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# *Exploring Flow Chemistry for the Synthesis and Scale-up of Small Organic Molecules*

MICHELE RUGGERI

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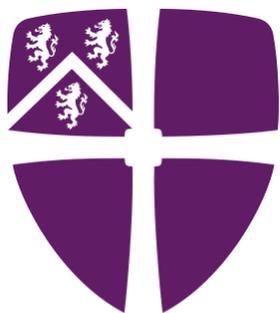
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**Durham**  
**University**

**Exploring Flow Chemistry for the Synthesis and Scale-up of  
Small Organic Molecules**

**A thesis submitted for the partial fulfilment of the requirement for the**

**Degree of**

**Doctor of Philosophy**

In the faculty of Science of Durham University

By

Michele Ruggeri

**Durham University**

**Department of Chemistry**

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South Road

Durham

2020

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## Materials and Methods

**Chemicals:** The chemicals used were obtained from the companies Sigma-Aldrich / Fluka, Alfa Aesar, TCI or Fluorochem and were used without further purification.

**Chromatography:** For the TLC chromatography Merck TLC Aluminium oxide 60 F254 with glass backing were used. Detection was carried out either by UV absorption or by treatment of the plate with an acidic solution of potassium permanganate and drying using a hand held hot-air dryer.

**NMR-Spectroscopy:** The NMR spectra were recorded on a Bruker Avance-400 and Varian VNMR-700 spectrometer in the indicated solvent at a temperature of 297 K. Commercially available deuterated chloroform, methanol or DMSO was used as a solvent. The spectra were always set to the reference value of the solvent, for example chloroform (for  $^1\text{H}$ -NMR spectra to 7.26 ppm and for  $^{13}\text{C}$ -NMR spectra to 77.00 ppm). For the exact analysis and assignment of the signals in more complex compounds, COSY, HSQC and HMBC spectra were additionally added. Chemical shifts were reported in ppm and coupling constants J in hertz (Hz). The following abbreviations were used for the multiplicities of the signals: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

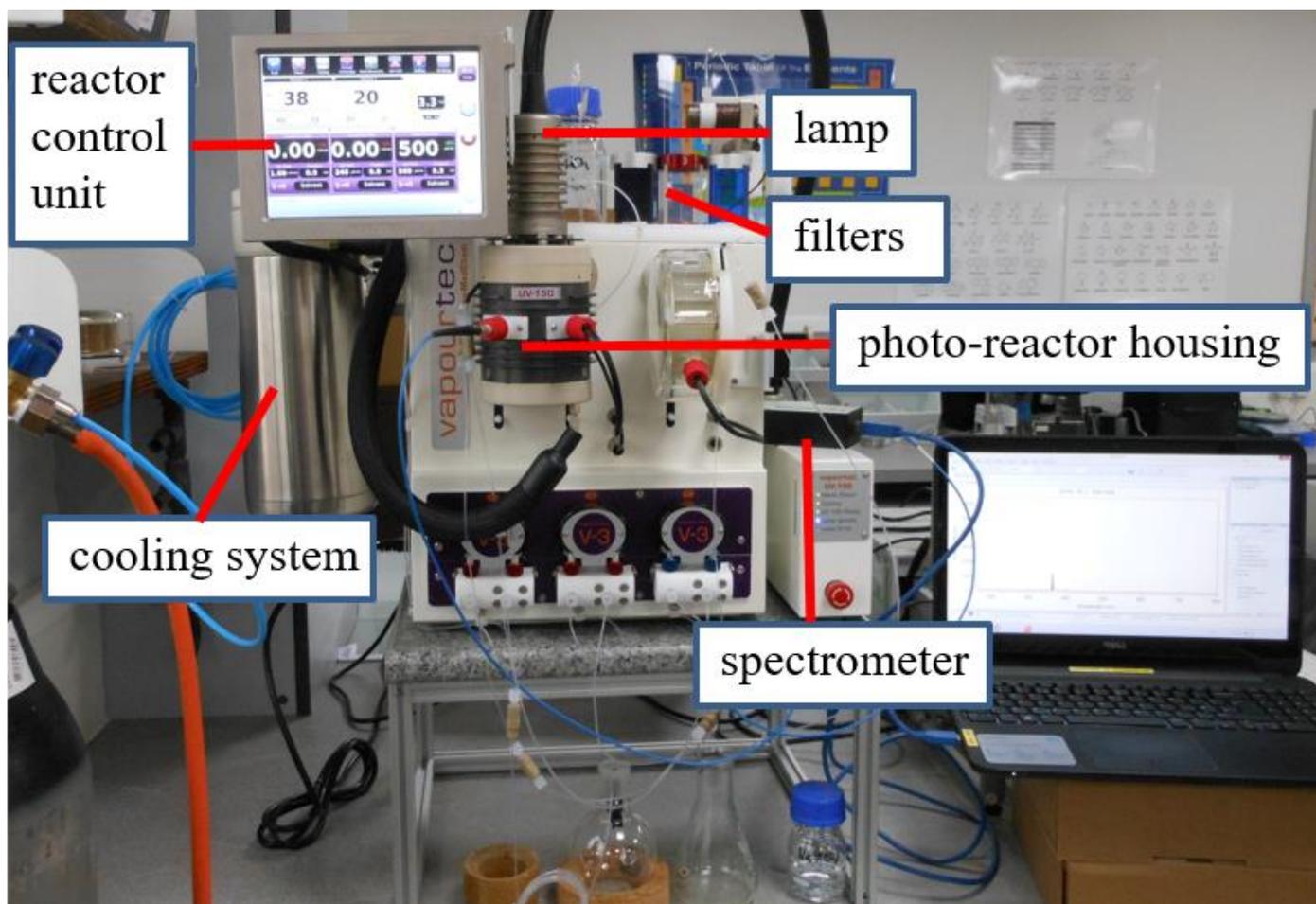
**MS-Spectroscopy:** GCMS spectra were obtained using an Agilent 6890N gas chromatograph coupled with an Agilent 5973 inert mass selective detector operating in EI mode with a custom-built Anature auto sampler/injector or by Durham University Mass Spectrometry service. Electrospray (ES) mass spectra were obtained using a TQD mass spectrometer (Waters UK, Ltd; all were obtained by Durham University Mass Spectrometry service).

**IR-Spectroscopy:** The infrared spectra were recorded with a PerkinElmer Spectrum One IR spectrometer. The samples were measured by the ATR method (attenuated total reflection). The evaluation was limited to the bands characteristic of the compound. The position of the absorption bands in the IR spectrum was expressed in wave numbers  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ).

**Melting point determination:** The melting point was determined using an Electrothermal 9100 capillary melting point device. The melting point range was recorded for the determination of melting points for resinous solids.

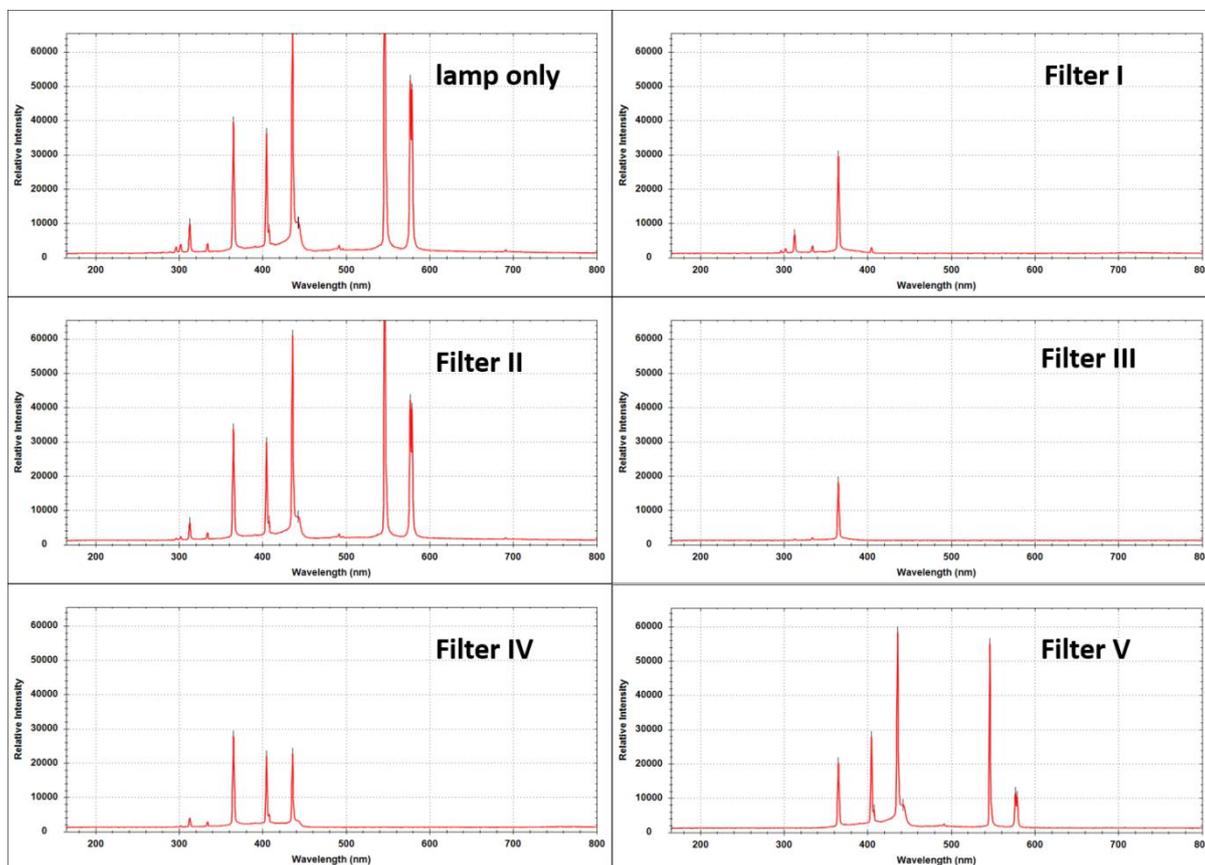
## Photo-reactor set-up:

For performing all of the reactions a commercially available Vapourtec E-series system comprising of three peristaltic pumps and a UV-150 photo-reactor was used. Temperature control of the photo-reactor was achieved via an attached Dewar filled with solid CO<sub>2</sub> and attached to a N<sub>2</sub>-cylinder (see image below). The photochemical reactions were monitored via a portable ExemplarLS spectrometer providing information through continuous recording of emission/transmission spectra. Different filters (see next page for details) were used and placed in between the high intensity medium pressure lamp and the reactor coil (FEP 10 mL volume).



## Emission spectra of different filters used

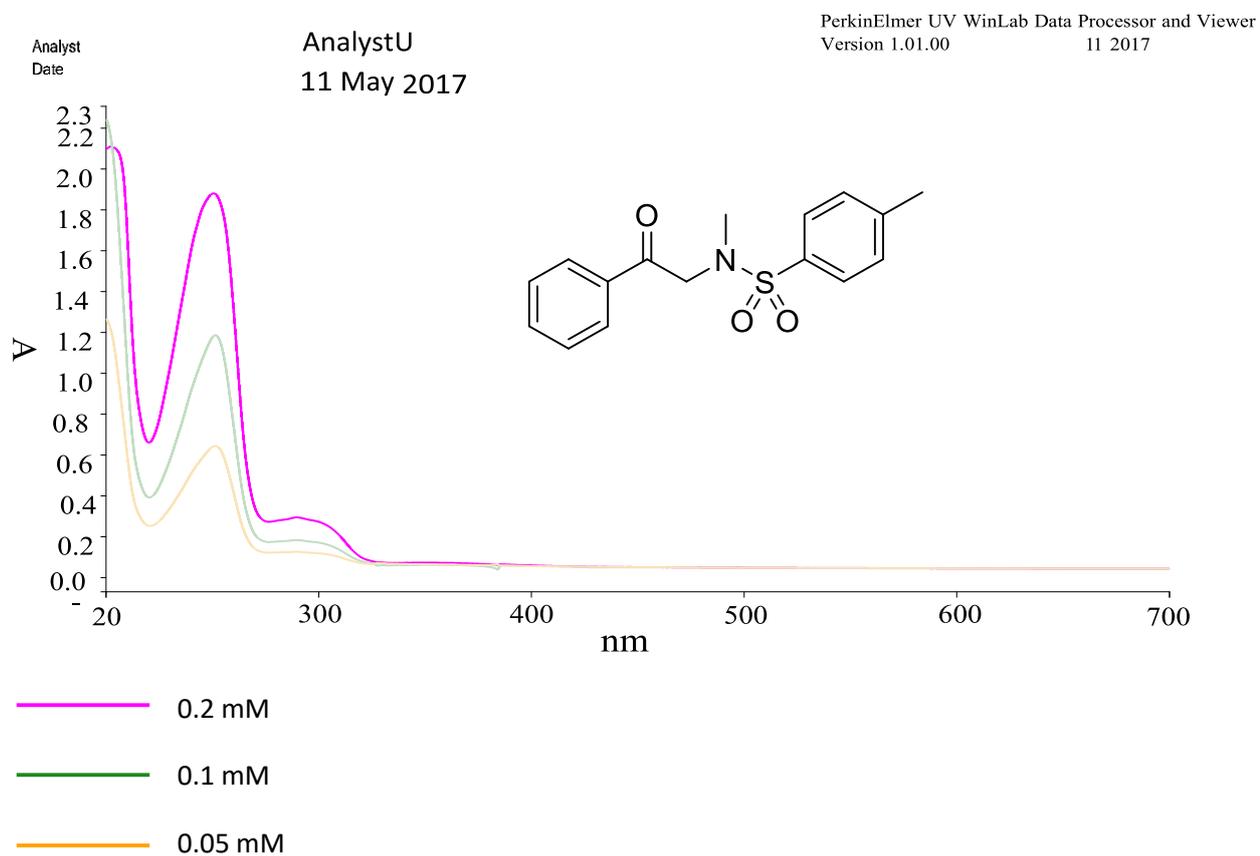
Shown below are the emission spectra recorded for various filters using water as solvent at 50% lamp power setting (80 W) using a portable ExemplarLS spectrometer. For the reaction performed in this work was used a medium pressure mercury lamp 150 W at 100% power fitted with the gold wavelength filter selector ( $\lambda=415\text{-}220\text{ nm}$  transmission).



# Photochemical flow synthesis of 3-hydroxyazetidines

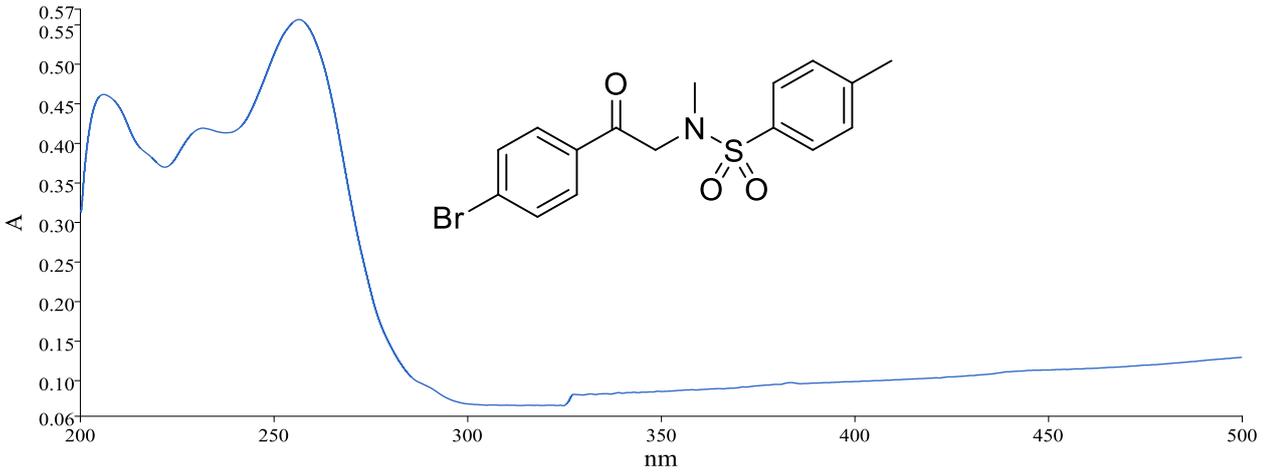
## UV-Vis recording of spectra.

The UV-Vis spectrum of compounds **1a**, **2a**, **6a**, **16a** and **18a**.



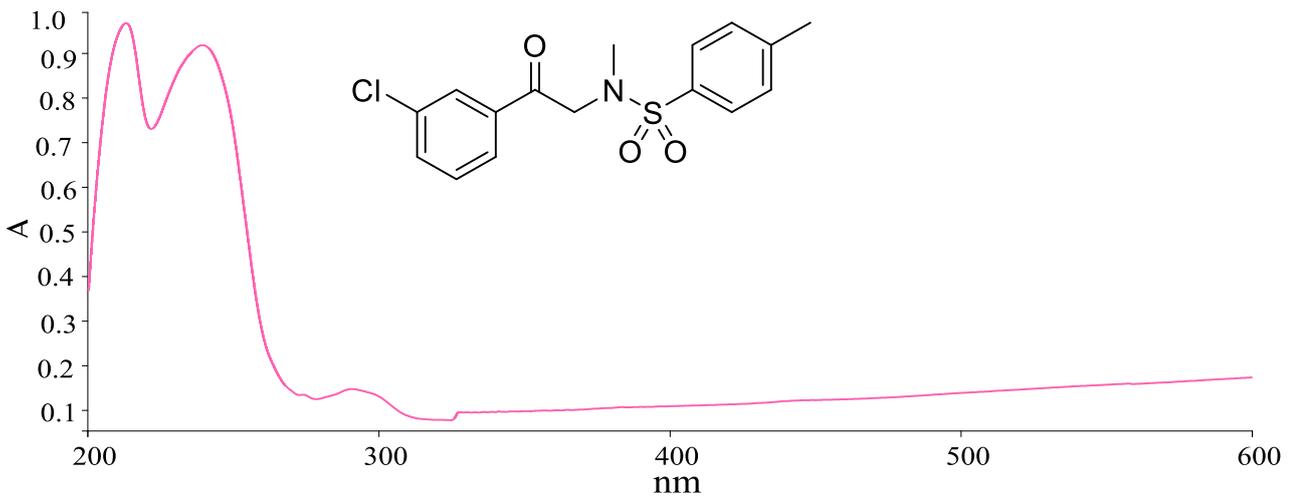
Analyst  
Date

AnalystUG  
04 May 2017 12:13

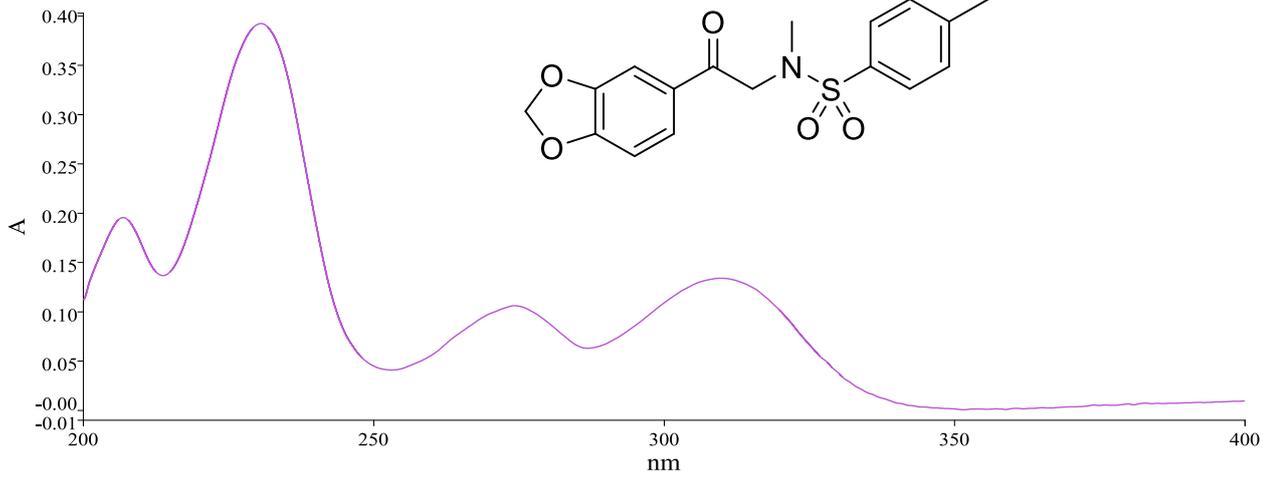


Analyst  
Date

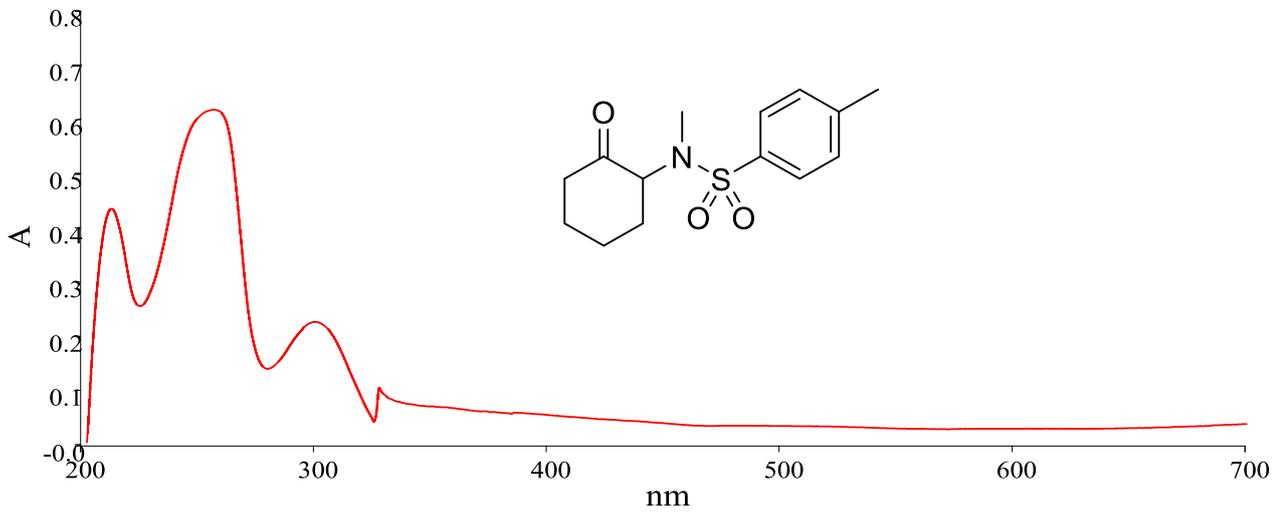
AnalvstU  
04 Mav2017



Analyst  
Date AnalystUG  
04 May 2017 12:16

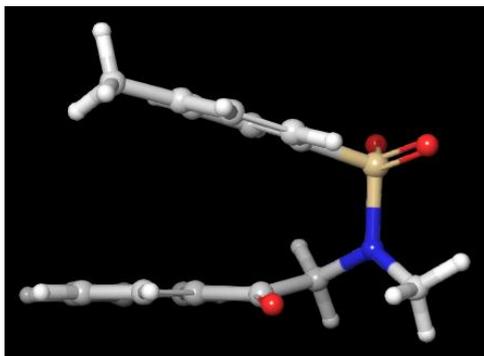


Analyst  
Date AnalystUG  
04May2017 12:09

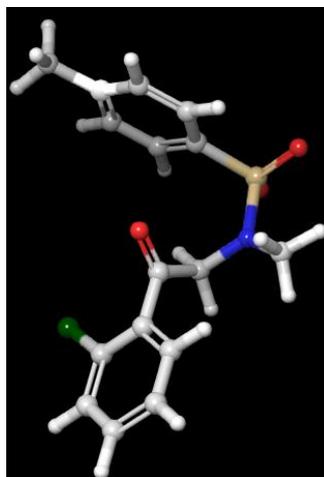


## 5. Molecular conformation modelling

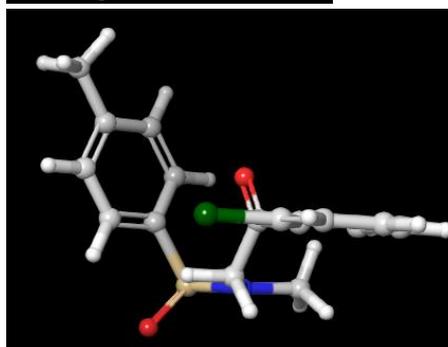
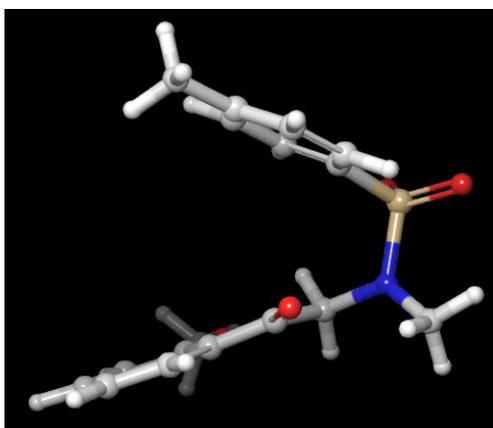
Unsubstituted (H):



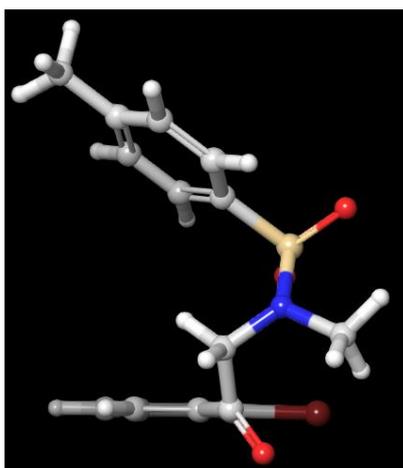
Orto-Cl:



Orto-OMe:



Orto-Br:



Orto-Me:

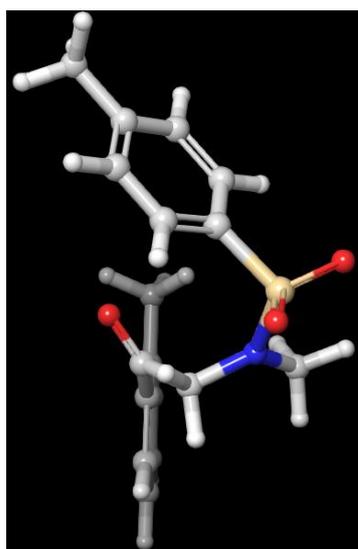


Table of Schrodinger Maestro calculated data:

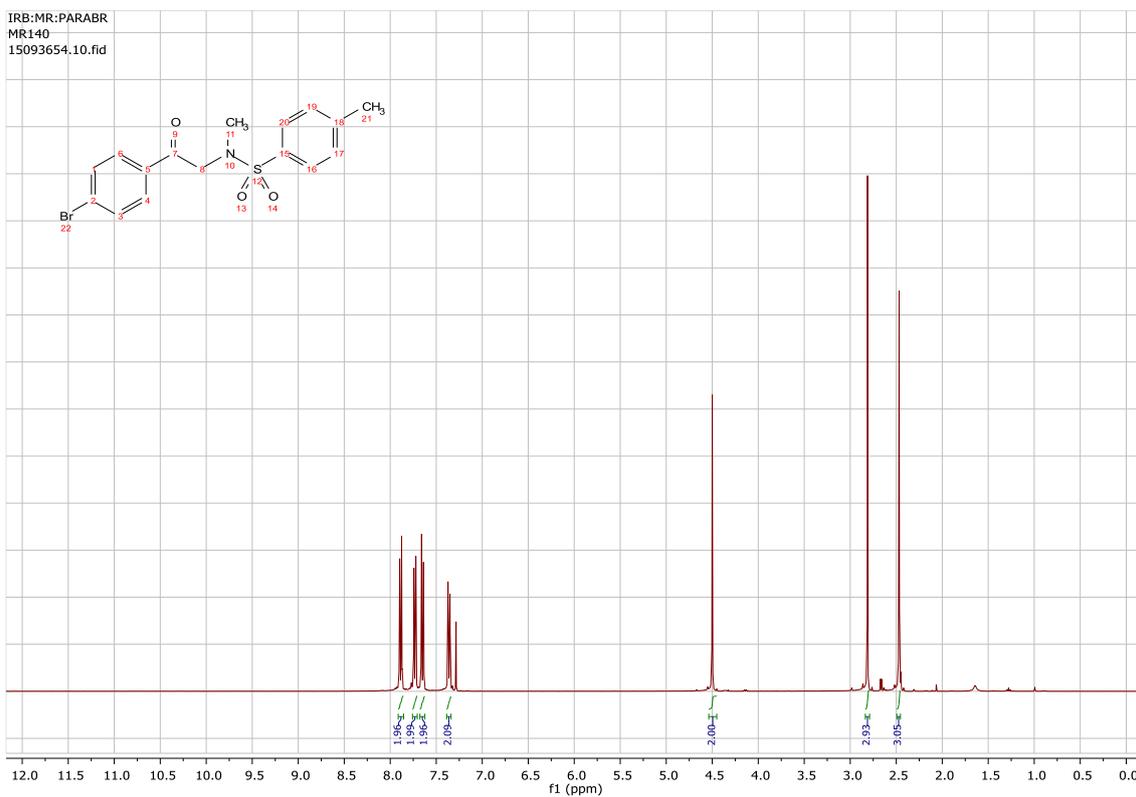
	Potential Energy <sup>1</sup>	Dihedral angle <sup>1,2</sup> (°)	Atomic Distance <sup>1,3</sup> (Å)	Conversion/Yield (%)
o-H	76.4	11.2	2.53	90/76
o-OMe	19.6	-8.0	2.45	100/82
o-Cl	77.7	91.4	3.09	100/61
o-Br	76.9	-65.7	2.70	100/40
o-Me	68.2	39.1	3.77	50/30

<sup>1</sup>Calculated from the minimized structure in Schrodinger Maestro software using the OPLS3e force field in water with no constraints <sup>2</sup>Dihedral angle between carbonyl and aryl ring <sup>3</sup>Distance from ketone oxygen to closest hydrogen on the *N*-methyl that needs to be abstracted during the reaction

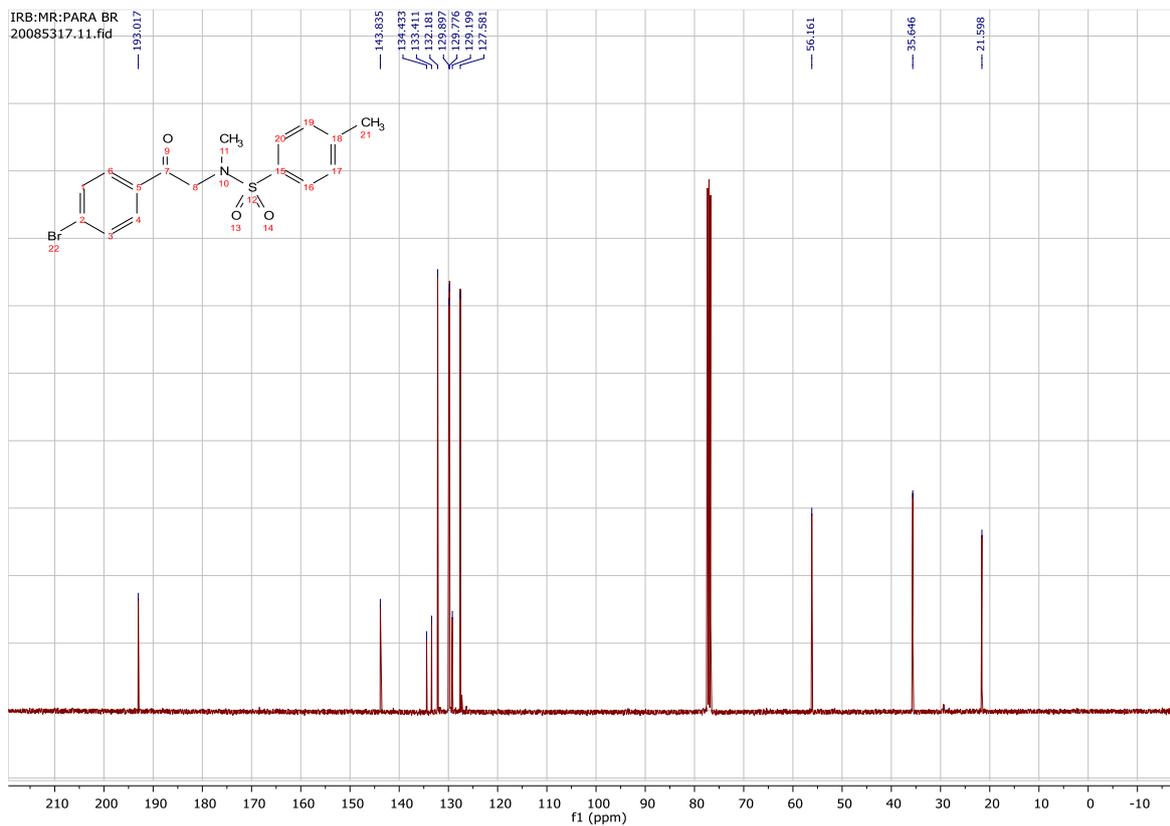
## **Starting material experimental spectra**



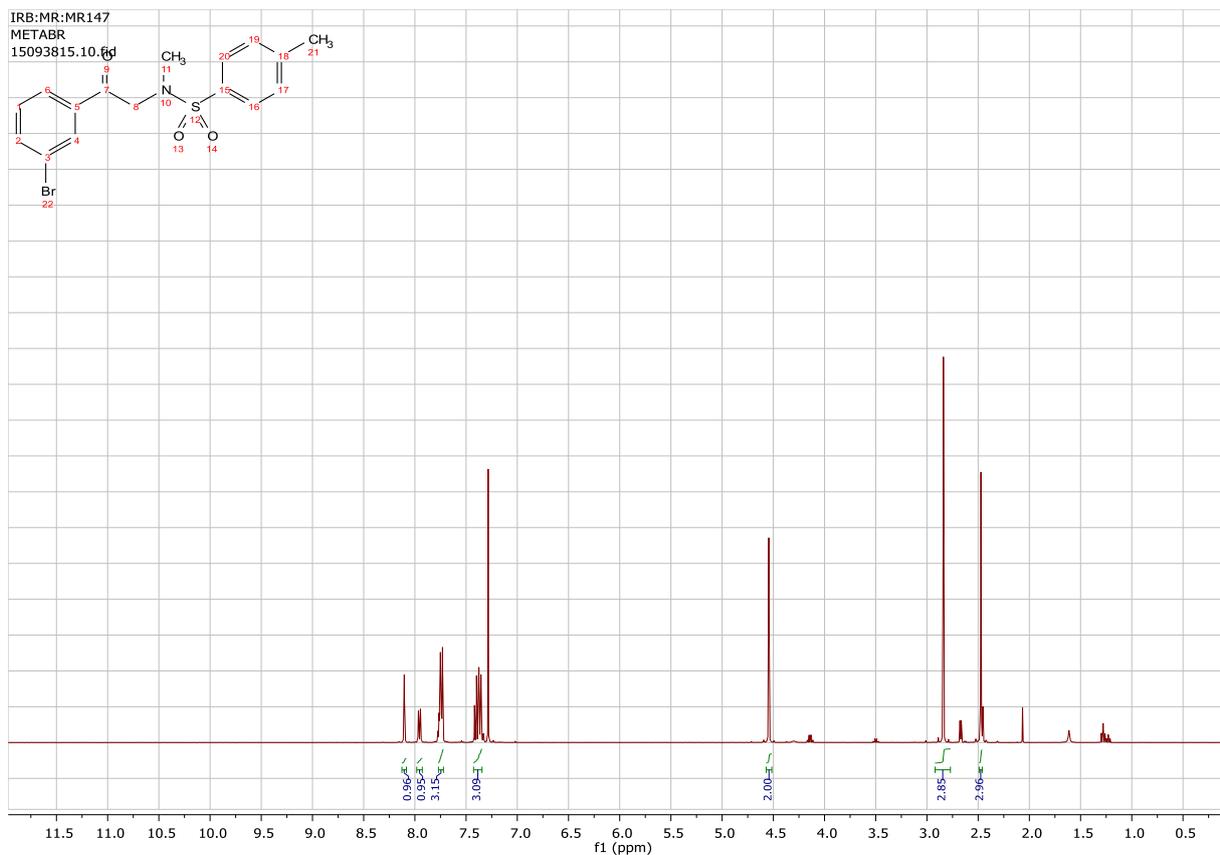
# Compound 1-118a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



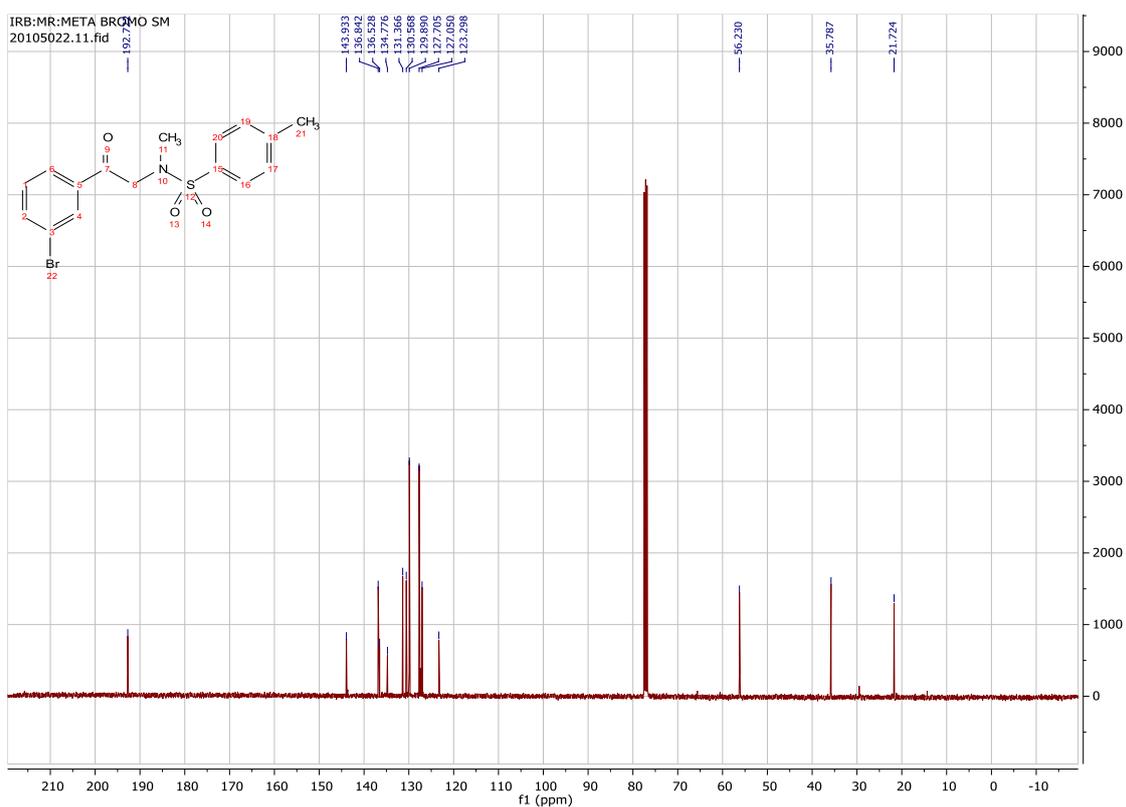
# Compound 1-118a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



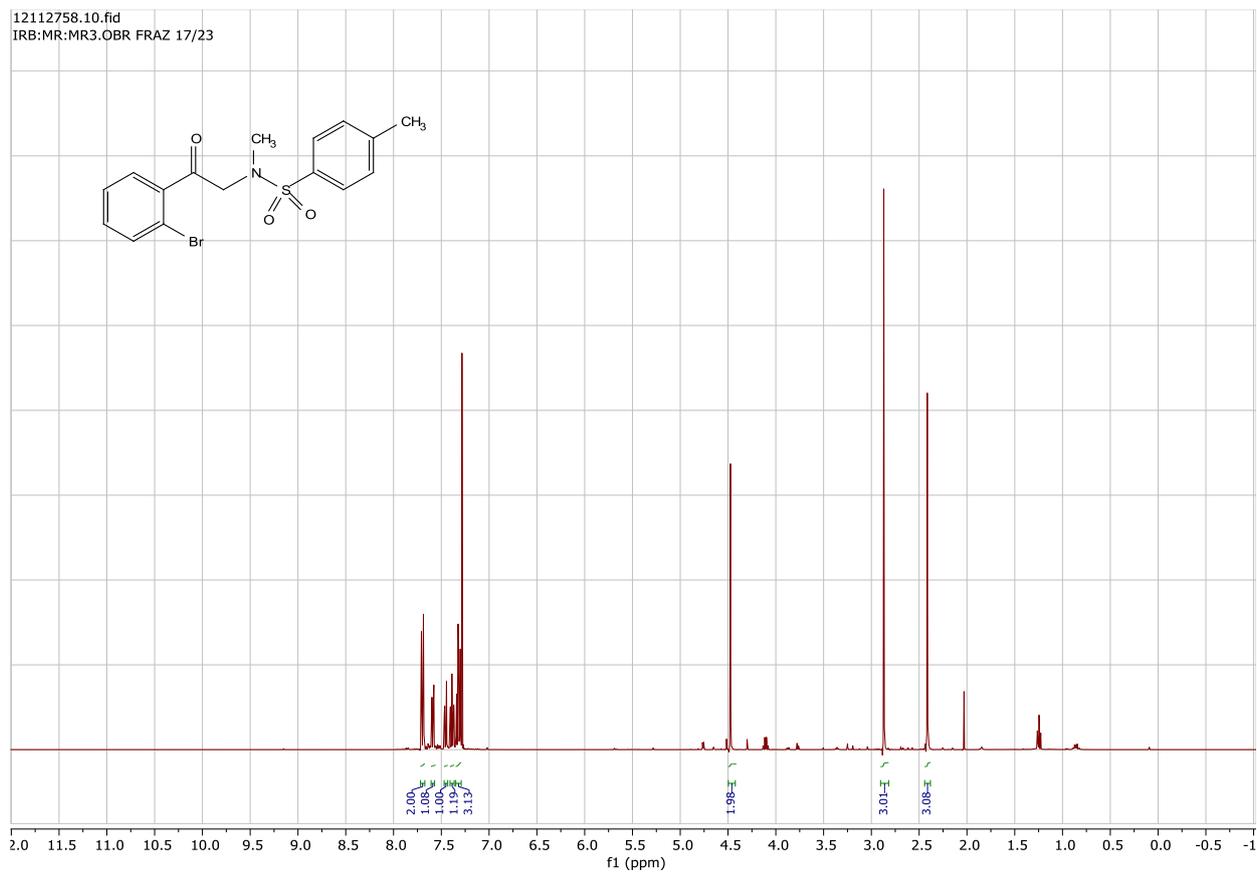
# Compound 1-119a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



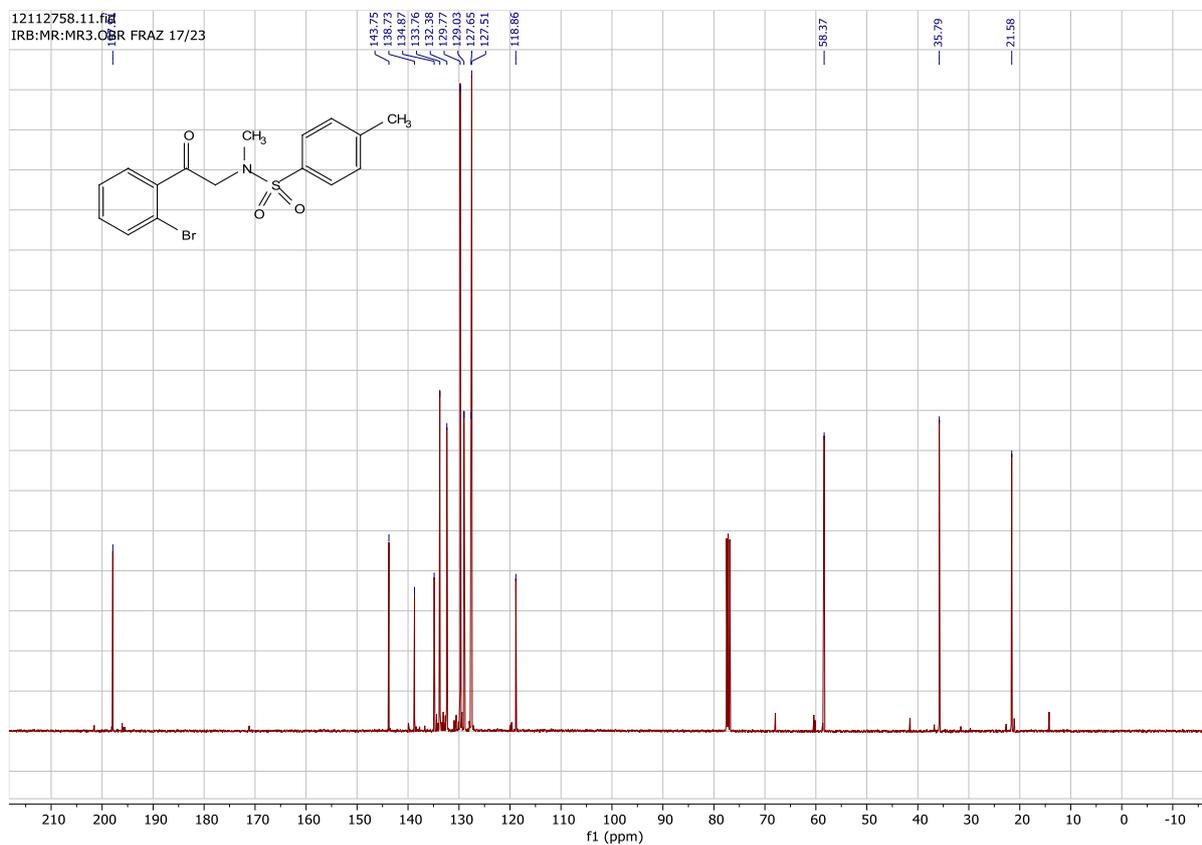
# Compound 1-119a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



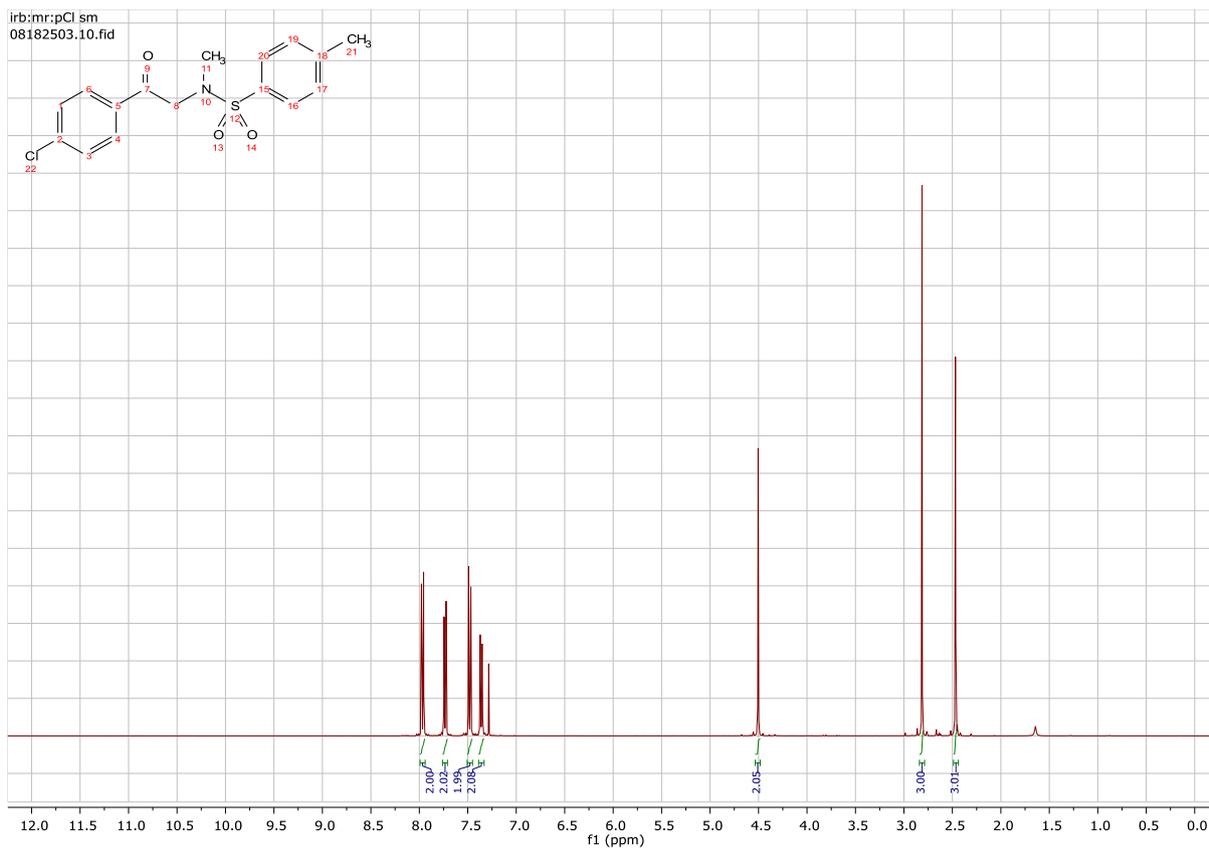
# Compound 1-120a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



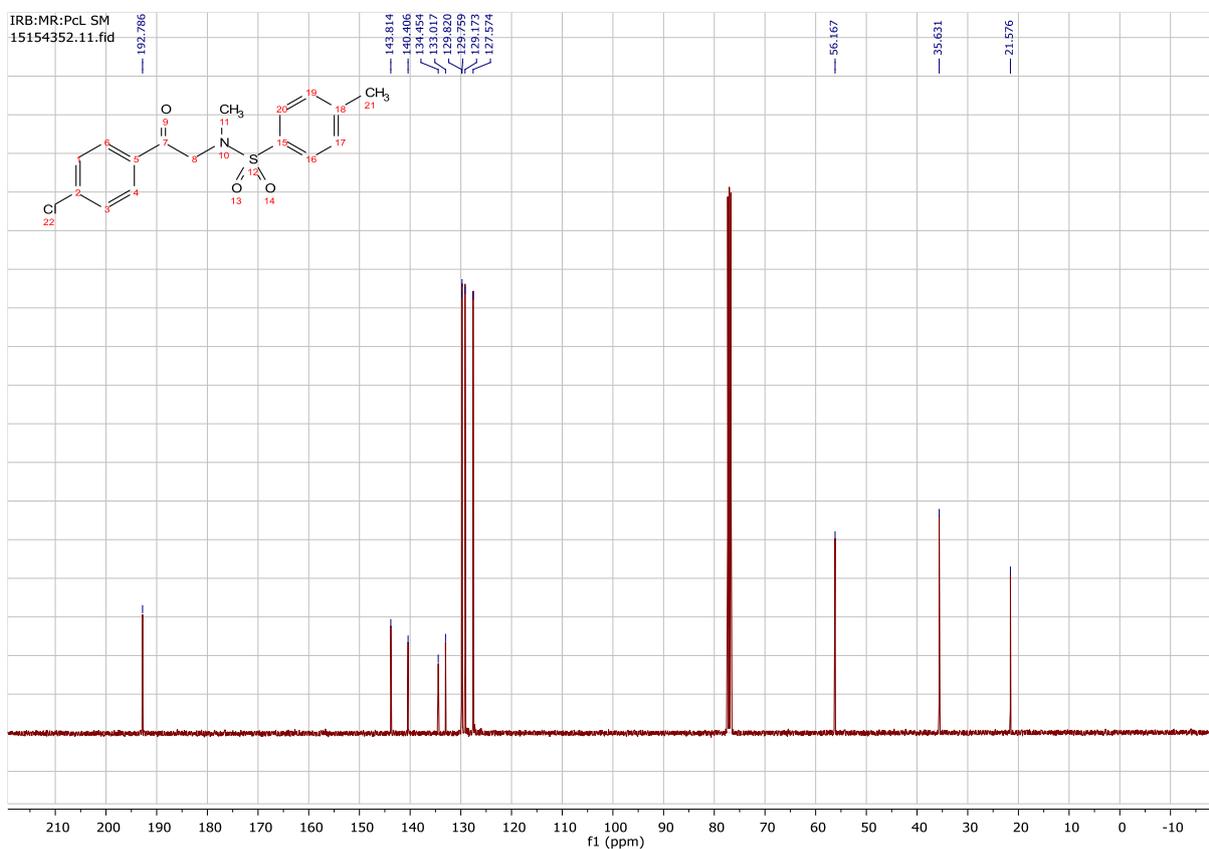
# Compound 1-120a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



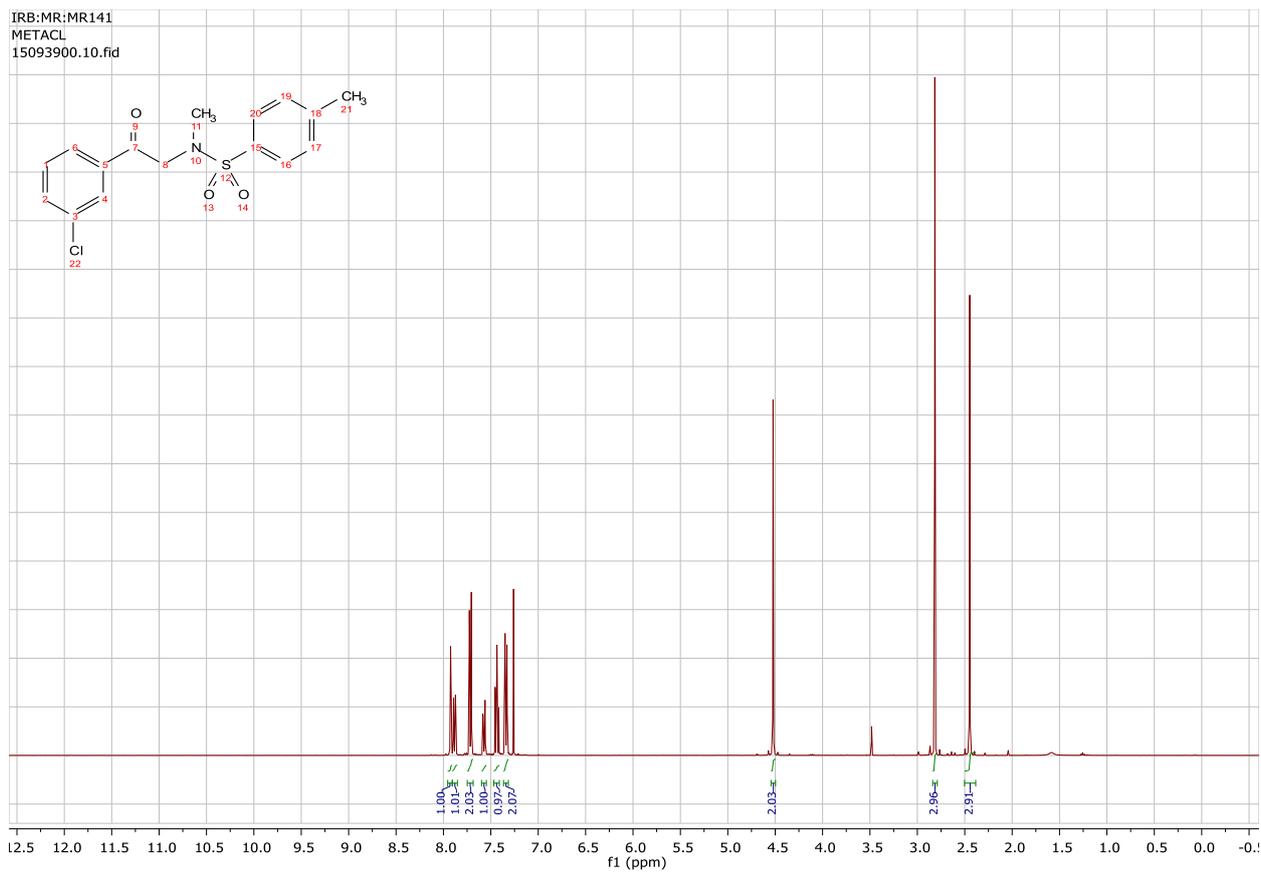
# Compound 1-121a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



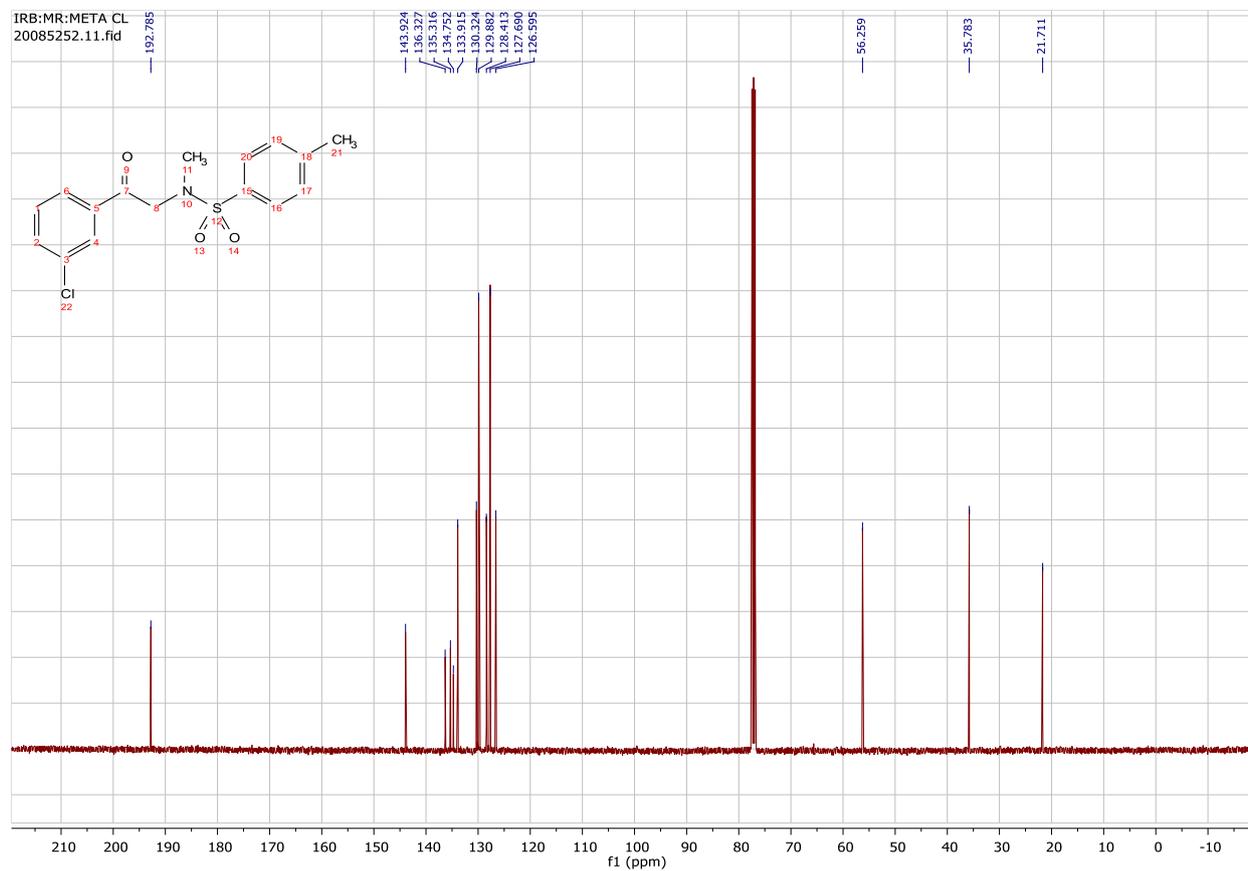
# Compound 1-121a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



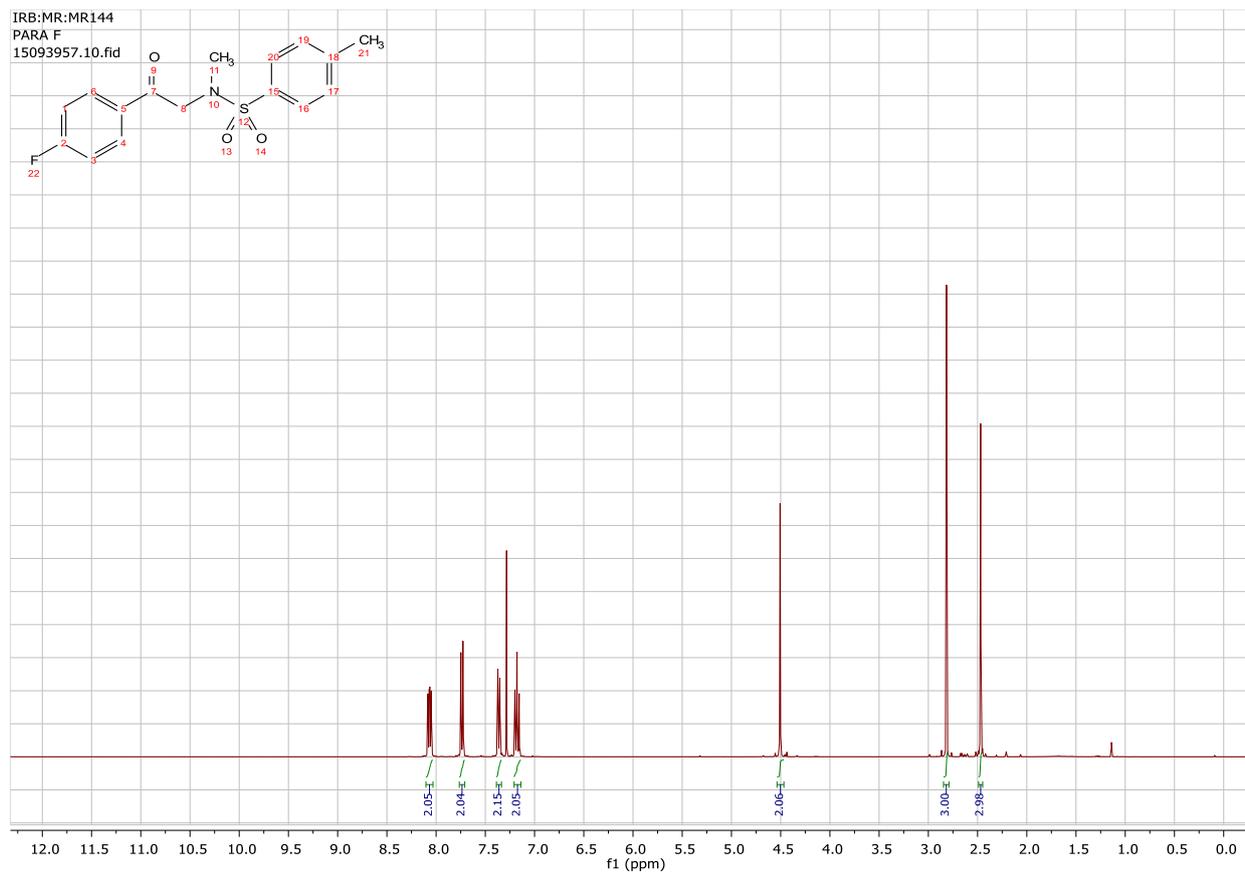
# Compound 1-122a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



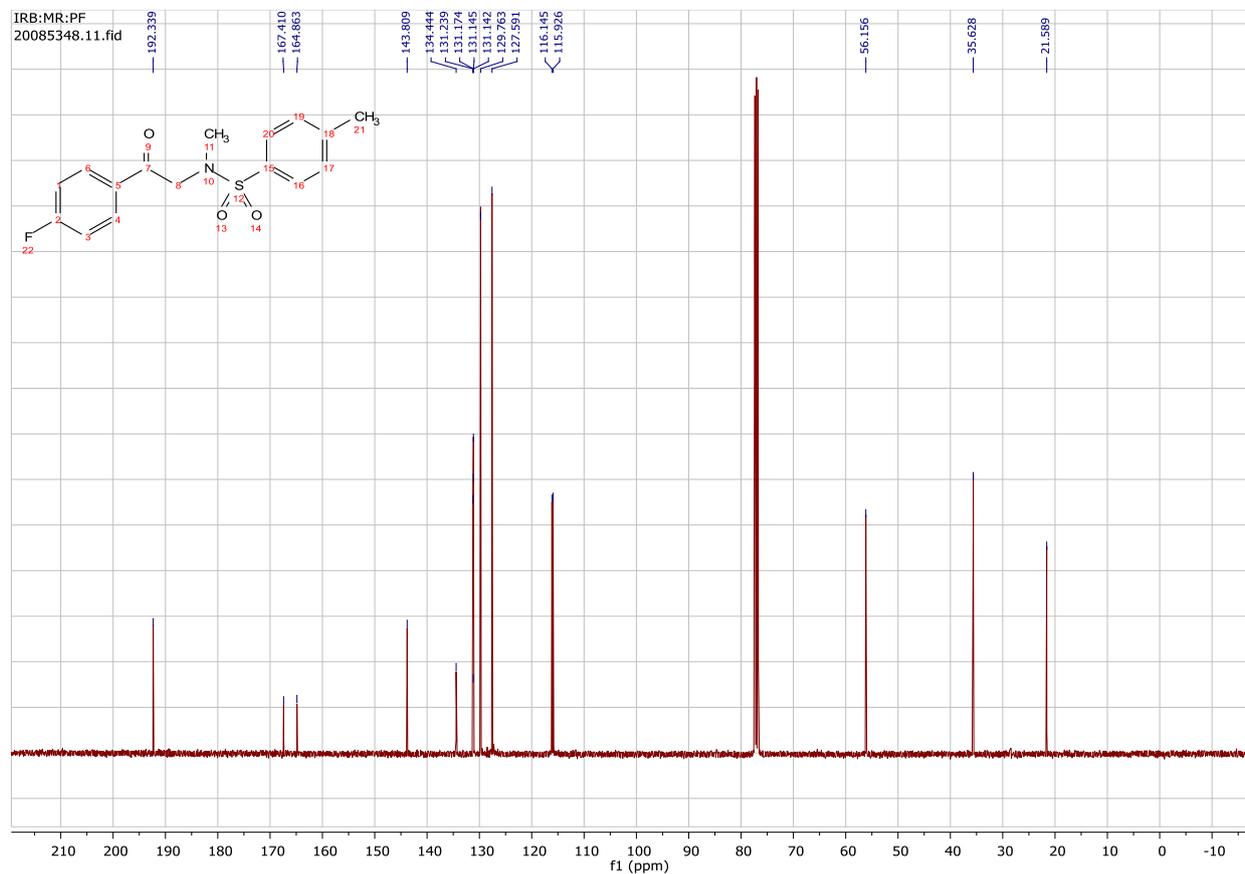
# Compound 1-122a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



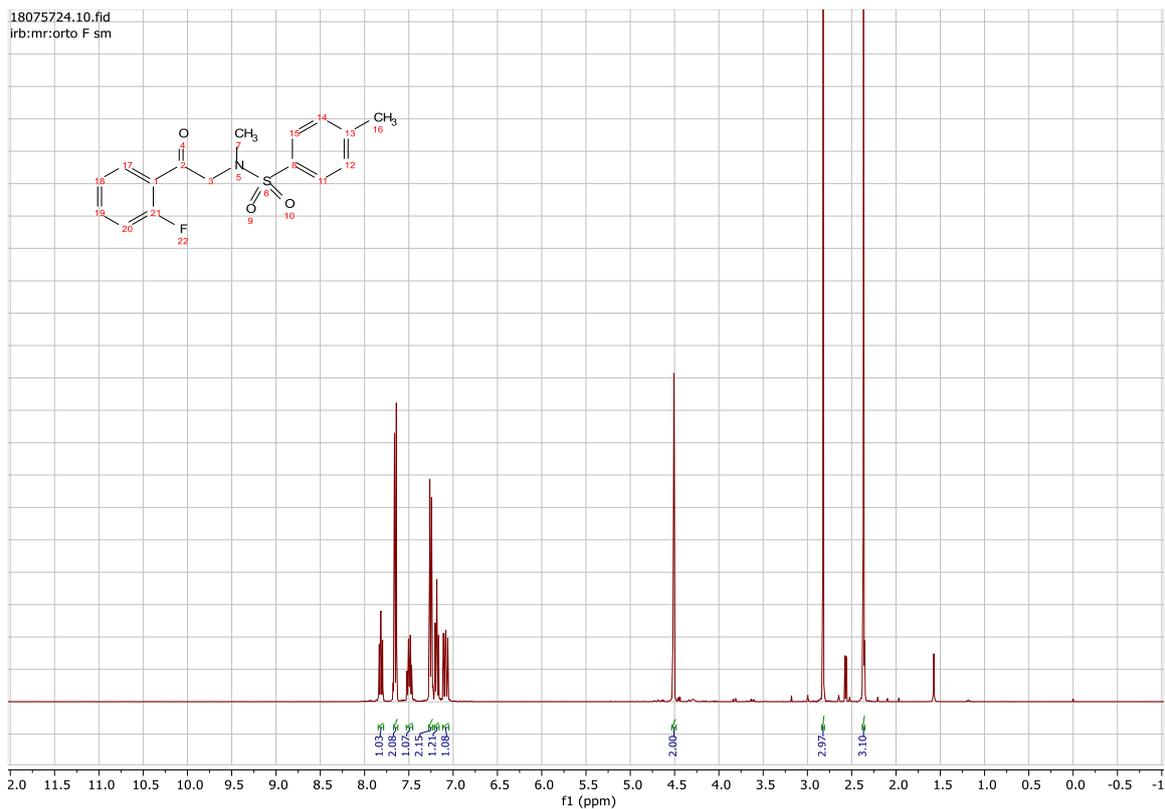
# Compound 1-124a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



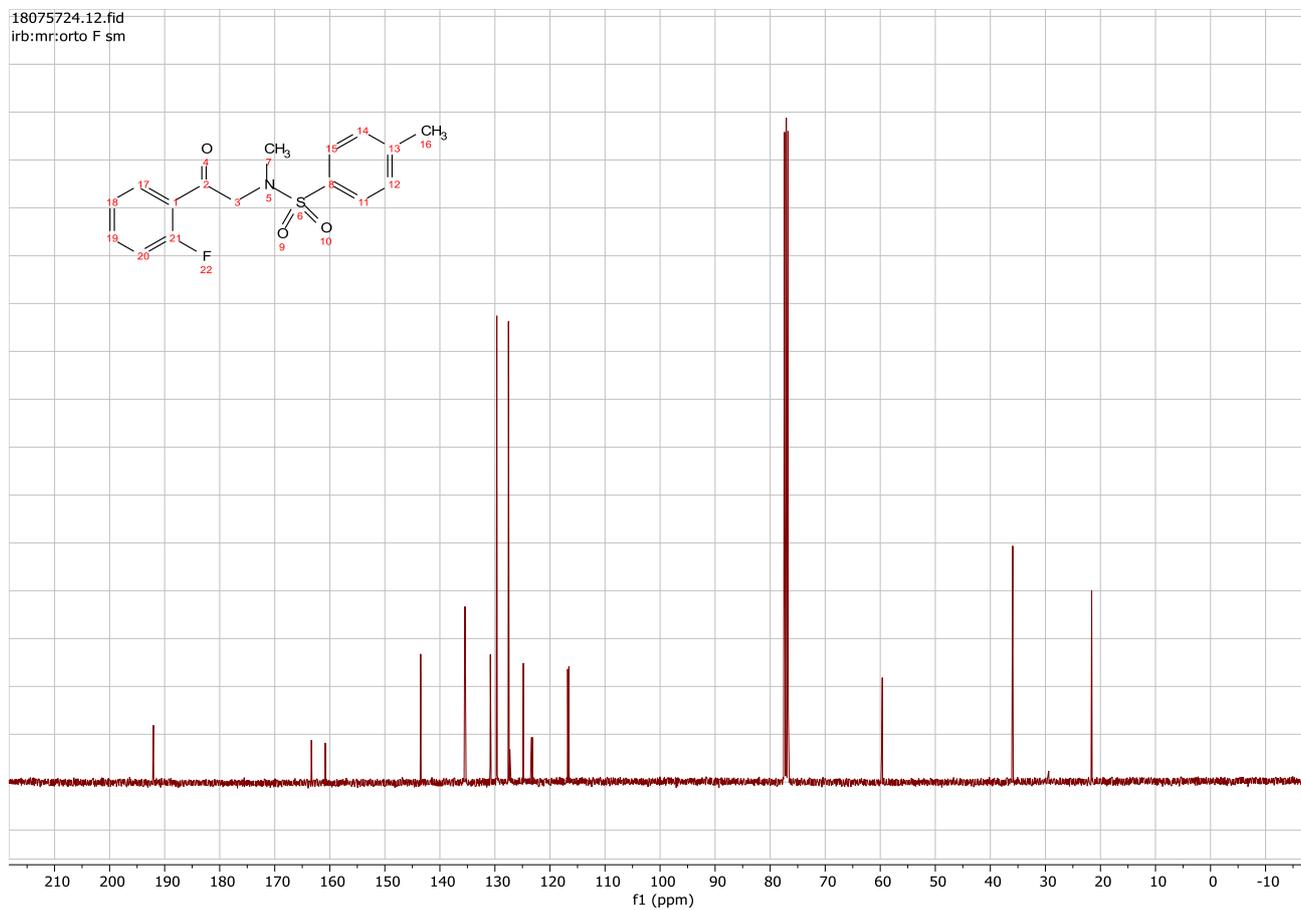
# Compound 1-124a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



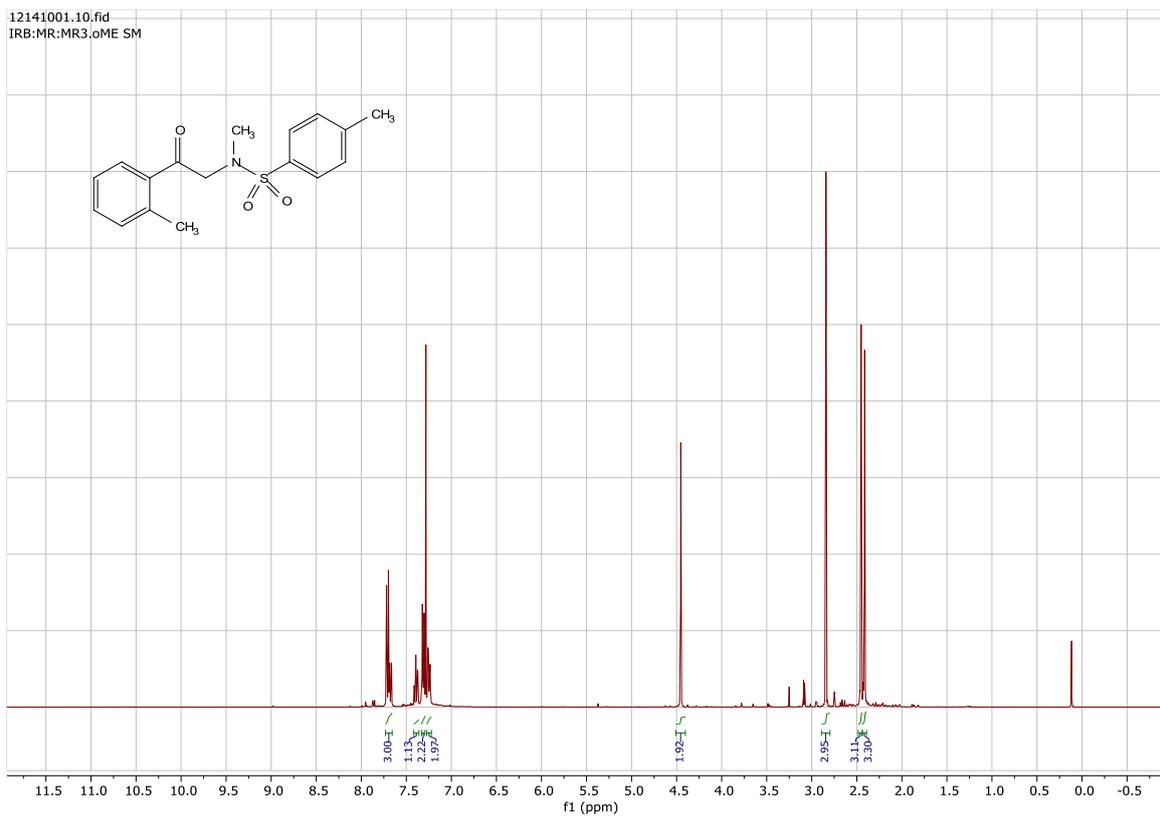
# Compound 1-125a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



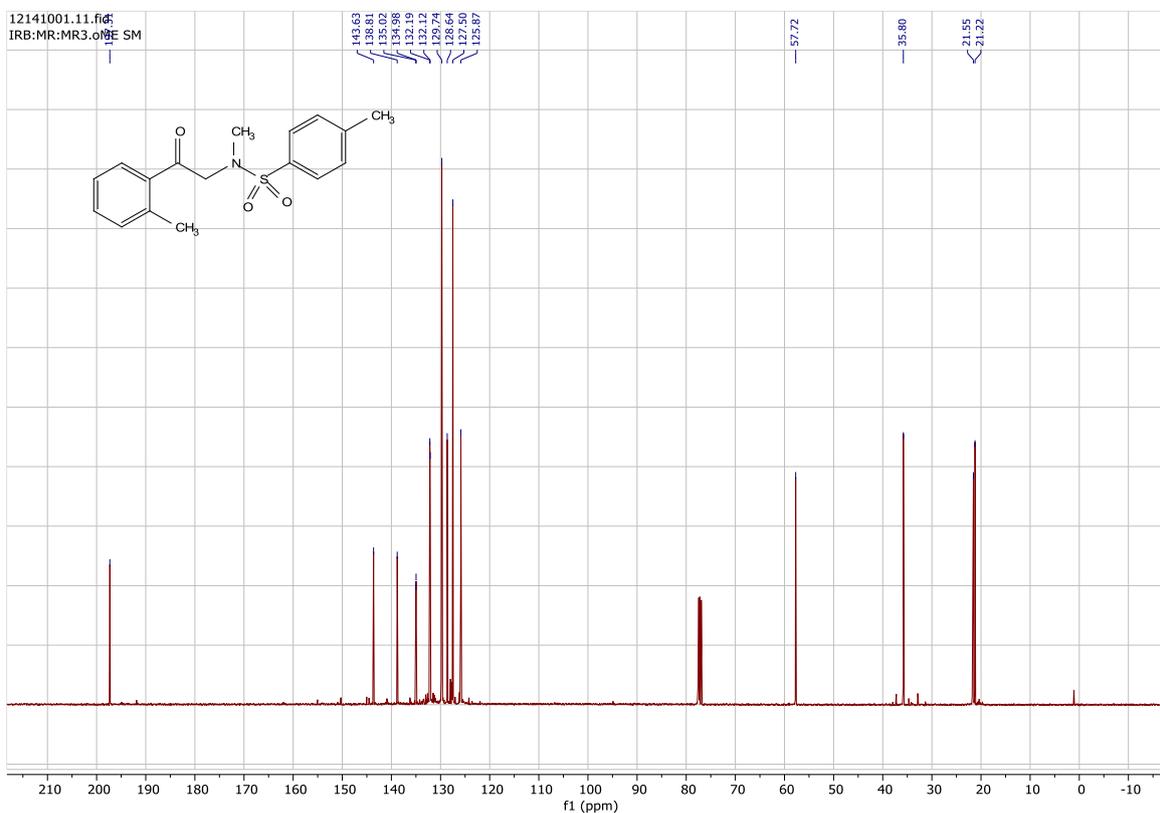
# Compound 1-125a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



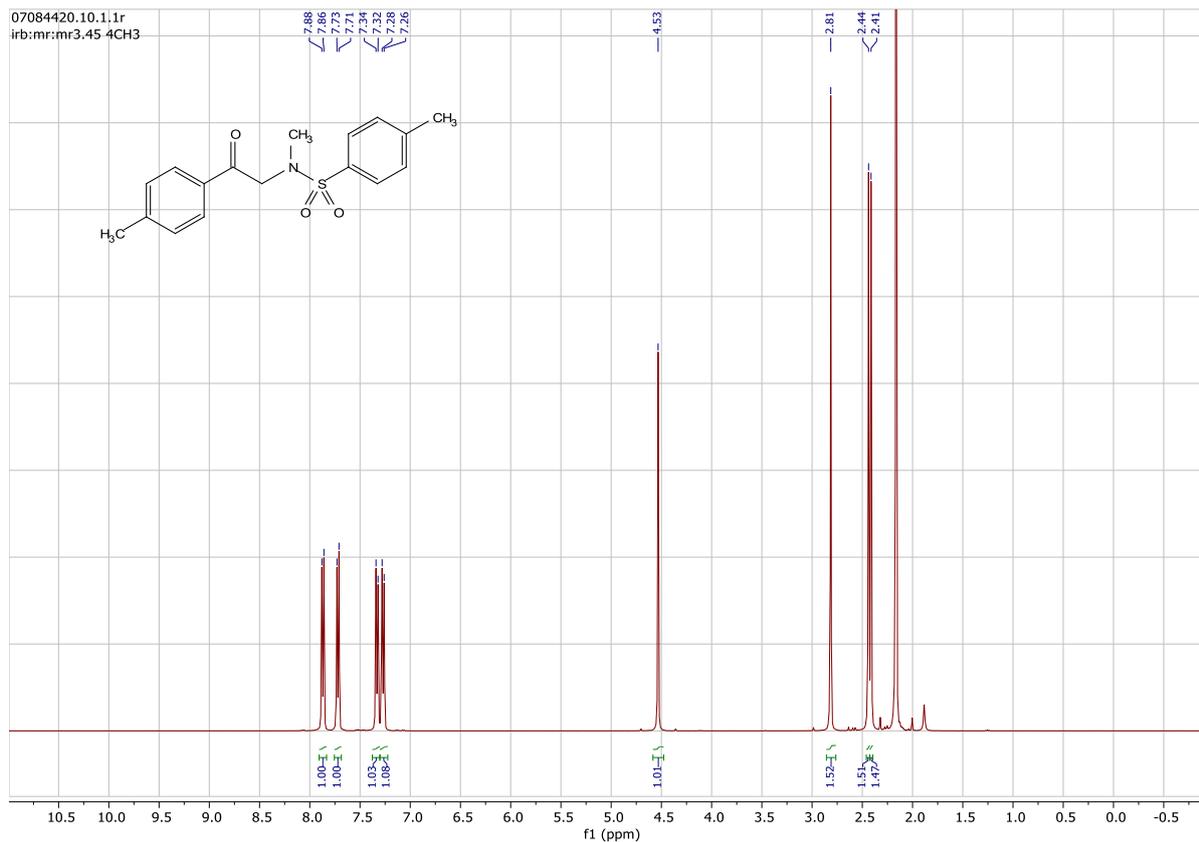
# Compound 1-126a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



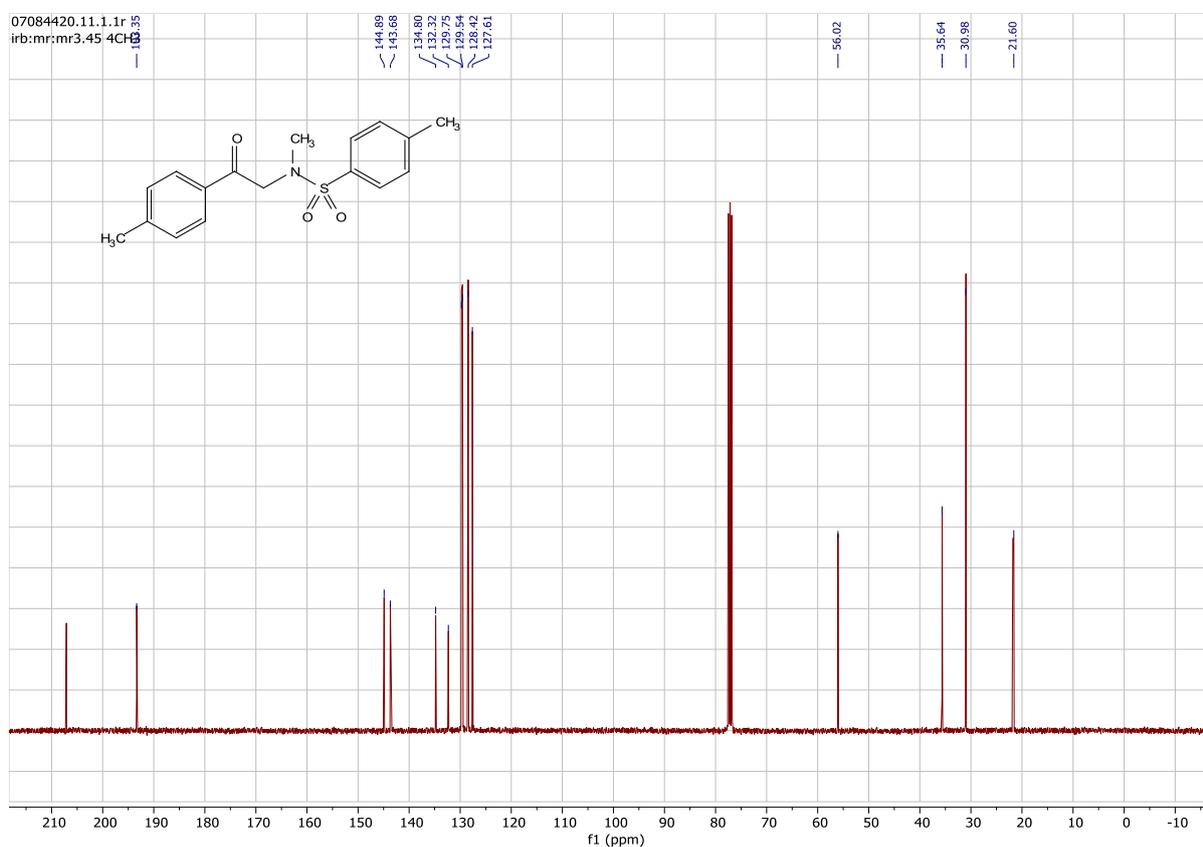
# Compound 1-126a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



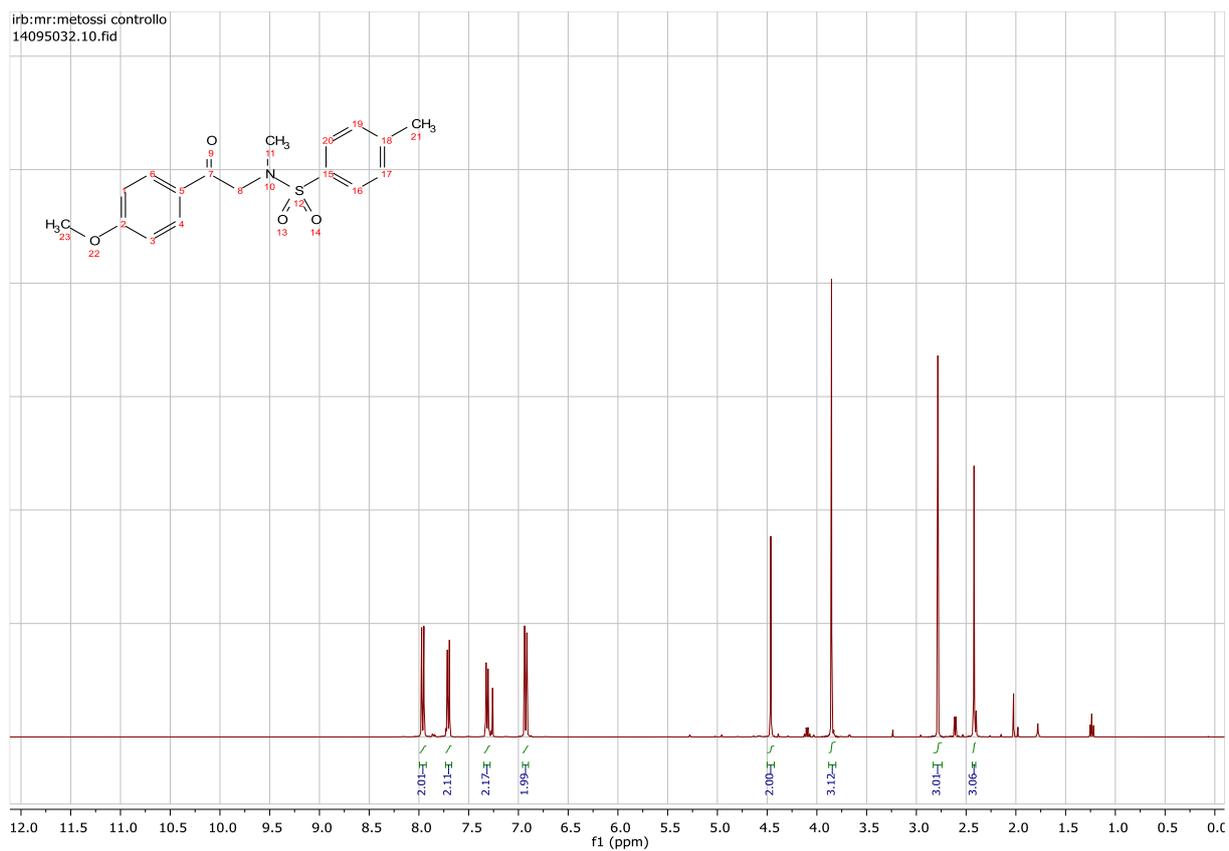
# Compound 1-127a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



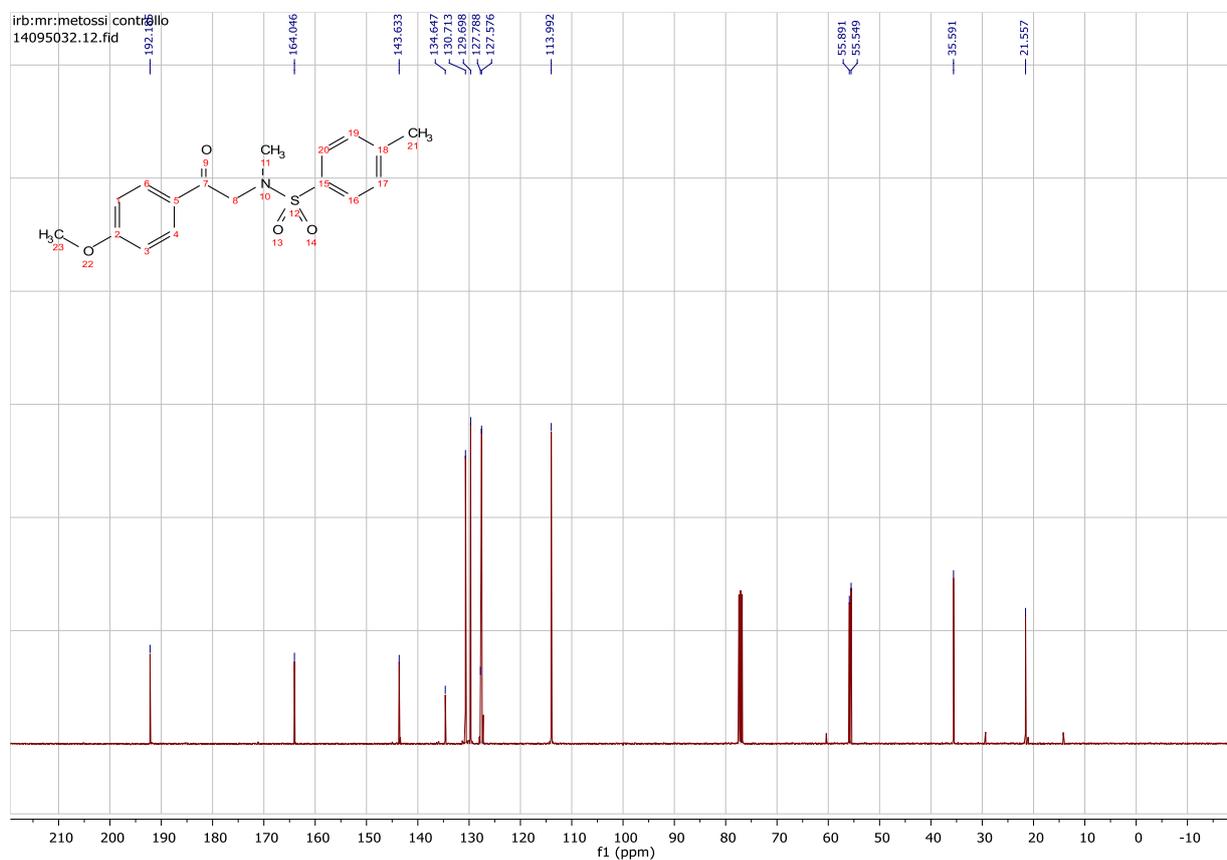
# Compound 1-127a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



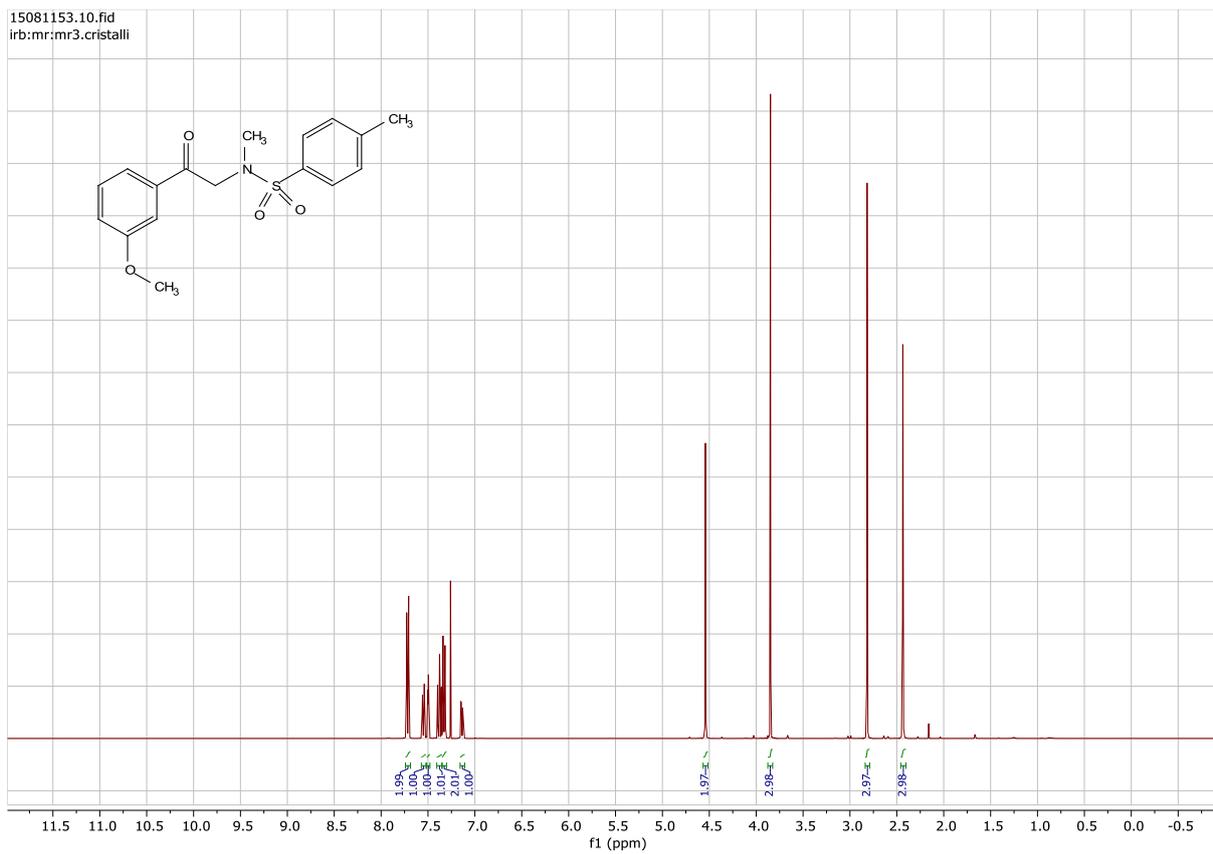
# Compound 1-128a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



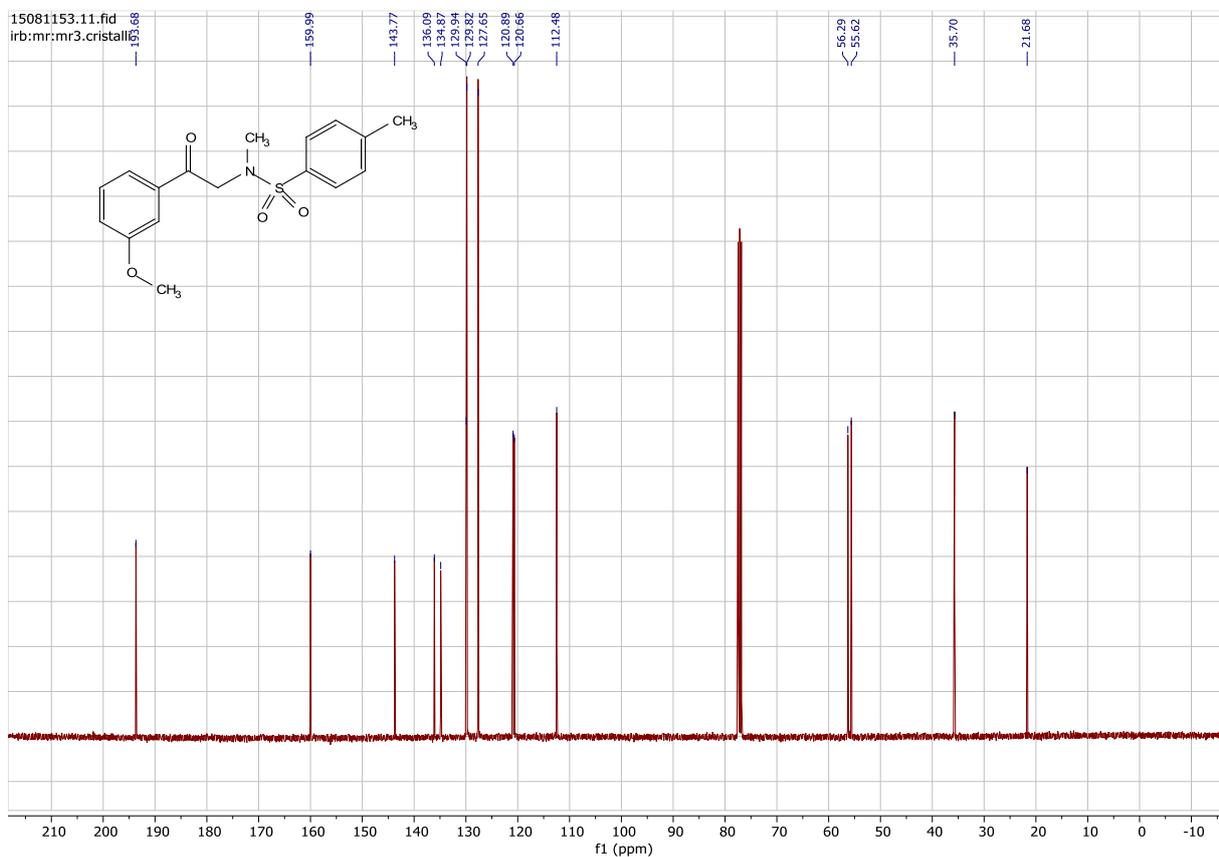
# Compound 1-128a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



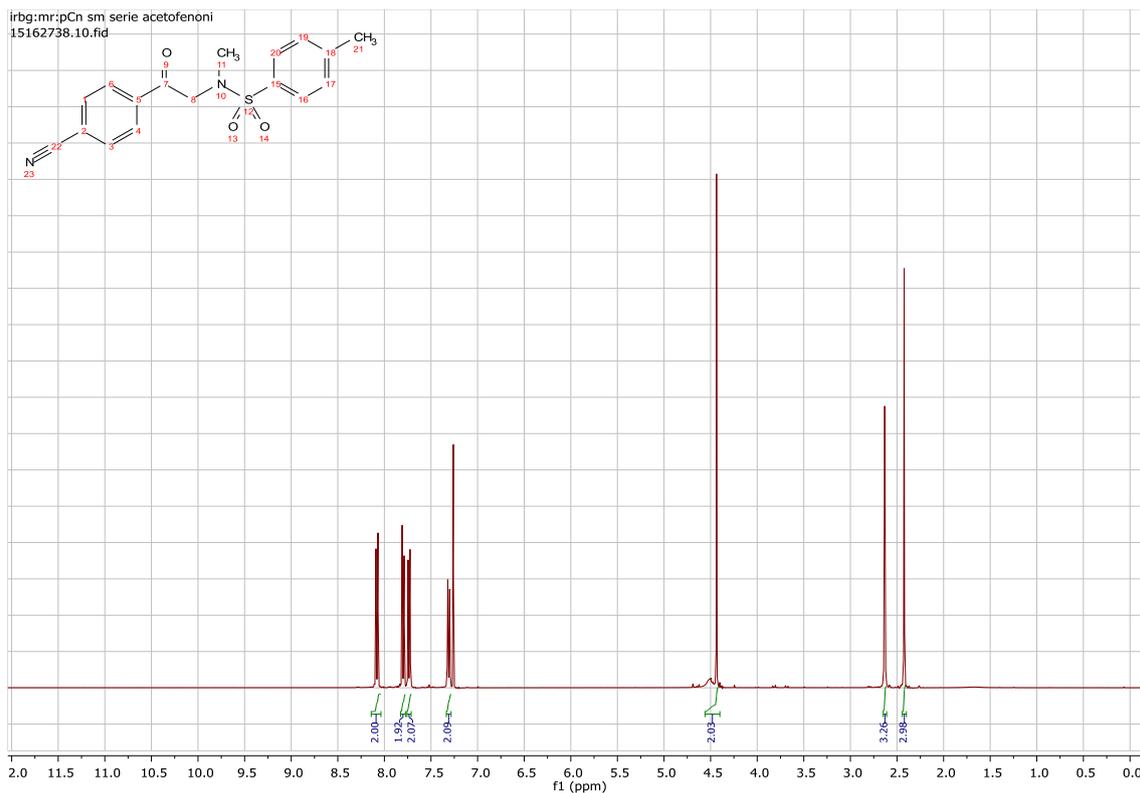
# Compound 1-129a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



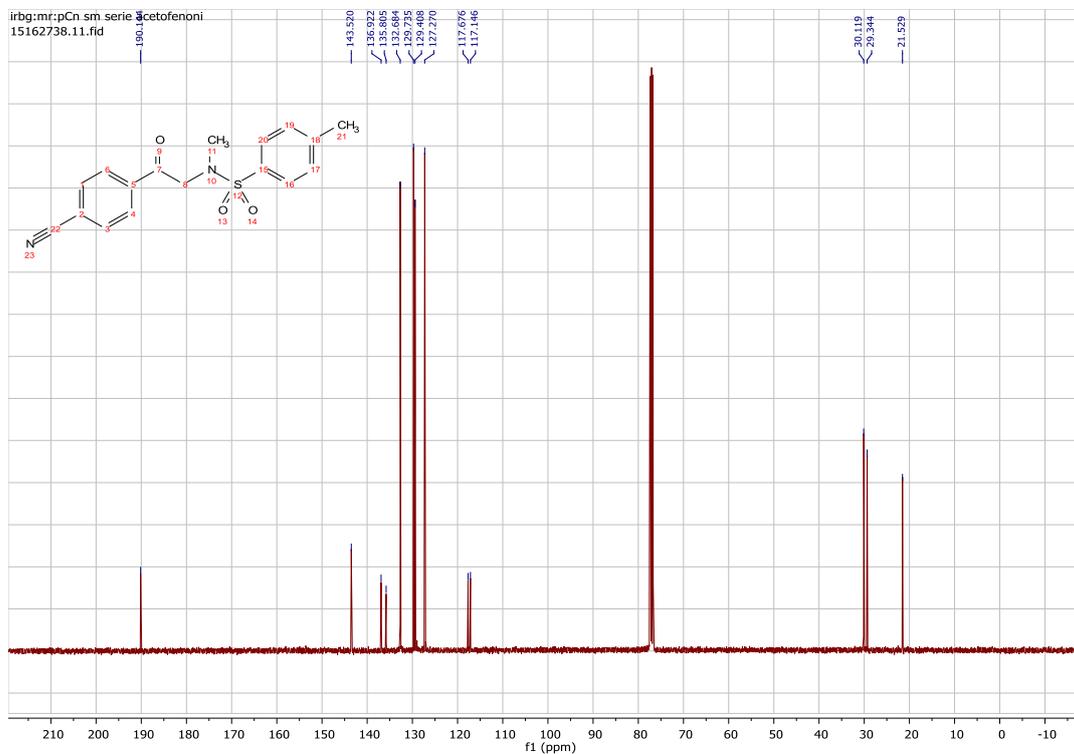
# Compound 1-129a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



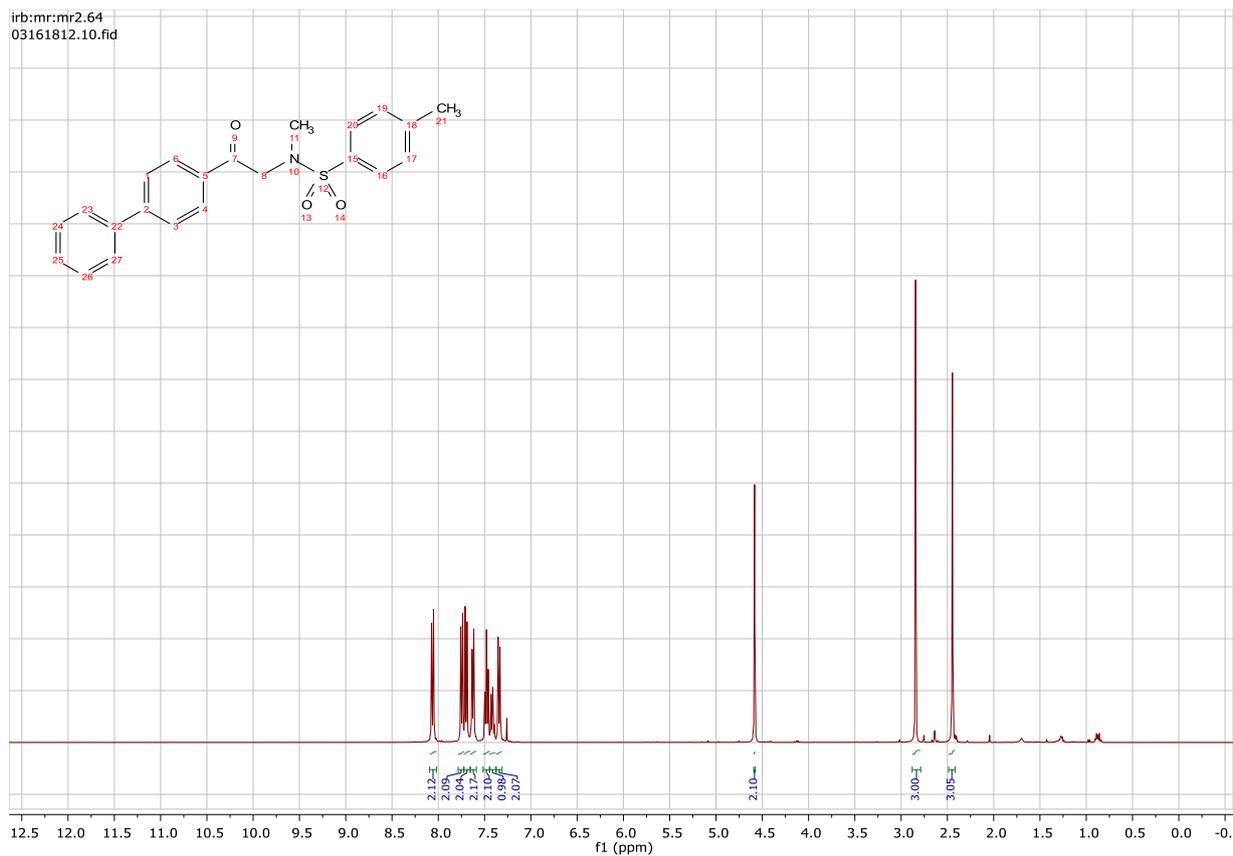
# Compound 1-131a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



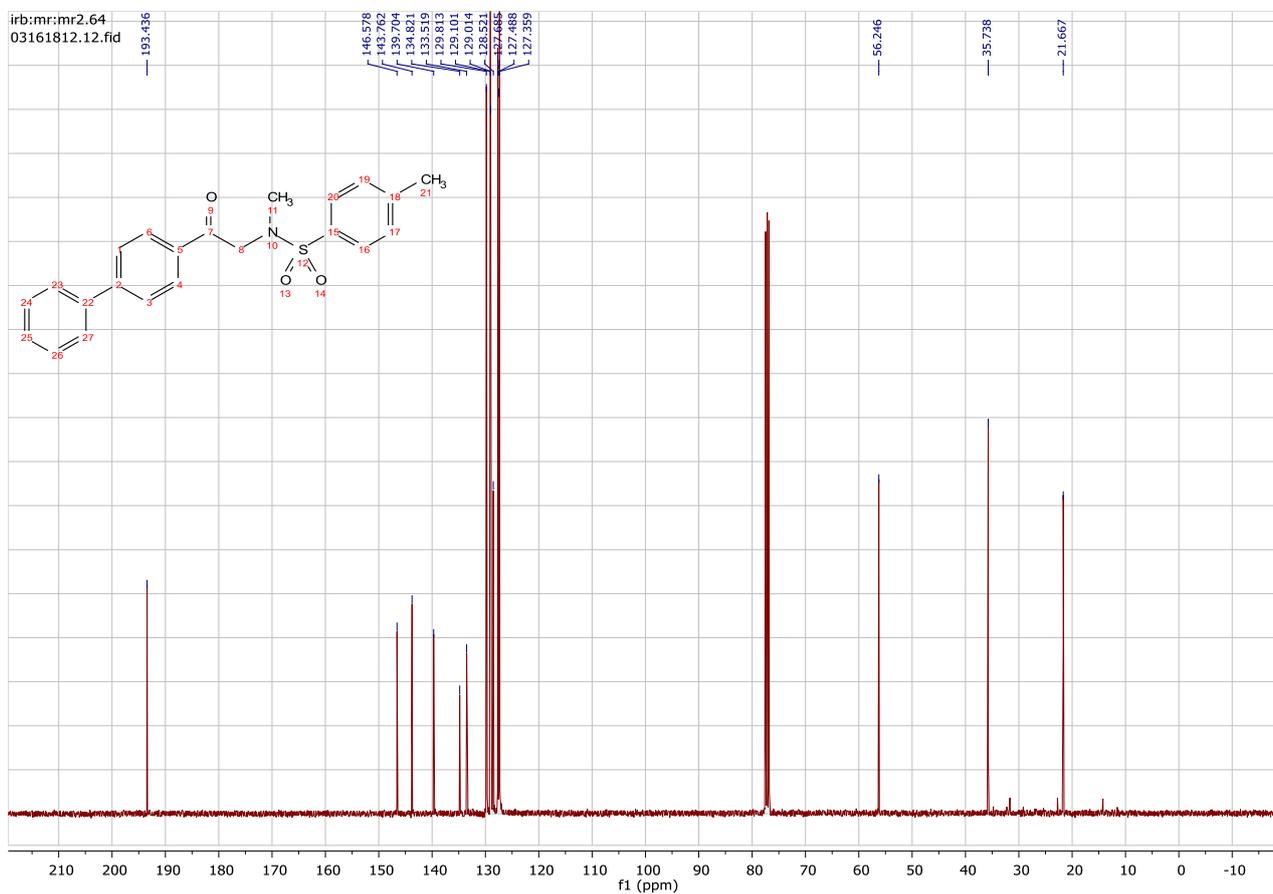
# Compound 1-131a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



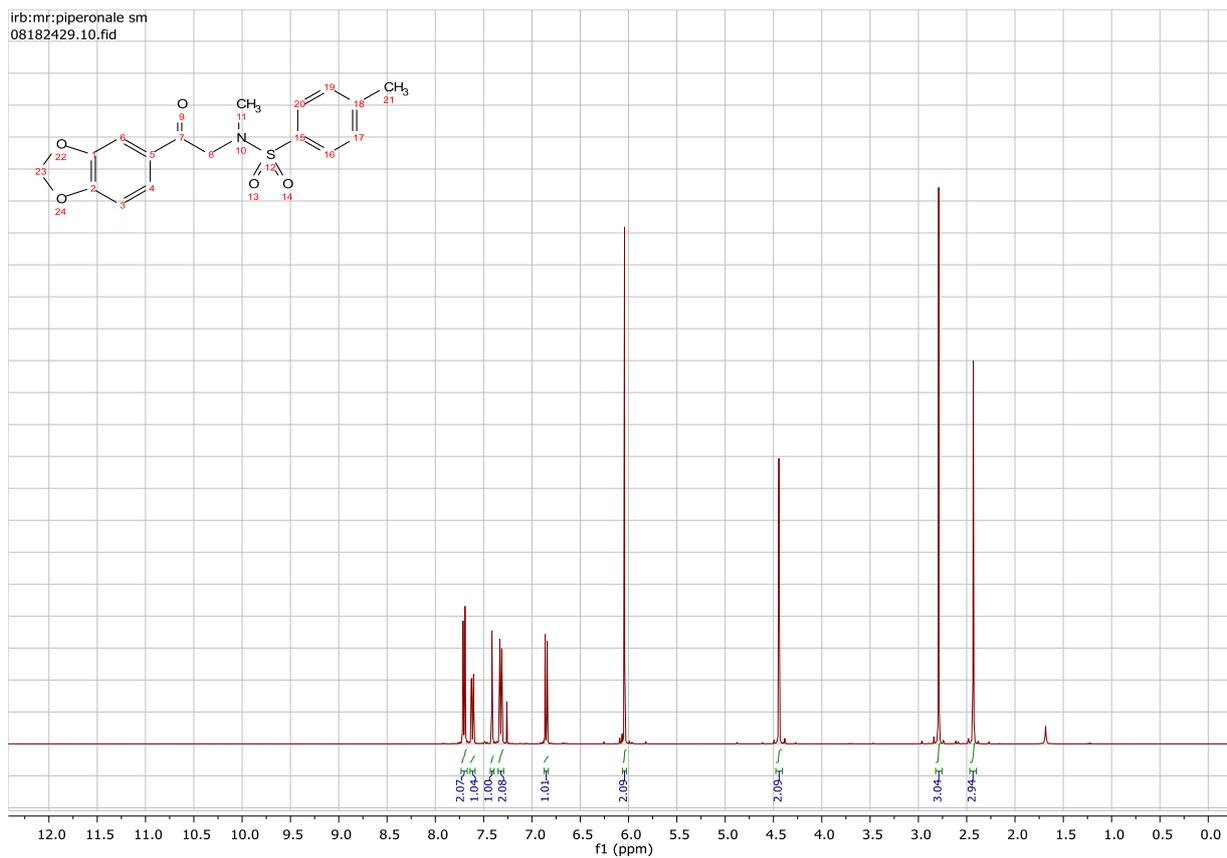
# Compound 1-132a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



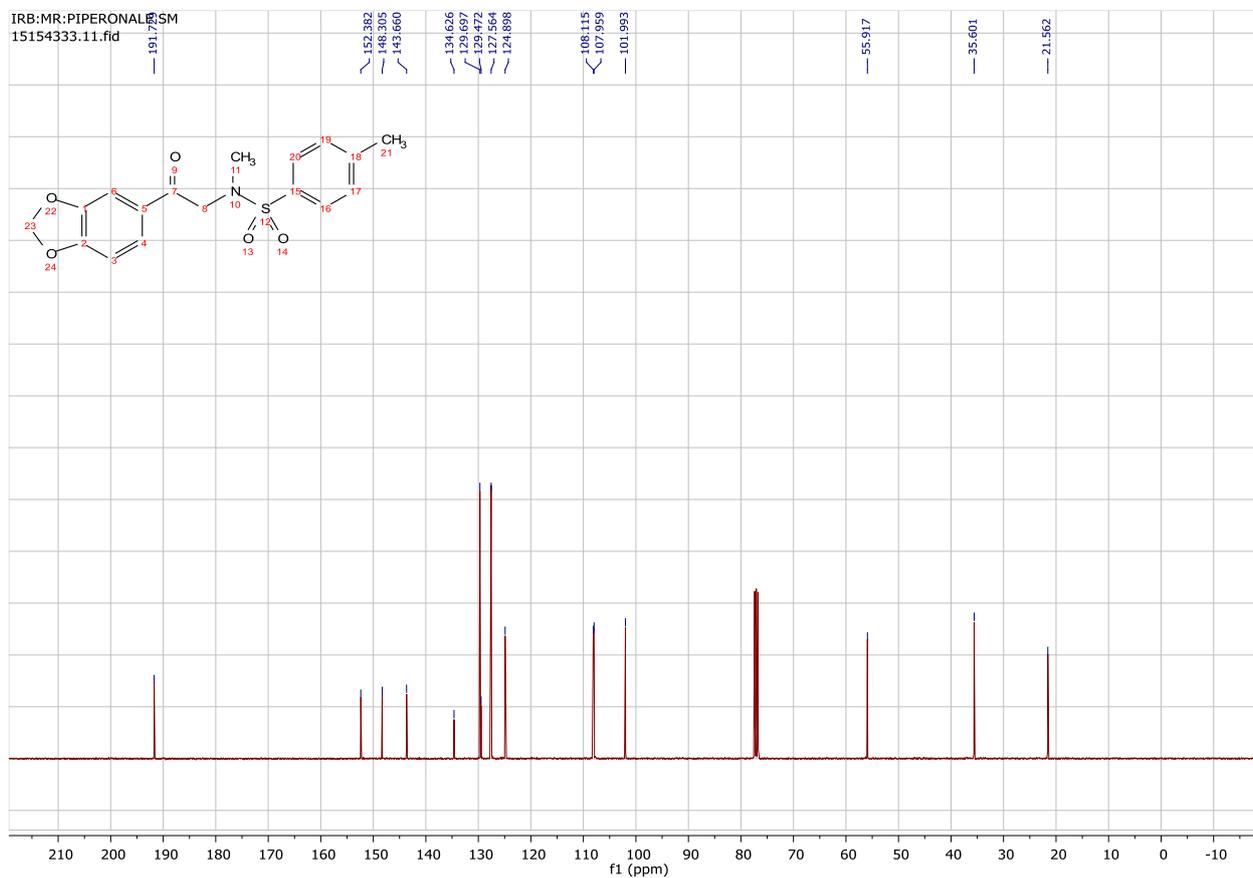
# Compound 1-132a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



# Compound 1-133a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )

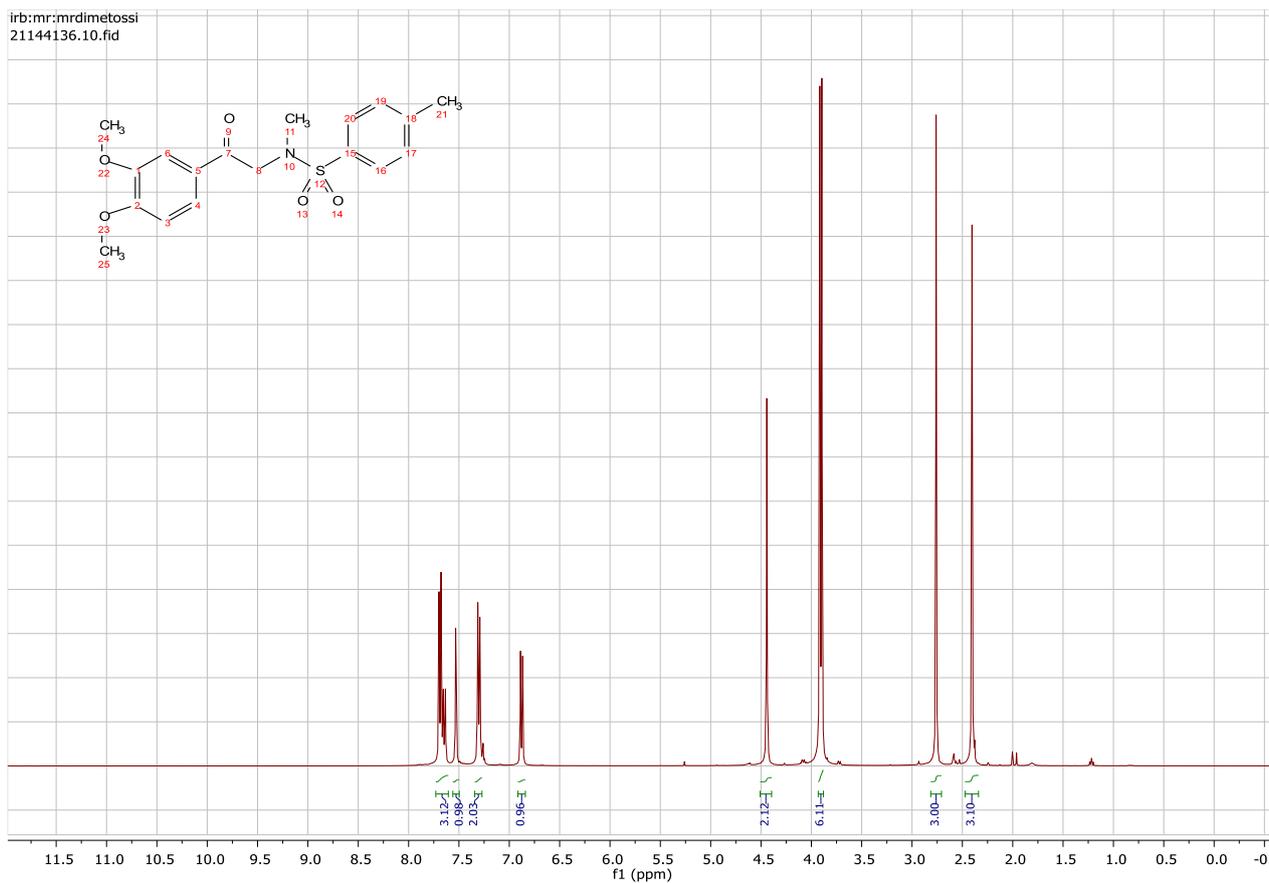


# Compound 1-133a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



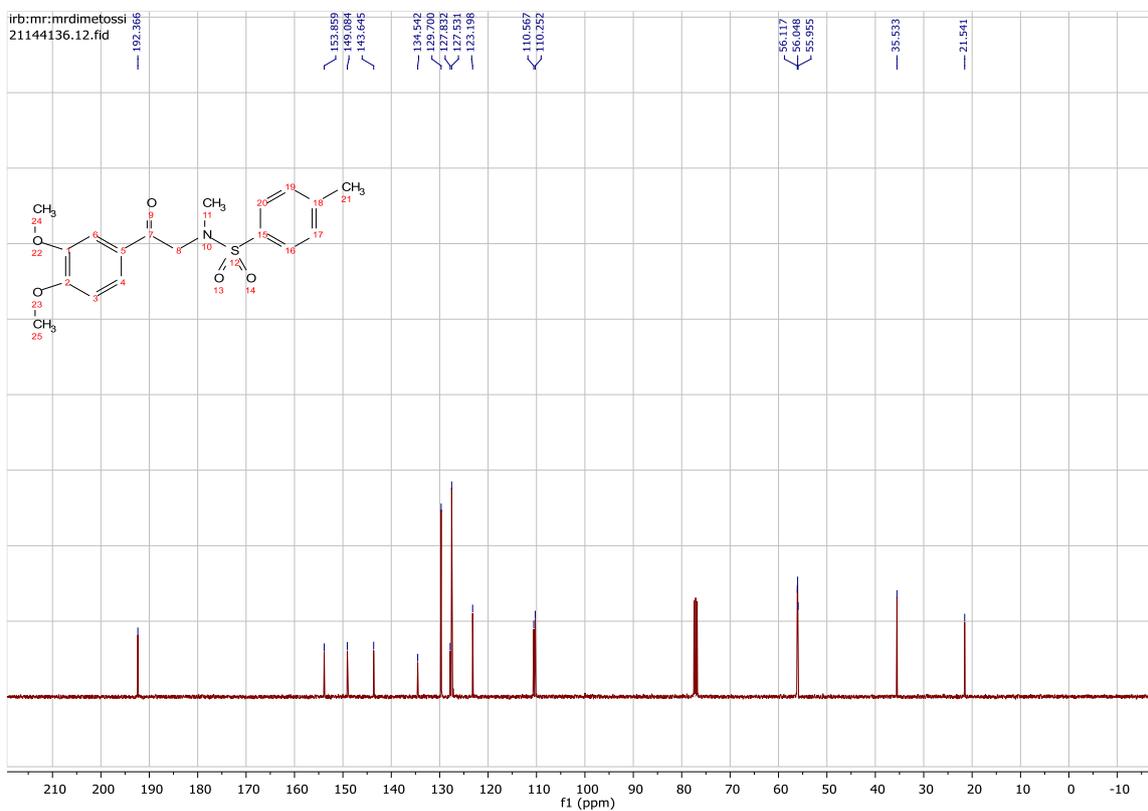
# Compound 1-134a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )

irb:mr:mrdimetossi  
21144136.10.fid



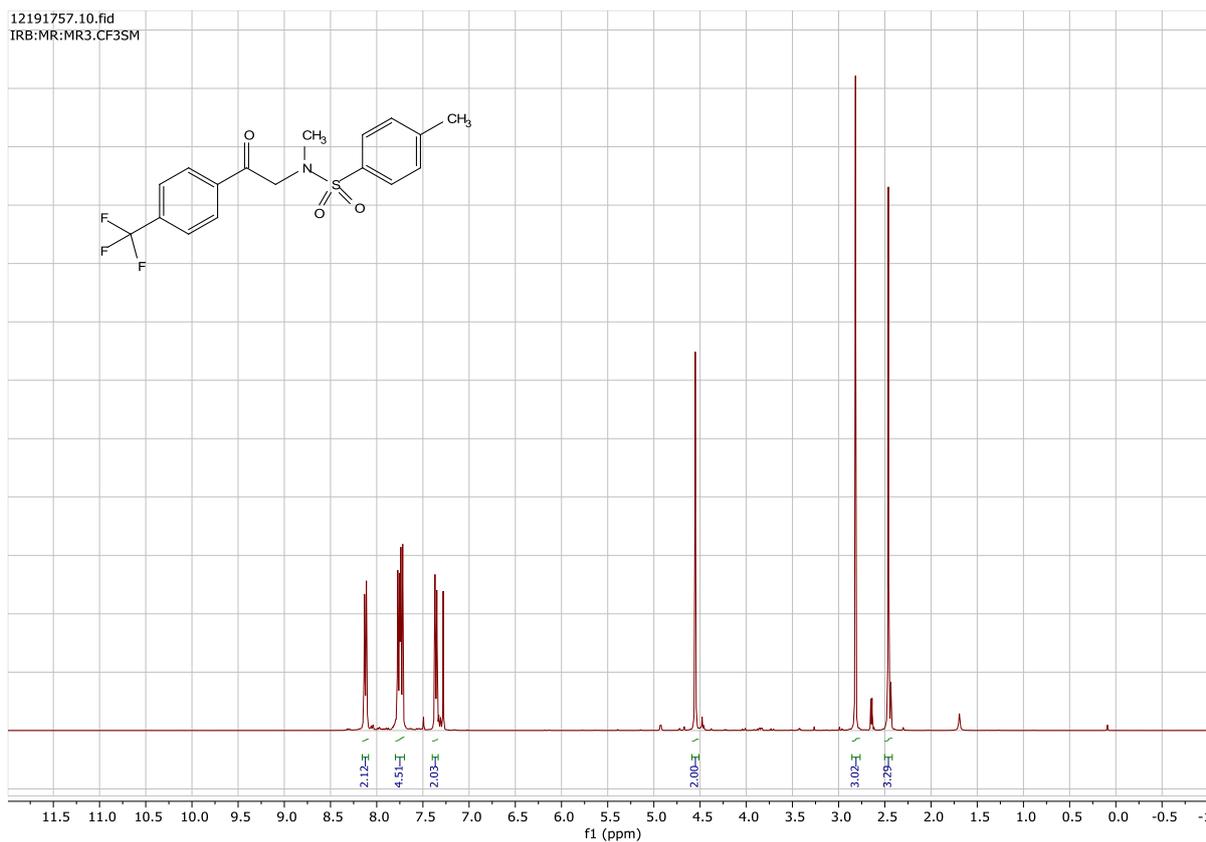
# Compound 1-134a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )

irb:mr:mrdimetossi  
21144136.12.fid



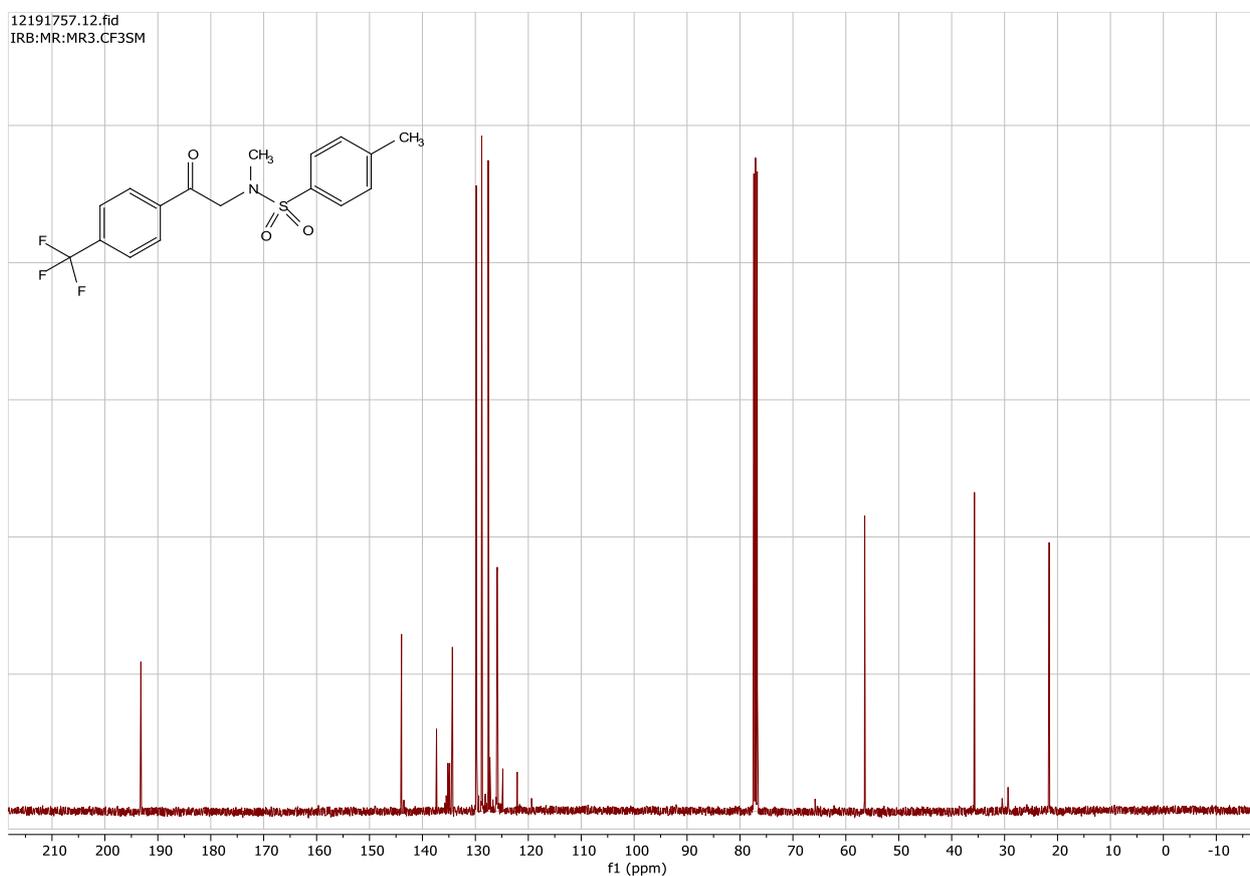
# Compound 1-135a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)

12191757.10.fid  
IRB:MR:MR3.CF3SM

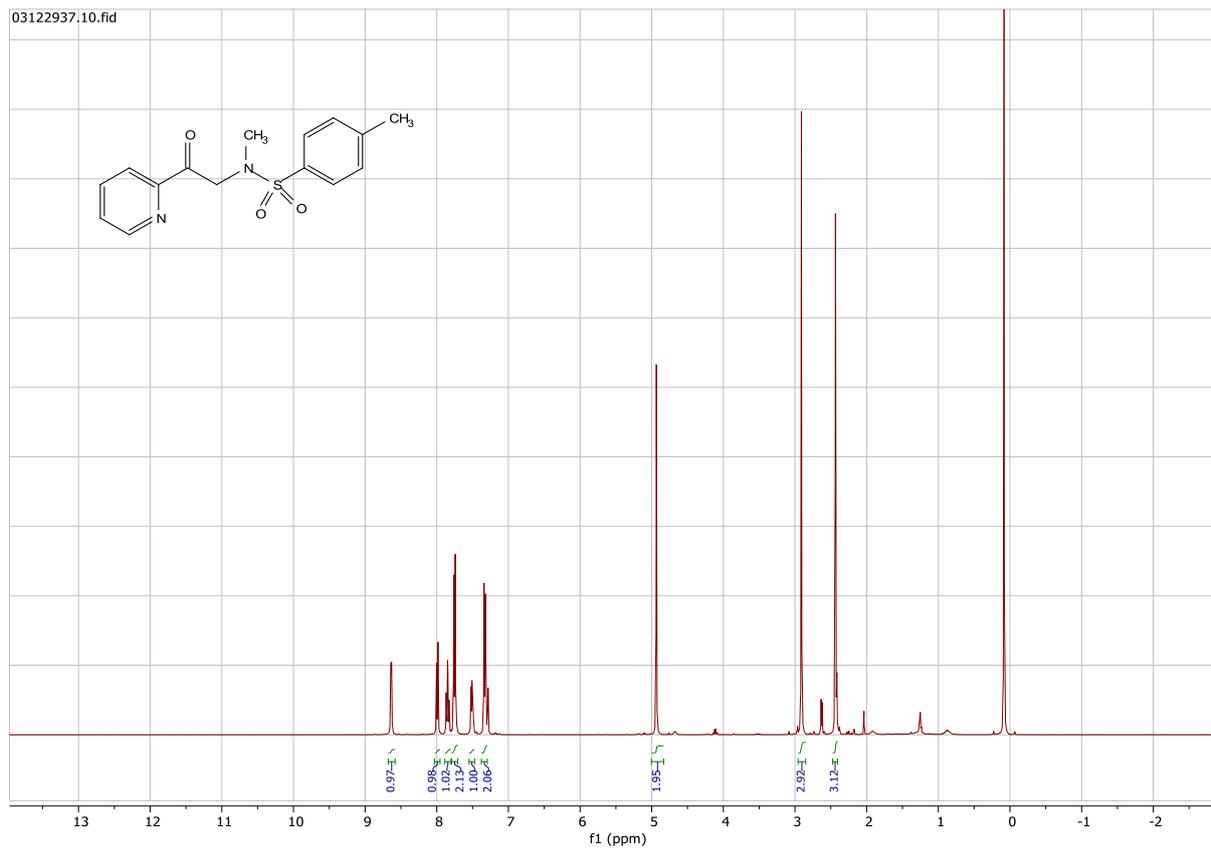


# Compound 1-135a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

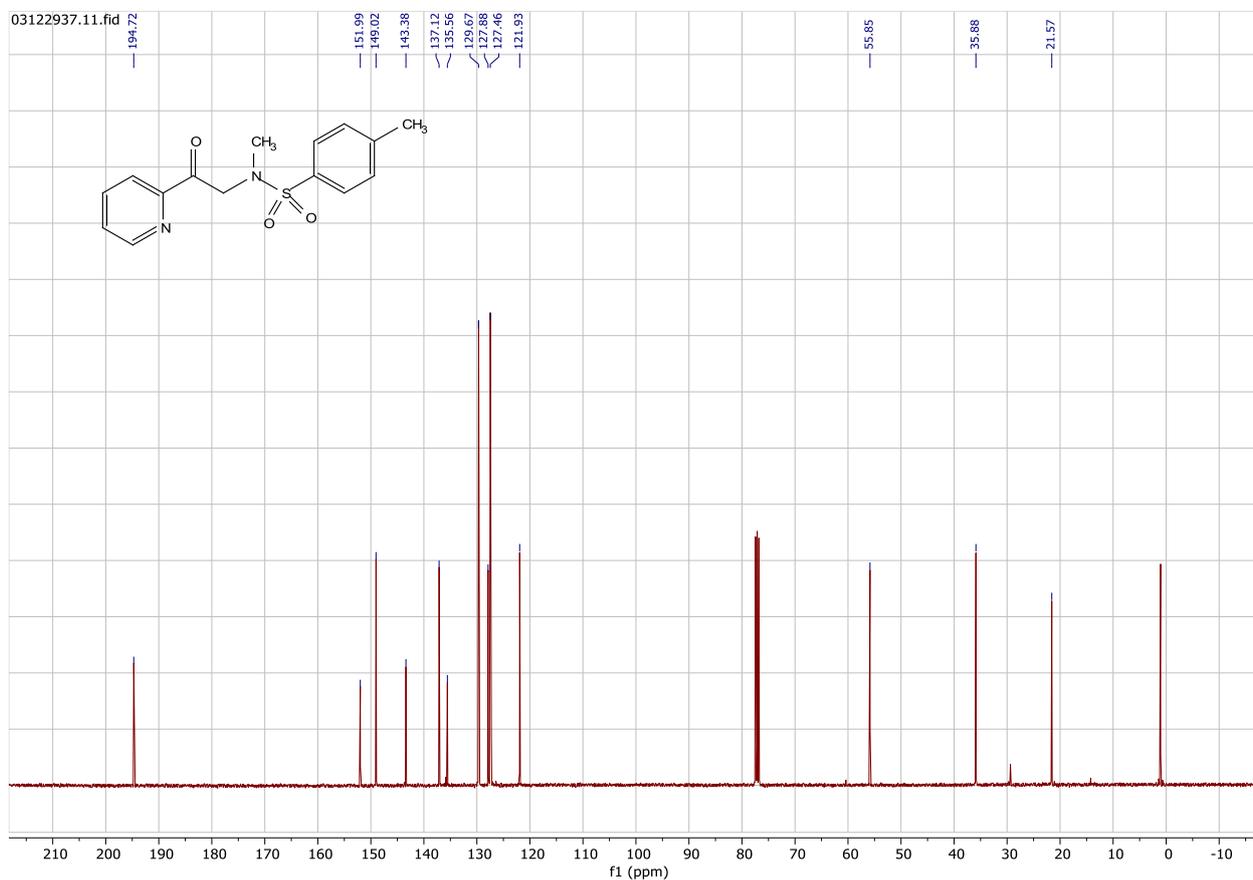
12191757.12.fid  
IRB:MR:MR3.CF3SM



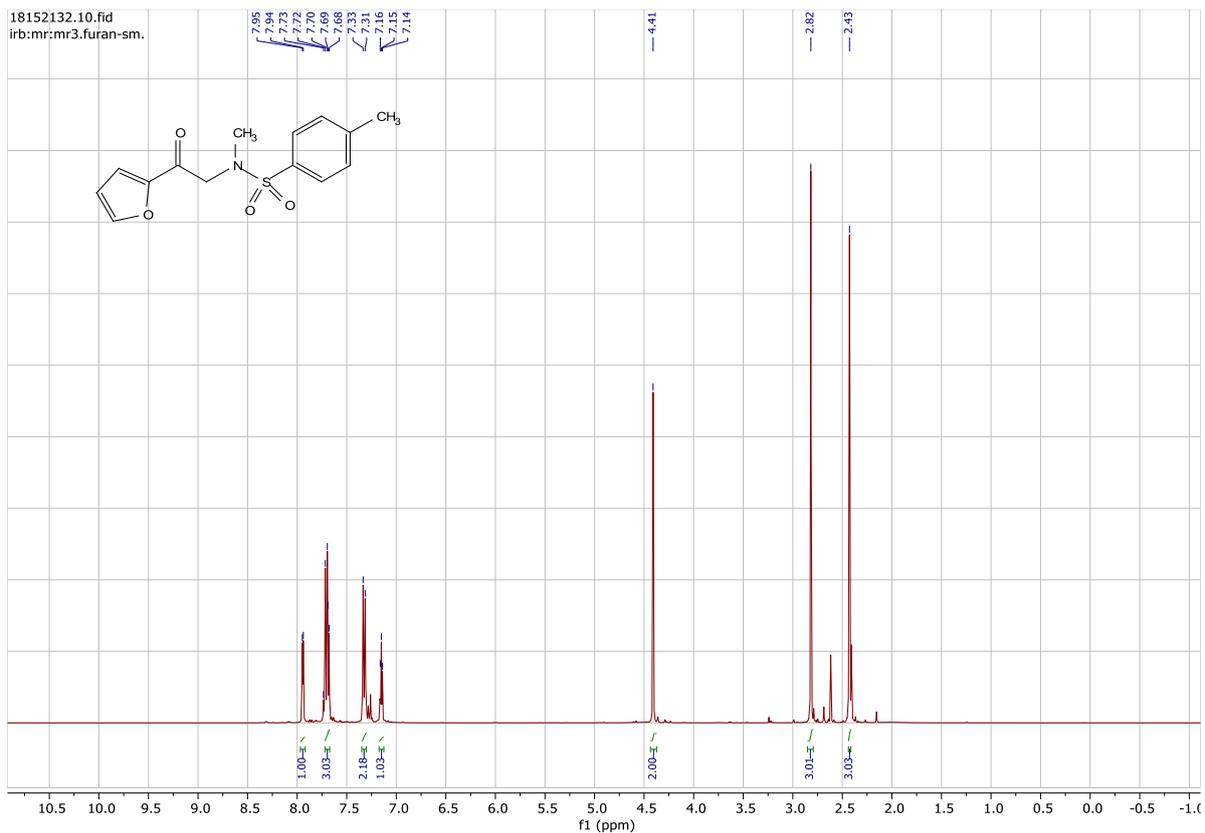
# Compound 1-136a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



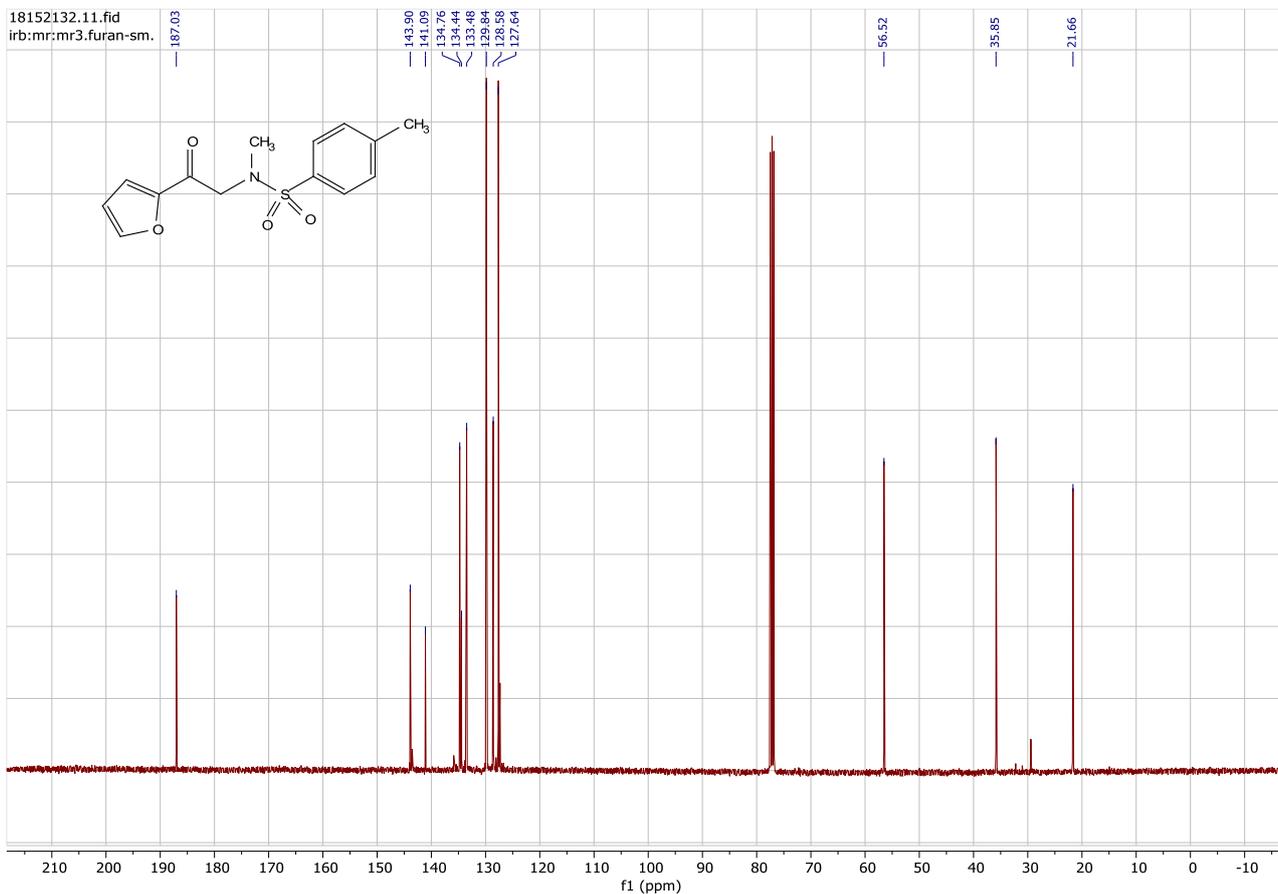
# Compound 1-136a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



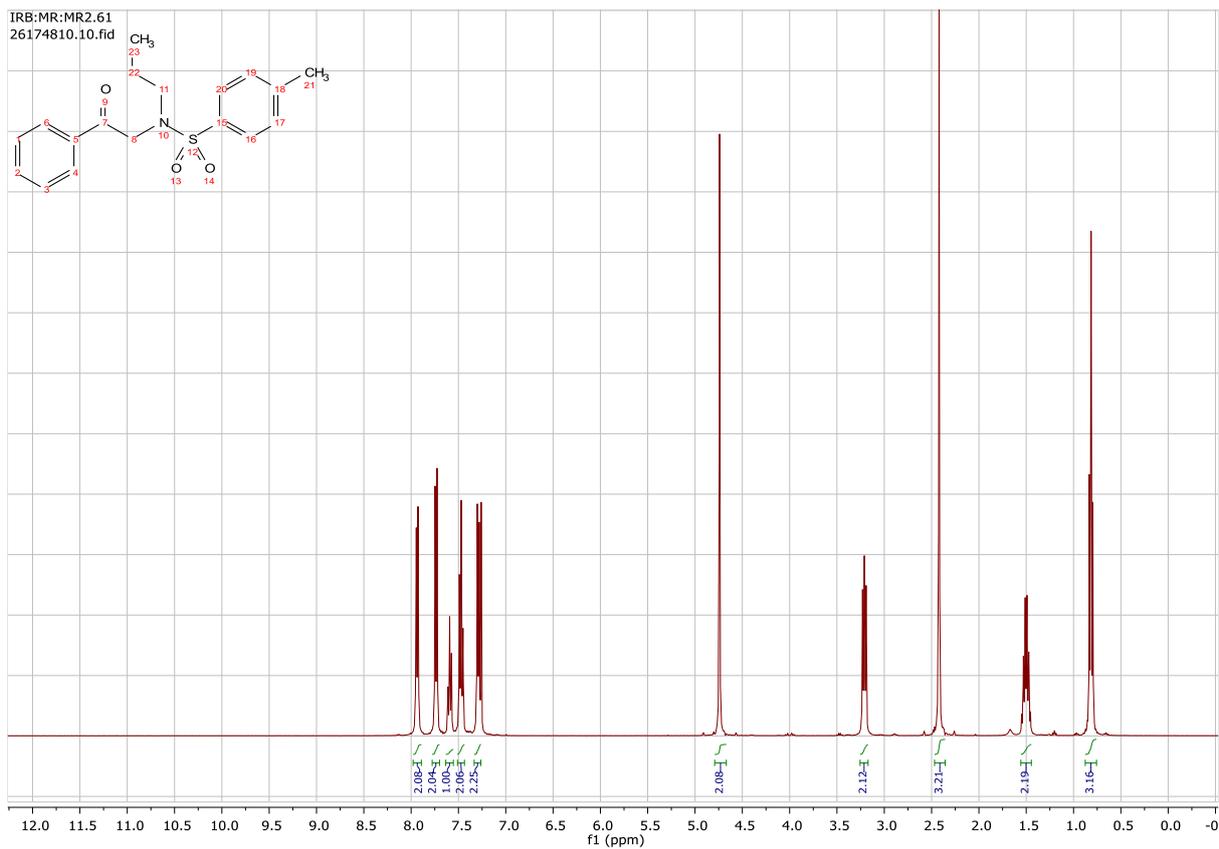
# Compound 1-137a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



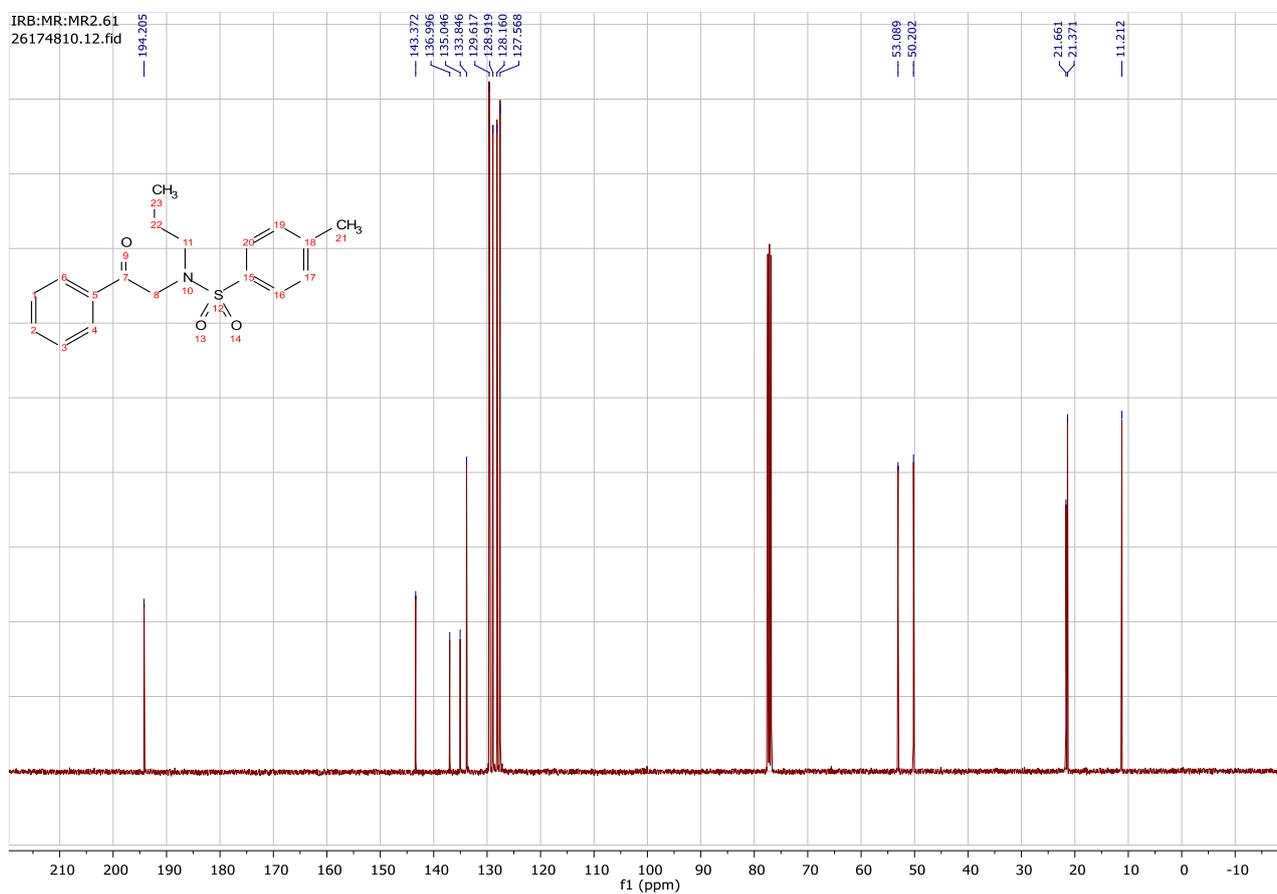
# Compound 1-137a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



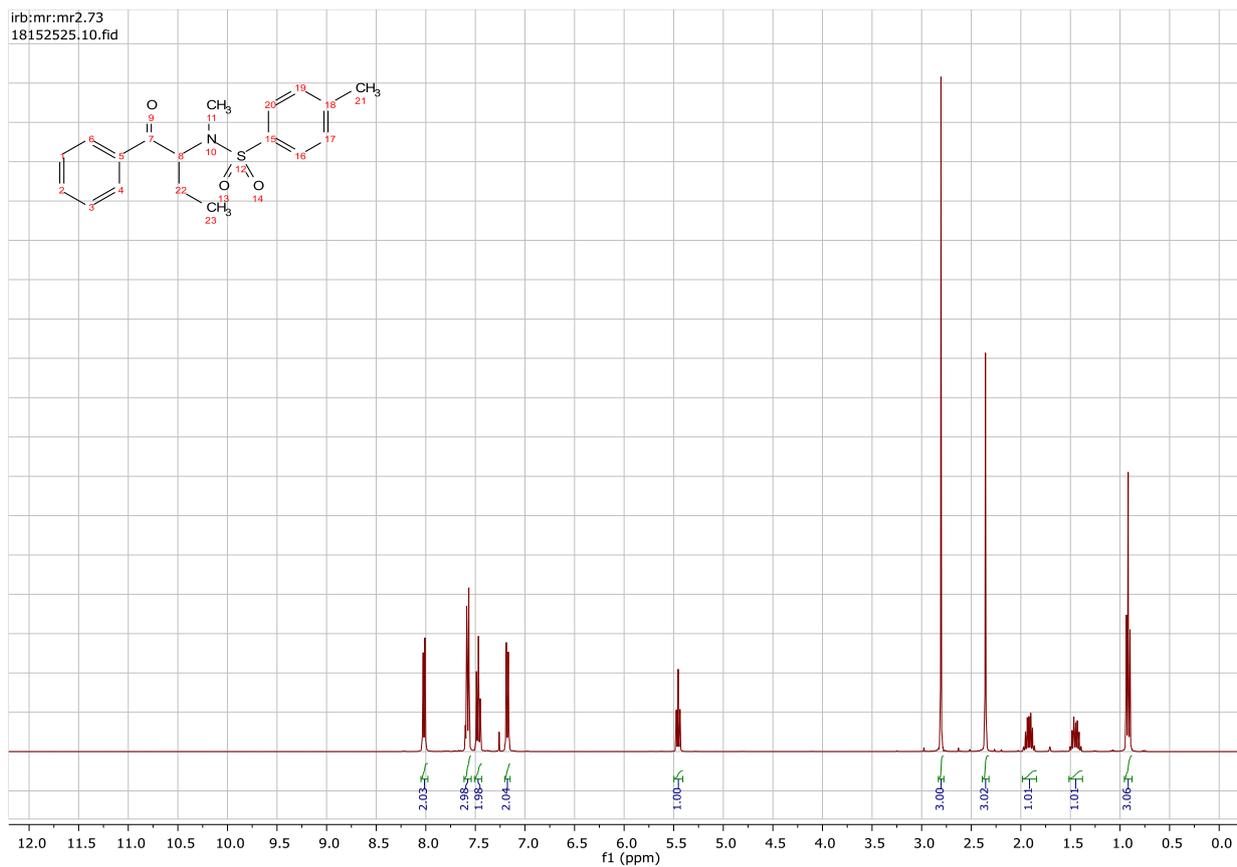
# Compound 1-139a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



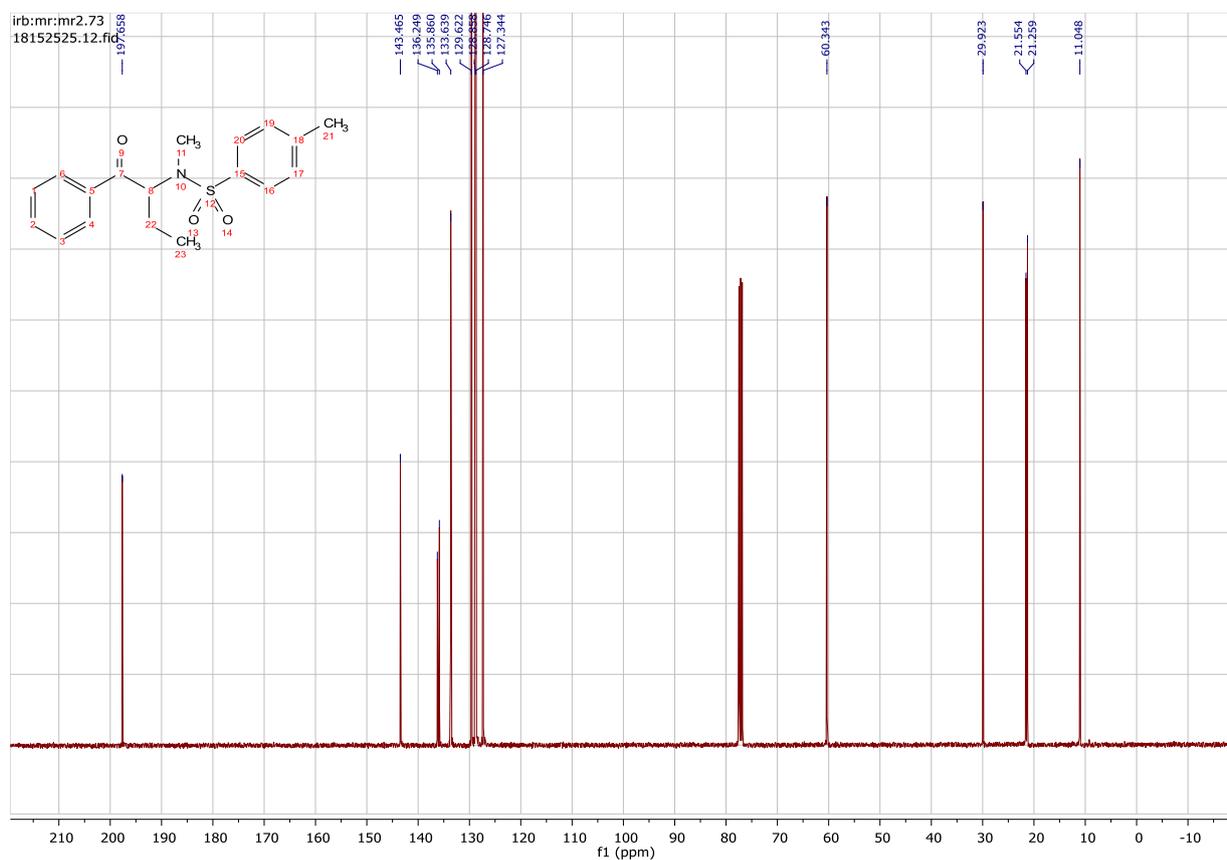
# Compound 1-139a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



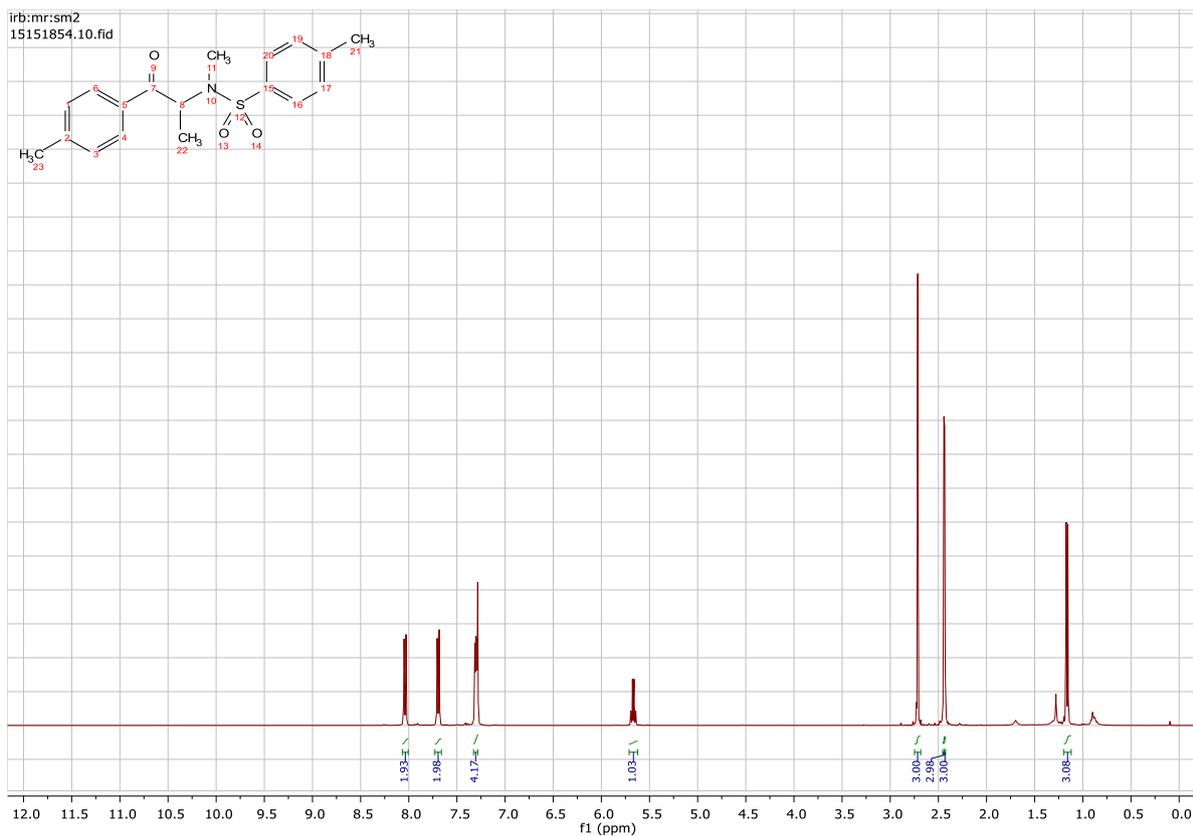
# Compound 1-140a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



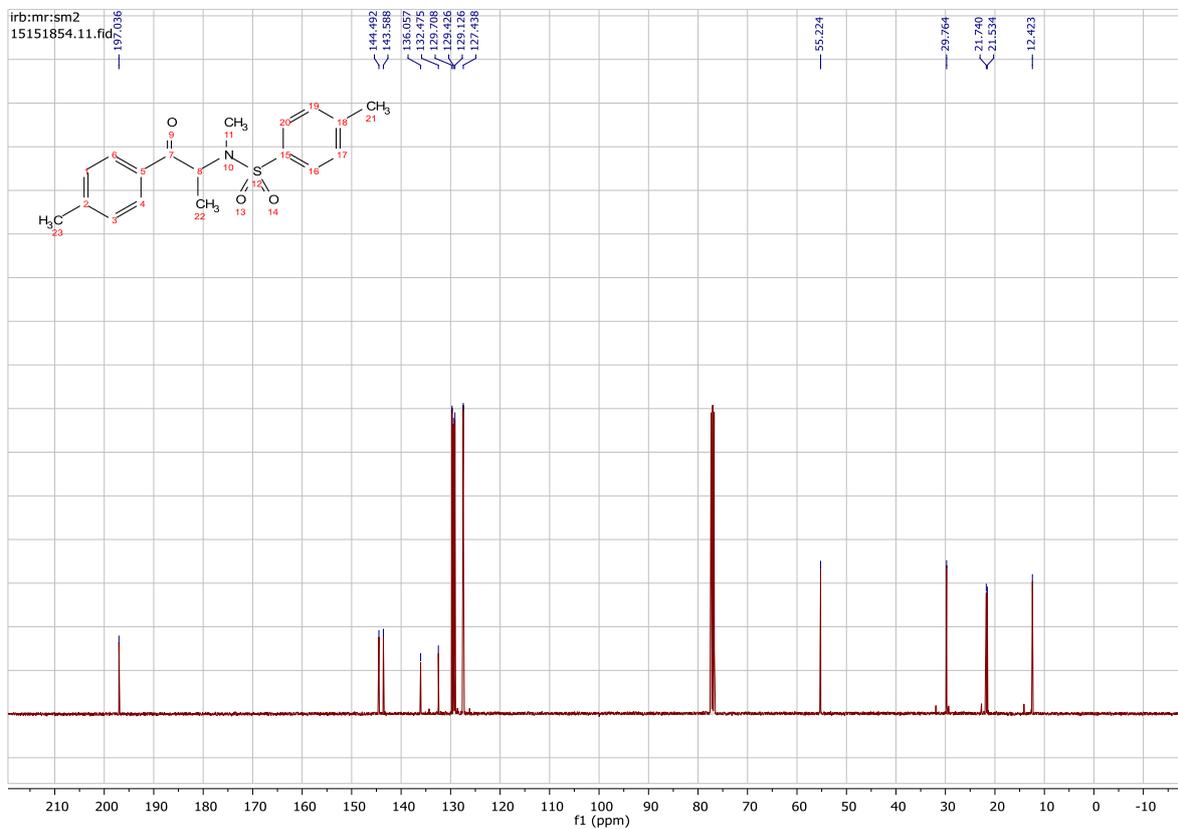
# Compound 1-140a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



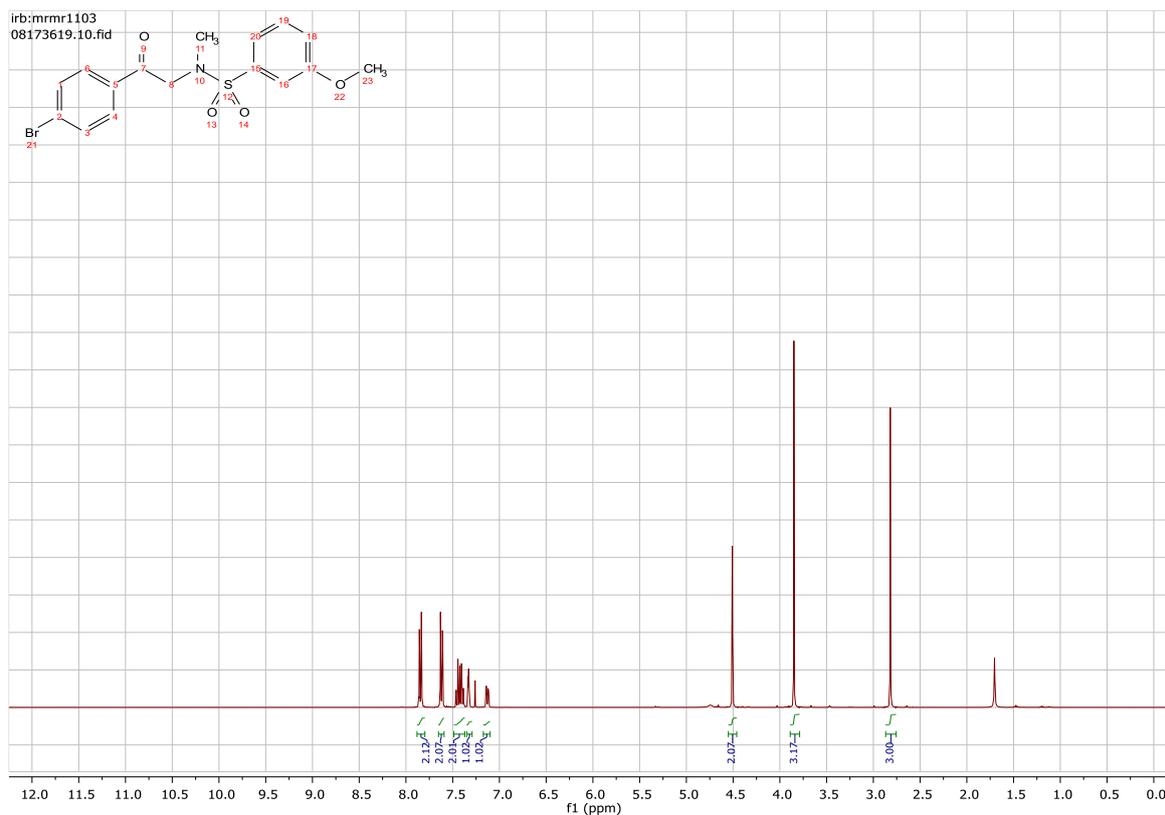
# Compound 1-142a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



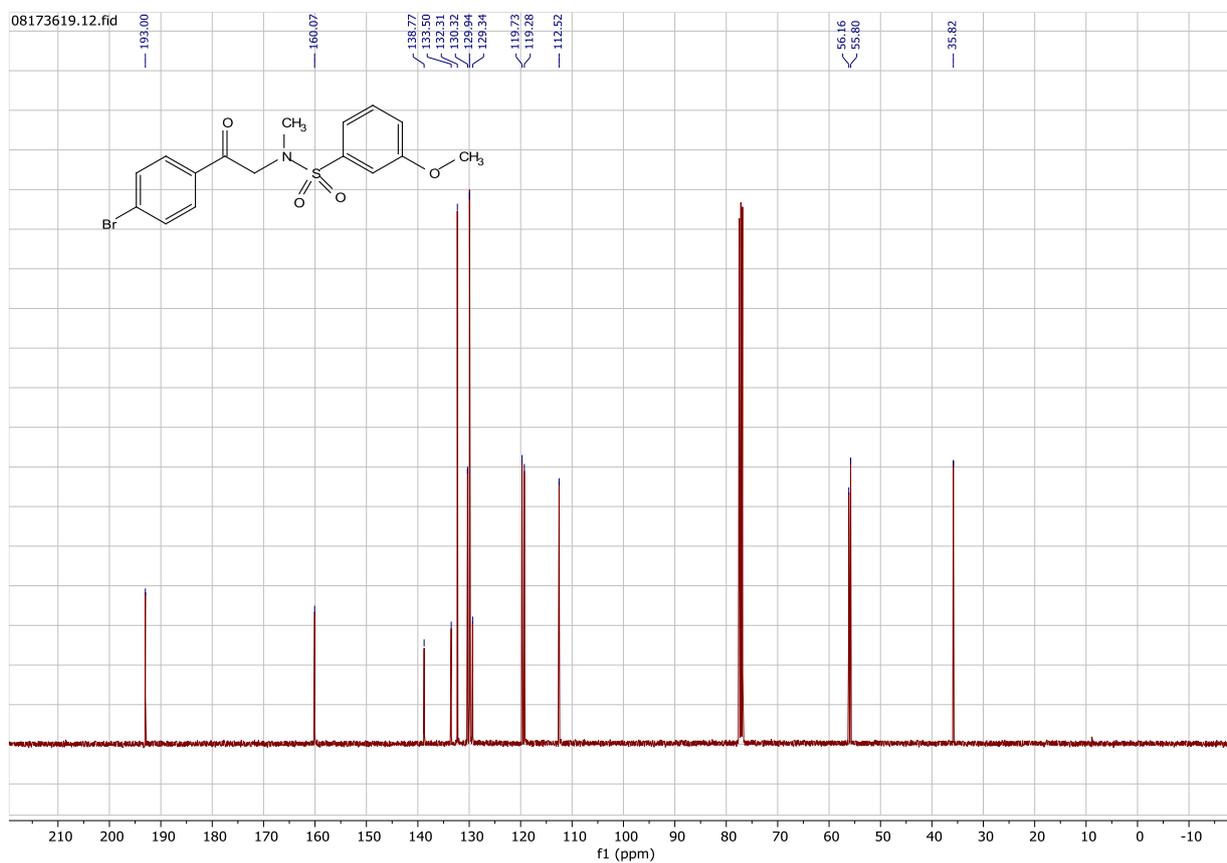
# Compound 1-142a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



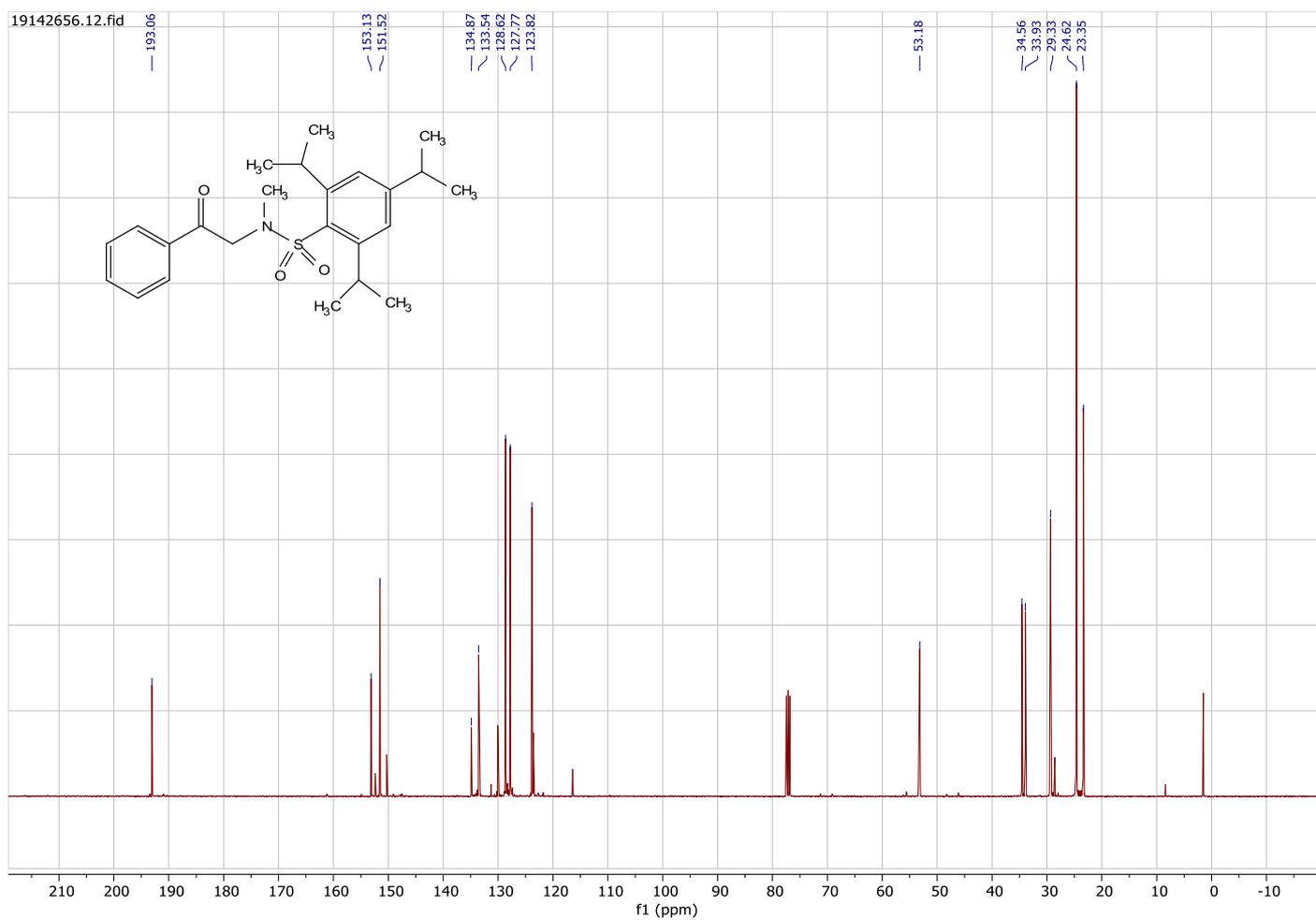
# Compound 1-143a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



# Compound 1-143a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )

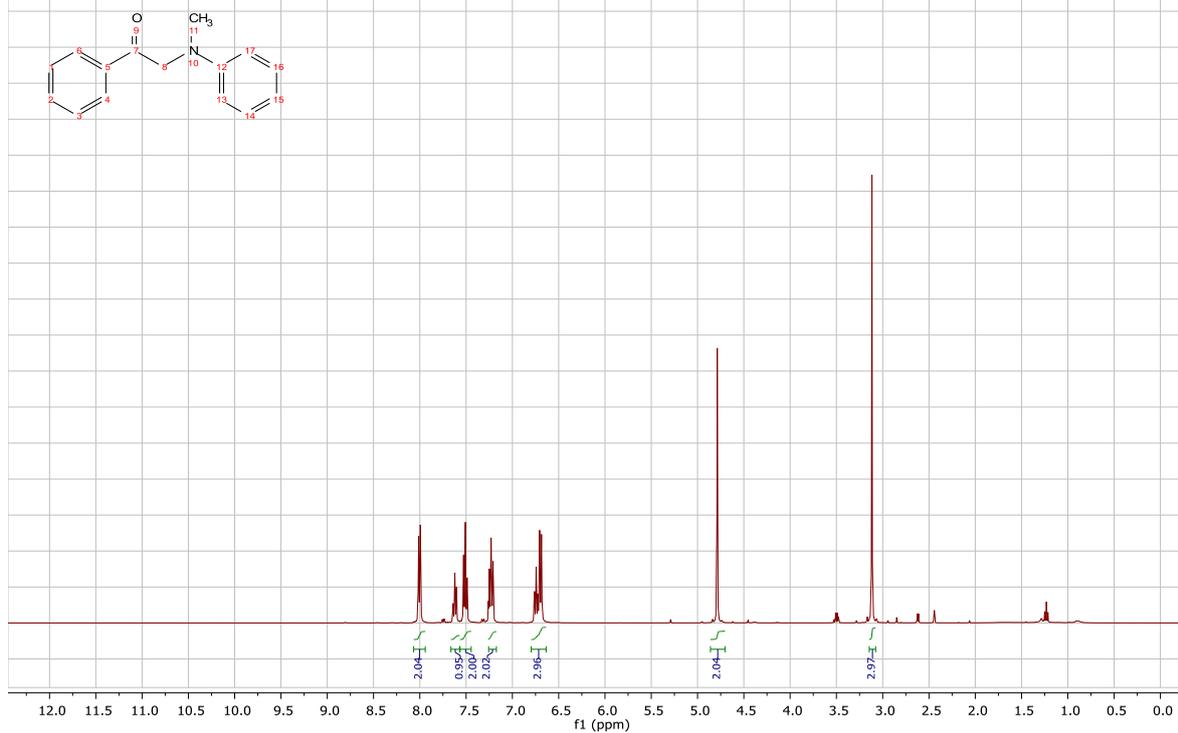


# Compound 1-144a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



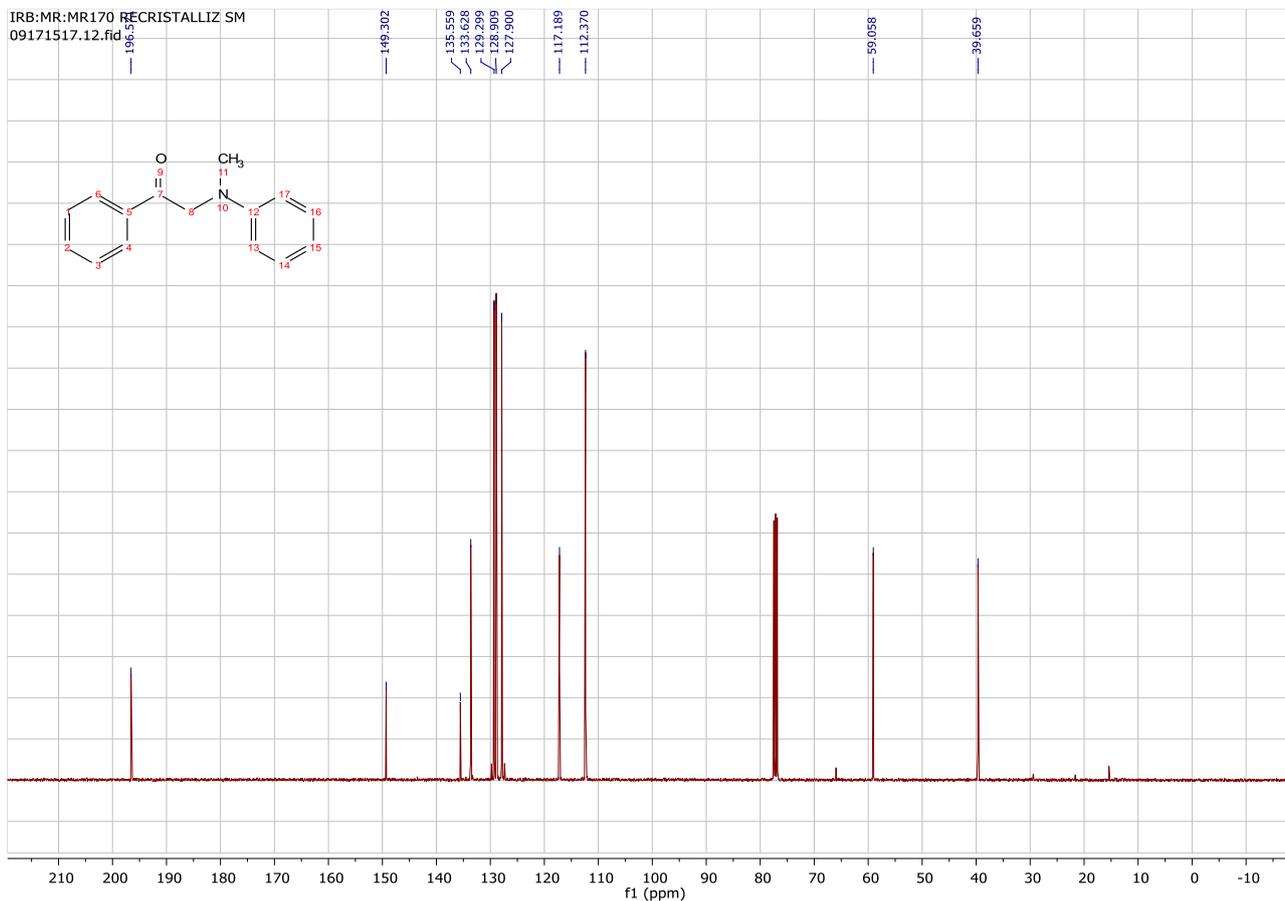
# Compound 1-146a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )

IRB:MR:MR170 RECRISTALLIZ SM  
09171517.10.fid

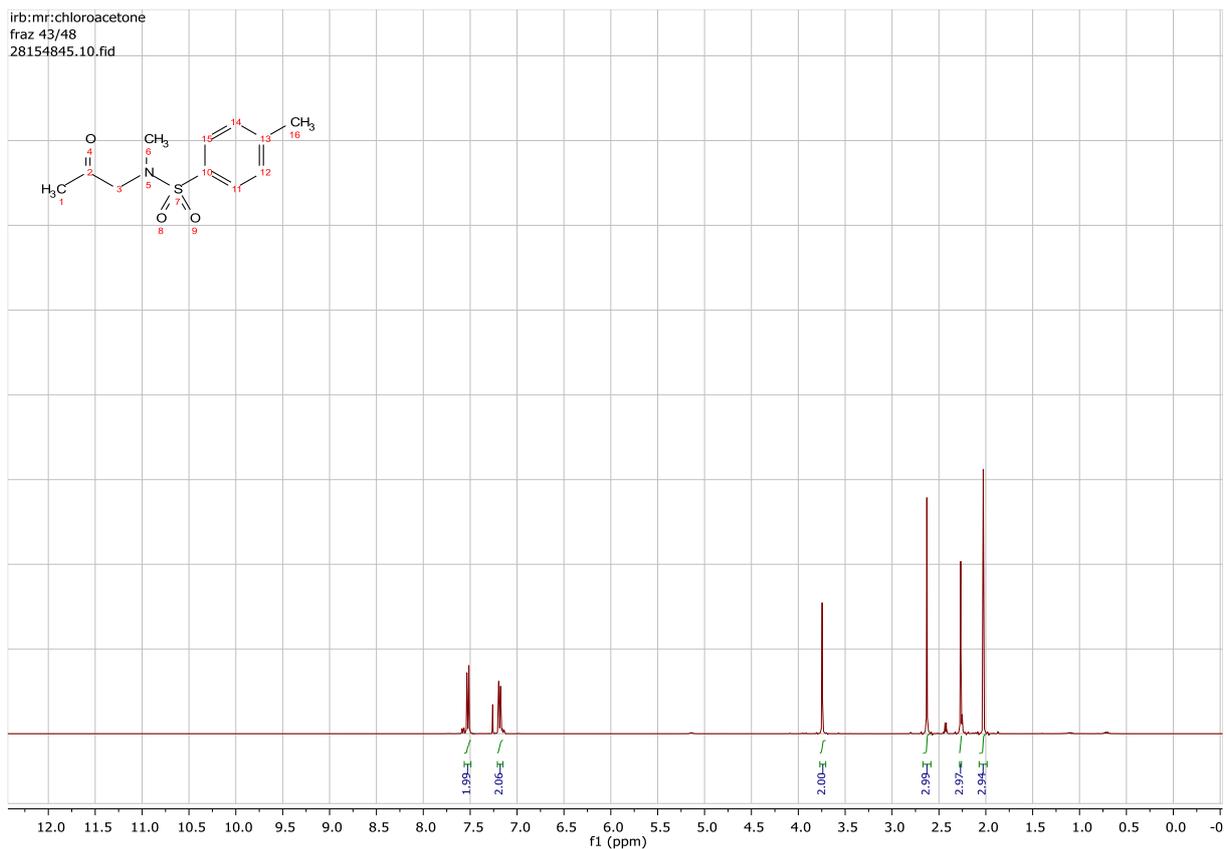


# Compound 1-146a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )

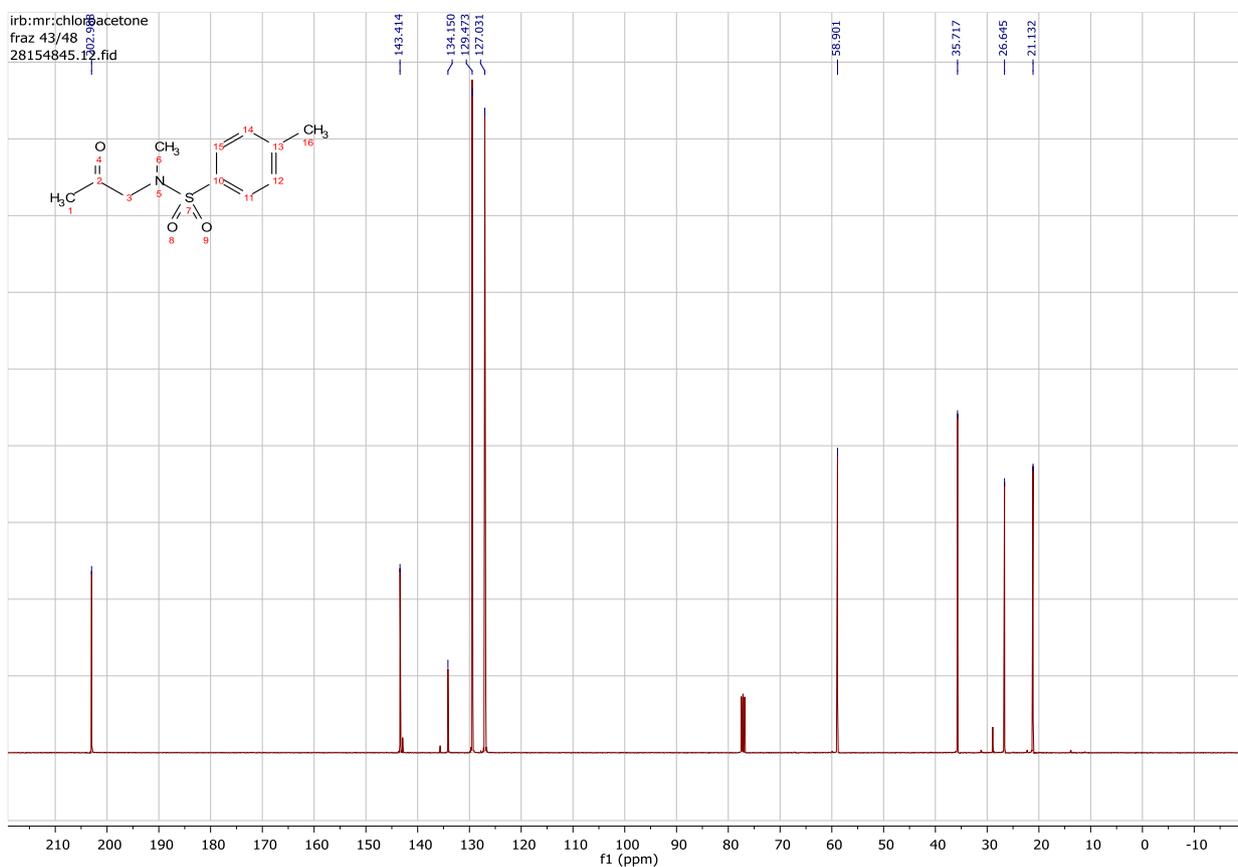
IRB:MR:MR170 RECRISTALLIZ SM  
09171517.12.fid



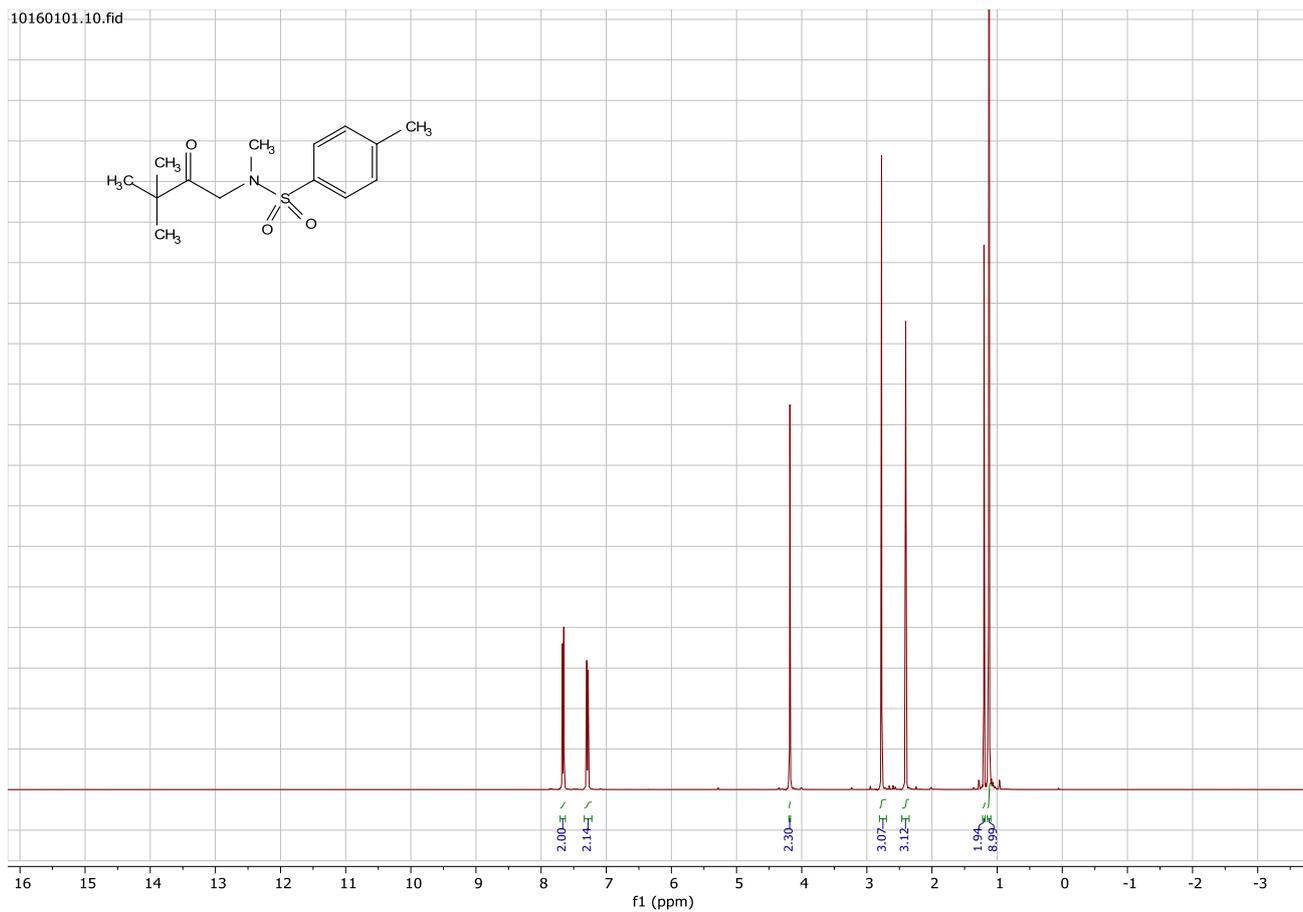
# Compound 1-151a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



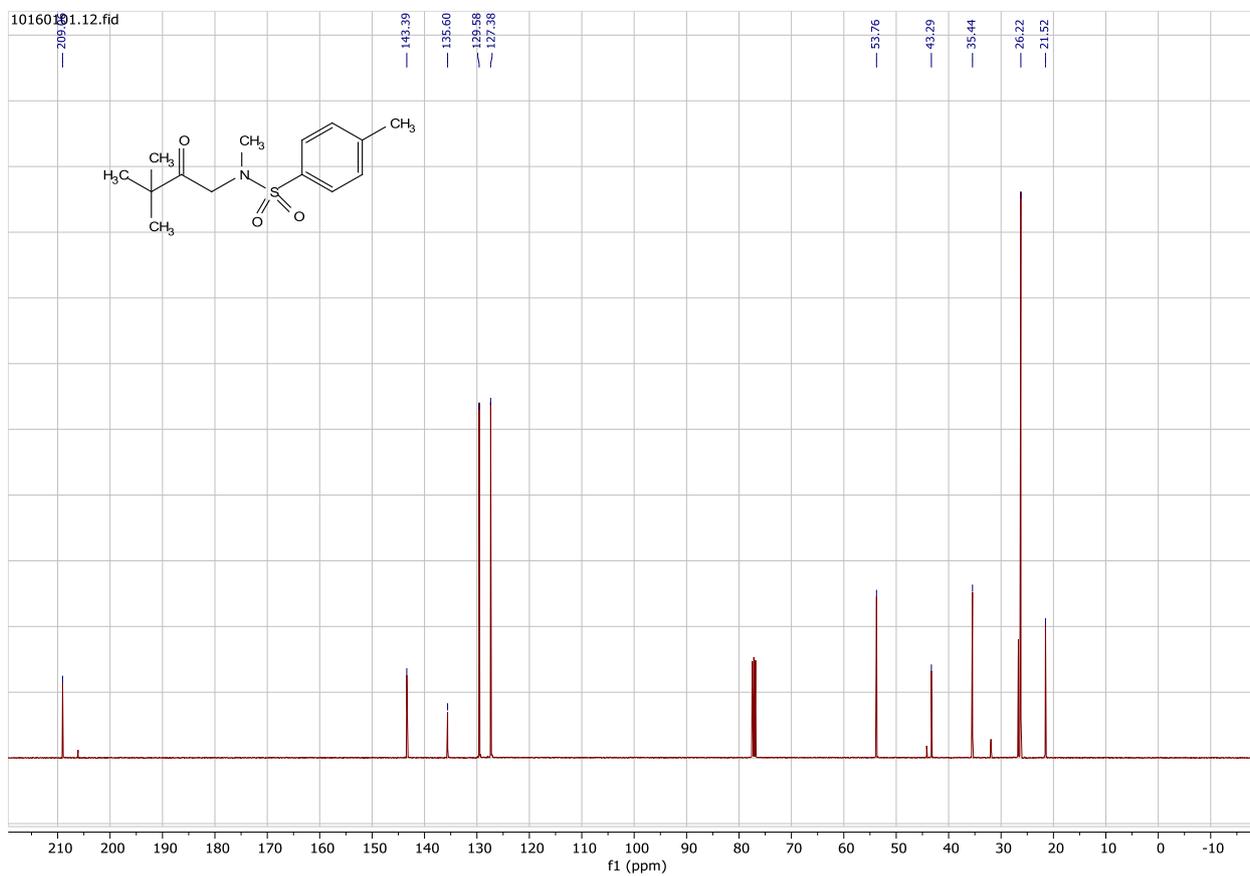
# Compound 1-151a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



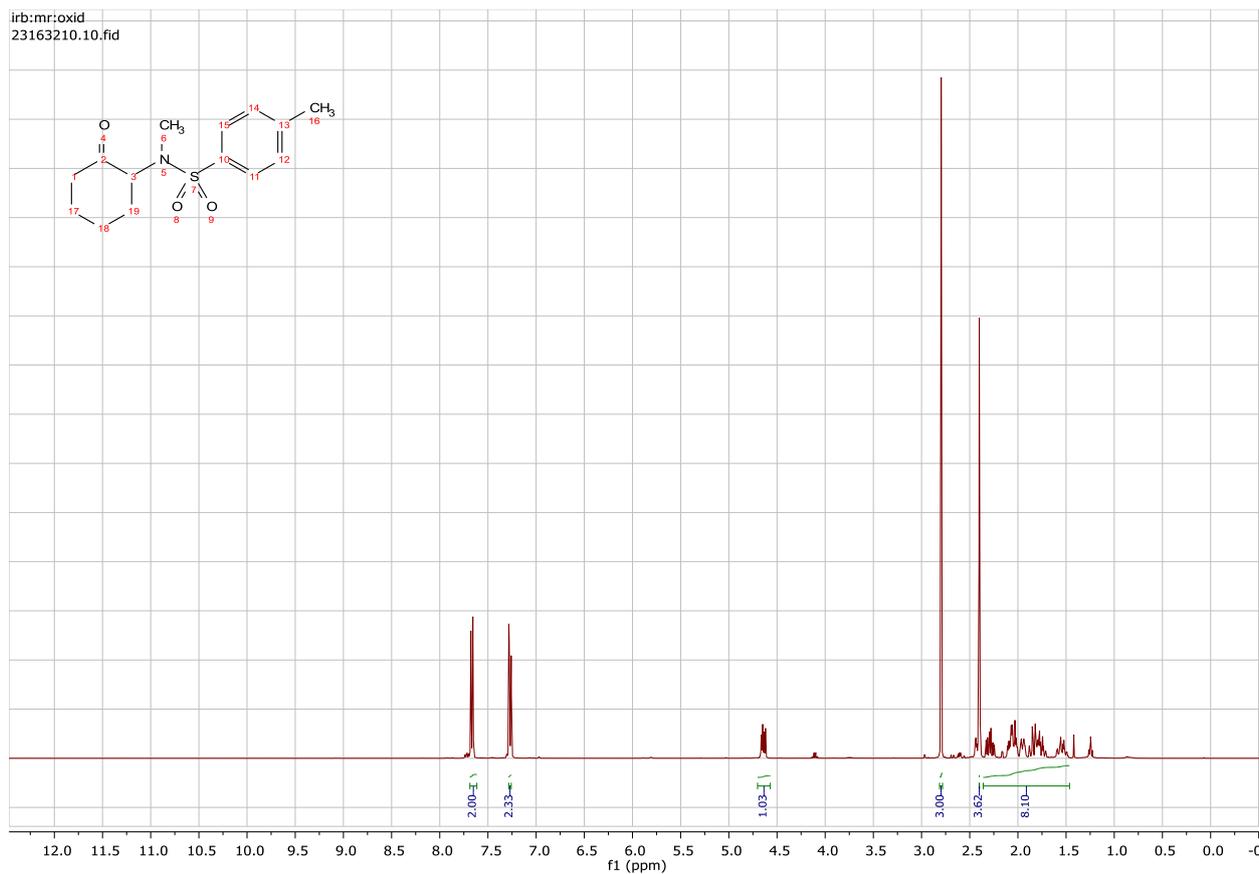
# Compound 1-152a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



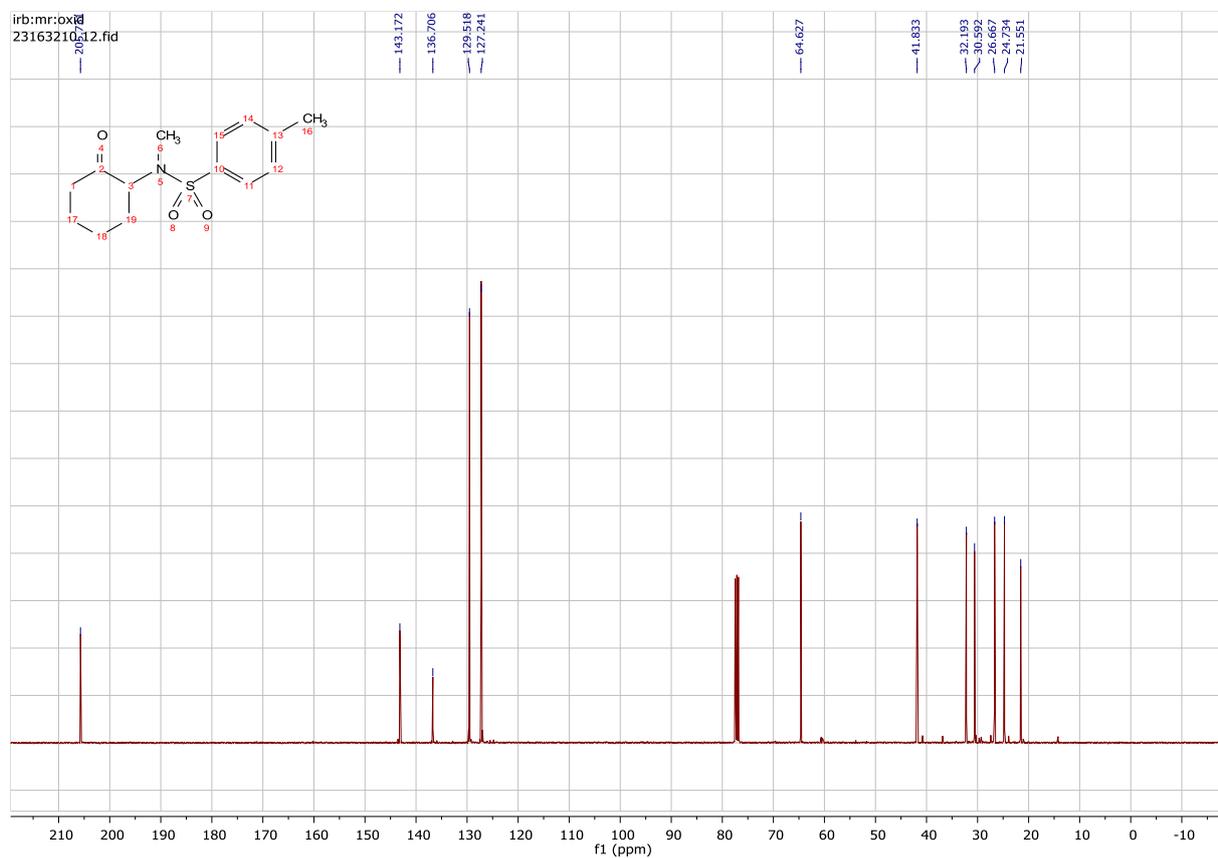
# Compound 1-152a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



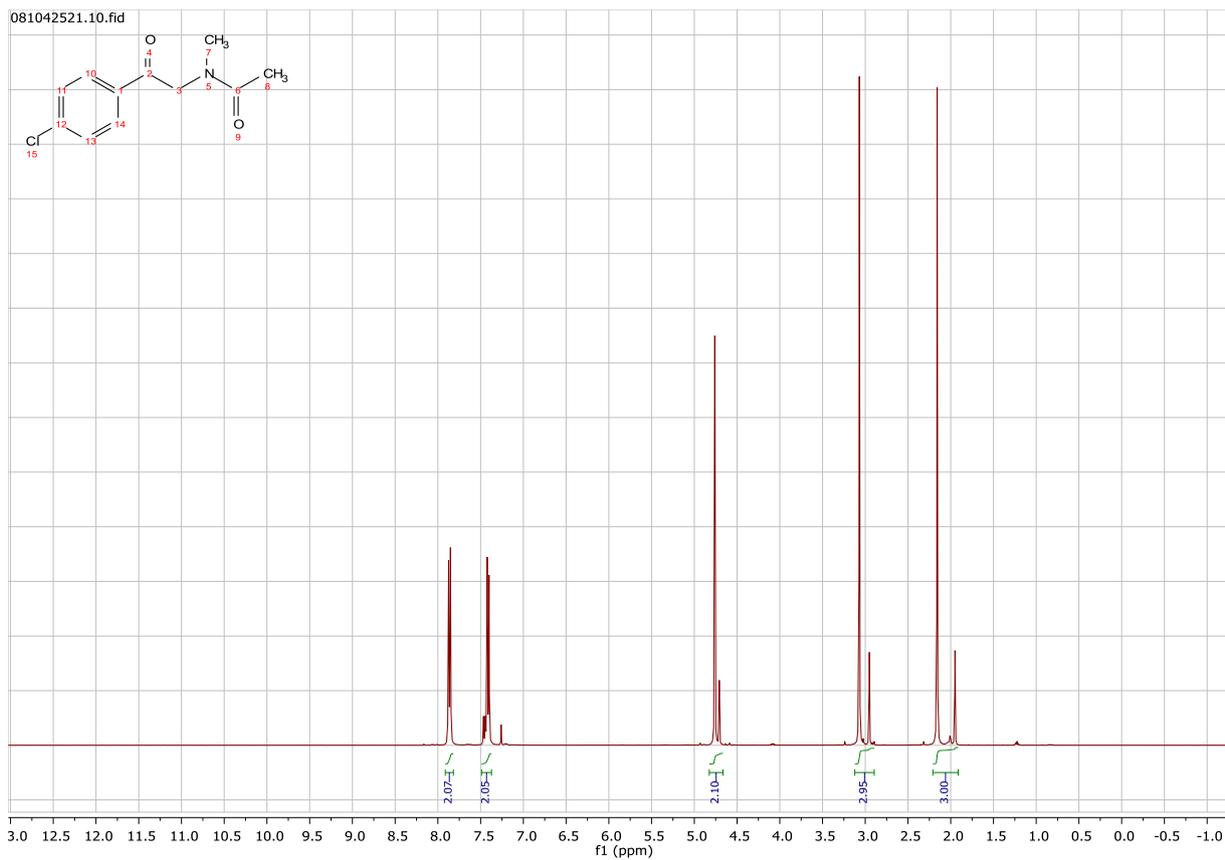
# Compound 1-150a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



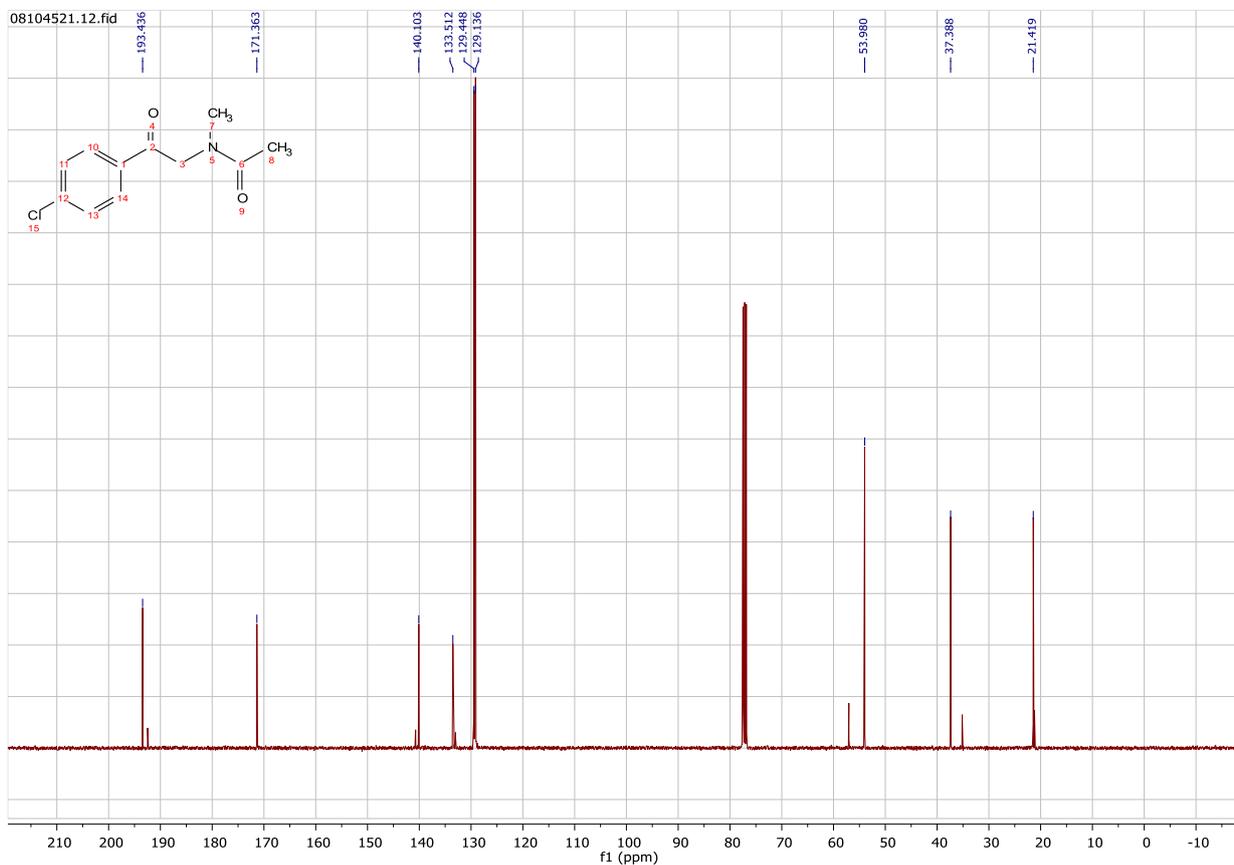
# Compound 1-150a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



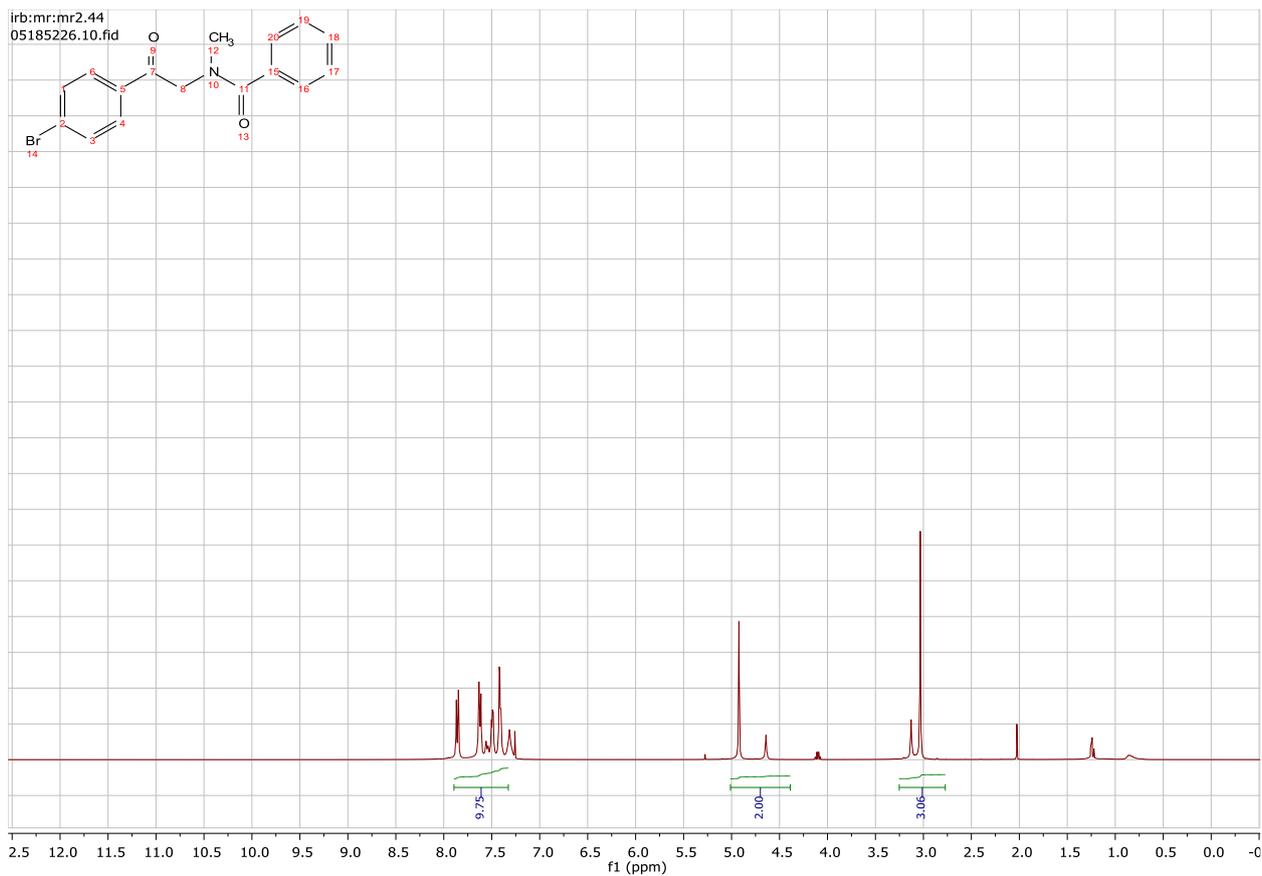
# Compound 1-156a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



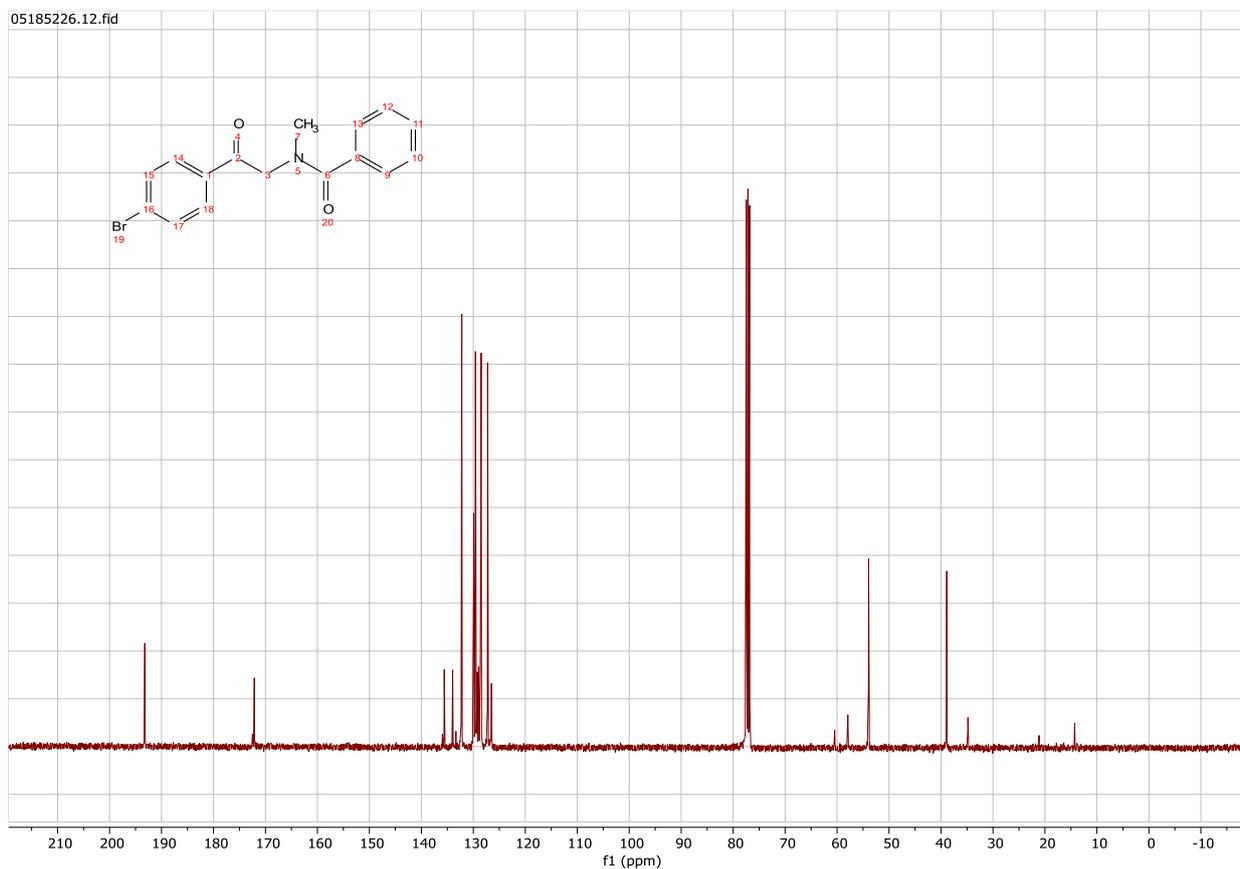
# Compound 1-156a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



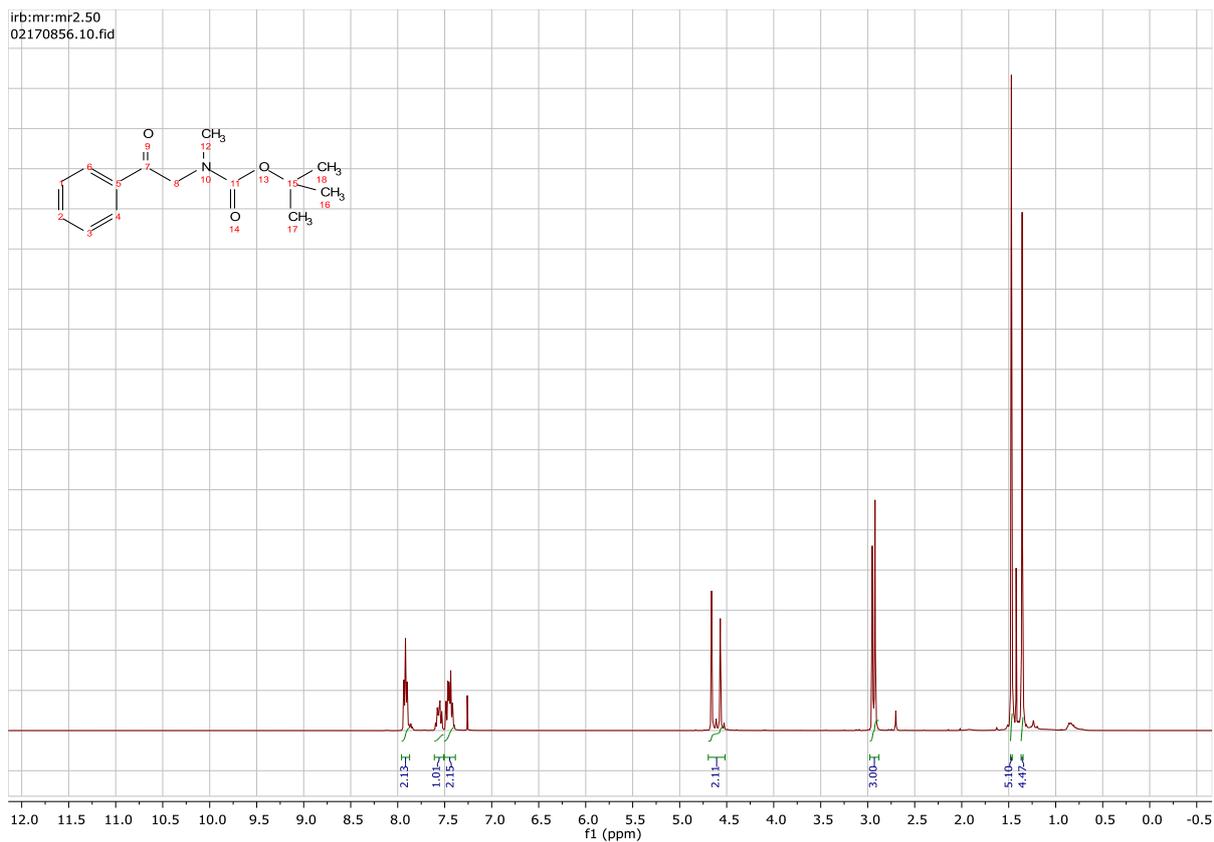
# Compound 1-157a $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



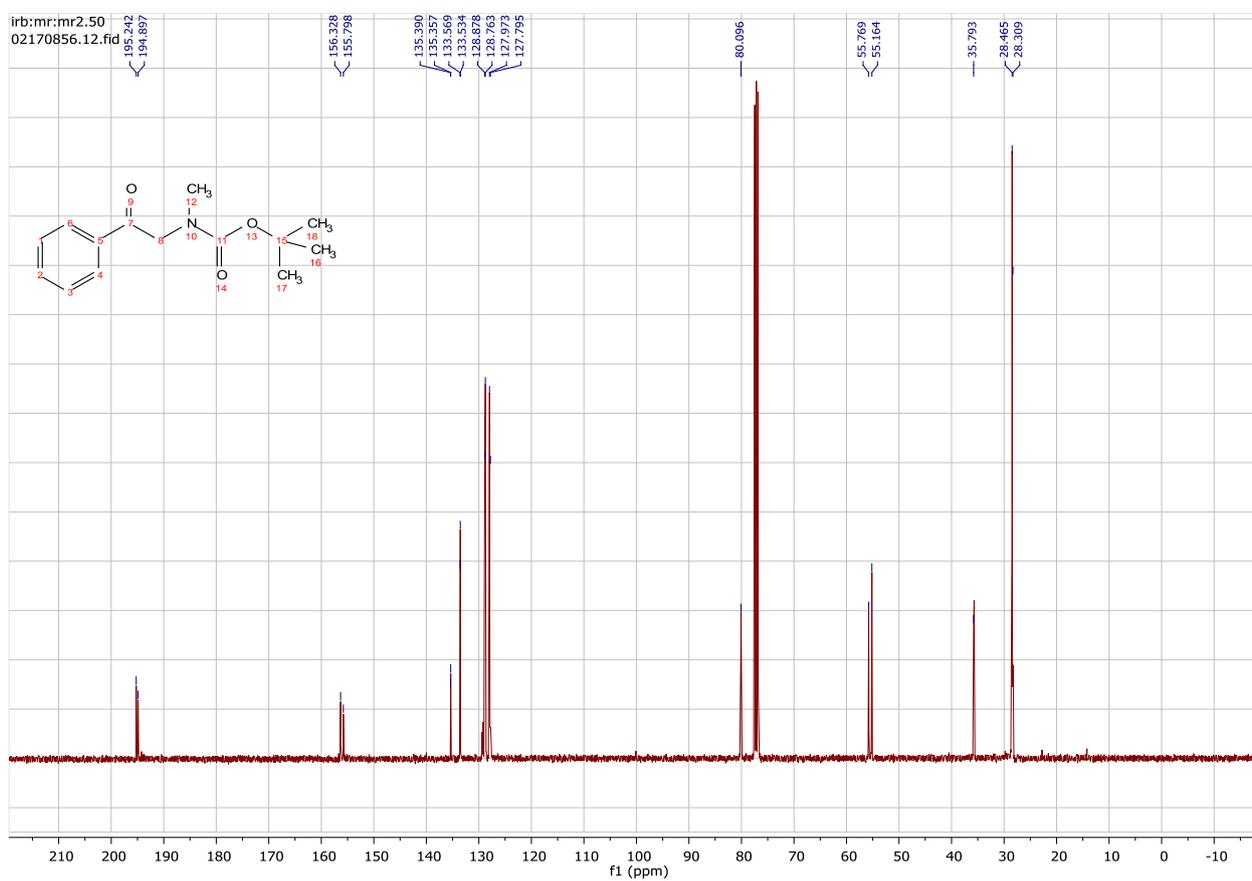
# Compound 1-157a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



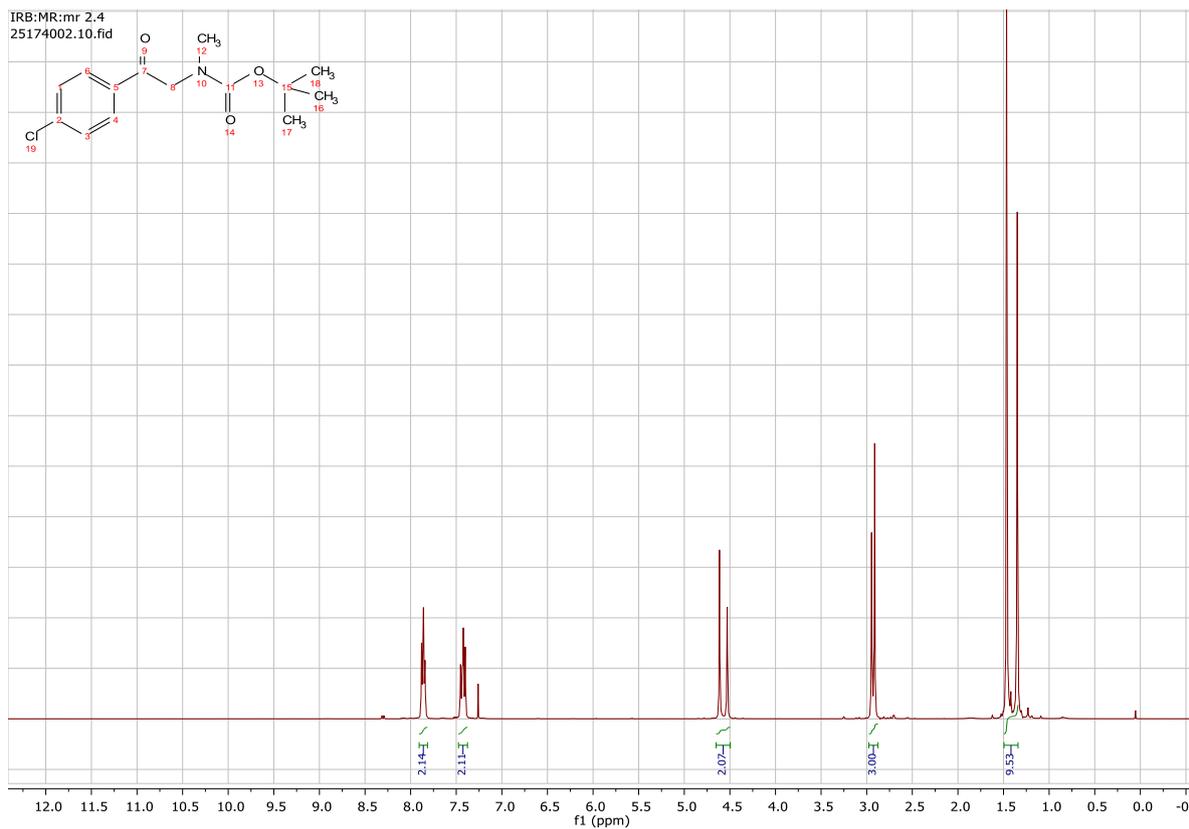
# Compound 1-153a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



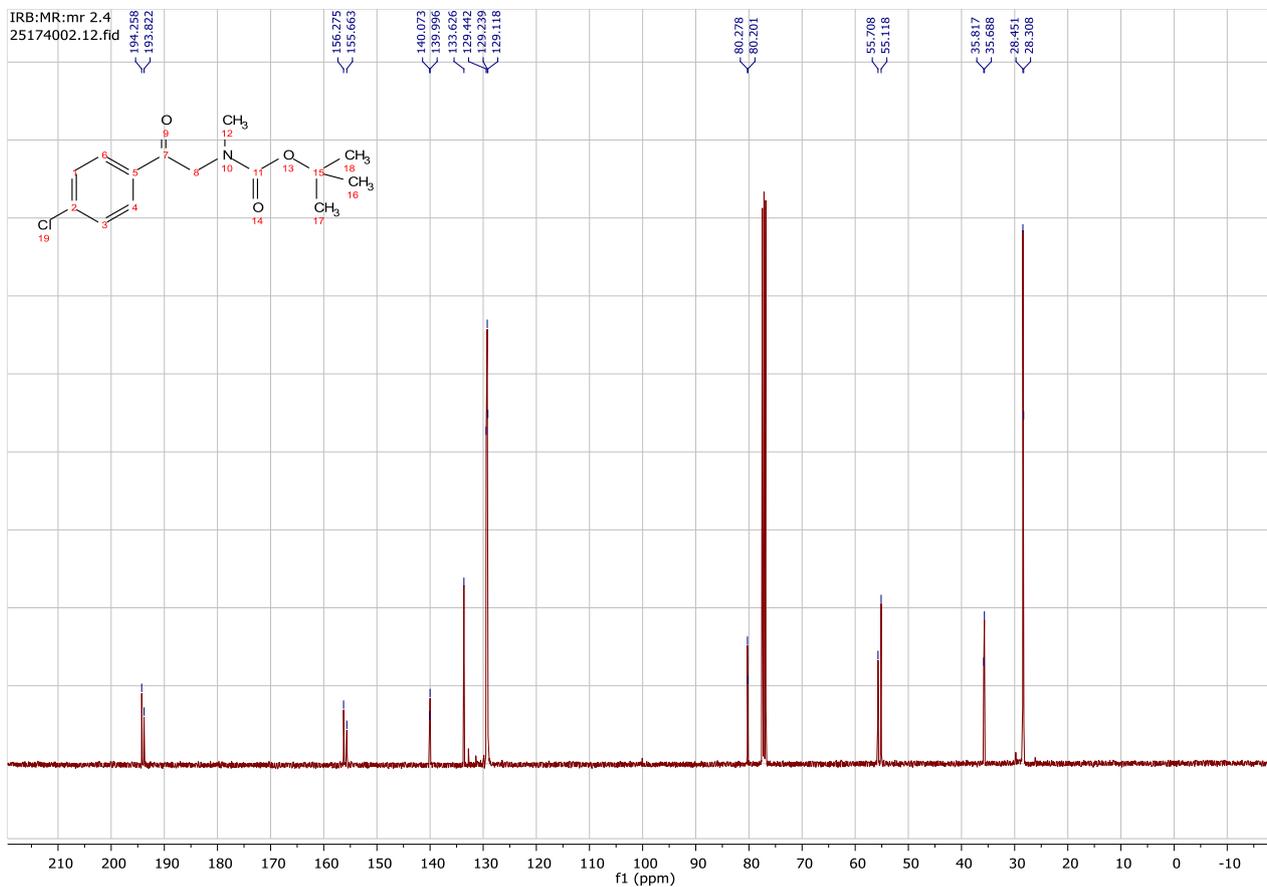
# Compound 1-153a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



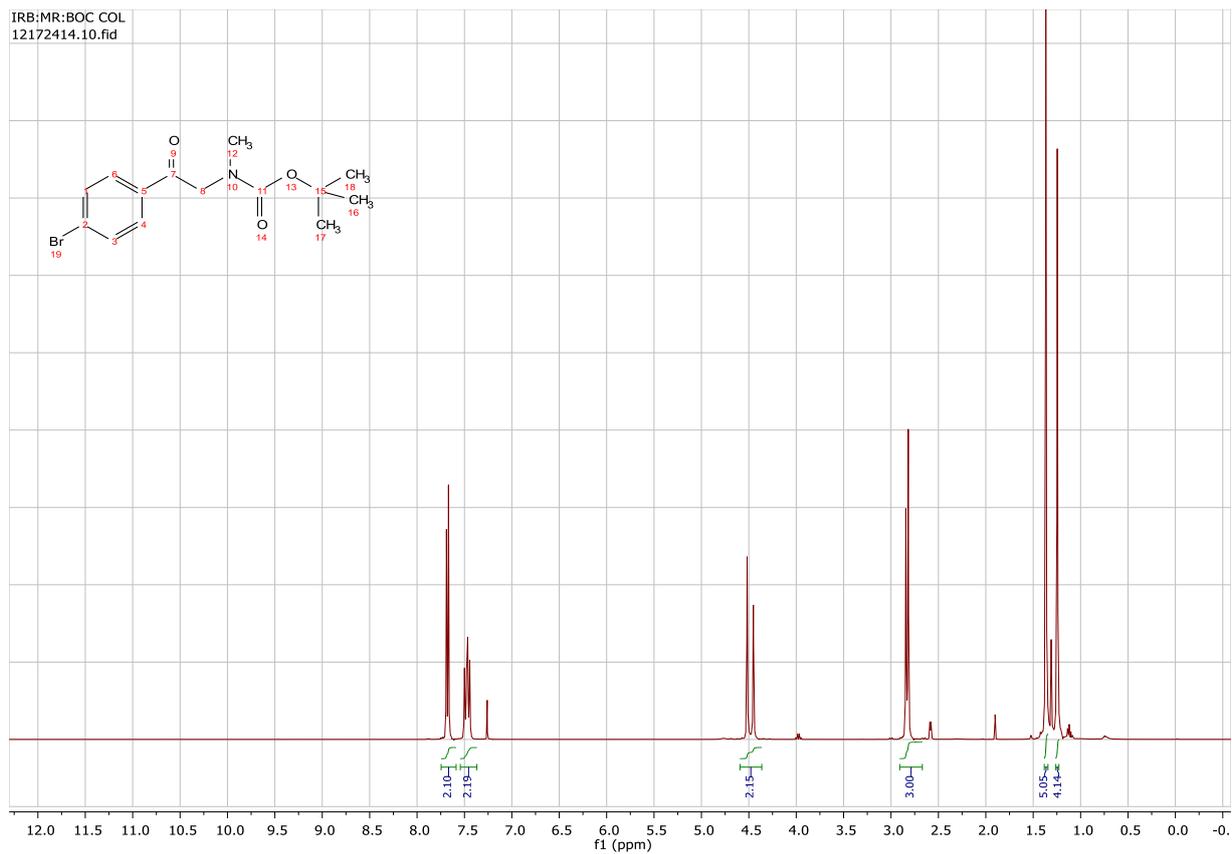
# Compound 1-154a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



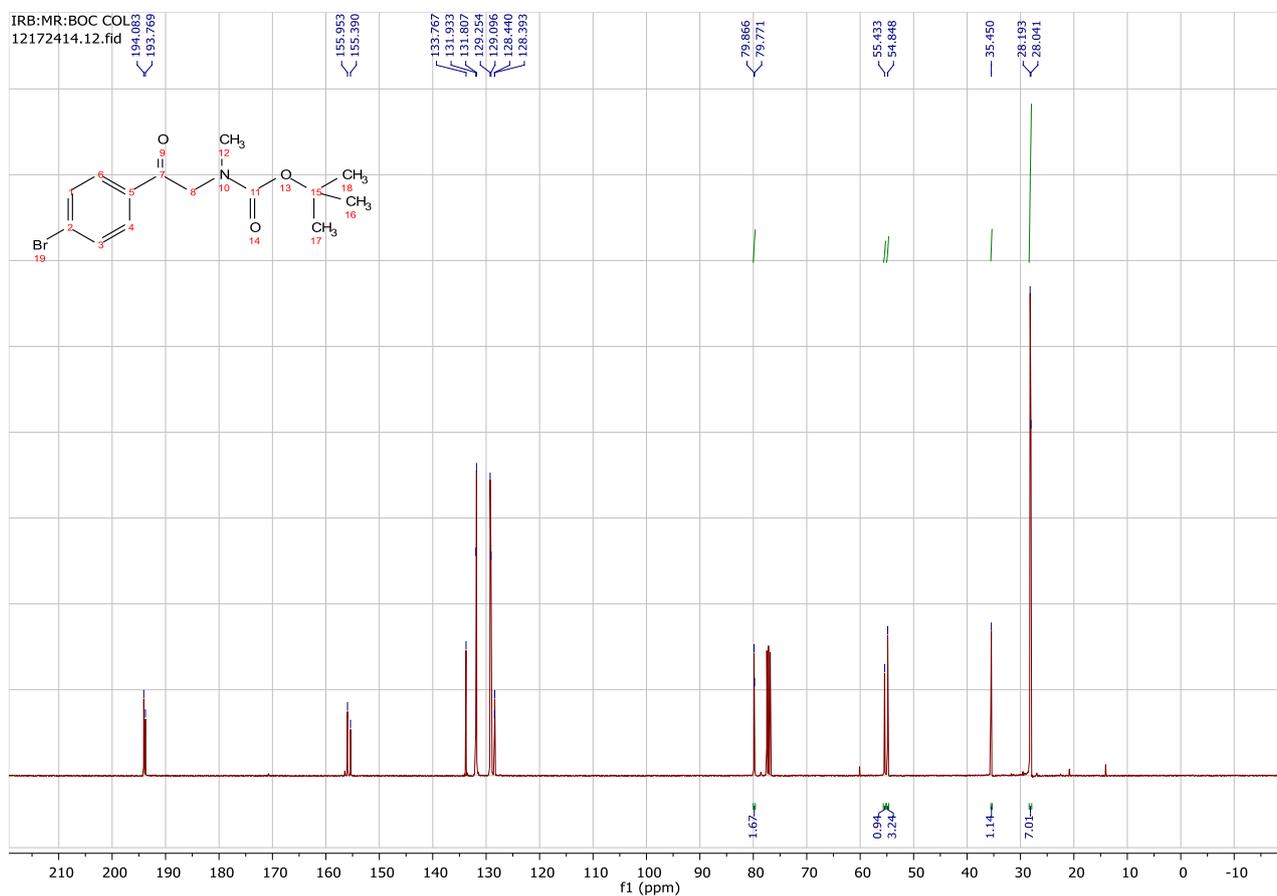
# Compound 1-154a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



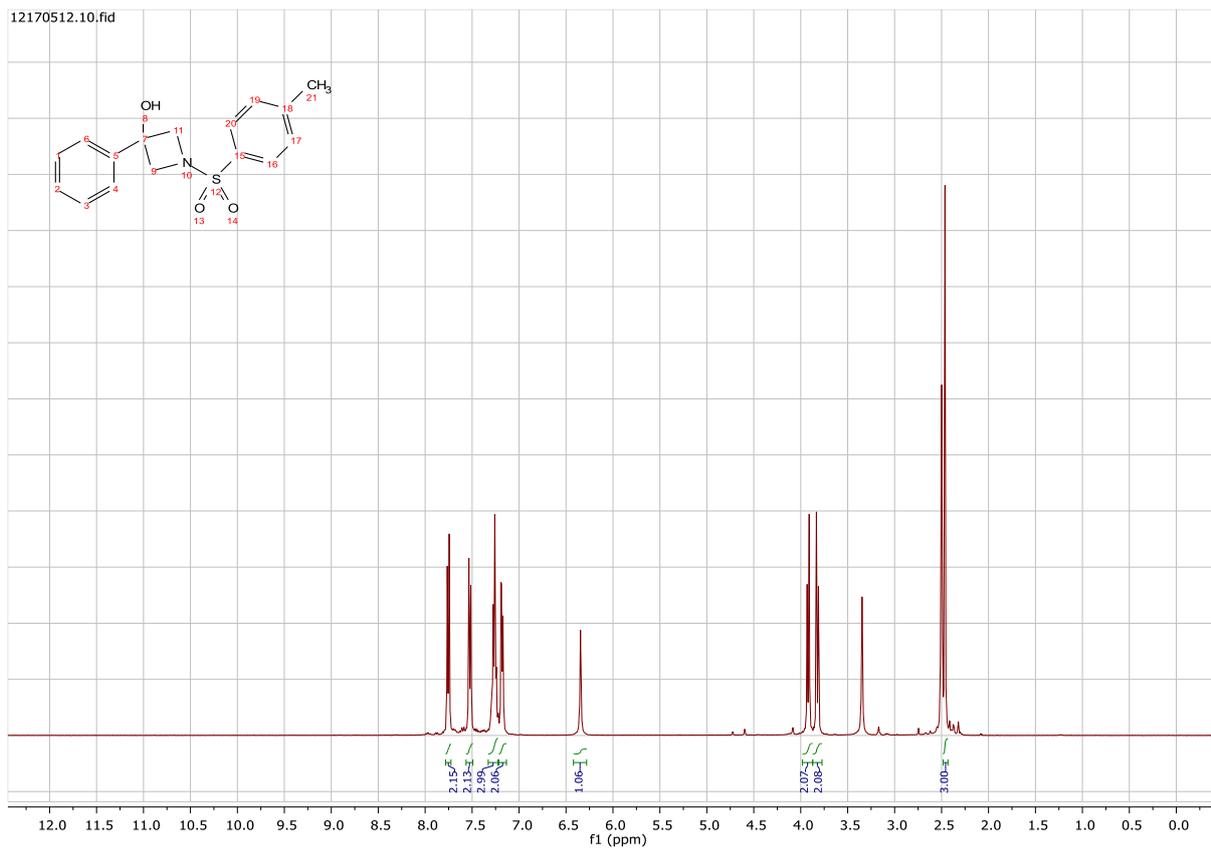
# Compound 1-155a <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



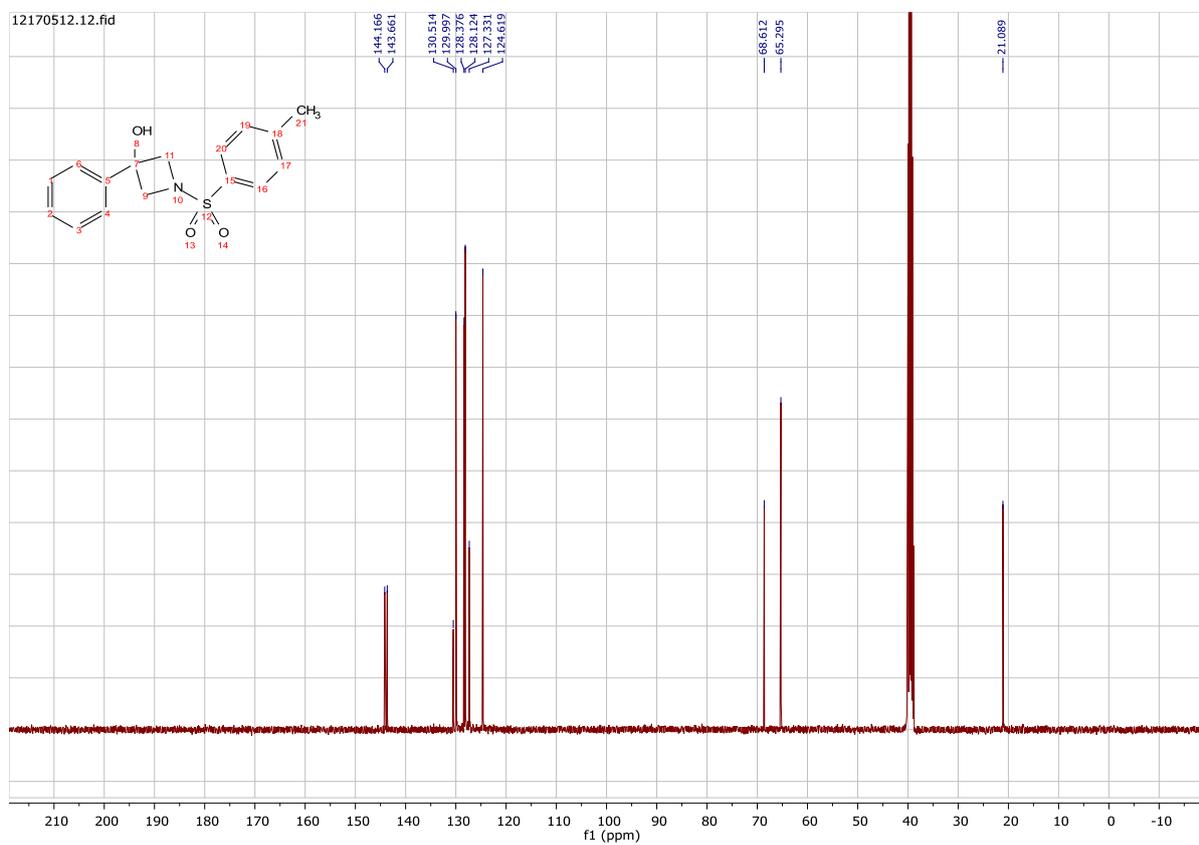
# Compound 1-155a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



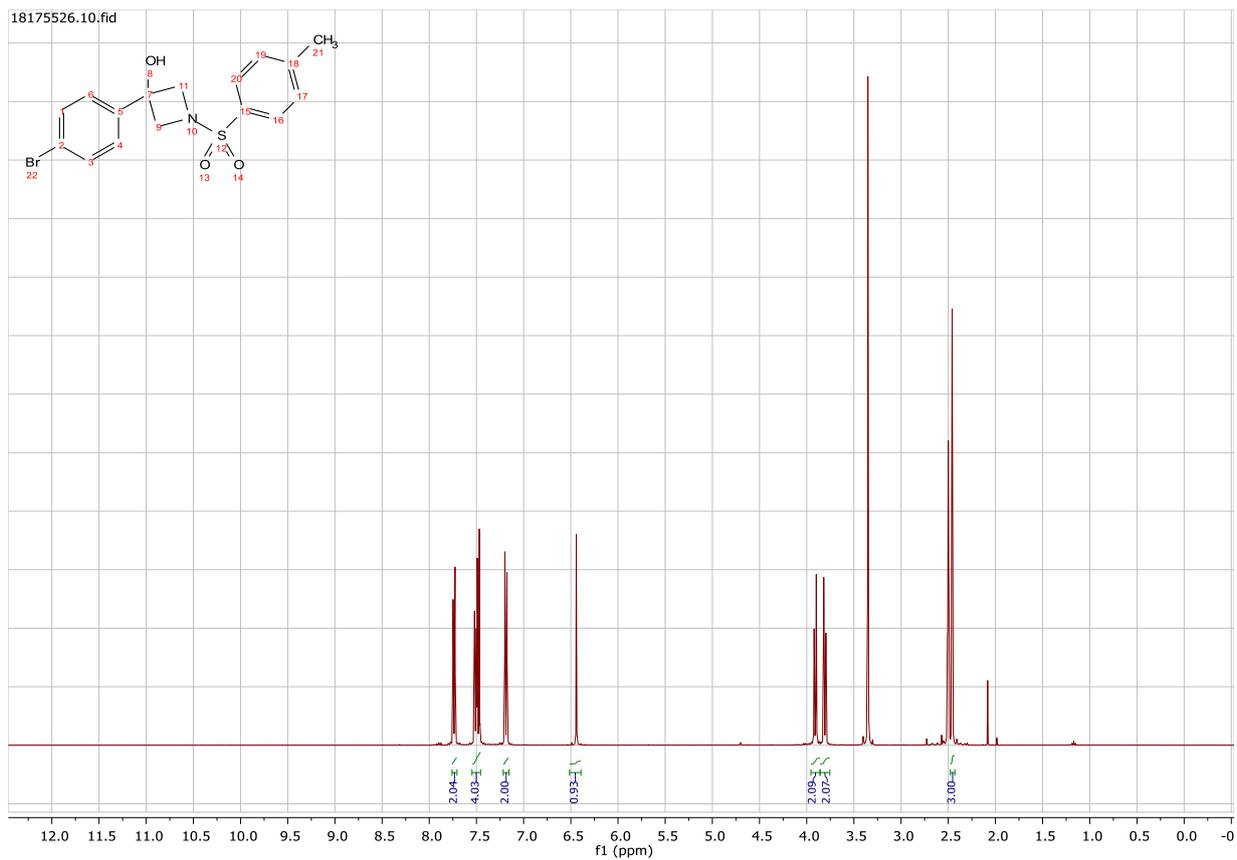
# Compound 1-115 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



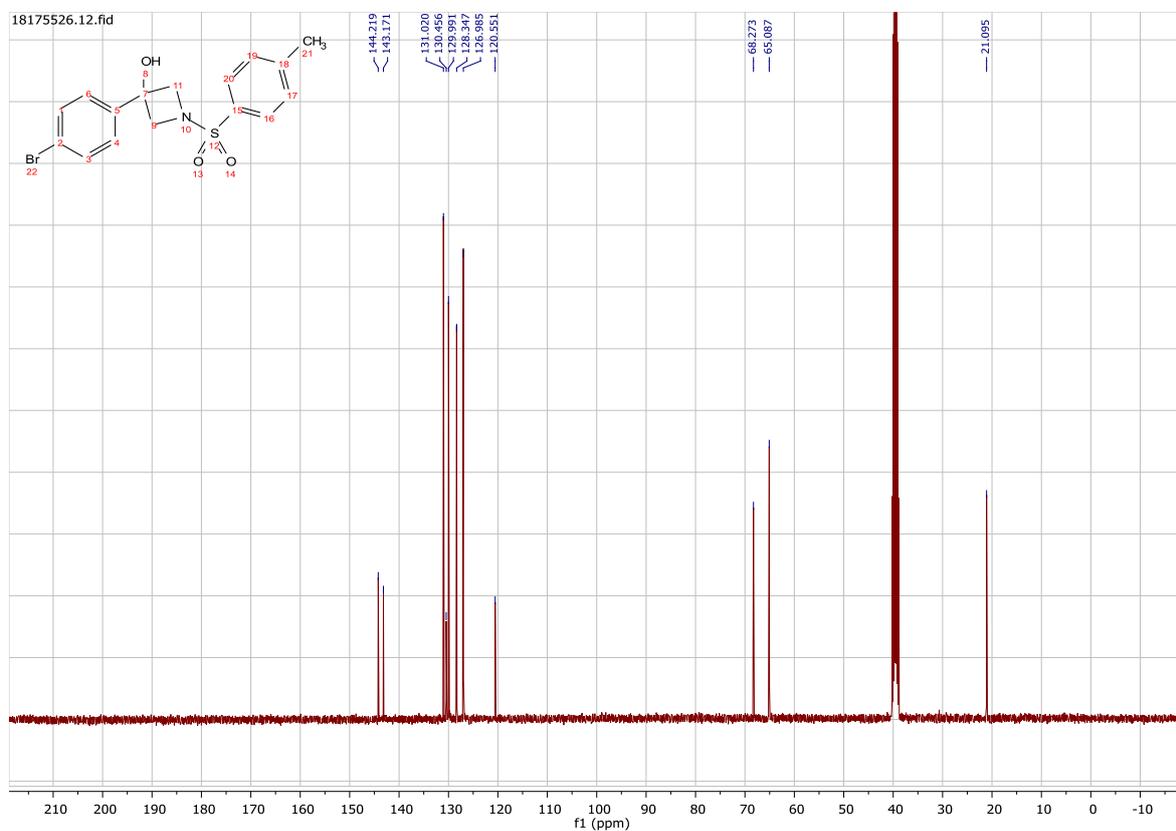
# Compound 1-115a <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



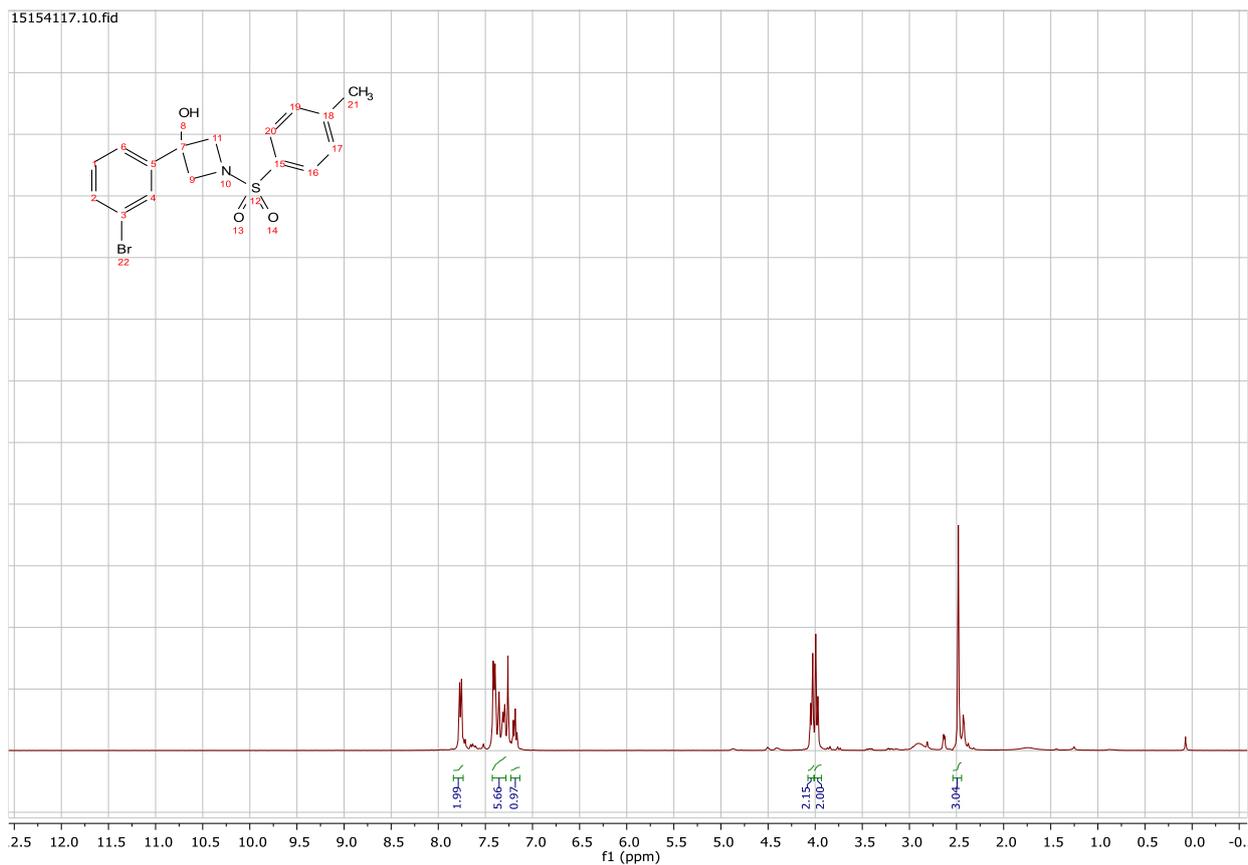
# Compound 1-118 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



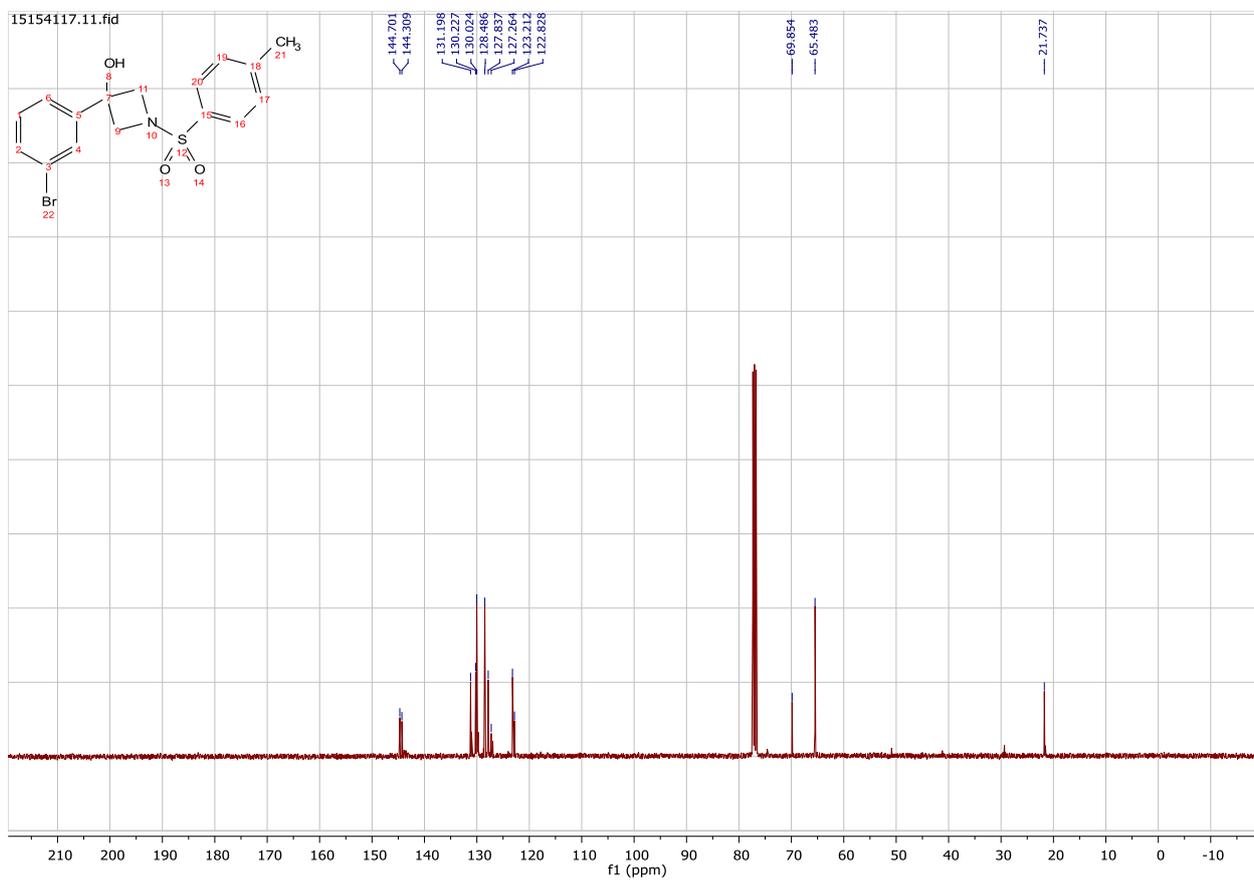
# Compound 1-118 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



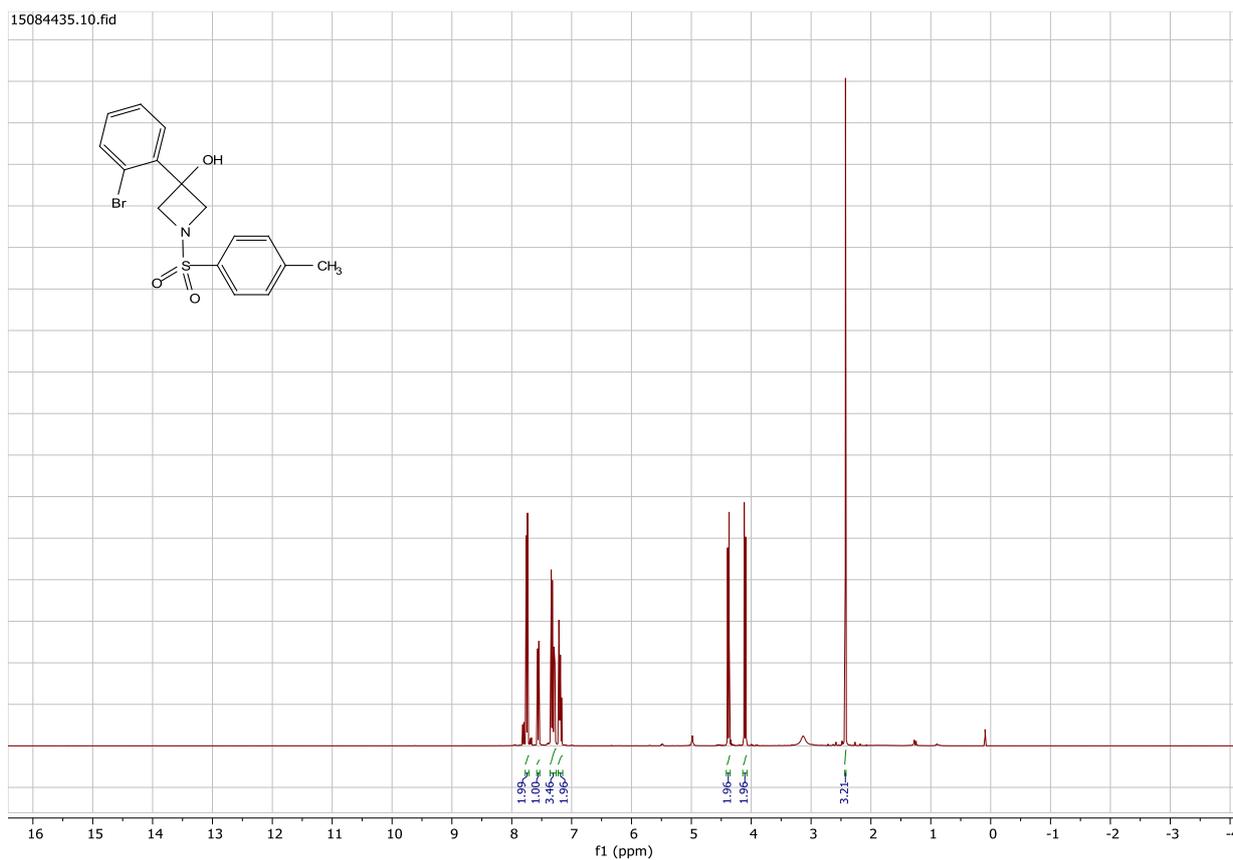
# Compound 1-119 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



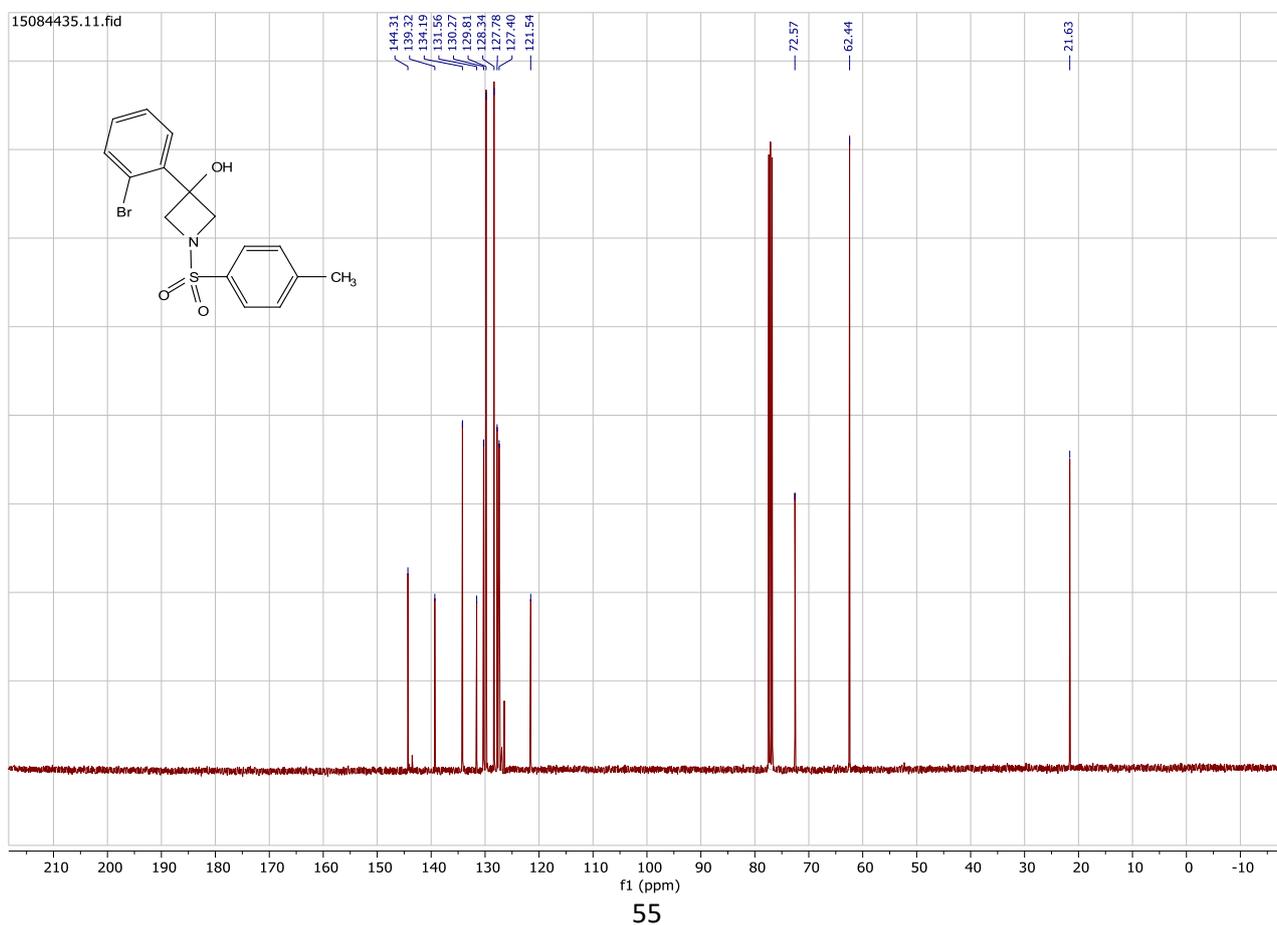
# Compound 1-119 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



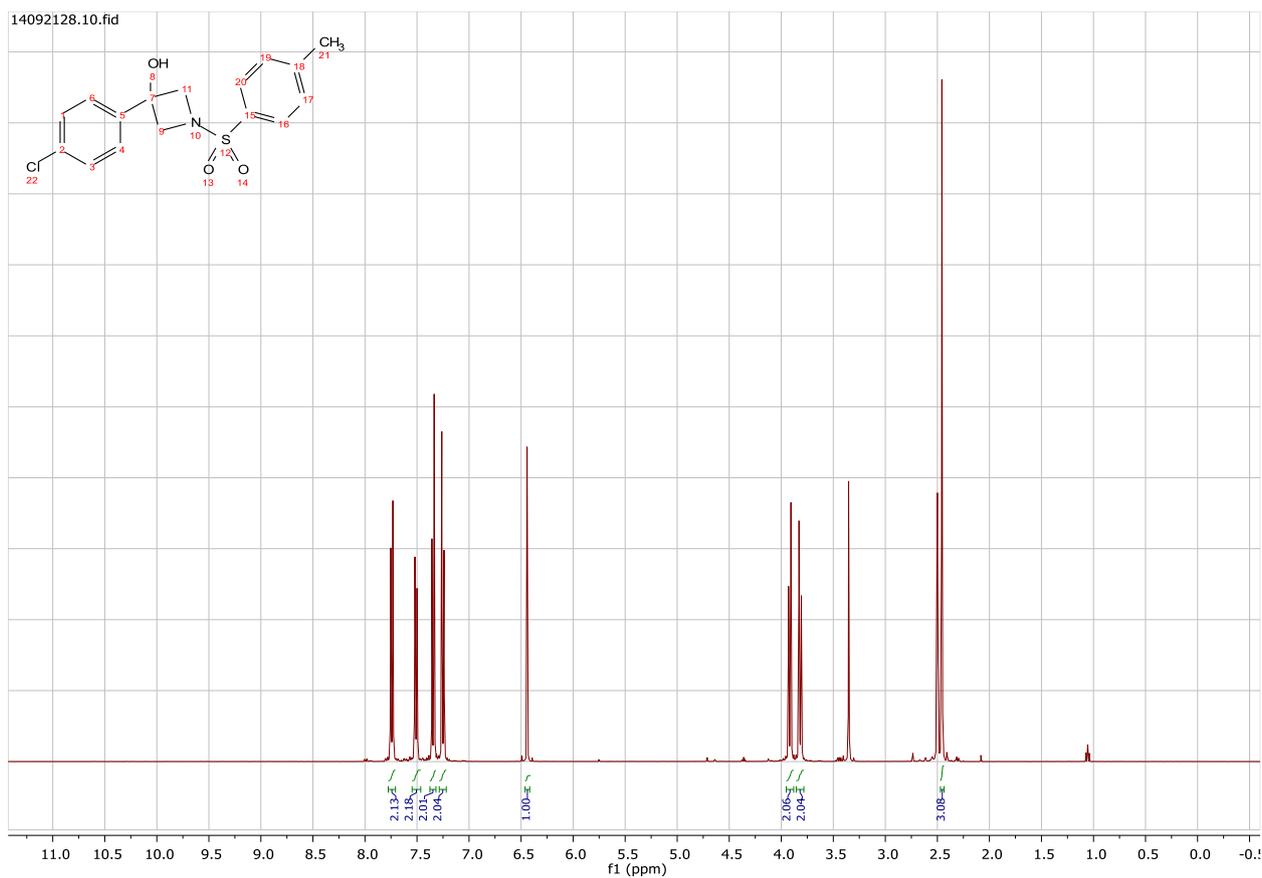
# Compound 1-120 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



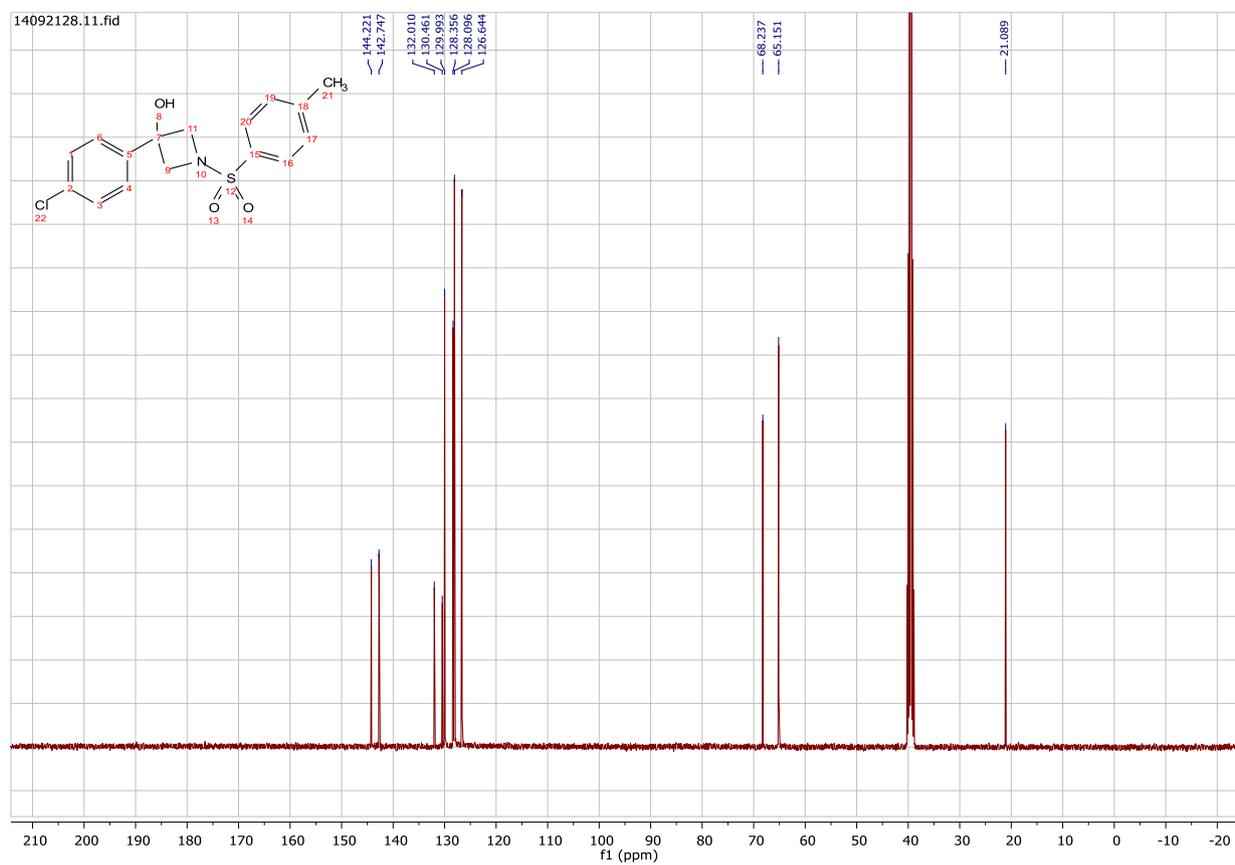
# Compound 1-120 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



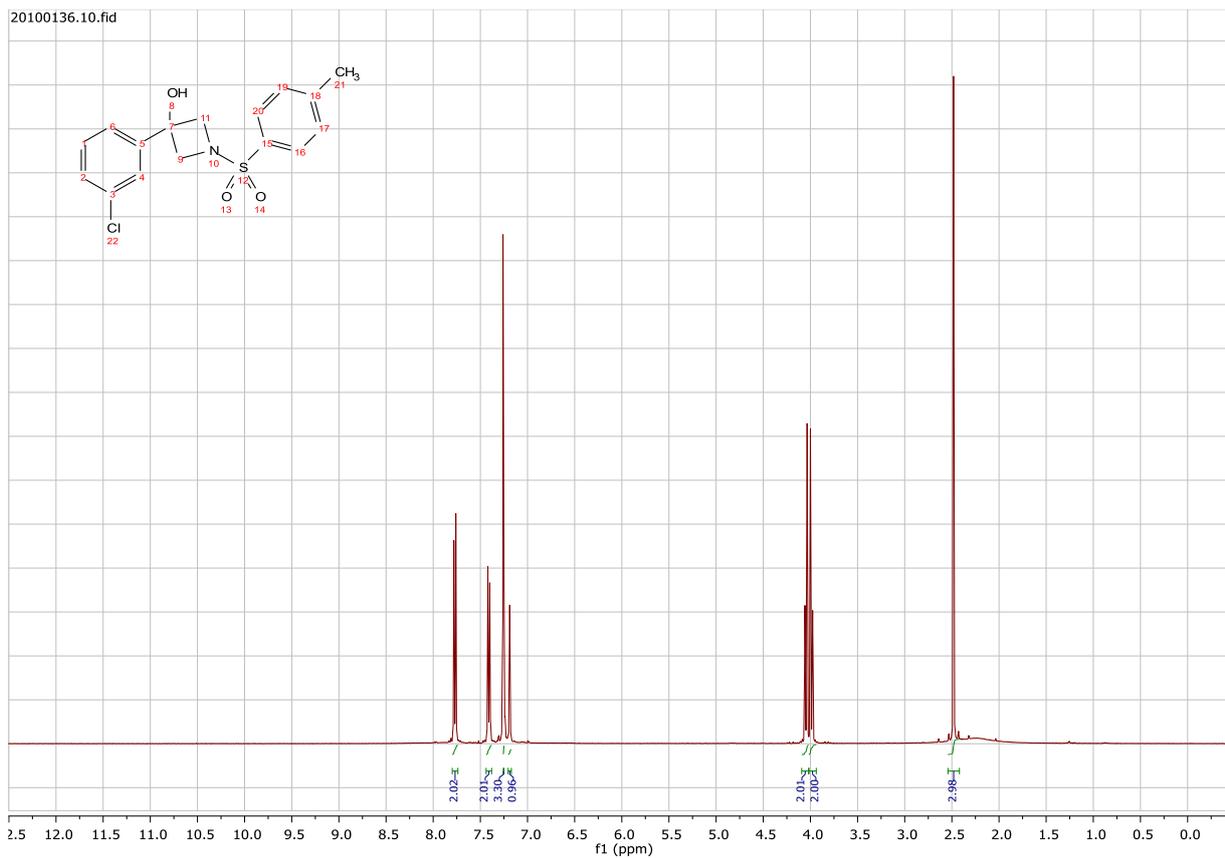
# Compound 1-121 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



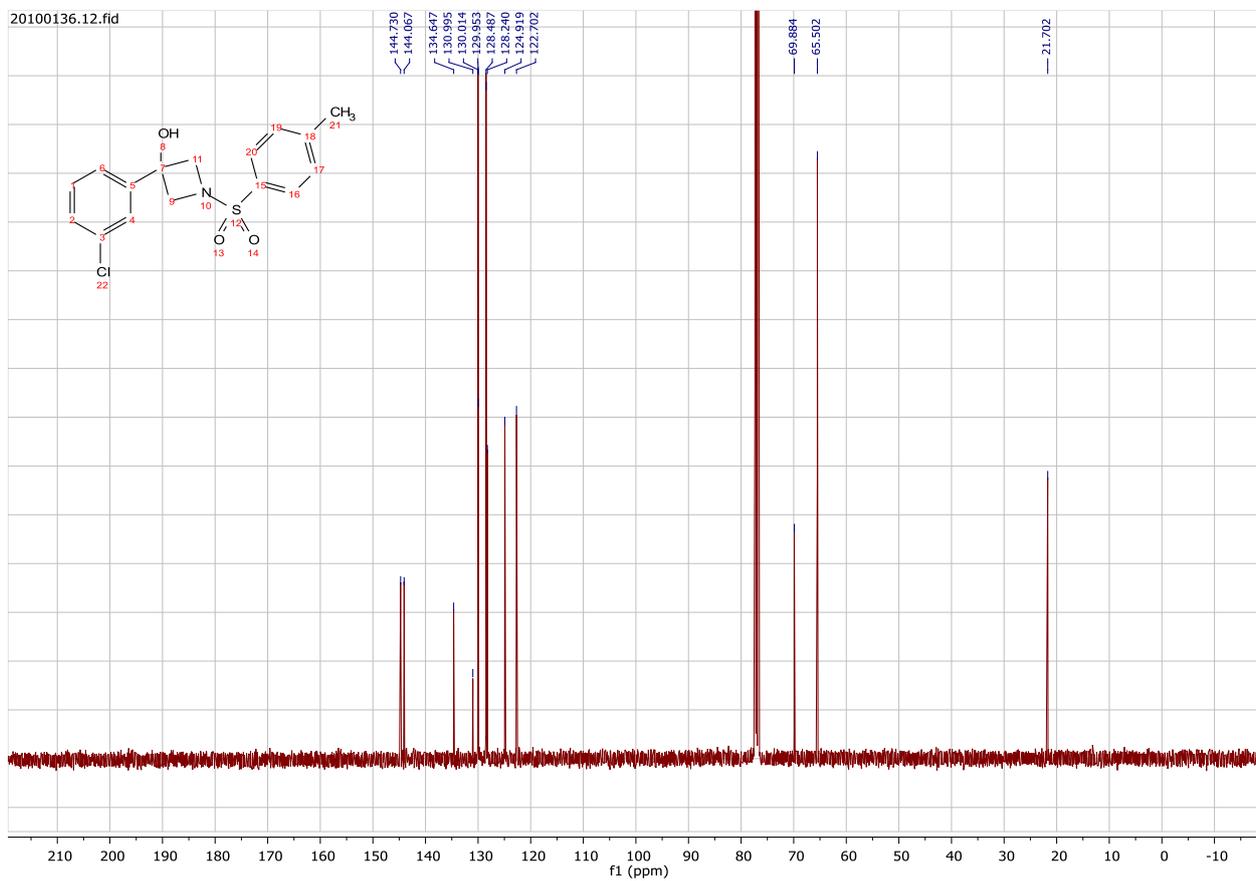
# Compound 1-121 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



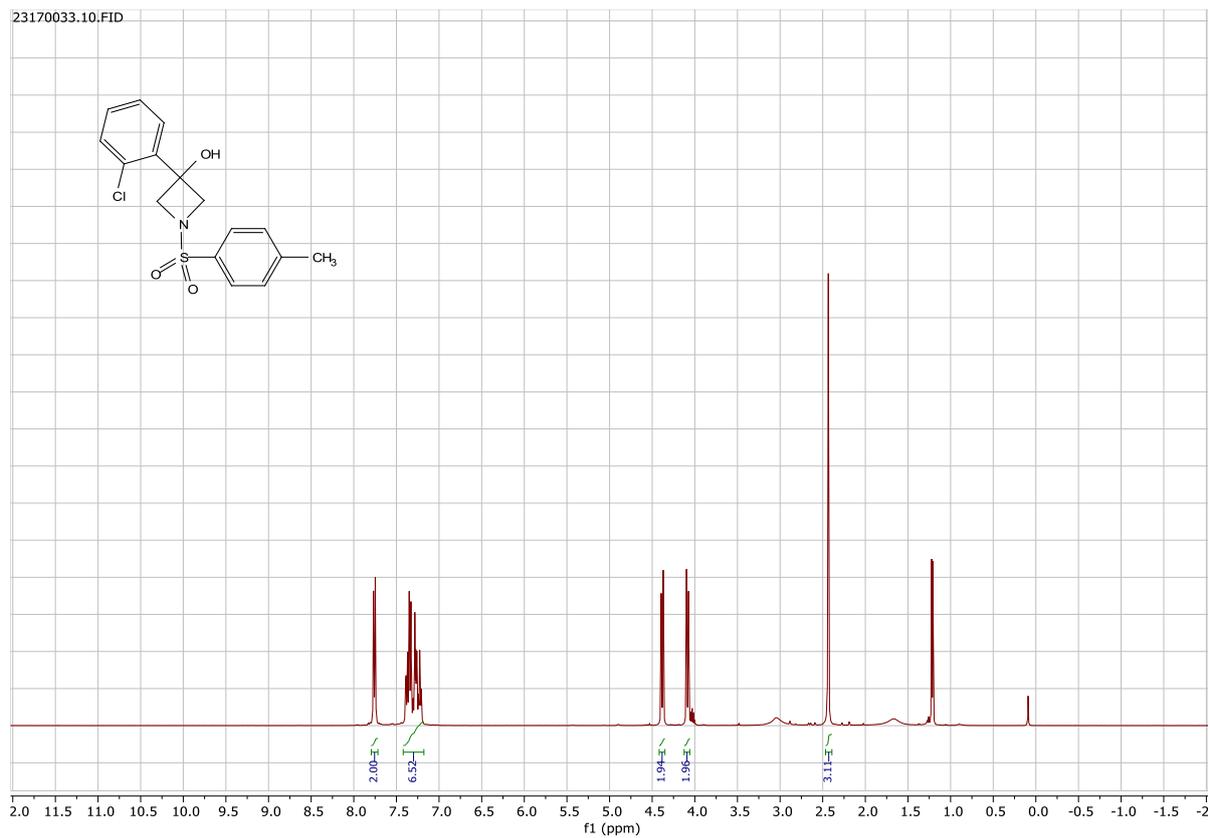
# Compound 1-122 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



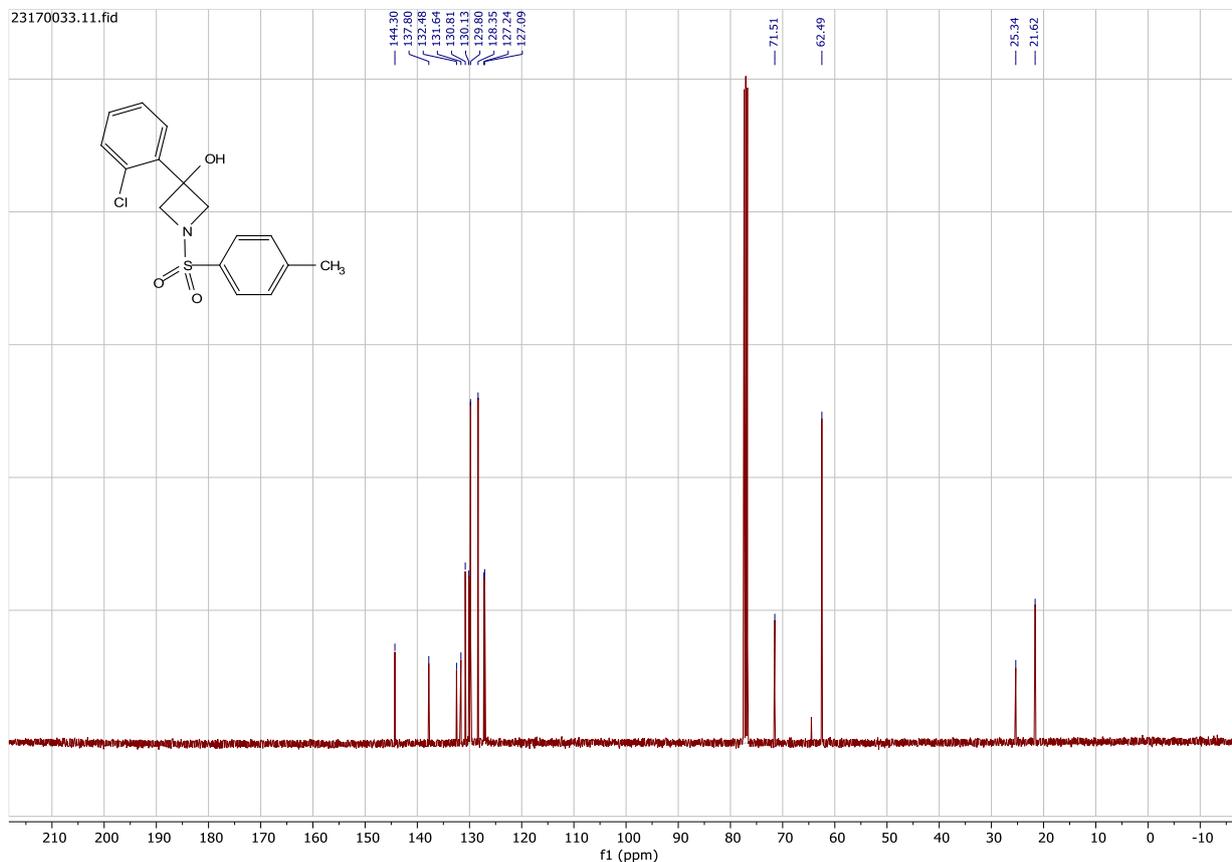
# Compound 1-122 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



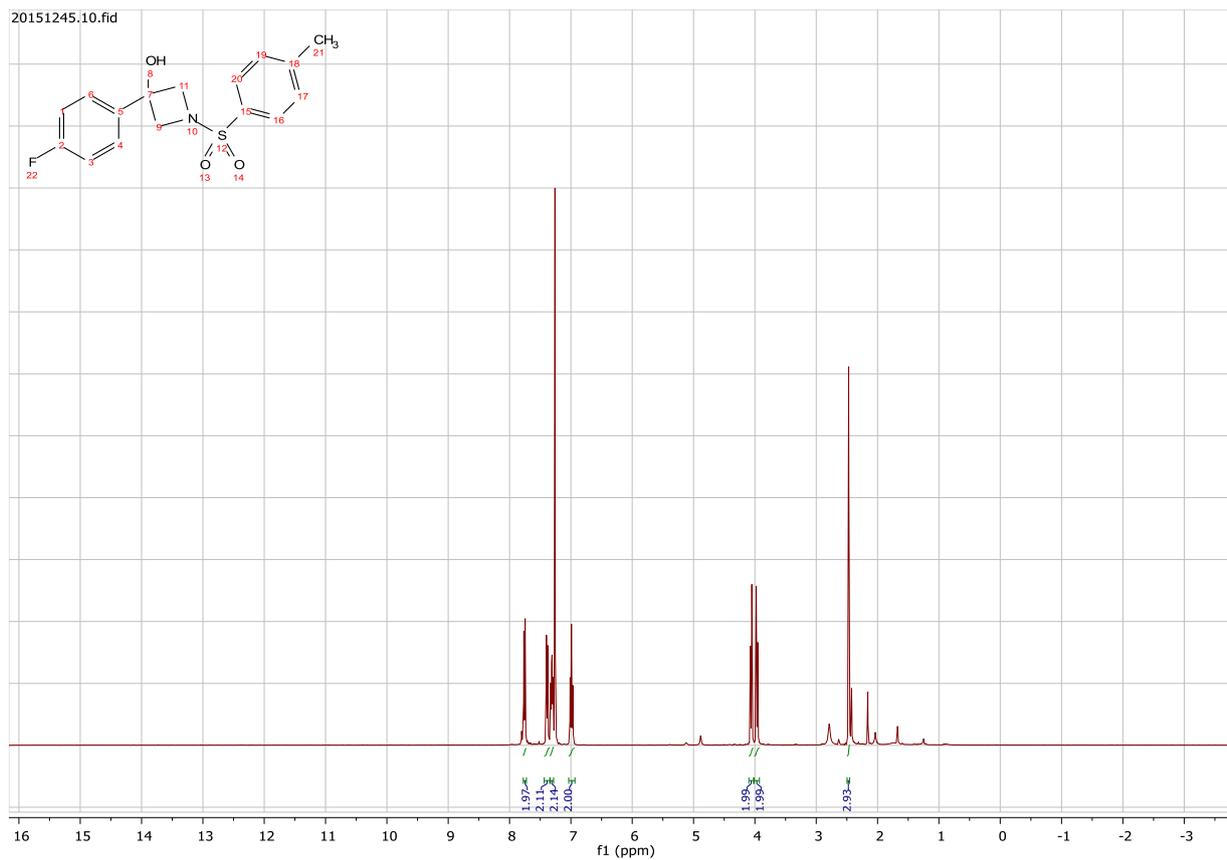
# Compound 1-123 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



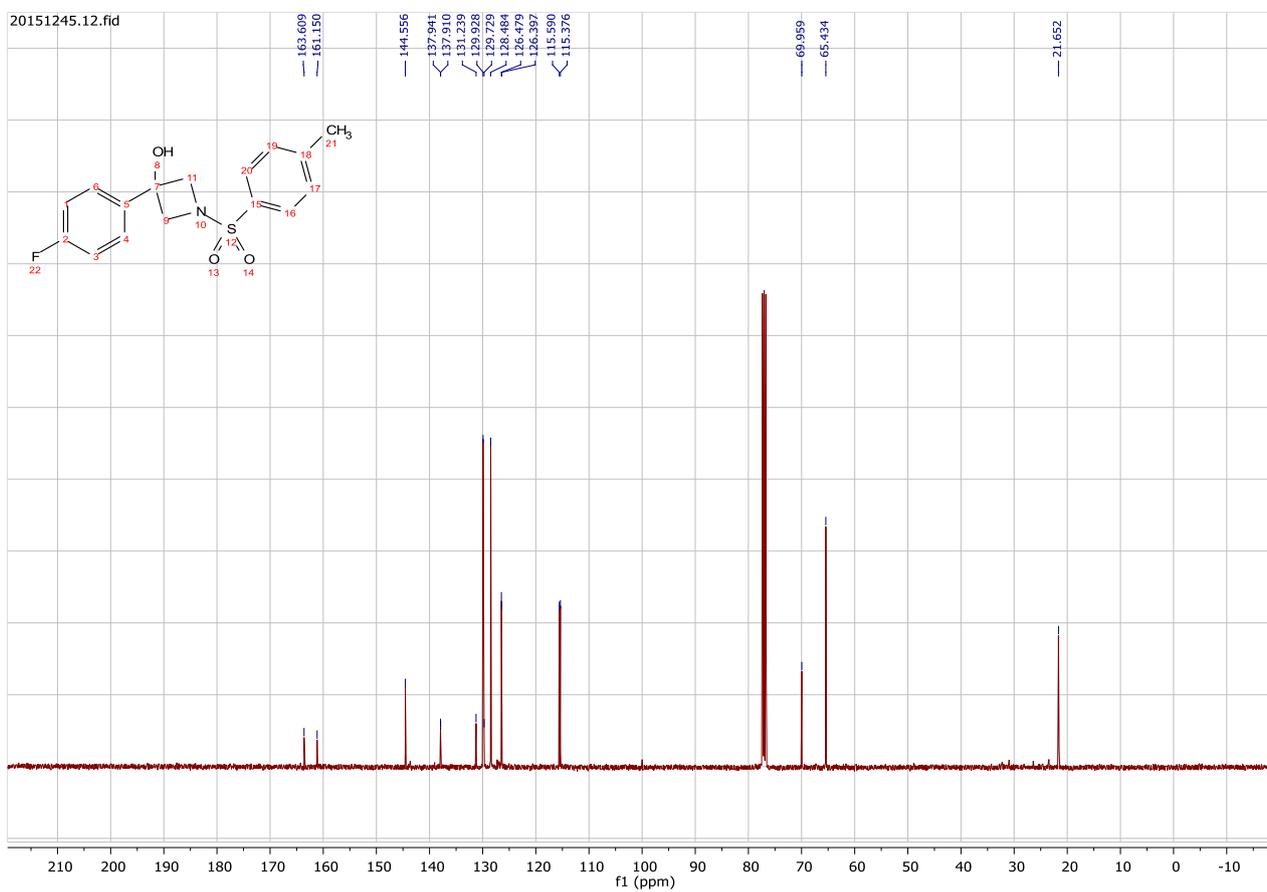
# Compound 1-123 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



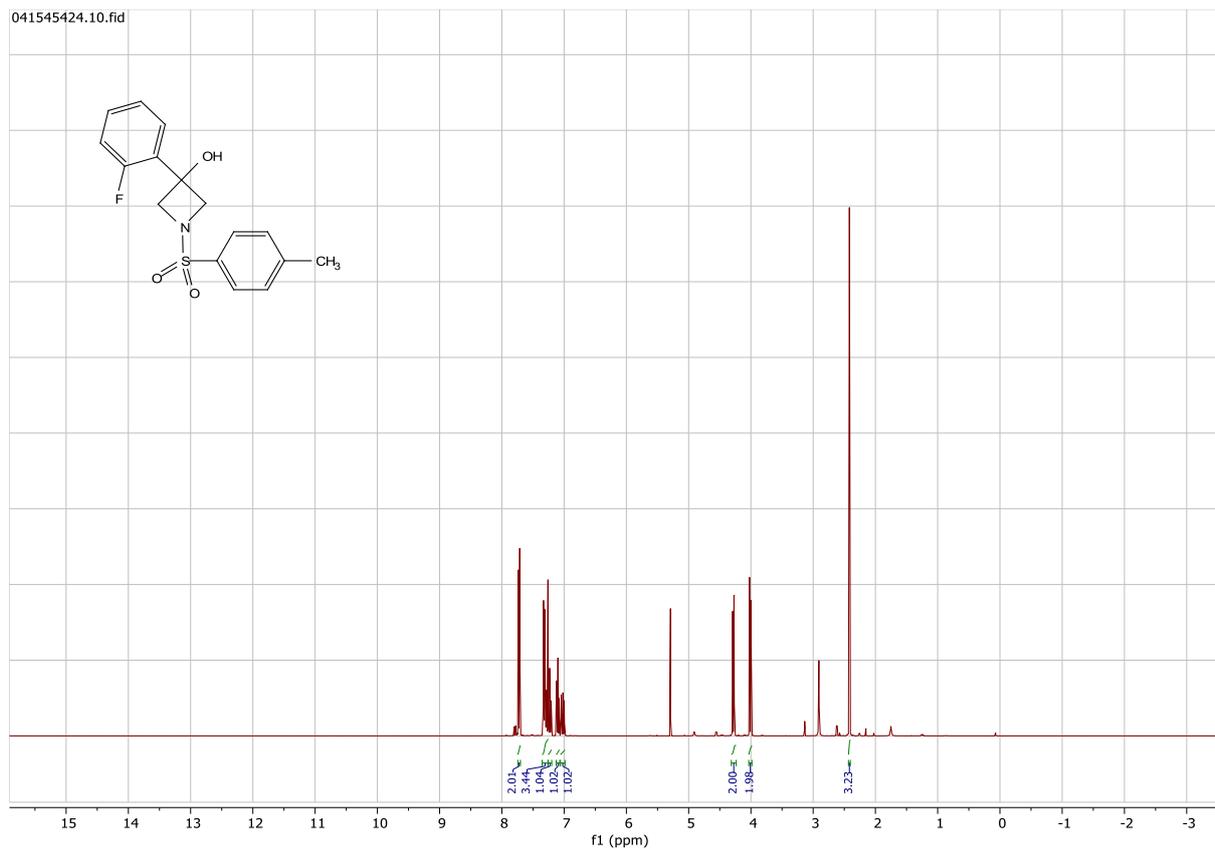
# Compound 1-124 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



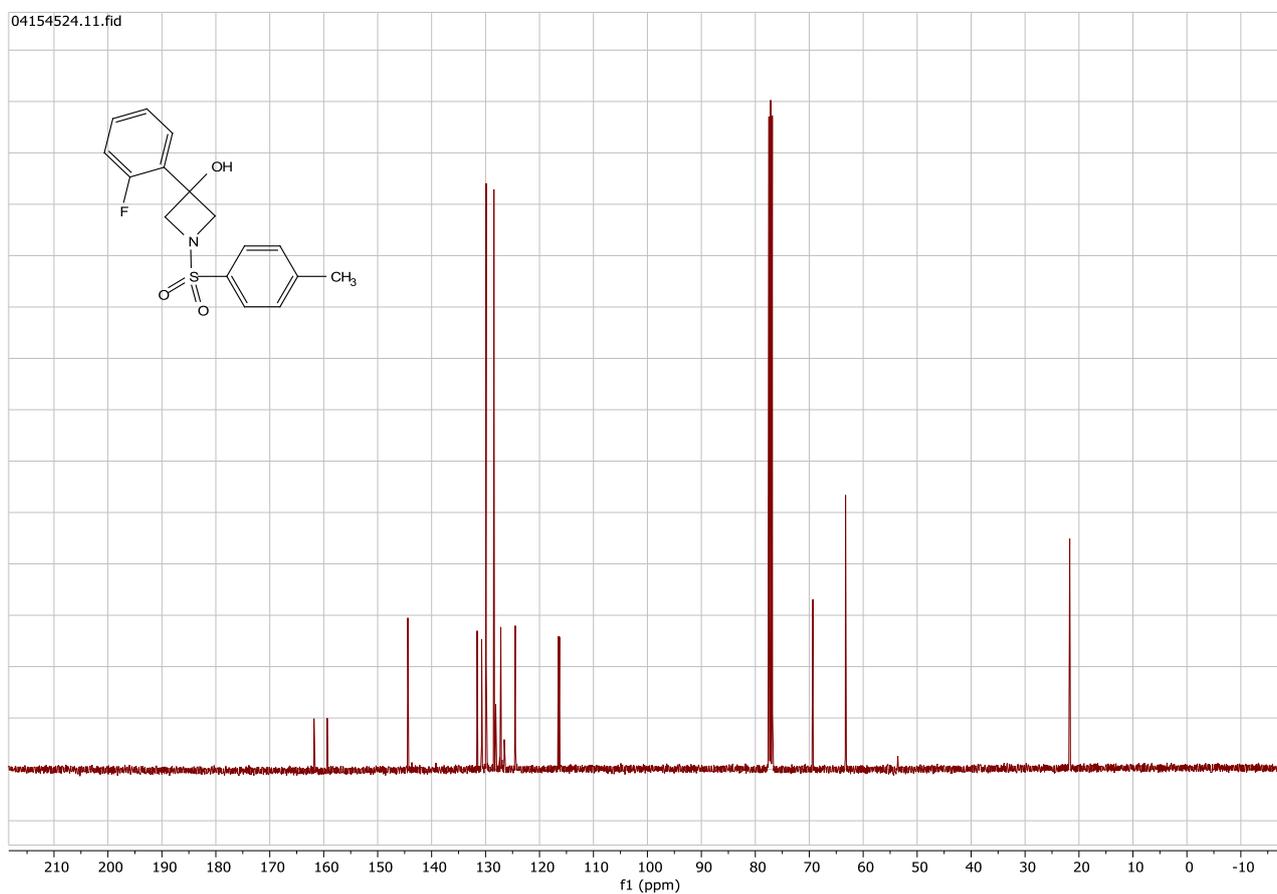
# Compound 1-124 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



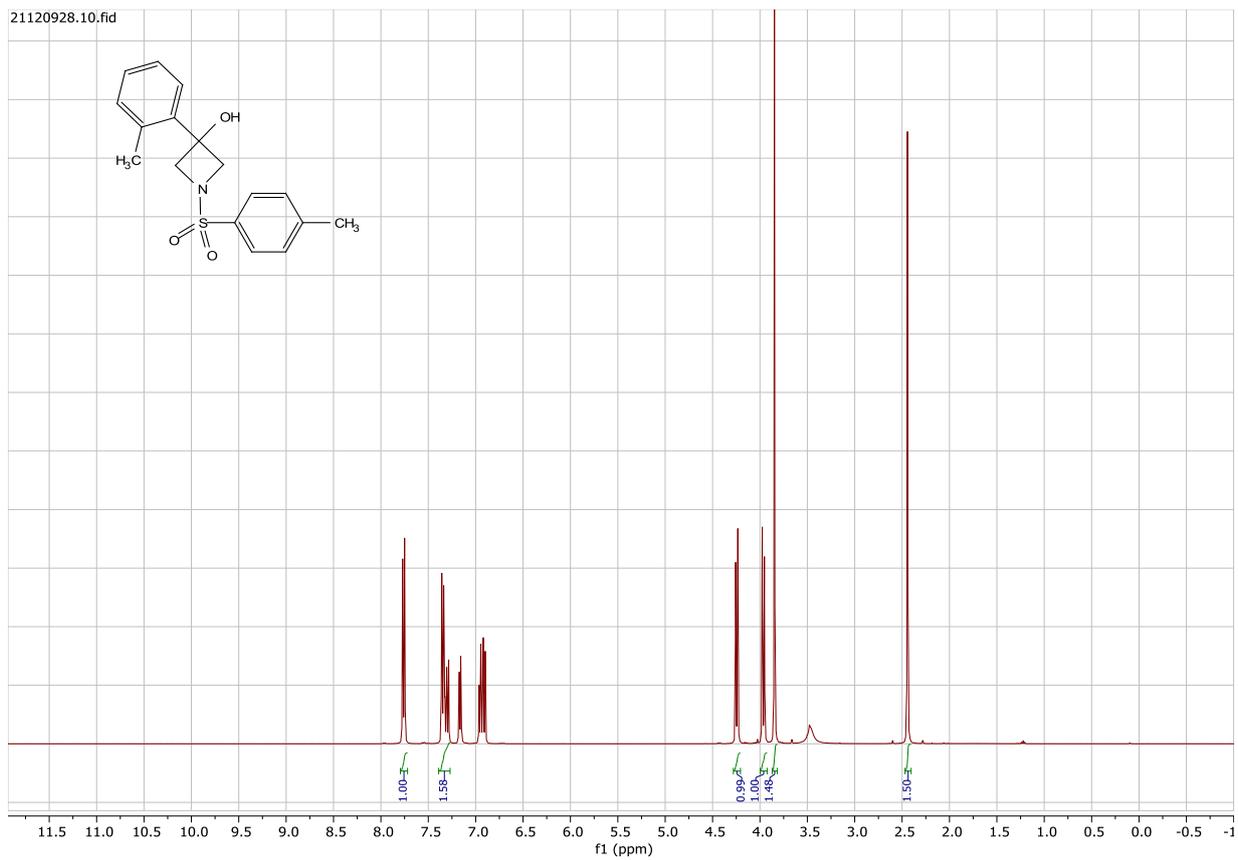
# Compound 1-125 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



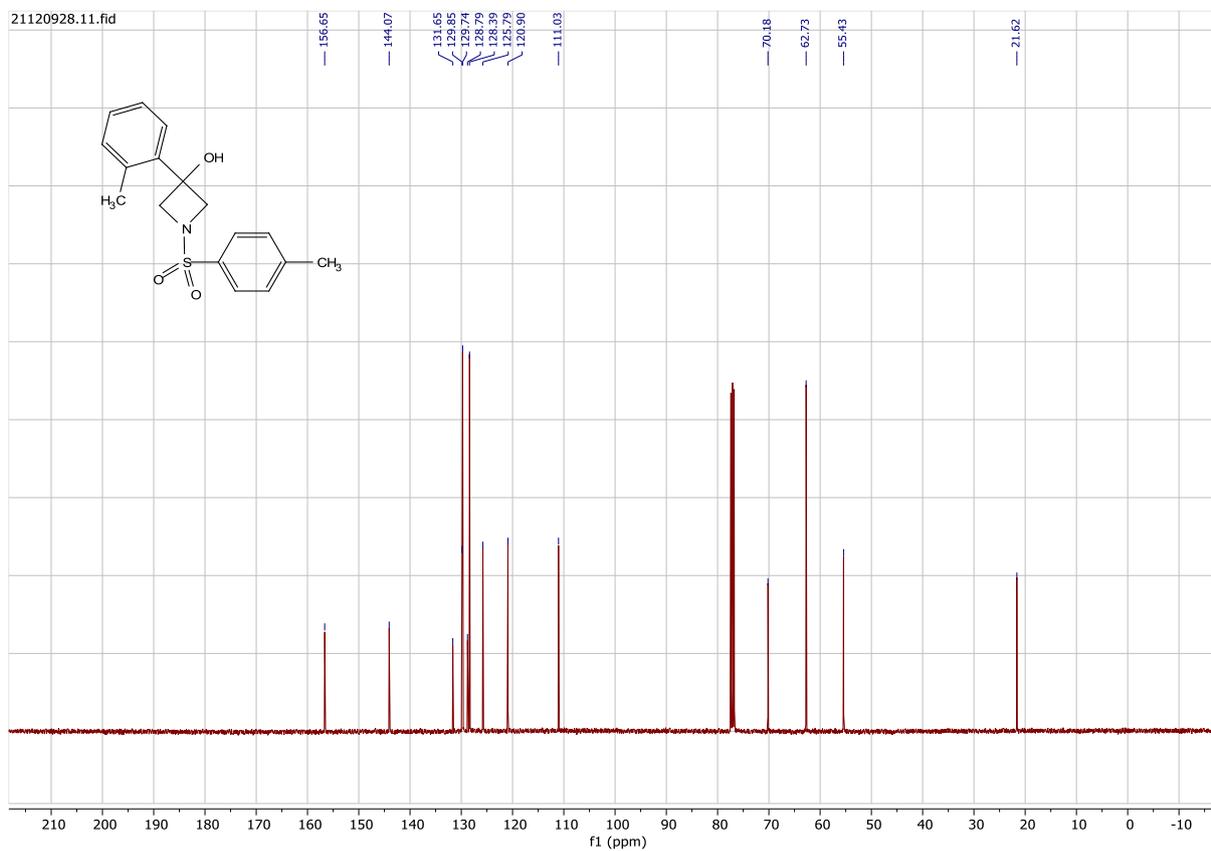
# Compound 1-125 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



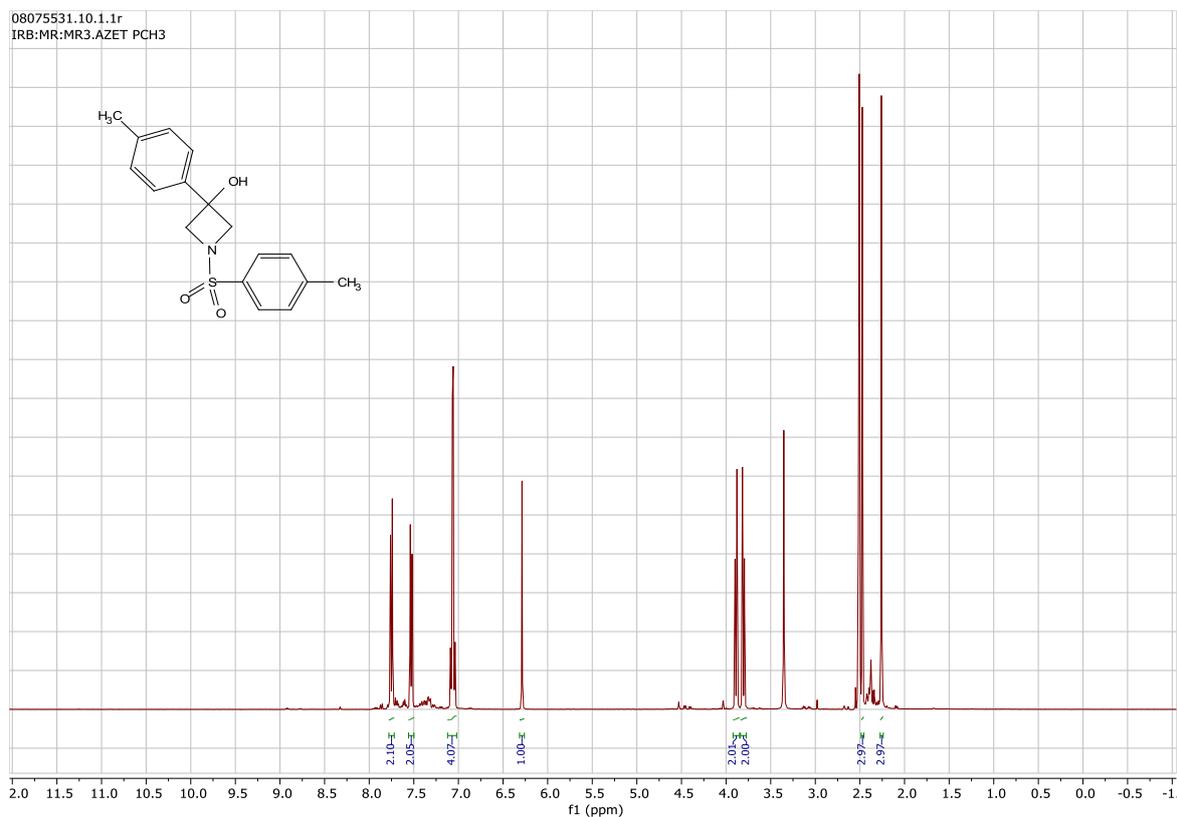
# Compound 1-126 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



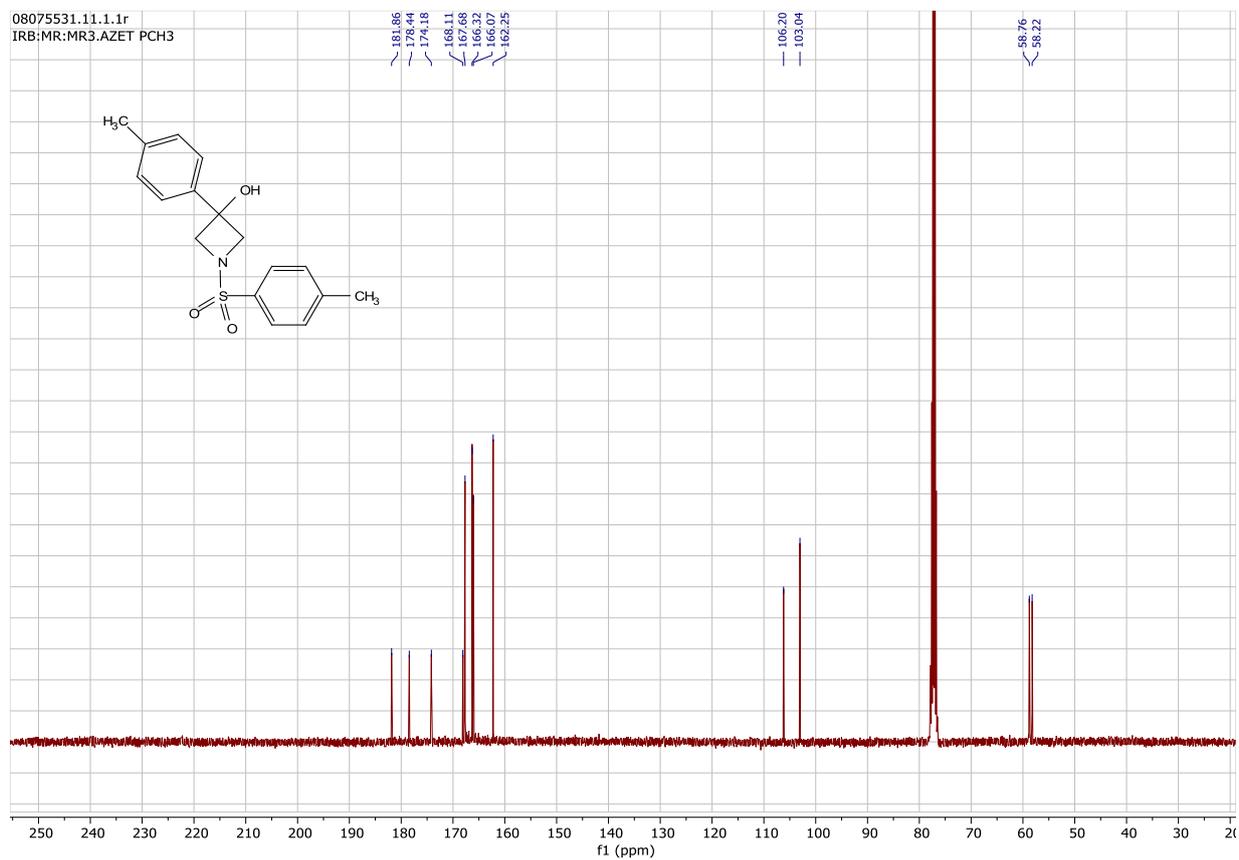
# Compound 1-126 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



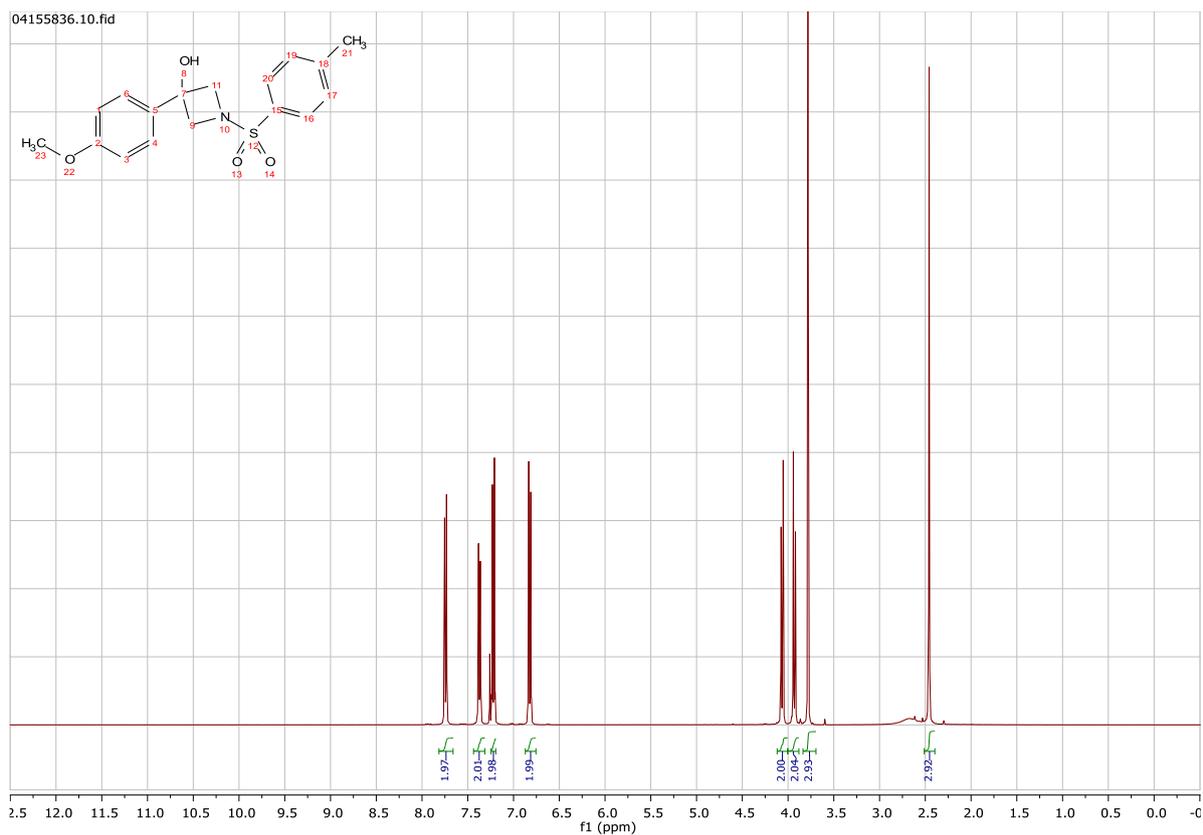
# Compound 1-127 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



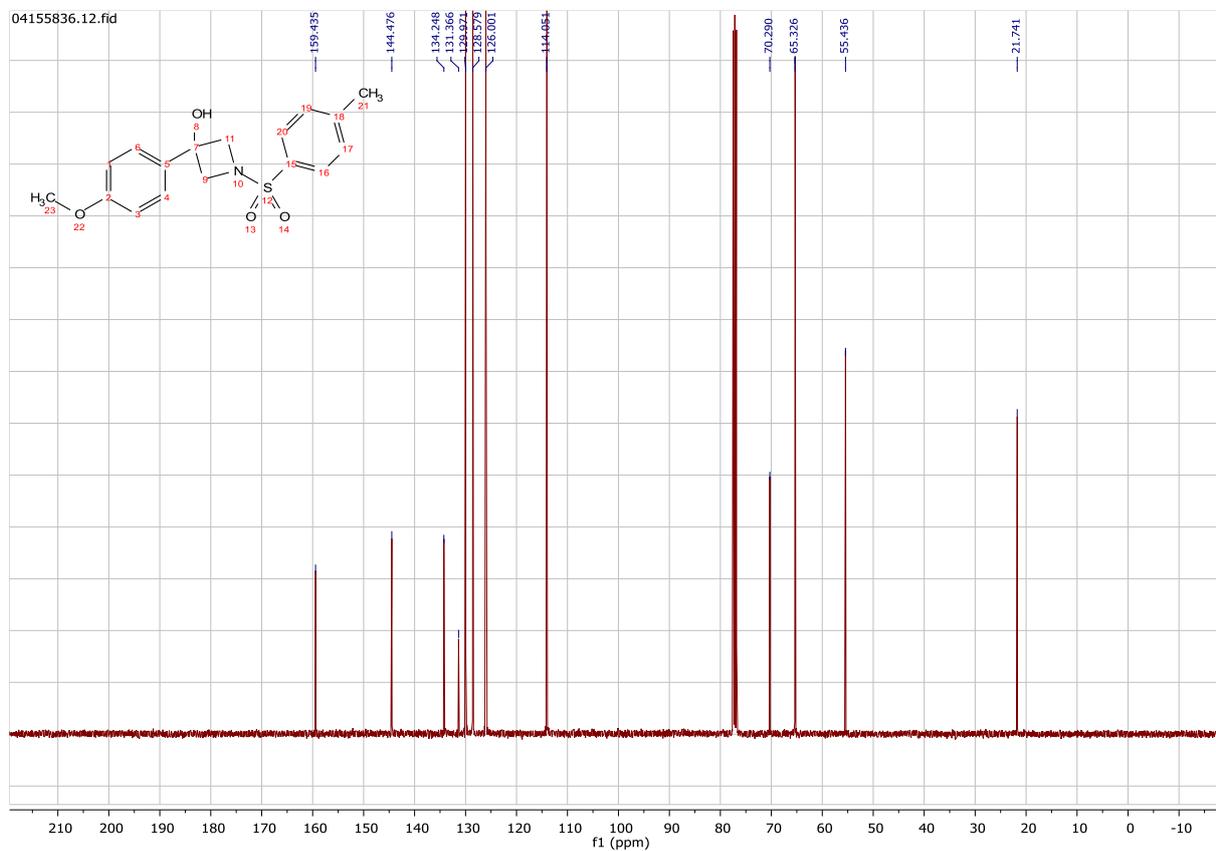
# Compound 1-127 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



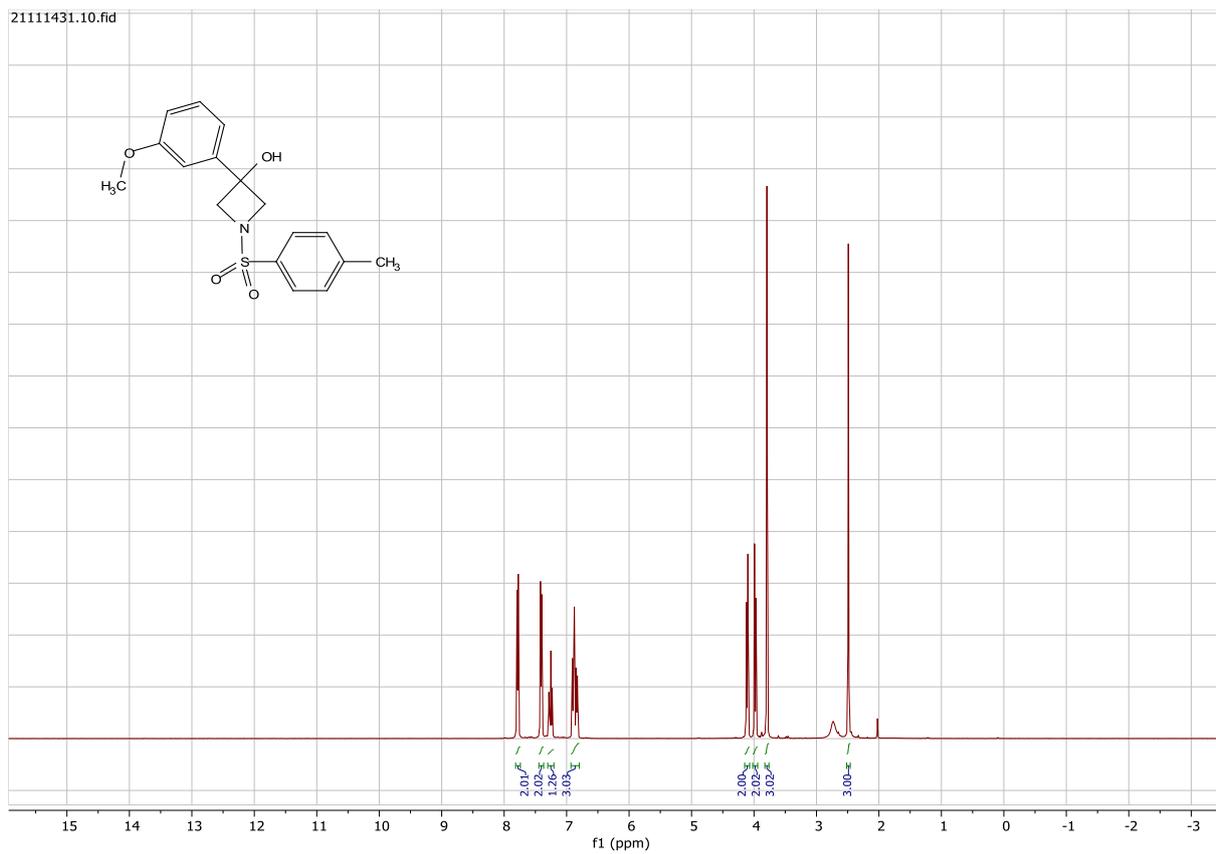
# Compound 1-128 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



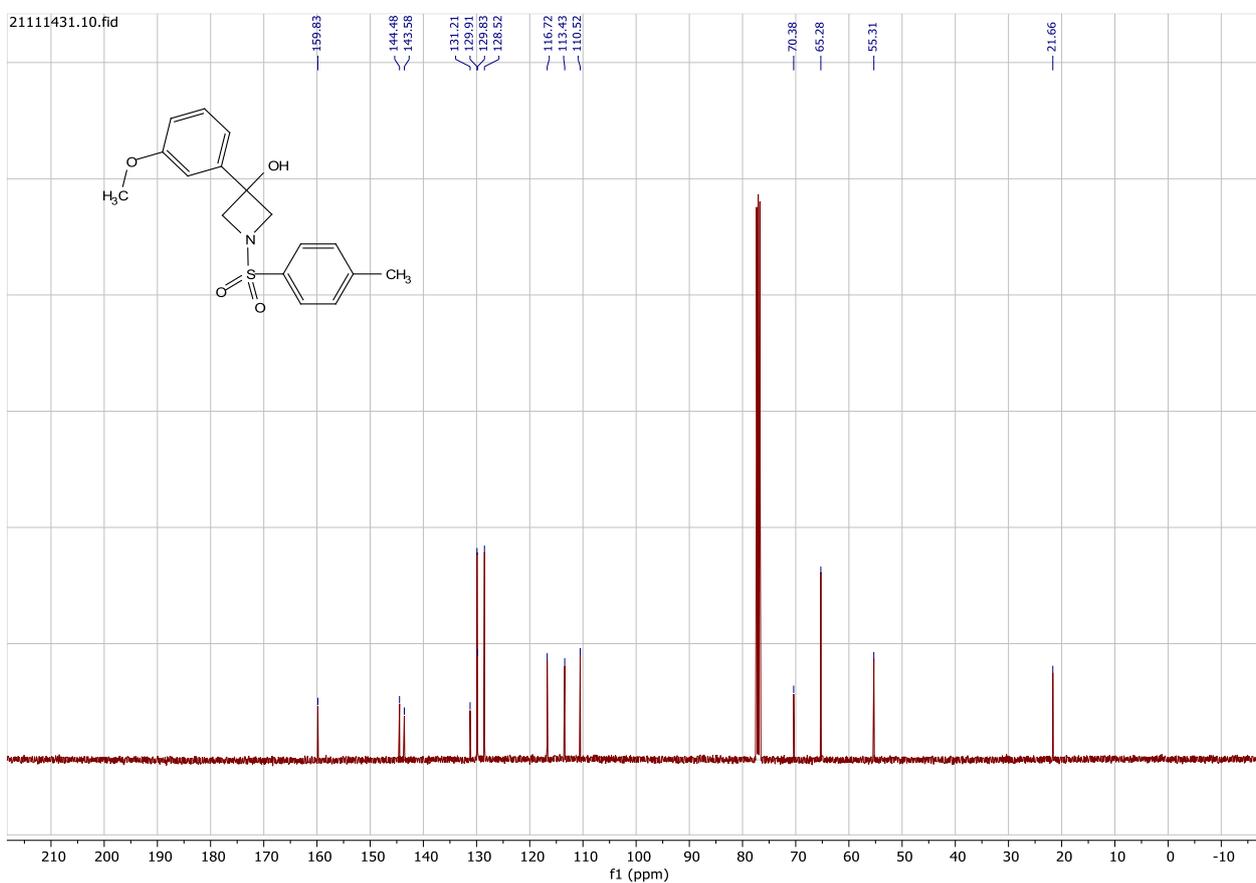
# Compound 1-128 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



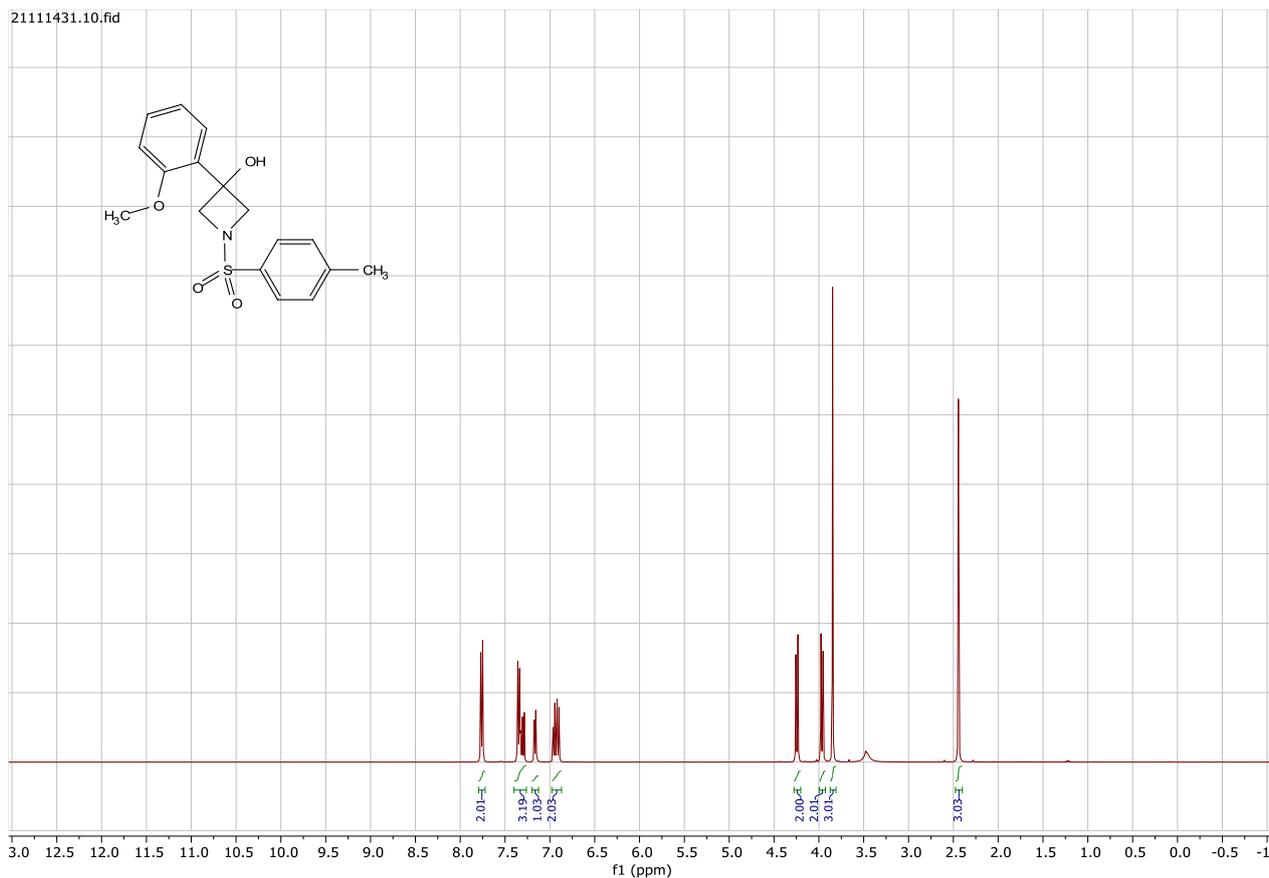
# Compound 1-129 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



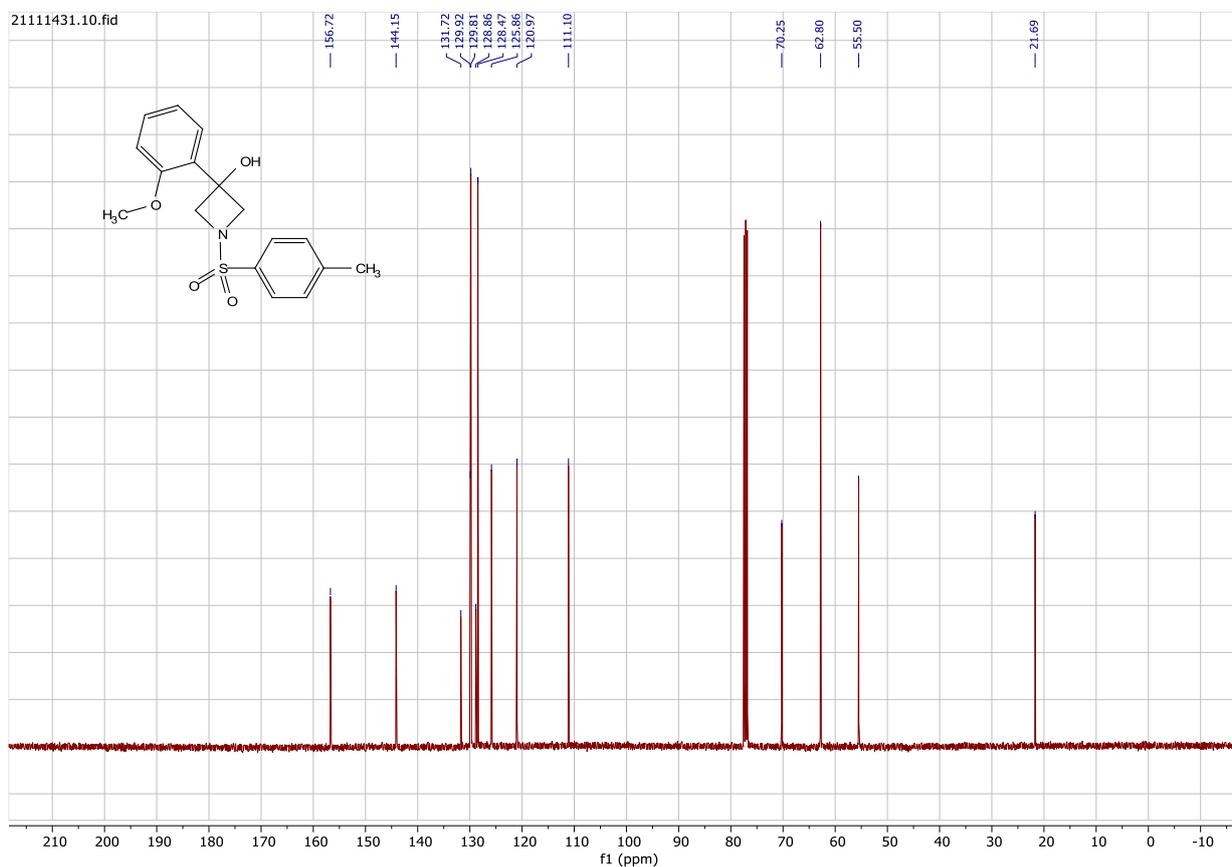
# Compound 1-129 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



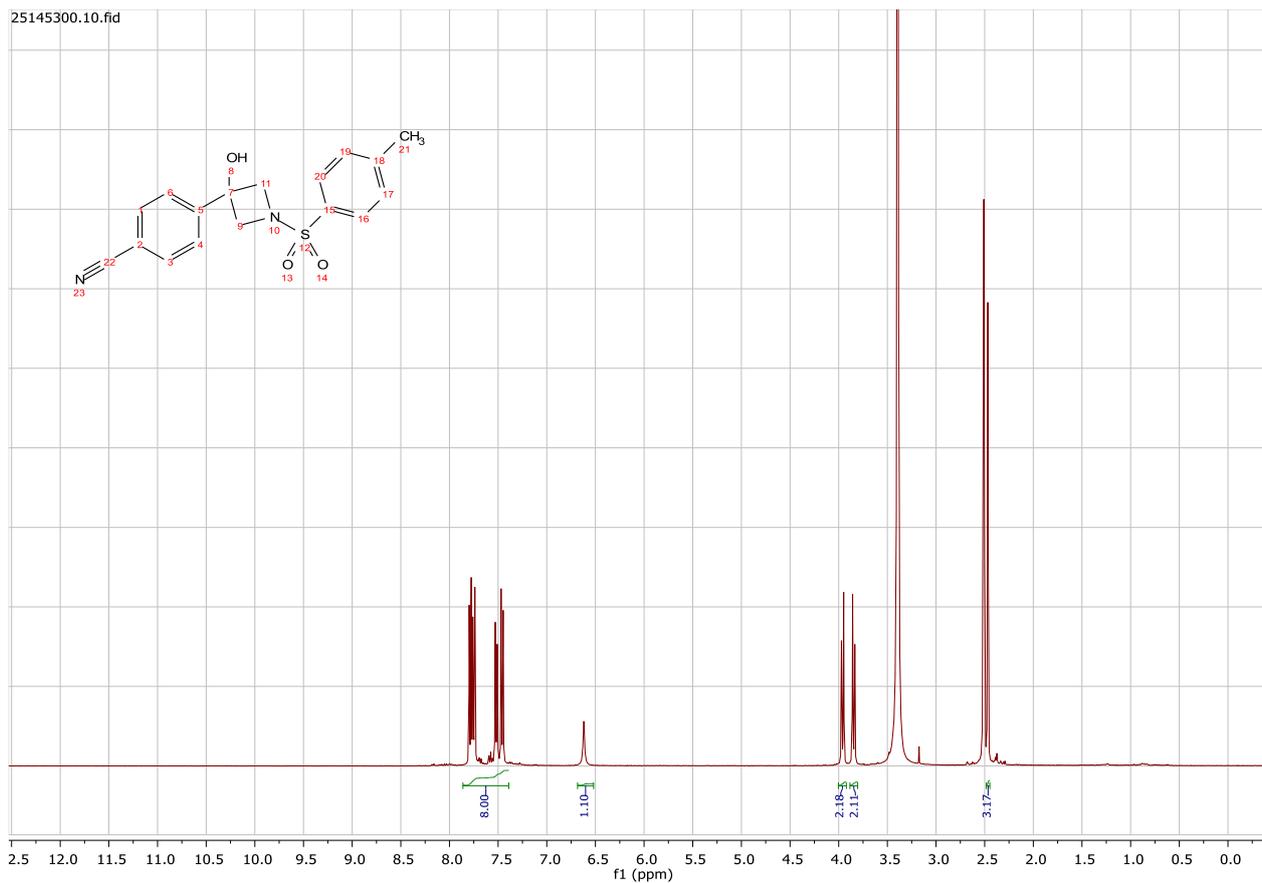
# Compound 1-130 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



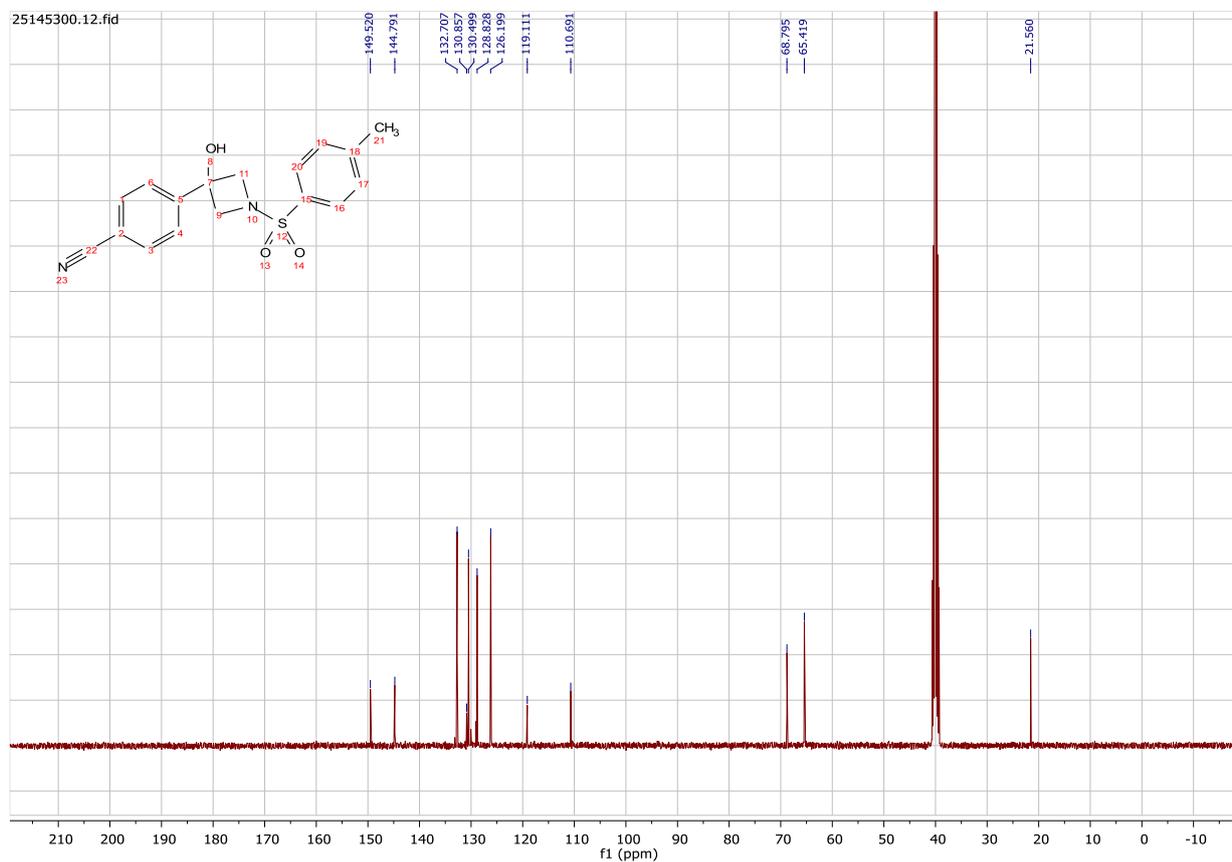
# Compound 1-130 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



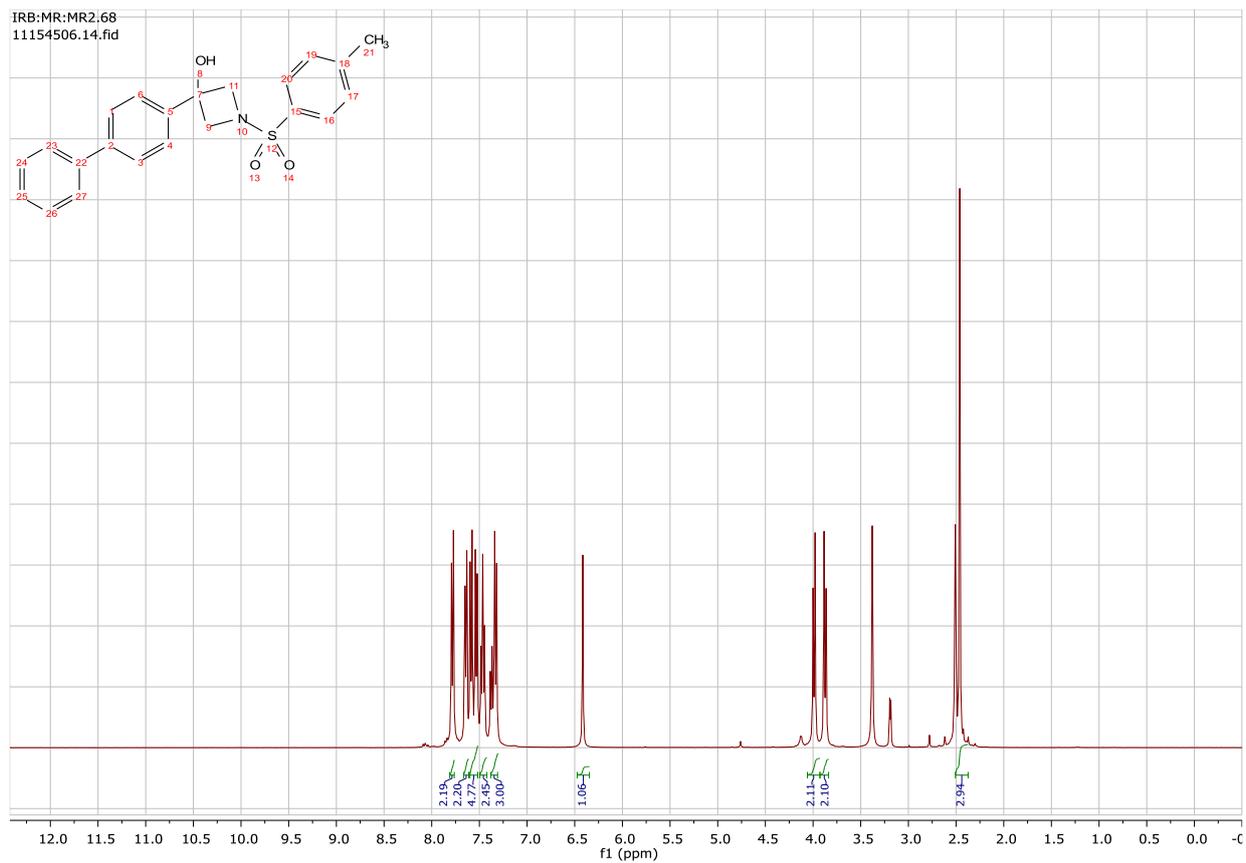
# Compound 1-131 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



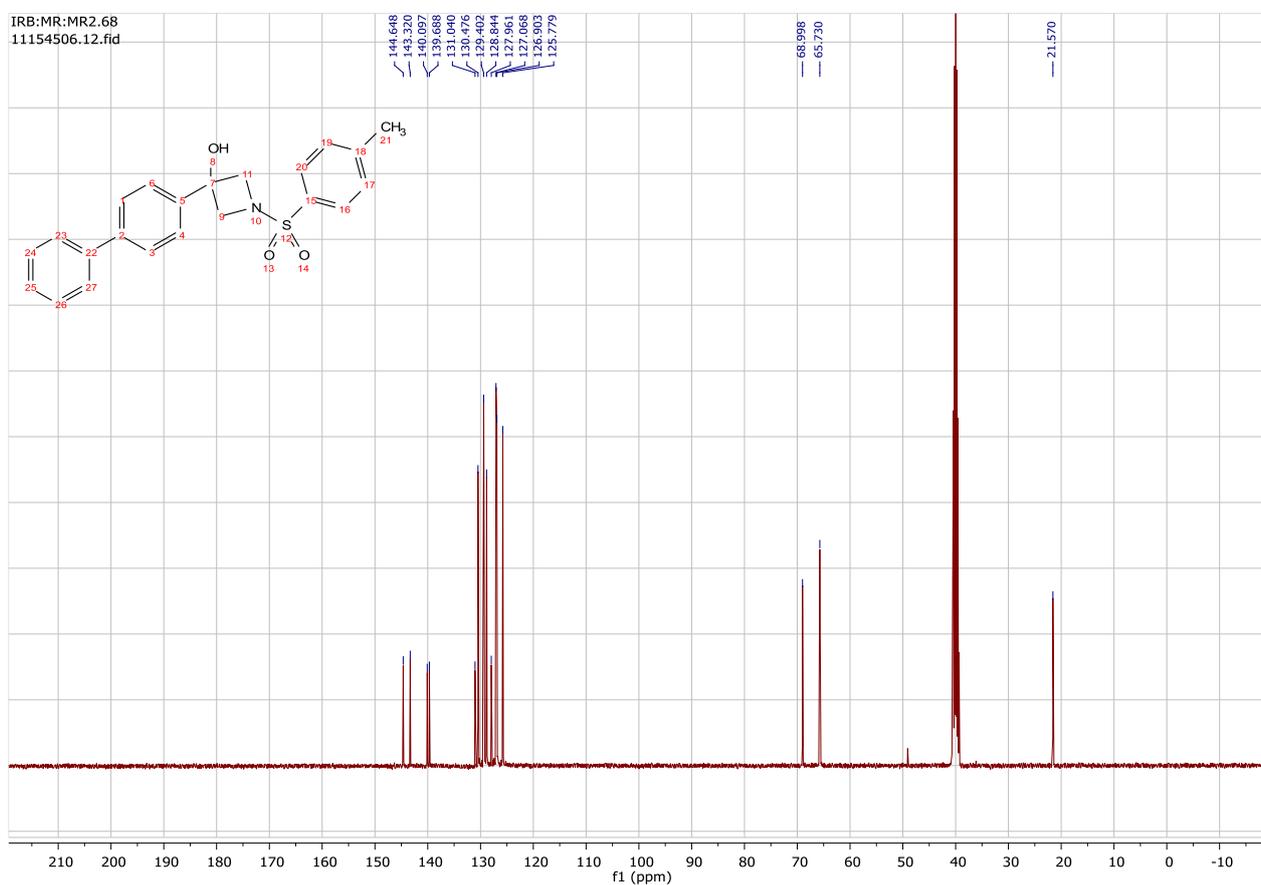
# Compound 1-131 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



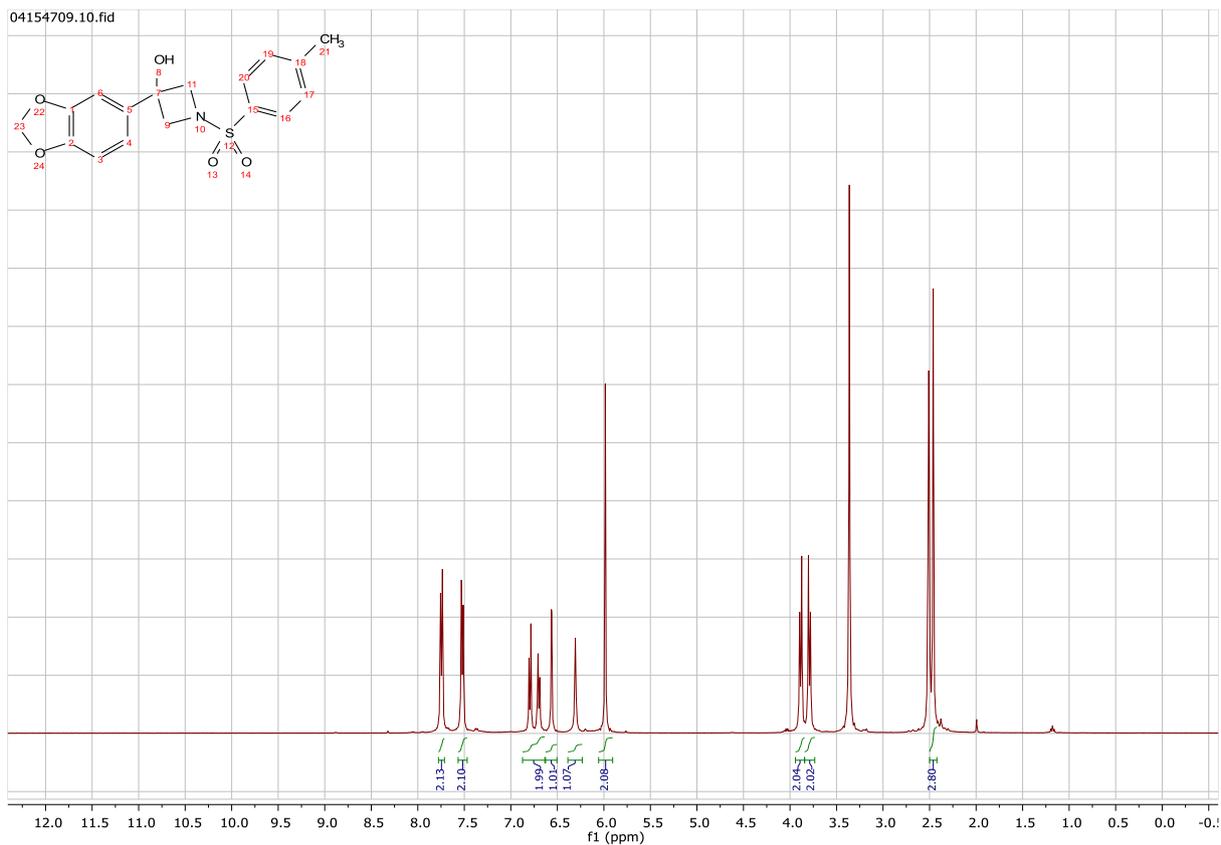
# Compound 1-132 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



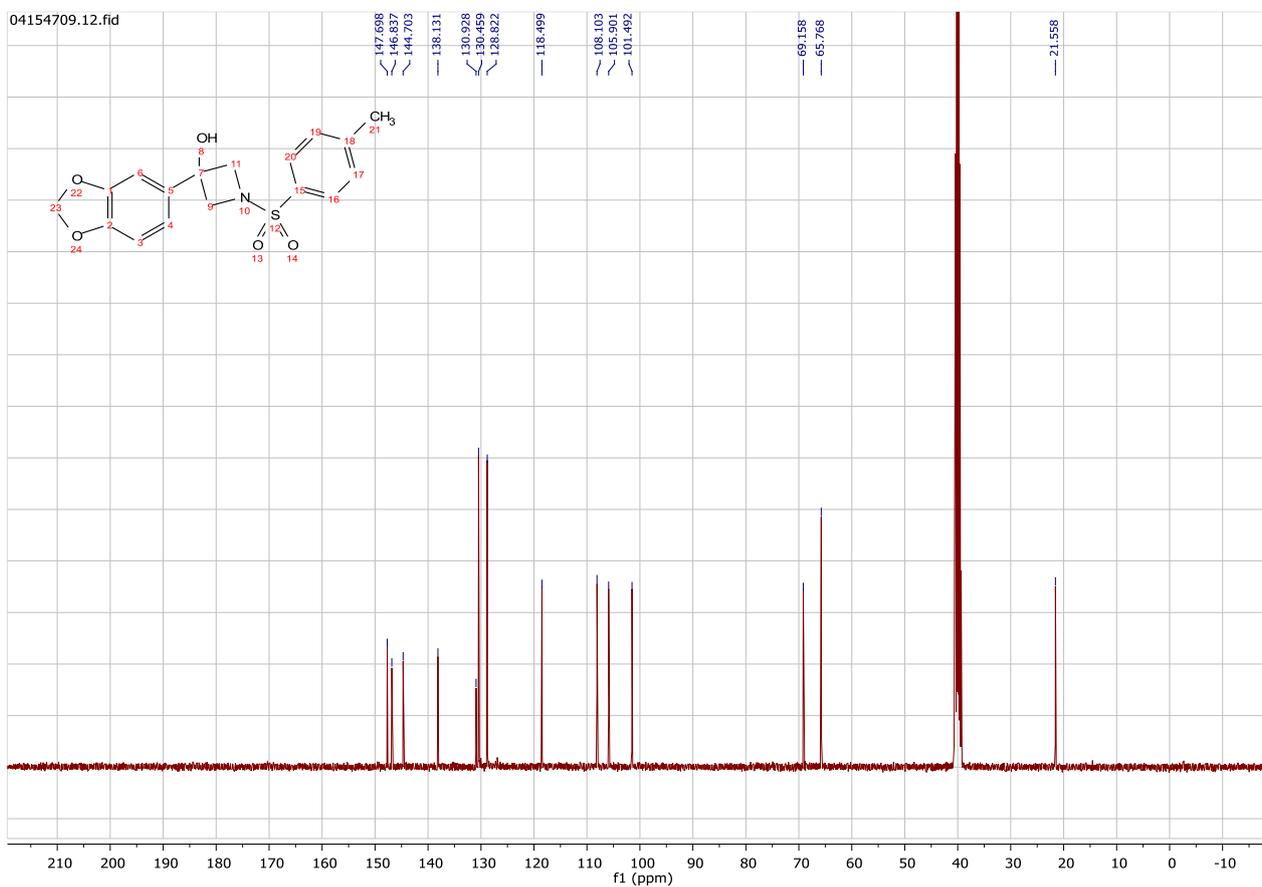
# Compound 1-132 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



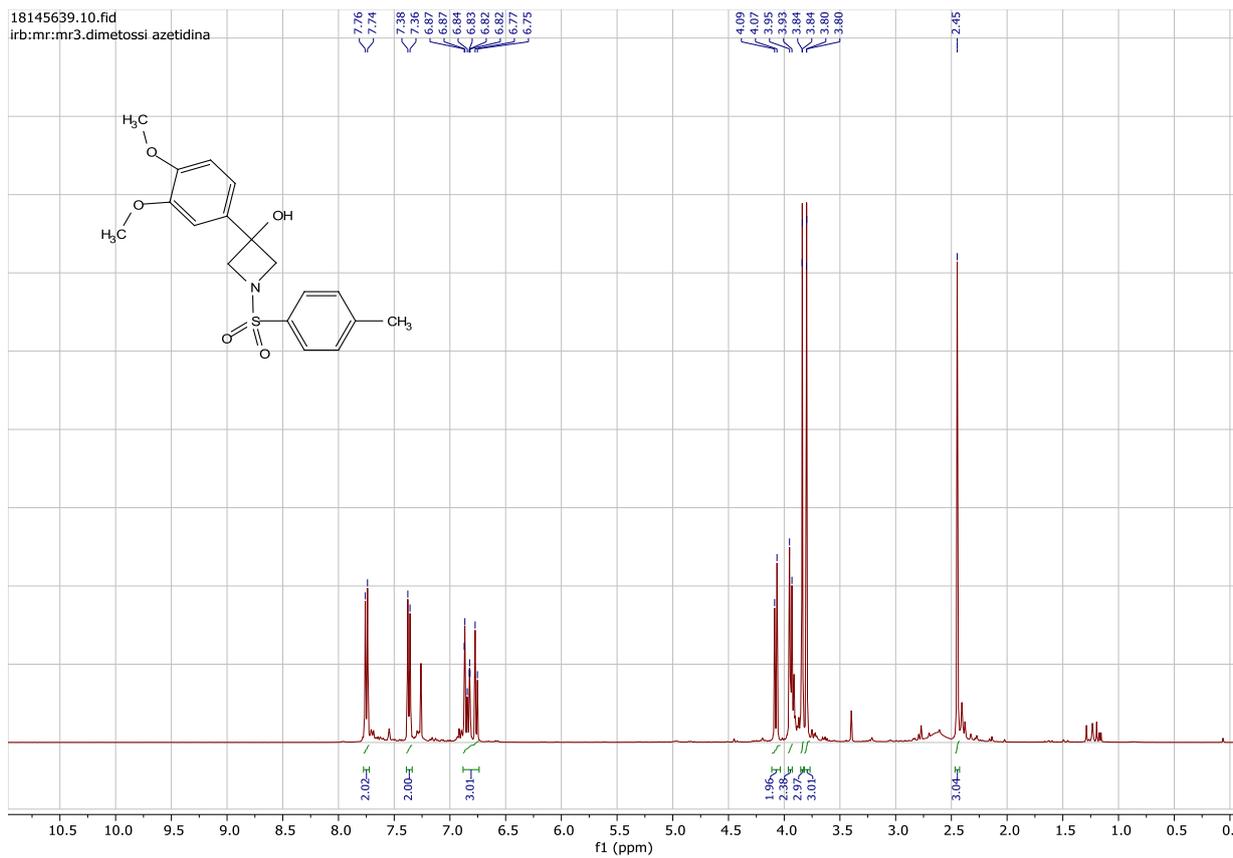
# Compound 1-133 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



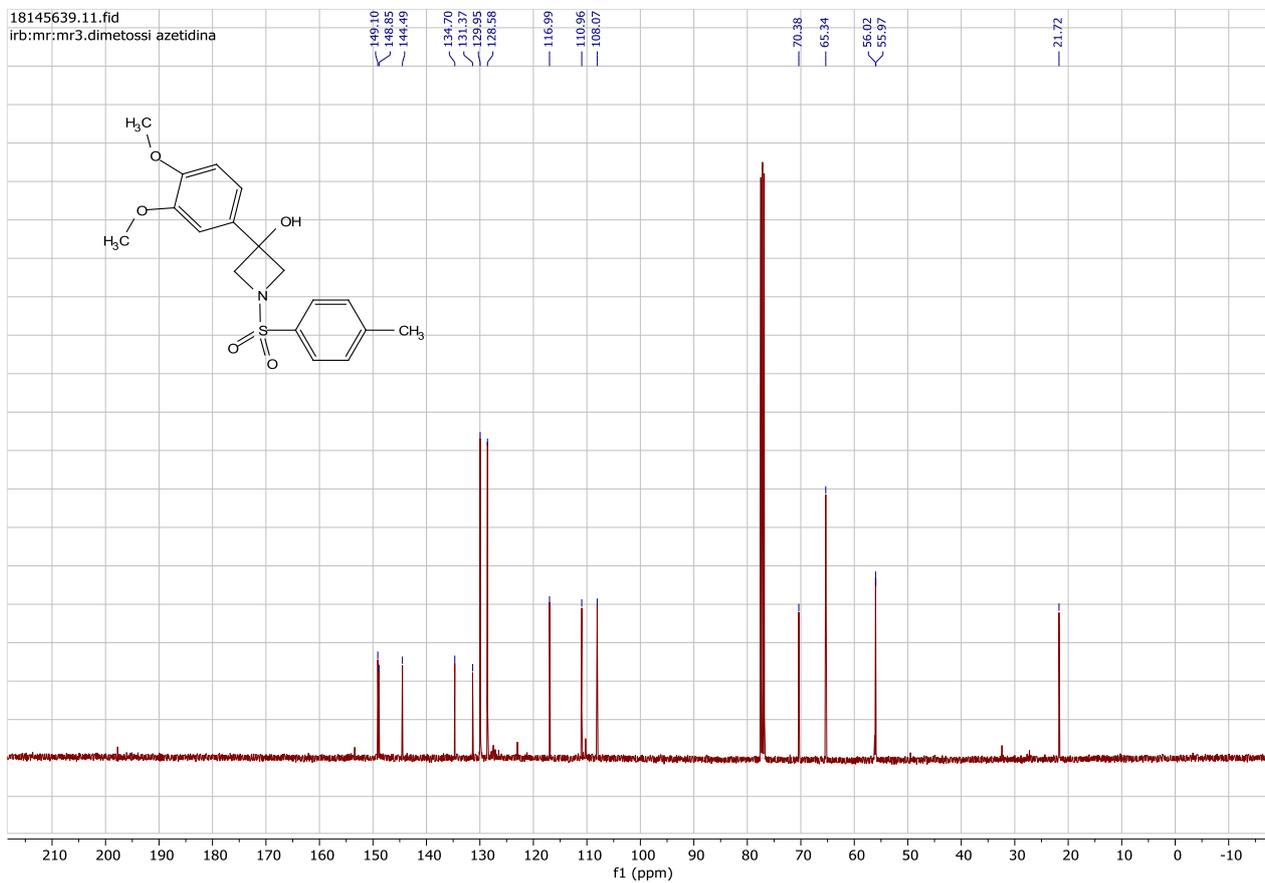
# Compound 1-133 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



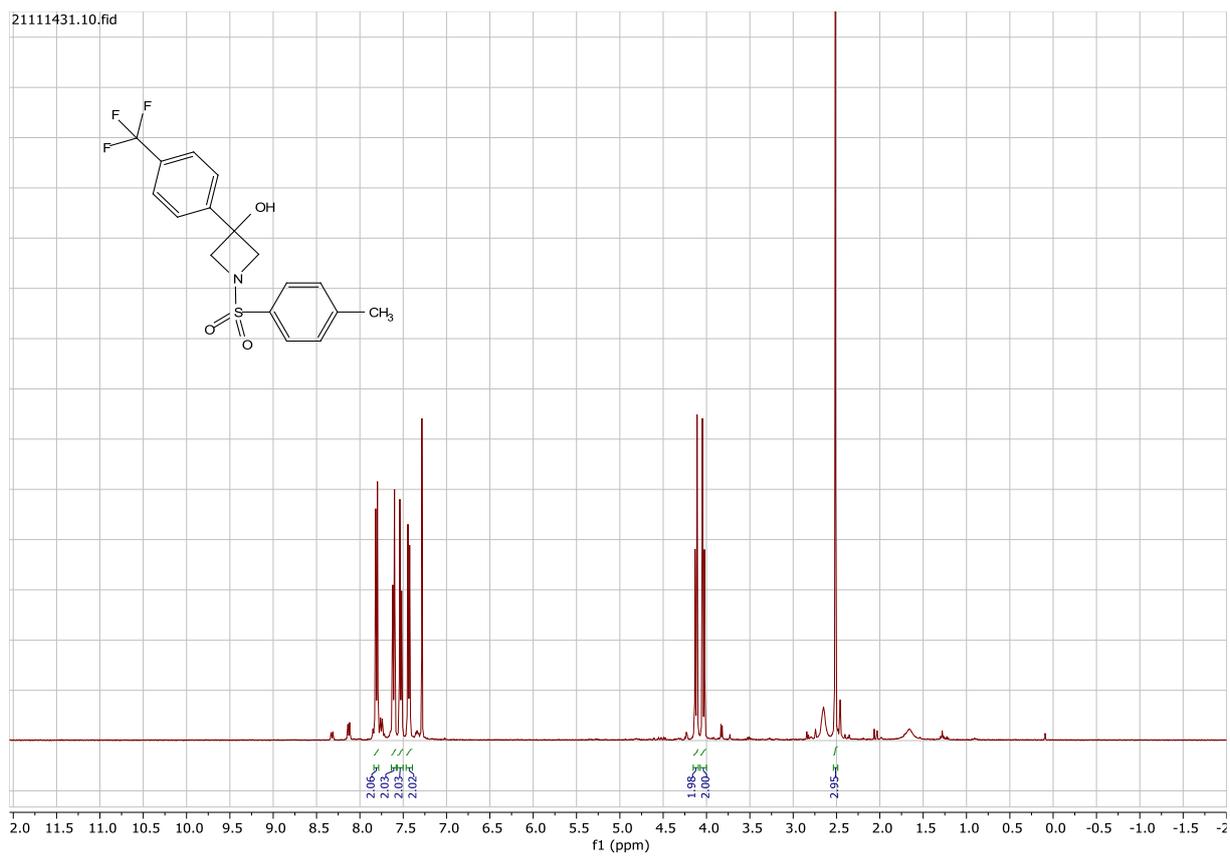
# Compound 1-134 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



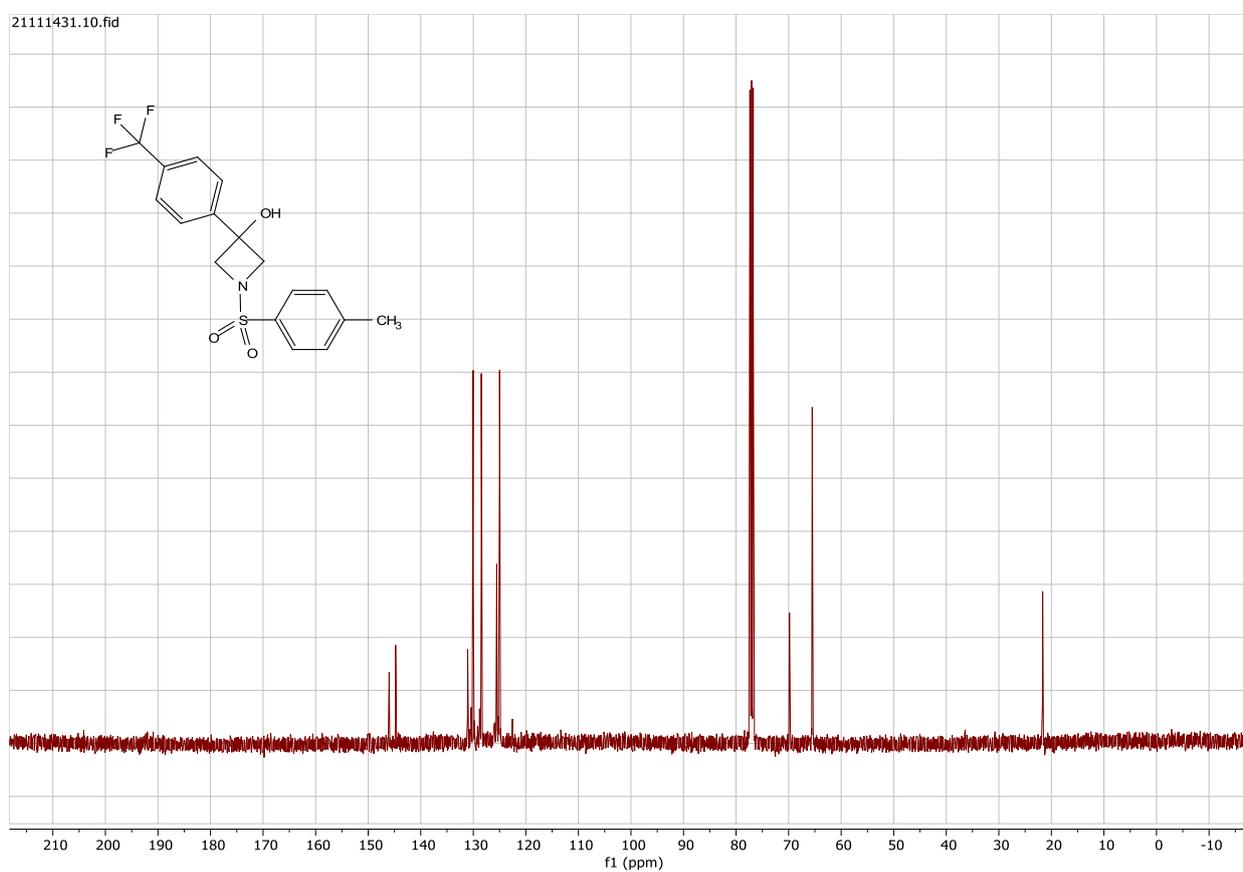
# Compound 1-134 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



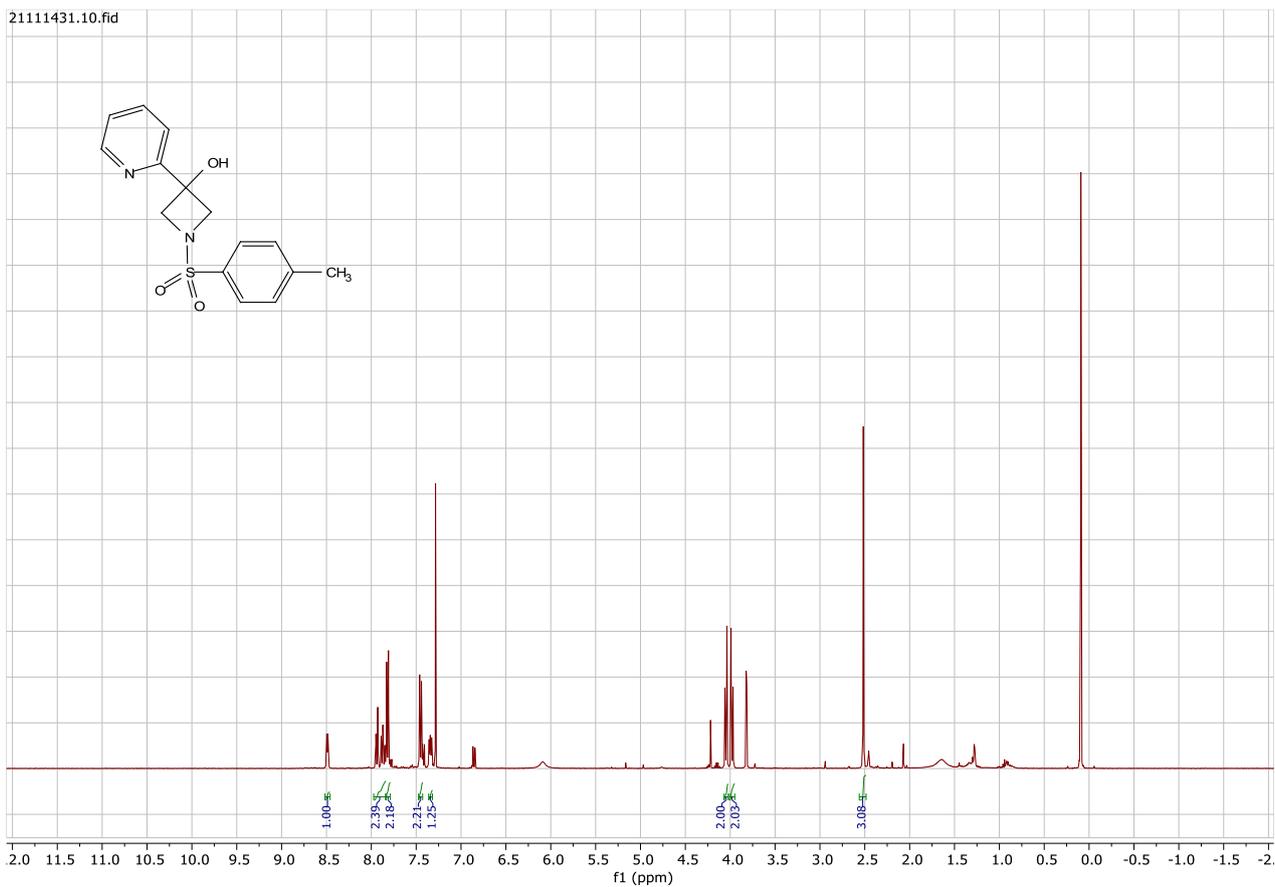
# Compound 1-135 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



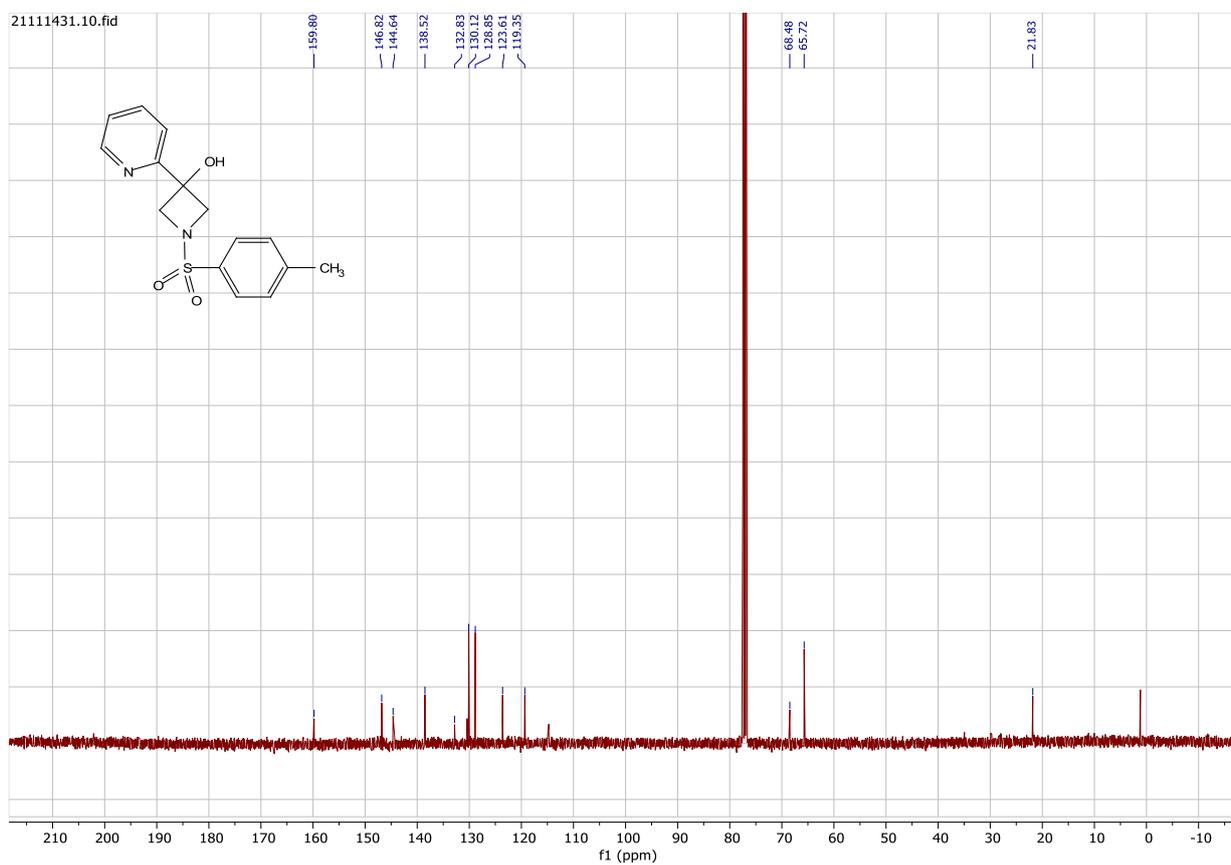
# Compound 1-135 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



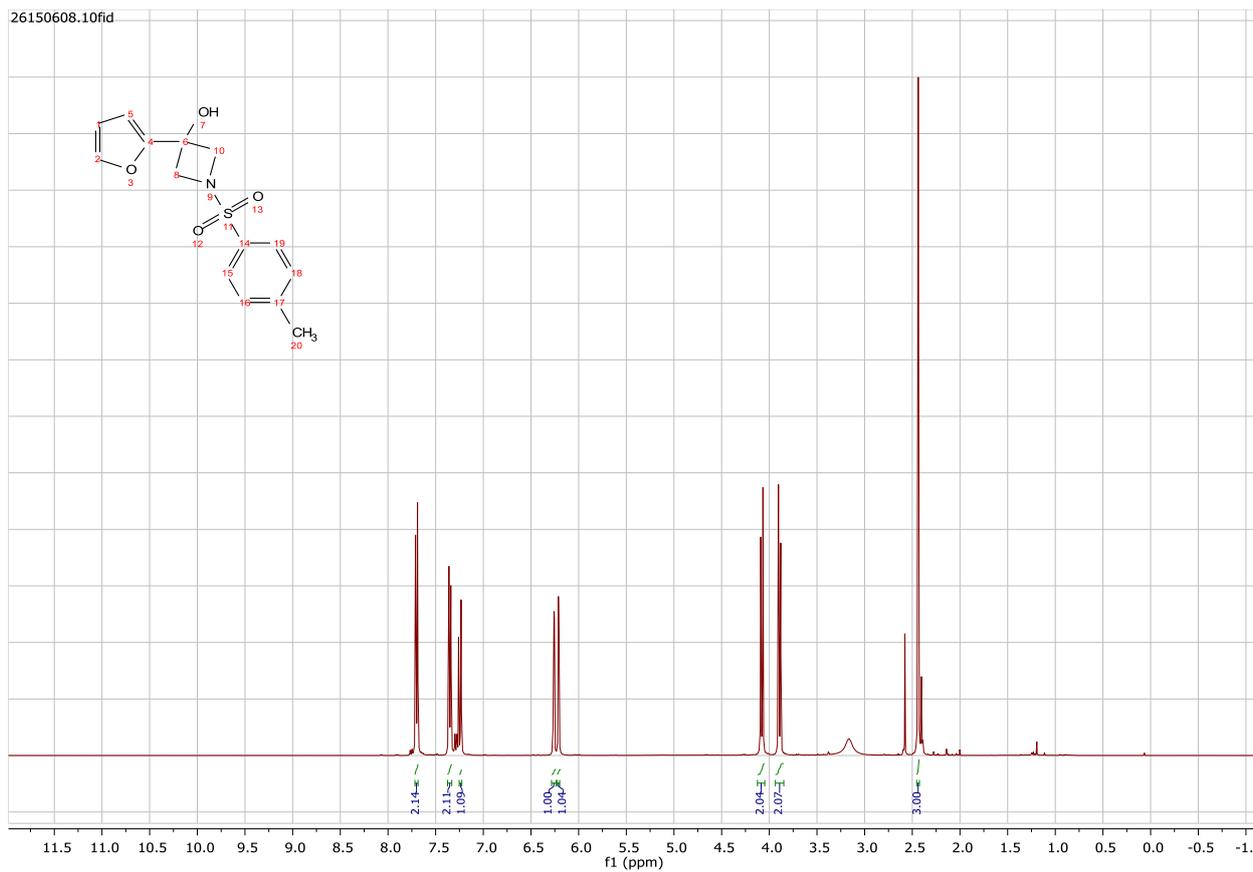
# Compound 1-136 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



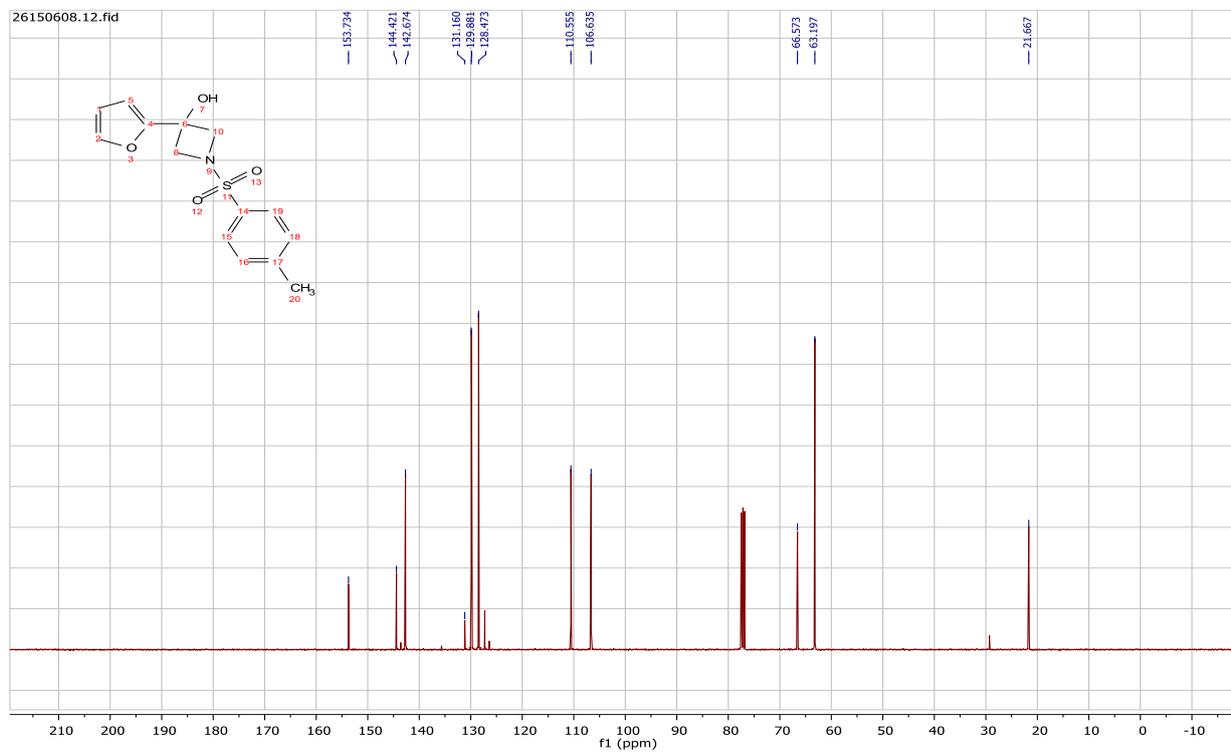
# Compound 1-136 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



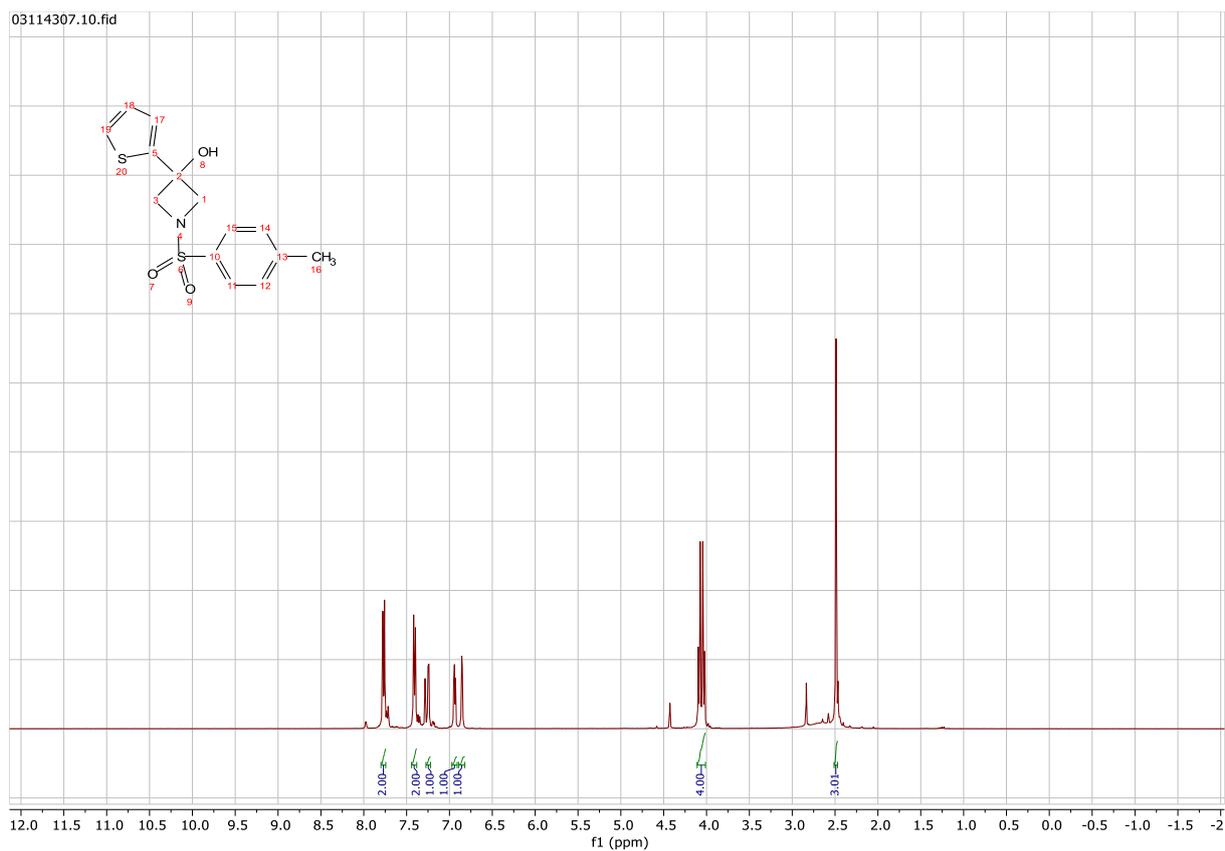
# Compound 1-137 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



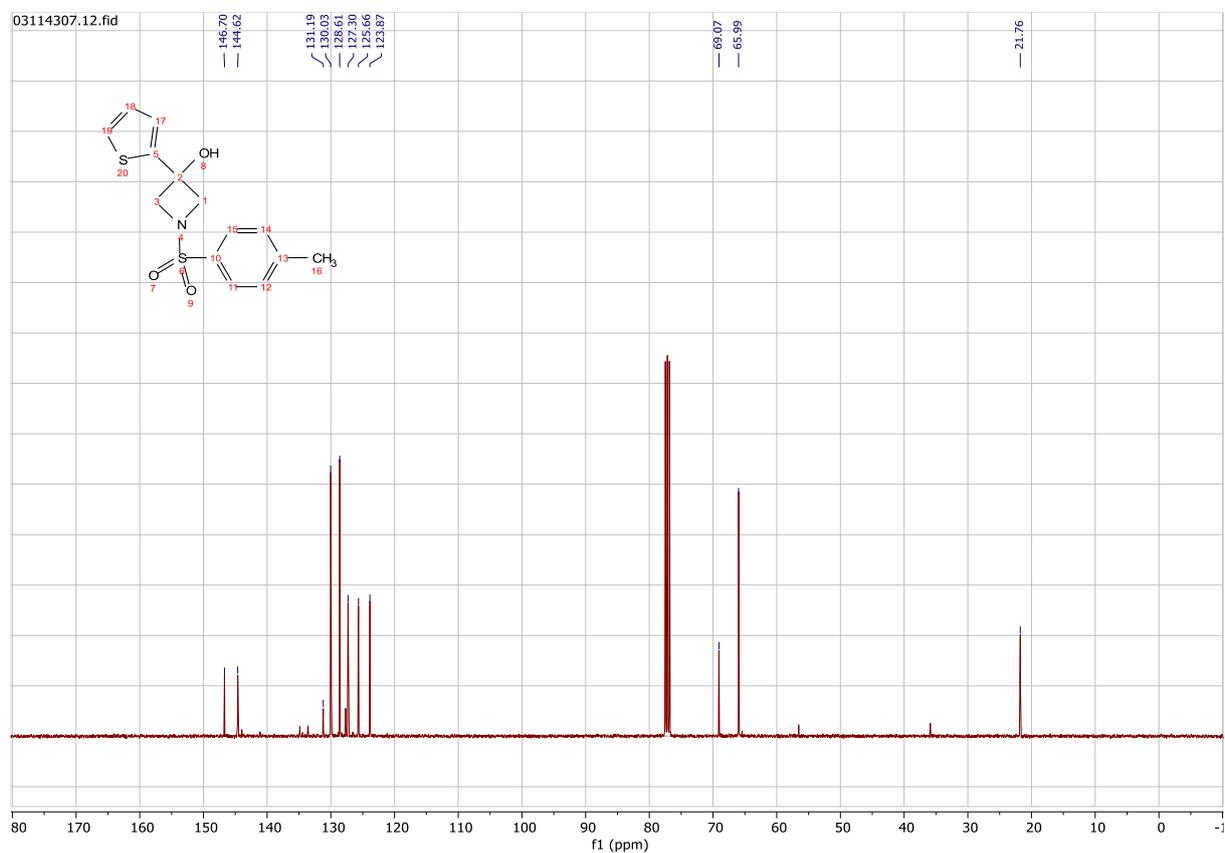
# Compound 1-137 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



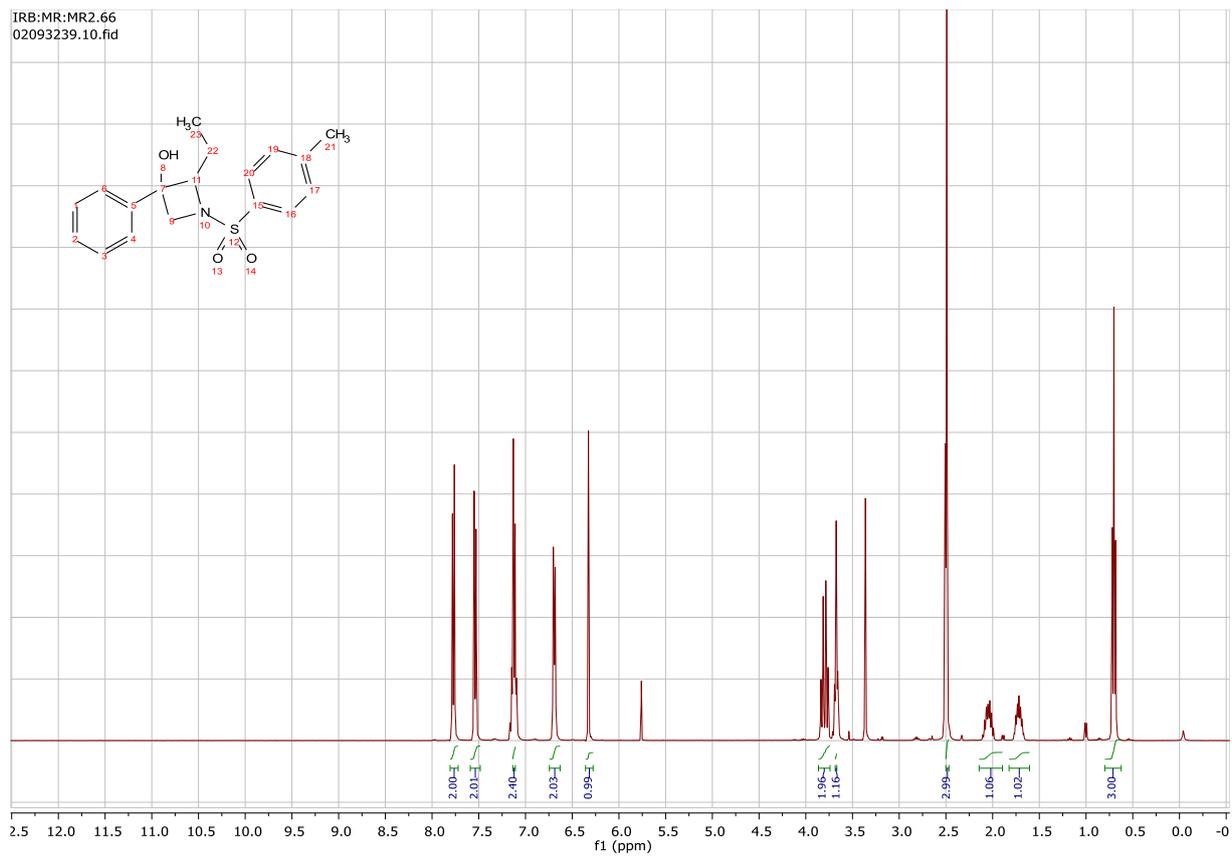
# Compound 1-138 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



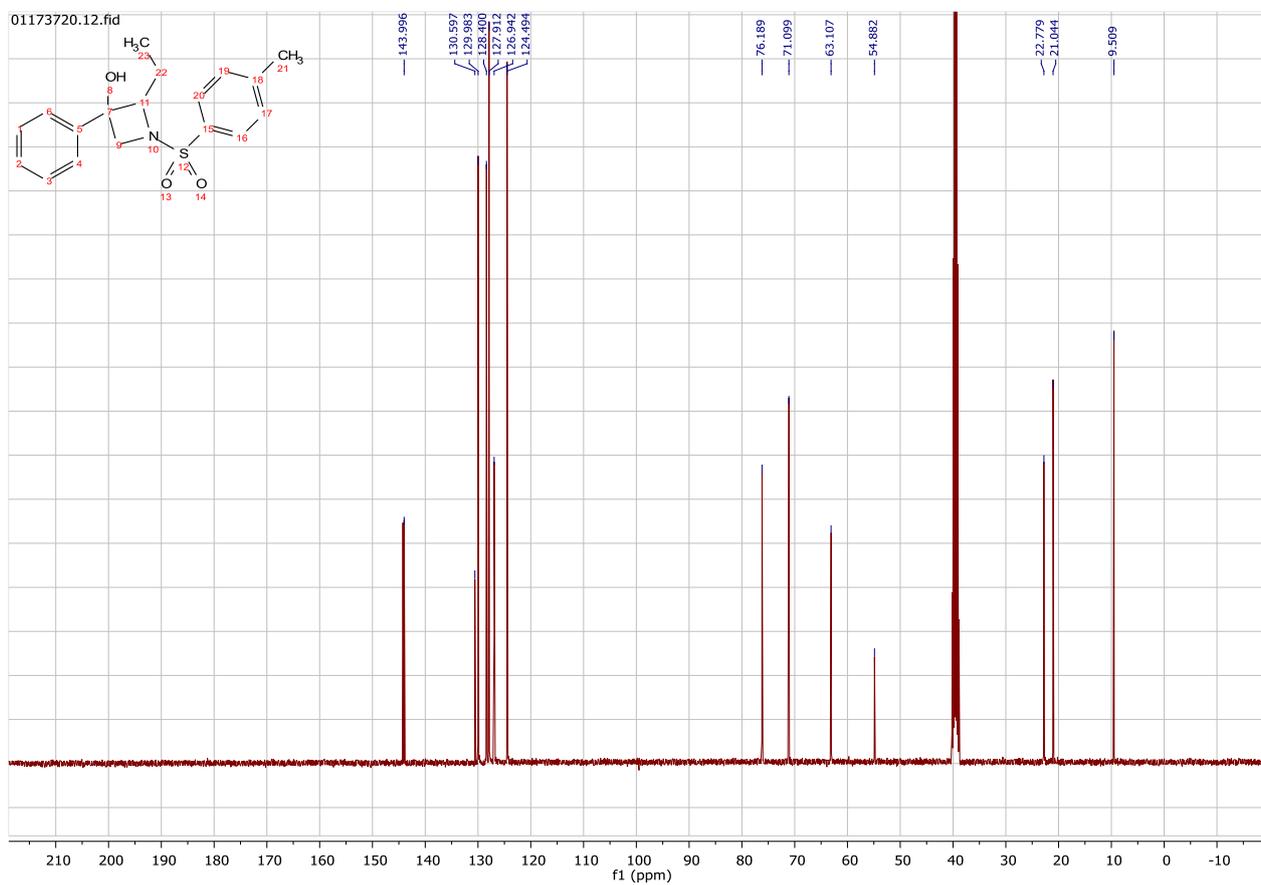
# Compound 1-138 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



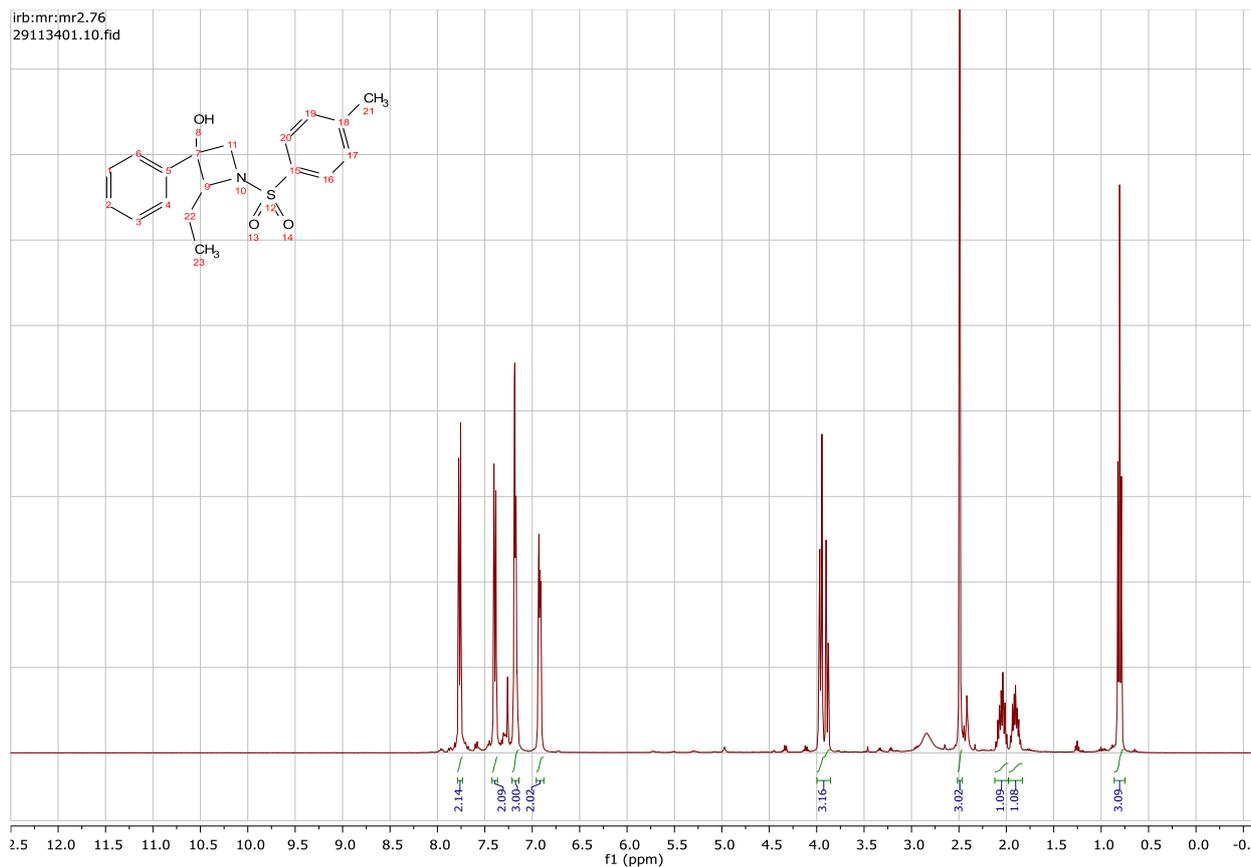
# Compound 1-139 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



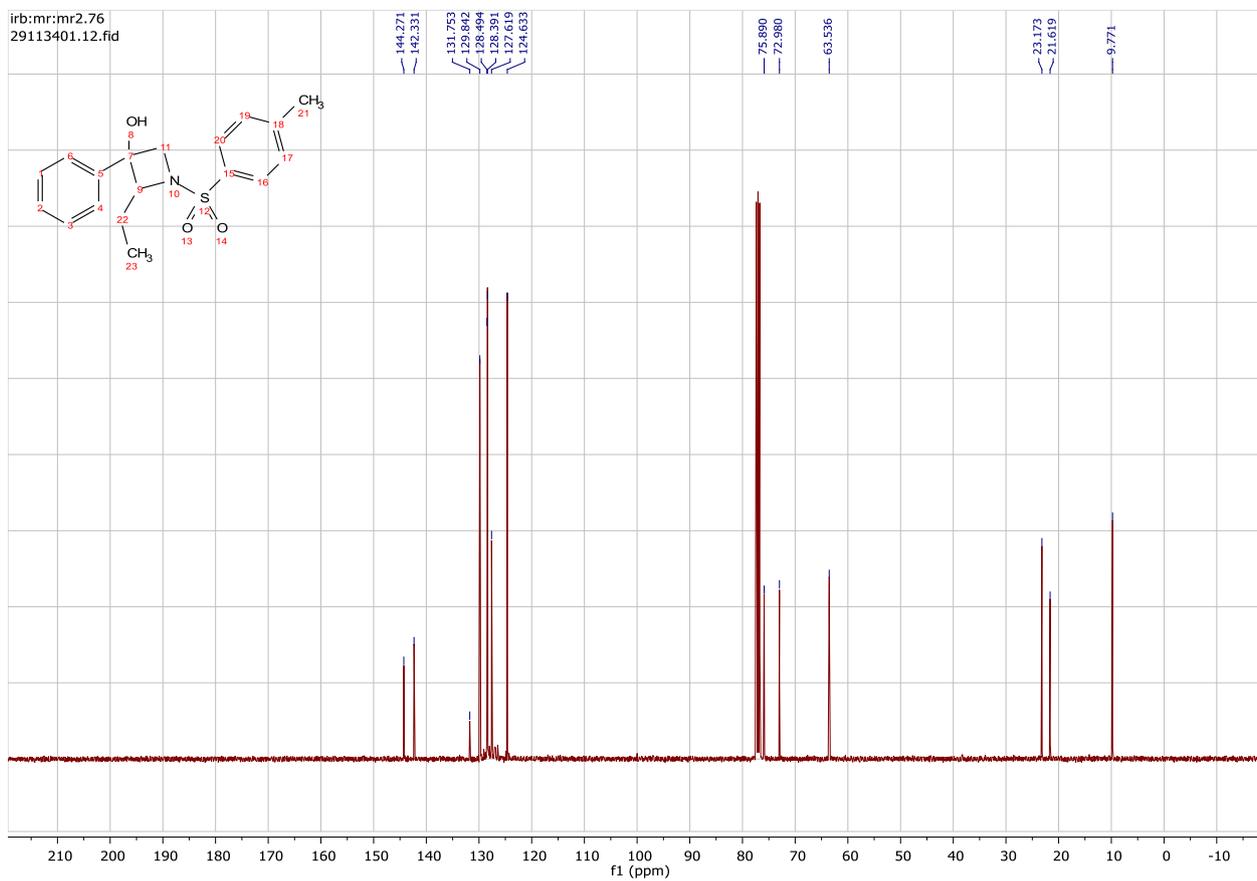
# Compound 1-139 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



# Compound 1-140 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)

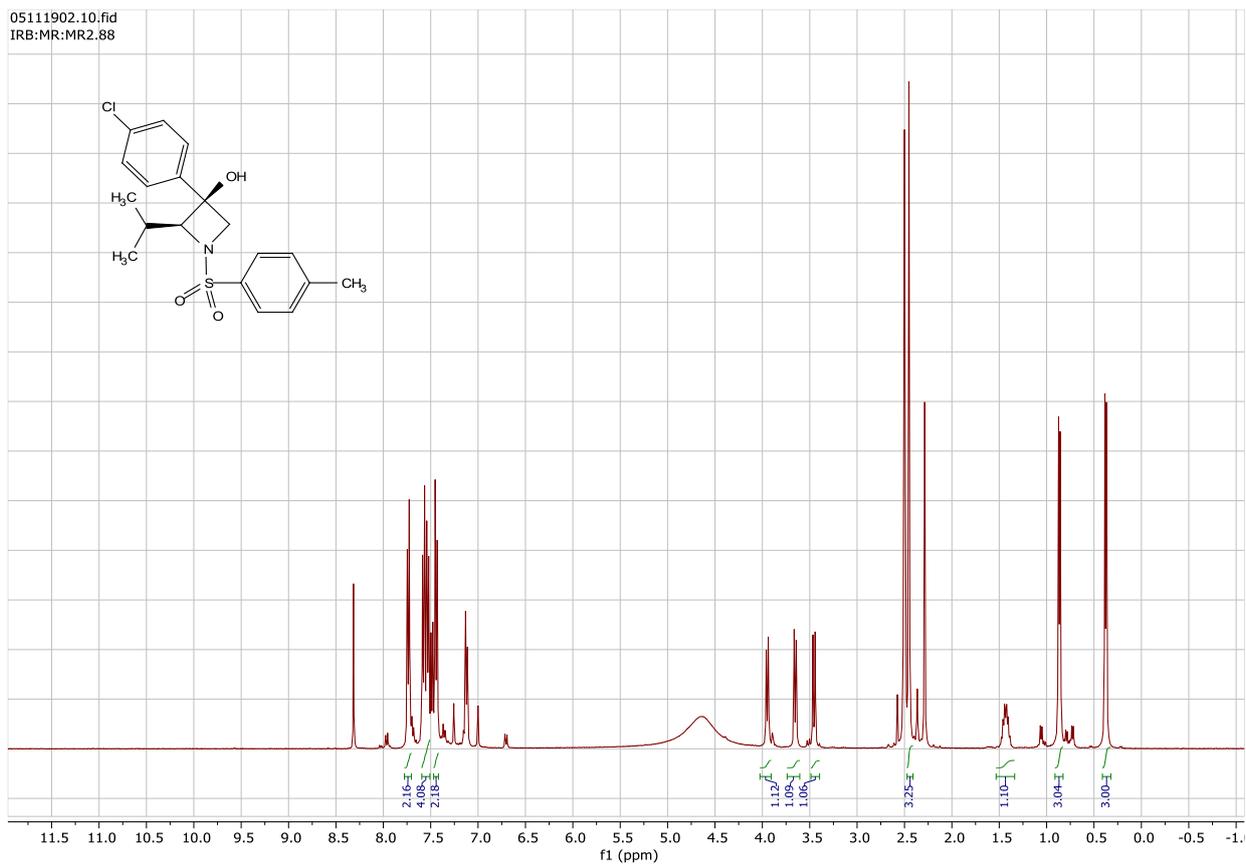


# Compound 1-140 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



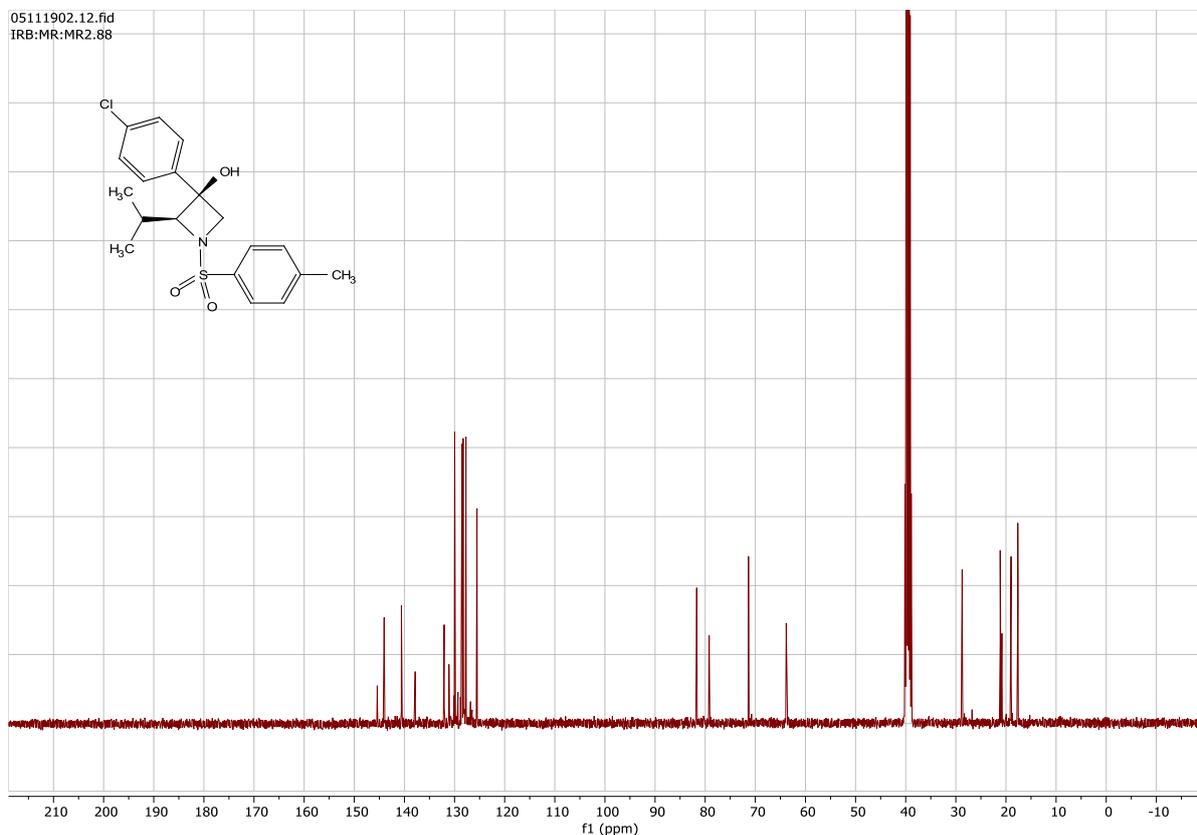
# Compound 1-141 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )

05111902.10.fid  
IRB:MR:MR2.88

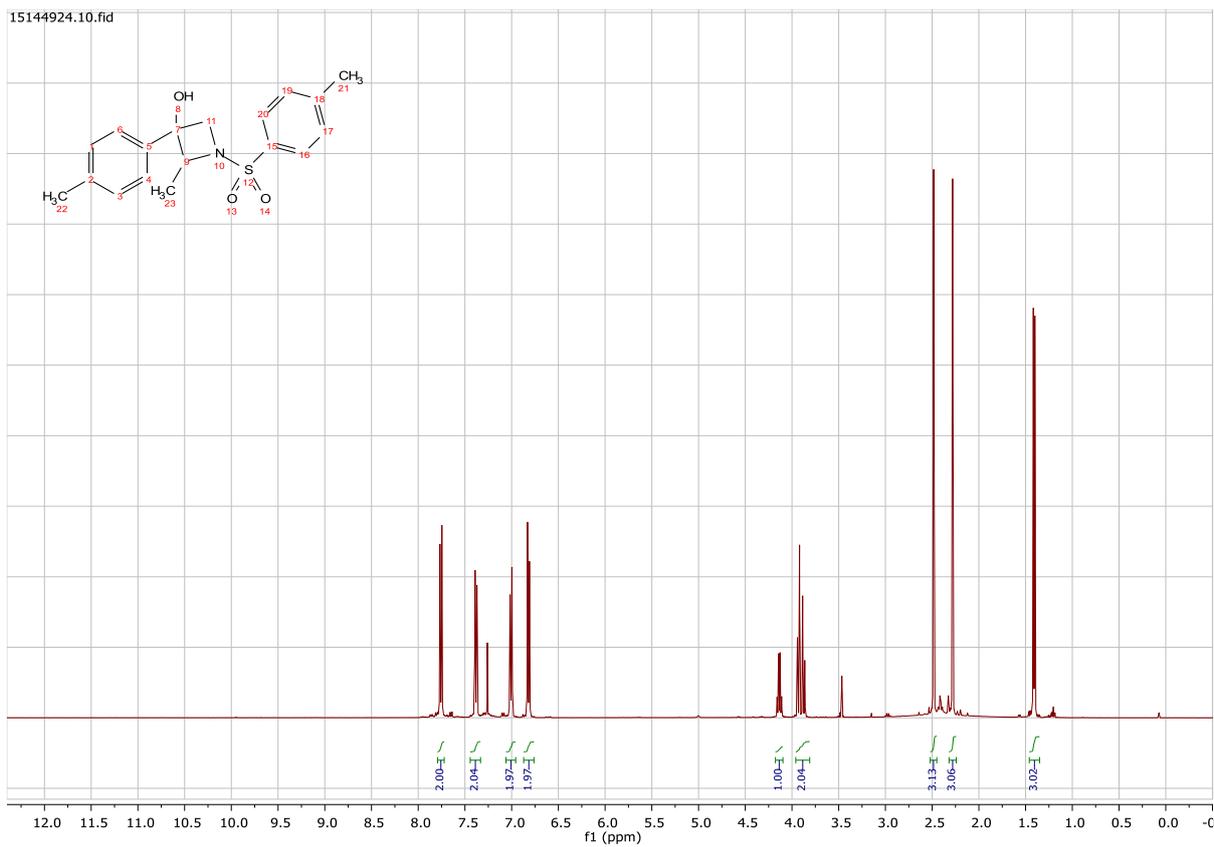


# Compound 1-141 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )

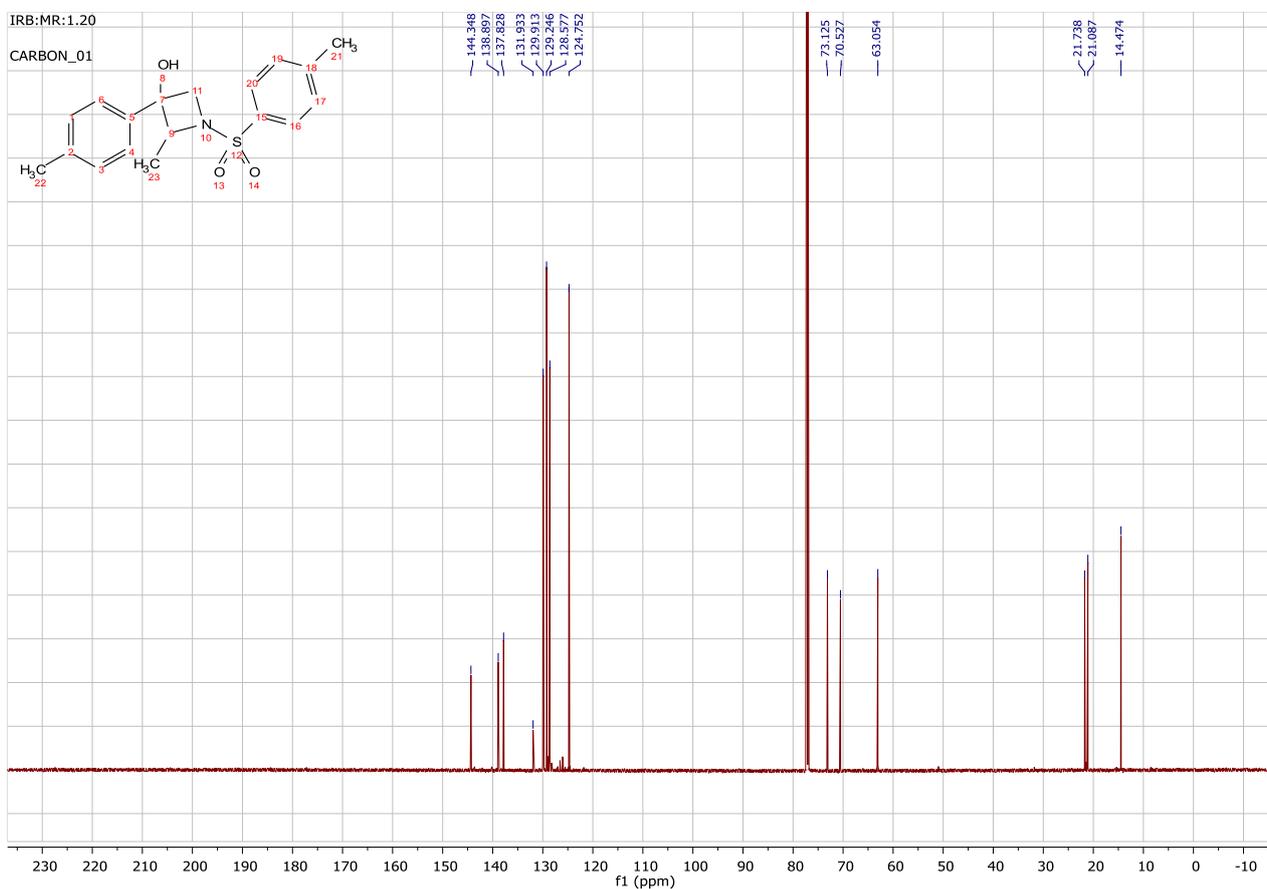
05111902.12.fid  
IRB:MR:MR2.88



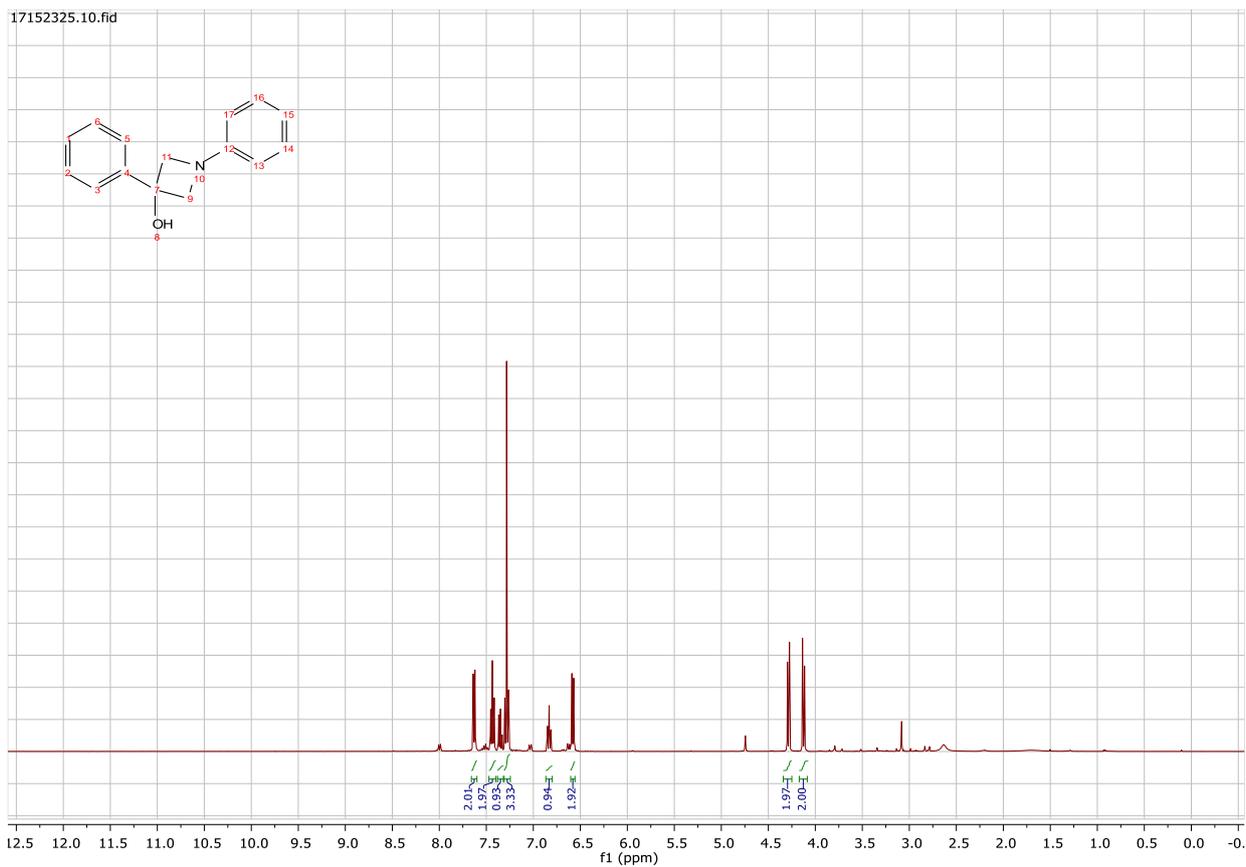
# Compound 1-142 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



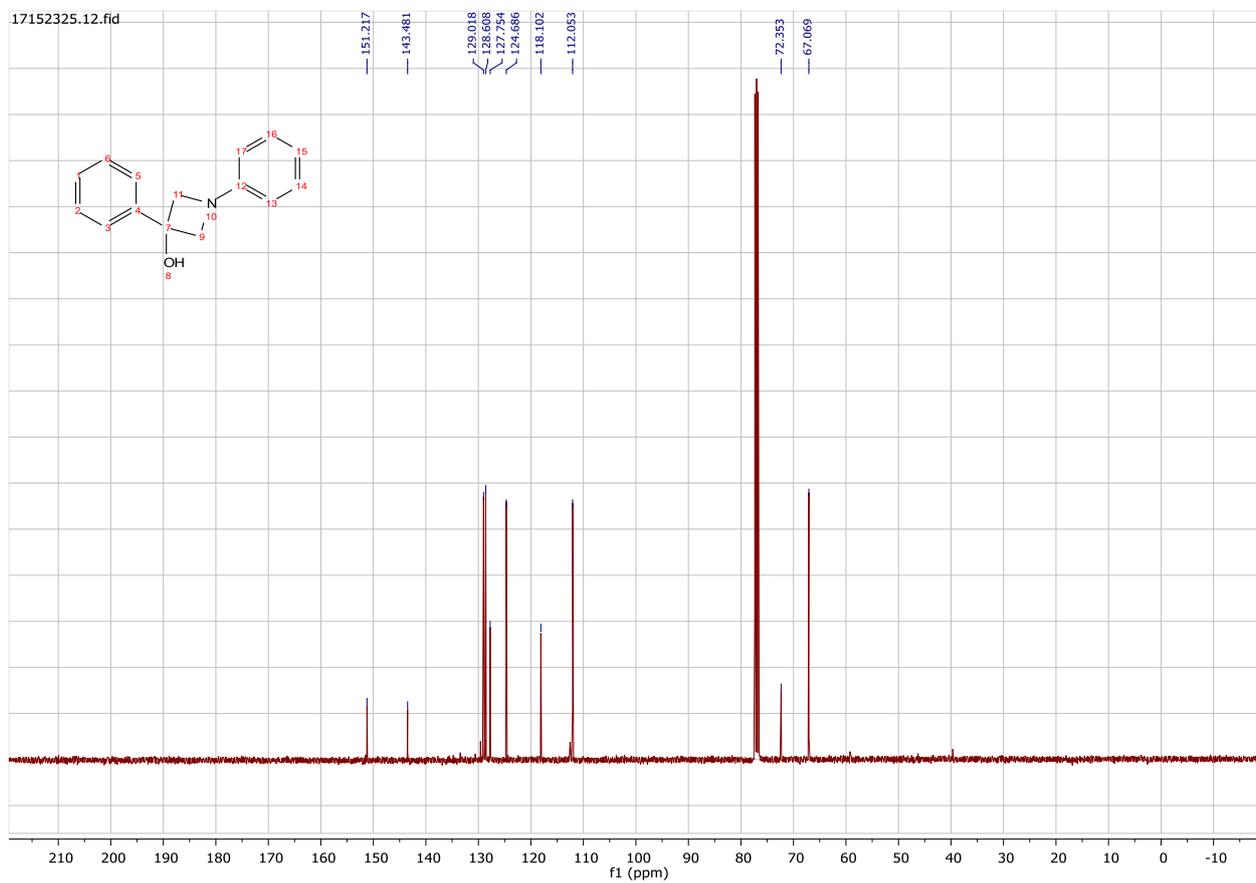
# Compound 1-142 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



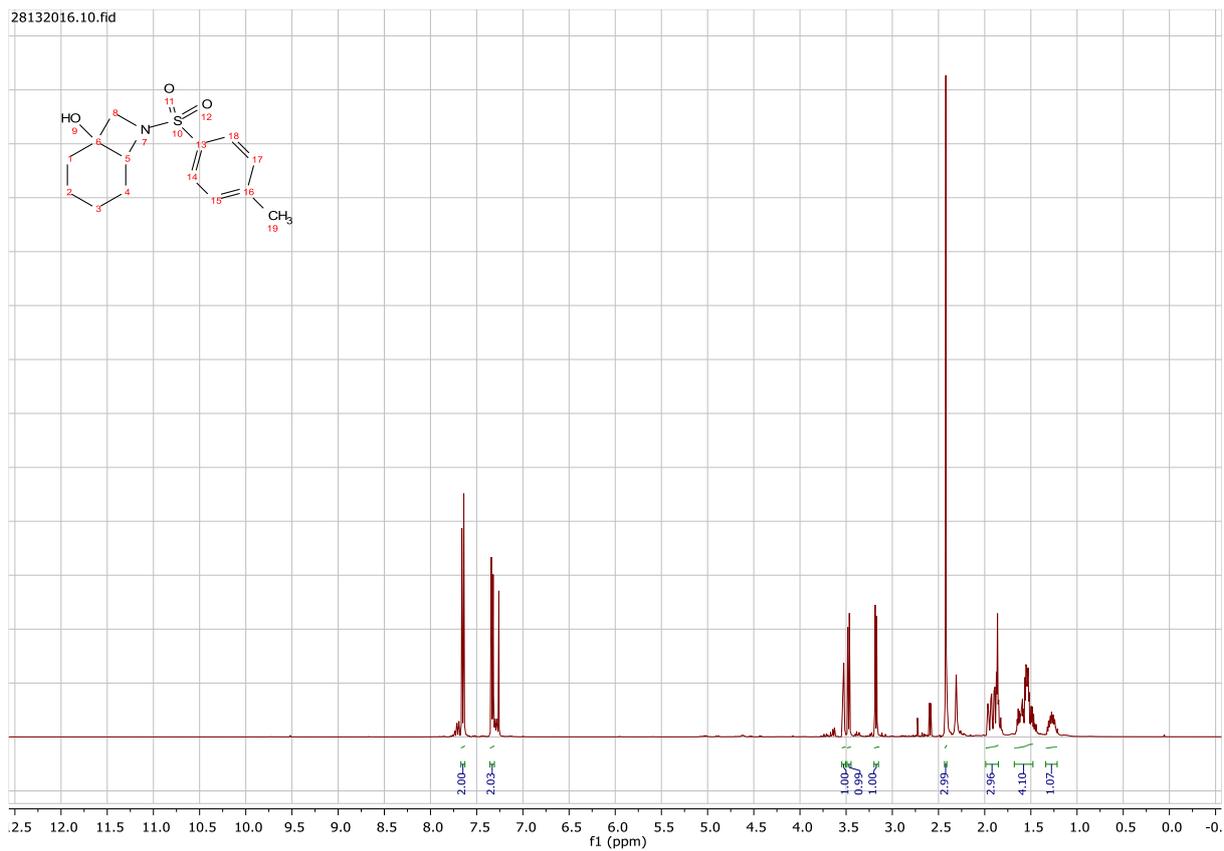
# Compound 1-146 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



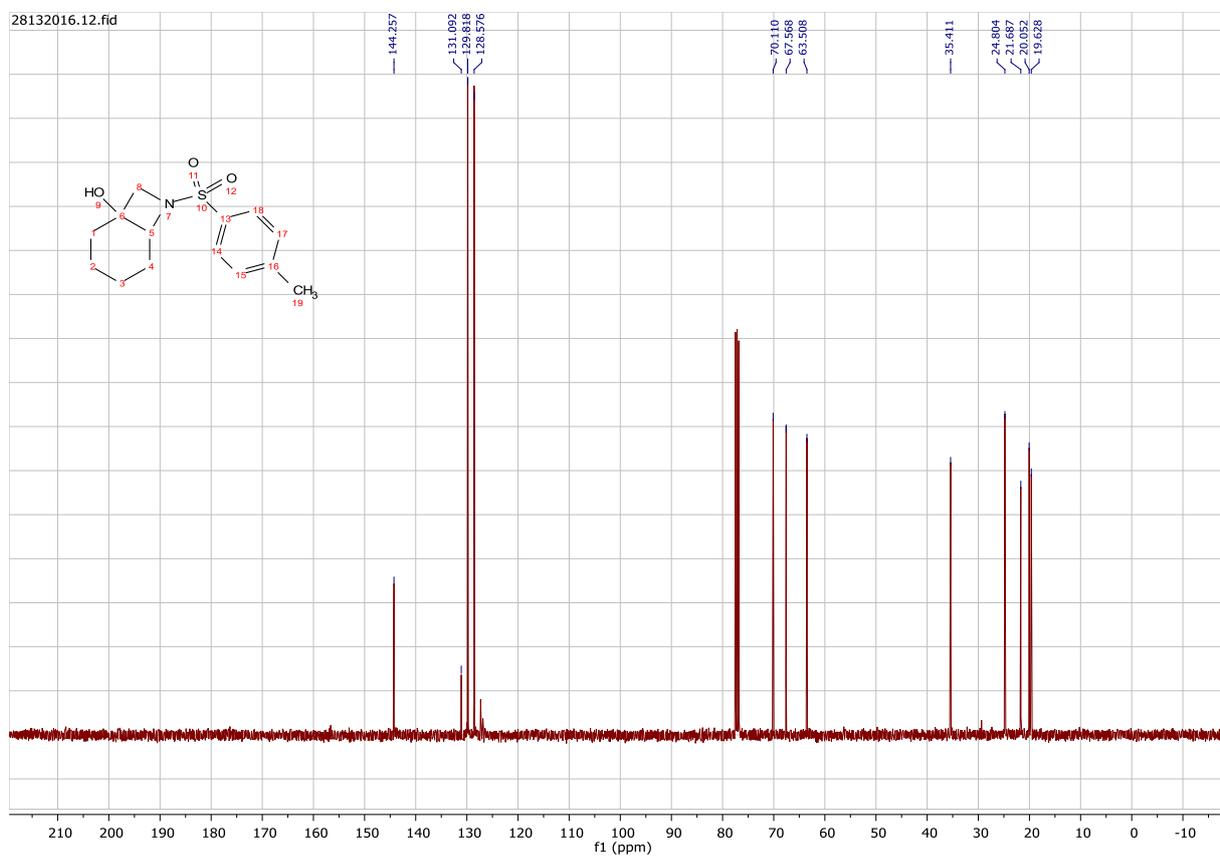
# Compound 1-146 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



# Compound 1-150 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )

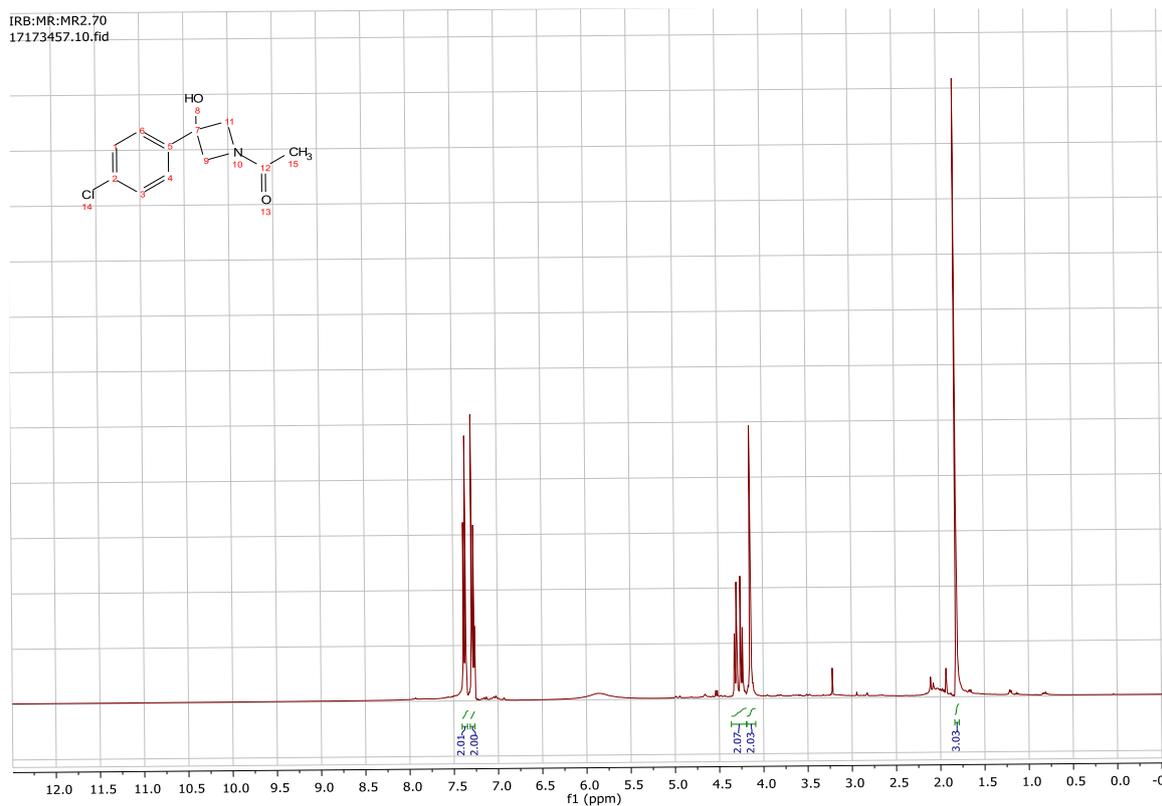


# Compound 1-150 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



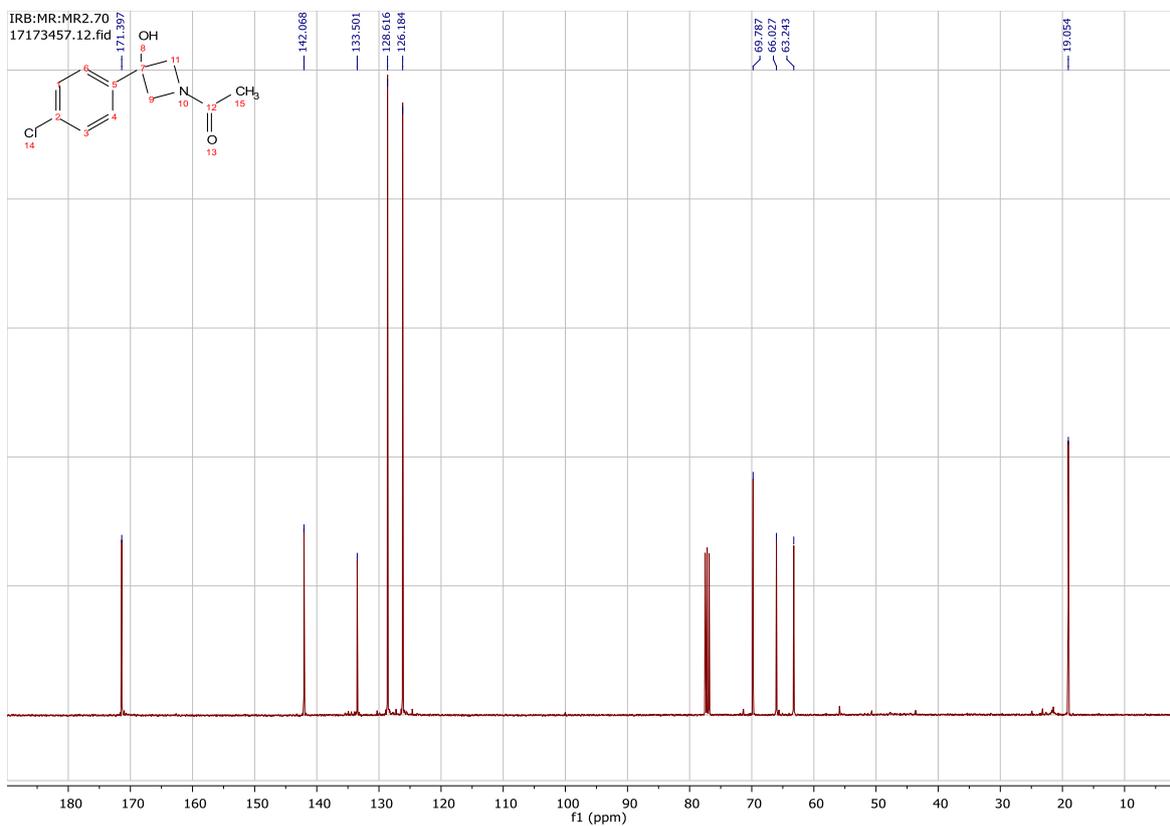
# Compound 1-156 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )

IRB:MR:MR2.70  
17173457.10.fid

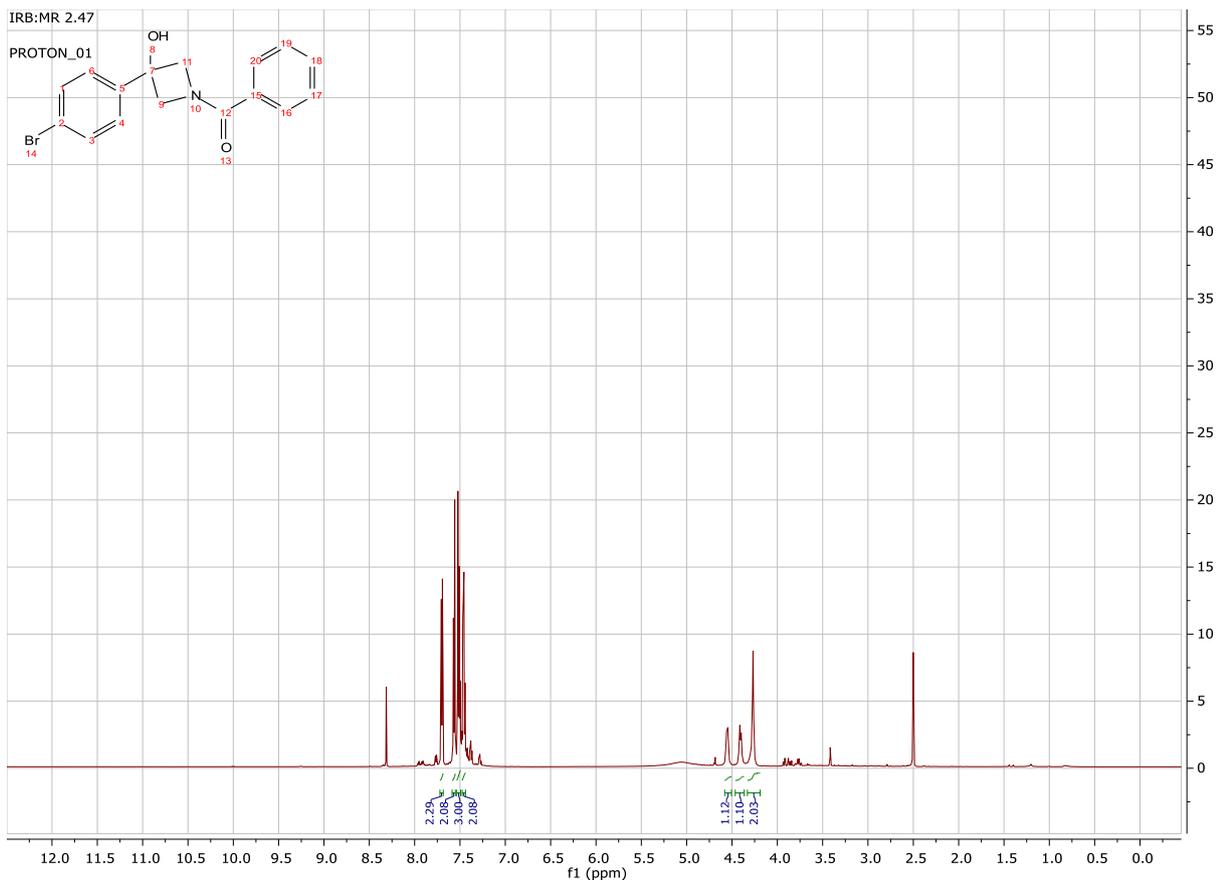


# Compound 1-156 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )

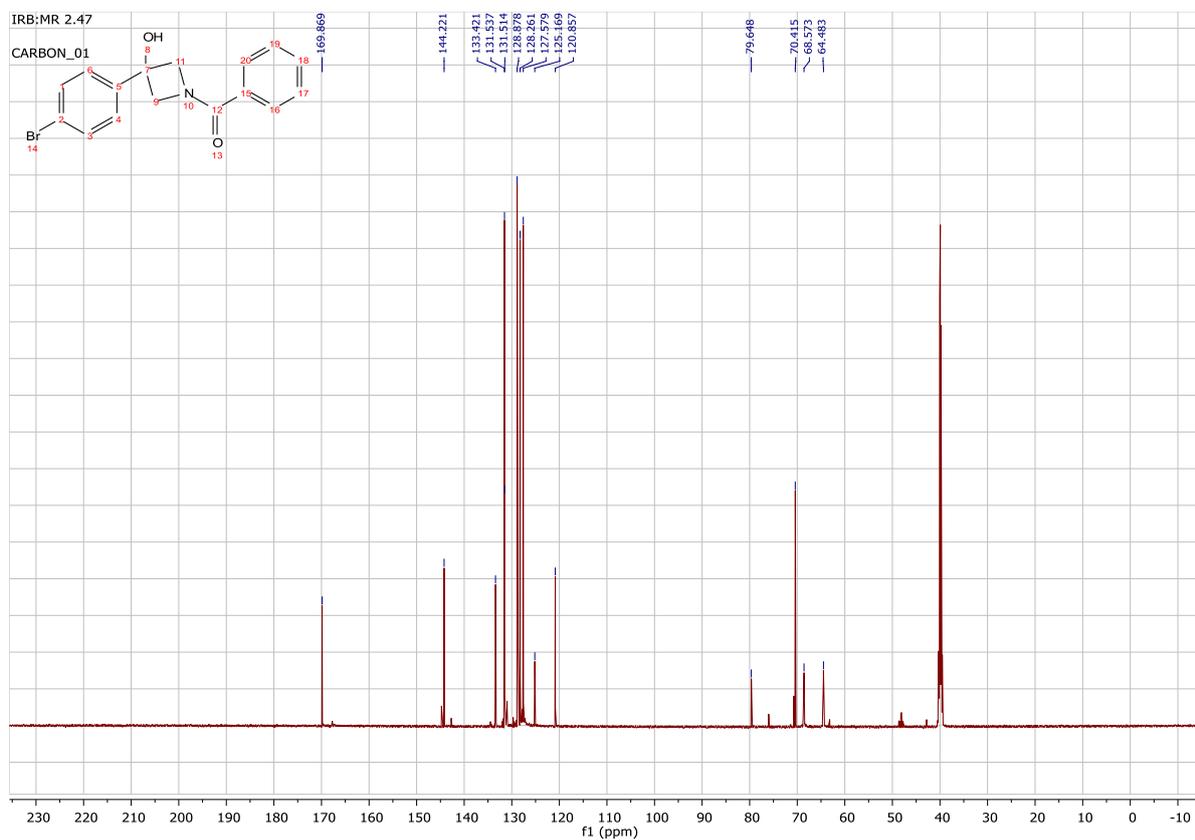
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17173457.12.fid



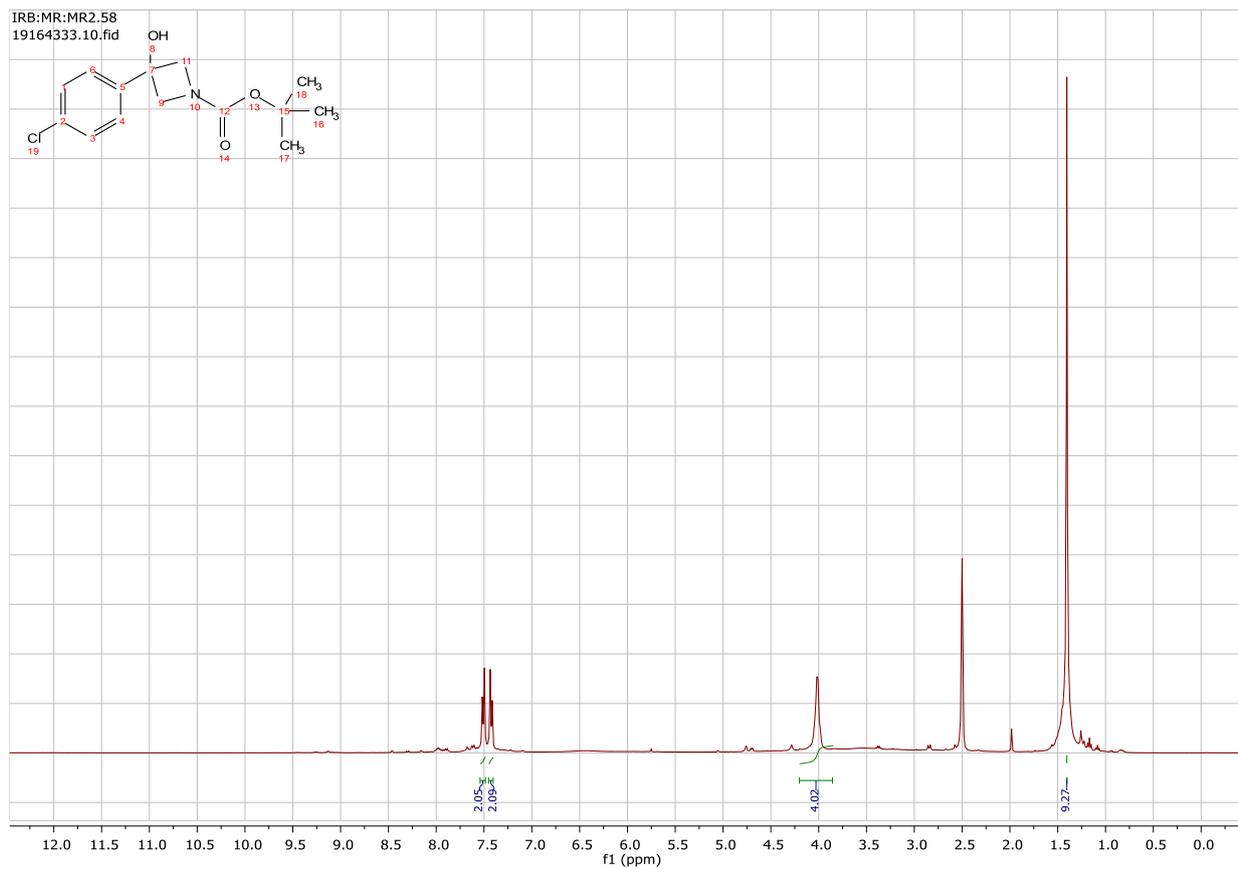
# Compound 1-157 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



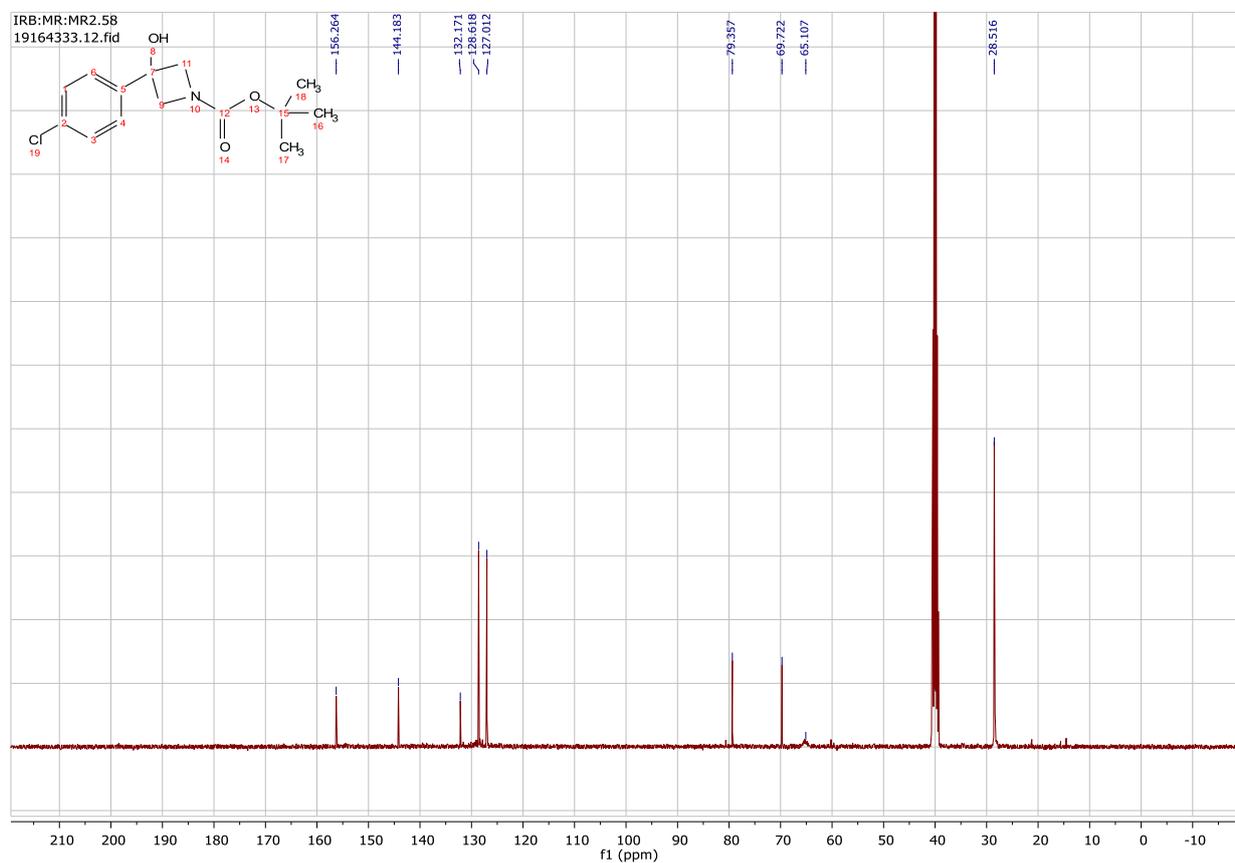
# Compound 1-157 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



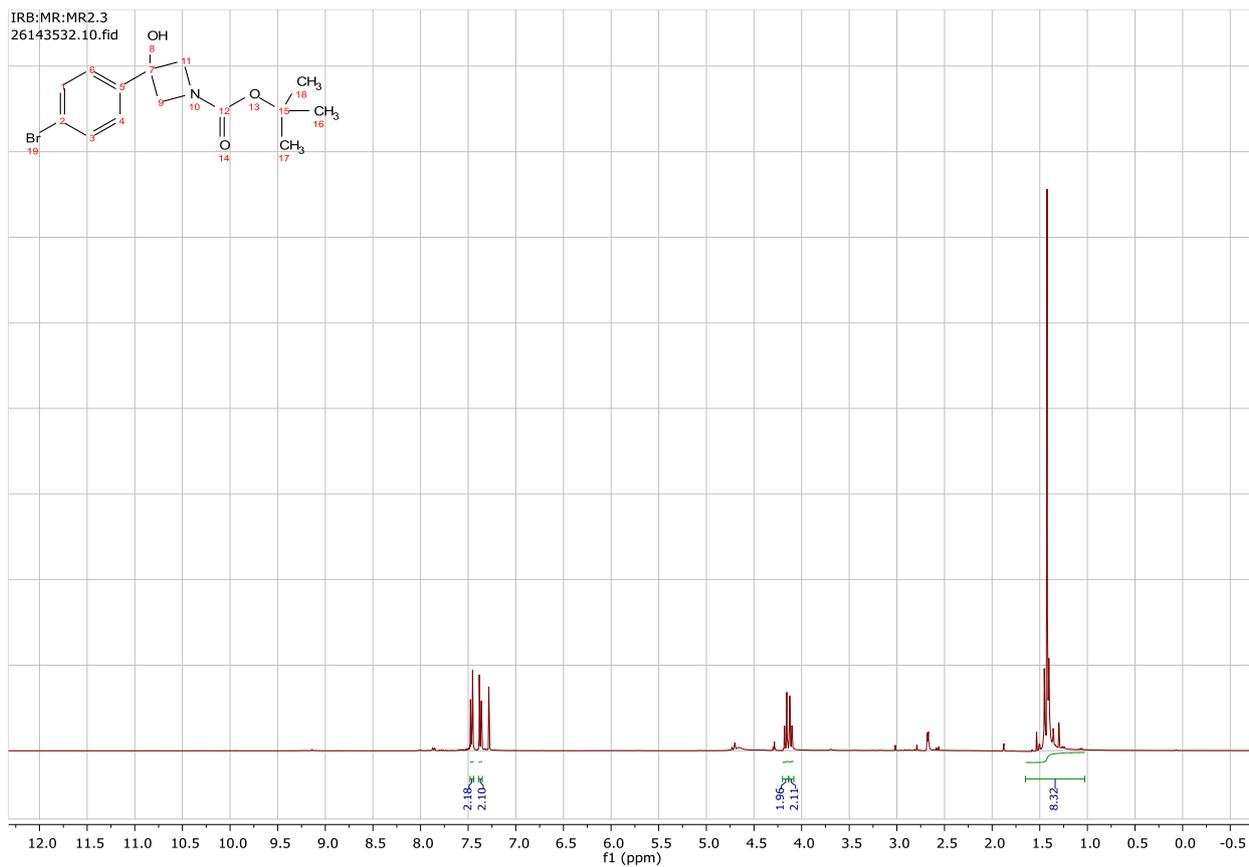
# Compound 1-154 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



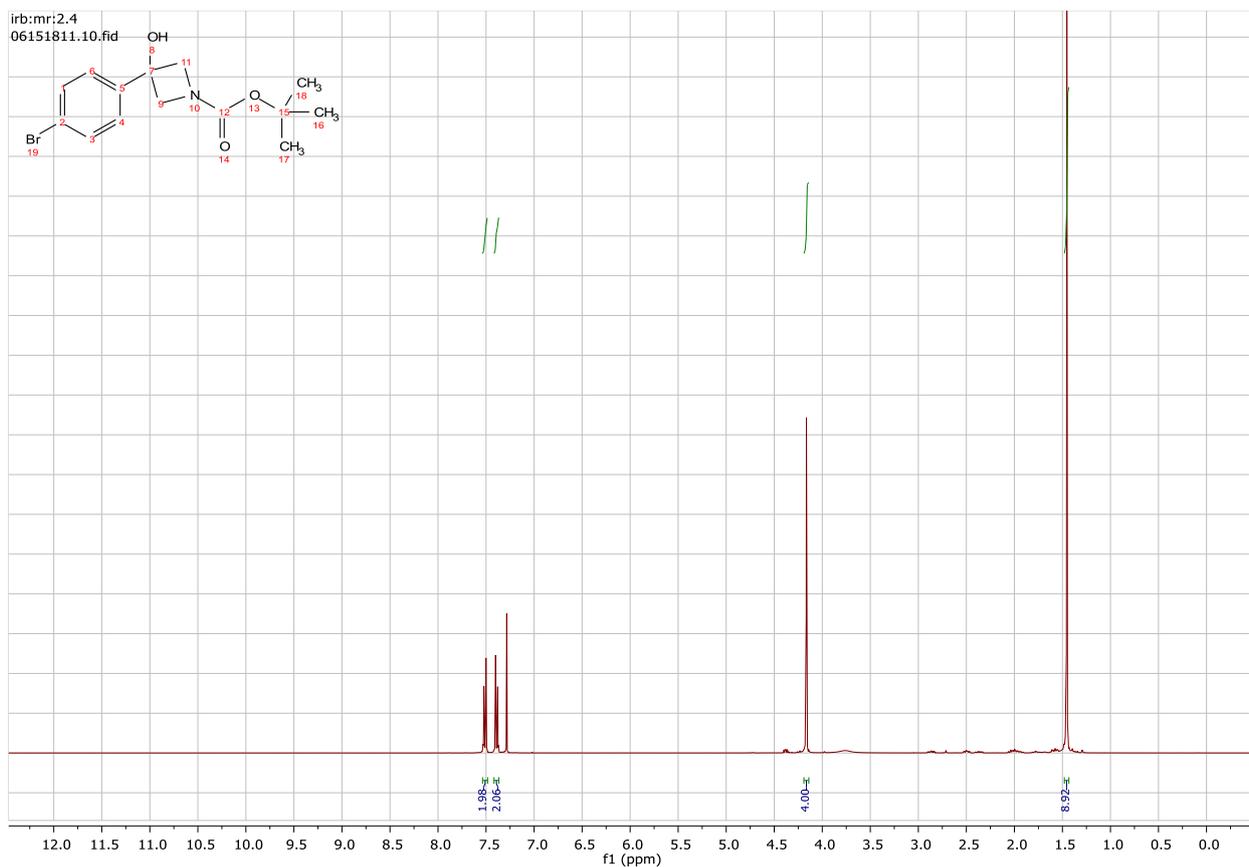
# Compound 1-154 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



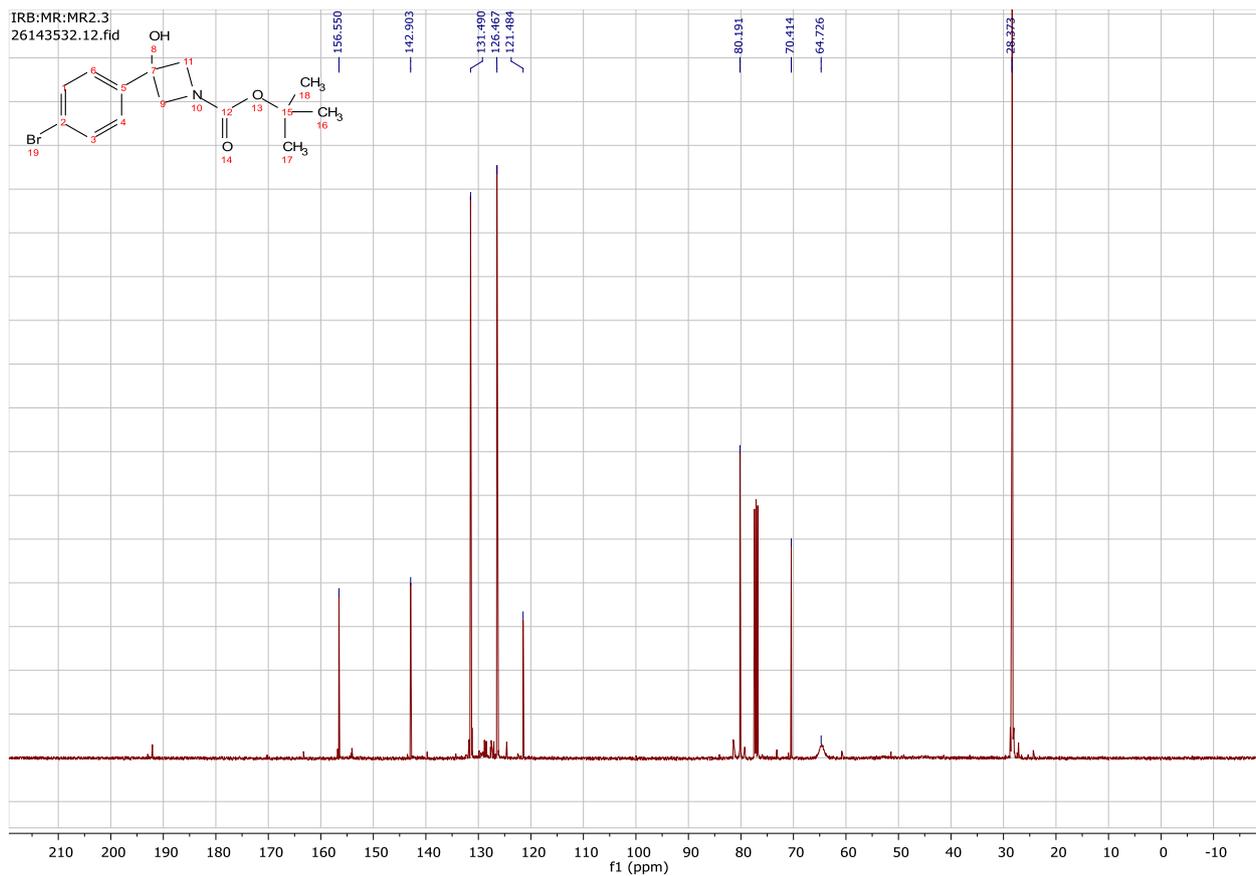
# Compound 1-155 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



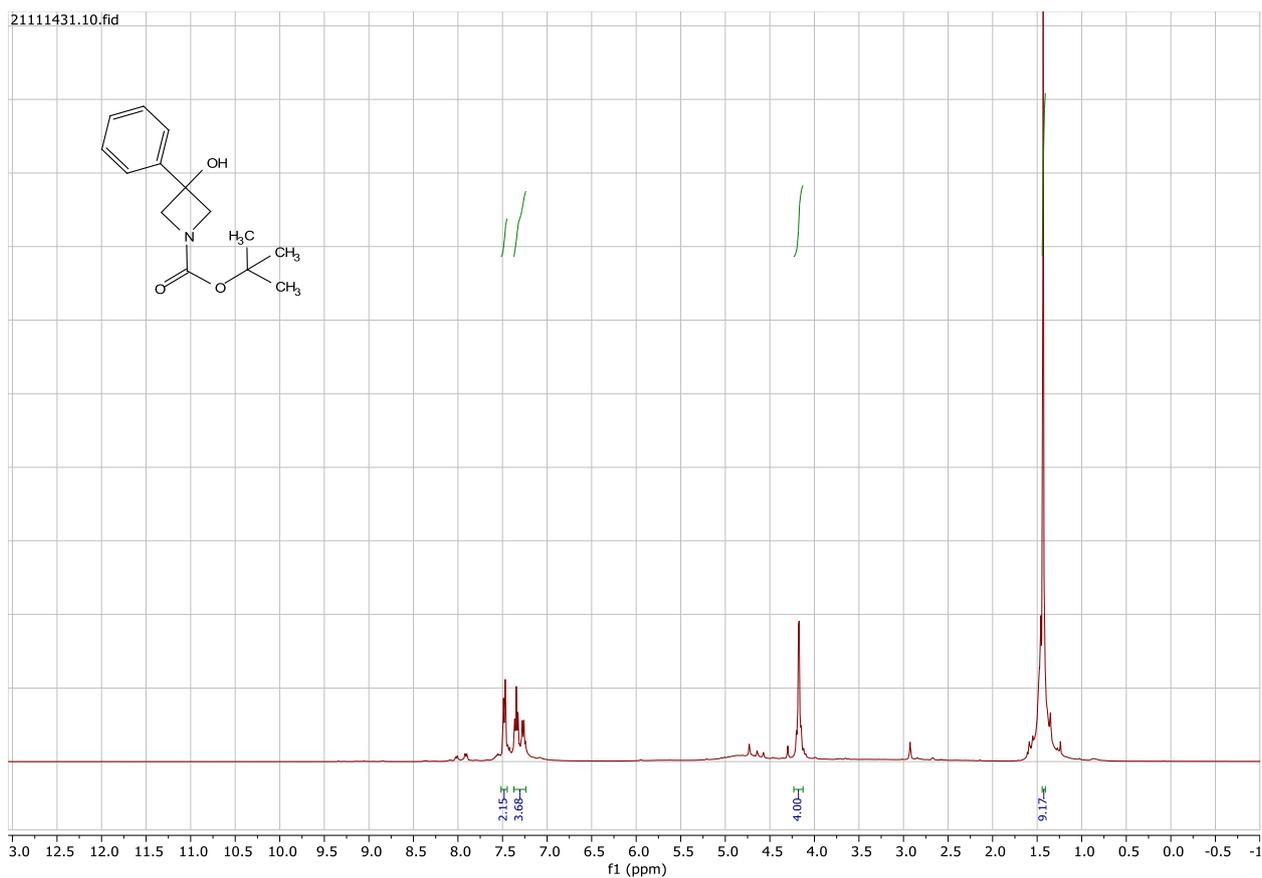
# Compound 1-155 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



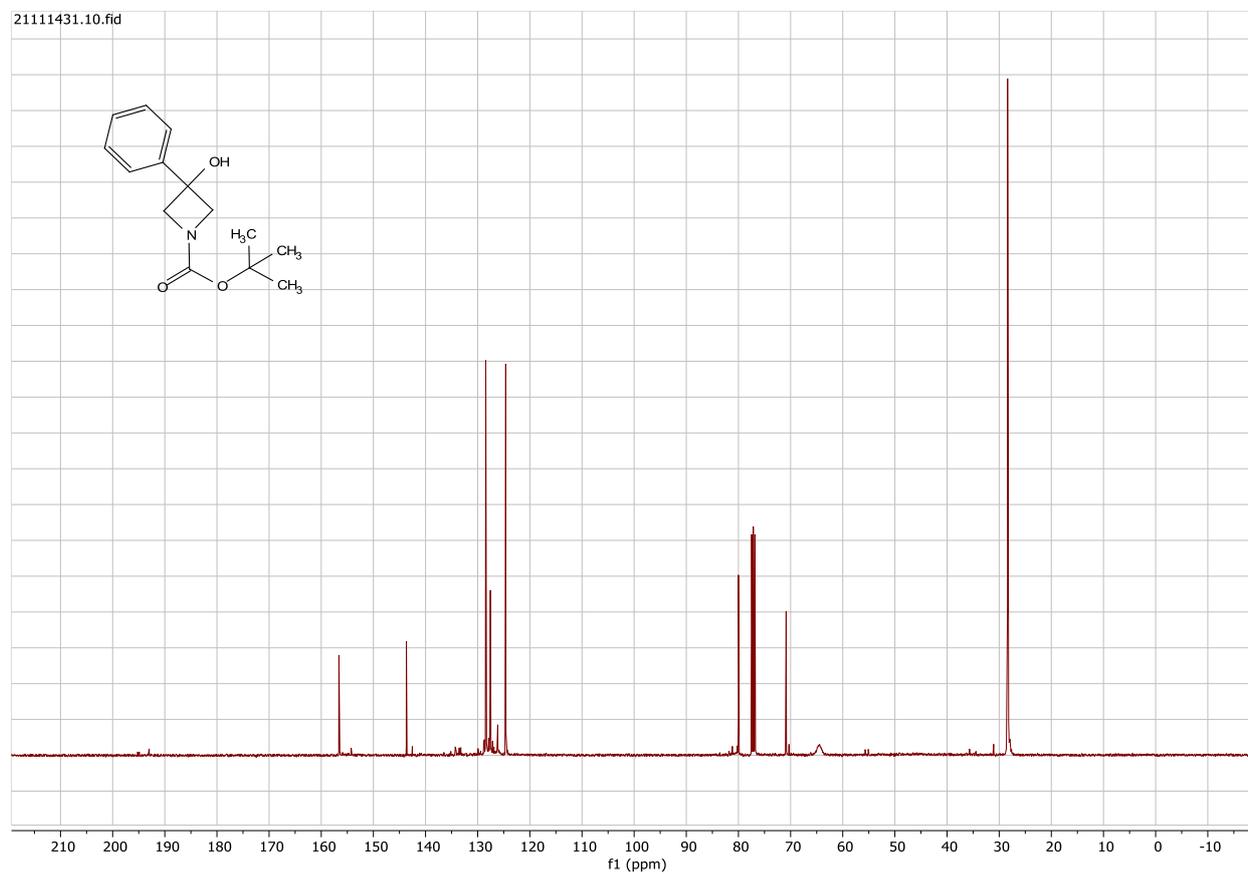
# Compound 1-155 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



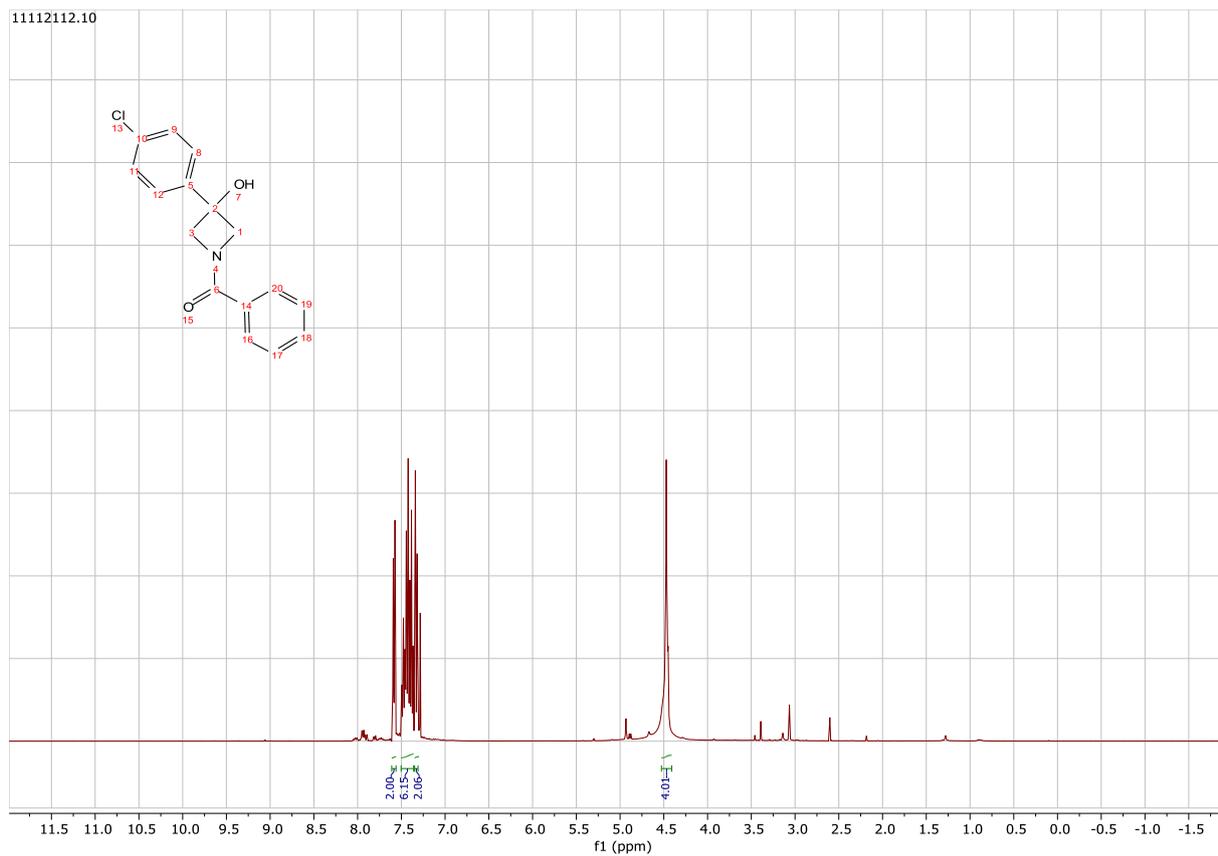
# Compound 1-153 $^1\text{H}$ NMR (101 MHz, $\text{CDCl}_3$ )



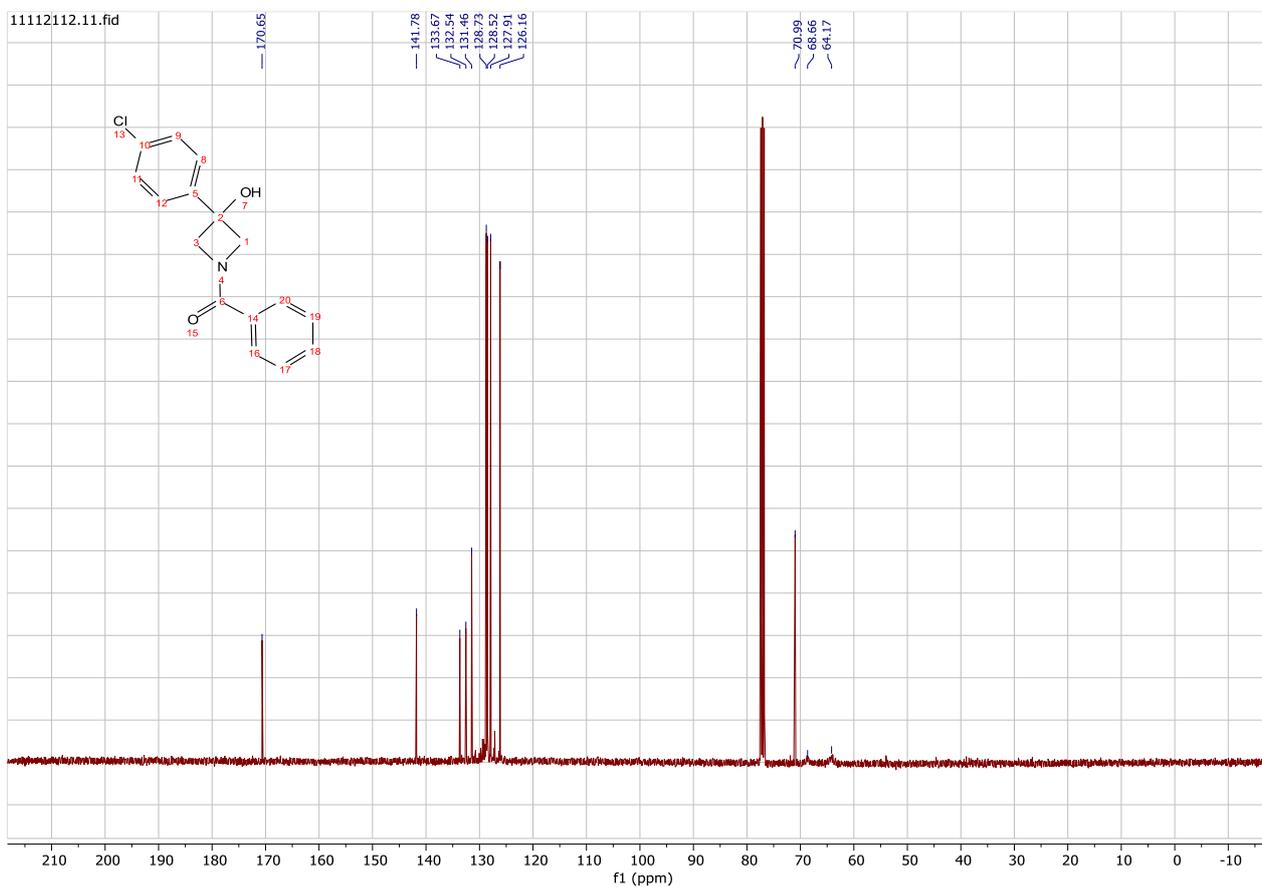
# Compound 1-153 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )



# Compound 1-158 <sup>1</sup>H NMR (101 MHz, CDCl<sub>3</sub>)



# Compound 1-158 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



## 9. References

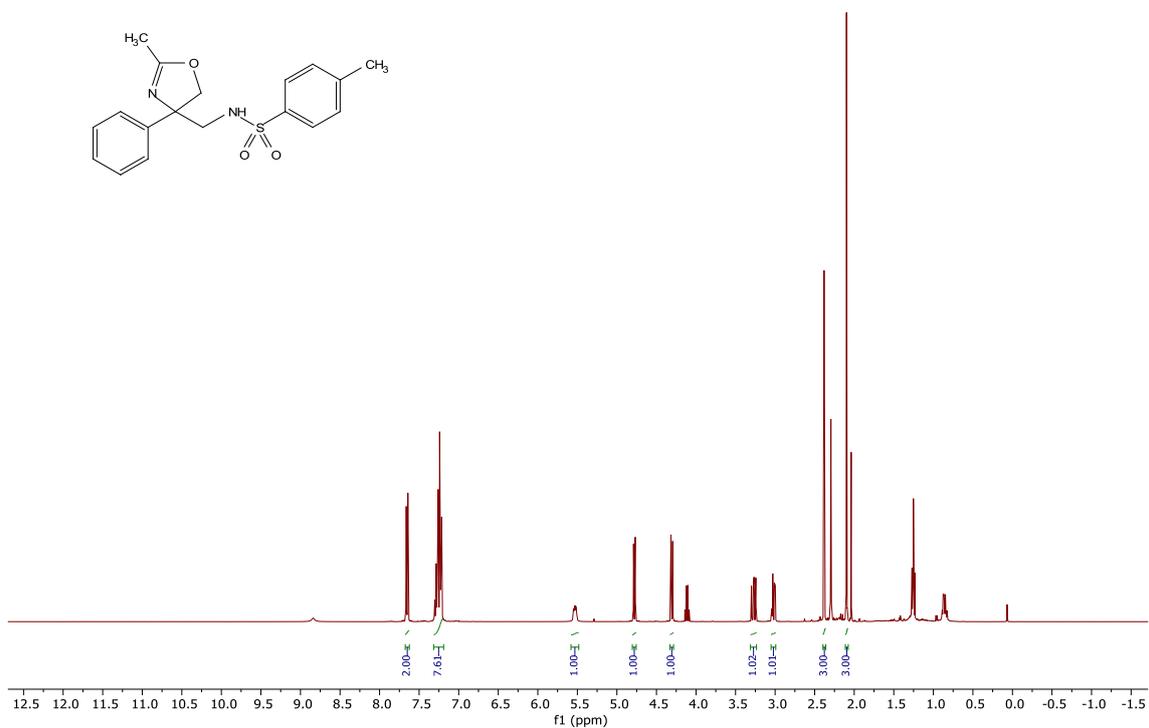
- [1] M. Liu, X. Mao, C. Ye, H. Huang, J. K. Nicholson, J. C. Lindon, *J. Magn. Res.* **1998**, *132*, 125–129.
- [2] R. W. Adams, C. M. Holroyd, J. A. Aguilar, M. Nilsson, G. A. Morris, *Chem. Commun.* **2013**, *49*, 358–360.
- [3] J. A. Aguilar, S. J. Kenwright, *Analyst* **2016**, *141*, 236–242.
- [4] N. Ishida, Y. Shimamoto, M. Murakami, *Angew. Chem.* **2012**, *51*, 11750–1175.
- [5] W. Li, Y. Duan, M. Zhang, J. Cheng, C. Zhu, *Chem. Comm.* **2016**, *48*, 7596–7599.
- [6] S. Miyata T. Kumamoto T. Ishikawa, *Helvetica Chim*

## Chapter 2

**A rearrangement of 3-hydroxyazetidines into 2-oxazolines.**

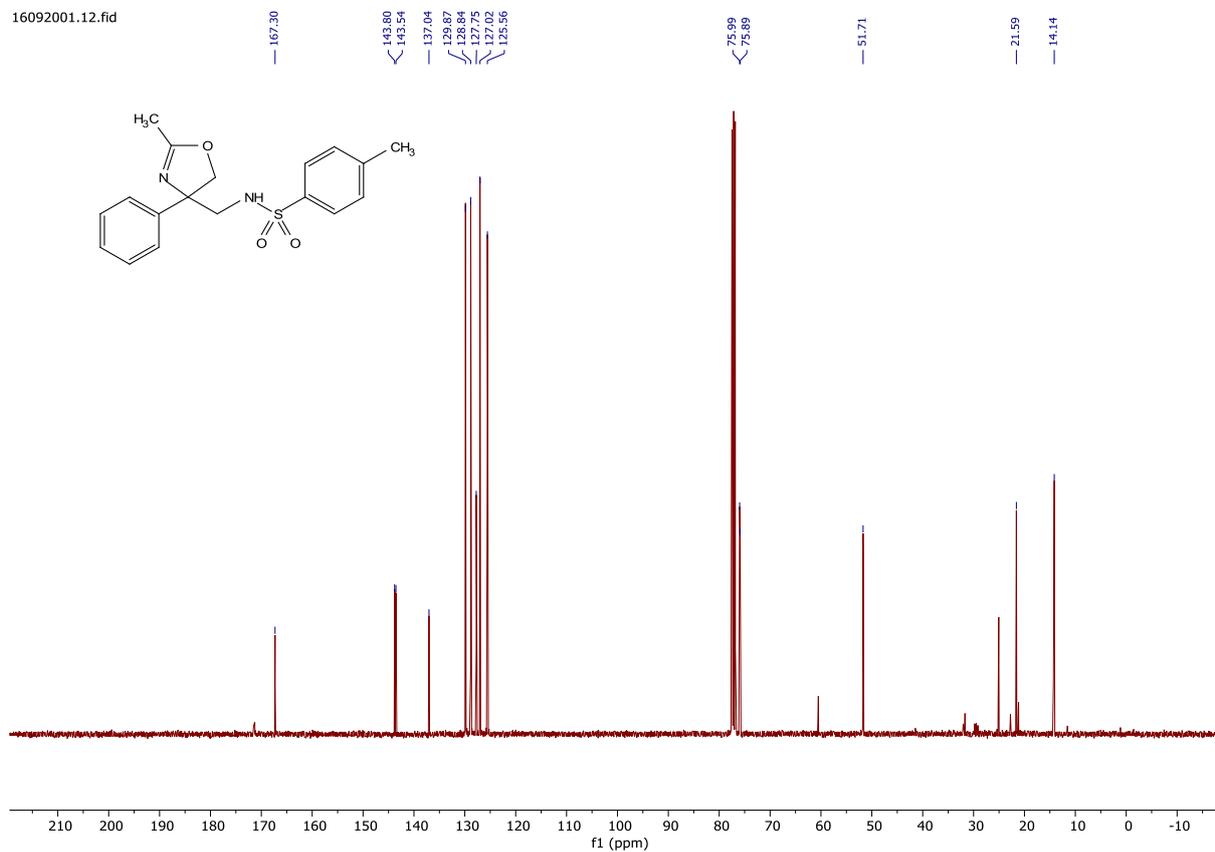
# Compound 2-164 $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )

16092001.10.fid



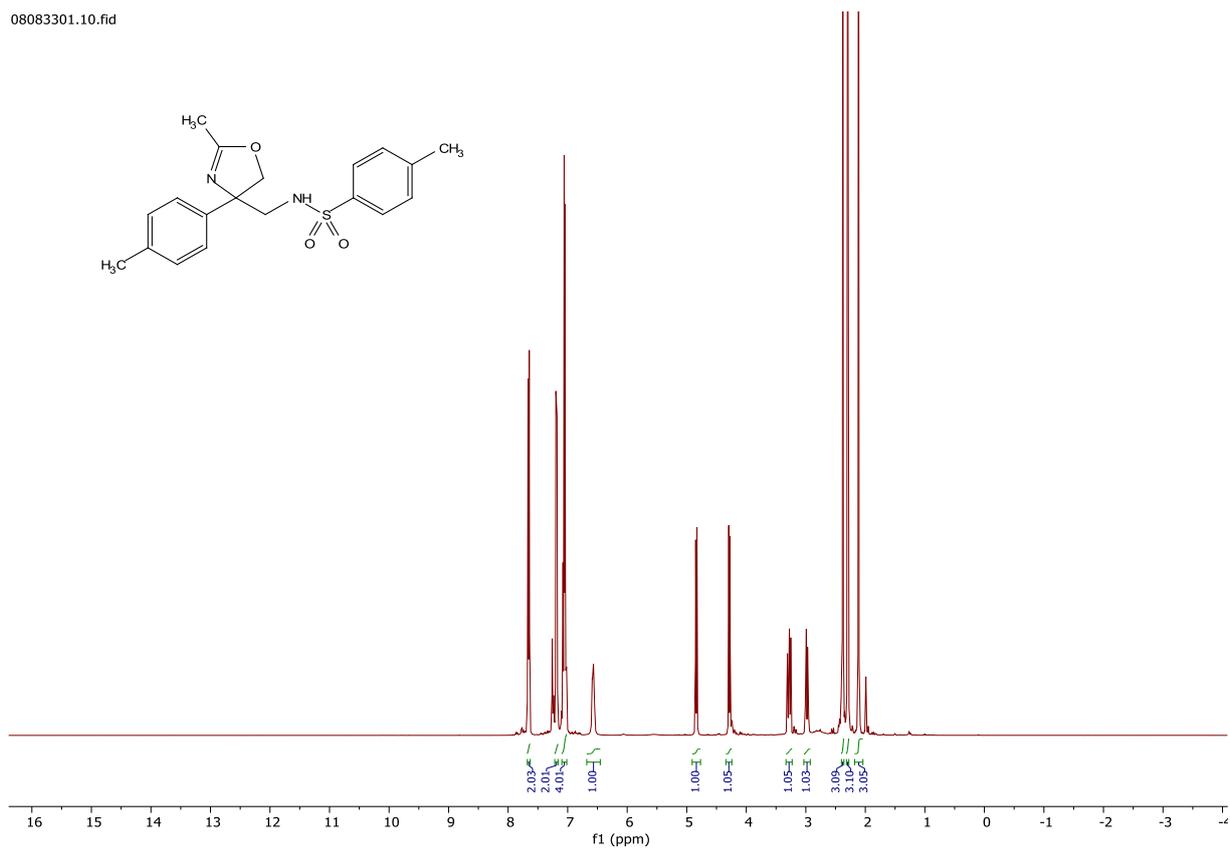
# Compound 2-164 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )

16092001.12.fid



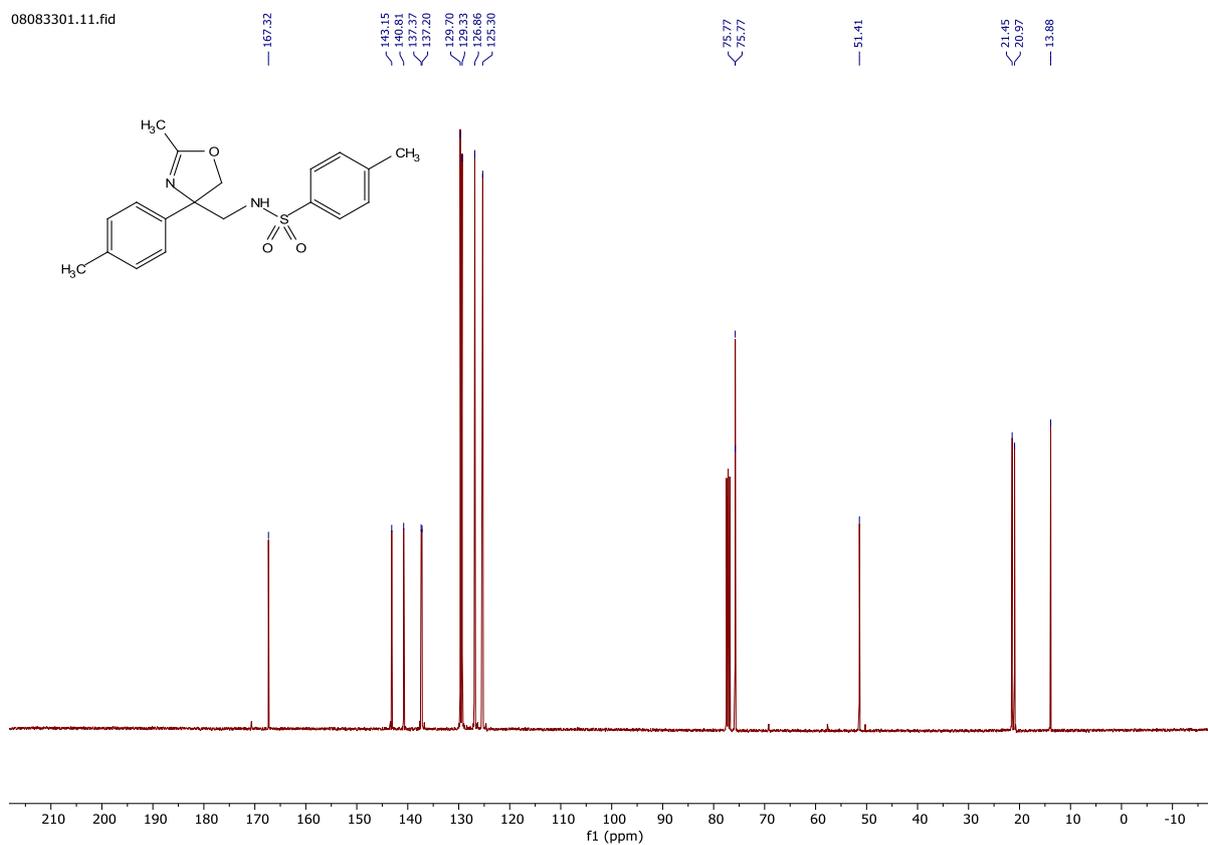
# Compound 2-165 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

08083301.10.fid

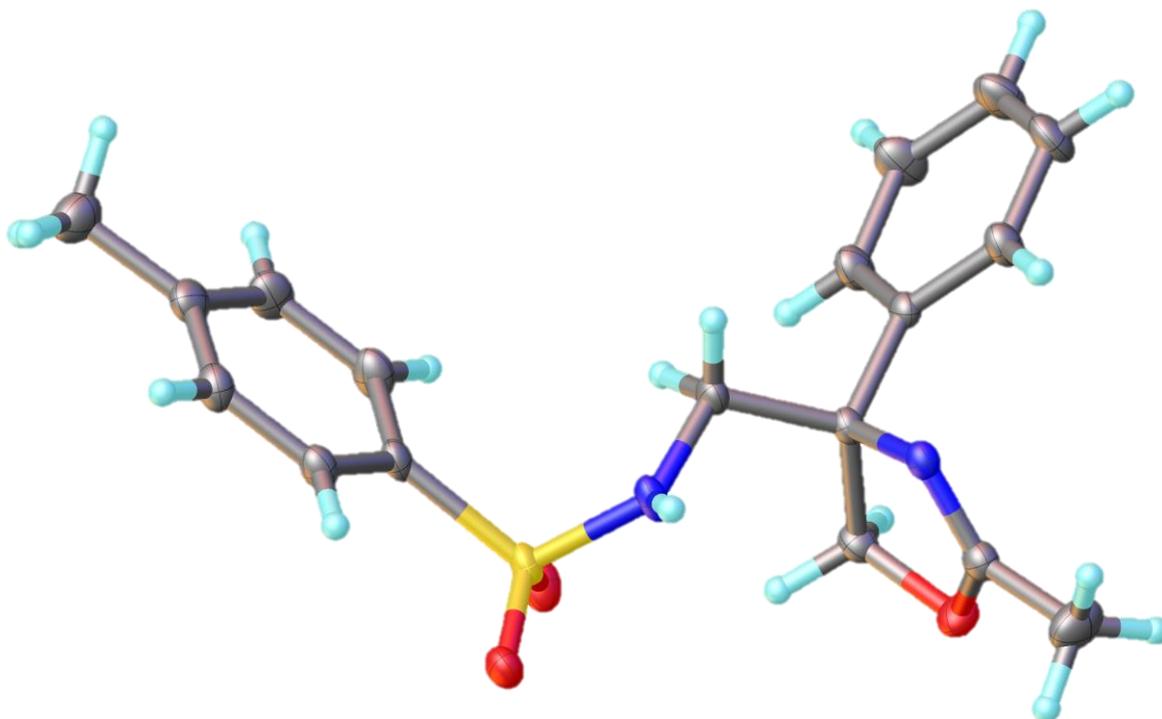


# Compound 2-165 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

08083301.11.fid



## Compound 2-164 X-ray structure



*Atomic displacement ellipsoids are drawn at the 50% probability level.*

Compound 4-2 was crystallised by solvent evaporation using a mixture Hexane: EtOAc

### Experimental

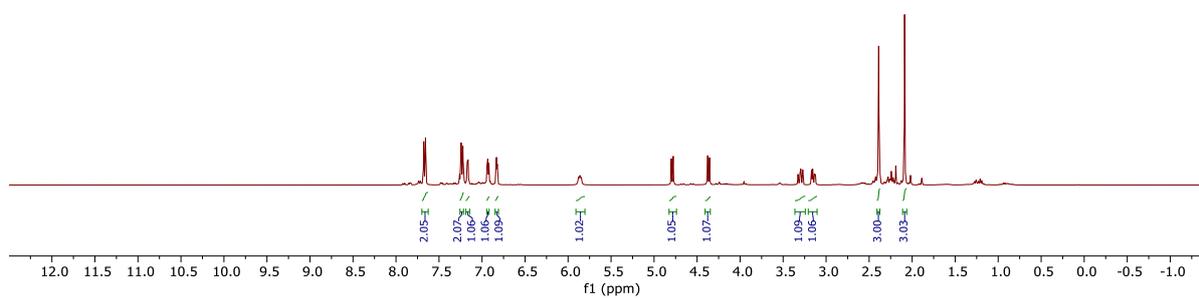
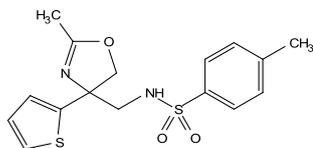
Single crystals of  $C_{25}H_{22}BrClN_2O_4S$  were A suitable crystal was selected on a D8V\_Mo diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 1) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 2) Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
- 3) Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

**Crystal Data** for  $C_{25}H_{22}BrClN_2O_4S$  ( $M = 561.86$  g/mol): triclinic, space group P-1 (no. 2),  $a = 8.9040(5)$  Å,  $b = 11.4226(7)$  Å,  $c = 11.9517(7)$  Å,  $\alpha = 81.001(2)^\circ$ ,  $\beta = 89.408(2)^\circ$ ,  $\gamma = 77.106(2)^\circ$ ,  $V = 1169.95(12)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 120$  K,  $\mu(\text{MoK}\alpha) = 1.997$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.595$  g/cm<sup>3</sup>, 26308 reflections measured ( $4.648^\circ \leq 2\theta \leq 60.274^\circ$ ), 6888 unique ( $R_{\text{int}} = 0.0395$ ,  $R_{\text{sigma}} = 0.0415$ ) which were used in all calculations. The final  $R_1$  was 0.0374 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1019 (all data).

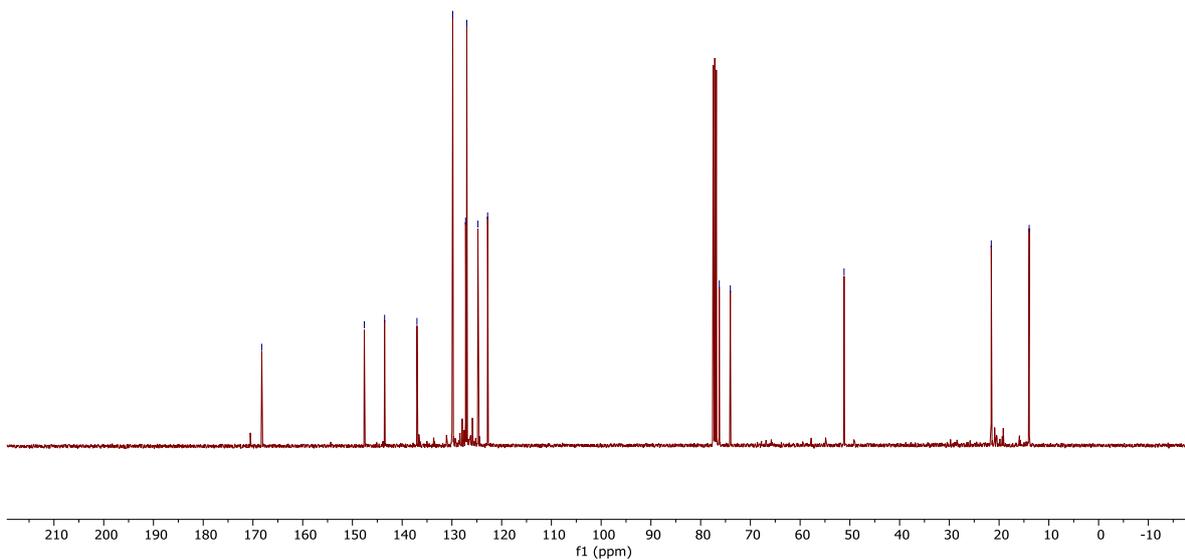
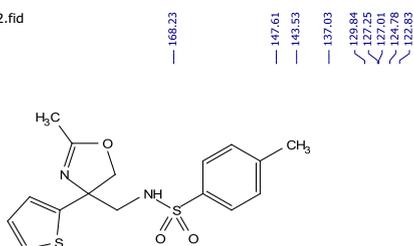
# Compound 2-166 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

24160644.10.fid



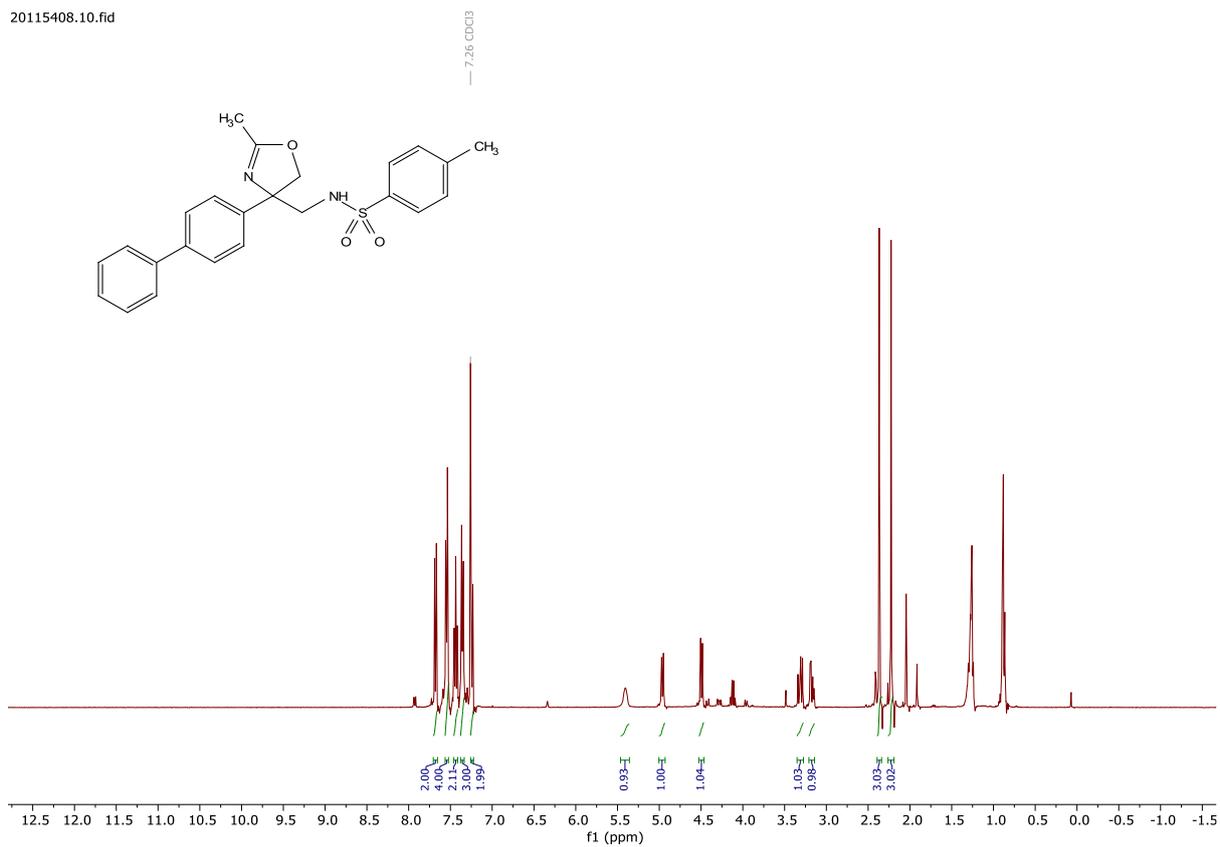
# Compound 2-166 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

24160644.12.fid



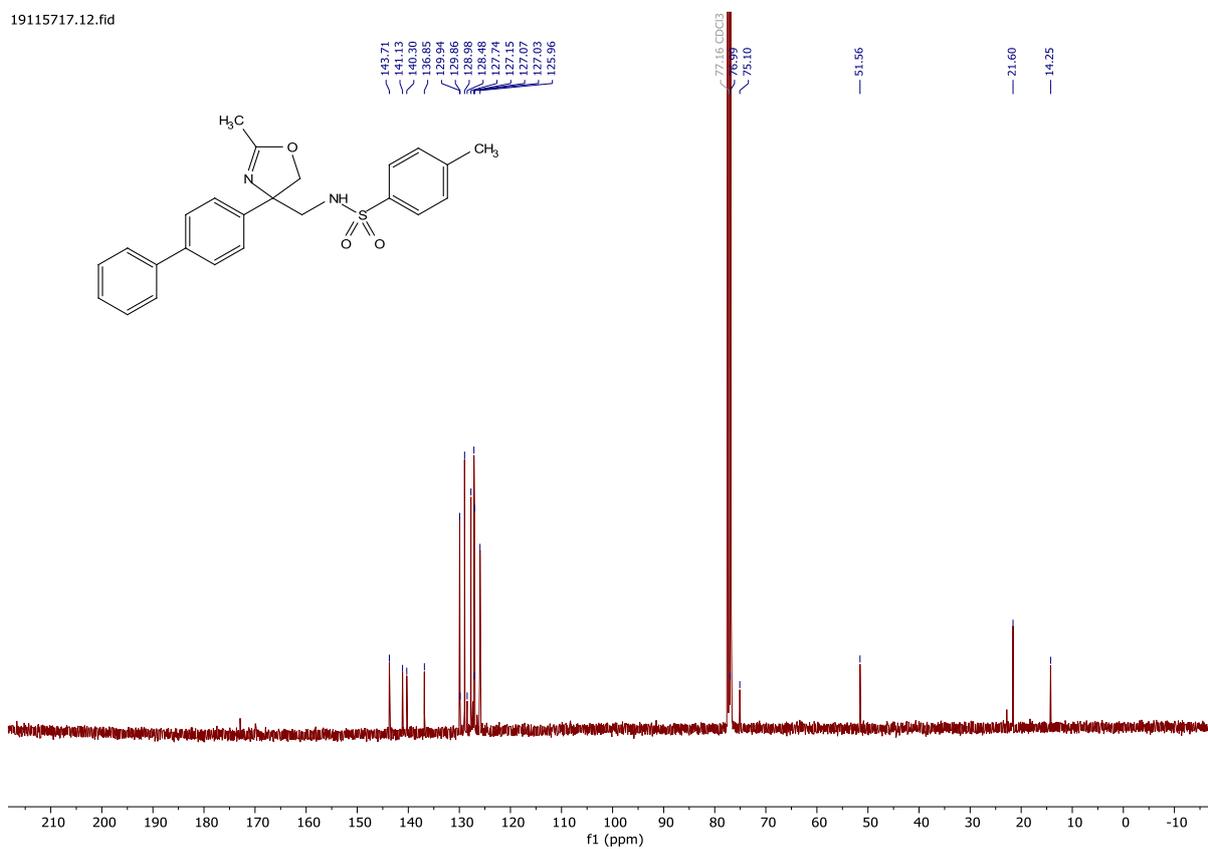
# Compound 2-167 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

20115408.10.fid



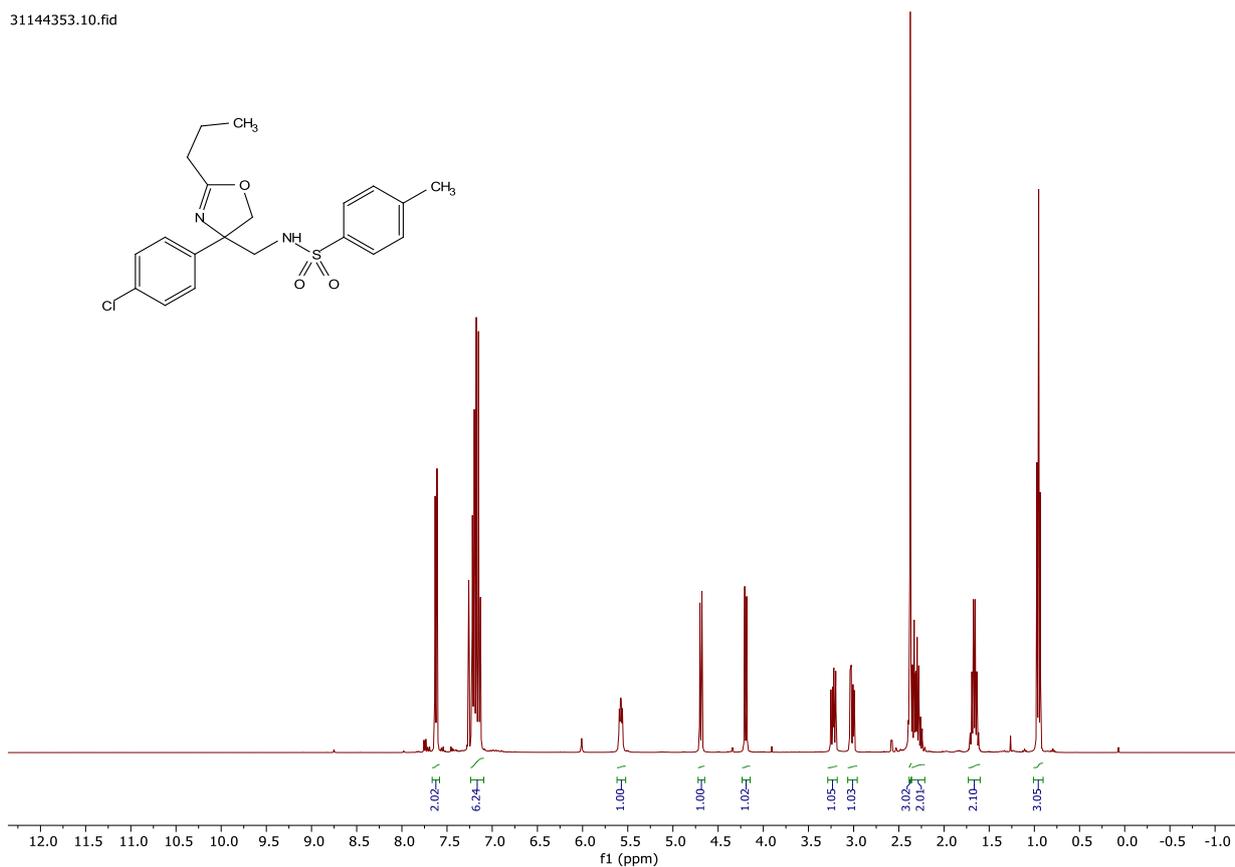
# Compound 2-167 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

19115717.12.fid



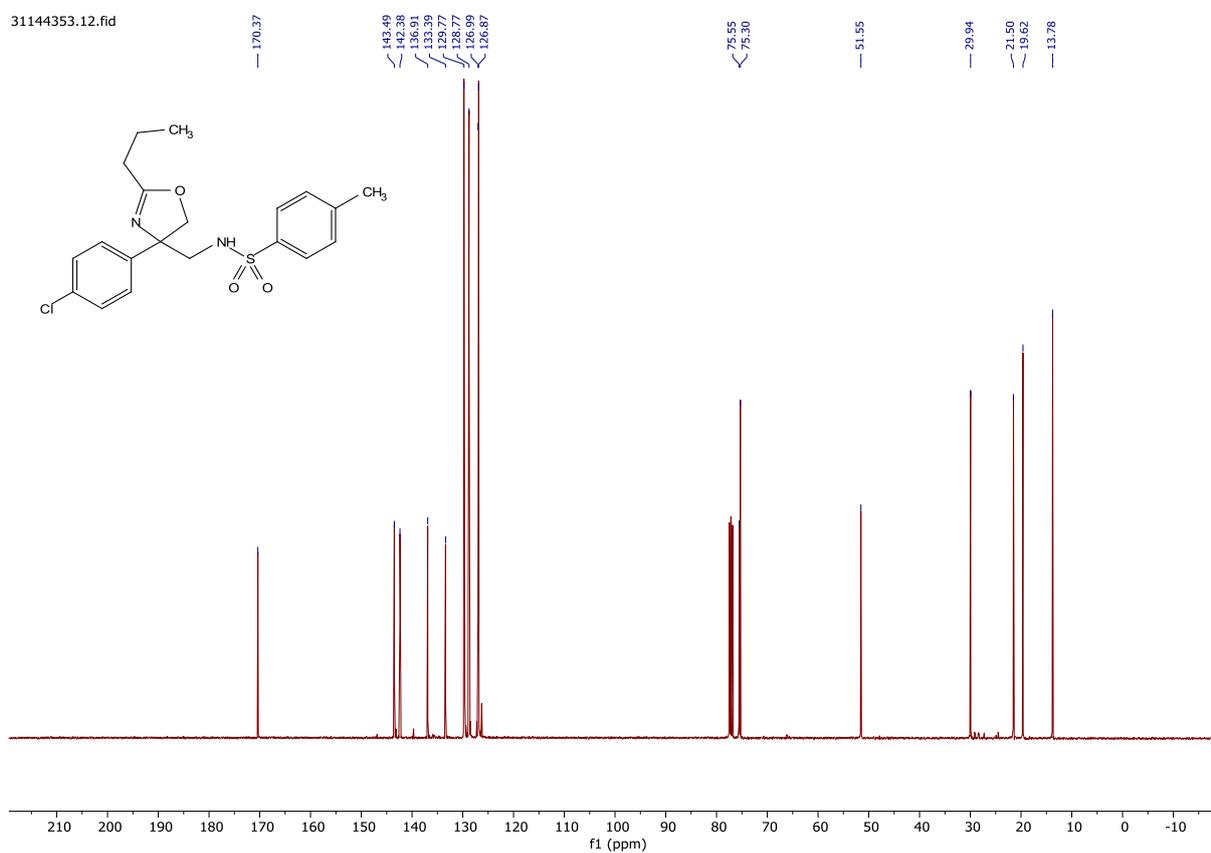
# Compound 2-168 $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )

31144353.10.fid



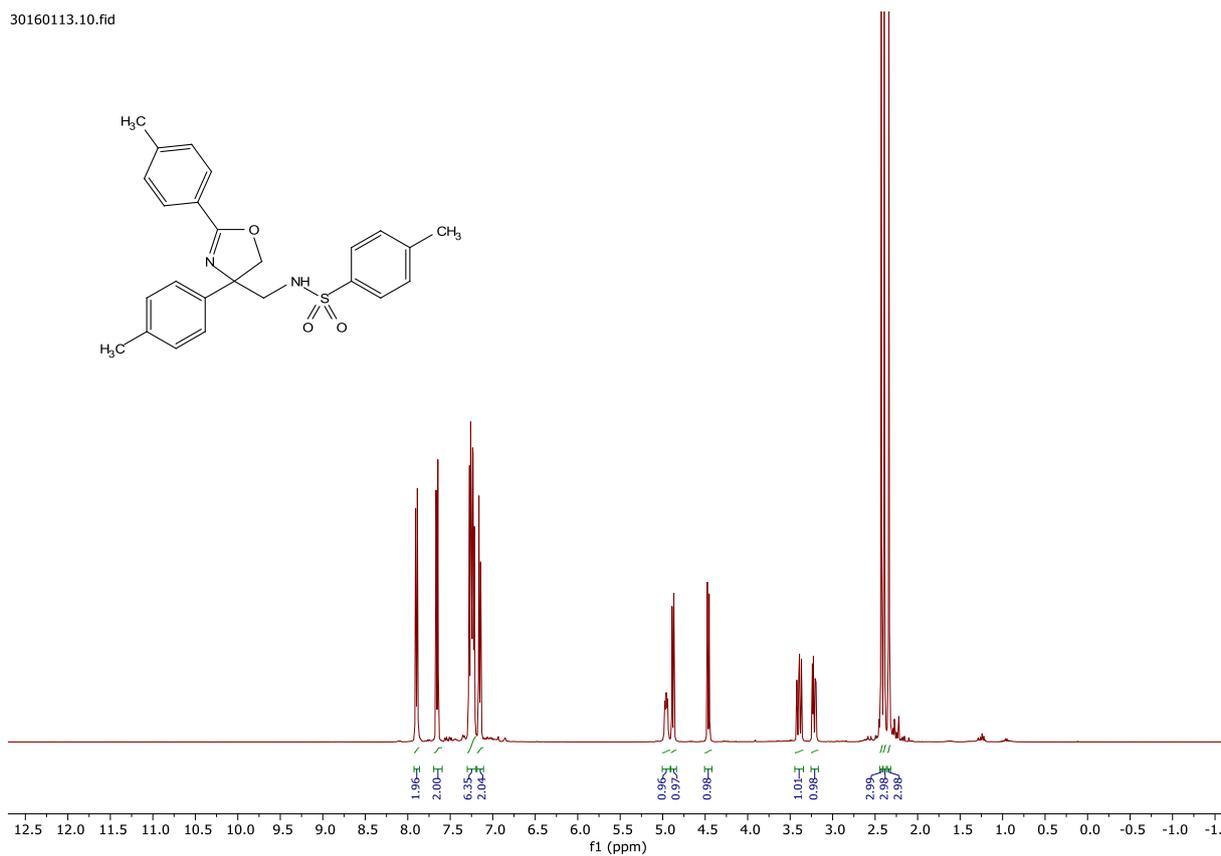
# Compound 2-168 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )

31144353.12.fid



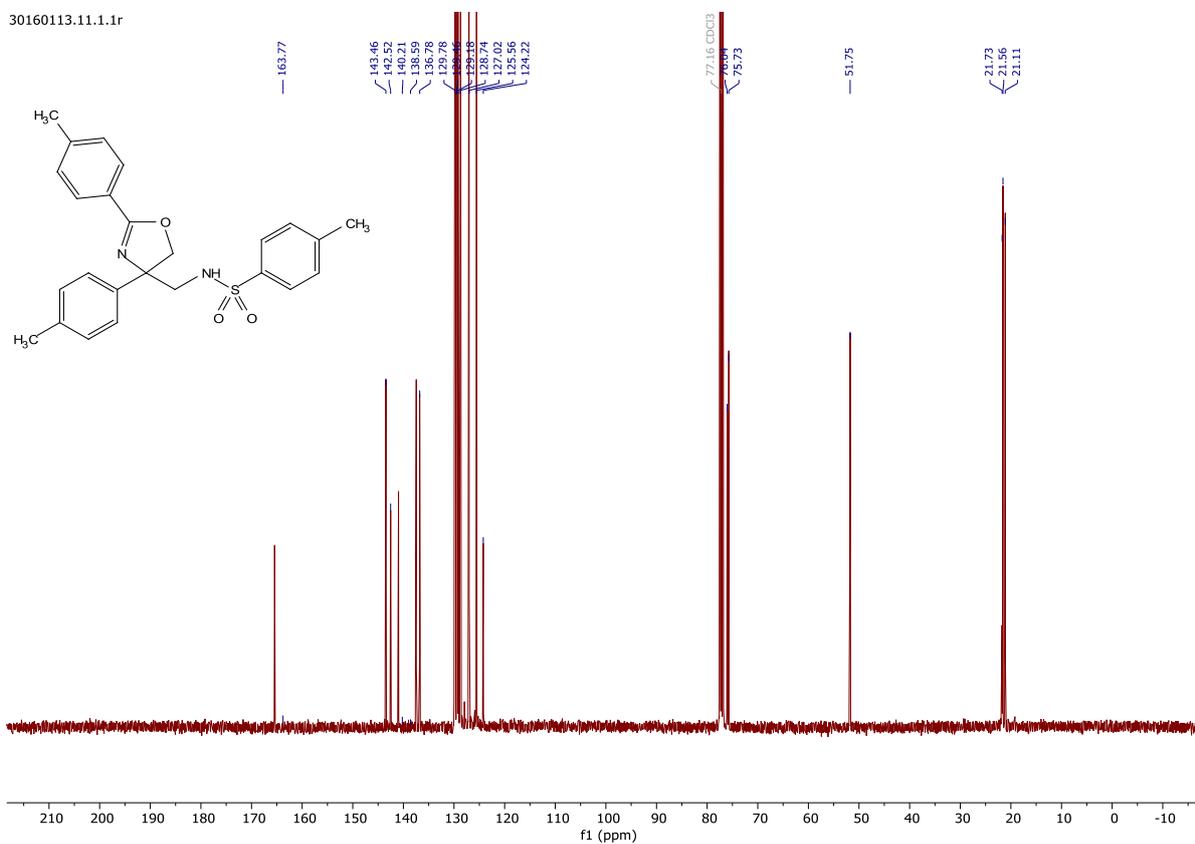
# Compound 2-169 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

30160113.10.fid



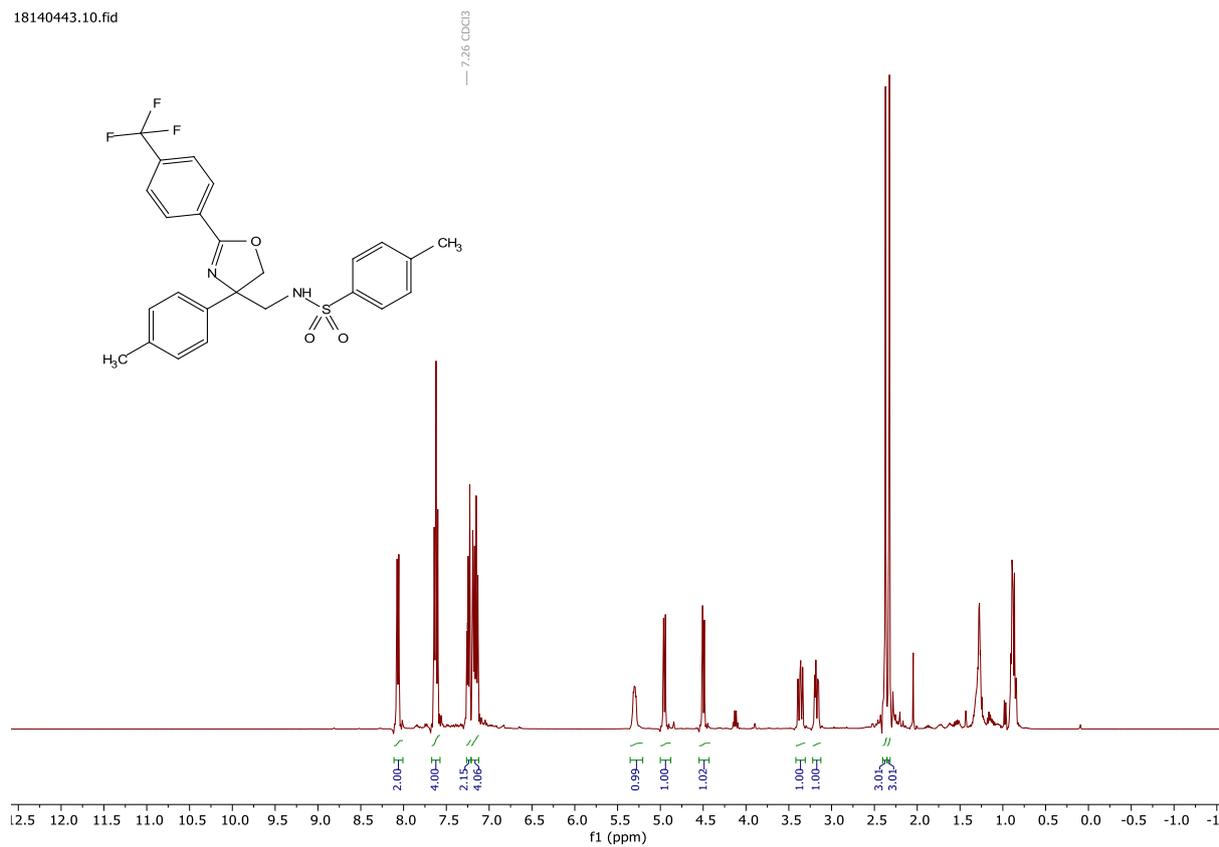
# Compound 2-169 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

30160113.11.1.1r



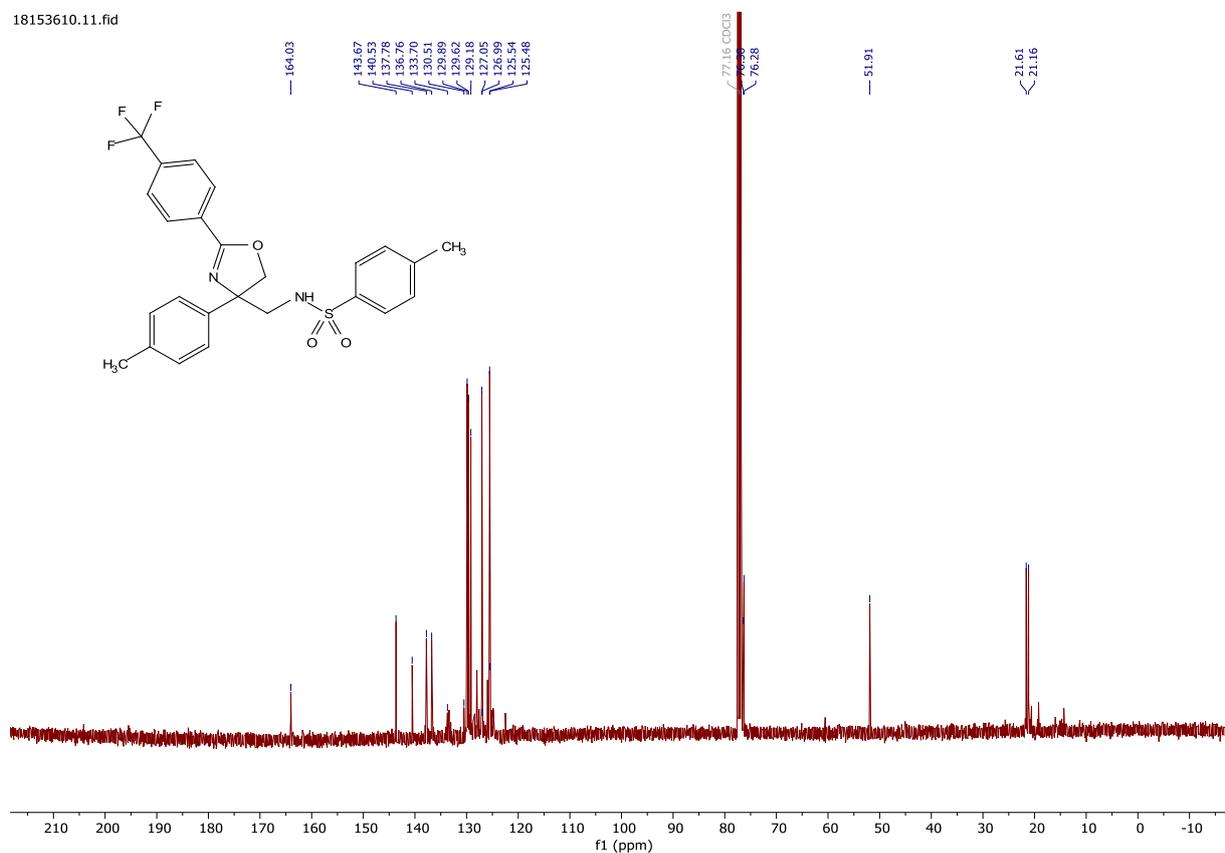
# Compound 2-170 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

18140443.10.fid



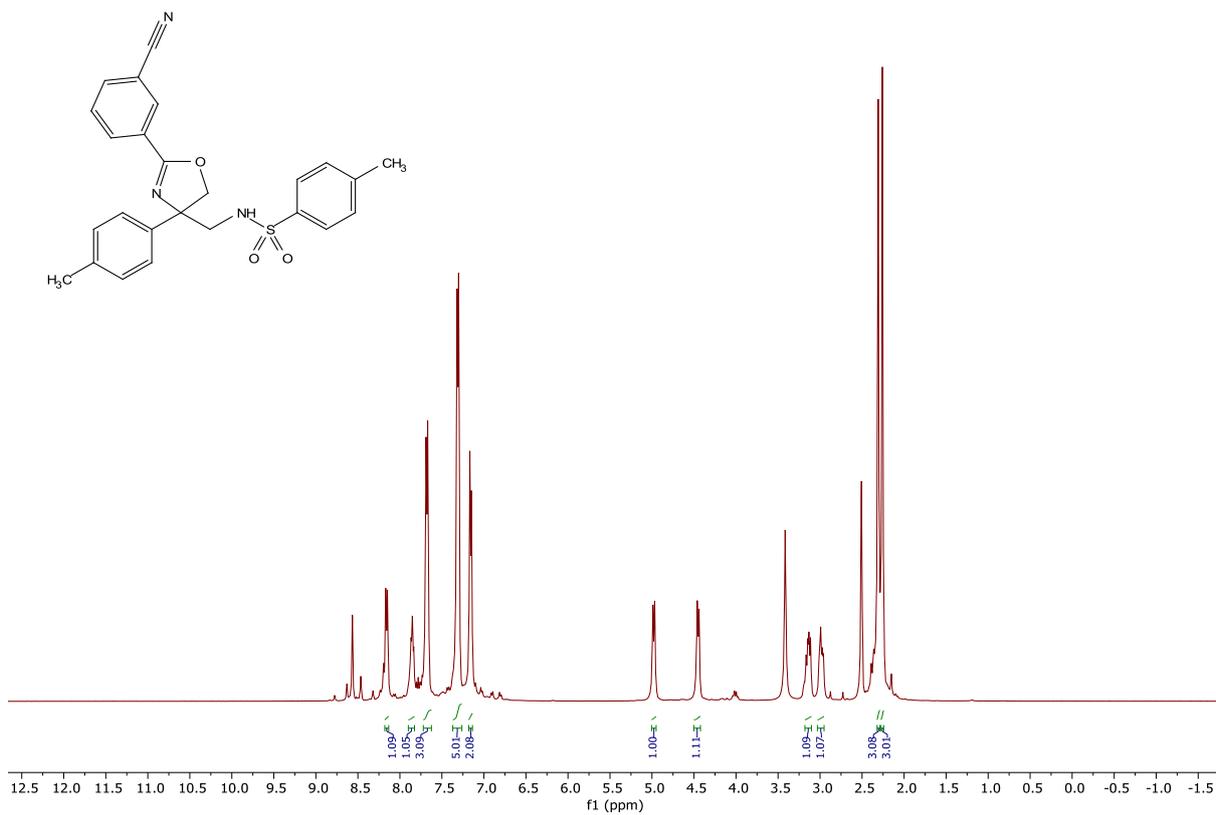
# Compound 2-170 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

18153610.11.fid



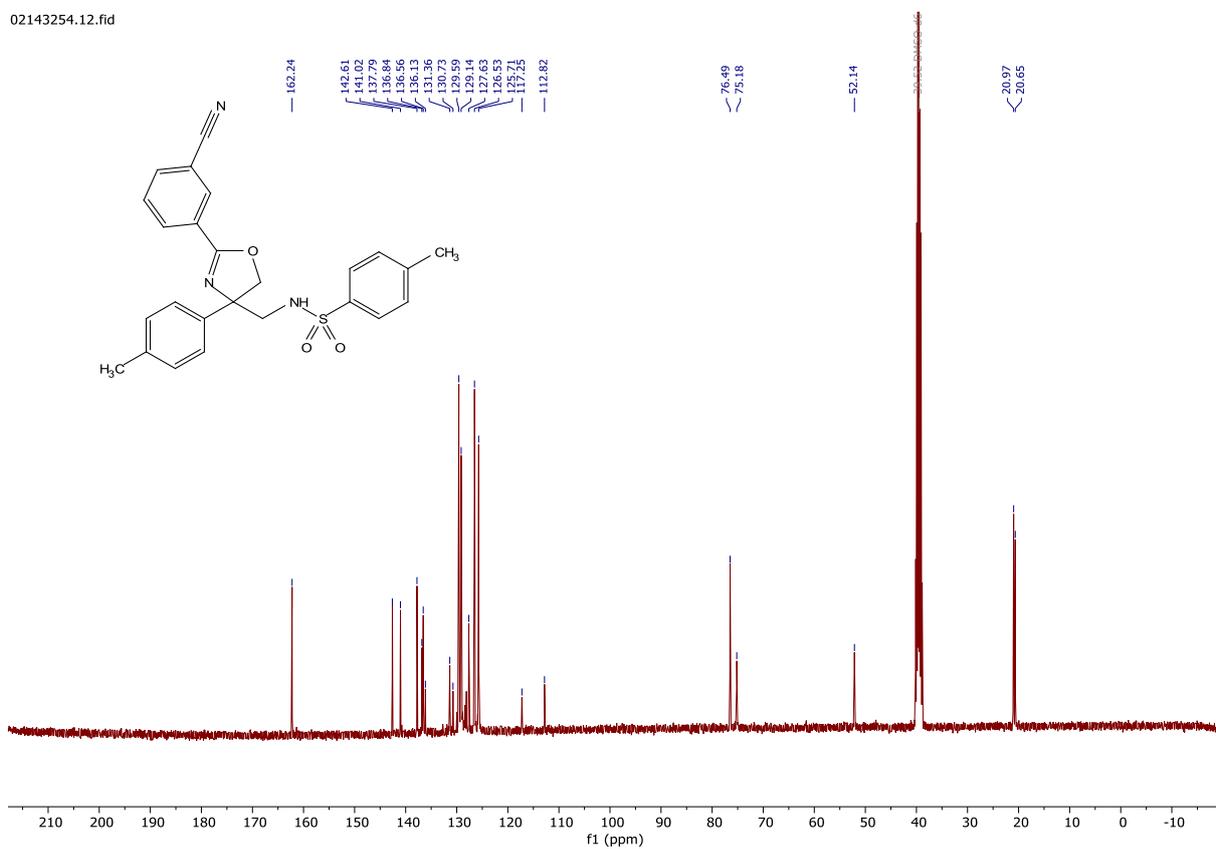
# Compound 2-171 <sup>1</sup>H NMR (400 MHz, DMSO)

02143254.10.fid



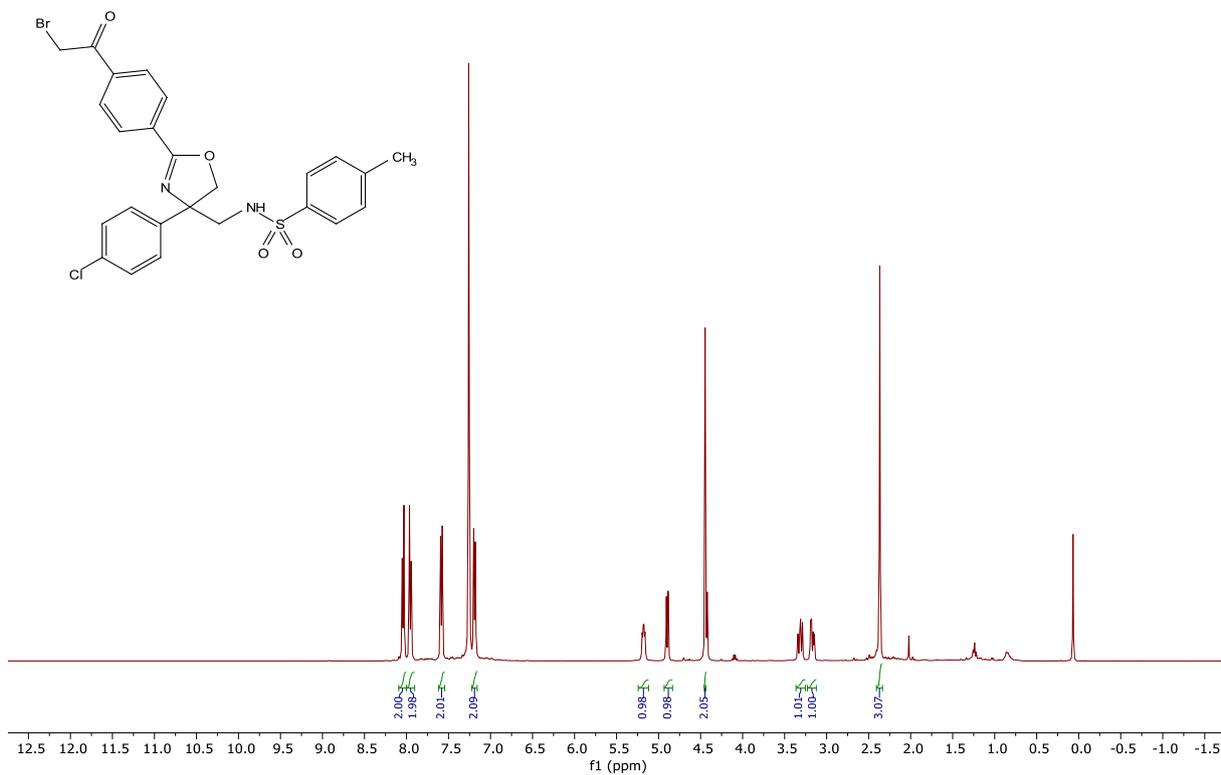
# Compound 2-171 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO)

02143254.12.fid



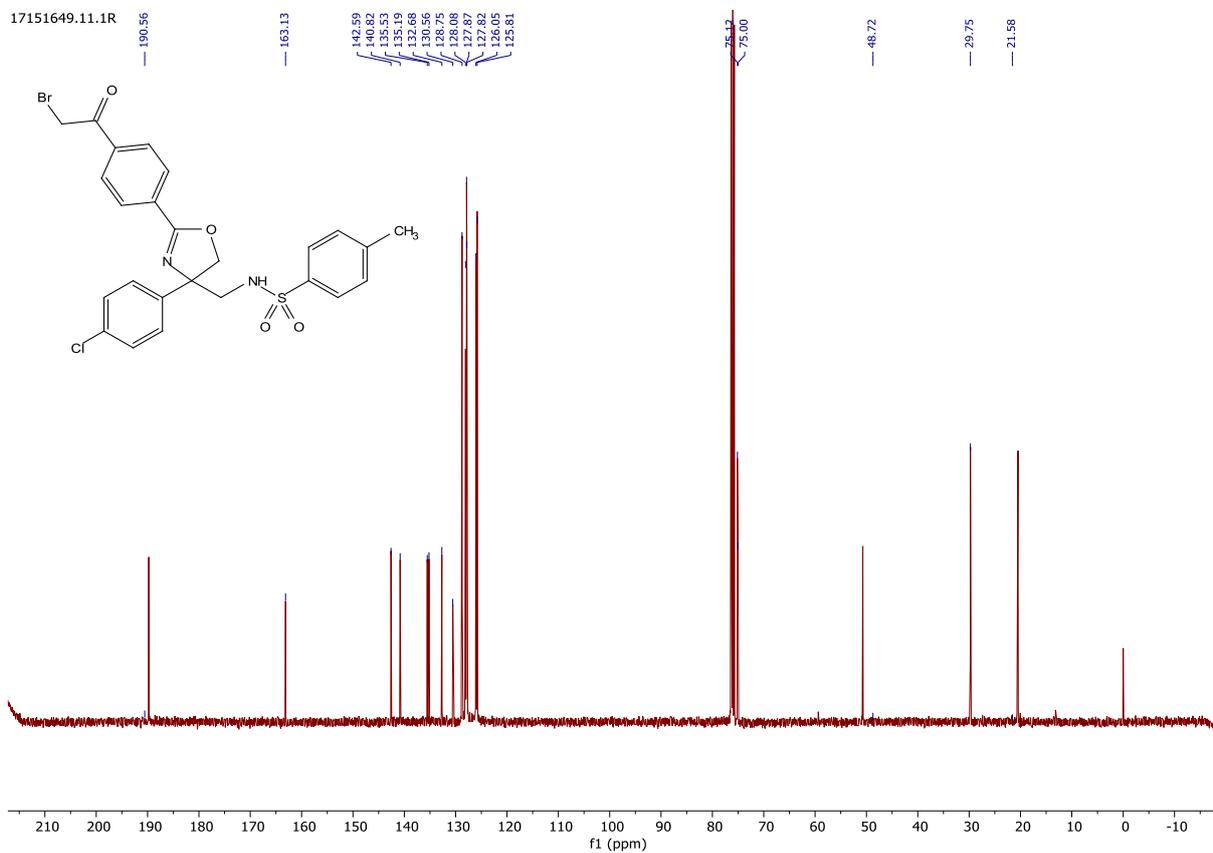
# Compound 2-172 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

17151649.10.fid



# Compound 2-172 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

17151649.11.1R





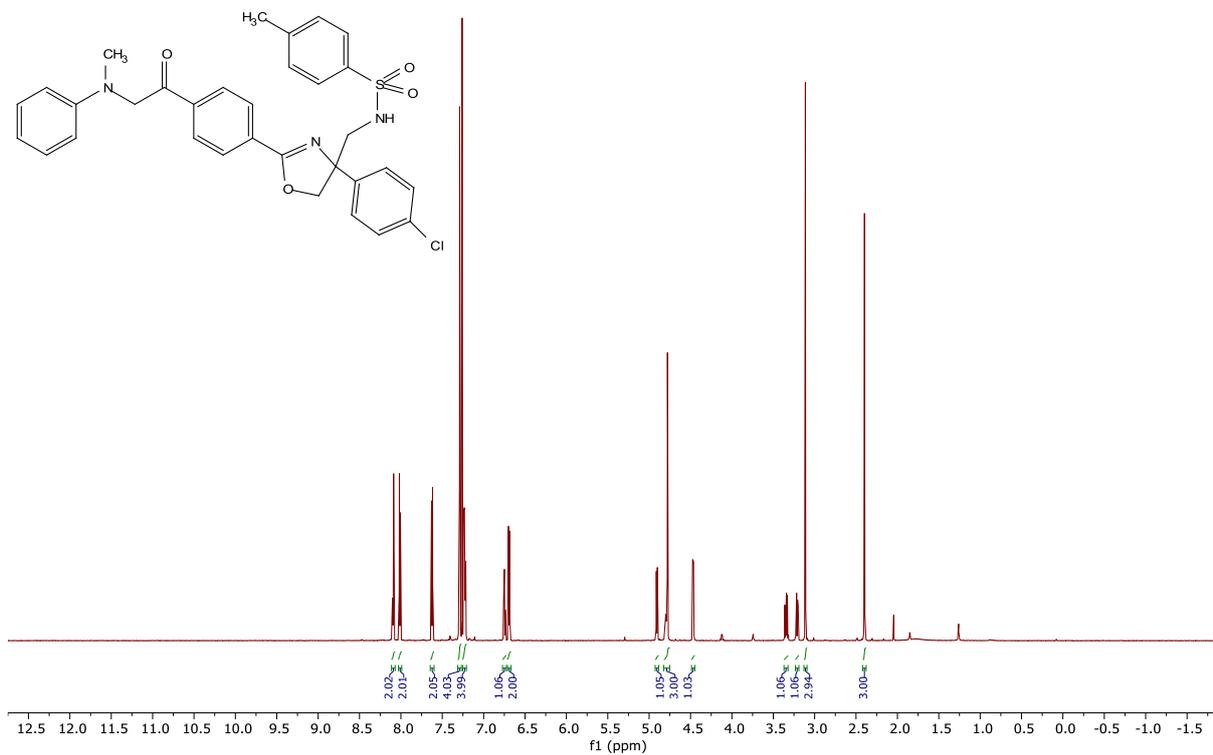
Single crystals of  $C_{25}H_{22}BrClN_2O_4S$  were A suitable crystal was selected on a D8V\_Mo diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 1) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 2) Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
- 3) Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

**Crystal Data** for  $C_{25}H_{22}BrClN_2O_4S$  ( $M = 561.86$  g/mol): triclinic, space group P-1 (no. 2),  $a = 8.9040(5)$  Å,  $b = 11.4226(7)$  Å,  $c = 11.9517(7)$  Å,  $\alpha = 81.001(2)^\circ$ ,  $\beta = 89.408(2)^\circ$ ,  $\gamma = 77.106(2)^\circ$ ,  $V = 1169.95(12)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 120$  K,  $\mu(\text{MoK}\alpha) = 1.997$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.595$  g/cm<sup>3</sup>, 26308 reflections measured ( $4.648^\circ \leq 2\theta \leq 60.274^\circ$ ), 6888 unique ( $R_{\text{int}} = 0.0395$ ,  $R_{\text{sigma}} = 0.0415$ ) which were used in all calculations. The final  $R_1$  was 0.0374 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1019 (all data).

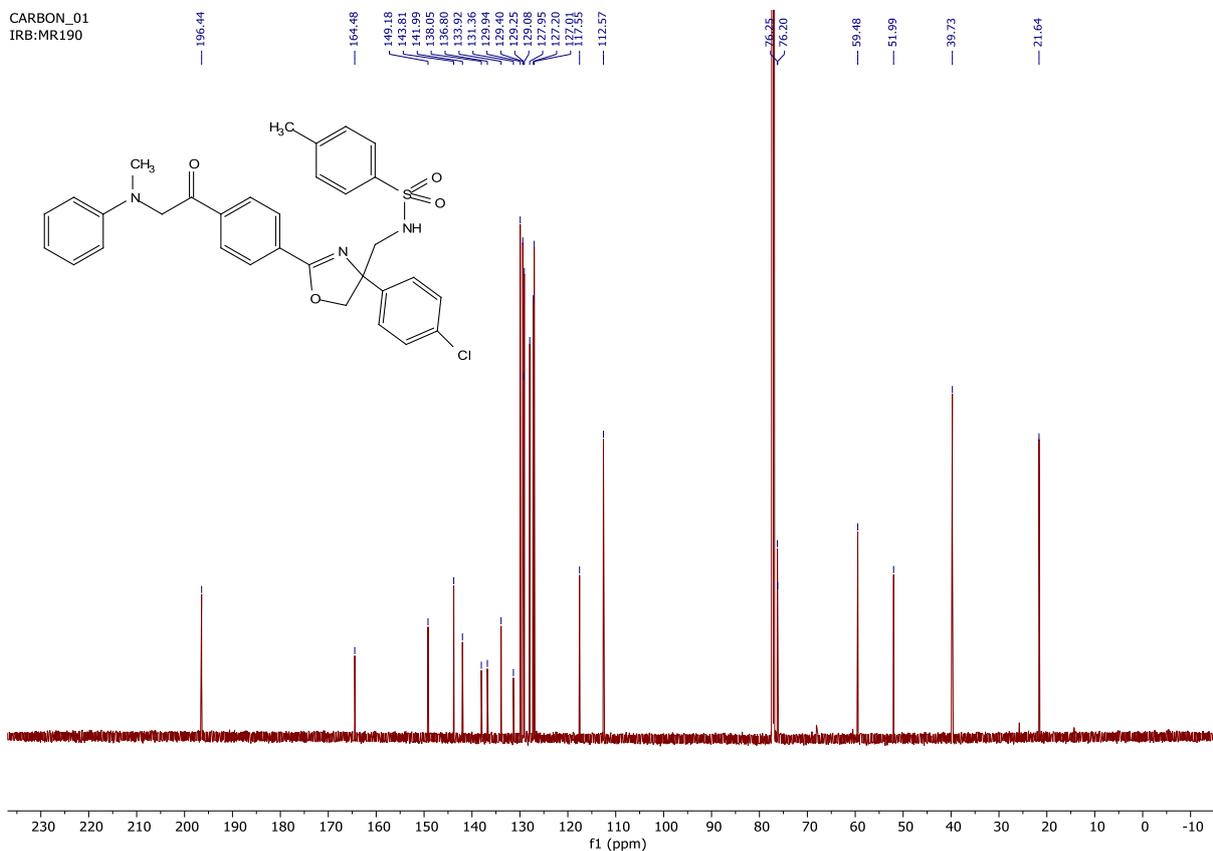
# Compound 2-173 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

PROTON\_01  
IRB:MR190



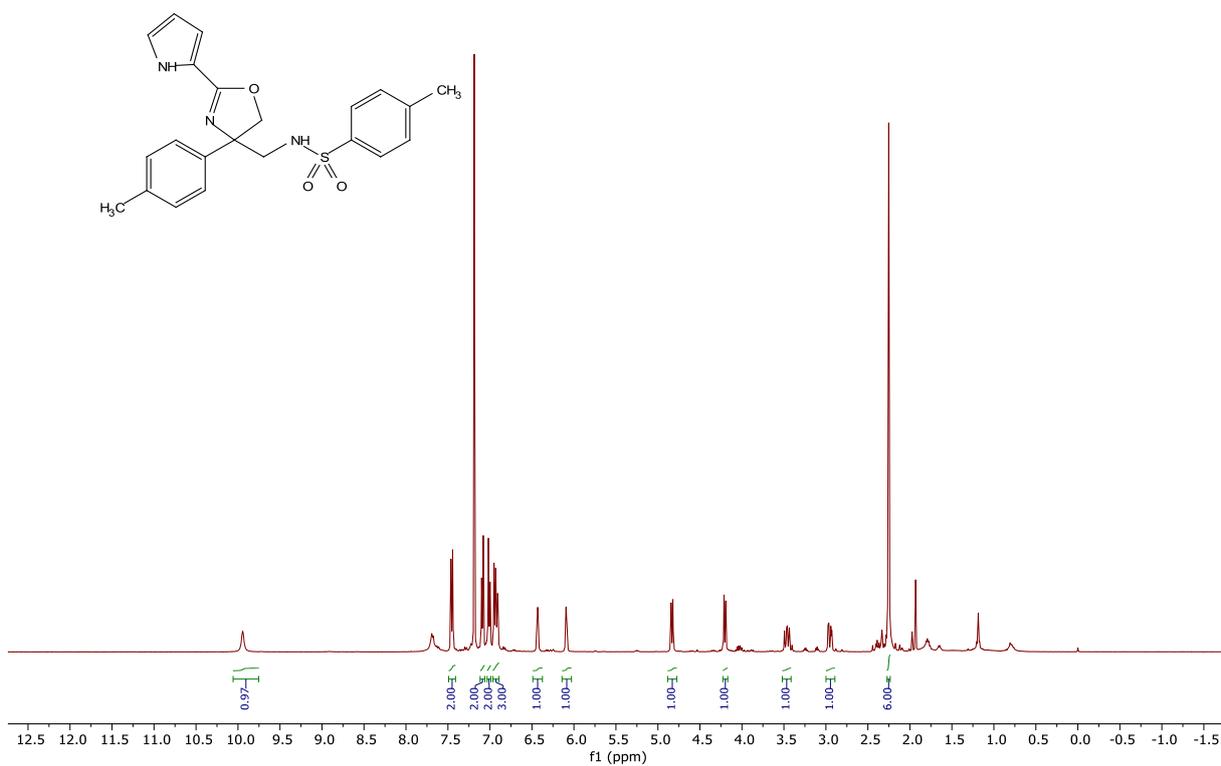
# Compound 2-173 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

CARBON\_01  
IRB:MR190



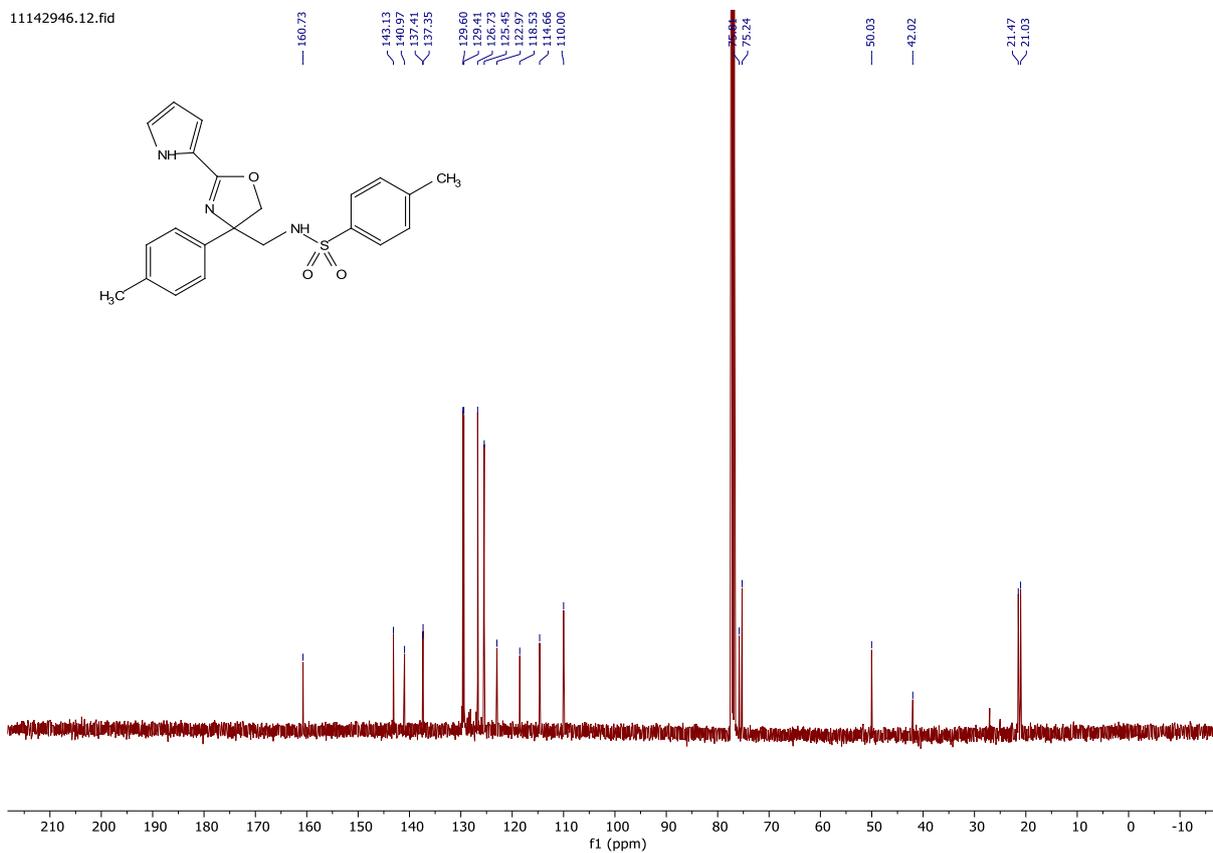
# Compound 2-174 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

11142946.10.fid



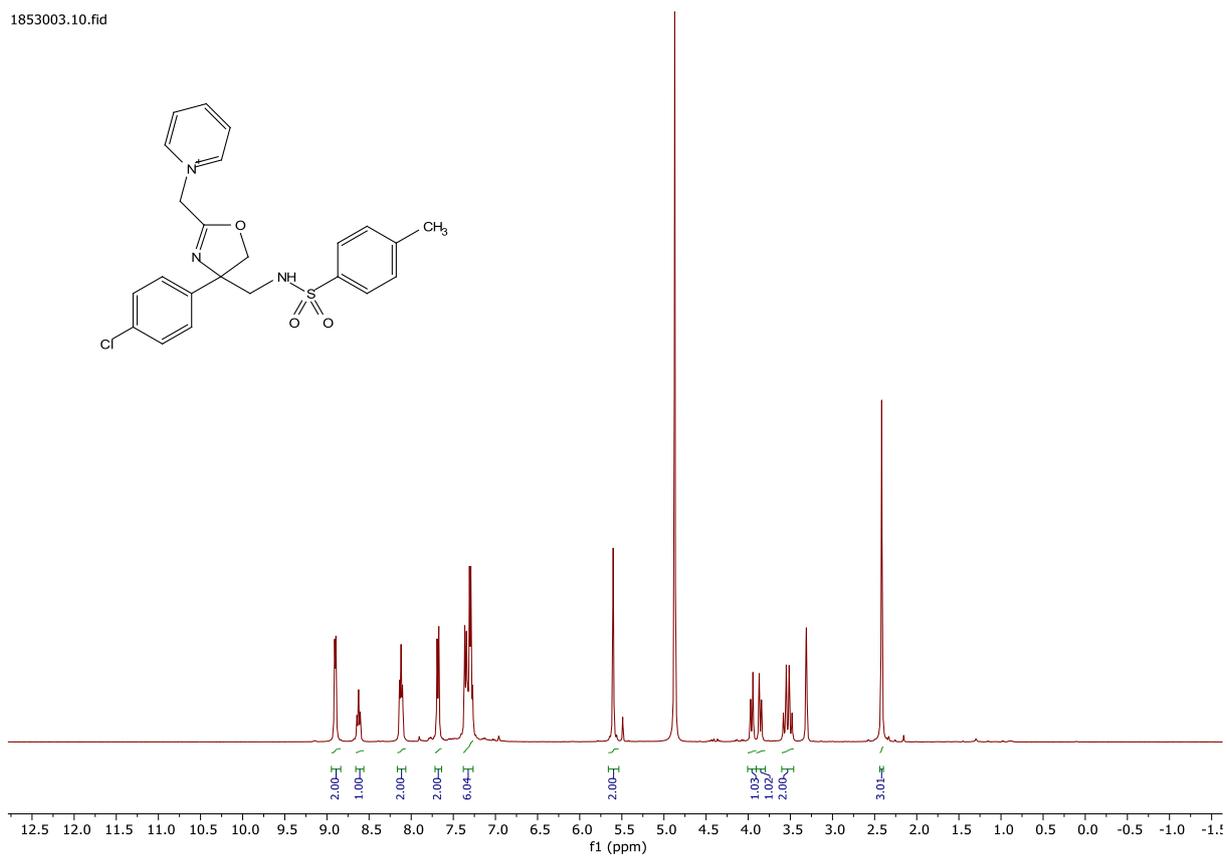
# Compound 2-174 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

11142946.12.fid



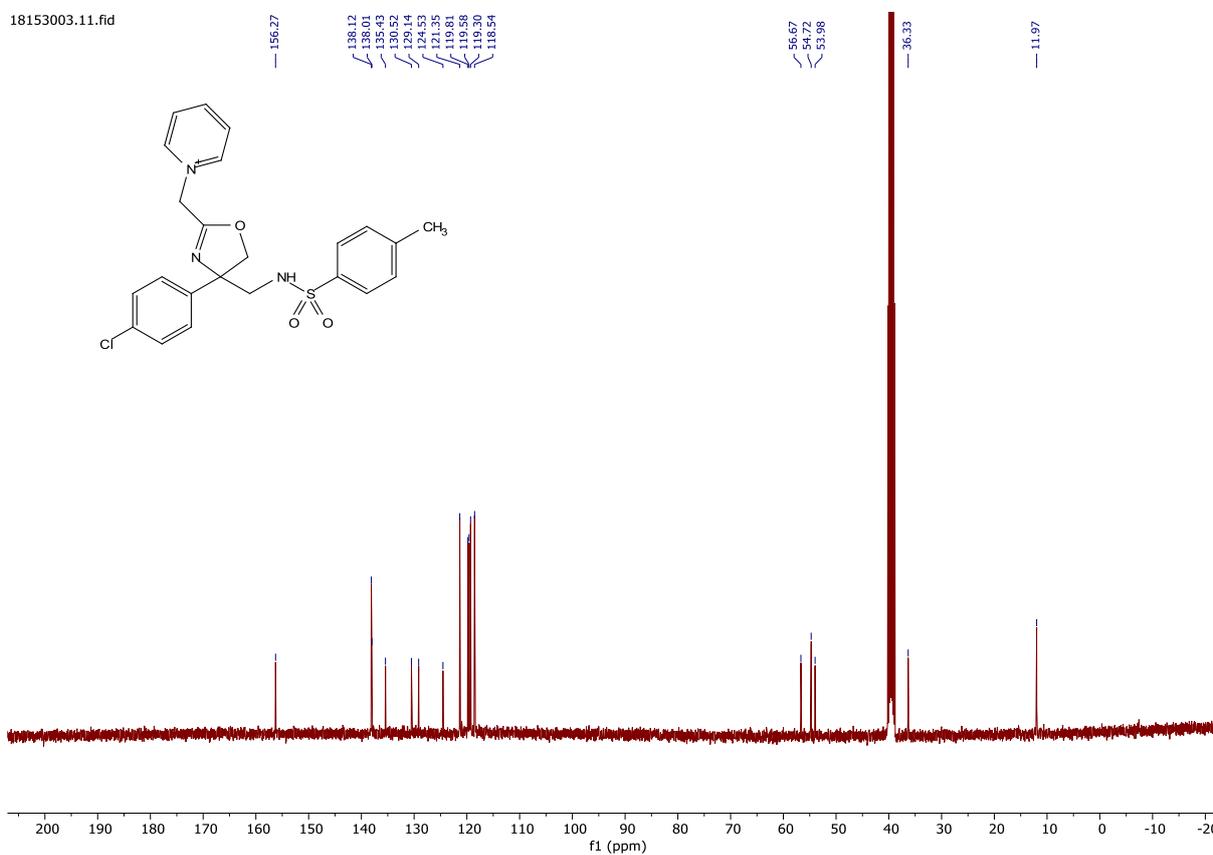
# Compound 2-175 <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)

1853003.10.fid



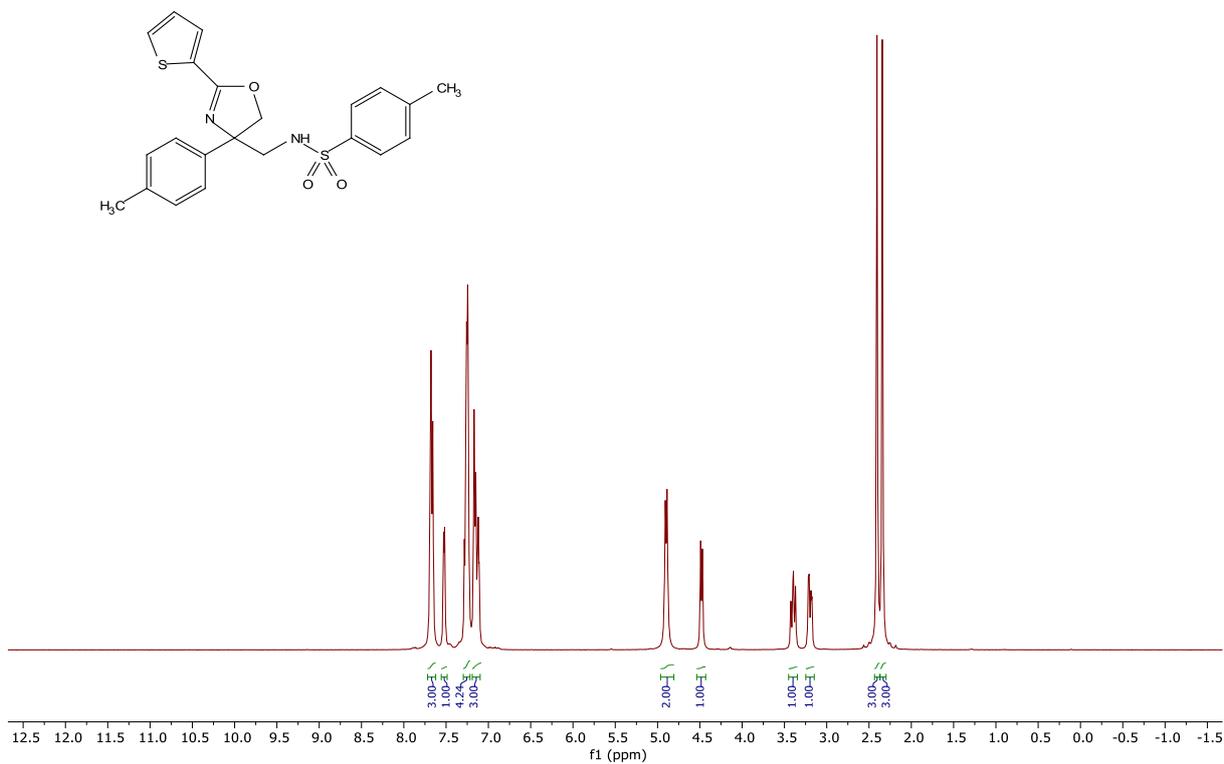
# Compound 2-175 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD)

18153003.11.fid



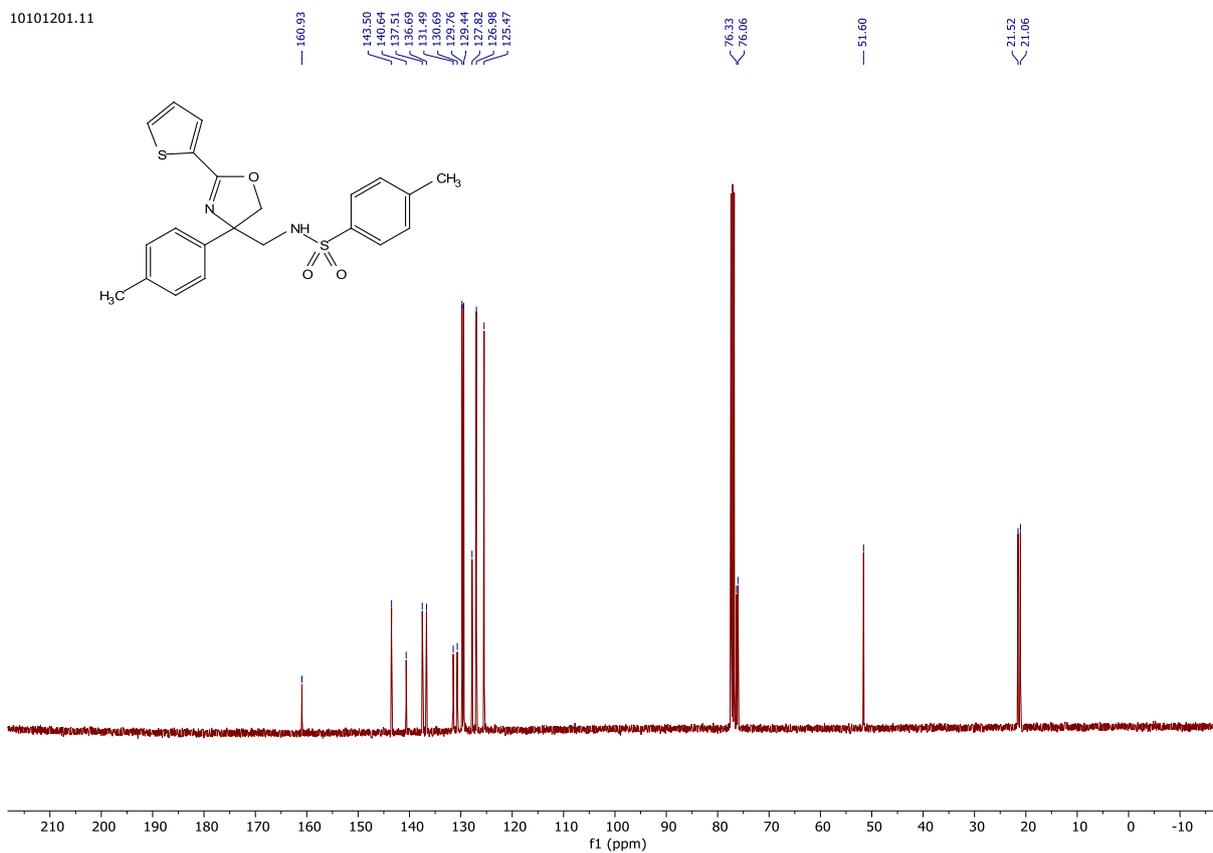
# Compound 2-176 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

10101201.10.fid

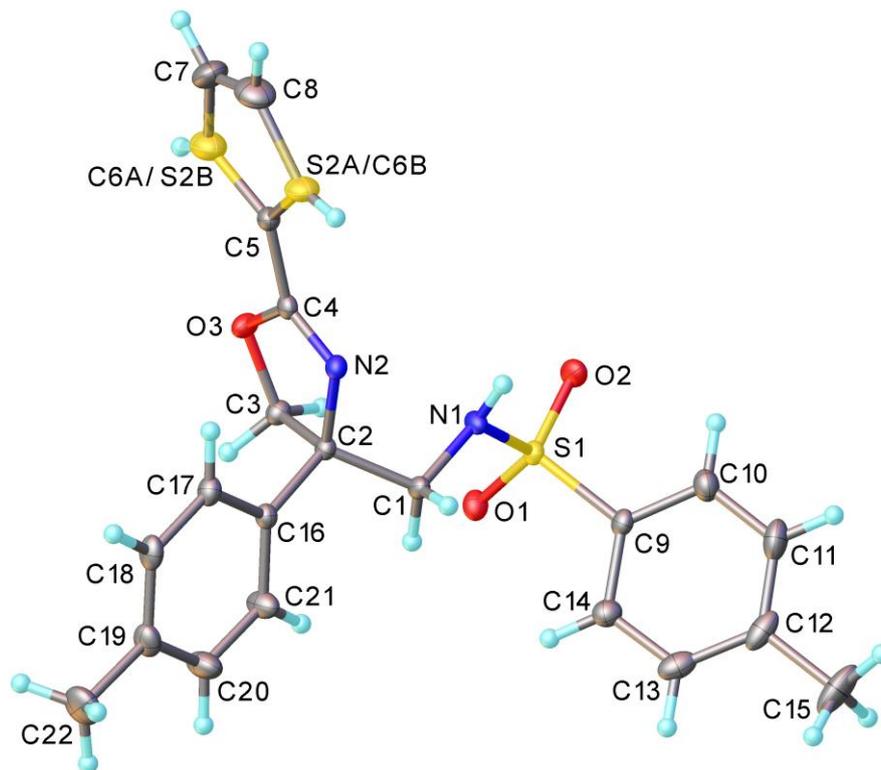


# Compound 2-176 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

10101201.11



## Compound 2-176 X-ray structure



*Atomic displacement ellipsoids are drawn at the 50% probability level.*

Compound 4-13 was crystallised by solvent evaporation using a mixture Hexane: EtOAc

### Experimental

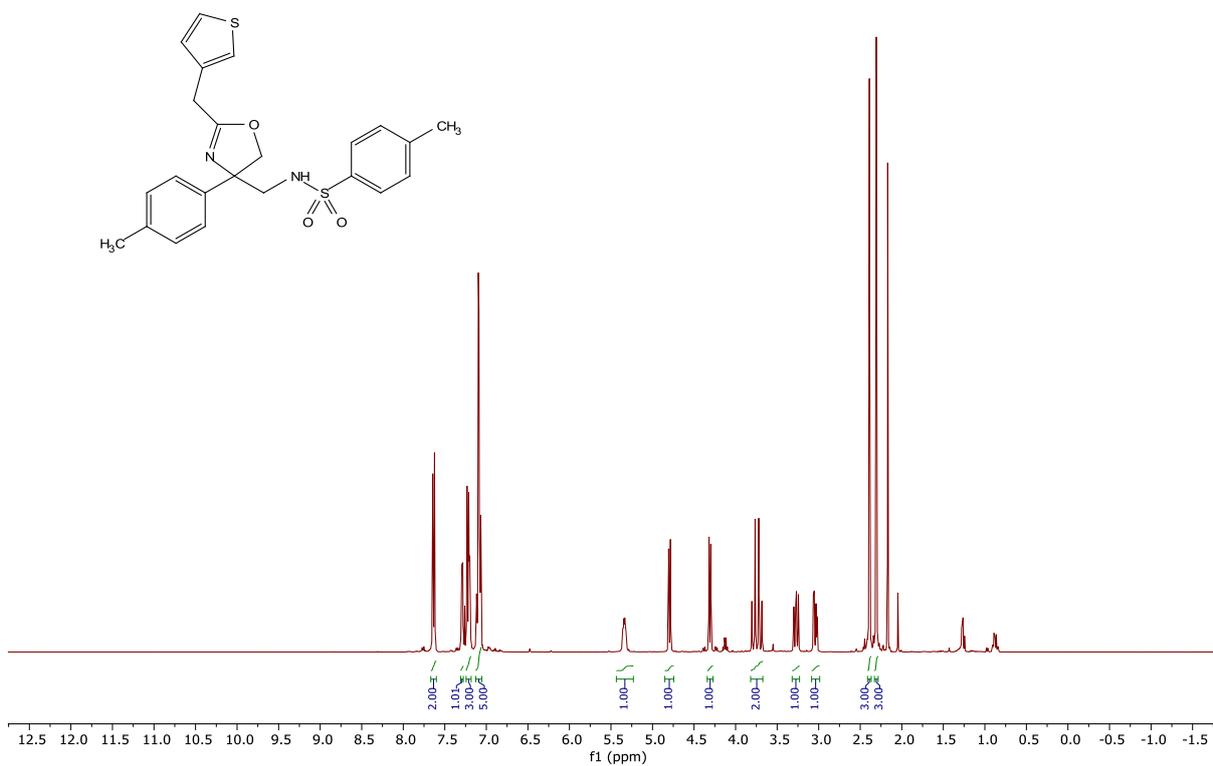
Single crystals of  $C_{23}H_{22}Cl_3DN_2O_3S$  were A suitable crystal was selected on a D8V\_Mo diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 4) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 5) Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
- 6) Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

**Crystal Data** for  $C_{23}H_{22}Cl_3DN_2O_3S_2$  ( $M = 546.91$  g/mol): triclinic, space group P-1 (no. 2),  $a = 9.8161(6)$  Å,  $b = 15.6907(9)$  Å,  $c = 17.1093(10)$  Å,  $\alpha = 85.923(2)^\circ$ ,  $\beta = 75.425(2)^\circ$ ,  $\gamma = 81.516(2)^\circ$ ,  $V = 2520.9(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 120$  K,  $\mu(\text{MoK}\alpha) = 0.558$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.441$  g/cm<sup>3</sup>, 56721 reflections measured ( $4.326^\circ \leq 2\theta \leq 60.262^\circ$ ), 14845 unique ( $R_{\text{int}} = 0.0561$ ,  $R_{\text{sigma}} = 0.0555$ ) which were used in all calculations. The final  $R_1$  was 0.0504 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1321 (all data)

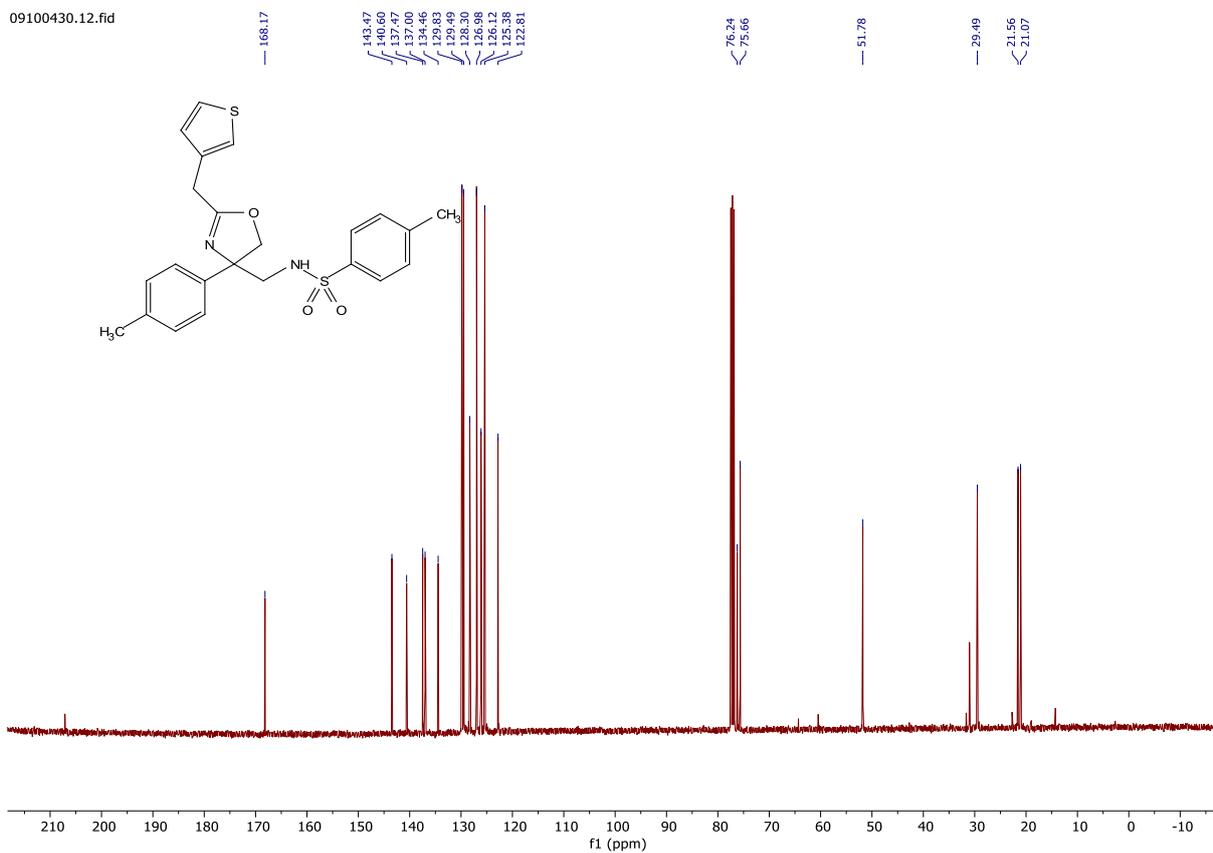
# Compound 2-177 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

09100430.10.fid



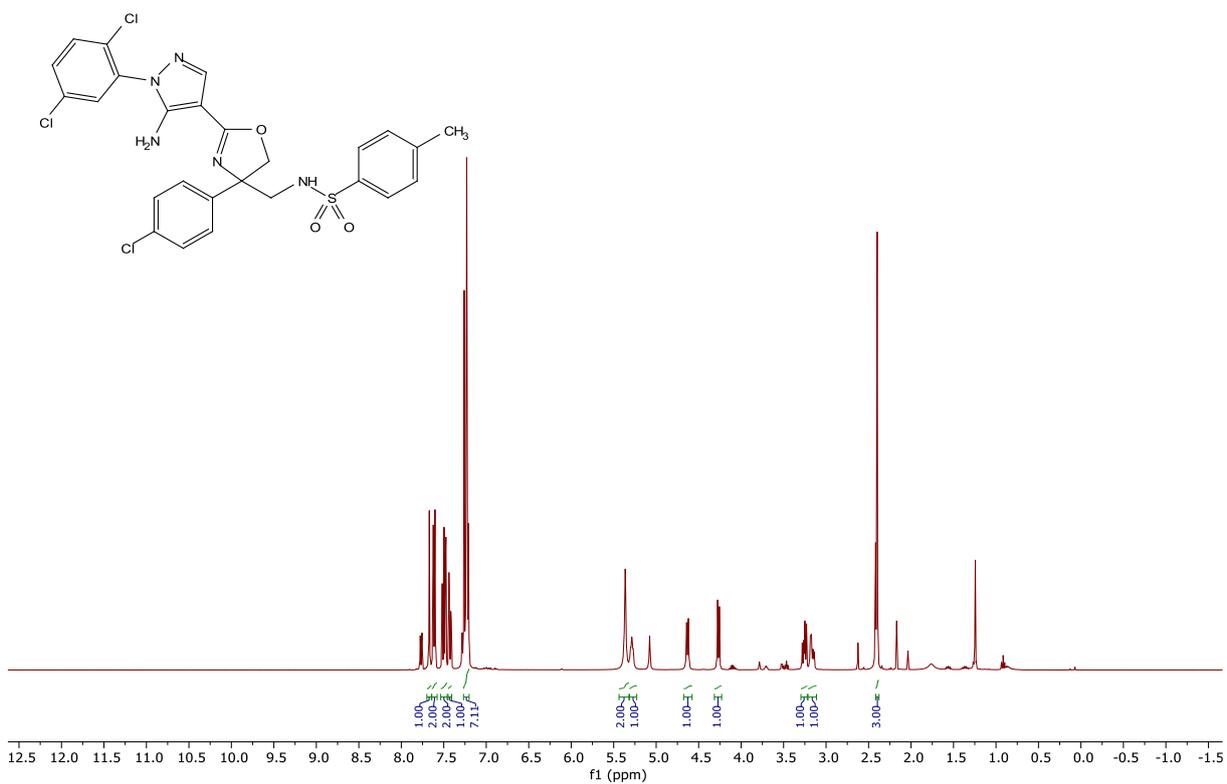
# Compound 2-177 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

09100430.12.fid



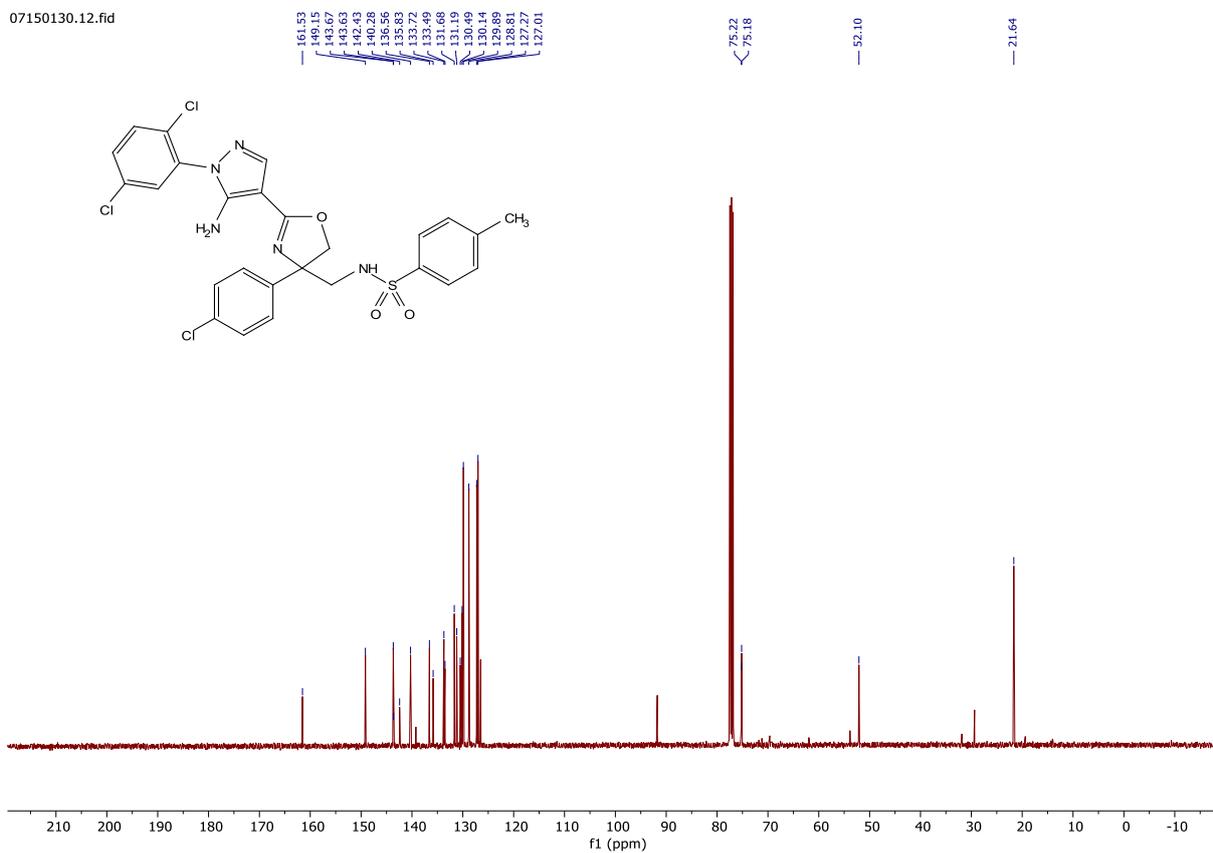
# Compound 2-175 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

07150130.10.fid



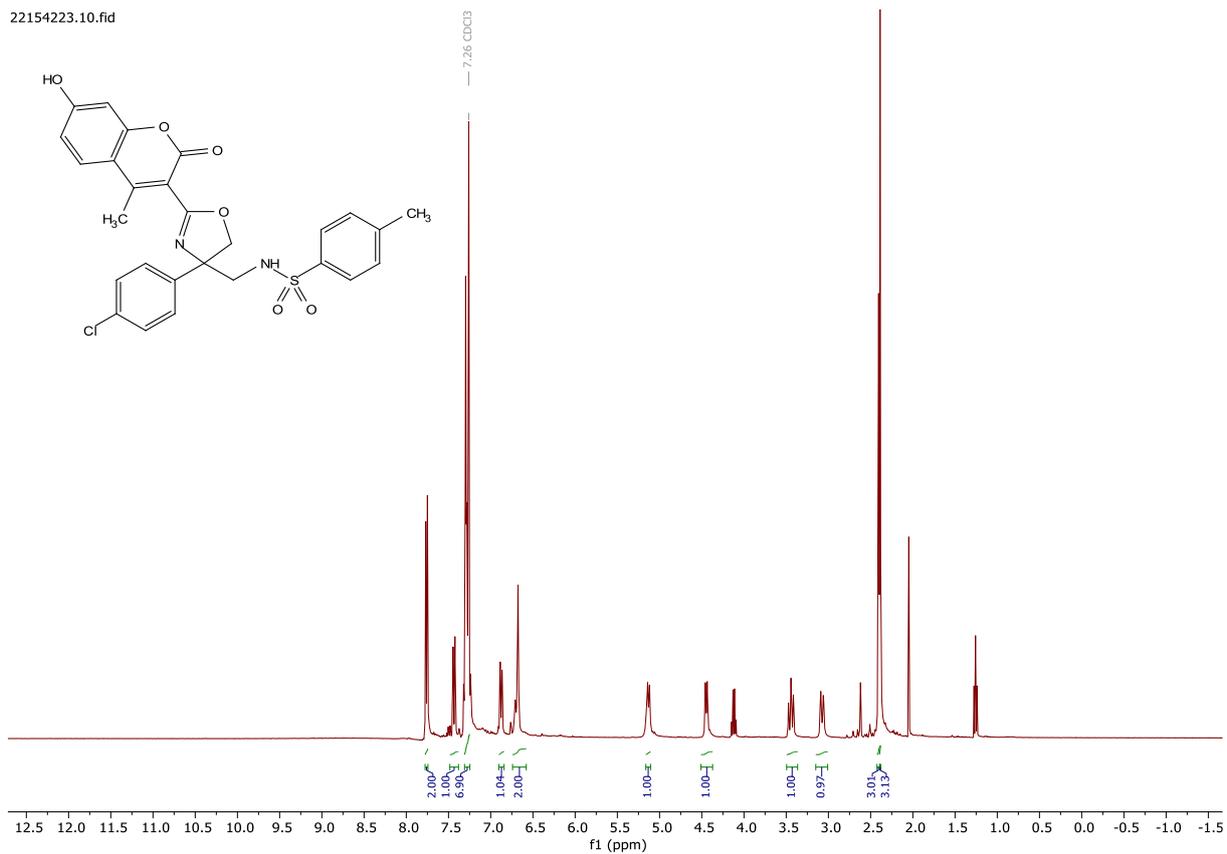
# Compound 2-178 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

07150130.12.fid



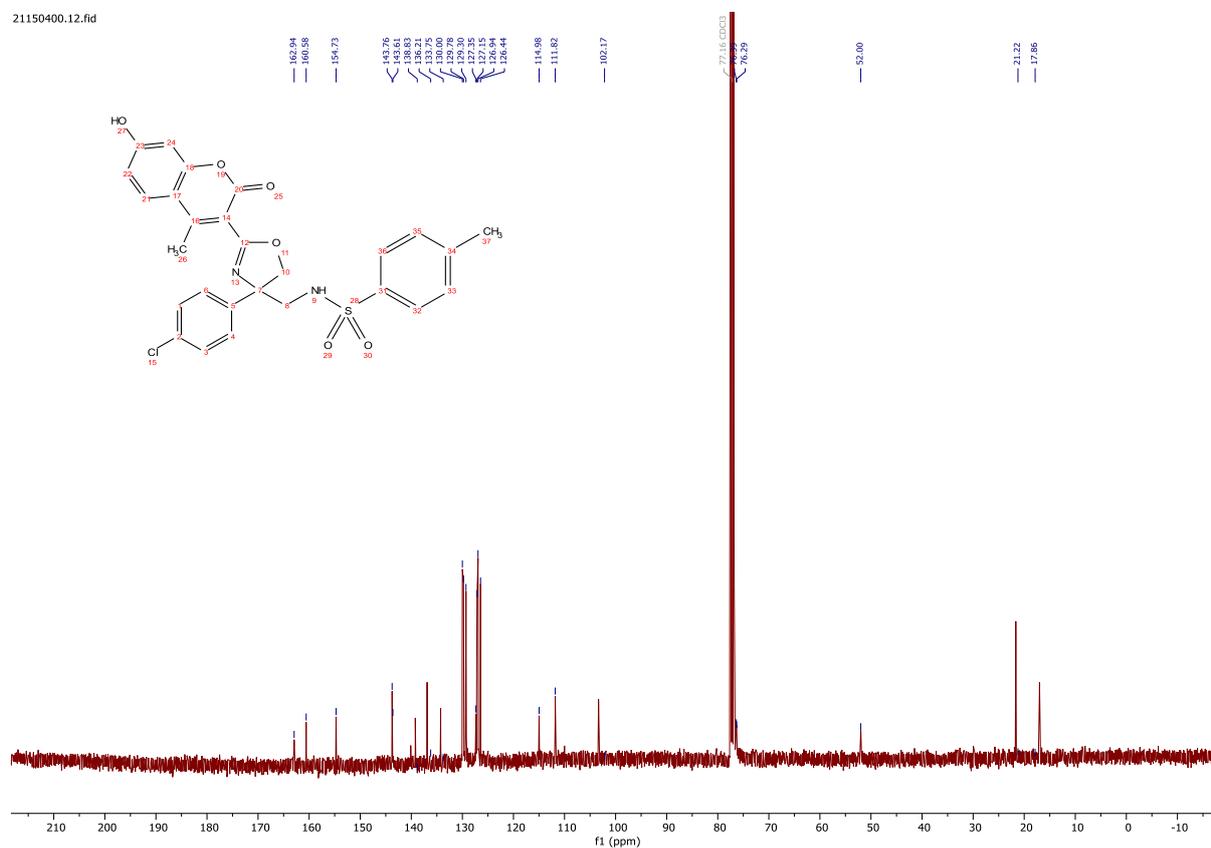
# Compound 2-179 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

22154223.10.fid



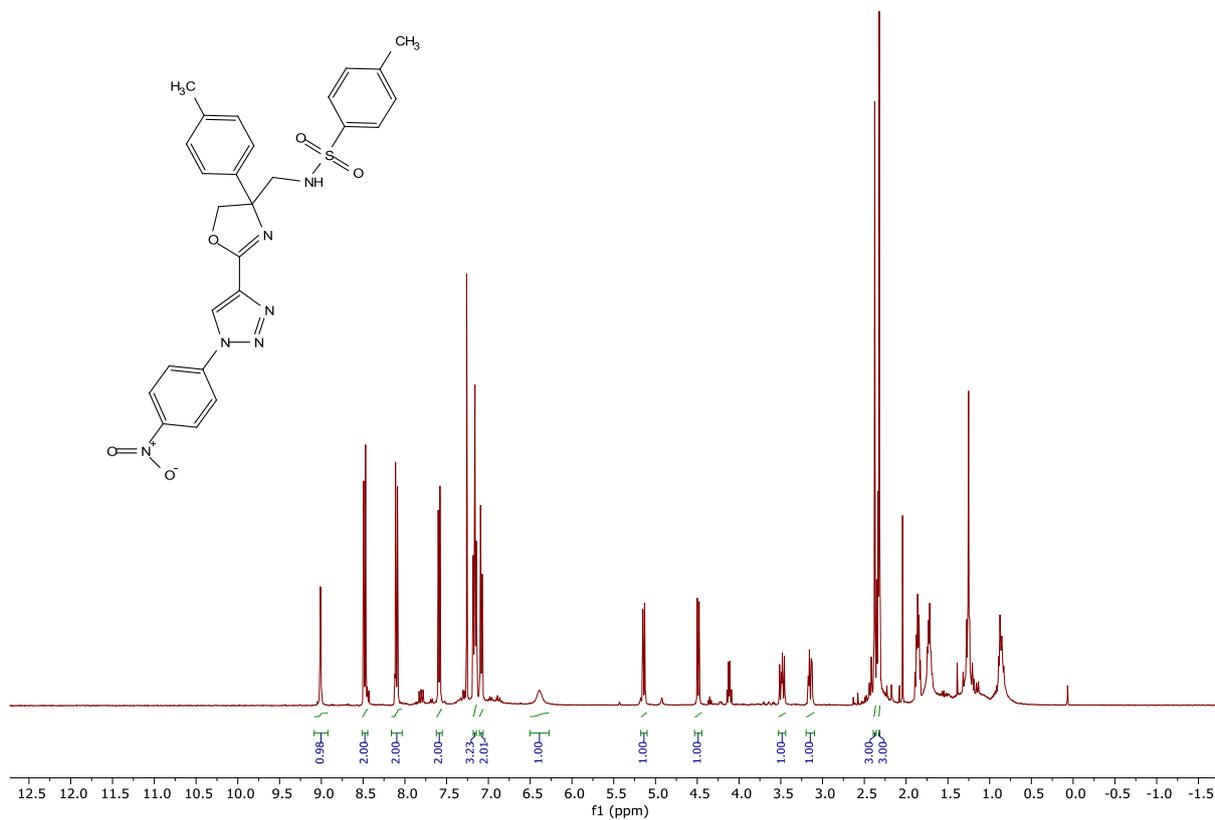
# Compound 2-179 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

21150400.12.fid



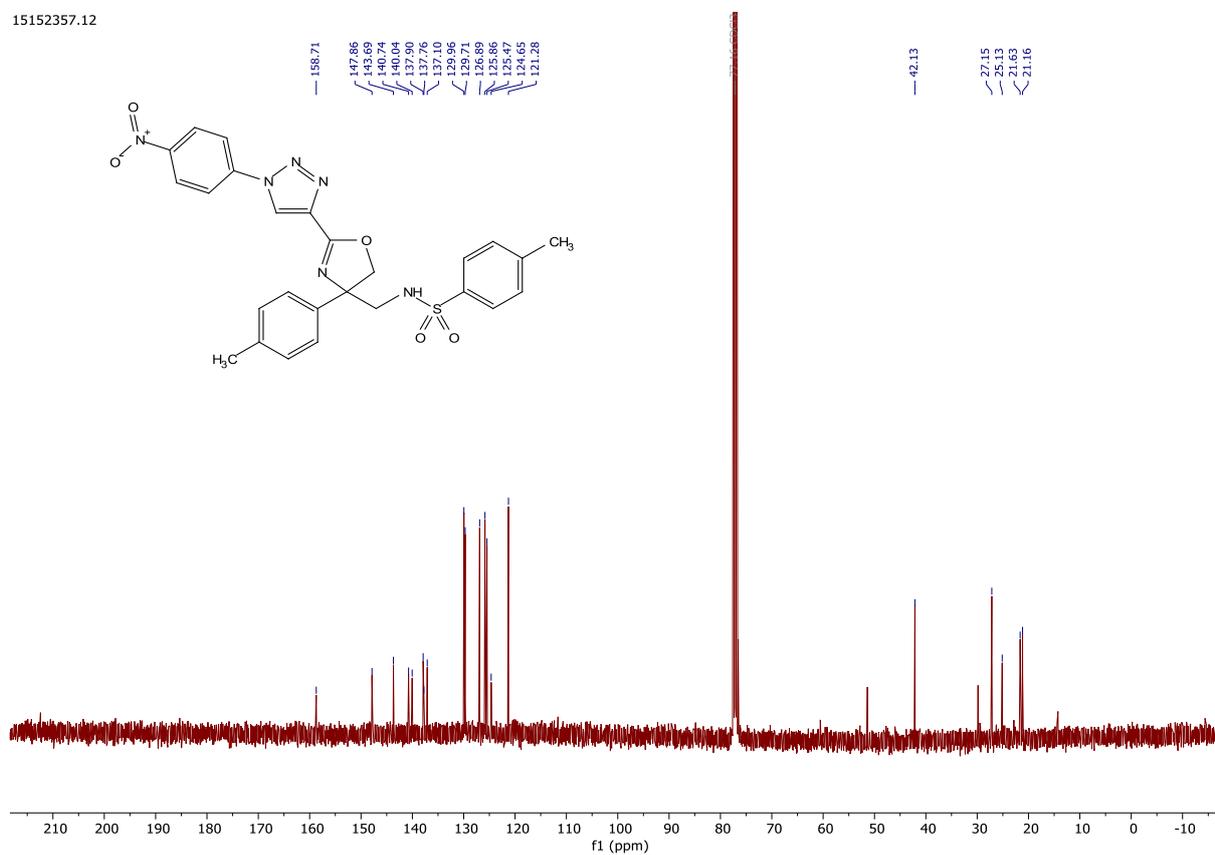
# Compound 2-180 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

15152357.10



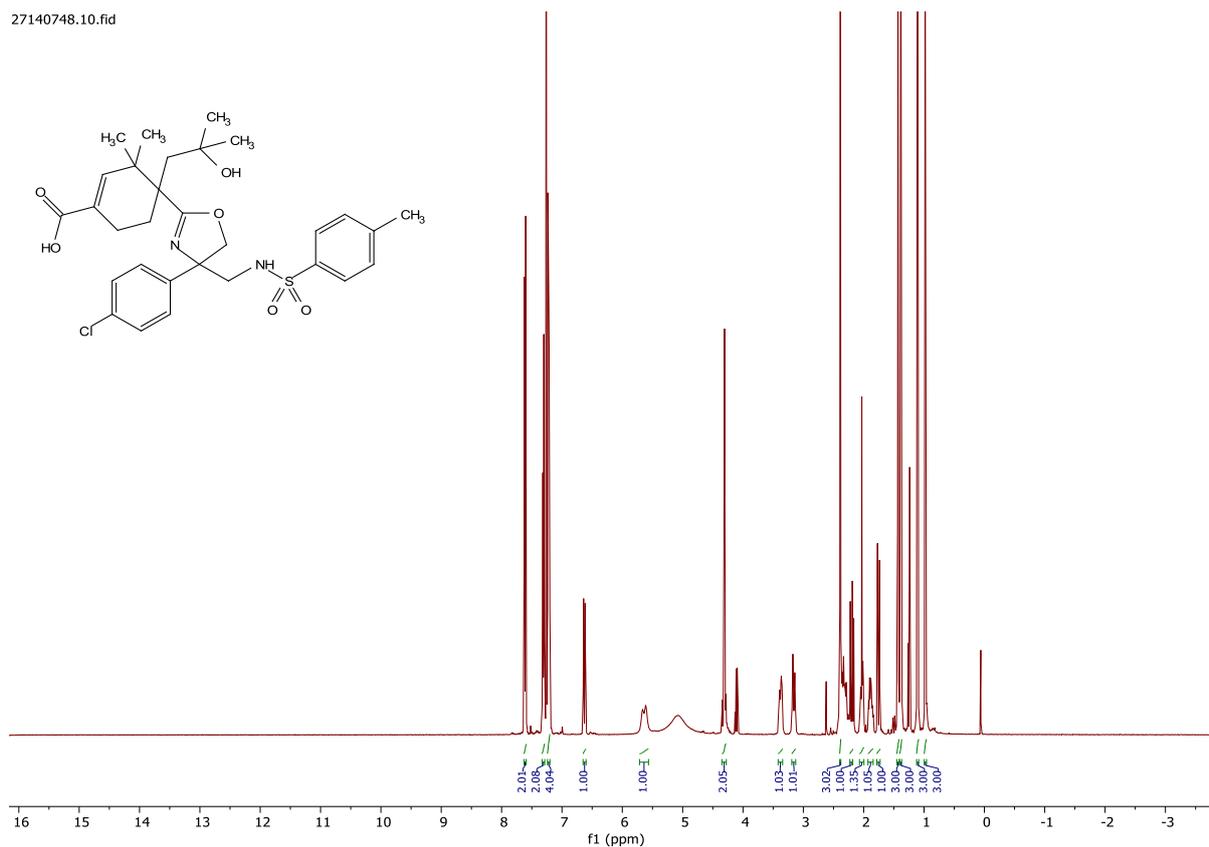
# Compound 2-180 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

15152357.12



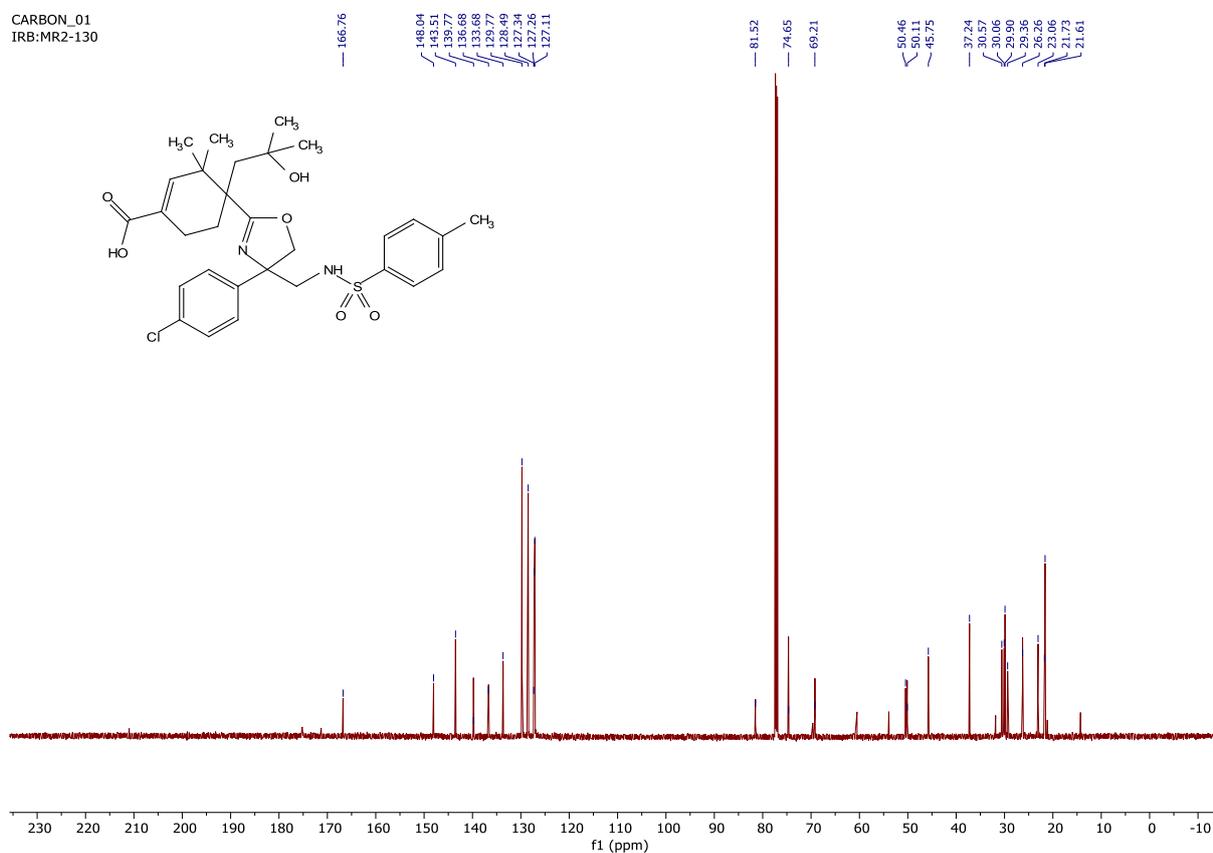
# Compound 2-181 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

27140748.10.fid



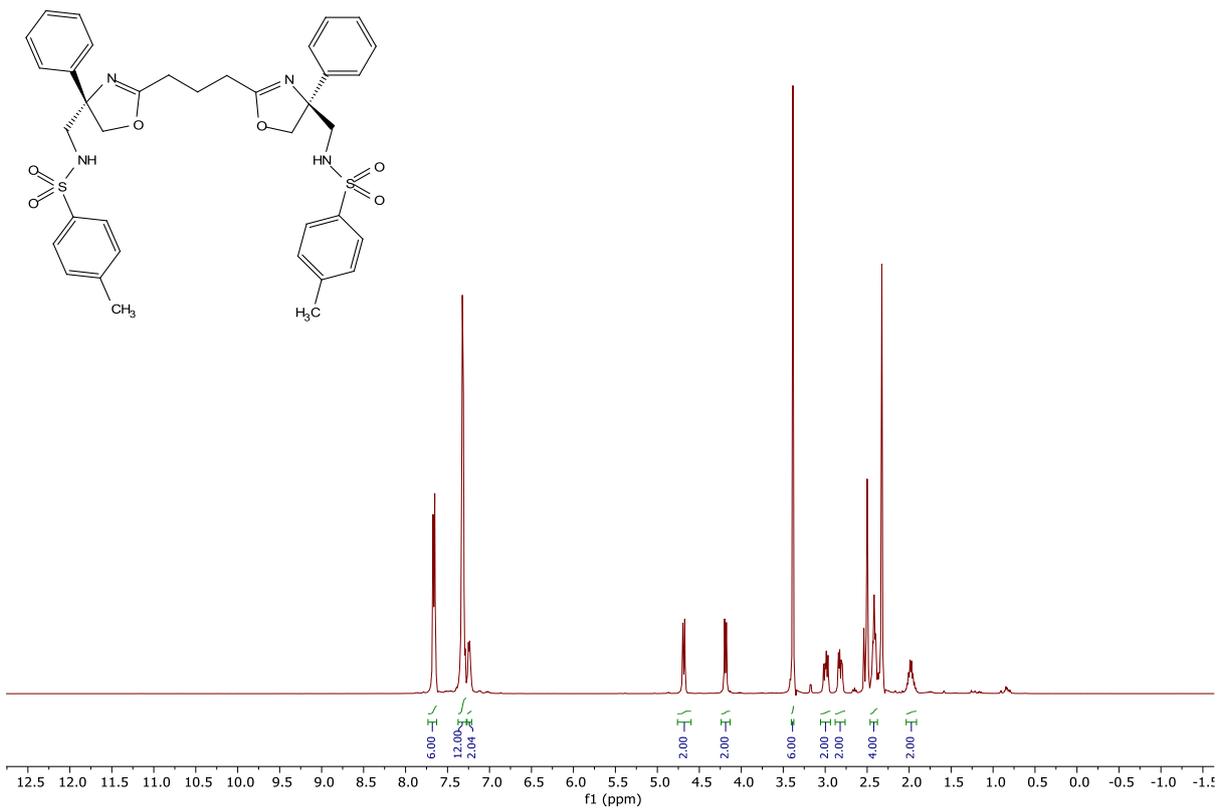
# Compound 2-181 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

CARBON\_01  
IRB:MR2-130



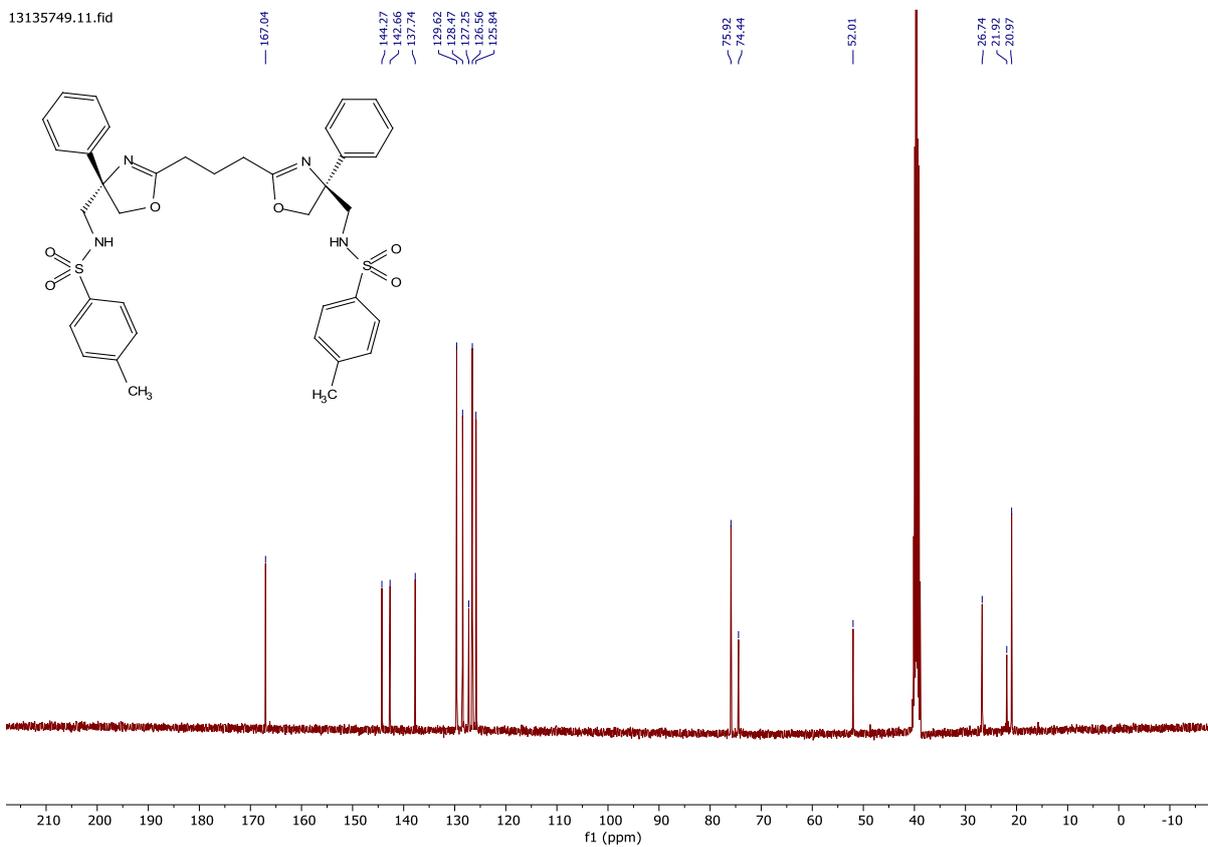
# Compound 2-193 <sup>1</sup>H NMR (400 MHz, DMSO)

13135749.10.fid

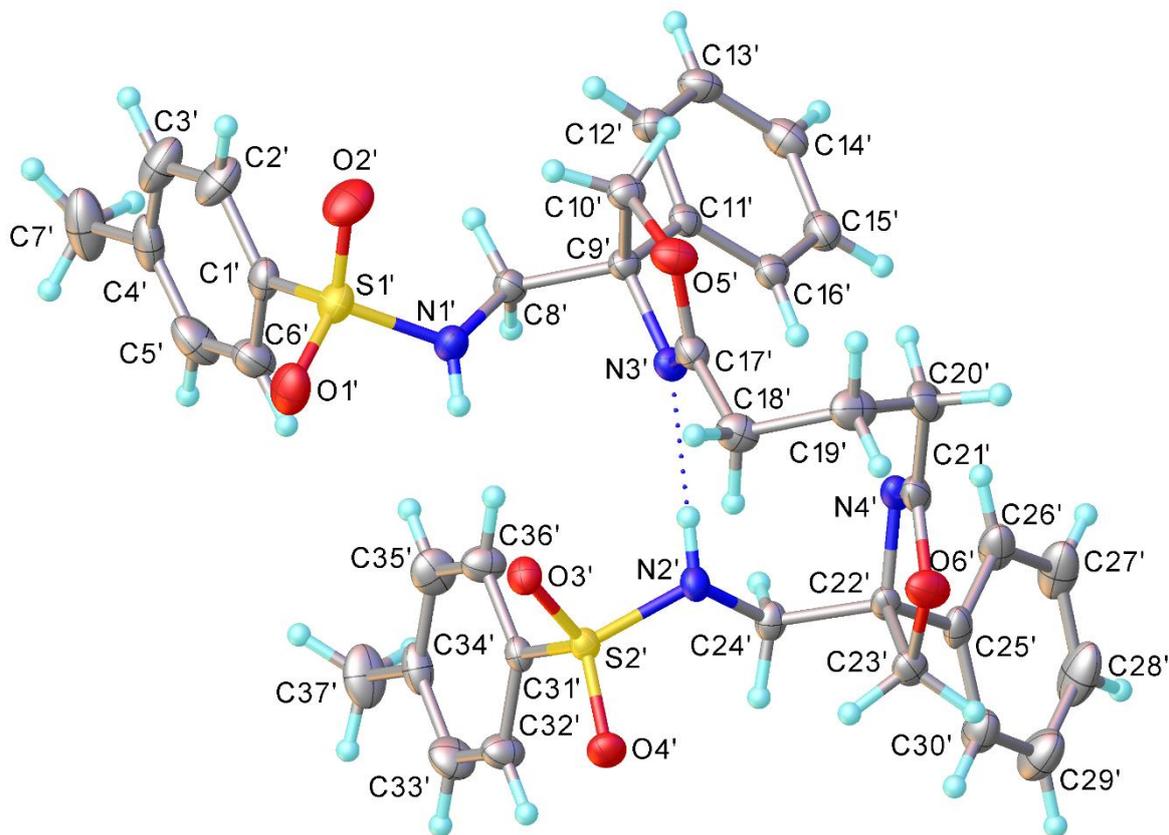


# Compound 2-193 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO)

13135749.11.fid



## Compound 2-193 X-ray structure



*Atomic displacement ellipsoids are drawn at the 50% probability level.*

Compound 4-20 was crystallised by solvent evaporation using a mixture Hexane: EtOAc

### Experimental

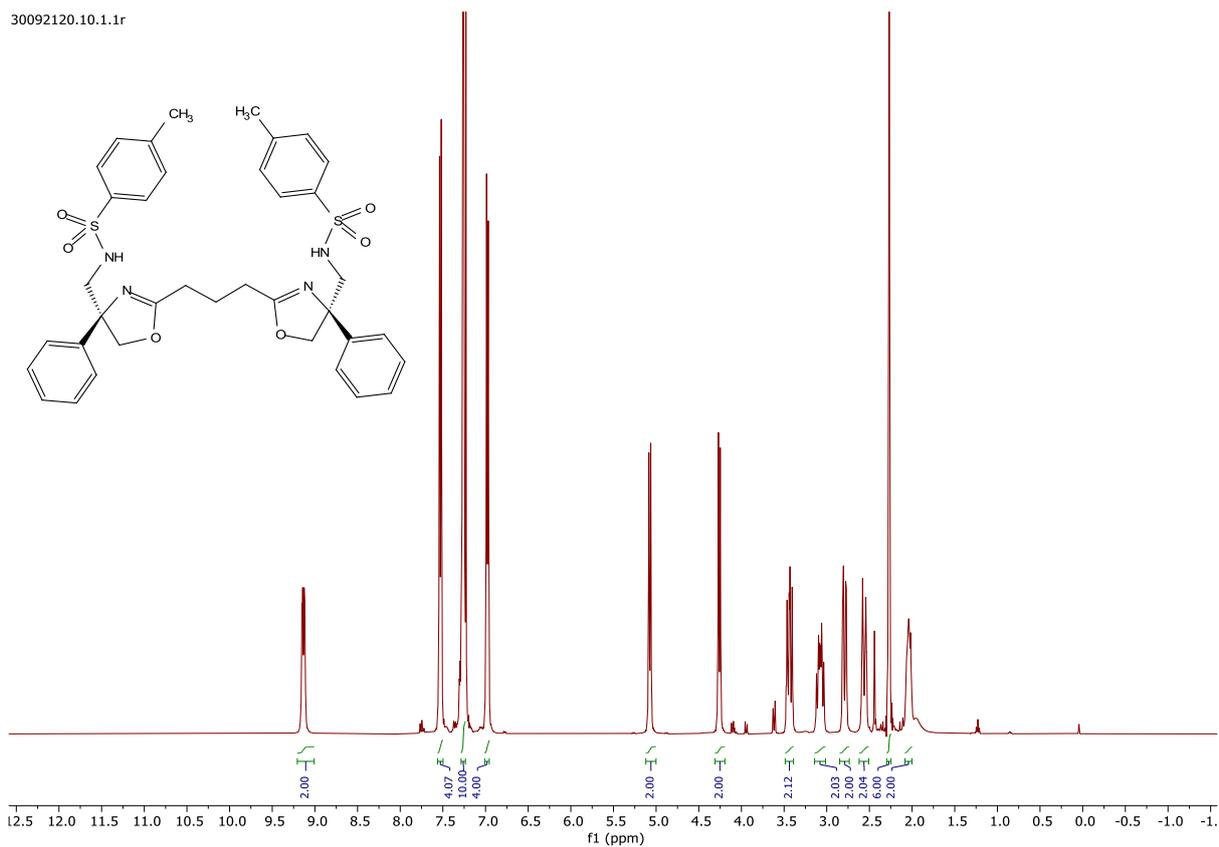
Single crystals of  $C_{37}H_{41}N_4O_6S_2$  were A suitable crystal was selected on a D8V\_Mo diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 7) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
- 8) Sheldrick, G.M. (2008). *Acta Cryst.* A64, 112-122.
- 9) Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

**Crystal Data for C<sub>37</sub>H<sub>40</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub> (*M* = 710.98 g/mol): monoclinic, space group P2<sub>1</sub>/c (no. 14), *a* = 11.8945(9) Å, *b* = 21.4091(15) Å, *c* = 28.158(2) Å, *β* = 96.410(3)°, *V* = 7125.5(9) Å<sup>3</sup>, *Z* = 8, *T* = 120 K, *μ*(MoKα) = 0.202 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.325 g/cm<sup>3</sup>, 139564 reflections measured (3.888° ≤ 2Θ ≤ 58°), 19071 unique (*R*<sub>int</sub> = 0.0453, *R*<sub>sigma</sub> = 0.0323) which were used in all calculations. The final *R*<sub>1</sub> was 0.0522 (*I* > 2σ(*I*)) and *wR*<sub>2</sub> was 0.1309 (all data)**

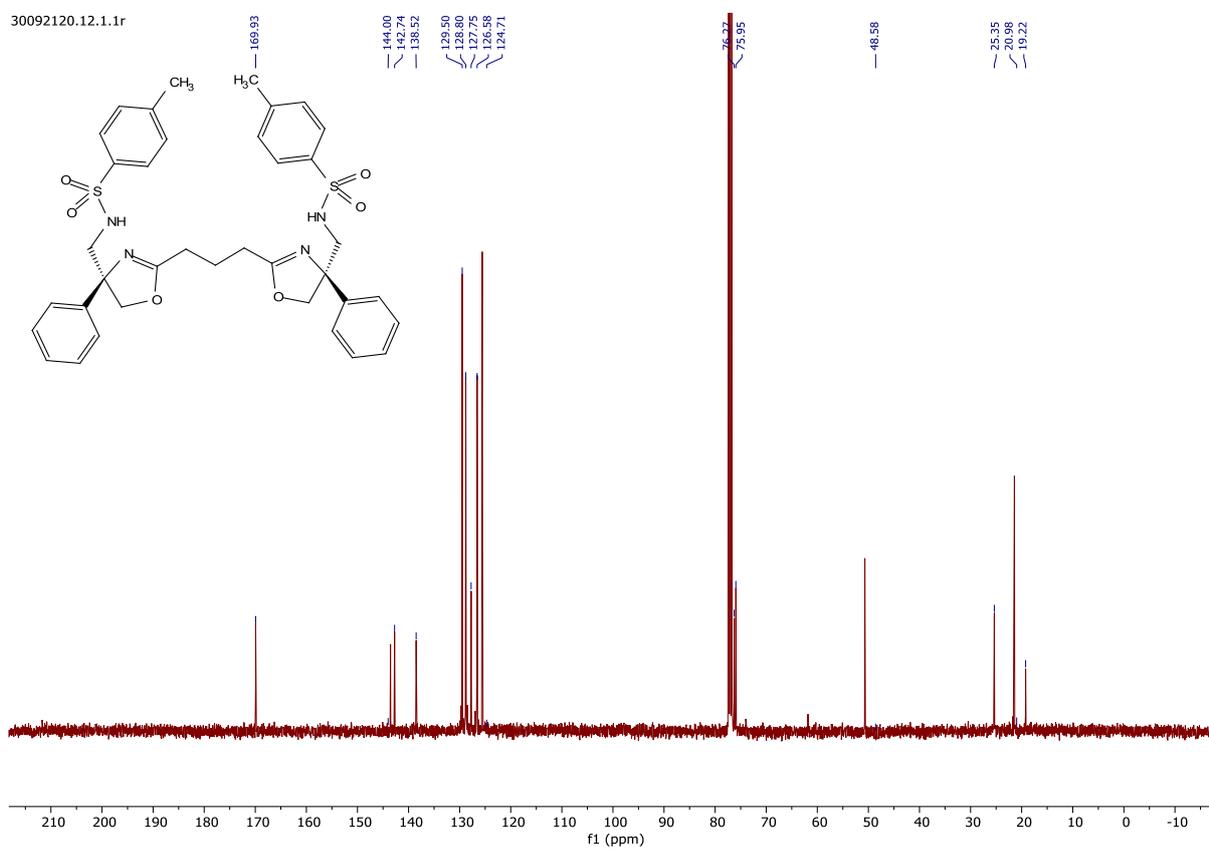
# Compound 2-194 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

30092120.10.1.1r

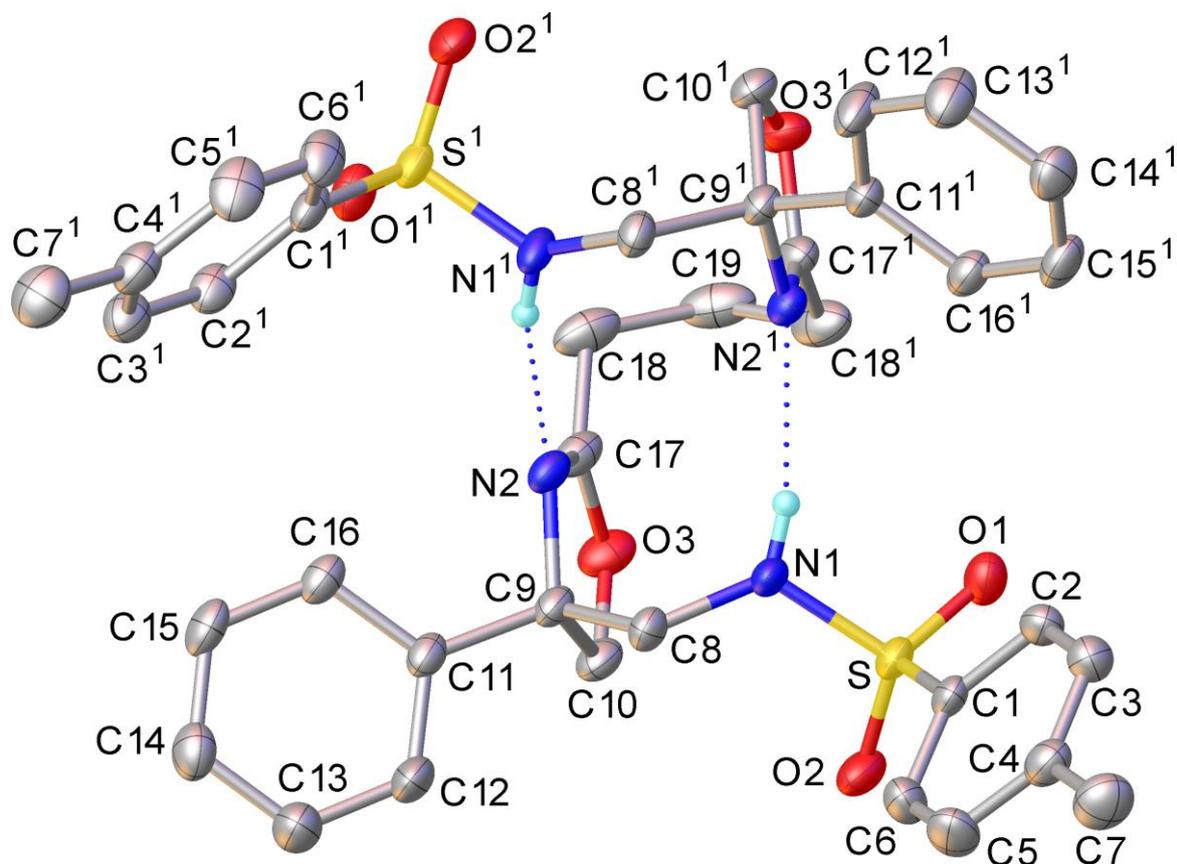


# Compound 2-194 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

30092120.12.1.1r



## Compound 2-194 X-ray structure



Atomic displacement ellipsoids are drawn at the 50% probability level.

Compound 4-21 was crystallised by solvent evaporation using a mixture Hexane: EtOAc

### Experimental

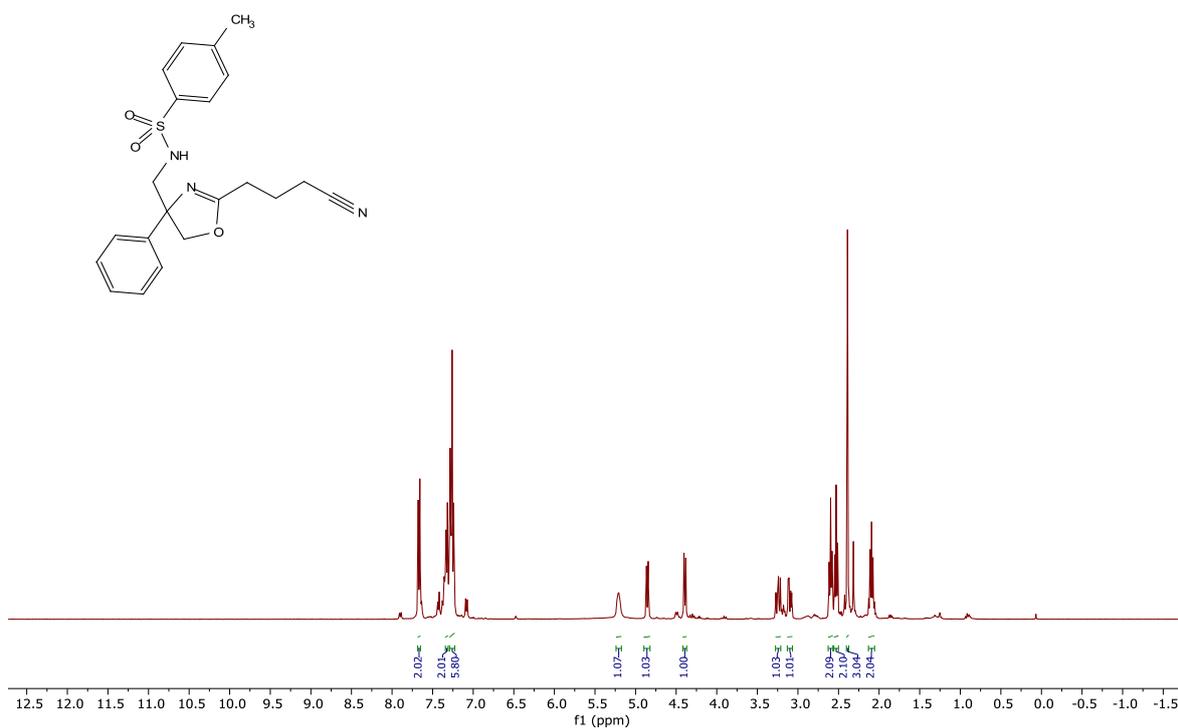
Single crystals of  $C_{37}H_{40}N_4O_6S_2$  were A suitable crystal was selected on a D8V\_Mo diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 1) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
- 2) Sheldrick, G.M. (2008). *Acta Cryst.* A64, 112-122.
- 3) Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

**Crystal Data** for  $C_{37}H_{40}N_4O_6S_2$  ( $M = 700.85$  g/mol): monoclinic, space group  $C2/c$  (no. 15),  $a = 15.0965(9)$  Å,  $b = 12.1682(7)$  Å,  $c = 21.8118(12)$  Å,  $\beta = 94.212(2)^\circ$ ,  $V = 3995.9(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 120$  K,  $\mu(\text{MoK}\alpha) = 0.179$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.165$  g/cm<sup>3</sup>, 36802 reflections measured ( $4.304^\circ \leq 2\theta \leq 54.962^\circ$ ), 4596 unique ( $R_{\text{int}} = 0.0435$ ,  $R_{\text{sigma}} = 0.0288$ ) which were used in all calculations. The final  $R_1$  was 0.0385 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1092 (all data).

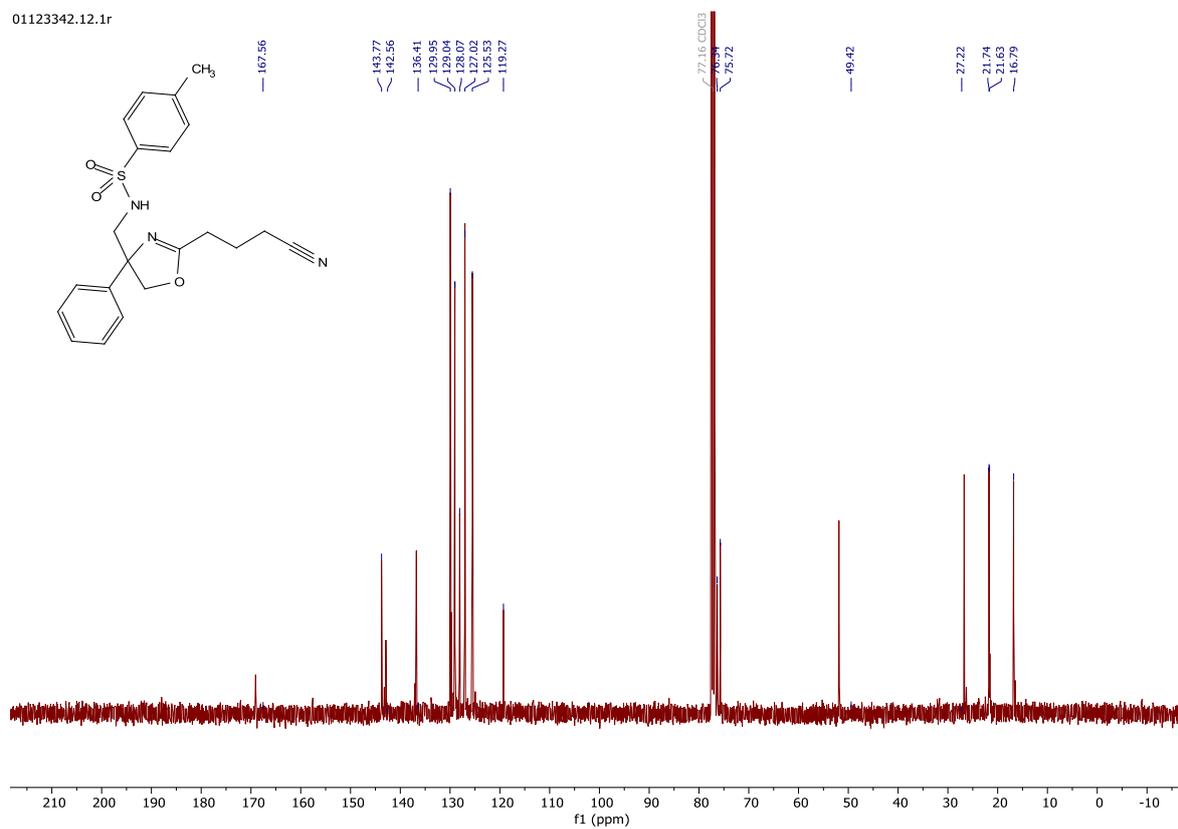
# Compound 2-195 $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )

01123342.10.1.1r



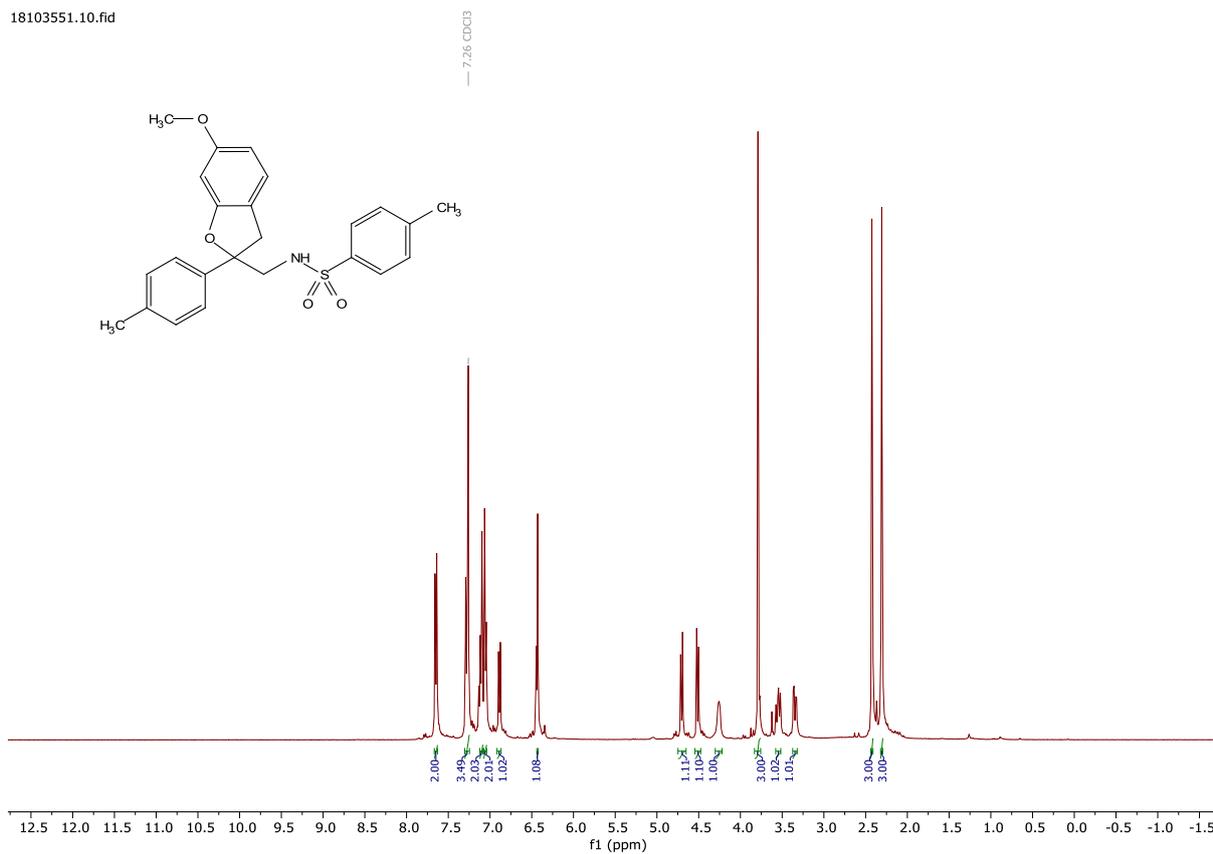
# Compound 2-195 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )

01123342.12.1r



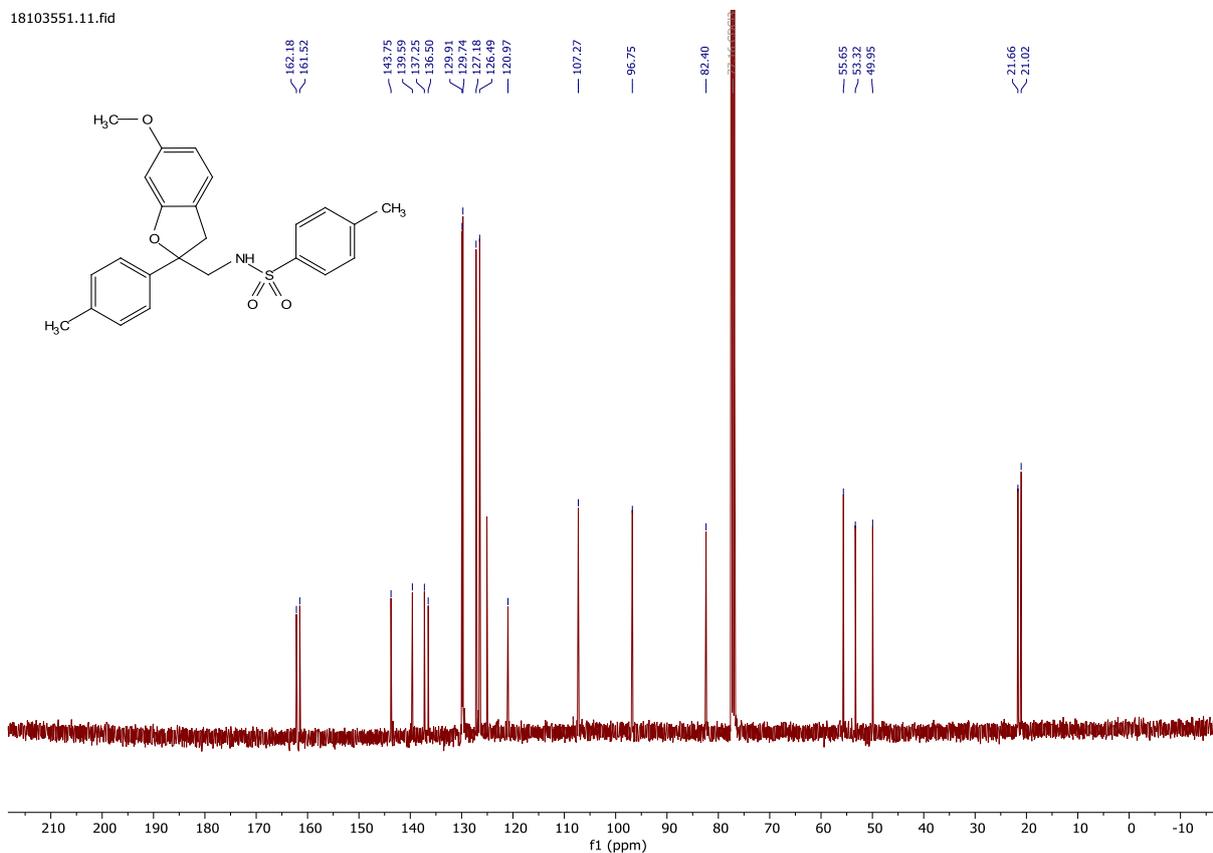
# Compound 2-197 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

18103551.10.fid

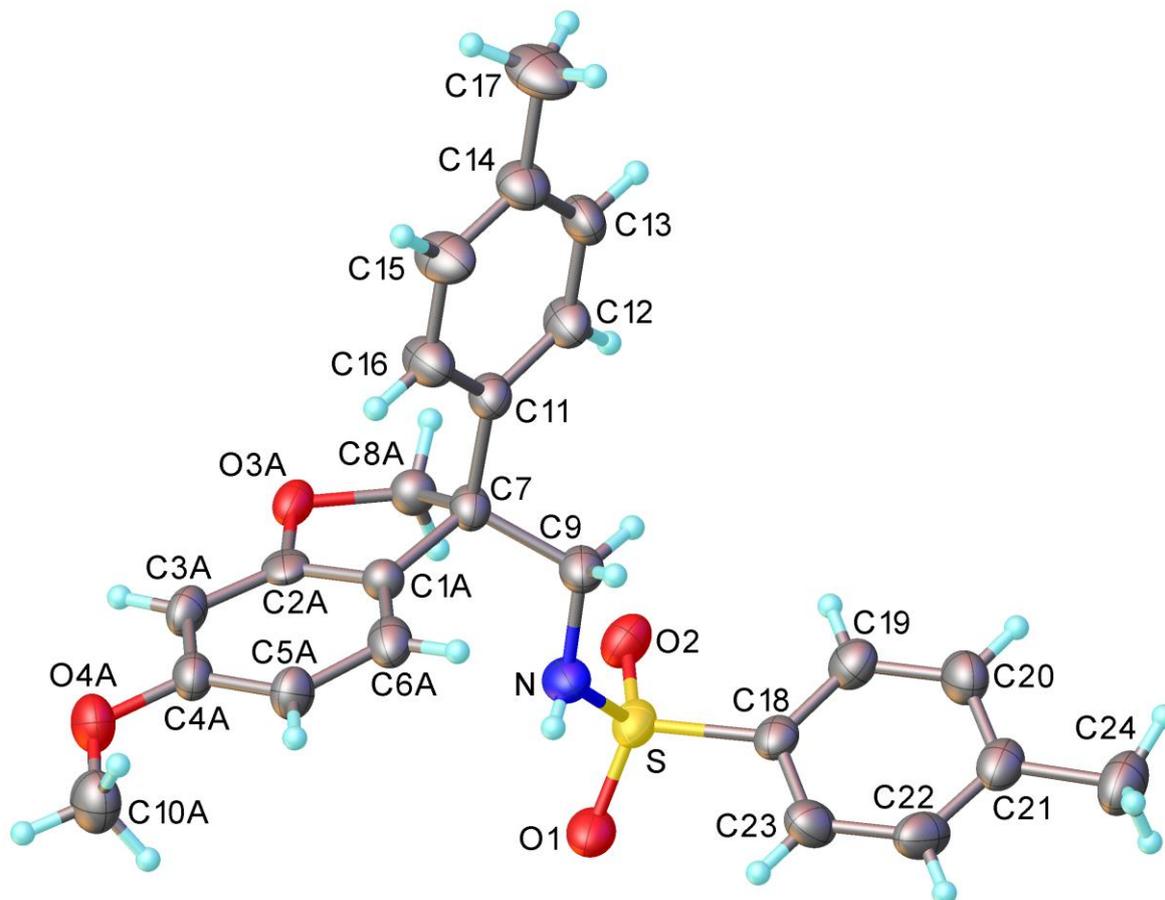


# Compound 2-197 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

18103551.11.fid



## Compound 2-197 X-ray structure



*Atomic displacement ellipsoids are drawn at the 50% probability level.*

Compound 4-7 was crystallised by solvent evaporation using a mixture Hexane: EtOAc

### Experimental

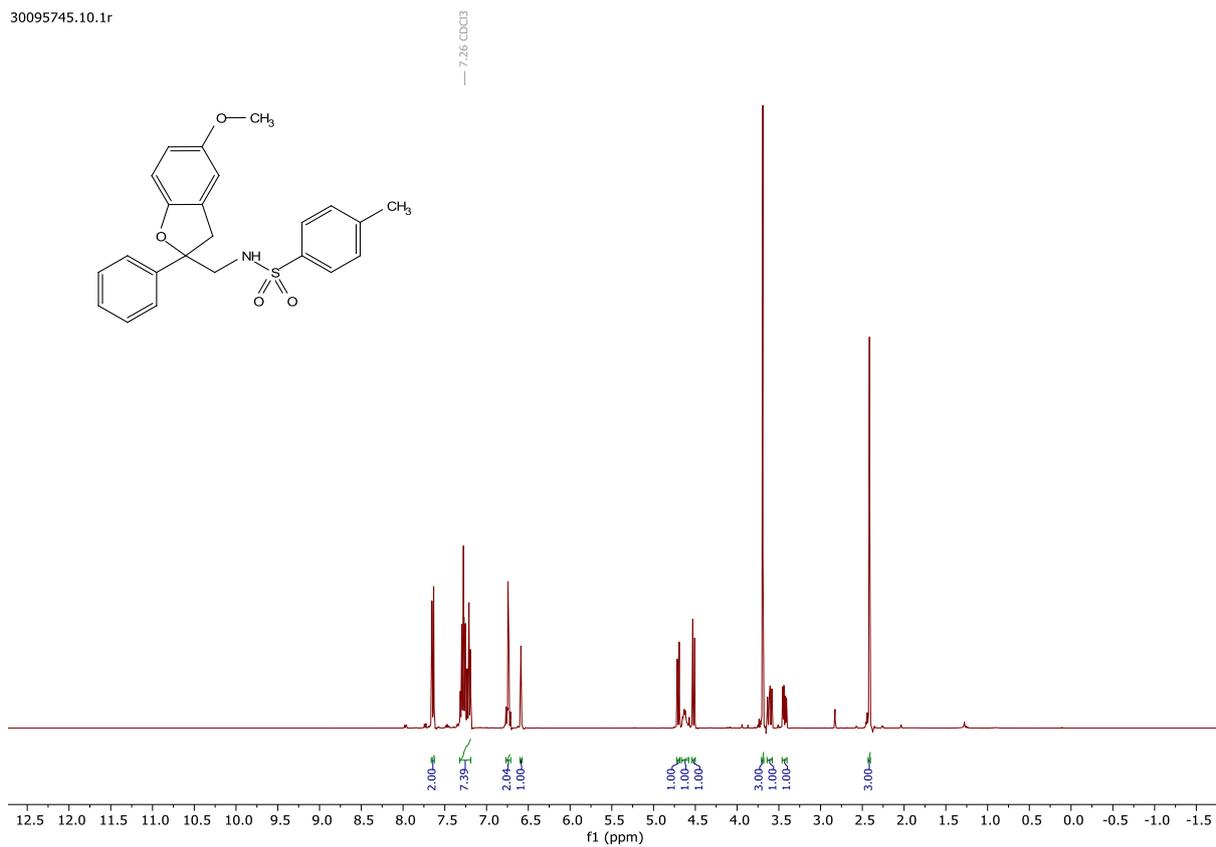
Single crystals of  $C_{24}H_{25}NO_4S$  were A suitable crystal was selected on a D8V\_Mo diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 4) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 5) Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
- 6) Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

**Crystal Data** **Crystal Data** for  $C_{24}H_{25}NO_4S$  ( $M = 423.51$  g/mol): monoclinic, space group  $P2_1/n$  (no. 14),  $a = 10.9761(8)$  Å,  $b = 11.2566(8)$  Å,  $c = 17.2670(13)$  Å,  $\beta = 98.209(2)^\circ$ ,  $V = 2111.5(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 120$  K,  $\mu(\text{MoK}\alpha) = 0.184$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.332$  g/cm<sup>3</sup>, 32741 reflections measured ( $4.146^\circ \leq 2\theta \leq 50.17^\circ$ ), 3761 unique ( $R_{\text{int}} = 0.0775$ ,  $R_{\text{sigma}} = 0.0604$ ) which were used in all calculations. The final  $R_1$  was 0.0489 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1210 (all data).

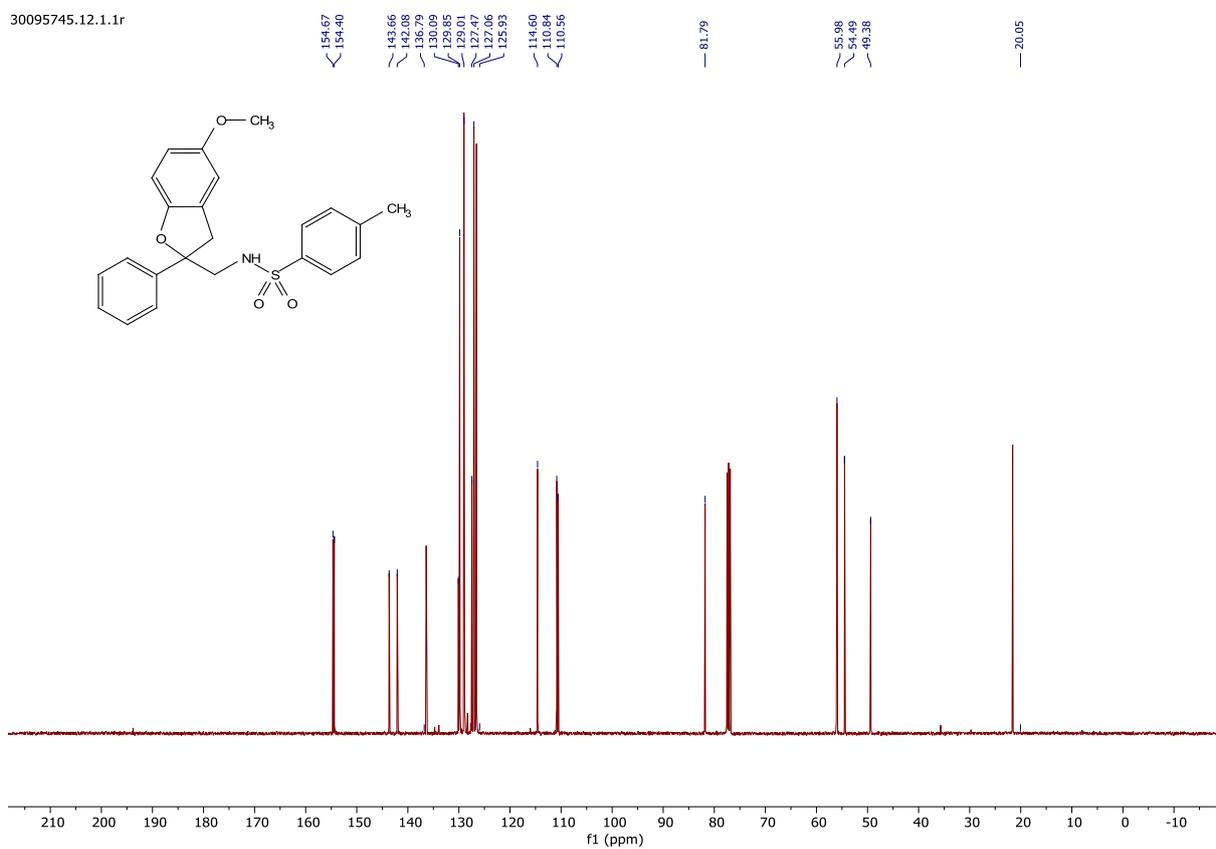
# Compound 2-199 $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )

30095745.10.1r



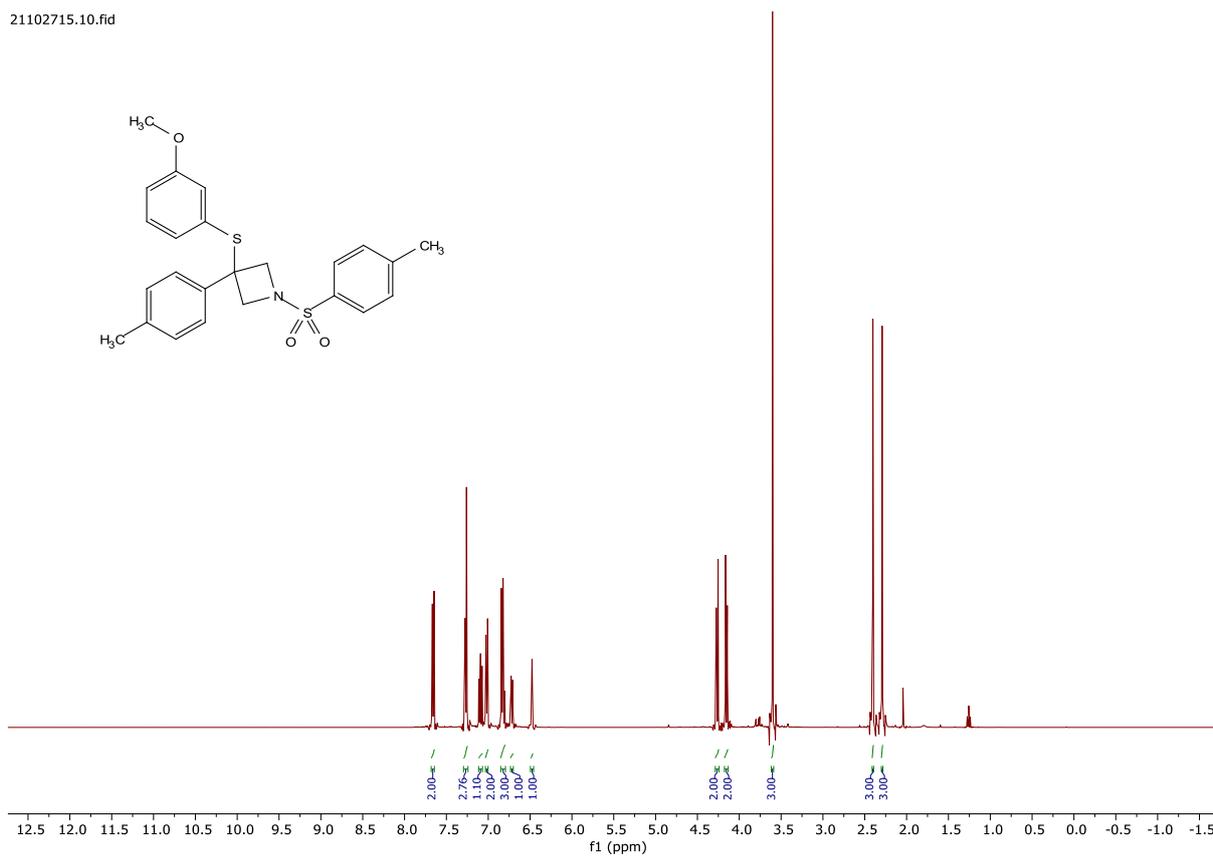
# Compound 2-199 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )

30095745.12.1.1r



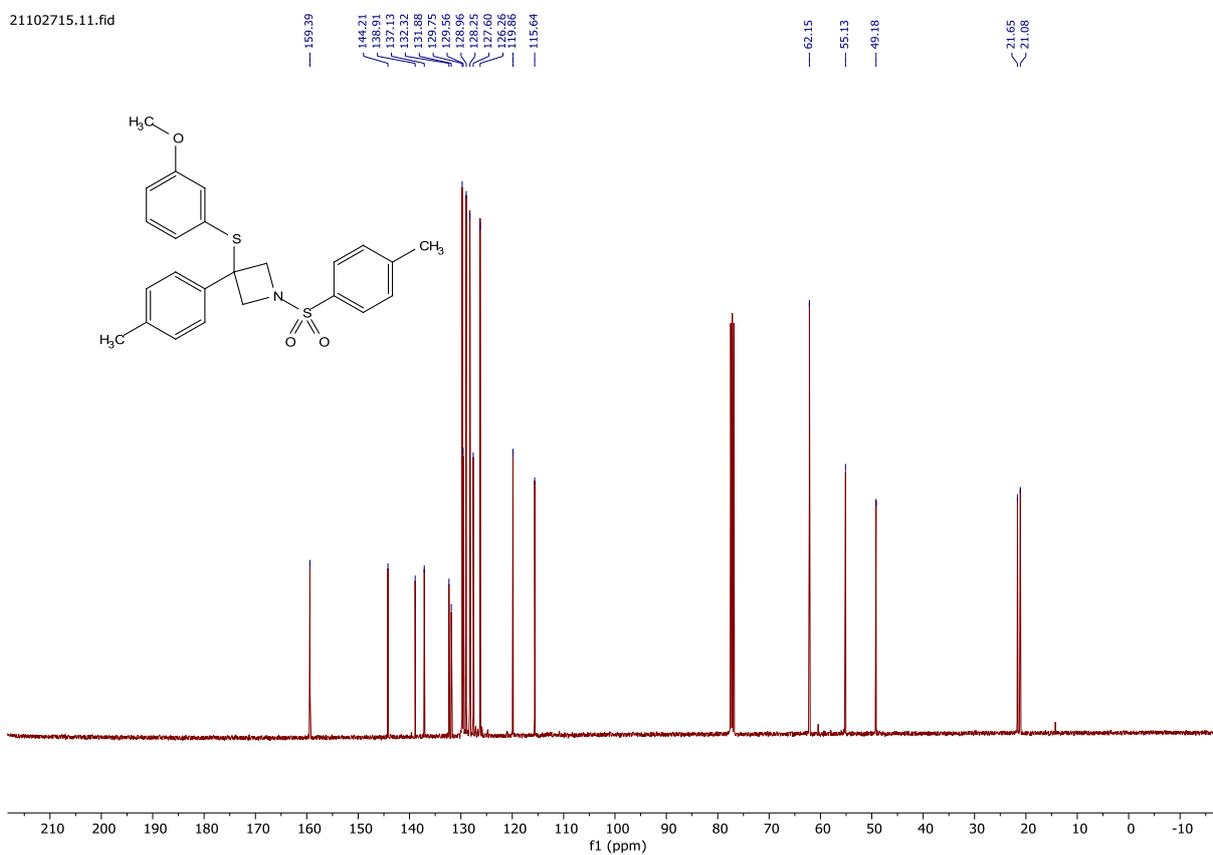
# Compound 2-201 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

21102715.10.fid

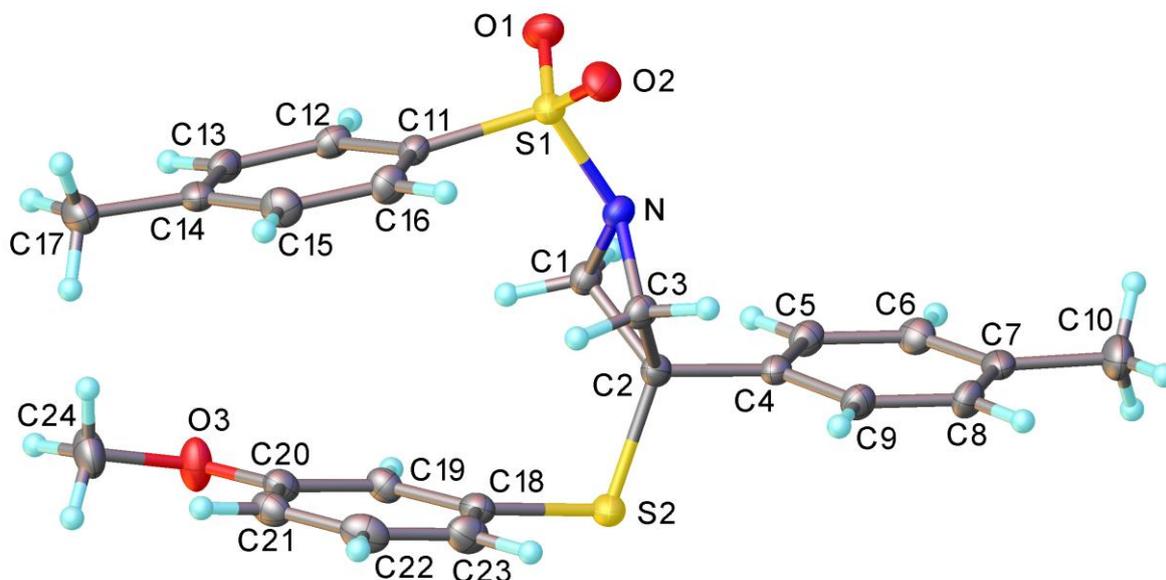


# Compound 2-201 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

21102715.11.fid



## Compound 2-202 X-ray structure



*Atomic displacement ellipsoids are drawn at the 50% probability level.*

Compound 9 was crystallised by solvent evaporation using a mixture Hexane: EtOAc

### Experimental

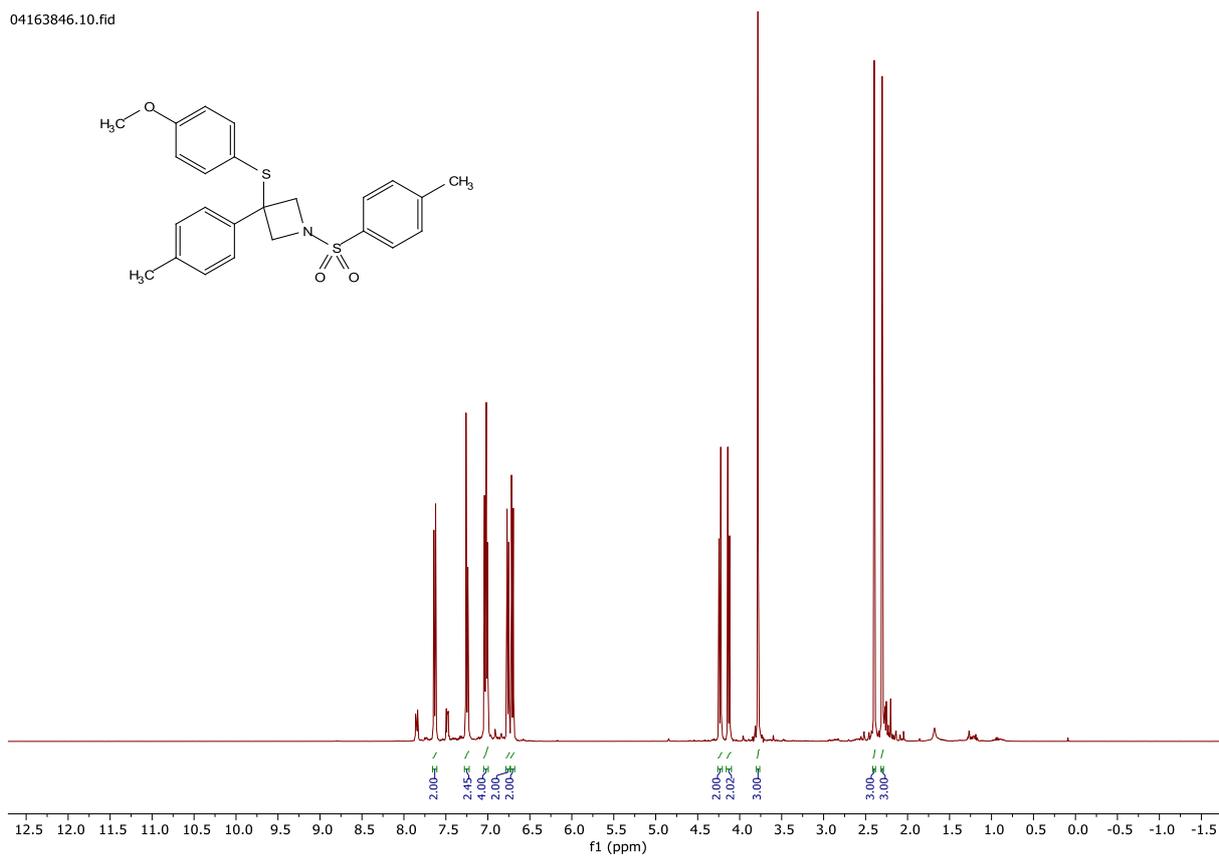
Single crystals of  $C_{24}H_{25}NO_3S_2$  were A suitable crystal was selected on a D8V\_Mo diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 1) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
- 2) Sheldrick, G.M. (2008). *Acta Cryst.* A64, 112-122.
- 3) Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

**Crystal Data** for  $C_{24}H_{25}NO_3S_2$  ( $M = 439.57$  g/mol): triclinic, space group P-1 (no. 2),  $a = 5.9971(2)$  Å,  $b = 19.0997(8)$  Å,  $c = 20.3305(8)$  Å,  $\alpha = 69.0014(14)^\circ$ ,  $\beta = 87.1419(16)^\circ$ ,  $\gamma = 87.6311(16)^\circ$ ,  $V = 2170.67(15)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 120$  K,  $\mu(\text{MoK}\alpha) = 0.271$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.345$  g/cm<sup>3</sup>, 45131 reflections measured ( $4.082^\circ \leq 2\theta \leq 57.398^\circ$ ), 11184 unique ( $R_{\text{int}} = 0.0425$ ,  $R_{\text{sigma}} = 0.0437$ ) which were used in all calculations. The final  $R_1$  was 0.0386 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1009 (all data).

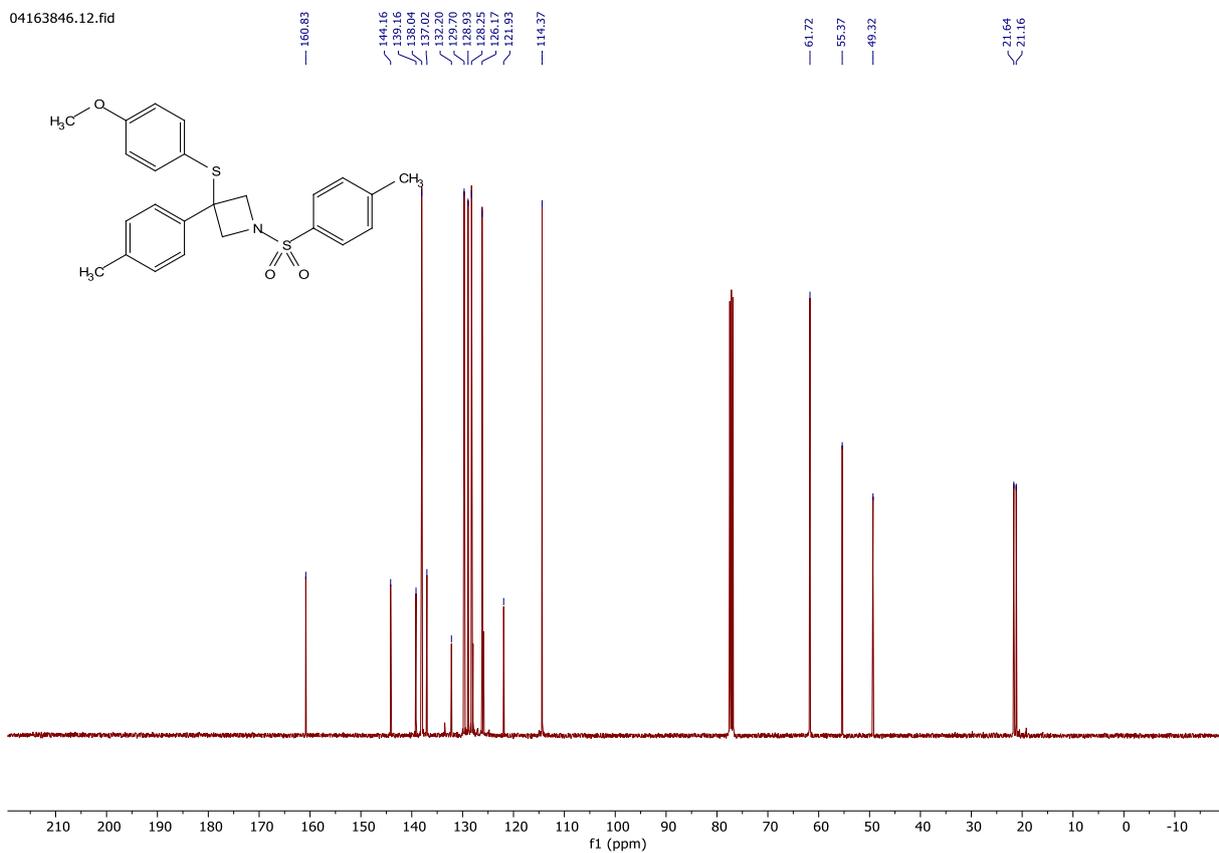
# Compound 2-203 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

04163846.10.fid



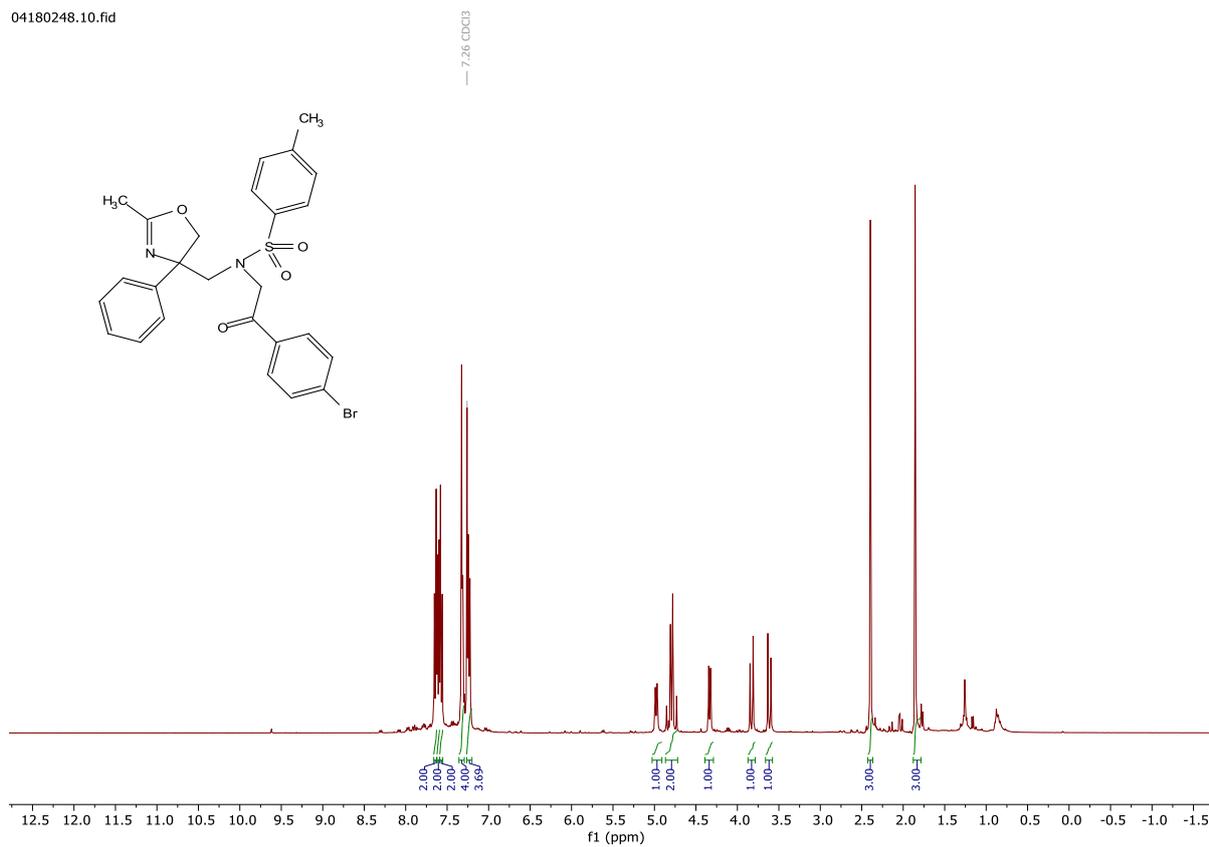
# Compound 2-203 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

04163846.12.fid



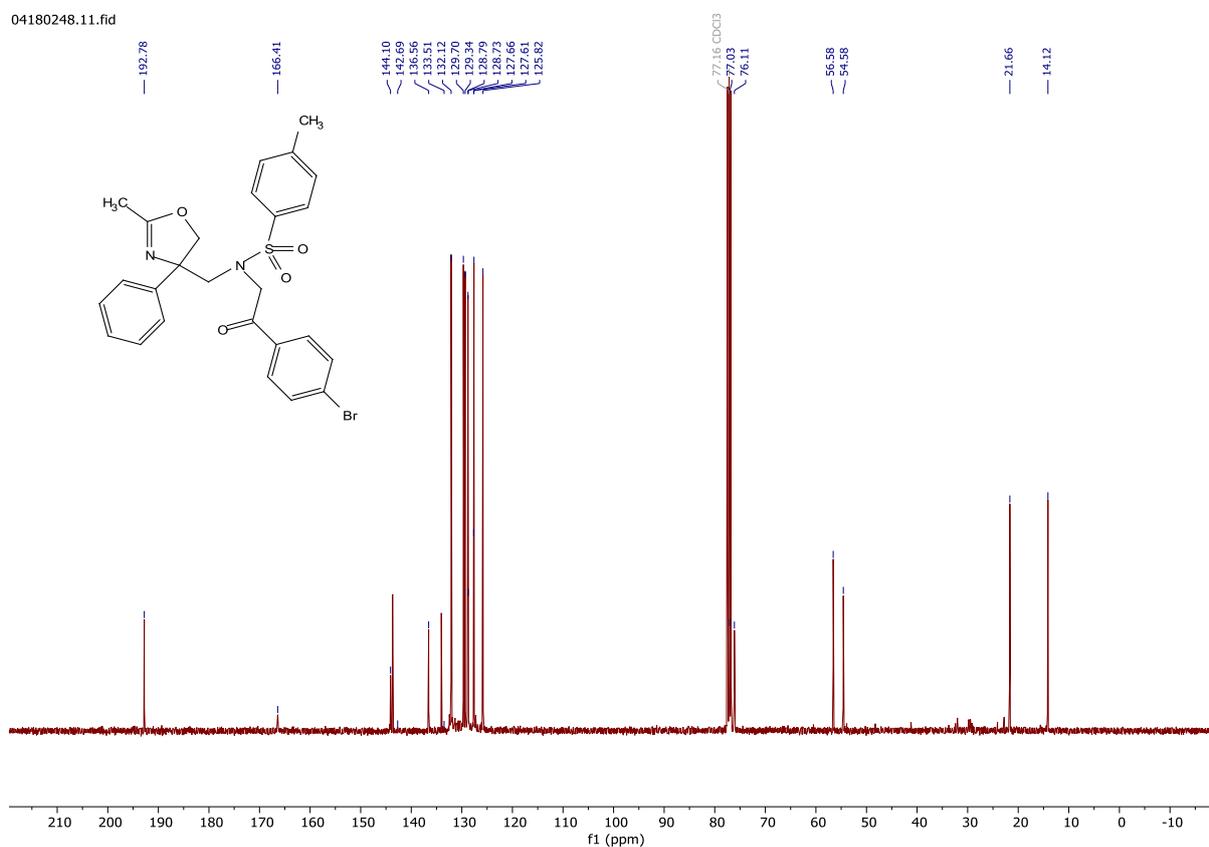
# Compound 2-205 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

04180248.10.fid



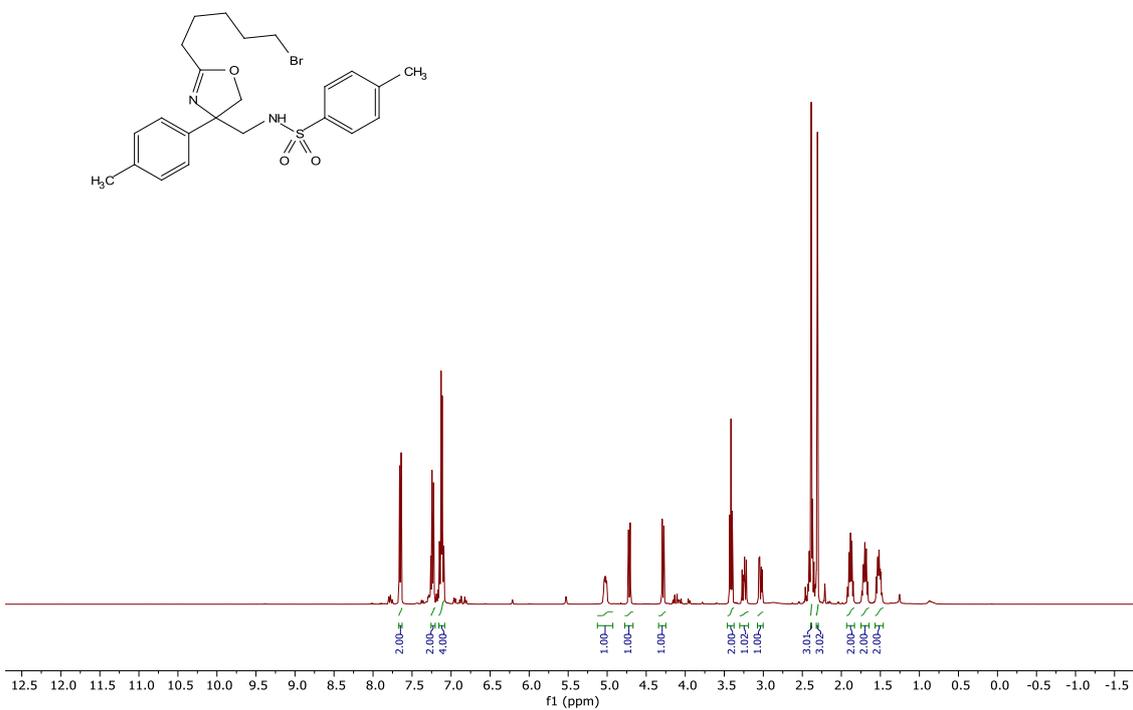
# Compound 2-205 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

04180248.11.fid



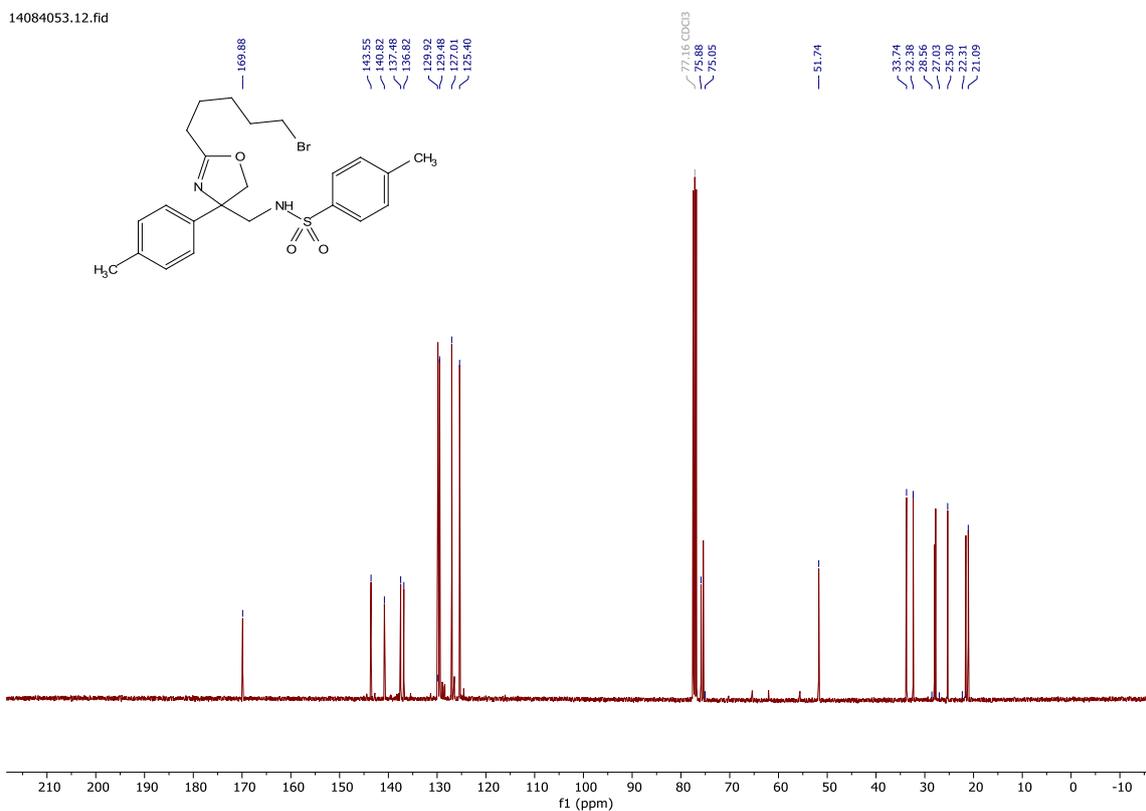
# Compound 2-206 $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )

14084053.10.FID

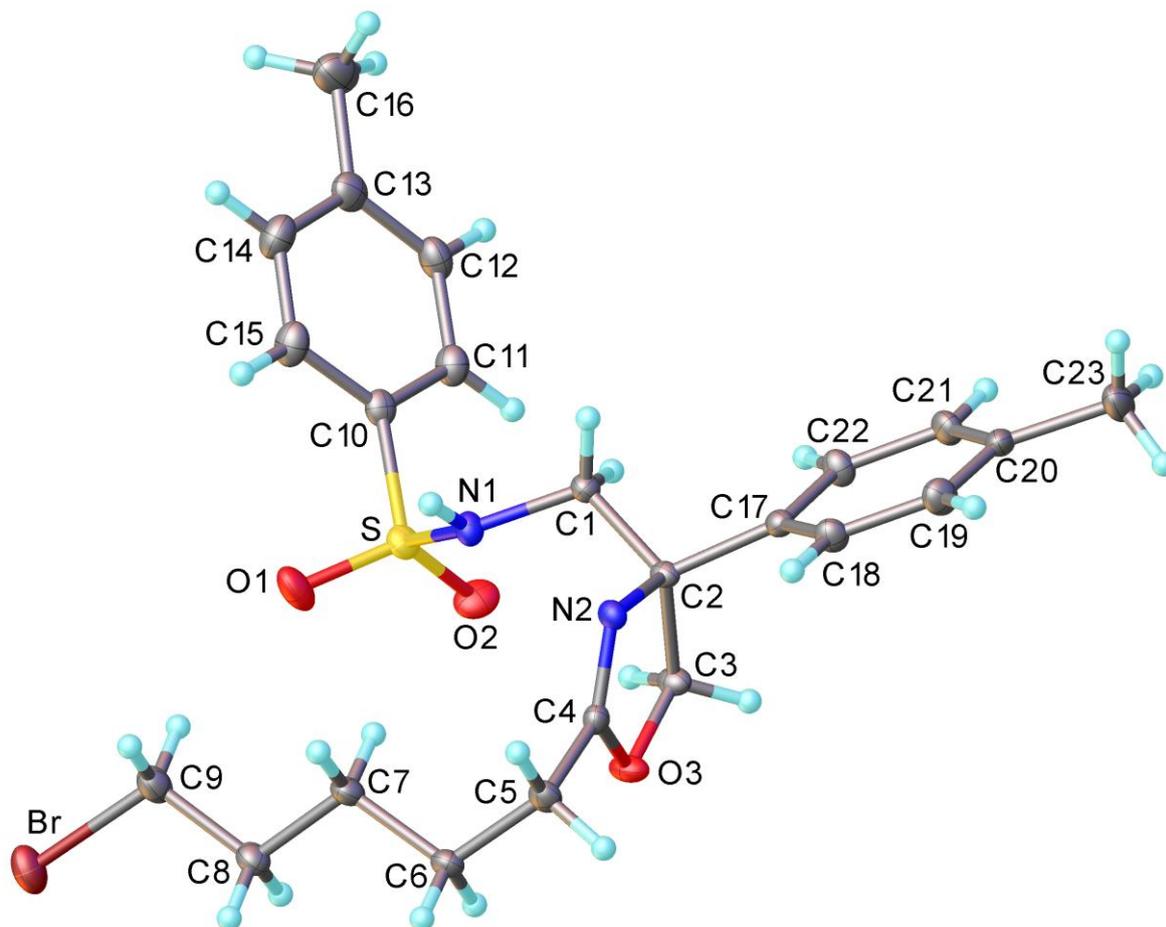


# Compound 2-206 $^{13}\text{C}\{^1\text{H}\}$ NMR (101MHz, $\text{CDCl}_3$ )

14084053.12.fid



## Compound 2-206 X-ray structure



Atomic displacement ellipsoids are drawn at the 50% probability level.

Compound 4-23 was crystallised by solvent evaporation using a mixture Hexane: EtOAc

### Experimental

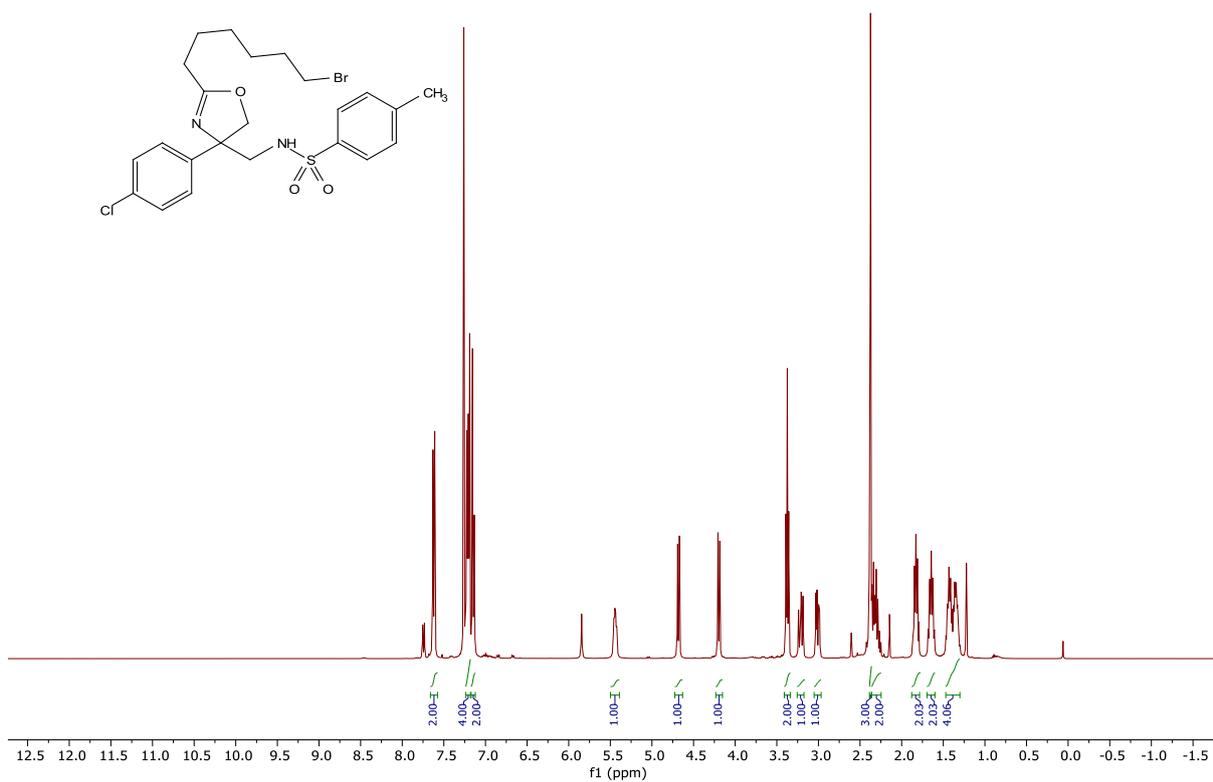
Single crystals of  $C_{23}H_{29}BrN_2O_3S$  were A suitable crystal was selected on a D8V\_Mo diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 1) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
- 2) Sheldrick, G.M. (2008). *Acta Cryst.* A64, 112-122.
- 3) Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

**Crystal Data** for  $C_{23}H_{29}BrN_2O_3S$  ( $M = 493.45$  g/mol): monoclinic, space group  $P2_1/n$  (no. 14),  $a = 12.7711(8)$  Å,  $b = 11.4910(7)$  Å,  $c = 16.0665(10)$  Å,  $\beta = 101.628(2)^\circ$ ,  $V = 2309.4(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 120$  K,  $\mu(\text{MoK}\alpha) = 1.897$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.419$  g/cm<sup>3</sup>, 58322 reflections measured ( $4.39^\circ \leq 2\theta \leq 65.146^\circ$ ), 8408 unique ( $R_{\text{int}} = 0.0386$ ,  $R_{\text{sigma}} = 0.0274$ ) which were used in all calculations. The final  $R_1$  was 0.0306 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0844 (all data).

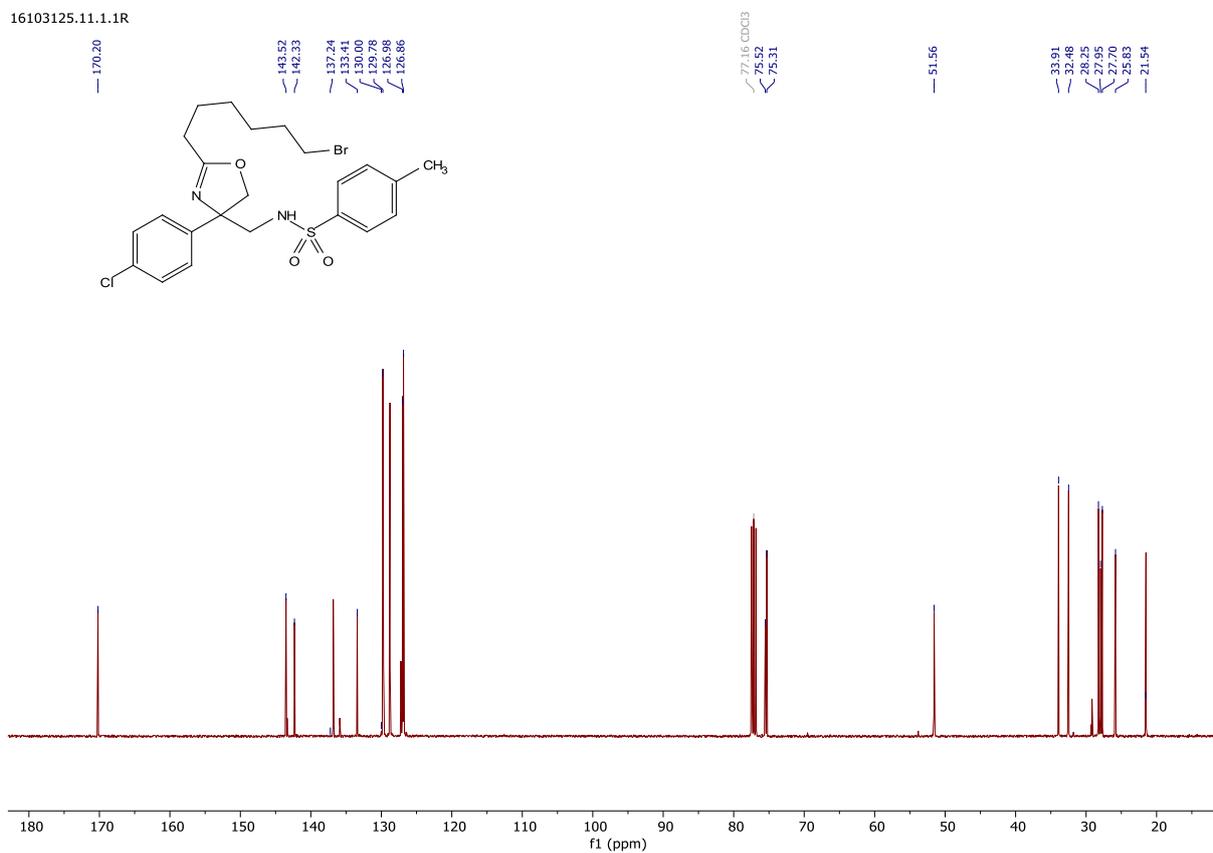
# Compound 2-207 $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )

16144408.10.FID



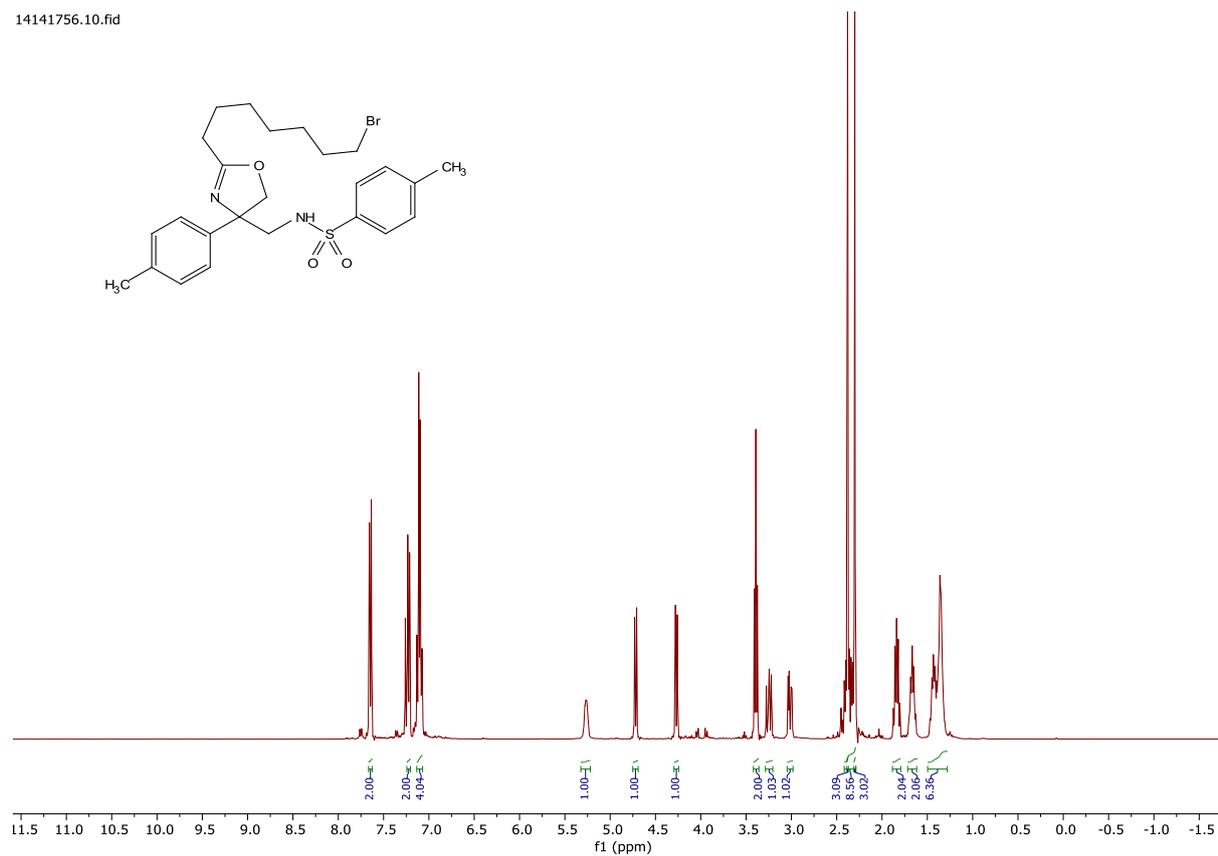
# Compound 2-207 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )

16103125.11.1.1R



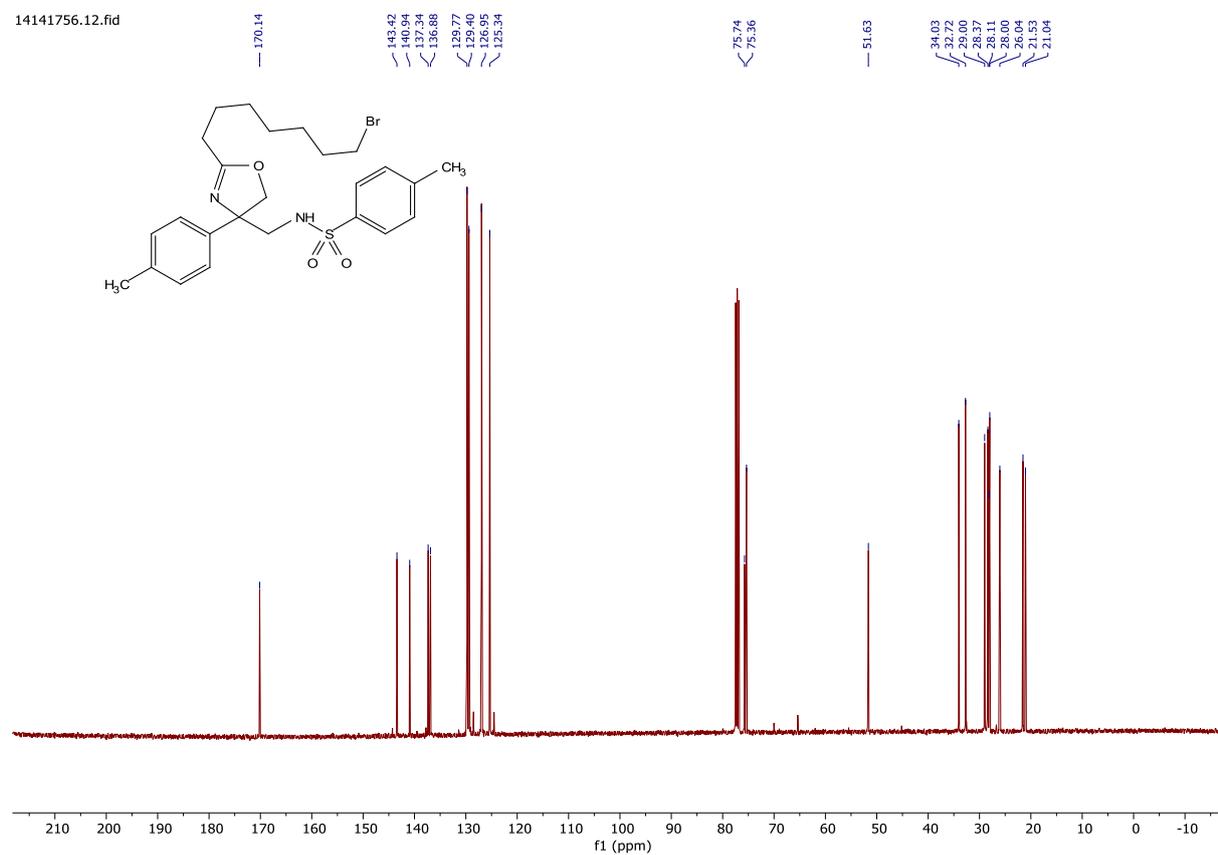
# Compound 2-209 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

14141756.10.fid



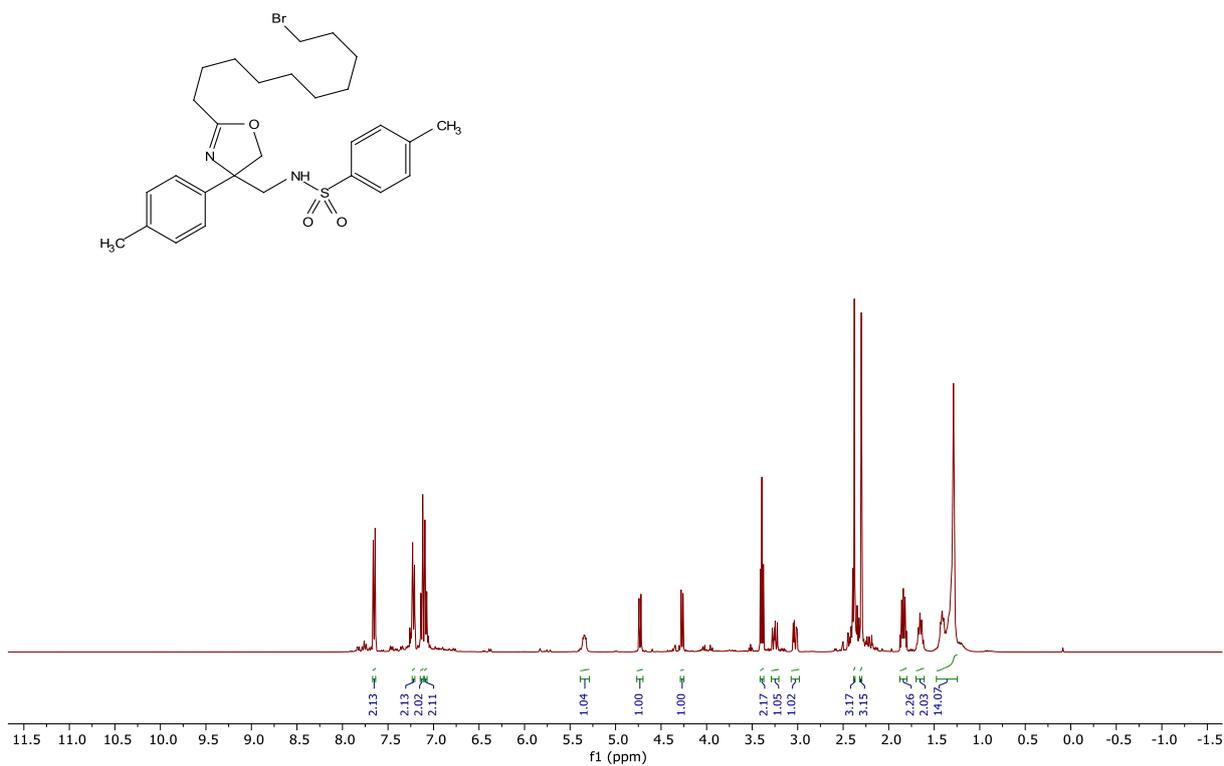
# Compound 2-209 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

14141756.12.fid



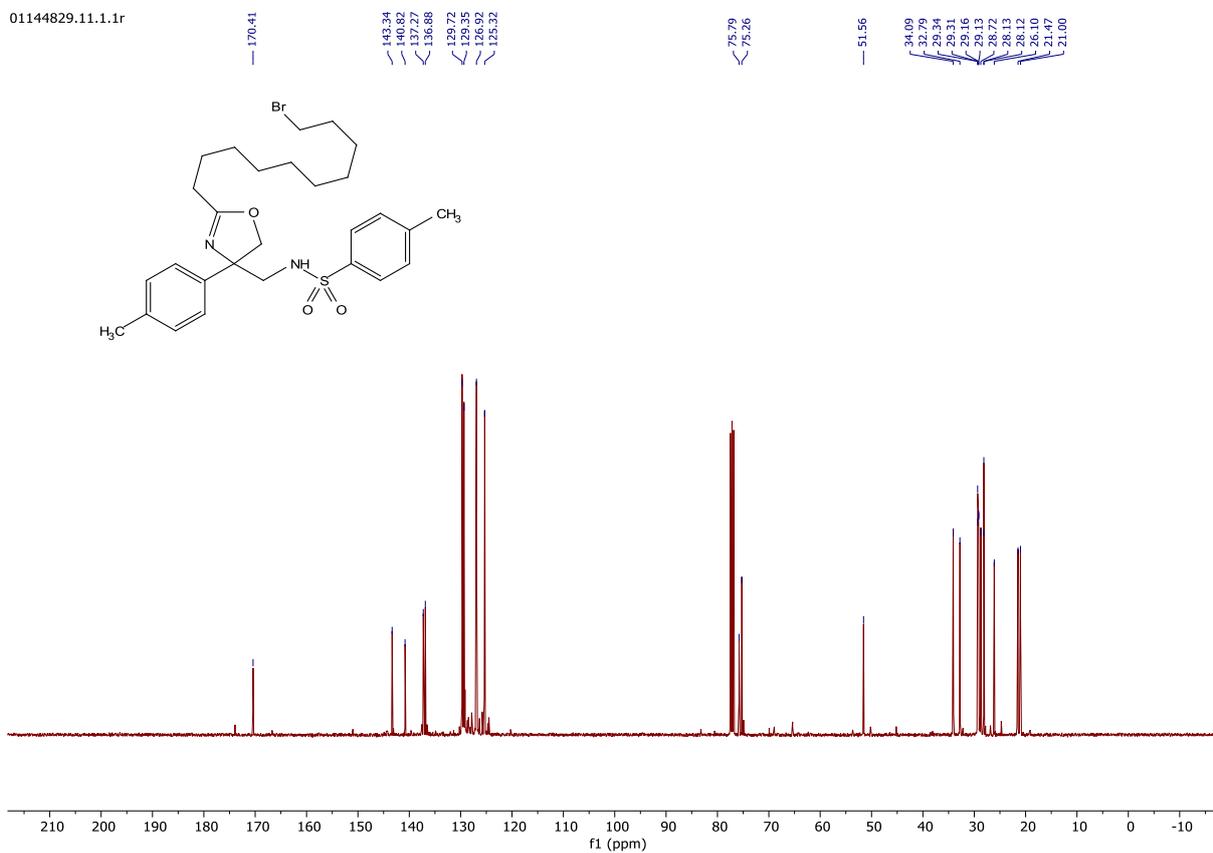
# Compound 2-210 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

01144829.10.fid



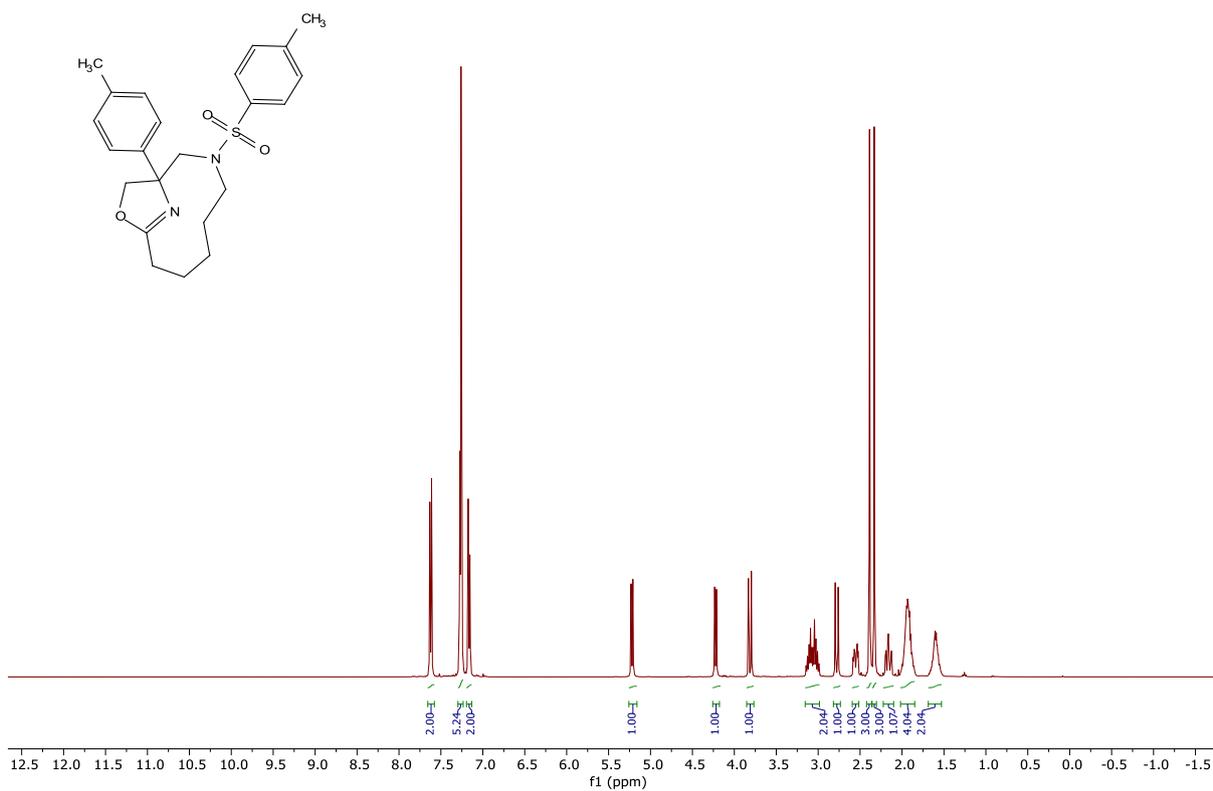
# Compound 2-210 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

01144829.11.1.1r



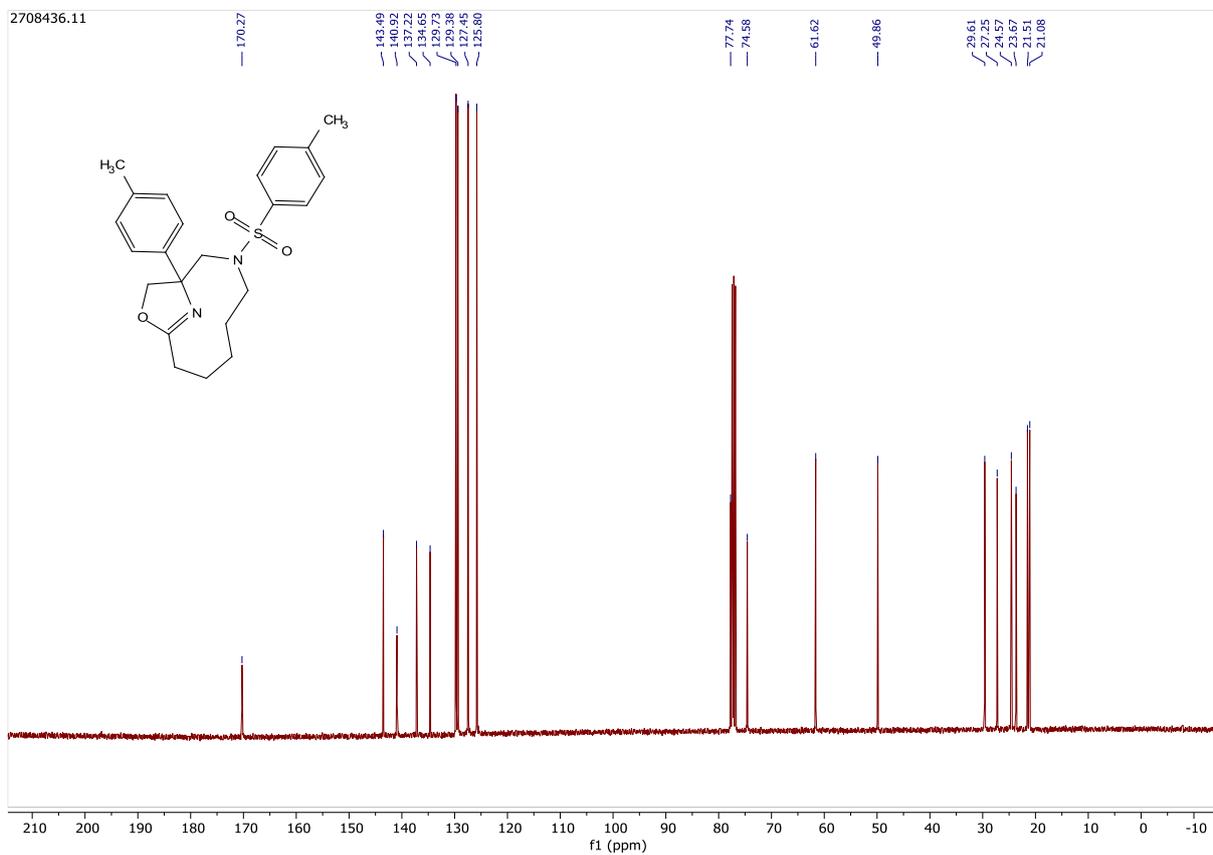
# Compound 2-211 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

2708436.10

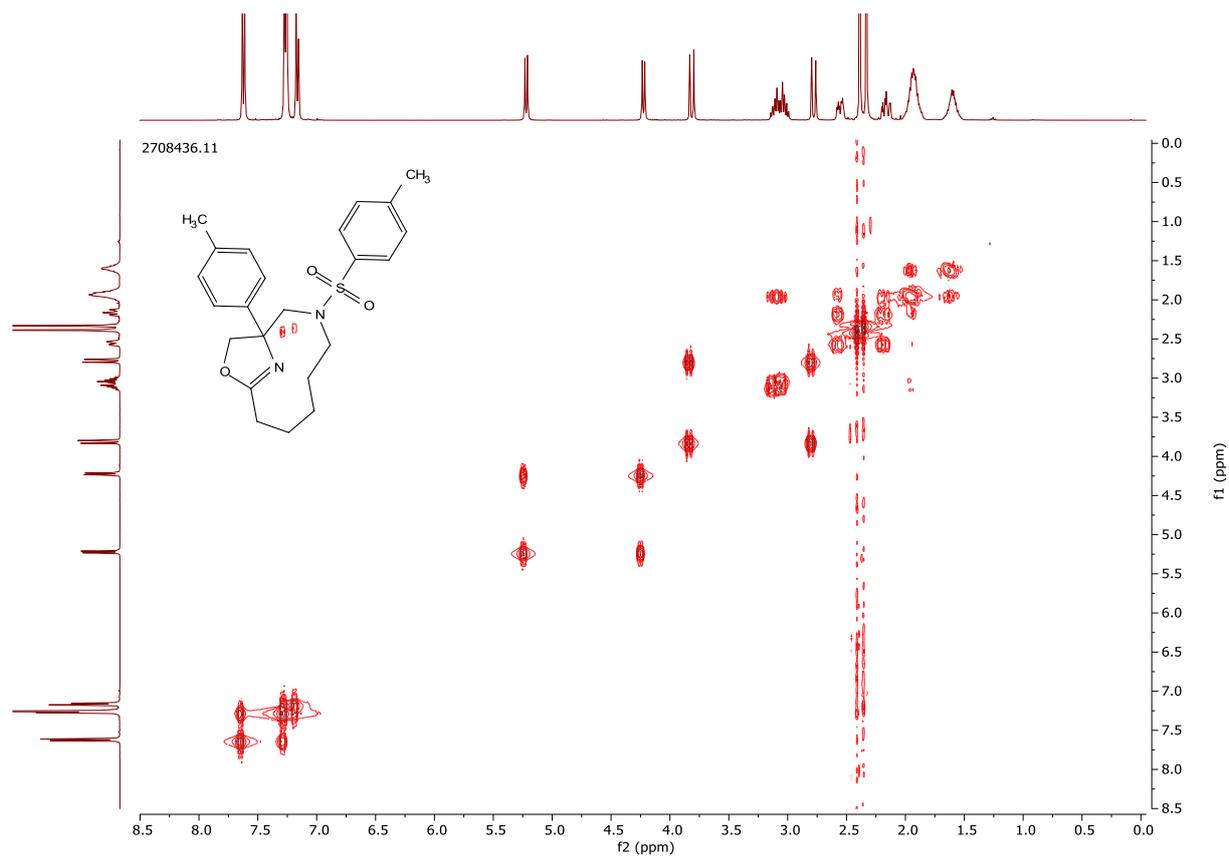


# Compound 2-211 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

2708436.11

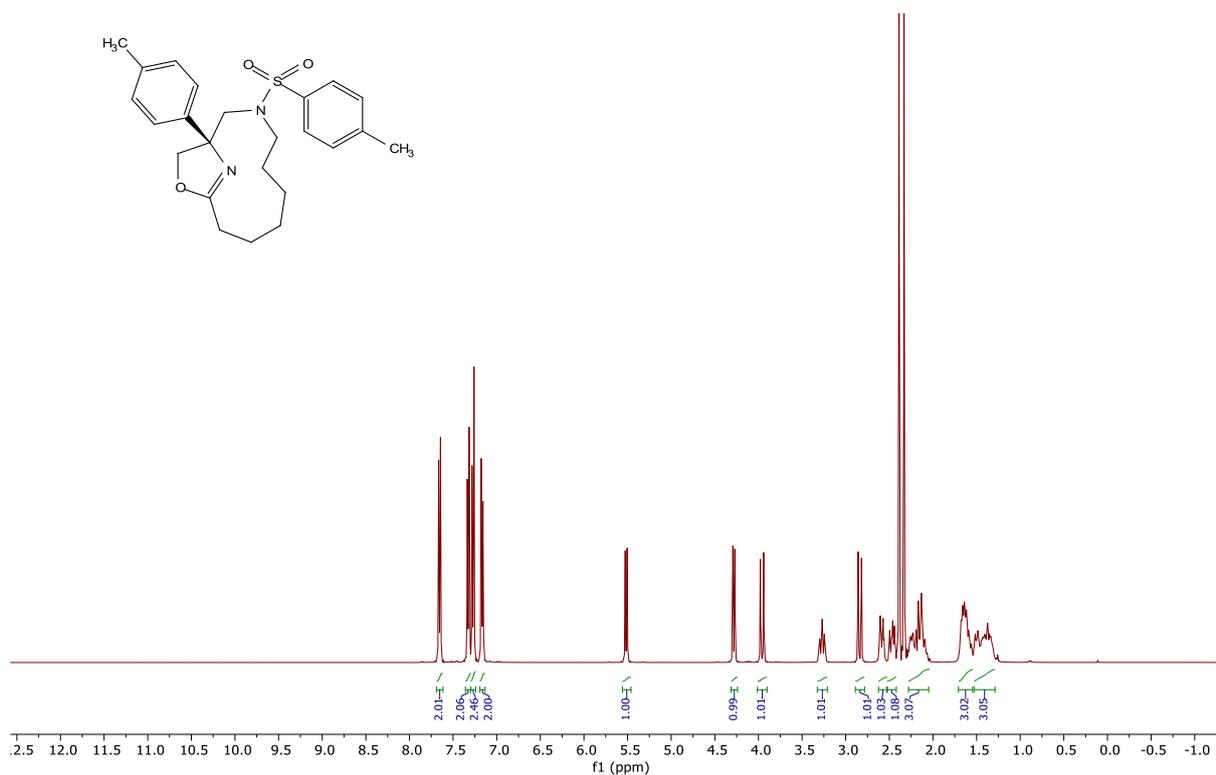


# Compound 2-211, COSY (400 MHz, CDCl<sub>3</sub>)



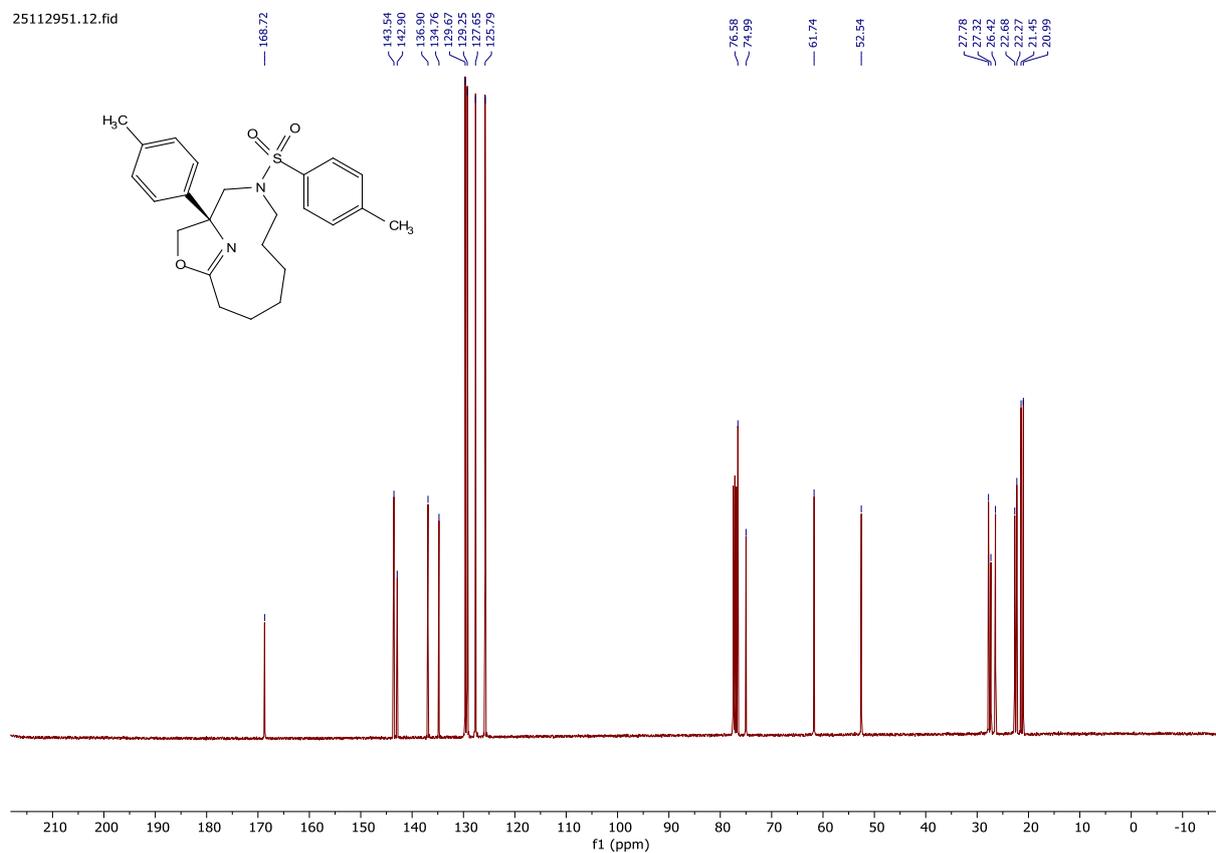
# Compound 2-212 $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )

25112951.10.fid

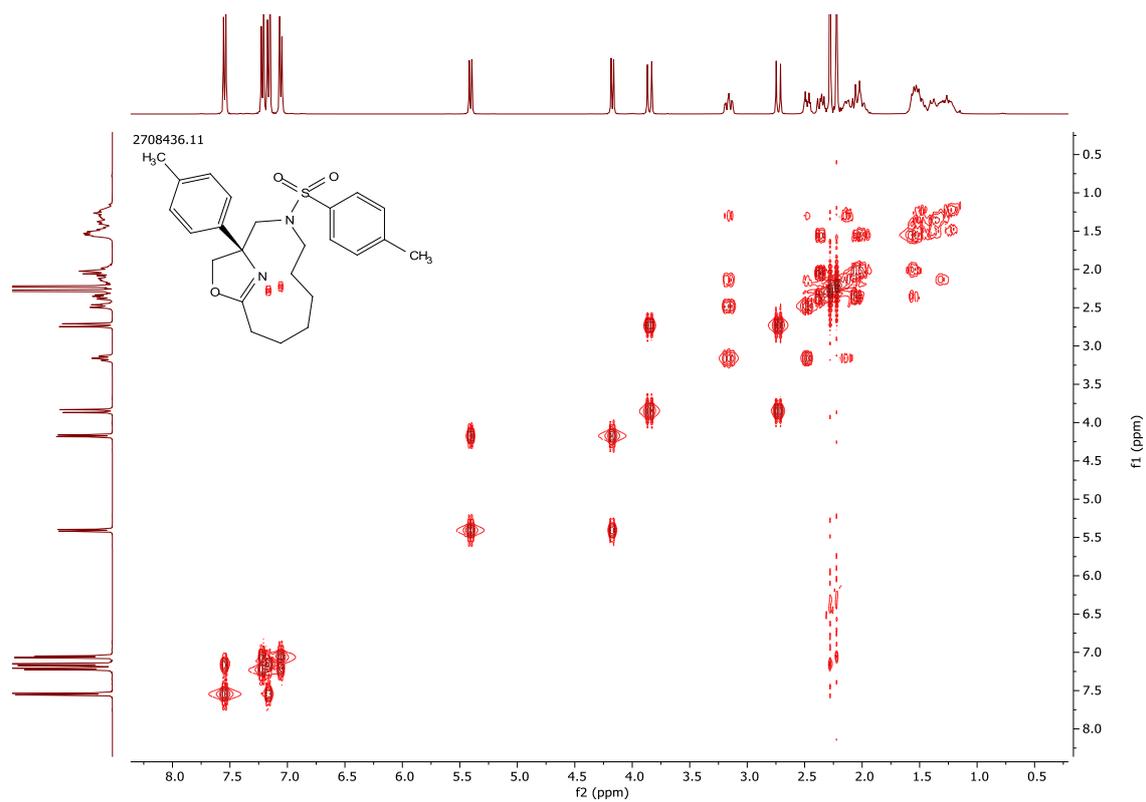


# Compound 2-212 $^{13}\text{C}$ { $^1\text{H}$ } NMR (101 MHz, $\text{CDCl}_3$ )

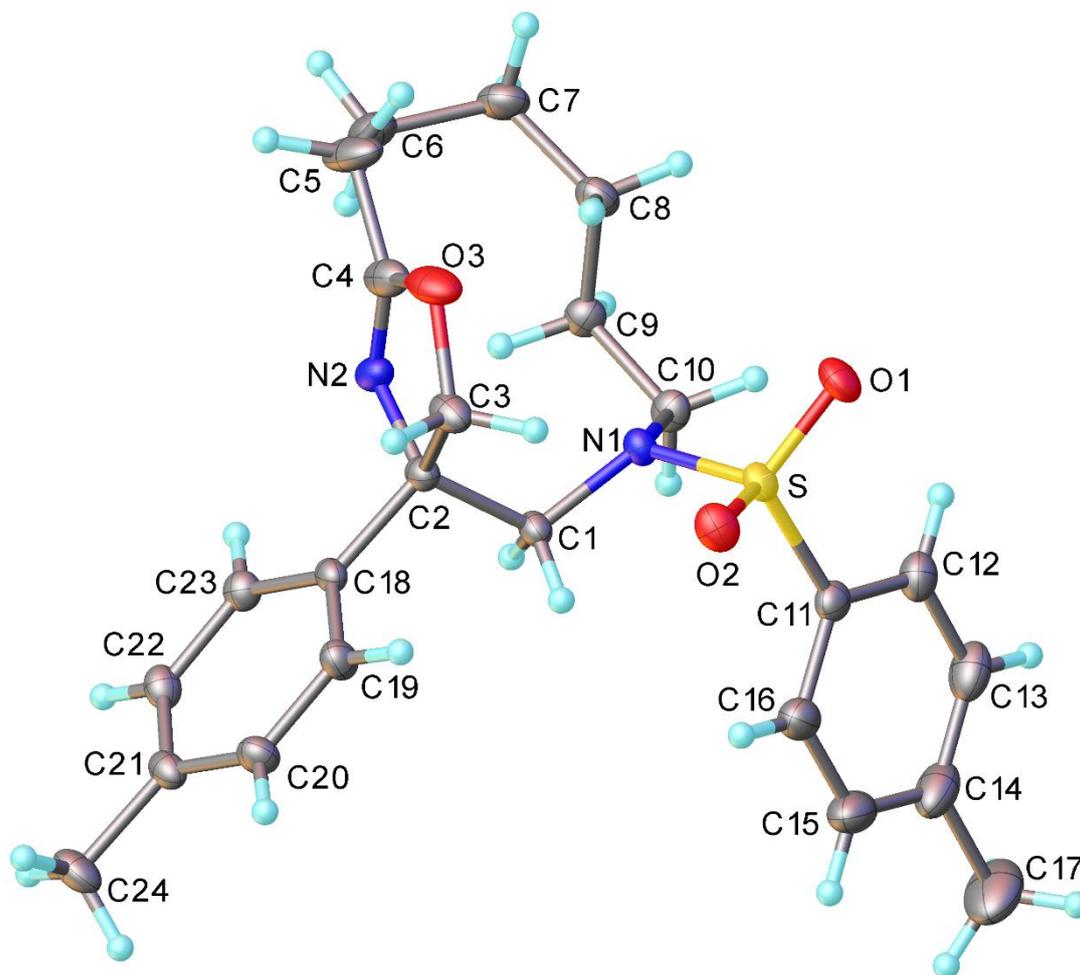
25112951.12.fid



# Compound 2-212 COSY (400 MHz, CDCl<sub>3</sub>)



## Compound 2-212 X-ray structure



*Atomic displacement ellipsoids are drawn at the 50% probability level.*

Compound 14-2 was crystallised by solvent evaporation using a mixture Hexane: EtOAc

### Experimental

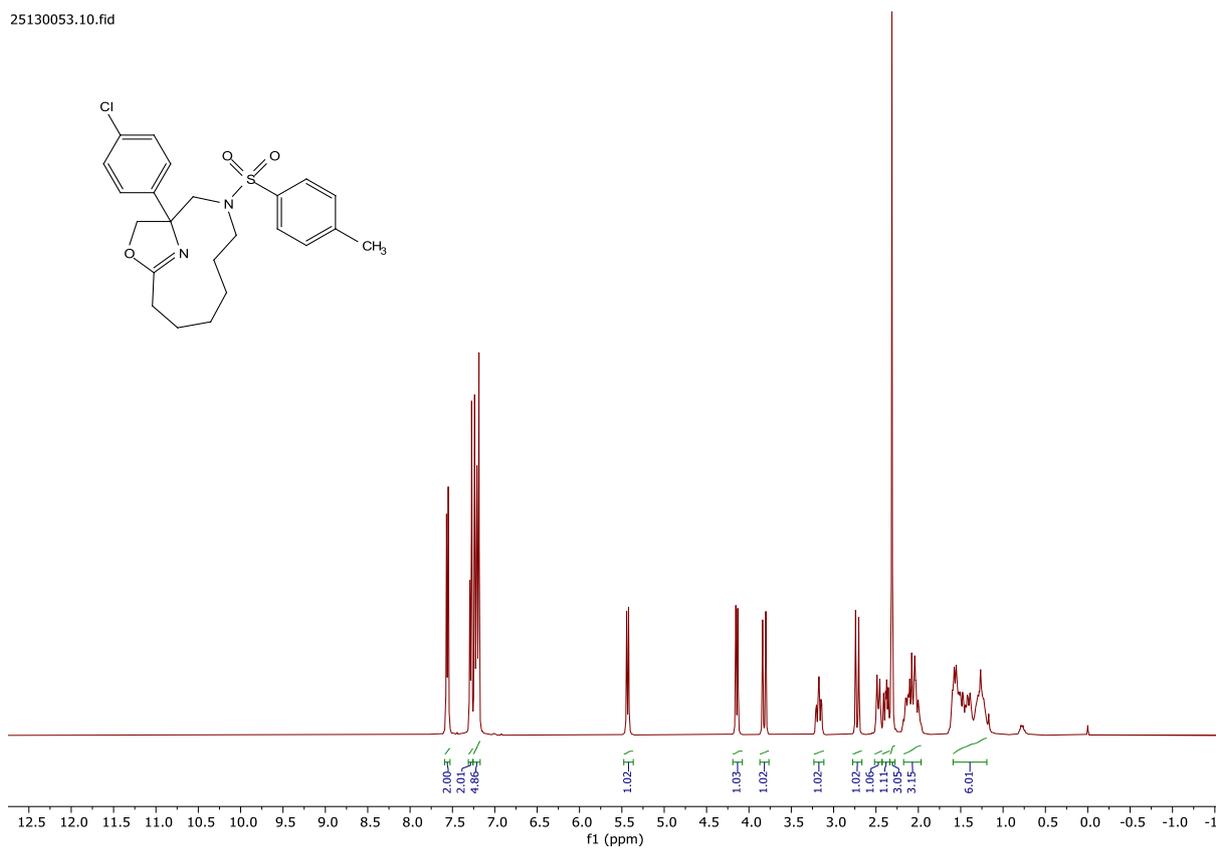
Single crystals of  $C_{24}H_{30}N_2O_3S$  were A suitable crystal was selected on a D8V\_Mo diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 1) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 2) Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
- 3) Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

**Crystal Data** for  $C_{24}H_{30}N_2O_3S$  ( $M = 426.56$  g/mol): monoclinic, space group  $P2_1/n$  (no. 14),  $a = 10.5538(7)$  Å,  $b = 21.7626(14)$  Å,  $c = 10.9319(7)$  Å,  $\beta = 116.908(2)^\circ$ ,  $V = 2239.0(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 120$  K,  $\mu(\text{MoK}\alpha) = 0.172$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.265$  g/cm<sup>3</sup>, 49376 reflections measured ( $4.452^\circ \leq 2\theta \leq 59.99^\circ$ ), 6522 unique ( $R_{\text{int}} = 0.0418$ ,  $R_{\text{sigma}} = 0.0287$ ) which were used in all calculations. The final  $R_1$  was 0.0399 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1099 (all data).

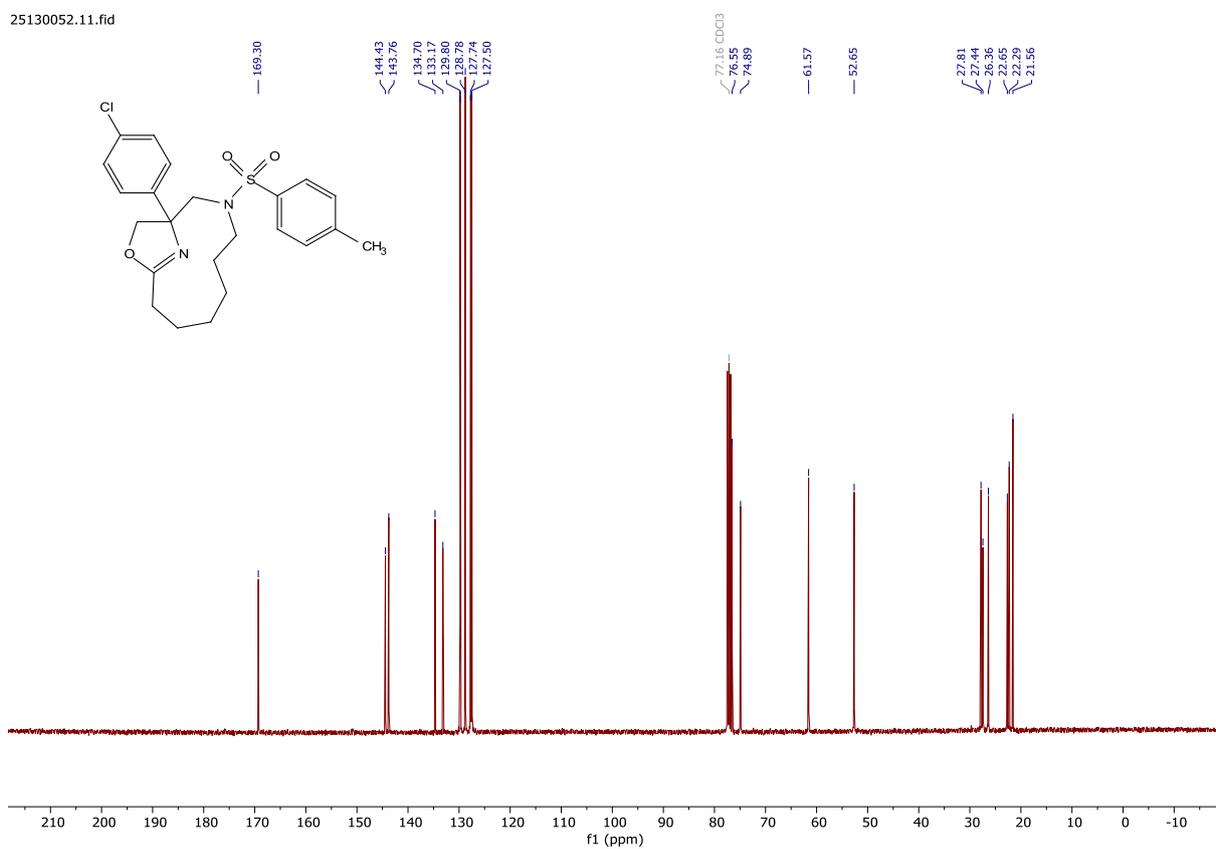
# Compound 2-213 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

25130053.10.fid

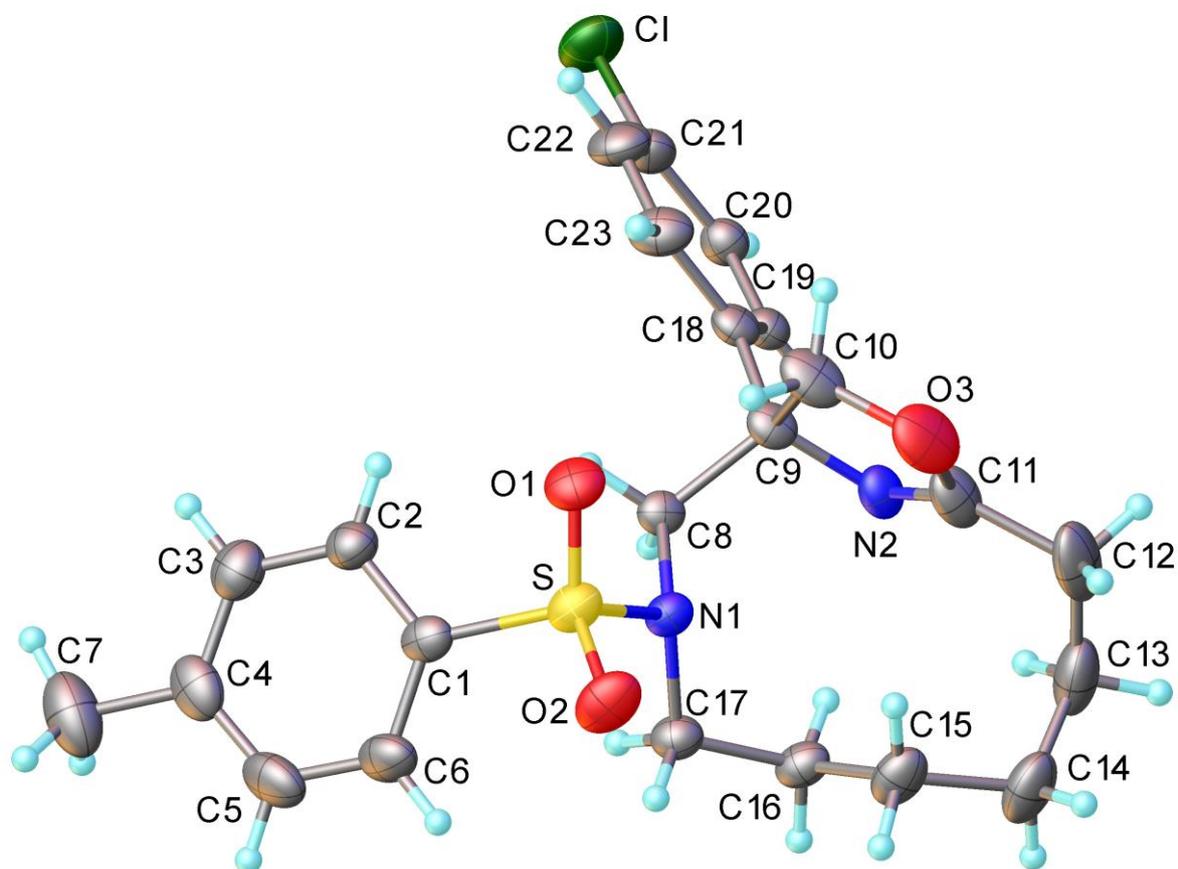


# Compound 2-213 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

25130052.11.fid



## Compound 2-213 X-ray structure



*Atomic displacement ellipsoids are drawn at the 50% probability level.*

Compound 14-3 was crystallised by solvent evaporation using a mixture Hexane: EtOAc

### Experimental

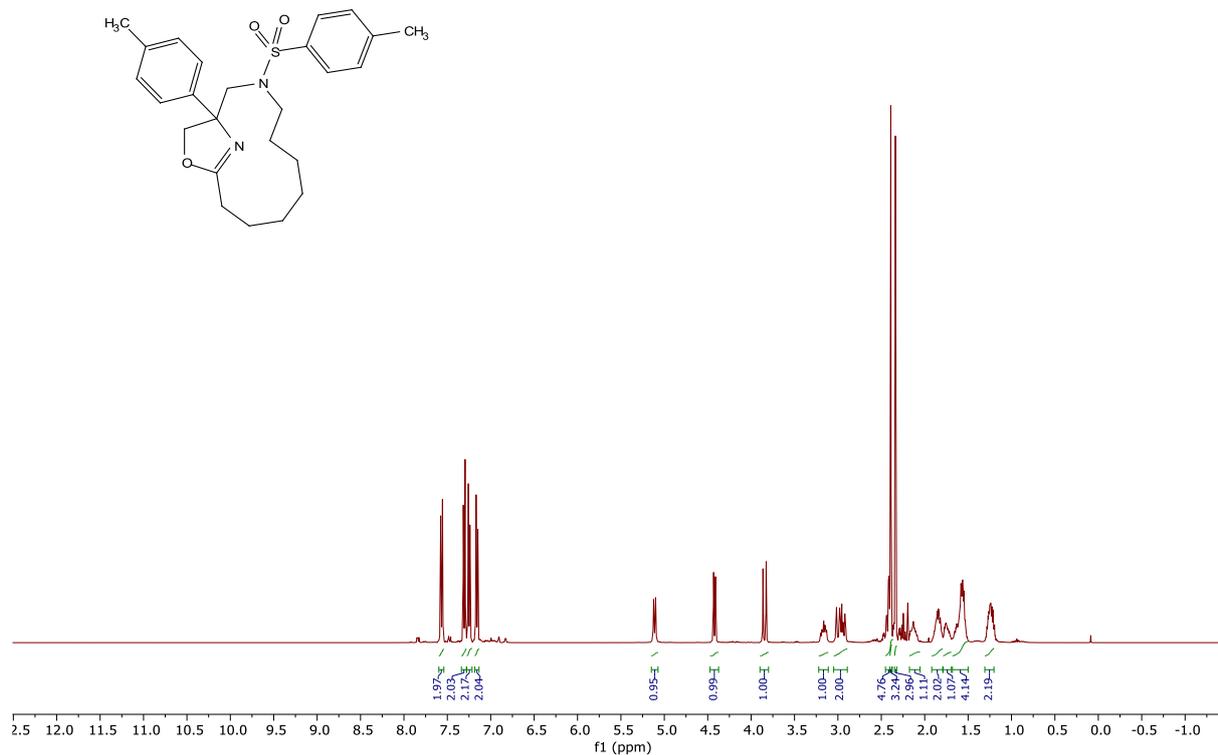
Single crystals of  $C_{23}H_{27}ClN_2O_3S$  were A suitable crystal was selected on a D8V\_Mo diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 1) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 2) Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
- 3) Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

**Crystal Data** for  $C_{23}H_{27}ClN_2O_3S$  ( $M = 446.97$  g/mol): triclinic, space group P-1 (no. 2),  $a = 5.8929(3)$  Å,  $b = 17.3978(9)$  Å,  $c = 21.6160(12)$  Å,  $\alpha = 89.719(2)^\circ$ ,  $\beta = 89.096(2)^\circ$ ,  $\gamma = 81.028(2)^\circ$ ,  $V = 2188.8(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 120$  K,  $\mu(\text{MoK}\alpha) = 0.298$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.356$  g/cm<sup>3</sup>, 34462 reflections measured ( $4.448^\circ \leq 2\theta \leq 50.052^\circ$ ), 7680 unique ( $R_{\text{int}} = 0.0507$ ,  $R_{\text{sigma}} = 0.0566$ ) which were used in all calculations. The final  $R_1$  was 0.0648 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1636 (all data).

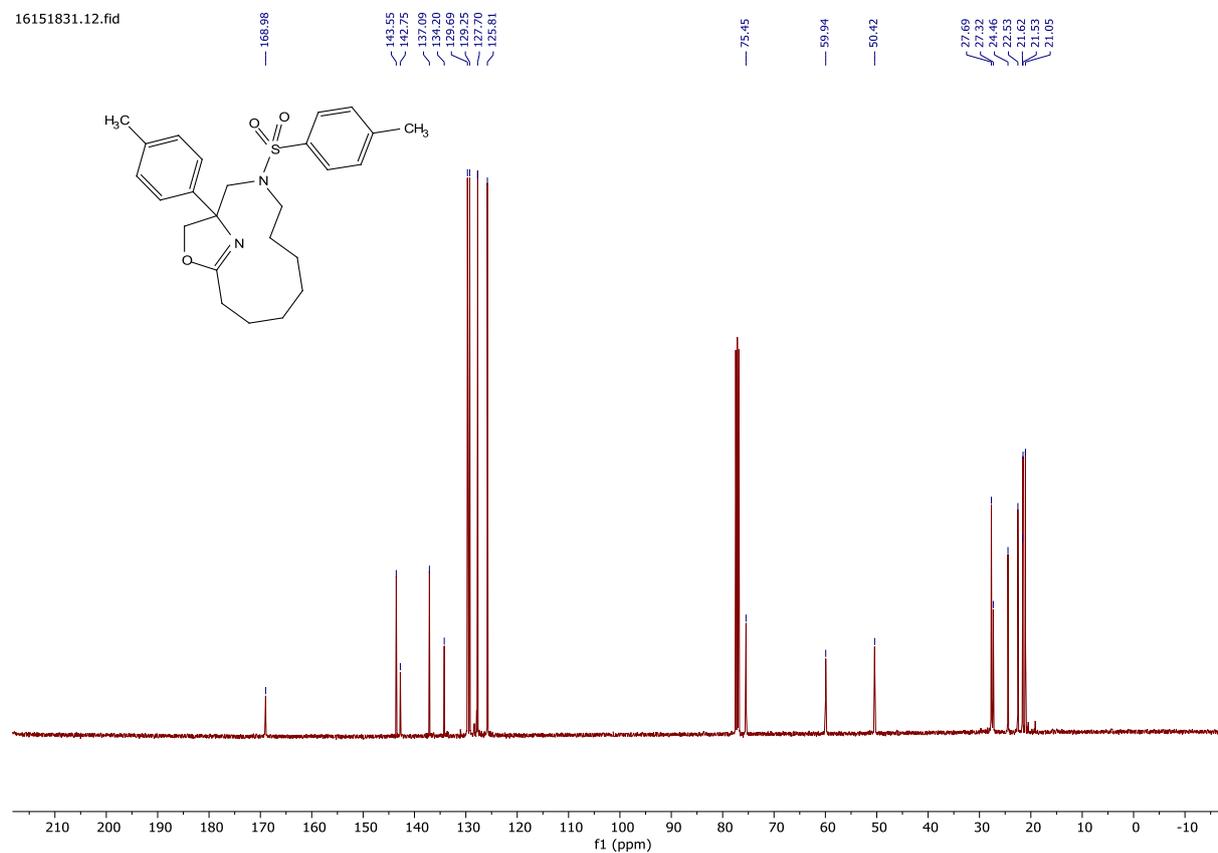
# Compound 2-214 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

17092709.10.fid

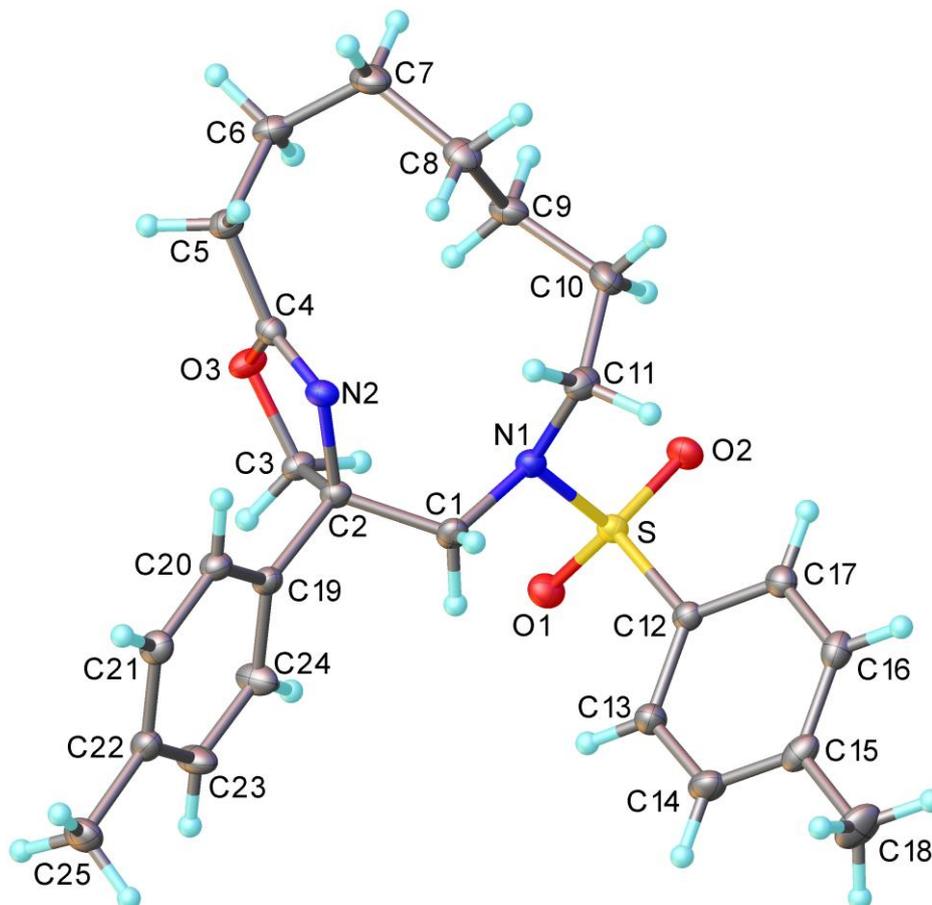


# Compound 2-214 <sup>13</sup>C{<sup>1</sup>H} NMR (400 MHz, CDCl<sub>3</sub>)

16151831.12.fid



## Compound 2-214 X-ray structure



Atomic displacement ellipsoids are drawn at the 50% probability level.

Compound 14-4 was crystallised by solvent evaporation using a mixture Hexane: EtOAc

### Experimental

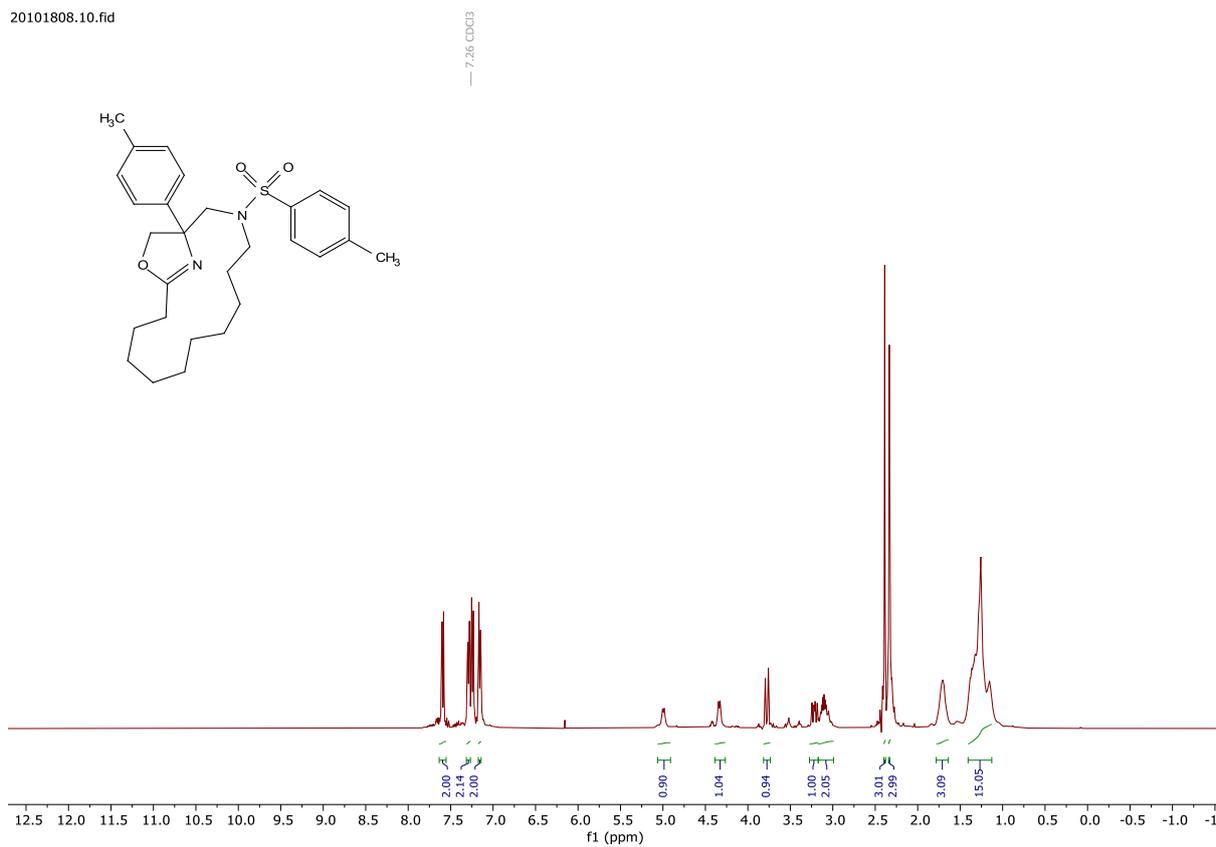
Single crystals of  $C_{25}H_{32}N_2O_3S$  were A suitable crystal was selected on a D8V\_Mo diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 1) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
- 2) Sheldrick, G.M. (2008). *Acta Cryst.* A64, 112-122.
- 3) Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

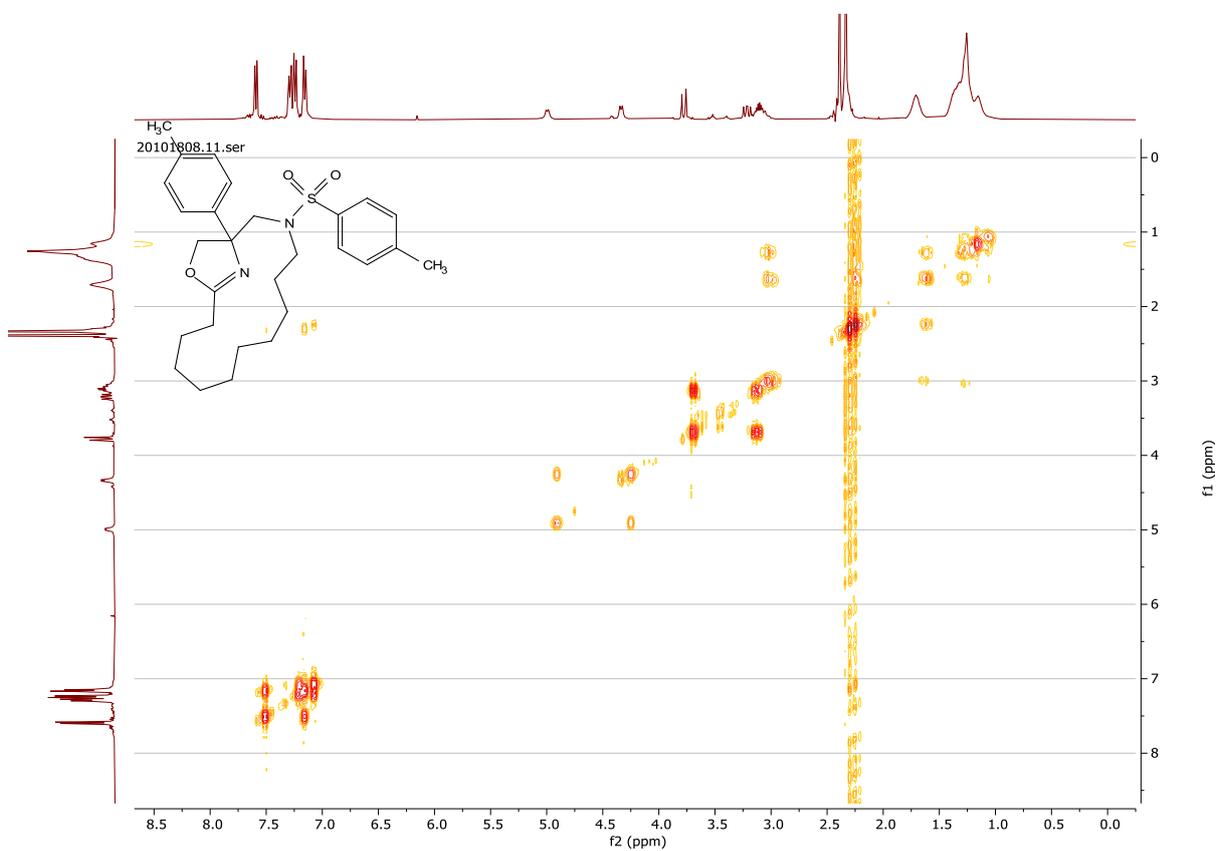
**Crystal Data** for  $C_{25}H_{32}N_2O_3S$  ( $M = 440.58$  g/mol): monoclinic, space group  $P2_1/n$  (no. 14),  $a = 10.5408(7)$  Å,  $b = 11.4873(7)$  Å,  $c = 19.3042(13)$  Å,  $\beta = 102.914(2)^\circ$ ,  $V = 2278.3(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 120$  K,  $\mu(\text{MoK}\alpha) = 0.171$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.284$  g/cm<sup>3</sup>, 49671 reflections measured ( $4.33^\circ \leq 2\theta \leq 60.254^\circ$ ), 6697 unique ( $R_{\text{int}} = 0.0431$ ,  $R_{\text{sigma}} = 0.0318$ ) which were used in all calculations. The final  $R_1$  was 0.0396 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1044 (all data).

# Compound 2-215 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

20101808.10.fid

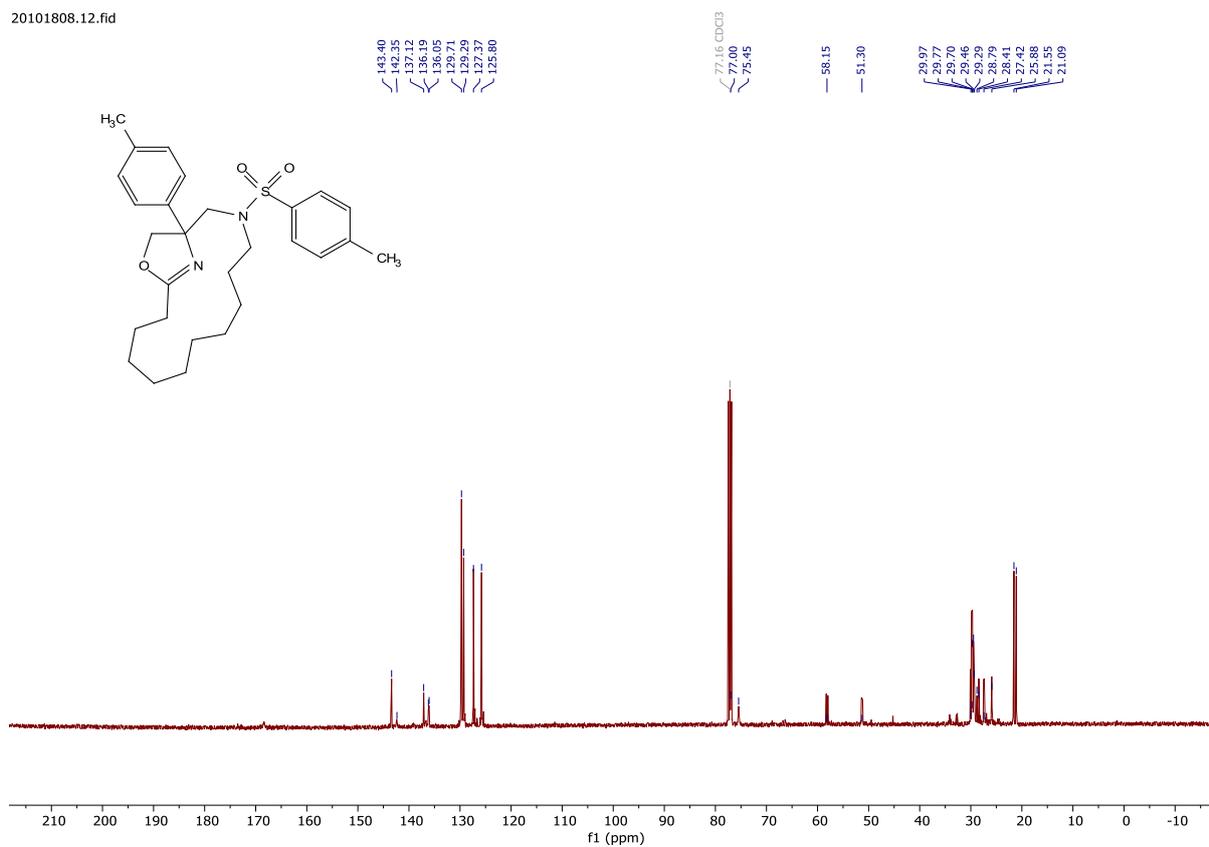


# Compound 2-215 COSY (400 MHz, CDCl<sub>3</sub>)



# Compound 2-215 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{CDCl}_3$ )

20101808.12.fid



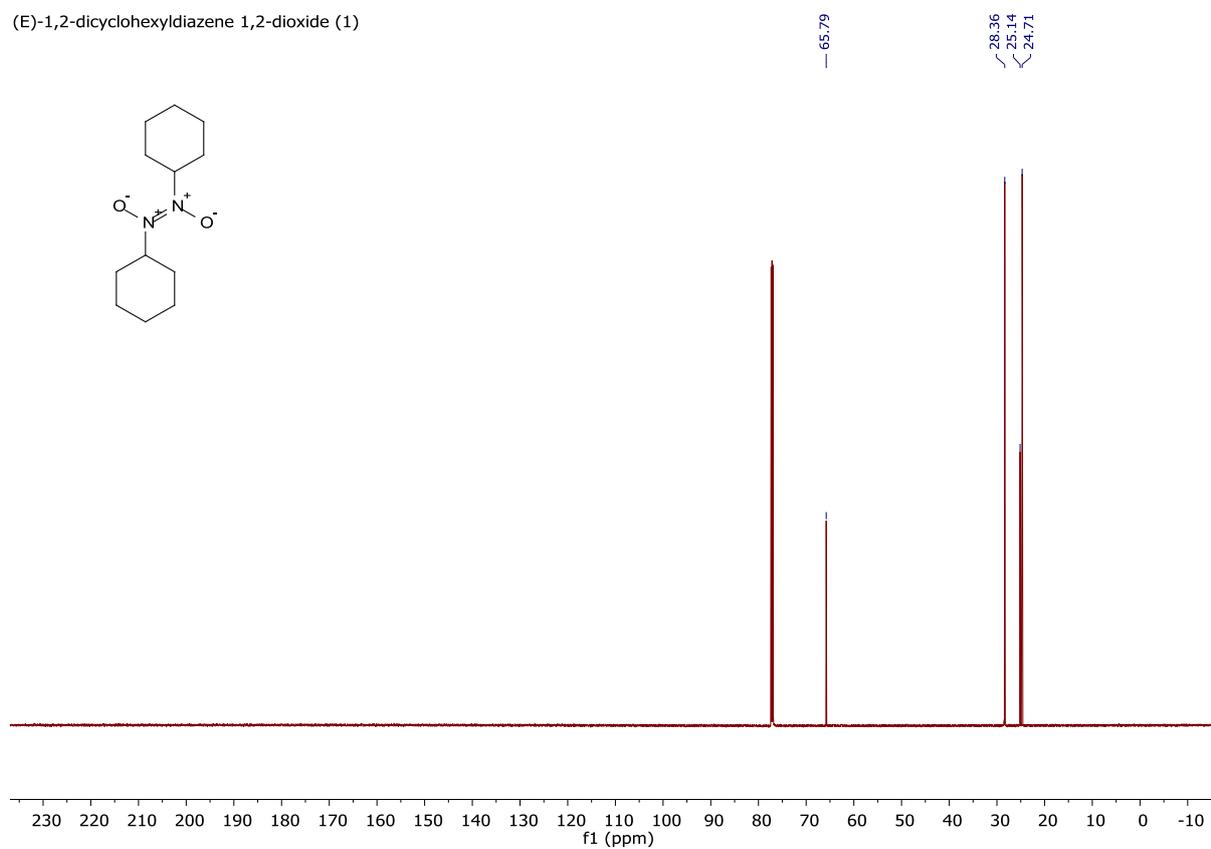
*ica Acta*, **2007** 90, 1420–1438.

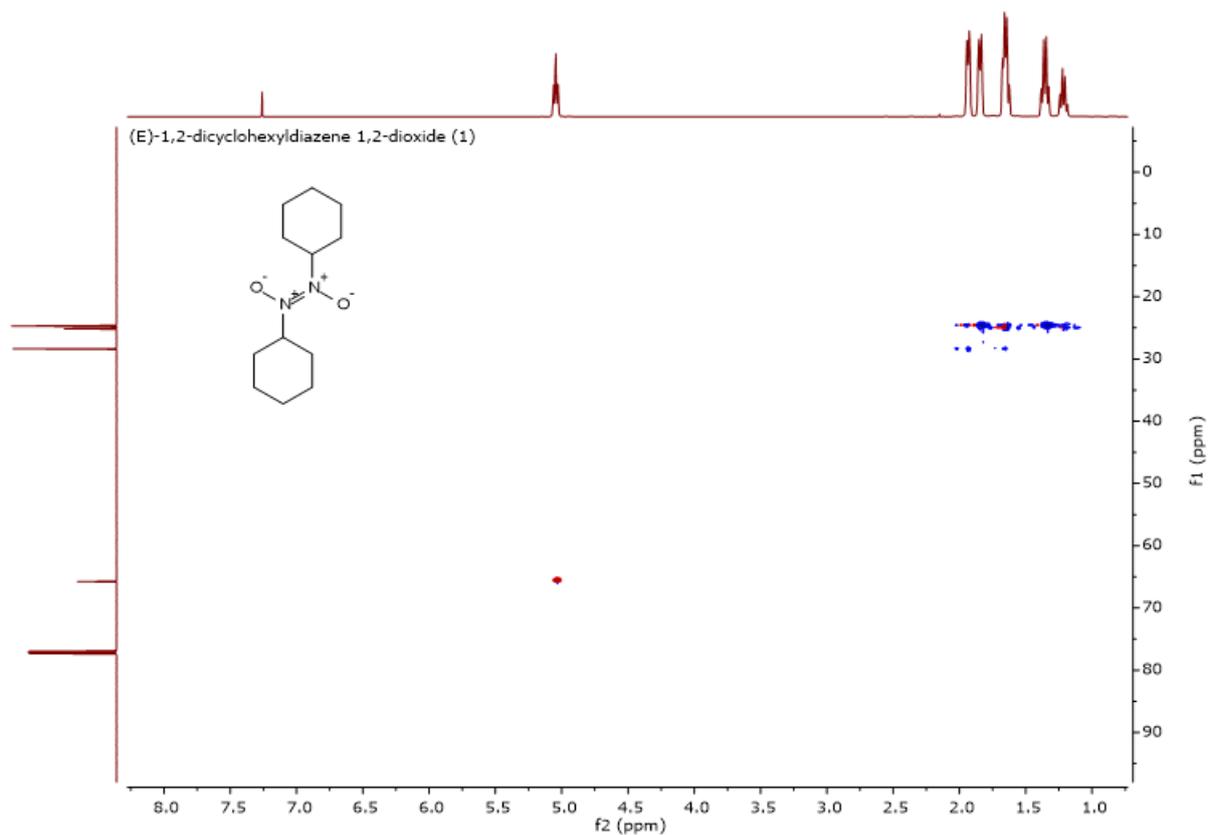
[7] K. Raja, Erum. A. Klumpp, Douglas, *Tetrahedron*, **2011**, 67, 4494–4497.

## Chapter 3: Exploring Photoflow Promoted Oximation of Alkanes

### Compound **3-176** $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, $\text{CDCl}_3$ )

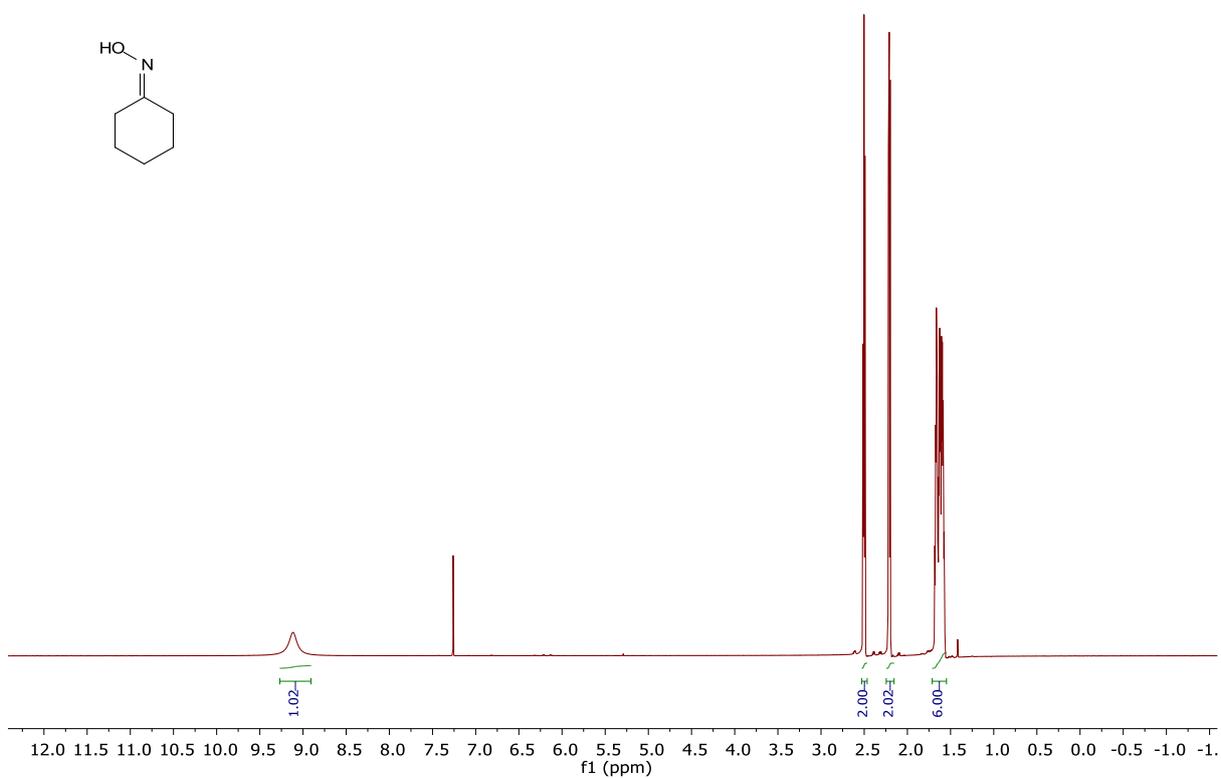
(E)-1,2-dicyclohexyldiazene 1,2-dioxide (1)



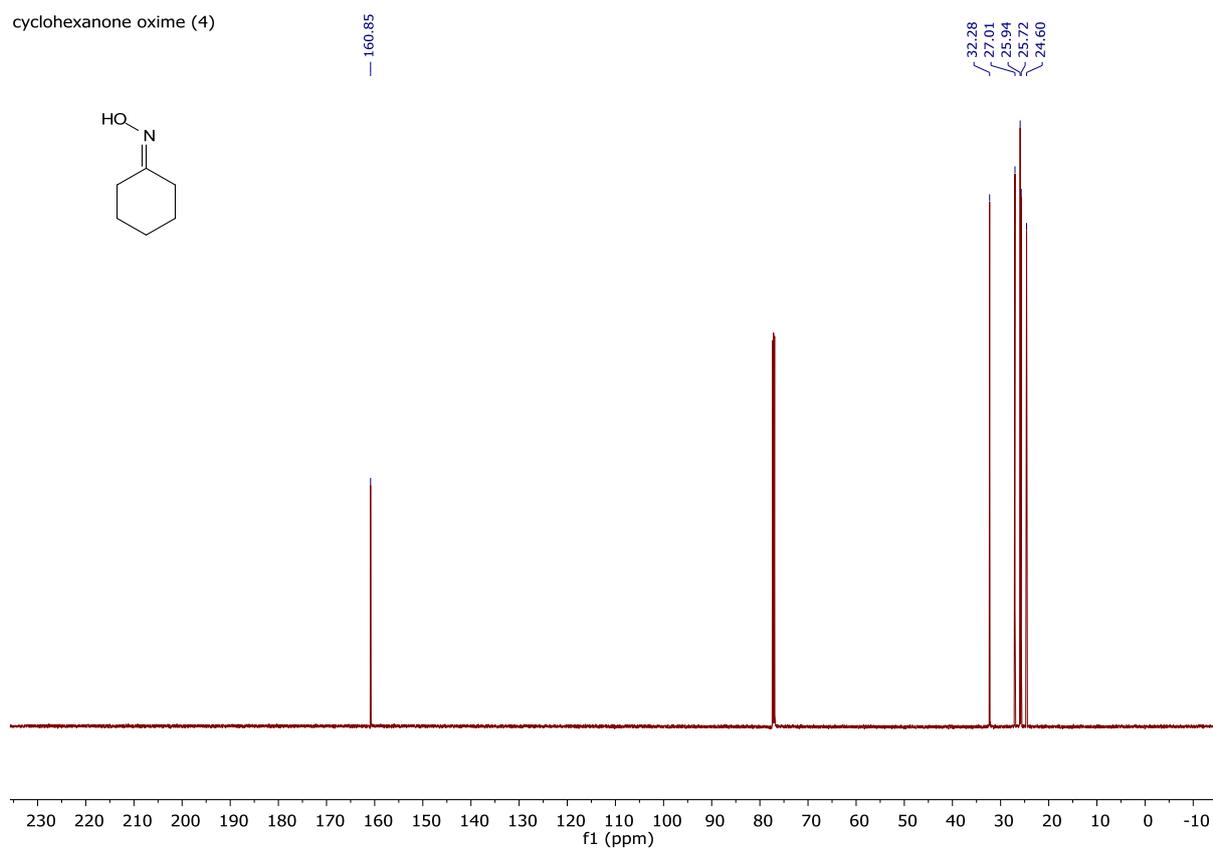


### Compound 3-7 $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )

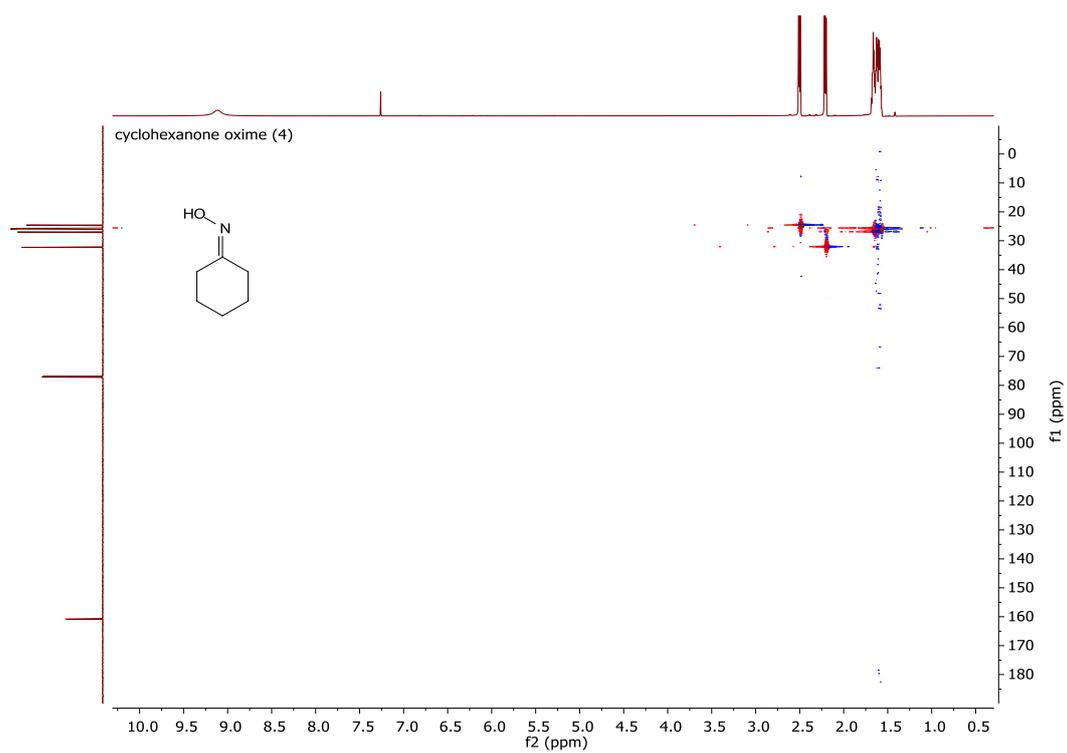
cyclohexanone oxime (4)



# Compound 3-7 $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, $\text{CDCl}_3$ )

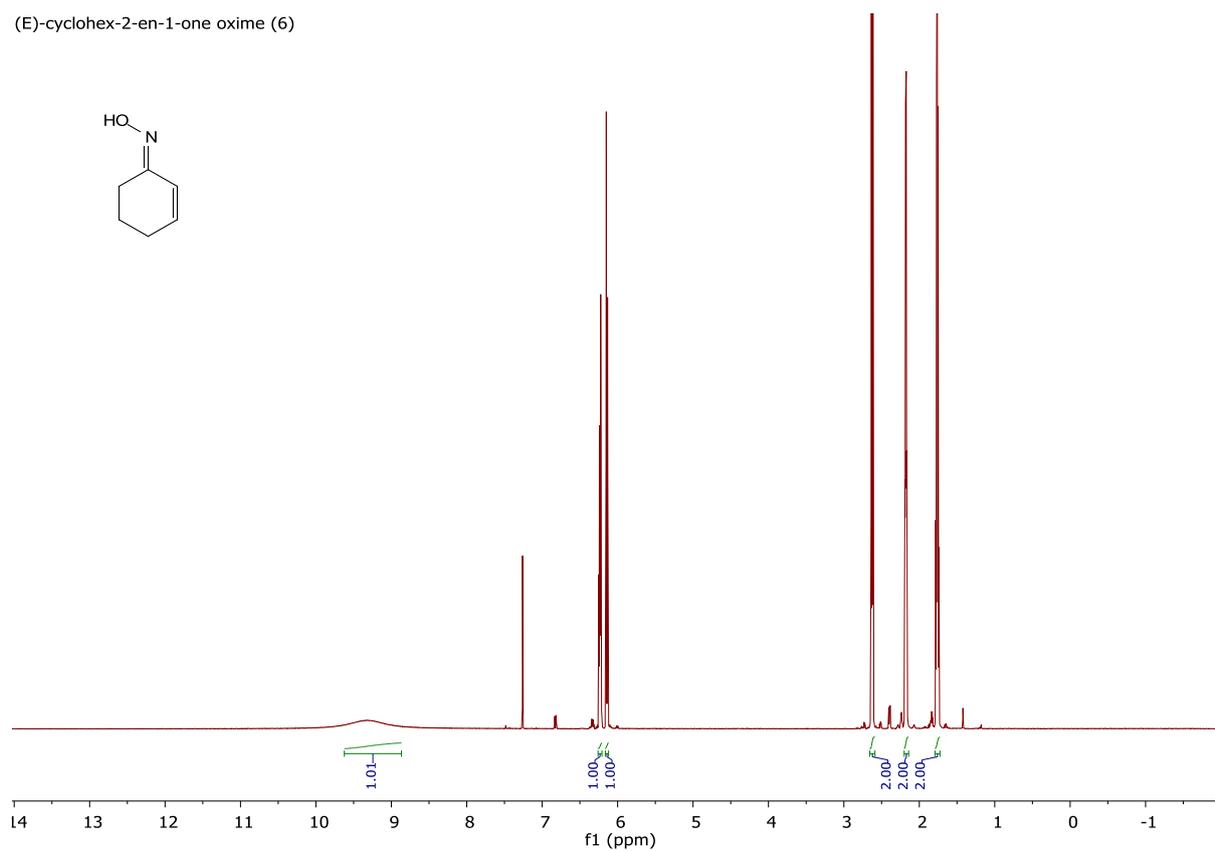


# Compound 3-7 HSQC (600 MHz, $\text{CDCl}_3$ )



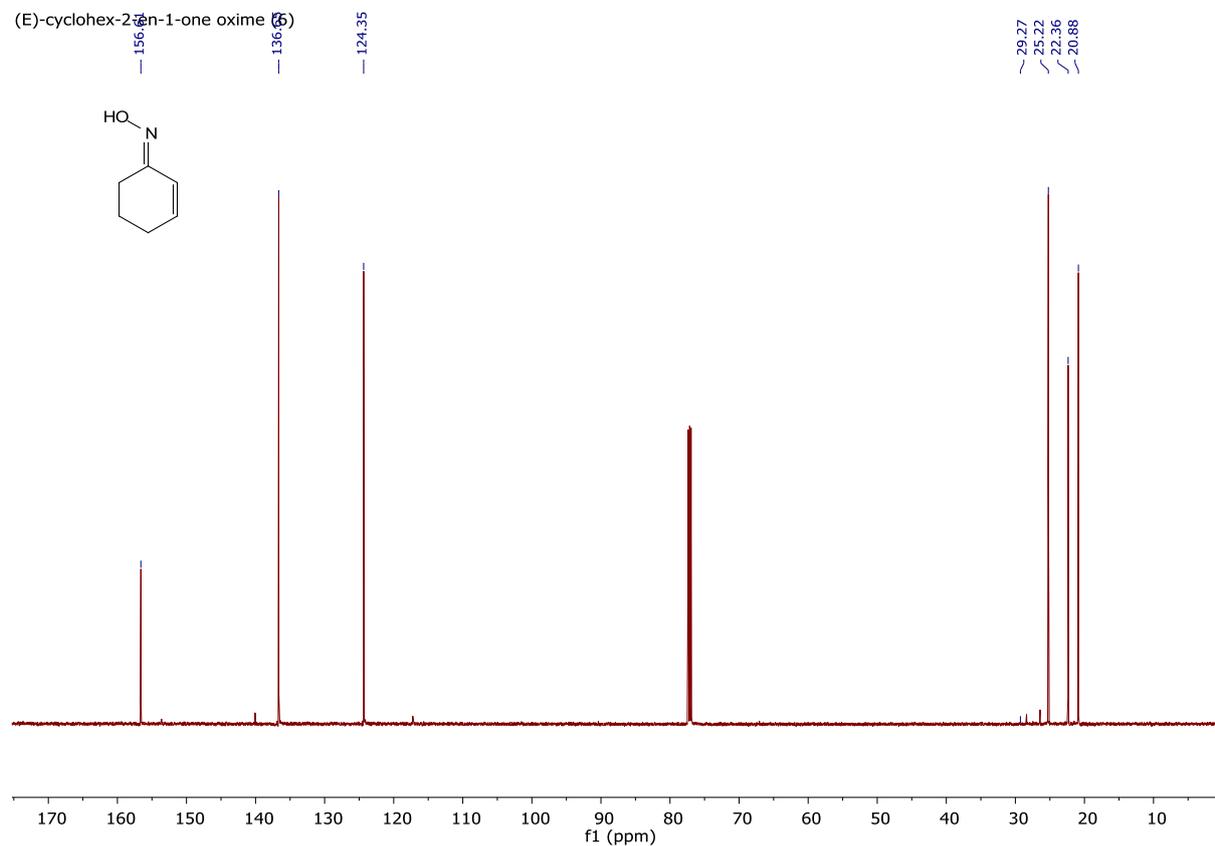
# Compound 3-187a $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

(E)-cyclohex-2-en-1-one oxime (6)

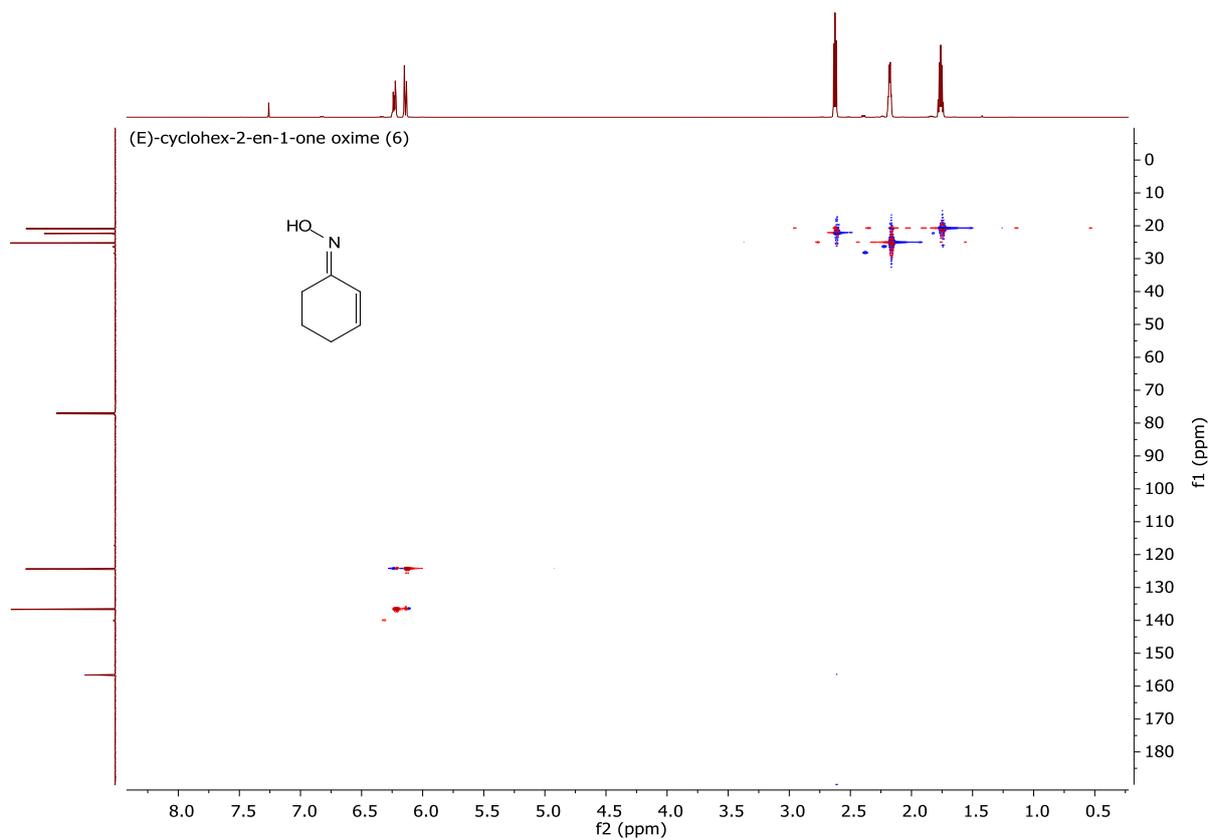


# Compound 3-187a $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, $\text{CDCl}_3$ )

(E)-cyclohex-2-en-1-one oxime (6)

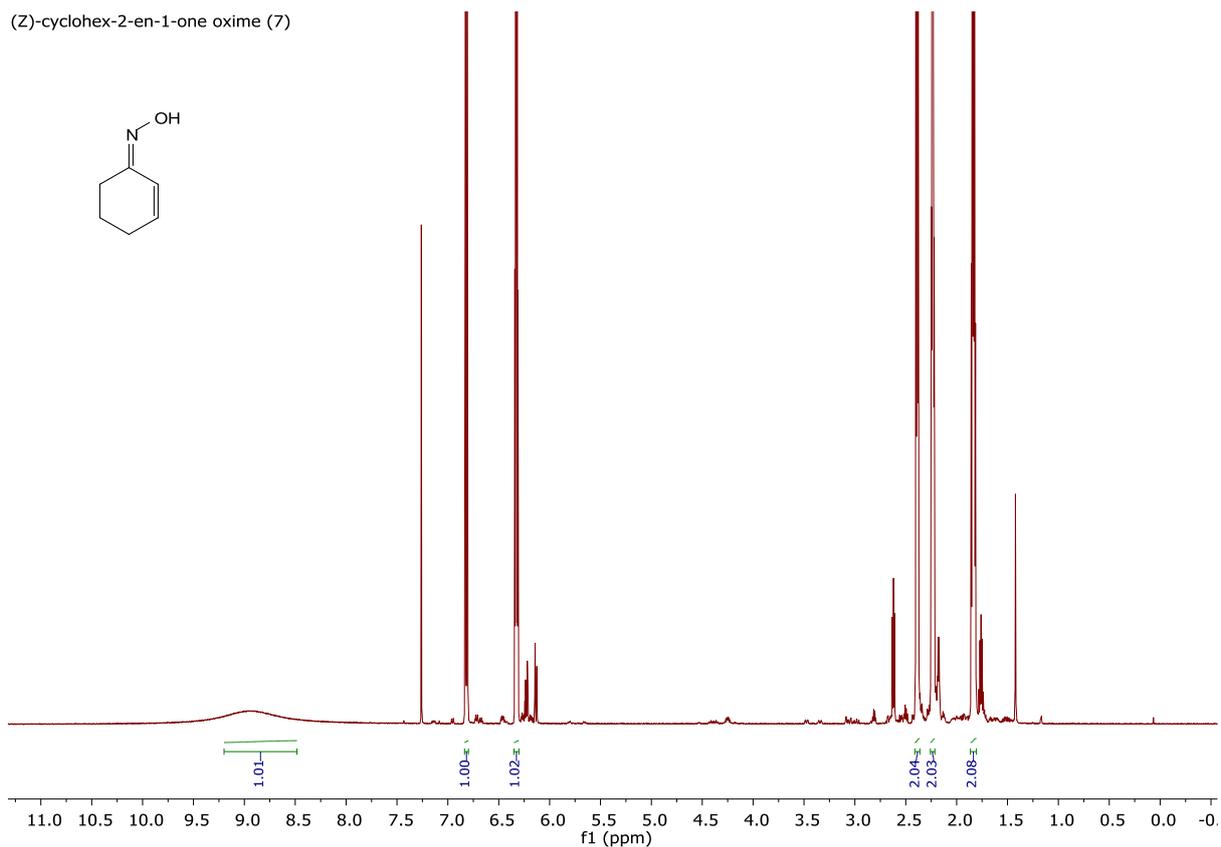


# Compound 3-187 HSQC (600 MHz, CDCl<sub>3</sub>)



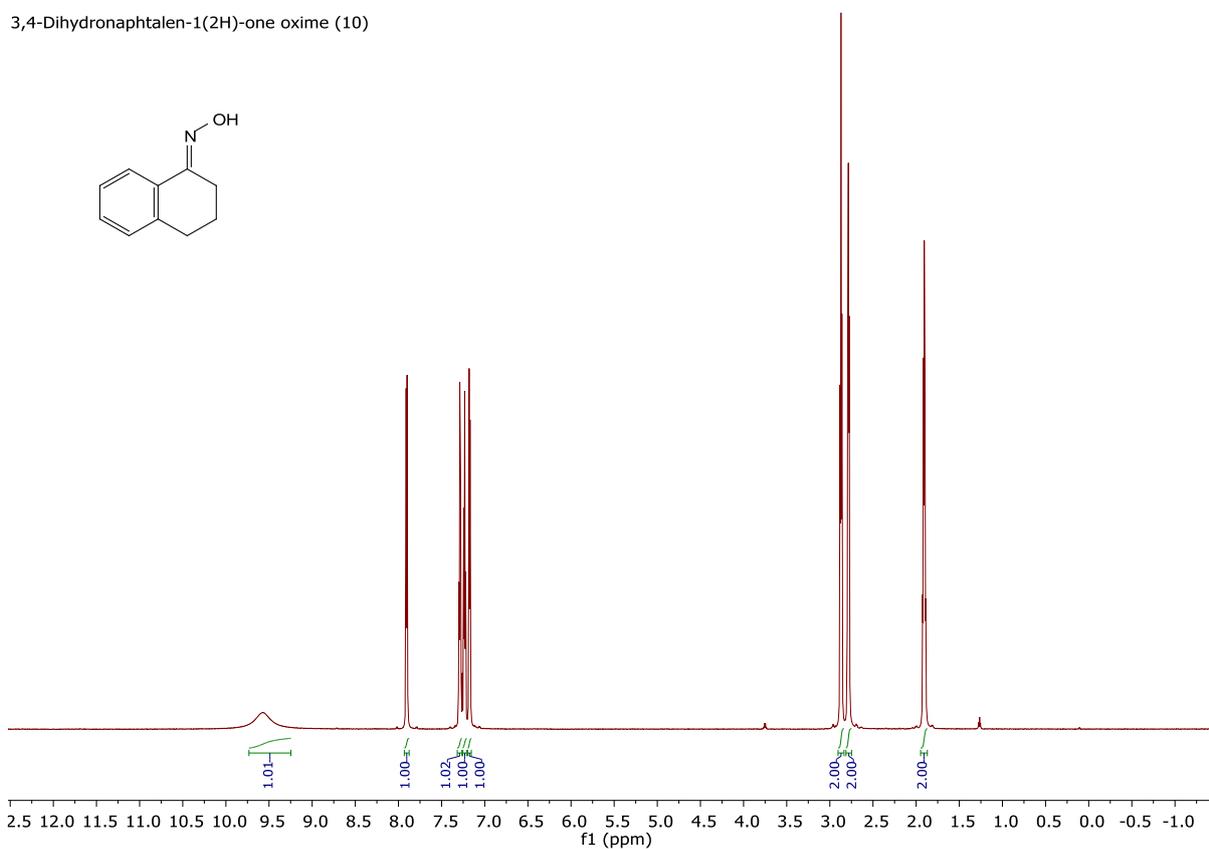
# Compound 3-187b $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

(Z)-cyclohex-2-en-1-one oxime (7)



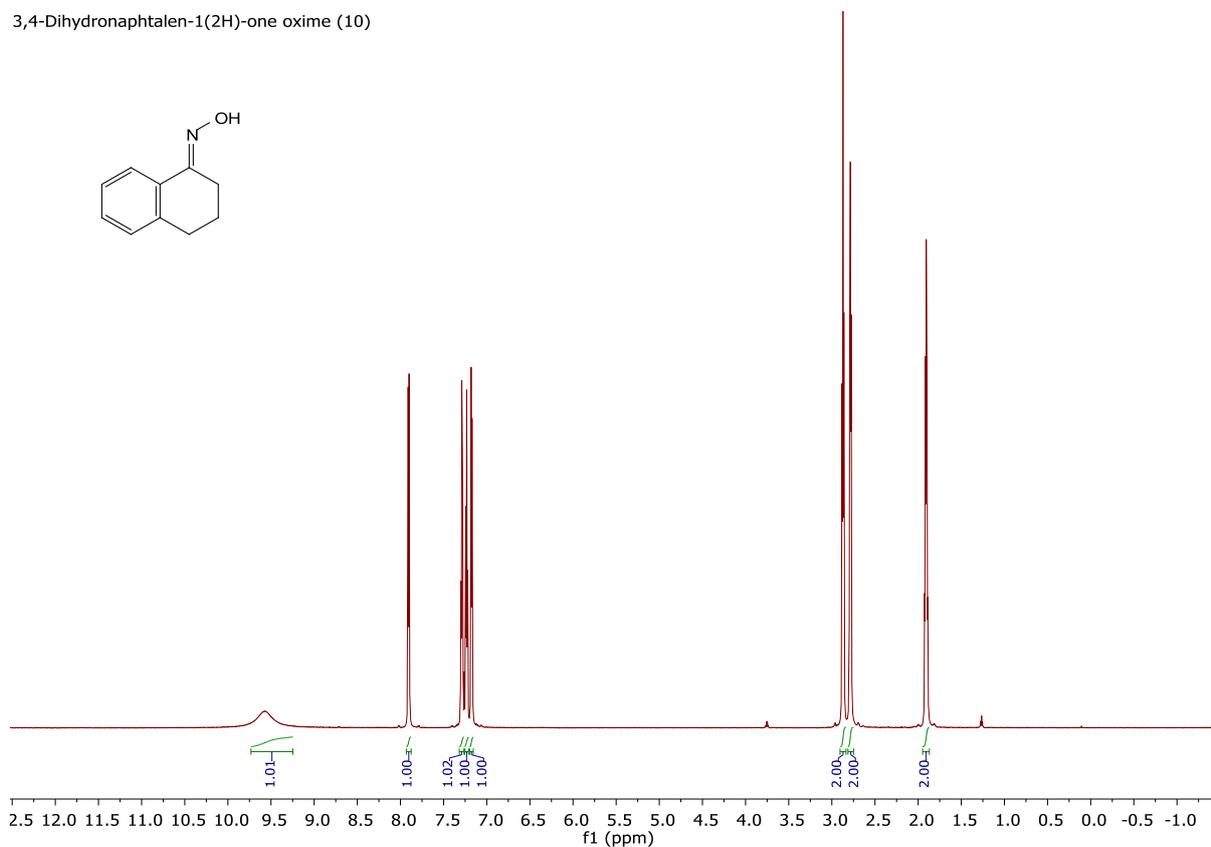
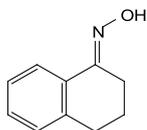
# Compound 3-187b $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, $\text{CDCl}_3$ )

3,4-Dihydronaphthalen-1(2H)-one oxime (10)



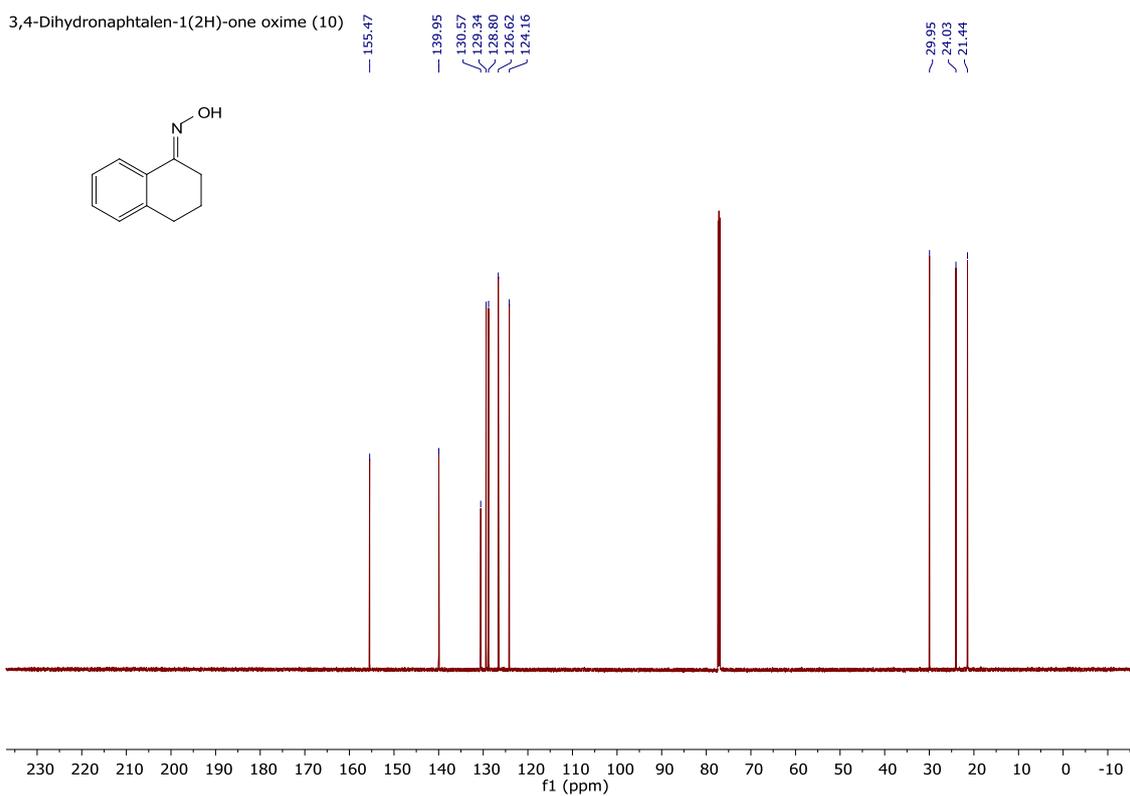
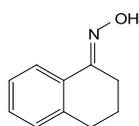
# Compound 3-196b $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

3,4-Dihydronaphthalen-1(2H)-one oxime (10)

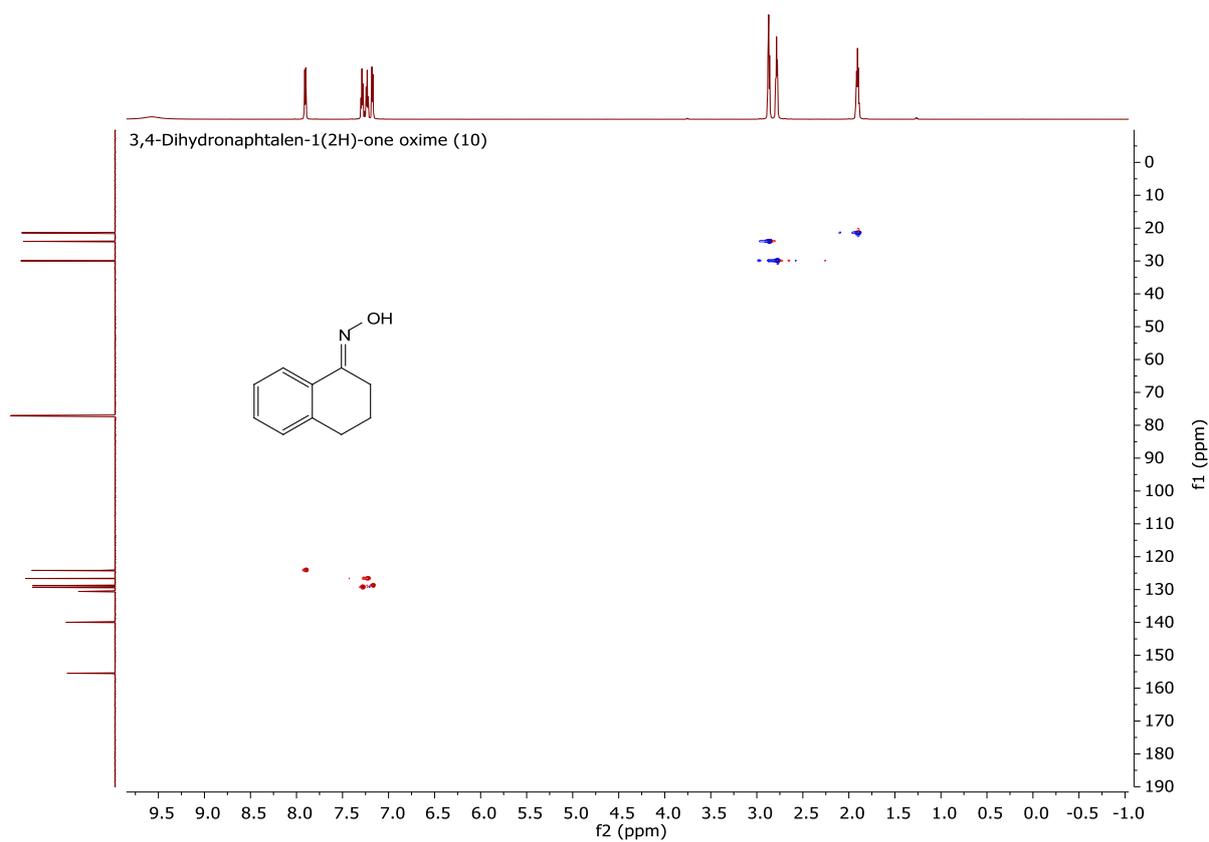


# Compound 3-196b $^{13}\text{C}\{^1\text{H}\}$ NMR (600 MHz, $\text{CDCl}_3$ )

3,4-Dihydronaphthalen-1(2H)-one oxime (10)

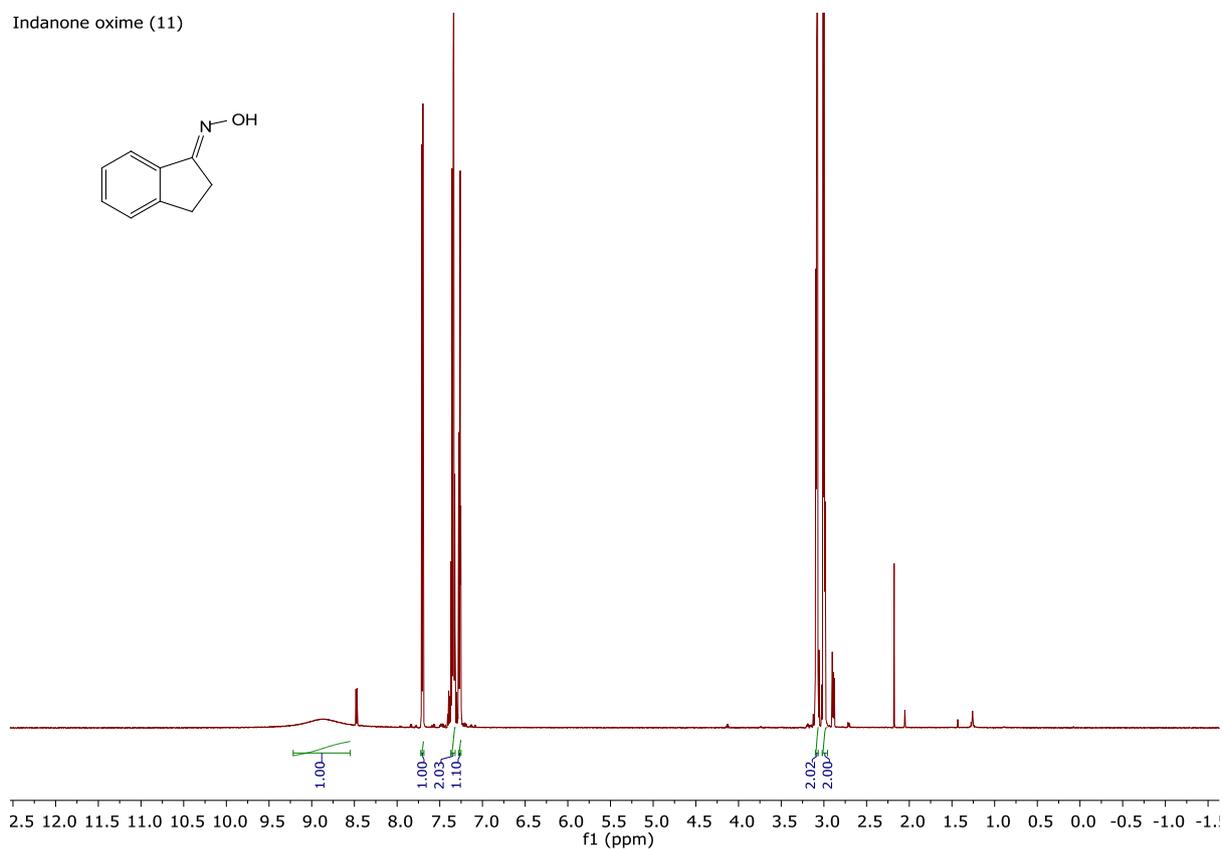


## Compound 3-196 HSQC (600 MHz, CDCl<sub>3</sub>)



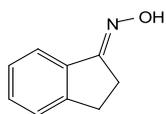
## Compound 3-197b <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)

Indanone oxime (11)



# Compound 3-197b $^{13}\text{C}\{^1\text{H}\}$ NMR (600 MHz, $\text{CDCl}_3$ )

1-Indanone oxime (11)



164.19

148.57

136.06

130.57

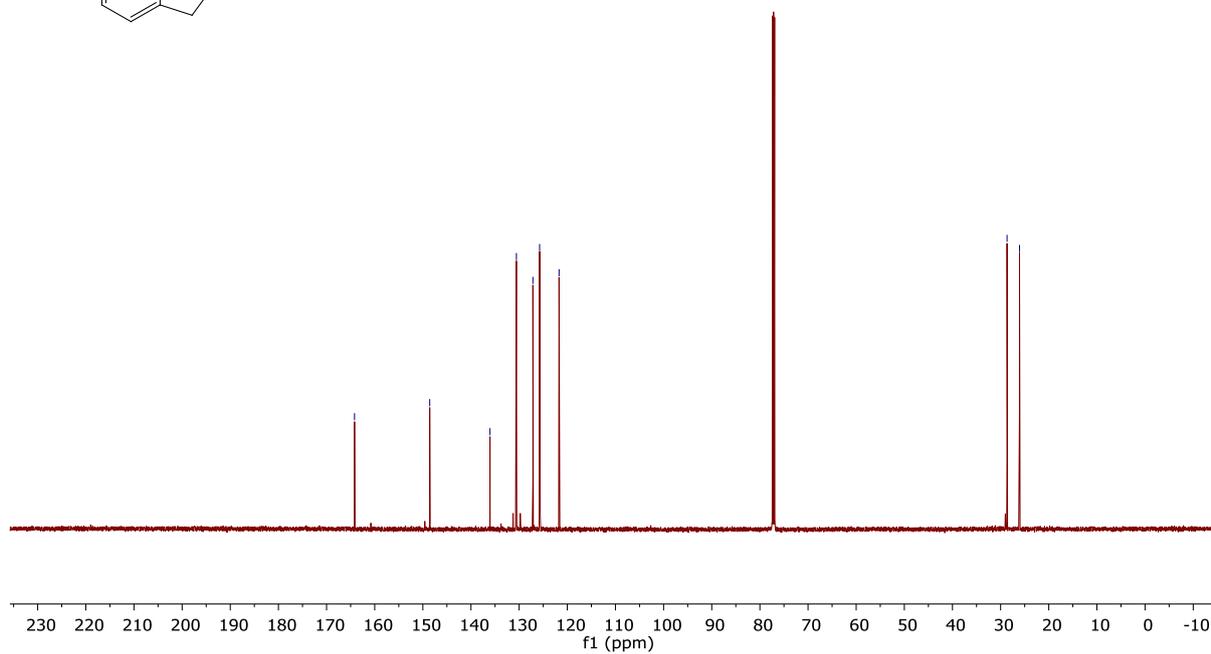
127.15

125.75

121.71

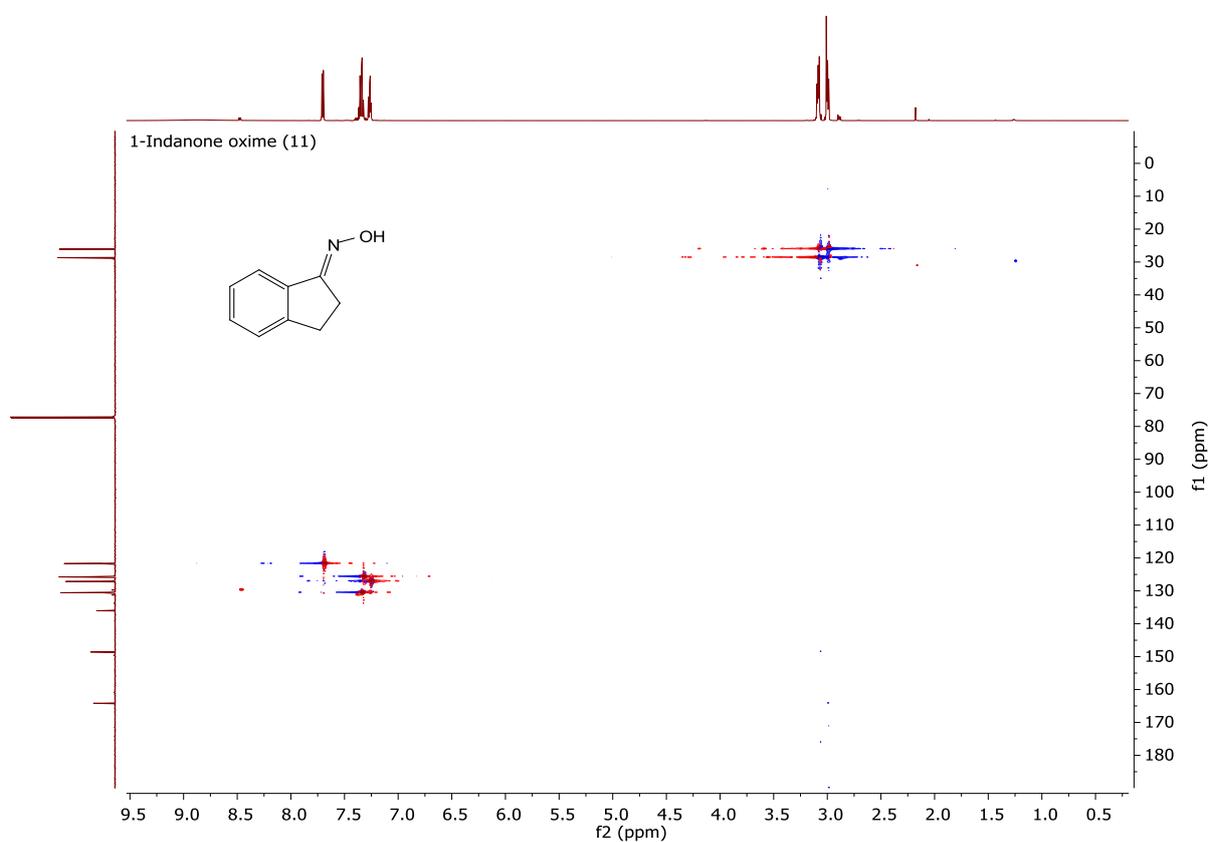
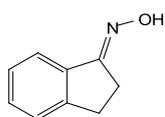
28.67

26.08



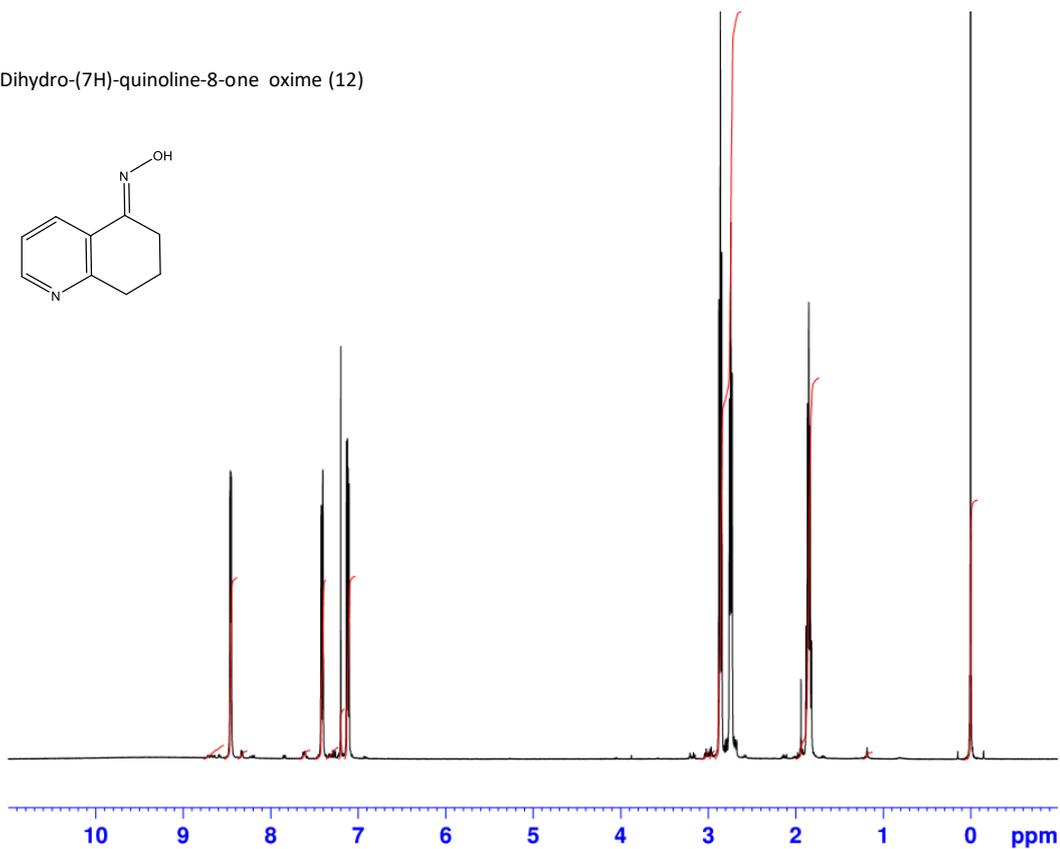
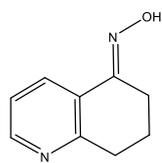
# Compound 3-197 HSQC (600 MHz, $\text{CDCl}_3$ )

1-Indanone oxime (11)



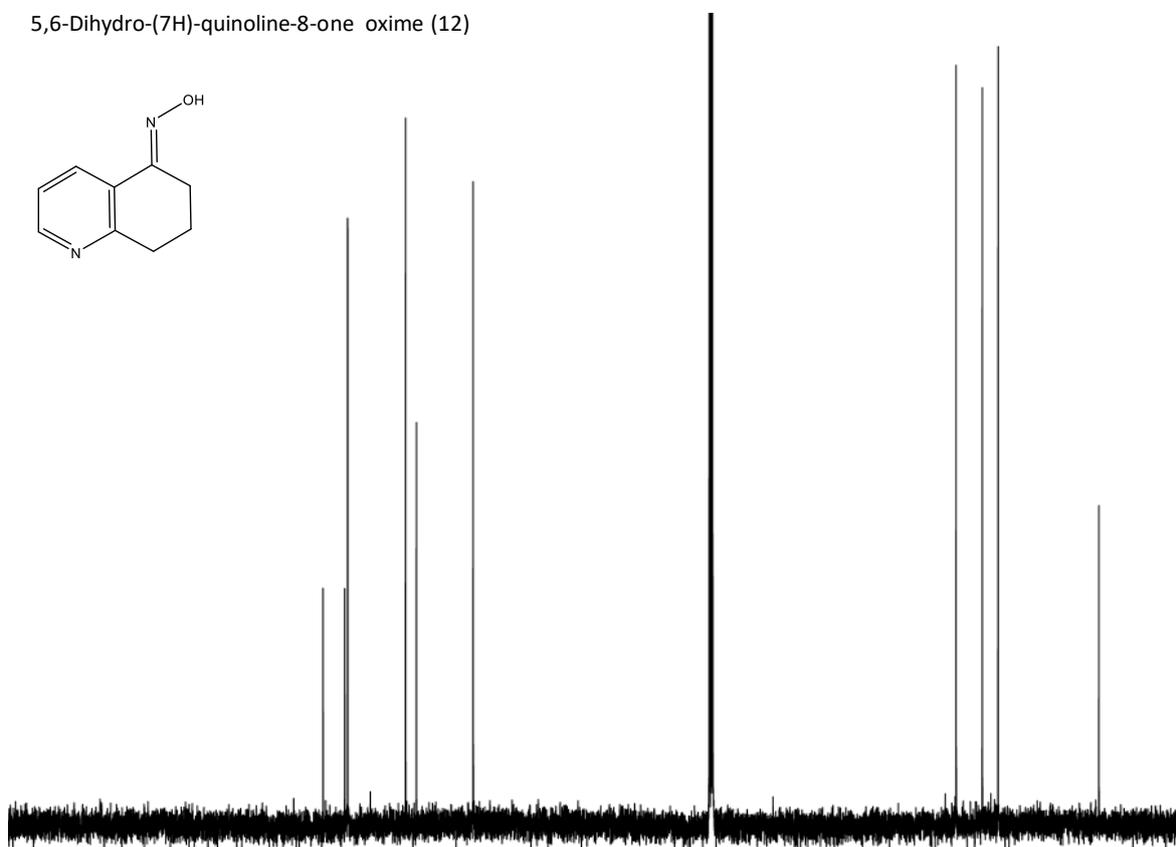
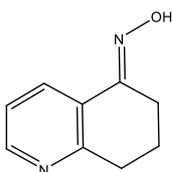
# Compound 3-198 $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

5,6-Dihydro-(7H)-quinoline-8-one oxime (12)



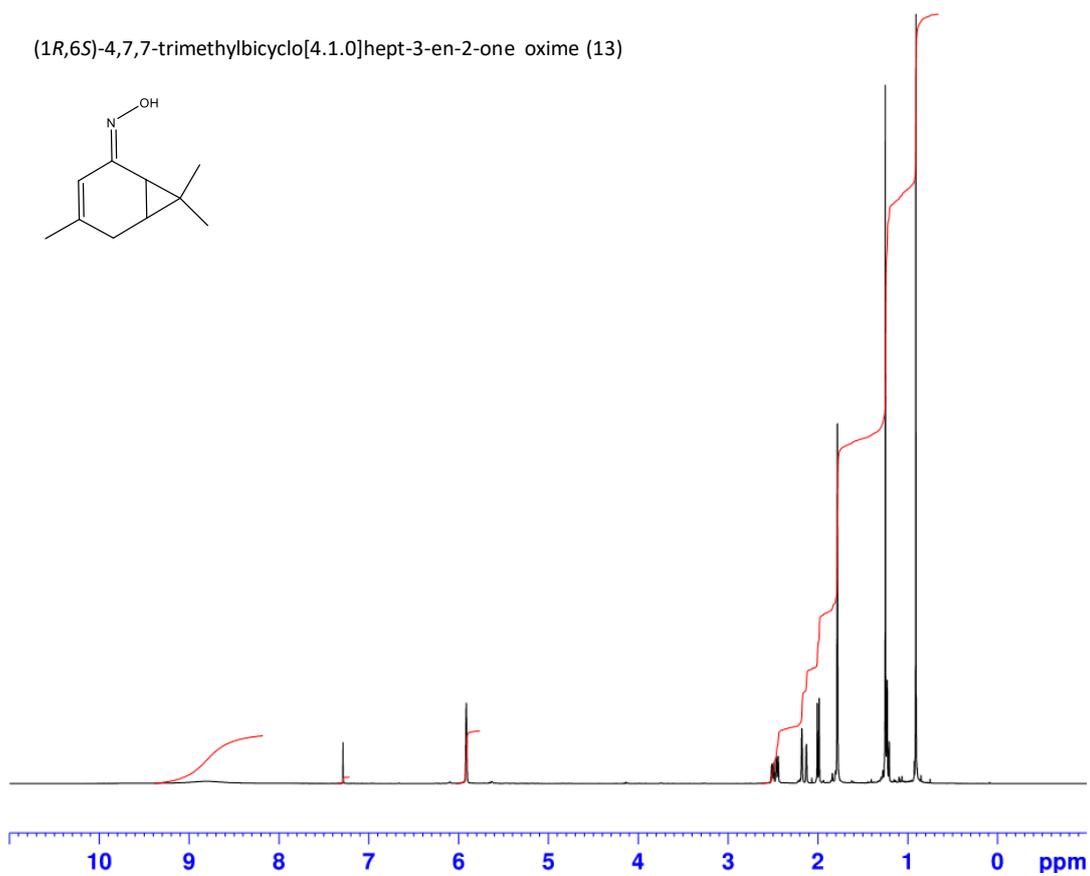
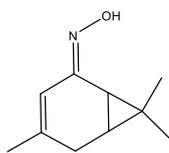
# Compound 3-198 $^{13}\text{C}\{^1\text{H}\}$ NMR (600 MHz, $\text{CDCl}_3$ )

5,6-Dihydro-(7H)-quinoline-8-one oxime (12)



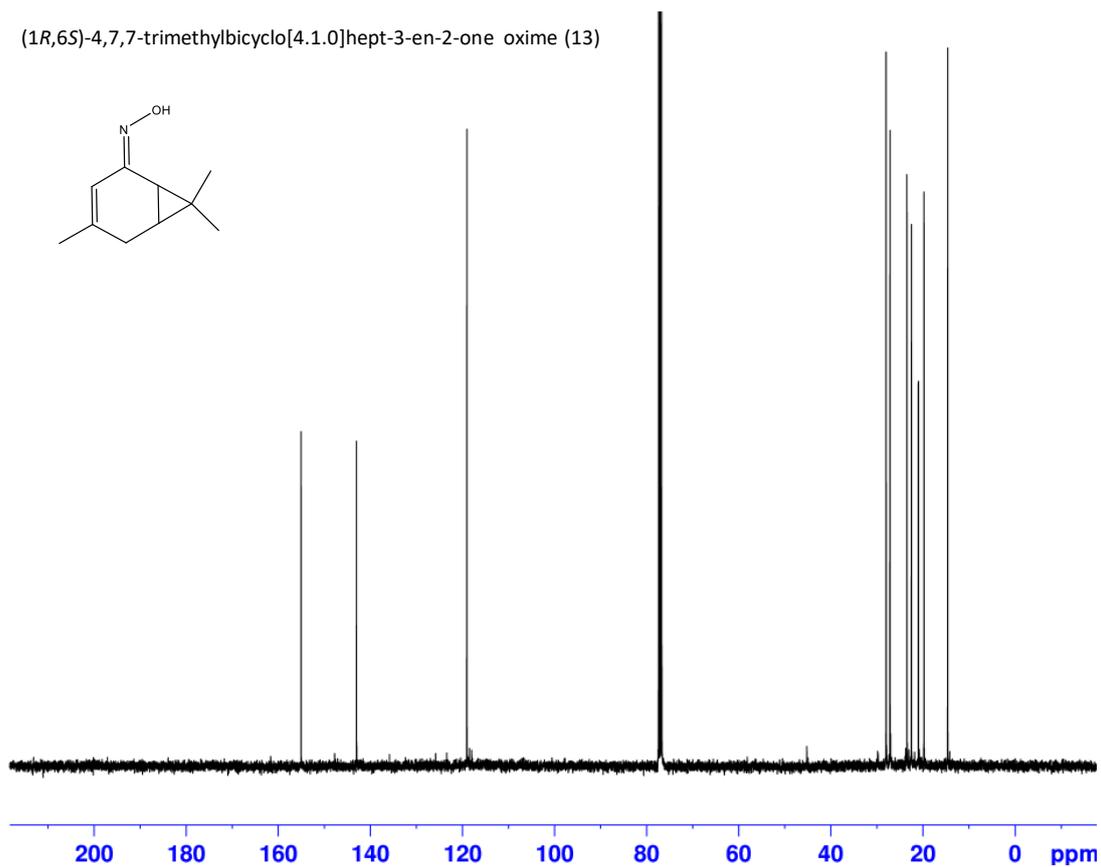
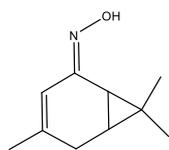
# Compound 3-199 $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

(1*R*,6*S*)-4,7,7-trimethylbicyclo[4.1.0]hept-3-en-2-one oxime (13)



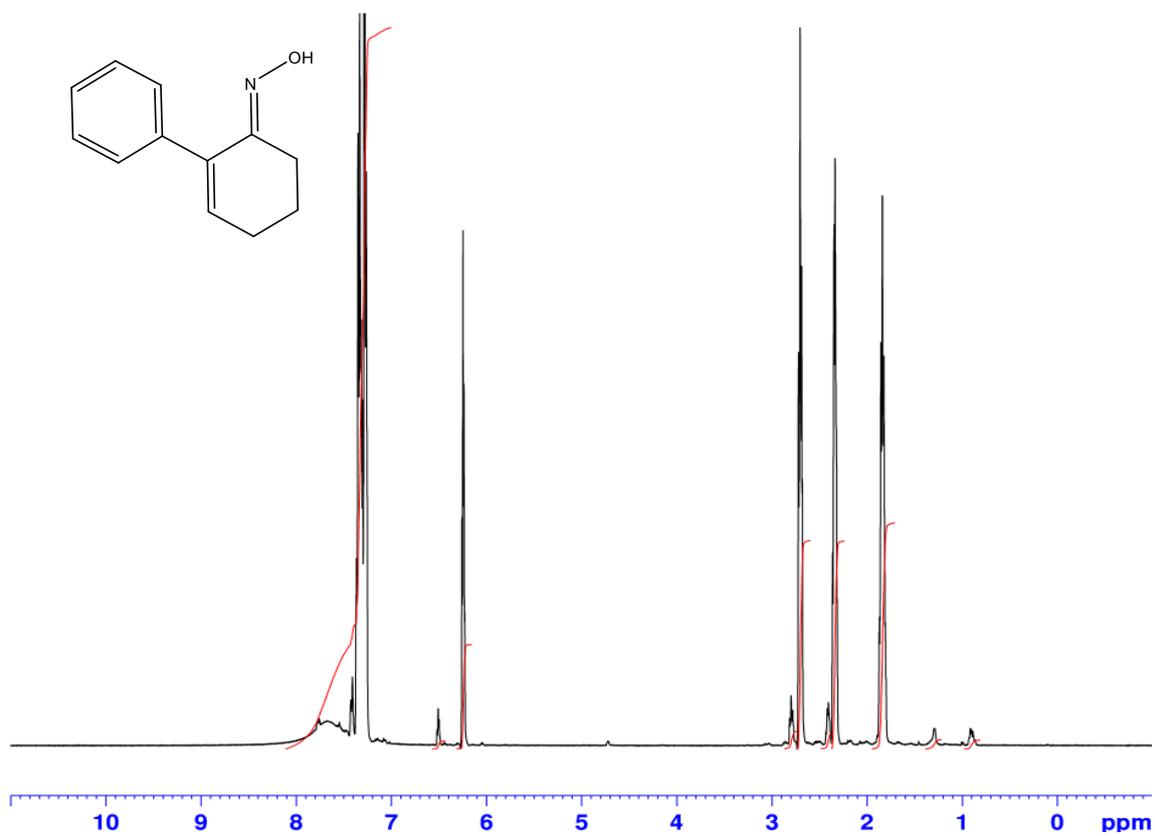
Compound **3-199**  $^{13}\text{C}\{^1\text{H}\}$  NMR (600 MHz,  $\text{CDCl}_3$ )

(1*R*,6*S*)-4,7,7-trimethylbicyclo[4.1.0]hept-3-en-2-one oxime (13)



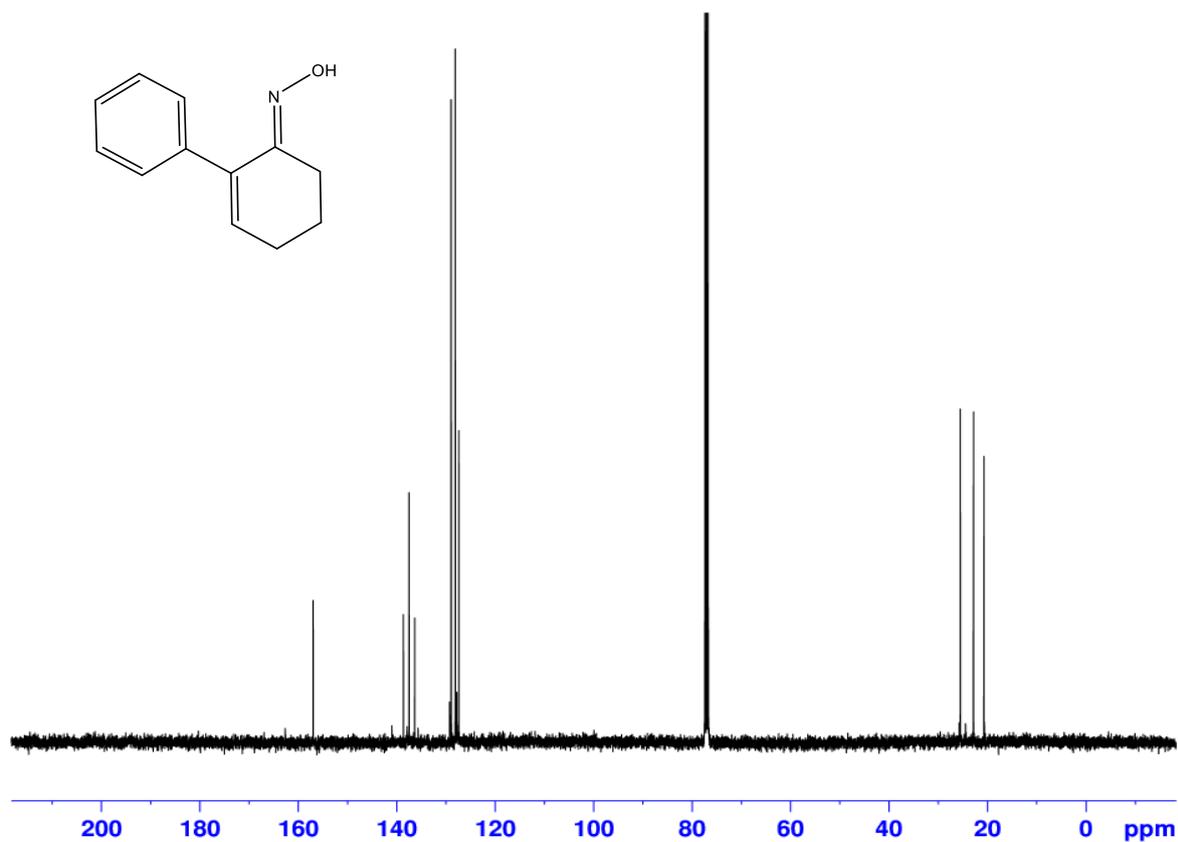
# Compound 3-200 $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

(E)-2-phenyl-2-cyclohexen-1-one oxime (14)



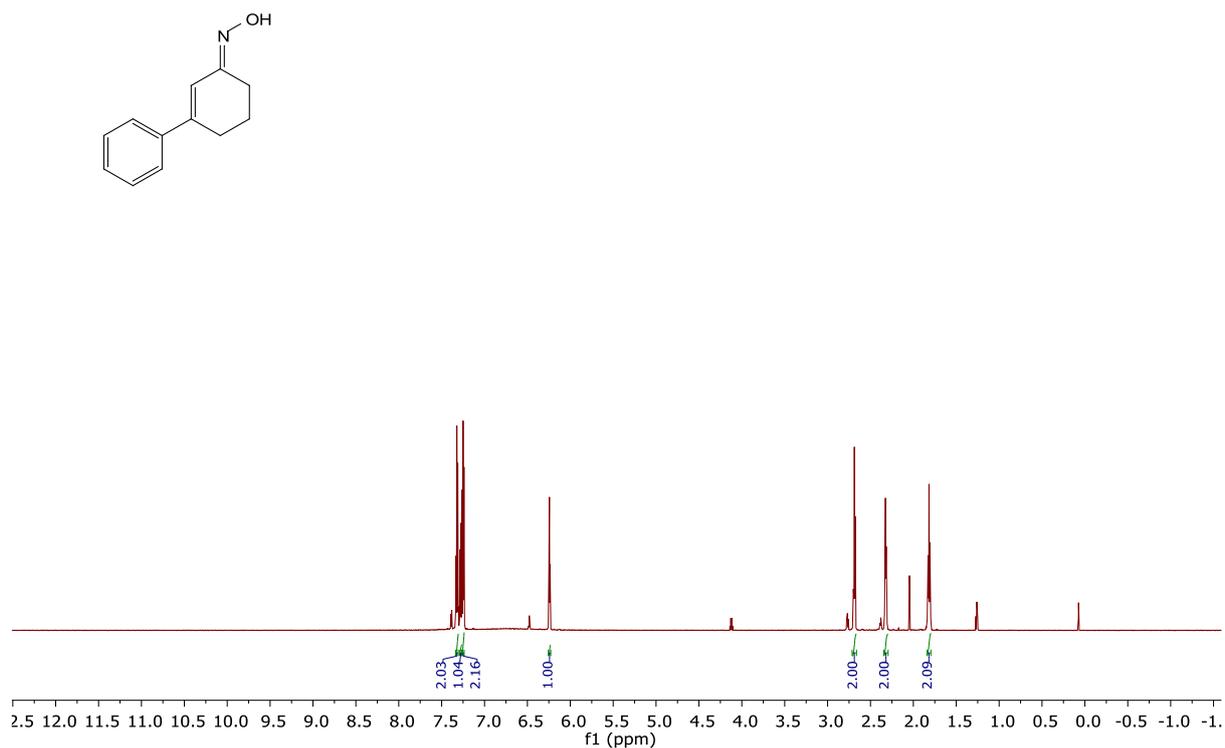
# Compound 3-200 $^{13}\text{C}\{^1\text{H}\}$ NMR (600 MHz, $\text{CDCl}_3$ )

(E)-2-phenyl-2-cyclohexen-1-one oxime (14)



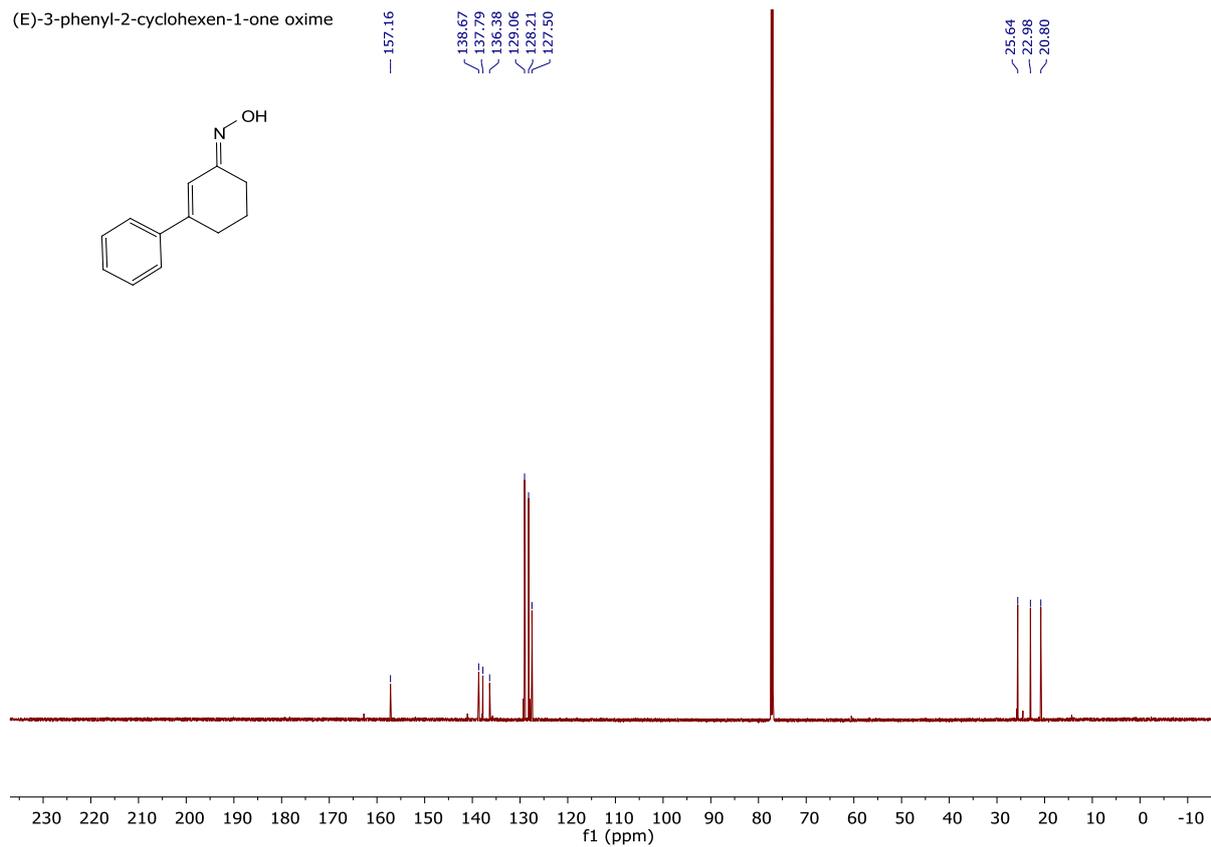
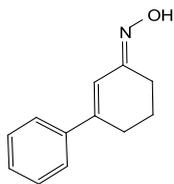
# Compound 3-201 $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

(E)-3-Phenyl-2-cyclohexen-1-one oxime (15)



# Compound **3-201** $^{13}\text{C}\{^1\text{H}\}$ NMR (600 MHz, $\text{CDCl}_3$ )

(E)-3-phenyl-2-cyclohexen-1-one oxime



# Compound 3-201 HSQC (600 MHz, CDCl<sub>3</sub>)

