Supporting Information

A catalyst and solvent-free protocol for sustainable synthesis of fused 4*H*-pyran derivatives

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Experimental section

General

4-Hydroxycoumarin, 3-methyl-1-phenyl-5-pyrazolone and all the aldehydes were procured from Sigma-Aldrich. All the solvents were obtained from Merck and Otto Chemie. All the reactions were completed on REMI 2MLH thermo-mechanical stirrer. TLC analysis was carried out using silica gel GF-254 from SRL (Alfa Aesar). Melting points were obtained on a digital apparatus and are uncorrected. IR spectra were done in potassium bromide (KBr) pellets on a Perkin-Elmer 10.4.00 IR spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectral analysis were done on Bruker (Avance-II 400 MHz), Varian-AS 400 NMR, and Bruker BioSpin GmbH spectrometers using tetramethylsilane (TMS) as an internal standard and DMSO-d_6 or $CDCl_3$ as a solvent. Crystal data were collected with a Super Nova, single source at offset/far, HyPix3000 diffractometer (CCD) using graphite monochromated MoKa radiation (k¼0.71073 Å) at 296 K. HRMS spectra was recorded on high resolution mass spectrometer **XEVO G2-XS QTOF.**

General procedure for the preparation of functionalized fused 4*H*-pyrans:

First, a dried 5 ml round bottom flask was equipped by teflon coated magnet and charged with a combination of 3-methyl-1-phenyl-1*H*-pyrazol-5(4H)-one/4-hydroxycoumarin (1 mmol), aromatic aldehydes (1 mmol), and NMSM (1 mmol). The mixture of all reagents was heated at 110 ^{o}C with stirring for mentioned time under neat conditions. Progress of the reactions was monitored by TLC. After completion of the reaction as indicated by TLC, the resulting precipitate was cooled and 2 ml of ethanol was added to stirr for 5 min. Next, the precipitate was filtered and washed with cold ethanol. After that, purification of the crude was done by recrystallization from hot acetonitrile to yield the pure products.

II. Crystallographic Description

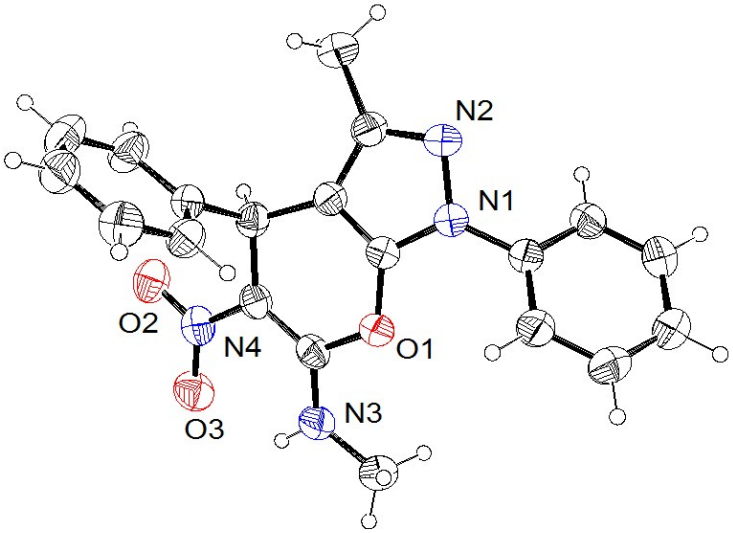


Fig 2. ORTEP representation of compound **4a** (CCDC 1901104)

Table 1. Crystal data for **4a** (CCDC 1901104)

Empirical formula	$C_{20}H_{18}N_4O_3$
Formula weight	362.38
Wavelength	0.71073 Å
Temperature	293(2) K
Crystal system, space group	Monoclinic, P-2
Unit cell dimension (Å)	a = 10.7875 (3) alpha = 90 deg. b = 20.8262 (4) beta = 99.106(2) deg. c = 8.0335 (2) gamma = 90 deg.
Volume	1782.08(8) $Å^3$
Z, Calculated density	4, 1.351 g/cm^3
Absorption coefficient	0.094 mm^{-1}
F (000)	760.0
Absorption correction	multi-scan
Reflection collected	21157
Theta range for data collection	6.456 to 54.798 deg.
Goodness-of-fit on F^2	1.070

Table 2. Crystal data for **6b** (CCDC 1901105)

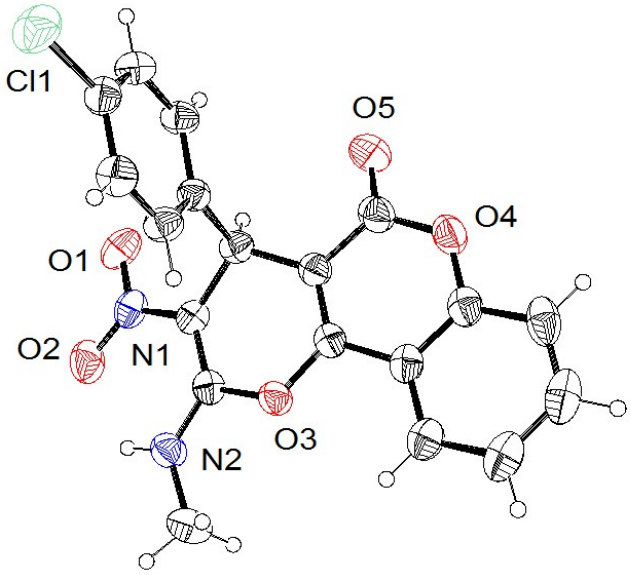
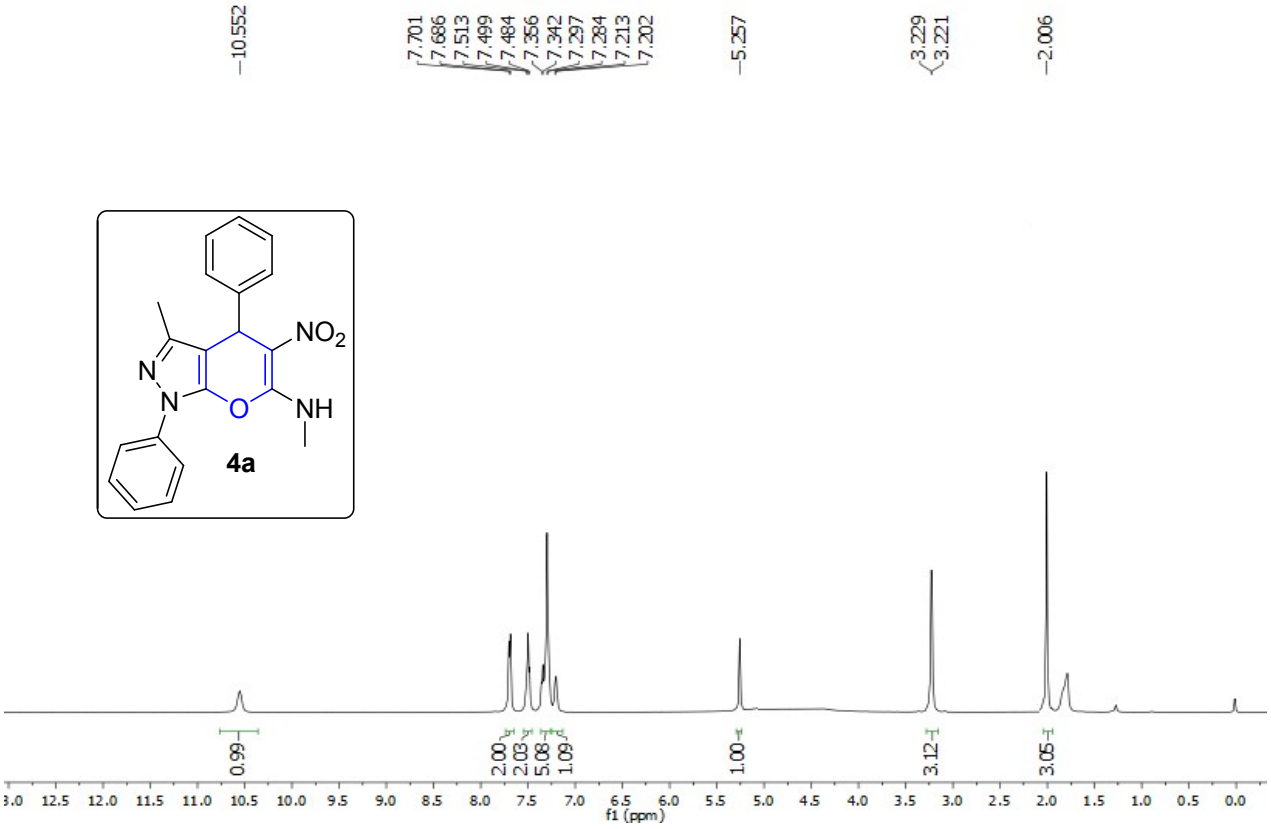


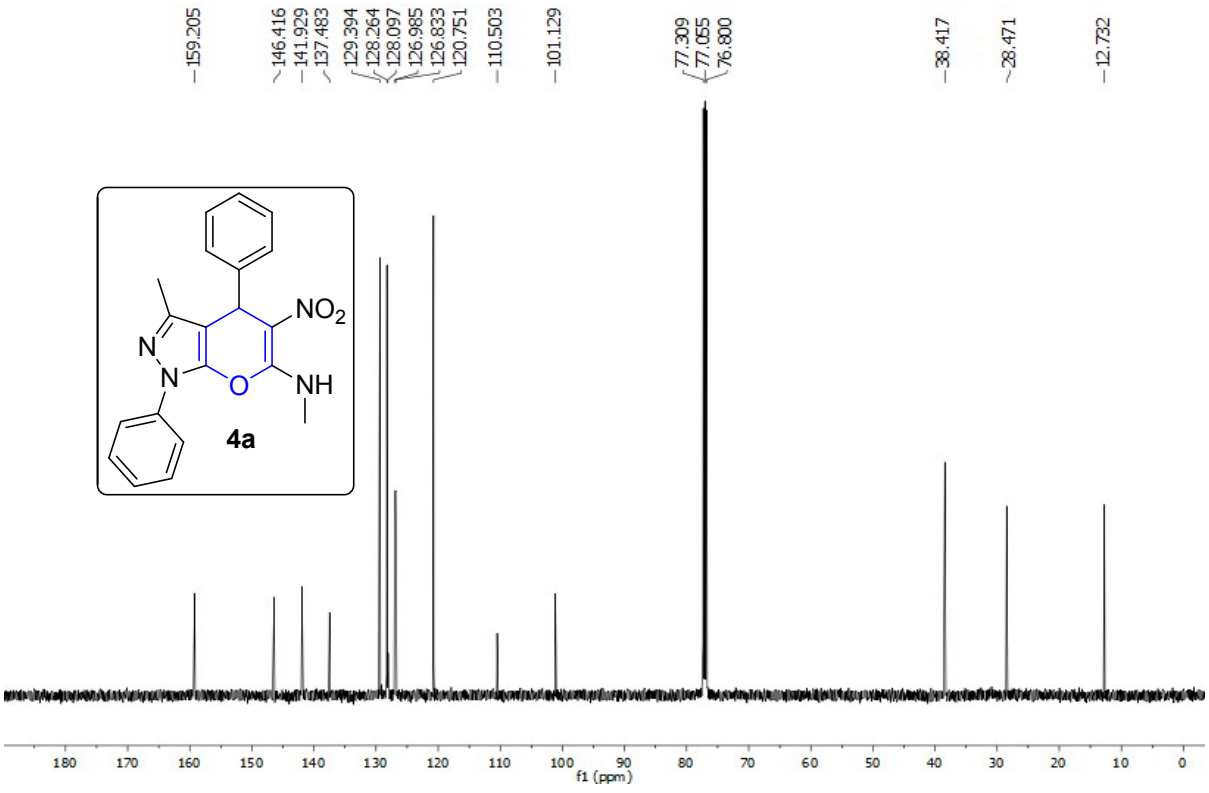
Fig 3.ORTEP representation of compound **6b** (CCDC1901105)

Empirical formula	$C_{19}H_{13}ClN_2O_5$
Formula weight	384.76
Wavelength	0.71073 Å
Temperature	293(2) K
Crystal system, space group	Monoclinic, P-2
Unit cell dimension (Å)	a = 8.5412(2) alpha = 90.0 deg. b = 13.1791(3) beta = 96.973(2) deg. c = 14.8906 (3) gamma = 90.0 deg.
Volume	1663.77(6) $Å^3$
Z, Calculated density	4, 1.536 g/cm^3
Absorption coefficient	0.266 mm^{-1}
F (000)	792.0
Absorption correction	multi-scan
Reflection collected	3695
Theta range for data collection	6.594 to 54.844 deg.
Goodness-of-fit on F^2	1.090

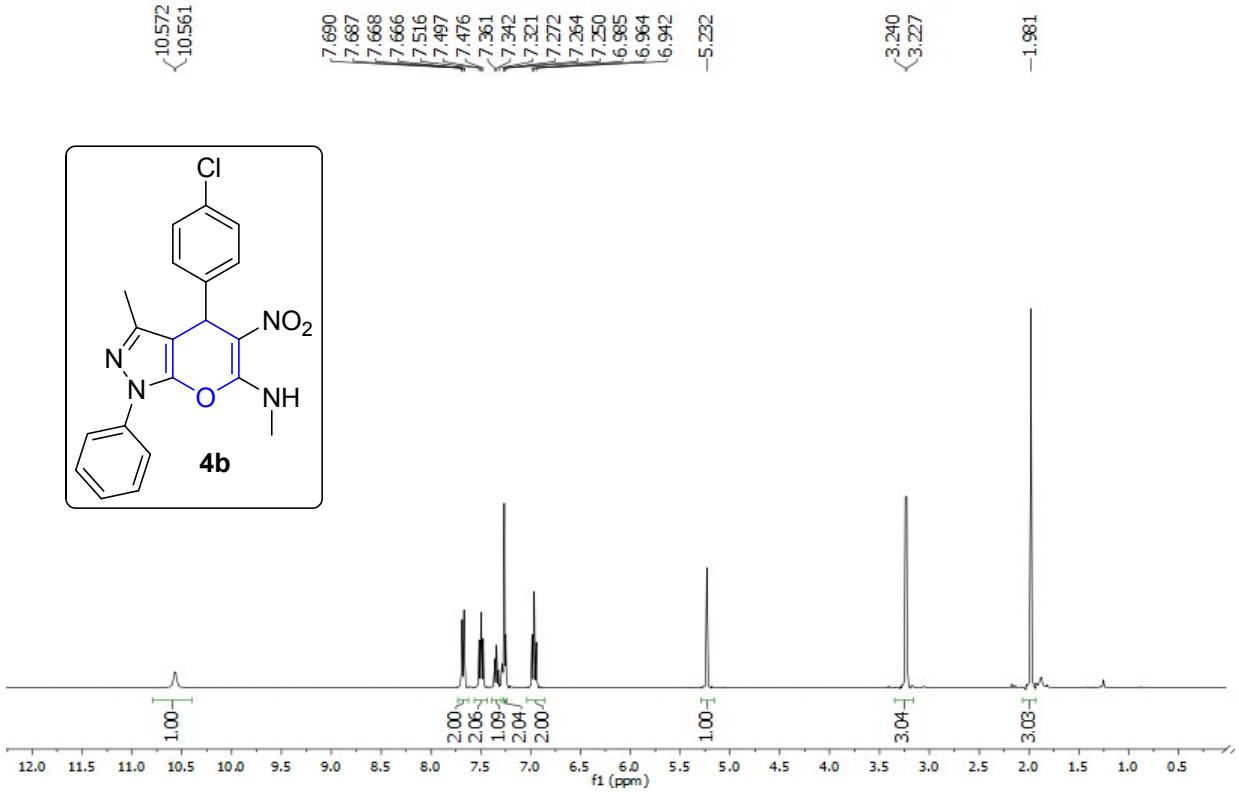
III. Copies of ^{1}H and ^{13}C NMR spectra:

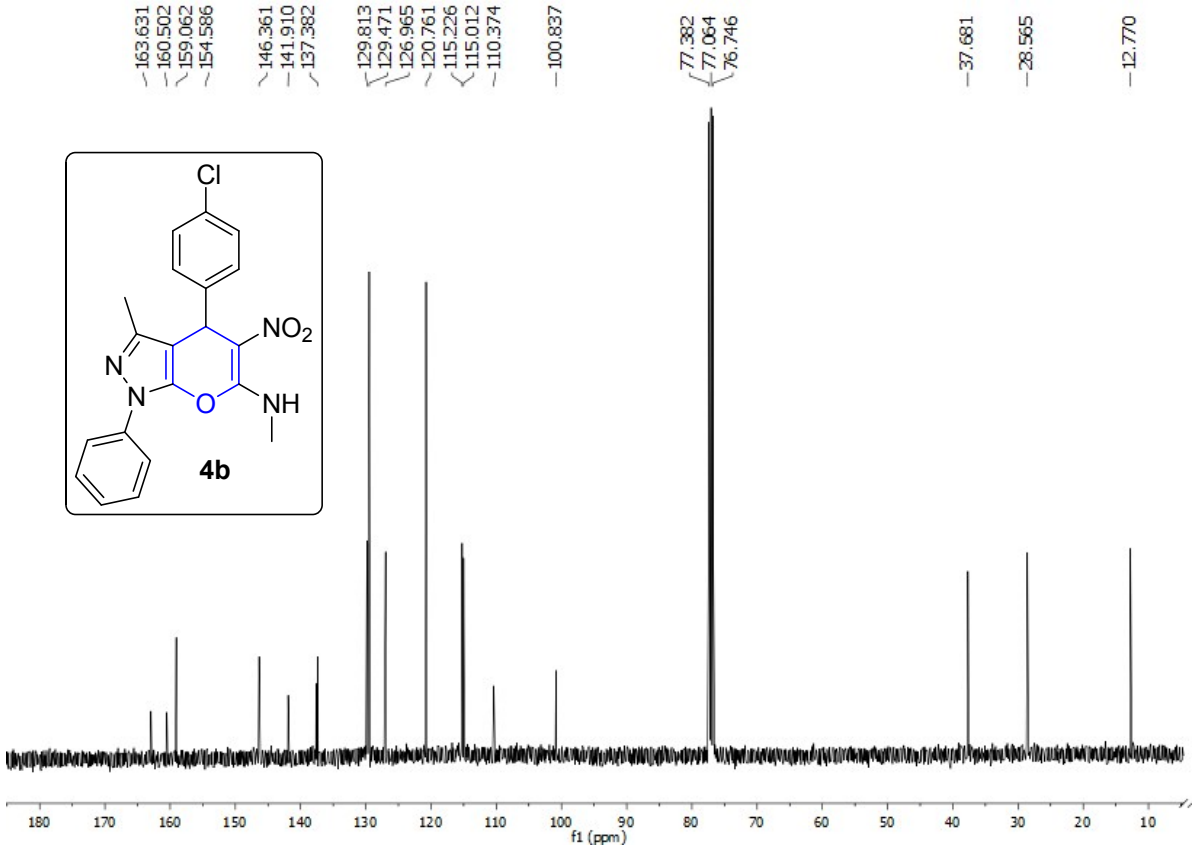
N,3-Dimethyl-5-nitro-1, 4-diphenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4a)



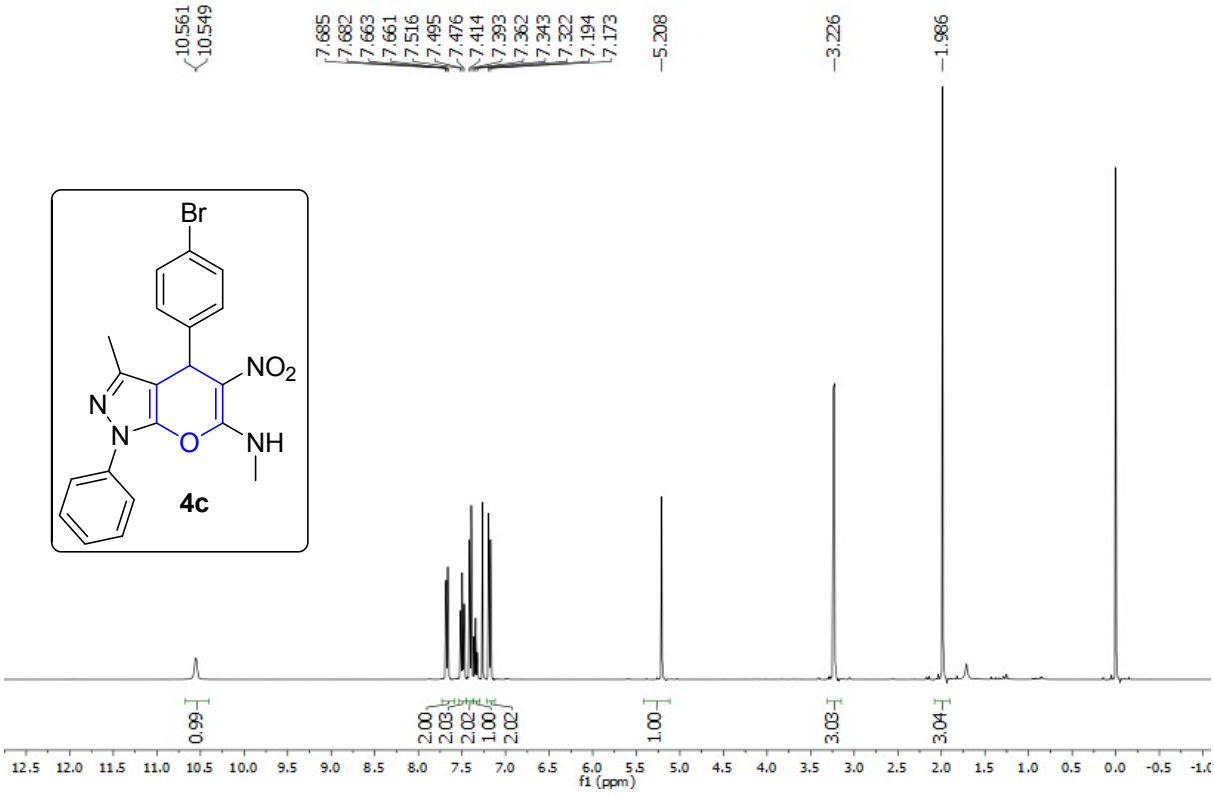


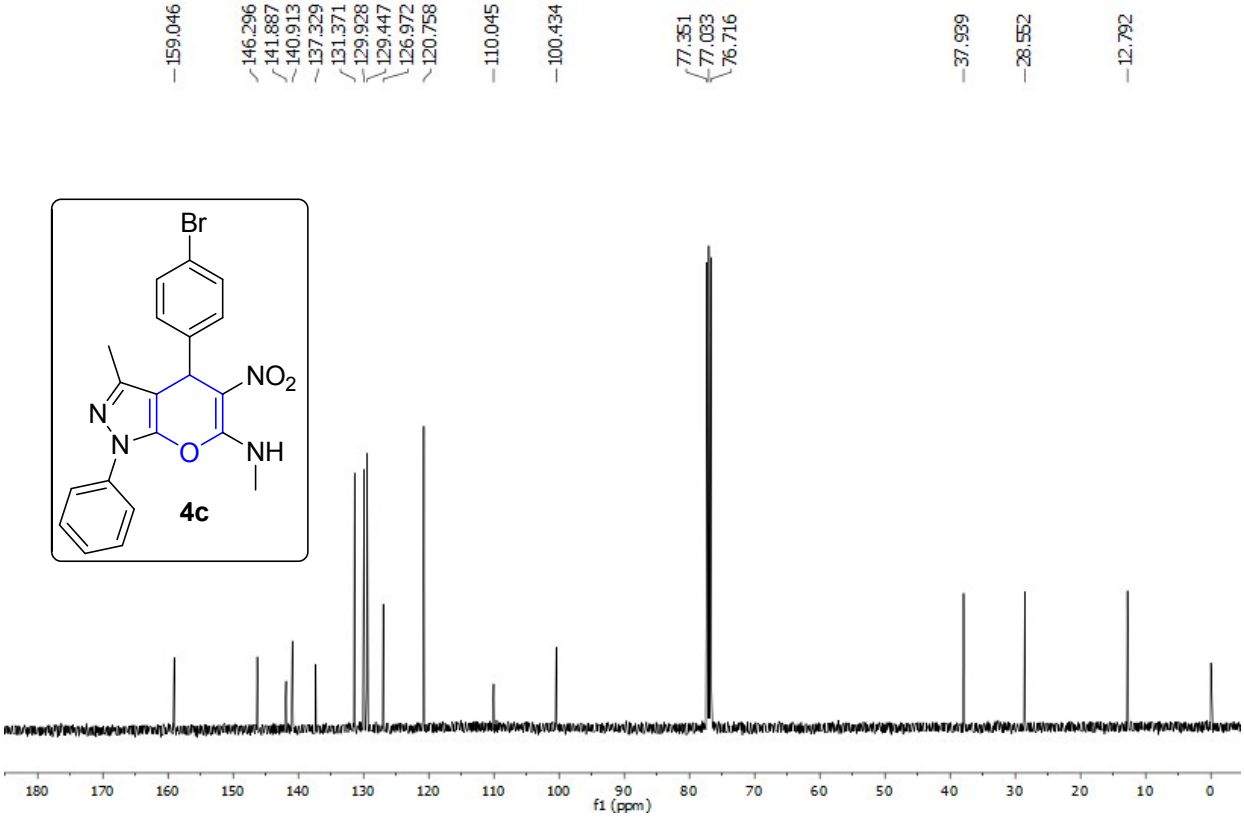
4-(4-Chlorophenyl)-N,3-dimethyl-5-nitro-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4b)



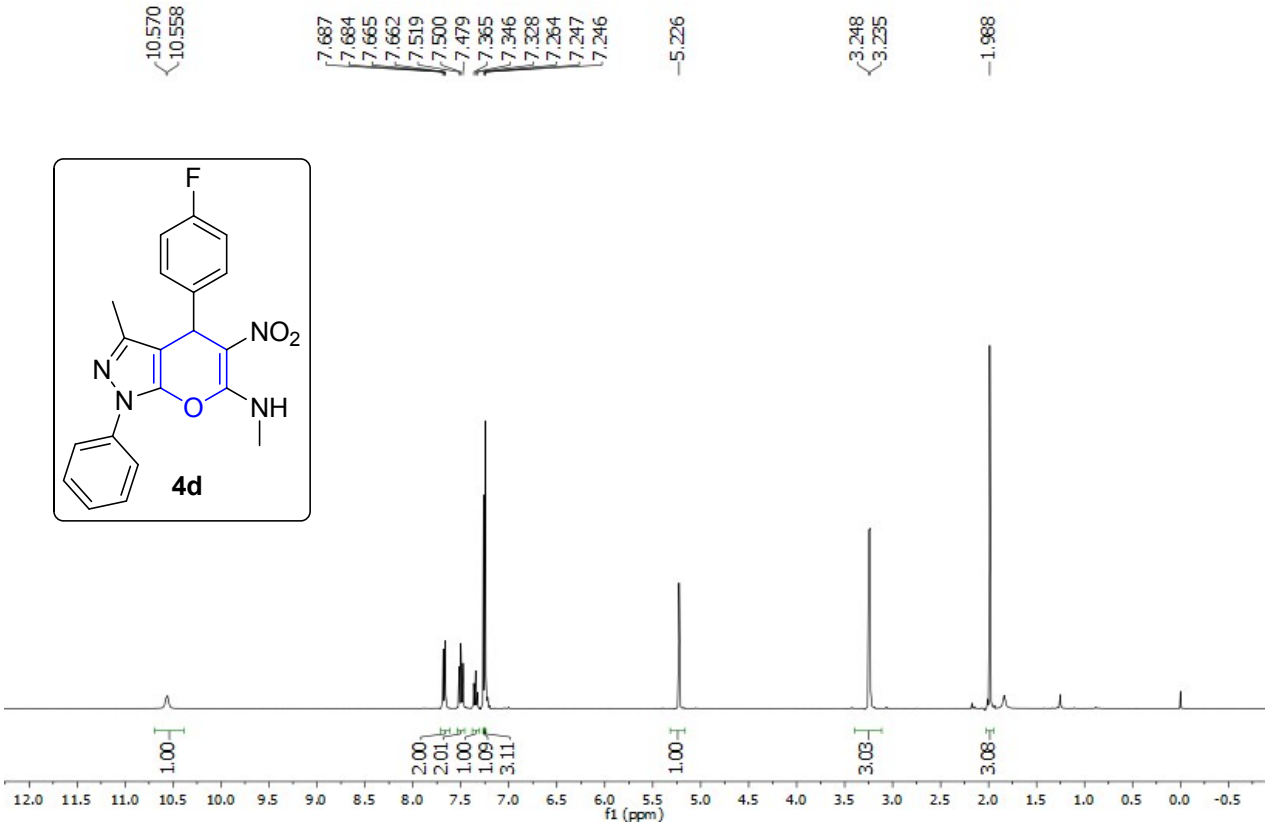


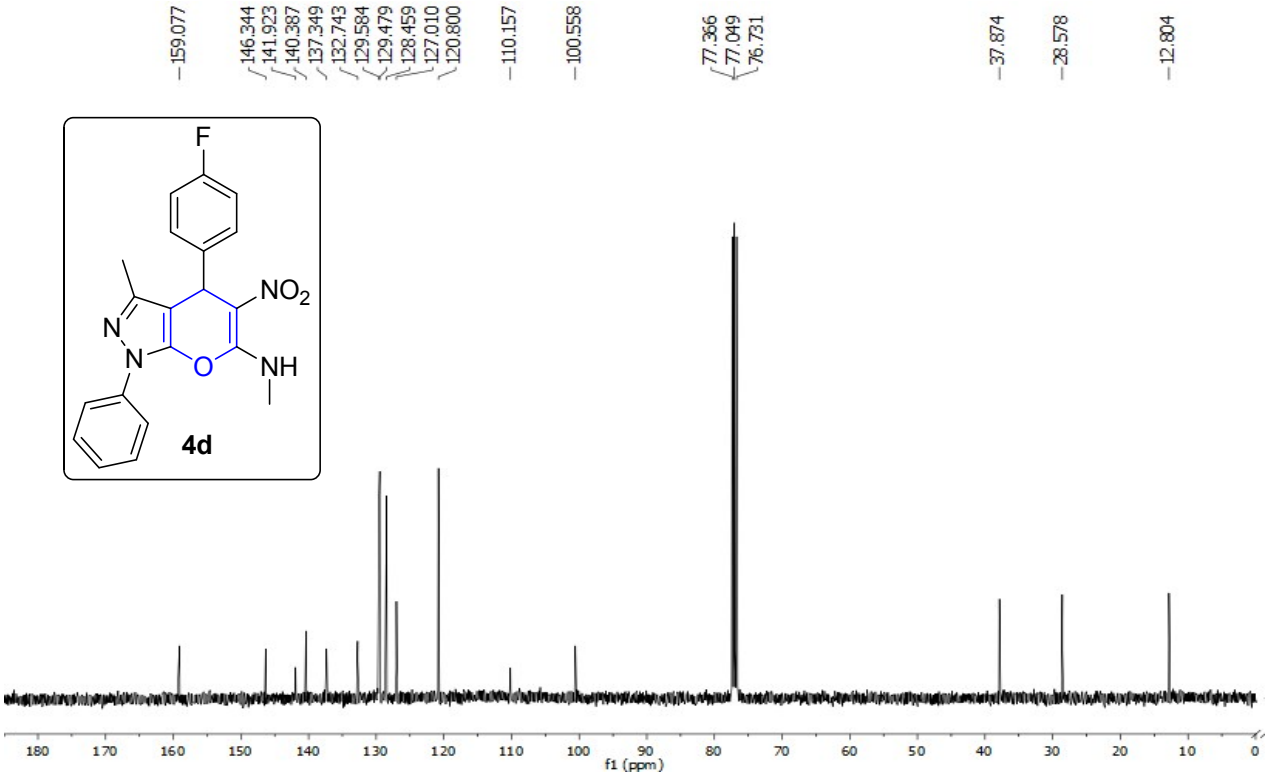
4-(4-Bromophenyl)-N,3-dimethyl-5-nitro-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4c)



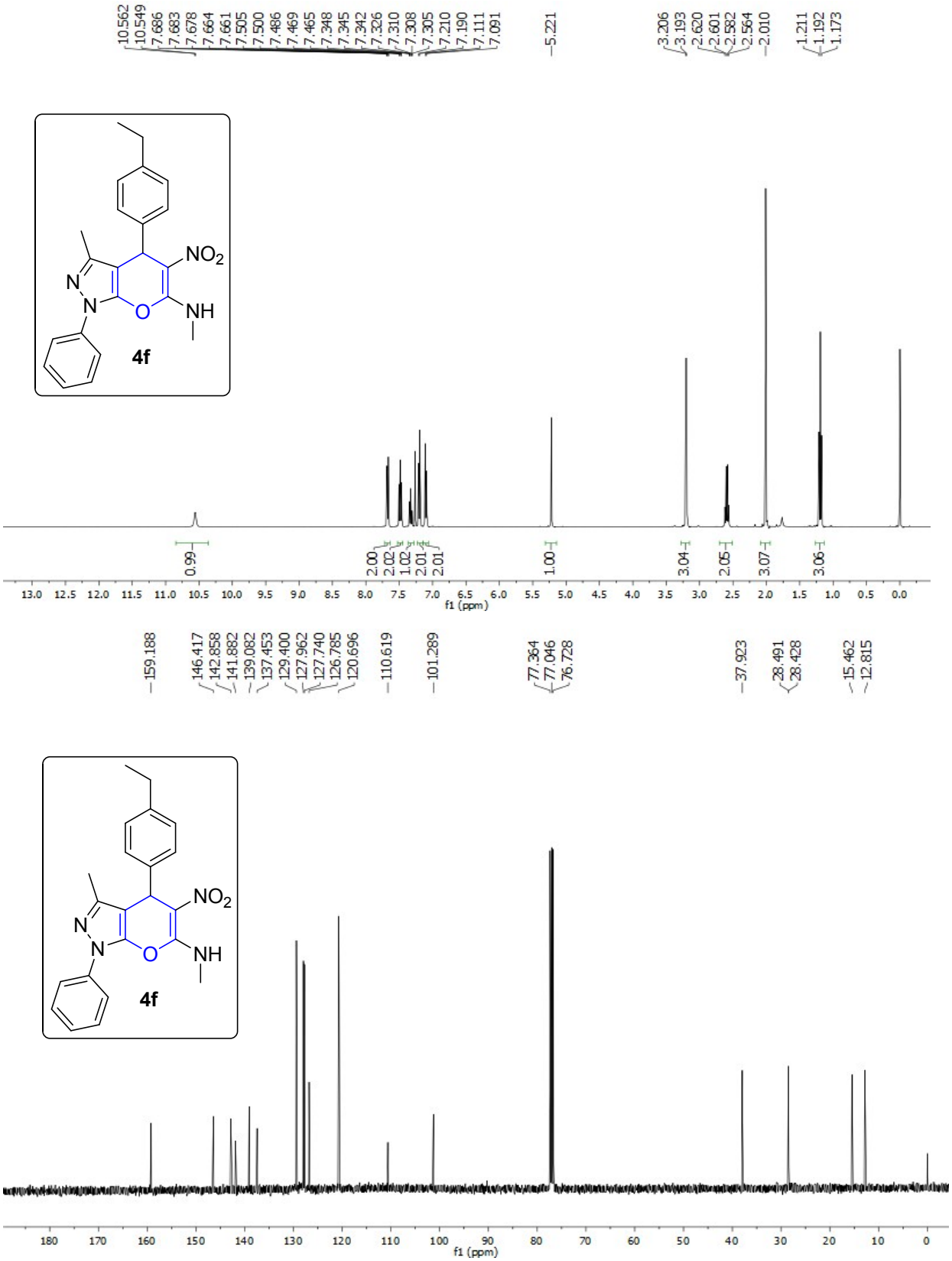


4-(4-Fluorophenyl)-N, 3-dimethyl-5-nitro-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4d)

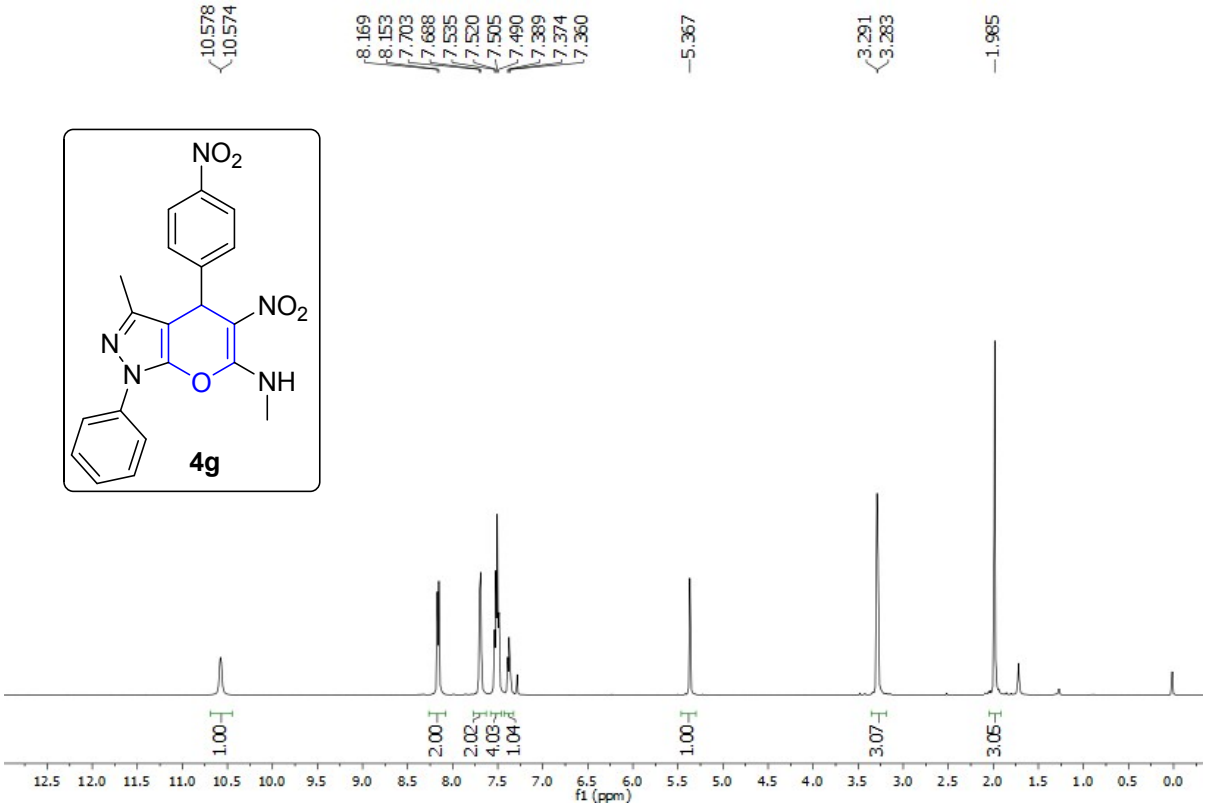


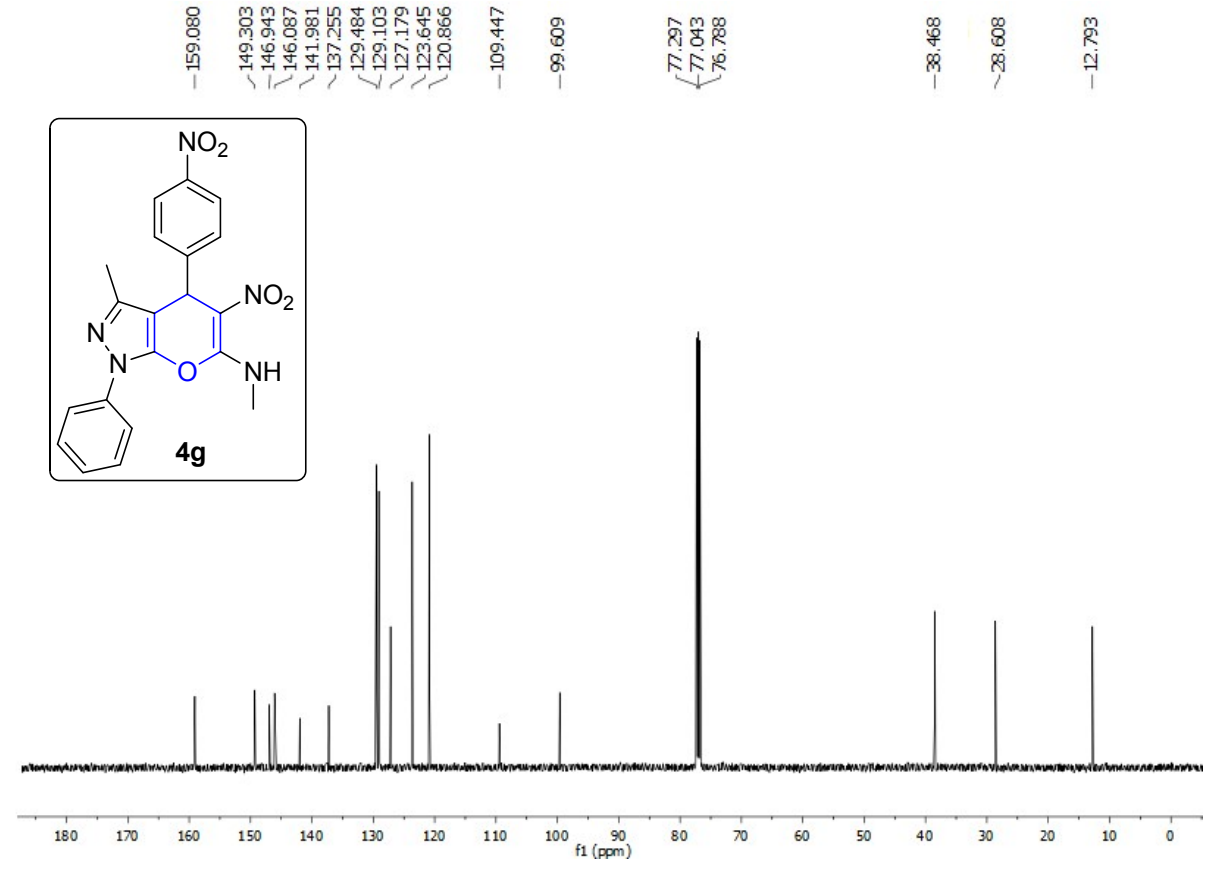


4-(4-Ethylphenyl)-N,3-dimethyl-5-nitro-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4f)

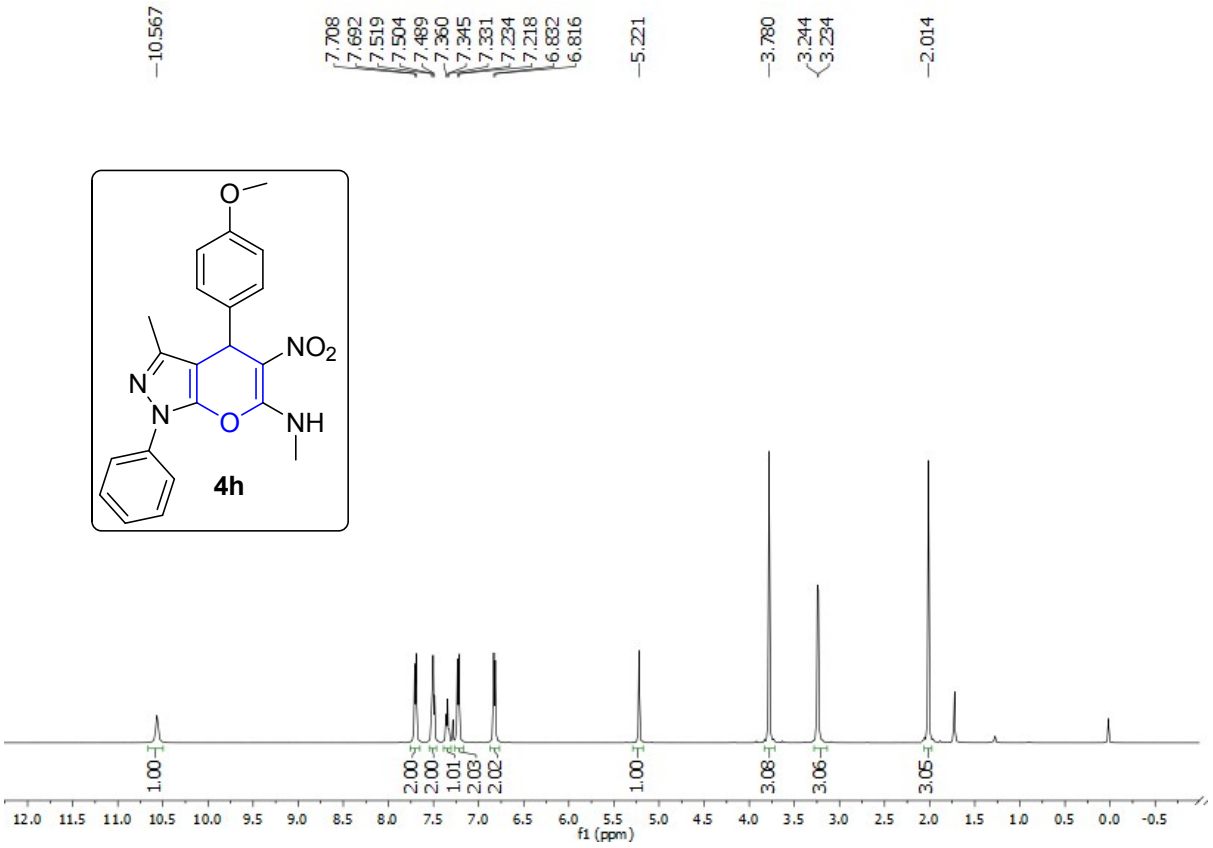


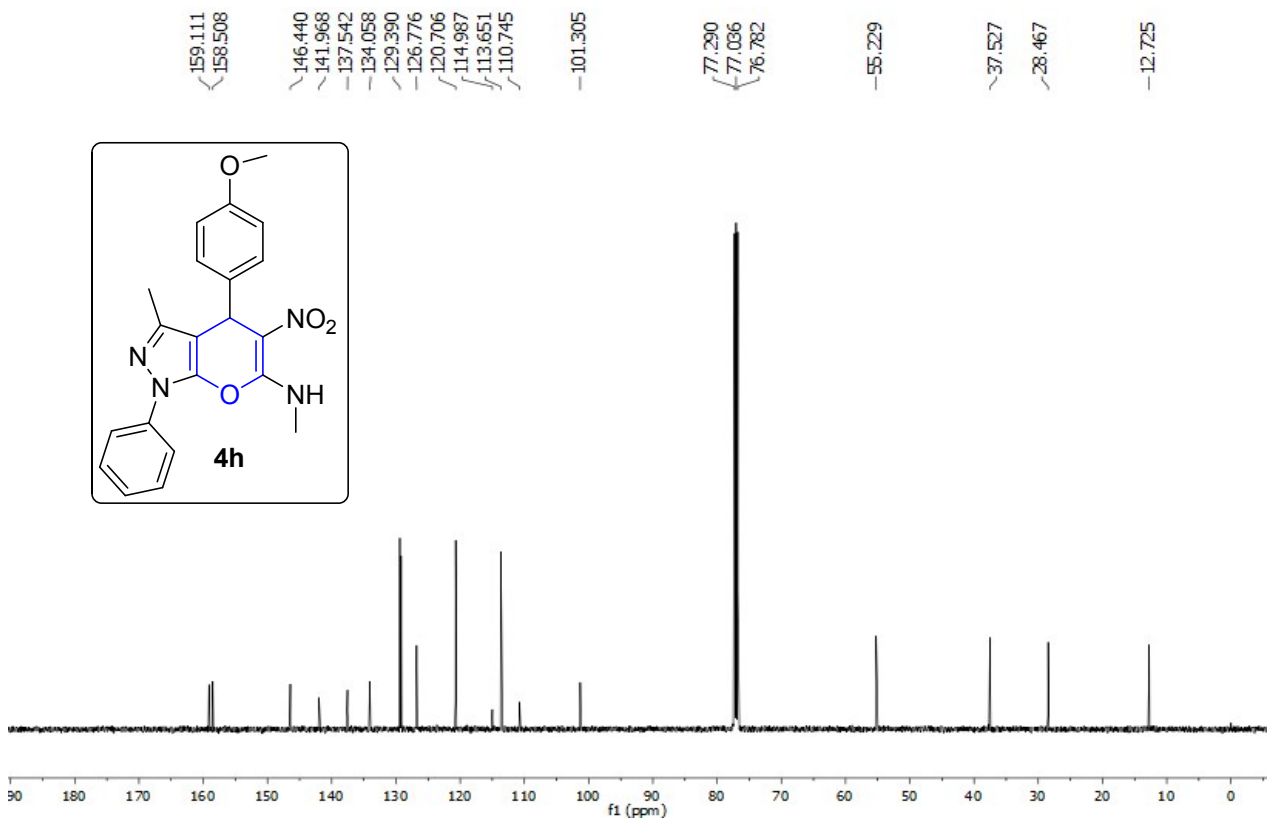
N, 3-Dimethyl-5-nitro-4-(4-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4g)



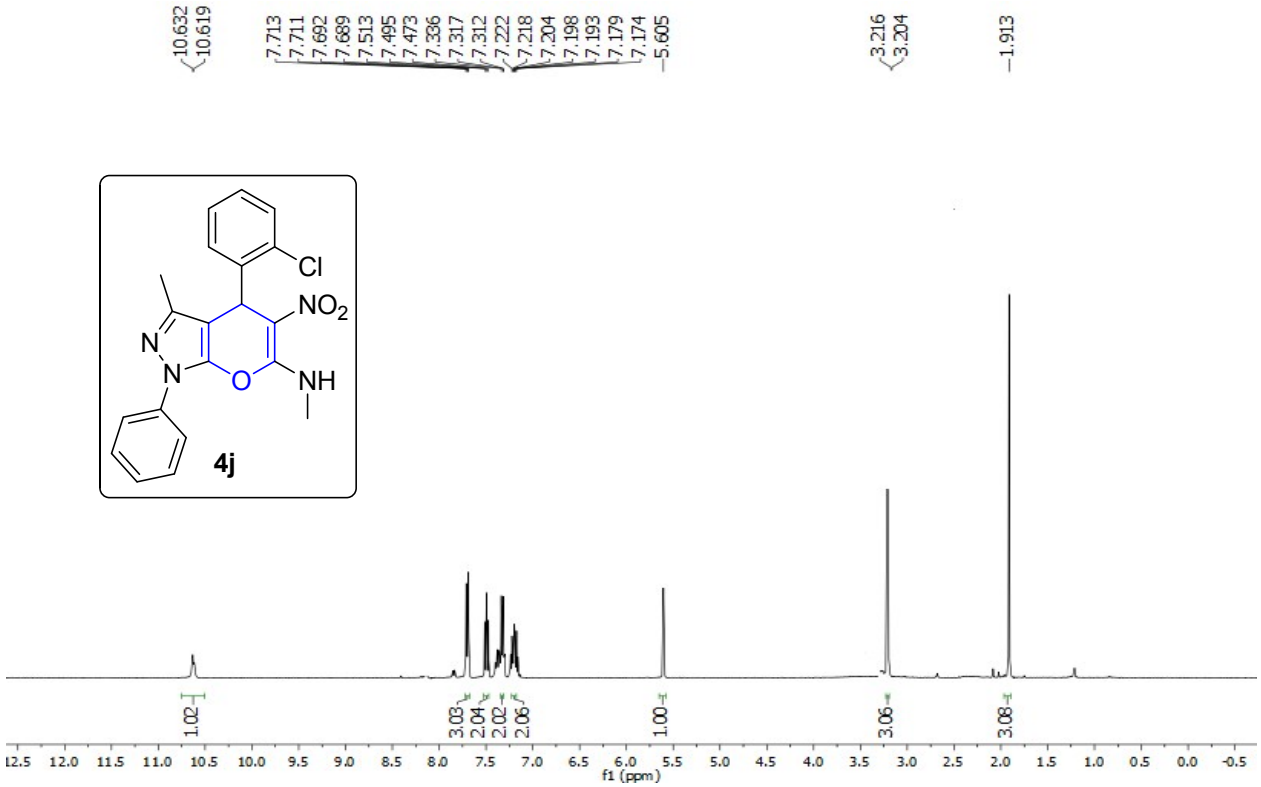


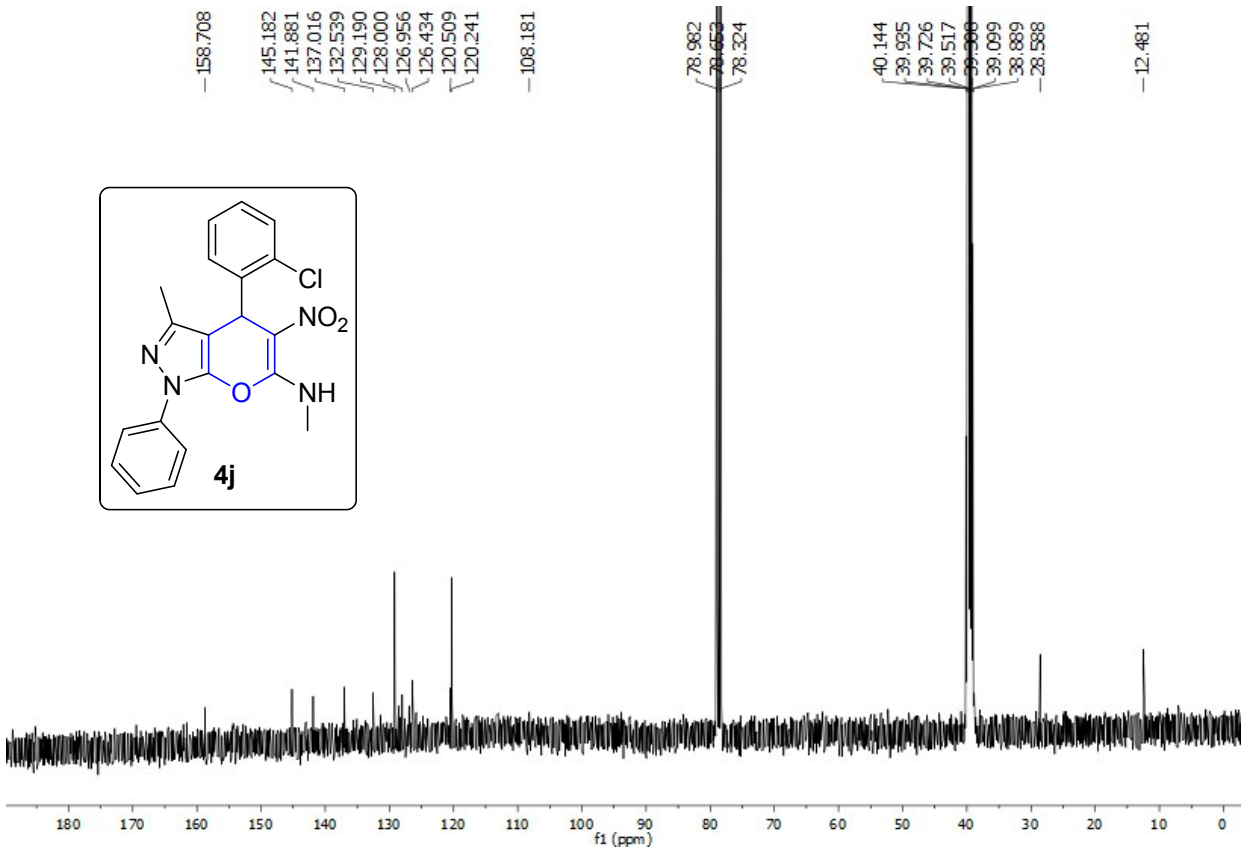
4-(4-Methoxyphenyl)-N,3-dimethyl-5-nitro-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4h)



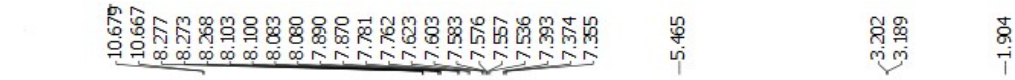


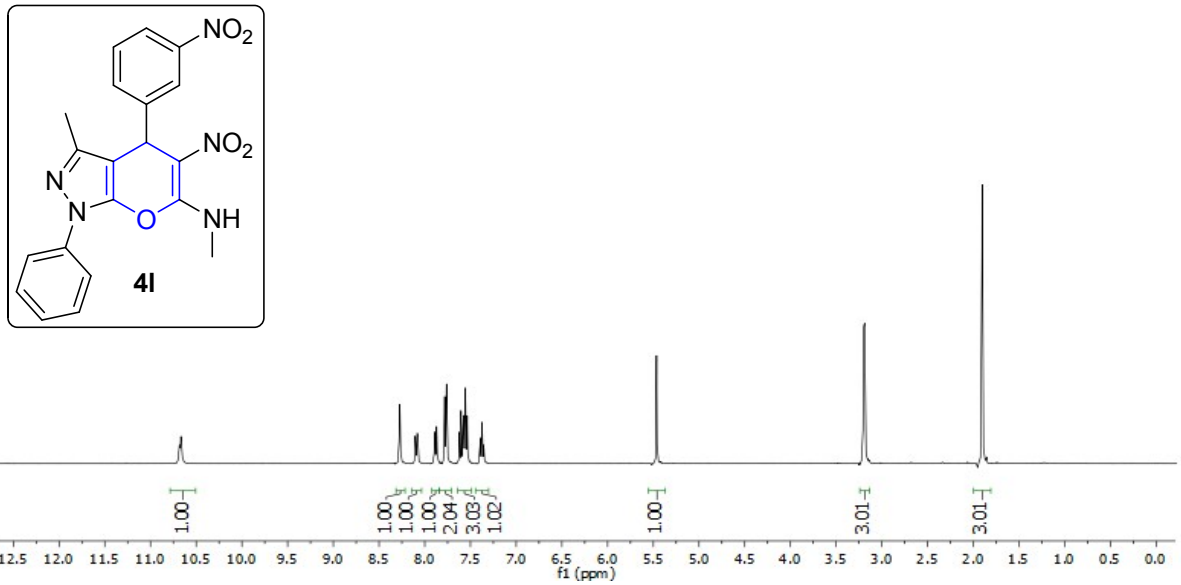
4-(2-Chlorophenyl)-N,3-dimethyl-5-nitro-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4j)

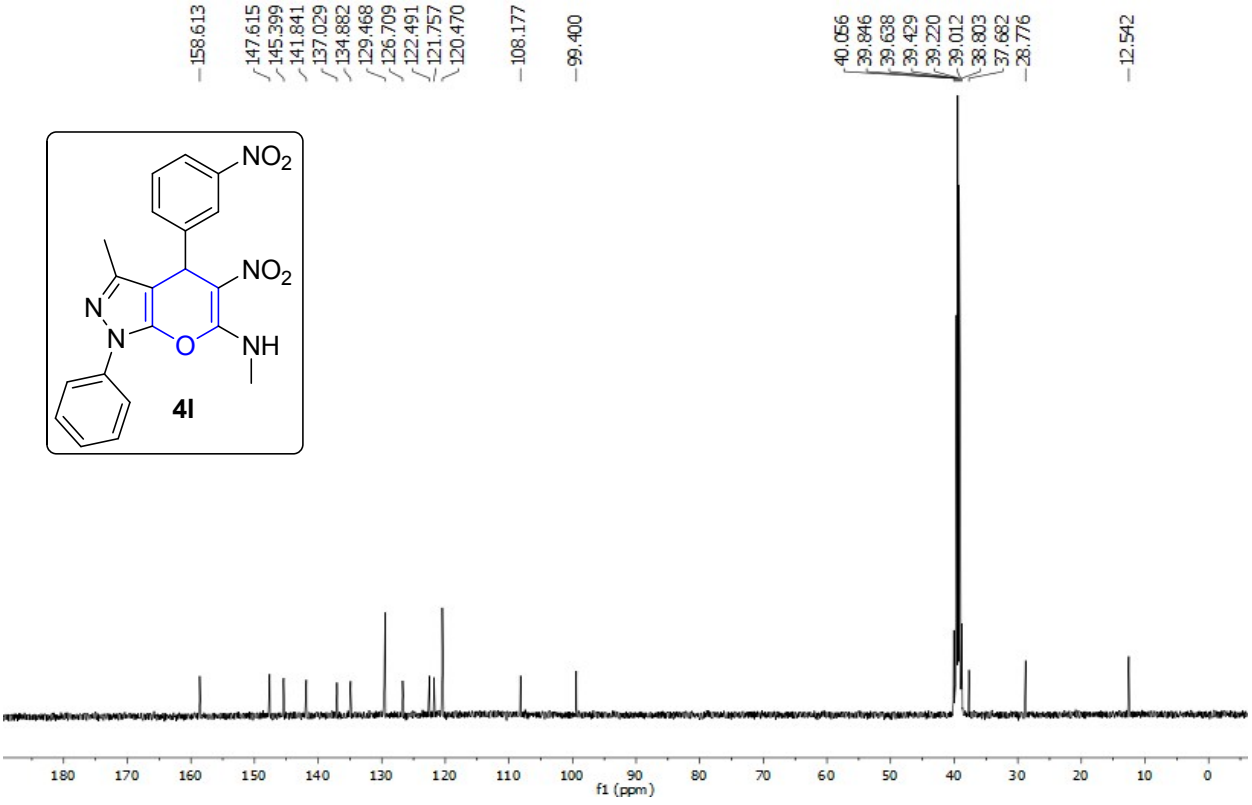




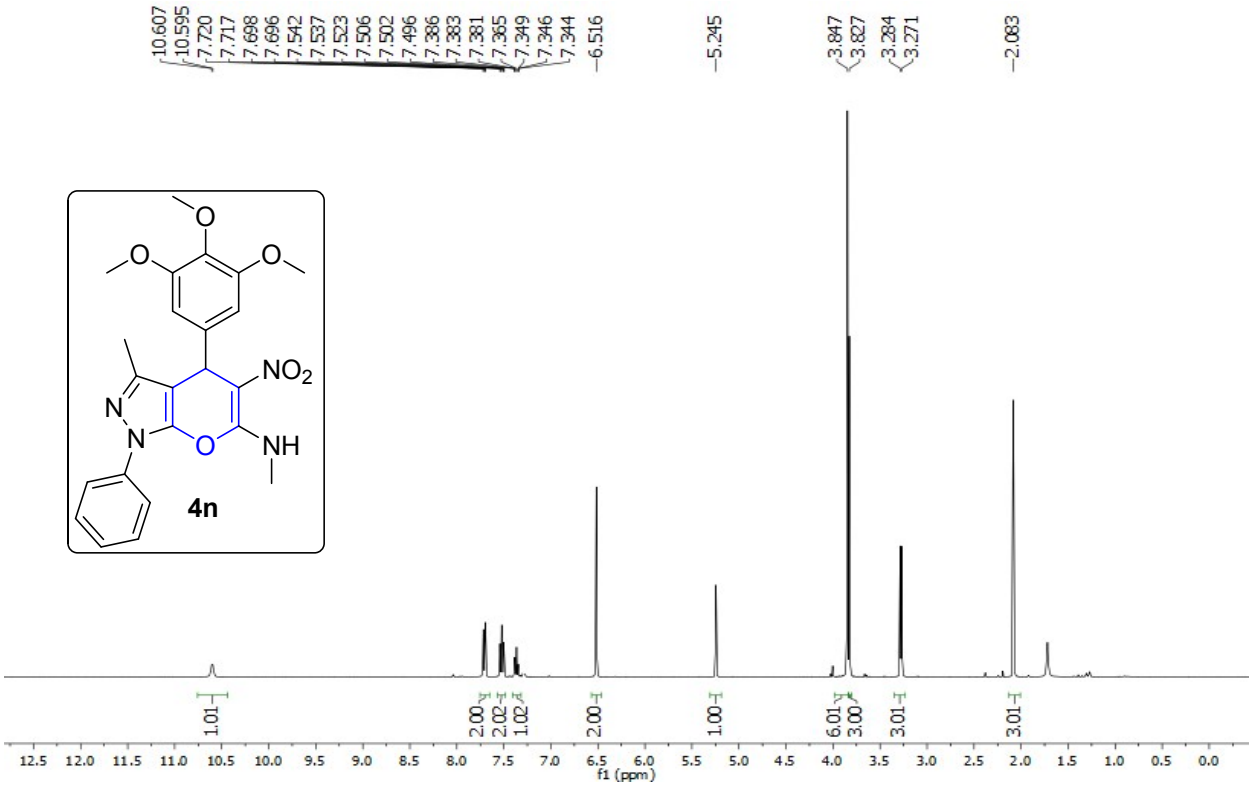
N, 3-Dimethyl-5-nitro-4-(3-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4l)

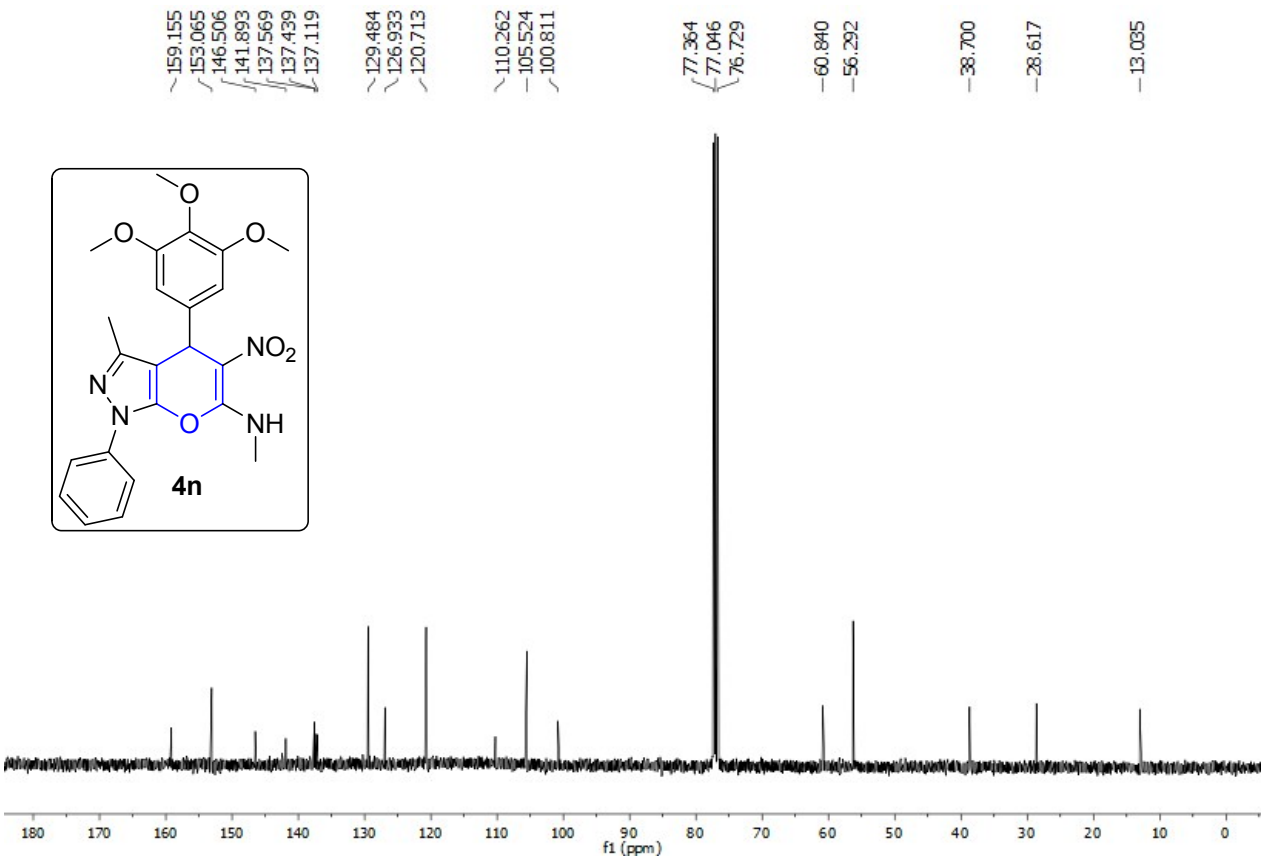




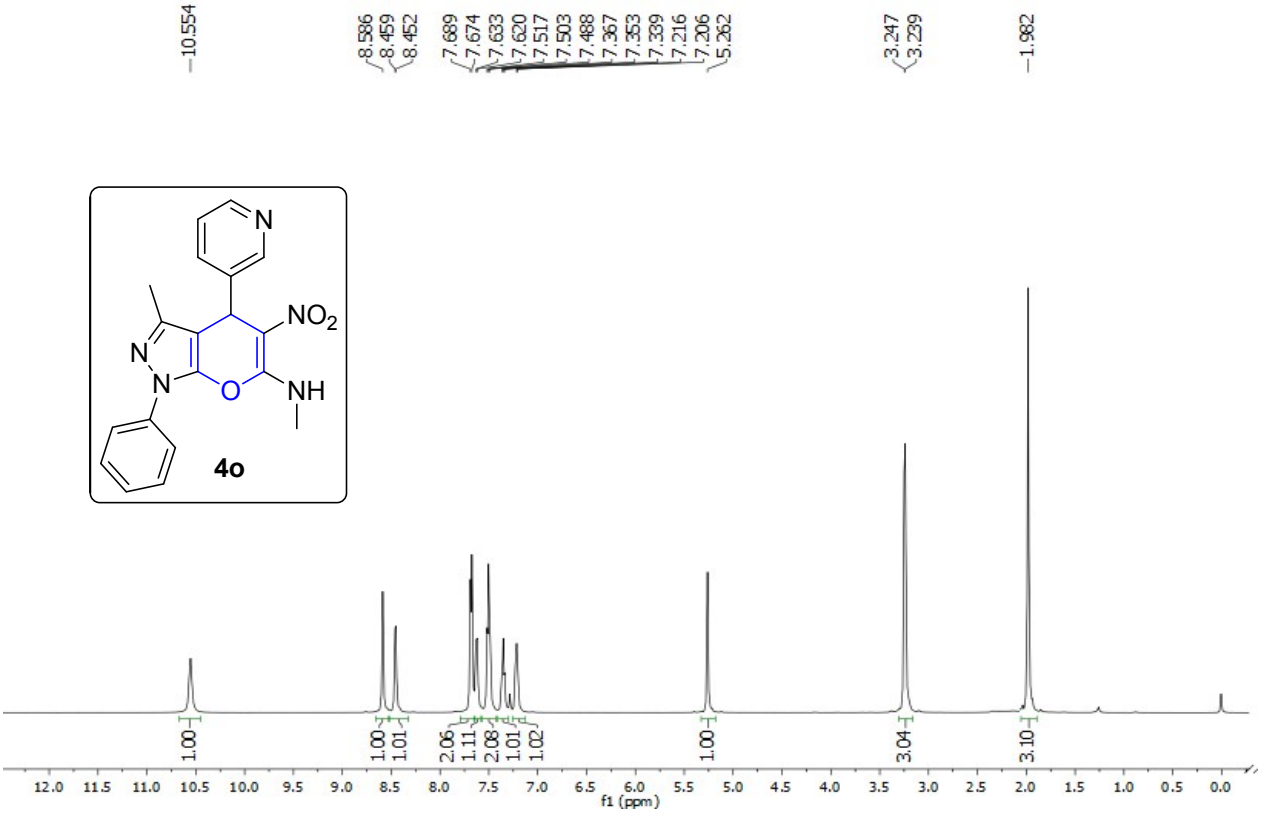


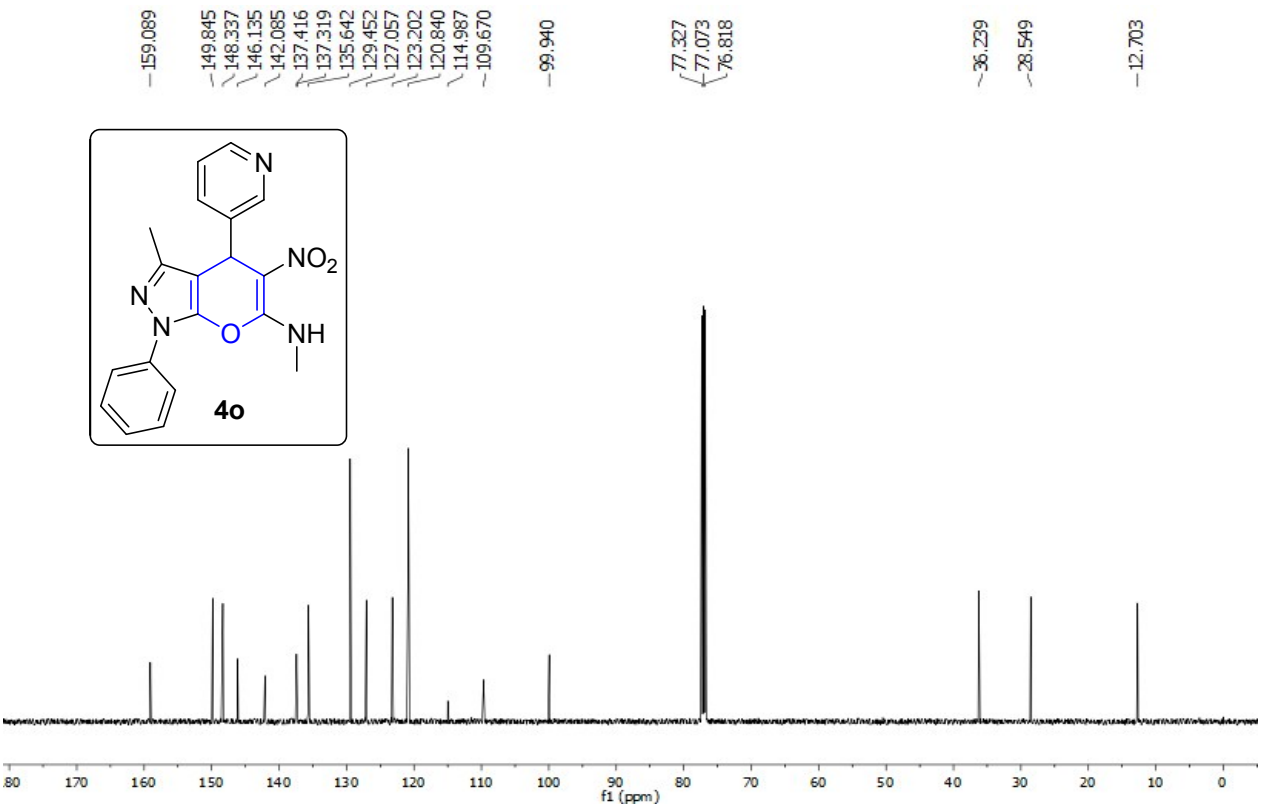
N, 3-Dimethyl-5-nitro-1-phenyl-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4n)



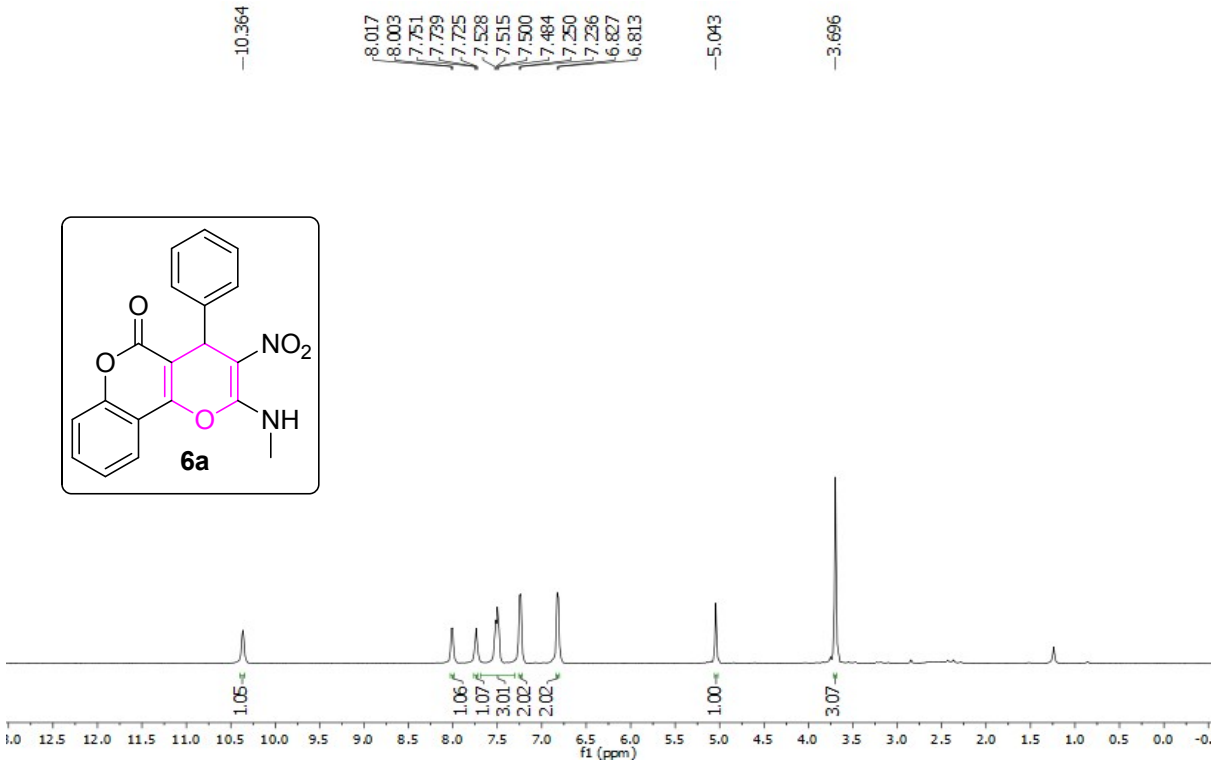


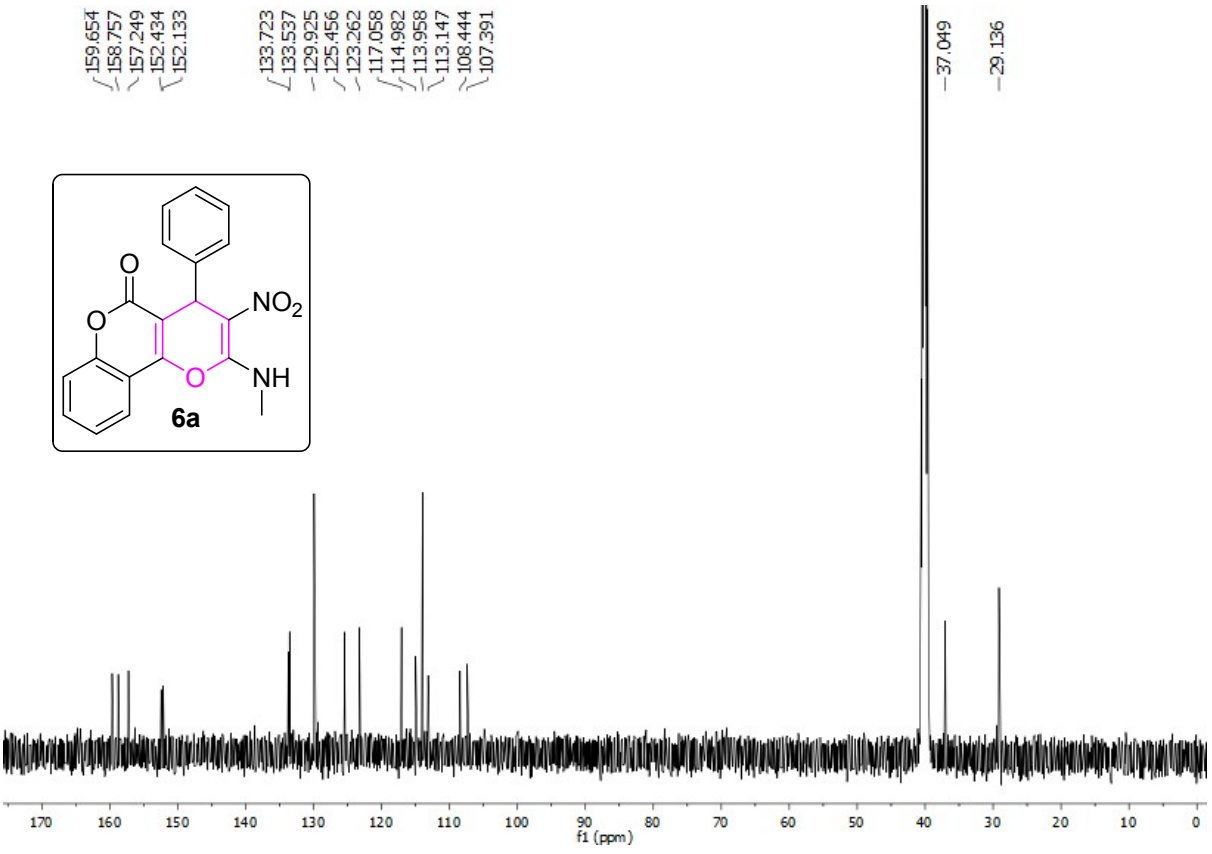
N,3-Dimethyl-5-nitro-1-phenyl-4-(pyridin-3-yl)-1, 4-dihydropyrano[2,3-c]pyrazol-6-amine (4o)



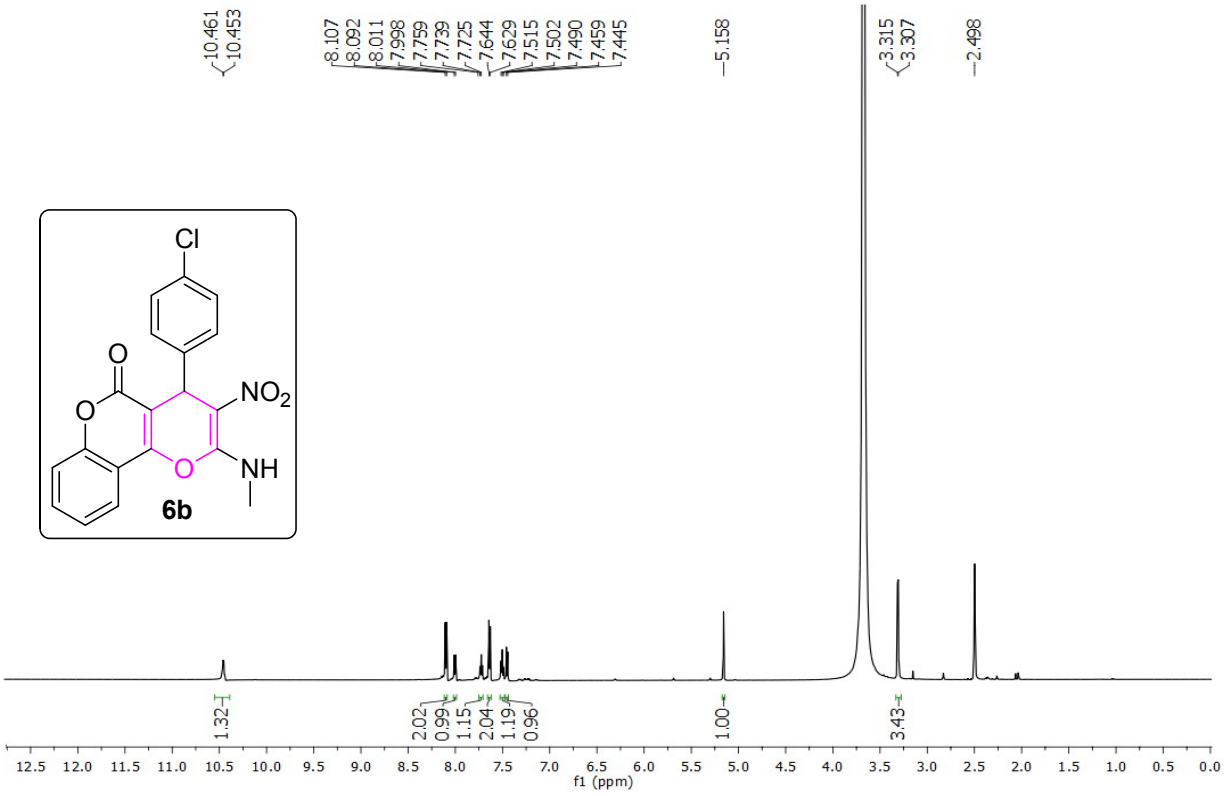


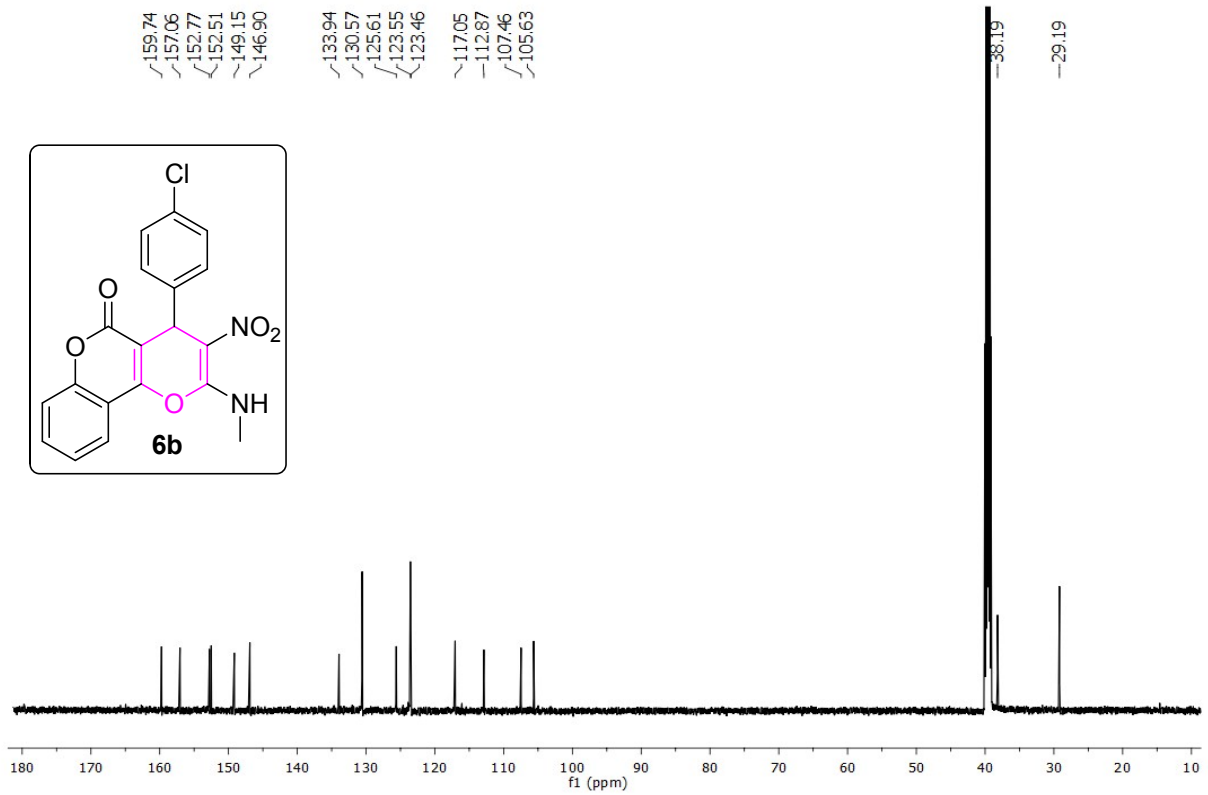
2-(Methylamino)-3-nitro-4-phenylpyrano[3,2-c]chromen-5(4H)-one (6a):



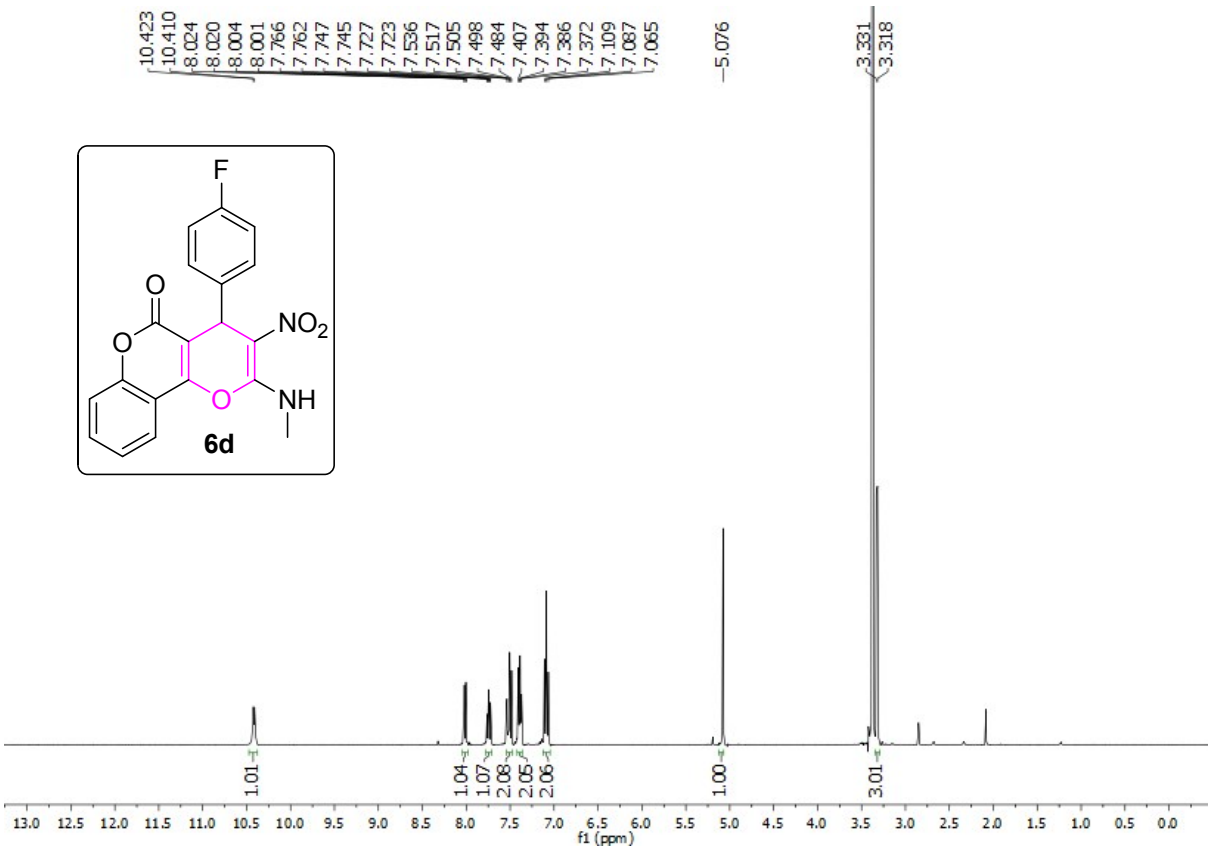


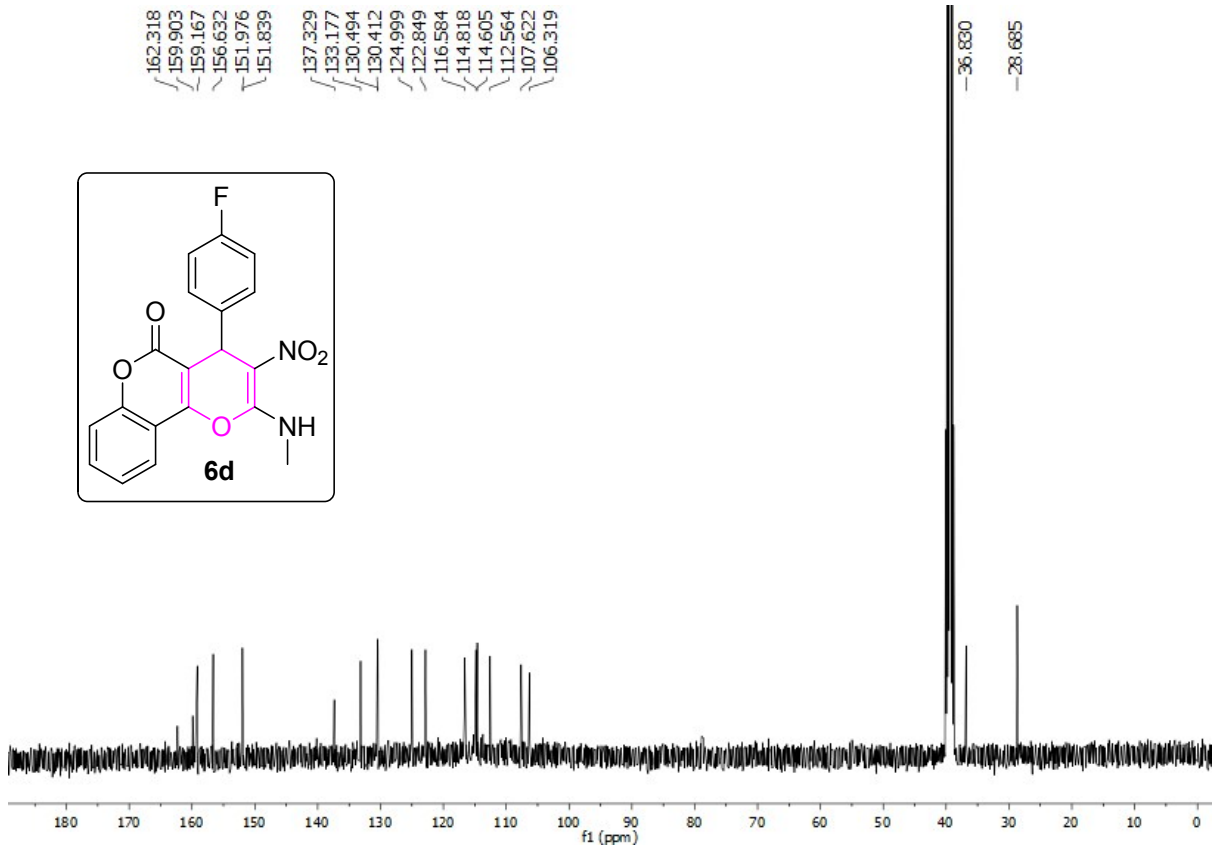
4-(4-chlorophenyl)-2-(methylamino)-3-nitropyrano[3,2-c]chromen-5(4H)-one (6b):



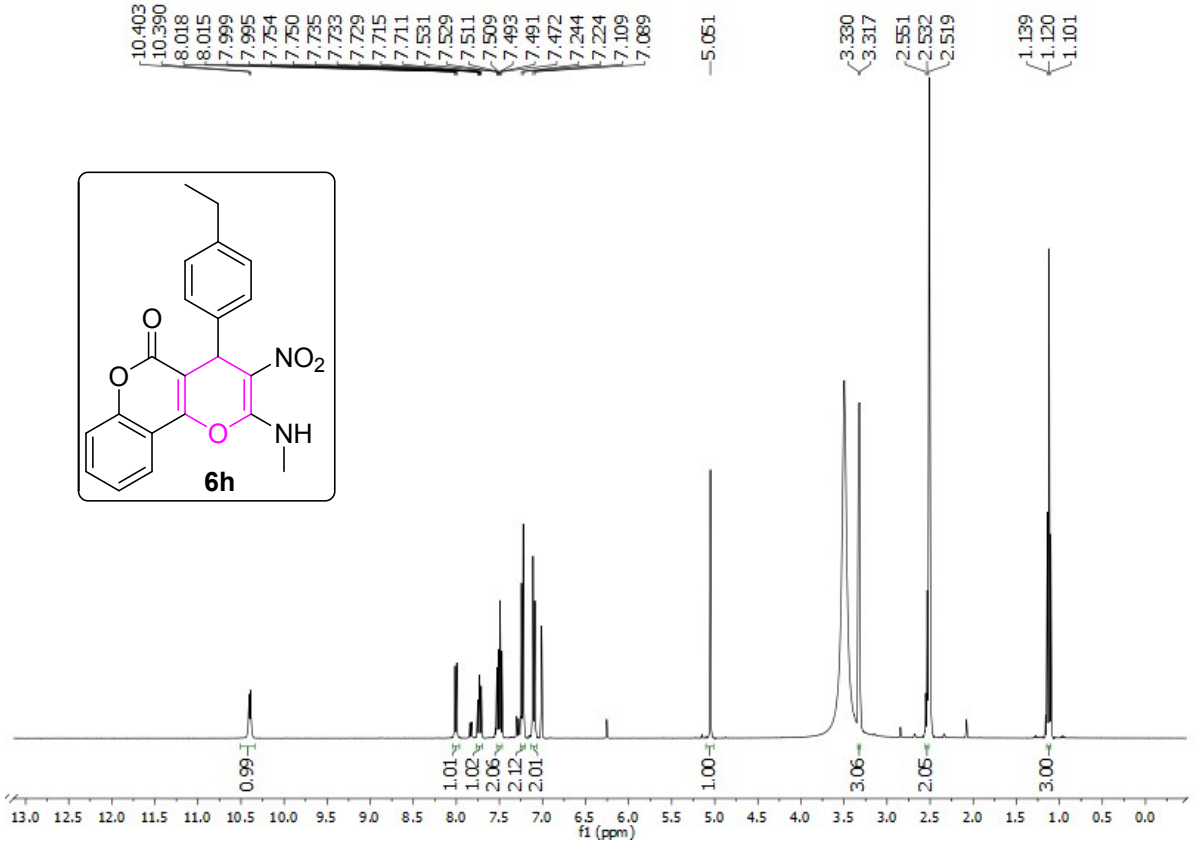


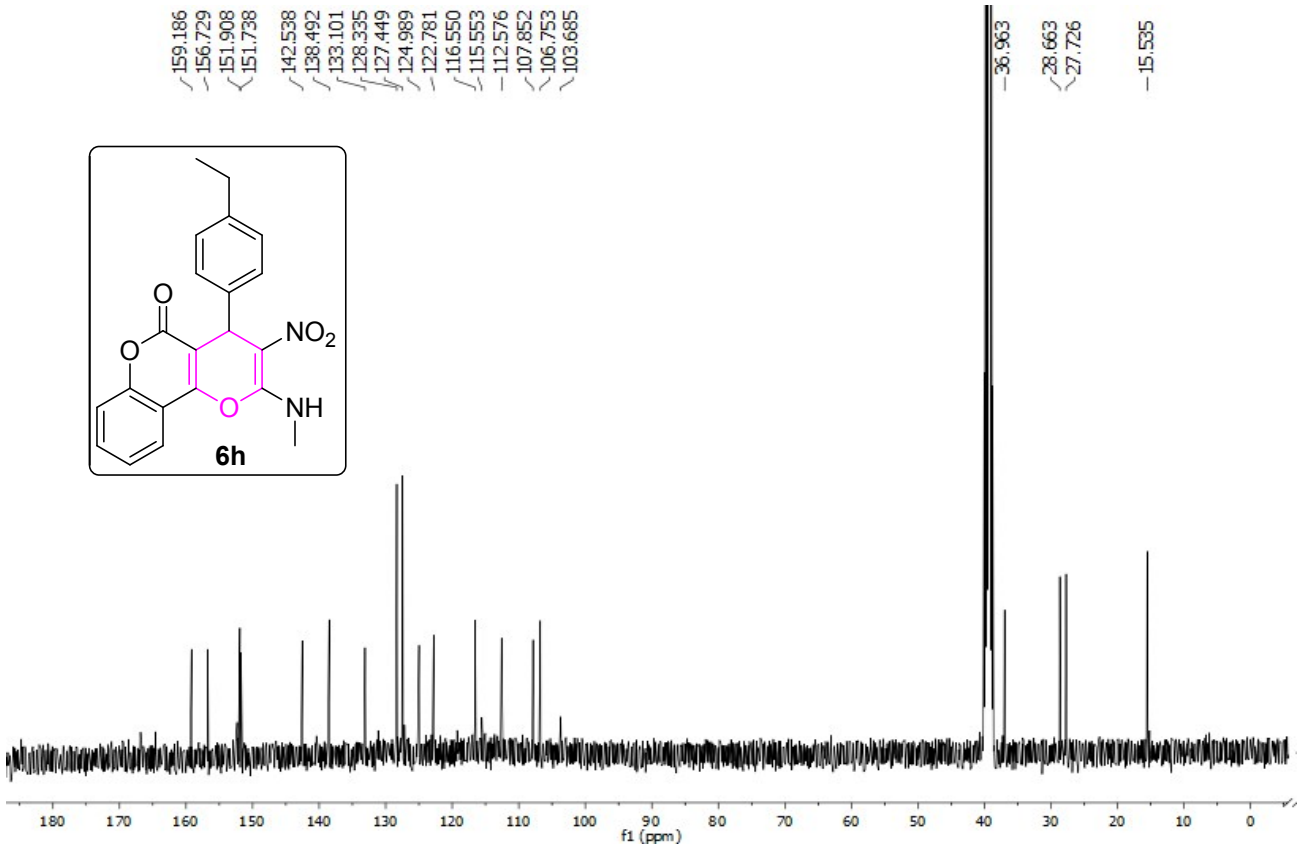
4-(4-Fluorophenyl)-2-(methylamino)-3-nitropyrano[3,2-c]chromen-5(4H)-one (6d)





4-(4-Ethylphenyl)-2-(methylamino)-3-nitropyrano[3,2-c]chromen-5(4H)-one (6h)





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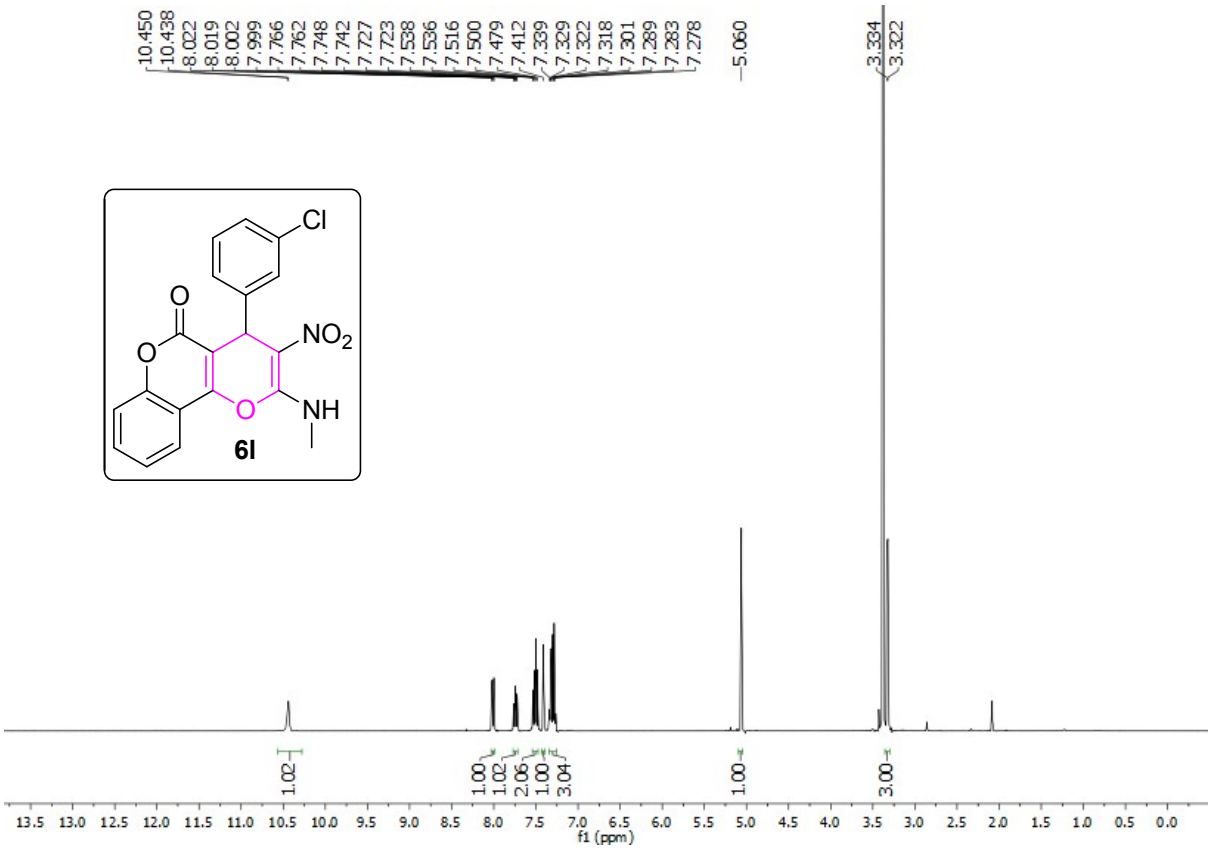
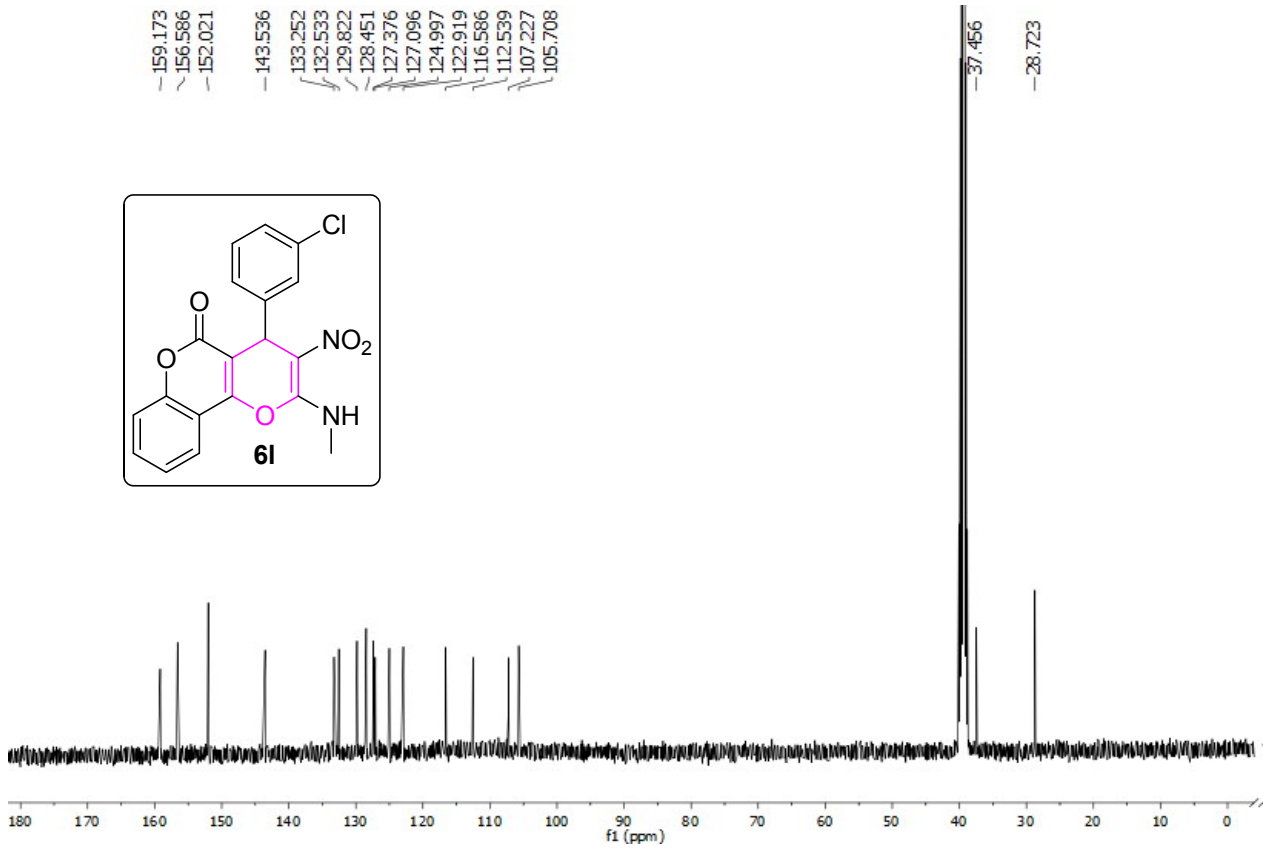
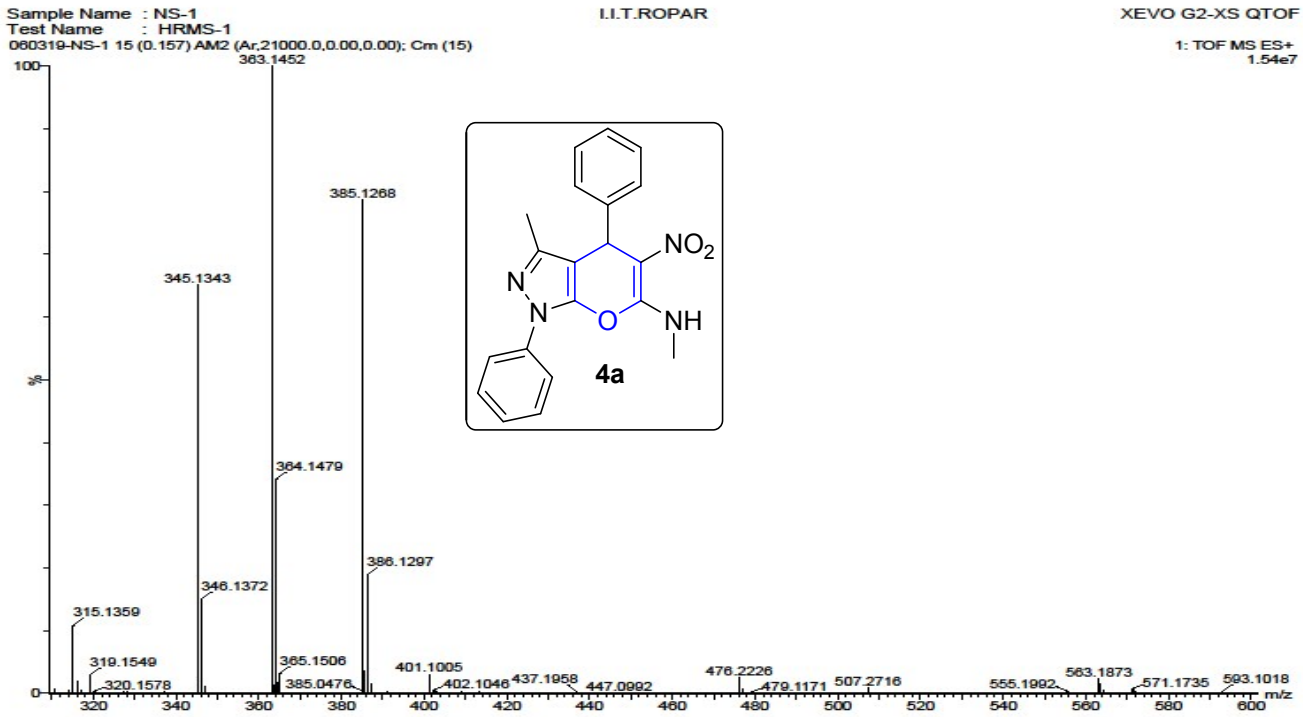




IV. HRMS spectra of selected compounds

(4a) ***N,3-Dimethyl-5-nitro-1,4-diphenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine***



(6a) ***2-(Methylamino)-3-nitro-4-phenylpyrano[3,2-c]chromen-5(4H)-one***