ELECTRONIC SUPPLENTARY INFORMATION

NEW JOURNAL OF CHEMISTRY

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

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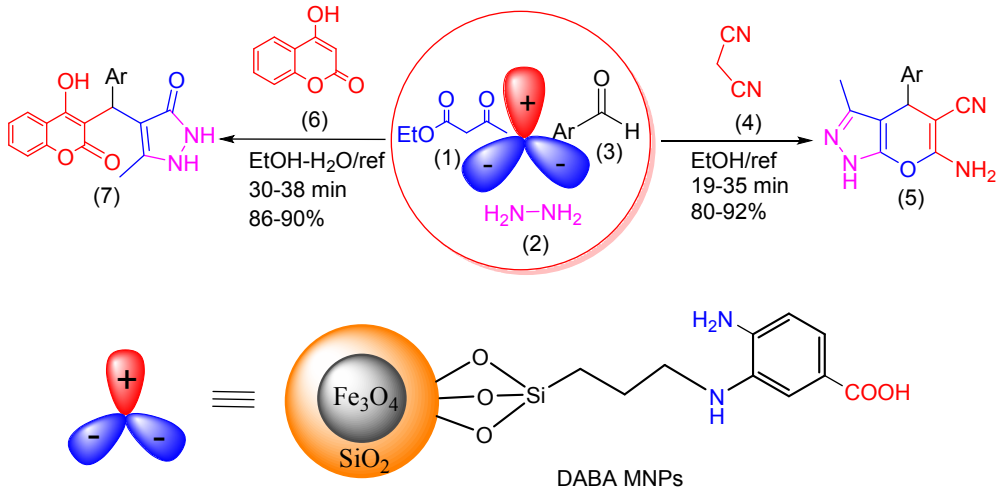

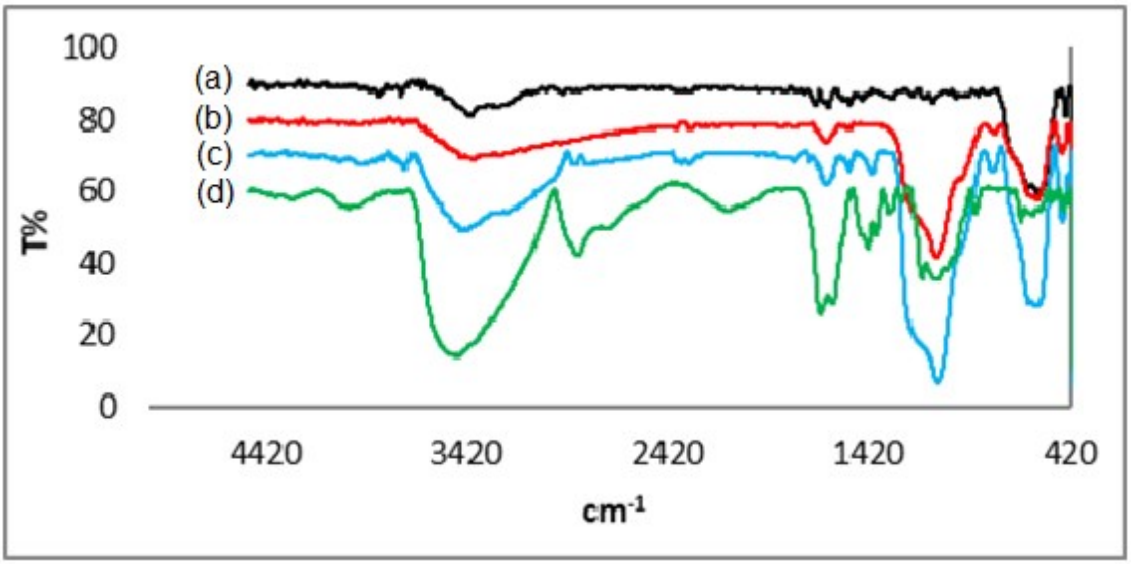

Fig. 1. FT-IR spectra of the Fe_3O_4 (**a**), Fe_3O_4@SiO_2 (**b**), Fe_3O_4@SiO_2@CPTS (**c**) and Fe_3O_4@SiO_2@PTS-DABA (**d**).

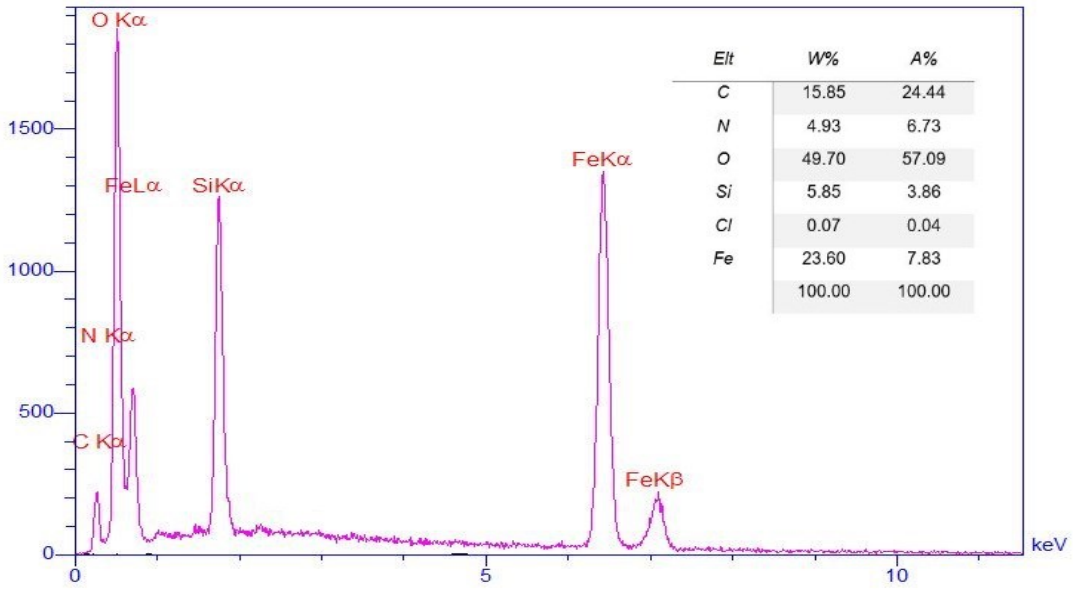

Fig. 2. Energy dispersive spectroscopy (EDS) pattern of the Fe_3O_4@SiO_2@PTS-DABA.

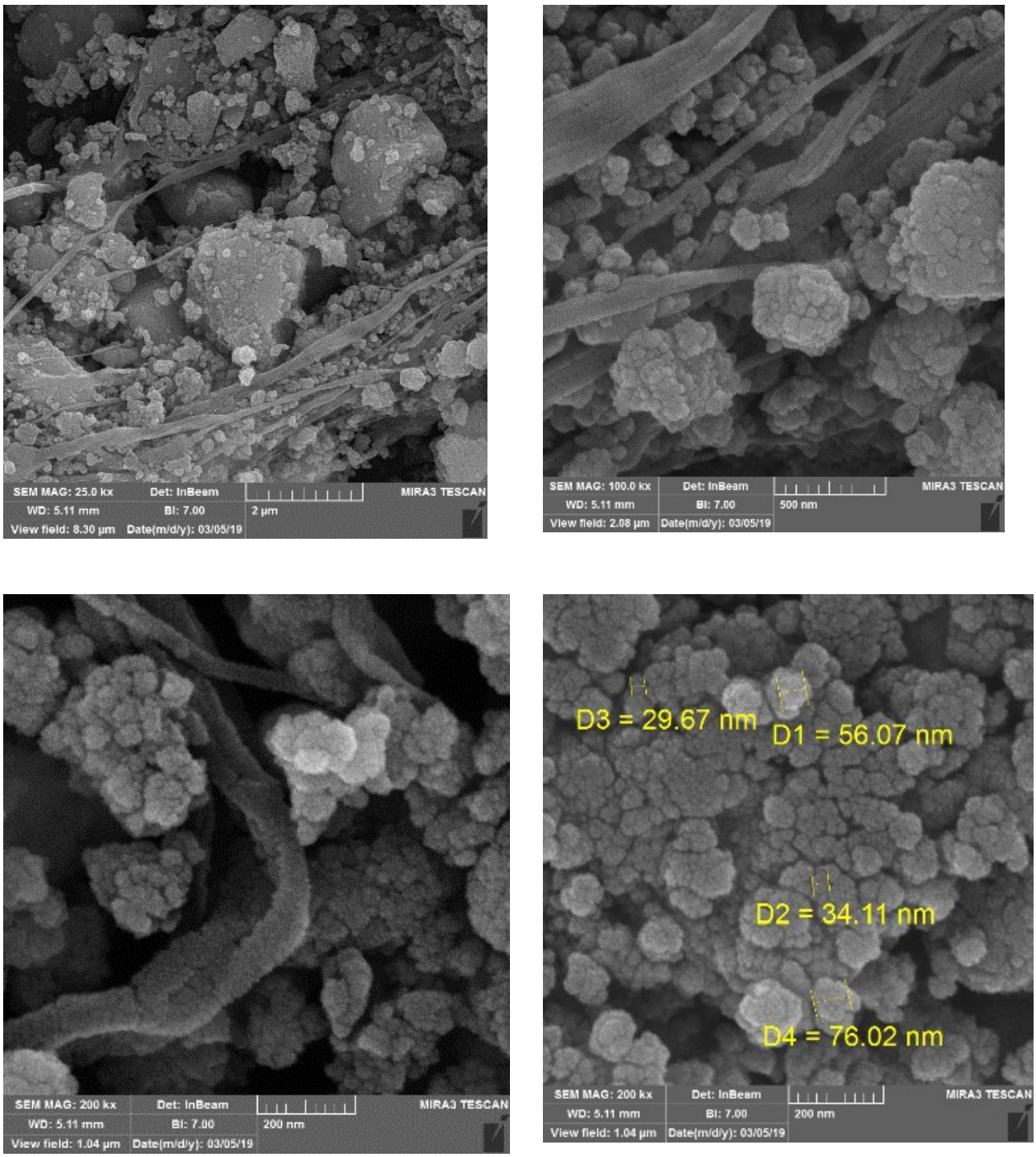

Fig. 3. FESEM images of the Fe_3O_4@SiO_2@PTS-DABA catalyst.

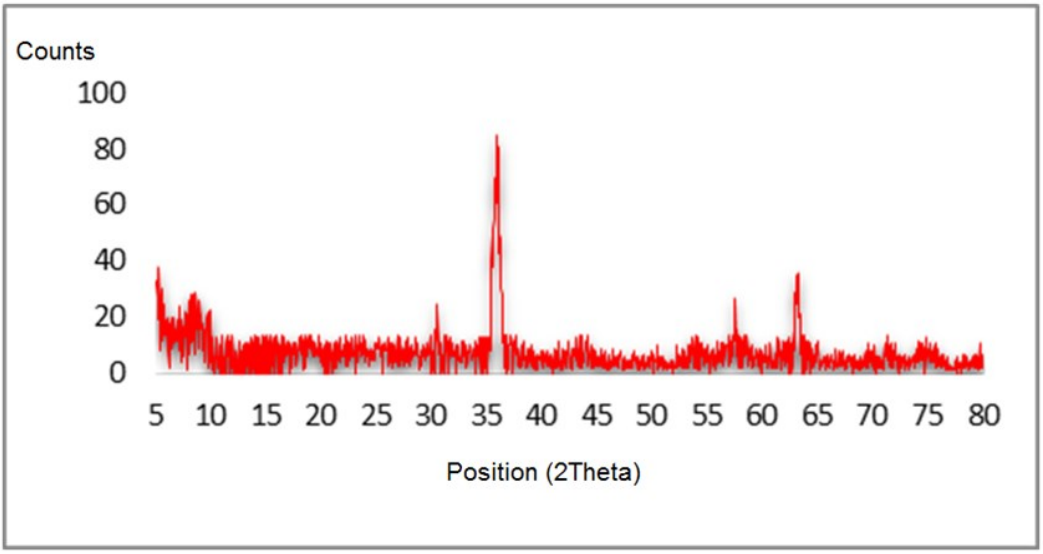

Fig.4. X-Ray diffraction (XRD) pattern of the Fe_3O_4@SiO_2@PTS-DABA.

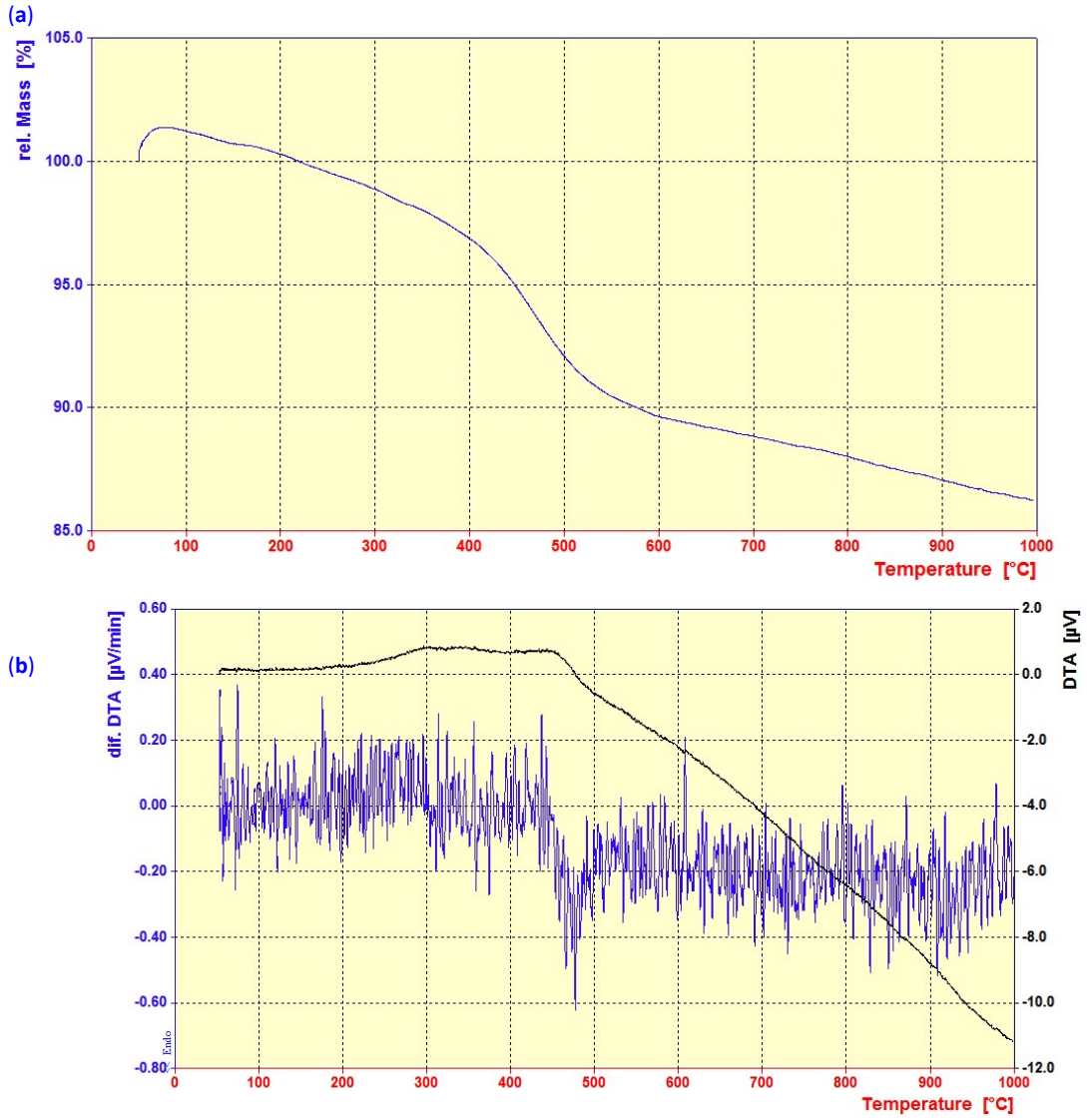

Fig. 5. (**a**) TGA and (**b**) DTA curves of the Fe_3O_4@SiO_2@PTS-DABA catalyst.

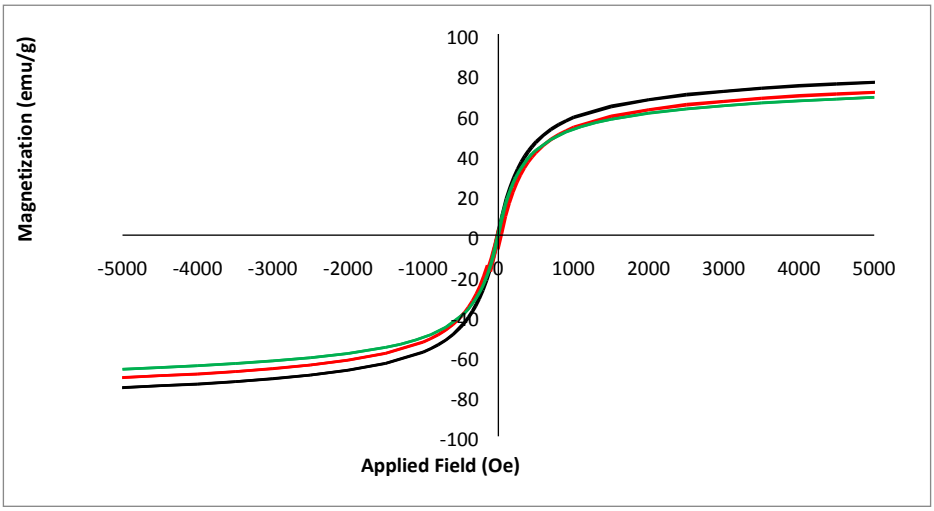

Fig. 6. Magnetization curves of the (black) Fe_3O_4, (red) Fe_3O_4@SiO_2, (green) Fe_3O_4@SiO_2@PTS-DABA.

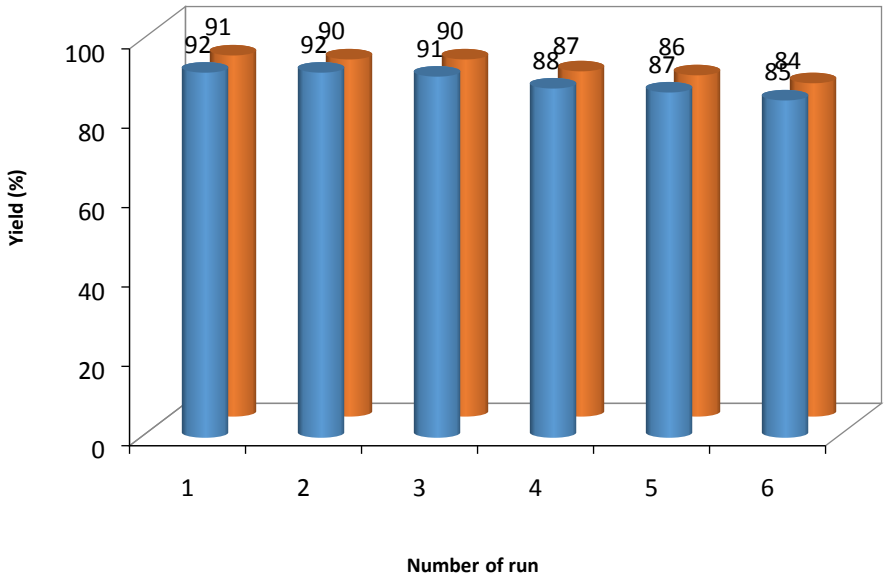

Fig. 7. Reusability of Fe_3O_4@SiO_2@PTS-DABA for the synthesis of **6a** (blue diagram) and 7a (red diagram).

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 ^{o}C; FT-IR (KBr, cm^{-1}) υ = 3407 (NH), 3303 and 3367 (NH_2), 2187 (CN), 1608 (C=N), 1602 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 1.79 (s, 3H, CH_3), 4.61 (s, 1H, CH), 6.90 (s, 2H, 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).

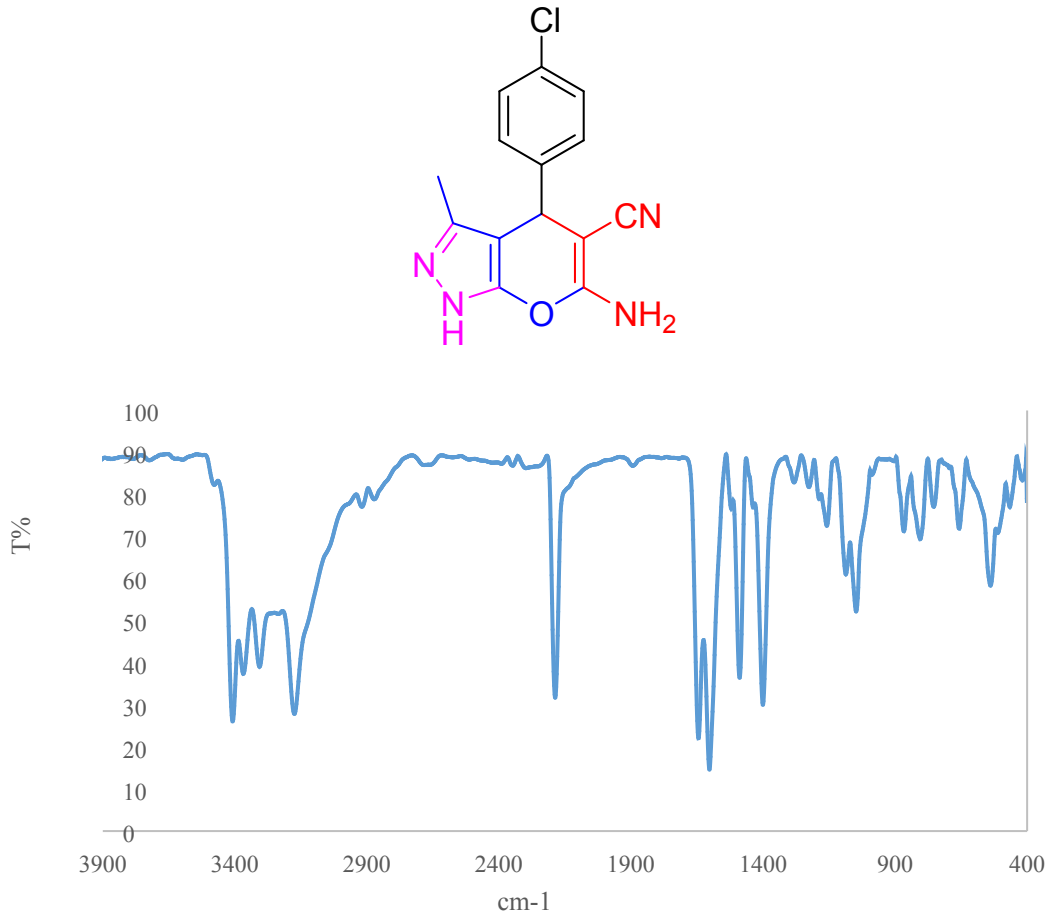

Fig. 8. FT-IR spectrum of 6-amino-4-(4-chlorophenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**5a**).

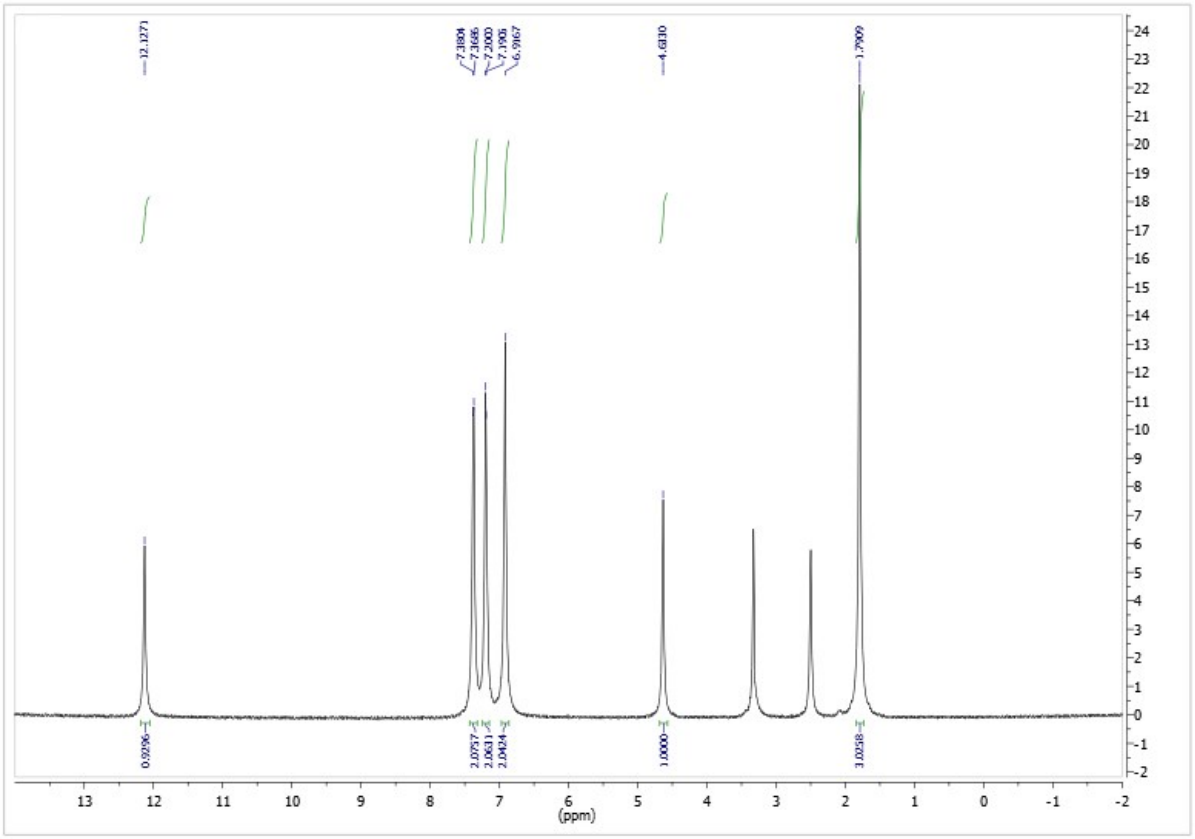

Fig. 9. ^{1}H NMR spectrum of 6-amino-4-(4-chlorophenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**5a**).

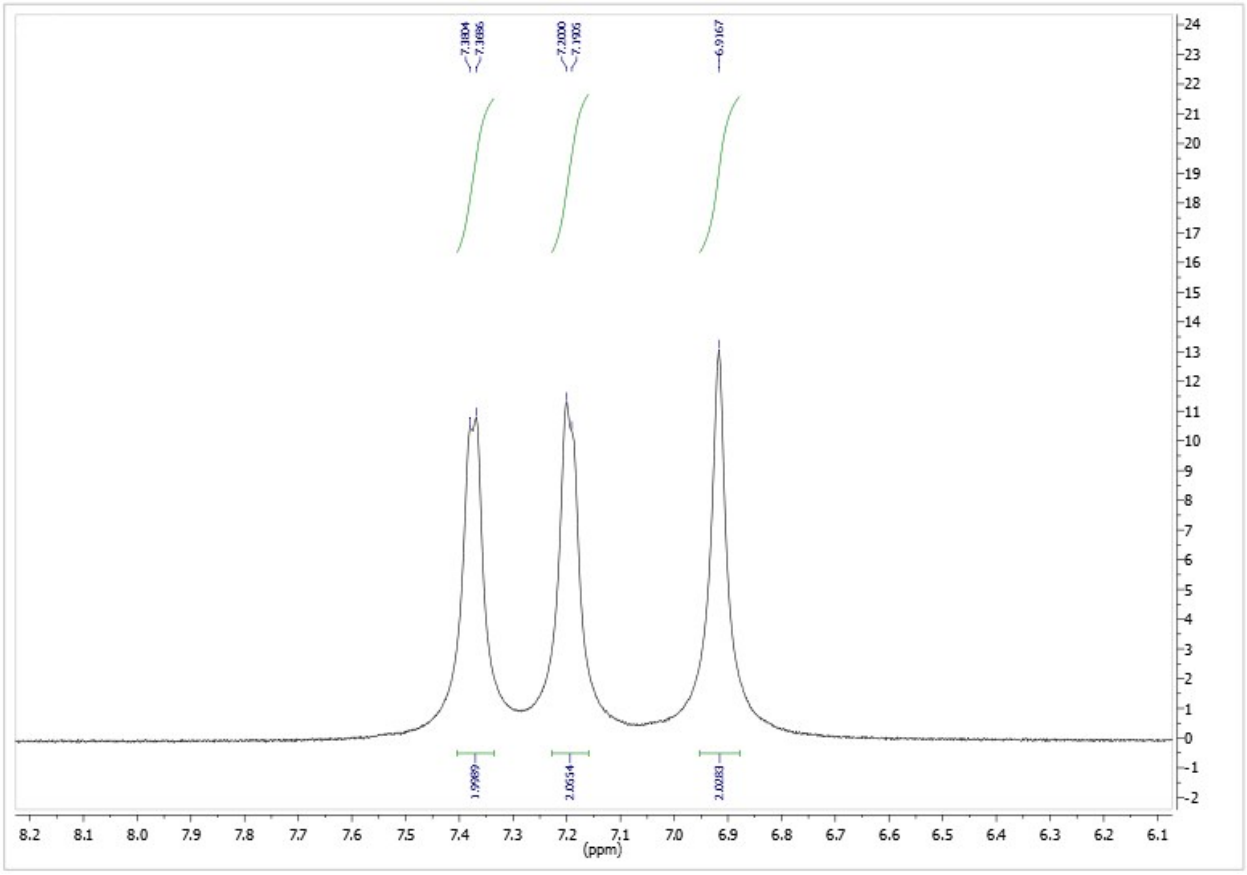

Fig. 10. Expanded aromatic region of ^{1}H NMR spectrum of 6-amino-4-(4-chlorophenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**5a**).

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

White solid, m.p. 209-211 ^{o}C; FT-IR (KBr, cm^{-1}): υ = 3402 (NH), 3245 and 3186 (NH_2), 2189 (CN), 1639 (C=N), 1600 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.79 (s, 3H, CH_3), 2.26 (s, 3H, Ar-CH_3), 4.53 (s, 1H, C-4), 6.82 (s, 2H, 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).

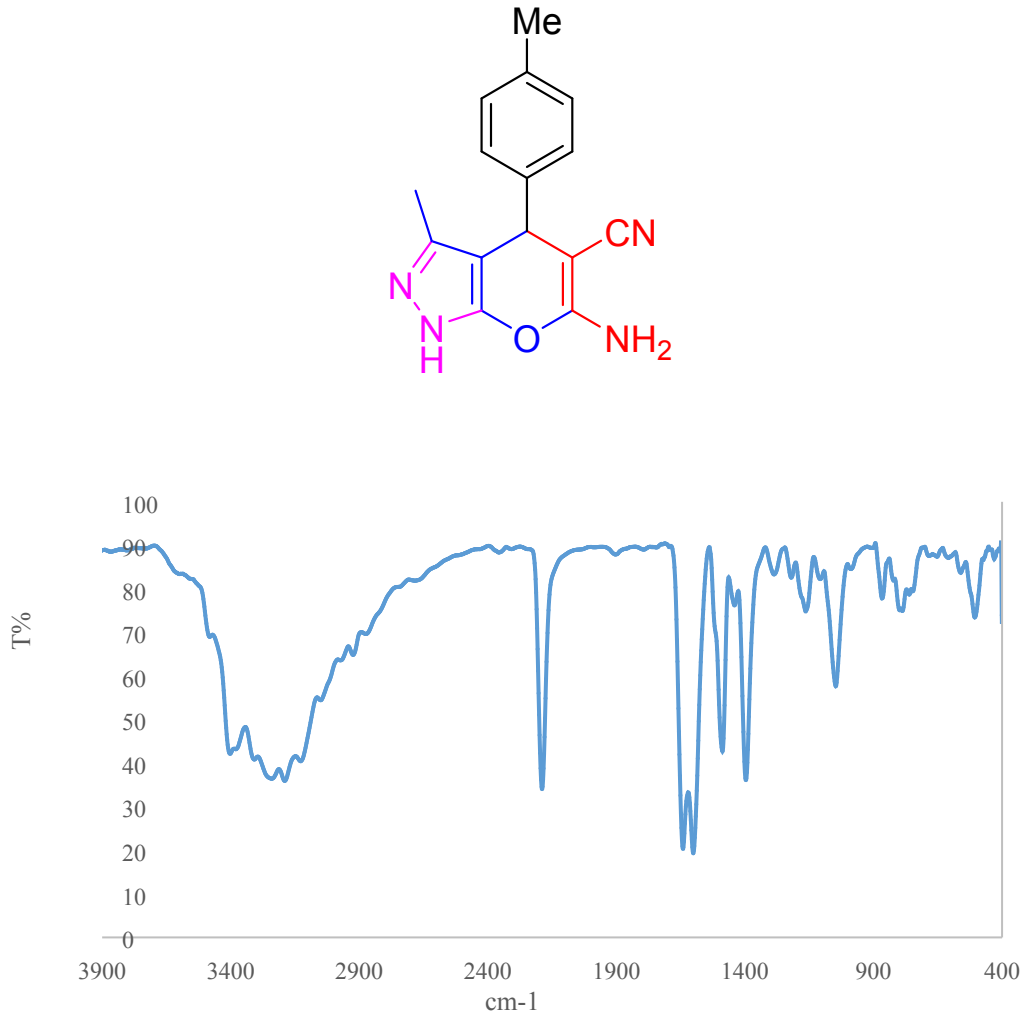

Fig. 11. FT-IR spectrum of 6-amino-4-(4-methylphenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**5g**).

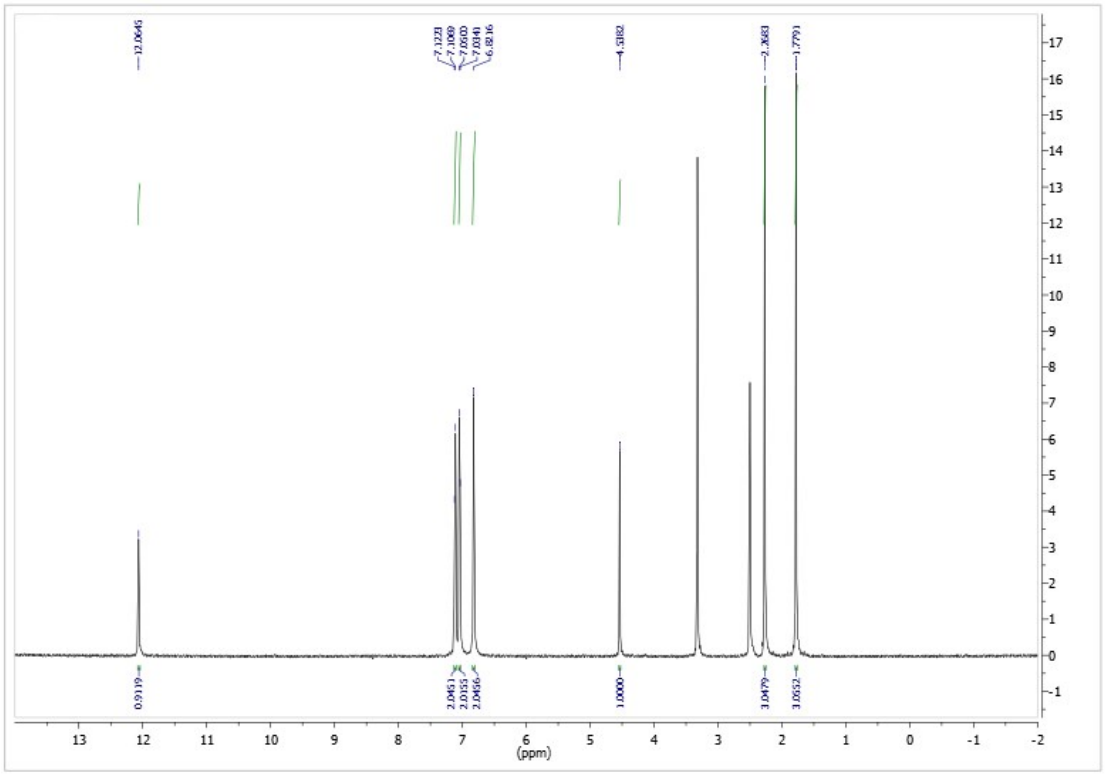

Fig. 12. ^{1}H NMR spectrum of 6-amino-4-(4-methylphenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**5g**).

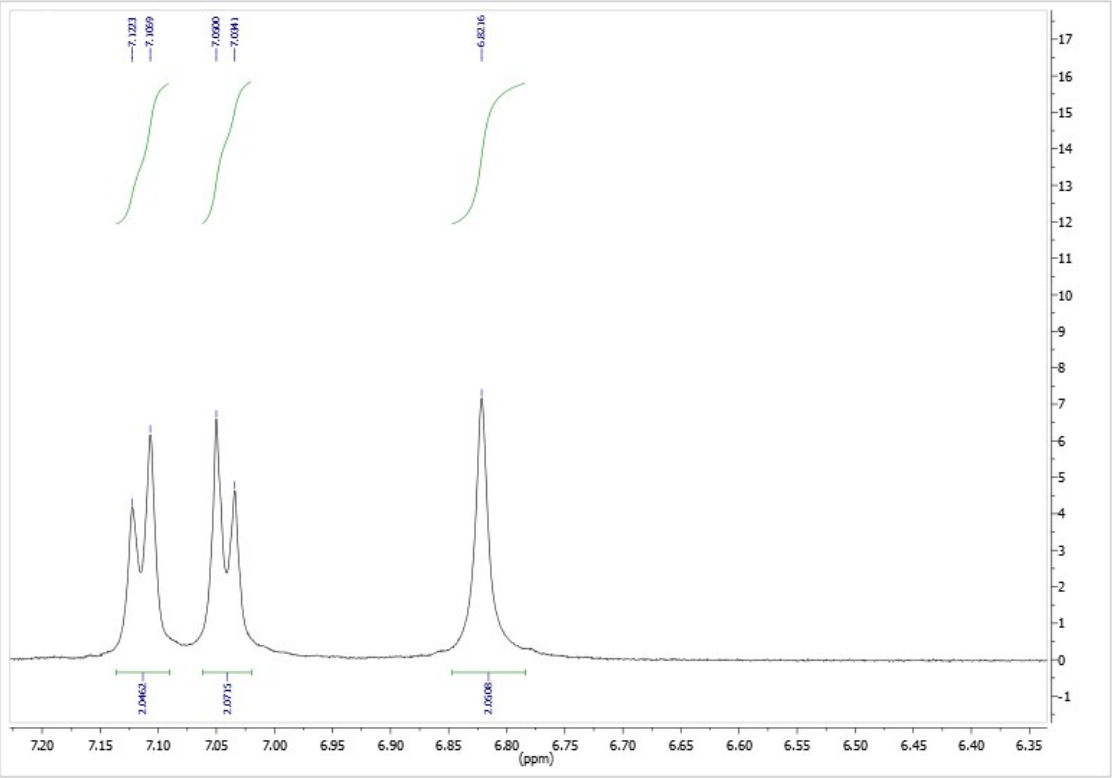

Fig. 13. Expanded aromatic region of ^{1}H NMR spectrum of 6-amino-4-(4-methyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**5g**).

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 ^{o}C; FT-IR (KBr, cm^{-1}): υ = 3035, 2727, 1616, 1539, 1357, 1184, 1041, 752; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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).

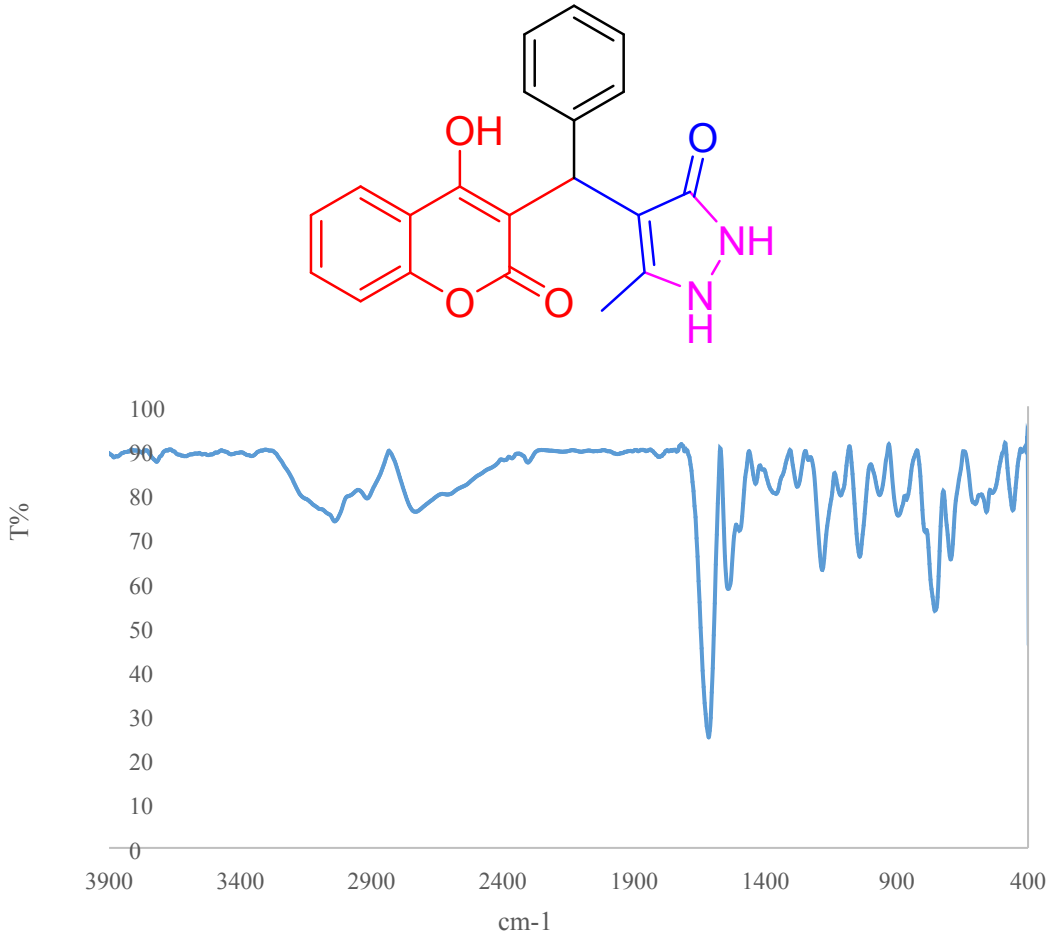

Fig. 14. FT-IR spectrum of 4-((4-hydroxy-2-oxo-2*H*-chromen-3-yl)(phenyl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (**7a**).

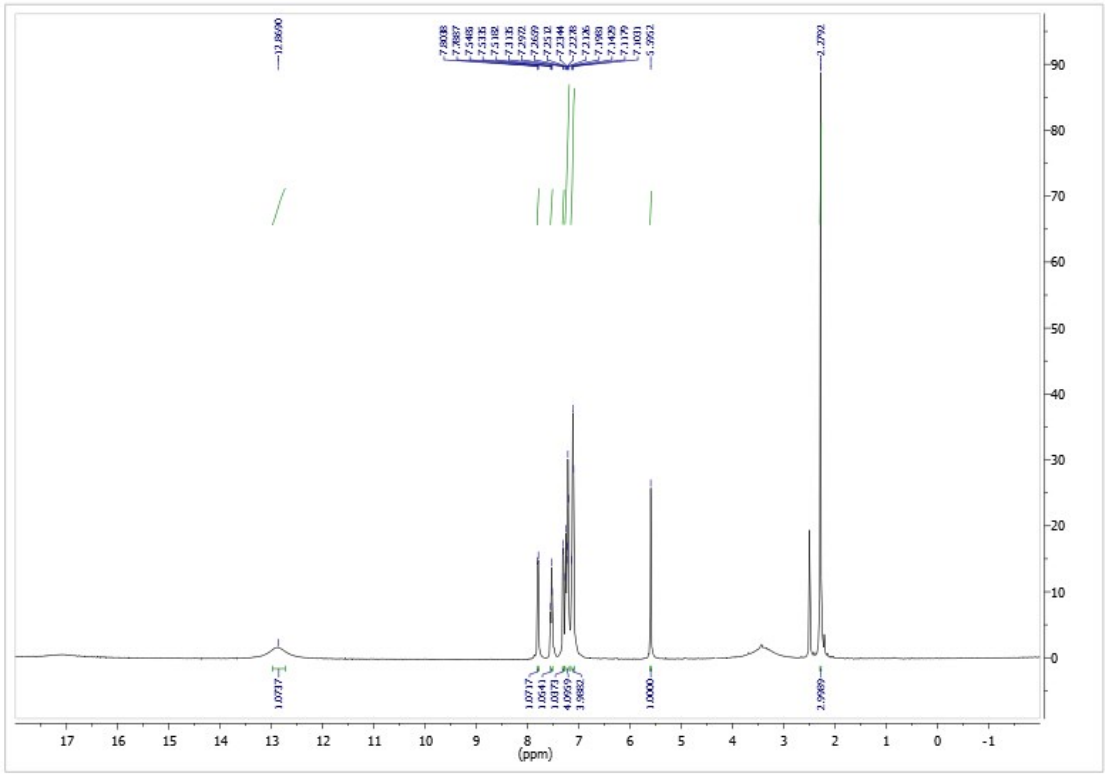

Fig. 15. [1]H NMR spectrum of 4-((4-hydroxy-2-oxo-2*H*-chromen-3-yl)(phenyl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (**7a**).

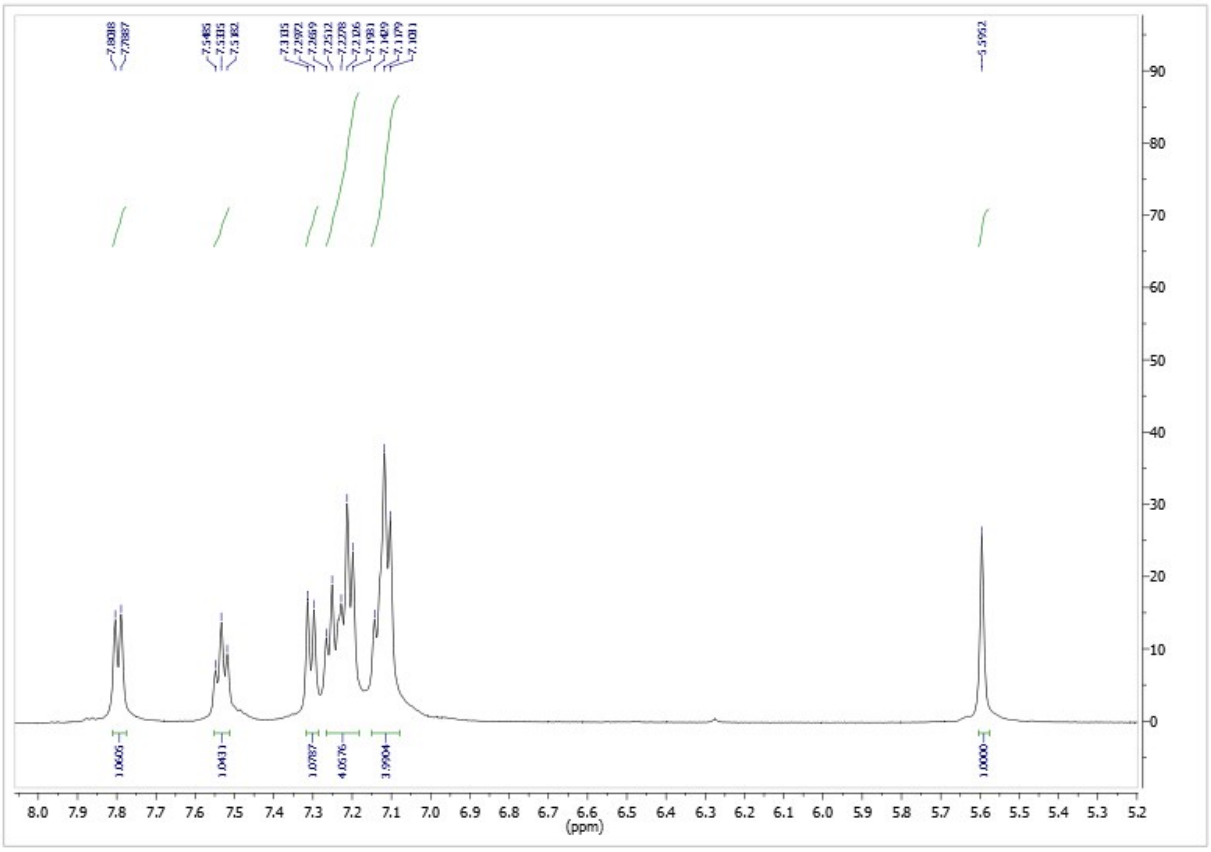

Fig. 16. Expanded aromatic region of ^{1}H NMR spectrum of 4-((4-hydroxy-2-oxo-2*H*-chromen-3-yl)(phenyl)methyl)-5-methyl-1,2-dihydro-3*H*-pyrazol-3-one (**7a**).