Supporting Information

Synthesis and Structure of Binuclear Arene Ru(II) N^O Chelating Complexes: Synthesis of Pyrimidinones via Acceptorless Dehydrogenative Annulation Using alcohols

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1. Experimental Materials and Methods

Commercially available $RuCl_3.3H_2O$ was used as supplied from Loba Chemie Pvt. Ltd. The solvents were freshly distilled before use following the standard procedures.[1] The Ru(II) precursor $[(\eta^6\text{-cymene})_2RuCl_2]_2$ was prepared by reported literature method.[2] The microanalysis of carbon, hydrogen and nitrogen were recorded by an analytical function testing Vario EL III CHNS elemental analyzer at the Sophisticated Test and Instrumentation Centre (STIC), Cochin University, Cochin. The Fourier Transform infrared spectra of complexes were recorded in KBr pellets with a Perkin-Elmer 597 spectrophotometers in the range 4000–400 cm^{-1}. The NMR spectra were recorded in $CDCl_3$ with a Bruker 400 MHz instrument using TMS as the internal reference. Chemical shifts are given in ppm referenced to solvents. A Micro mass thermo-scientific LTQ XL mass spectrometer was used for High-Resolution Mass Spectrometry of the complexes. The electronic spectra of the complexes in acetonitrile solution were recorded with a Jasco V-730 UV-Vis Varian spectrophotometer in the range 800-200 nm.

X-ray crystallographic data collection

Single crystals of complex **3** was grown by slow evaporation of a dichloromethane in methanol solution at room temperature. A single crystal of suitable size was covered with Paratone oil, mounted on the top of a glass fiber, and transferred to a Bruker AXS Kappa APEX II single crystal X-ray diffractometer using monochromated MoKα radiation (λ = 0.71073). Data were collected at 293 K. The structure was solved by direct methods using SIR-97 and was refined by the full matrix least-squares method on F 2 with SHELXL-97.[3] Non-hydrogen atoms were refined with anisotropy thermal parameters. All hydrogen atoms were geometrically fixed and collected to refine using a riding model. Frame integration and data reduction were performed using the Bruker SAINT Plus (Version 7.06a) software.[4] The multiscan absorption corrections were applied to the data using SADABS software. In addition, the solvent masking procedure was used to determine the structure of the RpCl compound (**BC3**). The obtained data did not allow for the unambiguous determination of the solvent

molecules in the complex structure. Figure 3 was drawn with ORTEP and the structural data have been deposited at the Cambridge Crystallographic Data Centre: CCDC 2248640.

2. Table S1. Crystal data and structure refinement for the complex 3

Crystal data	Complex 3
Empirical formula	$C_{40}H_{41}Cl_3N_2O_2Ru_2$
Formula weight	920.34
Colour	red
CCDC number	2248640
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	'P -1'
a (Å)	9.2909(3)
b (Å)	9.9699(4)
c (Å)	21.8283(9)
α (°)	97.571(3)
β (°)	97.284(3)
γ (°)	92.445(3)
Volume (Å^3)	1984.51(13)
Z	2
Crystal_density $\rho_{calcd.}$ (Mg m^{-3})	1.490
Absorption coefficient(μ) (mm-1)	0.998
F(000)	900
Crystal size (mm)	0.28 x 0.09 x 0.06
Theta range (°)	6.982 to 59.078
Limiting indices	-12 ≤ h ≤ 9 -12 ≤ k ≤ 11 -24 ≤ l ≤ 29
Reflections collected/unique	18069

Data/restraints/parameters Goodness-of – fit on F2	9316/0/459 1.131
Final R indices [I>2σ(I)] R indices (all data) Largest diff. Peak and hole(e oA -3)	0.0639, 0.1249 0.0991, 0.1414 1.33/-1.33

Table S2. Selected bond lengths (Å) and bond angles (°) for the complex 3.

Bond lengths (Å)	
Ru(1) N(1)	2.096(4)
Ru(1) O(1)	2.060(4)
Ru(1) Cl(4)	2.4060(17)
Ru(2) N(2)	2.089(4)
Ru(2) O(2)	2.062 (4)
Ru(2) Cl(3)	2.4033(15)
N(1) N(2)	1.430(5)
N(1) C(8)	1.310 (6)
N(2) C(1)	1.309(6)
O(1) C(1)	1.283(6)
O(2) C(8)	1.287(6)
Bond angles (°)	
O(1) Ru(1) N(1)	76.48 (15)
O(1) Ru(1) Cl(4)	84.81 (13)
N(1) Ru(1) Cl(4)	84.13 (12)
O(2) Ru(2) N(2)	76.15 (15)
O(2) Ru(2) Cl(3)	85.66 (12)
N(1) N(2) Ru(1)	113.3(3)
N(1) N(2) Ru(2)	113.8 (3)
O(1) C(1) N(2)	123.9(5)
C(8) N(1) Ru(1)	134.6(4)
C(1) N(2) Ru(2)	134.2 (4)

3. FT-IR spectra of the complexes BC1-BC3

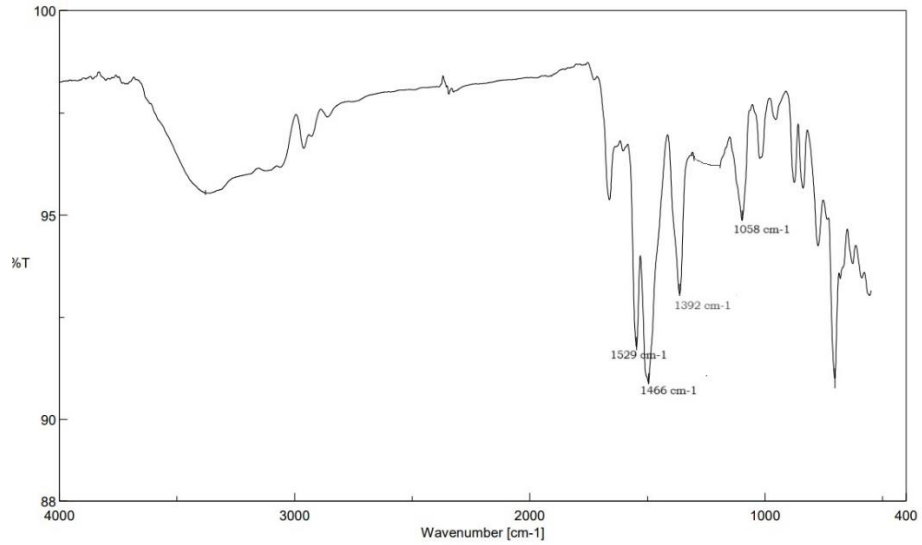

Figure S1. FT-IR spectrum of BC**1** in $CDCl_3$

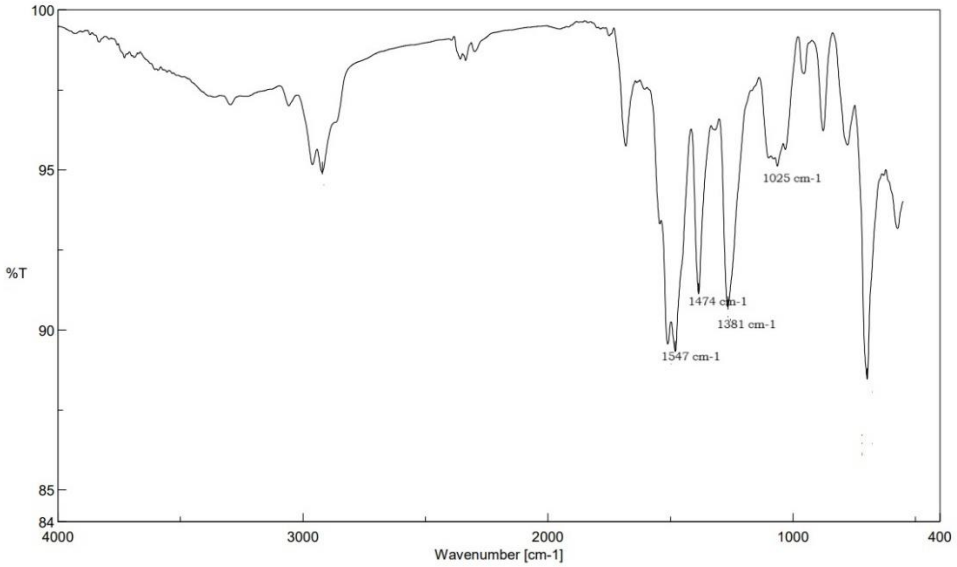

Figure S2. FT-IR spectrum of BC**2**

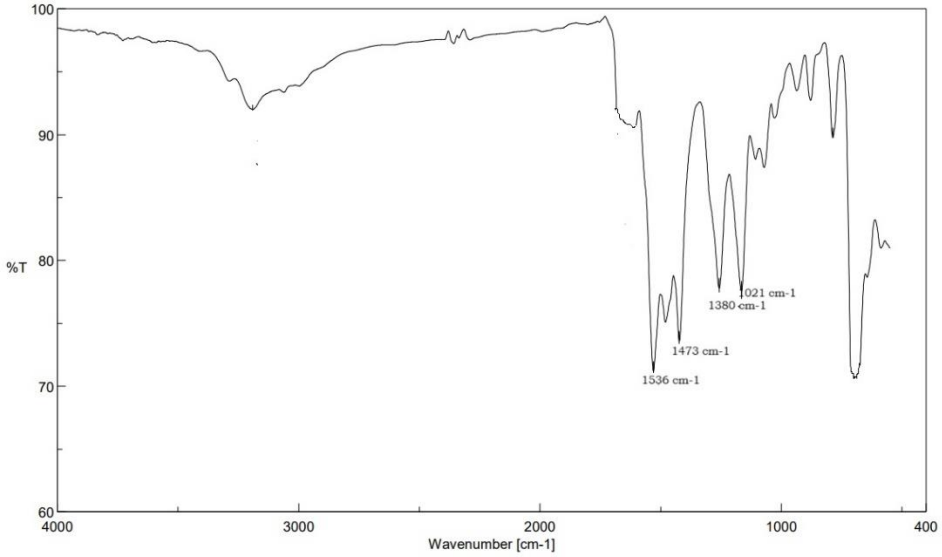

Figure S3. FT-IR spectrum of BC**3**

4. NMR spectra of the complexes BC1-BC3

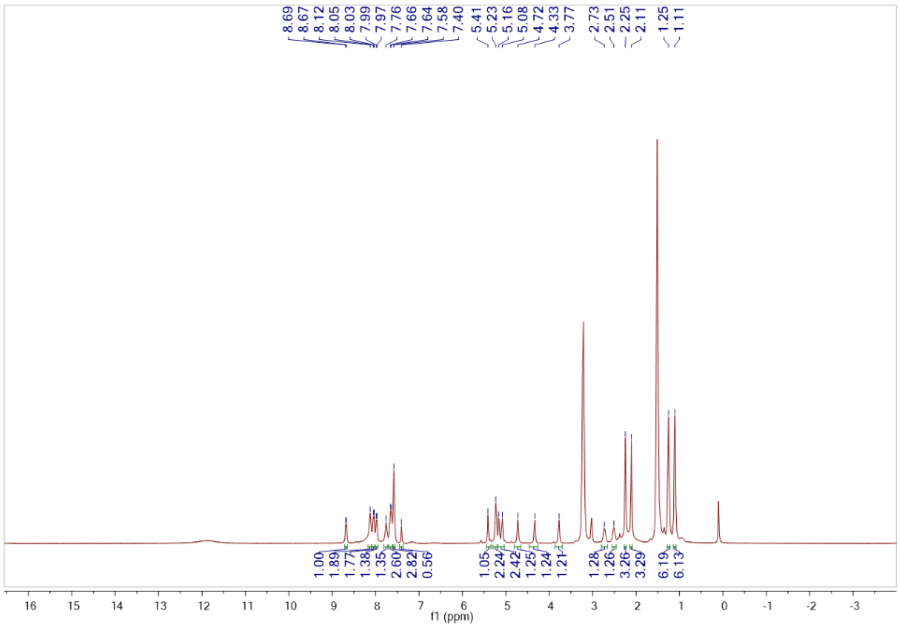

Figure S4. ^{1}H NMR spectrum of BC**1** in $CDCl_3$ (400 MHz, 293 K)

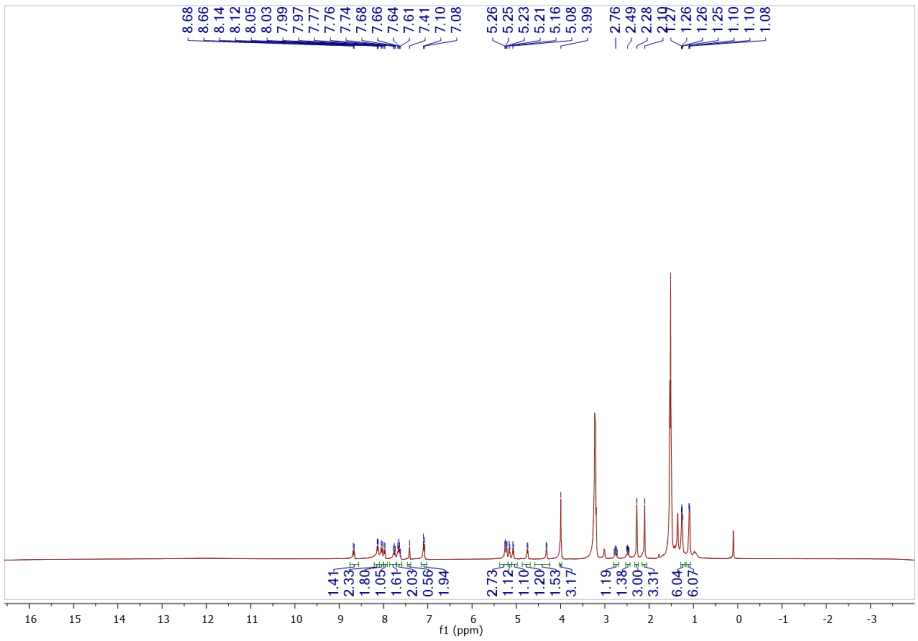

Figure S5. ^{1}H NMR spectrum of BC**2** in $CDCl_3$ (400 MHz, 293 K)

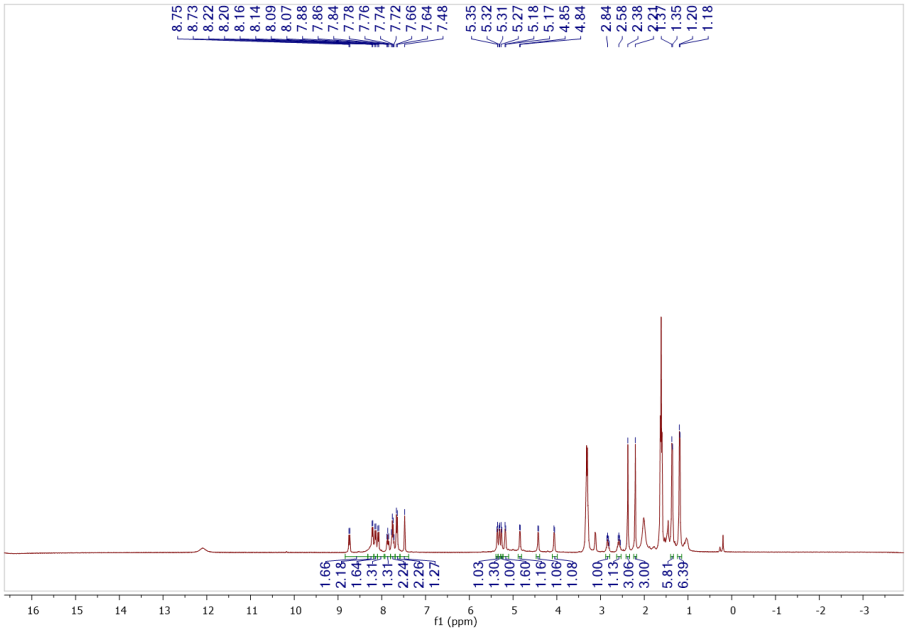

Figure S6. ^{1}H NMR spectrum of complex **3** in $CDCl_3$ (400 MHz, 293 K)

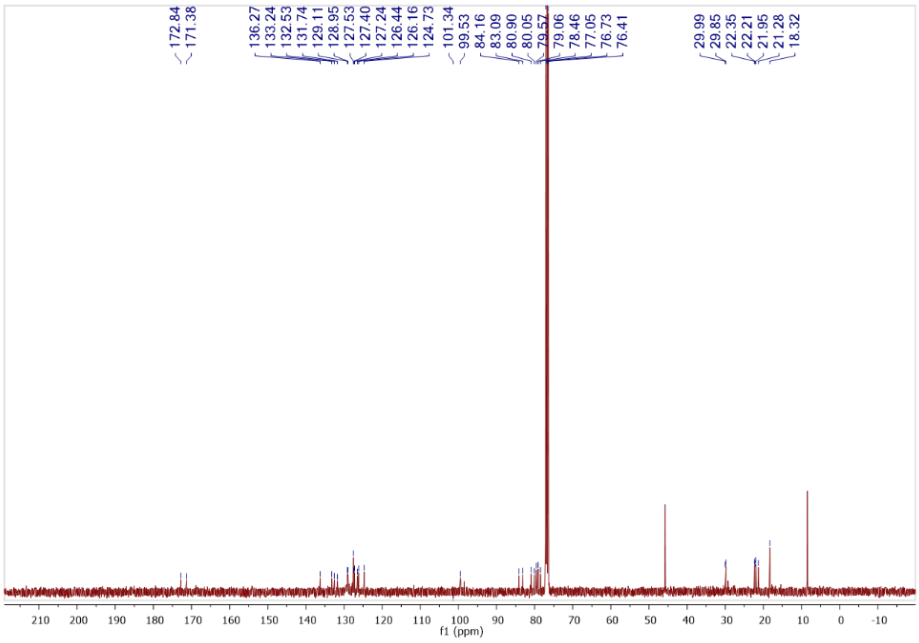

Figure S7. ^{13}C NMR spectrum of BC**1** in $CDCl_3$ (400 MHz, 293 K)

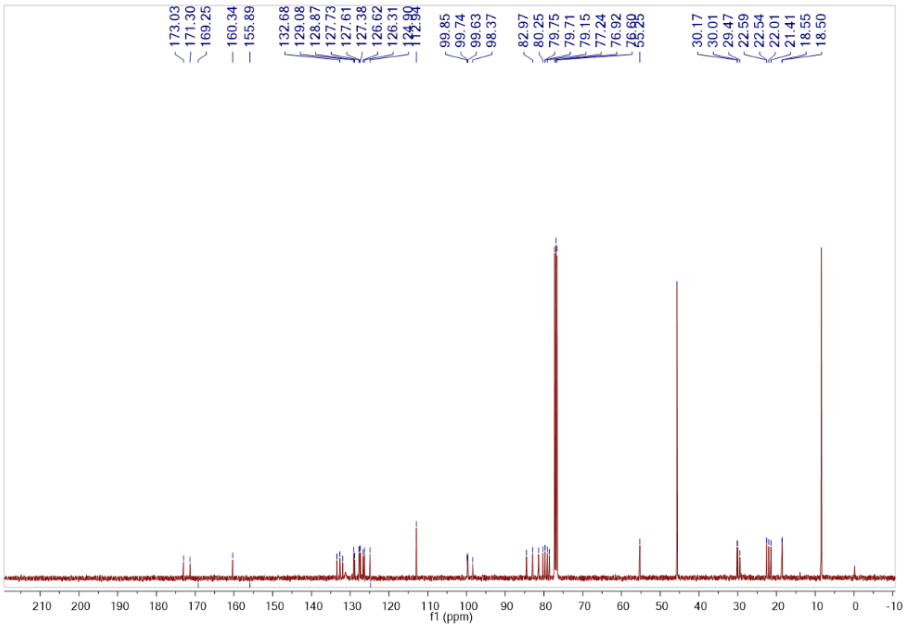

Figure S8. ^{13}C NMR spectrum of BC**2** in $CDCl_3$ (400 MHz, 293 K)

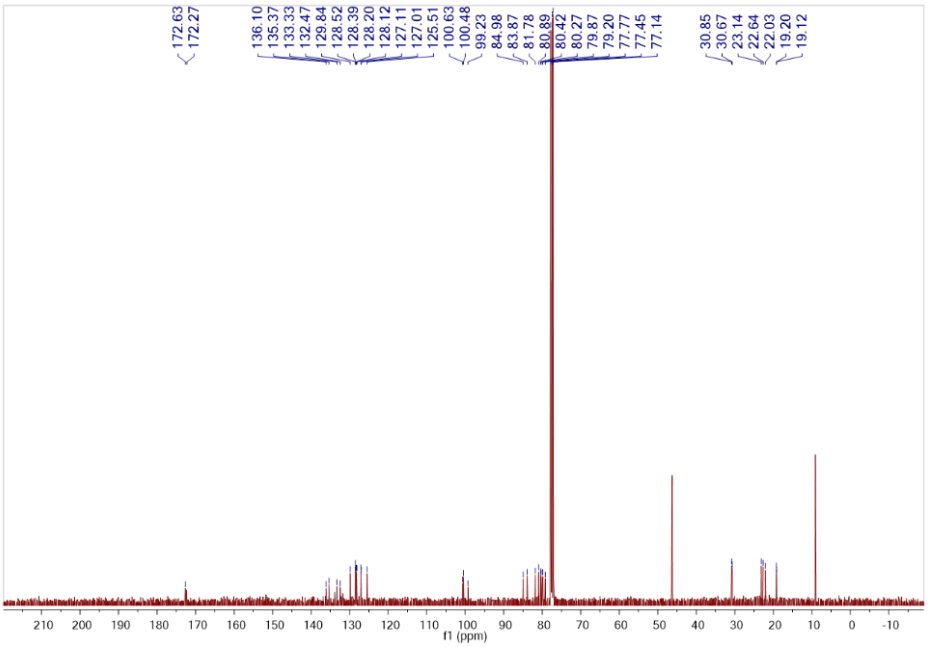

Figure S9. ^{13}C NMR spectrum of BC**3** in $CDCl_3$ (400 MHz, 293 K)

5. Spectral data of the dehydrogenative coupling of alcohols, pyrimidinone products and intermediates

Benzaldehyde**(1a')**[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.00 (s, 1H), 8.14 – 8.09 (m, 1H), 7.88 – 7.83 (m, 1H), 7.65 – 7.57 (m, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.63, 171.35, 136.36, 134.55, 133.67, 130.17, 129.79, 129.53, 129.03, 128.49.

4-methylbenzaldehyde **(1b')** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.93 (s, 1H), 7.75 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 7.7 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.06, 145.57, 134.16, 130.13, 129.84, 129.71, 129.13, 21.81.

4-isopropylbenzaldehyde (**1c'**), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.89 (d, J = 5.6 Hz, 1H), 7.73 (s, 2H), 7.29 (s, 2H), 2.89 (dd, J = 13.3, 6.6 Hz, 1H), 1.19 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ: 191.84, 156.06, 134.52, 129.93, 127.07, 34.37, 23.53.

4-methoxybenzaldehyde (**1d'**), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.93 (s, 1H), 7.41 (d, J = 7.3 Hz, 2H), 7.35 (s, 1H), 7.18 – 7.08 (m, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.02, 160.06, 137.76, 129.97, 123.27, 121.24, 112.15, 55.29, 55.25.

2,5-dimethoxybenzaldehyde (**1e'**), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.43 (s, 1H), 7.32 (d, J = 3.1 Hz, 1H), 7.13 (dd, J = 9.0, 3.2 Hz, 1H), 6.94 (d, J = 9.1 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.54, 156.70, 153.58, 124.90, 123.42, 113.34, 110.44, 56.17, 55.81.

3,4-dimethoxybenzaldehyde (**1f'**), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.85 (s, 1H), 7.51 – 7.34 (m, 2H), 6.98 (d, J = 8.1 Hz, 1H), 3.97 (d, J = 2.9 Hz, 3H), 3.94 (d, J = 3.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.77, 154.40, 149.53, 130.06, 126.72, 110.38, 108.89, 56.08, 55.88.

3-hydroxybenzaldehyde (**1g'**), ^{1}H NMR (400 MHz, DMSO) δ: 9.96 (s, 1H), 9.90 (s, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 6.9 Hz, 1H), 7.26 (s, 1H), 7.10 (d, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ: 192.99, 157.94, 137.60, 130.22, 121.76, 121.04, 114.62.

4-chlorobenzaldehyde (**1h'**), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.97 (s, 1H), 7.83 (dd, J = 17.4, 8.4 Hz, 2H), 7.51 (dd, J = 20.4, 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.83, 140.79, 134.70, 130.87, 129.39.

3-chlorobenzaldehyde (**1i'**), ^{1}H NMR (400 MHz, DMSO) δ: 9.94 (s, 1H), 7.85 (s, 2H), 7.60 – 7.52 (m, 2H), 7.45 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ: 191.68, 166.01, 137.71, 134.05, 133.94, 133.29, 132.81, 132.43, 130.82, 130.26, 128.80, 127.73.

2,6-dichlorobenzaldehyde (**1j'**), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.48 (s, 1H), 7.39 (s, 3H). 13C NMR (100 MHz, $CDCl_3$) δ: 188.79, 136.82, 133.67, 130.34, 129.78.

3-bromobenzaldehyde (**1k'**), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.96 (d, J = 6.2 Hz, 1H), 8.01 (d, J = 5.8 Hz, 1H), 7.78 (dd, J = 15.7, 6.2 Hz, 2H), 7.49 – 7.34 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.81, 137.98, 137.33, 132.37, 130.66, 128.42, 123.38.

2-bromobenzaldehyde (**1l'**), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.37 (s, 1H), 8.01 – 7.84 (m, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.45 (dd, J = 9.0, 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.91, 135.37, 133.92, 133.53, 129.89, 127.94, 127.15.

6-oxo-2,4-diphenyl-1,6-dihydropyrimidine-5-carbonitrile (**4a**)^{1}H NMR (400 MHz, DMSO) δ: 9.53 (s, 1H), 8.32 (d, J = 3.4 Hz, 1H), 7.95 (d, J = 3.7 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.74 (t, J = 7.3 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.53 (d, J = 3.5 Hz, 1H), 7.47 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ: 173.24, 167.71, 165.95, 164.63, 138.72, 138.20, 133.64, 130.08, 129.74, 128.93, 128.38, 128.26, 128.13, 128.10, 128.08, 128.04, 119.89, 90.87.

6-oxo-2-phenyl-4-(p-tolyl)-1,6-dihydropyrimidine-5-carbonitrile (**4b**) ^{1}H NMR (400 MHz, DMSO) δ 8.08 (d, J = 7.9 Hz, 2H), 7.98 – 7.85 (m, 2H), 7.75 (d, J = 15.6 Hz, 1H), 7.45 (s, 3H), 7.36 (d, J = 2.9 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ: 188.57, 143.60, 135.03, 134.69, 130.47, 129.31, 128.85, 128.79, 128.63, 122.00, 97.60, 21.14.

4-(4-isopropylphenyl)-6-oxo-2-phenyl-1,6-dihydropyrimidine-5-carbonitrile (**4c**) ^{1}H NMR (400 MHz, DMSO) δ: 9.63 (s, 1H), 8.27 – 8.22 (m, 1H), 7.87 (d, J = 7.8 Hz, 2H), 7.74 (t, J = 7.3 Hz, 1H), 7.62 (t, J = 7.6 Hz, 2H), 7.44 (s, 3H), 3.11 (dt, J = 13.4, 6.7 Hz, 1H), 1.25 (d, J = 6.7 Hz, 6H). ^{13}C NMR (1001 MHz, DMSO) δ: 177.28, 172.89, 165.99, 164.54, 138.81, 133.61, 129.94, 128.91, 128.43, 128.29, 128.09, 127.97, 119.04, 91.08, 21.09.

4-(4-methoxyphenyl)-6-oxo-2-phenyl-1,6-dihydropyrimidine-5-carbonitrile (**4d**) ^{1}H NMR (400 MHz, DMSO) δ: 8.34 (s, 1H), 8.01 (d, J = 7.8 Hz, 2H), 7.91 (d, J = 7.2 Hz, 1H), 7.48 (s, 4H), 7.09 (d, J = 7.6 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ: 170.87, 167.94, 166.89, 163.09, 160.83, 137.51, 134.19, 131.20, 130.51, 130.01, 128.92, 128.16, 128.11, 127.95, 127.45, 119.79, 113.56, 90.62, 55.30.

6-oxo-2-phenyl-4-(3,4,5-trimethoxyphenyl)-1,6-dihydropyrimidine-5-carbonitrile (**4e**) ^{1}H NMR (400 MHz, DMSO) δ: 8.37 (s, 1H), 7.96 (d, J = 61.2 Hz, 1H), 7.45 (s, 4H), 7.29 (s, 2H), 3.87 (s, 6H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ: 172.73, 166.91, 164.18, 152.37, 139.10, 138.70, 133.70, 131.18, 129.86, 128.04, 127.93, 127.44, 120.69, 105.86, 90.34, 60.10, 55.92.

4-(4-chlorophenyl)-6-oxo-2-phenyl-1,6-dihydropyrimidine-5-carbonitrile (**4f**) ^{1}H NMR (400 MHz, DMSO) δ 8.32 (d, J = 5.4 Hz, 1H), 7.97 – 7.87 (m, 1H), 7.59 (d, J = 10.5 Hz, 1H), 7.49 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ 166.12, 163.38, 139.85, 137.23, 132.96, 130.66, 130.19, 129.82, 128.17, 127.95, 127.01, 119.08, 91.92.

4-(4-bromophenyl)-6-oxo-2-phenyl-1,6-dihydropyrimidine-5-carbonitrile (**4g**) ^{1}H NMR (400 MHz, DMSO) δ: 8.32 (s, 1H), 7.96 – 7.87 (m, 2H), 7.59 (d, J = 9.5 Hz, 3H), 7.49 (s, 4H). ^{13}C NMR (100 MHz, DMSO) δ: 170.03, 166.12, 163.39, 139.84, 137.23, 132.97, 130.67, 130.19, 129.83, 128.18, 127.96, 127.01, 119.06, 91.93.

4-(4-fluorophenyl)-6-oxo-2-phenyl-1,6-dihydropyrimidine-5-carbonitrile (**4h**) ^{1}H NMR (400 MHz, DMSO) δ: 8.34 (s, 2H), 8.05 (s, 2H), 7.45 (d, J = 41.1 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 170.01, 166.61, 164.28, 163.06, 162.26, 162.14, 136.96, 134.09, 130.78, 128.22, 121.06, 121.01, 119.12, 115.33, 115.11, 91.71, 90.67.

6-oxo-2-phenyl-4-(thiophen-2-yl)-1,6-dihydropyrimidine-5-carbonitrile (**4i**) ^{1}H NMR (400 MHz, DMSO) δ: 9.52 (s, 1H), 8.32 (d, J = 3.2 Hz, 1H), 8.18 (d, J = 3.5 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 4.9 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.34 – 7.16 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ: 172.90, 165.90, 164.32, 159.21, 143.04, 138.41, 133.65, 130.42, 130.20, 128.93, 128.32, 128.09, 127.98, 127.91, 120.30, 86.69.

4-([1,1'-biphenyl]-4-yl)-6-oxo-2-phenyl-1,6-dihydropyrimidine-5-carbonitrile (**4j**) ^{1}H NMR (400 MHz, DMSO) δ: 10.06 (s, 1H), 8.05 (s, 3H), 7.99 (s, 5H), 7.92 (s, 4H), 7.74 (d, J = 9.7 Hz, 9H), 7.48 (d, J = 8.8 Hz, 9H).

4-isopropyl-6-oxo-2-phenyl-1,6-dihydropyrimidine-5-carbonitrile (**4k**) ^{1}H NMR (400 MHz, DMSO) δ: 8.39 (s, 1H), 8.22 (s, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 7.9 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ: 160.02, 151.95, 134.25, 132.19, 131.71, 129.92, 127.94, 120.92, 113.83, 102.88, 61.16, 38.75, 38.54, 38.33, 38.12, 37.91, 37.71, 37.50, 12.56.

2-methyl-6-oxo-4-(p-tolyl)-1,6-dihydropyrimidine-5-carbonitrile(**5a**)

^{1}H NMR (400 MHz, DMSO) δ 8.34 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 2.40 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 167.28, 161.97, 157.89, 154.91, 144.38, 130.95, 129.92, 129.28, 129.06, 128.66, 115.76, 101.08, 62.22, 21.31, 13.95.

4-(4-methoxyphenyl)-2-methyl-6-oxo-1,6-dihydropyrimidine-5-carbonitrile (**5b**)

^{1}H NMR (400 MHz, DMSO) δ 8.32 (s, 1H), 7.78 (s, 2H), 7.20 (s, 1H), 3.86 (d, *J* = 26.4 Hz, 3H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 162.39, 158.59, 154.81, 154.16, 153.51, 148.69, 126.74, 123.97, 116.39, 112.95, 111.89, 98.46, 55.90, 55.49, 14.02.

4-(2,5-dimethoxyphenyl)-2-methyl-6-oxo-1,6-dihydropyrimidine-5-carbonitrile (**5c**)

^{1}H NMR (400 MHz, DMSO) δ 8.54 (s, 1H), 7.71 (d, *J* = 2.8 Hz, 1H), 7.25 (dd, *J* = 9.1, 2.9 Hz, 1H), 7.16 (d, *J* = 9.2 Hz, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 161.92, 153.42, 152.68, 148.50, 121.57, 119.87, 115.69, 113.39, 112.45, 102.12, 62.32, 56.38, 55.51, 13.94.

4-(3-chlorophenyl)-2-methyl-6-oxo-1,6-dihydropyrimidine-5-carbonitrile (**5d**)

^{1}H NMR (400 MHz, DMSO) δ: 8.39 (s, 1H), 8.23 (s, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ: 161.38, 153.31, 135.60, 133.55, 133.06, 131.28, 129.28, 122.27, 115.19, 104.25, 88.23, 62.51, 13.91.

4-(4-bromophenyl)-2-methyl-6-oxo-1,6-dihydropyrimidine-5-carbonitrile (**5e**)

1H NMR (400 MHz, DMSO) δ 8.39 (s, 1H), 8.23 (s, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.55 (t, J = 7.9 Hz, 1H), 1.32 (d, J = 7.1 Hz, 3H). 13C NMR (101 MHz, DMSO) δ 161.38, 153.31, 135.60, 133.55, 133.06, 131.28, 129.28, 122.27, 115.19, 104.25, 88.23, 62.51, 13.91.

2-amino-4-(2,5-dimethoxyphenyl)-6-oxo-1,6-dihydropyrimidine-5-carbonitrile (**6a**)

1H NMR (400 MHz, DMSO) δ 8.31 (s, 1H), 7.60 (s, 3H), 7.08 (s, 2H), 3.83 (s, 3H), 3.76 (s, 3H). 13C NMR (101 MHz, DMSO) δ 164.99, 158.63, 152.65, 152.19, 142.58, 121.85, 118.76, 118.09, 112.75, 112.65, 112.13, 102.14, 79.14, 56.08, 55.39.

2-amino-4-(2,3-dimethoxyphenyl)-6-oxo-1,6-dihydropyrimidine-5-carbonitrile (**6b**)
1H NMR (400 MHz, DMSO) δ 8.29 (s, 2H), 7.76 (s, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.18 (d, J = 8.5 Hz, 2H), 3.88 (s, 3H), 3.81 (s, 3H). 13C NMR (101 MHz, DMSO) δ 162.37, 154.78, 153.50, 148.67, 126.74, 123.96, 116.37, 112.91, 111.85, 98.42, 55.88, 55.46.

2-amino-4-(4-chlorophenyl)-6-oxo-1,6-dihydropyrimidine-5-carbonitrile (**6c**)

1H NMR (400 MHz, DMSO) δ 8.41 (s, 1H), 8.07 (s, 2H), 7.68 (s, 2H), 7.52 (d, J = 37.9 Hz, 2H). 13C NMR (101 MHz, DMSO) δ 166.53, 161.32, 153.64, 137.86, 132.40, 131.09, 129.44, 128.66, 115.26, 103.40, 91.52, 62.44, 13.92.

2-amino-4-(3-chlorophenyl)-6-oxo-1,6-dihydropyrimidine-5-carbonitrile (**6d**)

1H NMR (400 MHz, DMSO) δ 8.42 (s, 1H), 7.91 – 7.88 (m, 2H), 7.71 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 8.0 Hz, 2H). 13C NMR (101 MHz, DMSO) δ 166.04, 161.32, 153.41, 149.16, 133.30, 132.89, 132.66, 130.61, 128.78, 127.88, 115.84, 104.75, 101.01, 95.39, 62.52, 13.92.

ethyl-2-cyano-3-phenylacrylate (**2a'**)

^{1}H NMR (400 MHz, DMSO) δ: 8.66 (s, 1H), 8.41 (s, 1H), 8.18 (s, 1H), 7.80 (d, *J* = 7.4 Hz, 4H), 7.43 (s, 5H), 7.29 (d, *J* = 3.6 Hz, 5H), 4.30 (d, *J* = 11.0 Hz, 1H), 1.22 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ: 163.70, 137.49, 136.68, 135.66, 128.99, 128.63, 127.99, 127.69, 127.08, 126.89, 112.49, 111.96, 104.46, 61.20, 19.50.
2,4,6-triphenyl-1,3,5-triazine

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.81 – 8.71 (m, 5H), 7.69 – 7.48 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.68, 136.27, 132.55, 129.00, 128.68, 128.51, 127.33.

6-amino-3-bromo-4-phenylpyridin-2(1H)-one (Bropirimine)

^{1}H NMR (400 MHz, DMSO) δ: 7.95 (d, J = 7.3 Hz, 3H), 7.63 (t, J = 7.4 Hz, 2H), 7.52 (d, J = 7.6 Hz, 2H), 7.49 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ: 193.07, 167.32, 162.96, 137.08, 136.22, 132.84, 130.72, 129.23, 128.54, 115.82, 93.44.

5. NMR spectra for catalytic products:

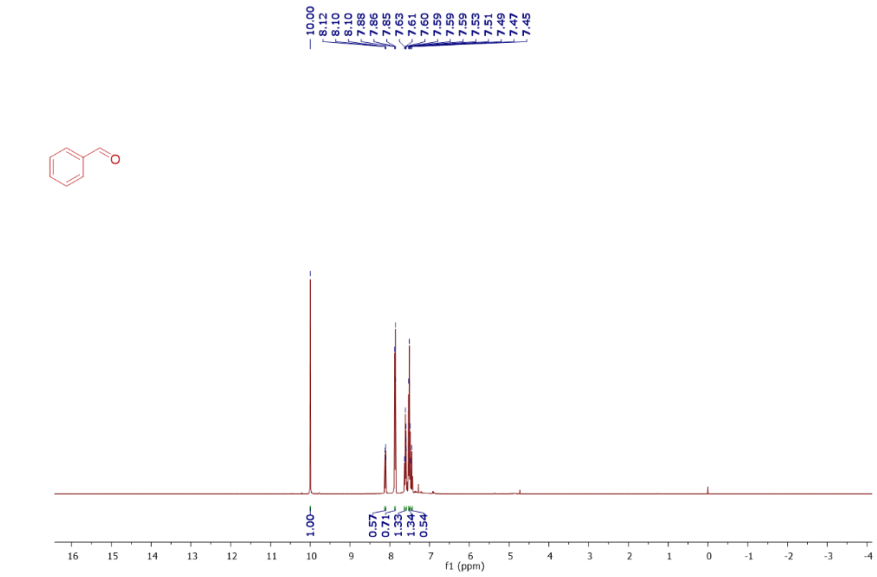

Figure S10: ^{1}H NMR spectrum for (**1a'**) in $CDCl_3$ (400MHz, 300K)

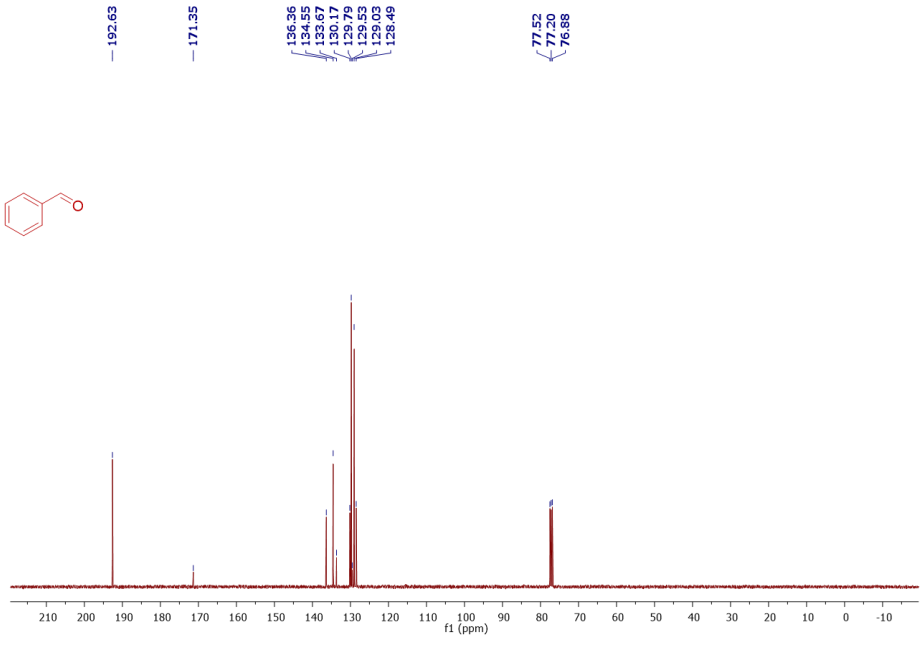

Figure S11: ^{13}C NMR spectrum for (**1a'**) in $CDCl_3$ (100MHz, 300K)

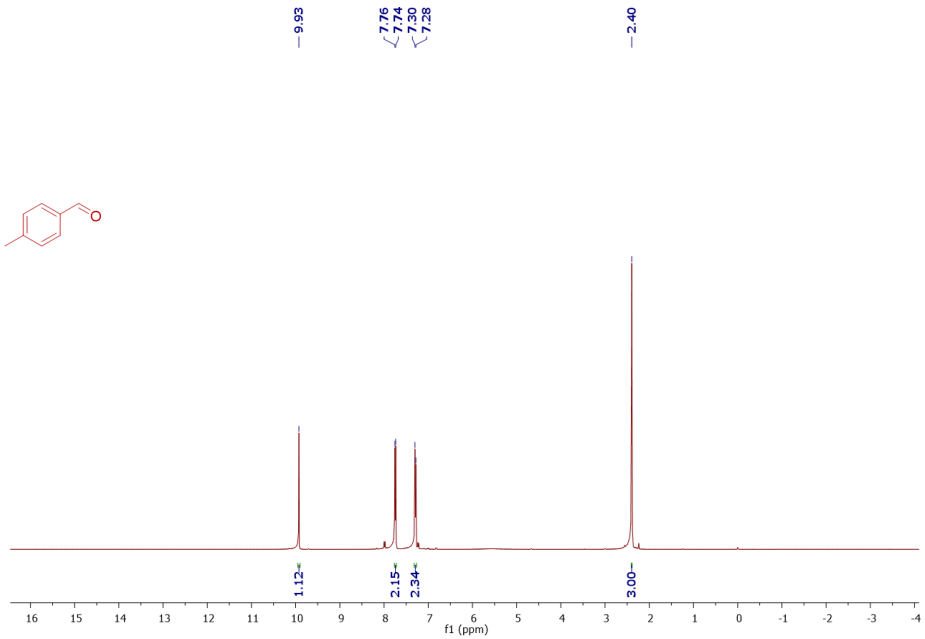

Figure S12: ^{1}H NMR spectrum for (**1b'**) in $CDCl_3$ (400MHz, 300K)

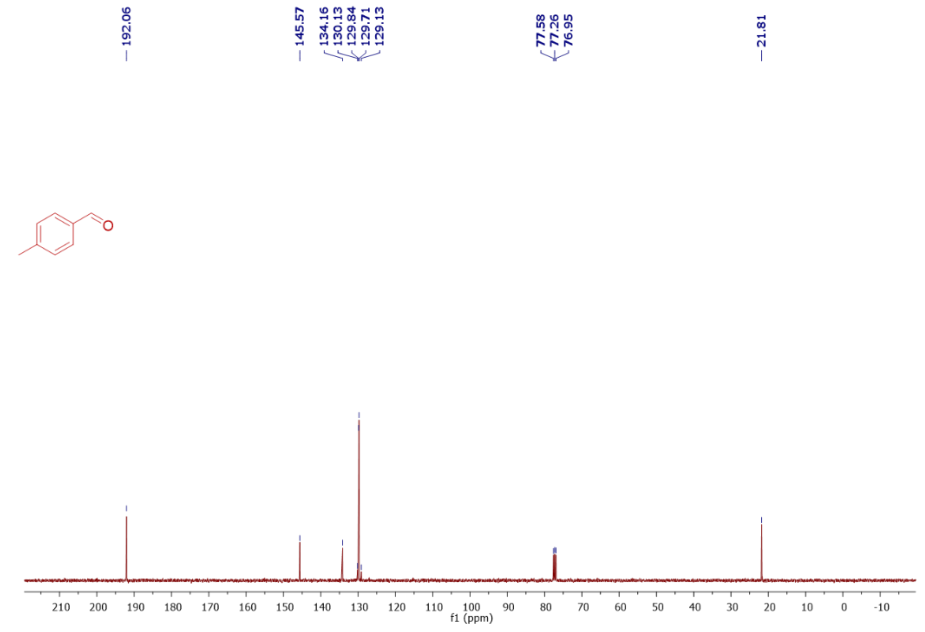

Figure S13: ^{13}C NMR spectrum for (**1b'**) in $CDCl_3$ (100MHz, 300K)

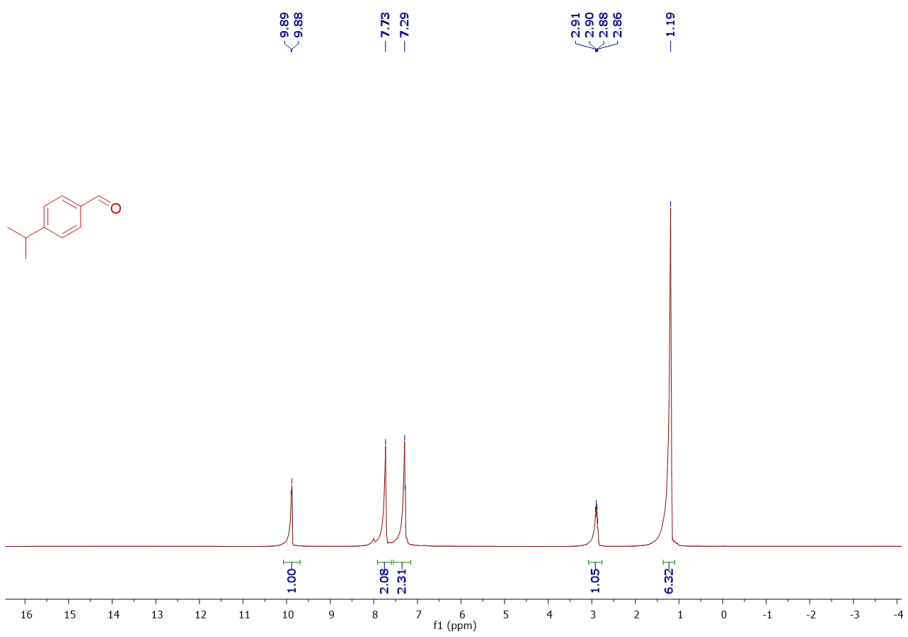

Figure S14: ^{1}H NMR spectrum for (**1c'**) in $CDCl_3$ (400MHz, 300K)

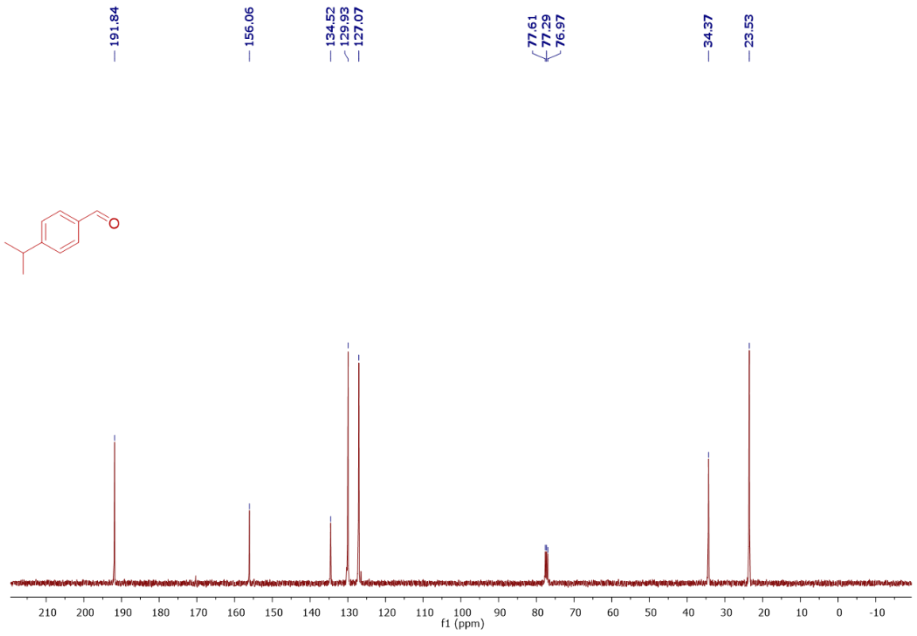

Figure S15: ^{13}C NMR spectrum for (**1c'**) in $CDCl_3$ (100MHz, 300K)

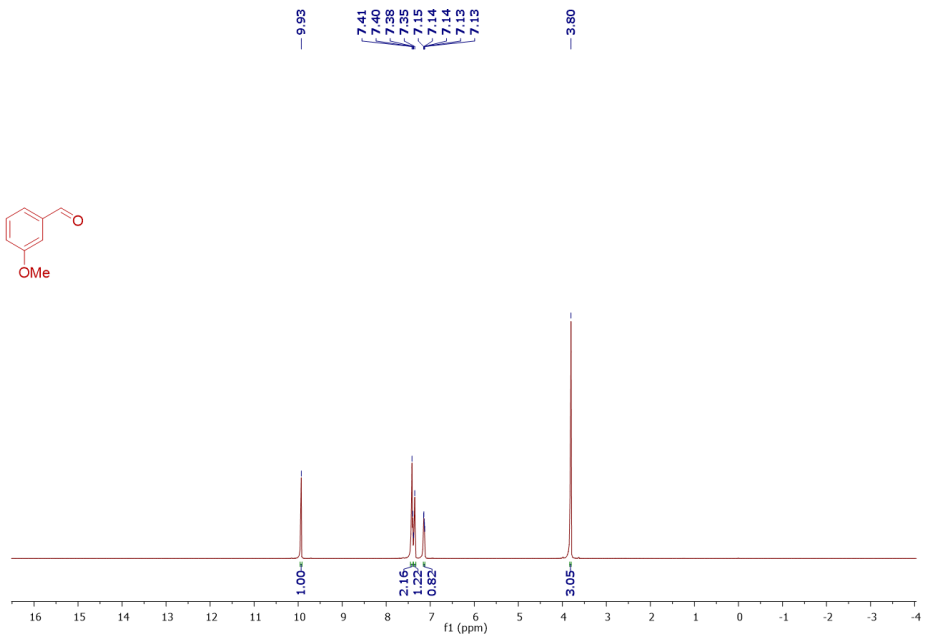

Figure S16: ^{1}H NMR spectrum for (**1d'**) in $CDCl_3$ (400MHz, 300K)

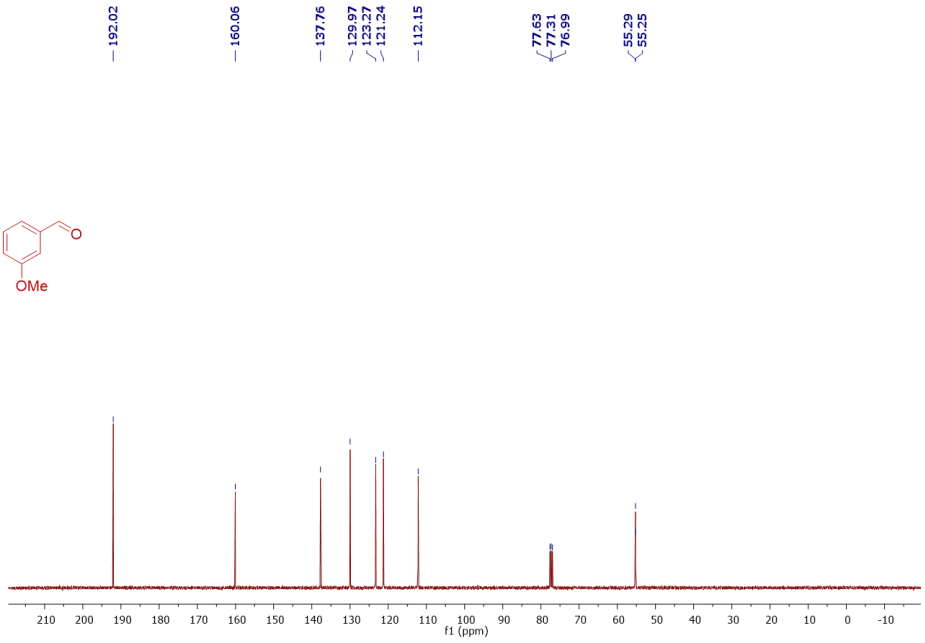

Figure S17: ^{13}C NMR spectrum for (**1d'**) in $CDCl_3$ (100MHz, 300K)

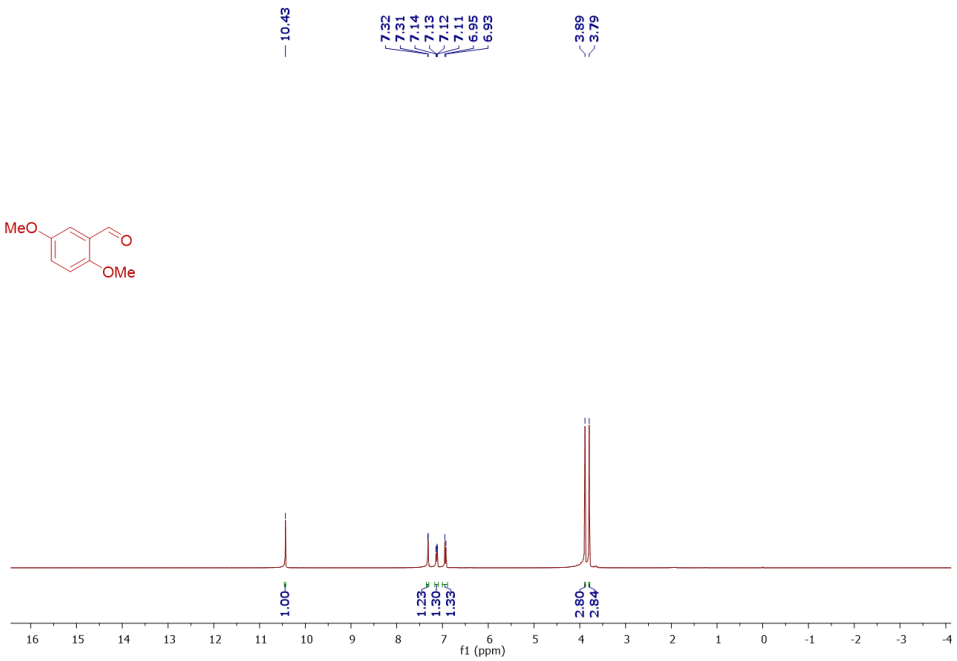

Figure S18: ^{1}H NMR spectrum for (**1e'**) in $CDCl_3$ (400MHz, 300K)

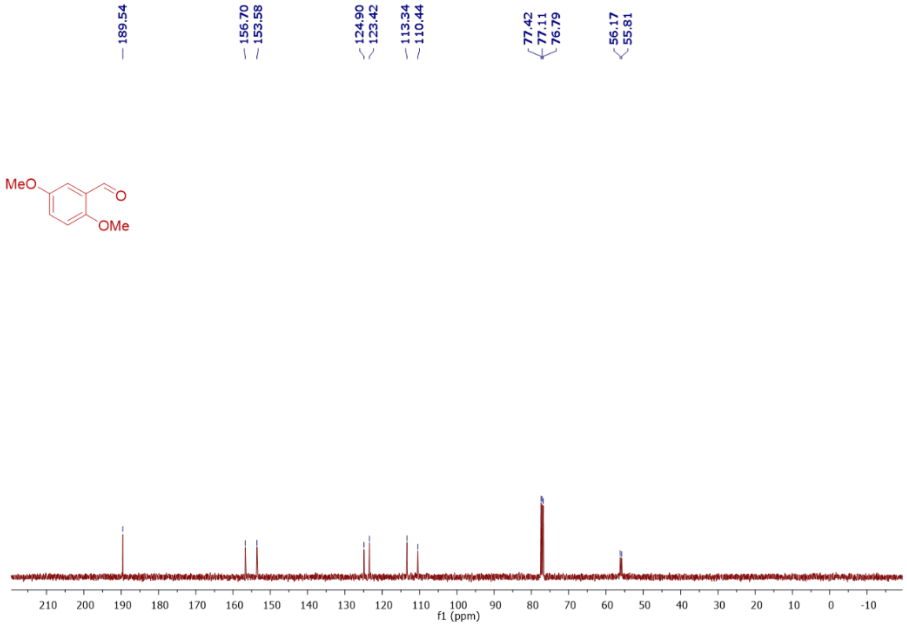

Figure S19: ^{13}C NMR spectrum for (**1e'**) in $CDCl_3$ (100MHz, 300K)

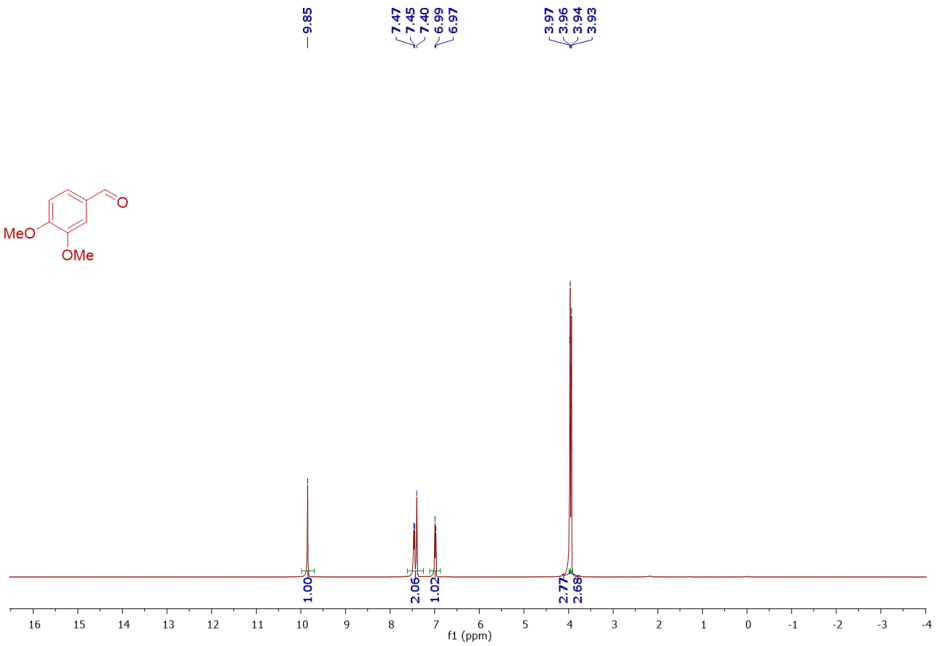

Figure S20: ^{1}H NMR spectrum for (**1f'**) in $CDCl_3$ (400MHz, 300K)

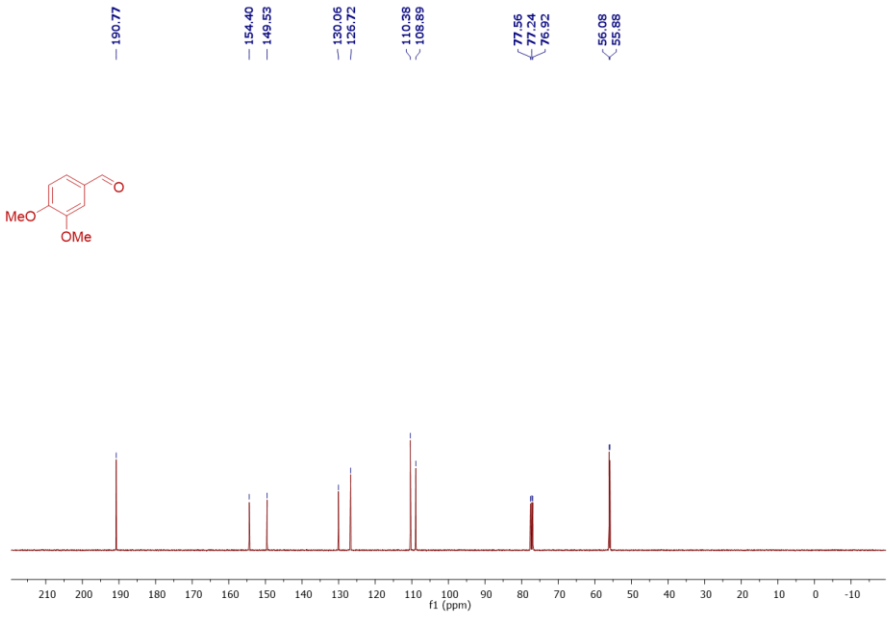

Figure S21: ^{13}C NMR spectrum for (**1f'**) in $CDCl_3$ (100MHz, 300K)

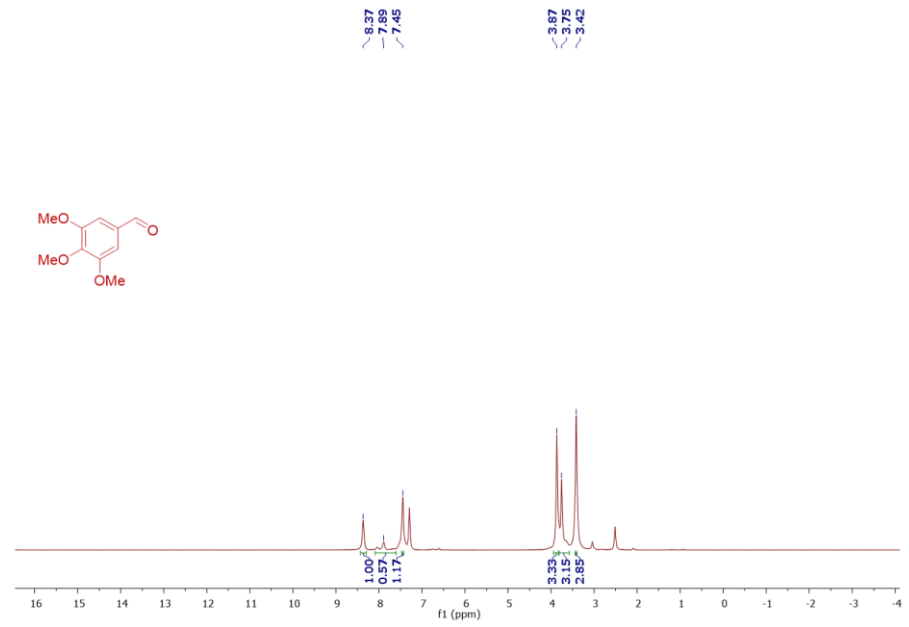

Figure S22: ^{1}H NMR spectrum for (**1g'**) in $CDCl_3$ (400MHz, 300K)

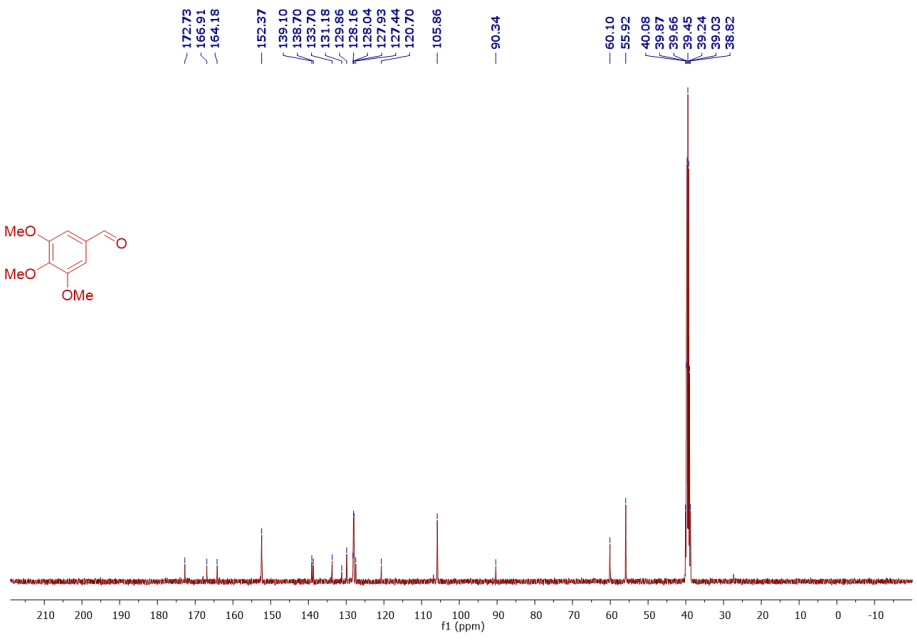

Figure S23: ^{13}C NMR spectrum for (**1g'**) in $CDCl_3$ (100MHz, 300K)

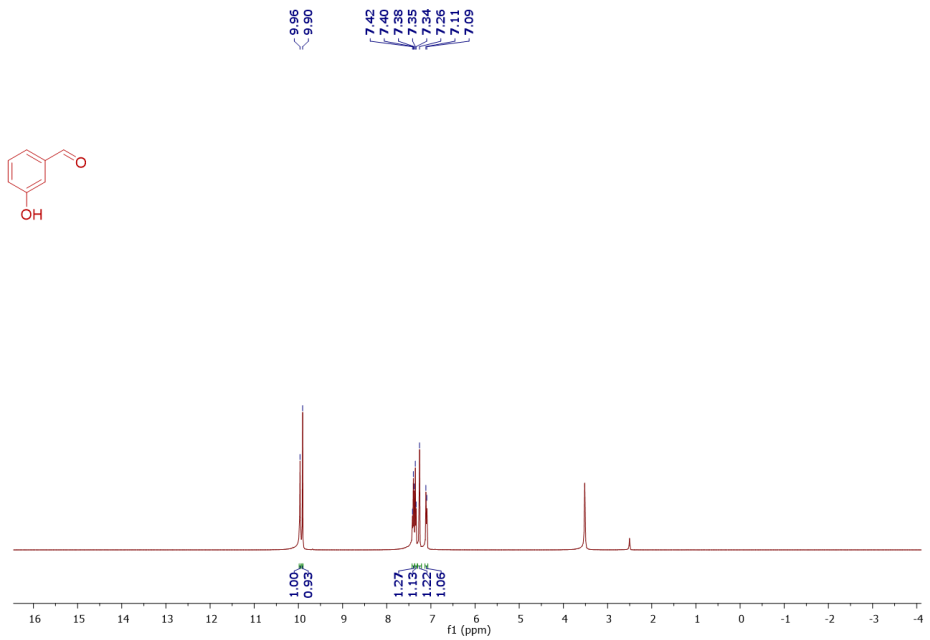

Figure S24: ^{1}H NMR spectrum for (**1h'**) in $CDCl_3$ (400MHz, 300K)

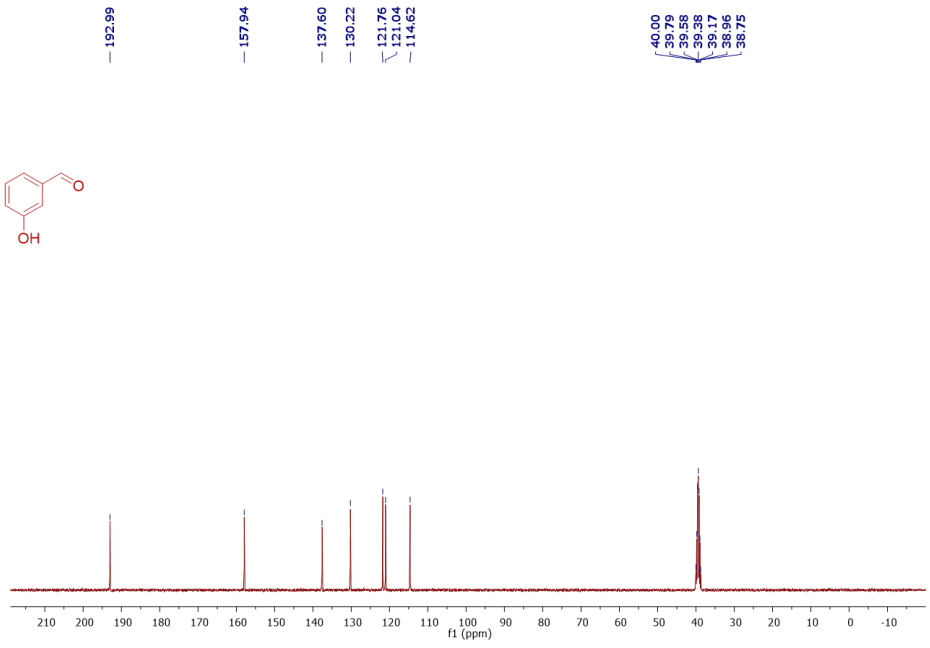

Figure S25: ^{13}C NMR spectrum for (**1h'**) in $CDCl_3$ (100MHz, 300K)

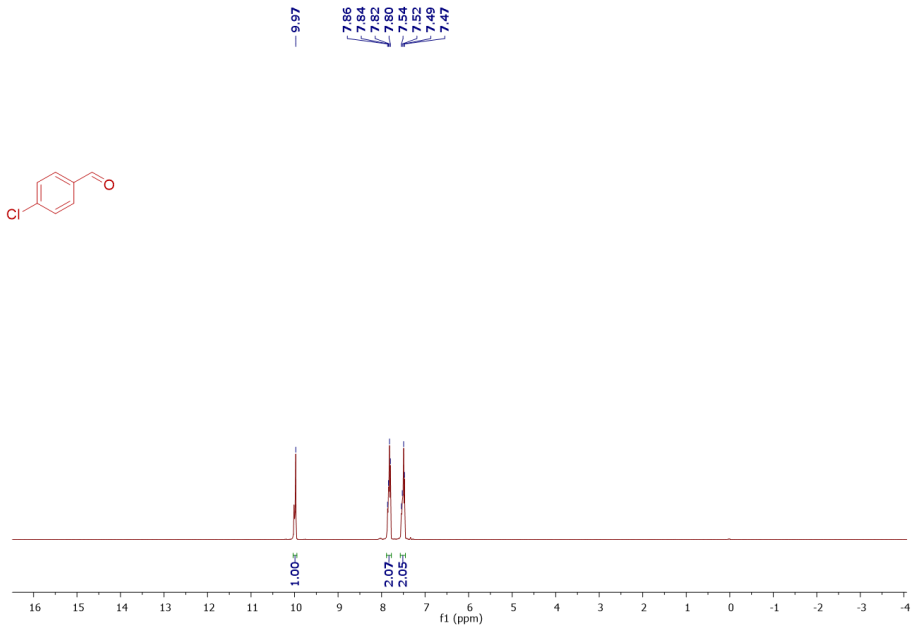

Figure S26: ^{1}H NMR spectrum for (**1i'**) in $CDCl_3$ (400MHz, 300K)

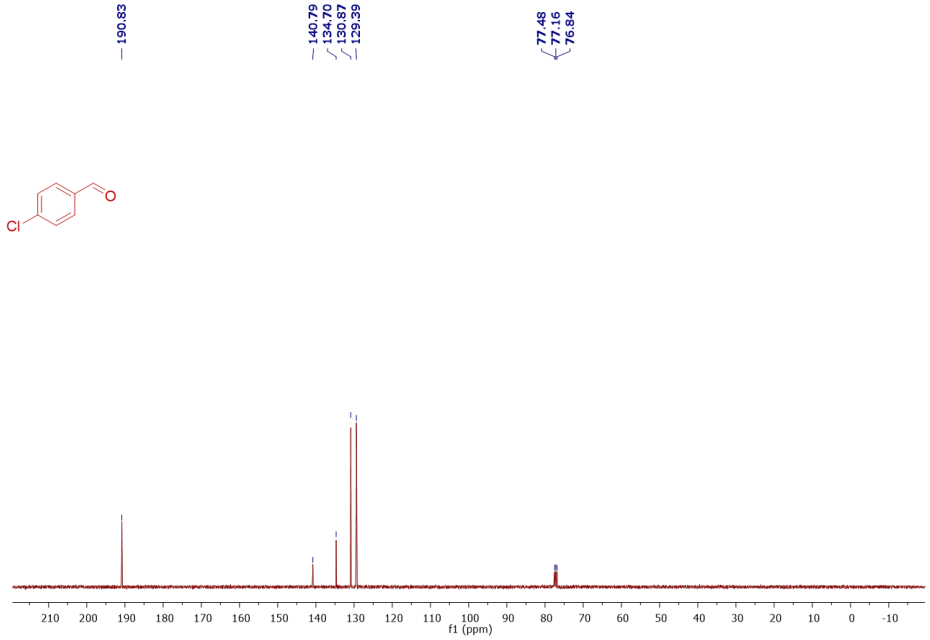

Figure S27: ^{13}C NMR spectrum for (**1i'**) in $CDCl_3$ (100MHz, 300K)

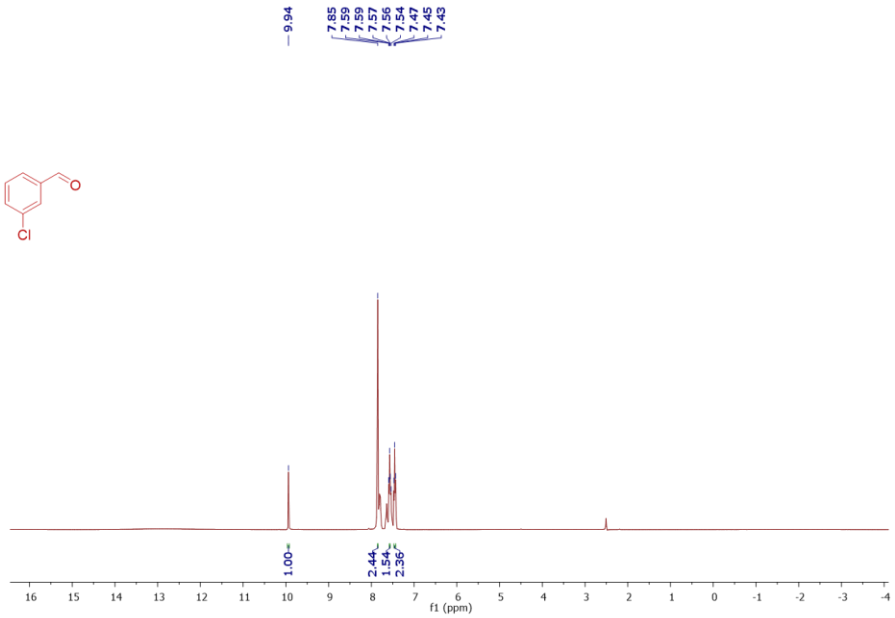

Figure S28: ^{1}H NMR spectrum for (**1j'**) in $CDCl_3$ (400MHz, 300K)

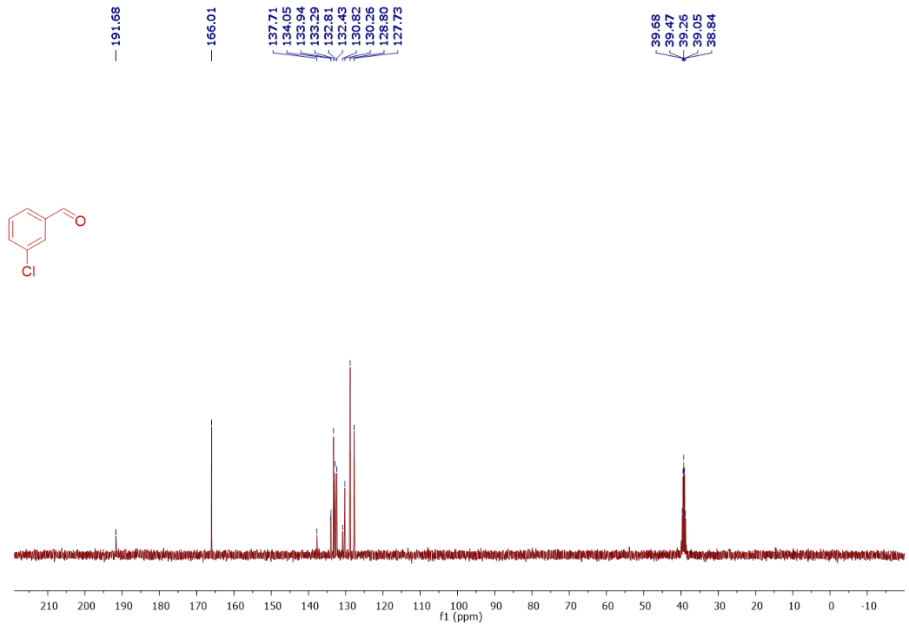

Figure S29: ^{13}C NMR spectrum for (**1j'**) in $CDCl_3$ (100MHz, 300K)

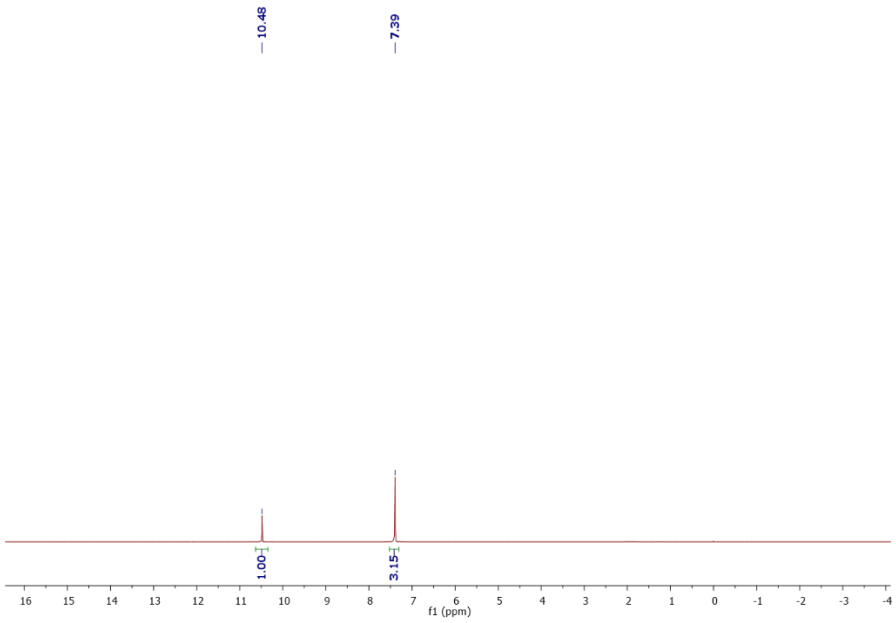

Figure S30: ^{1}H NMR spectrum for (**1k'**) in $CDCl_3$ (400MHz, 300K)

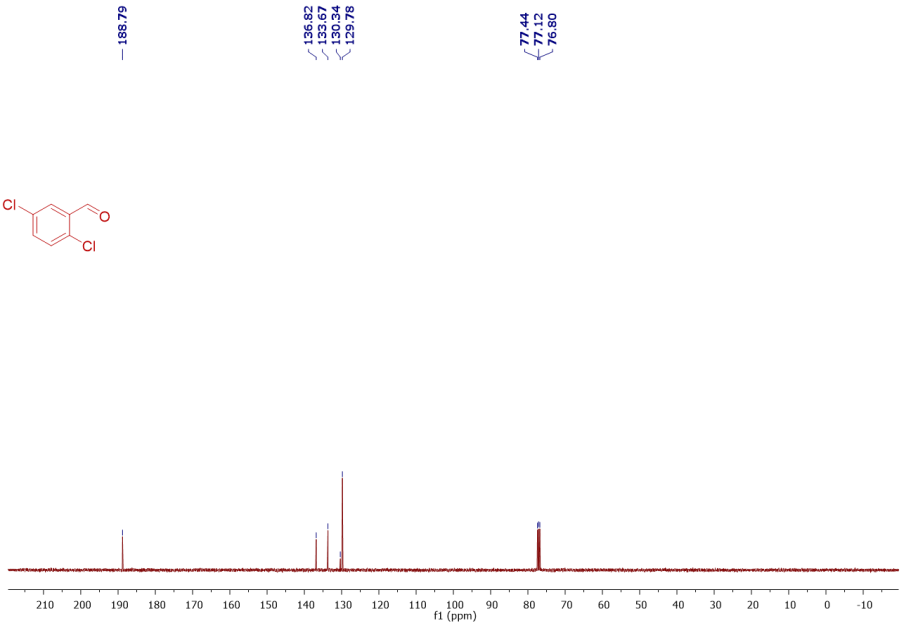

Figure S31: ^{13}C NMR spectrum for (**1k'**) in $CDCl_3$ (100MHz, 300K).

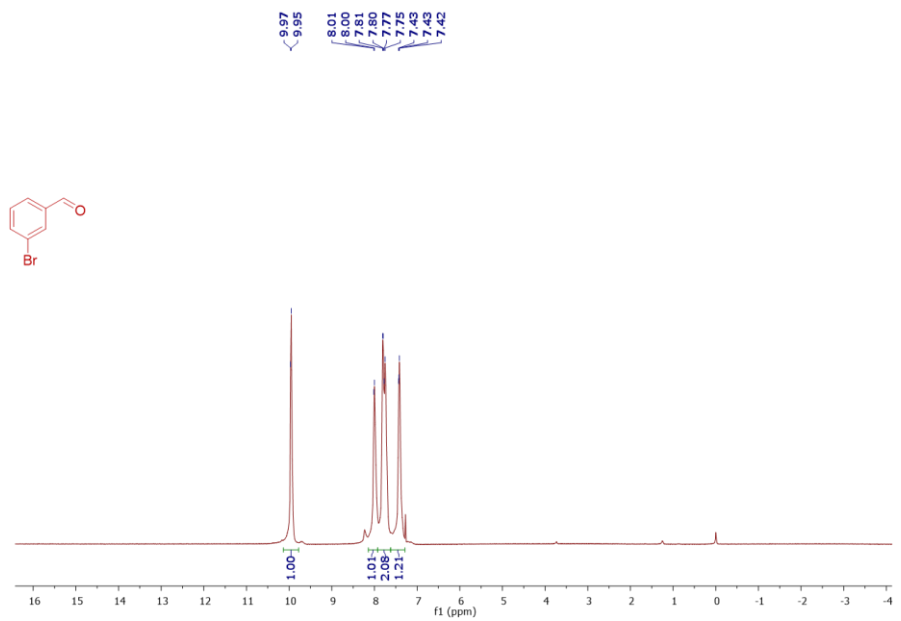

Figure S32: ^{1}H NMR spectrum for (**1l'**) in $CDCl_3$ (400MHz, 300K)

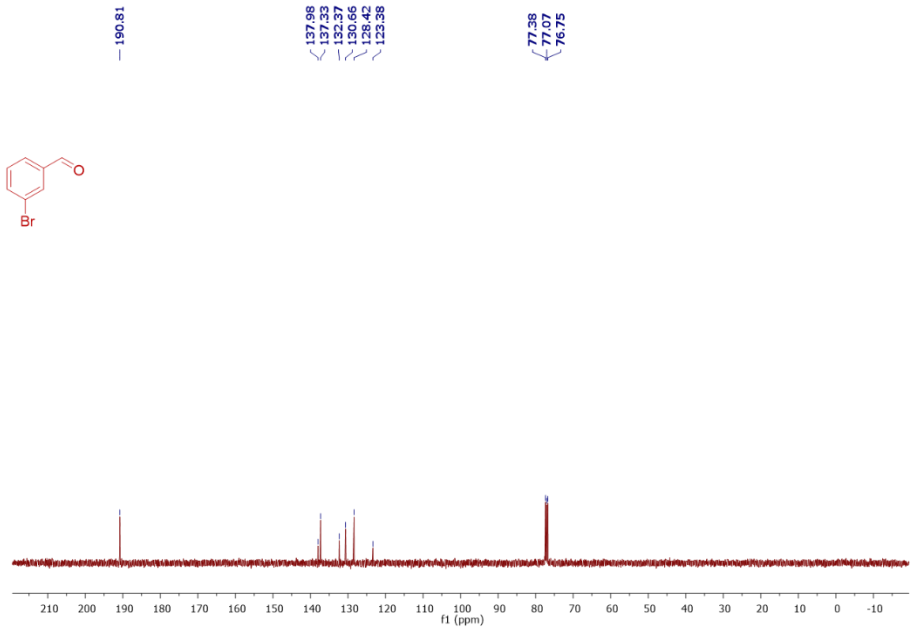

Figure S33: ^{13}C NMR spectrum for (**1l'**) in $CDCl_3$ (100MHz, 300K)

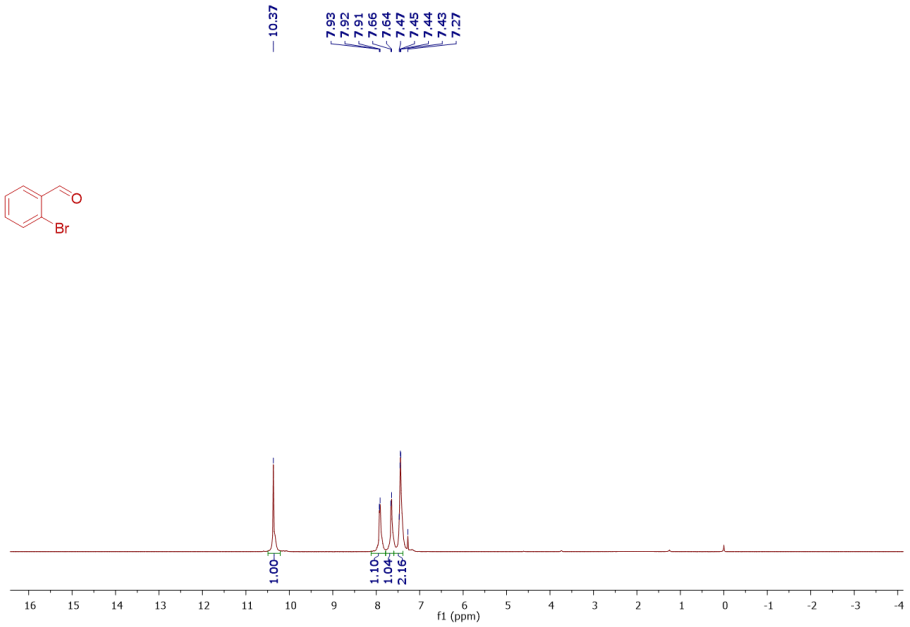

Figure S34: ^{1}H NMR spectrum for (**1m'**) in $CDCl_3$ (400MHz, 300K)

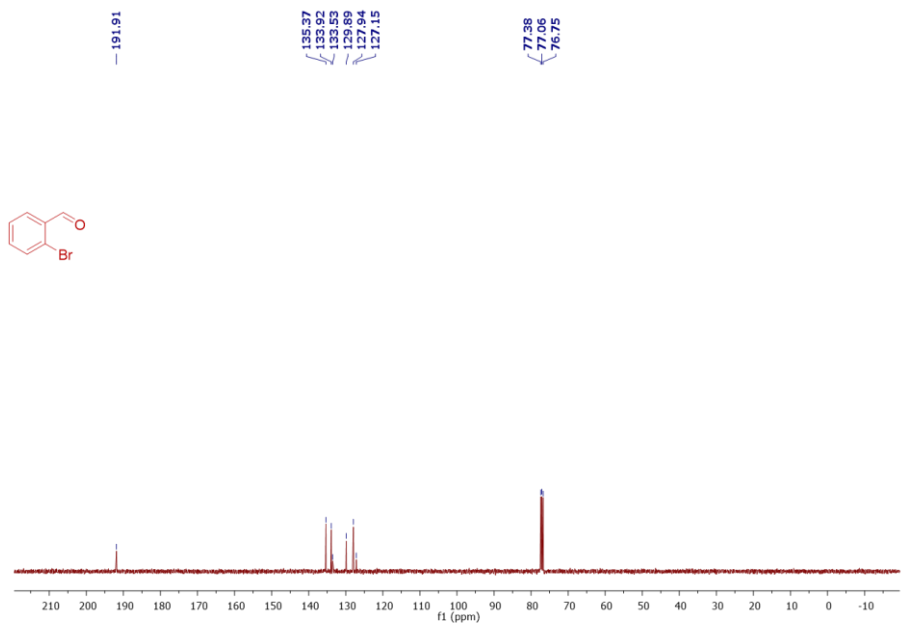

Figure S35: ^{13}C NMR spectrum for (**1m'**) in $CDCl_3$ (100MHz, 300K)

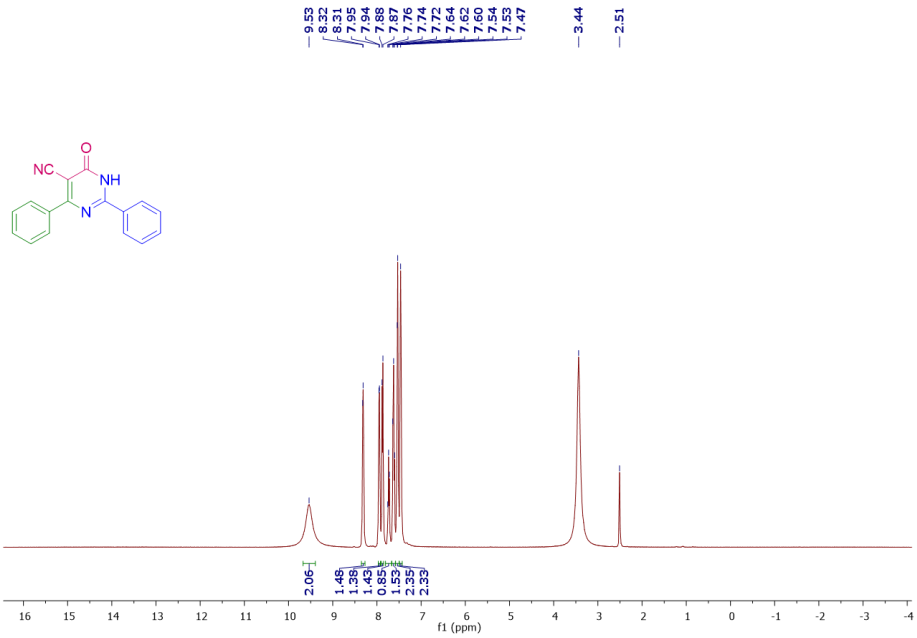

Figure S36: ^{1}H NMR spectrum for (**4a**) in DMSO (400MHz, 300K)

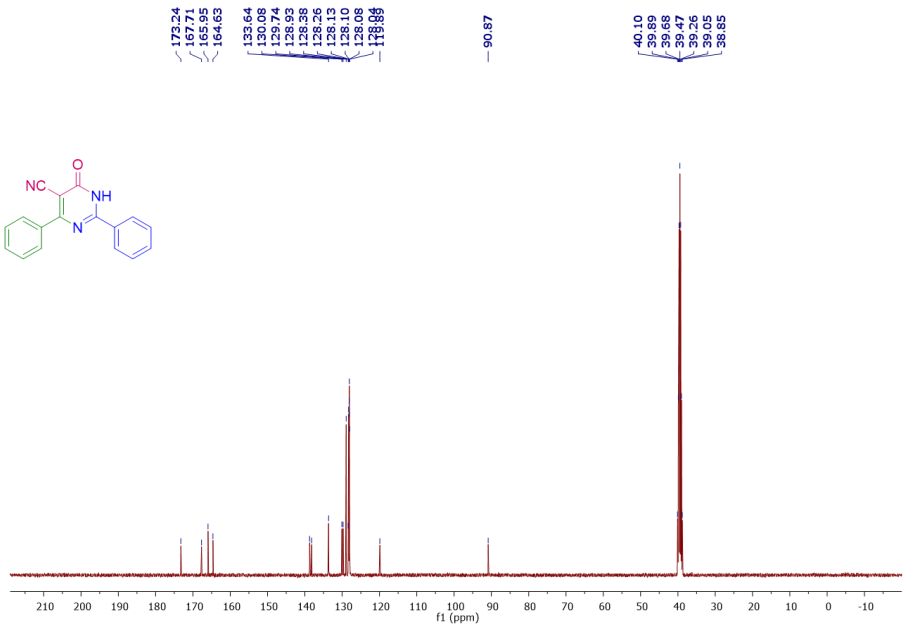

Figure S37: ^{13}C NMR spectrum for (**4a**) in DMSO (100MHz, 300K)

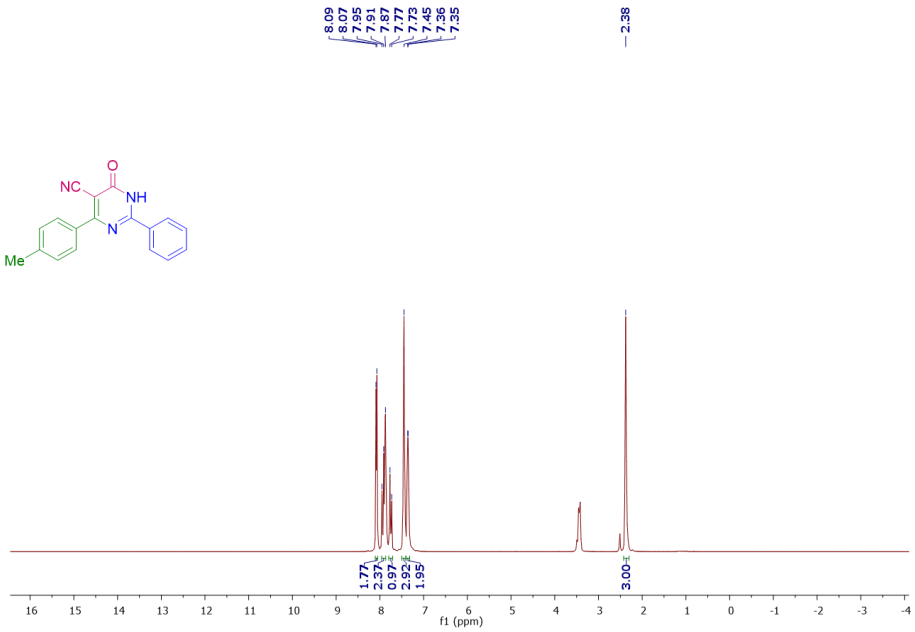

Figure S38: ^{1}H NMR spectrum for (**4b**) in DMSO (400MHz, 300K)

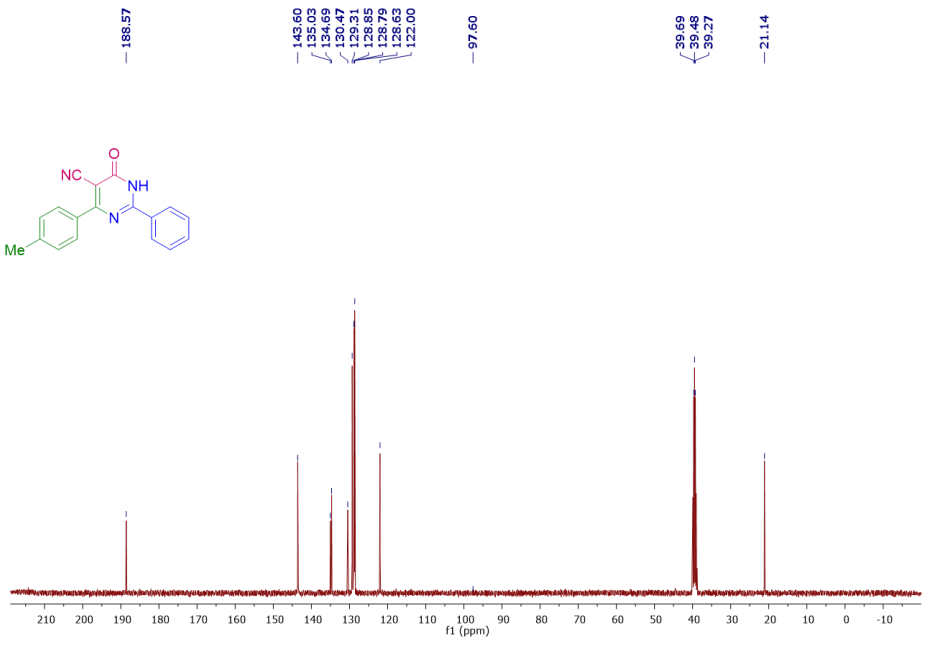

Figure S39: ^{13}C NMR spectrum for (**4b**) in DMSO (100MHz, 300K)

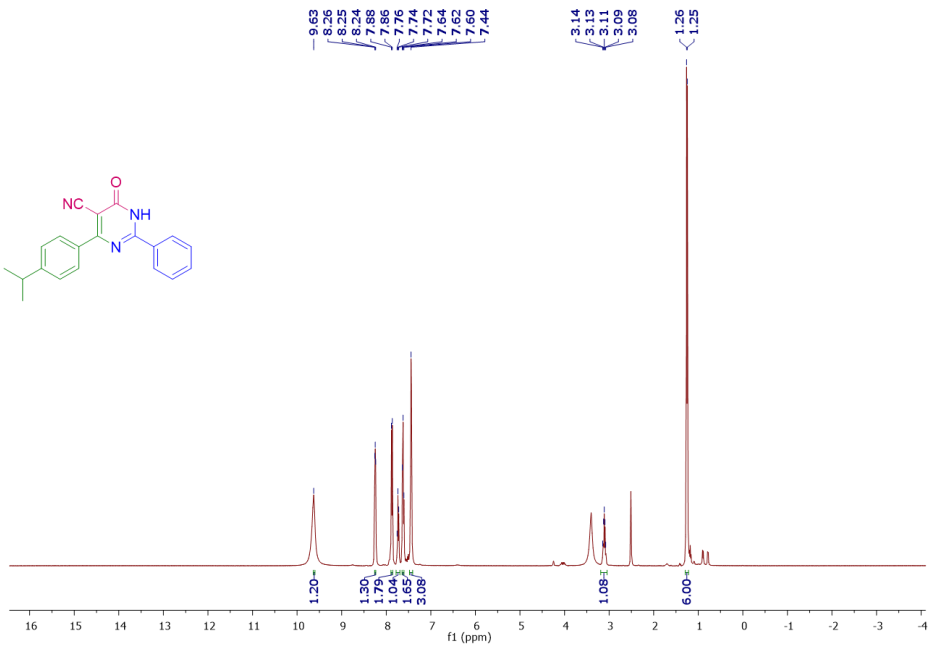

Figure S40: ^{1}H NMR spectrum for (**4c**) in DMSO (400MHz, 300K)

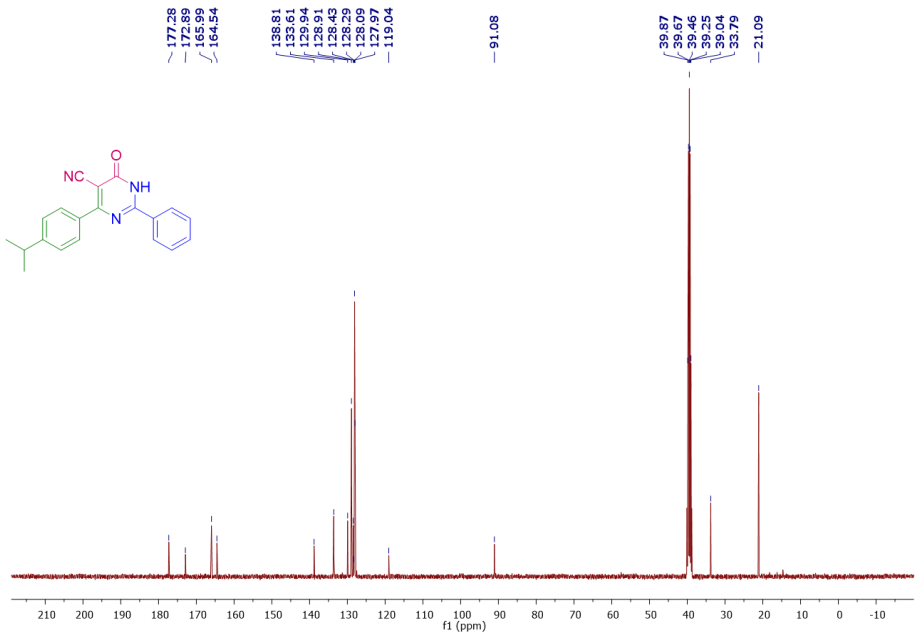

Figure S41: ^{13}C NMR spectrum for (**4c**) in DMSO (100MHz, 300K)

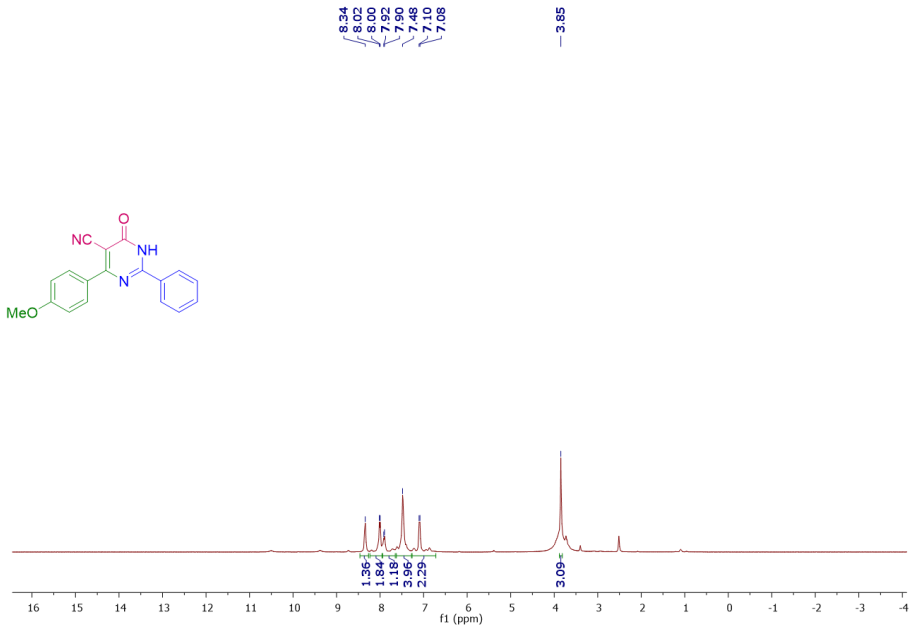

Figure S42: ^{1}H NMR spectrum for (**4d**) in DMSO (400MHz, 300K)

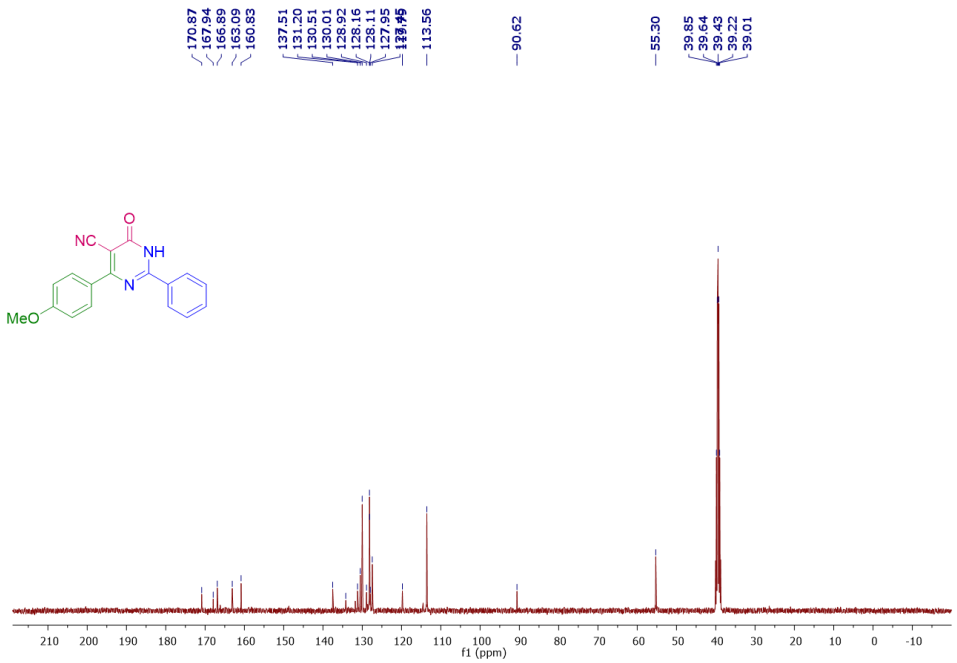

Figure S43: ^{13}C NMR spectrum for (**4d**) in DMSO (100MHz, 300K)

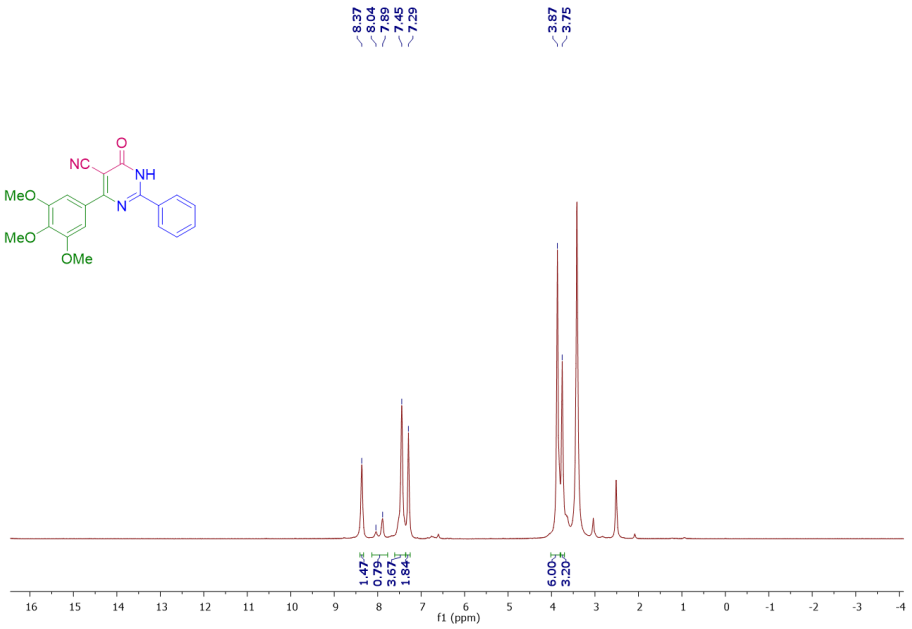

Figure S44: ^{1}H NMR spectrum for (**4e**) in DMSO (400MHz, 300K)

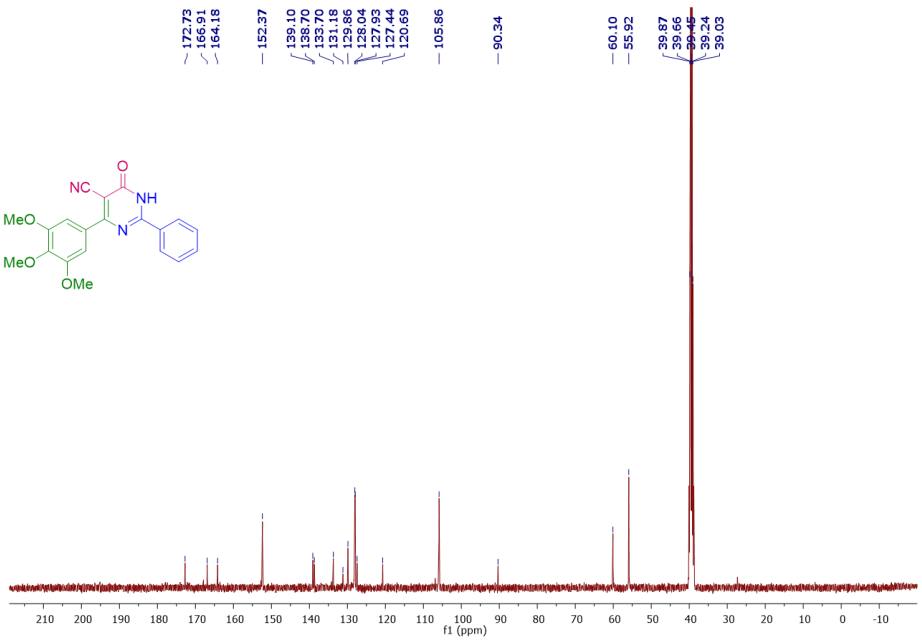

Figure S45: ^{13}C NMR spectrum for (**4e**) in DMSO (100MHz, 300K).

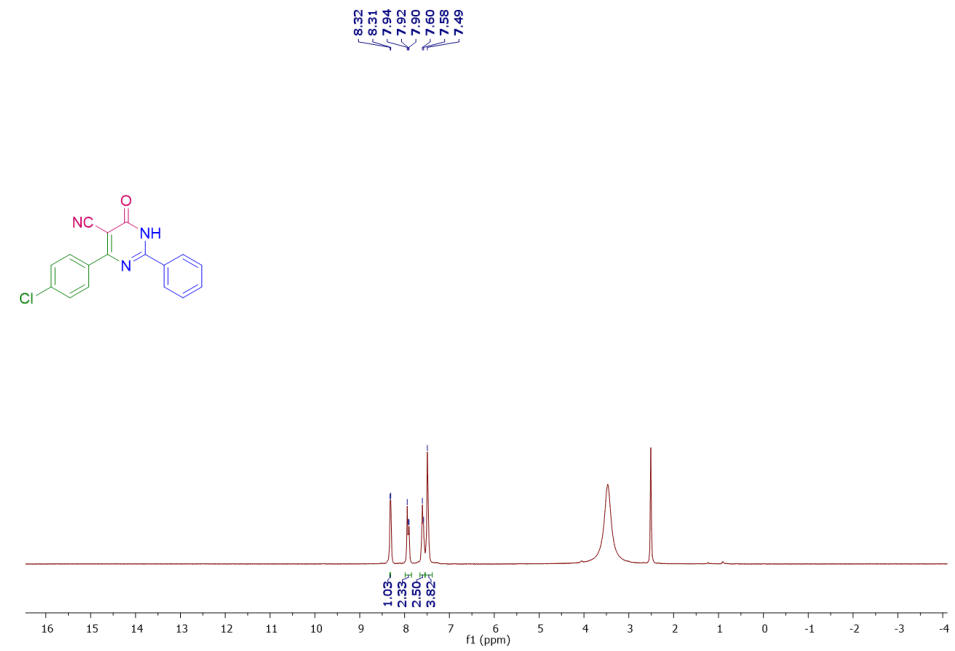

Figure S46: ^{1}H NMR spectrum for (**4f**) in DMSO (400MHz, 300K)

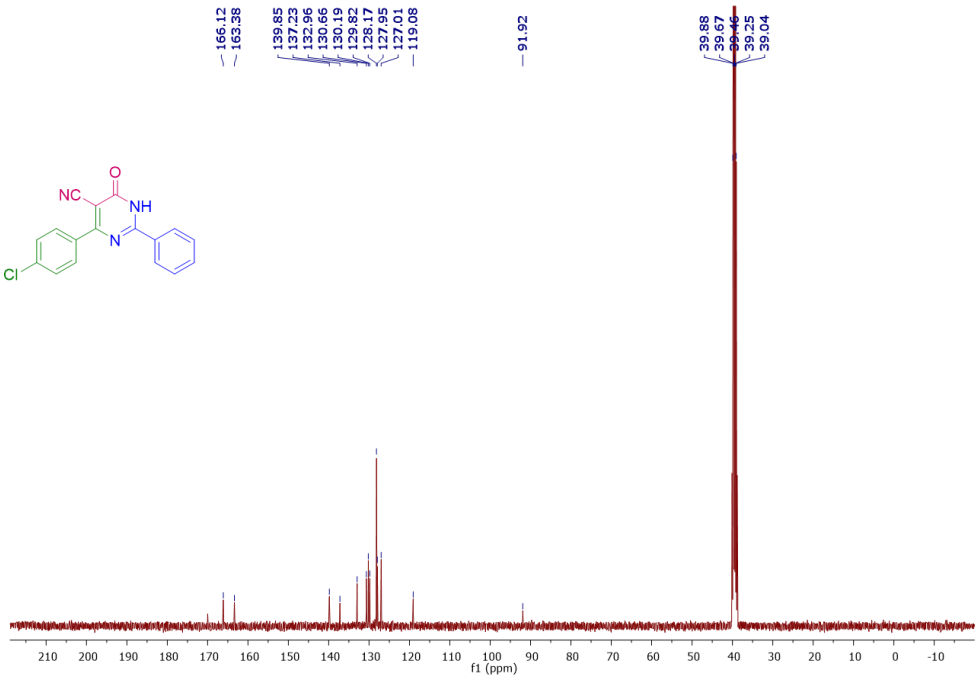

Figure S47: ^{13}C NMR spectrum for (**4f**) in DMSO (100MHz, 300K)

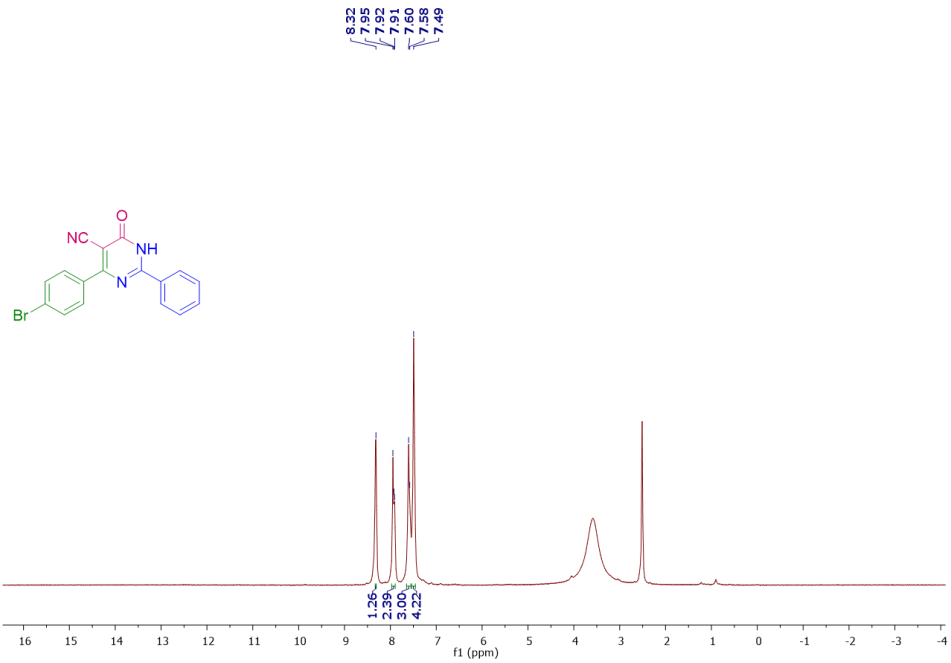

Figure S48: ^{1}H NMR spectrum for (**4g**) in DMSO (400MHz, 300K)

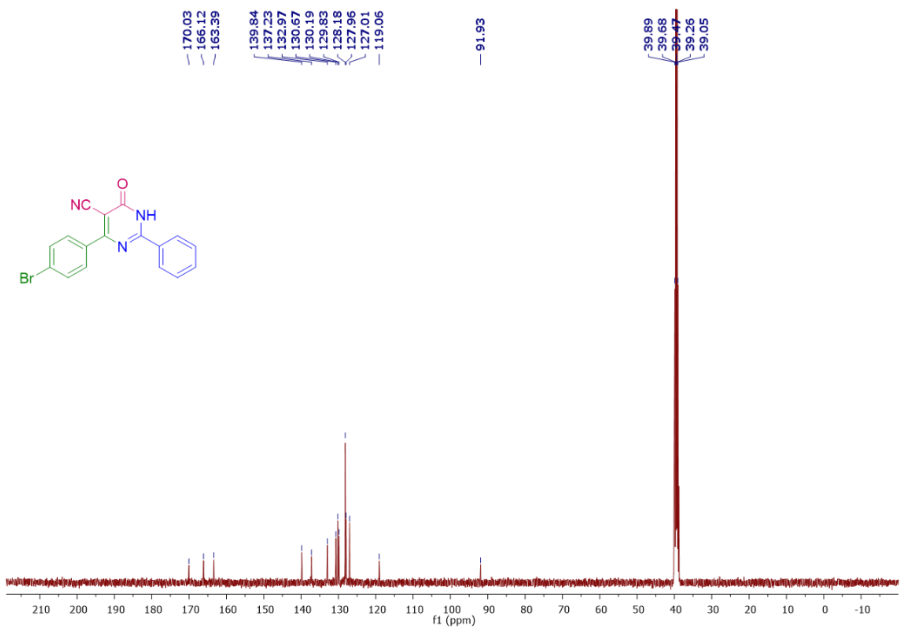

Figure S49: ^{13}C NMR spectrum for (**4g**) in DMSO (100MHz, 300K)

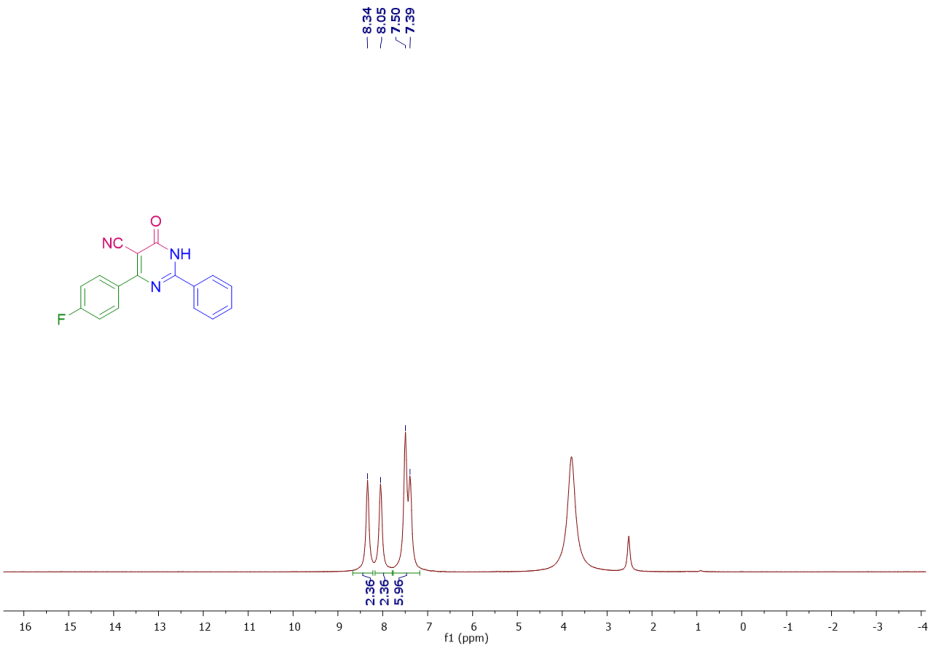

Figure S50: ^{1}H NMR spectrum for (**4h**) in DMSO (400MHz, 300K)

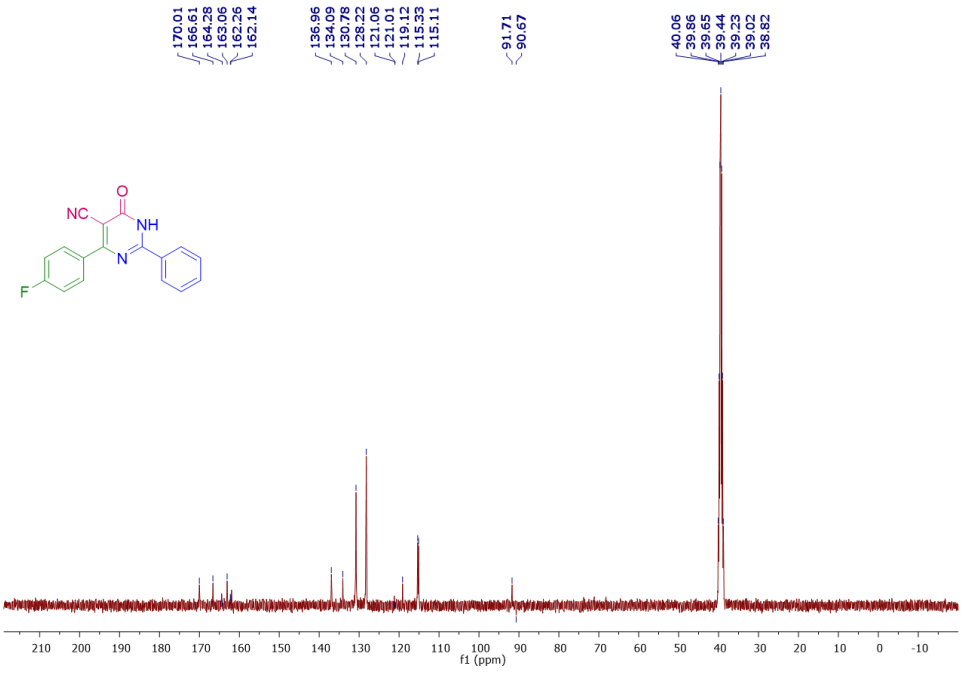

Figure S51: ^{13}C NMR spectrum for (**4h**) in DMSO (100MHz, 300K)

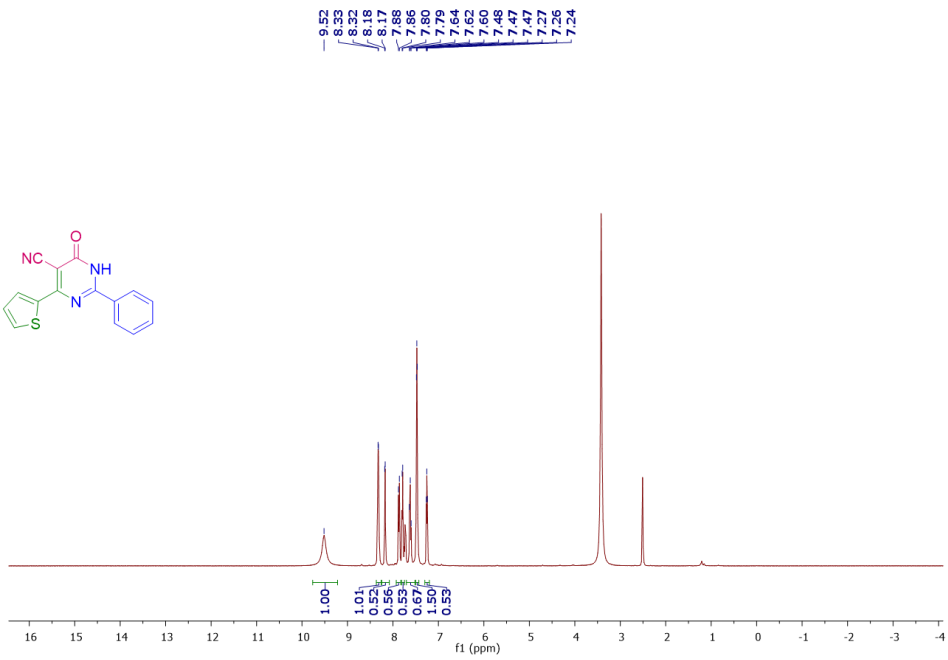

Figure S52: ^{1}H NMR spectrum for (**4i**) in DMSO (400MHz, 300K)

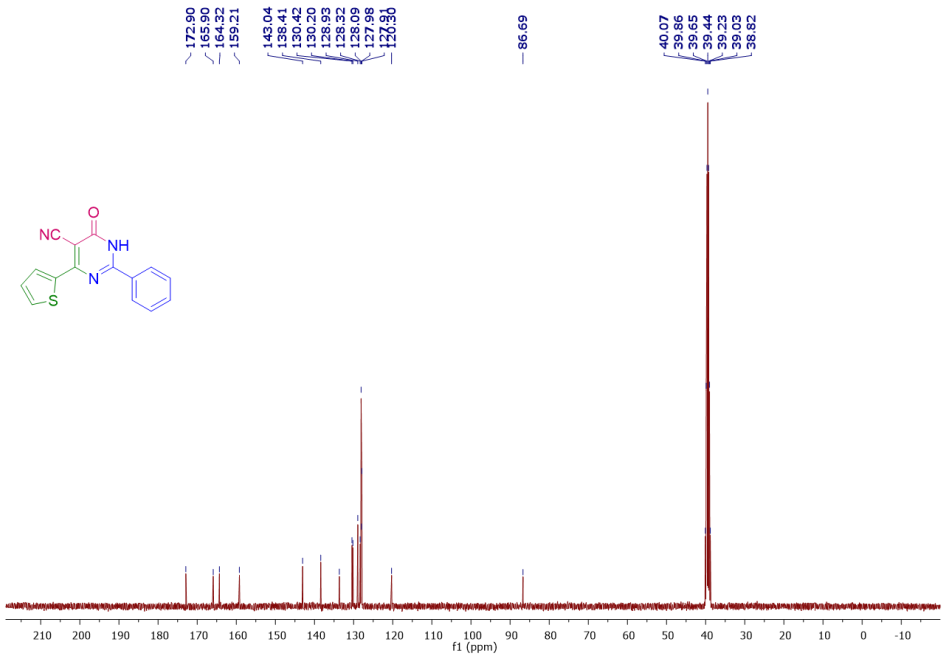

Figure S53: ^{13}C NMR spectrum for (**4i**) in DMSO (100MHz, 300K)

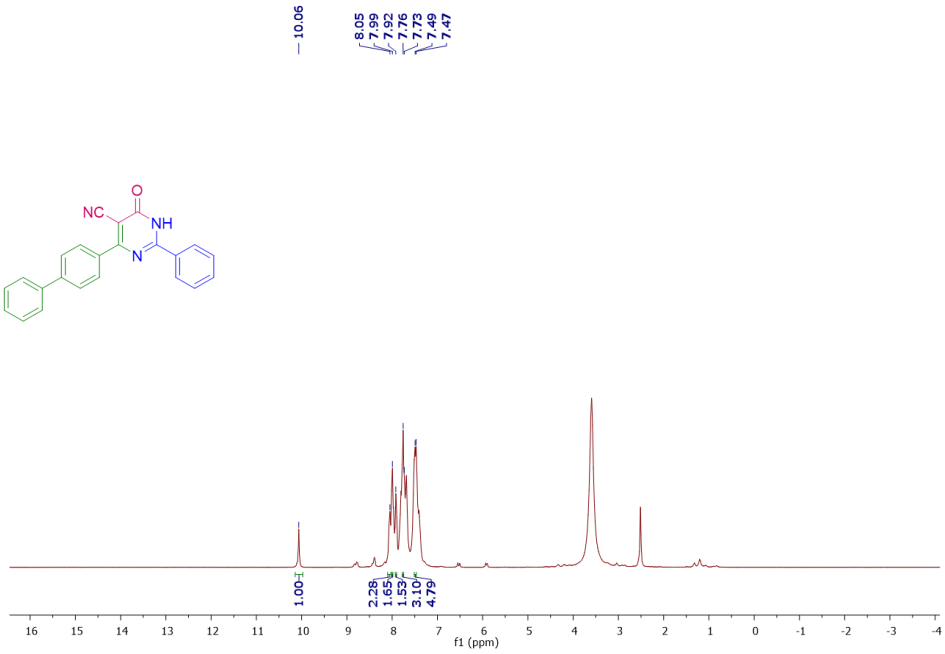

Figure S54: ^{1}H NMR spectrum for (**4j**) in DMSO (400MHz, 300K)

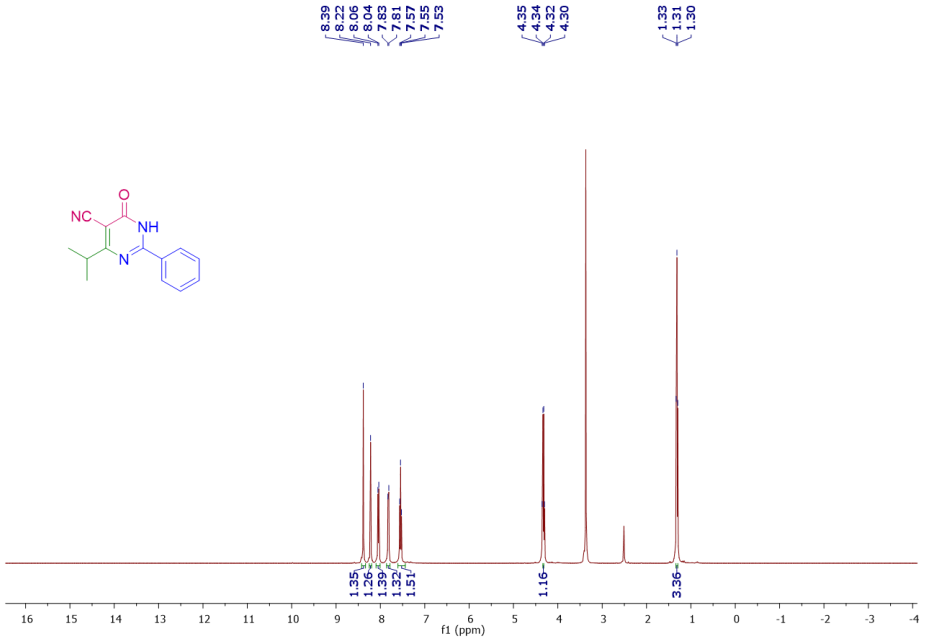

Figure S55: ^{1}H NMR spectrum for (**4k**) in DMSO (400MHz, 300K)

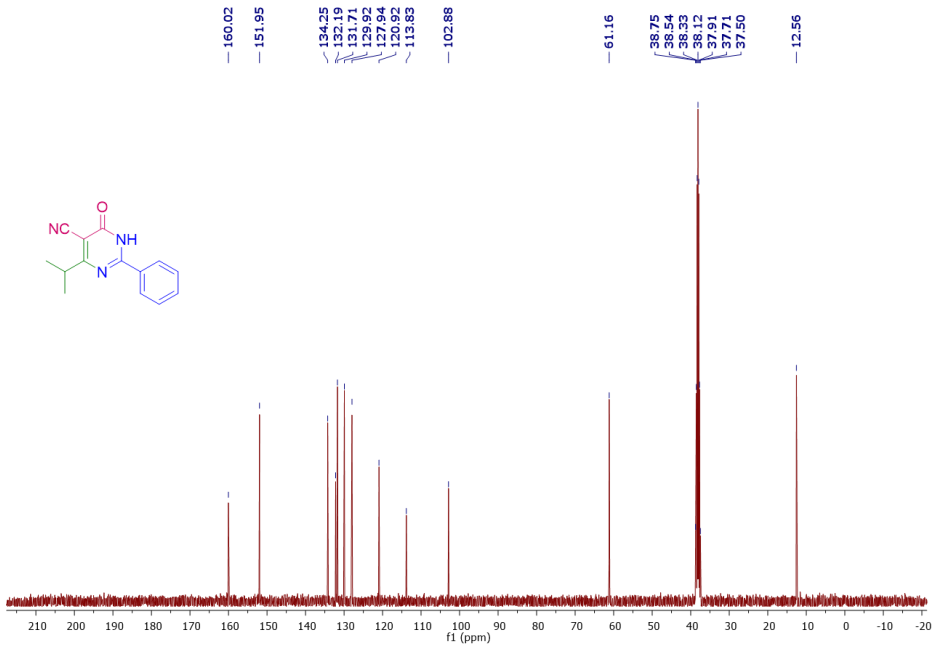

Figure S56: ^{13}C NMR spectrum for (**4k**) in DMSO (100MHz, 300K)

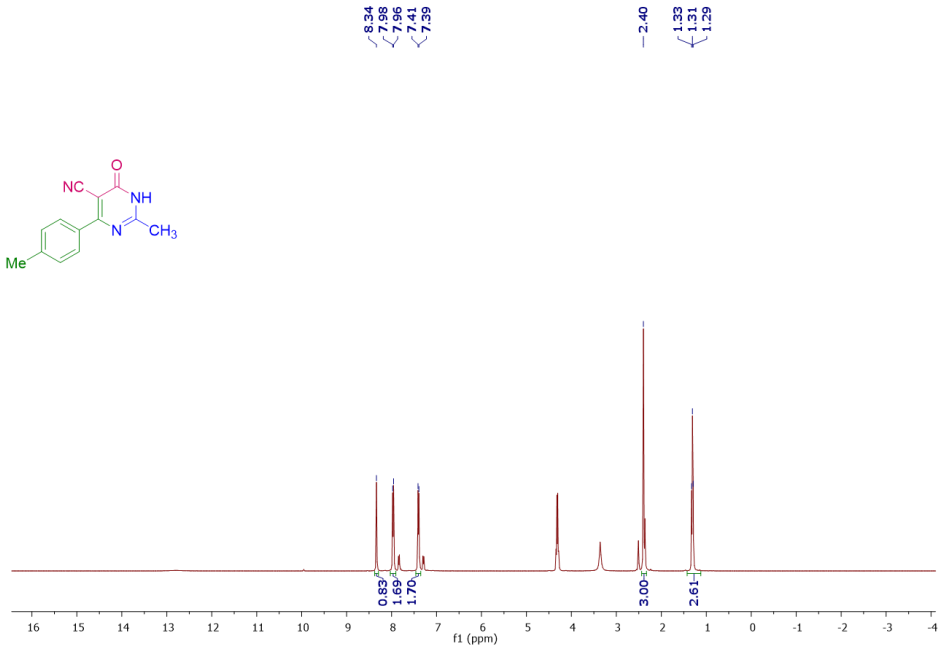

Figure S57: ^{1}H NMR spectrum for (**5a**) in DMSO (400MHz, 300K)

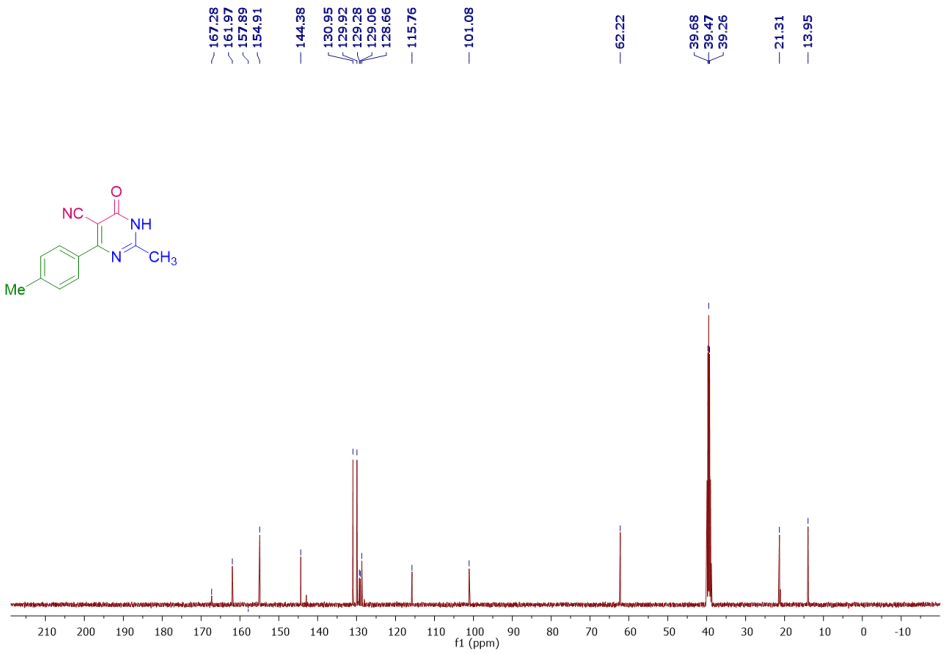

Figure S58: ^{13}C NMR spectrum for (**5a**) in DMSO (100MHz, 300K)

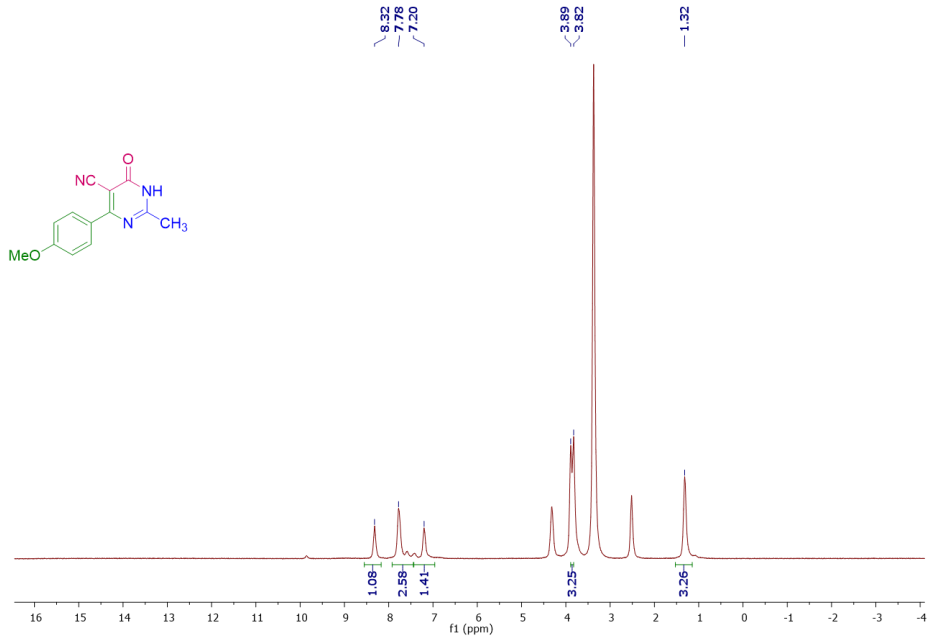

Figure S59: ^{1}H NMR spectrum for (**5b**) in DMSO (400MHz, 300K)

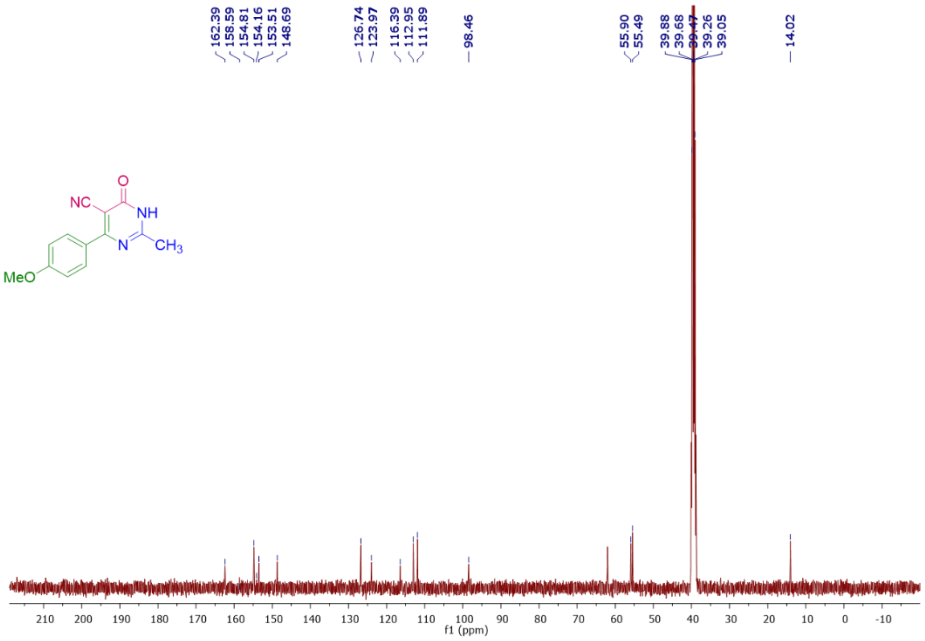

Figure S60: ^{13}C NMR spectrum for (**5b**) in DMSO (100MHz, 300K)

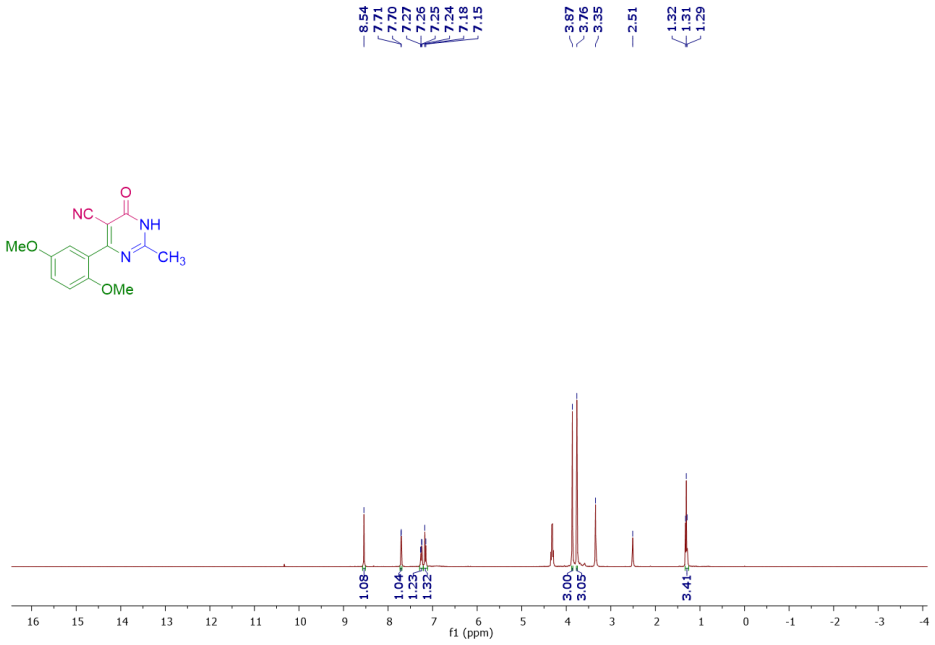

Figure S61: ^{1}H NMR spectrum for (**5c**) in DMSO (400MHz, 300K)

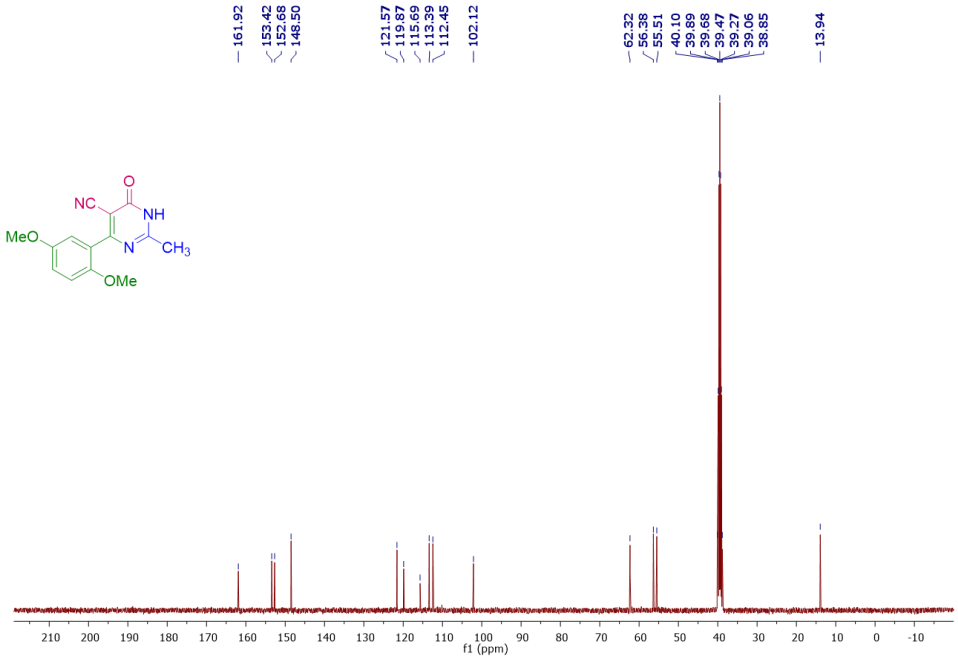

Figure S62: ^{13}C NMR spectrum for (**5c**) in DMSO (100MHz, 300K)

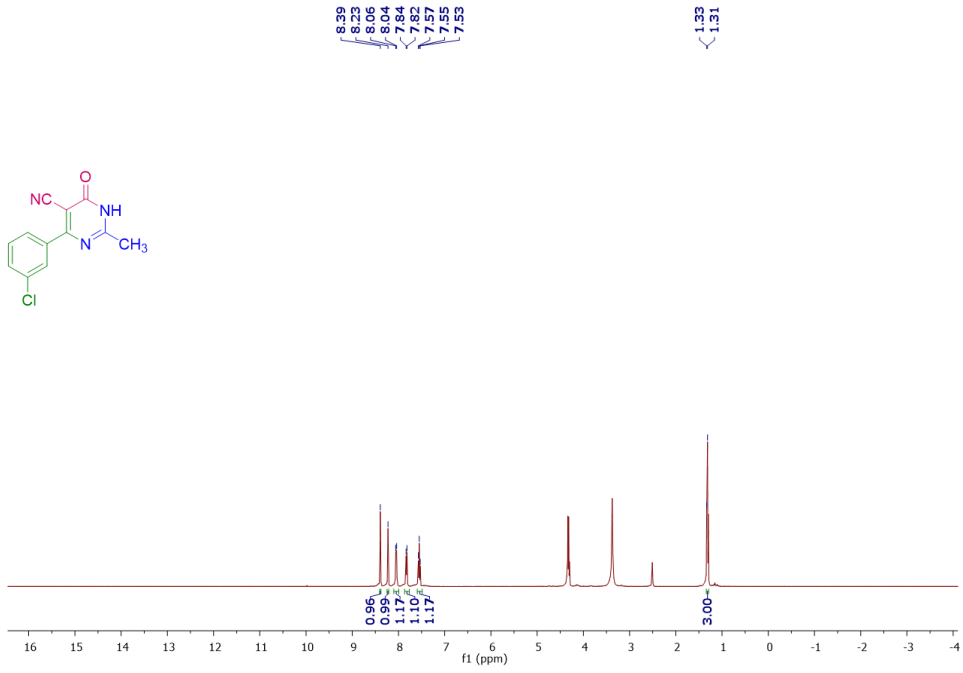

Figure S63: ^{1}H NMR spectrum for (**5d**) in DMSO (400MHz, 300K).

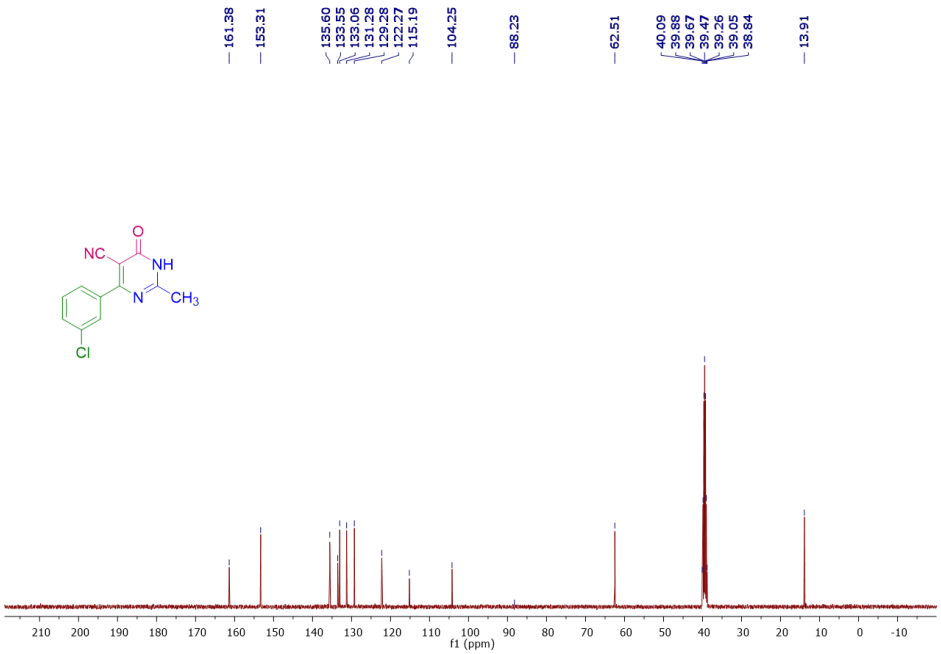

Figure S64: ^{13}C NMR spectrum for (**5d**) in DMSO (100MHz, 300K).

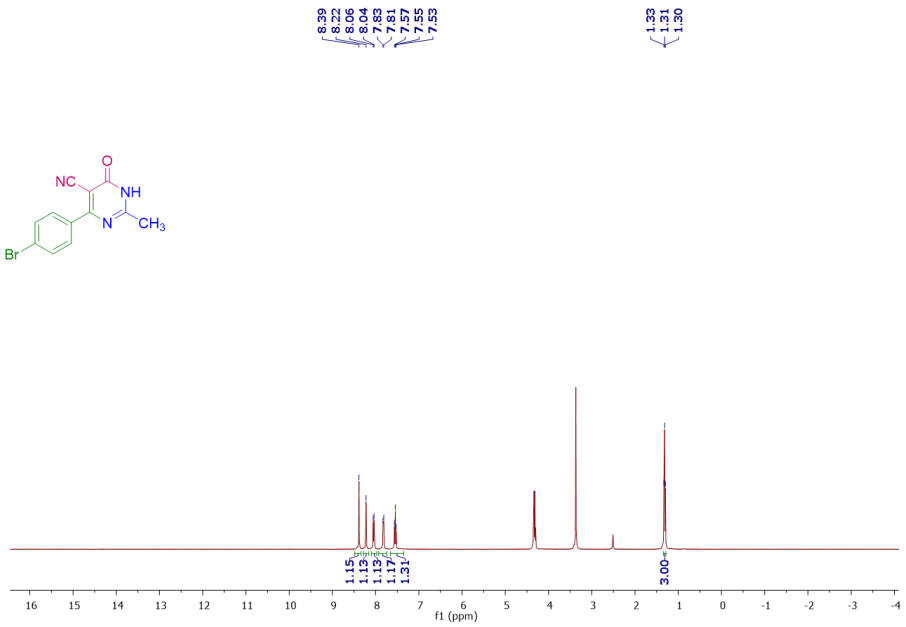

Figure S65: ^{1}H NMR spectrum for (**5e**) in DMSO (400MHz, 300K)

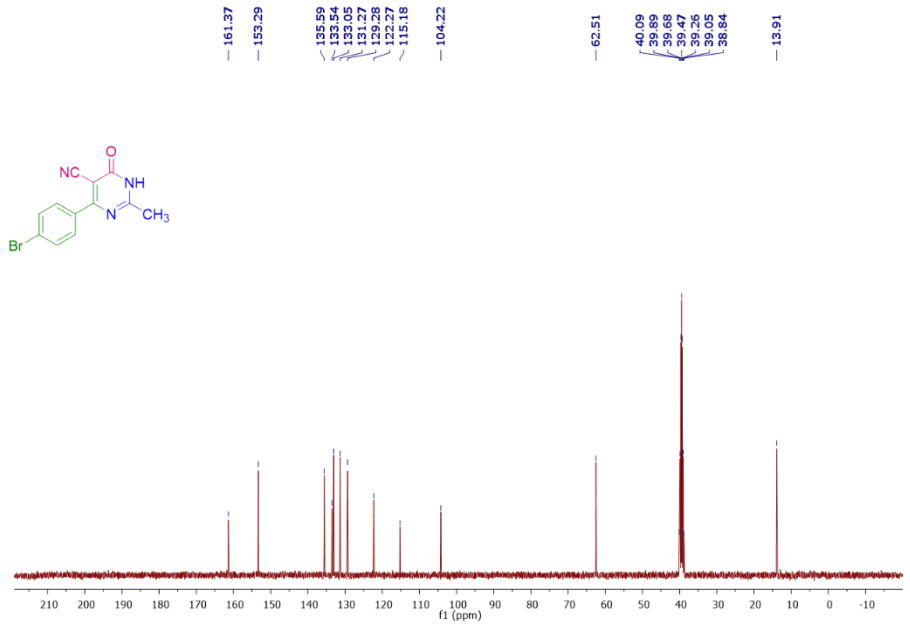

Figure S66: ^{13}C NMR spectrum for (**5e**) in DMSO (100MHz, 300K)

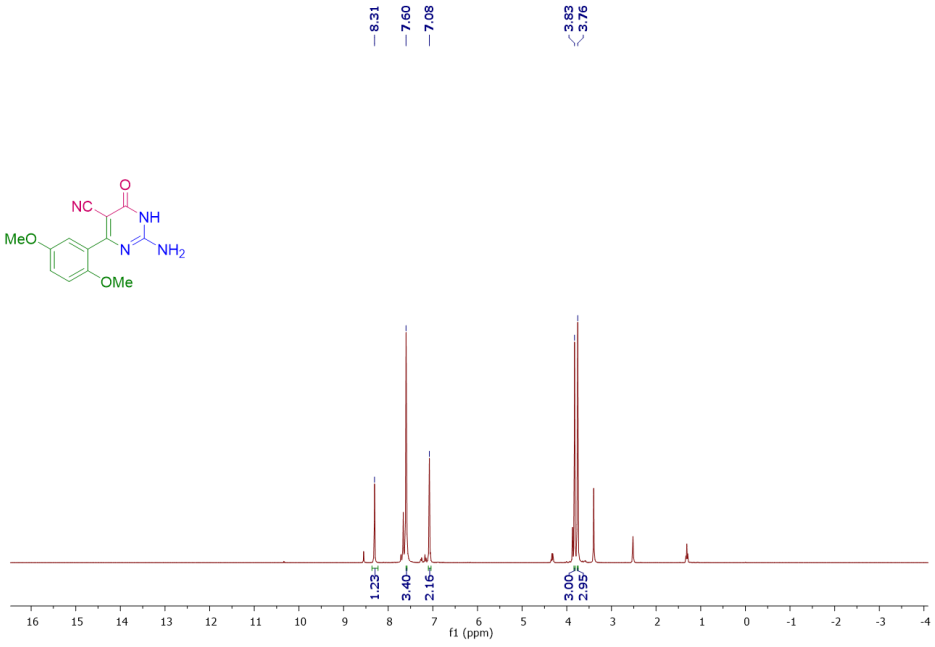

Figure S67: ^{1}H NMR spectrum for (**6a**) in DMSO (400MHz, 300K).

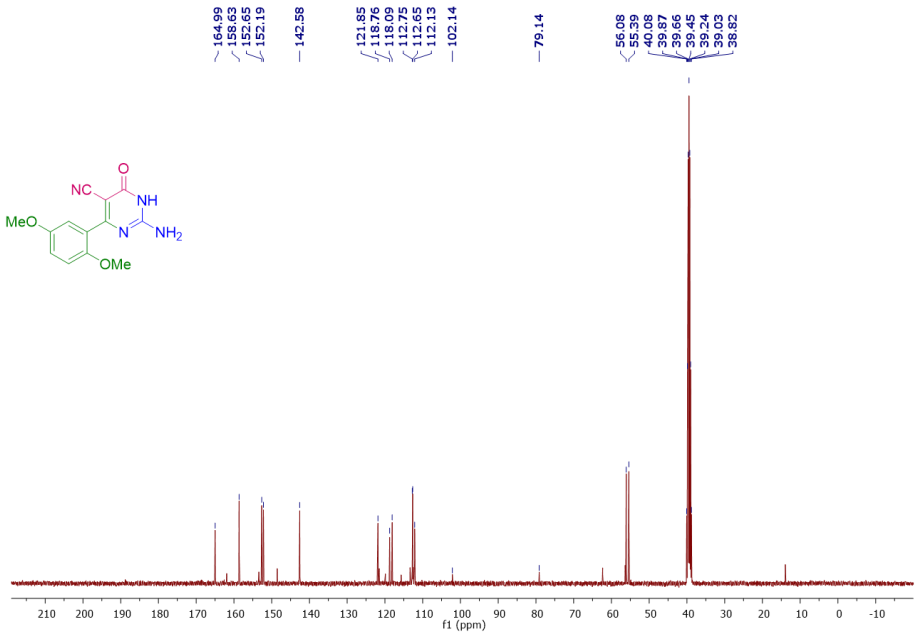

Figure S68: ^{13}C NMR spectrum for (**6a**) in DMSO (100MHz, 300K).

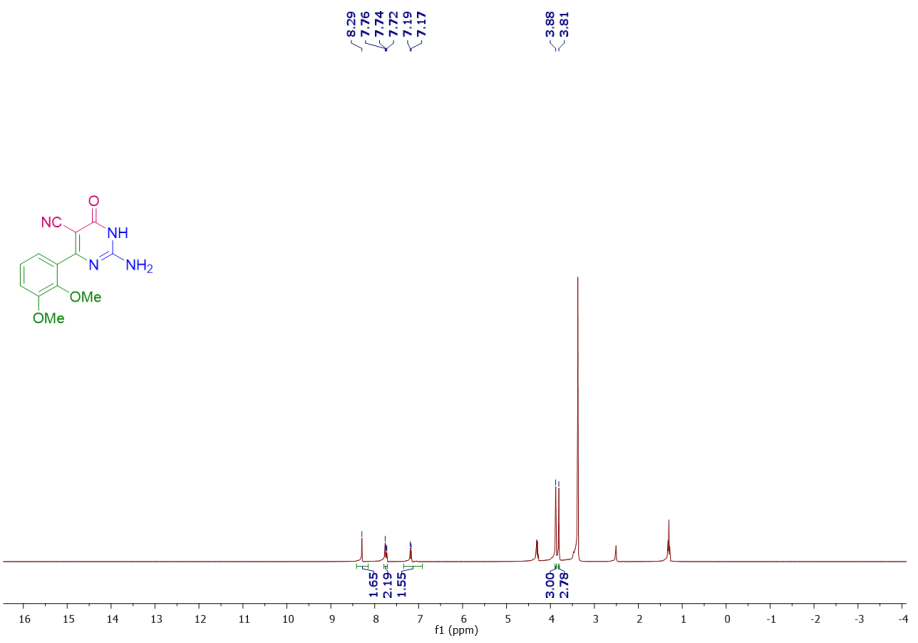

Figure S69: ^{1}H NMR spectrum for (**6b**) in DMSO (400MHz, 300K).

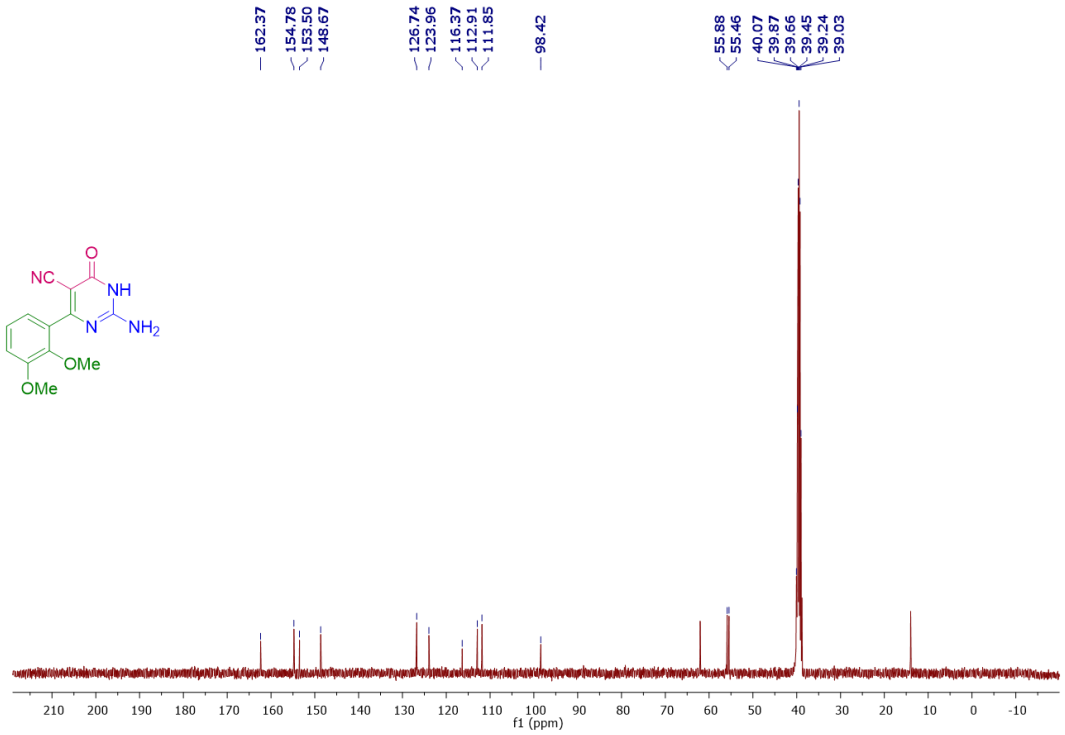

Figure S70: ^{13}C NMR spectrum for (**6b**) in DMSO (100MHz, 300K).

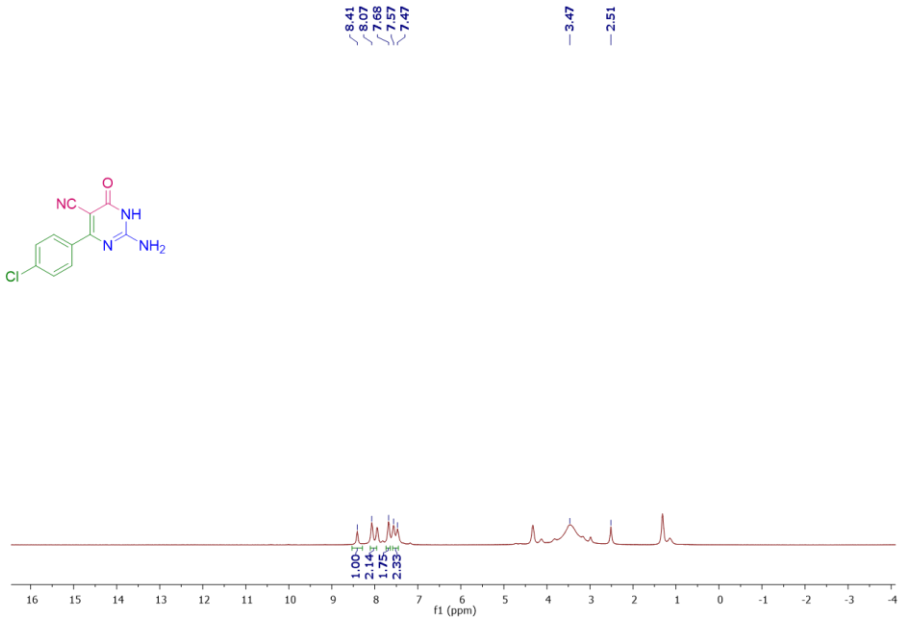

Figure S71: ^{1}H NMR spectrum for (**6c**) in DMSO (400MHz, 300K).

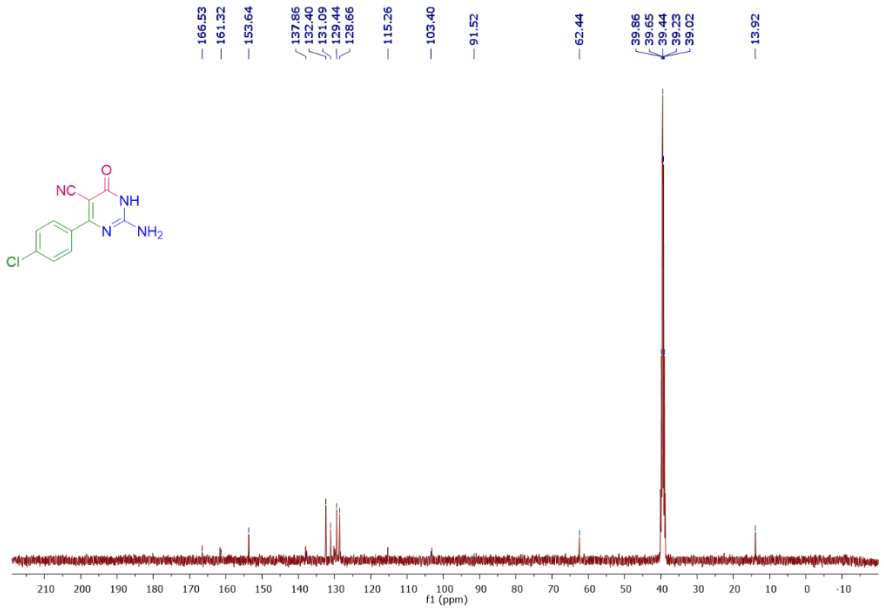

Figure S72: ^{13}C NMR spectrum for (**6c**) in DMSO (100MHz, 300K).

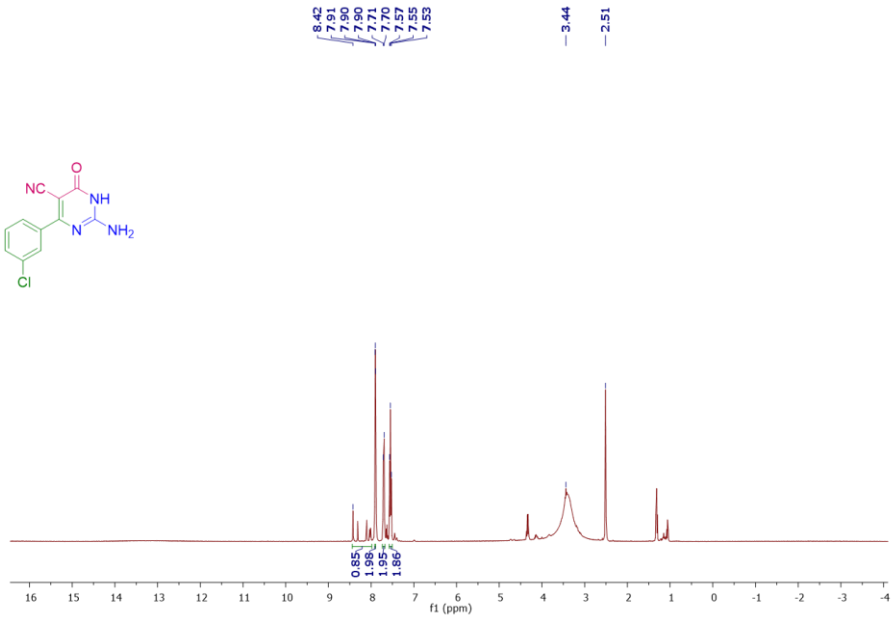

Figure S73: ^{1}H NMR spectrum for (**6d**) in DMSO (400MHz, 300K).

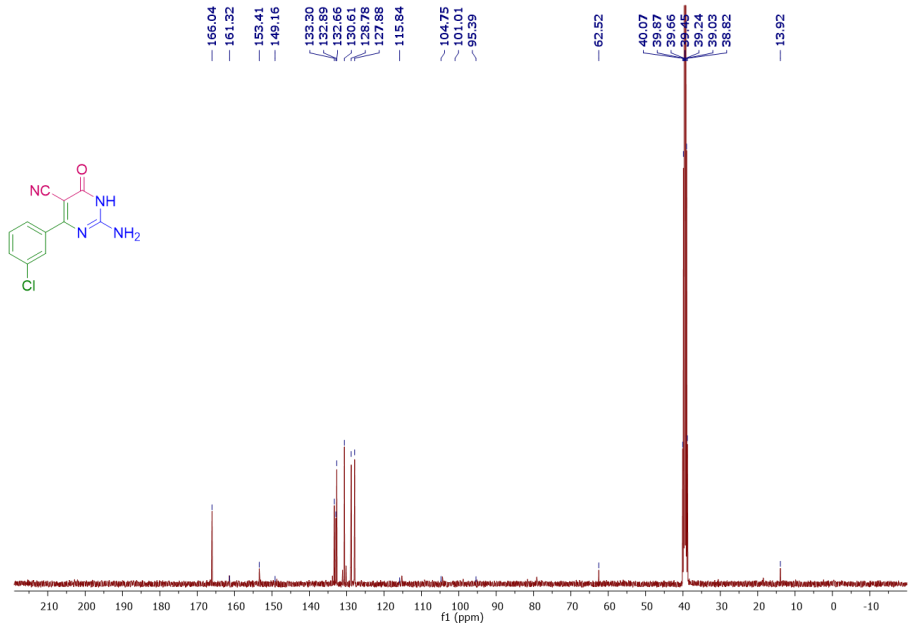

Figure S74: ^{13}C NMR spectrum for (**6d**) in DMSO (100MHz, 300K).

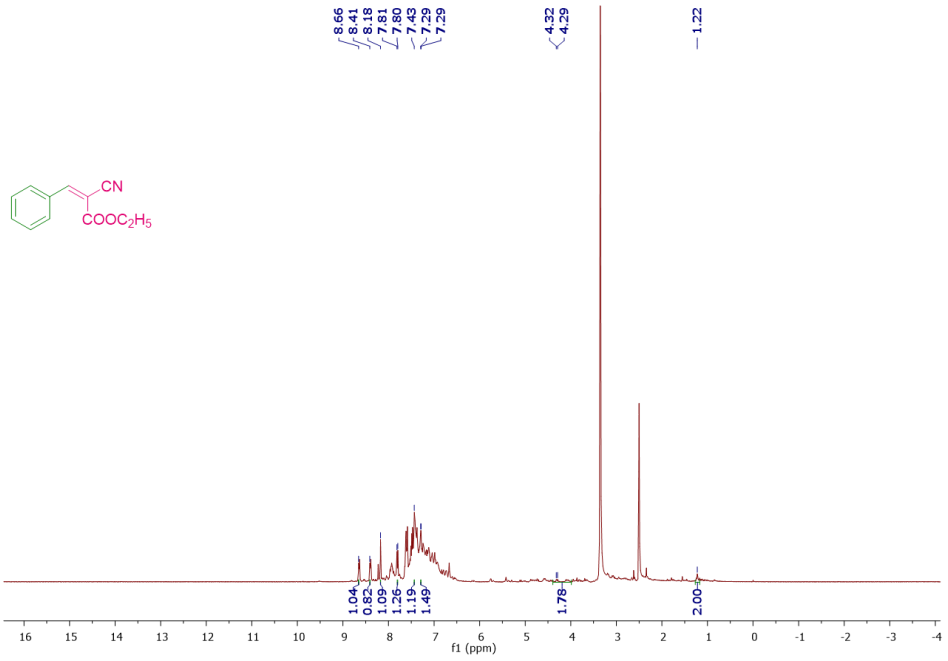

Figure S75: ^{1}H NMR spectrum for (**2a'**) in DMSO (400MHz, 300K).

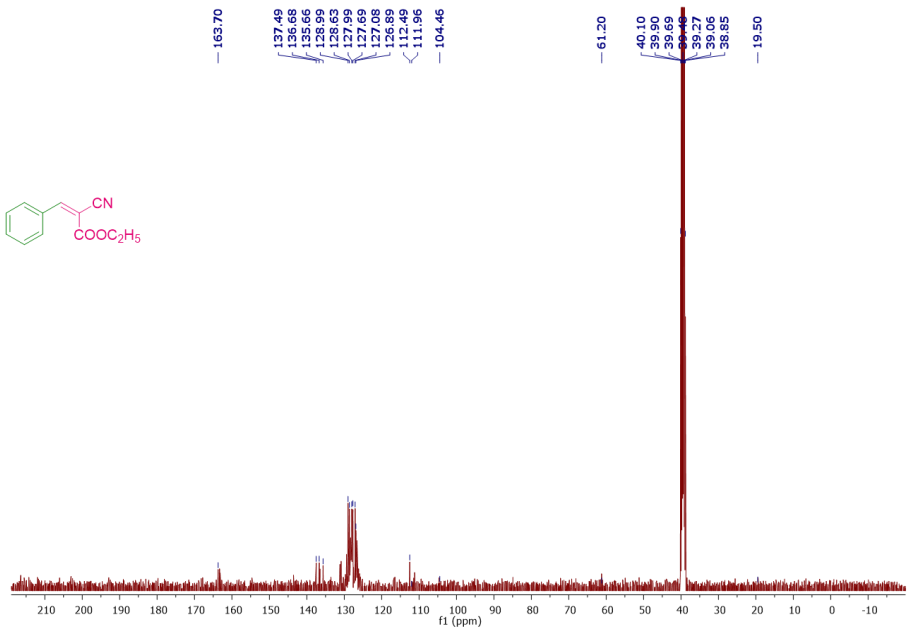

Figure S76: ^{13}C NMR spectrum for (**2a'**) in DMSO (100MHz, 300K).

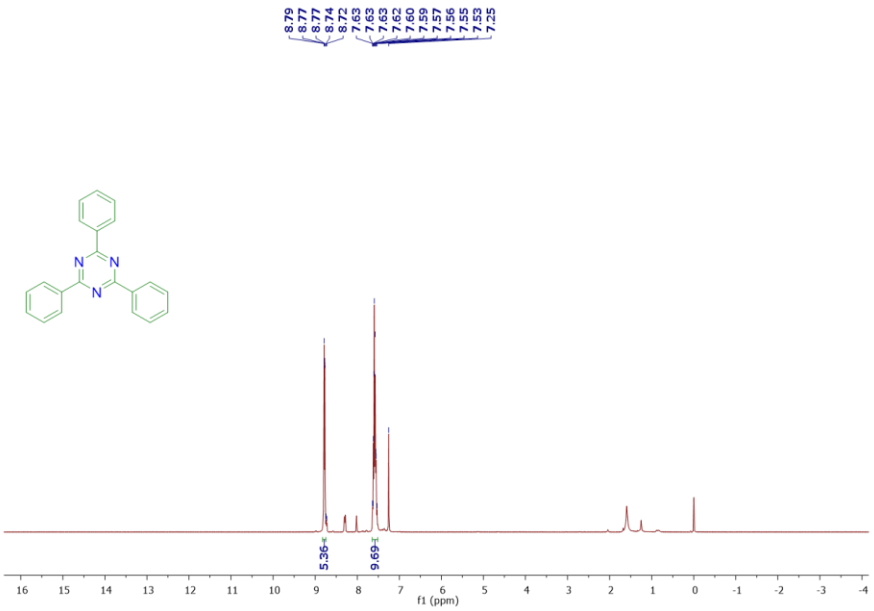

Figure S77: ^{1}H NMR spectrum for 2,4,6-triphenyl-1,3,5-triazine in DMSO (400MHz, 300K).

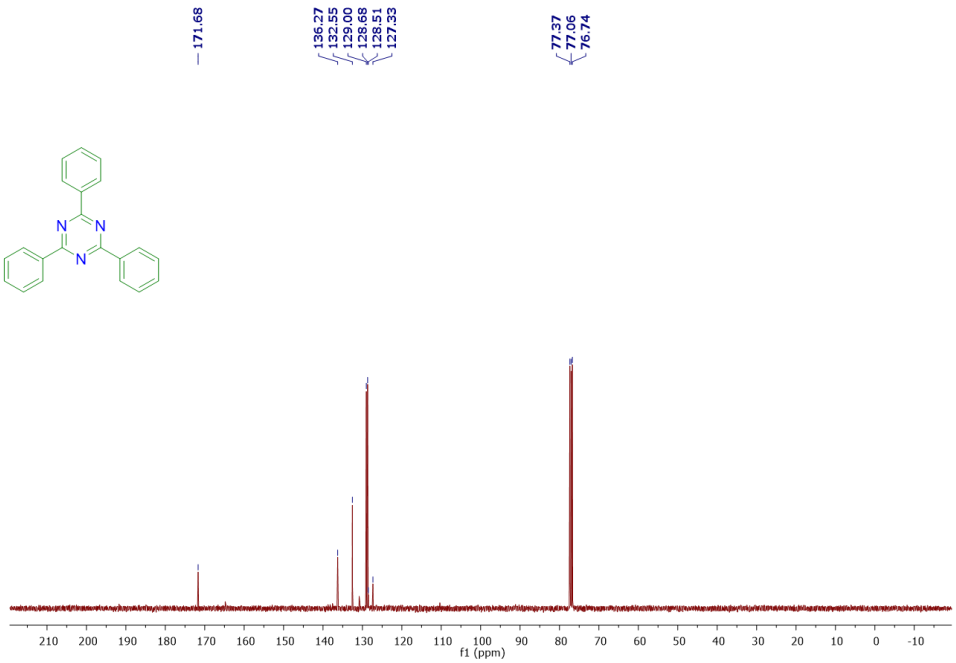

Figure S78: ^{13}C NMR spectrum for 2,4,6-triphenyl-1,3,5-triazinein DMSO (100MHz, 300K).

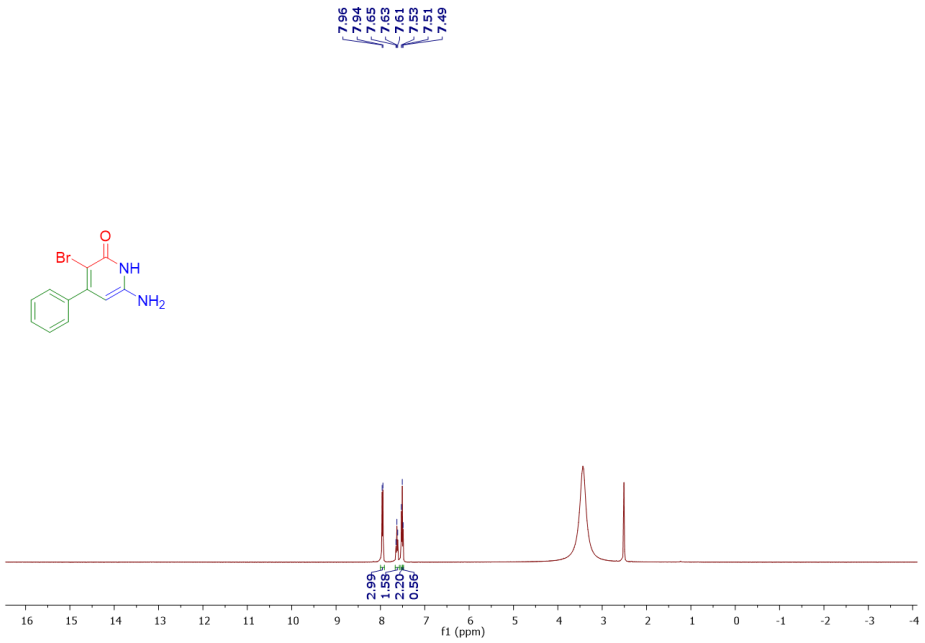

Figure S79: ^{1}H NMR spectrum for (**bropirimine)** in DMSO (400MHz, 300K).

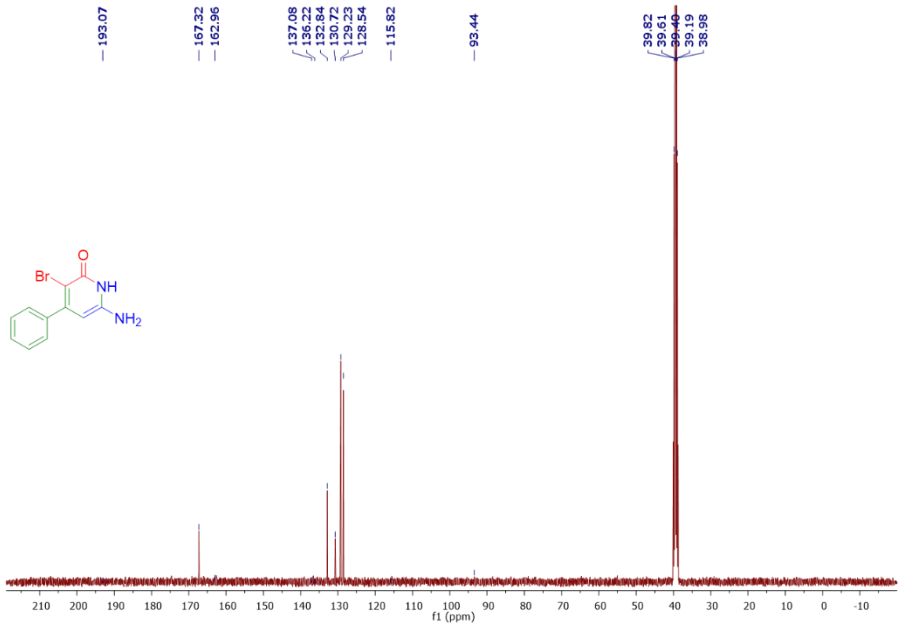

Figure S80: ^{13}C NMR spectrum for (**bropirimine**) in DMSO (100MHz, 300K).

6. References

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