

# Supporting Information

## Synthesis of Benzofuro[3,2-*b*]indol-3-one Derivatives via Dearomative (3 + 2) Cycloaddition of 2-Nitrobenzofurans and *para*-Quinamines

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Jun-Qing Yin,<sup>1</sup> Ming-Qiang Zhou<sup>2,\*</sup> and Zhen-Hua Wang<sup>1,\*</sup>

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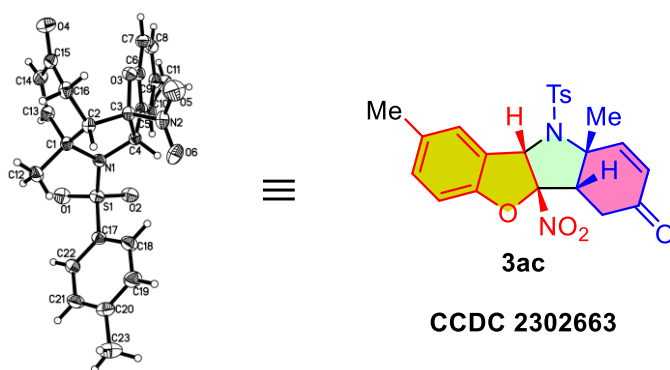
wangzhenhua@cdu.edu.cn

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## 1. Crystal data and structure refinement

Single crystals of compound **3ac** were prepared through dissolving the sample in mixture solvent of EtOH/DCM (1/1) at room temperature and crystalizing by slow evaporation of solvent. A suitable crystal was selected for structure determination on a 'Oxford Gemini E' diffractometer. The crystal was kept at 293 K during data collection. Using Olex2<sup>1</sup>, the structure was solved with the ShelXT<sup>2</sup> structure solution program using Intrinsic Phasing and refined with the ShelXL<sup>3</sup> refinement package using Least Squares minimization.



ORTEP of **3ac** (at the 50% probability level)

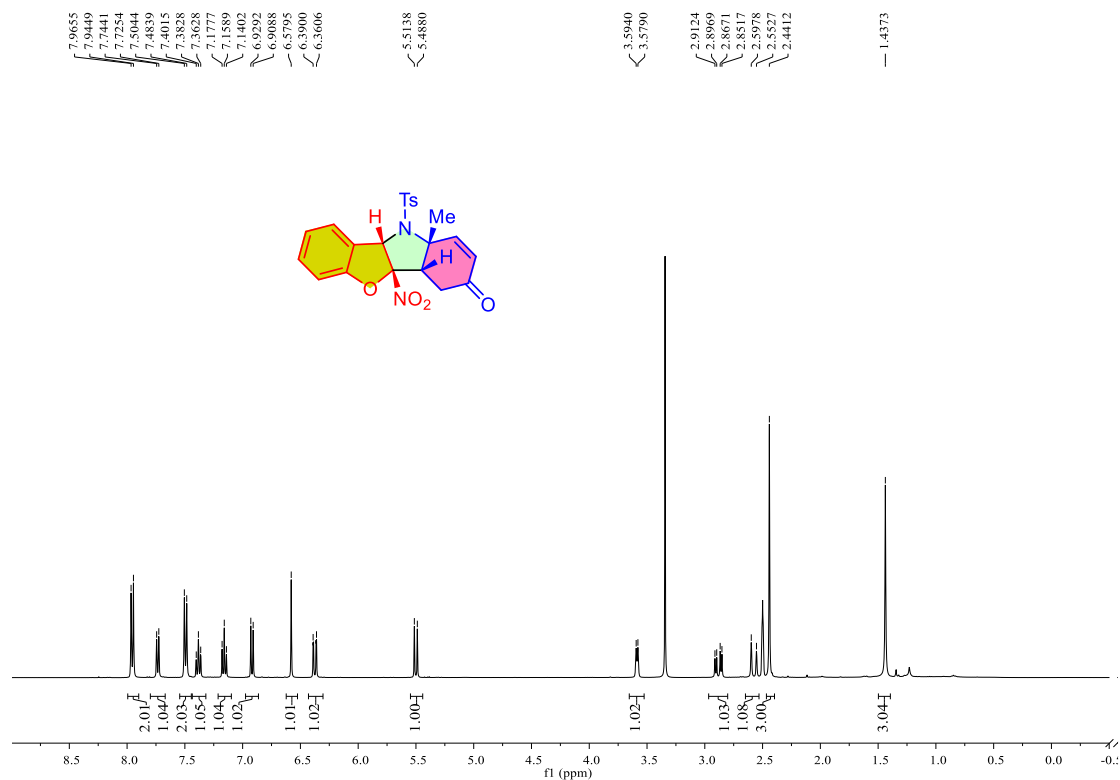
Identification code	<b>3ac</b>
Empirical formula	C <sub>23</sub> H <sub>22</sub> N <sub>2</sub> O <sub>6</sub> S
Formula weight	454.48
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	12.1191(4)
b/Å	12.9353(5)
c/Å	14.2184(5)
α/°	90
β/°	91.613(3)
γ/°	90
Volume/Å <sup>3</sup>	2228.06(13)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.355
μ/mm <sup>-1</sup>	1.656
F(000)	952.0
Crystal size/mm <sup>3</sup>	0.14 × 0.12 × 0.08
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.298 to 134.142
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16

Reflections collected	20024
Independent reflections	3979 [ $R_{\text{int}} = 0.0558$ , $R_{\text{sigma}} = 0.0363$ ]
Data/restraints/parameters	3979/0/292
Goodness-of-fit on $F^2$	1.041
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0435$ , $wR_2 = 0.1165$
Final R indexes [all data]	$R_1 = 0.0538$ , $wR_2 = 0.1277$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.26/-0.27

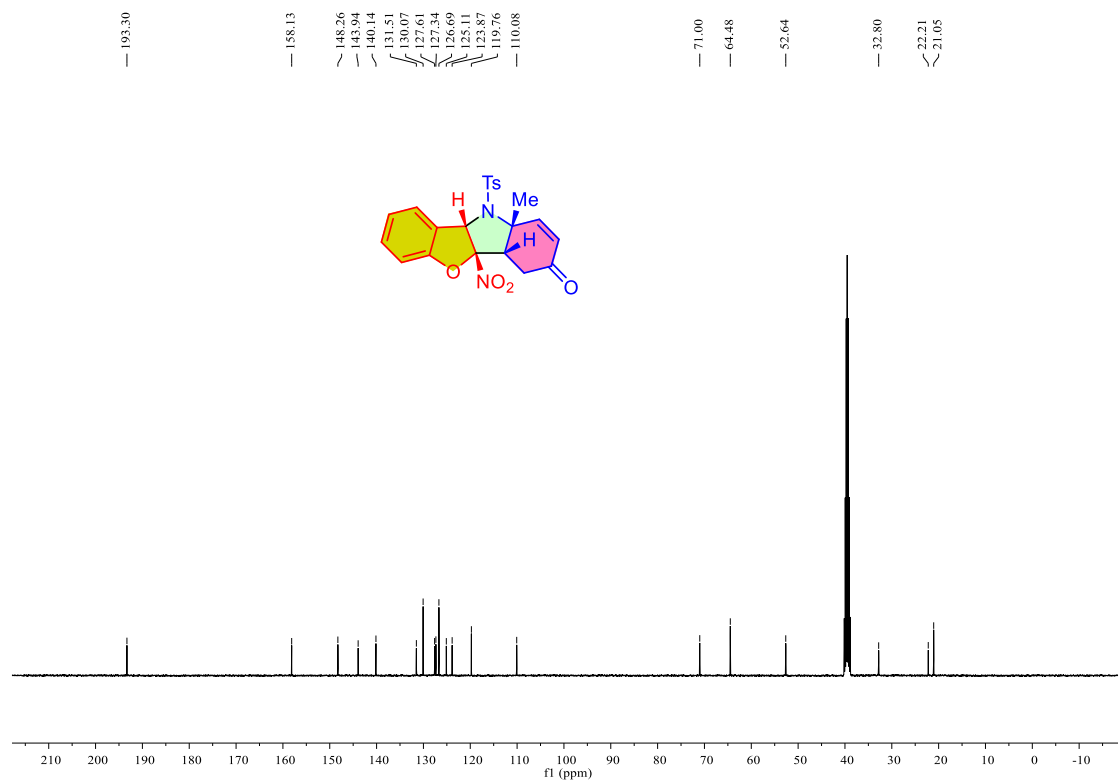
1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.*, **2009**, *42*, 339-341.
2. Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3-8.
3. Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3-8.

## 2. Copies of $^1\text{H}$ , $^{13}\text{C}$ NMR spectra for compounds 3, 4, 5, and 6

### $^1\text{H}$ NMR (400 MHz, $\text{DMSO}-d_6$ ) of 3aa

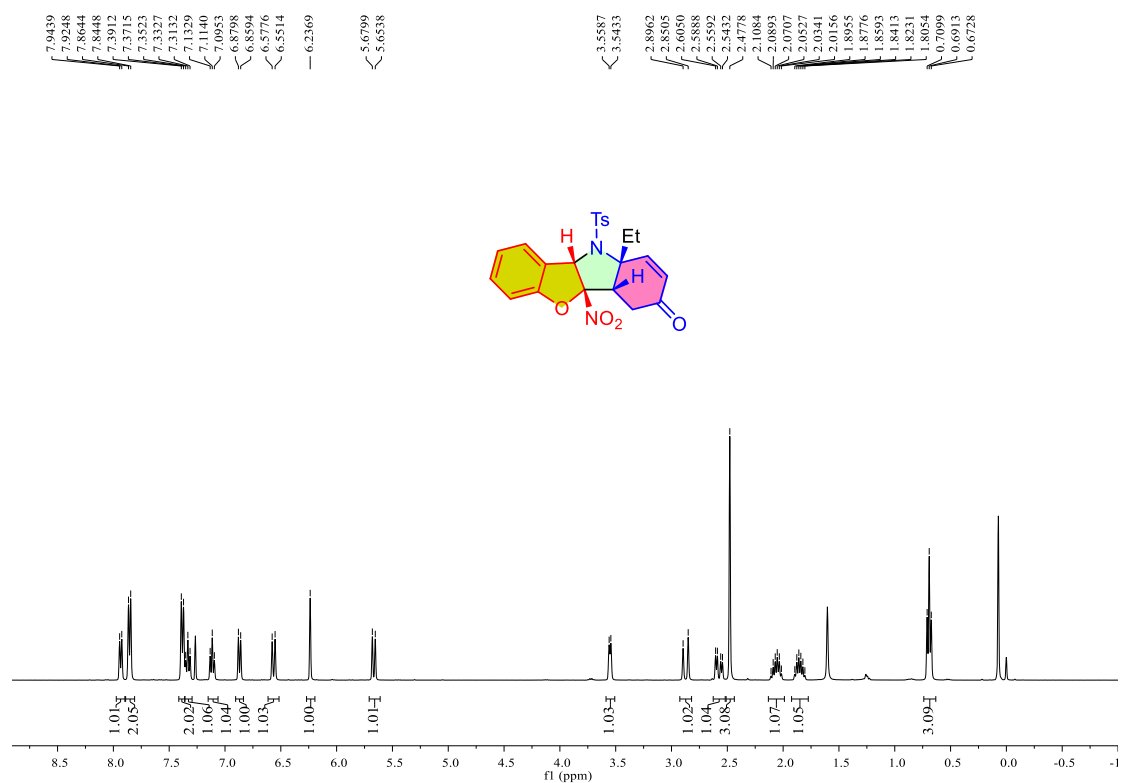


### $^{13}\text{C}$ NMR (101 MHz, $\text{DMSO}-d_6$ ) of 3aa

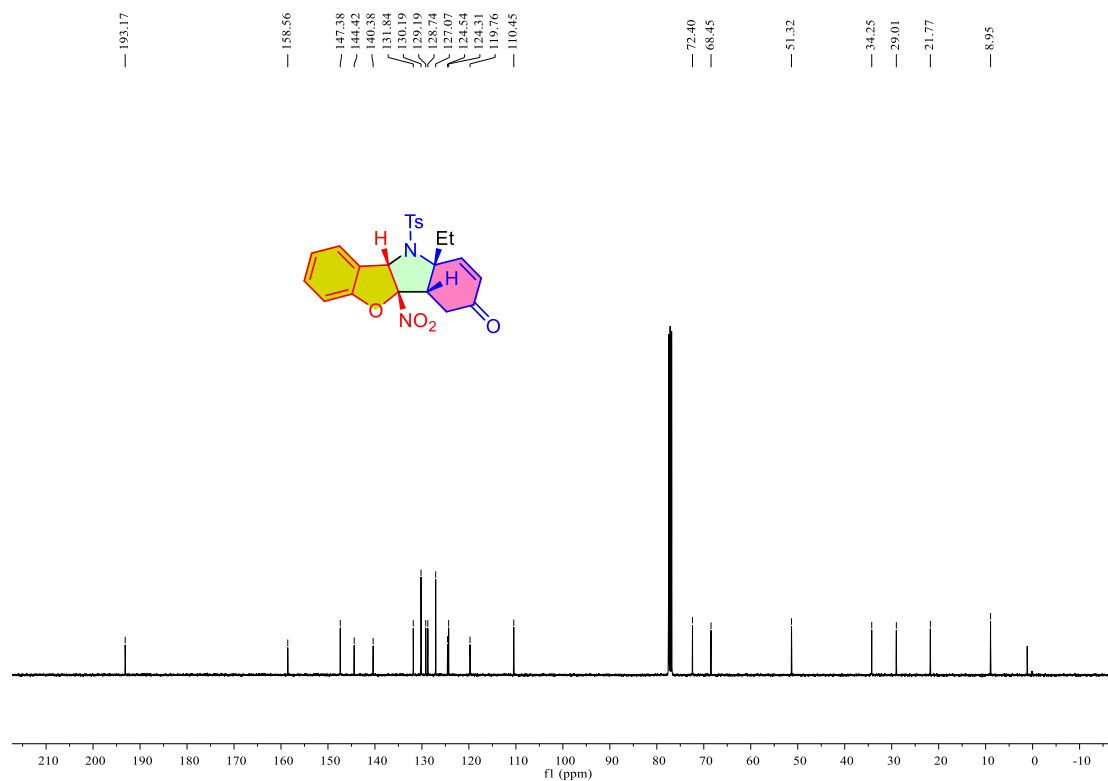




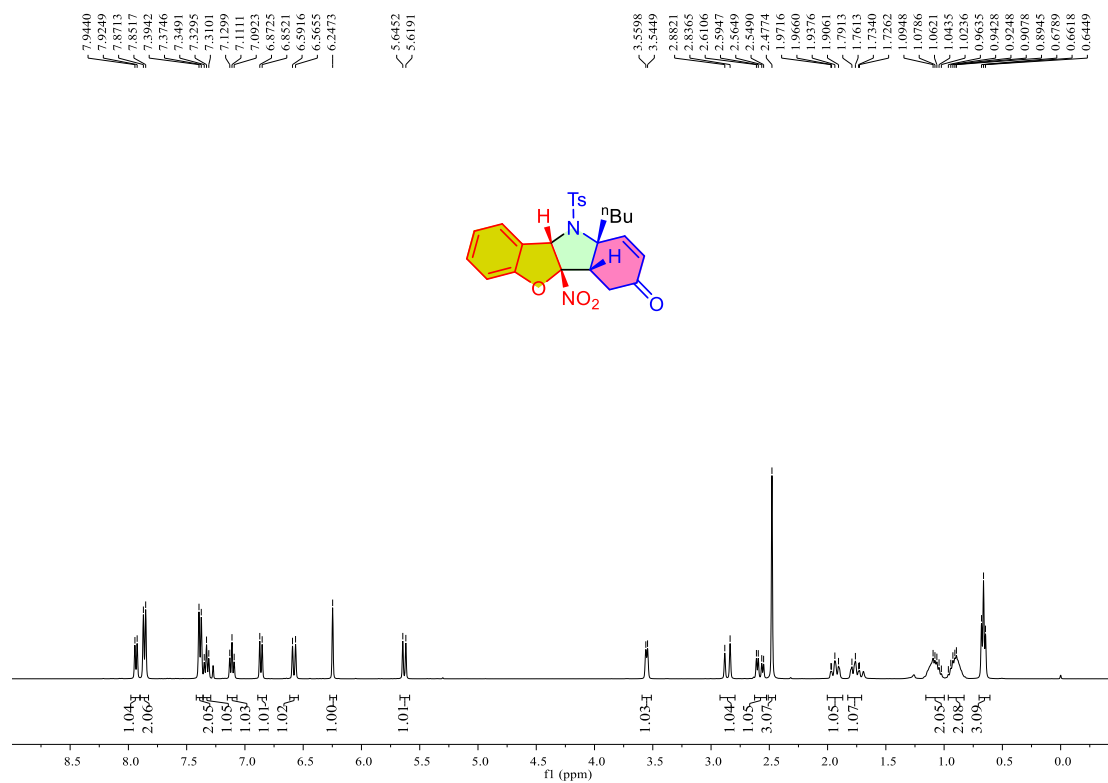
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ba**



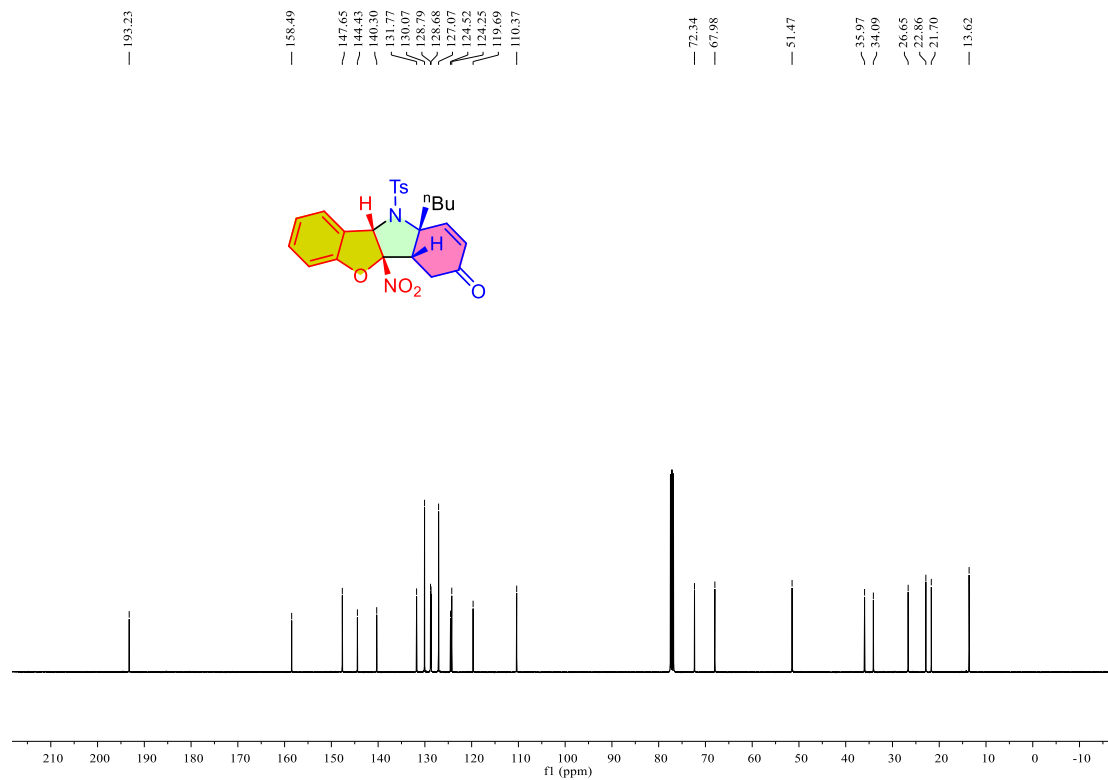
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ba**



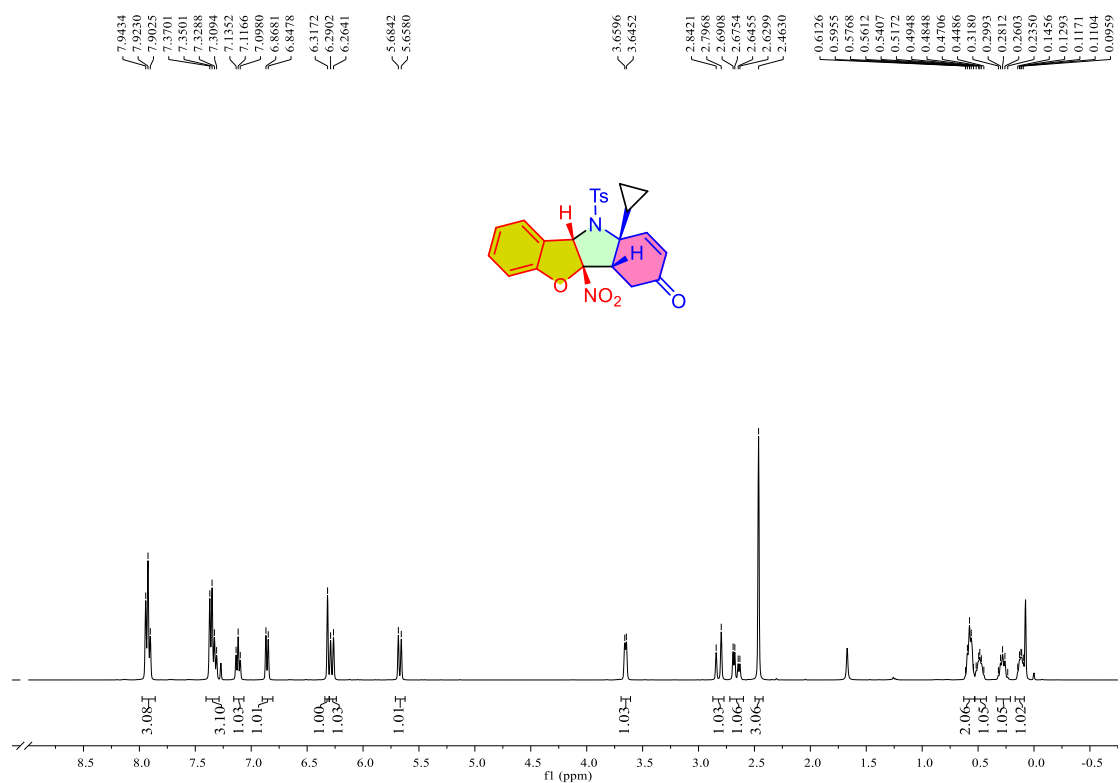
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ca**



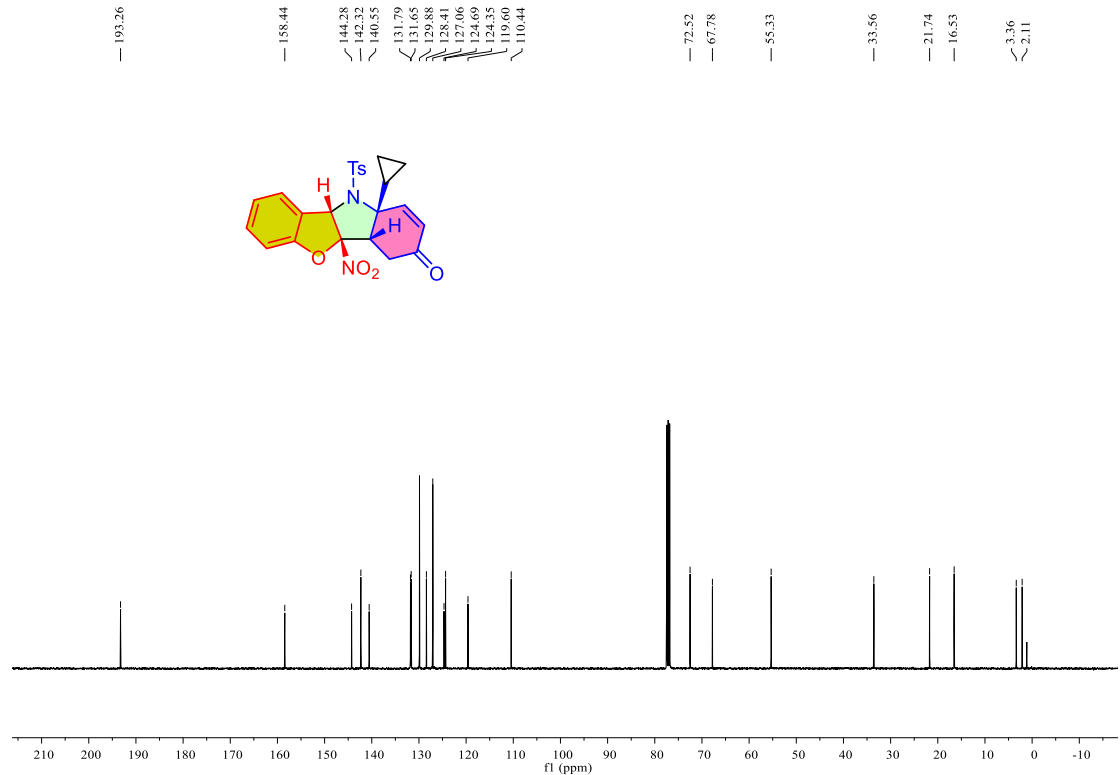
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3ca**



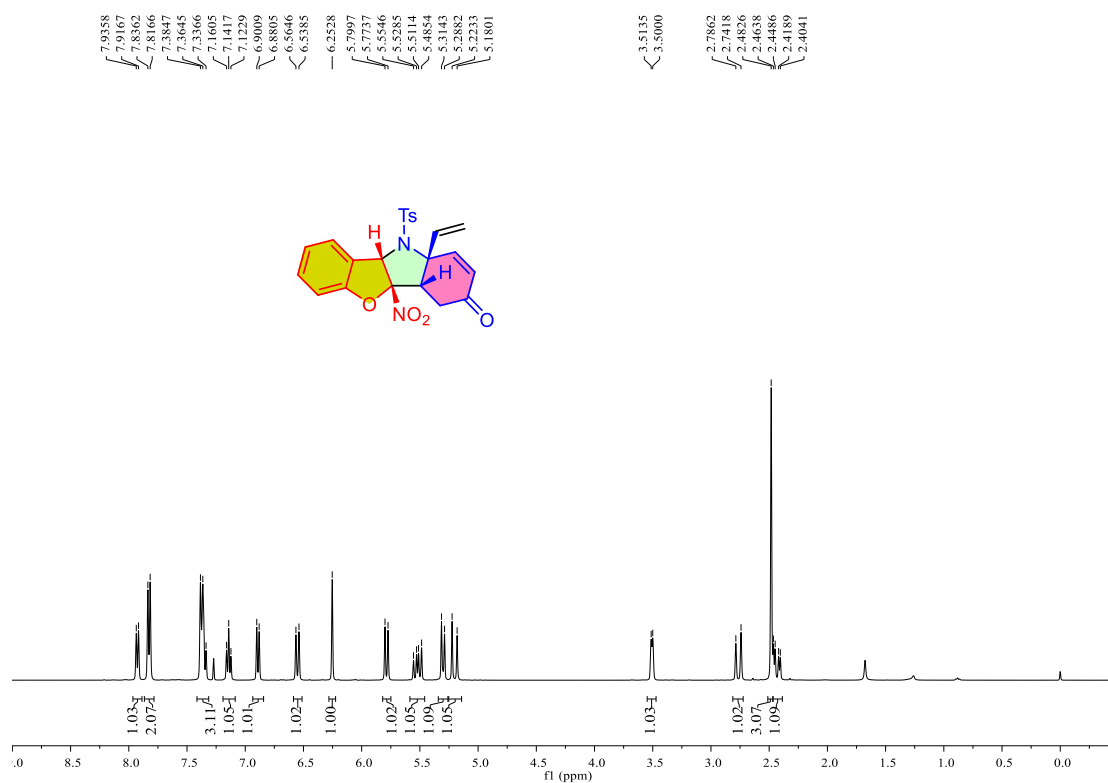
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3da**



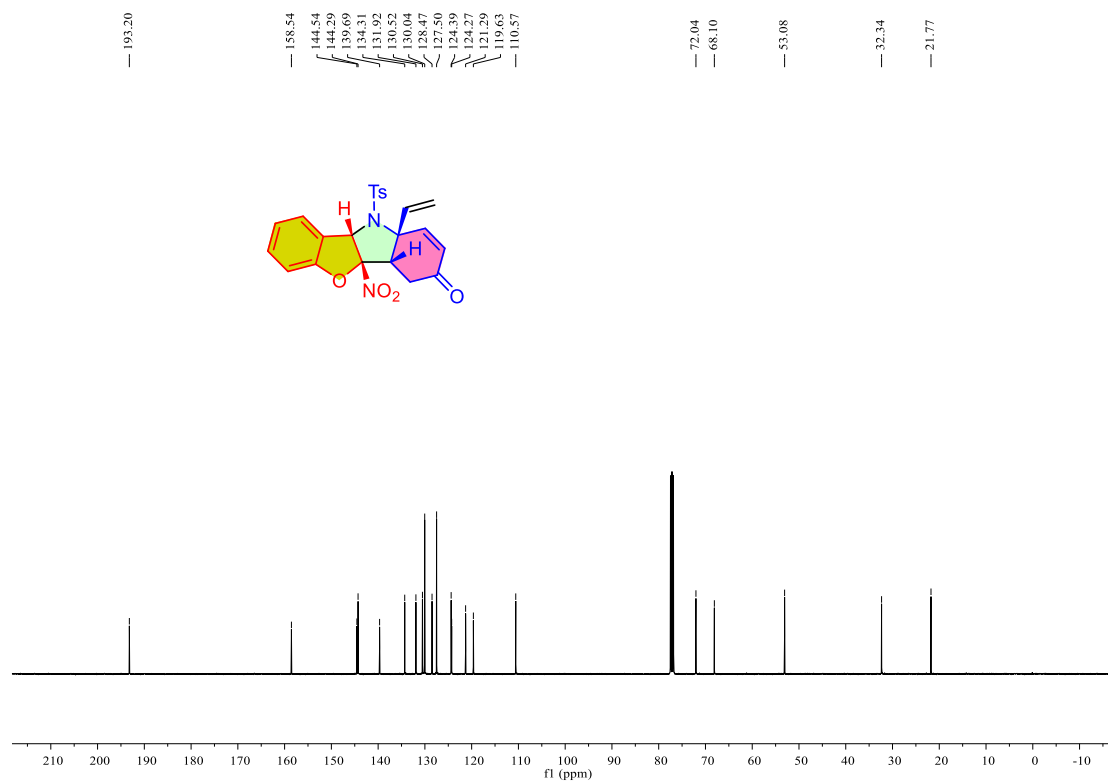
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3da**



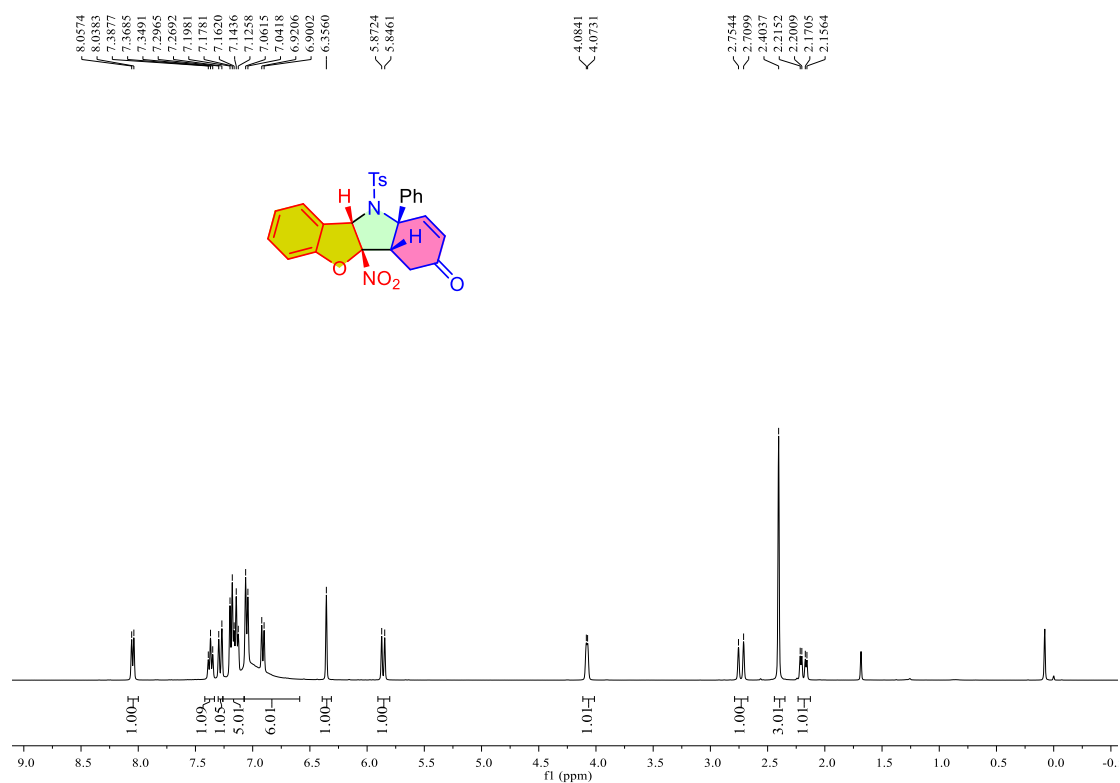
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ea**



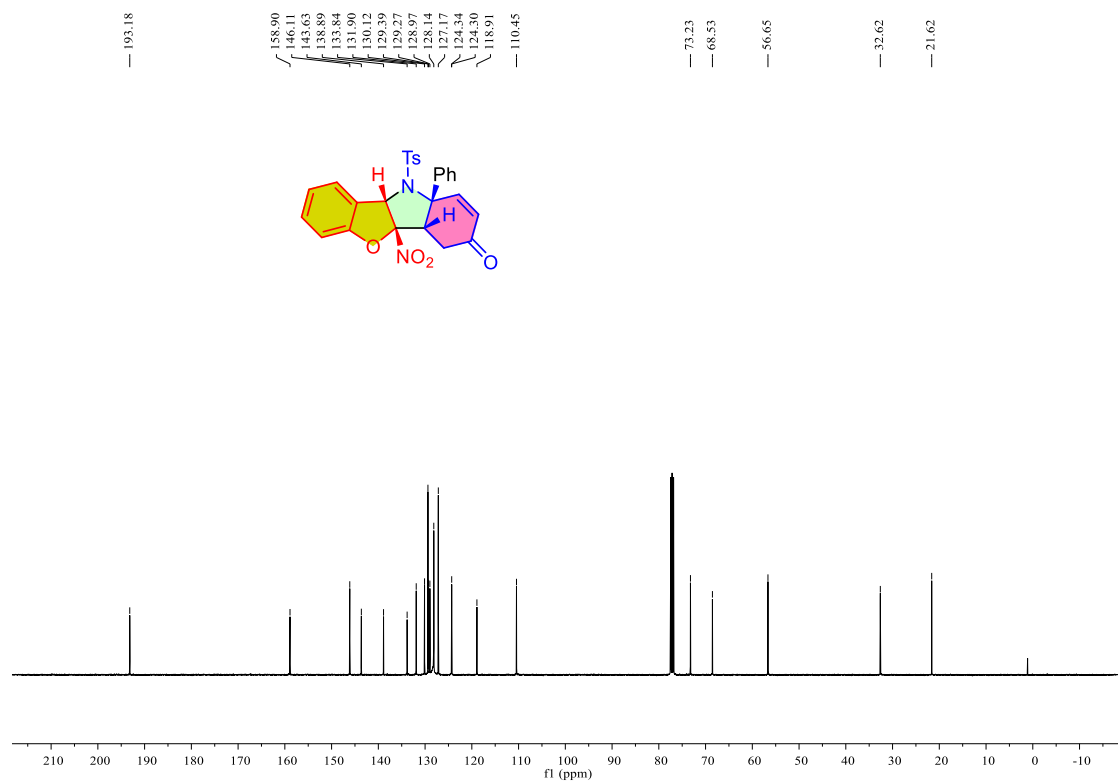
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ea**



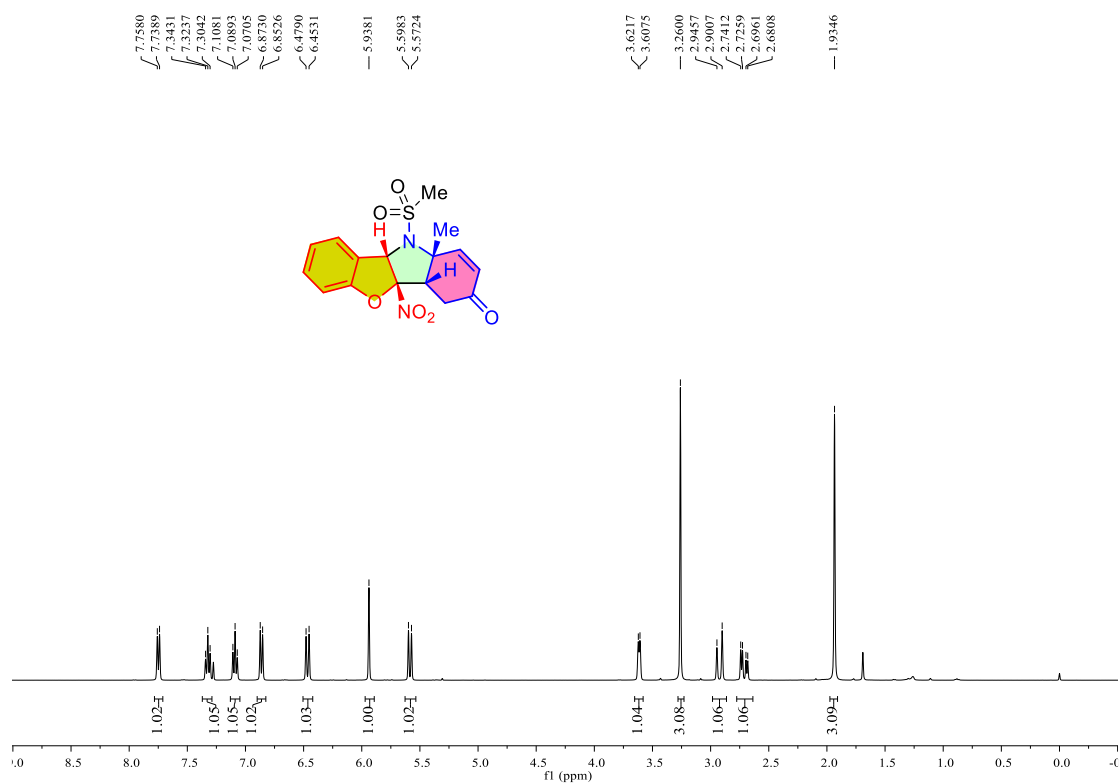
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3fa**



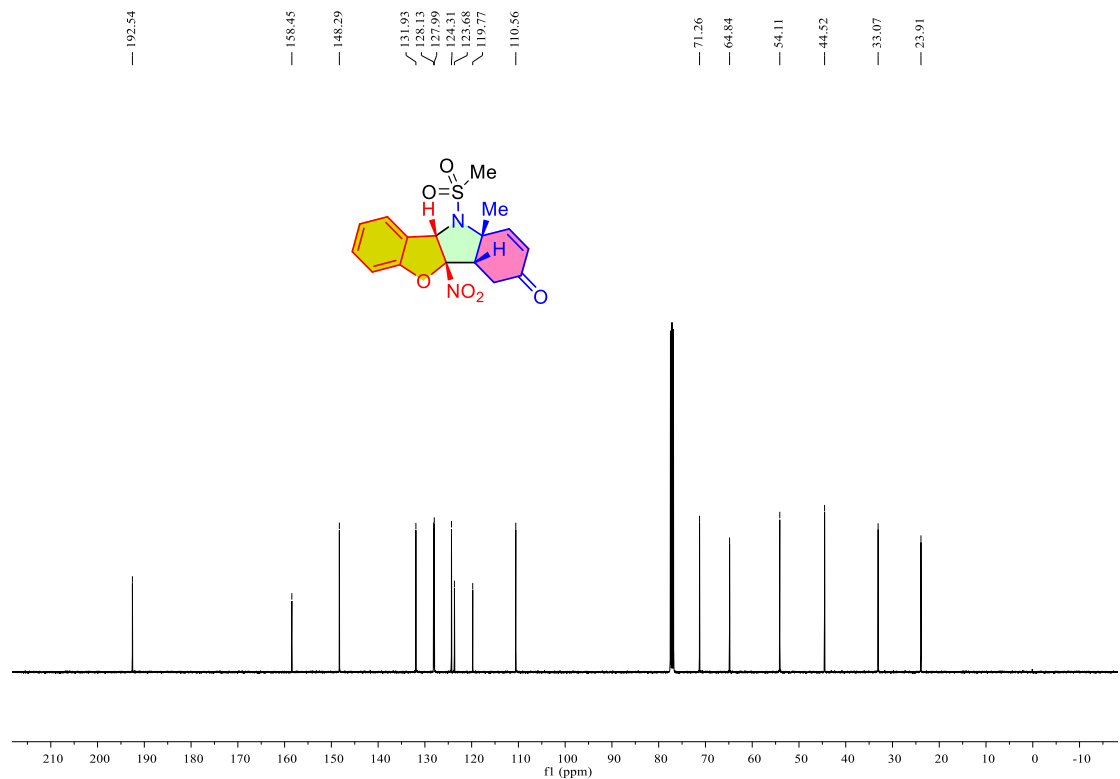
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3fa**



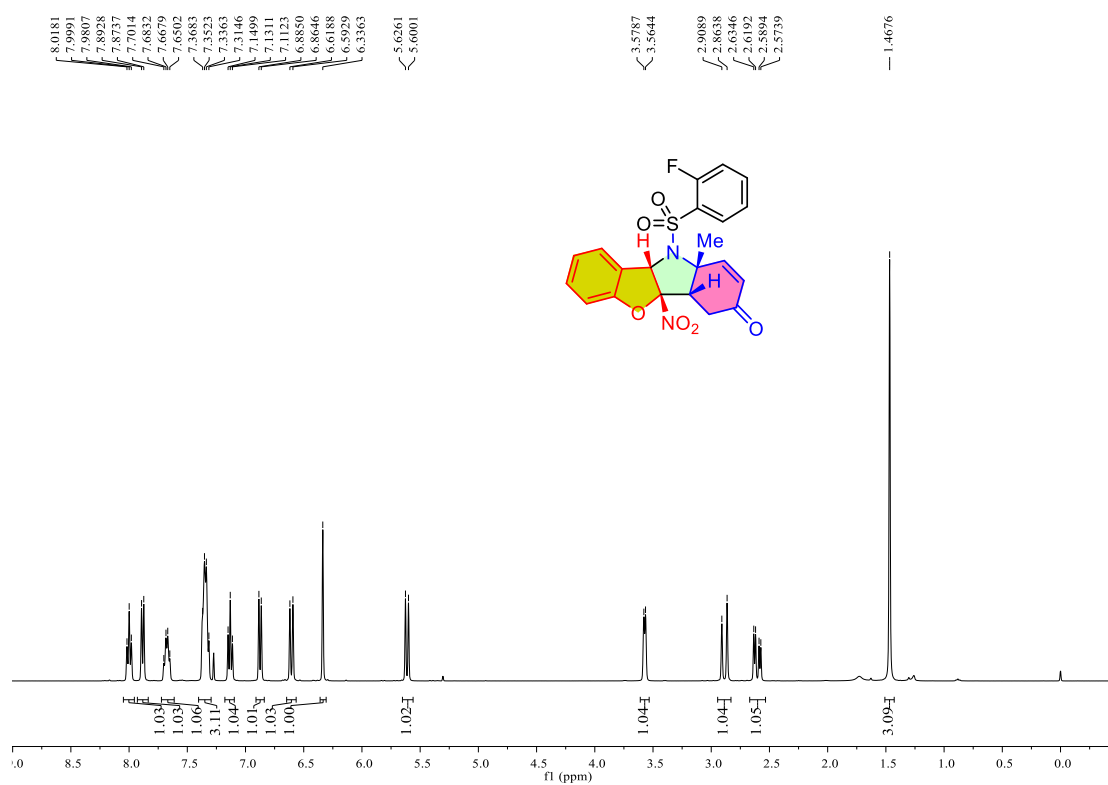
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ga**



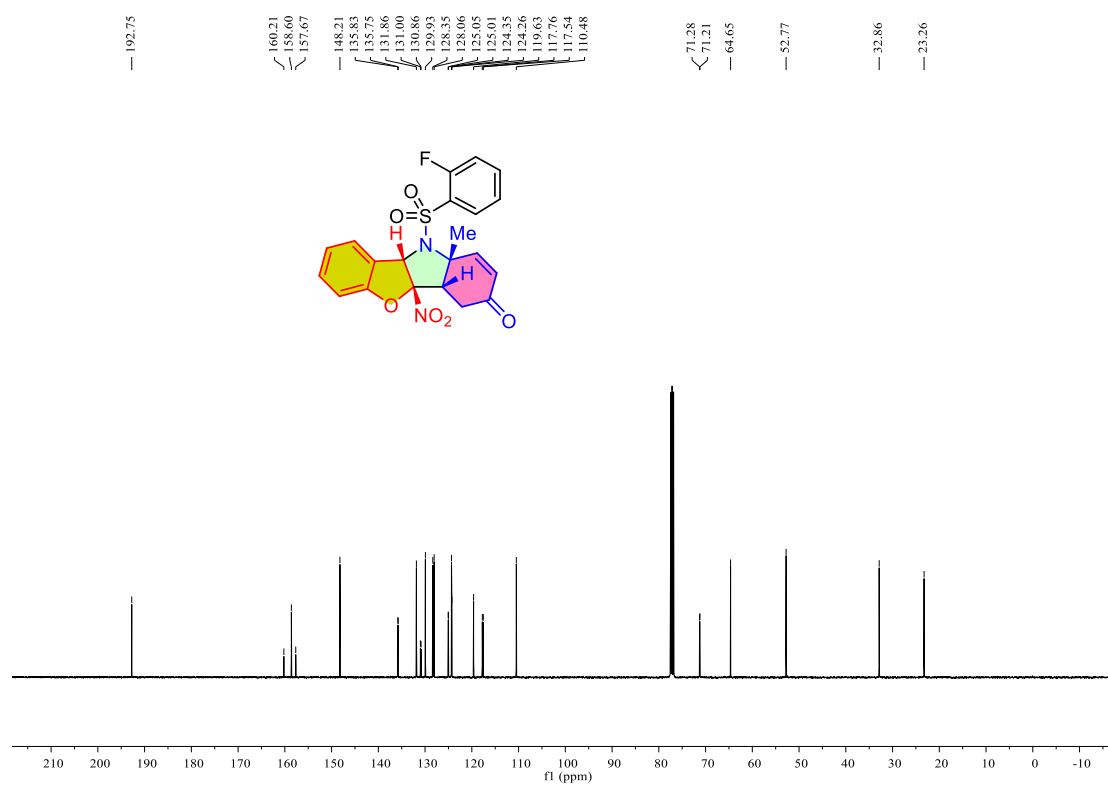
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ga**



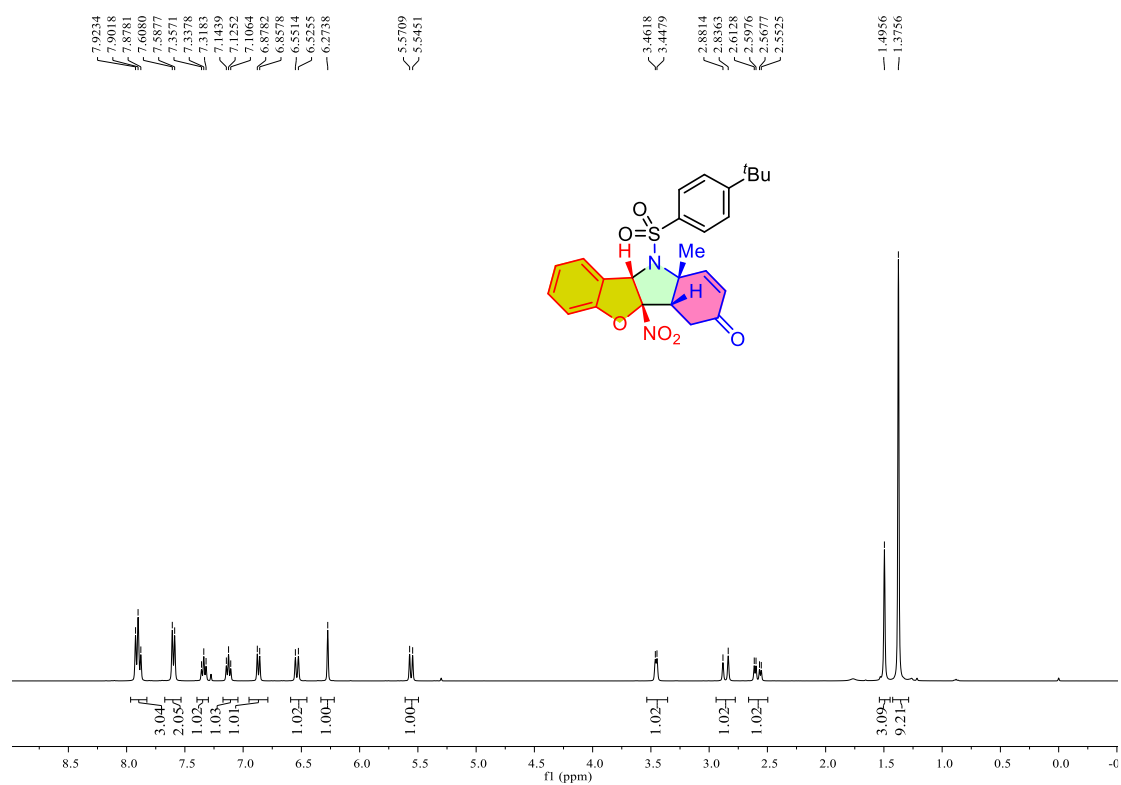
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ha**



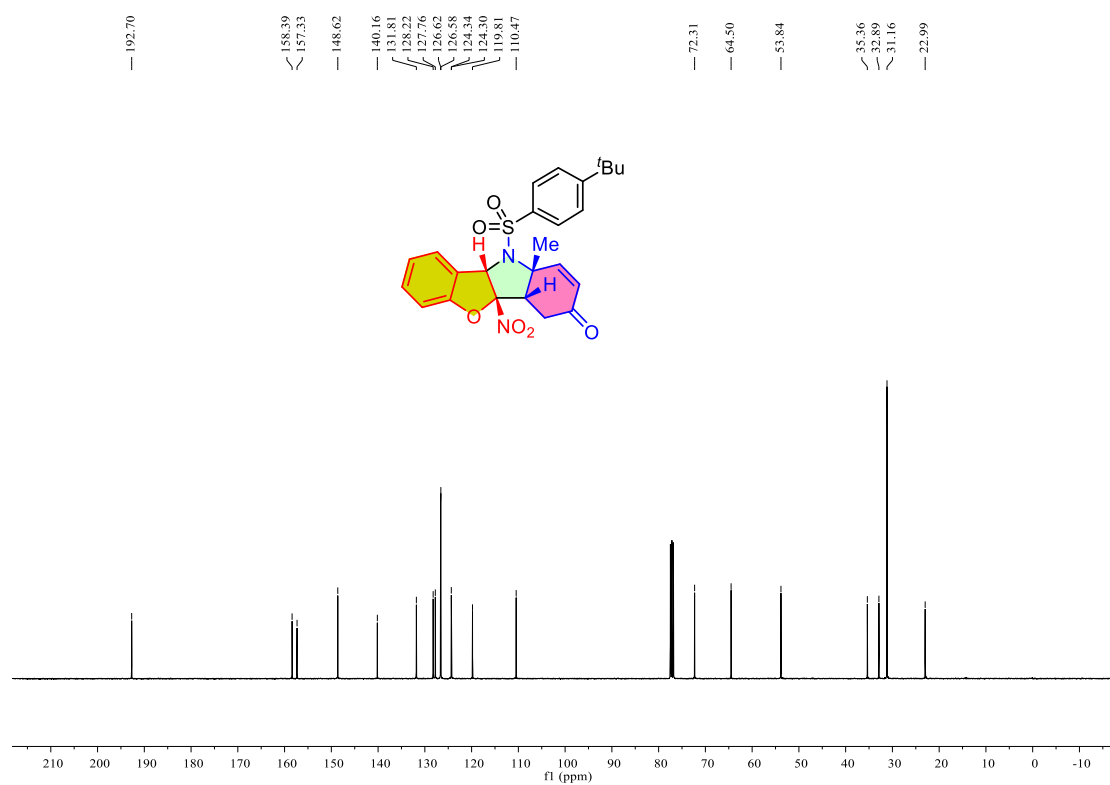
<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ha**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ia**

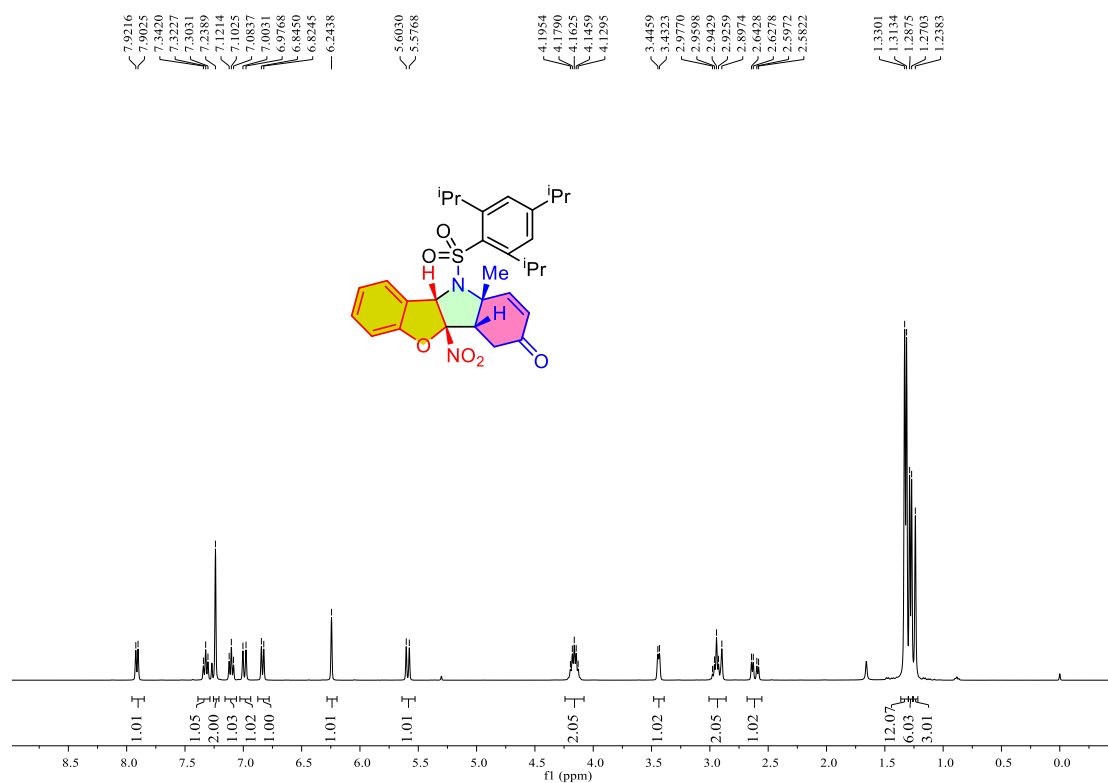


<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ia**

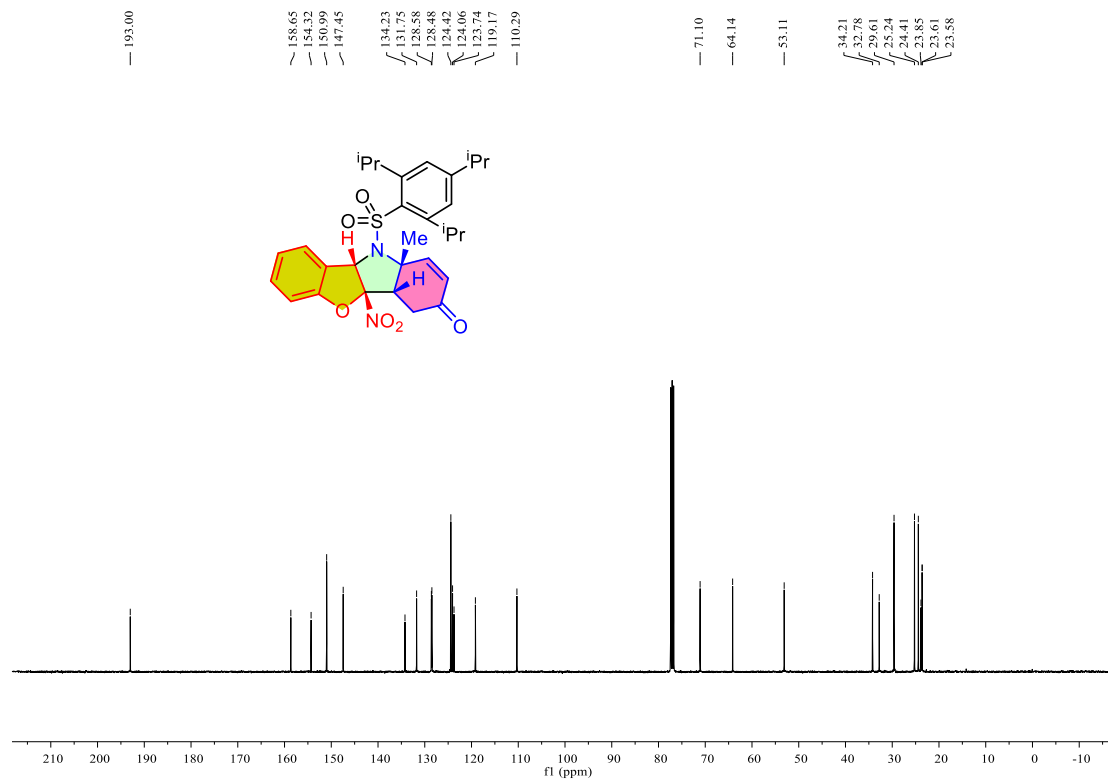




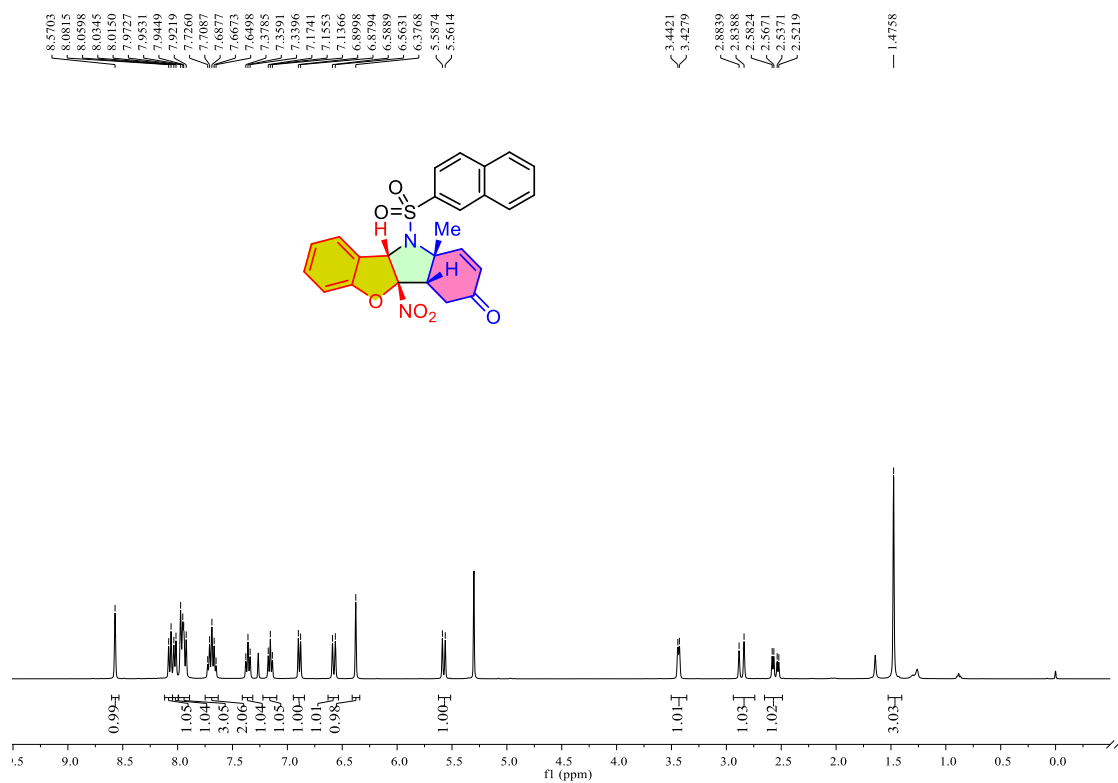
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ja**



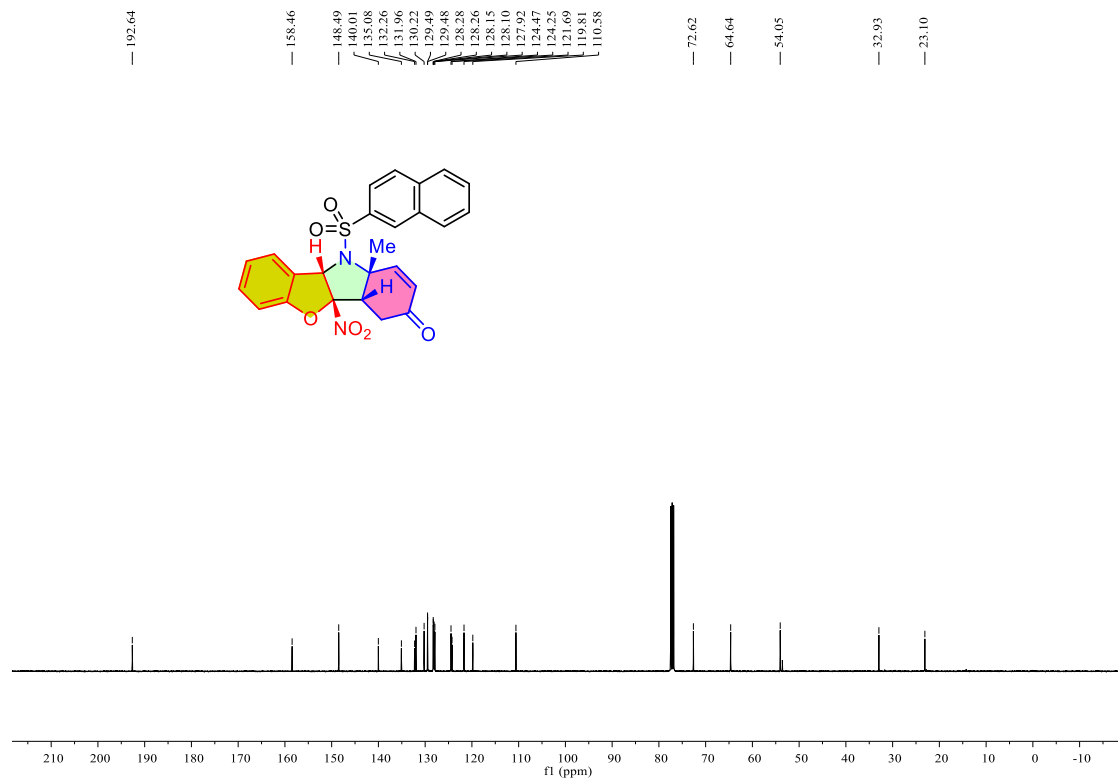
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ja**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ka**



<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ka**



Chemical structure of compound 10: CC1=C(C(=O)N1C2=CC=CC=C2C3=CC=CC=C3O3)C(=O)N1C2=CC=CC=C2C3=CC=CC=C3O3

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound 10. The x-axis represents the chemical shift in ppm, ranging from 0.0 to 8.5. The spectrum shows several multiplets and singlets. Integration values are provided below the baseline.

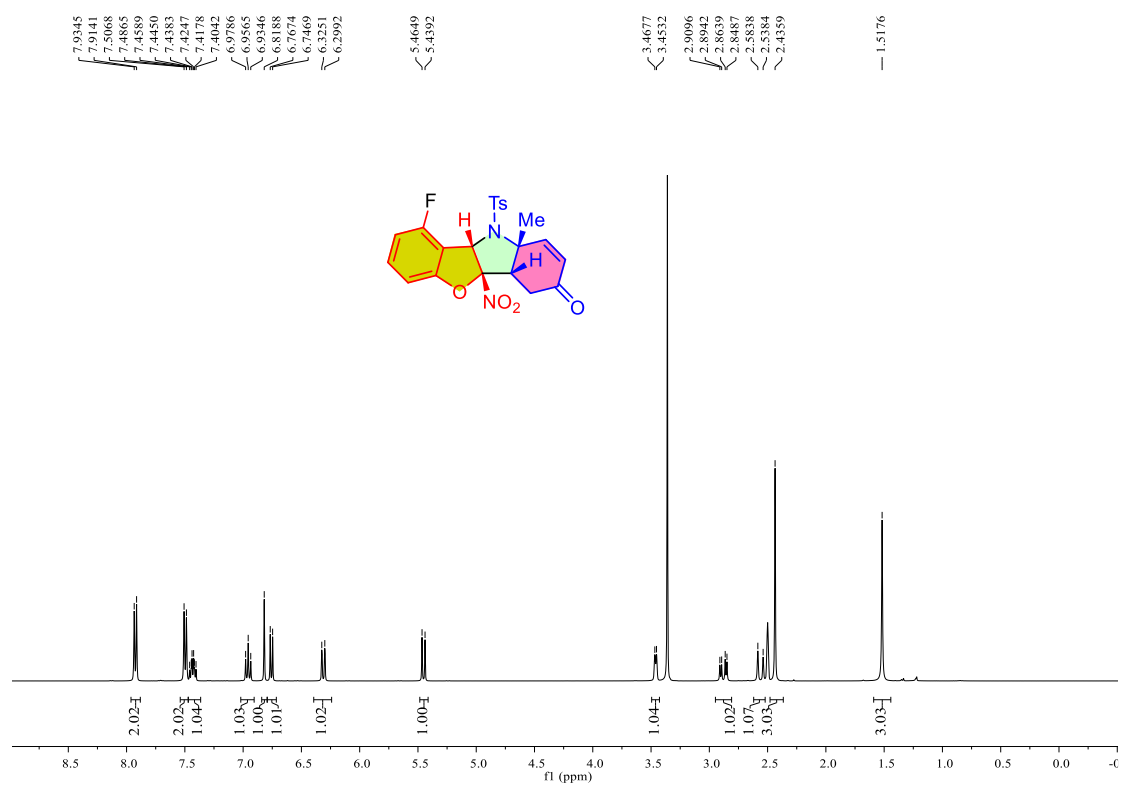
Chemical Shift (ppm)	Integration
7.8428, 7.8237, 7.7680, 7.7615, 7.7067, 7.6945, 7.6855, 7.5489, 7.5388, 7.1610, 7.1497, 7.1279, 7.1090, 6.8887, 6.8682, 6.4615, 6.4356	1.02, 1.02, 1.00, 1.04, 2.07, 1.02, 1.04, 1.00
5.5963, 5.5704	1.03
3.5167, 3.5024	1.03
2.8910, 2.8458, 2.6558, 2.6403, 2.6105, 2.5951	1.05
1.7112	3.02

Chemical structure of the compound is shown above the spectrum. The structure is a complex molecule featuring a benzene ring, a furan ring, a pyridine ring, and a thienothiopyran ring system. The structure is color-coded: the benzene ring is yellow, the furan ring is orange, the pyridine ring is green, and the thienothiopyran ring is blue. The structure is labeled with  $\text{H}$ ,  $\text{Me}$ ,  $\text{NO}_2$ , and  $\text{S}$ .

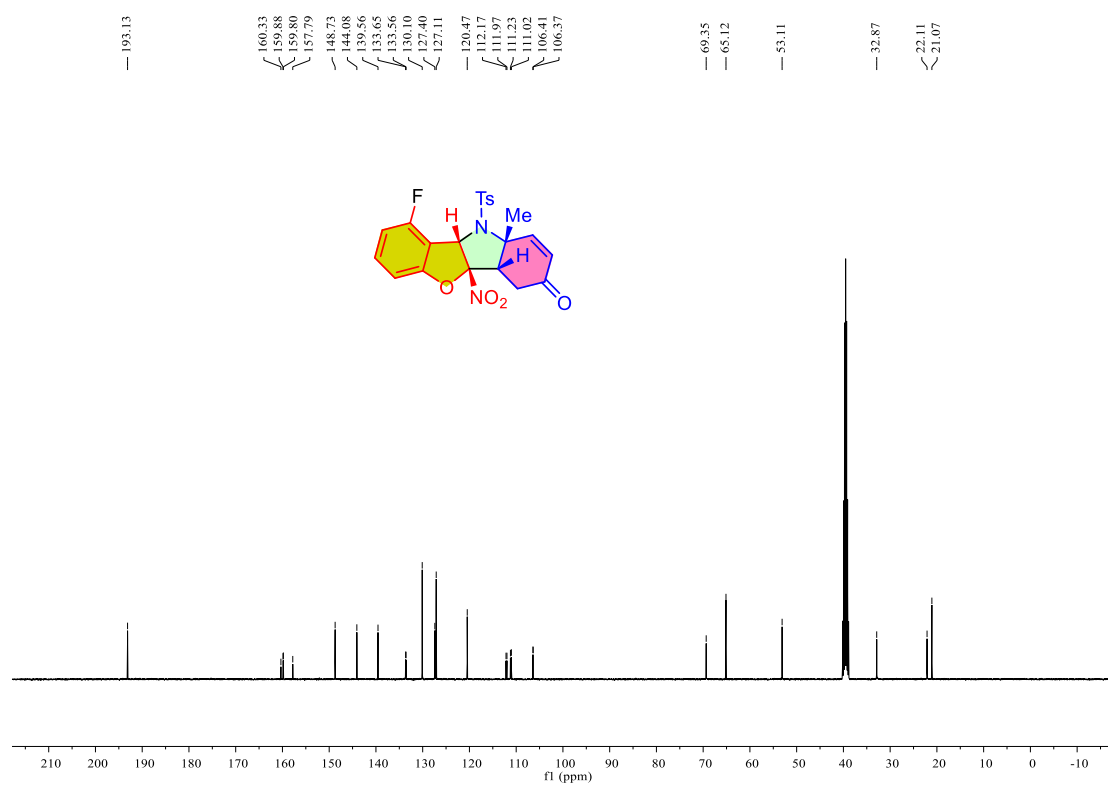
Chemical shift values (ppm) are listed above the spectrum:

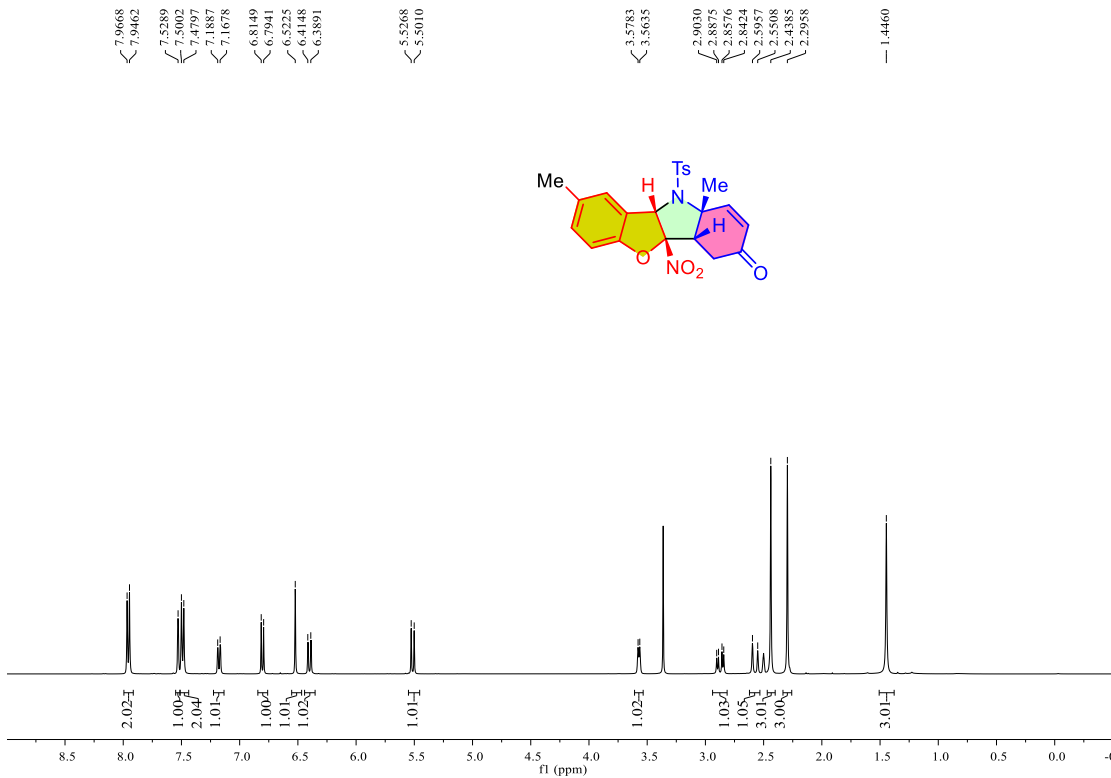
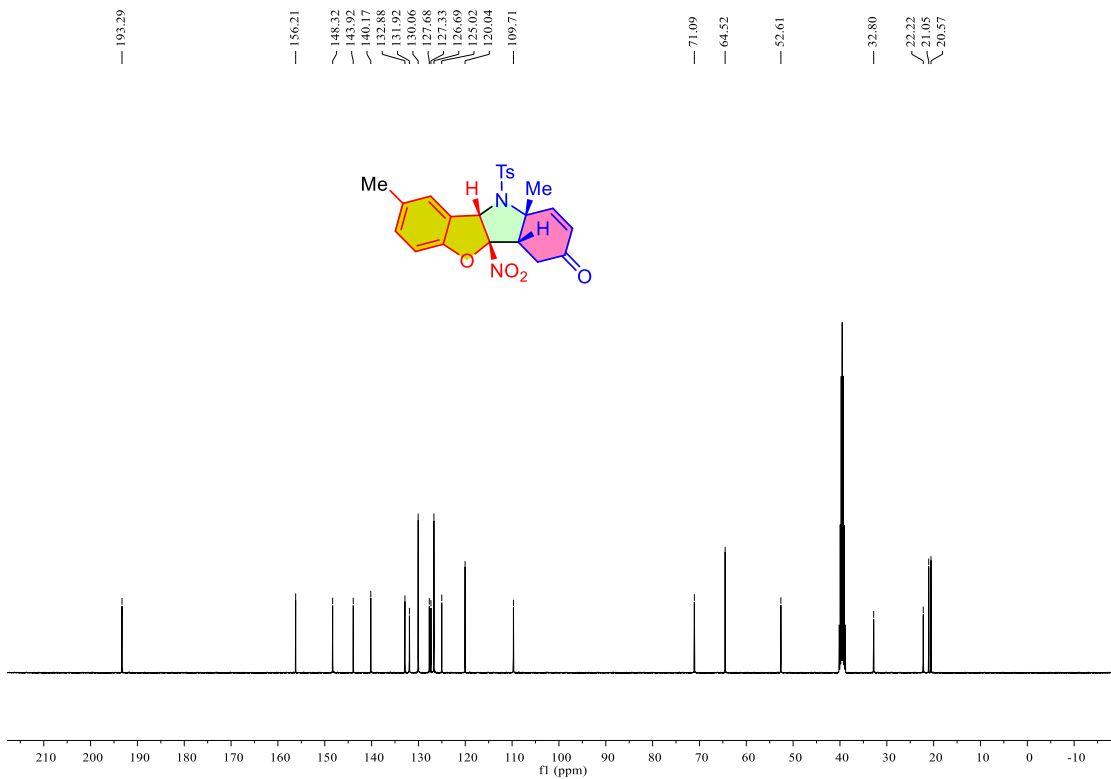
- 192.55
- 158.41
- 148.26
- 143.58
- 132.81
- 132.66
- 131.96
- 128.11
- 127.77
- 127.59
- 124.35
- 123.86
- 119.75
- 110.58
- 71.59
- 65.33
- 53.40
- 32.90
- 22.73

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

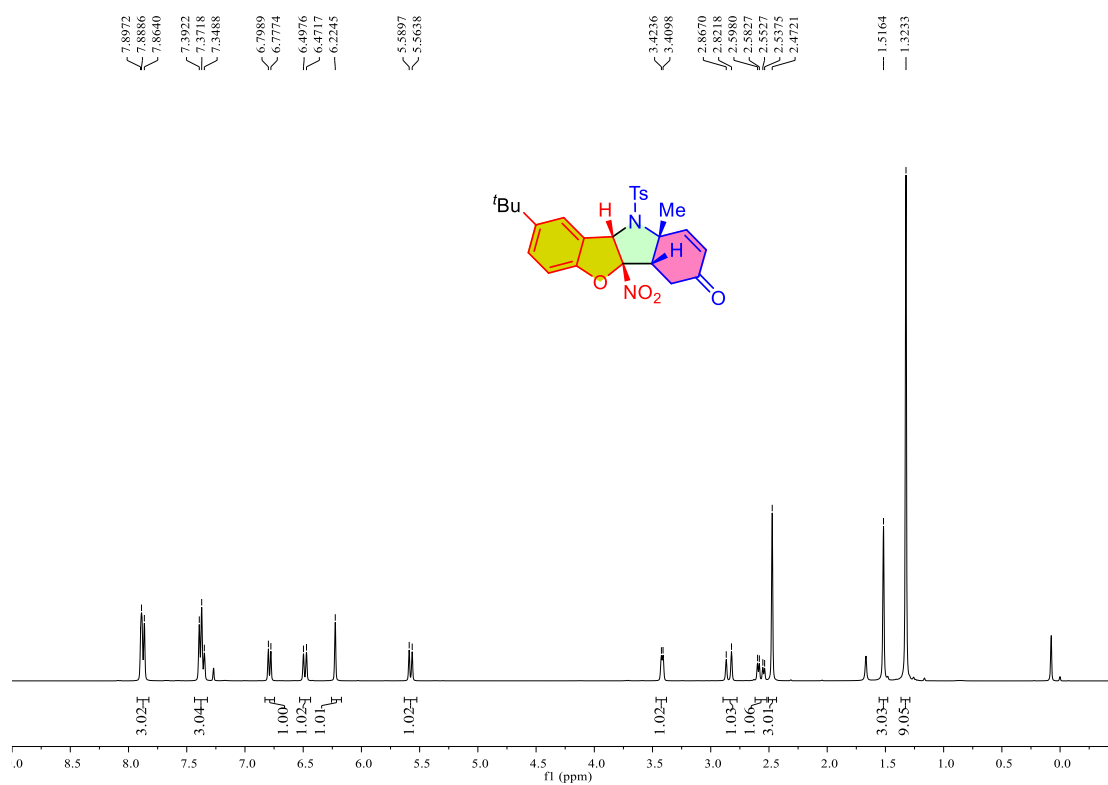


<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3ab**

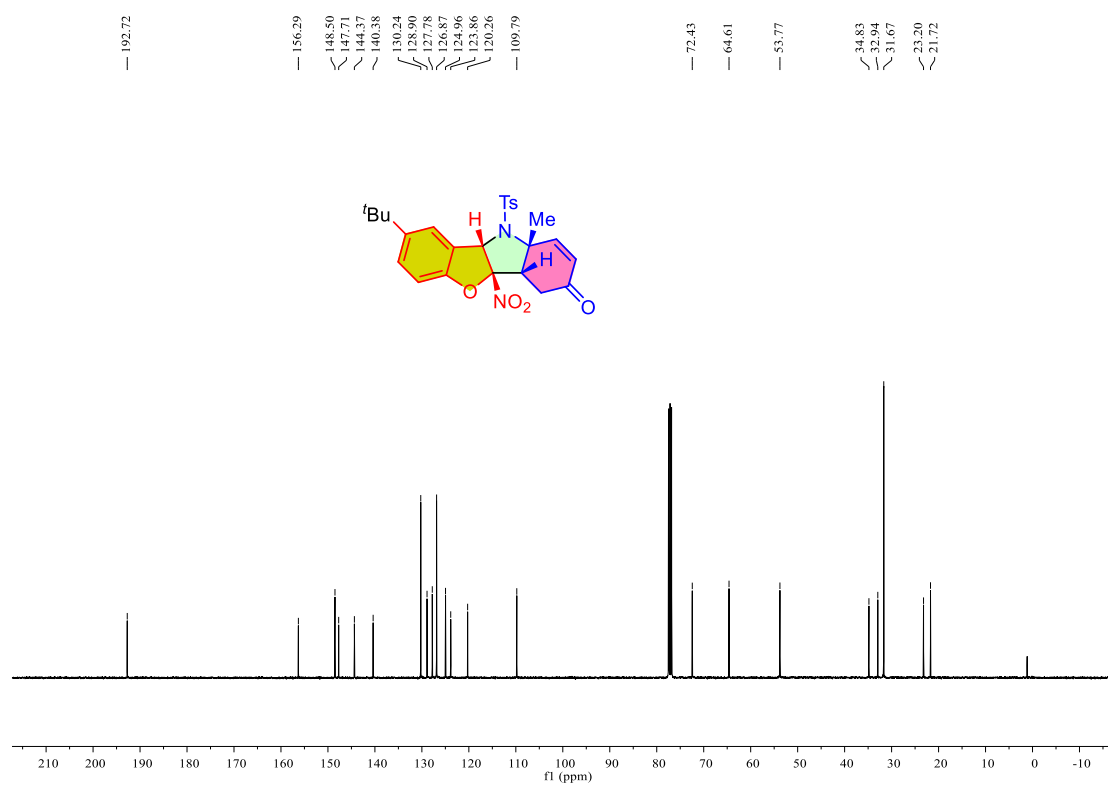


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ac** $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3ac**

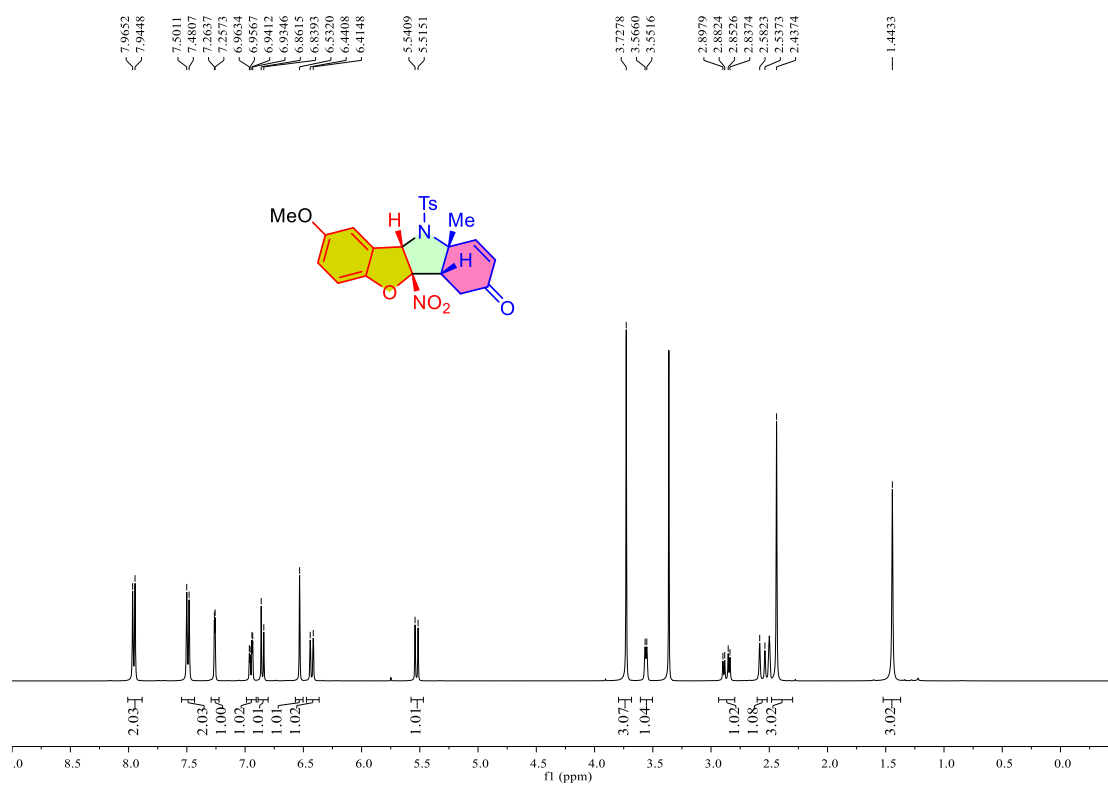
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ad**



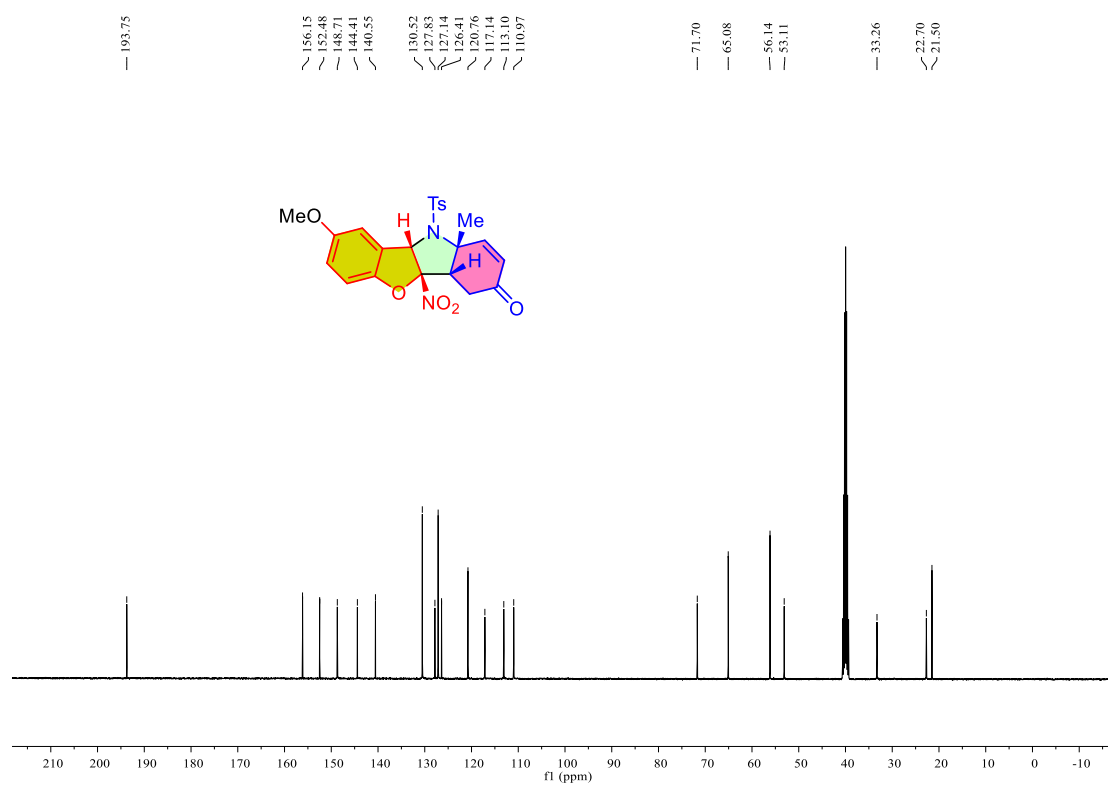
<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ad**



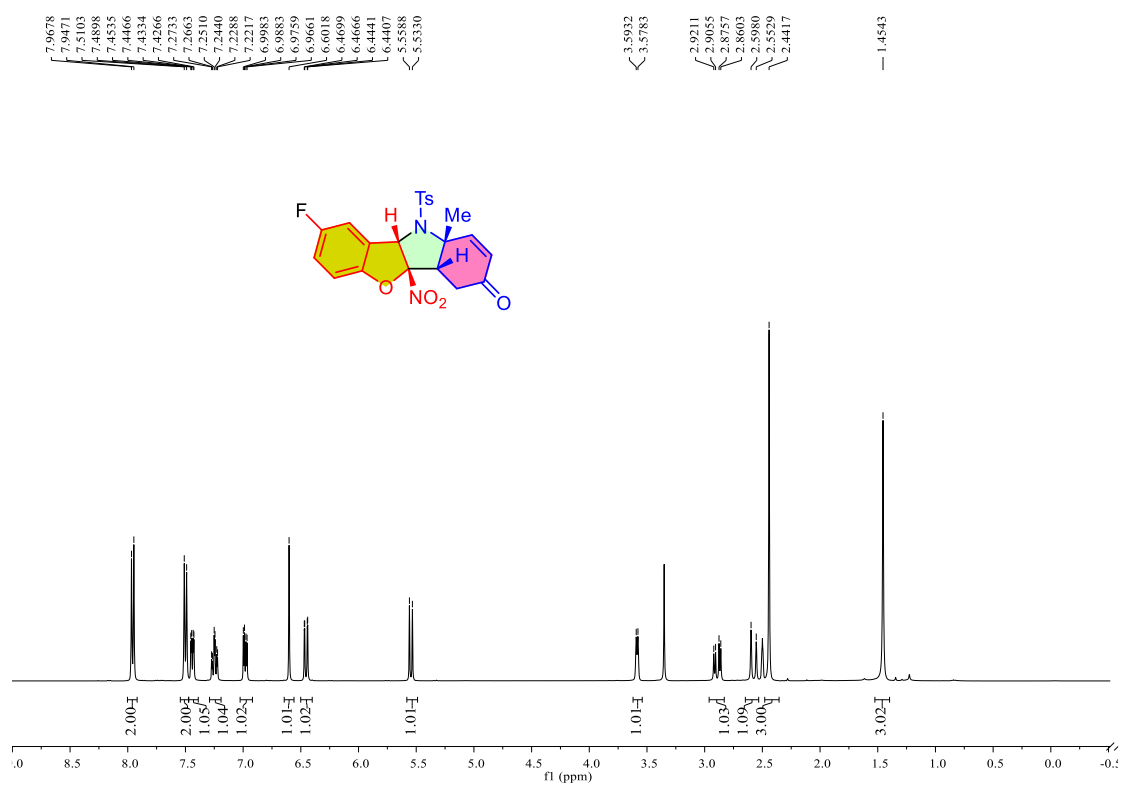
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ae**



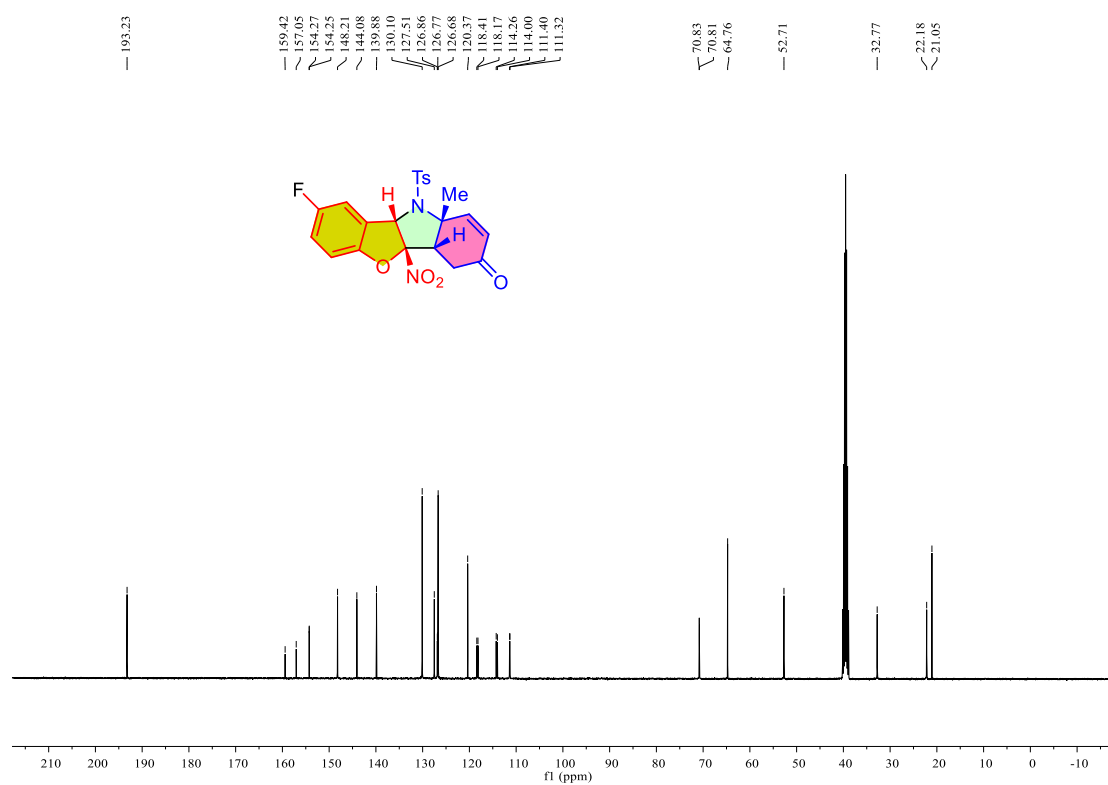
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ae**



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

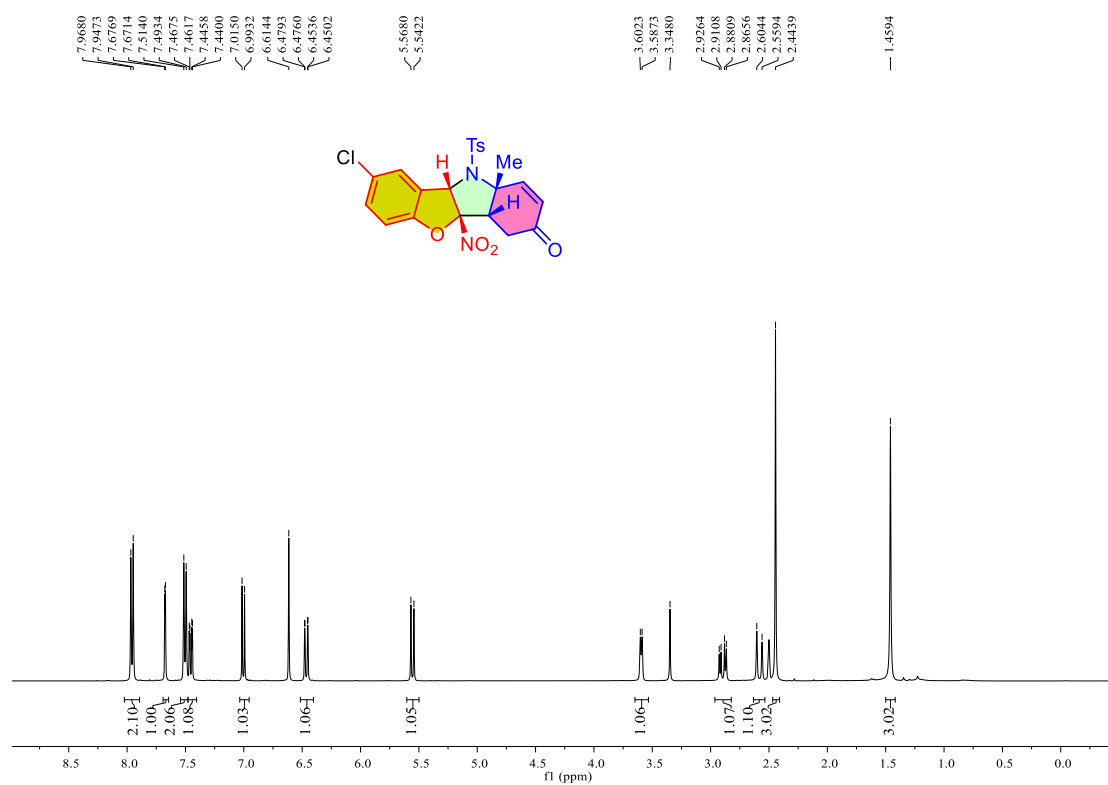


<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3af**

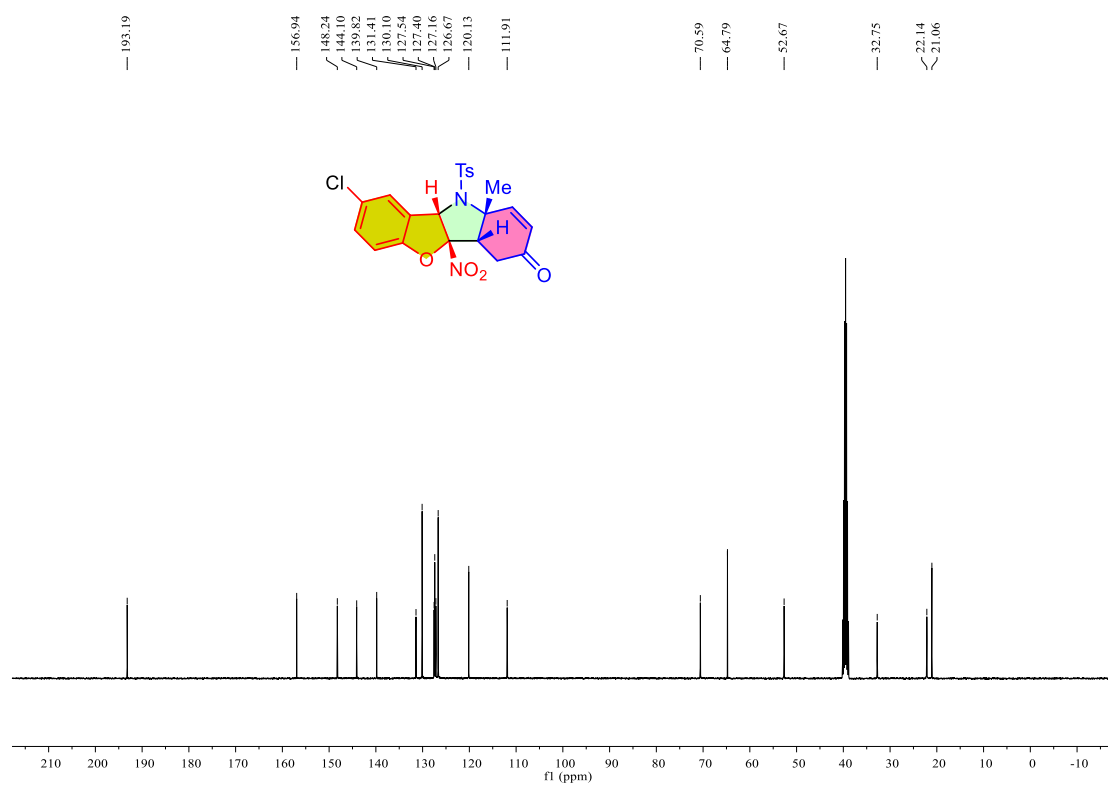




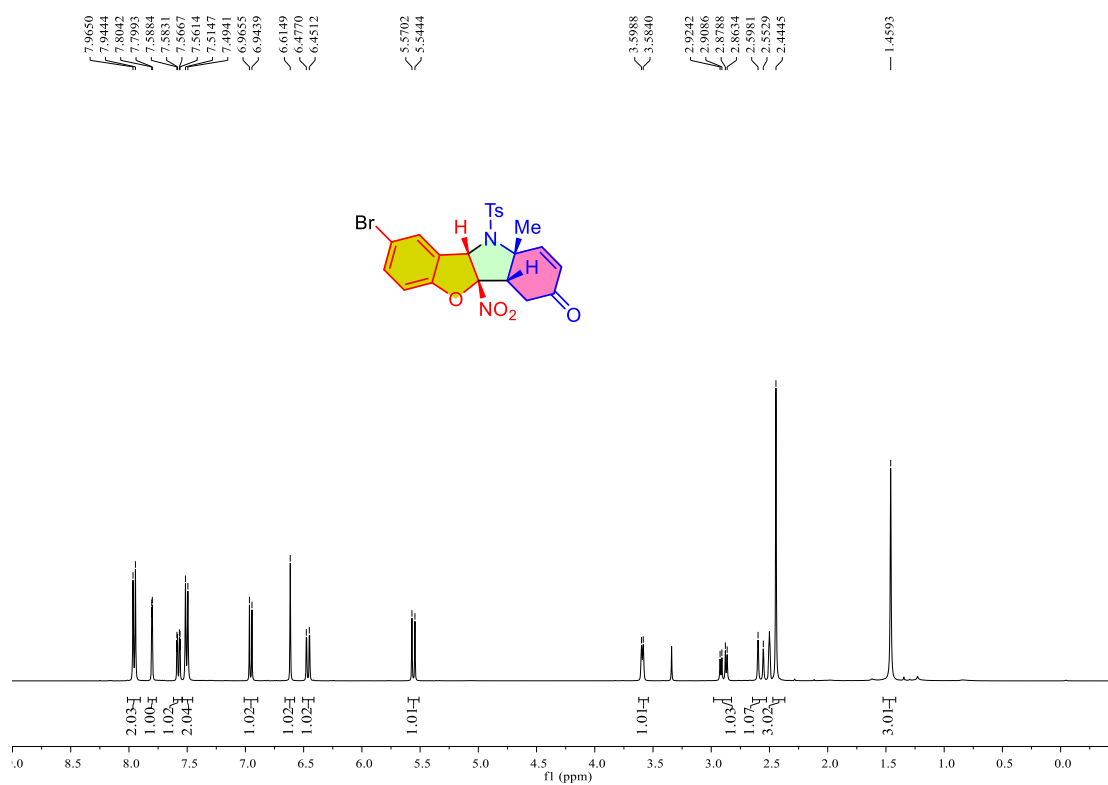
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ag**



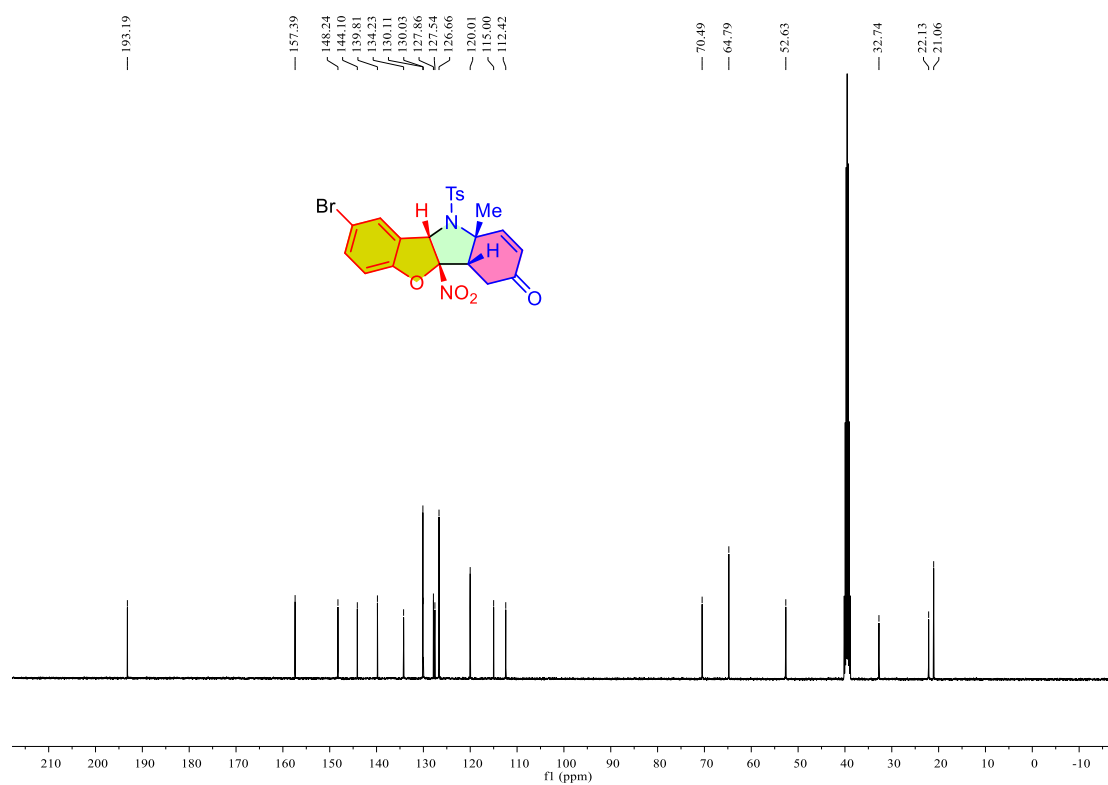
<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ag**



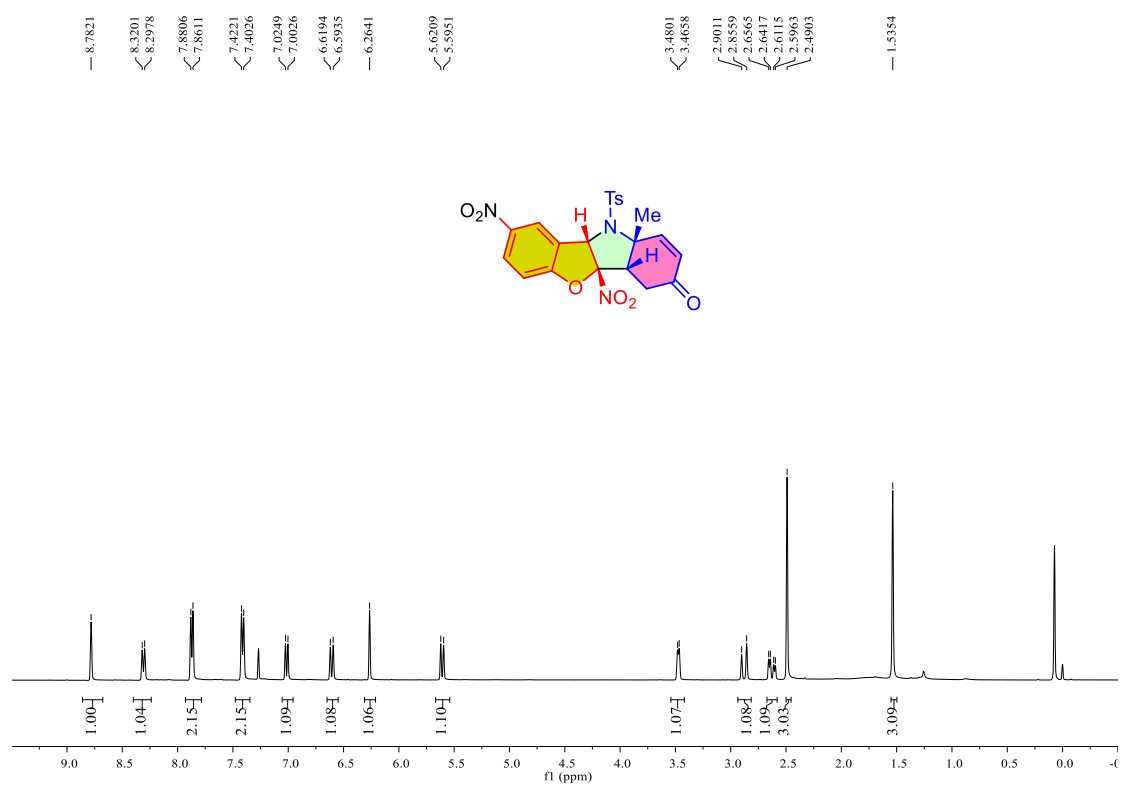
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **3ah**



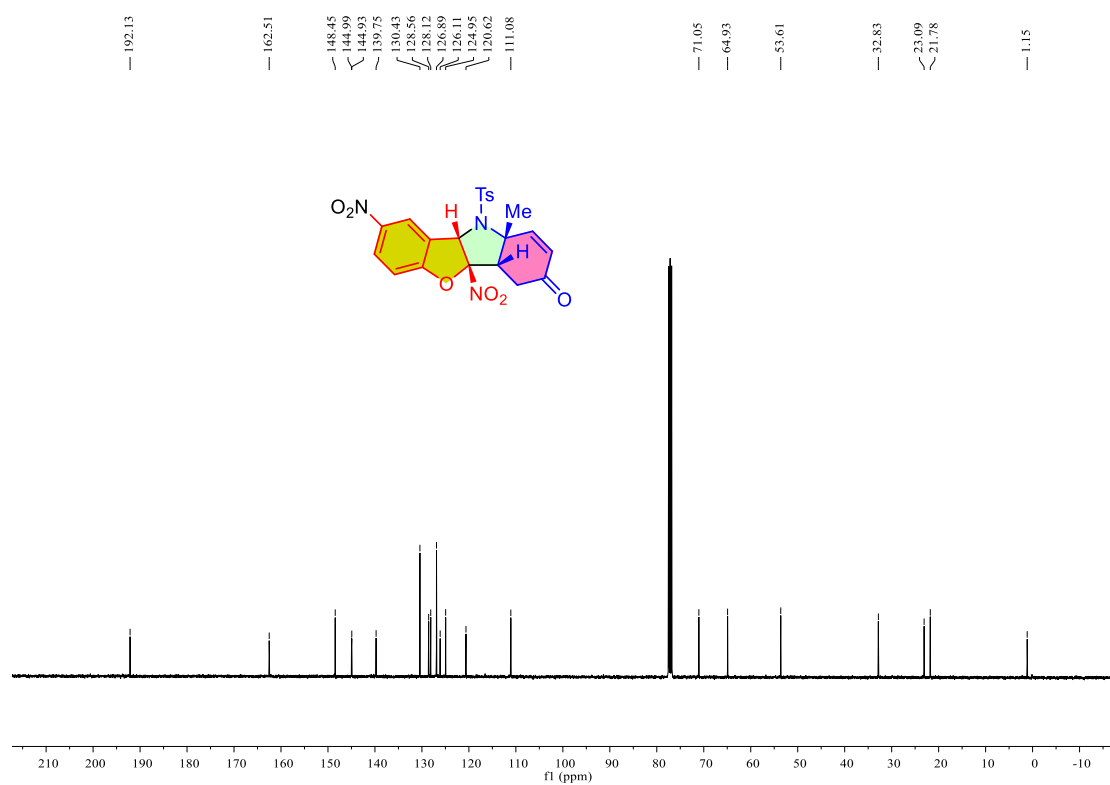
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3ah**



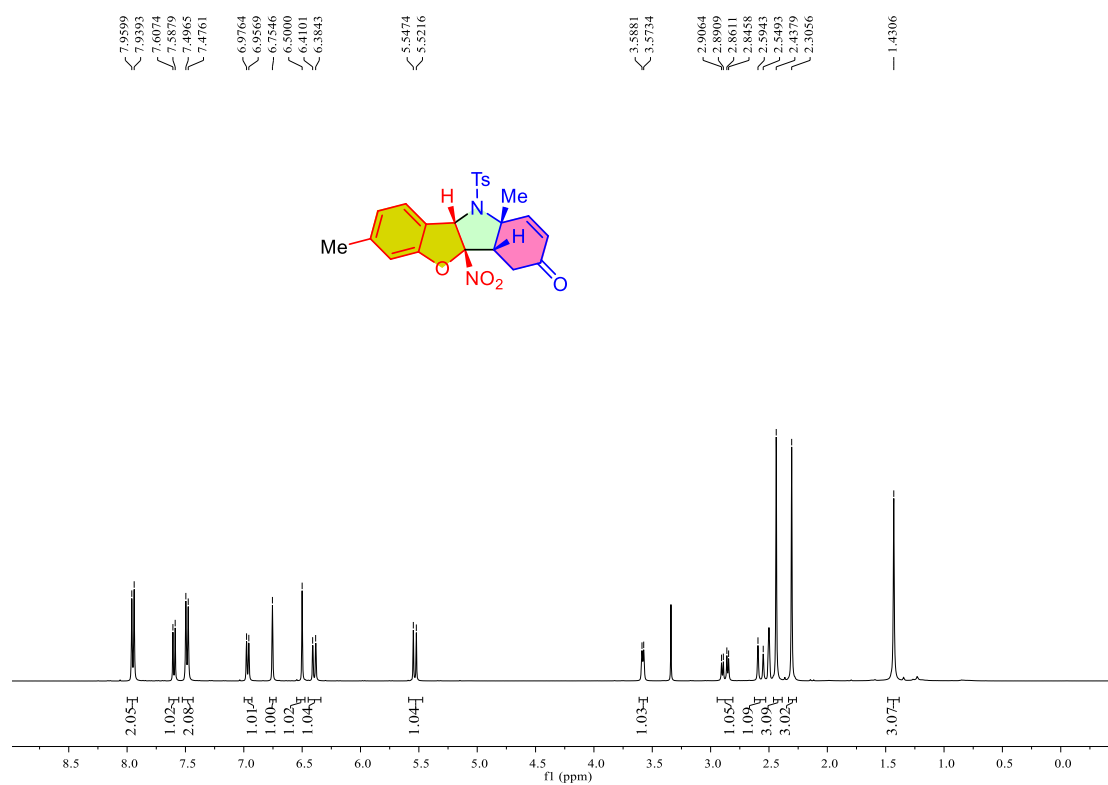
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ai**



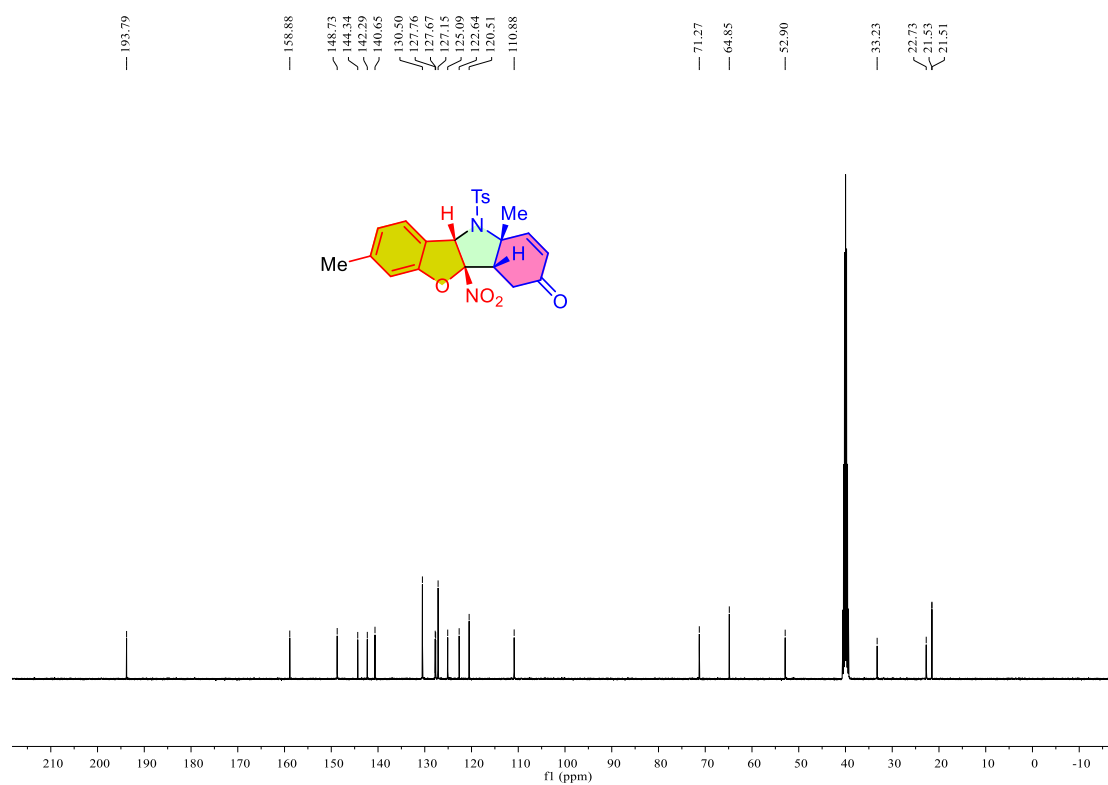
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ai**



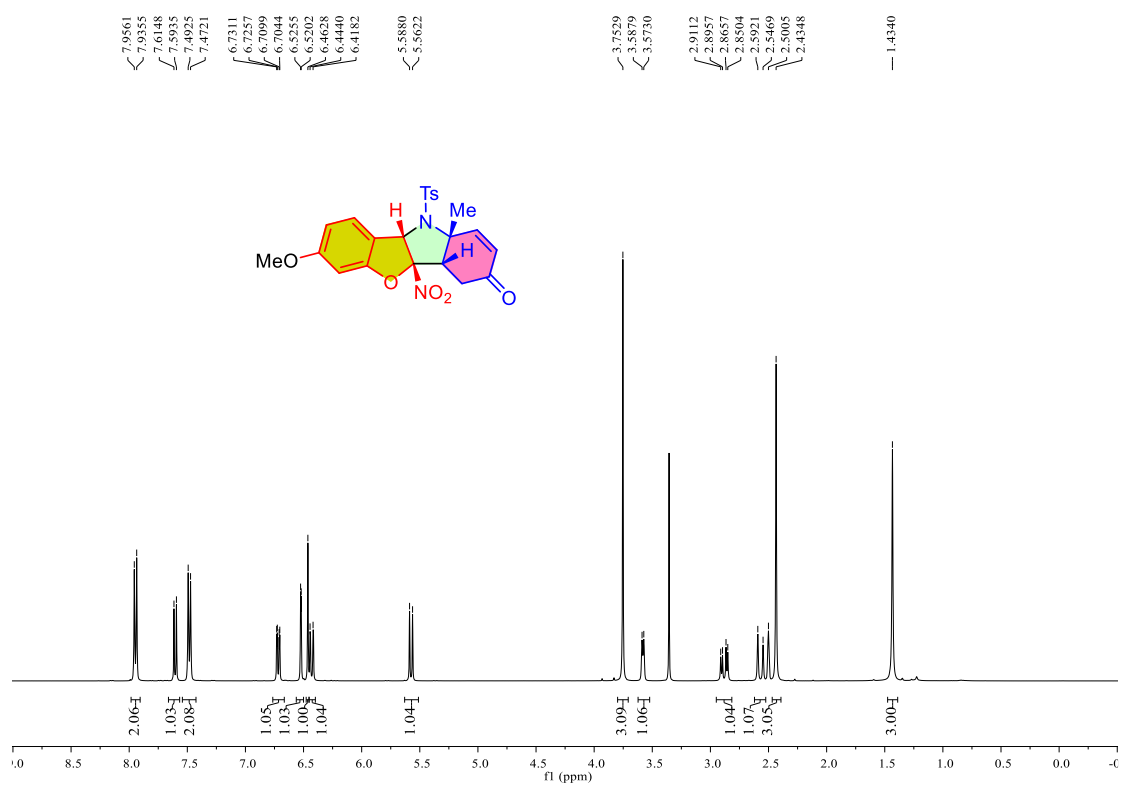
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **3aj**



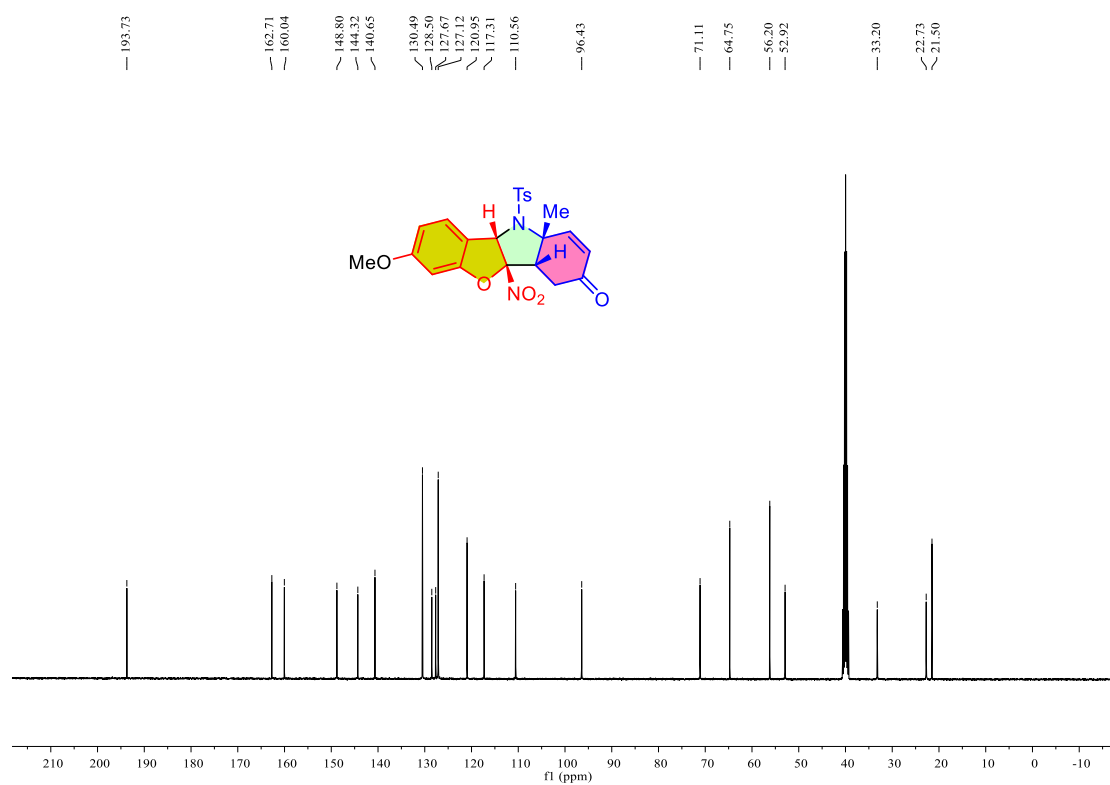
<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3aj**



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



<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3ak**



**Chemical structure of compound 10:** Cc1c(C(=O)O)c2c(c1)cc(F)cc2N(C(=O)O)C(=O)O

**<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>):**

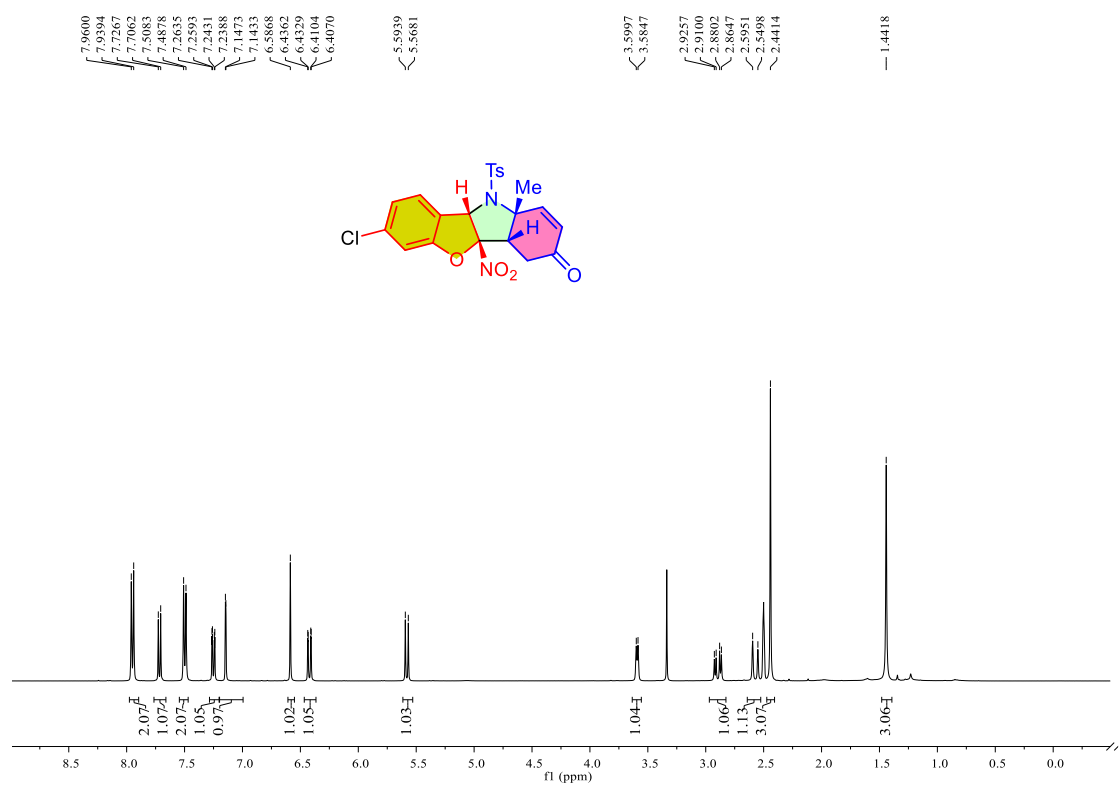
Chemical Shift (ppm)	Integration
1.4454	3.02
2.497	3.00
2.603	1.03
2.881	1.00
3.588	1.00
5.563	1.00
6.442	1.00
6.940	1.00
7.015	0.99
7.032	1.01
7.334	1.99
7.739	1.01
7.942	2.00

Chemical structure of compound 10 is shown above the  $^1\text{H}$  NMR spectrum. The structure is a tricyclic system with a fluorinated benzene ring, a furan ring, and a pyrrolidine ring. The pyrrolidine ring is substituted with a methyl group (Me), a tosyl group (Ts), and a nitro group ( $\text{NO}_2$ ). The furan ring is substituted with a fluorine atom (F). The benzene ring is substituted with a fluorine atom (F).

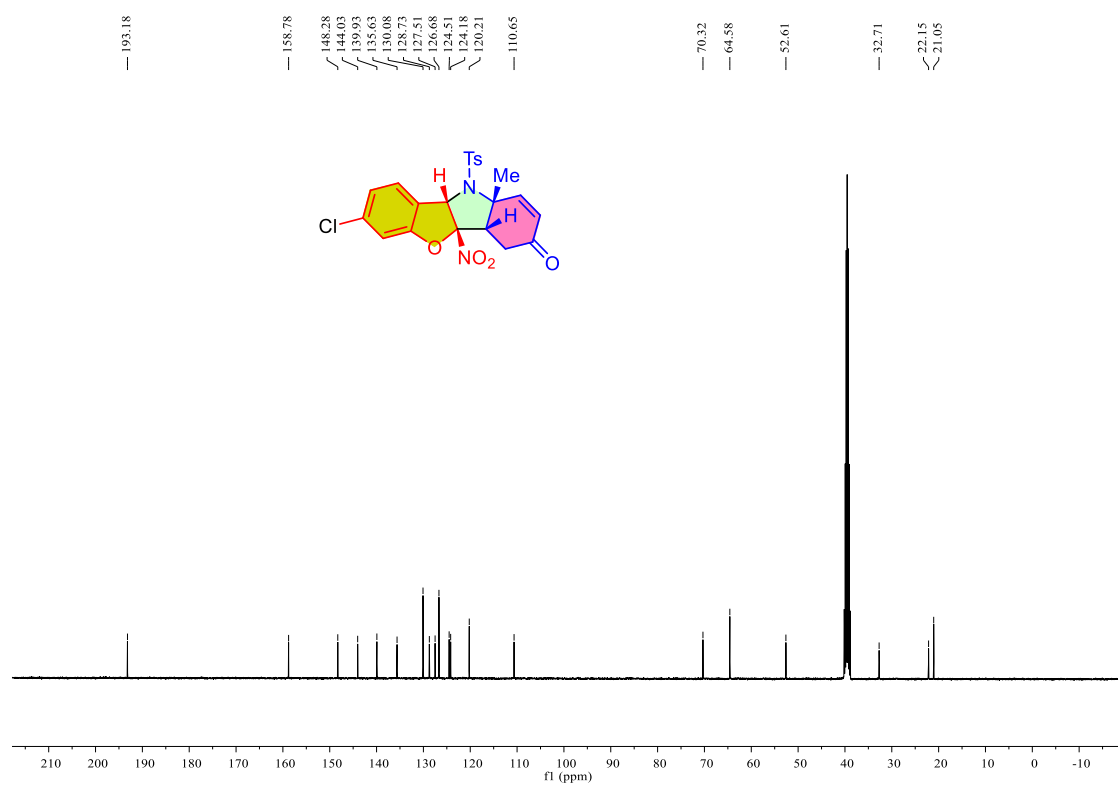
$^{13}\text{C}$  NMR peaks (ppm): 193.17, 165.22, 162.76, 159.17, 159.03, 148.33, 144.00, 140.01, 130.08, 128.85, 128.44, 127.40, 126.68, 121.55, 121.52, 120.55, 111.05, 110.82, 98.87, 98.59, 70.28, 64.51, 52.64, 32.71, 22.17, 21.05.

$^1\text{H}$  NMR peaks (ppm): 7.8, 7.6, 7.4, 7.2, 7.0, 6.8, 6.6, 6.4, 6.2, 6.0, 5.8, 5.6, 5.4, 5.2, 5.0, 4.8, 4.6, 4.4, 4.2, 4.0, 3.8, 3.6, 3.4, 3.2, 3.0, 2.8, 2.6, 2.4, 2.2, 2.0, 1.8, 1.6, 1.4, 1.2, 1.0, 0.8, 0.6, 0.4, 0.2, 0.0.

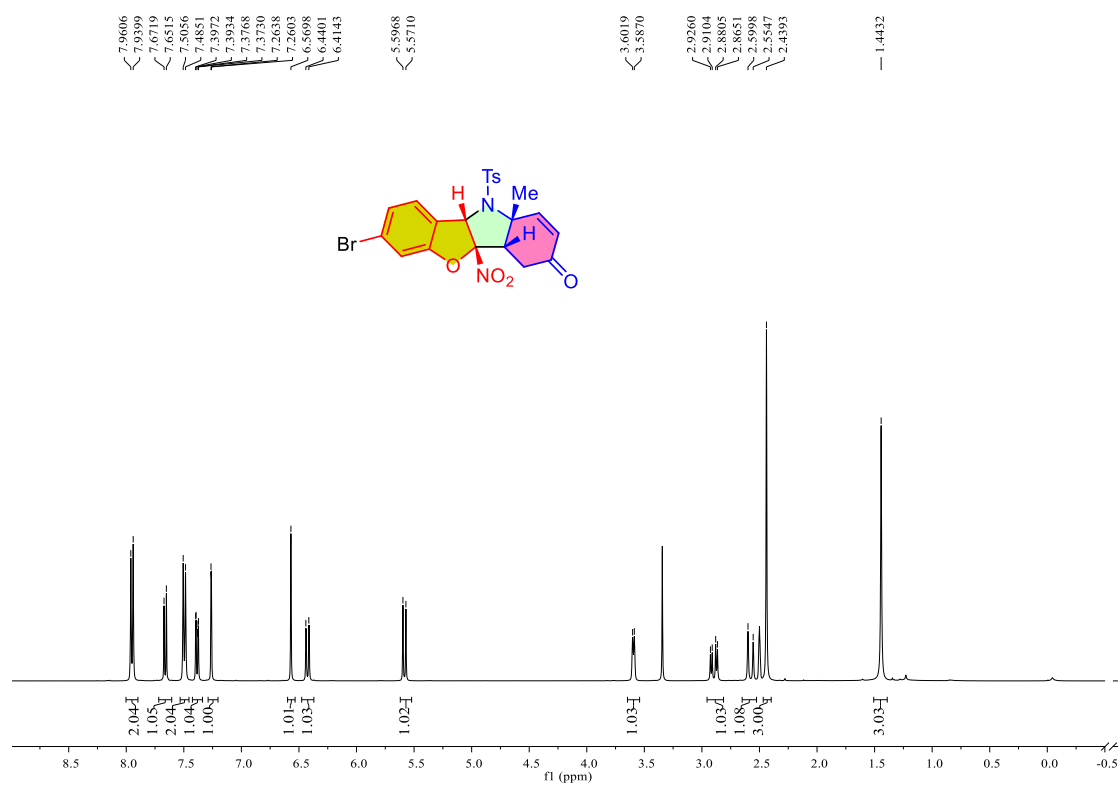
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **3am**



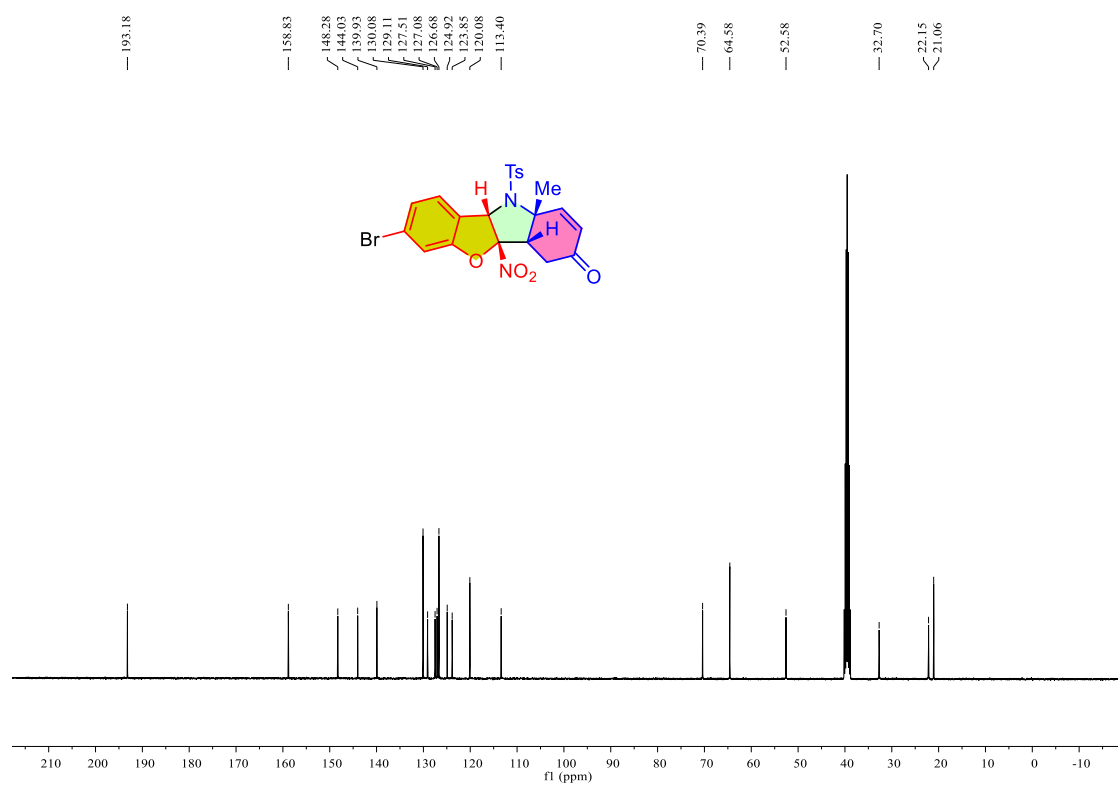
<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3am**



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

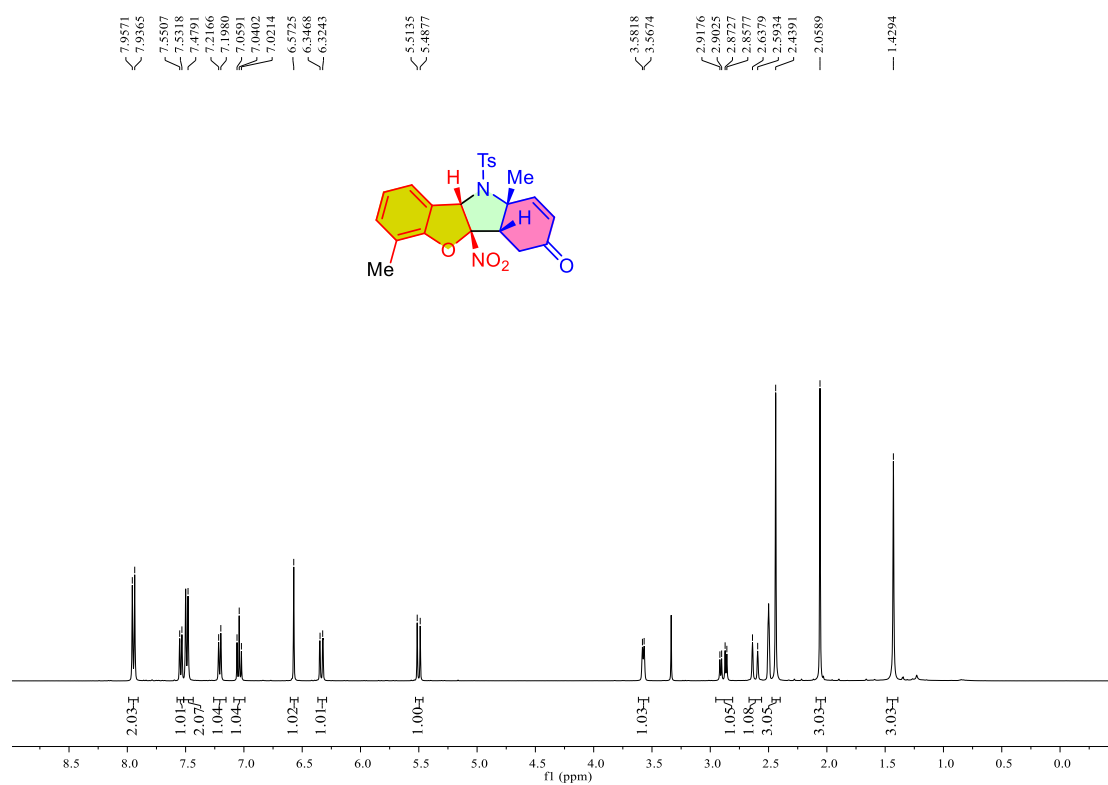


<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3an**

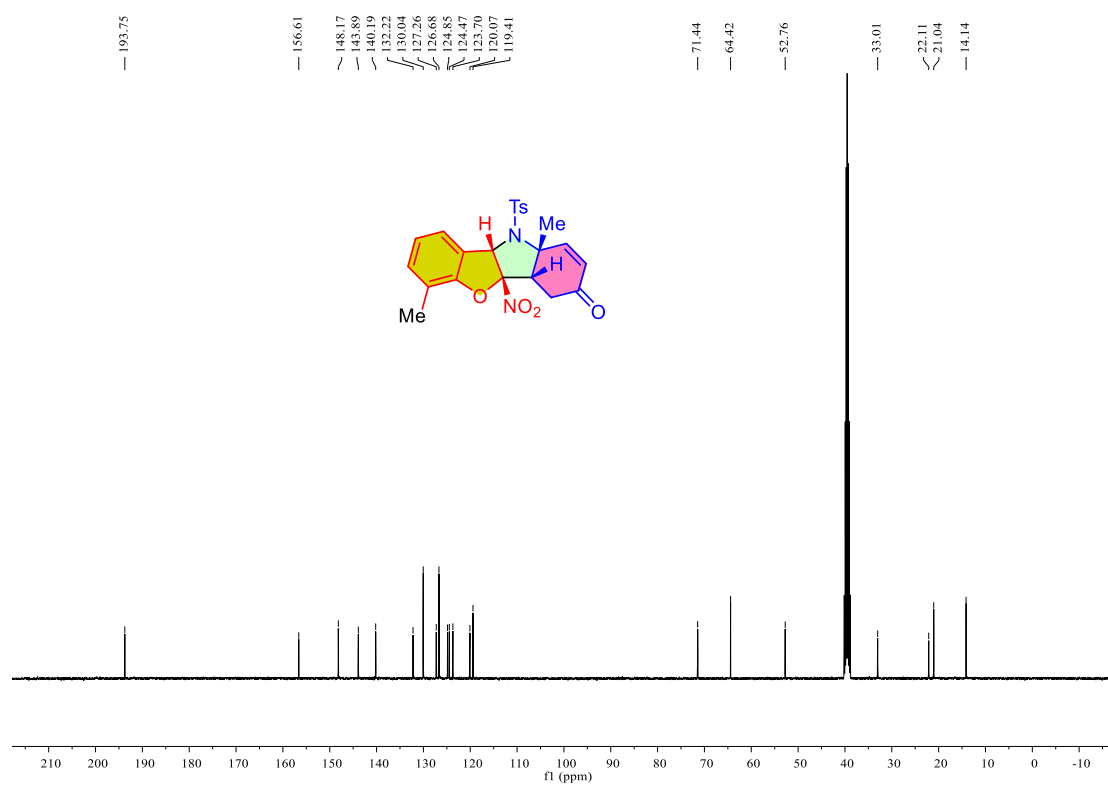




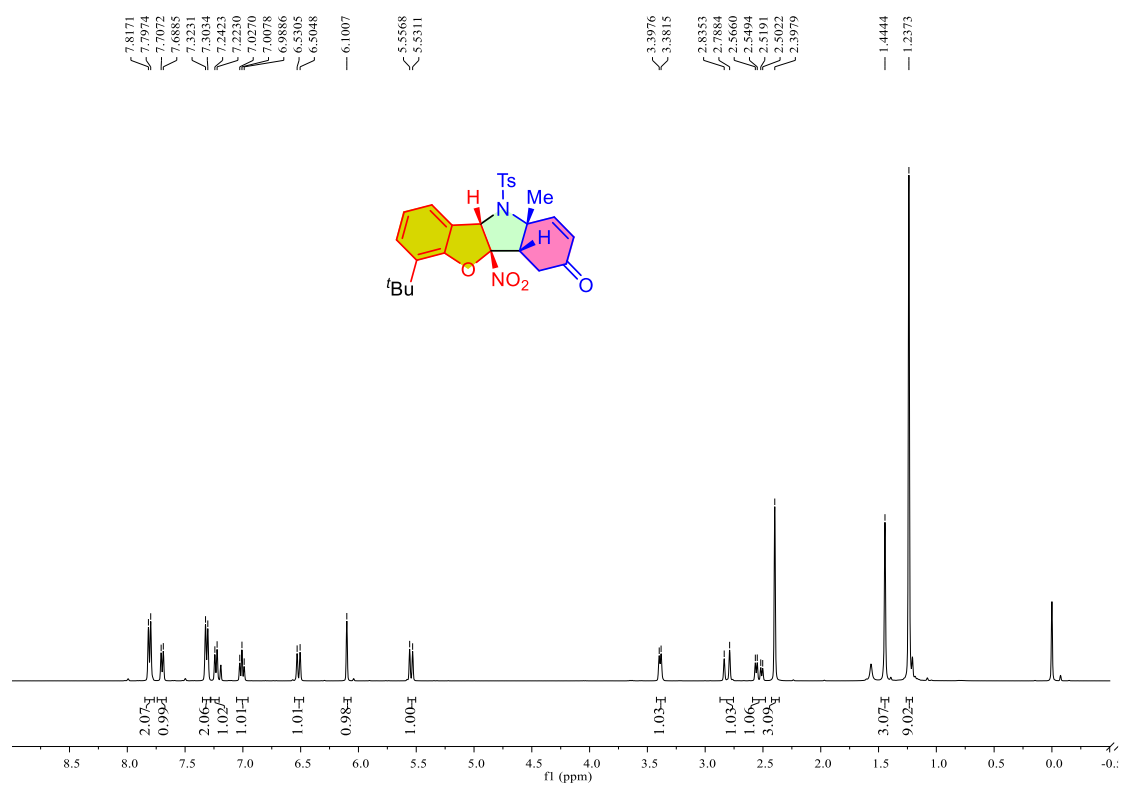
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **3ao**



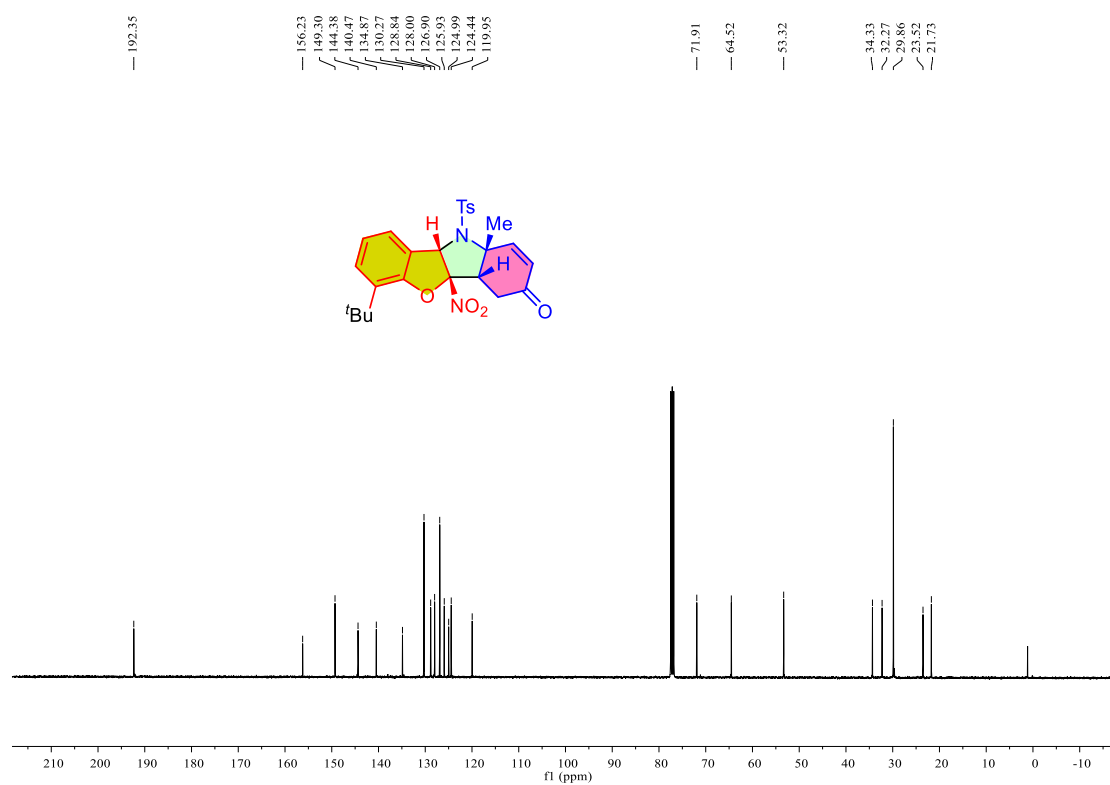
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3ao**



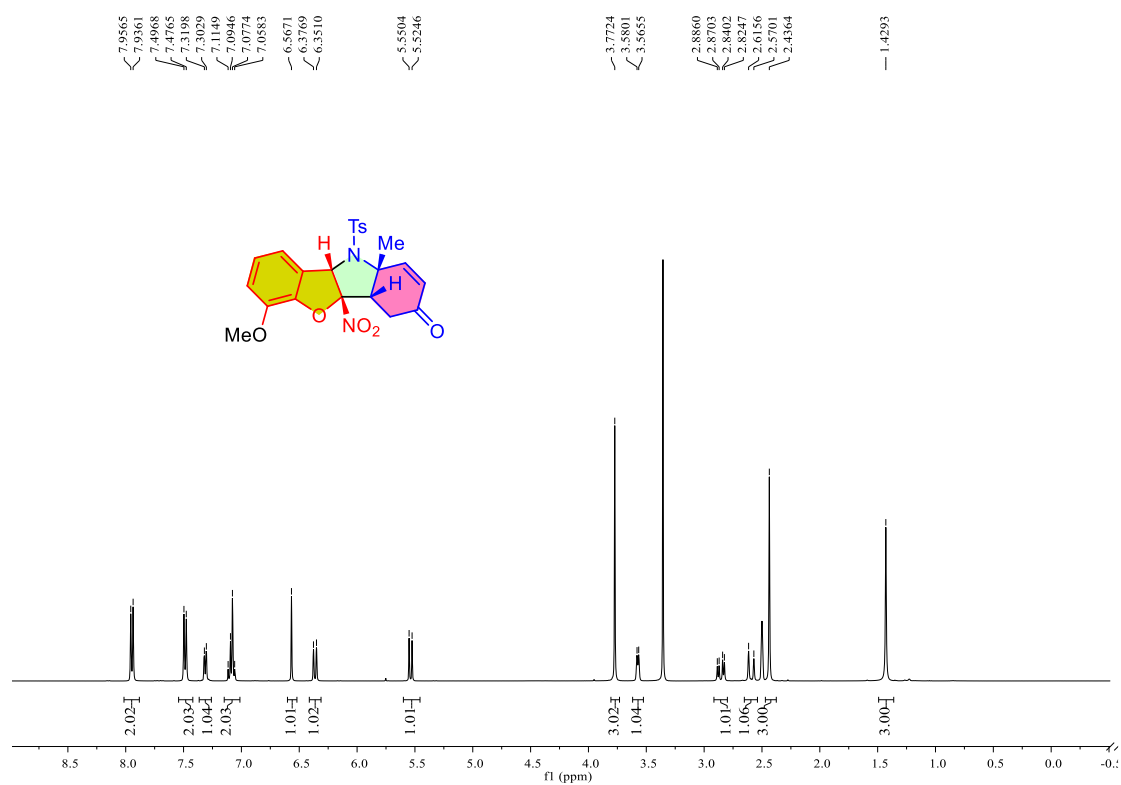
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ap**



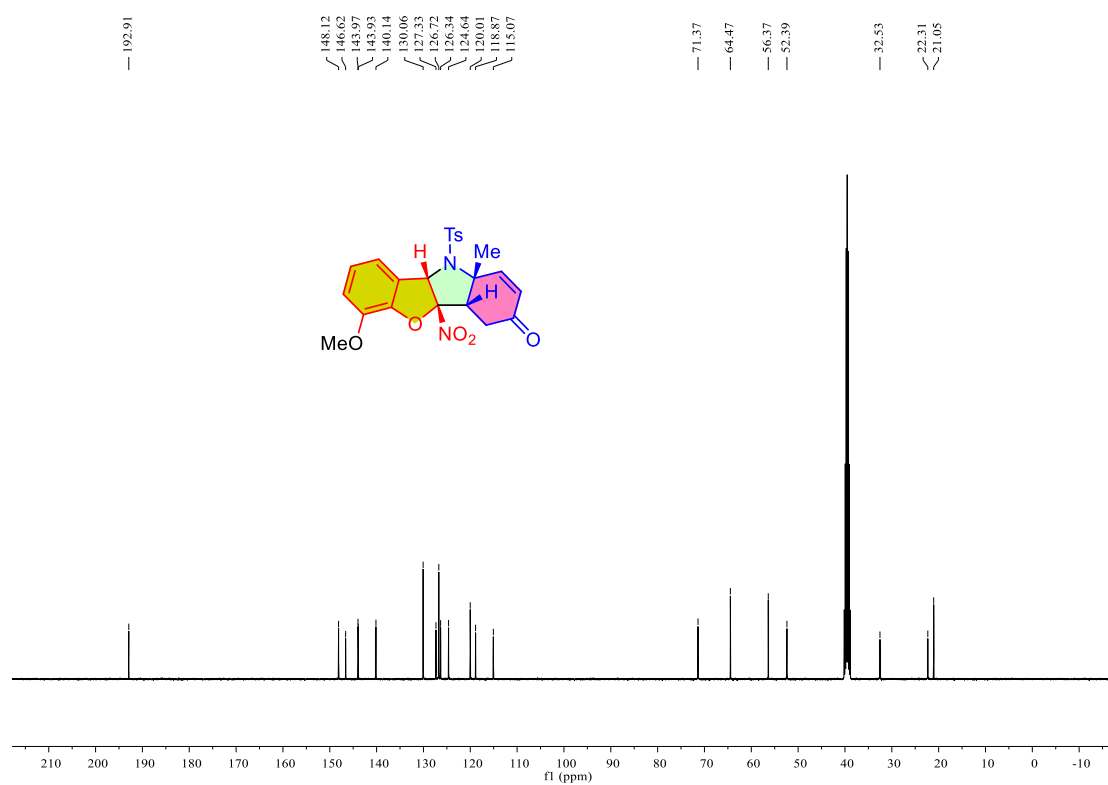
<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ap**



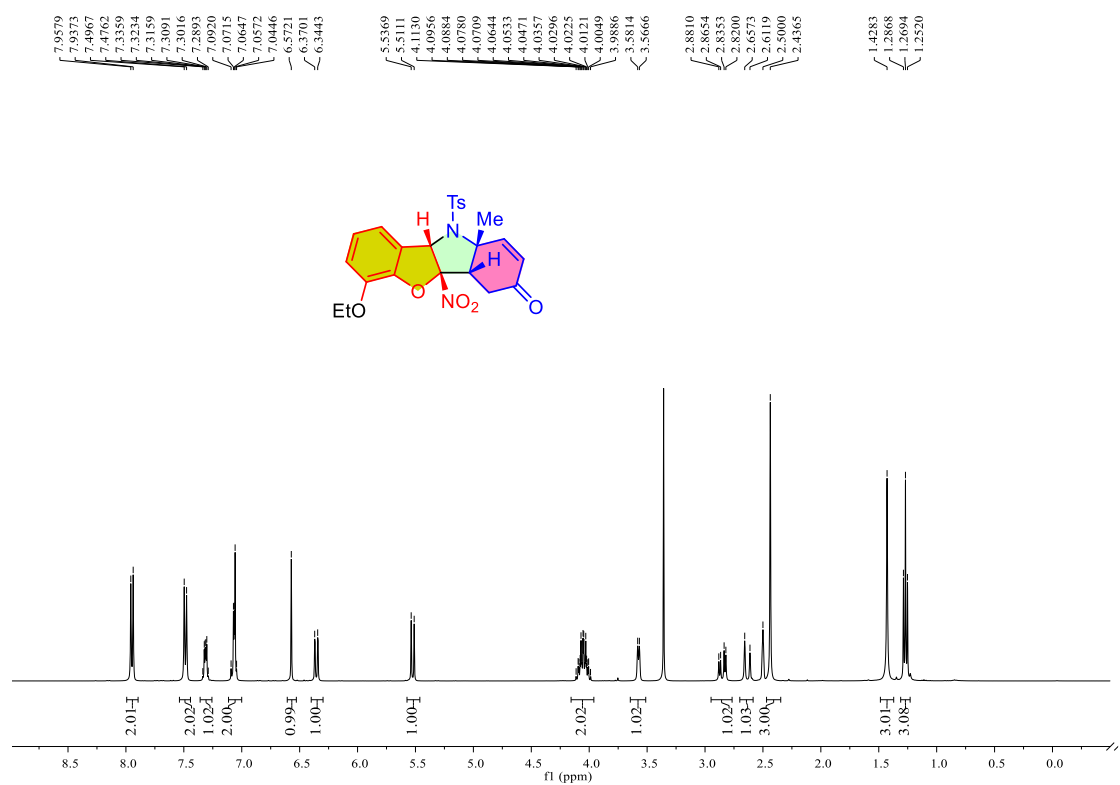
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **3aq**



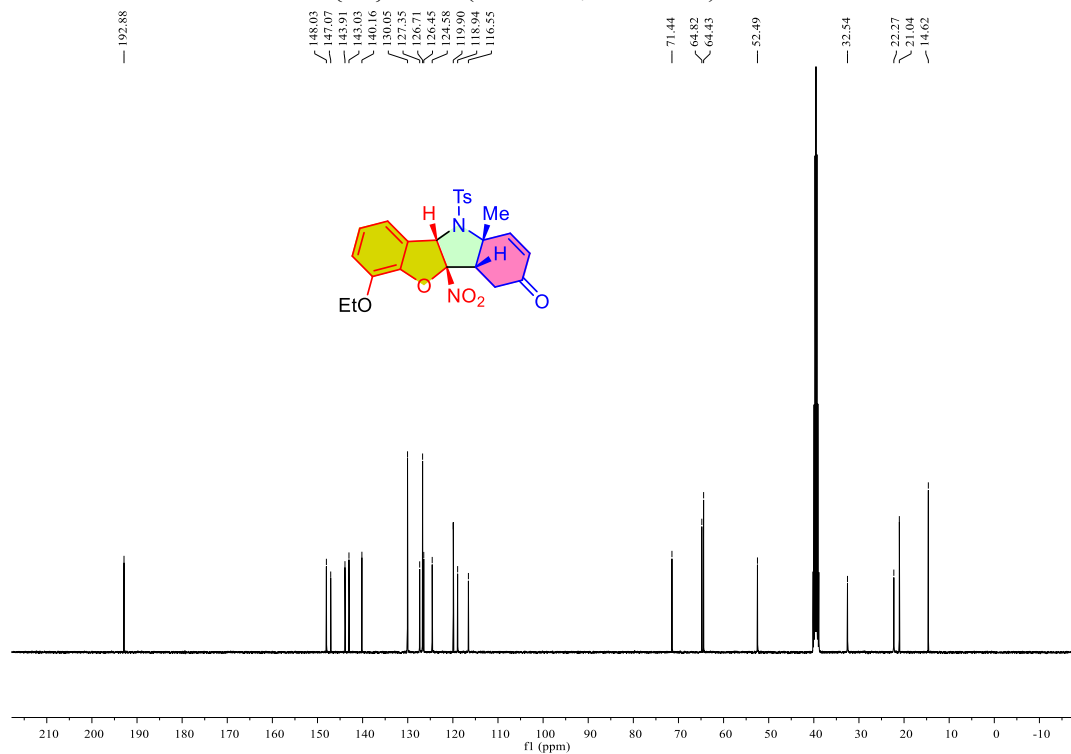
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3aq**



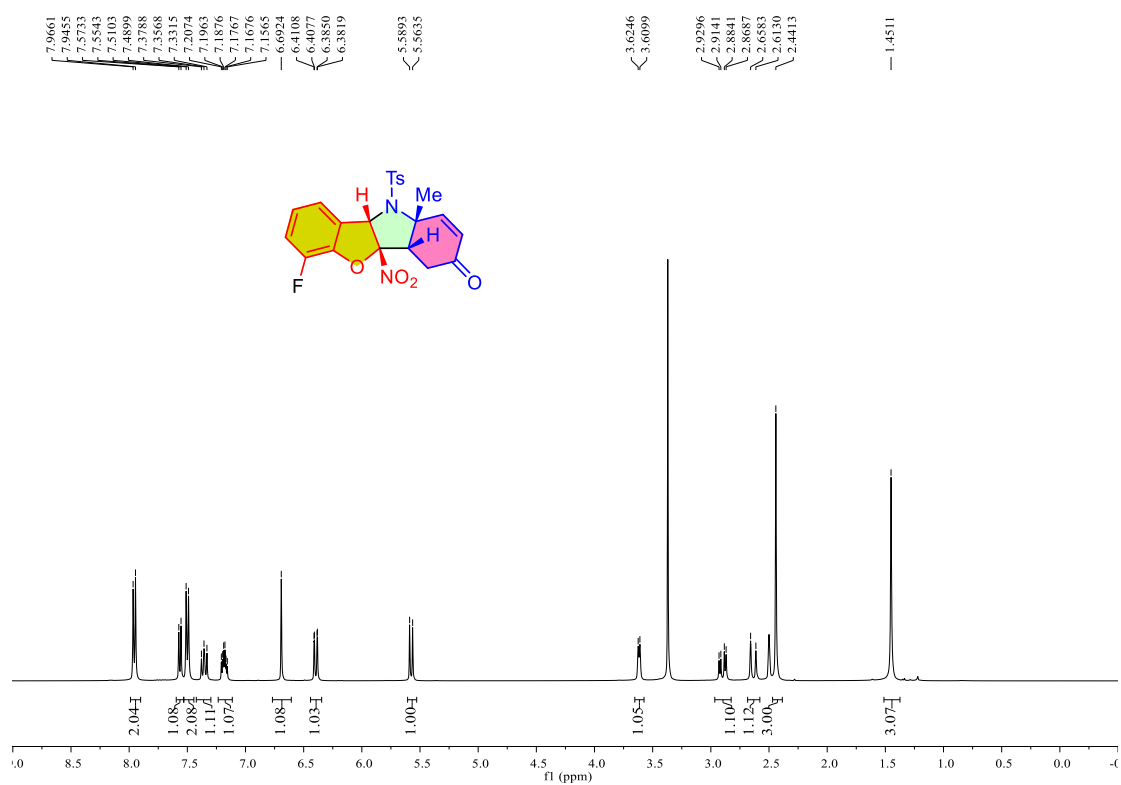
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **3ar**



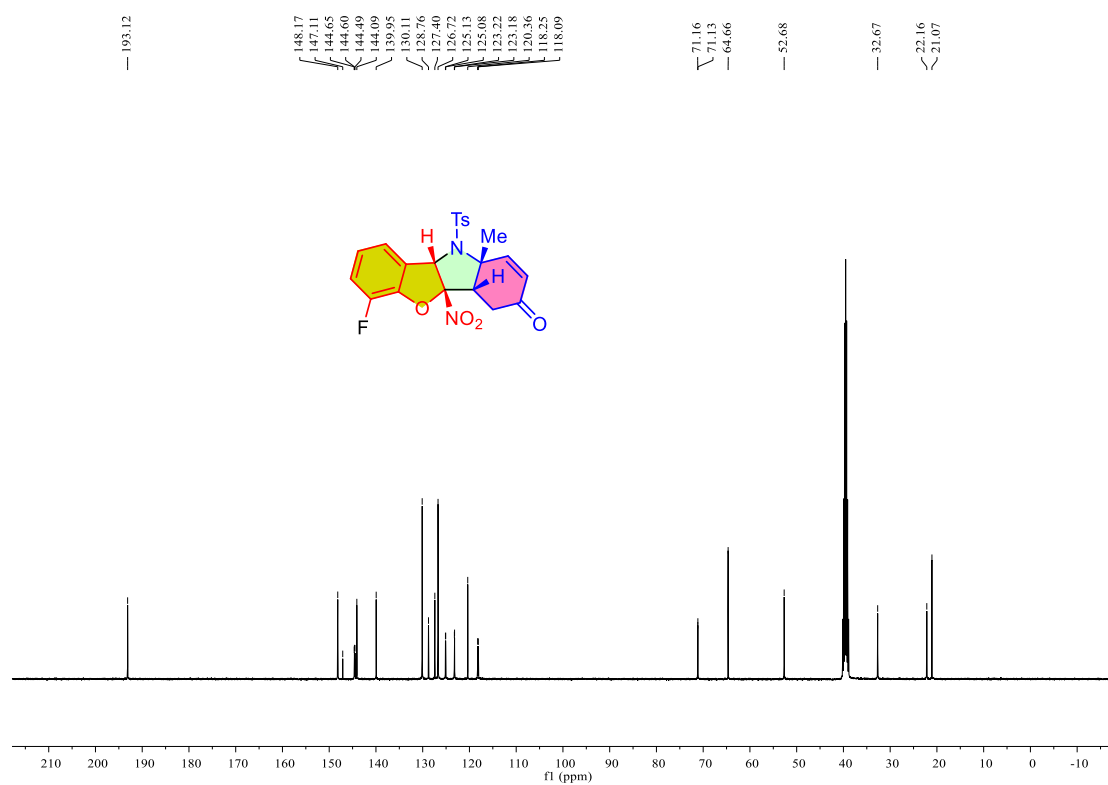
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3ar**



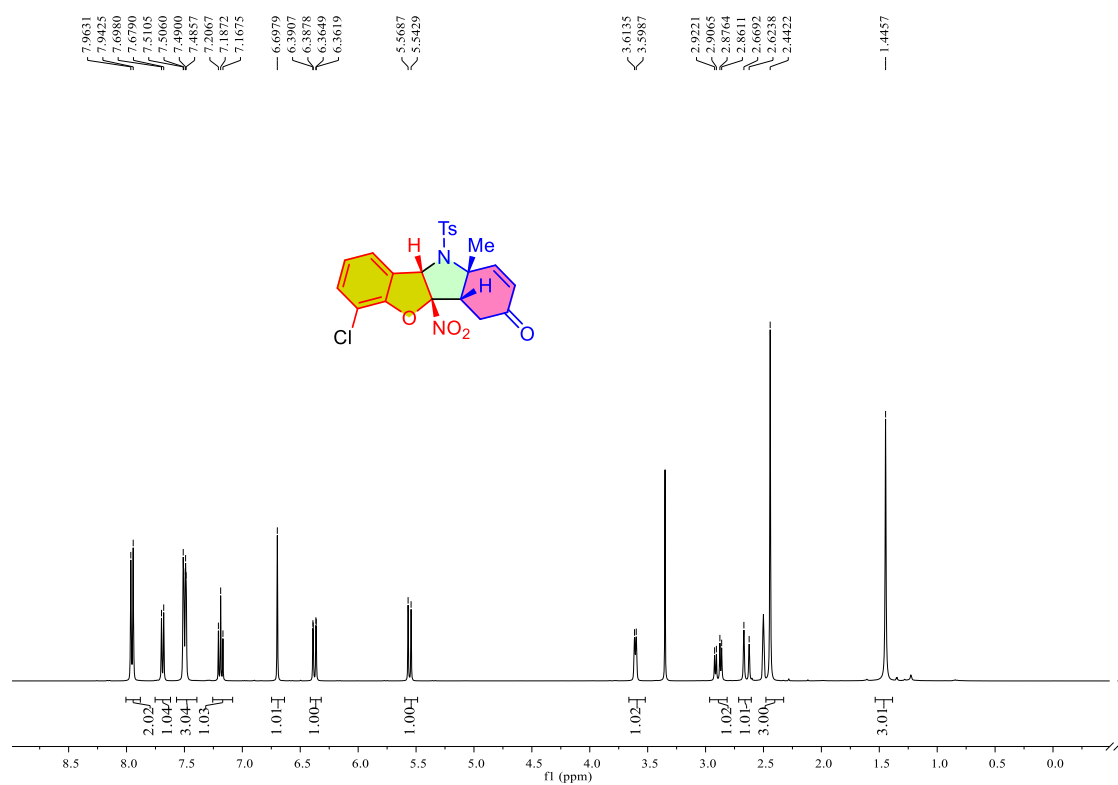
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **3as**



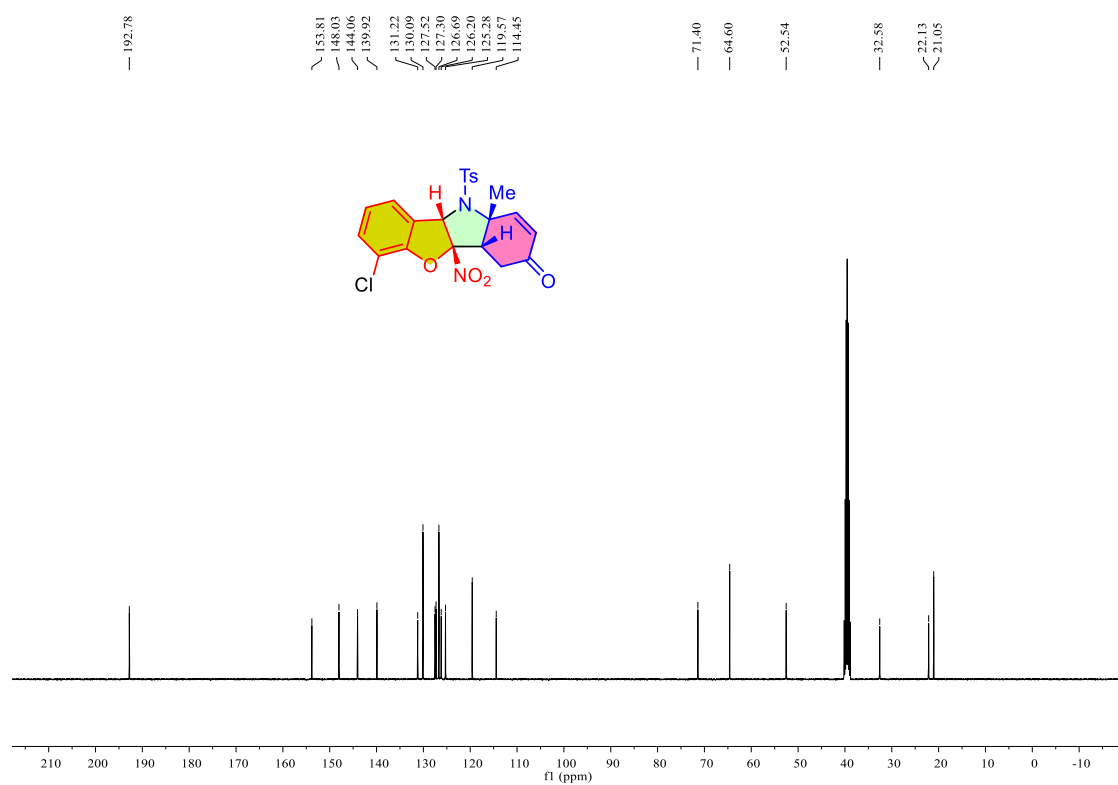
<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3as**



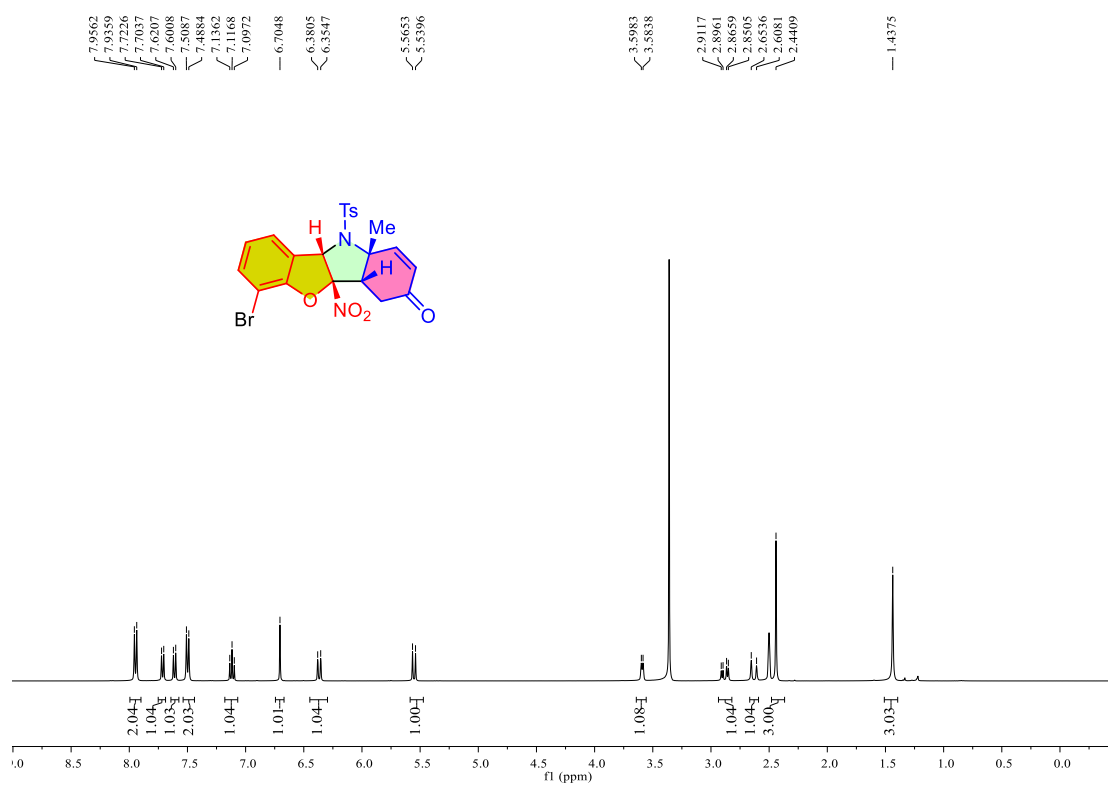
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **3at**



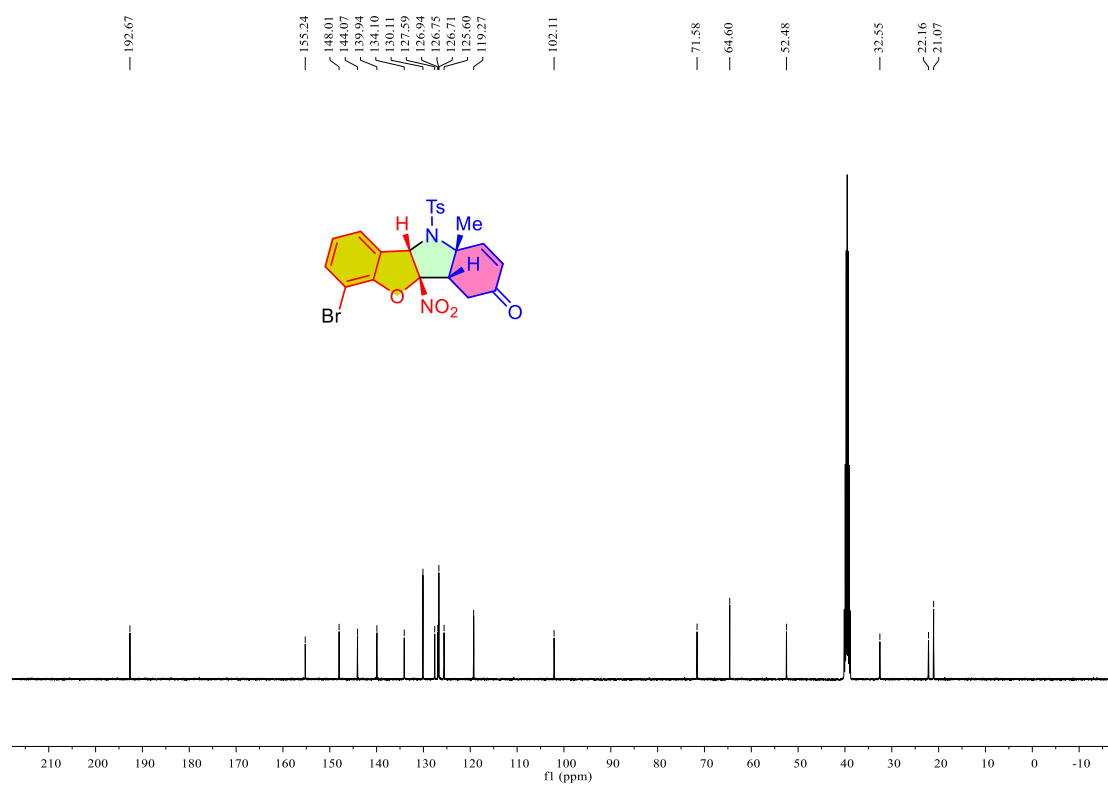
<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3at**



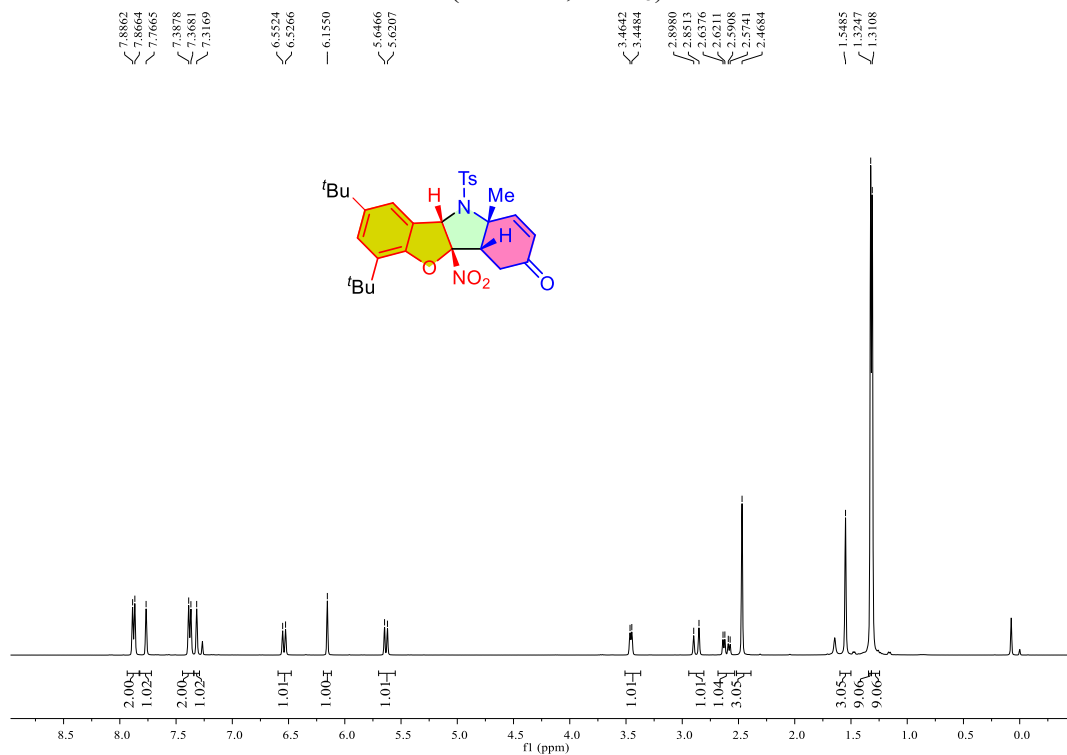
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **3au**



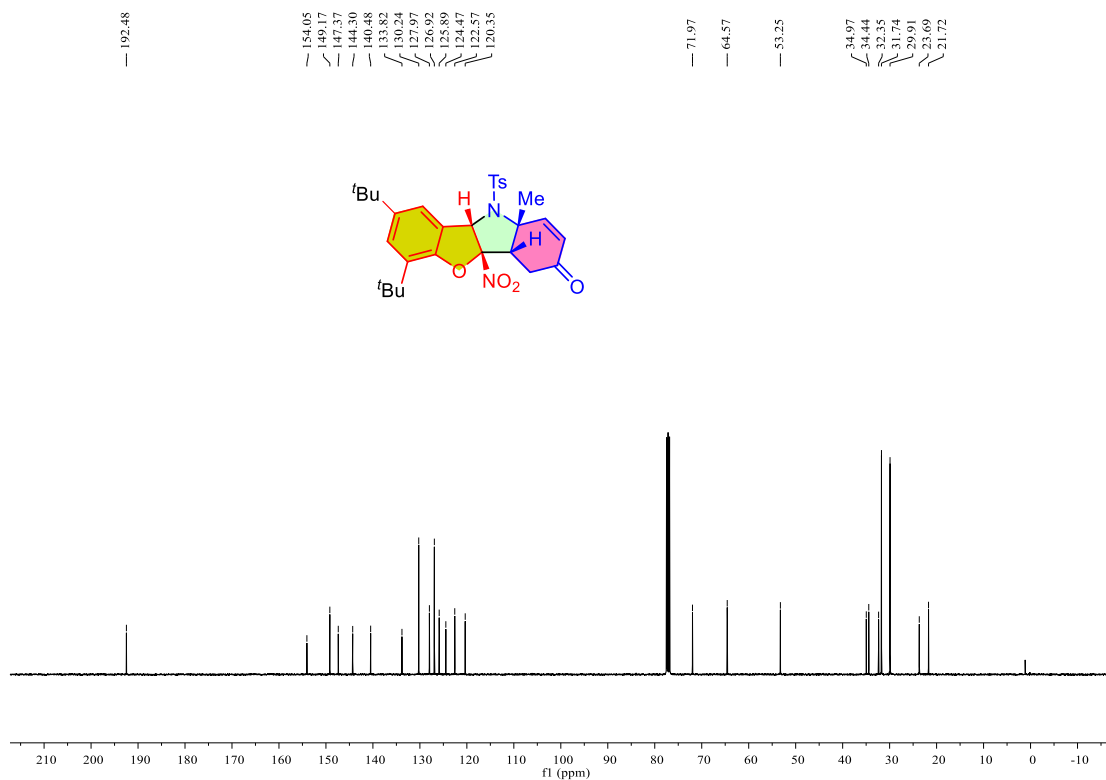
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3au**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3av**

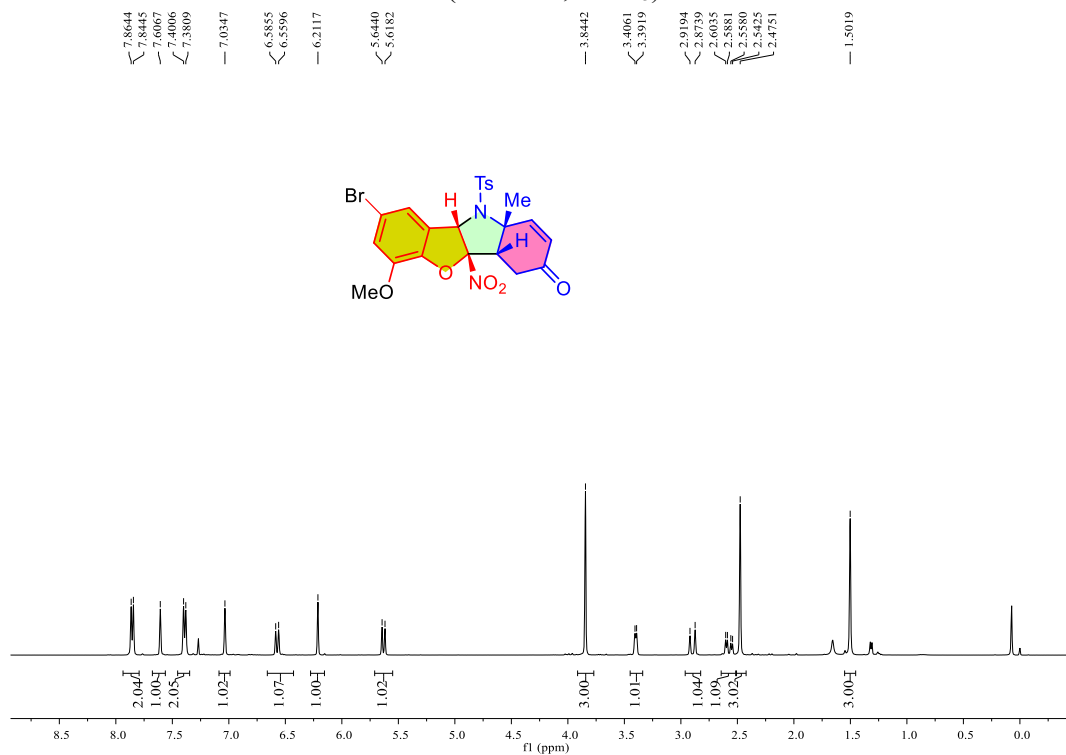


<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3av**

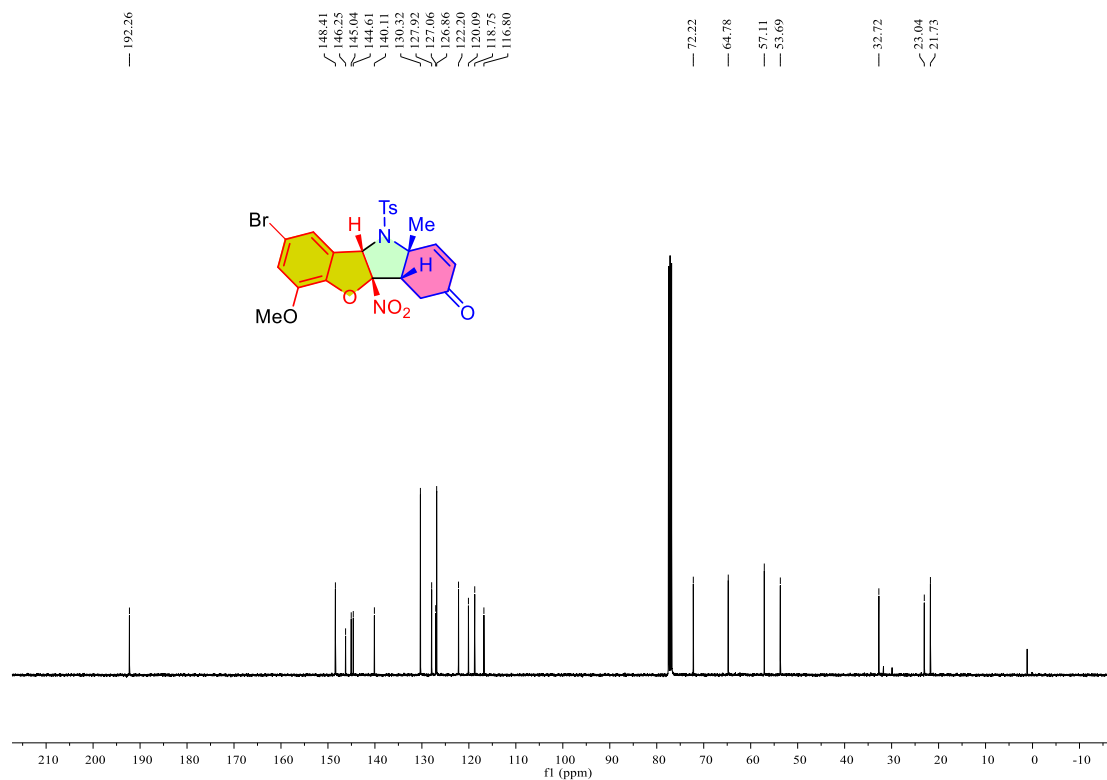




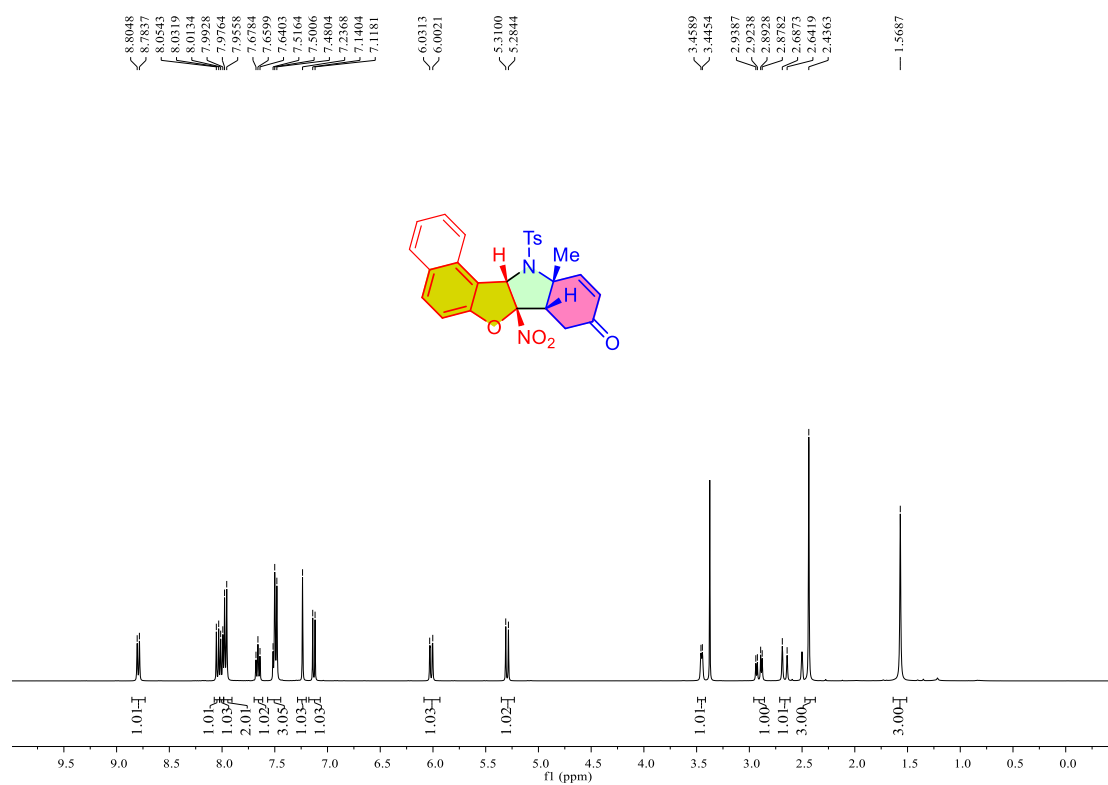
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3aw**



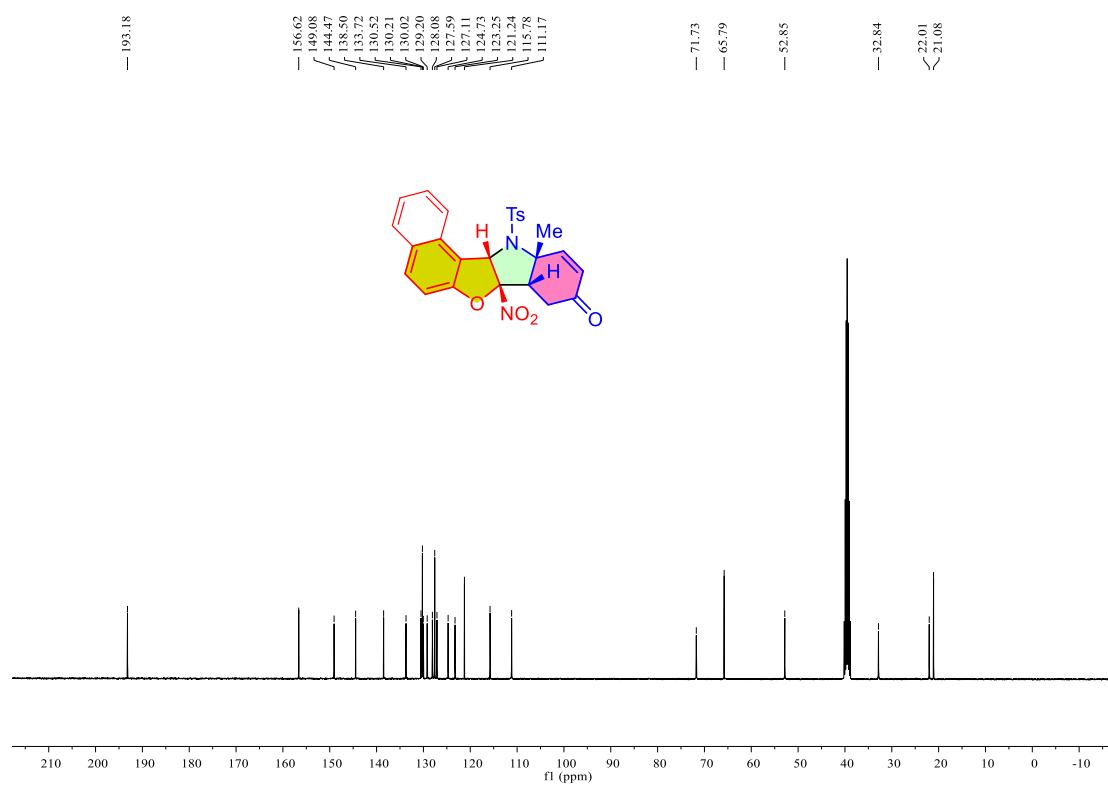
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3aw**



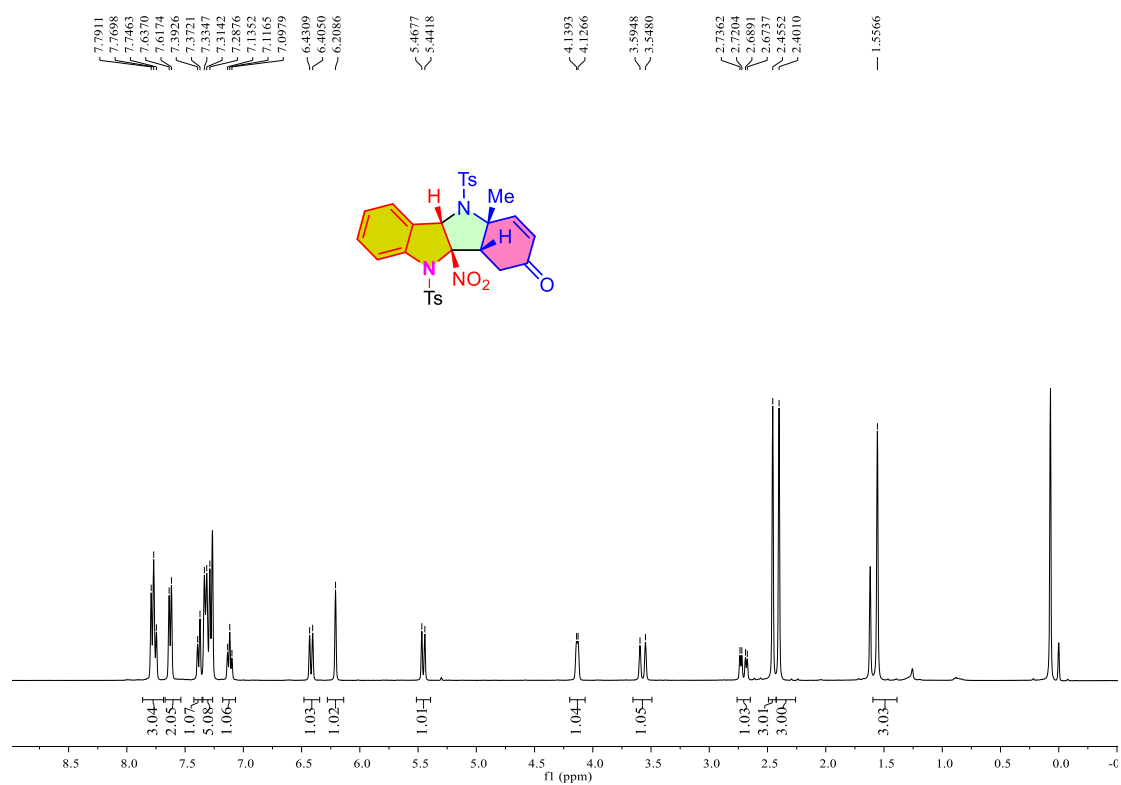
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) of **3ax**



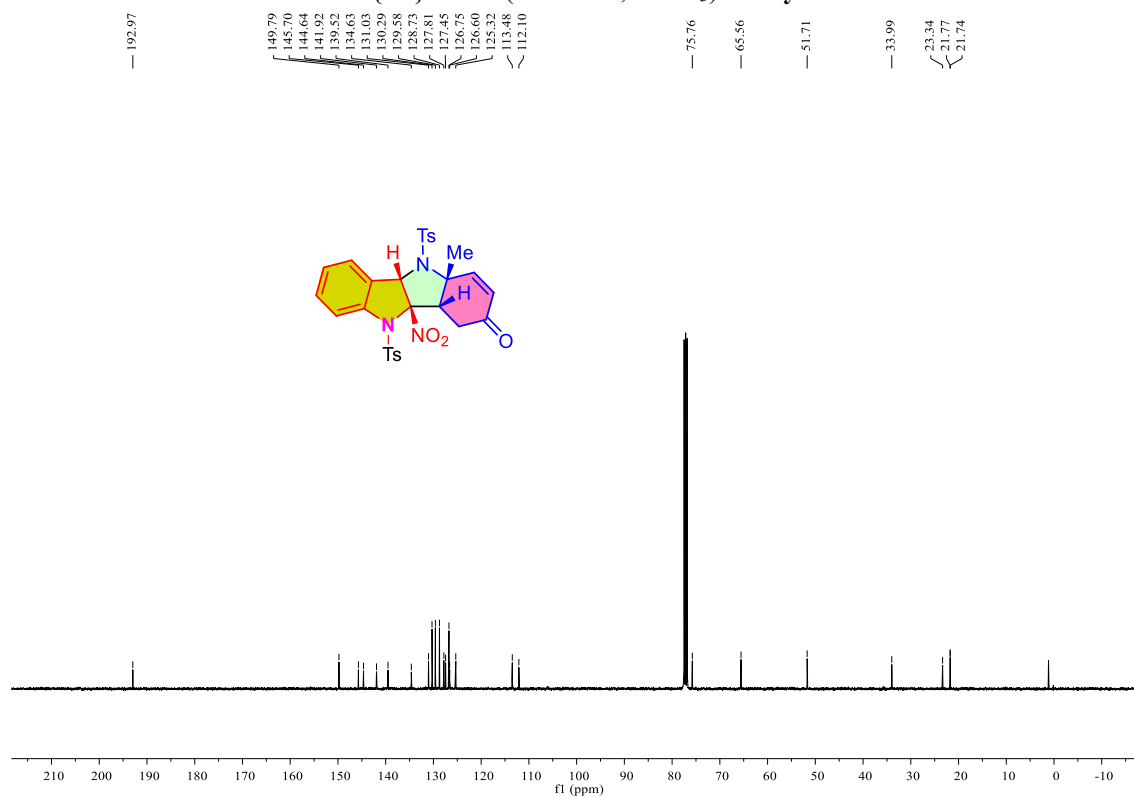
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) of **3ax**



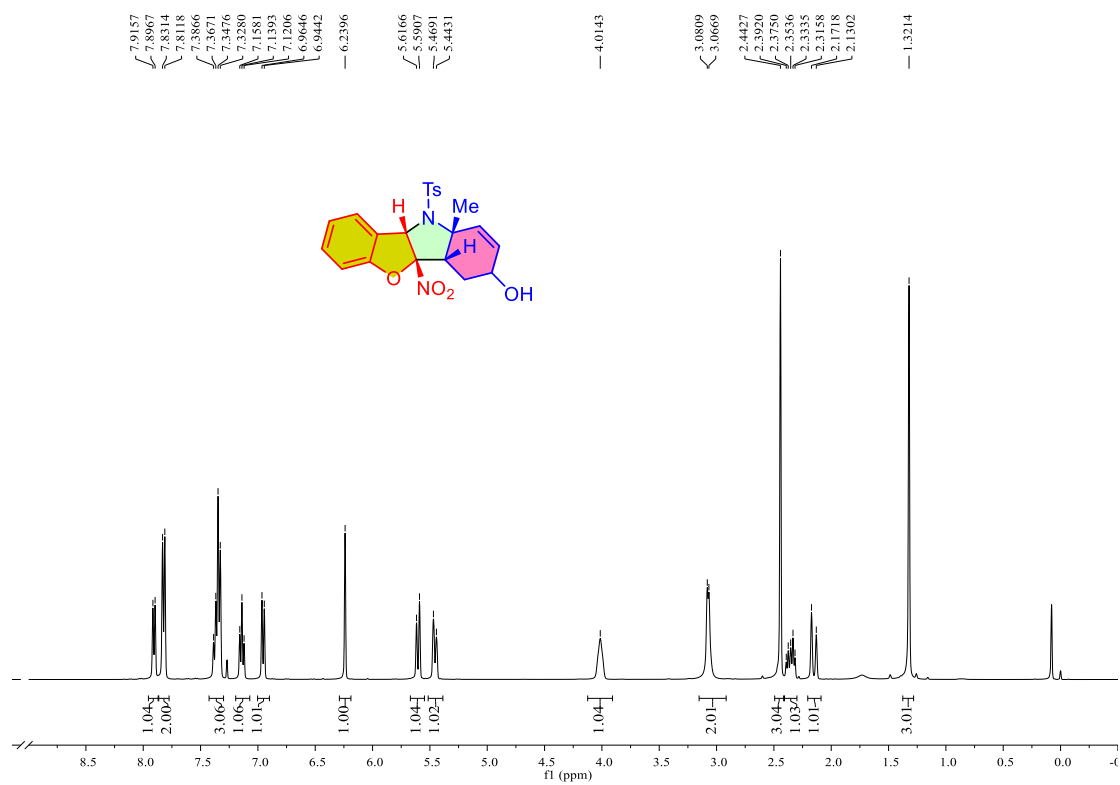
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ay**



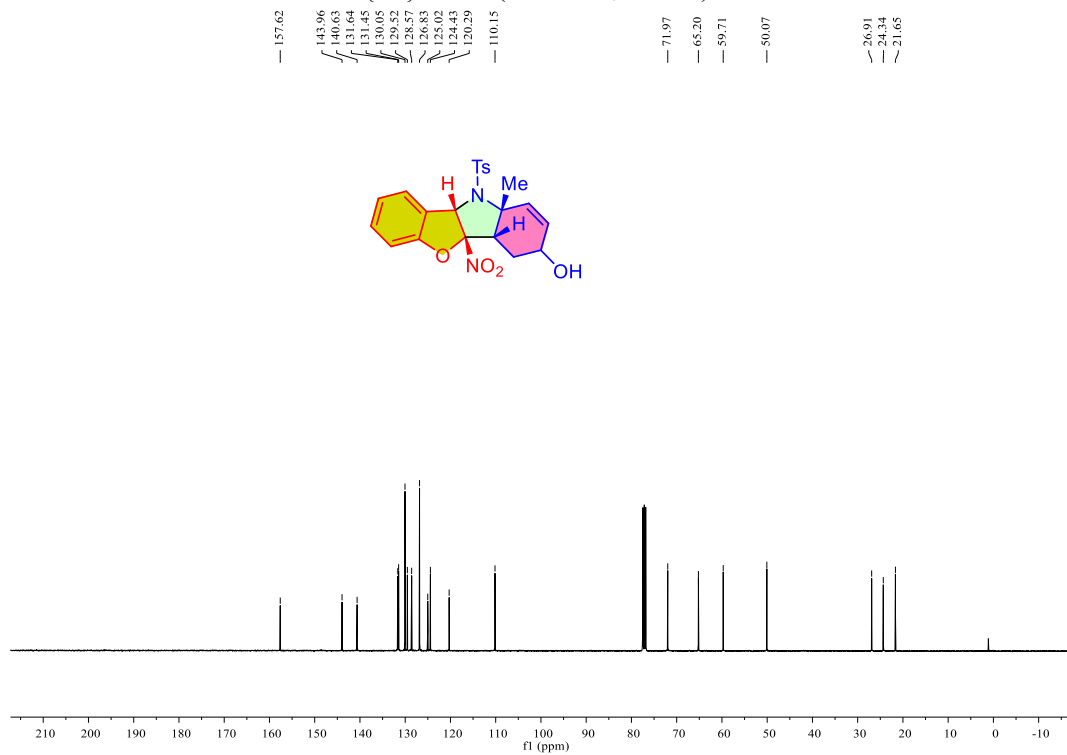
<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **3ay**



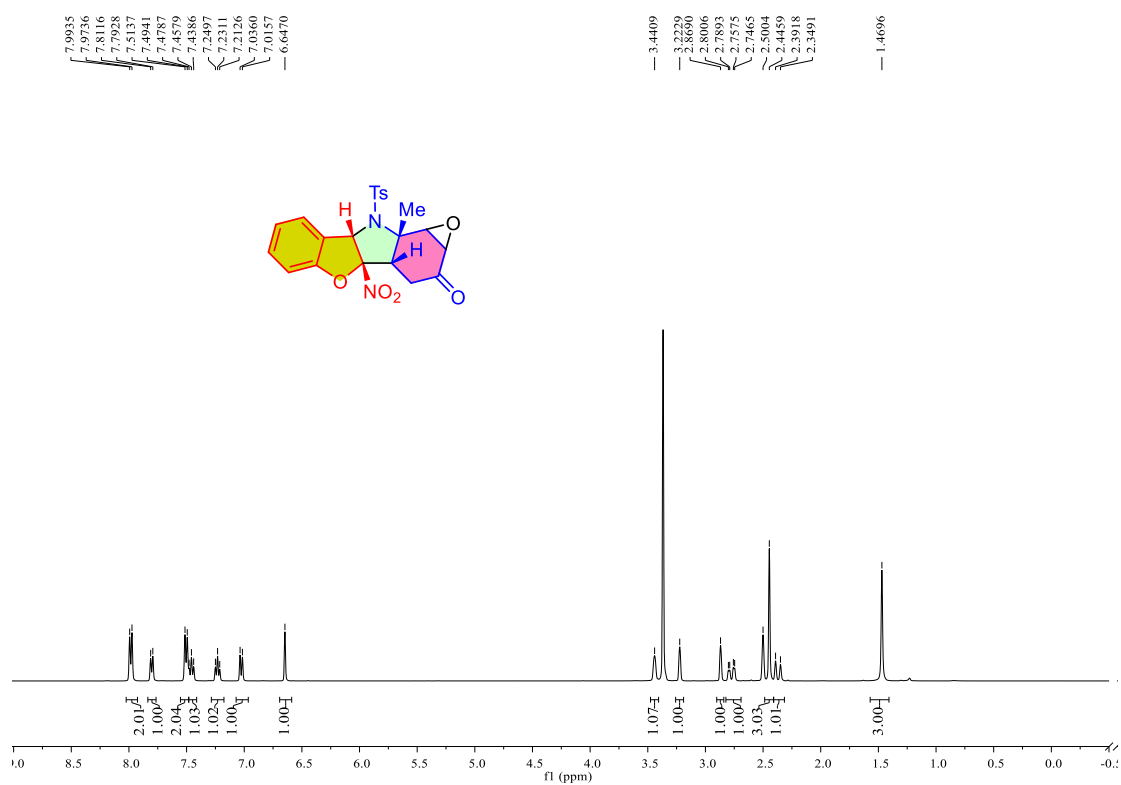
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **4**



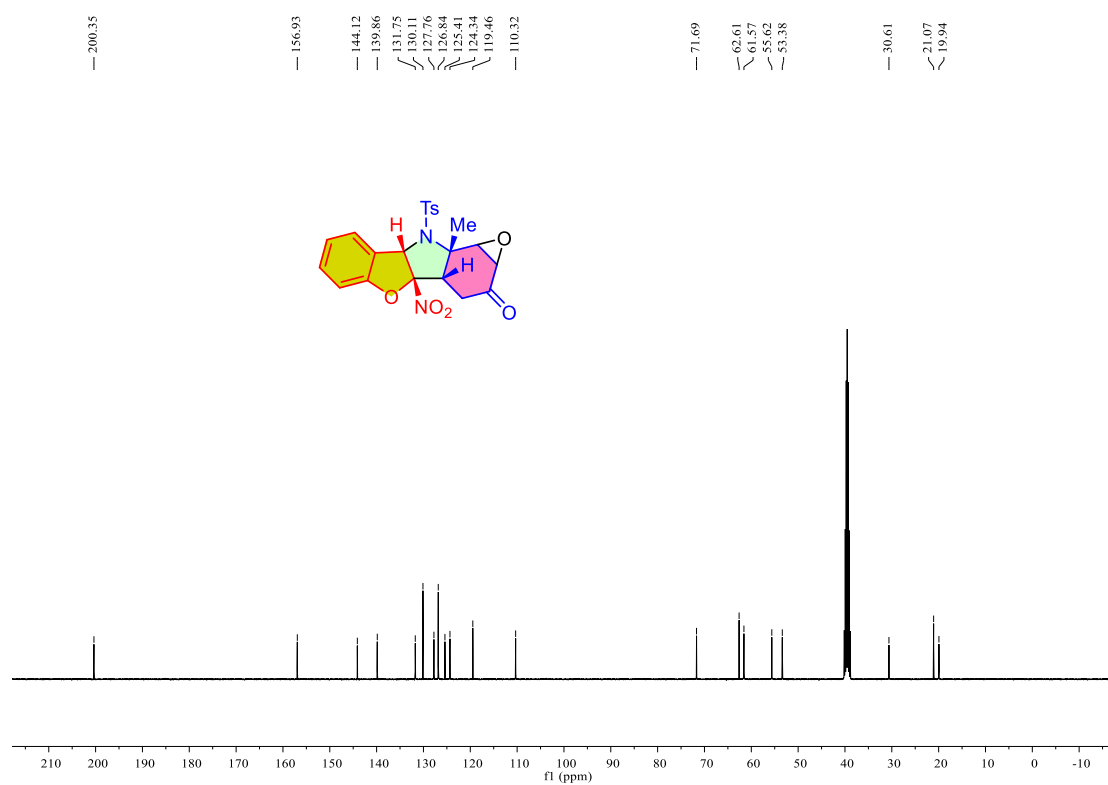
<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **4**



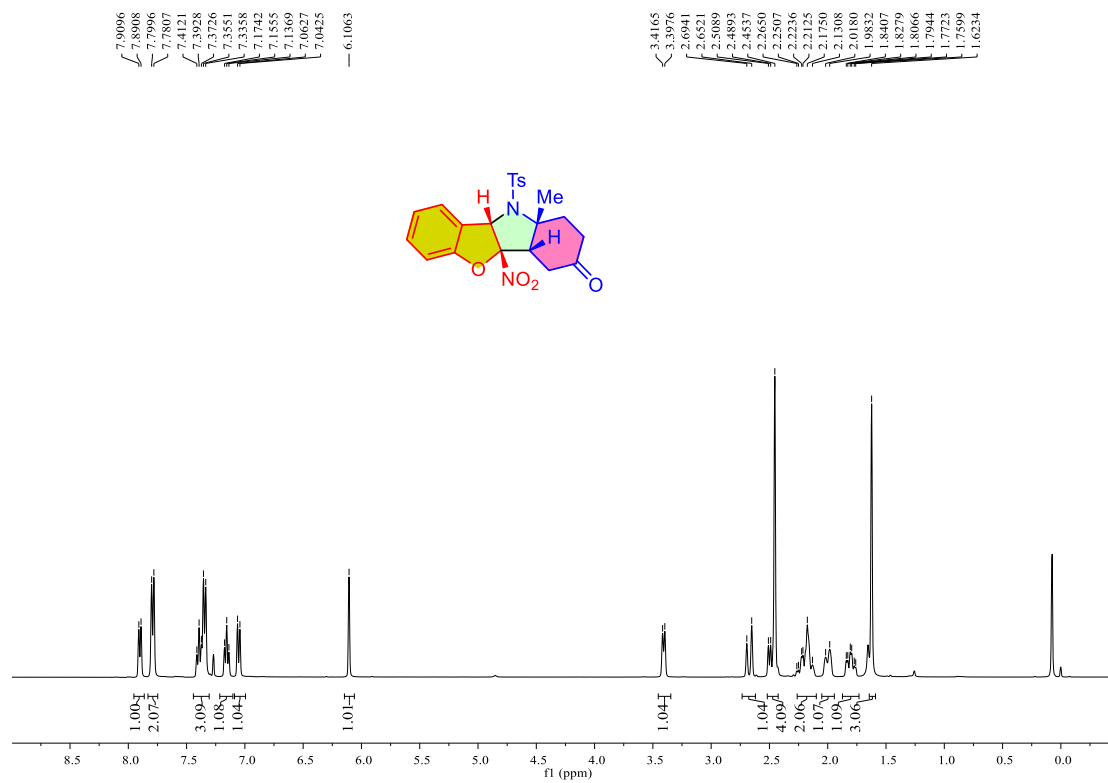
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **5**



<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **5**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **6**



<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) of **6**

