Supporting Information

for

Mechanochemical Synthesis of 1,2,6-Thiadiazine 1-Oxides from Sulfonimidamides and the Fluorescence Properties of the Products

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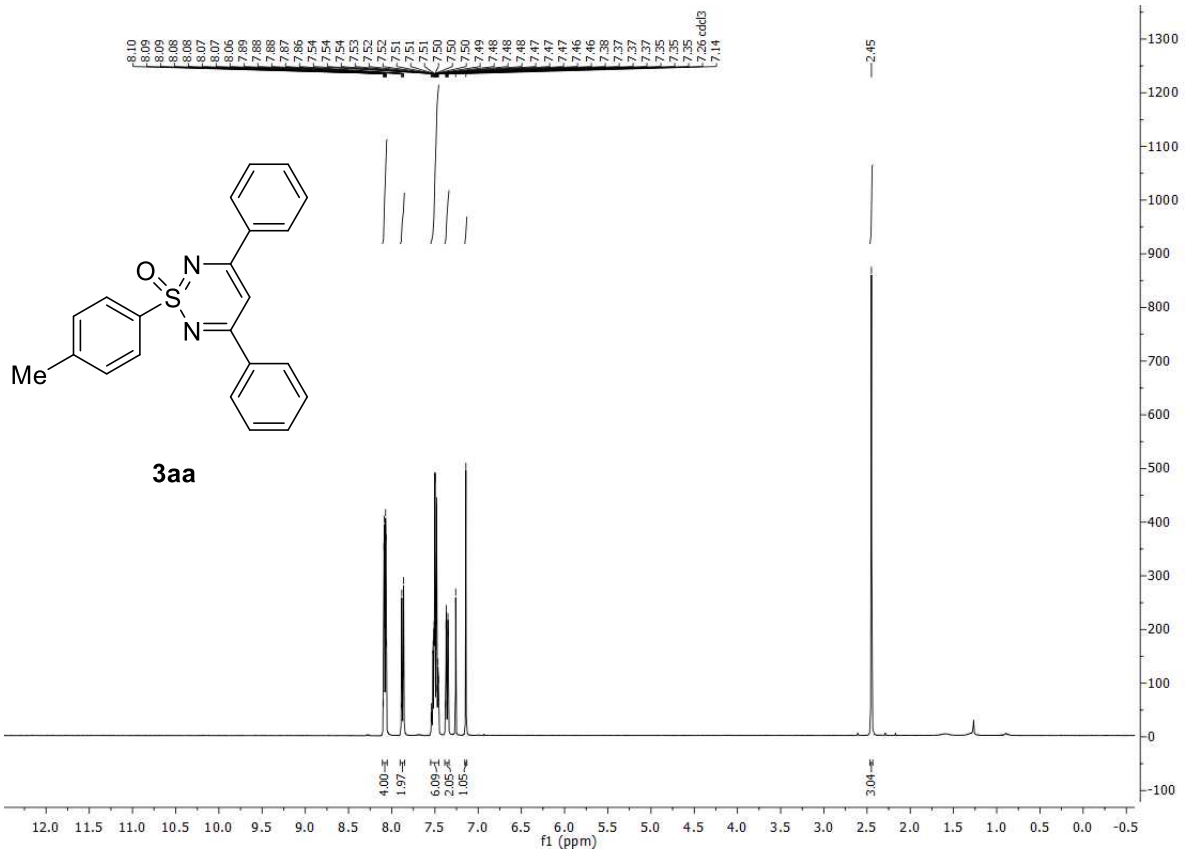
1. Ball mill equipment

The mechanochemical reactions were carried out in a RETSCH Mixer Mill MM 400. Reactions on a 1 mmol scale were performed in stainless steel milling vessels (10 mL volumetric capacity) with three stainless steel milling balls (7 mm in diameter). All other mechanochemical reactions were done in stainless steel milling vessels (5 mL volumetric capacity) and two stainless steel milling balls (7 mm in diameter).

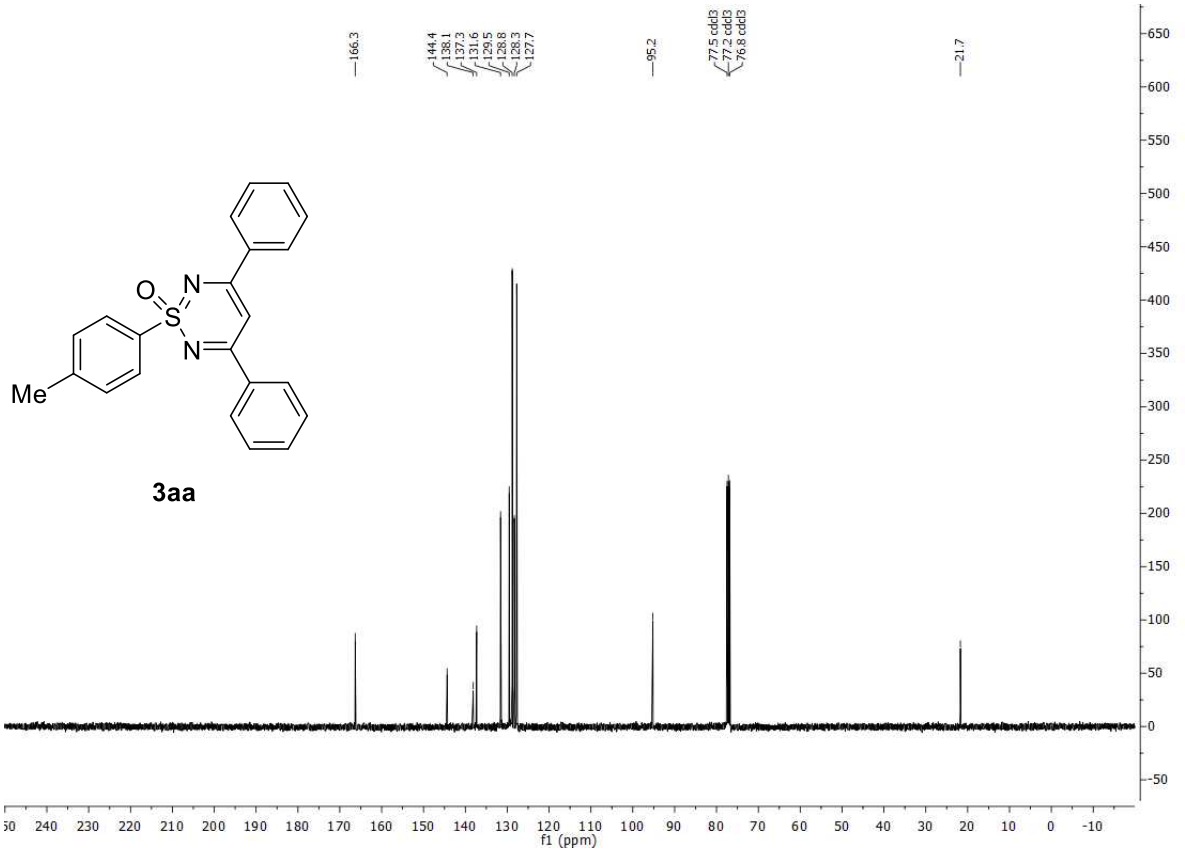
Figure S1. Stainless steel milling vessels used in mechanochemical reactions; left: 5 mL, right: 10 mL.

2. NMR spectra

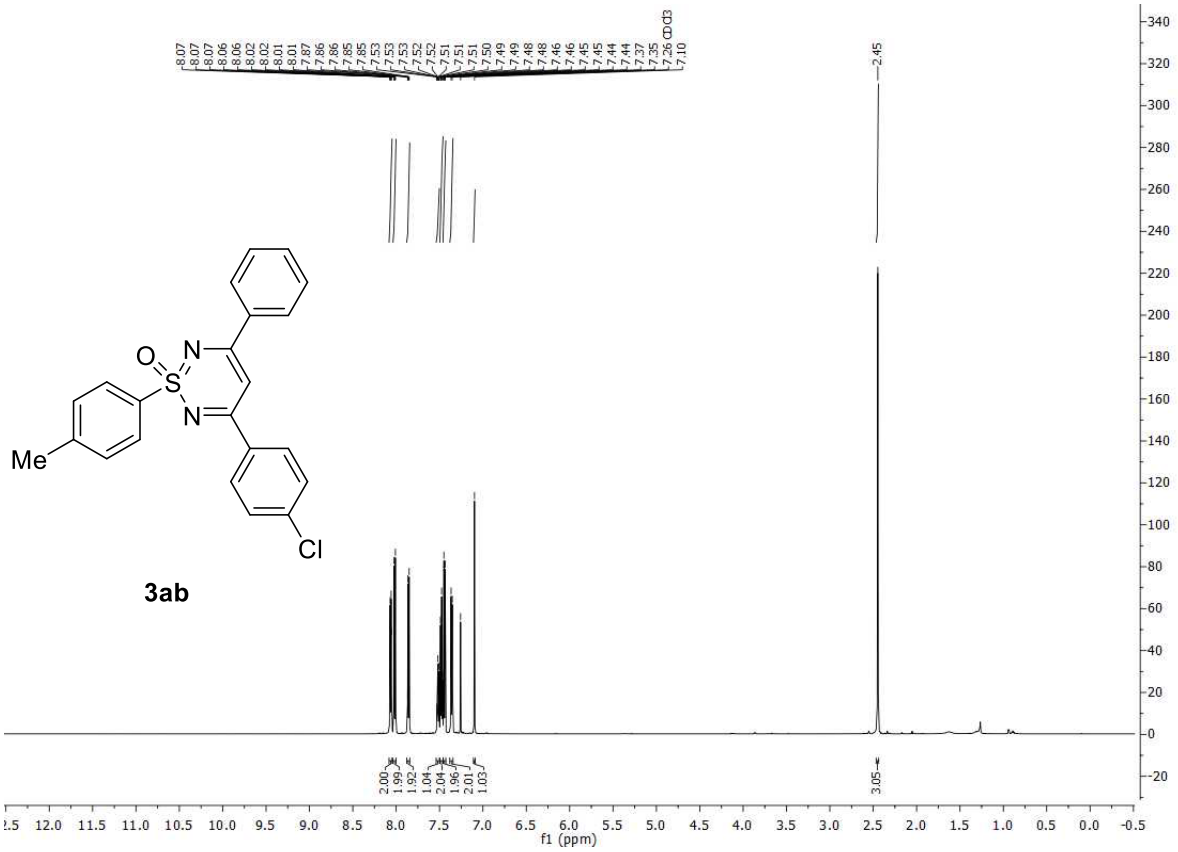
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aa**



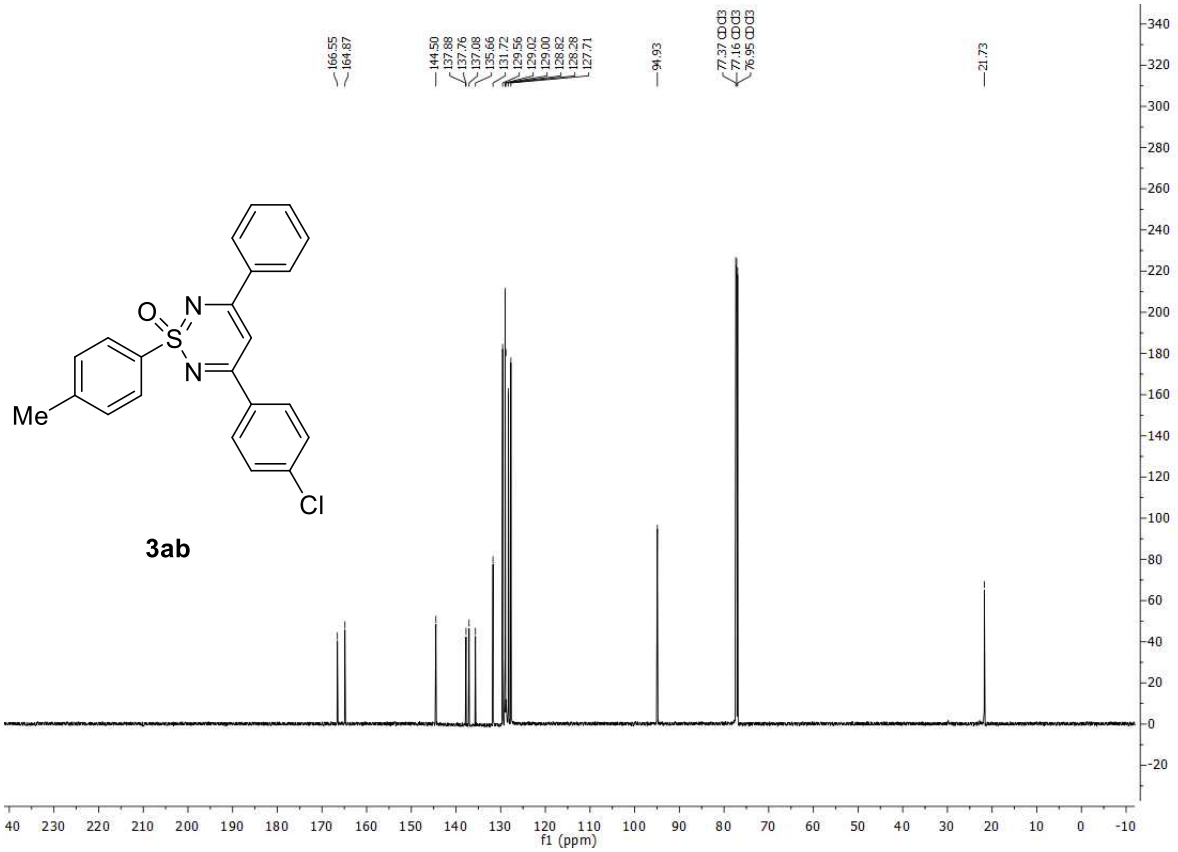
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **3aa**



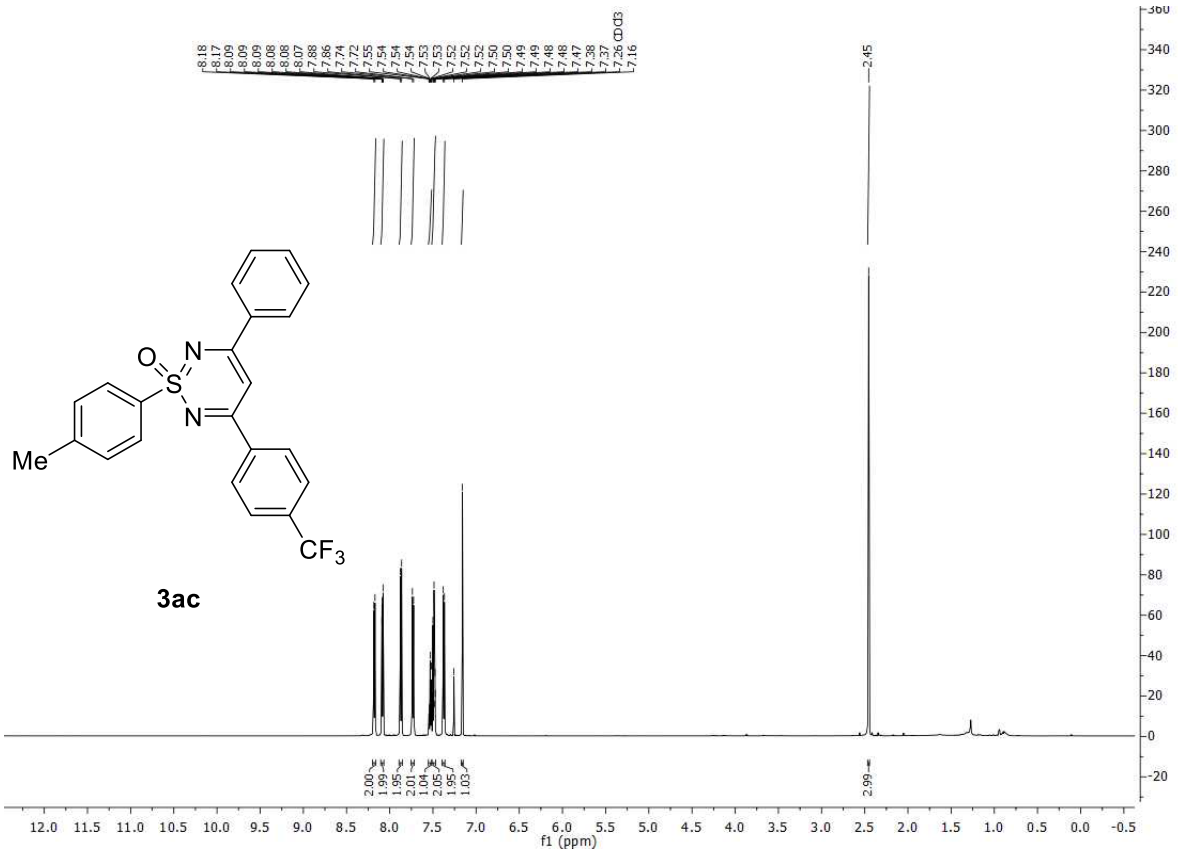
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **3ab**



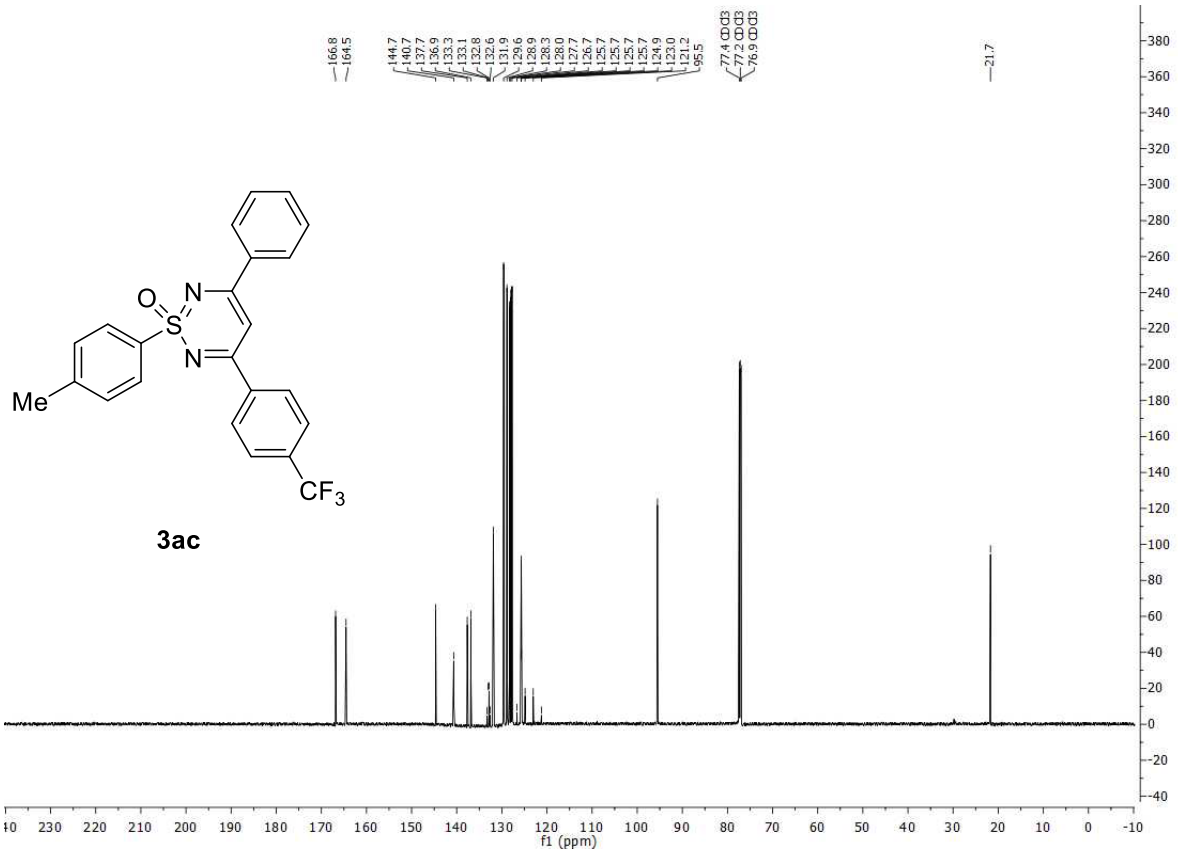
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of compound **3ab**



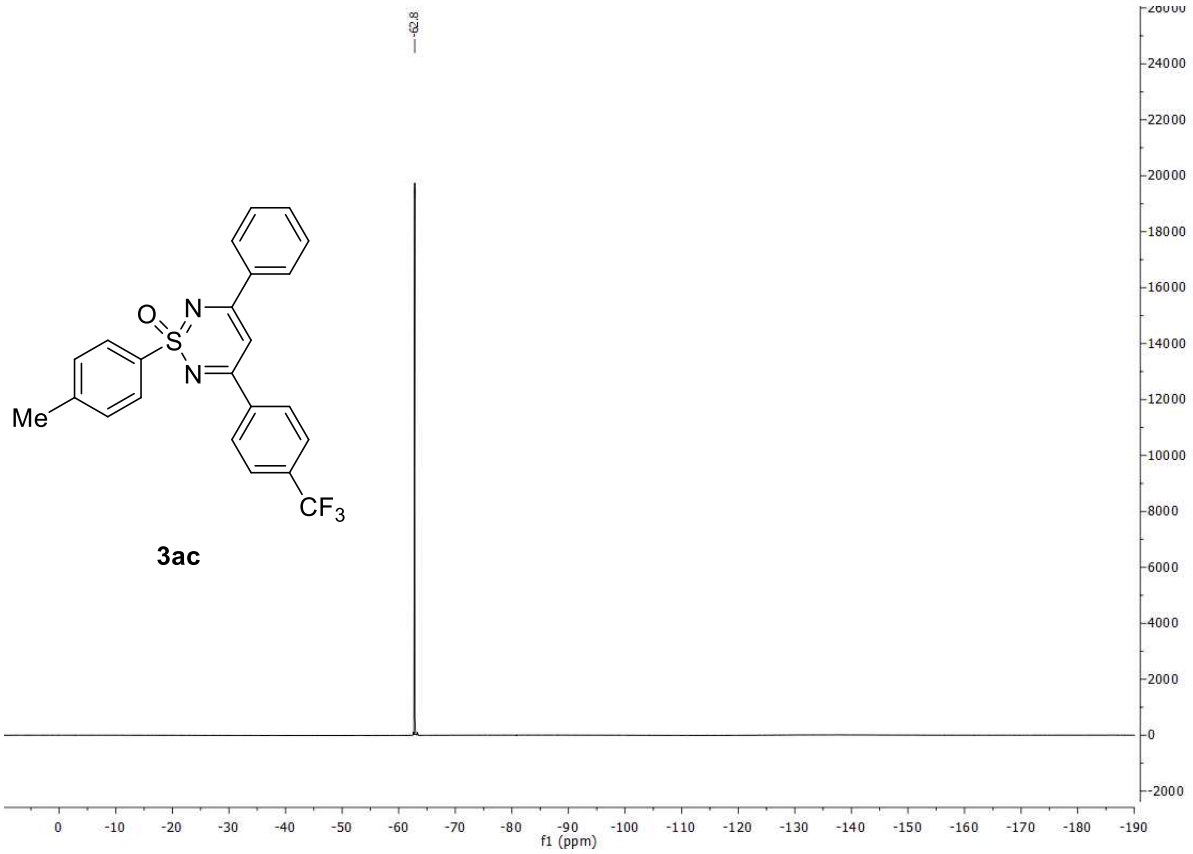
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **3ac**



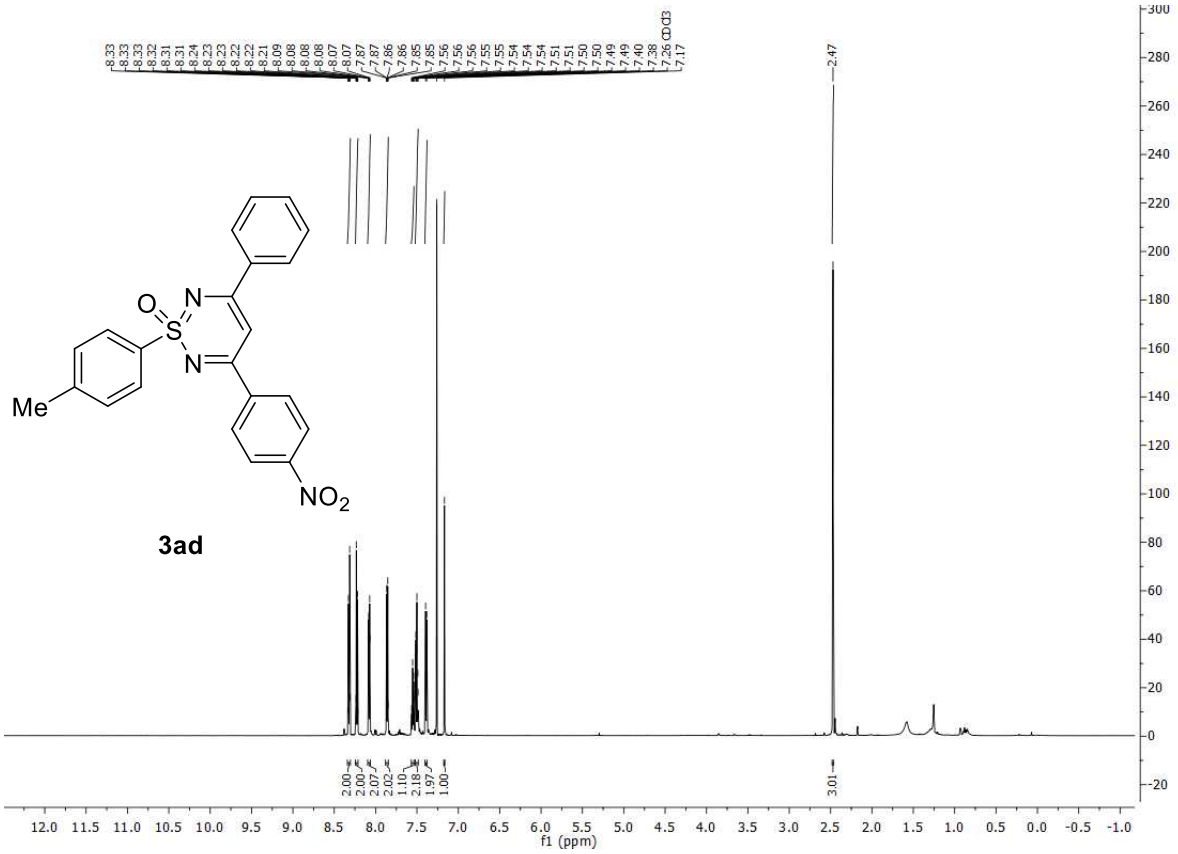
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of compound **3ac**



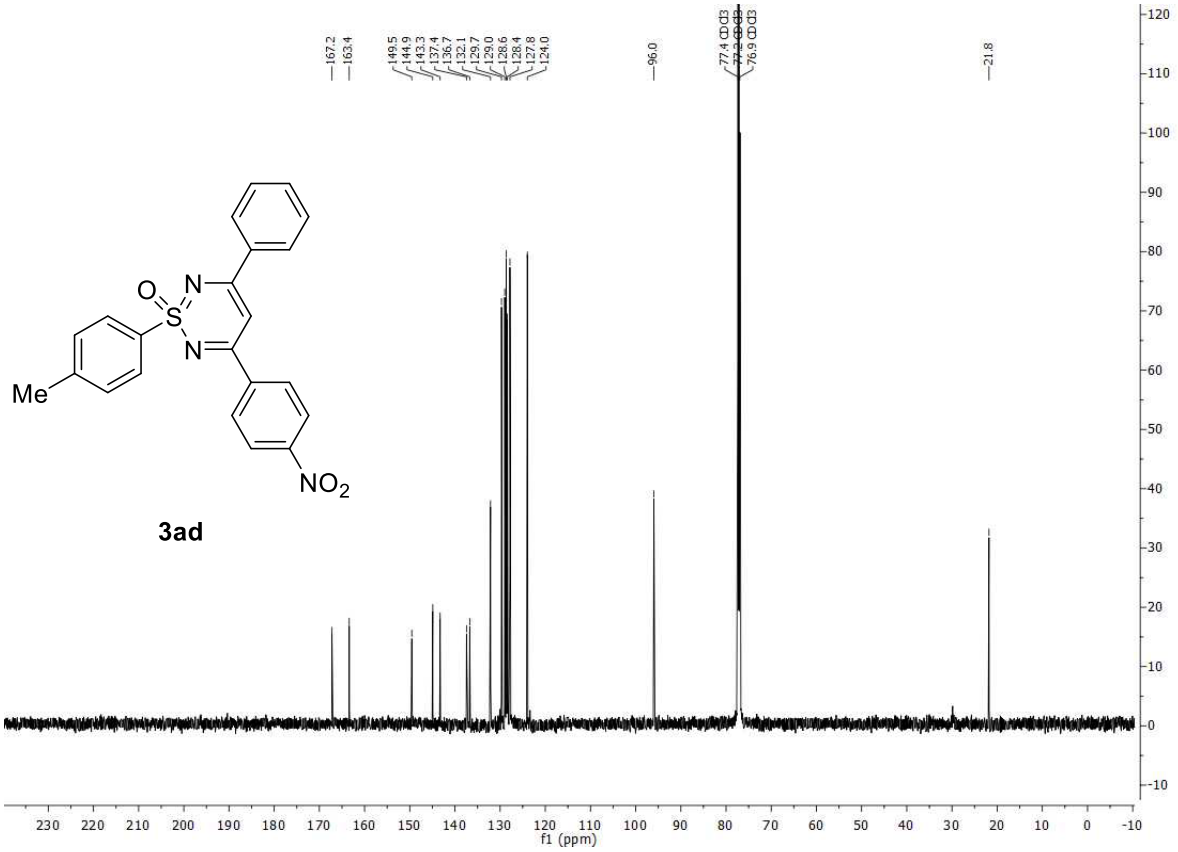
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3ac**



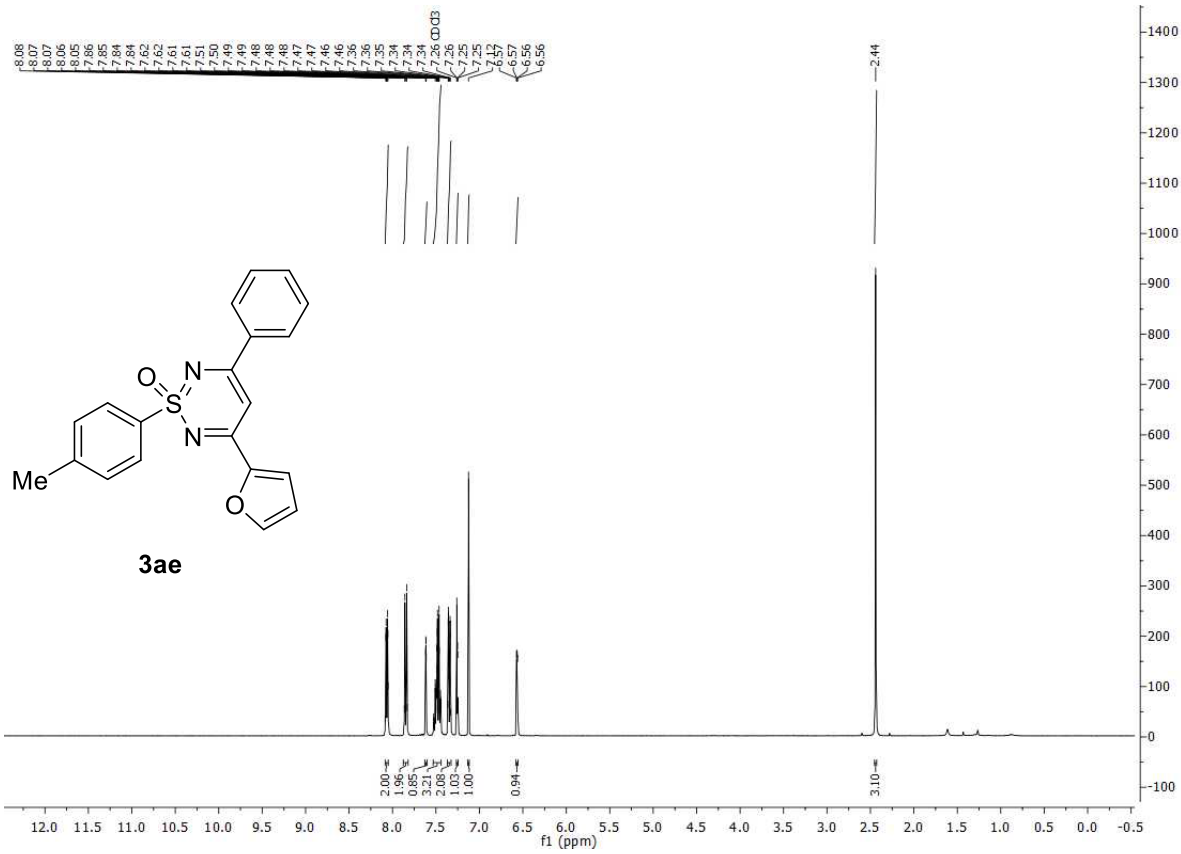
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **3ad**



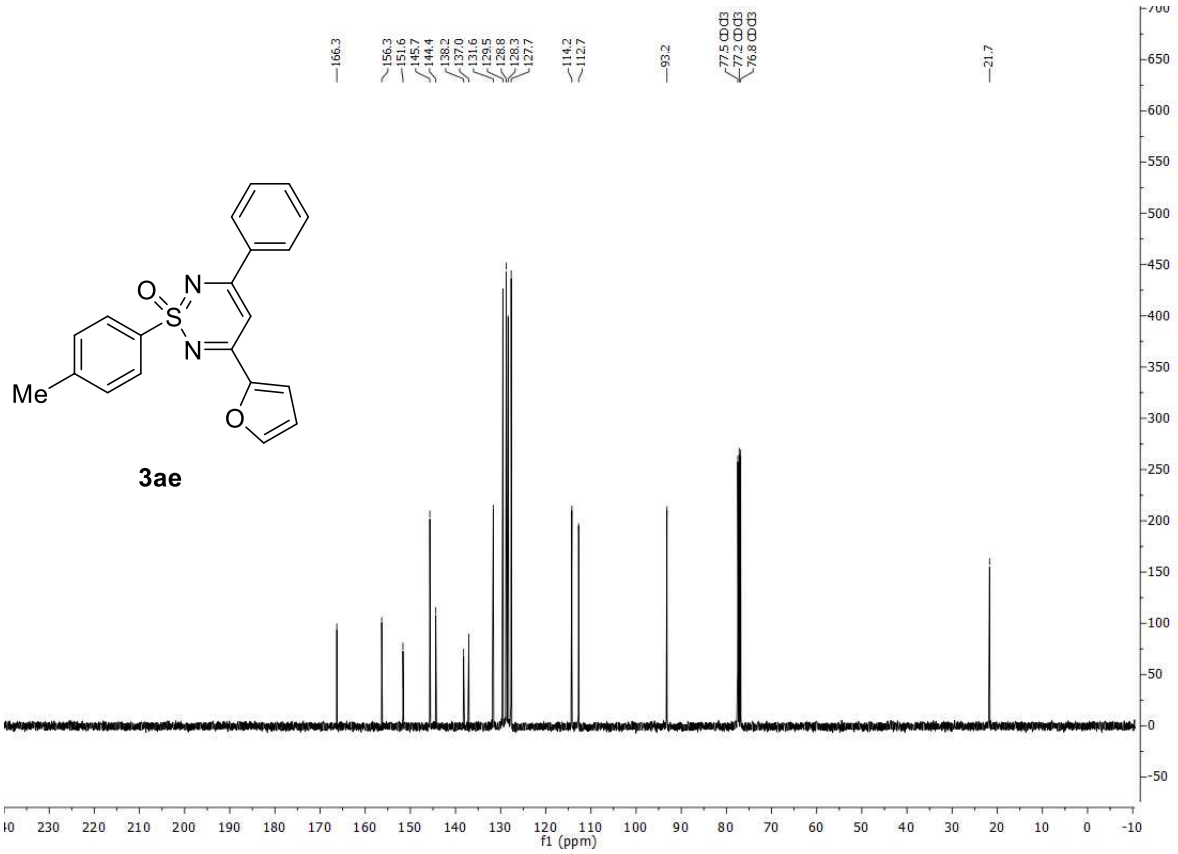
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of compound **3ad**



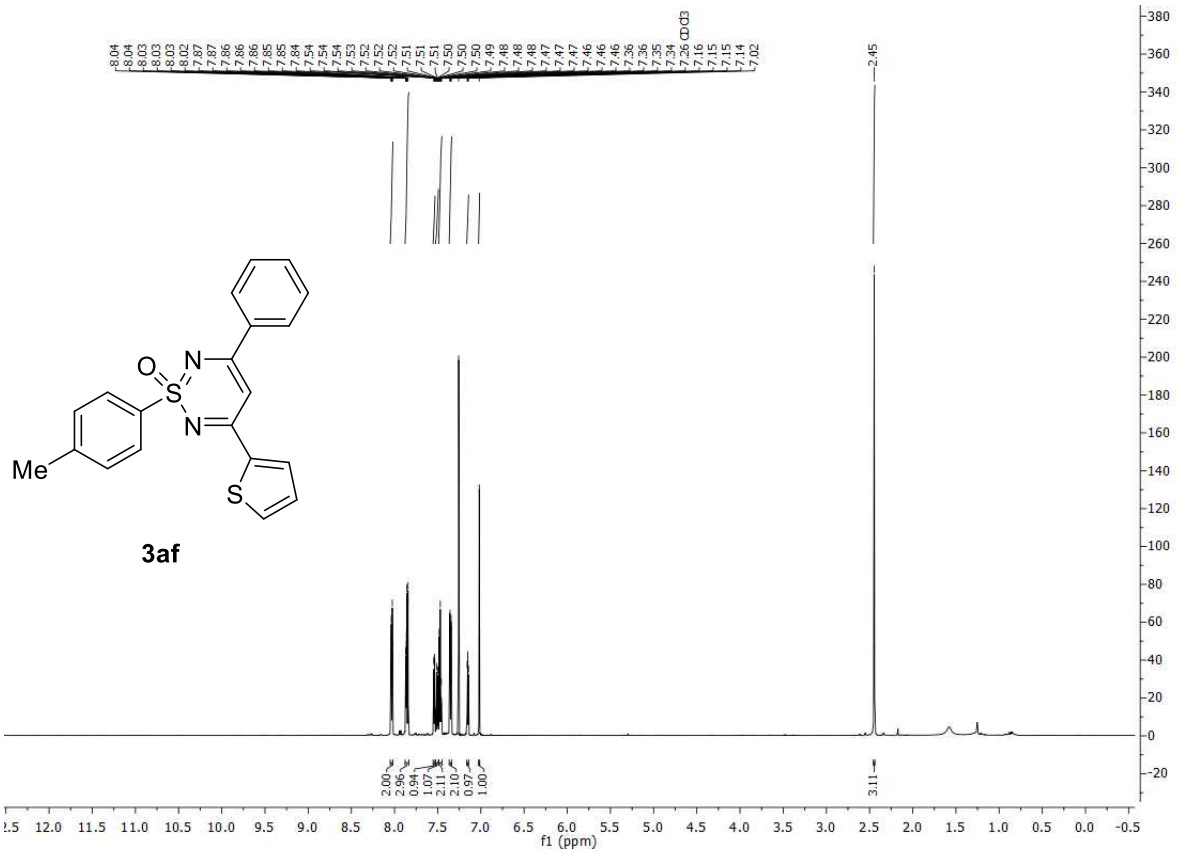
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ae**



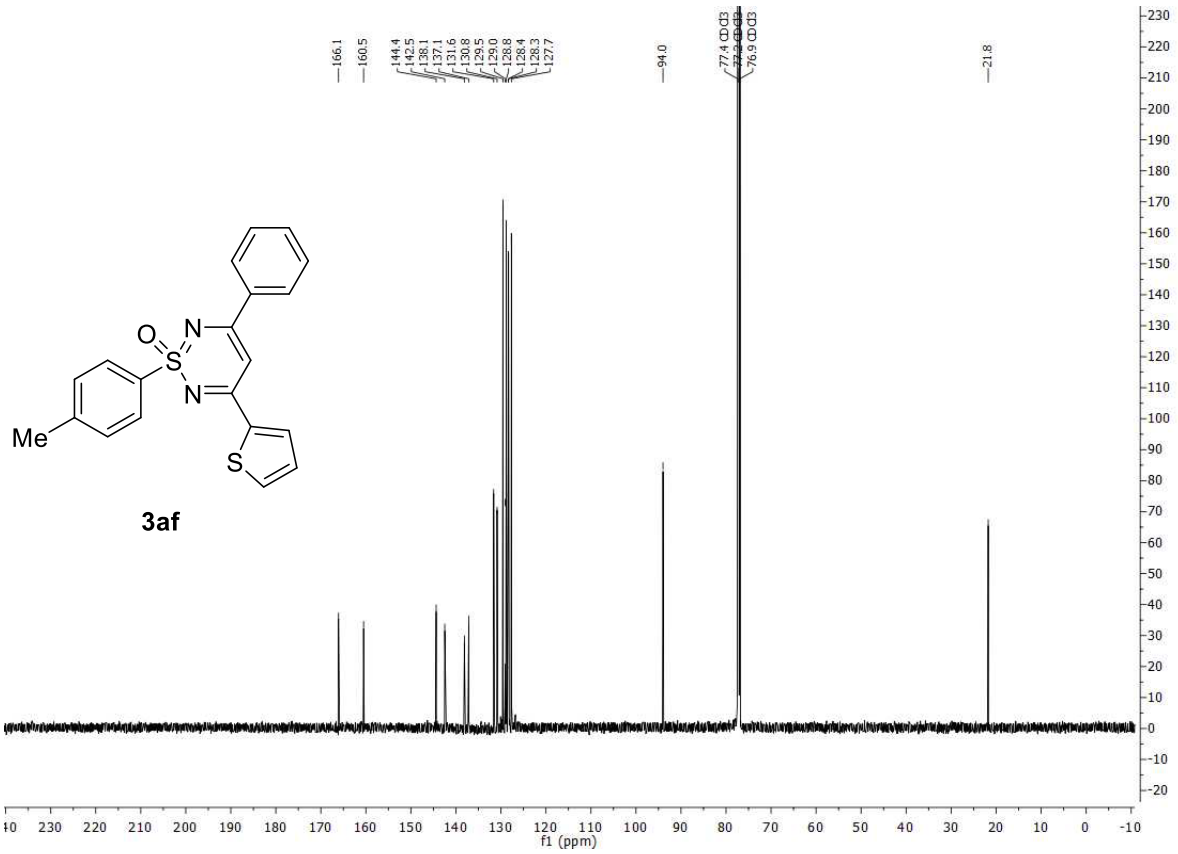
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ae**



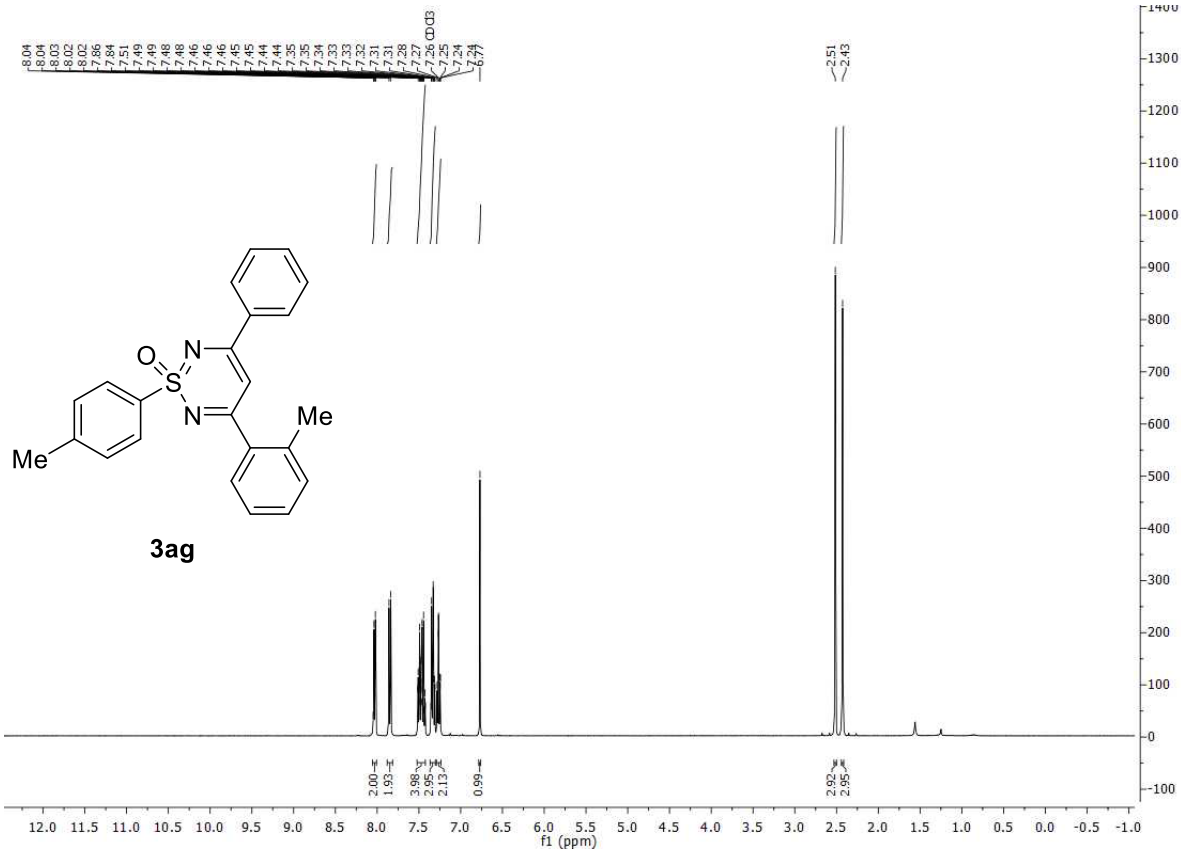
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **3af**



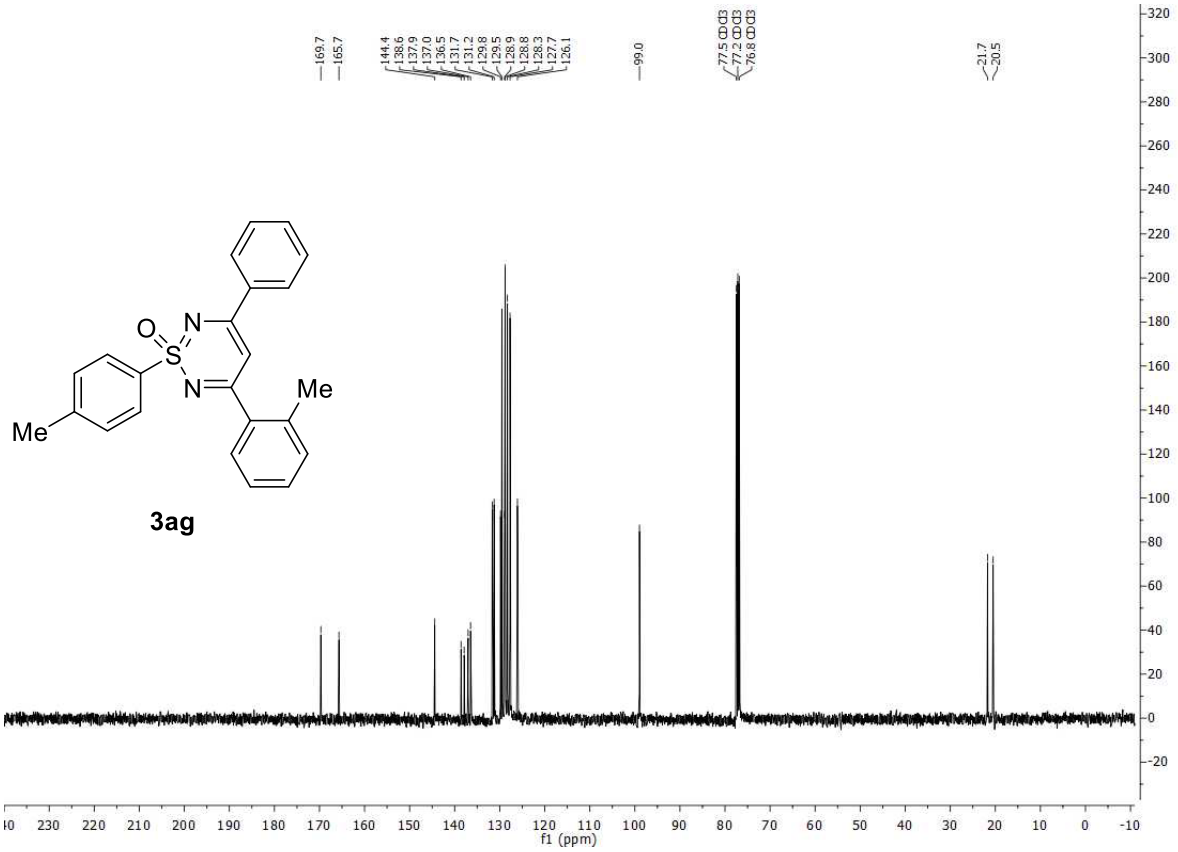
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of compound **3af**



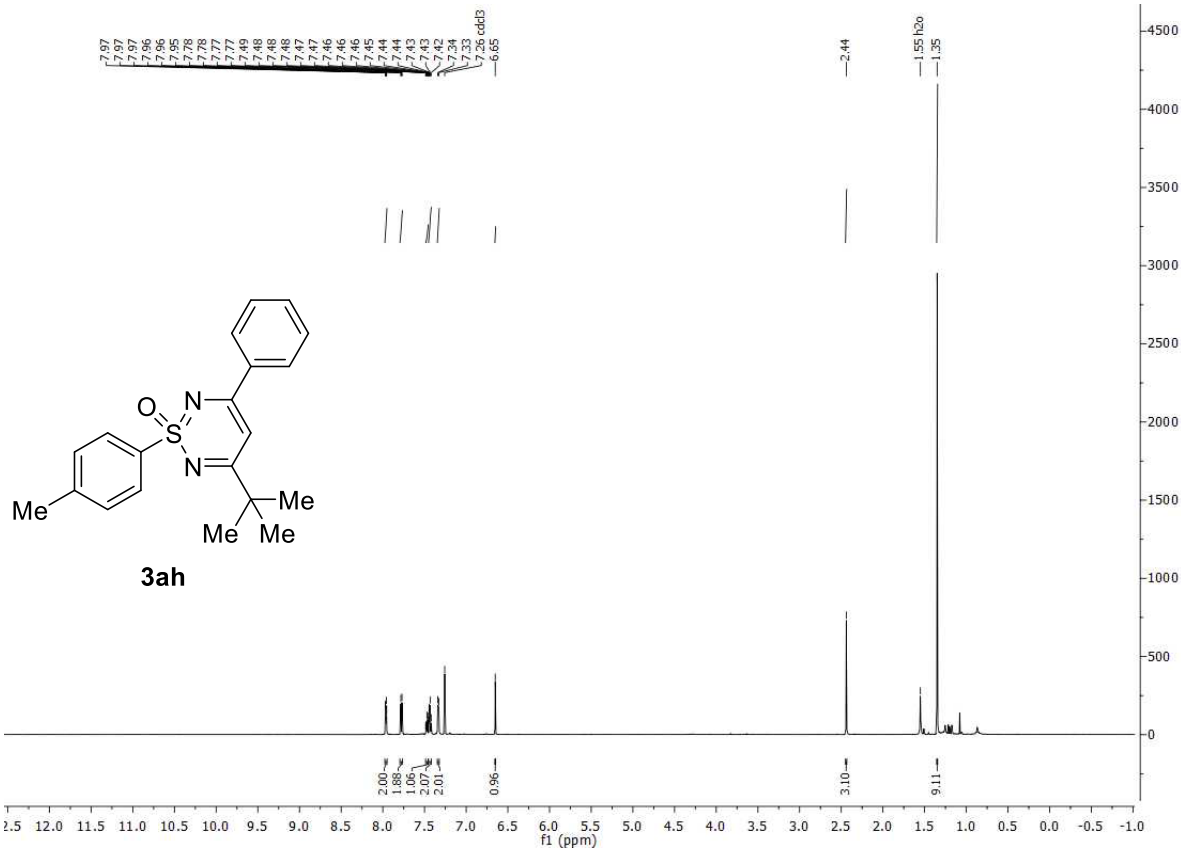
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ag**



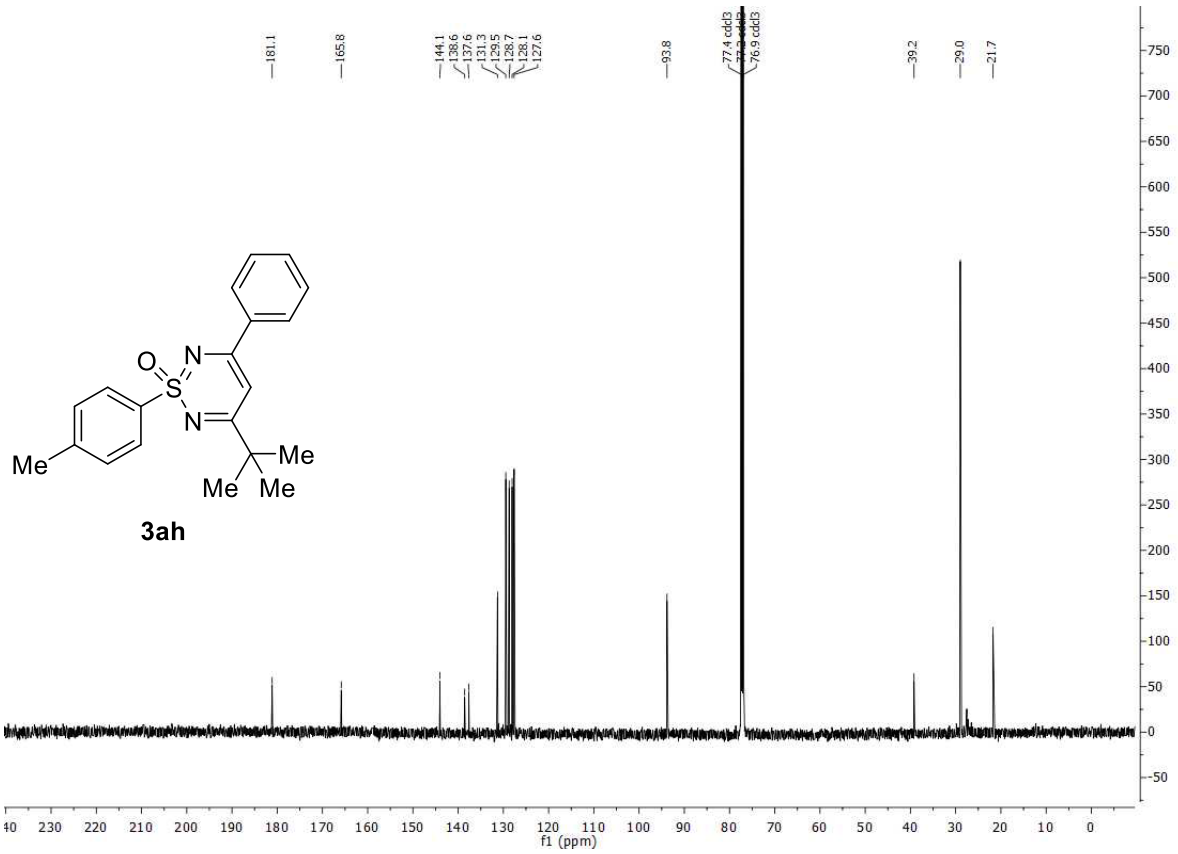
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ag**



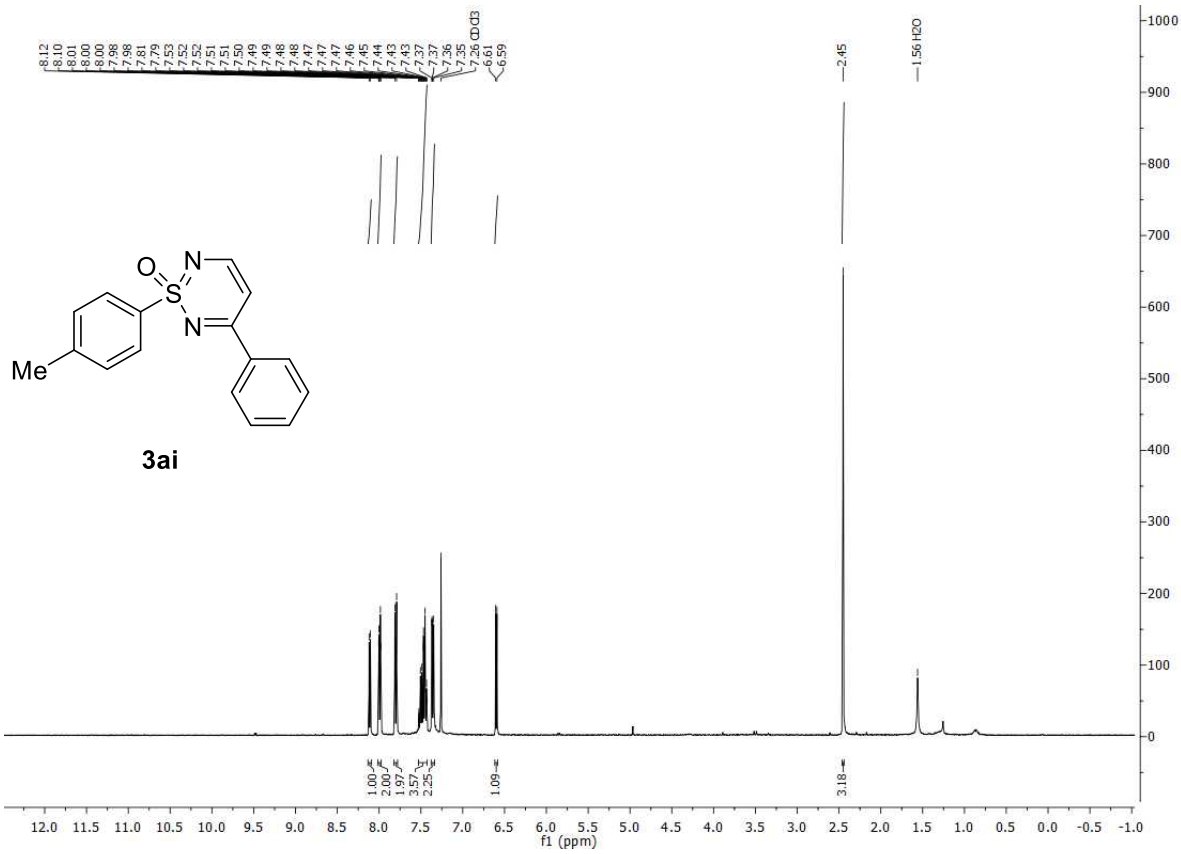
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **3ah**



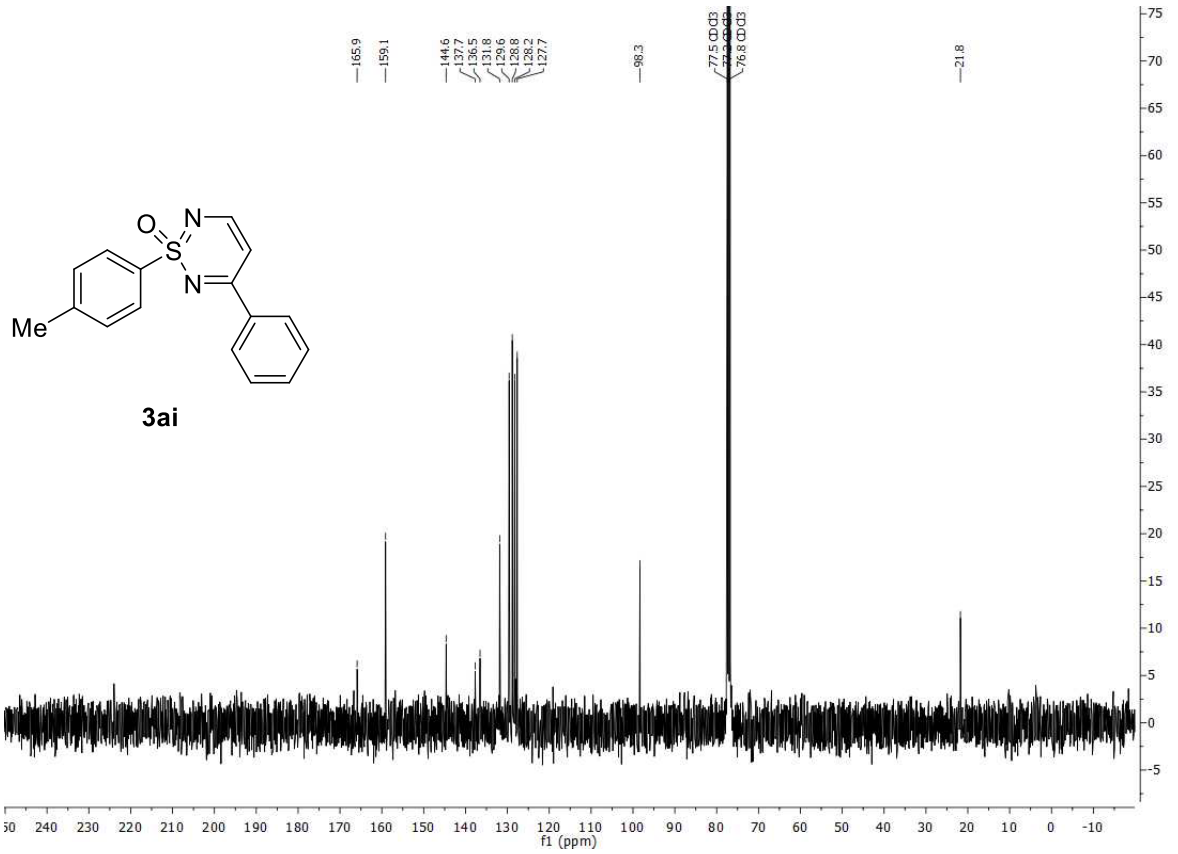
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of compound **3ah**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ai**

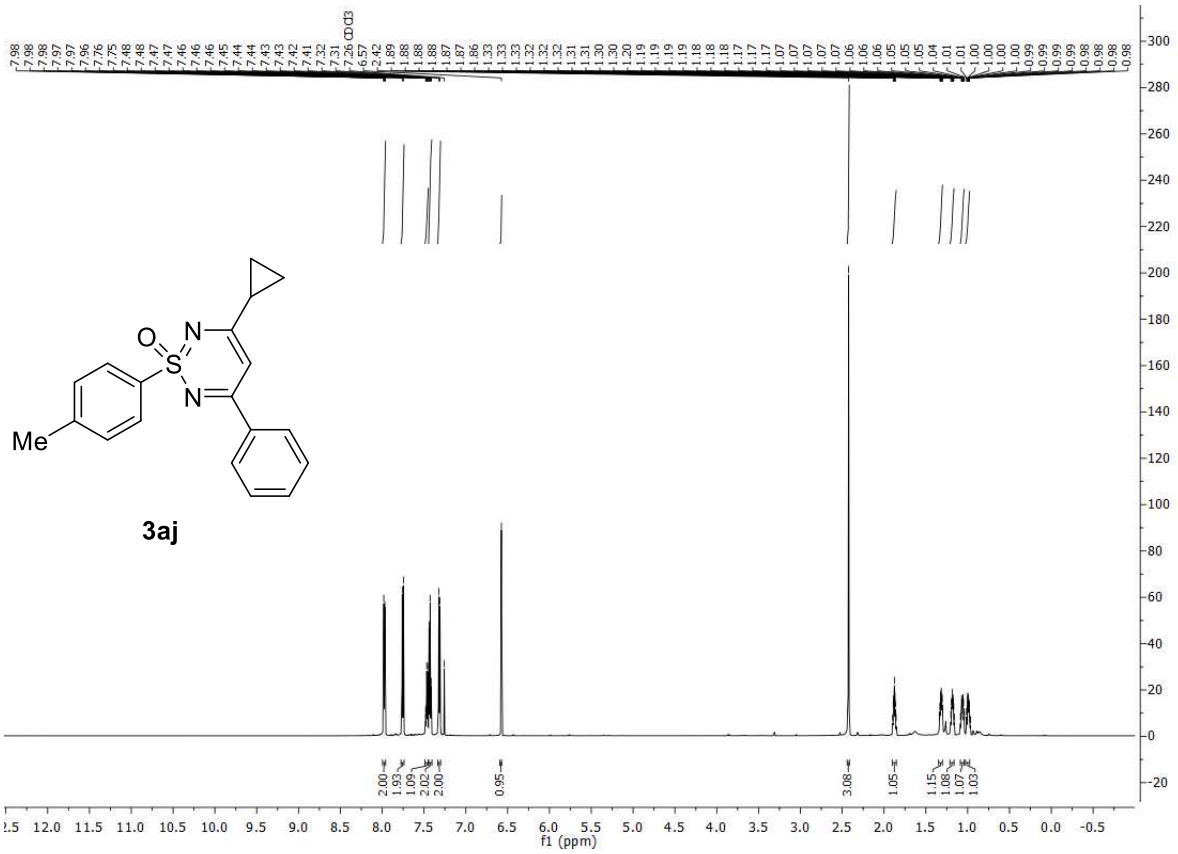


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ai**



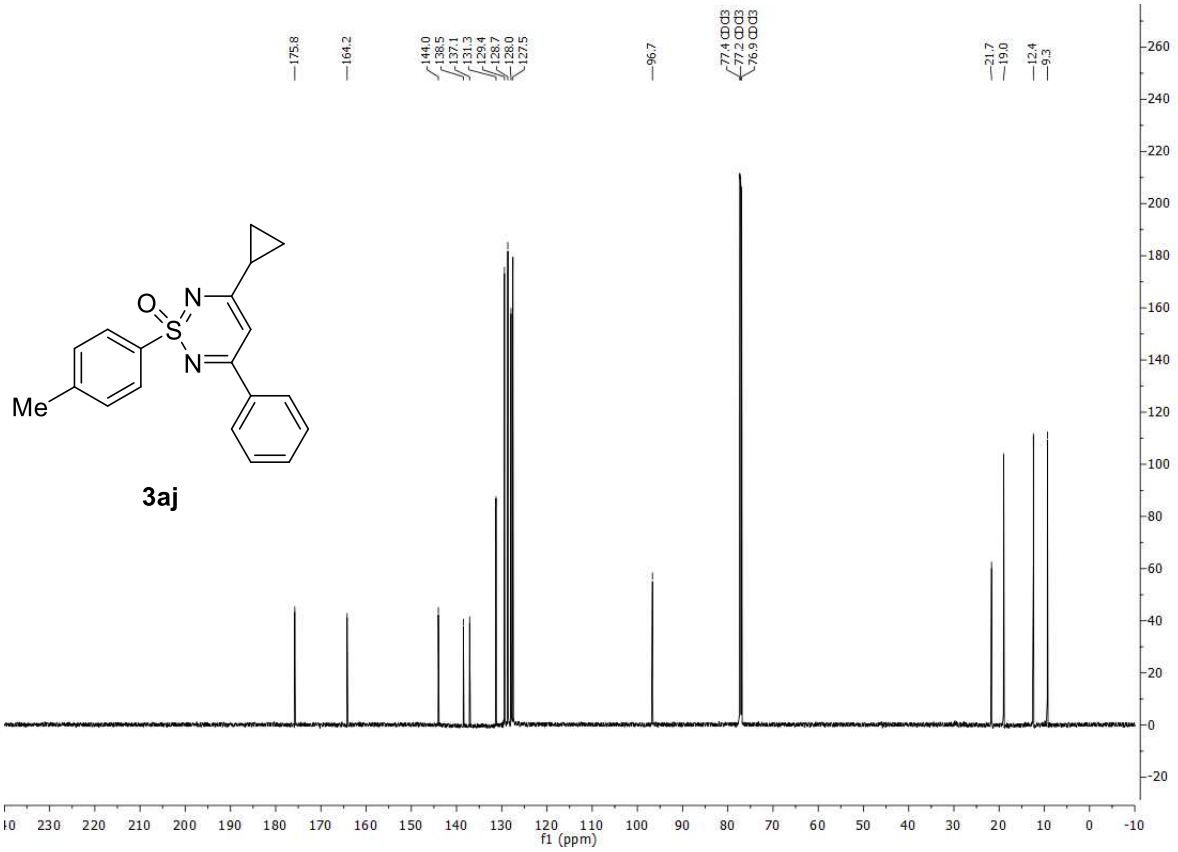
3ai

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aj**

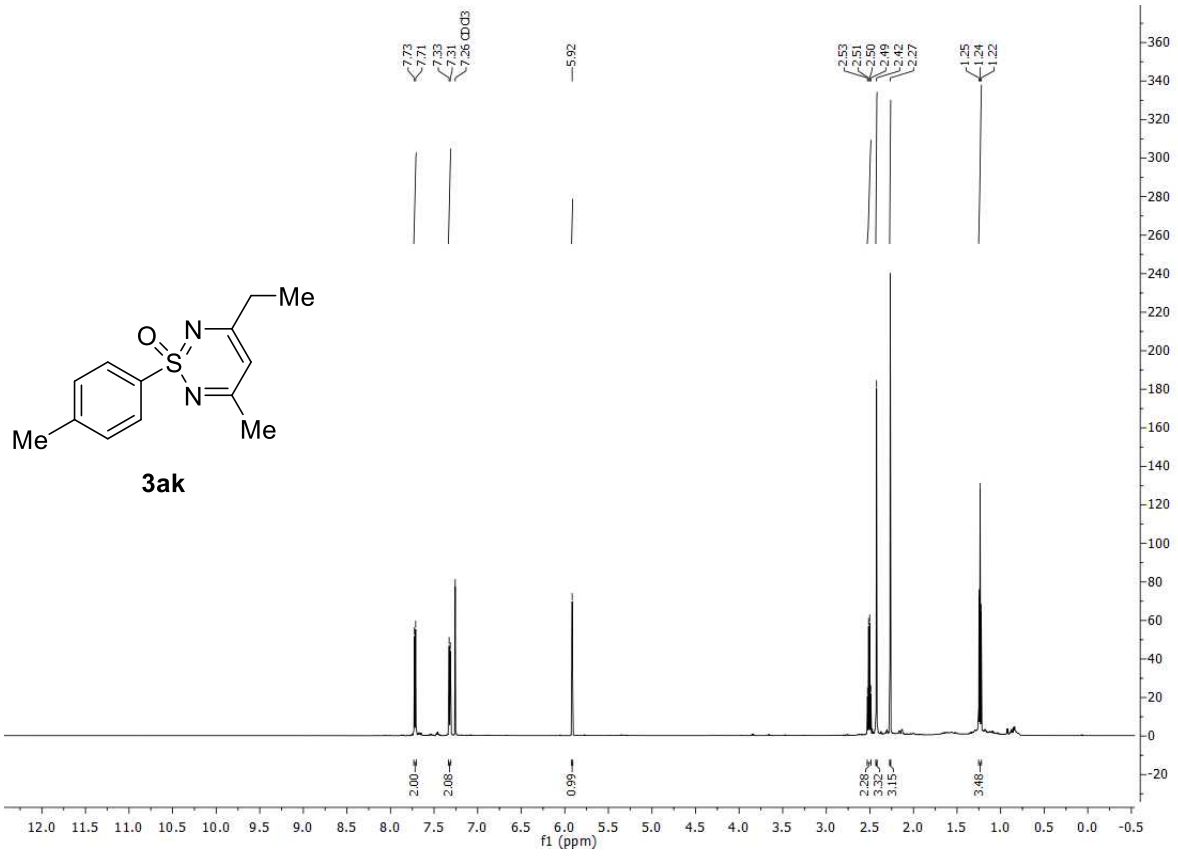


3aj

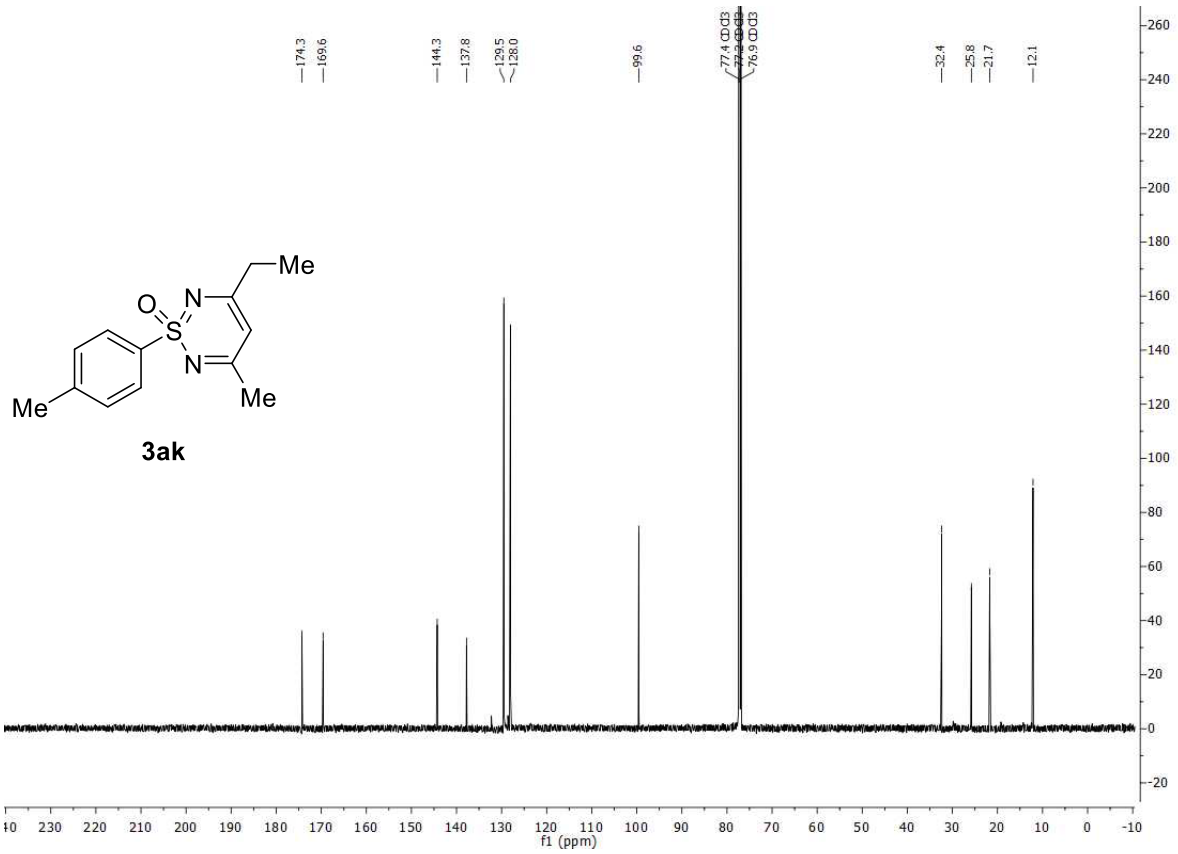
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3aj**



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **3ak**

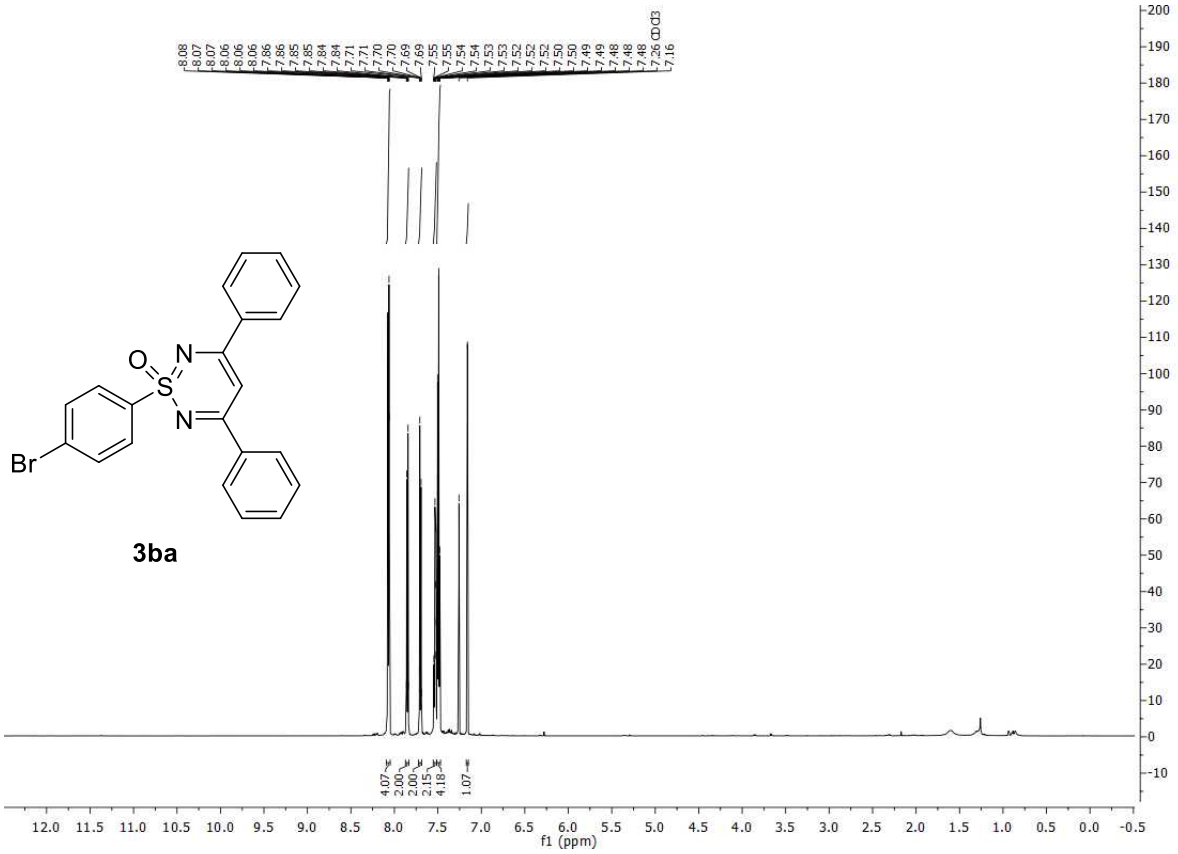


$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of compound **3ak**



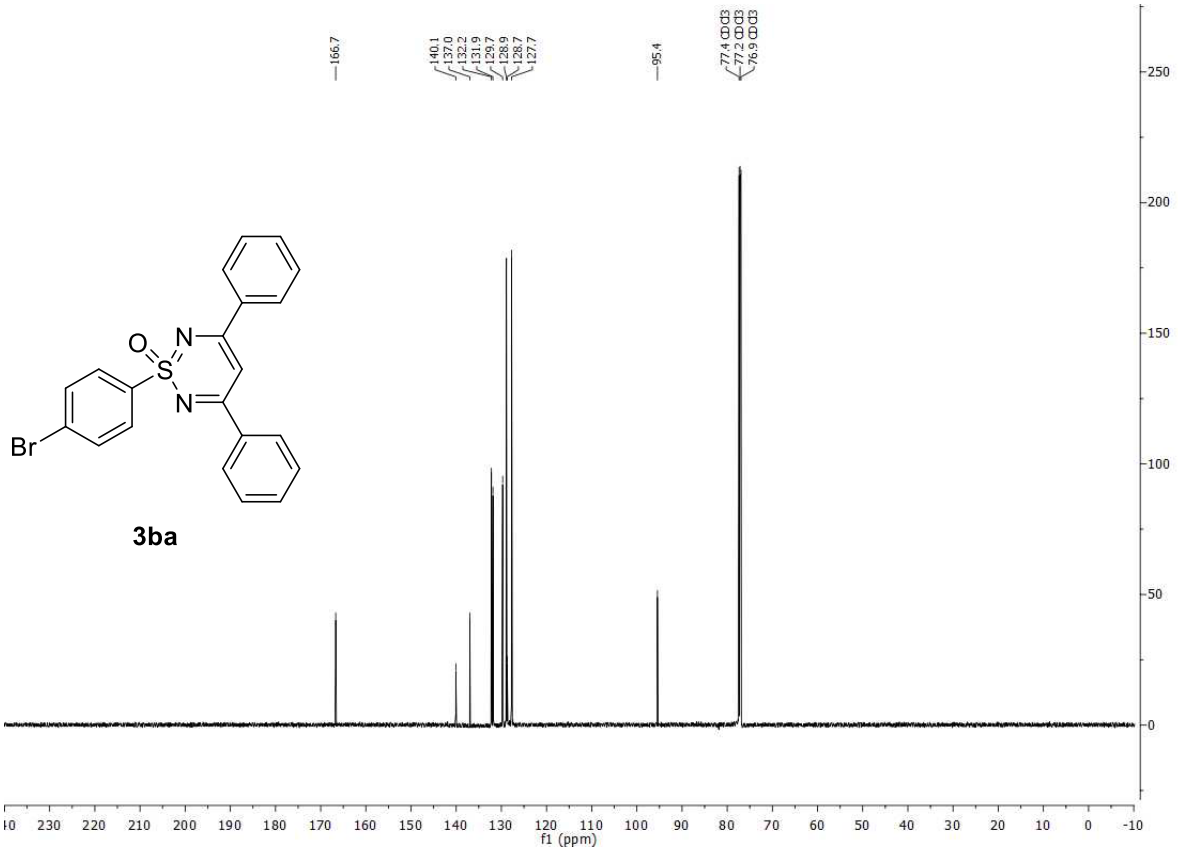
3ak

^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **3ba**

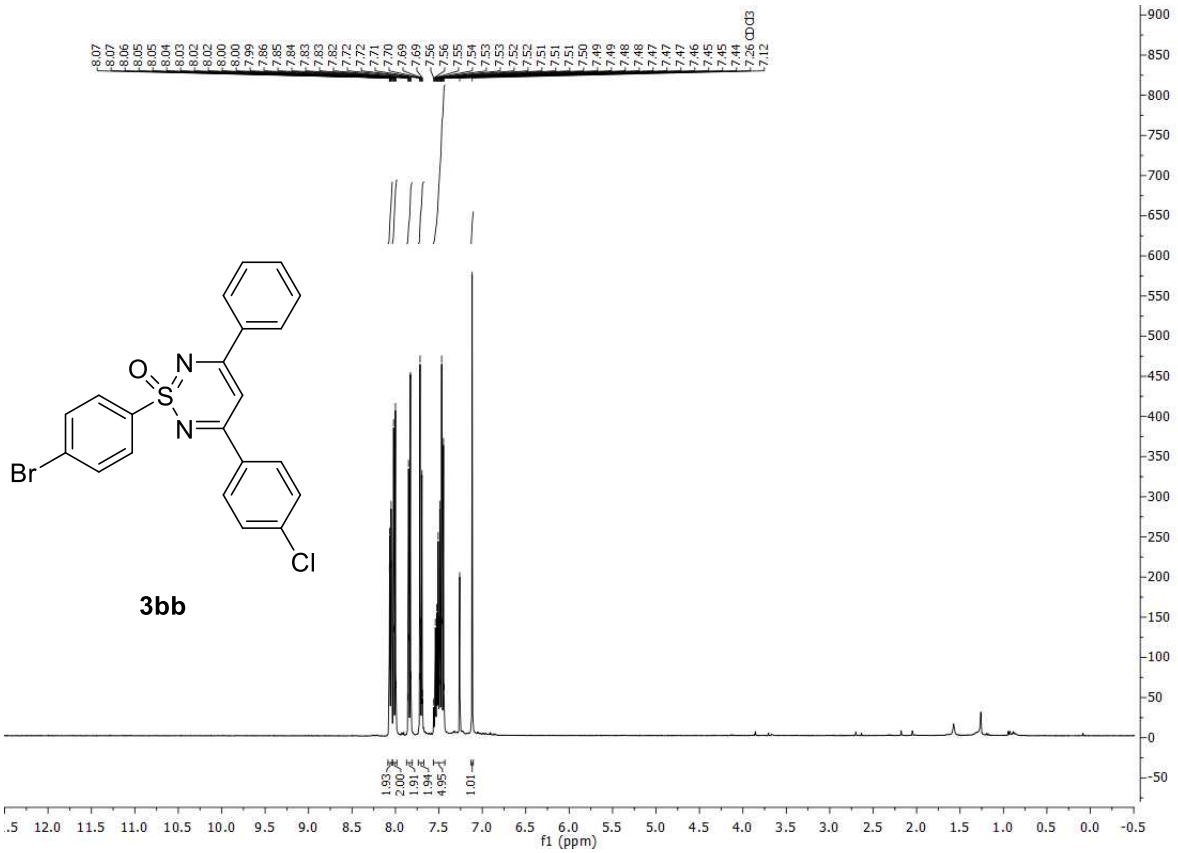


3ba

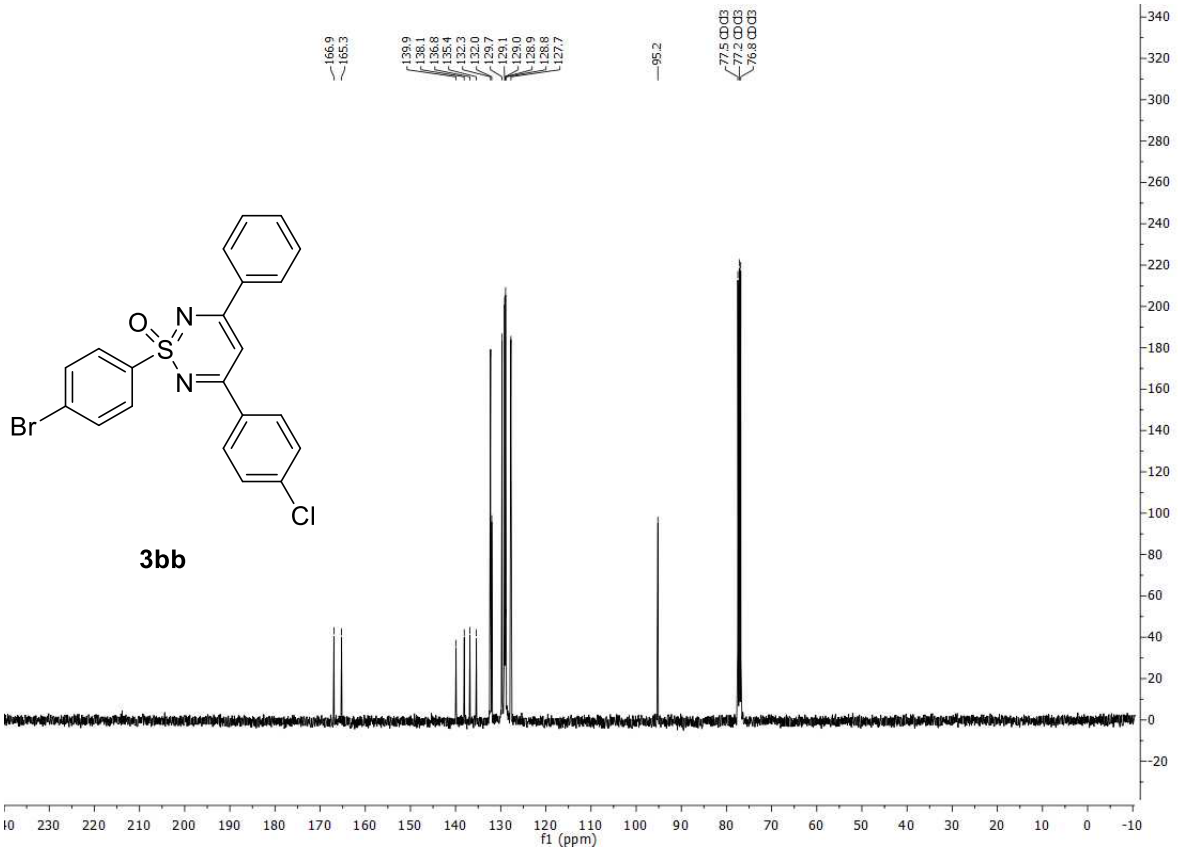
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of compound **3ba**



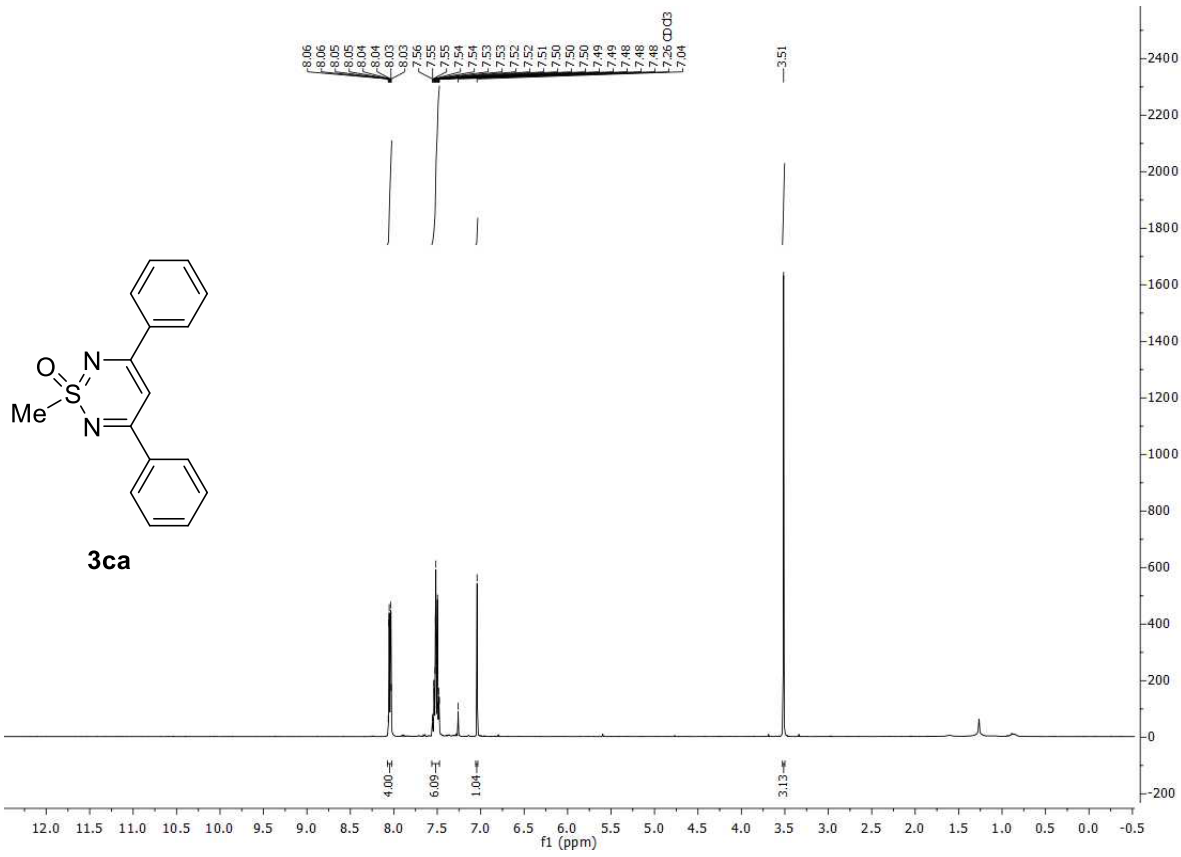
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3bb**



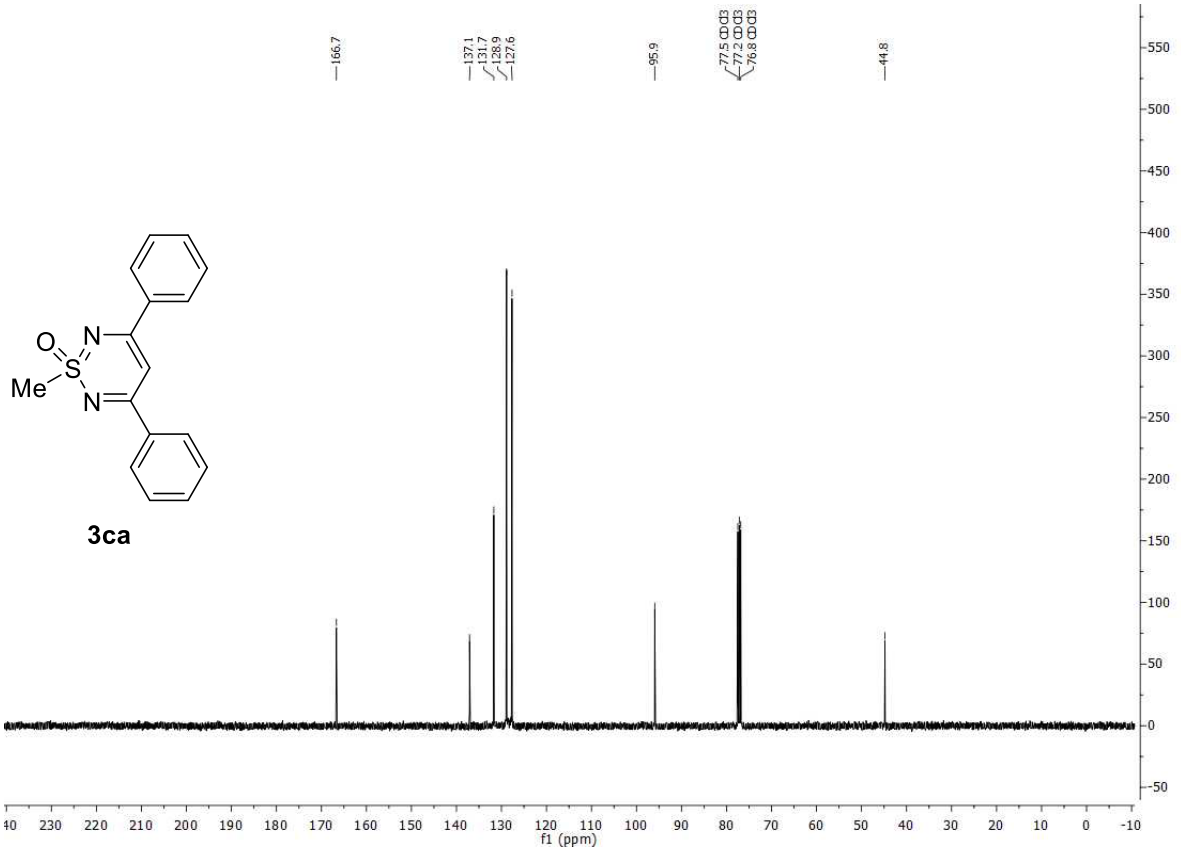
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3bb**



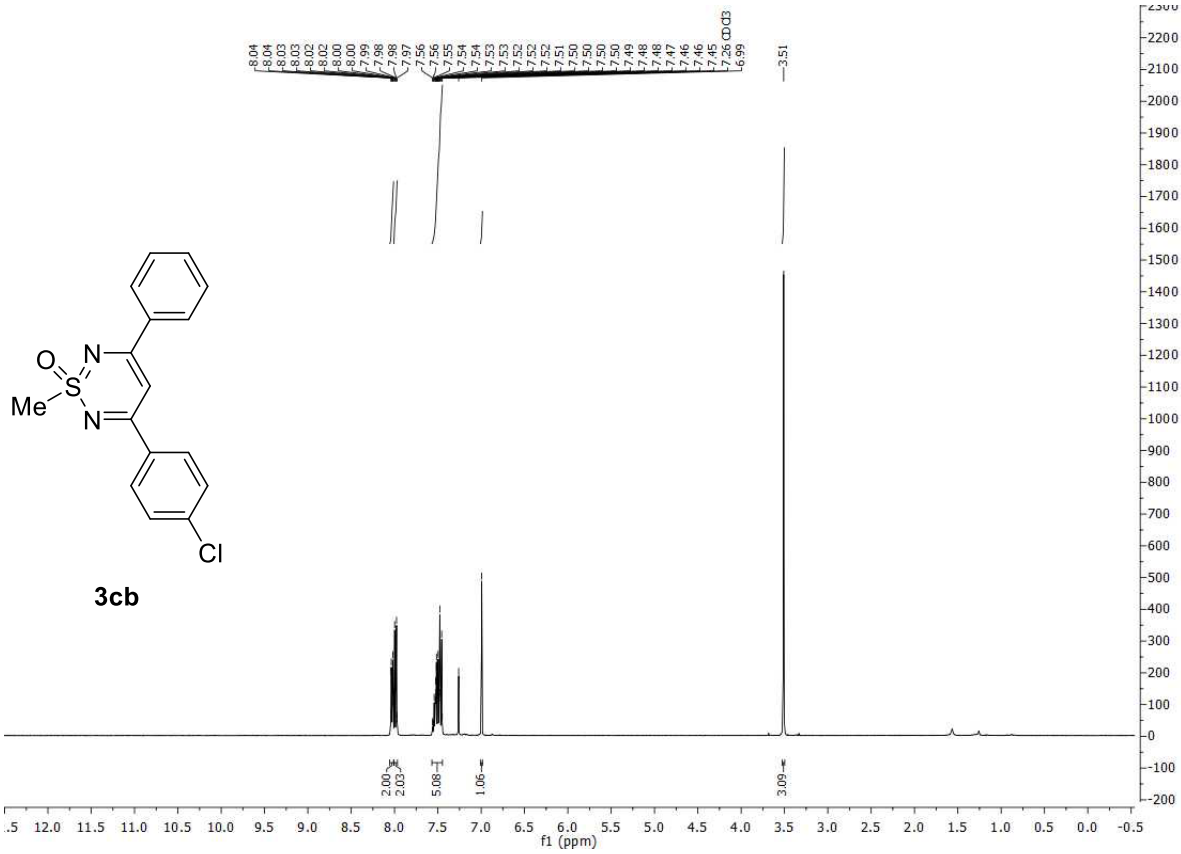
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ca**



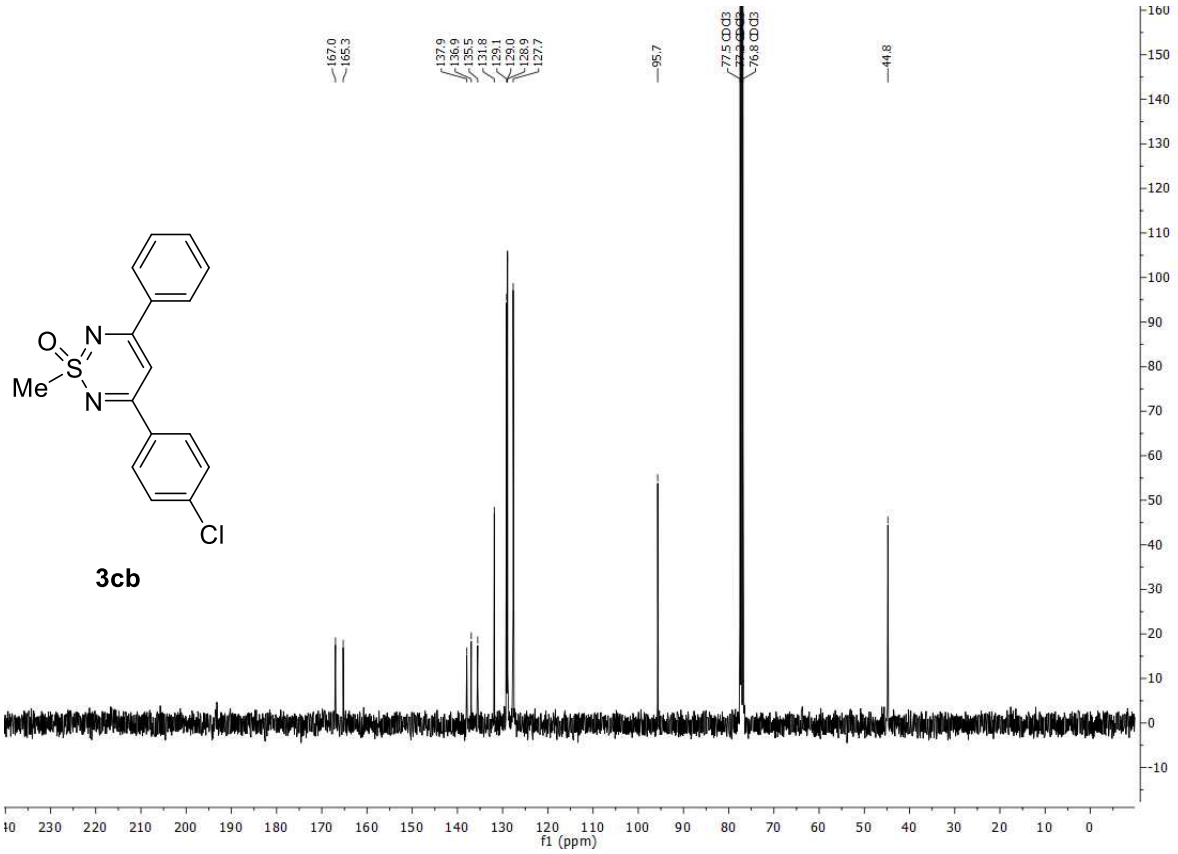
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ca**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3cb**



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3cb**



3. Photophysical properties

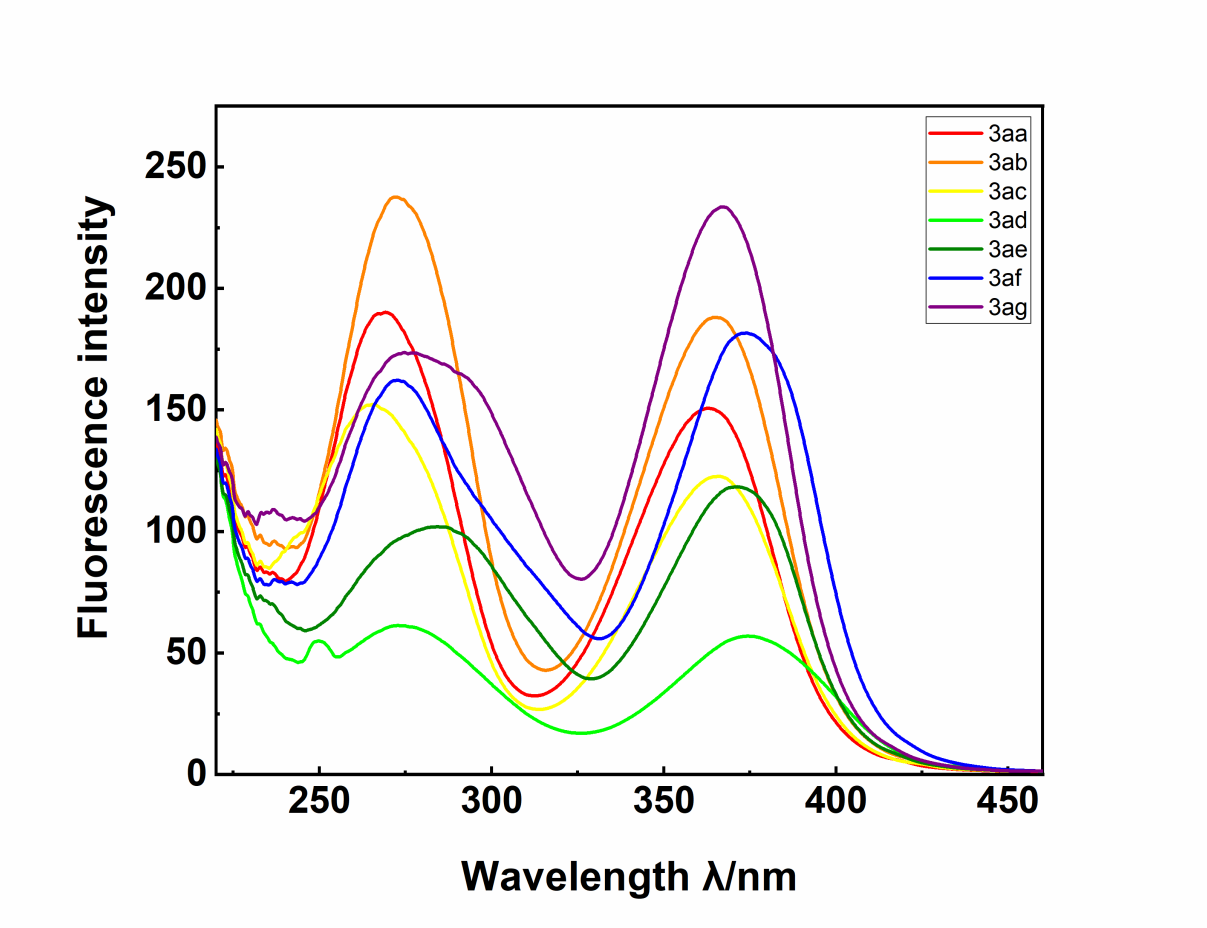


Figure S2. Fluorescence excitation spectra of **3aa**-**3ag** in 1,4-dioxane (0.02 mM), the emission wavelengths were 480 nm for **3aa** and **3ae**, 484 nm for **3ab**, 488 nm for **3ac**, 505 nm for **3ad**, 485 nm for **3af** and 478 nm for **3ag**. Small bands at half wavelengths (around 250 nm) are caused by the second order diffraction of the grating.

Table S1. Spectral and photophysical properties of compounds **3aa-3ag** in 1,4-dioxane: absorption maximum λ^{abs}_{max}, absorption coefficient maximum ε_{max}, fluorescence maximum λ^{flo}_{max}, fluorescence quantum yield φ determined using quinine sulfate as a reference.

Compound	λ^{abs}_{max} / *nm*	ε_{max} / 10^4 *L mol*$^{-1}$ *cm*$^{-1}$	λ^{flo}_{max} / *nm*	φ
3aa	364	1.43	477	0.23
3ab	366	1.72	478	0.26
3ac	367	1.48	481	0.15
3ad	377	1.12	506	0.14
3ae	375	1.94	477	0.15
3af	376	1.79	479	0.25
3ag	368	1.93	475	0.28

The fluorescence quantum yield was determined using quinine sulfate as reference:

$$\phi_f^i = \frac{F^i f_s n_i^2}{F^s f_i n_s^2} \phi_f^s$$

ϕ_f^i and ϕ_f^s are the fluorescence quantum yield of the investigated compound in 1,4-dioxane and quinine sulfate in 0.05 M H_2SO_4, respectively. F^i and F^s are the integrated intensities, and f_x is the absorption factor ($f_x = 1 - 10^{-A_x}$ with the absorbance A). The refractive indices of the sample and reference solution (1,4-dioxane and water) are n_i and n_s, respectively.

4. References

(1) Schöbel, J.-H.; Passia, M. T.; Wolter, N. A.; Puttreddy, R.; Rissanen, K.; Bolm, C. 1,2,6-Thiadiazine 1-Oxides: Unsaturated Three-Dimensional S,N-Heterocycles from Sulfonimidamides. *Org. Lett.* **2020**, *22*, 2702–2706.

(2) Brouwer, A. M. Standards for photoluminescence quantum yield measurements in solution. *Pure Appl. Chem.* **2011**, *83*, 2213–2228.