

**Copper(II)-catalyzed (3+2) cycloaddition of 2*H*-azirines to 6-membered cyclic enols as a route to pyrrolo[3,2-*c*]quinolone, chromeno[3,4-*b*]pyrrole, and naphtho[1,8-*ef*]indole scaffolds**

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St. Petersburg, 199034, Russia.

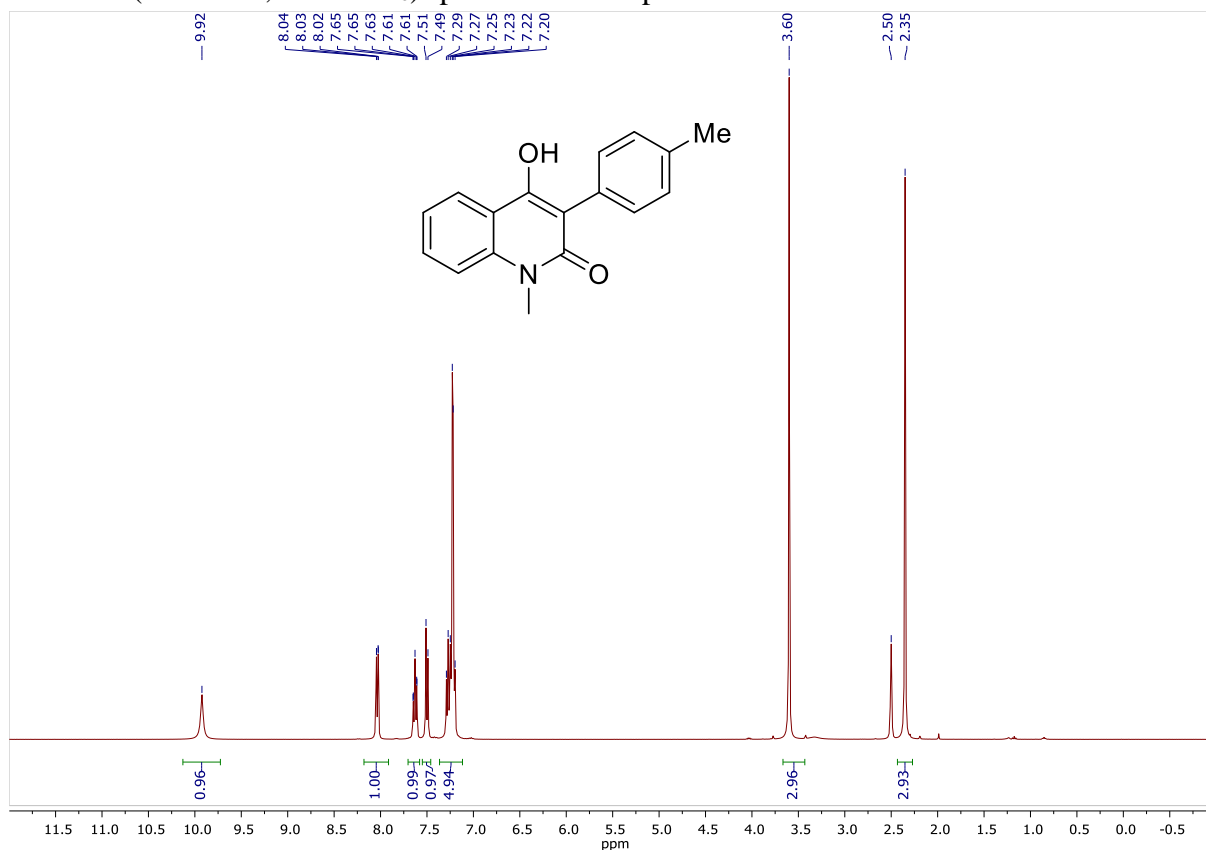
E-mail: *n.rostovskiy@spbu.ru*, *m.novikov@spbu.ru*

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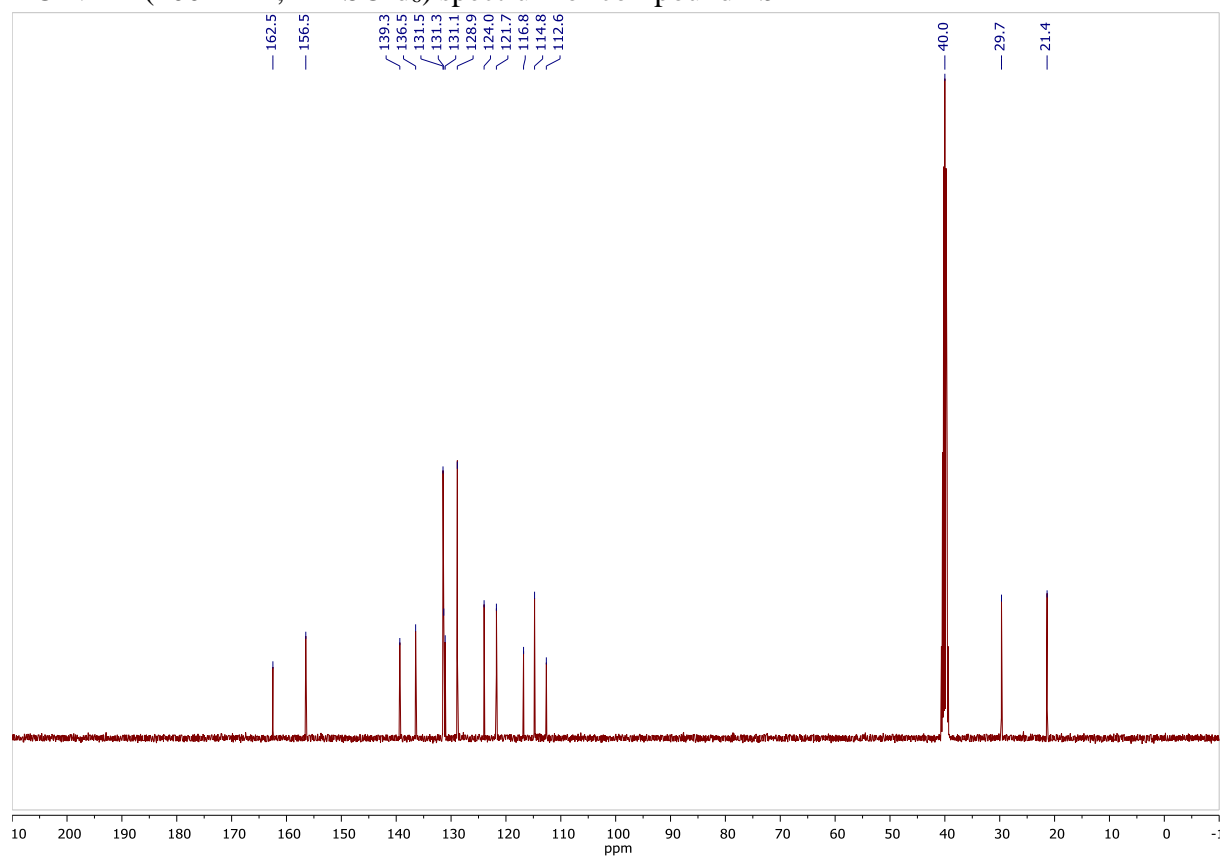
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## NMR Spectra of New Compounds

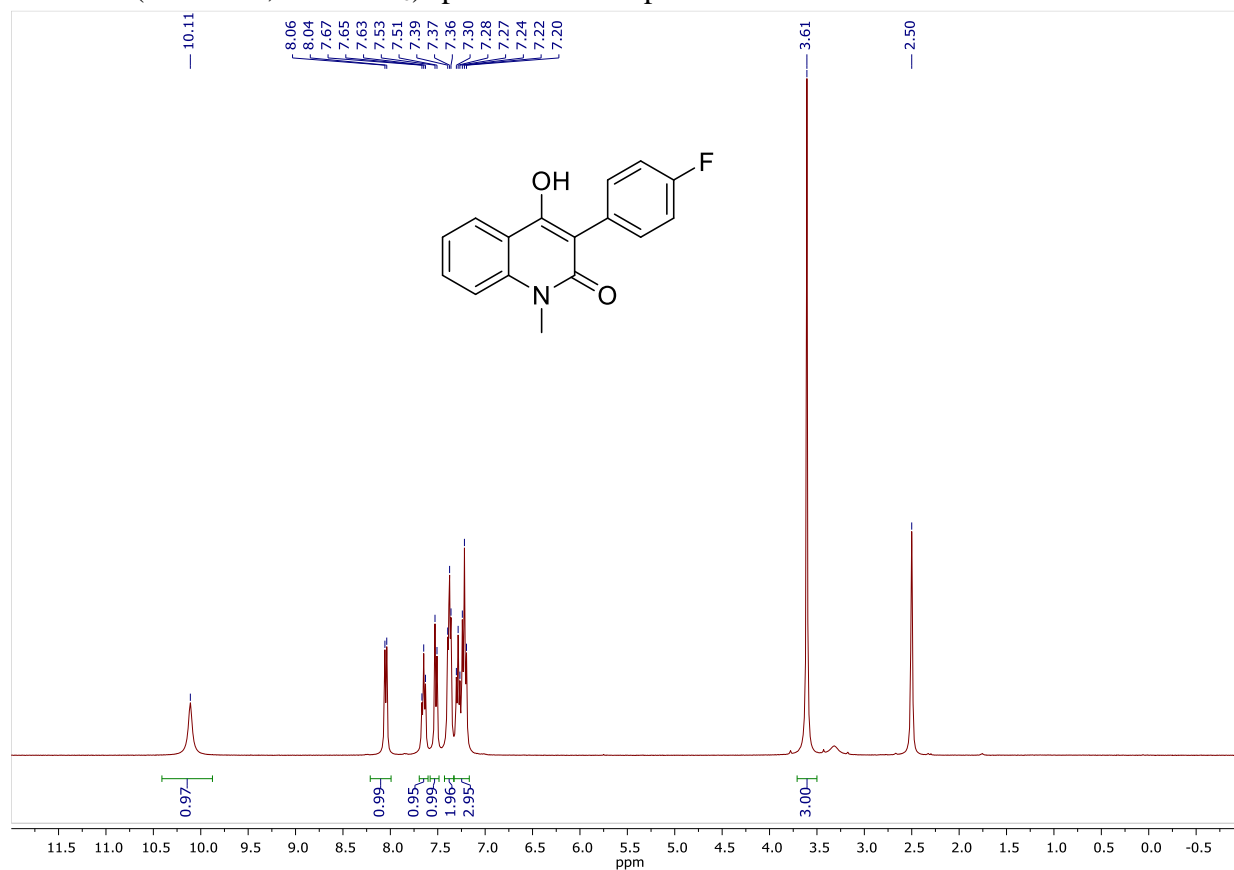
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1b**



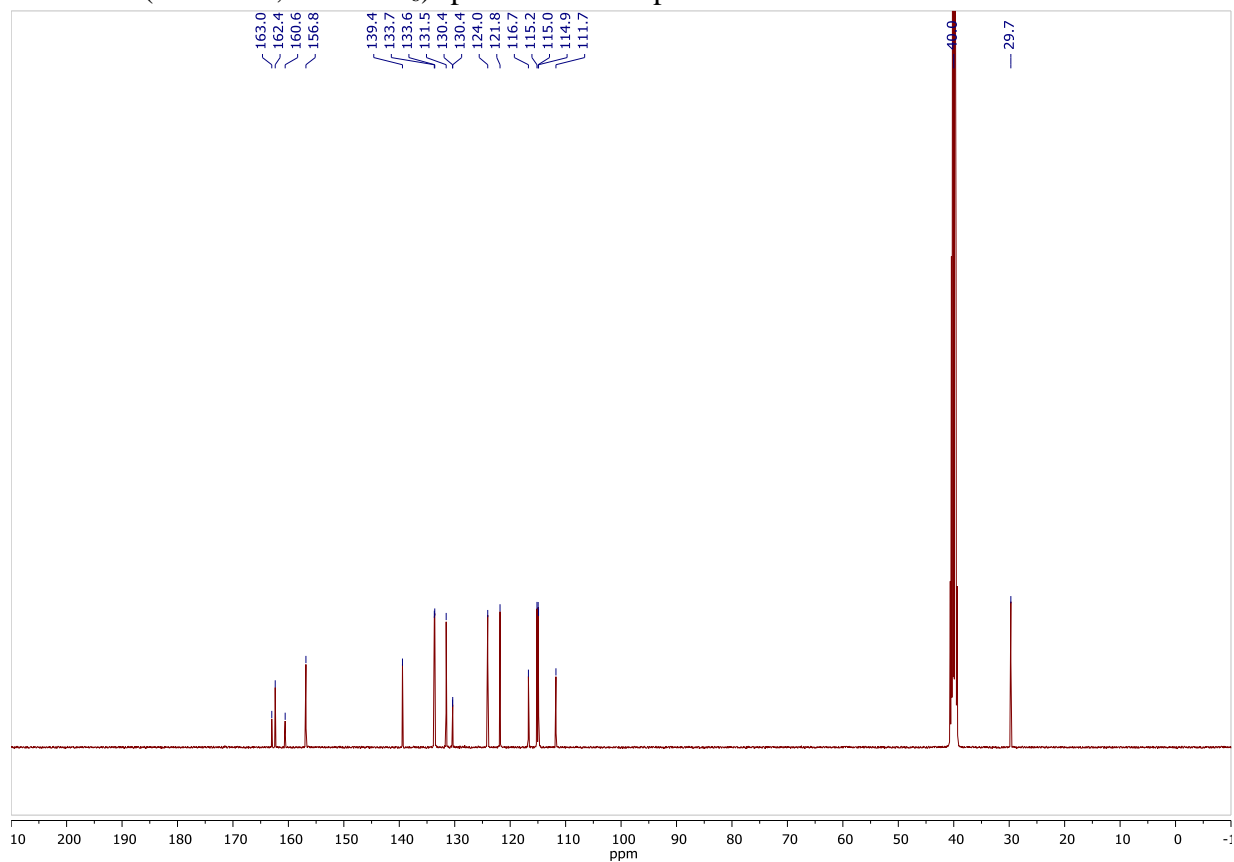
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1b**



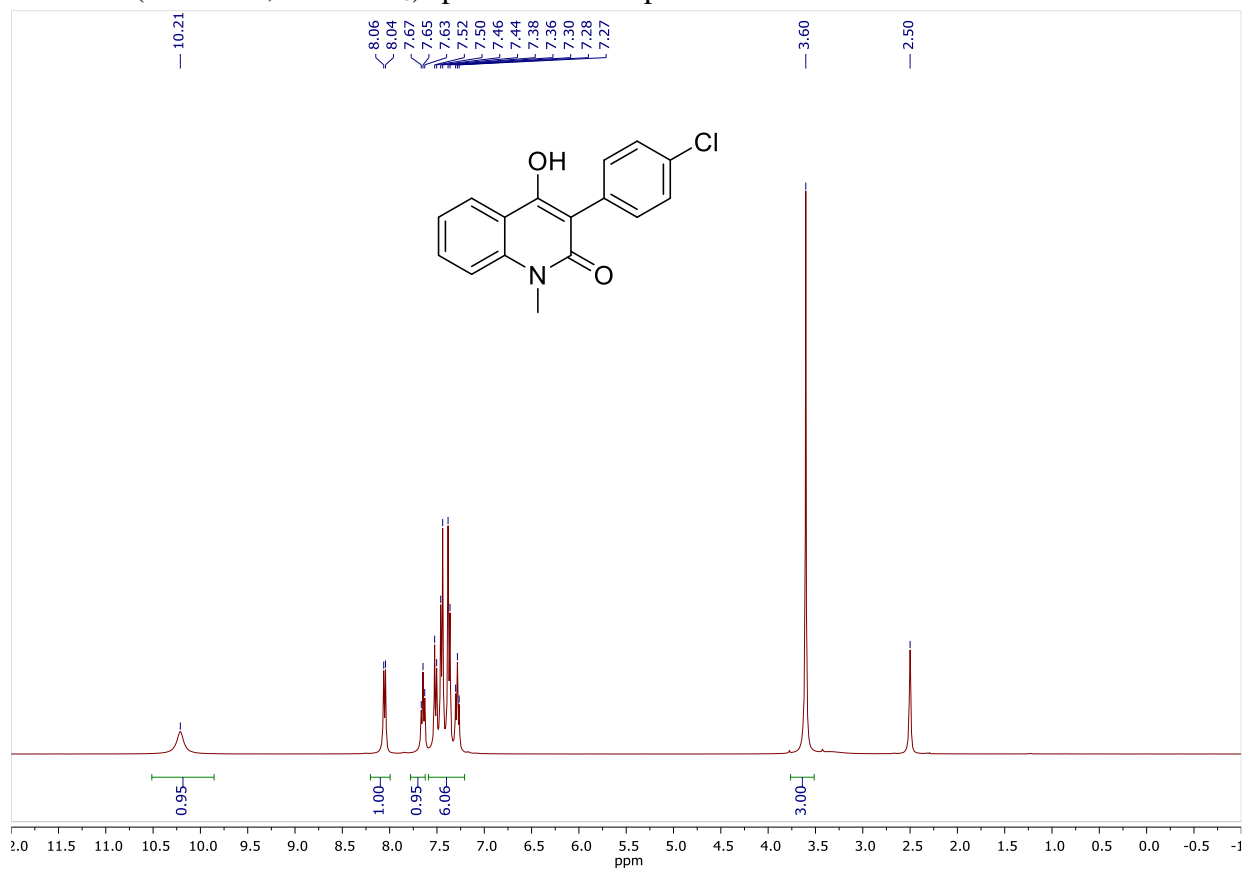
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1d**



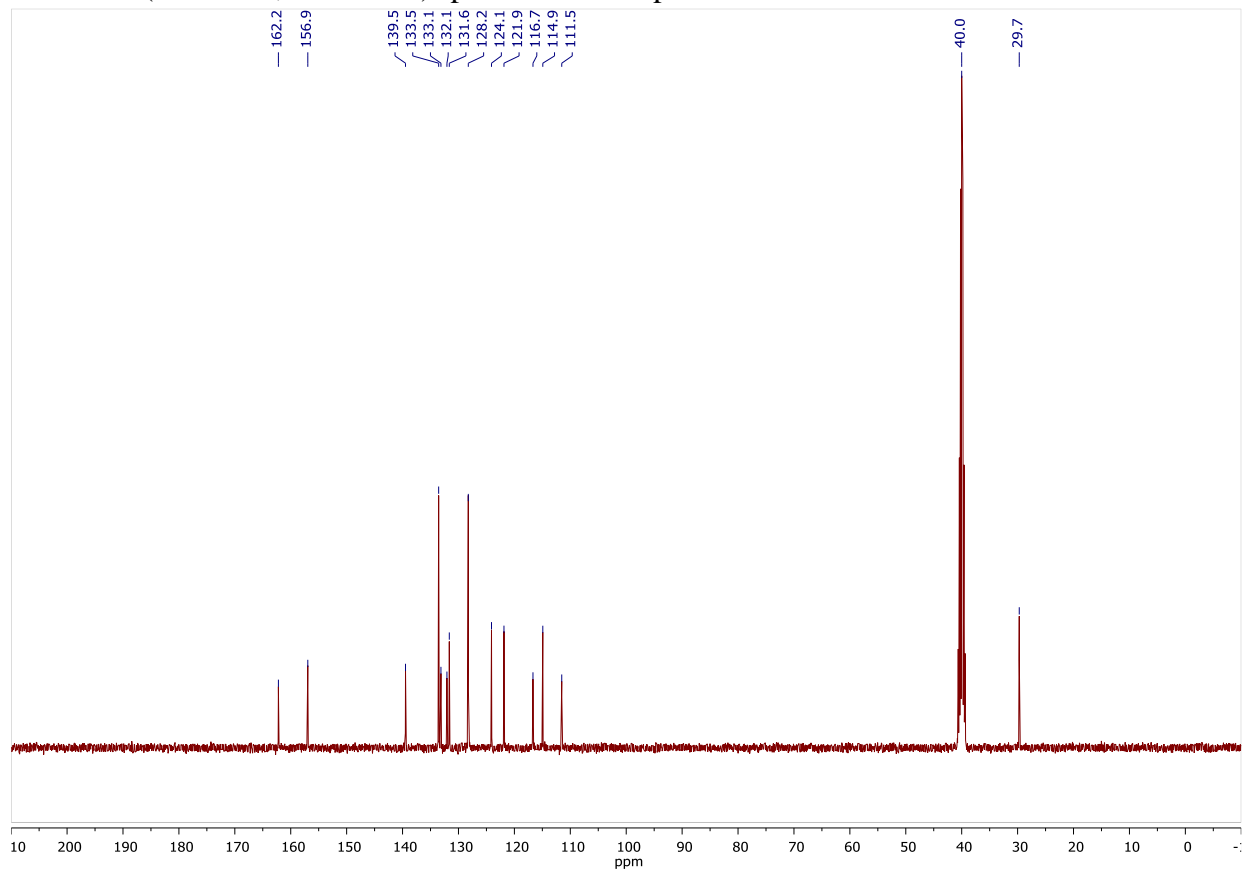
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1d**



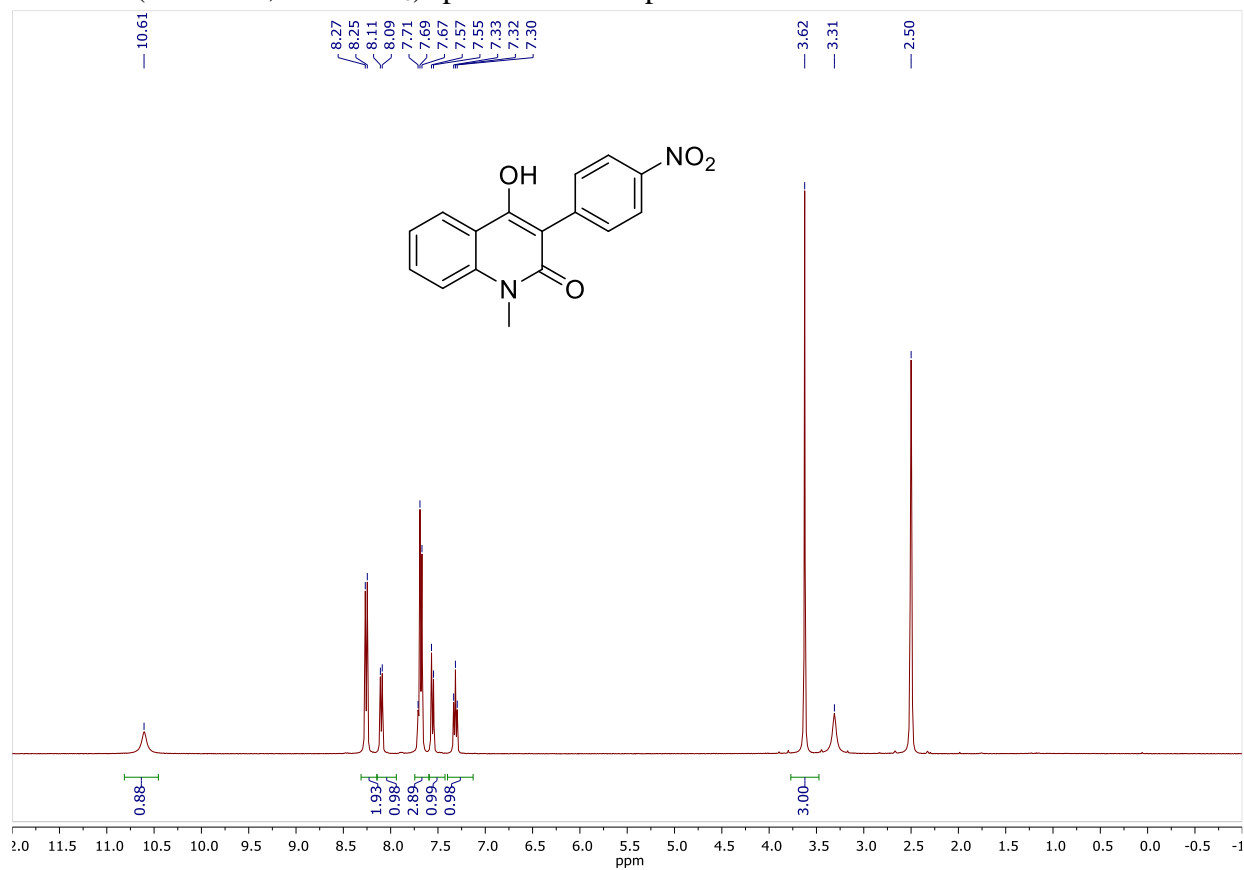
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1e**



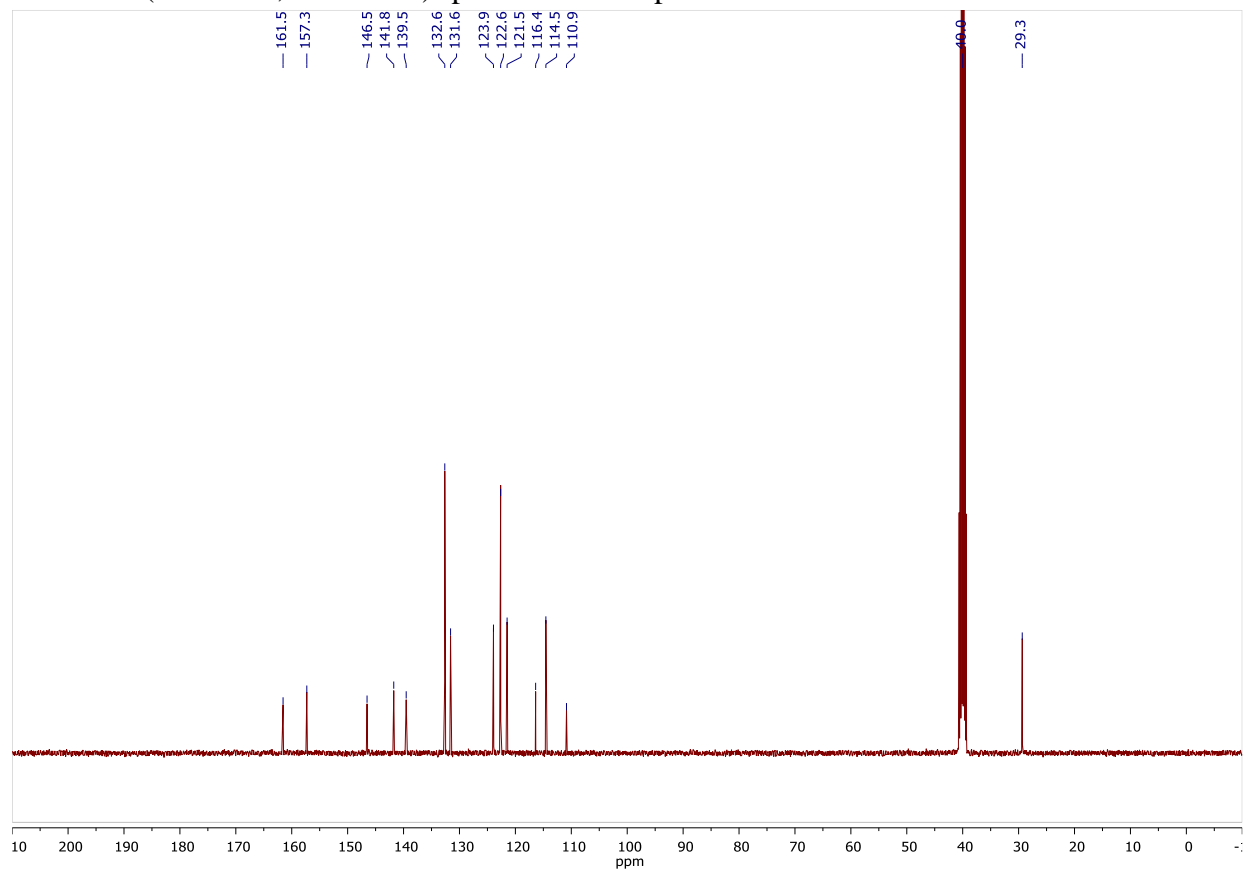
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1e**



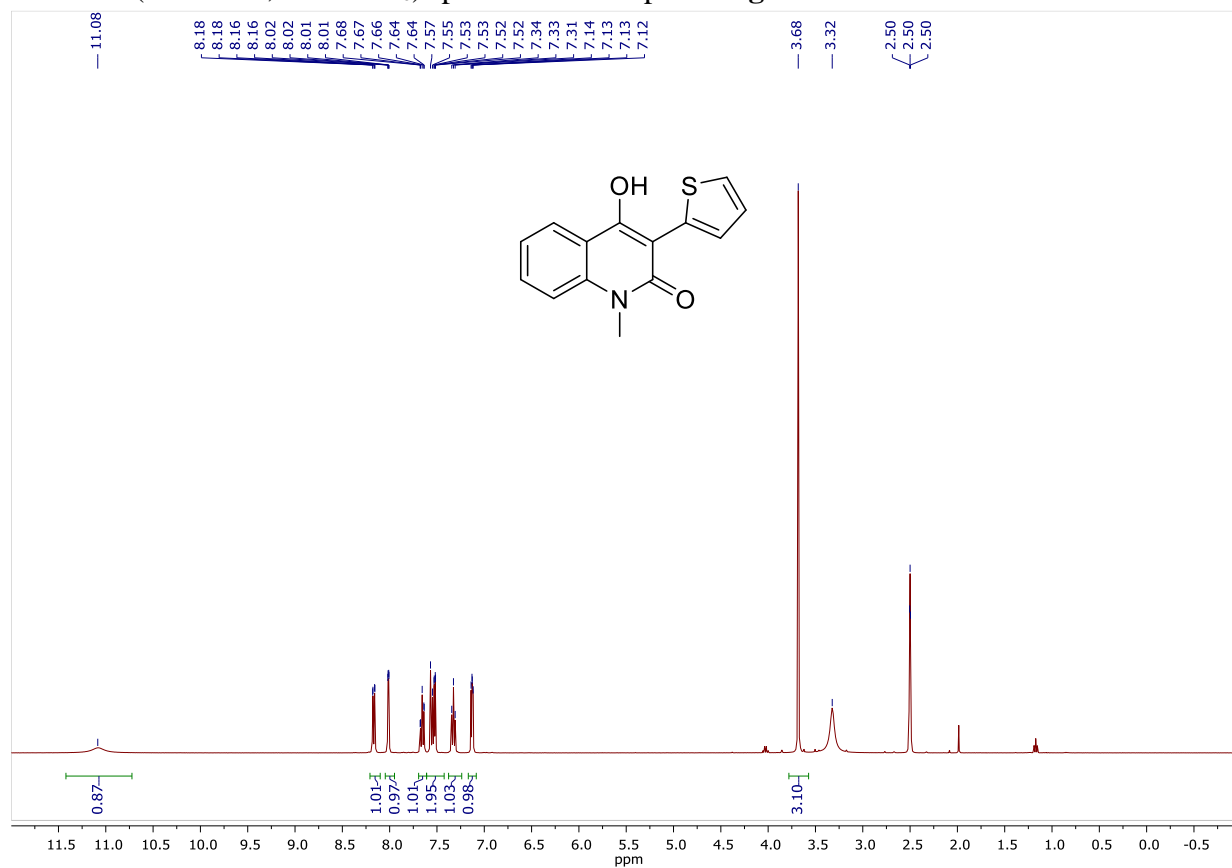
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1f**



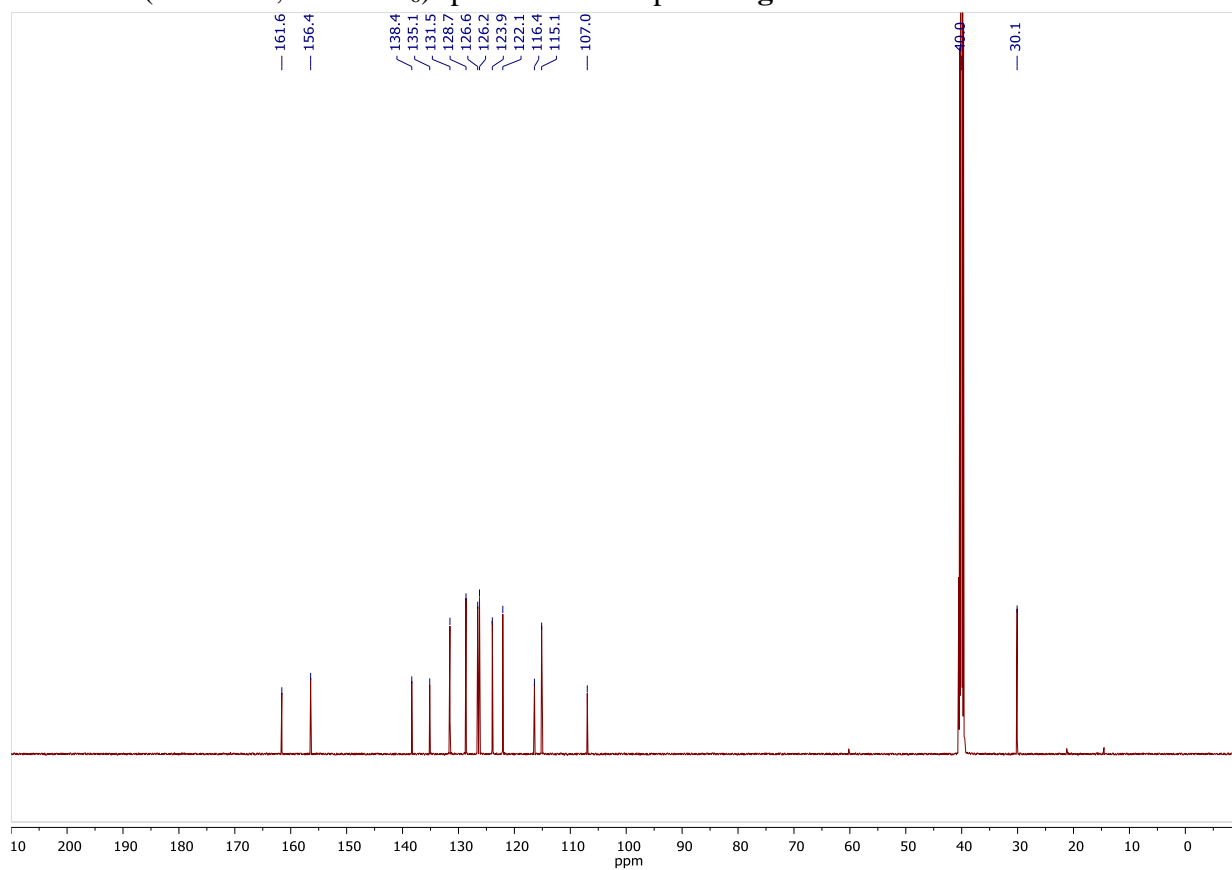
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1f**



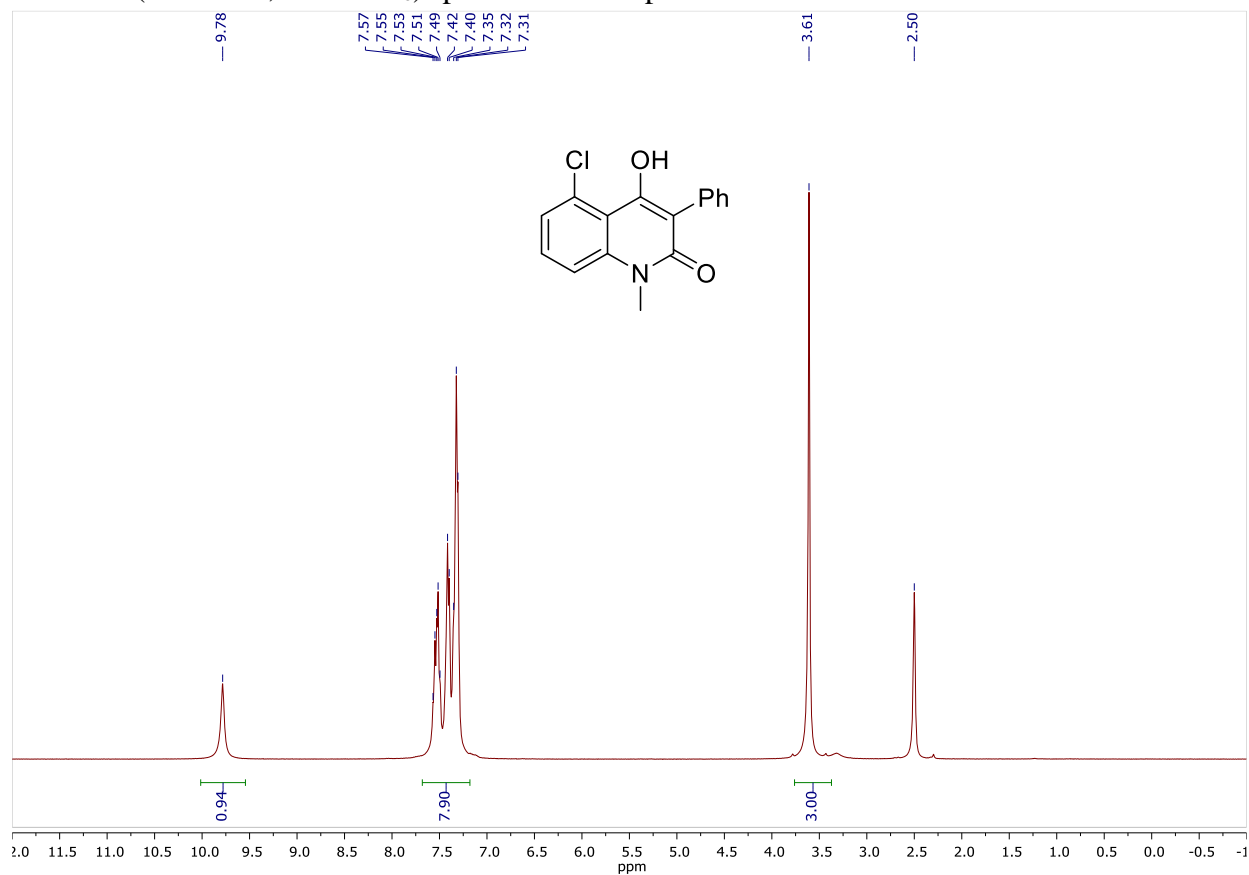
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1g**



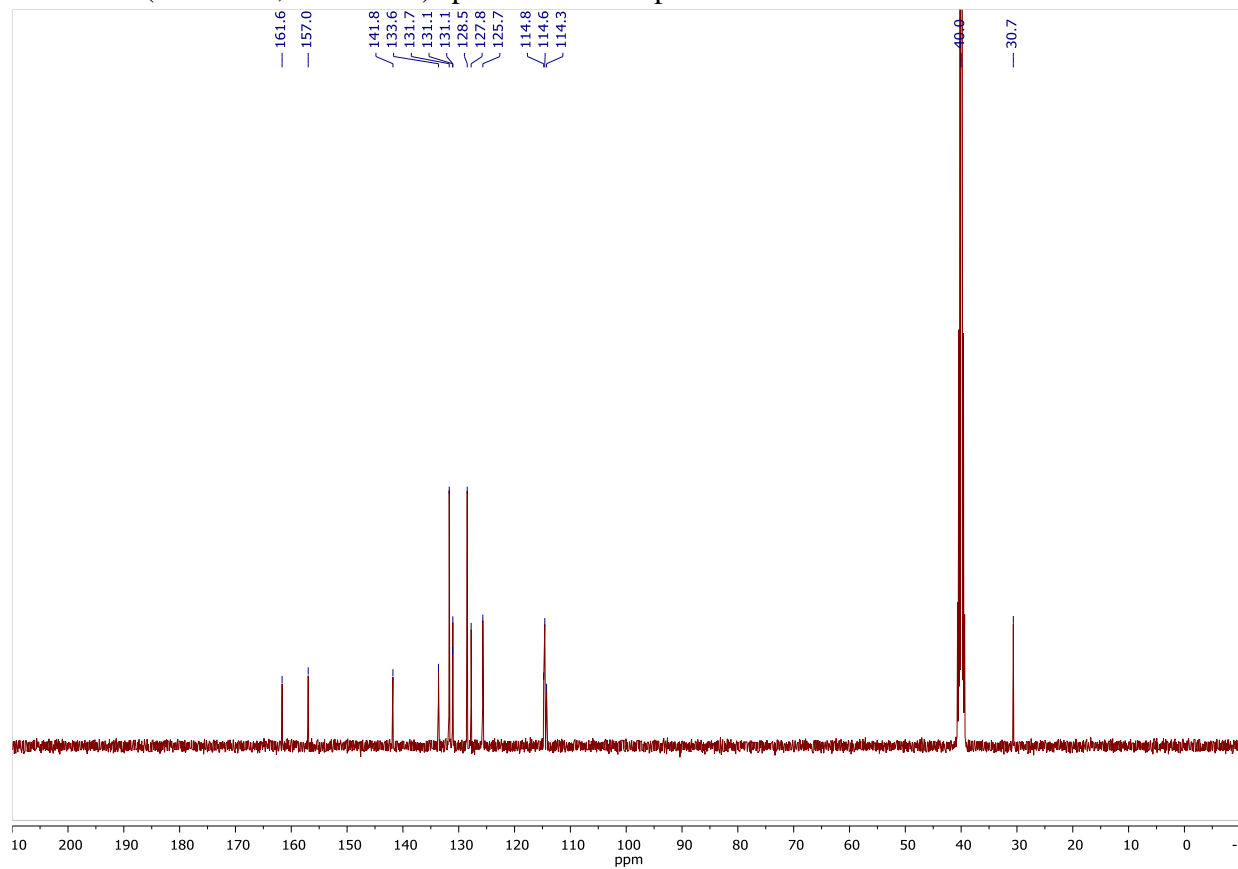
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1g**



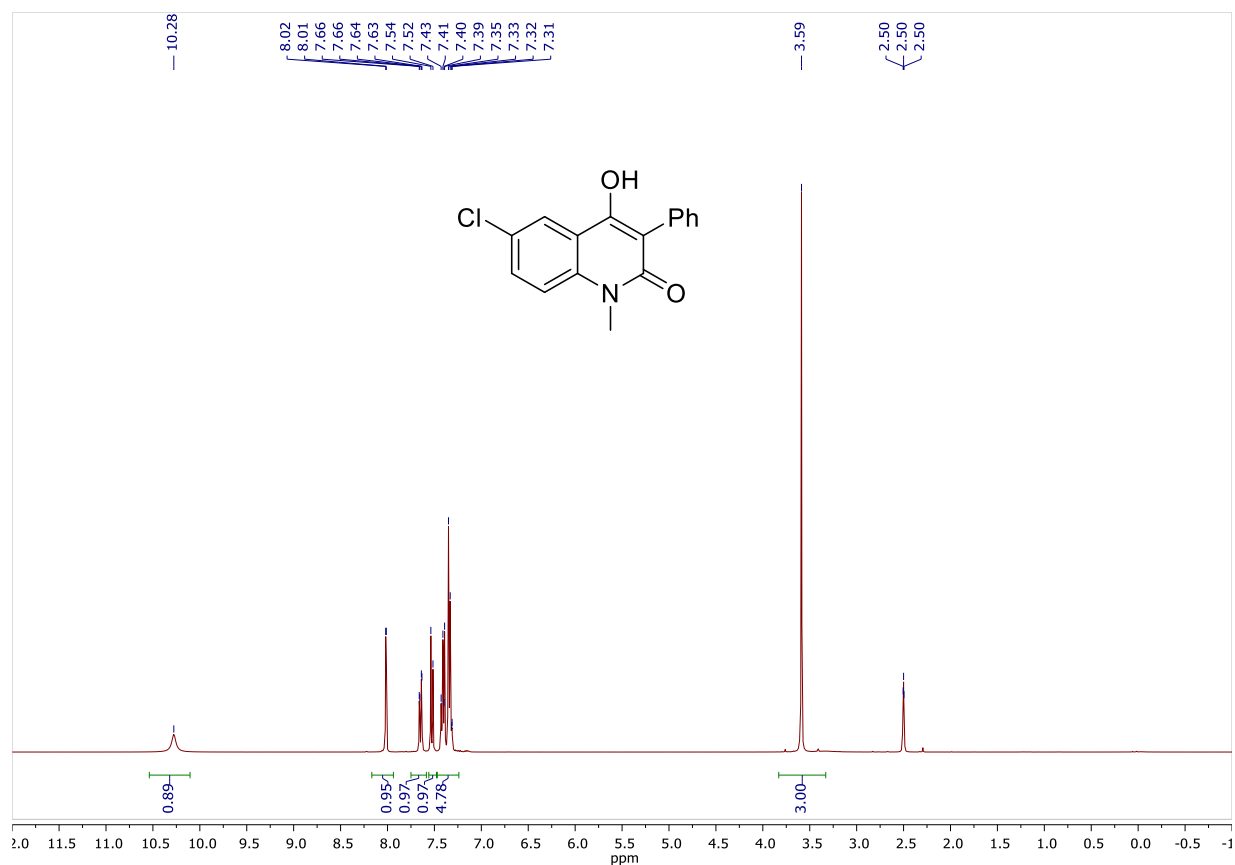
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1h**



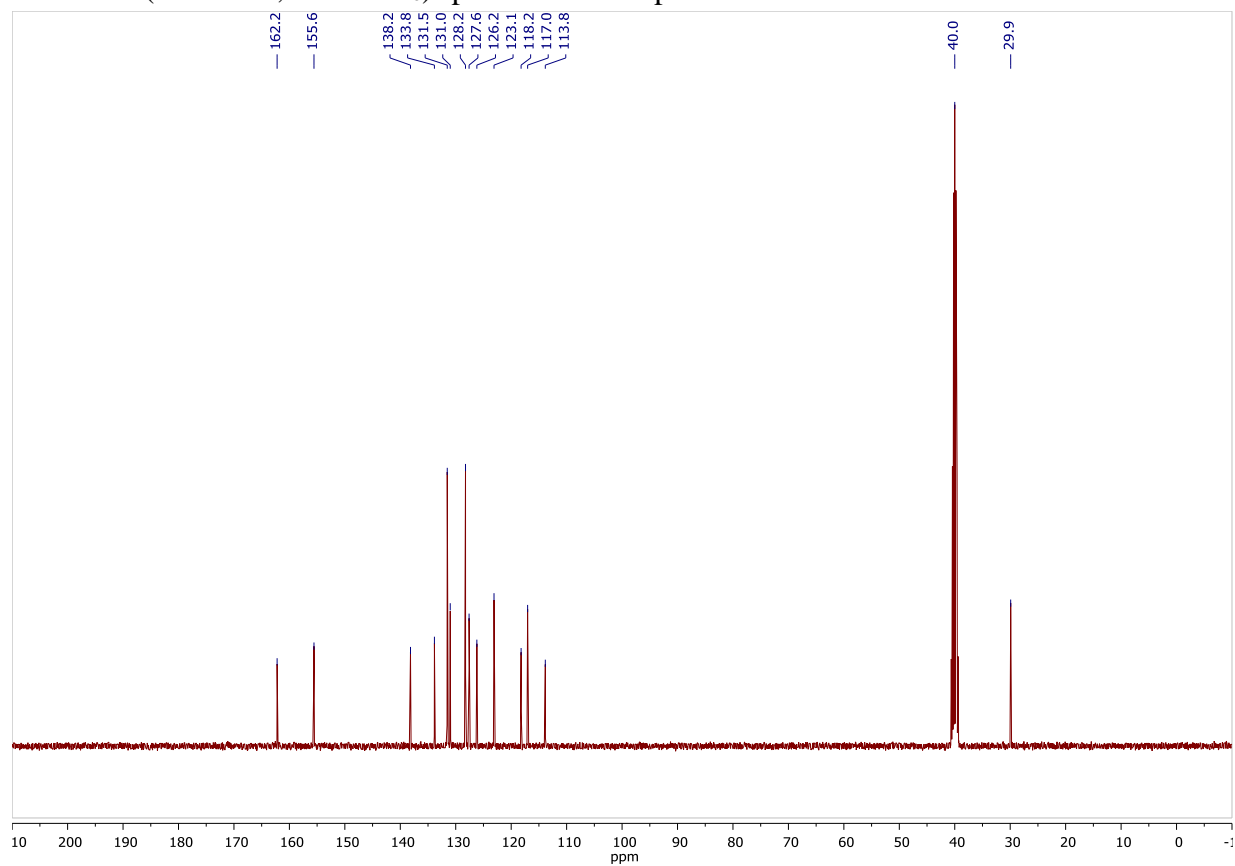
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1h**



$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1i**

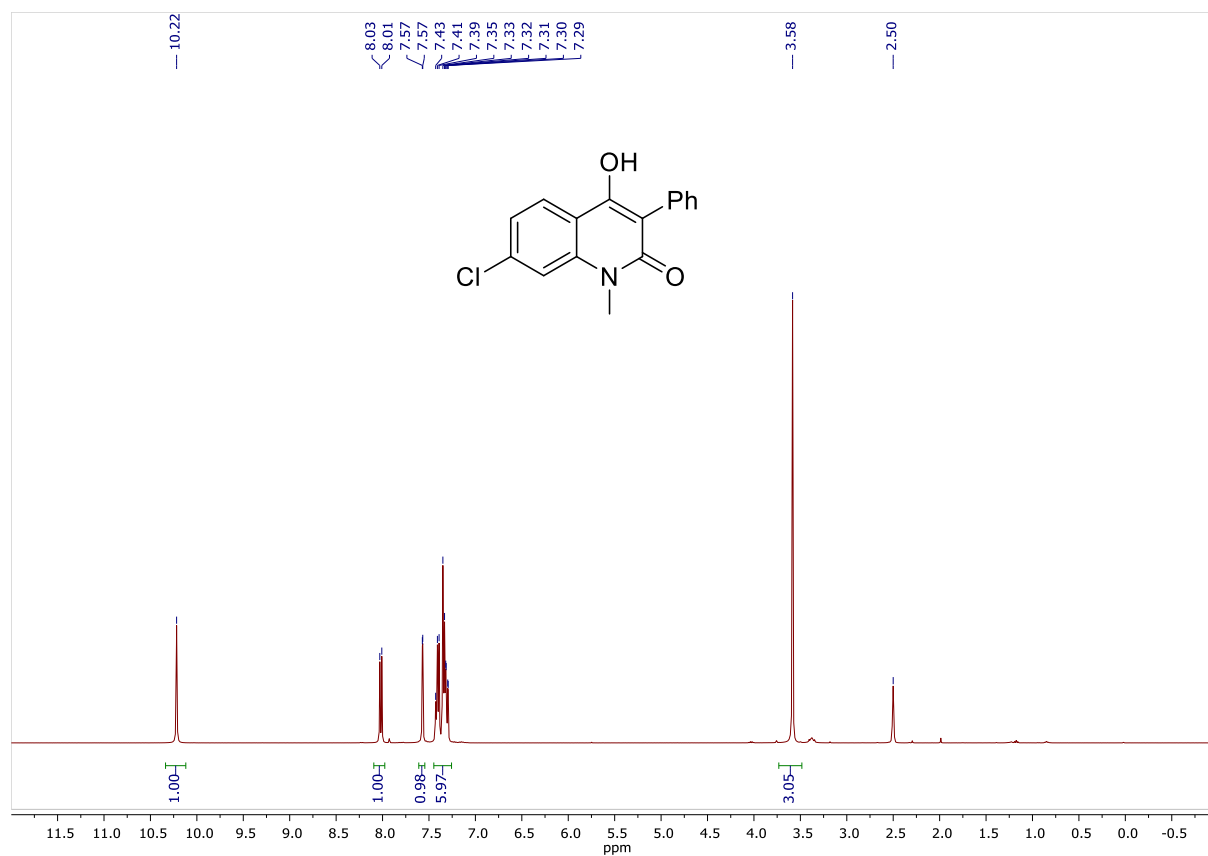


$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **1i**

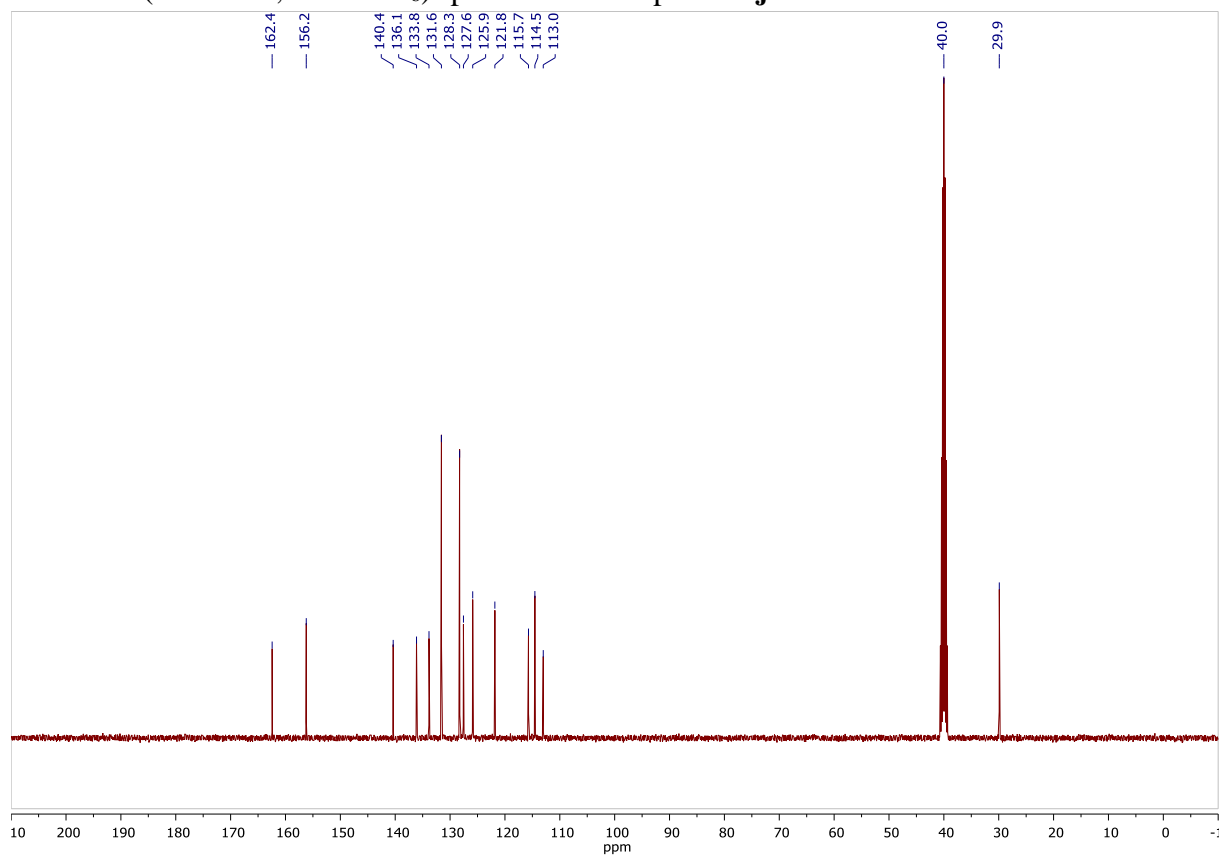




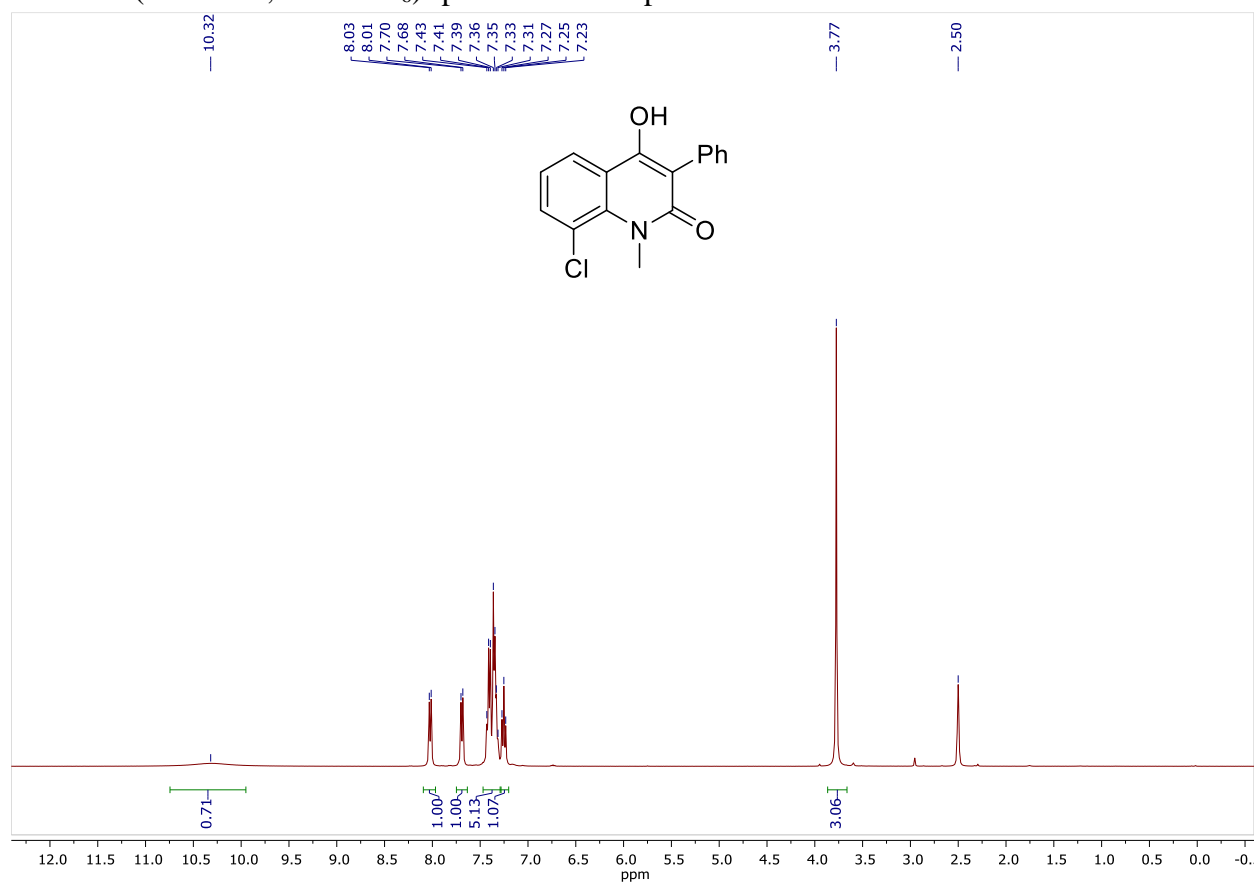
$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) spectrum of compound **1j**



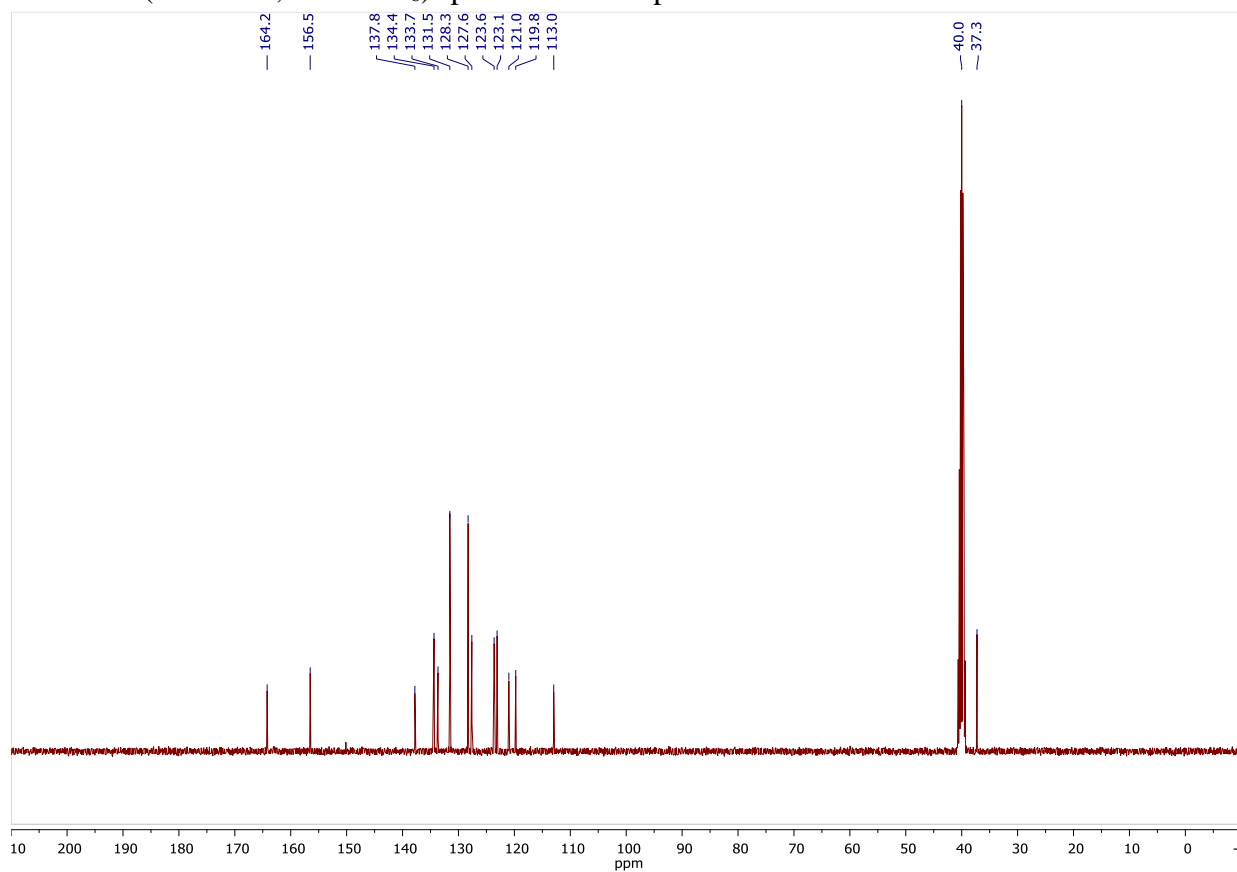
$^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ) spectrum of compound **1j**



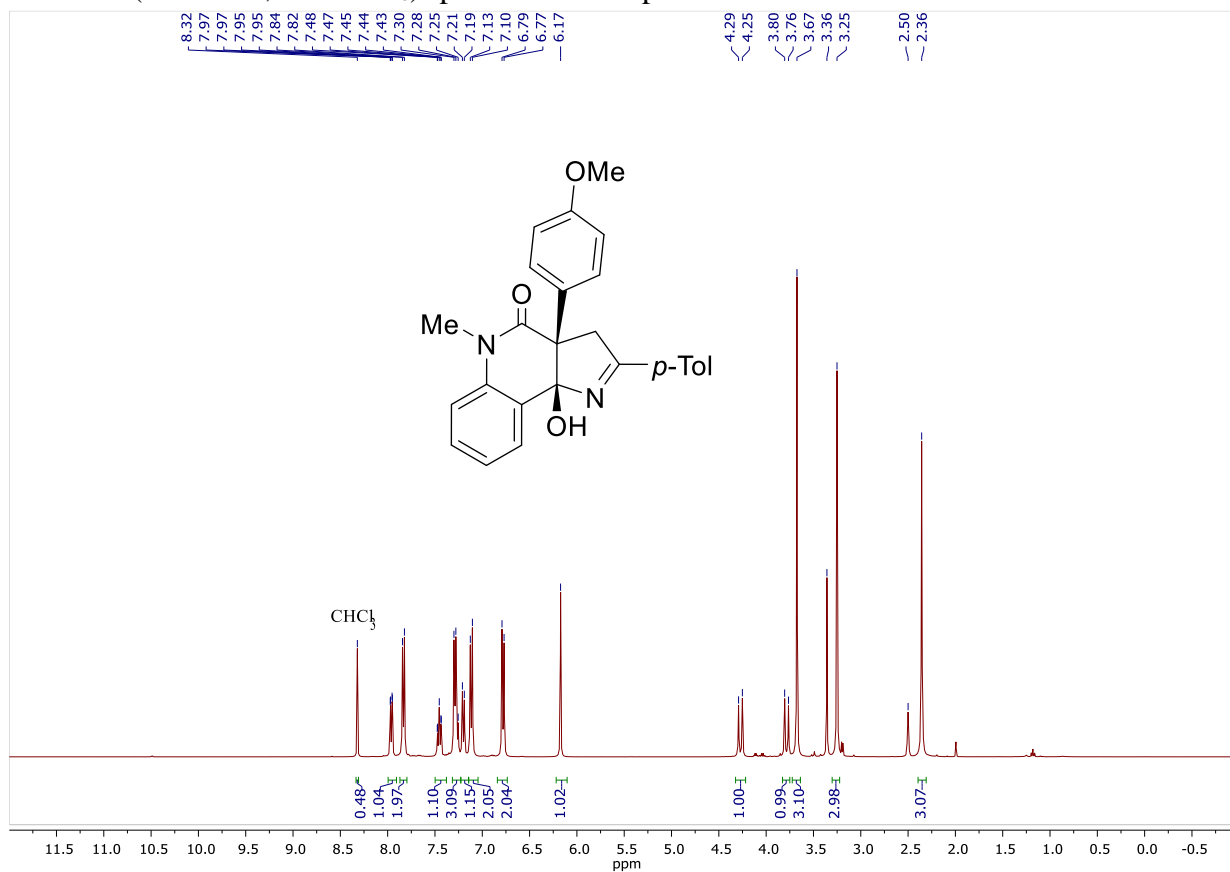
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of compound **1k**



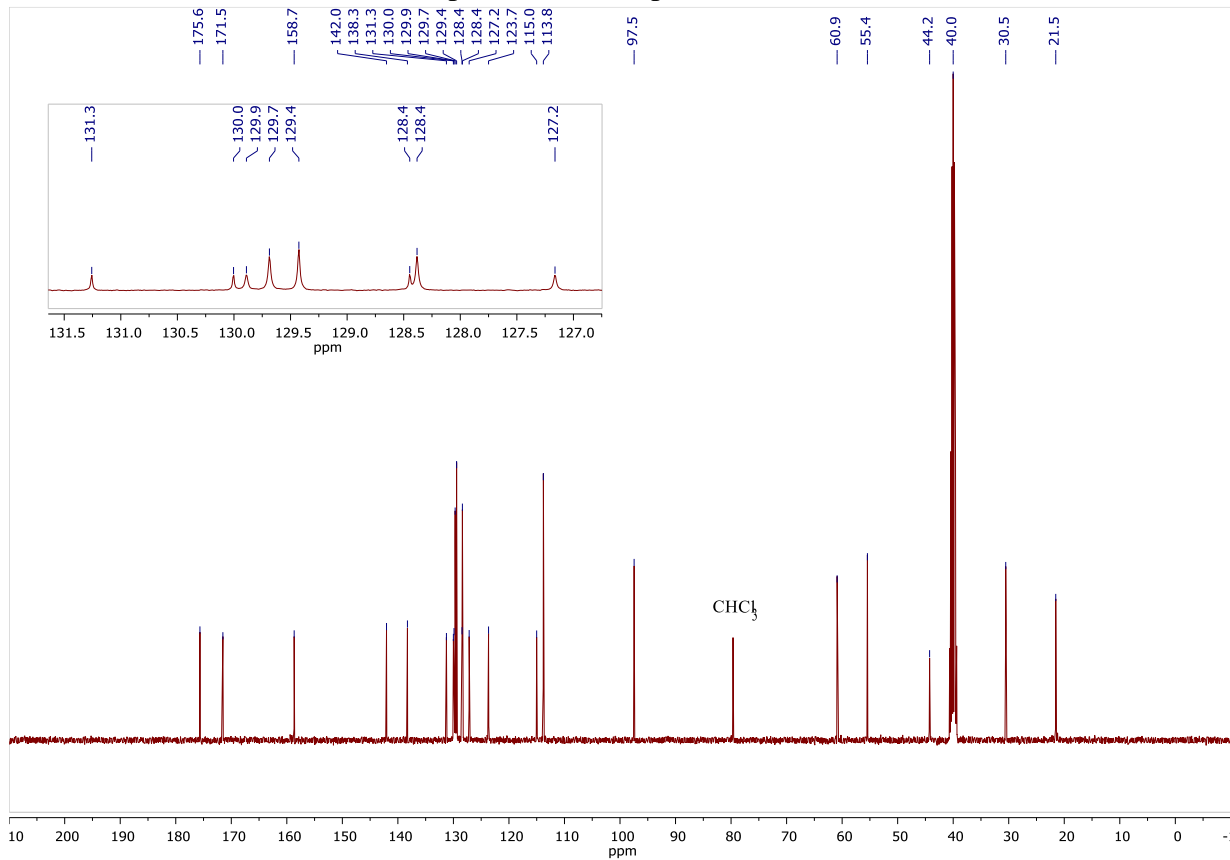
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of compound **1k**



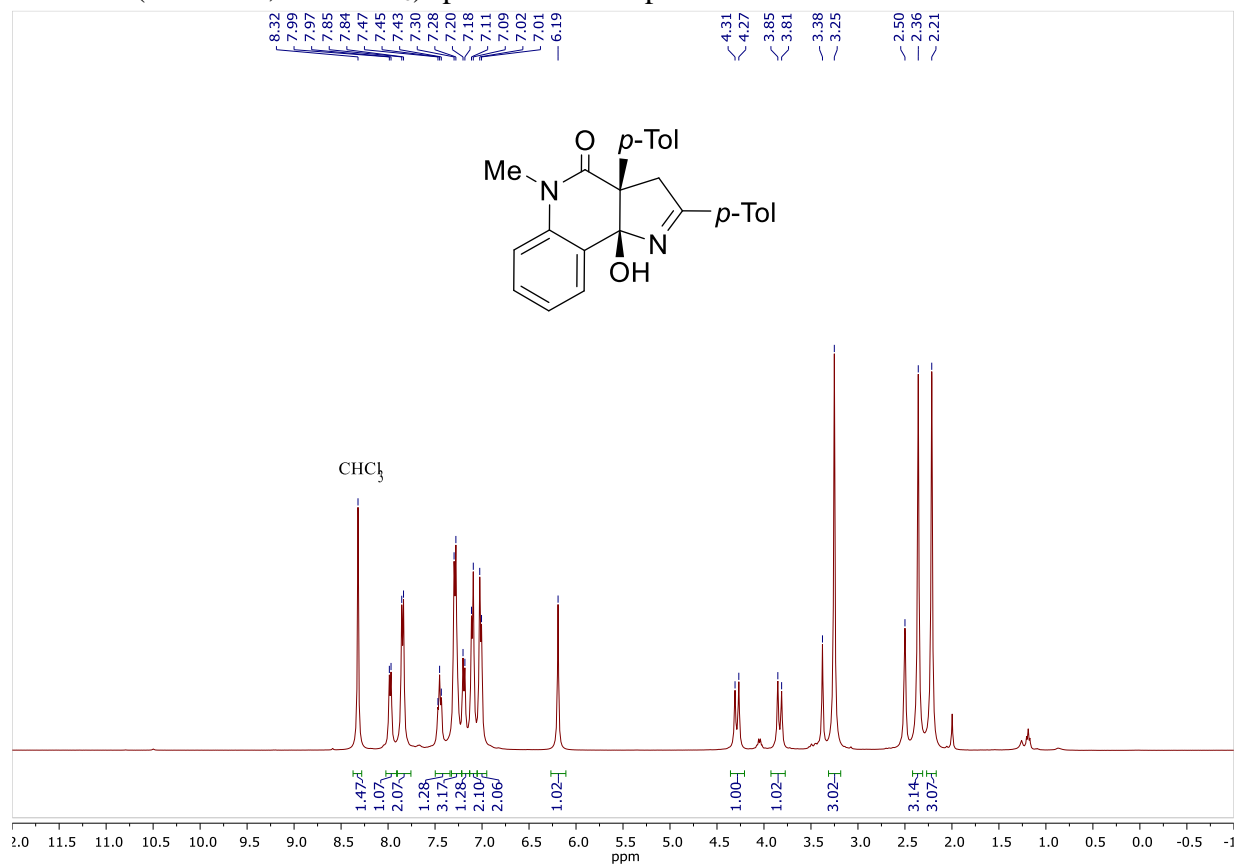
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3a**



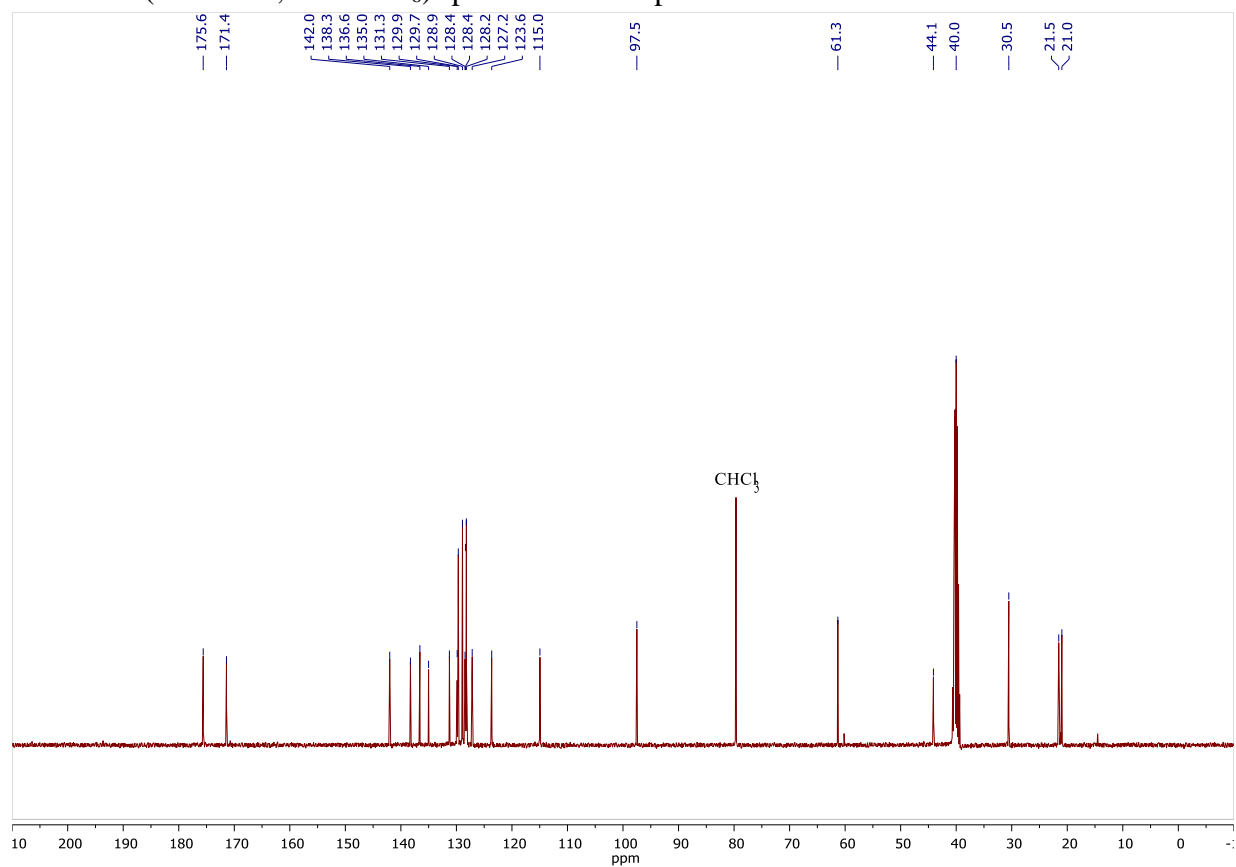
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3a**



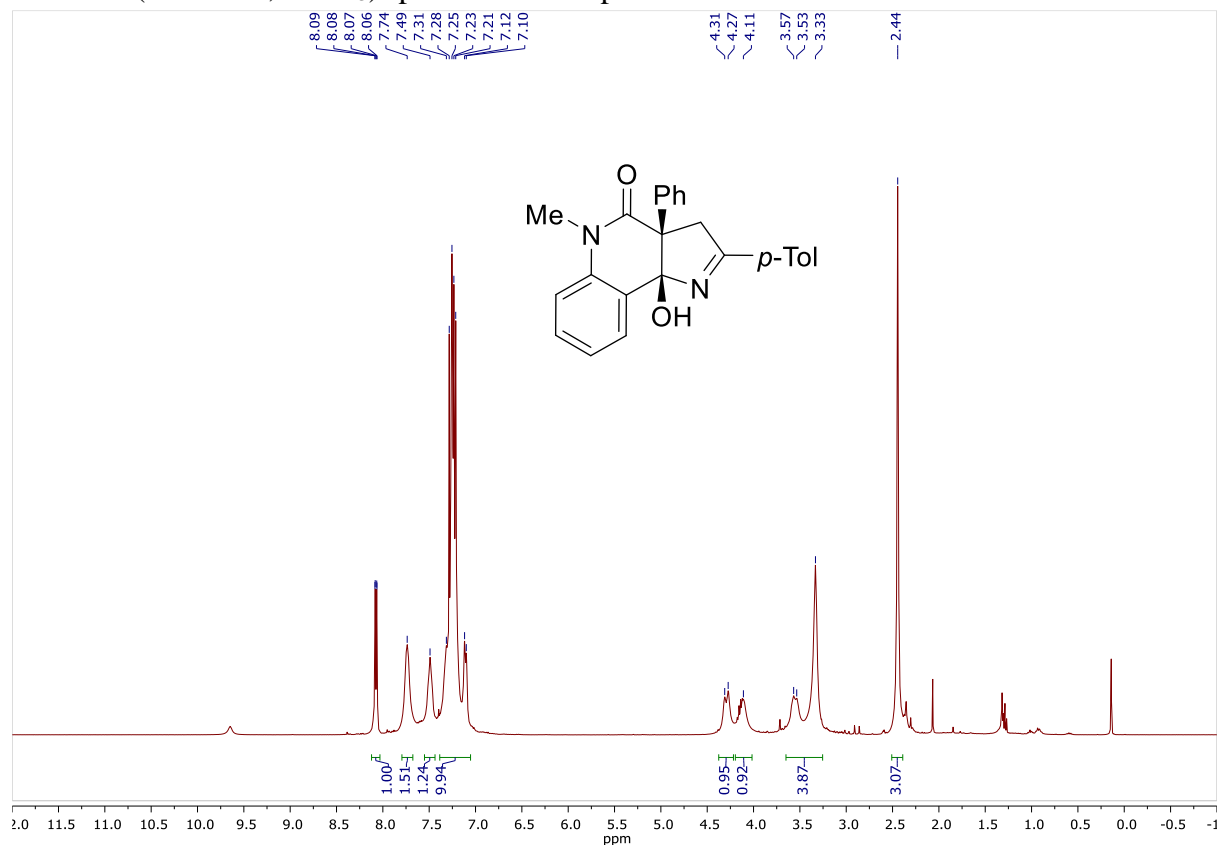
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3b**



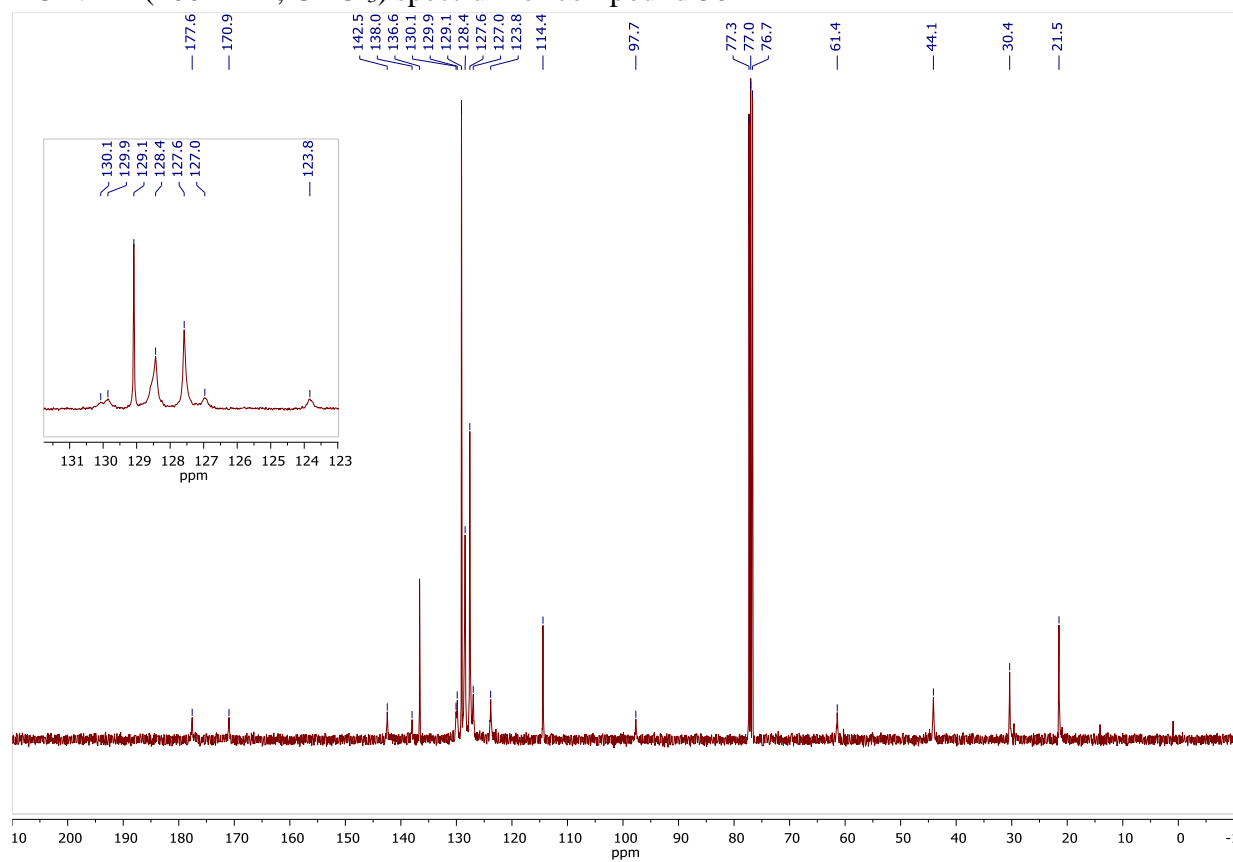
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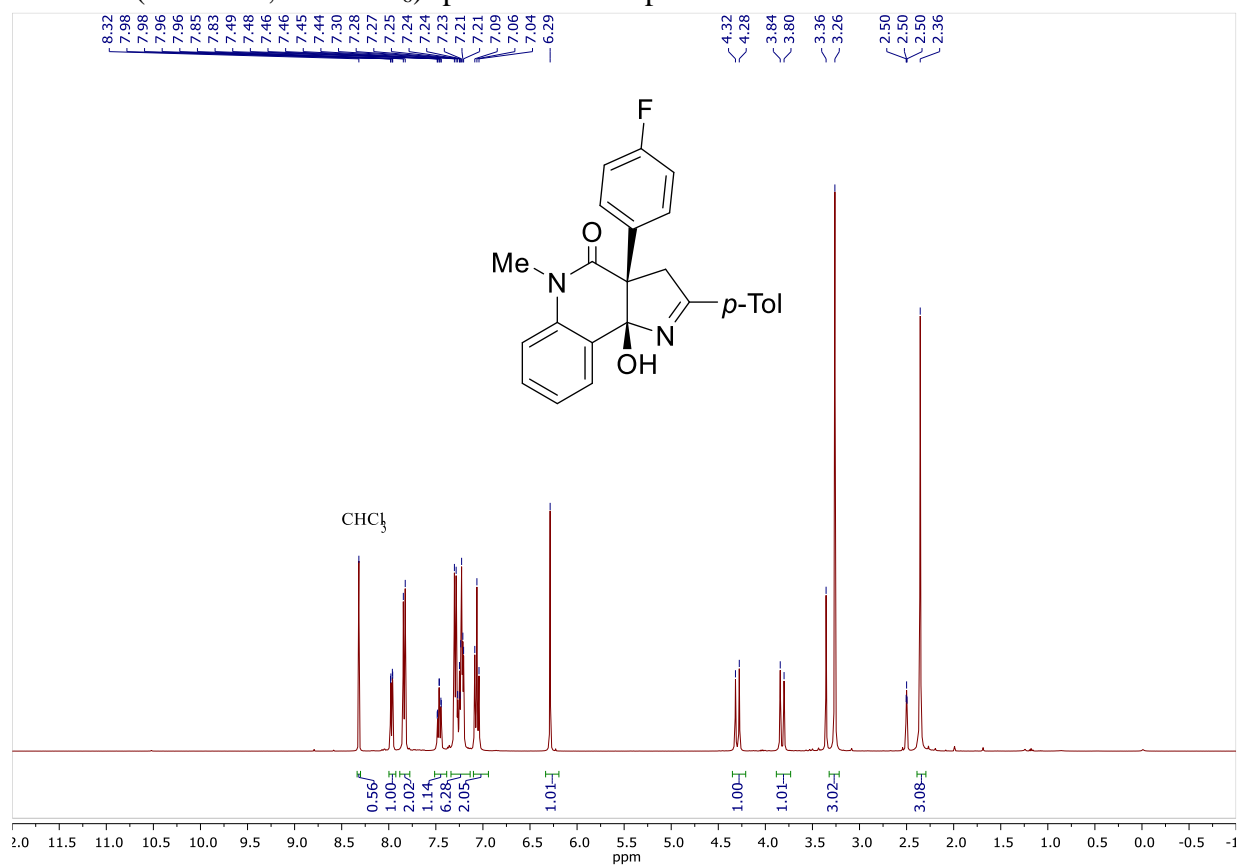
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3c**



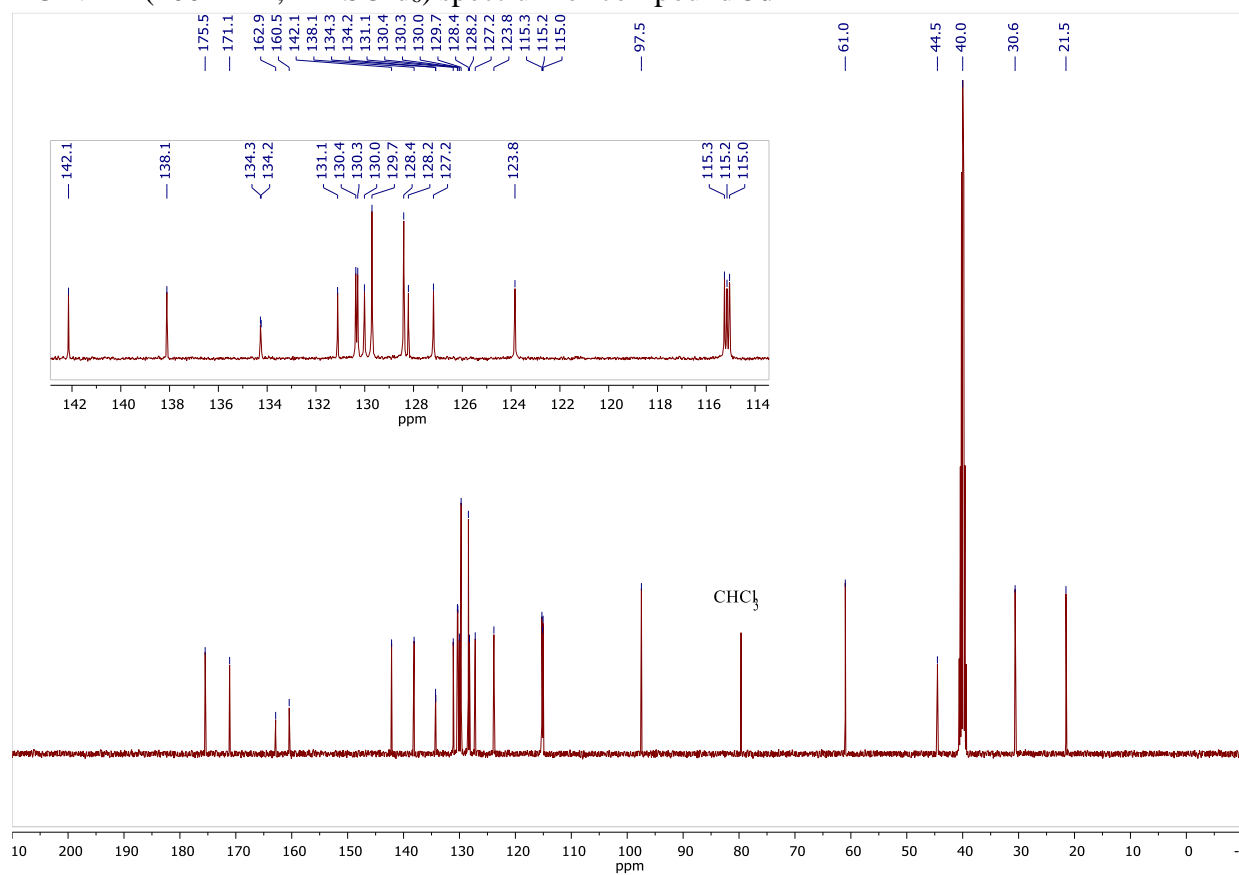
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3c**



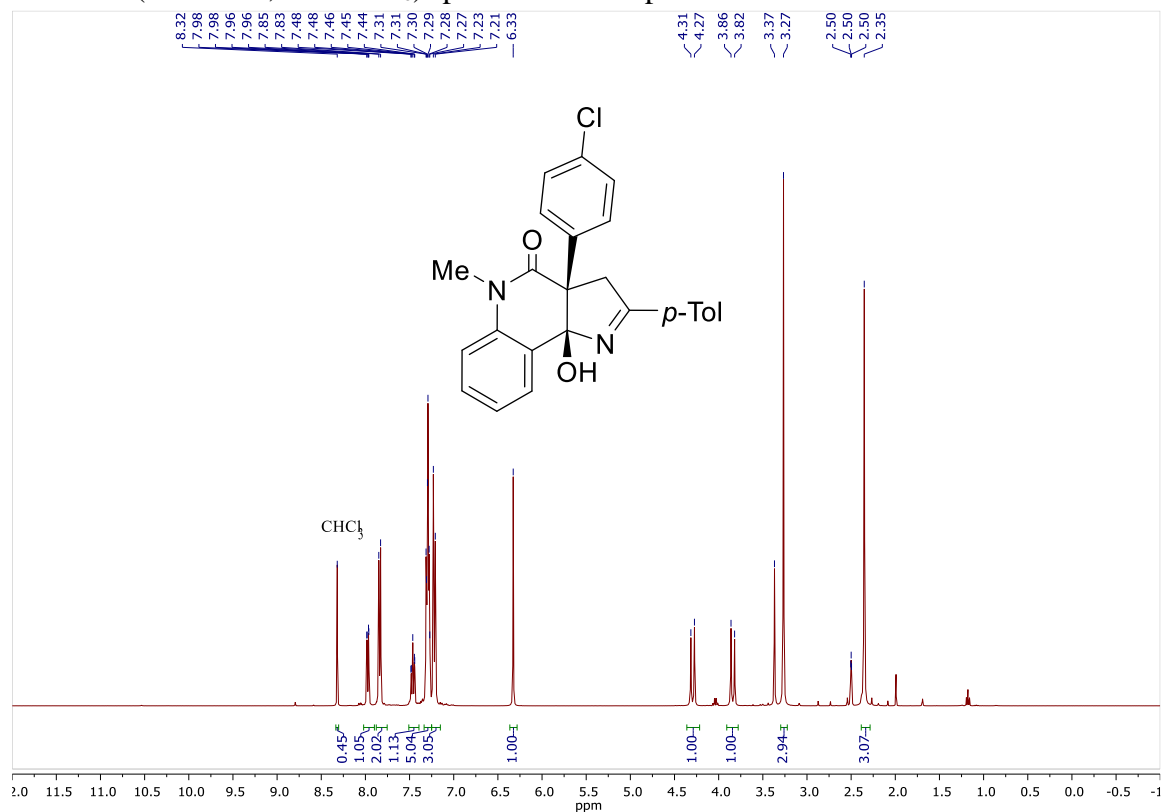
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3d**



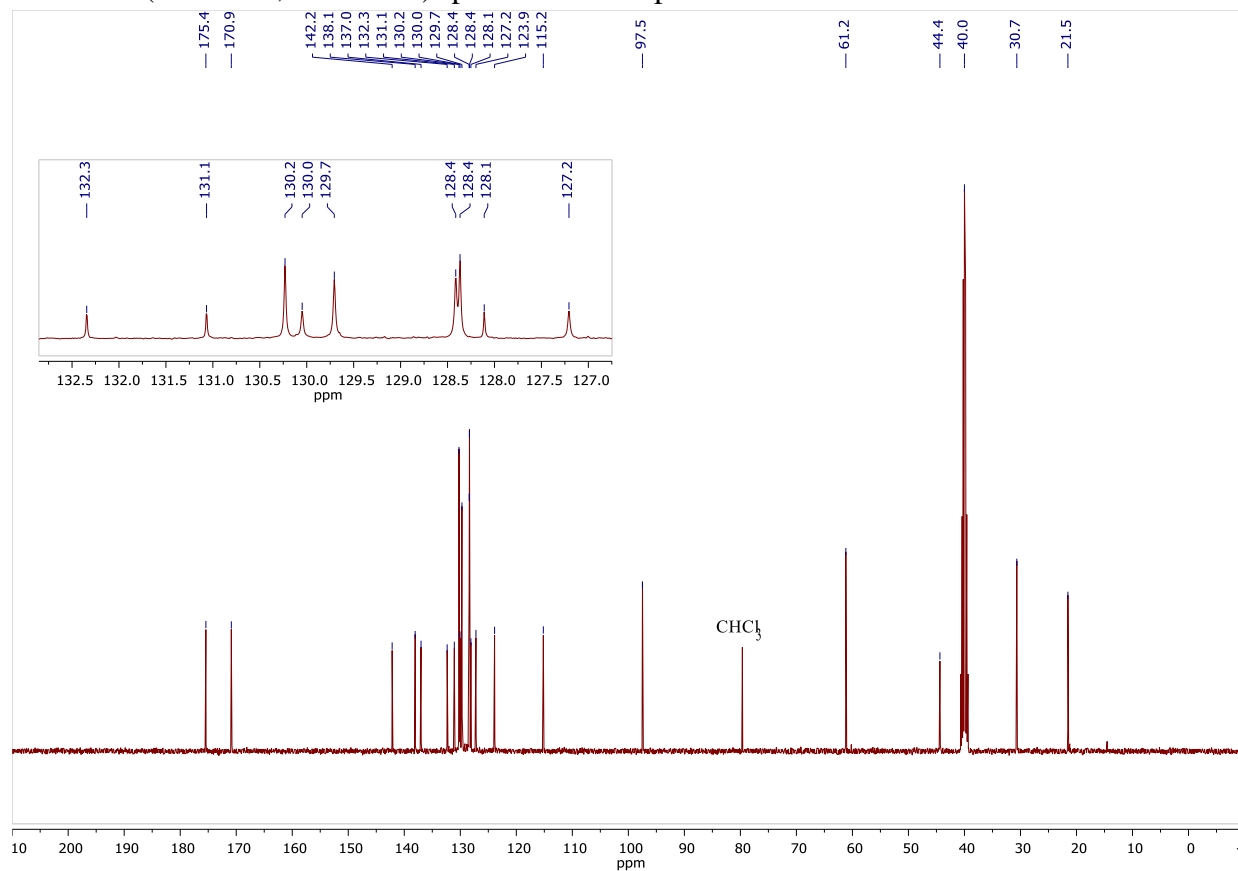
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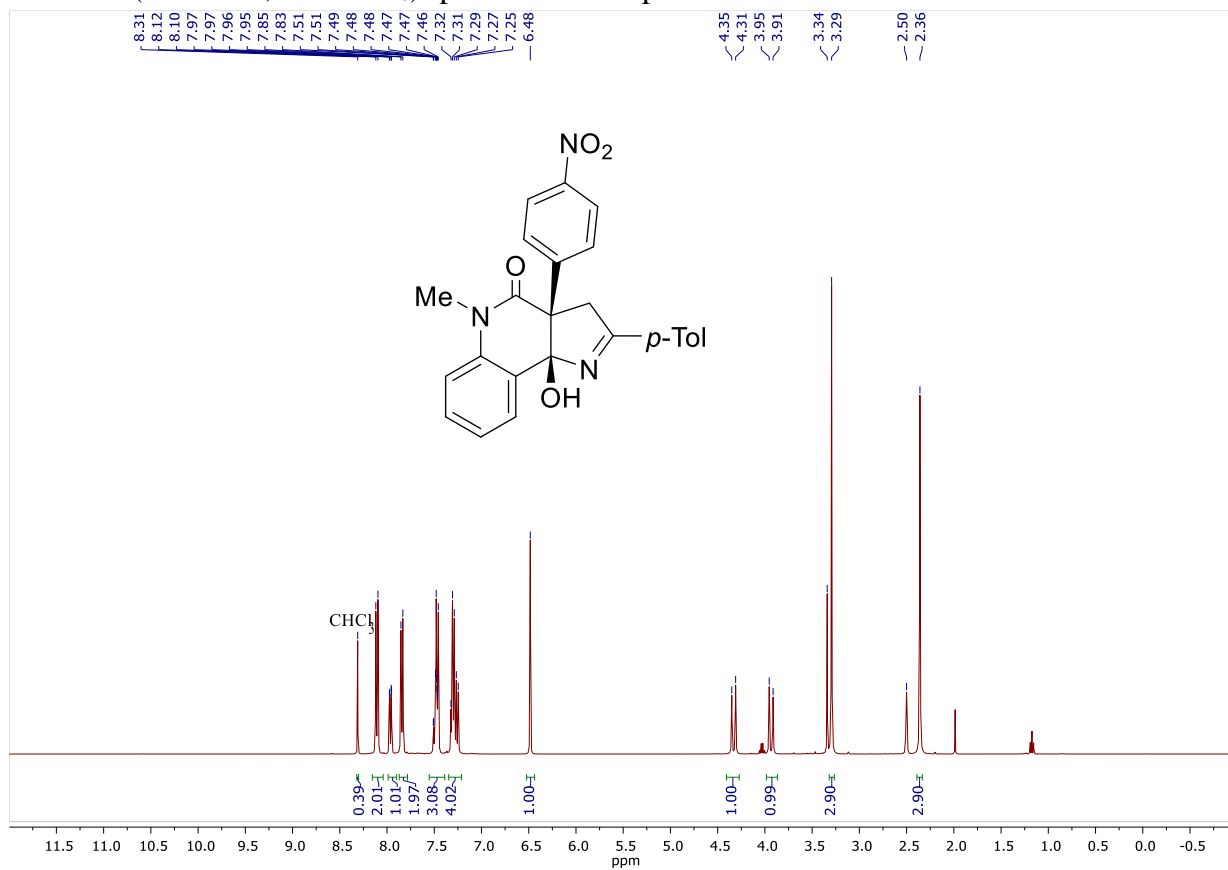
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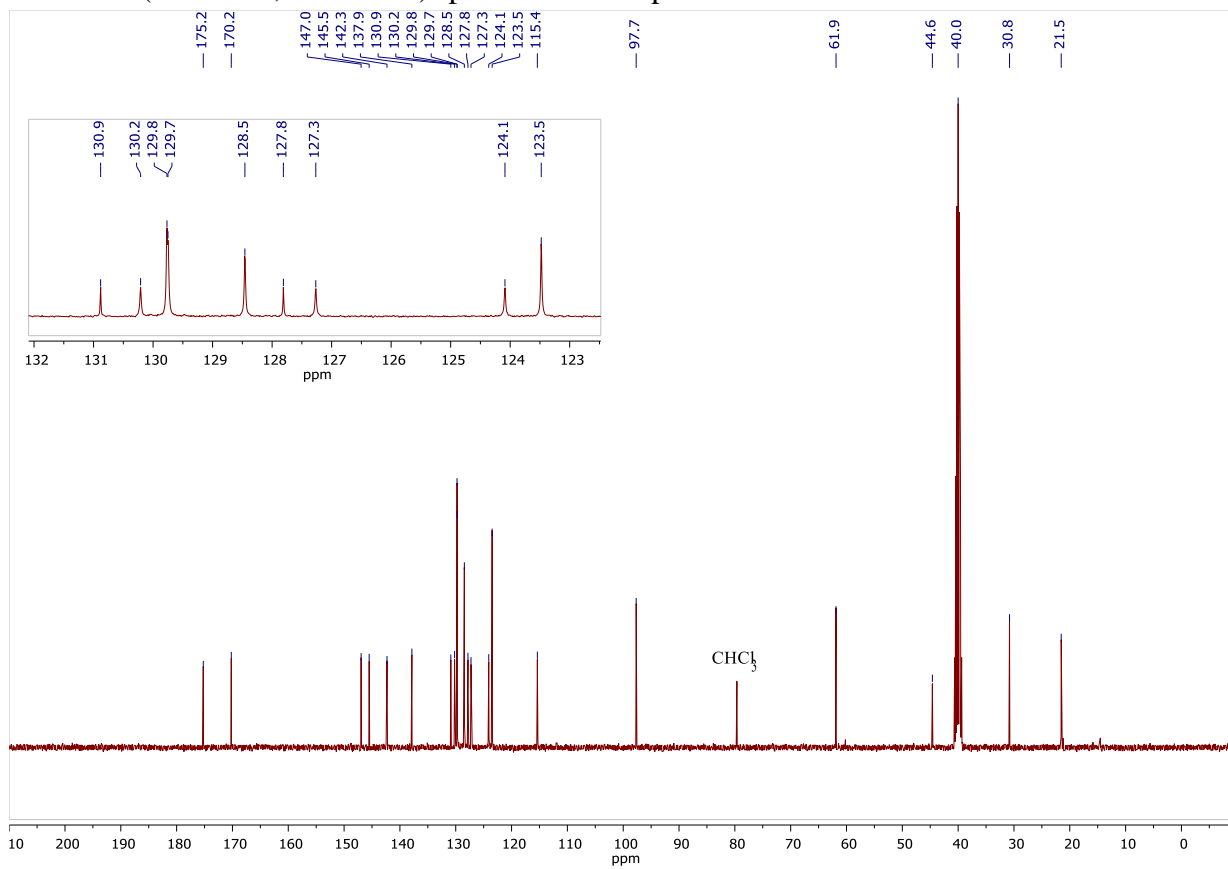
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3e**



$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3f**

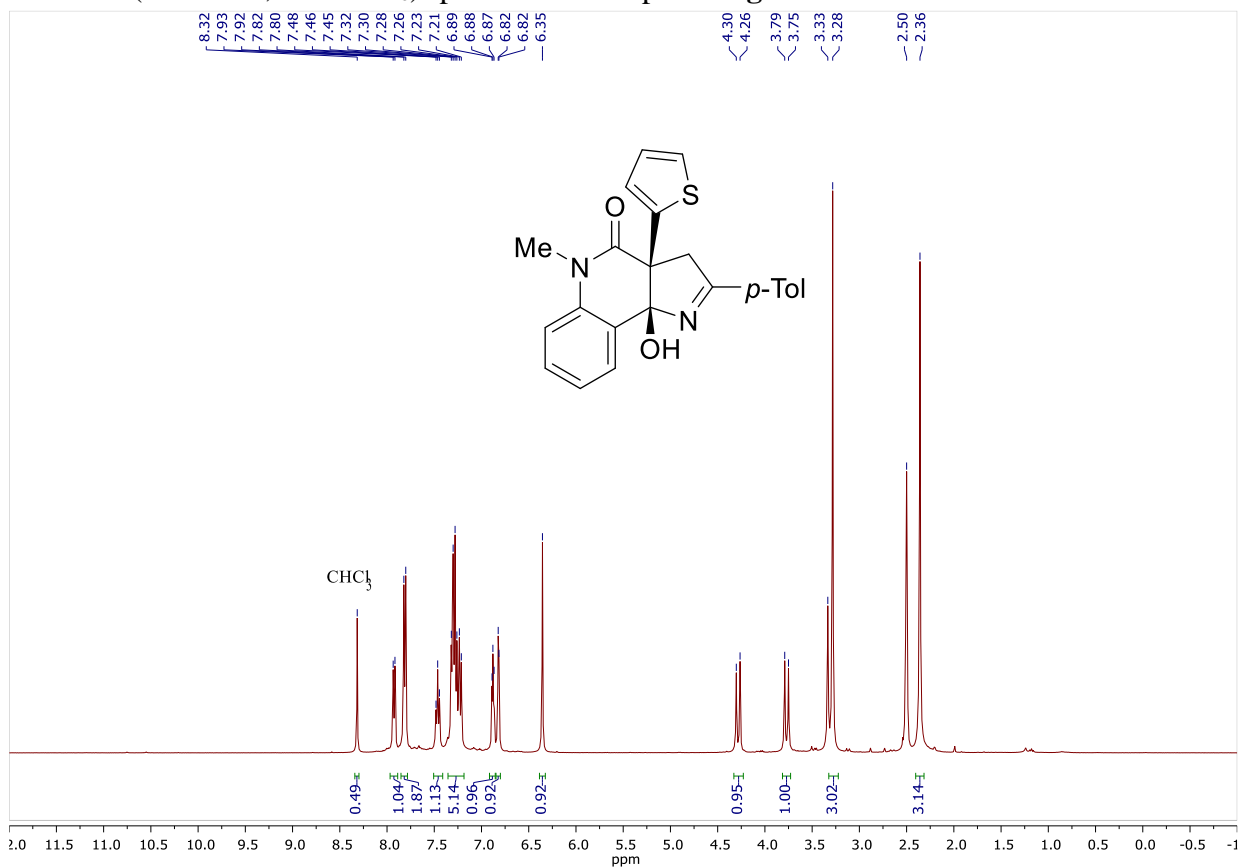


$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3f**

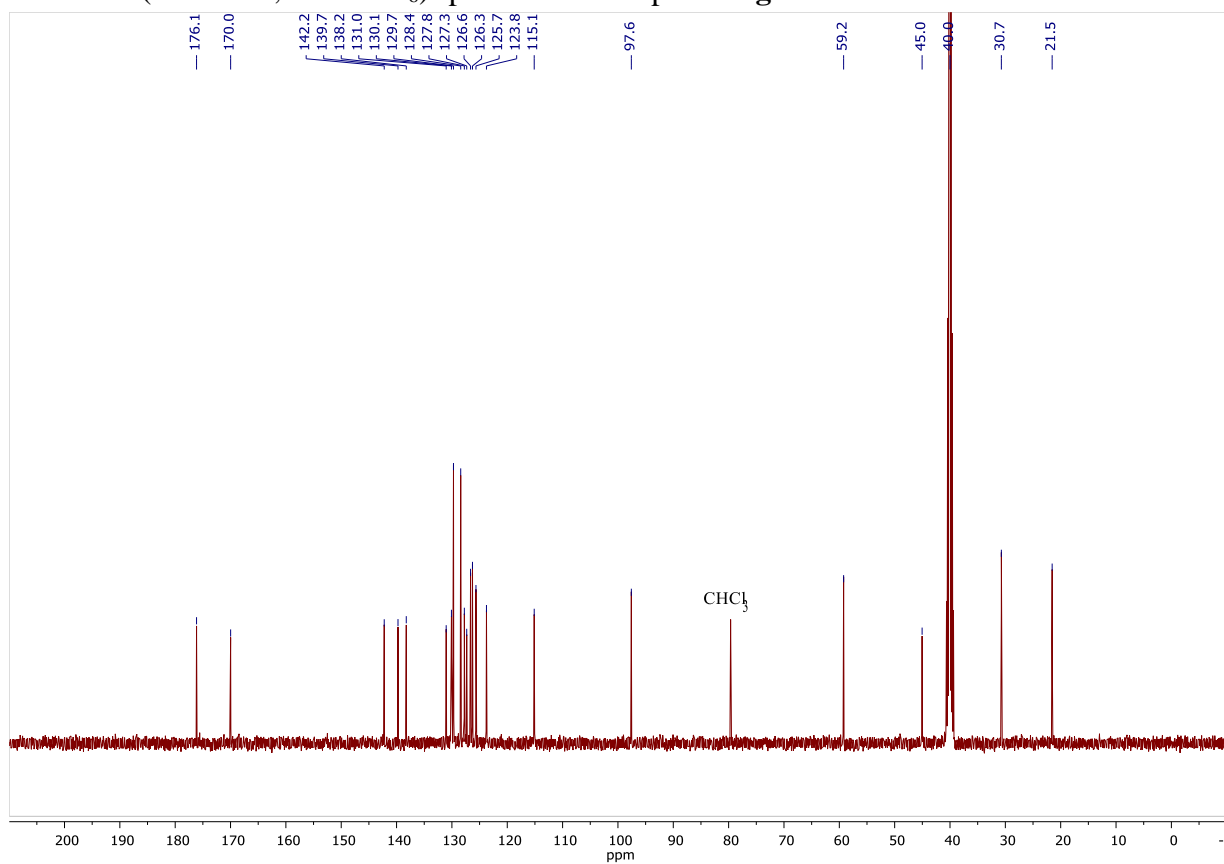




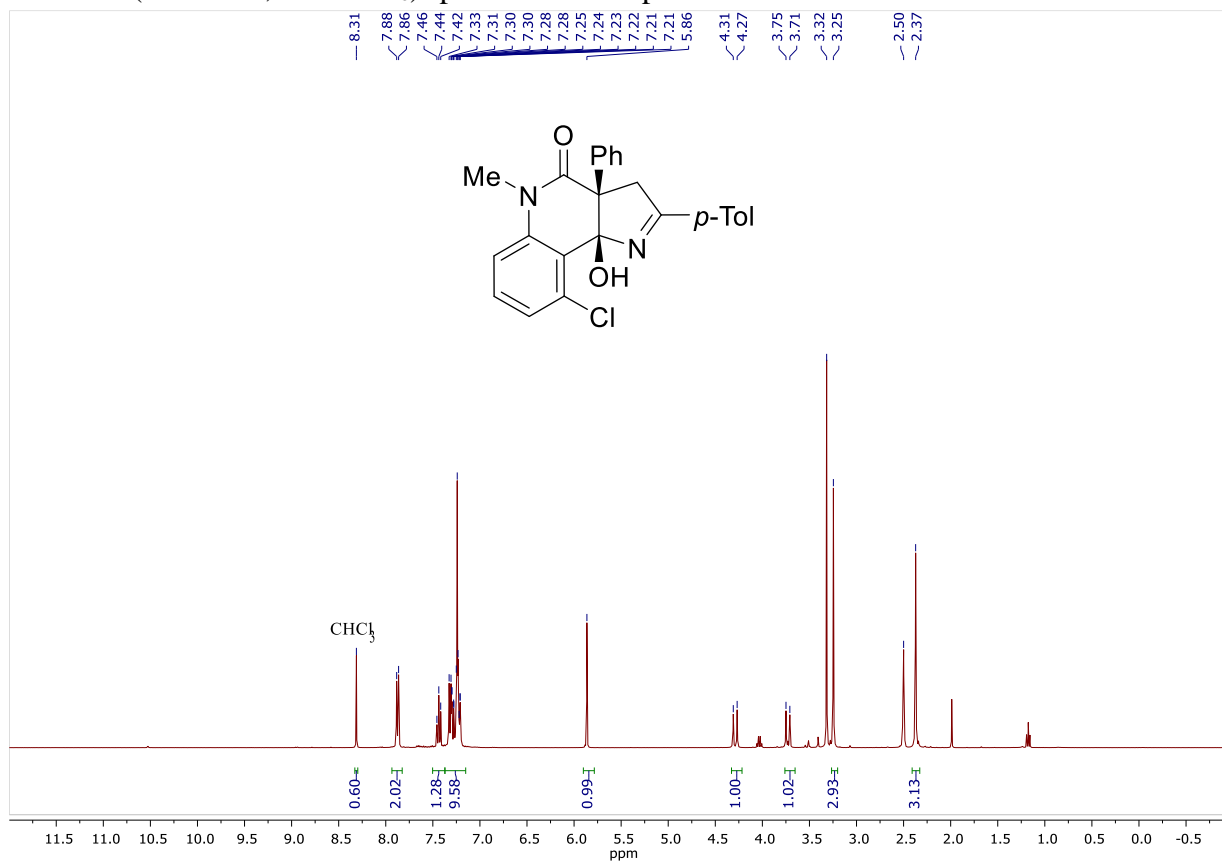
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3g**



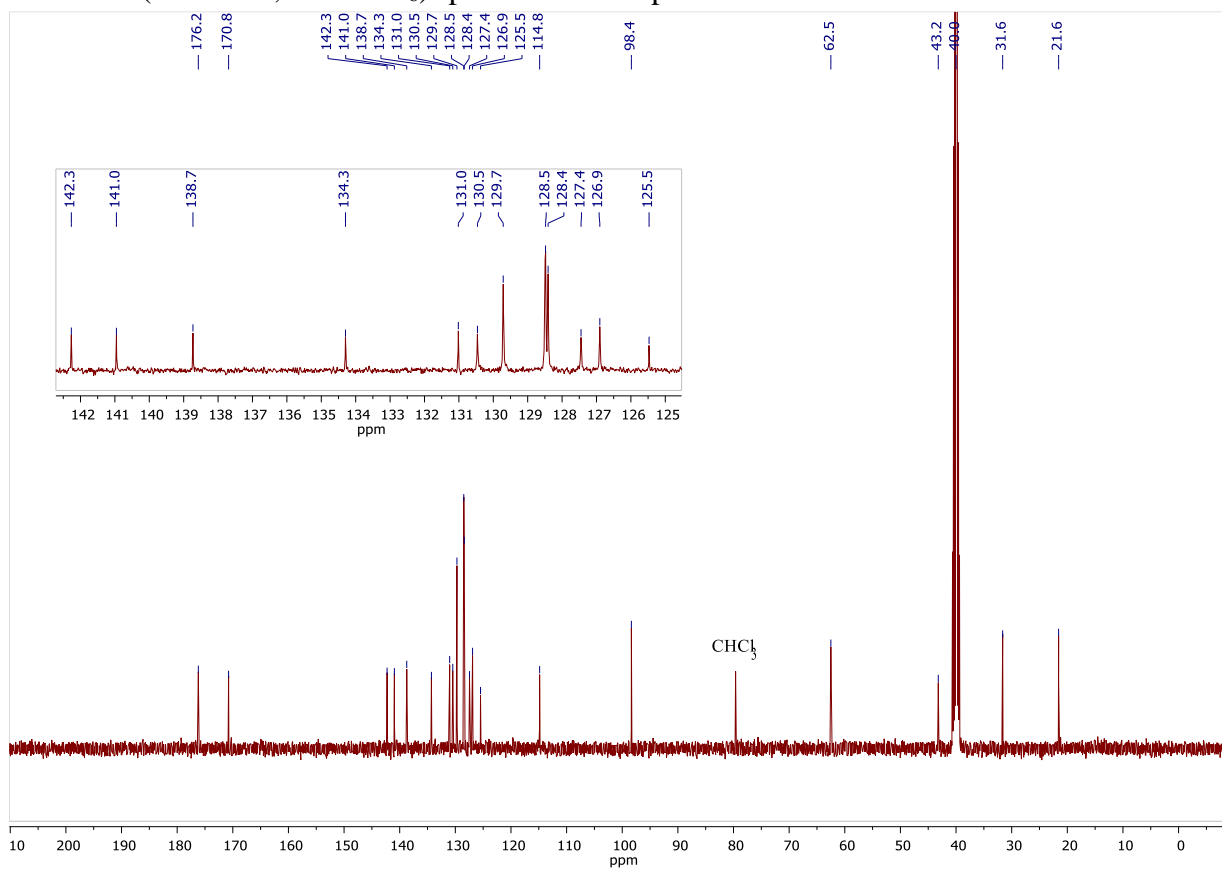
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3g**



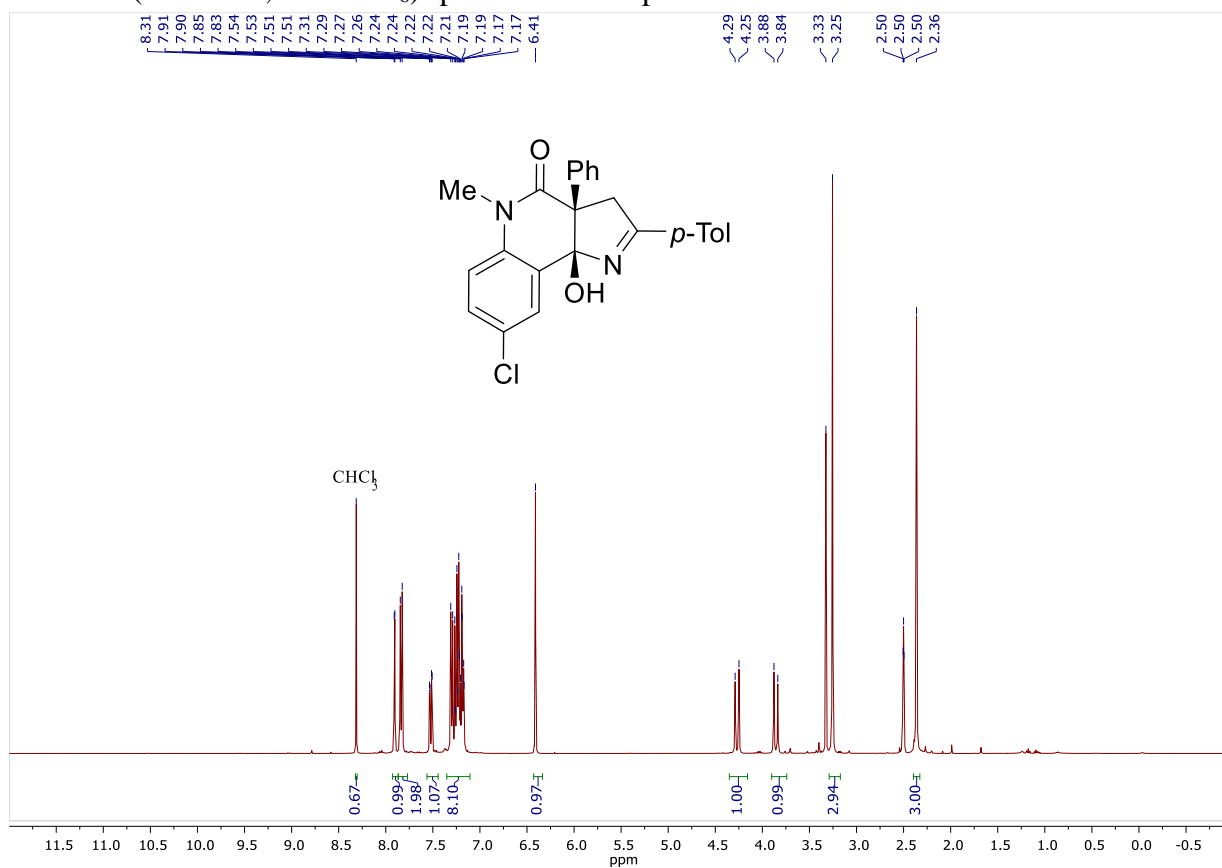
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3h**



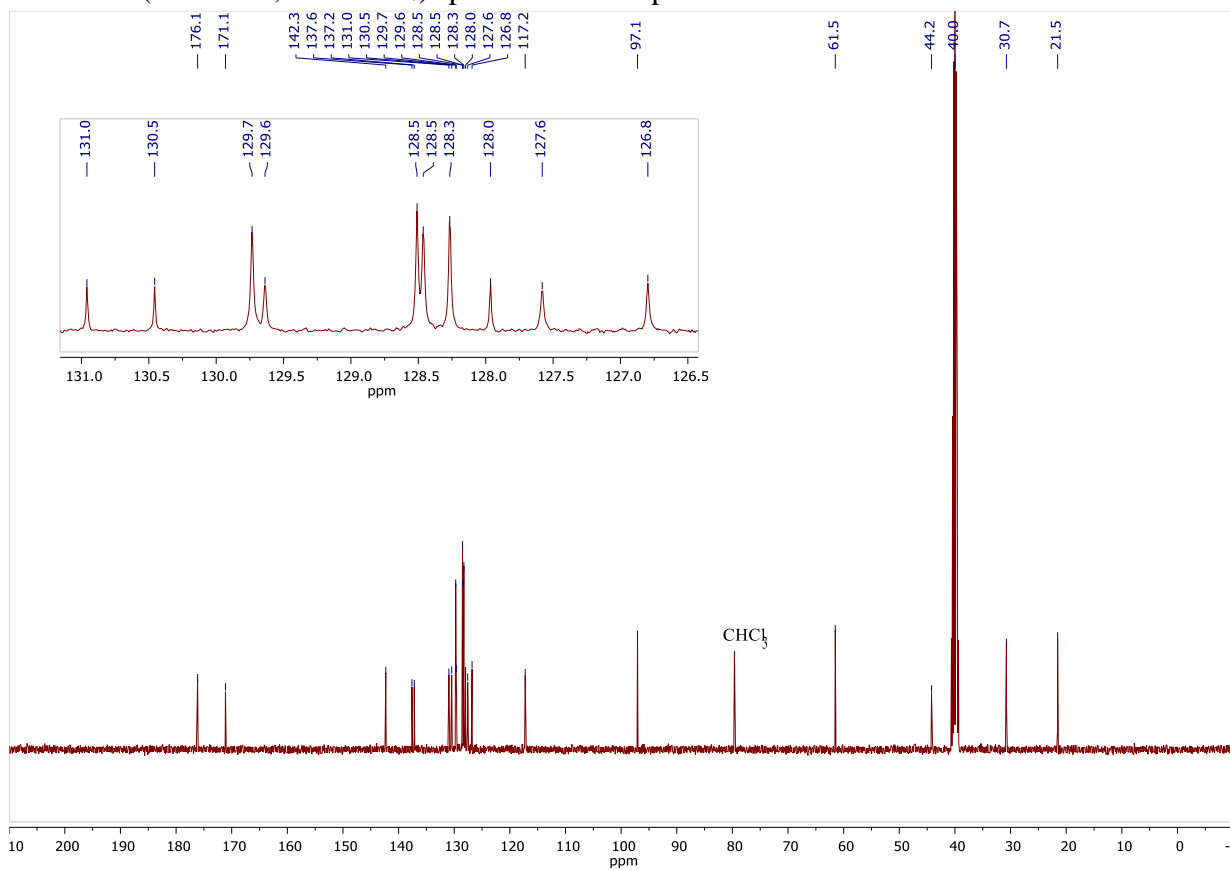
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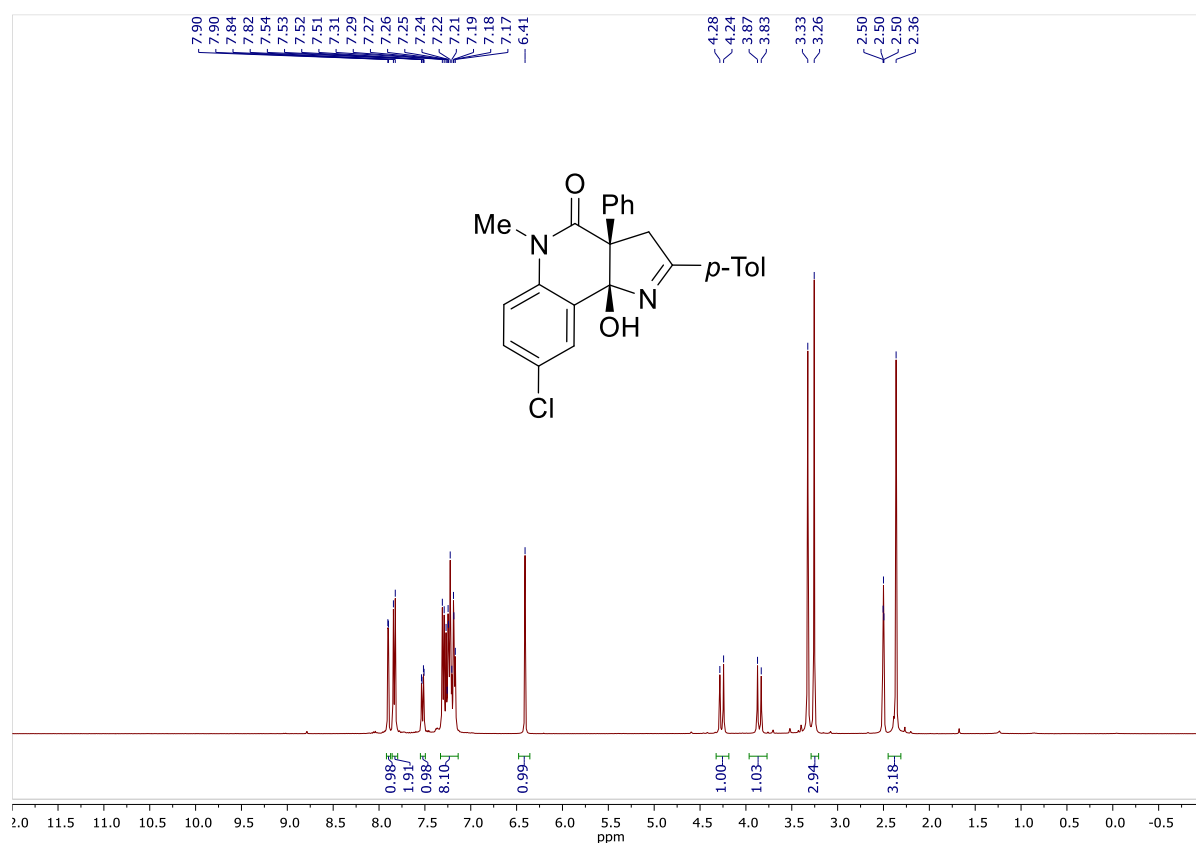
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of compound **3i**



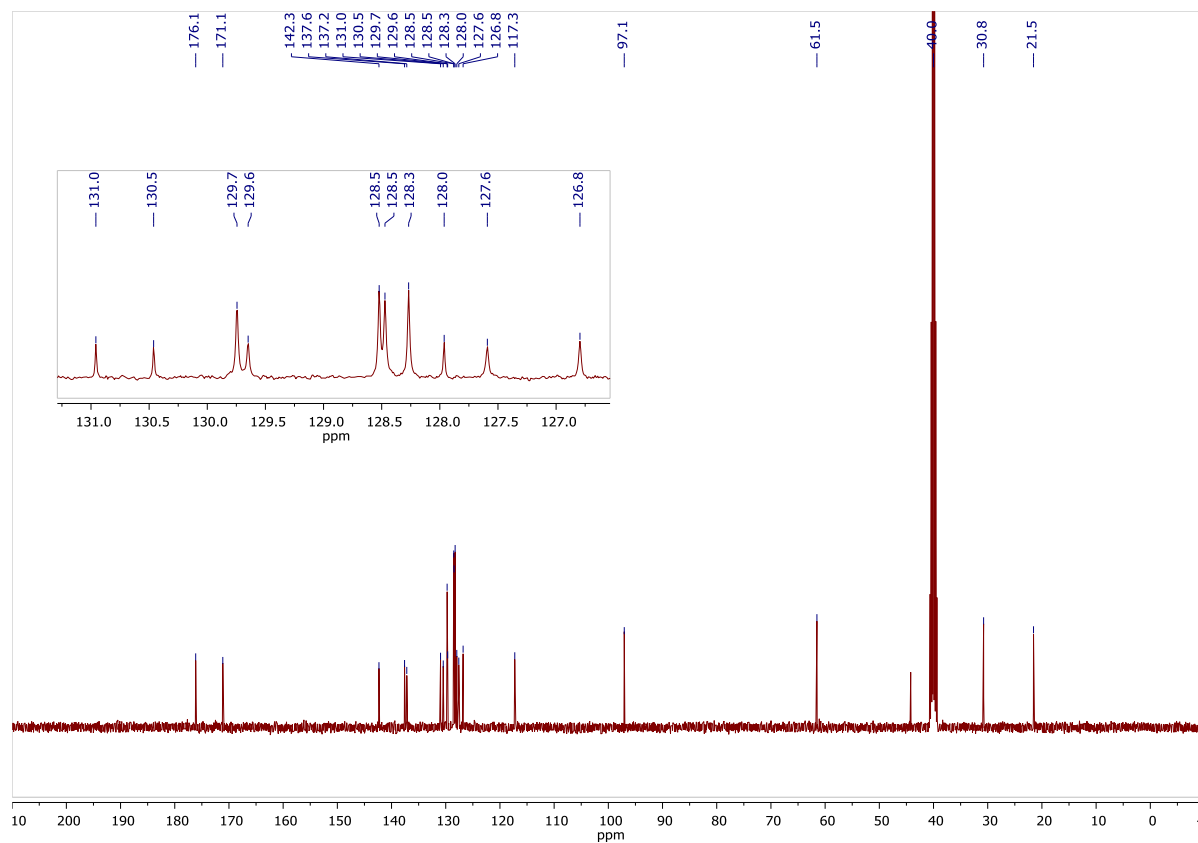
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of compound **3i**



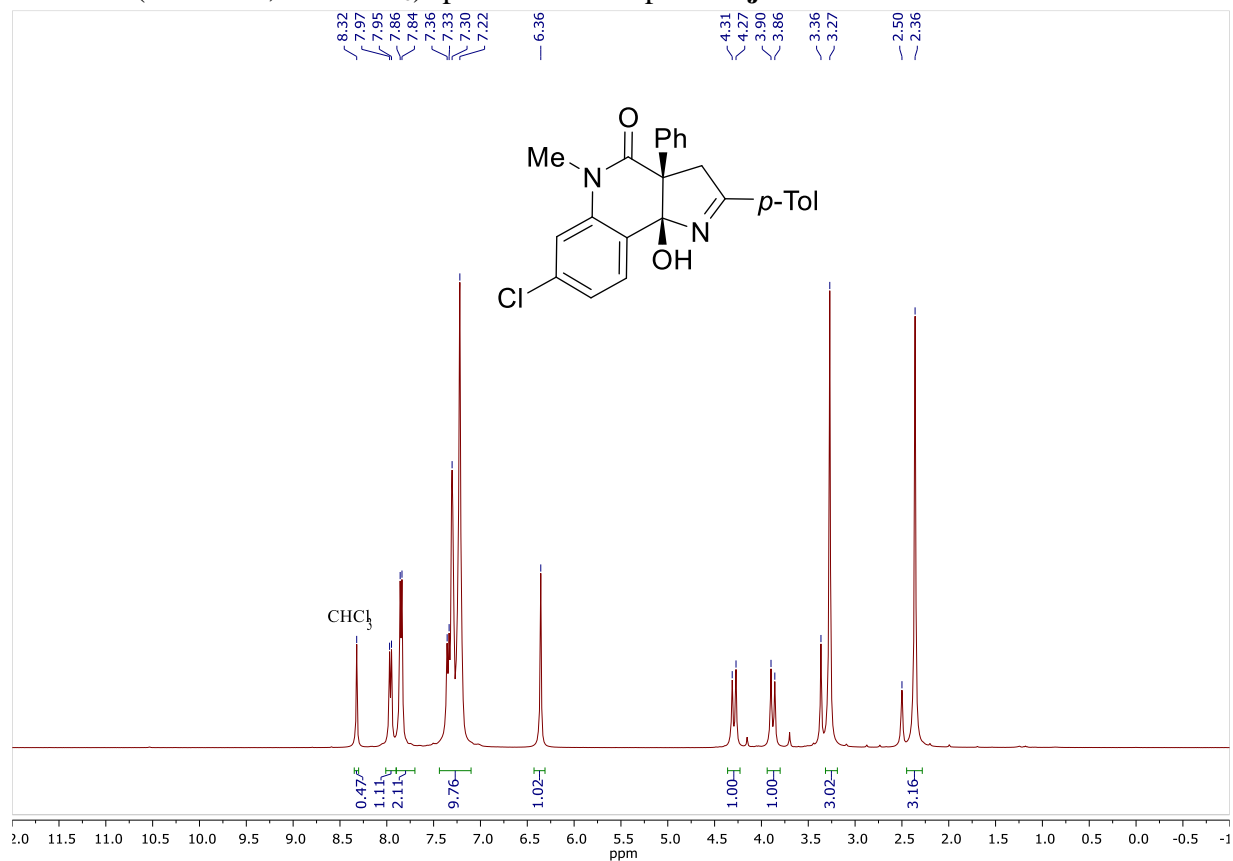
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3i** prepared by evaporation of  $\text{DMSO-d}_6$  solution of solvate **3i** with  $\text{CHCl}_3$



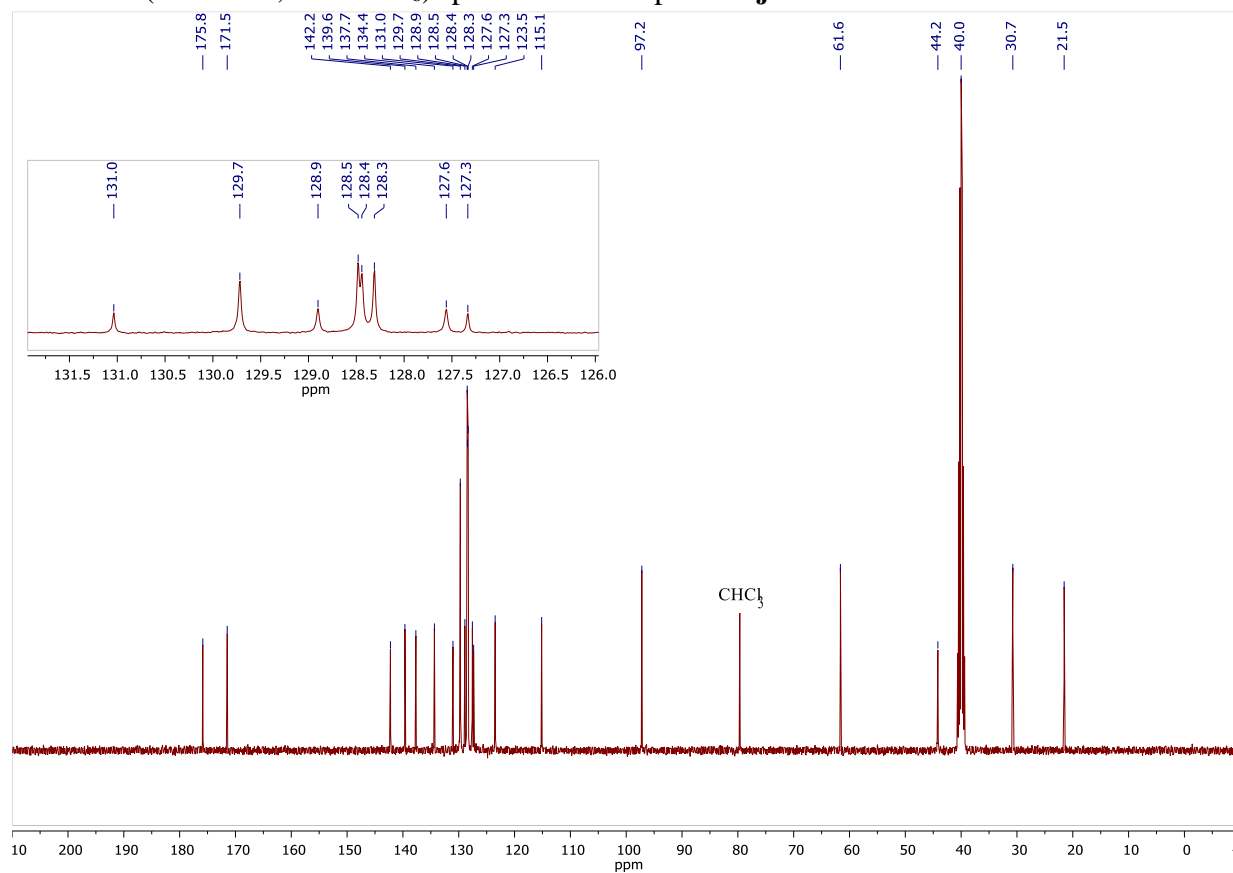
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3i** prepared by evaporation of  $\text{DMSO-d}_6$  solution of solvate **3i** with  $\text{CHCl}_3$



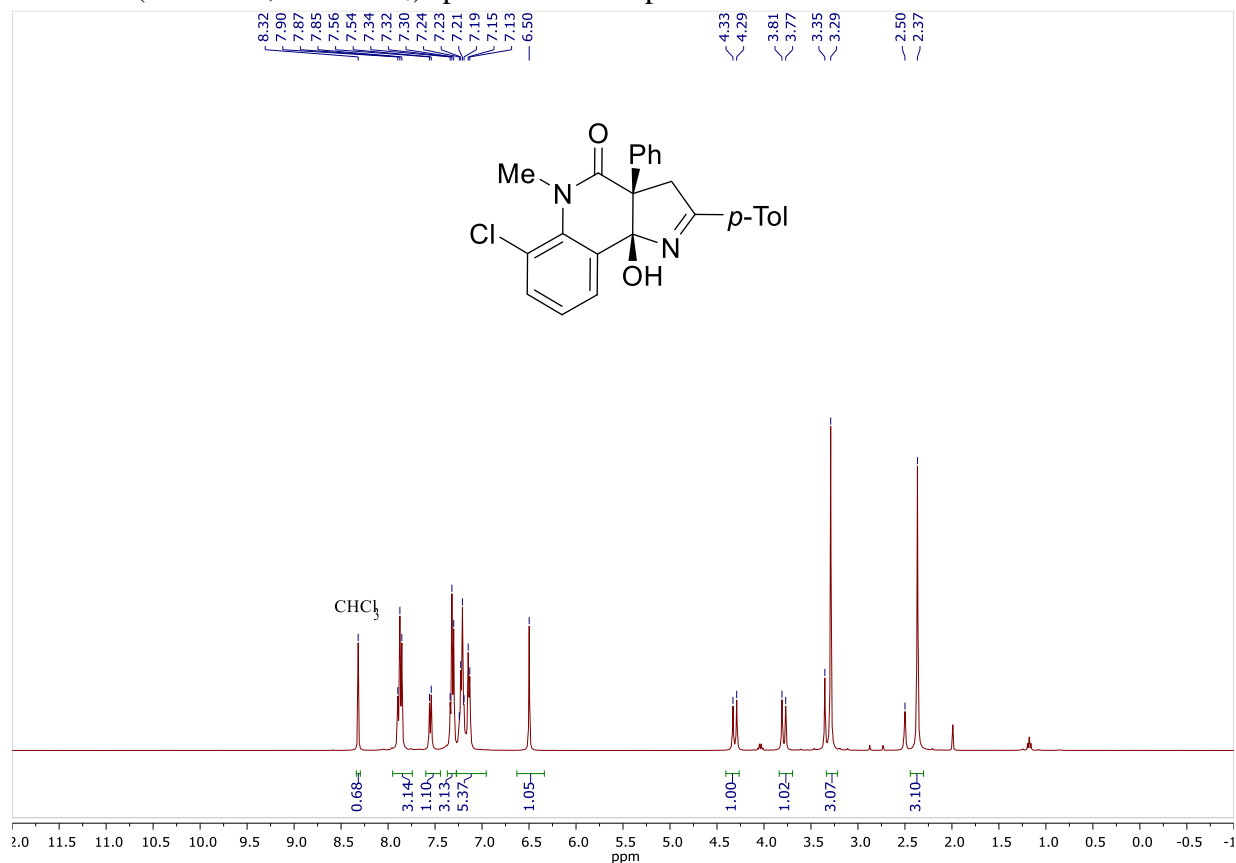
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3j**



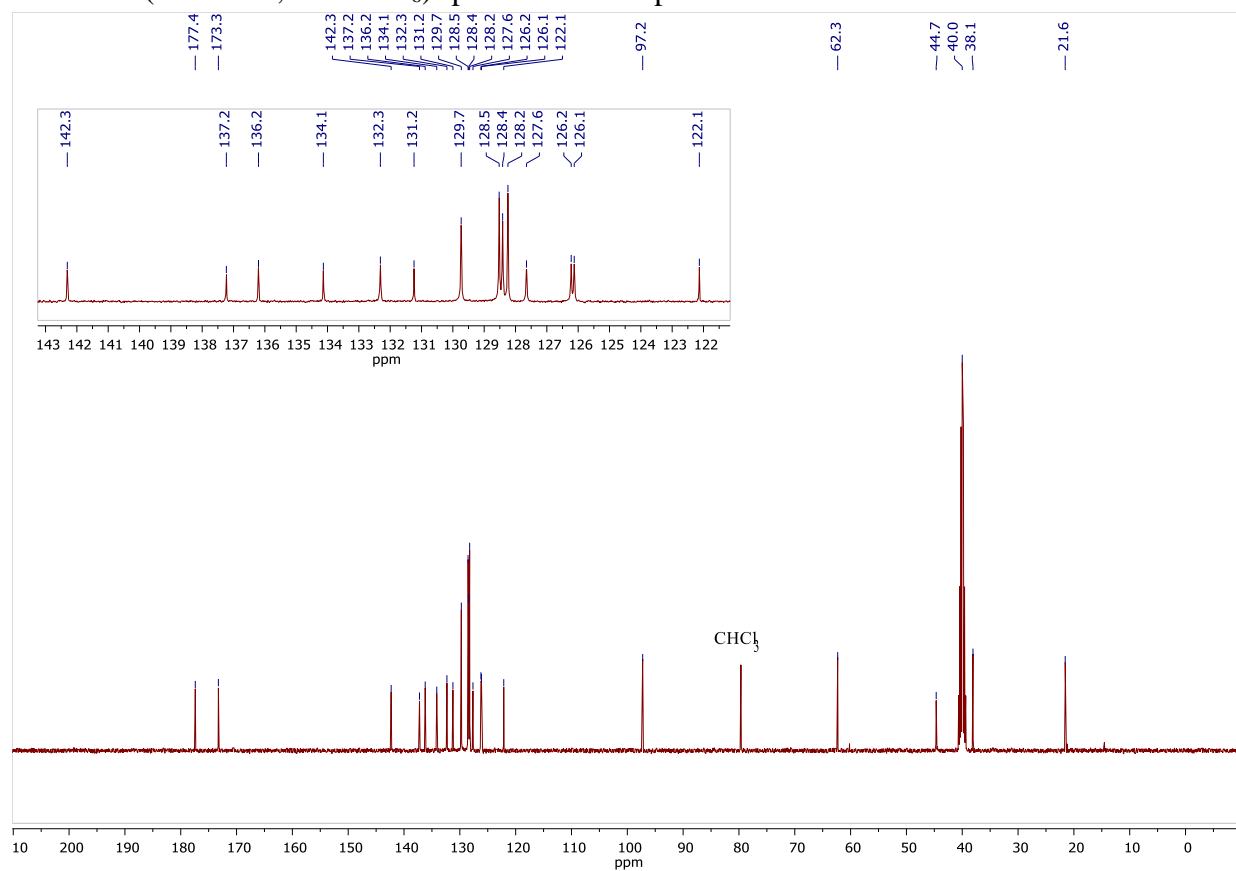
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3j**



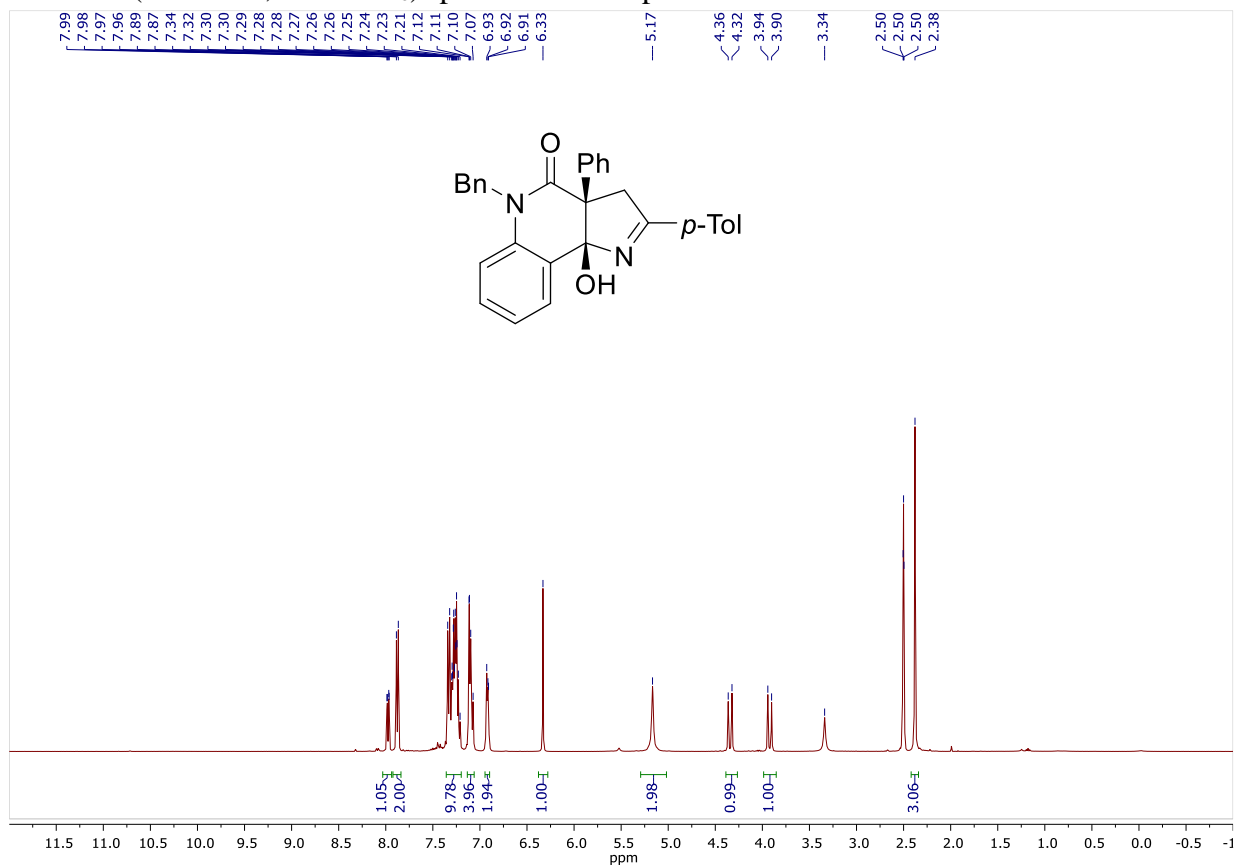
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3k**



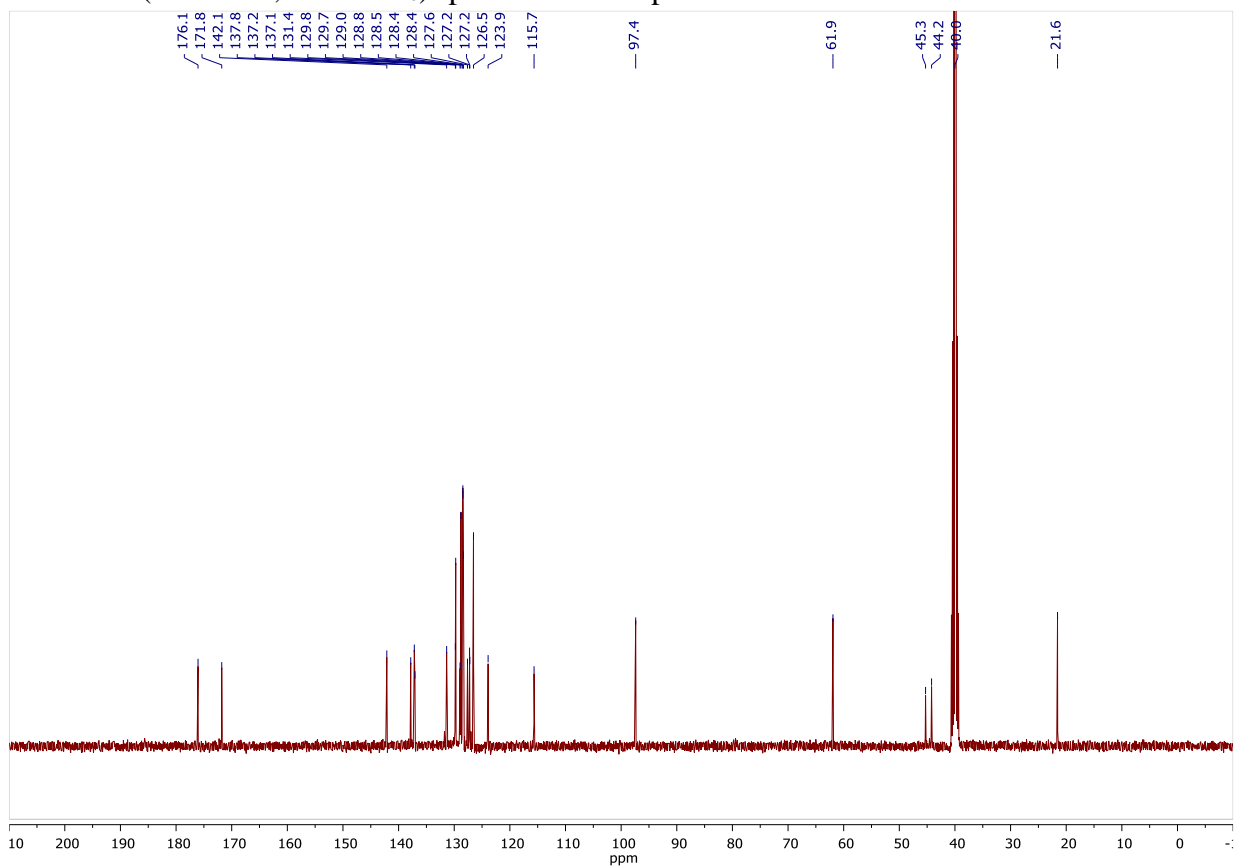
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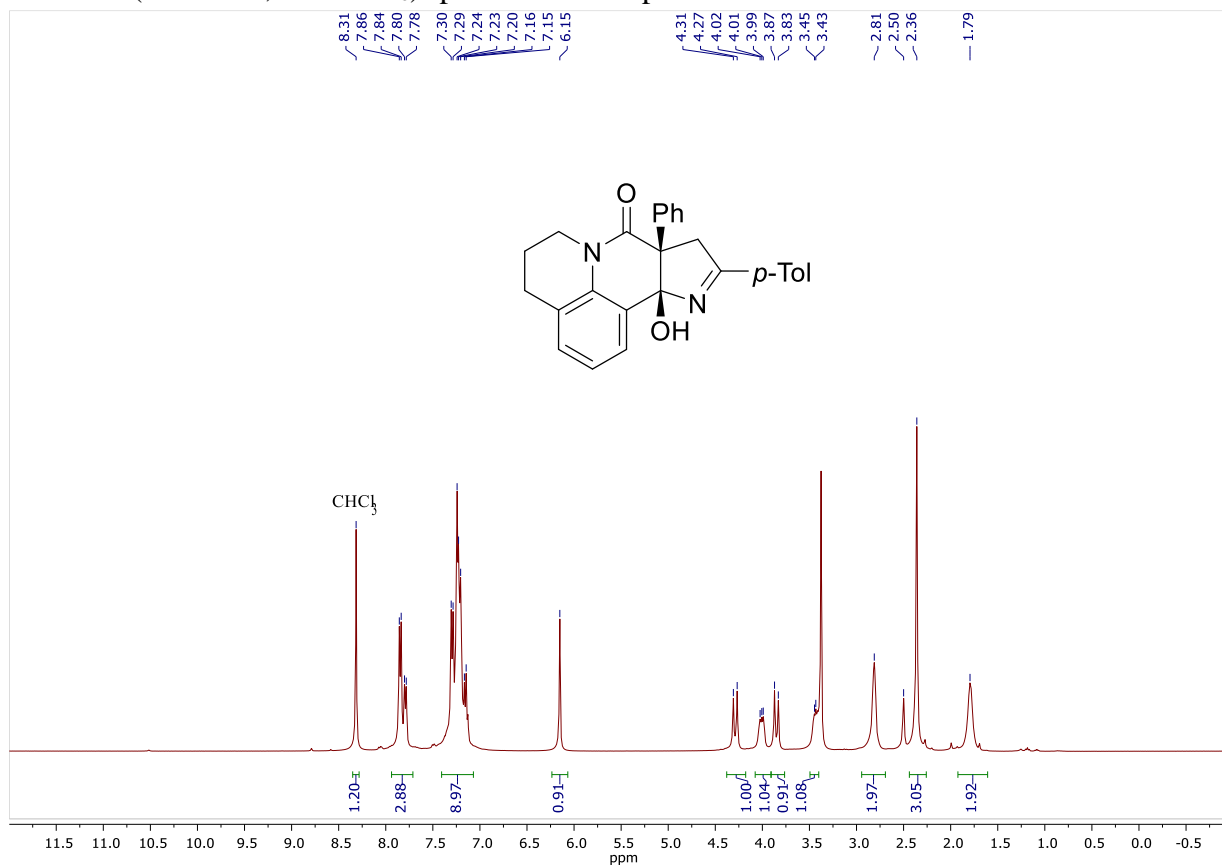
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) spectrum of compound **3l**



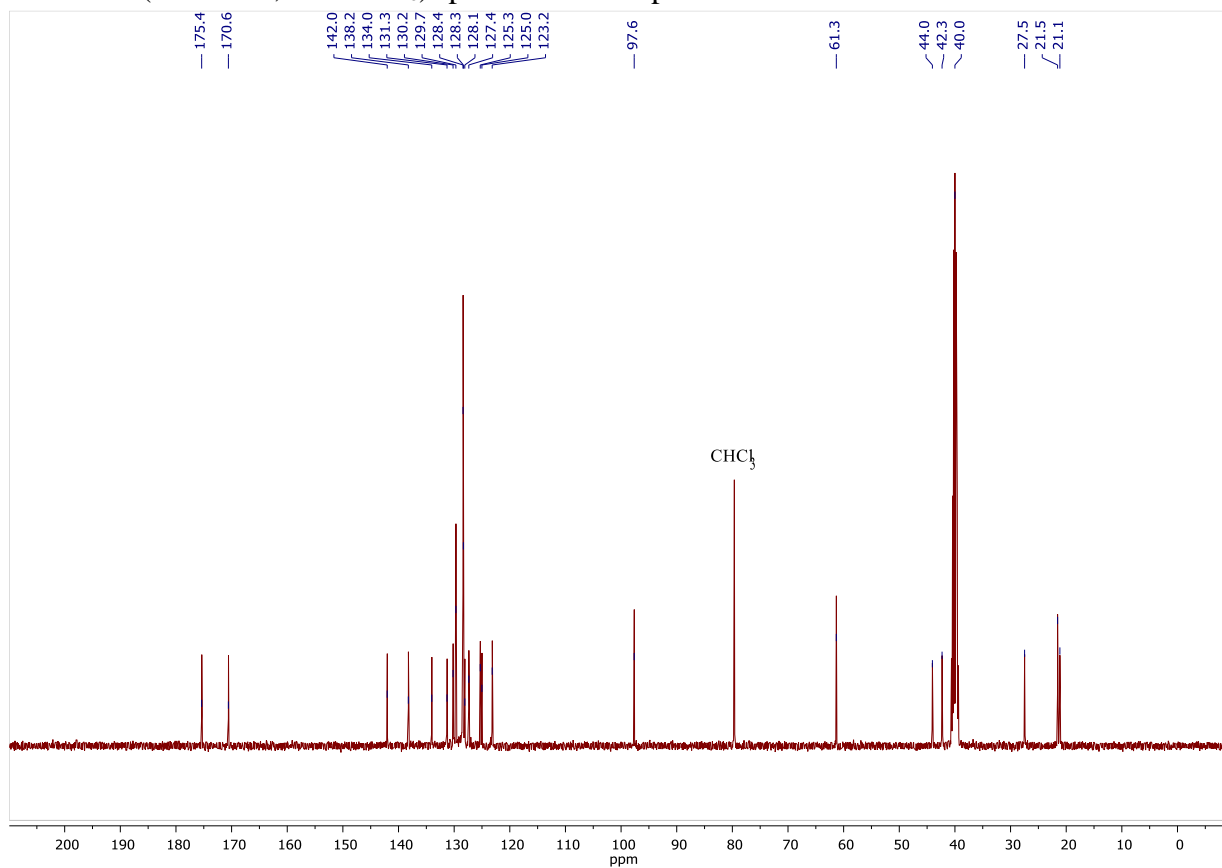
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectrum of compound **3l**



$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3m**

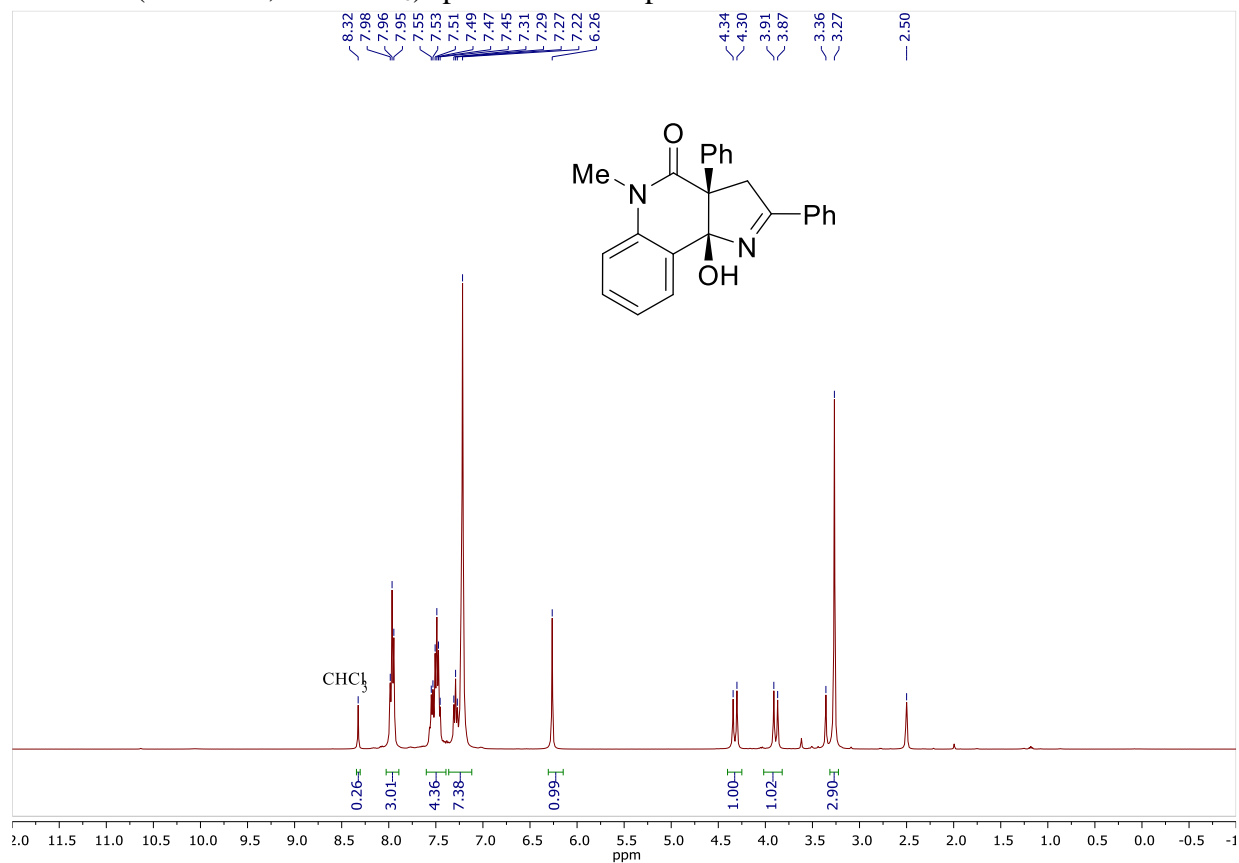


$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **3m**

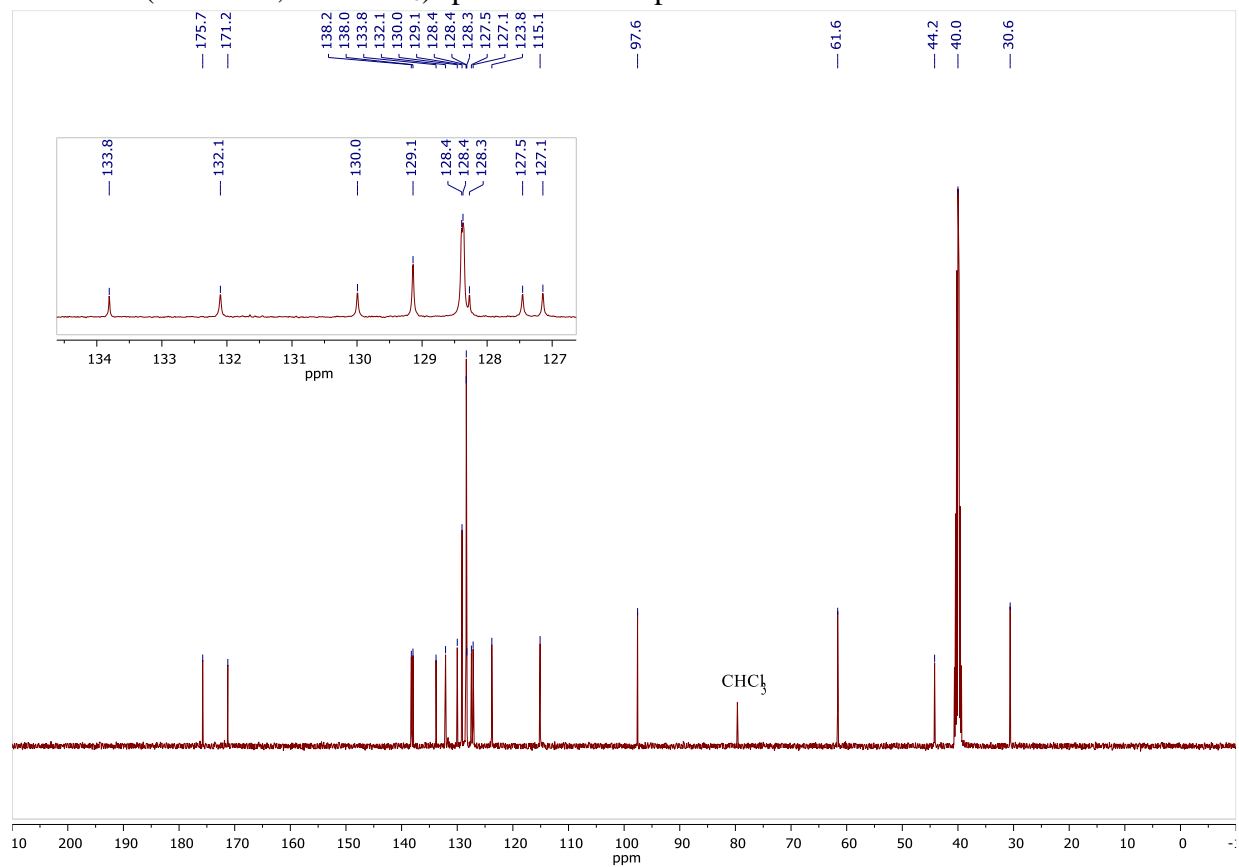




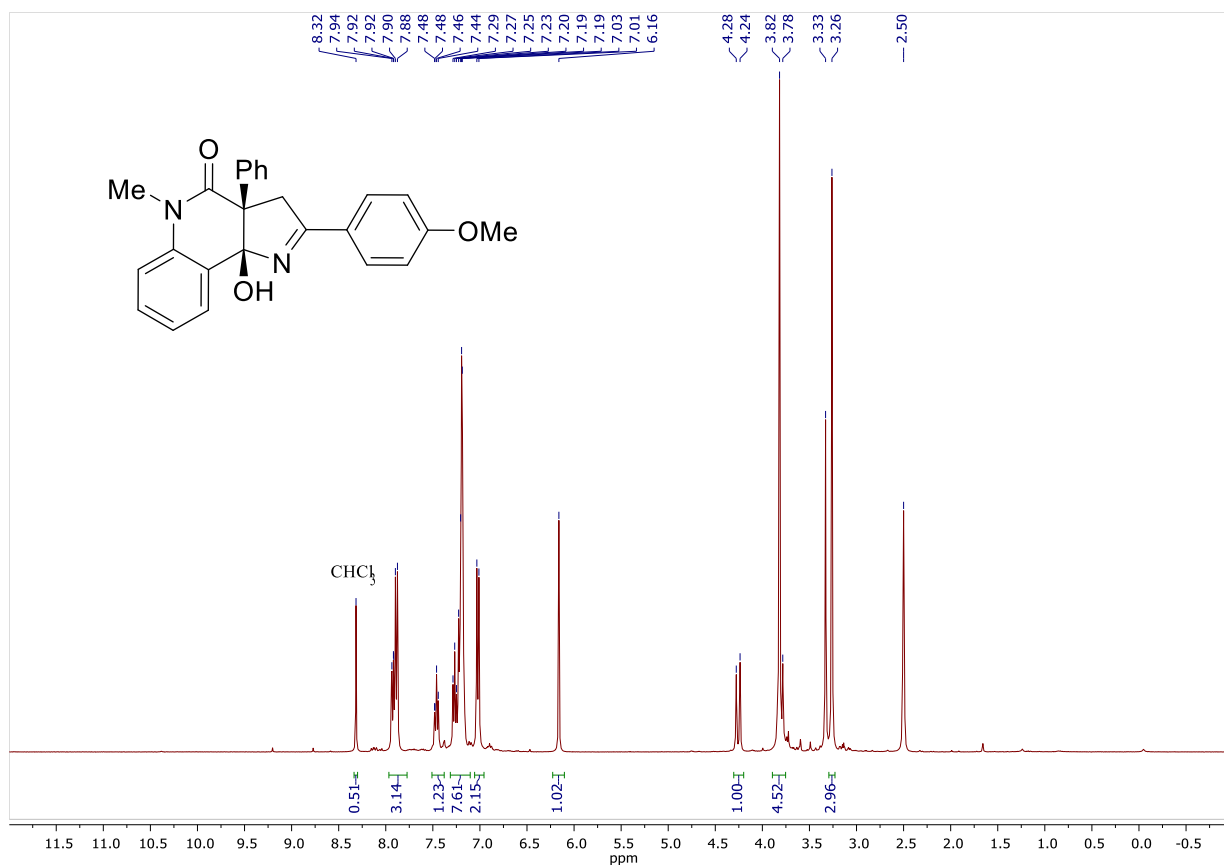
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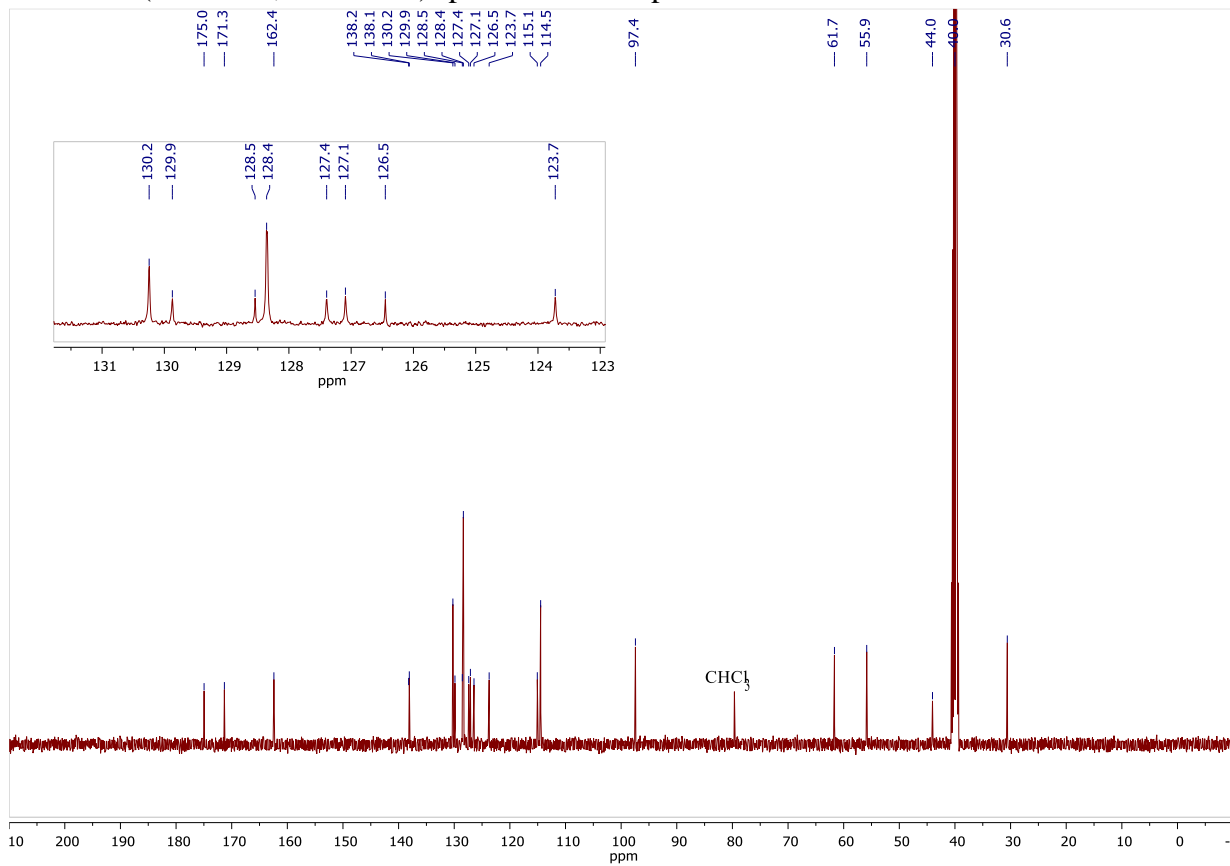
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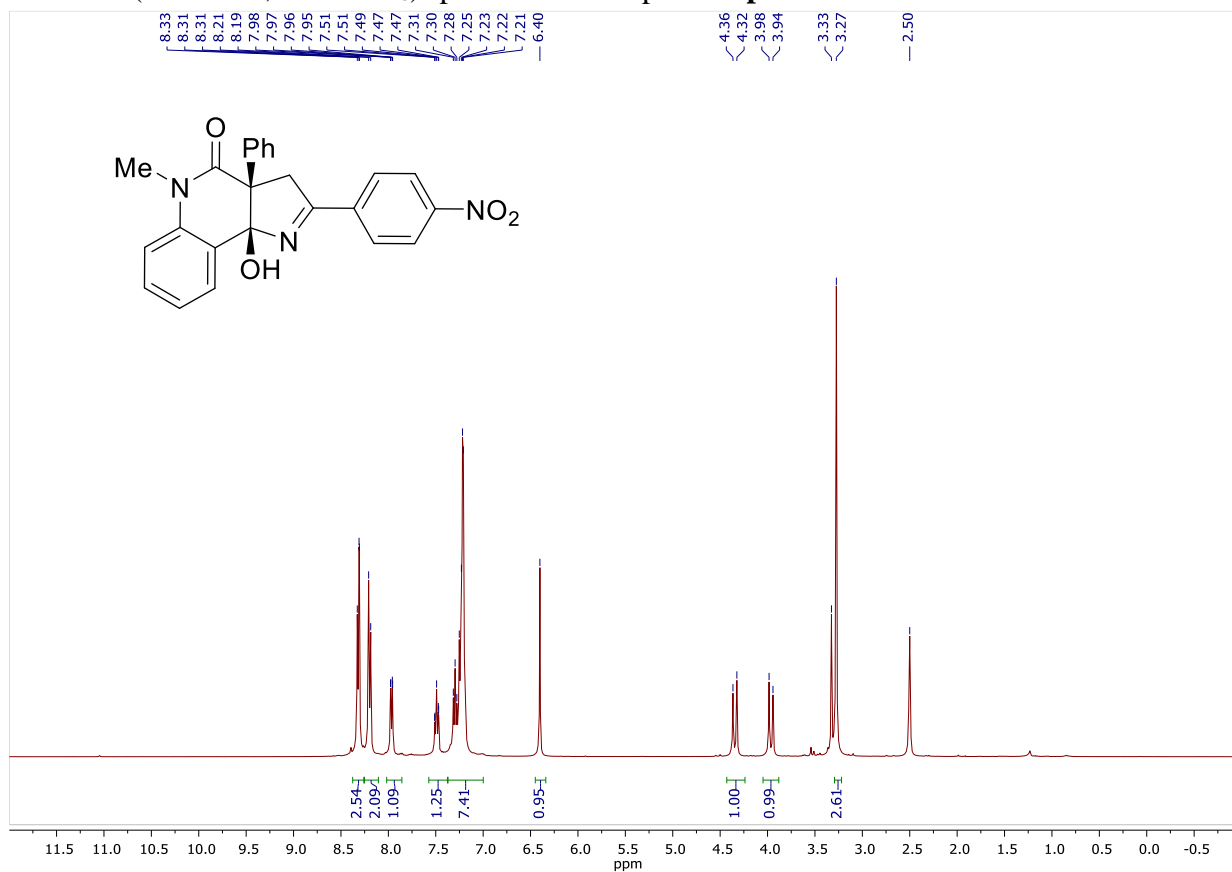
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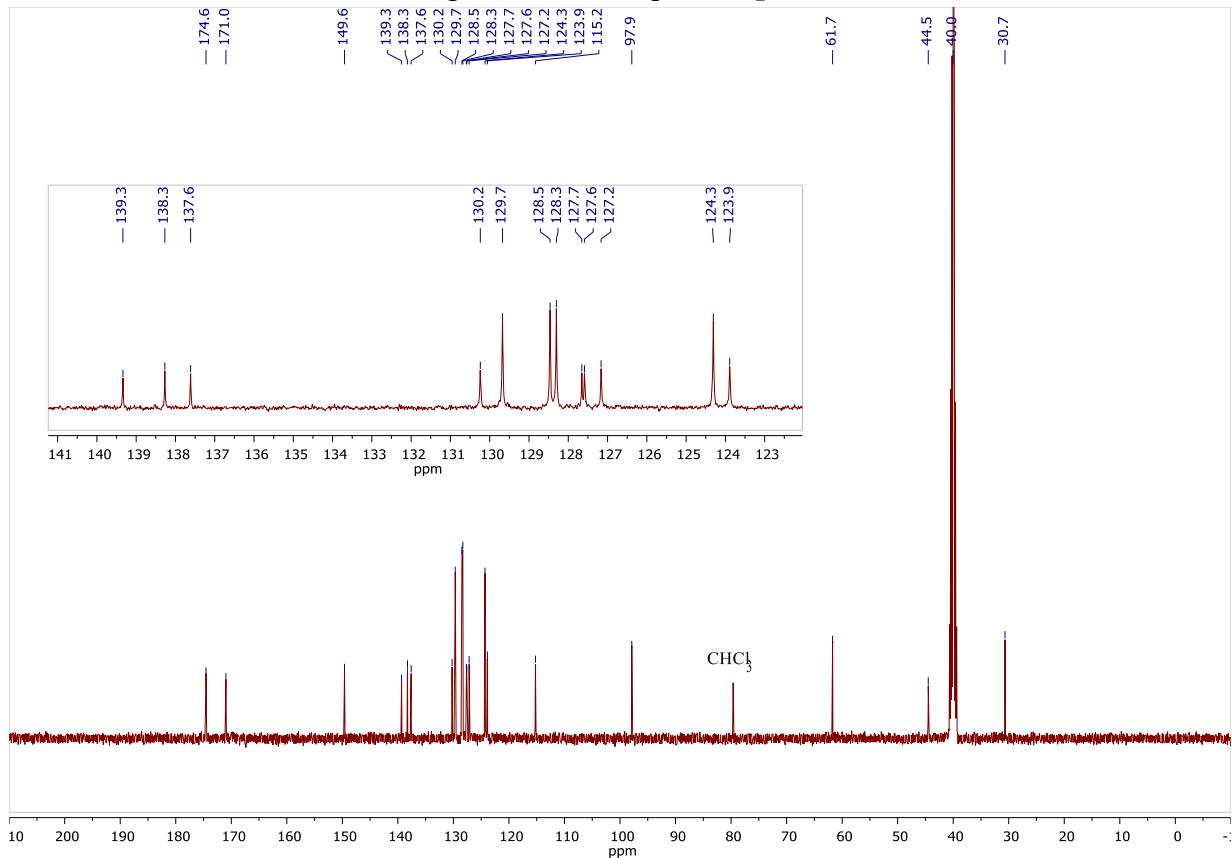
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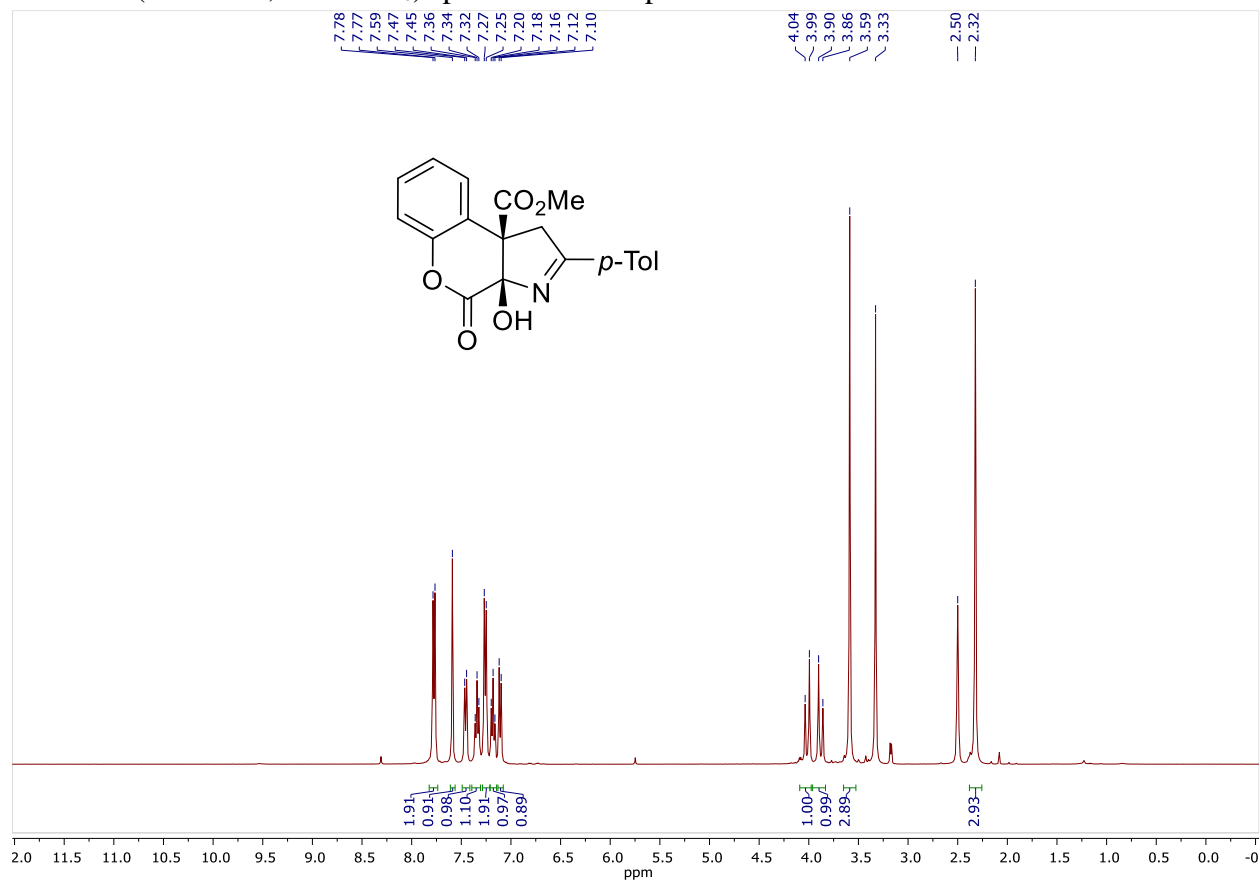
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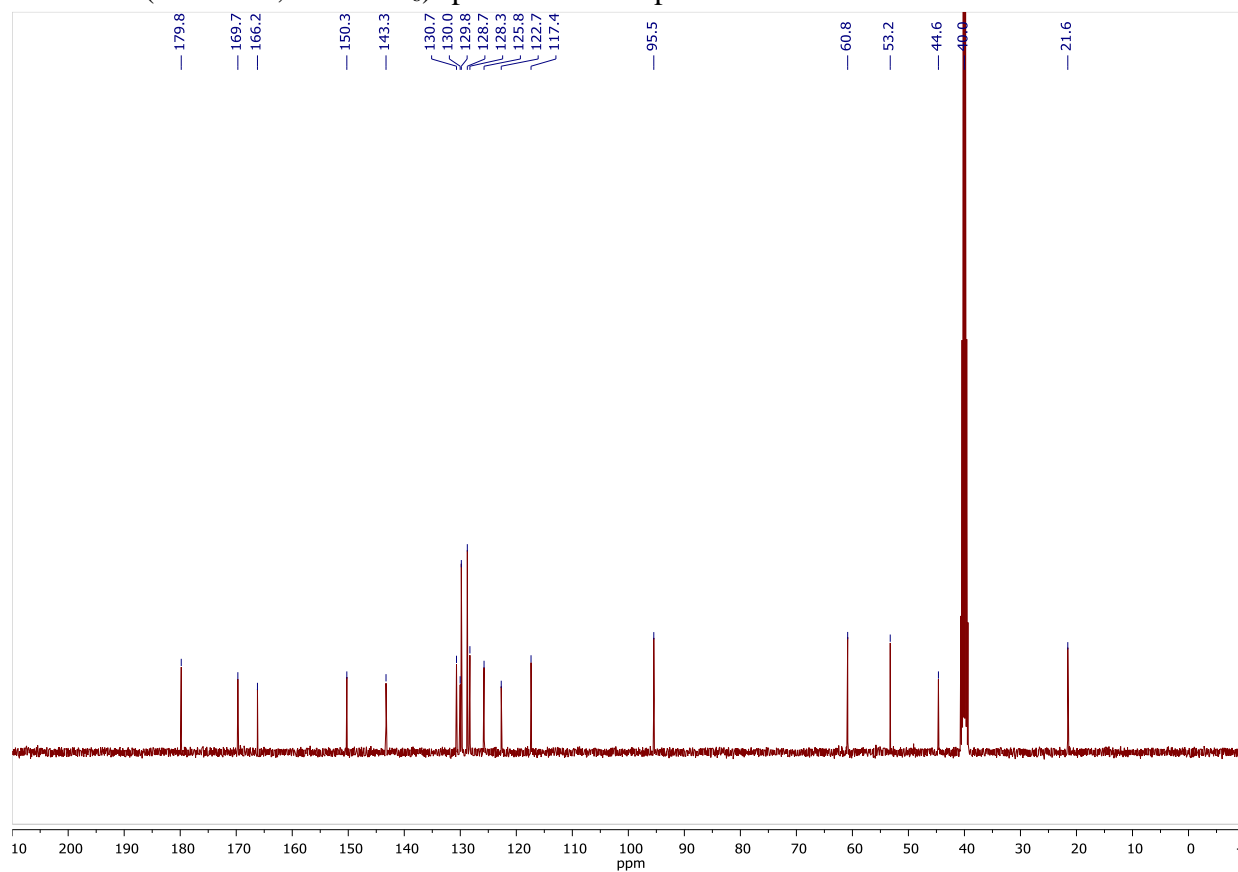
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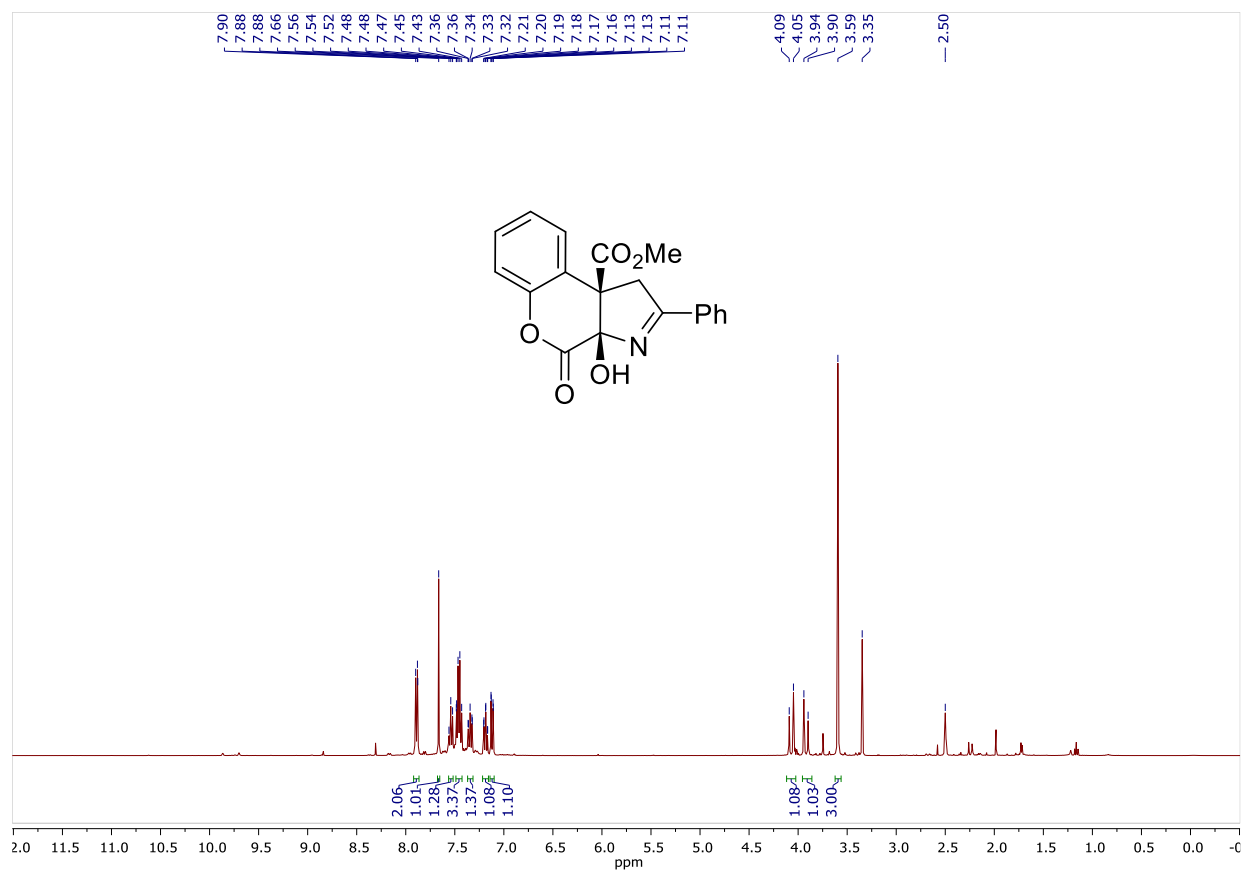
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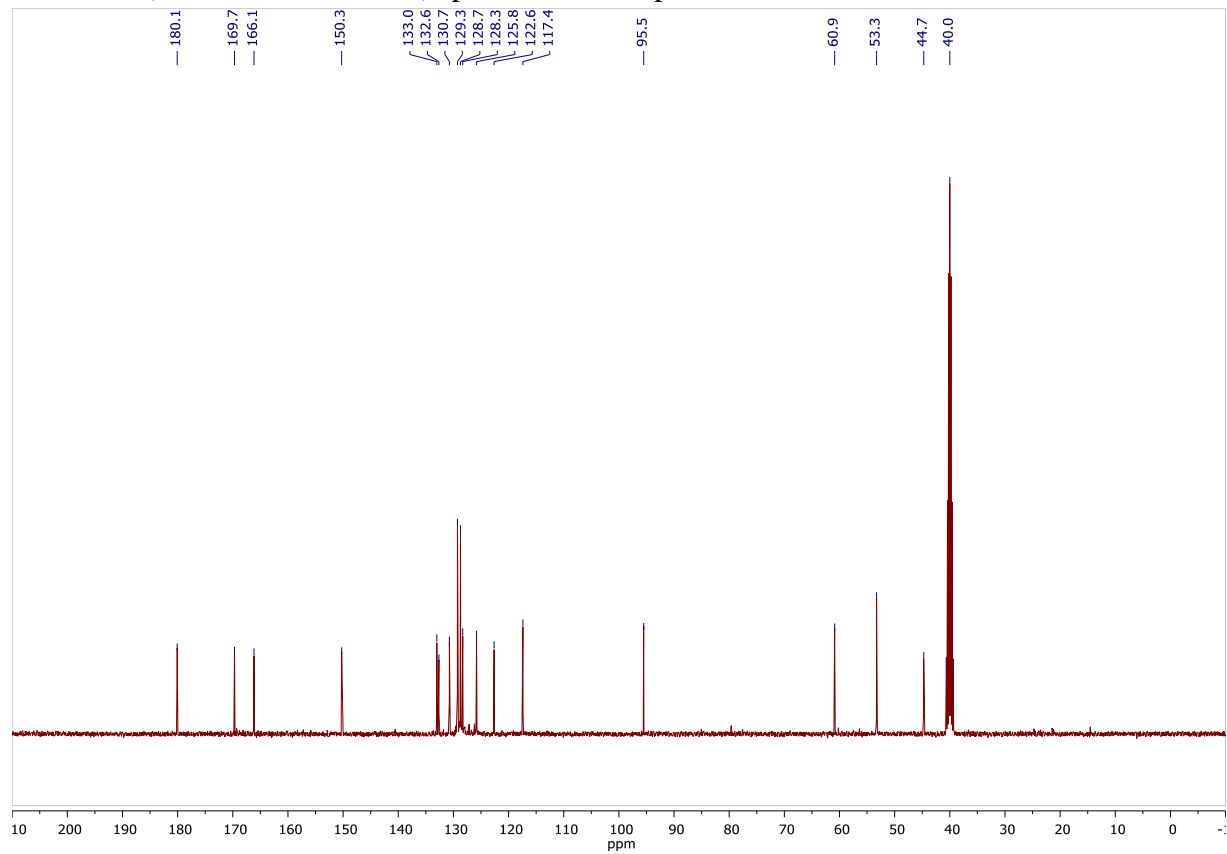
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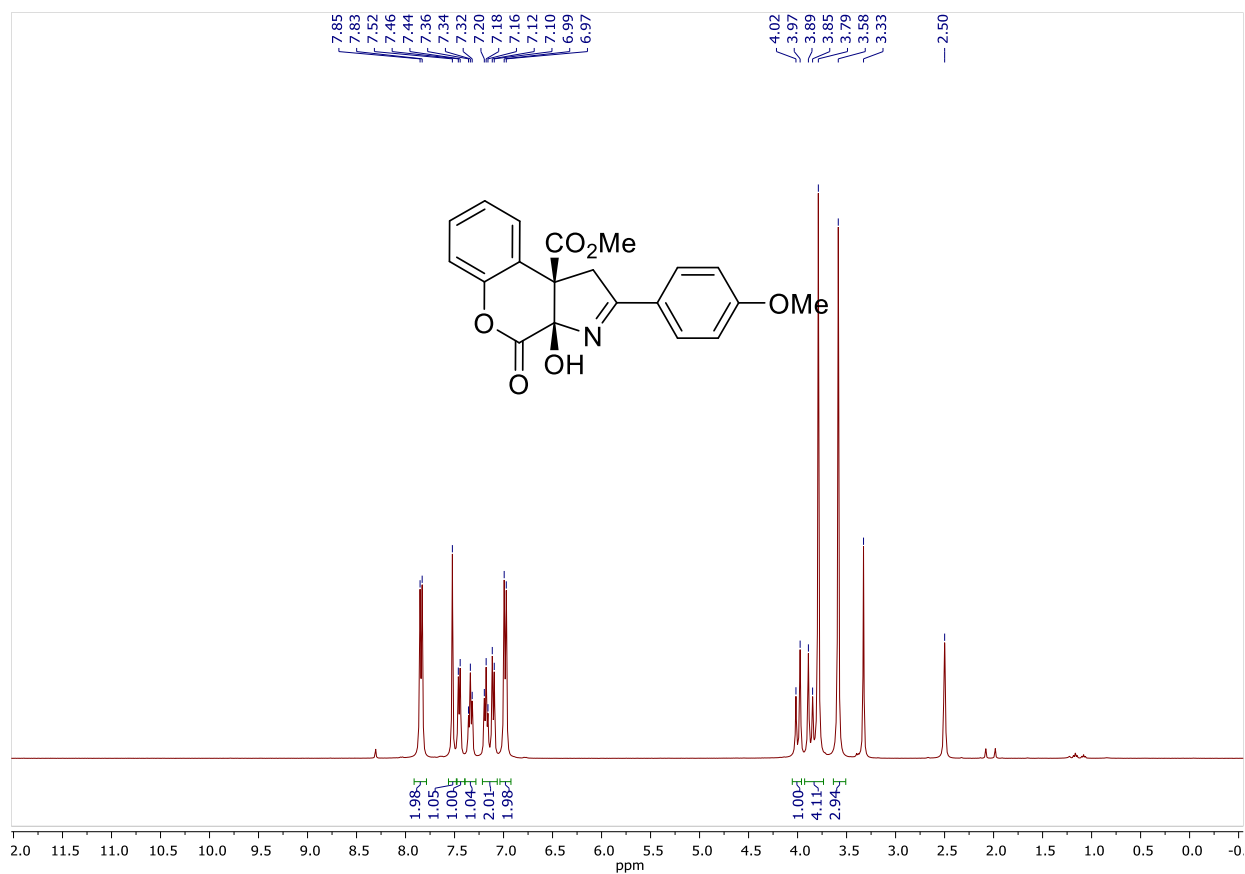
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **6b**



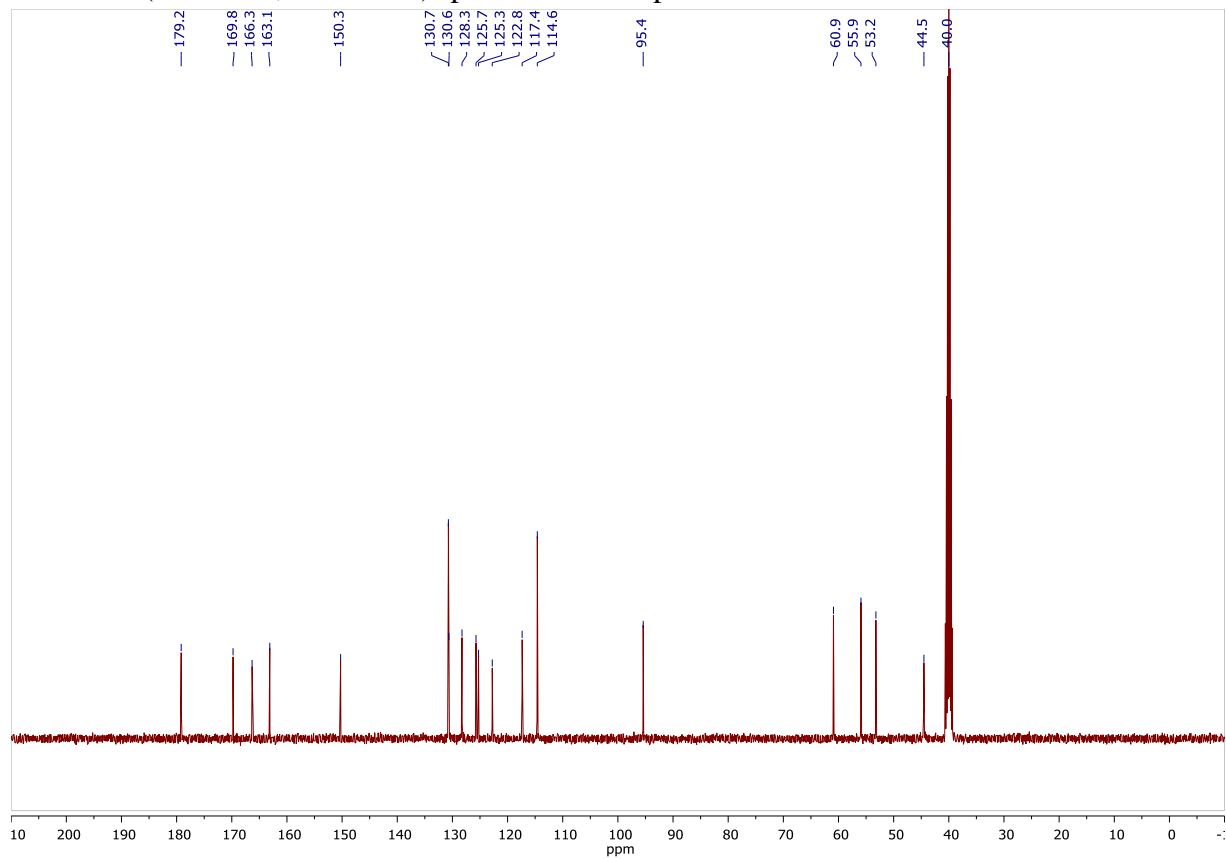
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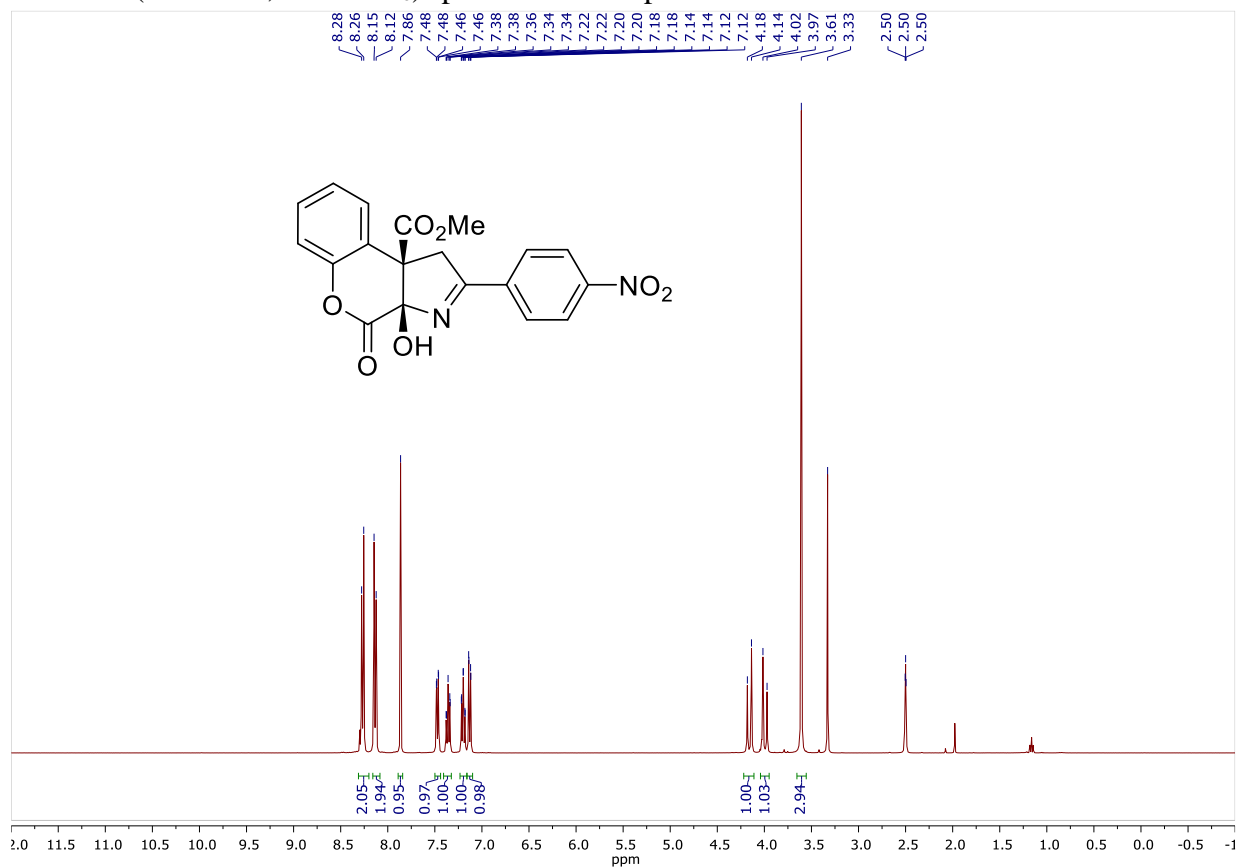
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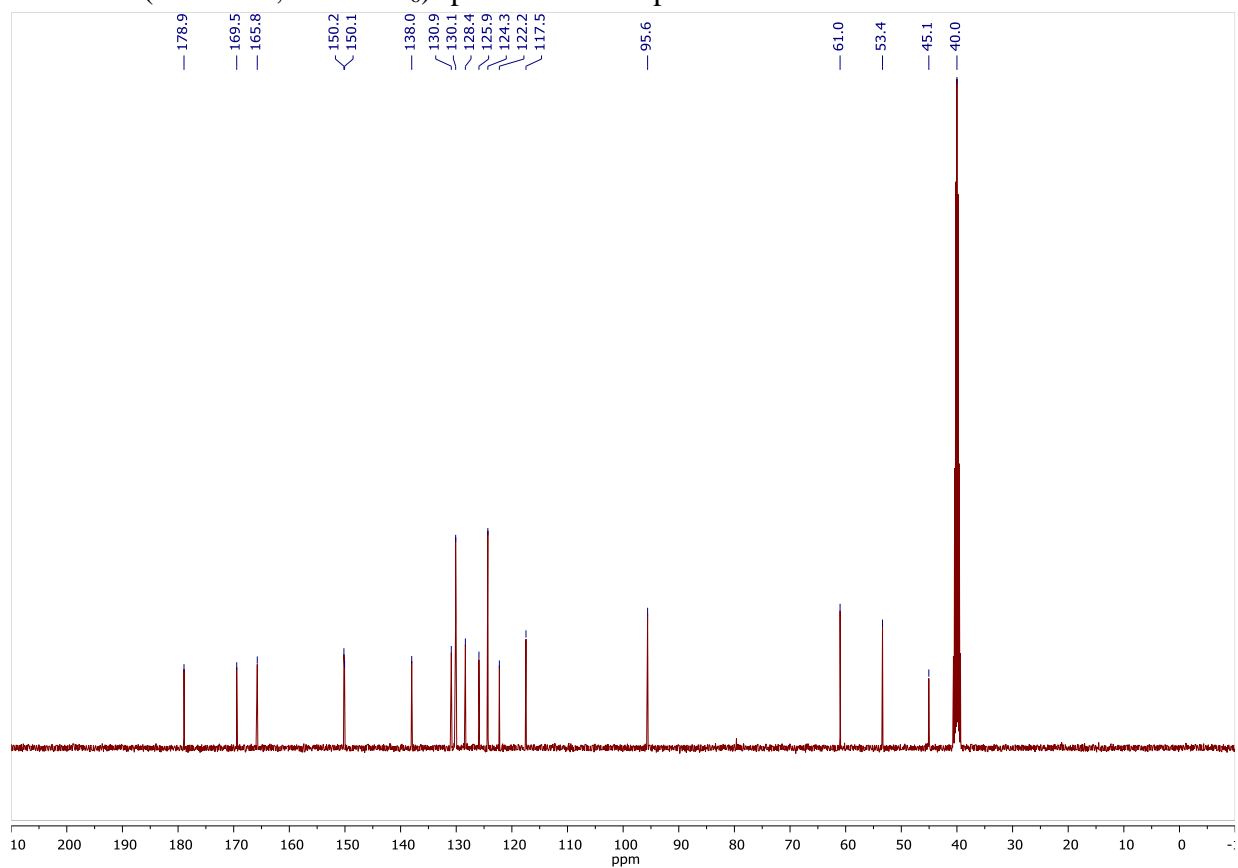
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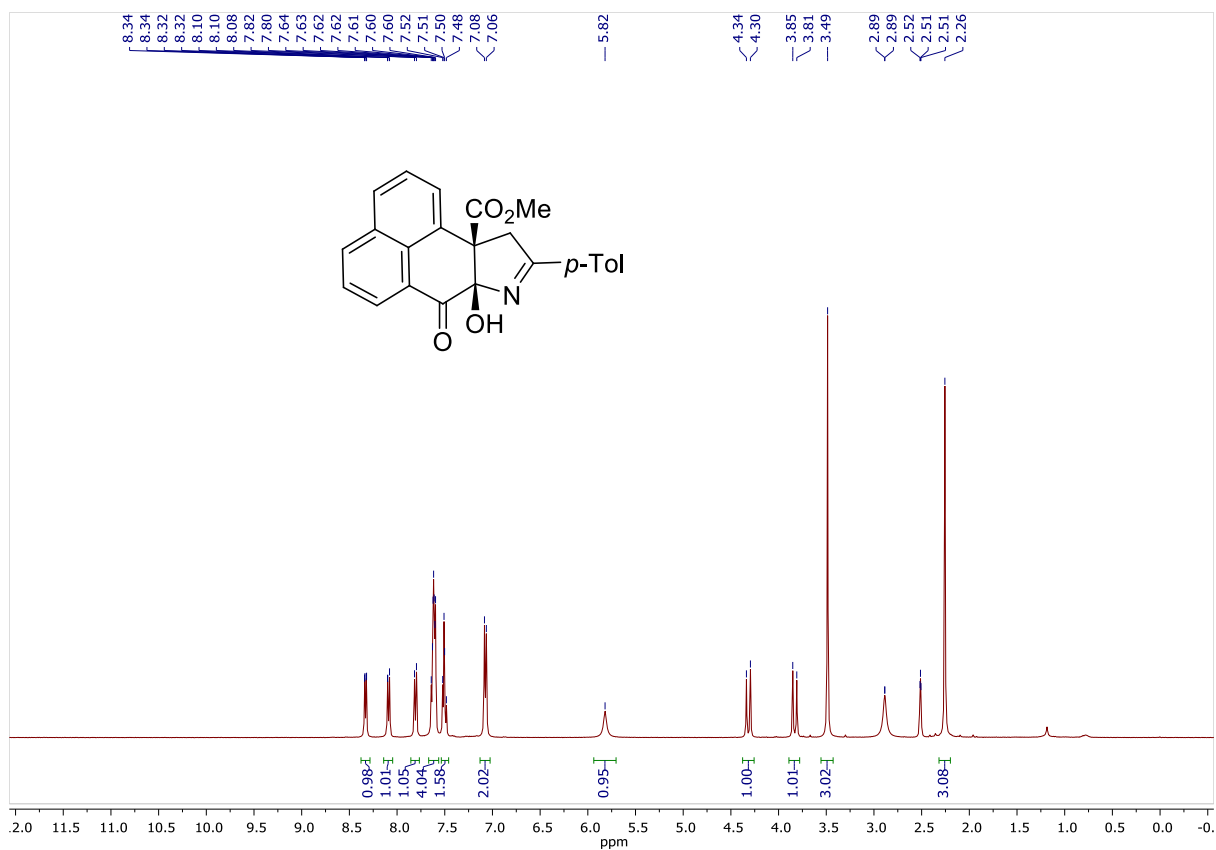
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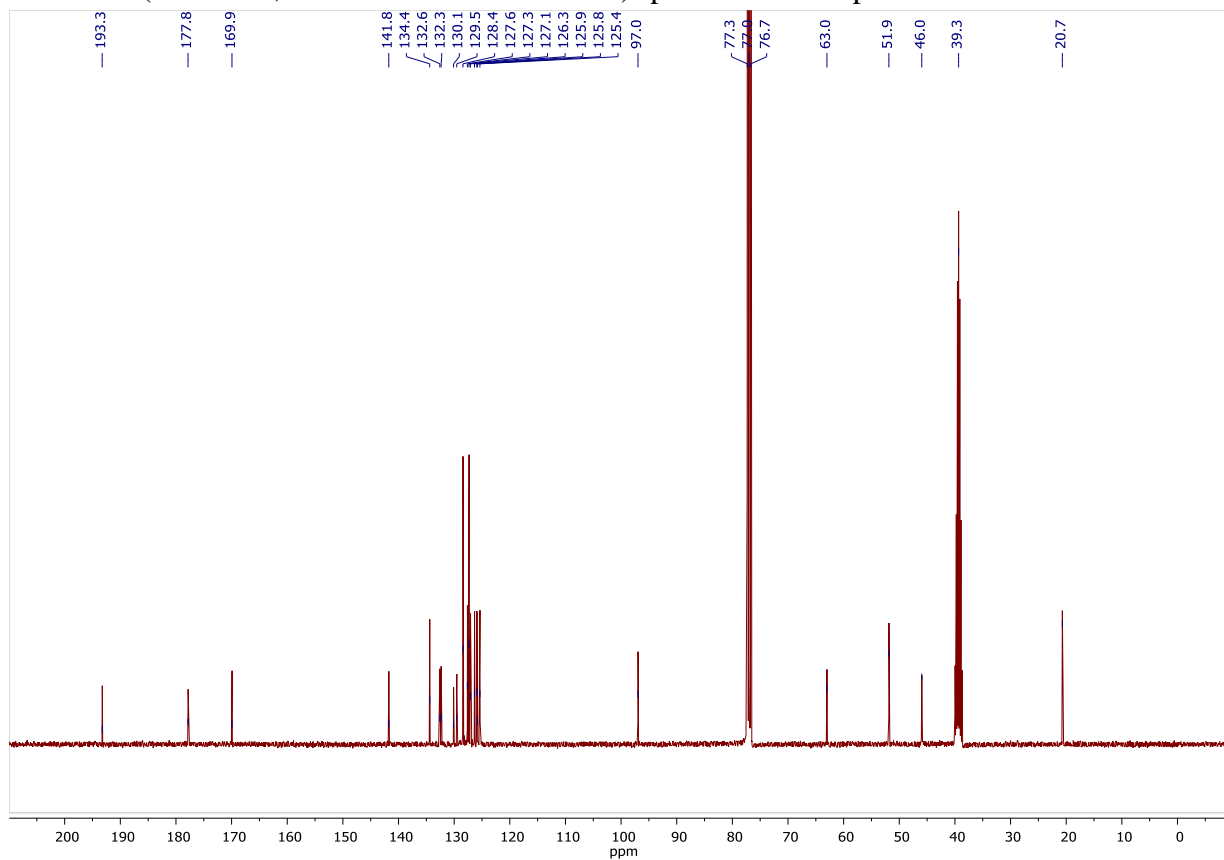
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **6d**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{DMSO-d}_6$  mixture) spectrum of compound **8**

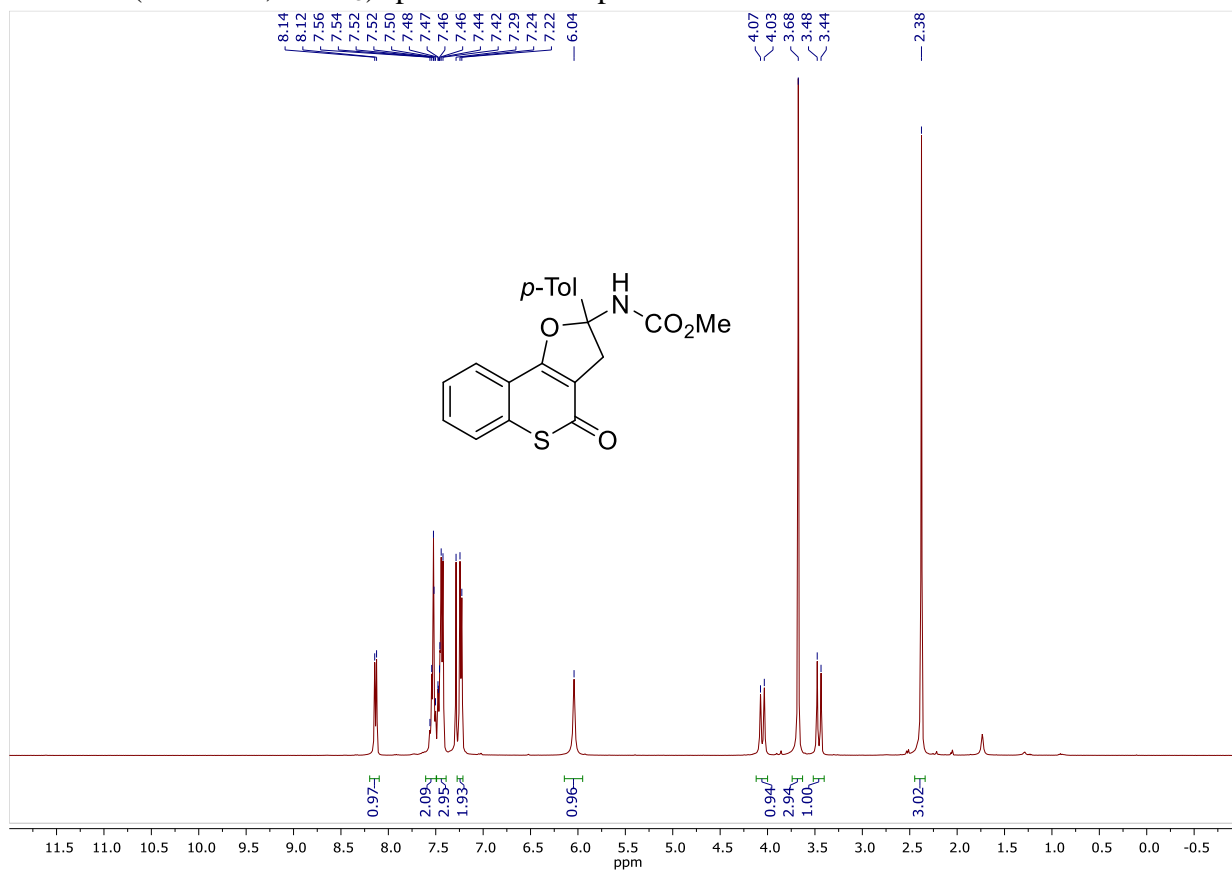


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3/\text{DMSO-d}_6$  mixture) spectrum of compound **8**

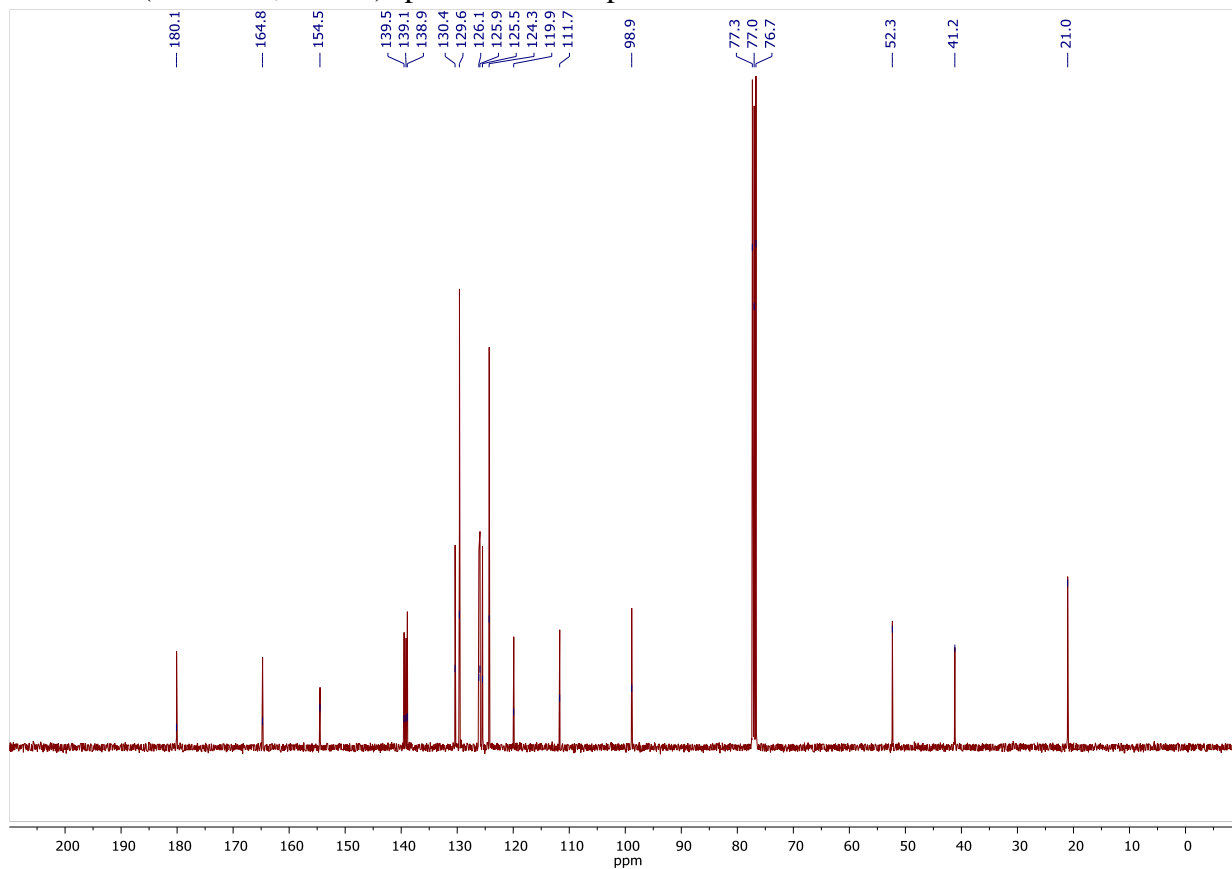




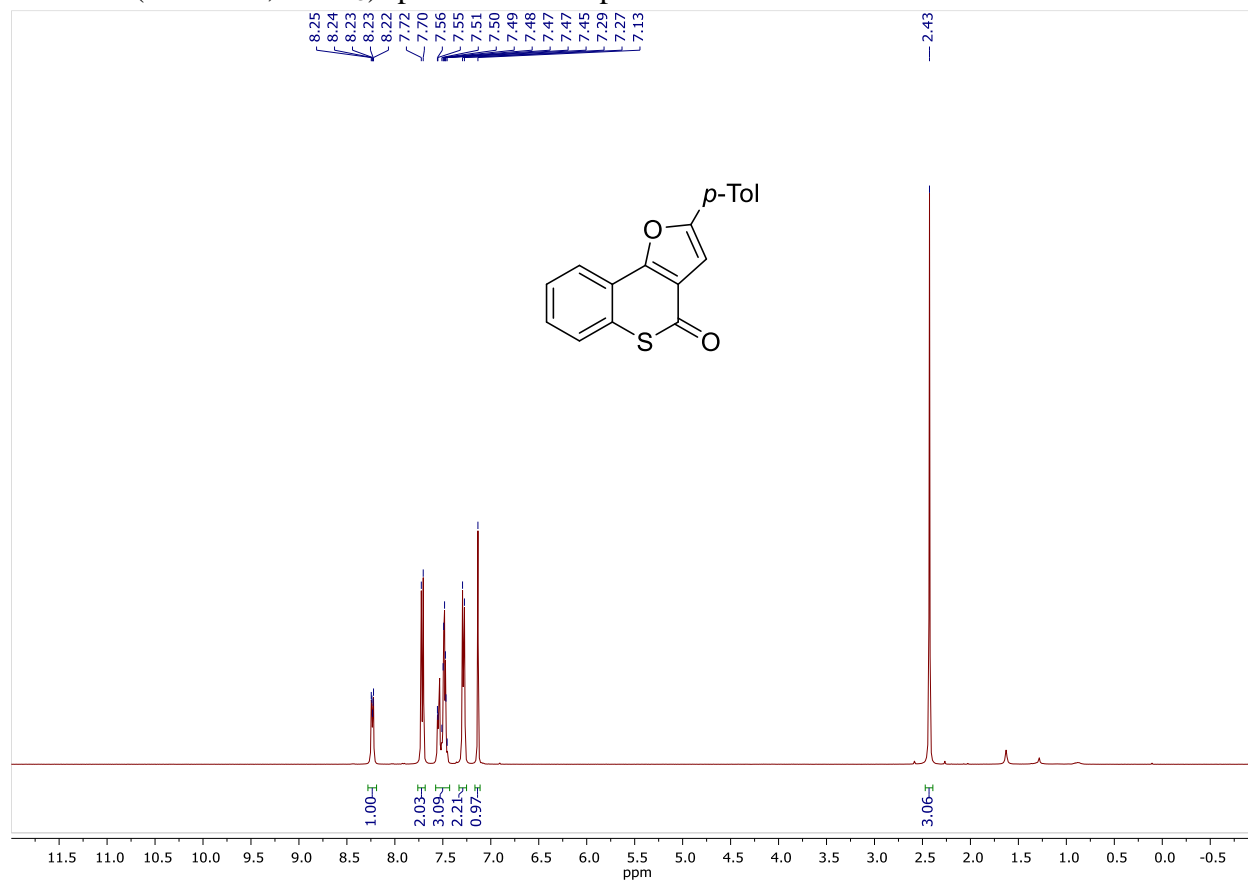
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **15**



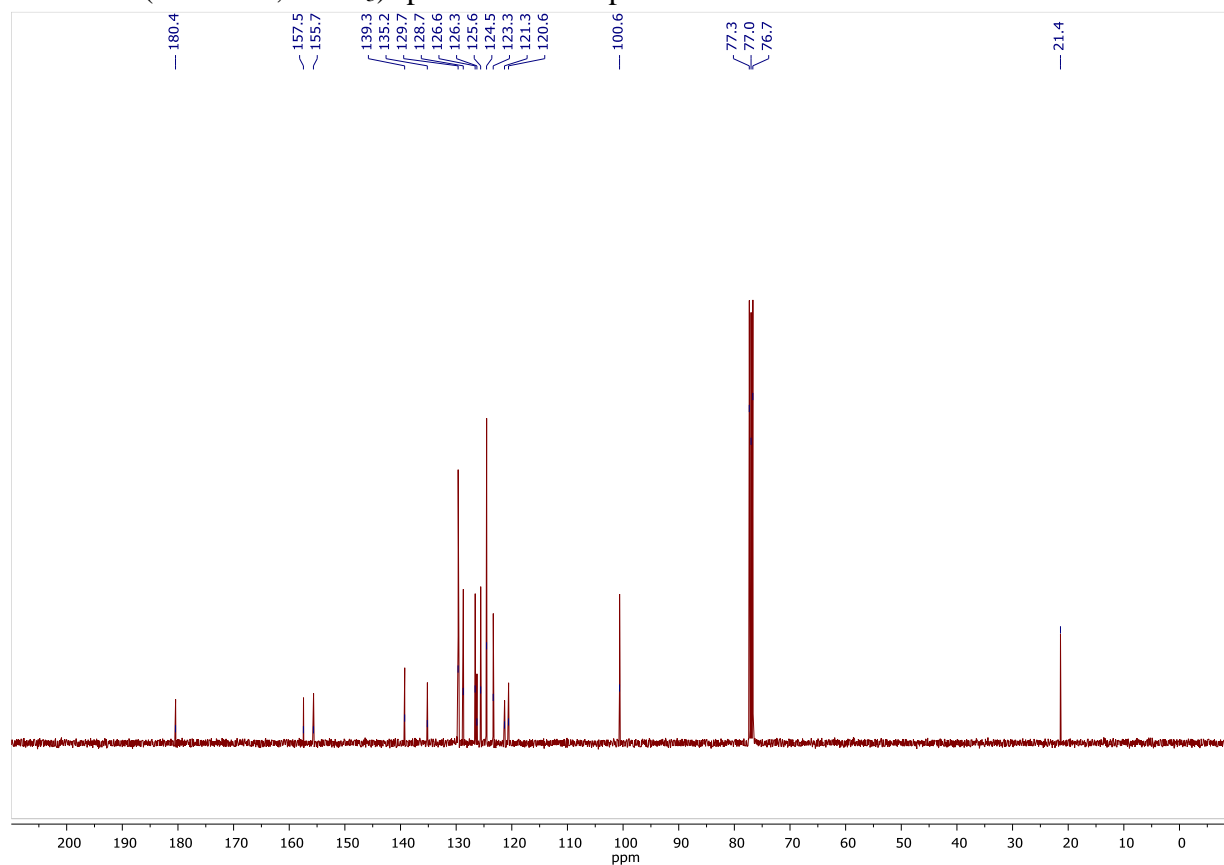
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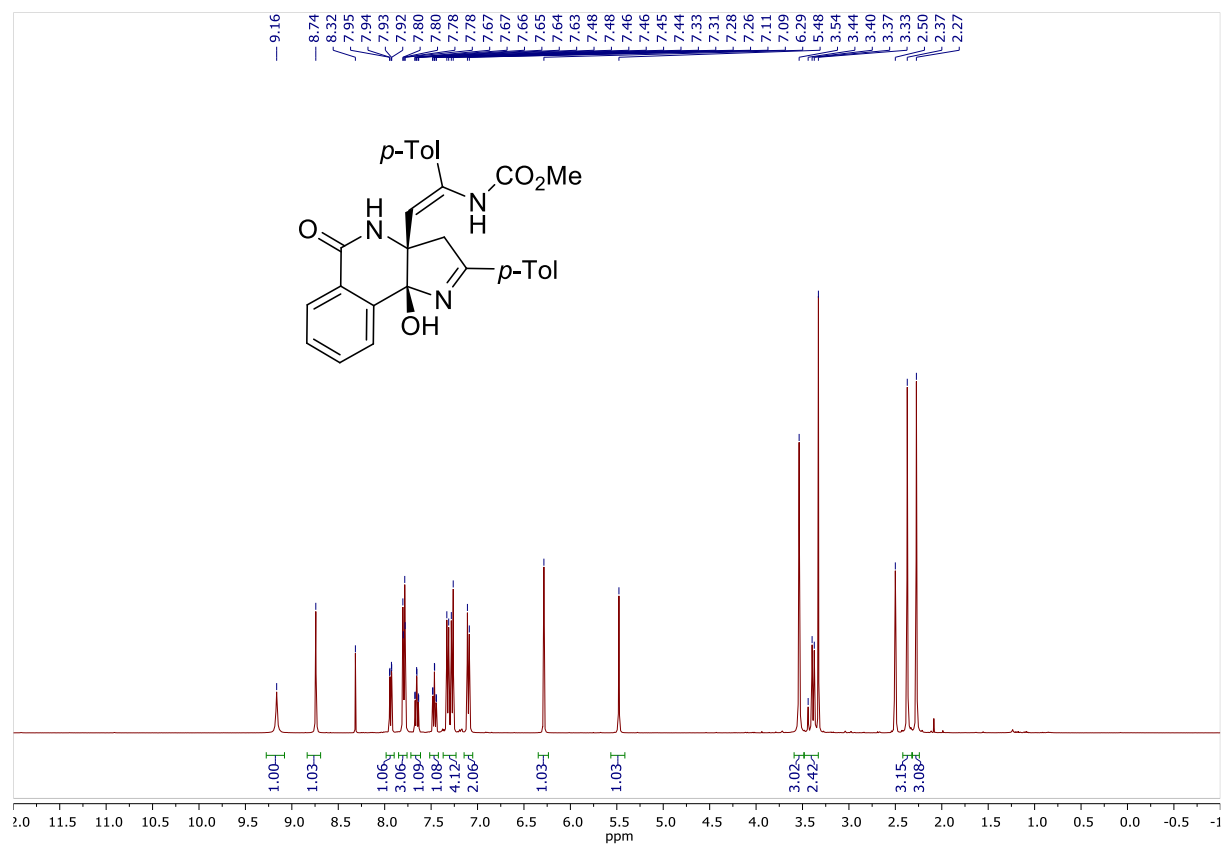
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **16**



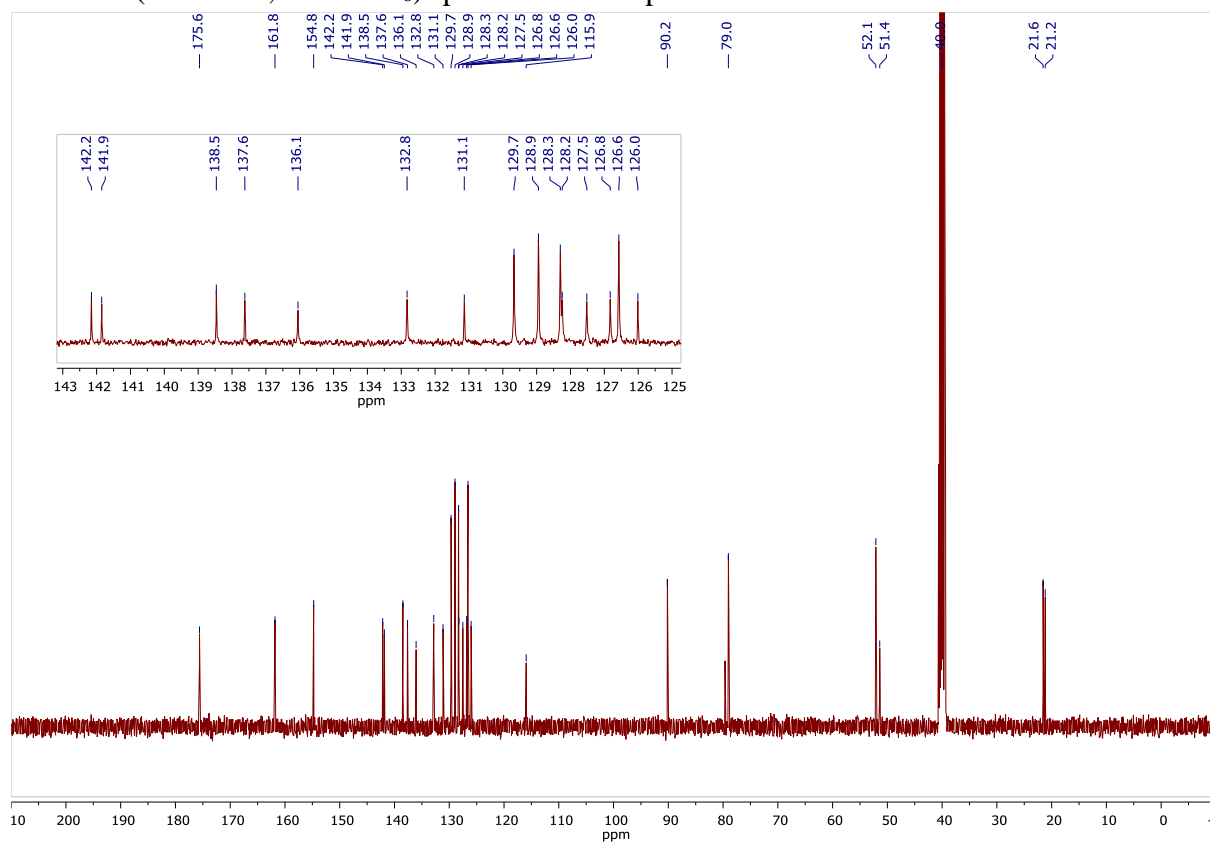
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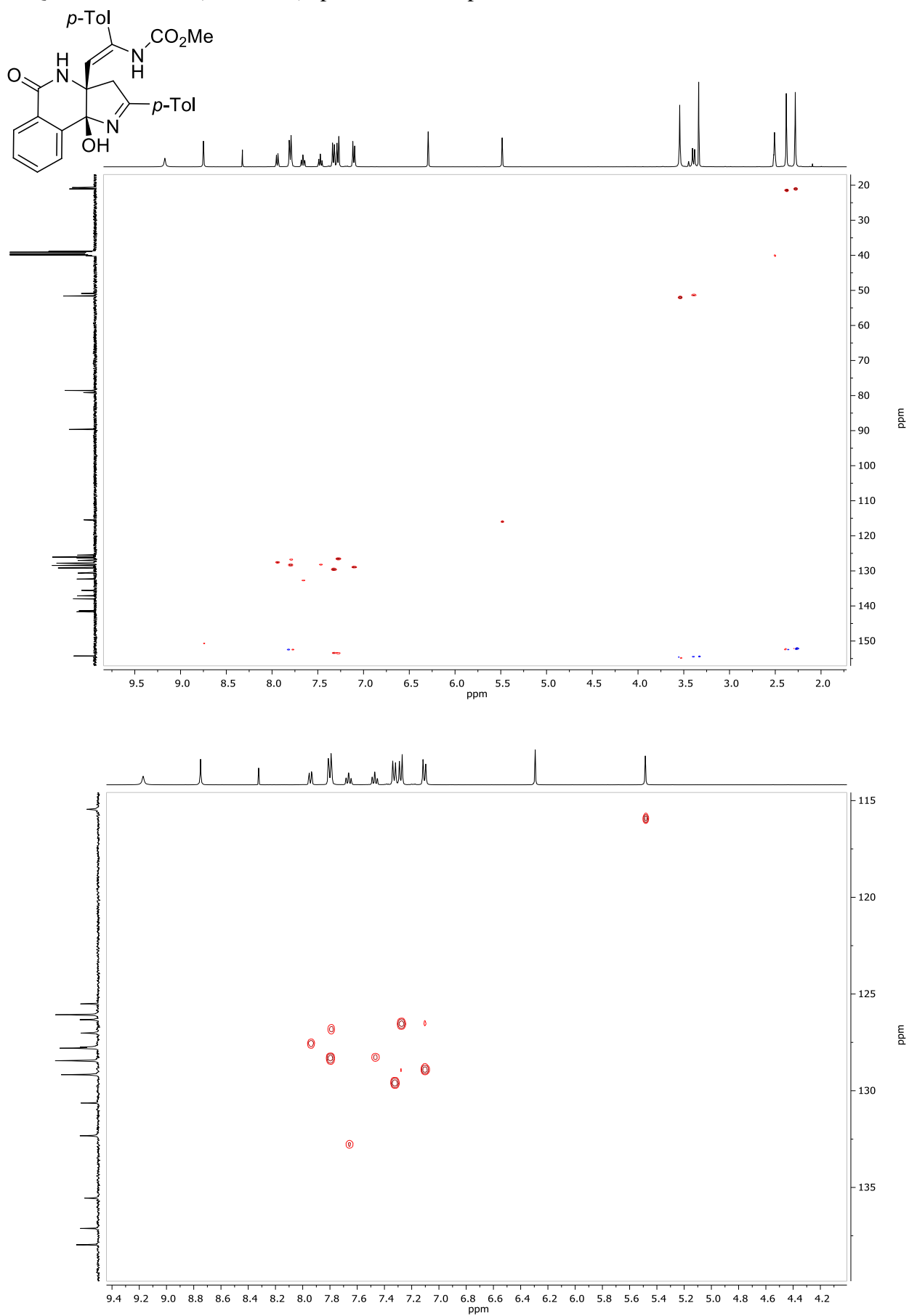
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **18**

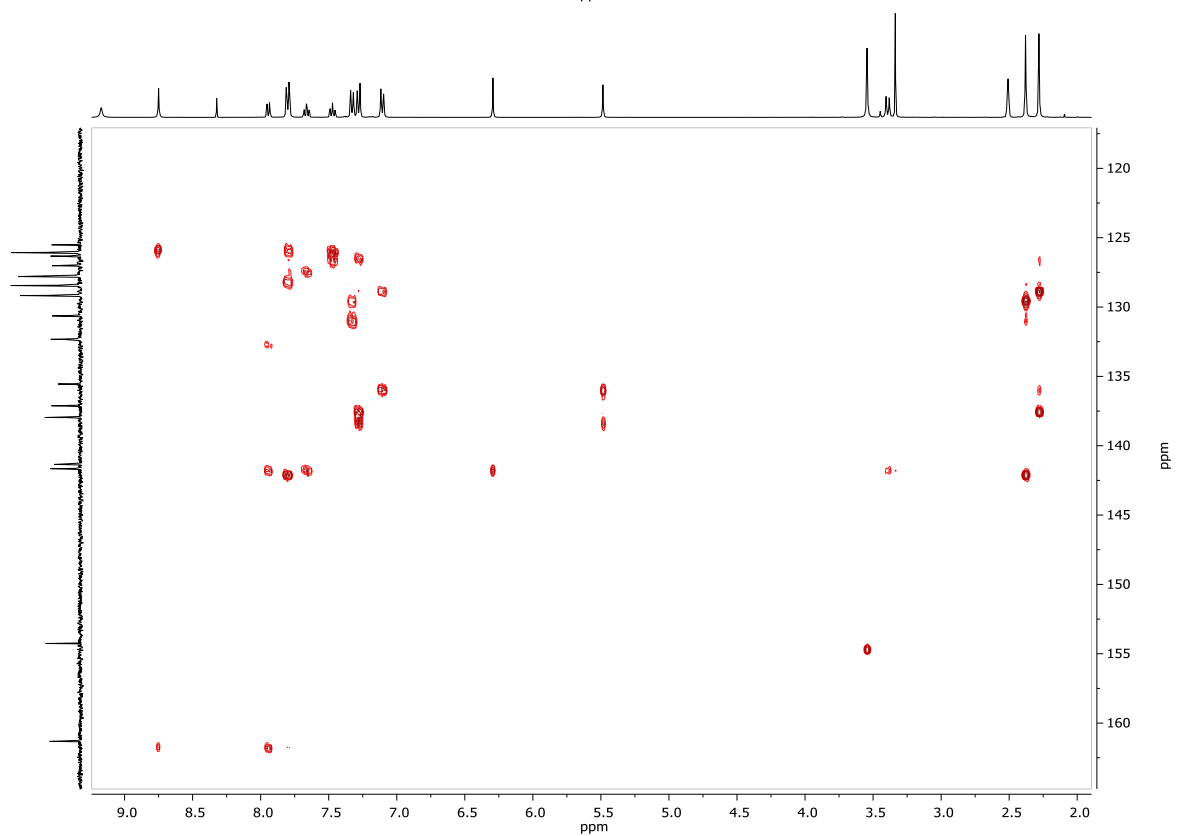
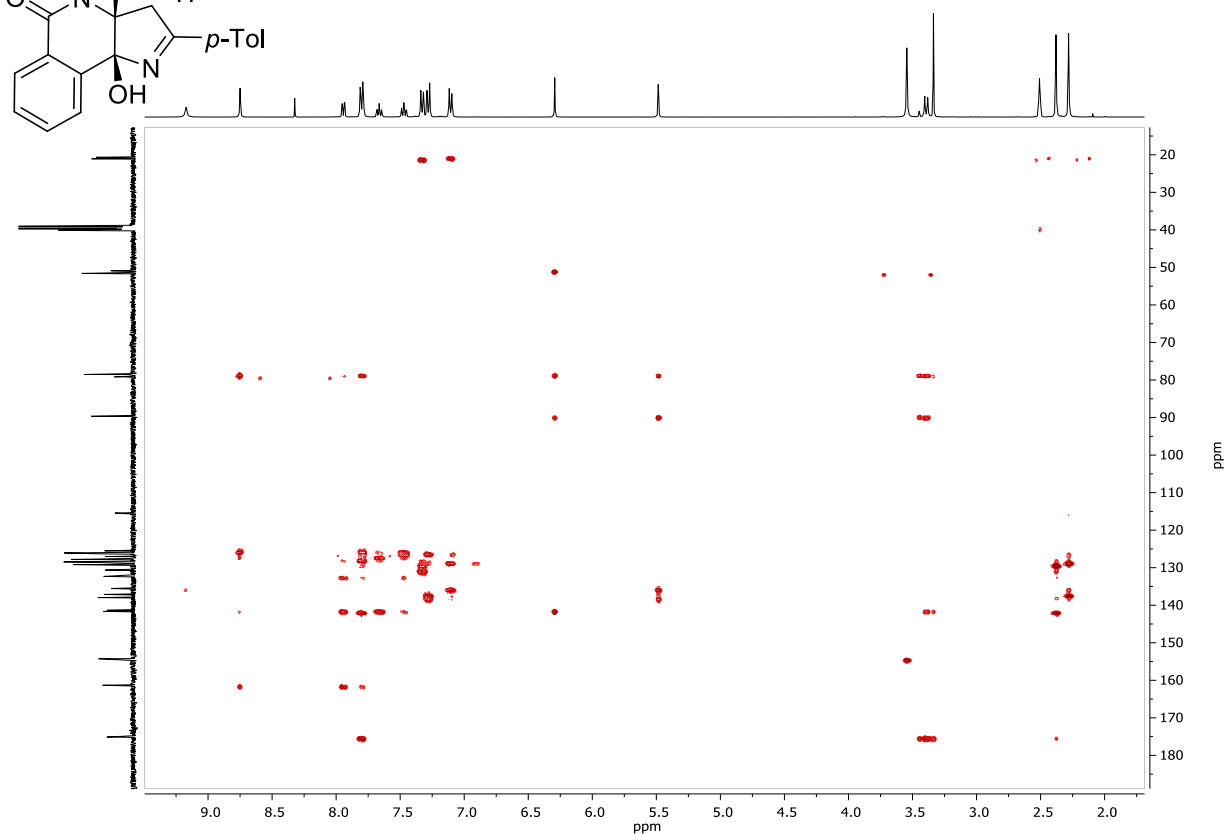


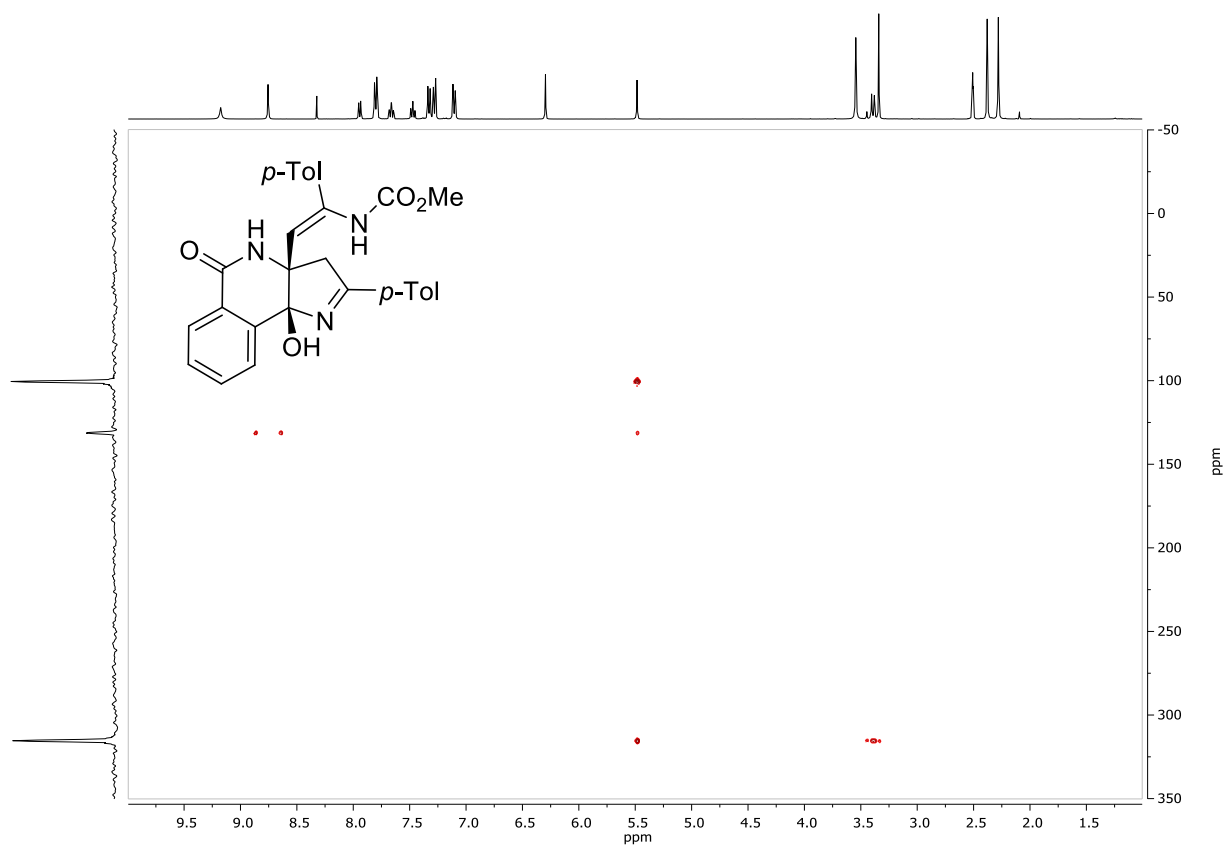
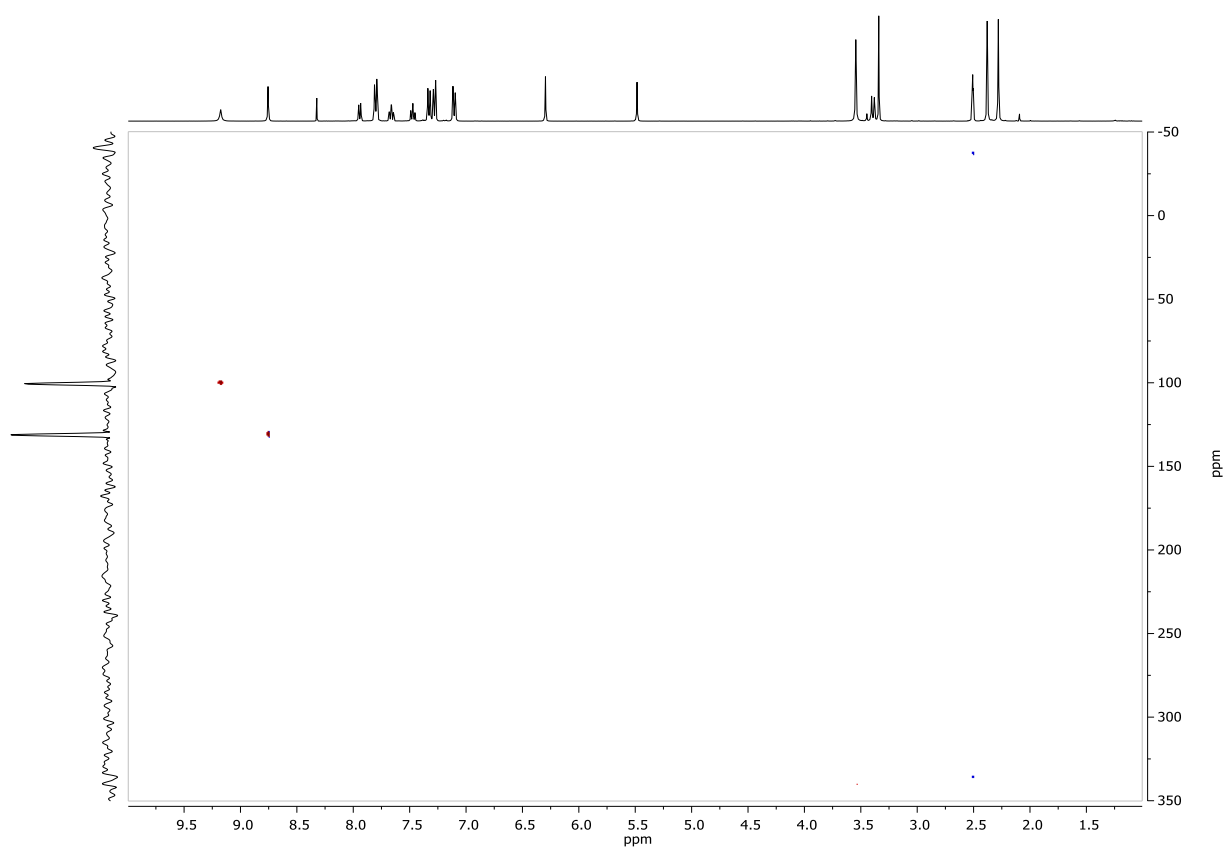
$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of compound **18**



HSQC  $^1\text{H}$ - $^{13}\text{C}$  NMR (DMSO- $d_6$ ) spectrum of compound **18**



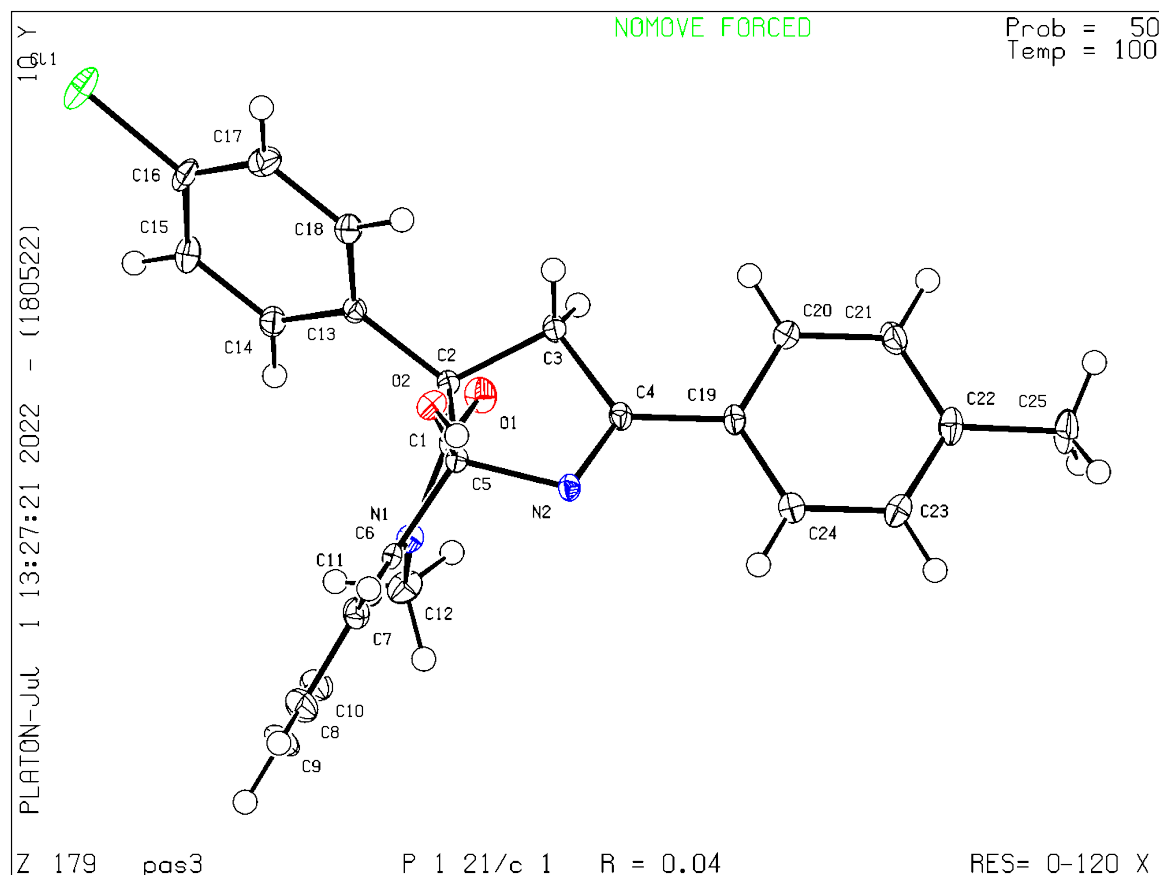


HMBC  $^1\text{H}$ - $^{15}\text{N}$  (DMSO- $\text{d}_6$ ) spectrum of compound **18**HSQC  $^1\text{H}$ - $^{15}\text{N}$  NMR ( $\text{DMSO-d}_6$ ) spectrum of compound **18**

## 2. X-ray Data

### Crystallographic data of compound **3e** (CCDC 1535459)

Single crystal of compound **3e** was grown by slow evaporation of hexane-diethyl ether solution. A suitable crystal was selected and studied on a Agilent Technologies Xcalibur Eos diffractometer. The crystal was kept at 100(2) 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 minimization.



**Figure S1.** Molecular structure of compound **3e**, displacement parameters are drawn at 50% probability level.

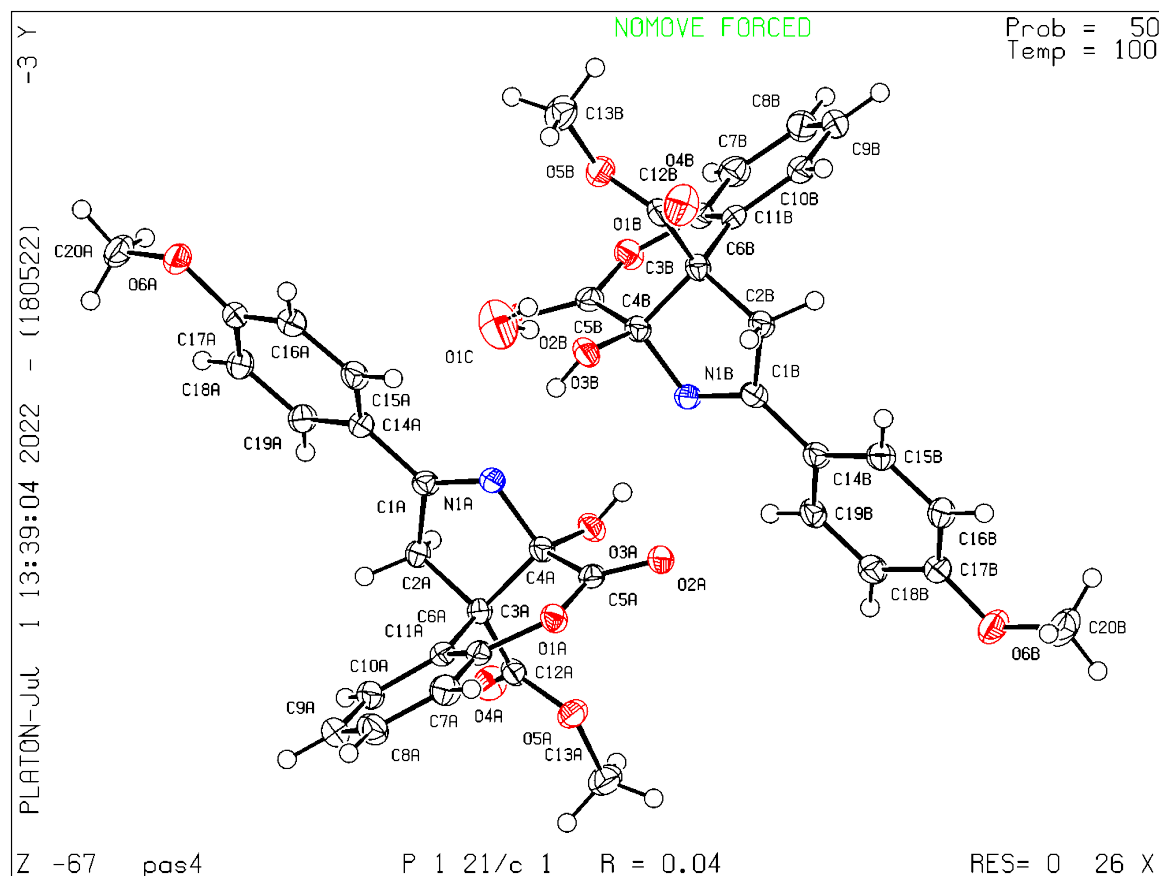
**Table S1 Crystal data and structure refinement for 3e.**

Empirical formula	C <sub>25</sub> H <sub>21</sub> N <sub>2</sub> O <sub>2</sub> Cl
Formula weight	416.89
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	12.0877(6)
b/Å	9.3537(4)
c/Å	18.5922(10)
α/°	90
β/°	105.038(5)
γ/°	90
Volume/Å <sup>3</sup>	2030.15(18)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.364
μ/mm <sup>-1</sup>	0.213
F(000)	872.0
Crystal size/mm <sup>3</sup>	0.34 × 0.18 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.29 to 55
Index ranges	-11 ≤ h ≤ 15, -11 ≤ k ≤ 12, -21 ≤ l ≤ 24
Reflections collected	11952
Independent reflections	4647 [R <sub>int</sub> = 0.0263, R <sub>sigma</sub> = 0.0345]
Data/restraints/parameters	4647/0/274
Goodness-of-fit on F <sup>2</sup>	1.020
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0373, wR <sub>2</sub> = 0.0888
Final R indexes [all data]	R <sub>1</sub> = 0.0476, wR <sub>2</sub> = 0.0957
Largest diff. peak/hole / e Å <sup>-3</sup>	0.36/-0.30



### Crystallographic data of compound **6c** (CCDC 2182542)

Single crystal of compound **6c** was grown by slow evaporation of EtOAc-hexane solution. A suitable crystal was selected and studied on an Agilent Technologies Supernova diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [4] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimization.



**Figure S2.** Molecular structure of compound **6c**, displacement parameters are drawn at 50% probability level.

**Table S2 Crystal data and structure refinement for 6c.**

Empirical formula	C <sub>20</sub> H <sub>17.46</sub> NO <sub>6.23</sub>
Formula weight	371.45
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	18.9991(6)
b/Å	11.0188(2)
c/Å	17.6331(7)
α/°	90
β/°	107.678(4)
γ/°	90
Volume/Å <sup>3</sup>	3517.1(2)
Z	8
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.403
μ/mm <sup>-1</sup>	0.882
F(000)	1554.0
Crystal size/mm <sup>3</sup>	0.45 × 0.34 × 0.26
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.396 to 144.988
Index ranges	-23 ≤ h ≤ 22, -13 ≤ k ≤ 5, -20 ≤ l ≤ 21
Reflections collected	12891
Independent reflections	6683 [R <sub>int</sub> = 0.0310, R <sub>sigma</sub> = 0.0355]
Data/restraints/parameters	6683/0/505
Goodness-of-fit on F <sup>2</sup>	1.077
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0409, wR <sub>2</sub> = 0.1090
Final R indexes [all data]	R <sub>1</sub> = 0.0591, wR <sub>2</sub> = 0.1335
Largest diff. peak/hole / e Å <sup>-3</sup>	0.34/-0.30

### 3. References

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3. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.
4. Sheldrick, G.M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst.* **2015**, *A71*, 3–8.