

Supporting Information

Cu(II) immobilized on poly (guanidine-sulfonamide) functionalized MgFe₂O₄@Bentonite: a novel magnetic nanocatalyst for the synthesis of 1,4-dihydropyrano[2,3-c]pyrazole

Sedigheh Alavinia, Ramin Ghorbani-Vaghei*, Ramin Ghiai, Alireza Gharakhani,
Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan,
6517838683, Iran

*Corresponding author; E-mail: rgvaghei@yahoo.com & ghorbani@basu.ac.ir

Fax: +98(81)38380647

General procedure for the synthesis of substituted 1,4-dihydropyrano[2,3-c]pyrazole derivatives

Benzaldehyde (1 mmol), malononitrile (1 mmol), ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), and Bentonite@MgFe₂O₄@PGSA/Cu (10 mg) was stirred in water solvent at room temperature. After completion of the reaction (monitored by TLC), Bentonite@MgFe₂O₄@PGSA/Cu catalyst was isolated by external magnet, washed with EtOH and EtOAc (2 × 5 mL) and dried under vacuum. The title compounds were obtained in their crystalline forms by recrystallization of ethanol solution (Scheme 1).

Spectral data for products.

6-Amino-4-(2-hydroxy-3-methoxy)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

white solid; IR (KBr) (ν_{\max} , cm⁻¹) 3468-3382, 3185, 2185, 3300-3500; ¹H NMR (400 MHz, CDCl₃-d₆): δ (ppm) 1.96 (3H, s), 3.79 (3H, s), 4.60 (1H, s), 6.55-6.97 (5H, m), 10.39 (2H, br); ¹³C NMR (75 MHz, CDCl₃-d₆) δ (ppm): 10.35, 29.26, 56.04, 105.43, 110.56, 120.53, 121.31, 124.34, 124.76, 136.95, 138.35, 147.16, 159.55, 160.51.

6-Amino-3-methyl-4-(naphthalene-1-yl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

white solid; IR (KBr) (ν_{\max} , cm⁻¹) 3375, 3310, 3156, 2191; ¹H NMR (400 MHz, CDCl₃-d₆): δ (ppm) 1.76 (3H, s), 4.78 (1H, s), 6.92-6.95 (2H, s), 7.23-7.91 (7H, m), 12.16 (1H, s); ¹³C NMR (75 MHz, CDCl₃-d₆) δ (ppm): 10.18, 36.97, 57.56, 97.85, 121.26, 126.16, 126.21, 126.29, 126.70, 128.00, 128.14, 128.85, 132.59, 133.28, 136.29, 142.16, 155.29, 161.39

6-Amino-4-(4-Bisphenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

white solid; IR (KBr) (ν_{\max} , cm⁻¹): 3391, 3367, 3167, 2187; ¹H-NMR: (CDCl₃-d₆) δ (ppm) = 1.84 (3H, s), 4.66 (1H, s), 6.91 (2H, s), 7.25-7.67 (9H, m), 12.13 (1H, s)

¹³C-NMR: (CDCl₃-d₆) δ (ppm) = 10.29, 36.32, 57.52, 98.01, 121.32, 127.03, 127.24, 127.80, 128.50, 129.37, 136.10, 139.01, 140.27, 144.21, 155.25, 161.40

6-Amino-4-(4-fluorophenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

white solid; IR (KBr) (ν_{\max} , cm^{-1}):3360,3233,3119,2195 ; $^1\text{H-NMR}$: ($\text{CDCl}_3\text{-d}_6$) δ (ppm) 1.78(3H, s), 4.63 (1H, s), 6.89 (2H, s), 7.11-7.22 (4H, m),12.12 (H, s)

6-Amino-4-(3-nitrophenyl)-1,4- dihydropyrano[2,3,c]pyrazole-5-carbonitrile

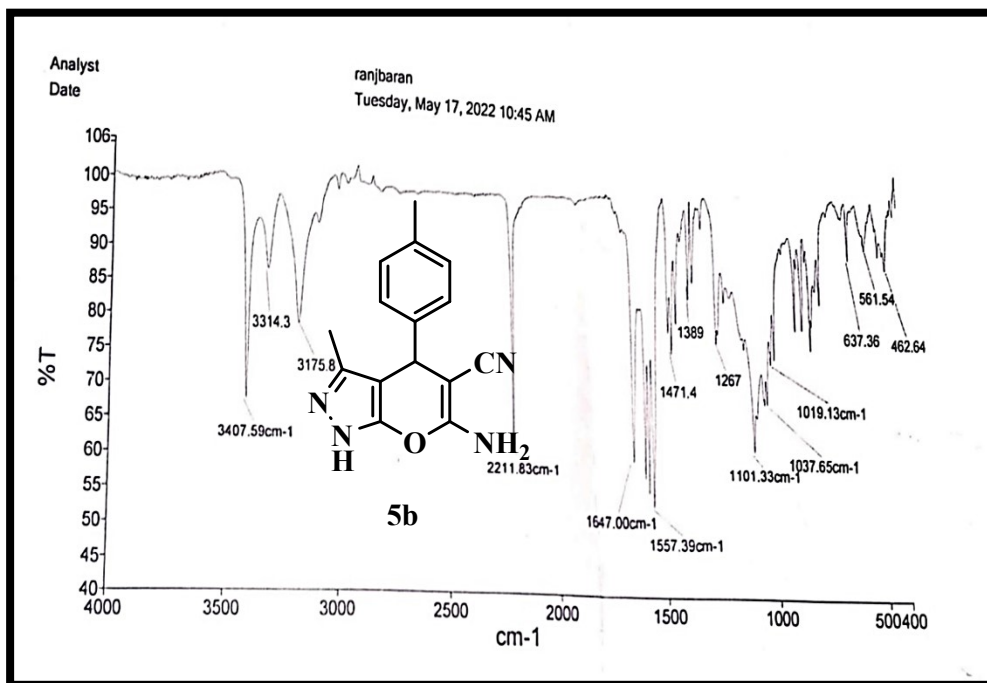
white solid; IR (KBr) (ν_{\max} , cm^{-1}) 3474,3117,3223,2195 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3\text{-d}_6$) δ (ppm): 1.81 (3H,s), 4.88 (1H,s), 7.06 (2H,s), 7.68-8.03(4H,m), 12.21 (1H,s)

6-Amino-4-(3-bromophenyl)-3-methyl-1,4- dihydropyrano[2,3,c]pyrazole-5-carbonitrile

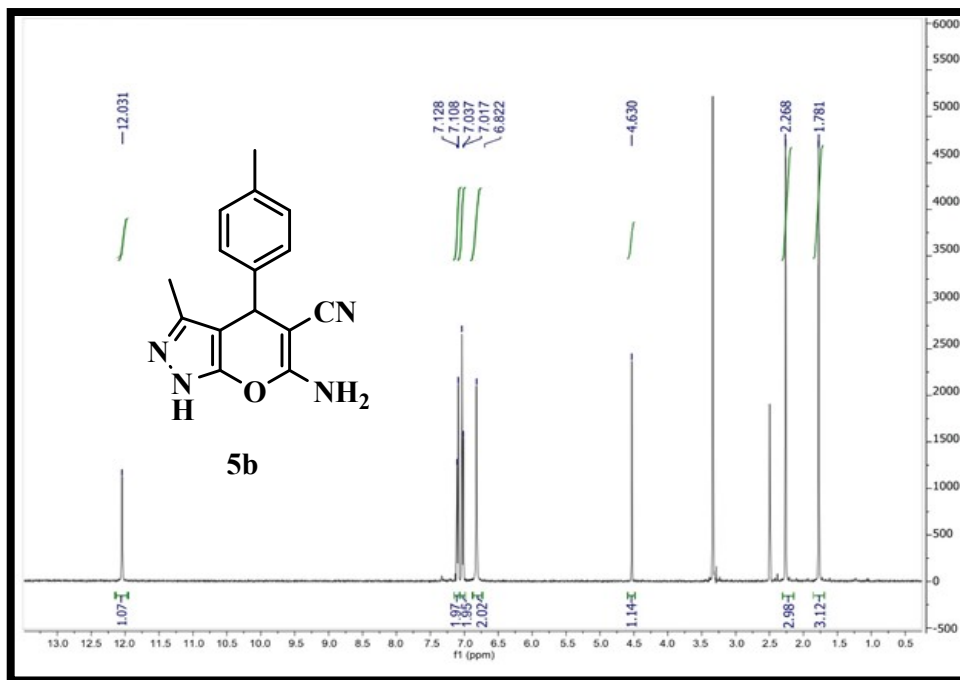
White solid; IR (KBr) (ν_{\max} , cm^{-1}) 3410,3320,3194,2191 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 1.82 (3H, CH_3 , s), 4.66 (1H, s), 6.99-7.41 (6H,ArH, m), 12.17(1H,NH, s)

6-Amino-4-(furan-2-yl)-3-methyl-1,4- dihydropyrano[2,3,c]pyrazole-5-carbonitrile

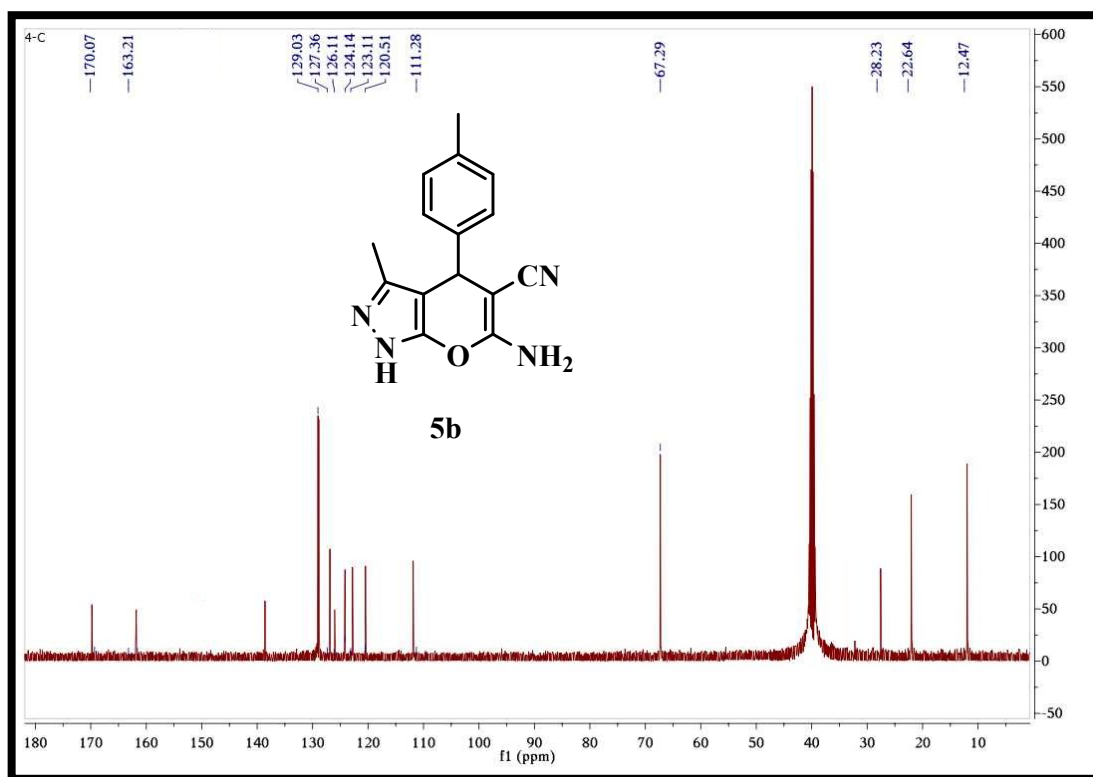
Yellow solid; IR (KBr) (ν_{\max} , cm^{-1}) 3419,3323,3055,2172 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3\text{-d}_6$): δ (ppm) 2.16 (3H, CH_3 , s), 4.96 (1H, s), 6.36-7.71 (5H, NH_2 ,m), 12.53 (1H,NH, s)



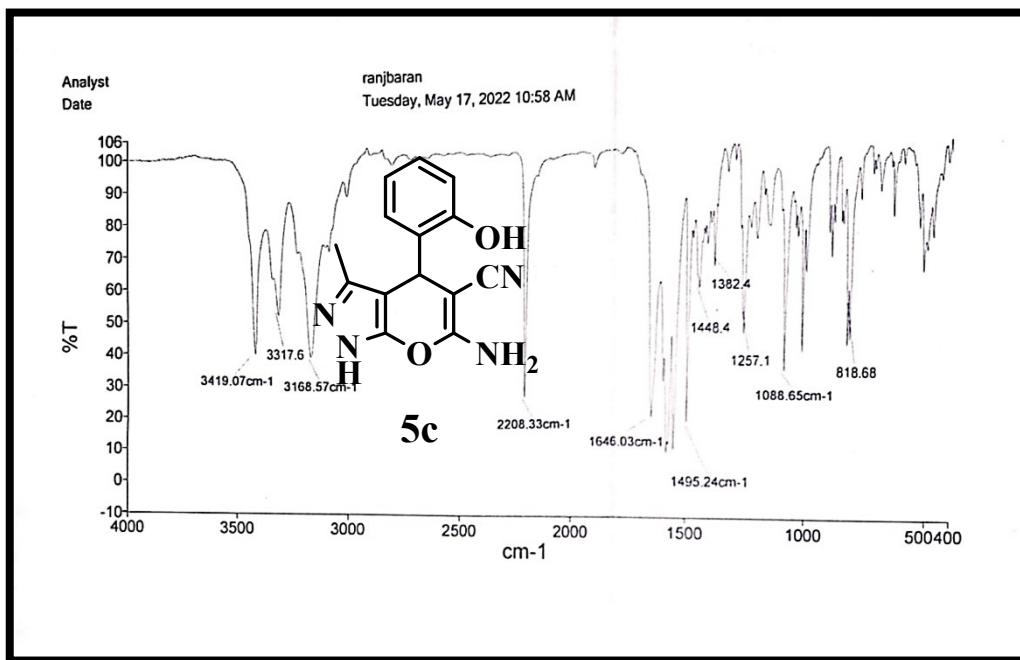
FT-IR spectra of compound 5b



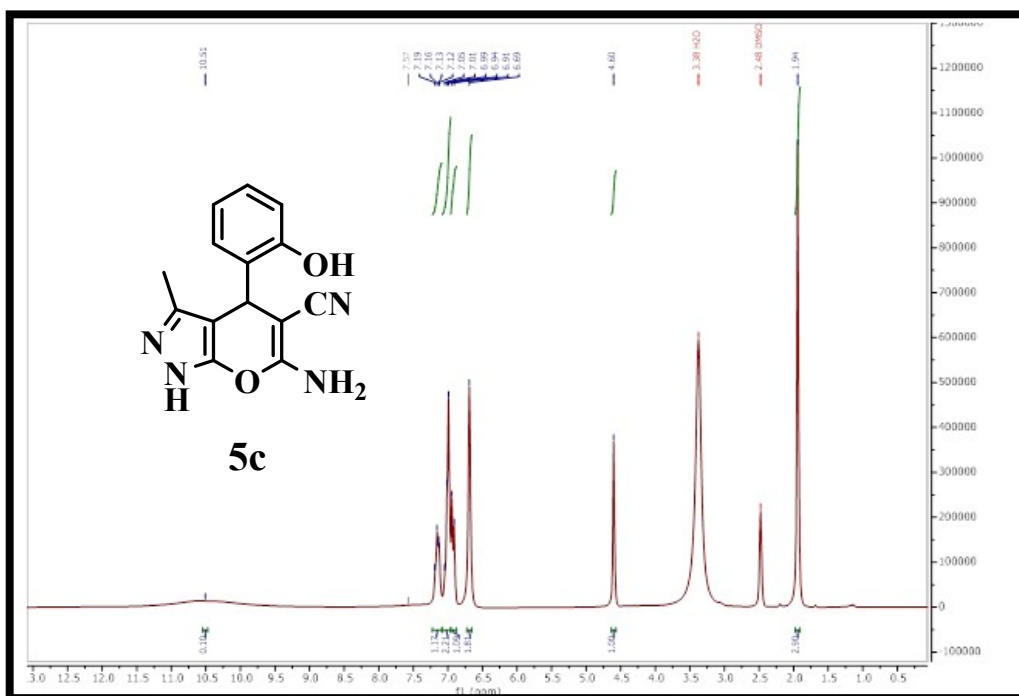
¹H NMR spectra of compound 5b



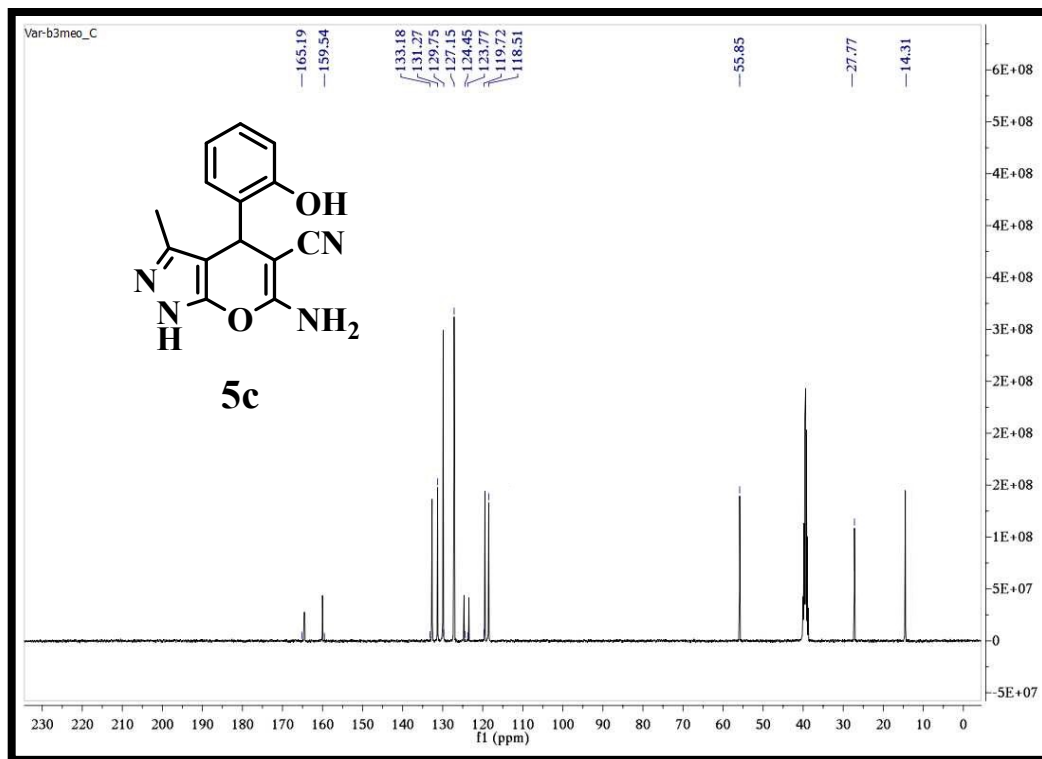
¹³C NMR spectra of compound 5b



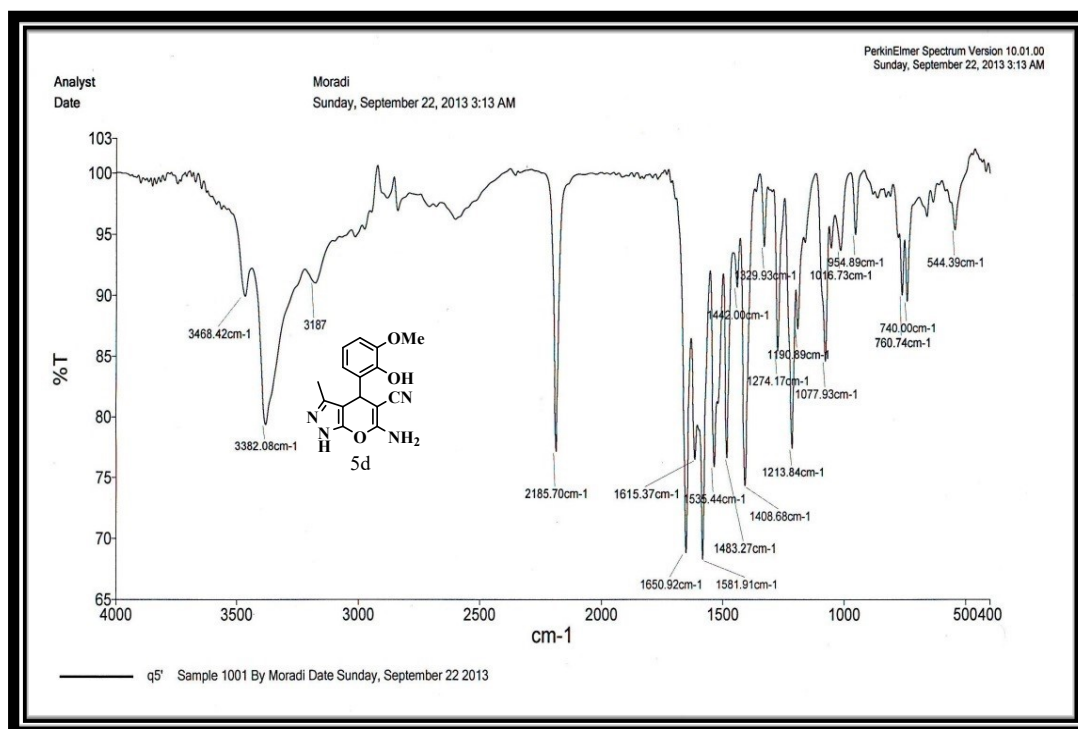
FT-IR spectra of compound 5c



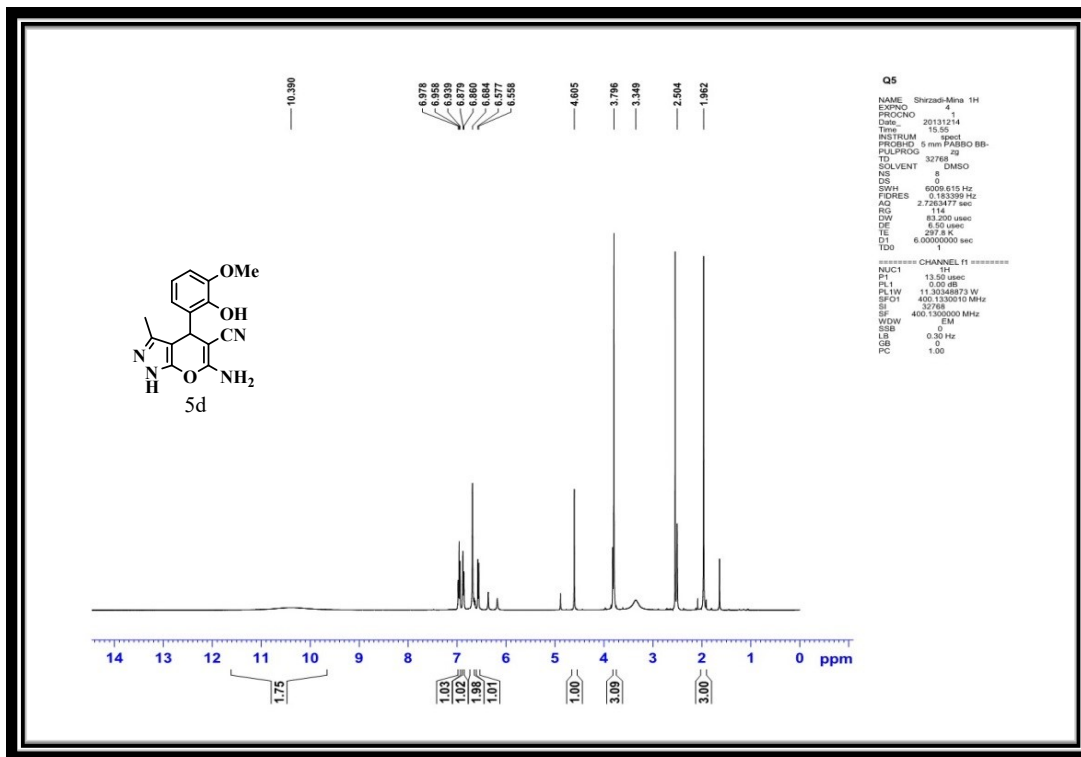
¹H NMR spectra of compound 5c



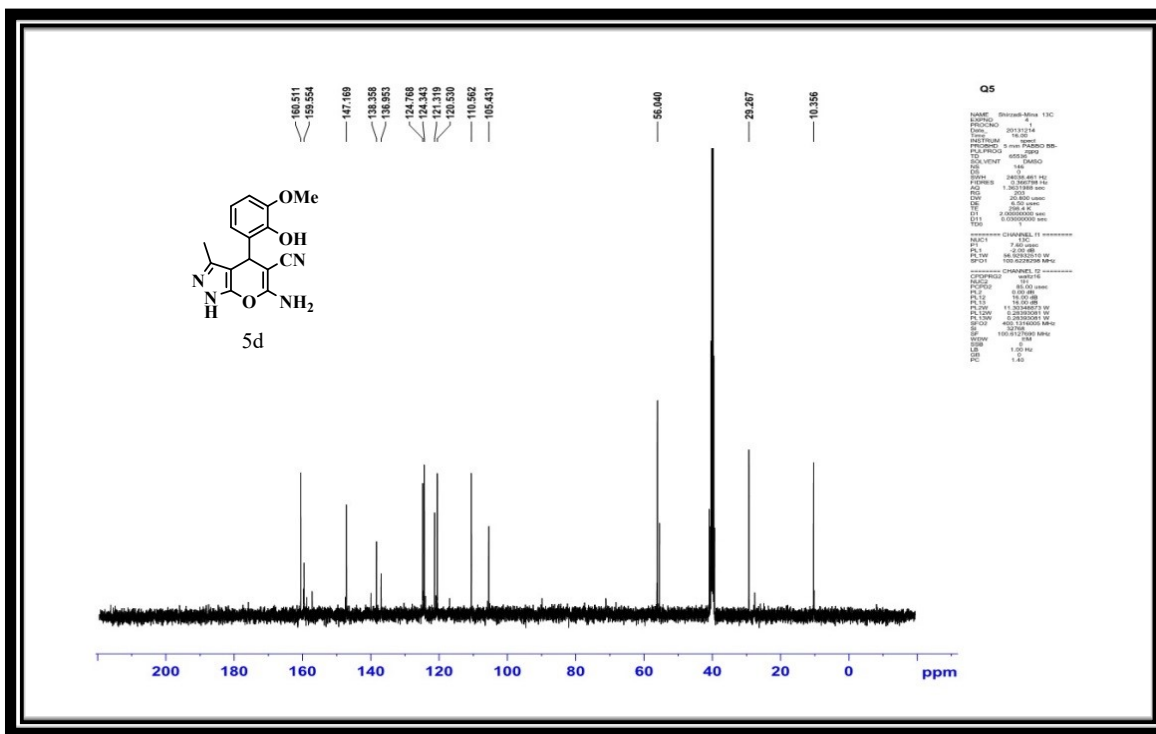
¹³C NMR spectra of compound **5c**



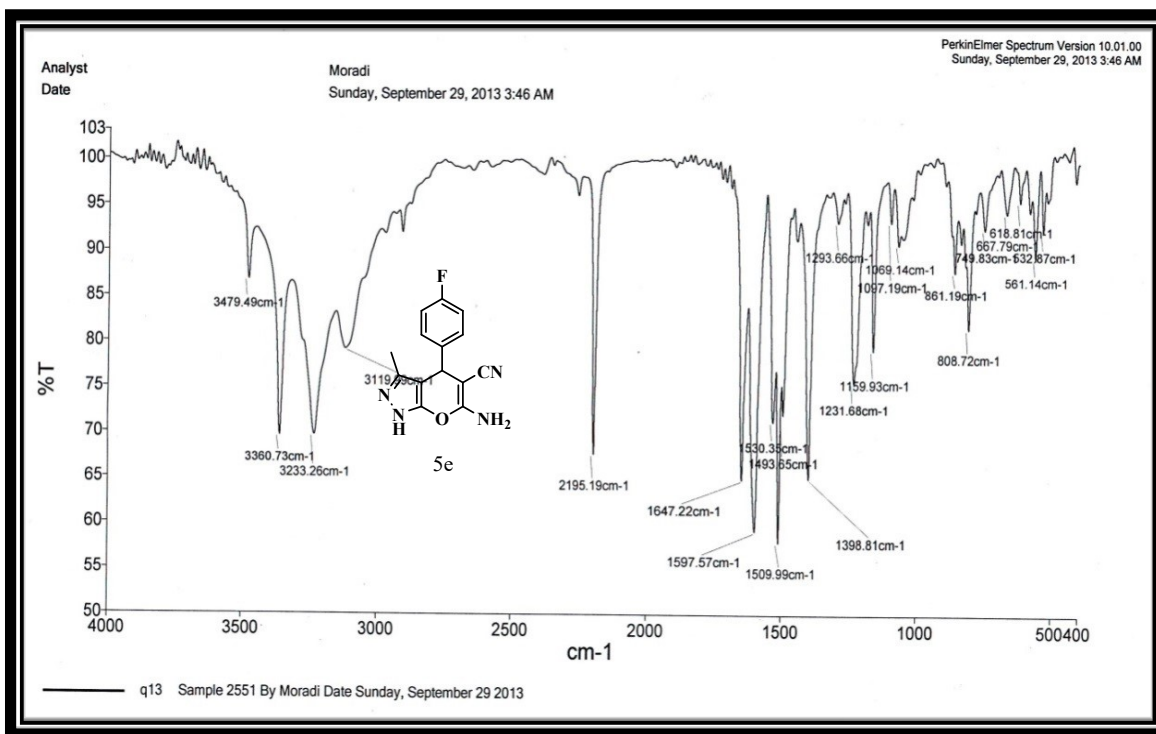
FT-IR spectra of compound **5d**



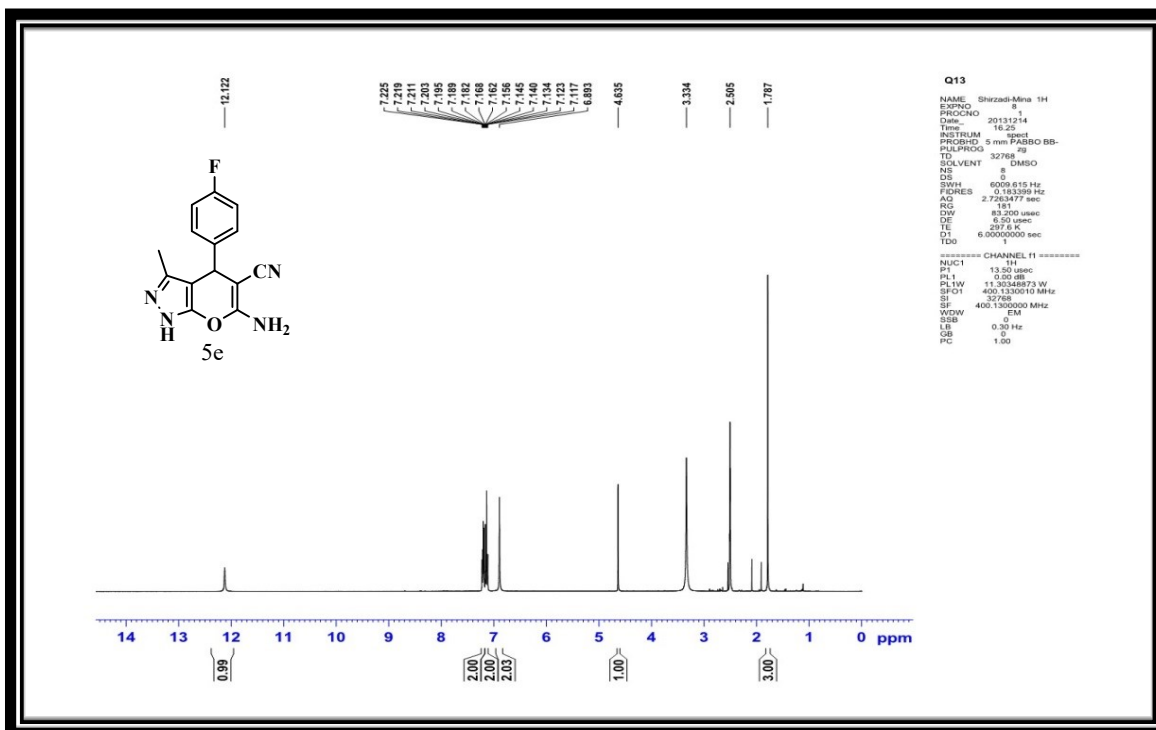
¹H NMR spectra of compound 5d



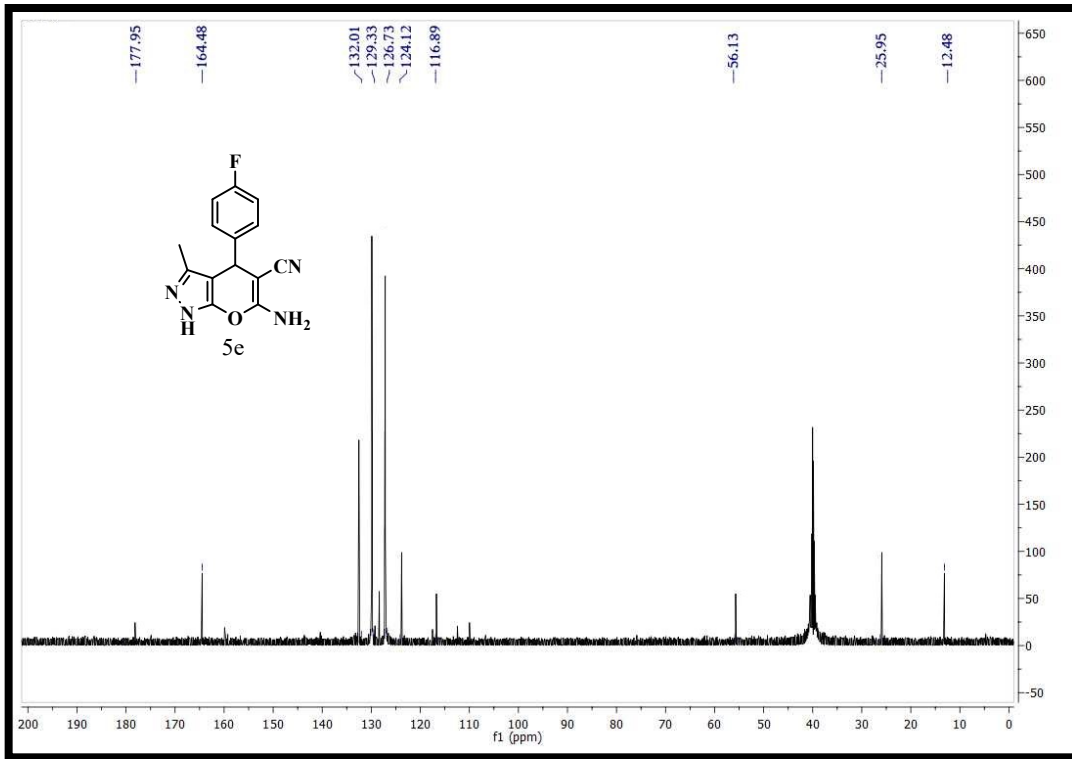
¹³C NMR spectra of compound 5d



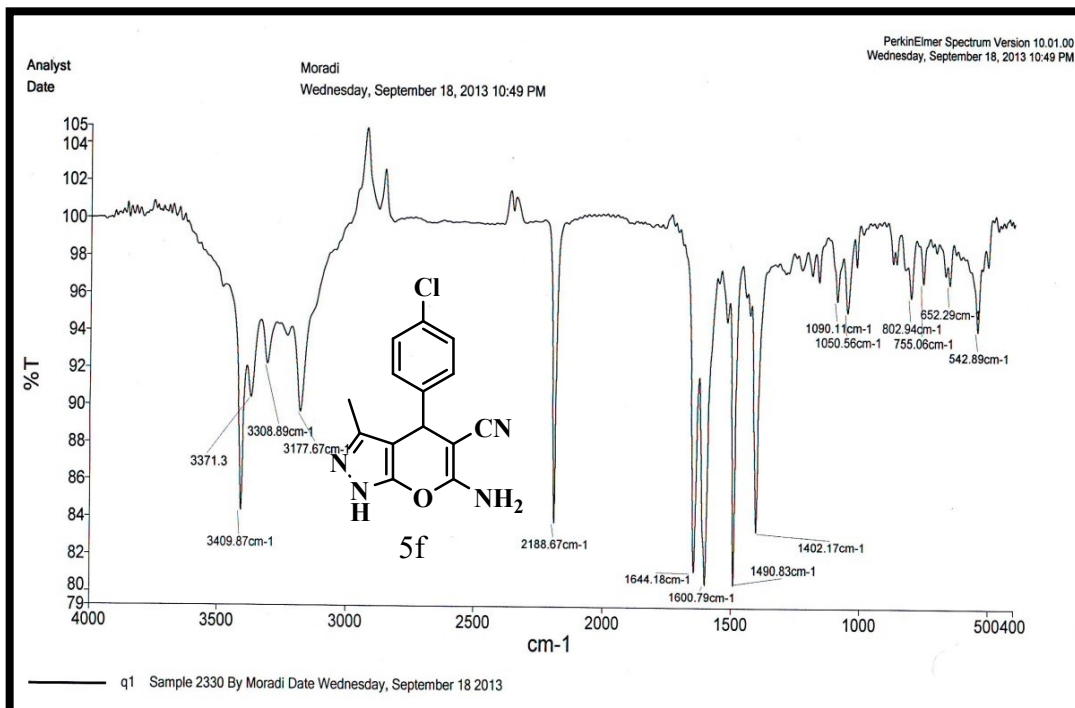
FT-IR spectra of compound 5e



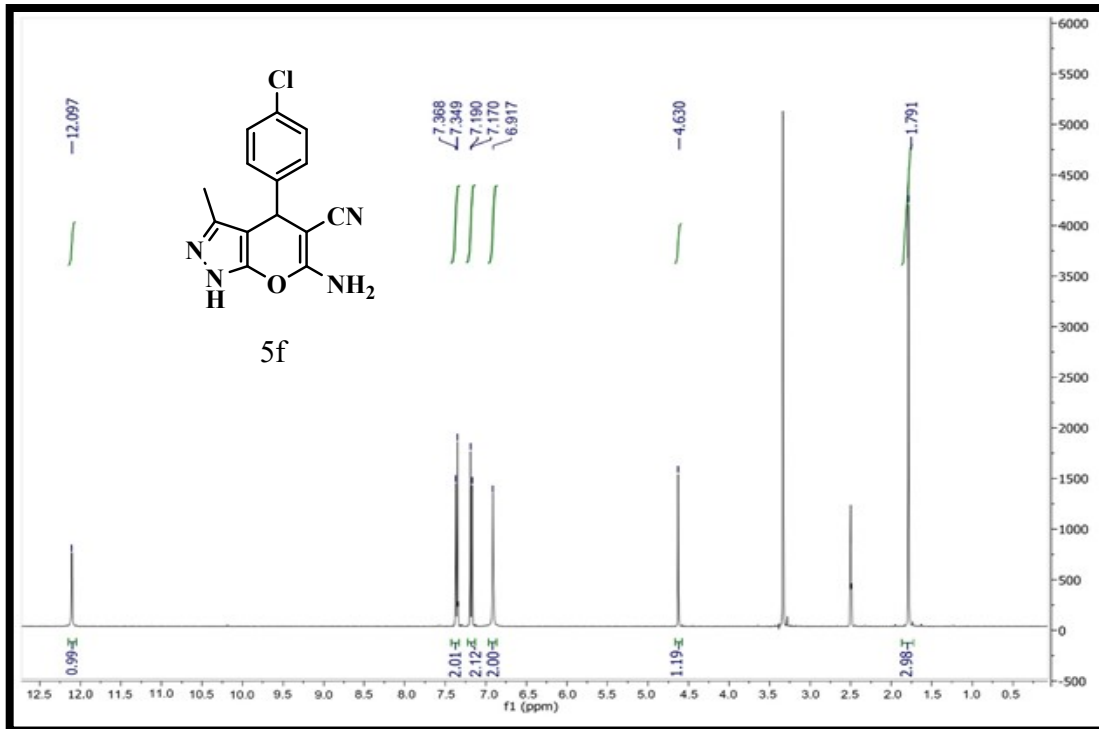
¹H NMR spectra of compound 5e



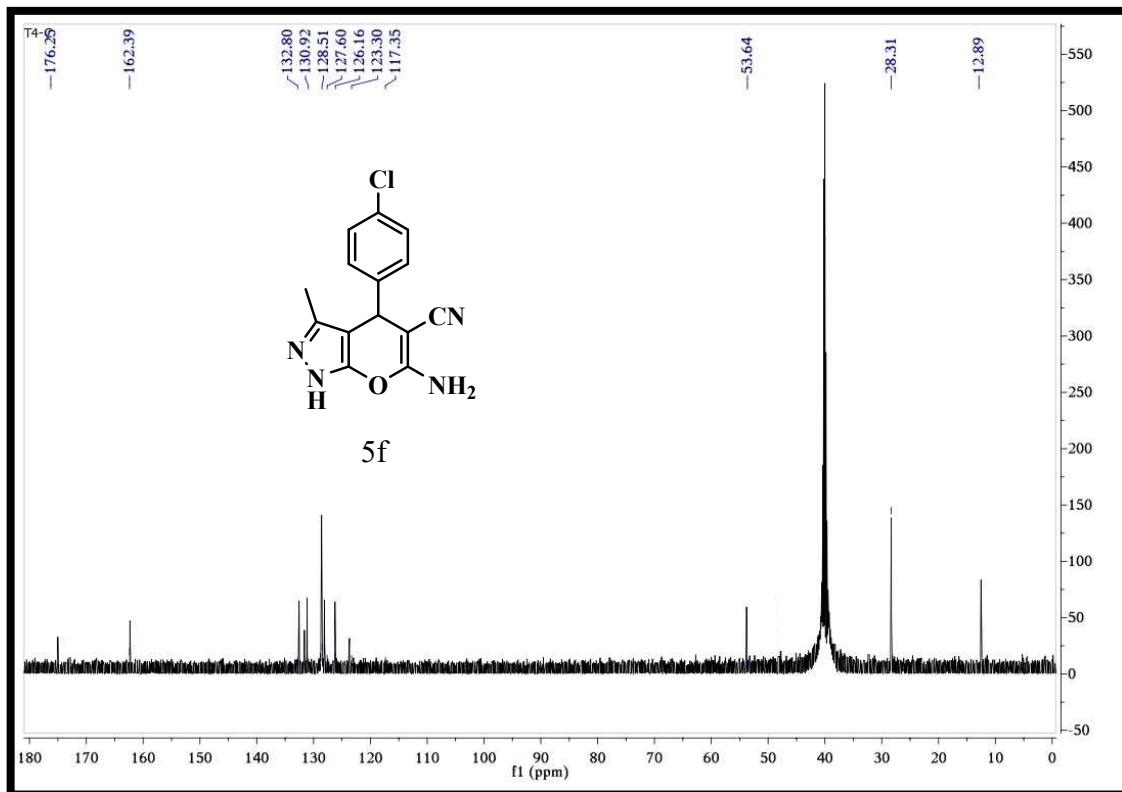
¹³C NMR spectra of compound 5e



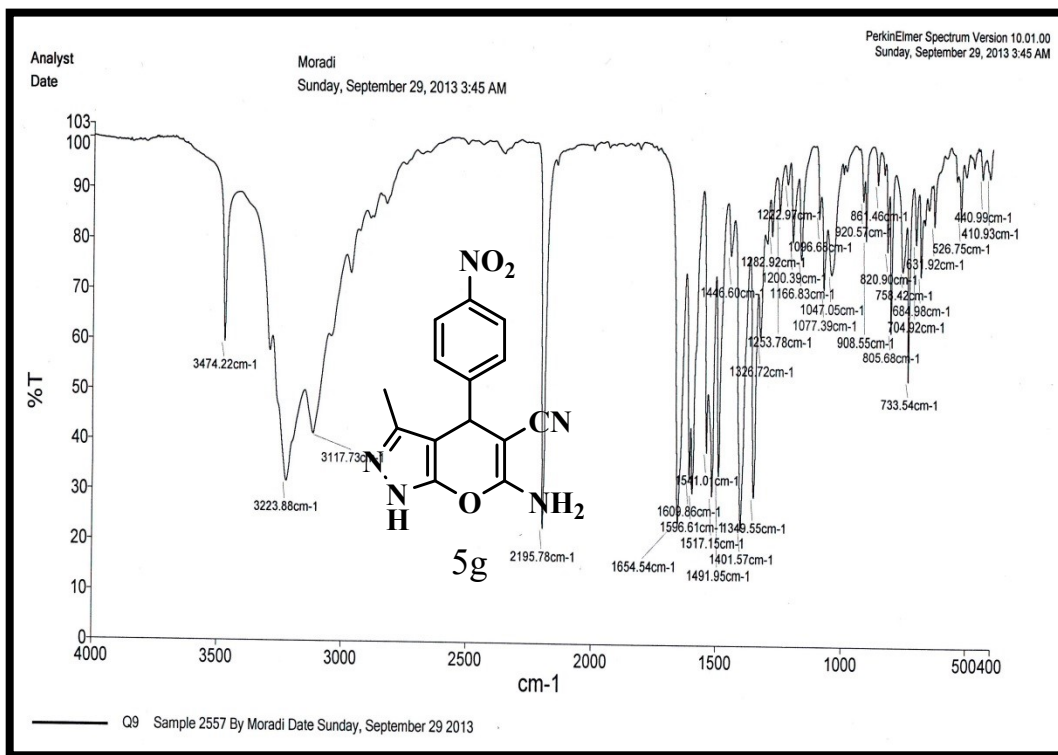
FT-IR spectra of compound 5f



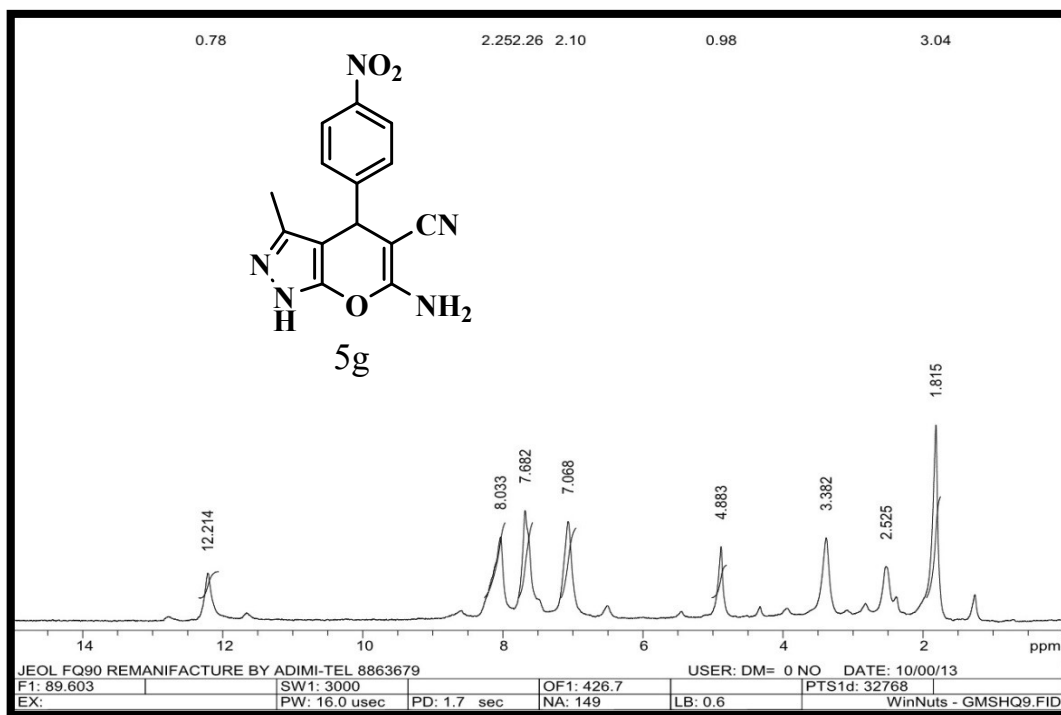
¹H NMR spectra of compound 5f

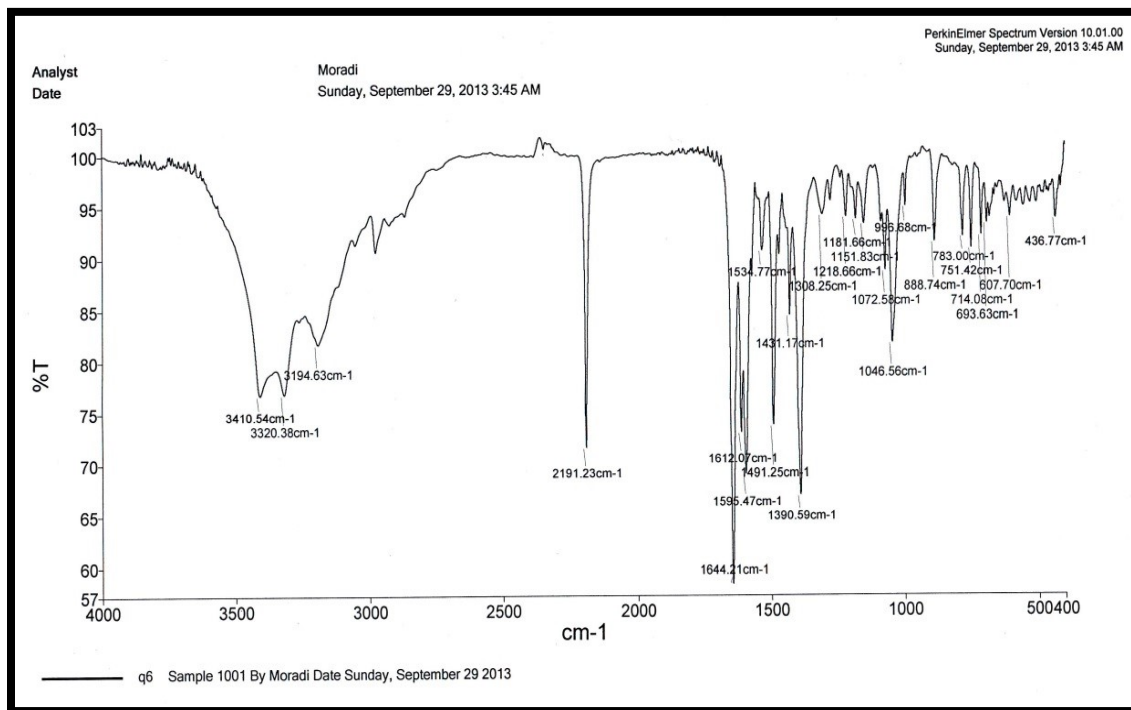


¹³CNMR spectra of compound 5f

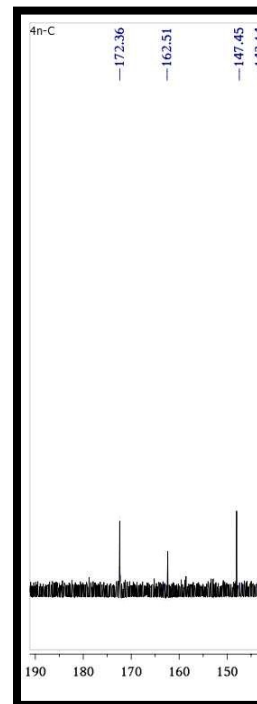


FT-IR spectra of compound 5g

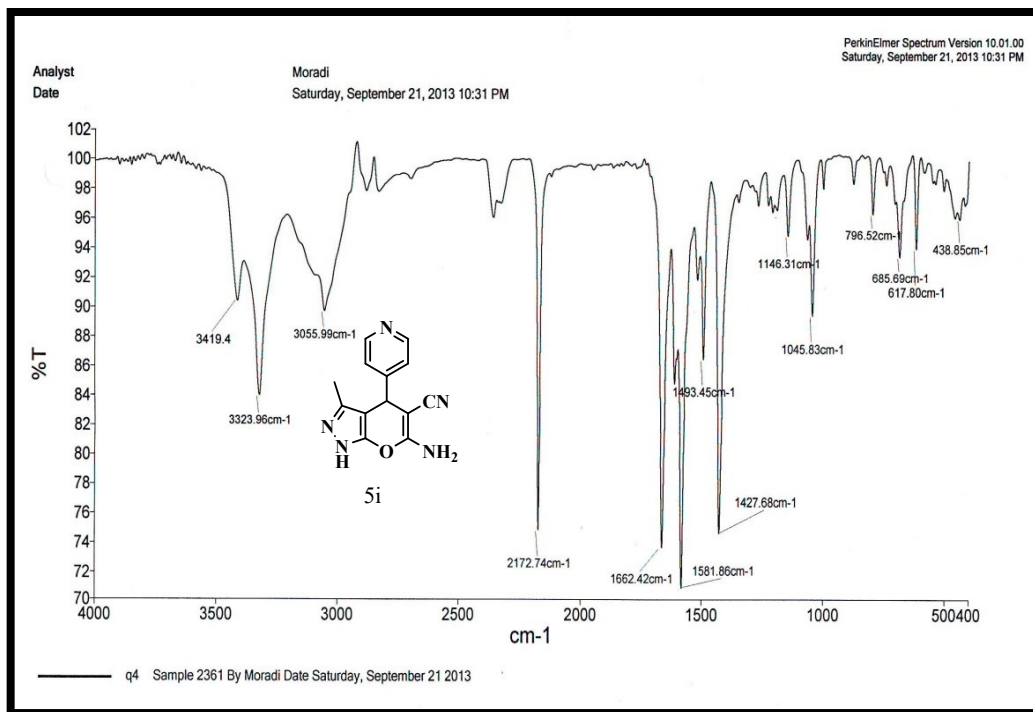




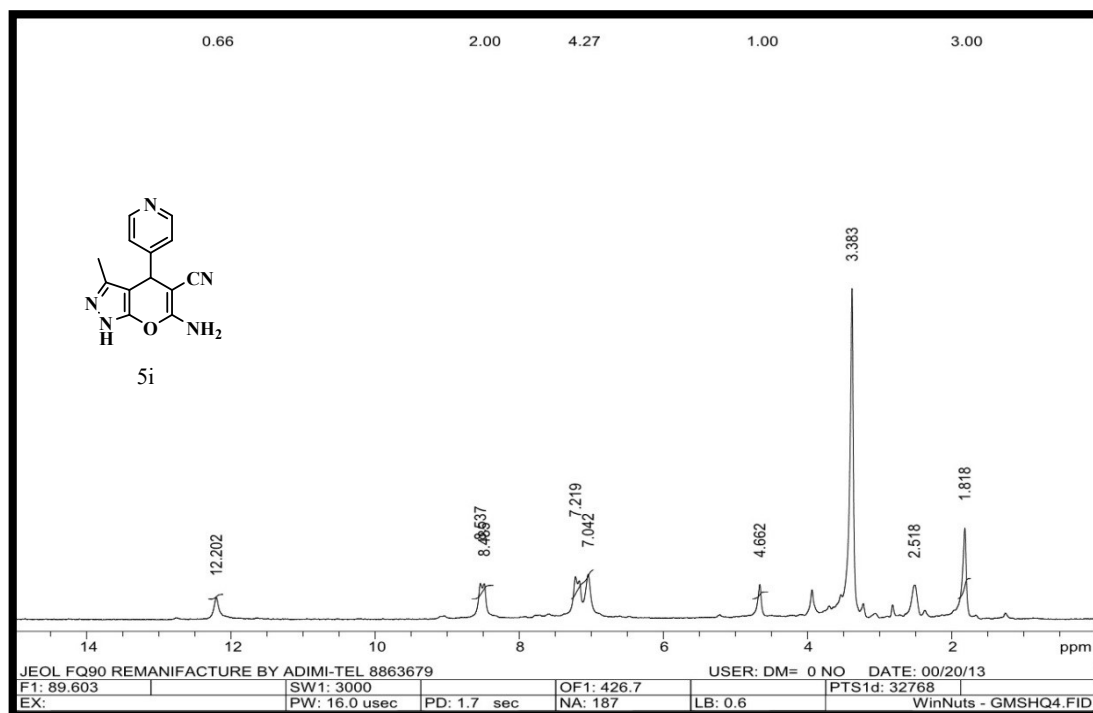
**¹H NMR
R
spectra
of
compound
5g**



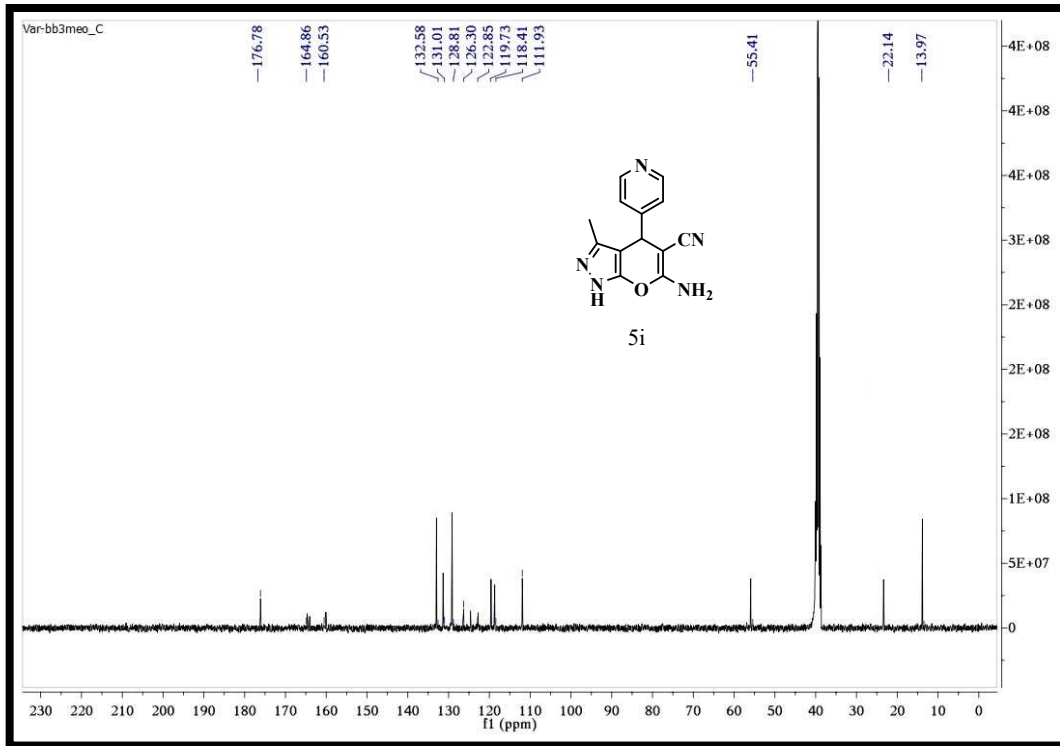
¹³C NMR spectra of compound 5g



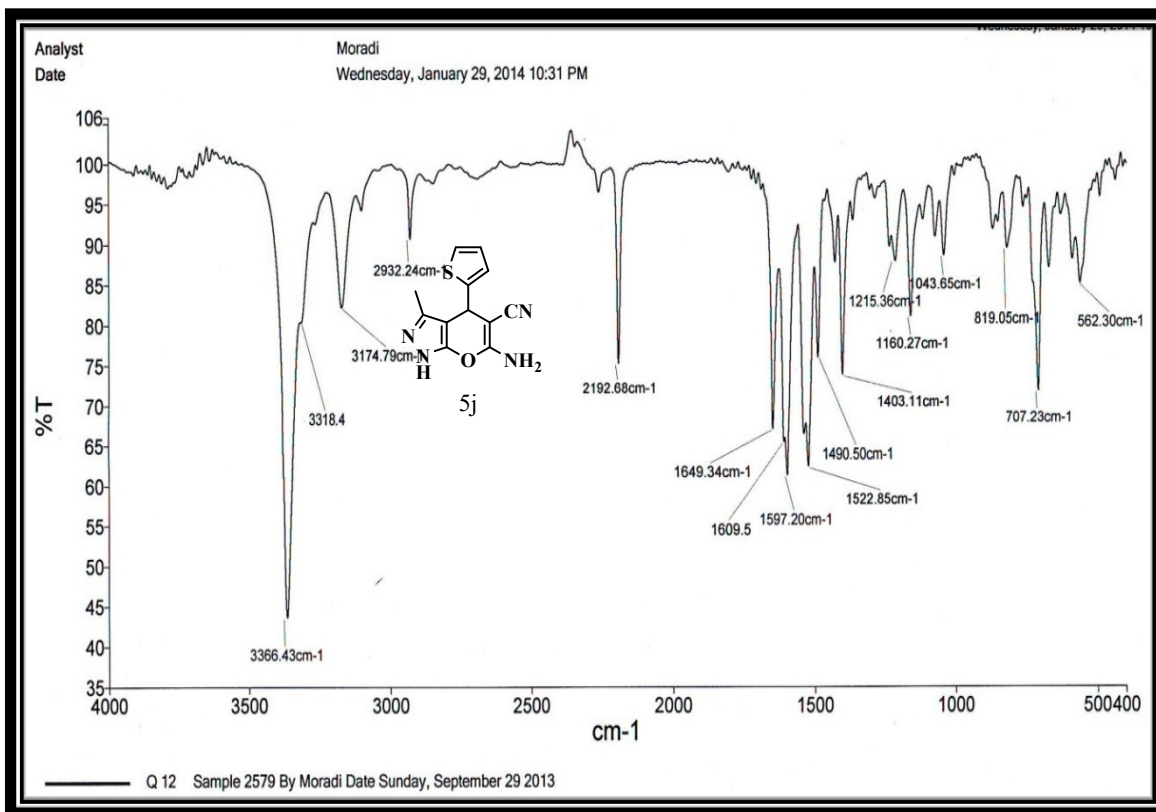
FT-IR spectra of compound 5i



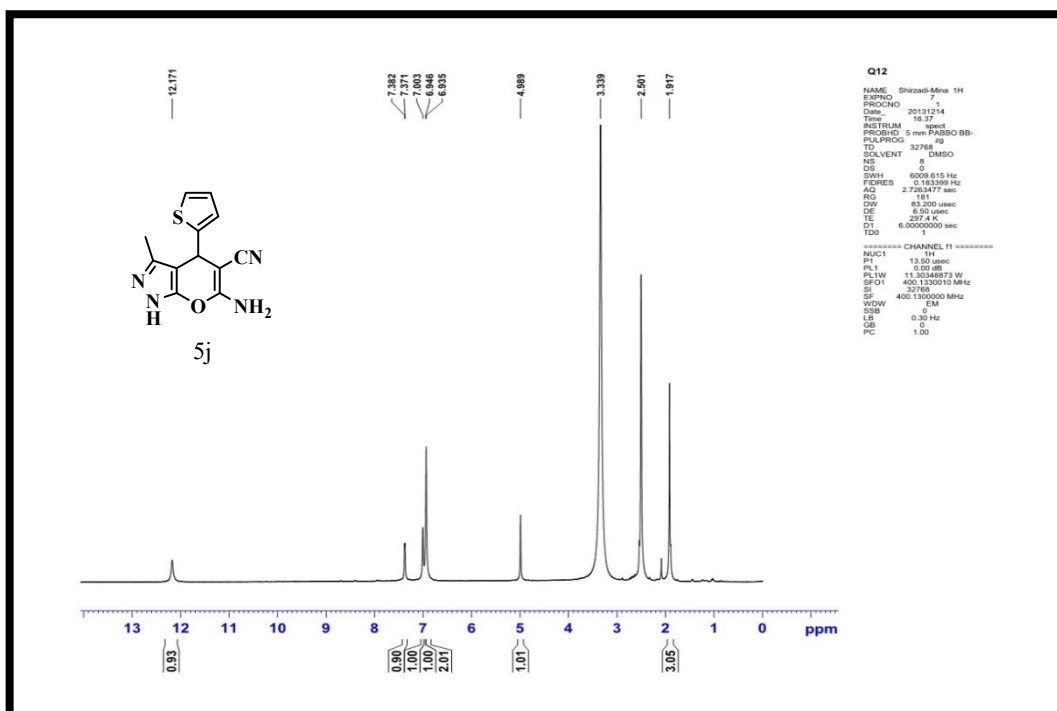
¹H NMR spectra of compound 5i



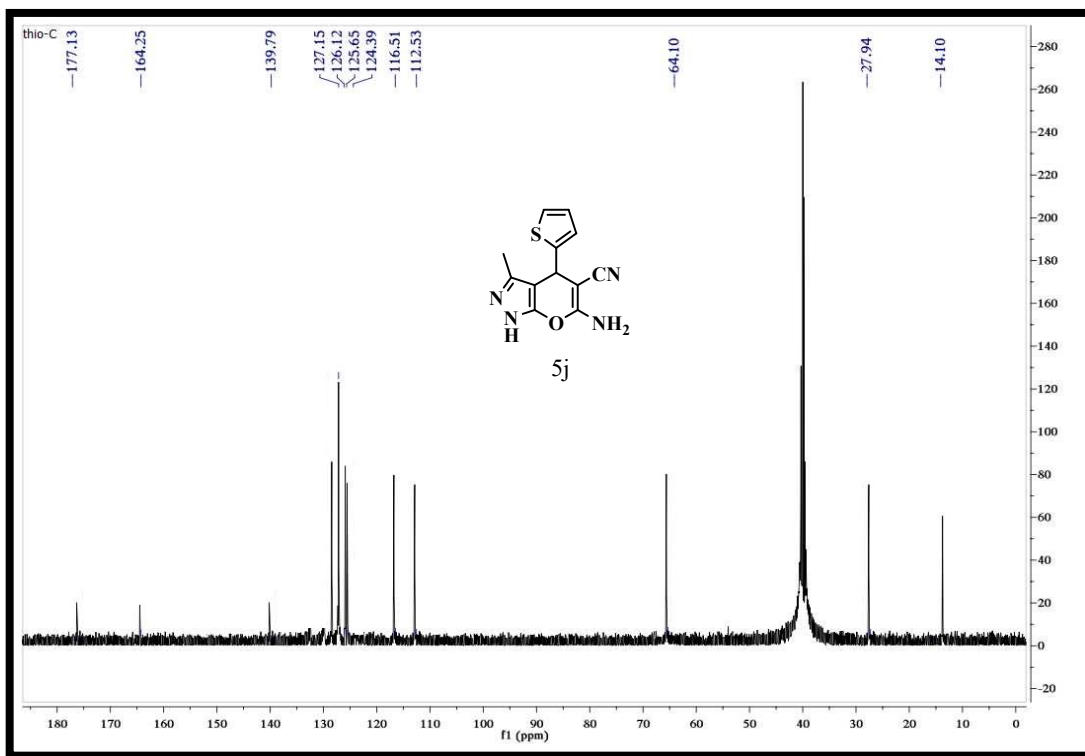
¹³CNMR spectra of compound 5i



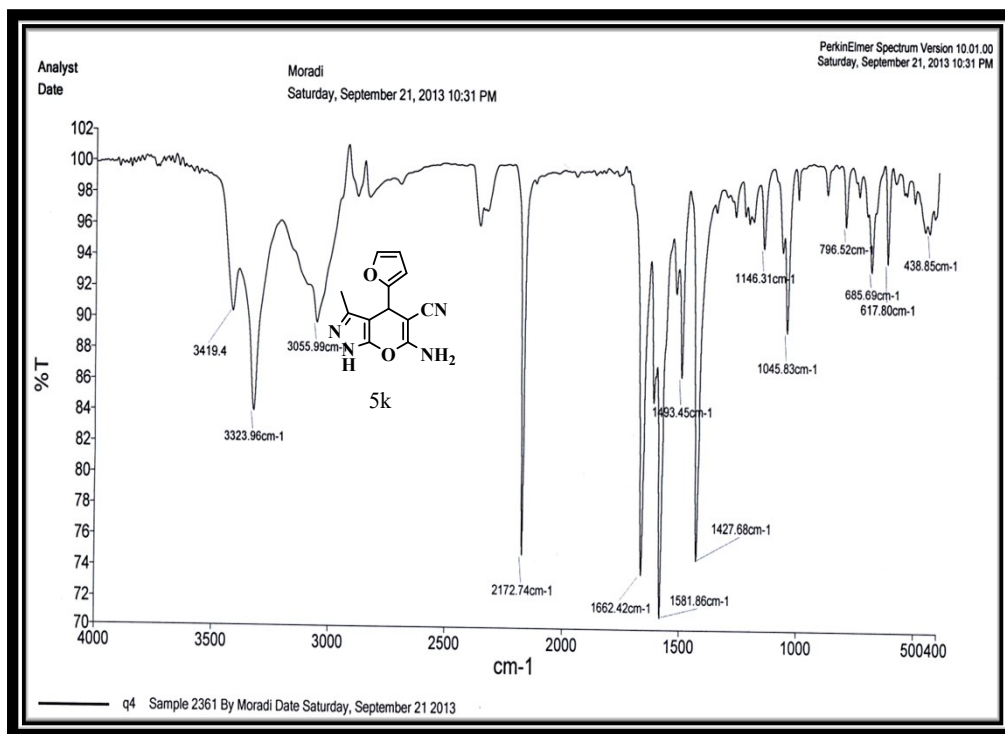
FT-IR spectra of compound 5j



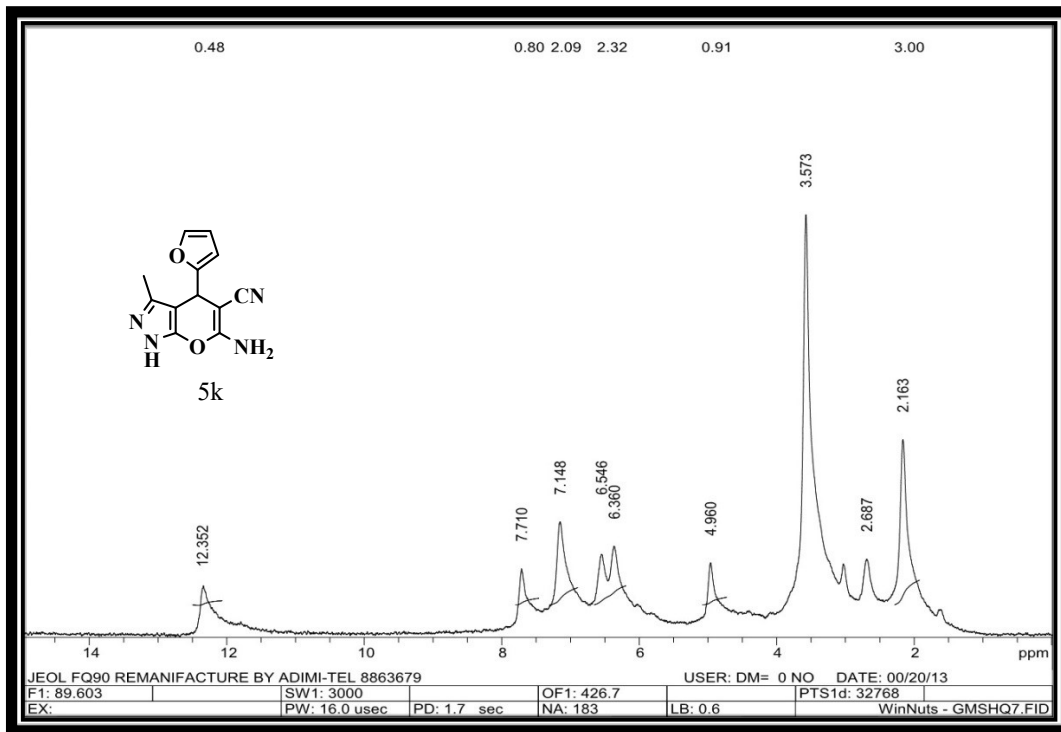
¹H NMR spectra of compound 5j



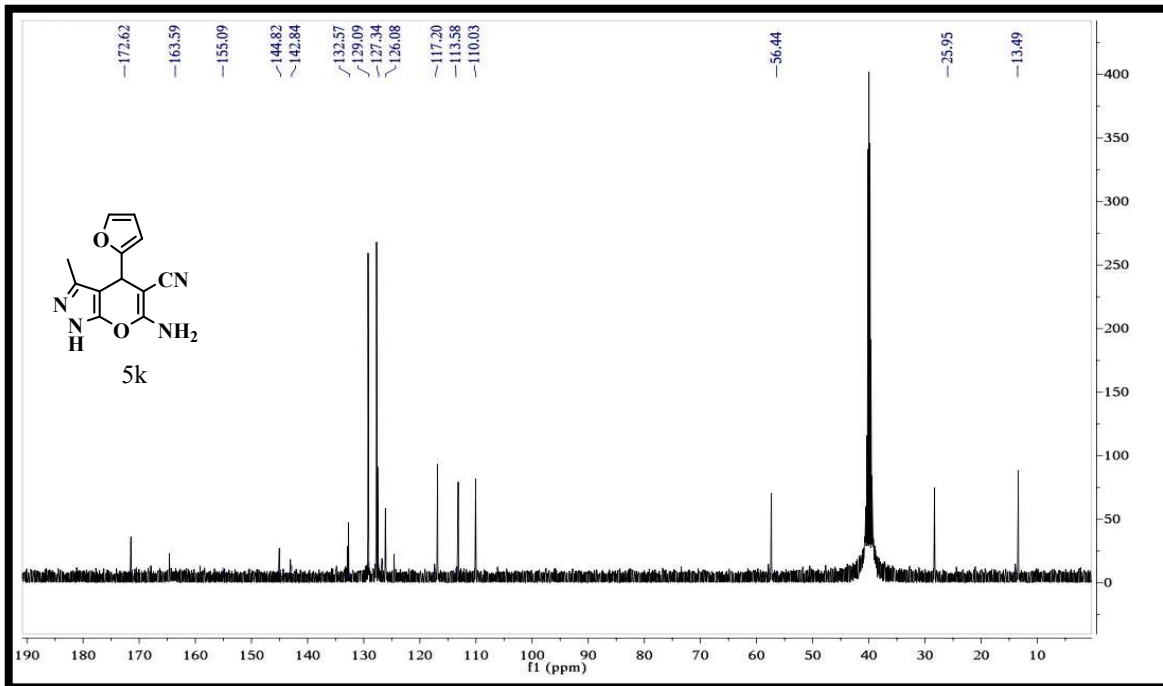
¹³CNMR spectra of compound 5j



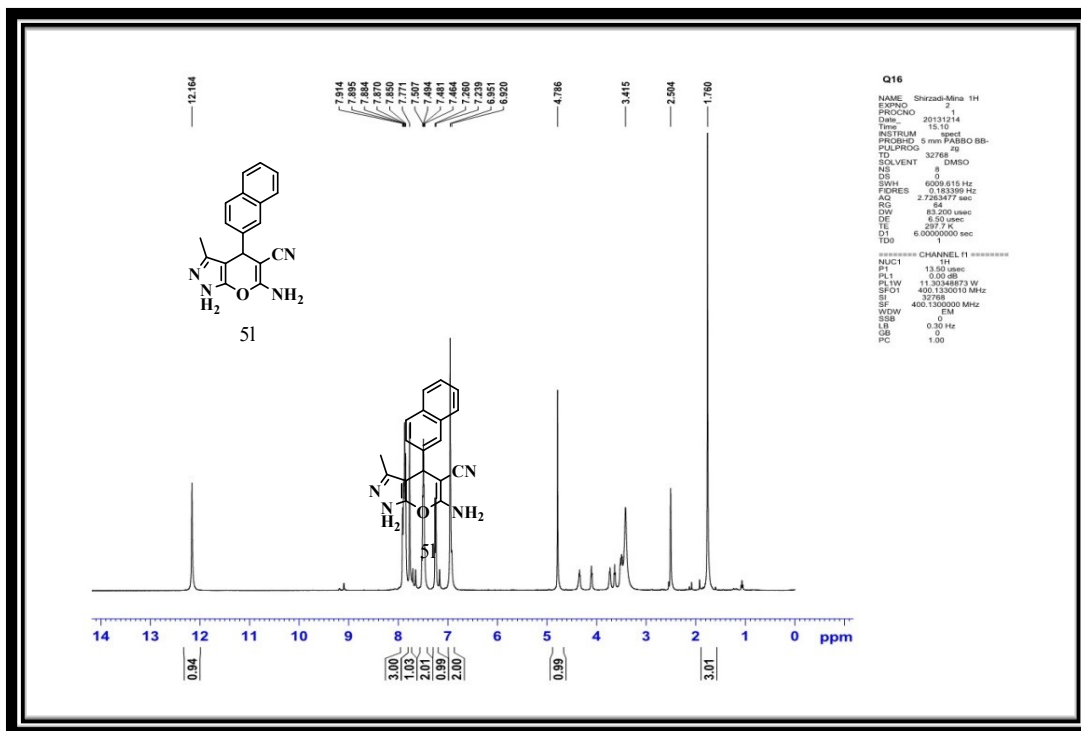
FT-IR spectra of compound 5k



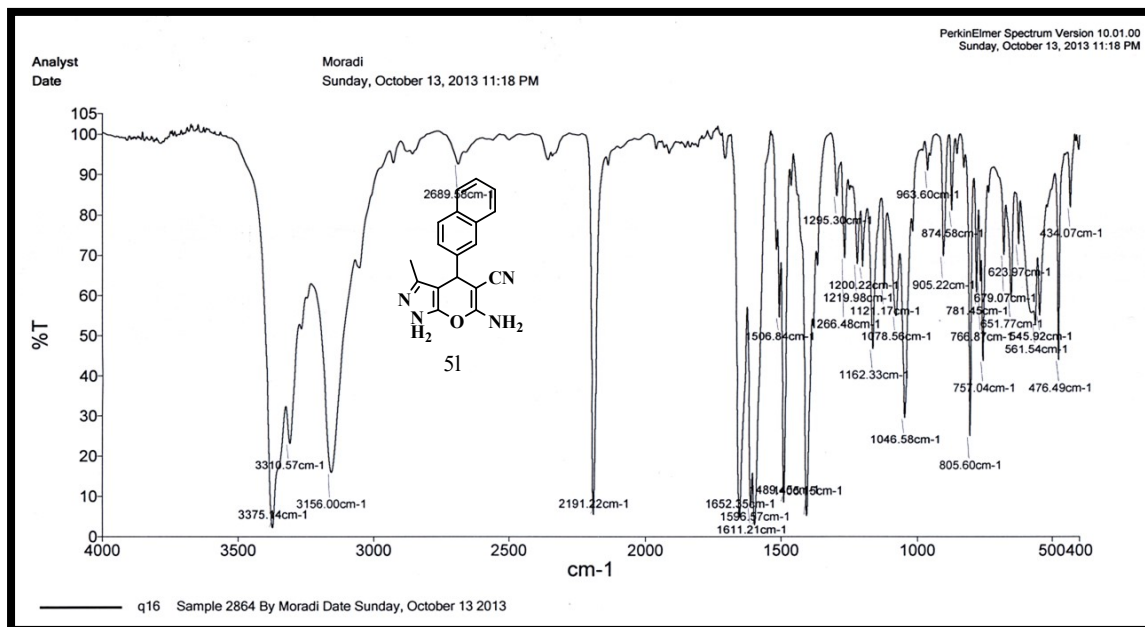
¹³C NMR spectra of compound 5k

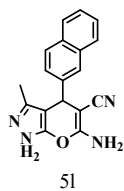


¹³CNMR spectra of compound 5k



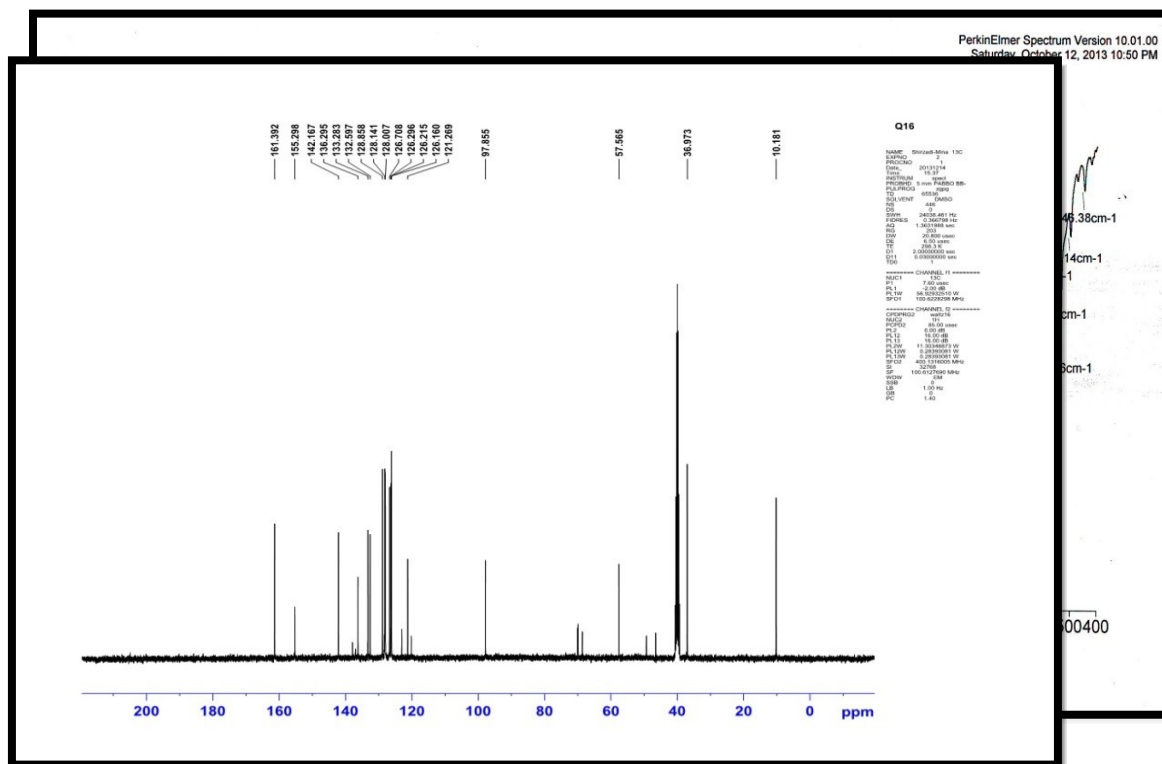
¹HNMR spectra of compound 5l





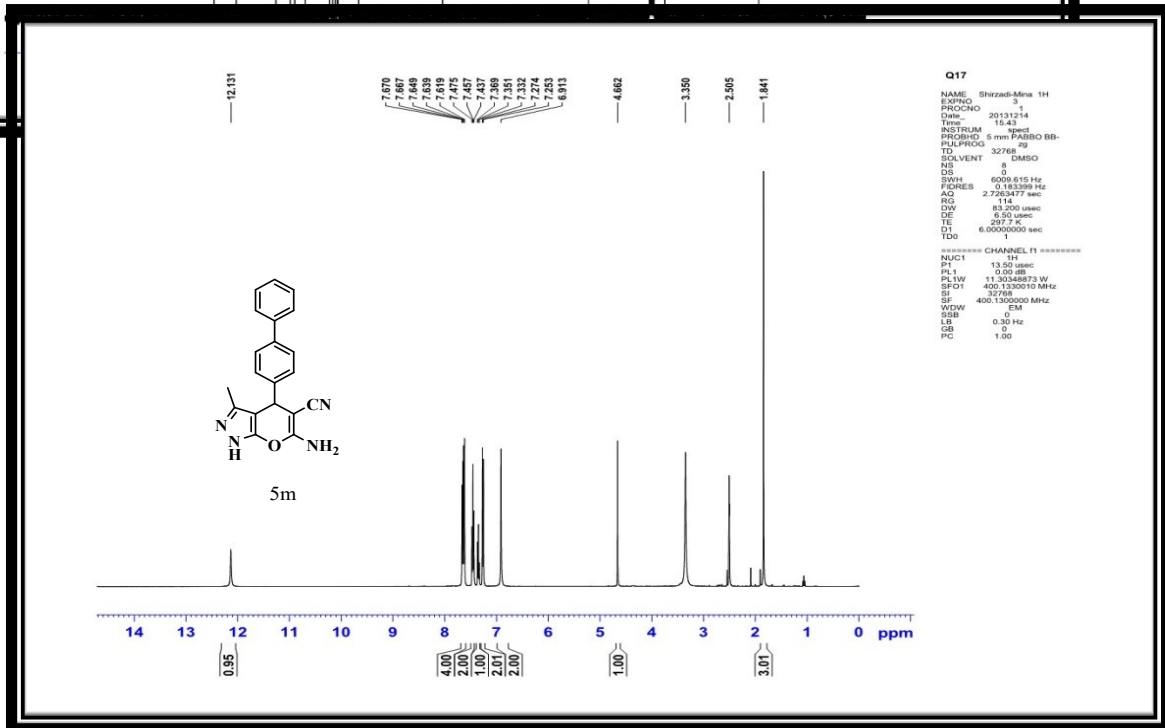
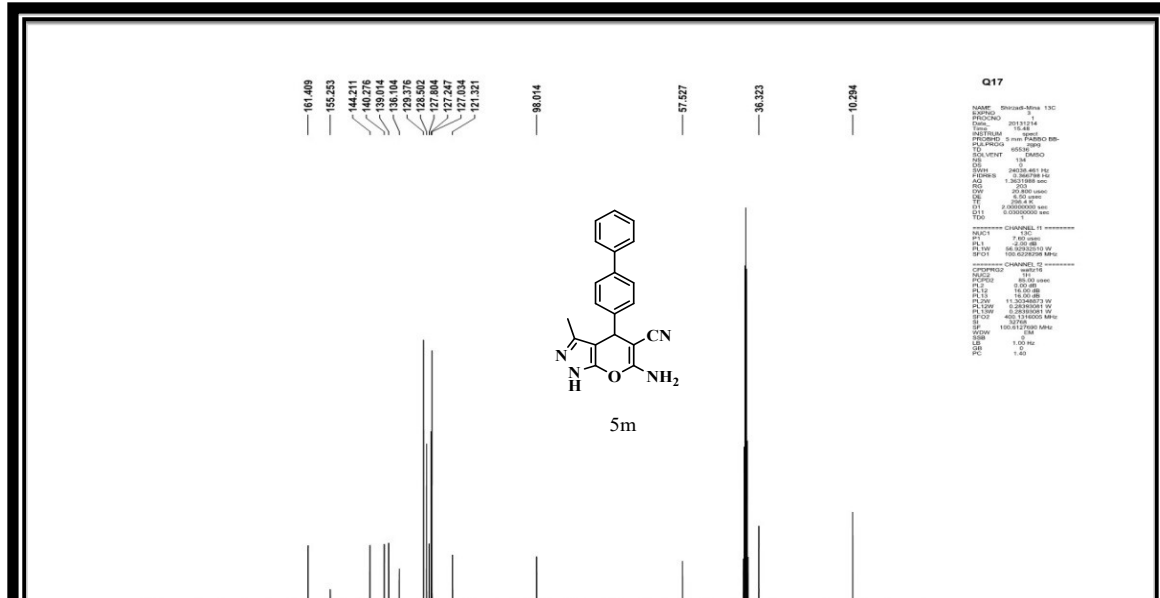
¹³CNMR spectra of compound 51

b



FTIR spectra of compound 5m

¹HNMR spectra of compound 5m



¹³CNMR spectra of compound 5m

