Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

Oxidative Cyclization of *N*-Acylhydrazones. Development of Highly Selective Turn-on Fluorescent Chemodosimeters for Cu^{2+}

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1. Figures S1-S8

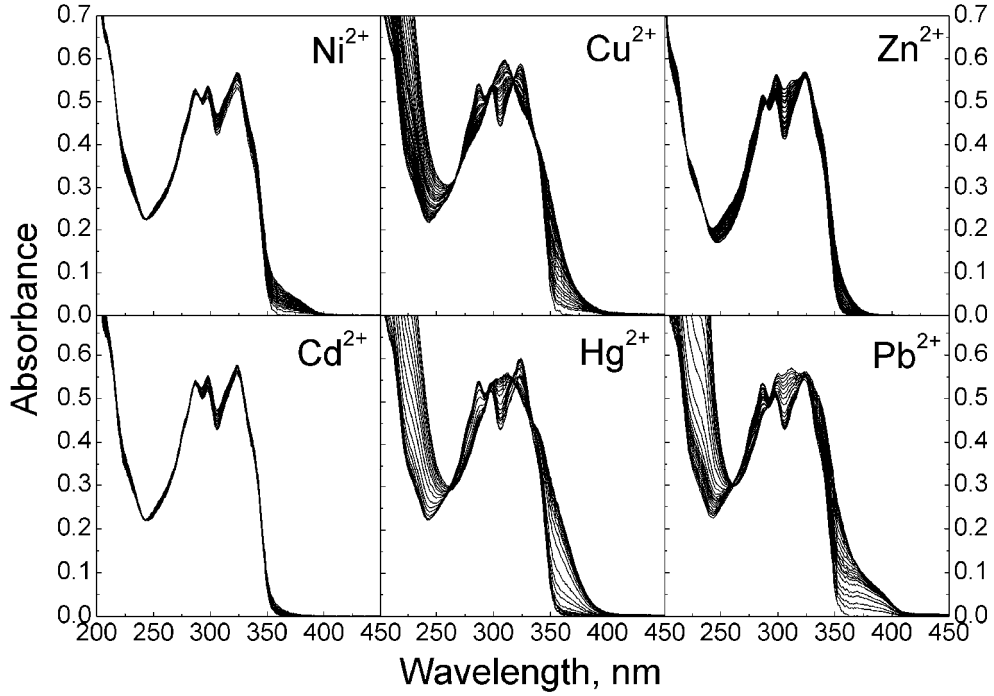


Figure S1. Absorption spectra of **2a** (20 μM) in CH_3CN in the presence of given metal ion of increasing concentration. Concentrations of metal ions increased in the same manner from 0 to 250 μM.

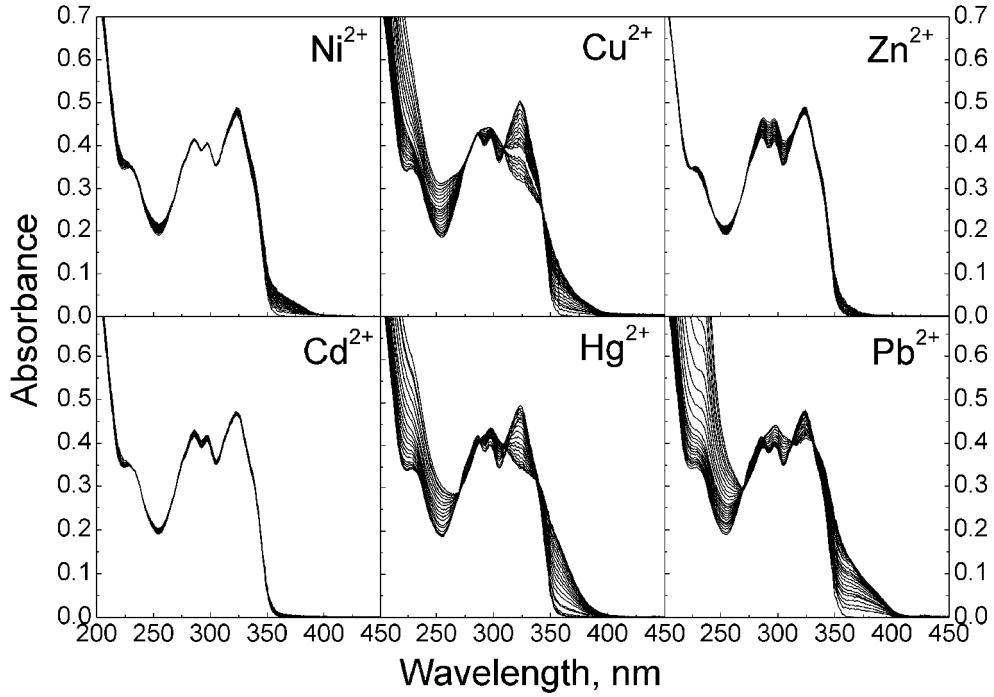


Figure S2. Absorption spectra of **2b** (20 μM) in CH_3CN in the presence of given metal ion of increasing concentration. Concentrations of metal ions increased in the same manner from 0 to 250 μM.

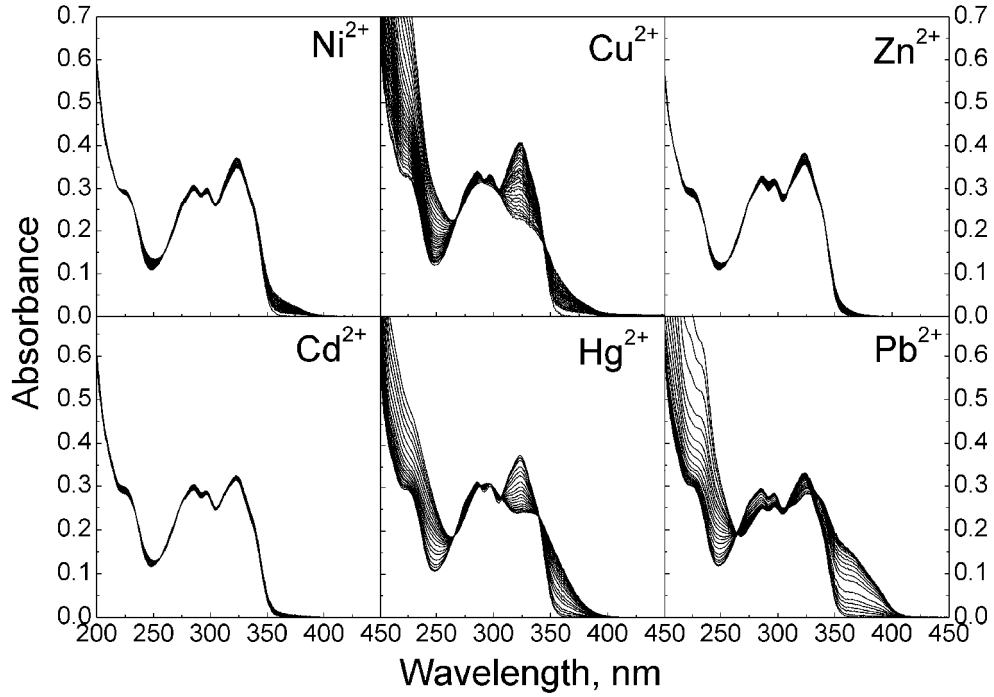


Figure S3. Absorption spectra of **2c** (20 μM) in CH_3CN in the presence of given metal ion of increasing concentration. Concentrations of metal ions increased in the same manner from 0 to 250 μM.

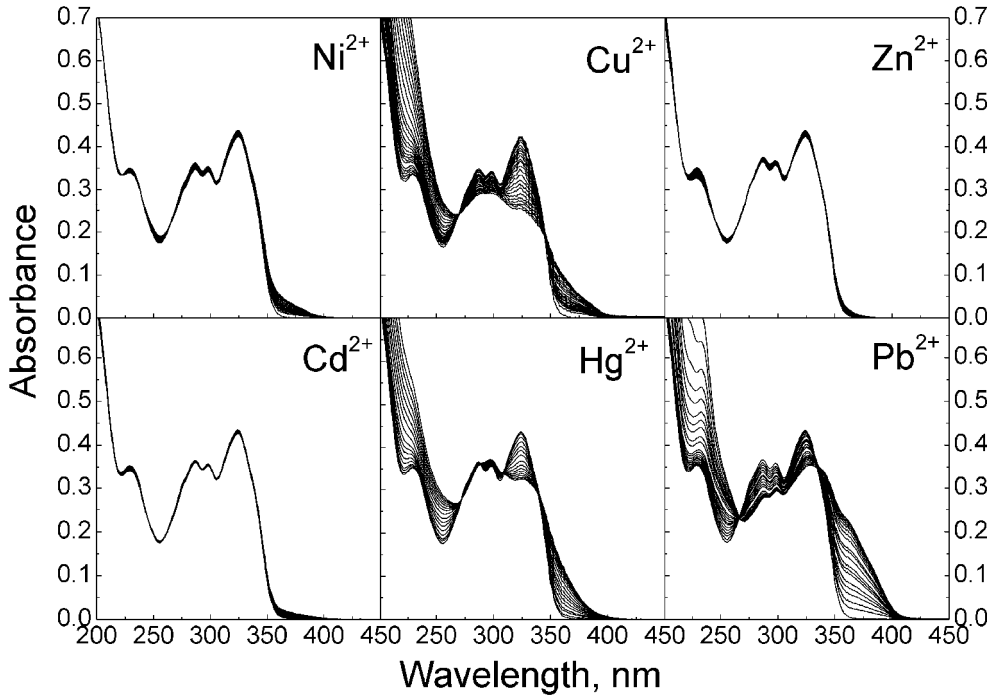


Figure S4. Absorption spectra of **2d** (20 μM) in CH_3CN in the presence of given metal ion of increasing concentration. Concentrations of metal ions increased in the same manner from 0 to 250 μM.

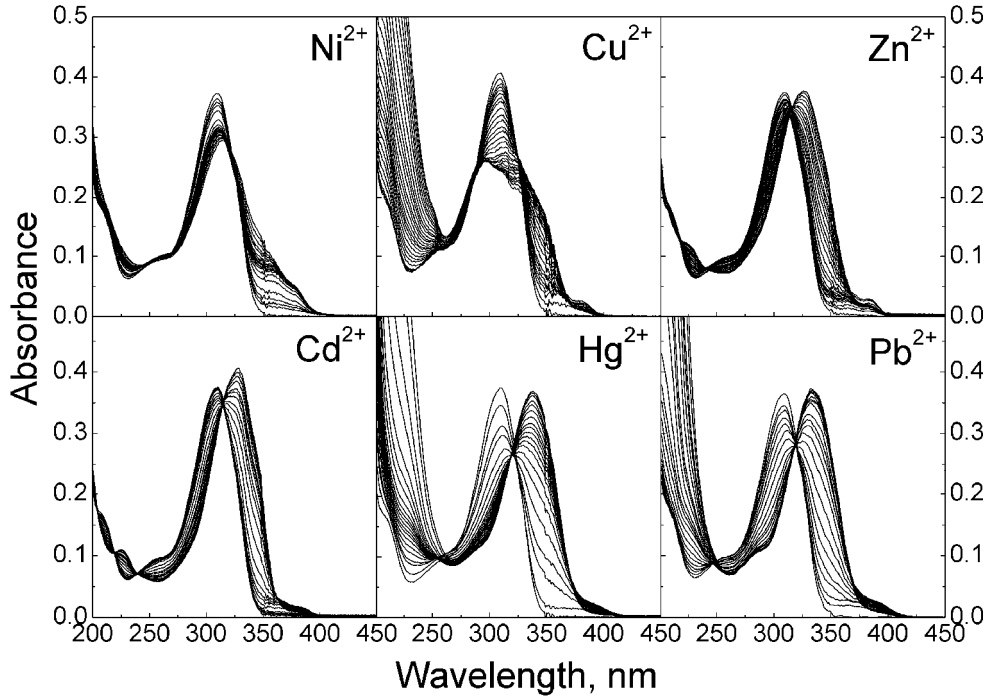


Figure S5. Absorption spectra of **3a** (10 μM) in CH_3CN in the presence of given metal ion of increasing concentration. Concentrations of metal ions increased in the same manner from 0 to 250 μM.

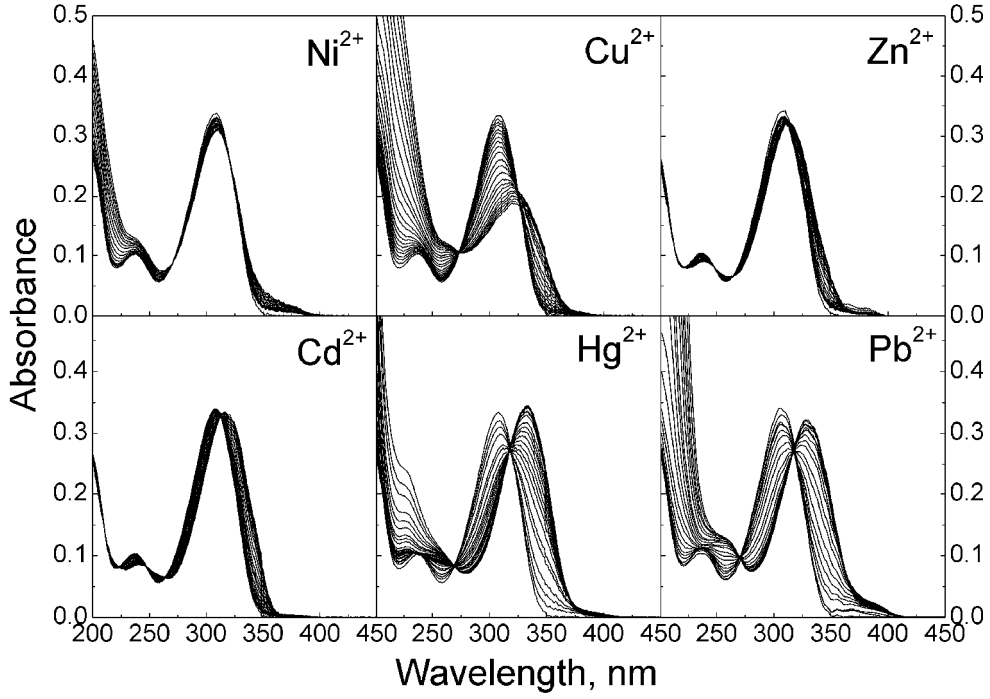


Figure S6. Absorption spectra of **3b** (10 μM) in CH_3CN in the presence of given metal ion of increasing concentration. Concentrations of metal ions increased in the same manner from 0 to 250 μM.

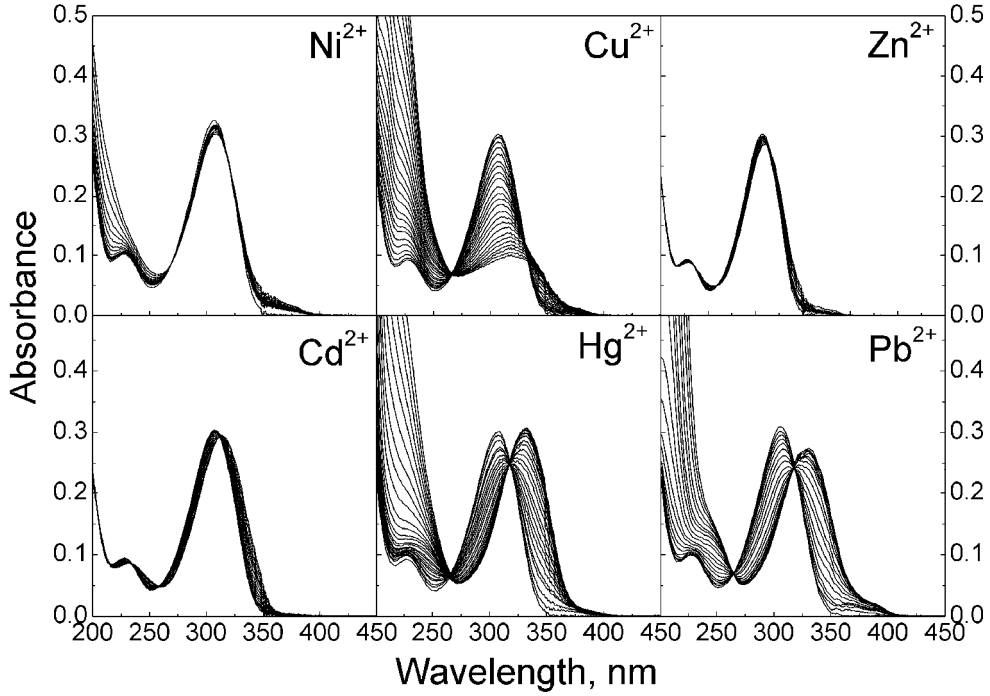


Figure S7. Absorption spectra of **3c** (10 μM) in CH_3CN in the presence of given metal ion of increasing concentration. Concentrations of metal ions increased in the same manner from 0 to 250 μM.

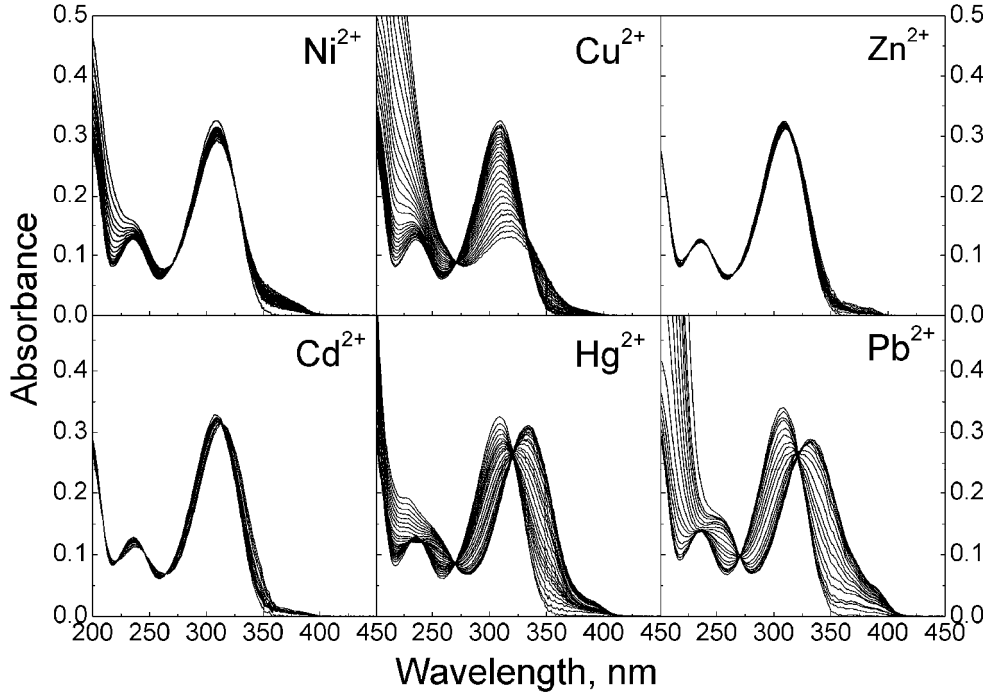


Figure S8. Absorption spectra of **3d** (10 μM) in CH_3CN in the presence of given metal ion of increasing concentration. Concentrations of metal ions increased in the same manner from 0 to 250 μM.

2. Figure S9

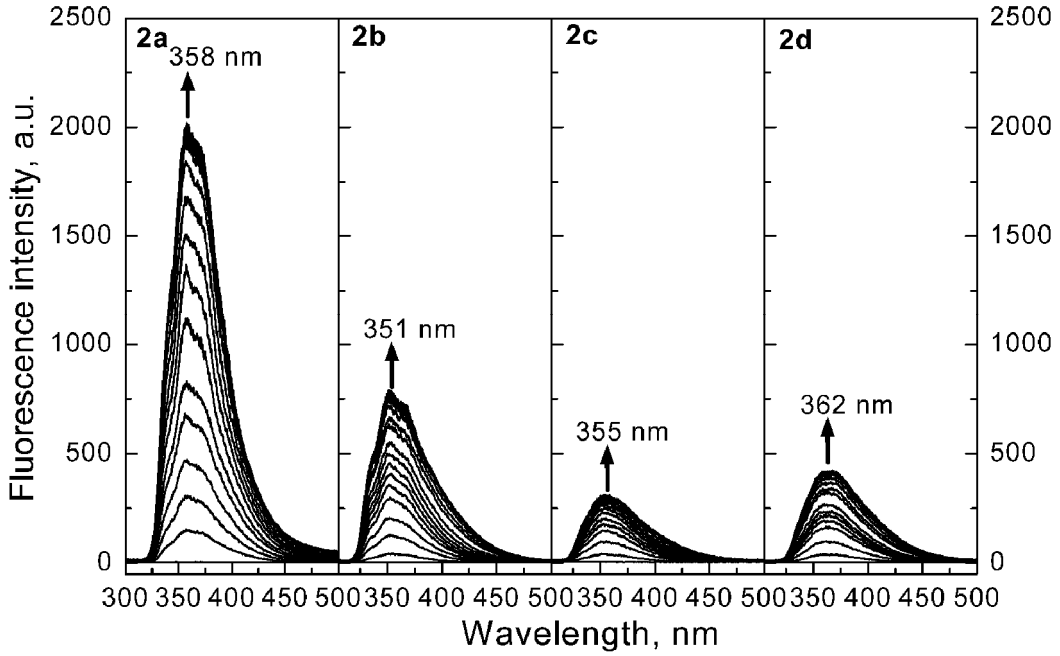


Figure S9. Fluorescence spectra of **2** in CH_3CN in the presence of increasing concentration of $Cu(ClO_4)_2$. [**2**] = 10 μM.

3. Figure S10

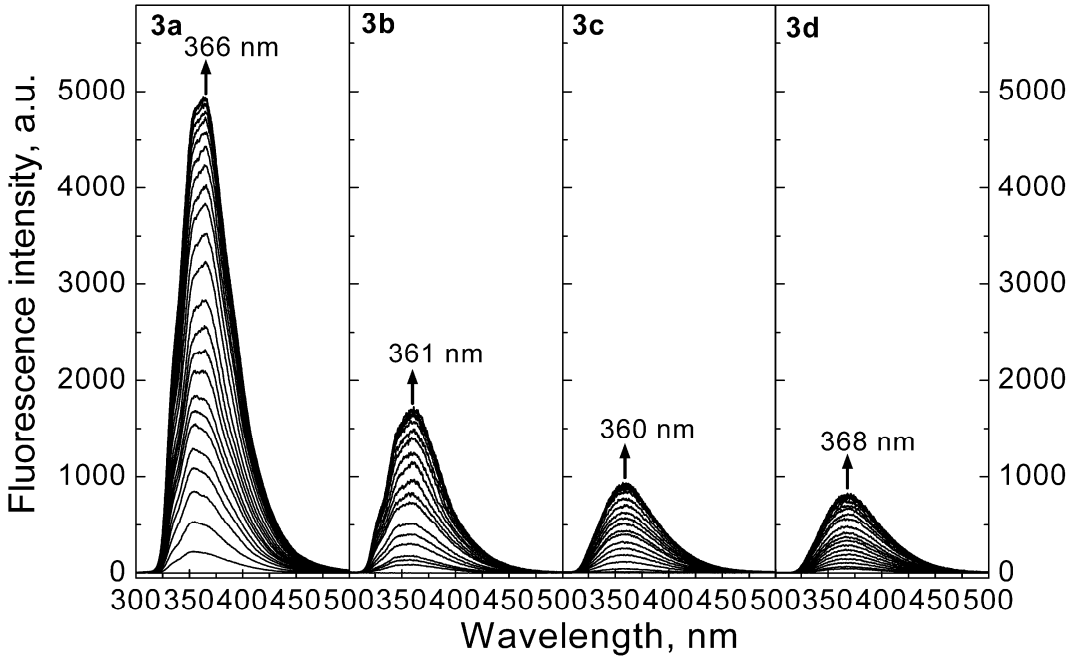


Figure S10. Fluorescence spectra of **3** in CH_3CN in the presence of increasing concentration of $Cu(ClO_4)_2$. [**3**] = 10 μM.

4. Table S1

Table S1. Absorption and fluorescence spectral parameters of **13**

	λ_{abs}, nm	ε, 10^4 M^{-1} cm^{-1}	λ_{flu}, nm	Φ [a]
13a	300	4.37	353/366	0.725
13b	294	3.98	347/361	0.719
13c	291	3.81	360	0.719
13d	295	3.76	368	0.720

[a] Fluorescence quantum yield of **13** was measured using quinine sulfate as a standard (0.546 in 0.5 M H_2SO_4: Demas, J. N.; Crobys, G. A. *J. Phys. Chem.* **1971**, *75*, 991-1024). The measurement error was up to 5%.

5. Figure S11

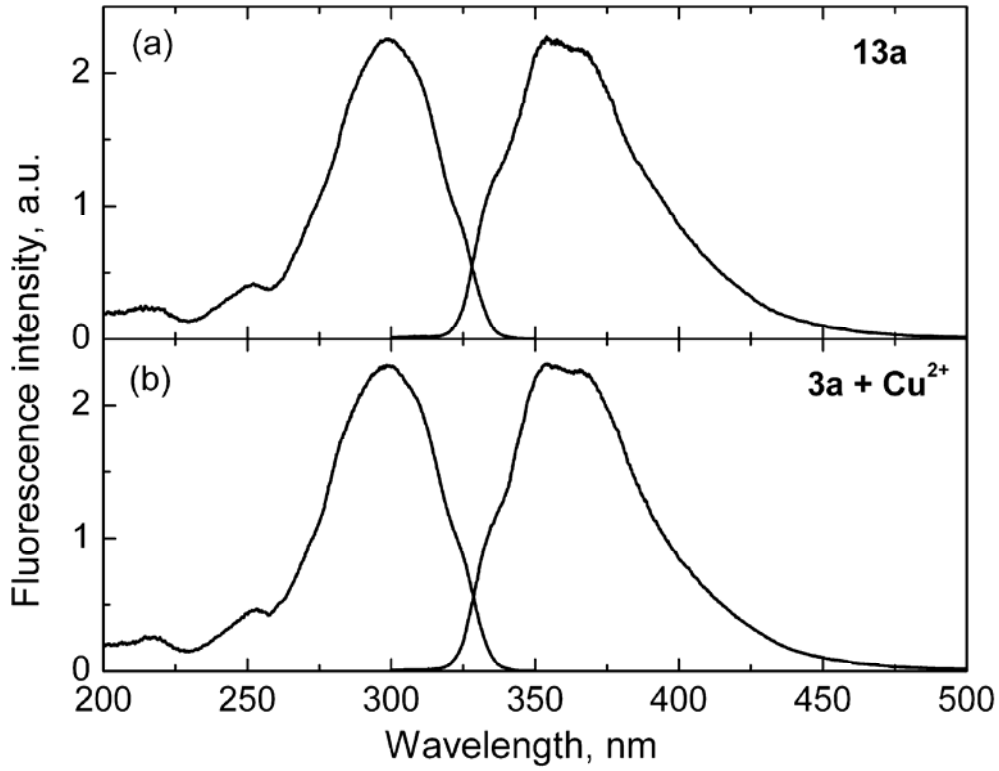


Figure S11. Fluorescence excitation and emission spectra of (a) the oxidation product **13a** and (b) **3a** in the presence of 1.0 equivalent Cu^{2+} in CH_3CN

6. Figure S12

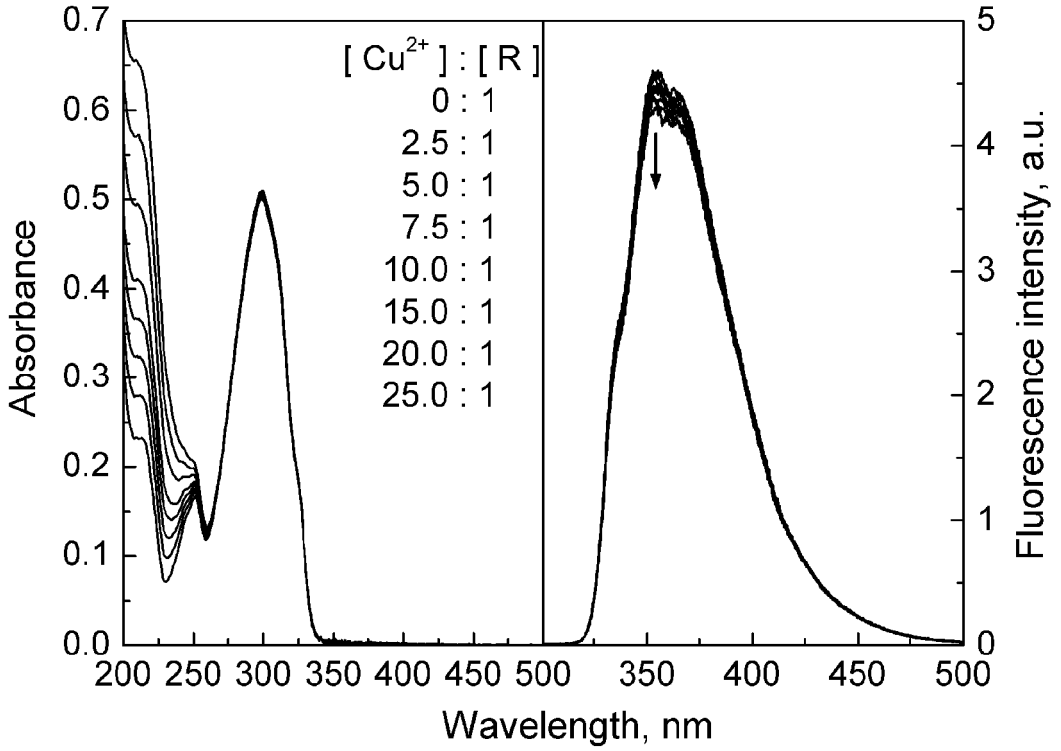


Figure S12. Absorption and fluorescence spectra of **13a** (10 μM) in CH_3CN in the presence of increasing concentration of Cu^{2+}. The excitation wavelength for acquiring fluorescence spetra was 283 nm.

7. Figure S13

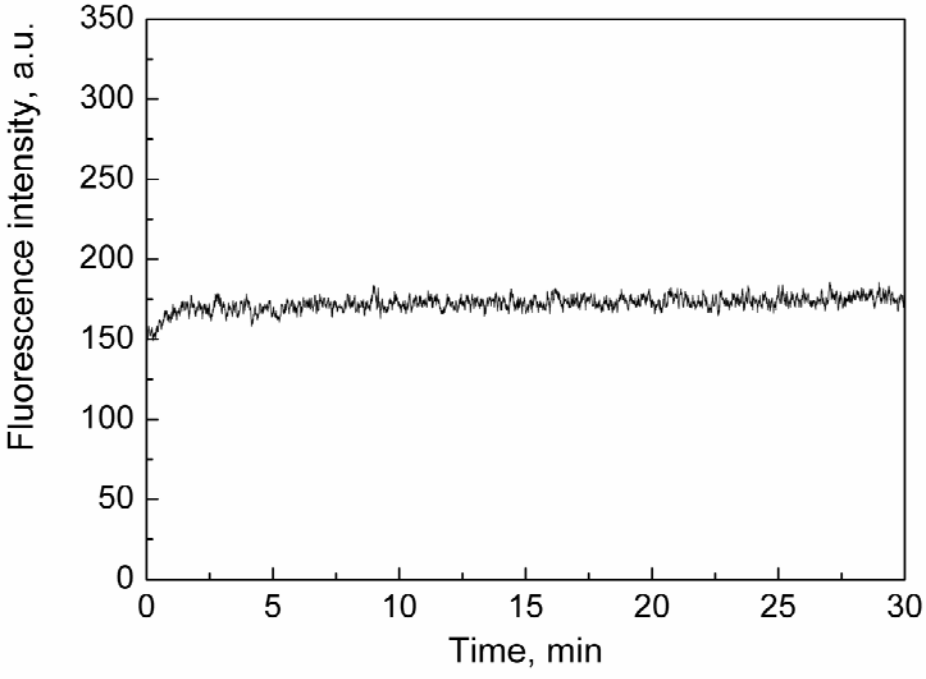


Figure S13. Time scan of fluorescence intensity of **3a** (0.5 μM) in CH_3CN in the presence of 0.5 equiv. of Cu^{2+}. The excitation and emission wavelength were 283 nm and 360 nm, respectively.

8. Figure S14

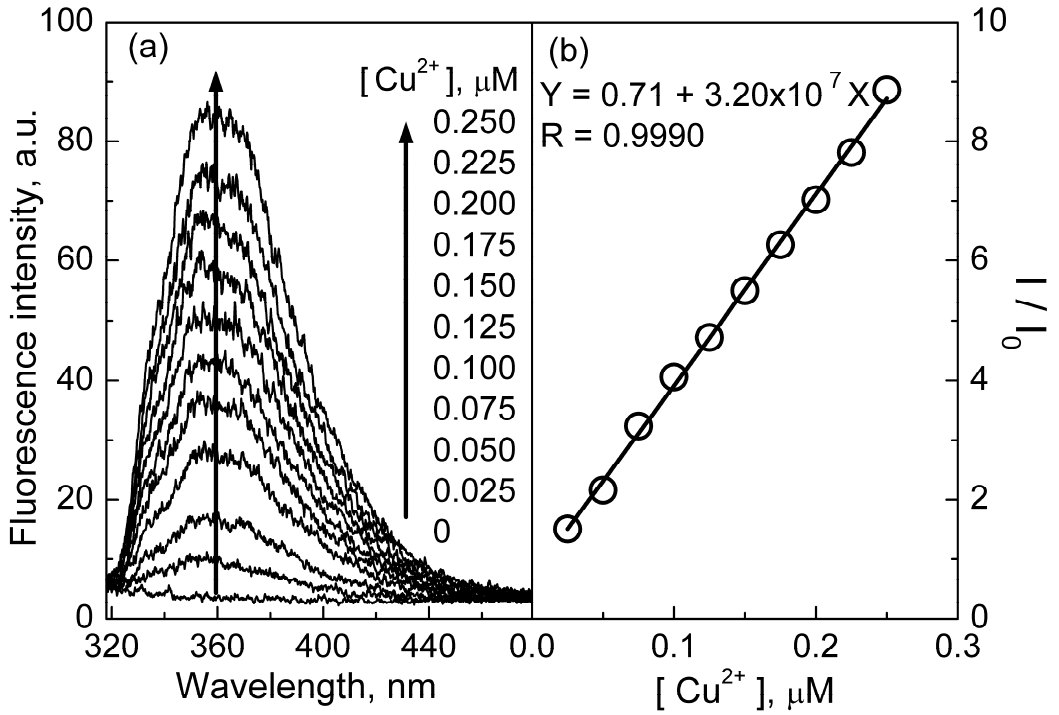


Figure S14. (a) Fluorescence spectra of **3a** (0.5 μM) in CH_3CN in the presence of increasing concentration of $Cu(ClO_4)_2$ and (b) linear response curve. Excitation wavelength was 283 nm.

9. Optimization of assay conditions in aqueous solution

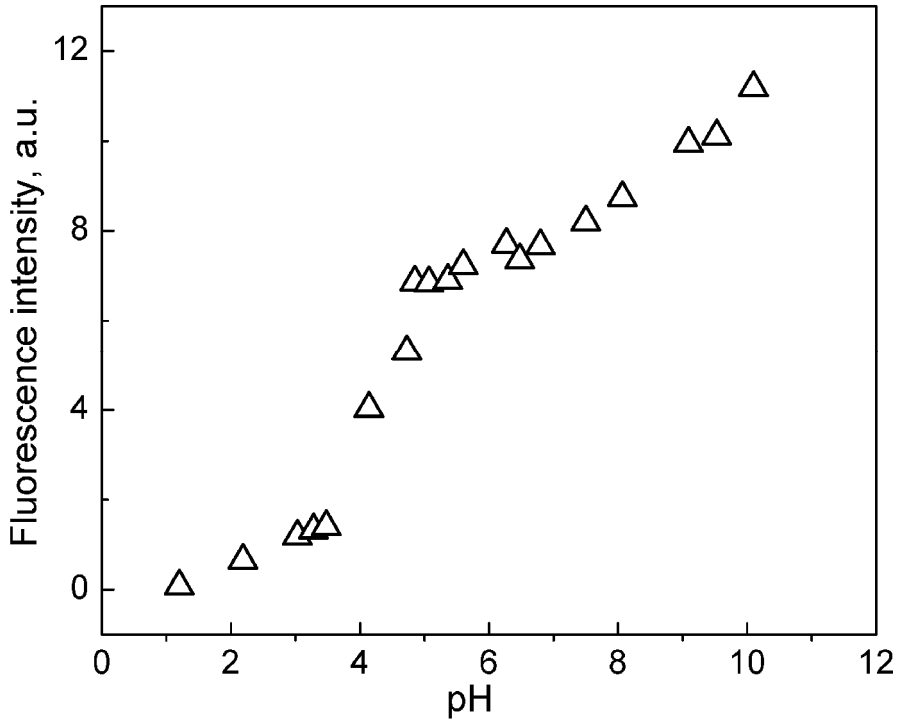


Figure S15. Plots of the fluorescence intensity of **3a** (10 μM) in the presence of 25 equiv. of Cu^{2+} as a function of pH of CH_3CN-H_2O (1:1, v/v) solution

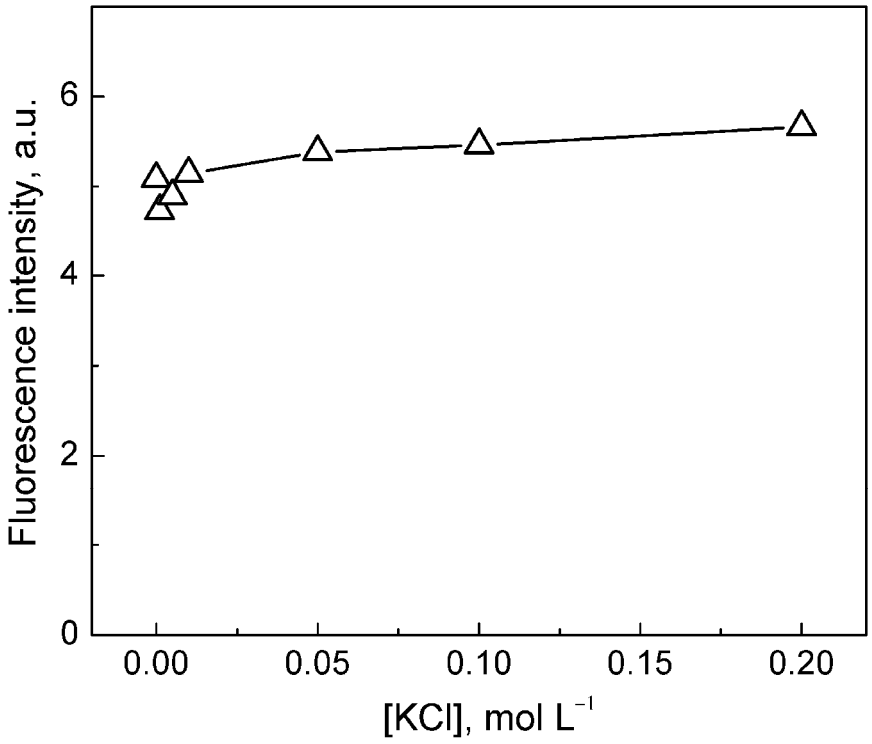


Figure S16. Ionic strength effect (KCl) of the fluorescence of **3a** in the presence of 25 equiv. of Cu^{2+} in CH_3CN-H_2O (1:1, v/v). [KCl] = 0 - 0.2 M.

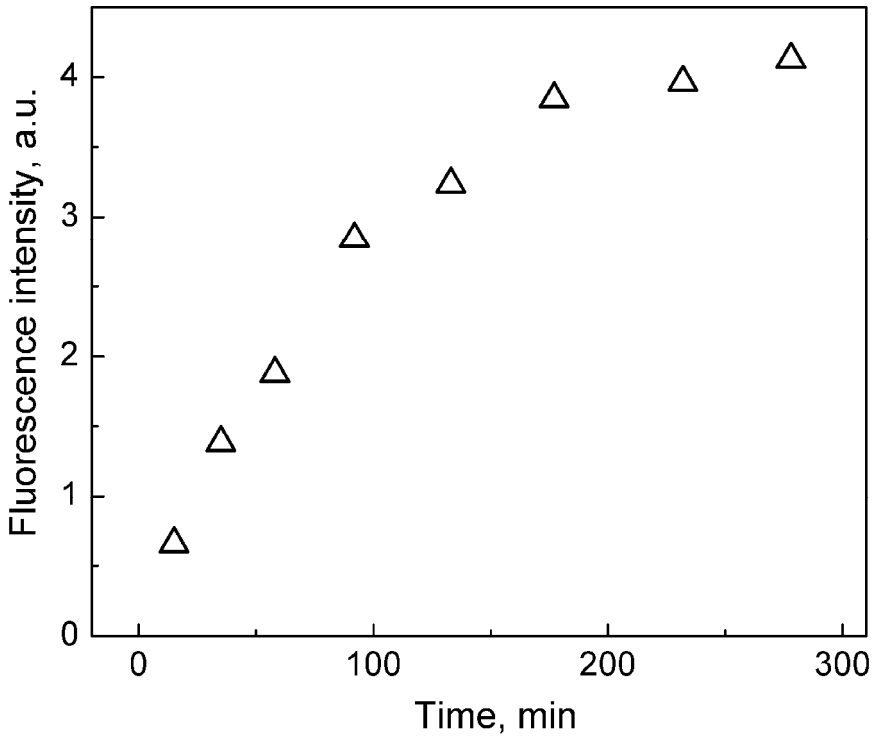


Figure S17. Influence of reaction duration on the fluorescence of **3a** in the presence of 25 equivalents of Cu^{2+} in a mixture of CH_3CN and Tris-HCl (5 mM, pH 7.2, KCl 0.1 M) aqueous buffer solution (20/80, v/v) at 50°C

10. Figure S18

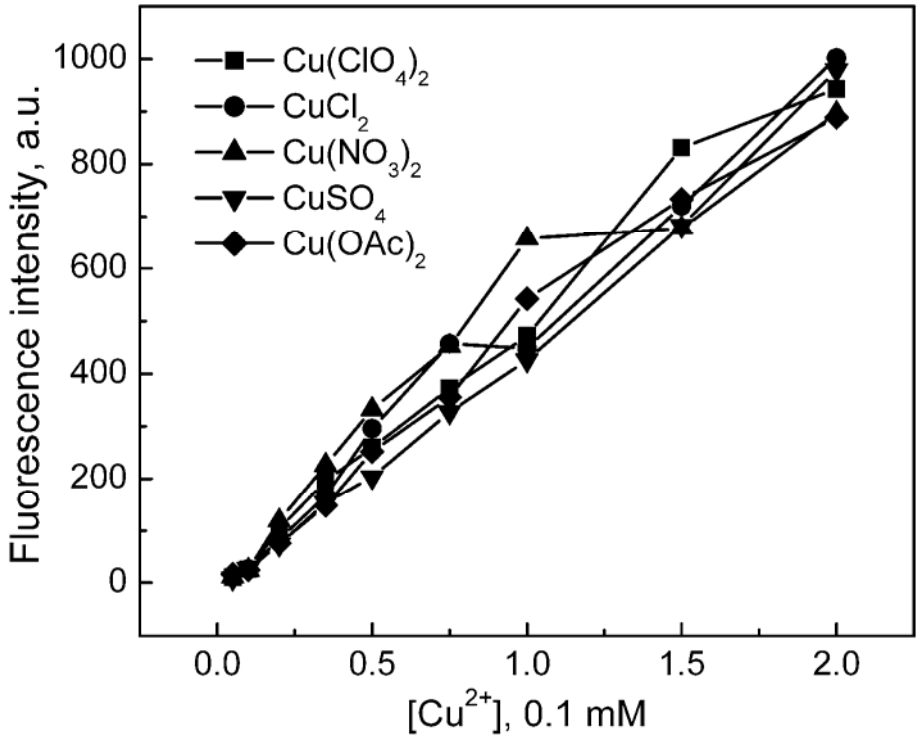
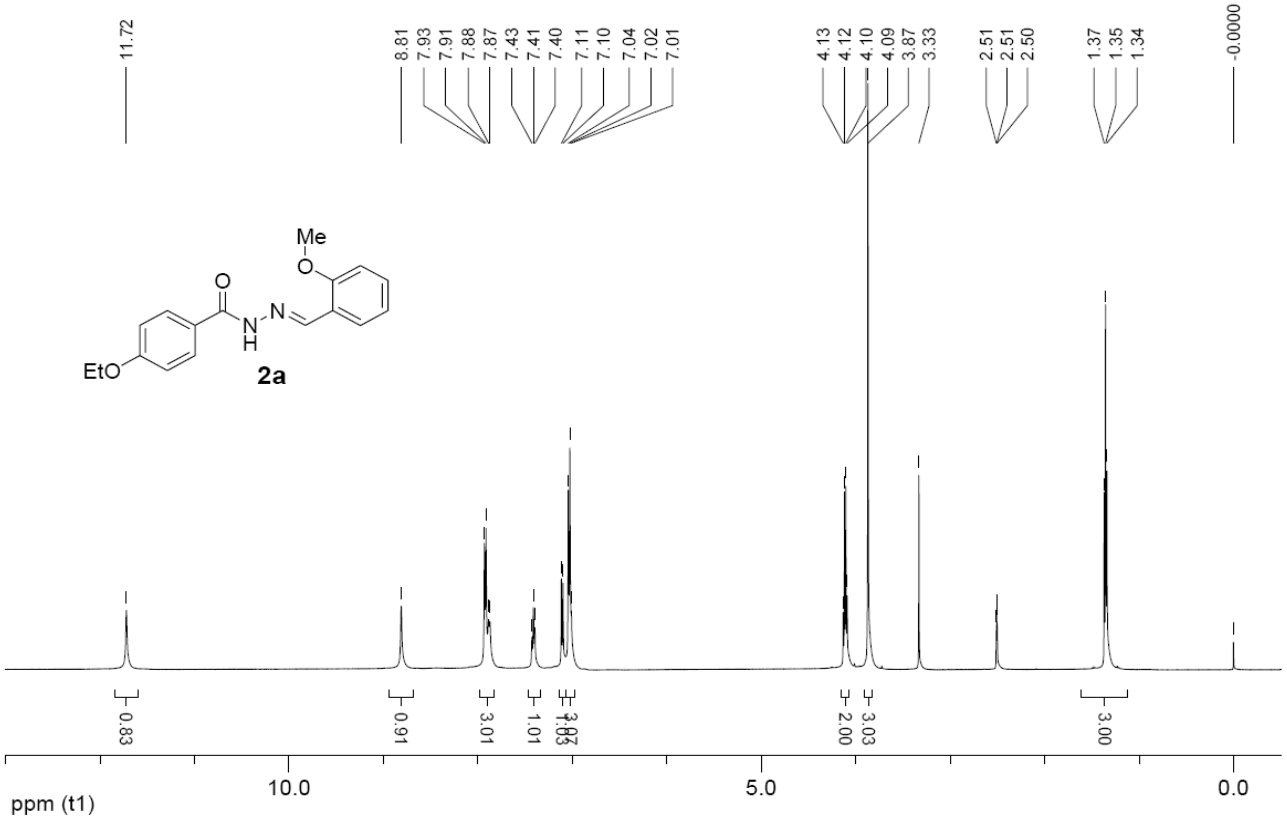


Figure S18. Fluorescent response of **3a** toward Cu^{2+} with varied counter anion in a mixture of CH_3CN and Tris-HCl (5 mM, pH 7.2, 0.1 M KCl) aqueous buffer solution (20/80, v/v)

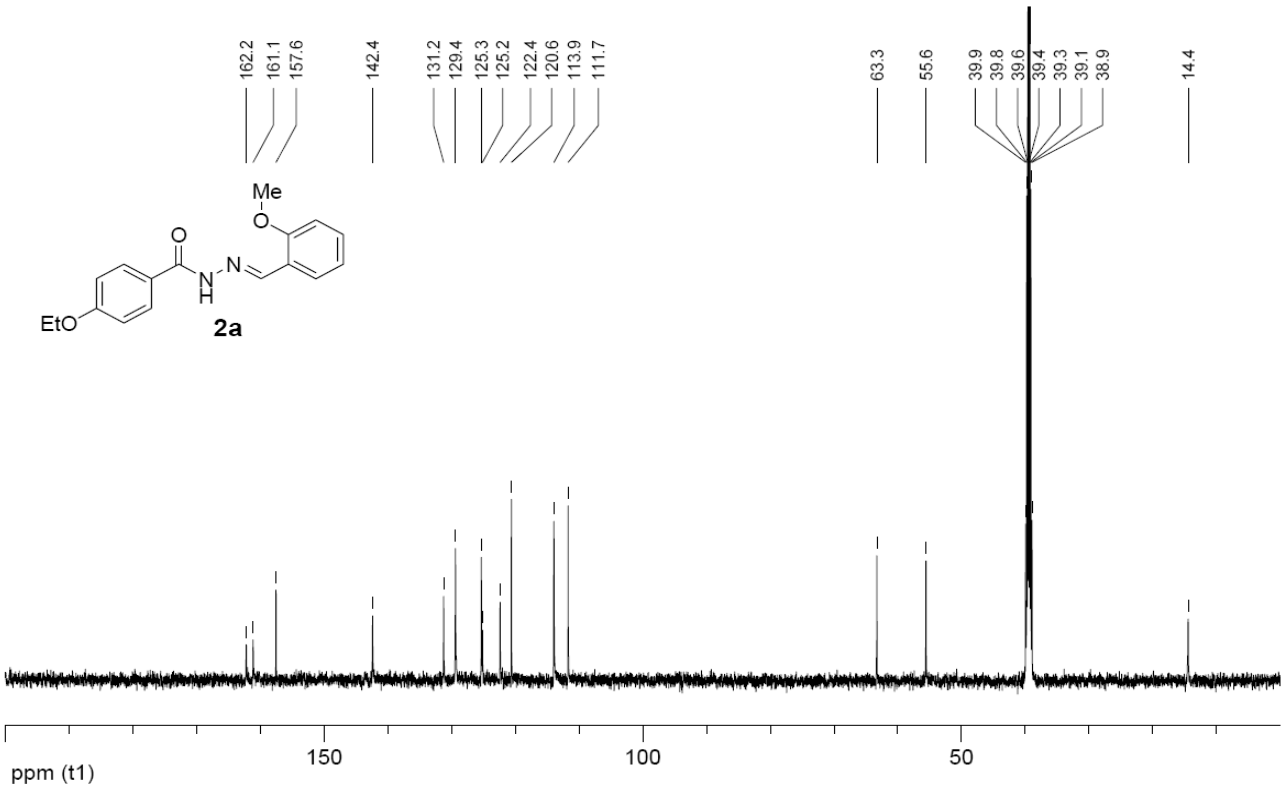
11. ^{1}H NMR and ^{13}C NMR spectra of compounds 2-13

***N'*-(2-Methoxybenzylidene)-4-ethoxybenzohydrazide (2a)**:

^{1}H NMR (500MHz, DMSO-d_6)

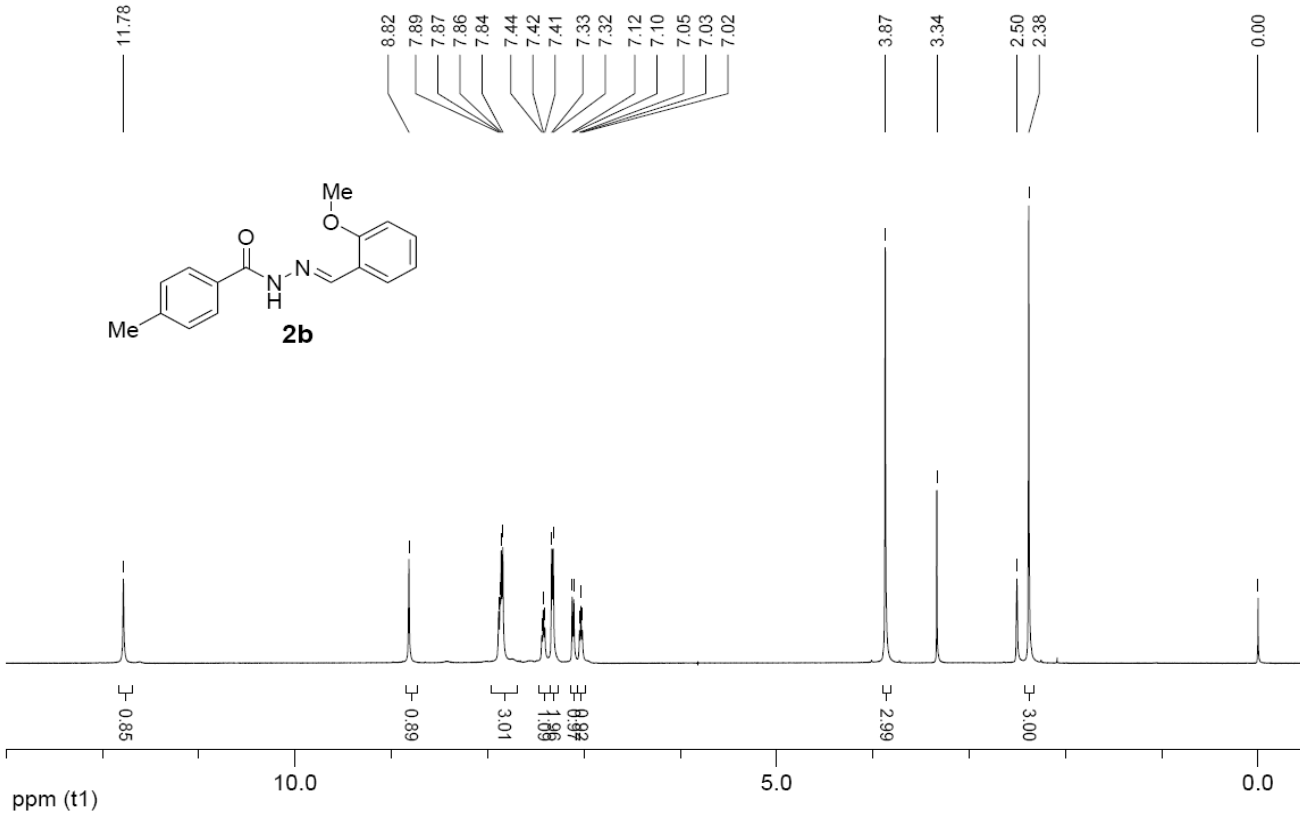


^{13}C NMR (125MHz, DMSO-d_6)

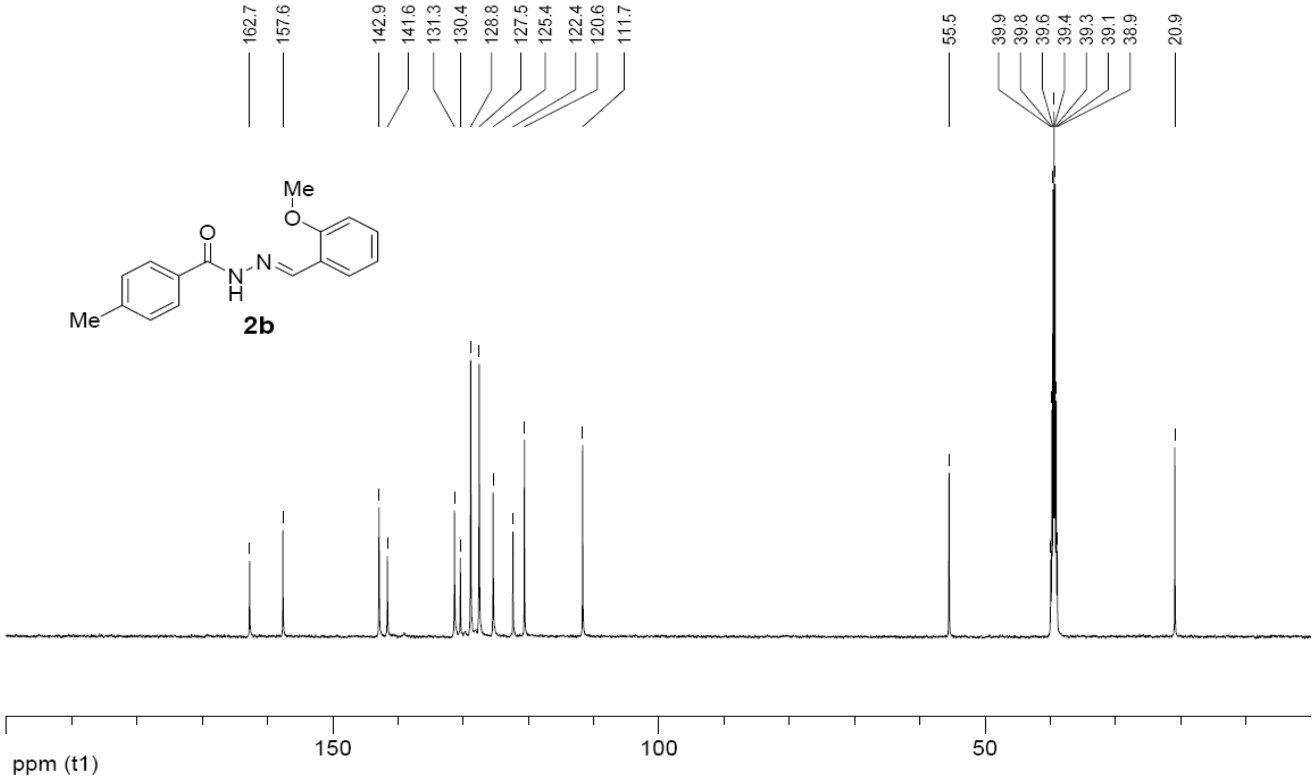


***N'*-(2-Methoxybenzylidene)-4-methylbenzohydrazide (2b)**:

^{1}H NMR (500MHz, DMSO-d_6)

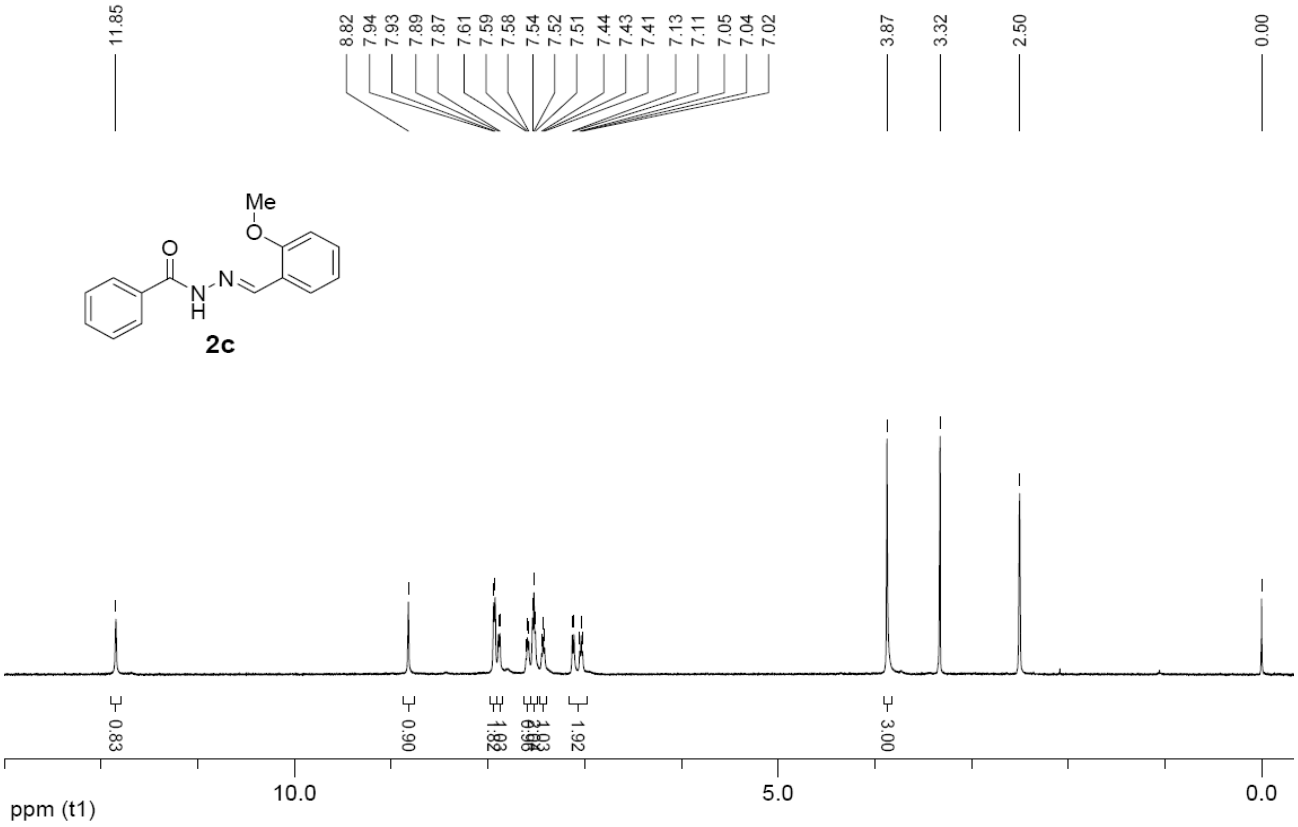


^{13}C NMR (125MHz, DMSO-d_6)

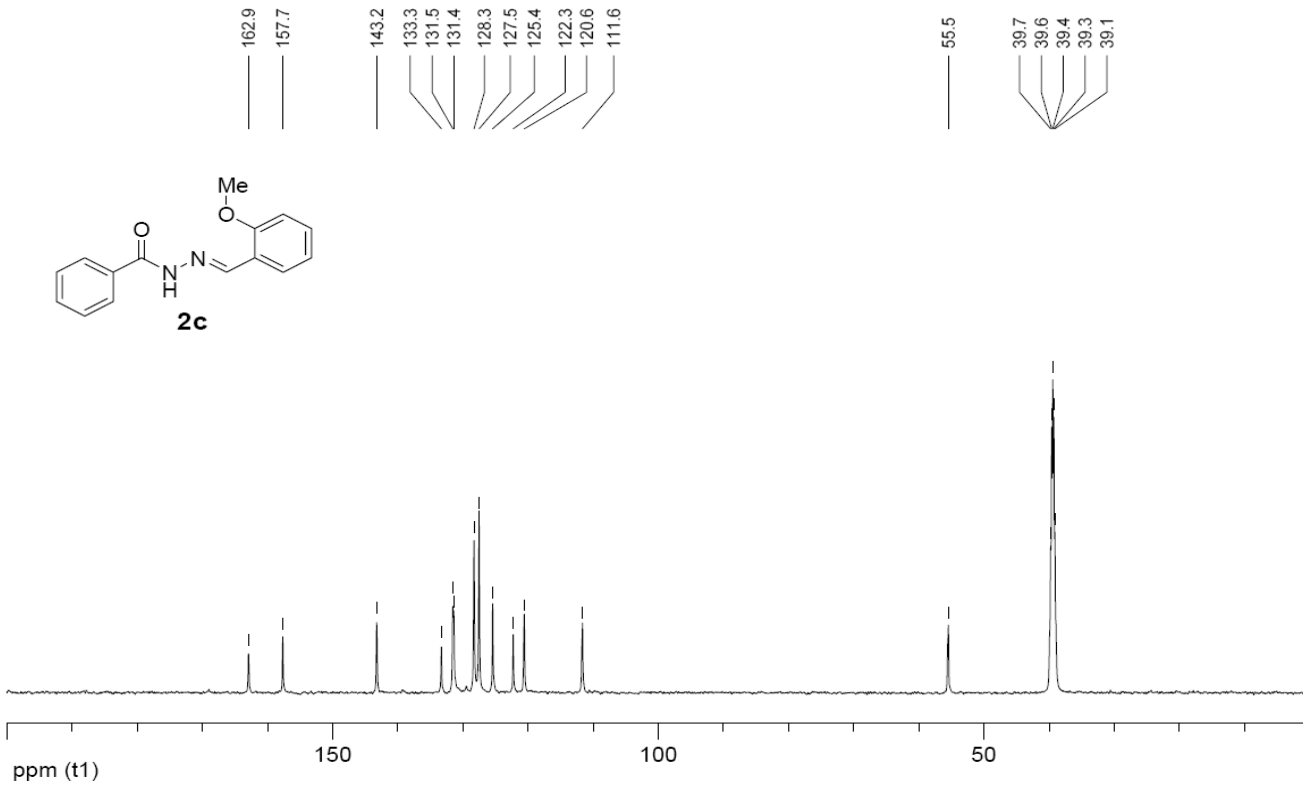


***N'*-(2-Methoxybenzylidene)benzohydrazide (2c)**:

^{1}H NMR (500MHz, DMSO-d_6)

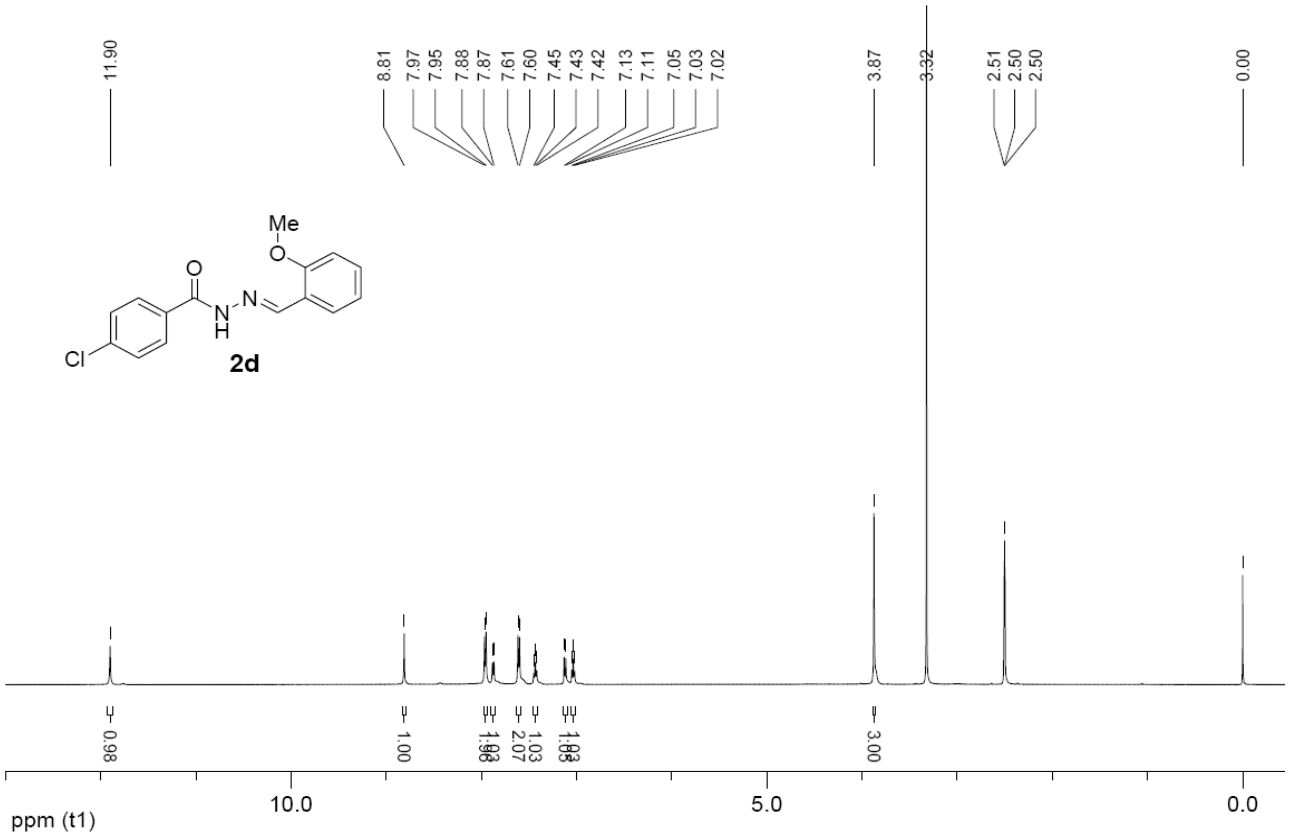


^{13}C NMR (125MHz, DMSO-d_6)

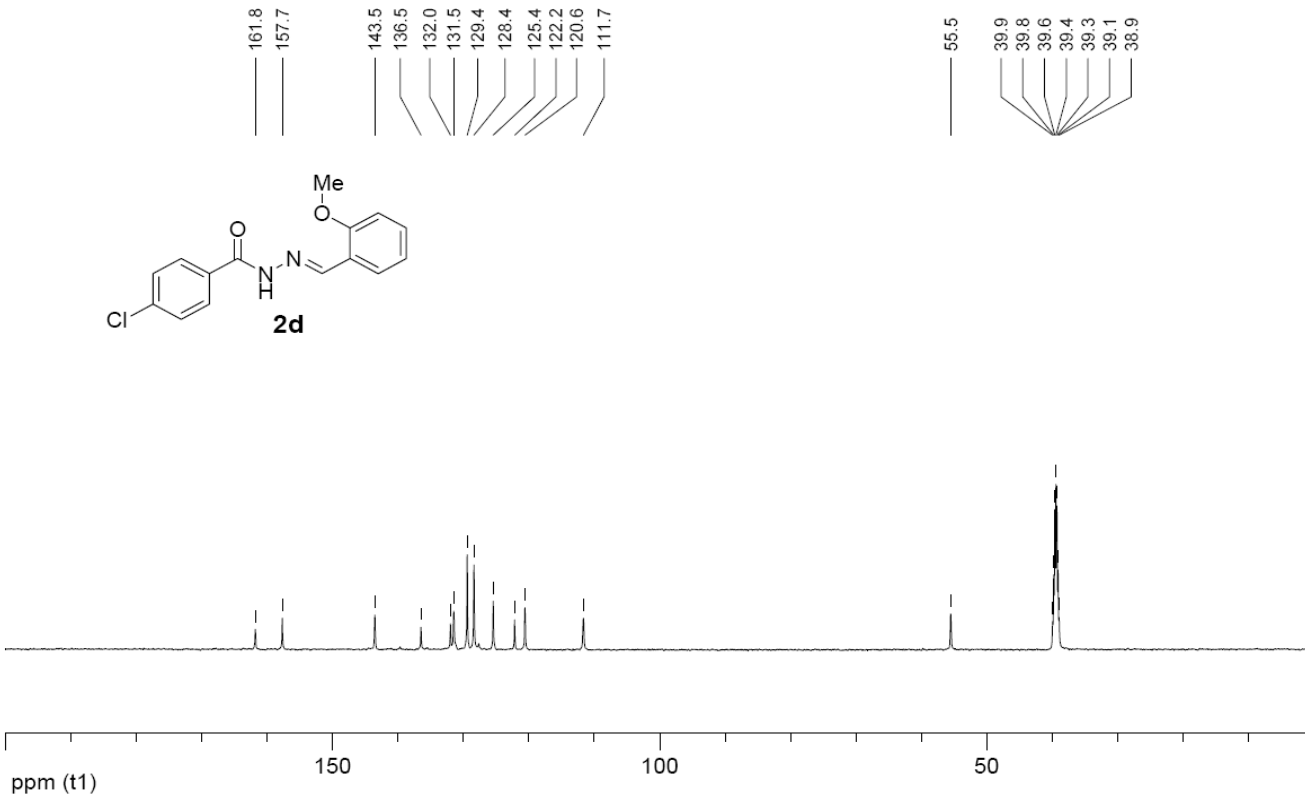


***N'*-(2-Methoxybenzylidene)-4-chlorobenzohydrazide (2d)**:

^{1}H NMR (500MHz, DMSO-d_6)

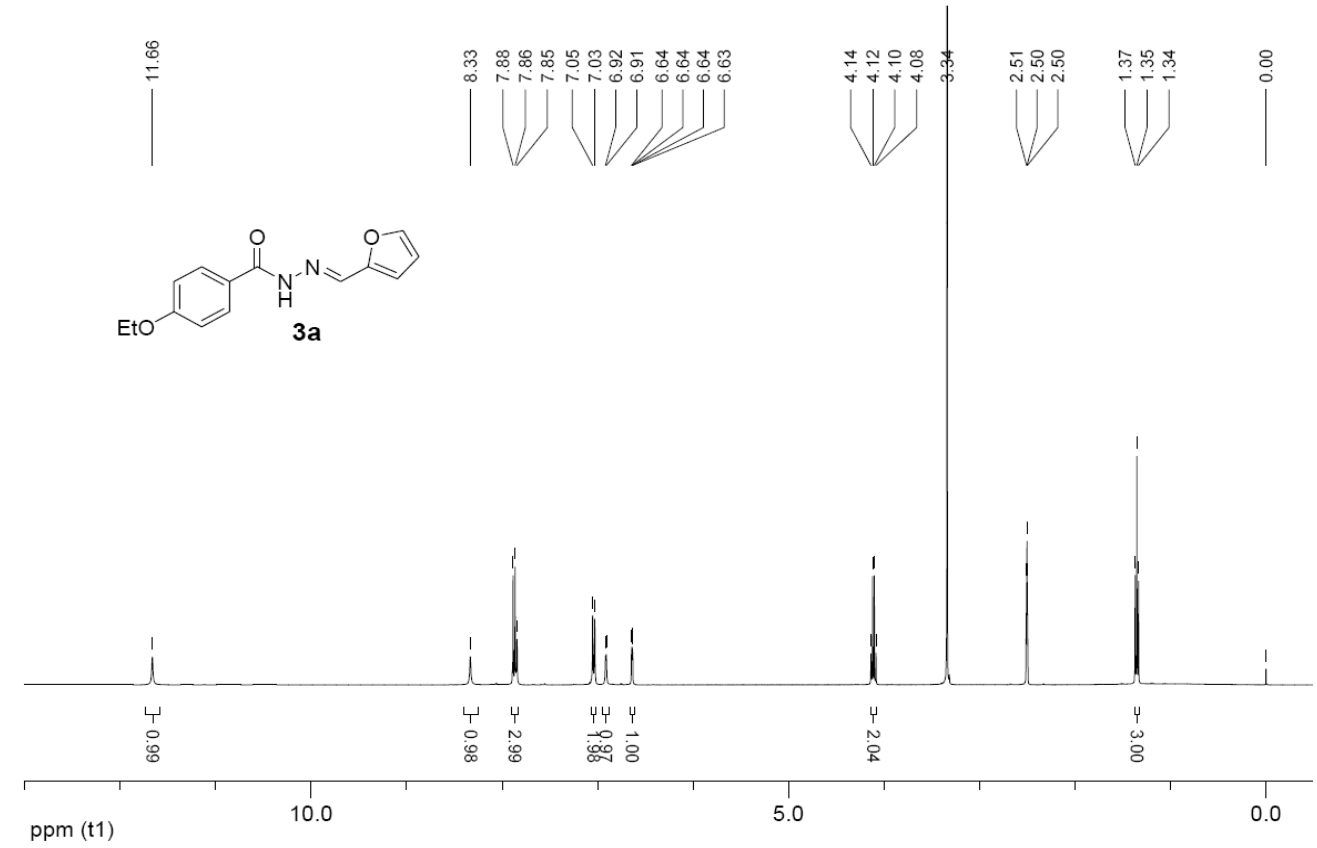


^{13}C NMR (125MHz, DMSO-d_6)

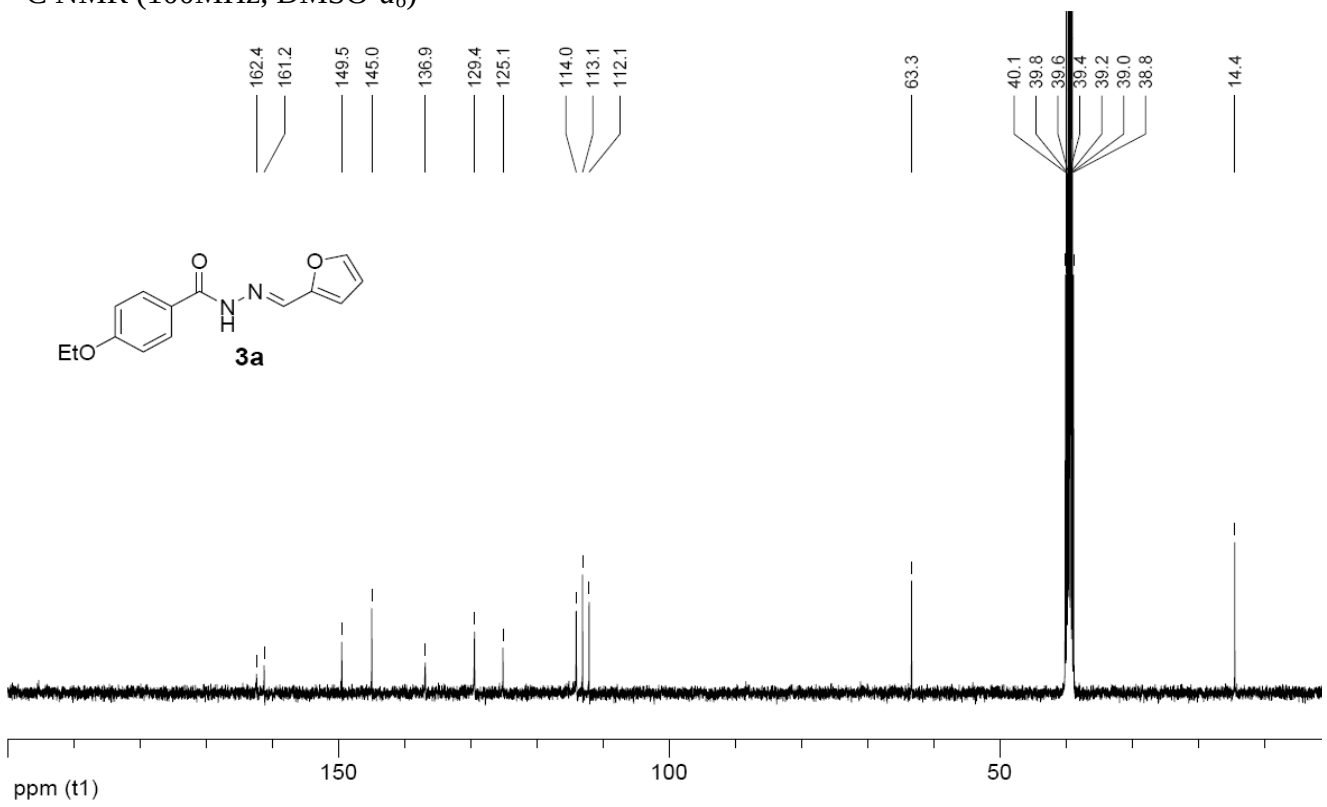


4-Ethoxy-*N'*-(furan-2-ylmethylene)benzohydrazide (3a):

^{1}H NMR (400MHz, DMSO-d_6)

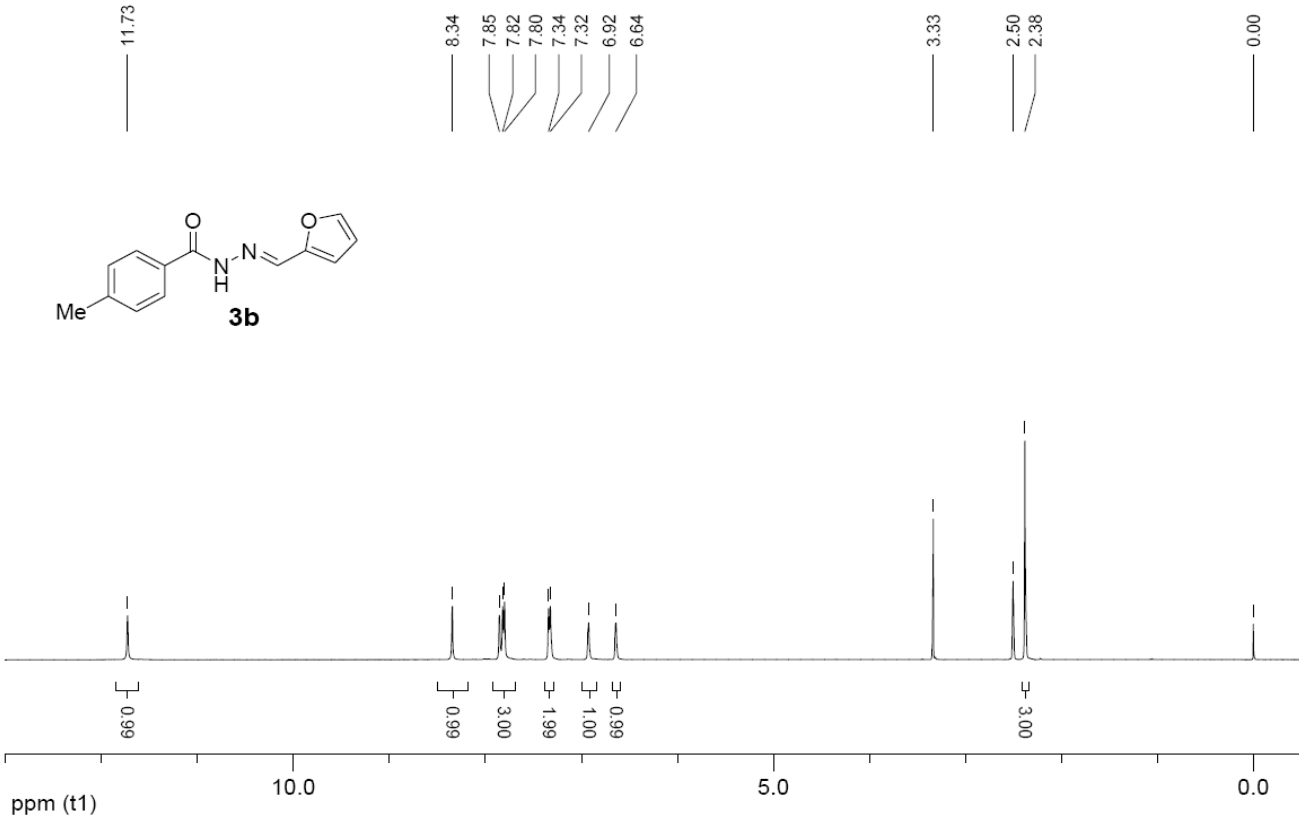


^{13}C NMR (100MHz, DMSO-d_6)

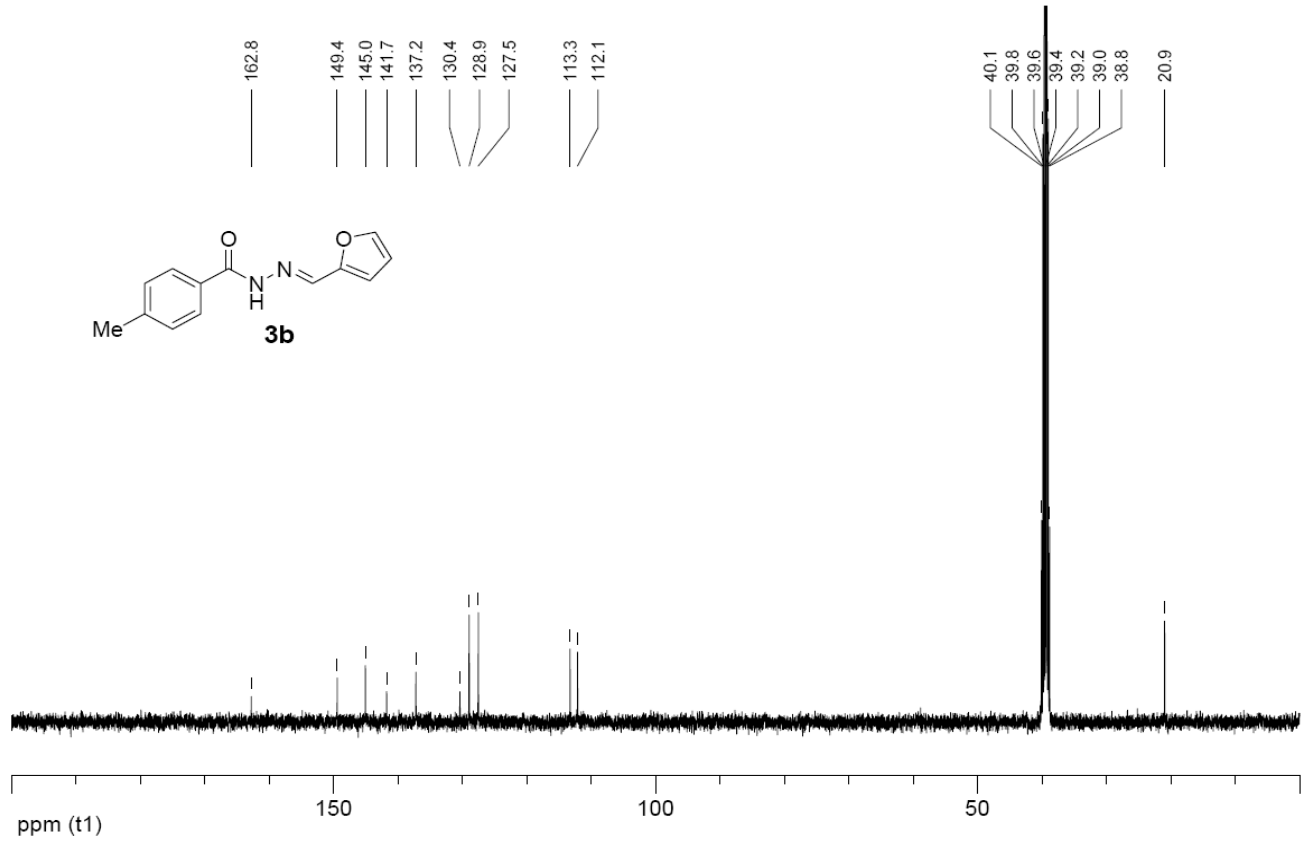


***N'*-(Furan-2-ylmethylene)-4-methylbenzohydrazide (3b)**:

^{1}H NMR (400MHz, DMSO-d_6)

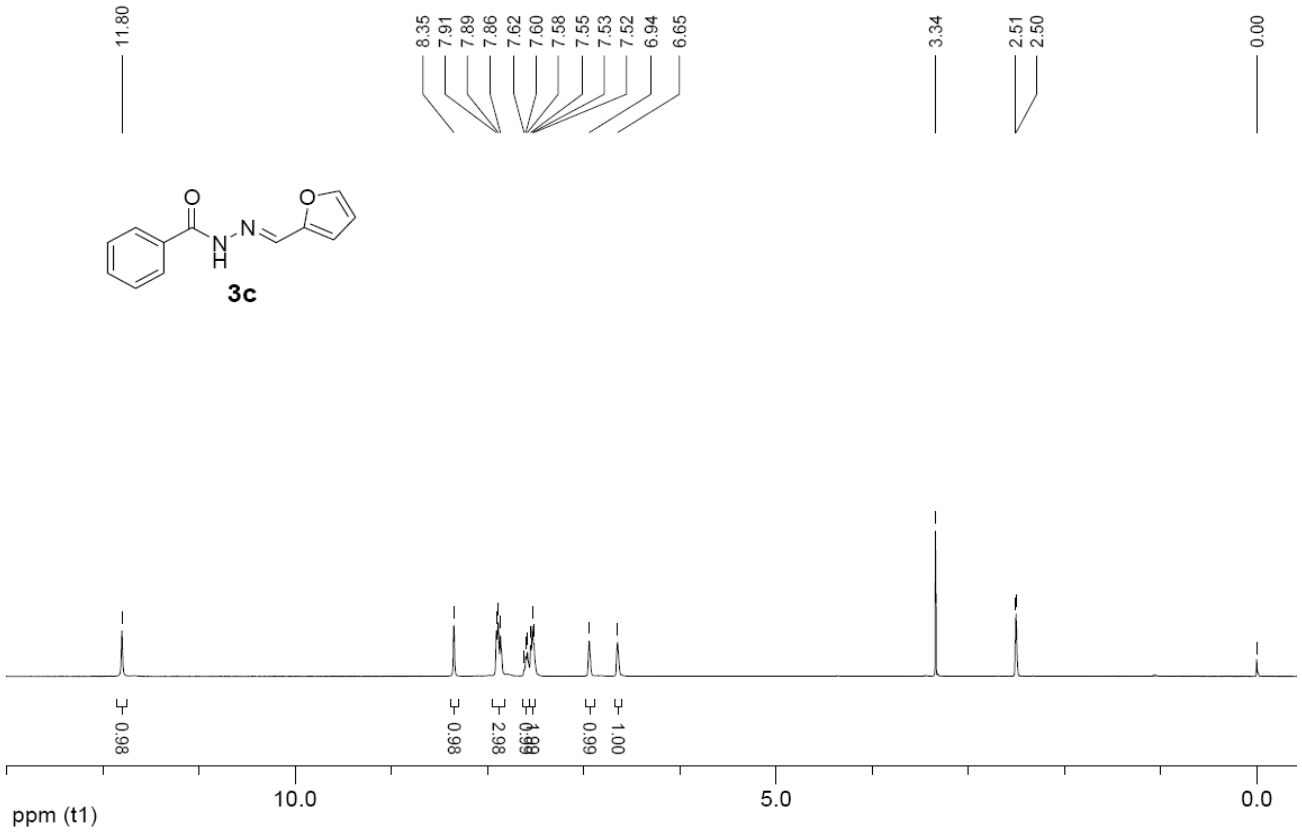


^{13}C NMR (100MHz, DMSO-d_6)

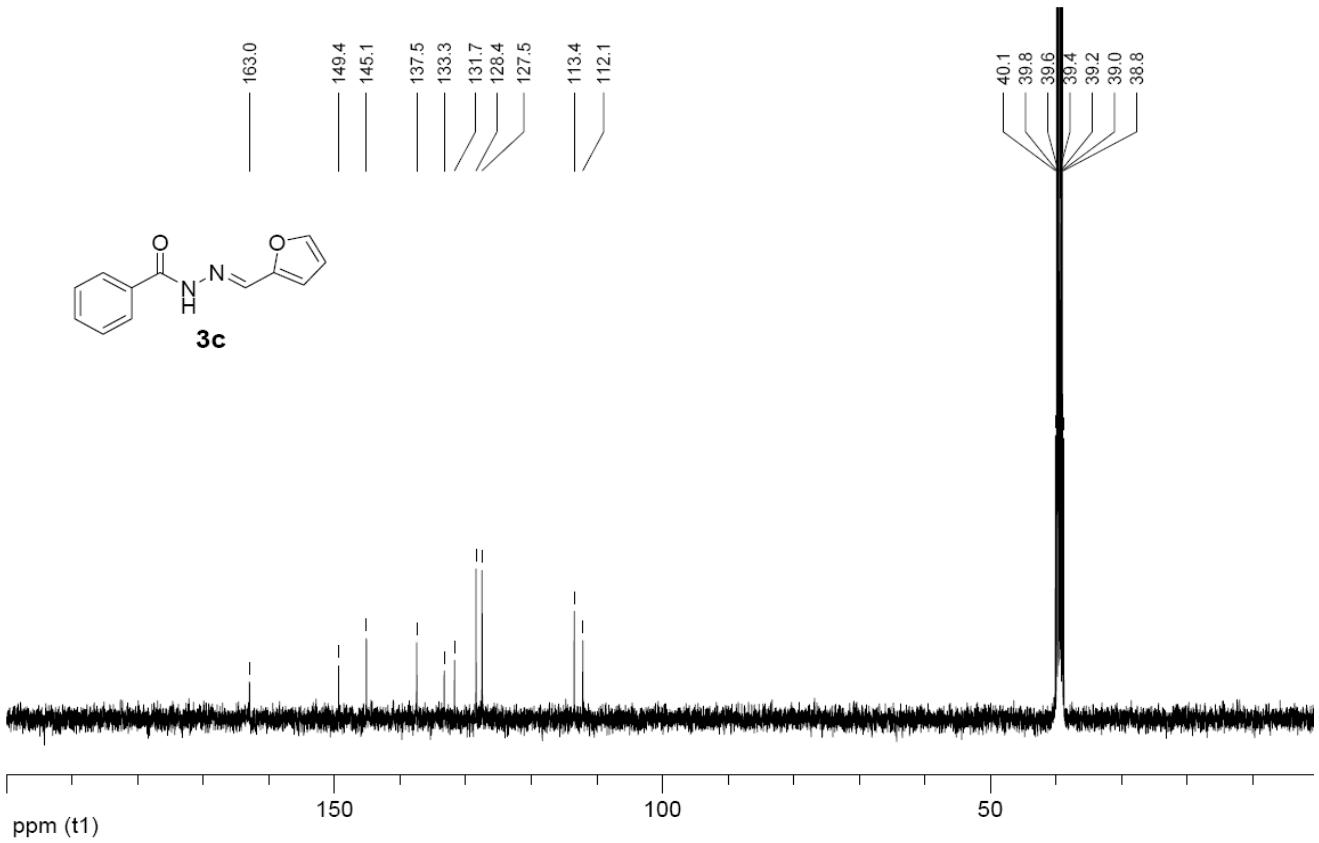


***N'*-(Furan-2-ylmethylene)benzohydrazide (3c)**:

^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (100MHz, DMSO-d_6)



4-Chloro-*N'*-(furan-2-ylmethylene)benzohydrazide (3d):

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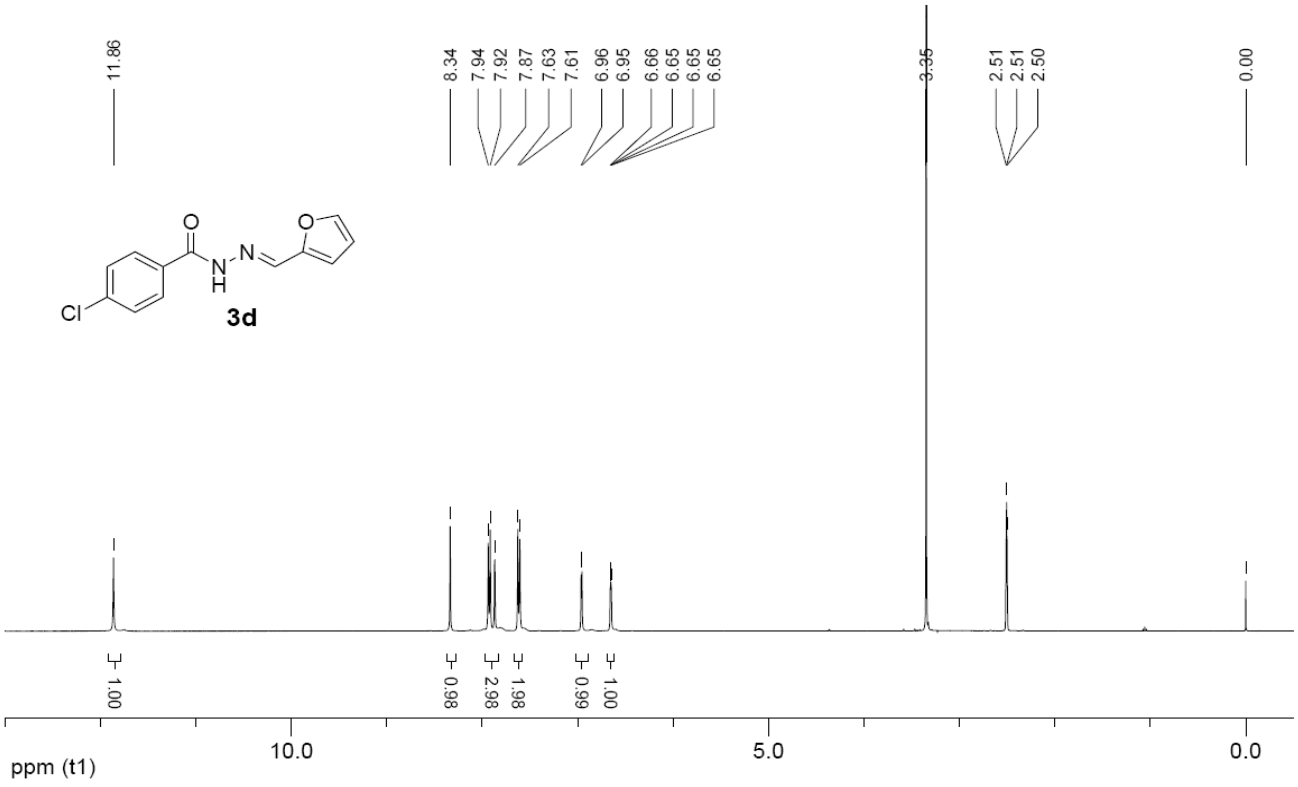
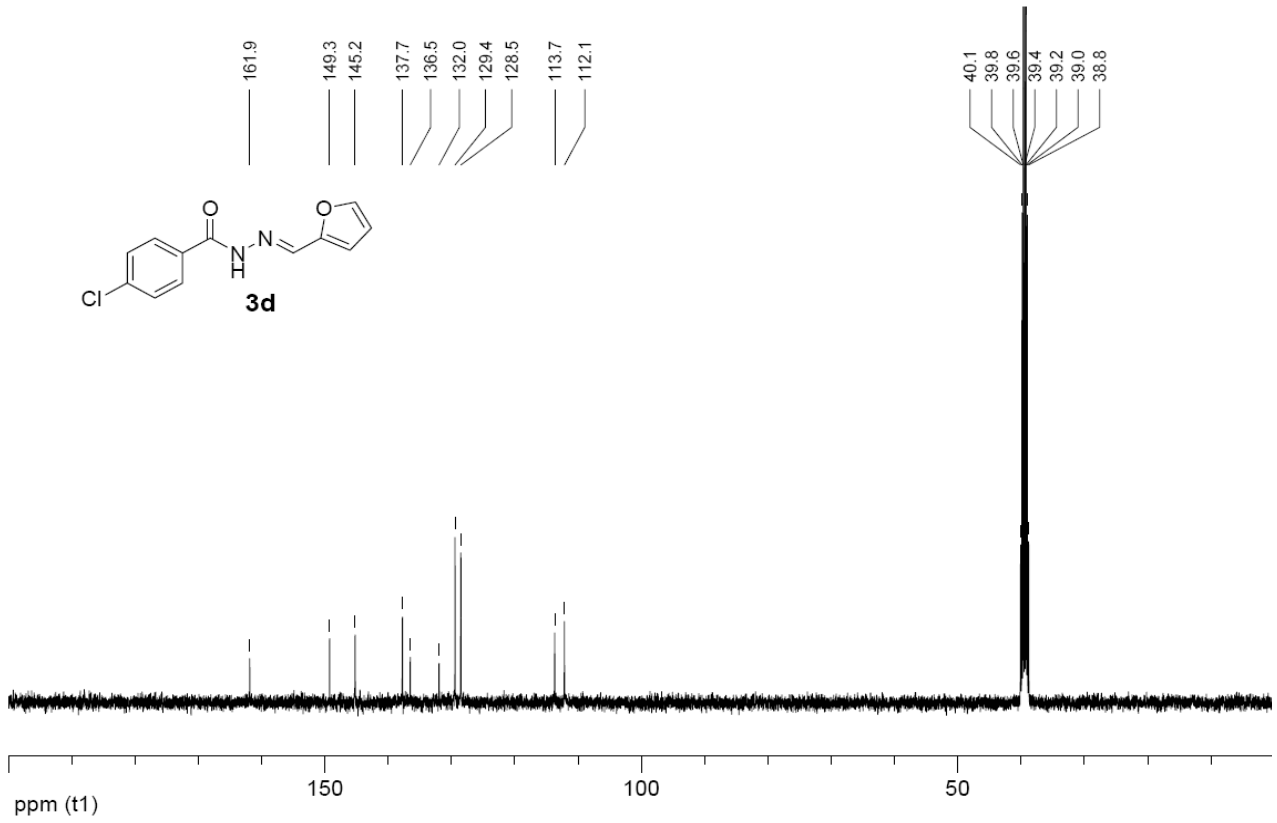
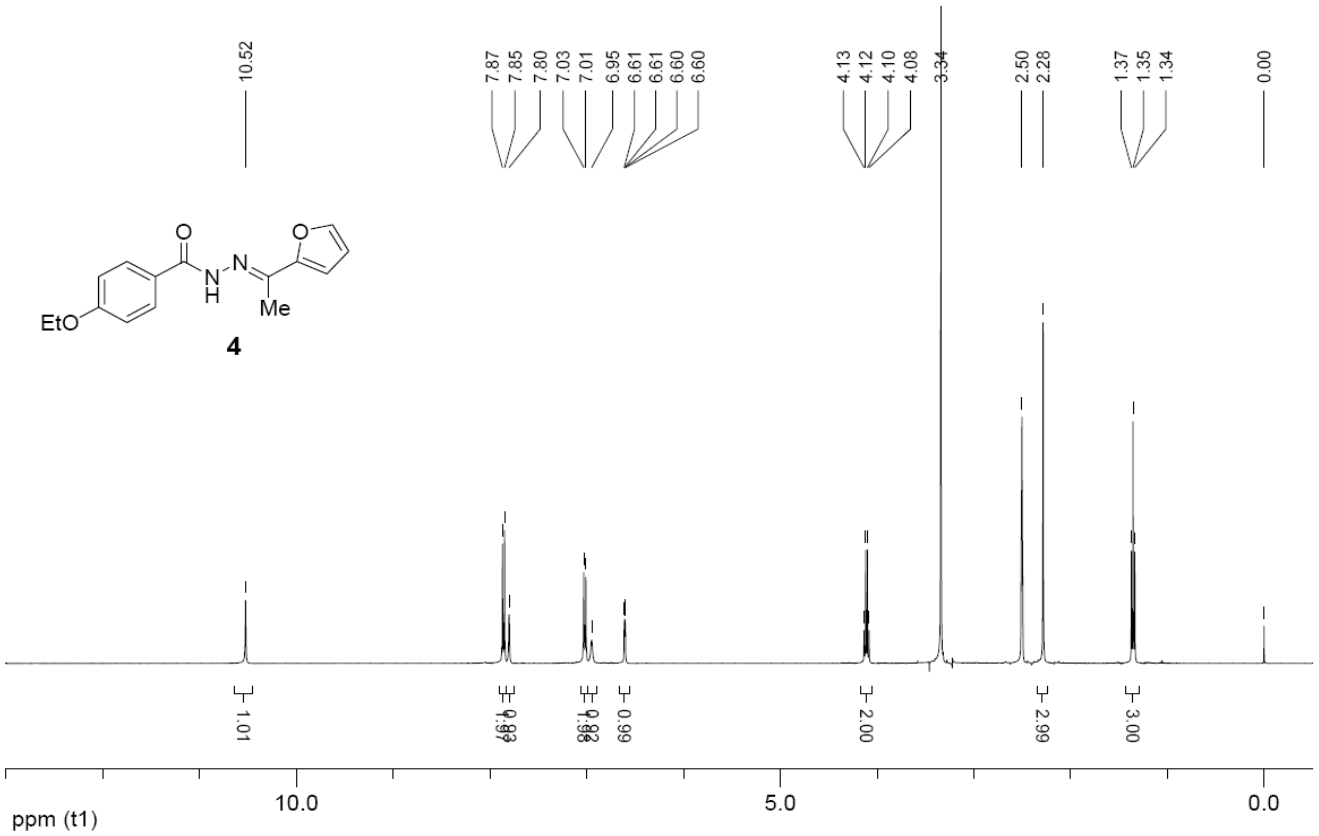


^{13}C NMR (100MHz, DMSO-d_6)

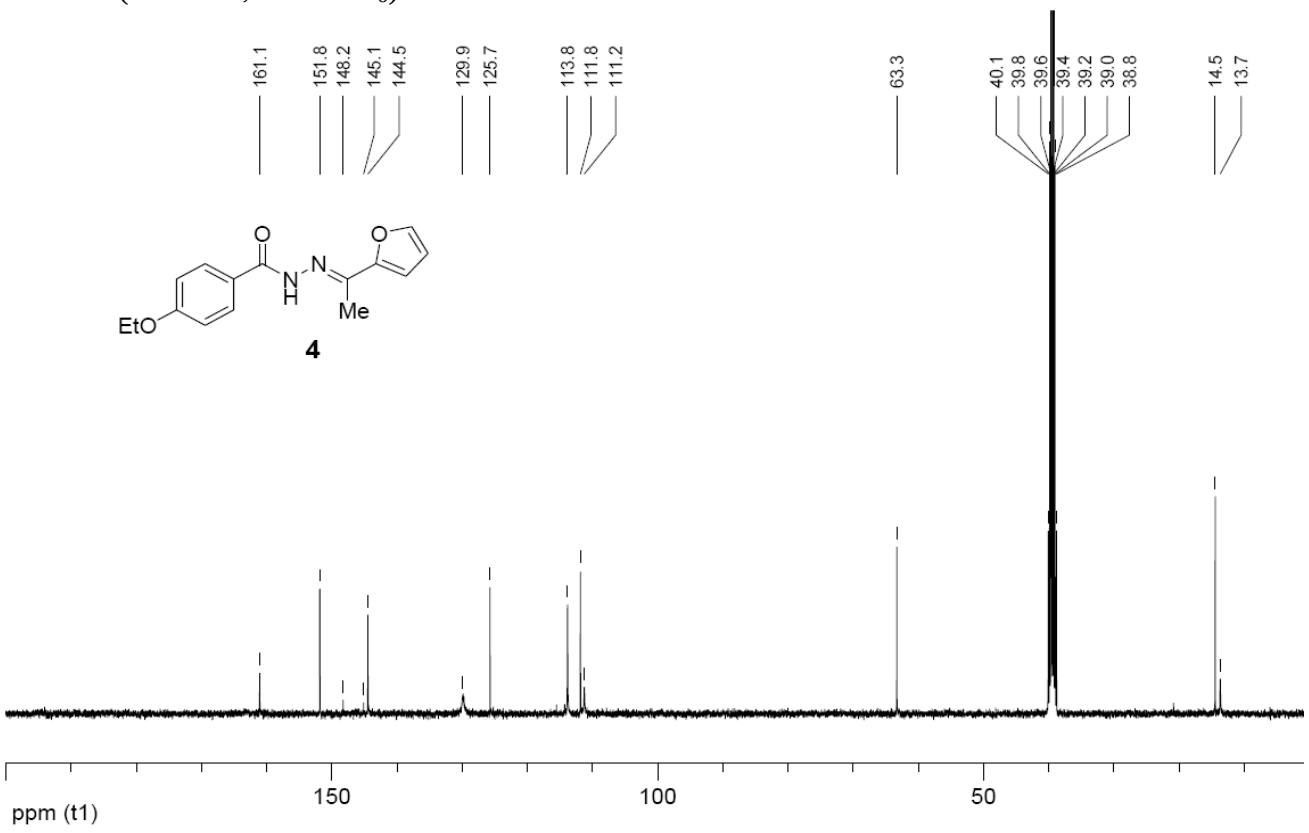


4-Ethoxy-*N'*-(1-(furan-2-yl)ethylidene)benzohydrazide (4):

^{1}H NMR (400MHz, DMSO-d_6)

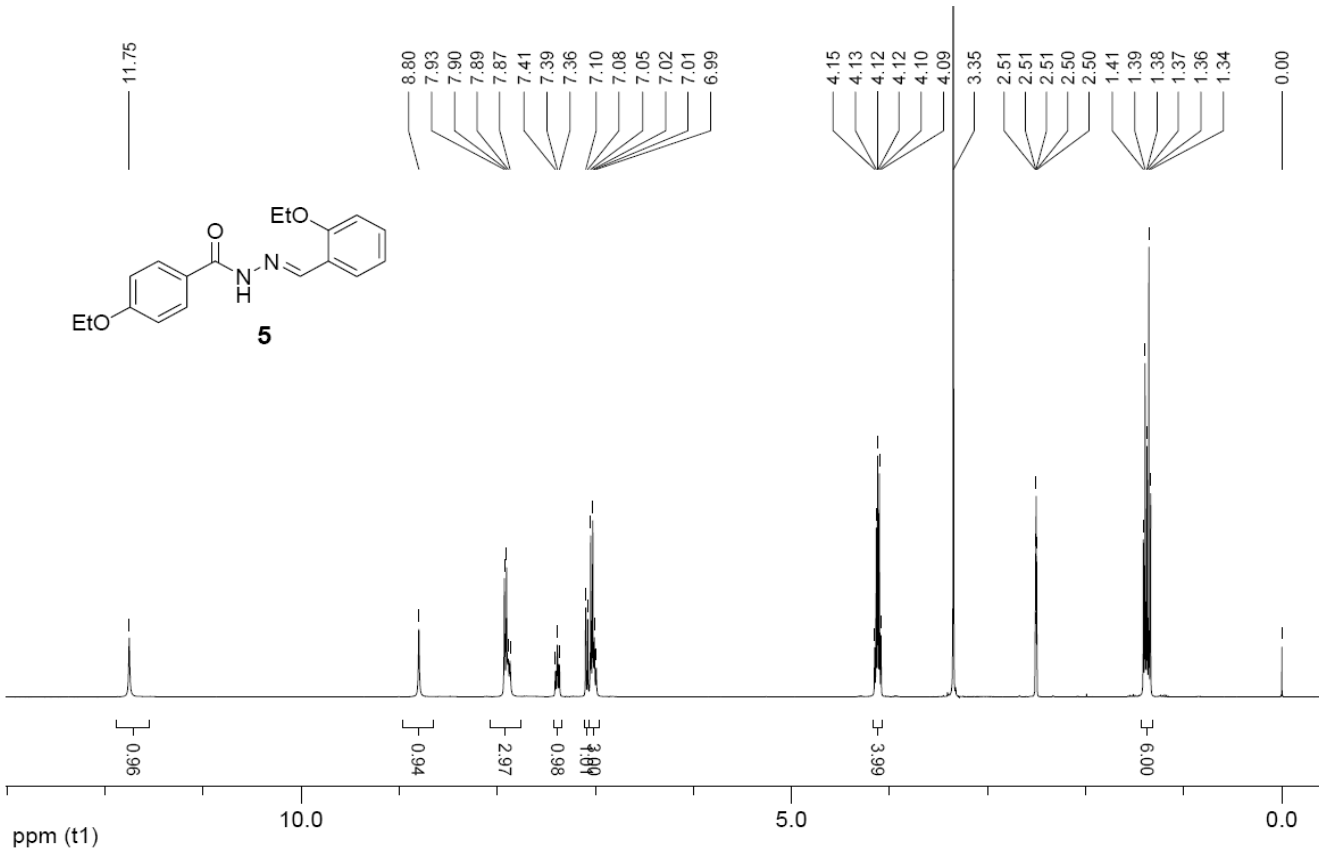


^{13}C NMR (100MHz, DMSO-d_6)

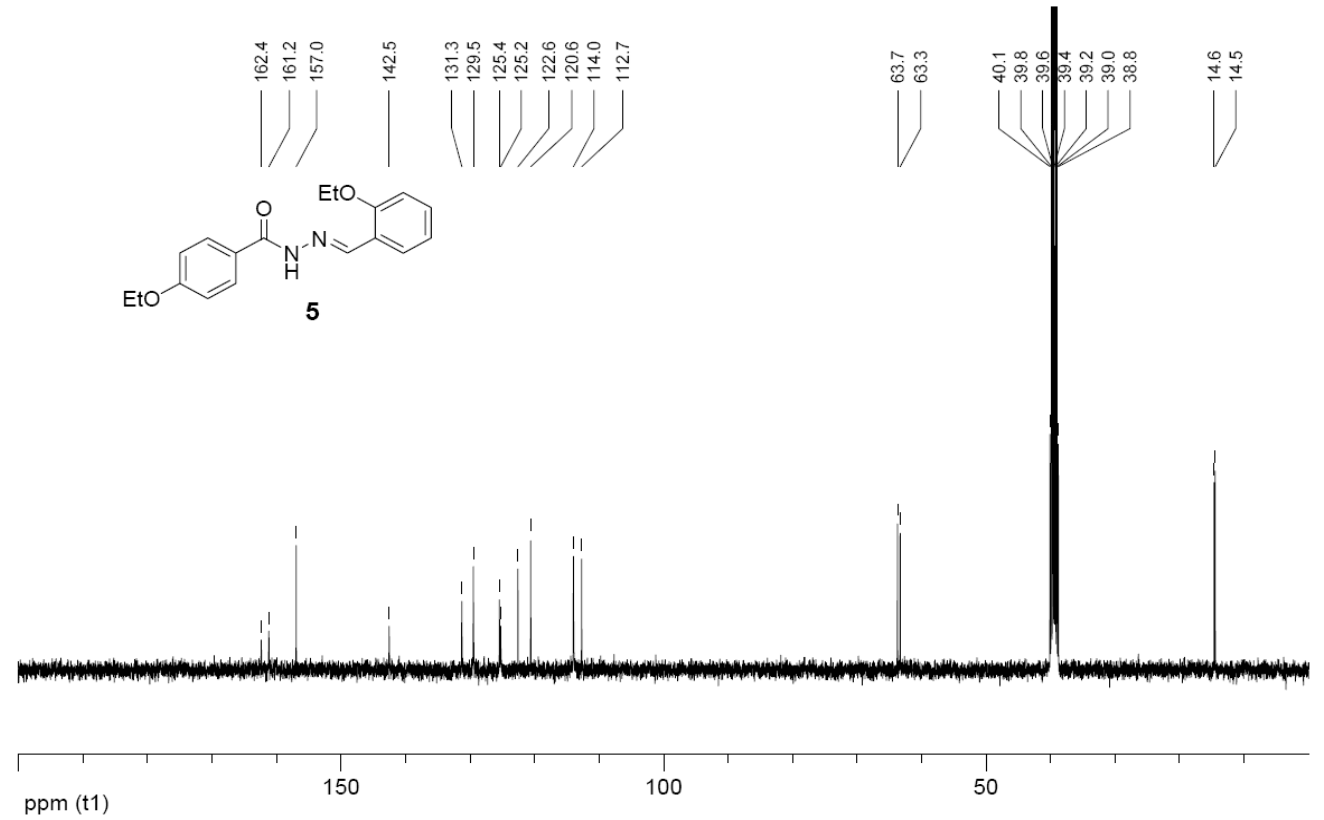


***N'*-(2-Ethoxybenzylidene)-4-ethoxybenzohydrazide (5)**:

^{1}H NMR (400MHz, DMSO-d_6)

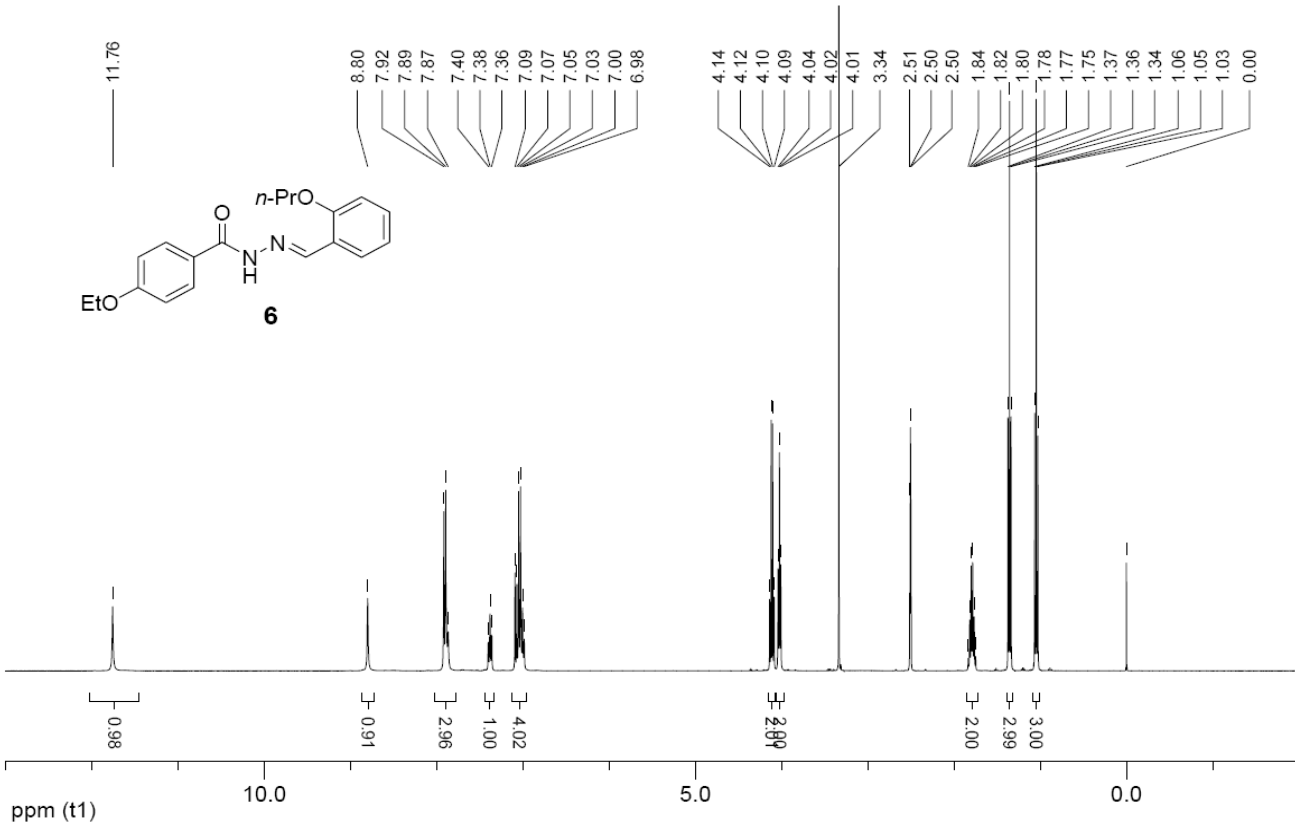


^{13}C NMR (100MHz, DMSO-d_6)

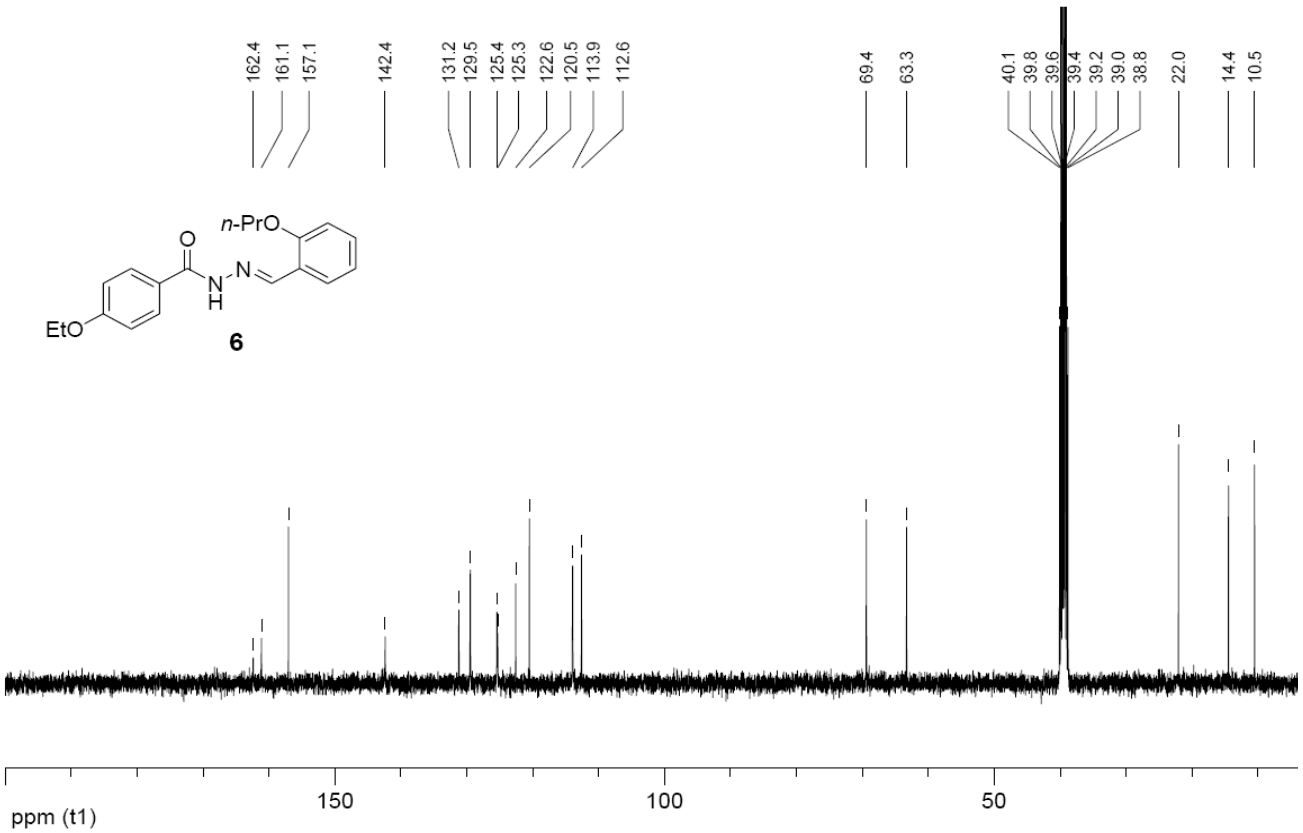


***N'*-(2-Propoxybenzylidene)-4-ethoxybenzohydrazide (6)**:

^{1}H NMR (400MHz, DMSO-d_6)

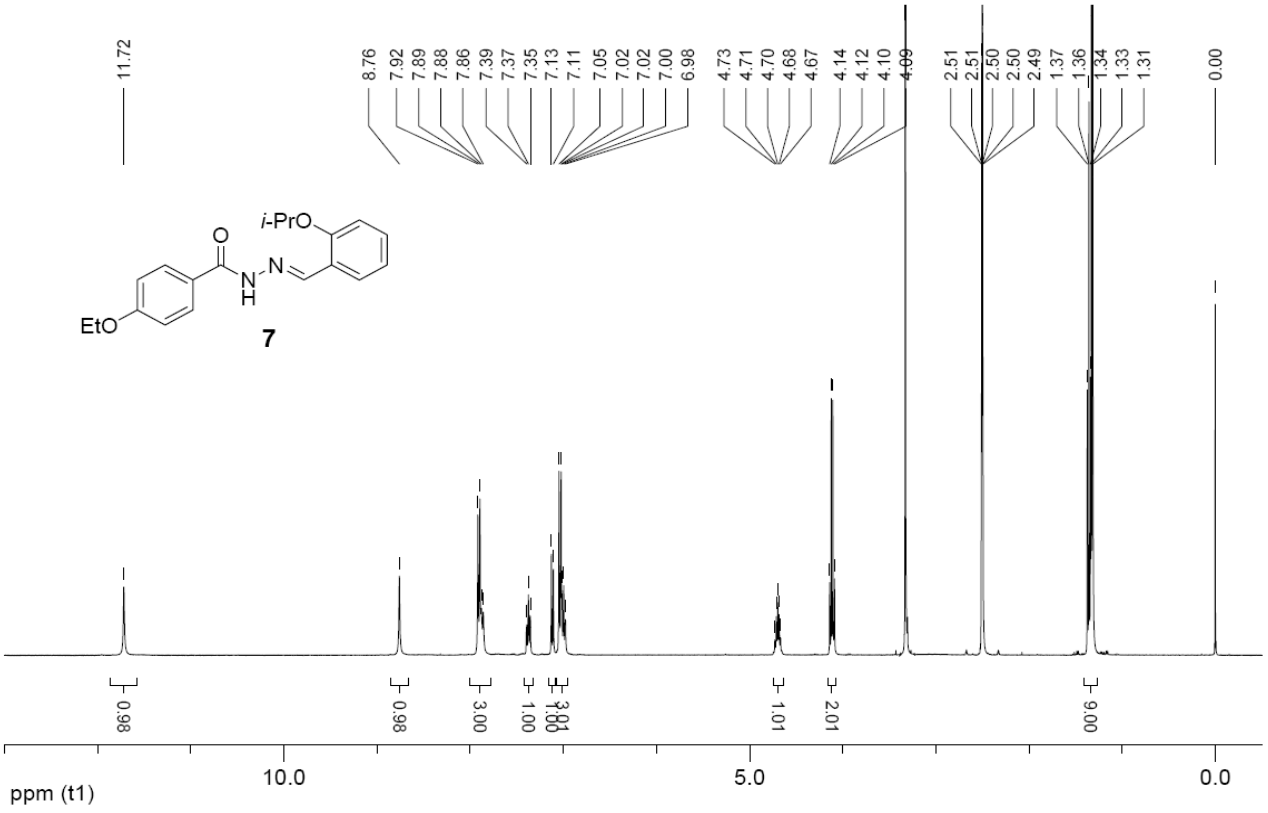


^{13}C NMR (100MHz, DMSO-d_6)

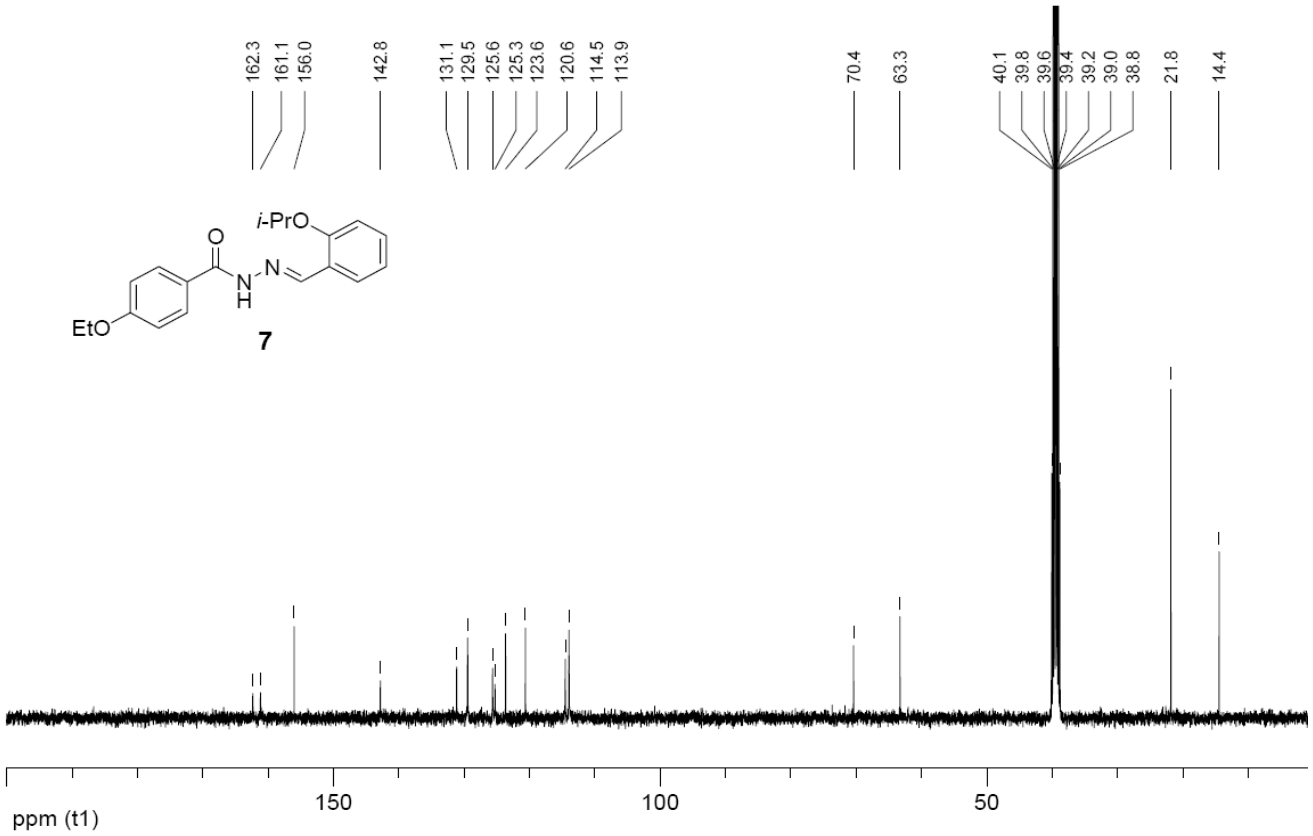


***N'*-(2-Isopropoxybenzylidene)-4-ethoxybenzohydrazide (7)**:

^{1}H NMR (400MHz, DMSO-d_6)

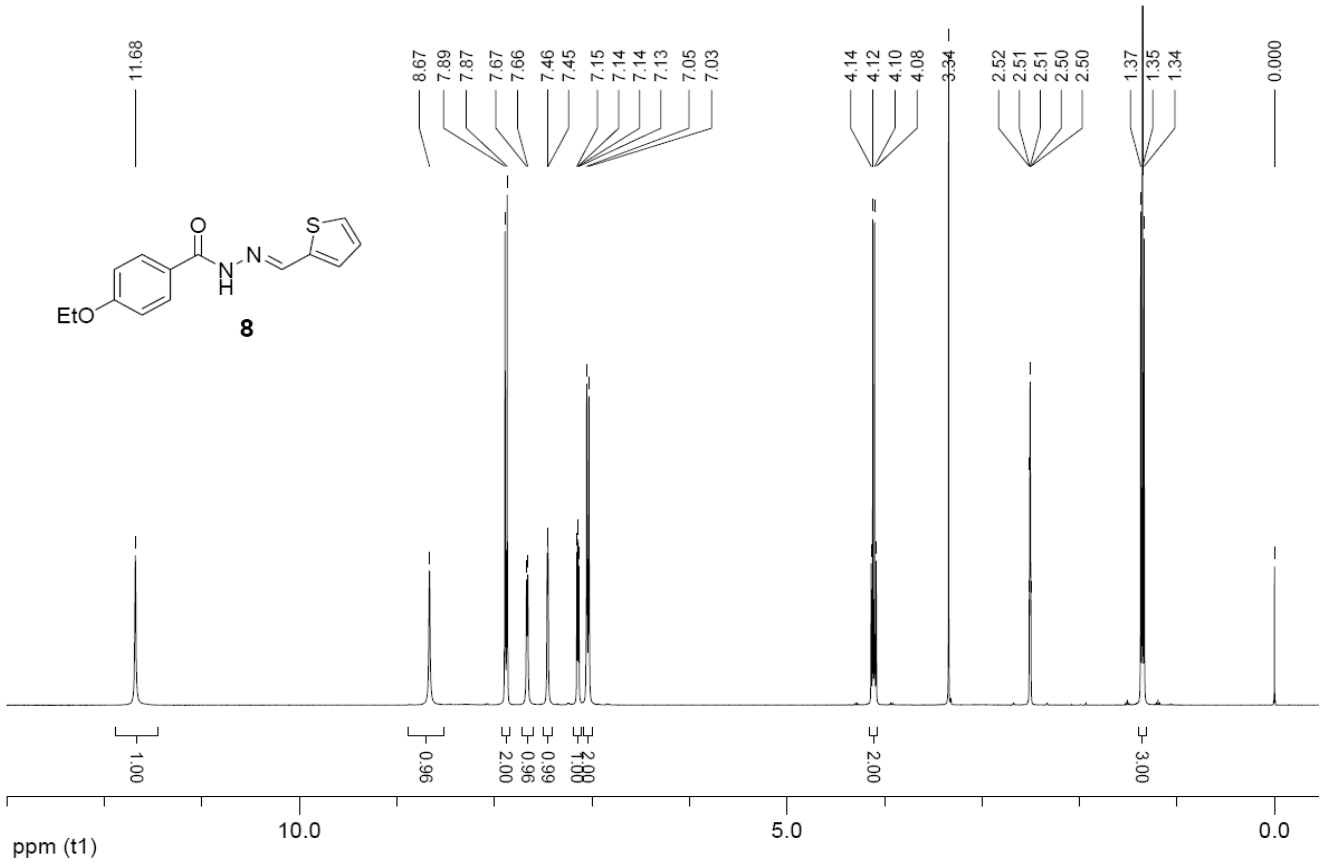


^{13}C NMR (100MHz, DMSO-d_6)

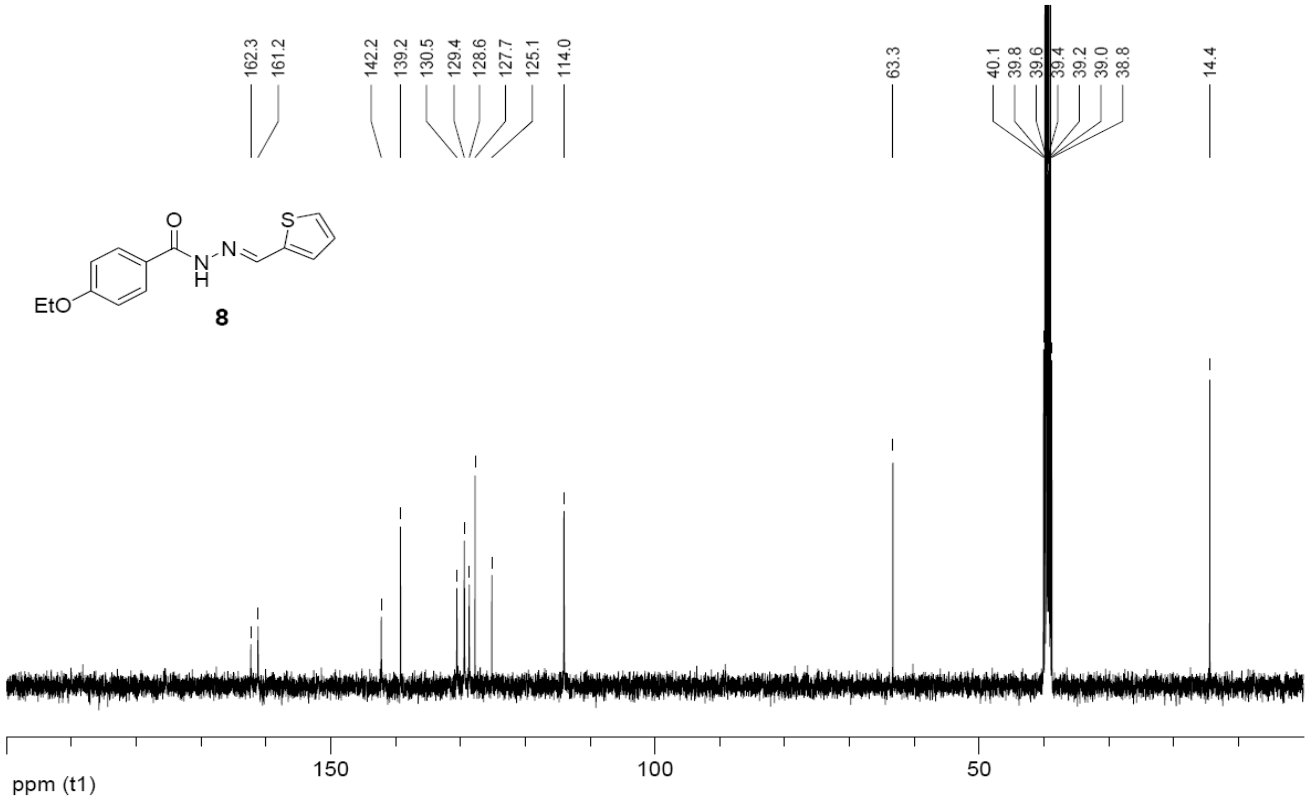


4-Ethoxy-*N'*-(thiophen-2-ylmethylene)benzohydrazide (8) :

^{1}H NMR (400MHz, DMSO-d_6)



^{13}C NMR (100MHz, DMSO-d_6)



***N'*-Benzylidene-4-ethoxybenzohydrazide (9)**:

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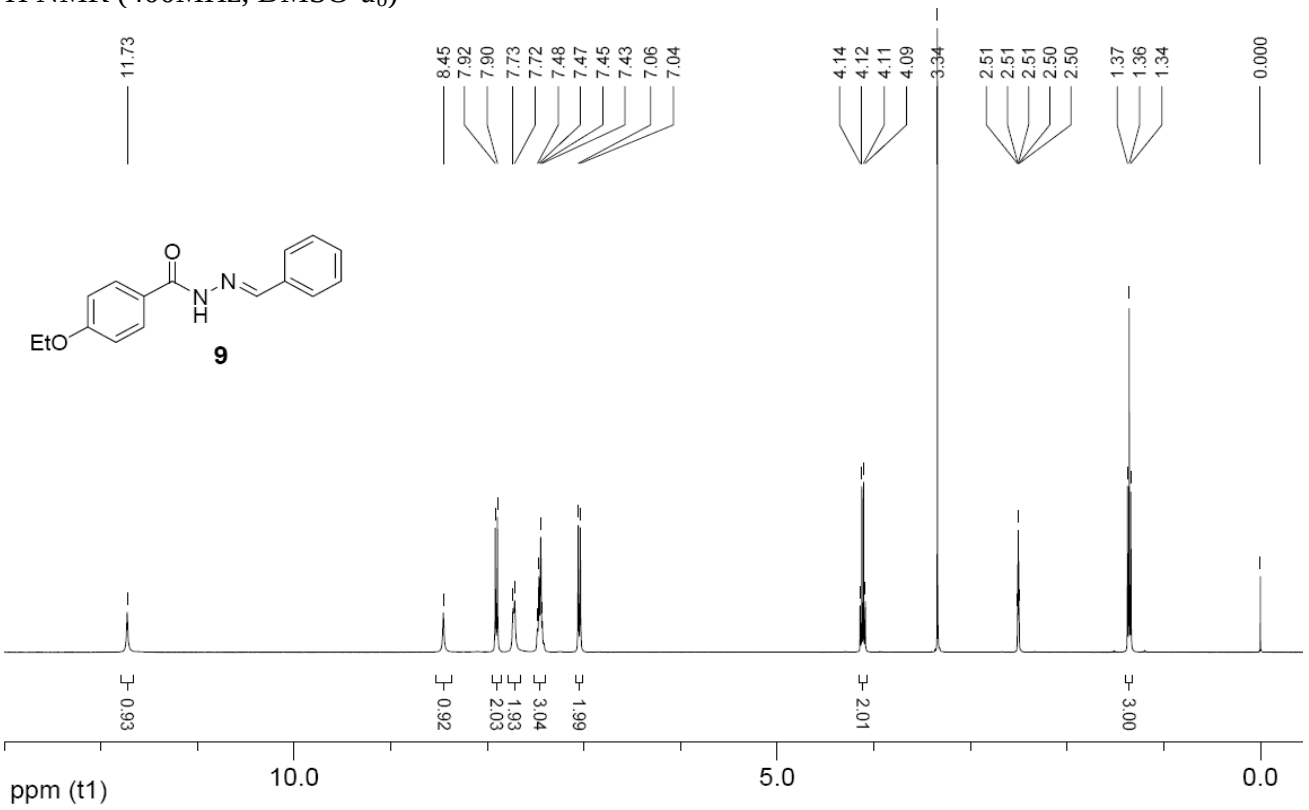
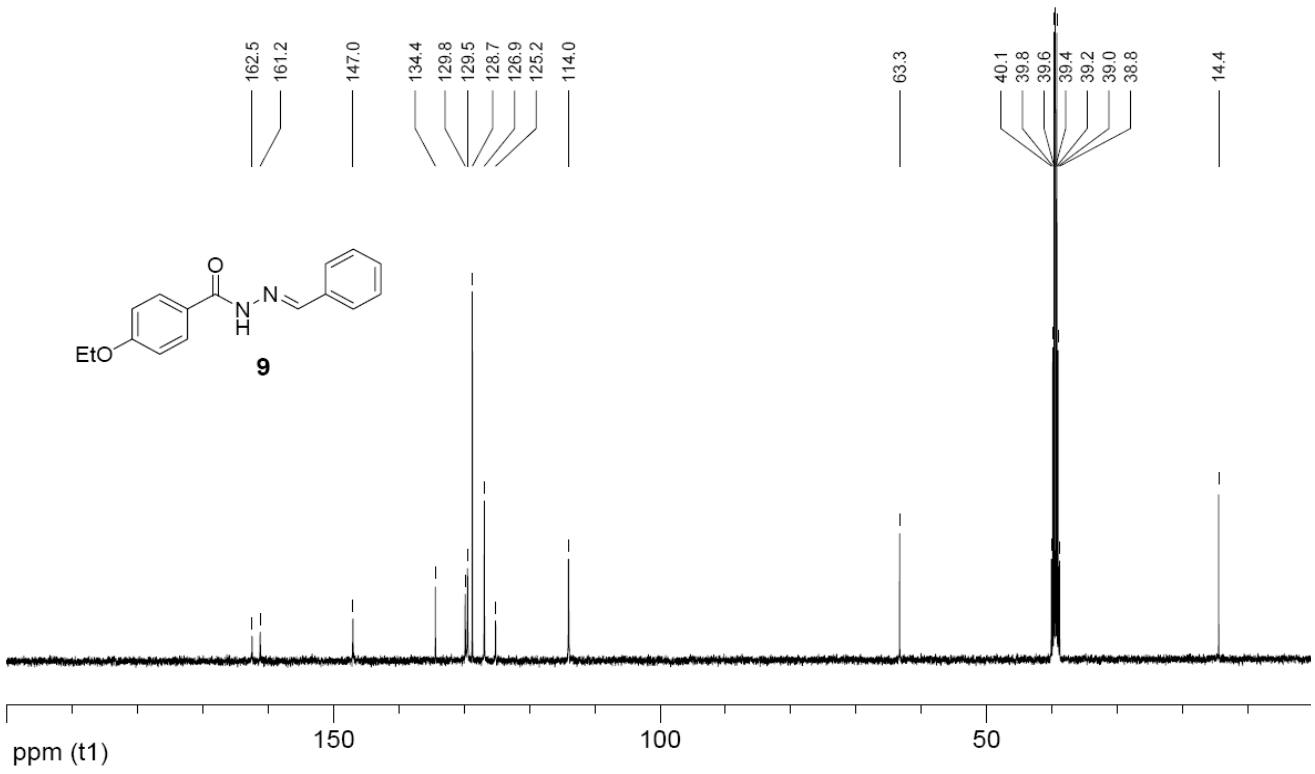
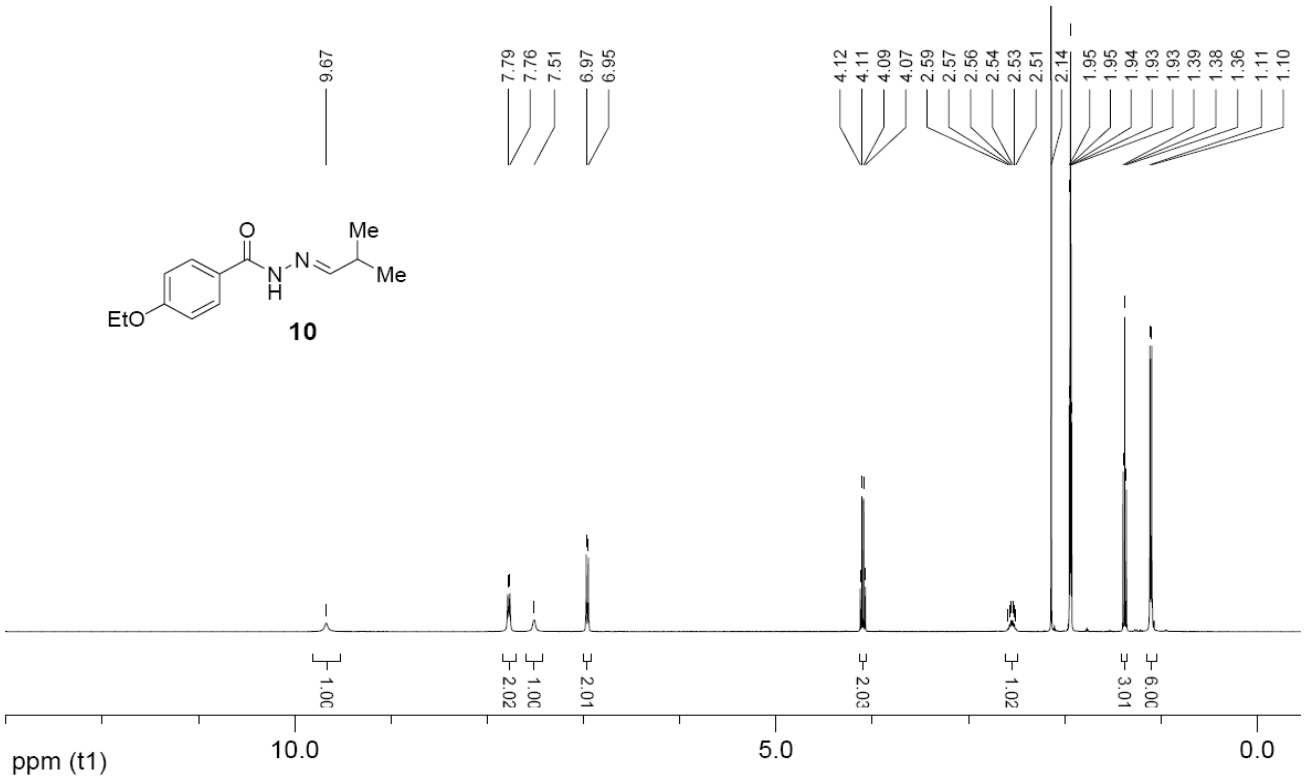


^{13}C NMR (100MHz, DMSO-d_6)

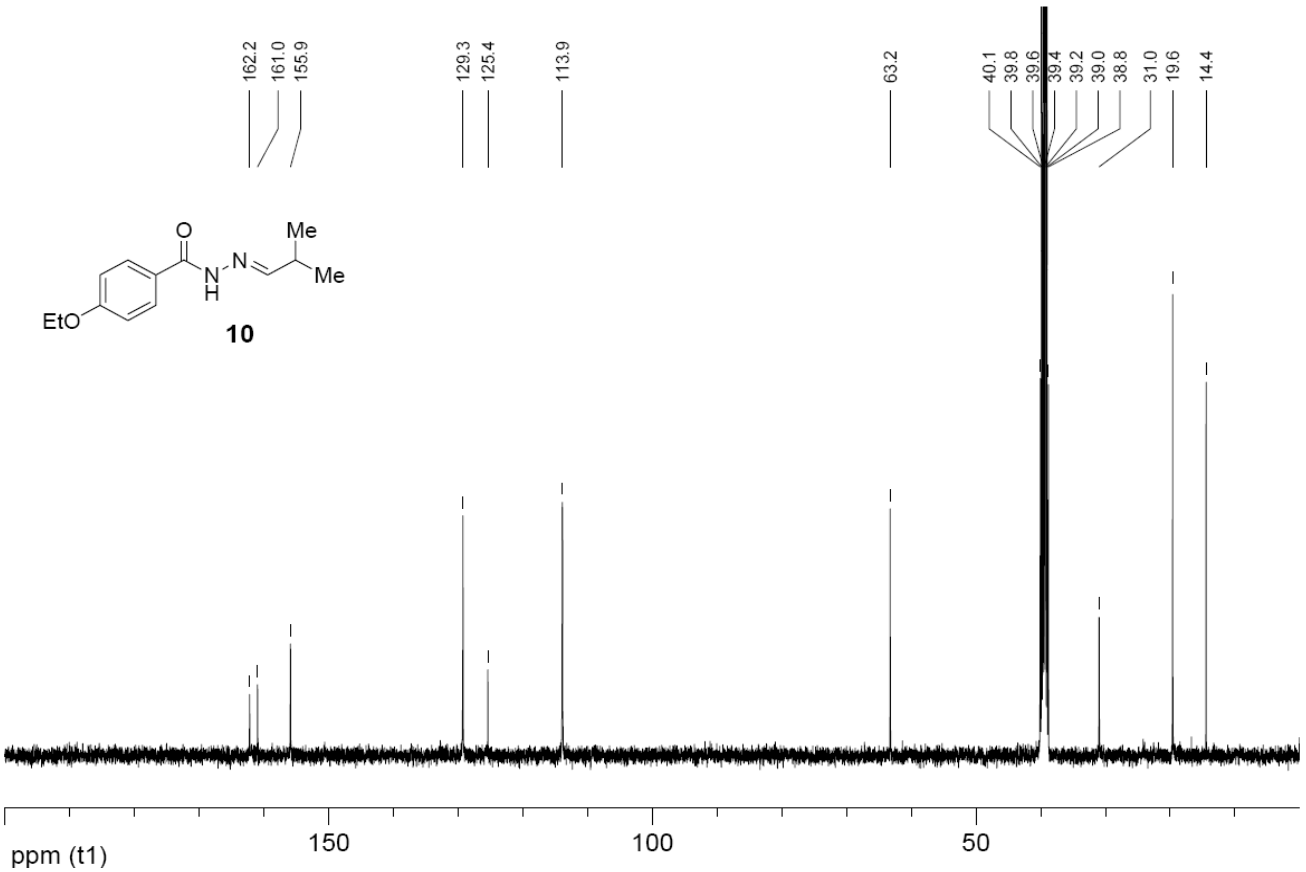


4-Ethoxy-*N'*-(2-methylpropylidene)benzohydrazide(10):

^{1}H NMR (400MHz, CD_3CN)

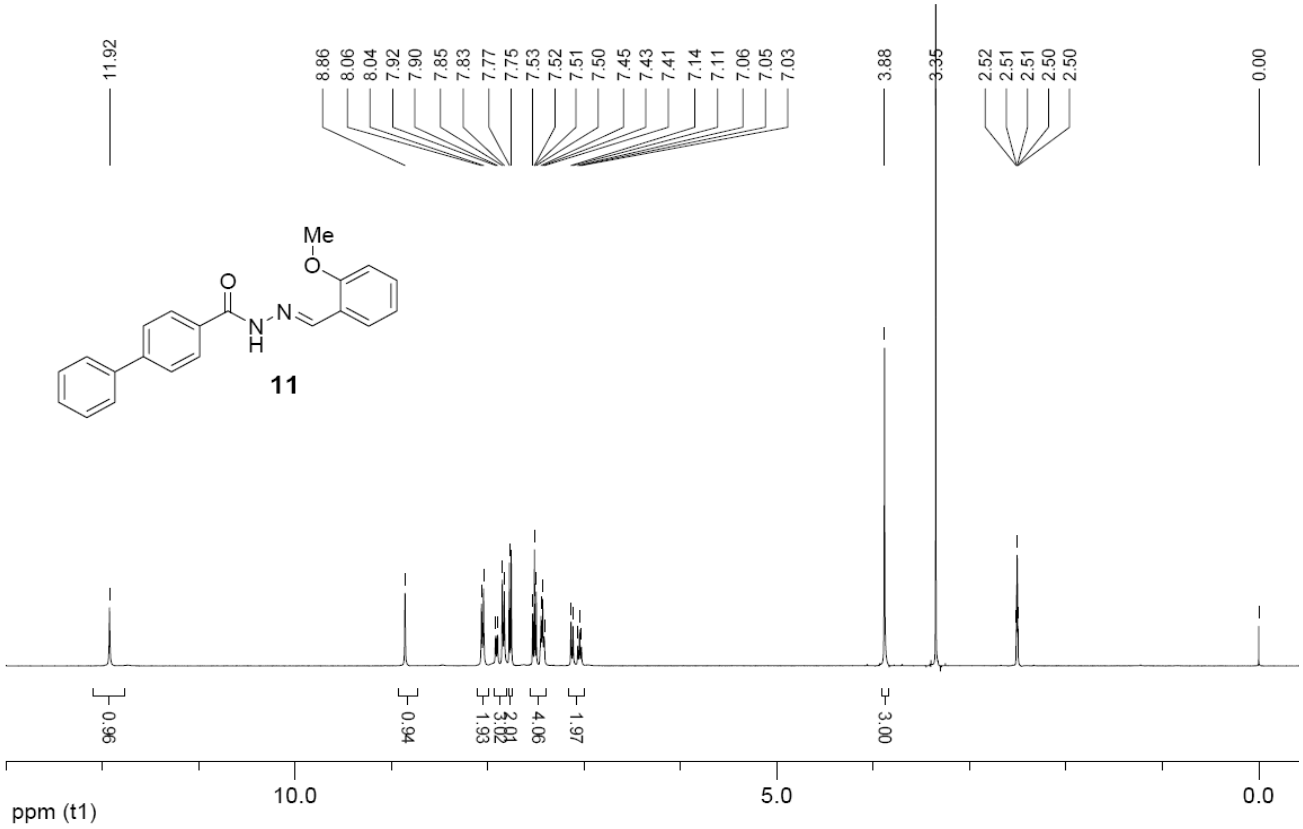


^{13}C NMR (400MHz, DMSO-d_6)

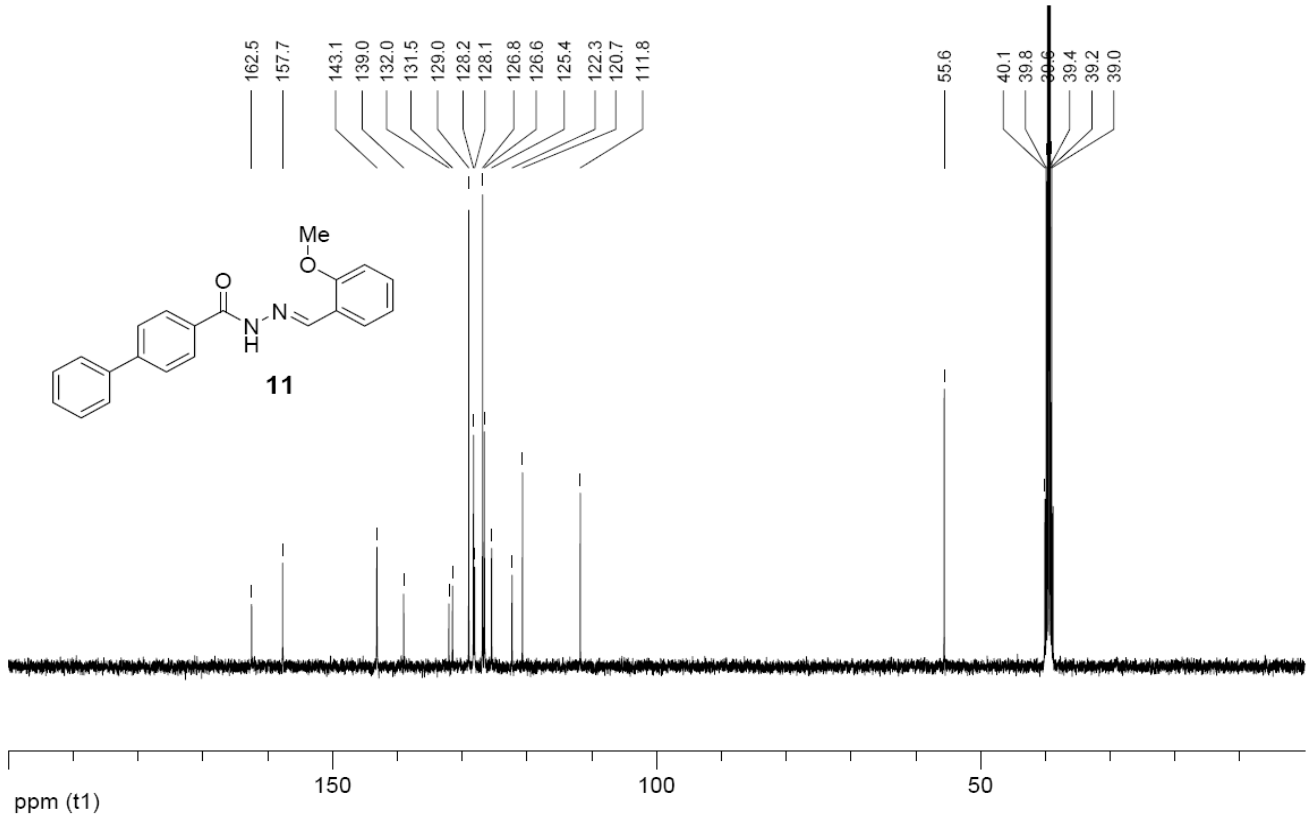


4-Penyl-*N'*-(2-methoxybenzylidene)benzohydrazide (11):

^{1}H NMR (400MHz, DMSO-d_6)

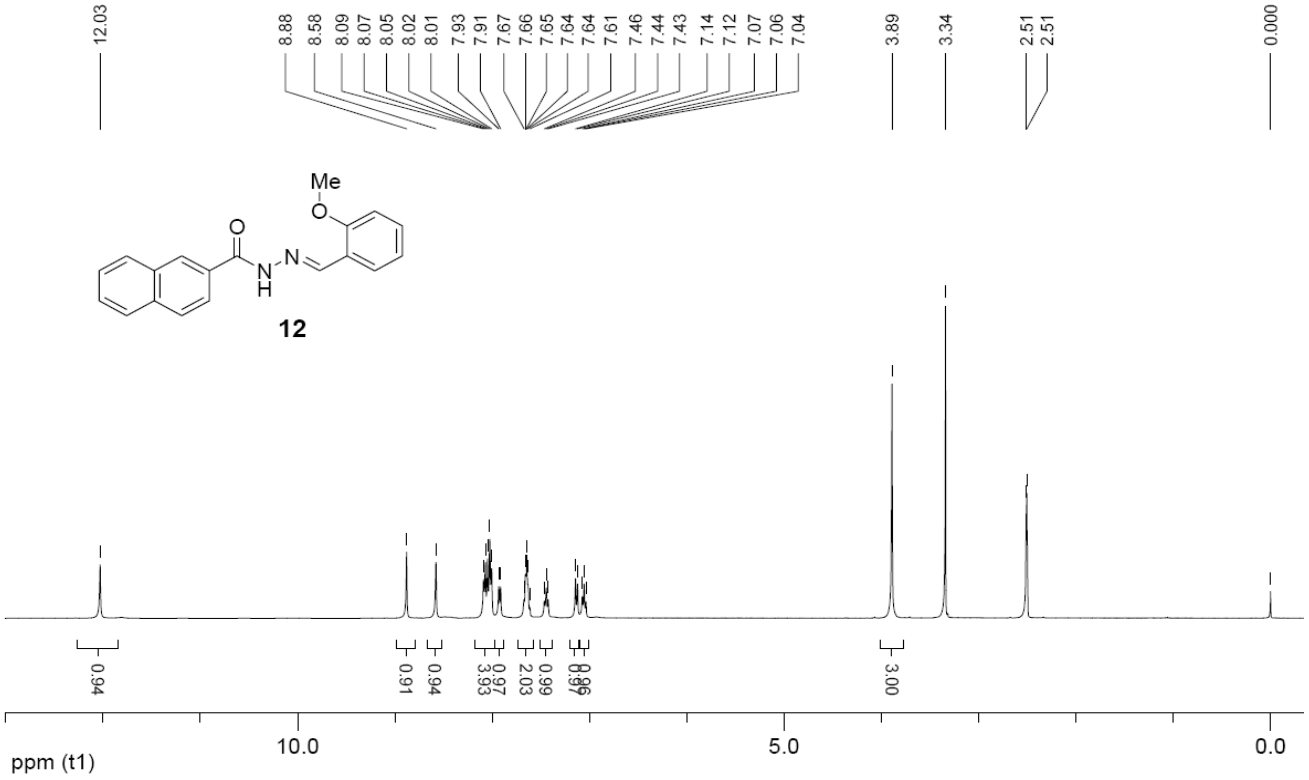


^{13}C NMR (100MHz, DMSO-d_6)

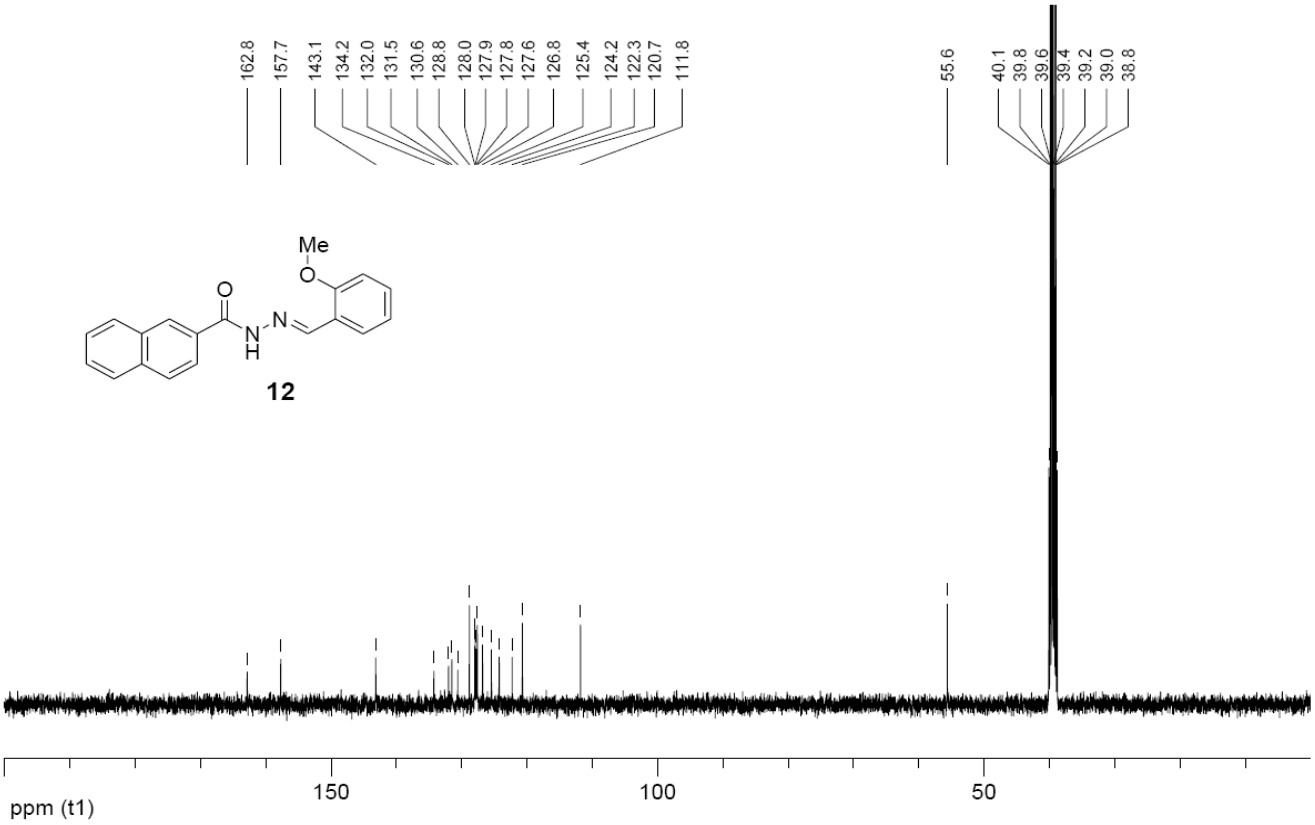


***N'*-(2-Methoxybenzylidene)-2-naphthohydrazide (12)**:

^{1}H NMR (400MHz, DMSO-d_6)

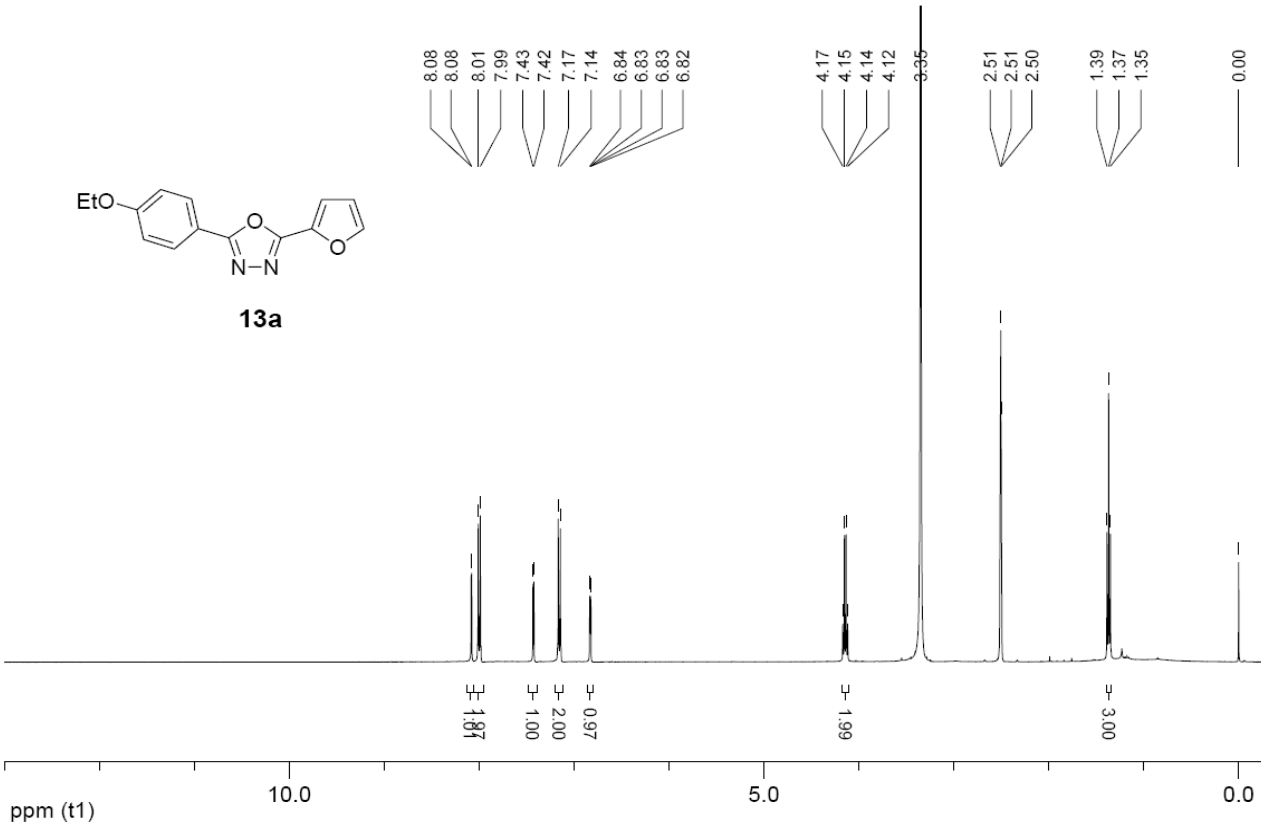


^{13}C NMR (100MHz, DMSO-d_6)

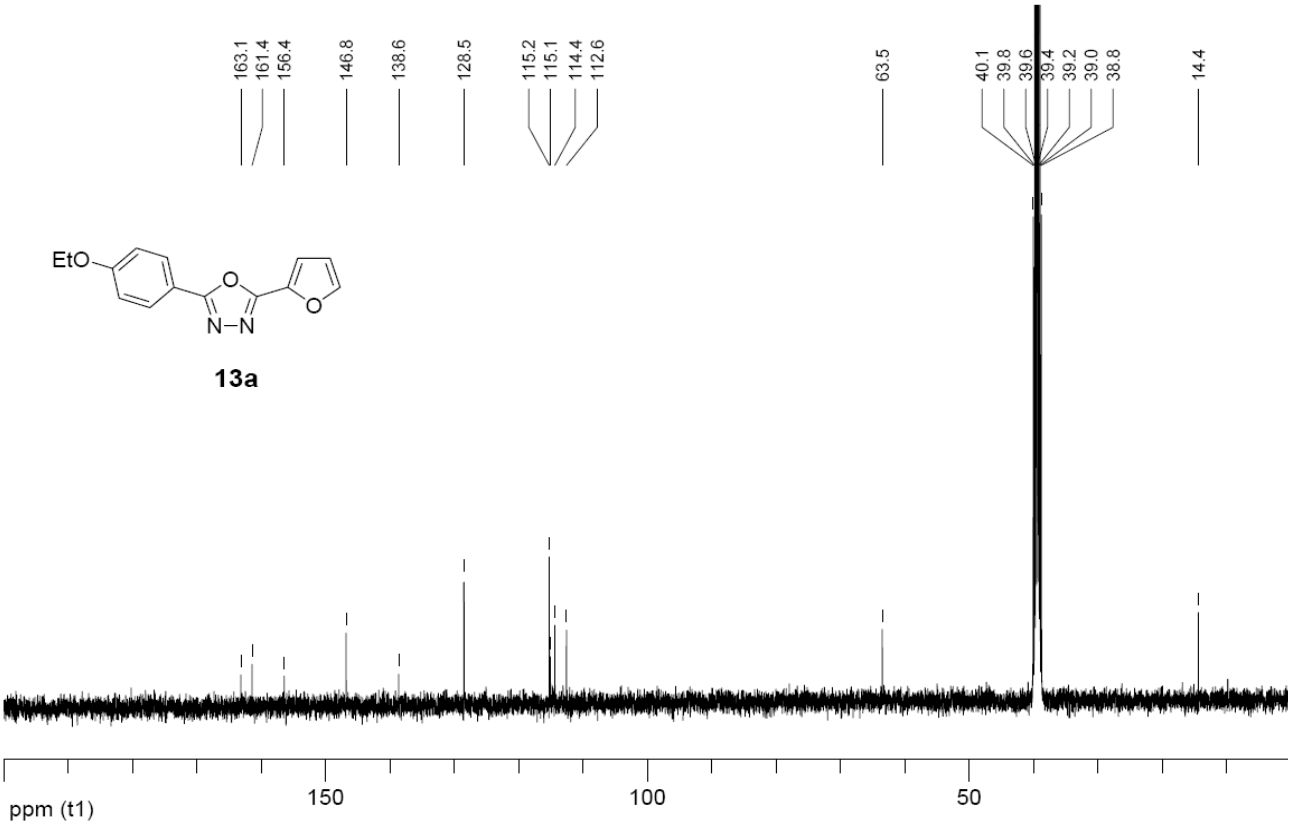


2-(4-Ethoxyphenyl)-5-furan-2-yl-1,3,4-oxadiazole (13a):

^{1}H NMR (400MHz, DMSO-d_6)

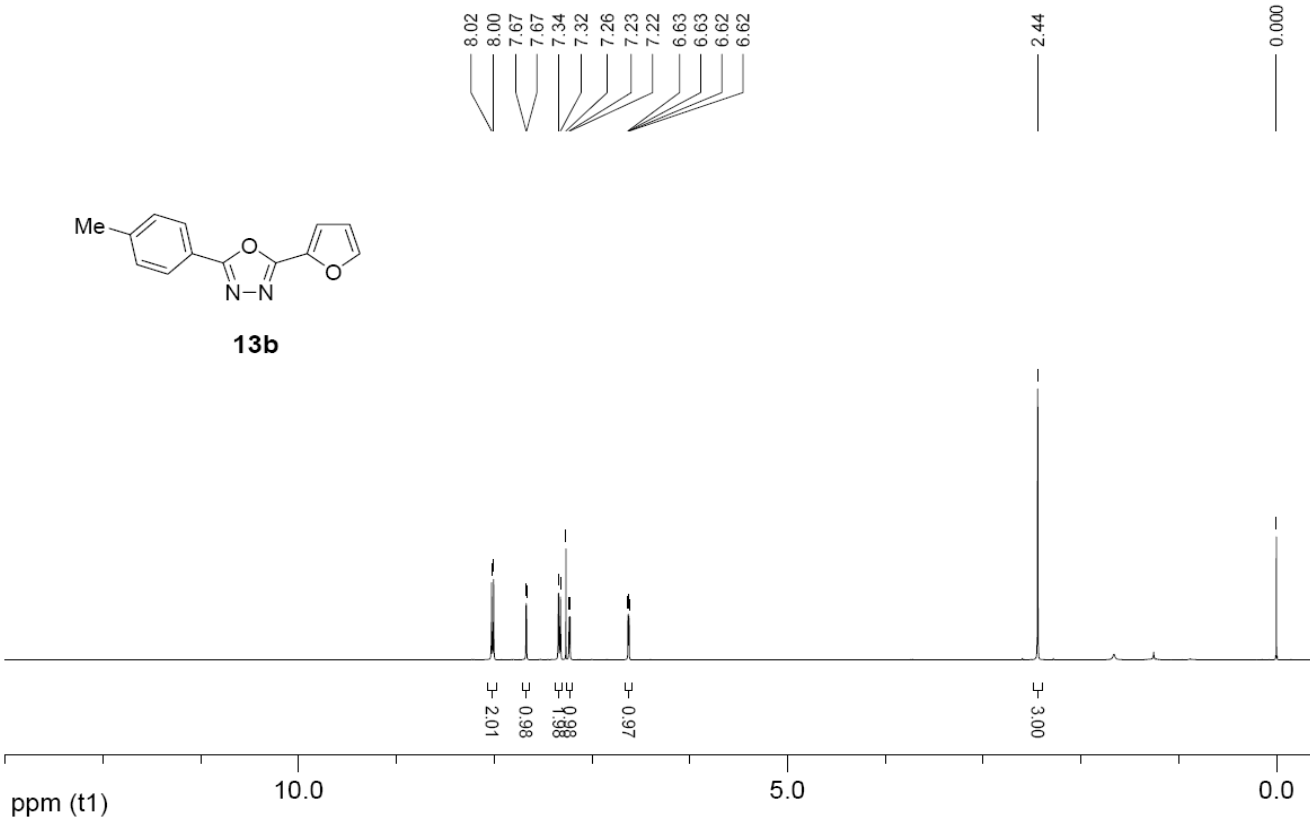


^{13}C NMR (100MHz, DMSO-d_6)

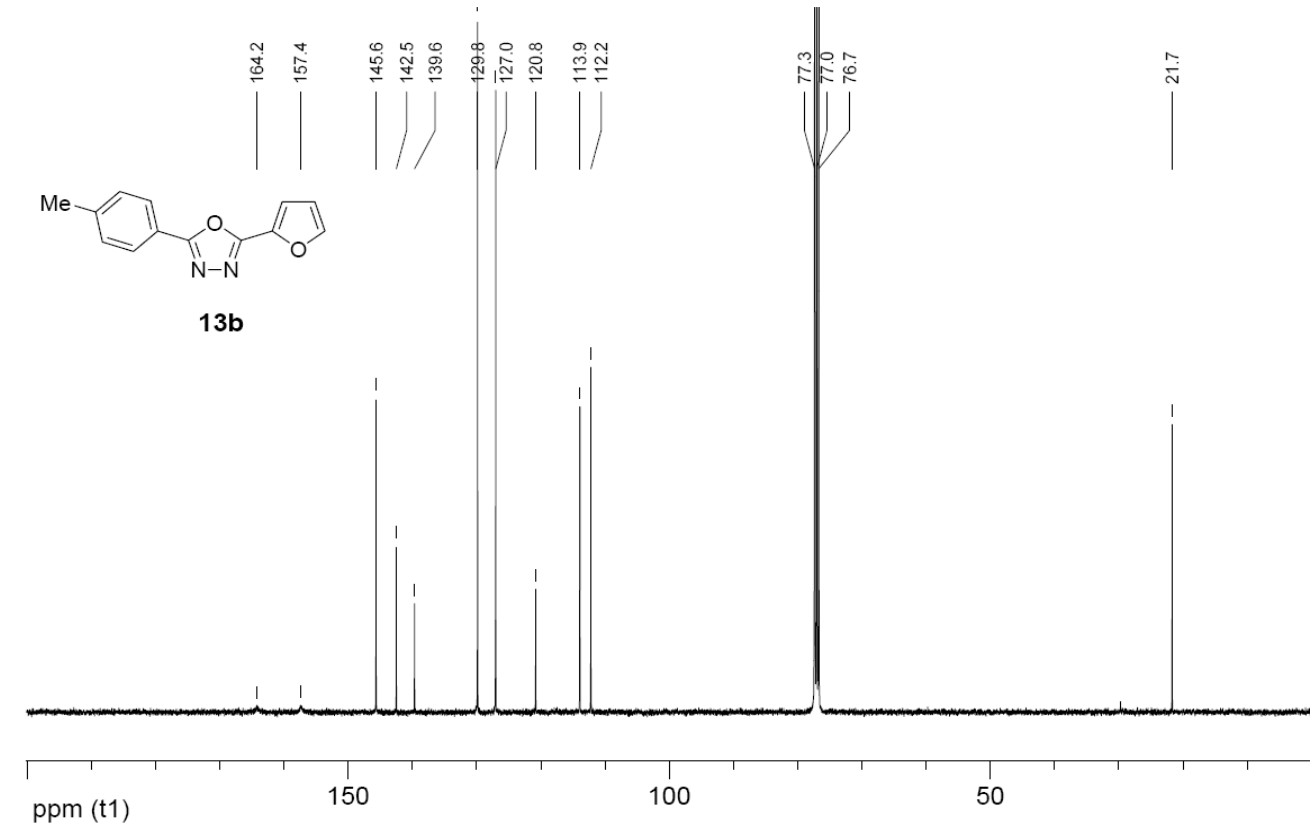


2-Furan-2-yl-5-*p*-tolyl-1,3,4-oxadiazole (13b):

^{1}H NMR (400MHz, $CDCl_3$)

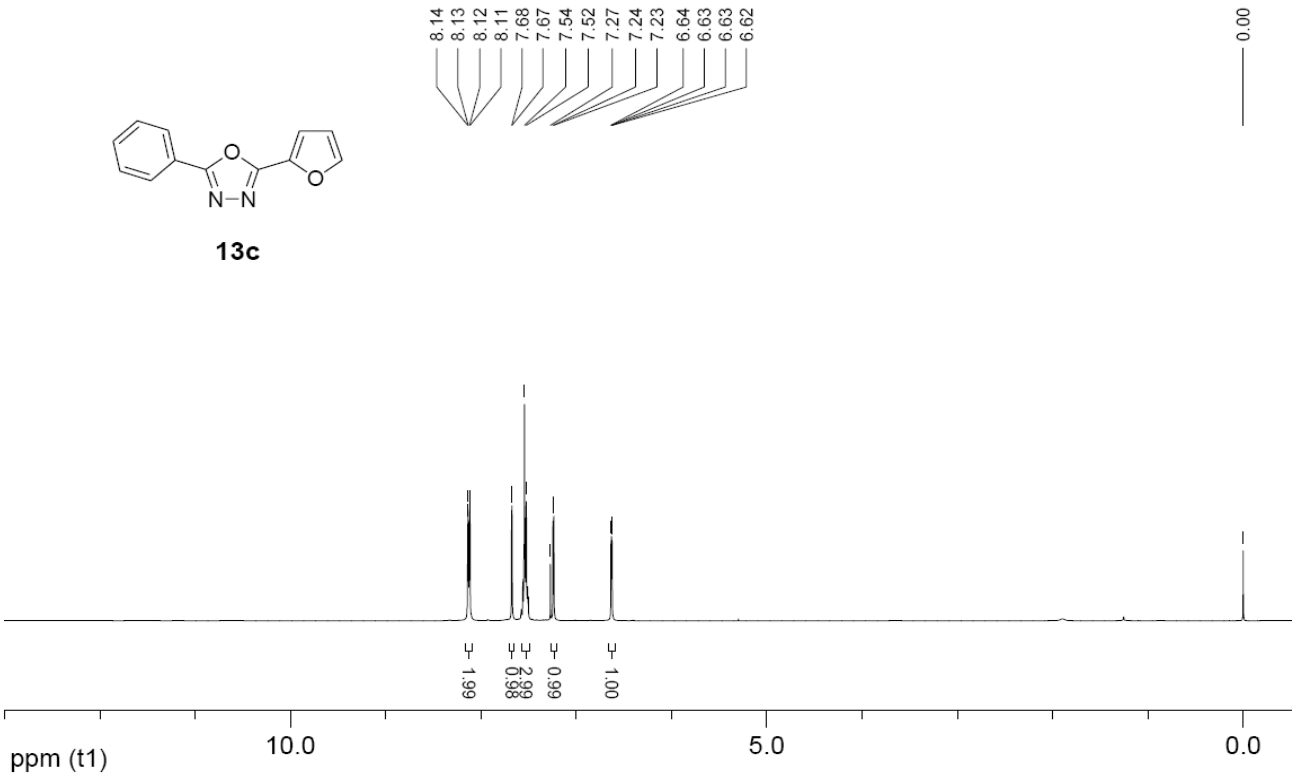


^{13}C NMR (100MHz, $CDCl_3$)

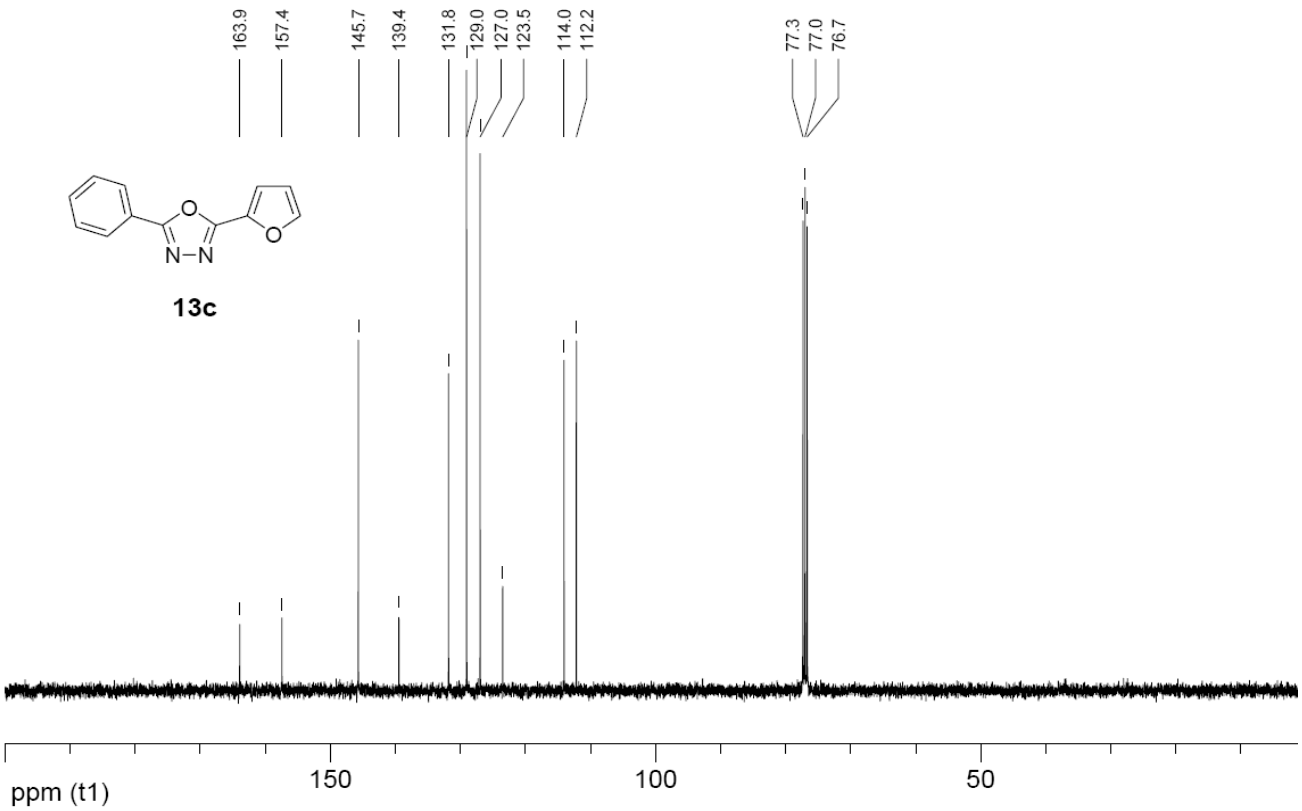


2-Furan-2-yl-5-phenyl-1,3,4-oxadiazole (13c):

^{1}H NMR (400MHz, $CDCl_3$)

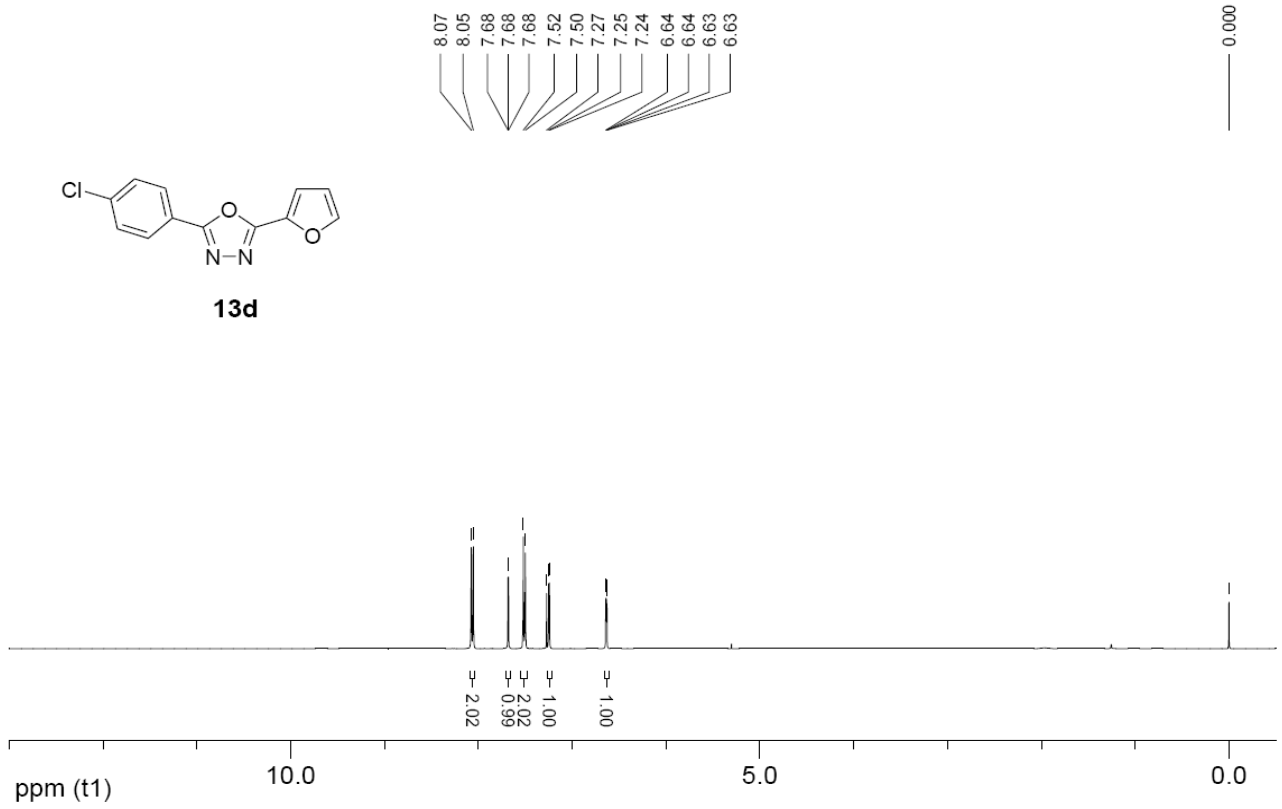


^{13}C NMR (100MHz, $CDCl_3$)



2-(4-Chlorophenyl)-5-furan-2-yl-1,3,4-oxadiazole (13d):

^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (100MHz, $CDCl_3$)