Electronic Supplementary Material (ESI) for RSC Advances.

Novel iron doped calcium oxalates as promising heterogeneous catalysts for one-pot multi-component synthesis of pyranopyrazoles

Kranthi Kumar Gangu, Suresh Maddila, Surya Narayana Maddila and Sreekantha B Jonnalagadda*

*School of Chemistry & Physics, University of KwaZulu-Natal, Westville Campus, Chiltern Hills, Durban-4000, South Africa

*Corresponding Author: Prof. Sreekantha B. Jonnalagadda
School of Chemistry & Physics,
University of KwaZulu-Natal,
Durban 4000, South Africa.
Tel.: +27 31 2607325,
Fax: +27 31 2603091
E-mail address: jonnalagaddas@ukzn.ac.za

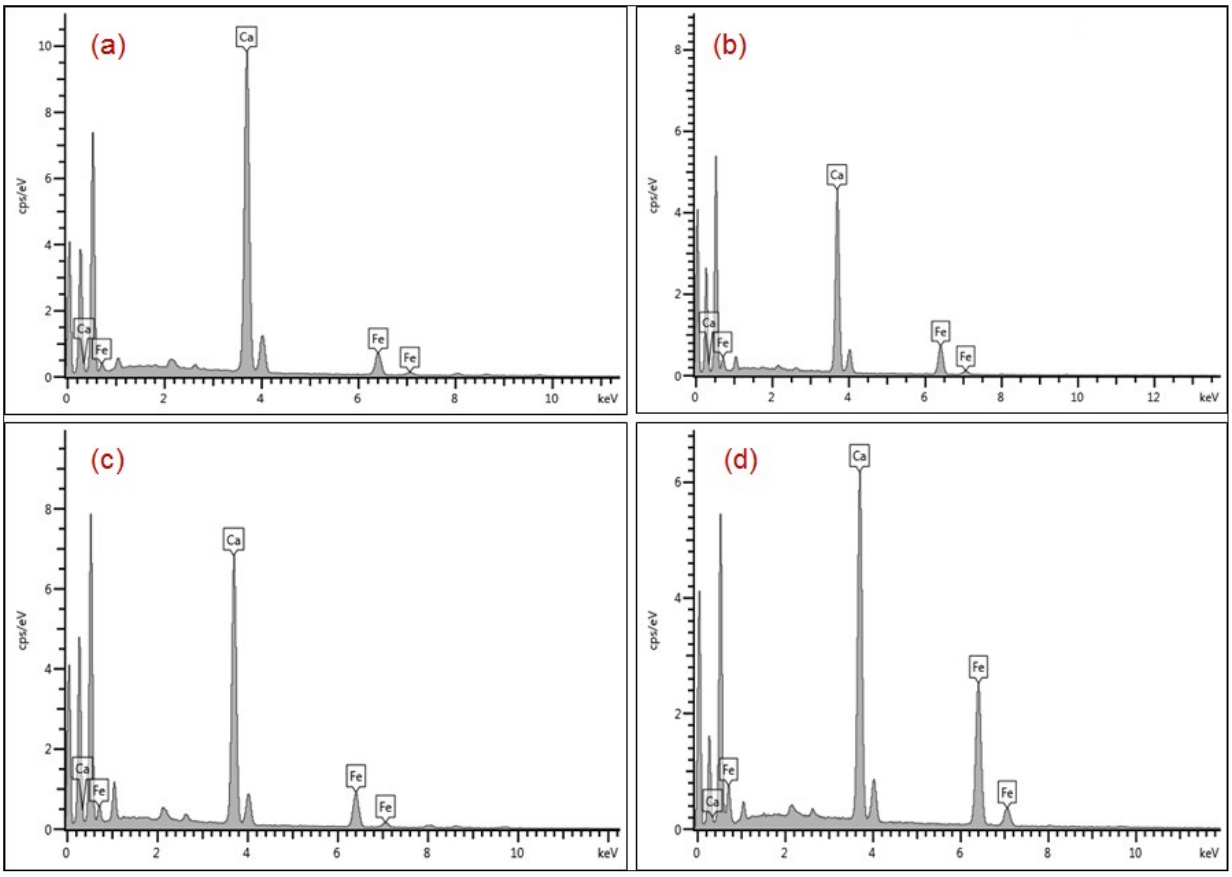


Fig. S1. EDX spectra of (a) 0.5 Fe-CaOx/glu (b) 1.0 Fe-CaOx/glu (c) 2.0 Fe-CaOx/glu (d) 3.0 Fe-CaOx/glu

Table S1: Optimization of the amount of 2.0 Fe-CaOx/glu as catalyst in the model reaction[a]

Entry	Catalyst (mg)	Time (min)	Yield (%)
1	10	15	91
2	20	10	98
3	30	10	96
4	40	10	94
5	50	15	92

[a]Reaction conditions: 3-fluoro benzaldehyde (1.0 mmol), malononitrile (1.0 mmol), hydrazine hydrate (1.0 mmol), dimethyl acetylenedicarboxylic acid (1.0 mmol), catalyst (20 mg) and ethanol (5.0 mL) were refluxed at 50 ^{o}C

.

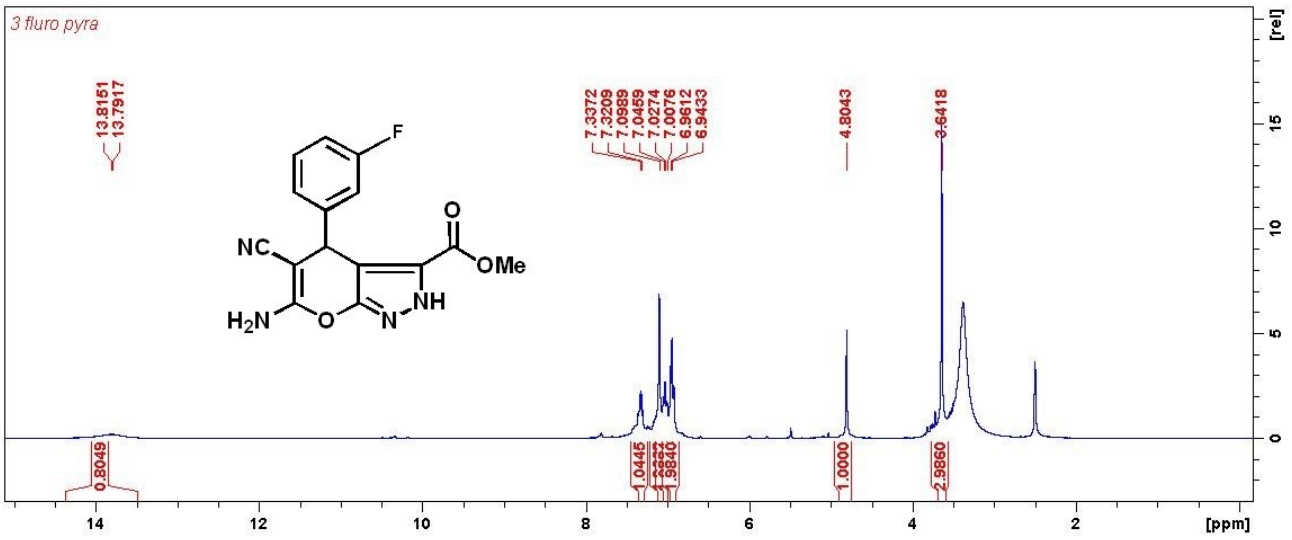


Fig. S2. ^{1}H-NMR spectrum of methyl 6-amino-5-cyano-4-(3-fluorophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate

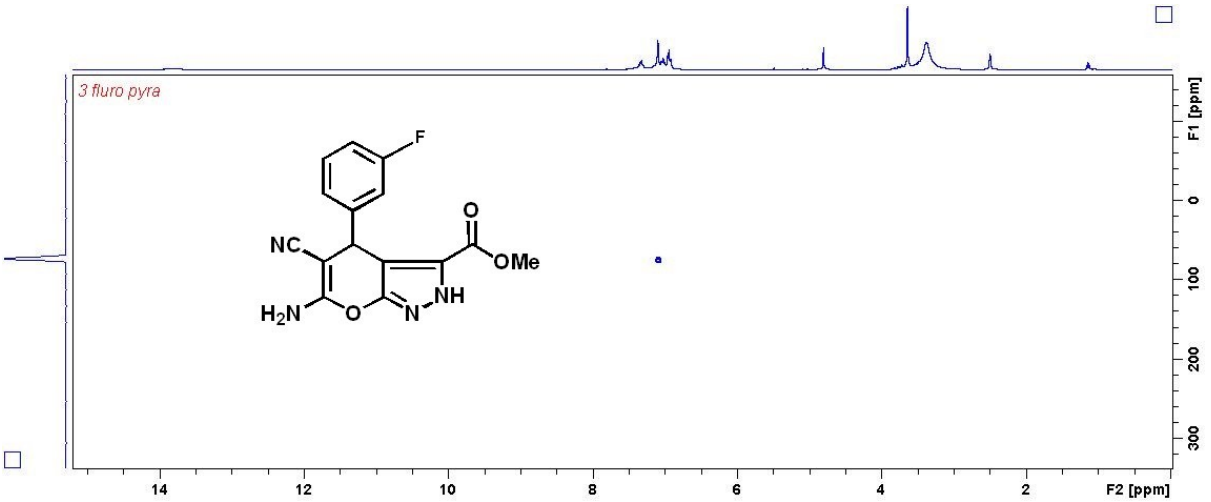


Fig. S3. ^{15}N-NMR spectrum of methyl 6-amino-5-cyano-4-(3-fluorophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate

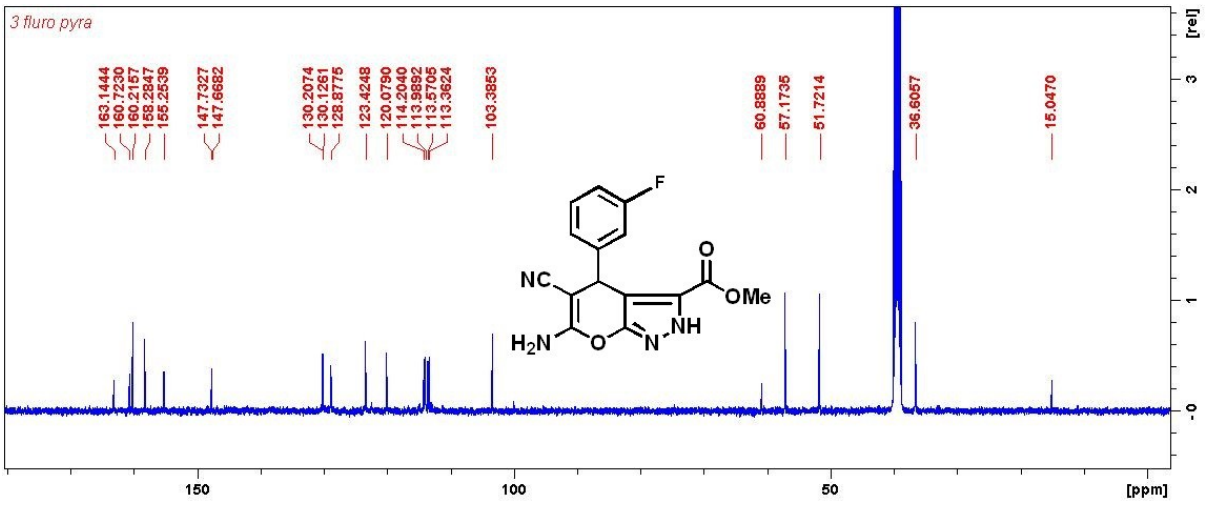


Fig. S4. ^{13}C-NMR spectrum of methyl 6-amino-5-cyano-4-(3-fluorophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate

Spectral data of products:

Entry 1:

6-amino-4-(4-Methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile;-.^{1}H NMR (400 MHz, DMSO-d_6) 3.65 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 4.68 (s, 1H, CH), 6.83 (d, J = 8.52 Hz, 2H, ArH), 6.99 (s, 1H, NH_2) 7.03 (t, J = 8.88 Hz, 2H, ArH), 13.69 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): 36.19, 51.71, 54.92, 58.03, 113.53, 114.56, 128.34, 129.93, 137.03, 157.85, 160.02, 160.44; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 7.08 (s, 2H, NH_2).

Entry 2:

6-amino-4-(4-Bromophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile;-.^{1}H NMR (400 MHz, DMSO-d_6) 3.64 (s, 3H, OCH_3), 4.75 (s, 1H, CH), 7.08 (s, 1H, NH_2), 7.47 (d, J = 8.28 Hz, 2H, ArH), 7.72 (d, J = 8.36 Hz, 1H, ArH), 7.82 (d, J = 8.48 Hz, 1H, ArH), 13.77 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): 32.23, 51.62, 56.28, 103.92, 109.77, 115.35, 119.45, 122.00, 133.56, 151.04, 153.11, 156.47, 160.74; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 7.08 (s, 2H, NH_2).

Entry 3:

6-amino-4-(4-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile;-.^{1}H NMR (400 MHz, DMSO-d_6) 3.66 (s, 3H, OCH_3), 4.78 (s, 1H, CH), 7.06 (s, 1H, NH_2), 7.16 (d, J = 5.68 Hz, 2H, ArH), 7.35 (d, J = 5.52 Hz, 2H, ArH), 13.78 (s, 1H, NH). ^{13}C NMR (100

MHz, DMSO-d_6): 36.98, 52.23, 57.88, 104.11, 120.57, 128.69, 129.77, 144.32, 155.78, 158.78, 160.72; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 7.06 (s, 2H, NH_2).

Entry 4:

6-amino-4-(3-Hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile;-.^{1}H NMR (400 MHz, DMSO-d_6) 3.66 (s, 3H, OCH_3), 4.63 (s, 1H, CH), 6.53 (s, 1H, ArH), 6.59 – 6.62 (m, 2H, ArH), 6.83 (s, 1H, NH_2) 7.09 (t, *J* = 7.8 Hz, 1H, ArH), 9.29 (s, 1H, OH), 13.24 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): 36.14, 57.26, 97.66, 113.80, 114.10, 118.15, 120.77, 129.23, 135.53, 145.93, 154.73, 157.39, 160.80; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 6.83 (s, 2H, NH_2).

Entry 5:

6-amino-4-(2-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile;-.^{1}H NMR (400 MHz, DMSO-d_6) 3.57 (s, 3H, OCH_3), 5.26 (s, 1H, CH), 7.05 (s, 1H, NH_2), 7.21 – 7.25 (m, 2H, ArH), 7.38 (dd, *J* = 7.68 Hz, 0.96 Hz, 1H, ArH), 7.56 – 7.59 (m, 1H, ArH), 13.76 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): 32.71, 51.62, 56.86, 104.21, 111.45, 120.53, 121.24, 123.23, 128.45, 137.25, 146.39, 152.25, 155.82, 158.46, 160.42; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 7.05 (s, 2H, NH_2).

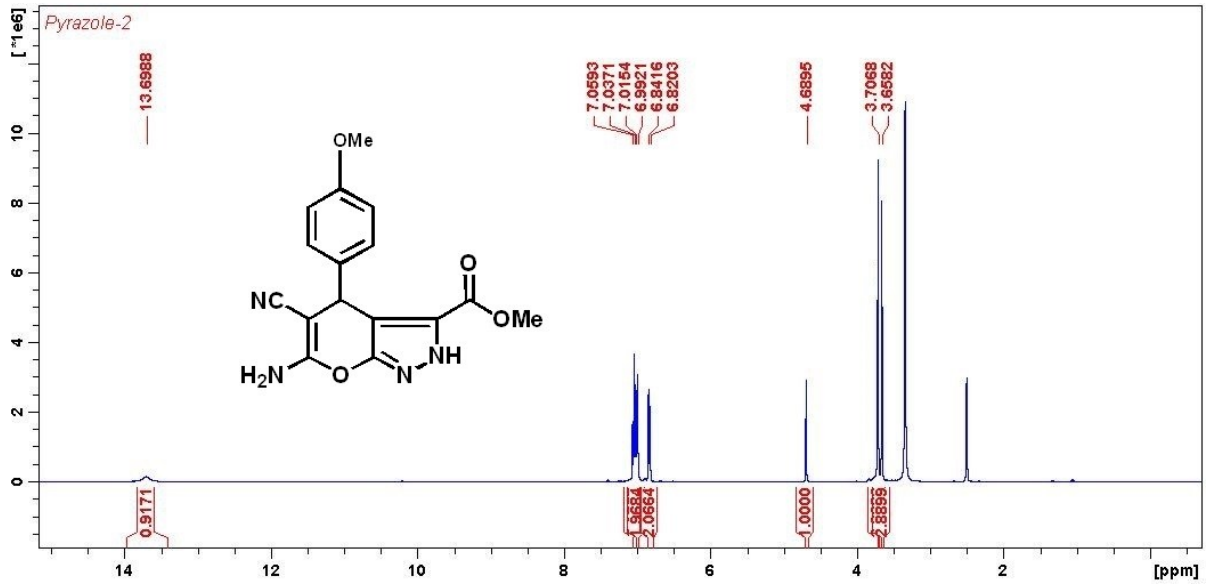
Entry 6:

6-amino-5-cyano-4-(thiophen-2-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate;- ^{1}H NMR (400 MHz, DMSO-d_6) 3.75 (s, 3H, OCH_3), 5.14 (s, 1H, CH), 6.92 (t, *J* = 0.96 Hz, 1H, ArH,), 6.96 (d, *J* = 1.88 Hz, 1H, ArH), 7.12 (s, 2H, NH_2), 7.34 (d, *J* = 3.56 Hz, 1H, ArH), 13.81 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): 31.13, 32.59, 52.39, 58.22, 104.70, 120.60, 124.71, 125.08, 127.09, 128.75, 129.36, 131.44, 134.22, 138.88, 149.91, 155.36, 156.23, 158.93, 160.92; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 7.12 (s, 2H, NH_2).

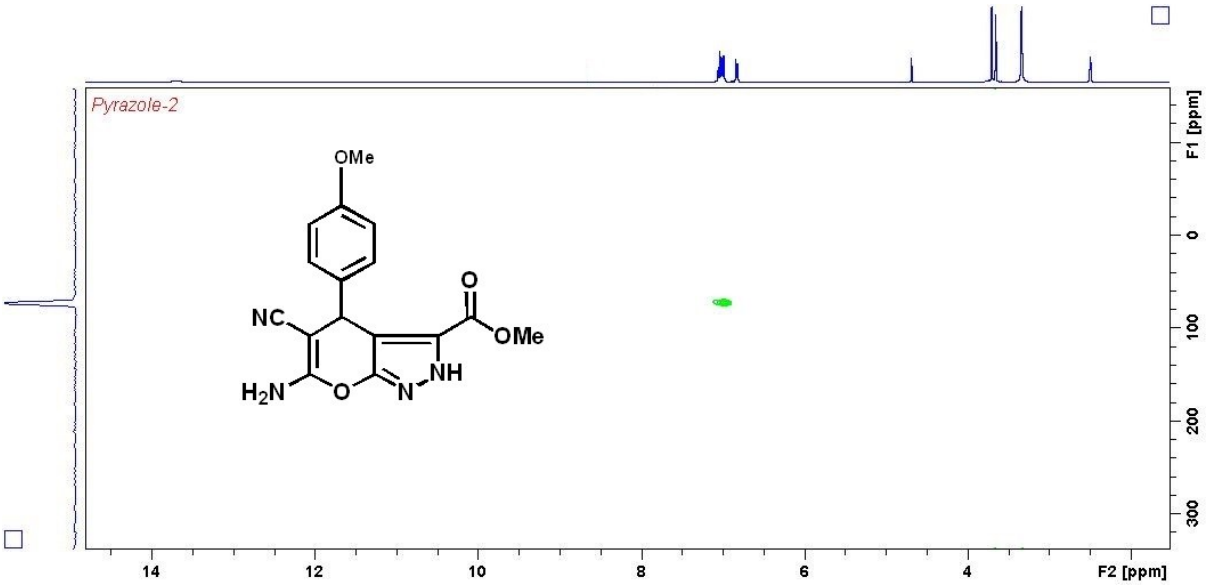
Entry 7:

6-amino-5-cyano-4-(furan-2-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate;- ^{1}H NMR (400 MHz, DMSO-d_6) 3.75 (s, 3H, OCH_3), 4.93 (s, 1H, CH), 6.16 (d, *J* = 2.08 Hz, 1H, ArH,), 6.35 (d, *J* = 0.96 Hz, 1H, ArH), 7.10 (s, 2H, NH_2), 7.48 (d, *J* = 1.52 Hz, 1H, ArH), 13.78 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): 31.18, 52.38, 55.20, 101.96, 105.96, 110.79, 120.50, 129.43, 142.46, 155.72, 158.97, 161.42; ^{15}N NMR (40.55 MHz, DMSO-d_6) δ 7.10 (s, 2H, NH_2).

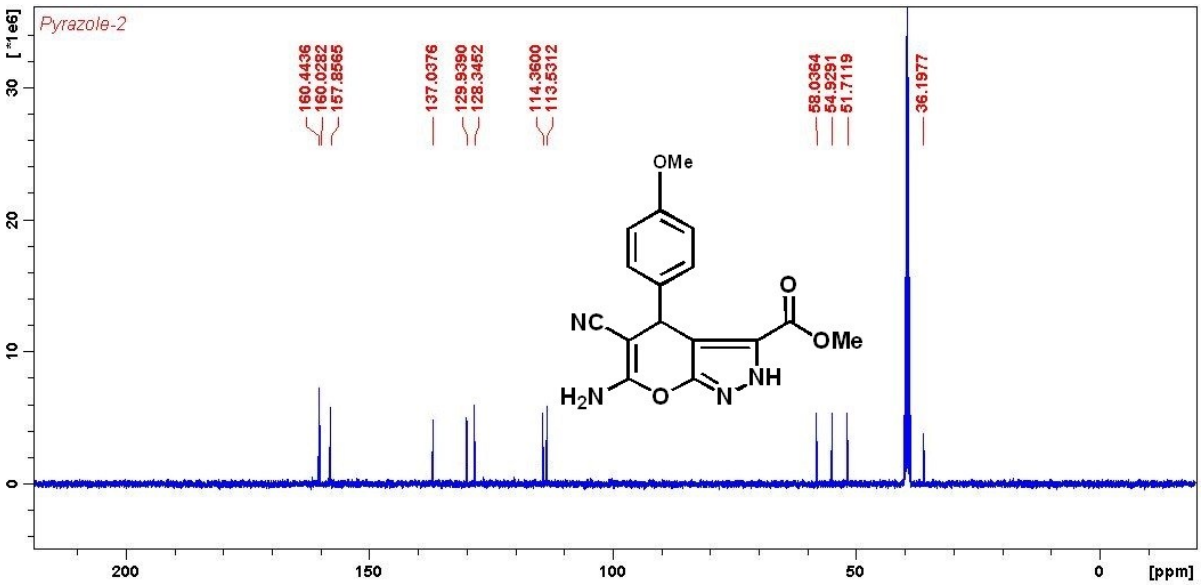
Entry 1:



^{1}H NMR spectrum of 6-amino-4-(4-Methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

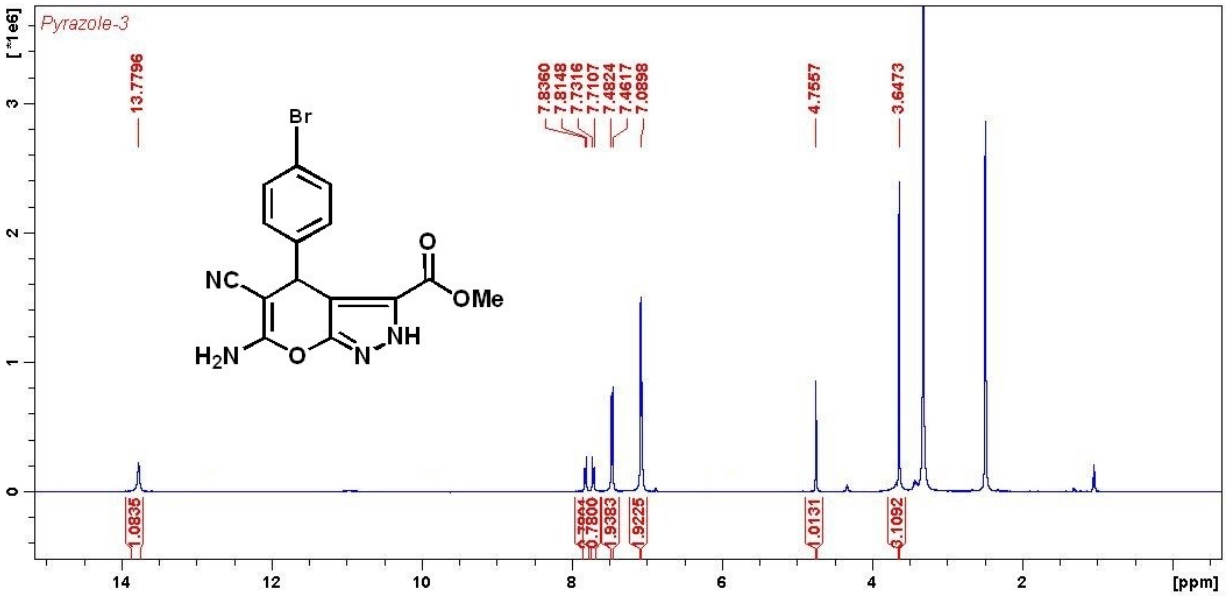


^{15}N NMR spectrum of 6-amino-4-(4-Methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

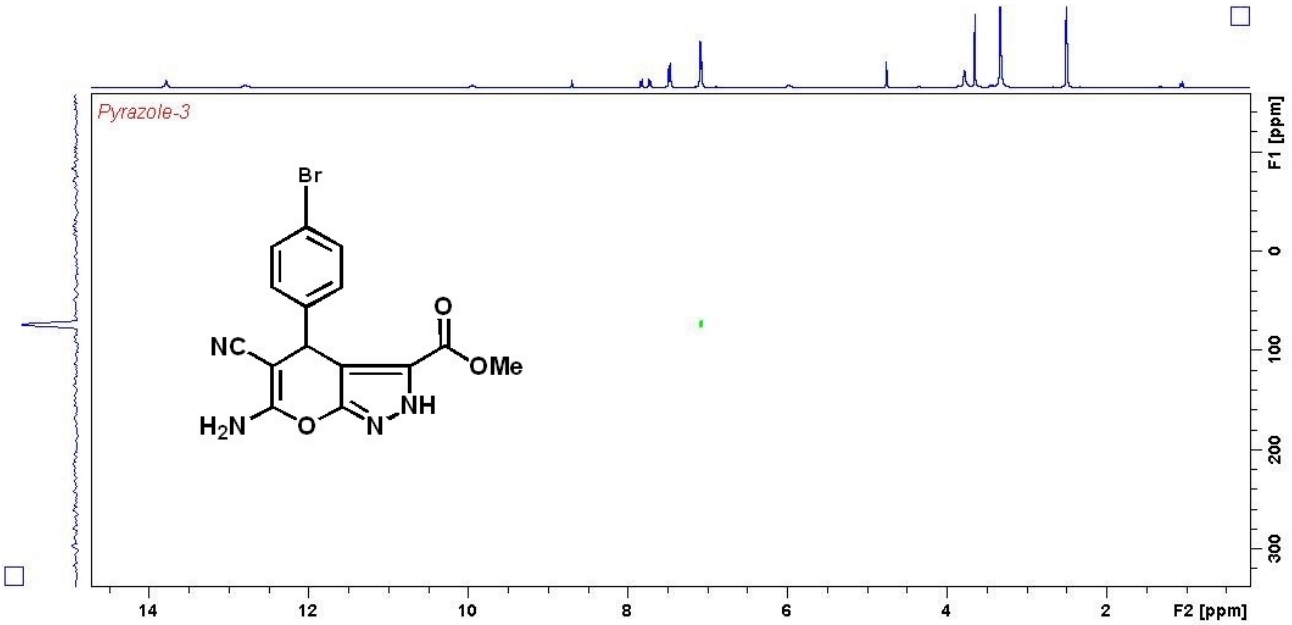


^{13}C NMR spectrum of 6-amino-4-(4-Methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

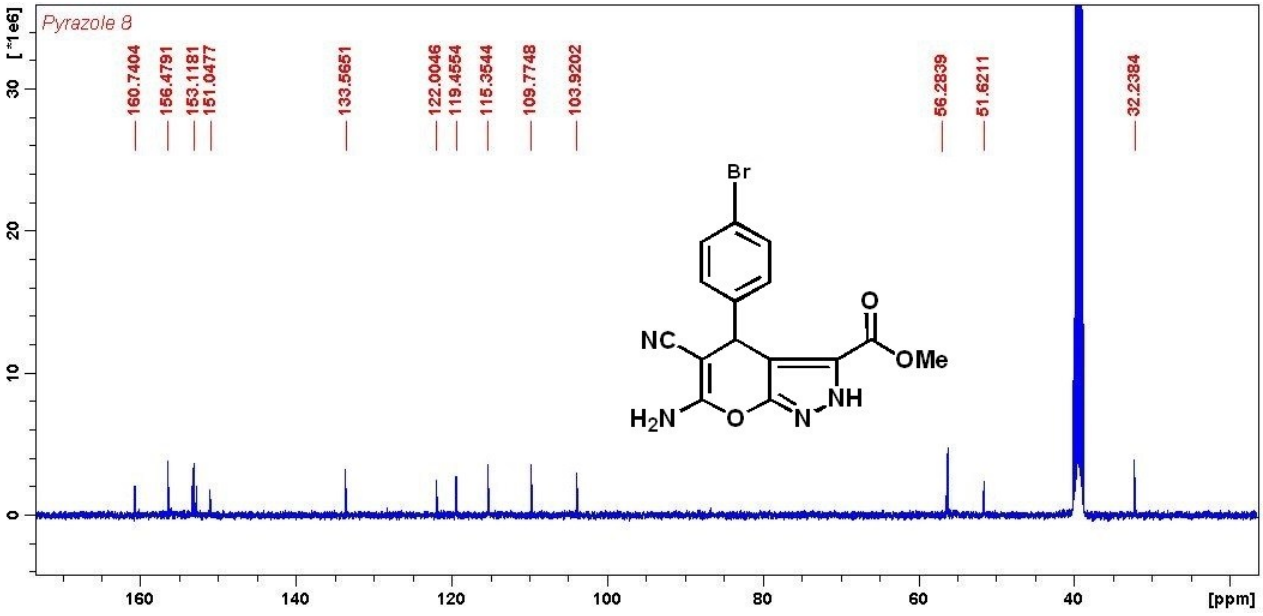
Entry 2:



^{1}H NMR spectrum of 6-amino-4-(4-Bromophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

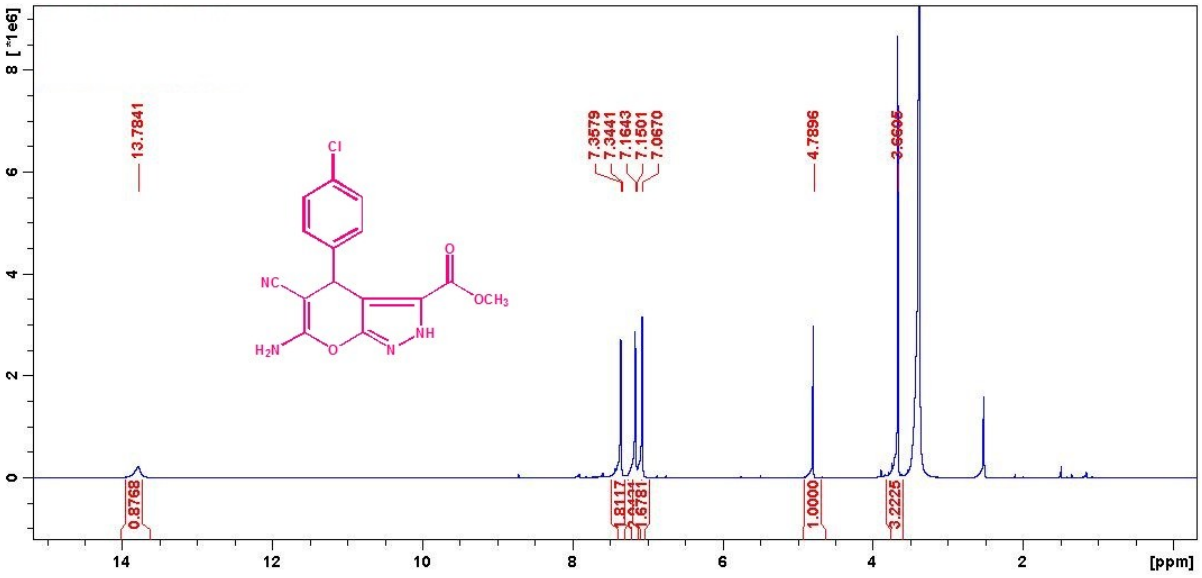


^{15}N NMR spectrum of 6-amino-4-(4-Bromophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

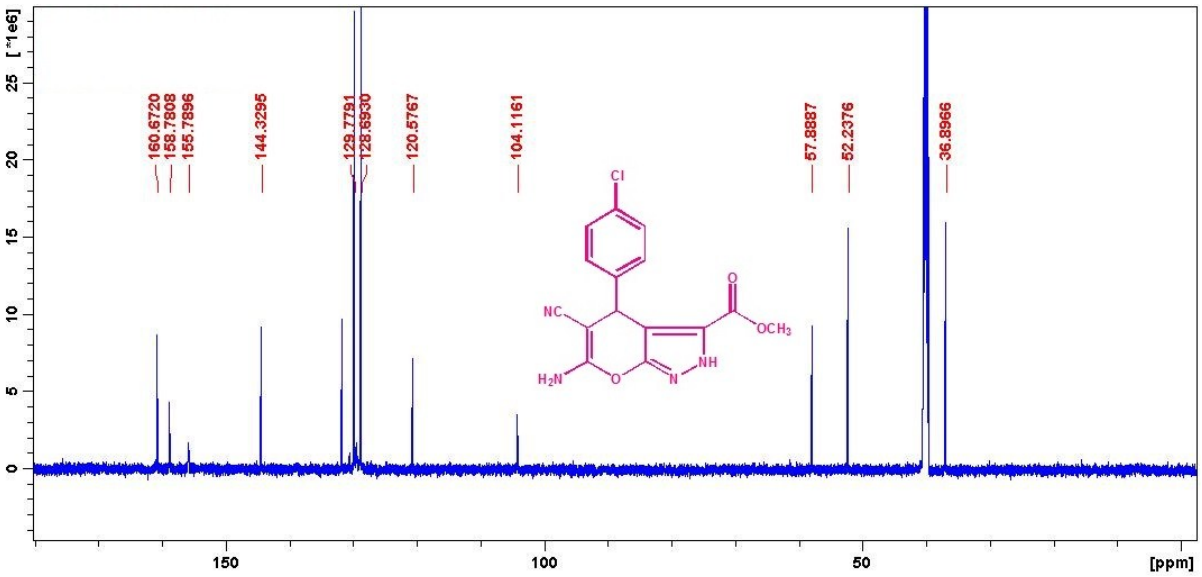


^{13}C NMR spectrum of 6-amino-4-(4-Bromophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

Entry 3:

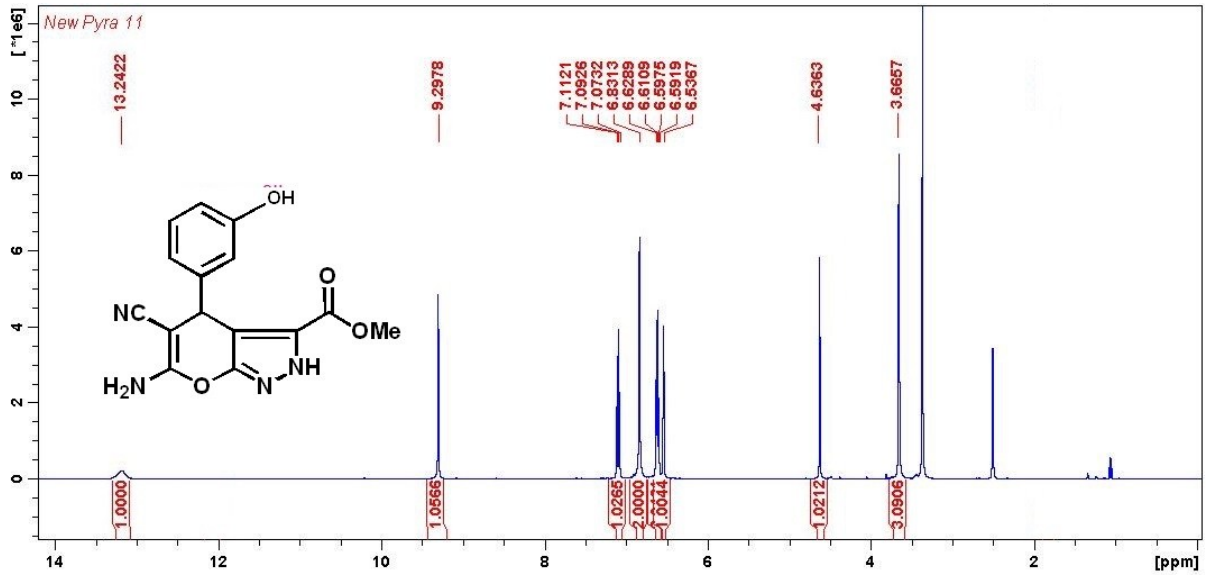


^{1}H NMR spectrum of 6-amino-4-(4-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

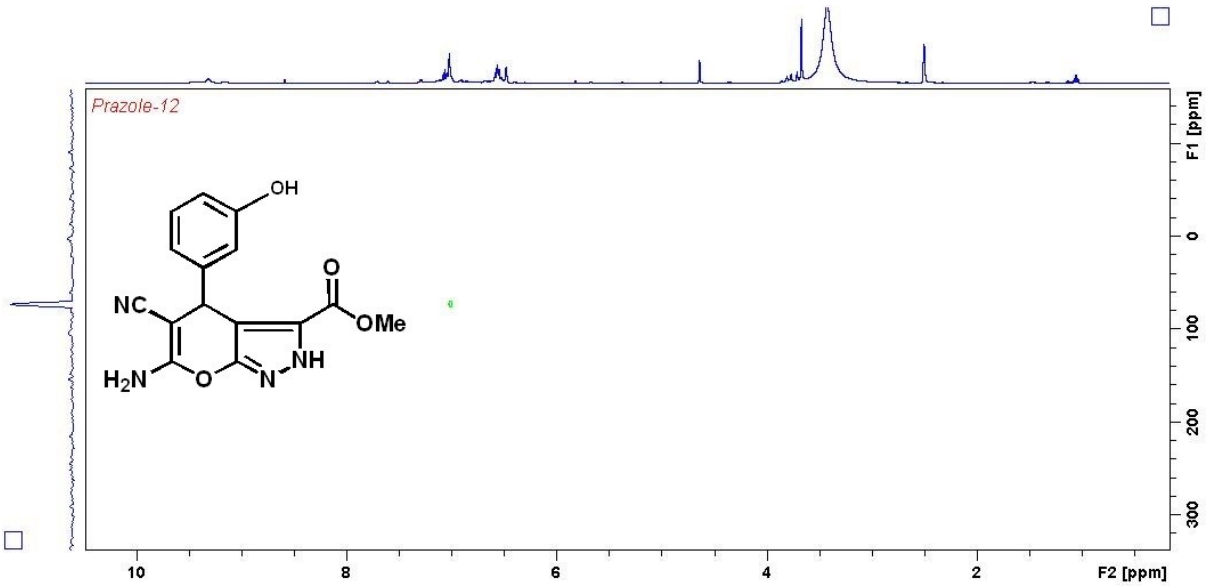


^{13}C NMR spectrum of 6-amino-4-(4-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

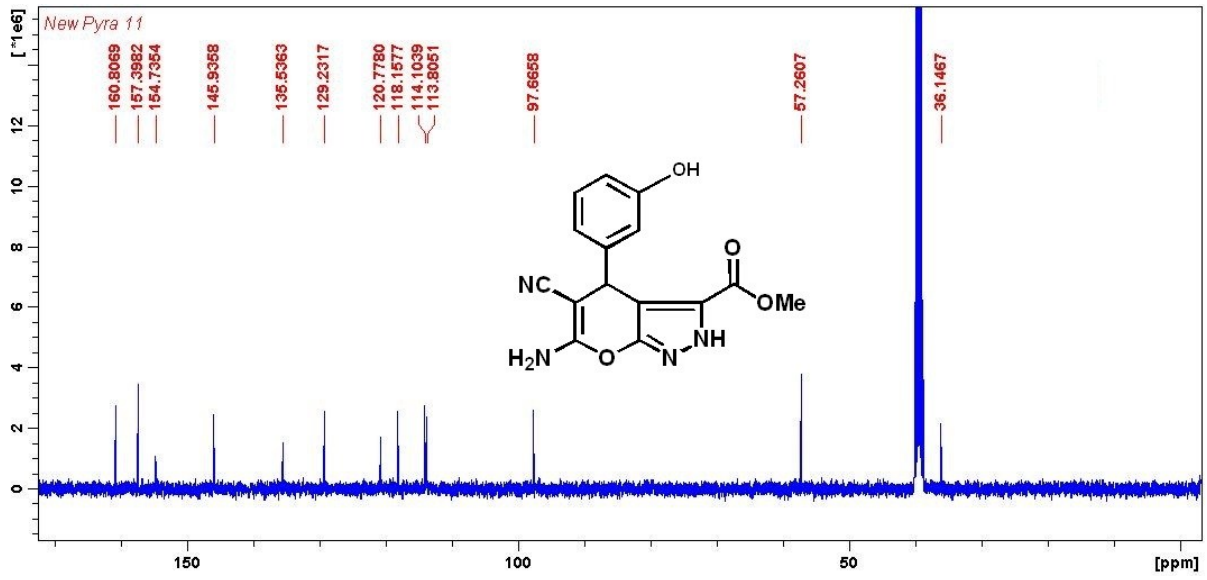
Entry 4:



^{1}H NMR spectrum of 6-amino-4-(3-Hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

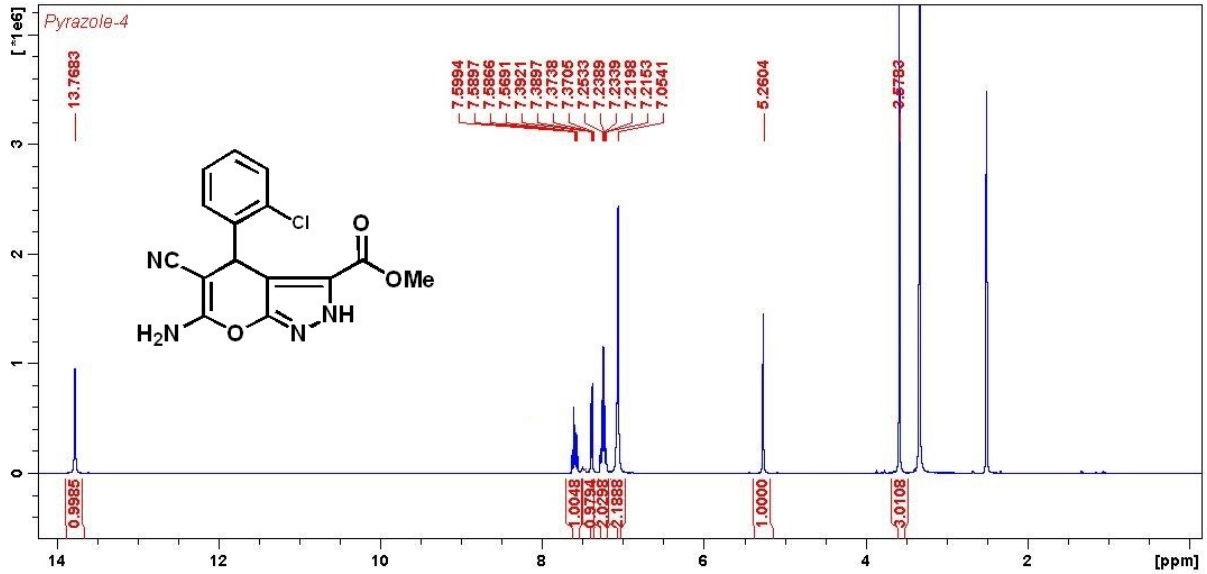


^{15}N NMR spectrum of 6-amino-4-(3-Hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

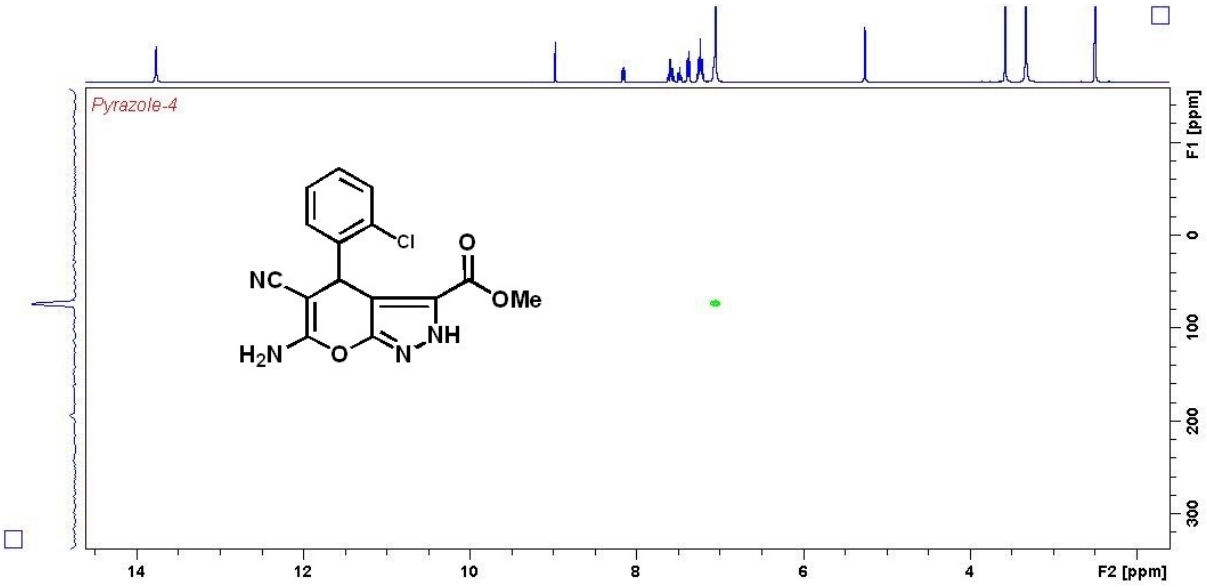


^{13}C NMR spectrum of 6-amino-4-(3-Hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

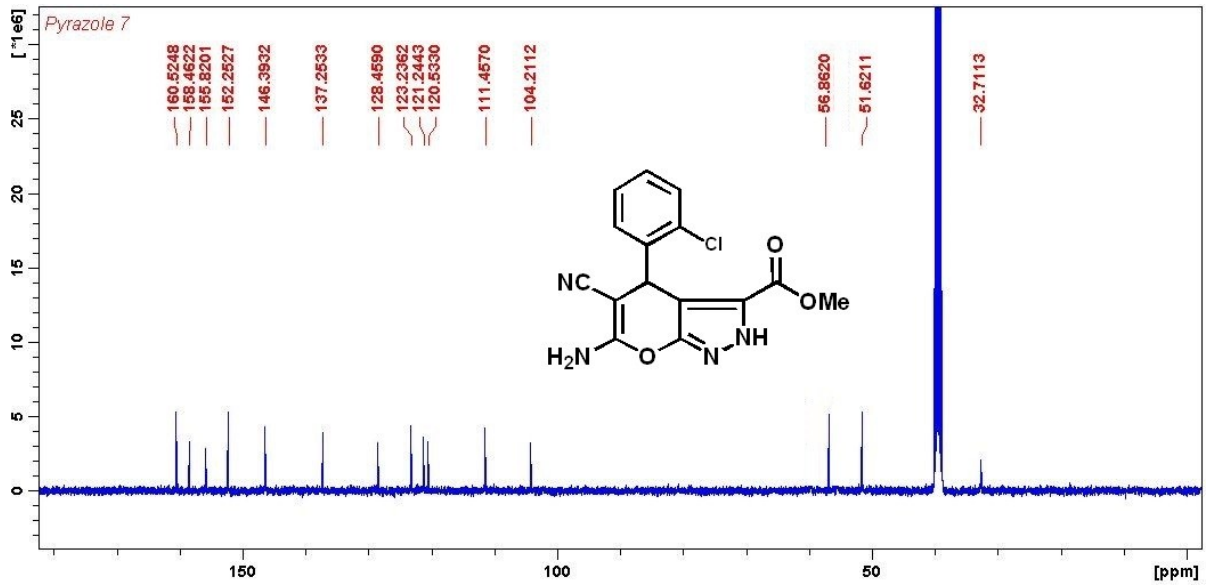
Entry 5:



^{1}H NMR spectrum of 6-amino-4-(2-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

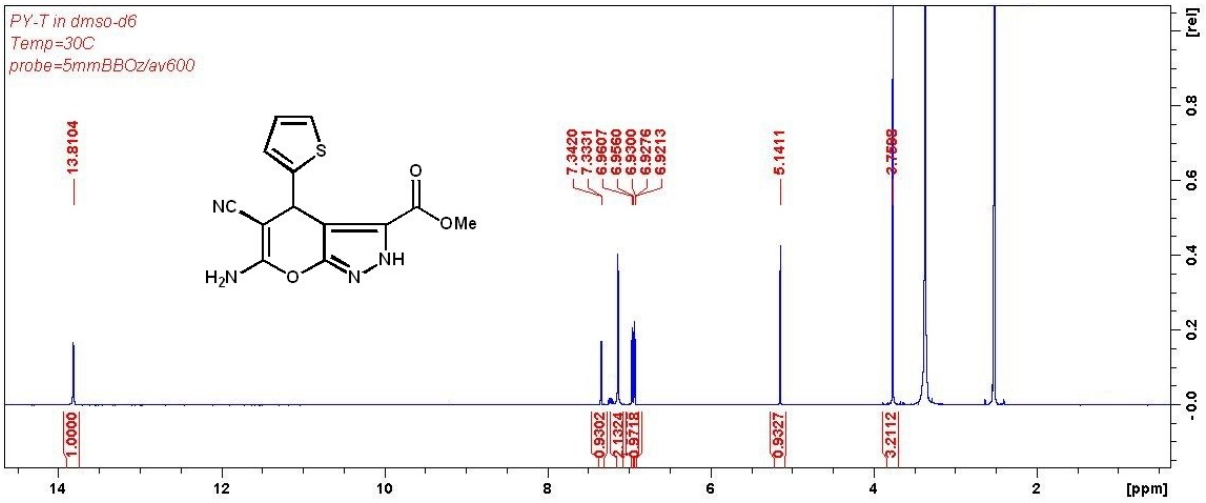


^{15}N NMR spectrum of 6-amino-4-(2-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

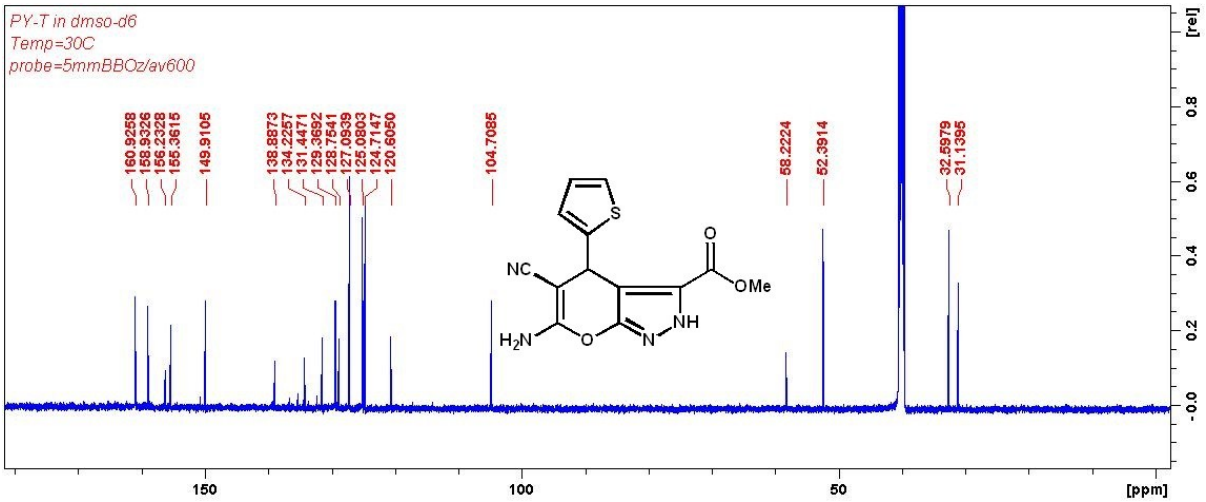


^{13}C NMR spectrum of 6-amino-4-(2-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

Entry 6:

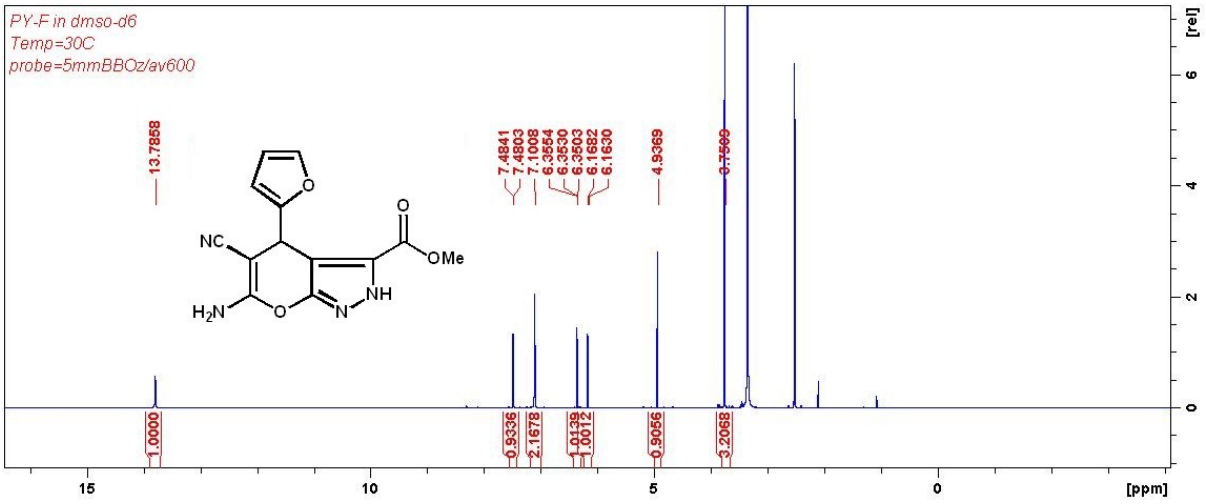


^{1}H NMR spectrum of 6-amino-5-cyano-4-(thiophen-2-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate

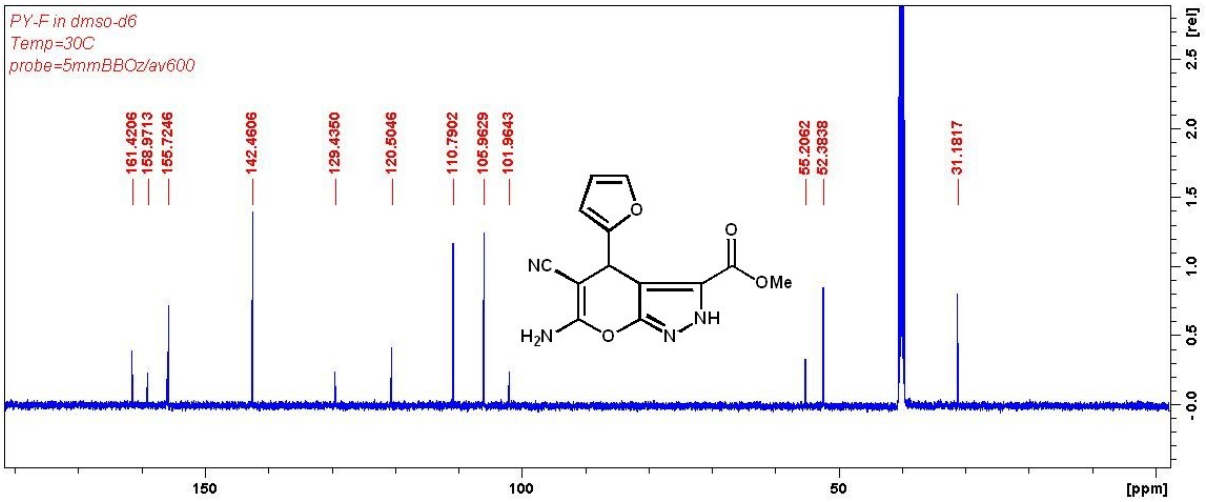


^{13}C NMR spectrum of 6-amino-5-cyano-4-(thiophen-2-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate

Entry 7:



^{1}H NMR spectrum of 6-amino-5-cyano-4-(furan-2-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate



^{13}C NMR spectrum of 6-amino-5-cyano-4-(furan-2-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate