

Supporting Information

MgFe₂O₄@Tris magnetic nanoparticles: an effective and powerful catalyst for one-pot synthesis of pyrazolopyranopyrimidine and tetrahydrodipyrzoloypyridine derivatives

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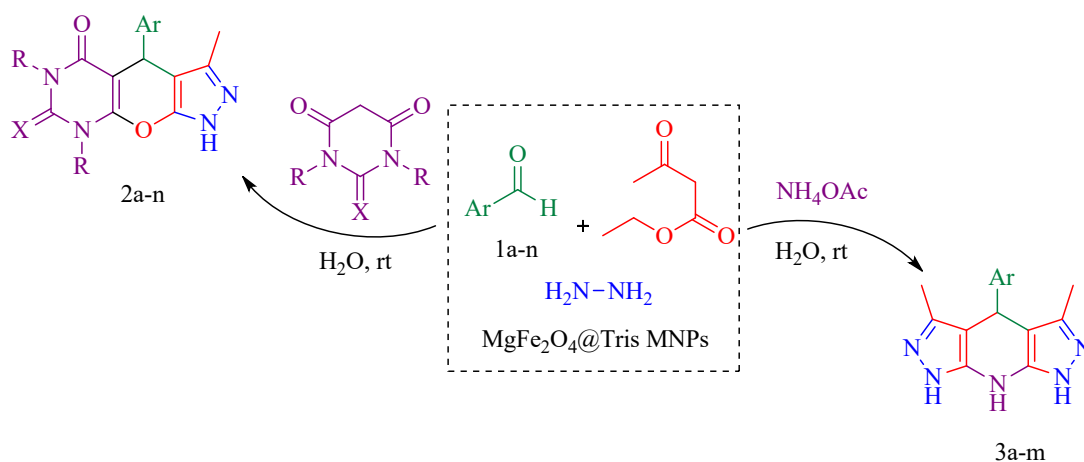
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Abstract

Magnesium (Mg) as a metal has wide applications, but its use in chemical reactions is rarely reported. Currently, magnesium catalytic processes are being developed to synthesize basic chemical compounds. Therefore, an effective and recyclable nano-catalyst was synthesized using MgFe₂O₄@Tris in this study. The structure of the MgFe₂O₄@Tris was characterized by various techniques including Fourier-transform infrared (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and vibrating sample magnetometer (VSM) techniques. Finally, the catalytic activity of this nano-catalyst was evaluated for the synthesis of pyrazolopyranopyrimidine and tetrahydrodipyrzoloypyridine derivatives. Among the advantages of this catalyst are its high catalytic activity, high yields, use of environmentally friendly solvents, easy magnetic separation, and the possibility of reusing the catalyst.

General information about the equipment, solvents and raw materials used

All reactants used in this research were purchased from Merck, Fluka, or Sigma-Aldrich Chemical Companies. The melting points were defined by Barnstead Electrothermal 9100 in capillary tubes. The Infrared (IR) spectra of samples were recorded in KBr pellets using a VRTEX 70 spectrophotometer (Bruker, Germany). ¹³C and ¹H NMR spectra (in Hertz) were obtained by Bruker DRX-250 AVANCE instrument in DMSO-*d*₆ as the solvent and TMS as the internal standard. Energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) were accomplished and utilized a Czech TESCAN instrument. Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (PerkinElmer-STA6000, USA), and magnetic measurements of the nanocatalyst were obtained using a vibrating sample magnetometer (VSM; MDKB). X-ray diffraction (XRD) was collected using a Holland Philips PW1730 and TEM of the MNPs was recorded with a Philips-EM 208S TEM.



Scheme S1. Synthesis of pyrazolopyranopyrimidines and tetrahydrodipyrzoloypyridine using MgFe₂O₄@Tris MNPs

Data on the physical properties of pyrazolopyranopyrimidines

3-Methyl-4-(4-chlorophenyl)-6,8-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7(1H,4H)-dione (2a) (Table 2, Entry 1)

White solid; Yield: 98%; M.p. 218-220°C.

3-Methyl-4-phenyl-6,8-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7(1H,4H)-dione (2b) (Table 2, Entry 2)

White solid; Yield: 98%; M.p. 215-218°C.

3-Methyl-4-(4-methoxyphenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7 (6H,8H)-diones (2c) (Table 2, Entry 3)

Yellow solid; Yield: 97%; M.p. 226-228°C.

3-Methyl-4-(2-methoxyphenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7 (6H,8H)-diones (2e) (Table 2, Entry 5)

Pale yellow solid; Yield: 92%; M.p. 228-230°C.

3-Methyl-4-(3-hydroxyphenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7 (6H,8H)-diones (2f) (Table 2, Entry 6)

Pale yellow solid; Yield: 94%; M.p. 278-280°C.

3-Methyl-4-(4-bromophenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7 (6H,8H)-diones (2h) (Table 2, Entry 8)

White solid; Yield: 95%; M.p. 210-212°C.

4-(4-Methoxyphenyl)-3-methyl-7-thioxo-4,6,7,8-tetrahydropyrazolo[5,6]pyrano[2,3-d]pyrimidine-5(1H)-one (2j) (Table 2, Entry 10)

yellow solid; Yield: 92%; M.p. 224-225°C.

4-phenyl-3-methyl-7-thioxo-4,6,7,8-tetrahydropyrazolo[5,6]pyrano[2,3-d]pyrimidine-5(1H)-one (2k) (Table 2, Entry 11)

yellow solid; Yield: 94%; M.p. 219-220°C.

4-(2-hydroxyphenyl)-3-methyl-7-thioxo-4,6,7,8-tetrahydropyrazolo[5,6]pyrano[2,3-d]pyrimidine-5(1H)-one (2l) (Table 2, Entry 12)

yellow solid; Yield: 95%; M.p. 267-270°C.

4-(4-Chlorophenyl)-3,6,8-trimethyl-6,8-dihydropyrazolo(4',3':5,6)pyrano(2,3-d)pyrimidine-5,7(1H,4H)-dione (2n) (Table 2, Entry 14)

White solid; Yield: 98%; M.p. 200-202°C.

4-(2-Methoxyphenyl)-3-methyl-7-thioxo-4,6,7,8-tetrahydropyrazolo[5,6]pyrano[2,3-d]pyrimidine-5(1H)-one (2m) (Table 2, Entry 13)

yellow solid; Yield: 97%; M.p. 222-225°C; IR (KBr): 3468, 3130, 2891, 1609, 1544, 1391, 1287, 1242 cm⁻¹; ¹H NMR (250 MHz, DMSO-d₆) δ (ppm): 13.5 (br, 1H), 11.42 (s, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.10 (t, J = 7.9 Hz, 1H), 6.80 (dd, J

= 12.4, 7.4 Hz, 2H), 5.63 (s, 1H), 3.71 (s, 1H), 3.64 (s, 3H), 3.42 (q, J = 7.3 Hz, 1H), 2.26 (s, 3H), 1.03 (t, J = 7.2 Hz, 1H);
¹³C NMR (63 MHz, DMSO-d₆) δ (ppm): 173.18, 163.75, 159.89, 157.13, 144.36, 130.32, 128.85, 127.56, 120.00, 111.17, 106.09, 95.32, 56.50, 55.76, 26.53, 10.60.

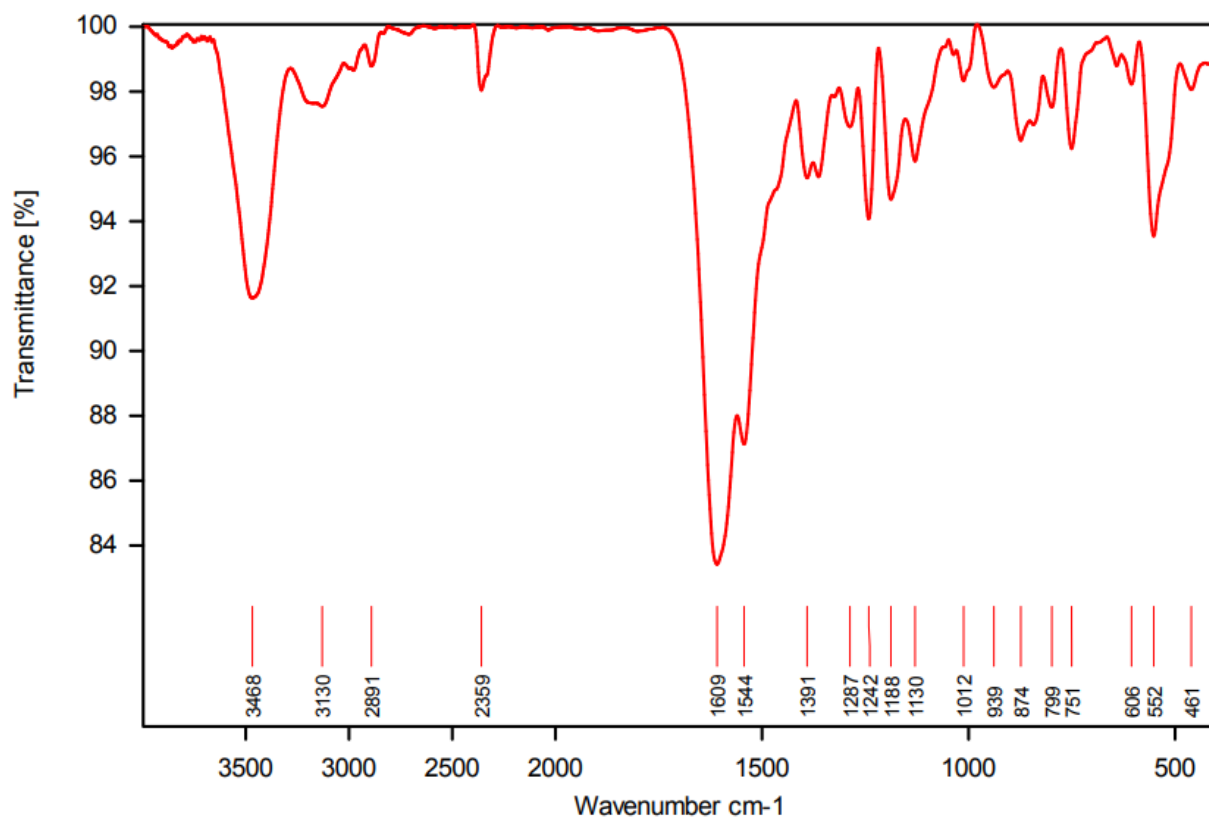
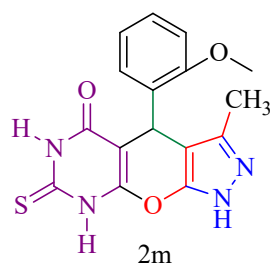


Figure S1. The FT-IR spectrum of 4-(2-Methoxyphenyl)-3-methyl-7-thioxo-4,6,7,8- tetrahydropyrazolo[5,6]pyrano[2,3-d]pyrimidine-5(1H)-one (2m) (Table 2, Entry 13)

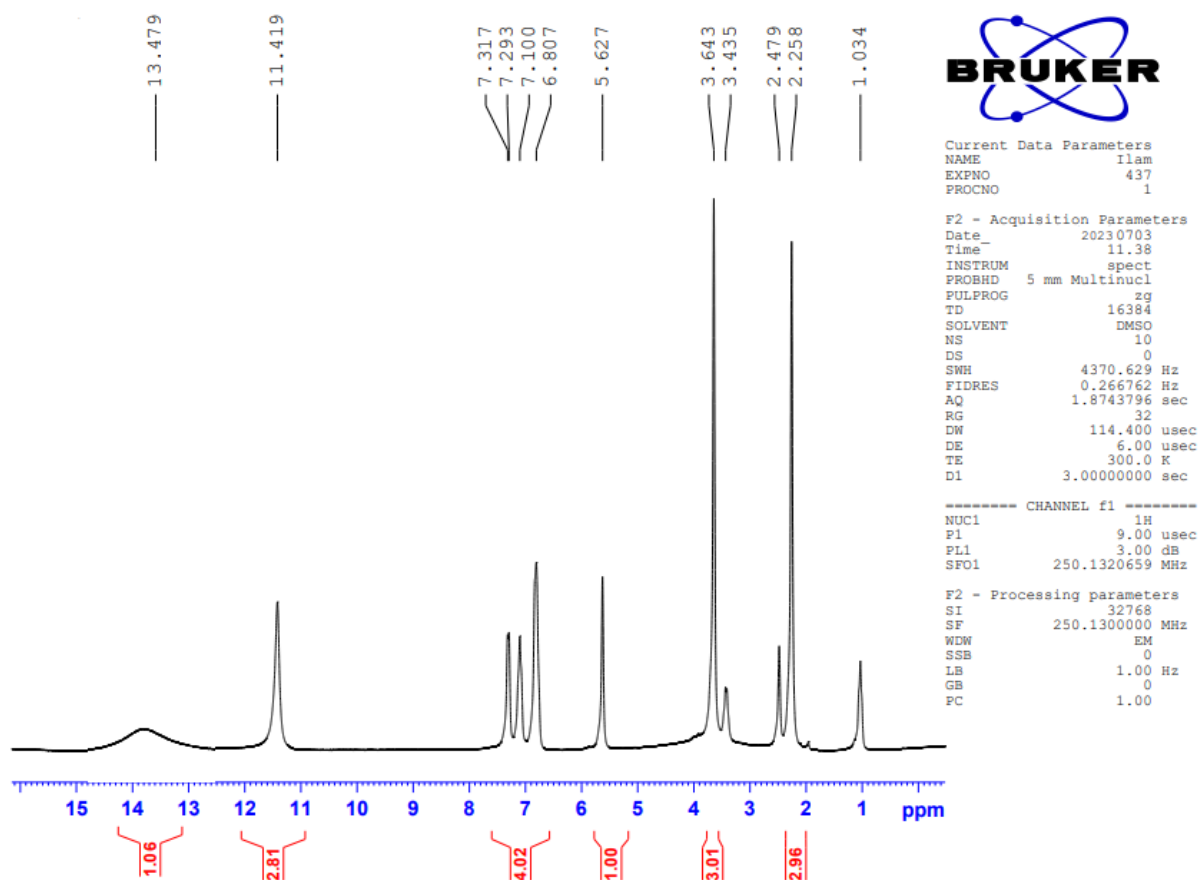


Figure S2. The ^1H NMR spectrum of 4-(2-Methoxyphenyl)-3-methyl-7-thioxo-4,6,7,8- tetrahydropyrazolo[5,6]pyrano[2,3-d]pyrimidine-5(1H)-one (2m) (Table 2, Entry 13)

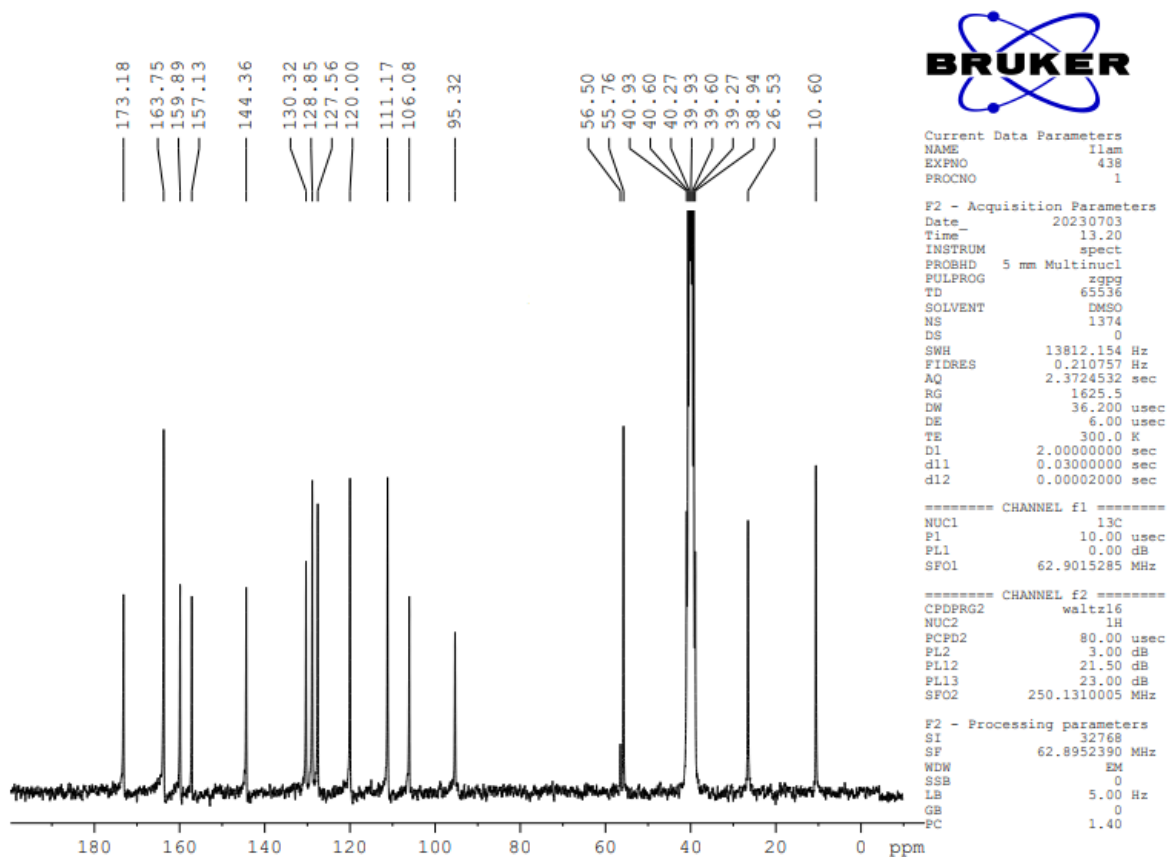
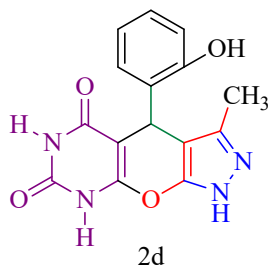


Figure S3. The ^{13}C NMR spectrum of 4-(2-Methoxyphenyl)-3-methyl-7-thioxo-4,6,7,8-tetrahydropyrazolo[5,6]pyrano[2,3-d]pyrimidine-5(1H)-one (2m) (Table 2, Entry 13)

3-Methyl-4-(2-hydroxyphenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7(6H,8H)-diones (2d)
(Table 2, Entry 4)

yellow solid; Yield: 97%; M.p. 264-268°C; ^1H NMR (250 MHz, DMSO- d_6) δ (ppm): 13.3 (br, 1H), 10.08 (s, 3H), 7.25 (s, 2H), 6.90 (s, 2H), 6.62 (s, 4H), 5.54 (s, 1H), 4.50 (s, 1H), 4.11 (s, 1H), 2.19 (s, 6H), 1.26 (s, 2H); ^{13}C NMR (63 MHz, DMSO- d_6) δ (ppm): 165.3, 160.99, 155.09, 151.00, 144.1, 132.9, 132.0, 129.24, 126.96, 118.51, 115.22, 106.1, 90.91, 81, 26. 18.92, 10.79.



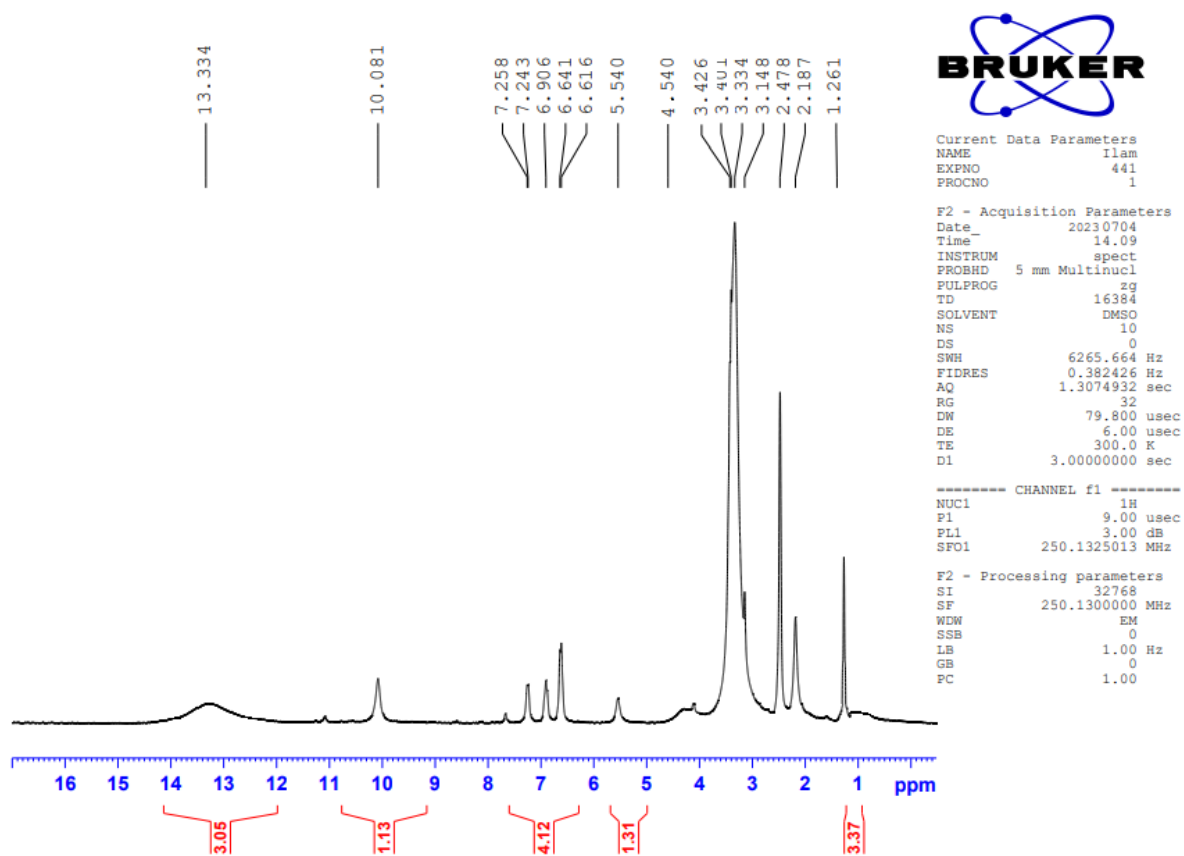


Figure S4. The ^1H NMR spectrum of 3-Methyl-4-(2-hydroxyphenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7 (6H,8H)-diones (2f) (Table 2, Entry 4)

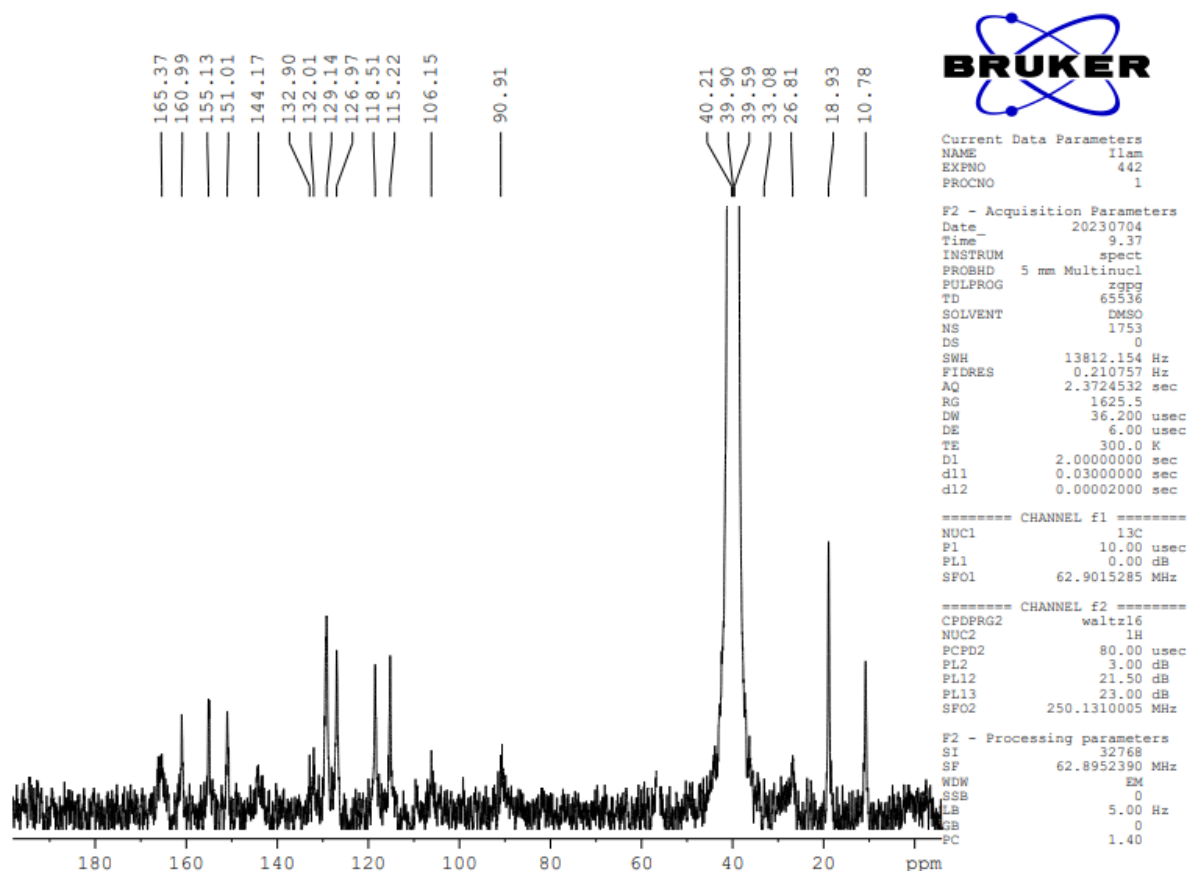
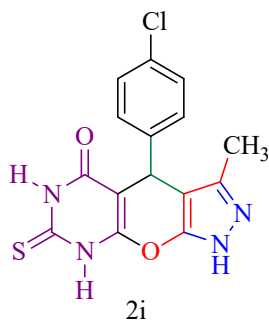


Figure S5. The ^{13}C NMR spectrum of 3-Methyl-4-(2-hydroxyphenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7 (6H,8H)-diones (2d) (Table 2, Entry 4)

4-(4-chlorophenyl)-3-methyl-7-thioxo-4,6,7,8-tetrahydropyrazolo[5,6]pyrano[2,3-d]pyrimidine-5(1H)-one (2i)
(Table 2, Entry 9)

White solid; Yield: 98%; M.p. 224-226°C; IR (KBr): 3418, 2873, 1597, 1533, 1351, 1308, 1190 cm^{-1} ; ^1H NMR (250 MHz, DMSO- d_6) δ (ppm): 11.49 (s, 2H), 7.24 (s, 2H), 7.03 (s, 2H), 5.39 (s, 1H), 2.23 (s, 3H); ^{13}C NMR (63 MHz, DMSO- d_6) δ (ppm): 173.61, 163.73, 159.51, 144.21, 141.34, 130.57, 129.00, 128.27, 105.50, 96.23, 30.67, 10.38.



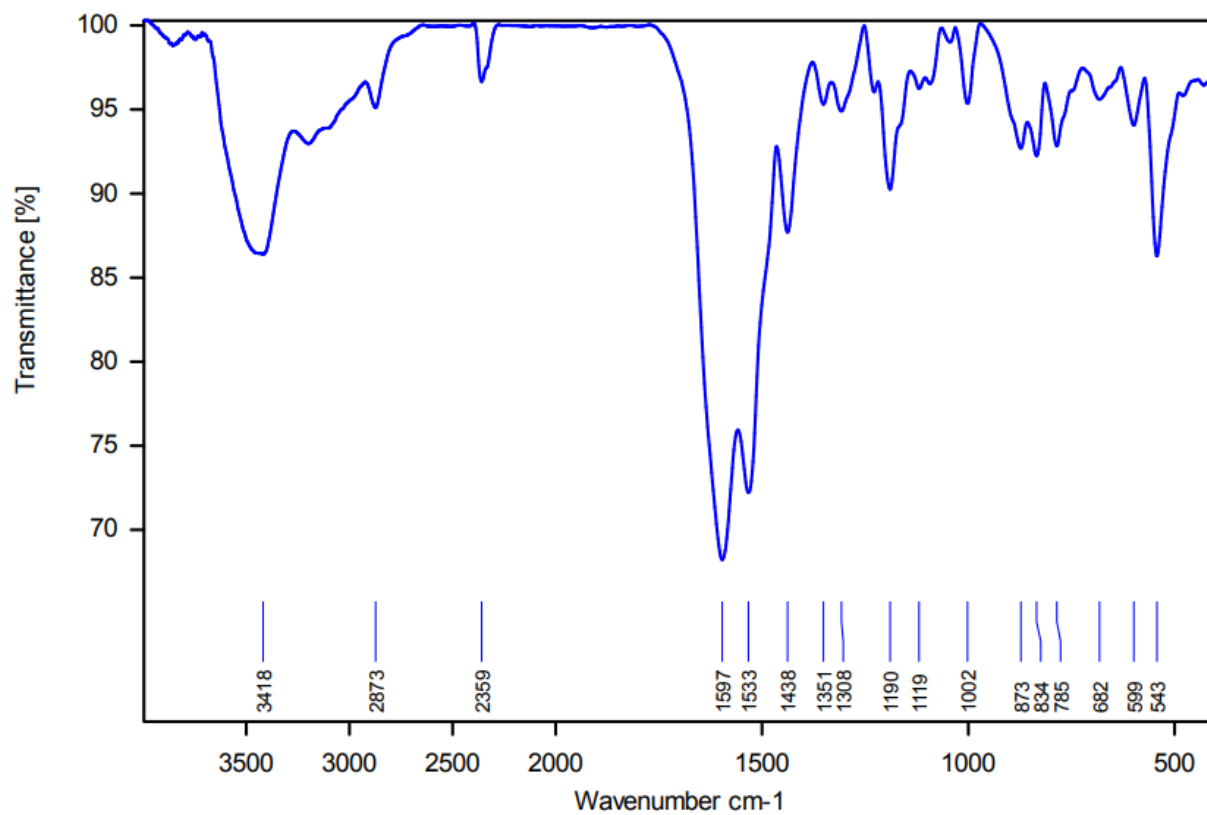


Figure S6. The FT-IR spectrum of 4-(4-chlorophenyl)-3-methyl-7-thioxo-4,6,7,8-tetrahydropyrazolo [5,6]pyrano[2,3-d]pyrimidine-5(1H)-one (2i) (Table 2, Entry 9)

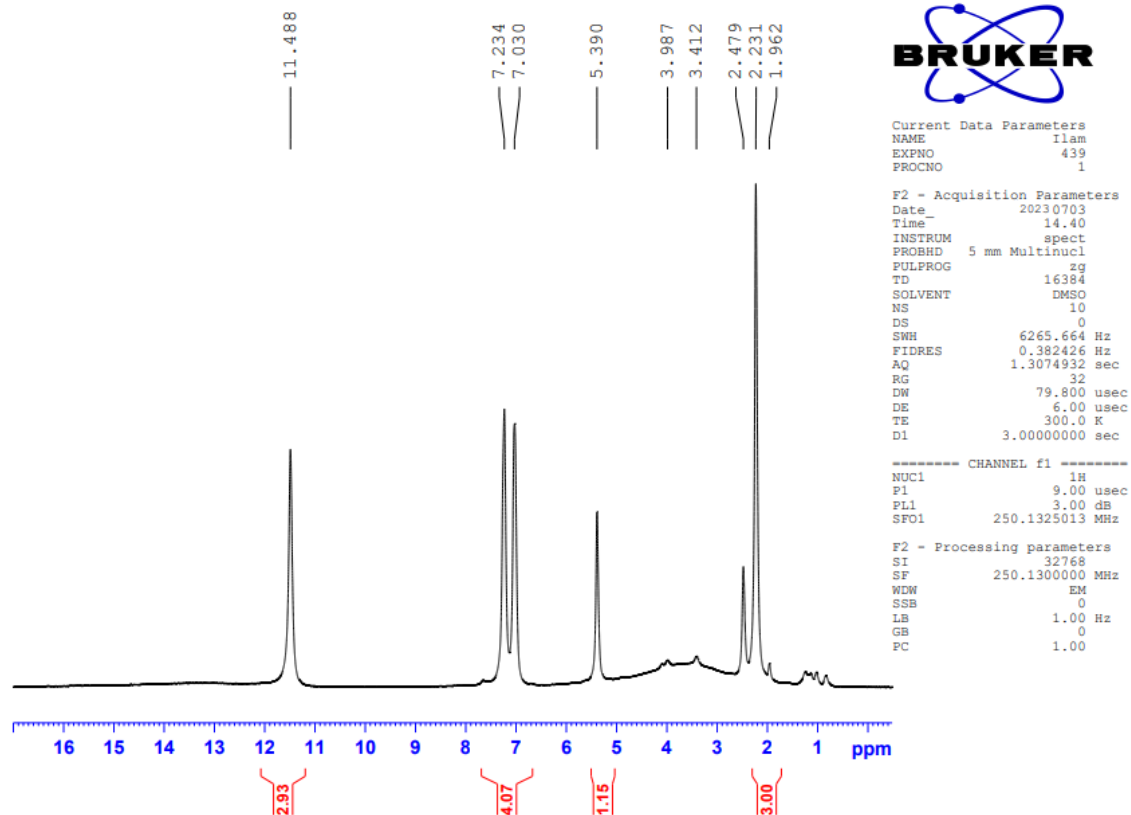


Figure S7. The ^1H NMR spectrum of 4-(4-chlorophenyl)-3-methyl-7-thioxo-4,6,7,8-tetrahydropyrazolo[5,6]pyrano[2,3-d]pyrimidine-5(1H)-one (2i) (Table 2, Entry 9)

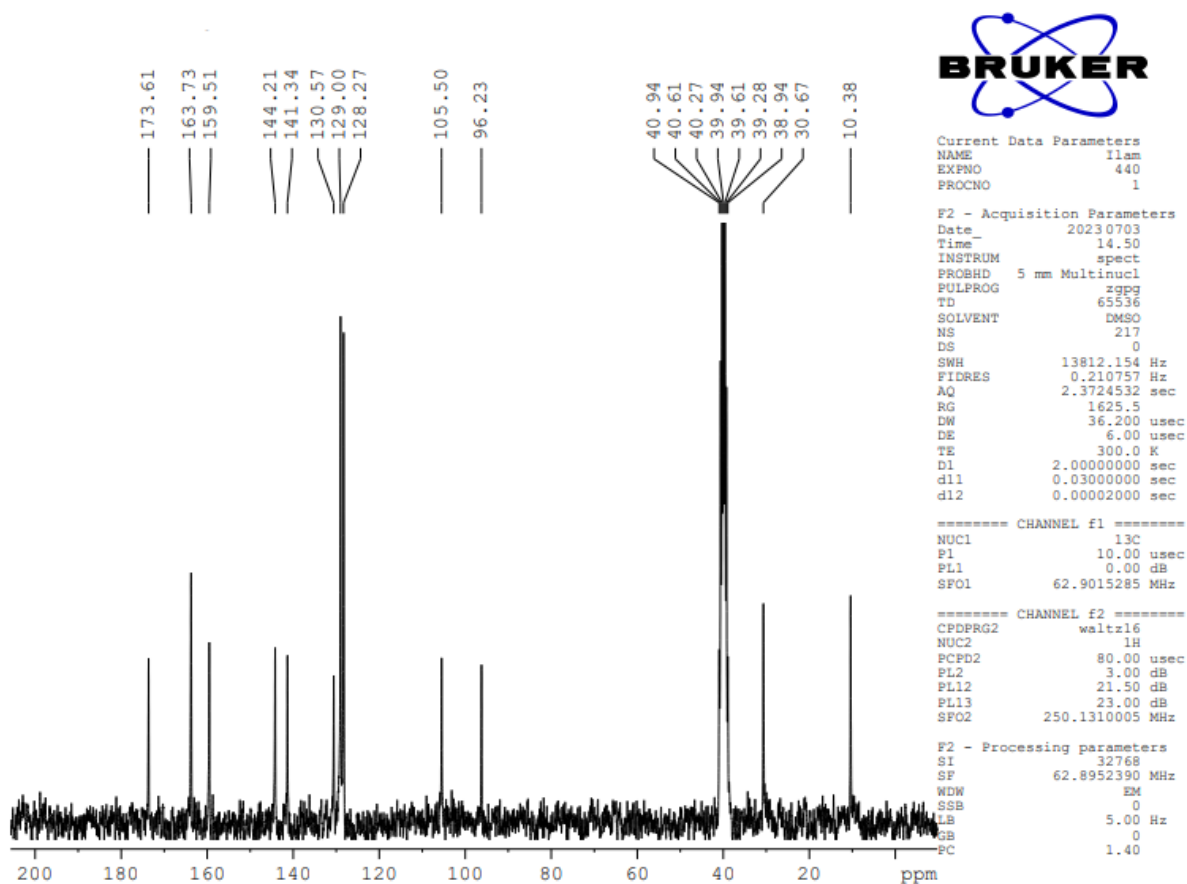
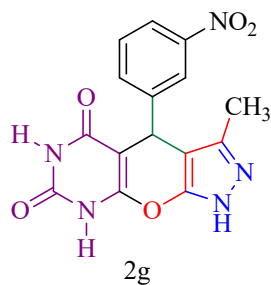


Figure S8. The ^{13}C NMR spectrum of 4-(4-chlorophenyl)-3-methyl-7-thioxo-4,6,7,8-tetrahydropyrazolo[5,6]pyrano[2,3-d]pyrimidine-5(1H)-one (2i) (Table 2, Entry 9)

3-Methyl-4-(3-nitrophenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7(6H,8H)-diones (2g) (Table 2, Entry 7)

white solid; Yield: 80%; M.p. 266-268°C; IR (KBr): 3616, 3497, 3160, 2924, 1712, 1585, 1527, 1479, 1299, 1231, 1184, 548 cm^{-1} ; ^1H NMR (250 MHz, DMSO- d_6) δ (ppm): 13.24 (s, 1H), 10.27 (s, 4H), 7.99 (s, 2H), 7.85 (s, 2H), 7.51 (s, 4H), 5.52 (s, 2H), 2.25 (s, 5H); ^{13}C NMR (63 MHz, DMSO- d_6) δ (ppm): 165.32, 160.47, 151.17, 148.16, 145.65, 144.29, 134.28, 129.89, 121.58, 121.20, 105.26, 91.34, 31.24, 10.46.



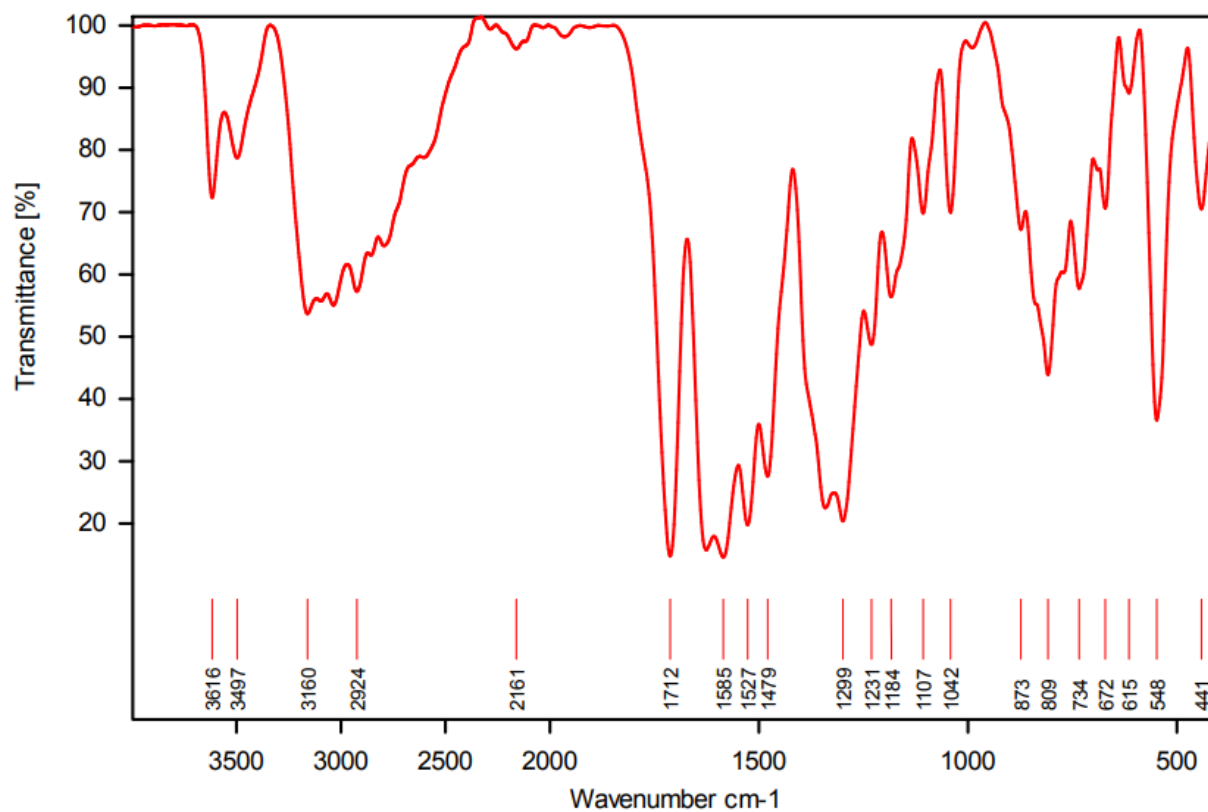


Figure S9. The FT-IR spectrum of 3-Methyl-4-(3-nitrophenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7(6H,8H)-diones (2g) (Table 2, Entry 7)

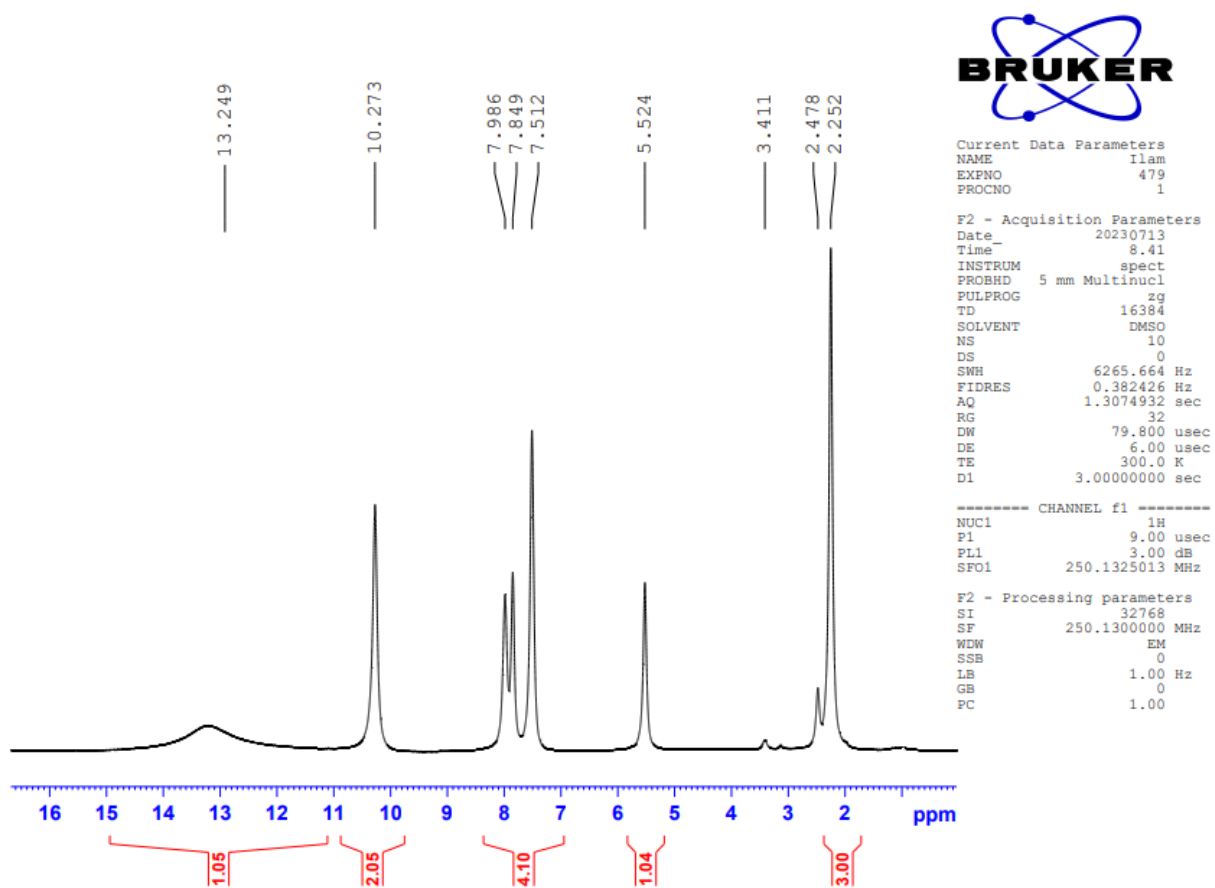


Figure S10. The ^1H NMR spectrum of 3-Methyl-4-(3-nitrophenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7(6H,8H)-diones (2g) (Table 2, Entry 7)

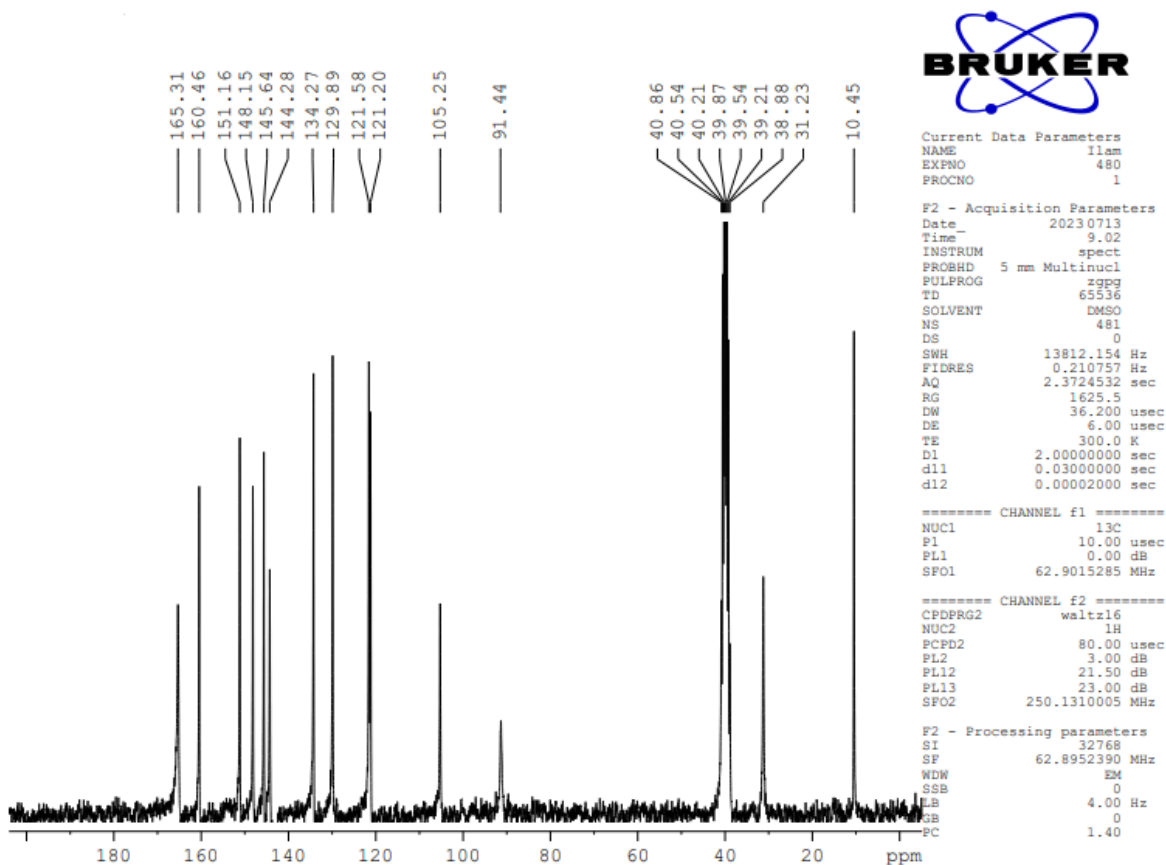


Figure S11. The ^{13}C NMR spectrum of 3-Methyl-4-(3-nitrophenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3-d]pyrimidine-5,7(6H,8H)-diones (2g) (Table 2, Entry 7)

Data on the physical properties of tetrahydrodipyrzolo[3,4-b;4',3'-e]pyridines

3,5-Dimethyl-4-(4-chlorophenyl)-1,4,7,8-tetrahydrodipyrzolo[3,4-b;4',3'-e]pyridine (3a) (Table 4, Entry 1)

white solid; Yield: 98%; M.p. 252-254°C.

3,5-Dimethyl-4-(4-methoxyphenyl)-1,4,7,8-tetrahydrodipyrzolo[3,4-b;4',3'-e]pyridine (3c) (Table 4, Entry 3)

Cream solid; Yield: 90%; M.p. 187-190°C.

3,5-Dimethyl-4-(2-nitrophenyl)-1,4,7,8-tetrahydrodipyrzolo[3,4-b;4',3'-e]pyridine (3e) (Table 4, Entry 5)

Cream solid; Yield: 88%; M.p. 189-190°C.

3,5-Dimethyl-4-(4-bromophenyl)-1,4,7,8-tetrahydrodipyrzolo[3,4-b;4',3'-e]pyridine (3g) (Table 4, Entry 7)

Pale yellow solid; Yield: 91%; M.p. 169-170°C.

3,5-Dimethyl-4-(4-hydroxyphenyl)-1,4,7,8-tetrahydrodipyrzolo[3,4-b;4',3'-e]pyridine (3h) (Table 4, Entry 8)

white solid; Yield: 92%; M.p. 269-270°C.

3,5-Dimethyl-4-(2-chlorophenyl)-1,4,7,8-tetrahydrodipyrzolo[3,4-b;4',3'-e]pyridine (3i) (Table 4, Entry 9)

pale brown solid; Yield: 90%; M.p. 165-167°C.

3,5-Dimethyl-4-(4-nitrophenyl)-1,4,7,8-tetrahydrodipyrzolo[3,4-b;4',3'-e]pyridine (3j) (Table 4, Entry 10)

Cream solid; Yield: 80%; M.p. 298-300°C.

3,5-Dimethyl-4-(3-bromophenyl)-1,4,7,8-tetrahydrodipyrzolo[3,4-b;4',3'-e]pyridine (3k) (Table 4, Entry 11)

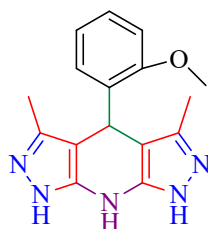
Cream solid; Yield: 91%; M.p. 247-248°C.

4- (1,4,7,8-Tetrahydro-3,5-dimethyldipyrzolo[3,4-b;4',3'-e] pyridin-4-yl)-N,N-dimethyl aniline (3l) (Table 4, Entry 12)

yellow solid; Yield: 90%; M.p. 240-243°C.

3,5-Dimethyl-4-(2-methoxyphenyl)-1,4,7,8-tetrahydrodipyrzolo[3,4-b;4',3'-e]pyridine (3d) (Table 4, Entry 4)

Pale yellow solid; Yield: 93%; M.p. 180-182°C; IR (KBr): 3218, 2929, 1730, 1598, 1462, 1281, 1032, 751 cm⁻¹.



3d

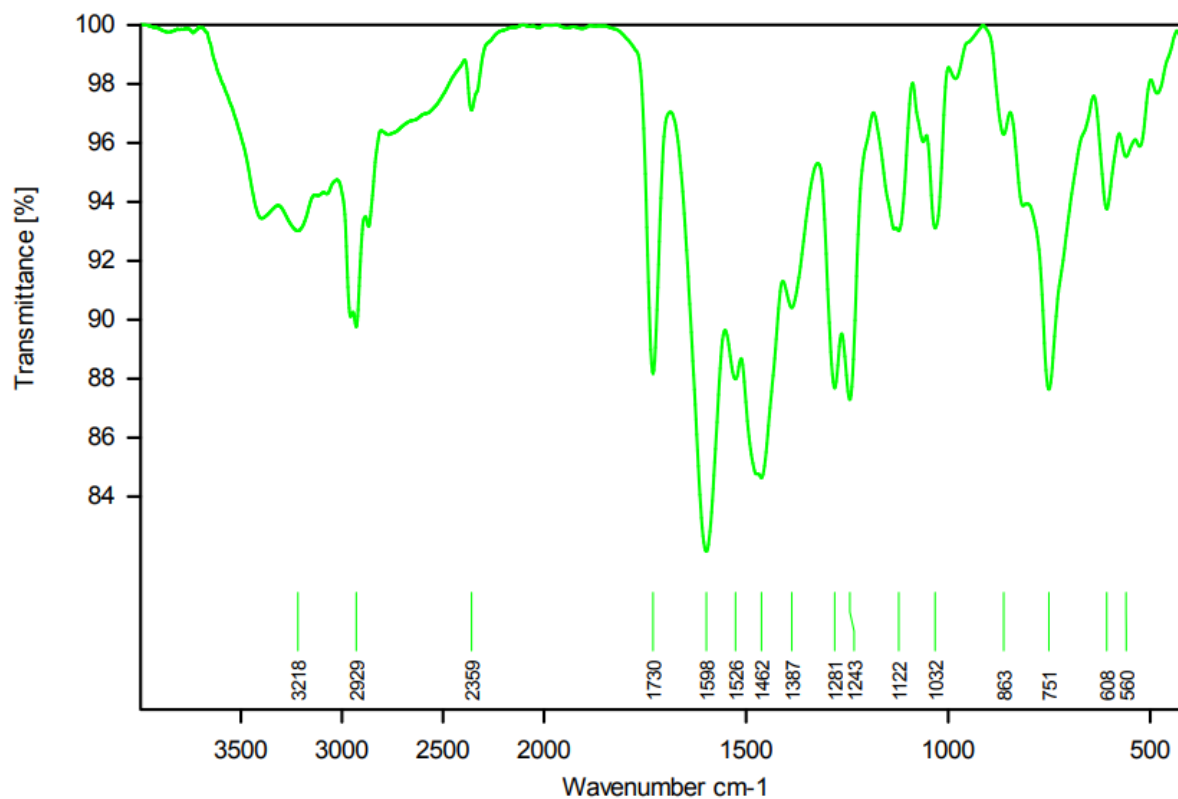


Figure S12. The FT-IR spectrum of 3,5-Dimethyl-4-(2-methoxyphenyl)-1,4,7,8-tetrahydropyrazolo[3,4-b;4',3'-e]pyridine (3d) (Table 4, Entry 4)

1,4,7,8-Tetrahydro-3,5-dimethyl-4-phenyldipyrzolo-[3,4- b:4',3'-e]pyridine (3b) (Table 4, Entry 2)

white solid; Yield: 98%; M.p. 241-243°C; IR (KBr): 3362, 2725, 1606, 1486, 1448, 1143, 727 cm⁻¹; ¹H NMR (250 MHz, DMSO-d₆) δ (ppm): 11.24 (s, 4H), 7.13 (s, 5H), 4.80 (s, 1H), 2.05 (s, 7H), 1.03 (s, 1H); ¹³C NMR (63 MHz, DMSO-d₆) δ (ppm): 161.53, 143.82, 140.22, 128.14, 127.91, 125.82, 104.67, 33.21, 10.81.

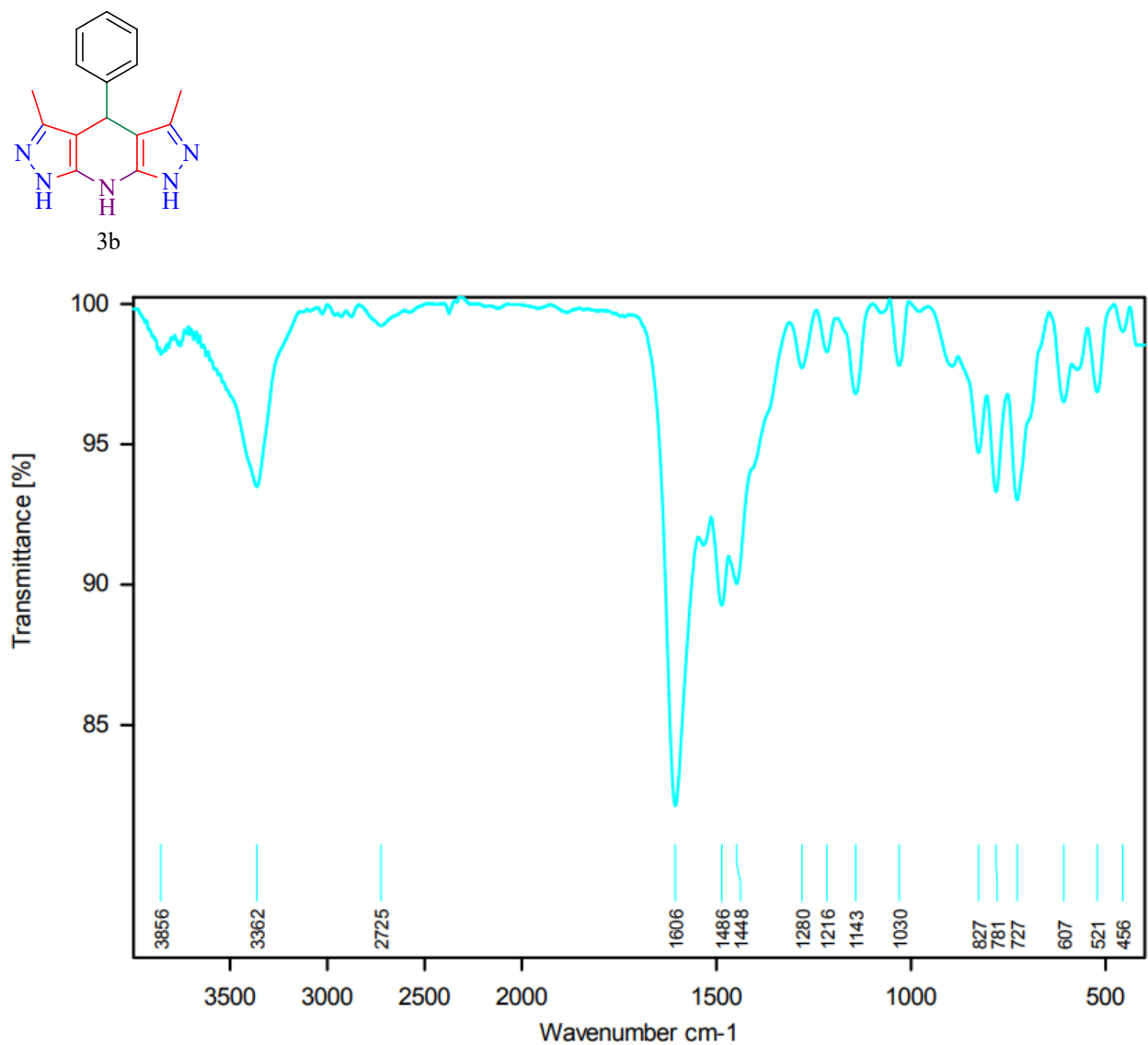


Figure S13. The FT-IR spectrum of 1,4,7,8-Tetrahydro-3,5-dimethyl-4-phenyldipyrzolo-[3,4- b:4',3'-e]pyridine (3b) (Table 4, Entry 2)

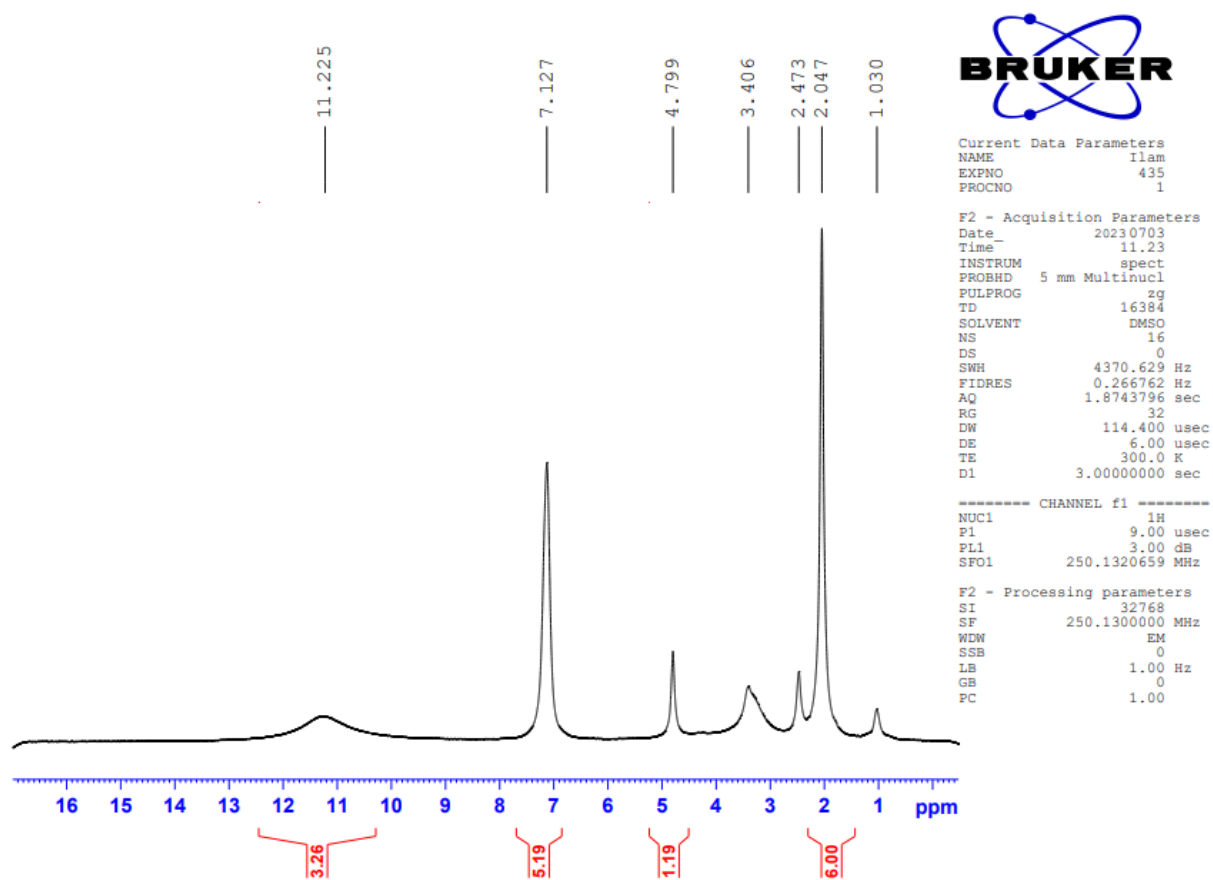


Figure S14. The ^1H NMR spectrum of 1,4,7,8-Tetrahydro-3,5-dimethyl-4-phenyldipyrzolo-[3,4- b:4',3'-e]pyridine (3b) (Table 4, Entry 2)

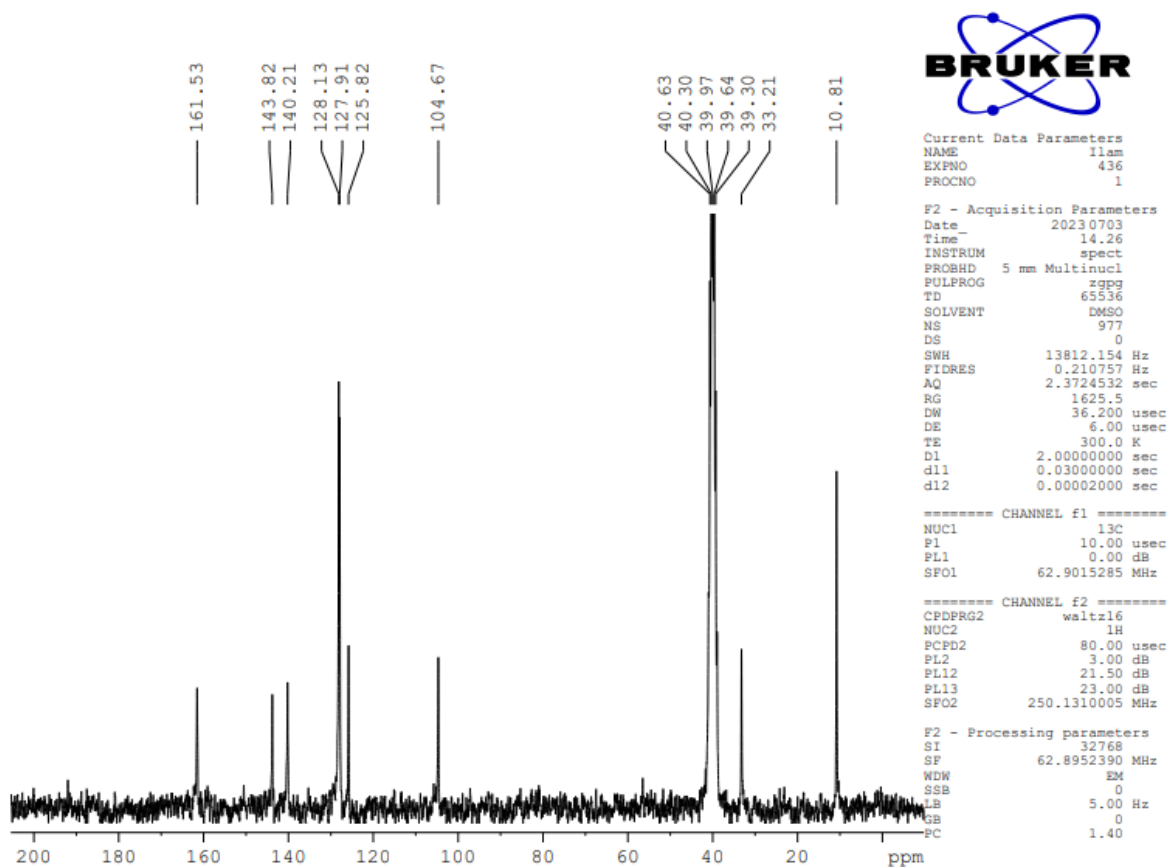
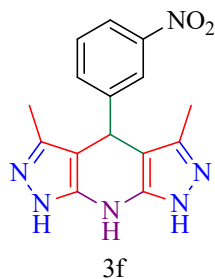


Figure S15. The ^{13}C NMR spectrum of 1,4,7,8-Tetrahydro-3,5-dimethyl-4-phenyldipyrzolo-[3,4- b:4',3'-e]pyridine (3b) (Table 4, Entry 2)

3,5-Dimethyl-4-(3-nitrophenyl)-1,4,7,8-tetrahydrodipyrzolo[3,4-b;4',3'-e]pyridine (3f) (Table 4, Entry 6)

Cream solid; Yield: 85%; M.p. 284-286°C; ^1H NMR (250 MHz, DMSO- d_6) δ (ppm): 11.35 (s, 4H), 7.97 (d, J = 16.4 Hz, 2H), 7.53 (s, 2H), 4.96 (s, 1H), 2.08 (s, 5H); ^{13}C NMR (63 MHz, DMSO- d_6) δ (ppm): 161.35, 146.26, 148.04, 140.34, 135.04, 129.66, 122.39, 121.14, 103.76, 33.02, 10.73.



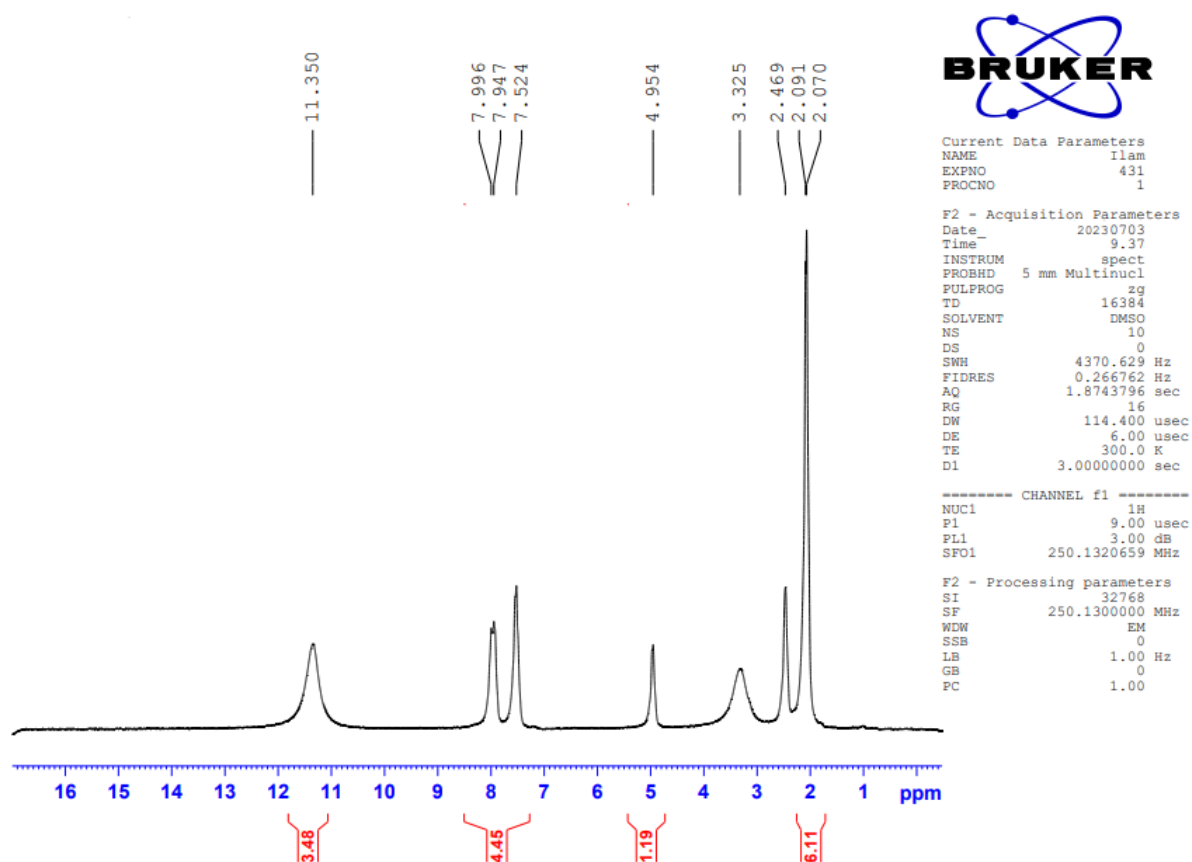


Figure S16. The ^1H NMR spectrum of 3,5-Dimethyl-4-(3-nitrophenyl)-1,4,7,8-tetrahydridiprazolo[3,4-b;4',3'-e]pyridine (3f) (Table 4, Entry 6)

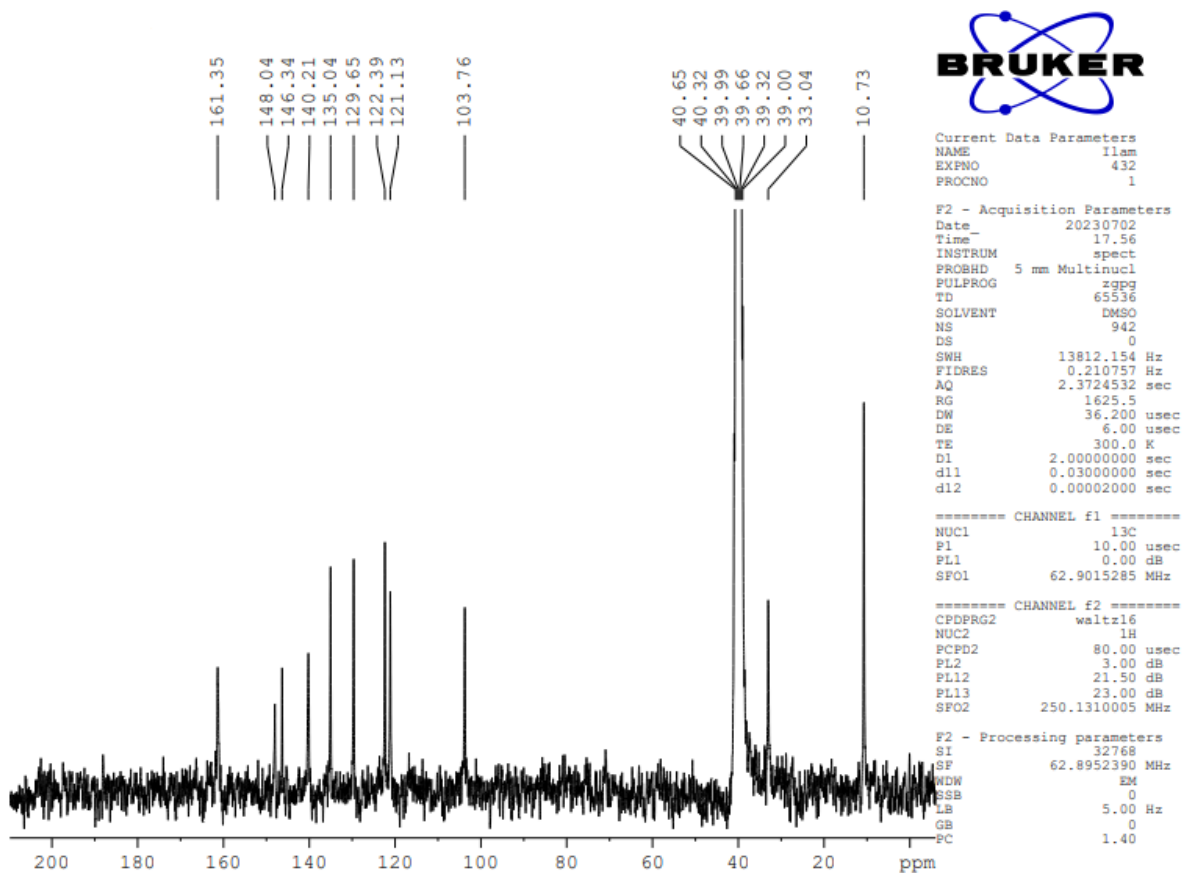
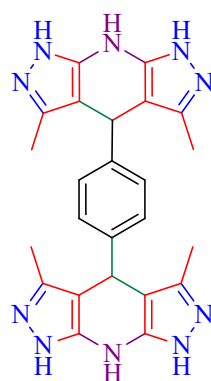


Figure S17. The ^{13}C NMR spectrum of 3,5-Dimethyl-4-(3-nitrophenyl)-1,4,7,8-tetrahydridipyrzolo[3,4-b;4',3'-e]pyridine (3f) (Table 4, Entry 3)

1,4-Bis[(1,4,7,8-Tetrahydro-3,5-dimethyldipyrzolo[3,4-b:40,30-e]pyridin-4-yl)] benzene (3m) (Table 4, Entry 13)

Pale orange solid; Yield: 96%; M.p. >300 °C; IR (KBr): 3401, 1602, 1457, 1215, 1136, 785, 593 cm^{-1} ; ^1H NMR (250 MHz, DMSO- d_6) δ (ppm): 11.31 (s, 3H), 6.93 (s, 2H), 4.68 (s, 1H), 2.03 (s, 7H), 1.02 (s, 2H); ^{13}C NMR (63 MHz, DMSO- d_6) δ (ppm): 168.25, 161.65, 140.36, 127.23, 109.50, 32.81, 10.79.



3m

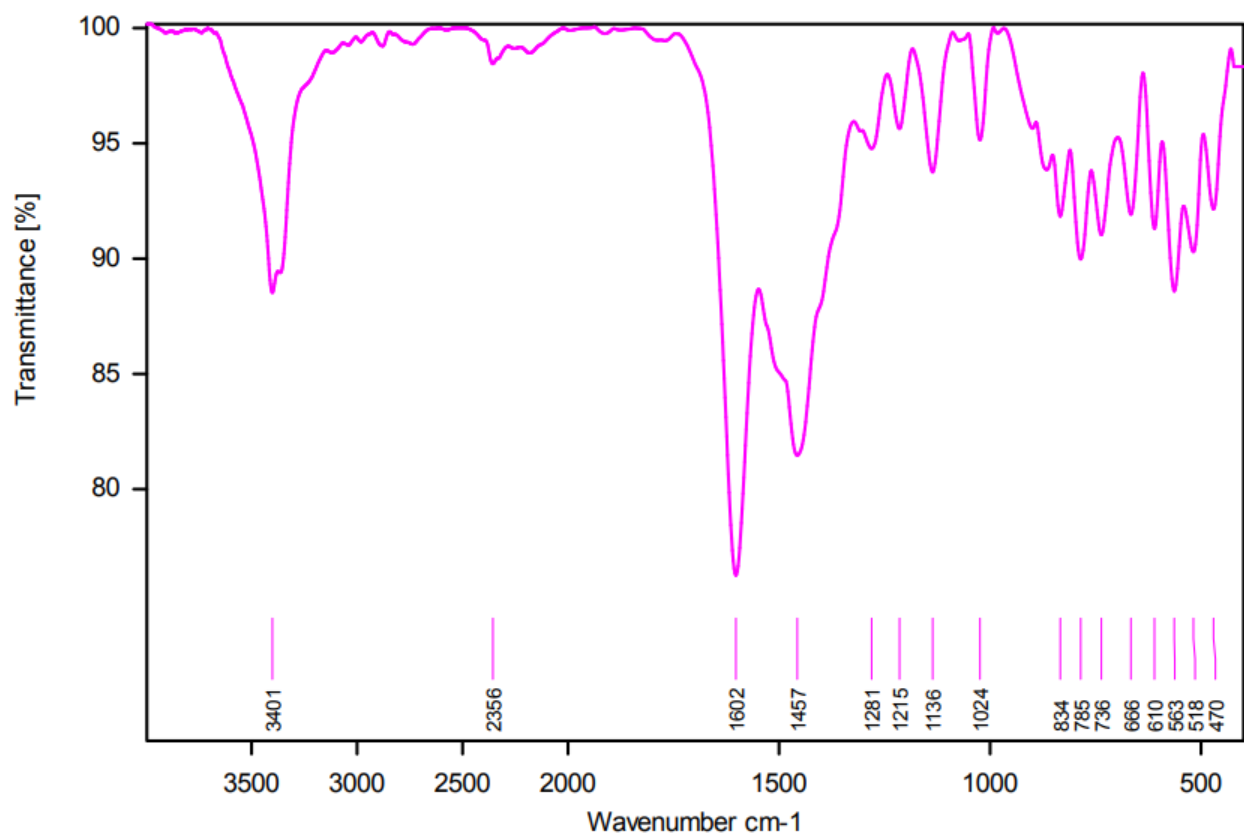


Figure S18. The FT-IR spectrum of 1,4-Bis[(1,4,7,8-Tetrahydro-3,5-dimethyldipyrzolo[3,4-b:4',3'-e]pyridin-4-yl)]benzene (3m) (Table 4, Entry 13)

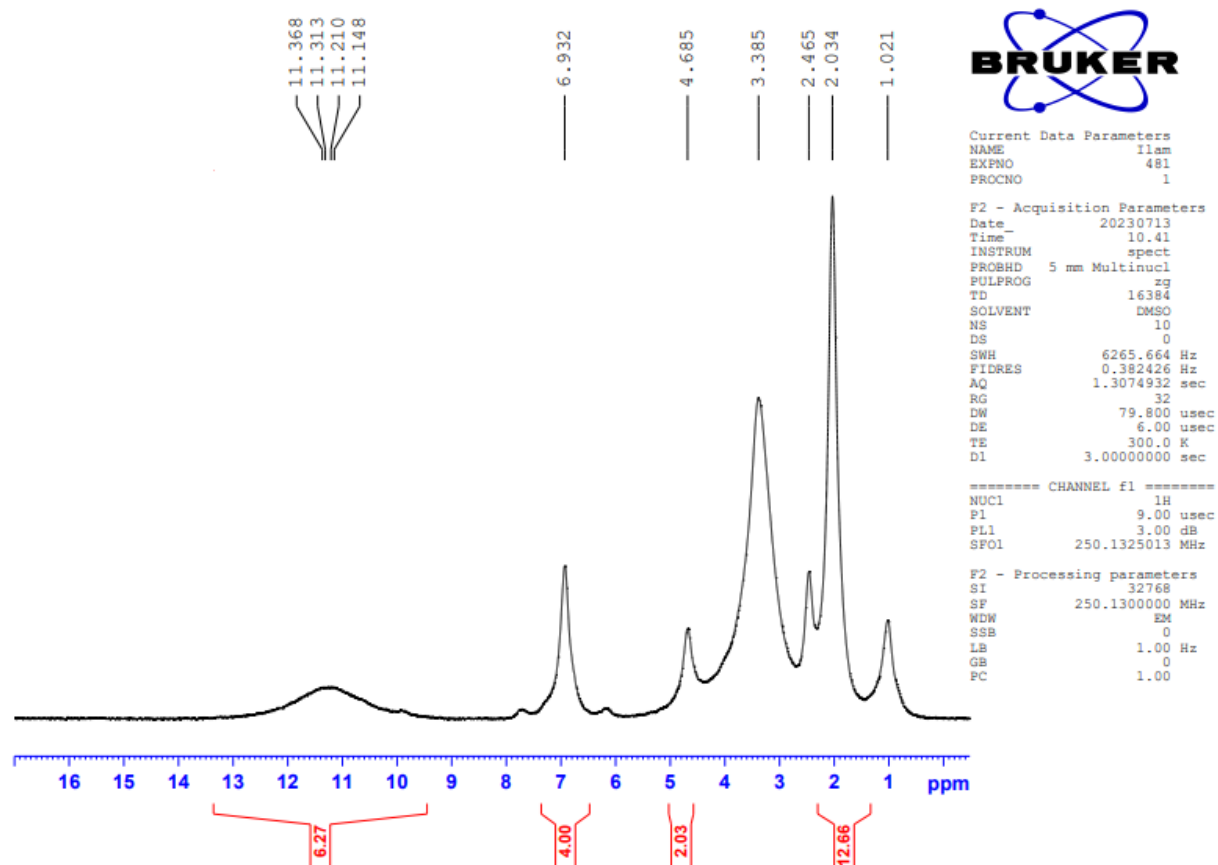


Figure S19. The ^1H NMR spectrum of 1,4-Bis[(1,4,7,8-Tetrahydro-3,5-dimethyldipyrzolo[3,4-b:40,30-e]pyridin-4-yl)] benzene (3m) (Table 4, Entry 13)

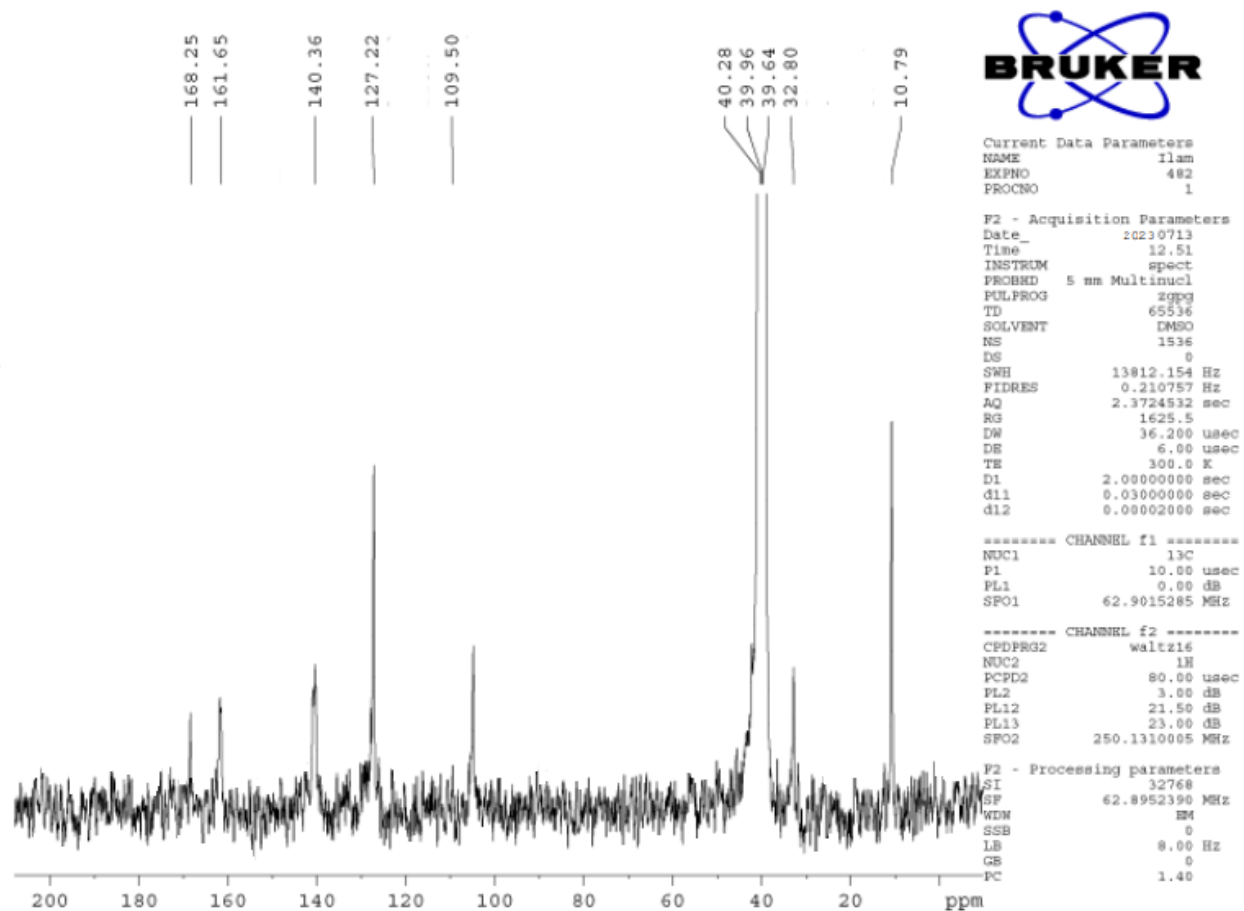


Figure S20. The ^{13}C NMR spectrum of 1,4-Bis[(1,4,7,8-Tetrahydro-3,5-dimethyldipyrzolo[3,4-b:4',3'-e]pyridin-4-yl)] benzene (3m) (Table 4, Entry 13)