Supporting Information

Green and efficient synthesis of 5-amino-1*H*-pyrazole-5-carbonitriles utilizing novel modified LDH

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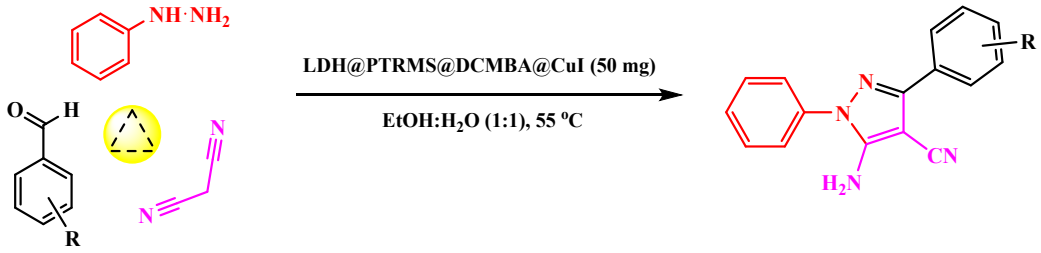
General procedure for the one-pot synthesis of 5-amino-1*H*-pyrazole-5-carbonitriles

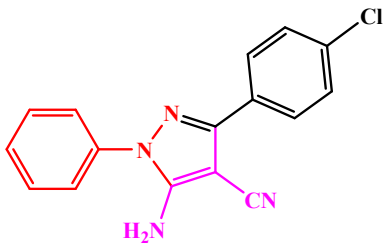


In a standard experimental procedure, the following components were combined in a 5 mL round-bottomed flask: In a test tube containing phenyl hydrazine (1 mmol), benzaldehyde derivatives (1 mmol), malononitrile (1 mmol), and the LDH@PTRMS@DCMBA@CuI catalyst (0.05 g), the mixture was stirred at 55 °C using a magnetic stirrer for an appropriate period of time. The advancement of the reaction was tracked using TLC (n-hexane/ethyl acetate: 0.5:0.5 mL) to observe the transformation of reactants into products. Once the reaction reached completion and the desired compound was obtained, the mixture was allowed to cool to room temperature. To isolate the catalyst, 3 mL of either hot ethanol or chloroform was introduced into the reaction mixture.

Subsequently, the catalyst (LDH@PTRMS@DCMBA@CuI) was separated through centrifugation, thoroughly washed, and subsequently dried in an oven at 60 °C to remove any residual solvent and moisture. The solvent of the reaction mixture was evaporated, and the products were recrystallized with ethanol, yielding the compounds with high yield. The products were identified using FTIR, ^{1}H NMR, and ^{13}C NMR spectra, and the melting points of all products were recorded.

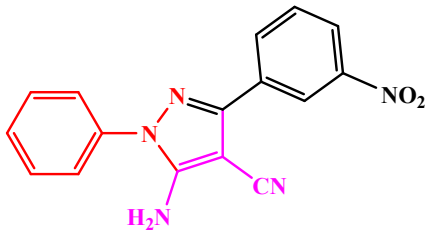
Spectral Data:

S1. 5-amino-3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (4b)

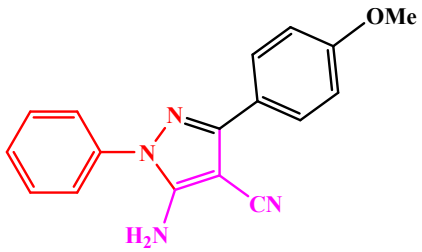


M.p. 190-192 °C, FT-IR (KBr, ν cm^{-1}): 3447, 3346, 3313, 3208, 3055, 2928, 2206, 1632, 1600, 1519, 1489, 1259, 1135, 1084, 914, 829, 749, 509; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.62 (t, J = 11.5 Hz, 5H), 7.40 – 7.28 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 7.7 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 153.12, 144.40, 142.44, 135.81, 133.90, 130.91, 129.46, 129.31, 129.03, 128.81, 128.33, 127.25, 120.33, 112.79.

S2. 5-amino-3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (4c)



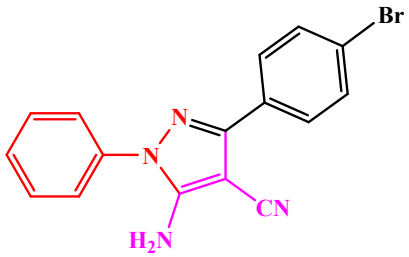
M.p. 128-130 °C, FT-IR (KBr, ν cm^{-1}): 3442, 3305, 3221, 3058, 2928, 2205, 1600, 1583, 1514, 1485, 1258, 1139, 905, 822, 758, 511; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.70 (s, 2H), 7.53 (t, J = 8.0 Hz, 1H), 7.32 (t, J = 7.8 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.94 (t, J = 7.2 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 148.69, 143.90, 137.35, 134.64, 133.90, 131.41, 130.19, 129.79, 129.47, 124.51, 122.54, 120.91, 112.99.



S3. 5-amino-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (4e)

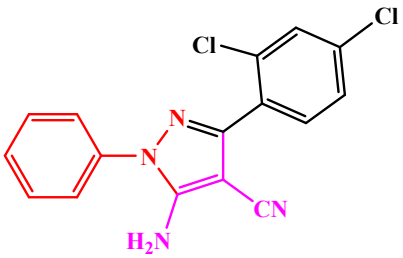
M.p. 107-109 °C, FT-IR (KBr, ν cm^{-1}): 3445, 3340, 3315, 3210, 3055, 2954, 2206, 1597, 1508, 1441, 1295, 1246, 1175, 1129, 1028, 821, 684, 532; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.27 – 7.46 (m, 4H), 7.31 (s, 1H), 7.25 (s, 1H), 7.10 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.86 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 160.08, 151.20, 144.52, 137.98, 131.96, 130.22, 129.21, 127.67, 119.87, 114.27, 114.06, 112.76, 55.28.

S4. 5-amino-3-(4-bromophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (4f)



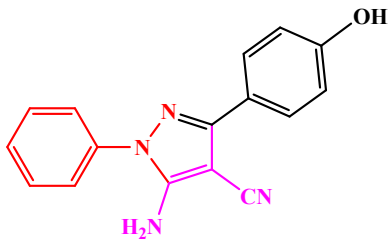
M.p. 161-163 °C, FT-IR (KBr, ν cm^{-1}): 3447, 3345, 3314, 3218, 3047, 2954, 2836, 2204, 1588, 1508, 1440, 1295, 1246, 1129, 1175, 1028, 921, 839, 746, 531; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.59 (d, J = 4.1 Hz, 2H), 7.51 (d, J = 3.8 Hz, 4H), 7.41 – 7.26 (m, 2H), 7.11 (d, J = 7.4 Hz, 2H), 6.91 (d, J = 6.3 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 144.32, 135.79, 134.27, 132.42, 131.96, 131.69, 131.22, 130.12, 129.29, 128.28, 127.48, 122.10, 120.32, 112.76.

S5. 5-amino-3-(2,4-dichlorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (4g)



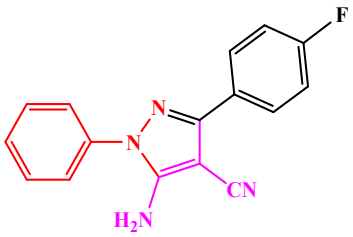
M.p. 160-161 °C, FT-IR (KBr, ν cm^{-1}): 3414, 3311, 3200, 3052, 2210, 1600, 1576, 1504, 1445, 1262, 1233, 1134, 1070, 913, 836, 754, 508; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.8 Hz, 4H), 7.33 (d, *J* = 16.4 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.03 (s, 1H), 6.92 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (63 MHz, DMSO) δ 157.05, 145.07, 132.88, 132.53, 132.08, 131.49, 131.27, 130.69, 129.62, 128.70, 128.11, 127.38, 120.00, 112.75.

S6. 5-amino-3-(4-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (4h)



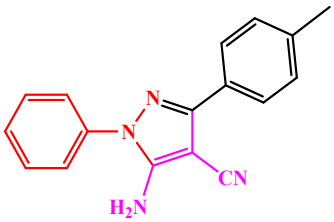
M.p. 206-208 °C, FT-IR (KBr, ν cm^{-1}): 3479, 3368, 3347, 3233, 3055, 2923, 2210, 1642, 1597, 1520, 1448, 1274, 1228, 1172, 918, 829, 697, 513. ^{1}H NMR (250 MHz, DMSO-d_6) δ 9.74 (s, 1H), 7.98 – 7.62 (m, 2H), 7.47 (d, *J* = 27.5 Hz, 5H), 6.90 (s, 2H), 6.67 (s, 2H). ^{13}C NMR (63 MHz, DMSO) δ 158.77, 153.17, 150.94, 137.93, 129.92, 128.30, 127.89, 126.09, 124.65, 122.59, 115.97, 115.38.

S7. 5-amino-3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (4i)



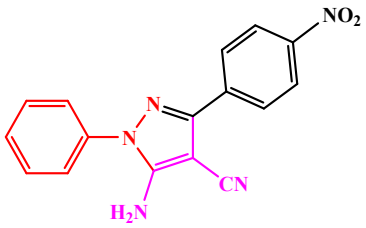
M.p. 163-165 °C, FT-IR (KBr, ν cm^{-1}): 3462, 3345, 3312, 3215, 3055, 2207, 1600, 1577, 1504, 1446, 1262, 1233, 1135, 1092, 836, 753, 693; ^{1}H NMR (250 MHz, DMSO-*d*6) δ 8.28 (s, 1H), 8.11 – 7.74 (m, 2H), 7.55 (s, 2H), 7.43 (d, *J* = 6.9 Hz, 2H), 7.32 (d, *J* = 9.3 Hz, 2H), 6.87 (s, 2H); ^{13}C NMR (63 MHz, DMSO) δ 164.21, 160.41, 153.37, 145.75, 135.79, 132.89, 129.97, 129.53, 128.57, 127.93, 124.77, 119.19, 116.56, 116.18, 115.86, 112.44.

S8. 5-amino-1-phenyl-3-(p-tolyl)-1*H*-pyrazole-4-carbonitrile (4j)



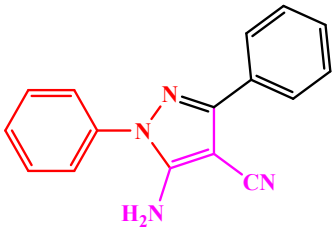
M.p. 116-118 °C, FT-IR (KBr, ν cm^{-1}): 3460, 3422, 3351, 3172, 3036, 2930, 2225, 1650, 1605, 1588, 1577, 1451, 1414, 1376, 1222, 1192, 939, 815, 615, 521; ^{1}H NMR (250 MHz, DMSO-*d*6) δ 8.46 (s, 2H), 7.85 (s, 2H), 7.62 – 7.17 (m, 5H), 6.75 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (63 MHz, DMSO) δ 161.77, 156.69, 146.13, 133.17, 131.13, 130.61, 129.92, 129.20, 128.91, 128.10, 124.40, 114.85, 21.91.

S9. 5-amino-3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile (4d)



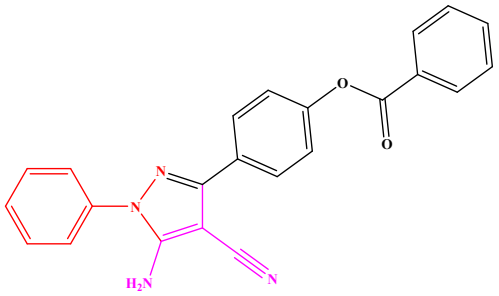
M.p. 163-164 °C, FT-IR (KBr, ν cm^{-1}): 3419, 3355, 3315, 3196, 3028, 2210, 1635, 1602, 1566, 1522, 1443, 1398, 1288, 1261, 1066, 1026, 929, 882, 756, 751, 508; ^{1}H NMR (250 MHz,) δ 8.01 (s, 2H), 7.49 (d, *J* = 23.5 Hz, 2H), 7.19 (s, 5H), 6.73 (s, 2H); ^{13}C NMR (63 MHz, DMSO) δ 165.00, 150.65, 145.71, 135.97, 134.75, 134.50, 131.58, 130.28, 129.46, 127.04, 123.32, 122.63, 119.24, 112.49.

S10. 5-amino-1,3-diphenyl-1*H*-pyrazole-4-carbonitrile (4a)



M.p. 159-161°C, FT-IR (KBr, ν cm^{-1}): 3450, 3313, 3195, 2209, 1637, 1593, 1566, 1494, 1443, 1261, 1136, 1066, 929, 882, 756, 692, 508; ^{1}H NMR (250 MHz, DMSO-*d*6) δ 7.83 (s, 2H), 7.63 – 7.46 (m, 2H), 7.39 – 7.16 (m, 4H), 7.04 (s, 2H), 6.73 (s, 2H); ^{13}C NMR (63 MHz, DMSO) δ 153.38, 145.76, 136.90, 129.95, 129.54, 129.26, 129.07, 128.34, 126.44, 126.06, 124.79, 119.16, 112.45.

S11. 4-(5-amino-4-cyano-1-phenyl-1*H*-pyrazol-3-yl)phenyl benzoate (4k)



M.p. 225-227 °C, FT-IR (KBr, ν cm^{-1}): 3485, 3387, 3291, 3179, 3060, 2895, 2201, 1733, 1643, 1570, 1500, 1450, 1410, 1355, 1311, 1249, 1129, 1081, 918, 885, 815, 752, 701, 531, 509; ^{1}H NMR (250 MHz, DMSO-*d*6) δ 8.26 – 8.00 (m, 2H), 7.87 (s, 1H), 7.80 – 7.68 (m, 2H), 7.58 (s, 5H), 7.29 (s, 2H), 7.07 (s, 2H), 6.73 (s, 2H); ^{13}C NMR (63 MHz, DMSO) δ 160.64, 153.35, 151.82, 146.13, 132.90, 131.56, 130.74, 129.98, 129.53, 128.53, 124.80, 122.62, 119.14, 115.92.

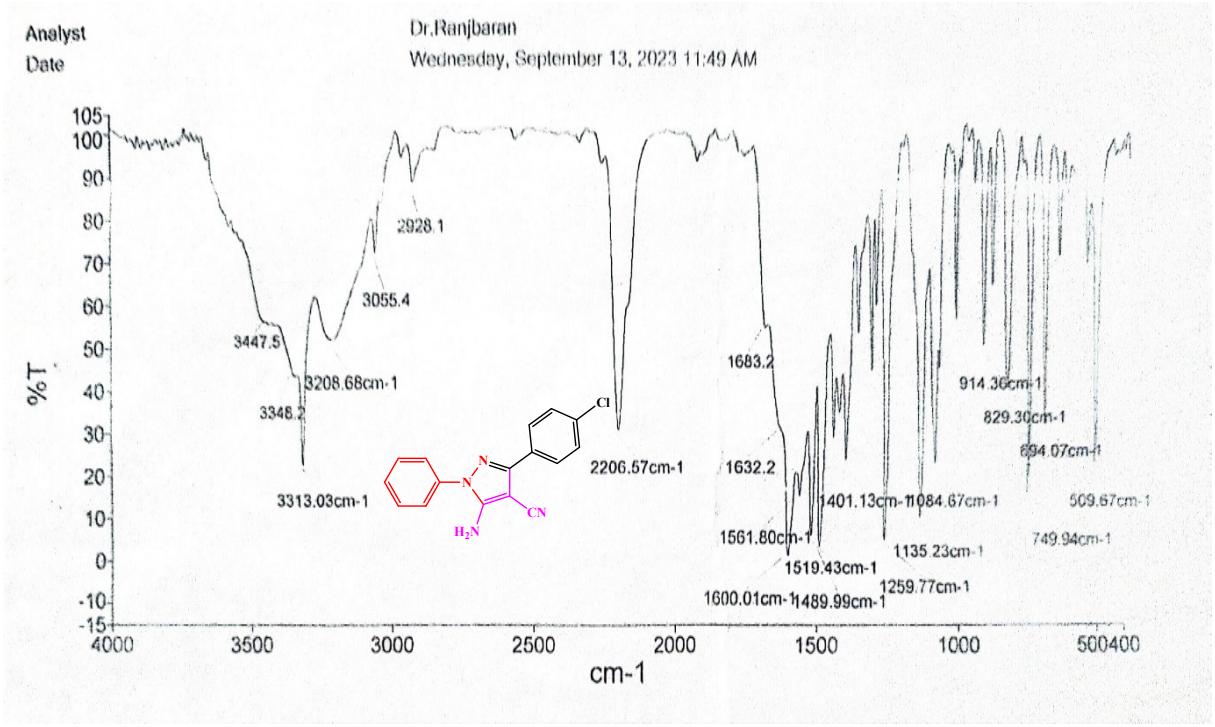


Fig. S1. The FTIR spectrum of 5-amino-3-(4-chlorophenyl)-1-phenyl-1H-pyrazole-4-carbonitrile

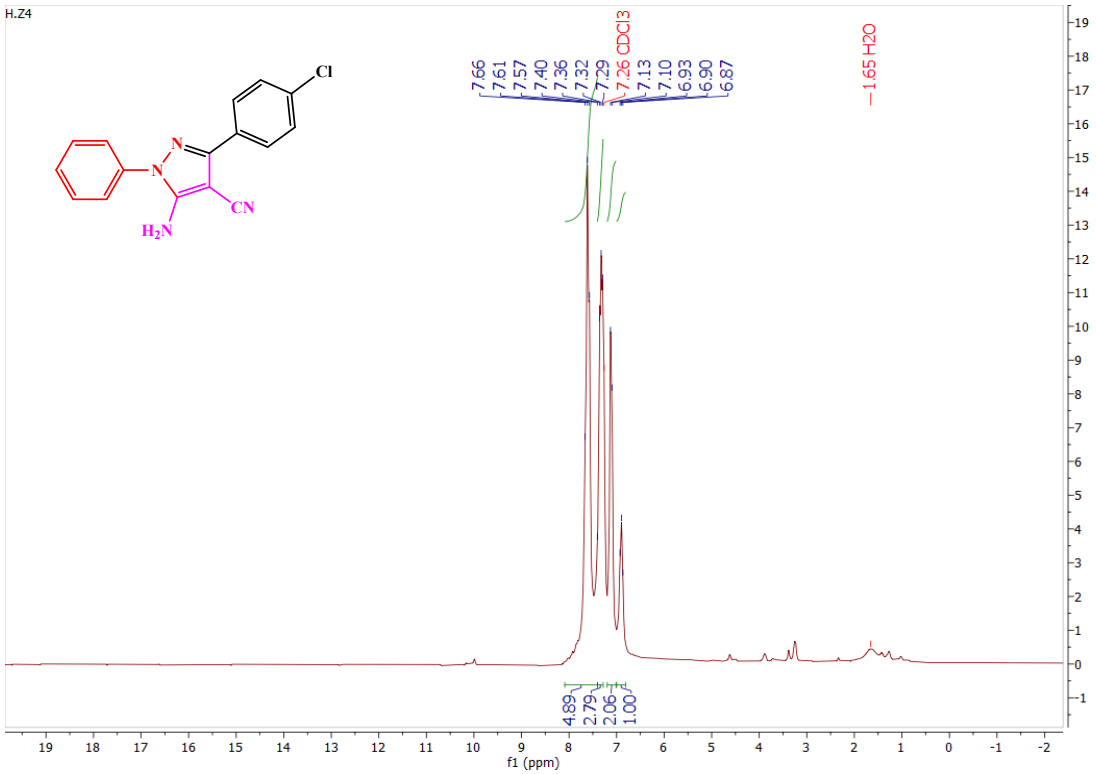


Fig. S2. The ^{1}H NMR spectrum of 5-amino-3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in $CDCl_3$ solvent

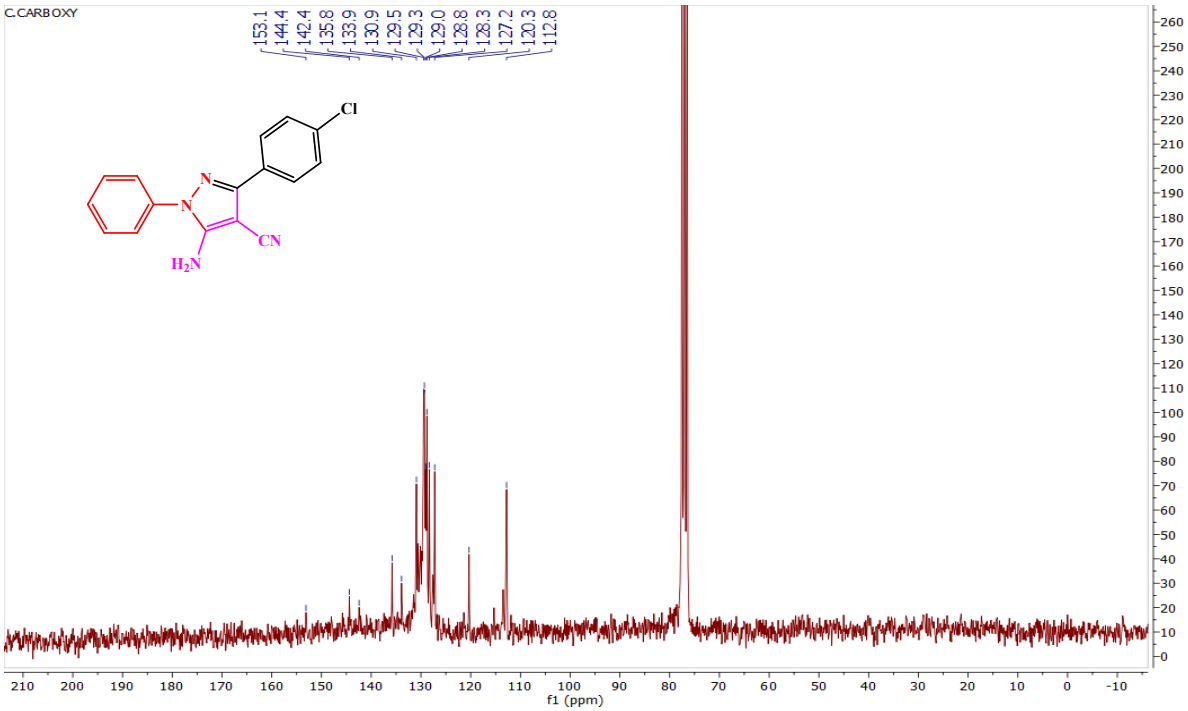


Fig. S3. The ^{13}C NMR spectrum of 5-amino-3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in $CDCl_3$ solvent

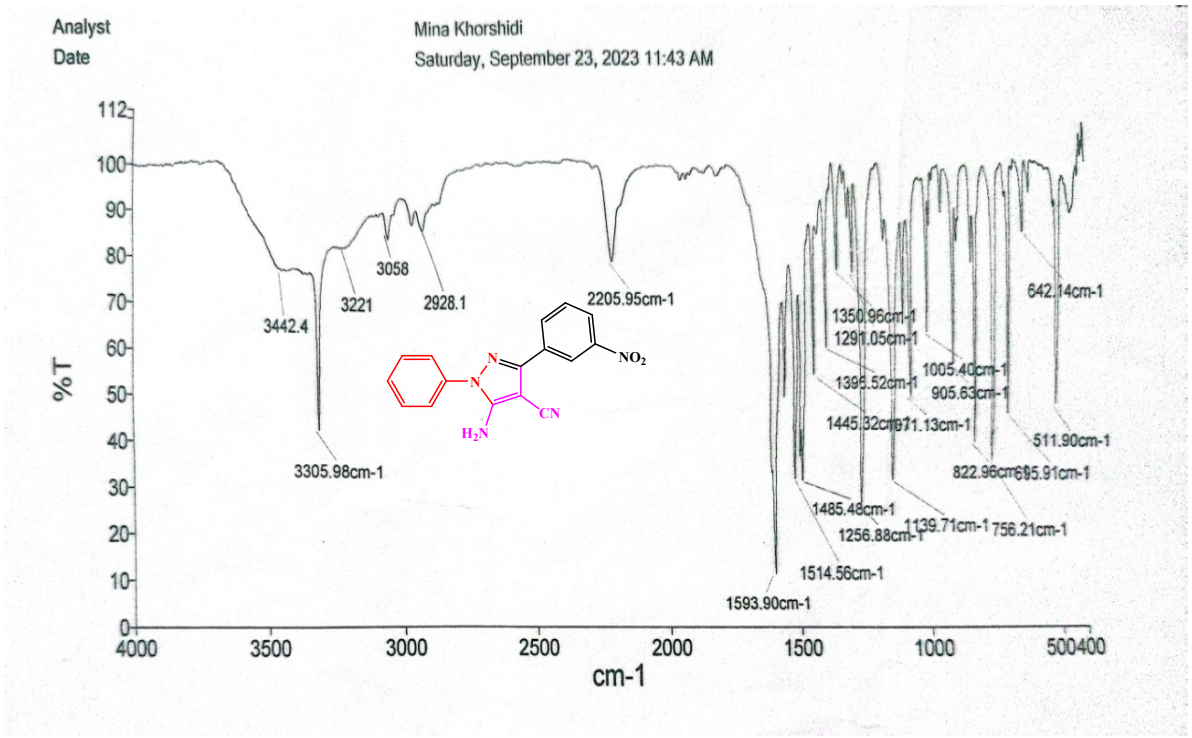


Fig. S4. The FTIR spectrum of 5-amino-3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile

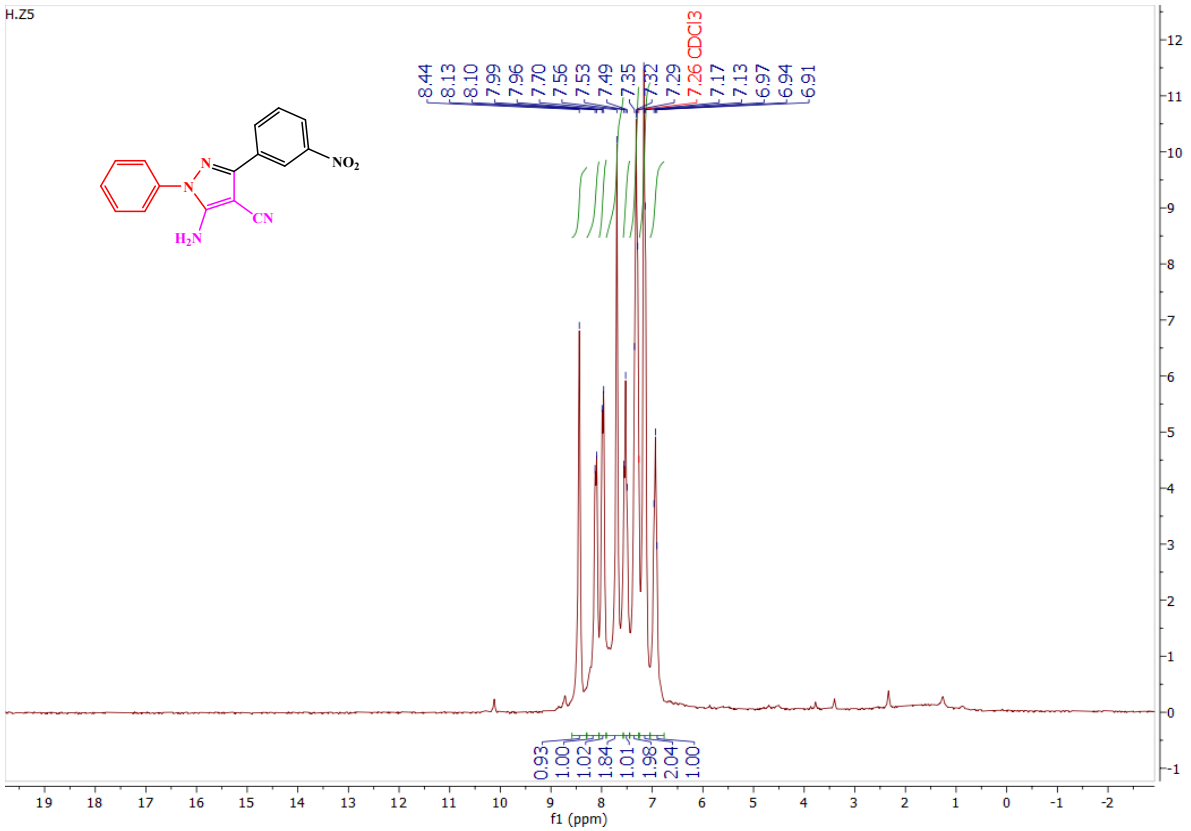


Fig. S5. The ^{1}H NMR spectrum of 5-amino-3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in $CDCl_3$ solvent

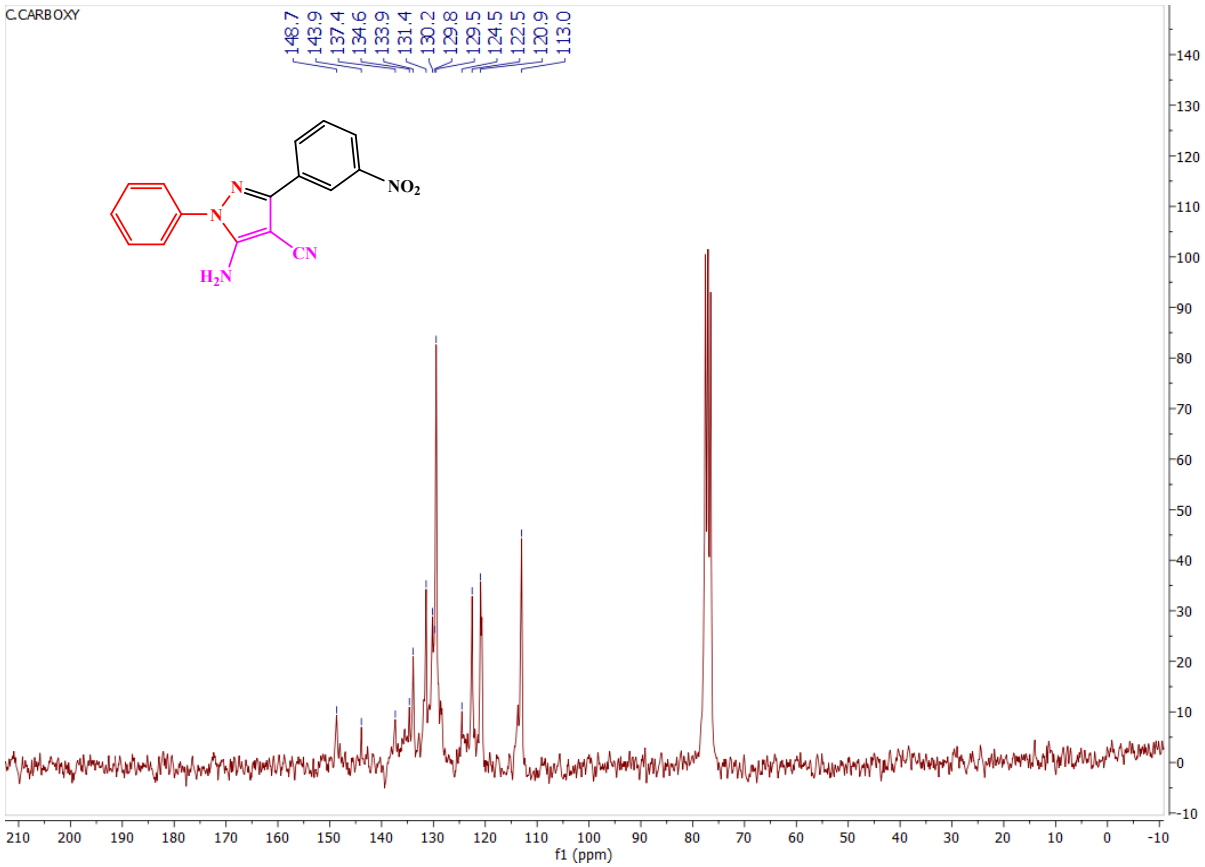


Fig. S6. The ^{13}C NMR spectrum of 5-amino-3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in $CDCl_3$ solvent

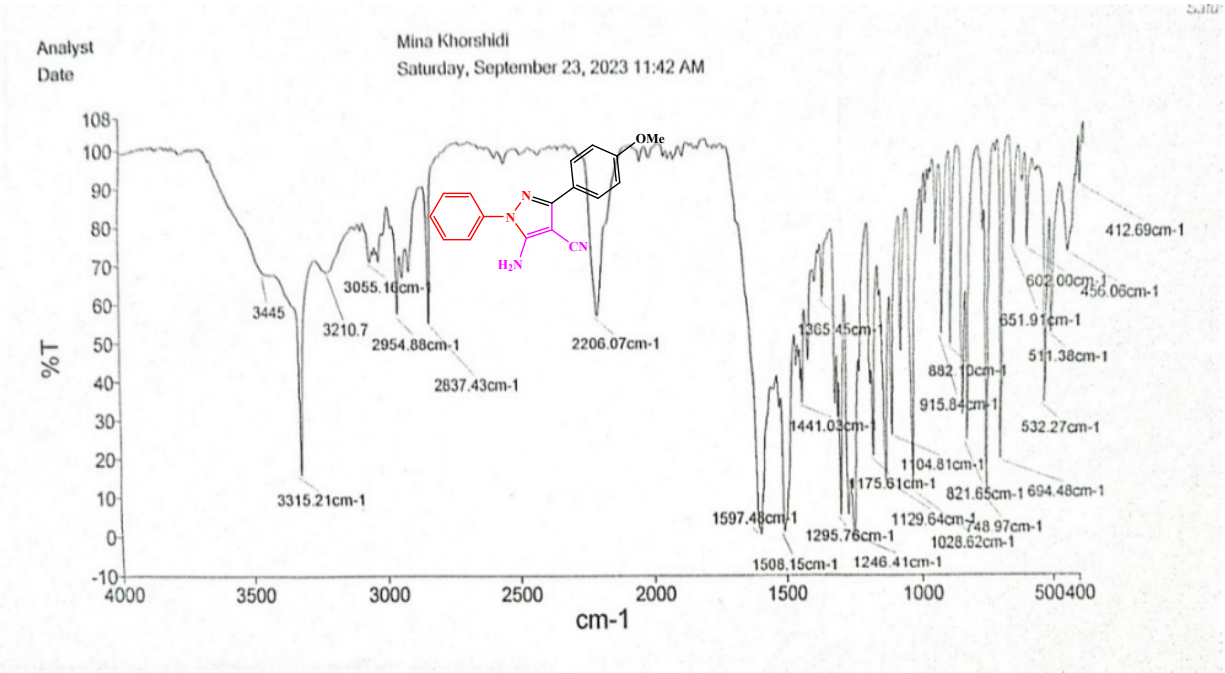


Fig. S7. The FTIR spectrum of 5-amino-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile

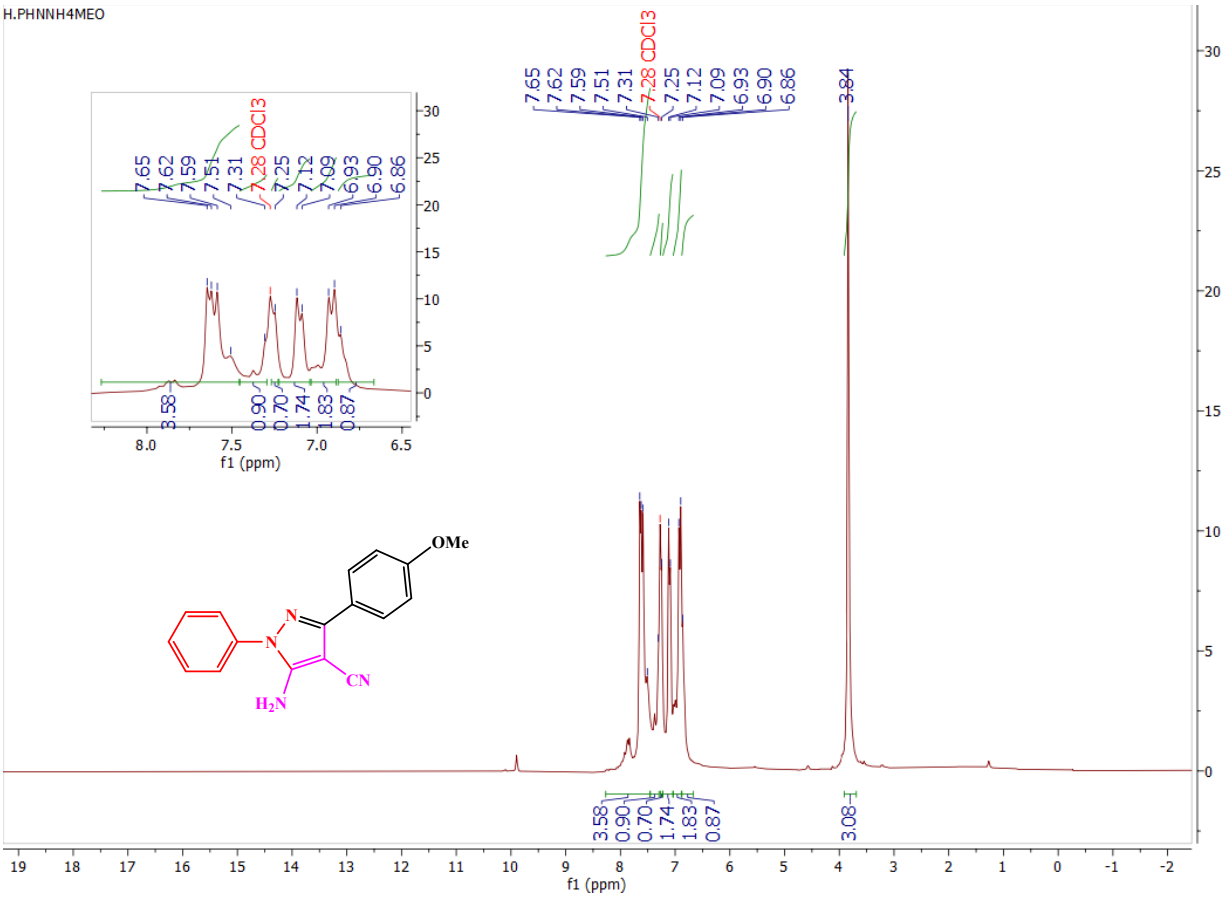


Fig. S8. The ^{1}H NMR spectrum of 5-amino-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in $CDCl_3$ solvent

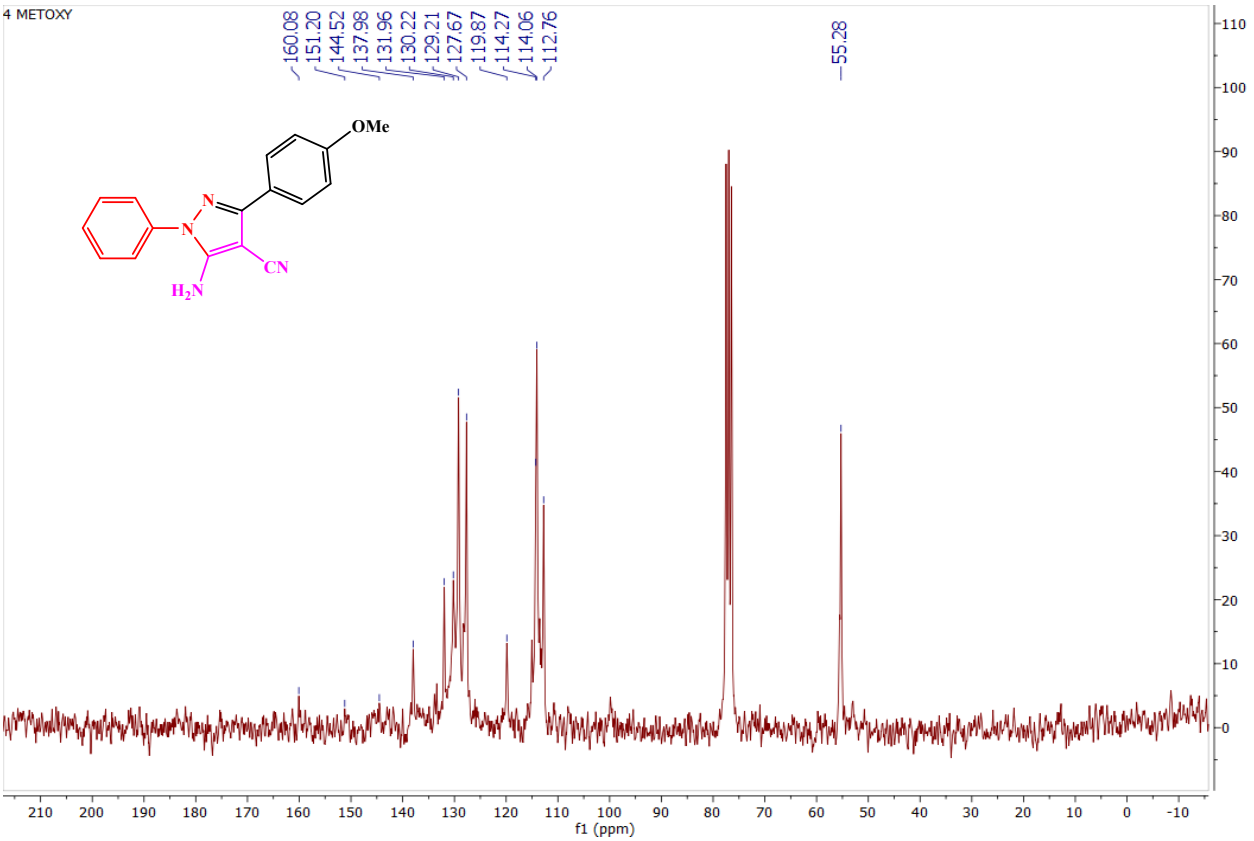


Fig. S9. The ^{13}C NMR spectrum of 5-amino-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in $CDCl_3$ solvent

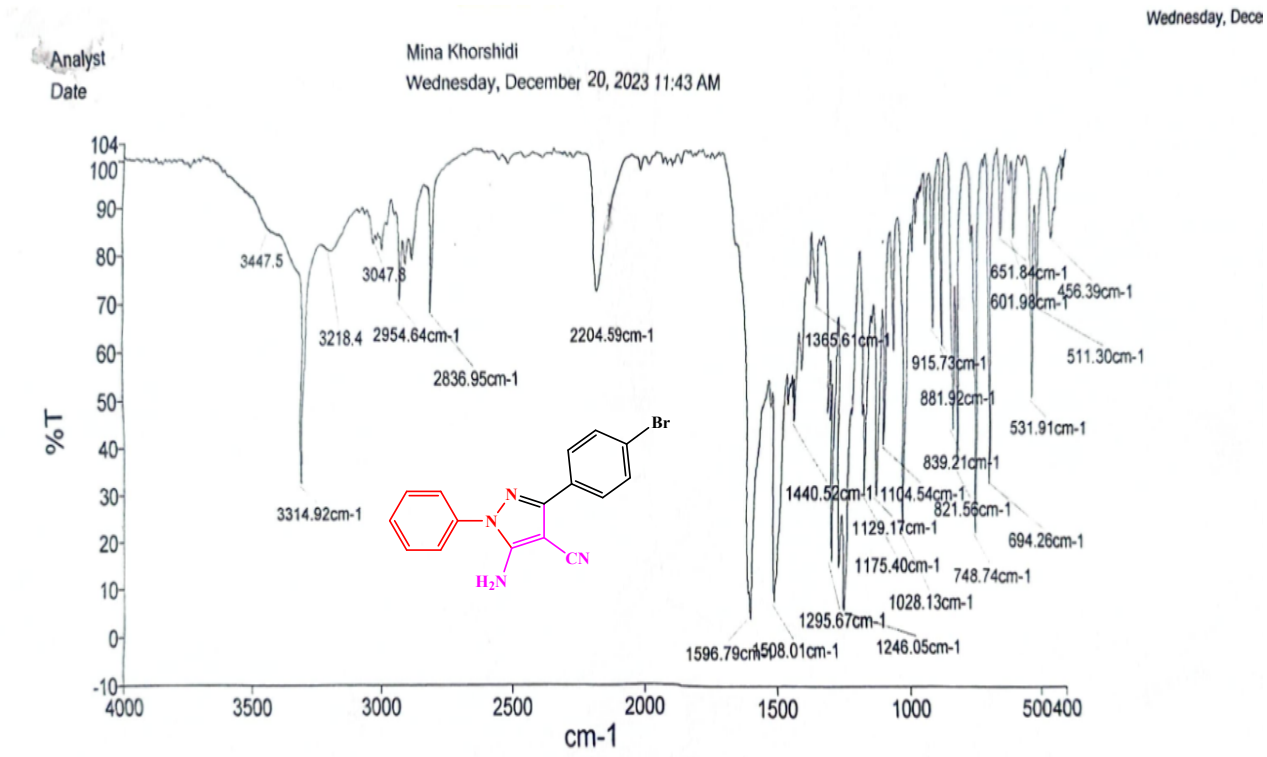


Fig. S10. The FTIR spectrum of 5-amino-3-(4-bromophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile

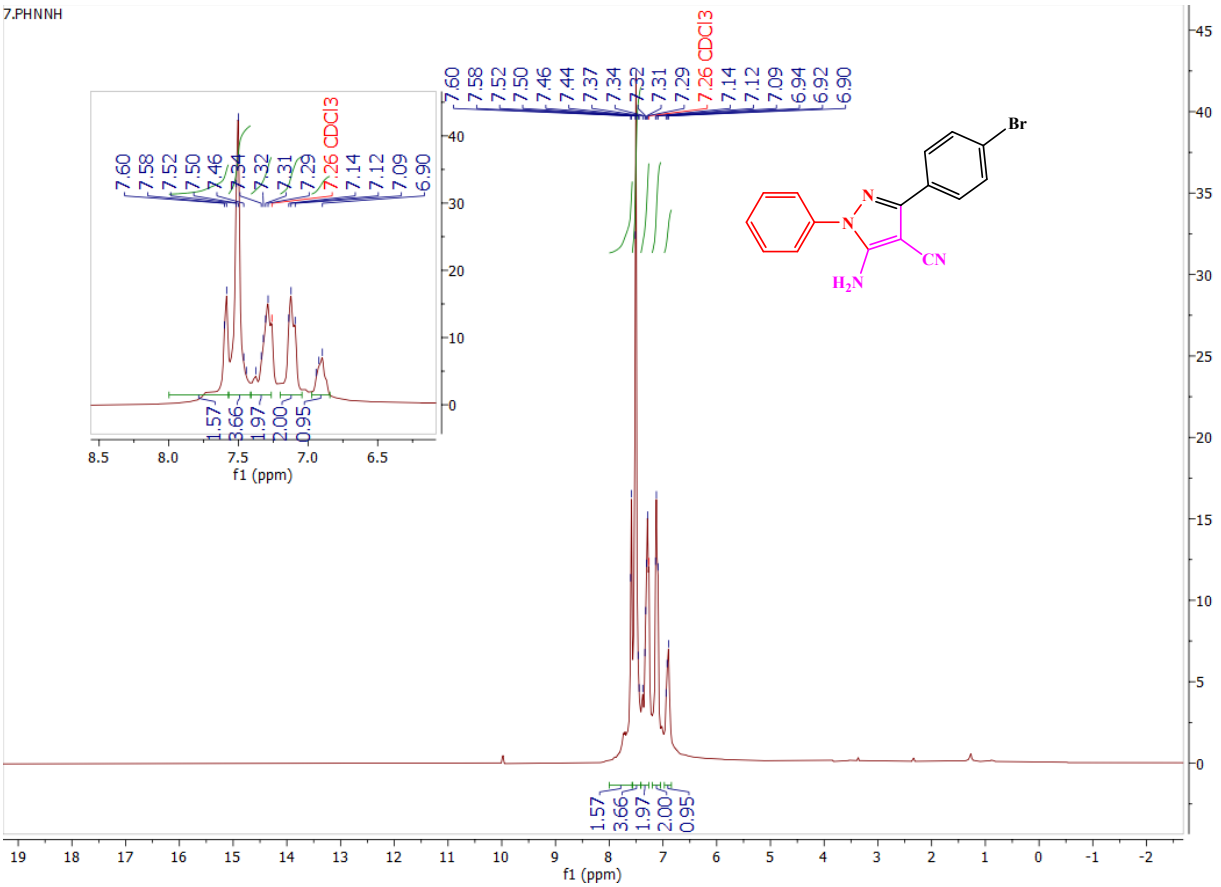


Fig. S11. The ^{1}H NMR spectrum of 5-amino-3-(4-bromophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in $CDCl_3$ solvent

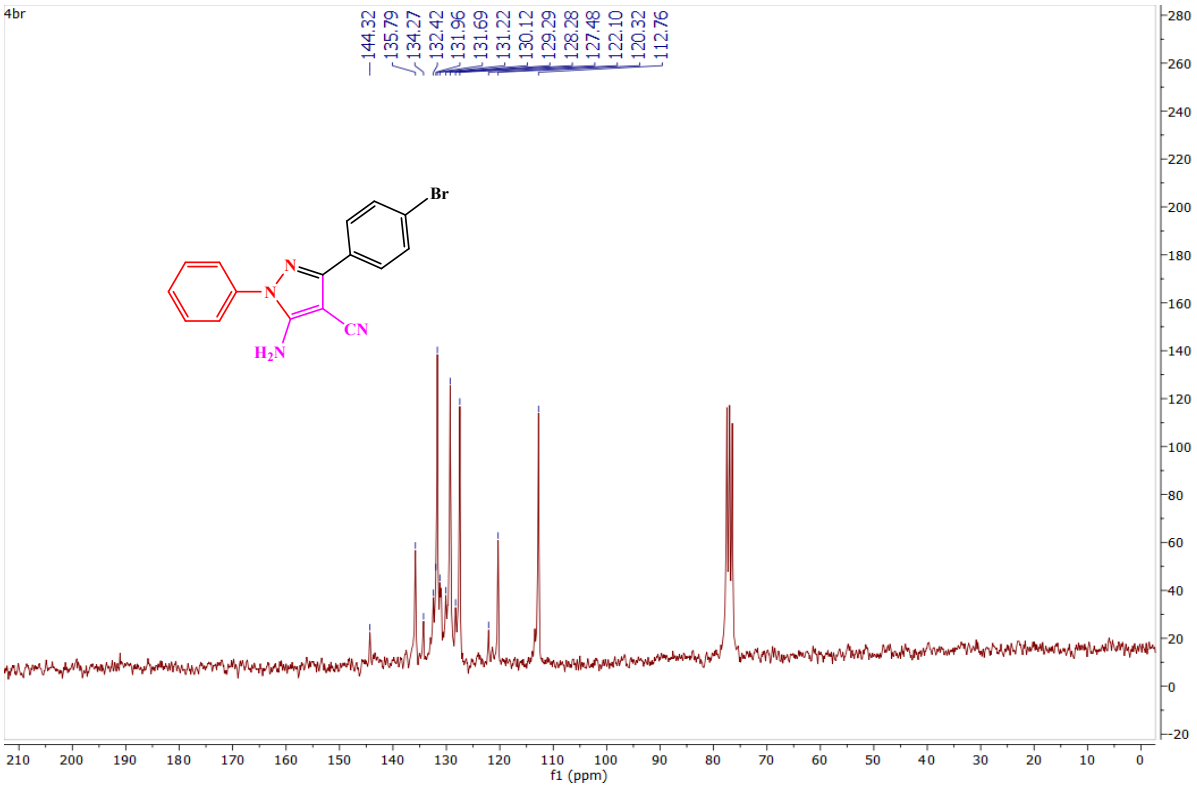


Fig. S12. The ^{13}C NMR spectrum of 5-amino-3-(4-bromophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in $CDCl_3$ solvent

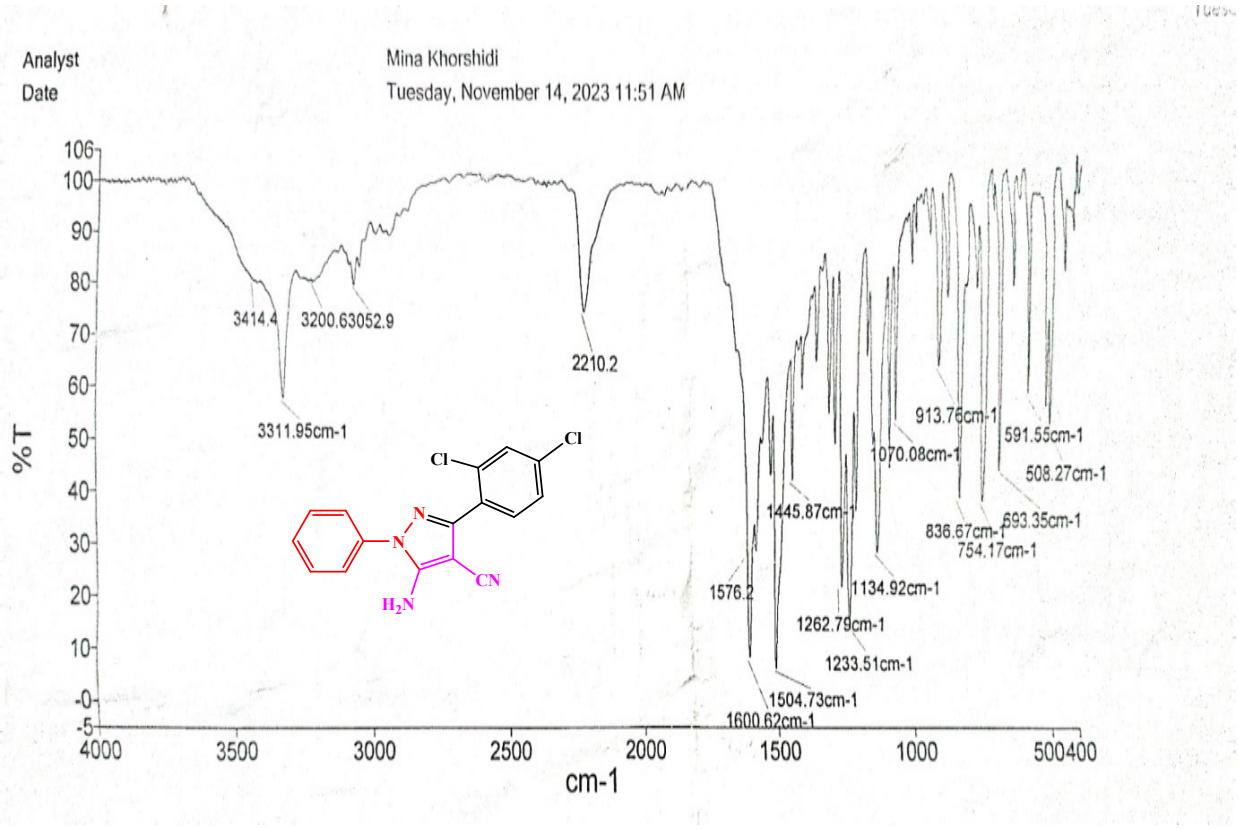


Fig. S13. The FTIR spectrum of 5-amino-3-(2,4-dichlorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile

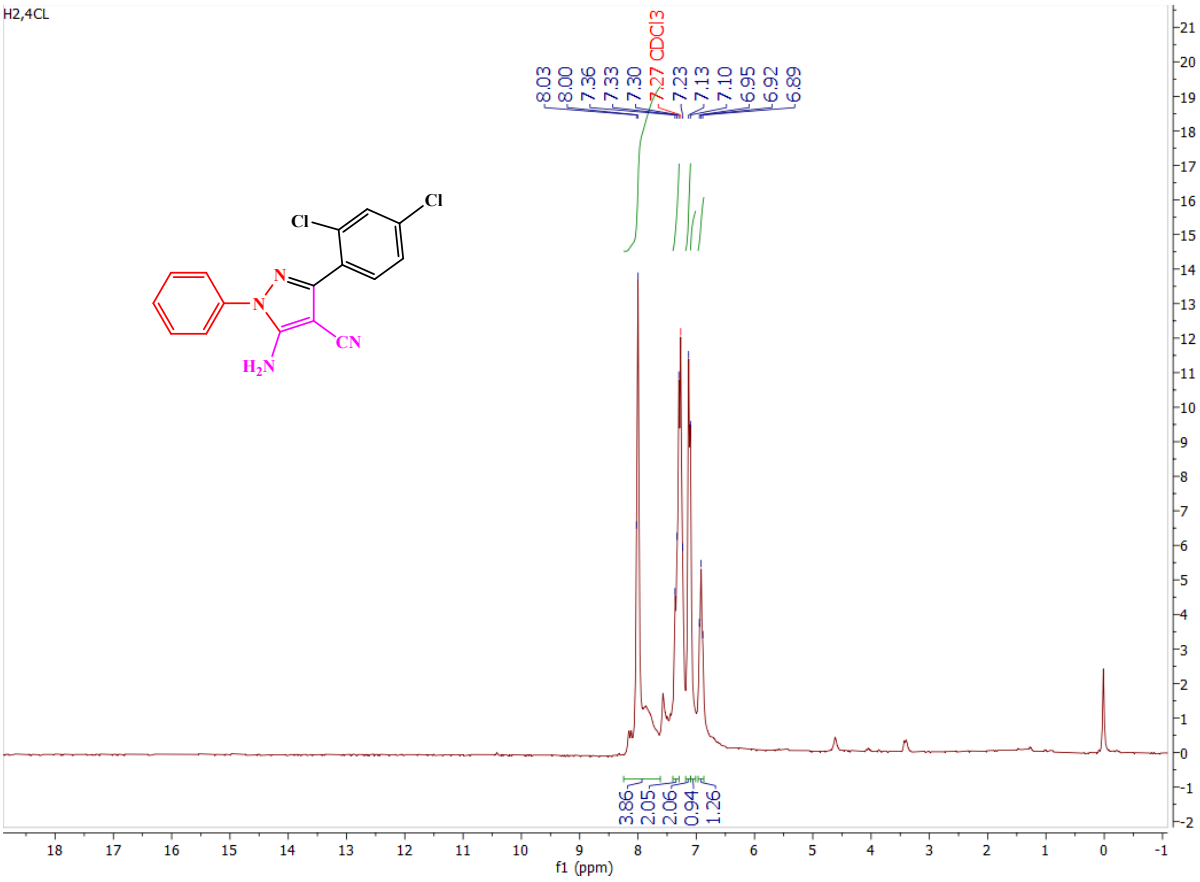


Fig. S14. The ^{1}H NMR spectrum of 5-amino-3-(2,4-dichlorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in $CDCl_3$ solvent

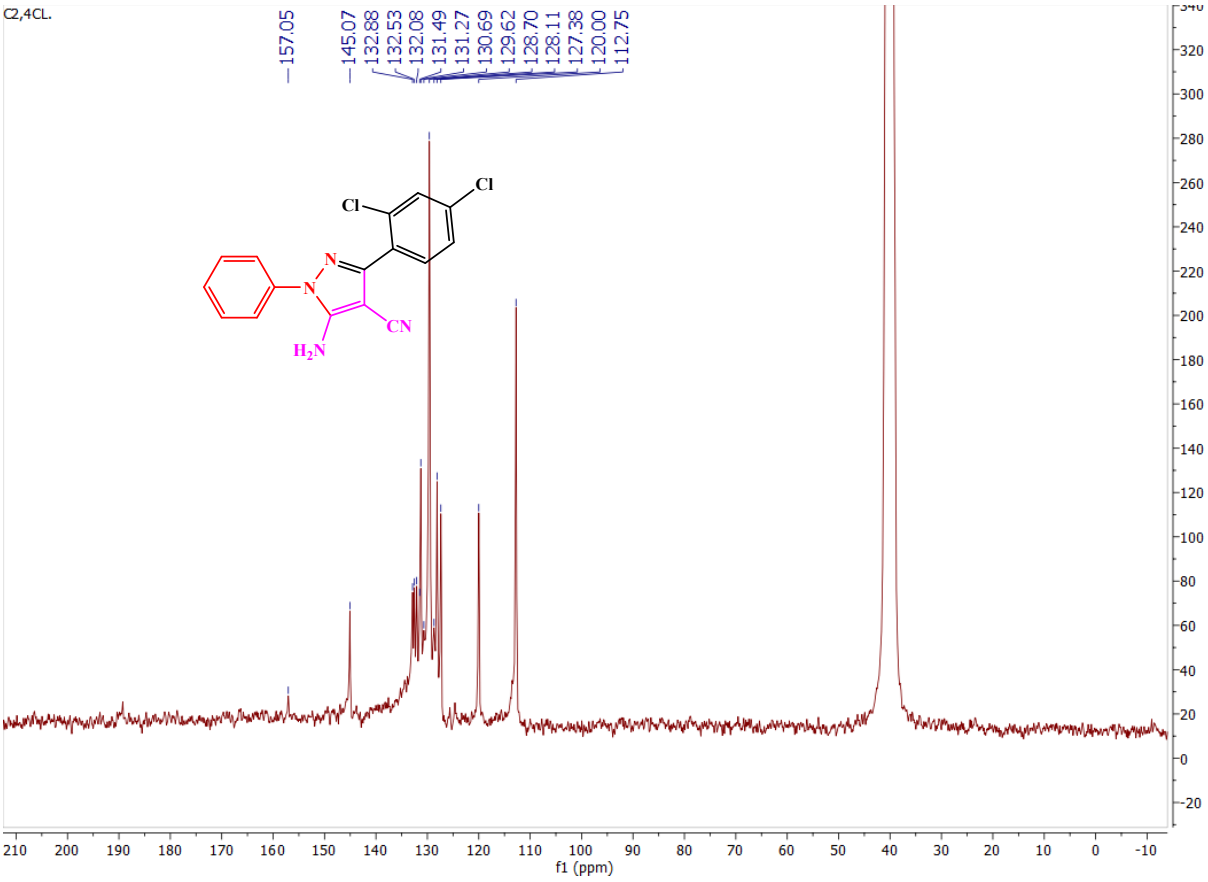


Fig. S15. The ^{13}C NMR spectrum of 5-amino-3-(2,4-dichlorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in DMSO solvent

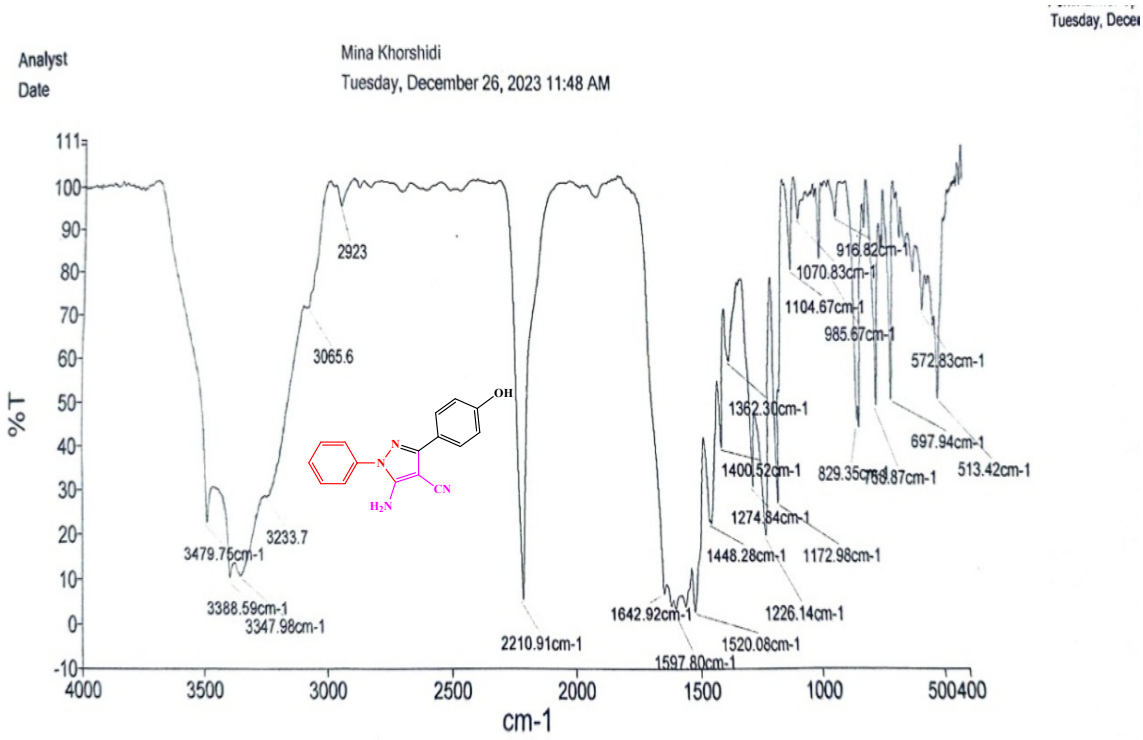


Fig. S16. The FTIR spectrum of 5-amino-3-(4-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile

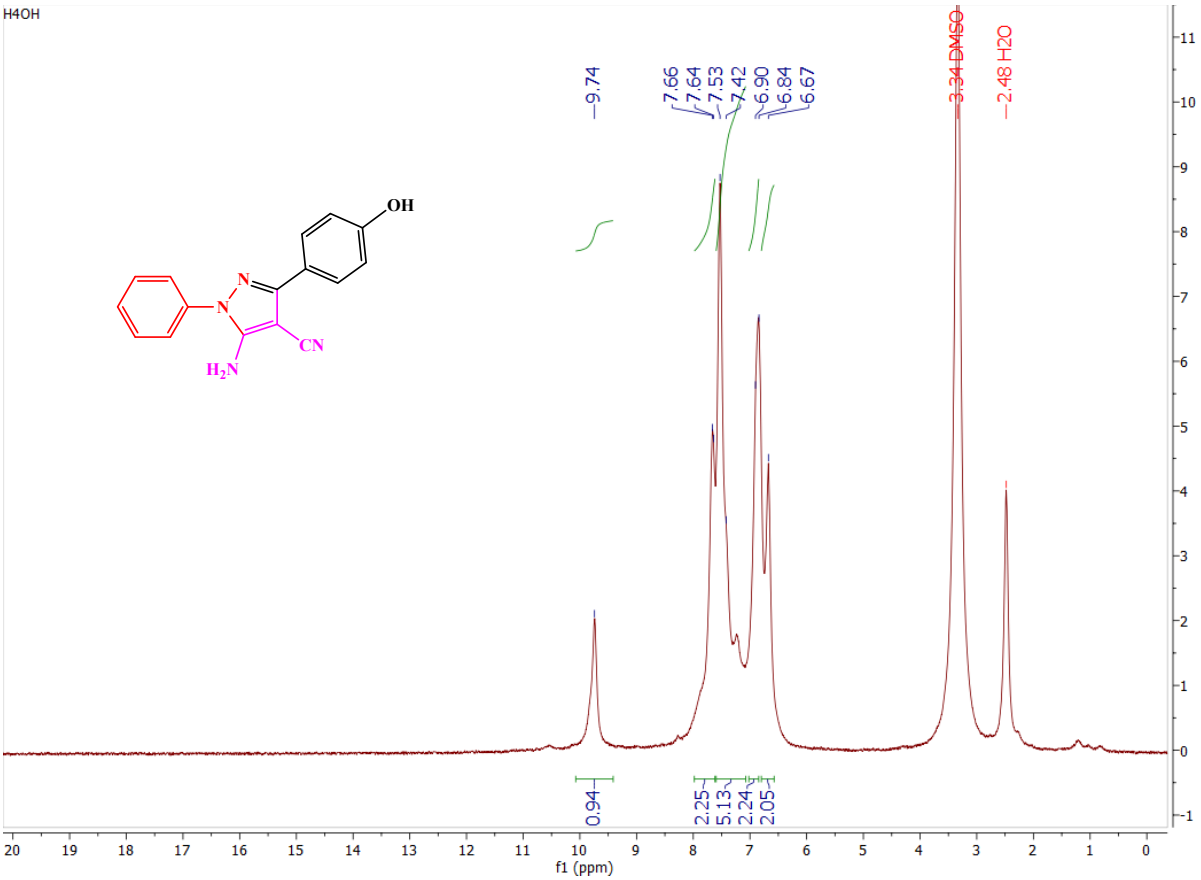


Fig. S17. The ^{1}H NMR spectrum of 5-amino-3-(4-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in DMSO solvent

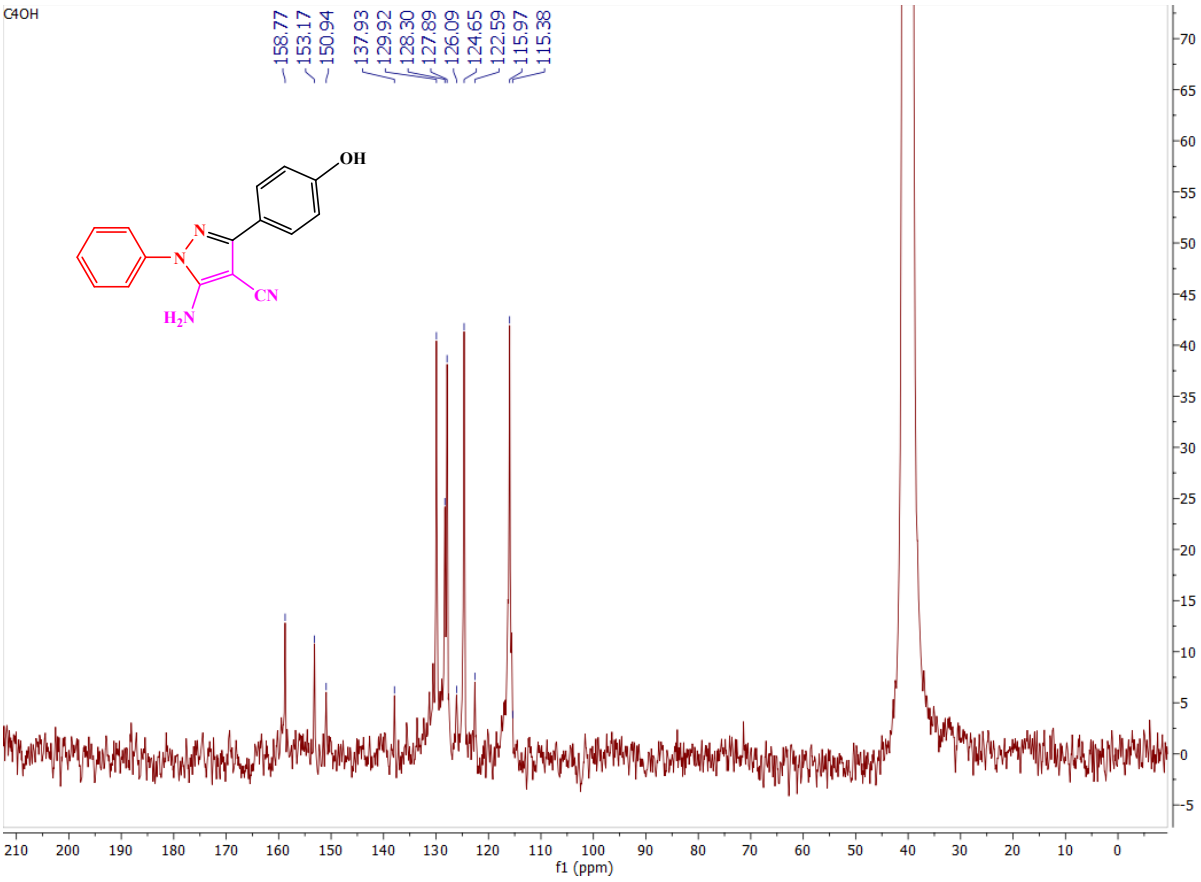


Fig. S18. The ^{13}C NMR spectrum of 5-amino-3-(4-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in DMSO solvent

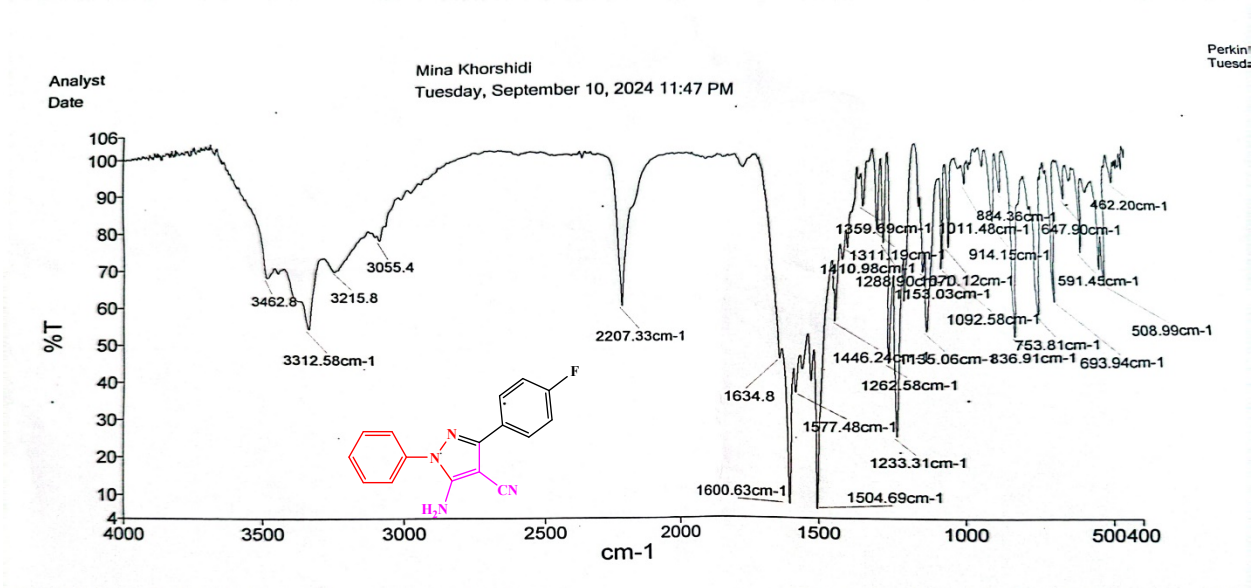


Fig. S19. The FTIR spectrum of 5-amino-3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile

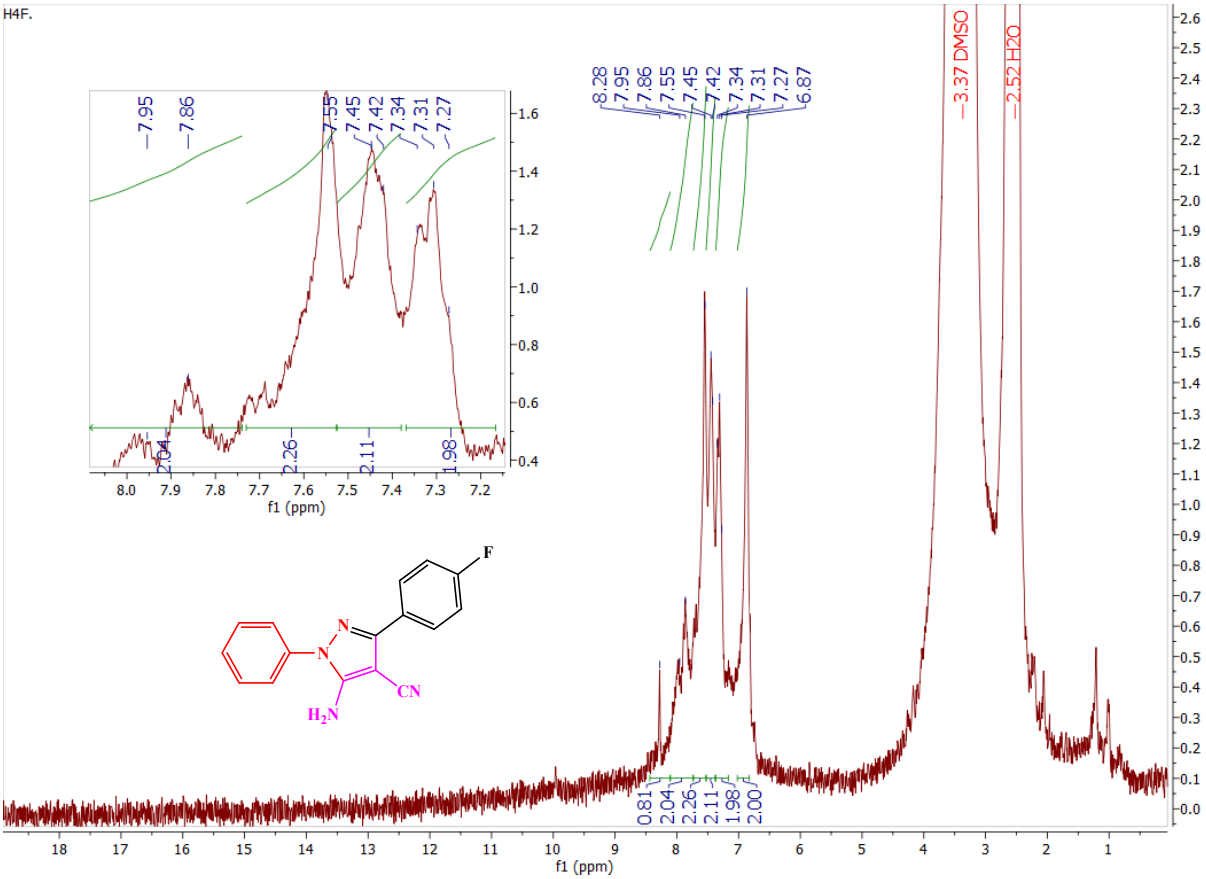


Fig. S20. The ^{1}H NMR spectrum of 5-amino-3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in DMSO solvent

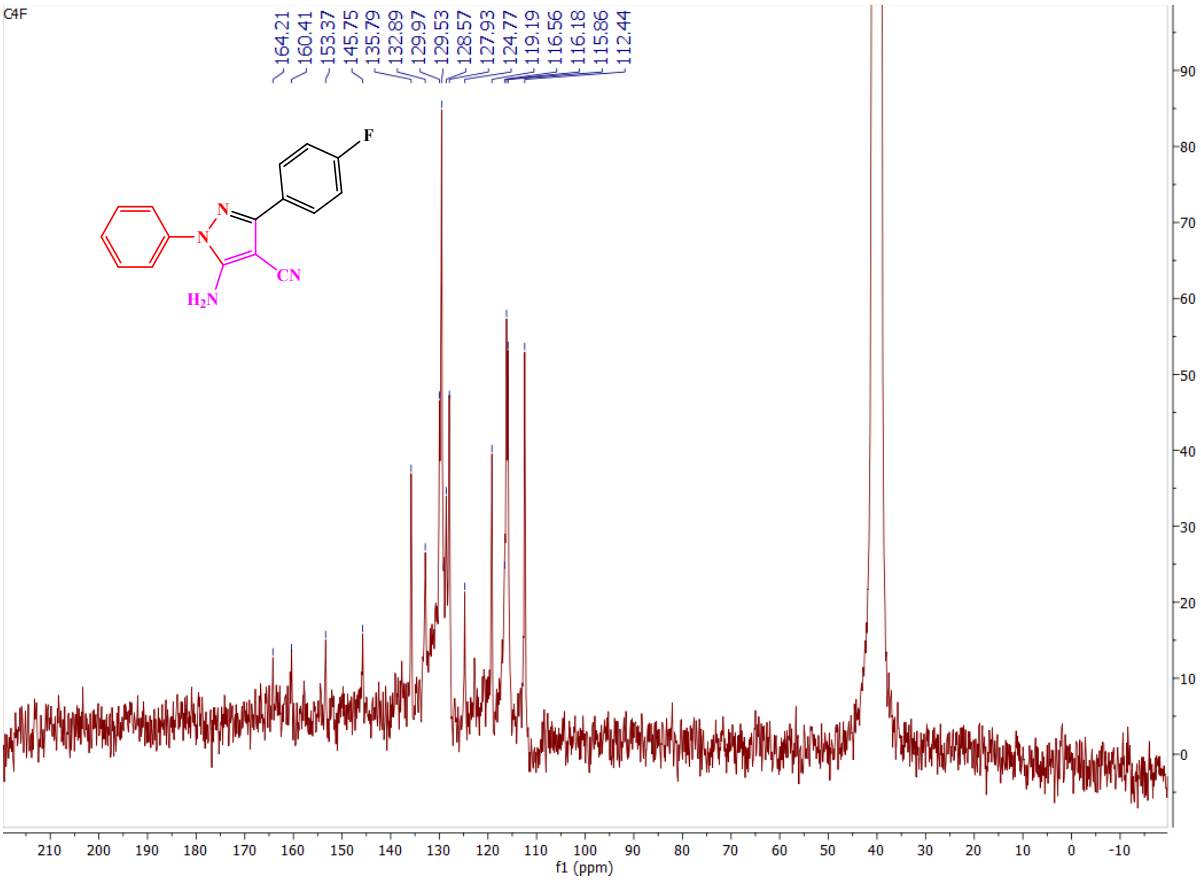


Fig. S21. The ^{13}C NMR spectrum of 5-amino-3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in DMSO solvent

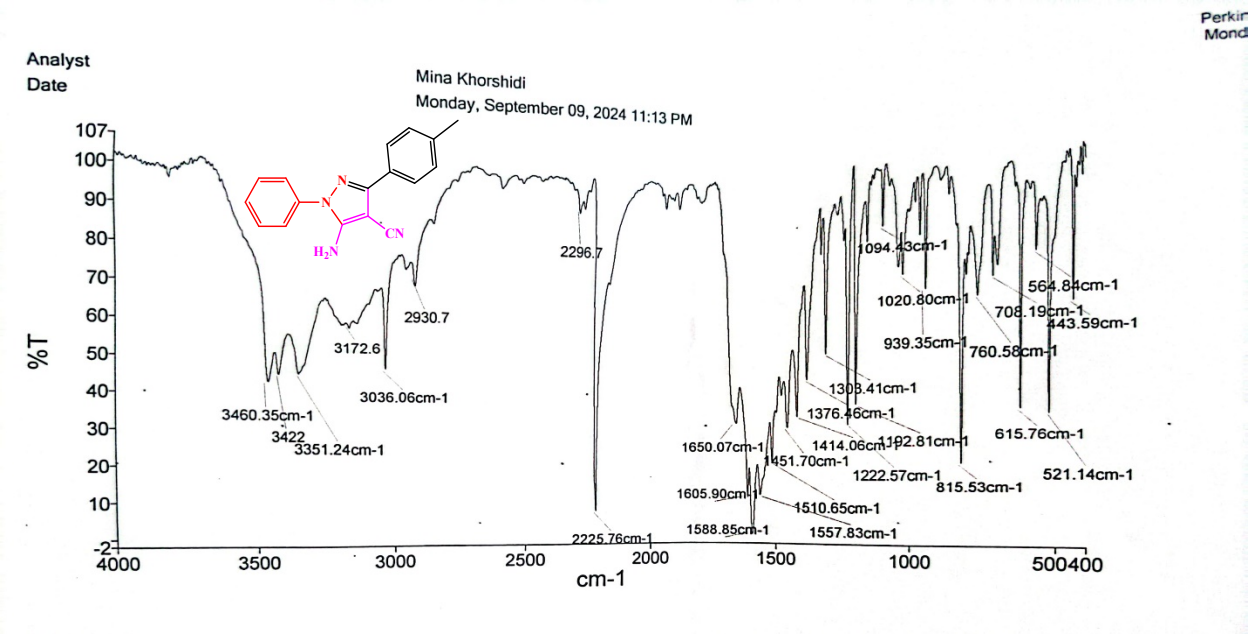


Fig. S22. The FTIR spectrum of 5-amino-1-phenyl-3-(p-tolyl)-1*H*-pyrazole-4-carbonitrile

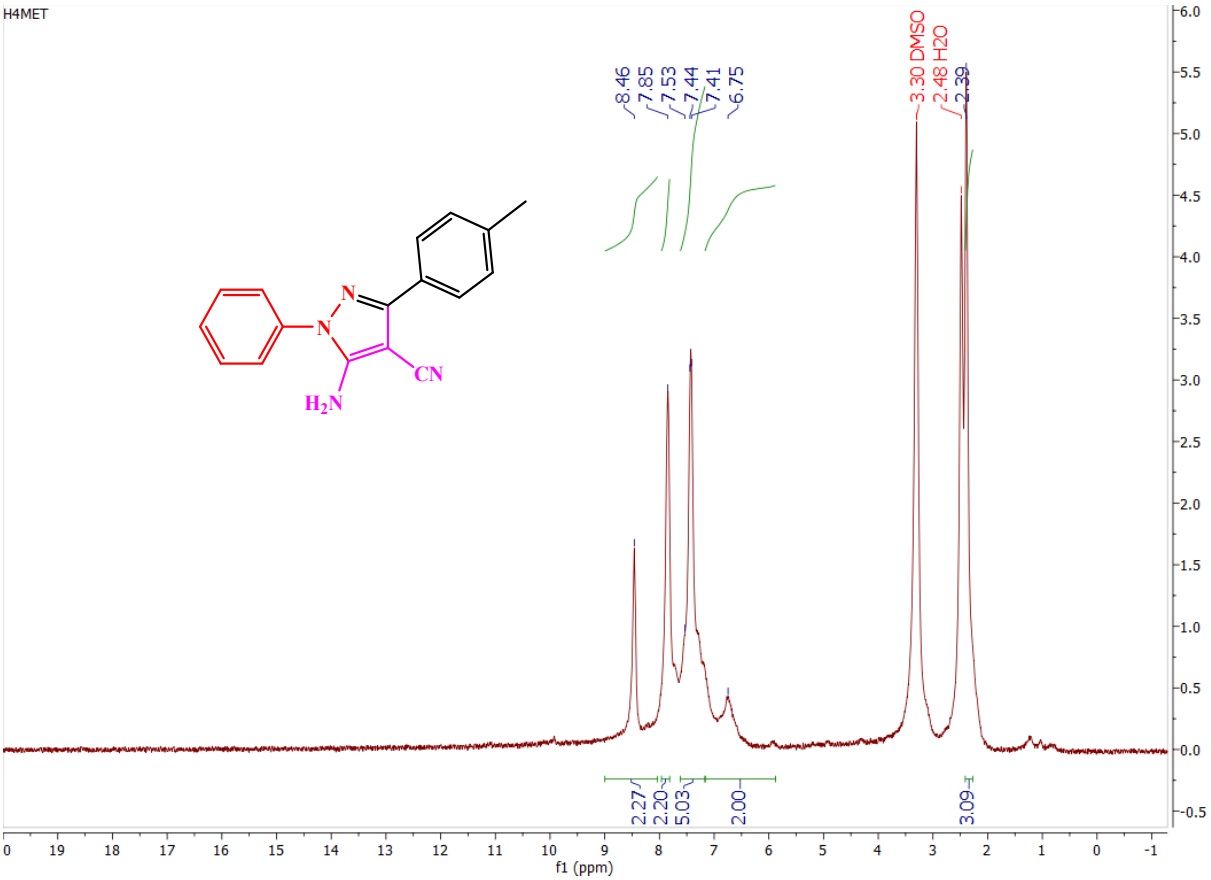


Fig. S23. The ^{1}H NMR spectrum of 5-amino-1-phenyl-3-(p-tolyl)-1*H*-pyrazole-4-carbonitrile in DMSO solvent

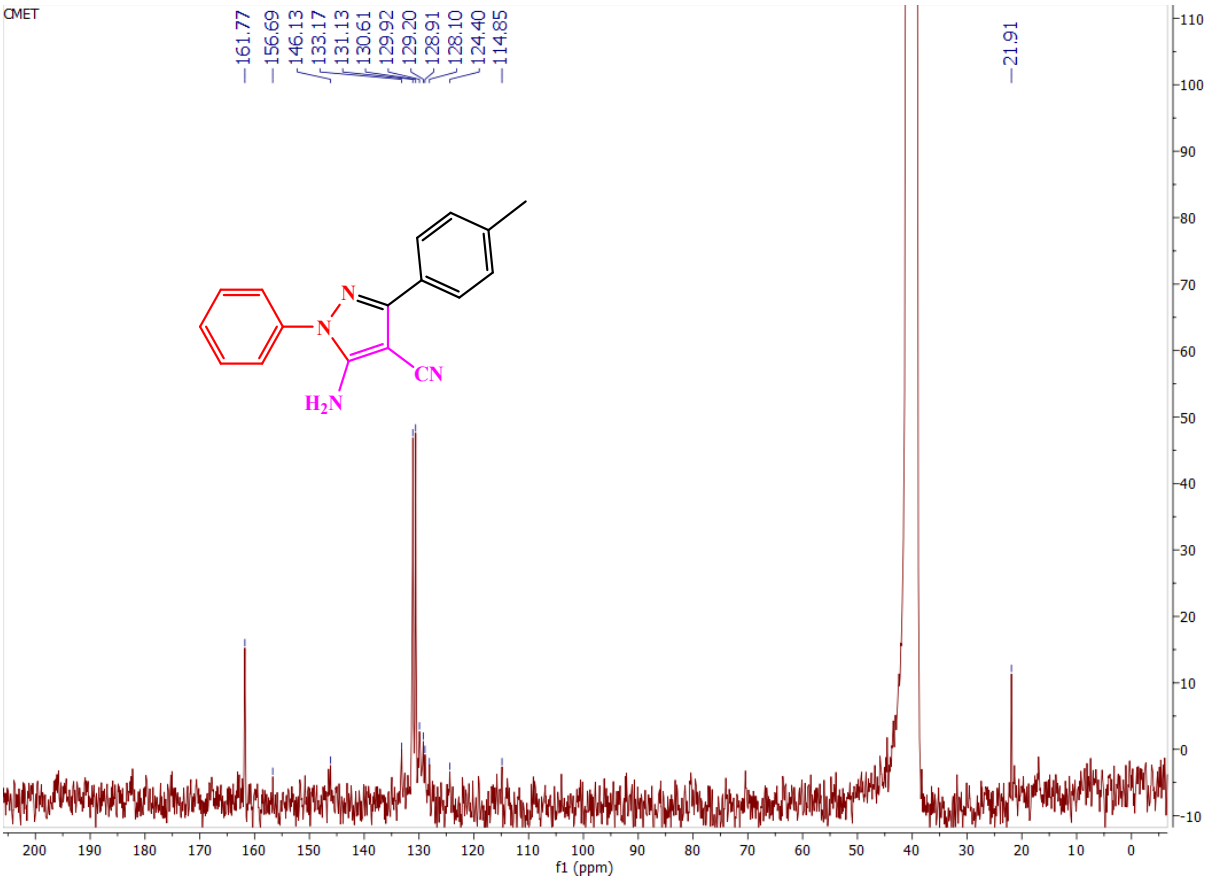


Fig. S24. The ^{13}C NMR spectrum of 5-amino-1-phenyl-3-(p-tolyl)-1*H*-pyrazole-4-carbonitrile in DMSO solvent

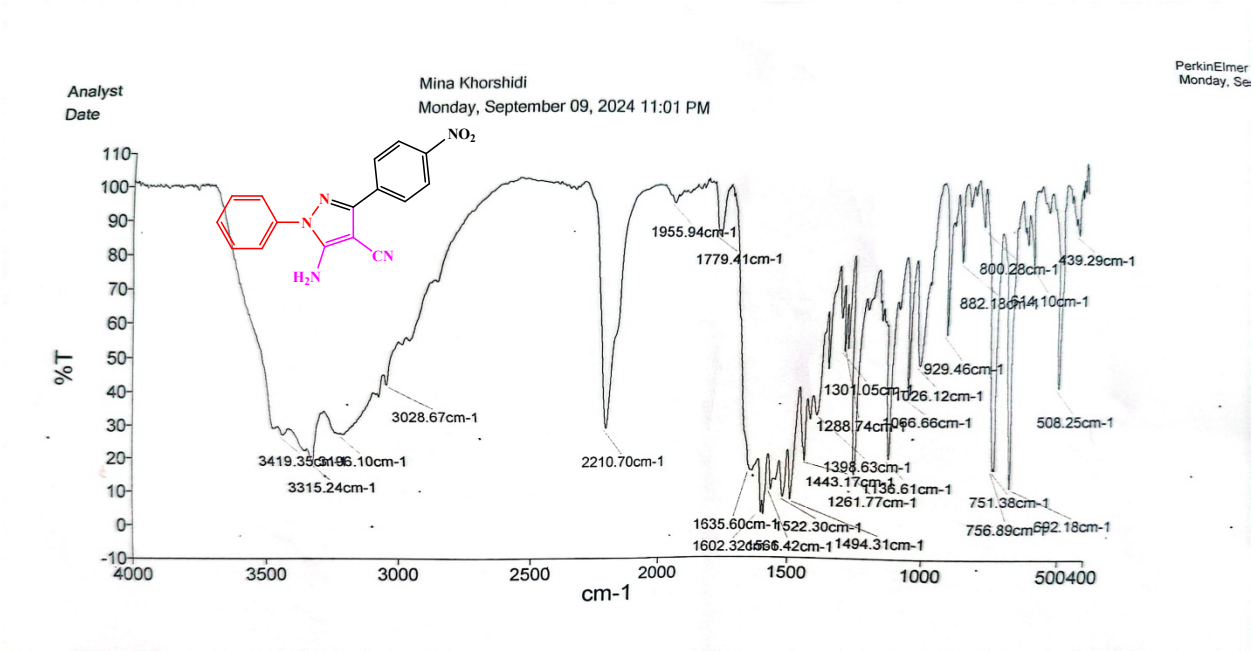


Fig. S25. The FTIR spectrum of 5-amino-3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile

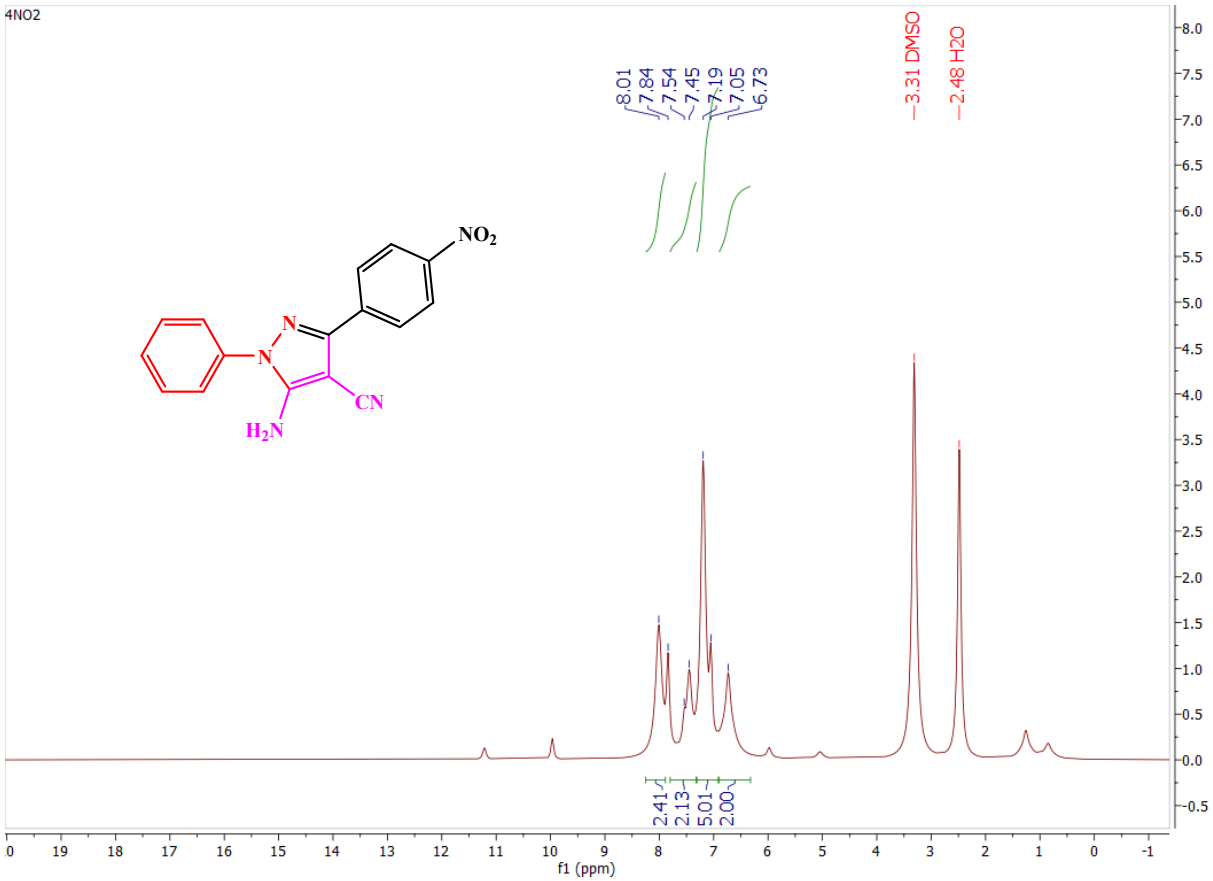


Fig. S26. The ^{1}H NMR spectrum of 5-amino-3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in DMSO solvent

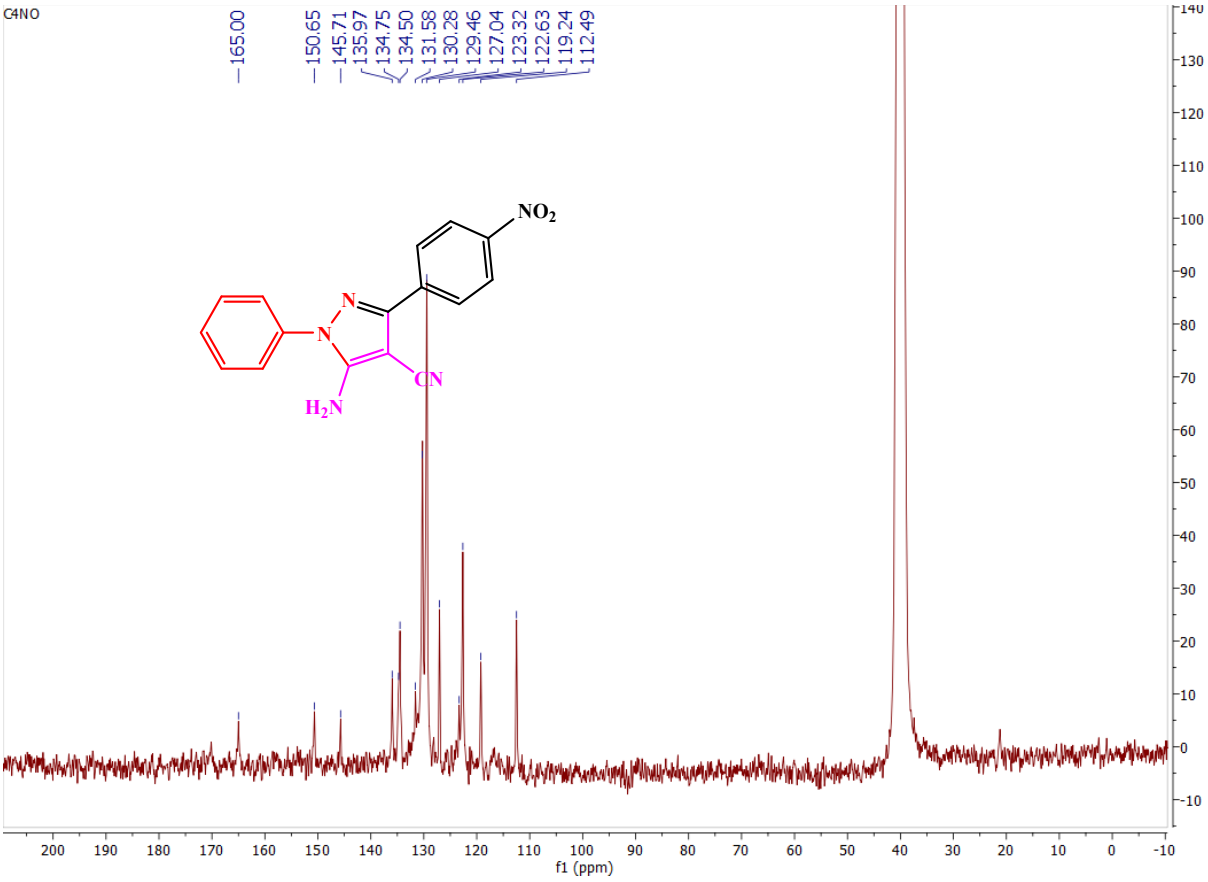


Fig. S27. The ^{13}C NMR spectrum of 5-amino-3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile in DMSO solvent

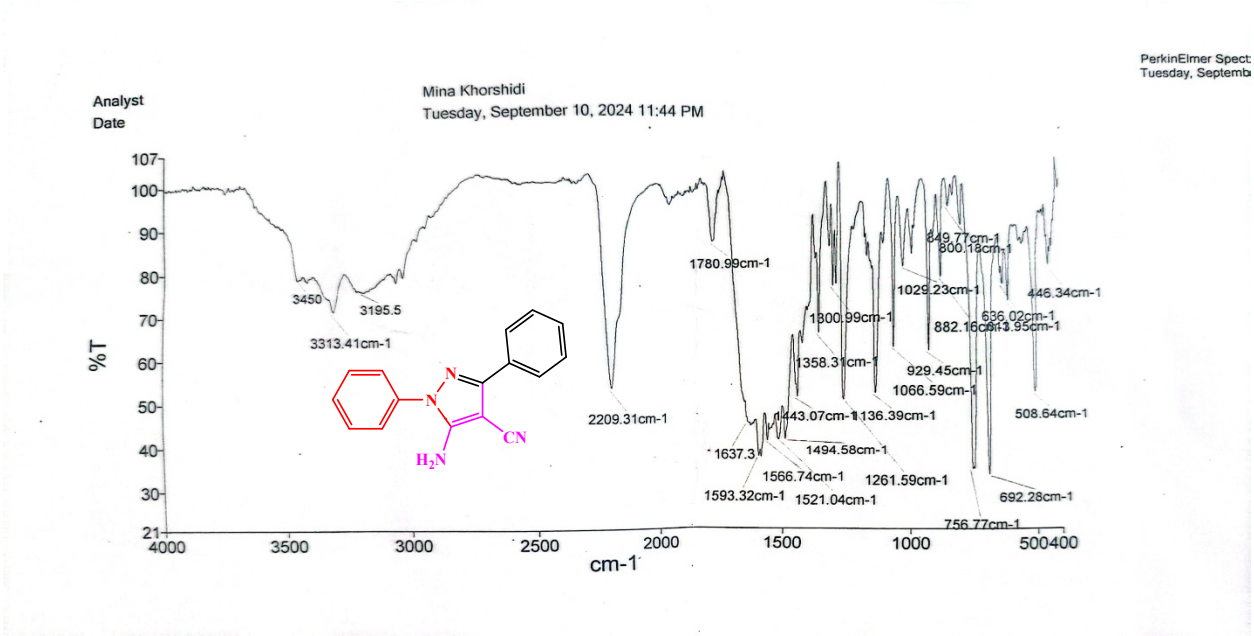


Fig. S28. The FTIR spectrum of 5-amino-1,3-diphenyl-1*H*-pyrazole-4-carbonitrile

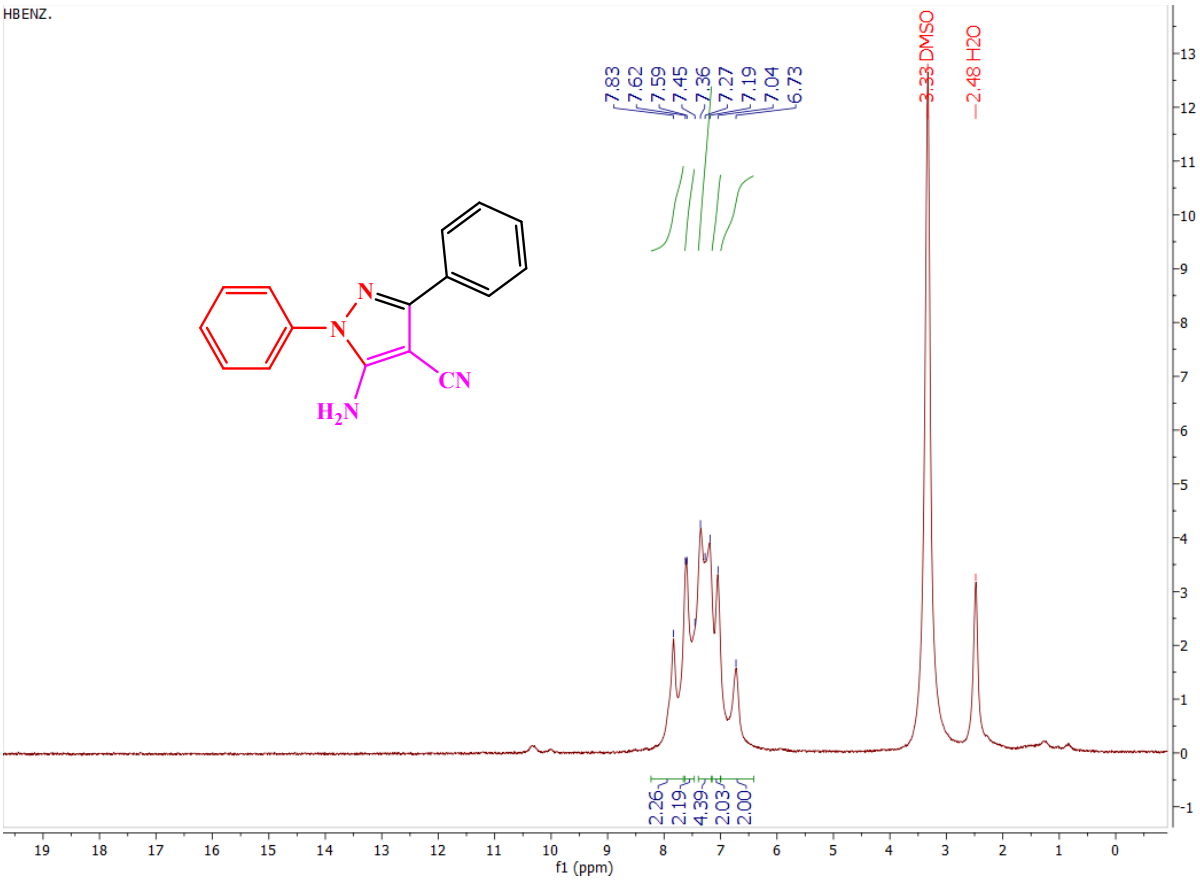


Fig. S29. The ^{1}H NMR spectrum of 5-amino-1,3-diphenyl-1*H*-pyrazole-4-carbonitrile in DMSO solvent

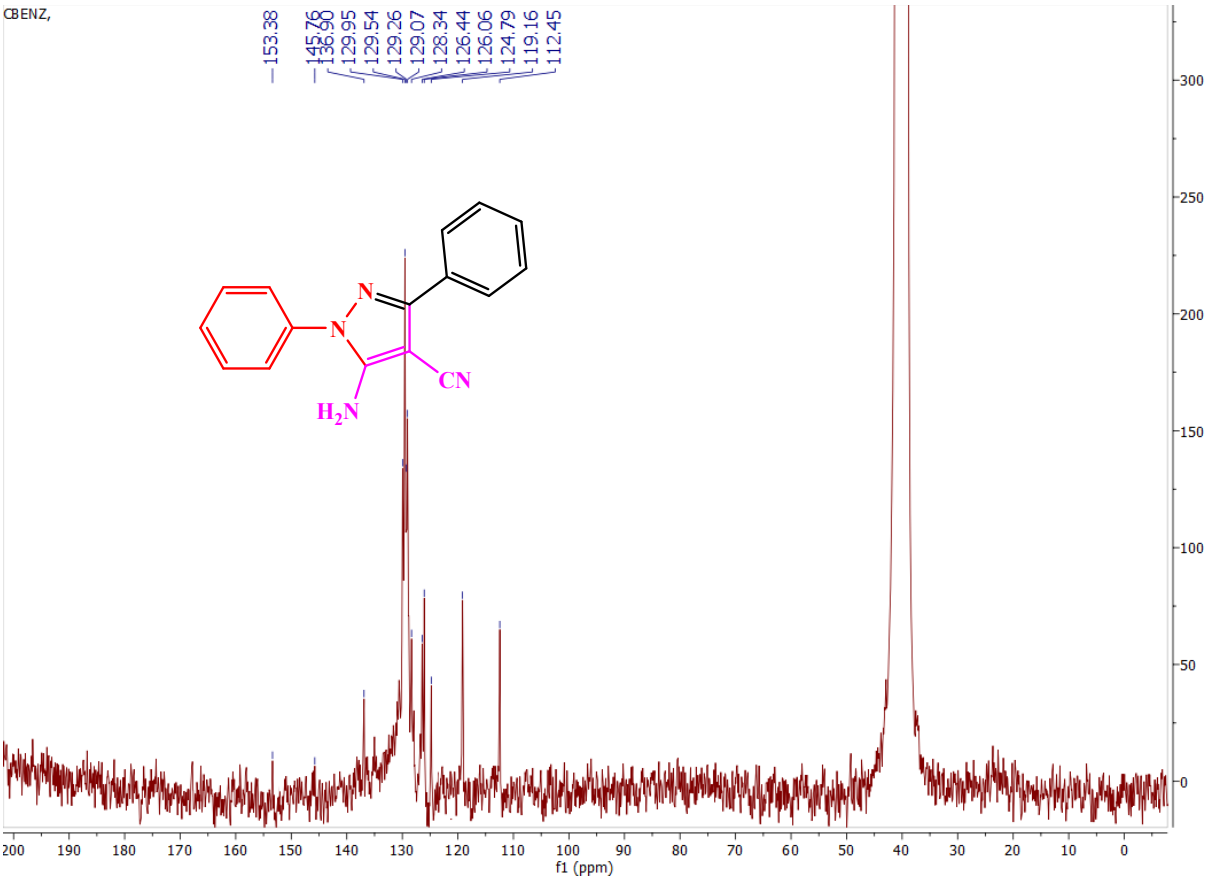


Fig. S30. The ^{13}C NMR spectrum of 5-amino-1,3-diphenyl-1*H*-pyrazole-4-carbonitrile in DMSO solvent

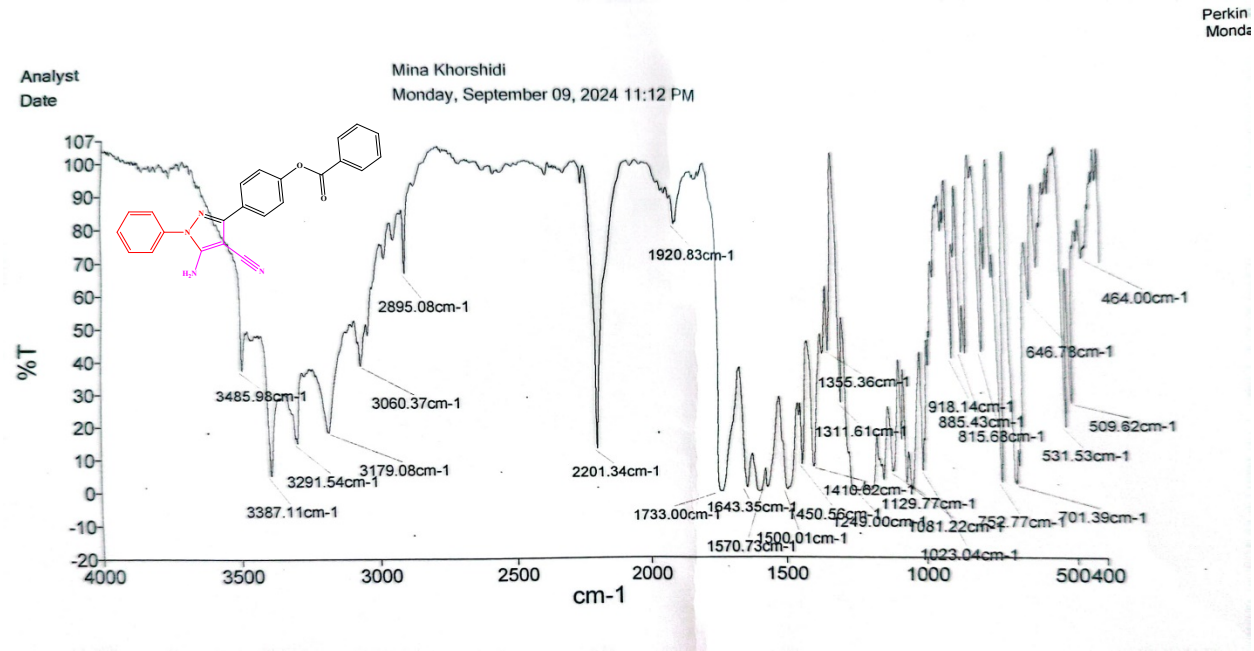


Fig. S31. The FTIR spectrum of 4-(5-amino-4-cyano-1-phenyl-1*H*-pyrazol-3-yl)phenyl benzoate

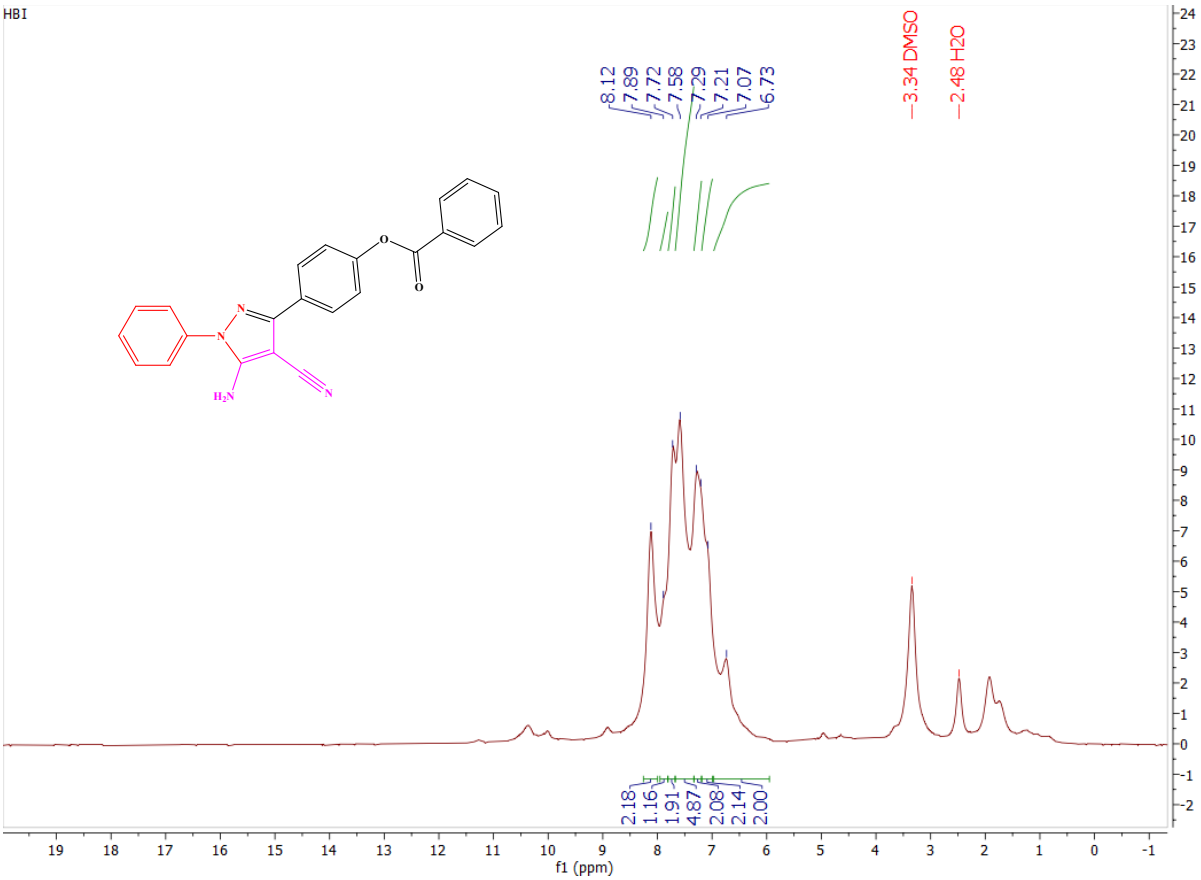


Fig. S32. The ^{1}H NMR spectrum of 4-(5-amino-4-cyano-1-phenyl-1*H*-pyrazol-3-yl)phenyl benzoate in DMSO solvent

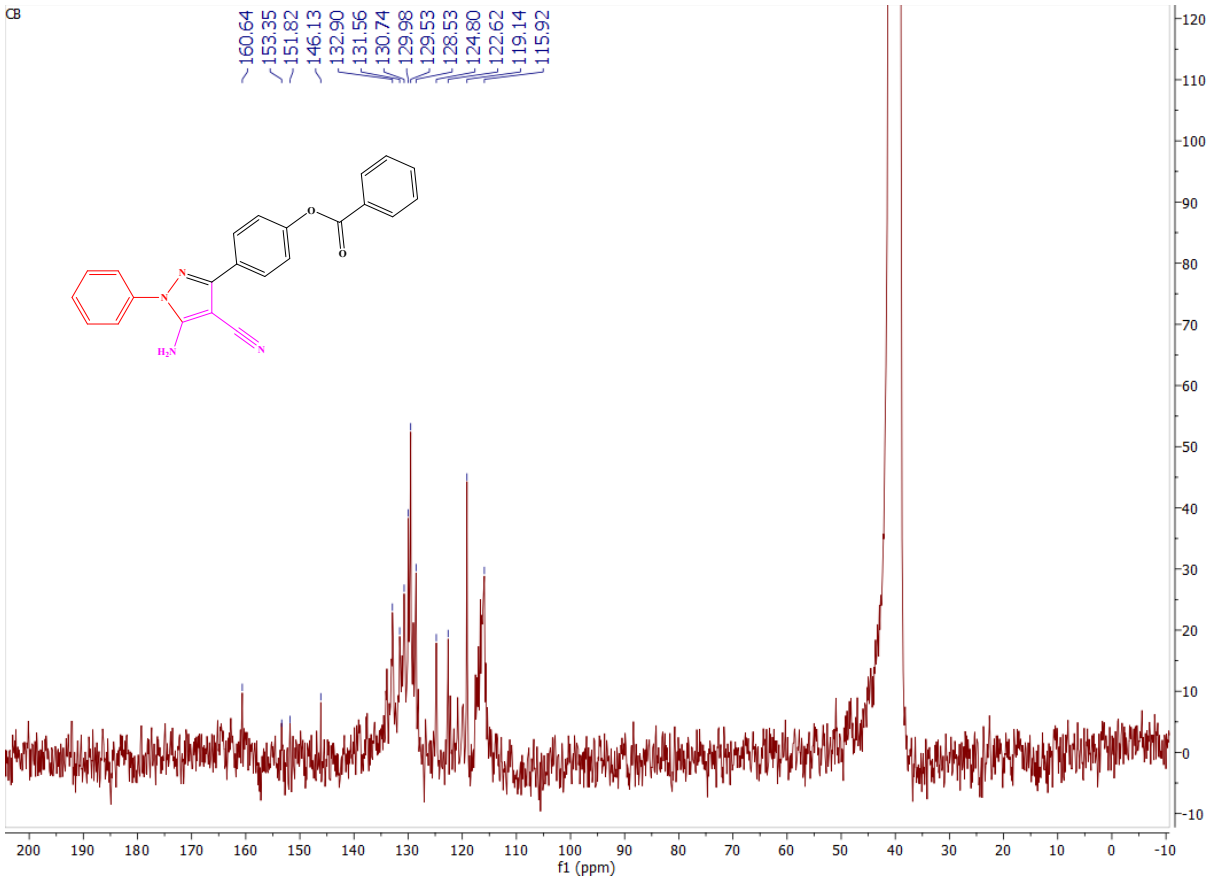


Fig. S33. The ^{13}C NMR spectrum of 4-(5-amino-4-cyano-1-phenyl-1*H*-pyrazol-3-yl)phenyl benzoate in DMSO solvent