

Catalytic applications of {[HMIM]C(NO₂)₃}: as a nano ionic liquid for the synthesis of pyrazole derivatives under green conditions and a mechanistic investigation with a new approach

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Supplementary data:

Fig. S1. The mass spectrum of 1-methylimidazolium trinitromethanide as a nano ionic liquid catalyst

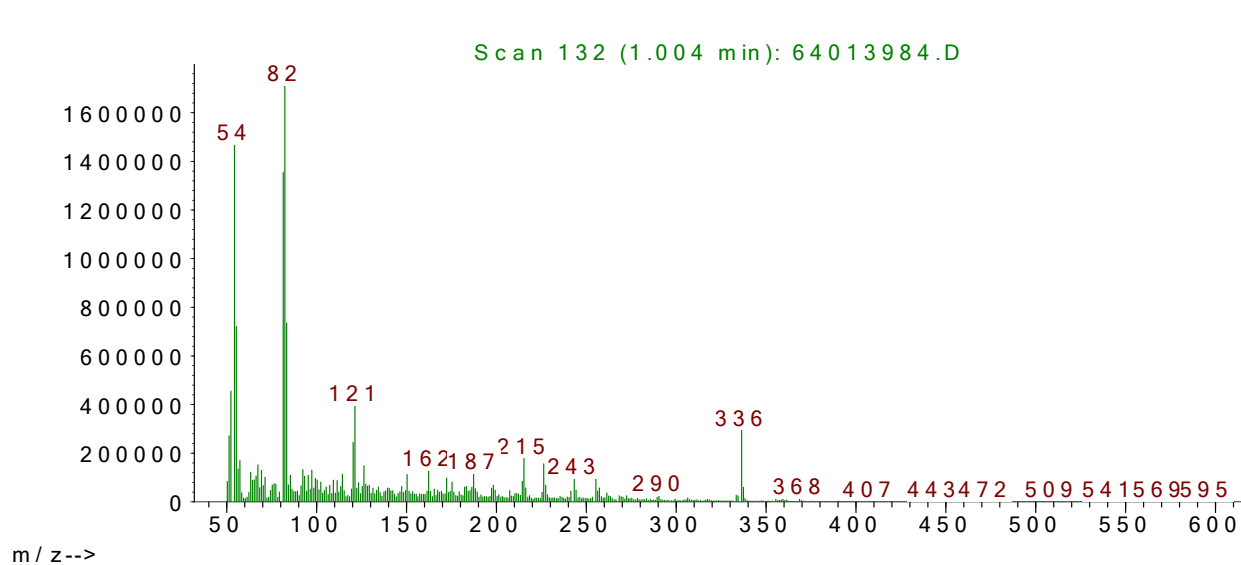


Fig. S2. The mass spectrum of 1-methylimidazolium trinitromethanide as a nano ionic liquid catalyst

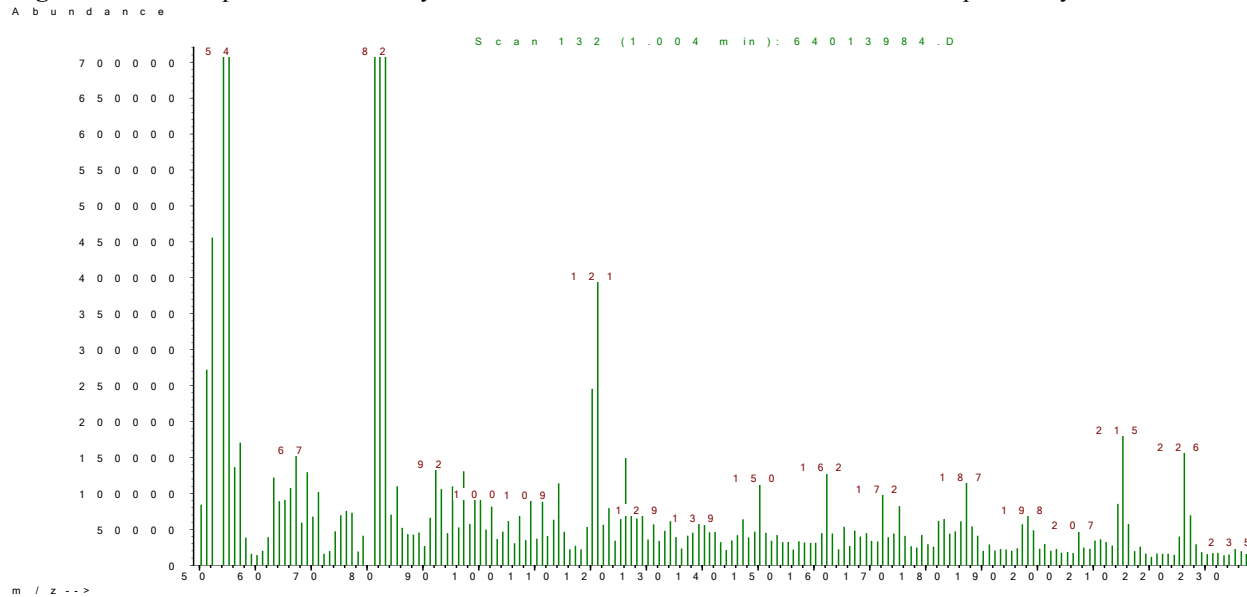


Fig. S3. The IR spectrum of 1-methylimidazolium trinitromethanide as a nano ionic liquid catalyst

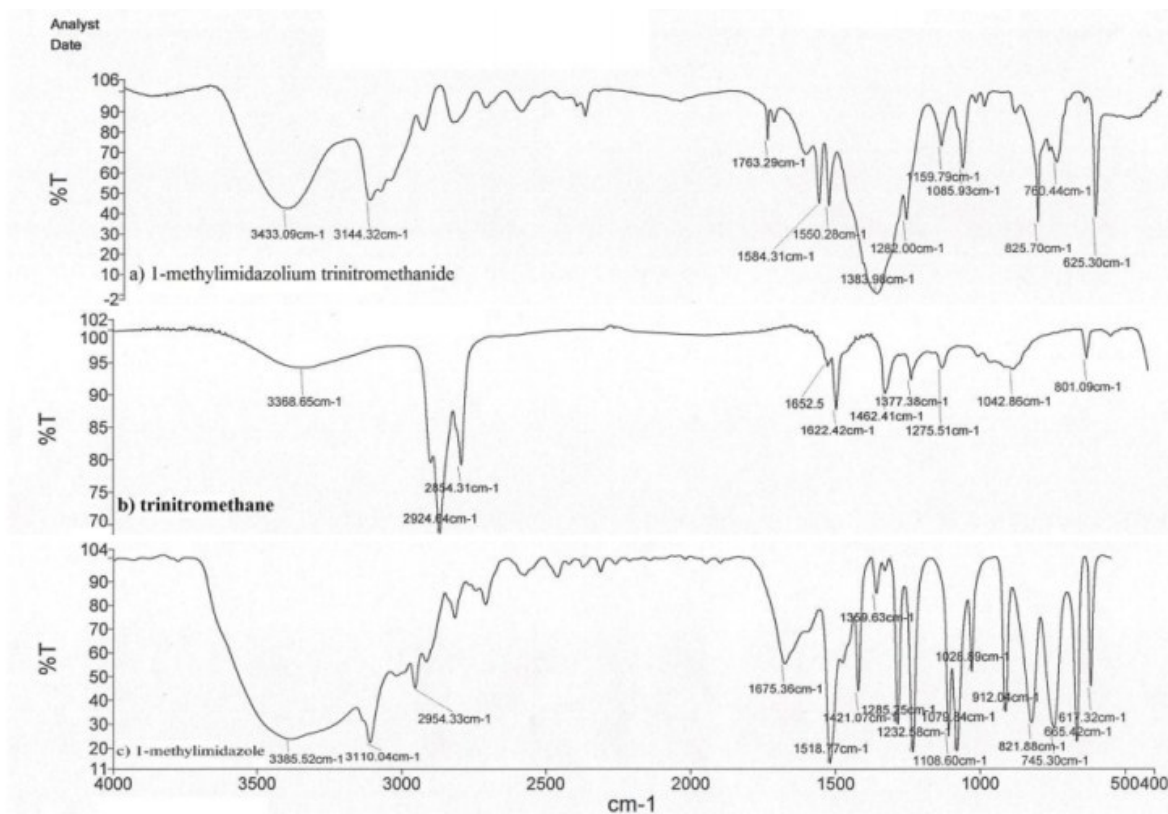


Fig. S4. The ¹H NMR spectrum of 1-methylimidazolium trinitromethanide as a nano ionic liquid catalyst

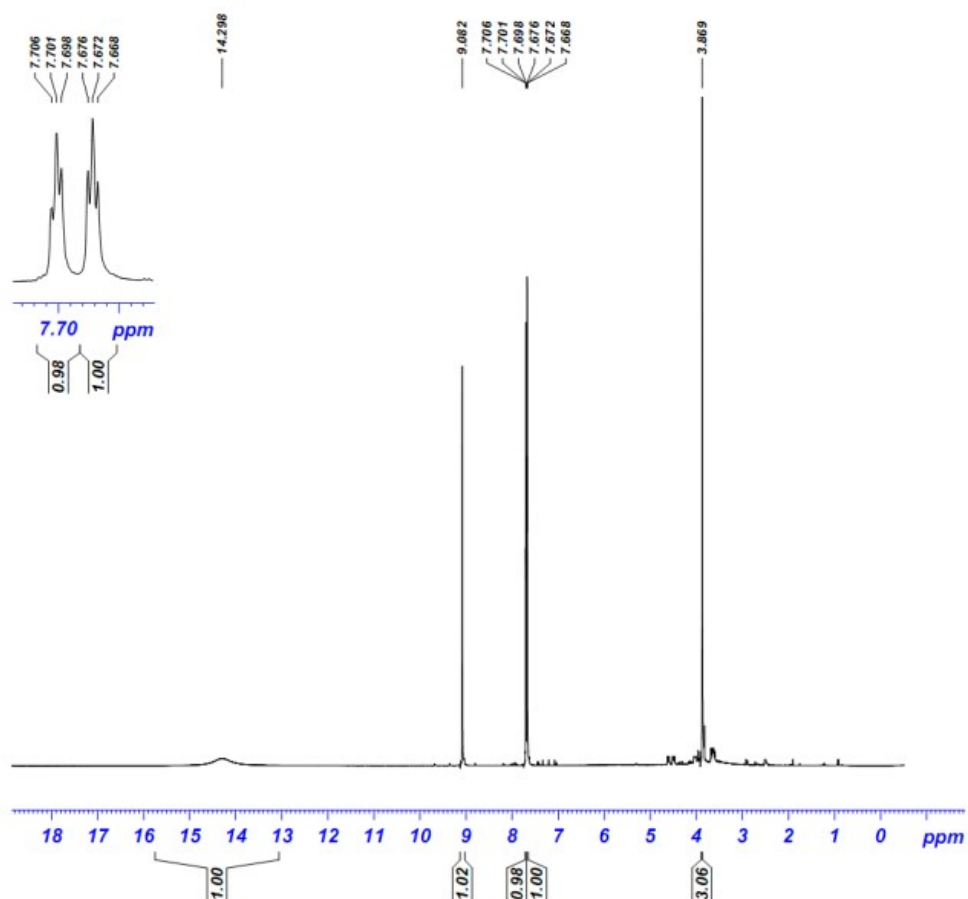


Fig. S5. The ^{13}C NMR spectrum of 1-methylimidazolium trinitromethanide as a nano ionic liquid

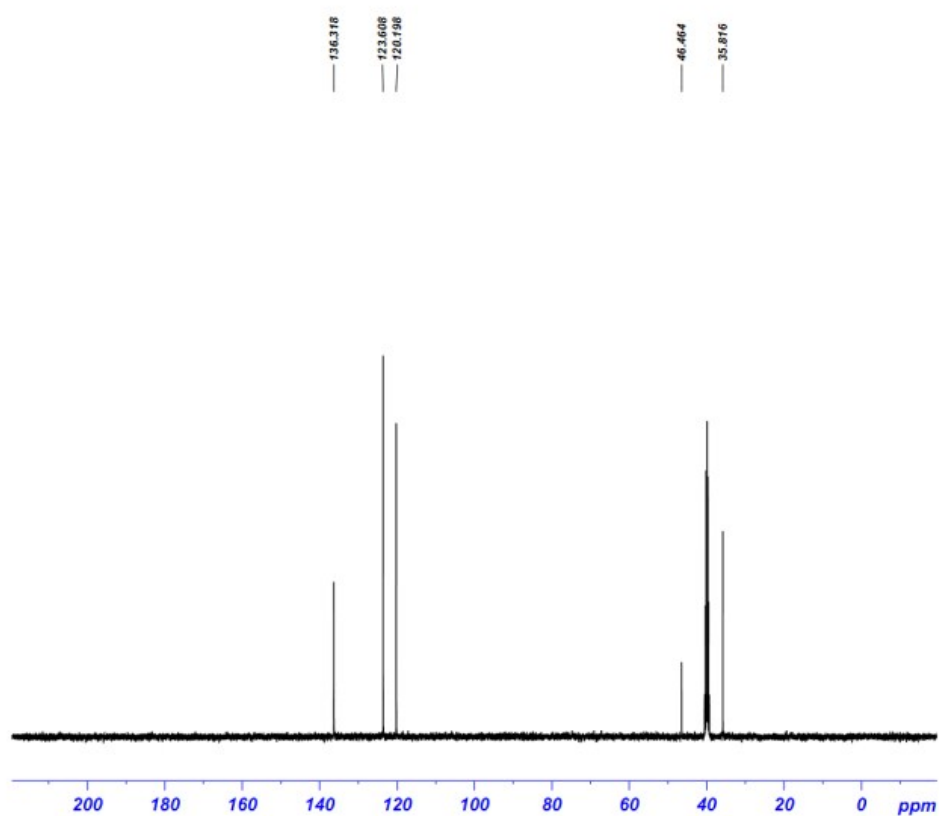


Fig. S6. The thermogravimetry (TG) illustrations of nano ionic liquid catalyst

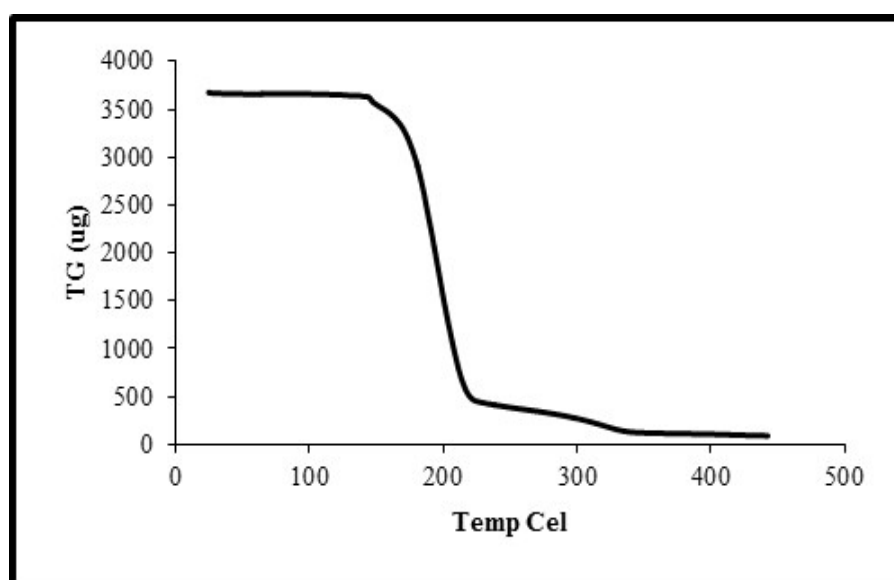


Fig. S7. The derivative thermogravimetry (DTG) illustrations of nano ionic liquid catalyst

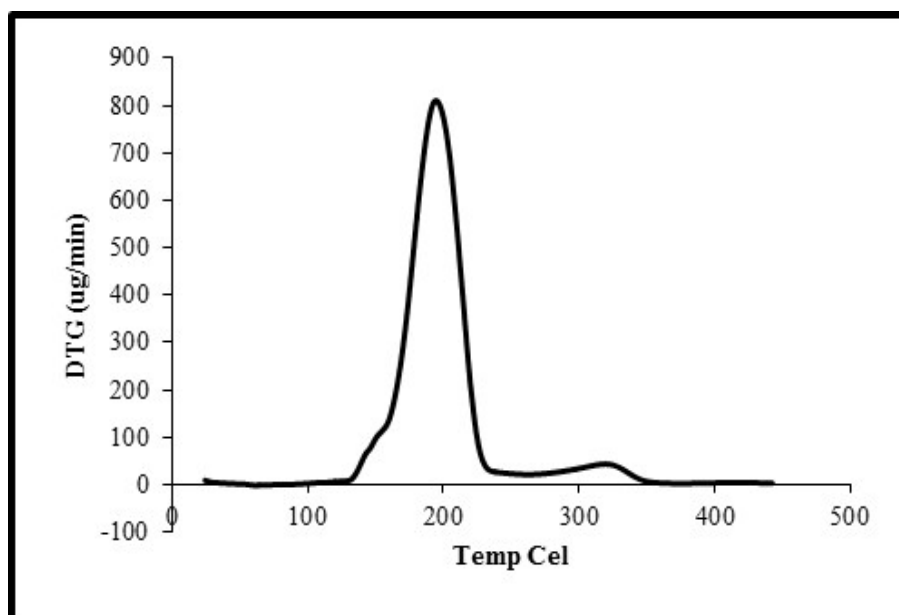


Fig. S8. The XRD pattern of the nano ionic liquid catalyst

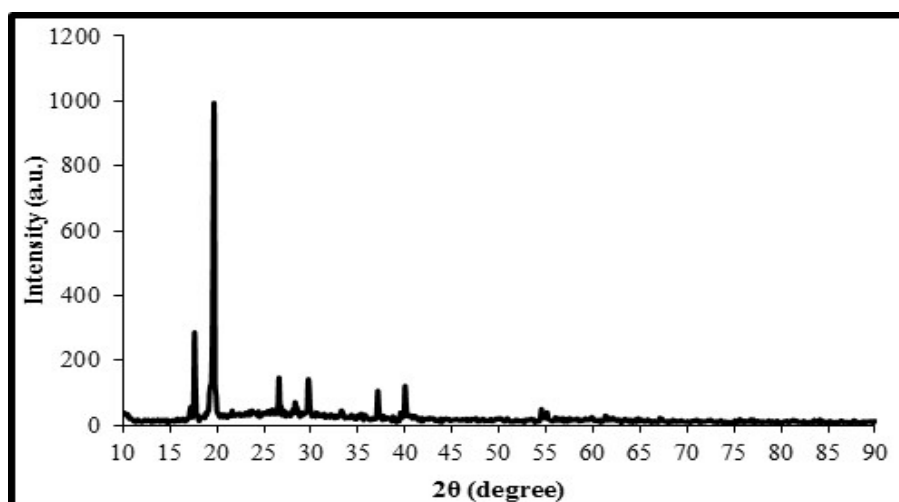


Table S1. XRD data for the nano ionic liquid catalyst

Entry	2θ	Peak width [FWHM] (degree)	Size [nm]	Inter planer distance [nm]
1	17.60	0.18	44.68	0.503314
2	19.70	0.22	36.67	0.450109
3	26.60	0.18	45.37	0.334710
4	29.70	0.25	62.45	0.089457
5	37.10	0.21	39.51	0.242037
6	40.00	0.19	44.68	0.225132

Fig. S9. The transmission electron microscopy (TEM) of 1-methylimidazolium trinitromethanide as a nano ionic liquid

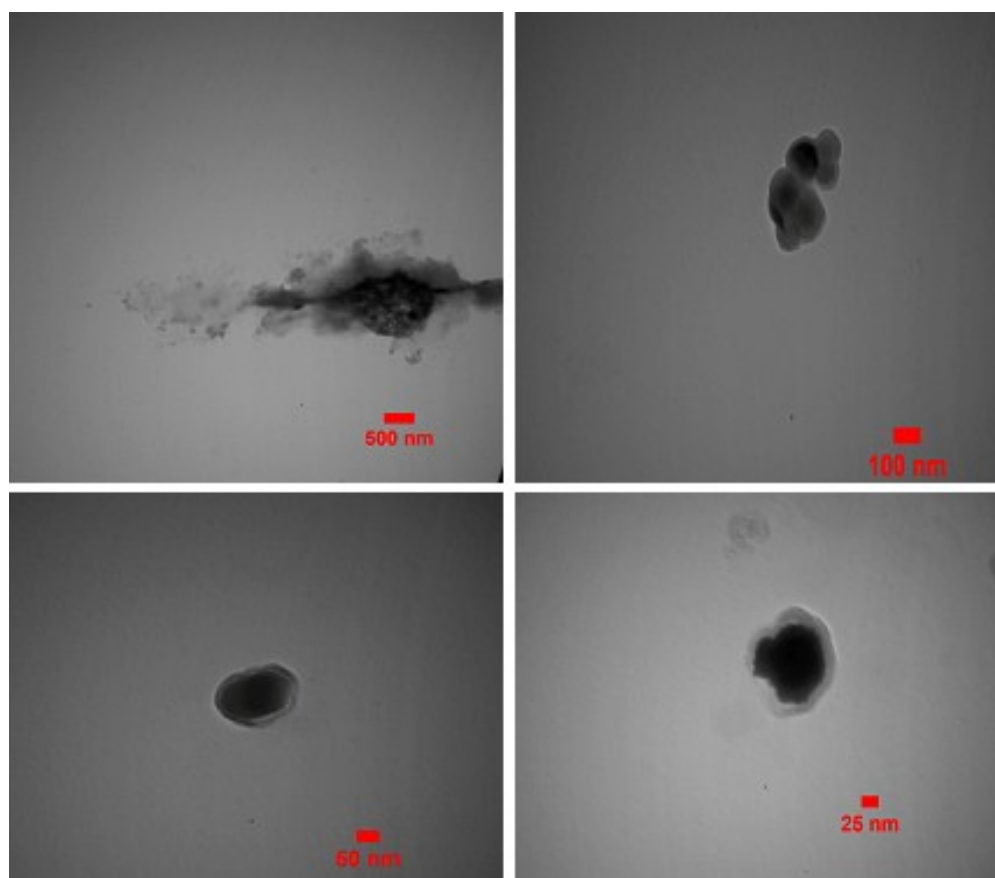


Fig. S10. The IR spectrum of 5-amino-3-(naphthalen-1-yl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 3)

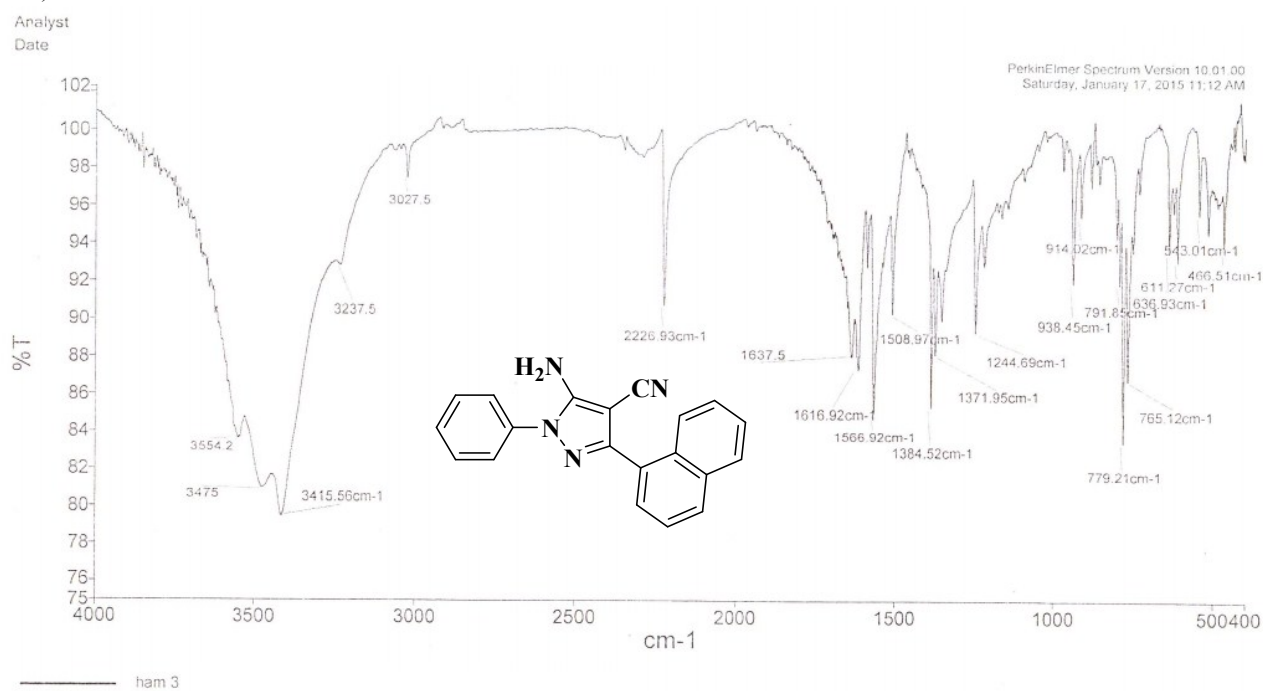


Fig. S11. The ^1H NMR spectrum of 5-amino-3-(naphthalen-1-yl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 3)

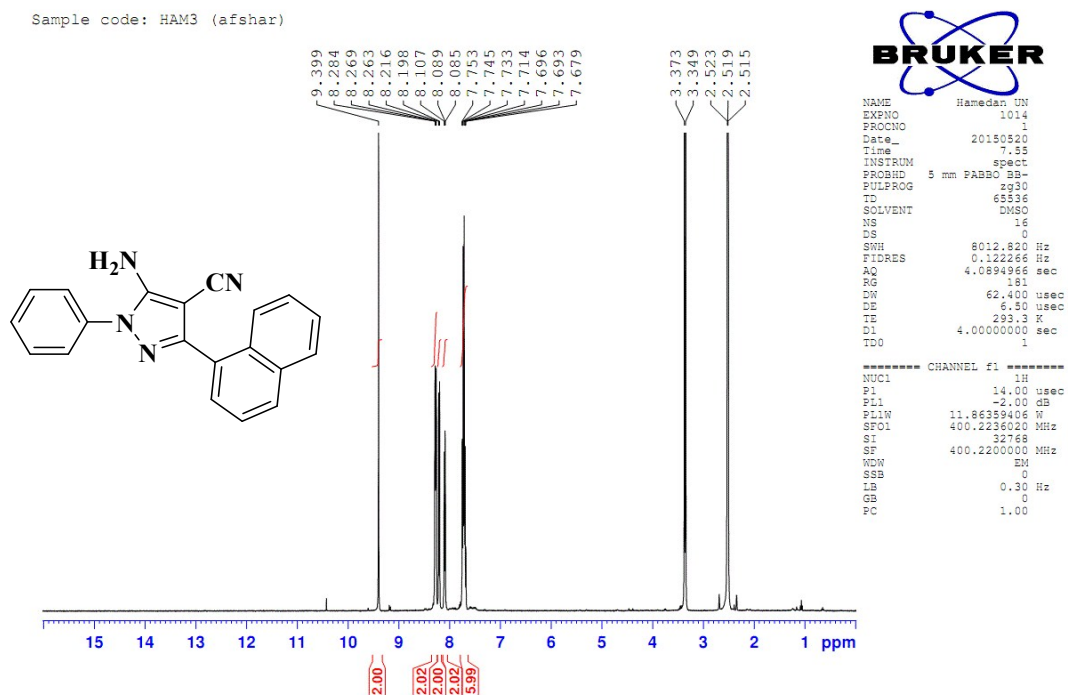


Fig. S12. The ^1H NMR spectrum of 5-amino-3-(naphthalen-1-yl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 3)

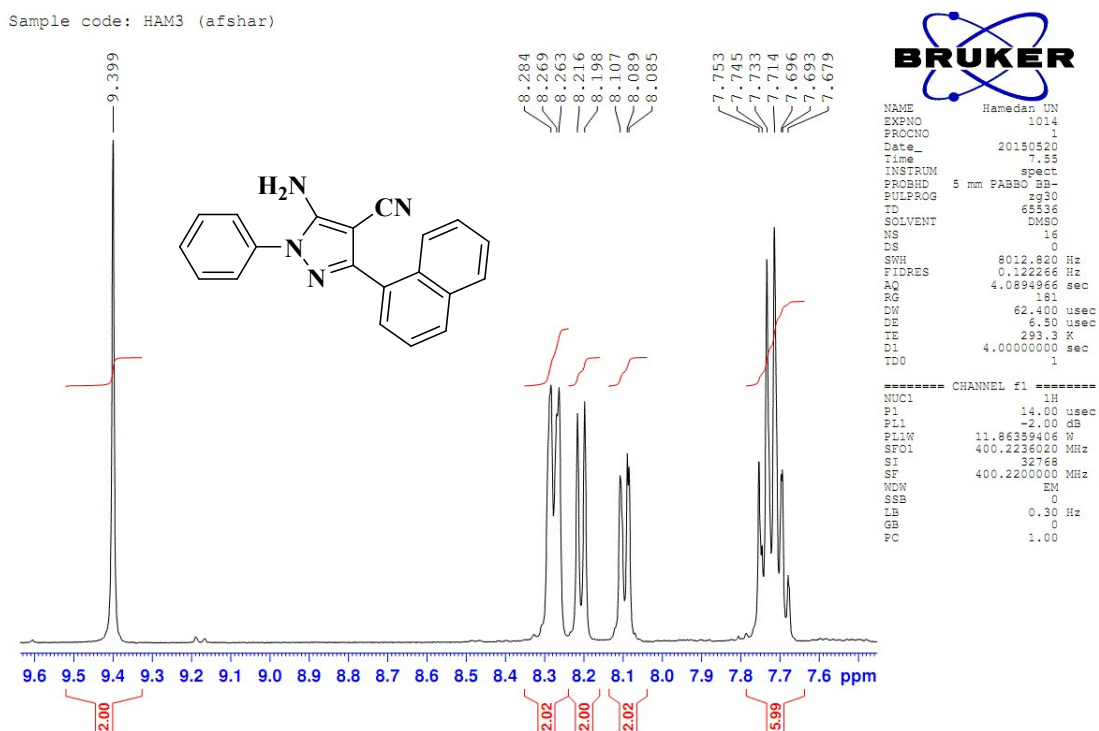


Fig. S13. The ^{13}C NMR spectrum of 5-amino-3-(naphthalen-1-yl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 3)

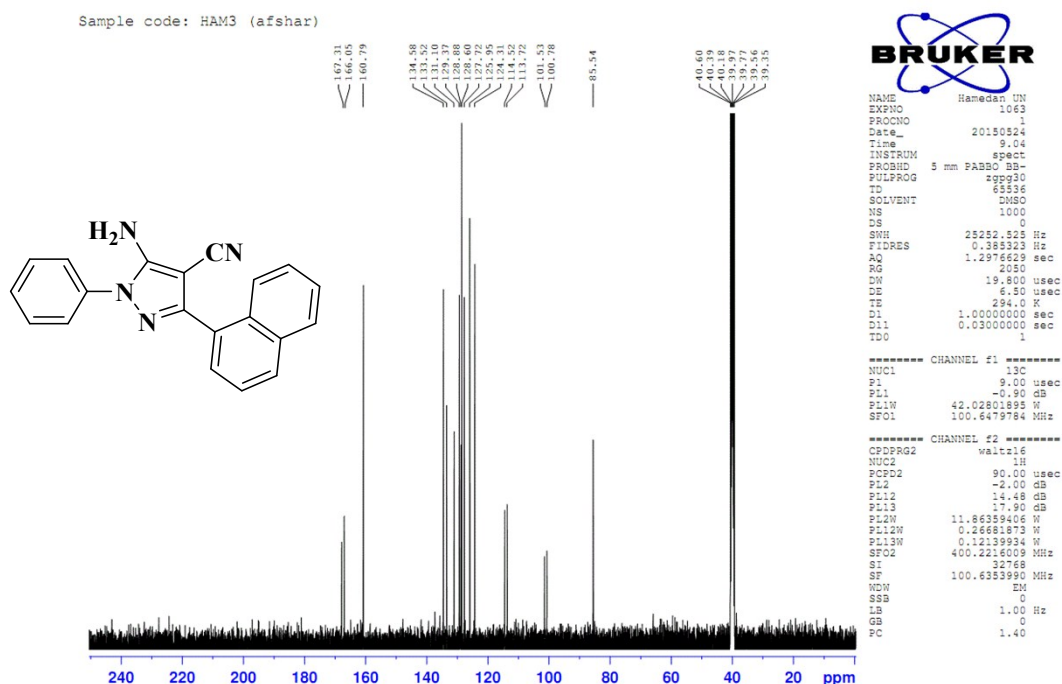


Fig. S14. The ^{13}C NMR spectrum of 5-amino-3-(naphthalen-1-yl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 3)

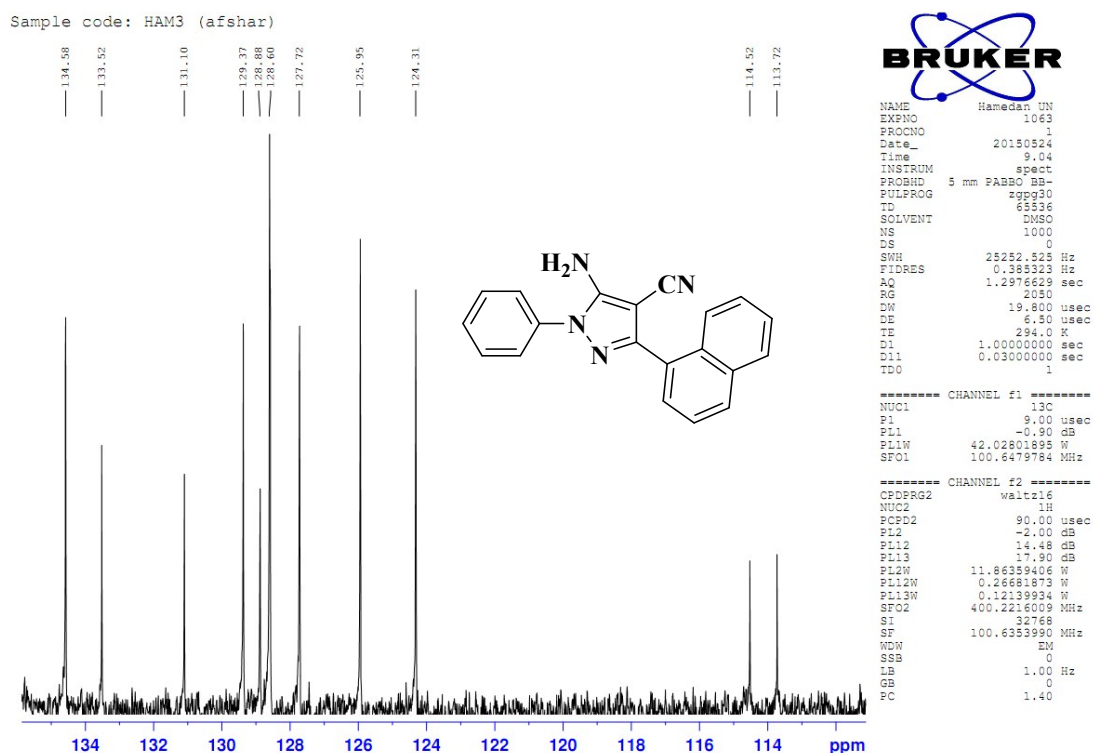


Fig. S15. The IR spectrum of 5-amino-1-phenyl-3-(1-phenylprop-1-en-2-yl)-1*H*-pyrazole-4-carbonitrile (Table 3, entry 4)

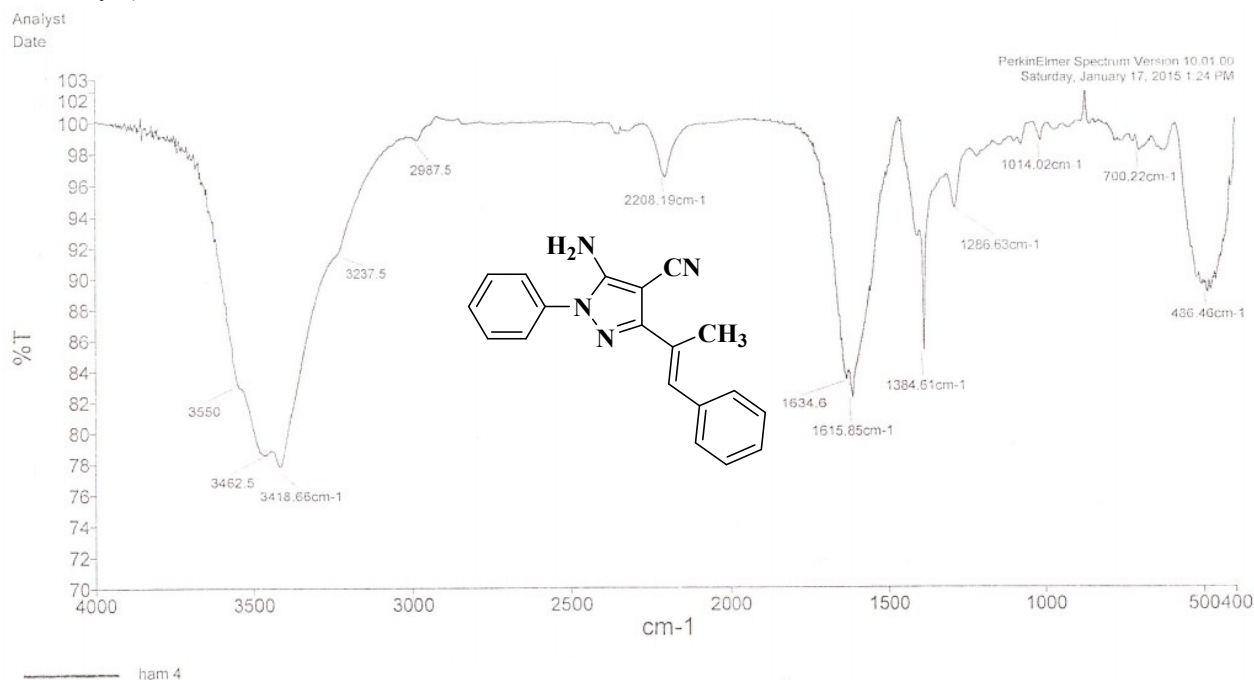


Fig. S16. The ^1H NMR spectrum of 5-amino-1-phenyl-3-(1-phenylprop-1-en-2-yl)-1*H*-pyrazole-4-carbonitrile (Table 3, entry 4)

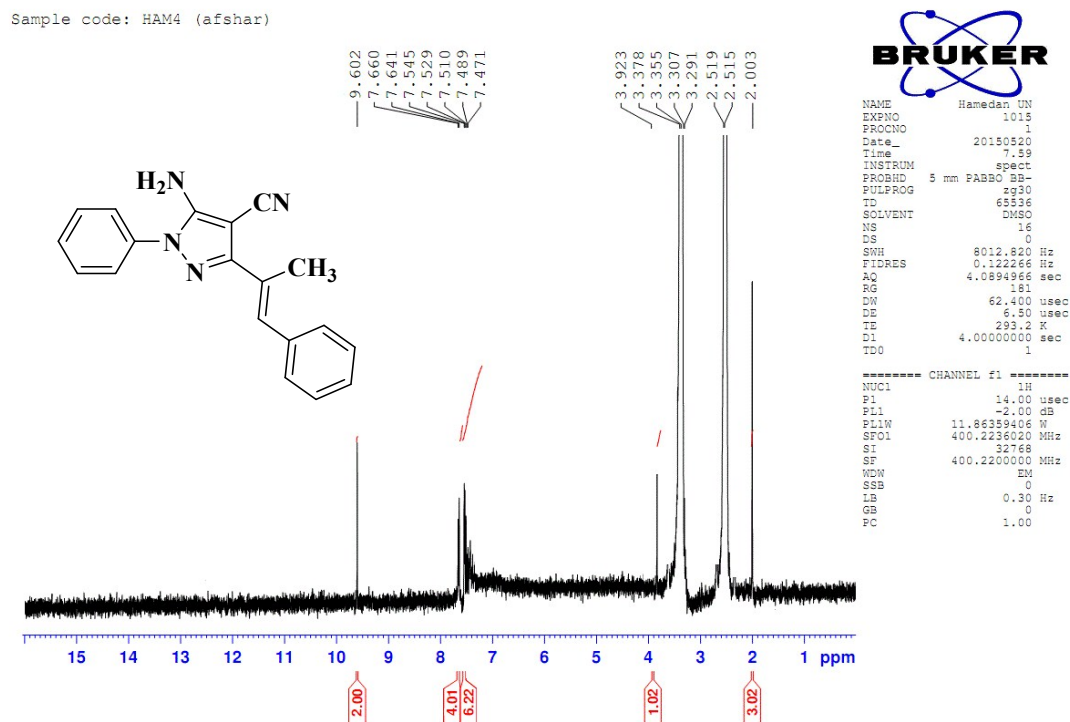


Fig. S17. The ^1H NMR spectrum of 5-amino-1-phenyl-3-(1-phenylprop-1-en-2-yl)-1H-pyrazole-4-carbonitrile (Table 3, entry 4)

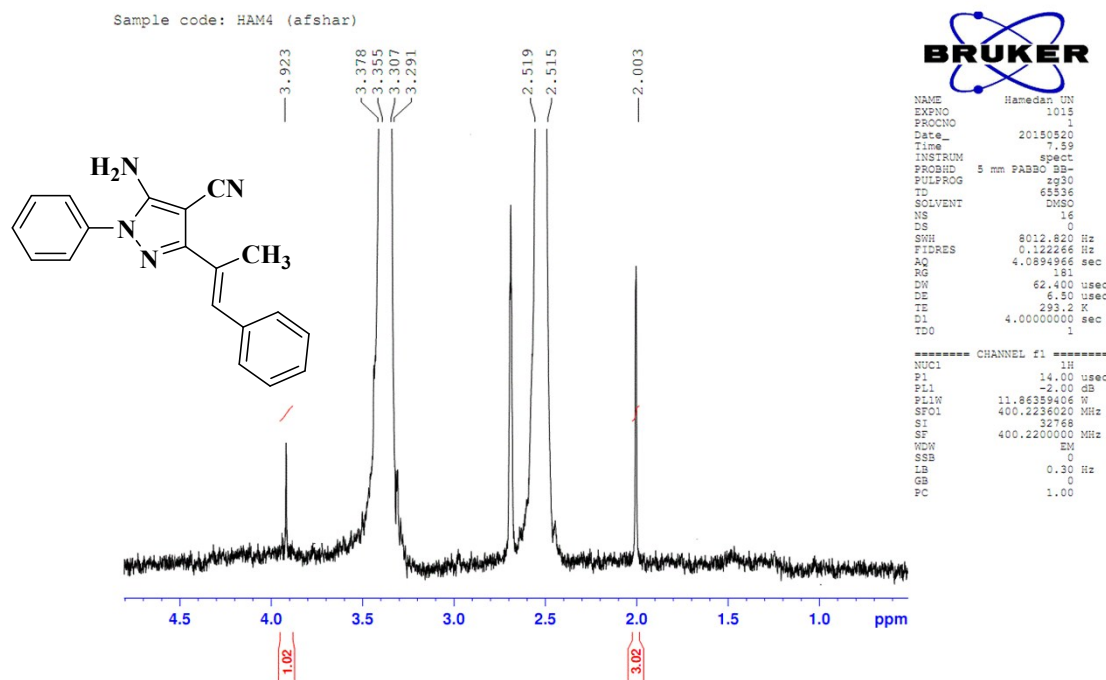


Fig. S18. The ^1H NMR spectrum of 5-amino-1-phenyl-3-(1-phenylprop-1-en-2-yl)-1H-pyrazole-4-carbonitrile (Table 3, entry 4)

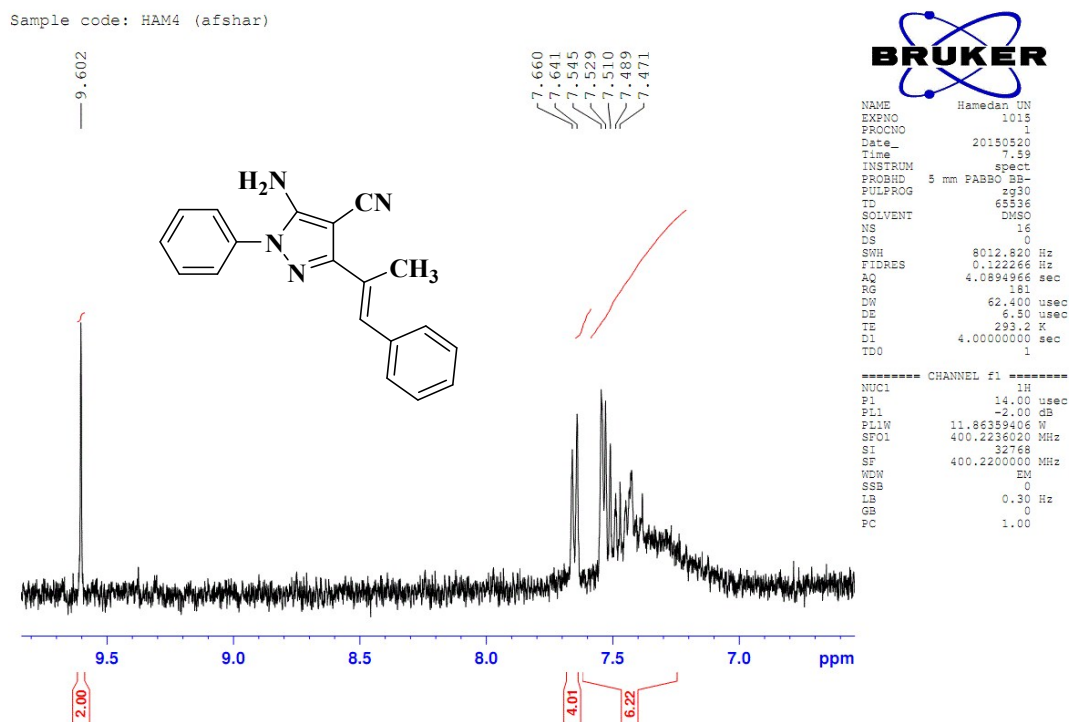


Fig. S19. The ^{13}C NMR spectrum of 5-amino-1-phenyl-3-(1-phenylprop-1-en-2-yl)-1*H*-pyrazole-4-carbonitrile (Table 3, entry 4)

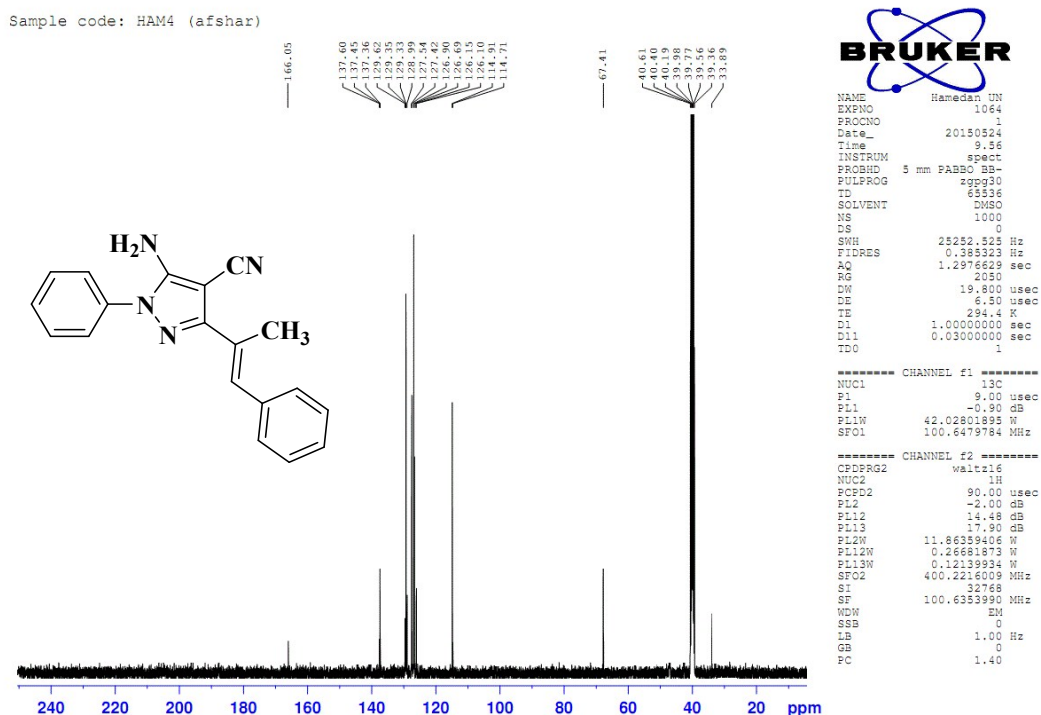


Fig. S20. The ^{13}C NMR spectrum of 5-amino-1-phenyl-3-(1-phenylprop-1-en-2-yl)-1*H*-pyrazole-4-carbonitrile (Table 3, entry 4)

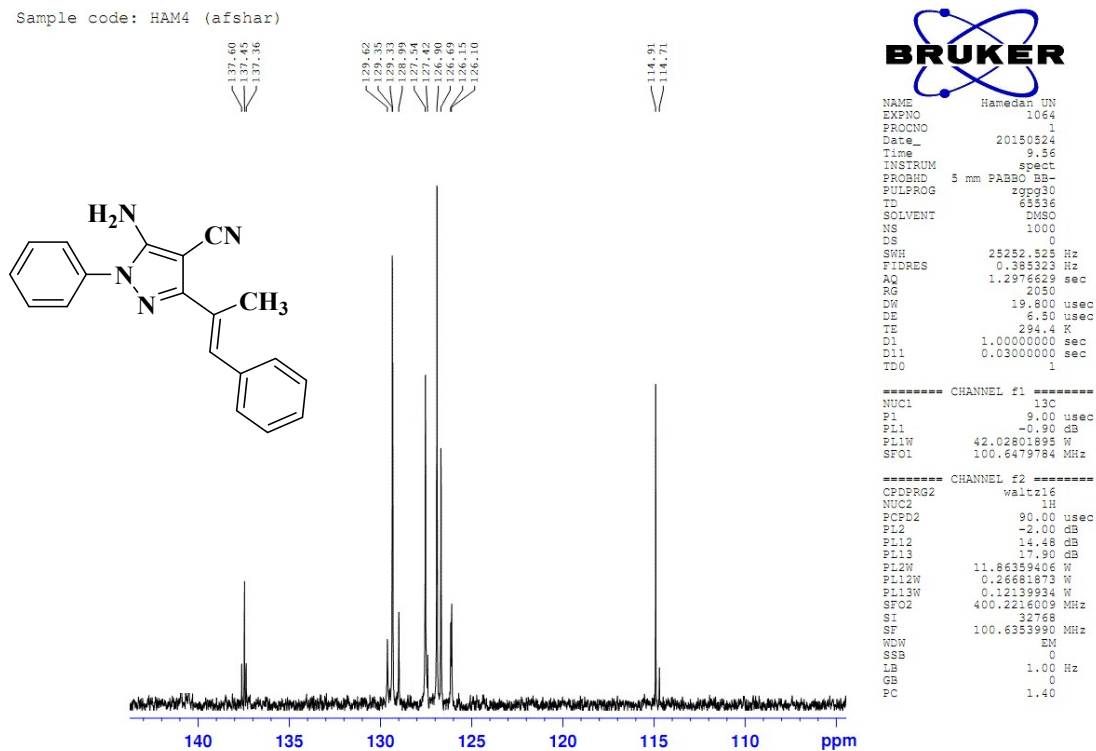


Fig. S21. The IR spectrum of 5-amino-3-(2-hydroxy-3-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 5)

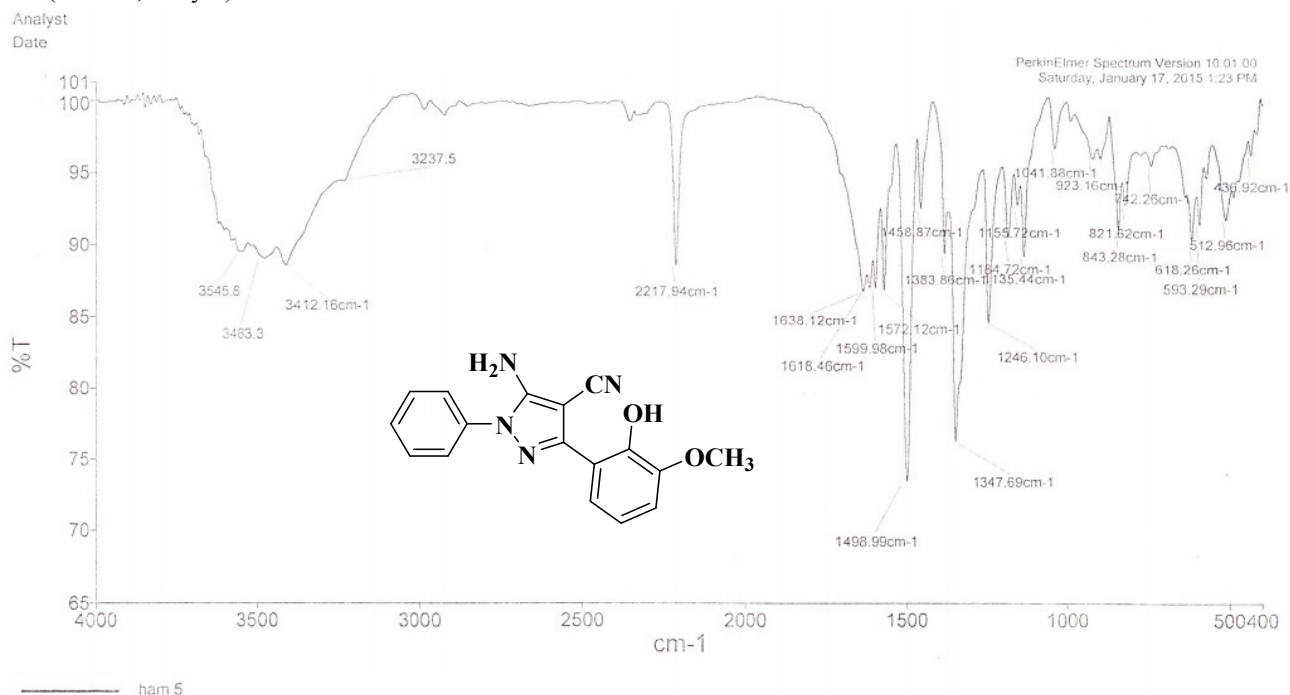


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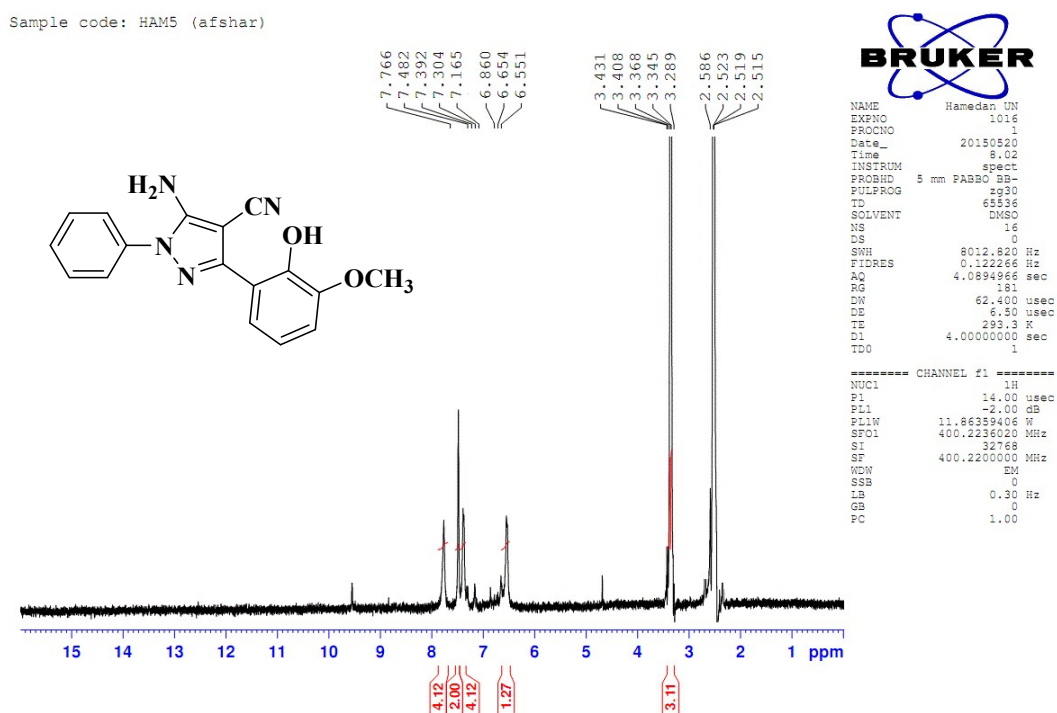


Fig. S23. The ^1H NMR spectrum of 5-amino-3-(2-hydroxy-3-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 5)

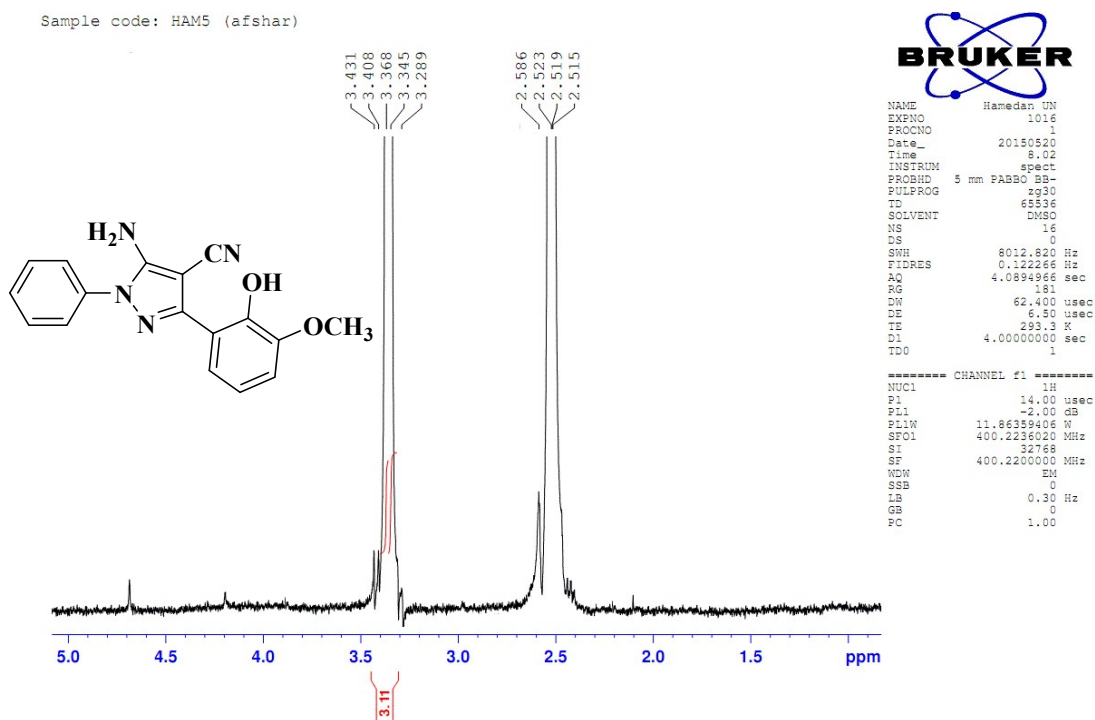


Fig. S24. The ^1H NMR spectrum of 5-amino-3-(2-hydroxy-3-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 5)

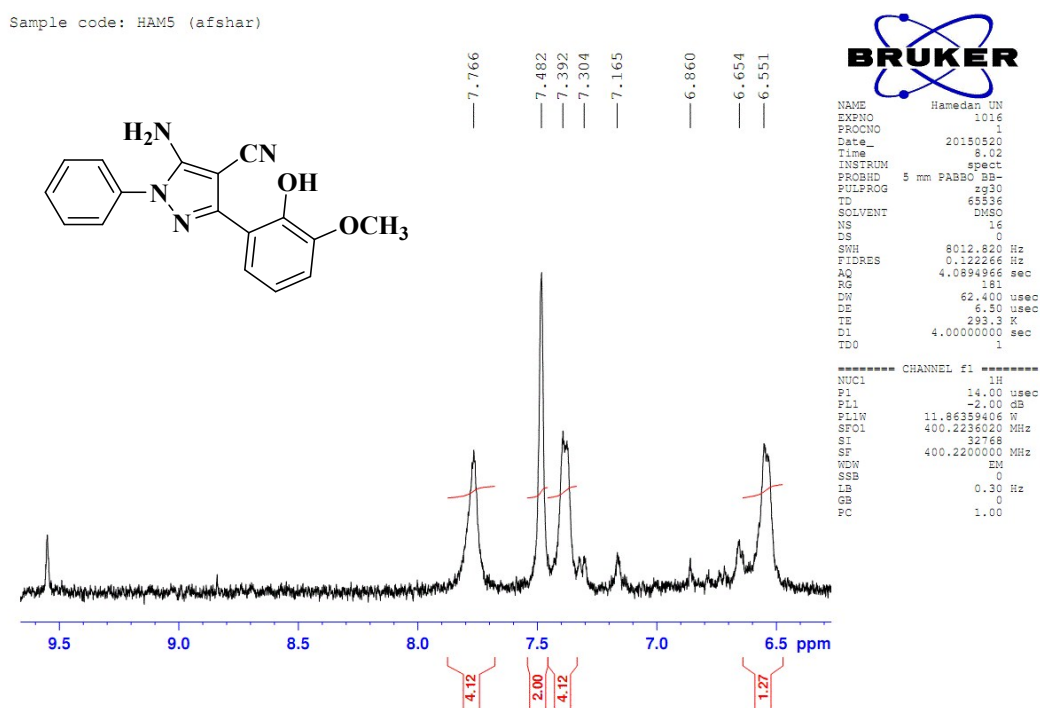


Fig. S25. The ^{13}C NMR spectrum of 5-amino-3-(2-hydroxy-3-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 5)

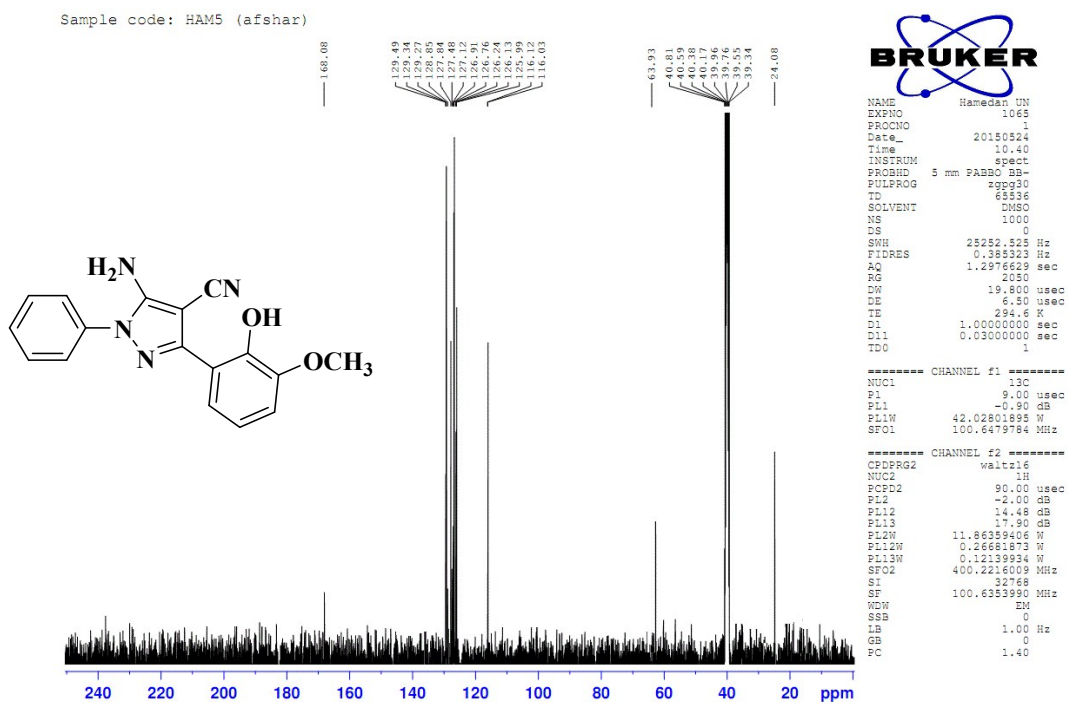


Fig. S26. The ^{13}C NMR spectrum of 5-amino-3-(2-hydroxy-3-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 5)

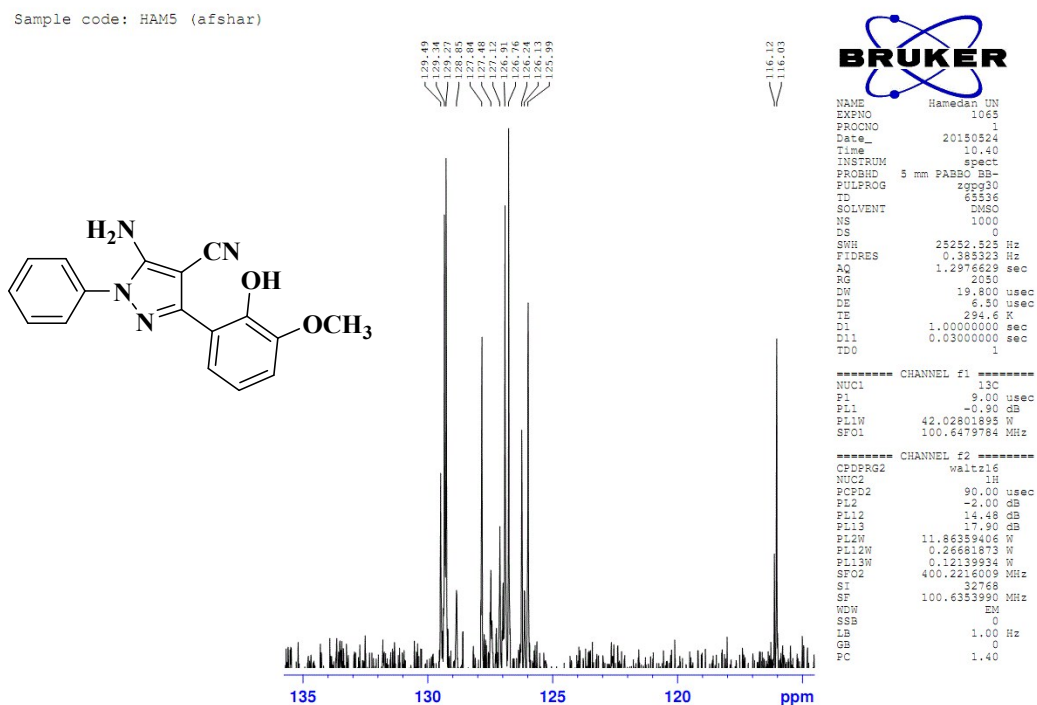


Fig. S27. The IR spectrum of 5-amino-3-(3-ethoxy-4-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (Table 3, entry 6)

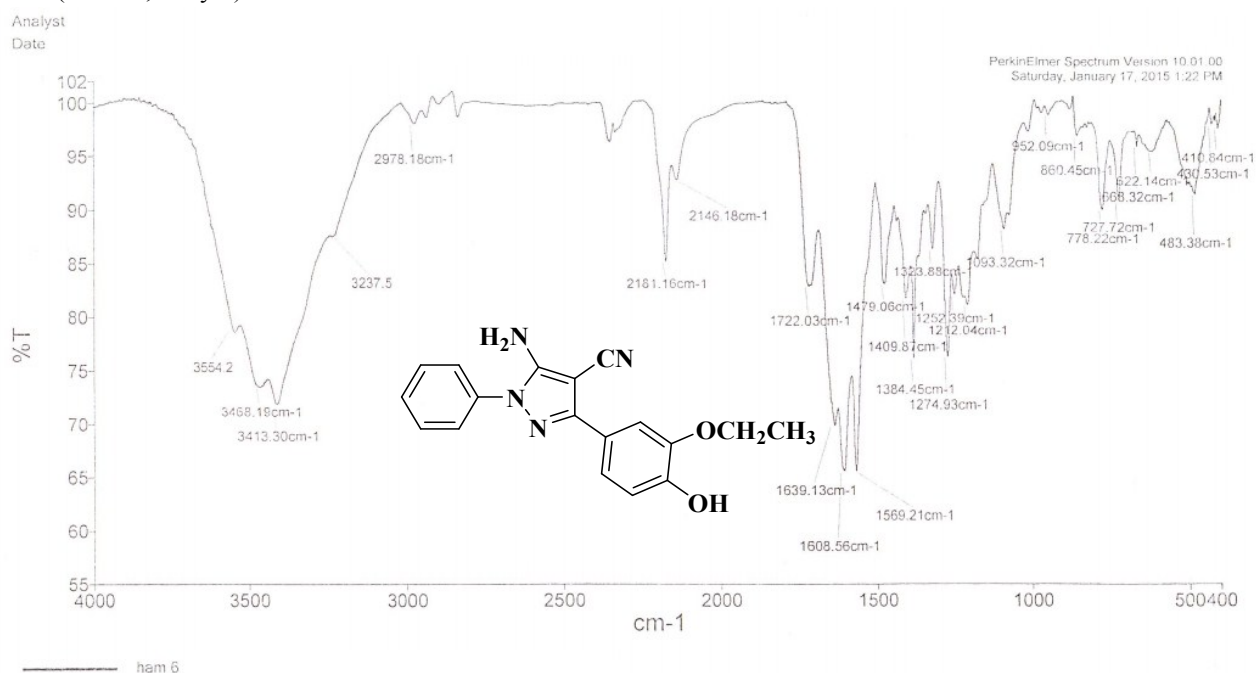


Fig. S28. The ¹H NMR spectrum of 5-amino-3-(3-ethoxy-4-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (Table 3, entry 6)

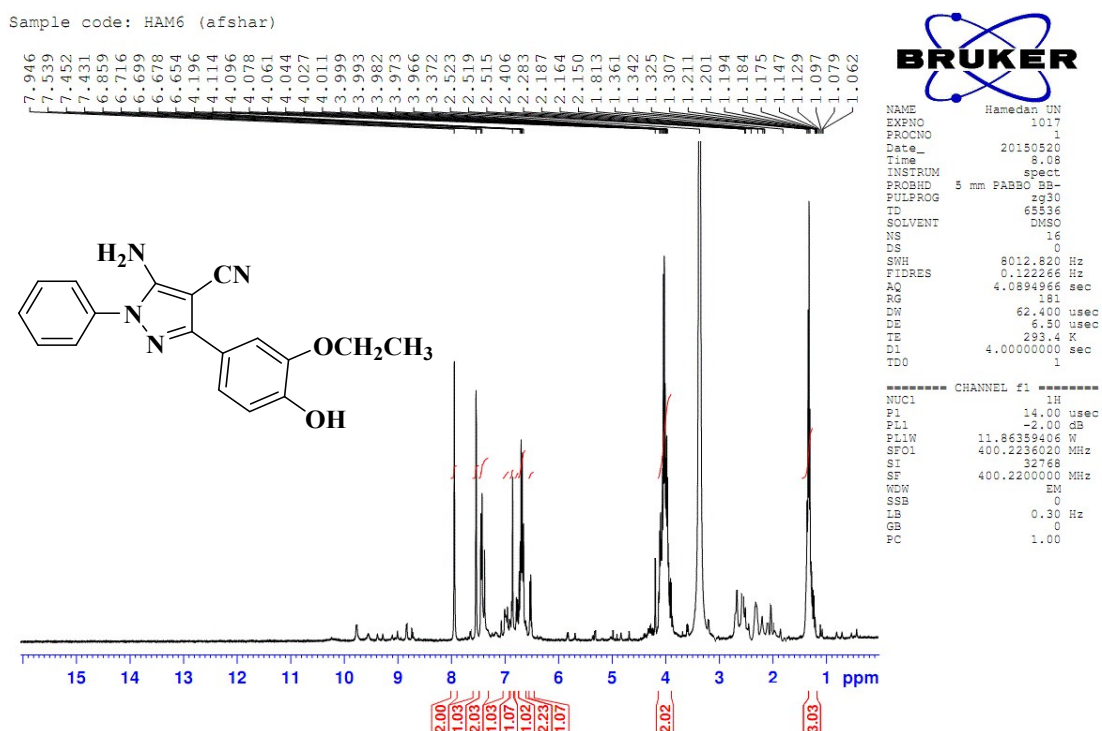


Fig. S30. The ¹H NMR spectrum of 5-amino-3-(3-ethoxy-4-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 6)



Fig. S31. The ^{13}C NMR spectrum of 5-amino-3-(3-ethoxy-4-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 6)

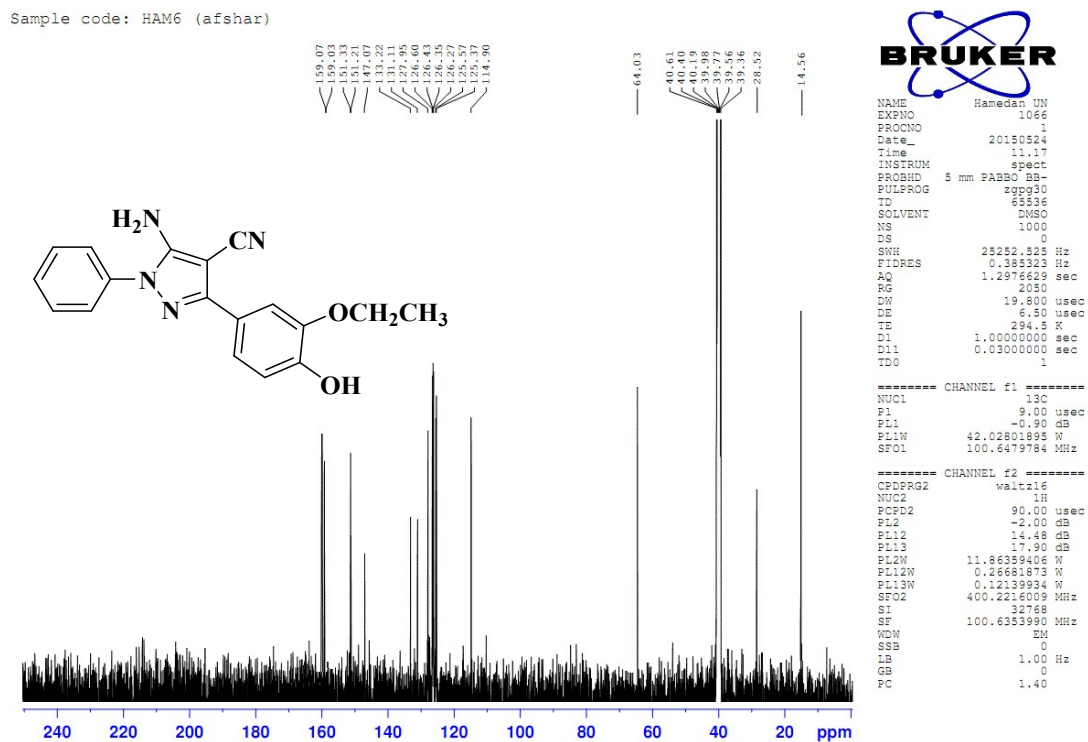


Fig. S32. The ^{13}C NMR spectrum of 5-amino-3-(3-ethoxy-4-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 6)

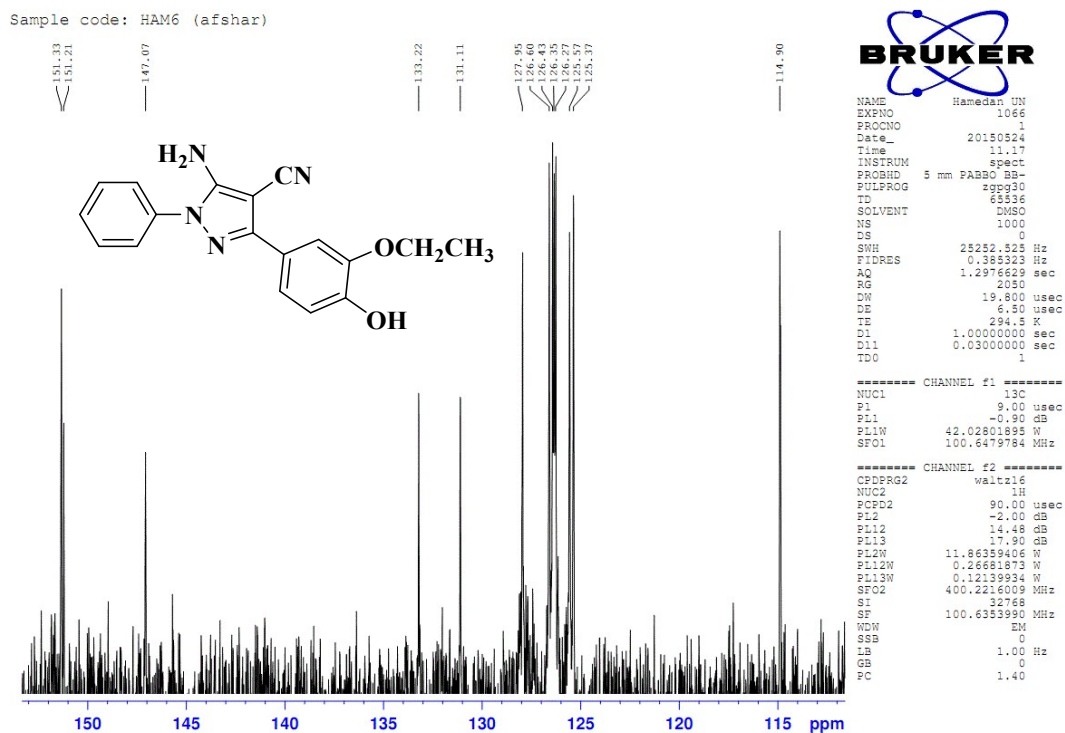


Fig. S33. The IR spectrum of 5-amino-3-(naphthalen-2-yl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 9)

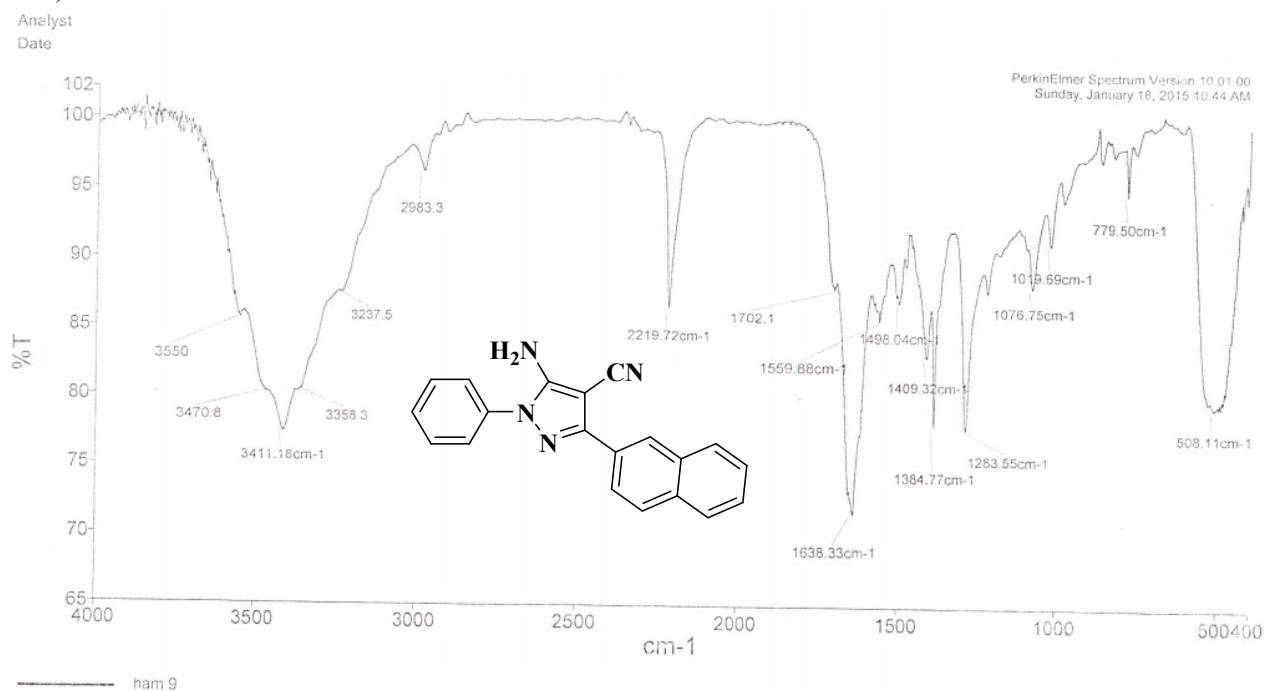


Fig. S34. The ¹H NMR spectrum of 5-amino-3-(3-ethoxy-4-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 9)

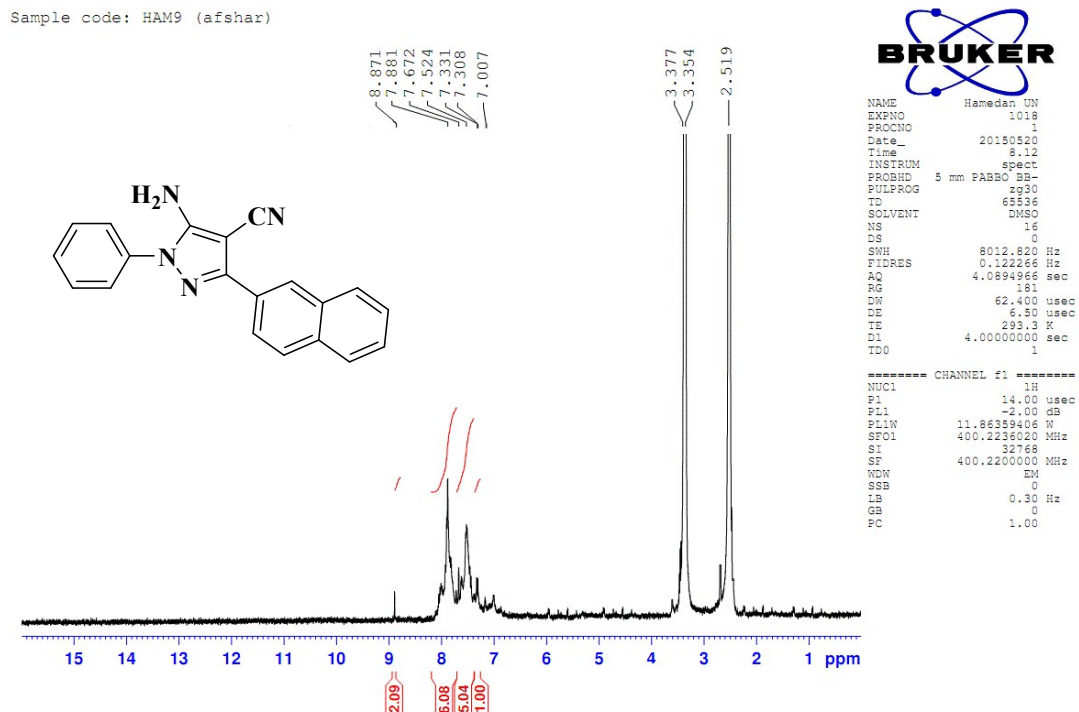


Fig. S35. The ^1H NMR spectrum of 5-amino-3-(naphthalen-2-yl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 9)

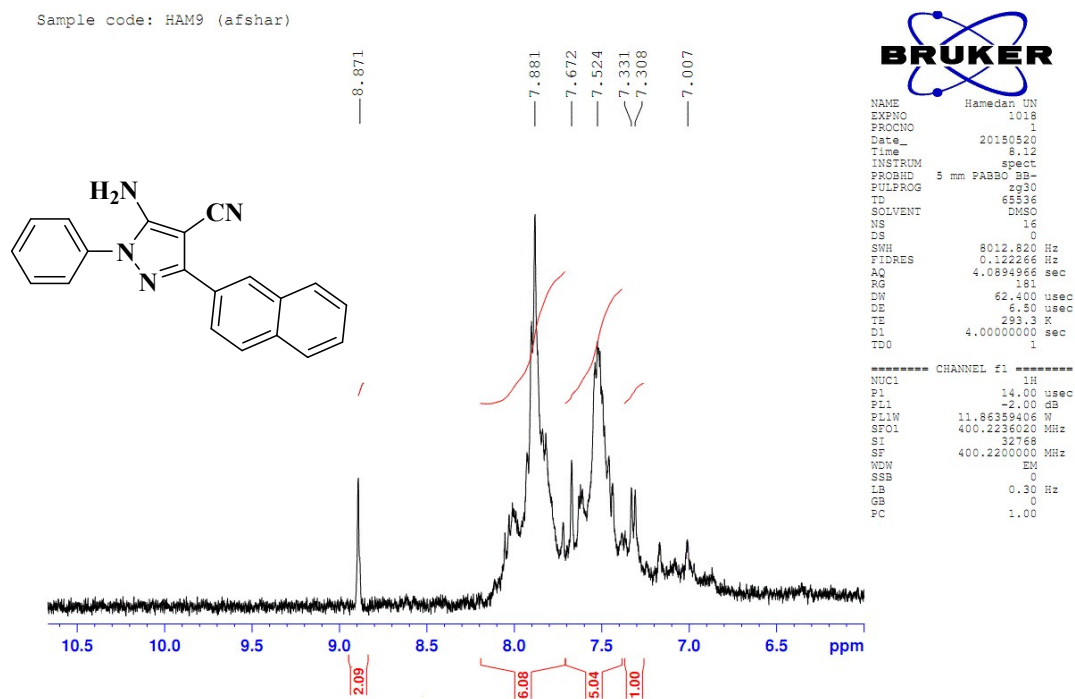


Fig. S36. The ^{13}C NMR spectrum of 5-amino-3-(naphthalen-2-yl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 9)

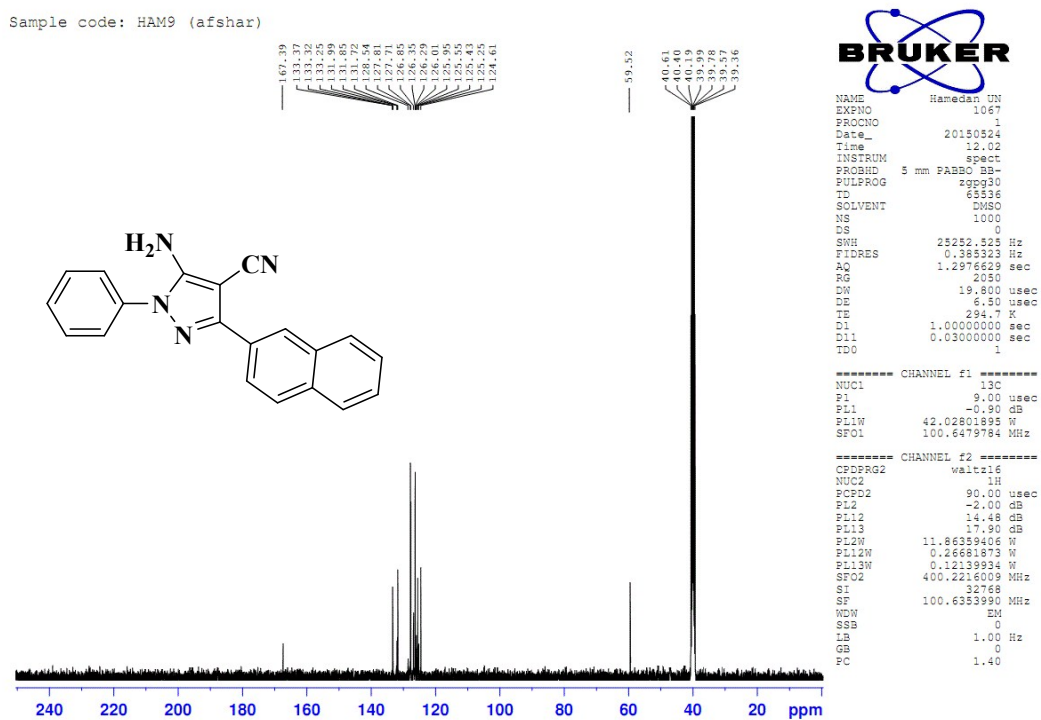


Fig. S37. The ^{13}C NMR spectrum of 5-amino-3-(naphthalen-2-yl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 9)

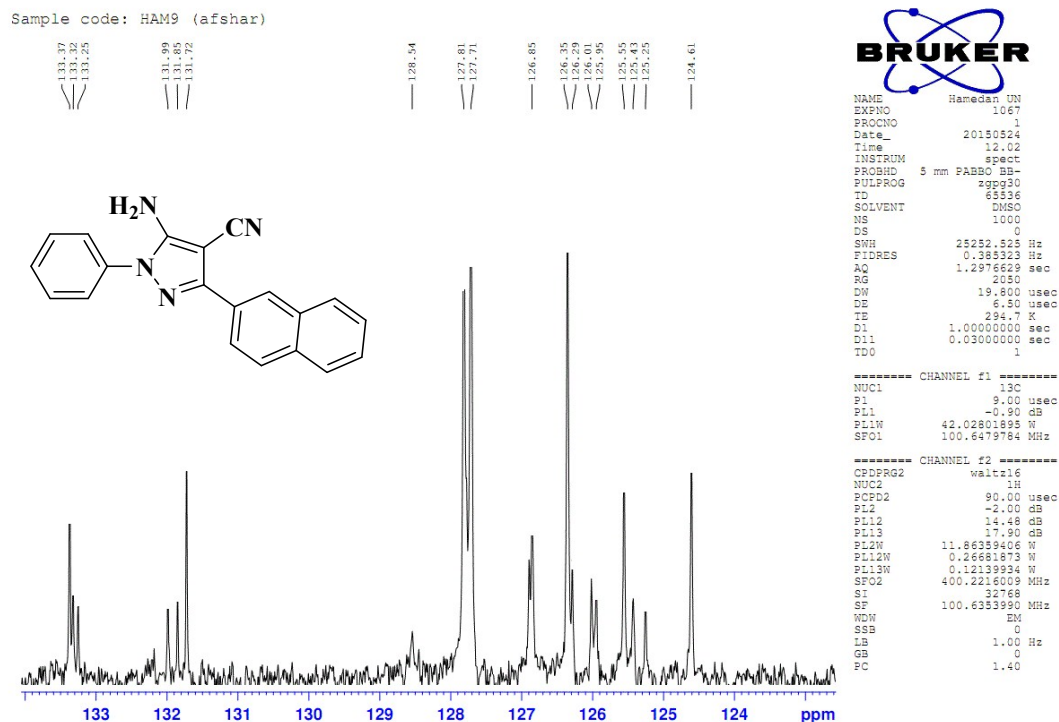


Fig. S38. The IR spectrum of 5-amino-3-(2,4-dichlorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (Table 3, entry 11)

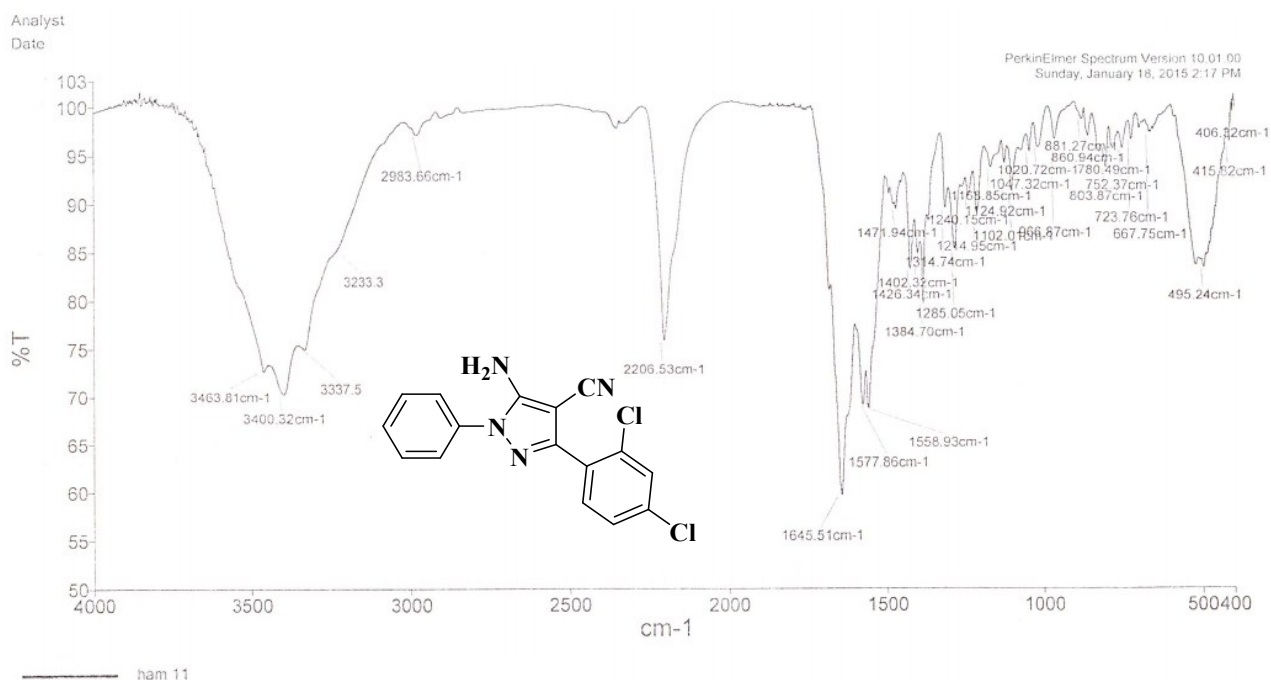


Fig. S39. The ^1H NMR spectrum of 5-amino-3-(2,4-dichlorophenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (Table 3, entry 11)

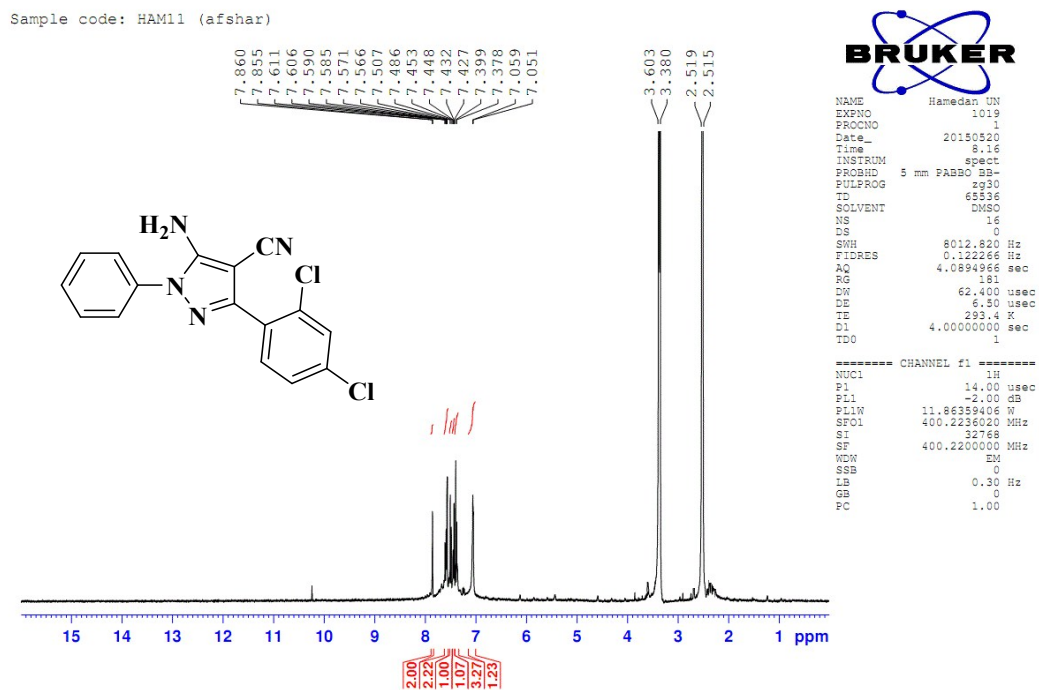


Fig. S40. The ^1H NMR spectrum of 5-amino-3-(2,4-dichlorophenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (Table 3, entry 11)

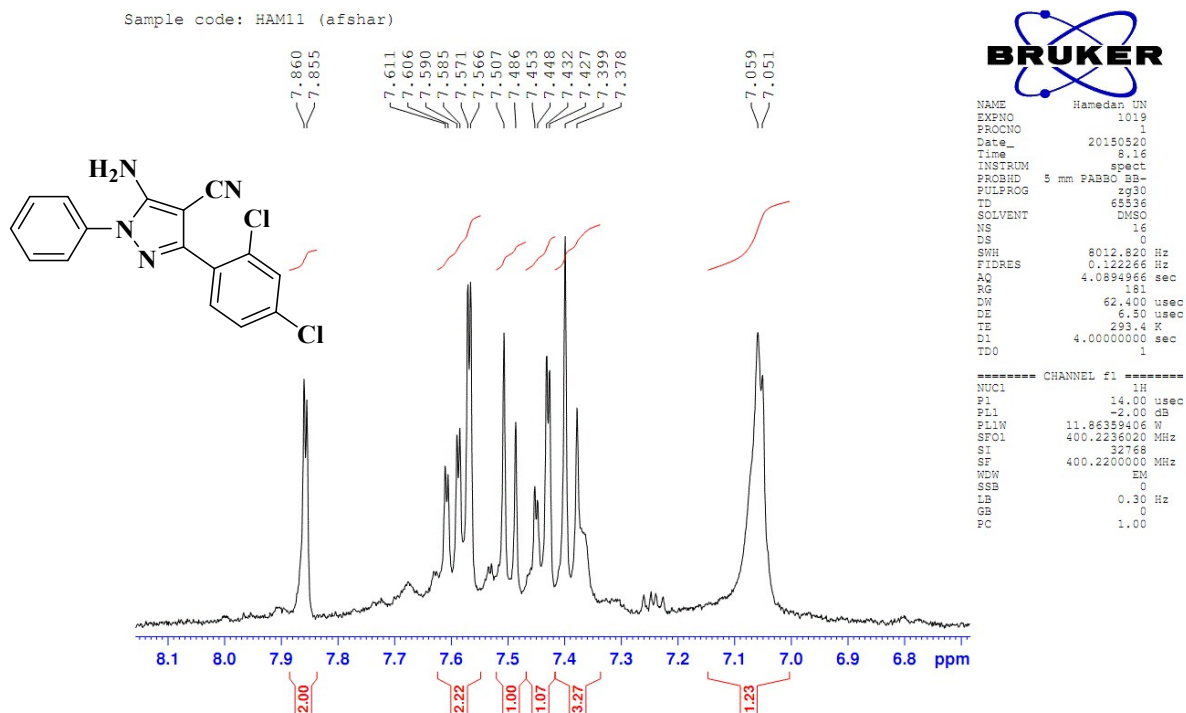


Fig. S41. The ^{13}C NMR spectrum of 5-amino-3-(2,4-dichlorophenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (Table 3, entry 11)

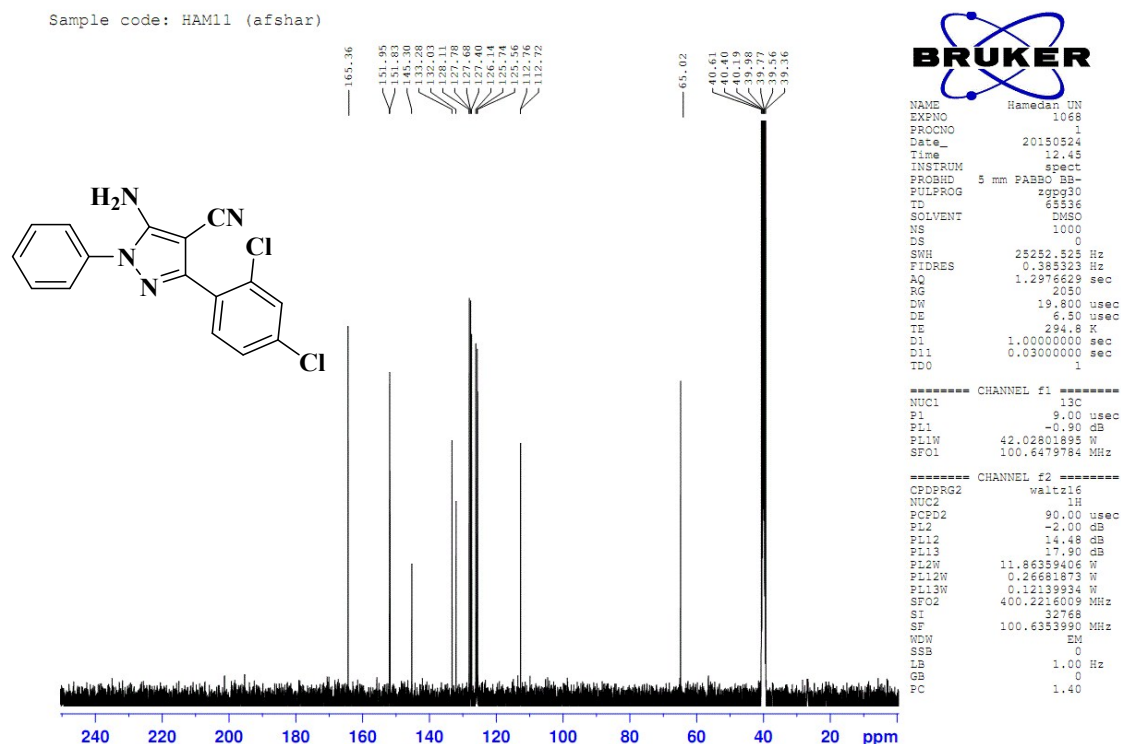


Fig. S42. The ^{13}C NMR spectrum of 5-amino-3-(2,4-dichlorophenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (Table 3, entry 11)

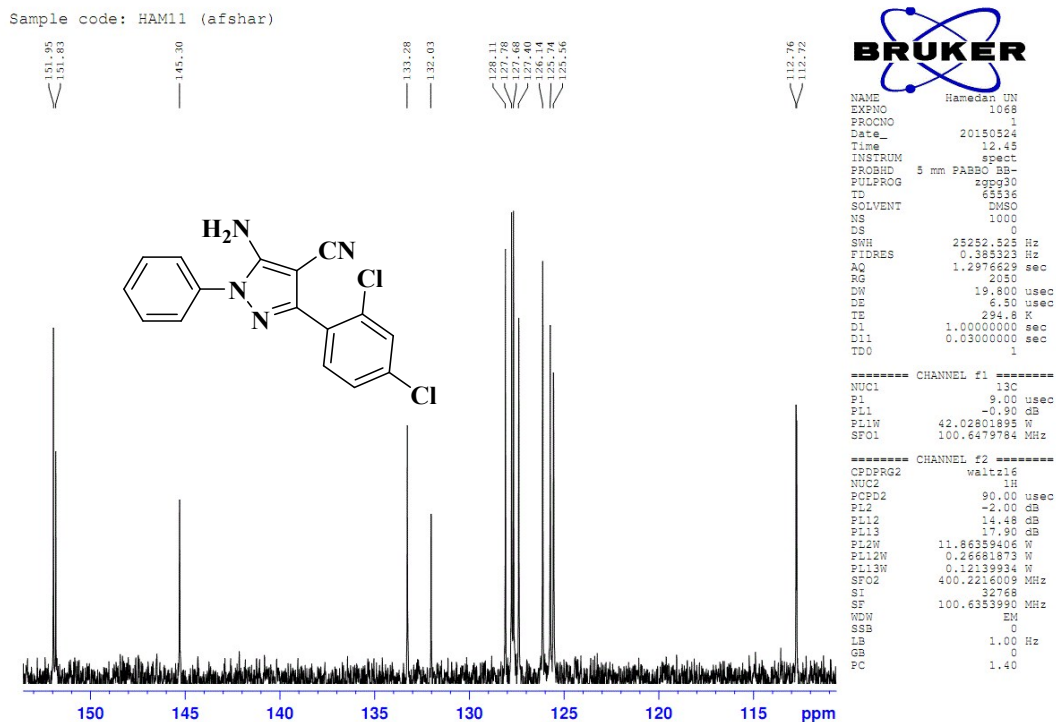


Fig. S43. The IR spectrum of 5-amino-1-phenyl-3-(pyridin-4-yl)-1*H*-pyrazole-4-carbonitrile (Table 3, entry 12)

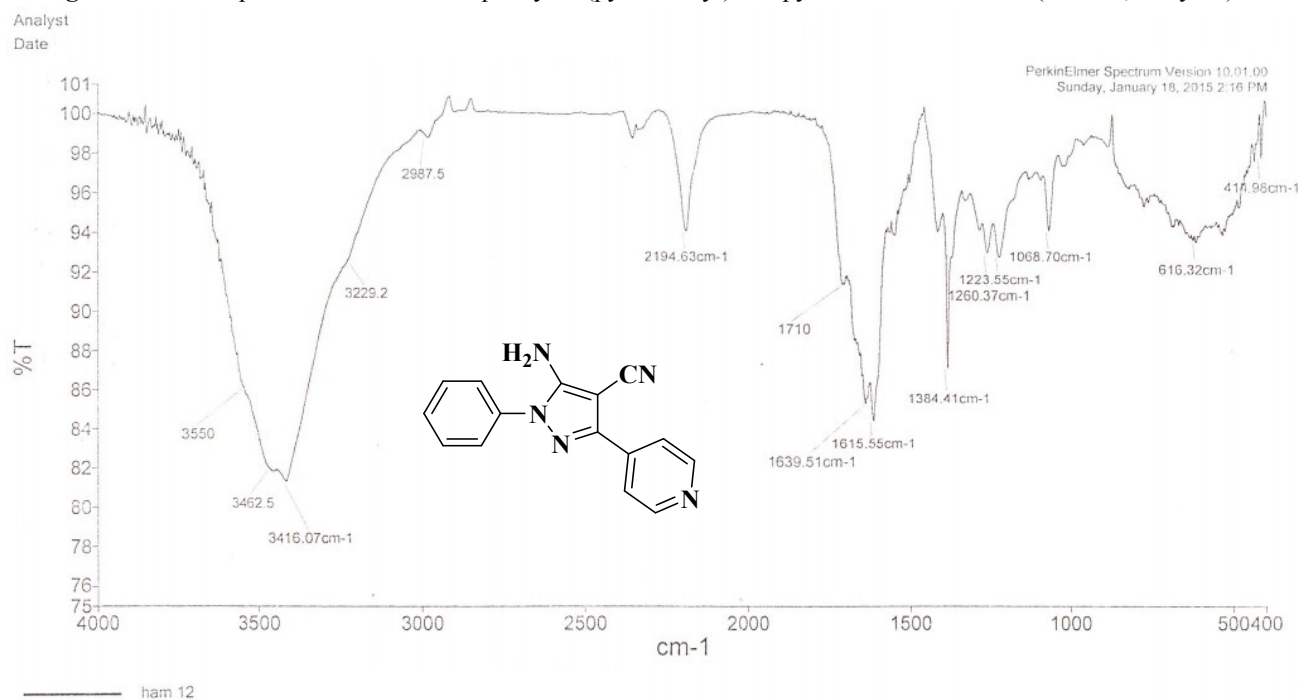


Fig. S44. The ^1H NMR spectrum of 5-amino-1-phenyl-3-(pyridin-4-yl)-1*H*-pyrazole-4-carbonitrile (Table 3, entry 12)

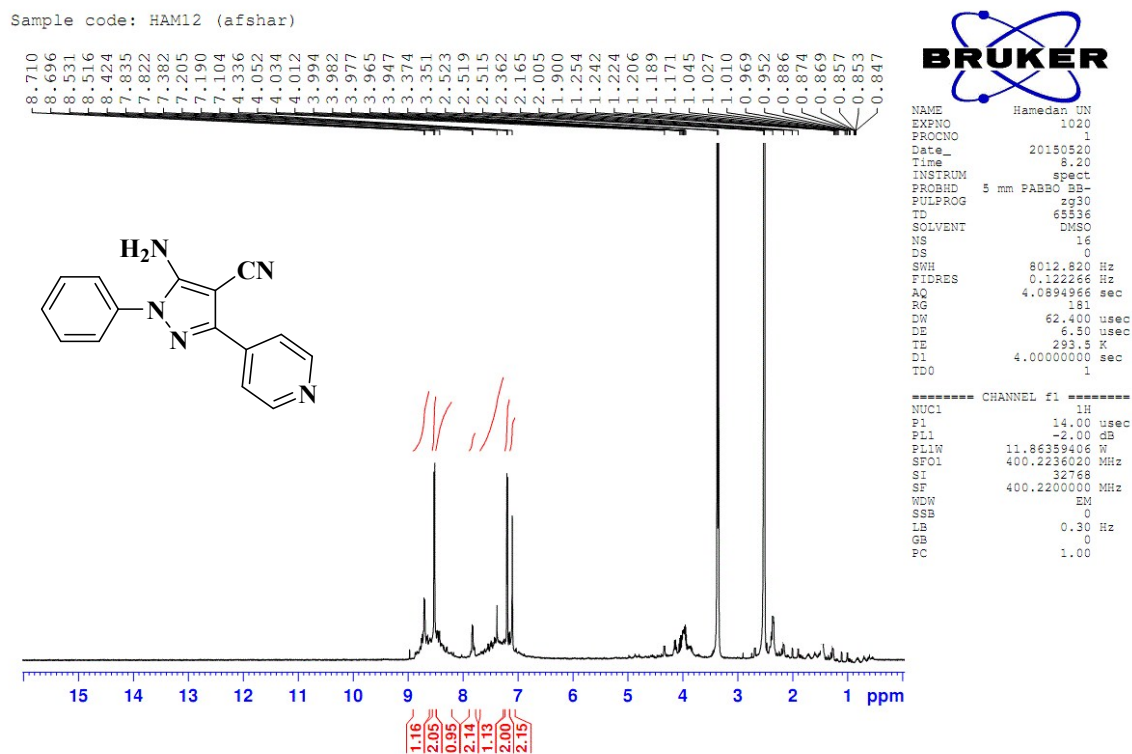


Fig. S45. The ^1H NMR spectrum of 5-amino-1-phenyl-3-(pyridin-4-yl)-1*H*-pyrazole-4-carbonitrile (Table 3, entry 12)

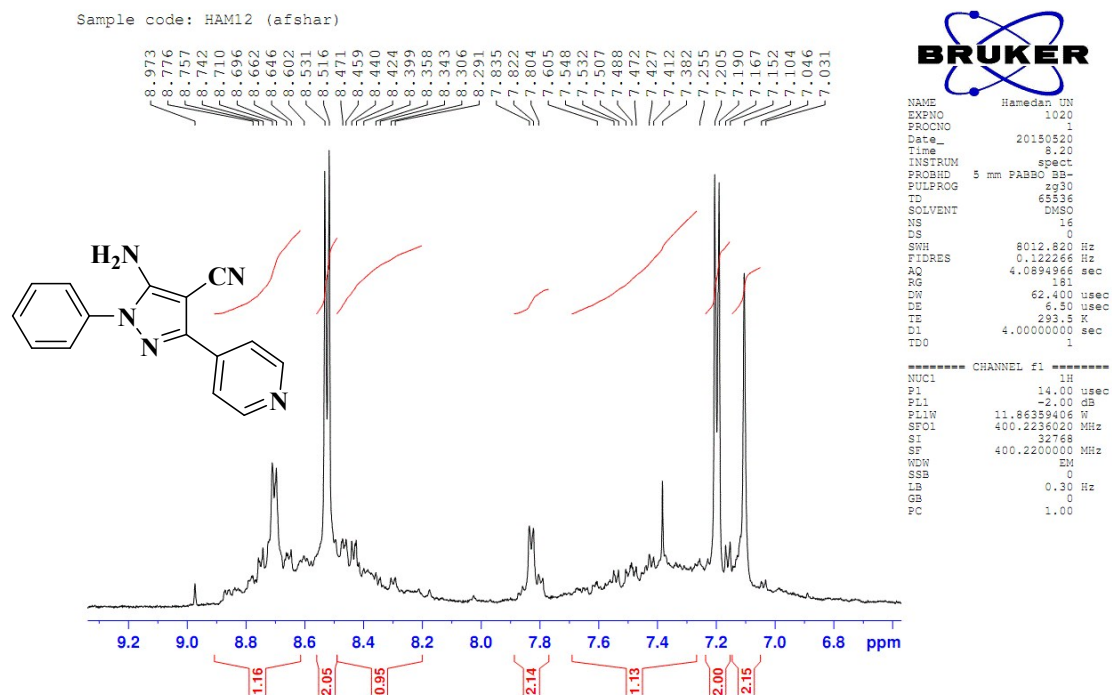


Fig. S46. The ^{13}C NMR spectrum of 5-amino-1-phenyl-3-(pyridin-4-yl)-1*H*-pyrazole-4-carbonitrile (Table 3, entry 12)

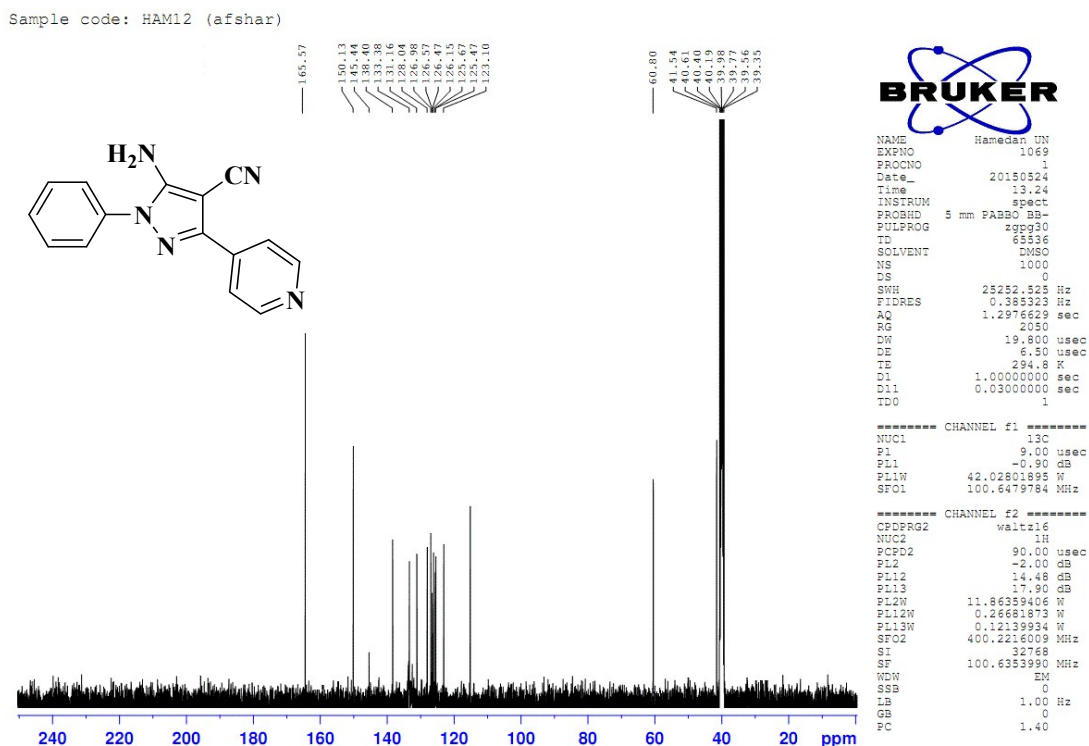


Fig. S47. The ^{13}C NMR spectrum of 5-amino-1-phenyl-3-(pyridin-4-yl)-1*H*-pyrazole-4-carbonitrile (Table 3, entry 12)

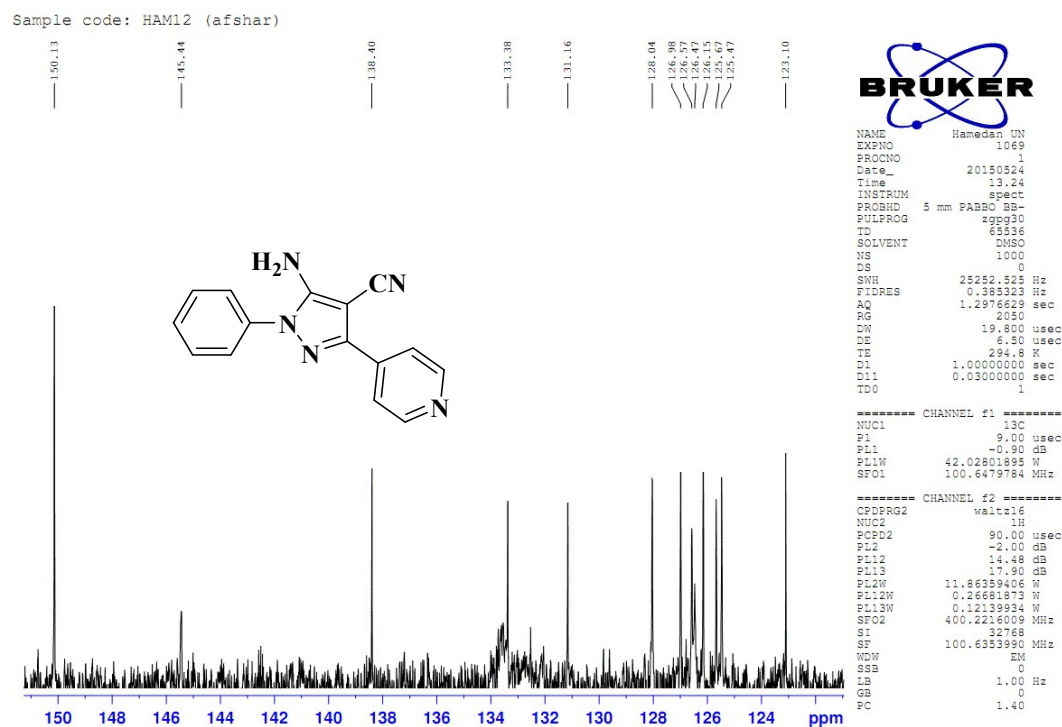


Fig. S48. The IR spectrum of 6-amino-3-methyl-4-(naphthalen-1-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 3)

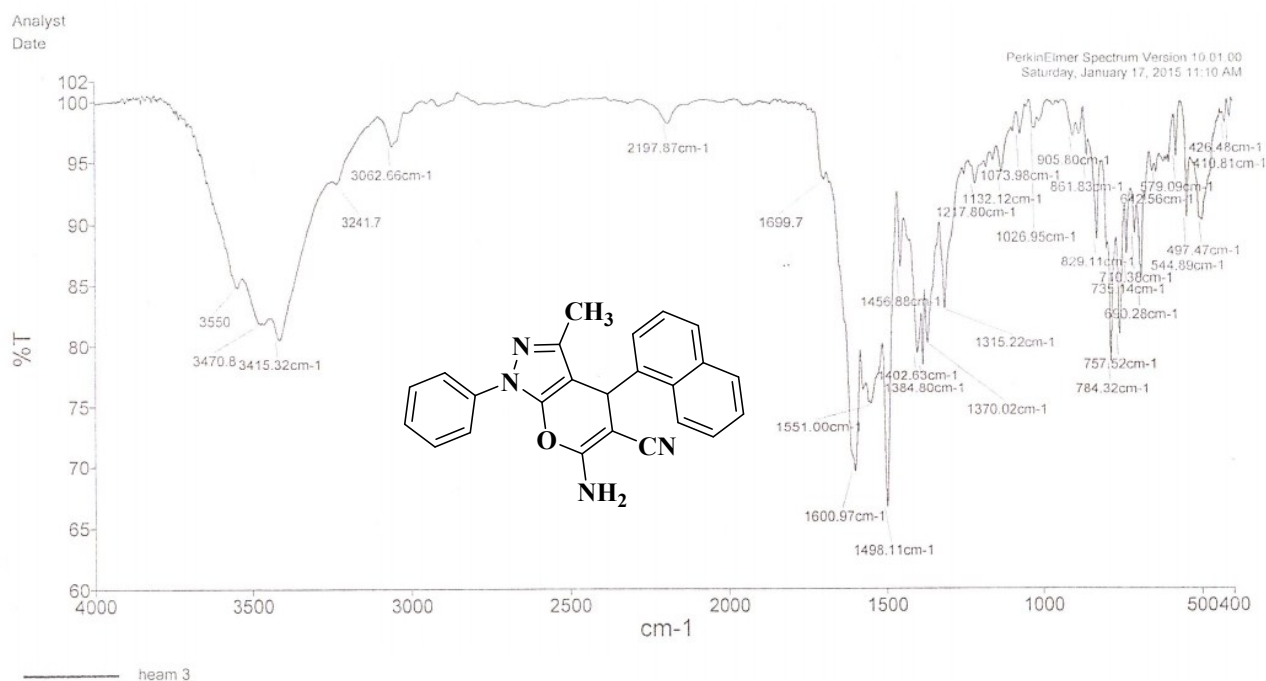


Fig. S49. The ^1H NMR spectrum of 6-amino-3-methyl-4-(naphthalen-1-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 3)

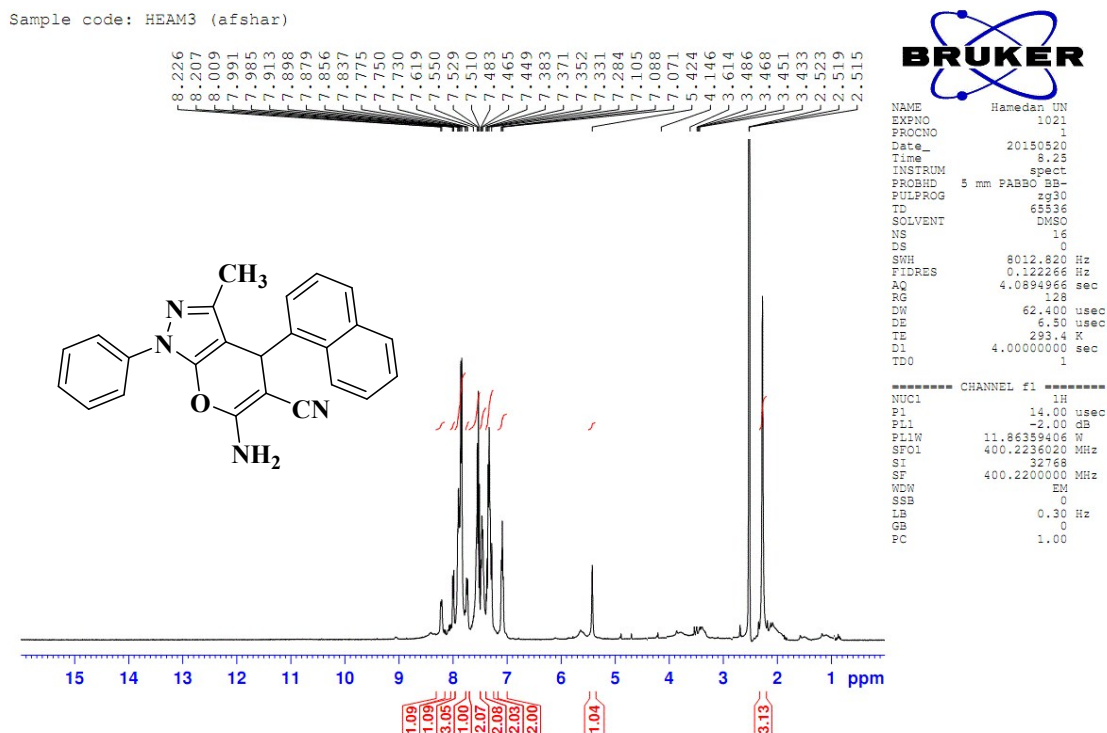


Fig. S50. The ^1H NMR spectrum of 6-amino-3-methyl-4-(naphthalen-1-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 3)

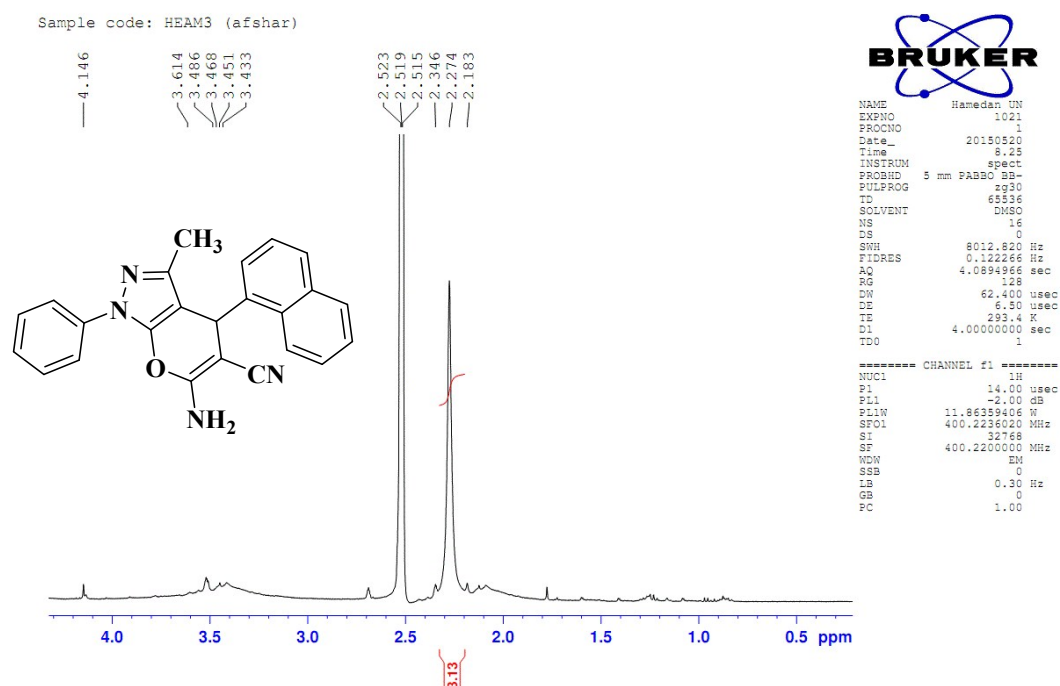


Fig. S51. The ^1H NMR spectrum of 6-amino-3-methyl-4-(naphthalen-1-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 3)

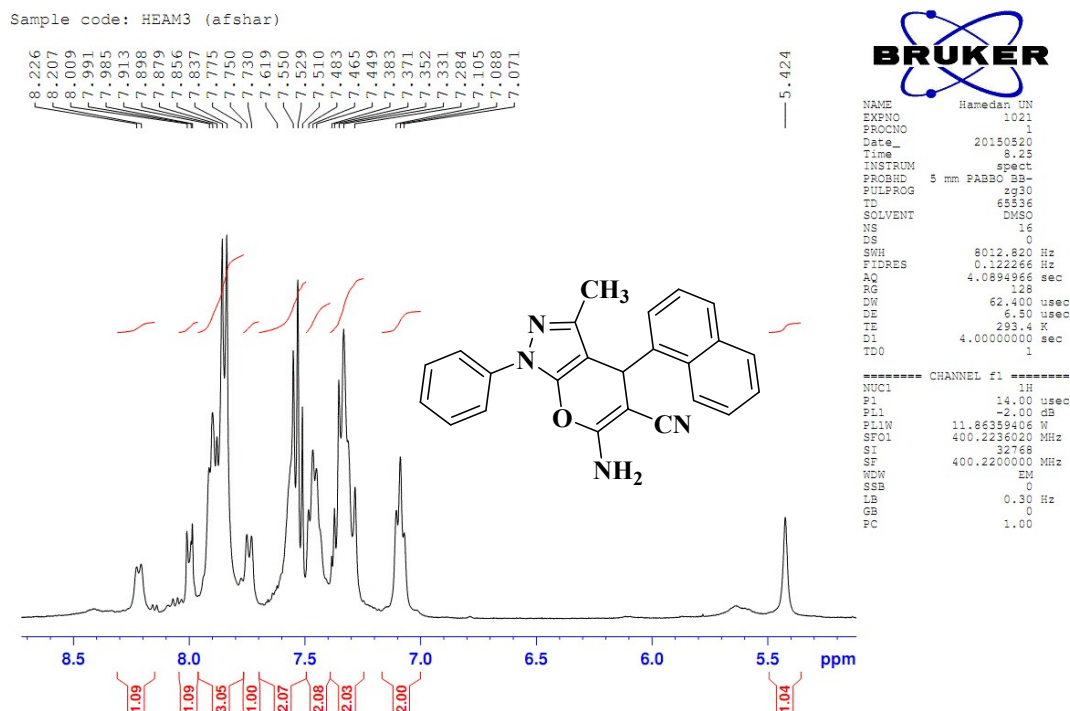


Fig. S52. The ^{13}C NMR spectrum of 6-amino-3-methyl-4-(naphthalen-1-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 3)

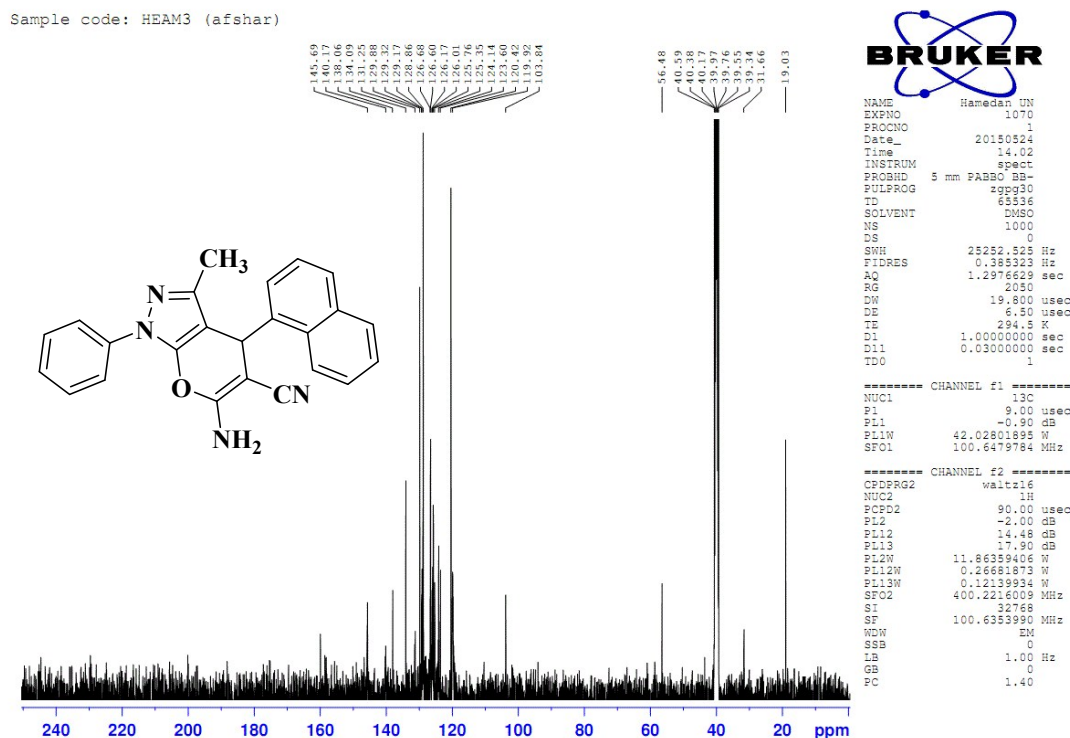


Fig. S53. The ^{13}C NMR spectrum of 6-amino-3-methyl-4-(naphthalen-1-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 3)

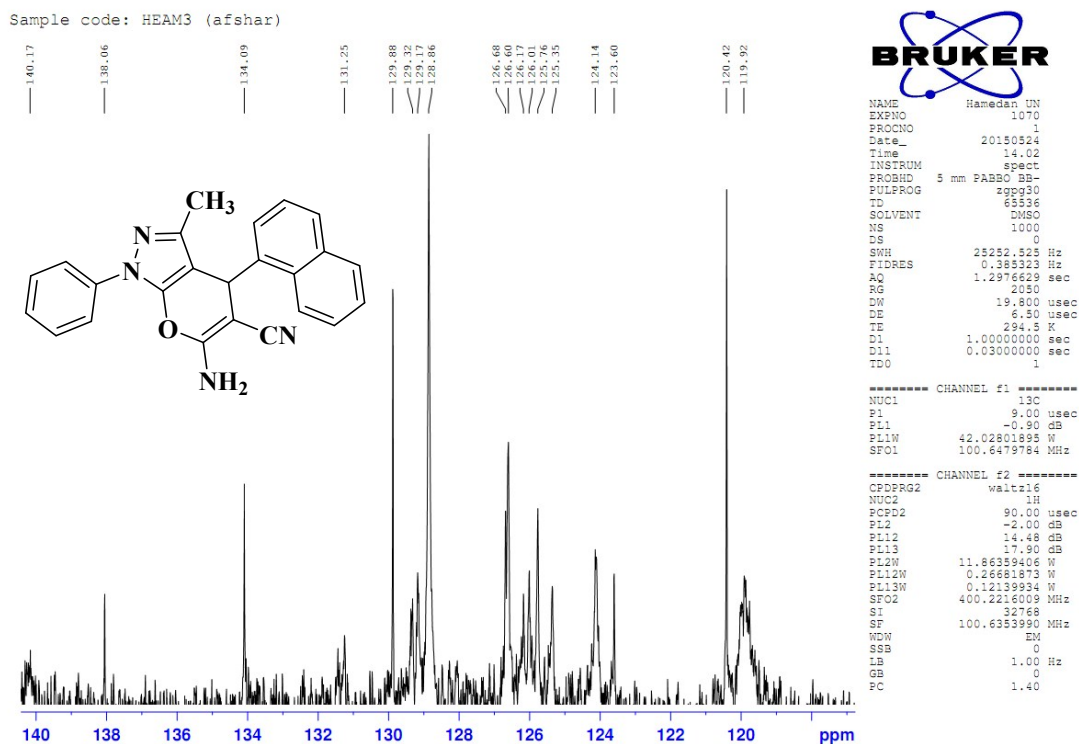


Fig. S54. The IR spectrum of 6-amino-3-methyl-1-phenyl-4-(1-phenylprop-1-en-2-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 4)

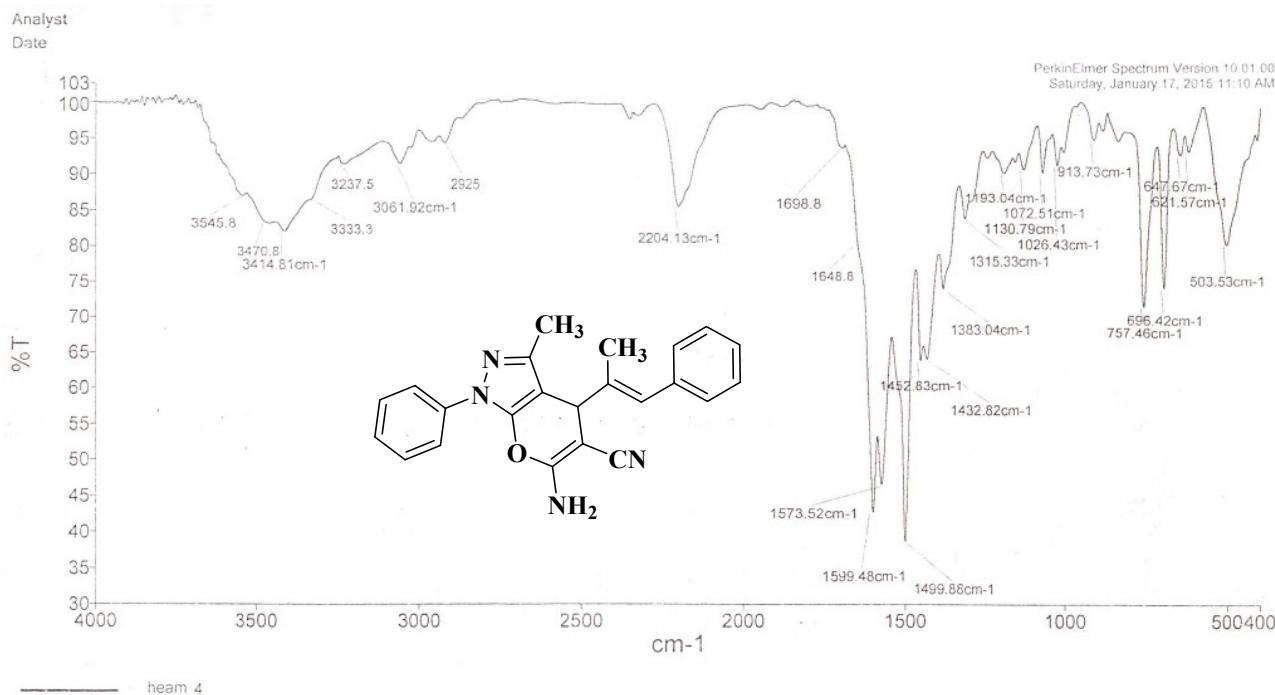


Fig. S55. The ^1H NMR spectrum of 6-amino-3-methyl-1-phenyl-4-(1-phenylprop-1-en-2-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 4)

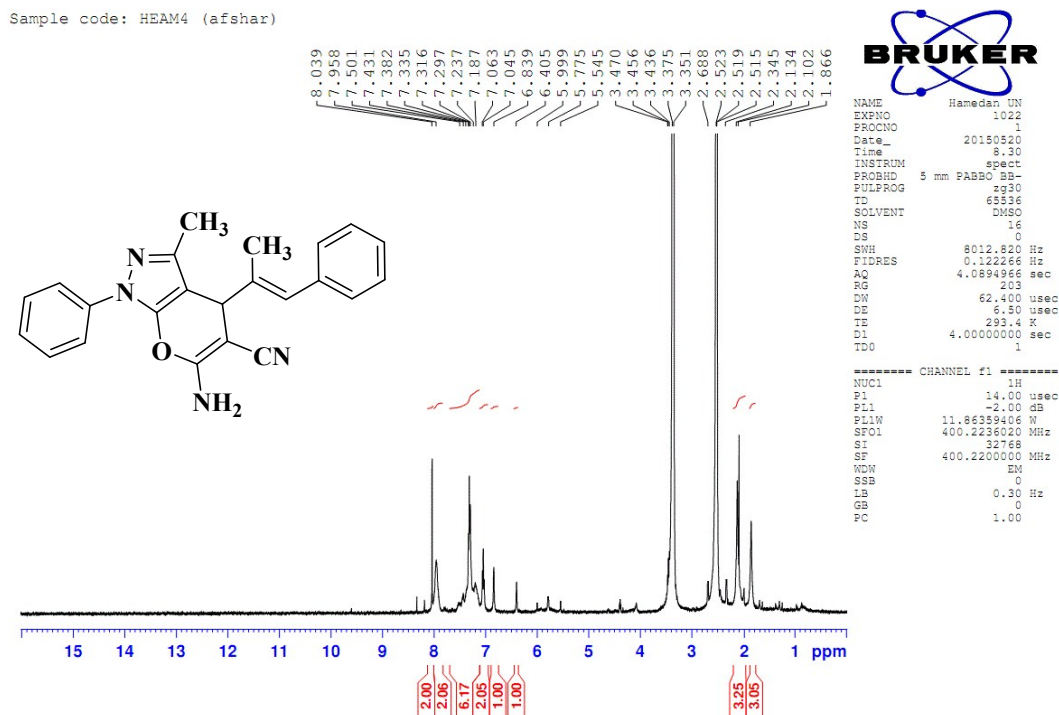


Fig. S56. The ^1H NMR spectrum of 6-amino-3-methyl-1-phenyl-4-(1-phenylprop-1-en-2-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 4)

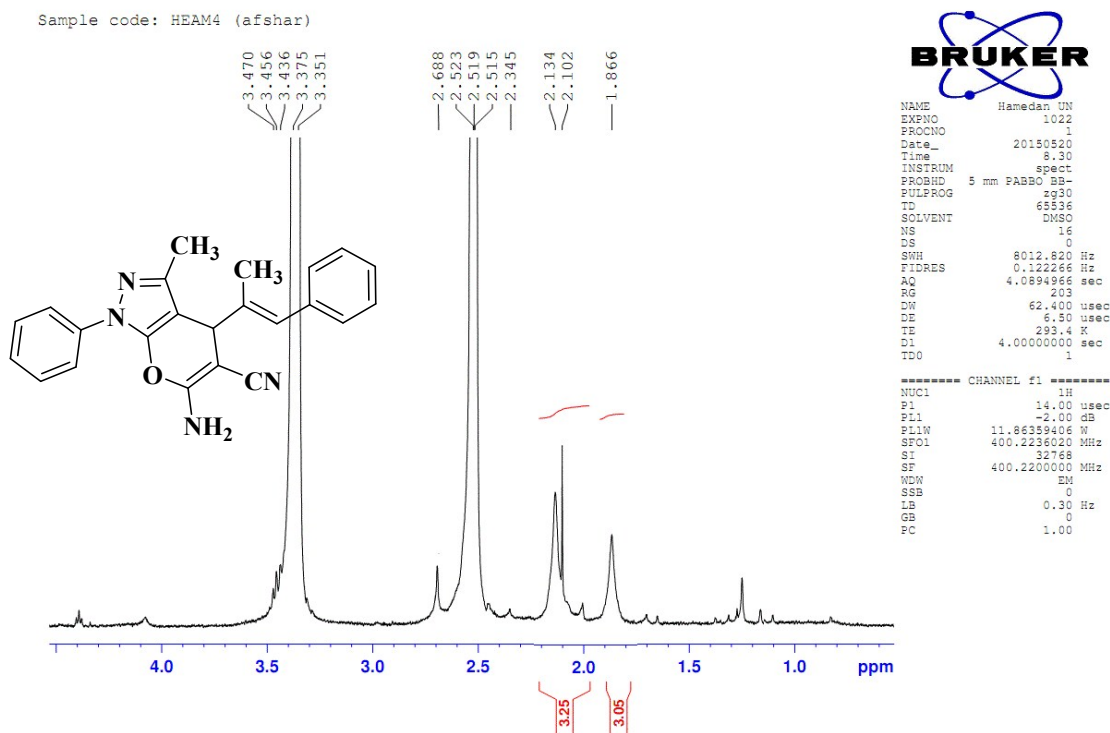


Fig. S57. The ^1H NMR spectrum of 6-amino-3-methyl-1-phenyl-4-(1-phenylprop-1-en-2-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 4)

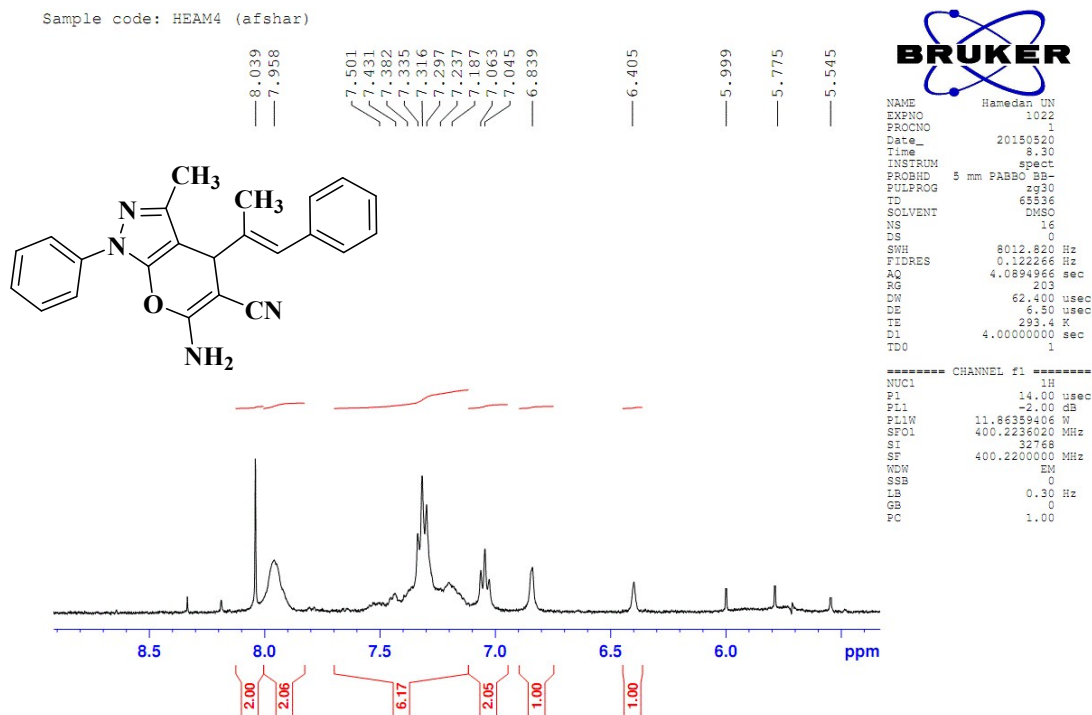


Fig. S58. The ^{13}C NMR spectrum of 6-amino-3-methyl-1-phenyl-4-(1-phenylprop-1-en-2-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 4)

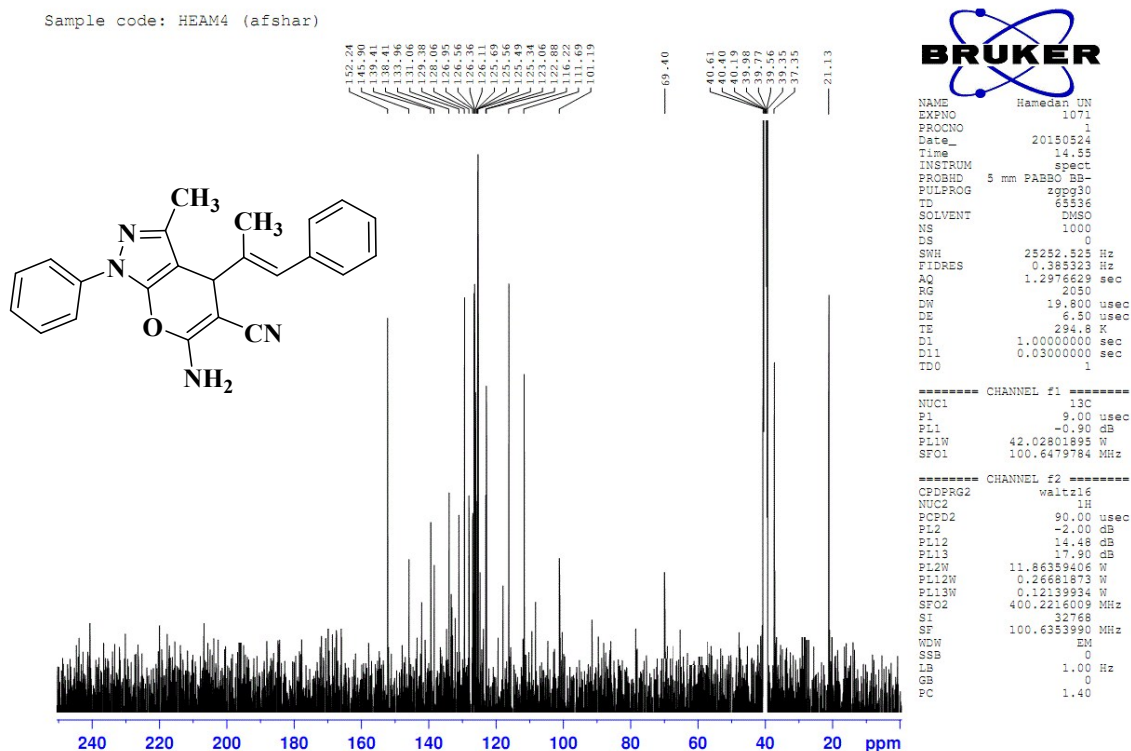


Fig. S59. The ^{13}C NMR spectrum of 6-amino-3-methyl-1-phenyl-4-(1-phenylprop-1-en-2-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 4)

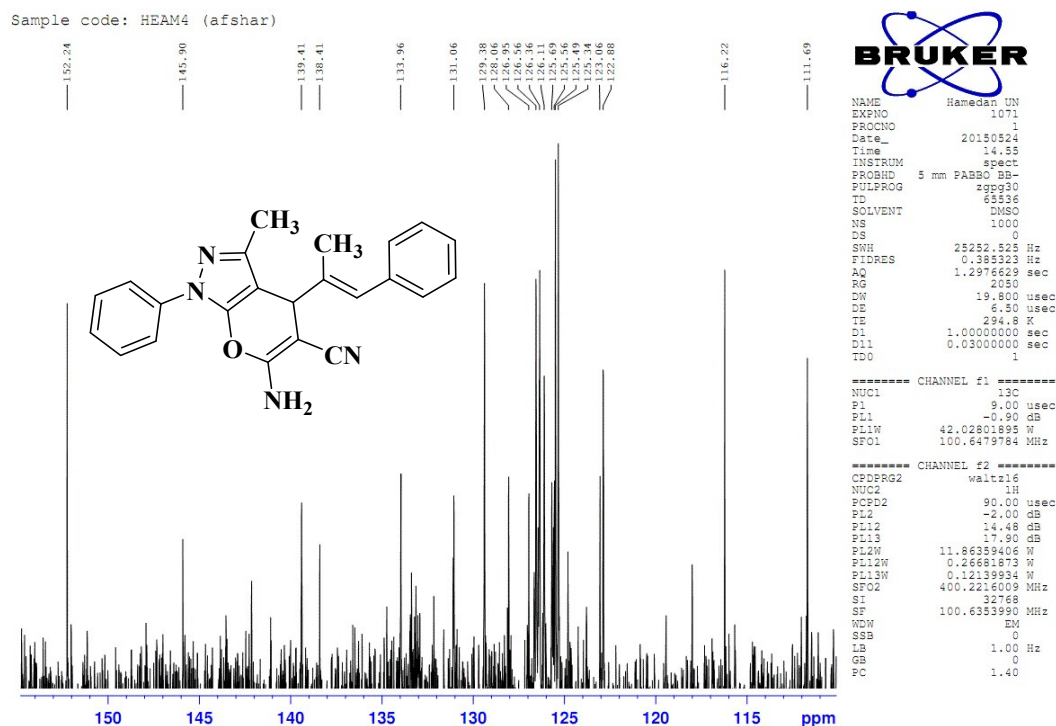


Fig. S60. The IR spectrum of 6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 5)

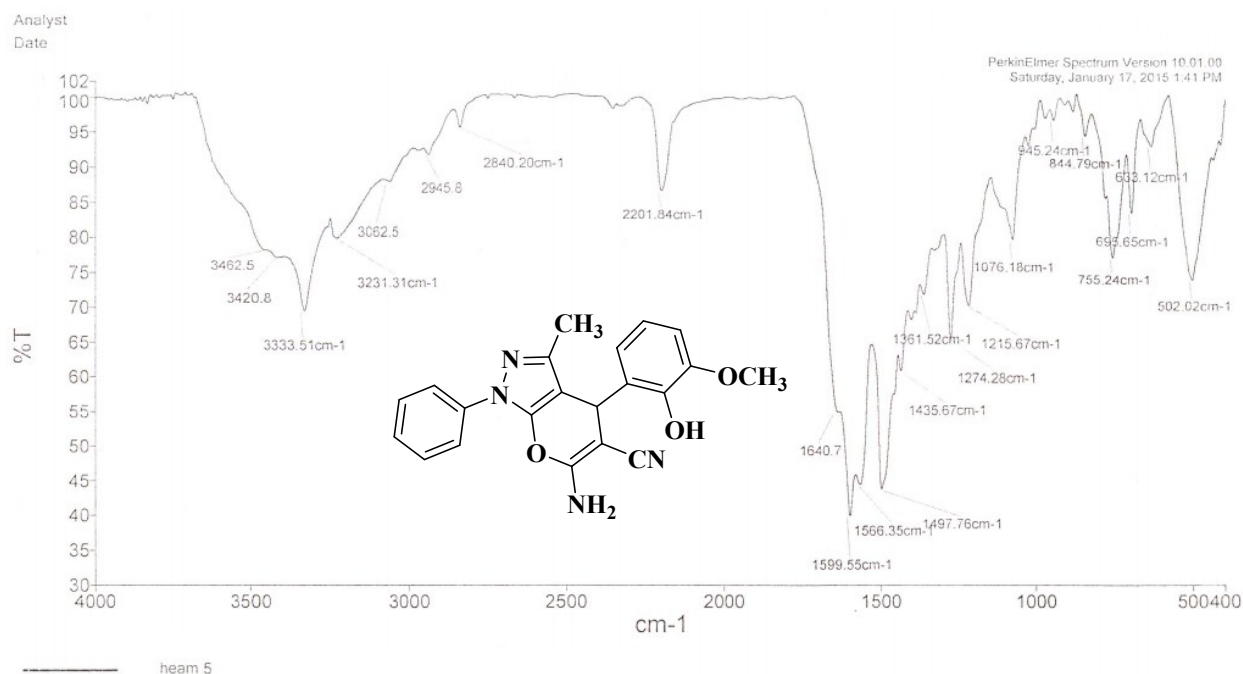


Fig. S61. The ^1H NMR spectrum of 6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 5)

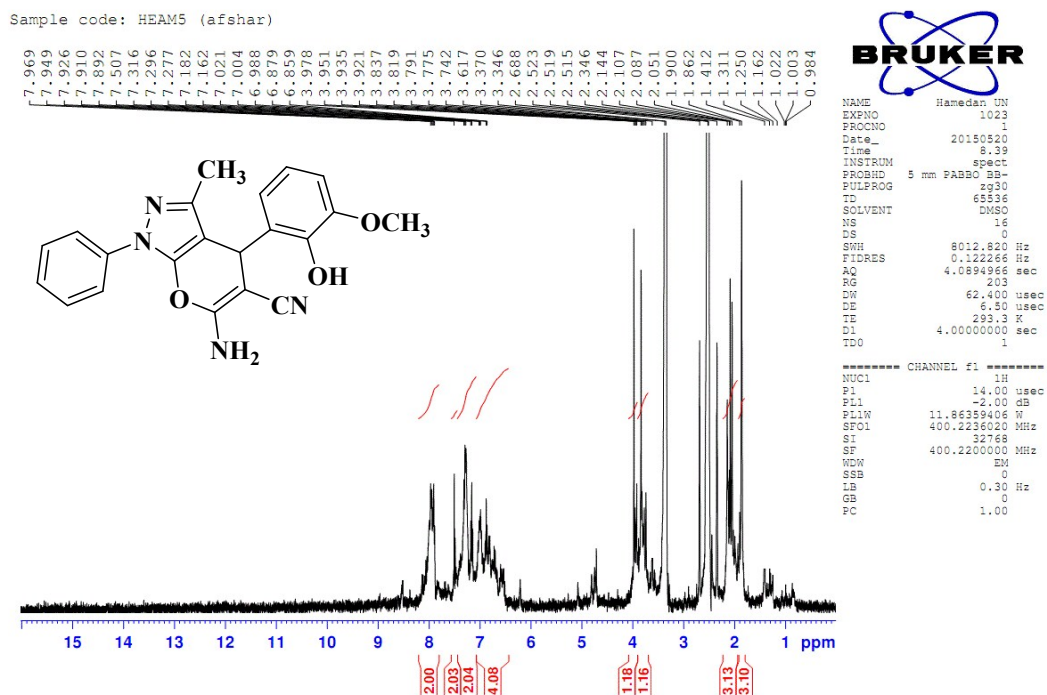


Fig. S62. The ^1H NMR spectrum of 6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 5)

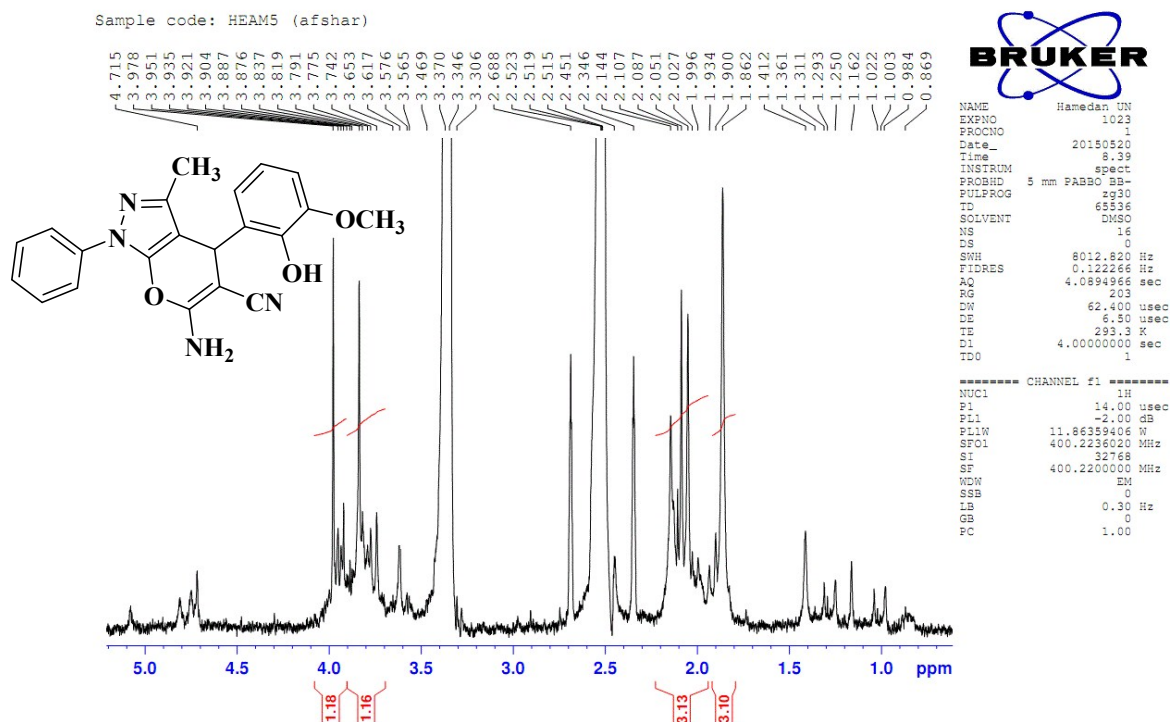


Fig. S63. The ^1H NMR spectrum of 6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 5)

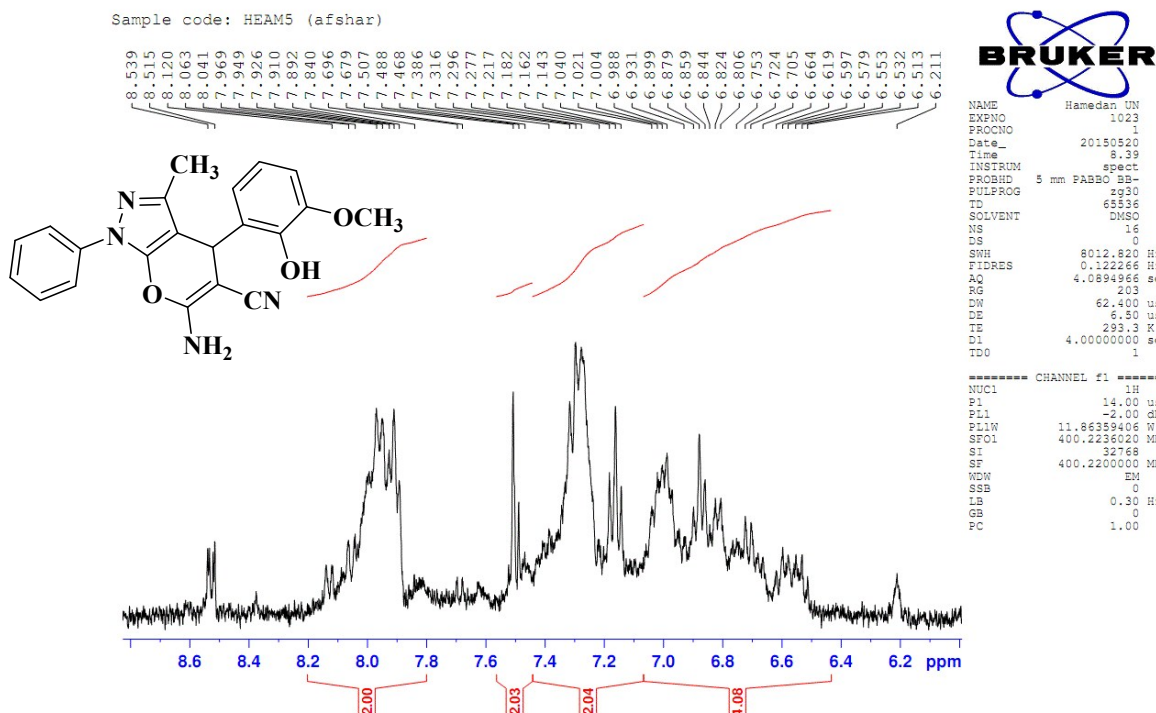


Fig. S64. The ^{13}C NMR spectrum of 6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 5)

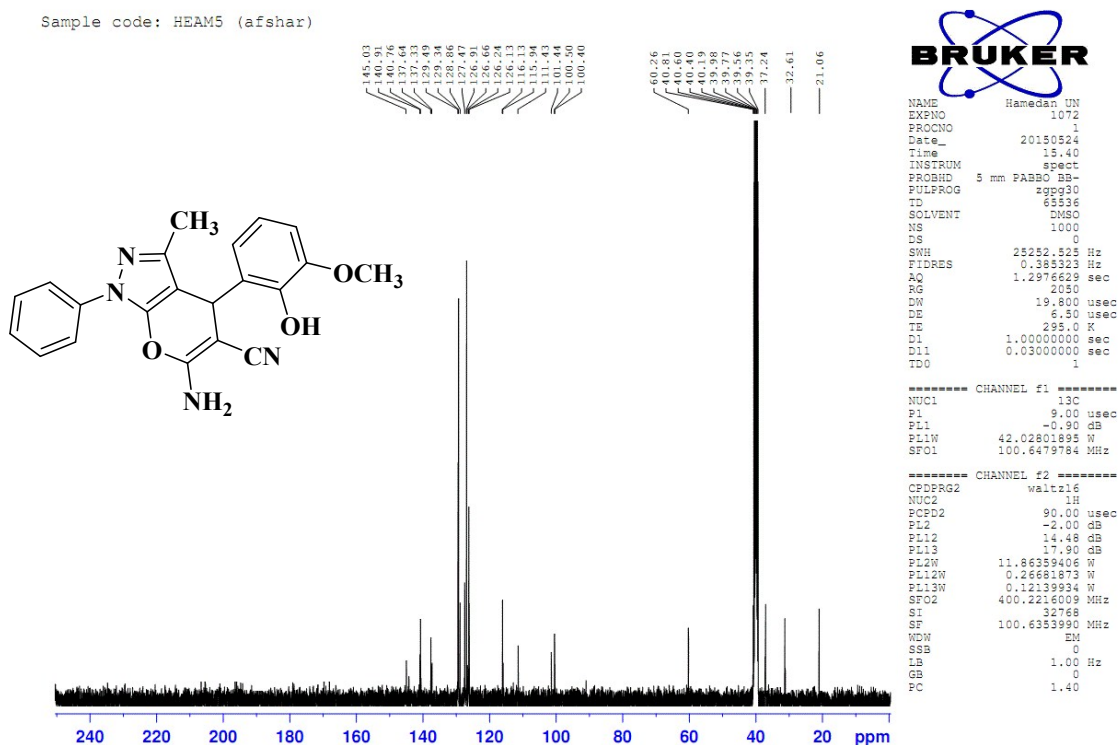


Fig. S65. The ^{13}C NMR spectrum of 6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 5)

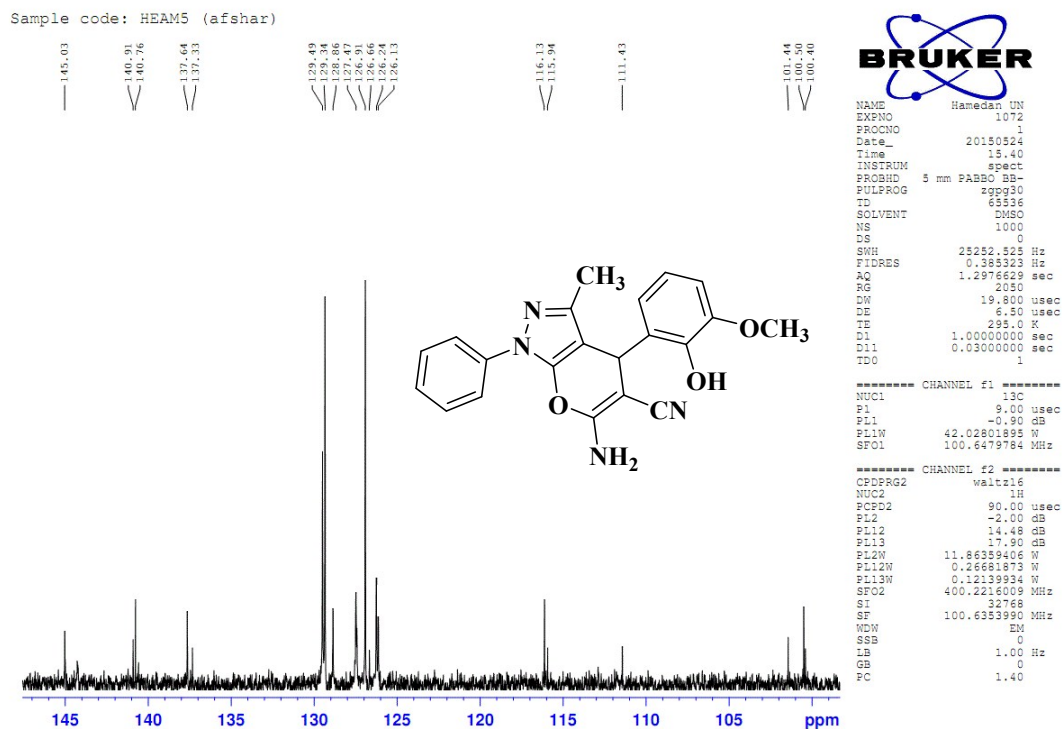


Fig. S66. The IR spectrum of 6-amino-4-(3-ethoxy-4-hydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 6)

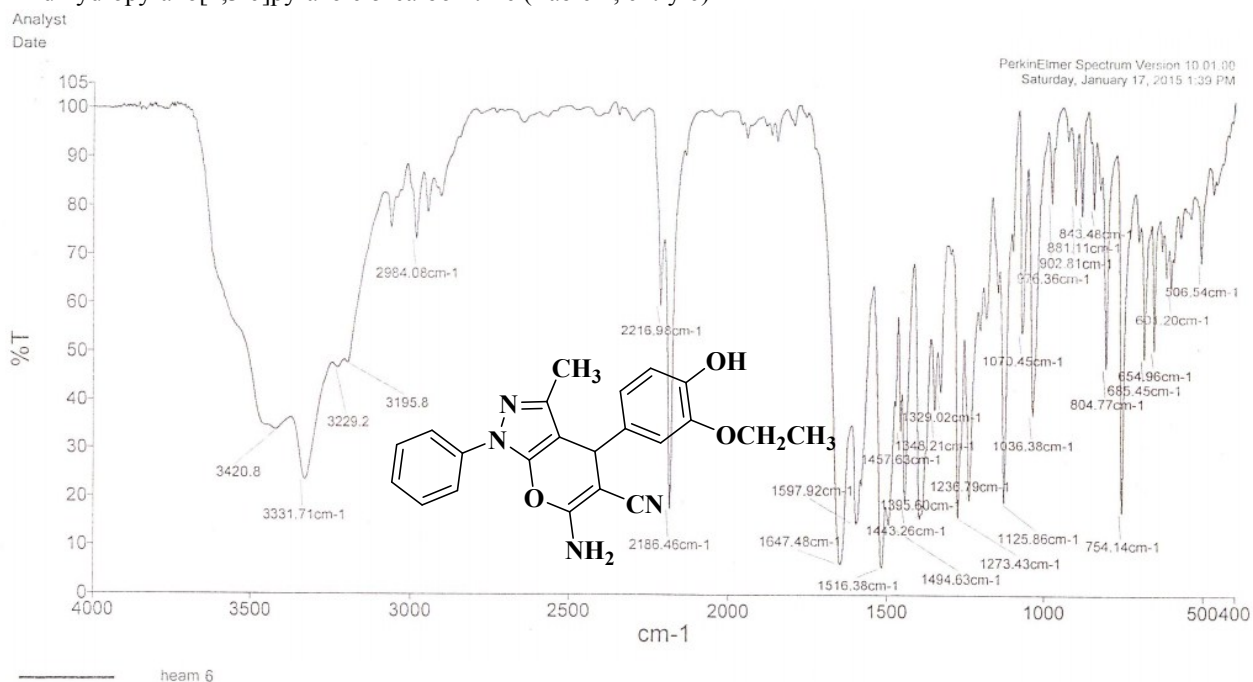


Fig. S67. The ^1H NMR spectrum of 6-amino-4-(3-ethoxy-4-hydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 6)

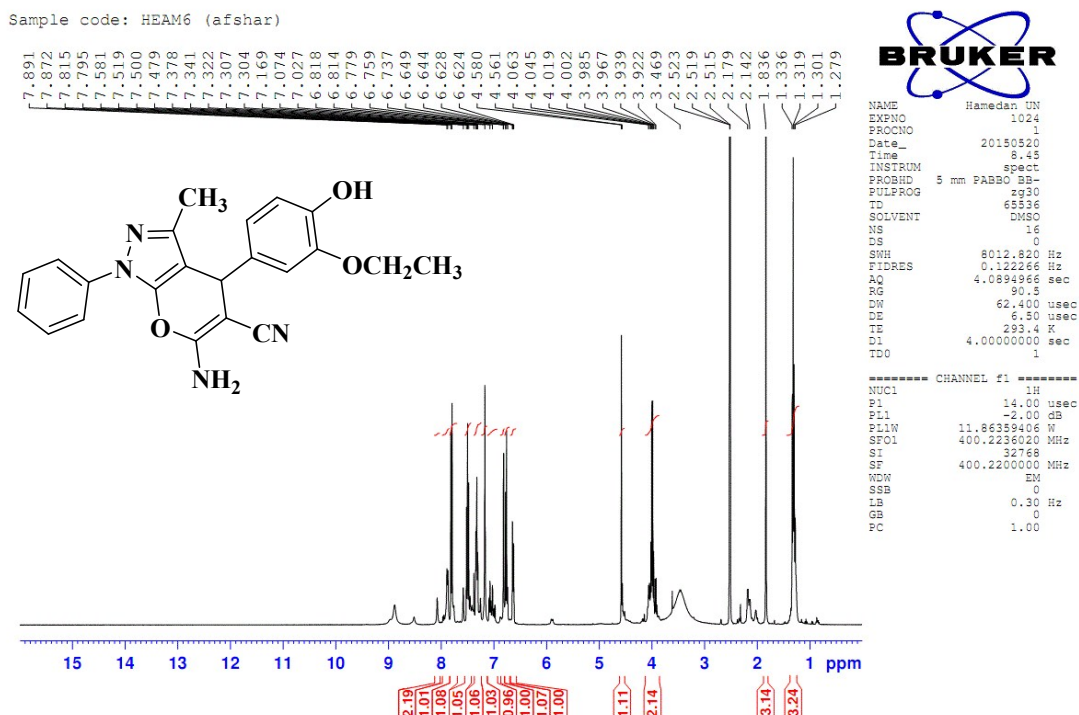


Fig. S68. The ^1H NMR spectrum of 6-amino-4-(3-ethoxy-4-hydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 6)

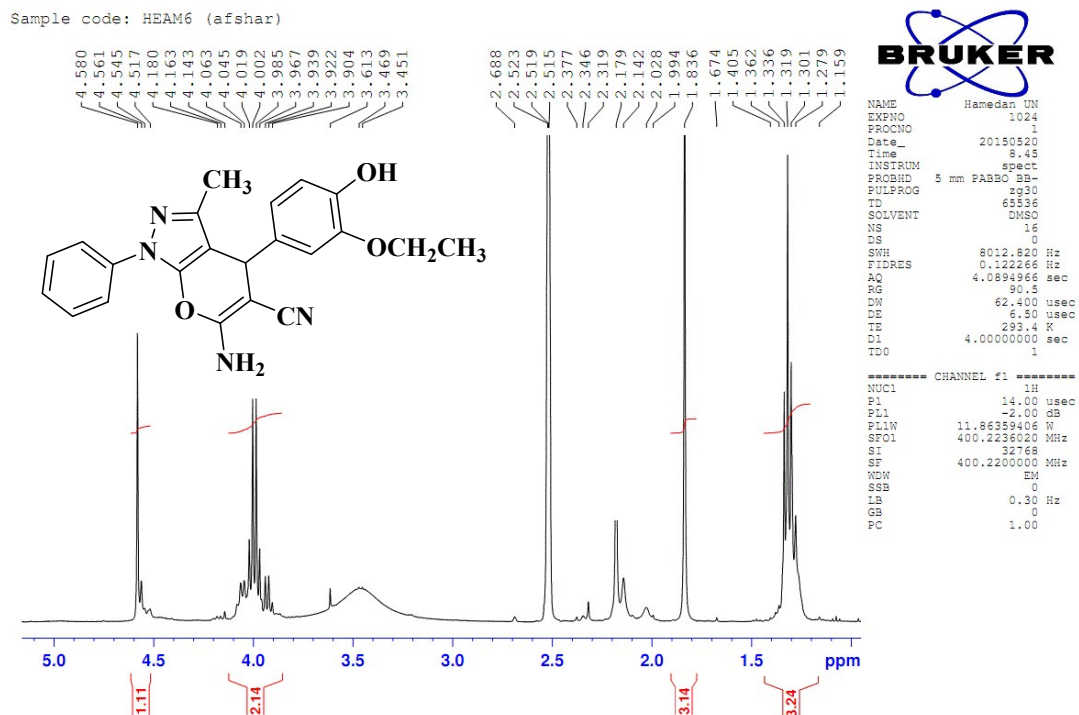


Fig. S69. The ^1H NMR spectrum of 6-amino-4-(3-ethoxy-4-hydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 6)

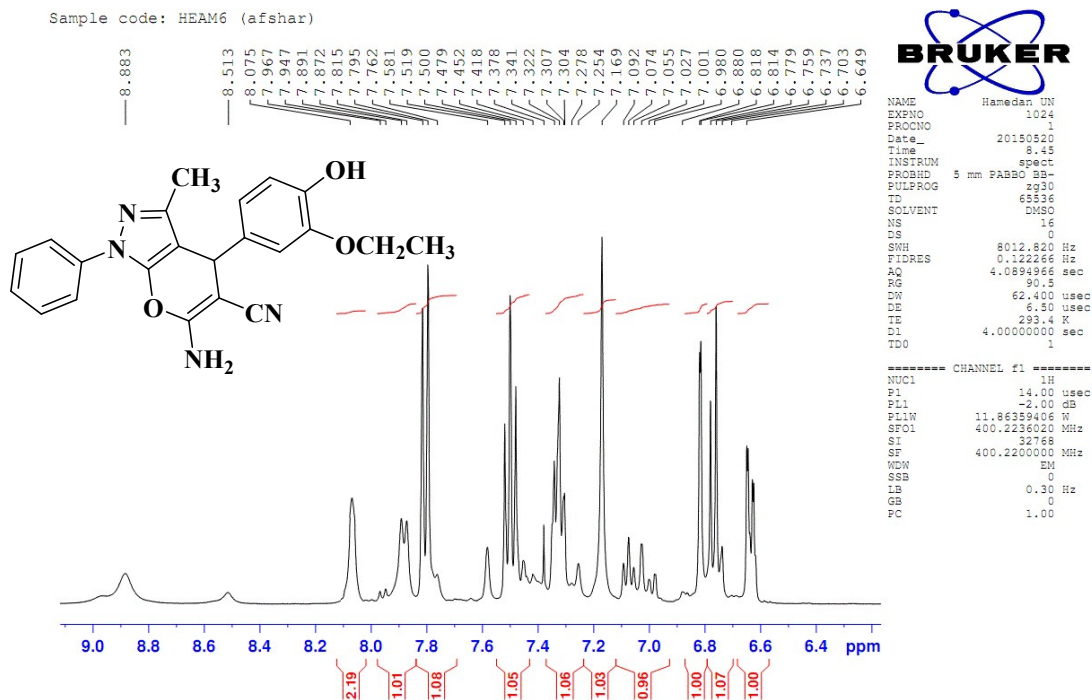


Fig. S70. The ^{13}C NMR spectrum of 6-amino-4-(3-ethoxy-4-hydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 6)

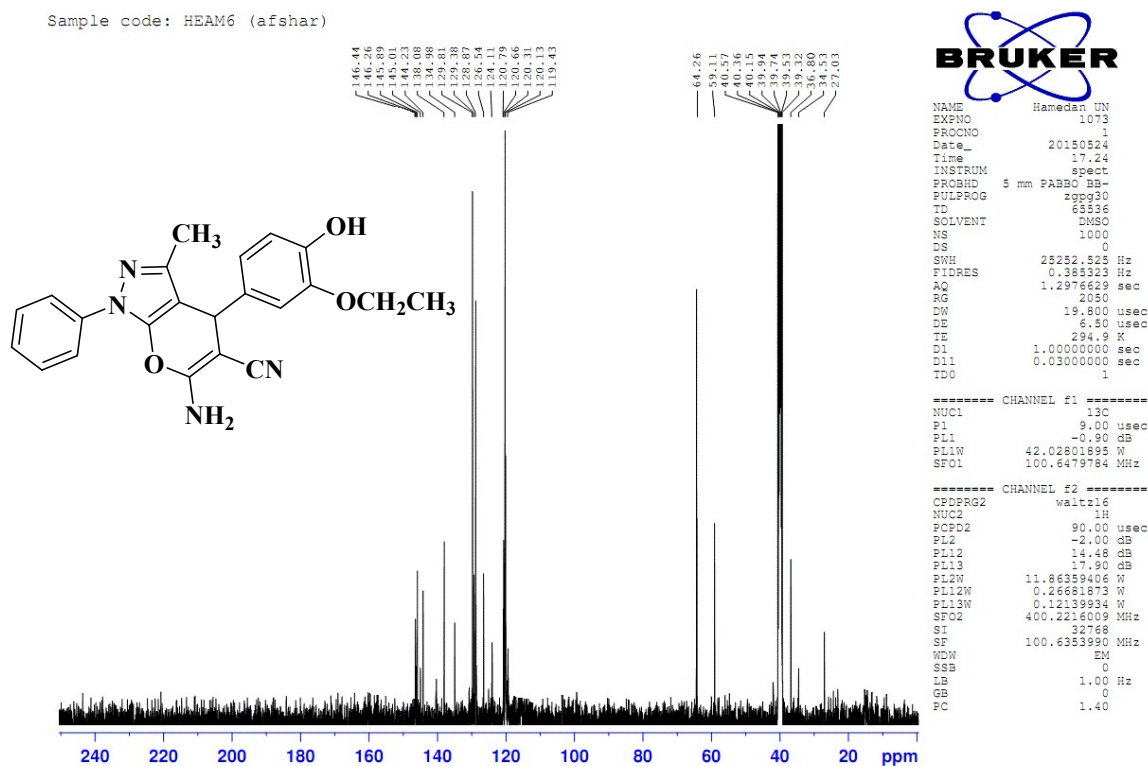


Fig. S71. The ^{13}C NMR spectrum of 6-amino-4-(3-ethoxy-4-hydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 6)

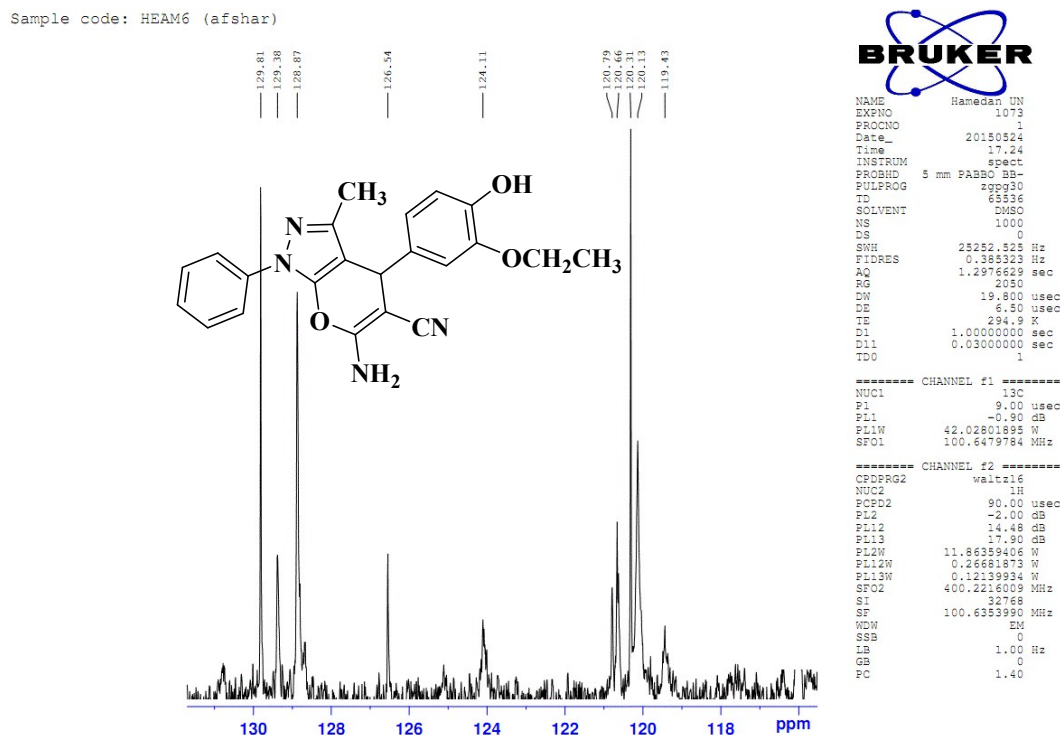


Fig. S72. The ^{13}C NMR spectrum of 6-amino-4-(3-ethoxy-4-hydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 6)

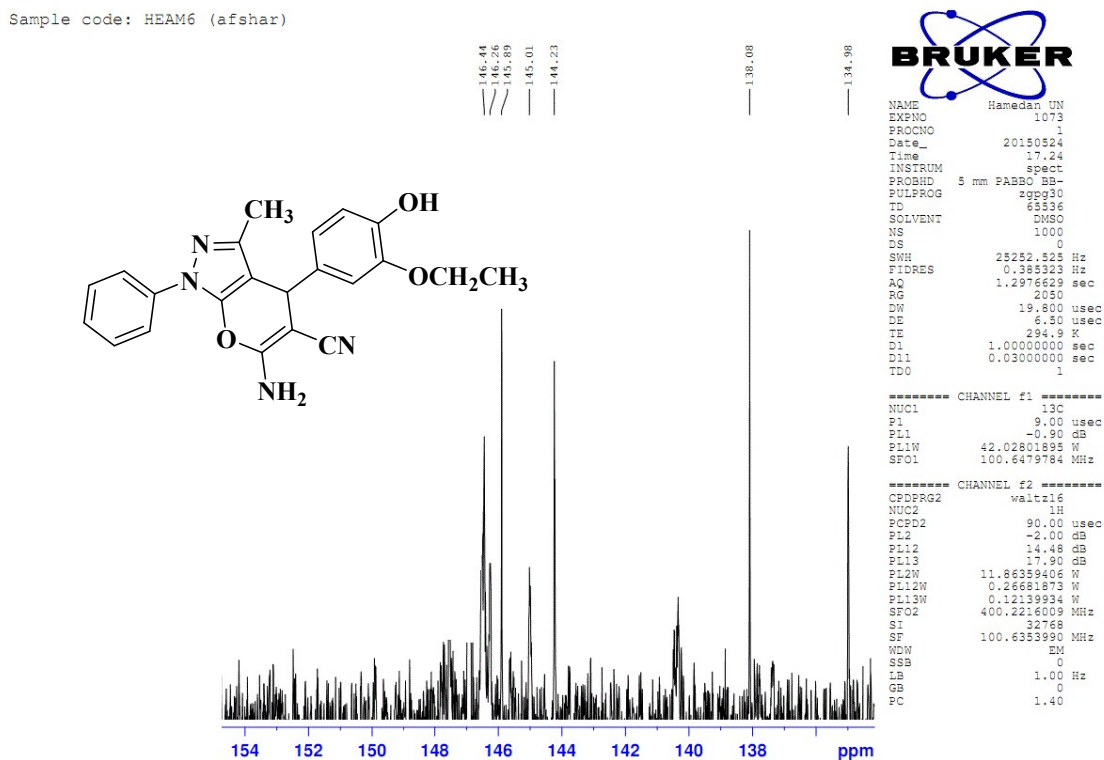


Fig. S73. The IR spectrum of 6-amino-3-methyl-4-(3-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 7)

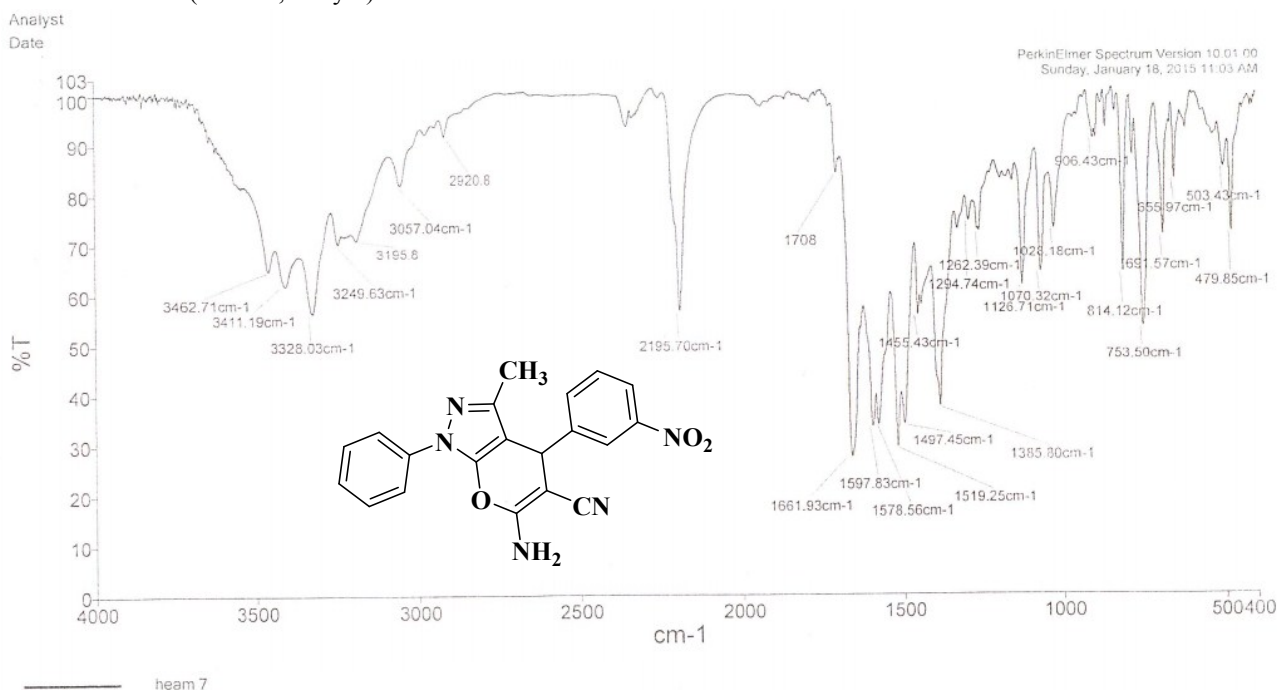


Fig. S74. The ^1H NMR spectrum of 6-amino-3-methyl-4-(3-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 7)

Sample code: HEAM7 (afshar)

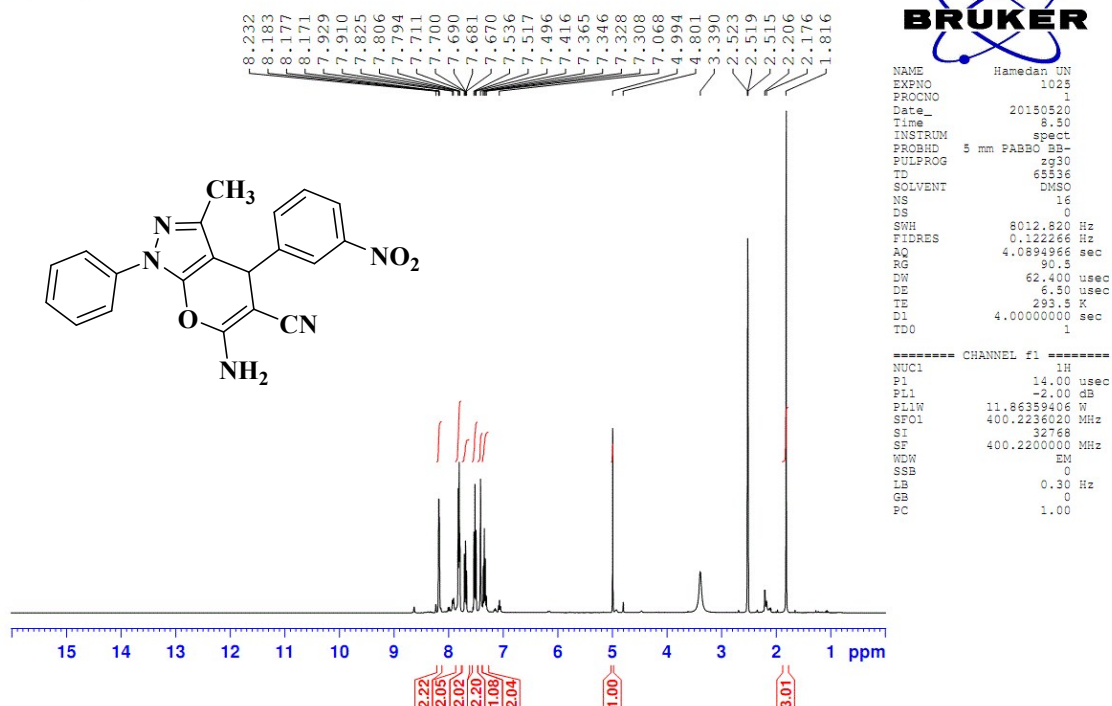


Fig. S75. The ^1H NMR spectrum of 6-amino-3-methyl-4-(3-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 7)

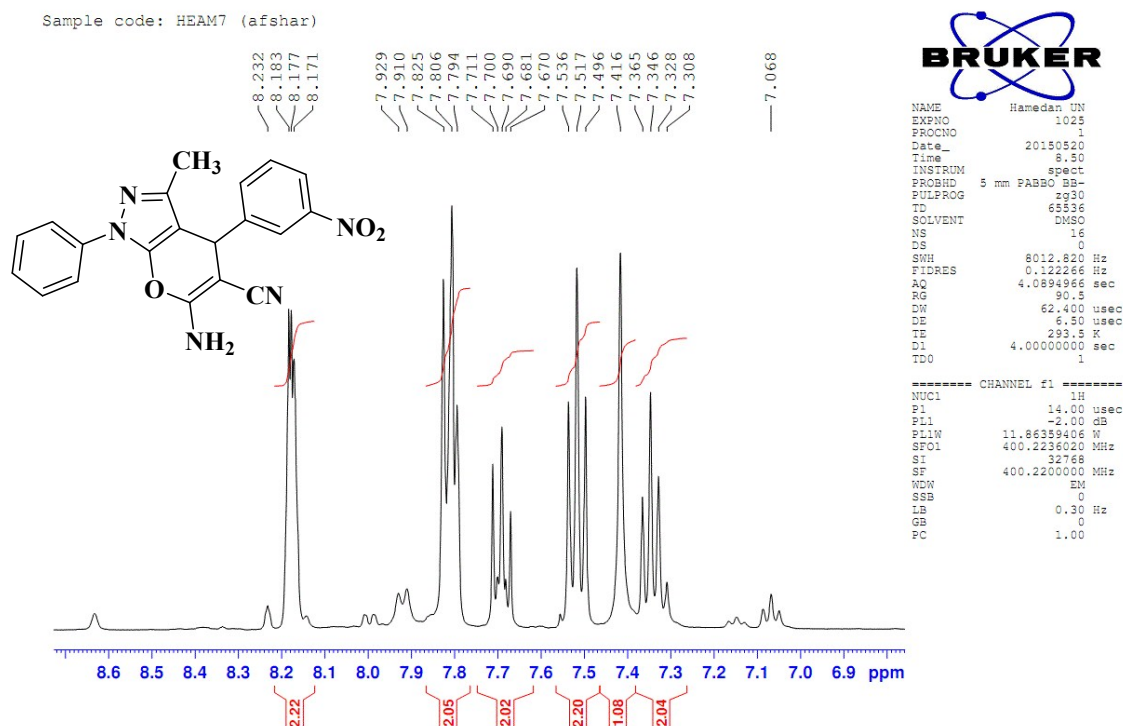


Fig. S76. The ^{13}C NMR spectrum of 6-amino-3-methyl-4-(3-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 7)

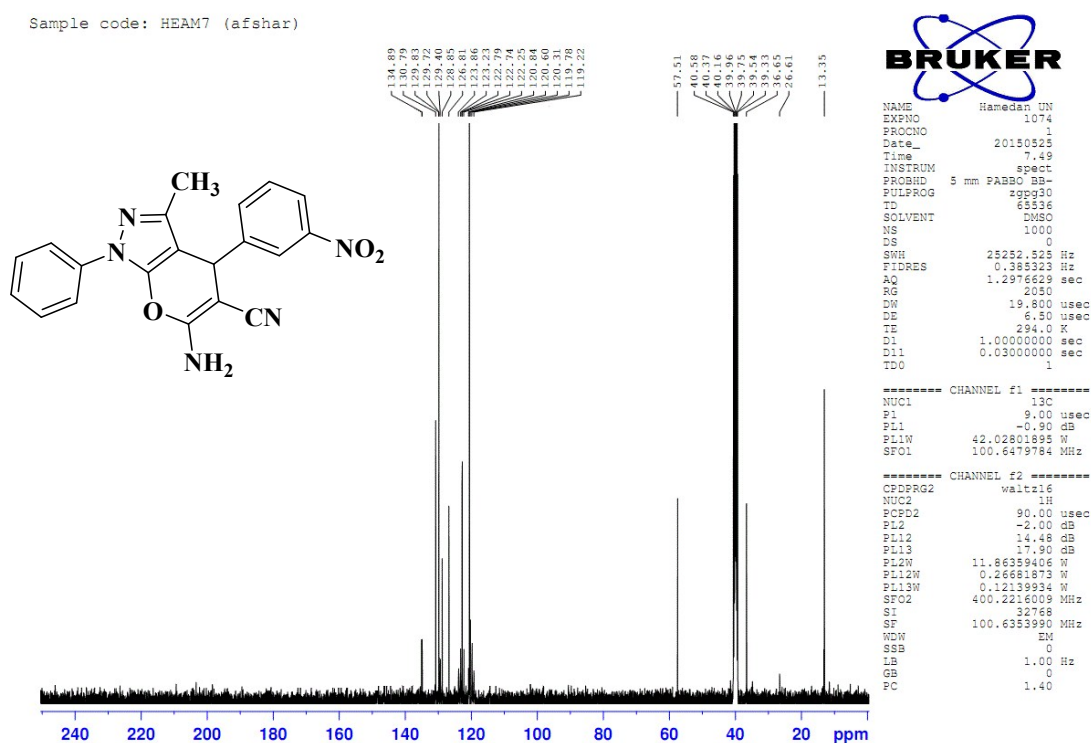


Fig. S77. The ^{13}C NMR spectrum of 6-amino-3-methyl-4-(3-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 7)

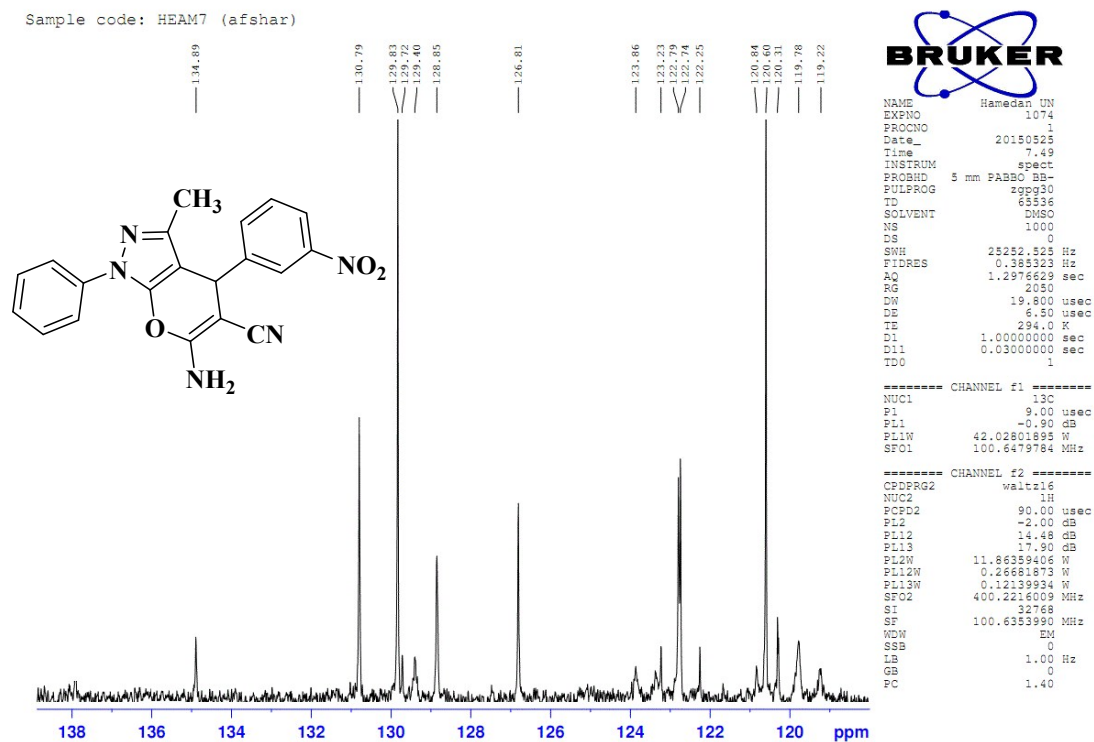


Fig. S78. The IR spectrum of 6-amino-3-methyl-4-(naphthalen-2-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 9)

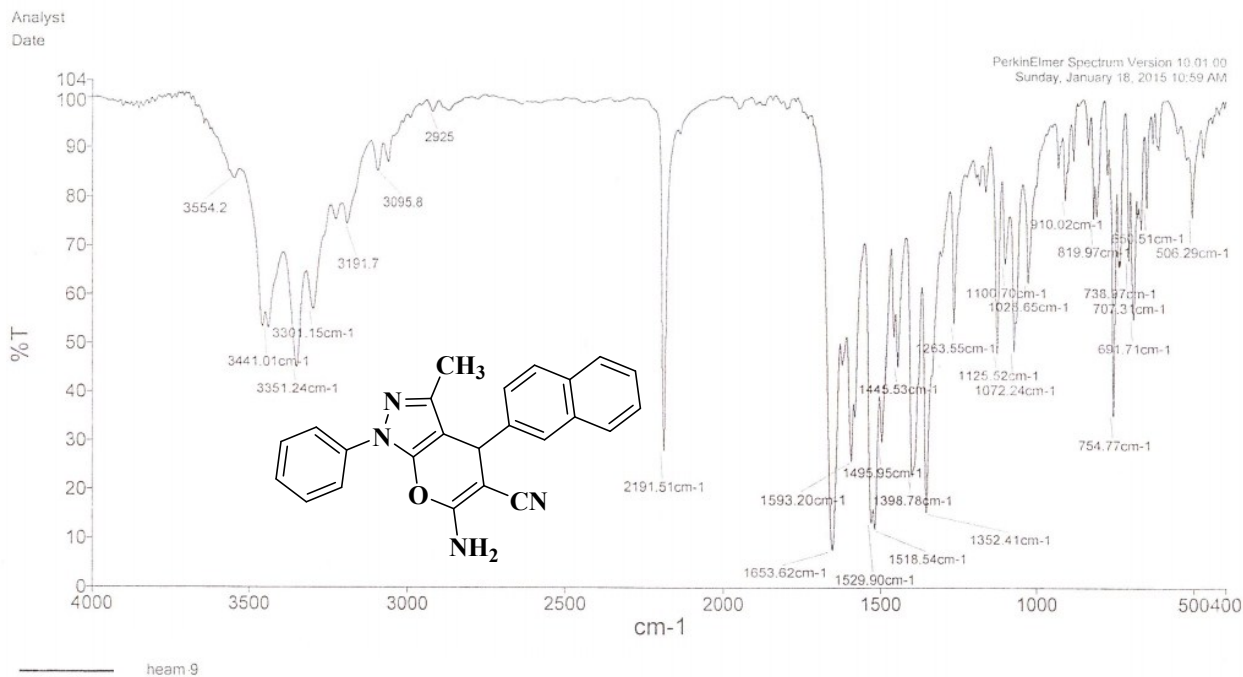


Fig. S79. The ^1H NMR spectrum of 6-amino-3-methyl-4-(naphthalen-2-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 9)

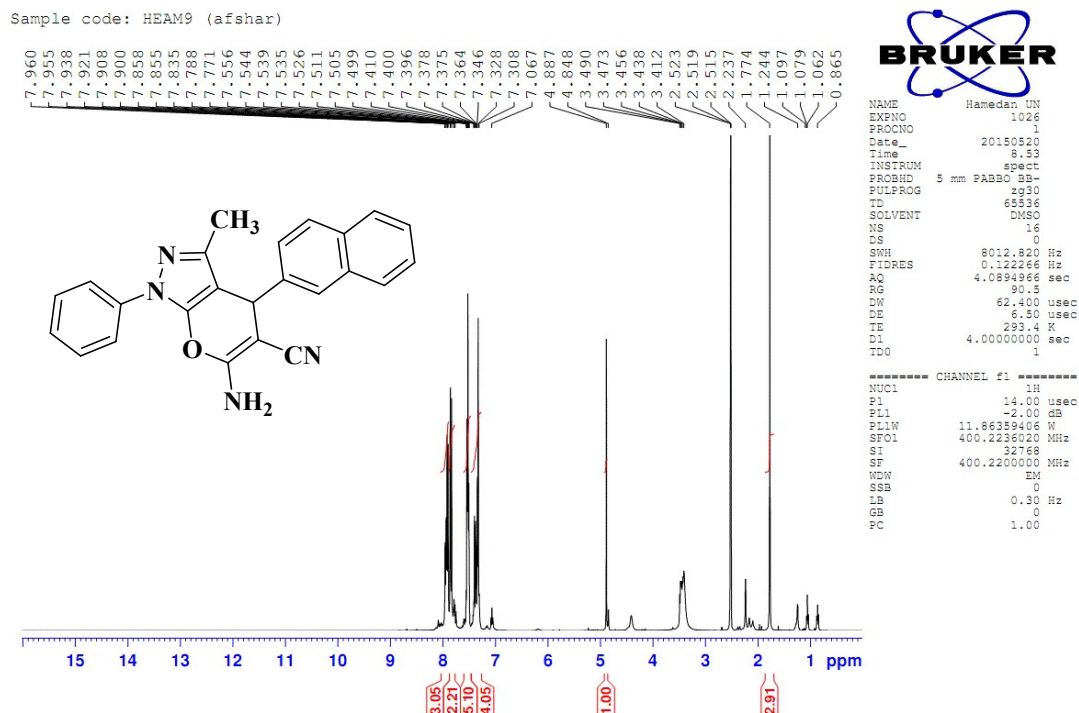


Fig. S80. The ^1H NMR spectrum of 6-amino-3-methyl-4-(naphthalen-2-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 9)

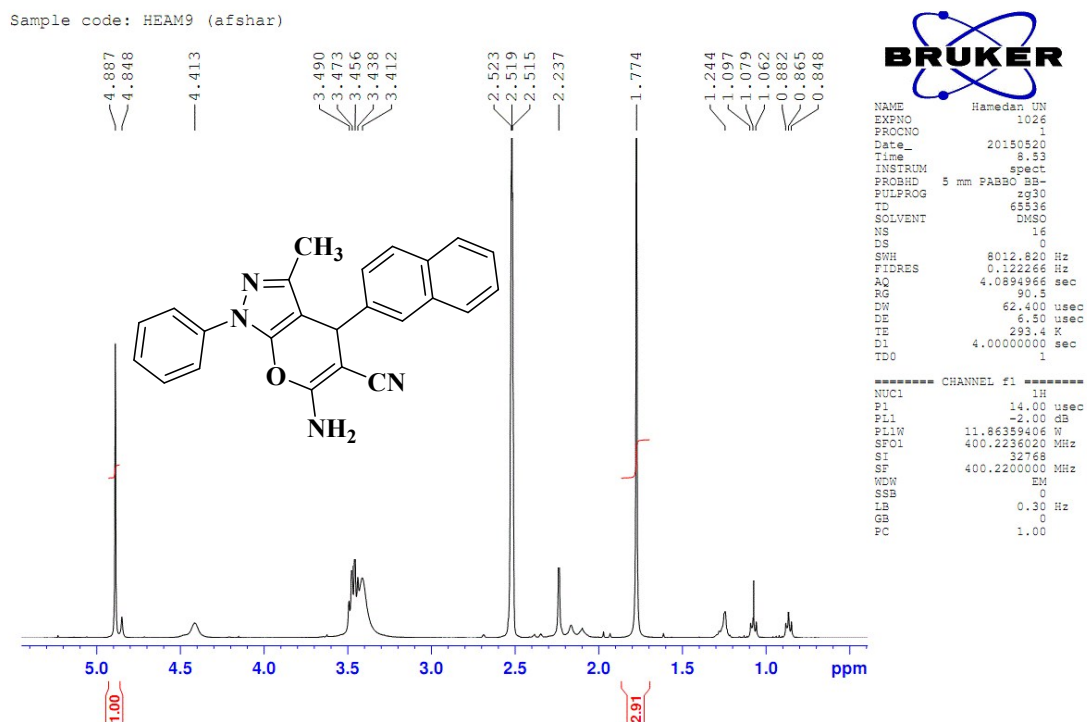


Fig. S81. The ^1H NMR spectrum of 6-amino-3-methyl-4-(naphthalen-2-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 9)

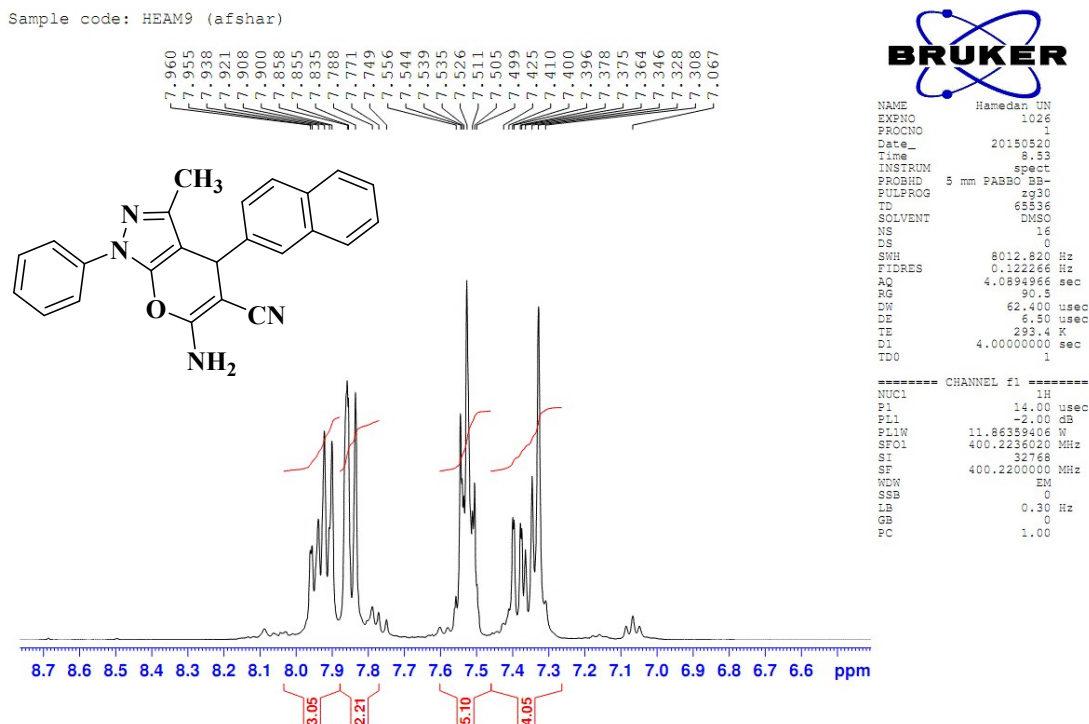


Fig. S82. The ^{13}C NMR spectrum of 6-amino-3-methyl-4-(naphthalen-2-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 9)

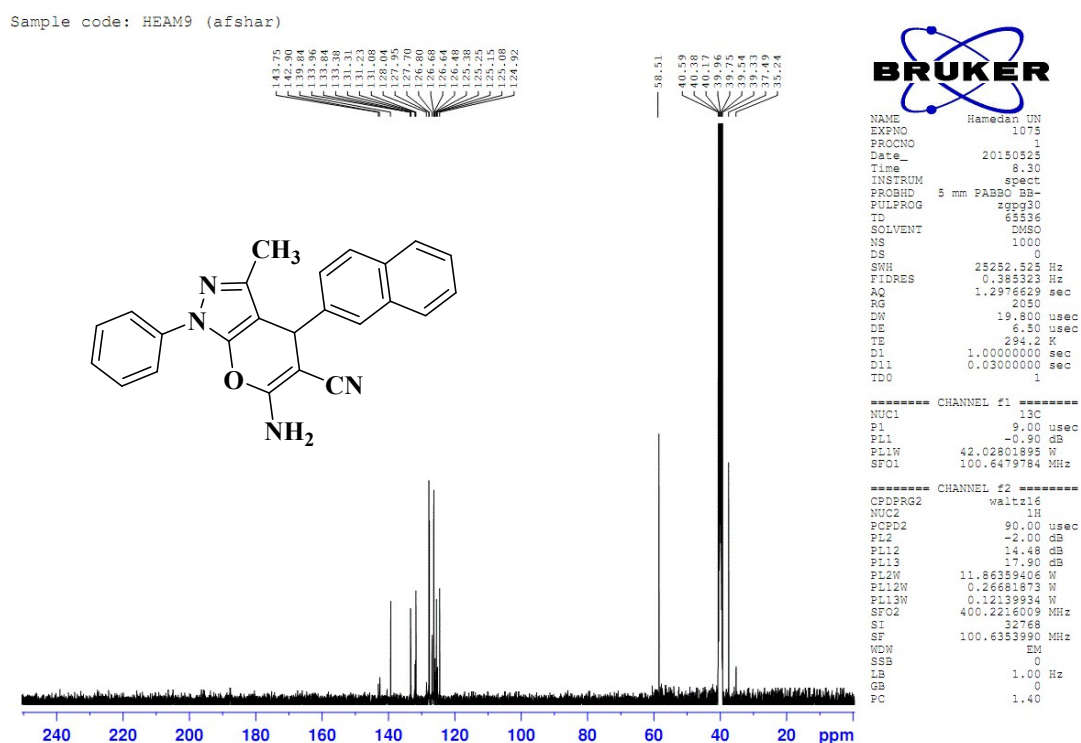


Fig. S83. The ^{13}C NMR spectrum of 6-amino-3-methyl-4-(naphthalen-2-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 9)

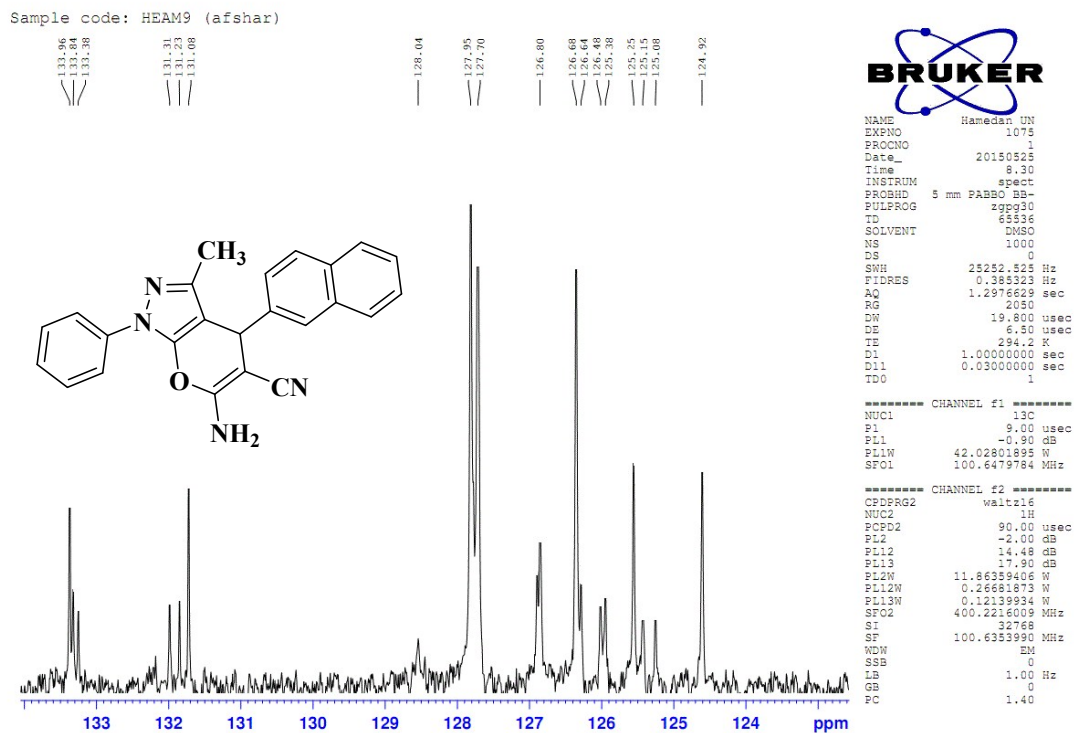


Fig. S84. The IR spectrum of 6-amino-4-(3,4-dihydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 10)

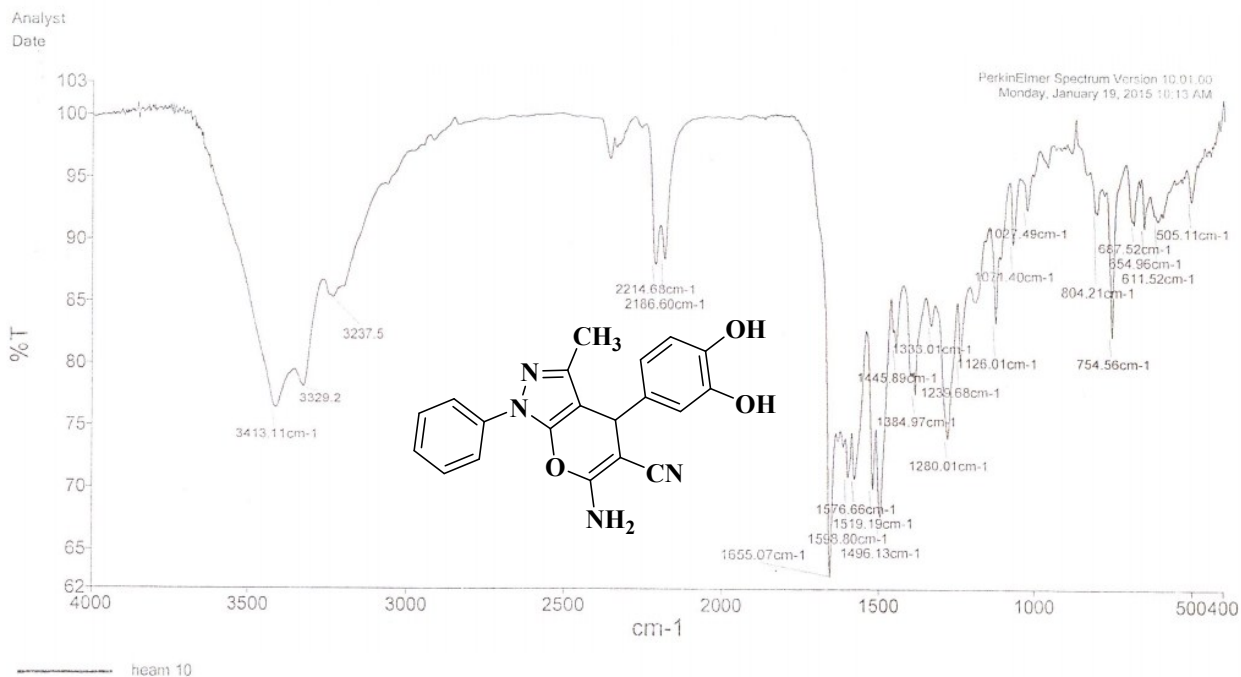


Fig. S85. The ^1H NMR spectrum of 6-amino-4-(3,4-dihydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 10)

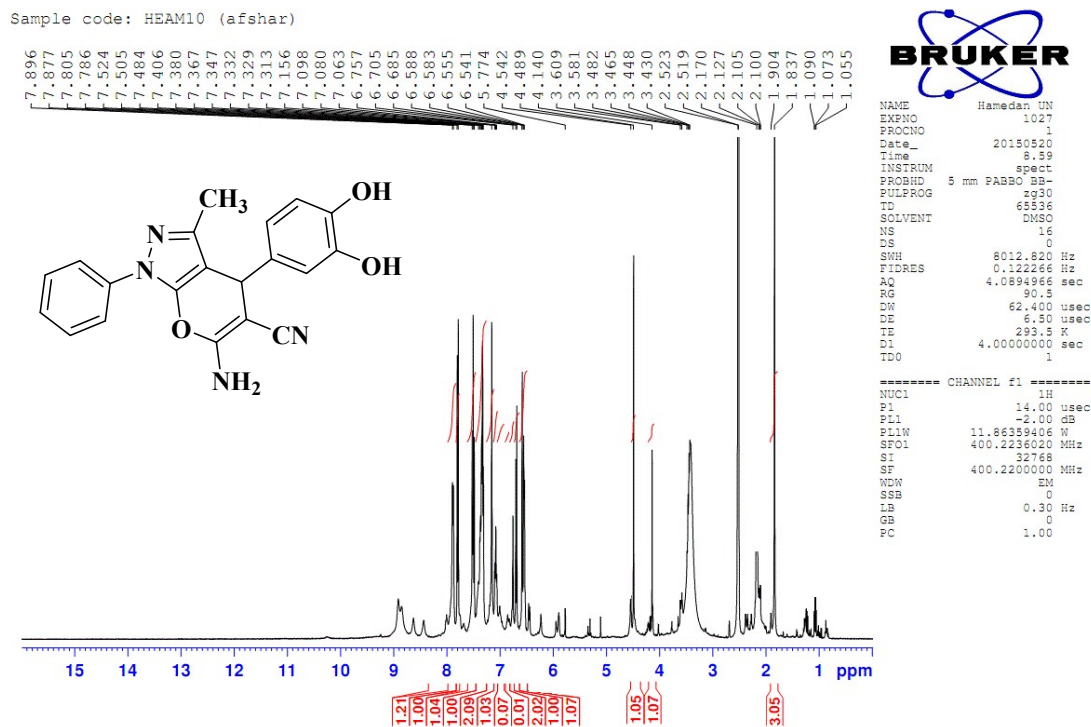


Fig. S86. The ^1H NMR spectrum of 6-amino-4-(3,4-dihydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 10)

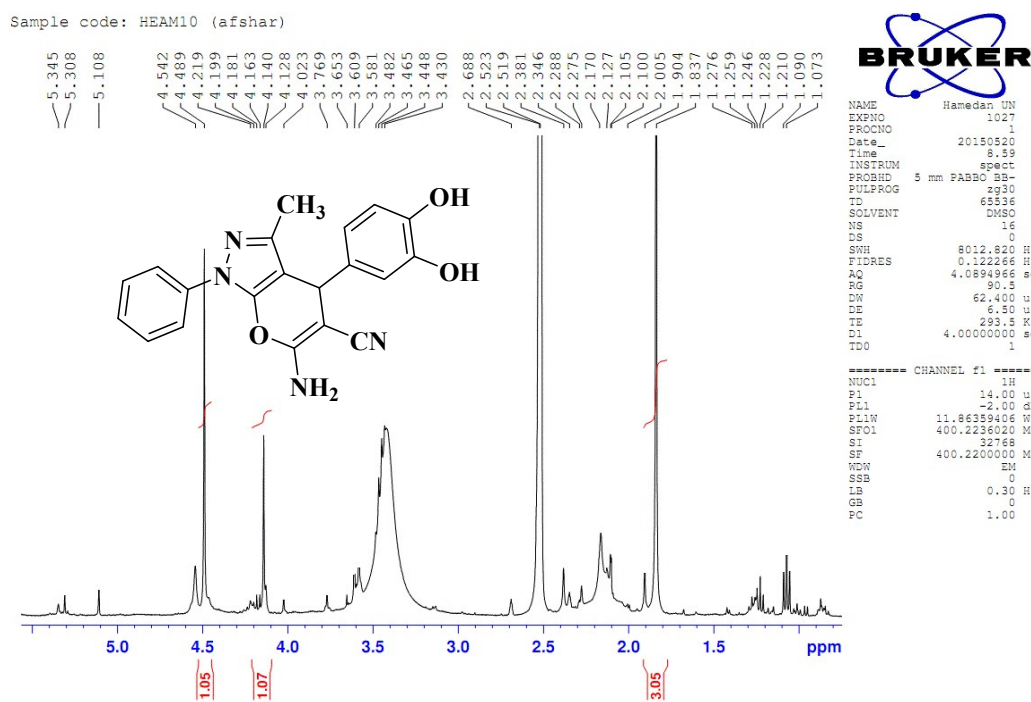


Fig. S87. The ^1H NMR spectrum of 6-amino-4-(3,4-dihydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 10)

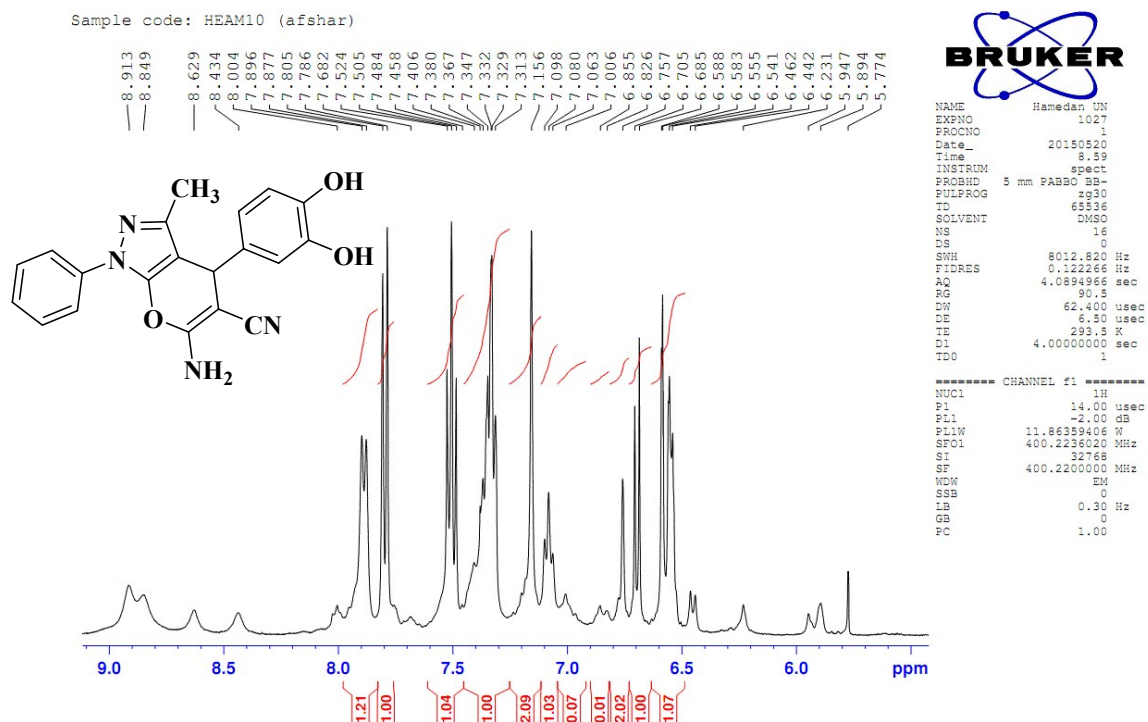


Fig. S88. The ^{13}C NMR spectrum of 6-amino-4-(3,4-dihydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 10)

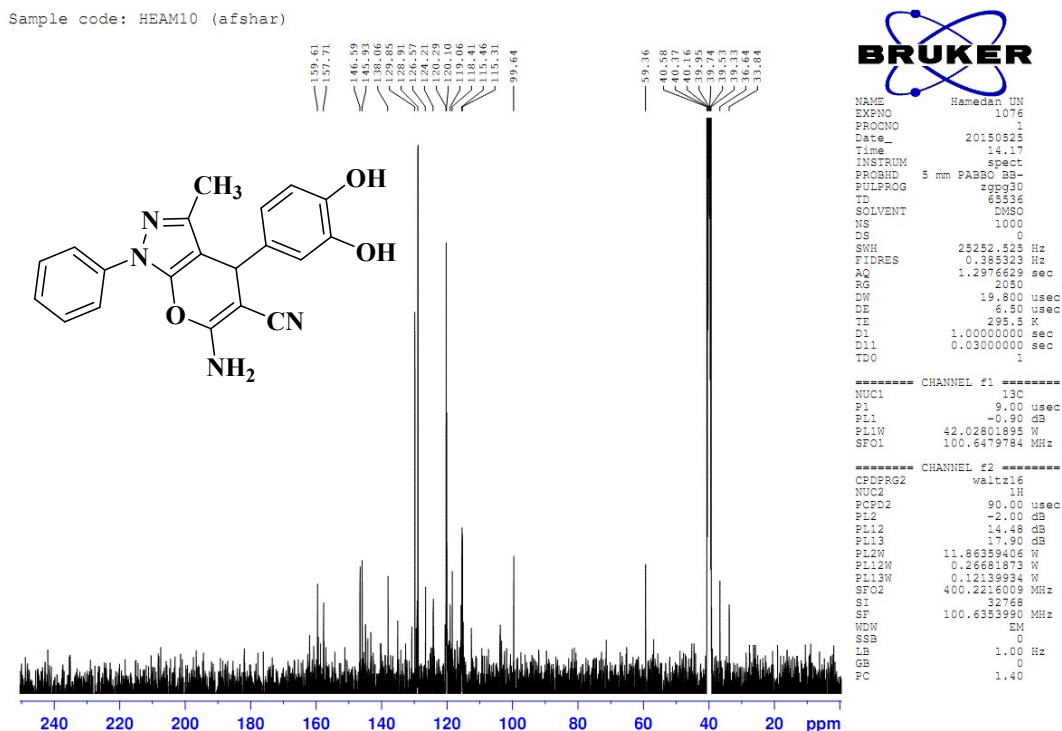


Fig. S89. The ^{13}C NMR spectrum of 6-amino-4-(3,4-dihydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 10)

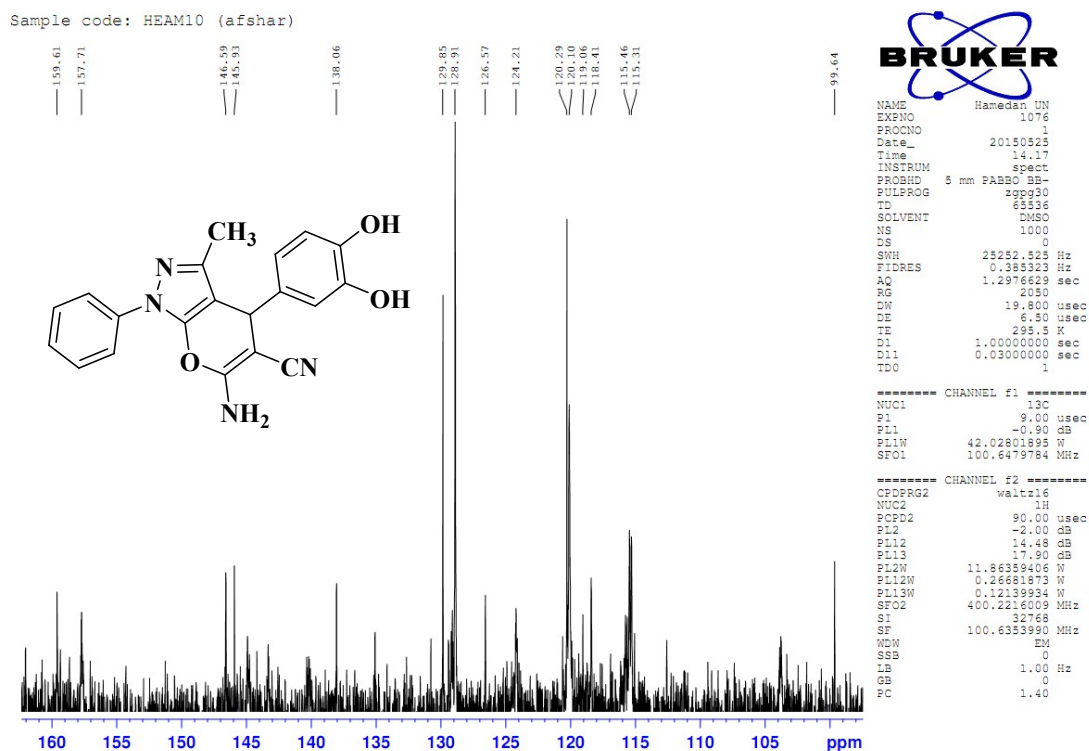


Fig. S90. The IR spectrum of 6-amino-3-methyl-1-phenyl-4-(pyridin-4-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 12)

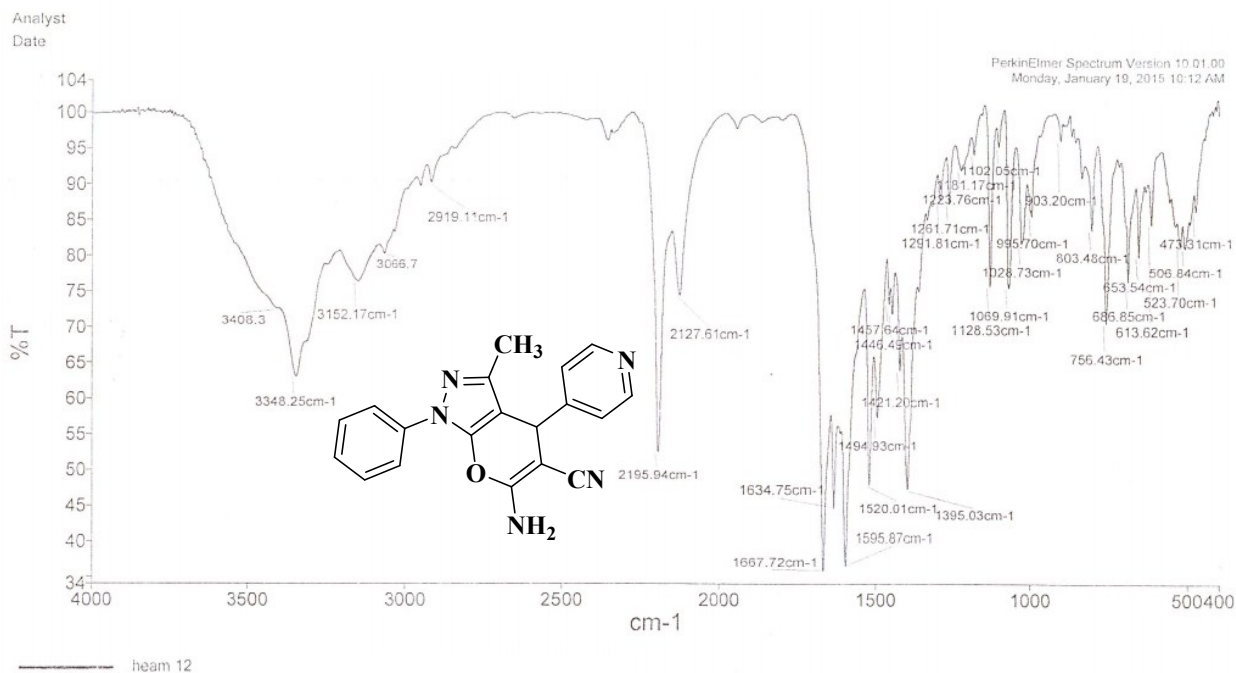


Fig. S91. The ^1H NMR spectrum of 6-amino-3-methyl-1-phenyl-4-(pyridin-4-yl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (Table 4, entry 12)

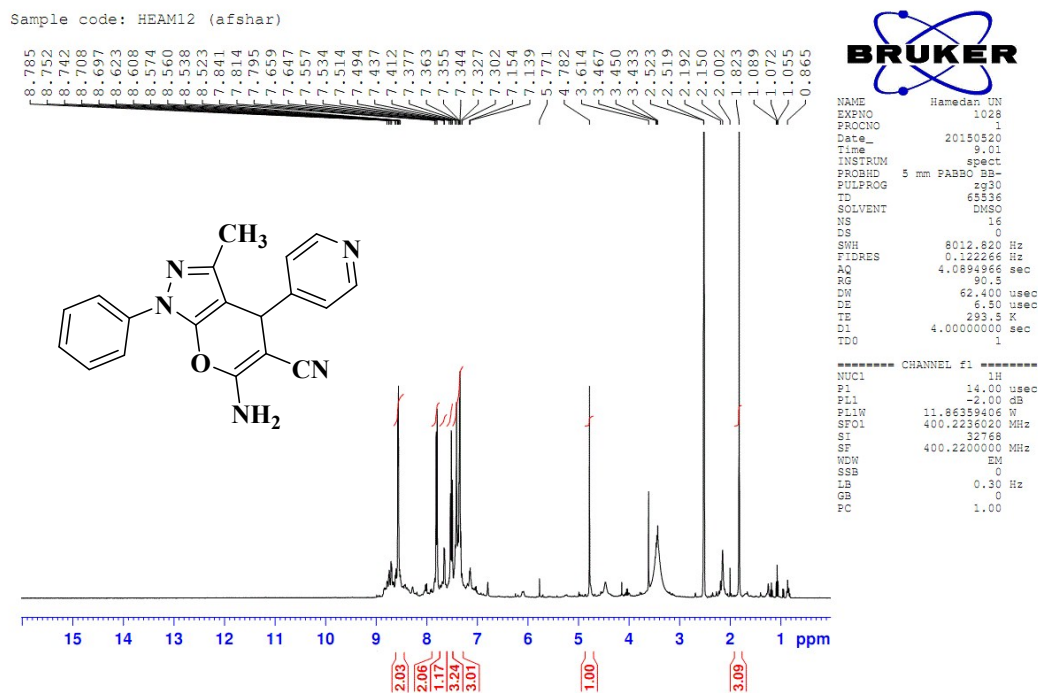


Fig. S92. The ^1H NMR spectrum of 6-amino-3-methyl-1-phenyl-4-(pyridin-4-yl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (Table 4, entry 12)

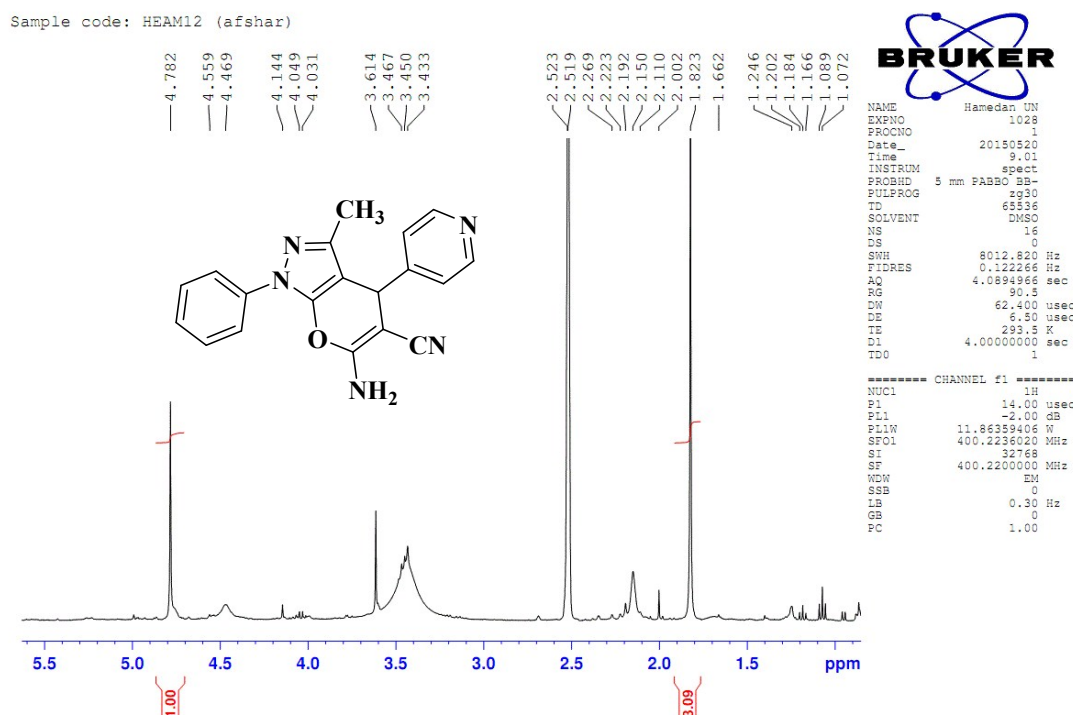


Fig. S93. The ^1H NMR spectrum of 6-amino-3-methyl-1-phenyl-4-(pyridin-4-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 12)

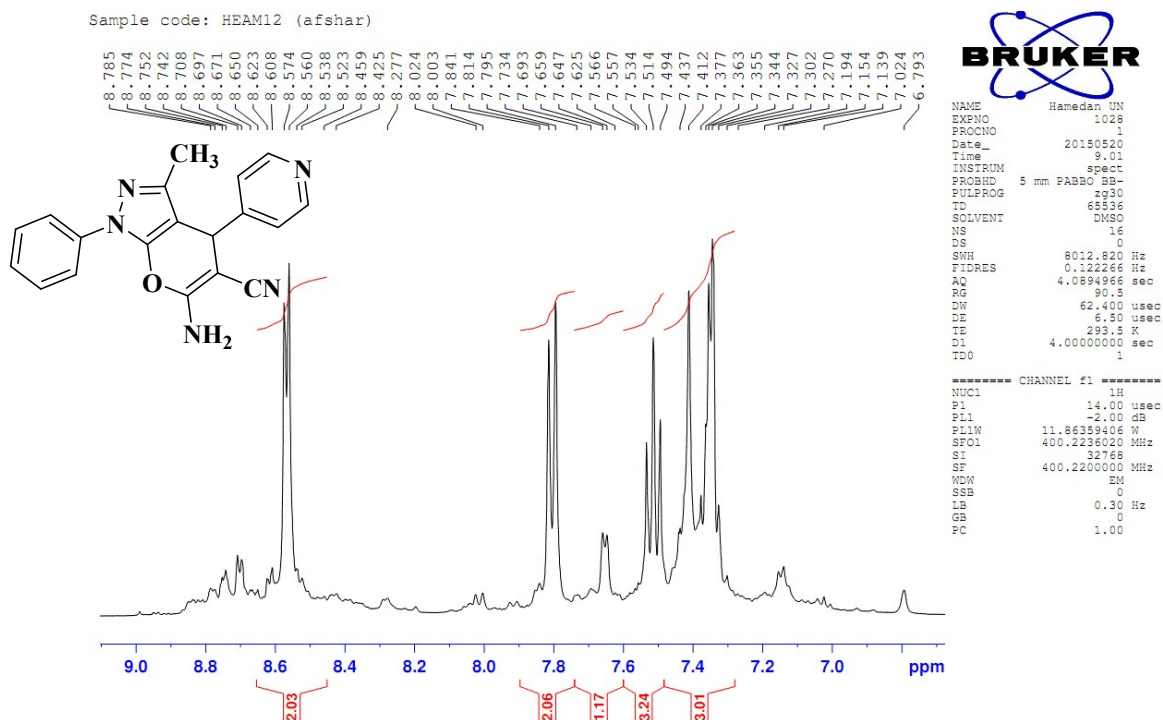


Fig. S94. The ^{13}C NMR spectrum of 6-amino-3-methyl-1-phenyl-4-(pyridin-4-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 12)

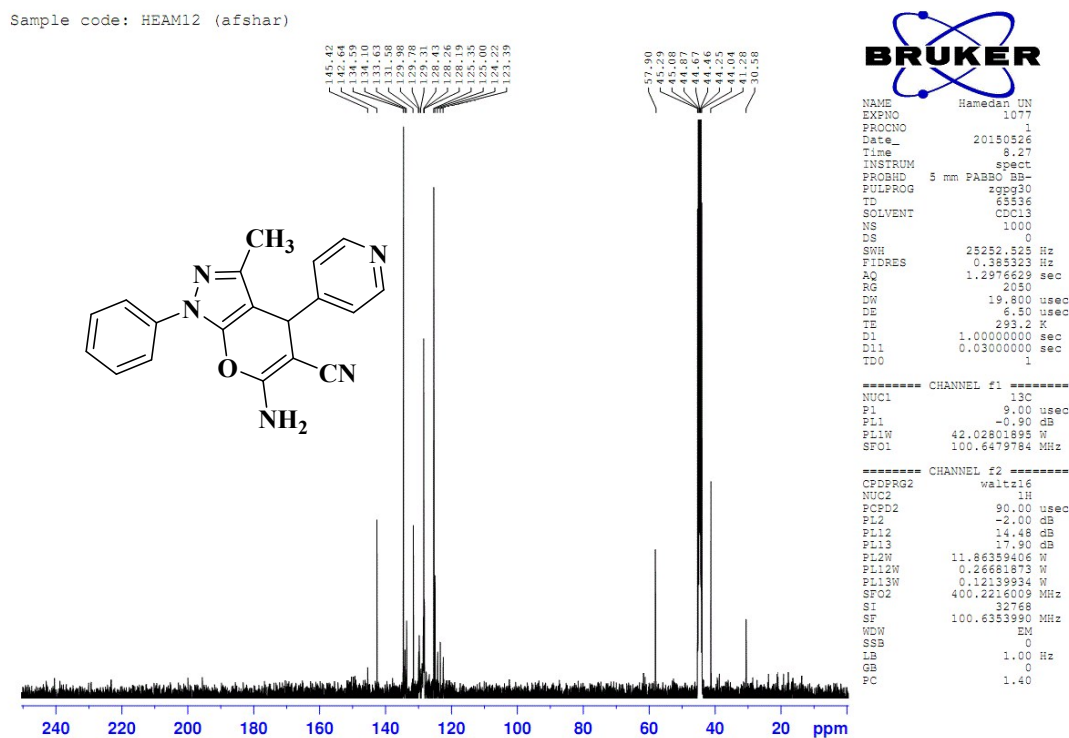


Fig. S95. The ^{13}C NMR spectrum of 6-amino-3-methyl-1-phenyl-4-(pyridin-4-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 12)

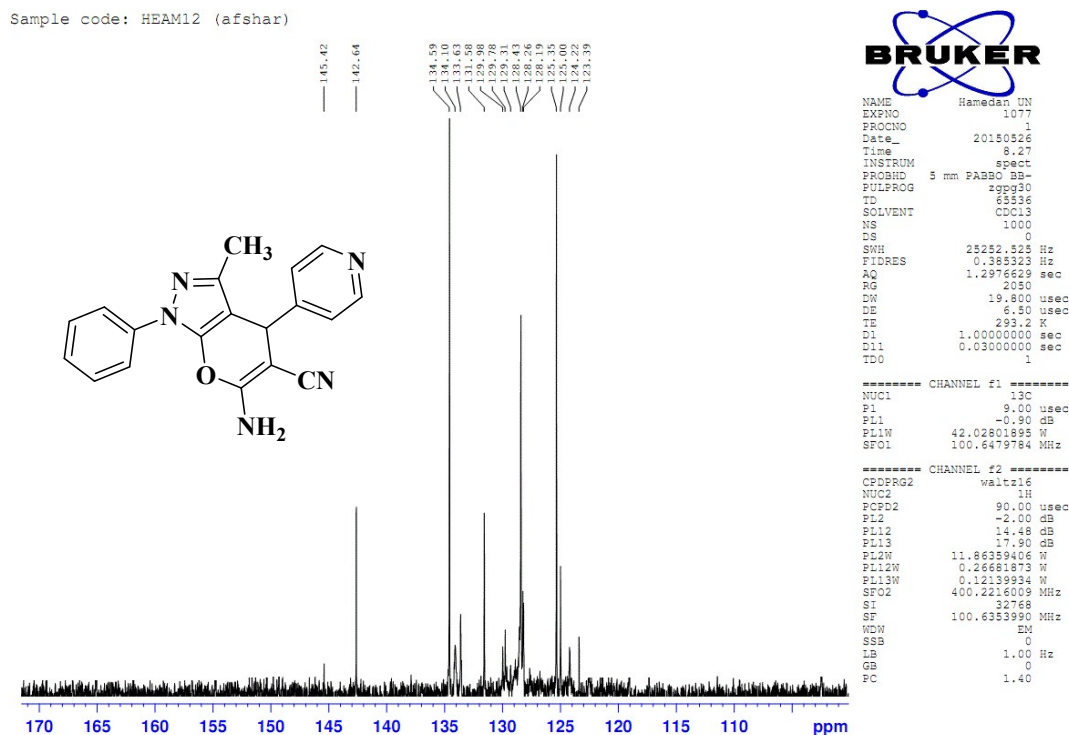


Fig. S96. The ^{13}C NMR spectrum of 6-amino-3-methyl-1-phenyl-4-(pyridin-4-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (Table 4, entry 12)

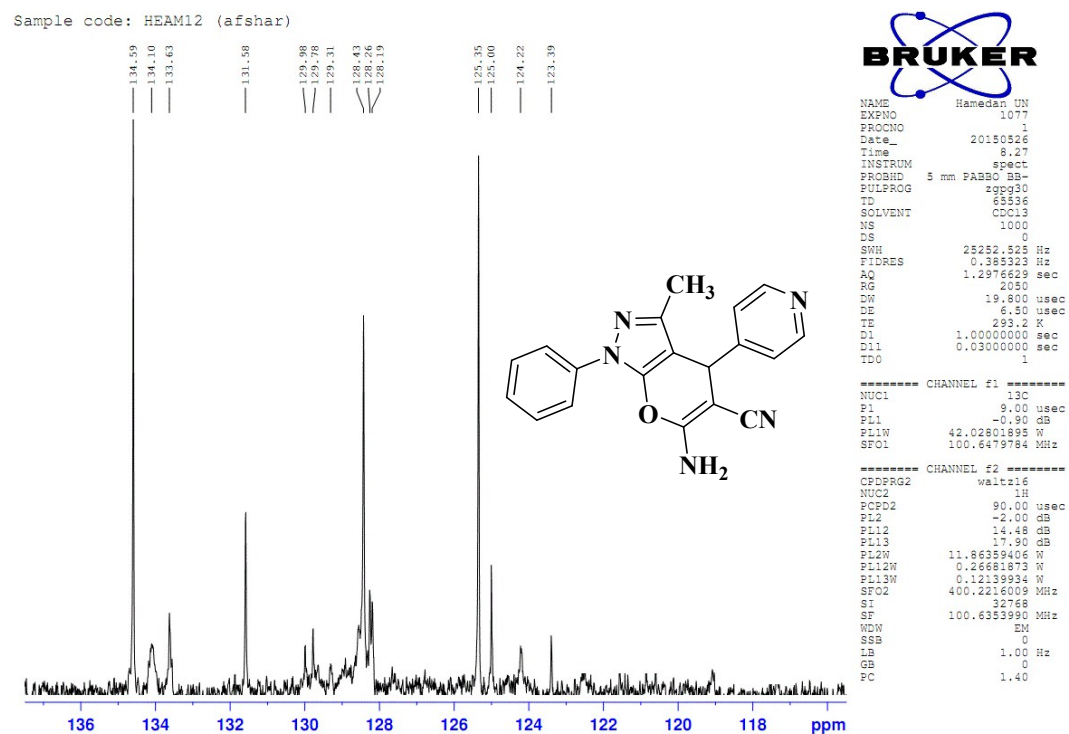


Fig. S97. The ^1H NMR spectrum of $\text{DMSO-}d_6$ with high intensity

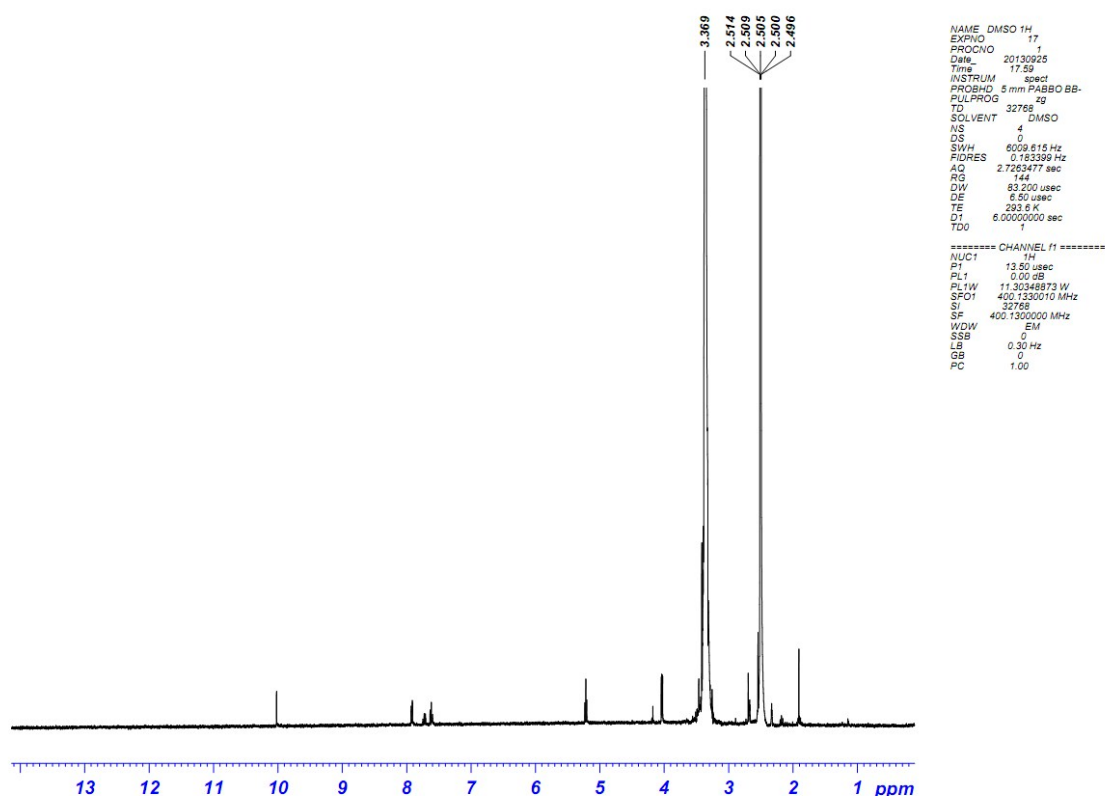


Fig. S98. The suggested mechanism for the in-situ oxidation-reduction in Cannizzaro reaction through unusual hydride transfer *via* anomeric effect.³⁸

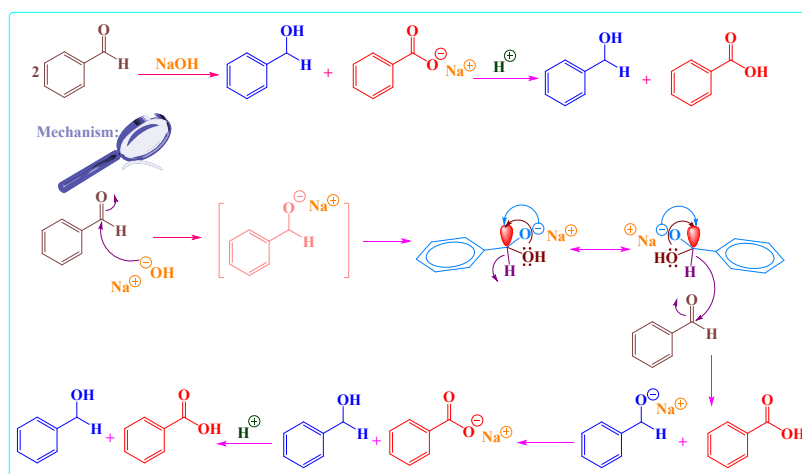


Table S1. Electronic energy, zero point energy and corrected electronic energy at B3LYP/TZVP level of theory.

Compounds	E _{el}	ZPE	E ₀
5	-836.1860291	0.247342	-835.938687
13-cis	-837.3472824	0.270853	-837.076429
13-trans	-837.3506303	0.270885	-837.079746
14-cis	-837.3520203	0.270314	-837.081707
14-trans	-837.3533099	0.270423	-837.082887
15	-1490.3725943	0.299646	-1490.072948
TS	-1491.5012262	0.315863	-1491.185363
H₂	-1.179649	0.010072	-1.169577
HC(NO₂)₃	-654.2022471	0.054201	-654.148046

Table S2. Cartesian atomic coordinates of calculated structures at B3LYP/TZVP level of theory.

“5”			
N	-0.006137000	0.057827000	-0.052625000
N	0.032283000	0.016267000	1.321540000
C	1.305873000	-0.071027000	1.785564000
C	2.136664000	-0.054660000	0.665990000
C	1.249418000	0.027404000	-0.458257000
C	-1.183773000	-0.012479000	2.057697000
C	-1.322042000	0.737478000	3.225557000
C	-2.520224000	0.690870000	3.931276000
C	-3.580702000	-0.079027000	3.466912000
C	-3.441007000	-0.805546000	2.287000000
C	-2.245334000	-0.781144000	1.581805000
C	3.539410000	-0.117382000	0.746085000
N	4.687592000	-0.180609000	0.877136000
N	1.647915000	-0.117402000	3.111088000
C	1.569841000	0.092152000	-1.892413000
C	0.605014000	0.556835000	-2.797034000
C	0.881908000	0.615040000	-4.154938000
C	2.126380000	0.215171000	-4.636527000
C	3.090029000	-0.246018000	-3.747046000
C	2.816185000	-0.309208000	-2.385254000
H	-0.513420000	1.371762000	3.563675000
H	-2.627438000	1.275828000	4.836224000
H	-4.513842000	-0.106151000	4.015216000
H	-4.265932000	-1.400534000	1.915416000
H	-2.124100000	-1.335251000	0.661699000
H	0.974956000	-0.522642000	3.744420000
H	2.601131000	-0.396358000	3.291530000
H	-0.358187000	0.872449000	-2.419440000
H	0.126445000	0.979234000	-4.840674000
H	2.342585000	0.265281000	-5.696708000
H	4.060269000	-0.561105000	-4.110880000
H	3.577117000	-0.680055000	-1.712405000
“13-cis”			
N	-0.027851000	0.609765000	0.264125000
N	0.200328000	-0.220637000	1.407601000
C	1.522470000	-0.216644000	1.815307000
C	2.237083000	0.772914000	0.872719000
C	1.287905000	0.796610000	-0.366651000
C	-0.894163000	-0.961410000	1.908990000
C	-0.790035000	-1.721174000	3.082653000
C	-1.896658000	-2.424387000	3.543104000
C	-3.109782000	-2.388236000	2.864240000
C	-3.208250000	-1.631608000	1.702078000
C	-2.116243000	-0.919554000	1.223097000
C	3.635152000	0.457354000	0.648703000
N	4.755304000	0.233117000	0.506520000
N	2.007454000	-0.897626000	2.770167000
C	1.604166000	-0.234205000	-1.432280000
C	2.549445000	0.081042000	-2.410402000

C	2.881257000	-0.837396000	-3.399129000
C	2.267584000	-2.085306000	-3.422681000
C	1.319809000	-2.403821000	-2.456249000
C	0.986703000	-1.484280000	-1.466941000
H	2.198243000	1.758565000	1.352083000
H	1.298812000	1.786105000	-0.824068000
H	-0.365128000	1.510279000	0.603419000
H	0.149930000	-1.762513000	3.608181000
H	-1.800558000	-3.009311000	4.449910000
H	-3.964230000	-2.940312000	3.234810000
H	-4.142890000	-1.590891000	1.155798000
H	-2.198247000	-0.341960000	0.314969000
H	3.011997000	-0.762700000	2.848028000
H	3.033455000	1.051532000	-2.401714000
H	3.616457000	-0.576685000	-4.150295000
H	2.523550000	-2.803238000	-4.192107000
H	0.833119000	-3.371276000	-2.471087000
H	0.235523000	-1.739592000	-0.732599000

“13-trans”

N	0.017108000	0.267632000	0.245372000
N	0.188341000	-0.333150000	1.530285000
C	1.477461000	-0.193068000	2.015008000
C	2.248345000	0.584024000	0.923727000
C	1.374804000	0.327241000	-0.324210000
C	-0.918555000	-1.005066000	2.099639000
C	-0.887759000	-1.483543000	3.416421000
C	-2.003083000	-2.129664000	3.936743000
C	-3.154030000	-2.307198000	3.177533000
C	-3.180288000	-1.827013000	1.872619000
C	-2.078117000	-1.178585000	1.331800000
C	3.639703000	0.183371000	0.815600000
N	4.744676000	-0.129308000	0.732090000
N	1.904095000	-0.627867000	3.128558000
C	1.445071000	1.319570000	-1.462603000
C	0.536787000	1.183577000	-2.518365000
C	0.559883000	2.066824000	-3.589648000
C	1.499077000	3.094012000	-3.629289000
C	2.412558000	3.229404000	-2.591821000
C	2.385420000	2.348038000	-1.513736000
H	2.213154000	1.647467000	1.187796000
H	1.608824000	-0.675858000	-0.694457000
H	-0.318448000	1.222402000	0.388833000
H	0.003899000	-1.358086000	4.008361000
H	-1.963533000	-2.496634000	4.955283000
H	-4.016714000	-2.810658000	3.595304000
H	-4.066170000	-1.956386000	1.262554000
H	-2.102826000	-0.814114000	0.316138000
H	2.899178000	-0.453136000	3.239946000
H	-0.191725000	0.382442000	-2.493099000
H	-0.151713000	1.949802000	-4.397720000
H	1.520874000	3.780147000	-4.466845000

H	3.153316000	4.018889000	-2.617992000
H	3.119110000	2.466052000	-0.726706000

“14-cis”

C	0.180792000	0.214674000	-0.069281000
N	0.100553000	0.301655000	1.420248000
N	1.465318000	0.169421000	1.914479000
C	2.299269000	0.565757000	0.877544000
C	1.617726000	0.638848000	-0.302656000
C	1.674656000	0.584544000	3.262968000
C	2.741112000	0.029420000	3.977492000
C	2.974768000	0.420801000	5.291360000
C	2.131603000	1.336107000	5.913028000
C	1.050212000	1.859055000	5.209202000
C	0.818000000	1.493393000	3.888744000
N	3.625751000	0.779815000	1.095986000
C	2.204721000	0.934678000	-1.537403000
N	2.718469000	1.189251000	-2.545744000
C	-0.885407000	1.058629000	-0.739539000
C	-1.677188000	0.506583000	-1.744025000
C	-2.642908000	1.273798000	-2.390669000
C	-2.827393000	2.603048000	-2.031110000
C	-2.041067000	3.161661000	-1.025208000
C	-1.075403000	2.395423000	-0.386116000
H	0.038374000	-0.825615000	-0.399215000
H	-0.398042000	-0.507767000	1.776750000
H	3.363254000	-0.722808000	3.509155000
H	3.804861000	-0.011979000	5.836086000
H	2.305763000	1.627286000	6.941111000
H	0.382996000	2.564759000	5.689060000
H	-0.020526000	1.892518000	3.336268000
H	3.907714000	1.087022000	2.014342000
H	4.132237000	1.193685000	0.328297000
H	-1.536297000	-0.531013000	-2.026830000
H	-3.248577000	0.831717000	-3.172357000
H	-3.577980000	3.203229000	-2.530847000
H	-2.180425000	4.198278000	-0.742691000
H	-0.464538000	2.828786000	0.395510000

“14-trans”

C	-0.574381000	0.096967000	0.664624000
N	0.754179000	0.639338000	1.106688000
N	0.792436000	0.582095000	2.549567000
C	-0.438471000	0.142732000	3.011460000
C	-1.312553000	-0.063199000	1.981433000
C	2.037936000	0.254072000	3.152528000
C	2.342573000	0.769740000	4.416228000
C	3.547795000	0.442186000	5.030364000
C	4.470349000	-0.367761000	4.378760000
C	4.180828000	-0.845884000	3.102445000
C	2.973195000	-0.543760000	2.488016000
N	-0.670142000	-0.018886000	4.342598000

C	-2.621989000	-0.526446000	2.145214000
N	-3.702423000	-0.918742000	2.304027000
C	-1.197599000	1.012126000	-0.371223000
C	-1.077977000	0.705732000	-1.726625000
C	-1.602846000	1.554869000	-2.696066000
C	-2.255952000	2.722522000	-2.317172000
C	-2.383162000	3.035411000	-0.966444000
C	-1.858108000	2.185564000	-0.000133000
H	-0.414997000	-0.879388000	0.192120000
H	0.778672000	1.628736000	0.875913000
H	1.657027000	1.458658000	4.894119000
H	3.773178000	0.845859000	6.009845000
H	5.413890000	-0.609853000	4.851117000
H	4.899996000	-1.466751000	2.582098000
H	2.746141000	-0.900838000	1.493753000
H	0.125357000	-0.141801000	4.948971000
H	-1.486022000	-0.560782000	4.583817000
H	-0.574035000	-0.207214000	-2.023631000
H	-1.505280000	1.301983000	-3.744797000
H	-2.671182000	3.382314000	-3.069181000
H	-2.902679000	3.937021000	-0.665413000
H	-1.977934000	2.421256000	1.050766000

“15”

N	0.239468000	0.650312000	-0.406509000
N	-0.719917000	1.604263000	-0.104947000
C	-0.110540000	2.754019000	0.234170000
C	1.281150000	2.528833000	0.190871000
C	1.453459000	1.186995000	-0.198807000
C	-2.124807000	1.403780000	-0.328328000
C	-2.960378000	1.193859000	0.763873000
C	-4.321996000	1.020267000	0.542292000
C	-4.827961000	1.052020000	-0.752732000
C	-3.978685000	1.259788000	-1.836162000
C	-2.618314000	1.441428000	-1.629009000
C	2.239974000	3.531791000	0.433769000
N	2.969216000	4.401945000	0.647924000
N	-0.772966000	3.895994000	0.479878000
C	2.687066000	0.430279000	-0.393106000
C	2.749611000	-0.586517000	-1.354018000
C	3.924394000	-1.301054000	-1.535138000
C	5.046147000	-1.007047000	-0.767403000
C	4.991973000	0.003875000	0.188480000
C	3.821071000	0.721806000	0.377842000
H	-0.033475000	-0.410470000	-0.233779000
H	-2.543558000	1.125314000	1.760591000
H	-4.979408000	0.834713000	1.381397000
H	-5.886689000	0.900635000	-0.920771000
H	-4.373848000	1.270956000	-2.843563000
H	-1.943177000	1.595087000	-2.460777000
H	-0.261945000	4.699303000	0.805775000
H	-1.774937000	3.892606000	0.576416000

H	1.883607000	-0.817551000	-1.959260000
H	3.958360000	-2.093797000	-2.270646000
H	5.960815000	-1.569005000	-0.908967000
H	5.860625000	0.227716000	0.794285000
H	3.782828000	1.490813000	1.137435000
C	-0.543733000	-1.972815000	0.298335000
N	-1.303957000	-1.619904000	1.520519000
O	-0.747037000	-0.814542000	2.264404000
O	-2.420542000	-2.077618000	1.701775000
N	-1.443939000	-2.580024000	-0.712223000
O	-1.289677000	-3.732848000	-1.069908000
O	-2.301505000	-1.813991000	-1.147147000
N	0.610033000	-2.831899000	0.614269000
O	0.834988000	-3.134129000	1.777599000
O	1.305604000	-3.146742000	-0.344234000

“TS”

C	-0.163929000	1.969176000	-1.147815000
N	-0.126570000	1.925974000	0.249669000
N	1.235062000	1.736539000	0.617197000
C	1.996741000	2.090738000	-0.449355000
C	1.168768000	2.297535000	-1.558269000
C	1.611064000	1.915920000	1.995430000
C	2.018325000	0.809611000	2.733018000
C	2.391519000	0.986252000	4.062884000
C	2.345658000	2.250031000	4.640702000
C	1.925704000	3.349484000	3.894128000
C	1.557853000	3.187756000	2.565191000
N	3.324568000	2.256930000	-0.358556000
C	1.631554000	2.645343000	-2.836505000
N	2.062167000	2.936543000	-3.869924000
C	-1.417080000	2.388618000	-1.820297000
C	-1.618967000	2.106463000	-3.174623000
C	-2.779646000	2.525720000	-3.807041000
C	-3.756005000	3.217918000	-3.094472000
C	-3.562968000	3.494508000	-1.746031000
C	-2.397108000	3.085912000	-1.108237000
H	-0.256293000	0.424845000	-1.517140000
H	-0.706867000	1.213638000	0.685356000
H	2.020445000	-0.173334000	2.278789000
H	2.705596000	0.130347000	4.646174000
H	2.631318000	2.380628000	5.676982000
H	1.885728000	4.331834000	4.347369000
H	1.226304000	4.030770000	1.972241000
H	3.811170000	1.955875000	0.470223000
H	3.857702000	2.326940000	-1.210628000
H	-0.879140000	1.540993000	-3.726447000
H	-2.928025000	2.301061000	-4.855497000
H	-4.664493000	3.537117000	-3.589726000
H	-4.317620000	4.033788000	-1.187324000
H	-2.237097000	3.325136000	-0.065195000
C	-0.027761000	-1.859697000	-0.889648000

N	1.142764000	-2.407820000	-1.601327000
O	2.141873000	-1.697784000	-1.557583000
O	1.041567000	-3.466645000	-2.195528000
N	-1.293976000	-2.547558000	-1.213365000
O	-1.920088000	-3.094773000	-0.319227000
O	-1.622575000	-2.477392000	-2.388012000
N	0.199506000	-1.683800000	0.538366000
O	1.206582000	-2.137886000	1.064805000
O	-0.642515000	-0.990998000	1.117119000
H	-0.183799000	-0.487810000	-1.348000000

“H₂”

H	0.000000000	0.000000000	0.127995000
H	0.000000000	0.000000000	0.872005000

“HC(NO₂)₃”

C	-0.115261000	0.020833000	0.695374000
N	-0.967603000	-0.153456000	-0.558497000
O	-2.104061000	0.253121000	-0.429710000
O	-0.449735000	-0.646829000	-1.533171000
N	1.114850000	-0.878564000	0.611653000
O	2.170592000	-0.370380000	0.313758000
O	0.876636000	-2.045097000	0.848062000
N	0.319598000	1.478002000	0.824352000
O	0.262433000	2.176912000	-0.160439000
O	0.700689000	1.770924000	1.938981000
H	-0.699784000	-0.254863000	1.564697000

Figure S99. Total Energy along IRC

