

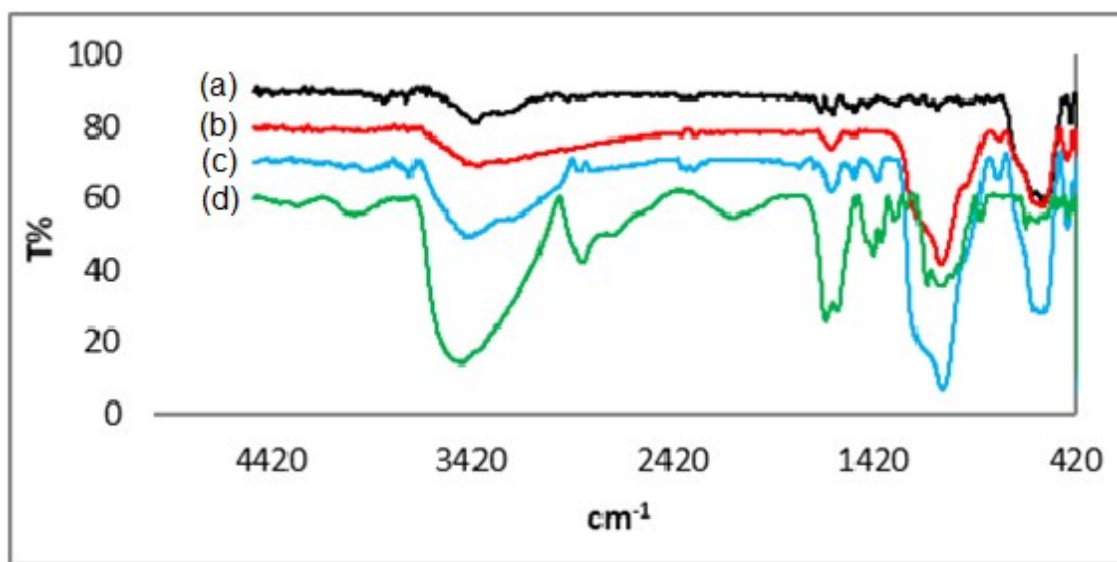
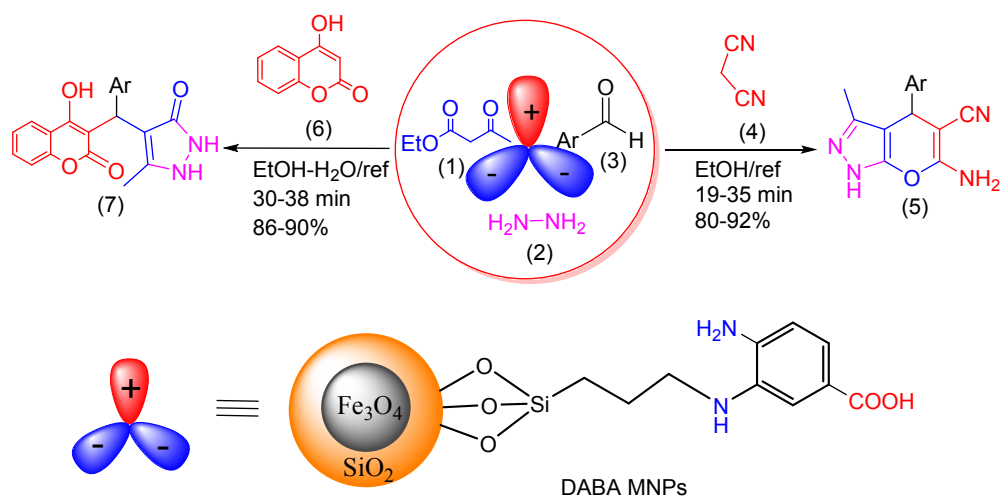
ELECTRONIC SUPPLEMENTARY INFORMATION

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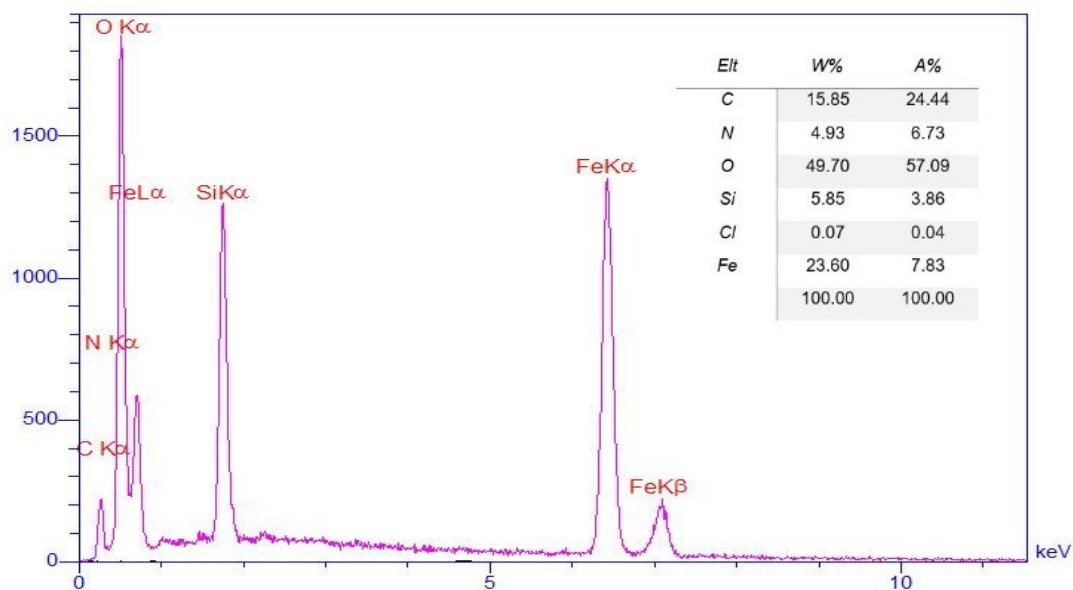
**DABA MNPs: a new and efficient magnetic bifunctional nanocatalyst for green synthesis of biologically active pyrano[2,3-*c*]pyrazole and benzylpyrazolyl coumarin derivatives**

Shahriar Karami, Mohammad G. Dekamin,\* Ehsan Valiey and Peyman Shakib

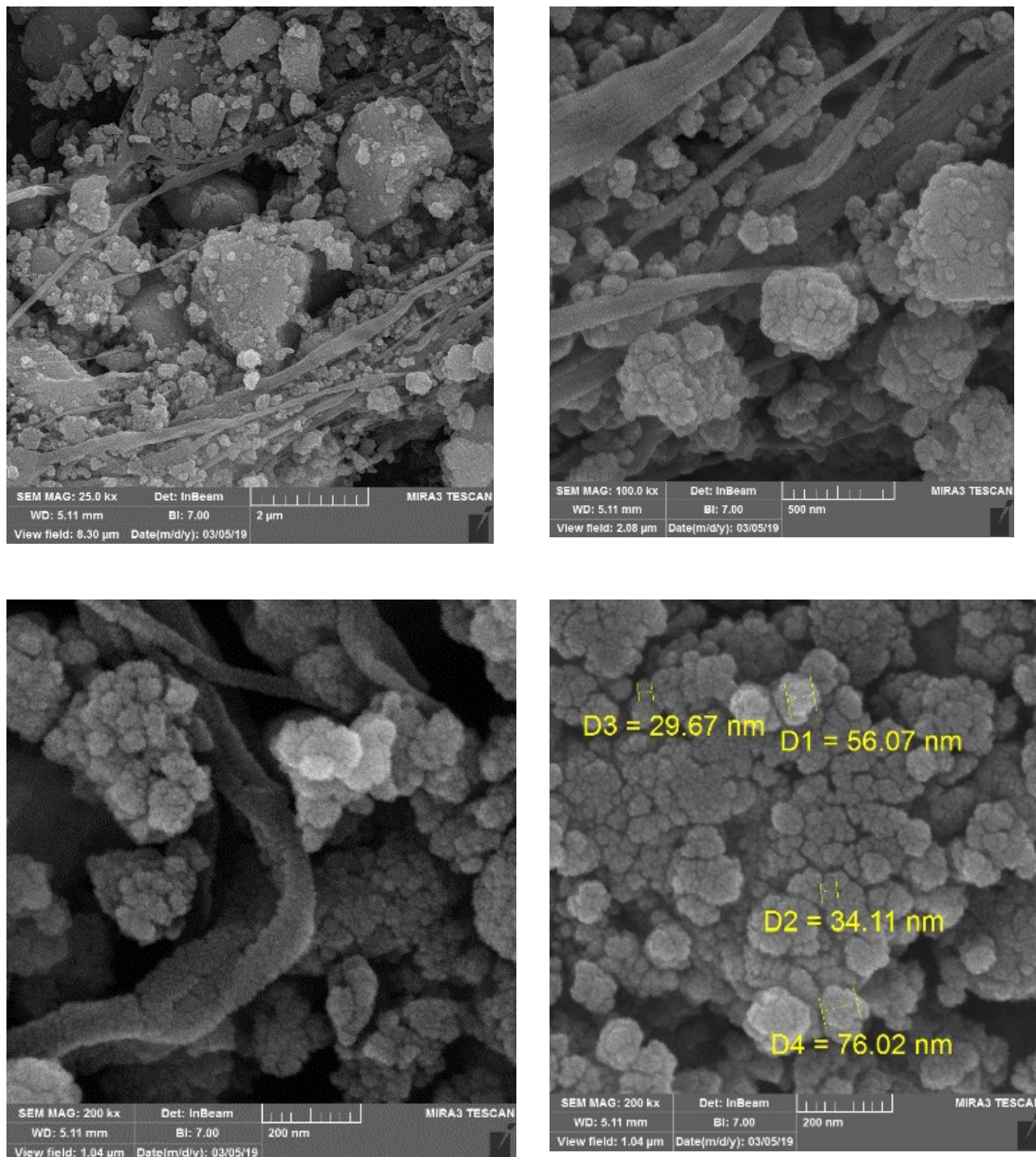
| Contents                                                                                                                                                                                                                       | Page |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| FT-IR spectra of the Fe <sub>3</sub> O <sub>4</sub> , Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> , Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @CPTS and Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PTS-DABA | 2    |
| Energy dispersive spectroscopy (EDS) pattern of Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PTS-DABA                                                                                                                     | 3    |
| Field emission scanning electron microscopy (FESEM) images of Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PTS-DABA                                                                                                       | 4    |
| X-Ray diffraction pattern of Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PTS-DABA                                                                                                                                        | 5    |
| Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) curves of the Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PTS-DABA catalyst                                                                     | 6    |
| Vibrating sample magnetometer (VSM) study of the Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PTS-DABA                                                                                                                    | 7    |
| Reusability of Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PTS-DABA for the synthesis of <b>6a</b> and <b>7a</b>                                                                                                         | 7    |
| FT-IR spectrum of 6-amino-4-(4-chlorophenyl)-3-methyl-1,4-dihydropyrano[2,3- <i>c</i> ]pyrazole-5-carbonitrile ( <b>5a</b> )                                                                                                   | 8    |
| <sup>1</sup> H NMR spectrum of 6-amino-4-(4-chlorophenyl)-3-methyl-1,4-dihydropyrano[2,3- <i>c</i> ]pyrazole-5-carbonitrile ( <b>5a</b> )                                                                                      | 9    |
| Expanded aromatic region of <sup>1</sup> H NMR spectrum of 6-amino-4-(4-chlorophenyl)-3-methyl-1,4-dihydropyrano[2,3- <i>c</i> ]pyrazole-5-carbonitrile ( <b>5a</b> )                                                          | 10   |
| FT-IR spectrum of 6-amino-4-(4-methylphenyl)-3-methyl-1,4-dihydropyrano[2,3- <i>c</i> ]pyrazole-5-carbonitrile ( <b>5g</b> )                                                                                                   | 11   |
| <sup>1</sup> H NMR spectrum of 6-amino-4-(4-methylphenyl)-3-methyl-1,4-dihydropyrano[2,3- <i>c</i> ]pyrazole-5-carbonitrile ( <b>5g</b> )                                                                                      | 12   |
| Expanded aromatic region of <sup>1</sup> H NMR spectrum of 6-amino-4-(4-methylphenyl)-3-methyl-1,4-dihydropyrano[2,3- <i>c</i> ]pyrazole-5-carbonitrile ( <b>5g</b> )                                                          | 13   |
| FT-IR Spectrum of 4-((4-hydroxy-2-oxo-2 <i>H</i> -chromen-3-yl)(phenyl)methyl)-5-methyl-1,2-dihydro-3 <i>H</i> -pyrazol-3-one ( <b>7a</b> )                                                                                    | 14   |
| <sup>1</sup> H NMR Spectrum of 4-((4-hydroxy-2-oxo-2 <i>H</i> -chromen-3-yl)(phenyl)methyl)-5-methyl-1,2-dihydro-3 <i>H</i> -pyrazol-3-one ( <b>7a</b> )                                                                       | 15   |
| Expanded aromatic region of <sup>1</sup> H NMR spectrum of 4-((4-hydroxy-2-oxo-2 <i>H</i> -chromen-3-yl)(phenyl)methyl)-5-methyl-1,2-dihydro-3 <i>H</i> -pyrazol-3-one ( <b>7a</b> )                                           | 16   |



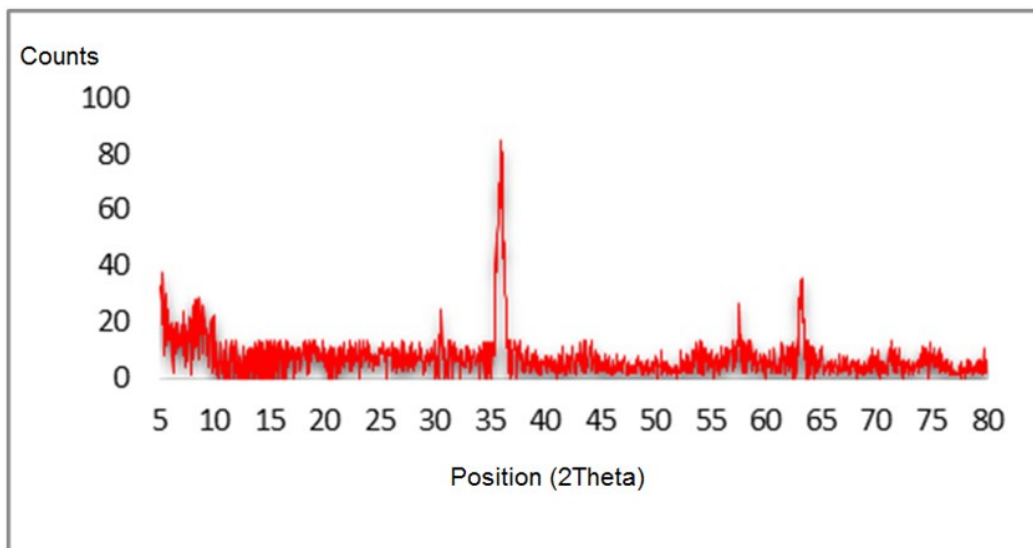
**Fig. 1.** FT-IR spectra of the Fe<sub>3</sub>O<sub>4</sub> (a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (b), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@CPTS (c) and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PTS-DABA (d).



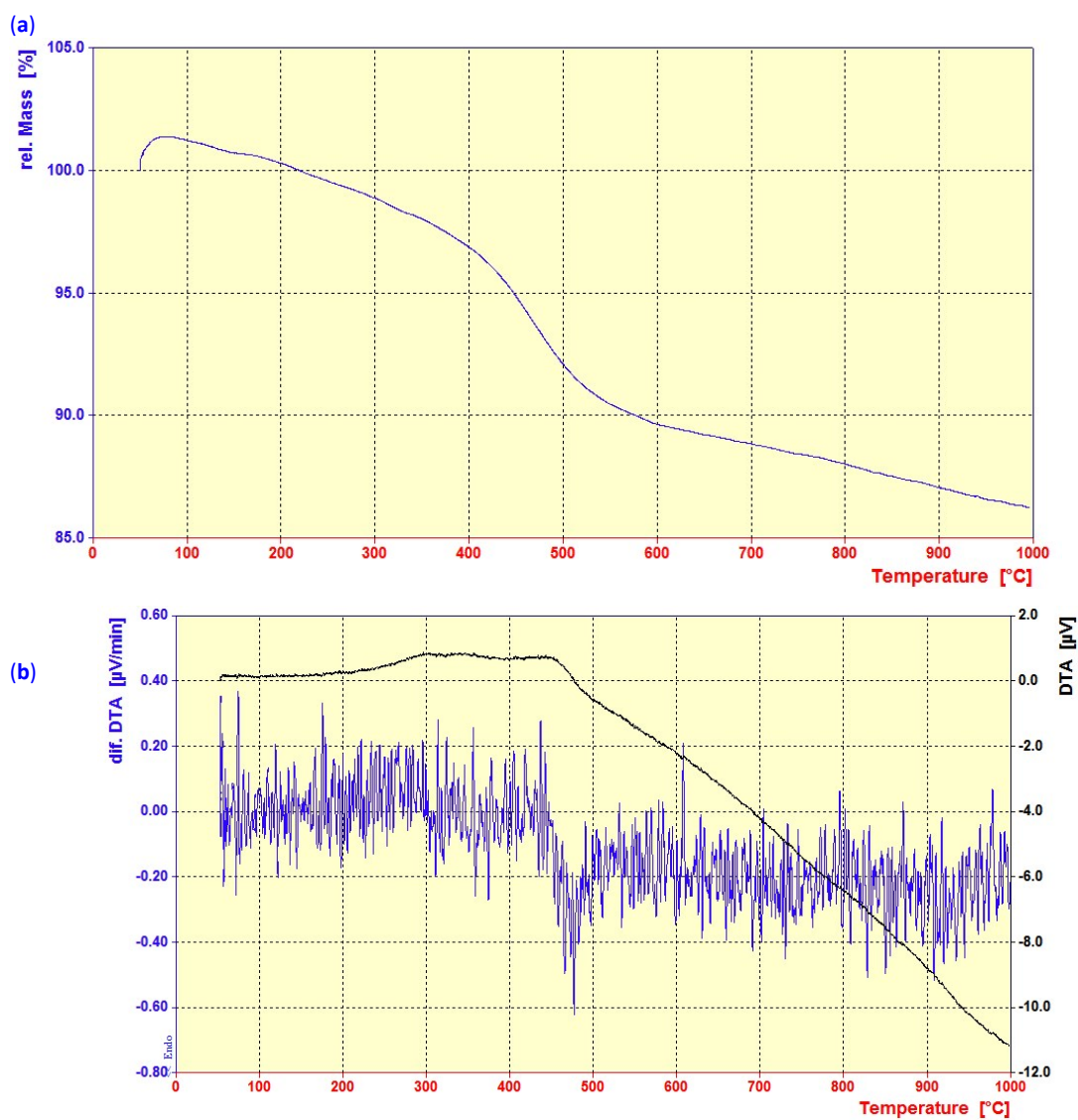
**Fig. 2.** Energy dispersive spectroscopy (EDS) pattern of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PTS-DABA}$ .



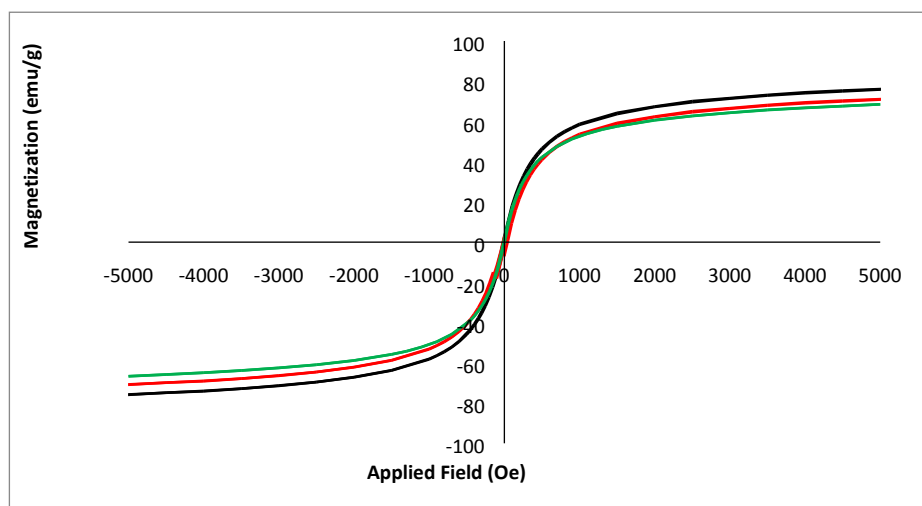
**Fig. 3.** FESEM images of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PTS-DABA}$  catalyst.



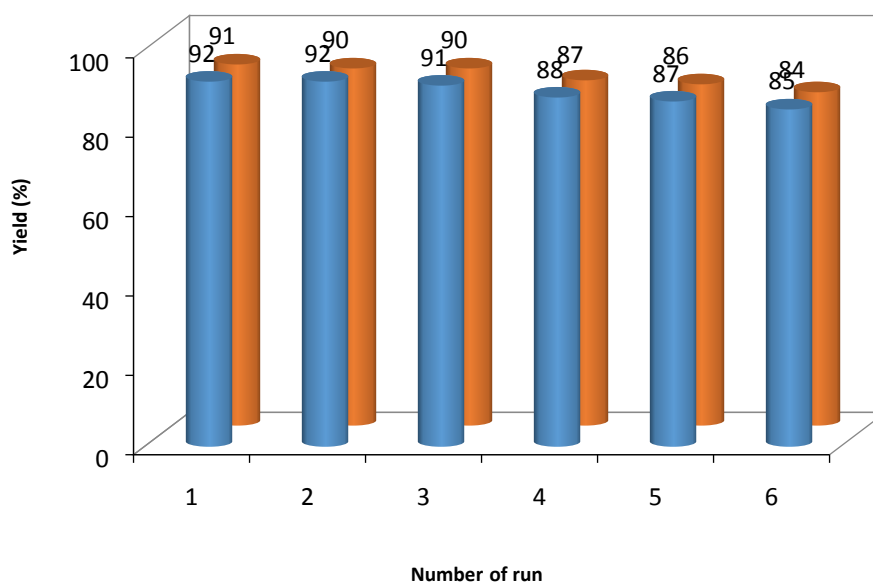
**Fig.4.** X-Ray diffraction (XRD) pattern of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PTS-DABA}$ .



**Fig. 5.** (a) TGA and (b) DTA curves of the  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{PTS-DABA}$  catalyst.



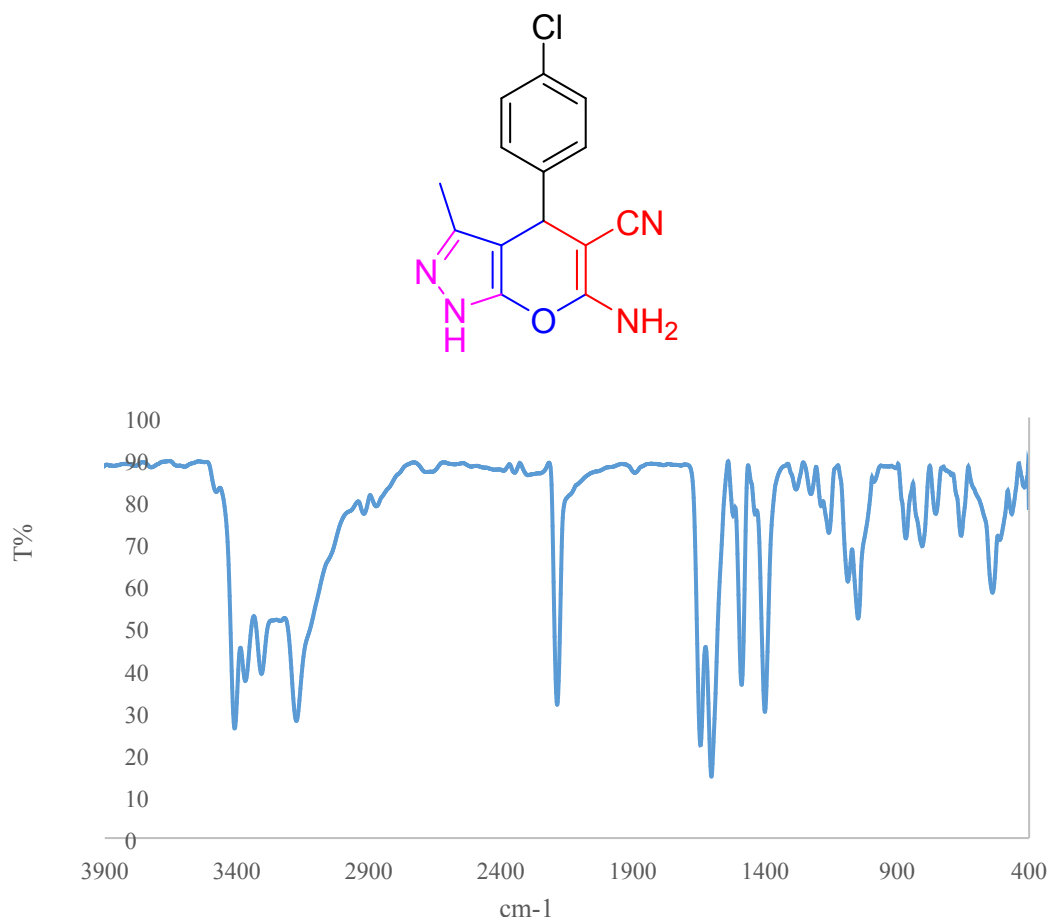
**Fig. 6.** Magnetization curves of the (black) Fe<sub>3</sub>O<sub>4</sub>, (red) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, (green) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PTS-DABA.



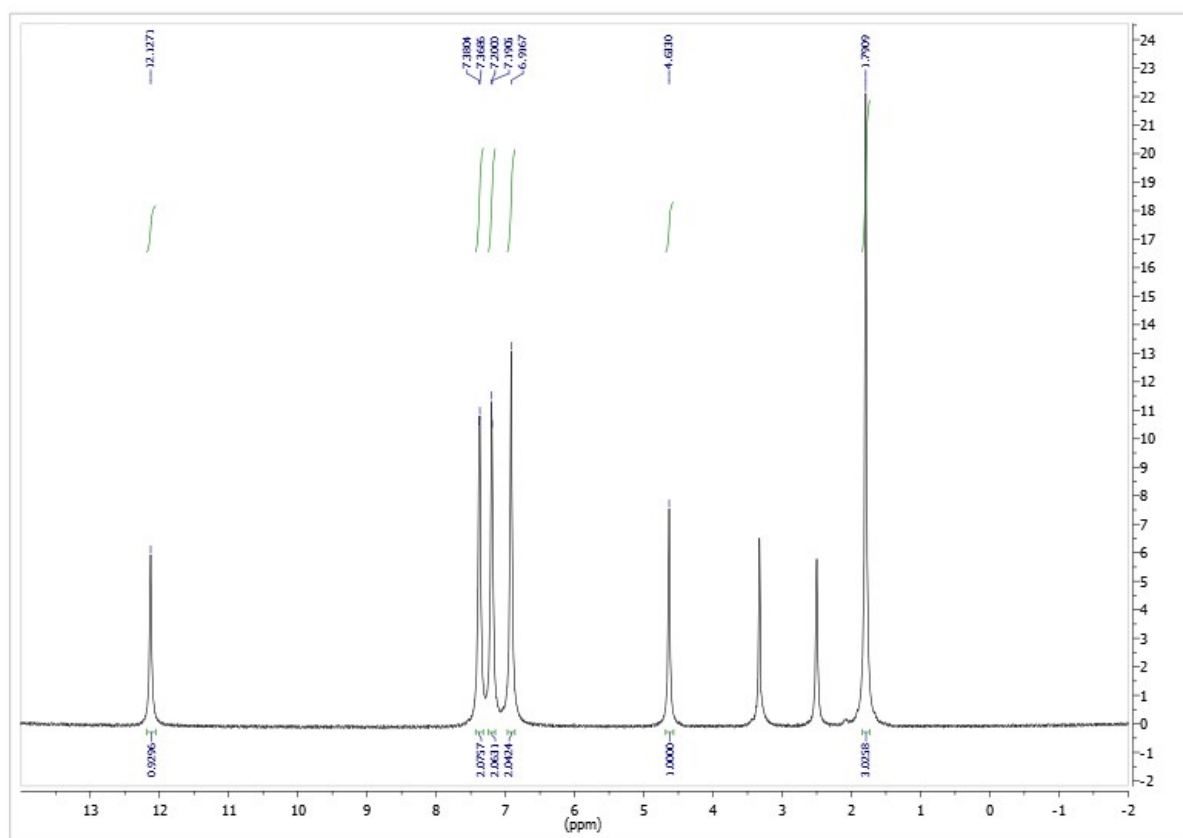
**Fig. 7.** Reusability of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PTS-DABA for the synthesis of **6a** (blue diagram) and **7a** (red diagram).

**Selected spectral data:****6-amino-4-(4-chlorophenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**5a**)**

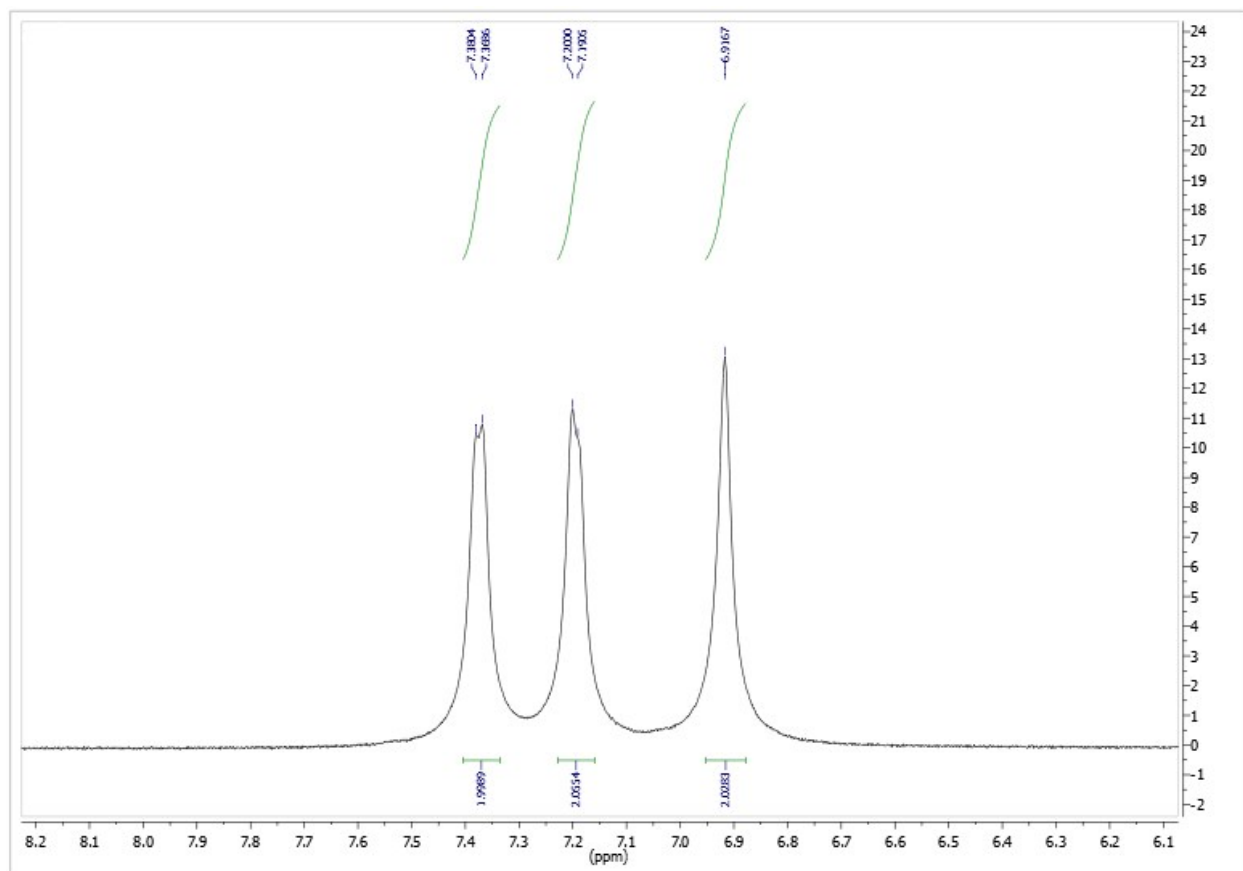
Light yellow solid, m.p. 233-235 °C; FT-IR (KBr,  $\text{cm}^{-1}$ )  $\nu$  = 3407 (NH), 3303 and 3367 ( $\text{NH}_2$ ), 2187 (CN), 1608 ( $\text{C}=\text{N}$ ), 1602 ( $\text{C}=\text{C}$ );  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ )  $\delta$  ppm 1.79 (s, 3H,  $\text{CH}_3$ ), 4.61 (s, 1H, CH), 6.90 (s, 2H,  $\text{NH}_2$ ), 7.19-7.20 (d, 2H,  $J$  = 5.0 Hz, Ar-H), 7.37-7.38 (d, 2H,  $J$  = 5.0 Hz, Ar-H), 12.12 (s, 1H, NH).



**Fig. 8.** FT-IR spectrum of 6-amino-4-(4-chlorophenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**5a**).



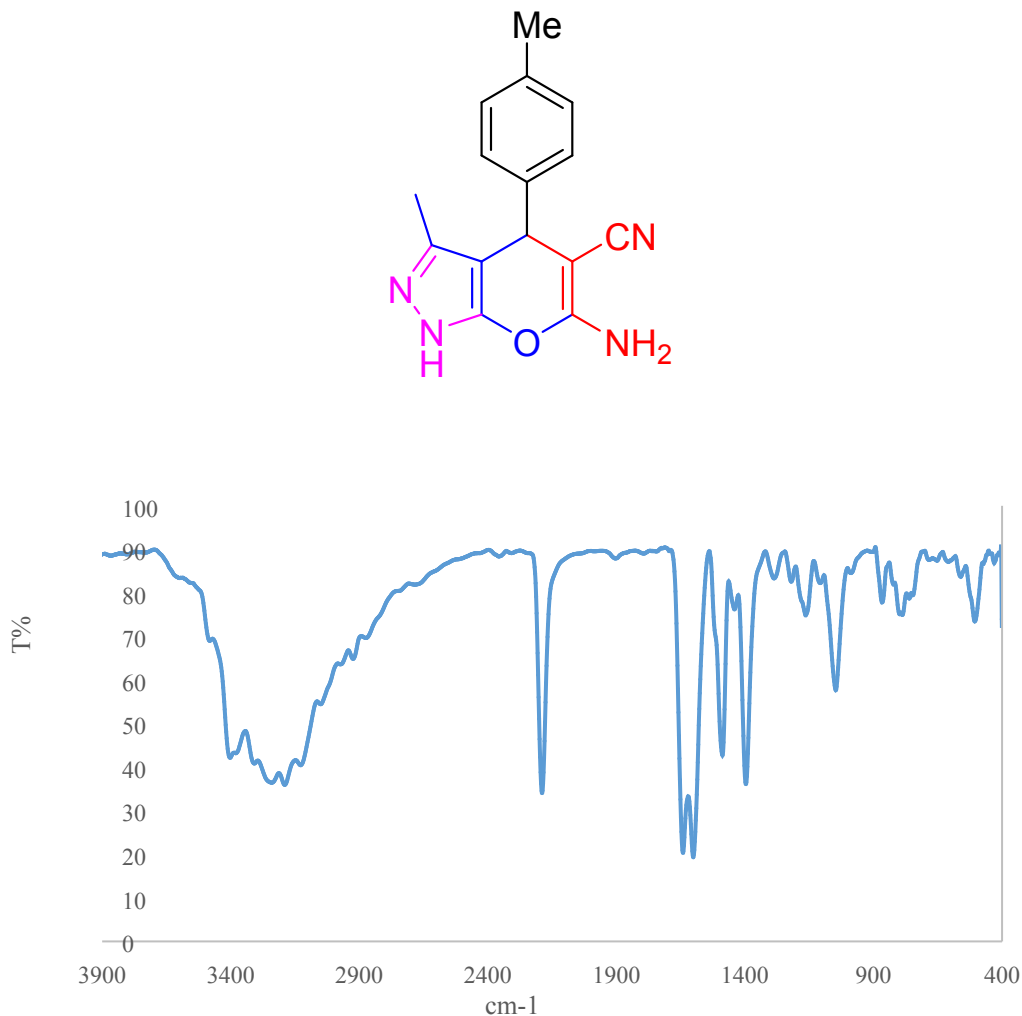
**Fig. 9.**  $^1\text{H}$  NMR spectrum of 6-amino-4-(4-chlorophenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**5a**).



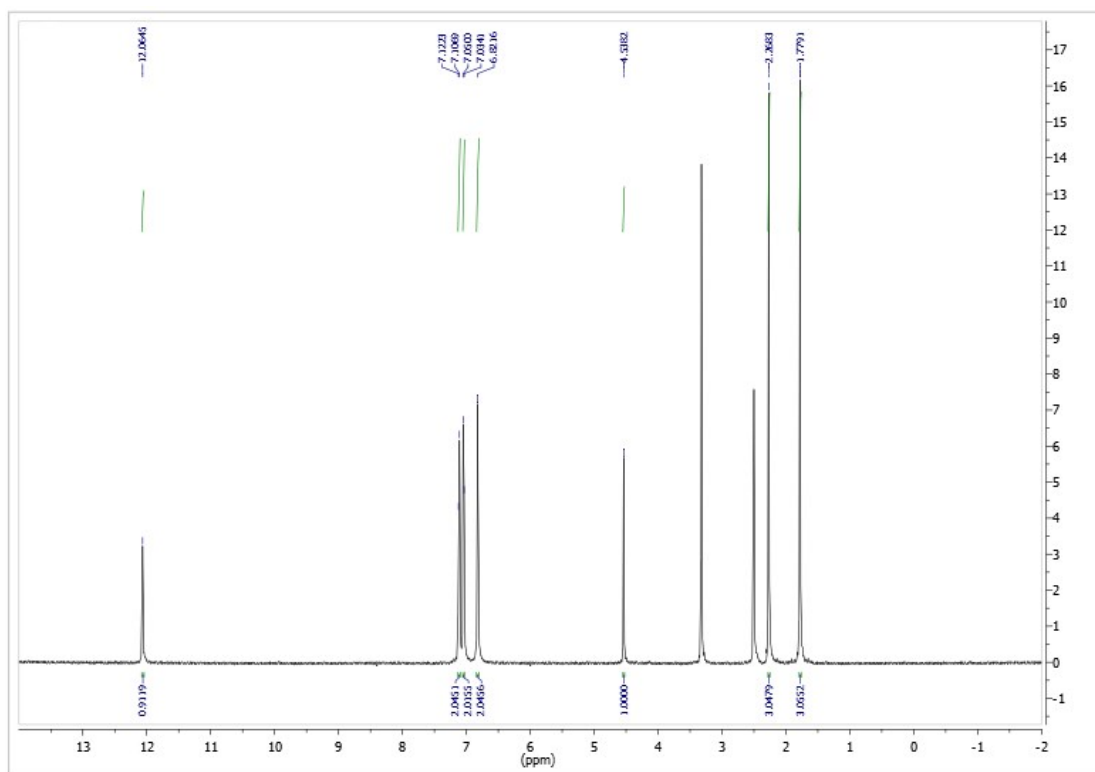
**Fig. 10.** Expanded aromatic region of  $^1\text{H}$  NMR spectrum of 6-amino-4-(4-chlorophenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**5a**).

**6-amino-4-(4-methylphenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (5g)**

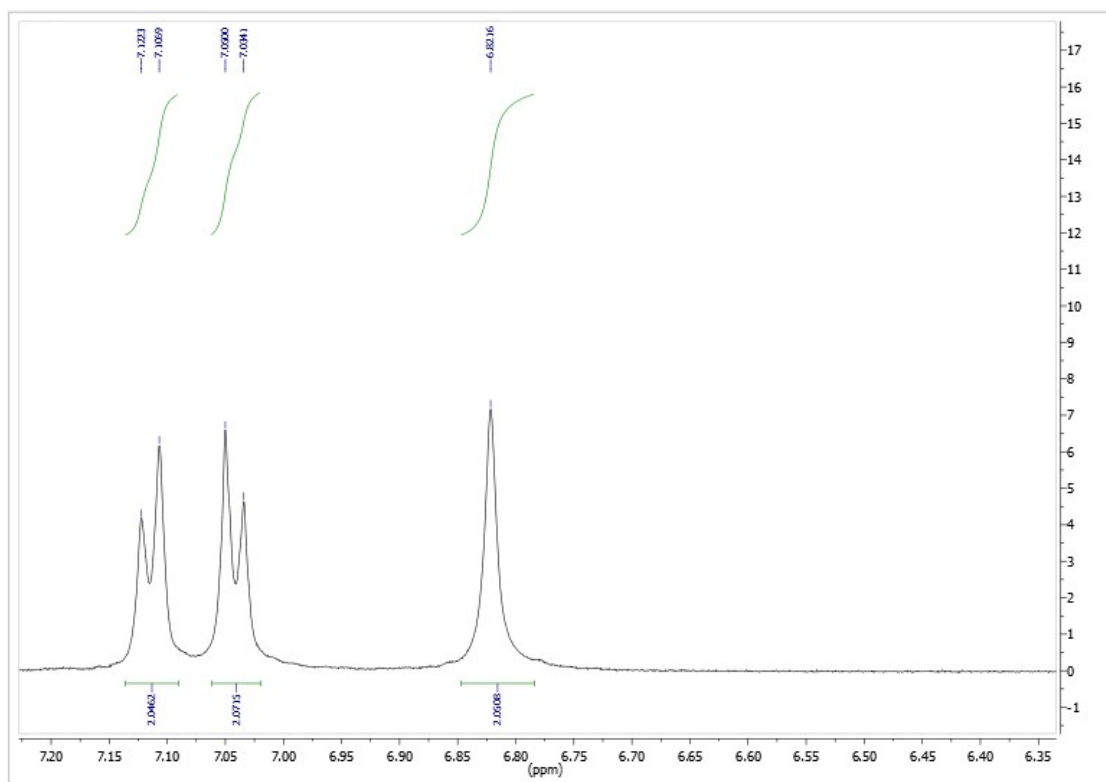
White solid, m.p. 209-211 °C; FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  = 3402 (NH), 3245 and 3186 ( $\text{NH}_2$ ), 2189 (CN), 1639 ( $\text{C}=\text{N}$ ), 1600 ( $\text{C}=\text{C}$ );  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  = 1.79 (s, 3H,  $\text{CH}_3$ ), 2.26 (s, 3H, Ar- $\text{CH}_3$ ), 4.53 (s, 1H, C-4), 6.82 (s, 2H,  $\text{NH}_2$ ), 7.03-7.05 (d, 2H,  $J$  = 10.0 Hz, Ar-H), 7.10-7.12 (d, 2H,  $J$  = 10.0 Hz, Ar-H), 12.06 (s, 1H, NH).



**Fig. 11.** FT-IR spectrum of 6-amino-4-(4-methylphenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (5g).



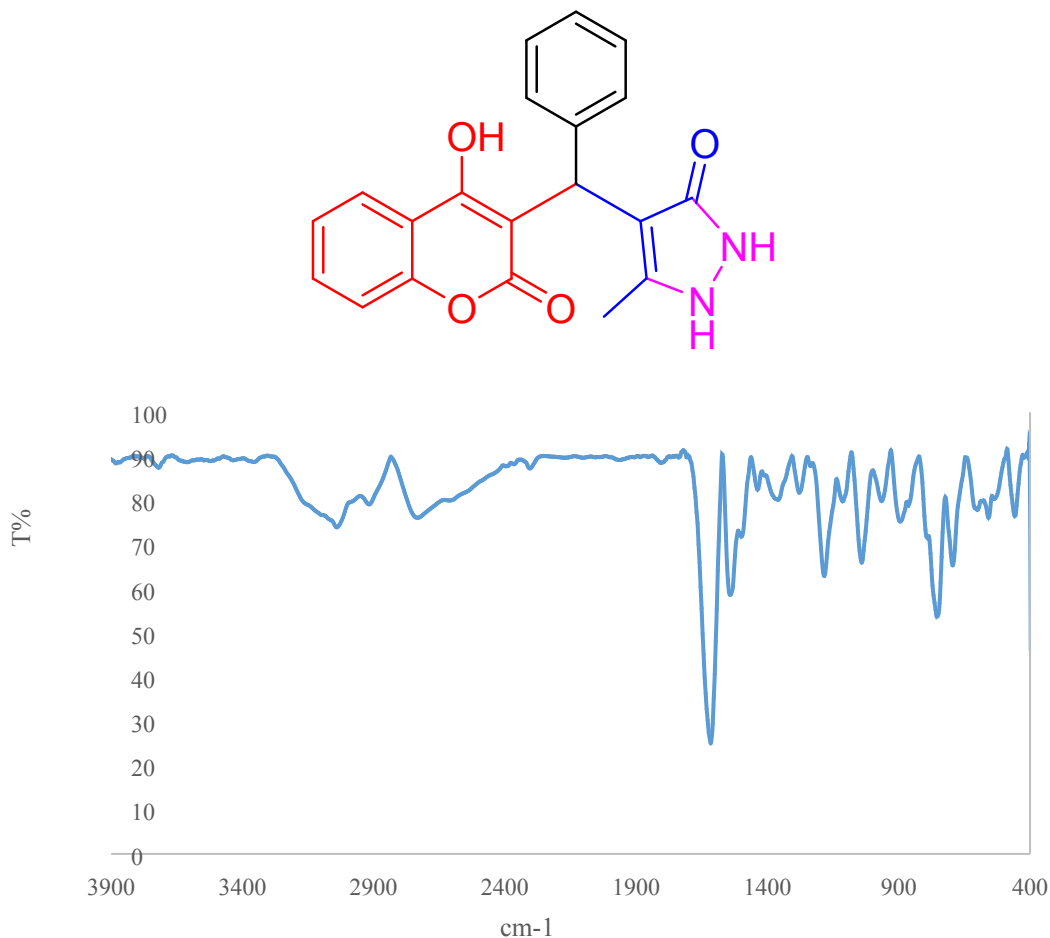
**Fig. 12.**  $^1\text{H}$  NMR spectrum of 6-amino-4-(4-methylphenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5g**).



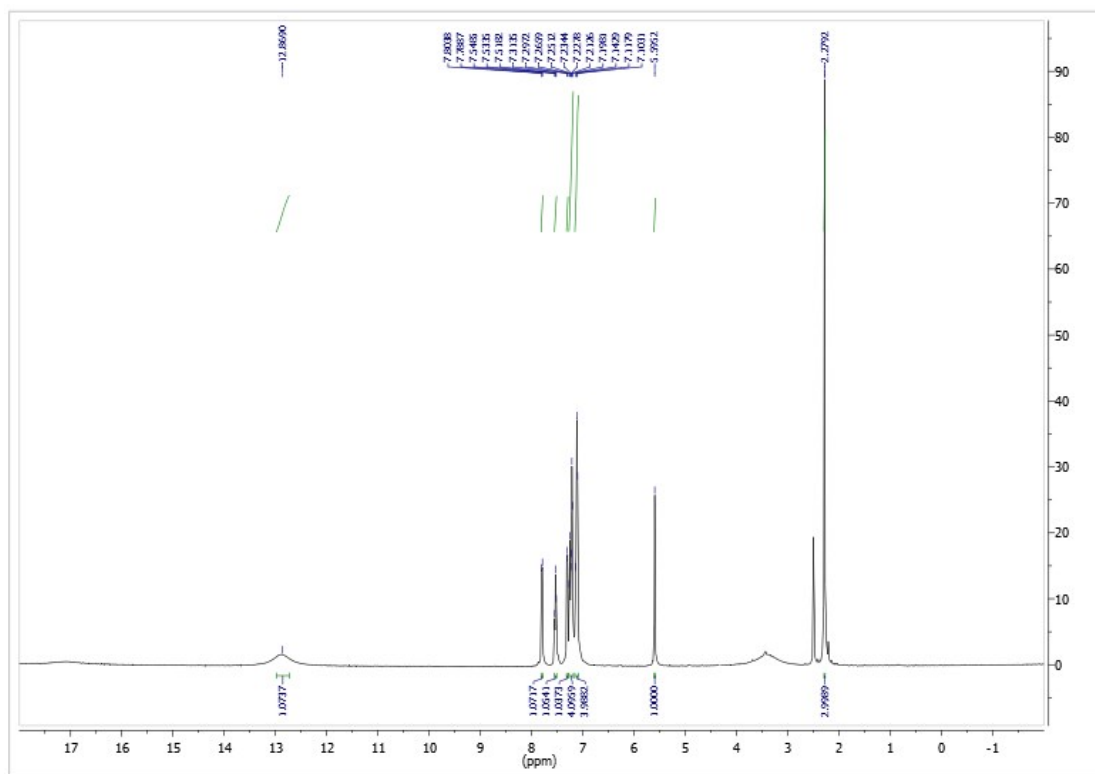
**Fig. 13.** Expanded aromatic region of <sup>1</sup>H NMR spectrum of 6-amino-4-(4-methyl)-3-methyl-1,4-dihydropyran[2,3-*c*]pyrazole-5-carbonitrile (**5g**).

**4-((4-hydroxy-2-oxo-2*H*-chromen-3-yl)(phenyl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (7a)**

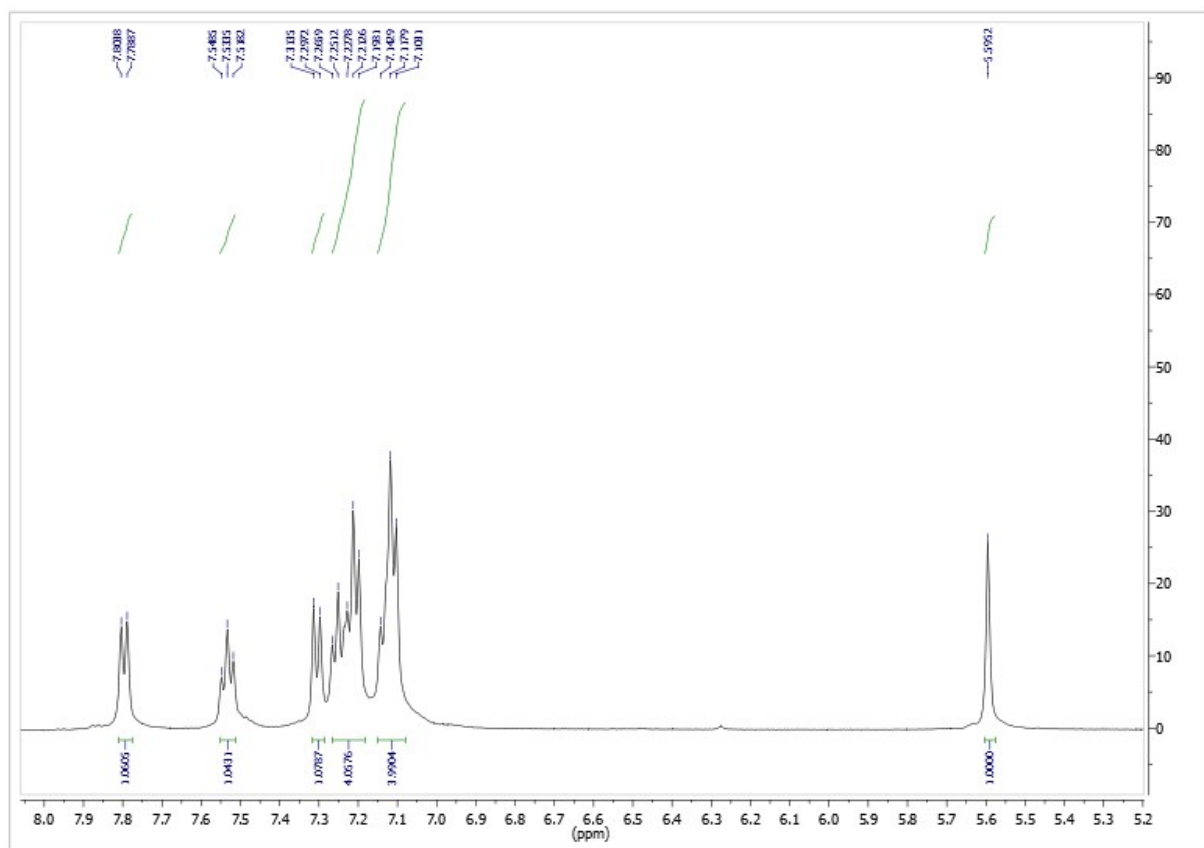
Cream crystalline solid, m.p. 231-233 °C; FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  = 3035, 2727, 1616, 1539, 1357, 1184, 1041, 752; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  2.27 (3H, s), 5.59 (1H, s), 7.10-7.14 (4H, m), 7.19-7.26 (4H, m), 7.29-7.31 (1H, d,  $J$  = 10.0), 7.51-7.54 (1H, t,  $J$  = 7.8 Hz), 7.78-7.80 (1H, d,  $J$  = 10.0), 12.89 (1H, s).



**Fig. 14.** FT-IR spectrum of 4-((4-hydroxy-2-oxo-2*H*-chromen-3-yl)(phenyl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (7a).



**Fig. 15.**  $^1\text{H}$  NMR spectrum of 4-((4-hydroxy-2-oxo-2*H*-chromen-3-yl)(phenyl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (**7a**).



**Fig. 16.** Expanded aromatic region of  $^1\text{H}$  NMR spectrum of 4-((4-hydroxy-2-oxo-2*H*-chromen-3-yl)(phenyl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (**7a**).