

SUPPORTING INFORMATION

A Novel Application of $\text{Co}_3\text{O}_4@\text{SiO}_2$ Nanocomposite as an Efficient and Robust Catalyst for the Preparation of Some Imidazolone Derivatives

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ABBREVIATIONS:

$\text{Co}_3\text{O}_4@\text{SiO}_2$ MNPs = Cobalt (II,III) oxide/porous-silicananocomposites.

EXPERIMENTAL PROCEDURE:

The $\text{Co}_3\text{O}_4@\text{SiO}_2$ MNPs were prepared according to the experimental procedure. All compounds afforded spectral data. The $\text{Co}_3\text{O}_4@\text{SiO}_2$ nanocomposites were prepared in two steps according to the procedure described by Ghasemzadeh *et al.* with some modifications [25].

First step, formation of cobalt (II,III) oxide (Co_3O_4) NPs: A warm (50 °C) solution including cobalt (II) nitrate hexa-hydrate (8.60 g) in ethanol (100 mL) was prepared with vigorous stirring and kept for 30 minutes. Then, oxalic acid (2.14 g) was quickly added to the solution and stirred at 50 °C for 2 hours. The formed precipitates of cobalt (II) oxalate were collected by centrifuge, washed with ethanol, dried at room temperature and finally calcined for 2 hours at 400 °C to produce the dark cobalt(II,III) oxide nanoparticles.

Second step, formation of $\text{Co}_3\text{O}_4@\text{SiO}_2$ core-shell nanocomposites: To a mixture containing Co_3O_4 nanoparticles (0.5 g), ethanol (350 mL) and cetyltrimethylammonium bromide (2.2 g) were added dropwise to a concentrated ammonia aqueous solution (40 mL, 28 wt%) under sonication for 20 minutes. Then, tetraethylorthosilicate (0.4 mL) in ethanol (10 mL) was added to the above mixture under ultrasound irradiation and stirred at room temperature for 20 hours. The Co_3O_4 /porous-silica core-shell nanocomposites were collected by centrifugation and washed three times with deionized water, and finally calcined at 600 °C for 6 hours.

SPECTROSCOPIC DATA:

The structure and magnetic characterization of $\text{Co}_3\text{O}_4@\text{SiO}_2$ were done by using various spectroscopic analyses including FT-IR, X-ray powder diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, and vibrating sample magnetometer.

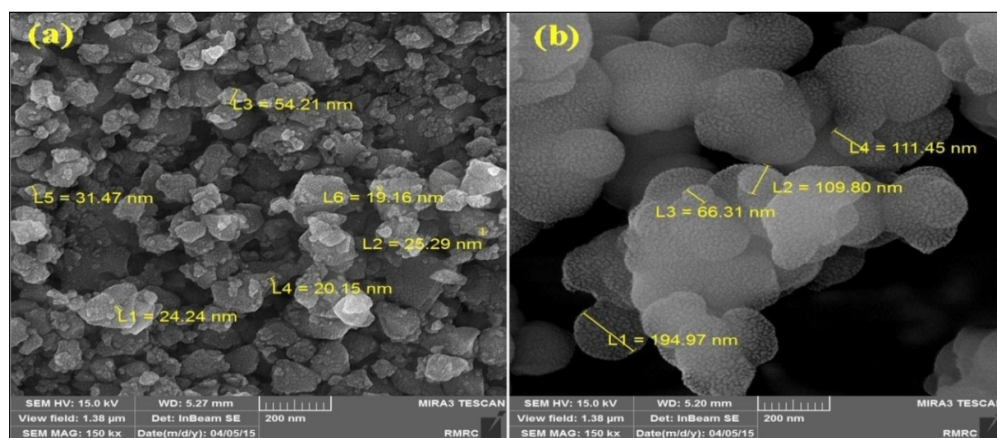


Fig S1. FE-SEM images of Co_3O_4 (a) and $\text{Co}_3\text{O}_4@\text{SiO}_2$ (b) MNPs.

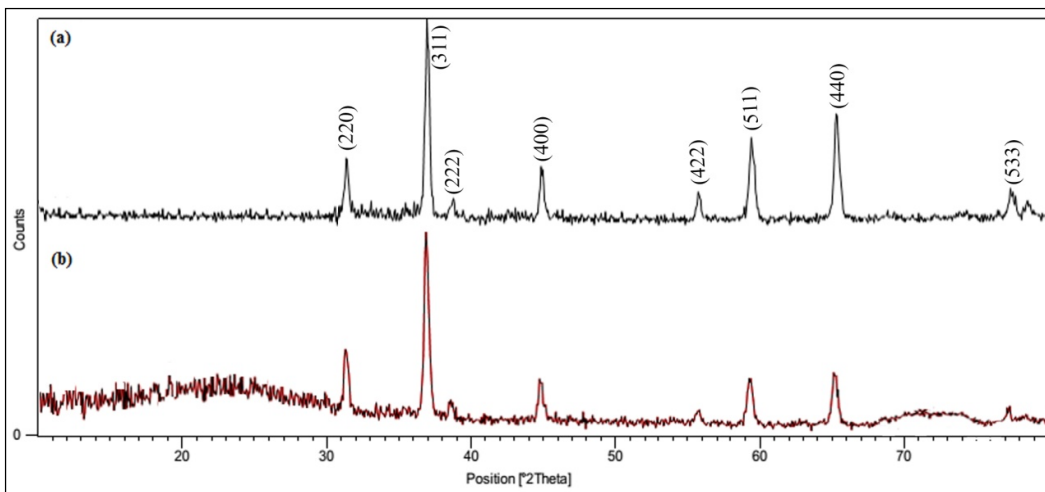


Fig. S2. X-ray diffraction of Co_3O_4 (a) and $\text{Co}_3\text{O}_4@\text{SiO}_2$ (b) MNPs.

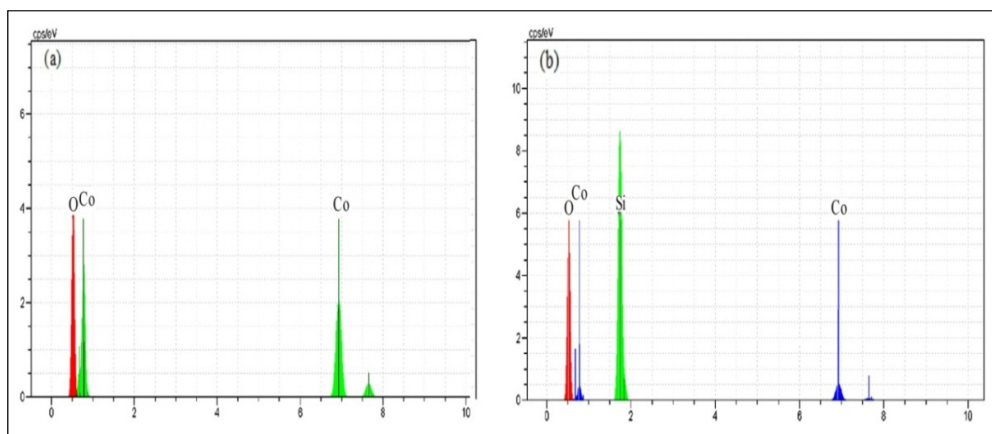


Fig. S3. EDX spectra of Co_3O_4 (a) and $\text{Co}_3\text{O}_4@\text{SiO}_2$ (b) MNPs.

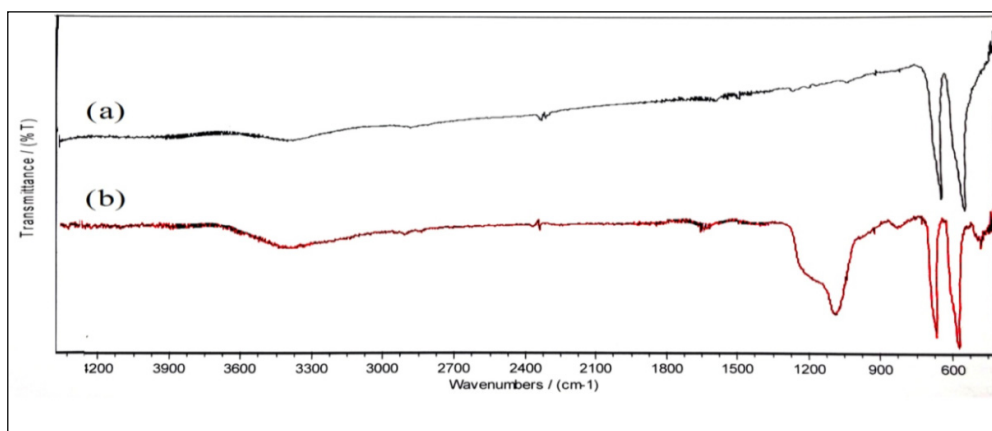


Fig. S4. Comparative FT-IR spectra of Co_3O_4 (a) and $\text{Co}_3\text{O}_4@\text{SiO}_2$ (b) MNPs.

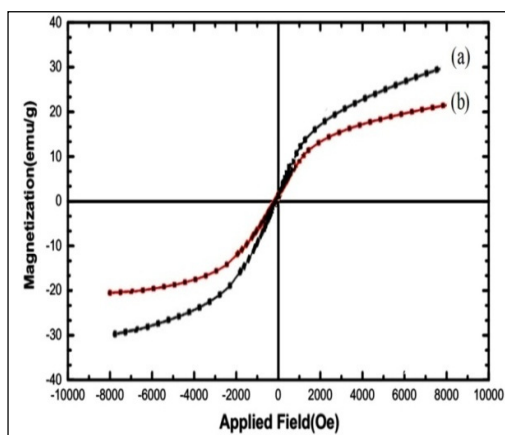


Fig. S5. VSM magnetization curves of the Co_3O_4 (a) and $\text{Co}_3\text{O}_4@\text{SiO}_2$ (b) MNPs.

5-(4-isopropylbenzylidene)-2-phenyl-3-(4-chlorophenyl)-3,5-dihydro-4(4H)-imidazolone (4a): Yellow solid; Yield 91%; m.p. (°C): 209-211; FT-IR (KBr) (ν_{\max} / cm^{-1}): 1651 (C=O, str., imidazolone ring), 1597 (C=N, str., imidazolone ring), 1095 (C-Cl, str., aromatic); ^1H NMR (400MHz, DMSO- d_6) δ (ppm): 1.18-1.36 (d, 6H, - $(\text{CH}_3)_2$), 2.89 (m, 1H, C-H $(\text{CH}_3)_2$), 7.12 (s, 1H, vinyl), 7.19-8.04 (m, 12H, ArH); MS (EI) (m/z): 400.91(M^+); Anal. Calcd. For $\text{C}_{25}\text{H}_{21}\text{ClN}_2\text{O}$: C 74.90, H 5.28, N 6.99; Found C 74.83, H 5.36, N 7.06. %.

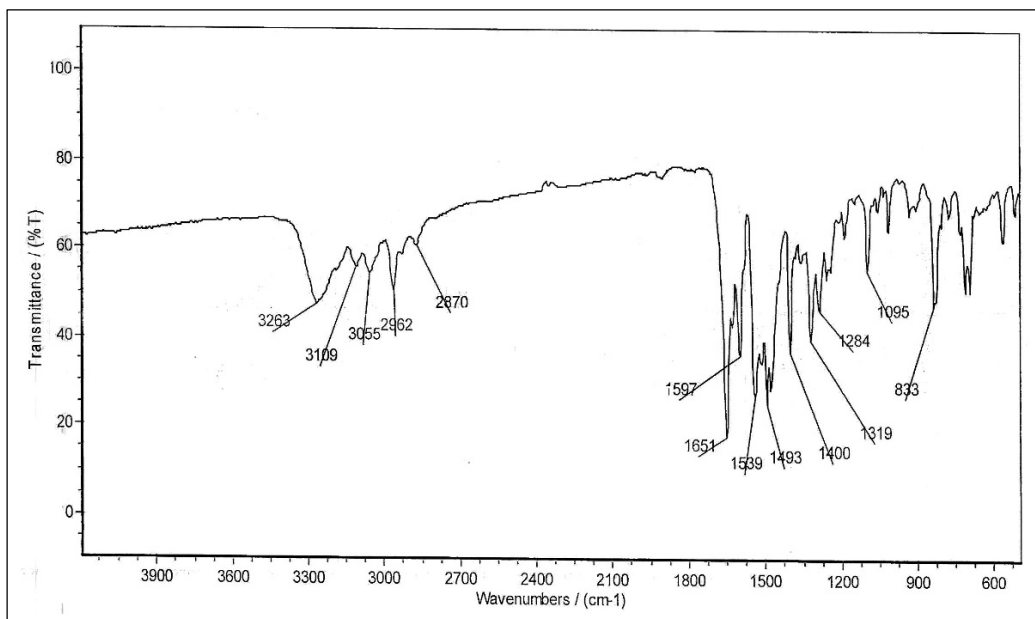


Fig. S6. FT-IR spectrum of 5-(4-isopropylbenzylidene)-2-phenyl-3-(4-chlorophenyl)-3,5-dihydro-4(4H)-imidazolone (4a).

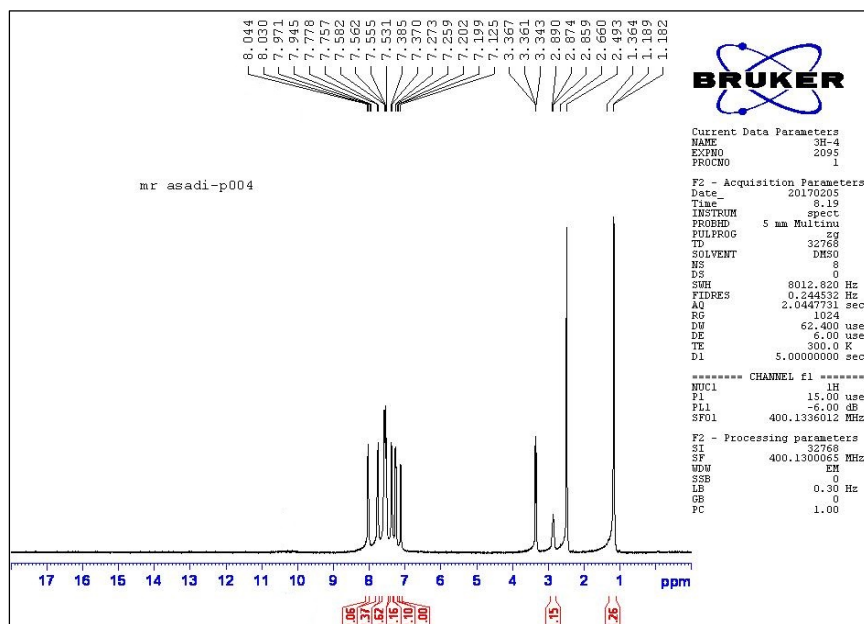


Fig. S7. ^1H NMR spectrum of 5-(4-isopropylbenzylidene)-2-phenyl-3-(4-chlorophenyl)-3,5-dihydro-4(4H)-imidazolone (4a).

5-(4-isopropylbenzylidene)-2-phenyl-3-(4-tolyl)-3,5-dihydro-4(H)-imidazolone (4b):

Yellow solid; m.p. (°C): 201-203; FT-IR (KBr) (ν_{\max} / cm^{-1}): 1651 (C=O, str., imidazolone ring), 1604 (C=N, str., imidazolone ring); $^1\text{H NMR}$ (400MHz, DMSO- d_6) δ (ppm): 1.16-1.18 (d, 6H, $-(\text{CH}_3)_2$), 2.25 (s, 3H, CH_3), 2.88 (m, 1H, C-H(CH_3) $_2$), 7.10 (s, 1H, vinyl), 7.12-8.03 (m, 12H, ArH); MS (EI) (m/z): 380.49(M^+); Anal. Calcd. For $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}$: C 82.07, H 6.36, N 7.36; Found C 82.14, H 6.28, N 7.42. %.

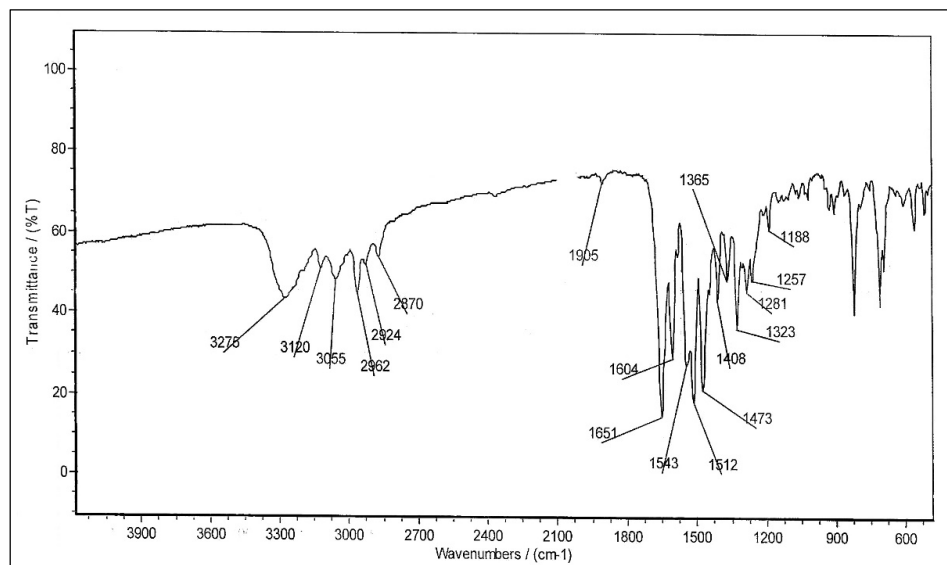


Fig. S8. FT-IR spectrum of 5-(4-isopropylbenzylidene)-2-phenyl-3-(4-tolyl)-3,5-dihydro-4(H)-imidazolone (4b).

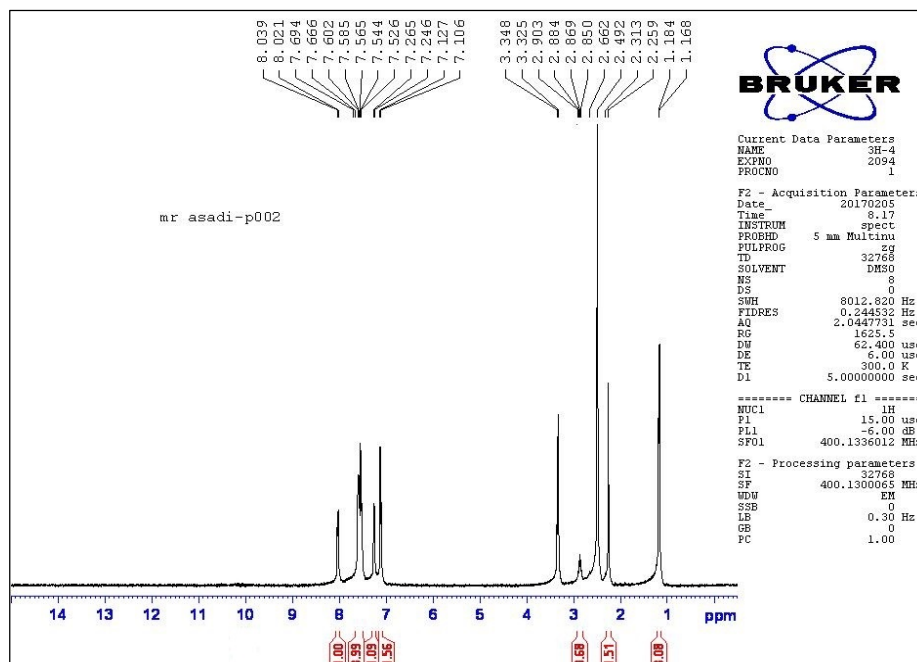


Fig. S9. $^1\text{H NMR}$ spectrum of 5-(4-isopropylbenzylidene)-2-phenyl-3-(4-tolyl)-3,5-dihydro-4(H)-imidazolone (4b).

5-(4-cyanobenzylidene)-2-phenyl-3-(4-tolyl)-3,5-dihydro-4(4H)-imidazolone (4c):

Yellow solid; m. p. (°C): 183-184; FT-IR (KBr) (ν_{\max} / cm^{-1}): 2225 (CN, medium), 1674 (C=O, str., imidazolone ring), 1601 (C=N, str., imidazolone ring); $^1\text{H NMR}$ (400MHz, DMSO- d_6) δ (ppm): 2.25 (s, 3H, CH₃), 7.09-7.13 (s, 1H, vinyl), 7.51-7.98 (m, 12H, ArH); MS (EI) (m/z): 363.42(M⁺); Anal. Calcd. For C₂₄H₁₇N₃O: C 79.32, H 4.72. N 11.56; Found C 79.41, H 4.65. N 11.48. %.

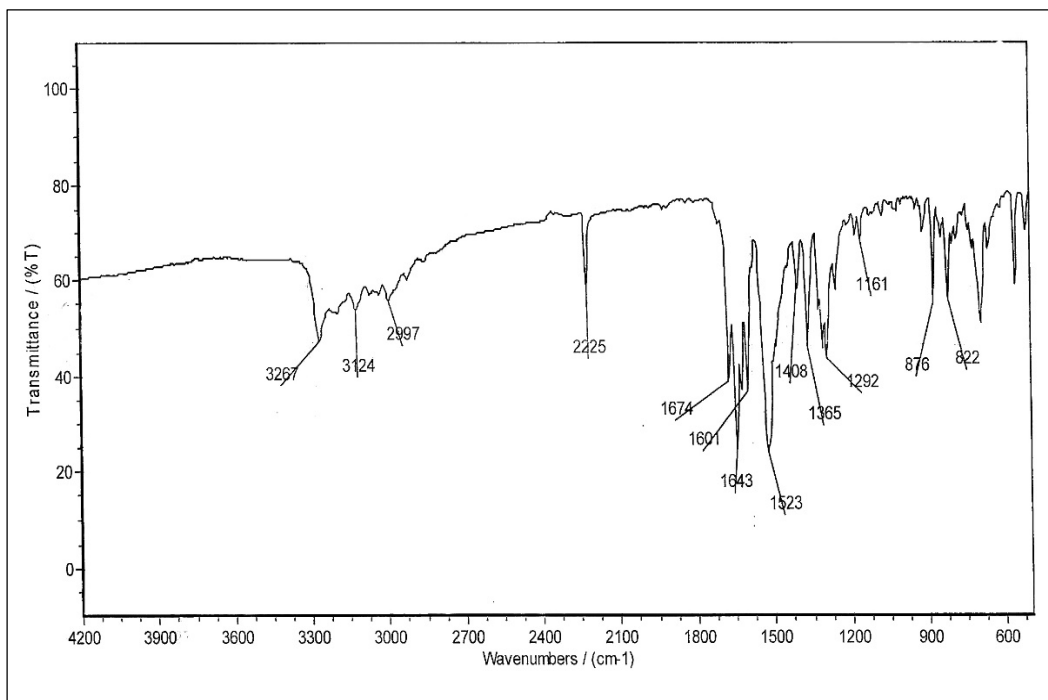


Fig. S10. FT-IR spectrum of 5-(4-cyanobenzylidene)-2-phenyl-3-(4-tolyl)-3,5-dihydro-4(4H)-imidazolone (4c).

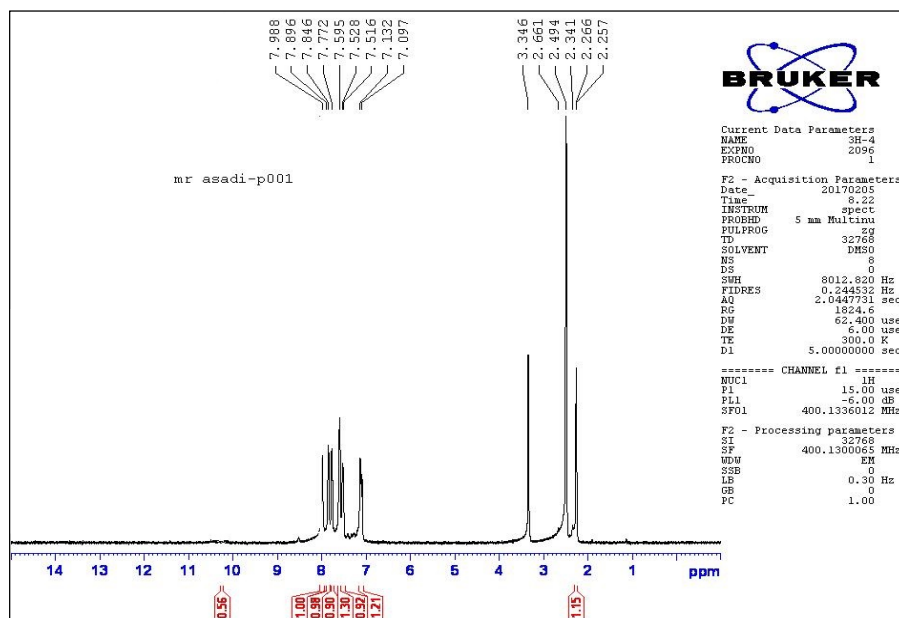


Fig. S11. $^1\text{H NMR}$ spectrum of 5-(4-cyanobenzylidene)-2-phenyl-3-(4-tolyl)-3,5-dihydro-4(4H)-imidazolone (4c).

5-(4-cyanobenzylidene)-2-phenyl-3-(4-chlorophenyl)-3,5-dihydro-4(4H)-imidazolone (4d): Yellow solid; m.p. (°C): 222-224; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 2225 (CN, medium), 1674 (C=O, str., imidazolone ring), 1597 (C=N, str., imidazolone ring), 1092 (C-Cl, str., aromatic); ^1H NMR (400MHz, DMSO- d_6) δ (ppm): 7.08 (s, 1H, vinyl), 7.10-8.00 (m, 12H, ArH); MS (EI) (m/z): 383.84(M^+); Anal. Calcd. For $\text{C}_{24}\text{H}_{17}\text{N}_3\text{O}$: C 71.97, H 3.68, N 10.95; Found C 71.88, H 3.75, N 11.03. %.

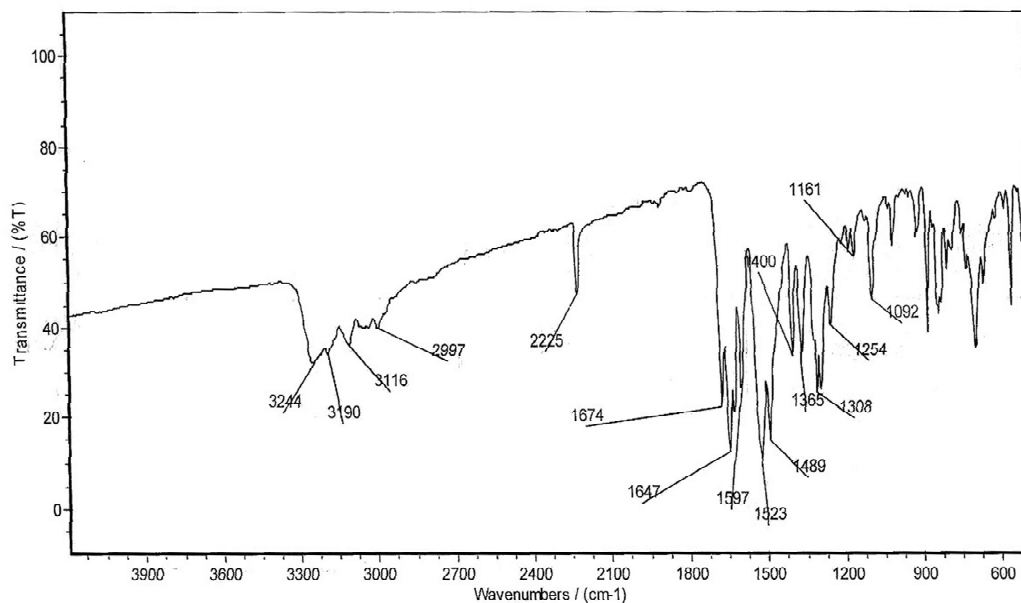


Fig. S12. FT-IR spectrum of 5-(4-cyanobenzylidene)-2-phenyl-3-(4-chlorophenyl)-3,5-dihydro-4(4H)-imidazolone (4d).

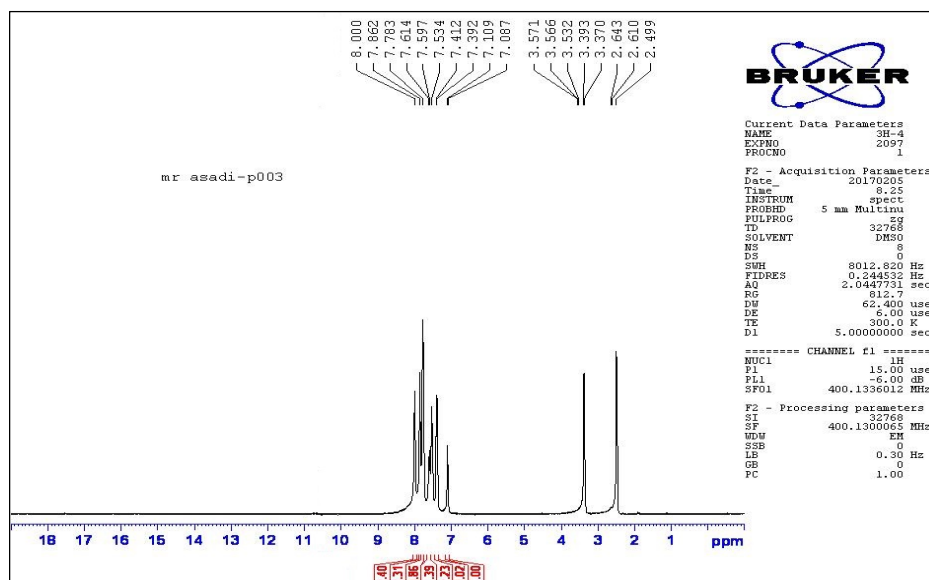


Fig. S13. ^1H NMR spectrum of 5-(4-cyanobenzylidene)-2-phenyl-3-(4-chlorophenyl)-3,5-dihydro-4(4H)-imidazolone (4d).

REFERENCE:

[25] M.A. Ghasemzadeh, B. Molaei, M.H. Abdollahi-Basir, F. Zamani, Preparation and catalytic study on a novel amino-functionalized silica-coated cobalt oxide nanocomposite for the synthesis of some indazoles, *Acta. Chim. Slov.* 64 (2017) 73-82.