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Supporting Information

Synthesis of 3-amino-substituted benzothiadiazine oxides by a palladium-catalysed cascade reaction

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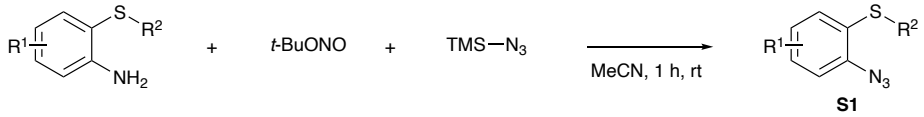
1. General information

All commercially available chemicals used in this work were obtained from Merck, Sigma-Aldrich, Alfa Aesar, Chempur, ACROS ORGANICS or abcr and were used as received. Triethylamine (99%) for synthesis was dried for several days over KOH prior use. Tetrakis-(triphenylphosphine)-palladium, 2-azido sulfoximines and aryl-substituted isonitriles were synthesised as indicated below. Tetrakis-(triphenylphosphine)-palladium was stored at –25 °C in an argon filled glove box (MBraun Labmaster 130). A small amount was transferred for use each time before the reaction set up. Dry and degassed DMF and DMSO were purchased from ACROS ORGANICS. All other dry and degassed solvents (DCM, THF, MeCN and Toluene) were purified by a Solvent Purification System MB-SPS-5 from MBRAUN. Ethyl acetate for column chromatography was distilled before use. Triethylamine (99%), *n*-pentane (technical grade), and MeOH (technical grade) were used without further purification. Chemical reactions under inert conditions were performed in oven dried (160 °C) Schlenk-tubes and -flasks using standard Schlenk techniques. Argon was used as inert gas. For heating oil baths or aluminium blocks on hotplates were used. All used stir bars were purified overnight in a solution of aqua regia. Thin layer chromatography was performed using ALUGRAM Xtra SIL G/UV_{254} from MACHEREY-NAGEL. For column chromatography silica gel 60 (0.063 – 0.2 mm or 0.04 – 0.063 mm) from MACHEREY-NAGEL under ambient pressure was used. Documented solvent mixtures for column chromatography are given as volume ratios (*V*/*V*).

Melting points were recorded on a Büchi B-540 melting point apparatus applying a heating rate of 5.0 °C/ min. Nuclear magnetic resonance (NMR) spectra were recorded in deuterated solvents ($CDCl_3$, $(CD_3)_2SO$) at room temperature using a Bruker Avance Neo 400 (400 MHz), Agilent VNMRS 400 (400 MHz), Bruker Avance Neo 600 (600 MHz) or an Agilent VNMRS 600 (600 MHz) spectrometer. The measured spectra were analysed using the software MestReNova (version: 14.3.0-30573) and documented in the following order: chemical shifts (δ) are given in parts per million, multiplicities are stated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), ddd (doublet of doublets of doublets) and coupling constants (J) are given in Hz. Chemical shifts are referenced to the residual signal of the undeuterated solvent. The measurement of infrared (IR) spectra was carried out on a PerkinElmer 100 FT/IR spectrometer. The documented IR bands are given as wavenumbers ν in cm^{-1}. For the measurement of high-resolution mass spectra (HRMS) a Thermo Scientific LTQ Orbitrap XL spectrometer applying electrospray ionization (ESI) or a Thermo Scientific Orbitrap Exploris GC 240 applying electron ionisation (EI) was used. An Elementar Vario EL was used for elemental analysis.

2. Experimental procedures

2.1 Experimental procedure for the synthesis of 2-azido sulfides (EP1)[S1,S2]

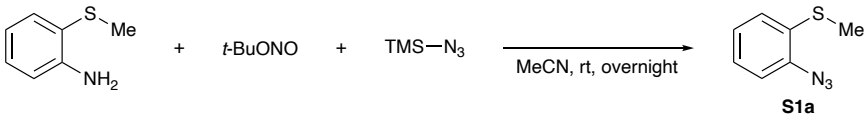


S1

2-Azido sulfides were synthesised according to previously published reports.[S1,S2] A solution of the corresponding thioaniline (4.0 mmol, 1.0 equiv.) in dry and degassed MeCN (8.0 mL) was cooled to 0 °C in an ice bath. To this solution *tert*-butyl nitrite (90% purity, 6.0 mmol, 0.79 mL, 1.5 equiv.) and trimethylsilyl azide (95% purity, 6.0 mmol, 0.83 mL, 1.5 equiv.) were added sequentially and dropwise, and the resulting mixture was stirred at 0 °C for 15 min. After stirring at room temperature for additionally 1 h, SiO_2 was added the volatiles were removed under reduced pressure. The product was obtained after purification by column chromatography on silica using pure *n*-pentane or *n*-pentane: EtOAc (99:1).

Safety note*: Although no hazardous reactions or explosions of 2-azido sulfides were observed during our studies, all azides should be treated with special care. In particular, gram-scale reactions should run behind a blast shield. Due to the extensive formation of nitrogen gas, the addition of trimethylsilyl azide must be done dropwise.*

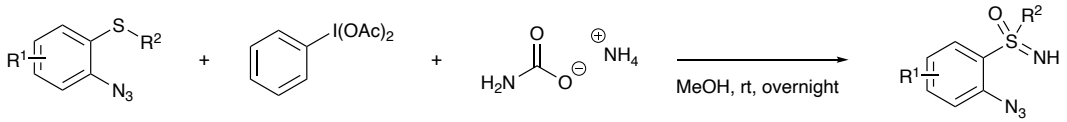
2.2 Experimental procedure for the gram-scale synthesis of 2-azido sulfide S1a (EP2)[S1,S2]



S1a

2-Azido sulfide **S1a** was synthesised according to the modified experimental procedure **EP1** based on previously published reports.[S1,S2] A solution of 2-(methylthio)aniline (32.0 mmol, 4593 mg, 1.0 equiv.) in dry and degassed MeCN (64.0 mL) was cooled to 0 °C in an ice bath. To this solution *tert*-butyl nitrite (90% purity, 48.0 mmol, 6.34 mL, 1.5 equiv.) and trimethylsilyl azide (95% purity, 48.0 mmol, 6.65 mL, 1.5 equiv.) were added sequentially and dropwise. The resulting solution was stirred overnight while slowly warming up to room temperature. SiO_2 was added, and the volatiles were removed under reduced pressure. The product was obtained after purification by column chromatography on silica (column diameter: ca. 4.5 cm, column length: ca. 30 cm) using pure *n*-pentane as a yellowish solid (4574 mg, 27.7 mmol, 87%).

2.3 Experimental procedure for the synthesis of 2-azido sulfoximines (EP3)[S2]



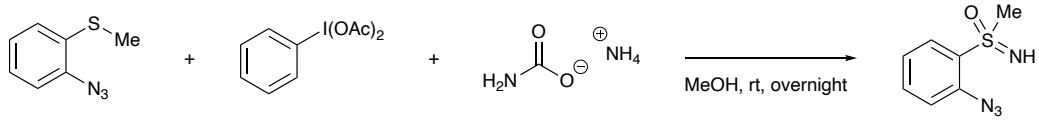
S1 **1**

2-Azido sulfoximines were synthesised according to our previous report.[S2] The corresponding azido sulfide (30.0 mmol, 1.0 equiv.), ammonium carbamate (60.0 mmol, 4684 mg, 2.0 equiv.), and bis(acetoxy)iodobenzene (97% purity, 75.0 mmol, 24905 mg, 2.5 equiv.) were charged in a round-bottom flask. MeOH (60.0 mL) was added, and the flask was closed tight immediately with a rubber septum and balloon. After stirring overnight at room temperature, SiO_2 was added. The volatiles were removed under reduced pressure and the product was purified twice by column chromatography on silica using *n*-pentane: EtOAc as gradient solution (1:0 → 1:1 → 0:1).

Safety note*: Although no hazardous reactions or explosions of 2-azido sulfoximines were observed during our studies, all azides should be treated with special care. In particular, gram-scale reactions should run behind a blast shield.*

Note*: Due to the complex reaction mixture (liquid/ solid/ gas) the reproducibility and yield (ca. ± 15%) is strongly affected by the used stir bar and stirring frequency (preferably low) especially on large scale. In order to guarantee reproducibility of the results at low catalyst loadings (0.25 mol% – 0.5 mol%), it is necessary to purify the corresponding 2-azido sulfoximine twice by column chromatography [even if the product is pure according to NMR and EA (below ± 0.3% deviation)].*

2.4 Experimental procedure for the gram-scale synthesis of 2-azido sulfoximine 1a (EP4)[S2]

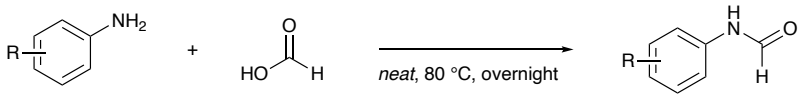


S1a **1a**

2-Azido sulfoximine **1a** was synthesised according to experimental procedure **EP3** based on our previous report.[S2] (2-Azidophenyl)(methyl)sulfane (**S1a**, 30 mmol, 4957 mg, 1.0 equiv.), ammonium carbamate (60.0 mmol, 4684 mg, 2.0 equiv.), and bis(acetoxy)iodobenzene (97% purity, 75 mmol, 24905 mg, 2.5 equiv.) were charged in a round bottom flask. MeOH (60.0 mL) was added, and the reaction flask was immediately tightly closed with a rubber septum and a balloon. After stirring overnight at room temperature, DCM and SiO_2 were added. The volatiles were removed under reduced pressure, and the product was purified twice by column chromatography on silica (column diameter: ca. 4.5 cm, column length: ca. 40 cm) using *n*-pentane: EtOAc as gradient solution (first column: 1:0 → 1:1 → 0:1, second column: 1:1 → 0:1). Compound **1a** was obtained as a yellowish solid (4512 mg, 23.0 mmol, 77%).

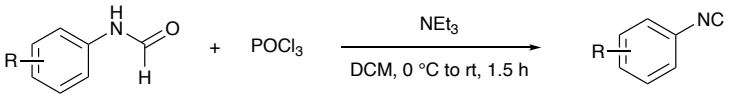
Note: *Due to the complex reaction mixture (liquid/ solid/ gas) the reproducibility and yield (± 15%) is strongly affected by the used stir bar and stirring frequency especially on large scale*

2.5 Experimental procedure for the synthesis of formamides (EP5)[S3]



Aromatic formamides were synthesised according to a modified literature procedure.[S3] In a screw cap reaction tube the corresponding aniline (16.0 mmol, 1.0 equiv.) was suspended in formic acid (19.2 mmol, 0.74 mL, 1.2 equiv.). The reaction tube was closed, and the corresponding suspension was stirred overnight at 80 °C in an aluminium block. After cooling to room temperature, the mixture was diluted with EtOAc (ca. 150 mL) and was washed sequentially with water (3 x 40 mL) and brine (3 x 40 mL). The organic phase was dried over $MgSO_4$, SiO_2 was added, and the volatiles were removed under reduced pressure. The desired formamide was obtained after column chromatography on silica using *n*-pentane: EtOAc (10:1).

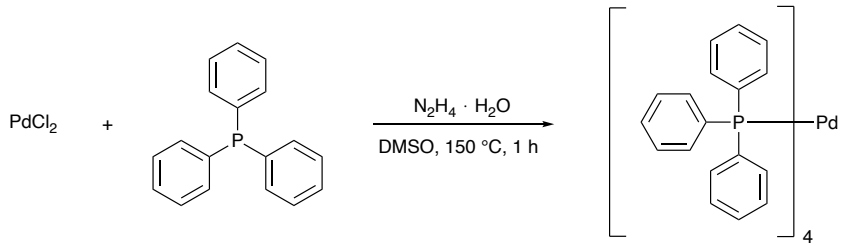
2.6 Experimental procedure for the synthesis of isonitriles (EP6)[S4]



Isonitriles were synthesised according to a modified literature procedure.[S4] The corresponding formamide (10 mmol, 1.0 equiv.) was dissolved in dry and degassed DCM (10.0 mL) and cooled to 0 °C in an ice bath. To this solution were dropwise added NEt_3 (34 mmol, 4.73 mL, 3.4 equiv.) and $POCl_3$ (11 mmol, 1.03 mL, 1.1 equiv.), and the resulting reaction mixture was stirred for 30 min at 0 °C and additionally 1 h at room temperature. The reaction was quenched by the addition of sat. aq. Na_2CO_3 solution. The aqueous phase was extracted with DCM (3 x 50 mL) and the combined organic layers were dried over $MgSO_4$. SiO_2 was added and the volatiles were removed under reduced pressure. Purification by column chromatography on silica using *n*-pentane: EtOAc as gradient solution (10:1 → 5:1) afforded the desired isonitriles.

Note*: Because of the highly exothermic reaction, the addition of $POCl_3$ should be done very carefully.* ***All aryl-substituted isocyanides should be stored in the freezer and used within days after synthesis.*** *Due to their penetrating odour, it is recommended to handle the isonitriles with special care inside a fume hood.*

2.7 Experimental procedure for the synthesis of tetrakis-(triphenylphosphine)-palladium (EP7)[S5]

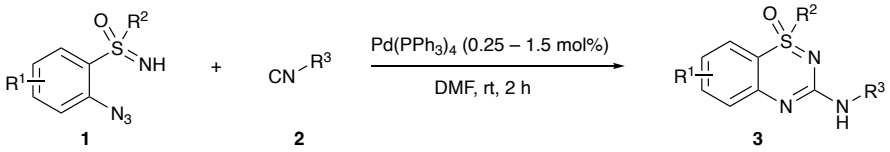


Tetrakis-(triphenylphosphine)-palladium was synthesised under strict inert conditions in oven dried (160 °C) glassware according to a modified literature procedure.[S5] Under argon atmosphere, $PdCl_2$ (4.23 mmol, 750 mg, 1.0 equiv.) and PPh_3 (21.2 mmol, 5547 mg, 5.0 equiv.) were suspended in dry and degassed DMSO (60 mL, degassed by bubbling argon through the solution). The resulting suspension was stirred at 150 °C in an oil bath until a clear solution was obtained (approx. 20 min). After additionally stirring for 30 min at 150 °C, hydrazine monohydrate (16.9 mmol, 0.84 mL, 4.0 equiv.) was added fast and dropwise to the hot solution and the mixture was vigorously stirred at 150 °C for 10 min. The reaction mixture was slowly cooled to room temperature, and the precipitate was collected by filtration under Schlenk conditions. The precipitate was washed thoroughly with degassed EtOH and Et_2O (degassed by bubbling argon through the solution). After drying in vacuum tetrakis-(triphenylphosphine)-palladium was obtained as a bright yellow solid (4620 mg, 4.0 mmol, 95%). The purity of the catalyst was checked by elemental analysis.

EA calcd for $C_{72}H_{60}P_4Pd$: C, 74.84; H, 5.23; found C, 74.93; H, 5.31.

***Note**: Tetrakis-(triphenylphosphine)-palladium was stored at –25 °C in an argon filled glove box. A small amount was transferred for use each time before the reaction set-up.*

2.8 Experimental procedure for the synthesis of 3-amino benzothiadiazine oxides (EP8)

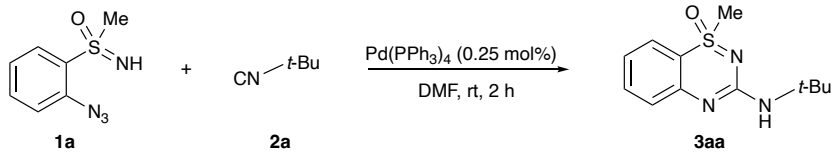


An oven dried Schlenk-tube was charged with tetrakis-(triphenylphosphine)-palladium (0.001–0.006 mmol, 1.2– 6.9 mg, 0.25–1.5 mol%) and the corresponding 2-azido sulfoximine (0.4 mmol, 1.0 equiv.) under air atmosphere. Next, the tube was evacuated and backfilled with argon three times. Dry and degassed DMF (2.0 mL) and the corresponding isonitrile (0.44 mmol, 1.1 equiv.) were added, and the resulting reaction mixture was stirred under argon atmosphere at room temperature for 2 h. The solution was diluted with EtOAc (ca. 40 mL), transferred in a separation funnel, and washed with brine (3 x ca. 25 mL). The organic layer was dried over $MgSO_4$, SiO_2 was added, and the volatiles were removed under reduced pressure. Purification by column chromatography on silica (column diameter:

ca. 2 cm, column length: ca. 30 cm) using *n*-pentane: EtOAc: NEt_3 as gradient solution (20:10:1 → 10:10:1) followed by filtration over active charcoal (glass pipet filled with ca. 0.5 cm celite, ca. 1.5 cm active charcoal, and ca. 0.5 cm sand) afforded the desired product.

Note**: Trace amounts of solvents can be removed by coevaporation with Et_2O and further freeze-drying overnight on Schlenk line. Filtration over active charcoal is necessary to remove trace amounts of unknown impurities.* ***The quality of the used azido sulfoximine is essential for the reproducibility of the reaction on very low catalyst loadings (0.25 mol% or 0.5 mol%). *Therefore, the used azido sulfoximine must be purified twice by column chromatography. Otherwise, higher amounts of catalyst (1.0 mol%) should be considered. Additionally, in case of aryl-substituted isonitriles the yield is strongly affected by their quality. Therefore, these isonitriles must be used within the next days after synthesis.*

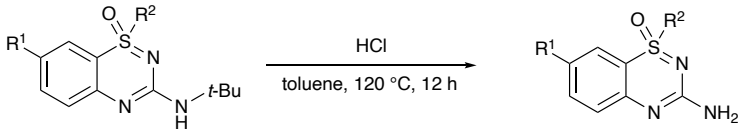
2.9 Experimental procedure for the gram-scale synthesis of benzothiadiazine oxide 3aa (EP9)



An oven dried Schlenk-flask was charged with tetrakis-(triphenylphosphine)-palladium (0.025 mmol, 14.4 mg, 0.25 mol%) and (2-azidophenyl)(imino)(methyl)-λ^6-sulfanone (**1a**, 981 mg, 5.0 mmol, 1.0 equiv.) under air atmosphere. Next, the flask was thoroughly evacuated and backfilled with argon four times. Dry and degassed DMF (25.0 mL) and 2-isocyano-2-methylpropane (**2a**, 98% purity, 626 µL, 0.55 mmol, 1.1 equiv.) were added, and the resulting reaction mixture was stirred under argon atmosphere at room temperature for 2 h. The solution was diluted with EtOAc (ca. 150 mL), transferred in a separation funnel, and washed with brine (3x ca. 75 mL). The combined aqueous phases were collected and extracted once with EtOAc (20 mL). The combined organic layers were dried over $MgSO_4$, SiO_2 was added, and the volatiles were removed under reduced pressure. Purification by column chromatography on silica (column diameter: ca. 3 cm, column length: ca. 30 cm) using *n*-pentane: EtOAc: NEt_3 as gradient solution (20:10:1 → 10:10:1) afforded the desired product as a colourless solid (**3aa**, 1201 mg, 4.78 mmol, 95%).

Note**: Further purification by filtration over active charcoal was not necessary.* ***The quality of the used azido sulfoximine is essential for reproducibility of the reaction. *Therefore, the used azido sulfoximine must be purified twice by column chromatography. Otherwise, higher amounts of catalyst should be considered.*

2.10 Experimental procedure for the deprotection of 3-(*tert*-butylamino)-substituted benzothiadiazine oxides (EP10)

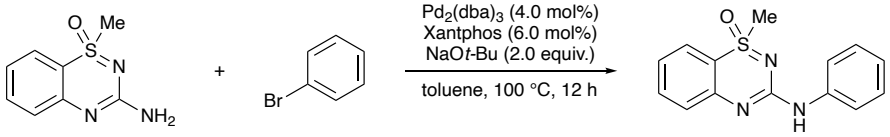


3aa: R^1 = H, R^2 = Me
3ca: R^1 = Cl, R^2 = Ph

4a: R^1 = H, R^2 = Me 86%
4c: R^1 = Cl, R^2 = Ph 69%

Compounds **4a** and **4c** were synthesised according to a modified literature procedure.[S6] In a screw cap reaction tube the corresponding 3-amino benzothiadiazine oxide (**3aa** or **3ca**, 1.0 mmol, 1.0 equiv.) was suspended in toluene (5.0 mL). Concentrated HCl (5.0 mL) was added, and the biphasic mixture was stirred vigorously at 120 °C for 12 h in a preheated aluminium block. After cooling down to room temperature, the mixture was diluted with EtOAc (ca. 75 mL) and basified with an aqueous solution of NaOH (ca. 3 M) until pH = 12. The aqueous layer was extracted with EtOAc (3x ca. 50 mL) and the combined organic layers were dried over $MgSO_4$. SiO_2 was added and the volatiles were removed under reduced pressure. Purification by column chromatography on silica (column diameter: ca. 3 cm, column length: ca. 30 cm) using EtOAc: MeOH (5:1) afforded the desired product.

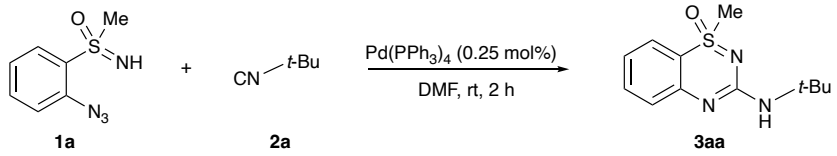
2.11 Experimental procedure for the Buchwald-Hartwig coupling of compound 4a (EP11)



4a + **5** → **3ah**: 58%

Compound **3ah** was synthesised according to a modified literature procedure.[S7] An oven dried Schlenk-tube was charged with tris(dibenzylideneacetone)dipalladium(0) (0.04 mmol, 18.3 mg, 4.0 mol%), Xantphos (0.03 mmol, 17.4 mg, 6 mol%), 3-amino-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (**4a**, 1.0 mmol, 195 mg, 2.0 equiv.), and NaO*t*-Bu (1.0 mmol, 96 mg, 2.0 equiv.) under air atmosphere. Next, the tube was evacuated and backfilled with argon three times. Dry and degassed toluene (1.0 mL) and bromobenzene (53 µL, 0.5 mmol, 1.0 equiv.) were added and the resulting suspension was stirred for 12 h in a preheated aluminium block at 100 °C. After cooling to room temperature, the reaction mixture was diluted with EtOAc (10 mL), filtered through a pad of Celite® and washed with EtOAc (ca. 30 mL). H_2O (ca. 30 mL) was added, and the aqueous layer was extracted with EtOAc (2 x ca. 20 mL). The combined organic layers were washed with brine (ca. 25 mL), and dried over $MgSO_4$. SiO_2 was added and the volatiles were removed under reduced pressure. Purification by column chromatography on silica (column diameter: ca. 3 cm, column length: ca. 30 cm) using *n*-pentane: EtOAc: NEt_3 as gradient solution (20:10:1 → 10:10:1) afforded the desired product as a colourless solid (**3ah**, 79 mg, 0.29 mmol, 58%).

3. Optimisation of reaction conditions and control experiments



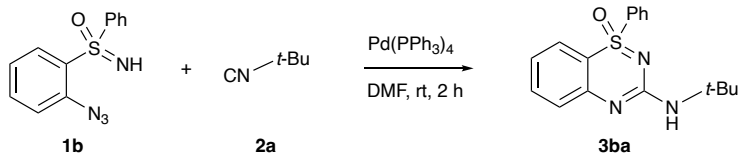
An oven dried Schlenk-tube was charged with the respective metal precatalyst and (2-azidophenyl)(imino)(methyl)-λ^6-sulfanone (**1a**, 78.5 mg, 0.4 mmol, 1.0 equiv.) under air atmosphere. Next, the tube was evacuated and filled with argon three times. Dry and degassed DMF (2.0 mL) and 2-isocyano-2-methylpropane (**2a**, 51 µL, 0.44 mmol, 1.1 equiv.) were added, and the resulting reaction mixture was stirred under argon atmosphere at room temperature for the indicated time. The solution was diluted with EtOAc (ca. 40 mL), transferred in a separation funnel, and washed with brine (3 x ca. 25 mL). The organic layer was dried over $MgSO_4$, SiO_2 was added, and the volatiles were removed under reduced pressure. Purification by column chromatography on silica (column diameter: ca. 2 cm, column length: ca. 30 cm) using *n*-pentane: EtOAc: NEt_3 as gradient solution (20:10:1 → 10:10:1) afforded the desired product.

Note: *In case of THF, DCM, MeCN and toluene as the solvent, no extraction was necessary.*

Table S1. Optimisation of the reaction conditions.[a]

entry	catalyst (mol%)	solvent	time (h)	yield (%)	entry[a]	catalyst (mol%)	solvent	time (h)	yield (%)
1	$Co(acac)_3$ (5.0)	DMF	12	0	11	$Pd(PPh_3)_4$ (0.25)	THF	12	15
2	$Cu(OAc)_2$ (5.0)	DMF	12	0	12	$Pd(PPh_3)_4$ (0.25)	DCM	12	96
3	$[Cp^*RhCl_2]_2$ (5.0)	DMF	12	75	13	$Pd(PPh_3)_4$ (0.25)	MeCN	12	97
4	$Pd(OAc)_2$ (5.0)	DMF	12	19	14	$Pd(PPh_3)_4$ (0.25)	toluene	12	66
5	$Pd(PPh_3)_4$ (5.0)	DMF	12	99	15	$Pd(PPh_3)_4$ (0.25)	DMF	2	98/97/98
6	$Pd(PPh_3)_4$ (2.5)	DMF	12	99	16[c]	$Pd(PPh_3)_4$ (0.25)	DMF	2	90
7	$Pd(PPh_3)_4$ (1.0)	DMF	12	99/99	17	–	DMF	2	0
8	$Pd(PPh_3)_4$ (0.5)	DMF	12	98	18	–	DMF	24	0
9	$Pd(PPh_3)_4$ (0.25)	DMF	12	98/99/98	19	PPh_3 (5.0)	DMF	24	0
10[b]	$Pd(PPh_3)_4$ (0.1)	DMF	12	*trace*					

[a]*Reaction conditions*: catalyst, **1a** (0.4 mmol), **2a** (0.44 mmol), solvent (2.0 mL) under inert conditions at rt for the indicated time. Yields after extraction and column chromatography. Multiple yields refer to reproduction experiments. [b]Up-scaled to 1.0 mmol of **1a**. [c]No inert atmosphere.



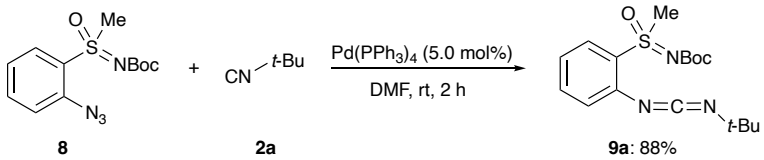
An oven dried Schlenk-tube was charged with $Pd(PPh_3)_4$ and (2-azidophenyl)(imino)(phenyl)-λ^6-sulfanone (**1b**, 103.3 mg, 0.4 mmol, 1.0 equiv.) under air atmosphere. Next, the tube was evacuated and filled with argon three times. Dry and degassed DMF (2.0 mL) and 2-isocyano-2-methylpropane (**2a**, 51 µL, 0.44 mmol, 1.1 equiv.) were added and the resulting reaction mixture was stirred under argon atmosphere at room temperature for 2 h. The solution was diluted with EtOAc (ca. 40 mL), transferred in a separation funnel, and washed with brine (3 x ca. 25 mL). The organic layer was dried over $MgSO_4$, SiO_2 was added, and the volatiles were removed under reduced pressure. Purification by column chromatography on silica (column diameter: ca. 2 cm, column length: ca. 30 cm) using *n*-pentane: EtOAc: NEt_3 as gradient solution (20:10:1 → 10:10:1) afforded the desired product.

Table S2. Optimisation of the reaction conditions for substituted azido sulfoximines.[a]

entry	catalyst (mol%)	solvent	time (h)	yield (%)
1	$Pd(PPh_3)_4$ (0.25)	DMF	2	16
2	$Pd(PPh_3)_4$ (0.5)	DMF	2	32
3	$Pd(PPh_3)_4$ (1.0)	DMF	2	63
4	$Pd(PPh_3)_4$ (1.5)	DMF	2	82

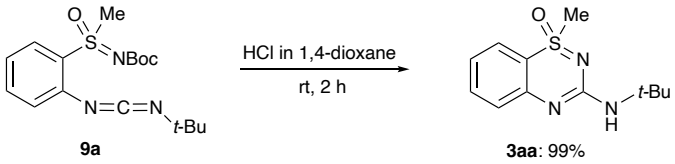
[a]*Reaction conditions*: $Pd(PPh_3)_4$, **1b** (0.4 mmol), **2a** (0.44mmol), DMF (2.0 mL) under inert conditions at rt for 2 h. Yields after extraction and column chromatography.

4. Mechanistic studies



8 **2a** **9a**: 88%

Compound **9a** was synthesised according to the modified experimental procedure **EP8**. An oven dried Schlenk-tube was charged with tetrakis-(triphenylphosphine)-palladium (0.05 mmol, 23.1 mg, 5.0 mol%) and *tert*-butyl [(2-azidophenyl)(methyl)(oxo)-λ^6-sulfaneylidene]carbamate (**8**, 0.4 mmol, 119 mg, 1.0 equiv.) under air atmosphere. Next, the tube was evacuated and backfilled with argon three times. Dry and degassed DMF (2.0 mL) and 2-isocyano-2-methylpropane (**2a**, 51 µL, 0.44 mmol, 1.1 equiv.) were added, and the resulting reaction mixture was stirred under argon atmosphere at room temperature for 2 h. The solution was diluted with EtOAc (ca. 40 mL), transferred in a separation funnel, and washed with brine (3 x ca. 25 mL). The organic layer was dried over $MgSO_4$, SiO_2 was added, and the volatiles were removed under reduced pressure. Purification by column chromatography on silica (SiO_2 0.04 – 0.063 mm, column diameter: ca. 2 cm, column length: ca. 50 cm) using *n*-pentane: DCM: EtOAc (10:2:1) afforded the desired product **9a** as a yellowish oil (124 mg, 0.35 mmol, 88%).



9a **3aa**: 99%

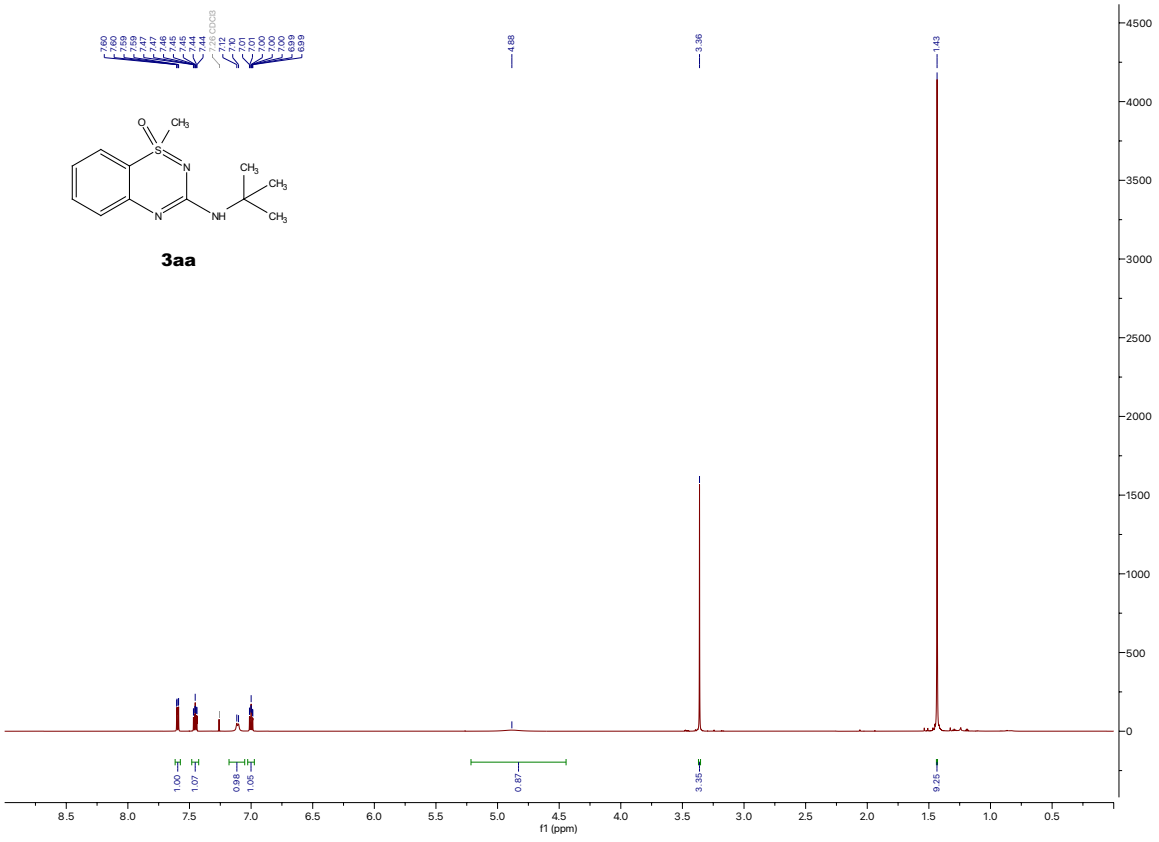
Compound **9a** was charged in a screw cap reaction tube and dissolved in a solution of HCl in dioxane (4 mol/L, 8.0 mmol, 2.0 mL, 20 equiv.). The reaction tube was closed, and the resulting solution was stirred at room temperature for 2 h. After this time the reaction mixture was basified by the addition of aq. conc. $NaHCO_3$ solution until pH = 8, transferred to a separation funnel and extracted with EtOAc (3x ca. 50 mL). The combined organic layers were dried over $MgSO_4$, SiO_2 was added, and the volatiles were removed under reduced pressure. Purification by column chromatography on silica (column diameter: ca. 2 cm, column length: ca. 15 cm) using *n*-pentane: EtOAc: NEt_3 (20:10:1) afforded the desired product **3aa** as a yellowish oil (99 mg, 0.39 mmol, 99%).

***Note**: All mechanistic experiments were performed twice.*

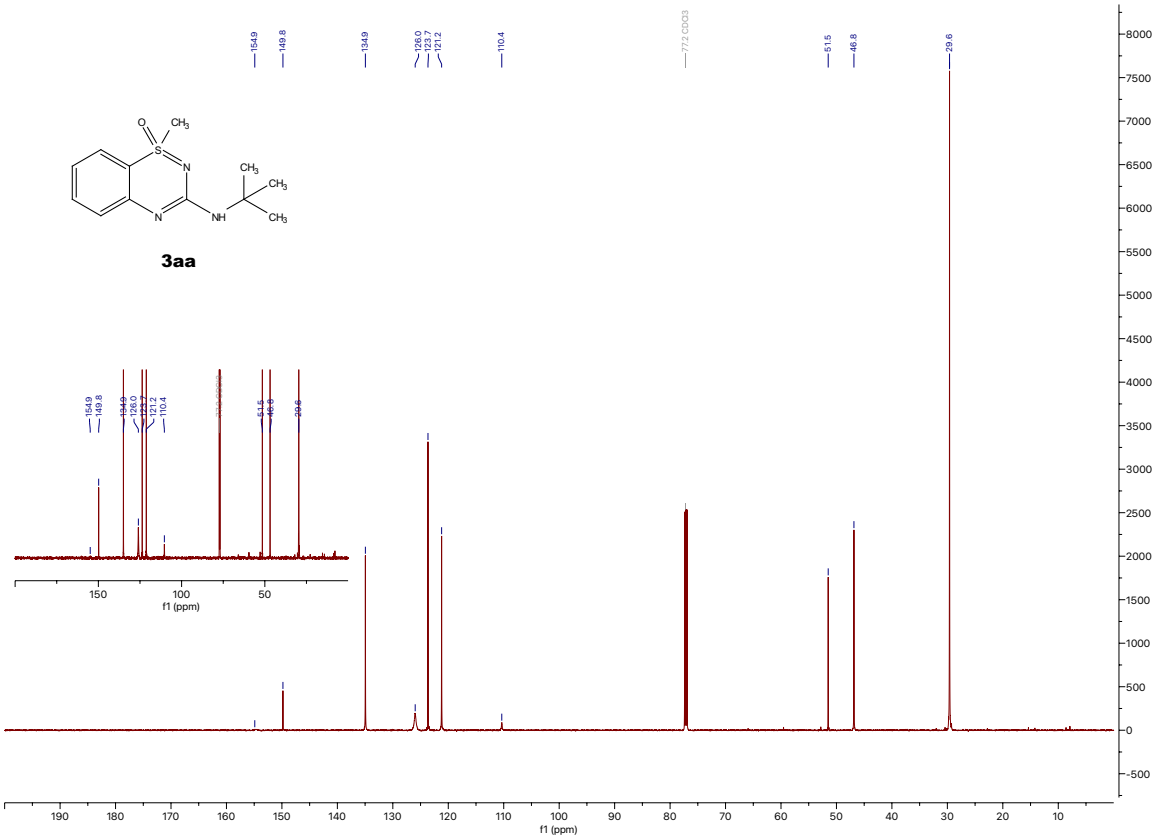
5. NMR studies

Due to the possible quadrupole moment of the nitrogen atoms, several signals in the ^{13}C {^{1}H} NMR spectrum of alkyl-substituted 3-amino benzothiadiazine oxides (**3aa**, **3ab**, **3ac**, **3ad**, **3af**, **3ba**, **3ca**, **3da** and **3ea**) are broad with low intensity. Therefore, the measurement of a highly concentrated sample (ca. 30–40 mg) with extended measurement time was necessary to observe all relevant signals. The signals affected are marked in bold. Alternatively, the samples could be measured in a mixture of $CDCl_3$ (ca. 0.7 mL) and conc. HCl (ca. two drops), which significantly improved the quality of the measured ^{13}C {^{1}H} NMR spectrum. In the following, the effect will be illustrated for compound **3aa**. The ^{13}C {^{1}H} NMR spectrum of all other acidified compounds can be found in sections 5. and 8.

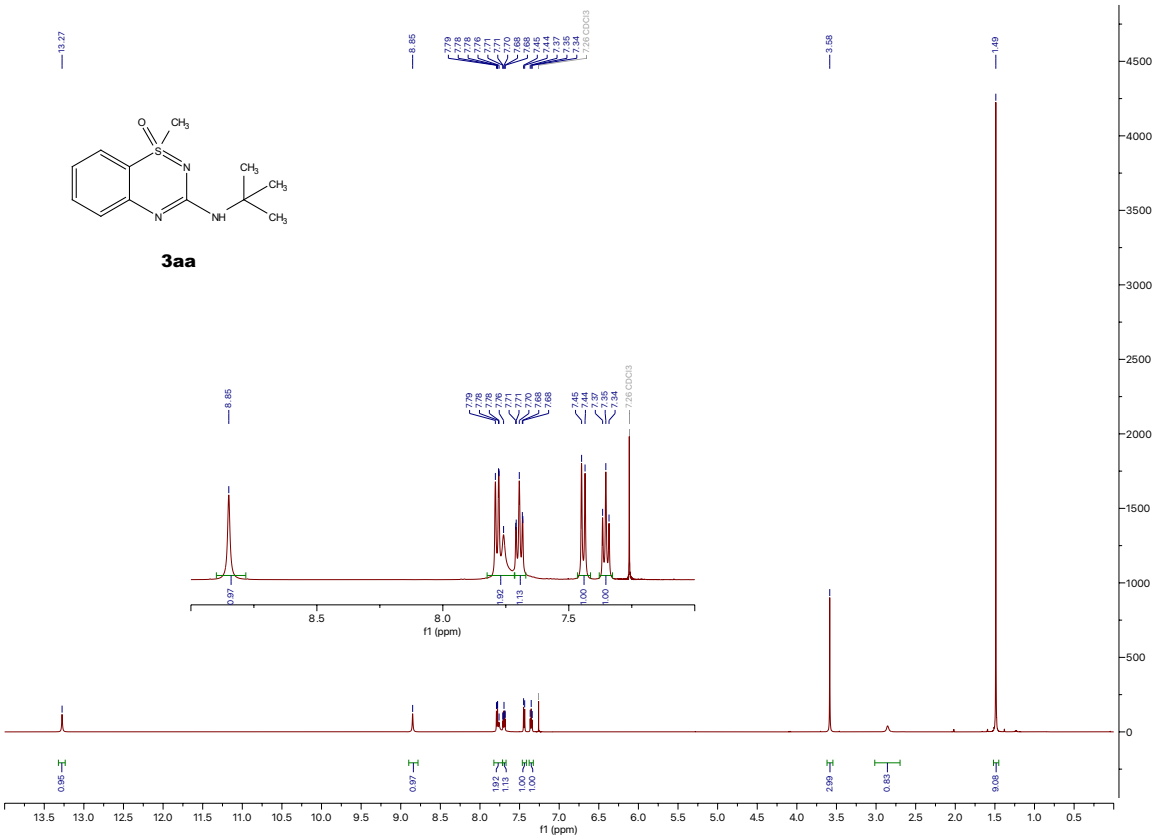
^{1}H NMR spectrum of compound **3aa** (600 MHz, $CDCl_3$)



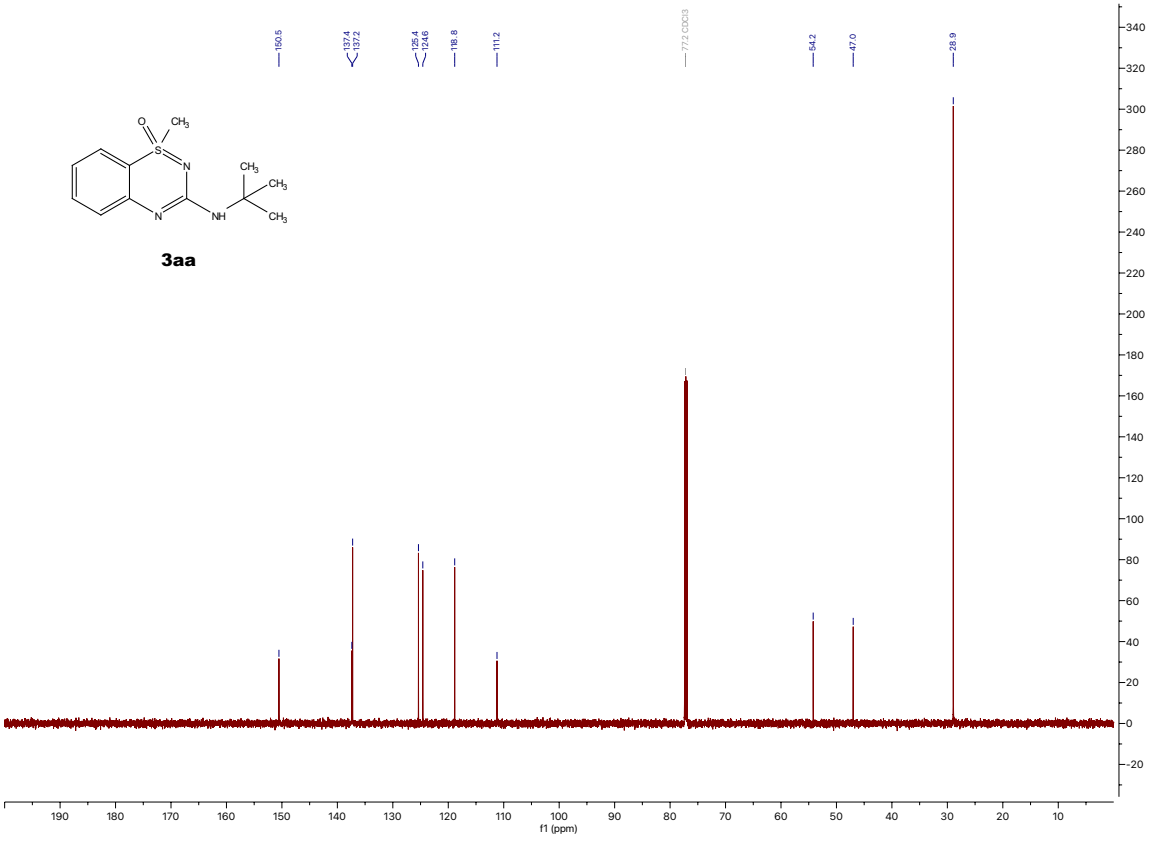
^{13}C {^{1}H} NMR spectrum of compound **3aa** (151 MHz, $CDCl_3$)



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



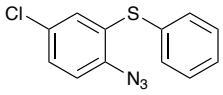
^{13}C {^{1}H} NMR spectrum of compound **3aa** (151 MHz, $CDCl_3$, HCl)



6. Characterisation Data

6.1 Starting materials

(2-Azido-5-chlorophenyl)(phenyl)sulfane (S1c)



Following the general experimental procedure **EP1**, compound **S1c** was obtained after purification by column chromatography (SiO_2, pure *n*-pentane) as a brownish solid (959 mg, 3.66 mmol, 92%).

Mp: 57 – 59 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 – 7.32 (m, 5H), 7.19 (dd, J = 8.5, 2.3 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 6.92 (d, J = 2.3 Hz, 1H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 136.8, 133.3, 132.0, 130.8, 130.6, 130.0, 129.9, 128.7, 127.6, 119.6 ppm.

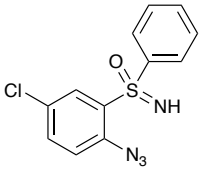
IR (ATR): ν = 3381, 3234, 3075, 2926, 2851, 2665, 2559, 2423, 2327, 2271, 2113, 1892, 1848, 1810, 1767, 1723, 1672, 1572, 1462, 1417, 1380, 1294, 1099, 1062, 1019, 998, 923, 863, 833, 799, 755, 693 cm^{-1}.

MS (100 eV, CI) m/z (%): 262 (21) $[M]^+$.

MS (70 eV, EI) m/z (%): 263 (23), 261 (32) $[M]^+$, 236 (9), 235 (19), 234 (41), 233 (52) $[M – N_2]$, 232 (100) $[M – HN_2]$, 198 (48), 171 (17), 156 (15), 154 (11), 129 (12), 109 (26), 95 (12), 77 (33), 51 (55).

EA calcd for $C_{12}H_8ClN_3S$: C, 55.07; H, 3.08; N, 16.06; found C, 55.33; H, 2.94; N, 16.62.

(2-Azido-5-chlorophenyl)(imino)(phenyl)-λ^6-sulfanone (1c)



2-Azido sulfoximine **1c** was synthesised according to the modified experimental procedure **EP3** based on our previous report.[S2] (2-Azido-5-chlorophenyl)(phenyl)sulfane (**S1c**, 5 mmol, 1309 mg, 1.0 equiv.), ammonium carbamate (10.0 mmol, 781 mg, 2.0 equiv.), and bis(acetoxy)iodobenzene (12.5 mmol, 4151 mg, 2.5 equiv.) were charged in a round bottom flask. MeOH (10.0 mL) was added, and the reaction flask was closed tight immediately with a rubber septum and balloon. After stirring overnight at room temperature, DCM and SiO_2 were added. The volatiles were removed under reduced pressure and the product was purified by column chromatography on silica using *n*-pentane: EtOAc as gradient solution (1:0 → 1:1 → 0:1). Compound **1c** was obtained as a yellowish solid (1259 mg, 4.3 mmol, 86%).

Mp: 143 – 147 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20 (d, J = 2.4 Hz, 1H), 8.11 – 8.02 (m, 2H), 7.62 – 7.57 (m, 1H), 7.54 – 7.50 (m, 2H), 7.49 (dd, J = 8.5, 2.5 Hz, 1H), 7.11 (d, J = 8.5 Hz, 1H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 141.2, 137.1, 135.0, 134.0, 133.3, 130.4, 130.1, 129.0 (2C), 121.4 ppm.

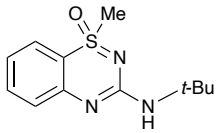
IR (ATR): ν = 3886, 3358, 3335, 3302, 3061, 2925, 2656, 2428, 2342, 2114, 1911, 1801, 1650, 1562, 1459, 1385, 1304, 1230, 1156, 1104, 1073, 930, 825, 761, 713, 686, 664 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{12}H_9ClN_4NaOS^+$ 315.0078; found 315.0068.

EA calcd for $C_{12}H_9ClN_4OS$: C, 49.24; H, 3.10; N, 19.14; found C, 48.99; H, 2.96; N, 18.89.

6.2 Benzothiadiazines

3-(*tert*-Butylamino)-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3aa)



Following the general experimental procedure **EP8** using 0.25 mol% of $Pd(PPh_3)_4$, compound **3aa** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a colourless solid (98 mg, 0.39 mmol, 98%).

Mp: 92 – 94 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60 (dd, J = 8.0, 1.6 Hz, 1H), 7.45 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H), 7.11 (d, J = 8.5 Hz, 1H), 7.00 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 4.88 (br s, 1H), 3.36 (s, 3H), 1.43 (s, 9H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = **154.9**, 149.8, 134.9, **126.0**, 123.7, 121.2, **110.4**, 51.5, 46.8, 29.6 ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$, HCl): δ = 150.5, 137.4, 137.2, 125.4, 124.6, 118.8, 111.2, 54.2, 47.0, 28.9 ppm.

^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ = 7.90 (dd, J = 8.1, 1.6 Hz, 1H), 7.48 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H), 7.10 – 6.81 (m, 2H), 6.37 (s, 1H), 3.62 (s, 3H), 1.38 (s, 9H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $(CD_3)_2SO$): δ = **153.3**, **148.6**, 134.2, **125.4**, 124.0, 120.5, **111.8**, 50.5, 44.8, 29.3 ppm.

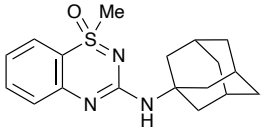
IR (ATR): ν = 3376, 2966, 2924, 2163, 1964, 1513, 1455, 1393, 1362, 1300, 1207, 1132, 1109, 1065, 1025, 967, 914, 844, 783, 756, 727, 668 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{18}N_3OS^+$ 252.1165; found 252.1164.

***Note**: Due to the possible quadrupole moment of the nitrogen atoms, several signals in the ^{13}C {^1H} NMR spectrum appear broad with low intensity. Therefore, the measurement of a highly*

concentrated sample (ca. 30–40 mg) with extended measurement time was necessary to observe all relevant signals. The signals affected are marked in bold. Alternatively, the sample could be measured in a mixture of $CDCl_3$ (ca. 0.7 mL) and conc. HCl (ca. two drops).

3-{[(3*s*,5*s*,7*s*)-Adamantan-1-yl]amino}-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3ab)



Following the general experimental procedure **EP8** using 0.25 mol% of $Pd(PPh_3)_4$, compound **3ab** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a yellowish solid (129 mg, 0.39 mmol, 98%).

Mp: 101 – 160 °C (*complex melting behaviour*)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 7.00 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 3.37 (s, 3H), 2.22 – 2.03 (m, 9H), 1.88 – 1.61 (m, 6H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = **154.6**, 149.4, 135.0, **125.5**, 123.7, 121.2, **110.3**, 52.1, 46.9, 42.3, 36.6, 29.7 ppm.

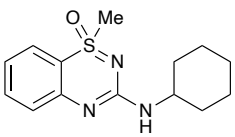
^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$, HCl): δ = 150.1, 137.4, 137.2, 125.3, 124.6, 118.8, 111.2, 55.0, 47.0, 41.3, 36.1, 29.5 ppm.

IR (ATR): ν = 3368, 2905, 2851, 2293, 2199, 2158, 1996, 1911, 1666, 1509, 1459, 1399, 1358, 1300, 1223, 1146, 1075, 966, 934, 845, 817, 757, 717, 667 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{24}N_3OS^+$ 330.1635; found 330.1624.

***Note**: Due to the possible quadrupole moment of the nitrogen atoms, several signals in the ^{13}C {^1H} NMR spectrum appear broad with low intensity. Therefore, the measurement of a highly concentrated sample (ca. 30–40 mg) with extended measurement time was necessary to observe all relevant signals. The signals affected are marked in bold. Alternatively, the sample could be measured in a mixture of $CDCl_3$ (ca. 0.7 mL) and conc. HCl (ca. two drops).*

3-(Cyclohexylamino)-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3ac)



Following the general experimental procedure **EP8** using 0.25 mol% of $Pd(PPh_3)_4$, compound **3ac** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a colourless solid (108 mg, 0.39 mmol, 98%).

Mp: 118 – 120 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60 (dd, J = 7.9, 1.5 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.12 (br m, 1H), 7.00 (t, J = 7.5 Hz, 1H), 4.88 (br s, 1H), 3.83 (br s, 1H), 3.37 (s, 3H), 2.16 – 1.90 (m, 2H), 1.83 – 1.65 (m, 2H), 1.66 – 1.53 (m, 1H), 1.42 – 1.32 (m, 2H), 1.23 – 1.09 (m, 3H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = **155.0**, 150.1, 135.1, **125.9**, 123.8, 121.2, **110.7**, 49.7, 47.0, 33.62, 33.55, 29.8, 25.8, 25.0 ppm.

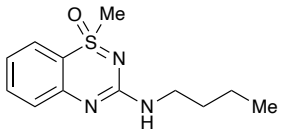
^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$, HCl): δ = 150.3, 137.4, 137.3, 125.4, 124.7, 118.9, 111.4, 51.1, 47.0, 32.24, 32.20, 25.3, 24.43, 24.36 ppm.

IR (ATR): ν = 3369, 3034, 2929, 2853, 2305, 2171, 2013, 1807, 1648, 1598, 1501, 1452, 1369, 1326, 1287, 1243, 1199, 1148, 1064, 972, 932, 891, 841, 786, 762, 715 cm^{-1}.

HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{14}H_{19}N_3OS^+$ 277.1243; found 277.1243.

***Note**: Due to the possible quadrupole moment of the nitrogen atoms, several signals in the ^{13}C {^1H} NMR spectrum appear broad with low intensity. Therefore, the measurement of a highly concentrated sample (ca. 30–40 mg) with extended measurement time was necessary to observe all relevant signals. The signals affected are marked in bold. Alternatively, the sample could be measured in a mixture of $CDCl_3$ (ca. 0.7 mL) and conc. HCl (ca. two drops).*

3-(Butylamino)-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3ad)



Following the general experimental procedure **EP8** using 0.5 mol% of $Pd(PPh_3)_4$, compound **3ad** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a colourless solid (93 mg, 0.37 mmol, 93%).

Mp: 93 – 95 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60 (dd, J = 8.0, 1.6 Hz, 1H), 7.46 (ddd, J = 8.6, 7.1, 1.6 Hz, 1H), 7.13 (br m, 1H), 7.10 – 6.97 (m, 1H), 3.40 – 3.37 (m, 2H), 3.36 (s, 3H), 1.61 – 1.46 (m, 2H), 1.42 – 1.31 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = **155.5**, 149.9, 135.1, **125.8**, 123.8, 121.3, **110.7**, 46.9, 41.1, 32.0, 20.1, 13.9 ppm.

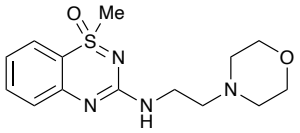
^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$, HCl): δ = 151.3, 137.3, 137.2, 125.5, 124.7, 118.9, 111.5, 47.1, 41.6, 31.0, 20.0, 13.7 ppm.

IR (ATR): ν = 3390, 3057, 3026, 2925, 2860, 2300, 2161, 2001, 1804, 1668, 1600, 1513, 1457, 1401, 1372, 1293, 1244, 1200, 114, 1065, 969, 923, 842, 755, 667 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{18}N_3OS^+$ 252.1165; found 252.1160.

***Note**: Due to the possible quadrupole moment of the nitrogen atoms, several signals in the ^{13}C {^1H} NMR spectrum appear broad with low intensity. Therefore, the measurement of a highly concentrated sample (ca. 30–40 mg) with extended measurement time was necessary to observe all relevant signals. The signals affected are marked in bold. Alternatively, the sample could be measured in a mixture of $CDCl_3$ (ca. 0.7 mL) and conc. HCl (ca. two drops).*

1-Methyl-3-[(2-morpholinoethyl)amino]-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3ae)



Following the general experimental procedure **EP8** using 0.5 mol% of $Pd(PPh_3)_4$, compound **3ae** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 10:10:1 → 10:5:1) as a yellowish oil (105 mg, 0.34 mmol, 85%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.16 (br m, 1H), 7.04 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 3.70 (t, *J* = 4.7 Hz, 4H), 3.63 – 3.45 (m, 2H), 3.38 (s, 3H), 2.54 (t, *J* = 6.0 Hz, 2H), 2.46 (s, 4H) ppm.

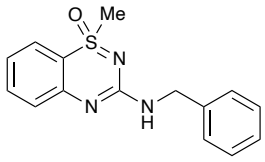
^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = **155.2**, 149.6, 135.2, **125.9**, 123.8, 121.6, **110.6**, 67.1, 57.4, 53.5, 47.0, 37.6 ppm.

IR (ATR): ν = 3281, 2925, 2860, 2241, 2162, 2030, 1625, 1520, 1460, 1235, 1113, 1072, 1010, 912, 855, 759, 726 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{21}N_4O_2S^+$ 309.1380; found 309.1375.

***Note**: Due to the possible quadrupole moment of the nitrogen atoms, several signals in the ^{13}C {^1H} NMR spectrum appear broad with low intensity. Therefore, the measurement of a highly concentrated sample (ca. 30–40 mg) with extended measurement time was necessary to observe all relevant signals. The signals affected are marked in bold. Acidification of the compound led to decomposition.*

3-(Benzylamino)-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3af)



Following the general experimental procedure **EP8** using 0.5 mol% of $Pd(PPh_3)_4$, compound **3af** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a colourless solid (109 mg, 0.38 mmol, 96%).

Mp: 118 – 121 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.63 (dd, J = 8.0, 1.6 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.37 – 7.28 (m, 4H), 7.26 – 7.22 (m, 1H), 7.15 (br m, 1H), 7.04 (t, J = 7.6 Hz, 1H), 4.70 – 4.56 (m, 2H), 3.35 (s, 3H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = **155.6**, 149.7, 139.2, 135.1, 128.6, 127.7, 127.3, **125.8**, 123.8, 121.6, **110.9**, 46.9, 45.4 ppm.

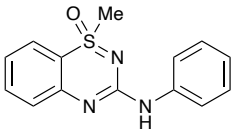
^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$, HCl): δ = 151.6, 137.3, 137.1, 136.0, 128.9, 128.0, 127.7, 125.8, 124.8, 118.9, 111.6, 47.0, 45.3 ppm.

IR (ATR): ν = 3615, 3380, 3236, 3025, 2922, 2856, 2303, 2165, 1964, 138, 1514, 1455, 1404, 1351, 1290, 1219, 1138, 1090, 1069, 1026, 962, 913, 844, 753, 698 cm^{-1}.

HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{15}H_{15}N_3OS^+$ 285.0930; found 285.0931.

***Note**: Due to the possible quadrupole moment of the nitrogen atoms, several signals in the ^{13}C {^1H} NMR spectrum appear broad with low intensity. Therefore, the measurement of a highly concentrated sample (ca. 30–40 mg) with extended measurement time was necessary to observe all relevant signals. The signals affected are marked in bold. Alternatively, the sample could be measured in a mixture of $CDCl_3$ (ca. 0.7 mL) and conc. HCl (ca. two drops).*

1-Methyl-3-(phenylamino)-1λ^4-benzo[e][1,2,4]thiadiazine 1-oxide (3ah)



Following the general experimental procedure **EP8** using 0.5 mol% of $Pd(PPh_3)_4$, compound **3ah** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a colourless solid (103 mg, 0.378 mmol, 94%).

Mp: 152 – 154 °C

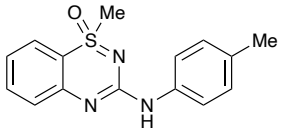
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.69 (dd, J = 8.0, 1.5 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.56 (ddd, J = 8.5, 7.1, 1.5 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.15 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.05 (tt, J = 7.3, 1.1 Hz, 1H), 3.45 (s, 3H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 152.6, 148.9, 139.1, 135.3, 128.9, 126.6, 123.8, 123.1, 122.8, 120.4, 111.5, 47.1 ppm.

IR (ATR): ν = 3343, 3007, 2922, 2323, 2159, 2096, 1801, 1731, 1595, 1553, 1505, 1453, 1400, 1324, 1280, 1213, 1132, 1075, 1026, 965, 899, 853, 833, 752, 691 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{14}N_3OS^+$ 272.0852; found 272.0847.

1-Methyl-3-(*p*-tolylamino)-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3ai)



Following the general experimental procedure **EP8** using 0.5 mol% of $Pd(PPh_3)_4$, compound **3ai** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a yellowish solid (106 mg, 0.37 mmol, 93%).

Mp: 72 – 141 °C (*complex melting behaviour*)

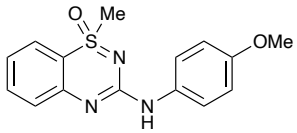
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.54 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.26 (dd, *J* = 8.7, 1.0 Hz, 1H), 7.17 – 7.08 (m, 3H), 3.44 (s, 3H), 2.32 (s, 3H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 152.8, 149.0, 136.4, 135.3, 132.8, 129.4, 126.4, 123.8, 122.5, 120.8, 111.4, 47.0, 20.9 ppm.

IR (ATR): ν = 3348, 3018, 2921, 2859, 2323, 2172, 2106, 1897, 1731, 1659, 1592, 1507, 1456, 1407, 1322, 1293, 1218, 1087, 1022, 966, 818, 784, 756, 665 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{16}N_3OS^+$ 286.1009; found 286.1001.

3-[(4-Methoxyphenyl)amino]-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3aj)



Following the general experimental procedure **EP8** using 0.5 mol% of $Pd(PPh_3)$, compound **3aj** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a yellowish solid (112 mg, 0.37 mmol, 93%).

Mp: 57 – 112 °C (*complex melting behaviour*)

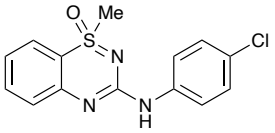
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.14 – 7.08 (m, 1H), 6.92 (br s, 1H), 6.86 (d, *J* = 9.0 Hz, 2H), 3.80 (d, *J* = 1.3 Hz, 3H), 3.43 (d, *J* = 1.3 Hz, 3H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 156.0, 153.1, 149.3, 135.2, 132.1, 126.5, 123.8, 122.7, 122.3, 114.2, 111.4, 55.6, 47.0 ppm.

IR (ATR): ν = 3345, 3003, 2924, 2837, 2319, 2062, 1872, 1595, 1506, 1456, 1411, 1284, 1218, 1176, 1096, 1029, 968, 830, 757, 666 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{16}N_3O_2S^+$ 302.0958; found 302.0950.

3-[(4-Chlorophenyl)amino]-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3ak)



Following the general experimental procedure **EP8** using 0.5 mol% of $Pd(PPh_3)_4$, compound **3ak** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a colourless solid (117 mg, 0.38 mmol, 96%).

Mp: 173 – 176 °C

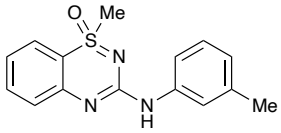
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.32 – 7.22 (m, 3H), 7.20 – 7.13 (m, 1H), 3.46 (s, 3H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 152.4, 148.8, 137.8, 135.4, 128.9, 127.9, 126.7, 123.8, 123.0, 121.5, 111.6, 47.1 ppm.

IR (ATR): ν = 3278, 3057, 3014, 2920, 2854, 2316, 2185, 2107, 2017, 1950, 1878, 1587, 1544, 1521, 1494, 1457, 1401, 1320, 1276, 1225, 1138, 1094, 1011, 958, 919, 850, 820, 785, 746, 700, 673 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{13}ClN_3OS^+$ 306.0462; found 306.0463.

1-Methyl-3-(*m*-tolylamino)-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3al)



Following the general experimental procedure **EP8** using 0.5 mol% of $Pd(PPh_3)_4$, compound **3al** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a colourless solid (106 mg, 0.37 mmol, 93%).

Mp: 121 – 123 °C

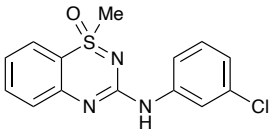
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.55 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.34 (s, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.17 – 7.11 (m, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 3.45 (s, 3H), 2.34 (s, 3H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 152.6, 148.9, 139.0, 138.7, 135.2, 128.8, 126.5, 124.0, 123.8, 122.7, 121.0, 117.7, 111.4, 47.0, 21.7 ppm.

IR (ATR): ν = 3348, 3019, 2922, 2252, 2163, 1928, 1600, 1556, 1511, 1453, 1406, 1309, 1221, 1168, 1131, 1085, 968, 908, 849, 757, 726 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{16}N_3OS^+$ 286.1009; found 286.1001.

3-[(3-Chlorophenyl)amino]-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3am)



Following the general experimental procedure **EP8** using 0.5 mol% of $Pd(PPh_3)_4$, compound **3am** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a yellowish solid (102 mg, 0.33 mmol, 83%).

Mp: 123 – 127 °C

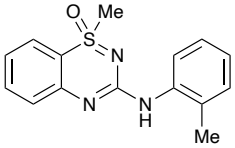
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.81 (s, 1H), 7.70 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.38 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.00 (dd, *J* = 8.0, 1.1 Hz, 1H), 3.47 (s, 3H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 152.2, 148.6, 140.5, 135.4, 134.5, 129.8, 126.8, 123.8, 123.2, 122.8, 120.0, 118.0, 111.6, 47.0 ppm.

IR (ATR): ν = 3343, 3062, 3009, 2924, 2253, 2162, 1930, 1662, 1590, 1553, 1506, 1455, 1404, 1303, 1219, 1166, 1078, 1027, 968, 902, 849, 758, 728, 685 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{13}ClN_3OS^+$ 306.0462; found 306.0455.

1-Methyl-3-(*o*-tolylamino)-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3an)



Following the general experimental procedure **EP8** using 0.5 mol% of $Pd(PPh_3)_4$, compound **3an** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as an off-white solid (108 mg, 0.38 mmol, 95%).

Mp: 183 – 187 °C

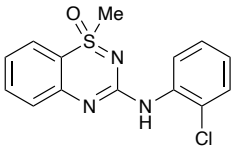
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.0 Hz, 1H), 7.67 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.53 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.19 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.13 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.05 (td, *J* = 7.5, 1.3 Hz, 1H), 6.79 (br s, 1H), 3.43 (s, 3H), 2.32 (s, 3H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 153.3, 149.0, 137.0, 135.2, 130.5, 129.7, 126.6, 126.4, 124.3, 123.7, 123.6, 122.5, 111.4, 46.9, 18.3 ppm.

IR (ATR): ν = 335, 3198, 3019, 2922, 2323, 2162, 2107, 1913, 1731, 1506, 1453, 1398, 1308, 1220, 1113, 1043, 966, 850, 753, 662 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{16}N_3OS^+$ 286.1009; found 286.1003.

3-[(2-Chlorophenyl)amino]-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3ao)



Following the general experimental procedure **EP8** using 0.5 mol% of $Pd(PPh_3)_4$, compound **3ao** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as an off-white solid (109 mg, 0.36 mmol, 89%).

Mp: 138 – 143 °C

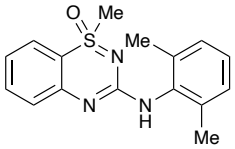
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.60 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.71 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.28 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 7.20 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 7.15 (br s, 1H), 6.97 (td, *J* = 7.7, 1.5 Hz, 1H), 3.48 (s, 3H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 152.1, 148.7, 136.0, 135.3, 129.2, 127.4, 127.0, 123.8, 123.3, 123.1, 122.9, 121.7, 111.8, 47.1 ppm.

IR (ATR): ν = 3410, 3058, 3013, 2924, 2854, 2303, 2166, 2073, 2022, 1800, 1733, 1598, 1558, 1511, 1459, 1434, 1289, 1238, 1208, 1083, 1028, 968, 934, 857, 835, 780, 749, 700 cm^{-1}.

HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{14}H_{12}ClN_3OS^+$ 305.0384; found 305.0382.

3-[(2,6-Dimethylphenyl)amino]-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3ap)



Following the general experimental procedure **EP8** using 0.5 mol% of $Pd(PPh_3)_4$, compound **3ap** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a colourless solid (109 mg, 0.36 mmol, 91%).

Mp: 213 – 216 °C

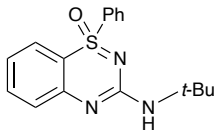
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 6.4 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.18 – 6.96 (m, 5H), 3.35 (s, 3H), 2.30 (s, 6H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 155.3, 149.5, 136.8, 135.3, 135.1, 128.2, 127.1, 125.4, 123.3, 121.9, 111.0, 46.7, 18.9 ppm.

IR (ATR): ν = 3190, 3026, 2922, 2854, 2324, 2191, 2102, 2020, 1808, 1607, 1560, 1457, 1394, 1311, 1289, 1214, 1164, 1136, 1095, 1028, 960, 918, 858, 823, 759, 658 cm^{-1}.

HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{16}H_{17}N_3OS^+$ 299.1087; found 299.1091.

3-(*tert*-Butylamino)-1-phenylbenzo[*e*][1,2,4]thiadiazine 1-oxide (3ba)



Following the general experimental procedure **EP8** using 1.5 mol% of $Pd(PPh_3)_4$, compound **3ba** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a colourless solid (103 mg, 0.33 mmol, 82%).

Mp: 119 – 128 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 – 7.83 (m, 2H), 7.65 – 7.59 (m, 1H), 7.58 – 7.52 (m, 2H), 7.40 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 6.88 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 1.46 (s, 9H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = **154.9**, 149.3, 141.1, 134.5, 133.6, 129.4, 128.4, **125.5**, 124.9, 121.4, **111.3**, 51.7, 29.7 ppm.

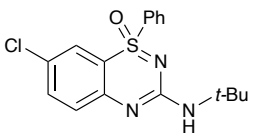
^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$, HCl): δ = 151.5, 138.0, 137.4, 136.6, 135.5, 130.3, 128.1, 125.5, 125.4, 118.7, 112.7, 54.3, 29.0 ppm.

IR (ATR): ν =3384, 3063, 2966, 2926, 2167, 1963, 1632, 1516, 1456, 1391, 1363, 1297, 1212, 1115, 1023, 983, 914, 853, 725, 684 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{20}N_3OS^+$ 314.1322; found 314.1315.

***Note**: Due to the possible quadrupole moment of the nitrogen atoms, several signals in the ^{13}C {^1H} NMR spectrum appear broad with low intensity. Therefore, the measurement of a highly concentrated sample (ca. 30–40 mg) with extended measurement time was necessary to observe all relevant signals. The signals affected are marked in bold. Alternatively, the sample could be measured in a mixture of $CDCl_3$ (ca. 0.7 mL) and conc. HCl (ca. two drops).*

3-(*tert*-Butylamino)-7-chloro-1-phenylbenzo[*e*][1,2,4]thiadiazine 1-oxide (3ca)



Following the general experimental procedure **EP8** using 1.5 mol% of of $Pd(PPh_3)_4$, compound **3ca** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a brownish solid (127 mg, 0.37 mmol, 91%).

Mp: 117 – 123 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 – 7.82 (m, 2H), 7.69 – 7.63 (m, 1H), 7.61 – 7.54 (m, 2H), 7.33 (dd, J = 9.0, 2.4 Hz, 1H), 7.19 (d, J = 2.4 Hz, 1H), 7.15 – 7.09 (m, 1H), 1.45 (s, 9H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = **154.7**, 147.7, 140.3, 135.0, 134.0, 129.6, 128.5, **127.1**, 125.6, 123.9, **111.9**, 51.8, 29.6 ppm.

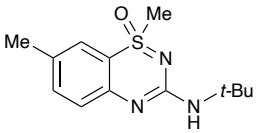
^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$, HCl): δ = 151.4, 137.3, 137.0, 135.9, 135.8, 130.5, 130.4, 128.2, 124.6, 120.4, 113.7, 54.5, 29.0 ppm.

IR (ATR): ν = 3427, 3064, 2966, 2925, 2329, 2252, 2114, 1977, 1903, 1731, 1635, 1516, 1456, 1363, 1295, 1212, 1116, 985, 909, 864, 829, 730, 685, 657 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{19}ClN_3OS^+$ 348.0932; found 348.0934.

***Note**: Due to the possible quadrupole moment of the nitrogen atoms, several signals in the ^{13}C {^1H} NMR spectrum appear broad with low intensity. Therefore, the measurement of a highly concentrated sample (ca. 30–40 mg) with extended measurement time was necessary to observe all relevant signals. The signals affected are marked in bold. Alternatively, the sample could be measured in a mixture of $CDCl_3$ (ca. 0.7 mL) and conc. HCl (ca. two drops).*

3-(*tert*-Butylamino)-1,7-dimethyl-1λ^4-benzo[*e*][1,2,4]thiadiazine (3da)



Following the general experimental procedure **EP8** using 1.5 mol% of $Pd(PPh_3)_4$, compound **3da** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a colourless solid (41 mg, 0.15 mmol, 39%).

Mp: 127 – 133 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 – 7.37 (m, 1H), 7.31 (dd, J = 8.5, 2.1 Hz, 1H), 7.06 (d, J = 8.5 Hz, 1H), 3.37 (s, 3H), 2.34 (s, 3H), 1.44 (s, 9H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = **147.1**, 136.7, **131.3**, 125.3, 122.8, **109.9**, 51.6, 46.9, 29.6, 20.9 ppm.

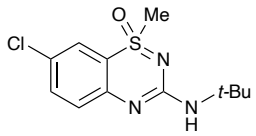
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, HCl): δ=150.5, 138.5, 135.9, 135.1, 123.7, 118.7, 110.9, 54.1, 46.9, 29.0, 21.0 ppm.

IR (ATR): ν = 3375, 3354, 2968, 2917, 2290, 2190, 2123, 1978, 1737, 1634, 1537, 1475, 1422, 1372, 1295, 1198, 1141, 11001, 1065, 990, 893, 833, 787, 730, 698 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{20}N_3OS^+$ 266.1322; found 266.1322.

Note**: Due to the possible quadrupole moment of the nitrogen atoms, several signals in the ^{13}C {^{1}H} NMR spectrum appear broad with low intensity. Therefore, the measurement of a highly concentrated sample (ca. 30–40 mg) with extended measurement time is necessary to observe all relevant signals. The signals affected are marked in bold.* ***The carbon signal (most probably) next to the nitrogen atoms could not be detected. *Alternatively, the sample could be measured in a mixture of $CDCl_3$ (ca. 0.7 mL) and conc. HCl (ca. two drops).*

3-(*tert*-Butylamino)-7-chloro-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (3ea)



Following the general experimental procedure **EP8** using 1.5 mol% of $Pd(PPh_3)_4$, compound **3ea** was obtained after purification by column chromatography (SiO_2, *n*-pentane: EtOAc: NEt_3, 20:10:1 → 10:10:1) as a colourless solid (63 mg, 0.22 mmol, 55%).

Mp: 165 – 172 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.57 (d, J = 2.4 Hz, 1H), 7.40 (dd, J = 9.0, 2.4 Hz, 1H), 7.12 – 7.06 (m, 1H), 3.38 (s, 3H), 1.43 (s, 9H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = **154.5**, 148.2, 135.4, **127.6**, 125.5, 122.9, **110.9**, 51.7, 46.9, 29.6 ppm.

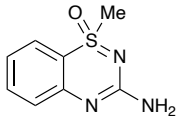
^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$, HCl): δ = 150.4, 137.6, 135.9, 130.5, 124.0, 120.5, 112.1, 54.5, 46.9, 28.9 ppm.

IR (ATR): ν = 3393, 3049, 2961, 2920, 2856, 2286, 2089, 1921, 1766, 1634, 1513, 1458, 1394, 1362, 1293, 1209, 1137, 1108, 1059, 964, 917, 886, 854, 830, 784, 750, 726 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{17}ClN_3OS^+$ 286.0775; found 286.0776.

***Note**: Due to the possible quadrupole moment of the nitrogen atoms, several signals in the ^{13}C {^{1}H} NMR spectrum appear broad with low intensity. Therefore, the measurement of a highly concentrated sample (ca. 30–40 mg) with extended measurement time was necessary to observe all relevant signals. The signals affected are marked in bold. Alternatively, the sample could be measured in a mixture of $CDCl_3$ (ca. 0.7 mL) and conc. HCl (ca. two drops).*

3-Amino-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (4a)



Following the general experimental procedure **EP10**, compound **4a** was obtained after purification by column chromatography (SiO_2, EtOAc: MeOH, 5:1) as a colourless solid (167 mg, 0.86 mmol, 86%).

Mp: 223 – 227 °C

^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ = 7.90 (dd, J = 8.0, 1.5 Hz, 1H), 7.48 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H), 7.03 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 6.99 (dd, J = 8.5, 1.1 Hz, 1H), 6.47 (br s, 2H), 3.62 (s, 3H) ppm.

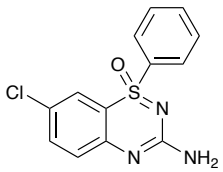
^{13}C {^{1}H} NMR (151 MHz, $(CD_3)_2SO$): δ = 156.0, 149.2, 134.3, 124.6, 124.2, 120.4, 111.3, 44.9 ppm.

IR (ATR): ν = 3650, 3430, 3309, 3032, 2920, 2782, 2727, 2328, 2114, 1993, 1923, 1646, 1602, 1550, 1507, 1461, 1392, 1293, 1211, 1133, 1081, 1020, 969, 944, 891, 840, 778, 742, 656 cm^{-1}.

HRMS (EI) *m/z*: $[M]^+$ calcd for $C_8H_9N_3OS^+$ 195.0461; found 195.0461.

EA calcd for $C_8H_9N_3OS$: C, 49.22; H, 4.65; N, 21.52; found C, 48.85; H, 4.66; N, 21.62.

3-Amino-7-chloro-1-phenylbenzo[*e*][1,2,4]thiadiazine 1-oxide (4c)



Following the general experimental procedure **EP10**, compound **4c** was obtained after purification by column chromatography (SiO_2, EtOAc: MeOH, 5:1) as a yellowish solid (201 mg, 0.69 mmol, 69%).

Mp: 223 – 225 °C

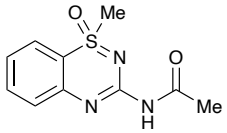
^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ = 7.93 – 7.87 (m, 2H), 7.81 – 7.75 (m, 1H), 7.74 – 7.67 (m, 2H), 7.47 (dd, J = 9.0, 2.5 Hz, 1H), 7.41 (d, J = 2.5 Hz, 1H), 7.06 (d, J = 9.0 Hz, 1H), 6.92 (br s, 2H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $(CD_3)_2SO$): δ = 156.4, 148.4, 139.5, 134.7, 134.3, 129.8, 128.3, 127.2, 123.7, 123.5, 111.6 ppm.

IR (ATR): ν = 3399, 3297, 3166, 2514, 2324, 2107, 1985, 1895, 1731, 1637, 1600, 1537, 1506, 1461, 1379, 1327, 1288, 1254, 1152, 1101, 997, 964, 886, 867, 829, 779, 731, 680 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{11}ClN_3OS^+$ 292.0306; found 292.0293.

***N*-(1-Methyl-1-oxido-1λ^4-benzo[*e*][1,2,4]thiadiazin-3-yl)acetamide (7)**



Compound **7** was synthesised according to a modified literature procedure.[S8] To a solution of 3-amino-1-methyl-1λ^4-benzo[*e*][1,2,4]thiadiazine 1-oxide (**4a**, 0.4 mmol, 78 mg, 1.0 equiv.) in dry and degassed MeCN (2.0 mL) was added acetic anhydride (0.7 mmol, 66 µL, 1.75 equiv.). Anhydrous cobalt(II) chloride (97% purity, 0.04 mmol, 5.4 mg, 10 mol%) was added and the resulting reaction mixture was stirred for 12 h at room temperature. SiO_2 was added and the volatiles were removed under reduced pressure. The product was purified by column chromatography on silica using *n*-pentane: EtOAc: NEt_3 (10:10:1). Compound **7** was obtained as a colourless solid (80 mg, 0.34 mmol, 85%).

Mp: 189 – 192 °C

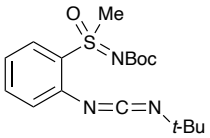
^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ = 10.05 (s, 1H), 8.11 (dd, J = 8.0, 1.5 Hz, 1H), 7.68 (ddd, J = 8.5, 7.2, 1.5 Hz, 1H), 7.36 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.32 – 7.23 (m, 1H), 3.82 (s, 3H), 2.19 (s, 3H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $(CD_3)_2SO$): δ = 169.5, 150.3, 146.5, 134.9, 126.3, 124.4, 124.3, 113.1, 44.8, 25.0 ppm.

IR (ATR): ν = 3322, 3068, 3008, 2920, 2854, 2656, 2322, 2191, 2108, 2023, 1998, 1933, 198, 1713, 1603, 1562, 1540, 1460, 1364, 1309, 1287, 1244, 1199, 1093, 1031, 989, 951, 853, 791, 751, 718 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{10}H_{12}N_3O_2S^+$ 238.0645; found 238.0644.

***tert*-Butyl [(2-{[(*tert*-butylimino)methylene]amino}phenyl)(methyl)(oxo)-λ^6-sulfaneylidene]carbamate (9a)**



Following the general experimental procedure **EP8** using 5.0 mol% of $Pd(PPh_3)_4$, compound **9a** was obtained after purification by column chromatography (SiO_2 0.04 – 0.063 mm, *n*-pentane: DCM: EtOAc, 10:2:1) as a yellowish oil (124 mg, 0.35 mmol, 88%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.06 (dd, J = 8.0, 1.5 Hz, 1H), 7.54 (td, J = 7.7, 1.6 Hz, 1H), 7.32 – 7.21 (m, 2H), 3.42 (s, 3H), 1.42 (s, 9H), 1.33 (s, 9H) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 157.3, 140.3, 134.7, 131.7, 130.9, 130.4, 125.0, 124.6, 80.1, 58.8, 42.6, 31.7, 28.2 ppm.

IR (ATR): ν = 2974, 2932, 2127, 1665, 1586, 1484, 1393, 1366, 1274, 1227, 1156, 1099, 1060, 966, 866, 760, 716 cm^{-1}.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{25}N_3NaO_3S^+$ 374.1509; found 374.1499.

7. X-Ray crystallographic studies

The single crystal X-ray data for **3ak** was collected at 120 K using an Agilent SuperNova dual wavelength diffractometer with an Atlas detector using mirror-monochromated Cu-Kα (λ = 1.54184 Å) radiation. The structure was solved by intrinsic phasing (SHELXT)[S9] and refined by full-matrix least squares on F^2 using Olex2,[S10] utilizing the SHELXL module.[S11] Anisotropic displacement parameters were assigned to non-H atoms and isotropic displacement parameters for all H atoms were constrained to multiples of the equivalent displacement parameters of their parent atoms with $U_{iso}(H) = 1.2\ U_{eq}(sp^2$ C/NH) or $U_{iso}(H) = 1.5\ U_{eq}(sp^3$ C) of their respective parent atoms. The X-ray single crystal data and CCDC number of **3ak** are included below.

Crystals suitable for single-crystal X-ray analysis were obtained by diffusion of *n*-pentane into a dichloromethane solution of **3ak**. Crystal data for **3ak**: $C_{14}H_{12}ClN_3OS$, M = 305.78, colourless needle, 0.02 × 0.04 × 0.22 mm, monoclinic, space group $P2_1$, a = 10.7651(5) Å, b = 4.8762(2) Å, c = 13.0778(5) Å, β = 106.910(5)°, V = 656.81(5) $Å^3$, Z = 2, D_{calc} = 1.546 gcm^{-3}, F(000) = 316, μ = 4.05 mm^{-1}, T = 120.0(1) K, θ_{max} = 74.4°, 2001 total reflections, 1877 with $I_o > 2\sigma(I_o)$, R_{int} = 0.030, 2001 data, 185 parameters, 1 restraint, GooF = 1.03, 0.46 < dΔρ < -0.34 $eÅ^{-3}$, $R[F^2 > 2\sigma(F^2)]$ = 0.043, $wR(F^2)$ = 0.112, Flack = –0.03(3), CCDC2240094.

8. References

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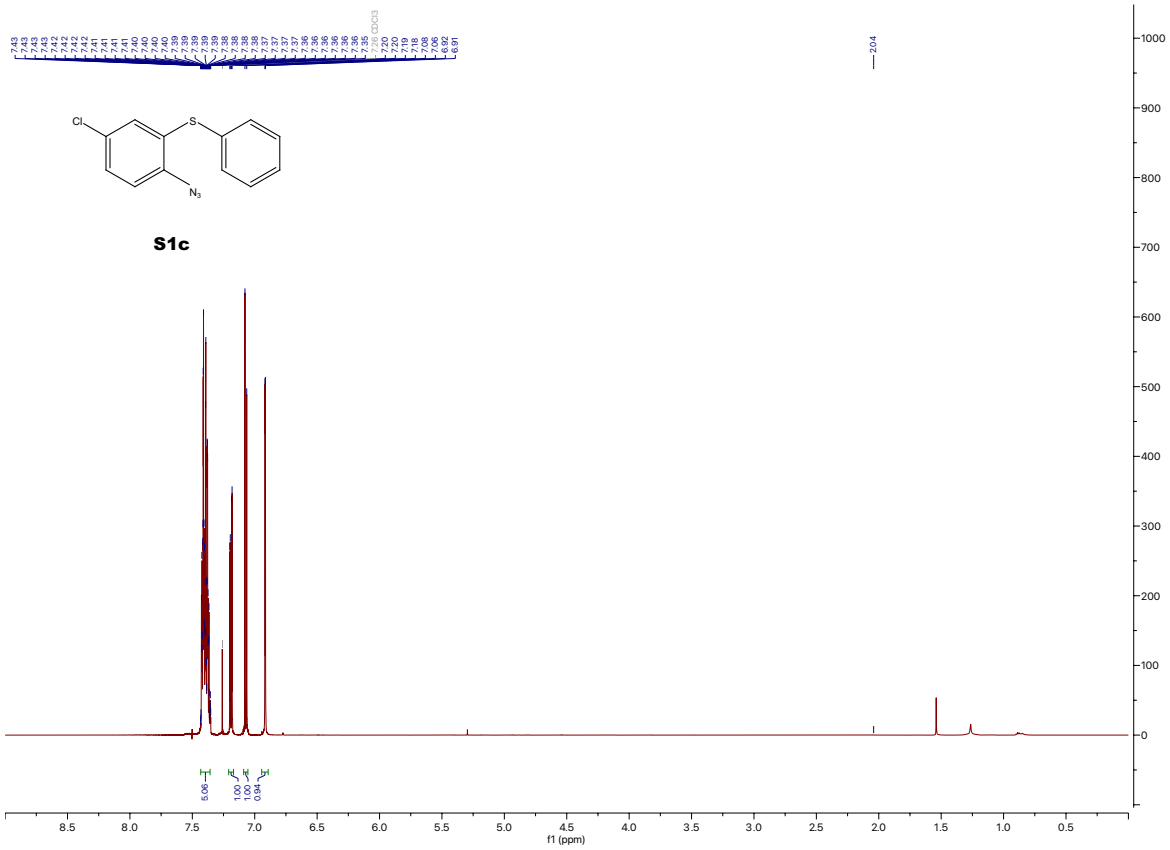
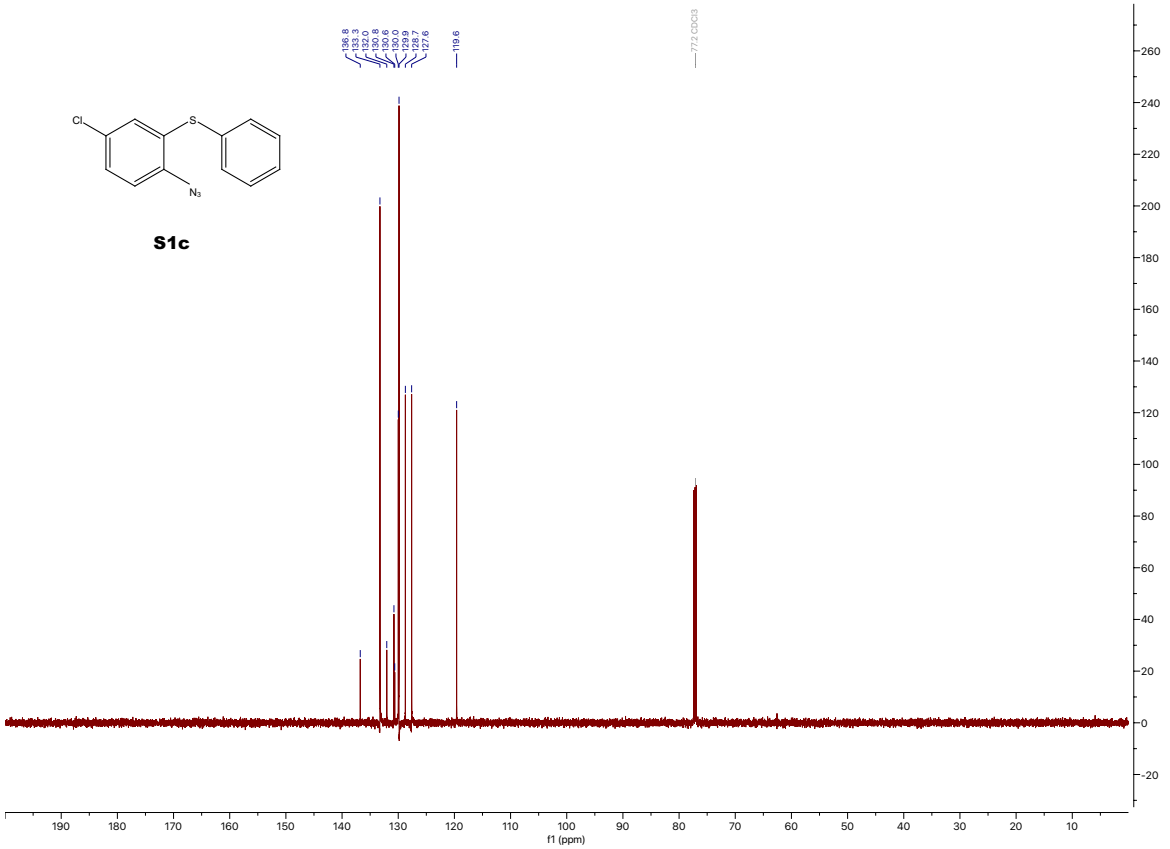
[S11] G. M. Sheldrick, *Acta Crystallogr. Sect. C,* 2015, **71**, 3–8.

9. NMR Spectra

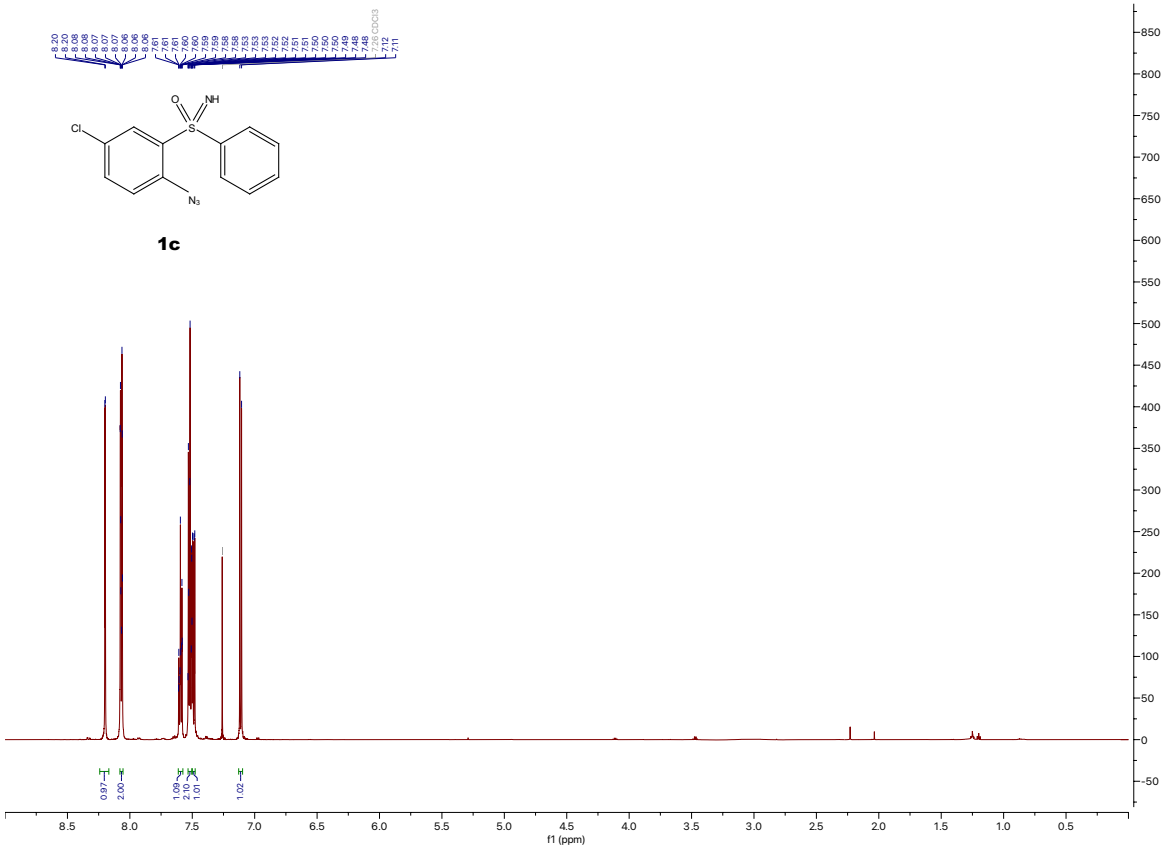
^{1}H NMR spectrum of compound **S1c** (600 MHz, $CDCl_3$)



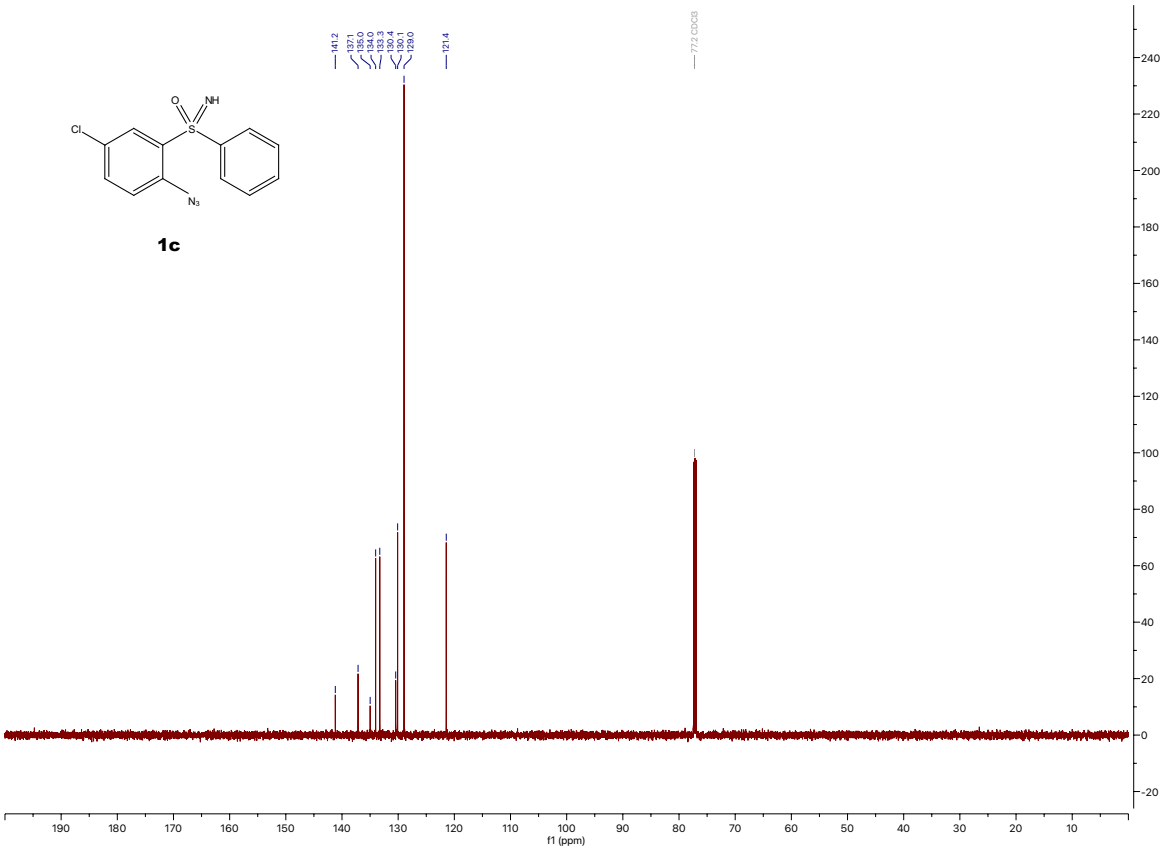
^{13}C {^{1}H} NMR spectrum of compound **S1c** (151 MHz, $CDCl_3$)



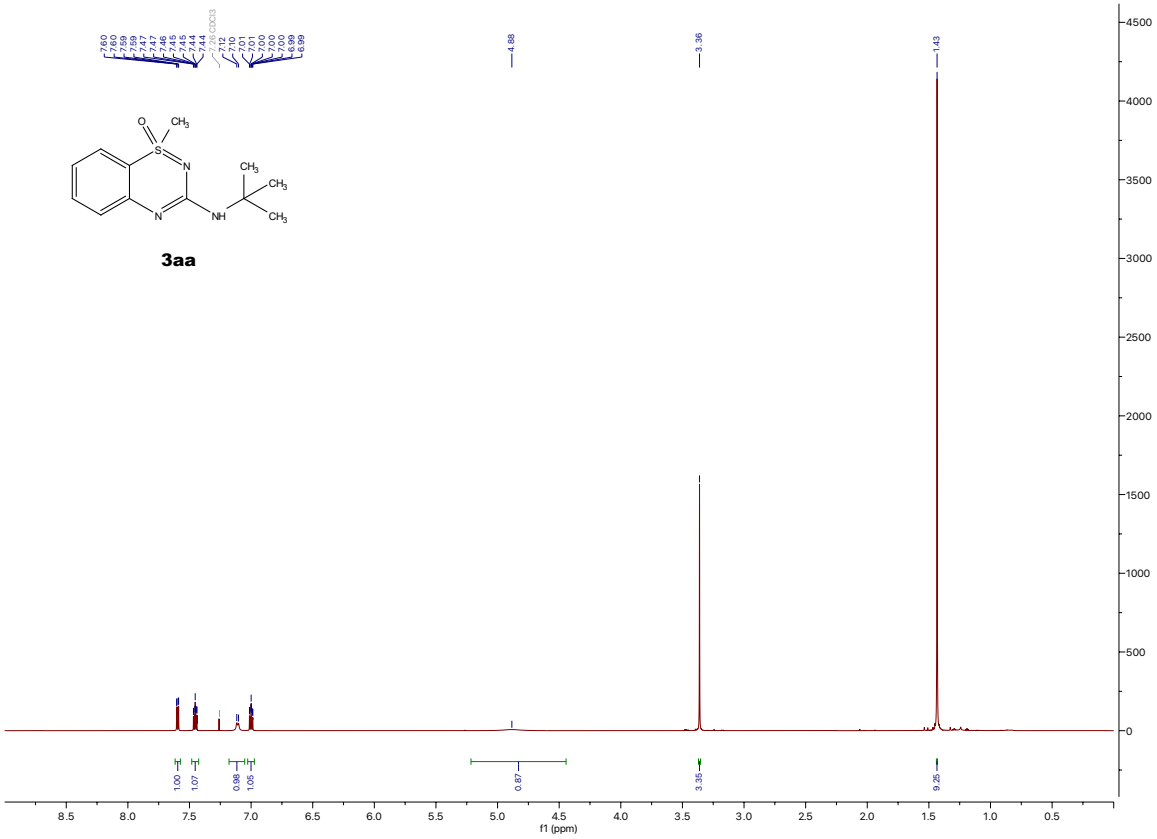
^{1}H NMR spectrum of compound **1c** (600 MHz, $CDCl_3$)



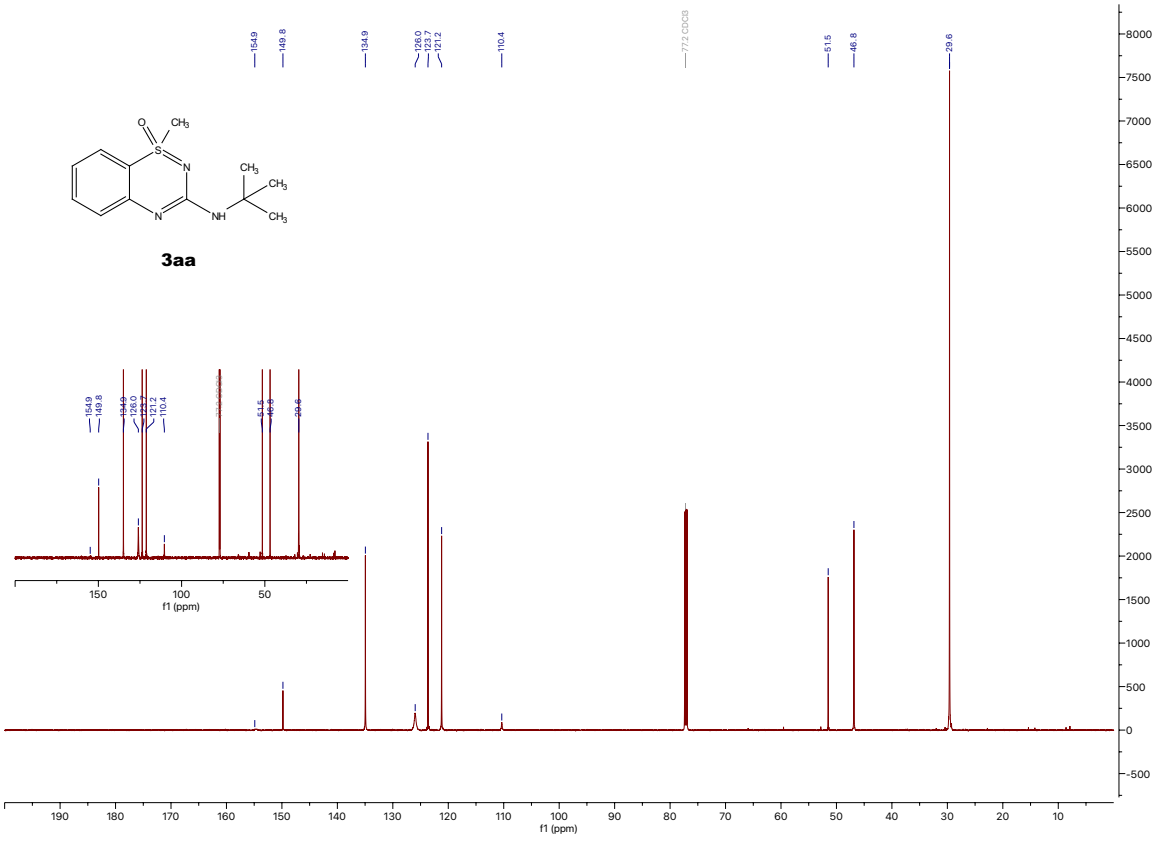
^{13}C {^{1}H} NMR spectrum of compound **1c** (151 MHz, $CDCl_3$)



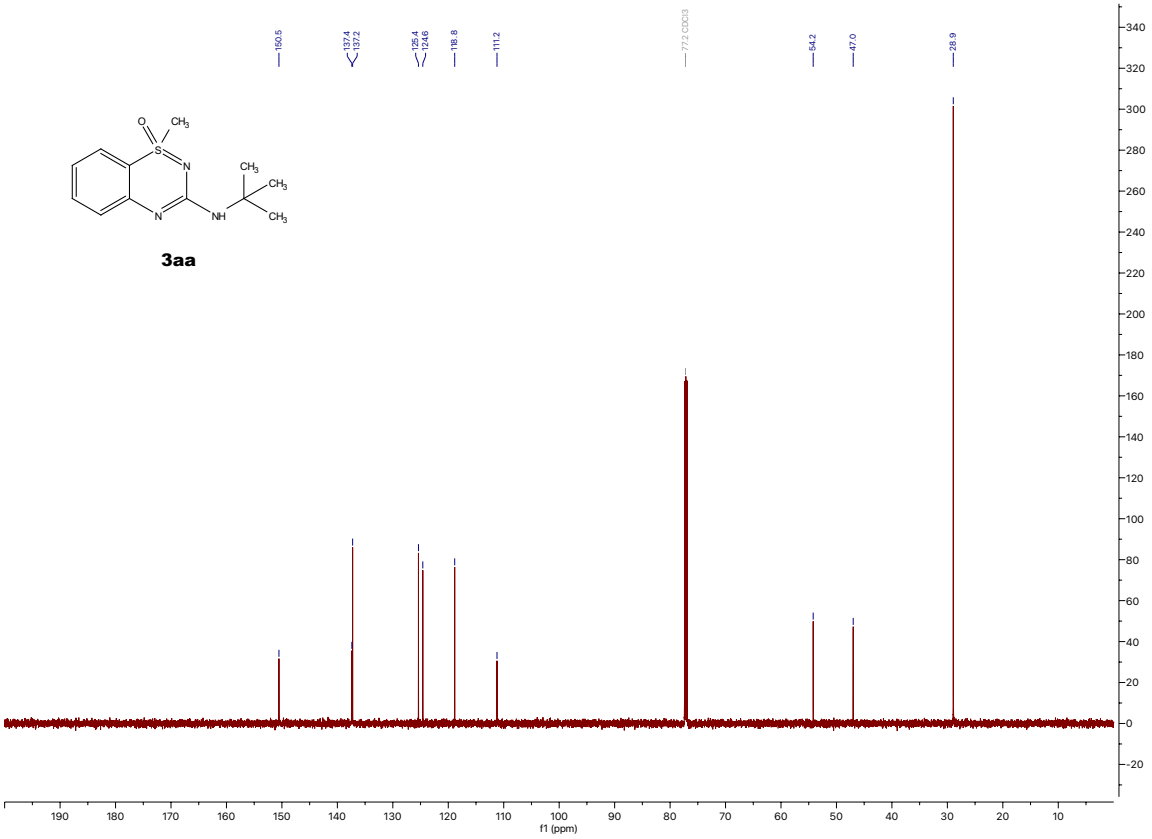
^{1}H NMR spectrum of compound **3aa** (600 MHz, $CDCl_3$)



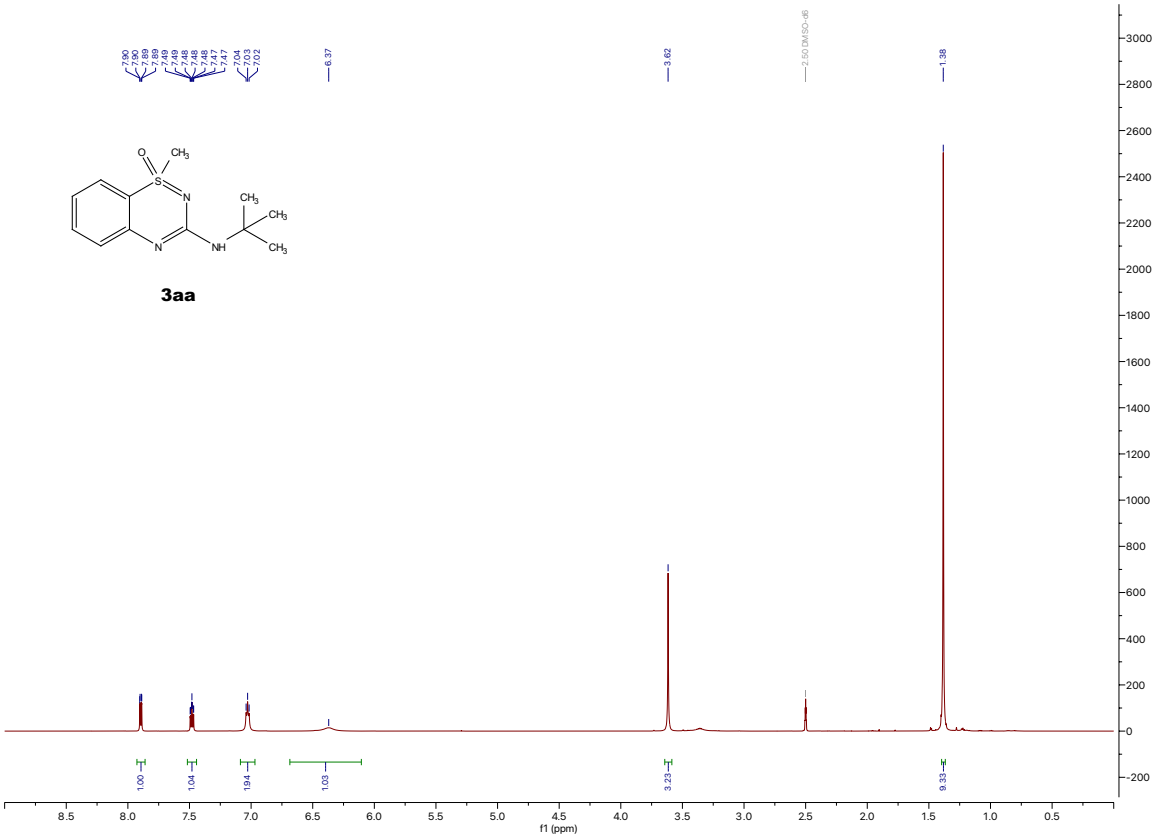
^{13}C {^{1}H} NMR spectrum of compound **3aa** (151 MHz, $CDCl_3$)



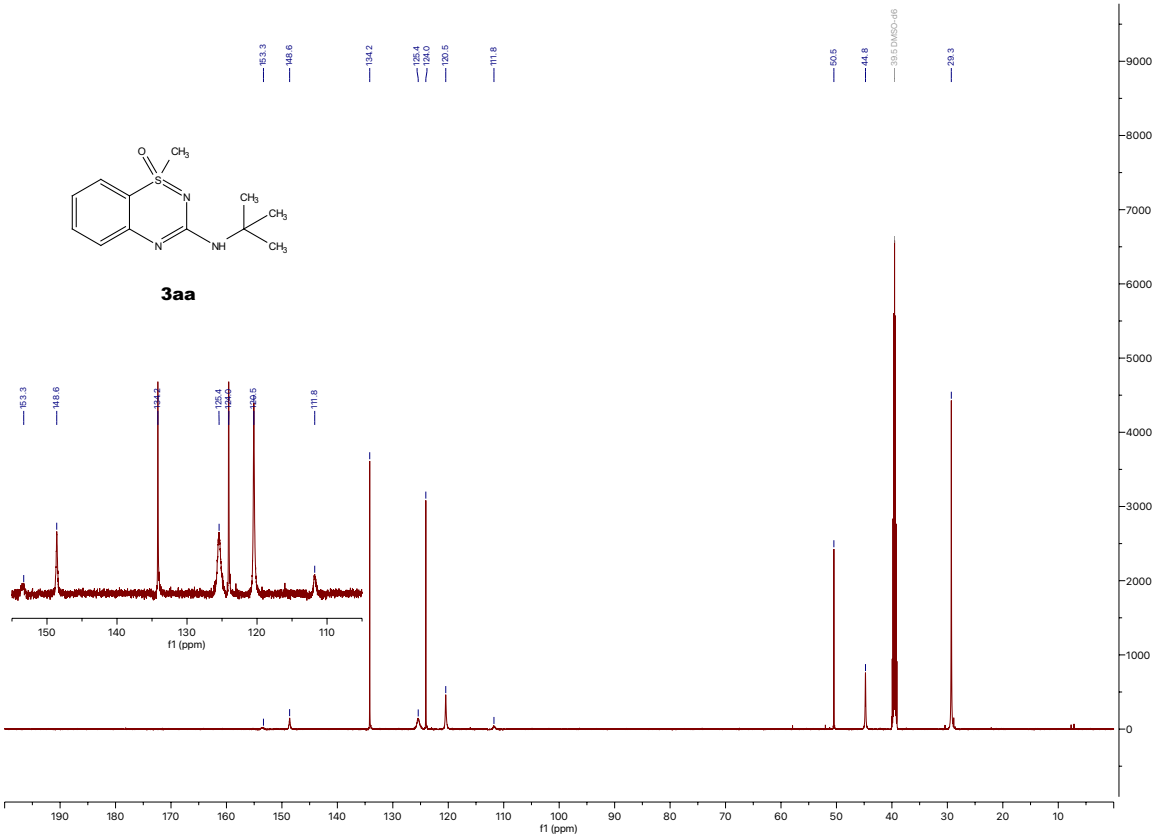
^{13}C {^{1}H} NMR spectrum of compound **3aa** (151 MHz, $CDCl_3$, HCl)



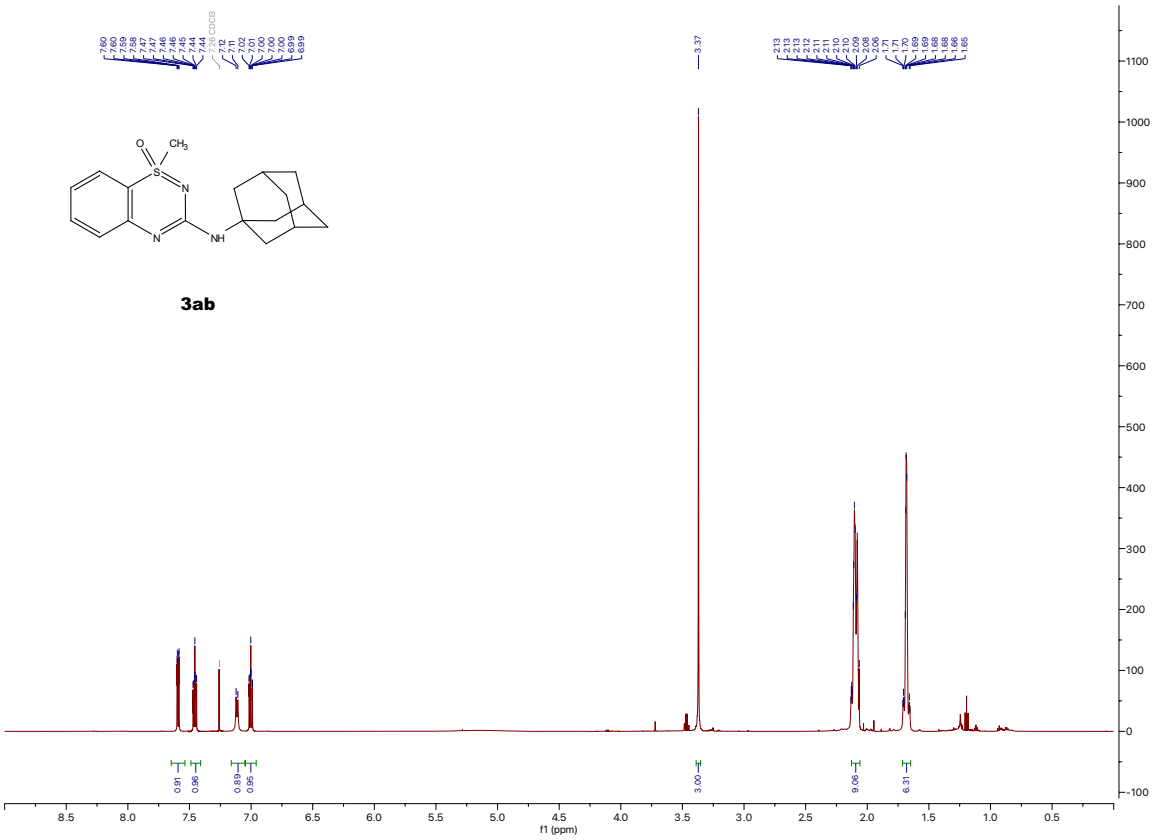
^{1}H NMR spectrum of compound **3aa** (600 MHz, $(CD_3)_2SO$)



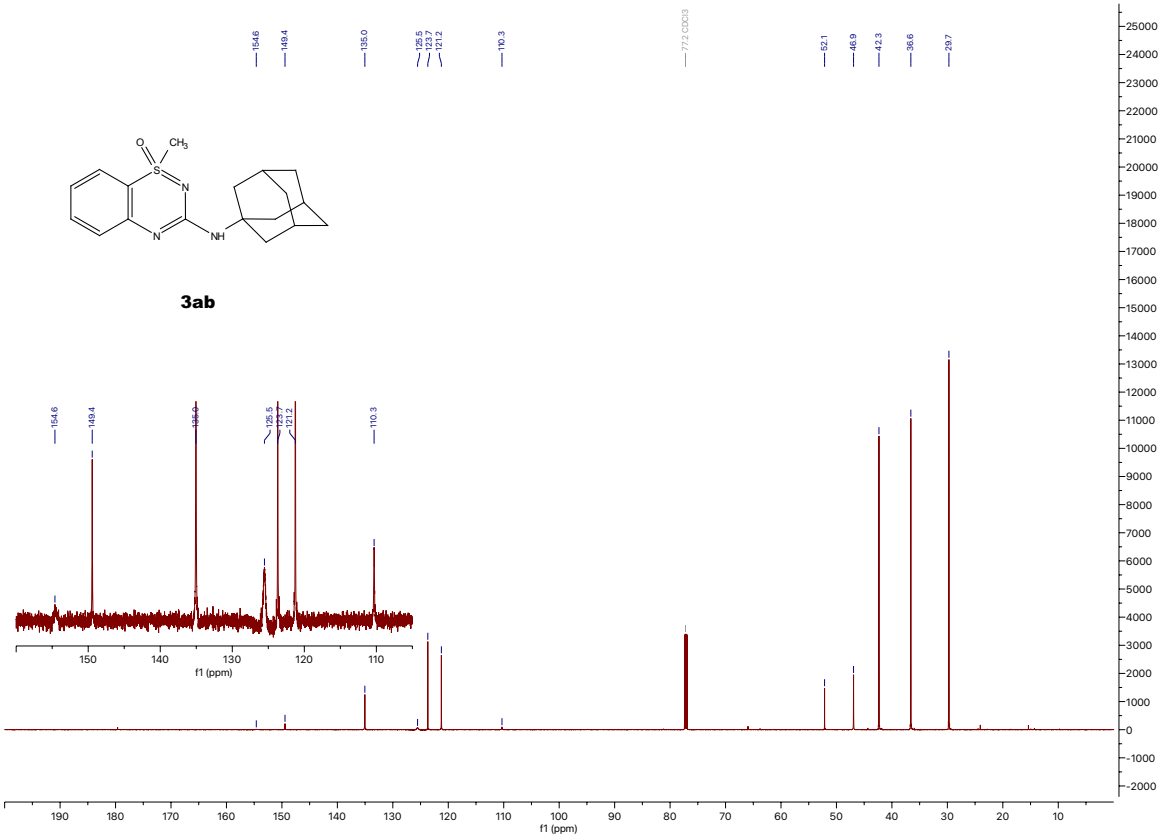
^{13}C {^{1}H} NMR spectrum of compound **3aa** (151 MHz, $(CD_3)_2SO$)



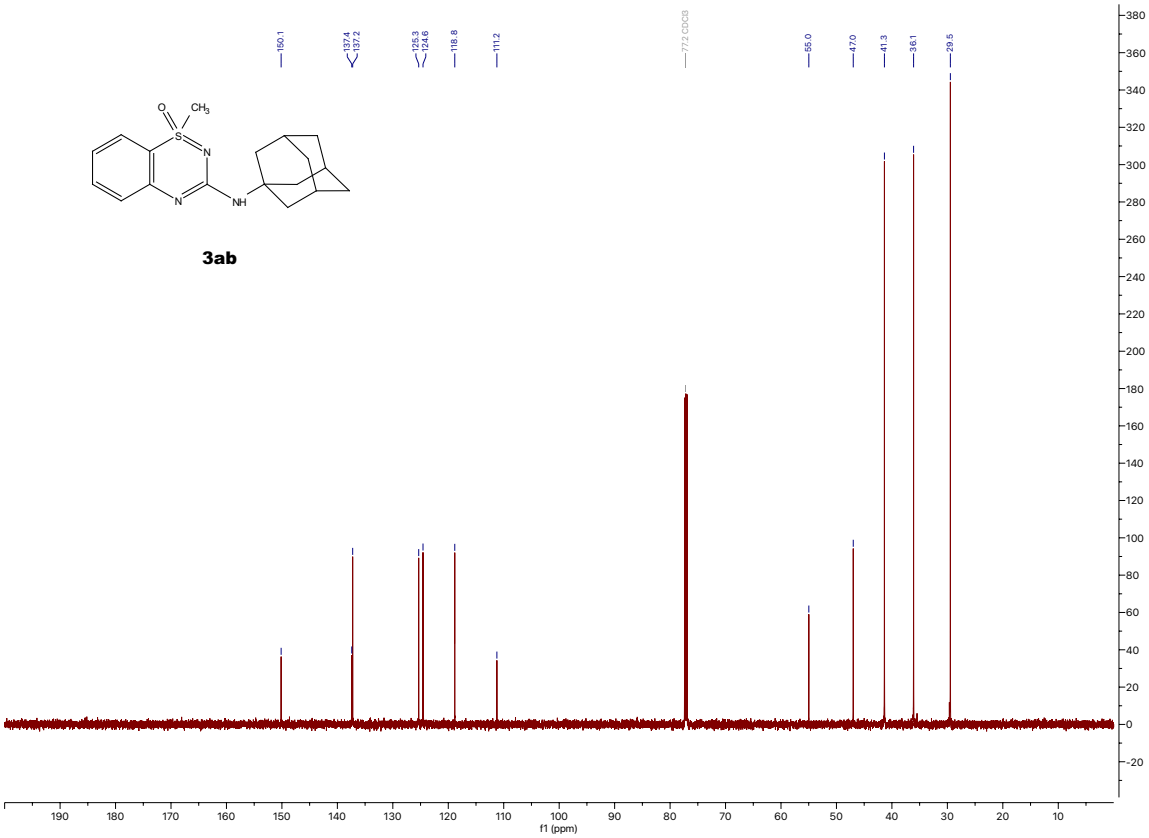
^{1}H NMR spectrum of compound **3ab** (600 MHz, $CDCl_3$)



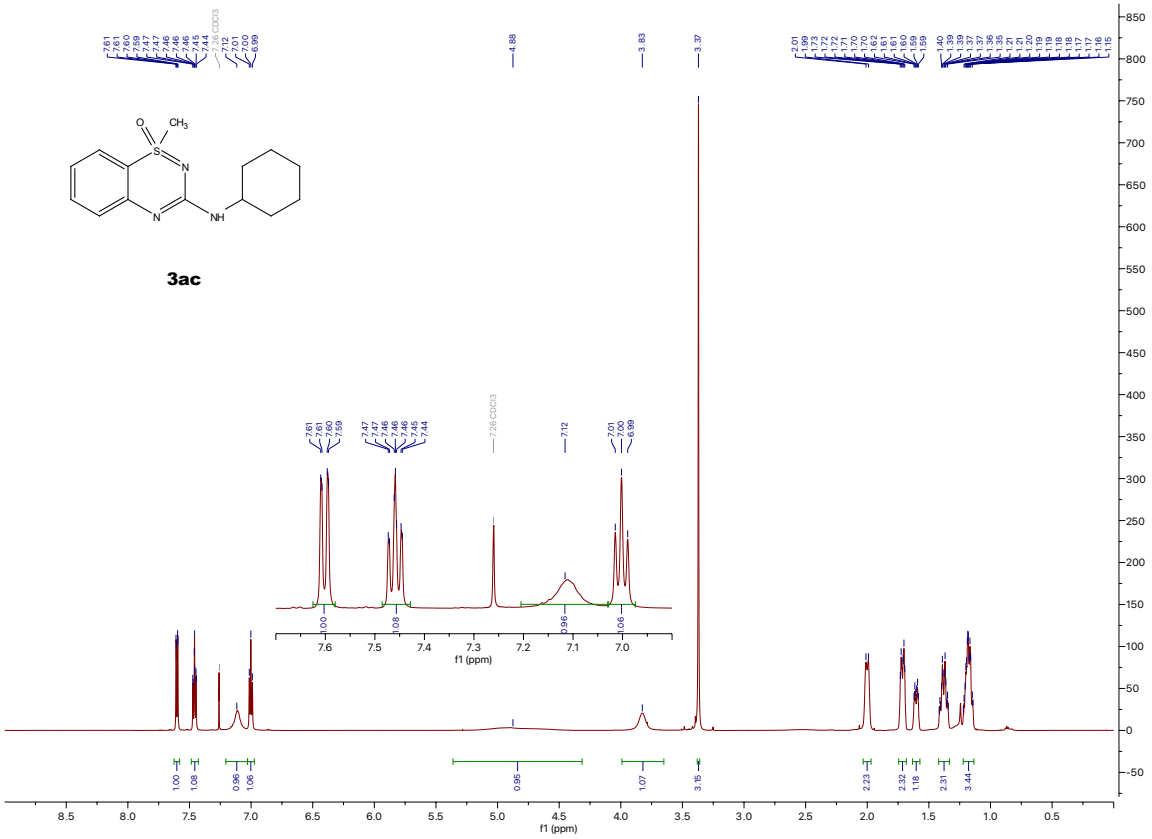
^{13}C {^{1}H} NMR spectrum of compound **3ab** (151 MHz, $CDCl_3$)



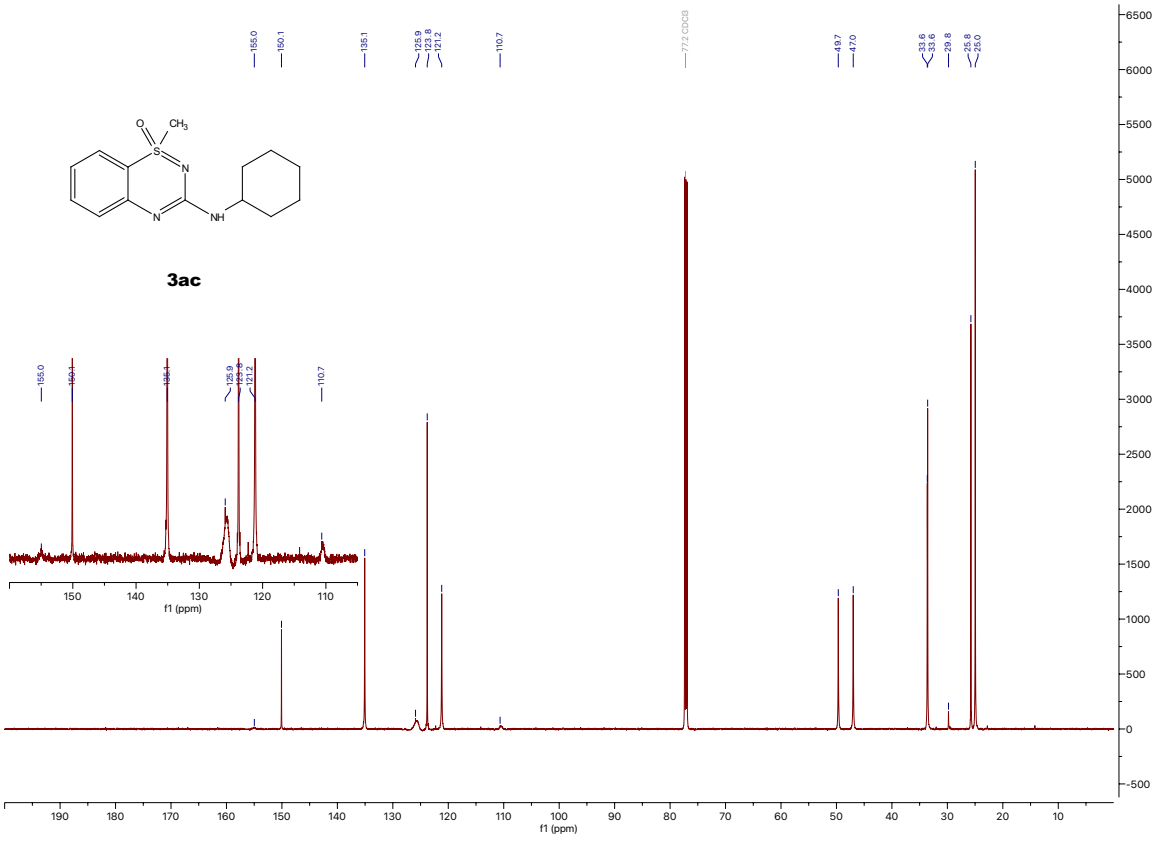
^{13}C {^{1}H} NMR spectrum of compound **3ab** (151 MHz, $CDCl_3$, HCl)



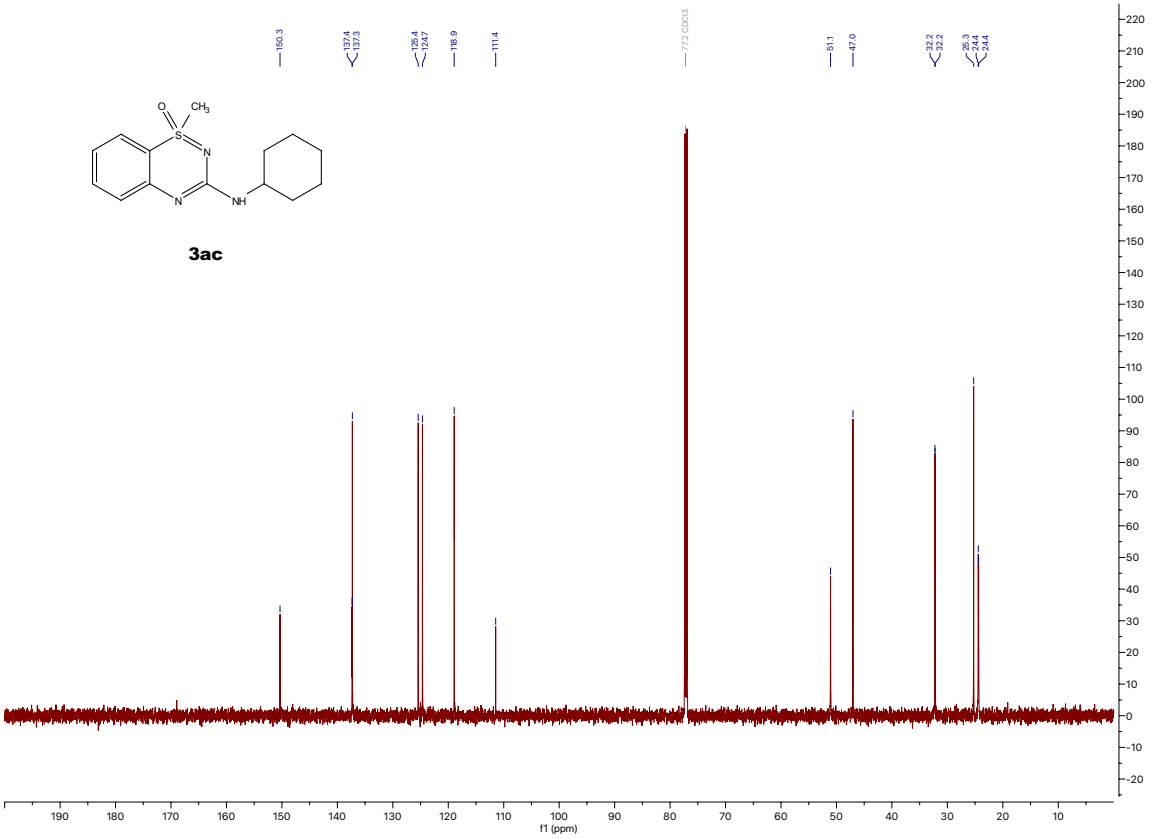
^{1}H NMR spectrum of compound **3ac** (600 MHz, $CDCl_3$)



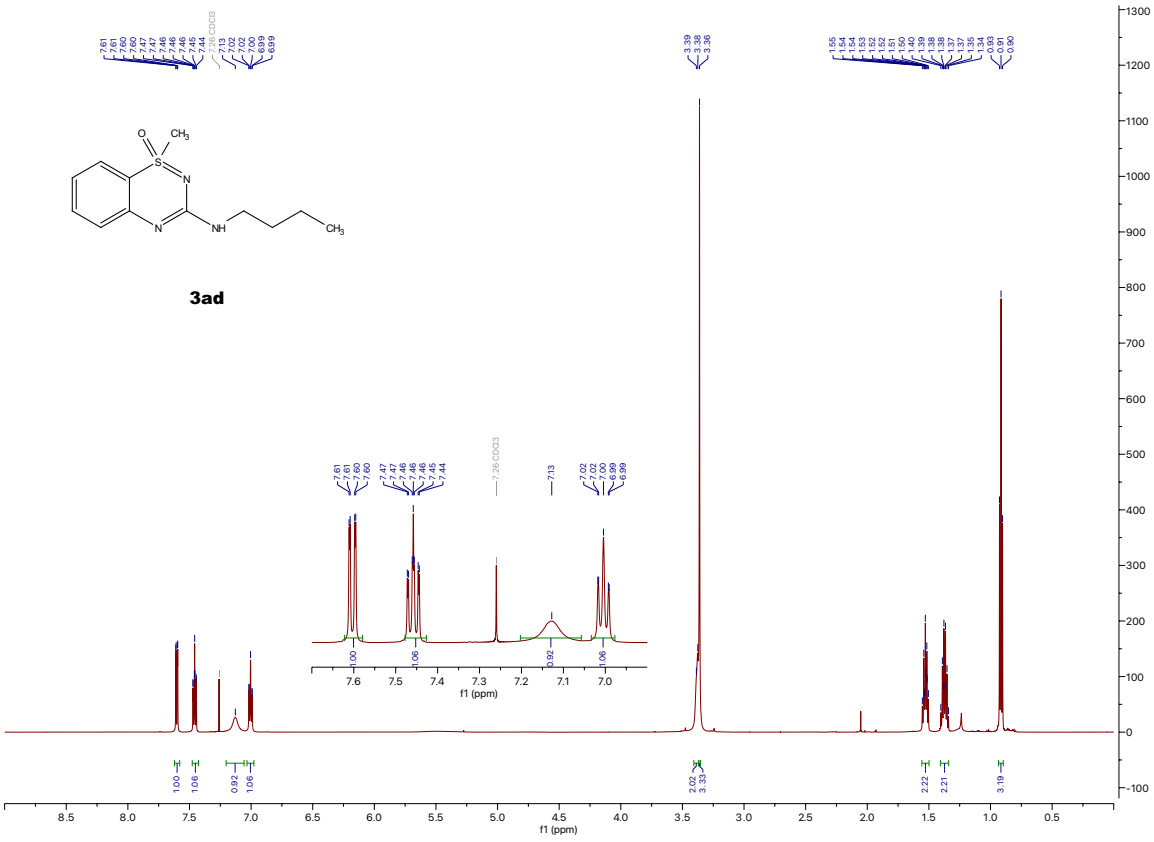
^{13}C {^{1}H} NMR spectrum of compound **3ac** (151 MHz, $CDCl_3$)



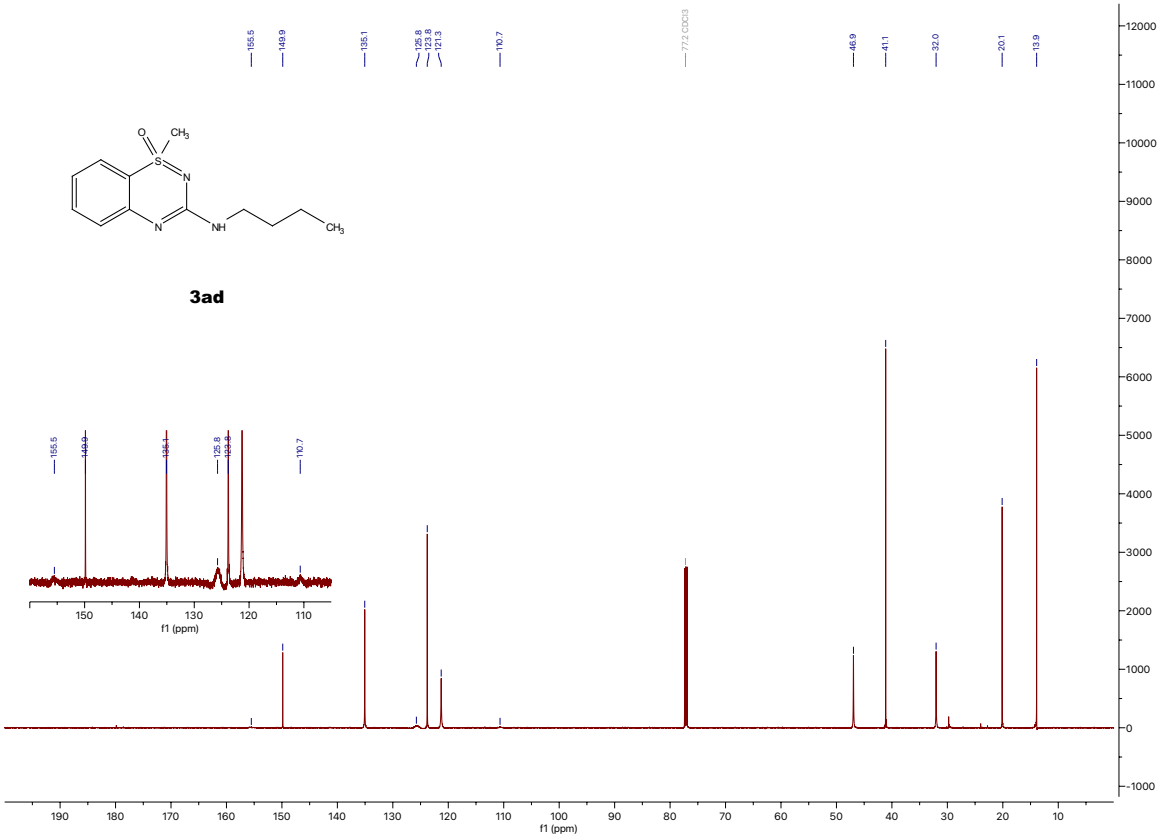
^{13}C {^{1}H} NMR spectrum of compound **3ac** (151 MHz, $CDCl_3$, HCl)



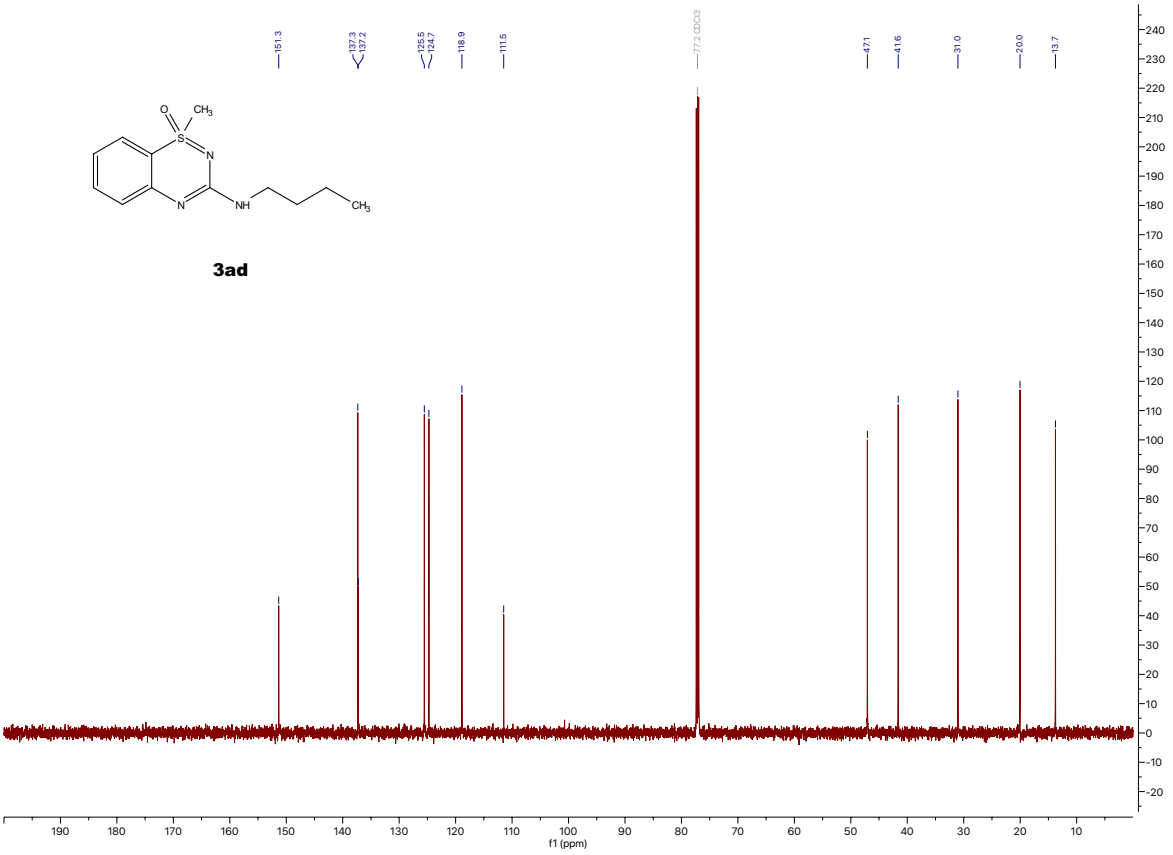
^{1}H NMR spectrum of compound **3ad** (600 MHz, $CDCl_3$)



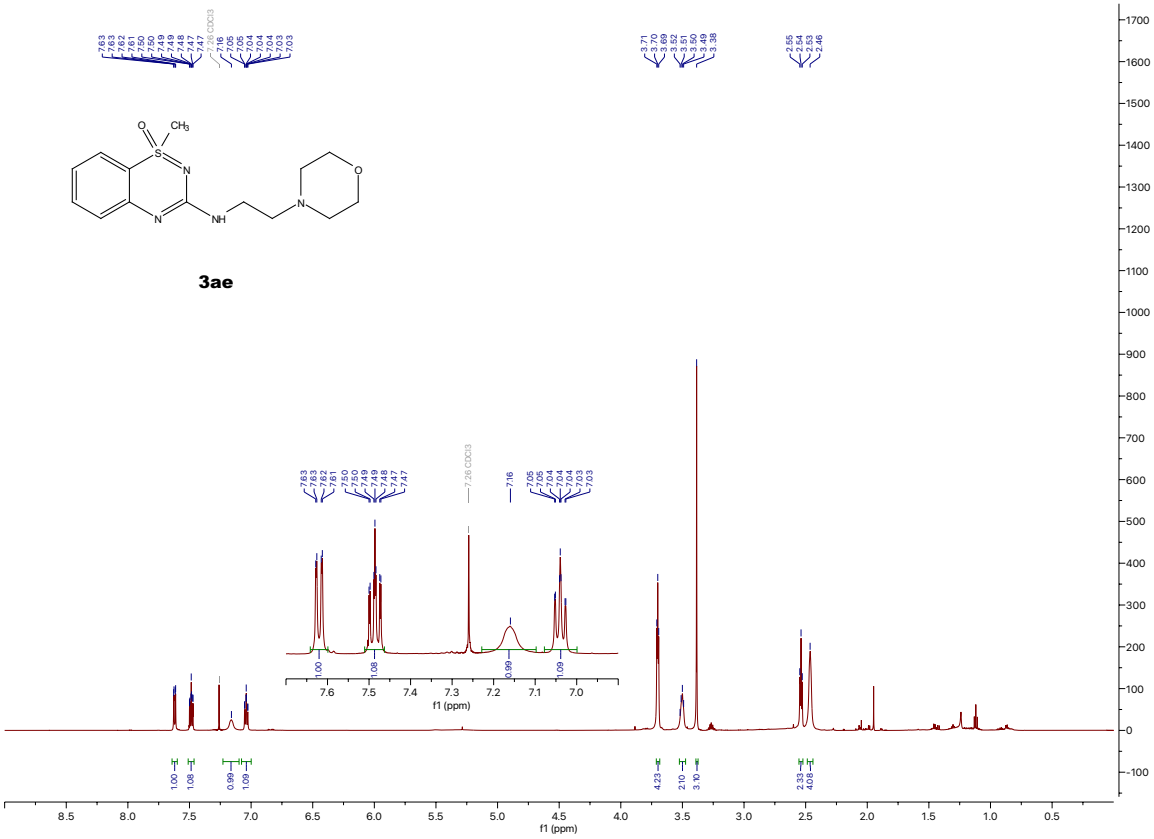
^{13}C {^{1}H} NMR spectrum of compound **3ad** (151 MHz, $CDCl_3$)



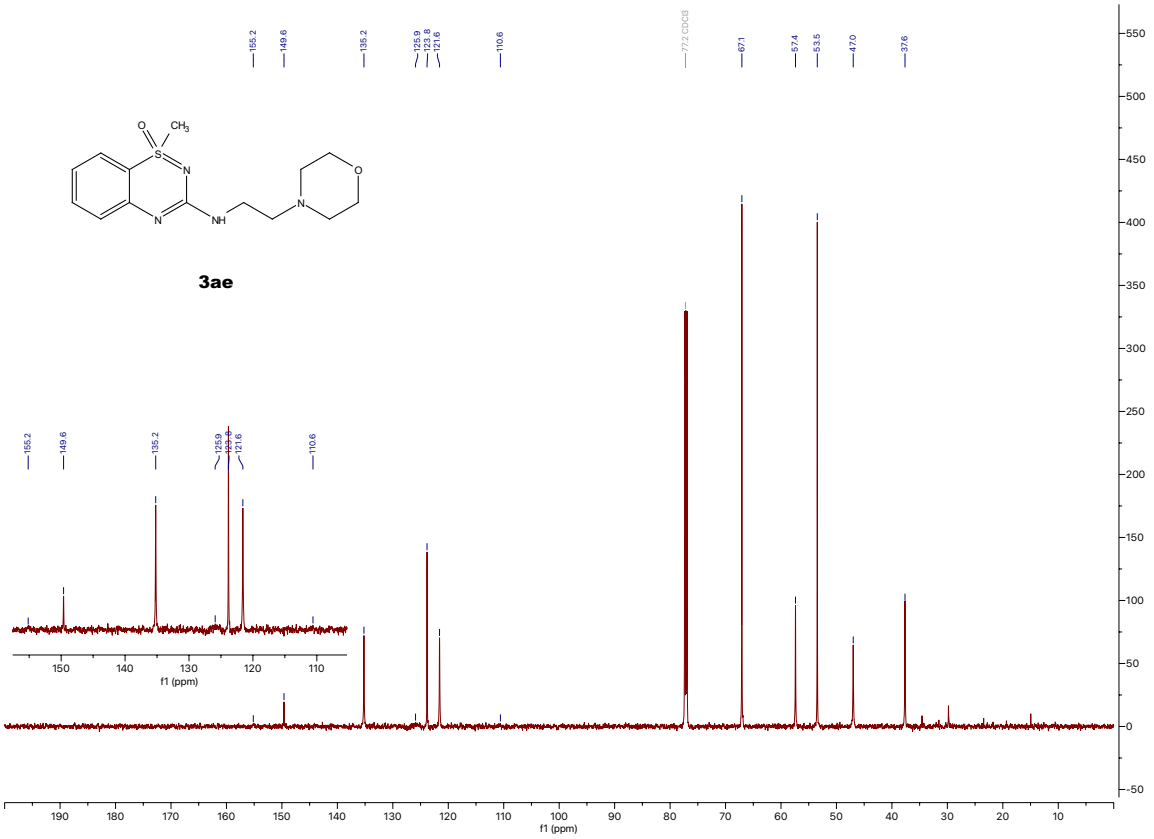
^{13}C {^{1}H} NMR spectrum of compound **3ad** (151 MHz, $CDCl_3$, HCl)



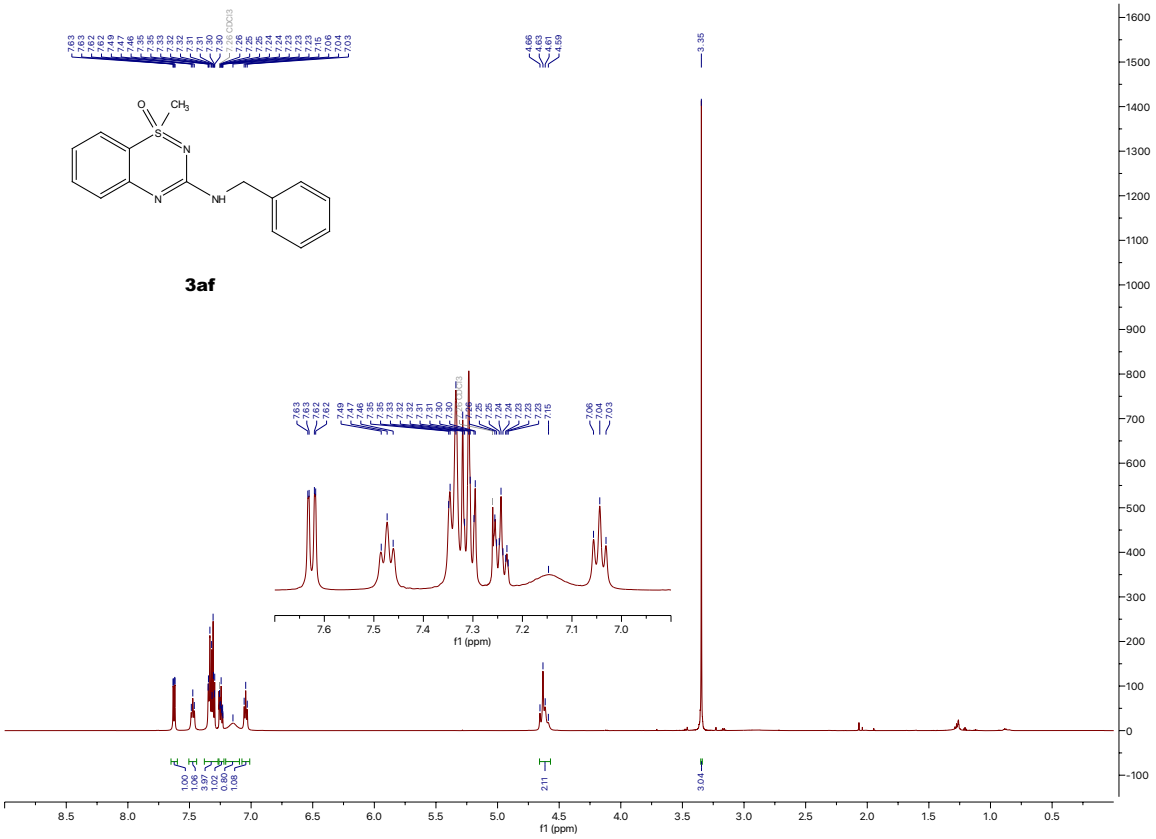
^{1}H NMR spectrum of compound **3ae** (600 MHz, $CDCl_3$)



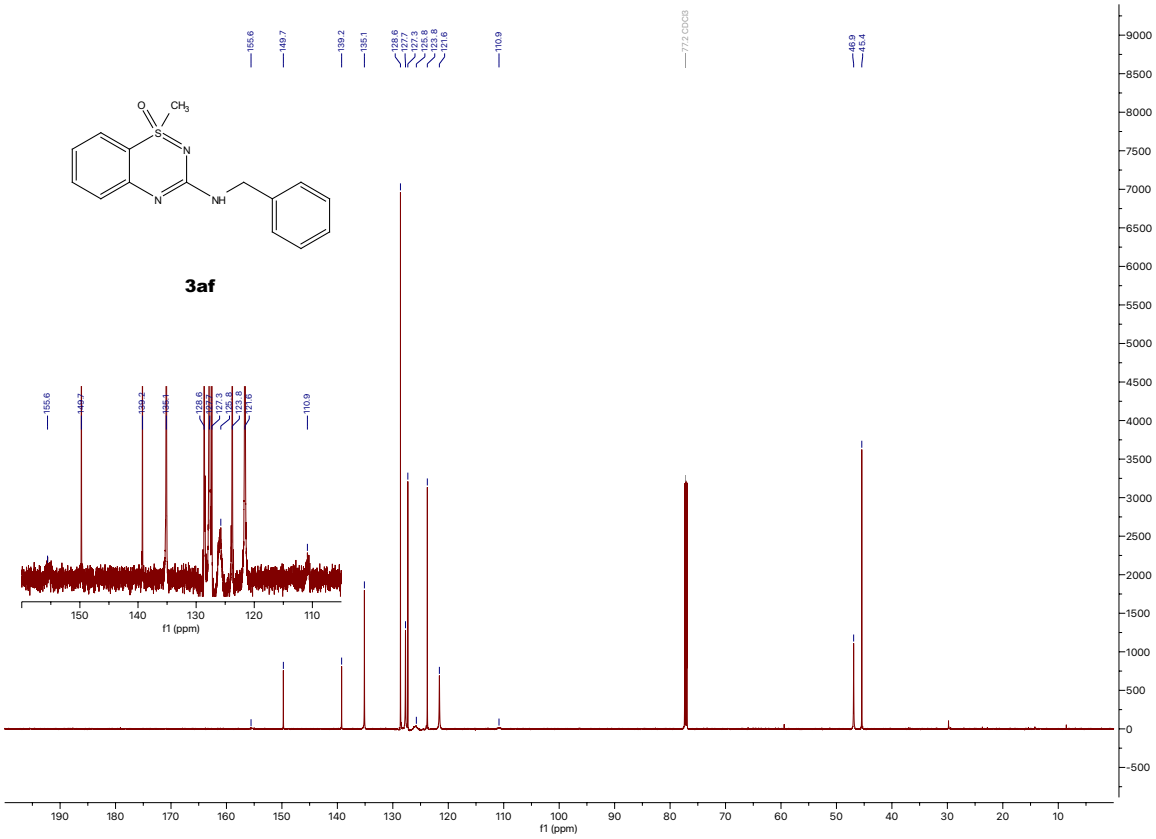
^{13}C {^{1}H} NMR spectrum of compound **3ae** (151 MHz, $CDCl_3$)



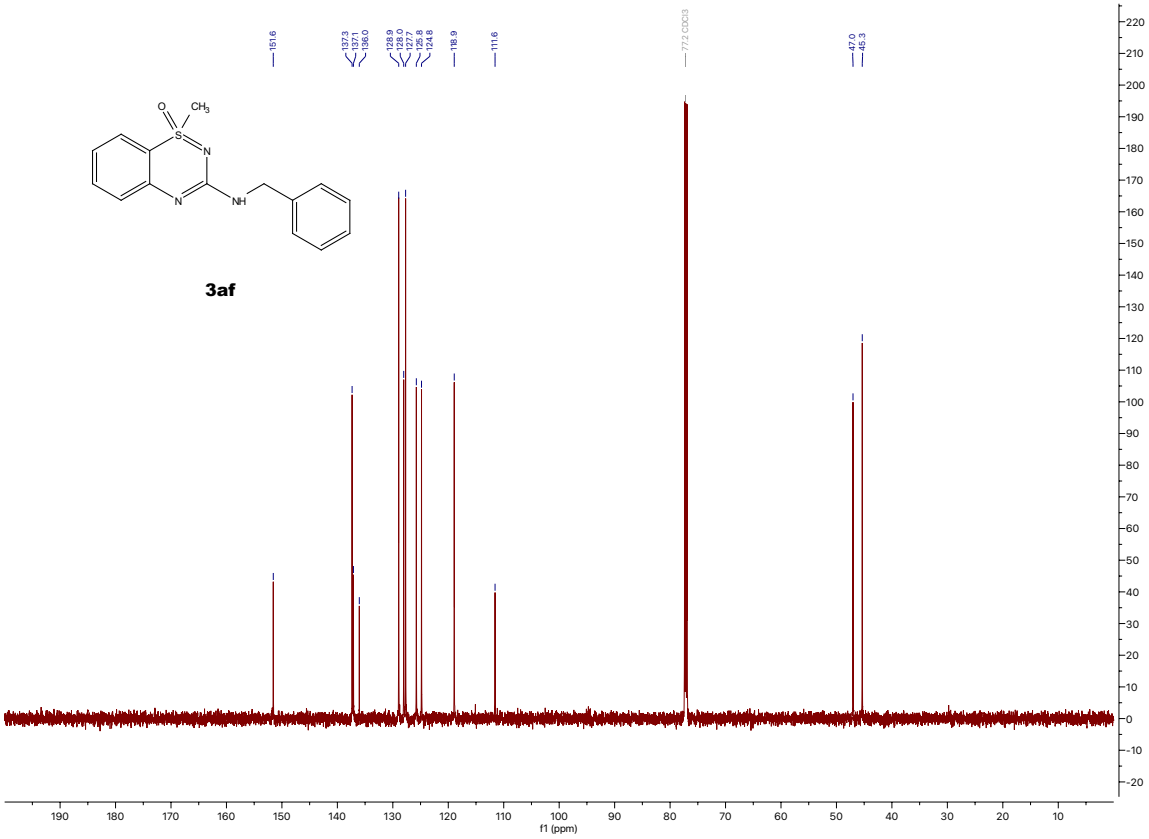
^{1}H NMR spectrum of compound **3af** (600 MHz, $CDCl_3$)



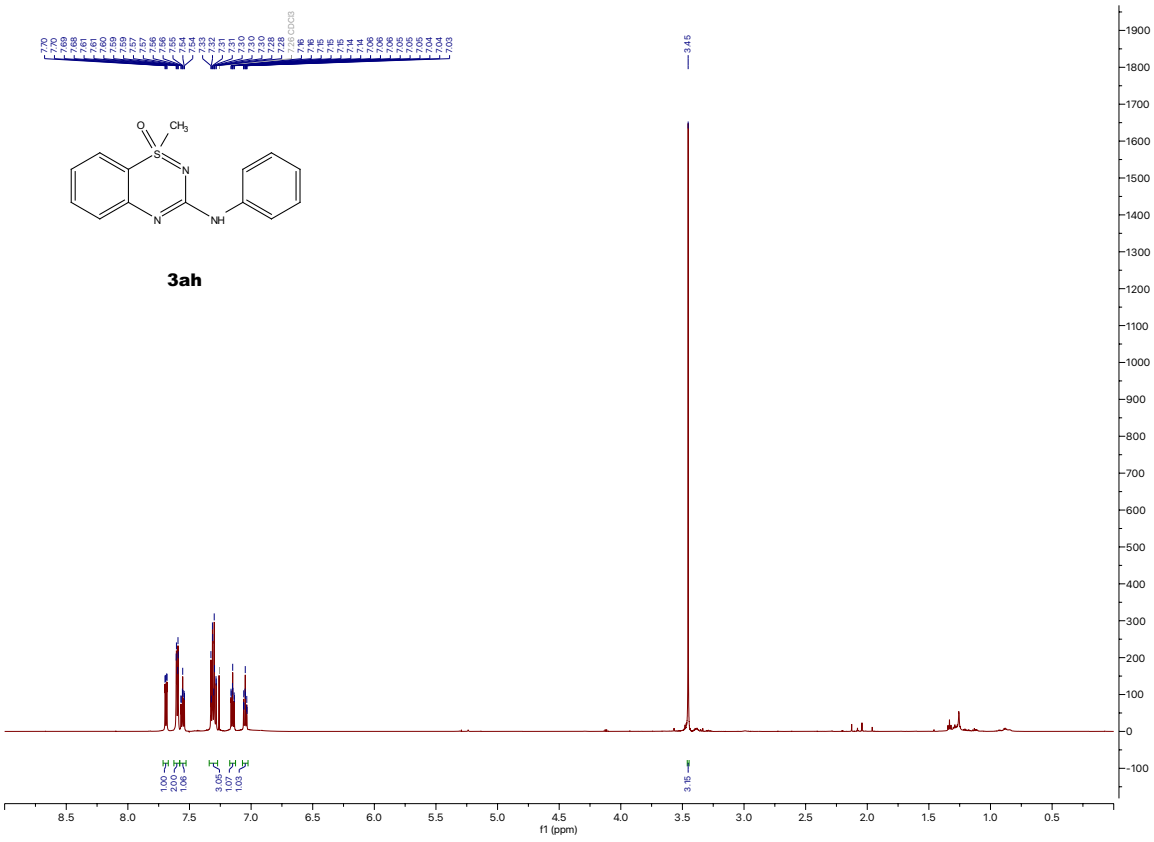
^{13}C {^{1}H} NMR spectrum of compound **3af** (151 MHz, $CDCl_3$)



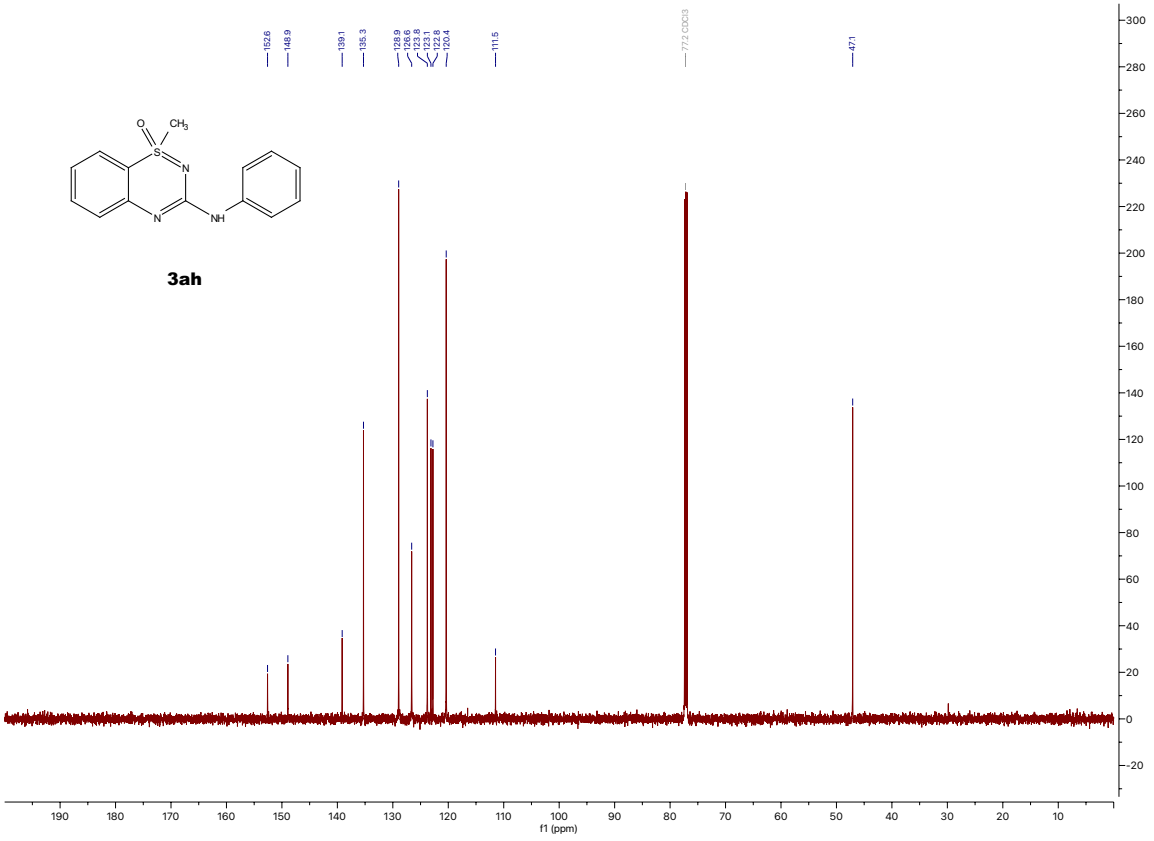
^{13}C {^{1}H} NMR spectrum of compound **3af** (151 MHz, $CDCl_3$, HCl)



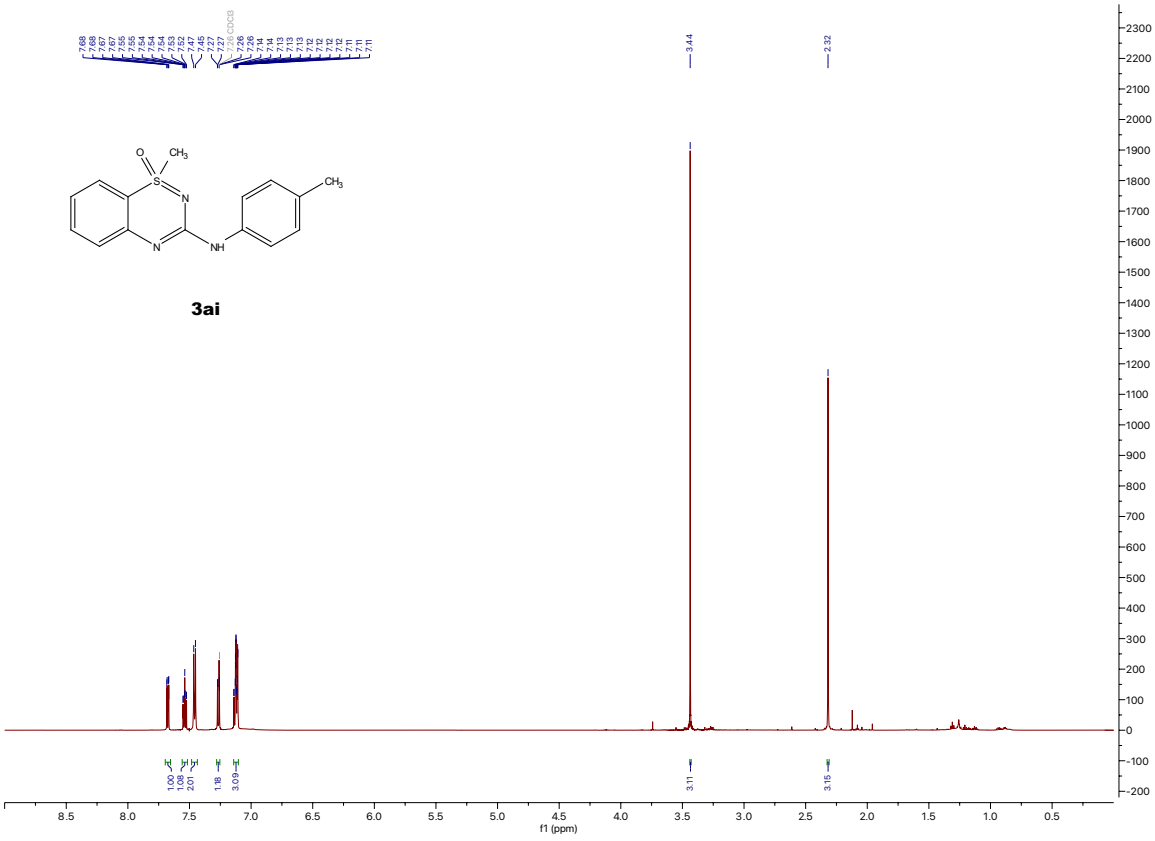
^{1}H NMR spectrum of compound **3ah** (600 MHz, $CDCl_3$)



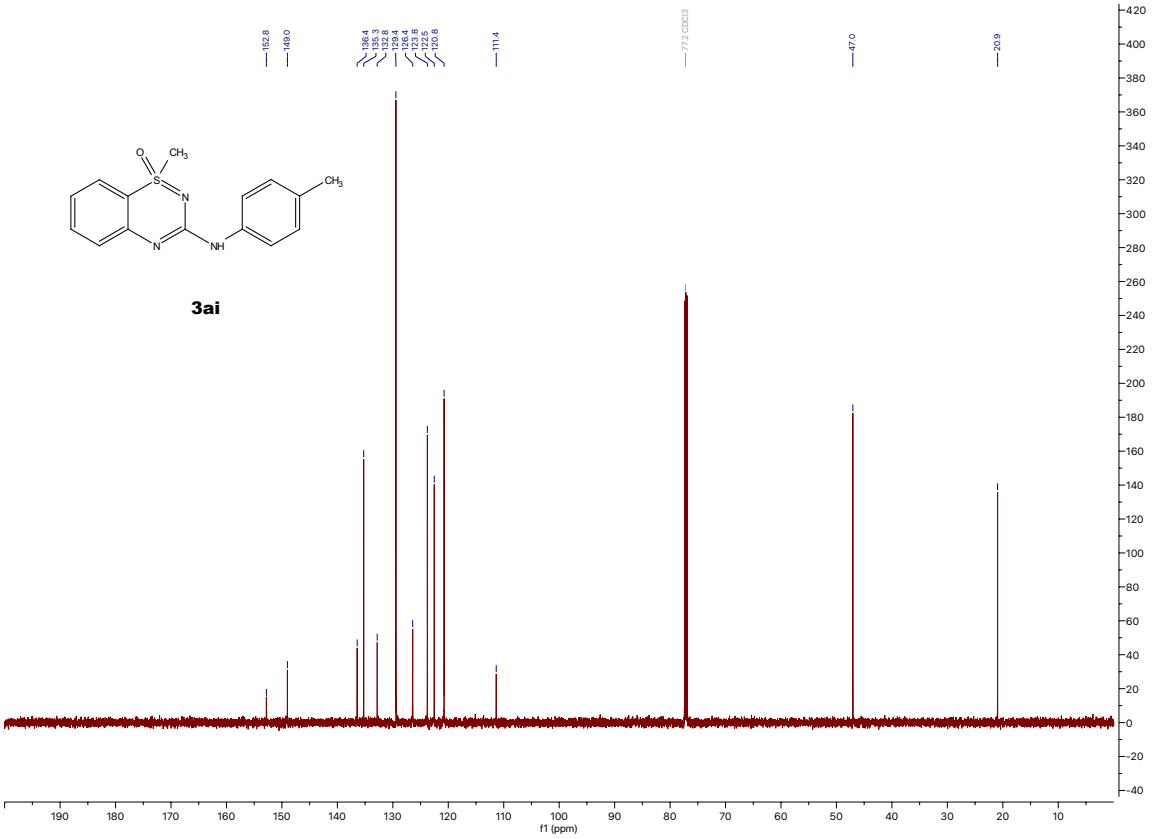
^{13}C {^{1}H} NMR spectrum of compound **3ah** (151 MHz, $CDCl_3$)



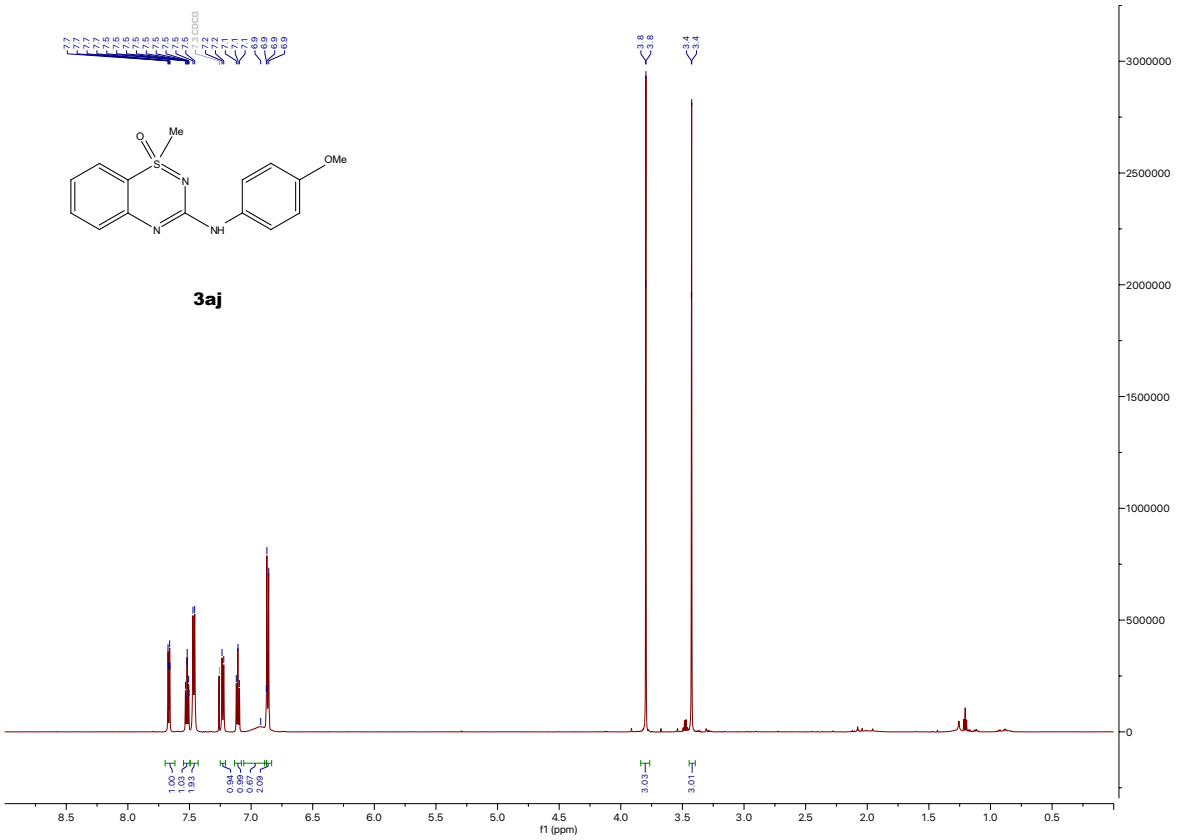
^{1}H NMR spectrum of compound **3ai** (600 MHz, $CDCl_3$)



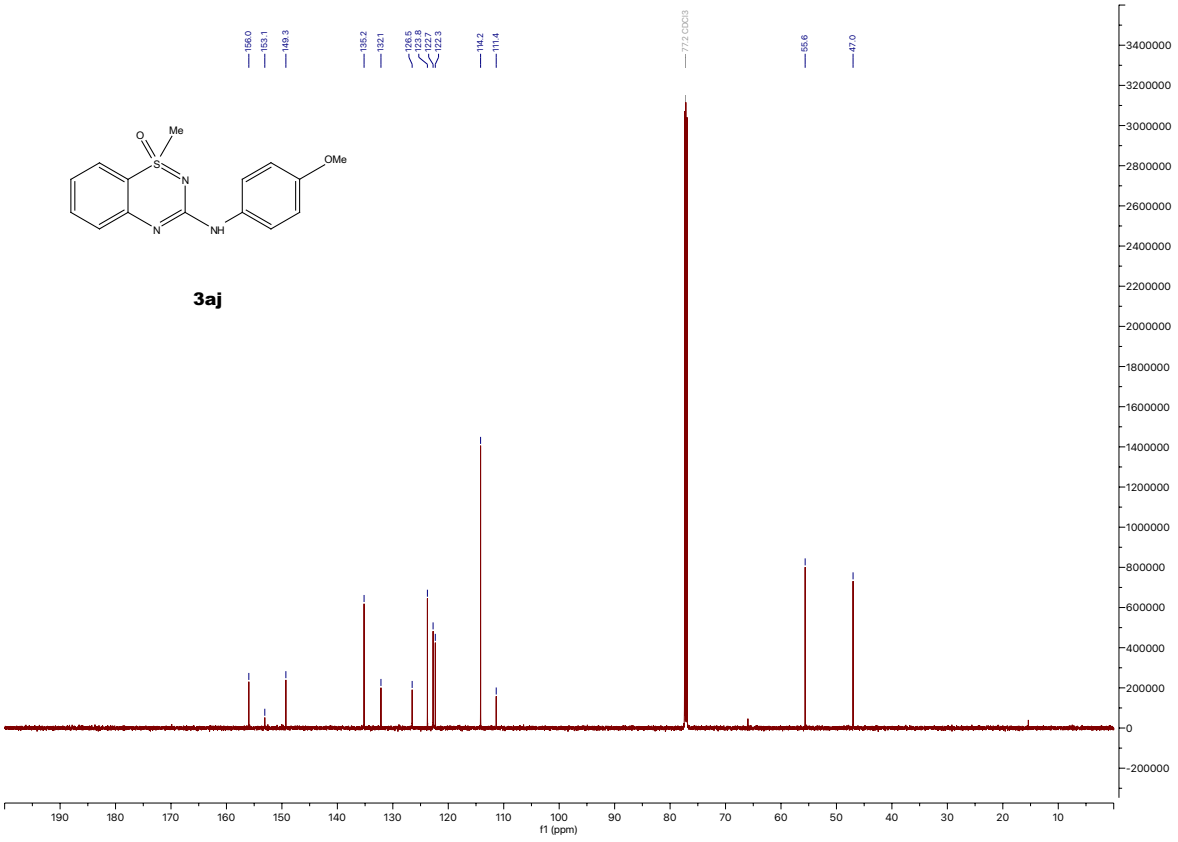
^{13}C {^{1}H} NMR spectrum of compound **3ai** (151 MHz, $CDCl_3$)



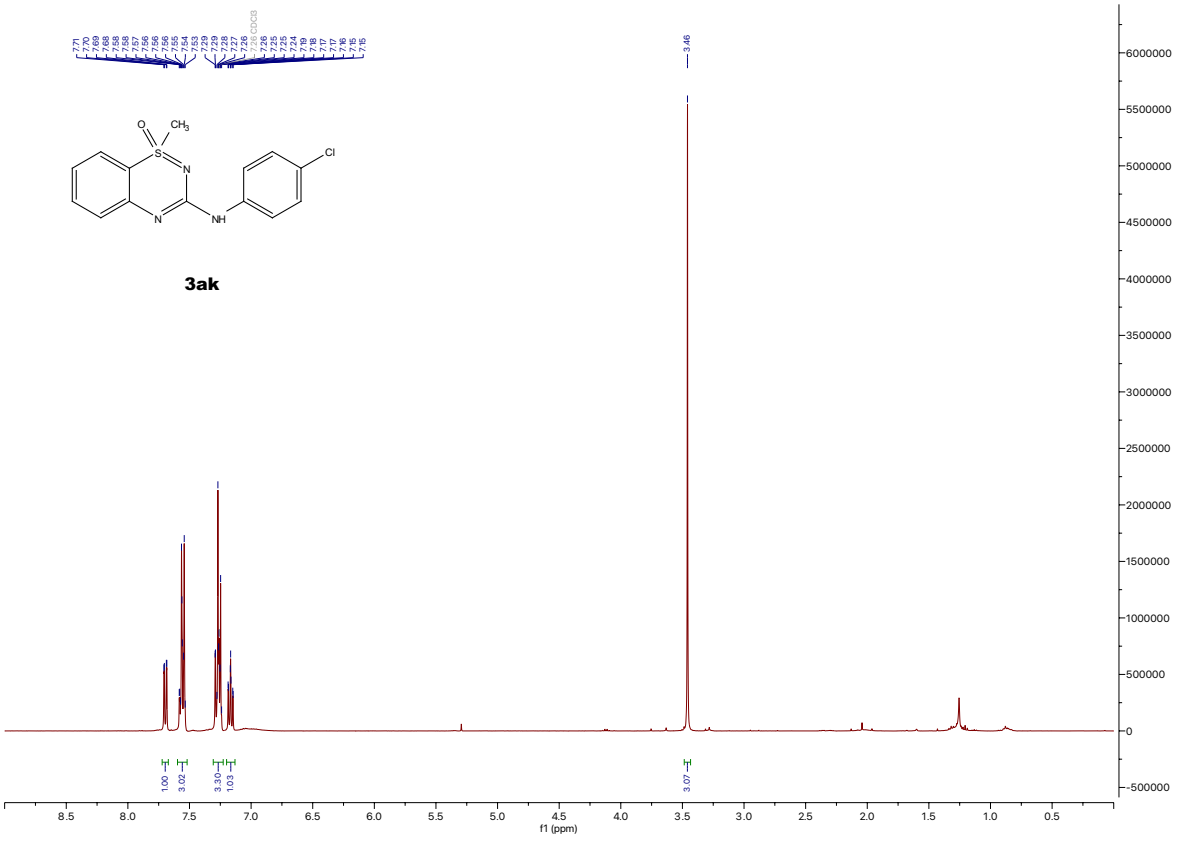
^{1}H NMR spectrum of compound **3aj** (600 MHz, $CDCl_3$)



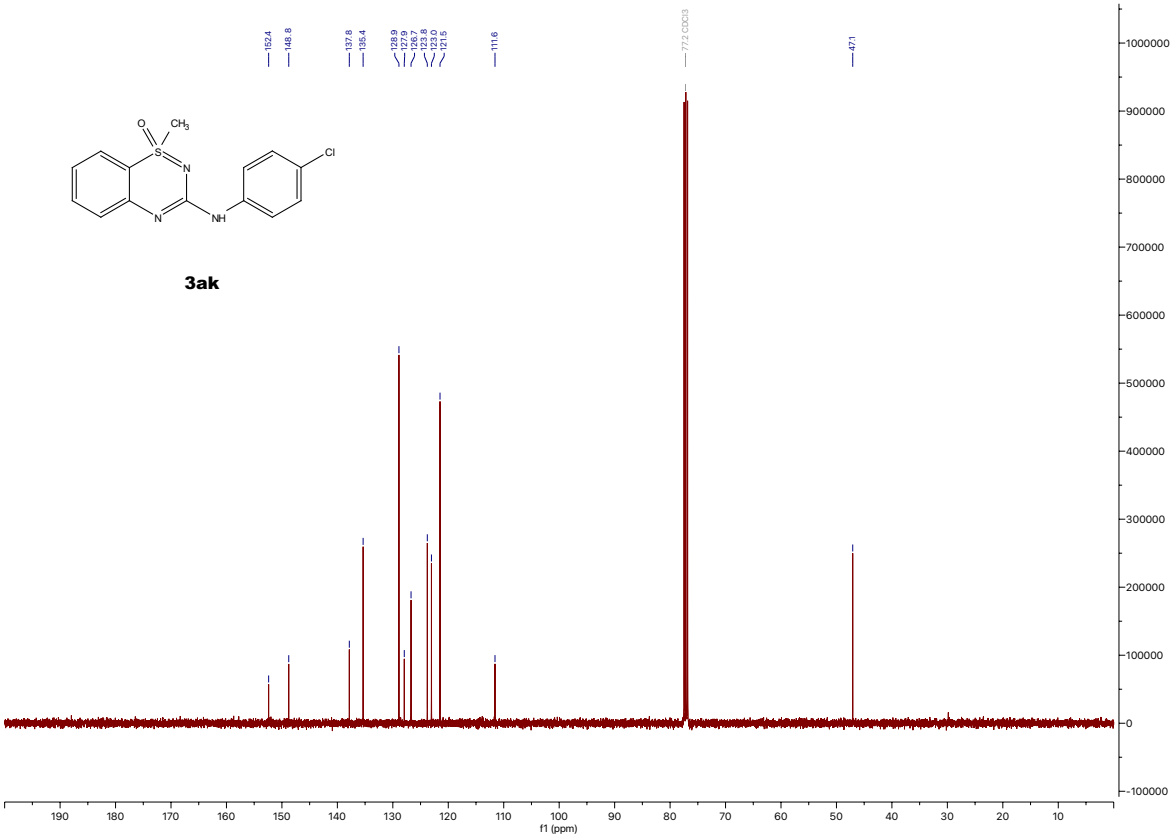
^{13}C {^{1}H} NMR spectrum of compound **3aj** (151 MHz, $CDCl_3$)



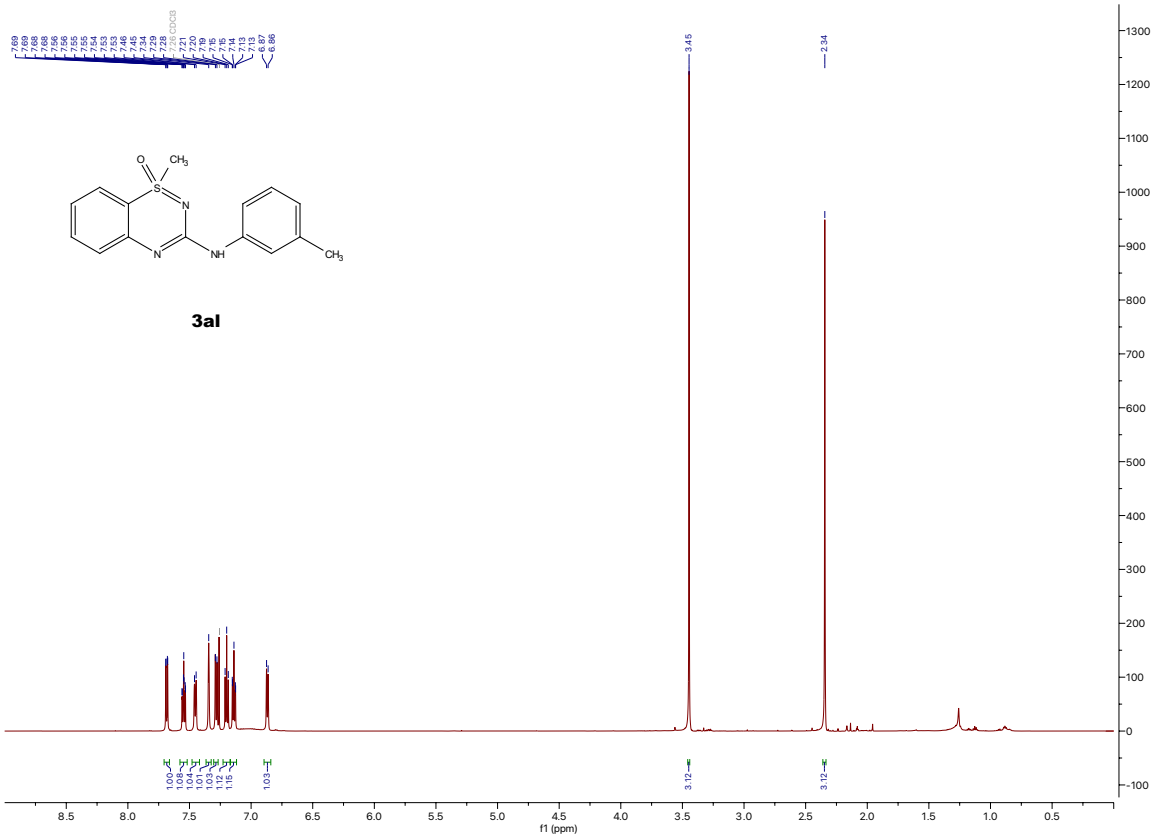
^{1}H NMR spectrum of compound **3ak** (600 MHz, $CDCl_3$)



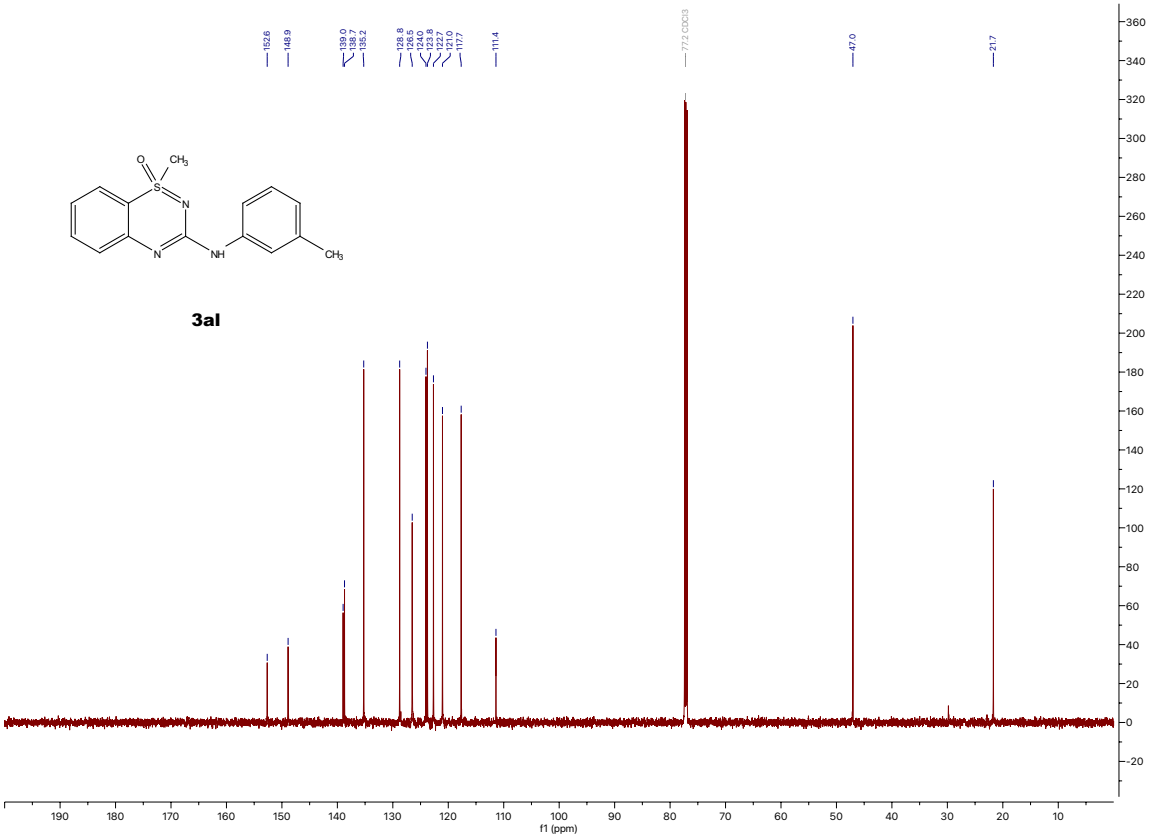
^{13}C {^{1}H} NMR spectrum of compound **3ak** (151 MHz, $CDCl_3$)



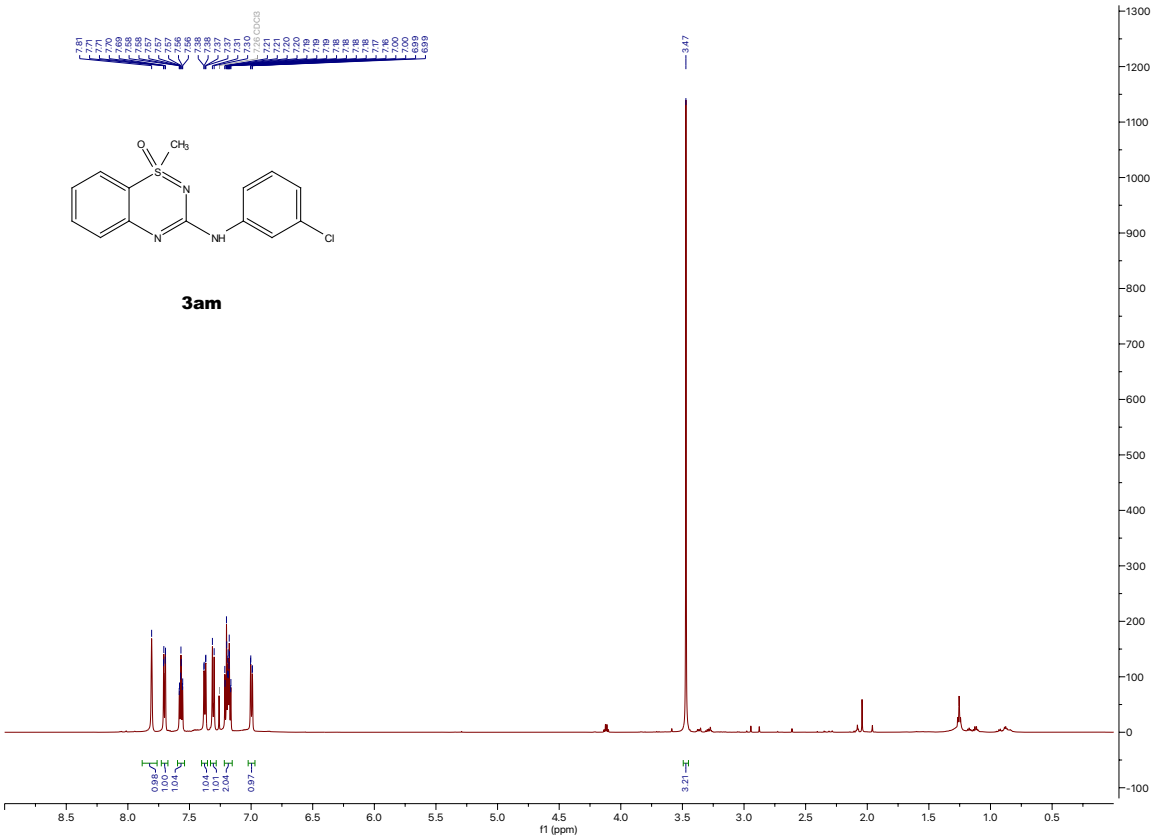
^{1}H NMR spectrum of compound **3al** (600 MHz, $CDCl_3$)



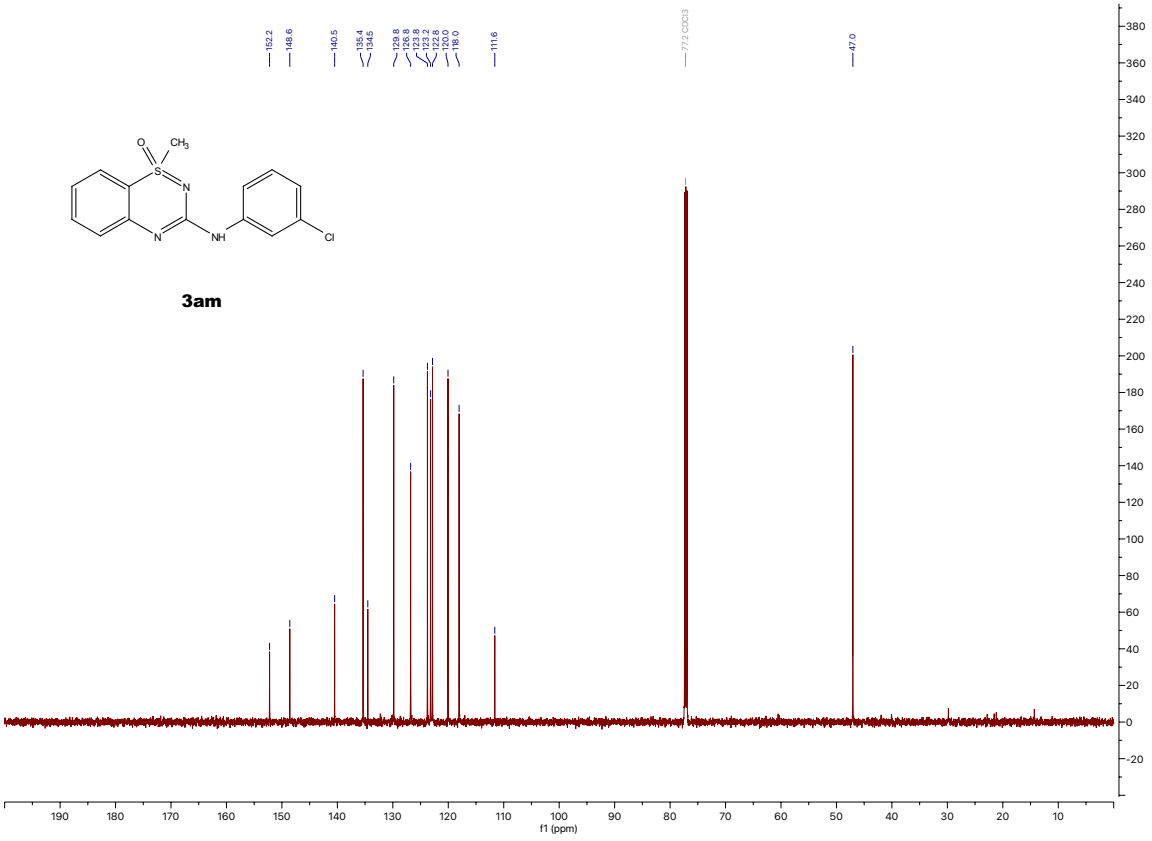
^{13}C {^{1}H} NMR spectrum of compound **3al** (151 MHz, $CDCl_3$)



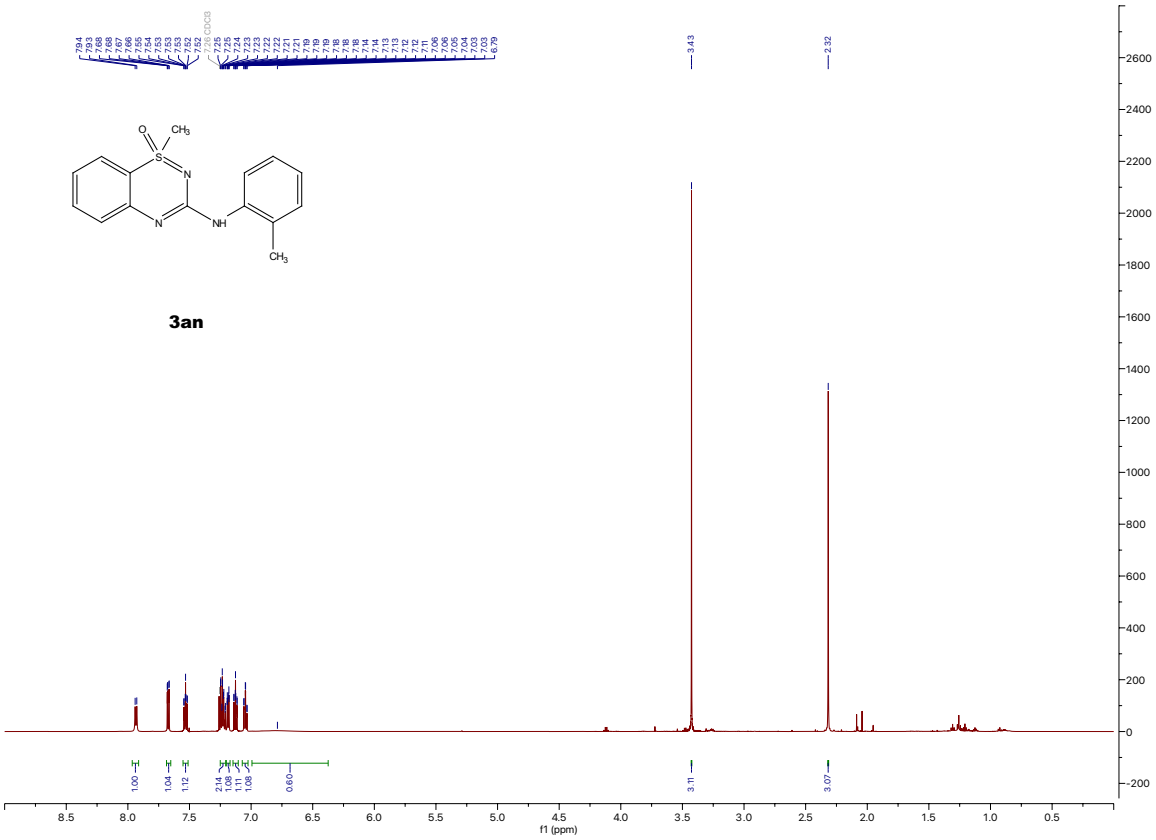
^{1}H NMR spectrum of compound **3am** (600 MHz, $CDCl_3$)



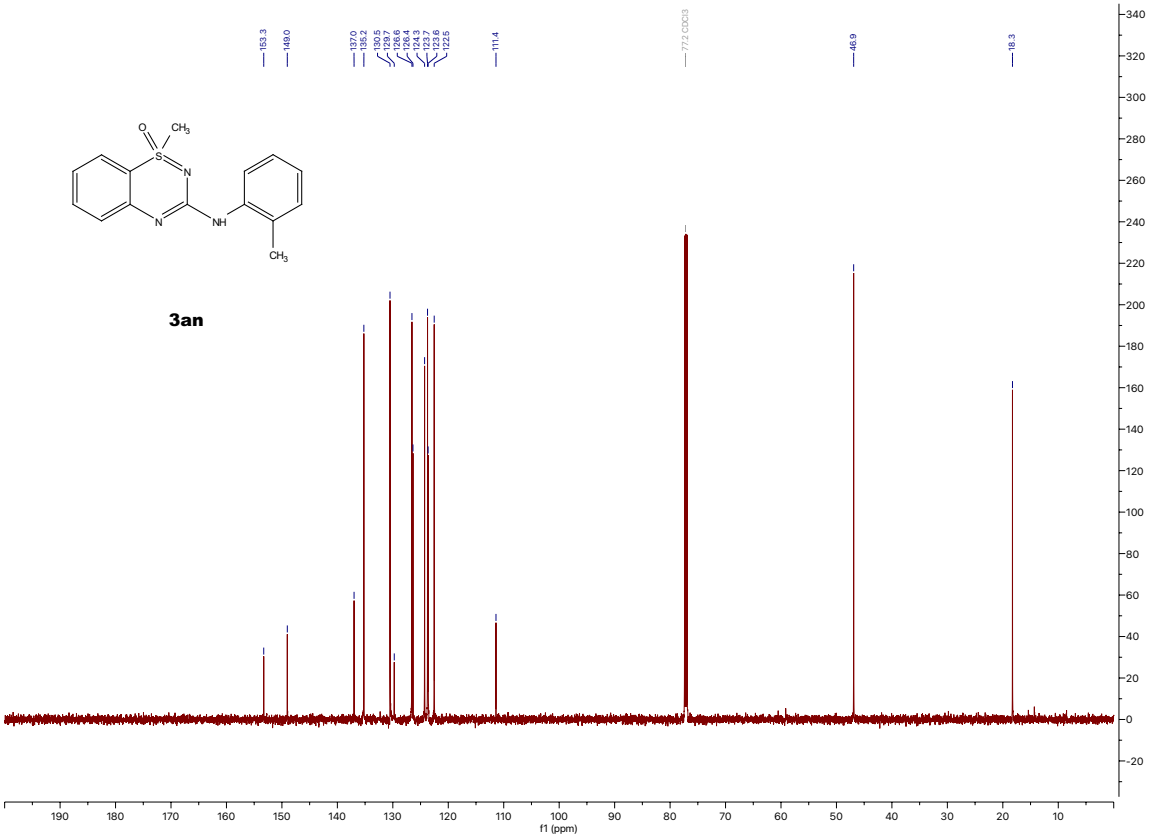
^{13}C {^{1}H} NMR spectrum of compound **3am** (151 MHz, $CDCl_3$)



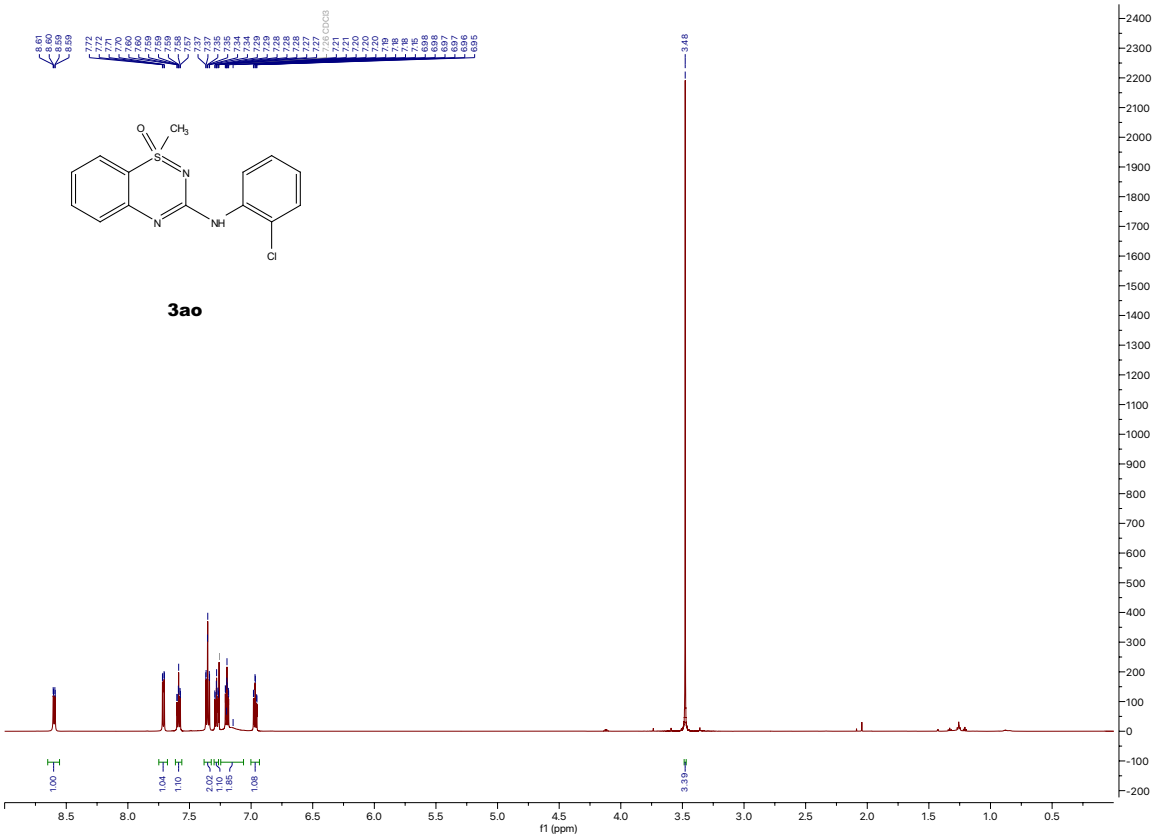
^{1}H NMR spectrum of compound **3an** (600 MHz, $CDCl_3$)



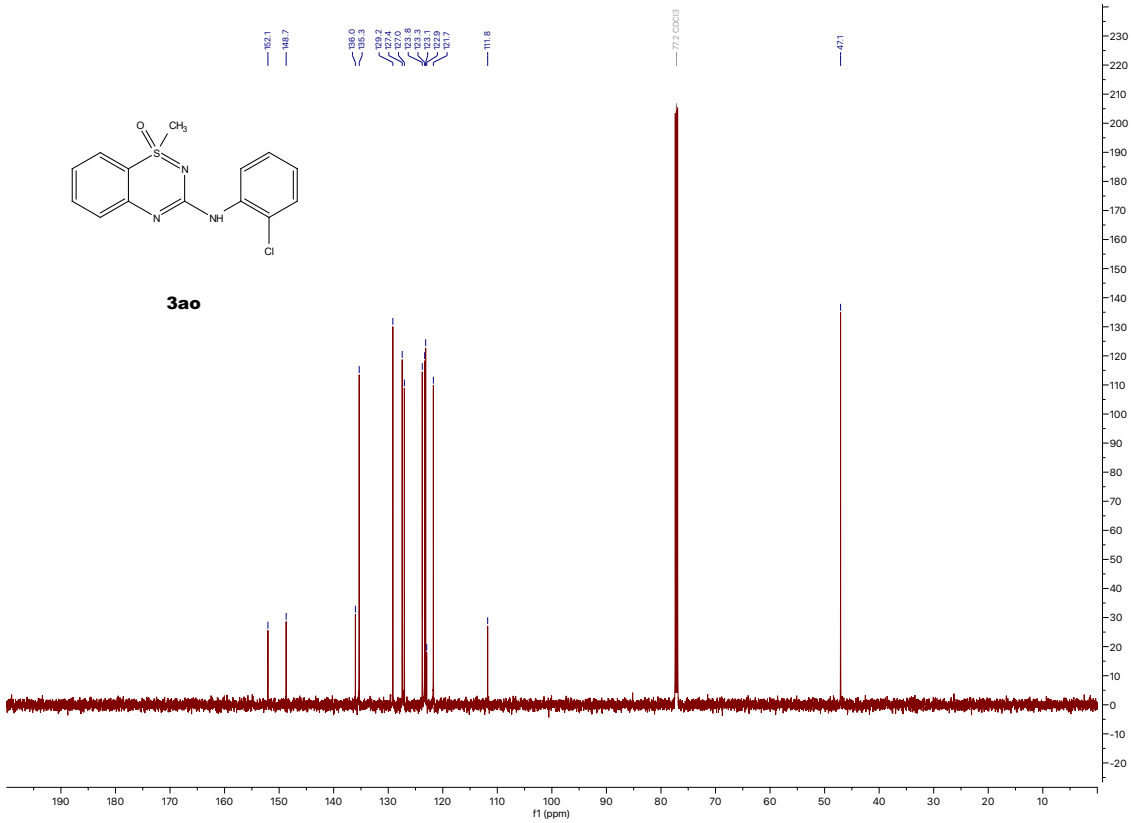
^{13}C {^{1}H} NMR spectrum of compound **3an** (151 MHz, $CDCl_3$)



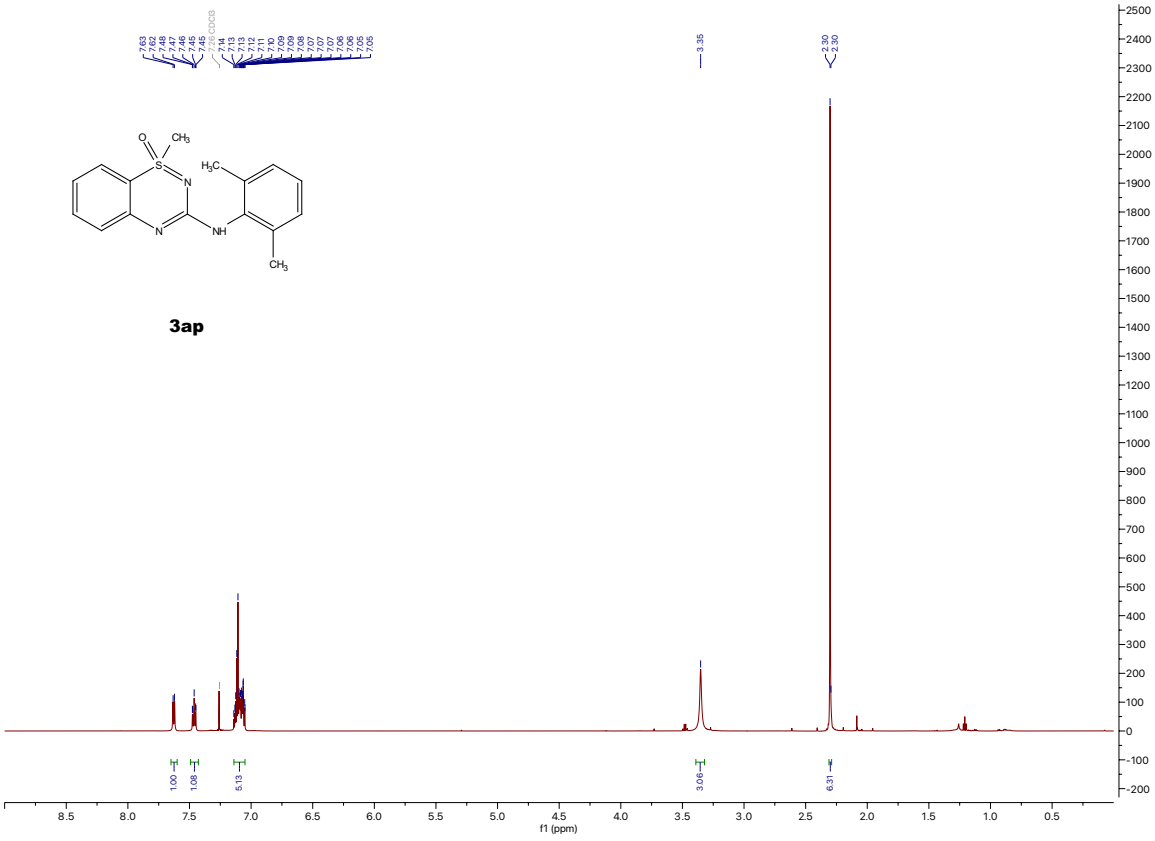
^{1}H NMR spectrum of compound **3ao** (600 MHz, $CDCl_3$)



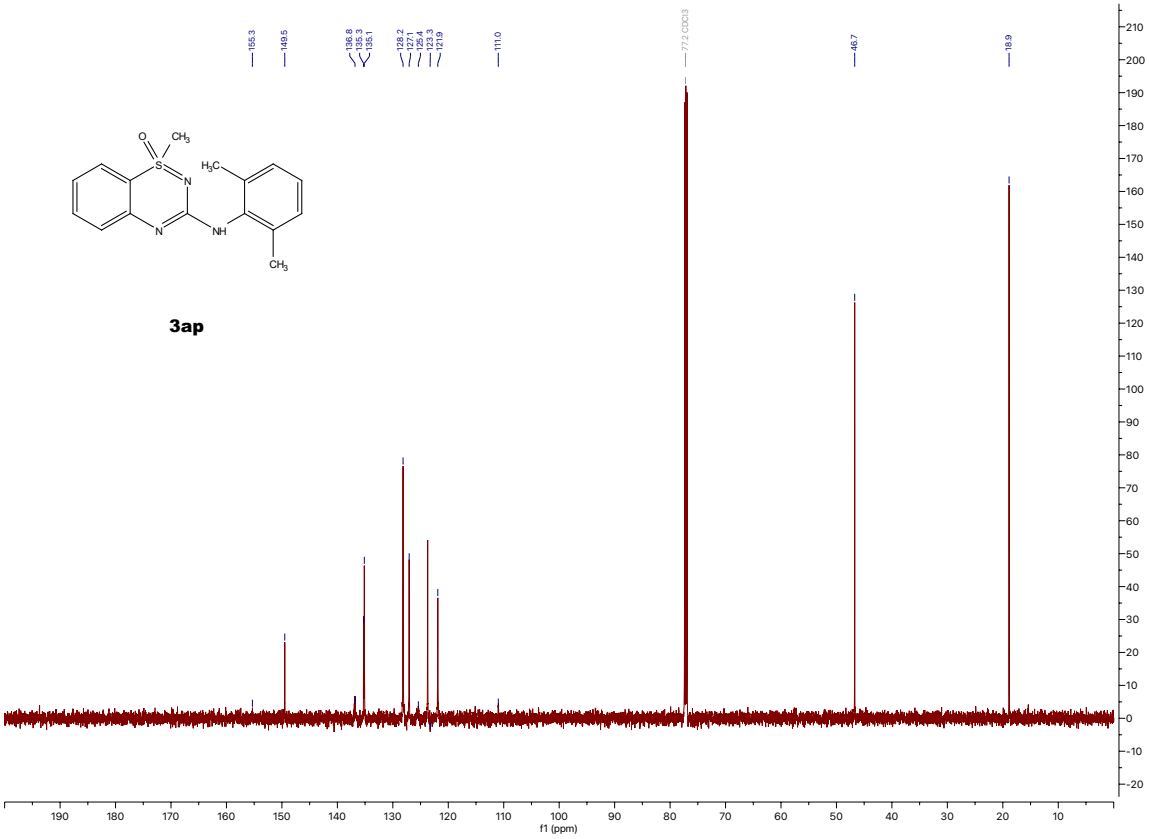
^{13}C {^{1}H} NMR spectrum of compound **3ao** (151 MHz, $CDCl_3$)



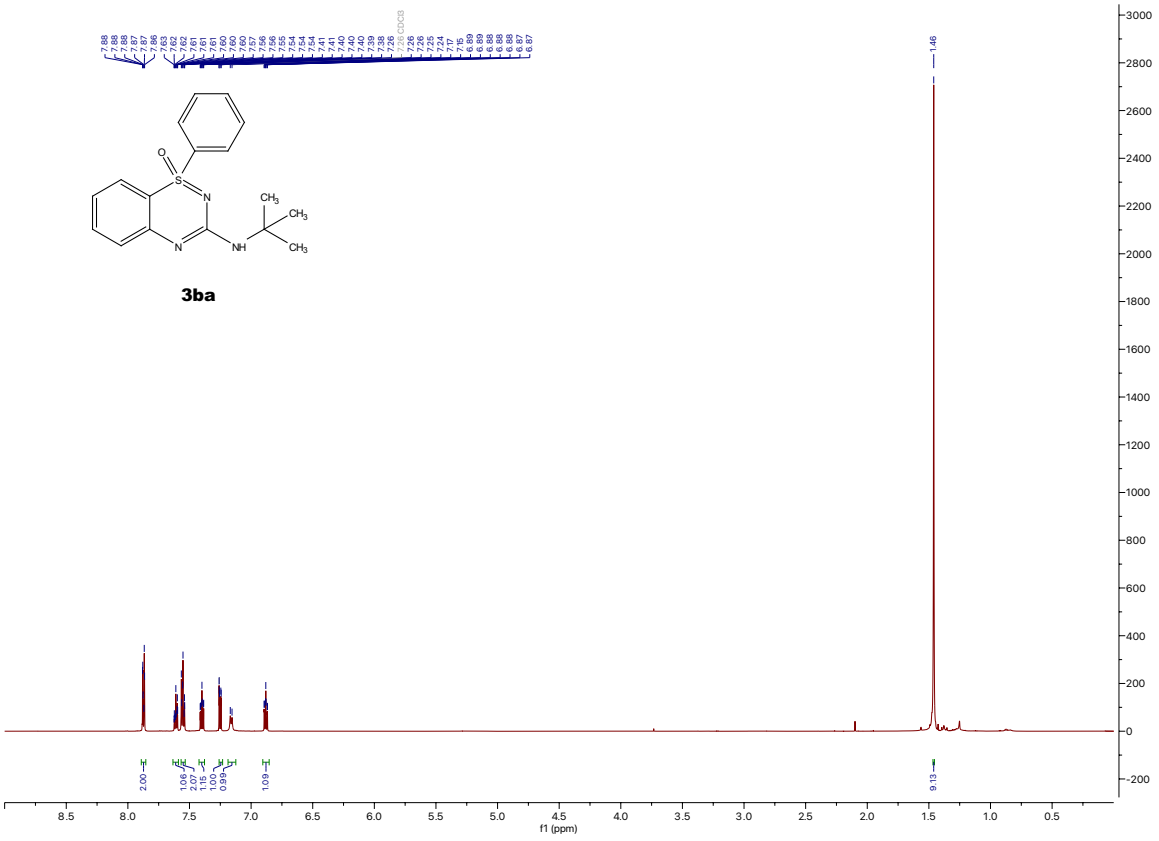
^{1}H NMR spectrum of compound **3ap** (600 MHz, $CDCl_3$)



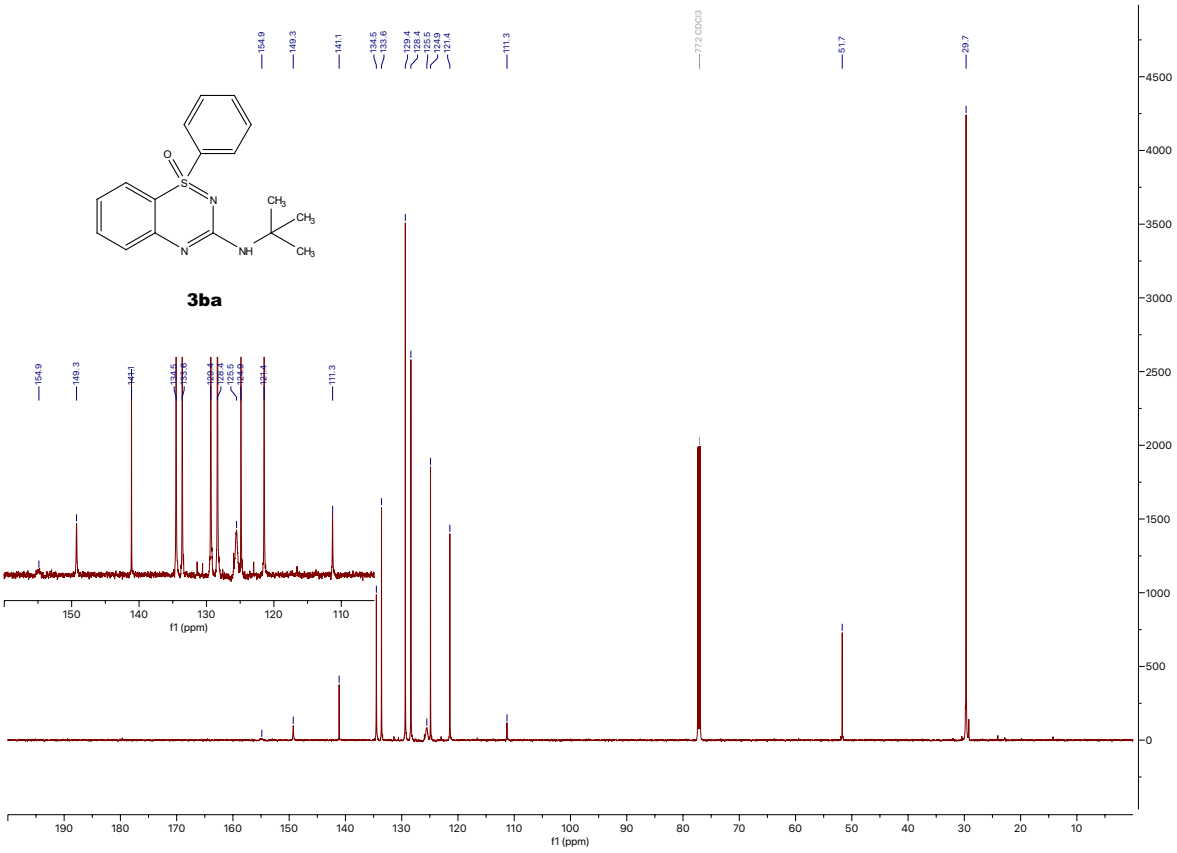
^{13}C {^{1}H} NMR spectrum of compound **3ap** (151 MHz, $CDCl_3$)



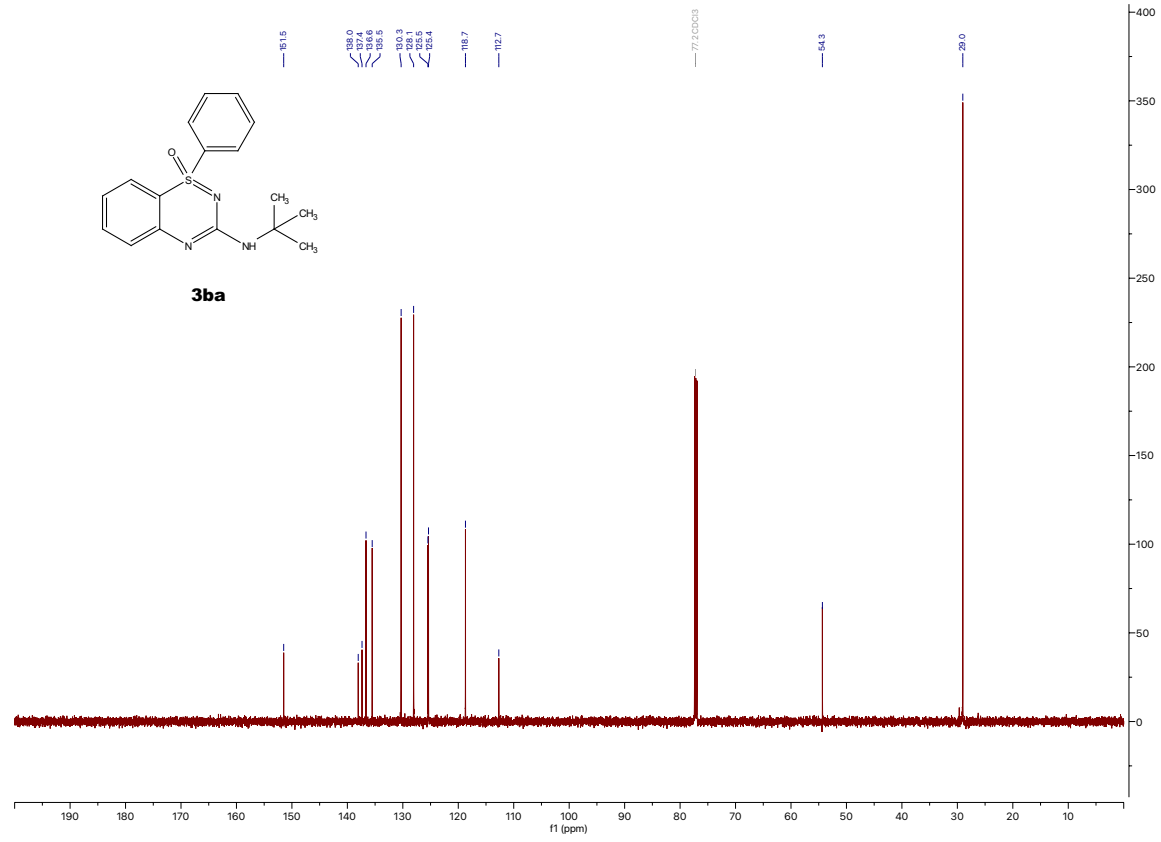
^{1}H NMR spectrum of compound **3ba** (600 MHz, $CDCl_3$)



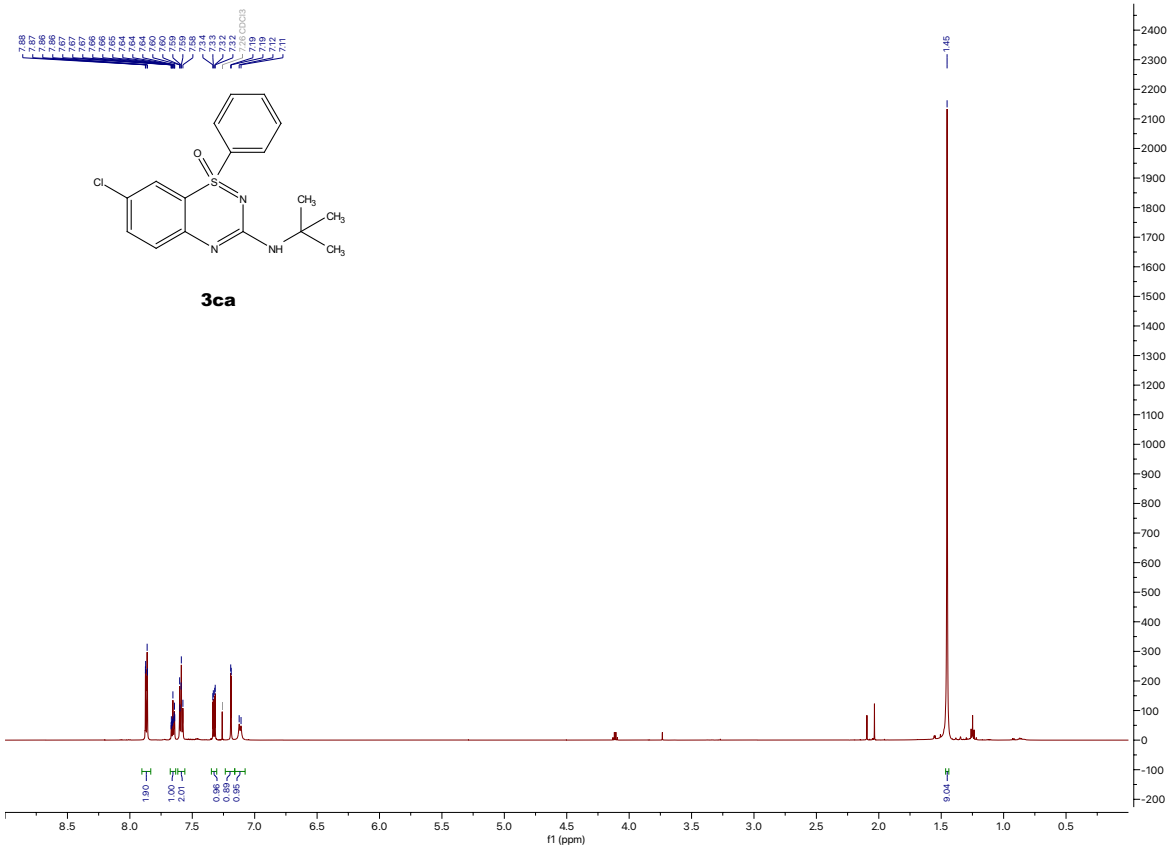
^{13}C {^{1}H} NMR spectrum of compound **3ba** (151 MHz, $CDCl_3$)



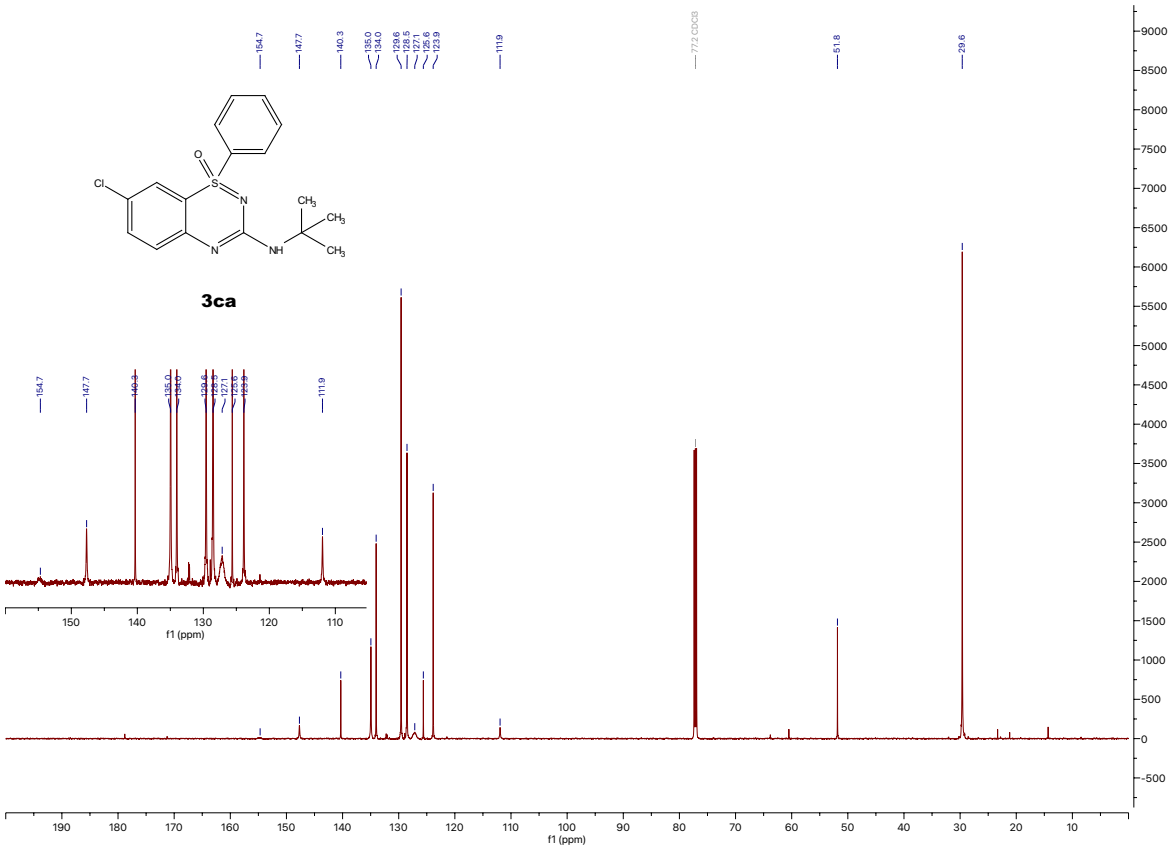
^{13}C {^{1}H} NMR spectrum of compound **3ba** (151 MHz, $CDCl_3$, HCl)



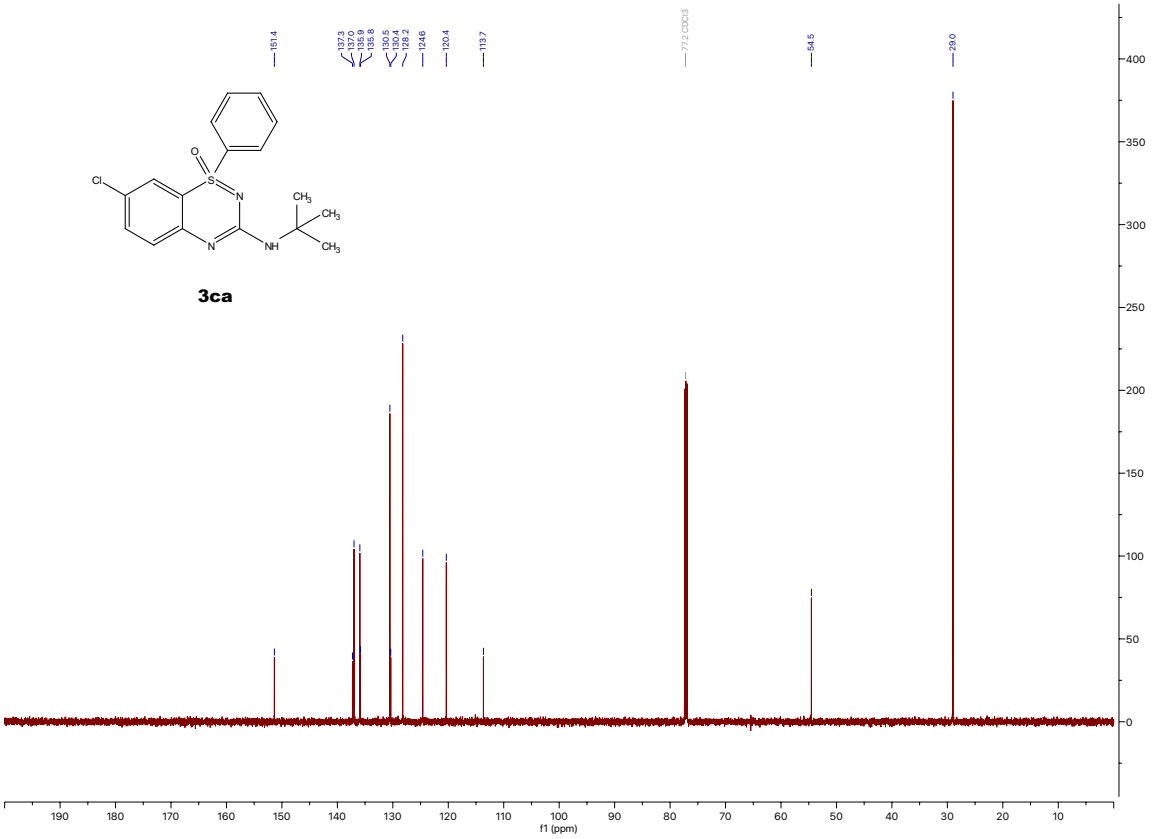
^{1}H NMR spectrum of compound **3ca** (600 MHz, $CDCl_3$)



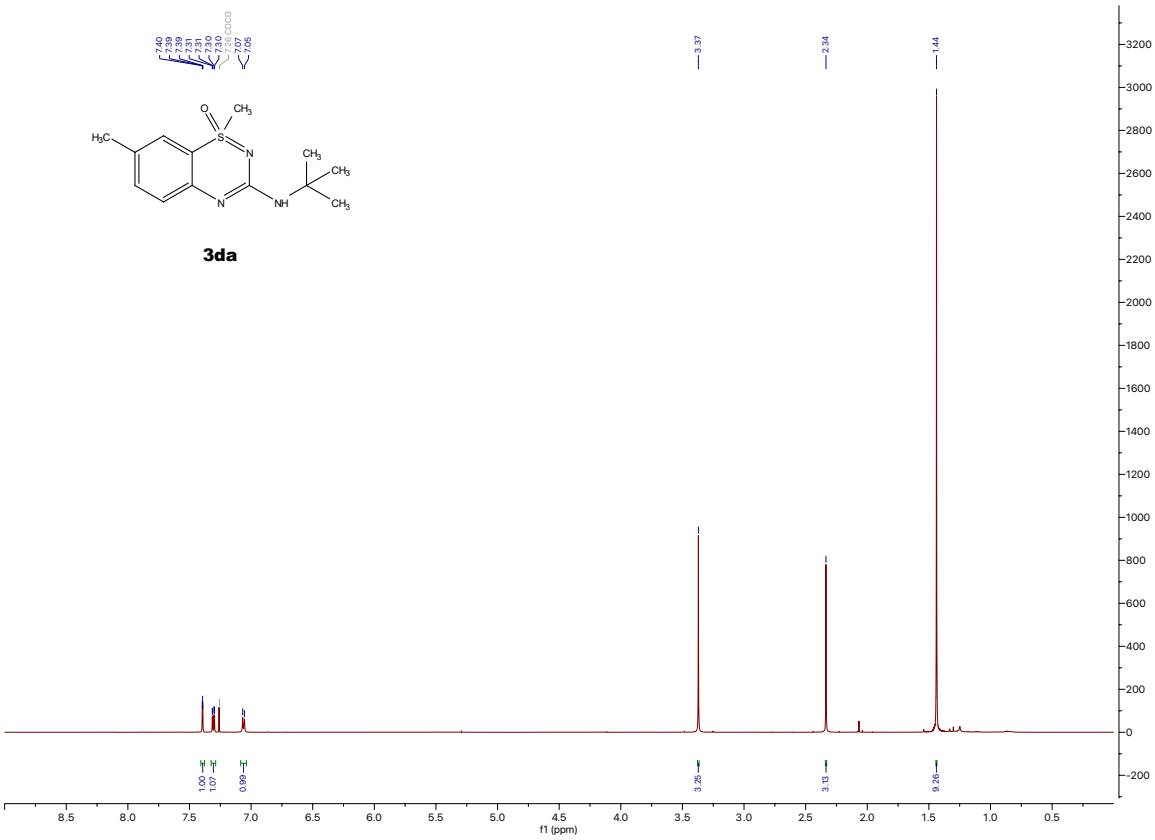
^{13}C {^{1}H} NMR spectrum of compound **3ca** (151 MHz, $CDCl_3$)



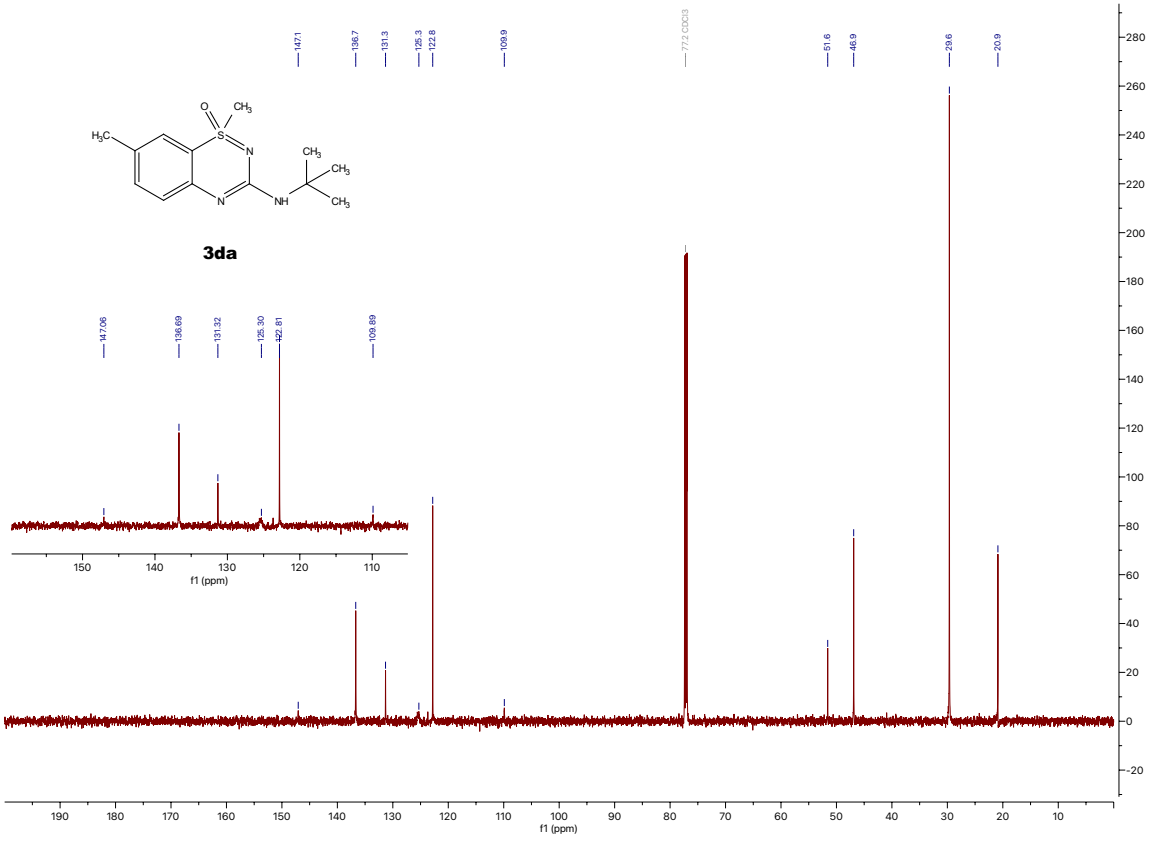
^{13}C {^{1}H} NMR spectrum of compound **3ca** (151 MHz, $CDCl_3$, HCl)



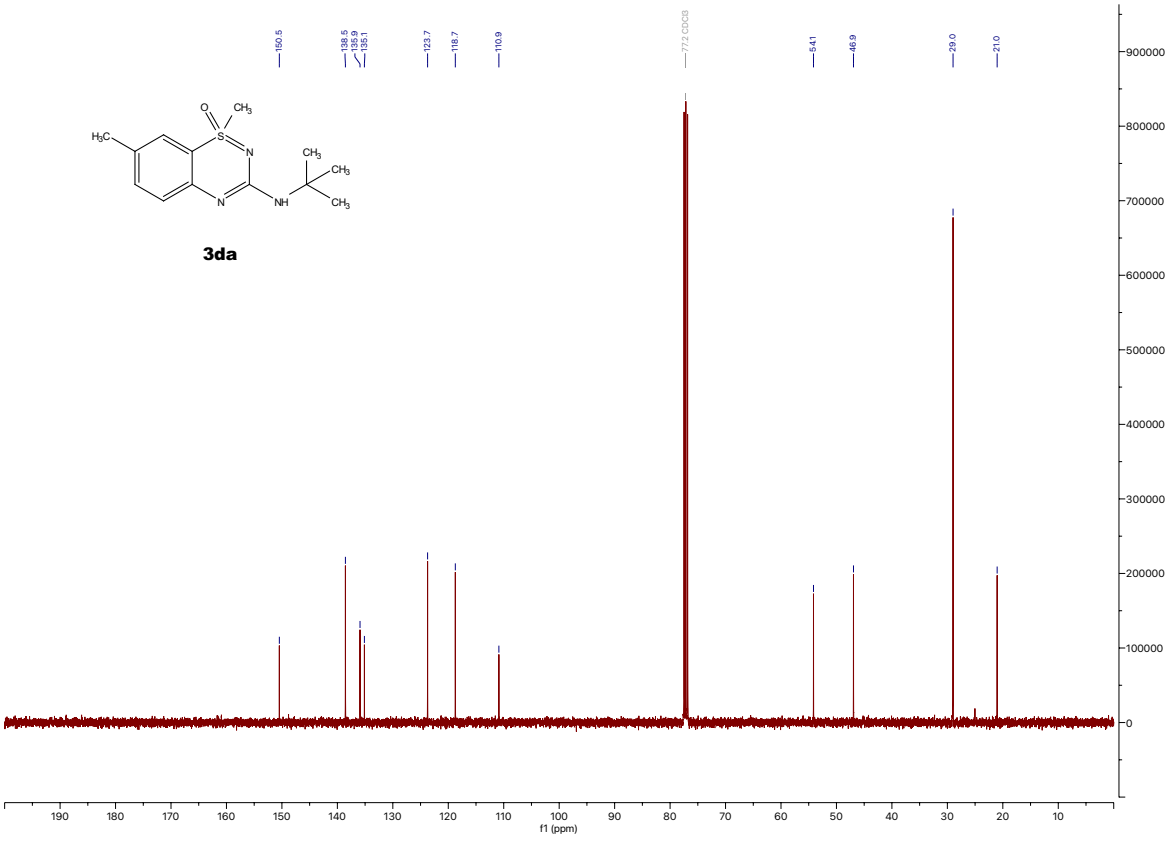
^{1}H NMR spectrum of compound **3da** (600 MHz, $CDCl_3$)



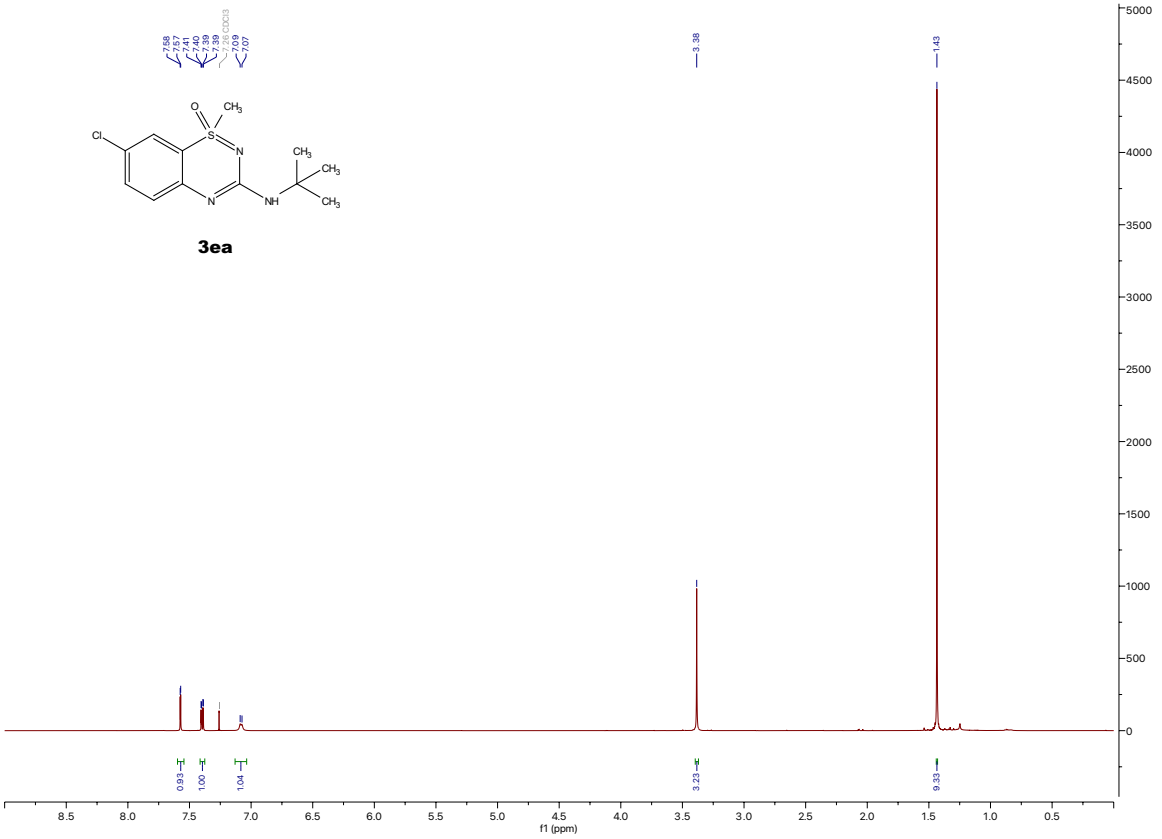
^{13}C {^{1}H} NMR spectrum of compound **3da** (151 MHz, $CDCl_3$)



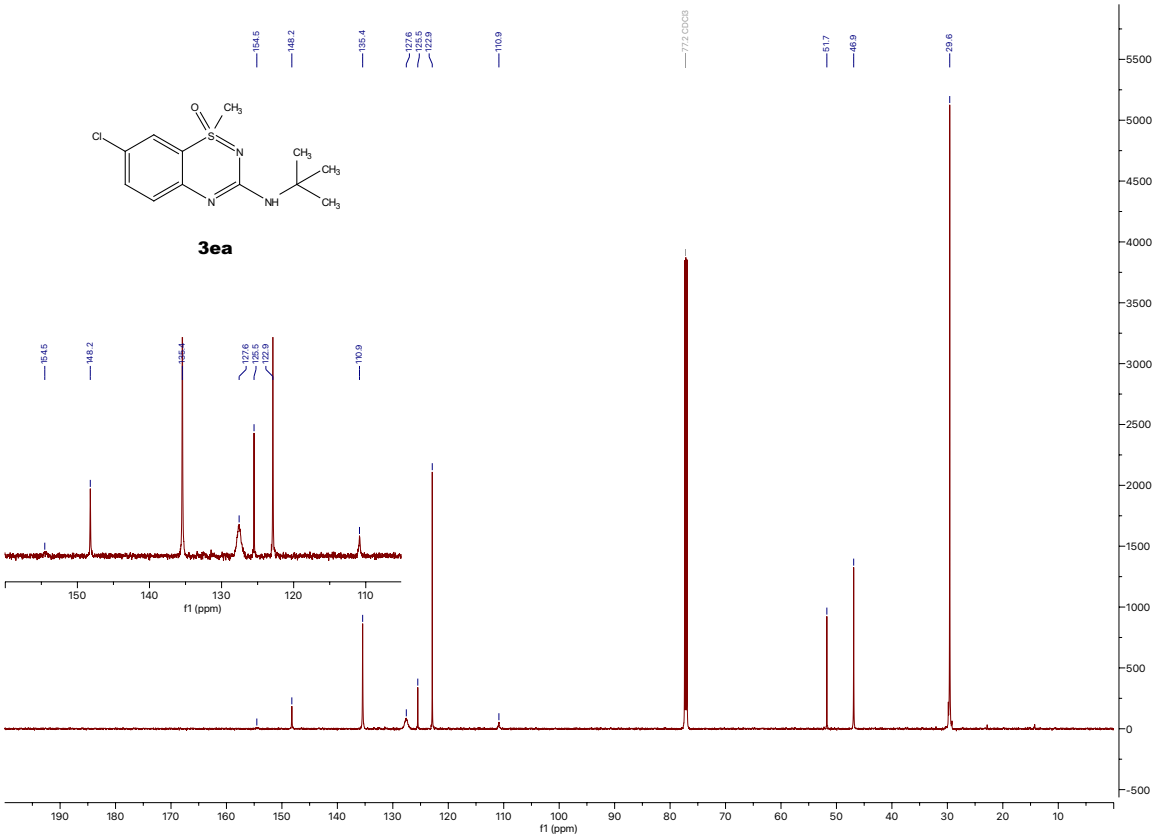
^{13}C {^{1}H} NMR spectrum of compound **3da** (151 MHz, $CDCl_3$, HCl)



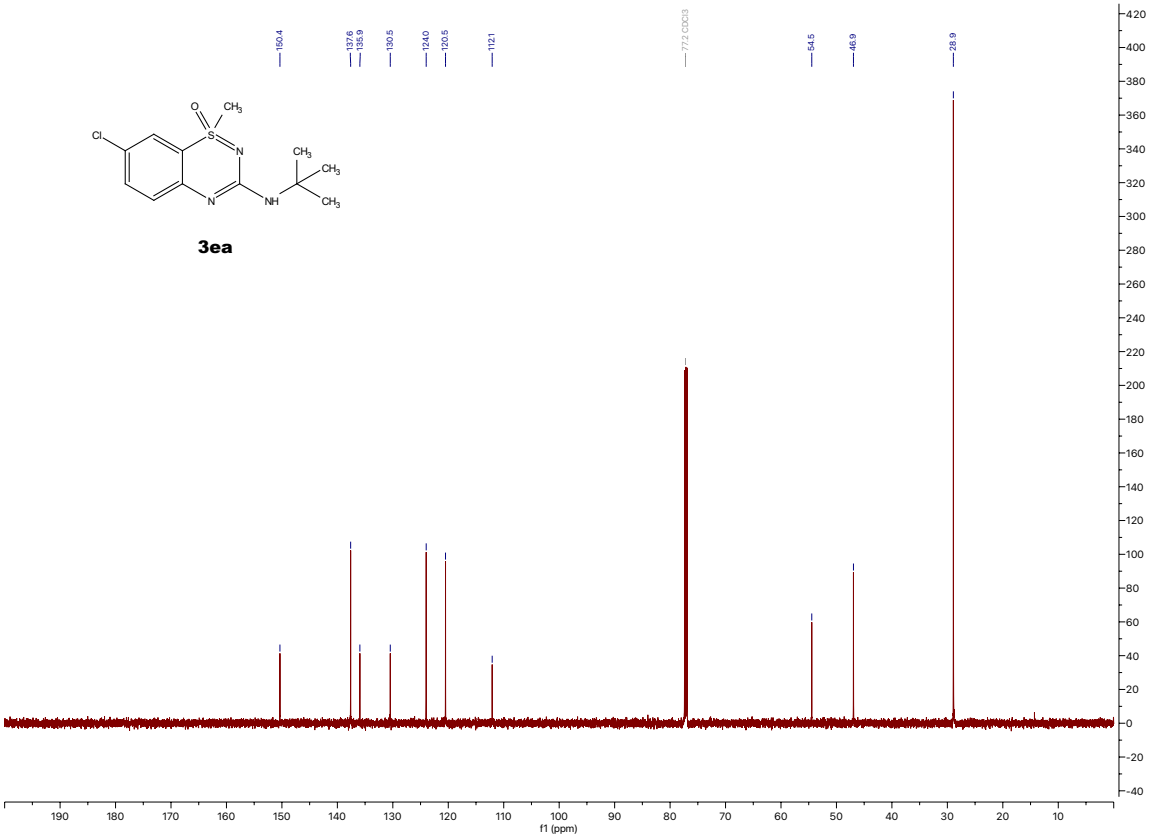
^{1}H NMR spectrum of compound **3ea** (600 MHz, $CDCl_3$)



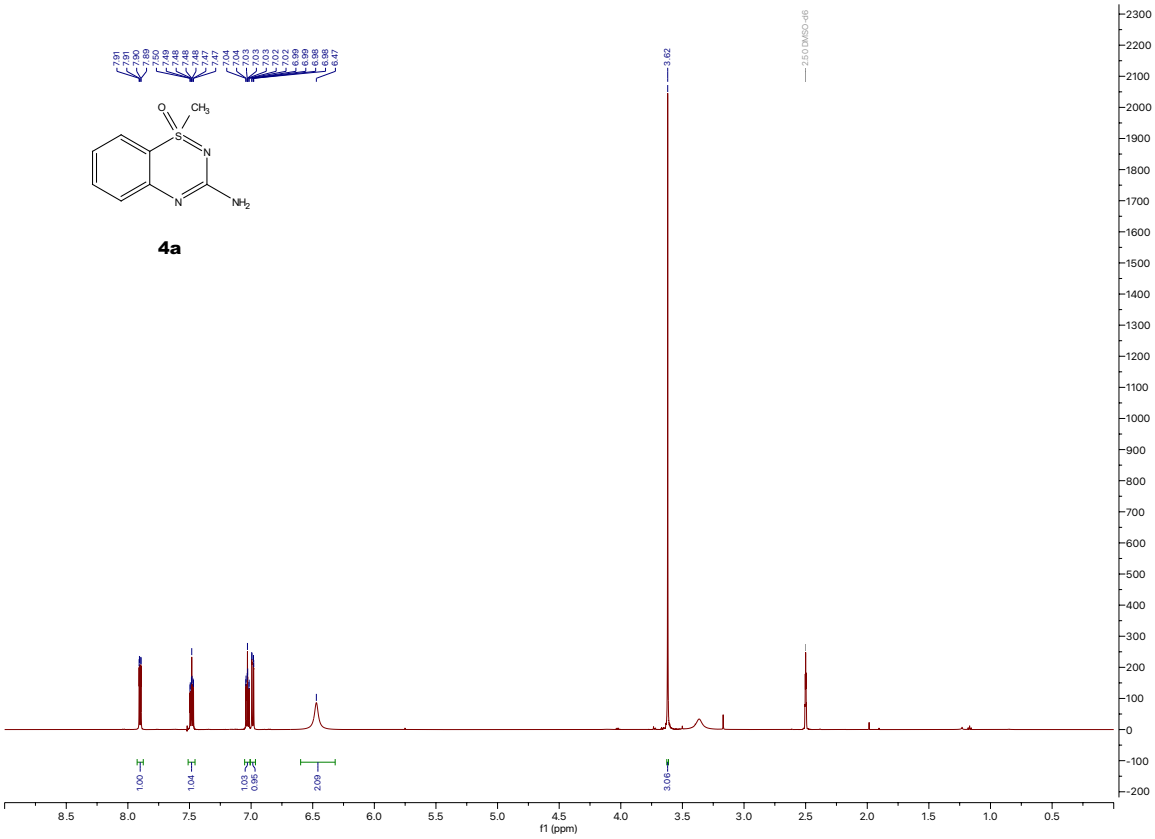
^{13}C {^{1}H} NMR spectrum of compound **3ea** (151 MHz, $CDCl_3$)



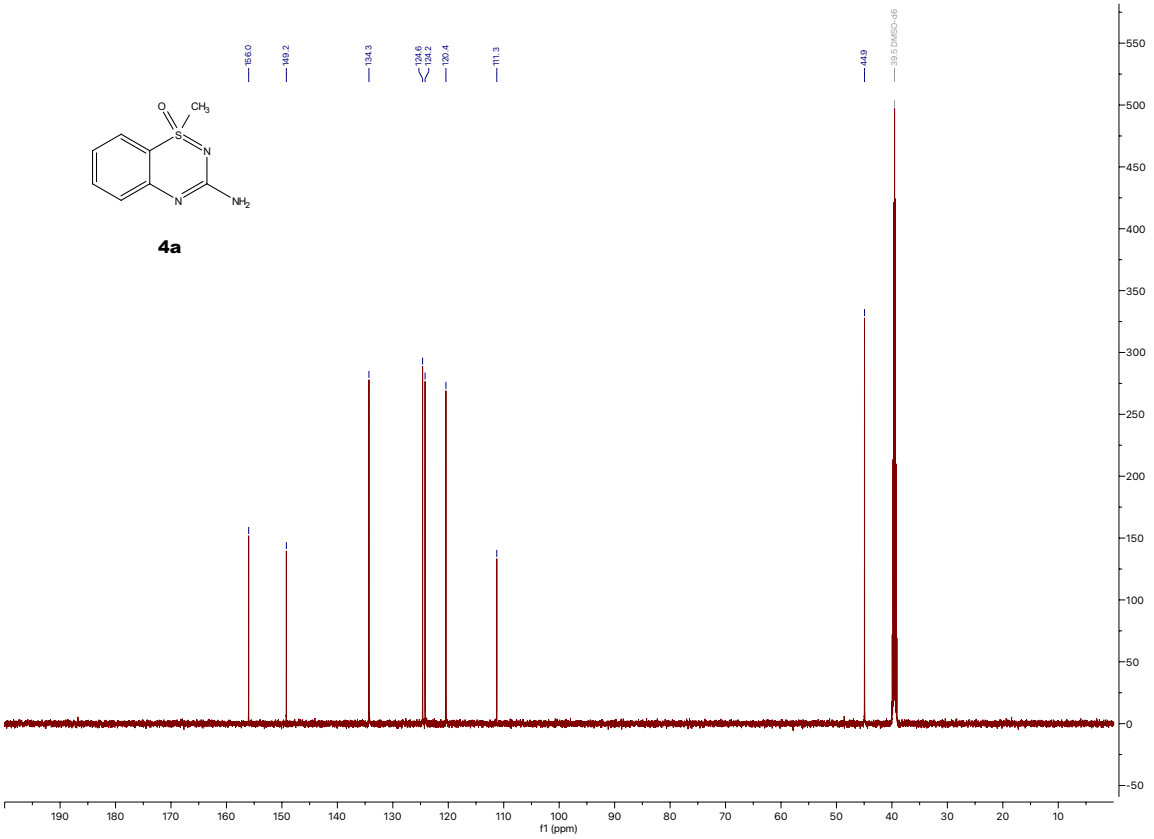
^{13}C {^{1}H} NMR spectrum of compound **3ea** (151 MHz, $CDCl_3$, HCl)



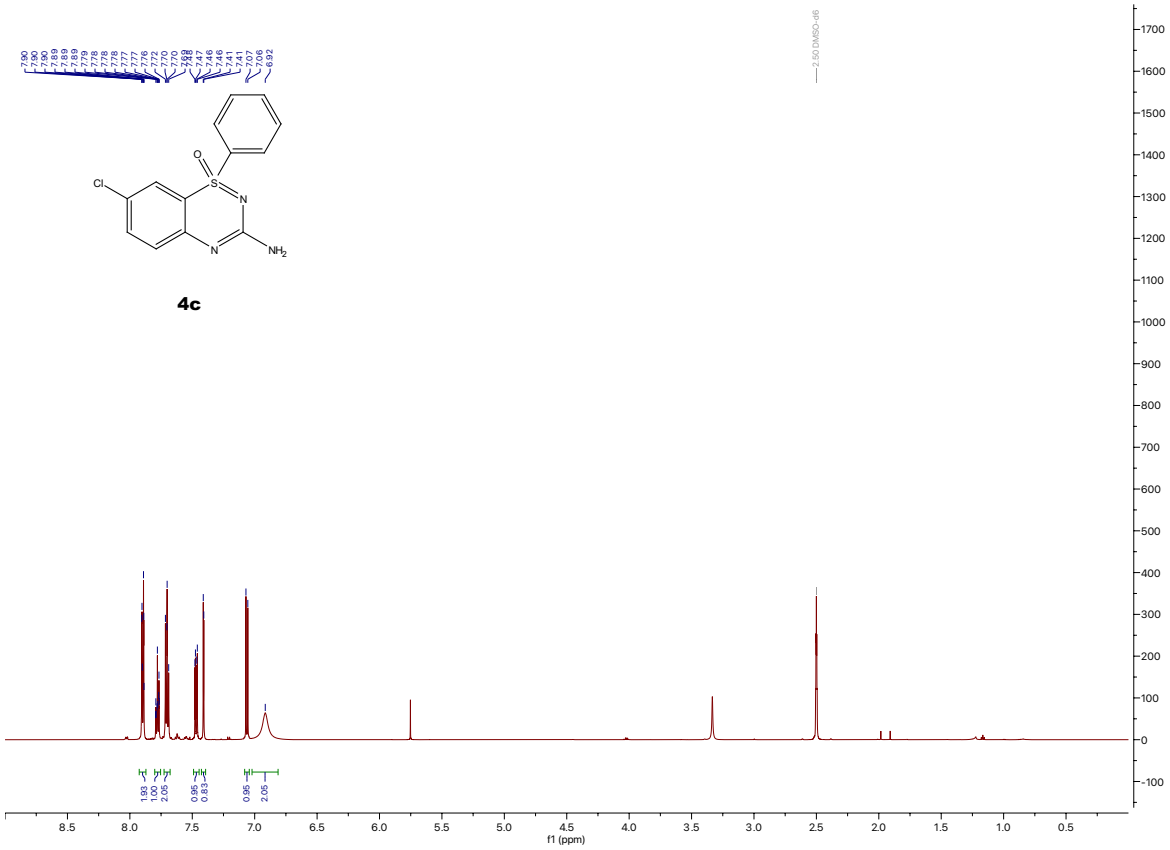
^{1}H NMR spectrum of compound **4a** (600 MHz, $(CD_3)_2SO$)



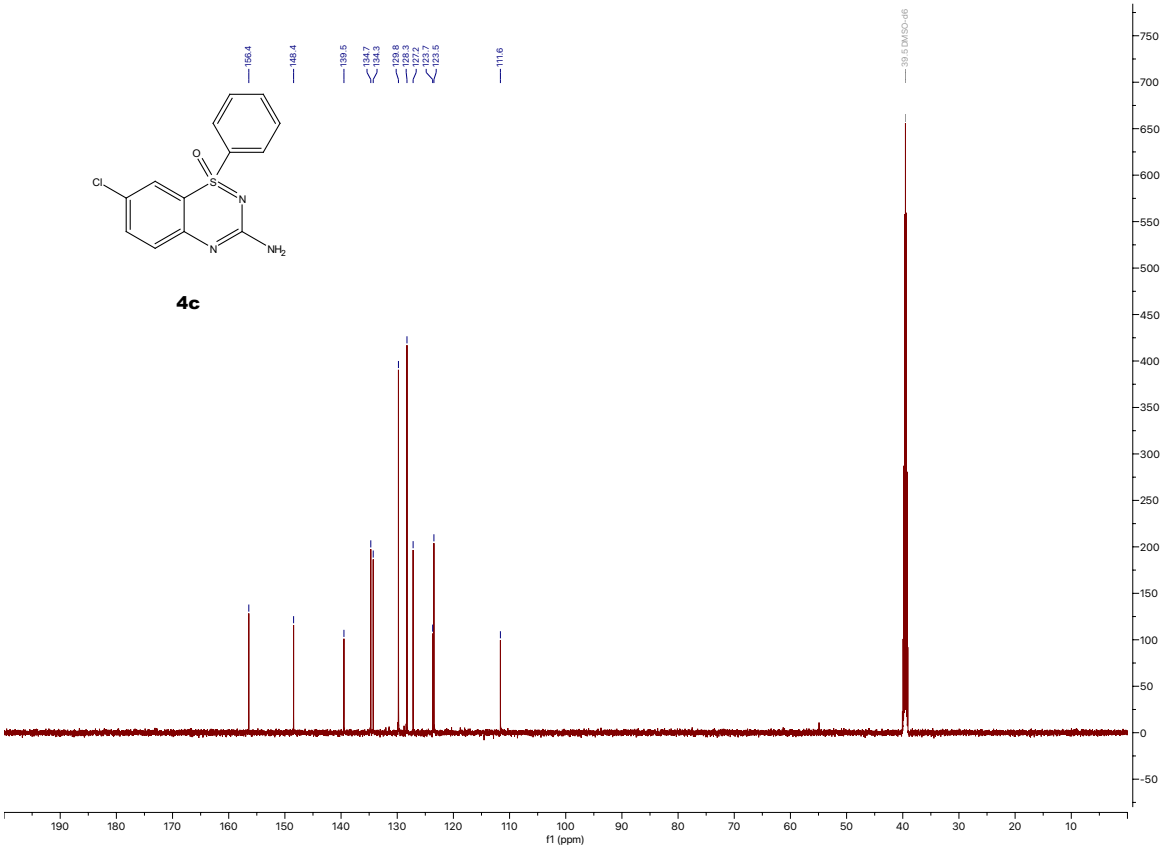
^{13}C {^{1}H} NMR spectrum of compound **4a** (151 MHz, $(CD_3)_2SO$)



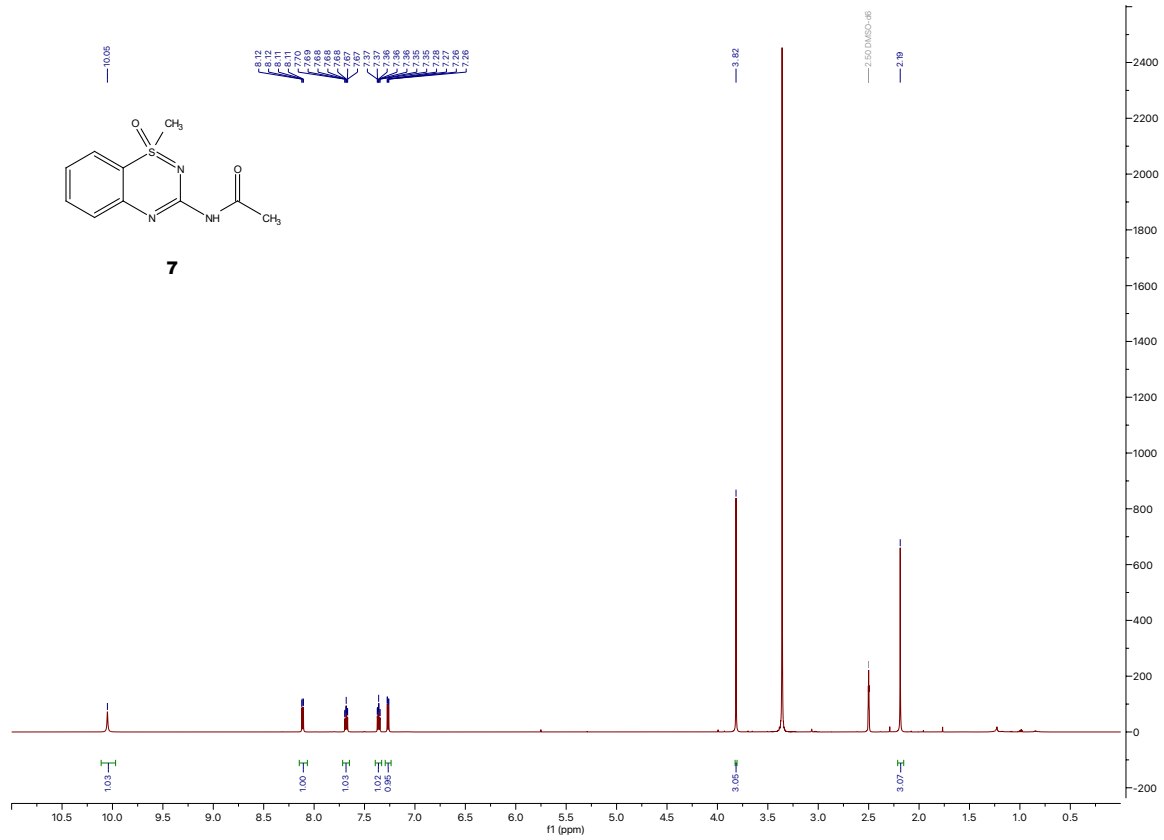
^{1}H NMR spectrum of compound **4c** (600 MHz, $(CD_3)_2SO$)



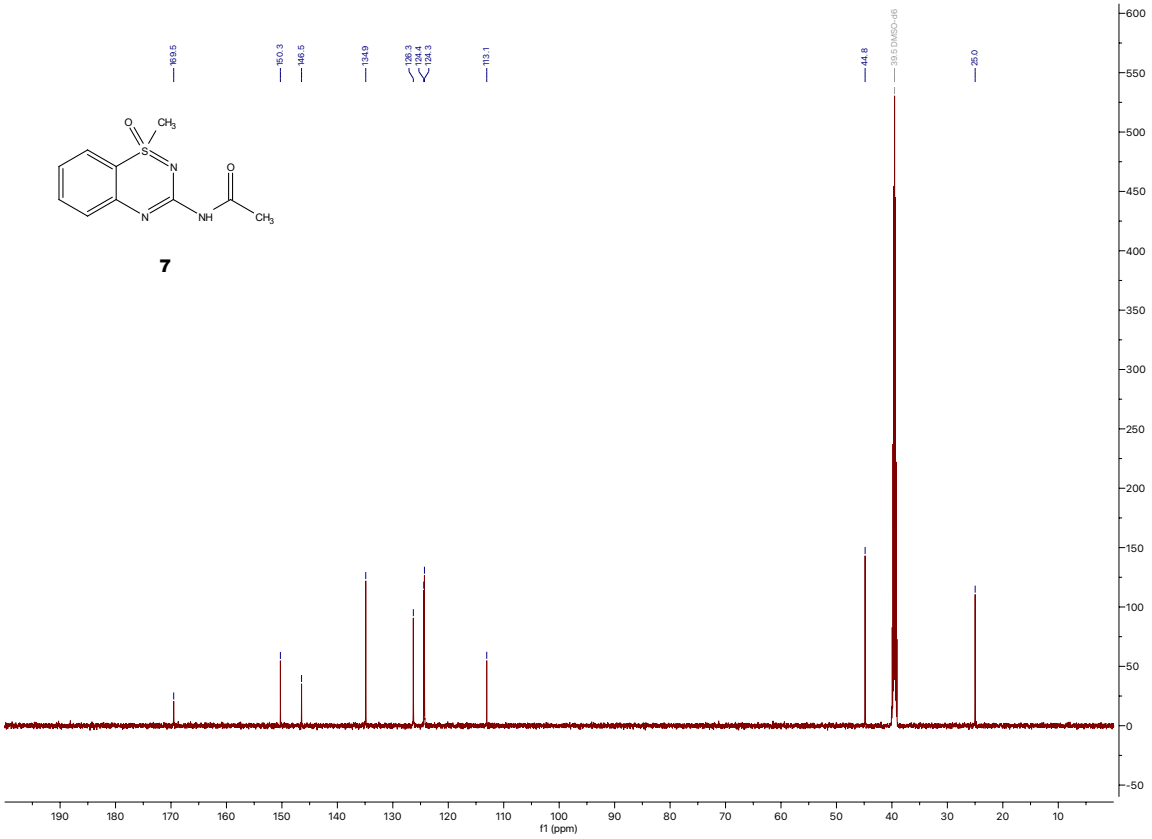
^{13}C {^{1}H} NMR spectrum of compound **4c** (151 MHz, $(CD_3)_2SO$)



^{1}H NMR spectrum of compound **7** (600 MHz, $(CD_3)_2SO$)

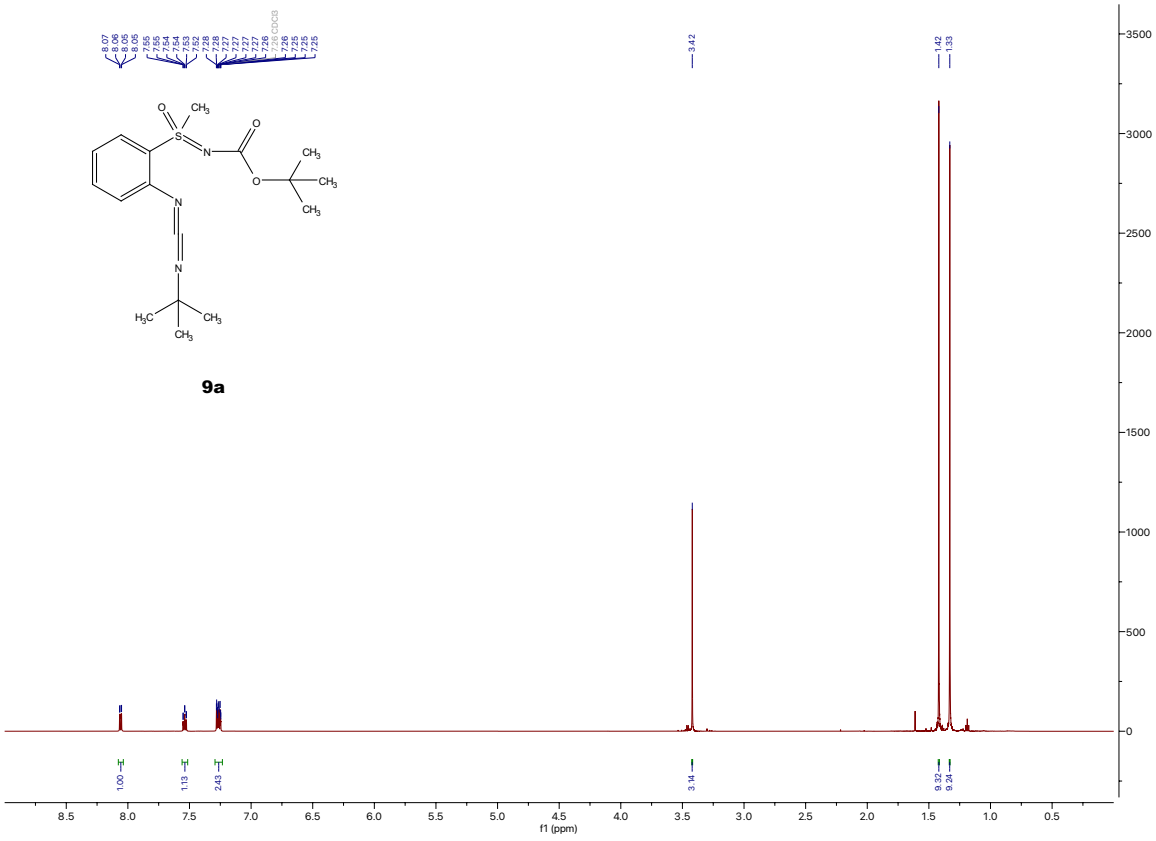


^{13}C {^{1}H} NMR spectrum of compound **7** (151 MHz, $(CD_3)_2SO$)



7

^{1}H NMR spectrum of compound **9a** (600 MHz, $CDCl_3$)



9a

^{13}C {^{1}H} NMR spectrum of compound **9a** (151 MHz, $CDCl_3$)