

# Sustainable Synthesis of Substituted 1,3,5-triazines by [ONO]- Pincer Supported Nickel(II) Complexes *via* Acceptorless Dehydrogenation Coupling Strategy

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## **1. Experimental section**

### **Methods and materials**

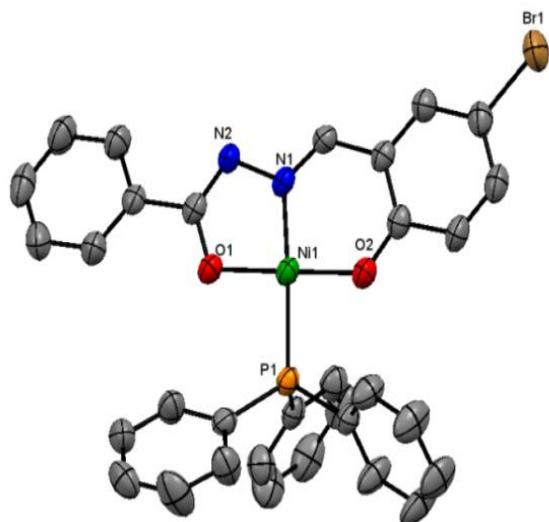
CHNS elemental Vario EL III elemental analyzer instrument was used to perform elemental analyses (C, H, and N). Perkin-Elmer 597 spectrophotometers have been used to record FT-IR spectra of the complexes in the range 4000–400 cm<sup>-1</sup>. Melting points were determined by Boetius micro heating table melting point apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in Bruker 400 MHz in using TMS as an internal standard. spectrometer using CDCl<sub>3</sub>/d<sub>6</sub>-DMSO as solvents on 400 and 100 MHz instruments respectively. The HRMS data was recorded in Agilent mass spectrometer 6350 using Q-TOF mass analyzer. Nickel precursor, [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (97%), Benzhydrazides (95–98%), solvents, benzamidine/guanidine hydrochloride and primary alcohols were purchased from commercial suppliers and used as received. Reagent grade solvents purchased from standard suppliers were purified and dried according to standard procedures.<sup>1</sup>

## 2. X-ray Crystallography

A single crystal with high quality and exhibiting good morphology was chosen for X-ray diffraction intensity measurements. The X-ray diffraction intensity data was collected at room temperature (293 K) on a Bruker D8 Quest Eco diffractometer using MoK $\alpha$  radiation (0.71073 Å). During the data collection, the crystal to detector distance was set to 4.5 cm. The data collection was monitored by APEX-III program suit.<sup>2</sup> further, the integration, Lorentz and polarization corrections and merging of data were carried out using SAINT. The absorption correction was performed by SADABS and the data was averaged using SORTAV software.<sup>3</sup> The hydrogen atoms of all C–H, N–H and O–H hydrogen bonds were located from the difference Fourier map and were refined isotropically. Idealized methyl group H-atom position was calculated geometrically [C–H = 0.96 Å]<sup>°</sup>and refined using riding model with Uiso(H) = 1.5 Ueq (C). The structure was solved by direct methods using SHELXS-2014<sup>4</sup>and refined by SHELXL-2014<sup>5</sup> programs incorporated to WINGX package.<sup>6</sup> The ORTEP of the molecule with displacement ellipsoids drawn at 50% probability level are shown in (Fig. 1). The molecular and packing diagrams were generated using the software MERCURY.<sup>7</sup> The CCDC number of complex **1** and **2** are **2247707** and **2247709** respectively.

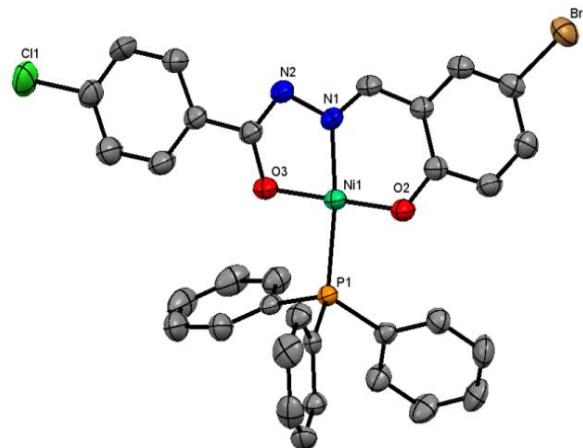
## Crystal Structures of Nickel(II)Pincer Complexes

Fortunately, the molecular architecture of ONO pincer-type nickel(II) complexes **1** and **2** were confirmed by single-crystal X-ray diffraction. The single crystals were grown by slow evaporation in equal ratio of dichloromethane and ethanol solvent mixture at room temperature. The complex **1** was crystallized in a monoclinic crystal system with a "P21/c" space group whereas the complex **2** was crystallized in an orthorhombic with "Pbca" space group. The single crystal XRD revealed that the hydrazone ligand is coordinated to nickel ion via phenolic oxygen(-OH), azomethine nitrogen(-N=CH-) and imidolate oxygen(=C=O) atoms. Therefore, the hydrazone ligands coordinates to the nickel ion via dibasic tridentate O<sup>2-</sup>N<sup>+</sup>O fashion with the formation of one five and one six membered chelated rings which generates an asymmetric pincer-type complex. The fourth position was occupied by the triphenylphosphine group and thus the complexes adopt a distorted square plane geometry around the Ni(II) ion. The bite angles of the complex **1** and **2** N(1)-Ni-O(1) 83.56°, N(1)-Ni-O(2) 95.51° and O(2)-Ni-(1)-N(1) 95.62°, N(1)-Ni(1)-O(3) 83.28° are respectively (**Figure 2 & 3**). The bond angles and distances of the square planar Ni(II) pincer complexes are comparable with other reported nickel complexes.<sup>37</sup>



**Figure S1. ORTEP view of the Complex 1 (CCDC: 2247707).** The thermal ellipsoids are drawn with a 30% probability level. All the hydrogen atoms are omitted for clarity. The selected bond distances (Å) and angles (°) Ni(1)-P(1) 2.2273(9), Ni(1)-O(1) 1.842(8), Ni(1)-O(2) 1.810(2), Ni(1)-N(1) 1.847(3), Br(1)-C(13) 1.899(4), P(1)-C(15) 1.823(3), P(1)-C(21) 1.821(3), P(1)-C(27) 1.816(3), O(1)-C(1) 1.314(4), O(2)-C(10) 1.311(4), N(1)-N(2)

1.397(3), N(1)-C(8) 1.285(4), N(2)-C(1) 1.293(4) and O(1)-Ni-(1)-P(1) 92.38(7), O(1)-Ni(1)-N(1) 83.56(10), O(2)-Ni(1)-N(1) 95(51), O(2)-Ni(1)-P(1) 88.37(8), O(2)-Ni(1)-O(1) 177.92(11), O(2)-Ni(1)-N(1) 95.51(11), N(1)-Ni(1)-P(1) 173.28(8), C(15)-P(1)-N(1) 117.91(10), C(15)-P(1)-C(21) 104.97(15) and C(21)-P(1)-Ni(1) 106.75(11).



**Figure S2. ORTEP view of the Complex 2(CCDC: 2247709).** The thermal ellipsoids are drawn with a 30% probability level. All the hydrogen atoms are omitted for clarity. The selected bond distances ( $\text{\AA}$ ) and angles ( $^{\circ}$ ) Ni(1)-P(1) 2.2439(9), Ni(1)-O(2) 1.816(2), Ni(1)-O(3) 1.827(2), Ni(1)-N(1) 1.856(3), Br(1)-C(13) 1.895(3), Cl(1)-C(5) 1.738(4), P(1)-C(15) 1.823(3), P(1)-C(21) 1.817(3), P(1)-C(27) 1.815(3), O(2)-C(10) 1.316(4), O(3)-C(1) 1.311(4), N(1)-N(2) 1.403(4), N(1)-C(8) 1.289(4), N(2)-C(1) 1.292(4) and O(2)-Ni-(1)-P(1) 92.82(7), O(2)-Ni(1)-O(3) 176.56(11), O(2)-Ni(1)-N(1) 95.62(11), O(3)-Ni(1)-P(1) 88.37(7), O(3)-Ni(1)-N(1) 83.28(11), N(1)-Ni(1)-P(1) 171.48(8), C(15)-P(1)-Ni(1) 119.91(10), C(21)-P(1)-Ni(1) 112.03(10) and C(21)-P(1)-C(15) 102.83(14), C(27)-P(1)-Ni(1) 126.4(2).

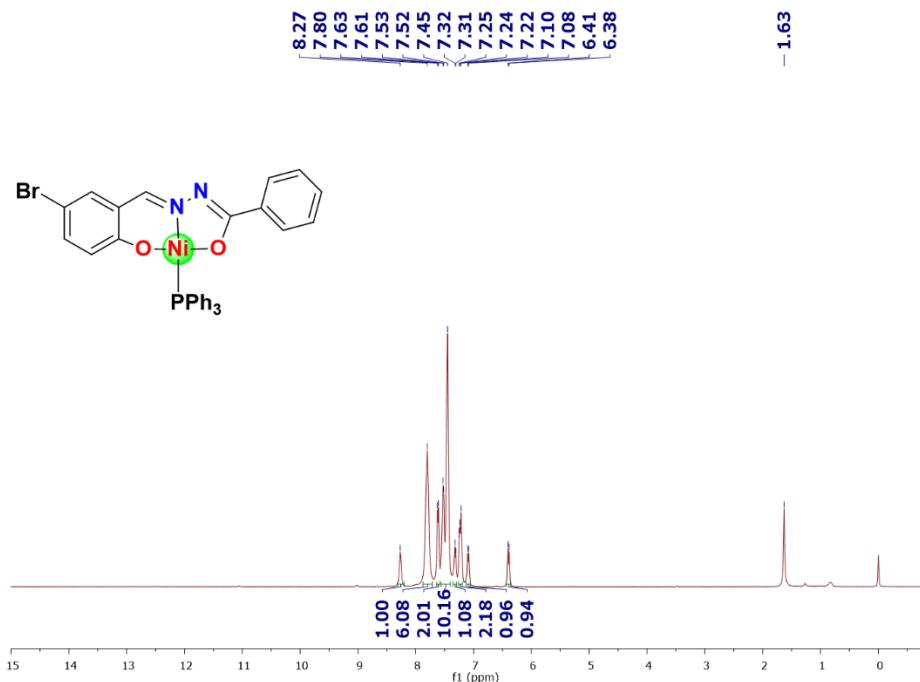
### 3. Crystallographic Refinement Parameters, bond angles and lengths

Identification code	Complex 1	Complex 2
Empirical formula	C <sub>32</sub> H <sub>24</sub> BrN <sub>2</sub> NiO <sub>2</sub> P	C <sub>32</sub> H <sub>23</sub> BrClN <sub>2</sub> NiO <sub>2</sub> P
Formula weight	638.12	672.56
Temperature/K	293(2)	293(2)
Crystal system	monoclinic	orthorhombic
Space group	P2 <sub>1</sub> /c	Pbca
a/Å	12.2894(8)	10.0944(4)
b/Å	20.7912(15)	18.3047(6)
c/Å	10.8663(8)	30.5513(12)
α/°	90	90
β/°	94.441(6)	90
γ/°	90	90
Volume/Å <sup>3</sup>	2768.1(3)	5645.2(3)
Z	4	8
ρcalcg/cm <sup>3</sup>	1.531	1.583
μ/mm <sup>-1</sup>	2.235	2.288
F(000)	1296.0	2720.0
Crystal size/mm <sup>3</sup>	0.26 × 0.18 × 0.06	0.31 × 0.13 × 0.07
Radiation	Mo Kα ( $\lambda = 0.71073$ )	Mo Kα ( $\lambda = 0.71073$ )
2Θ range for data collection/°	6.934 to 58.938	6.69 to 58.628
Index ranges	-16 ≤ h ≤ 13, -27 ≤ k ≤ 24, -13 ≤ l ≤ 14	-12 ≤ h ≤ 8, -17 ≤ k ≤ 25, -28 ≤ l ≤ 41
Reflections collected	14918	19300
Independent reflections	6639 [R <sub>int</sub> = 0.0445, R <sub>sigma</sub> = 0.0771]	6740 [R <sub>int</sub> = 0.0357, R <sub>sigma</sub> = 0.0465]
Data/restraints/parameters	6639/0/352	6740/0/361
Goodness-of-fit on F <sup>2</sup>	1.009	1.036
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0518, wR <sub>2</sub> = 0.0979	R <sub>1</sub> = 0.0511, wR <sub>2</sub> = 0.1027
Final R indexes [all data]	R <sub>1</sub> = 0.1011, wR <sub>2</sub> = 0.1173	R <sub>1</sub> = 0.0791, wR <sub>2</sub> = 0.1142
Largest diff. peak/hole / e Å <sup>-3</sup>	0.80/-0.84	0.97/-0.41

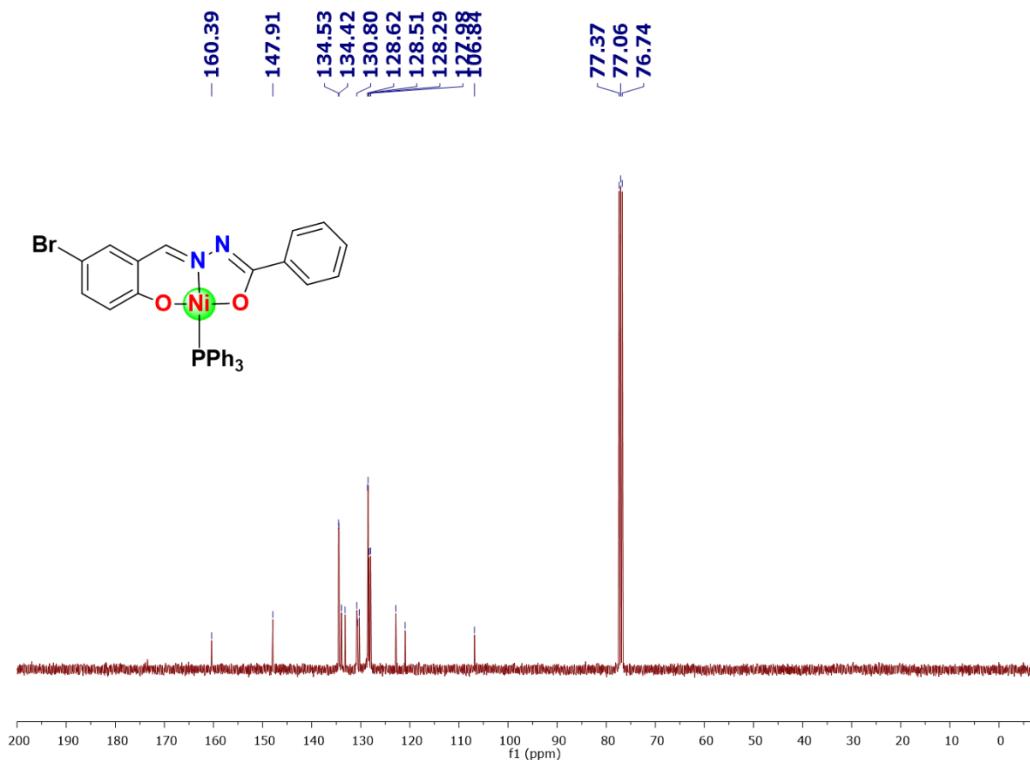
**Selected Bond Distances (Å) and Angles (deg) of Ni(II) Pincer Complexes 1 and 2**

Bond distances	Complex 1	Complex 2
Ni(1)-P(1)	2.2273(9)	2.2439(9)
Ni-O	Ni(1)-O(1) 1.842(8) Ni(1)-O(2) 1.810(2)	Ni(1)-O(2) 1.816(2) Ni(1)-O(3) 1.827(2)
Br(1)-C(13)	1.899(4)	1.895(3)
Ni(1)-N(1)	1.847(3)	1.856(3)
P(1)-C(15)	1.823(3),	1.823(3)
P(1)-C(21)	1.821(3),	1.817(3),
P(1)-C(27)	1.816(3),	1.815(3)
O-C	O(1)-C(1) 1.314(4), O(2)-C(10) 1.311(4),	O(2)-C(10) 1.316(4) O(3)-C(1) 1.311(4)
N(1)-N(2)	1.397(3),	1.403(4)
N(1)-C(8)	1.285(4),	1.289(4)
N(2)-C(1)	1.293(4)	1.292(4)
Bond Angles	Complex 1	Complex 2
1.	O(1)-Ni-(1)-P(1) 92.38(7)	O(2)-Ni-(1)-P(1) 92.82(7)
2.	O(1)-Ni(1)-N(1) 83.56(10)	O(2)-Ni(1)-O(3) 176.56(11)
3.	O(2)-Ni(1)-N(1) 95(51)	O(2)-Ni(1)-N(1) 95.62(11)
4.	O(2)-Ni(1)-P(1) 88.37(8)	O(3)-Ni(1)-P(1) 88.37(7)
5.	O(2)-Ni(1)-O(1) 177.92(11)	O(3)-Ni(1)-N(1) 83.28(11)
6.	N(1)-Ni(1)-P(1) 173.28(8)	N(1)-Ni(1)-P(1) 171.48(8)

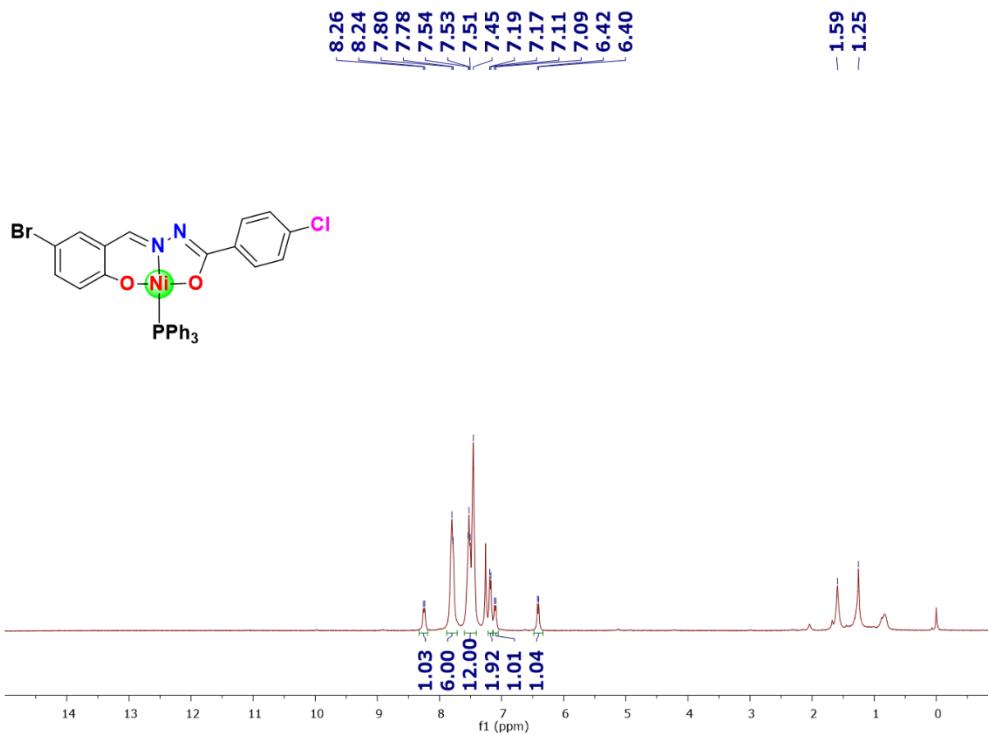
#### 4. NMR spectra of Ni(II) ONOpincer complexes 1-3



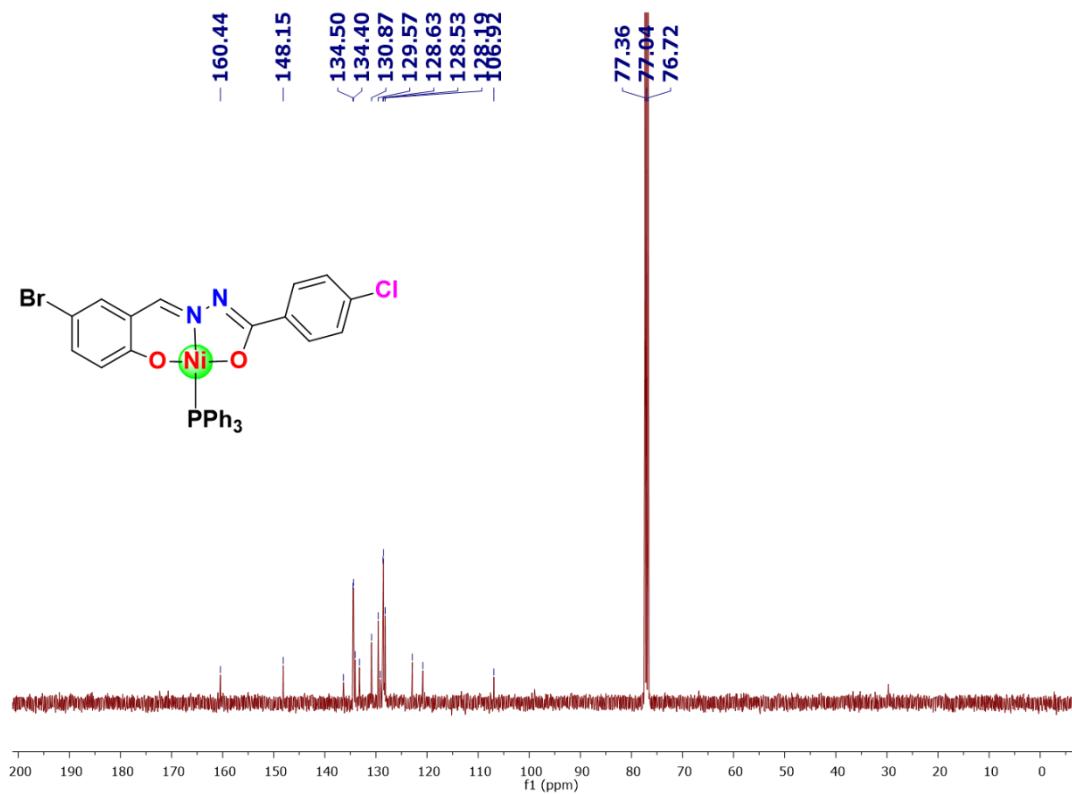
**Figure S3.**  $^1\text{H}$  NMR spectrum of complex **1** in  $\text{CDCl}_3$  (400 MHz, 300 K)



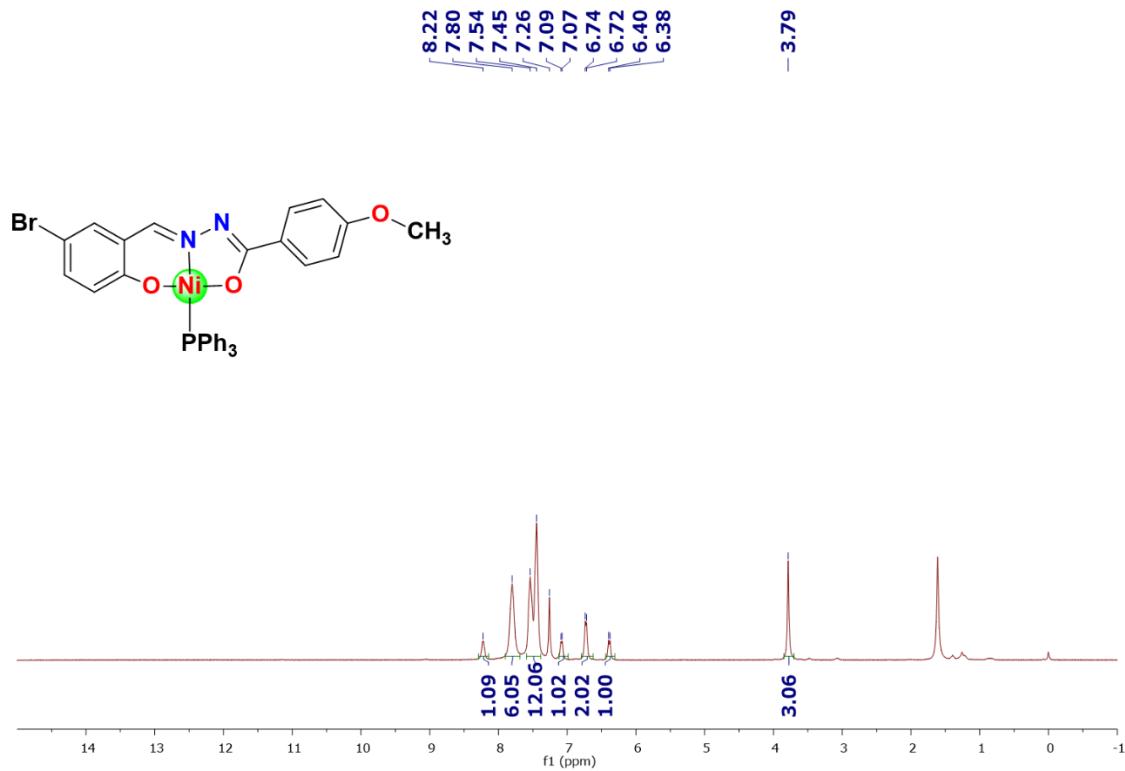
**Figure S4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **1** in  $\text{CDCl}_3$  (100 MHz, 300 K)



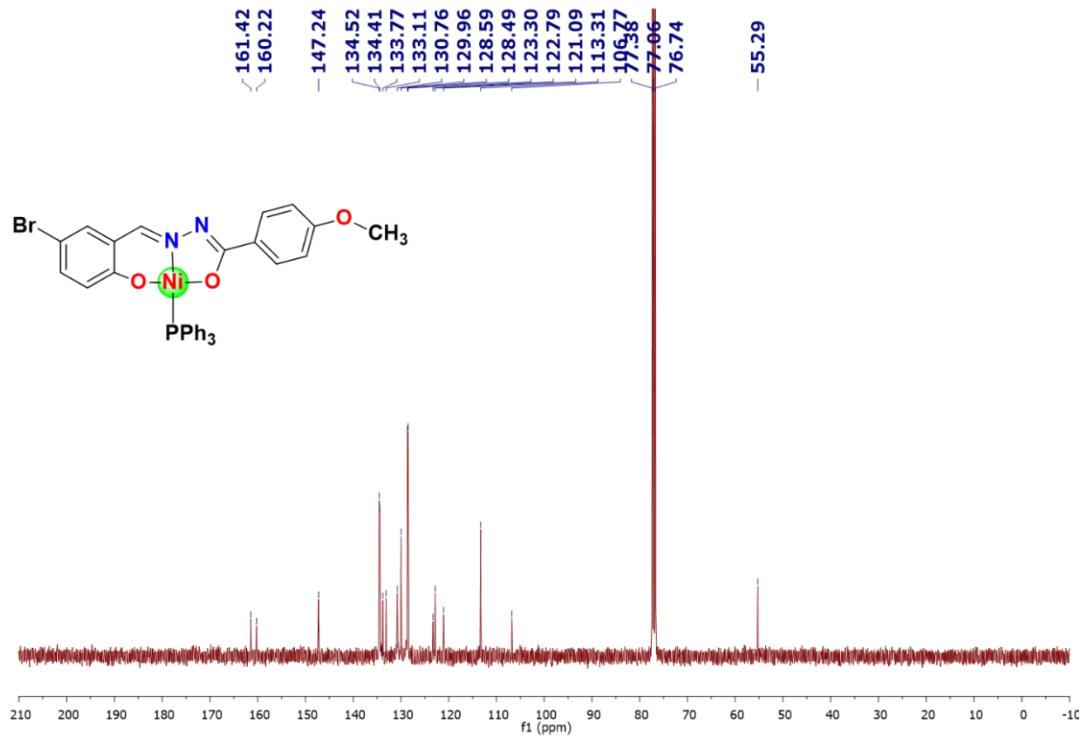
**Figure S5.**  $^1\text{H}$  NMR spectrum of complex **2** in  $\text{CDCl}_3$  (400 MHz, 300 K)



**Figure S6.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of complex **2** in  $\text{CDCl}_3$  (100 MHz, 300 K)

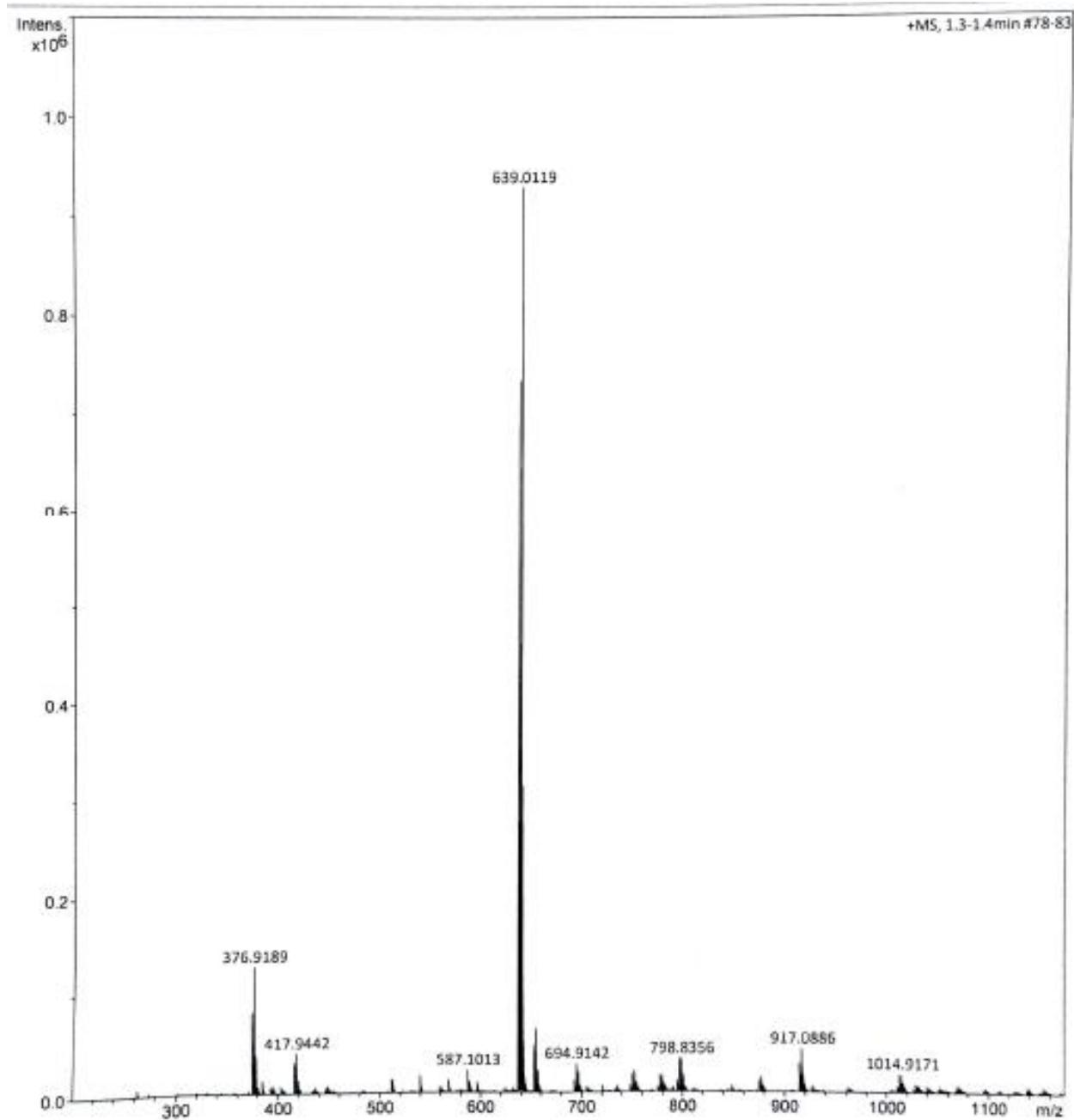


**Figure S7.**  $^1\text{H}$  NMR spectrum of complex **3** in  $\text{CDCl}_3$  (400 MHz, 300 K)

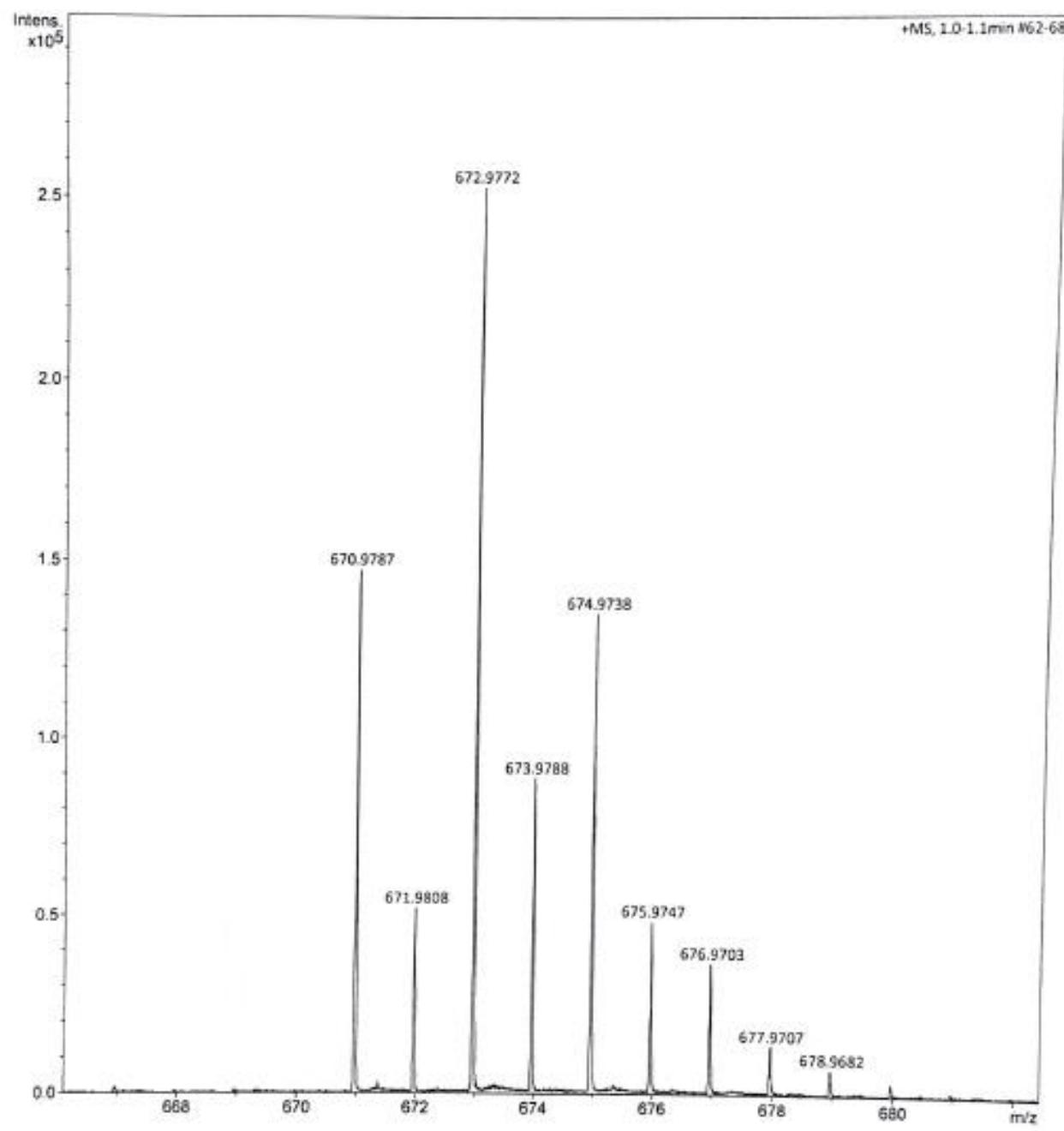


**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **3** in  $\text{CDCl}_3$  (100 MHz, 300 K)

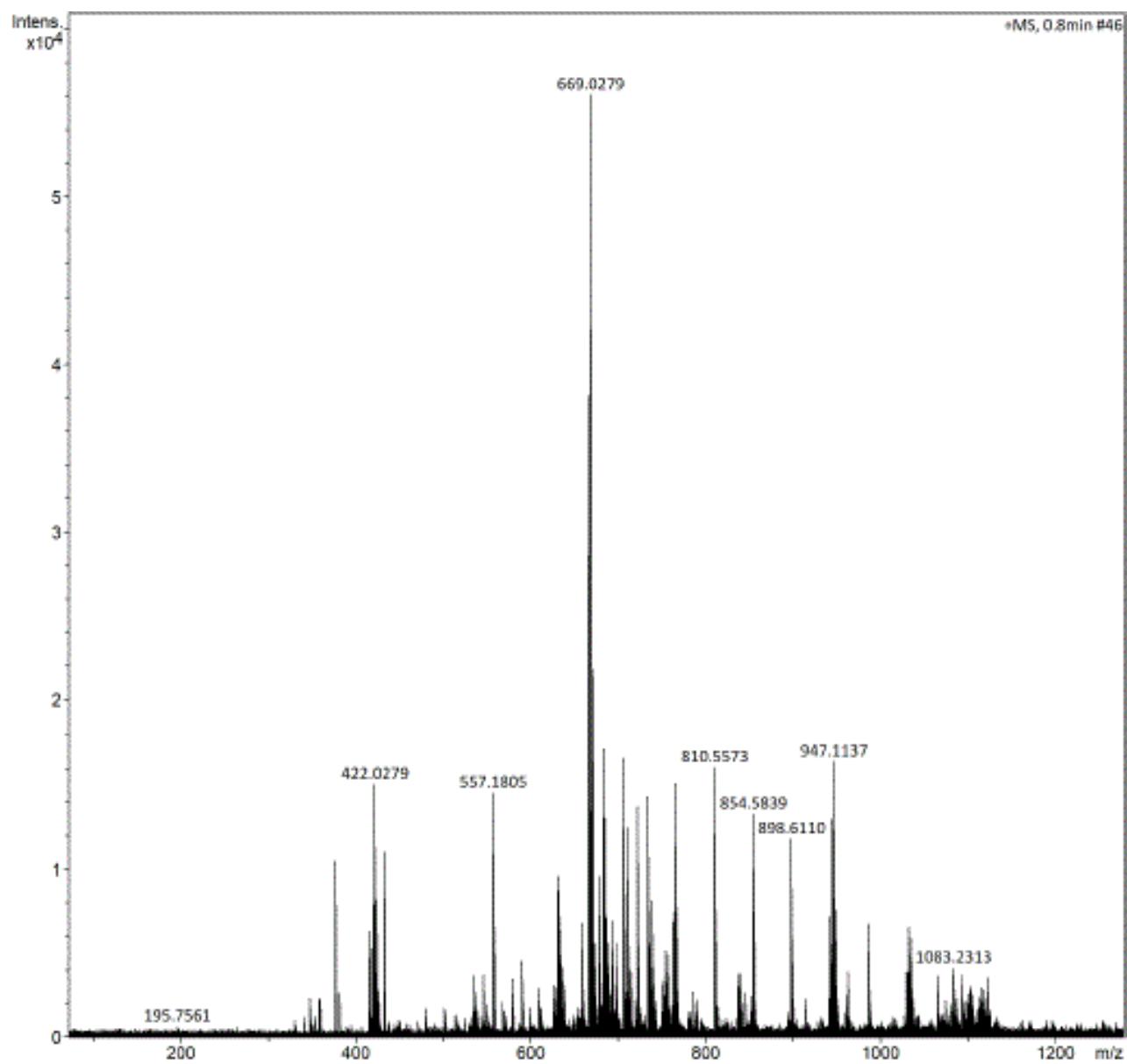
## 5. HRMS spectra of Ni(II) complexes 1-3



**Figure S9.** HRMS spectrum of complex 1



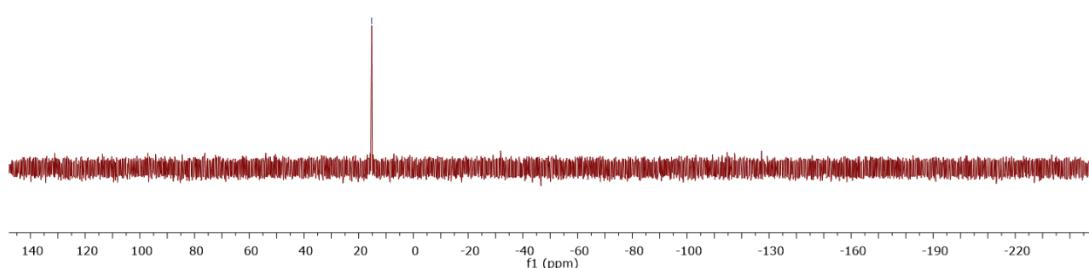
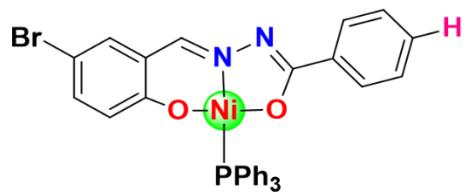
**Figure S10.** HRMS spectrum of complex 2



**Figure S11.** HRMS spectrum of complex **3**

PA-Ni-Br-H 31P  
PA-Ni-Br-H 31P

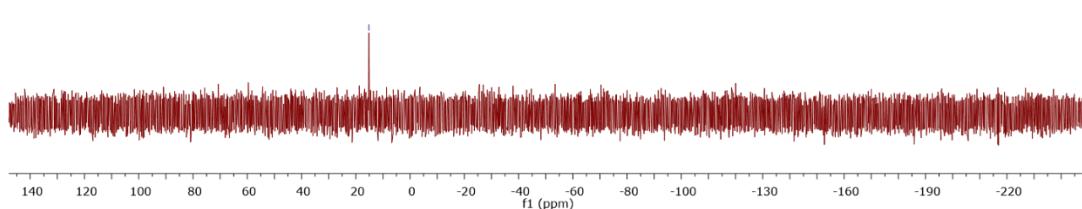
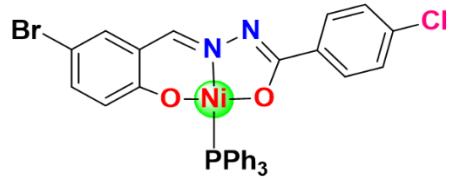
-15.25



**Figure S12.**  $^{31}\text{P}$  NMR spectrum of complex **1** in  $\text{CDCl}_3$  (100 MHz, 300 K)

PA-Ni-J-Cl 31P  
PA-Ni-J-Cl 31P

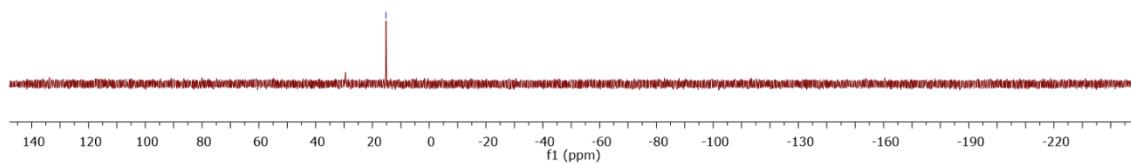
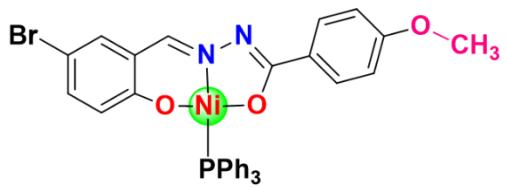
-15.14



**Figure S13.**  $^{31}\text{P}$  NMR spectrum of complex **2** in  $\text{CDCl}_3$  (100 MHz, 300 K)

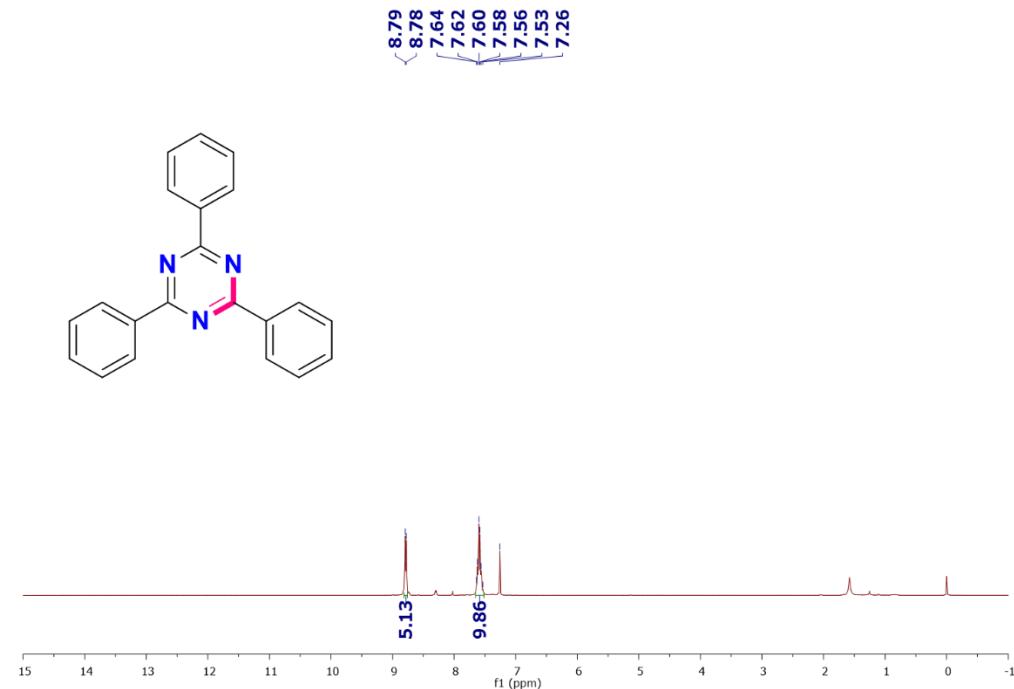
PA-Ni-J-OMe 31P  
PA-Ni-J-OMe 31P

- 15.24

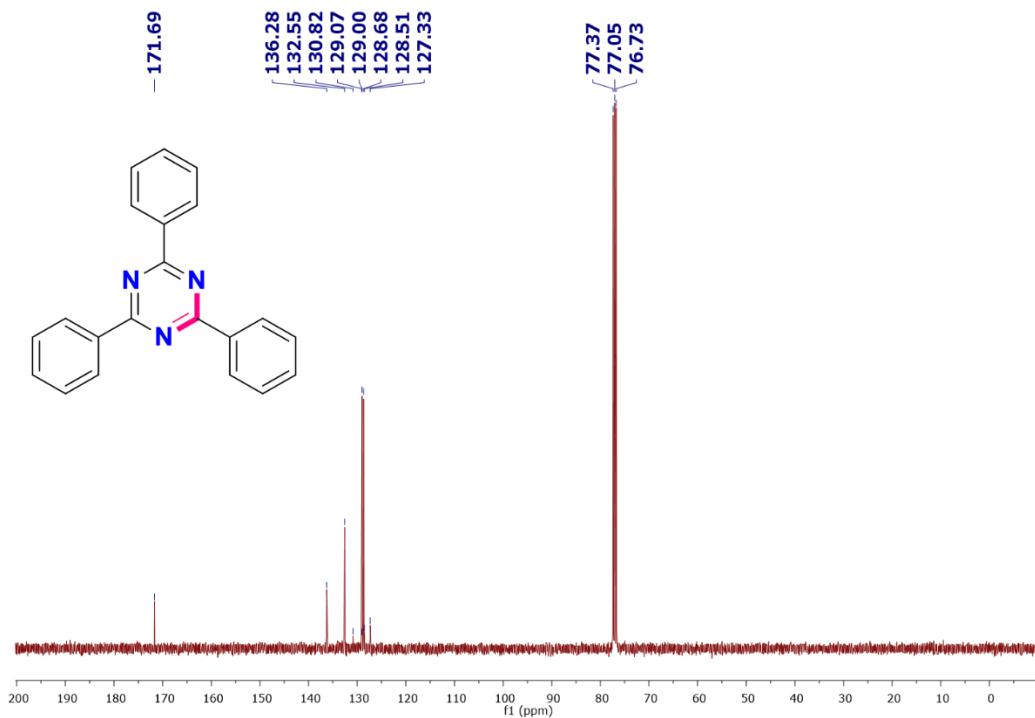


**Figure S14.**  ${}^3\text{1}\text{P}$  NMR spectrum of complex 3 in  $\text{CDCl}_3$  (100 MHz, 300 K)

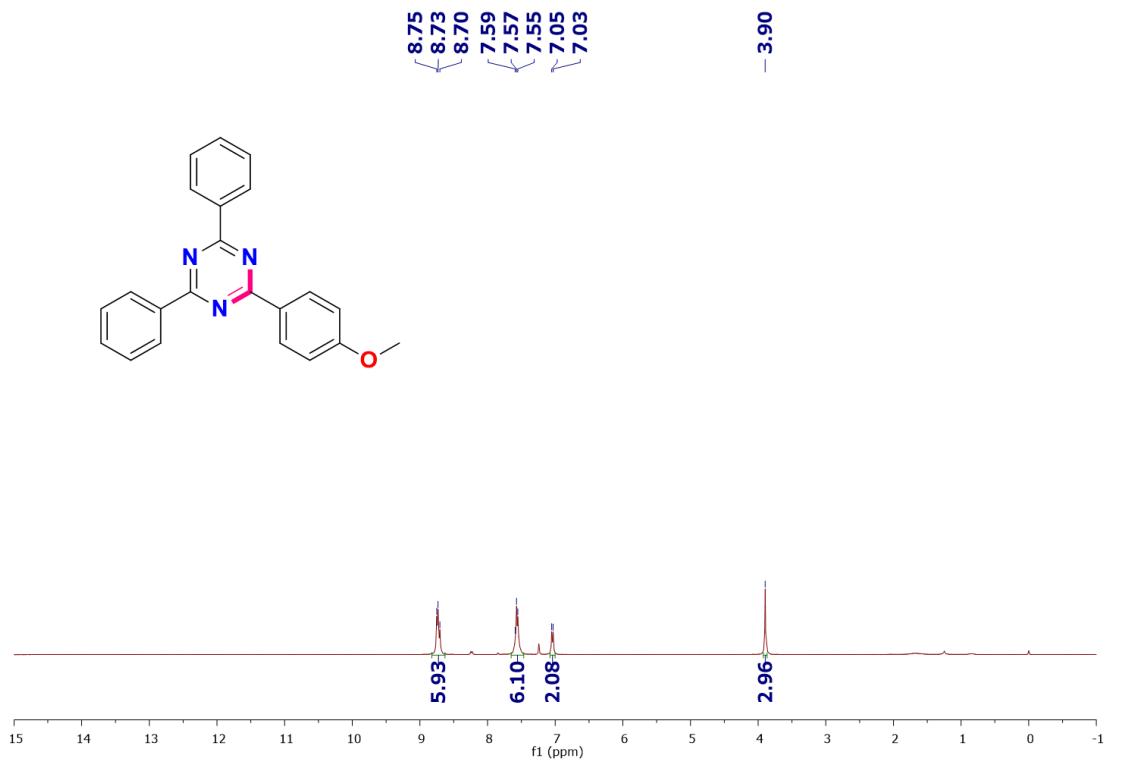
## 7. NMR Spectra of substituted 1,3,5-triazine products (3a-3t and 4a-4l)



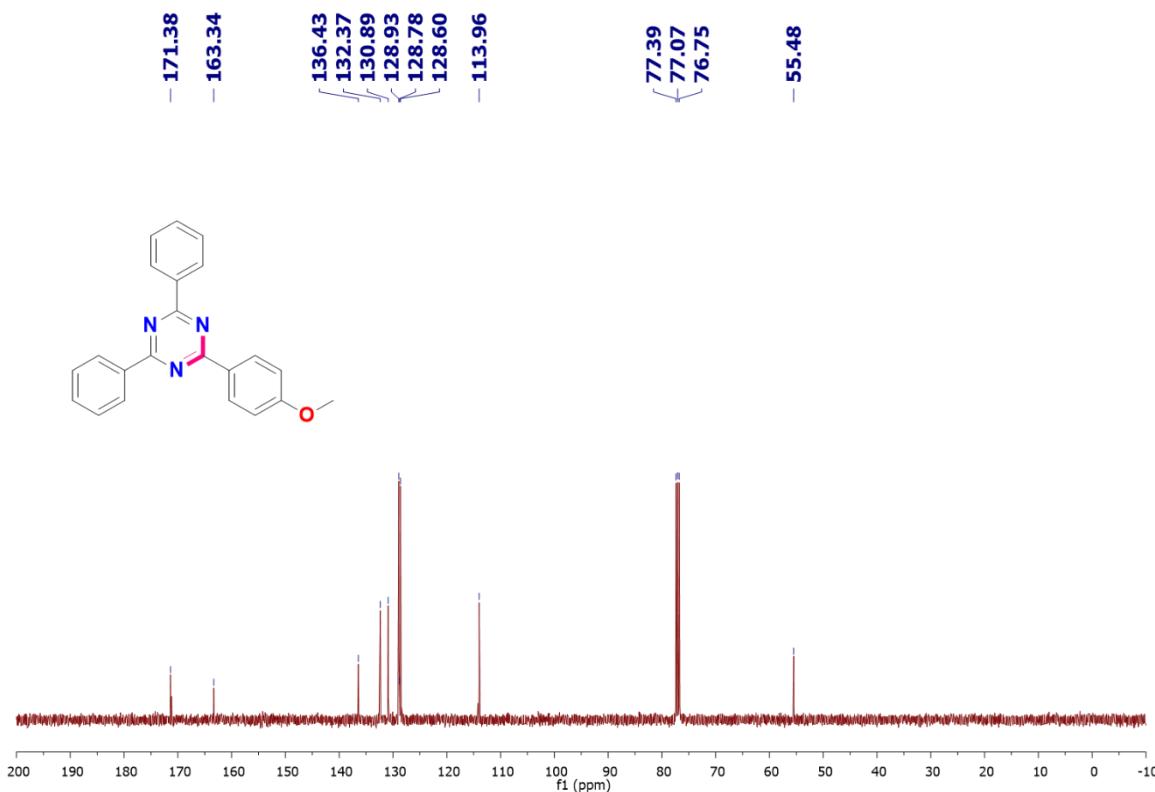
**Figure S15.**  $^1\text{H}$  NMR spectrum of 3a in  $\text{CDCl}_3$ (100 MHz, 300 K)



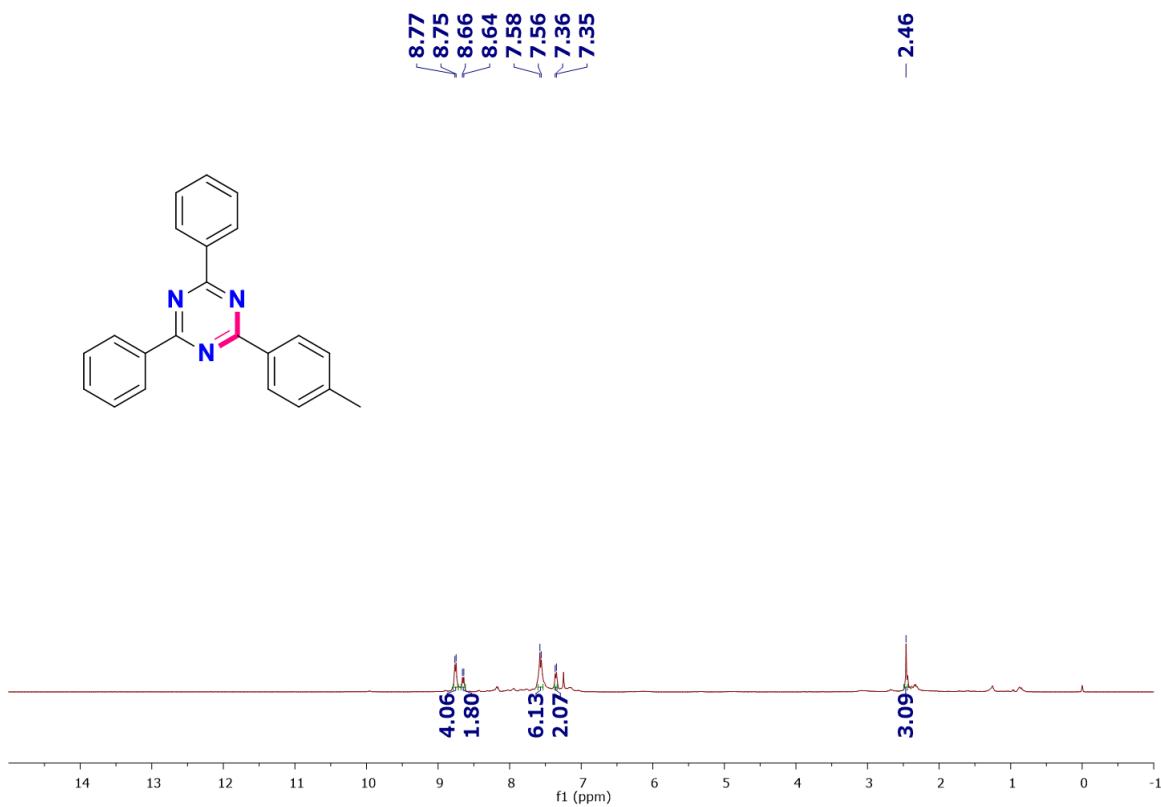
**Figure S16.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3a in  $\text{CDCl}_3$ (100 MHz, 300 K)



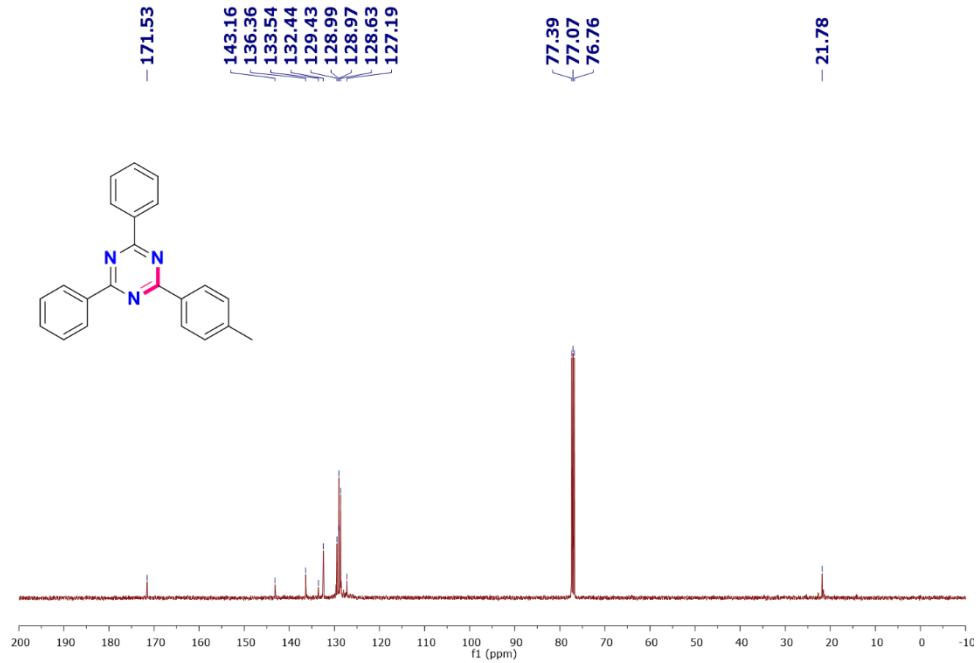
**Figure S17.**  $^1\text{H}$  NMR spectrum of **3b** in  $\text{CDCl}_3$ (100 MHz, 300 K)



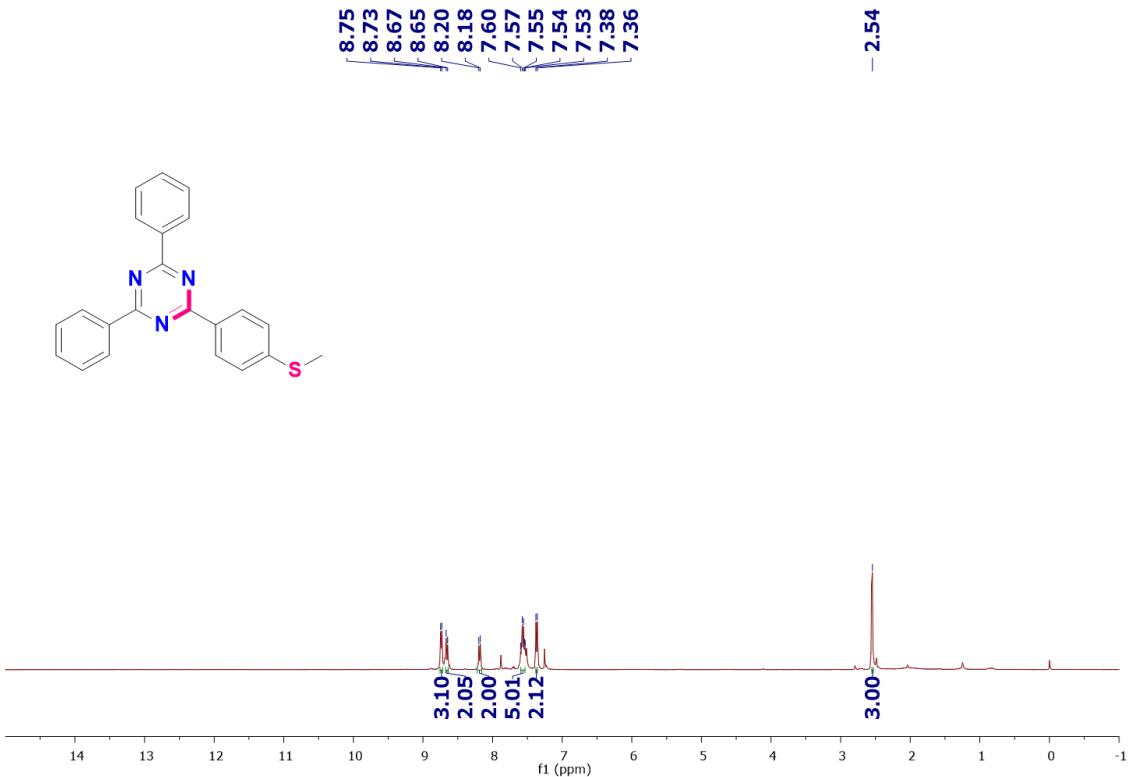
**Figure S18.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **3b** in  $\text{CDCl}_3$ (100 MHz, 300 K)



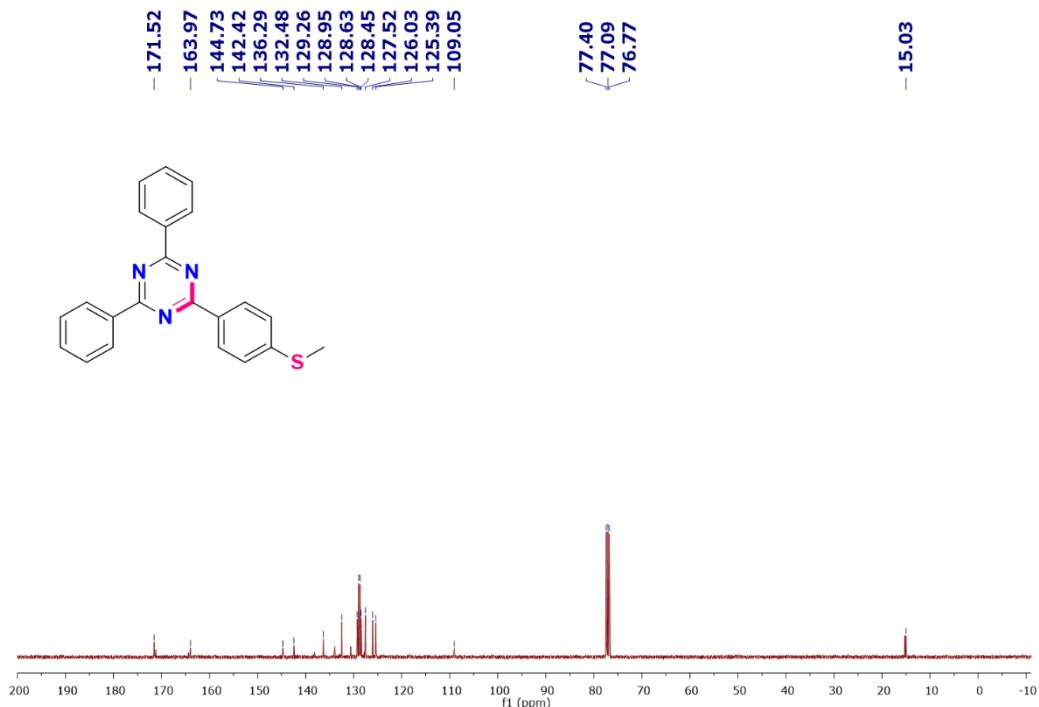
**Figure S19.**  $^1\text{H}$  NMR spectrum of **3c** in  $\text{CDCl}_3$ (100 MHz, 300 K)



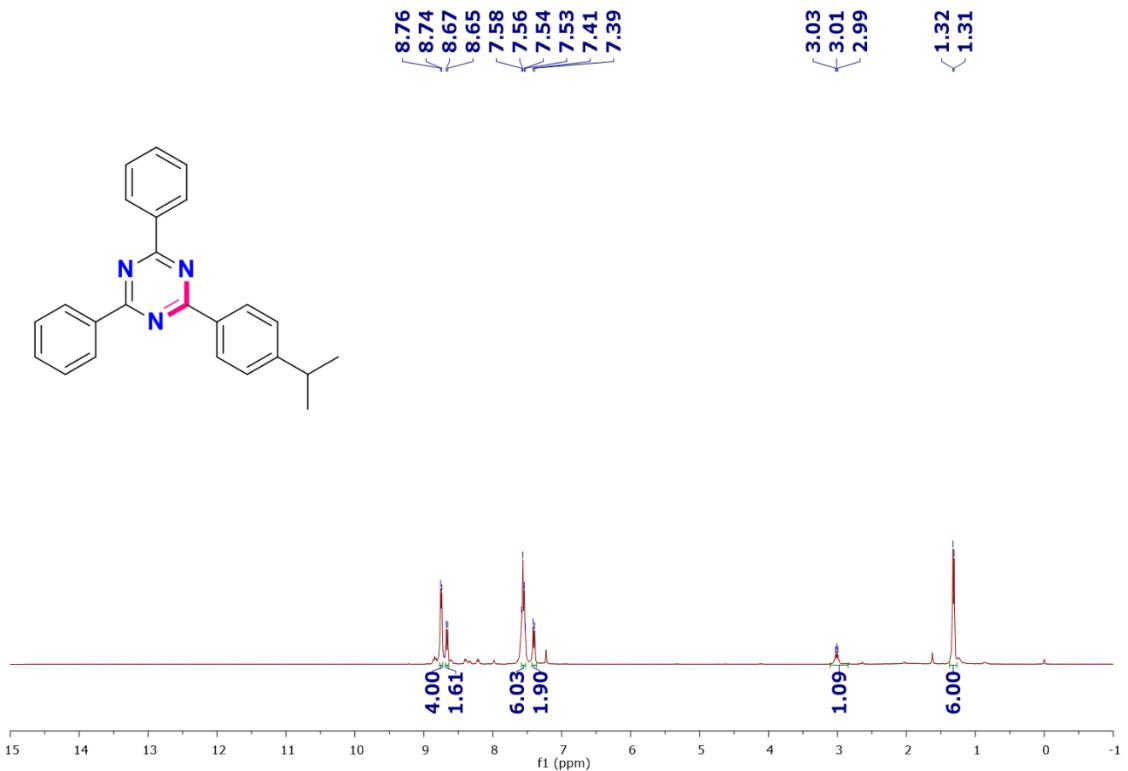
**Figure S20.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **3c** in  $\text{CDCl}_3$ (100 MHz, 300 K)



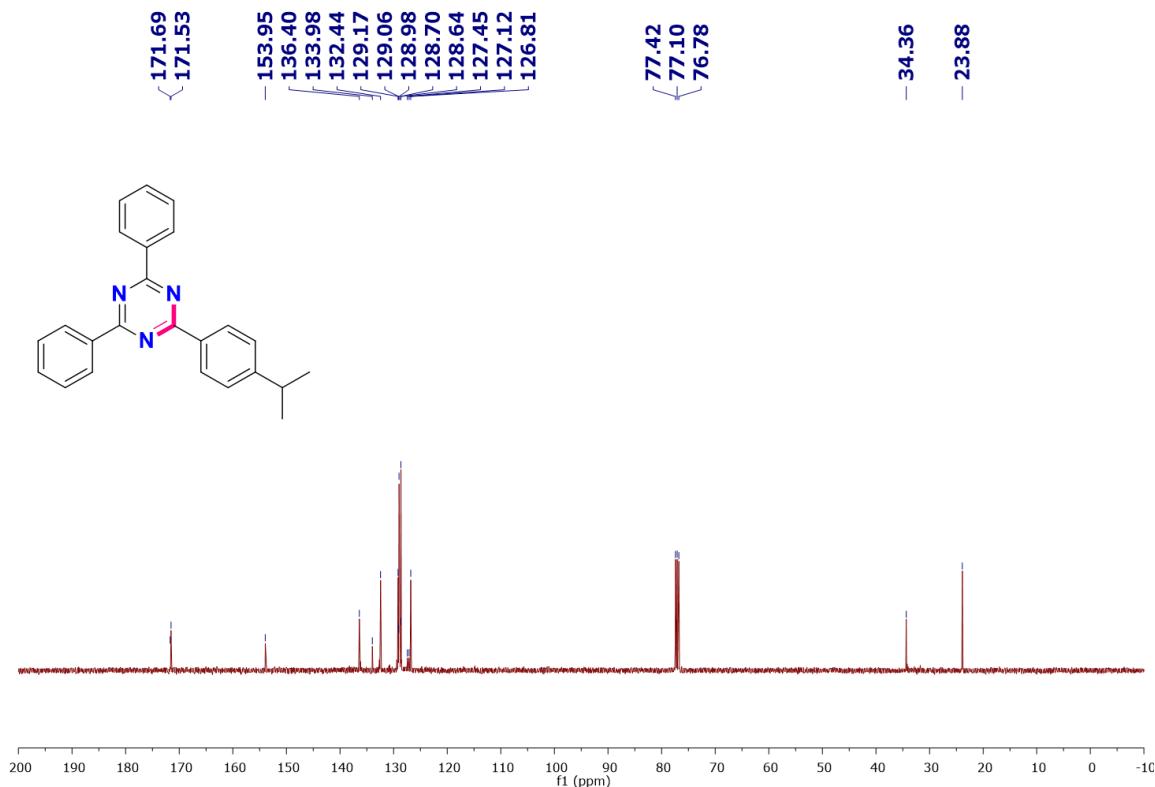
**Figure S21.**  $^1\text{H}$  NMR spectrum of **3d** in  $\text{CDCl}_3$ (100 MHz, 300 K)



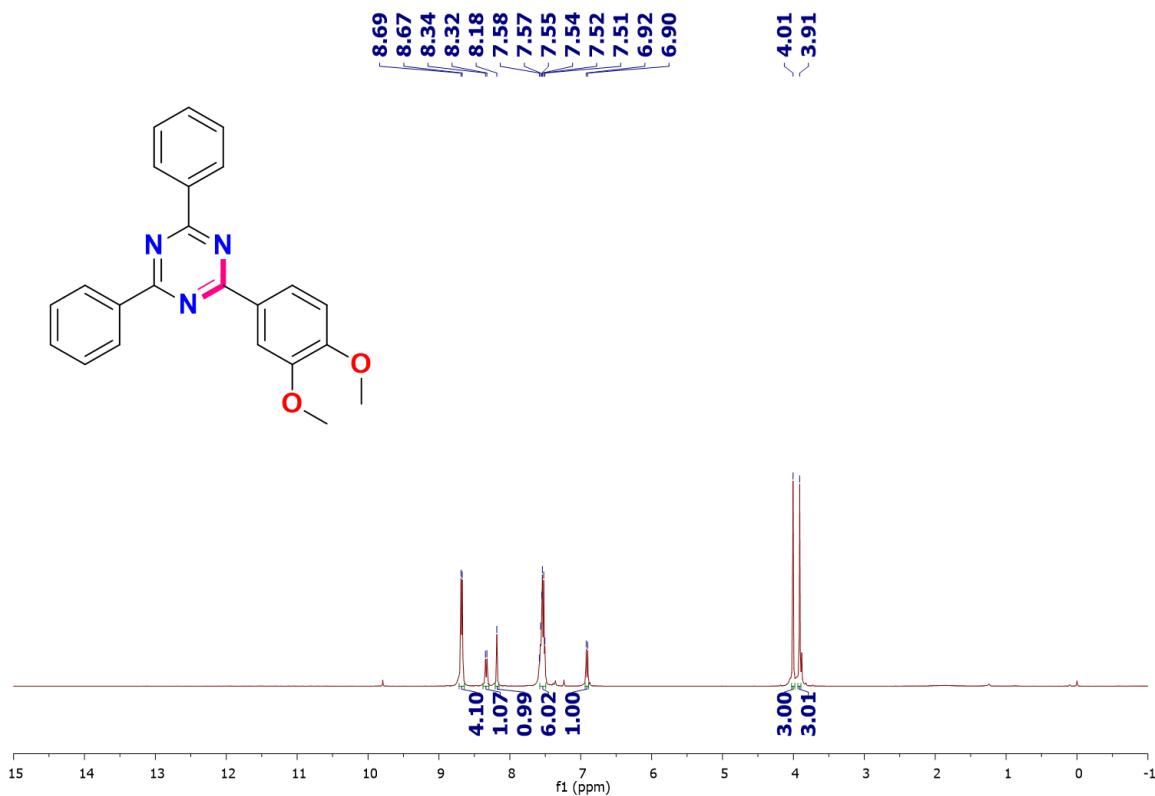
**Figure S22.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3d** in  $\text{CDCl}_3$ (100 MHz, 300 K)



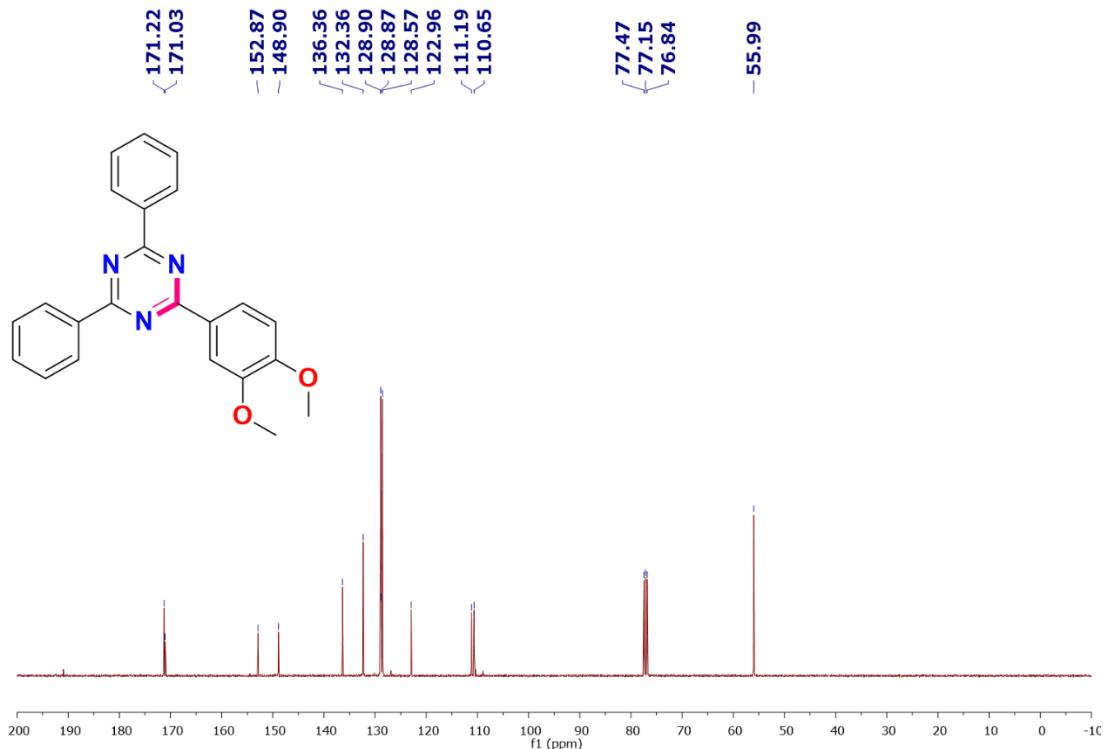
**Figure S23.** <sup>1</sup>H NMR spectrum of **3e** in CDCl<sub>3</sub>(100 MHz, 300 K)



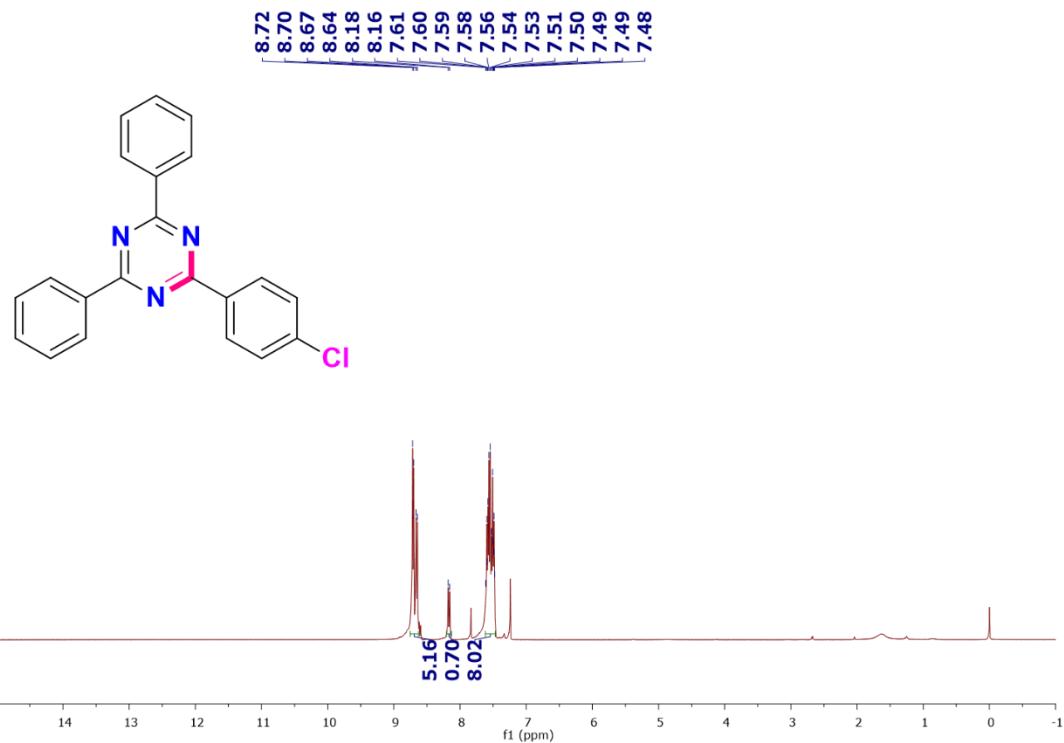
**Figure S24.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3e** in CDCl<sub>3</sub>(100 MHz, 300 K)



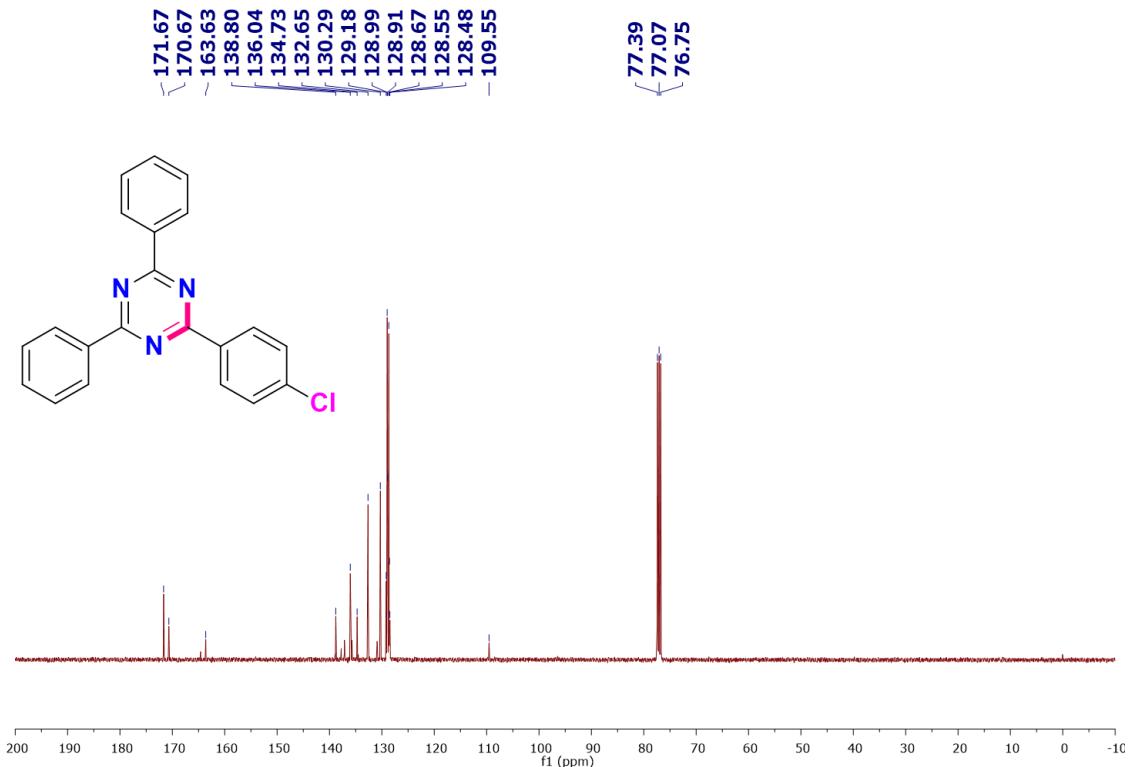
**Figure S25.**  $^1\text{H}$  NMR spectrum of **3f** in  $\text{CDCl}_3$ (100 MHz, 300 K)



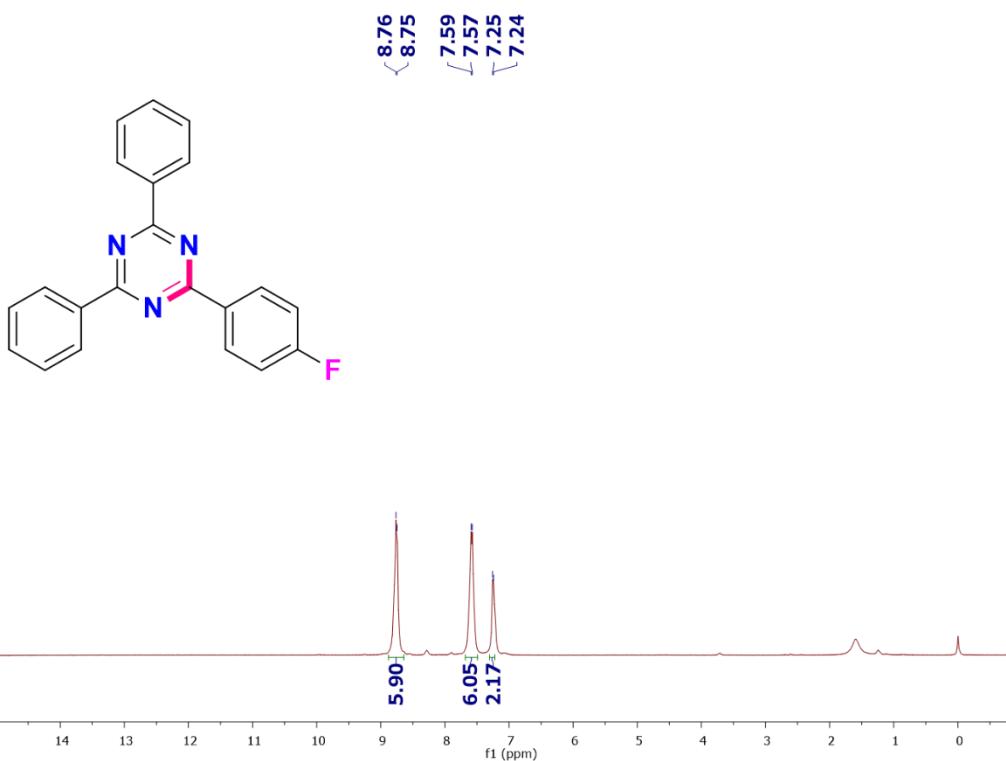
**Figure S26.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **3f** in  $\text{CDCl}_3$ (100 MHz, 300 K)



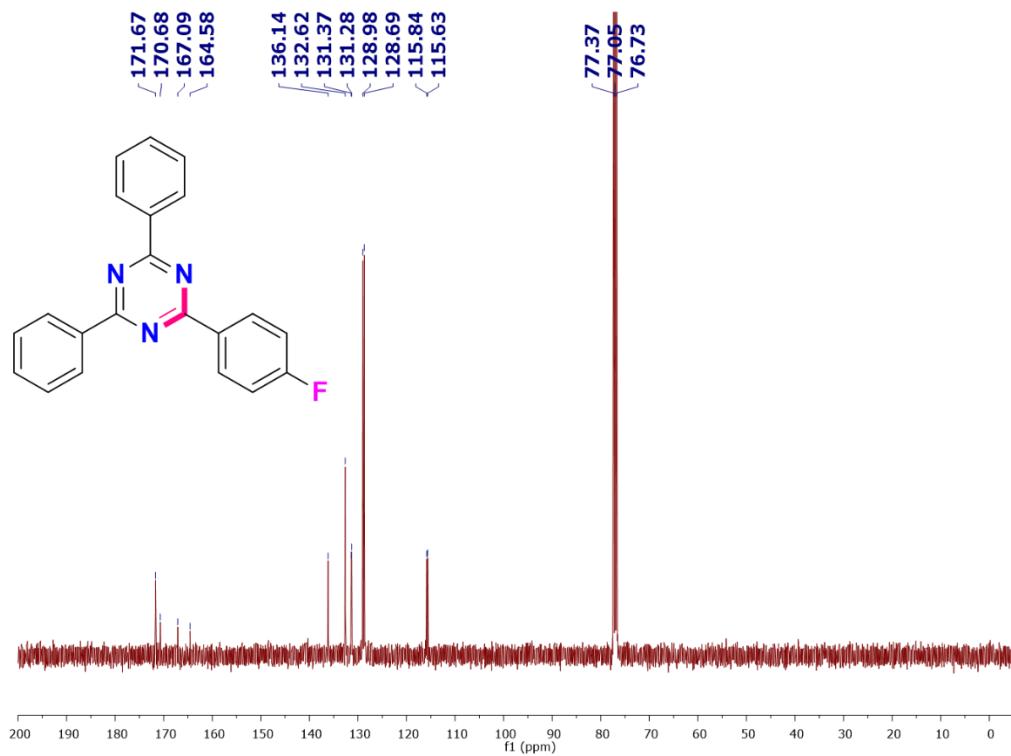
**Figure S27.** <sup>1</sup>H NMR spectrum of **3g** in CDCl<sub>3</sub>(100 MHz, 300 K)



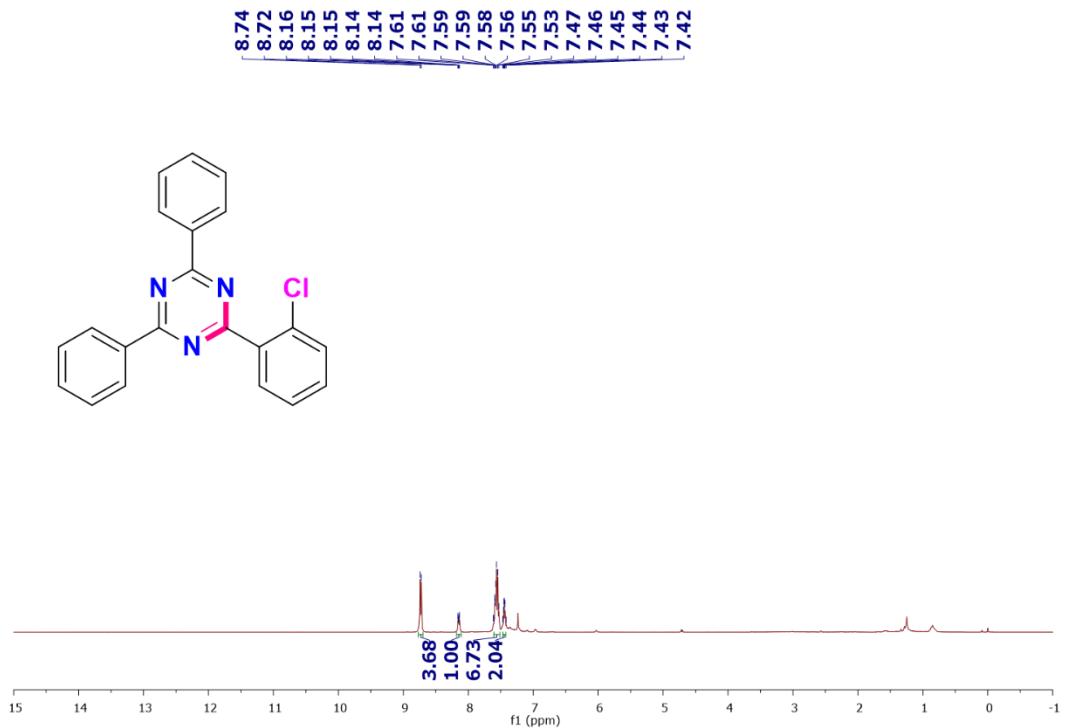
**Figure S28.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3g** in CDCl<sub>3</sub>(100 MHz, 300 K)



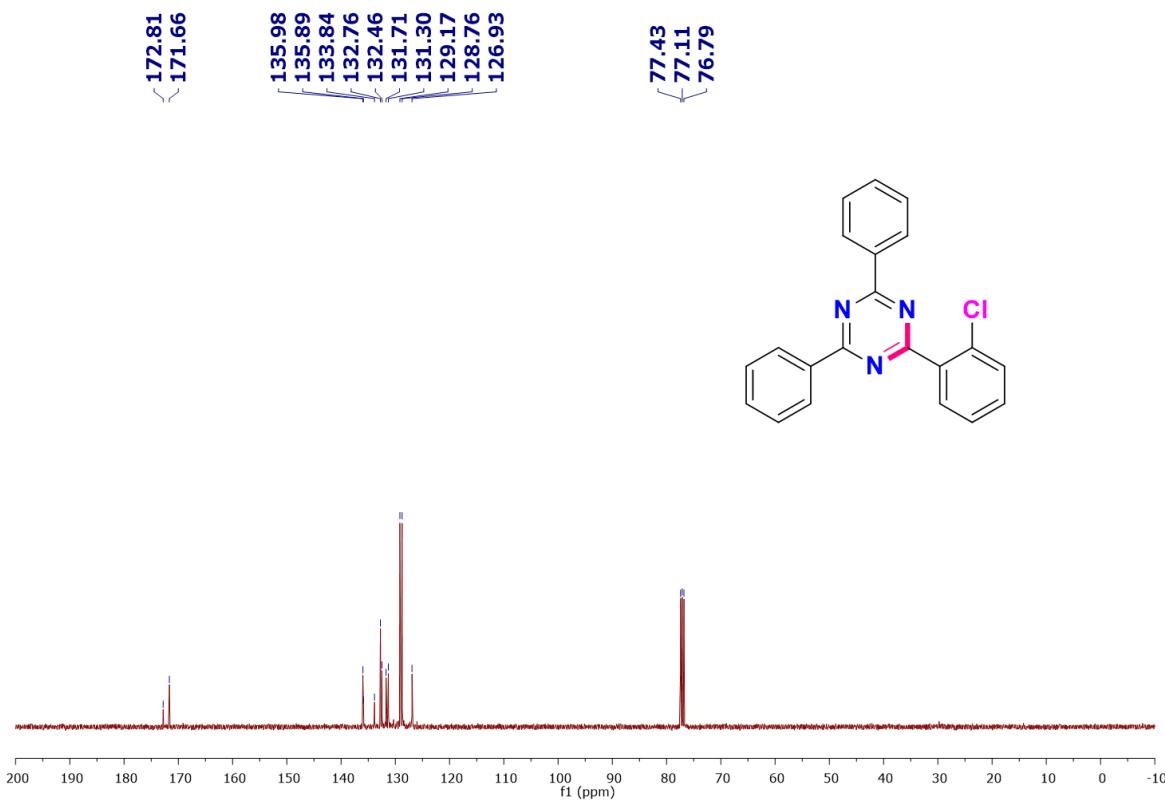
**Figure S29.**  $^1\text{H}$  NMR spectrum of **3h** in  $\text{CDCl}_3$ (100 MHz, 300 K)



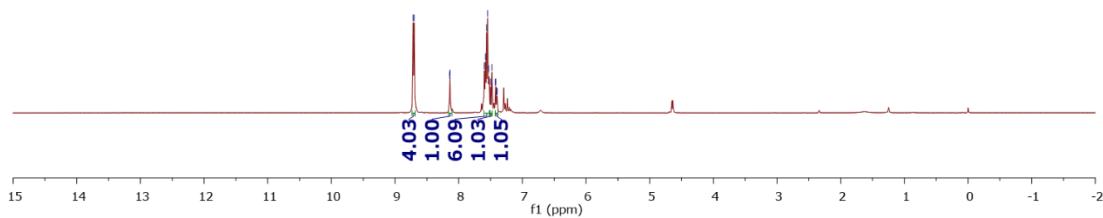
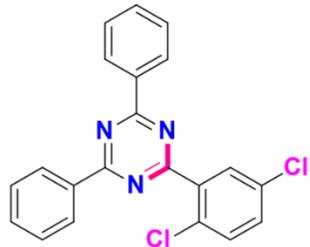
**Figure S30.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3h** in  $\text{CDCl}_3$ (100 MHz, 300 K)



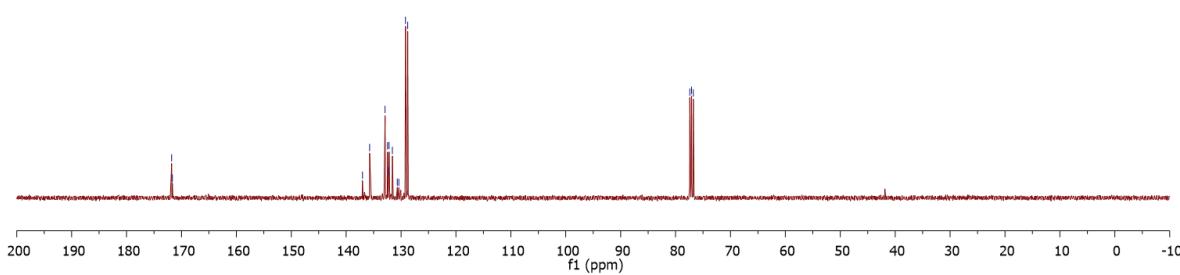
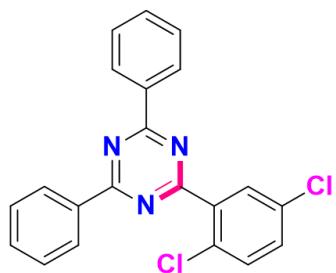
**Figure S31.** <sup>1</sup>H NMR spectrum of **3i** in CDCl<sub>3</sub>(100 MHz, 300 K)



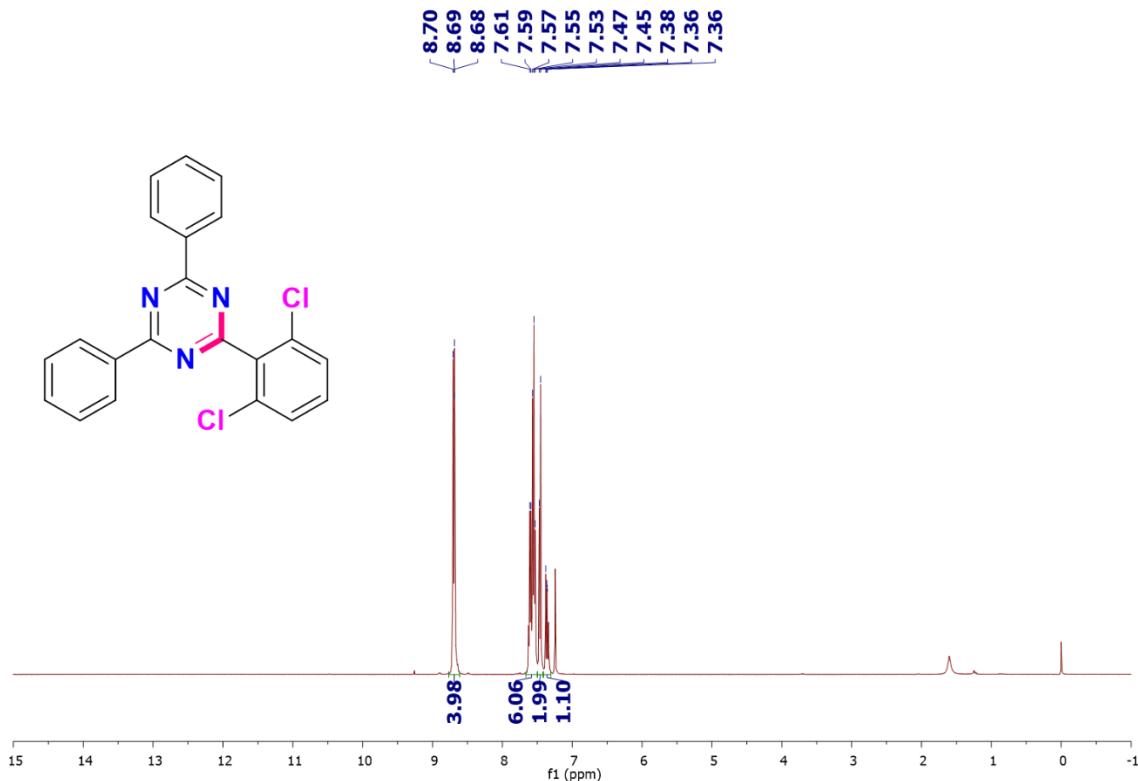
**Figure S32.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3i** in CDCl<sub>3</sub>(100 MHz, 300 K)



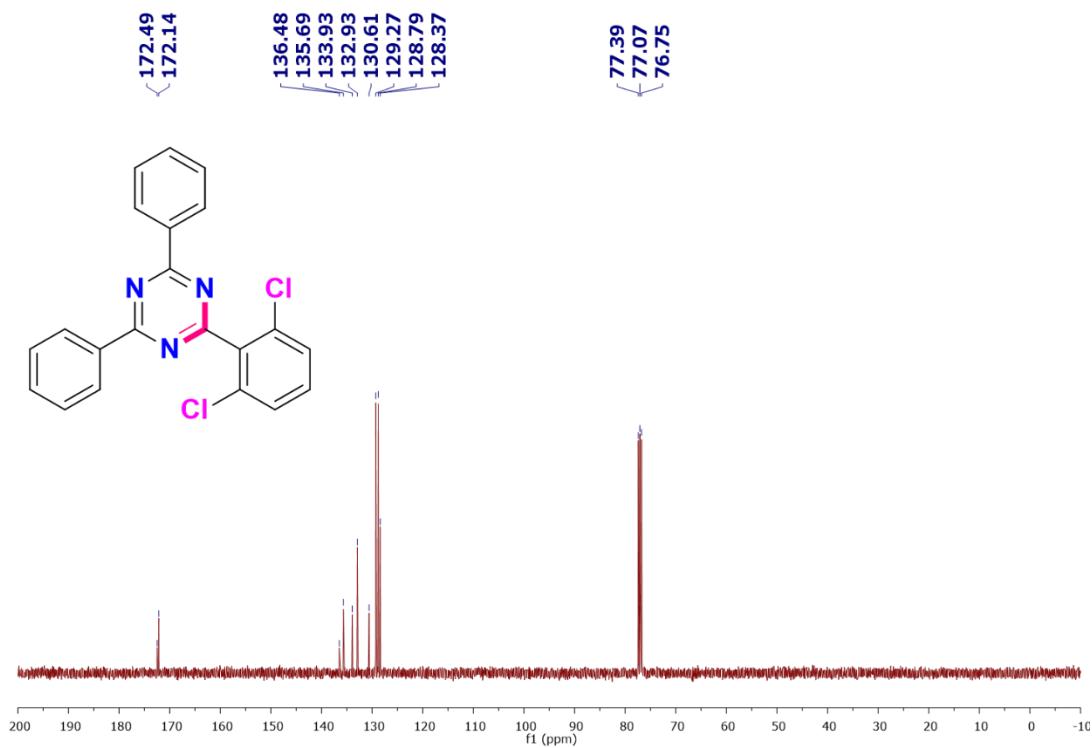
**Figure S33.**  $^1\text{H}$  NMR spectrum of **3j** in  $\text{CDCl}_3$  (100 MHz, 300 K)



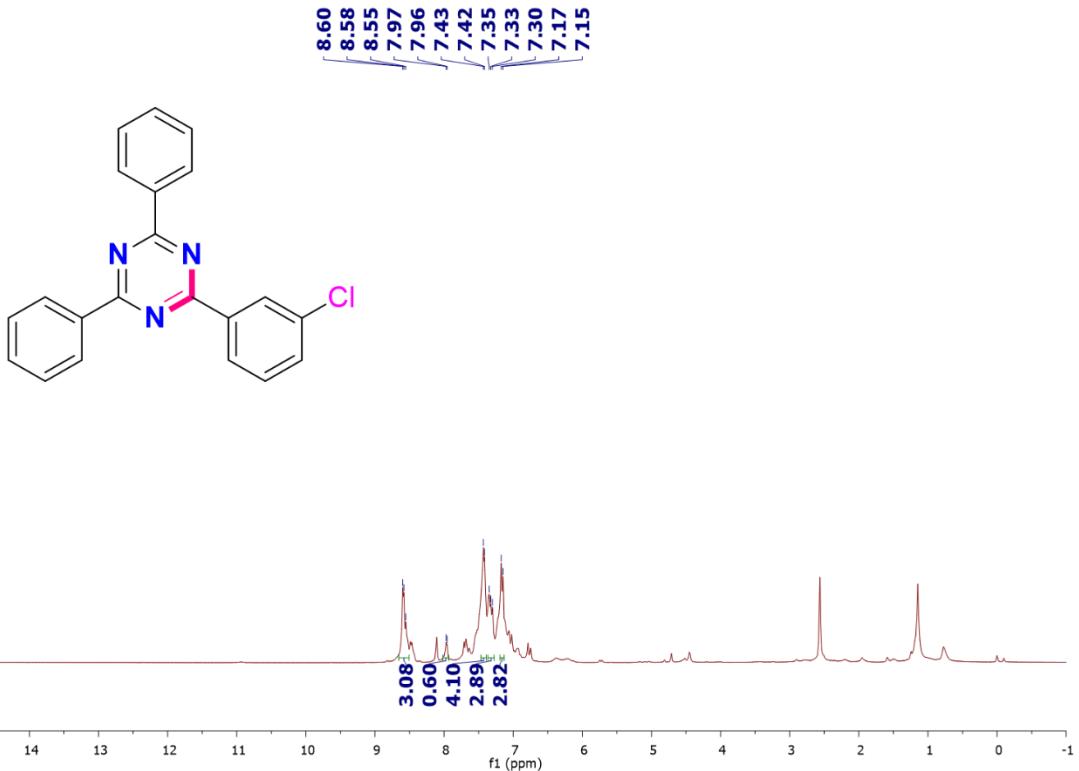
**Figure S34.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **3j** in  $\text{CDCl}_3$  (100 MHz, 300 K)



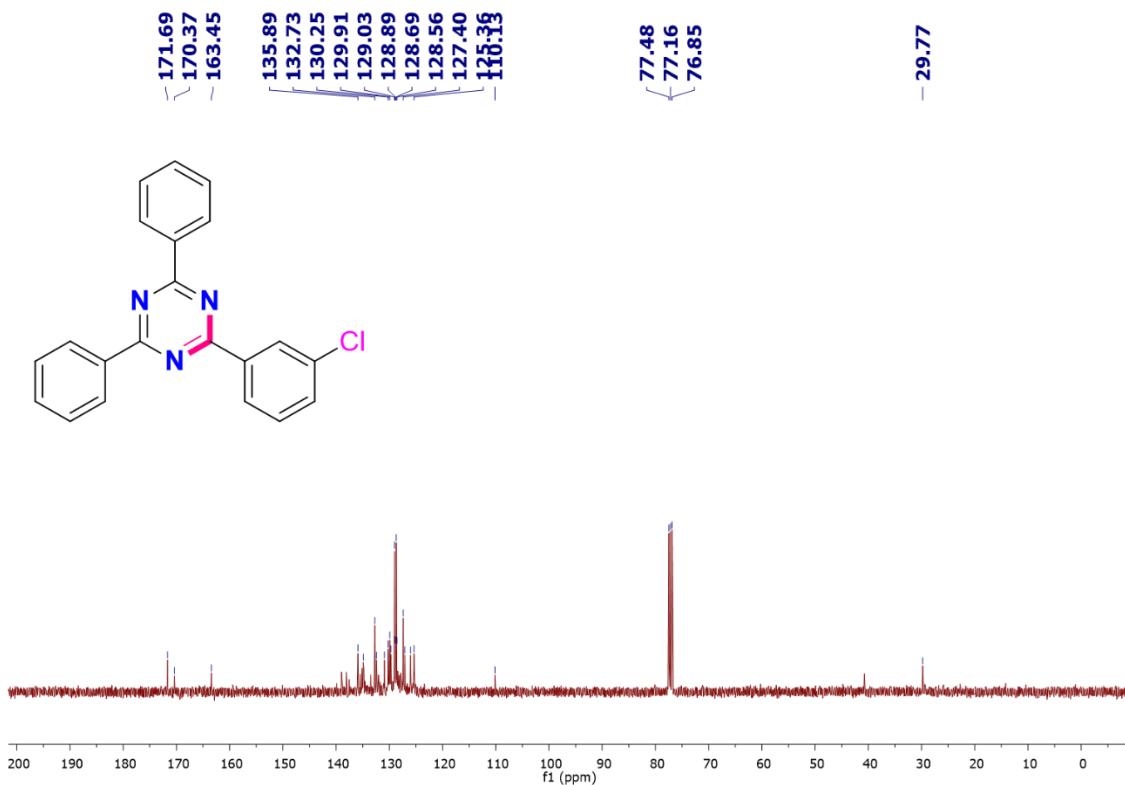
**Figure S35.**  $^1\text{H}$  NMR spectrum of **3k** in  $\text{CDCl}_3$ (100 MHz, 300 K)



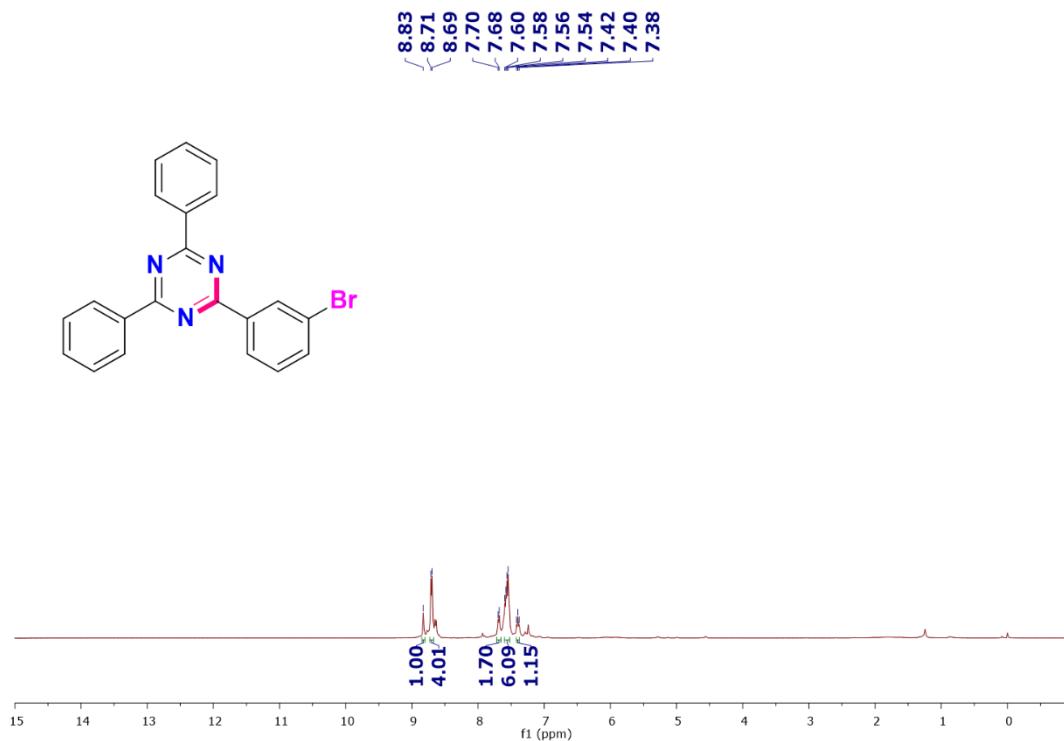
**Figure S36.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3k** in  $\text{CDCl}_3$ (100 MHz, 300 K)



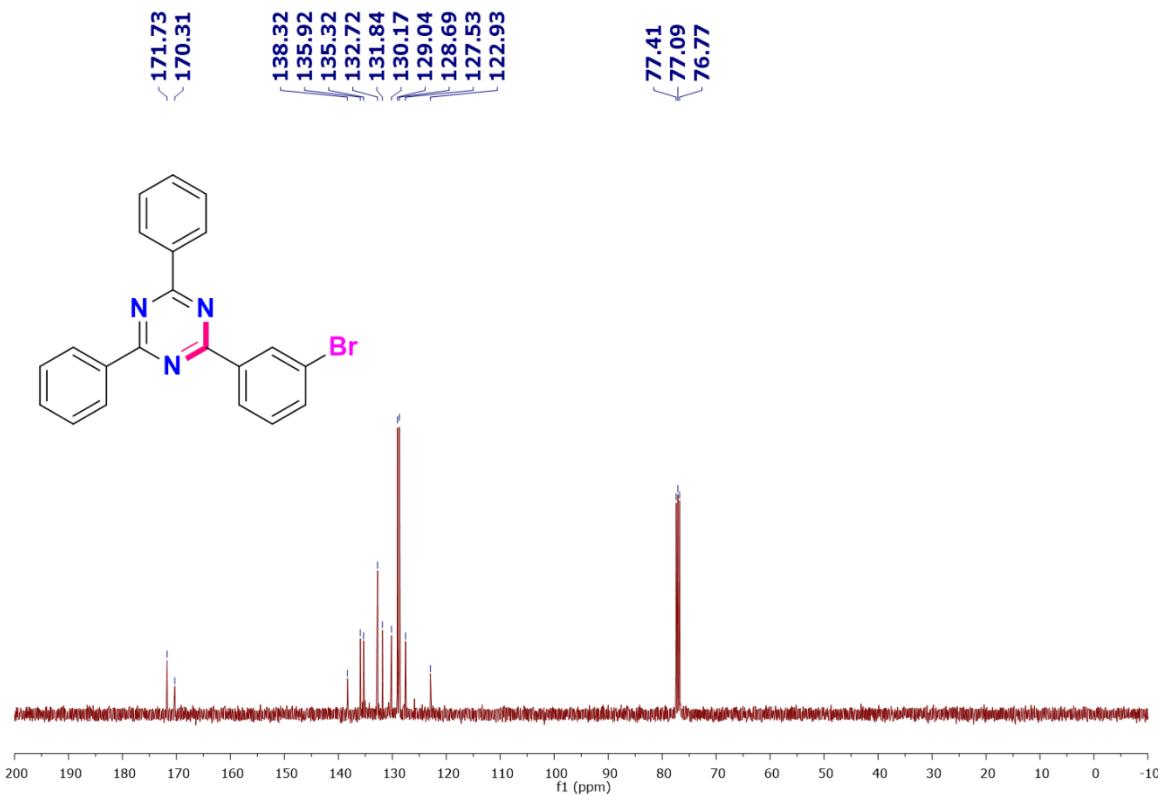
**Figure S37.**  $^1\text{H}$  NMR spectrum of **3l** in  $\text{CDCl}_3$ (100 MHz, 300 K)



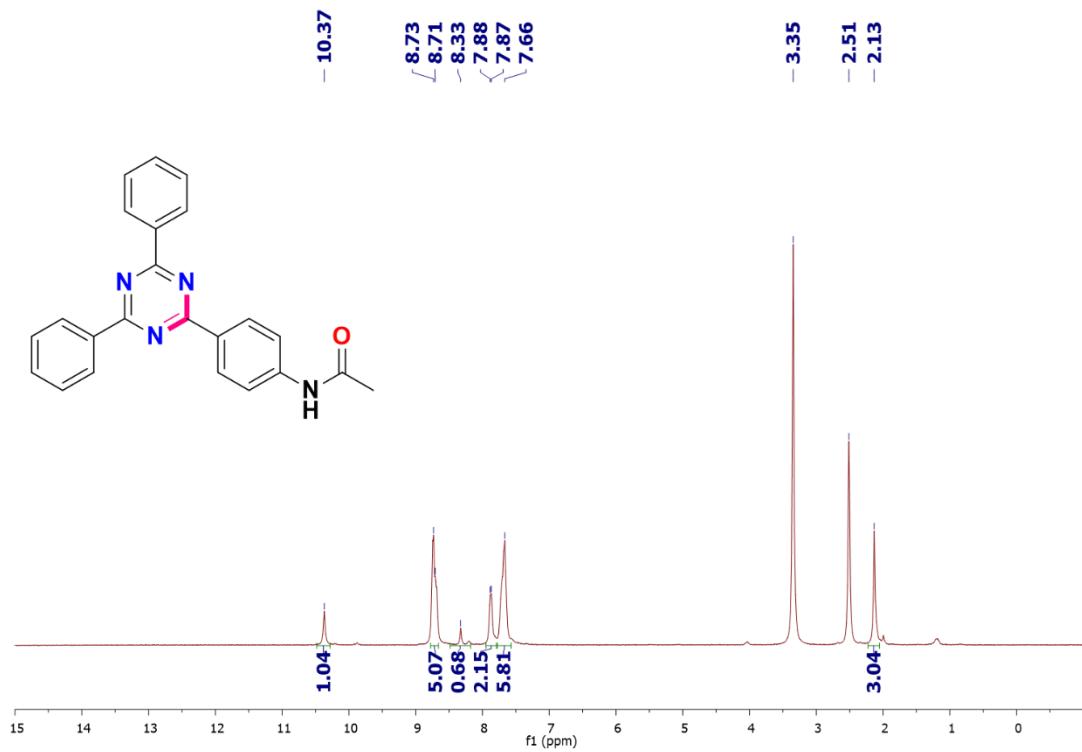
**Figure S38.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **3l** in  $\text{CDCl}_3$ (100 MHz, 300 K)



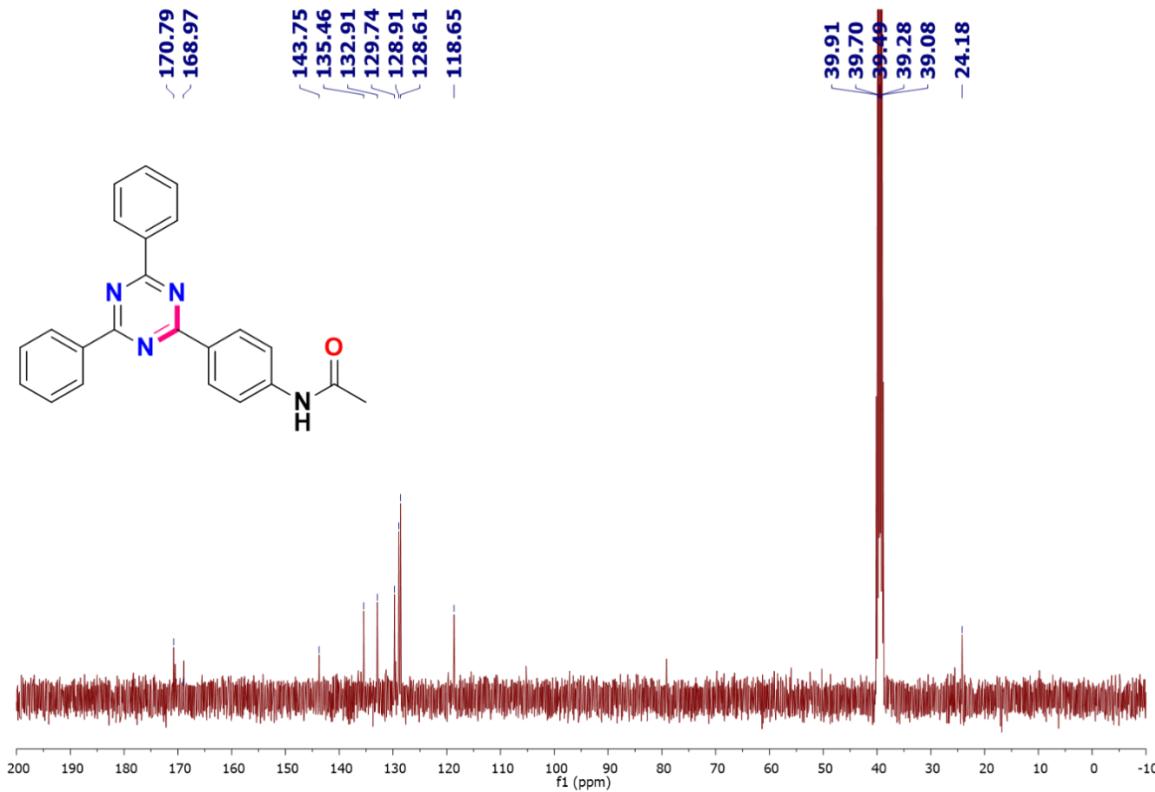
**Figure S39.** <sup>1</sup>H NMR spectrum of **3m** in CDCl<sub>3</sub>(100 MHz, 300 K)



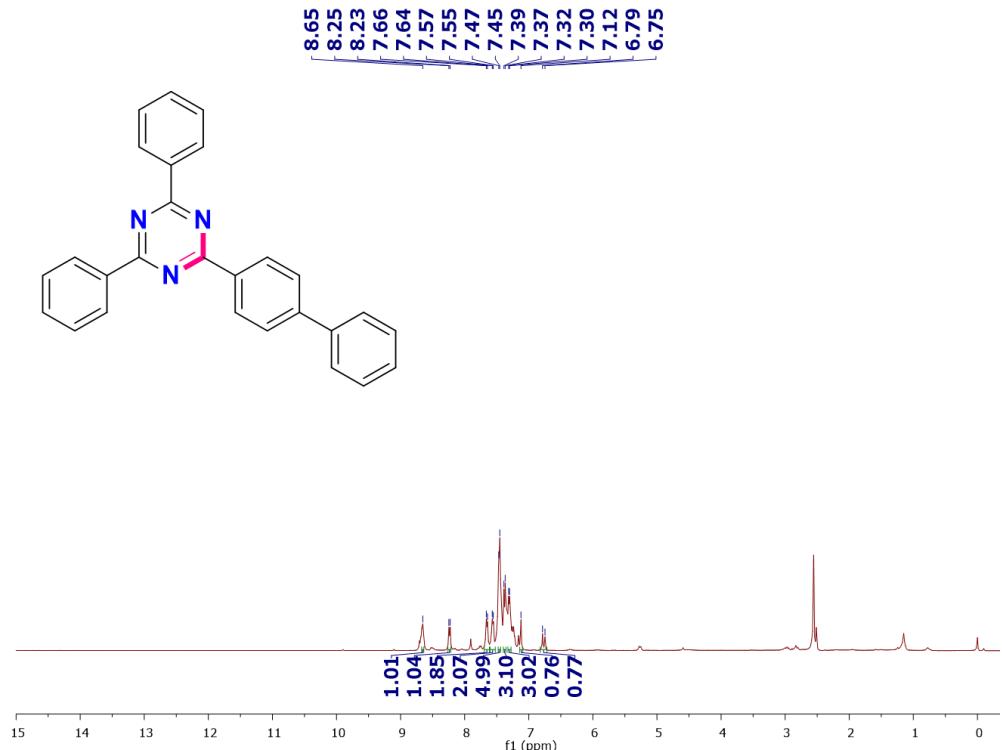
**Figure S40.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3m** in CDCl<sub>3</sub> (100 MHz, 300 K)



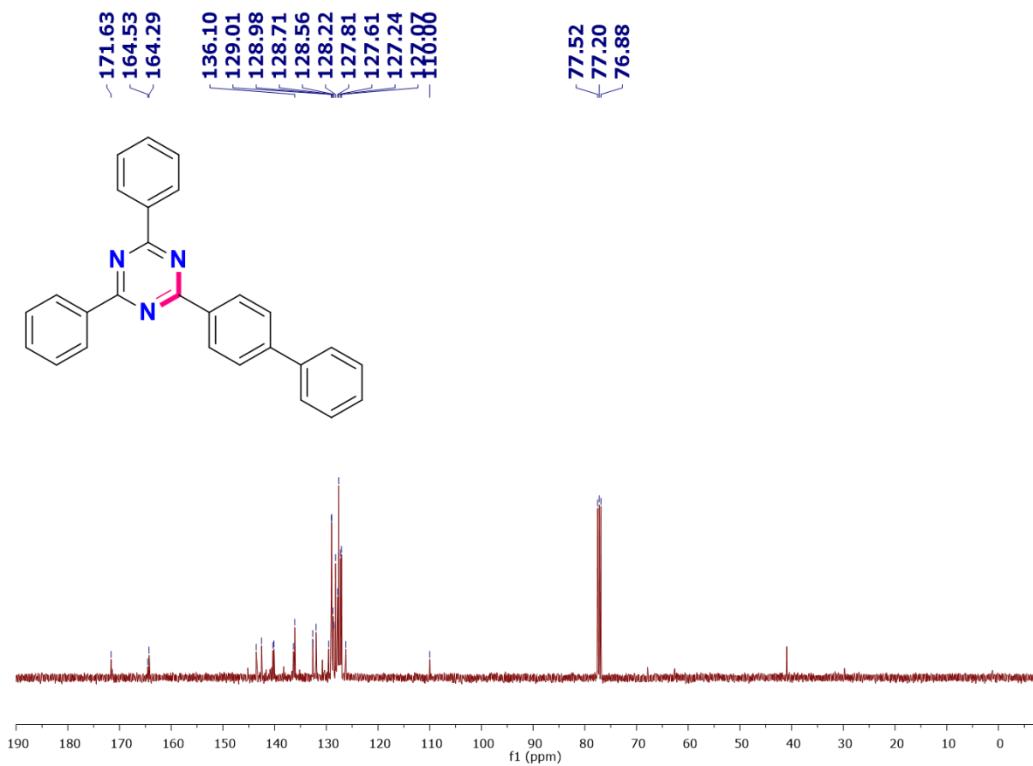
**Figure S41.**  $^1\text{H}$  NMR spectrum of **3n** in  $\text{DMSO-d}_6$ (100 MHz, 300 K)



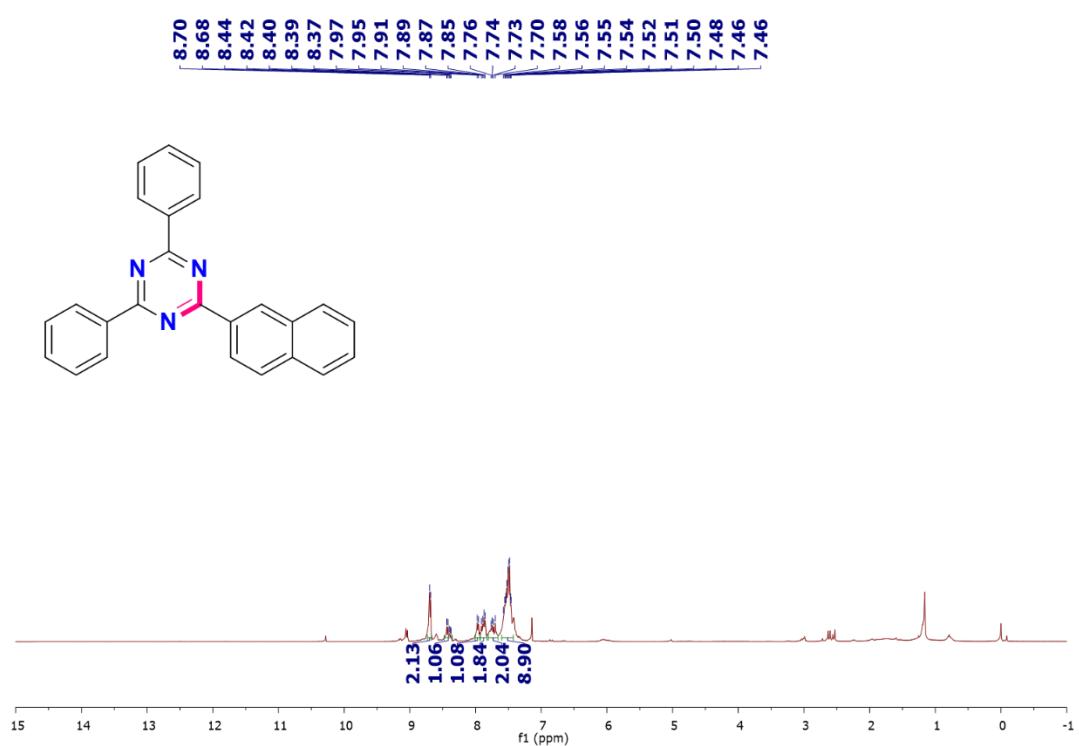
**Figure S42.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3n** in  $\text{DMSO-d}_6$ (100 MHz, 300 K)



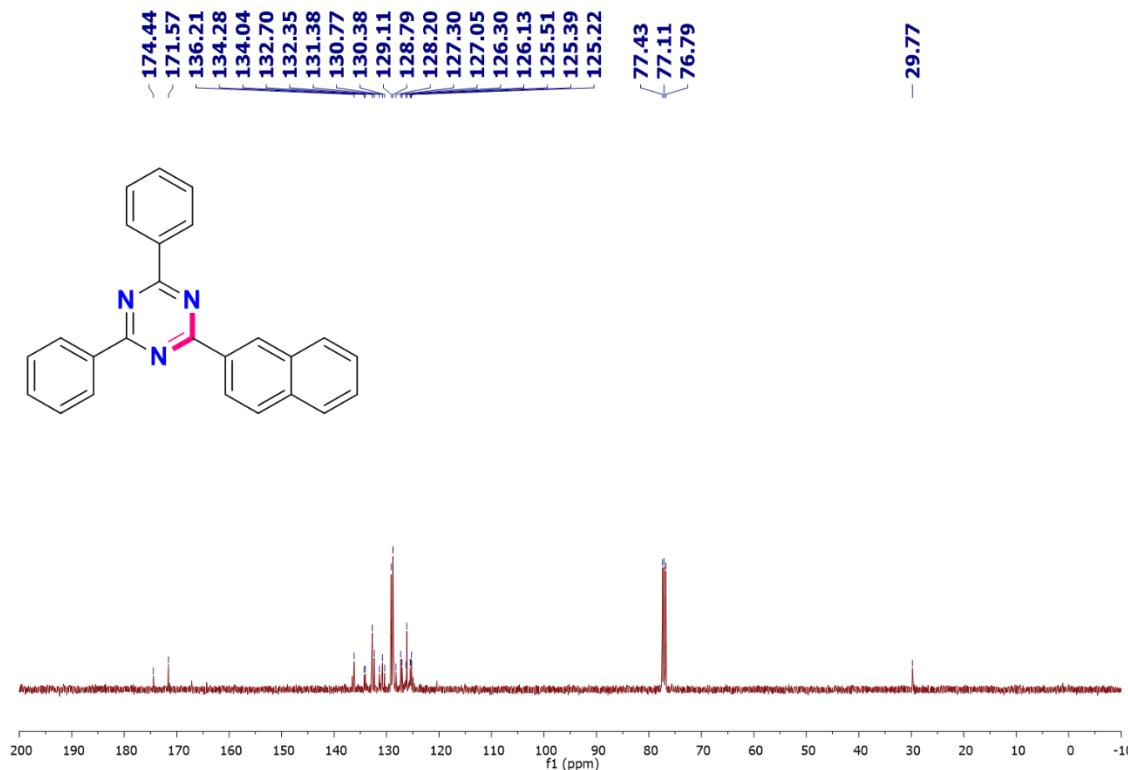
**Figure S43.**  $^1\text{H}$  NMR spectrum of **3o** in  $\text{CDCl}_3$ (100 MHz, 300 K)



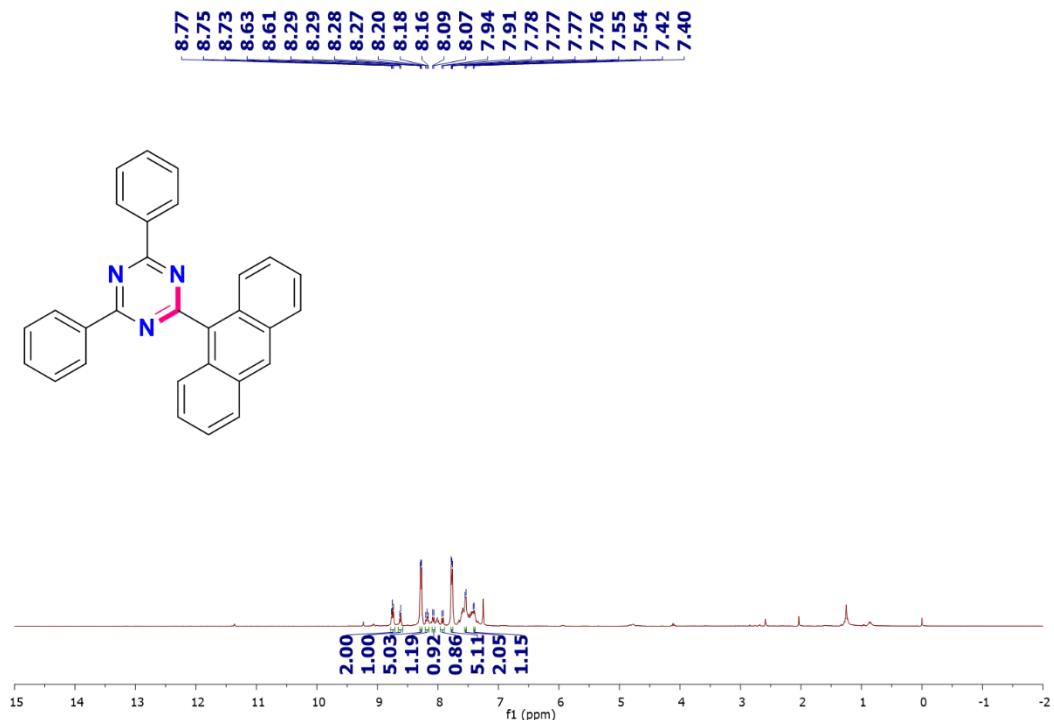
**Figure S44.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **3o** in  $\text{CDCl}_3$ (100 MHz, 300 K)



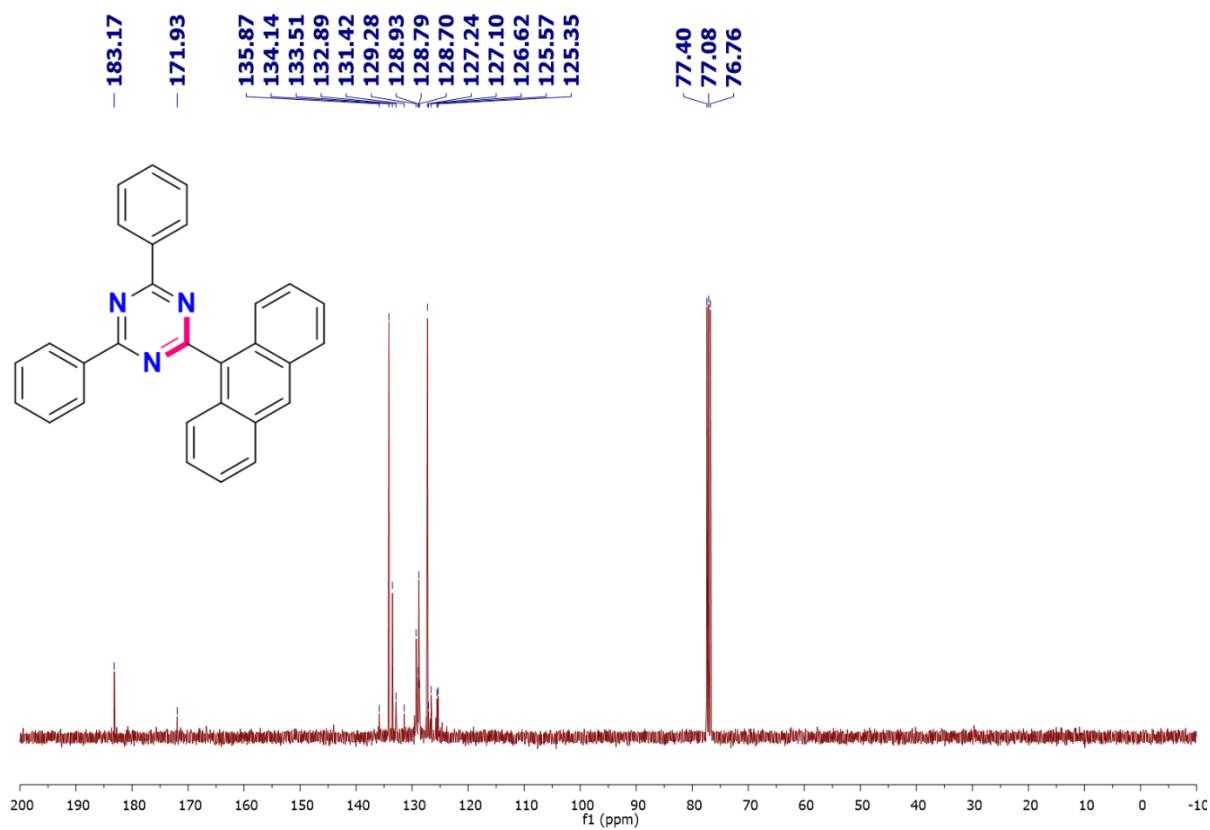
**Figure S45.** <sup>1</sup>H NMR spectrum of **3p** in CDCl<sub>3</sub>(100 MHz, 300 K)



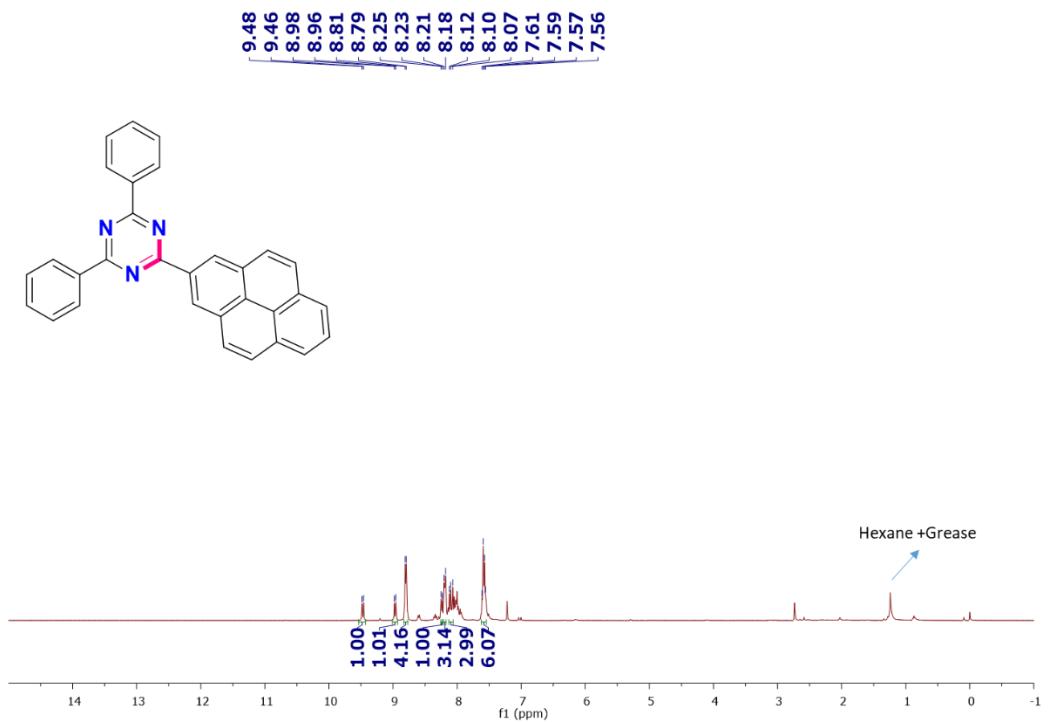
**Figure S46.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3p** in CDCl<sub>3</sub>(100 MHz, 300 K)



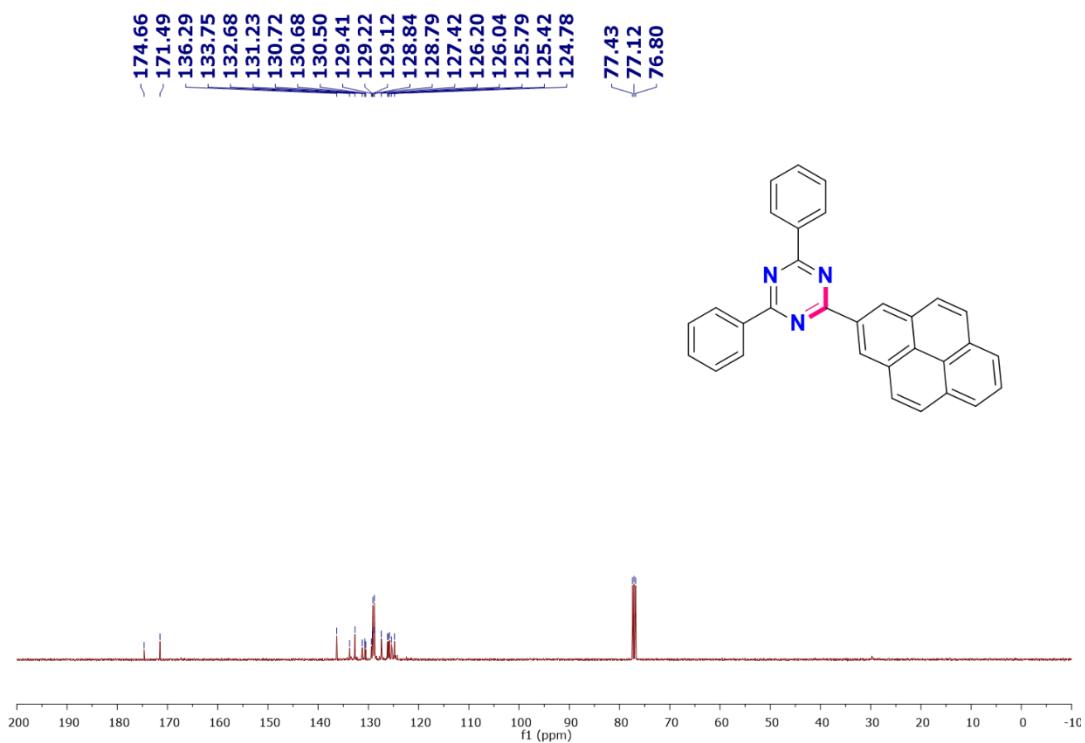
**Figure S47.**  $^1\text{H}$  NMR spectrum of **3q** in  $\text{CDCl}_3$  (100 MHz, 300 K)



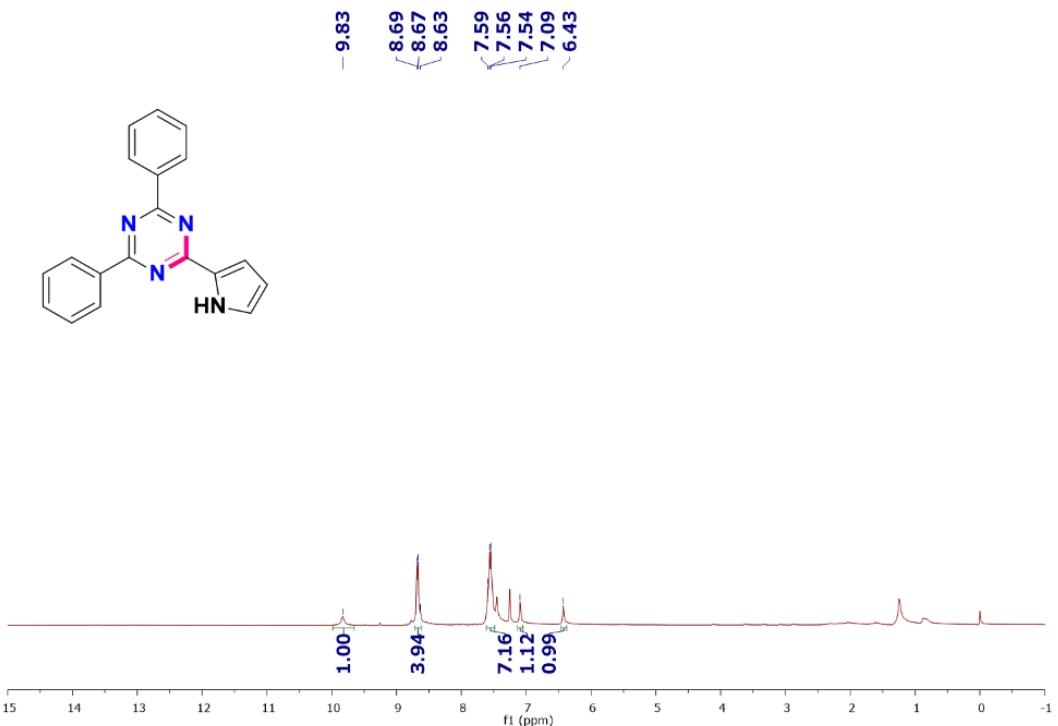
**Figure S48.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **3q** in  $\text{CDCl}_3$  (100 MHz, 300 K)



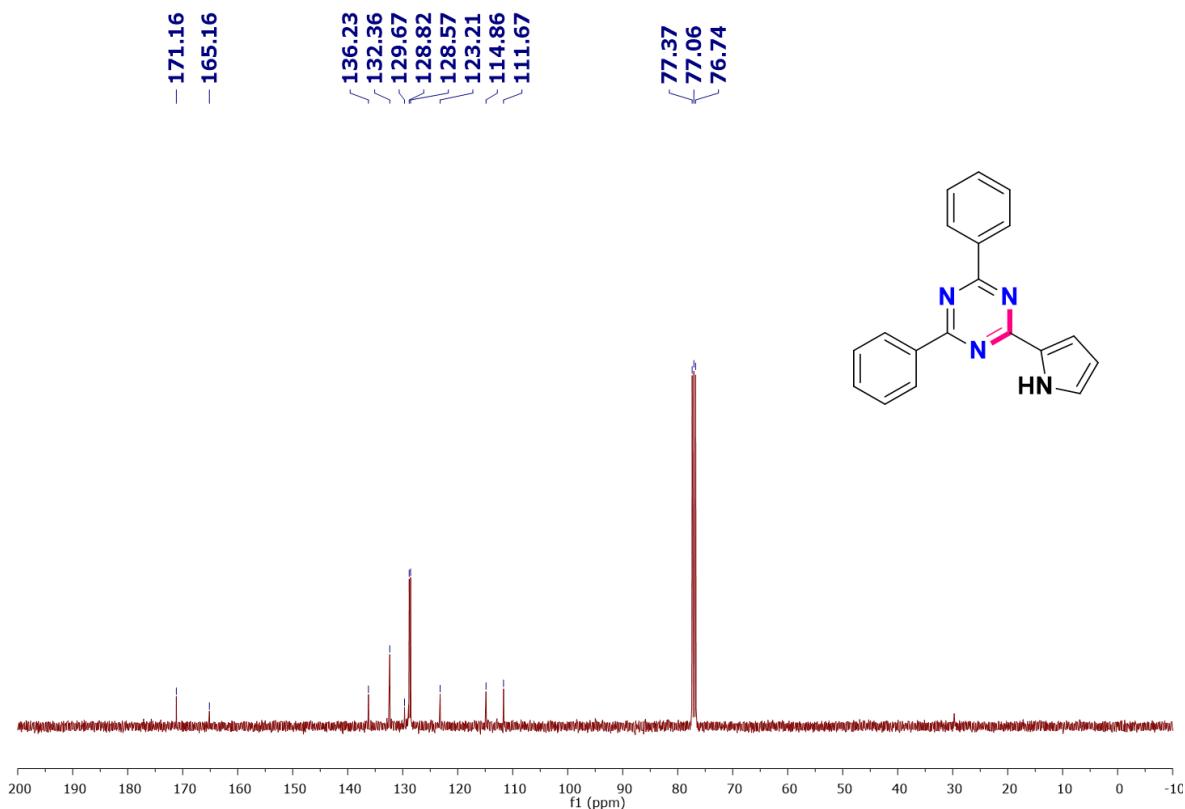
**Figure S49.**  $^1\text{H}$  NMR spectrum of **3r** in  $\text{CDCl}_3$ (100 MHz, 300 K)



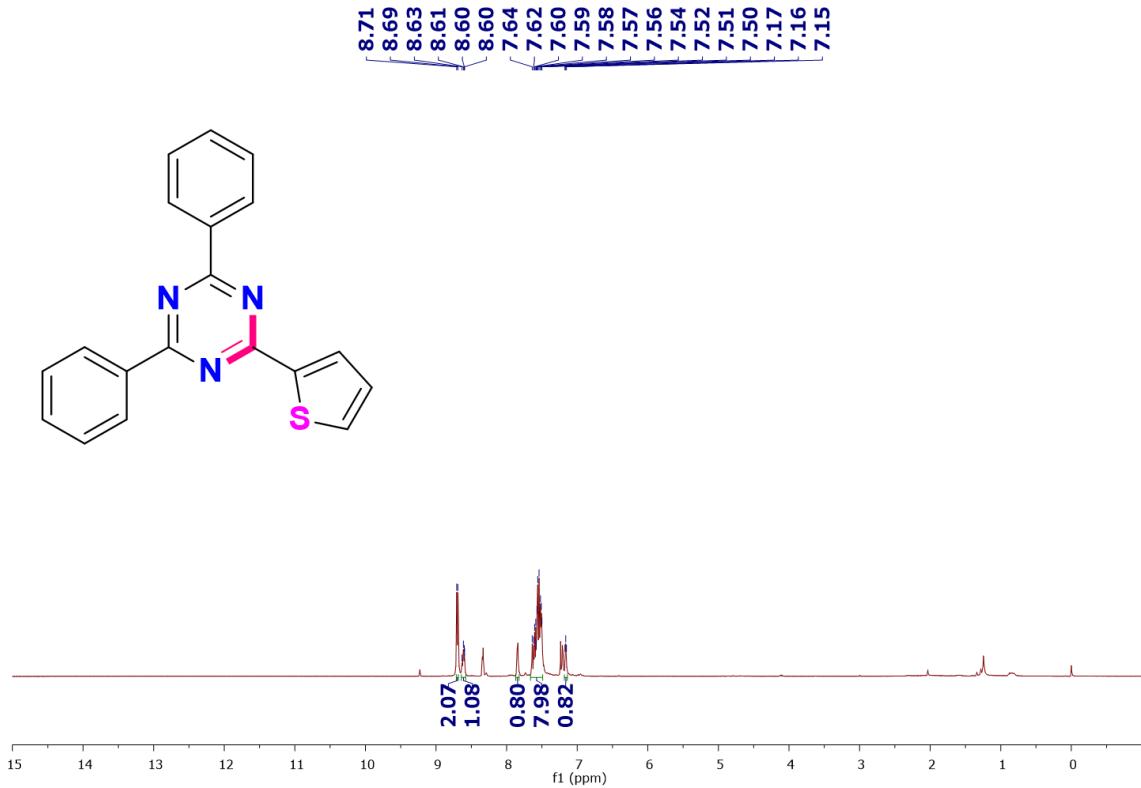
**Figure S50.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **3r** in  $\text{CDCl}_3$ (100 MHz, 300 K)



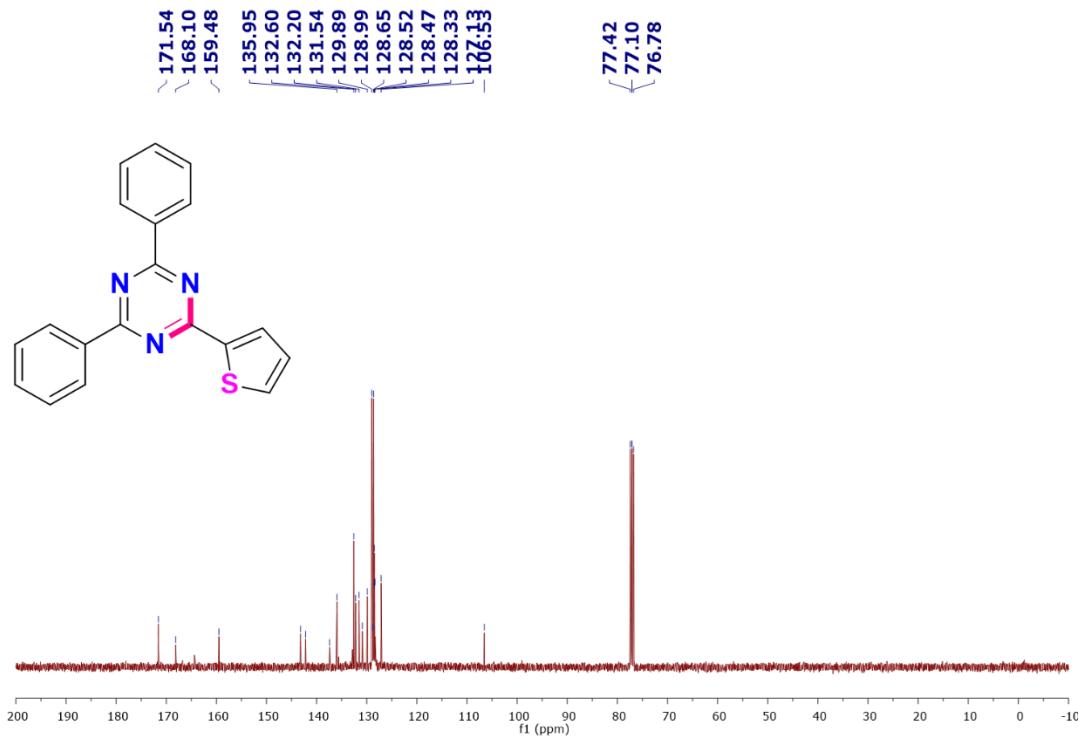
**Figure S51.** <sup>1</sup>H NMR spectrum of **3s** in CDCl<sub>3</sub>(100 MHz, 300 K)



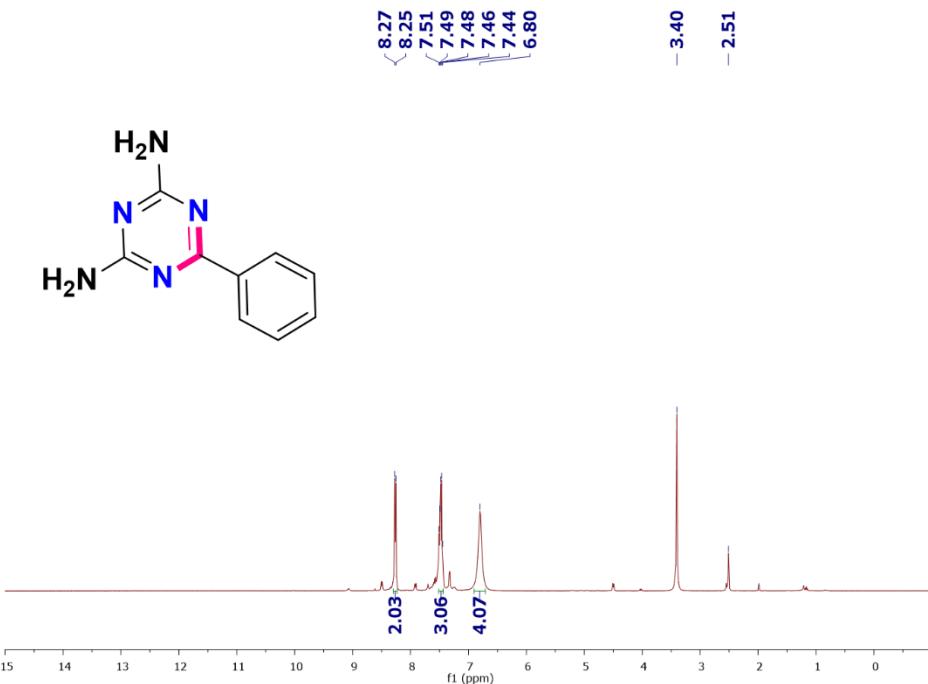
**Figure S52.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3s** in CDCl<sub>3</sub>(100 MHz, 300 K)



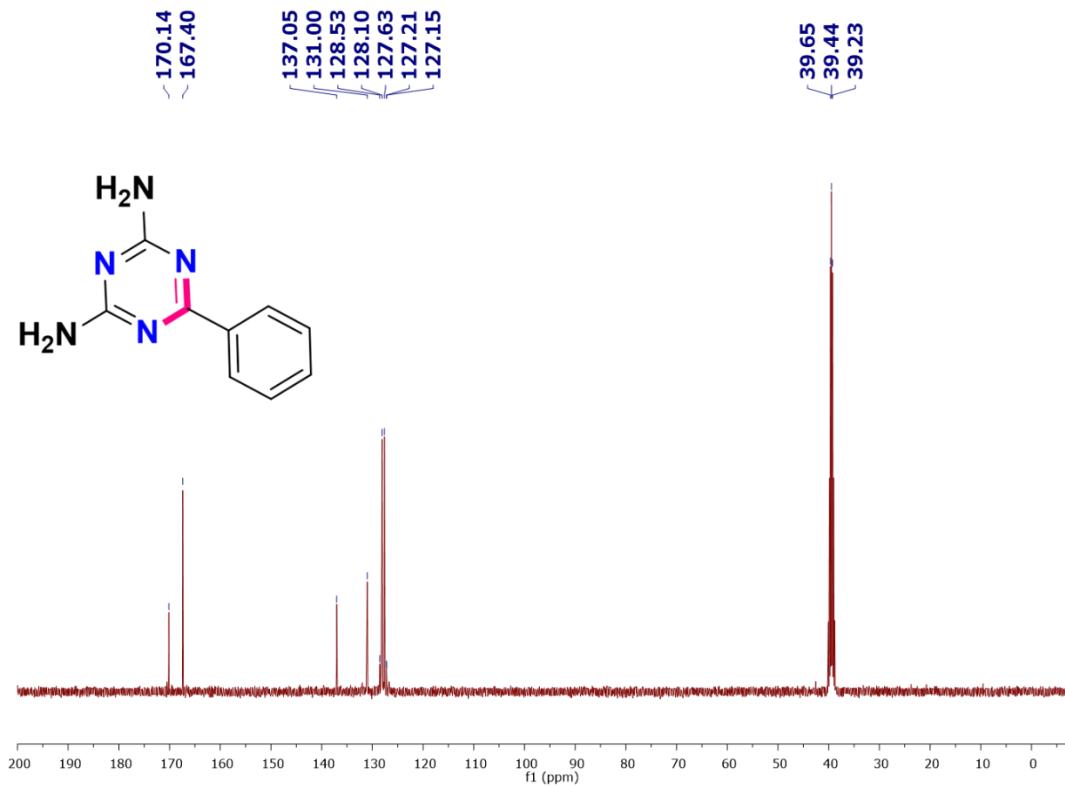
**Figure S53.** <sup>1</sup>H NMR spectrum of **3t** in CDCl<sub>3</sub>(100 MHz, 300 K)



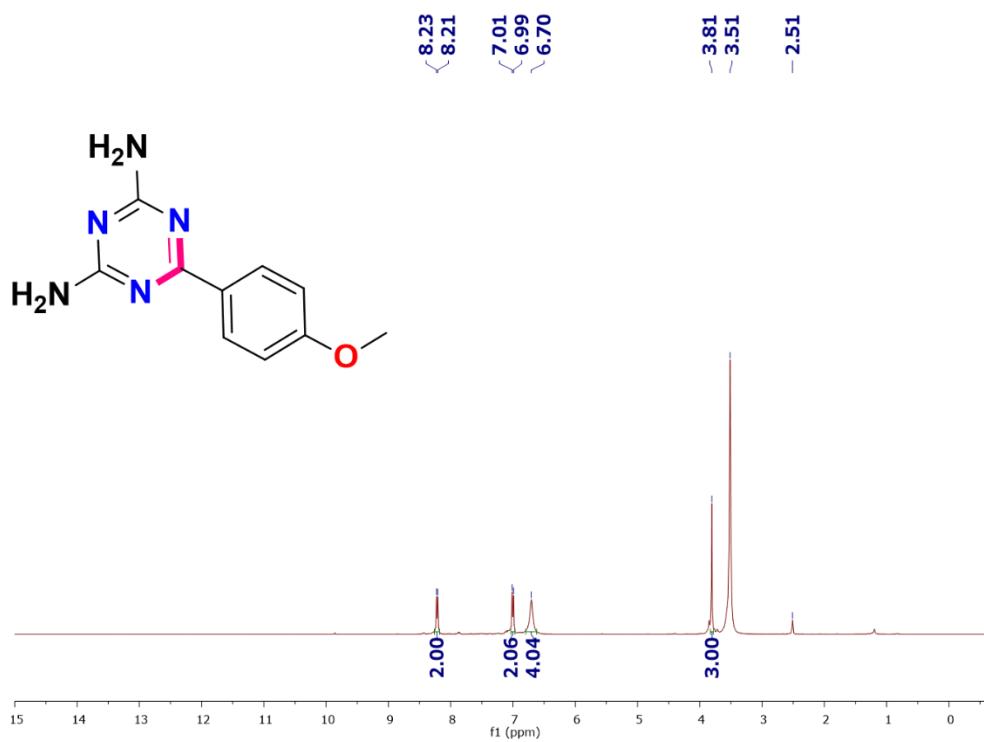
**Figure S54.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3t** in CDCl<sub>3</sub>(100 MHz, 300 K)



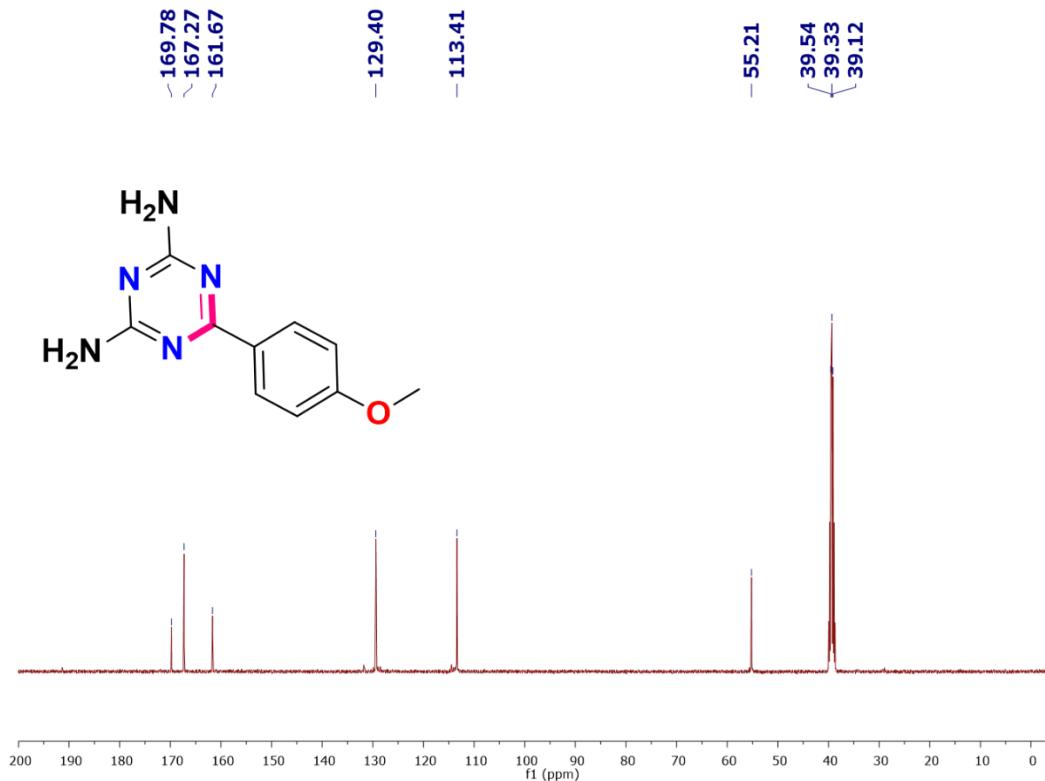
**Figure S55.**  $^1\text{H}$  NMR spectrum of **4a** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



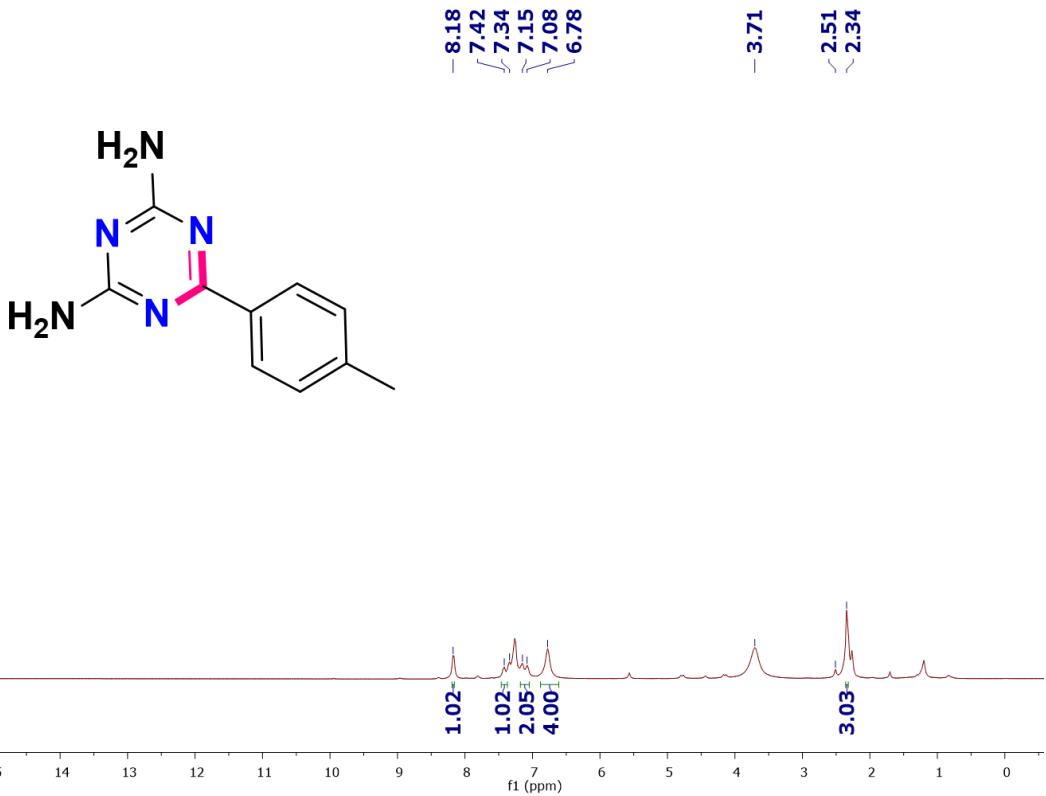
**Figure S56.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **4a** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



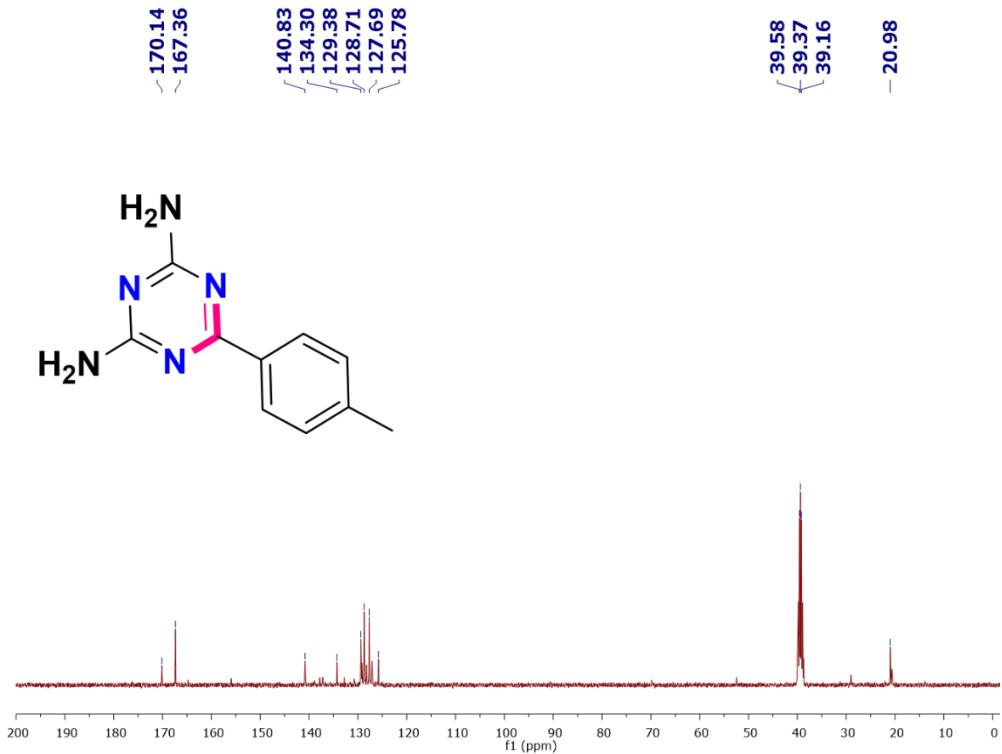
**Figure S547.**  $^1\text{H}$  NMR spectrum of **4b** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



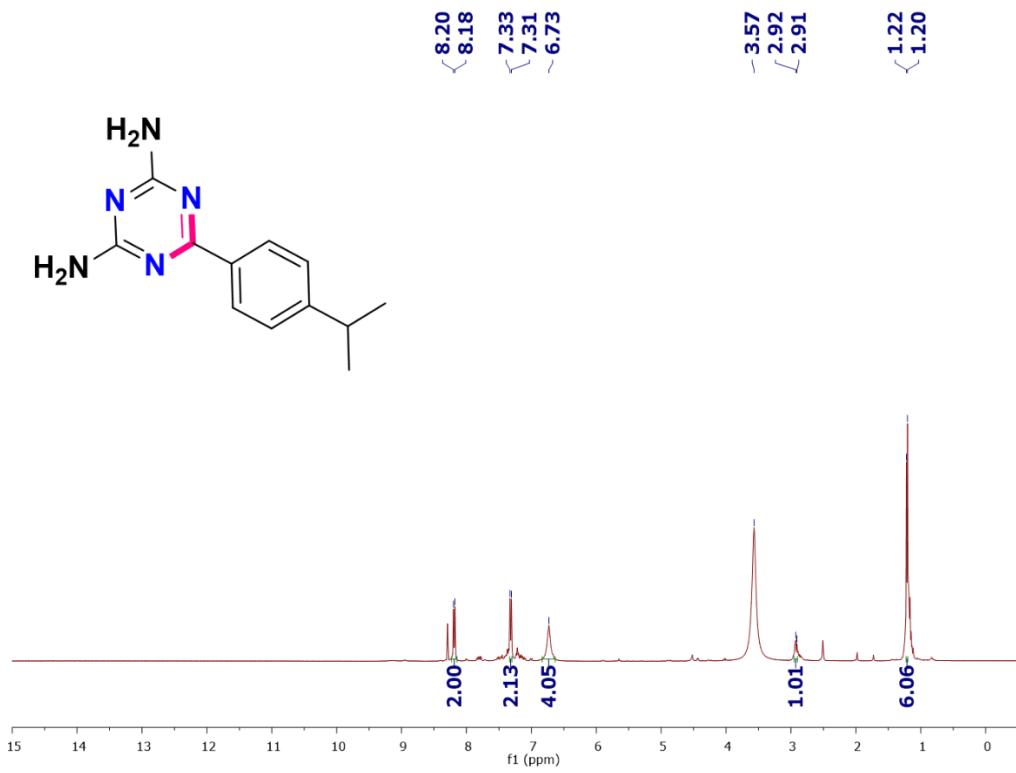
**Figure S58.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **4b** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



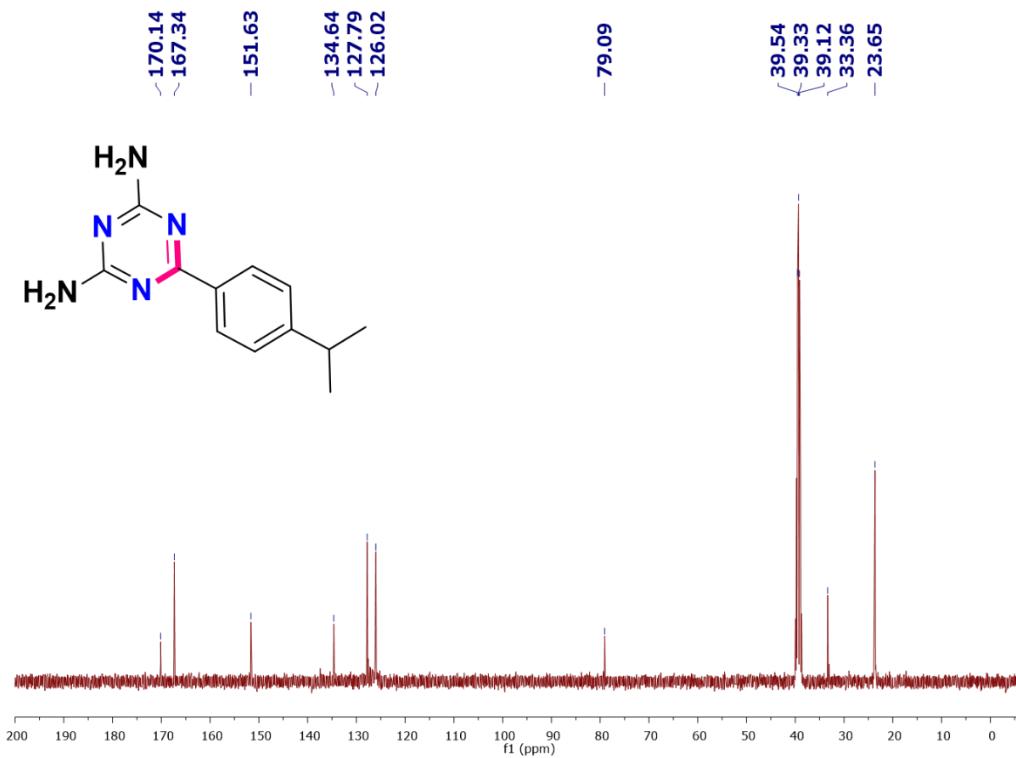
**Figure S59.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **4c** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



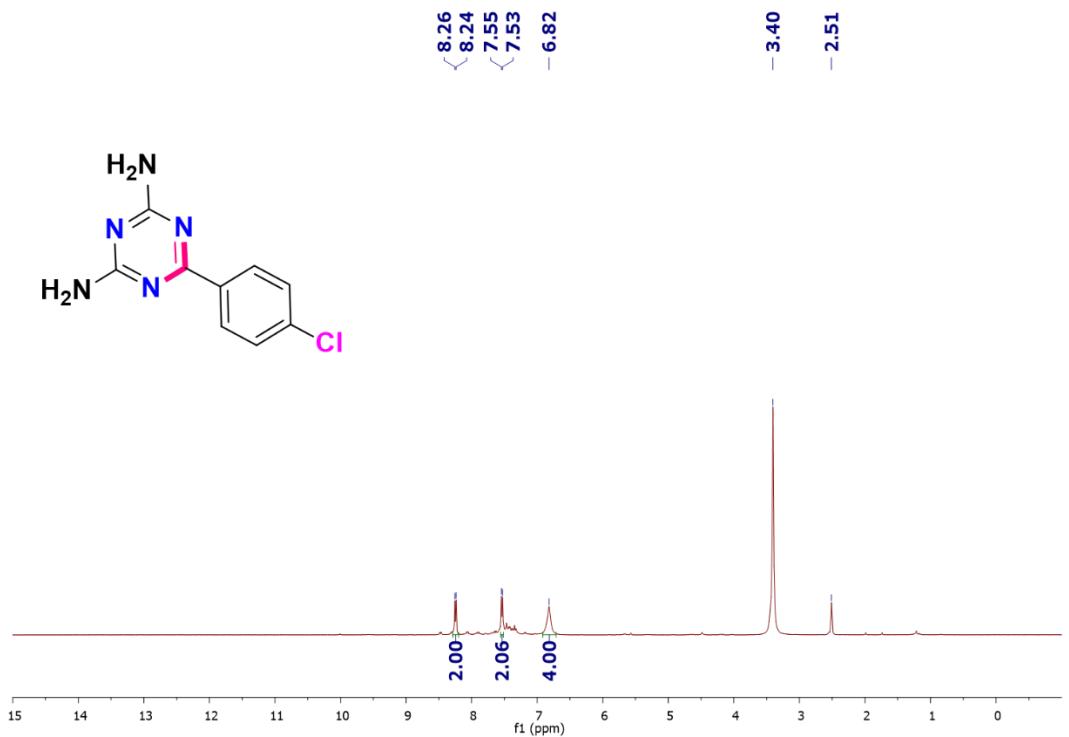
**Figure S60.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **4c** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



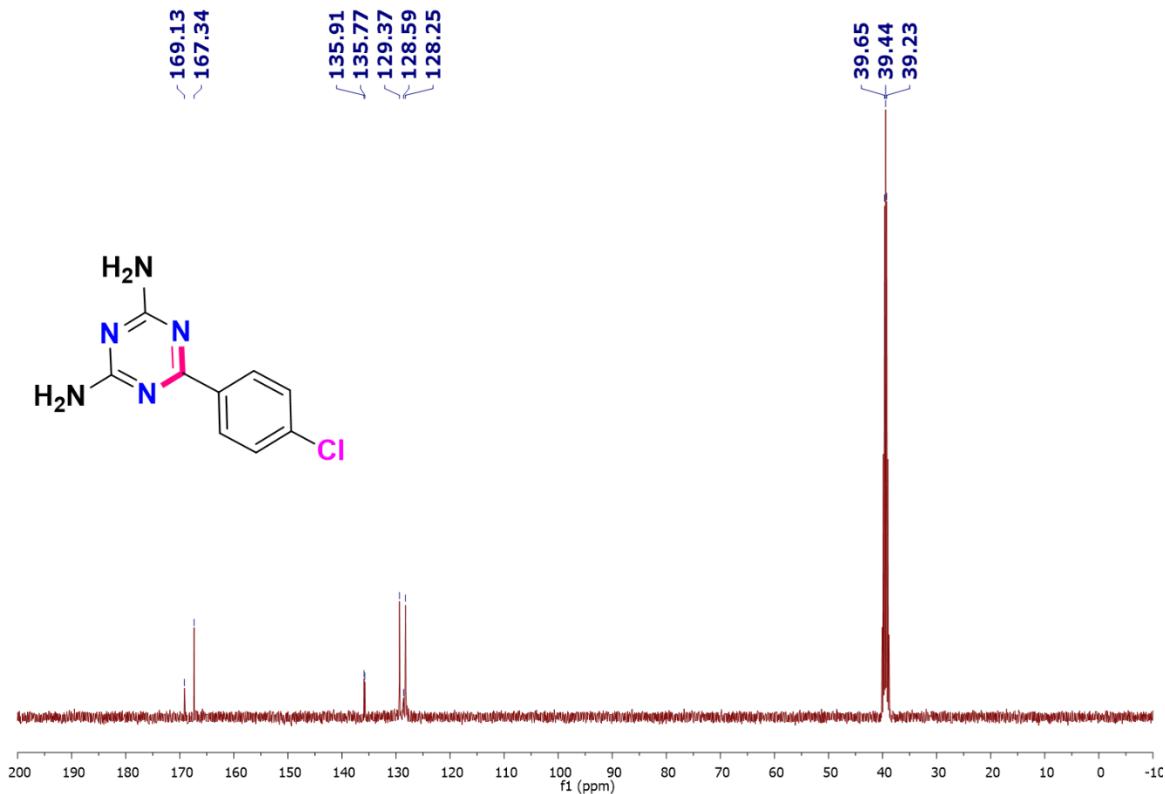
**Figure S61.**  $^1\text{H}$  NMR spectrum of **4d** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



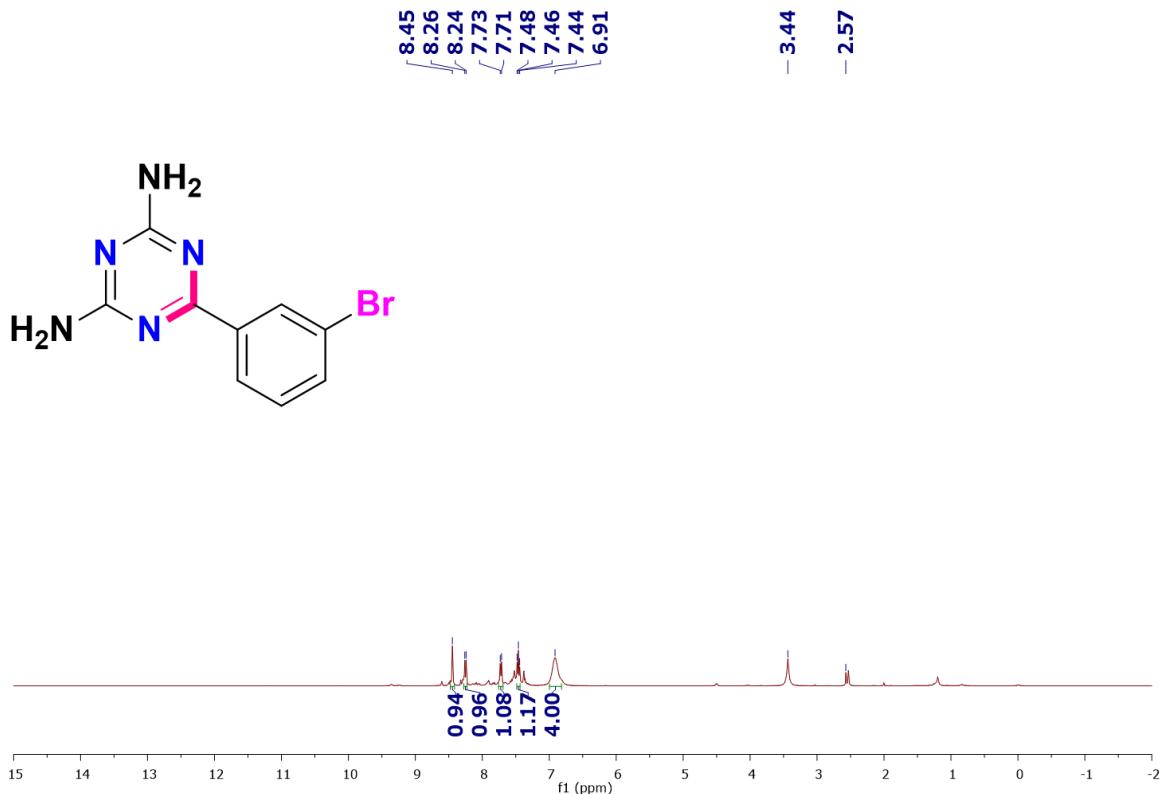
**Figure S62.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **4d** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



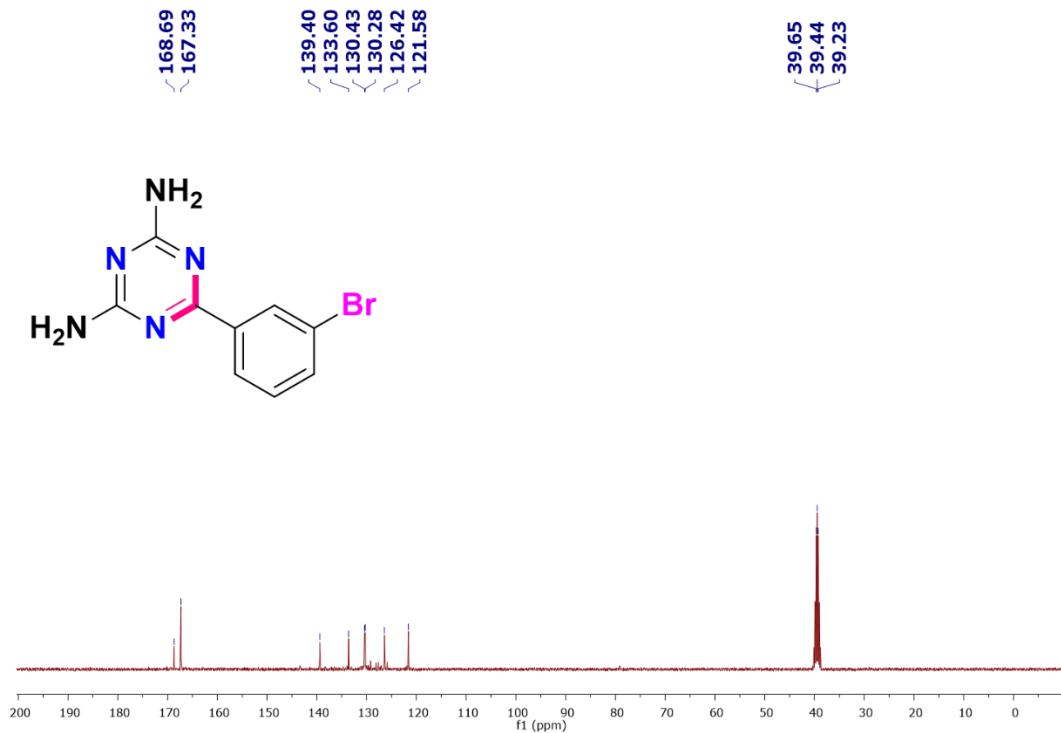
**Figure S63.**  $^1\text{H}$  NMR spectrum of **4e** in  $\text{DMSO-d}_6$  (400 MHz, 300 K)



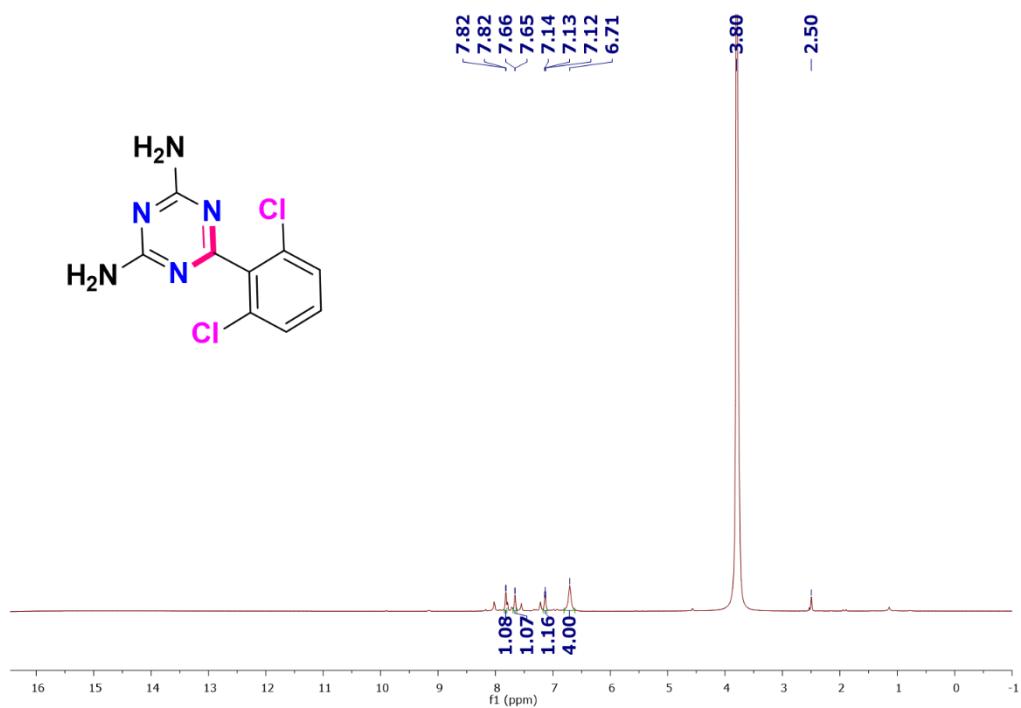
**Figure S64.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4e** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



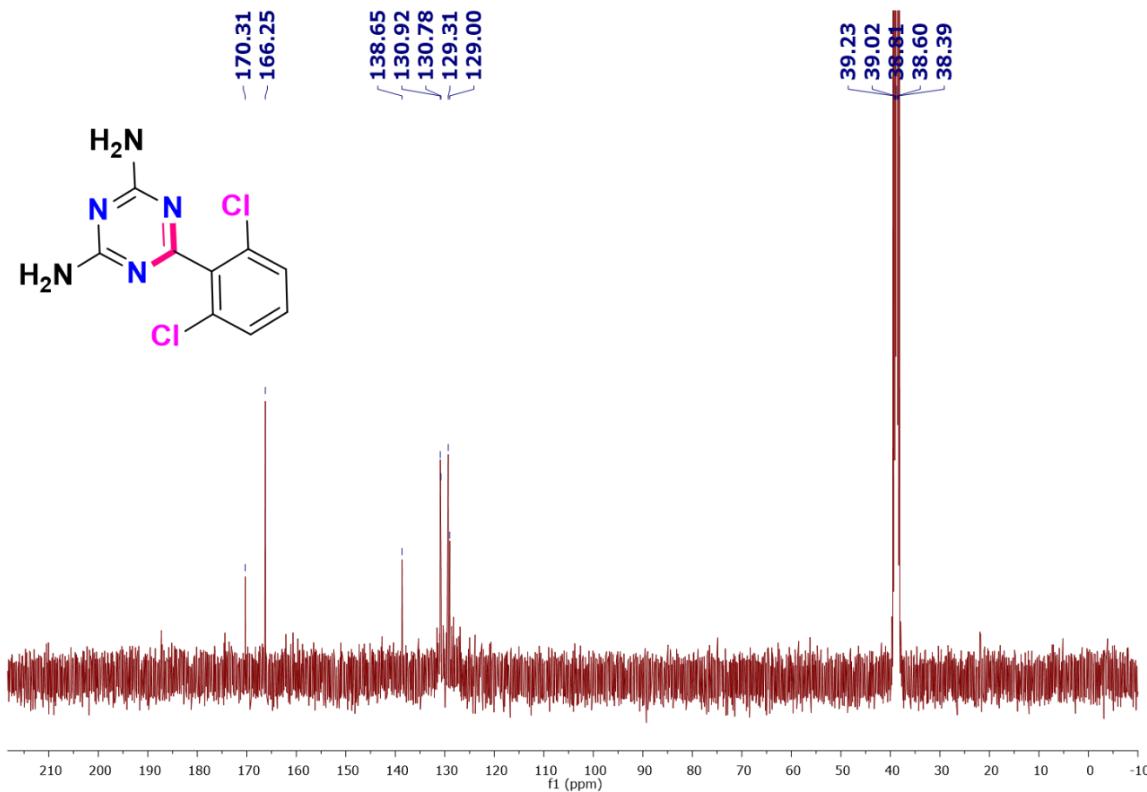
**Figure S65.** <sup>1</sup>H NMR spectrum of **4f** in DMSO-d<sub>6</sub> (400 MHz, 300 K)



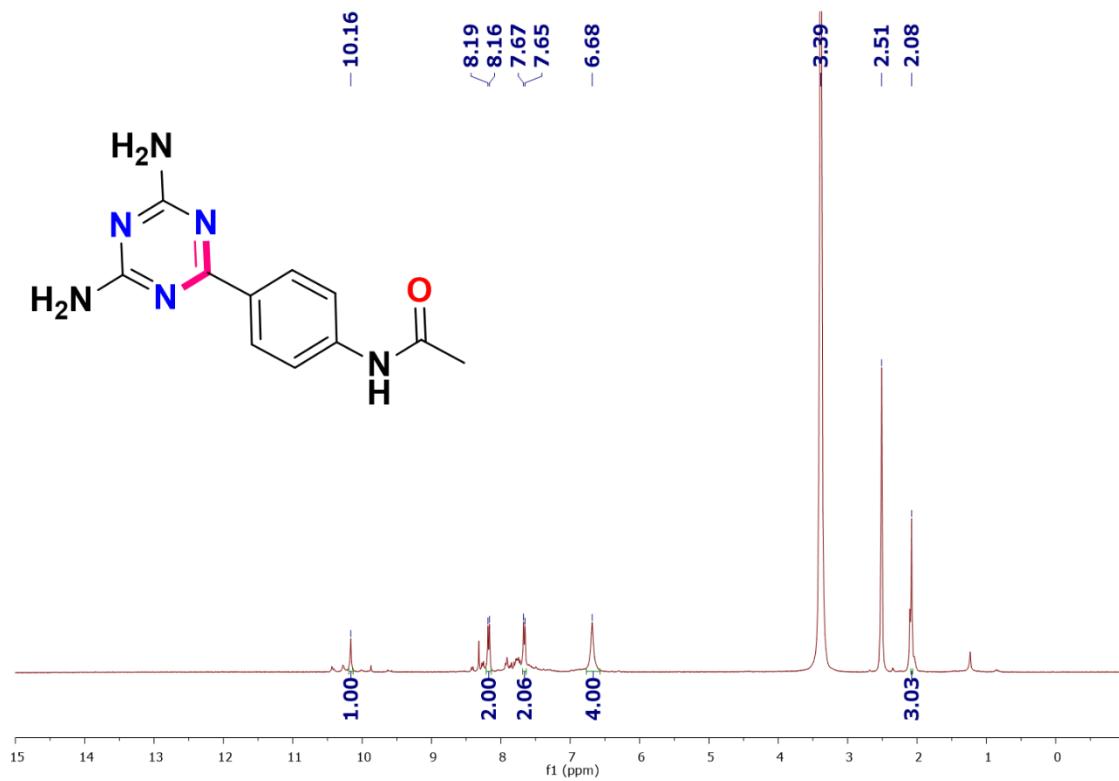
**Figure S66.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4f** in DMSO-d<sub>6</sub> (100 MHz, 300 K)



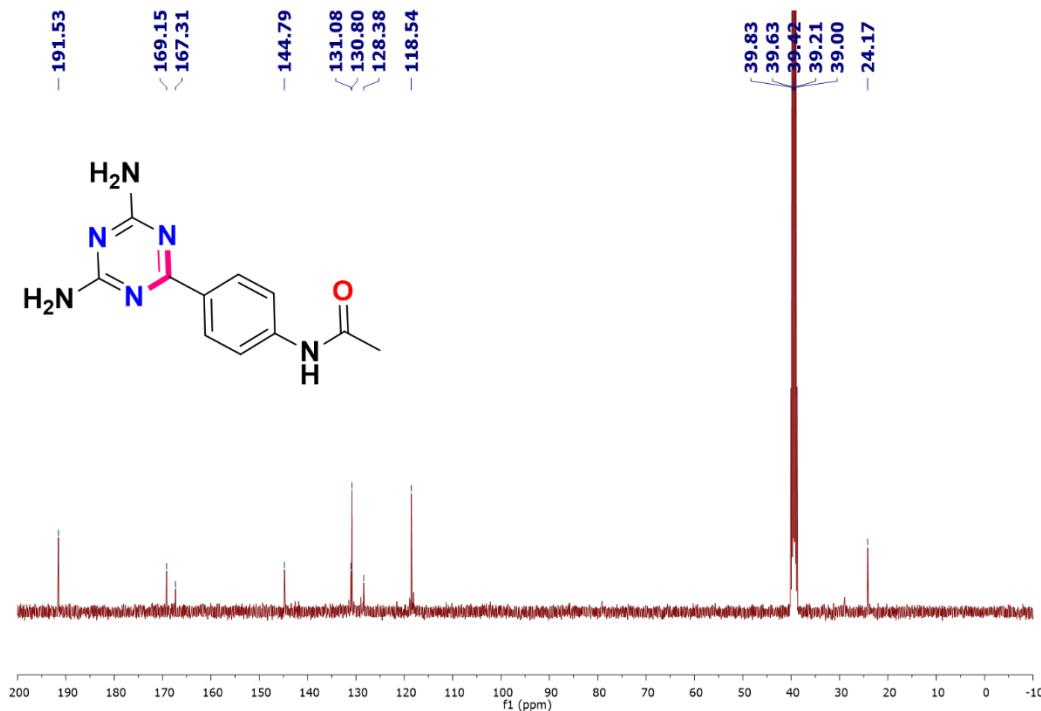
**Figure S67.**  $^1\text{H}$  NMR spectrum of **4g** in  $\text{DMSO-d}_6$  (400 MHz, 300 K)



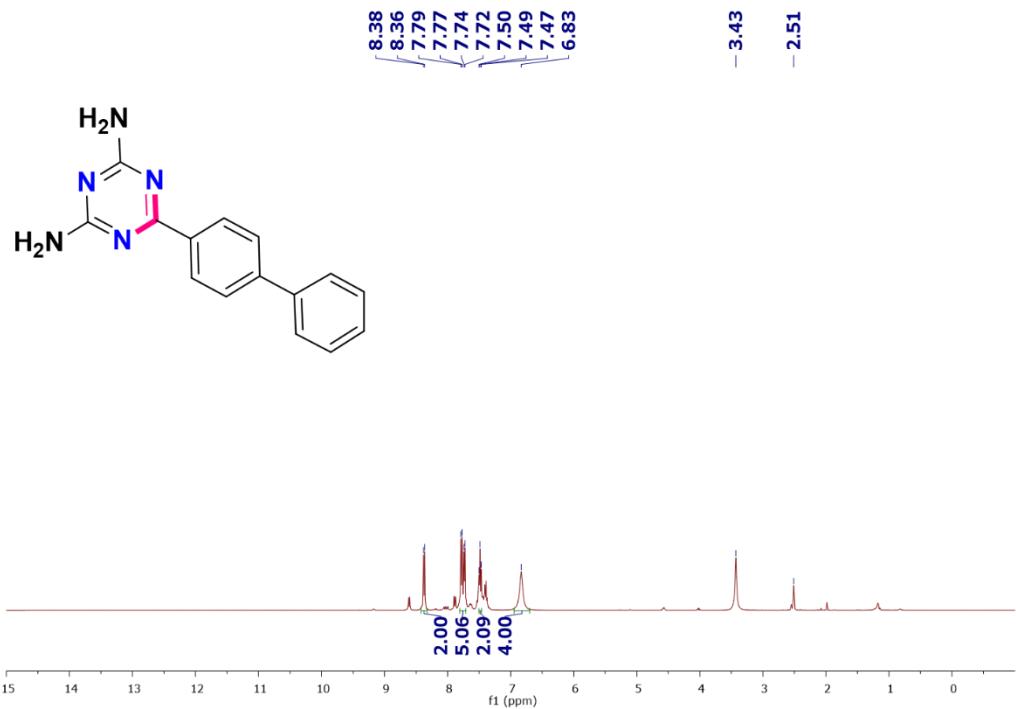
**Figure S68.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4g** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



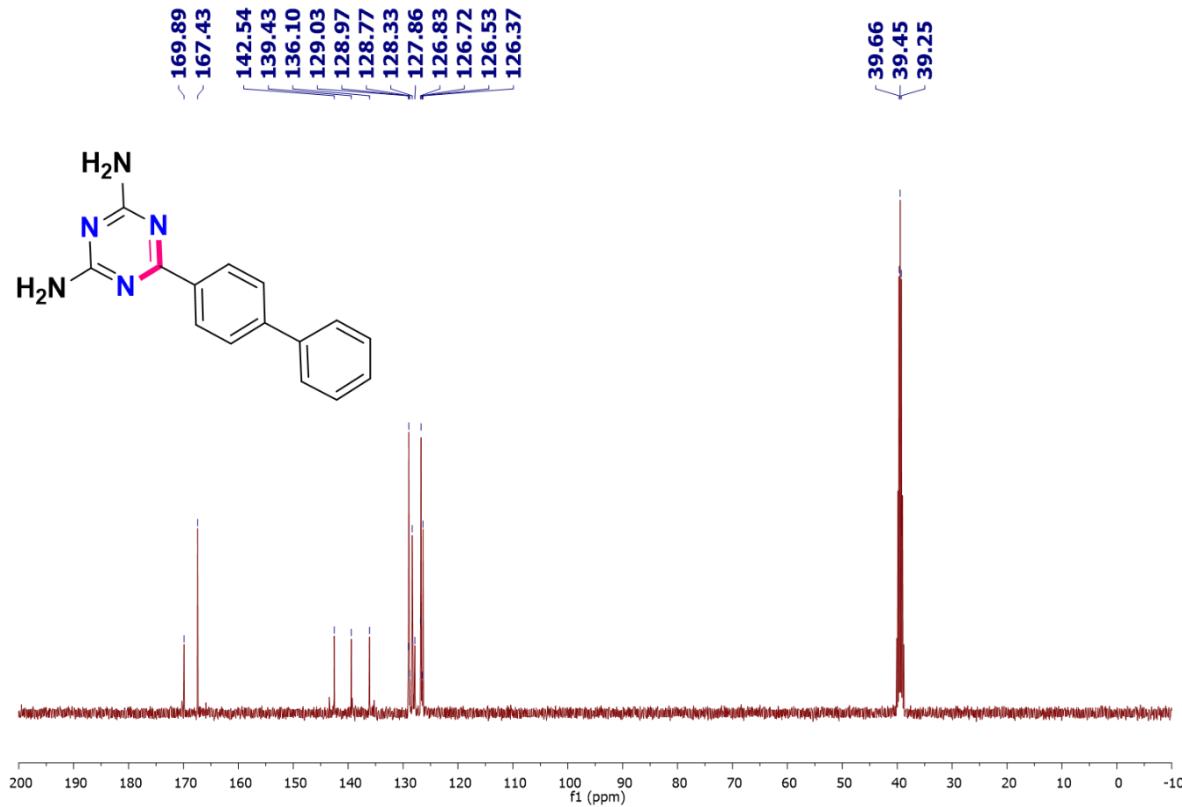
**Figure S69.**  $^1\text{H}$  NMR spectrum of **4h** in  $\text{DMSO-d}_6$  (400 MHz, 300 K)



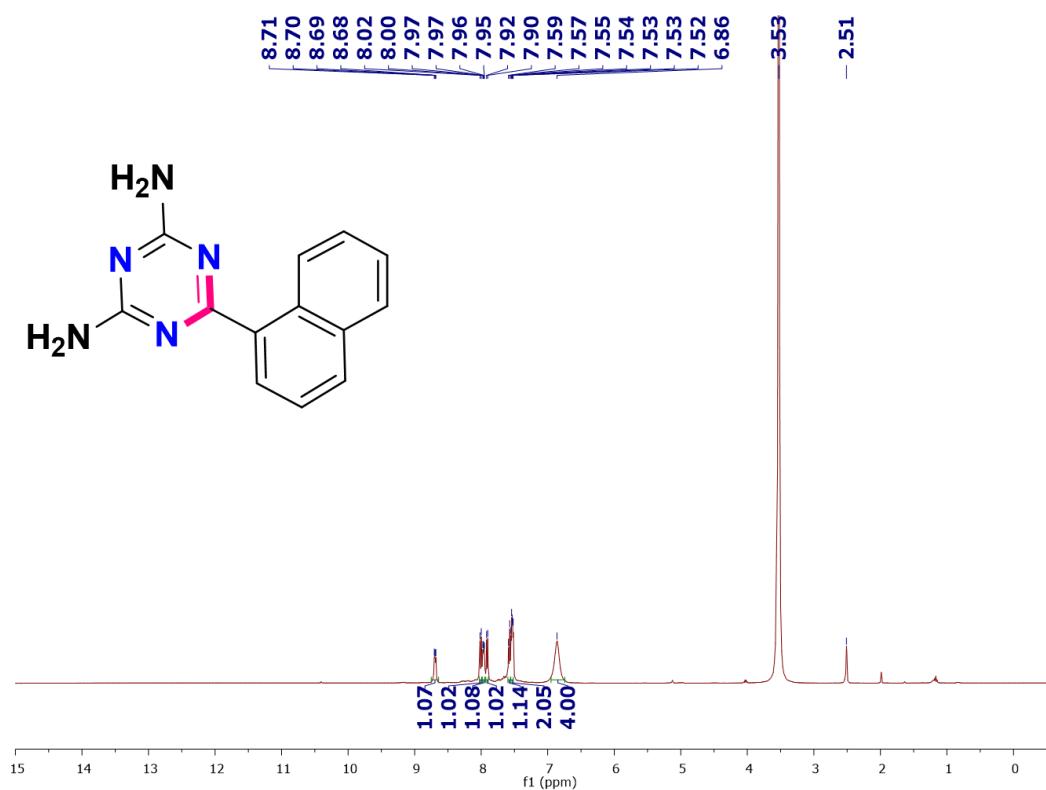
**Figure S70.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4h** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



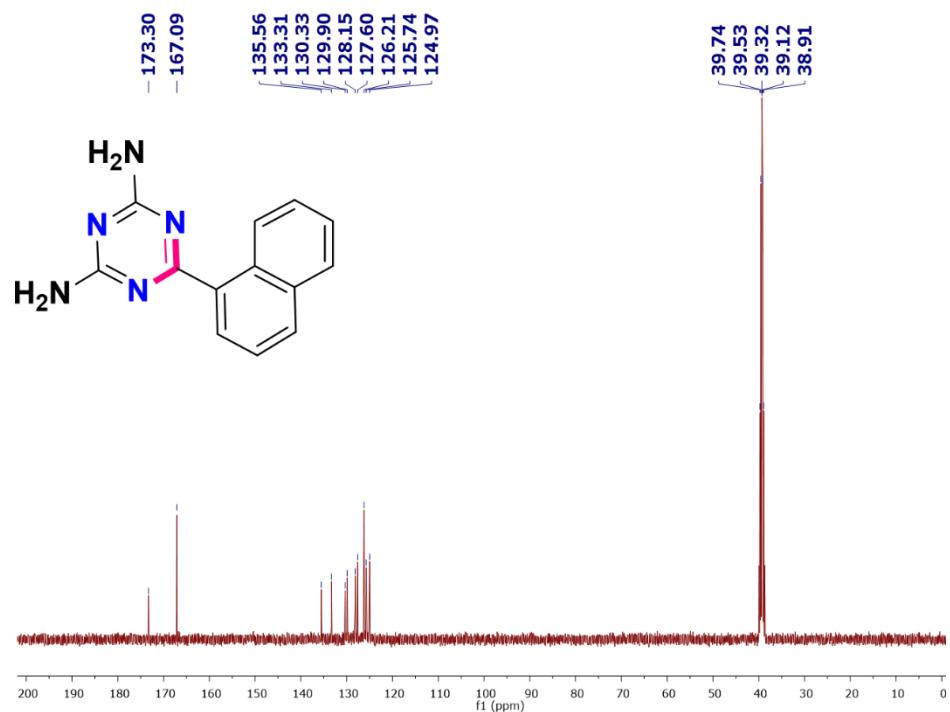
**Figure S71.**  $^1\text{H}$  NMR spectrum of **4i** in  $\text{DMSO-d}_6$  (400 MHz, 300 K)



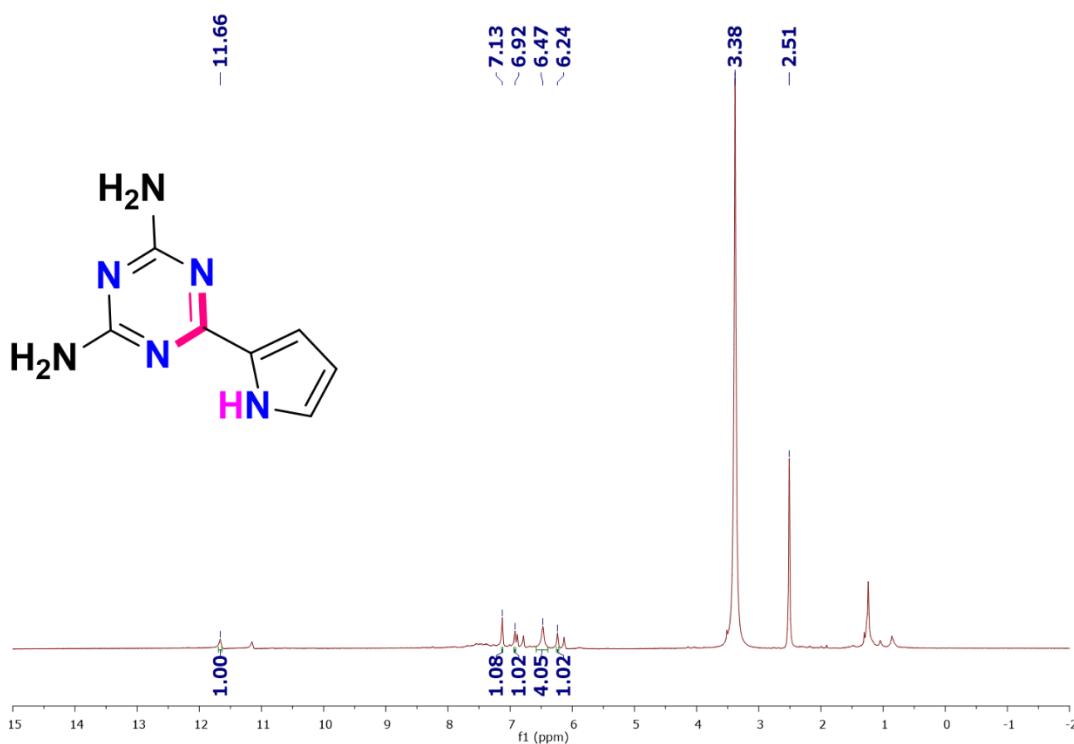
**Figure S72.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **4i** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



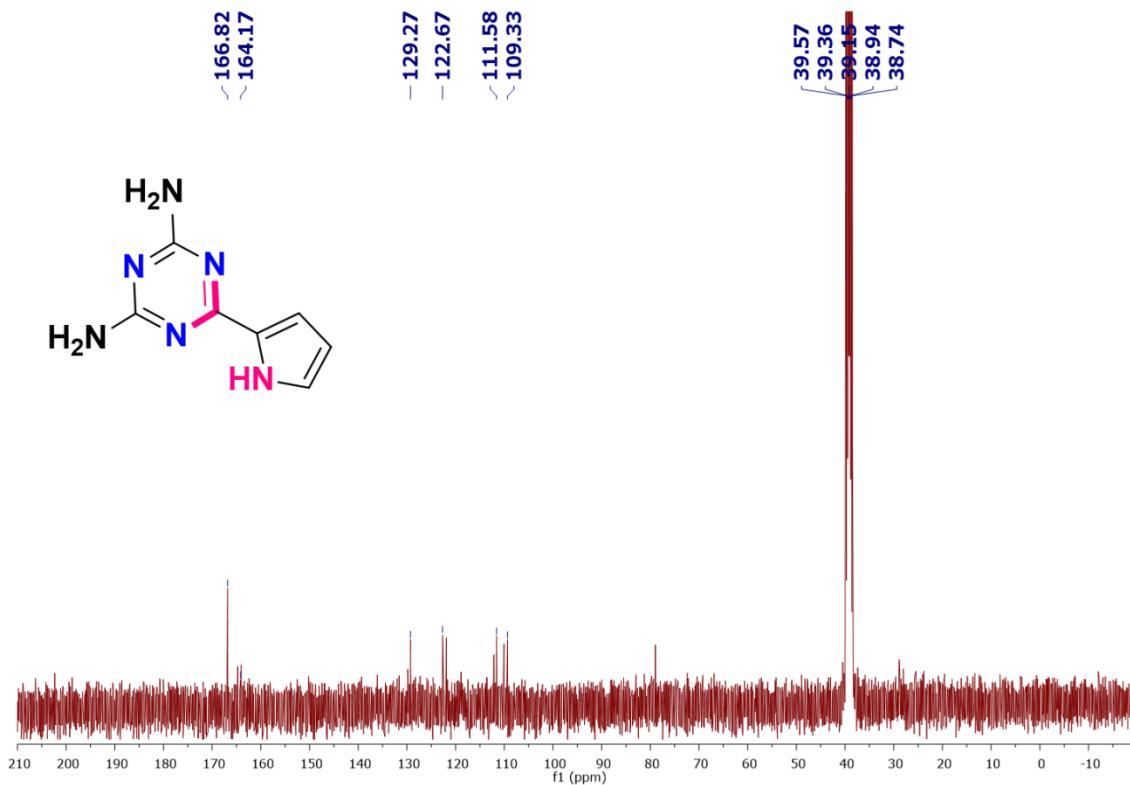
**Figure S73.**  $^1\text{H}$  NMR spectrum of **4j** in  $\text{DMSO-d}_6$  (400 MHz, 300 K)



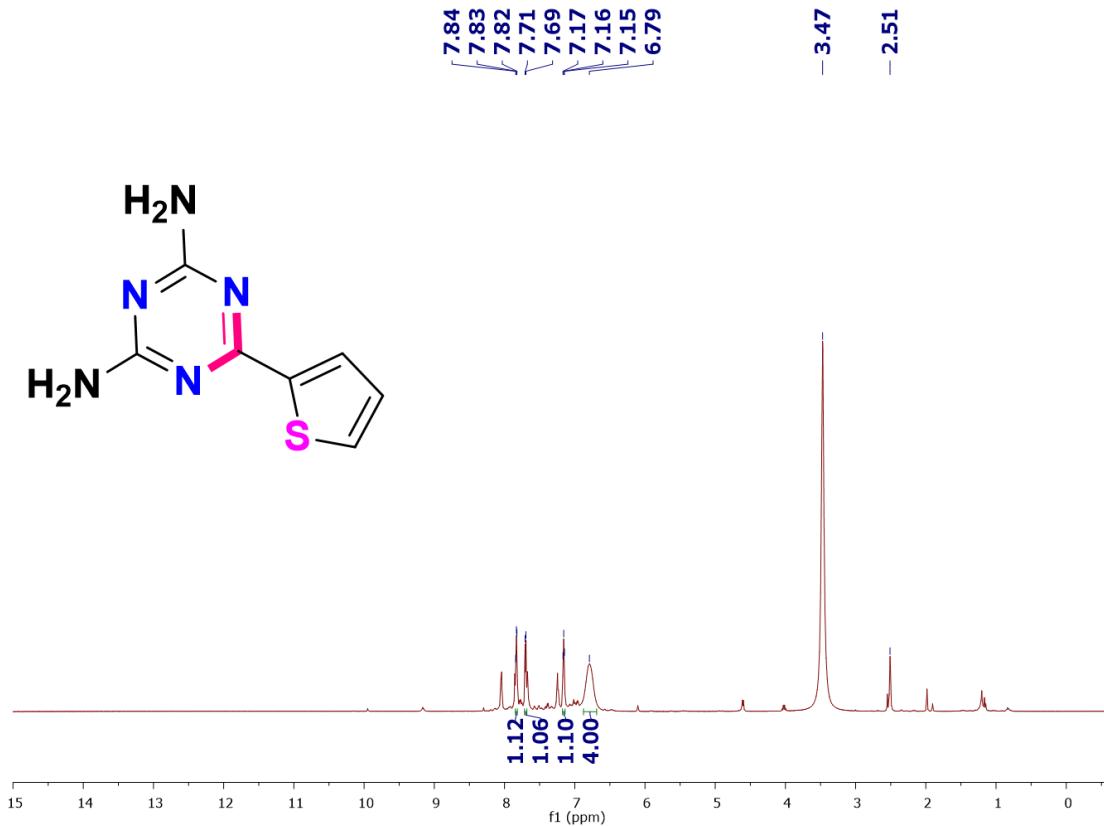
**Figure S74.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4j** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)



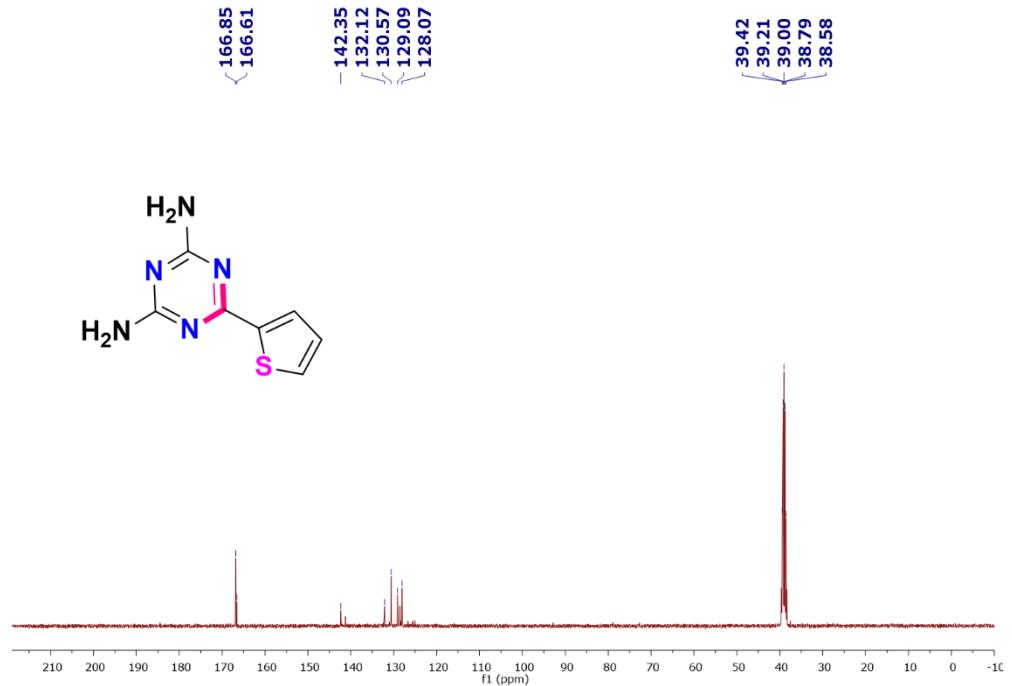
**Figure S75.**  $^1\text{H}$  NMR spectrum of **4k** in  $\text{DMSO-d}_6$  (400 MHz, 300 K)



**Figure S76.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **4k** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)

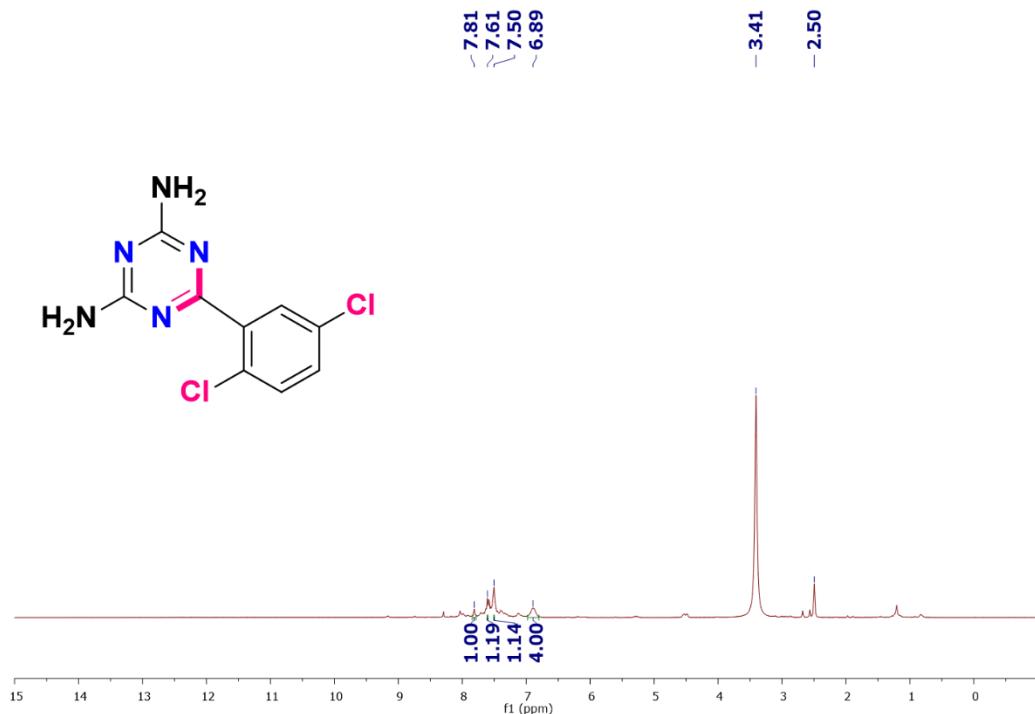


**Figure S77.**  $^1\text{H}$  NMR spectrum of **4l** in  $\text{DMSO-d}_6$  (400 MHz, 300 K)

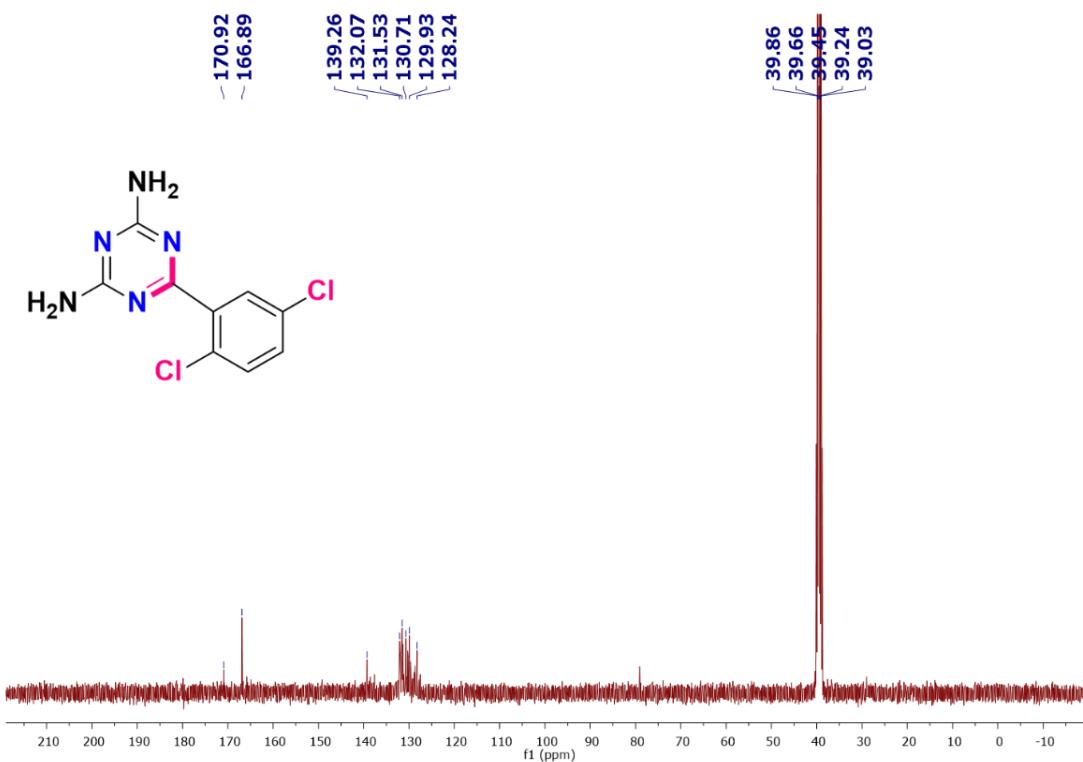


**Figure S78.**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of **4l** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)

**8. NMR spectra of Irsogladine drug (**4m**)**



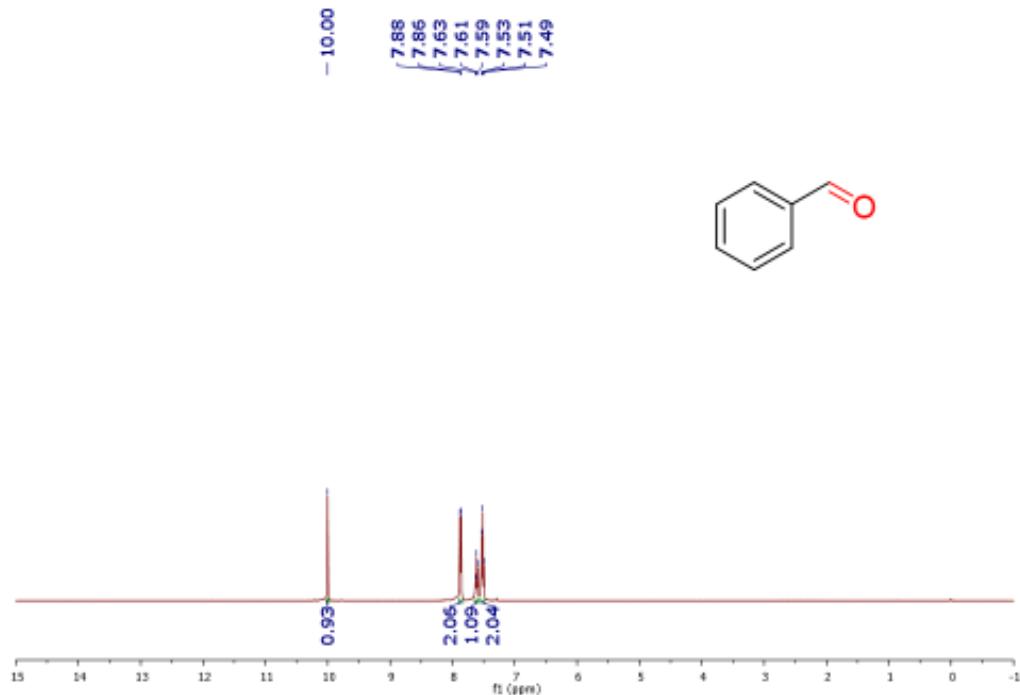
**Figure S79.**  $^1\text{H}$  NMR spectrum of **4m** in  $\text{DMSO-d}_6$  (400 MHz, 300 K)



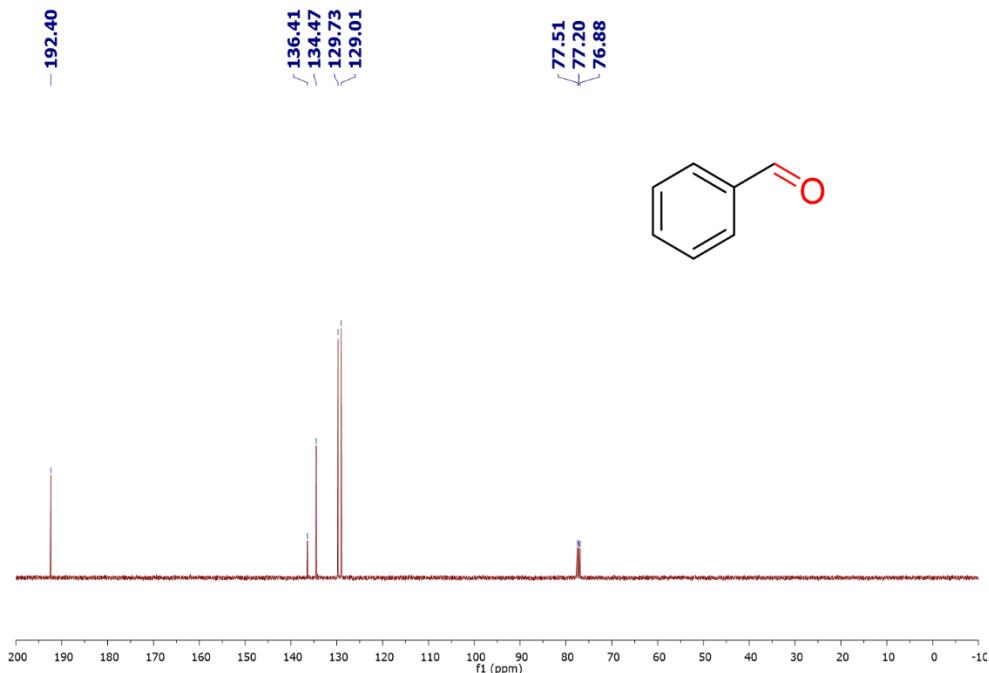
**Figure S80.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4m** in  $\text{DMSO-d}_6$  (100 MHz, 300 K)

## 9. NMR spectra of Intermediates:

### (i) Benzaldehyde (**1a'**)

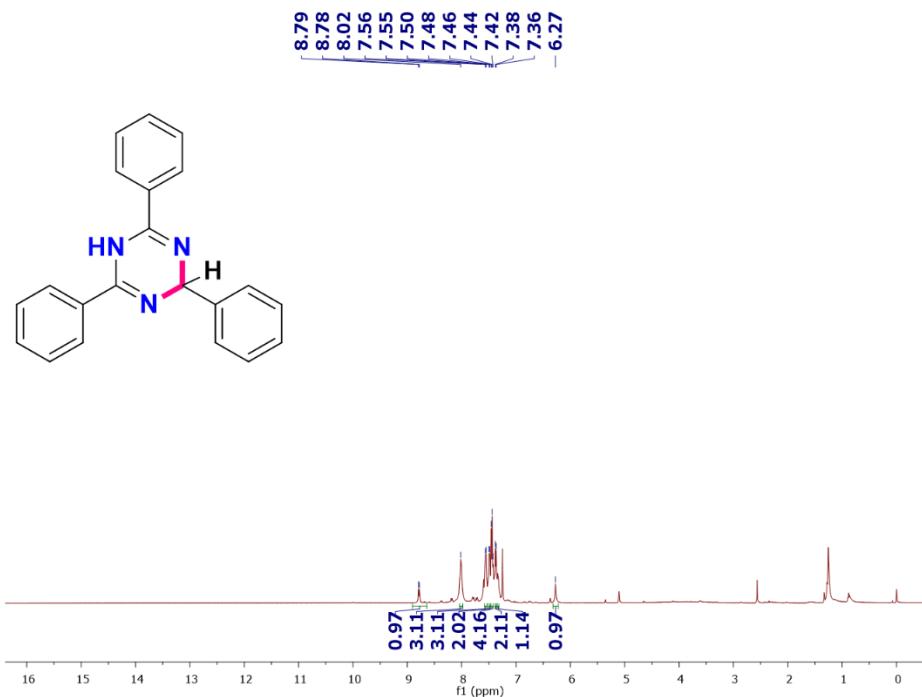


**Figure S81.**  $^1\text{H}$  NMR spectrum of **1a'** in  $\text{CDCl}_3$ (400 MHz, 300 K)

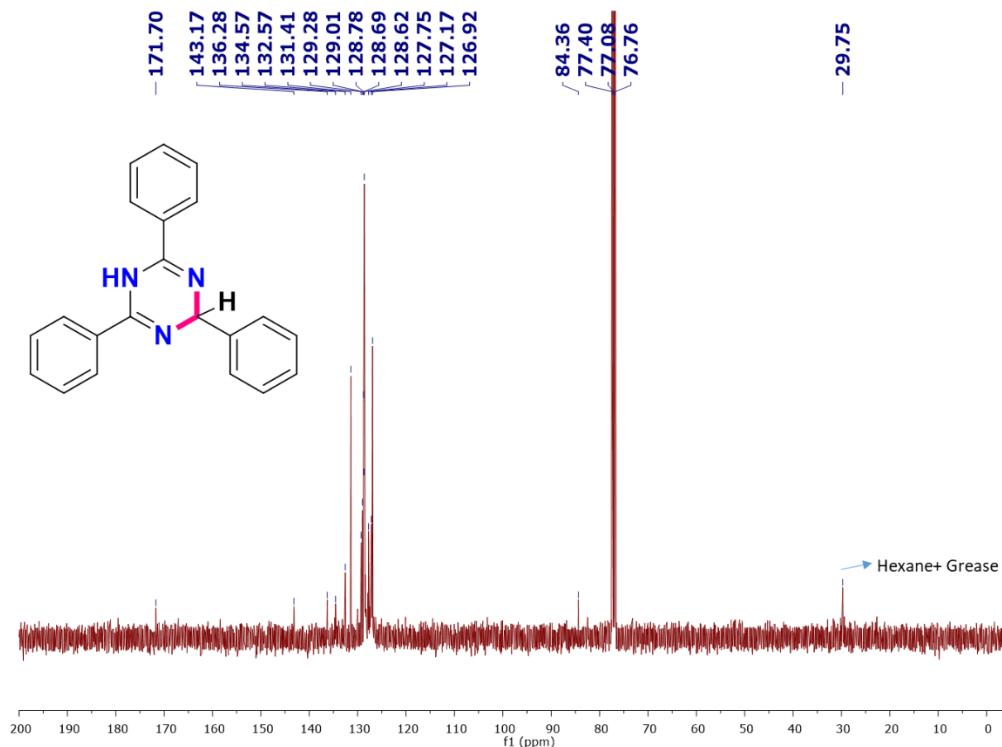


**Figure S82.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1a'** in  $\text{CDCl}_3$ (100 MHz, 300 K)

(ii) 2,4,6-triphenyl-1,4-dihydro-1,3,5-triazine (2a')



**Figure S83.** <sup>1</sup>H NMR spectrum of 2a' in CDCl<sub>3</sub>(400 MHz, 300 K)



**Figure S84.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 2a' in CDCl<sub>3</sub>(100 MHz, 300 K)

## 10. HRMS Spectra of new catalytic 1,3,5-Triazine derivatives

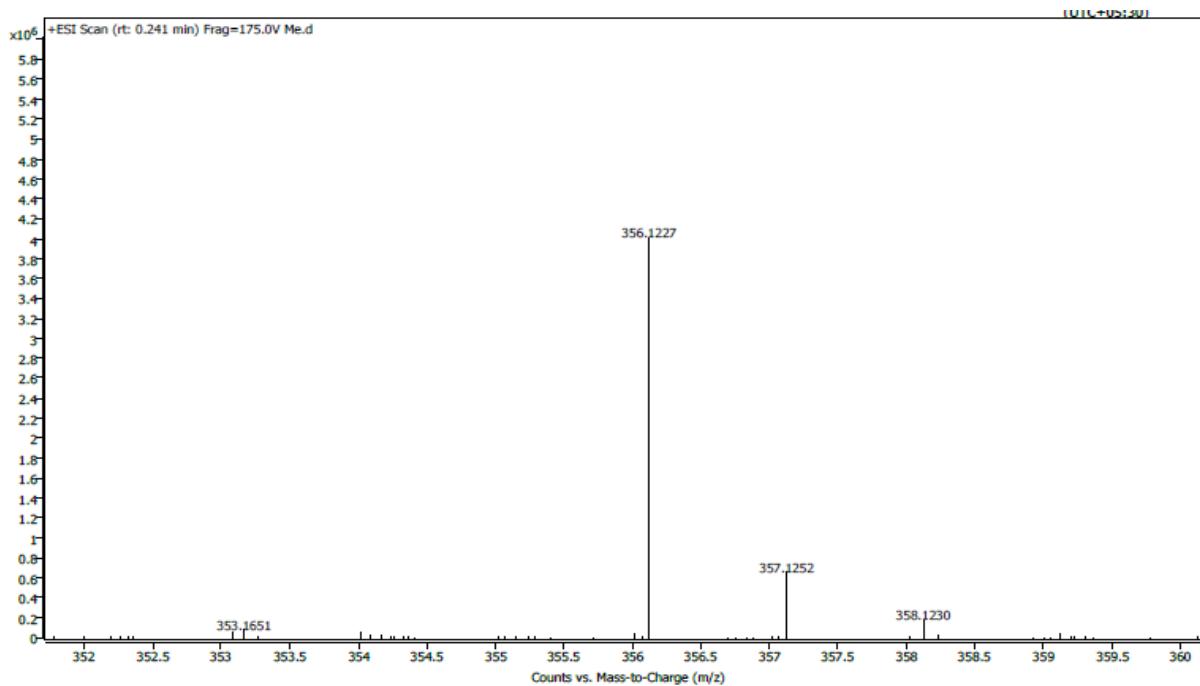


Figure S85. HRMSspectrum of3d

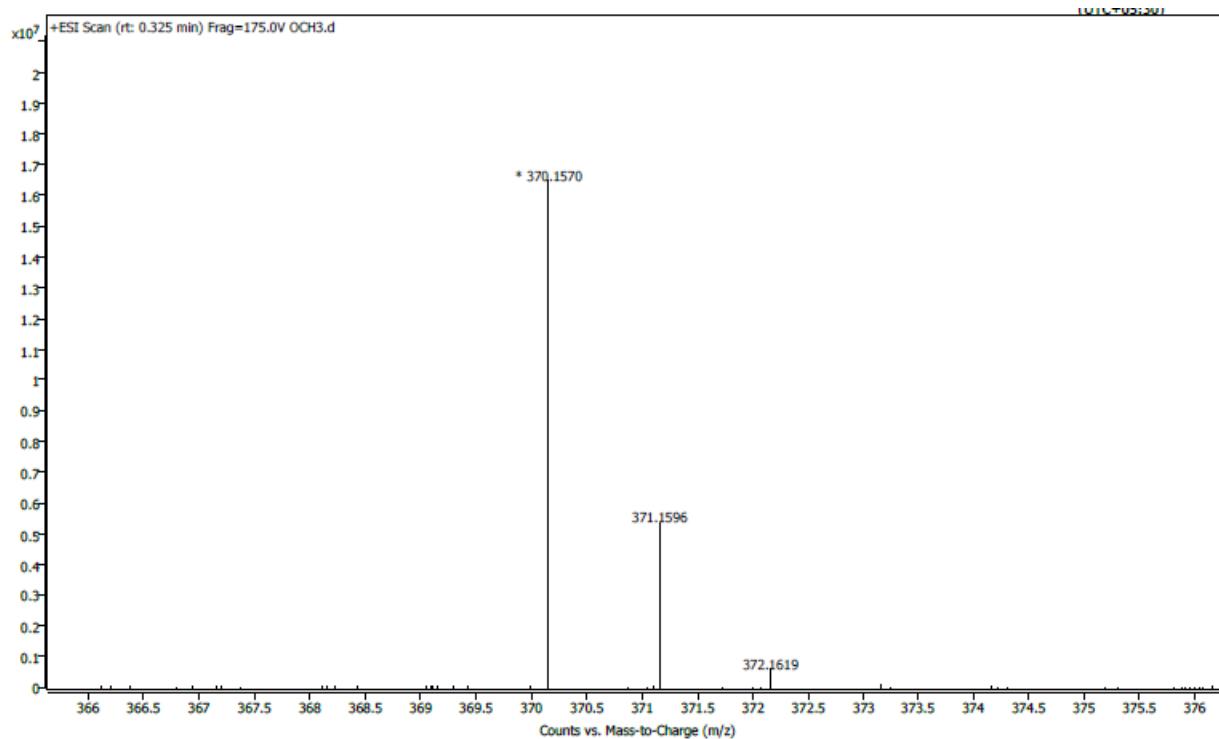


Figure S86. HRMSspectrum of3f

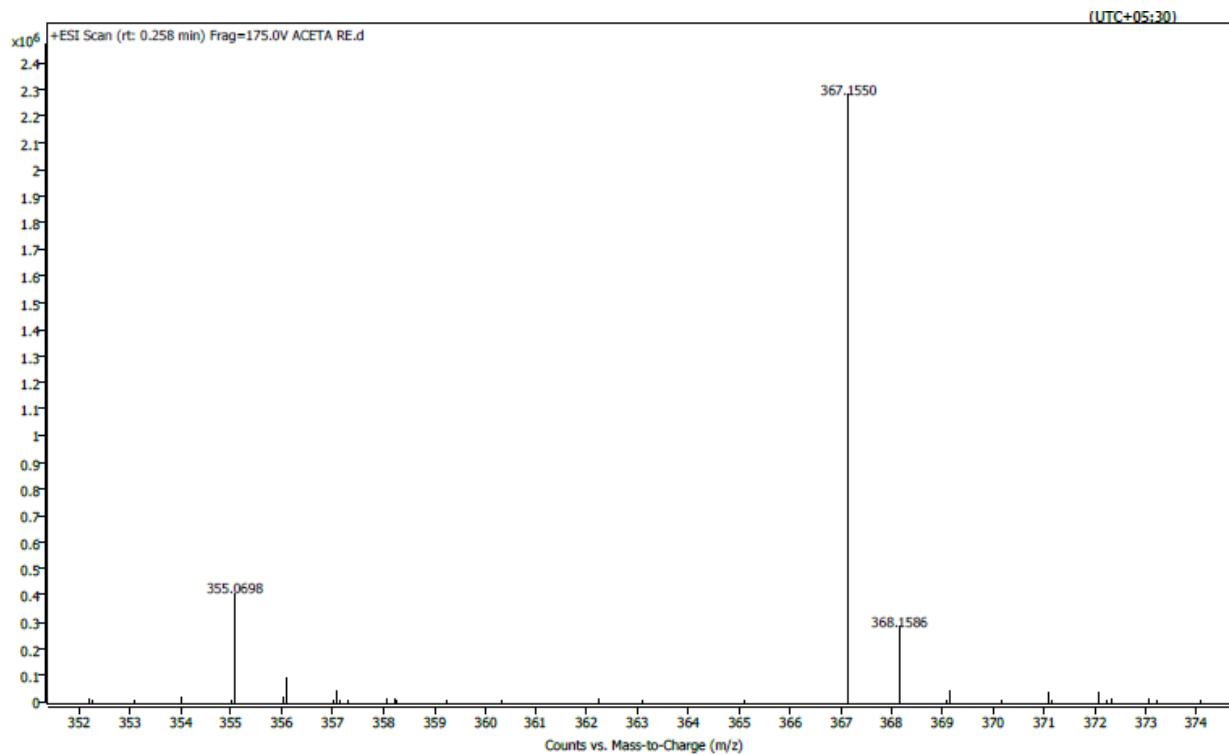


Figure S87. HRMSspectrum of<sup>3n</sup>

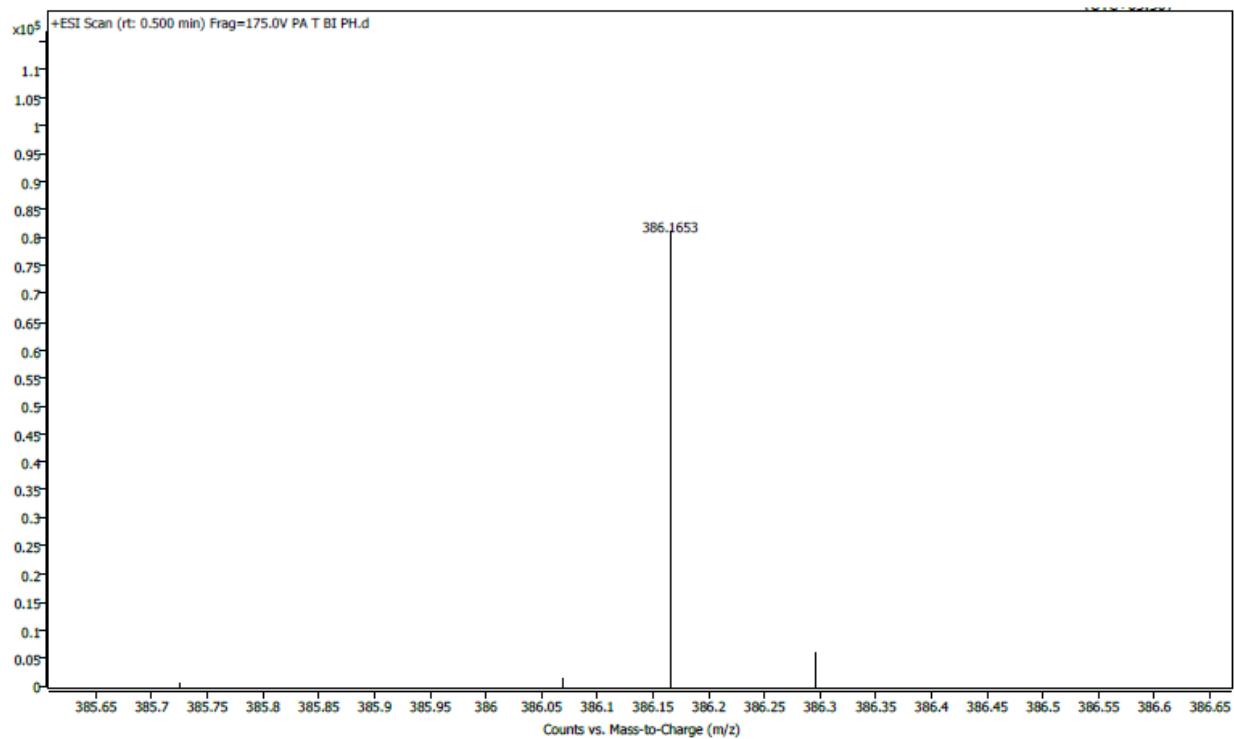


Figure S88. HRMSspectrum of<sup>3o</sup>

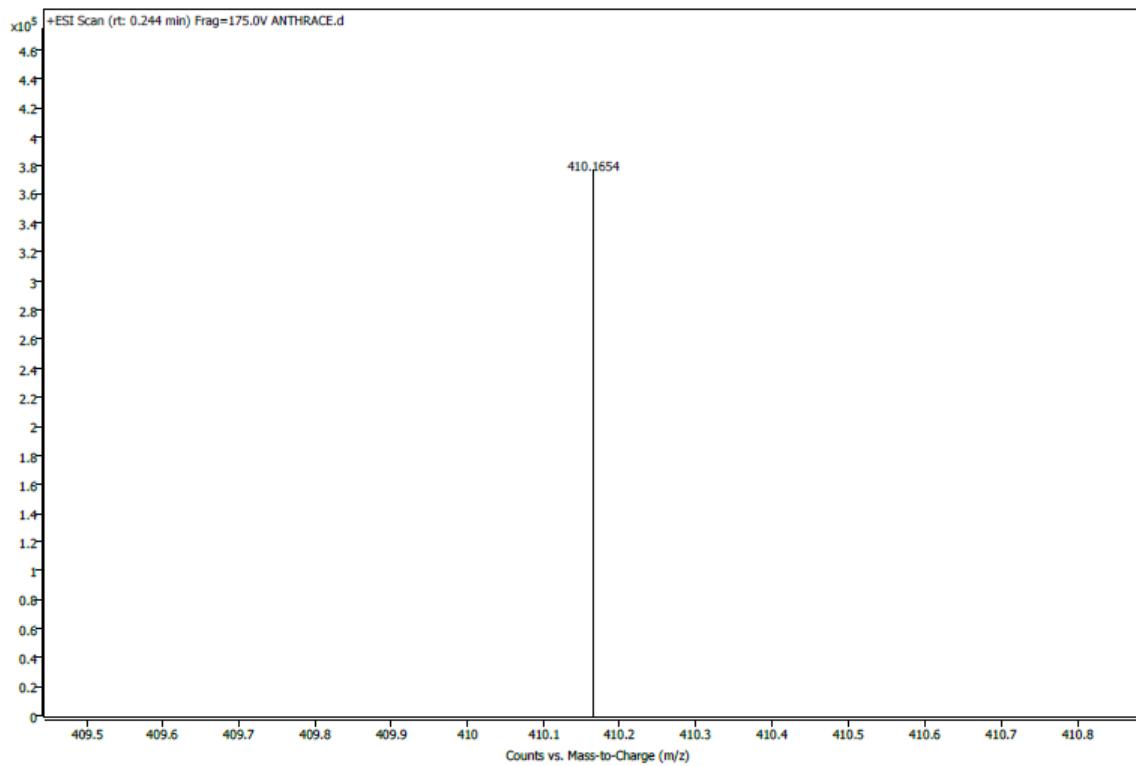


Figure S89. HRMSspectrum of3q

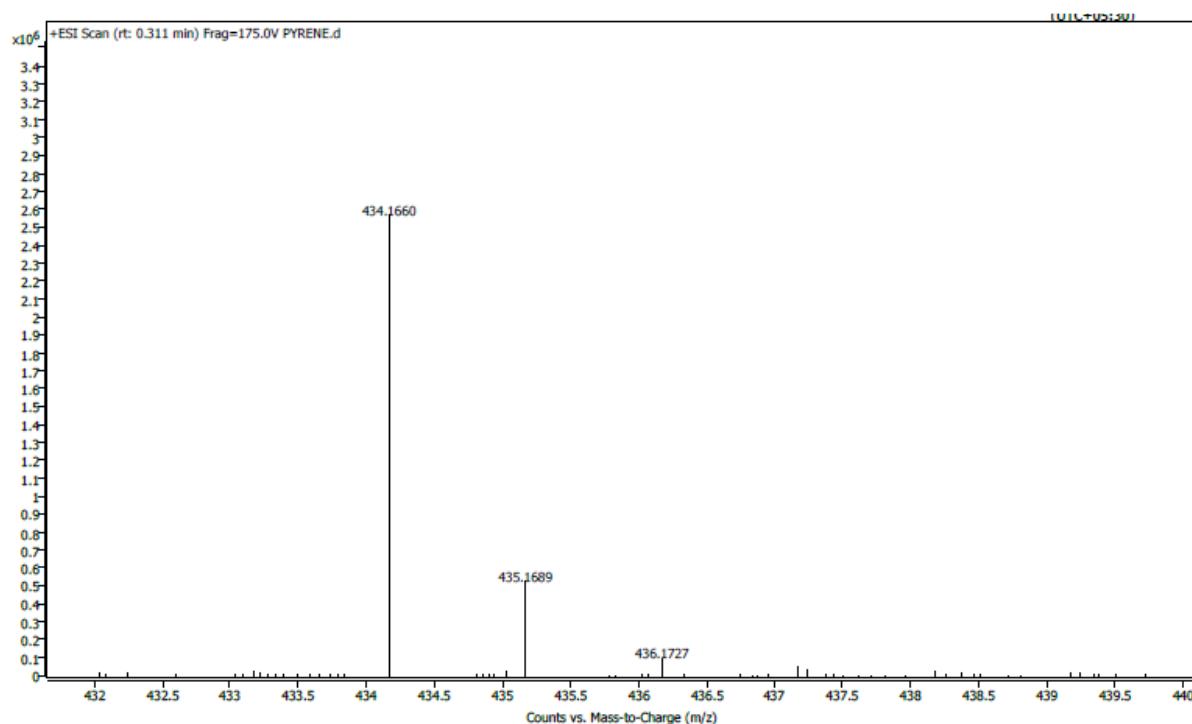
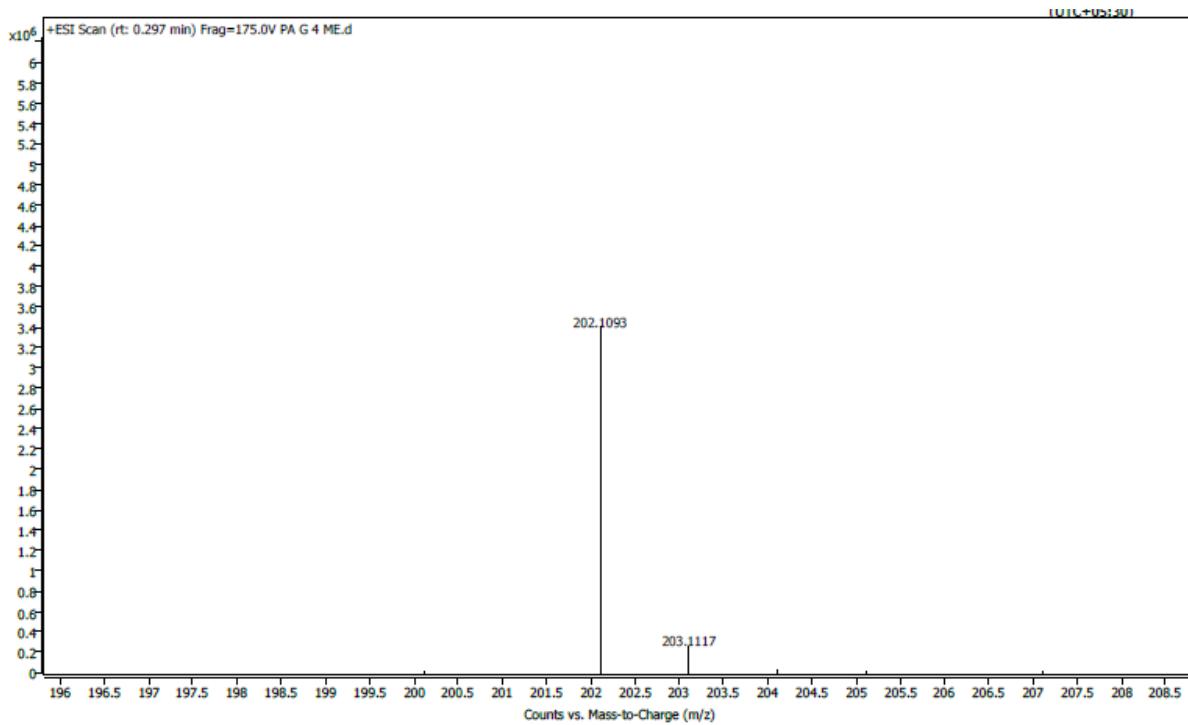
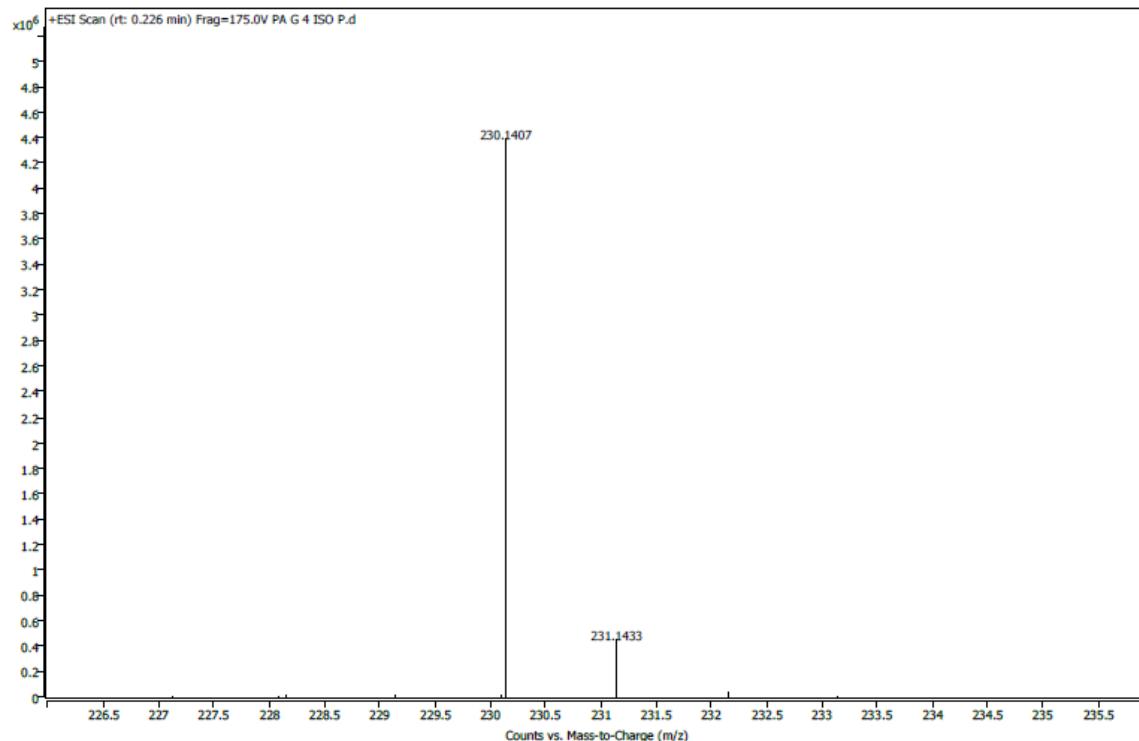


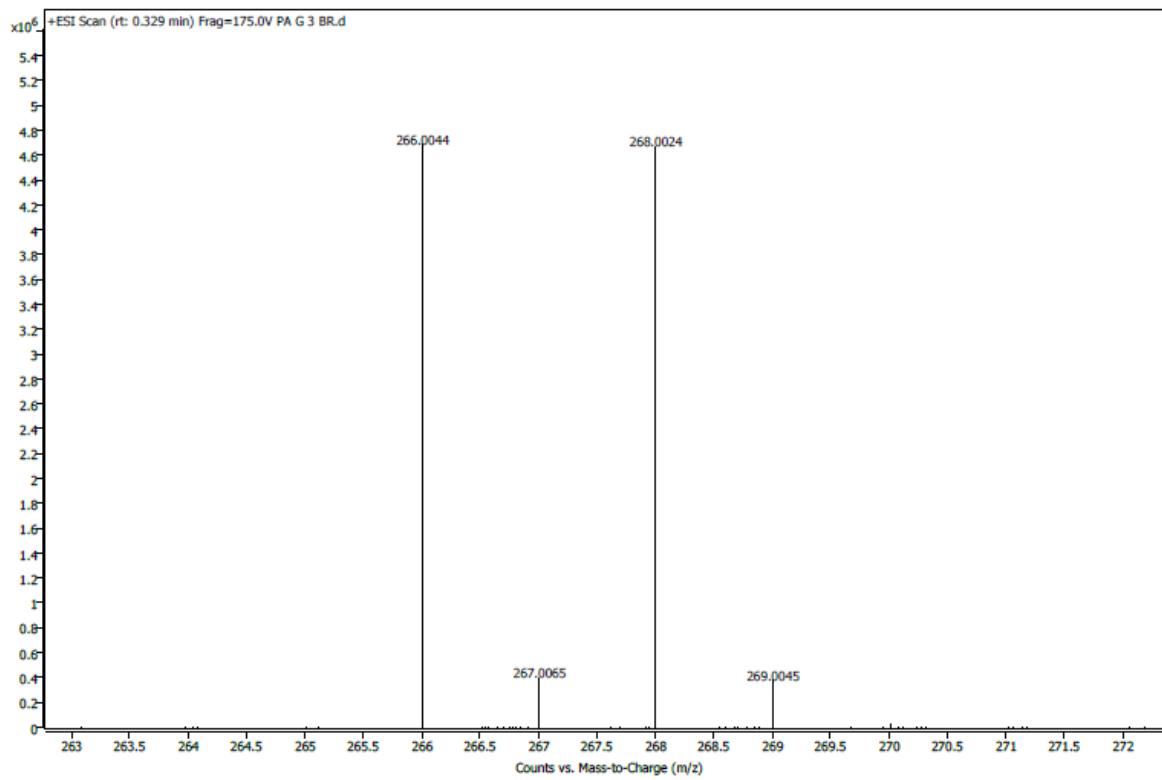
Figure S90. HRMSspectrum of3r



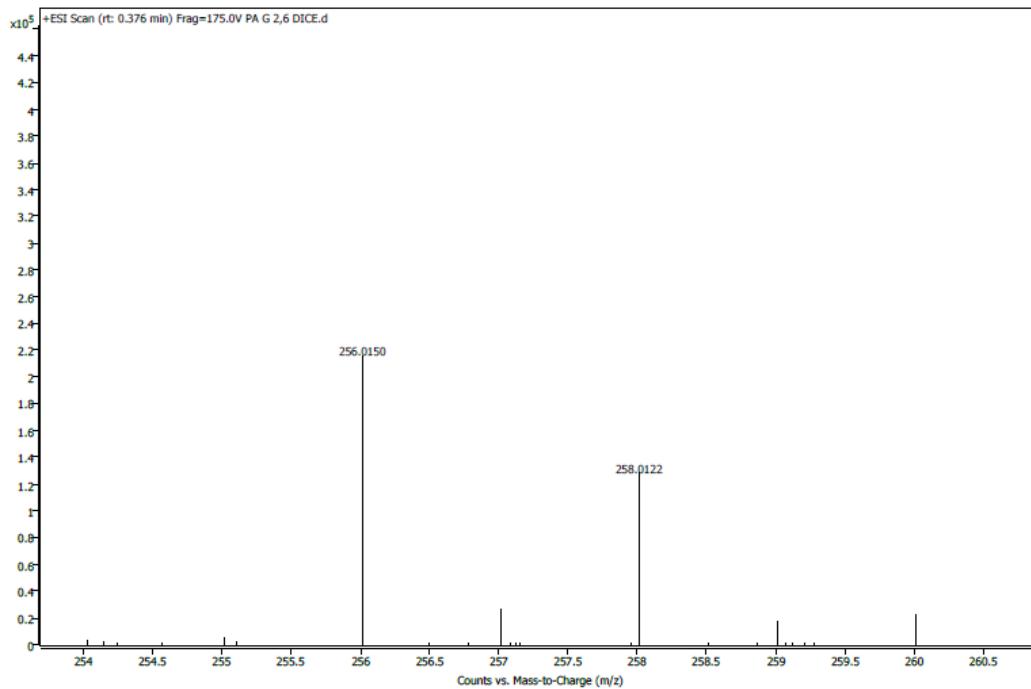
**Figure S91.** HRMSspectrum of**4c**



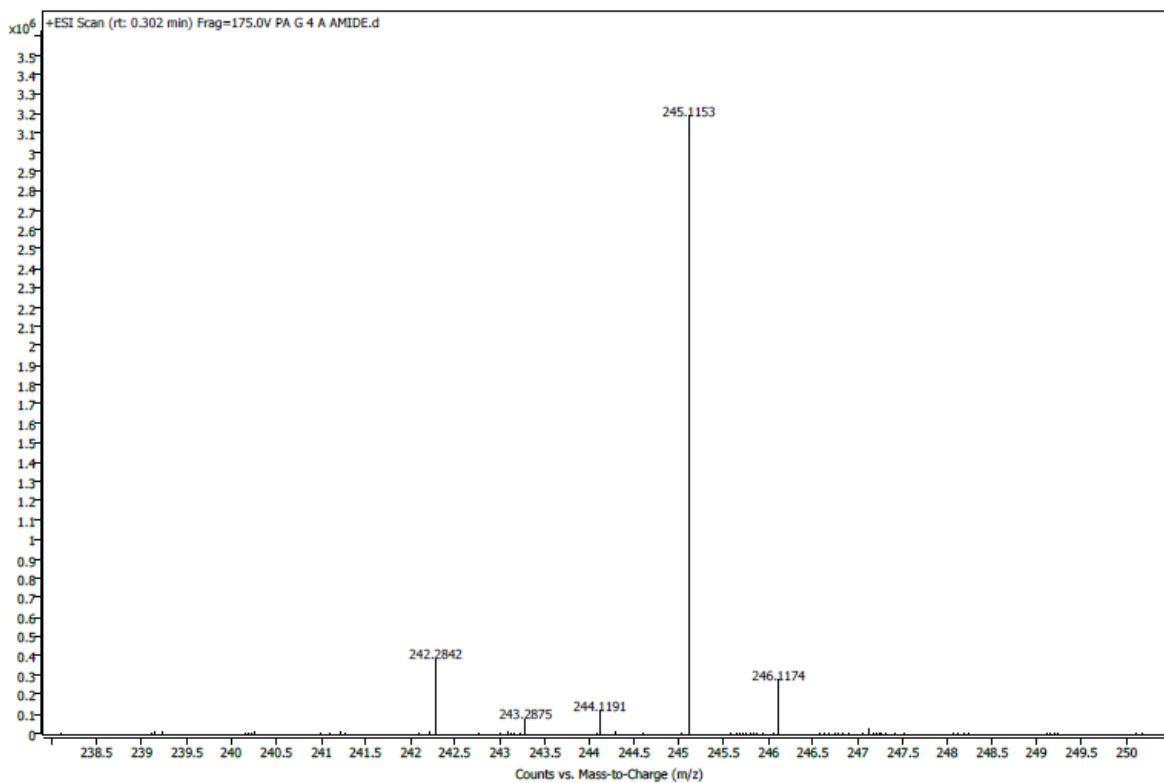
**Figure S92.** HRMSspectrum of**4d**



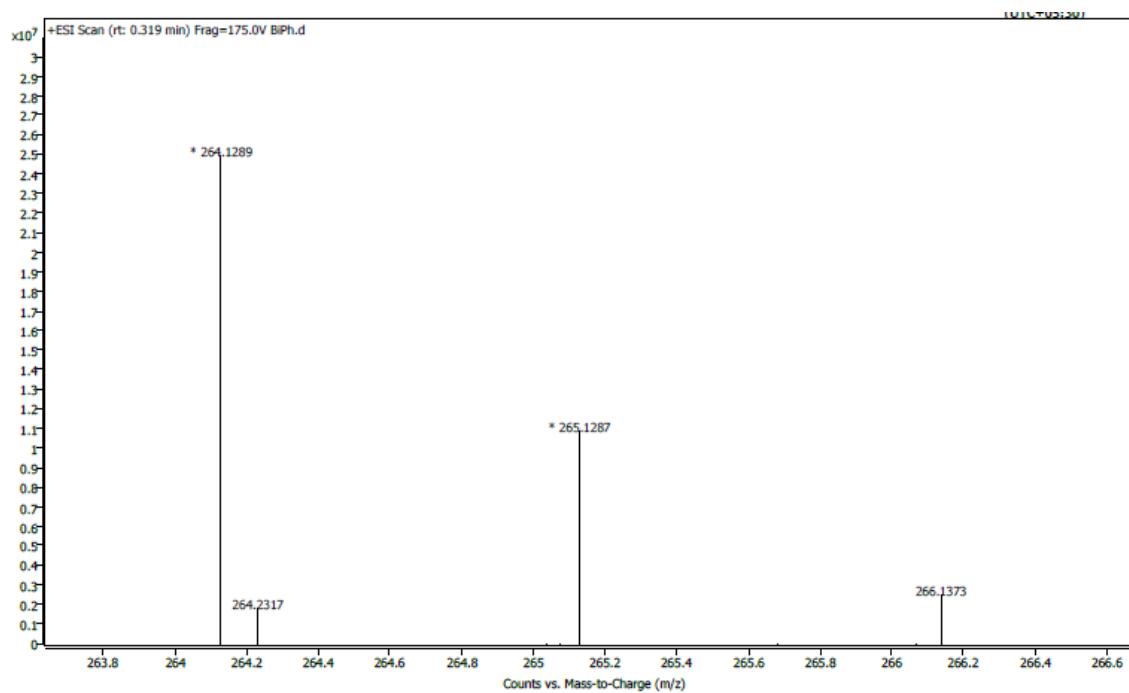
**Figure S93.** HRMSspectrum of**4f**



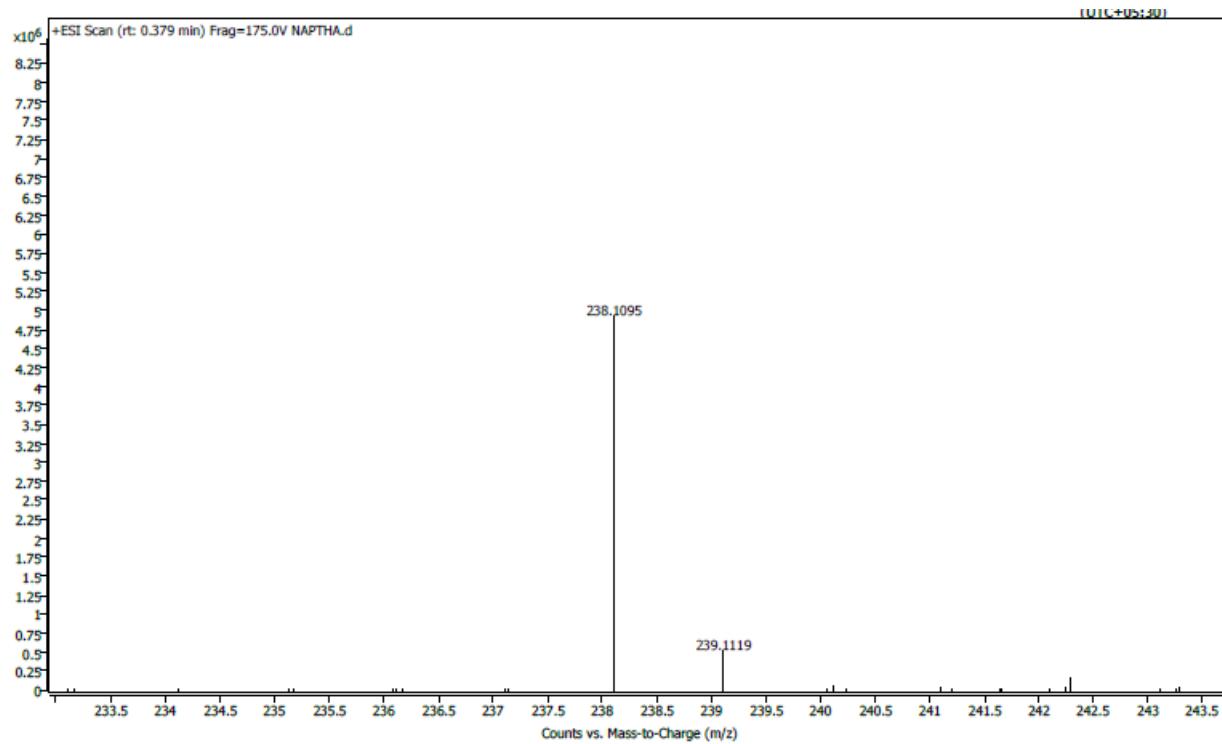
**Figure S94.** HRMSspectrum of**4g**



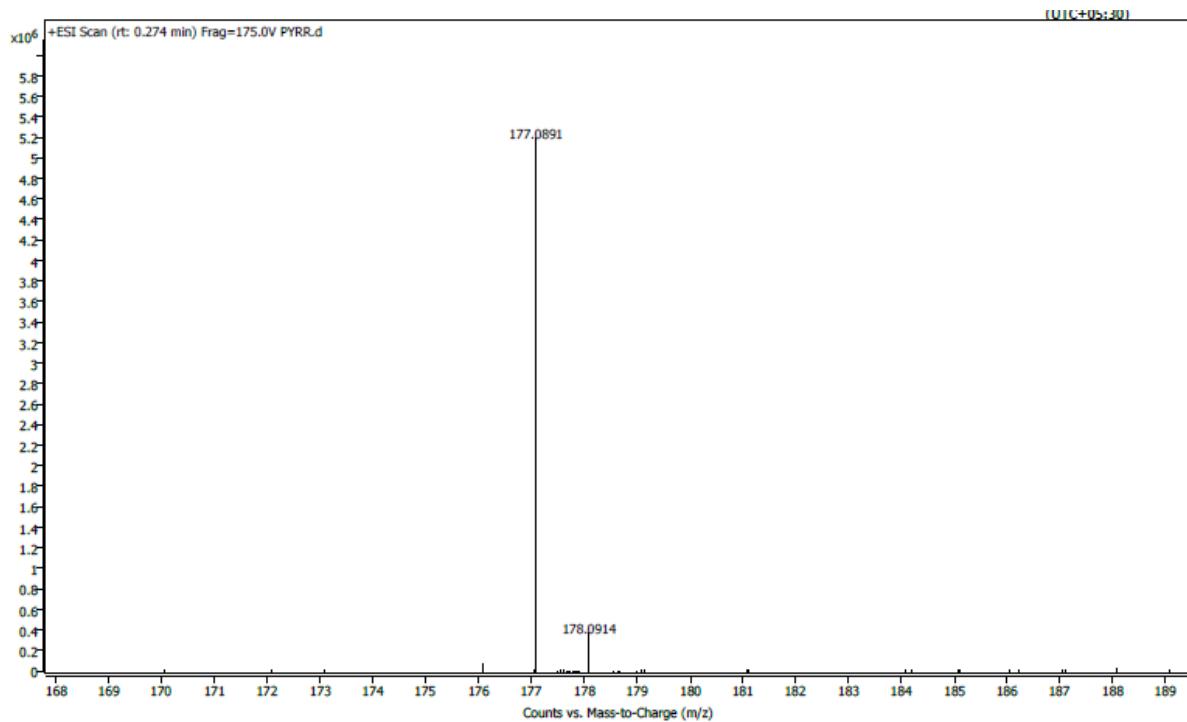
**Figure S95.** HRMSspectrum of 4h



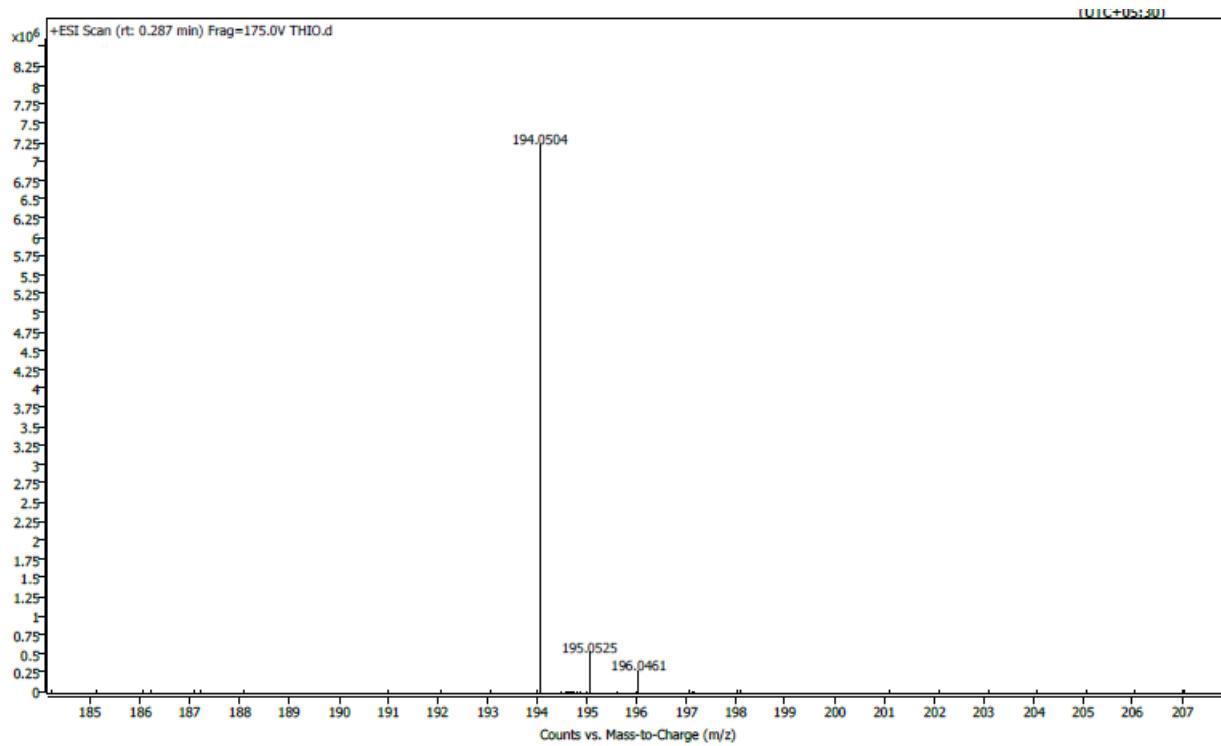
**Figure S96.** HRMSspectrum of 4i



**Figure S97.** HRMSspectrum of**4j**



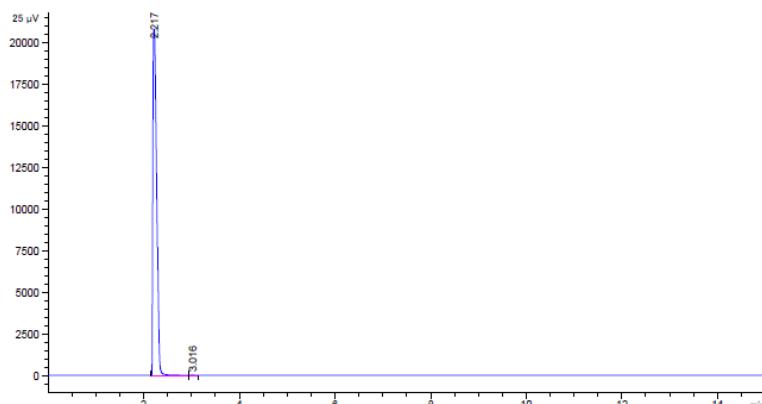
**Figure S98.** HRMSspectrum of**4k**



**Figure S99.** HRMSspectrum of **4l**

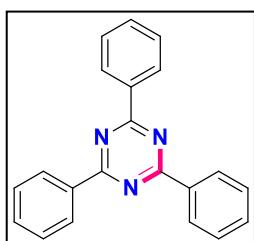
## 11. Confirmation of hydrogen gas

Benzyl alcohol (**1a**, 1.0 mmol), complex **3** (4 mol%), K<sub>2</sub>CO<sub>3</sub>(0.5 mmol), 3 mL of toluene were transferred in a dried 10 mL Schlenk flask. Then the reaction mixture was heated at 100 °C until the formation of H<sub>2</sub>. The GC analysis was performed using TCD detector confirming the liberation of hydrogen gas. Injection temperature = 50 °C, column temperature = 80 °C, detector temperature (TCD) = 180 °C, carrier gas = He<sub>2</sub>.

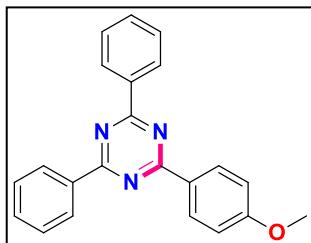


**Figure S100.** GCspectrum of H<sub>2</sub>gas

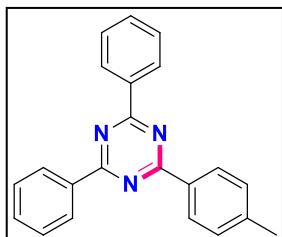
## 12. Characterization of isolated 1,3,5-triazine compounds



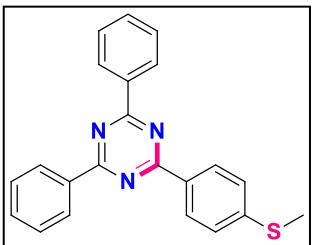
**2,4,6-triphenyl-1,3,5-triazine (3a)**<sup>10</sup>. Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and benzyl alcohol (108.14 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 540.10 mg, 87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.79 (d, *J* = 7.1 Hz, 5H), 7.76 – 7.44 (m, 10H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.6, 136.2, 132.5, 130.8, 129.0, 129.0, 128.6, 128.5, 127.3.



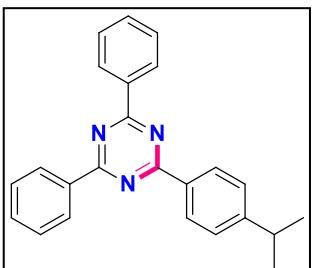
**2-(4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine (3b)**<sup>10</sup>. Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 4-Methoxybenzyl alcohol (138.16 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 598.01 mg, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.79 – 8.67 (m, 6H), 7.57 (t, *J* = 7.6 Hz, 6H), 7.04 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.3, 163.3, 136.4, 132.3, 130.8, 128.9, 128.7, 128.6, 113.9, 55.4.



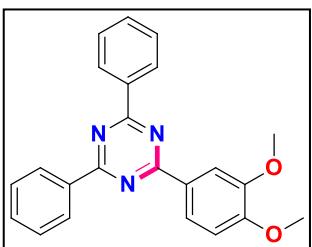
**2,4-diphenyl-6-(p-tolyl)-1,3,5-triazine (3c)**<sup>10</sup>. Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 4-Methylbenzyl alcohol (122.16 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 574.10 mg, 89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.76 (d, *J* = 6.7 Hz, 4H), 8.65 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 6H), 7.35 (d, *J* = 7.4 Hz, 2H), 2.46 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.5, 143.1, 136.3, 133.5, 132.4, 129.4, 128.9, 128.9, 128.6, 127.1, 21.7.



**2-(4-(methylthio)phenyl)-4,6-diphenyl-1,3,5-triazine(3d).** Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 4-(Methylthio)benzyl alcohol (154.23 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 584.42 mg, 82%). Mp: 213 °C (with decomposition). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.74 (d, *J* = 7.1 Hz, 3H), 8.66 (d, *J* = 8.5 Hz, 2H), 8.19 (d, *J* = 8.3 Hz, 2H), 7.73 – 7.44 (m, 5H), 7.37 (d, *J* = 8.3 Hz, 2H), 2.54 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.5, 163.9, 144.7, 142.4, 136.2, 132.4, 129.2, 128.9, 128.6, 128.4, 127.5, 126.0, 125.3, 109.0, 15.0. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup>Calcd for C<sub>22</sub>H<sub>18</sub>N<sub>3</sub>S 356.1221; Found 356.1227.

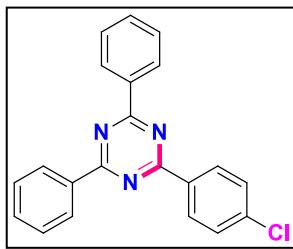


**2-(4-isopropylphenyl)-4,6-diphenyl-1,3,5-triazine(3e)**  
**10.**Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 4-Isopropylbenzyl alcohol (150.22 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 630.08 mg, 89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.81 – 8.62 (m, 3H), 8.44 (s, 1H), 8.23 (d, *J* = 7.5 Hz, 2H), 8.08 – 7.88 (m, 2H), 7.62 – 7.51 (m, 4H), 7.42 (s, 2H), 2.67 (d, *J* = 13.3 Hz, 1H), 1.29 (d, *J* = 26.7 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 165.0, 160.5, 138.1, 135.0, 130.7, 128.9, 128.5, 127.7, 127.5, 127.4, 127.1, 126.8, 126.7, 125.7, 110.2, 34.1, 23.9, 23.7.

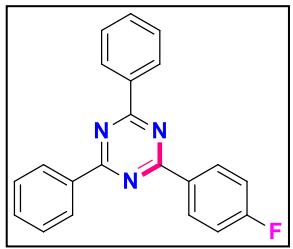


**2-(3,4-dimethoxyphenyl)-4,6-diphenyl-1,3,5-triazine (3f).**Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 3,4-Dimethoxybenzyl alcohol (Veratryl alcohol) (168.19 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 639.06 mg, 86%). Mp: 209 °C (with decomposition). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.68 (d, *J* = 7.1 Hz, 4H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.18 (s, 1H), 7.69 – 7.47 (m, 6H), 6.91 (d, *J* = 8.5 Hz, 1H), 4.01 (s, 3H), 3.91 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.2, 171.0,

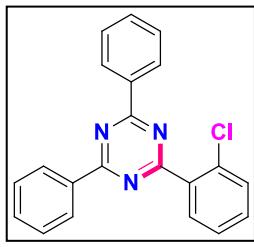
152.8, 148.9, 136.3, 132.3, 128.9, 128.8, 128.5, 122.9, 111.1, 110.6, 55.9. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup>Calcd for C<sub>23</sub>H<sub>20</sub>N<sub>3</sub>O<sub>2</sub> 370.1555; Found 370.1570.



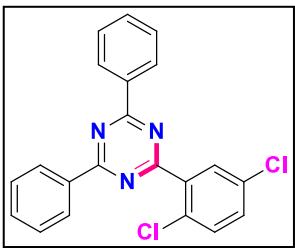
**2-(4-chlorophenyl)-4,6-diphenyl-1,3,5-triazine(3g)** <sup>10</sup>.Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 4-Chlorobenzyl alcohol (142.58 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: n-hexane: EtOAc = 20:1) as white solid (yield:530 mg, 77%). Mp: 196 °C (with decomposition). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.68 (dd, *J* = 21.2, 7.7 Hz, 5H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.68 – 7.40 (m, 8H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.6, 170.6, 163.6, 138.8, 136.0, 134.7, 132.6, 130.2, 129.1, 128.9, 128.9, 128.6, 128.5, 128.4, 109.5.



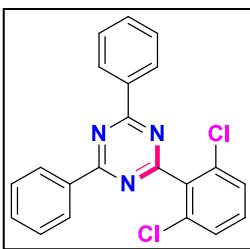
**2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (3h)** <sup>10</sup>.Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 4-Fluorobenzyl alcohol (126.12 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: n-hexane: EtOAc = 20:1) as white solid (yield:490.14 mg, 74%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.75 (d, *J* = 6.8 Hz, 6H), 7.58 (d, *J* = 7.0 Hz, 6H), 7.25 (d, *J* = 5.8 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.6, 170.6, 167.0, 164.5, 136.1, 132.6, 131.3, 131.2, 128.9, 128.6, 115.8, 115.6.



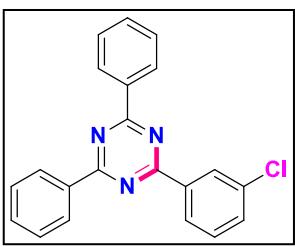
**2-(2-chlorophenyl)-4,6-diphenyl-1,3,5-triazine (3i)** <sup>10</sup>.Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 2-Chlorobenzyl alcohol (142.58 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: n-hexane: EtOAc = 20:1) as brown solid (yield:492.03 mg, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.73 (d, *J* = 7.0 Hz, 3H), 8.18 – 8.12 (m, 1H), 7.62 – 7.51 (m, 7H), 7.47 – 7.41 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO) δ 172.8, 171.6, 135.9, 135.8, 133.8, 132.7, 132.4, 131.7, 131.3, 129.1, 128.7, 126.9.



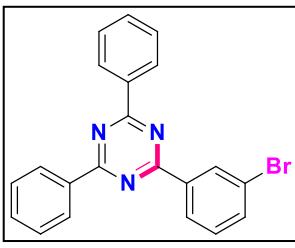
**2-(2,5-dichlorophenyl)-4,6-diphenyl-1,3,5-triazine (3j)**<sup>10</sup>. Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 2,5-Dichlorobenzyl alcohol (177.03 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 560.0 mg, 74%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.71 (d, *J* = 7.7 Hz, 4H), 8.14 (d, *J* = 2.1 Hz, 1H), 7.61 – 7.52 (m, 6H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.41 (dd, *J* = 8.5, 2.1 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.8, 171.6, 137.0, 135.7, 132.9, 132.4, 132.2, 132.1, 131.5, 130.6, 130.4, 129.1, 128.7.



**2-(2,6-dichlorophenyl)-4,6-diphenyl-1,3,5-triazine (3k)**<sup>10</sup>. Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 2,6-Dichlorobenzyl alcohol (177.03 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 511.20 mg, 67%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.74 – 8.64 (m, 4H), 7.64 – 7.50 (m, 6H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.41 – 7.29 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 172.4, 172.1, 136.4, 135.6, 133.9, 132.9, 130.6, 129.2, 128.7, 128.3.

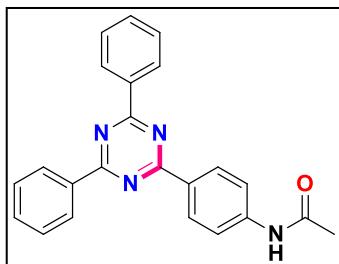


**2-(3-chlorophenyl)-4,6-diphenyl-1,3,5-triazine (3l)**<sup>10</sup>. Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 3-Chlorobenzyl alcohol (142.58 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 492.06 mg, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.65 – 8.50 (m, 3H), 7.96 (d, *J* = 5.8 Hz, 1H), 7.42 (d, *J* = 6.7 Hz, 4H), 7.38 – 7.26 (m, 3H), 7.16 (d, *J* = 10.8 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.6, 170.3, 163.4, 135.8, 134.9, 132.7, 132.4, 130.9, 130.2, 129.9, 129.6, 129.0, 128.8, 128.6, 128.5, 127.4, 127.0, 126.0, 125.3, 110.1.



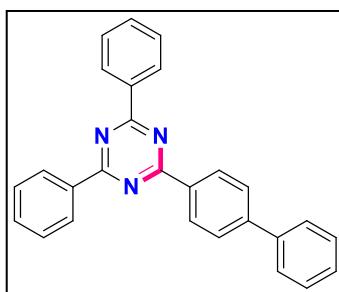
**2-(3-bromophenyl)-4,6-diphenyl-1,3,5-triazine (3m)**<sup>11</sup>. Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 3-bromobenzyl alcohol (187.03 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 581.03 mg, 74%). <sup>1</sup>H

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.82 (s, 1H), 8.70 (d, *J* = 7.1 Hz, 4H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.50 (m, 6H), 7.38 (dd, *J* = 15.6, 7.8 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.7, 170.3, 138.3, 135.9, 135.3, 132.7, 131.8, 130.1, 129.0, 128.7, 127.5, 125.9, 122.9, 122.8.

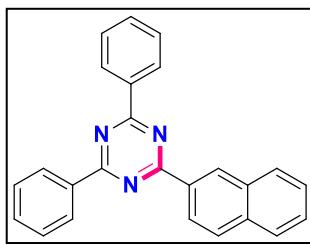


*N-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)acetamide* (3n).

Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 4-Acetamidobenzyl alcohol (165.19 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 583.31 mg, 78%). Mp: 223 °C (with decomposition). <sup>1</sup>H NMR (400 MHz, DMSO) δ 10.37 (s, 1H), 8.72 (d, *J* = 10.6 Hz, 5H), 8.33 (s, 1H), 7.87 (d, *J* = 6.6 Hz, 2H), 7.66 (s, 6H), 2.13 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO) δ 170.7, 168.9, 143.7, 135.4, 132.9, 129.7, 128.9, 128.6, 118.6, 24.1. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>19</sub>N<sub>4</sub>O 367.1559; Found 367.1550.

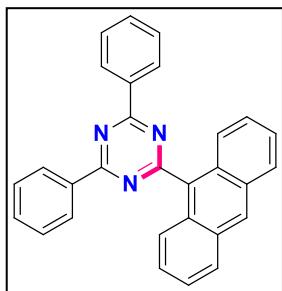


*2-([1,1'-biphenyl]-4-yl)-4,6-diphenyl-1,3,5-triazine* (3o). Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and Biphenyl-4-methanol (184.23 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 611.0 mg, 80%). Mp: 204 °C (with decomposition). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.65 (s, 1H), 8.24 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 6.5 Hz, 2H), 7.46 (d, *J* = 6.6 Hz, 5H), 7.38 (d, *J* = 8.1 Hz, 3H), 7.31 (d, *J* = 6.4 Hz, 3H), 7.12 (s, 1H), 6.77 (d, *J* = 15.4 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.6, 164.5, 164.2, 143.5, 142.5, 140.3, 140.1, 136.3, 136.1, 132.6, 132.5, 131.9, 129.5, 129.0, 128.9, 128.7, 128.5, 128.2, 127.8, 127.6, 127.2, 127.0, 126.2, 110.0. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>20</sub>N<sub>3</sub> 386.1657; Found 386.1653.

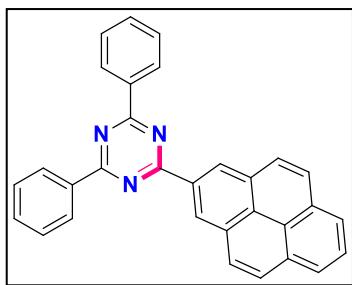


*2-(naphthalen-2-yl)-4,6-diphenyl-1,3,5-triazine* (3p)<sup>11</sup>. Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 1-Naphthalenemethanol (158.19 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as white solid (yield: 561.06 mg,

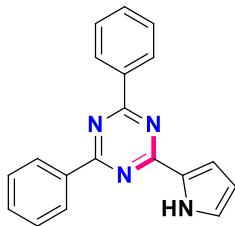
78%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.69 (d,  $J = 6.8$  Hz, 2H), 8.46 – 8.34 (m, 2H), 8.00 – 7.83 (m, 2H), 7.73 (dd,  $J = 16.2, 9.5$  Hz, 2H), 7.59 – 7.45 (m, 9H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 171.5, 136.2, 134.2, 134.0, 132.7, 132.3, 131.3, 130.7, 130.3, 129.1, 128.7, 128.2, 127.3, 127.0, 126.3, 126.1, 125.5, 125.3, 125.2.



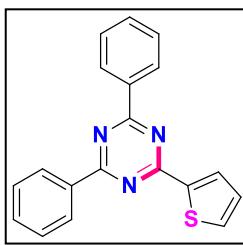
**2-(anthracen-9-yl)-4,6-diphenyl-1,3,5-triazine (3q).** Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 9-Anthracenemethanol (202.26 mg, 1.0 mmol). Column chromatography ( $\text{SiO}_2$ , Eluent: *n*-hexane:  $\text{EtOAc} = 20:1$ ) as brown solid (yield: 618.73 mg, 76%). Mp: 192 °C (with decomposition).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.75 (t,  $J = 6.5$  Hz, 2H), 8.62 (d,  $J = 7.3$  Hz, 1H), 8.28 (dd,  $J = 5.6, 3.4$  Hz, 5H), 8.18 (t,  $J = 8.6$  Hz, 1H), 8.08 (d,  $J = 8.3$  Hz, 1H), 7.92 (d,  $J = 8.6$  Hz, 1H), 7.77 (dd,  $J = 5.7, 3.3$  Hz, 5H), 7.54 (d,  $J = 7.6$  Hz, 2H), 7.41 (d,  $J = 7.1$  Hz, 1H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  183.1, 171.9, 135.8, 134.1, 133.5, 132.8, 131.4, 129.2, 128.9, 128.7, 128.7, 127.2, 127.1, 126.6, 125.5, 125.3. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for  $\text{C}_{29}\text{H}_{20}\text{N}_3$  410.1657; Found 410.1654.



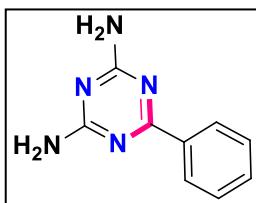
**2,4-diphenyl-6-(pyren-2-yl)-1,3,5-triazine (3r).** Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 1-Pyrenemethanol (232.28 mg, 1.0 mmol). Column chromatography ( $\text{SiO}_2$ , Eluent: *n*-hexane:  $\text{EtOAc} = 20:1$ ) as yellow solid (yield: 617.3 mg, 71%). Mp: 190 °C (with decomposition).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.47 (d,  $J = 9.4$  Hz, 1H), 8.97 (d,  $J = 8.0$  Hz, 1H), 8.80 (d,  $J = 7.1$  Hz, 4H), 8.24 (d,  $J = 7.9$  Hz, 1H), 8.19 (d,  $J = 9.9$  Hz, 3H), 8.13 – 8.05 (m, 3H), 7.62 – 7.54 (m, 6H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz, DMSO)  $\delta$  174.6, 171.4, 136.2, 133.7, 132.6, 131.2, 130.7, 130.6, 130.5, 129.4, 129.2, 129.1, 128.8, 128.7, 127.4, 126.2, 126.0, 125.7, 125.4, 124.7. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for  $\text{C}_{31}\text{H}_{20}\text{N}_3$  434.1657; Found 434.1660.



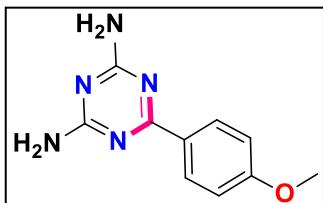
**2,4-diphenyl-6-(1H-pyrrol-2-yl)-1,3,5-triazine (3s)<sup>13</sup>.** Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and (1H-Pyrrol-2-yl)-methanol (97.12 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as brown solid (yield: 386.08 mg, 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.83 (s, 1H), 8.66 (t, *J* = 10.7 Hz, 4H), 7.67 – 7.45 (m, 7H), 7.09 (s, 1H), 6.43 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.1, 165.1, 136.2, 132.3, 129.6, 128.8, 128.5, 123.2, 114.8, 111.6.



**2,4-diphenyl-6-(thiophen-2-yl)-1,3,5-triazine (3t)<sup>13</sup>.** Following the general procedure, the title compound was synthesized by using benzamidine hydrochloride (313.22 mg, 2.0 mmol) and 2-Thiophenemethanol (114.17 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:1) as brown solid (yield: 398.71 mg, 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.70 (d, *J* = 6.9 Hz, 2H), 8.61 (dd, *J* = 9.7, 4.9 Hz, 1H), 7.84 (t, *J* = 5.7 Hz, 1H), 7.66 – 7.47 (m, 8H), 7.19 – 7.12 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.5, 168.1, 159.4, 143.1, 142.1, 137.3, 135.9, 132.6, 132.2, 131.5, 130.8, 129.8, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 127.1, 106.5.

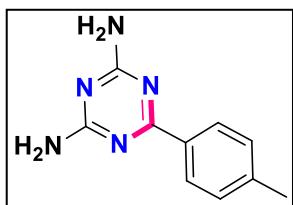


**6-phenyl-1,3,5-triazine-2,4-diamine (4a)<sup>12</sup>.** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and benzyl alcohol (108.14 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 328.01 mg, 86%). <sup>1</sup>H NMR (400 MHz, DMSO) δ 8.26 (d, *J* = 7.5 Hz, 2H), 7.65 – 7.38 (m, 3H), 6.80 (s, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO) δ 170.1, 167.4, 137.0, 131.0, 128.5, 128.1, 127.6, 127.2, 127.1.

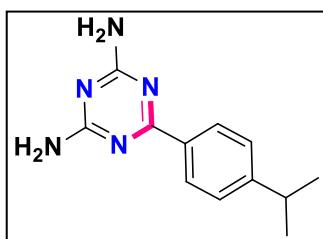


**6-(4-methoxyphenyl)-1,3,5-triazine-2,4-diamine (4b)<sup>14</sup>.** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and 4-Methoxybenzyl alcohol (138.16 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 398.06 mg, 92%). <sup>1</sup>H NMR (400 MHz,

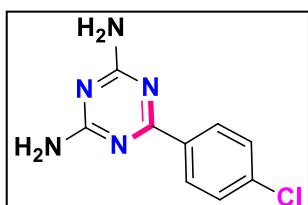
DMSO)  $\delta$  8.22 (d,  $J$  = 8.3 Hz, 2H), 7.00 (d,  $J$  = 8.7 Hz, 2H), 6.70 (s, 4H), 3.81 (s, 3H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz, DMSO)  $\delta$  169.7, 167.2, 161.6, 129.4, 113.4, 55.2.



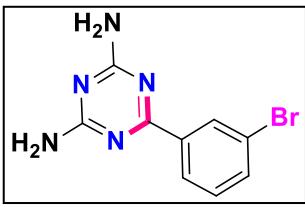
**6-(*p*-tolyl)-1,3,5-triazine-2,4-diamine (4c).** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and 4-methylbenzyl alcohol (122.16 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 354.70 mg, 89%). Mp: 231 °C (with decomposition).  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  8.18 (s, 1H), 7.38 (d,  $J$  = 31.2 Hz, 1H), 7.11 (d,  $J$  = 27.4 Hz, 2H), 6.78 (s, 4H), 2.34 (s, 3H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz, DMSO)  $\delta$  170.1, 167.3, 140.8, 134.3, 129.3, 128.7, 127.6, 125.7, 20.9. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup>Calcd for C<sub>10</sub>H<sub>12</sub>N<sub>5</sub> 202.1092; Found 202.1093.



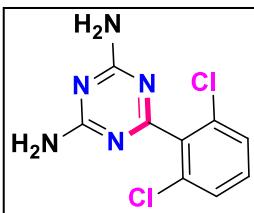
**6-(4-isopropylphenyl)-1,3,5-triazine-2,4-diamine (4d).** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and 4-isopropylbenzyl alcohol (150.22 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 402.04 mg, 88%). Mp: 233 °C (with decomposition).  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  8.19 (d,  $J$  = 8.2 Hz, 2H), 7.32 (d,  $J$  = 8.2 Hz, 2H), 6.73 (s, 4H), 2.92 (d,  $J$  = 6.8 Hz, 1H), 1.21 (d,  $J$  = 6.9 Hz, 6H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz, DMSO)  $\delta$  170.1, 167.3, 151.6, 134.6, 127.7, 126.0, 33.3, 23.6. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup>Calcd for C<sub>12</sub>H<sub>16</sub>N<sub>5</sub> 230.1405; Found 230.1407.



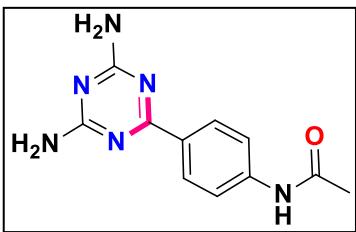
**6-(4-chlorophenyl)-1,3,5-triazine-2,4-diamine (4e).** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and 4-chlorobenzyl alcohol (126.12 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 295.90 mg, 72%).  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  8.25 (d,  $J$  = 8.3 Hz, 1H), 7.54 (d,  $J$  = 8.3 Hz, 2H), 6.82 (s, 2H).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz, DMSO)  $\delta$  169.1, 167.3, 135.9, 135.7, 129.3, 128.5, 128.2.



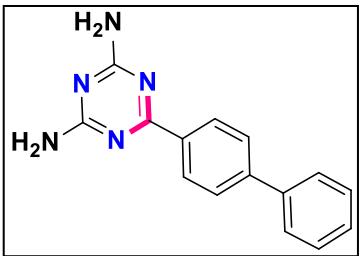
**6-(3-bromophenyl)-1,3,5-triazine-2,4-diamine (4f).** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and 3-Bromobenzyl alcohol (187.03 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 393.30 mg, 74%). Mp: 227 °C (with decomposition). <sup>1</sup>H NMR (400 MHz, DMSO) δ 8.45 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 6.91 (s, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO) δ 168.6, 167.3, 139.4, 133.6, 130.4, 130.2, 126.4, 121.5. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup>Calcd for C<sub>9</sub>H<sub>9</sub>BrN<sub>5</sub> 266.0041; Found 266.0044.



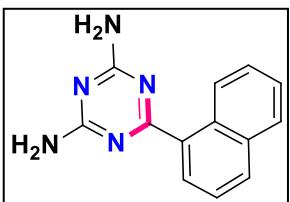
**6-(2,6-dichlorophenyl)-1,3,5-triazine-2,4-diamine (4g).** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and 2,6-Dichlorobenzyl alcohol (177.03 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 344.05 mg, 61%). Mp: 217 °C (with decomposition). <sup>1</sup>H NMR (400 MHz, DMSO) δ 7.82 (d, *J* = 2.9 Hz, 1H), 7.66 (d, *J* = 4.5 Hz, 1H), 7.15 – 7.10 (m, 1H), 6.71 (s, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO) δ 170.3, 166.2, 138.6, 130.9, 130.7, 129.3, 129.0. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup>Calcd for C<sub>9</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>5</sub> 256.0157; Found 256.0150.



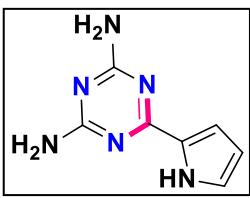
**N-(4-(4,6-diamino-1,3,5-triazin-2-yl)phenyl)acetamide (4h).** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and 4-Acetamidobenzyl alcohol (165.19 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 308.40 mg, 68%). Mp: 239 °C (with decomposition). <sup>1</sup>H NMR (400 MHz, DMSO) δ 10.16 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 6.68 (s, 4H), 2.08 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO) δ 191.5, 169.1, 167.3, 144.7, 131.0, 130.8, 128.3, 118.5, 24.1. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup>Calcd for C<sub>11</sub>H<sub>13</sub>N<sub>6</sub>O 245.1151; Found 245.1153.



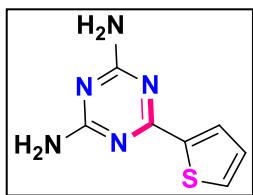
**6-([1,1'-biphenyl]-4-yl)-1,3,5-triazine-2,4-diamine (4i).** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and Biphenyl-4-methanol (184.23 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 391.06 mg, 74%). Mp: 221 °C (with decomposition). <sup>1</sup>H NMR (400 MHz, DMSO) δ 8.37 (d, *J* = 8.3 Hz, 2H), 7.76 (dd, *J* = 18.8, 7.9 Hz, 5H), 7.49 (t, *J* = 7.5 Hz, 2H), 6.83 (s, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO) δ 169.8, 167.4, 142.5, 139.4, 136.1, 129.0, 128.9, 128.7, 128.3, 127.8, 126.8, 126.7, 126.5, 126.3. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup>Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>5</sub> 264.1271; Found 264.1289.



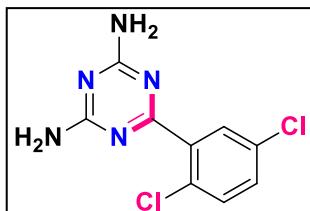
**6-(naphthalen-1-yl)-1,3,5-triazine-2,4-diamine (4j).** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and 1-Naphthalenemethanol (158.19 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 347.81 mg, 73%). Mp: 236 °C (with decomposition). <sup>1</sup>H NMR (400 MHz, DMSO) δ 8.69 (dd, *J* = 6.2, 3.5 Hz, 2H), 7.96 (ddd, *J* = 23.3, 18.8, 7.6 Hz, 3H), 7.69 – 7.29 (m, 2H), 6.86 (s, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO) δ 173.3, 167.0, 135.5, 133.3, 130.3, 129.9, 128.1, 127.6, 126.2, 125.7, 124.9. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup>Calcd for C<sub>13</sub>H<sub>12</sub>N<sub>5</sub> 238.1092; Found 238.1095.



**6-(1H-pyrrol-2-yl)-1,3,5-triazine-2,4-diamine (4k).** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and pyrrole-2-methanol (97.12 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 204.03 mg, 57%). Mp: 235 °C (with decomposition). <sup>1</sup>H NMR (400 MHz, DMSO) δ 11.66 (s, 1H), 7.13 (s, 1H), 6.92 (s, 1H), 6.47 (s, 2H), 6.24 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO) δ 166.8, 164.1, 129.2, 122.6, 111.5, 109.3. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup>Calcd for C<sub>7</sub>H<sub>9</sub>N<sub>6</sub> 177.0888; Found 177.0891.

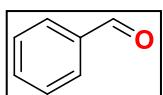


**6-(thiophen-2-yl)-1,3,5-triazine-2,4-diamine (4l).** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and 2-Thiophenemethanol (114.17 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 227.07 mg, 59%). Mp: 228 °C (with decomposition). <sup>1</sup>H NMR (400 MHz, DMSO) δ 7.85 – 7.81 (m, 1H), 7.70 (d, *J* = 4.8 Hz, 1H), 7.18 – 7.14 (m, 1H), 6.79 (s, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO) δ 166.8, 166.6, 142.3, 132.1, 130.5, 129.0, 128.0. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>8</sub>N<sub>5</sub>S 194.0500; Found 194.0504.

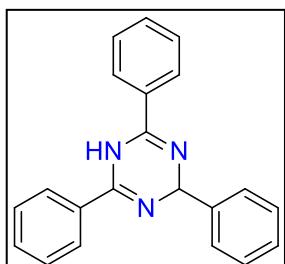


**6-(2,5-dichlorophenyl)-1,3,5-triazine-2,4-diamine (Irsogladine) (4m)<sup>15</sup>.** Following the general procedure, the title compound was synthesized by using guanidine hydrochloride (191.06 mg, 2.0 mmol) and 2,5-Dichlorobenzyl alcohol (177.03 mg, 1.0 mmol). Column chromatography (SiO<sub>2</sub>, Eluent: *n*-hexane: EtOAc = 20:3) as white solid (yield: 374.04 mg, 73%). <sup>1</sup>H NMR (400 MHz, DMSO) δ 7.81 (s, 1H), 7.61 (s, 1H), 7.50 (s, 1H), 6.89 (s, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 170.9, 166.8, 139.2, 132.0, 131.5, 130.7, 129.9, 128.2.

## Intermediates



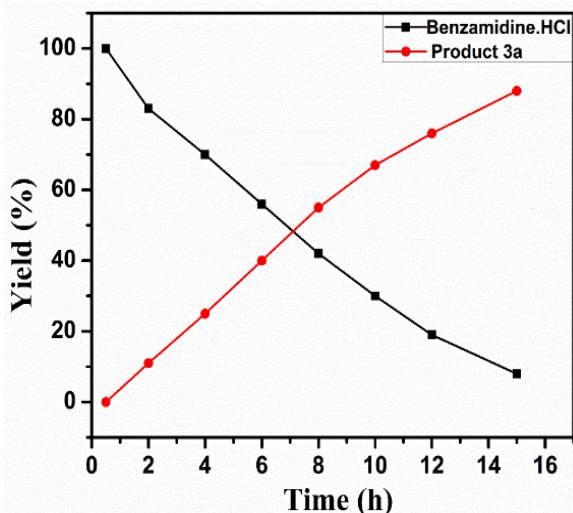
**Benzaldehyde (1a').**<sup>12</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.01 (s, 1H), 7.88 (d, *J* = 7.1 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 192.5, 134.5, 130.1, 129.8, 129.0, 128.5.



**2,4,6-triphenyl-1,4-dihydro-1,3,5-triazine (2a').**<sup>12</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.79 (d, *J* = 6.9 Hz, 1H), 8.02 (s, 3H), 7.56 (d, *J* = 6.8 Hz, 3H), 7.49 (d, *J* = 7.1 Hz, 2H), 7.46 – 7.41 (m, 4H), 7.37 (d, *J* = 6.7 Hz, 2H), 7.33 (d, *J* = 6.9 Hz, 1H), 6.27 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 171.7, 143.1, 136.2, 134.5, 132.5, 131.4, 129.2, 129.0, 128.7, 128.6, 128.6, 127.7, 127.1, 126.9, 84.3.

### 13. Kinetic experiment for time-conversion profile of the reaction

A series of eight different oven-dried round bottom flasks containing benzamidine hydrochloride (2 mmol), benzyl alcohol (1 mmol),  $K_2CO_3$  (0.5 mmol), and complex **3** (4 mol%) were added to each reaction vessel with 3 mL of dry toluene. All the flasks of reaction mixture were placed on separately preheated (100 °C) surfaces with stirring for 0.5 h, 2 h, 4 h, 6 h, 8 h, 10 h, 12 h, and 15 h. Subsequently, after reaching each time point, the corresponding flask was taken out and cooled to room temperature. The reaction mixture was passed through a bed of silica with ethyl acetate as an eluent. Further, the isolated products were analyzed by  $^1H$  NMR spectra. In the following, increasing the time at the constant temperature, the product formation was increased and decreasing the starting material.



**Figure S101.** Time-conversion profile of the reaction

## 14. Reference

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