiazolidin-4-ones.
3-(1H-benzo[d]imidazol-2-yl)-2-(5-bromo-2-hydroxyphenyl)thiazolidin-4-one (4c)

IR (KBr) \(\nu_{\text{max}}\) : 3412 (OH), 3348 (NH), 1690 (C=O), 1617, 1537 (C=N), 1467, 1369, 1274 (C=C), 1228 (C=N), 658 (C=S–C) cm\(^{-1}\);

\(^{13}\)C-NMR (75 MHz, DMSO-d\(_6\)) \(\delta_{C}\): 172.1, 154.1, 144.5, 139.8, 132.7, 128.8, 127.0, 124.4, 121.6, 121.5, 118.8, 117.5, 115.6, 111.8, 57.8, 32.1 ppm; MS (m/z, %): 311.1 (M\(^+\), 63), 238.1 (81), 220.1 (66), 160.1 (38), 118.1 (44), 77.1 (14), 58.1 (62), 43.1 (100).

3-(1H-benzo[d]imidazol-2-yl)-2-(3-methoxyphenyl)thiazolidin-4-one (4d)

IR (KBr) \(\nu_{\text{max}}\) : 3412 (OH), 3348 (NH), 1690 (C=O), 1617, 1537 (C=N), 1467, 1369, 1274 (C=C), 1228 (C=N), 658 (C=S–C) cm\(^{-1}\);

\(^{13}\)C-NMR (75 MHz, DMSO-d\(_6\)) \(\delta_{C}\): 172.1, 154.1, 144.5, 139.8, 132.7, 128.8, 127.0, 124.4, 121.6, 121.5, 118.8, 117.5, 115.6, 111.8, 57.8, 32.1 ppm; MS (m/z, %): 311.1 (M\(^+\), 63), 238.1 (81), 220.1 (66), 160.1 (38), 118.1 (44), 77.1 (14), 58.1 (62), 43.1 (100).

3-(1H-benzo[d]imidazol-2-yl)-2-(3-nitrophenyl)thiazolidin-4-one (4e)

IR (KBr) \(\nu_{\text{max}}\) : 3412 (OH), 3348 (NH), 1690 (C=O), 1617, 1537 (C=N), 1467, 1369, 1274 (C=C), 1228 (C=N), 658 (C=S–C) cm\(^{-1}\);

\(^{13}\)C-NMR (75 MHz, DMSO-d\(_6\)) \(\delta_{C}\): 172.1, 154.1, 144.5, 139.8, 132.7, 128.8, 127.0, 124.4, 121.6, 121.5, 118.8, 117.5, 115.6, 111.8, 57.8, 32.1 ppm; MS (m/z, %): 311.1 (M\(^+\), 63), 238.1 (81), 220.1 (66), 160.1 (38), 118.1 (44), 77.1 (14), 58.1 (62), 43.1 (100).

3-(1H-benzo[d]imidazol-2-yl)-2-(4-chlorophenyl)thiazolidin-4-one (4f)

White crystals; IR (KBr) \(\nu_{\text{max}}\) : 3324 (NH), 1708 (C=O), 1620, 1536 (C=N), 1488, 1450, 1366, 1270 (C=C), 1227, 1117, 1091 (C=N), 739, 722 (C=C), 658 (C=S–C) cm\(^{-1}\);

\(^{13}\)C-NMR (75 MHz, DMSO-d\(_6\)) \(\delta_{C}\): 171.6, 144.3, 144.1, 133.2, 130.6, 128.7, 127.9, 125.5 (2C), 123.8 (2C), 121.6, 60.8, 32.0 ppm; MS (m/z, %): 329.2 (M\(^+\), 80), 283 (60), 254.1 (100), 135.1 (45), 91.1 (26).

3-(1H-benzo[d]imidazol-2-yl)-2-(4-bromophenyl)thiazolidin-4-one (4g)

IR (KBr) \(\nu_{\text{max}}\) : 3324 (NH), 1708 (C=O), 1620, 1536 (C=N), 1488, 1450, 1366, 1270 (C=C), 1227, 1213, 1117 (C=N), 1108, 1009, 828, 739, 722, 658 (C=S–C), 500 cm\(^{-1}\);

\(^{13}\)C-NMR (300 MHz, DMSO-d\(_6\)) \(\delta_{C}\): 171.6, 144.3, 140.6, 132.4, 132.1, 128.6, 128.3 (d), 124.7, 124.6, 121.0, 119.7, 111.2, 60.9, 32.0, ppm; MS (m/z, %): 329.5 (M\(^+\), 100), 287.1 (21), 254.1 (59), 175.1 (24), 135.1 (76), 91.1 (41), 46.1 (77).

3-(1H-benzo[d]imidazol-2-yl)-2-(4-bromophenyl)thiazolidin-4-one (4h)

IR (KBr) \(\nu_{\text{max}}\) : 3413 (NH), 1706 (C=O), 1618, 1535 (C=N), 1486, 1450, 1369, 1270 (C=C), 1227, 1117 (C=N), 1006, 738, 722, 659 (C=S–C), 497 cm\(^{-1}\);

\(^{13}\)H-NMR (300 MHz, DMSO-d\(_6\)) \(\delta_{H}\): 12.42 (1H, s, NH), 7.49 (1H, d, J = 7.38 Hz, H-Ar), 7.35–7.44 (5H, q br, H-Ar), 7.06–7.11 (2H, m, H-Ar), 6.76 (1H, s, CH), 4.18 (1H, d, J = 16.50 Hz, SCH\(_2\)), 3.92 (1H, d, J = 16.53 Hz, SCH\(_2\)) ppm; \(^{13}\)C-NMR (75 MHz, DMSO-d\(_6\)) \(\delta_{C}\): 171.6, 144.3, 140.6, 132.4, 132.1, 128.6, 128.3 (d), 124.7, 124.6, 121.0, 119.7, 111.2, 60.9, 32.0, ppm; MS (m/z, %): 340 (M\(^+\), 100), 294.1 (86), 265.1 (39), 219.1 (37), 164.1 (27), 118.4 (43), 91.1 (28).

3-(1H-benzo[d]imidazol-2-yl)-2-(4-methoxyphenyl)thiazolidin-4-one (4i)

IR (KBr) \(\nu_{\text{max}}\) : 3378 (NH), 2961 (C–H), 1696 (C=O), 1622, 1545, 1493 (C=N), 1450, 1373 (C=C), 1270, 1251, (C=O), 1100 (C=N), 1118,753, 746, 644 (C=S–C) cm\(^{-1}\);

\(^{13}\)H-NMR (300 MHz, DMSO-d\(_6\)) \(\delta_{H}\): 12.44 (1H, s, NH), 7.51 (1H, d, J = 7.41, H-Ar), 7.36 (1H, d, J = 7.50, H-Ar), 7.25 (1H, t, J = 7.47, H-Ar), 7.03–7.13 (3H, m, H-Ar), 6.97 (1H, d, J = 7.14 Hz, H-Ar), 6.80 (1H, t, J = 7.47 Hz, H-Ar), 6.77 (1H, s, CH), 4.01 (1H, d, J = 16.47 Hz, SCH\(_2\)), 3.88 (1H, d, J =
16.23 Hz, \( \text{SCH}_2 \), 3.88 (3H, s, O\text{CH}_3) ppm; \(^{13}\text{C}-\text{NMR} (75 \text{ MHz}, \text{DMSO-}d_6) \delta_C: 172.0, 155.9, 144.5, 139.9, 132.8, 129.2, 128.5, 124.1, 121.7, 121.5, 120.3, 117.6, 111.9, 111.4, 57.6, 55.7, 32.0 ppm; MS (m/z, %): 326.2 (M\(^+\), 40), 294 (100), 220.1 (40), 91.2 (19), 46.1 (15).

3-(1H-benzo[d]imidazol-2-yl)-2-(4-methoxyphenyl)thiazolidin-4-one (4j)

IR (KBr) (\( \nu_{\max} \)): 3478 (NH), 1707 (C=O), 1638, 1617, 1540, 1511 (C=N), 1452, 1373 (C=C), 1270, 1254 (C=O), 1178 (C=N), 1116, 1026, 843, 726, 665 (C=S-C), 607 cm\(^{-1}\); \(^1\text{H}-\text{NMR} (300 \text{ MHz}, \text{DMSO-}d_6) \delta_H: 12.41 (1H, s, NH), 7.48 (1H, d, J = 7.14 Hz, H-Ar), 7.37 (1H, d, J = 7.53 Hz, H-Ar), 7.31 (2H, d, J = 8.61 Hz, H-Ar), 7.04–7.12 (2H, m, H-Ar), 6.83 (2H, d, J = 8.61 Hz, H-Ar), 6.71 (1H, s, CH), 4.17 (1H, d, J = 16.53 Hz, \text{SCH}_2), 3.91 (1H, d, J = 16.53 Hz, \text{SCH}_2), 3.68 (3H, s, O\text{CH}_3) ppm; \(^{13}\text{C}-\text{NMR} (75 \text{ MHz}, \text{DMSO-}d_6) \delta_C: 171.6, 158.9, 144.4, 133.2, 126.9, 121.6, 113.9, 113.7, 112.0, 61.5, 55.0, 32.2 ppm; MS (m/z, %): 325.2 (M\(^+\), 33), 279.1 (59), 250.1 (72), 165.1 (55), 135.1 (51), 118.1 (33), 91.1 (18).

2-2-10 3-(1H-benzo[d]imidazol-2-yl)-2-(3,4-dimethoxyphenyl)thiazolidin-4-one (4k)

IR (KBr) (\( \nu_{\max} \)): 3400 (NH), 1704 (C=O), 1637, 1617, 1537 (C=N), 1514, 1452 (C=C), 1273, 1256, 1239 (C=O), 1141 (C=N), 648 (C=S-C), 616, 478 cm\(^{-1}\); \(^1\text{H}-\text{NMR} (300 \text{ MHz}, \text{DMSO-}d_6) \delta_H: 12.42 (1H, s, NH), 7.48 (1H, d, J = 7.29 Hz, H-Ar), 7.38 (1H, d, J = 7.47 Hz, H-Ar), 7.05–7.13 (3H, m, H-Ar), 6.81 (2H, s, H-Ar), 6.70 (1H, s, CH), 4.16 (1H, d, J = 16.53 Hz, \text{SCH}_2), 3.90 (1H, d, J = 16.50 Hz, \text{SCH}_2), 3.72 (3H, s, O\text{CH}_3) ppm; \(^{13}\text{C}-\text{NMR} (75 \text{ MHz}, \text{DMSO-}d_6) \delta_C: 171.7, 148.8, 148.5, 144.4, 140.0, 133.4, 132.7, 121.7, 121.5, 117.7, 117.0, 111.8, 111.4, 109.7, 61.6, 55.4 (2C), 32.1 ppm; MS (m/z, %): 355.2 (M\(^+\), 100), 313.2 (61), 280.2 (50), 192.1 (17), 165.1 (81), 118.1 (30), 91.1 (18).

3-(1H-benzo[d]imidazol-2-yl)-2-(4-methylphenyl)thiazolidin-4-one (4l):

white crystals; IR (KBr) (\( \nu_{\max} \)): 3413 (NH), 1707 (C=O), 1638, 1617 (C=N), 1531, 1511, 1452, 1425, 1370, 1254, 1178 (C=N), 726, 665, 607 (C=S-C) cm\(^{-1}\); \(^1\text{H}-\text{NMR} (300 \text{ MHz}, \text{DMSO-}d_6) \delta_H: 12.41 (1H, br, NH), 7.51 (1H, d, J = 7.62 Hz, H-Ar), 7.38 (1H, d, J = 7.17 Hz, H-Ar), 7.27 (2H, d, J = 7.89 Hz, H-Ar), 7.03–7.11 (4H, m, CH), 6.71 (1H, s, H-Ar), 4.15 (1H, d, J = 16.53 Hz, \text{SCH}_2), 3.91 (1H, d, J = 16.56 Hz, \text{SCH}_2), 2.21 (3H, s, CH\(_3\)) ppm; \(^{13}\text{C}-\text{NMR} (75 \text{ MHz}, \text{DMSO-}d_6) \delta_C: 171.6, 144.4, 138.4, 137.3, 137.0, 136.8, 129.7, 129.5, 129.1, 128.9, 126.6, 125.3, 121.6, 119.8, 61.5, 32.12, 20.6 ppm; MS (m/z, %): 309.2 (M\(^+\), 100), 263.1 (71), 234.1 (75), 175.1 (27), 135.1 (74), 91.2 (26).
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