Green Synthesis of Pyrazolo-thiazolidine-4-ones Using Magnetic Nanocomposite of Multiwalled Carbon Nanotube

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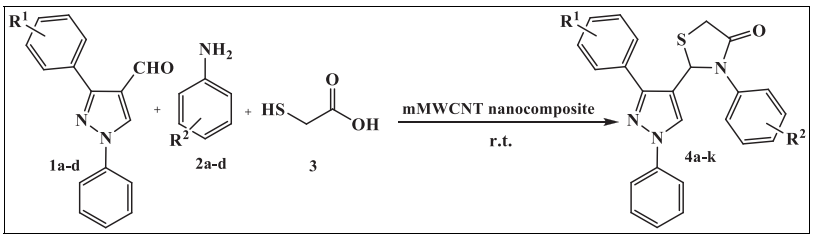

Magnetic multiwalled carbon nanotube nanocomposite as a recoverable catalyst for the synthesis of novel 1,3-thiazolidine-4-ones at room temperature in a one-pot procedure without additional organic solvents. IR, ^{1}HNMR, and ^{13}CNMR spectroscopies and elemental analysis were used for the identification of these compounds. Moreover, the catalyst could be easily recovered by magnetic separation and recycled for five runs without significant loss of its catalytic activity. All of synthesized compounds were characterized by IR, NMR, and elemental analyses.

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INTRODUCTION

Thiazolidine compounds are known to contribute to various pharmacological effects. Because of wide range of pharmacological activities, significant amount of research activities has been directed towards this class of compounds. Thiazolidines are used as antiseizure, fungicidal, antibacterial, antitubercular, anti-inflammatory, antiamoebic, antidiabetic, and local anesthetic agents [1,2]. Some of these compounds have also shown antiparkinsonism [3], antioxidant [4], anticonvulsant [5], hypoglycemic [6], and non-narcotic analgesic [7] activities. On the other hand, pyrazoles have shown antibacterial, antitumor, antiviral, antifungal, antitubercular, antiparasitic, anesthetic, antidiabetic, anti-inflammatory, analgesic, and insecticidal activities [8].

Development of the efficient and versatile methods for the synthesis of 1,3-thiazolidine-4-ones continues to be an active area of research, because of their important role in the realm of organic chemistry such as pharmaceutical and biological agricultural chemistry [1–8]. In recent years, a few reagents and media such as silica gel [9], silica chloride [10], Bi $(SCH_2COOH)_3$ [11], $ZnCl_2$ [12], HBTU [13], [BMIm][PF_6] [14], *Saccharomyces cerevisiae* [15], DCC [16], supported protic acid [17], and nano-Fe_3O_4@SiO_2 supported ionic liquid [18] have been employed for the synthesis of 1,3-thiazolidine-4-ones. However, some of the existing protocols suffer from the drawbacks as low yield, long reaction time, and leaving toxic residues. To the best of our knowledge, there is no report in the literature on the use of magnetic nanocomposite of multiwalled carbon nanotube (mMWCNT) as an effective catalyst for the regioselective synthesis of pyrazolo-1,3-thiazolidine-4-ones. Looking for the eco-friendly alternatives to classical syntheses [9–18] and in developing green chemistry [19–21], we report herein the regioselective synthesis of some novel pyrazolo-1,3-thiazolidine-4-ones at room temperature using the mMWCNT.

RESULTS AND DISCUSSION

In continuation of our ongoing studies to synthesize the heterocyclic and pharmaceutical compounds at mild and practical protocols [22–26], herein, we report our experimental results on synthesis of 2-pyrazolo-3-phenyl-1,3-thiazolidine-4-ones using various synthetized pyrazolecarbaldehydes, anilines, and thioglycolic acid in the presence of mMWCNT nanocomposite at room temperature (Scheme 1).

In order to optimize the model process and to examine efficiency of the novel catalyst in these reactions, several available catalysts or ionic liquids were chosen as the medium for comparison. In these experiments, pyrazolecarbaldehyde **1a**, 4-methoxy aniline **2a**, and thioglycolic acid **3** were mixed together with 10 mL of H_2O (entries 1–4 and 8–10) in the presence of various solid catalysts (0.1 g) or 2 mL of ionic liquids (entries 5–7) (Table 1). Among the tested catalysts or media, the

Scheme 1. Synthesis of novel 2-pyrazolo-3-phenyl-1,3-thiazolidine-4-ones using magnetic nanocomposite of multiwalled carbon nanotube (mMWCNT).

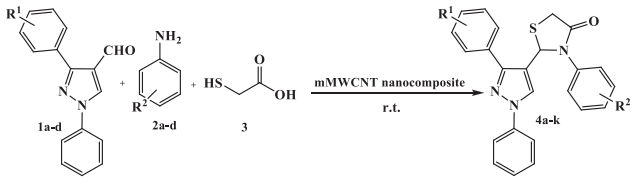

Table 1

Comparison of different catalysts or media for optimum synthesis of pyrazolo-thiazolidine-4-one **4a** at room temperature.

Entry	Catalyst[a,b] or Media[c]	Time (h)	Yield (%)
1	Silica gel	24	—
2	$ZnCl_2$	24	—
3	K10	24	—
4	*L*-proline	24	—
5	[BMIm][PF_6]	24	58
6	[BMIm]Br	24	72
7	[BMIm]HSO_4	24	83
8	Nano-SiO_2	12	70
9	Nano-Fe_3O_4	6	72
10	mMWCNT	1	92

mMWCNT, magnetic nanocomposite of multiwalled carbon nanotube.
[a]0.1 g of catalyst and 10 mL of H_2O (as a solvent) was used (entries 1–4).
[b]0.1 g of catalyst was used in solvent-free condition (entries 8–10).
[c]2 mL of ionic liquids were used (entries 5–7).

magnetic nanocomposite was the most appropriate catalyst for the reactions not only in high yield but also with high reaction rate (92% yield in 1 h) (Table 2). Moreover, our results showed that 0.1 g of mMWCNT is enough for the synthesis of pyrazolo-1,3-thiazolidine-4-one **4a** (Table 3).

Table 2 compares efficiencies for the synthesis of **4a** at various temperatures. It is clear that increasing the temperature has no effect in reaction time and yield. On the other hand, the best temperature for the synthesis of pyrazolo-thiazolidine-4-one **4a** was room temperature.

Investigation of the reaction scope revealed that various pyrazolcarbaldehydes and anilines can be utilized in this protocol (Table 4). It was shown that the synthesized aldehydes with electron-withdrawing groups reacted faster than those with electron-releasing groups. Meanwhile, it has been observed that better yields are obtained with substrates having electron-withdrawing groups (Table 4).

To evaluate the reusability of the magnetic nanocomposite, it was easily separated from the reaction medium by the super magnet and washed by H_2O. Then, the nanocomposite was distilled under vacuum to recover the solvent for reuse in subsequent reactions. After six successive runs, the recycled nanocomposite showed no loss in efficiency with regard to reaction time and yield (Table 5).

Table 2

The effect of temperature in the synthesis of pyrazolo-thiazolidine-4-one **4a** using magnetic nanocomposite of multiwalled carbon nanotube.

Entry	Temperature (°C)	Time (h)	Yield (%)[a]
1	100	2	92
2	80	1	93
3	60	1	92
4	RT	1	92

RT, room temperature.
[a]0.1 g of mMWCNT nanocomposite was used as a catalyst.

Table 3

Effect of magnetic nanocomposite of multiwalled carbon nanotube amount in the synthesis of **4a** at room temperature.

Entry	Catalyst amount (g)/1 mmol of aldehyde	Time (min)	Yield (%)
1	0.05	120	85
2	0.10	60	92
3	0.20	60	91
4	0.30	60	92

Table 4

Synthesis of pyrazolo-1,3-thiazolidine-4-ones (**4a–k**) using magnetic nanocomposite of multiwalled carbon nanotube.

Entry	Product[a]	R^1	R^2	Time (h)	Yield (%)[b]
1	**4a**	4-Cl	4-OCH_3	1	92
2	**4b**	H	4-OCH_3	1.5	90
3	**4c**	H	2-CH_3-4-NO_2	2	86
4	**4d**	4-Cl	2-CH_3-4-NO_2	2	90
5	**4e**	3-NO_2	2-CH_3-4-NO_2	2	90
6	**4f**	H	H	2	88
7	**4g**	H	4-NO_2	2	82
8	**4h**	4-Cl	4-NO_2	1.5	83
9	**4i**	3-NO_2	4-NO_2	2	83
10	**4j**	H	4-CH_3	2	85
11	**4k**	4-OH	4-NO_2	2	82

[a]All products were characterized by their physical constant, IR, NMR, and elemental analyses.
[b]Yields based upon the starting aldehyde.

Table 5

Evaluation of reusability of magnetic nanocomposite of multiwalled carbon nanotube for the synthesis of **4a**.

Run	1	2	3	4	5	6	7
Time (min)	60	60	60	60	60	60	90
Yield (%)	92	92	91	92	90	92	85

CONCLUSION

We have developed an efficient protocol for the synthesis of novel pyrazolo-1,3-thiazolidine-4-ones using mMWCNT nanocomposite as an effective and new catalyst. Simplicity and easy workup, together with the use of inexpensive, eco-friendly, and reusable nanocatalyst, are the notable features of this novel procedure. To the best of our knowledge, this is the first report on the synthesis of a new library of 1,3-thiazolidine-4-ones bearing pyrazole moiety that enhances the biological activity in aqueous media.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. Multiwalled carbon nanotube (98%) with outer diameter of 15–20 nm was purchased from Nanosany corporation (Mashhad, Iran). Other chemicals were purchased from Merck and Fluka and used as received. Melting points were measured on an Electro-thermal 9100 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker DRX 500 Avance spectrometer using $CDCl_3$ as solvent and TMS as internal standard. FT-IR spectra were recorded on a Shimadzu FT-IR-8400S spectrometer. Surface morphology of the magnetic nanocomposite was characterized under a Philips XL30 scanning electron microscope (The Netherlands). Crystal structure of the nanocomposite was determined by an X-ray diffractometer (Model 1830, Philips, The Netherlands) using Cu Kα radiation ($\lambda = 0.1541$ nm) at ambient temperature. Elemental analyses were recorded on a Carlo-Erba EA1110CNNO-S analyzer. Magnetic separation was conducted by a strong super magnet with 1.4 T magnetic field ($1 \times 3 \times 5$ cm^3).

The procedure for the synthesis of the mMWCNT nanocomposite. The synthesis of mMWCNT nanocomposite was carried out by the method described previously [27]. The X-ray diffractometer pattern in Fig. 1 shows successful incorporating of iron oxides nanoparticles into the multiwalled carbon nanotubes. The diffraction peaks at $2\theta = 26.2^{\circ}$ and 43.3° correspond to the structure of multiwalled carbon nanotubes. Moreover, the peaks at $2\theta = 30.3^{\circ}$, 35.6°, 43.3°, and 57.3° are related to maghemite or magnetite [28], and the peaks at $2\theta = 53.7^{\circ}$ and 62.8° may be assigned to hematite [29]. The scanning electron microscopic image of the magnetic nanocomposite (Fig. 2) clearly demonstrates successful coating of carbon nanotube surface by iron oxides nanoparticles with approximate size of 50 nm.

General procedure for preparation of 4a–k using mMWCNT nanocomposite. A mixture of pyrazolcarbaldehydes (1 mmol), various derivatives of aniline (1 mmol), thioglycolic acid (1 mmol), and mMWCNT nanocomposite (0.1 g) was stirred at room temperature for the required reaction times (1–2 h). The progress of the reaction was monitored by TLC (EtOAc : petroleum ether 1:3). After completion of the reaction, the product was dissolved in $CHCl_3$ (3×10 mL), and insoluble catalyst was separated using the super magnet. Then, the organic phase including the product and $CHCl_3$ was evaporated under vacuum, and the resulting crude material was purified by column chromatography. At last, the product was recrystallized from EtOH, and the pure products were collected in 82–92% yields.

2-(3-(4-Chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)-3-(4-methoxyphenyl)thiazolidin-4-one (4a). This compound was obtained as yellow solid, mp 242–244°C; FT-IR (KBr): 1502, 1541, 1600 (C=C aromatic), 1731 (C=O stretch), 2981 (C–H aliphatic), 3126 (C–H aromatic) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 3.28 (d, J = 15.3 Hz, 1H), 3.5 (d, J = 15.3 Hz, 1H), 3.52 (s, 3H, CH_3O), 5.48 (s, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.43–7.49 (m, 7H), 7.73–7.80 (m, 4H), 8.22 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ: 32.9, 40.4, 60.5, 118.0, 125.5, 127.4, 127.8, 128.4, 128.7, 129.5, 129.8, 133.6, 138.8, 143.1, 168.3 (C=O) ppm. *Anal.* Calcd for $C_{25}H_{20}ClN_3O_2S$: C, 65.00; H, 4.36; N, 9.10. Found: C, 65.02; H, 4.35; N, 9.08.

2-(1,3-Diphenyl-1H-pyrazol-4-yl)-3-(4-methoxyphenyl) thiazolidin-4-one (4b). This compound was obtained as yellow solid, mp 231–233°C; FT-IR (KBr): 1288 (C–O stretch aromatic), 1500, 1541, 1596 (C=C aromatic), 1737 (C=O stretch), 2977 (C–H aliphatic), 3058 (C–H aromatic) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 3.29 (d, J = 15.2 Hz, 1H), 3.49 (d, J = 15.2 Hz, 1H), 3.58 (s, 3H, CH_3O), 5.49 (s, 1H), 7.30 (td, J = 7.9,

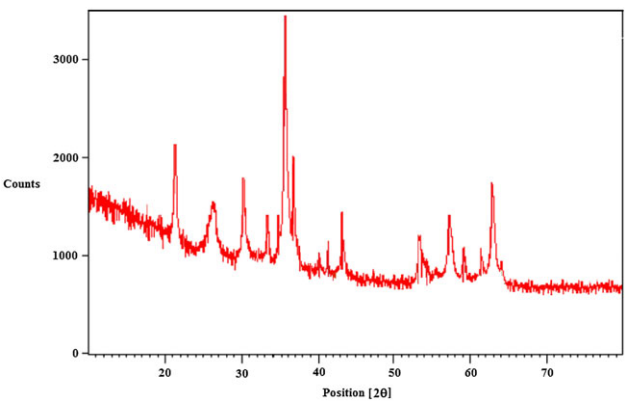

Figure 1. X-ray diffractometer pattern of magnetic nanocomposite of multiwalled carbon nanotube. [Color figure can be viewed at wileyonlinelibrary.com]

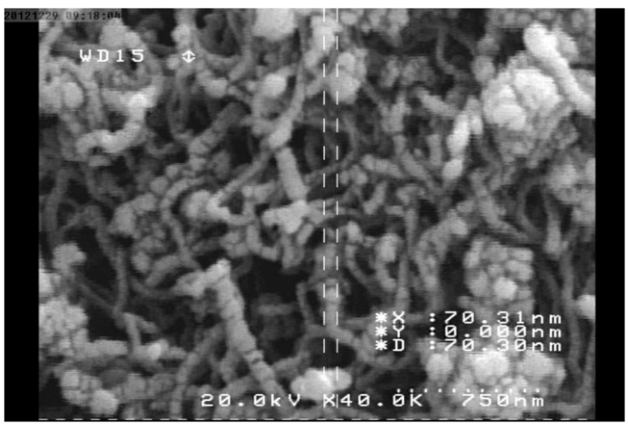

Figure 2. Scanning electron microscope image of magnetic nanocomposite of multiwalled carbon nanotube. [Color figure can be viewed at wileyonlinelibrary.com]

0.7 Hz, 2H), 7.37–7.41 (m, 2H), 7.45–7.48 (m, 6H), 7.76 (dd, *J* = 8.4, 0.6 Hz, 2H), 7.8 (d, *J* = 8.4 Hz, 2H), 8.09 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ: 32.9, 43.5, 60.5, 118.0, 125.7, 127.1, 127.3, 127.4, 127.5, 127.6, 128.4, 131.3, 138.6, 150.0, 168.8 (C=O) ppm. *Anal*. Calcd for $C_{25}H_{21}N_3O_2S$: C, 70.24; H, 4.95; N, 9.83. Found: C, 70.26; H, 4.97; N, 9.81.

2-(1,3-Diphenyl-1H-pyrazol-4-yl)-3-(2-methyl-4-nitrophenyl) thiazolidin-4-one (4c). This compound was obtained as orange solid, mp 237–239°C; FT-IR (KBr): 1363, 1541 (NO_2 stretch), 1450, 1500, 1596 (C=C aromatic), 1730 (C=O stretch), 2981 (C–H aliphatic), 3126 (C–H aromatic) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 3.30 (d, *J* = 15.2 Hz, 1H), 3.50 (d, *J* = 15.2 Hz, 1H), 3.58 (s, 3H, CH_3), 5.50 (s, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.40–7.42 (m, 1H), 7.45–7.49 (m, 7H), 7.75–7.78 (m, 2H), 7.80–7.82 (m, 2H), 8.23 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ: 30.9, 40.4, 43.5, 60.5, 60.6, 118.0, 125.7, 127.1, 127.3, 127.4, 127.5, 127.6, 128.4, 131.3, 138.6, 150.0, 168.8 (C=O) ppm. *Anal*. Calcd for $C_{25}H_{20}N_4O_3S$: C, 65.77; H, 4.42; N, 12.27. Found: C, 65.75; H, 4.39; N, 12.29.

2-(3-(4-Chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)-3-(2-methyl-4-nitrophenyl)thiazolidin-4-one (4d). This compound was obtained as orange solid, mp 240–242°C; FT-IR (KBr): 1400, 1539 (NO_2 stretch), 1454, 1500, 1598 (C=C aromatic), 1731 (C=O stretch), 2981 (C–H aliphatic), 3128 (C–H aromatic) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 3.24 (d, *J* = 15.2 Hz 1H), 3.49 (d, *J* = 15.2 Hz 1H), 3.55 (s, 1H, CH_3), 5.45 (s, 1H), 7.26–7.30 (m, 2H), 7.40–7.45 (m, 6H), 7.71–7.73 (m, 2H), 7.75–7.78 (m, 2H), 8.20 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ: 32.7, 40.3, 43.2, 60.4, 60.5, 117.8, 117.9, 125.7, 127.3, 127.6, 128.3, 128.6, 129.7, 133.1, 138.4, 148.7, 168.1(C=O) ppm. *Anal*. Calcd for $C_{25}H_{19}ClN_4O_3S$: C, 61.16; H, 3.90; N, 11.41. Found: C, 61.14; H, 3.87; N, 11.39.

3-(2-Methyl-4-nitrophenyl)-2-(3-(3-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)thiazolidin-4-one (4e). This compound was obtained as orange solid, mp 251–253°C; FT-IR (KBr): 1353, 1533 (NO_2 stretch) 1456, 1595 (C=C aromatic), 1731 (C=O stretch), 2981 (C–H aliphatic), 3128 (C–H aromatic) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 3.28 (d, *J* = 15.1 Hz, 1H), 3.34 (d, *J* = 15.1 Hz, 1H), 3.56 (s, 3H, CH_3), 5.52 (s, 1H), 7.31–7.35 (m, 1H), 7.45–7.48 (m, 3H), 7.64–7.66 (m, 2H), 7.66–7.76 (m, 3H), 8.21 (d, *J* = 2.0 Hz, 1H), 8.23 (d, *J* = 2.0 Hz, 1H), 8.25 (s, 1H), 8.72 (t, *J* = 1.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ: 32.8, 40.3, 60.4, 118.0, 118.3, 121.8, 122.3, 126.1, 127.7, 128.4, 128.5, 128.6, 133.1, 133.3, 138.3, 147.3, 147.4, 168.2 (C=O) ppm. *Anal*. Calcd for $C_{25}H_{19}N_5O_5S$: C, 59.87; H, 3.82; N, 13.96. Found: C, 59.85; H, 3.84; N, 13.95.

2-(1,3-Diphenyl-1H-pyrazol-4-yl)-3-phenylthiazolidin-4-one (4f). This compound was obtained as yellow solid, mp 221–223°C; FT-IR (KBr): 1498, 1539, 1596 (C=C aromatic), 1733 (C=O stretch), 2981 (C–H aliphatic), 3058 (C–H aromatic) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 3.29 (d, *J* = 15.1 Hz, 1H), 3.52 (d, *J* = 15.1 Hz, 1H), 5.53 (s, 1H), 7.18–7.30 (m, 2H), 7.40–7.44 (m, 2H) 7.46–7.52 (m, 6H), 7.77–7.85 (m, 5H), 8.26 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ: 43.5, 44.5, 119.0, 119.1, 126.7, 128.2, 128.3, 128.4, 128.6, 129.4, 132.4, 139.7, 151.1, 169.8 (C=O) ppm. *Anal*. Calcd for $C_{24}H_{19}N_3OS$: C, 72.52; H, 4.82; N, 10.57. Found: C, 72.50; H, 4.79; N, 10.59.

2-(1,3-Diphenyl-1H-pyrazol-4-yl)-3-(4-nitrophenyl)thiazolidin-4-one (4g). This compound was obtained as yellow solid, mp 234–236°C; FT-IR (KBr): 1361 (NO_2), 1542 (NO_2), 1730 (C=O, stretch), 2981 (C–H, aliphatic), 3060 (C–H aromatic) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 3.29 (d, *J* = 15.2 Hz, 1H), 3.50 (d, *J* = 15.2 Hz, 1H), 5.50 (s, 1H), 7.28–7.32 (m, 2H), 7.39–7.42 (m, 2H), 7.44–7.49 (m, 6H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.82 (dd, *J* = 8.5, 1.4 Hz, 2H), 8.23 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ: 32.9, 43.4, 117.3, 117.9, 118.0, 125.6, 126.7, 127.1, 127.2, 127.4, 127.5, 127.6, 127.7, 128.4, 131.2, 138.6, 150.0, 168.7 (C=O) ppm. *Anal*. Calcd for $C_{24}H_{18}N_4O_3S$: C, 65.14; H, 4.10; N, 12.66. Found: C, 65.12; H, 4.09; N, 12.63.

2-(3-(4-Chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)-3-(4-nitrophenyl)thiazolidin-4-one (4h). This compound was obtained as orange solid, mp 239–241°C; FT-IR (KBr): 1380 (NO_2 stretch), 1544 (NO_2 stretch), 1731 (C=O stretch), 2981 (C–H aliphatic) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 3.31 (d, *J* = 15.2 Hz, 1H), 3.53 (d, *J* = 15.2 Hz 1H), 5.51 (s, 1H), 7.36–7.37 (m, 1H), 7.46–7.50 (m, 5H), 7.52 (dd, *J* = 5.6, 3.2 Hz, 1H), 7.75–7.85 (m, 6H), 8.26 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ: 32.7, 44.0, 114.8, 118.2, 119.7, 123.9, 125.8, 128.4, 129.4, 129.8, 138.7, 150.3, 151.3, 170.3 (C=O) ppm. *Anal*. Calcd for $C_{24}H_{17}ClN_4O_3S$: C, 60.44; H, 3.59; N, 11.75. Found: C, 60.45; H, 3.61; N, 11.72.

3-(4-Nitrophenyl)-2-(3-(3-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)thiazolidin-4-one (4i). This compound was obtained as orange solid, mp 263–265°C; FT-IR (KBr): 1350 (NO_2 stretch), 1533 (NO_2 stretch), 1598, 1627 (C=C aromatic), 1731 (C=O stretch), 2923 (C–H aliphatic) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 3.30 (d, *J* = 15.3 Hz, 1H), 3.53 (d, *J* = 15.3 Hz, 1H), 5.54 (s, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.48–7.52 (m, 3H), 7.67 (t, *J* = 8.0 Hz, 2H), 7.76–7.80 (m, 3H), 8.24–8.76 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ: 43.3, 60.6, 118.1, 121.9, 122.4, 126.2, 127.8, 128.5, 128.6, 133.4, 168.7 (C=O) ppm. *Anal*. Calcd for $C_{24}H_{17}N_5O_5S$: C, 59.13; H, 3.51; N, 14.37. Found: C, 59.15; H, 3.49; N, 14.39.

2-(1,3-Diphenyl-1H-pyrazol-4-yl)-3-p-tolylthiazolidin-4-one (4j). This compound was obtained as yellow solid, mp 246–248°C; FT-IR (KBr): 1350, 1598, 1627 (C=C aromatic), 1731 (C=O stretch), 2923 (C–H aliphatic) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 3.32 (d, *J* = 15.2 Hz, 1H), 3.54 (d, *J* = 15.2 Hz, 1H), 3.63 (s, 3H, CH_3), 5.54 (s, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.48–7.55 (m, 6H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.85 (dd, *J* = 7.6, 1.2 Hz, 2H), 8.27 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ: 34.0, 41.48, 44.6, 119.0, 126.7, 128.2, 128.3, 128.5, 128.6, 129.0, 129.5, 129.7, 132.4, 139.7, 151.1, 169.8 (C=O) ppm. *Anal*. Calcd for $C_{25}H_{21}N_3OS$: C, 72.97; H, 5.14; N, 10.21. Found: C, 72.95; H, 5.15; N, 10.19.

2-(3-(4-Hydroxyphenyl)-1-phenyl-1H-pyrazol-4-yl)-3-(4-nitrophenyl)thiazolidin-4-one (4k). This compound was obtained as orange solid, mp 254–256°C; FT-IR (KBr): 1276 (C–O aromatic), 1347 (NO_2 stretch), 1502, 1533 (NO_2 stretch), 1602 (C=C aromatic), 1726 (C=O stretch), 2923 (C–H aliphatic), 3425 (O-H) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 3.32 (d, *J* = 15.3 Hz, 1H), 3.54 (d, *J* = 15.2 Hz, 1H), 5.48 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 7.29–7.39 (m, 3H), 7.49–7.51 (m, 4H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.75–7.78 (m, 3H), 8.22 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ: 33.9, 44.6, 115.6, 118.7, 119.1, 124.4, 126.7, 128.1, 129.5, 129.9, 139.6, 151.1, 156.3, 170.0 (C=O) ppm. *Anal*. Calcd for $C_{24}H_{18}N_4O_4S$: C, 62.87; H, 3.96; N, 12.22. Found: C, 62.86; H, 3.97; N, 12.20.

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