

Supporting Information for

C–H Sulfenylation via 1,3-Rearrangement of Sulfonyl Group in *N*-Protected 3-Bis-sulfonimidoindole Derivatives Using Fluorine Reagent

Kazuhiro Watanabe, Katsuhiko Moriyama,*

*Department of Chemistry, Graduate School of Science and Soft Molecular Activation Research Center, Chiba University,
Yayoi-cho 1-33, Inage-ku, Chiba, 263-8522, Japan*

moriyama@faculty.chiba-u.jp

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1. X-ray Diffraction Analysis of **2a**.

The single crystal of **2a** was obtained through vapor diffusion in EtOAc and hexane.

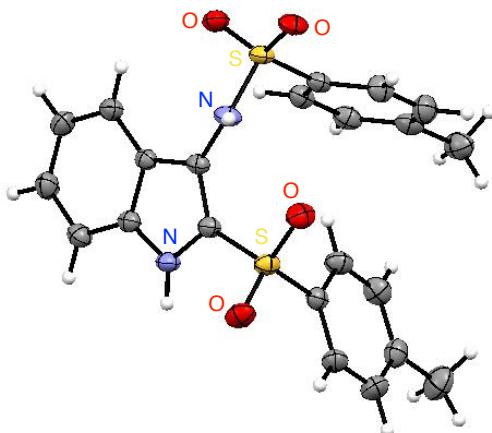


Figure S1. ORTEP drawing of **2a**. The ellipsoids correspond to 50% probability.

Formula	$C_{22}H_{20}N_2O_4S_2$	
Formula Weight	440.54	
Temperature	173 K	
Wavelength	1.54178 Å	
Crystal System	Monoclinic	
Space Group	C 1 2/c 1	
Unit Cell Dimensions	$a = 32.963(3)$ Å	$\alpha = 90^\circ$
	$b = 8.7052(9)$ Å	$\beta = 114.780(3)^\circ$
	$c = 15.5575(15)$ Å	$\gamma = 90^\circ$
Volume	$4053.2(7)$ Å ³	
Z Value	8	
Calculated Density	1.444 g cm ⁻³	
Absorption coeficiente	2.663 mm ⁻¹	
F(000)	1840	
Crystal size	$0.20 \times 0.10 \times 0.10$ mm ³	
Theta Range for Data Collection	2.9531-68.2925	
Index Ranges	$-37 \leq h \leq 39, -10 \leq k \leq 10, -18 \leq l \leq 18$	
Reflections Collected	3709	
Independent Reflections	3709 [R(int)=0.0182]	
Completeness to Theta = 68.302°	99.9%	
Refinement Method	Full-matrix least-squares on F ²	
Data/Restraints/Parameters	3709/0/273	
Goodness-of-Fit on F ²	1.366	
Final R Indices [I>2sigma(I)]	$R_1 = 0.0378$ and $wR_2 = 0.1432$	

R Indices (All Data)	$R_1 = 0.0387$ and $wR_2 = 0.1460$
Largest Diff. Peak and Hole	0.596 and $-0.582 \text{ e}^-/\text{\AA}$

2. X-ray Diffraction Analysis of **11**.

The single crystal of **11** was obtained through vapor diffusion in benzene and hexane.

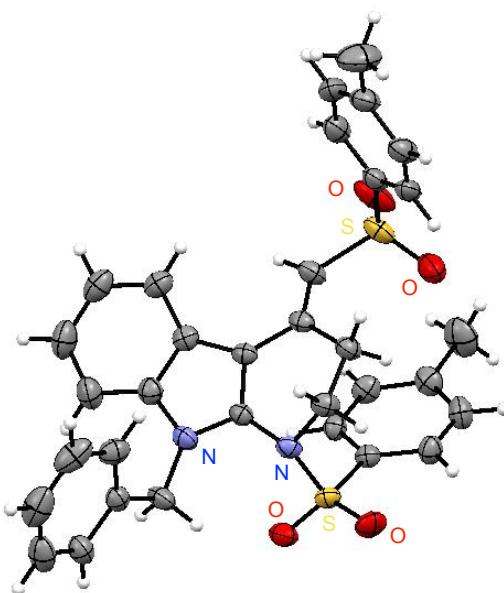


Figure S2. ORTEP drawing of **11**. The ellipsoids correspond to 50% probability.

Formula	$\text{C}_{33}\text{H}_{30}\text{N}_2\text{O}_4\text{S}_2$		
Formula Weight	582.71		
Temperature	173 K		
Wavelength	1.54178 Å		
Crystal System	Monoclinic		
Space Group	P 1 21/c 1		
Unit Cell Dimensions	$a = 13.1147(5) \text{ \AA}$	$\alpha = 90^\circ$	
	$b = 22.8270(8) \text{ \AA}$	$\beta = 98.306(2)^\circ$	
	$c = 9.7575(3) \text{ \AA}$	$\gamma = 90^\circ$	
Volume	$2890.46(17) \text{ \AA}^3$		
Z Value	4		
Calculated Density	1.339 g cm^{-3}		
Absorption coeficiente	2.005 mm^{-1}		
F(000)	1224		
Crystal size	$0.30 \times 0.020 \times 0.010 \text{ mm}^3$		

Theta Range for Data Collection	3.4057-68.1161
Index Ranges	-15 ≤ h ≤ 15, -23 ≤ k ≤ 27, -11 ≤ l ≤ 11
Reflections Collected	5276
Independent Reflections	5276 [R(int)=0.0507]
Completeness to Theta = 68.302°	99.8%
Refinement Method	Full-matrix least-squares on F ²
Data/Restraints/Parameters	5276/0/372
Goodness-of-Fit on F ²	1.048
Final R Indices [I>2sigma(I)]	R ₁ = 0.0394 and wR ₂ = 0.0948
R Indices (All Data)	R ₁ = 0.0525 and wR ₂ = 0.1014
Largest Diff. Peak and Hole	0.319 and -0.293 e ⁻ / Å

3. X-ray Diffraction Analysis of **12**.

The single crystal of **12** was obtained through vapor diffusion in THF and hexane.

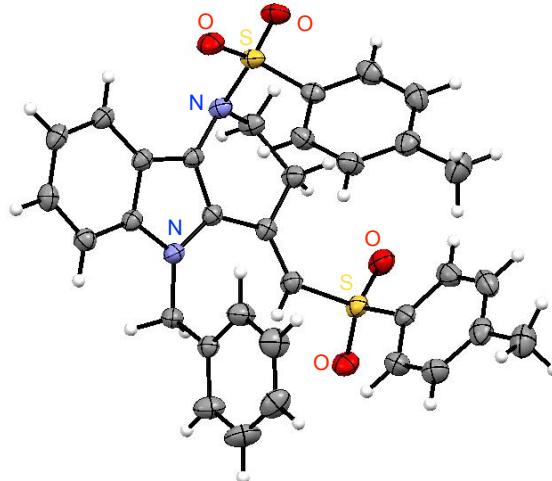
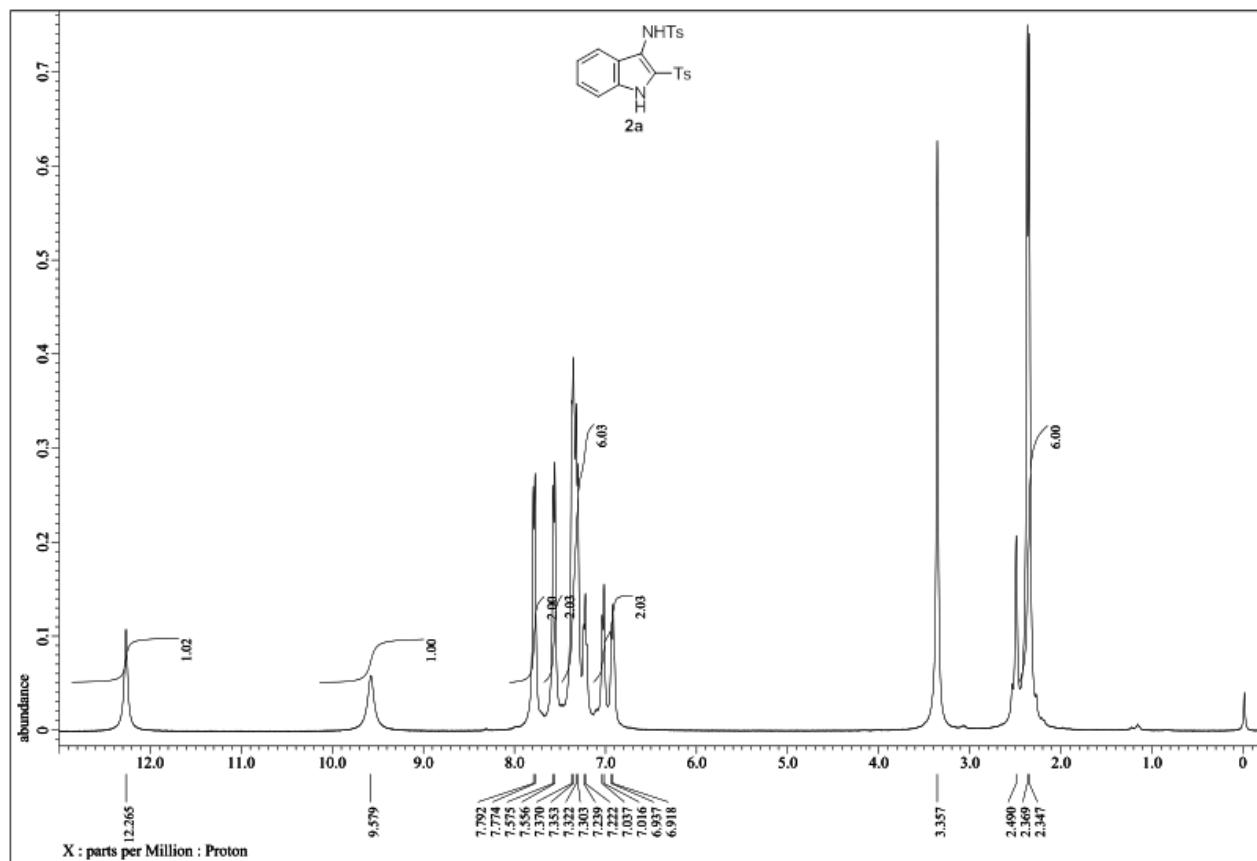


Figure S3. ORTEP drawing of **12**. The ellipsoids correspond to 50% probability.

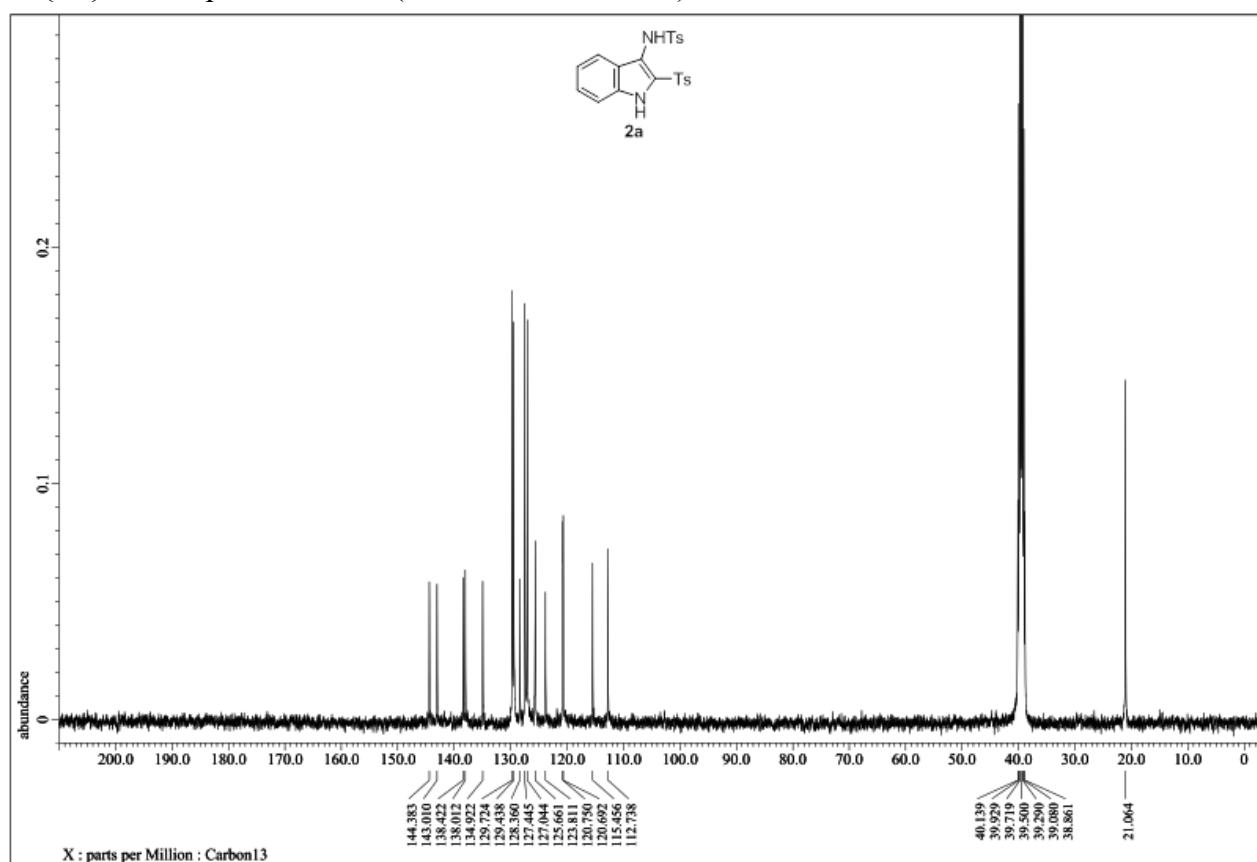
Formula	C ₃₃ H ₃₀ N ₂ O ₄ S ₂
Formula Weight	582.71
Temperature	173 K
Wavelength	1.54178 Å
Crystal System	Monoclinic
Space Group	P 1 21/n 1
Unit Cell Dimensions	$a = 9.7296(6)$ Å $\alpha = 90^\circ$ $b = 28.0212(17)$ Å $\beta = 106.7887(19)^\circ$

	$c = 10.7123(7) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$2796.1(3) \text{ \AA}^3$	
Z Value	4	
Calculated Density	1.384 g cm^{-3}	
Absorption coeficiente	2.073 mm^{-1}	
F(000)	1224	
Crystal size	$0.20 \times 0.10 \times 0.10 \text{ mm}^3$	
Theta Range for Data Collection	3.1542-68.2218	
Index Ranges	$-11 \leq h \leq 10, -33 \leq k \leq 31, -12 \leq l \leq 12$	
Reflections Collected	5044	
Independent Reflections	5044 [R(int)=0.0202]	
Completeness to Theta = 68.302°	99.8%	
Refinement Method	Full-matrix least-squares on F^2	
Data/Restraints/Parameters	5044/0/384	
Goodness-of-Fit on F^2	1.085	
Final R Indices [$I > 2\sigma(I)$]	$R_1 = 0.0368$ and $wR_2 = 0.0987$	
R Indices (All Data)	$R_1 = 0.0370$ and $wR_2 = 0.0989$	
Largest Diff. Peak and Hole	0.462 and $-0.308 \text{ e}^-/\text{\AA}$	

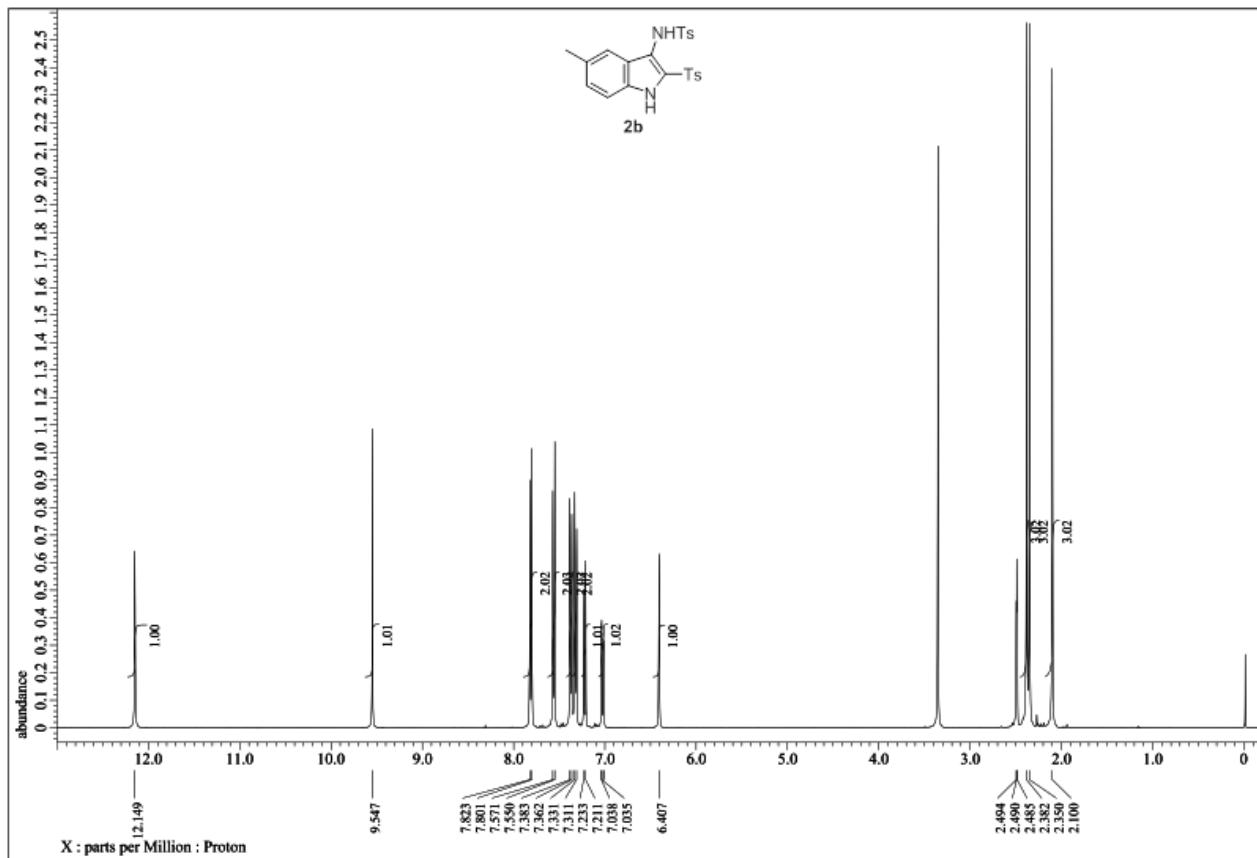
^1H NMR spectrum of **2a** (400 MHz, DMSO-*d*6)



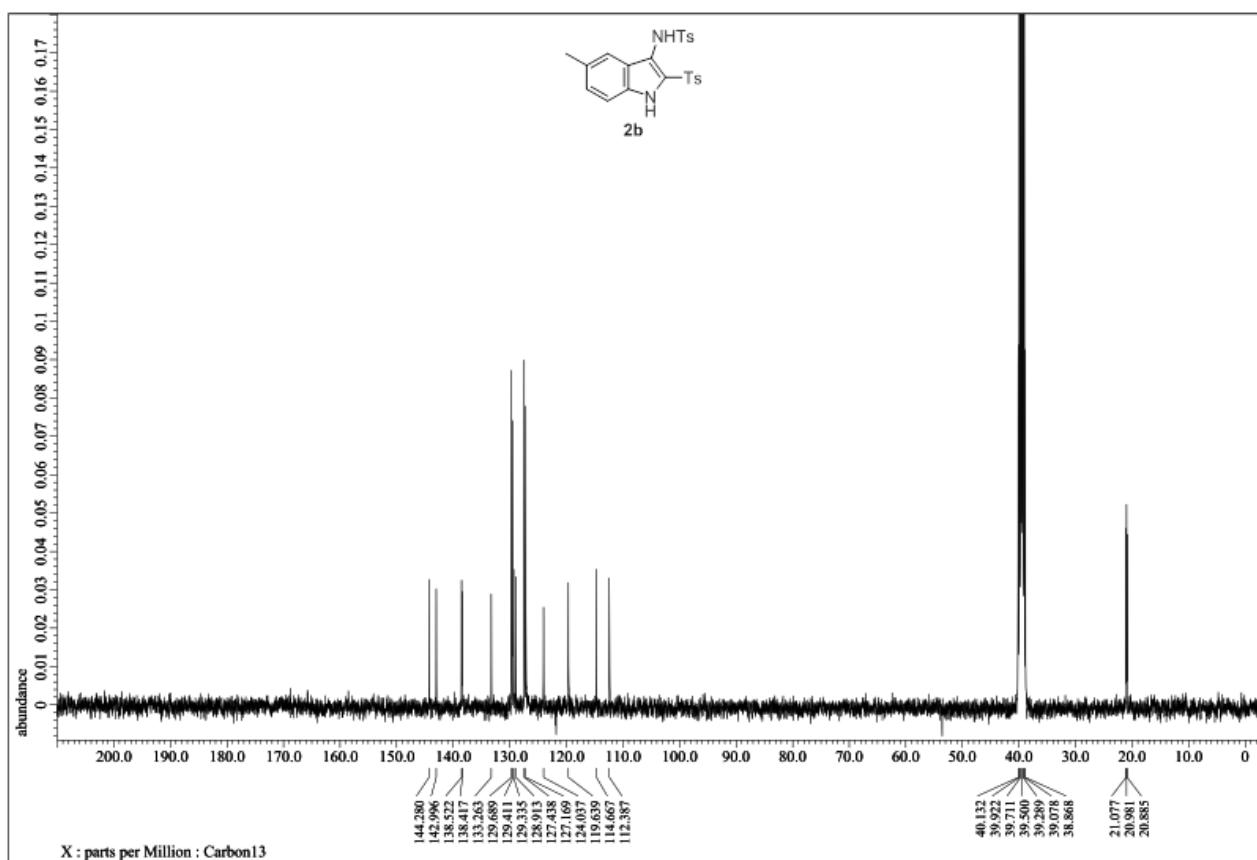
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2a** (400 MHz, DMSO-*d*6)



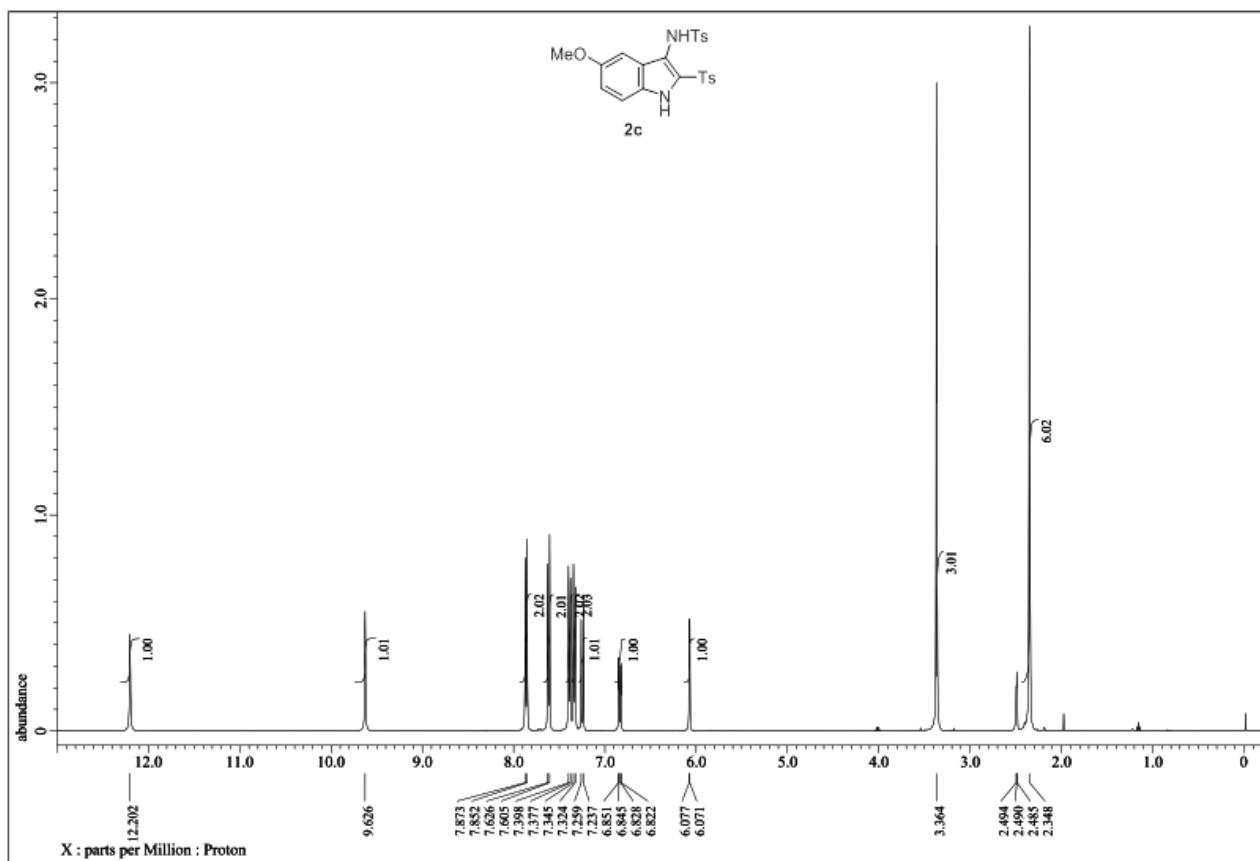
¹H NMR spectrum of **2b** (400 MHz, DMSO-*d*6)



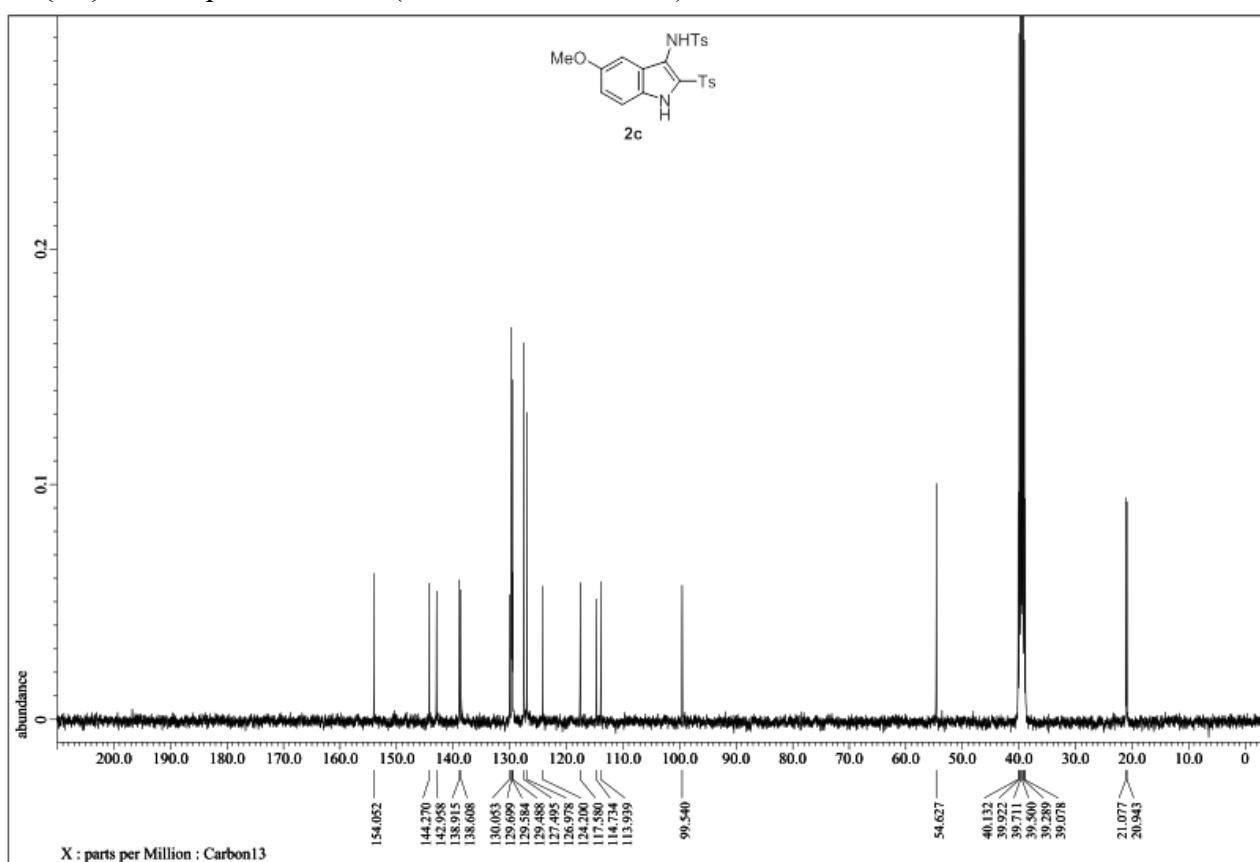
¹³C{¹H} NMR spectrum of **2b** (400 MHz, DMSO-*d*6)



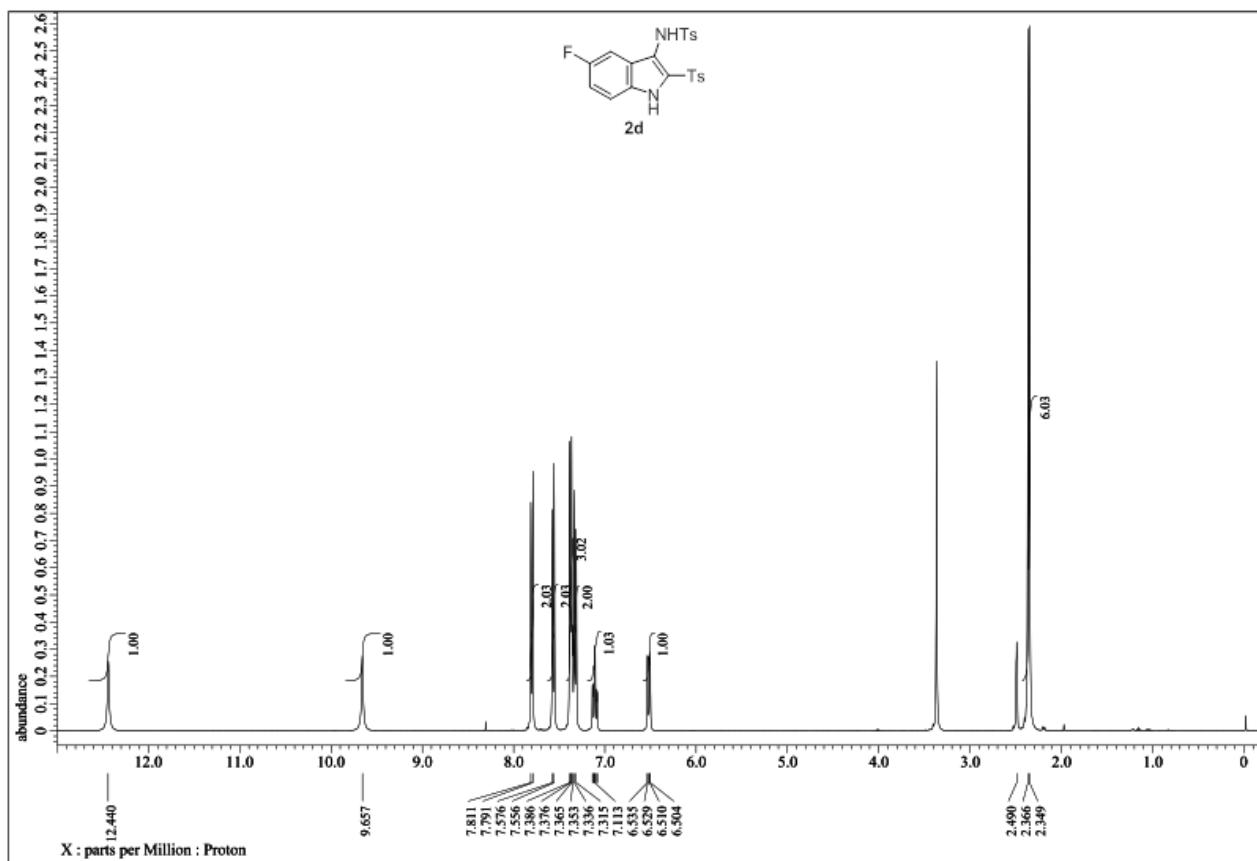
¹H NMR spectrum of **2c** (400 MHz, DMSO-*d*6)



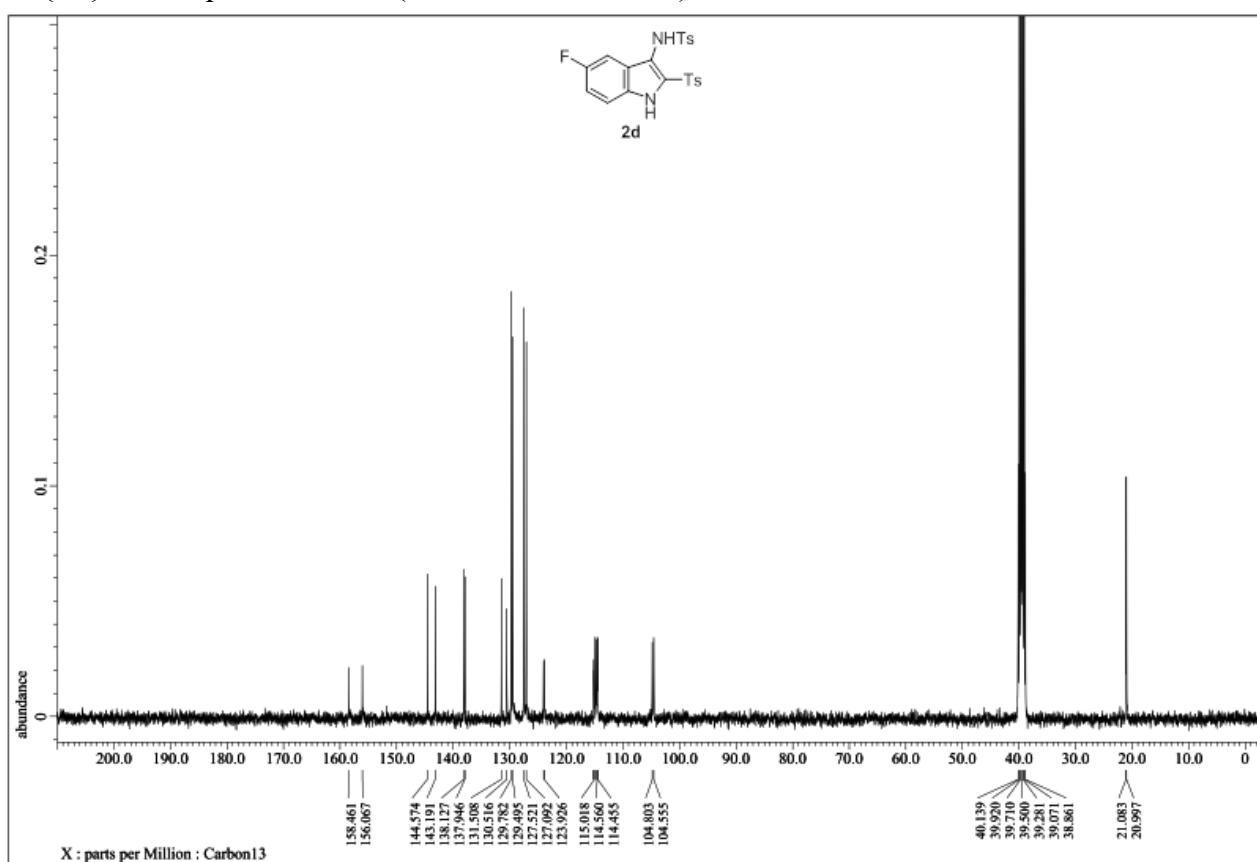
$^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2c** (400 MHz, DMSO-*d*6)



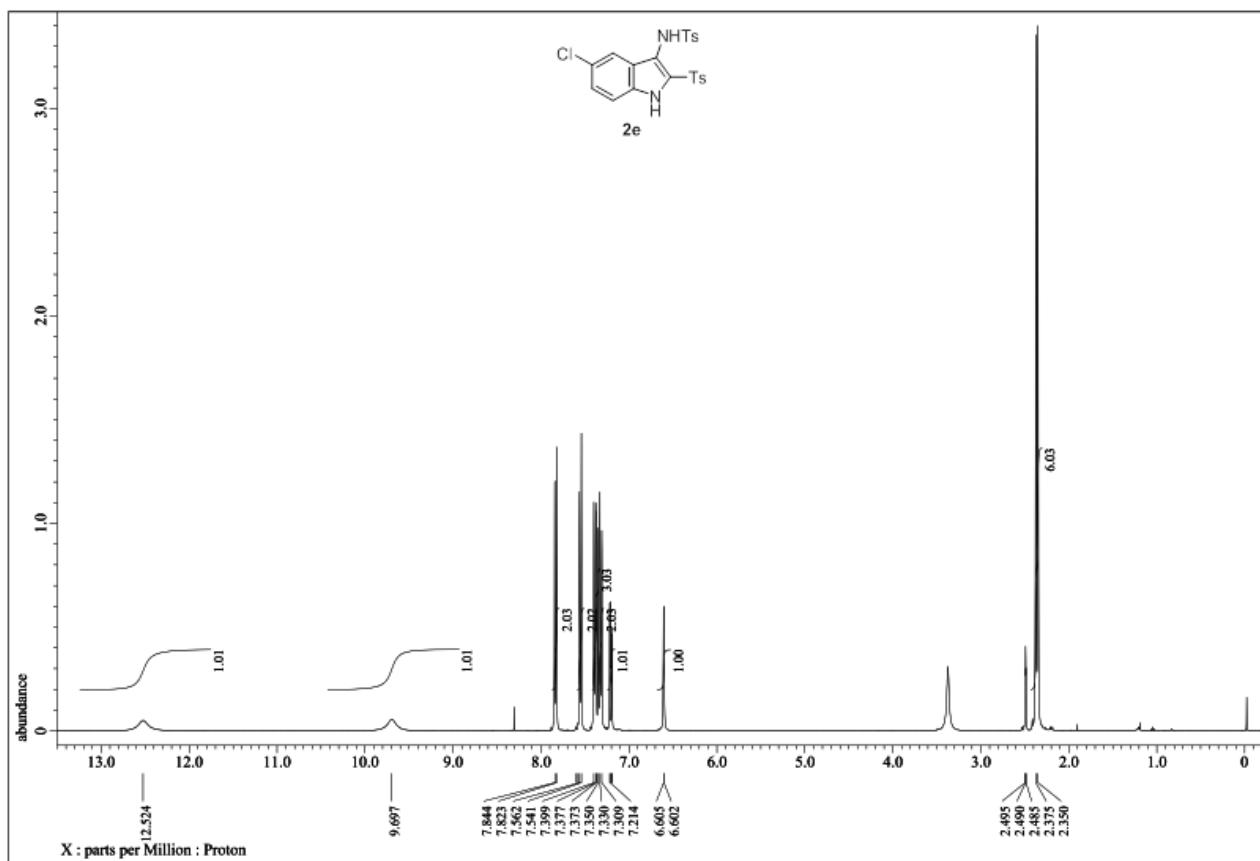
¹H NMR spectrum of **2d** (400 MHz, DMSO-*d*6)



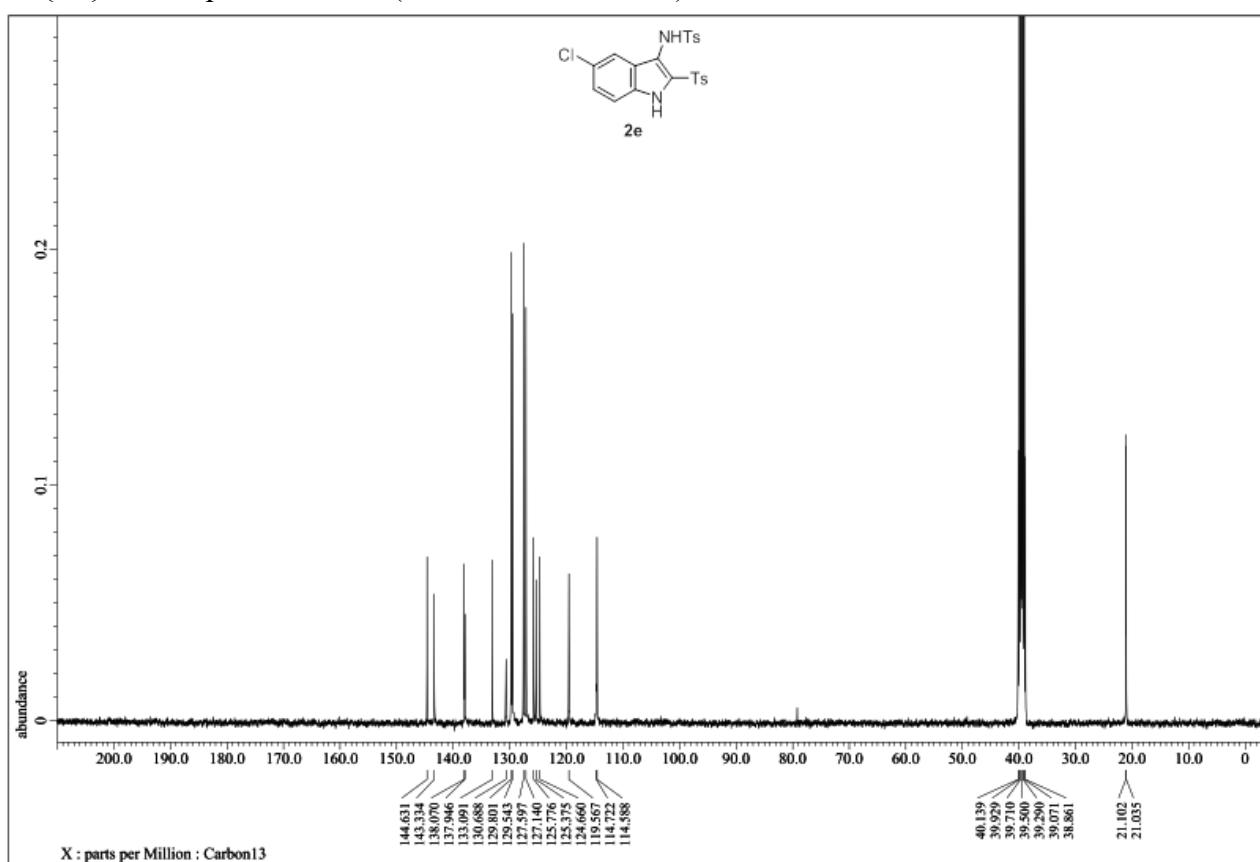
¹³C{¹H} NMR spectrum of **2d** (400 MHz, DMSO-*d*6)



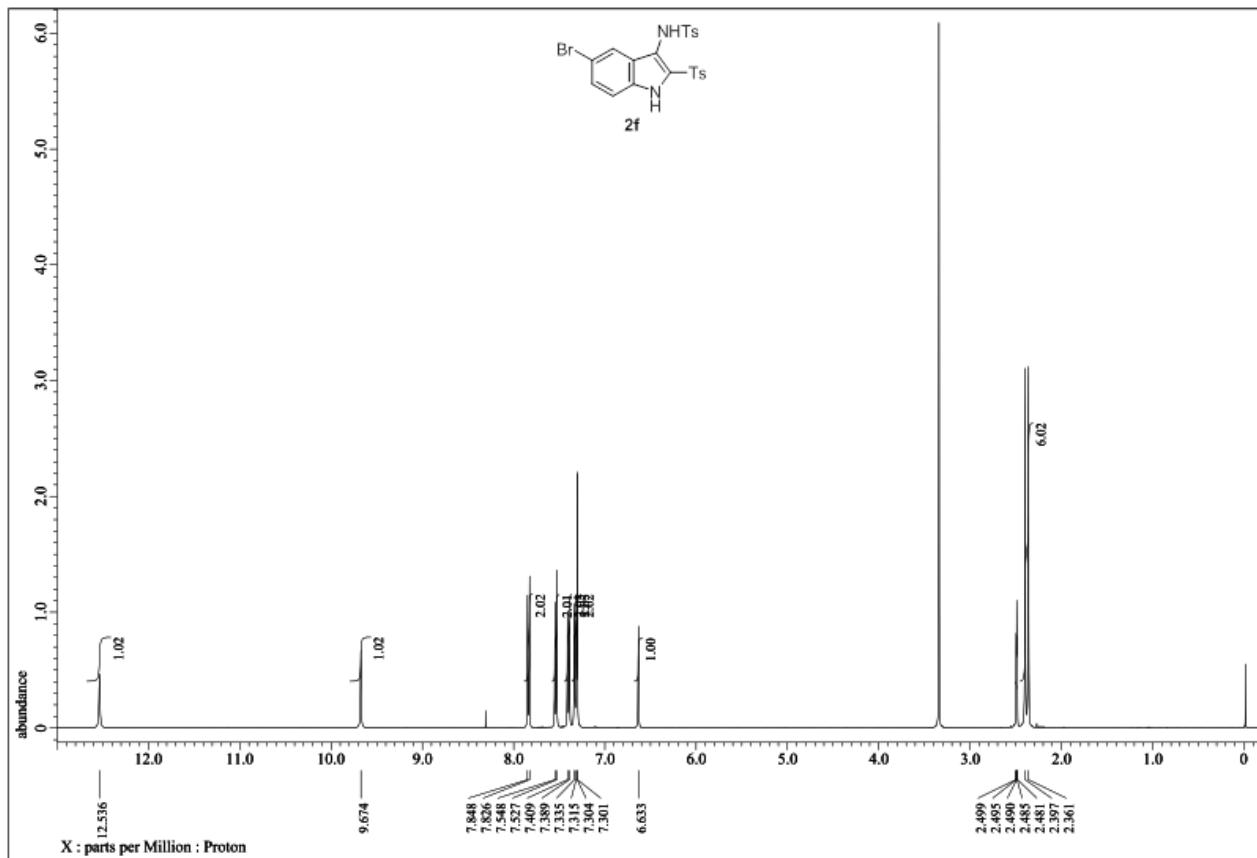
¹H NMR spectrum of **2e** (400 MHz, DMSO-*d*6)



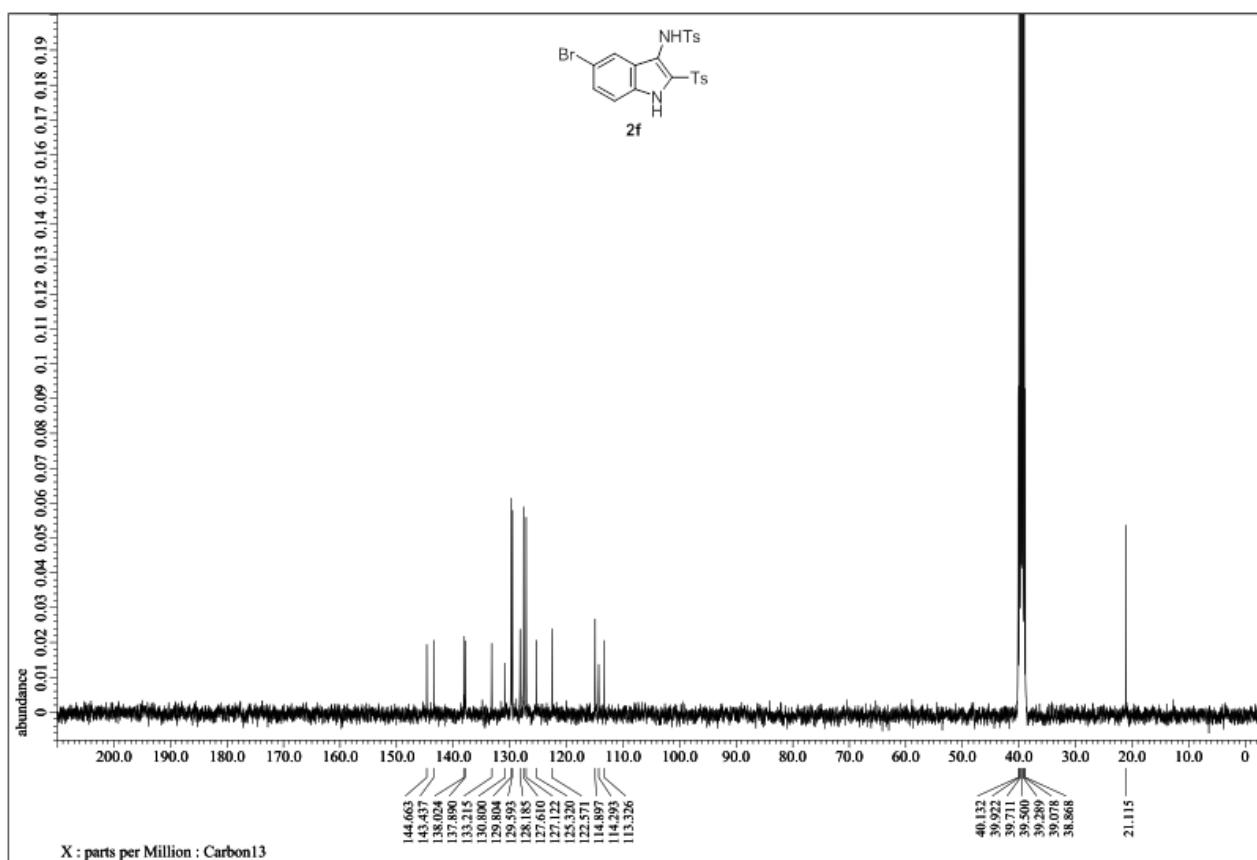
$^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2e** (400 MHz, DMSO-*d*6)



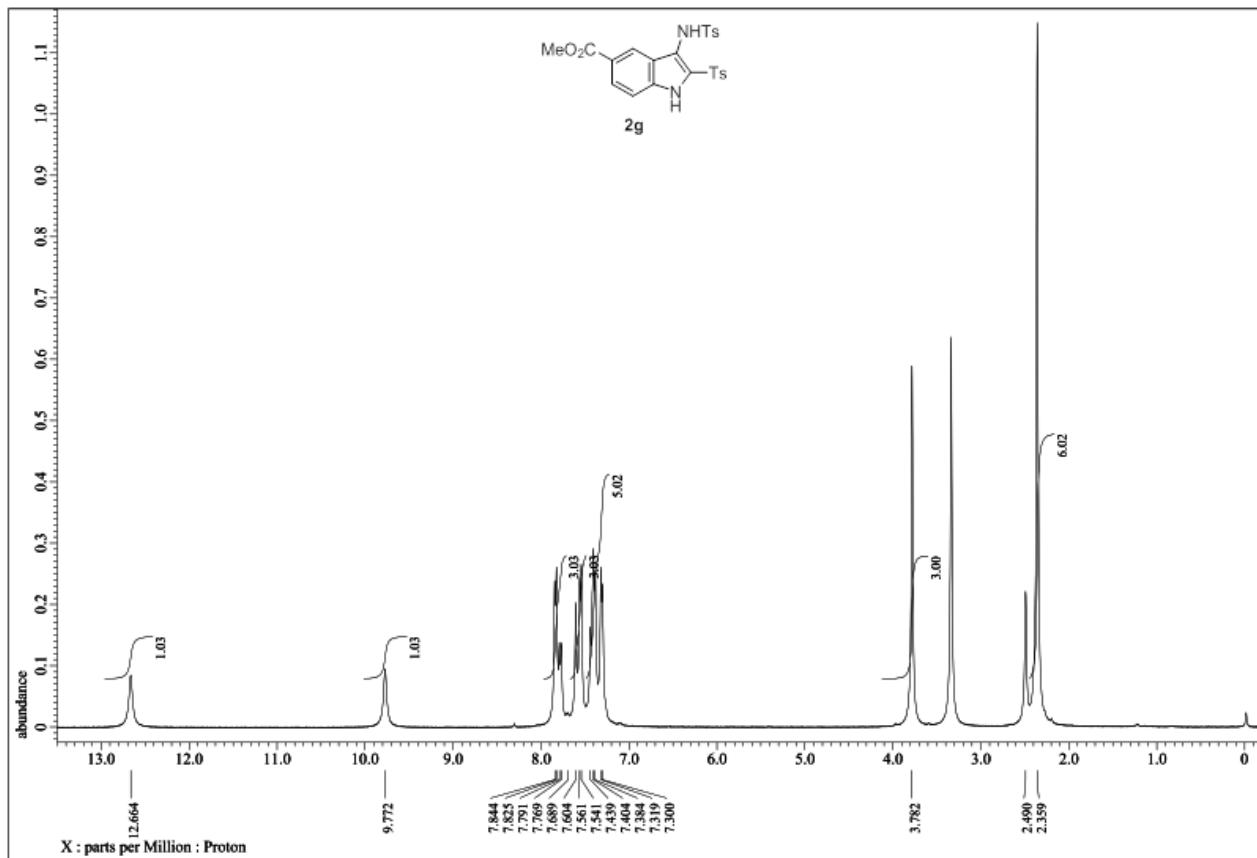
^1H NMR spectrum of **2f** (400 MHz, DMSO-*d*6)



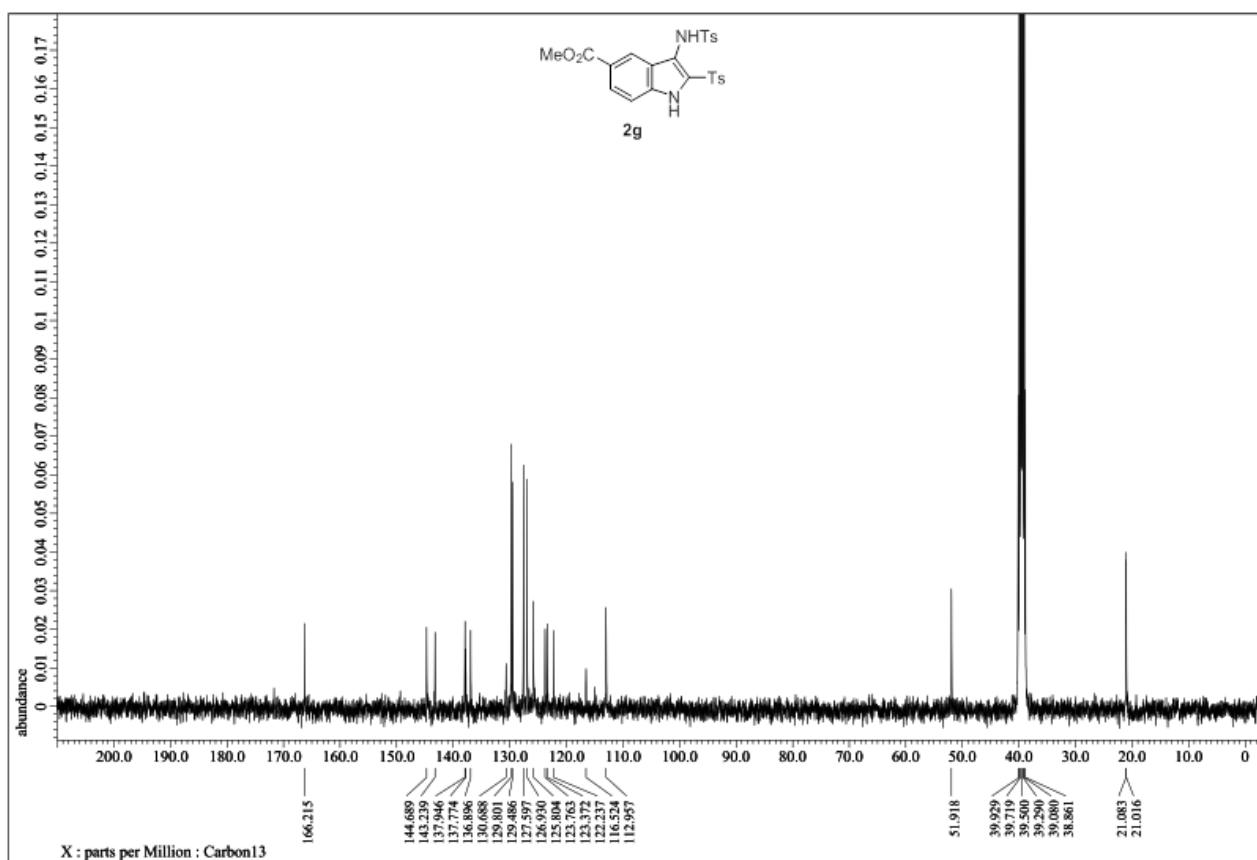
$^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2f** (400 MHz, DMSO-*d*6)



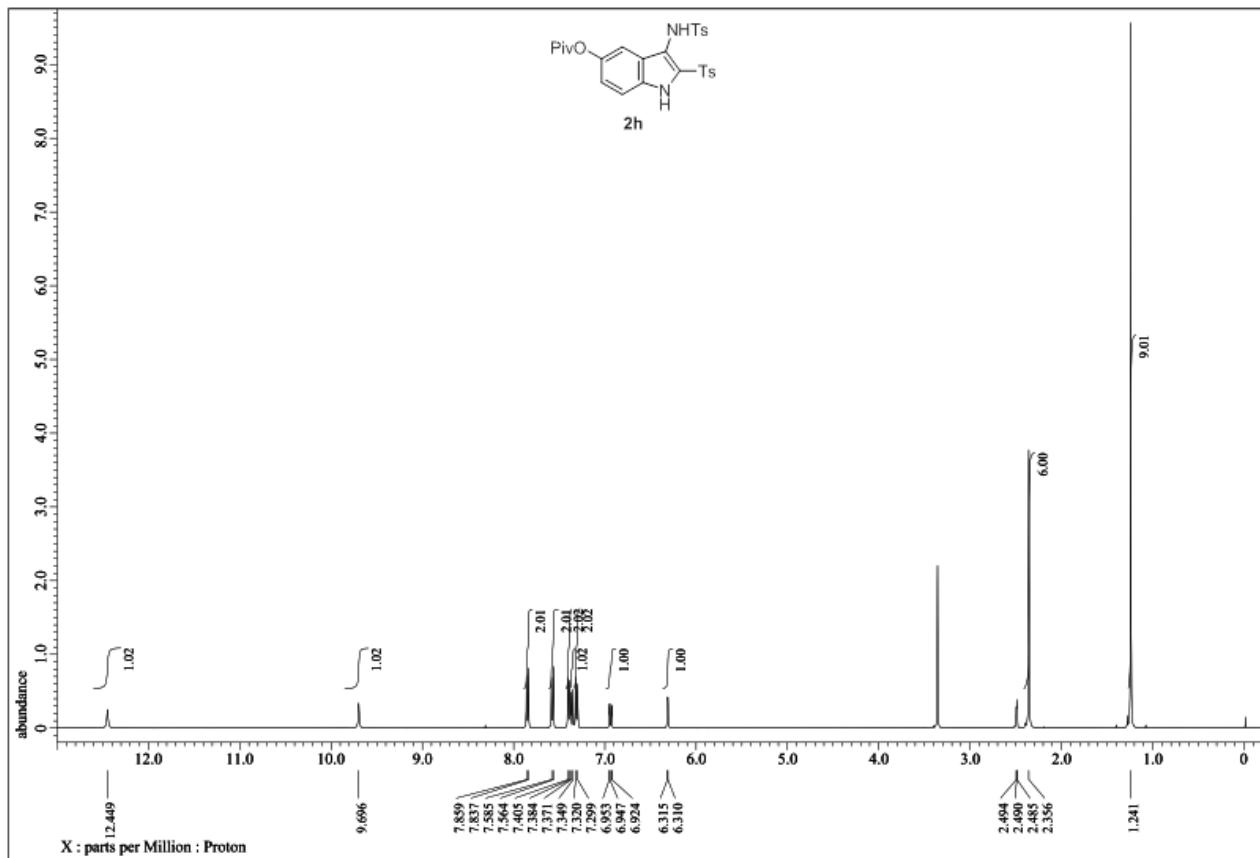
^1H NMR spectrum of **2g** (400 MHz, DMSO-*d*6)



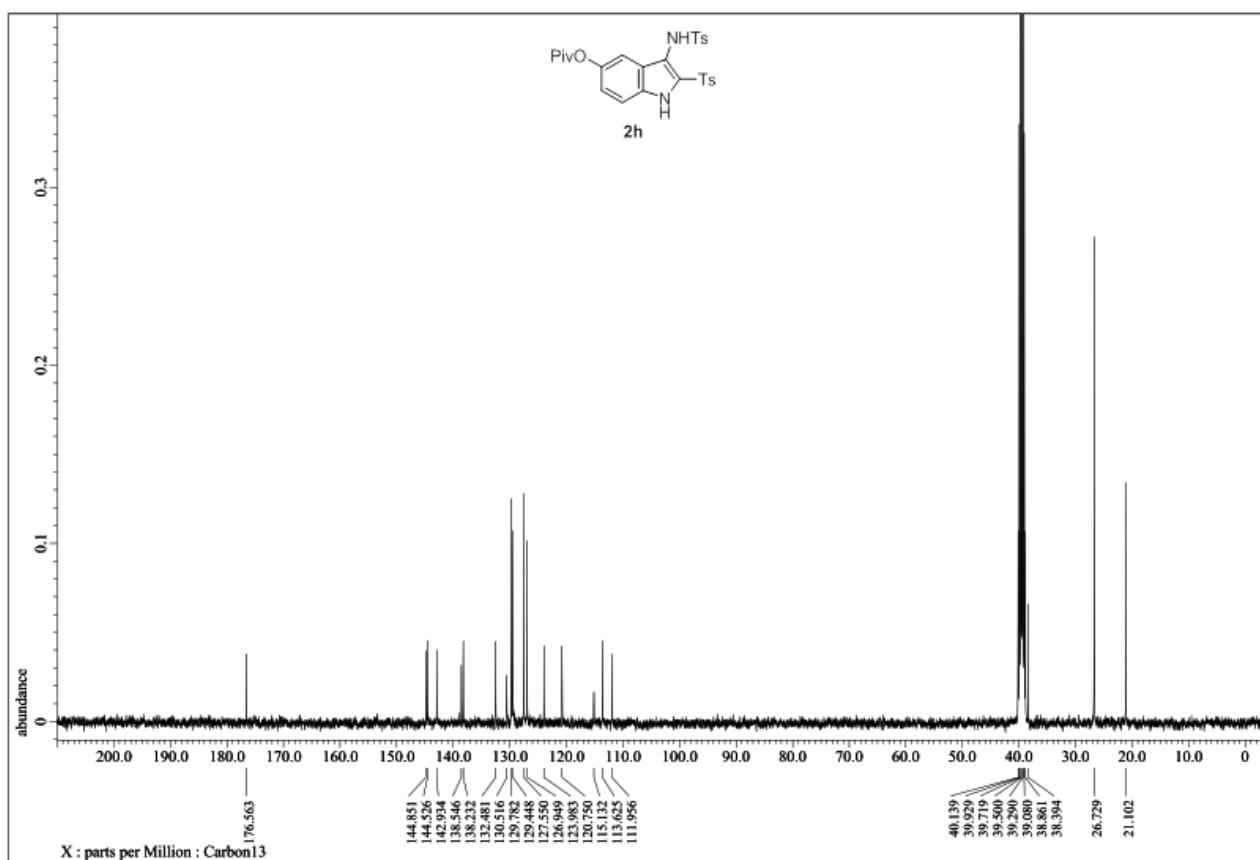
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2g** (400 MHz, DMSO-*d*6)



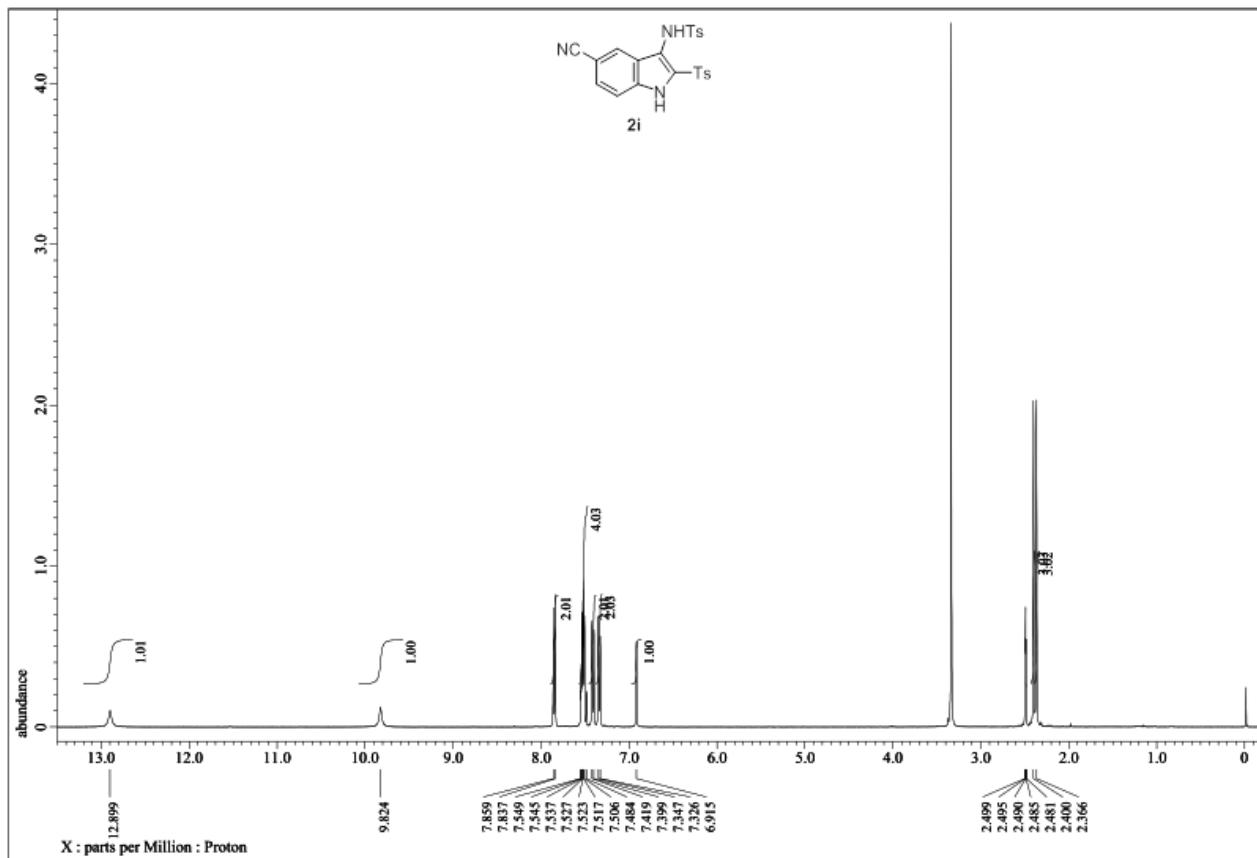
¹H NMR spectrum of **2h** (400 MHz, DMSO-*d*6)



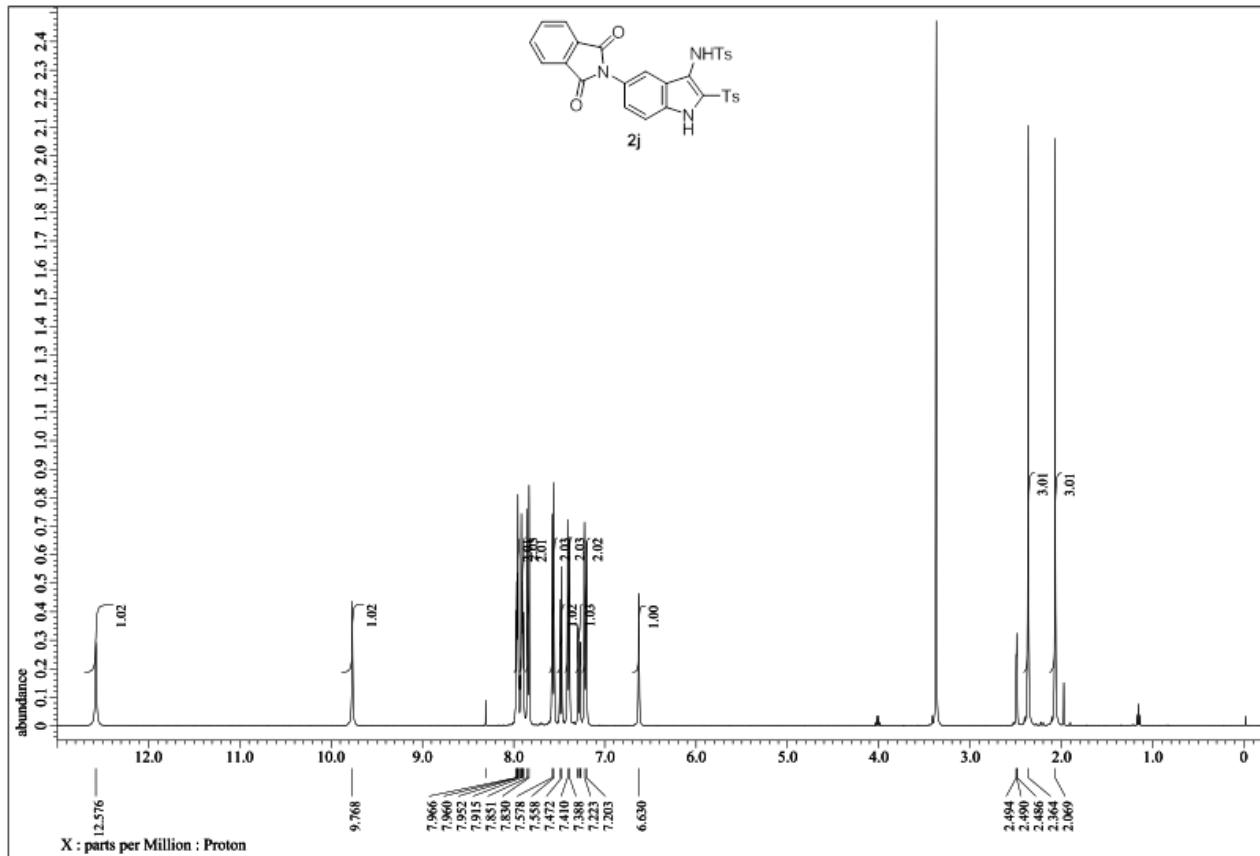
$^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2h** (400 MHz, DMSO-*d*6)



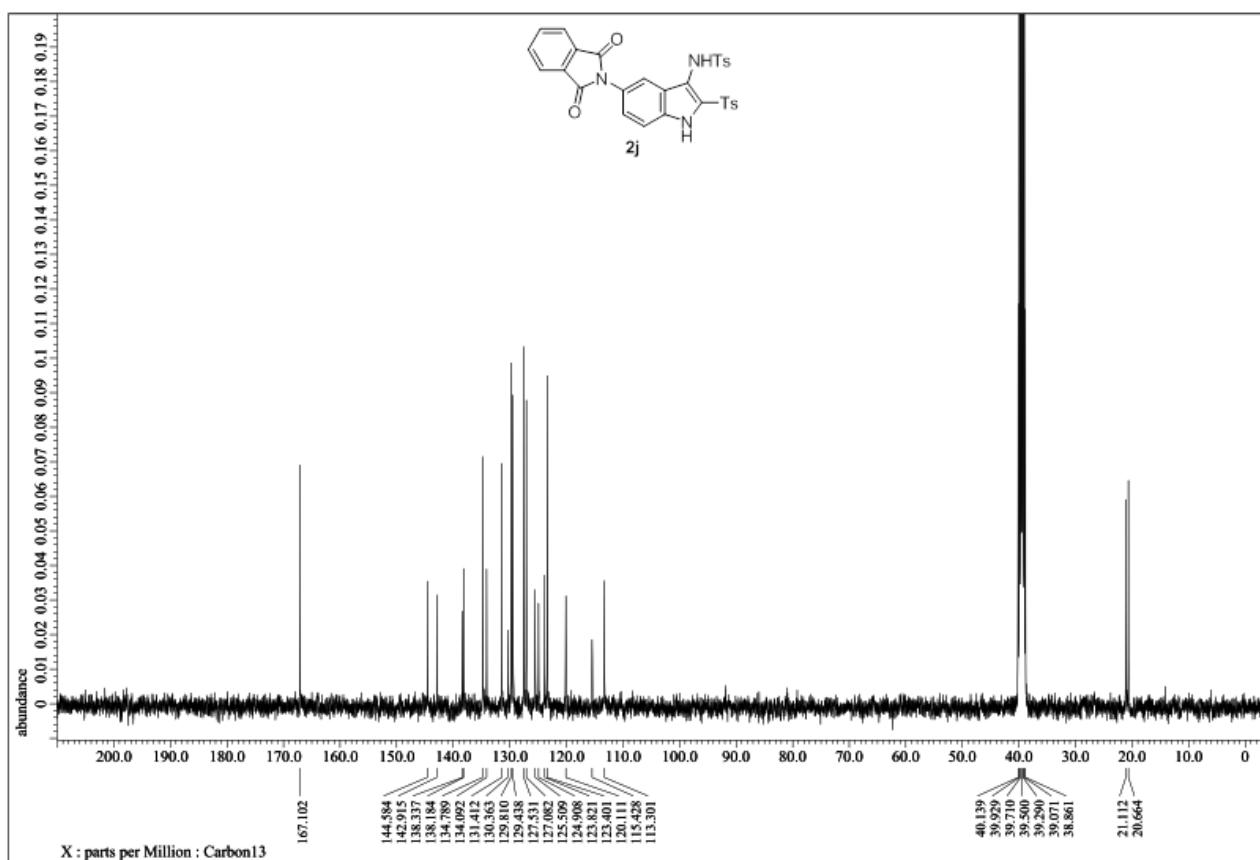
¹H NMR spectrum of **2i** (400 MHz, DMSO-*d*6)



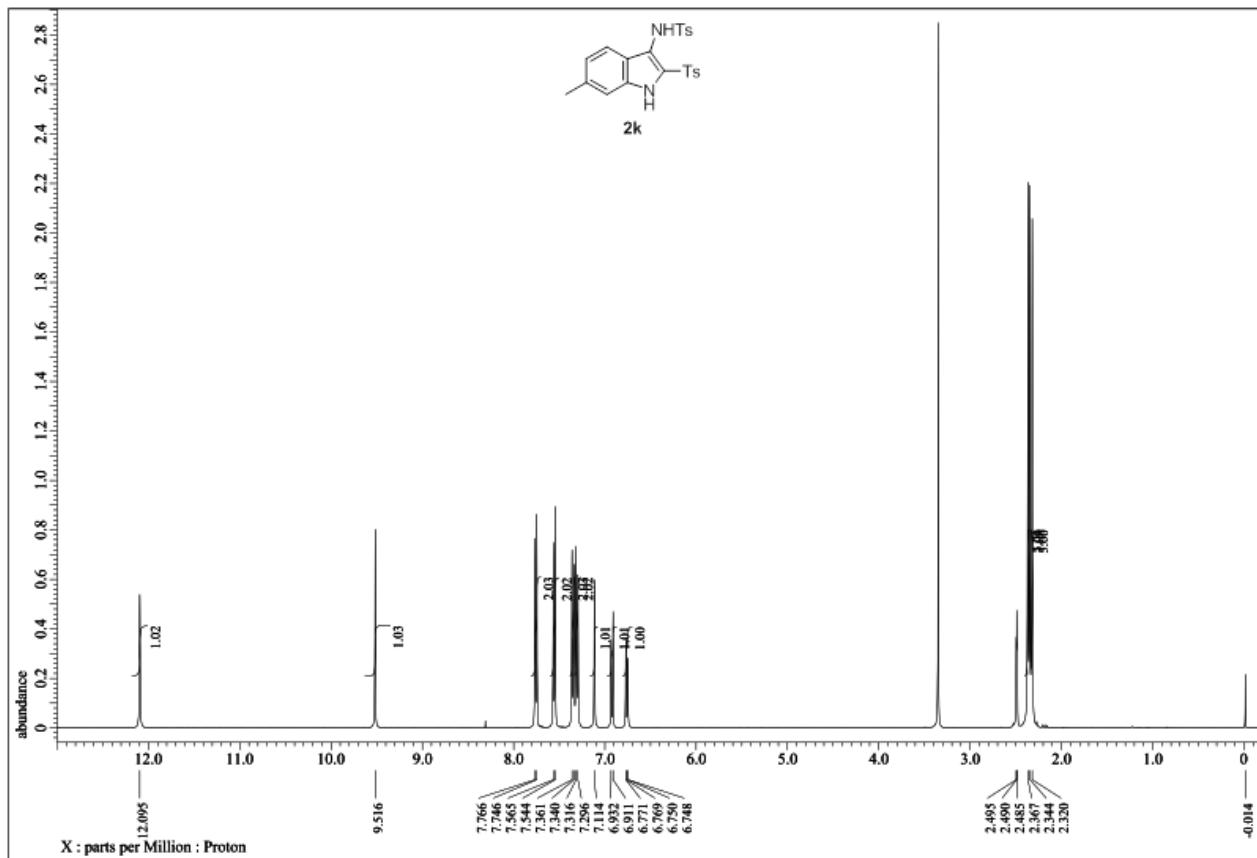
¹H NMR spectrum of **2j** (400 MHz, DMSO-*d*6)



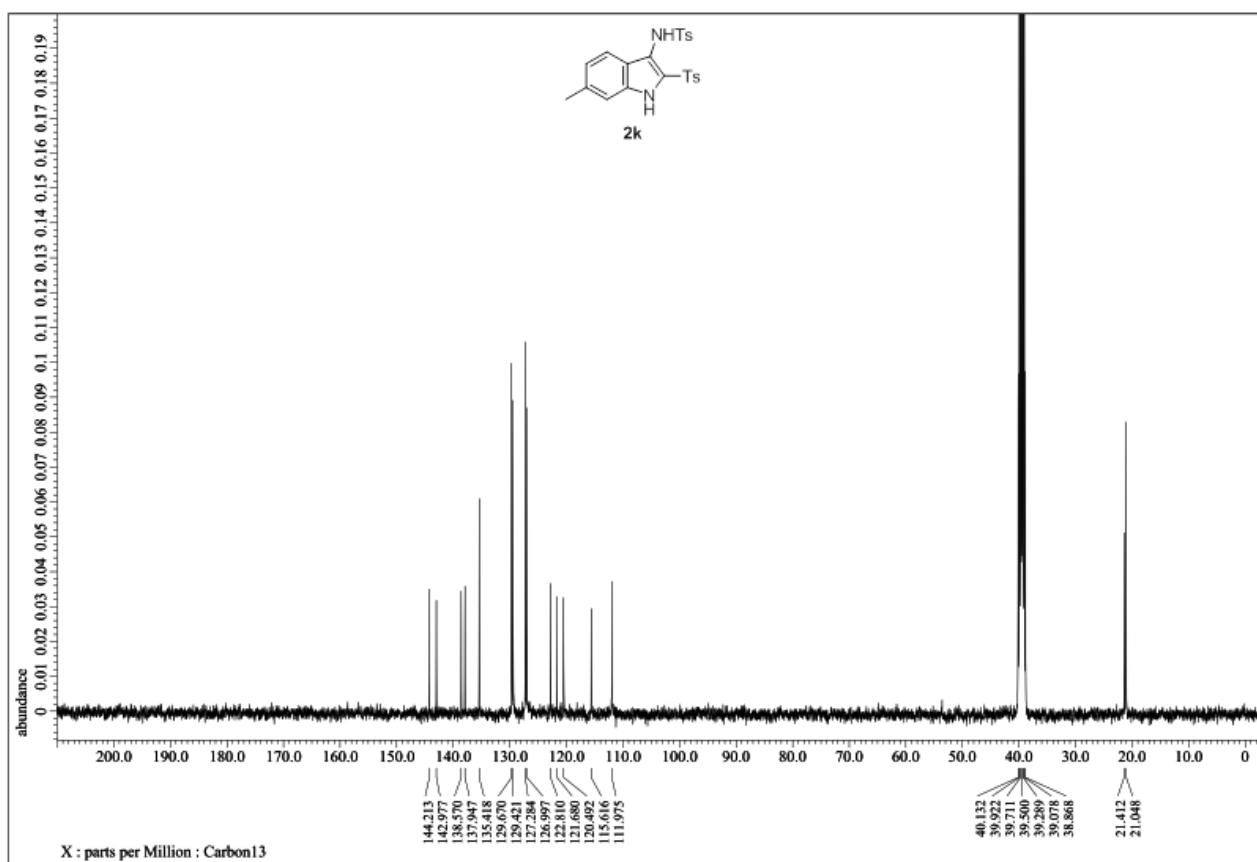
$^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2j** (400 MHz, DMSO-*d*6)



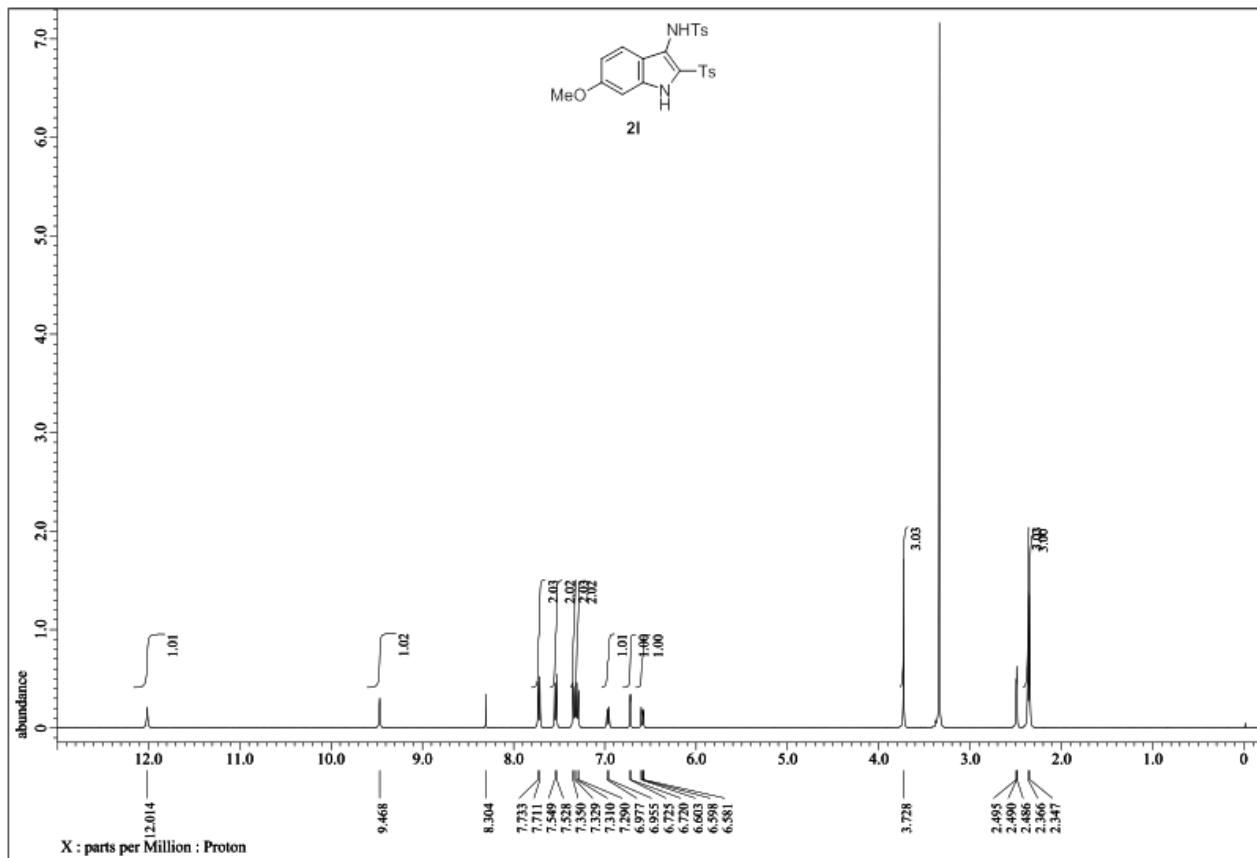
^1H NMR spectrum of **2k** (400 MHz, DMSO-*d*6)



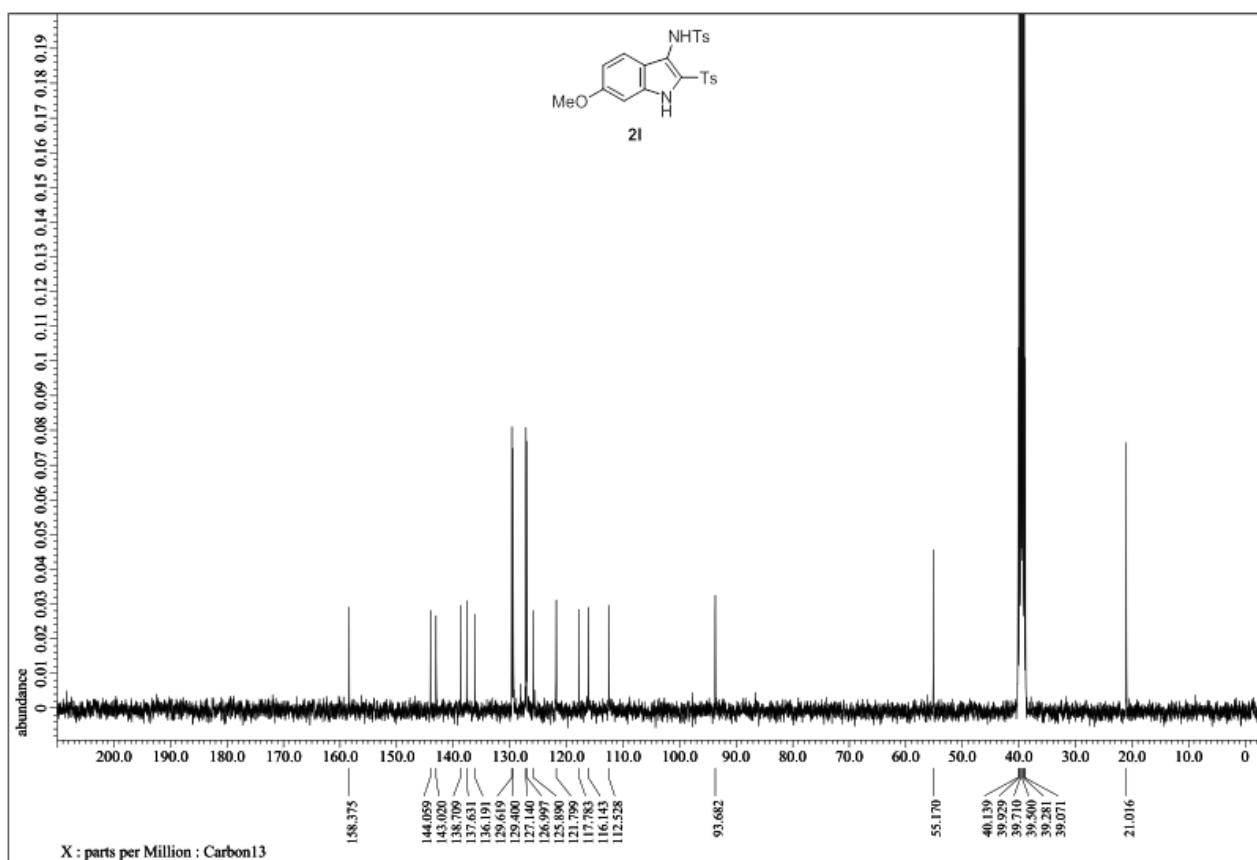
$^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2k** (400 MHz, DMSO-*d*6)



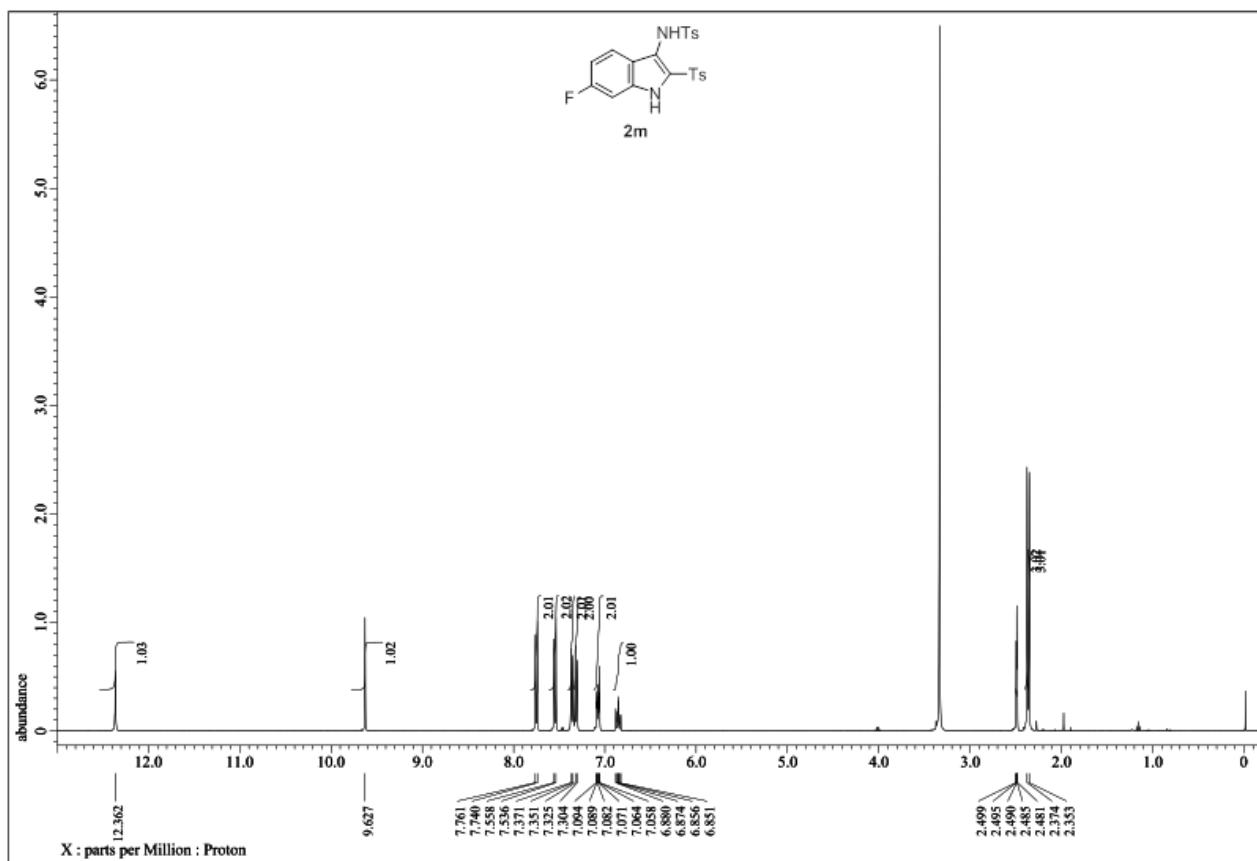
¹H NMR spectrum of **2l** (400 MHz, DMSO-*d*6)



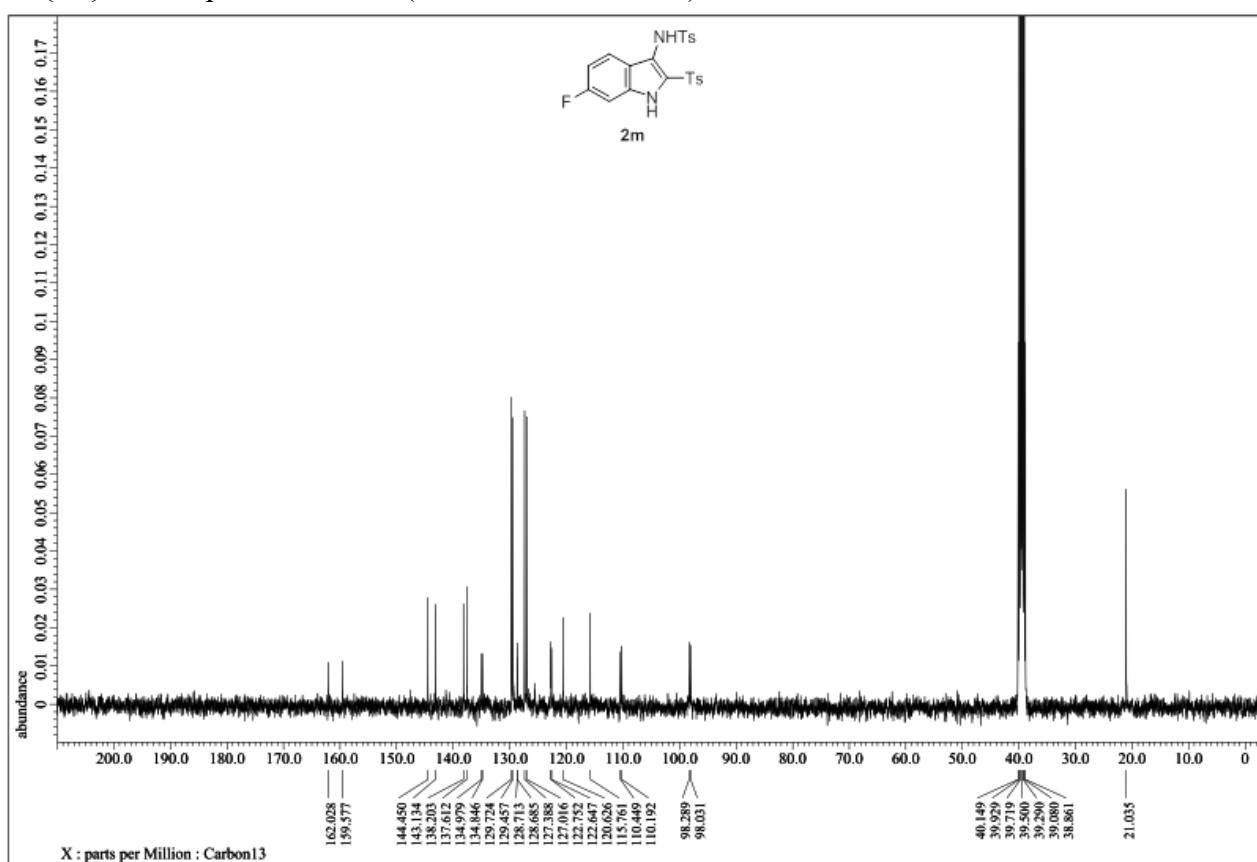
¹³C{¹H} NMR spectrum of **2l** (400 MHz, DMSO-*d*6)



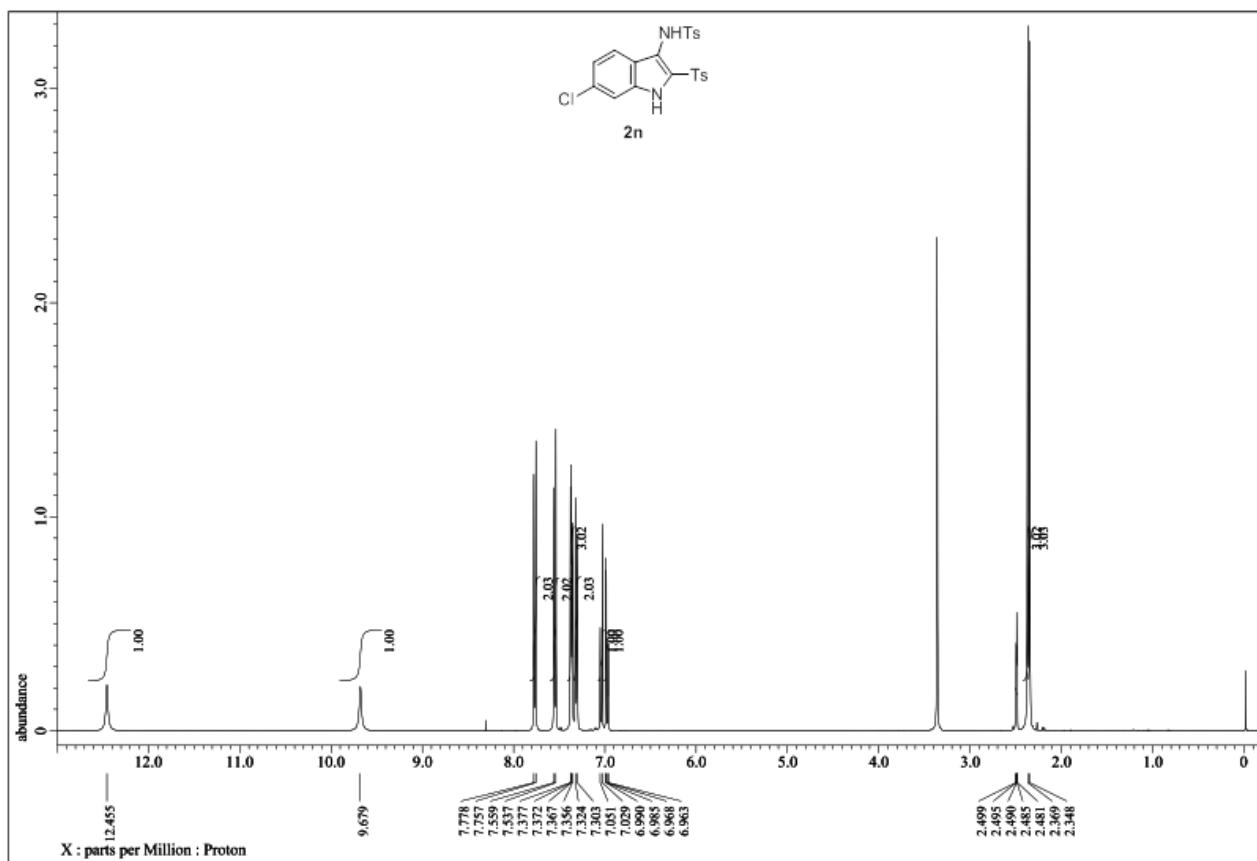
¹H NMR spectrum of **2m** (400 MHz, DMSO-*d*6)



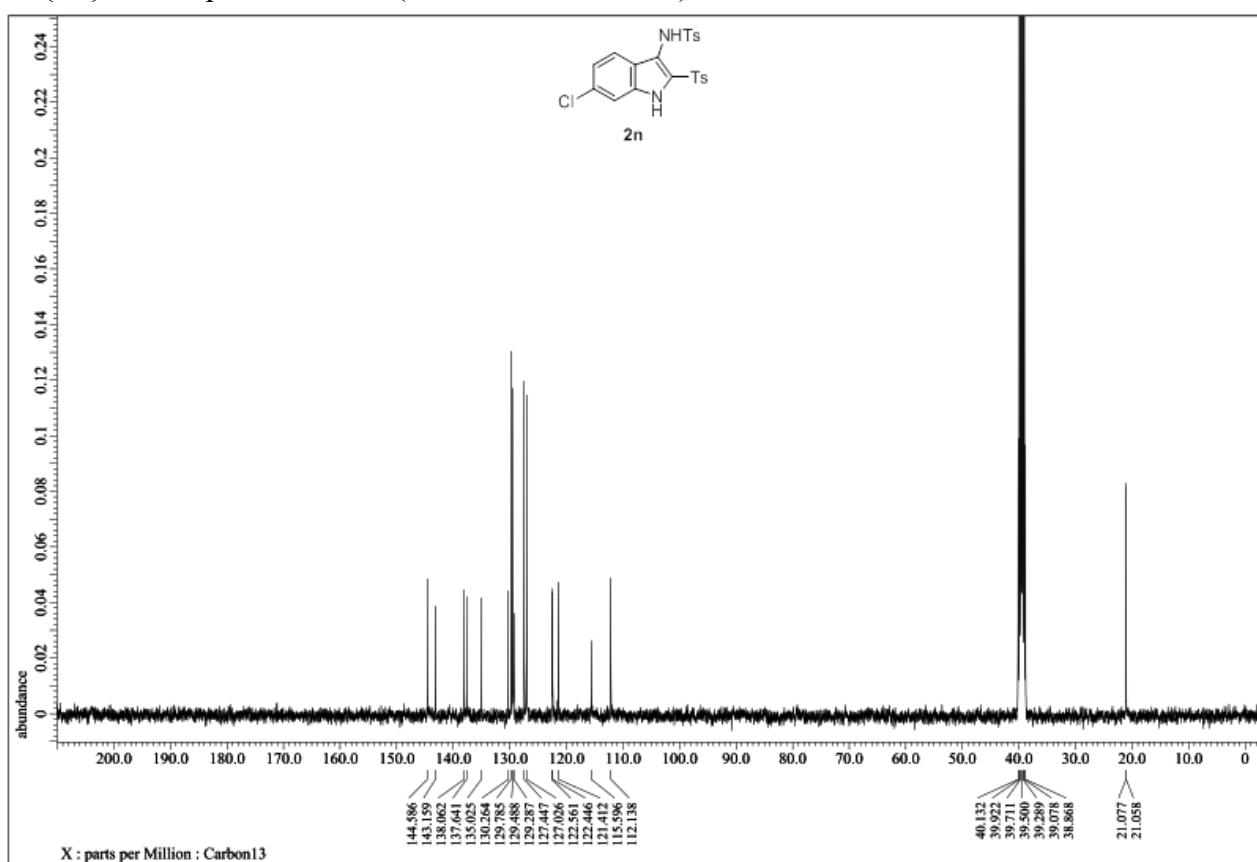
¹³C{¹H} NMR spectrum of **2m** (400 MHz, DMSO-*d*6)



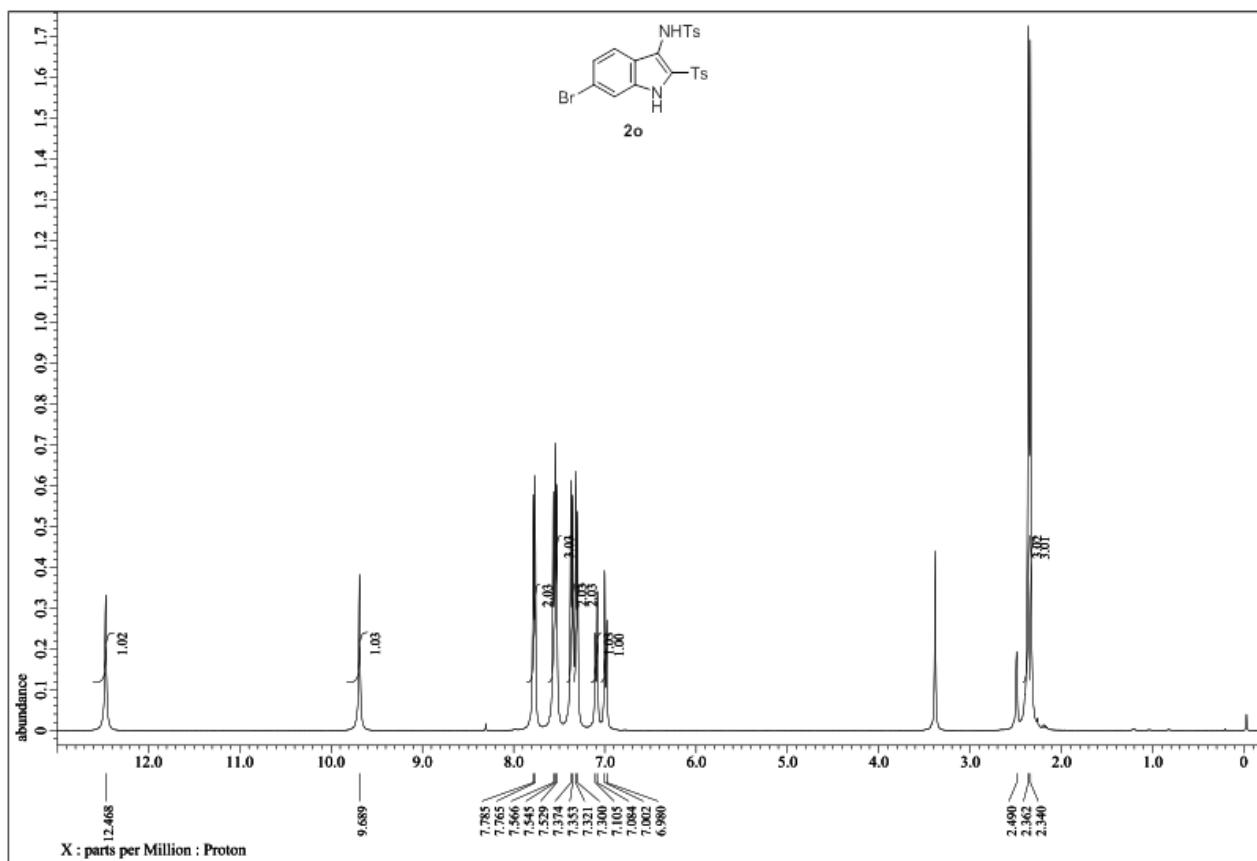
^1H NMR spectrum of **2n** (400 MHz, DMSO-*d*6)



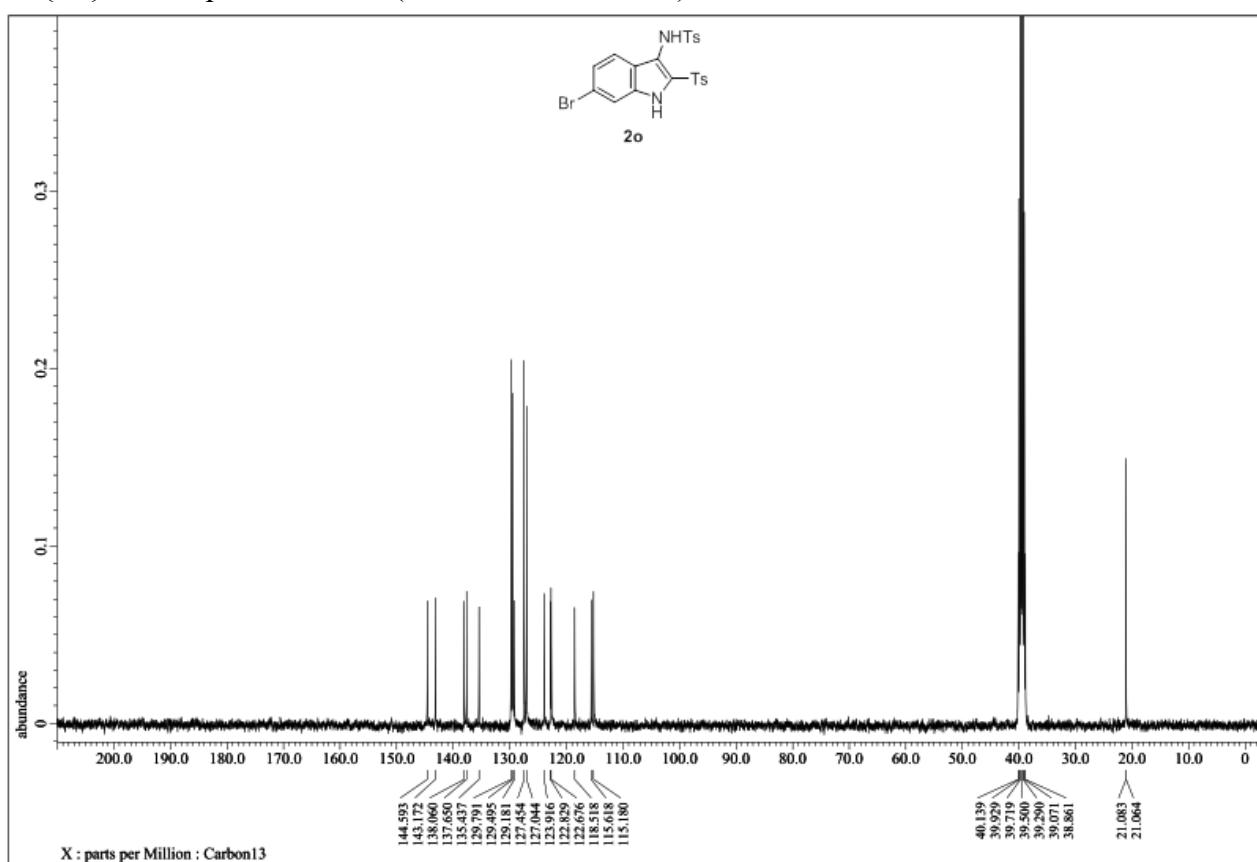
$^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2n** (400 MHz, DMSO-*d*6)



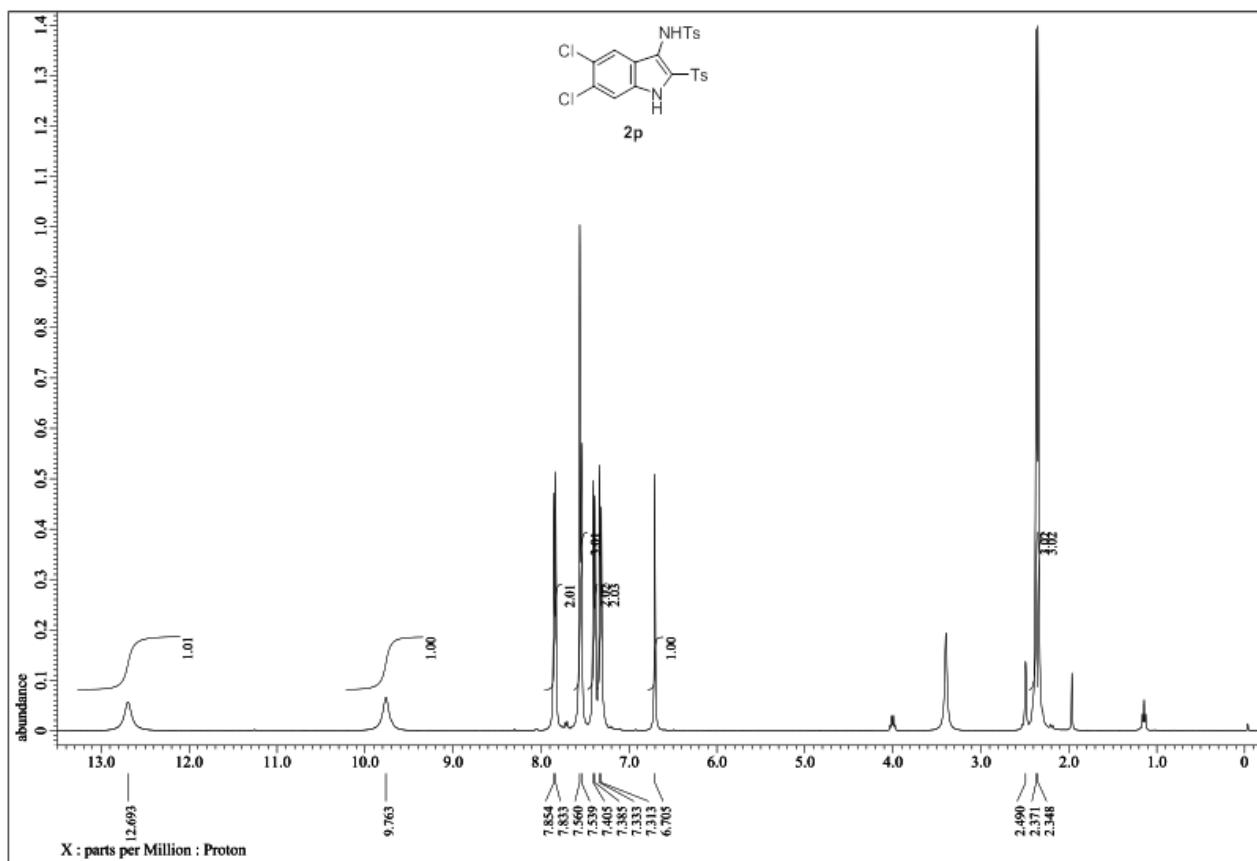
¹H NMR spectrum of **2o** (400 MHz, DMSO-*d*6)



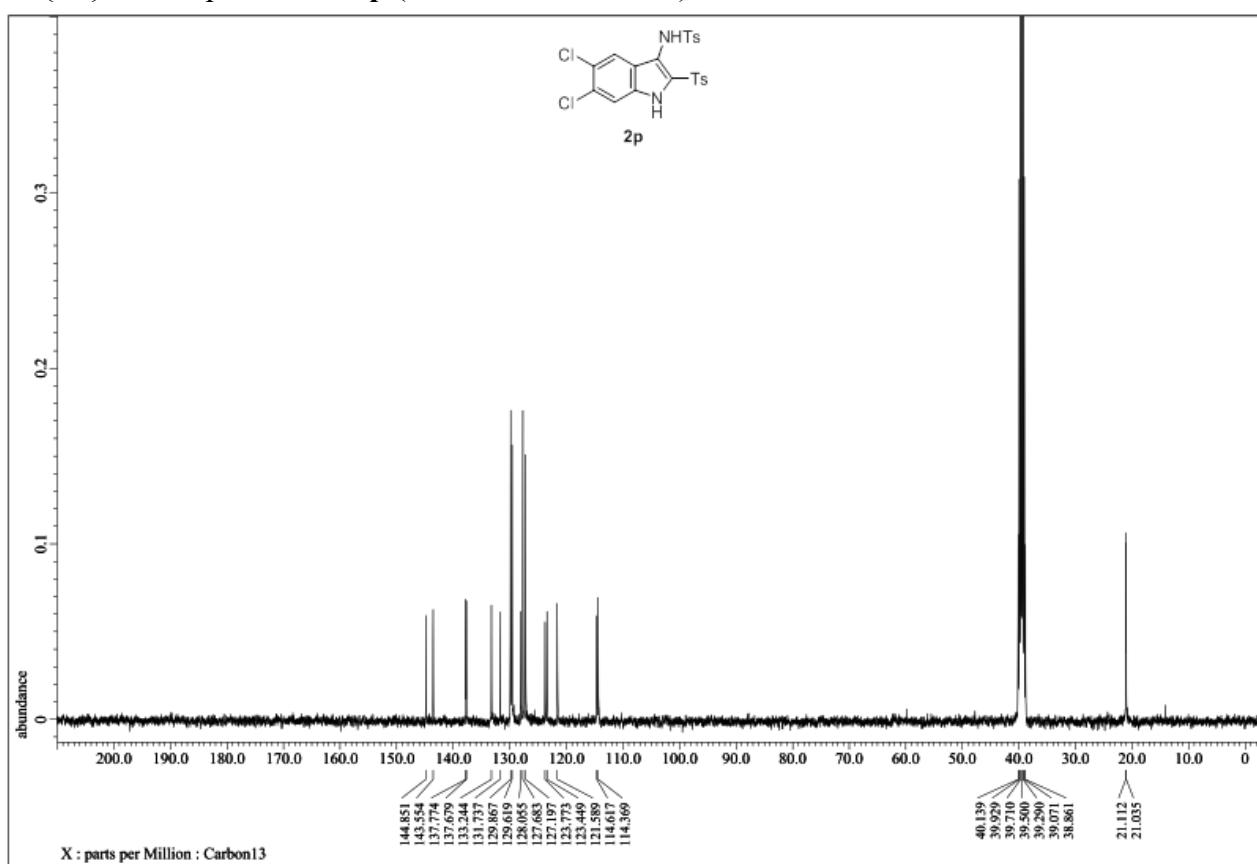
¹³C{¹H} NMR spectrum of **2o** (400 MHz, DMSO-*d*6)



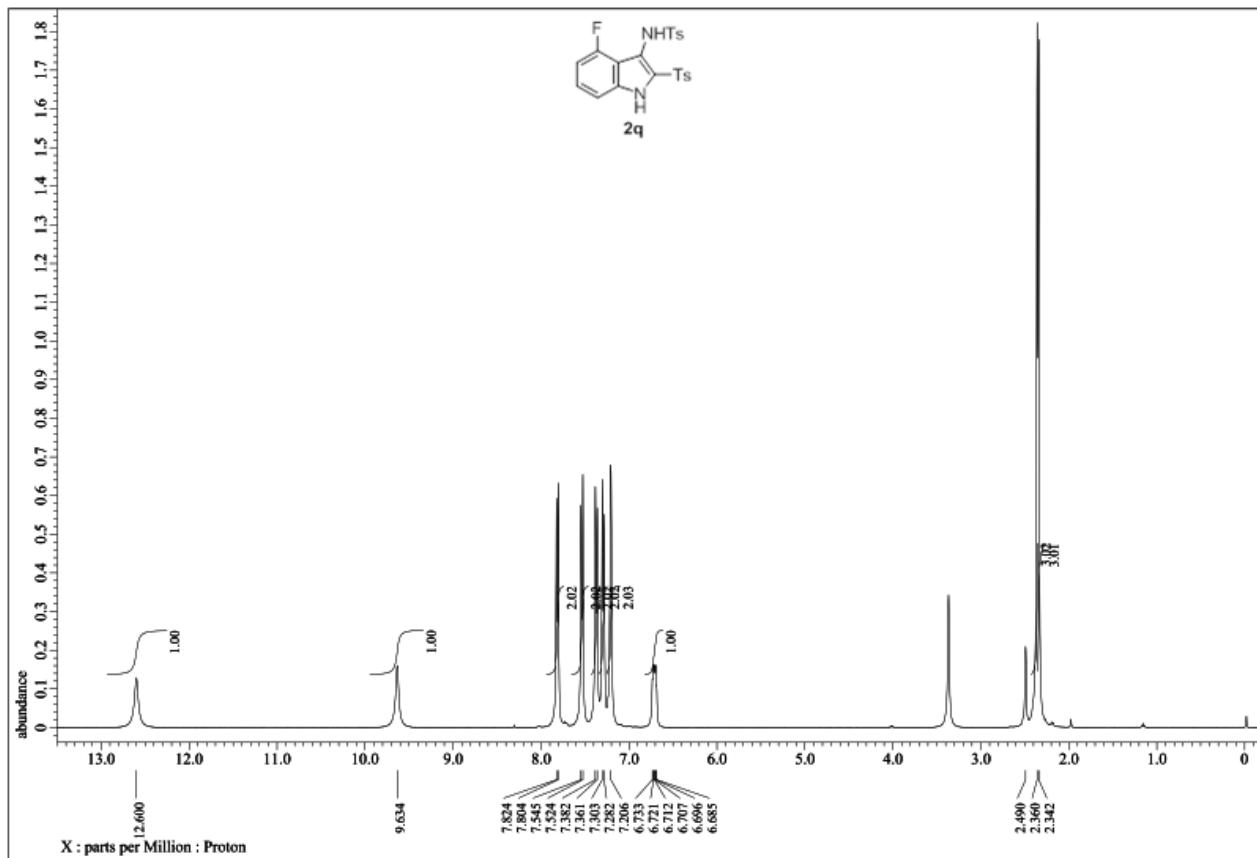
^1H NMR spectrum of **2p** (400 MHz, DMSO-*d*6)



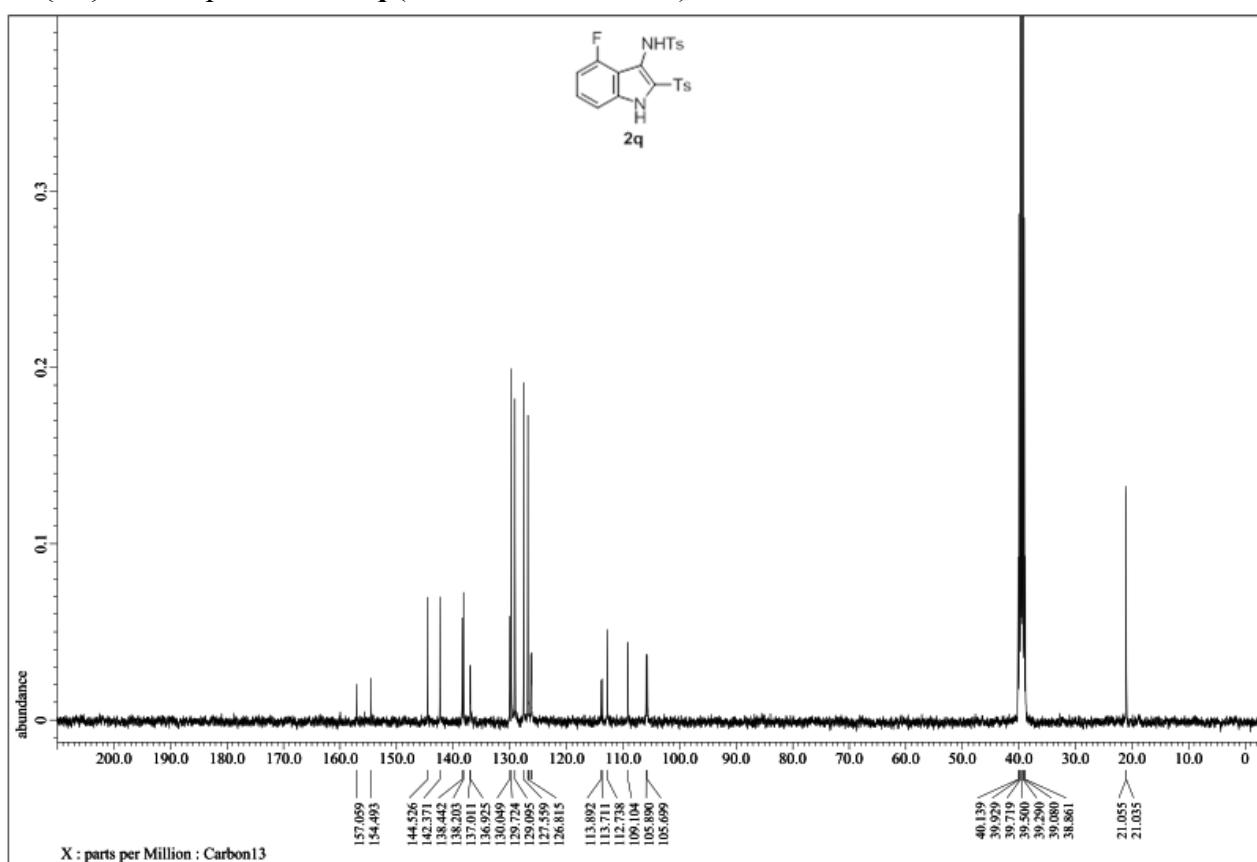
$^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2p** (400 MHz, DMSO-*d*6)



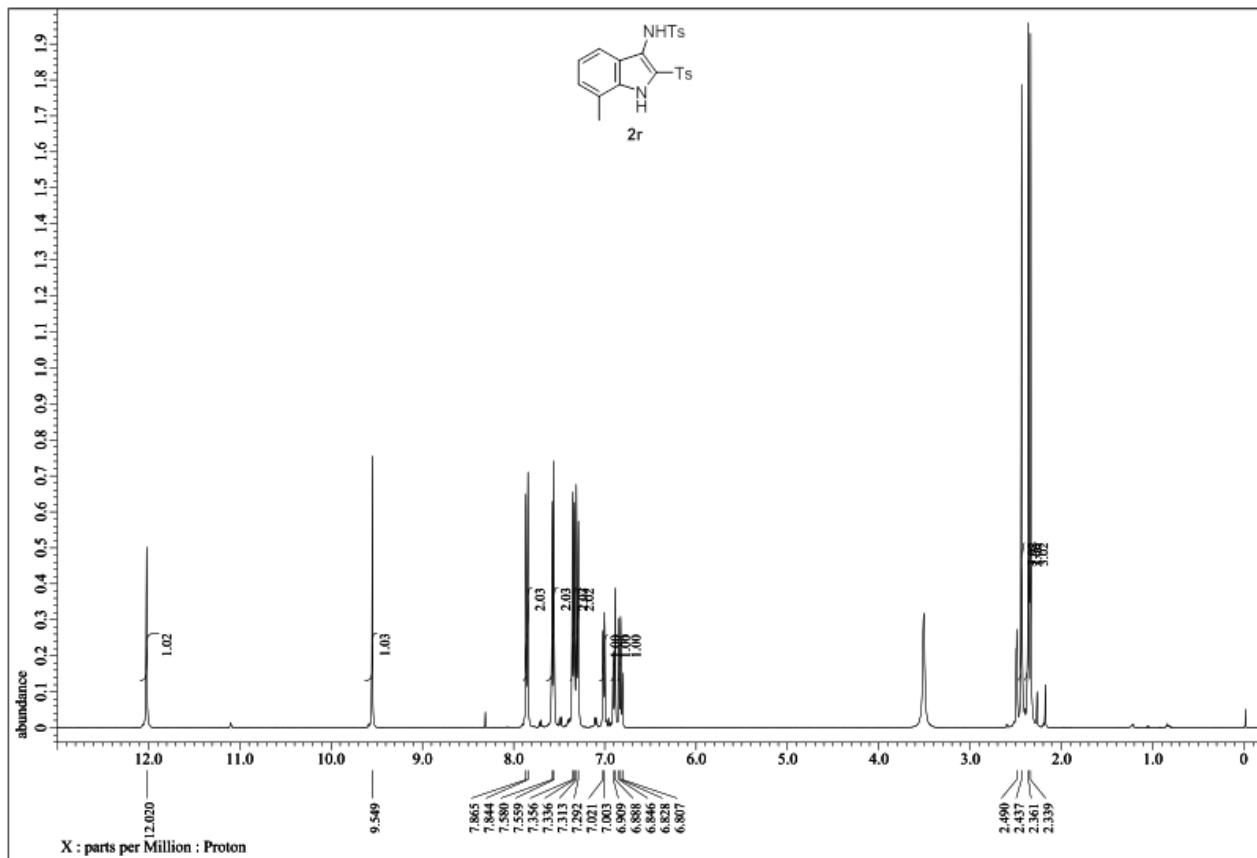
¹H NMR spectrum of **2q** (400 MHz, DMSO-*d*6)



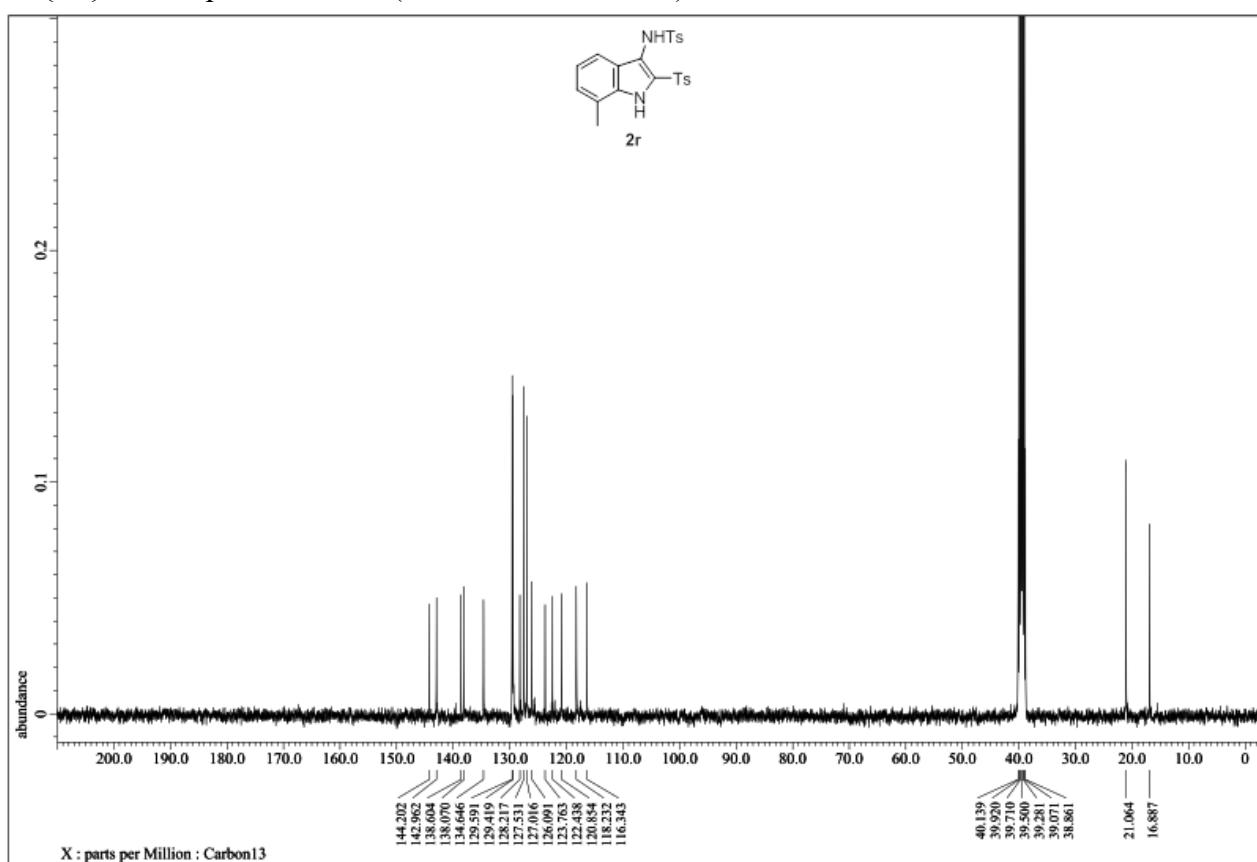
¹³C{¹H} NMR spectrum of **2q** (400 MHz, DMSO-*d*6)



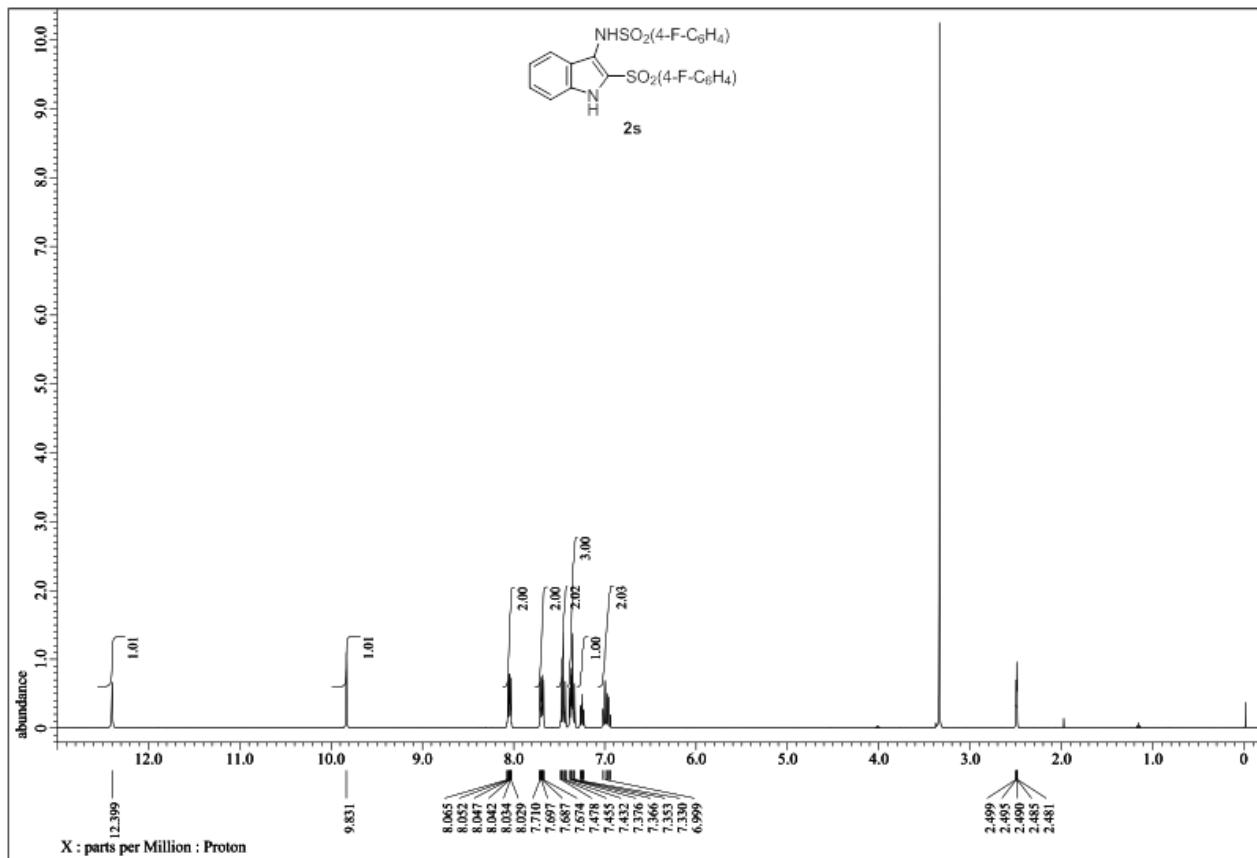
^1H NMR spectrum of **2r** (400 MHz, DMSO-*d*6)



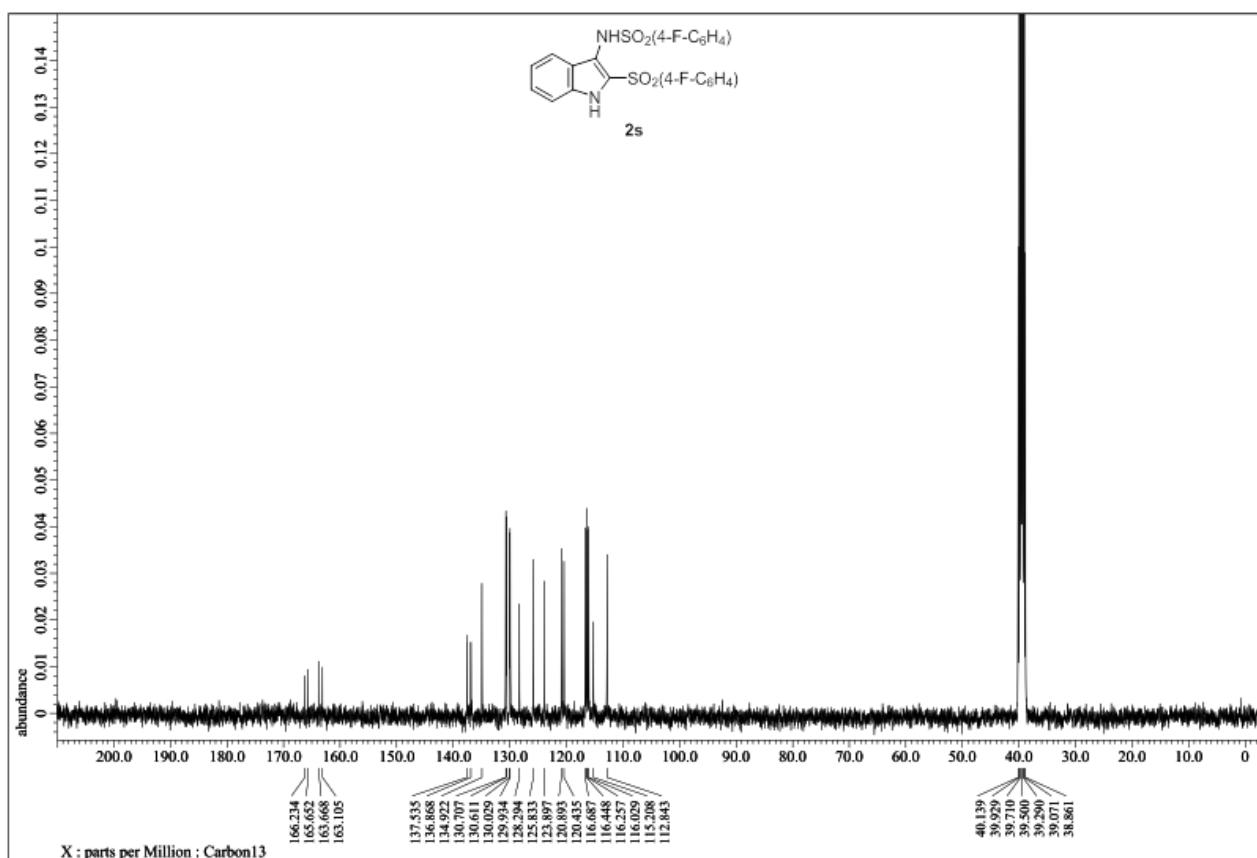
$^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2r** (400 MHz, DMSO-*d*6)



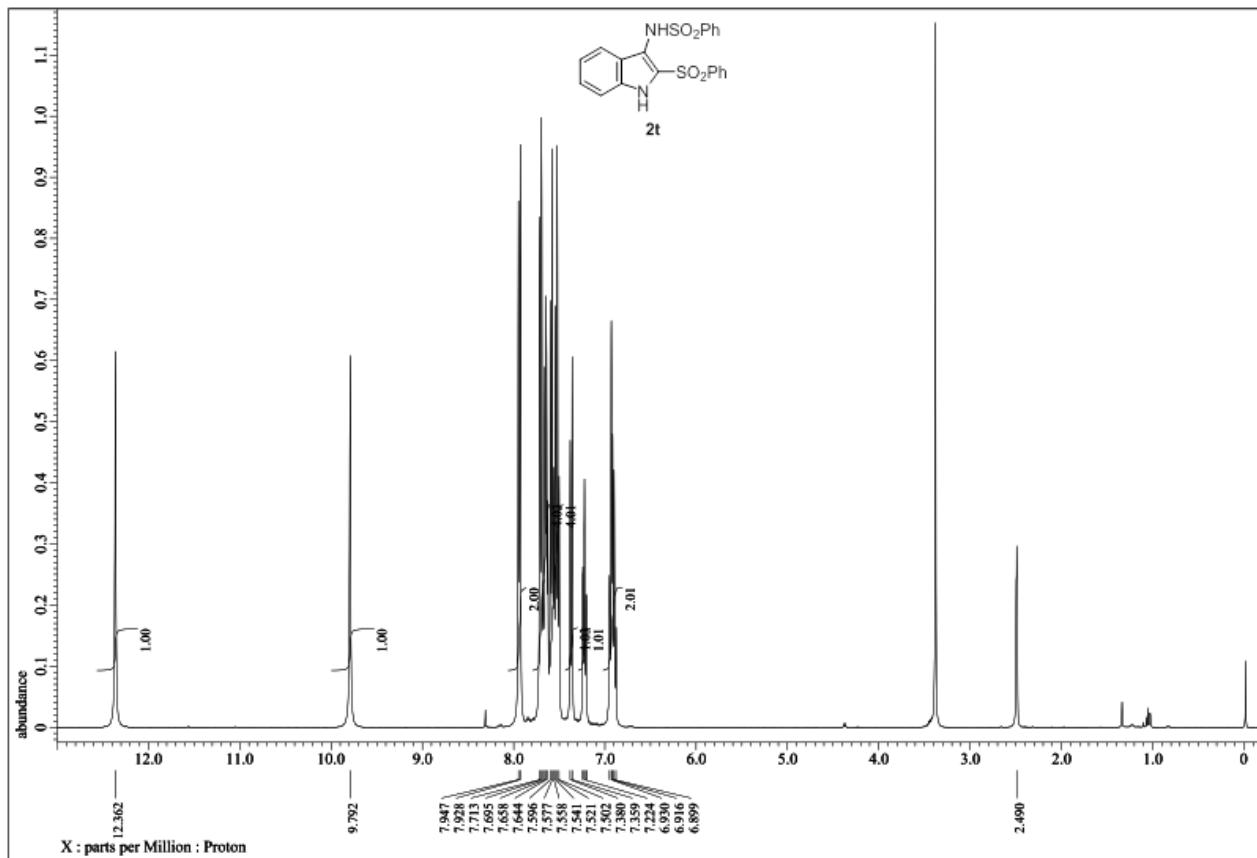
^1H NMR spectrum of **2s** (400 MHz, DMSO-*d*6)



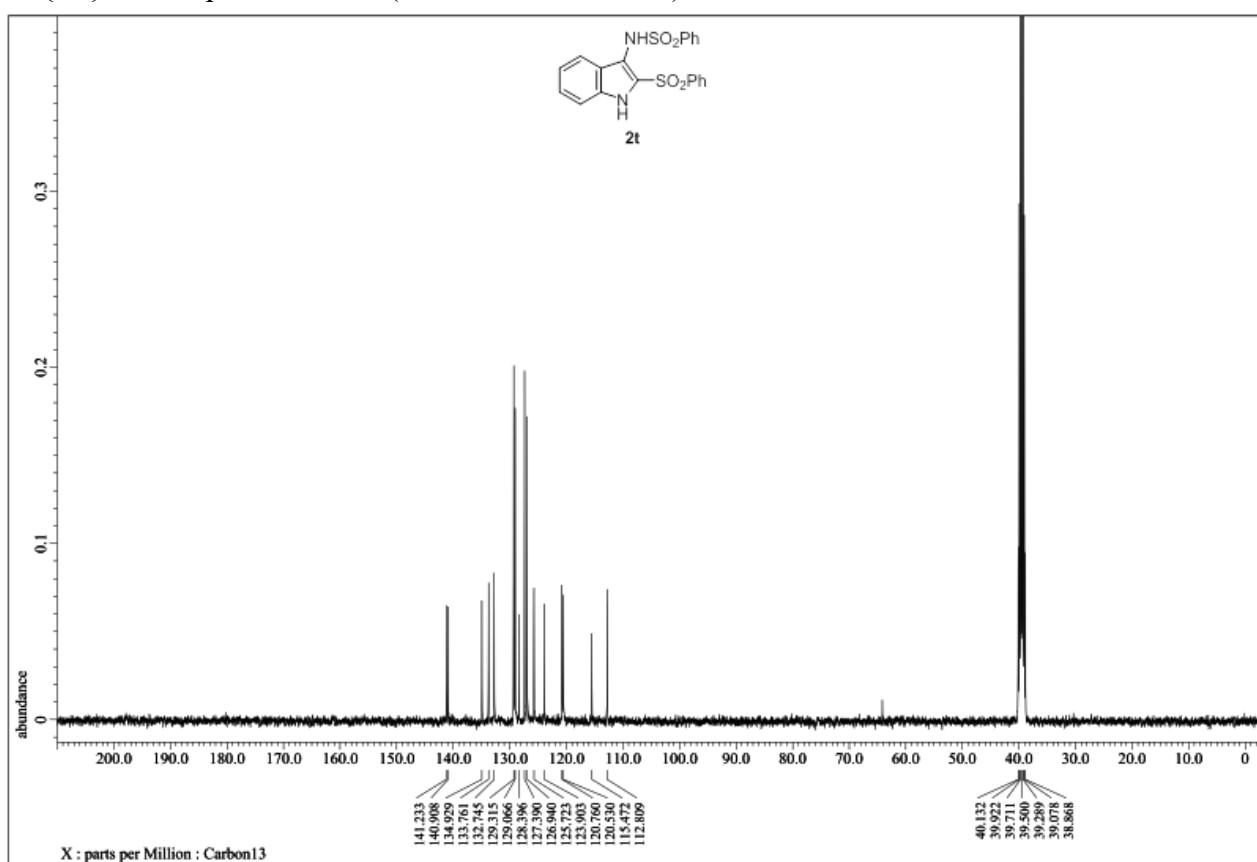
$^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2s** (400 MHz, DMSO-*d*6)



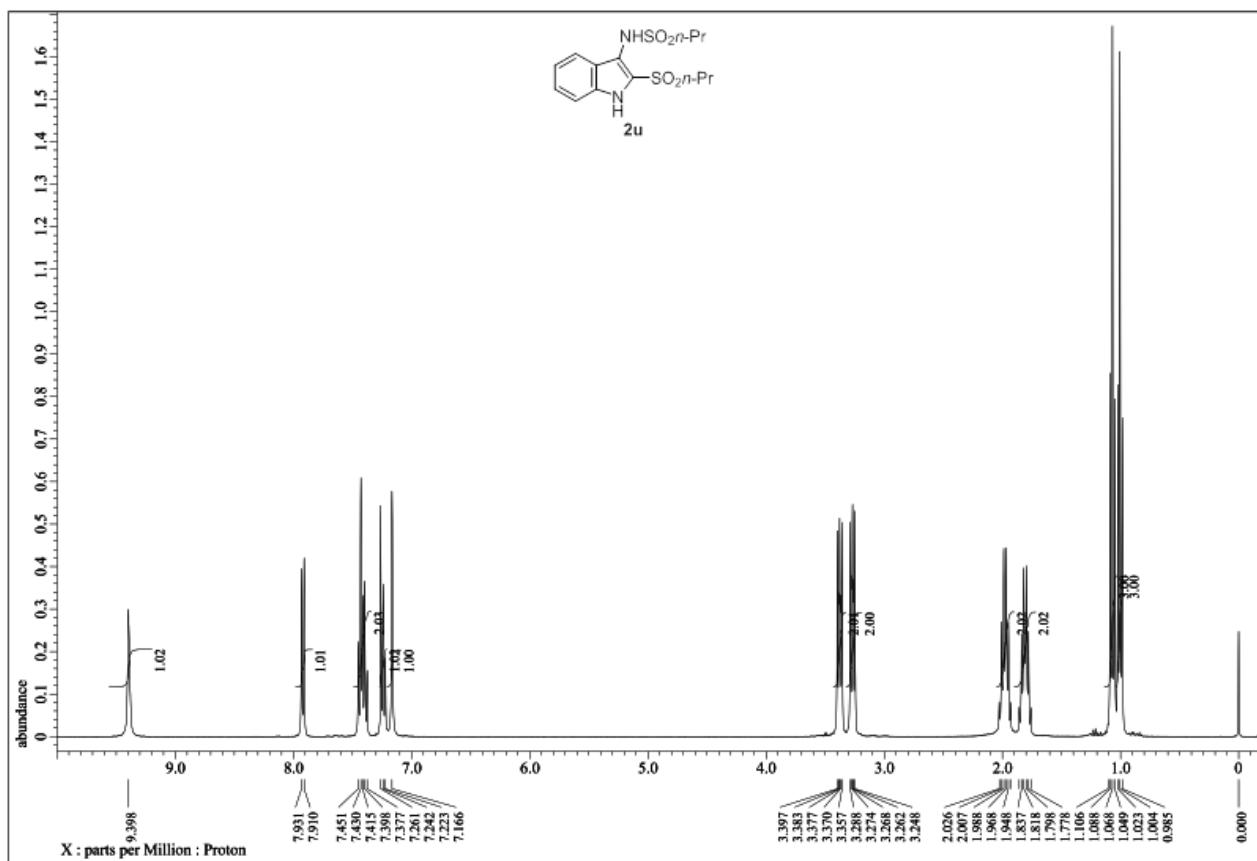
^1H NMR spectrum of **2t** (400 MHz, DMSO-*d*6)



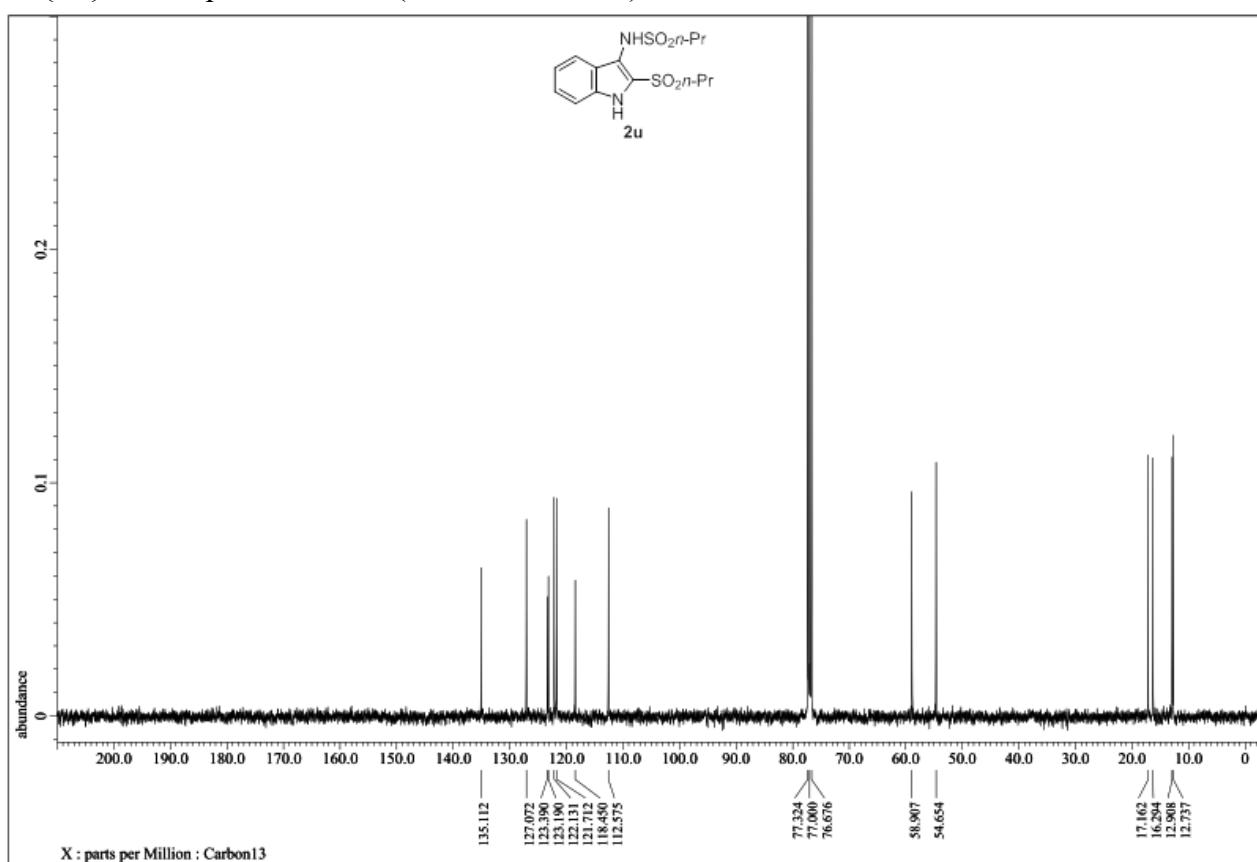
$^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2t** (400 MHz, DMSO-*d*6)



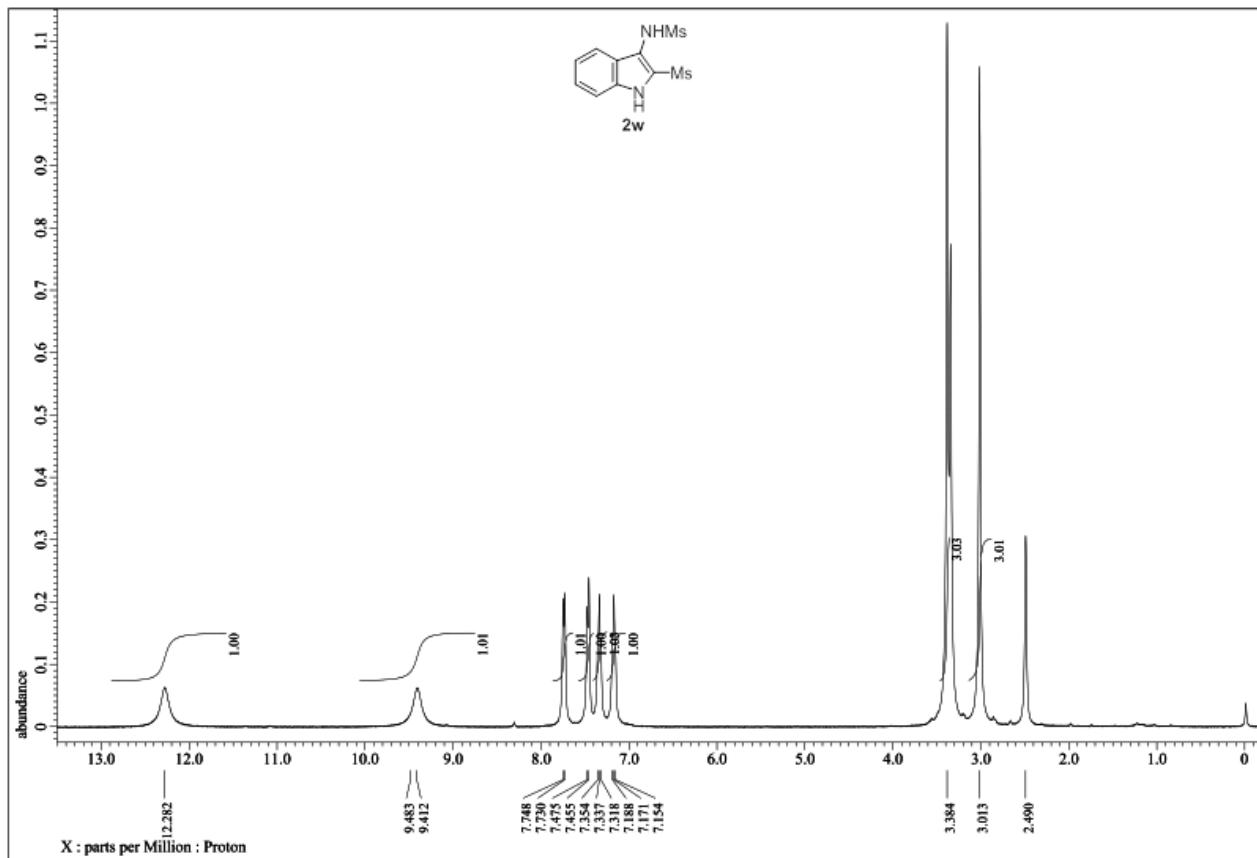
^1H NMR spectrum of **2u** (400 MHz, CDCl_3)



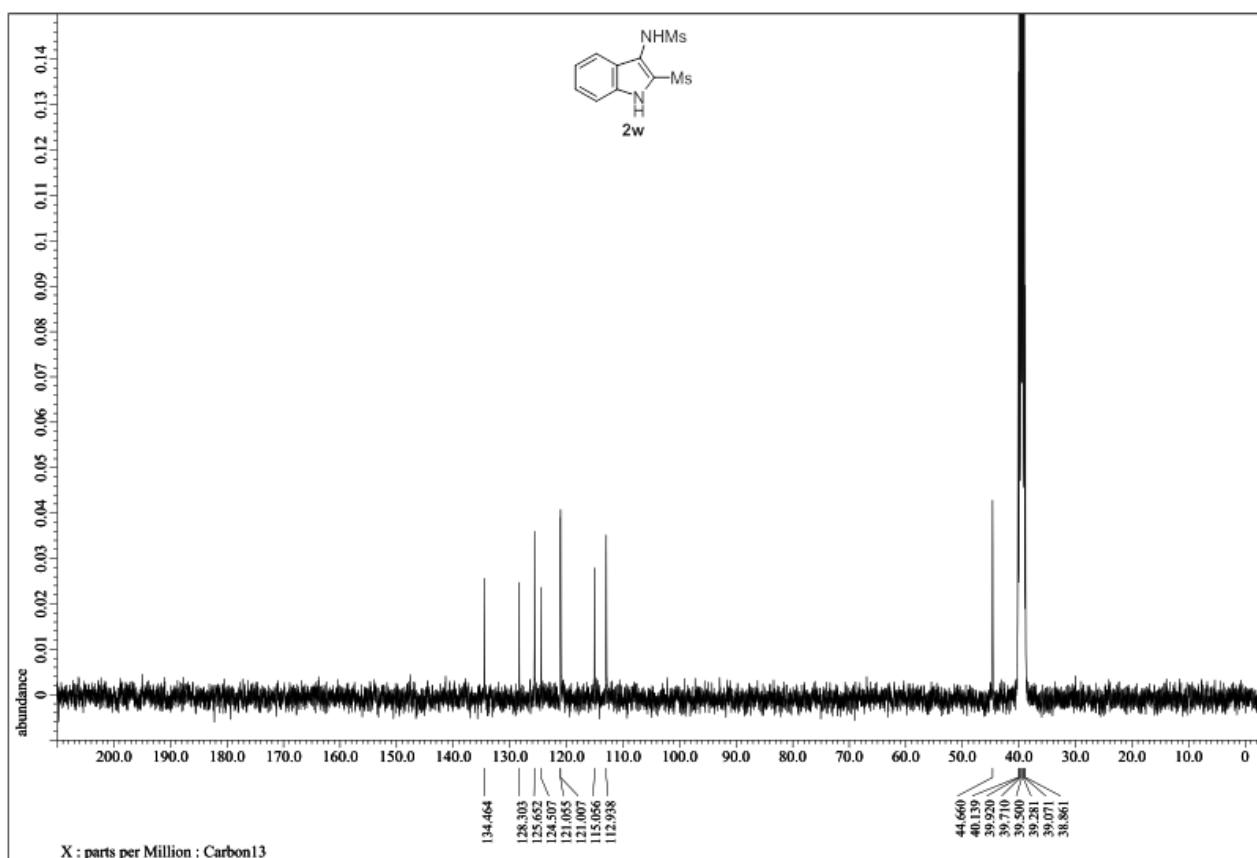
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2u** (400 MHz, CDCl_3)



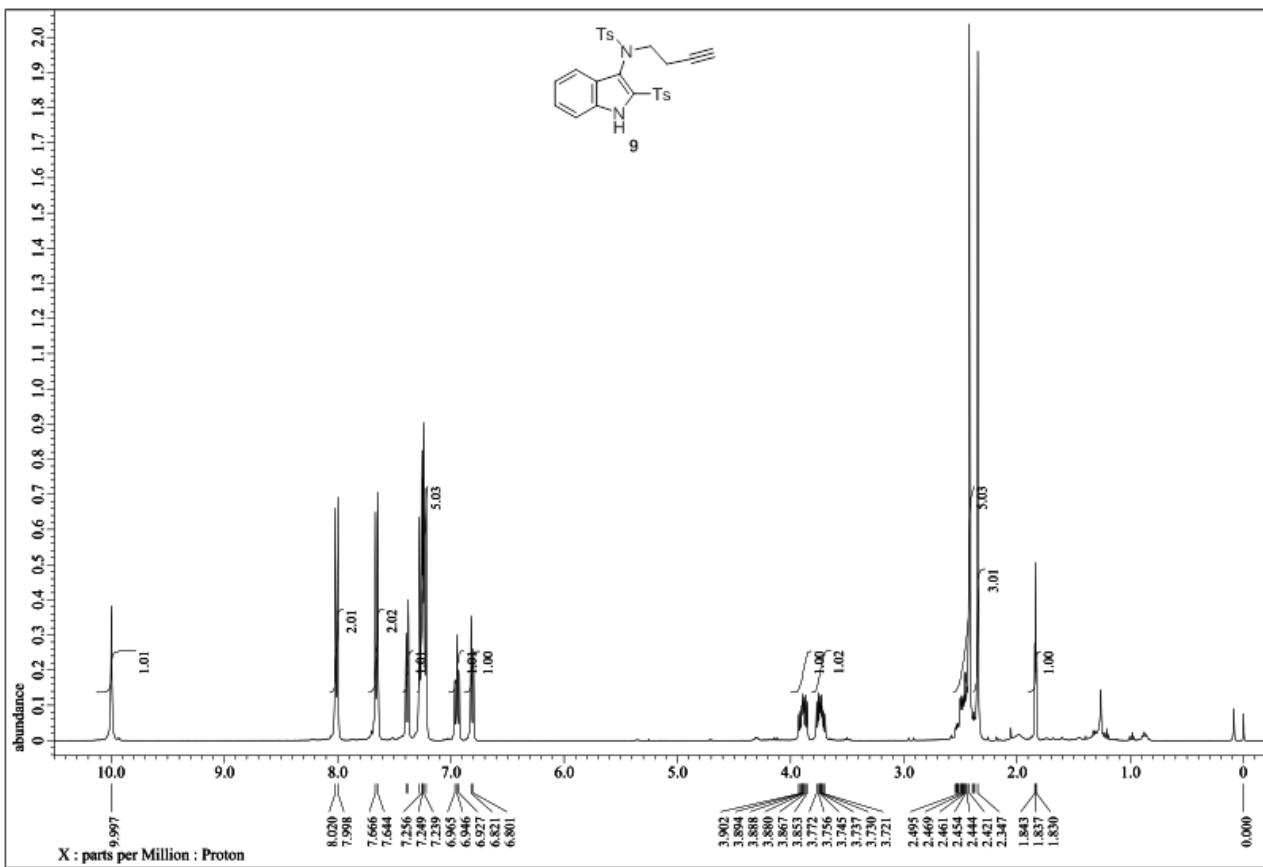
^1H NMR spectrum of **2w** (400 MHz, DMSO-*d*6)



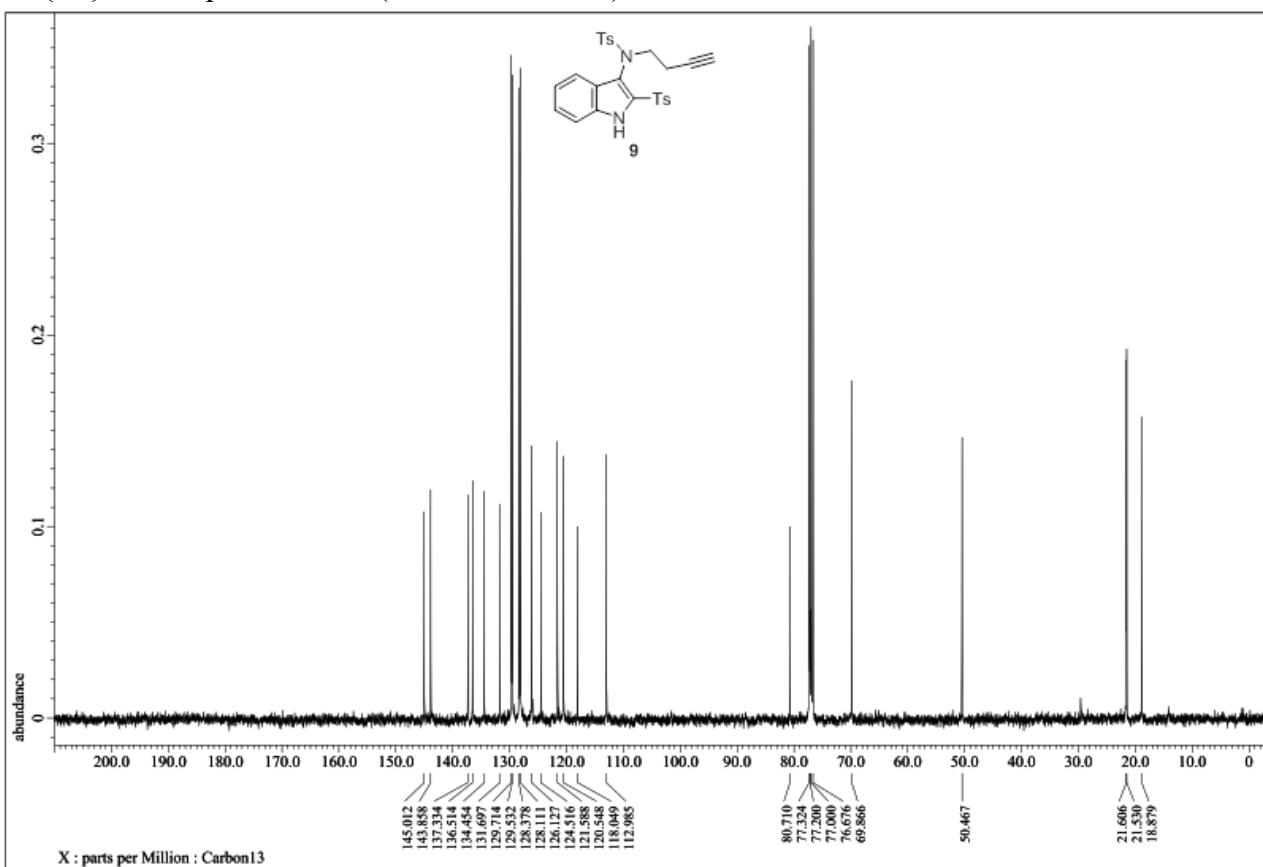
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2w** (400 MHz, DMSO-*d*6)



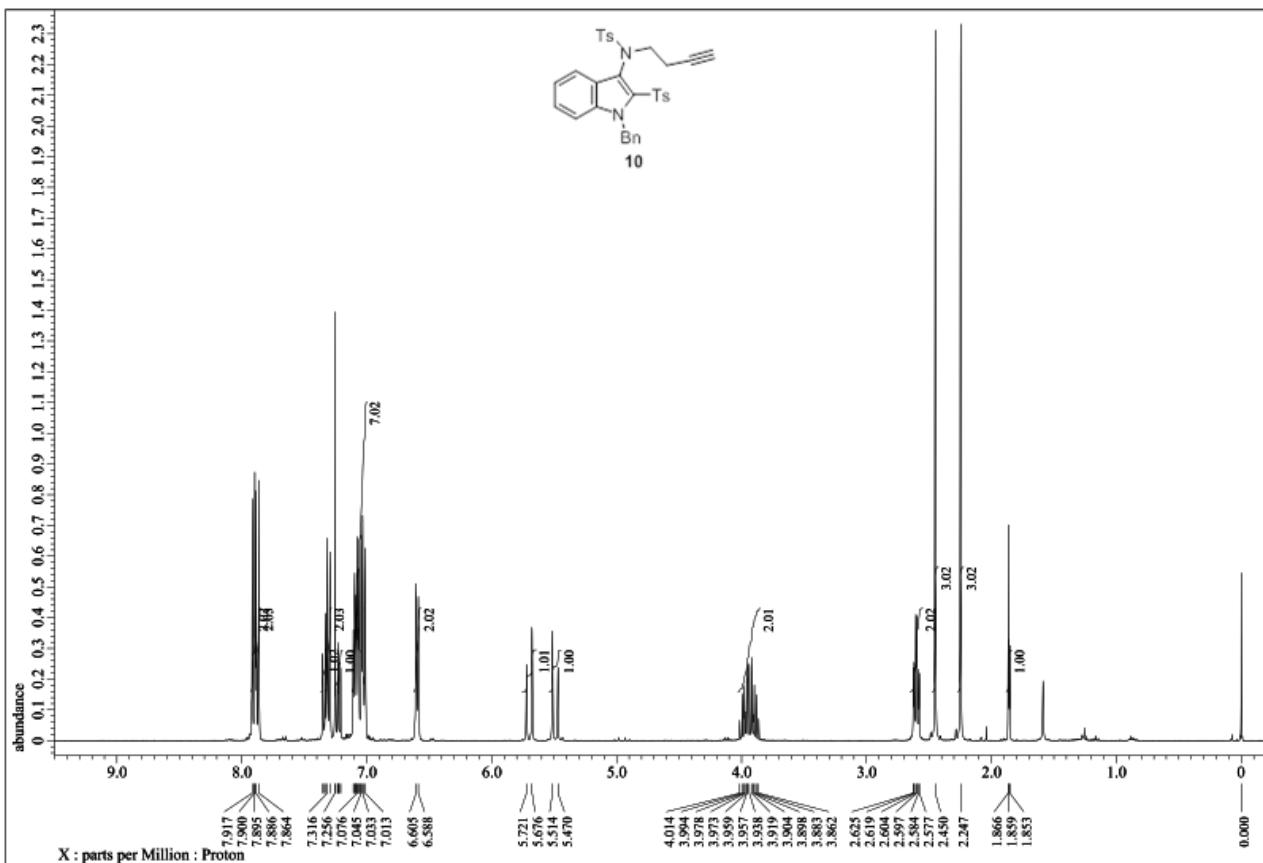
^1H NMR spectrum of **9** (400 MHz, CDCl_3)



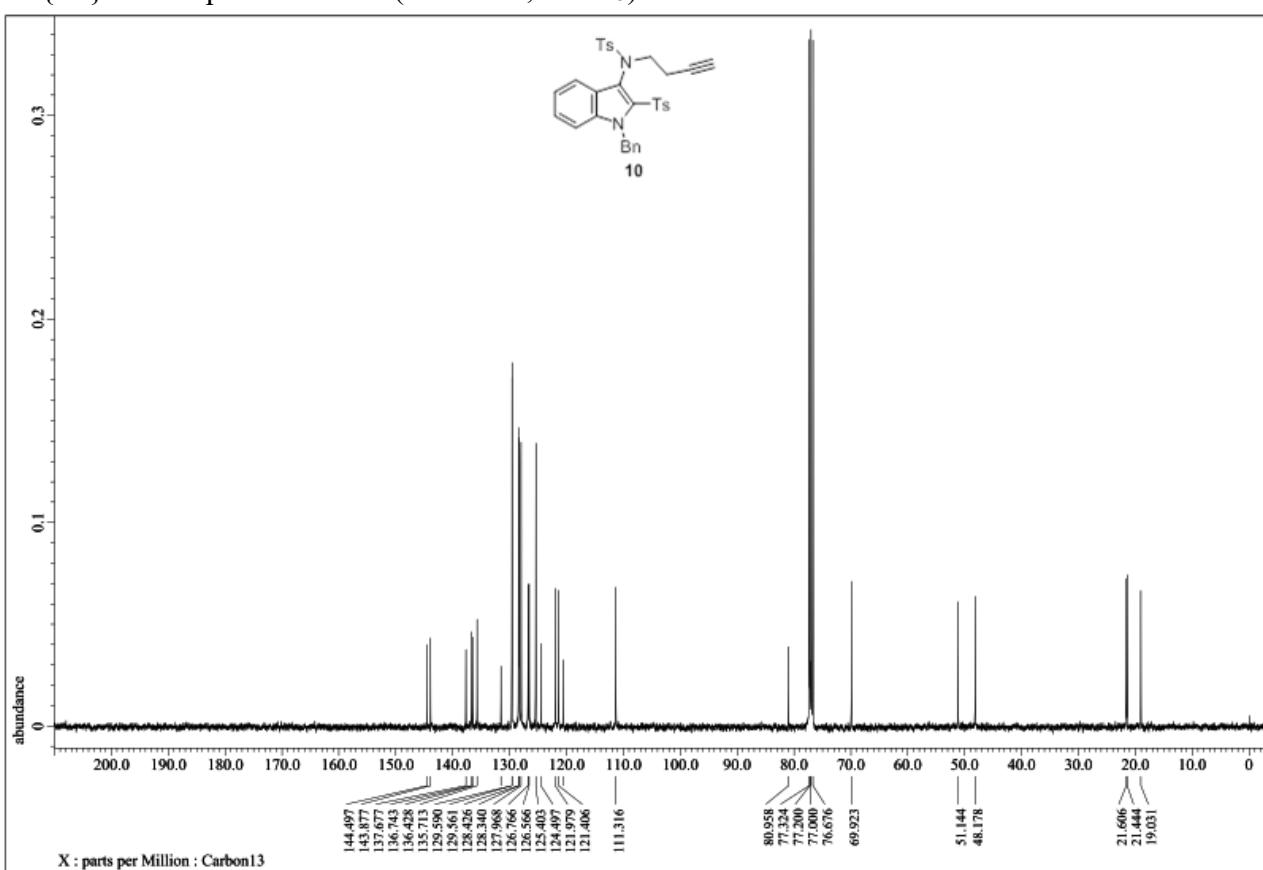
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** (400 MHz, CDCl_3)



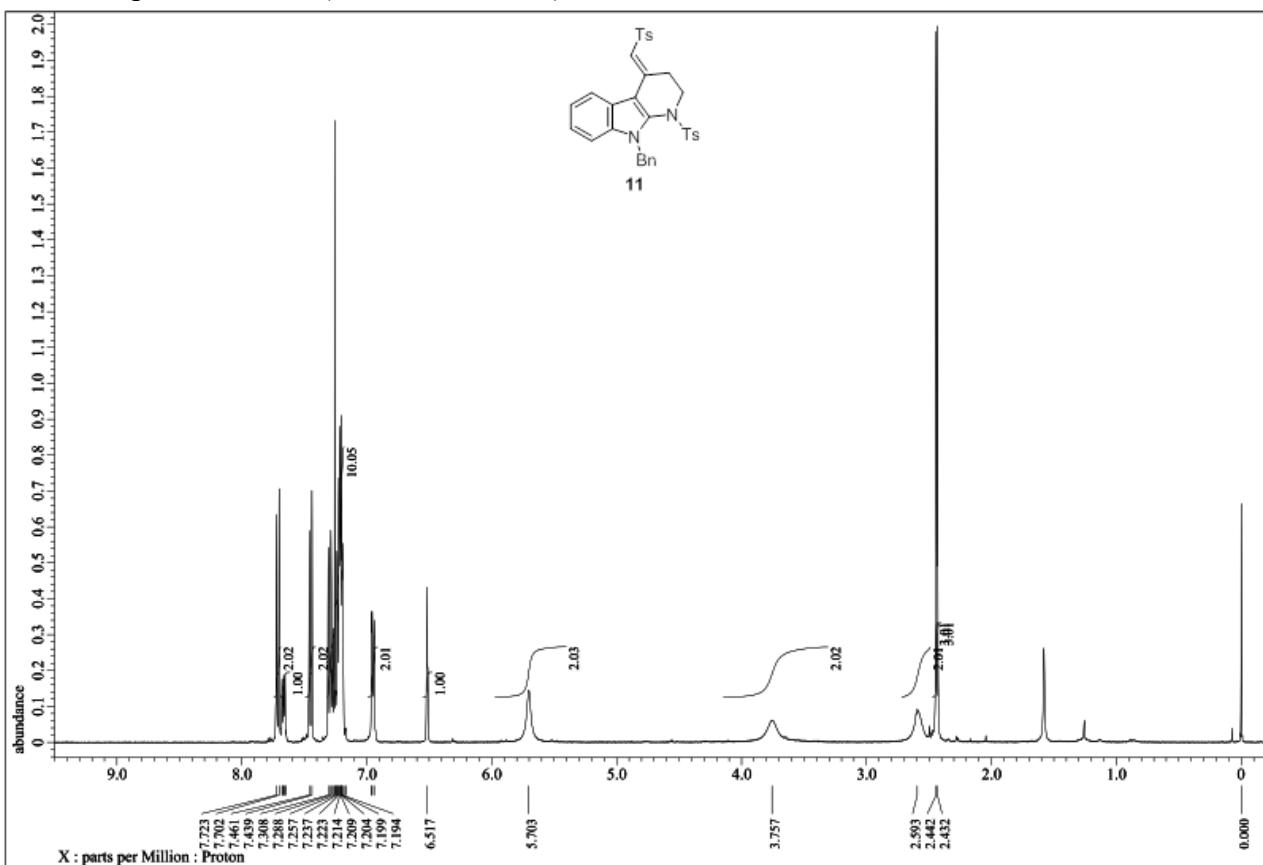
¹H NMR spectrum of **10** (400 MHz, CDCl₃)



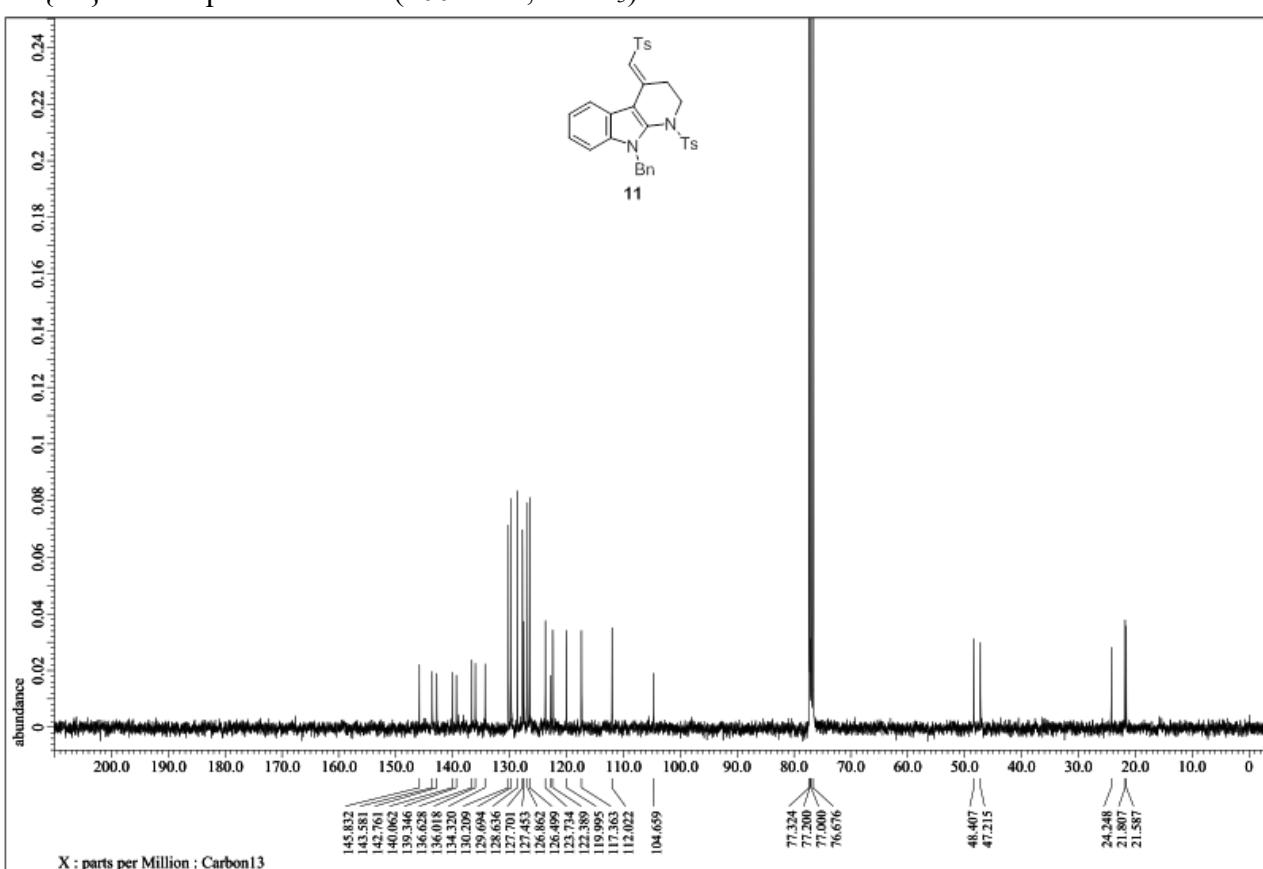
¹³C{¹H} NMR spectrum of **10** (400 MHz, CDCl₃)



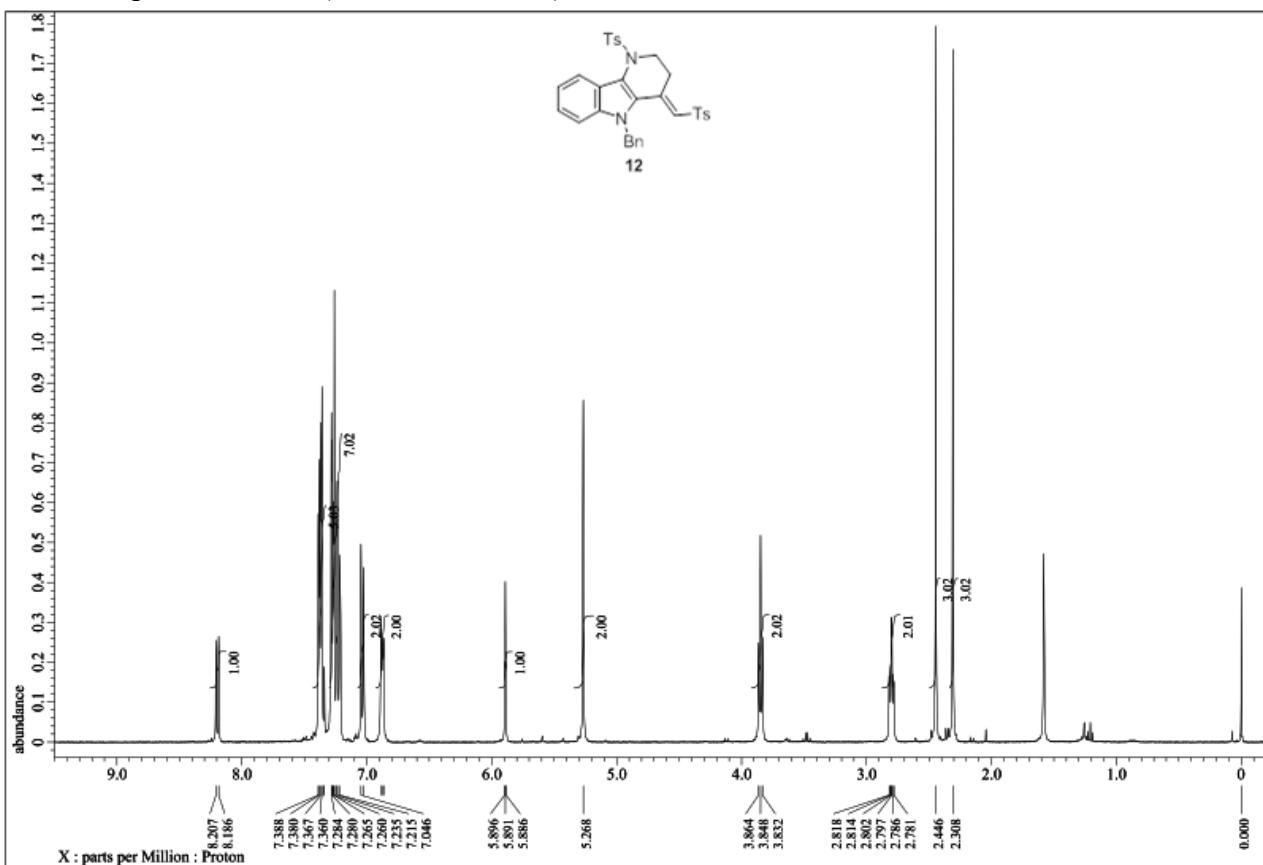
¹H NMR spectrum of **11** (400 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **11** (400 MHz, CDCl₃)



¹H NMR spectrum of **12** (400 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **12** (400 MHz, CDCl₃)

