Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

1. Experimental

1.1 Materials

Butyl-4-methylpyridinium tetrafloroborate (≥ 97) was procured from Sigma-Aldrich. Anhydrous ($FeCl_3$, 98%) and nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 97%) and hydrazine hydrate were purchased from HiMedia. Other chemicals used in the synthesis of pyrazolopyranopyrimidine and 1*H*-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives were procured from Alfa Aesar, Avra Synthesis and Loba Chemie chemical company respectively. **C**hemicals were used without processing. All the experimental procedure was carried out in the triply distilled water.

1.2 Characterization

Shimadzu spectrometer (FT-IR) was used for the recording of the Fourier transform infrared (FTIR) spectra. The samples were made *via* mixing sample (5 mg) with KBr (200 mg) to form pellets for measurement. The BET specific surface area was determined from N_2 adsorption−desorption isotherms at 77 K by using a Belsorb Mini-X analyzer. The sample was pretreated in a vacuum for 4 h at 200 °C to dehydrate the catalysts before N_2 adsorption. The Thermofisher Scientific Nexsa base X-ray photoelectron spectroscope was used to analyze the X-ray photoelectron spectrum of the nanostructure. High-Resolution Transmission electron micrographs (HR-TEM) were recorded on FEI, Tecnai G2, F30 transmission electron microscope with a field emission gun operating at 300 kV. It was also utilized to perform the EDX mapping and line scan of the sample. FEG-SEM images were recorded on a FEG-SEM-JSM-7600F Field Emission Scanning Electron Microscope. The powder X-ray diffraction (PXRD) spectroscopy was carried out on Smart lab, 9 kW rotating anode, at a scanning rate of 2º min^{-1} from 20–80 with Cu Kα radiation (λ = 1.5148 Å). Photoluminescence (PL) spectra were recorded on Hitachi F-4700 fluorescence spectrophotometer using xenon lamp as an excitation source. The magnetic property of the synthesized sample was explored with a vibrating sample magnetometer (VSM, Quantum Design, Model- Par 155, moment measurement range: 0.00001 to 10000 e.m.u.). The UV-Vis characterization of the synthesized sample was done on Perkin Elmer Model: UV -2450 UV-Vis- NIR spectrophotometer. The ^{1}H and ^{13}C NMR spectra of the products were carried out in $CDCl_3$/DMSO on Bruker Avance III (400 and 100 MHz). TGA was recorded on Perkin Elmer Simultaneous Thermal Analyser STA- 6000 having a heating rate of 10 °C/min. Commercially available Merck TLC Silica gel 60 aluminum plates were used for carrying out thin layer chromatography studies.

1.3 Catalyst Preparation

1.3.1 Synthesis of nanoceria (NC)

In the synthesis of nanoceria [1], the solution of cerium (IV) sulfate (5.2 g) in distilled water (50 mL) was formed with constant stirring for an hour. After this, pH 10 was maintained by

dropwise addition of NH_3 solution followed by continuous stirring for 4 h at 70 °C. The mixture was filtered under reduced pressure to obtain a solid residue followed by heating at 600 °C for 2 h under an air atmosphere. The obtained material was grounded and repeatedly washed with 1 M HCl solution followed by distilled water. Then, it was dried at 50 °C for 12 h in an oven.

1.3.2 Synthesis of tridoped nanoceria (TDNC)

For tri-doping of ceria, ionic liquid 1-butyl-4-methylpyridinium tetrafloroborate (1 g) was added to the already prepared nanoceria (5 g) in a silica crucible. This mixture was thoroughly mixed with grinding accompanied by calcination at 600 °C for 3 h. It was washed with water and dried in an oven at 80 °C for 24 h.

1.3.3 Synthesis of $NiFe_2O_4$/B, N and F-tridoped nanoceria (NFTDNC)

First of all, $NiFe_2O_4$ NPs were synthesized according to an earlier reported method. A solution of $FeCl_3$ (6.488 g, 0.04 mol) in distilled water (25 mL) was made under vigorous stirring. Similarly, $NiCl_2.6H_2O$ (4.754 g, 0.02 mol) was dissolved in distilled water (25 mL) and stirred to form its solution. Then, these solutions were mixed by continuous stirring at 60 ºC for 40 min. until a homogenous yellow-colored stock solution was formed. Its pH was maintained at 11 by the dropwise addition of NH_3 solution. It leads to the formation of reddish-brown color precipitates in the reaction mixture. After complete precipitation, these precipitates were filtered under reduced pressure and thoroughly washed with deionized water and ethanol. The obtained material was centrifuged for 10 min at 1000 rpm along with drying at 100 °C in an oven for 10 h. It was then ground in an agate mortar to obtain a fine powder.

$NiFe_2O_4$ NPs (1 g) and *B*, *N* and *F* tridoped nanoceria (5 g) were mixed in a silica crucible and heated at 650 °C for 3 h in a muffle furnace. The contrived nanomaterial *i.e.* $NiFe_2O_4$/*B*, *N, F*-tridoped nanoceria was repeatedly washed with deionized water along with ethyl acetate and ethanol followed by drying under vacuum at room temperature.

1.3.4 General procedure for $NiFe_2O_4$/B,N,F-tridoped nanoceria (NFTDNC) catalyzed synthesis of pyrazolopyranopyrimidine derivatives

To a mixture of ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol) in H_2O (5 mL) in a 50 mL round-bottom flask, $NiFe_2O_4$/*B*,*N,F*-tridoped nanoceria (NFTDNC) (0.030g) was added. The mixture was stirred at room temperature for 15 min. Then, aromatic aldehyde (1 mmol) and barbituric acid (1 mmol) were added to them. Thin-layer chromatography (TLC) was used to observe the progress of the reaction. The catalyst was recovered from the reaction mixture after the completion of the reaction. The products were filtered followed by recrystallization with ethanol. The structures of the synthesized products were established by ^{1}H NMR and ^{13}C NMR spectral data.

1.3.5 General procedure for preparation of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives by $NiFe_2O_4$/B,N,F-tridoped nanoceria (NFTDNC) nanomaterial

In a 50 mL round-bottom flask, phthalimide (1.0 mmol), $NiFe_2O_4$/*B*,*N,F*-tridoped nanoceria (NFTDNC) (0.050), hydrazine monohydrate (1.0 mmol) and H_2O (5 mL) were added. After stirring the reaction mixture for the desired time at 60 ºC, an aromatic aldehyde (1.0 mmol) and malononitrile (1.0 mmol) were added to it. The completion of the reaction was determined by employing thin-layer chromatography (TLC). The nanocatalyst was separated after the completion of the reaction. The pure compounds were obtained by recrystallization of the products with ethanol. The structures of the synthesized products were characterized using ^{1}H NMR and ^{13}C NMR techniques.

1.3.6 Preparation of dye solution for adsorption process

The sodium 4-{[4- (dimethylamino)phenyl] diazenyl}benzene−1-sulfonate *i.e.* methyl orange dye was procured from HiMedia and used as such. One gram of dye was dissolved in deionized water (1 L) to prepare a stock solution. It was diluted to form solutions of other appropriate concentrations

1.3.7 Batch mode adsorption experiments

In batch adsorption phenomena, the adsorption of MO dye on adsorption sites in NFTDNC from aqueous solution was evaluated for various variables, such as concentration of dye solution, the dosage of adsorbent, pH, temperature and contact time. The stock solution was diluted to form solutions of (5, 10, 20, 30, 40, 50 and 100 ppm) concentrations of MO dye. The 50 mL of dye solution were taken in the 100 mL round-bottomed flask with initial dye concentrations as (5, 10, 20, 30, 40, 50 and 100) ppm. At a particular instant, the effect of only one variable was studied keeping the other parameters constant. The adsorption variables viz. dosage effect, solution pH (3−10), the effect of temperature (283.15–333.15) K and contact time (10 min - 100 min), were optimized for adsorption MO dye. After the visual completion of the adsorption process, centrifugation was done to separate the adsorbent from the adsorbate solution. The UV–visible spectrophotometer (Model: T-90 UK) was used for the determination of absorbance of the filtrate at 464 nm (maximum absorption). The dye adsorbed at equilibrium *i.e.* qe (mg/g) was studied using Eq. (1).

$$qe = \left(\frac{C_o - C_e}{W}\right) V \qquad \textbf{(1)}$$

where V is the volume of solution, C_0 and Ce are initial and equilibrium concentrations of dye in the liquid phase (mg/L) and W is the weight of the adsorbent**.**

1.4 References

[1] V. Ramasamy, V. Mohana, V. Rajendran, Characterization of Ca doped CeO_2 quantum dots and their applications in photocatalytic degradation, OpenNano 3 (2018) 38-47.

2. Supplementary Tables

Table 1. EDX analysis of $NiFe_2O_4$ immobilized over *B,N,F* tridoped nanoceria (NFTDNC)

Element	Weight %	Atomic %
B K	6.25	26.20
N K	0.35	1.12
O K	12.27	34.75
F K	1.29	3.07
CeL	60.88	19.68
FeK	13.98	11.34
NiK	4.97	3.83

Table 2. Effect of concentration of catalyst on the synthesis of pyrazolopyranopyrimidine derivatives[a]

S.No	Amount of Catalyst (Wt %)	Time (min)	Yield (%)[b]
1	-	120	-
2	15	8	74
3	20	6	82
4	**30**	**2**	**90**
5	40	2	90
6	35	2	90

[a] **Optimized Reaction conditions:** ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), *o*-nitrobenzaldehyde (1 mmol), barbituric acid (1 mmol), water (5 mL) at room temperature.
[b] Isolated yield refers to yield obtained after crystallization with ethanol

Table 3. Effect of temperature in the synthesis of pyrazolopyranopyrimidine derivatives[a]

S. No.	Temperature (ºC)	Time (min)	Yield (%)[b]
1	80	2	90
2	70	2	90
3	60	2	90
4	50	2	90
5	**R.T.**	**2**	**90**

[a] **Optimized Reaction conditions:** ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), *o*-nitrobenzaldehyde (1 mmol), barbituric acid (1 mmol), nanocatalyst NFTDNC (30 wt %), water (5 mL).
[b] Isolated yield refers to yield obtained after crystallization with ethanol

Table 4. Effect of solvent in the synthesis of pyrazolopyranopyrimidine derivatives[a]

S. No.	Solvent	Temperature (ºC)	Time (min)	Yield (%)[b]
1	Solvent Free	R.T.	120	15
2	Ethanol	R.T.	10	75
3	Acetonitrile	R.T.	30	40
4	**Water**	**R.T.**	**2**	**90**
5	DMF	R.T.	30	54
6	Toluene	R.T.	30	20

[a] **Optimized Reaction conditions:** ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), *o*-nitrobenzaldehyde (1 mmol), barbituric acid (1 mmol), nanocatalyst NFTDNC (30 wt %) at room temperature.
[b] Isolated yield refers to yield obtained after crystallization with ethanol

Table 5. Screening of catalyst for the synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones derivatives [a]

S.No	Amount of Catalyst (Wt %)	Time (min)	Yield (%)[b]
1	-	120	-
2	**50**	**6**	**85**
3	60	6	85
4	40	8	80
5	35	10	70

[a] **Optimized Reaction conditions:** phthalimide (1 mmol), hydrazine hydrate (1 mmol), *m*-nitrobenzaldehyde (1 mmol), malononitrile(1 mmol), water (5 mL) at 60 ºC.
[b] Isolated yield refers to yield obtained after crystallization with ethanol

Table 6. Effect of temperature in the synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones derivatives [a]

S. No.	Temperature (ºC)	Time (min)	Yield (%)[b]
1	R.T.	60	-
2	40	60	15
3	50	60	40
4	**60**	**6**	**85**
5	70	6	85

[a] **Optimized Reaction conditions:** phthalimide (1 mmol), hydrazine hydrate (1 mmol), *m*-nitrobenzaldehyde (1 mmol), malononitrile(1 mmol), nanocatalyst NFTDNC (50 wt %), water (5 mL).
[b] Isolated yield refers to yield obtained after crystallization with ethanol

Table 7. Screening of solvent in the synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones derivatives [a]

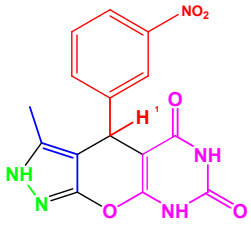
S. No.	Solvent	Temperature (ºC)	Time (min)	Yield (%)[b]
1	Solvent Free	60	120	20
2	Ethanol	60	120	60
3	Acetonitrile	60	120	50
4	**Water**	**60**	**6**	**85**
5	DMF	60	120	55
6	Toluene	60	120	-

[a] **Optimized Reaction conditions:** phthalimide (1 mmol), hydrazine hydrate (1 mmol), *m*-nitrobenzaldehyde (1 mmol), malononitrile(1 mmol), nanocatalyst NFTDNC (50 wt %), at 60 ºC.
[b] Isolated yield refers to yield obtained after crystallization with ethanol

3. Spectral data of the synthesized products of Pyrazolopyranopyrimidine and 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones derivatives

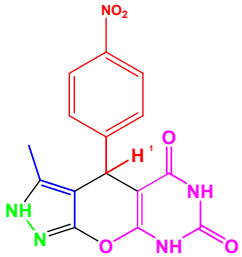
A. Pyrazolopyranopyrimidine derivatives

1



^{1}H NMR (400 MHz, DMSO): δ 10.31 (s, 3H), 10.08 (s, 1H), 8.84 (s, 1H), 8.66 (d, 1H), 8.50 (d, 1H), 8.29 (t, 1H), 5.48 (s, 1H).
^{13}C NMR (101 MHz, DMSO): δ 192.40, 160.88, 159.73, 151.19, 137.45, 135.51, 131.41, 129.02, 124.34, 122.92, 121.39, 56.65.

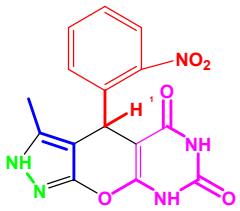
2



^{1}H NMR (400 MHz, DMSO): δ 10.35 (s, 3H), 10.09 (s, 1H), 8.38 (d, *J* = 8.7 Hz, 2H), 8.12 (d, *J* = 8.7 Hz, 2H), 5.95 (s, 1H).

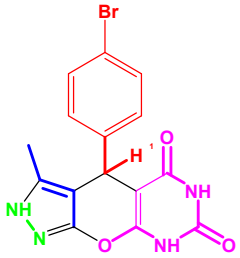
^{13}C NMR (101 MHz, DMSO): δ 192.95, 153.45, 151.20, 140.36, 131.11, 128.35, 128.22, 127.58, 127.18, 124.66, 123.64, 123.40, 81.63.

3



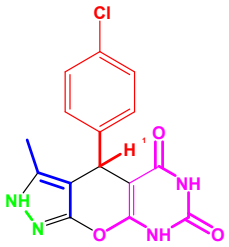
^{1}H NMR (400 MHz, DMSO): δ 10.32 (s, 3H), 7.98 (s, 1H), 7.90 (d, 1H), 7.85 (d, 1H), 7.52 (t, 1H), 7.43(t, 1H).
^{13}C NMR (101 MHz, DMSO): δ 192.48, 151.63,150.93, 147.34, 144.65, 143.33, 130.95, 121.34, 92.96, 52.18.

4



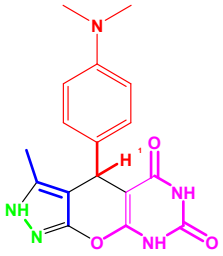
^{1}H NMR (400 MHz, DMSO): δ 10.38 (s, 3H), 8.01 (s, 1H), 7.54 (d, 2H), 7.46 (d, 2H).
^{13}C NMR (101 MHz, DMSO): δ 190.58, 152.63, 149.35, 145.78, 138.32, 131.92, 130.65, 122.43, 95.38, 62.9, 15.90.

5



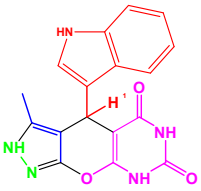
^{1}H NMR (400 MHz, DMSO): δ 10.30 (s, 3H), 8.30 (s, 1H), 7.58 (d, 2H), 7.49 (d, 2H).
^{13}C NMR (101 MHz, DMSO): δ 190.42, 153.63, 149.35, 146.43, 139.01, 133.91, 131.51, 129.35, 94.38, 65.90, 14.65.

6



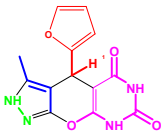
^{1}H NMR (400 MHz, DMSO): δ 10.28 (s, 3H), 8.20 (s, 1H), 7.12 (d, 2H), 7.6.68 (d, 2H).
^{13}C NMR (101 MHz, DMSO): δ 168.66, 152.54, 151.98, 149.63, 148.43, 131.49, 130.54, 112.78, 94.42, 62.93, 44.91, 16.61.

7



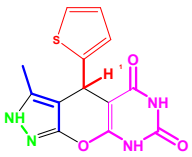
^{1}H NMR (400 MHz, DMSO) δ 12.15 (s, 2H), 9.87 (s, 2H), 8.23 (s, 2H), 8.06 (d, 1H), 7.50 (d, 1H), 7.26 – 7.22 (m, 2H).
^{13}C NMR (101 MHz, DMSO): δ 186.25, 139.30, 137.42, 124.34, 124.20, 122.90, 121.25, 118.47, 112.95, 90.52, 63.64, 16.68.

8



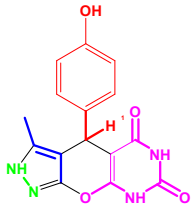
^{1}H NMR (400 MHz, DMSO) δ 10.68 (s, 3H), 8.36 (s, 1H), 7.32 (d, 1H), 6.52 (d, 1H), 6.26 (t, 1H).
^{13}C NMR (101 MHz, DMSO): δ 165.47, 150.63, 148.32, 144.85, 144.78, 141.94, 141.18, 117.92, 112.26, 108.60, 94.64, 48.56, 14.64.

9



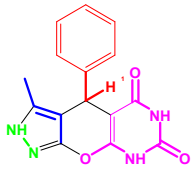
^{1}H NMR (400 MHz, DMSO) δ 10.42 (s, 3H), 8.34 (s, 1H), 7.26 (m, 2H), 6.98 (t, 1H).
^{13}C NMR (101 MHz, DMSO): δ 165.71, 154.48, 151.42, 150.98, 147.68, 140.94, 140.48, 127.26, 98.96, 90.94, 52.65, 14.49.

10



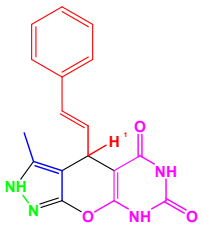
^{1}H NMR (400 MHz, DMSO) δ 10.51 (s, 3H), 8.14 (s, 1H), 7.08 (d, 2H), 6.62 (d, 2H).
^{13}C NMR (101 MHz, DMSO): δ 174.66, 156.78, 150.63, 149.53, 148.46, 131.91, 118.32, 94.38, 65.94, 16.69.

11



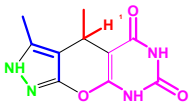
^{1}H NMR (400 MHz, DMSO): δ 10.45 (s, 3H), 8.34 (s, 1H), 7.36 (m, 2H), 7.22 (m, 3H).
^{13}C NMR (101 MHz, DMSO): δ 190.92, 152.65, 149.53, 148.46, 147.43, 140.41, 130.98, 130.82, 96.99, 62.93, 14.40.

12



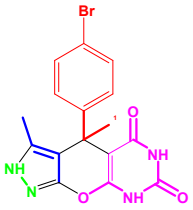
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.35 (s, 2H), 7.81 (d, 1H), 7.60 – 7.55 (m, 2H), 7.54 – 7.40 (m, 5H), 6.48 (d, 1H), 1.27 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.80, 159.10, 155.19, 146.96, 135.93, 134.07, 130.73, 128.98, 128.35, 122.81, 117.08, 107.11, 48.14.

13



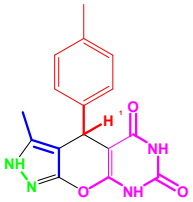
^{1}H NMR (400 MHz, DMSO): δ 10.26 (s, 3H), 5.06 (s, 1H), 1.47 (s, 3H).
^{13}C NMR (101 MHz, DMSO): δ 165.76, 154.63, 148.93, 144.46, 108.68, 52.06, 24.64, 14.68.

14



^{1}H NMR (400 MHz, DMSO): δ 10.32 (s, 3H), 7.48 (d, 2H), 7.32 (d, 3H), 1.67 (s, 3H).
^{13}C NMR (101 MHz, DMSO): δ 175.09, 160.62, 152.96, 150.01, 146.44, 146.02, 131.25, 130.25, 129.72, 122.87, 120.95, 111.10, 25.96, 14.41

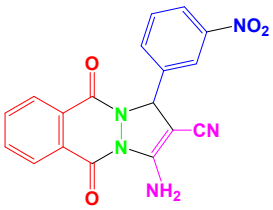
15



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 2H), 8.10 (d, 2H), 7.98 (d, 2H), 7.54 (s, 1H), 7.02 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.82, 146.97, 134.08, 130.73, 128.97, 128.35, 117.07, 29.70, 19.83.

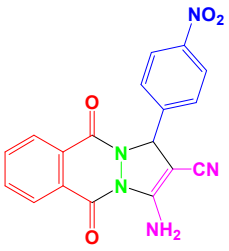
B. 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones derivatives

16



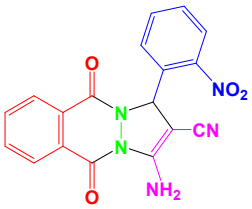
^{1}H NMR (400 MHz, DMSO): δ 11.34 (s, 2H), 8.55 (s, 1H), 8.44 (d, *J* = 8.1 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 7.86 (t, *J* = 8.1 Hz, 1H), 7.80 (s, 4H), 4.30 (s, 1H).
^{13}C NMR (101 MHz, DMSO): δ 169.98, 159.65, 148.36, 136.64, 135.51, 134.96, 132.75, 131.46, 129.00, 128.33, 124.87, 123.46, 114.02, 113.03, 85.47.

17



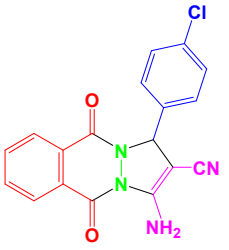
^{1}H NMR (400 MHz, DMSO): δ 11.33 (s, 2H), 8.34 (d, 2H), 8.09 (d, 2H), 7.80 (s, 4H), 4.29 (s, 1H).
^{13}C NMR (101 MHz, DMSO): δ 169.96, 159.69, 150.05, 136.99, 134.96, 132.77, 131.83, 131.10, 128.08, 124.66, 123.96, 123.46, 113.94, 112.87, 112.31, 86.54, 69.86.

18



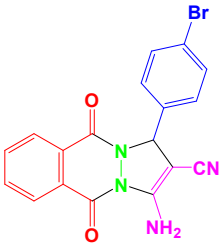
^{1}H NMR (400 MHz, DMSO): δ 11.33 (s, 2H), 8.02 (d, 1H), 7.64 (t, 1H), 7.40 (t, 1H), 7.32 (m, 4H), 7.22 (t, 1H), 5.36 (s, 1H).
^{13}C NMR (101 MHz, DMSO): δ166.22, 163.37, 157.75, 140.23, 134.76, 128.81, 128.68, 118.49, 68.92.

19



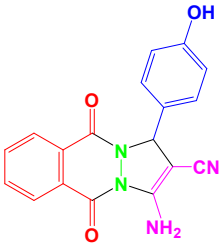
^{1}H NMR (400 MHz, DMSO): δ 11.34 (s, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.79 (s, 4H), 7.63 (d, *J* = 8.2 Hz, 2H), 4.28 (s, 1H).
^{13}C NMR (101 MHz, DMSO): δ 192.91, 169.97, 160.54, 139.58, 134.96, 132.76, 132.52, 131.66, 130.30, 130.05, 129.80, 123.46, 114.42, 113.40, 82.77.

20



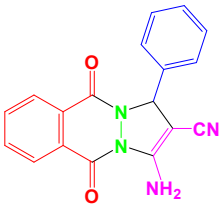
^{1}H NMR (400 MHz, DMSO): δ 11.28 (s, 2H), 7.56 (m, 4H), 7.42 (d, 2H), 7.18 (d, 2H), 4.38 (s, 1H).
^{13}C NMR (101 MHz, DMSO): δ 192.71, 164.72, 142.43, 131.08, 131.01, 130.96, 130.61, 127.32, 120.91, 118.49, 81.43.

21



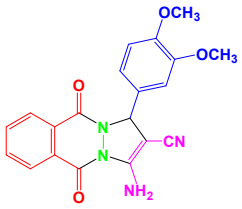
^{1}H NMR (400 MHz, DMSO): δ 11.33 (s, 2H), 7.52 (m, 4H), 7.01 (d, 2H), 6.64 (d, 2H), 4.28 (s, 1H).
^{13}C NMR (101 MHz, DMSO): δ 174.22, 164.73, 162.61, 140.42, 134.74, 134.60, 130.55, 130.01, 128.96, 118.49, 117.76, 117.17, 78.43.

22



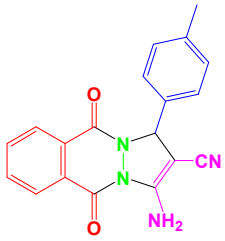
^{1}H NMR (400 MHz, DMSO): δ 11.36 (s, 2H), 7.48 (m, 4H), 7.27 (m, 5H), 4.26 (s, 1H).
^{13}C NMR (101 MHz, DMSO): δ 167.48, 165.46, 144.42, 134.46, 134.14, 134.01, 130.92, 130.46, 130.34, 129.96, 126.64, 125.46, 112.94, 77.96.

23



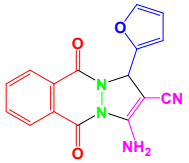
^{1}H NMR (400 MHz, DMSO): δ 11.33 (s, 2H), 7.80 (s, 4H), 7.55 (d, 1H), 7.47 – 7.32 (m, 1H), 7.09 (dd, 1H), 4.29 (s, 1H), 3.85 (s, 3H), 3.76 (s, 3H).
^{13}C NMR (101 MHz, DMSO): δ 169.97, 161.49, 161.05, 154.77, 149.08, 127.77, 126.78, 124.44, 124.12, 123.46, 115.23, 114.49, 112.26, 112.16, 109.39, 77.17, 56.45, 55.86.

24



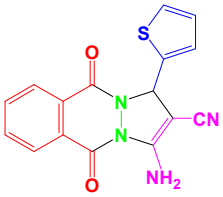
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (m, 6H), 7.31 (d, 2H), 3.74 (s, 1H), 1.72 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.04, 134.35, 132.83, 132.72, 132.30, 130.12, 128.95, 128.54, 123.63, 58.50, 18.43.

25



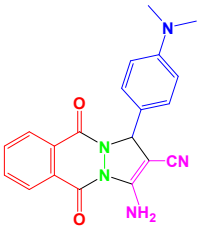
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.22 (s, 2H), 7.52 (m, 4H), 7.30 (d, 1H), 6.36 (t, 1H), 6.08 (d, 1H), 4.22 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 174.22. 162.83, 154.84, 142.45, 140.65, 134.74, 133.66, 130.92, 130.38, 118.05, 112.96, 110.45, 78.21.

26



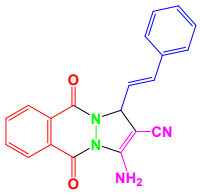
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.34 (s, 2H), 7.59 (m, 4H), 7.08 (d, 1H), 6.88 (t, 1H), 6.74 (d, 1H), 4.24 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 166.62, 161.83, 145.63, 138.73, 134.76, 134.66, 130.98, 128.83, 128.82, 118.84, 79.96.

27



^{1}H NMR (400 MHz, DMSO): δ 11.32 (s, 2H), 7.88 – 7.82 (m, 1H), 7.78 (s, 6H), 6.74 (d, 1H).
^{13}C NMR (101 MHz, DMSO): δ 190.93, 188.55, 169.95, 159.18, 154.75, 134.93, 134.10, 132.74, 123.44, 118.91, 116.04, 112.08, 111.41, 105.32, 68.61, 49.05.

28



^{1}H NMR (400 MHz, DMSO): δ 8.02 (s, 2H), 7.60 (m, 4H), 7.31 (d, 2H), 7.23 (m, 3H), 6.07 (d, 1H)< 5.02 (d,1H), 4.82 (d, 1H).
^{13}C NMR (101 MHz, DMSO): δ 166.22, 161.31, 137.76, 134.47, 133.64, 130.64, 130.21, 129.97, 128.74, 128.36, 122.57, 80.97.

C. ^{1}H NMR and ^{13}C NMR of some selected compounds

1

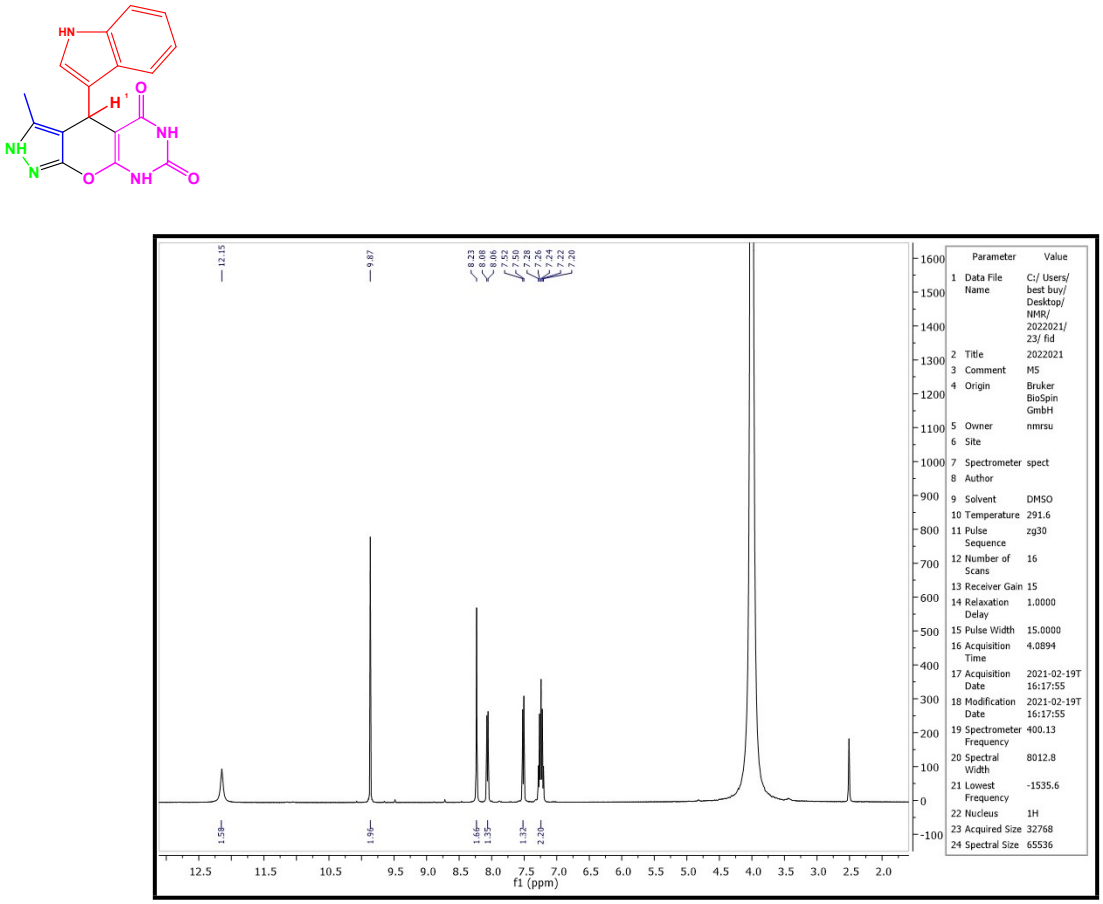


Figure 1. [1]HNMR of 3-Methyl-4-indolyl-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3*d*]pyrimidine-5,7(6*H*,8*H*) dione.

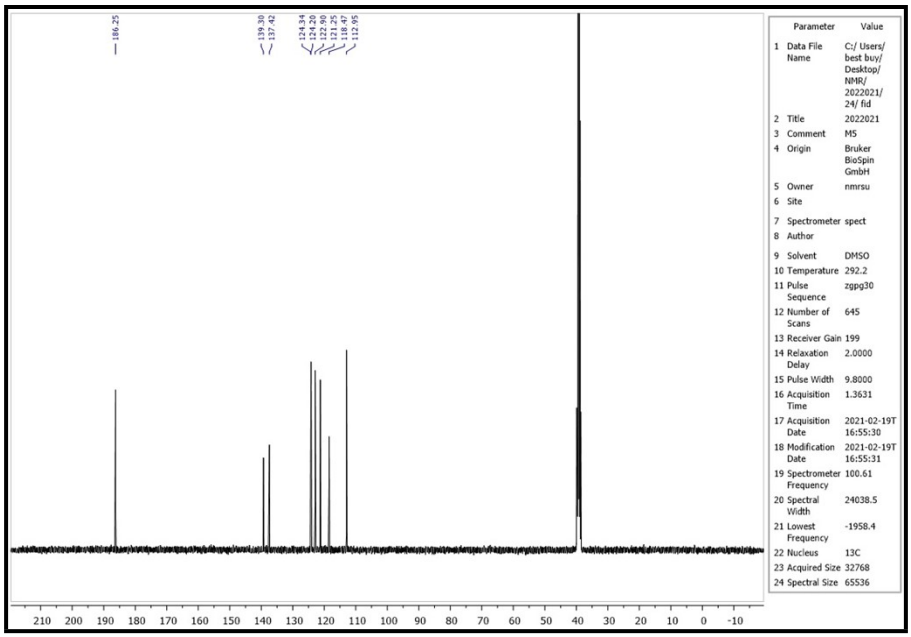
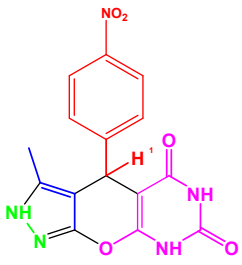


Figure 2. ^{13}CNMR of 3-Methyl-4-indolyl-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3*d*]pyrimidine-5,7(6*H*,8*H*) dione.

2.



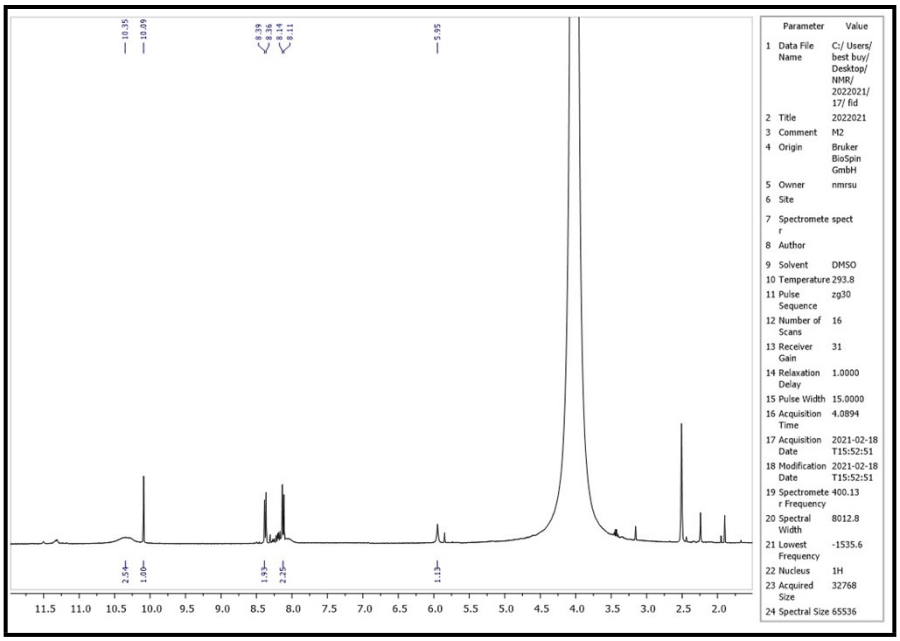


Figure 3. [1]HNMR of 3-Methyl-4-(4-nitrophenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3*d*]pyrimidine-5,7(6*H*,8*H*) dione.

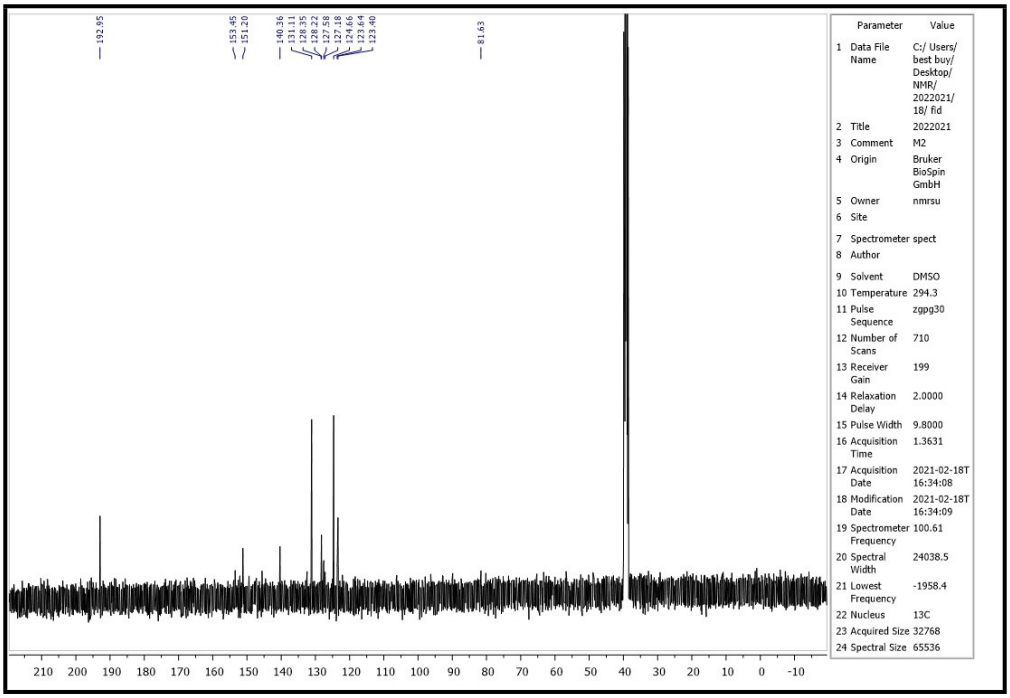
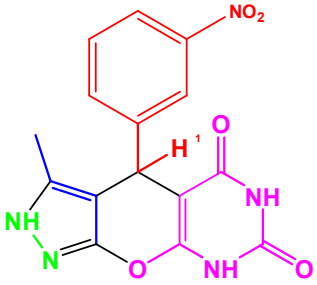


Figure 4. [13]CNMR of 3-Methyl-4-(4-nitrophenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3*d*]pyrimidine-5,7(6*H*,8*H*) dione.

3



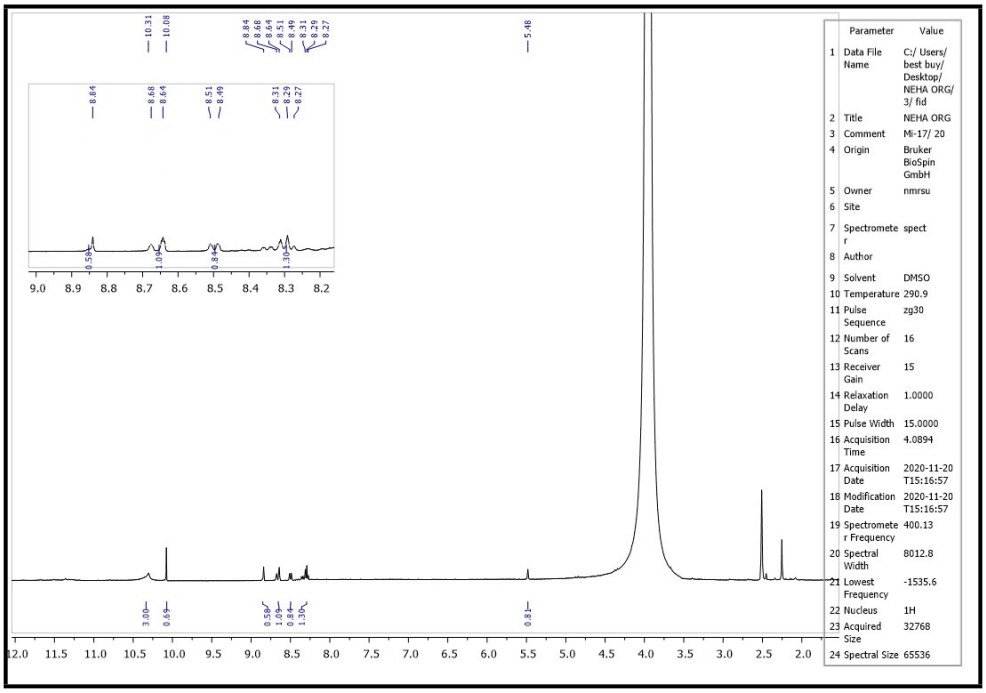
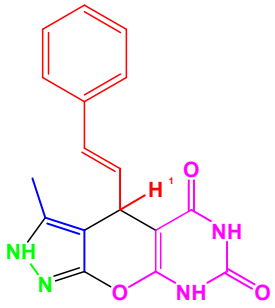


Figure 5. ^{13}CNMR of 3-Methyl-4-(3-nitrophenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3*d*]pyrimidine-5,7(6*H*,8*H*) dione.

4



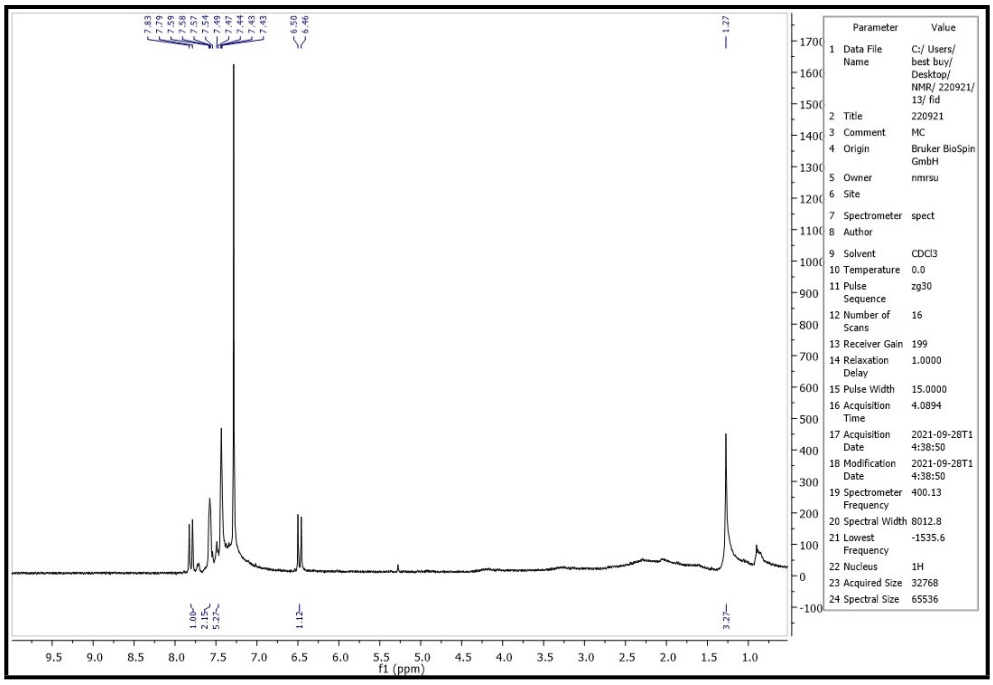


Figure 6. ^{1}HNMR of 3-Methyl-4-cinnamal-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3*d*]pyrimidine-5,7(6*H*,8*H*) dione.

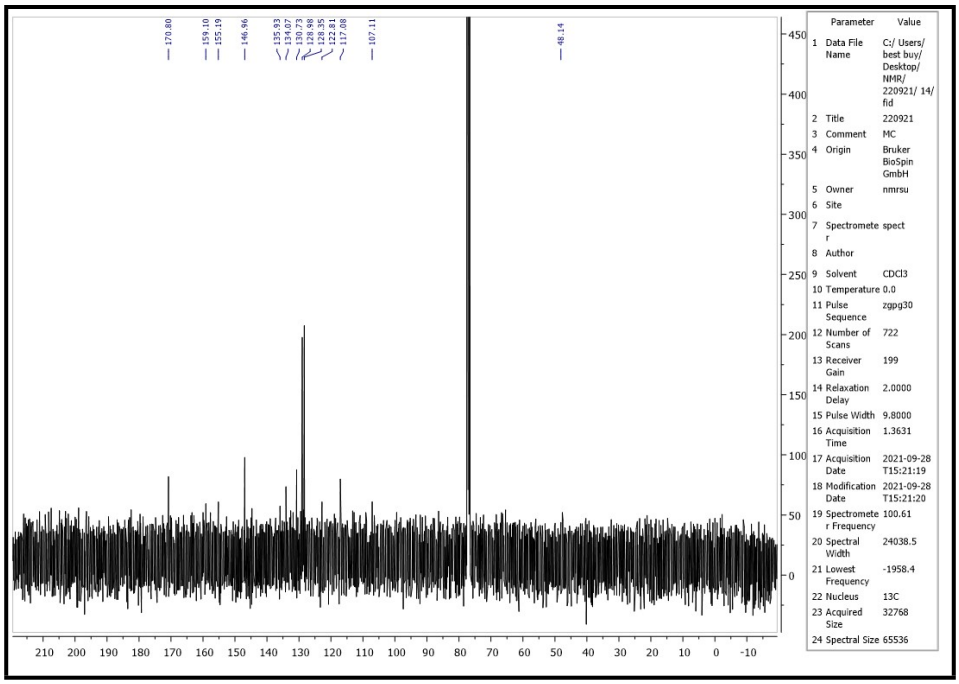
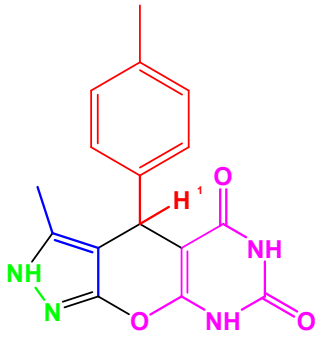


Figure 7. ^{13}CNMR of 3-Methyl-4-cinnamal-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3*d*]pyrimidine-5,7(6*H*,8*H*) dione.

5



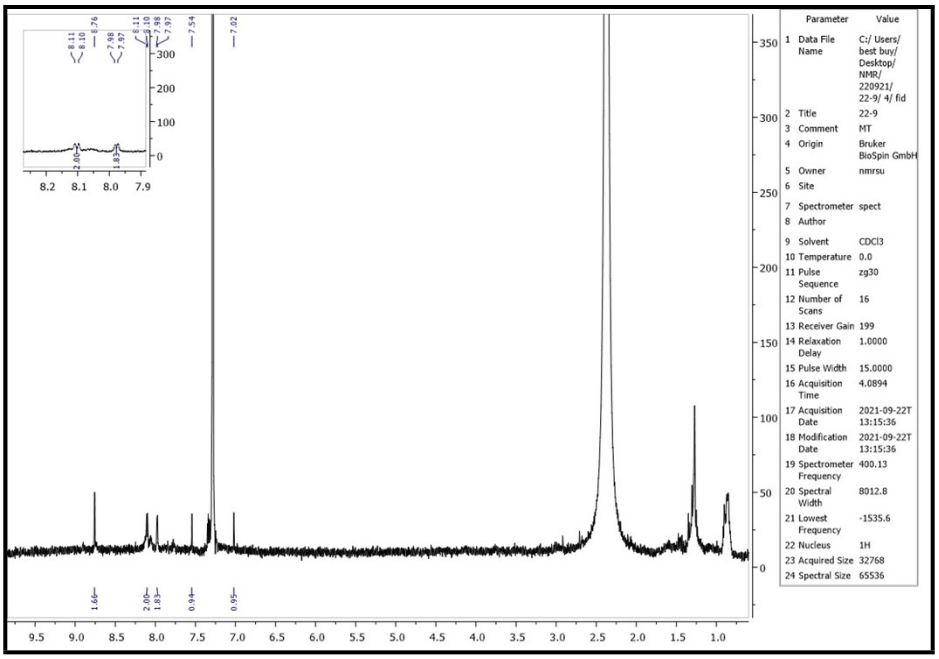


Figure 8. [1]HNMR of 3-Methyl-4-(4-methylphenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3*d*]pyrimidine-5,7(6*H*,8*H*) dione.

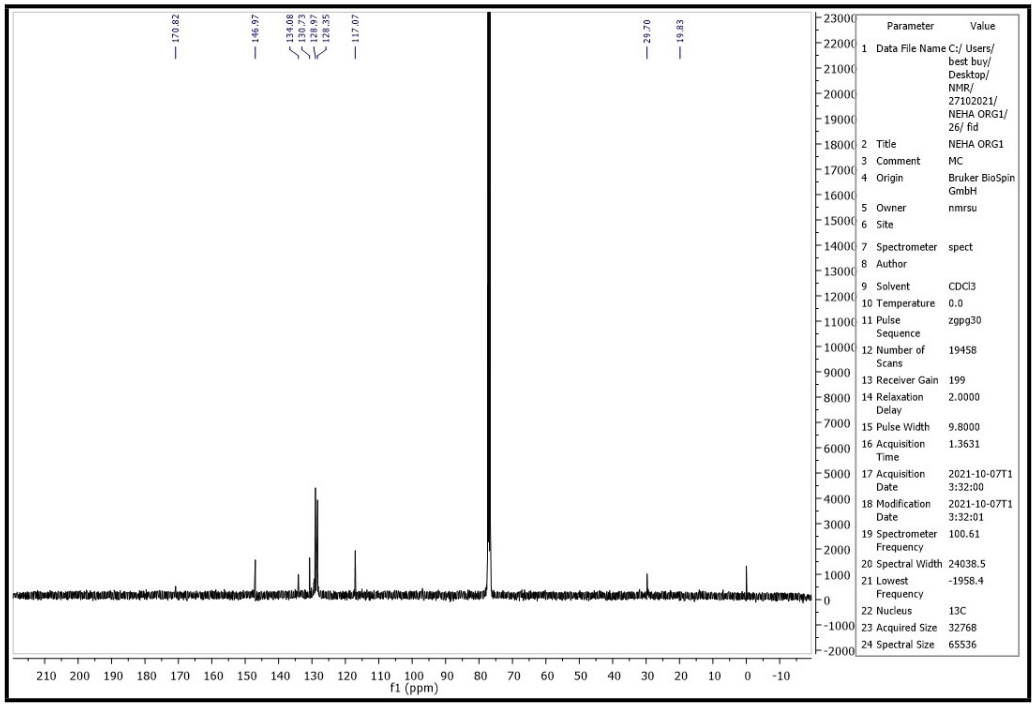
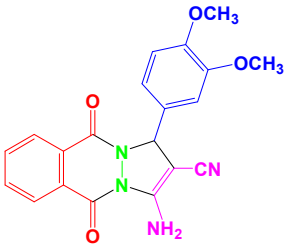


Figure 9. [13]CNMR of 3-Methyl-4-(4-methylphenyl)-1,4-dihydropyrazolo[4',3':5,6]pyrano[2,3*d*]pyrimidine-5,7(6*H*,8*H*) dione.

6



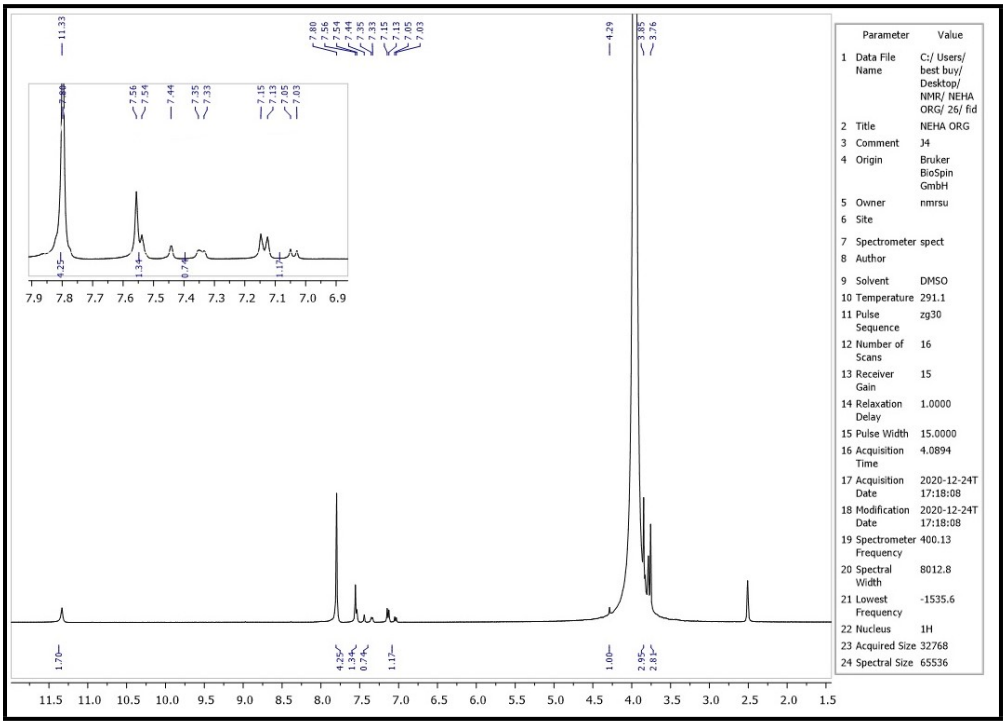


Figure 10. [1]HNMR of 3-Amino-1-(3,4-dimethoxyphenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*] phthalazine-2-carbonitrile.

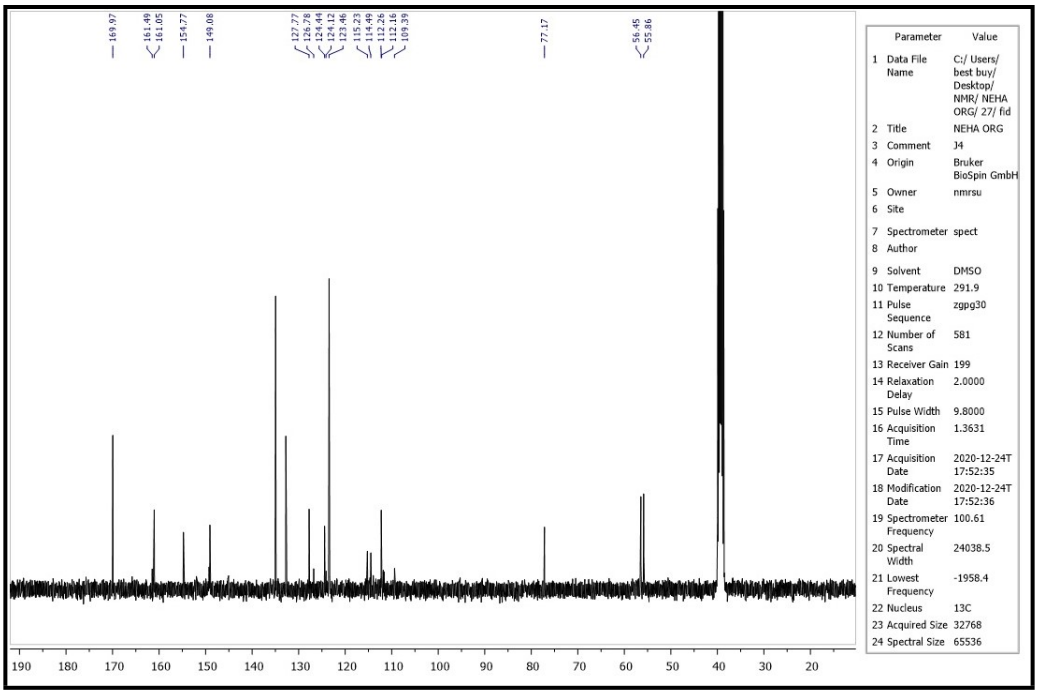
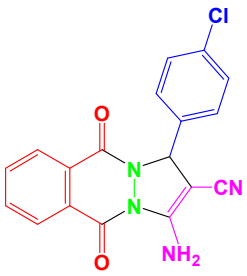


Figure 11. ^{13}CNMR of 3-Amino-1-(3,4-dimethoxyphenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*] phthalazine-2-carbonitrile.

7



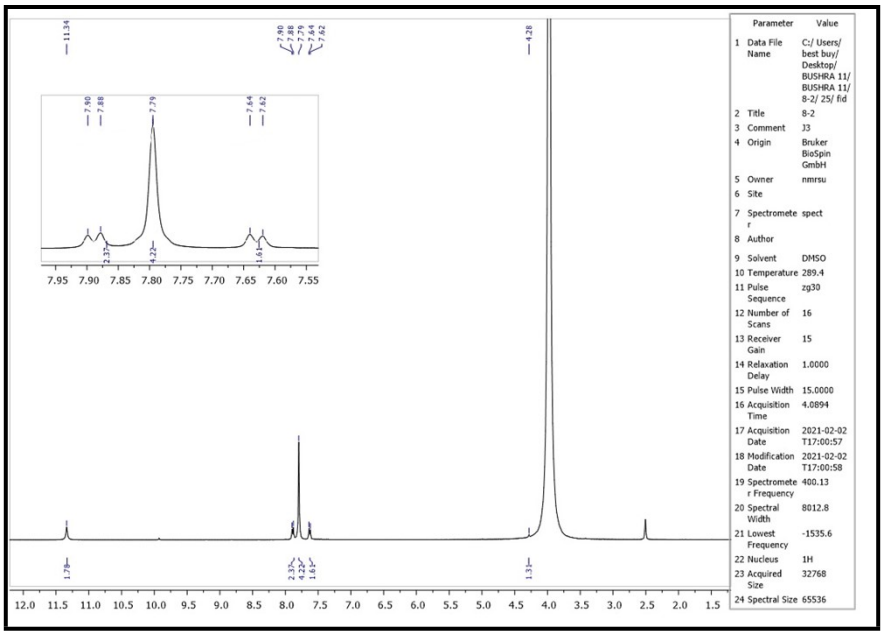


Figure 12. [1]HNMR of 3-Amino-1-(4-chlorophenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*] phthalazine-2-carbonitrile.

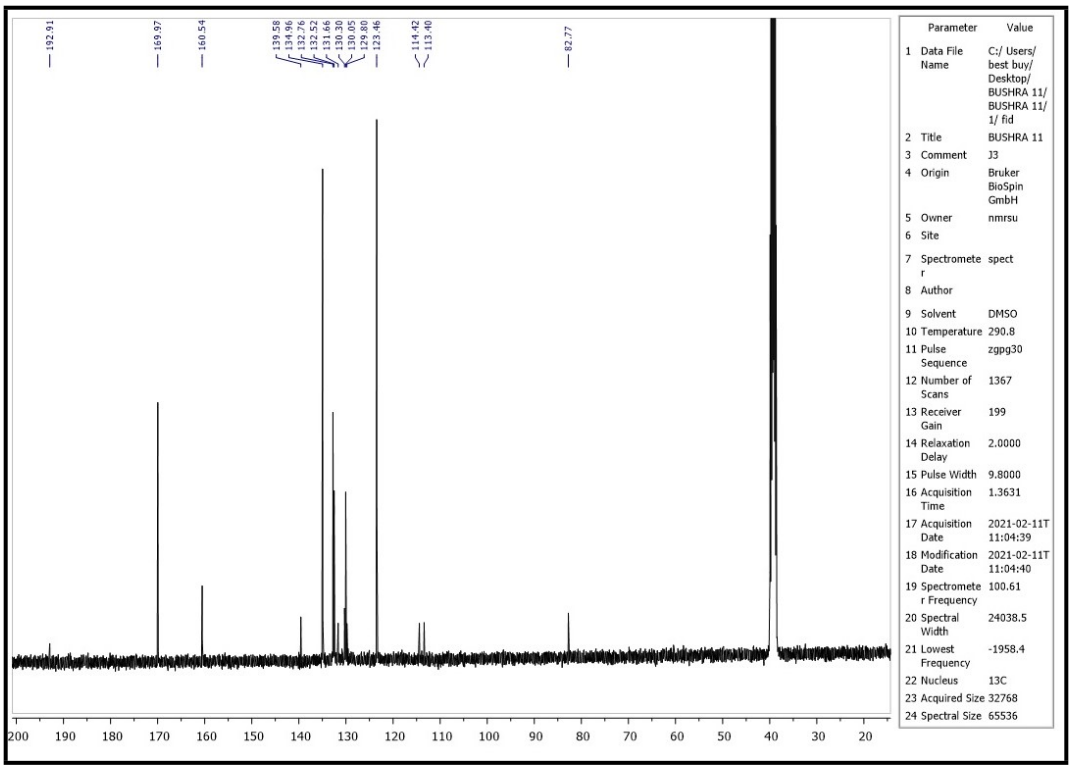
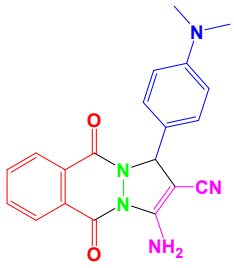


Figure 13. [13]CNMR of 3-Amino-1-(4-chlorophenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*] phthalazine-2-carbonitrile.

8



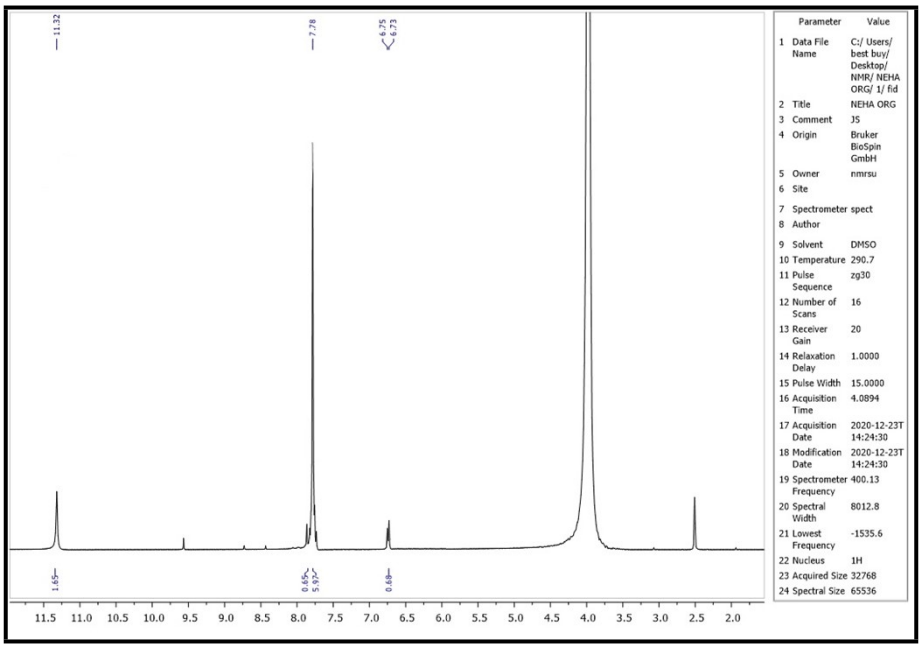


Figure 14. [1]HNMR of 3-Amino-1-(4-n,n-dimethylaminophenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*] phthalazine-2-carbonitrile.

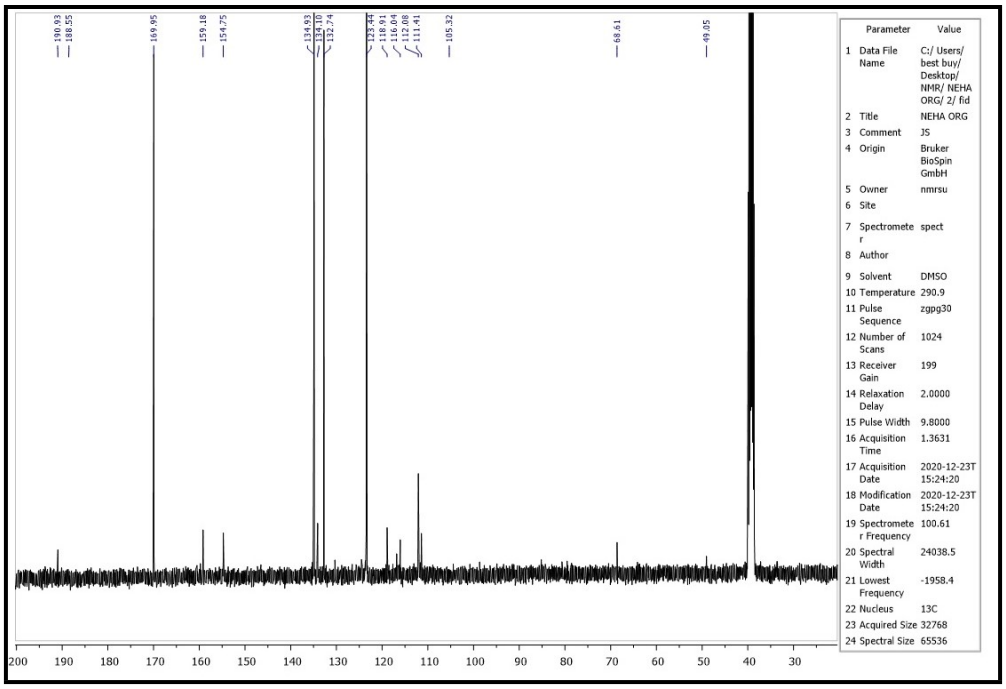
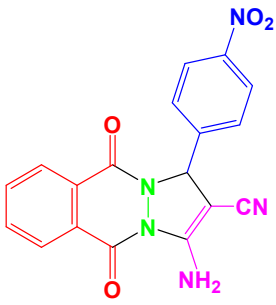


Figure 15. ^{13}CNMR of 3-Amino-1-(4-n,n-dimethylaminophenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*] phthalazine-2-carbonitrile.

9



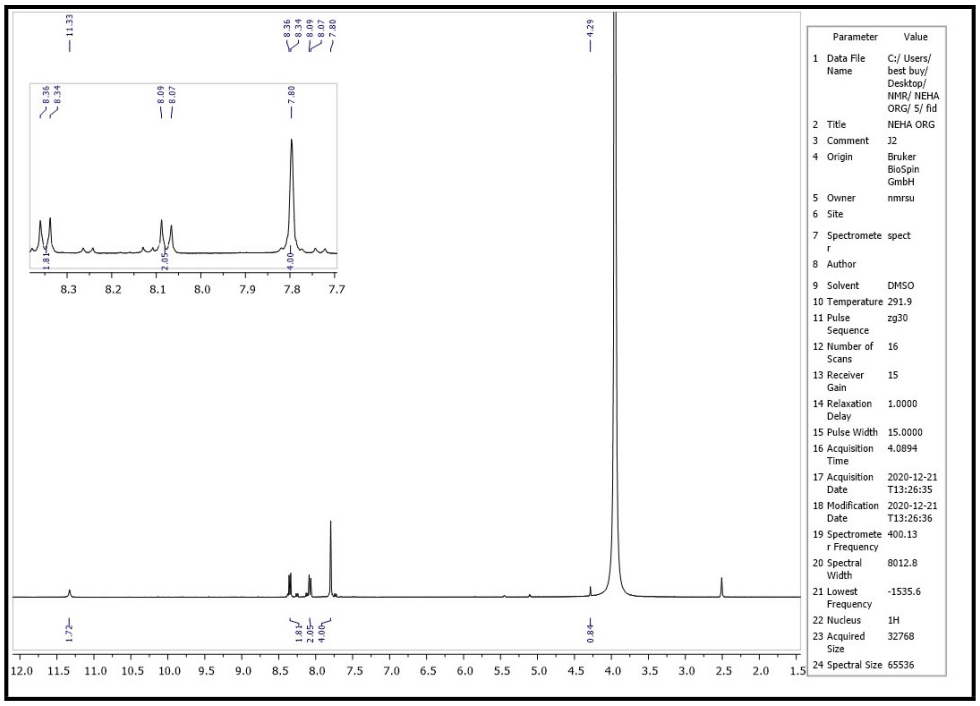


Figure 16. [1]HNMR of 3-Amino-1-(4-nitrophenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*] phthalazine-2-carbonitrile.

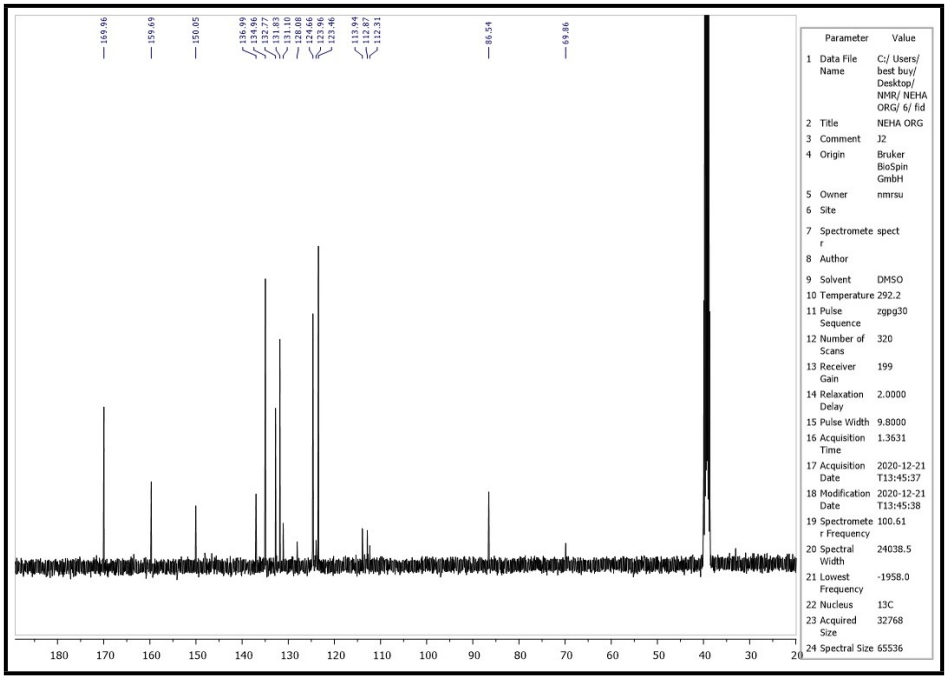
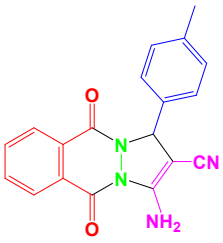


Figure 17. [13]CNMR of 3-Amino-1-(4-nitrophenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*] phthalazine-2-carbonitrile.

10



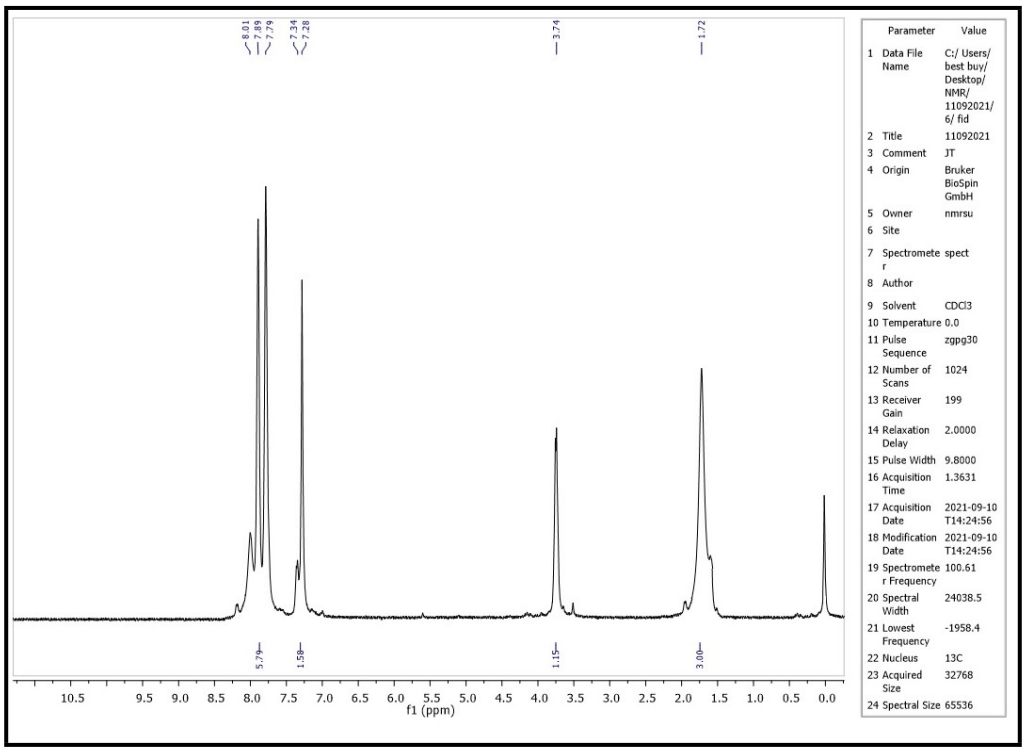


Figure 18. [1]HNMR of 3-Amino-1-(4-methylphenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*] phthalazine-2-carbonitrile.

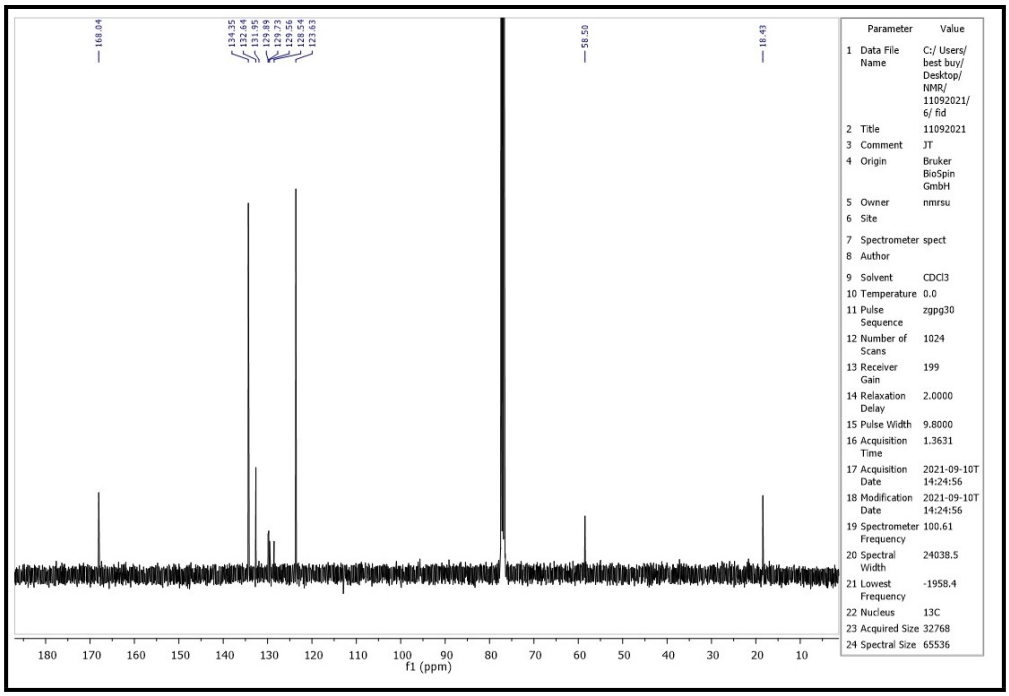
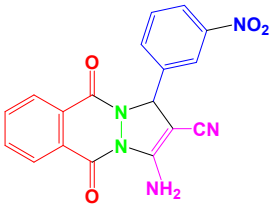


Figure 19. ^{13}CNMR of 3-Amino-1-(4-methylphenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*] phthalazine-2-carbonitrile.

11



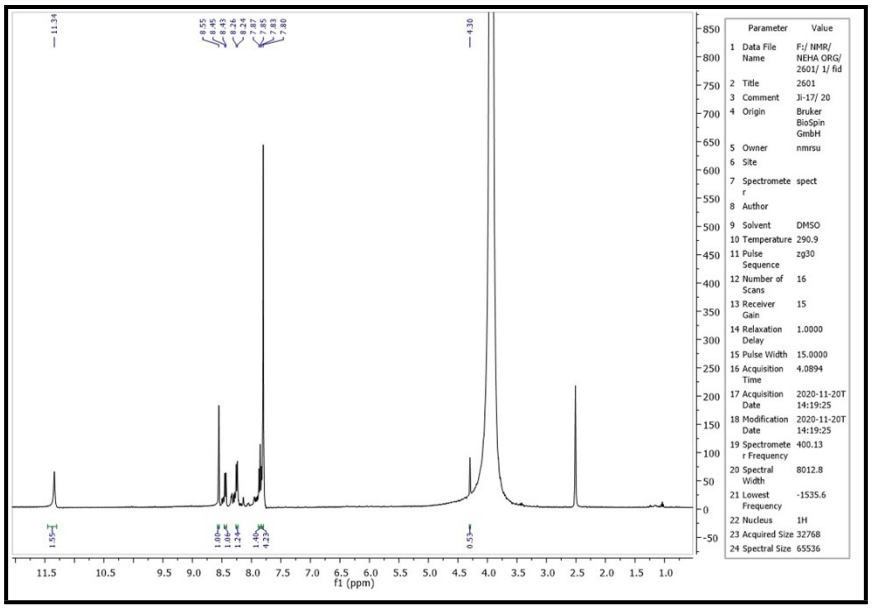


Figure 20. [1]HNMR of 3-Amino-1-(3-nitrolphenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*] phthalazine-2-carbonitrile.

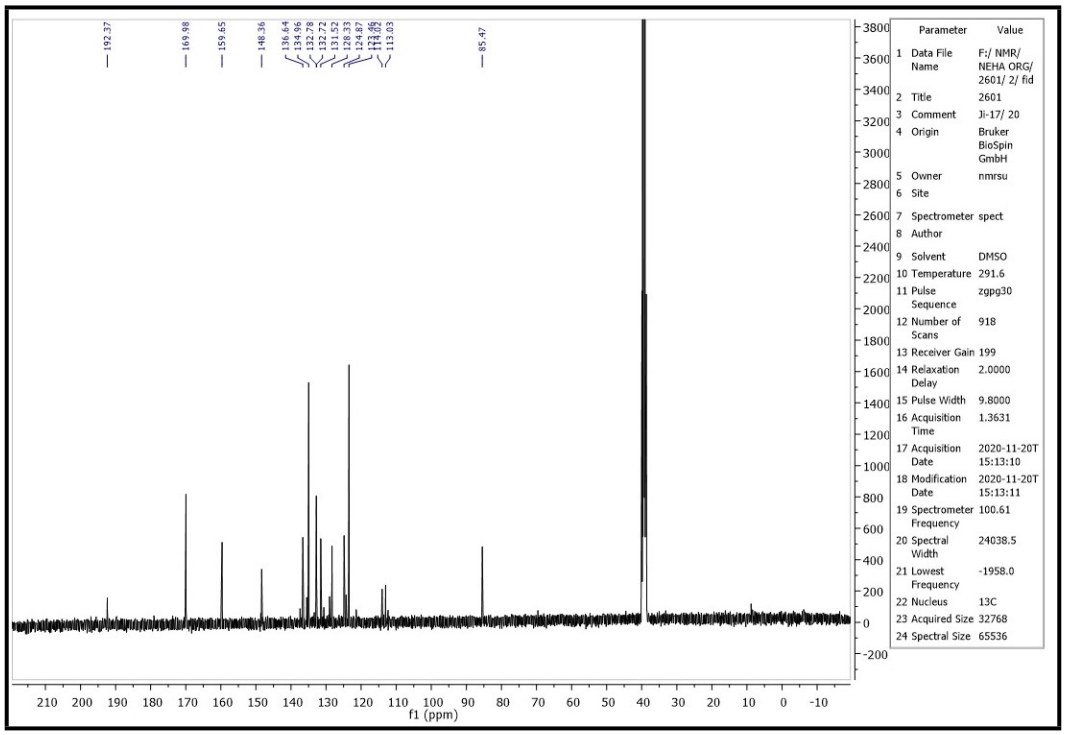


Figure 21. [13]CNMR of 3-Amino-1-(3-nitrolphenyl)-5,10-dihydro-5,10-dioxo-1*H*-pyrazolo[1,2-*b*] phthalazine-2-carbonitrile.