Supporting Information

Direct Access to *Bis*-*S*-Heterocycle via Copper-Catalyzed Three Component Tandem Cyclization Using S_8 as Sulfur Source

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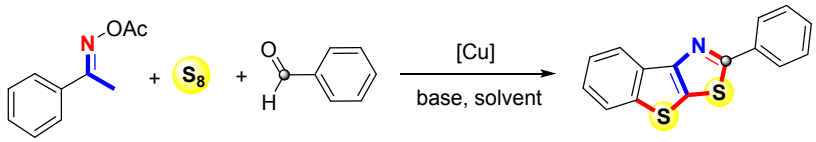
1. Optimization of Reaction Conditions

Table S1. Optimization of the reaction conditions [a]



1a **4a** **3aa**

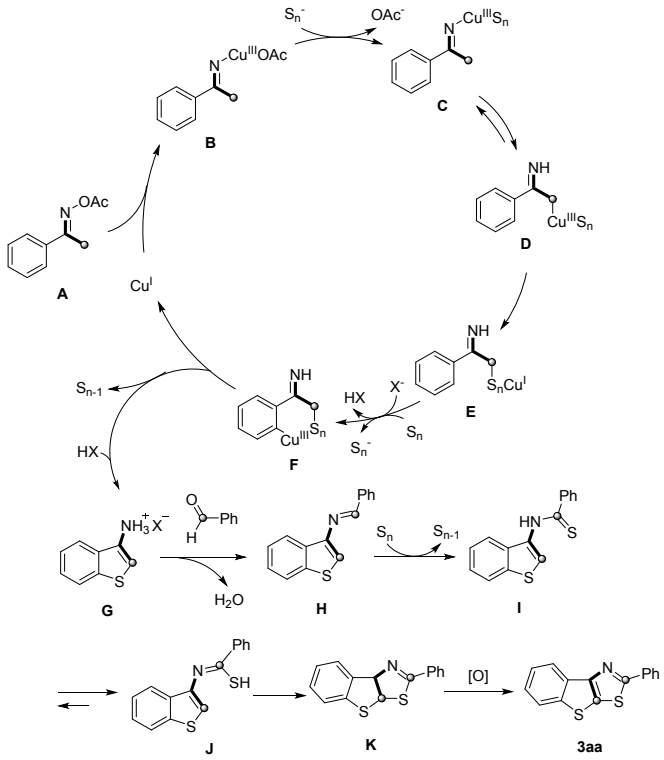
entry	solvent	base [b]	[Cu]	yield (%) [c]
1	DMSO	TBD	CuTC	66
2	DMSO	TBD	CuI	56
3	DMSO	TBD	$CuCl_2$	58
4	DMSO	TBD	CuCl	80
5	Hexane	TBD	CuCl	22
6	1,4-Dioxane	TBD	CuCl	trace
7	Toluene	TBD	CuCl	trace
8	NMP	TBD	CuCl	12
9	PhCl	TBD	CuCl	8
10	DMSO/Hexane (2:1)	TBD	CuCl	86 (81)
11	DMSO/Hexane (1:1)	TBD	CuCl	52
12	DMSO/Hexane (2:1)	TMEDA	CuCl	23
13	DMSO/Hexane (2:1)	DIPEA	CuCl	12
14	DMSO/Hexane (2:1)	DBU	CuCl	41

[a] Reaction conditions: **1a** (0.2 mmol), S_8 (0.05 mmol), **2a** (0.1 mmol), [Cu] (20 mol %), base (0.7 equiv), additive (0.5 equiv) in 1.5 mL of solvent at 120 °C under N2 for 22 h unless otherwise noted. [b] TBD = 1,5,7-triazabicyclo[4.4.0]-dec-5-ene. TMEDA = tetramethylethylenediamine. DIPEA = *N*,*N*-diisopropyl-ethylamine. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. [c] ^{1}H NMR yield using nitromethane as an internal standard. The number in parentheses is isolated yield.

2. Proposed Mechanism

A proposed mechanism with aldehyde as substrate is shown in Scheme S1. First, intermediate **B** is formed by the oxidative addition of Cu(I) to oxime esters. Coordination of the *in-situ* formed S_n^- to **B** gives intermediate **C** and simultaneously releases acetate. Subsequently, tautomerization of intermediate **C** affords the intermediate **D**,[1] which undergoes reductive elimination to form intermediate **E**.[2] The oxidation of Cu(I) species **E** by S_8 is followed by C–H activation and C–S bond reductive elimination to generate intermediate **G**.[3] Next, the condensation of **G** and benzaldehyde generates imine **H**, followed by the nucleophilic attack of S_8 and isomerization to afford intermediate **J**.[4] Finally, the intramolecular addition of sulfur moiety of **J** to arene and subsequent oxidation provides the desired product **3aa**.[5]

Scheme S1. Proposed Mechanism



Reference:

1 (a) X. Tang, W. Wu, W. Zeng and H. Jiang, *Acc. Chem. Res.*, 2018, **51**, 1092; (b) H. Huang, X. Ji, W. Wu and H. Jiang, *Chem. Soc. Rev.*, 2015, **44**, 1155.

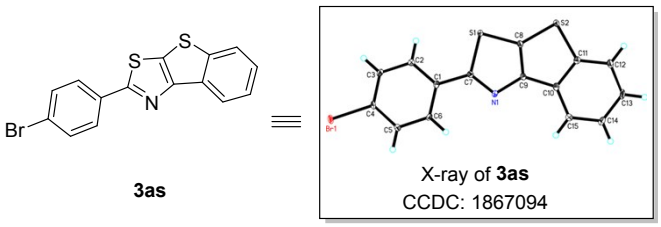
2 Y. Huang, D. Yan, X. Wang, P. Zhou, W. Wu and H. Jiang, *Chem. Commun.*, 2018, **54**, 1742.

3 (a) M. Wang, J. Wei, Q. Fan, X. Jiang, *Chem. Commun.*, 2017, **53**, 2918; (b) P. Dang, Z. Zheng, Y. Liang, *J. Org. Chem.*, 2017, **82**, 2263.

4 (a) J. Wei, Y. Li and X. Jiang, *Org. Lett.* 2016, **18**, 340; (b) H. Xu, H. Deng, Z. Li, H. Xiang and X. Zhou, *Eur. J. Org. Chem.*, **2013**, 7054.

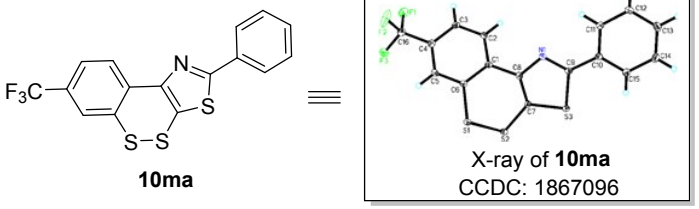
5 G. Revelant, S. Hesse and G. Kirsch, *Tetrahedron*, 2011, **67**, 9352.

3. X-ray Diffraction Parameters and Data for 3as



Compound	**3as**
CCDC	1867094
Empirical formula	$C_{15}H_8BrNS_2$
Formula weight	346.25
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
	a = 6.8836(3) Å α = 88.344(3) ° b = 7.0346(3) Å β = 89.963(3) ° c = 13.5790(5) Å γ = 79.153(4) °
Volume/Å^3	645.52(5)
Z	2
ρ_{calc}g/cm^3	1.781
μ/mm^{-1}	3.489
F(000)	344.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.9 to 49.986
Index ranges	-8 ≤ h ≤ 8, -8 ≤ k ≤ 8, -16 ≤ l ≤ 16
Reflections collected	9909
Independent reflections	2276 [R_{int} = 0.0447, R_{sigma} = 0.0370]
Data/restraints/parameters	2276/0/172
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0268, wR_2 = 0.0644
Final R indexes [all data]	R_1 = 0.0289, wR_2 = 0.0657
Largest diff. peak/hole / e Å^{-3}	0.49/-0.51

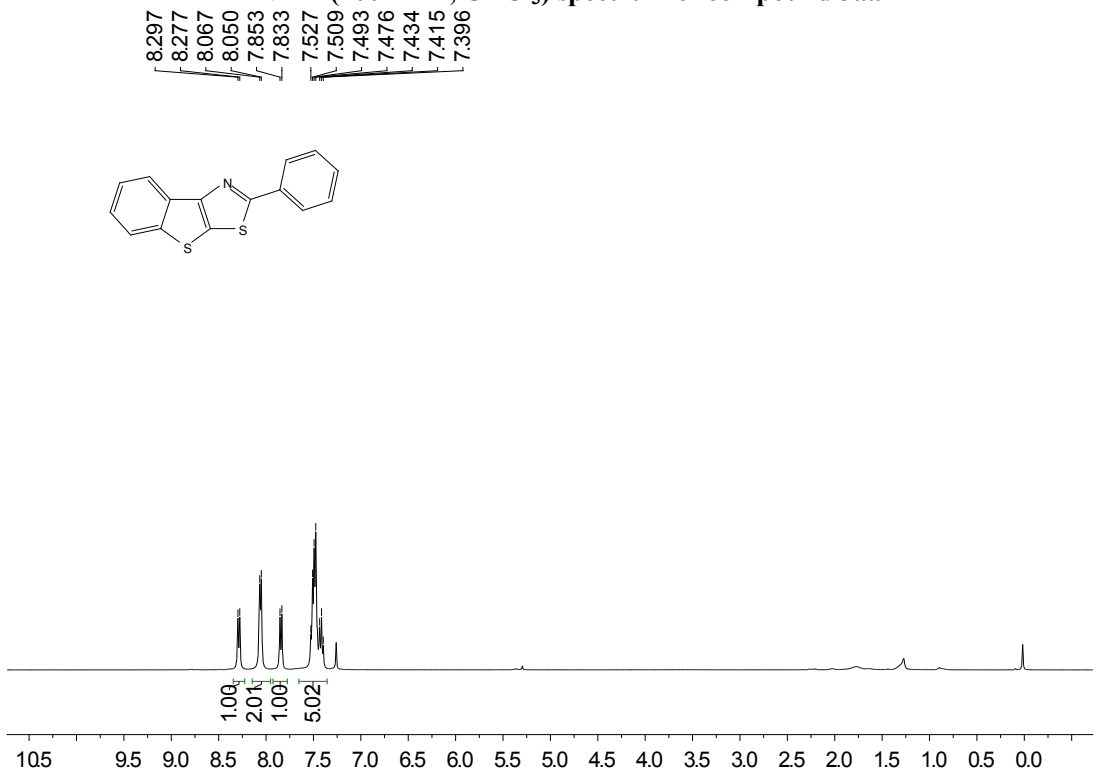
4. X-ray Diffraction Parameters and Data for 10ma



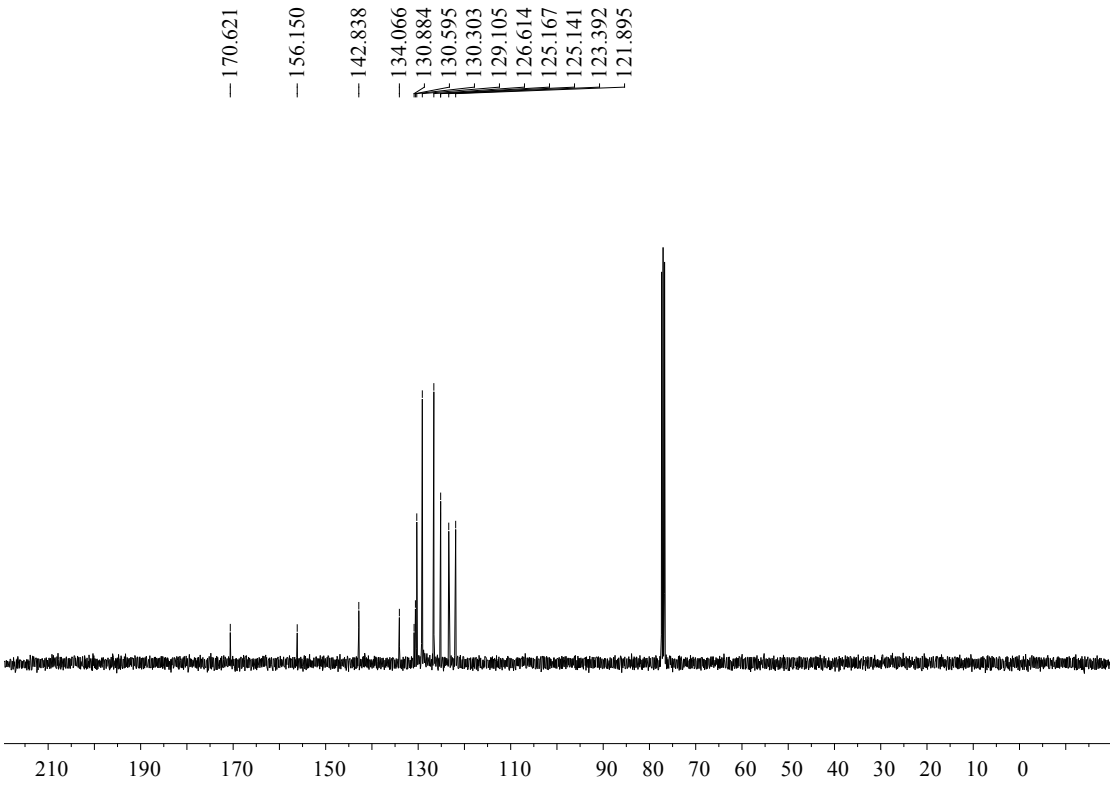
Compound	**10ma**
CCDC	1867096
Empirical formula	$C_{16}H_8F_3NS_3$
Formula weight	367.41
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
	a = 4.2674(3) Å α = 77.893(5) ° b = 12.9135(8) Å β = 87.653(5) ° c = 13.4730(8) Å γ = 86.789(5) °
Volume/Å^3	724.48(8)
Z	2
ρ_{calc}g/cm^3	1.684
μ/mm^{-1}	0.541
F(000)	372.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.98 to 50
Index ranges	-5 ≤ h ≤ 5, -15 ≤ k ≤ 15, -15 ≤ l ≤ 16
Reflections collected	6627
Independent reflections	2536 [R_{int} = 0.0275, R_{sigma} = 0.0387]
Data/restraints/parameters	2536/0/208
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0350, wR_2 = 0.0812
Final R indexes [all data]	R_1 = 0.0402, wR_2 = 0.0855
Largest diff. peak/hole / e Å^{-3}	0.45/-0.37

5. NMR Spectra for All Compounds

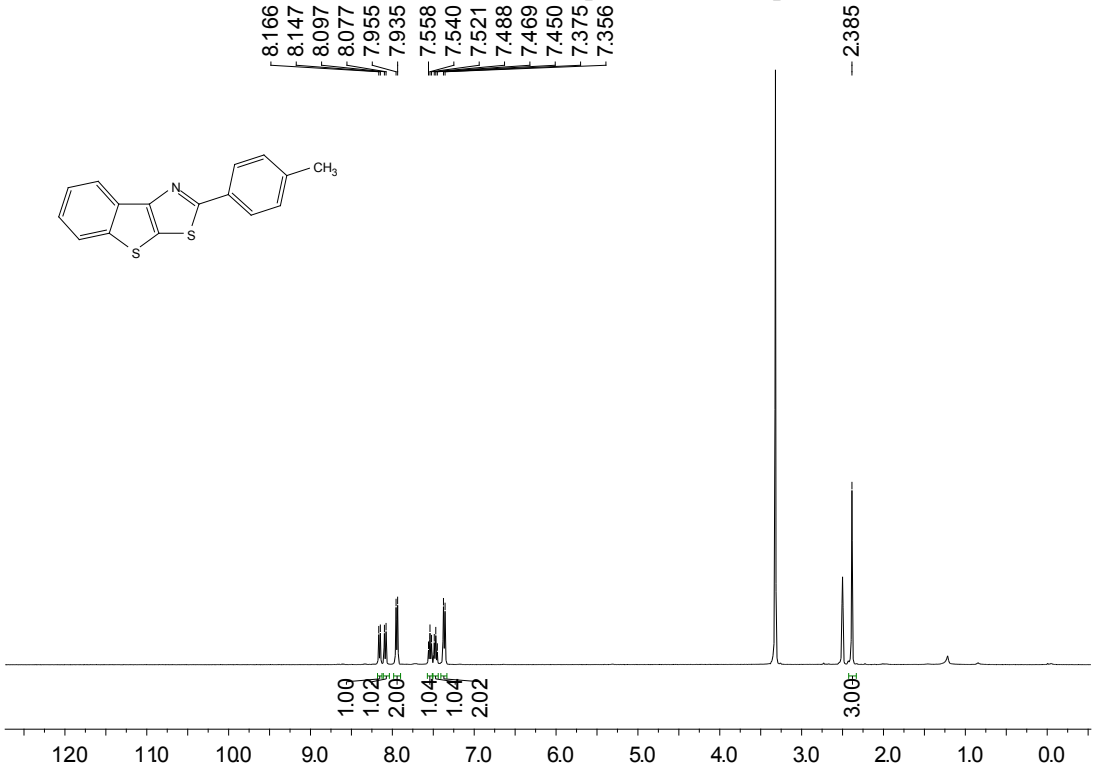
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3aa



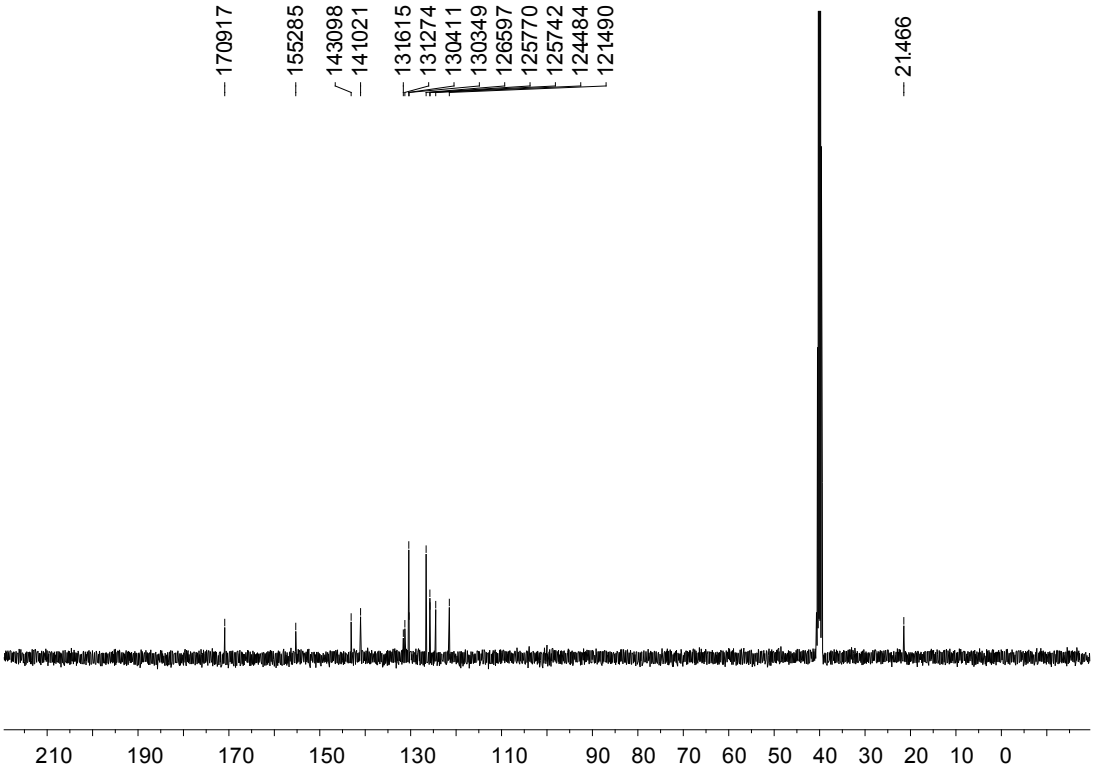
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3aa



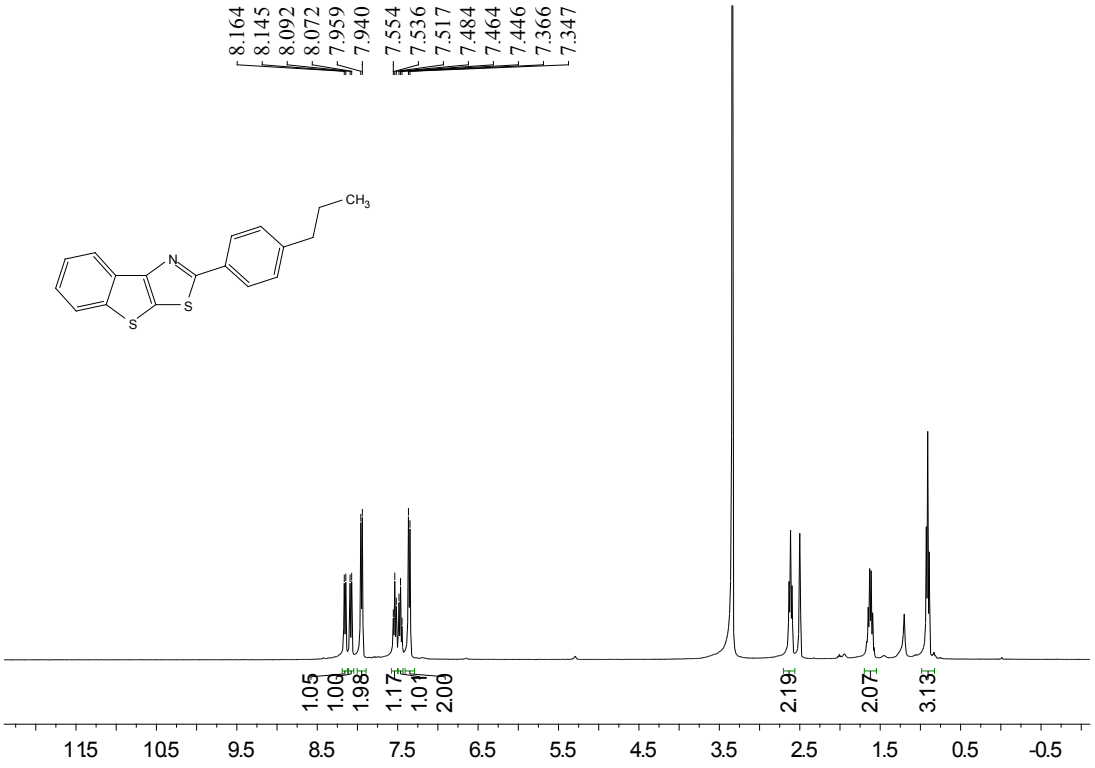
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3ab



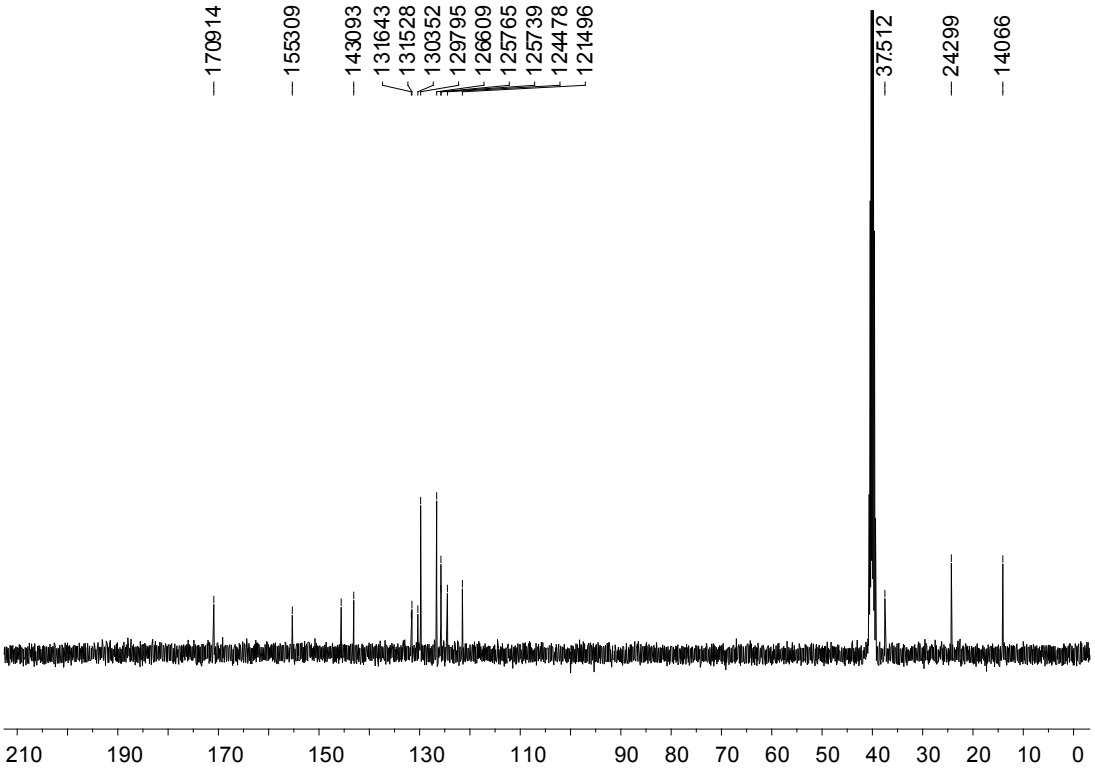
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ab



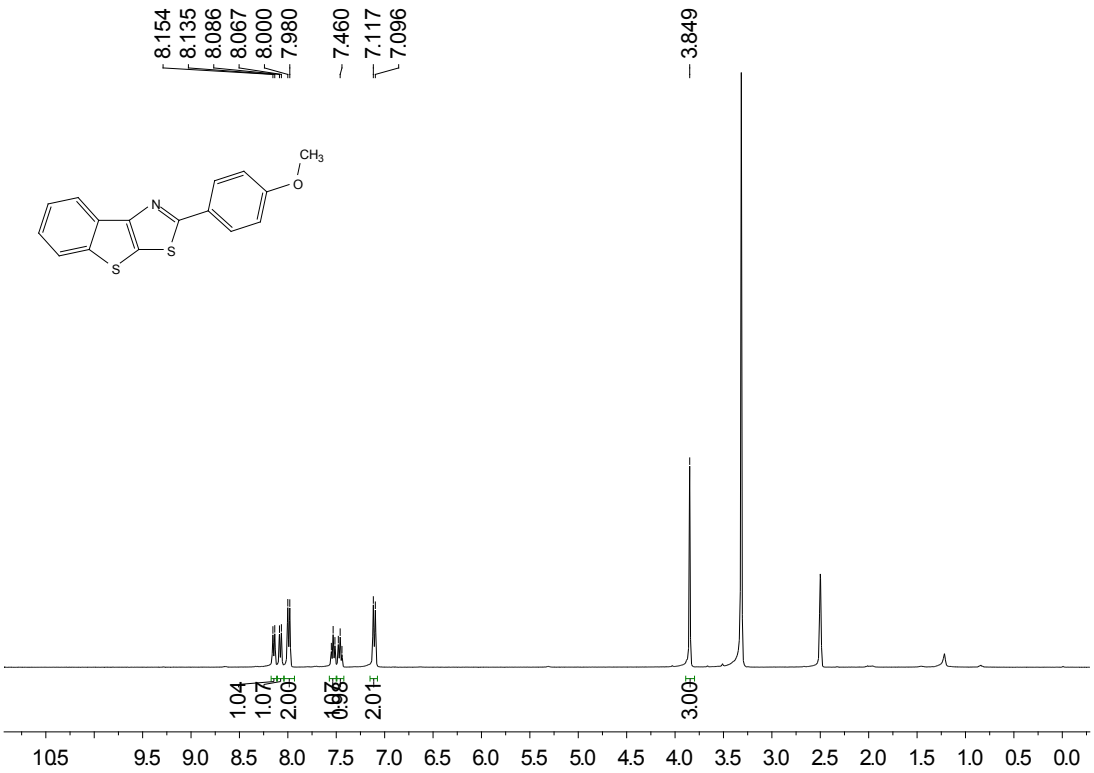
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3ac



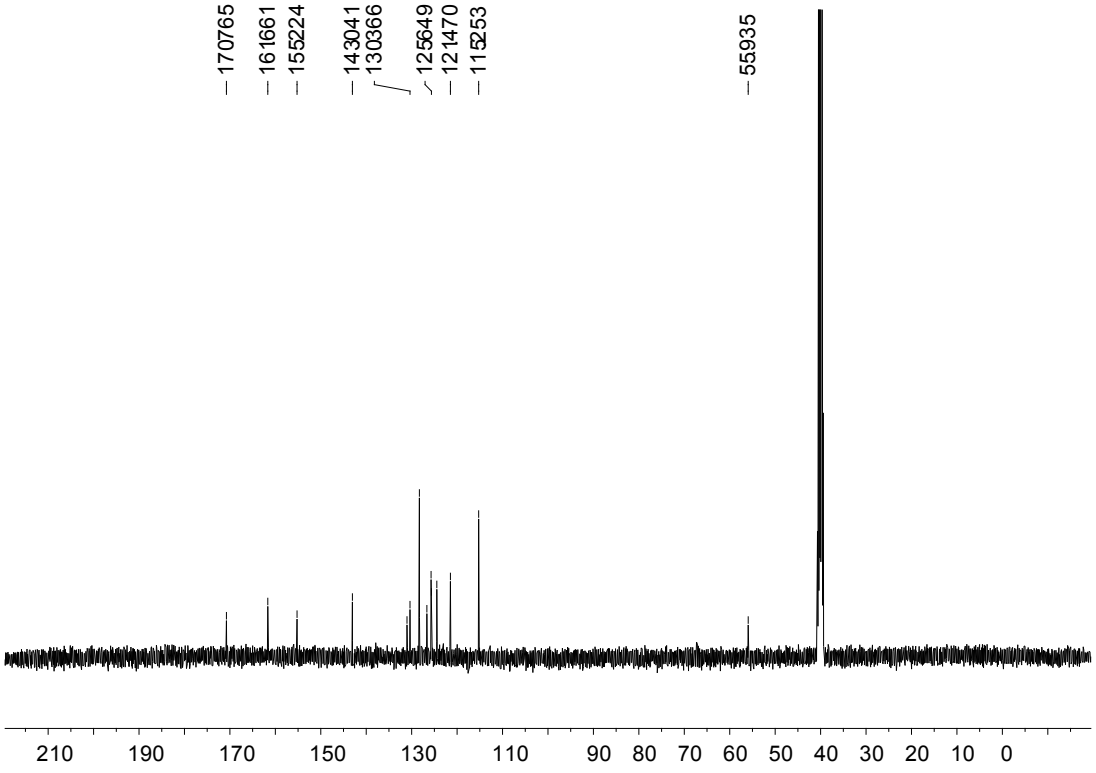
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ac



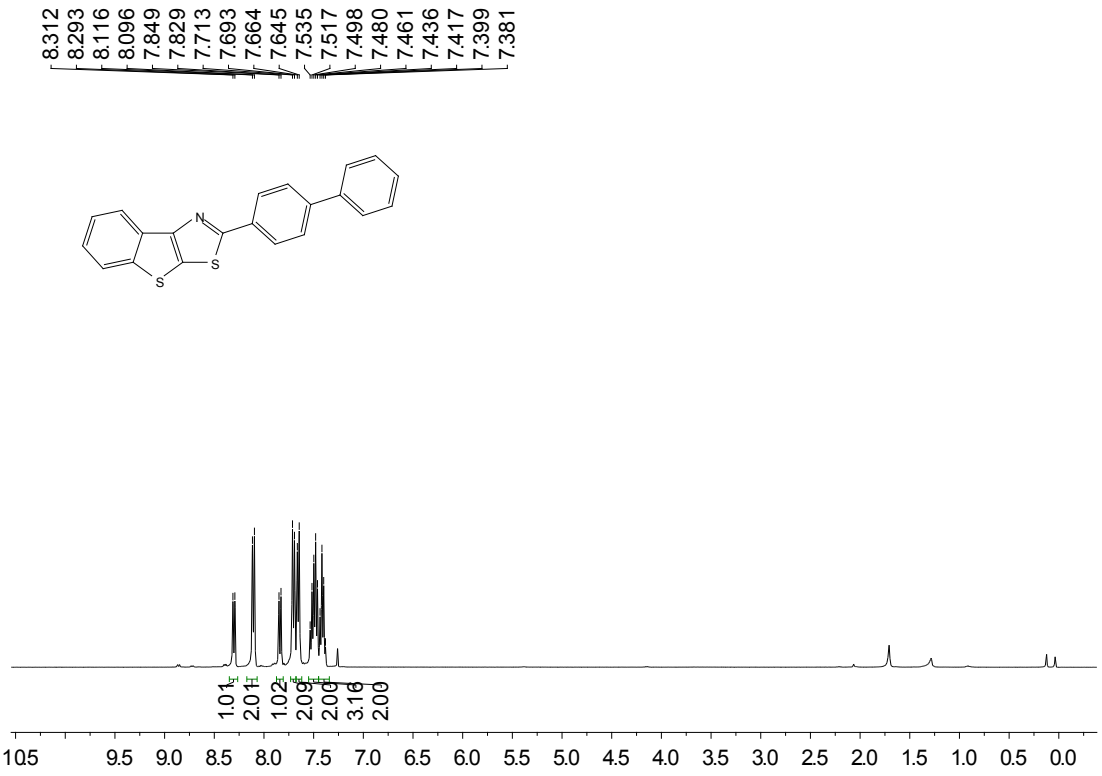
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3ad



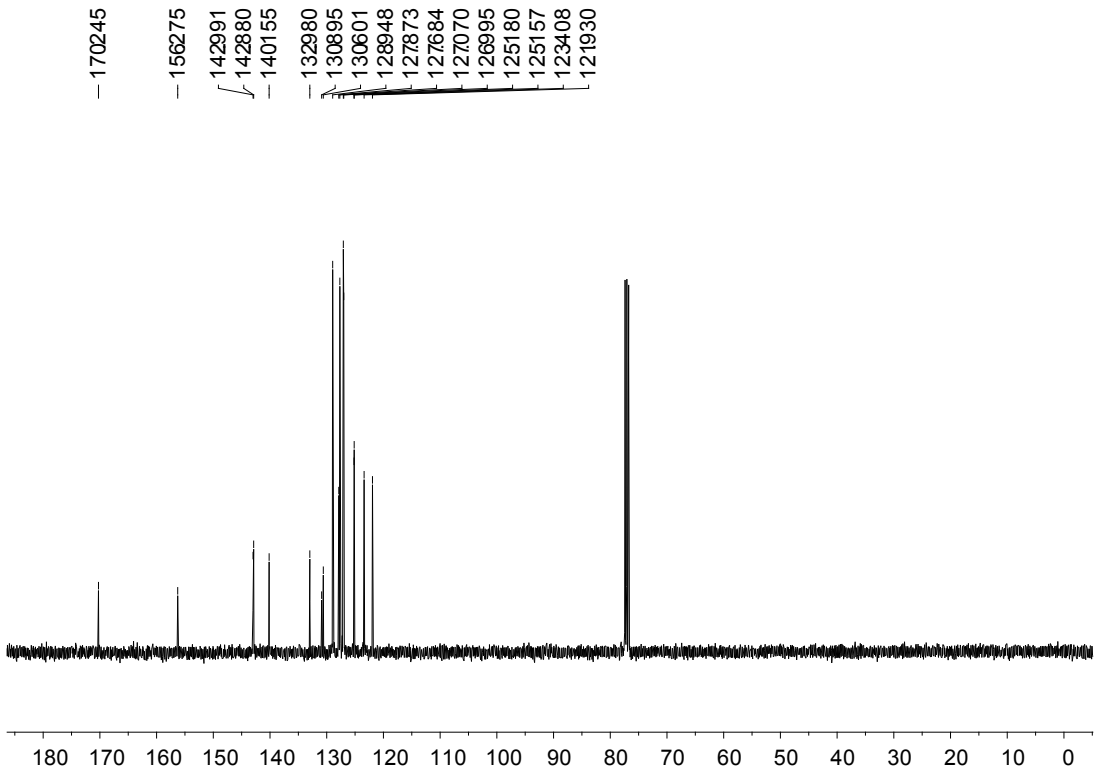
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ad



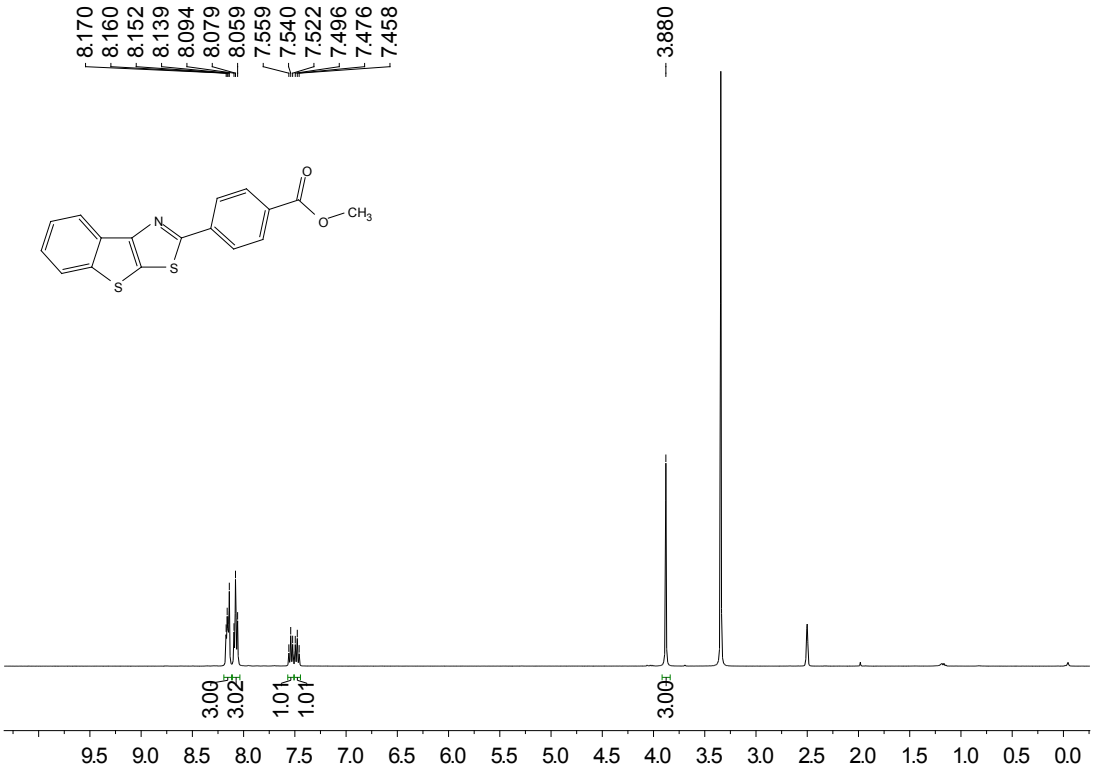
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3ae



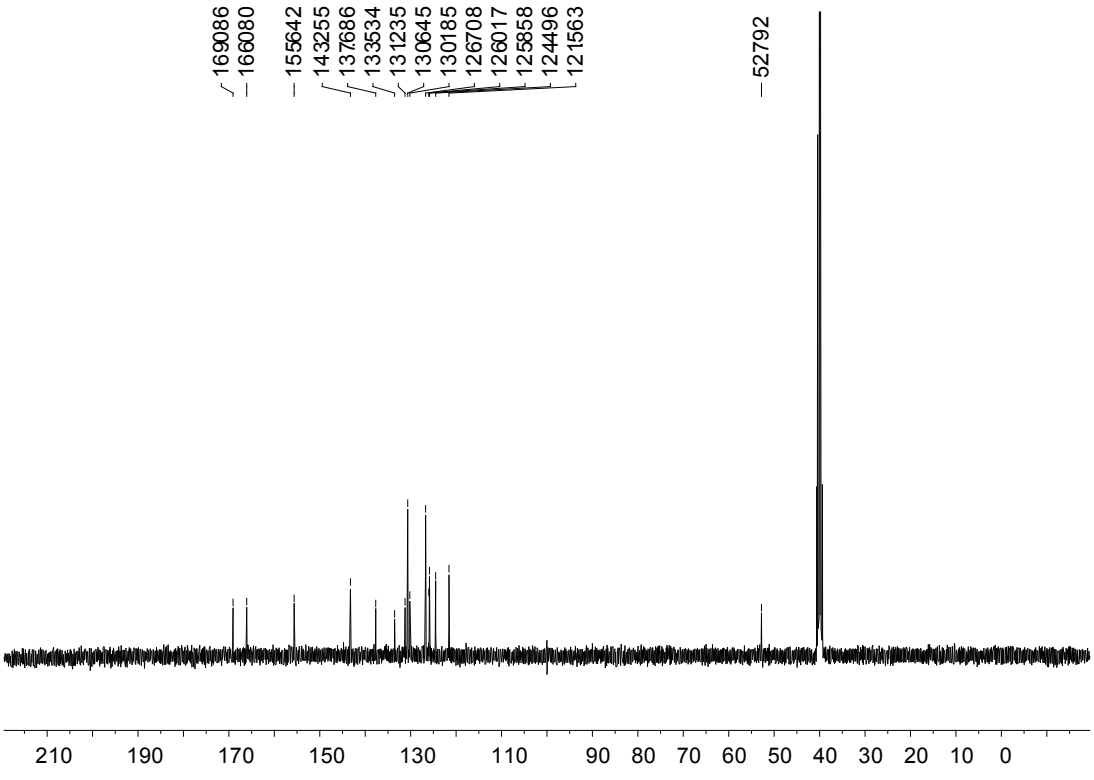
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3ae



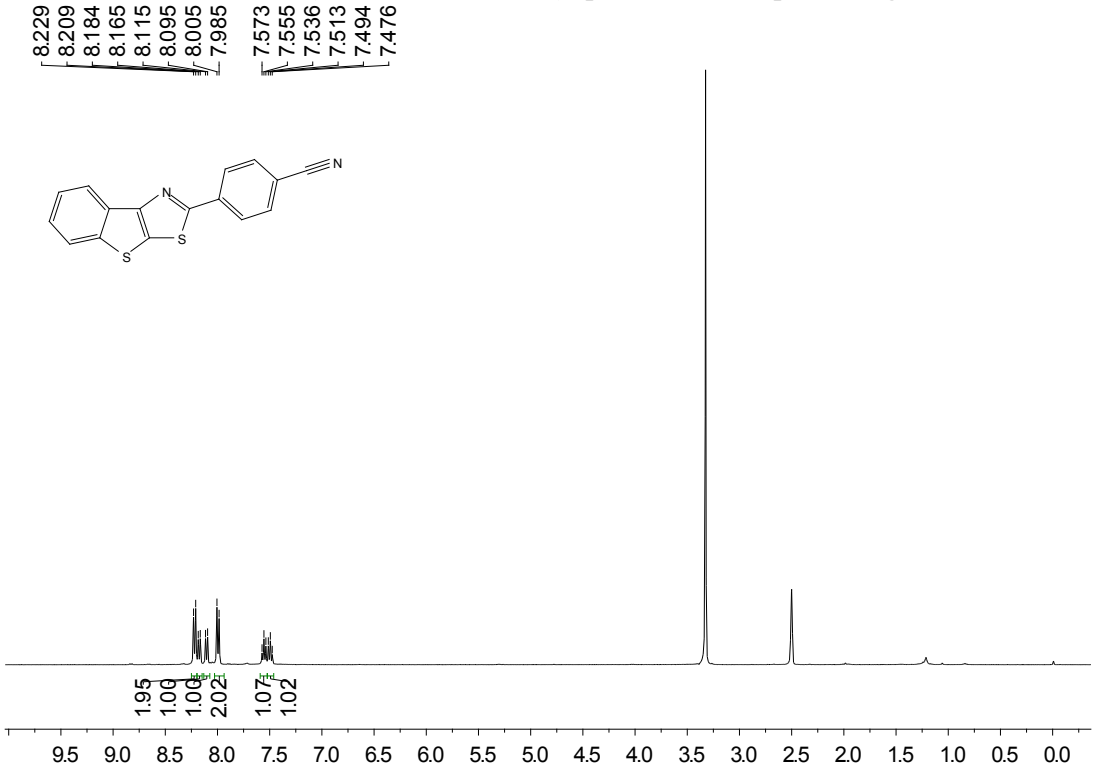
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3af



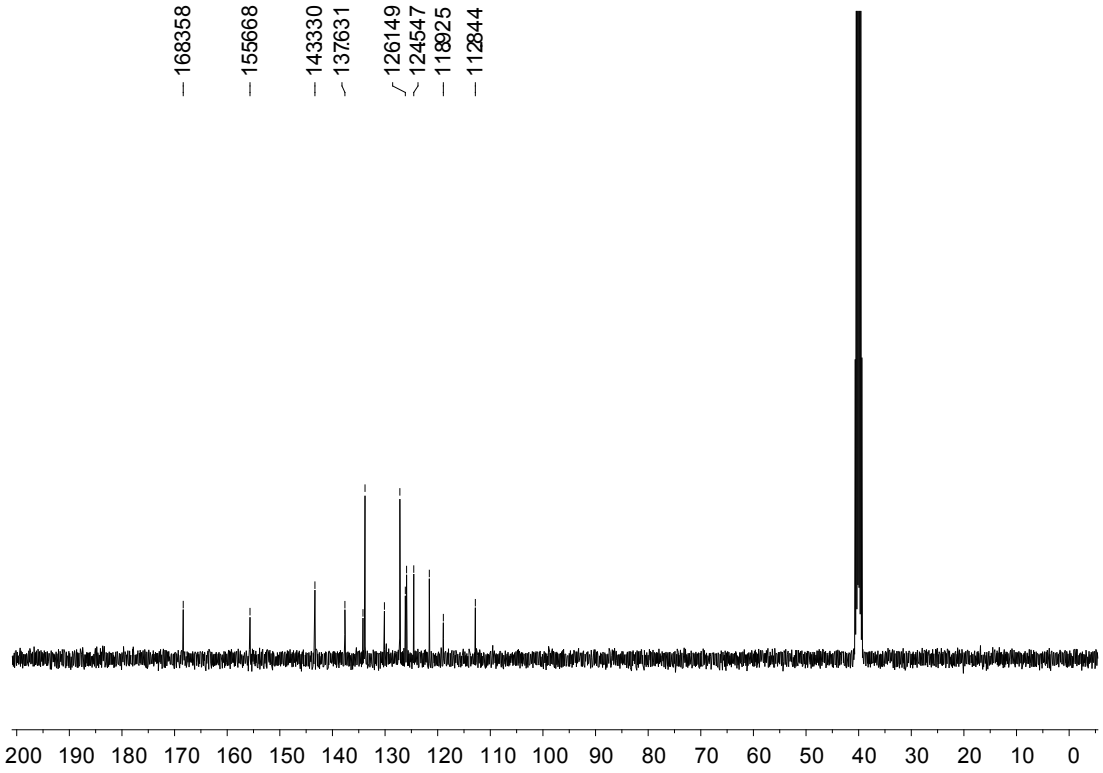
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3af



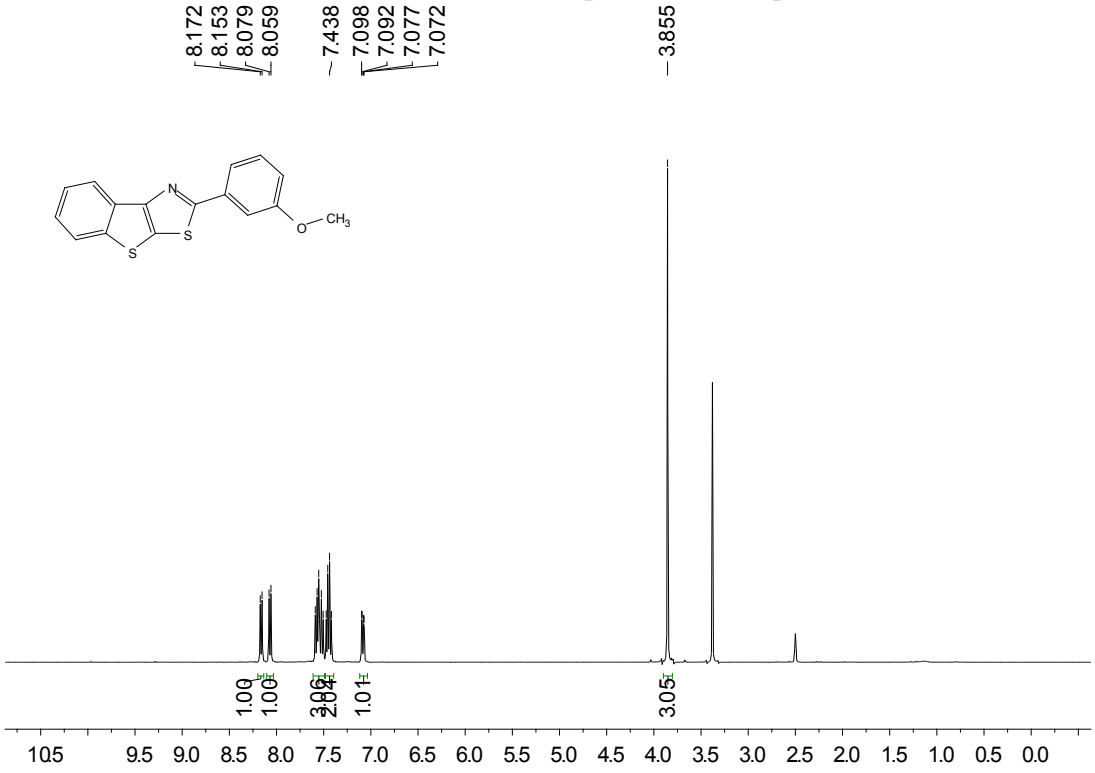
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3ag



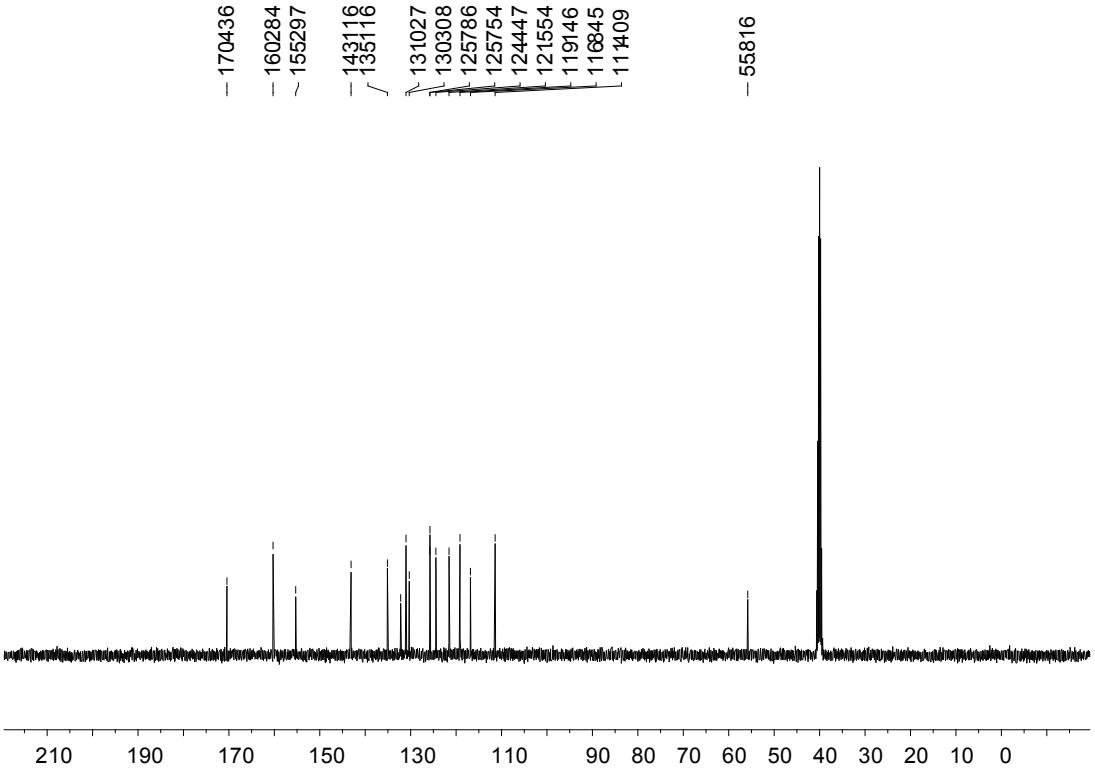
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ag



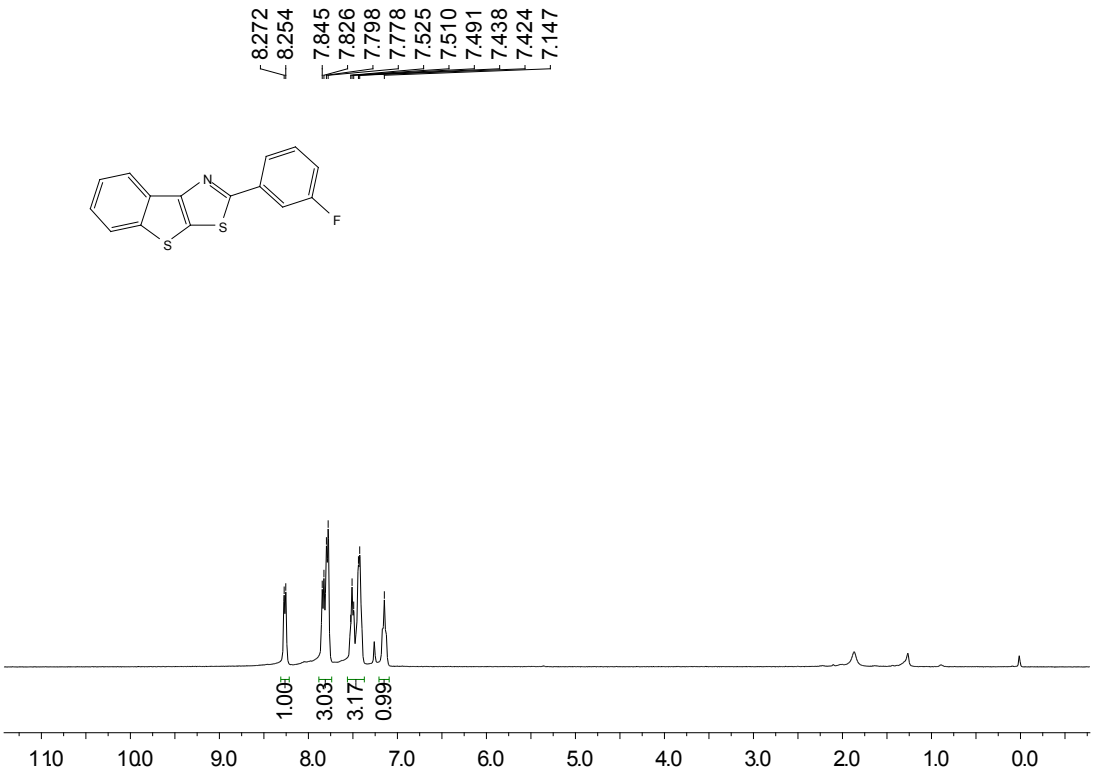
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3ah



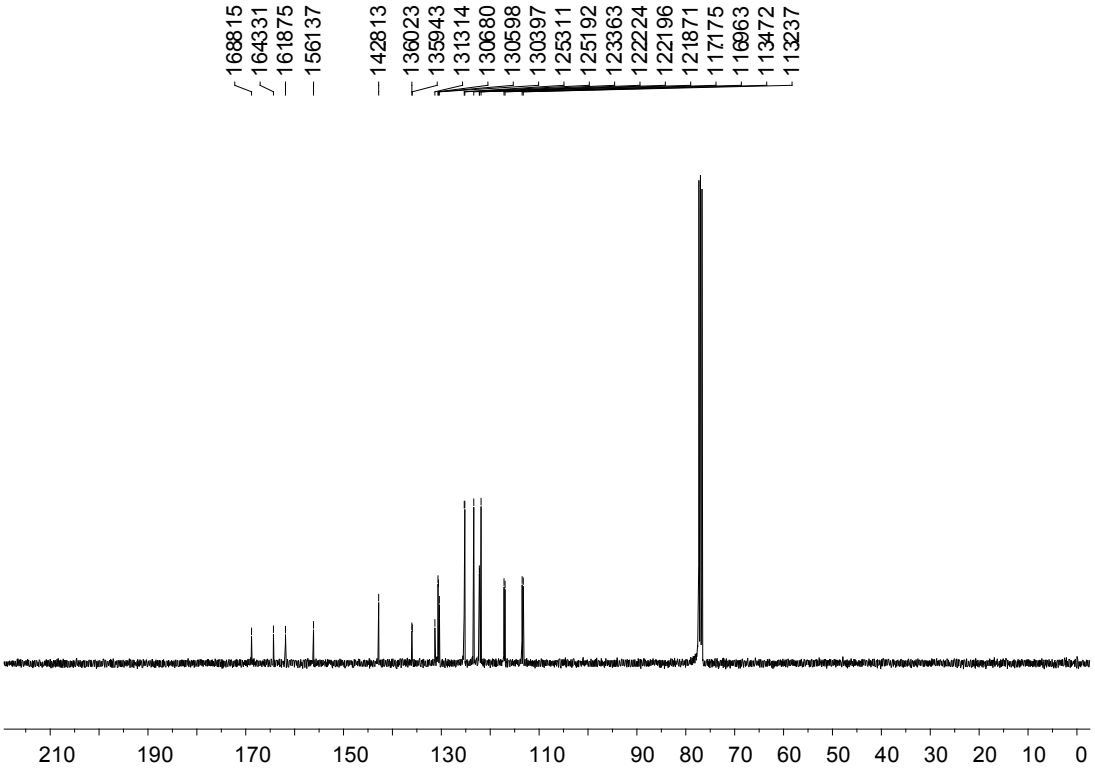
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ah



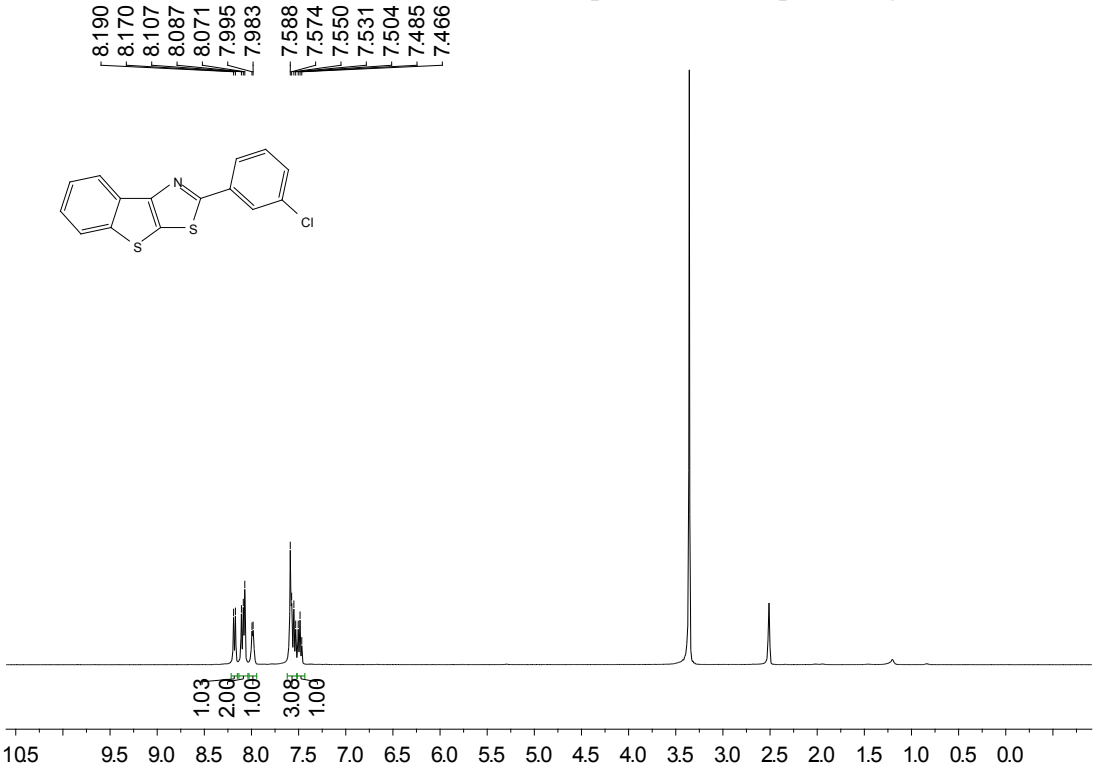
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3ai



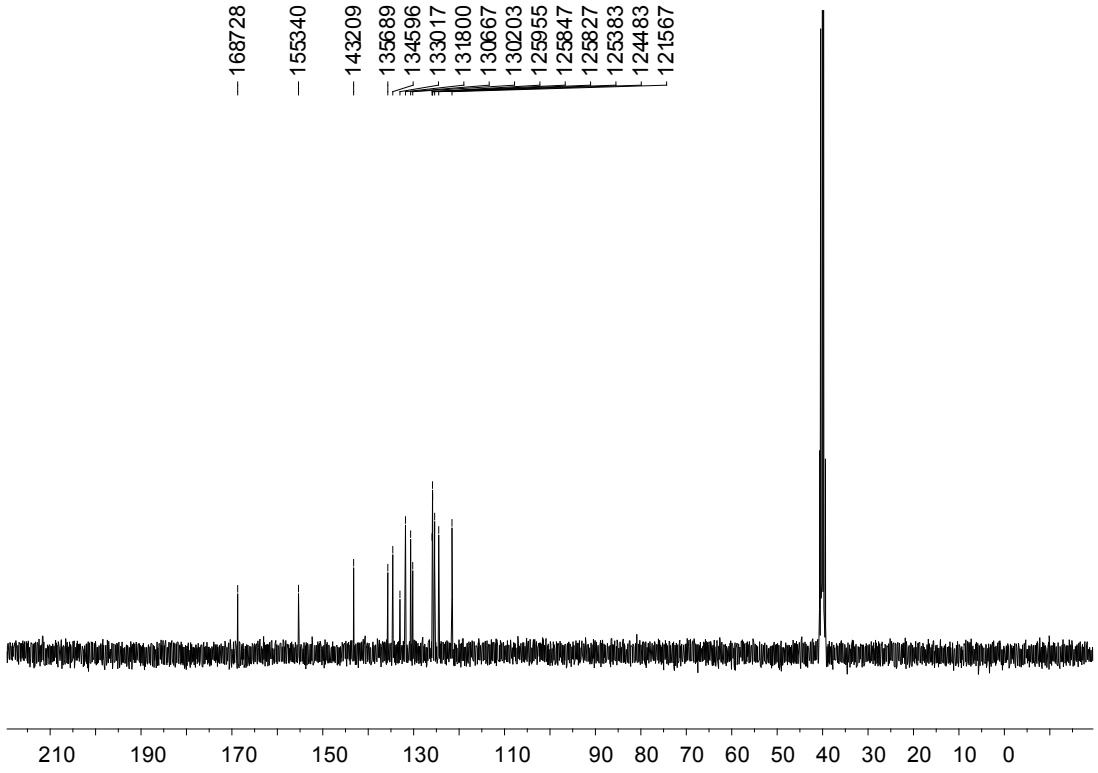
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3ai



^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3aj



^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3aj



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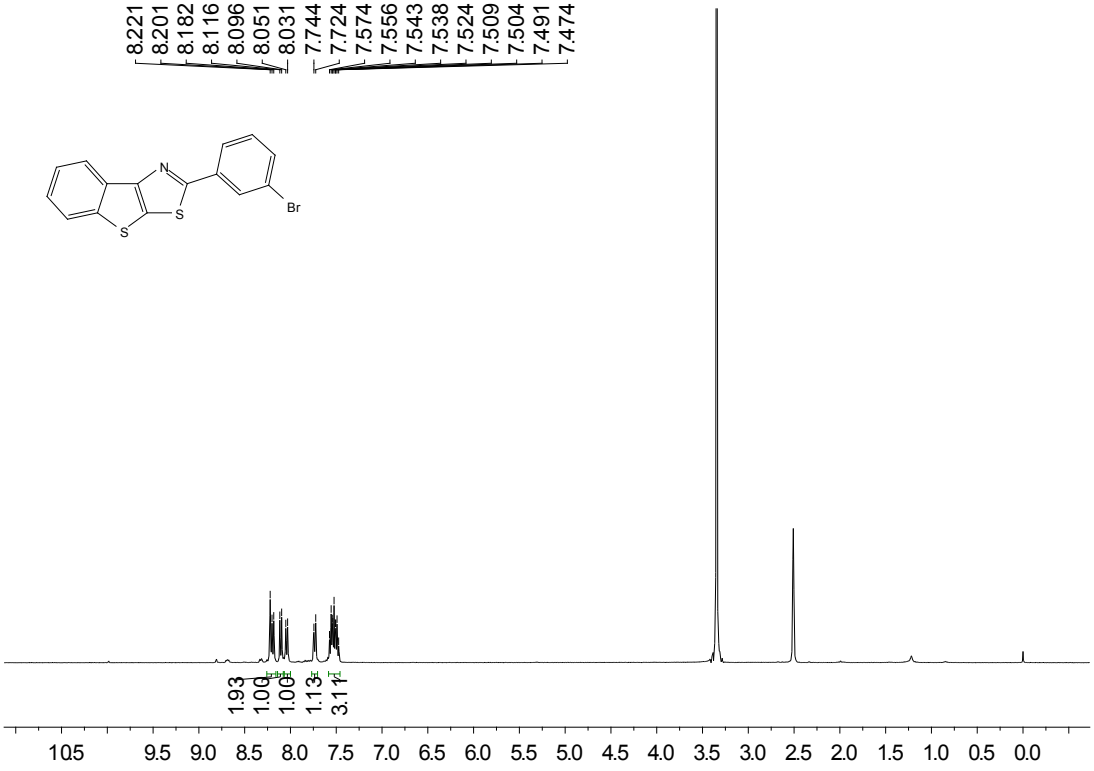
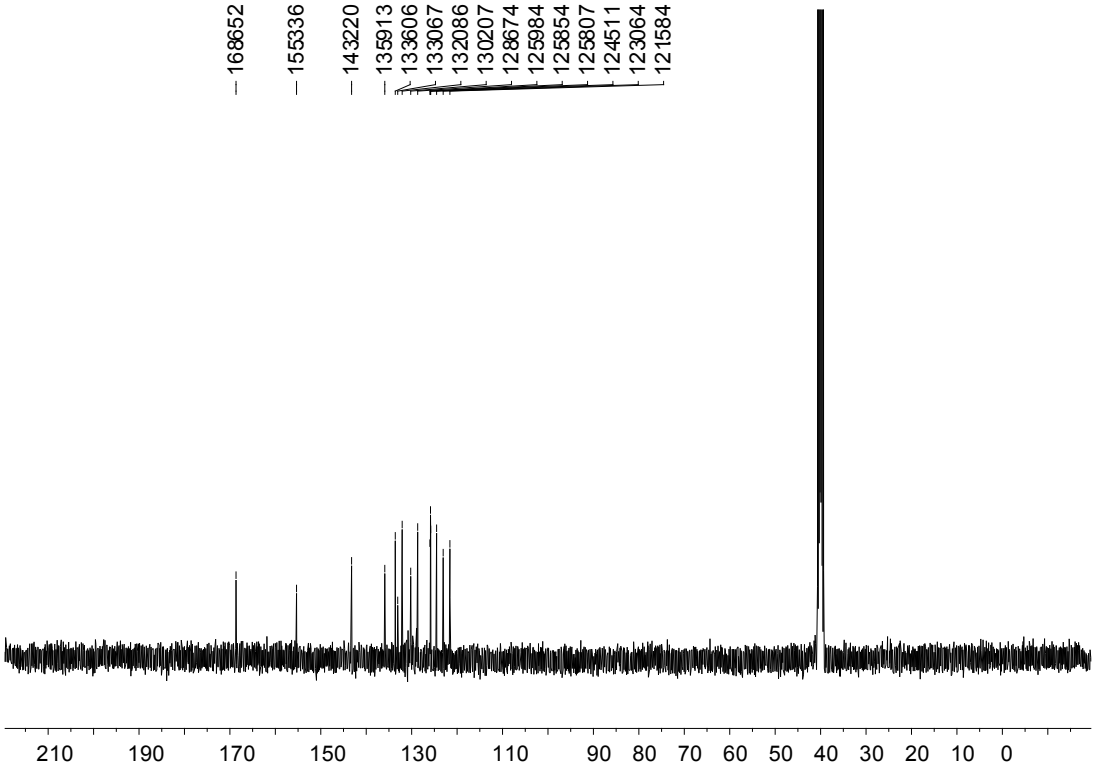
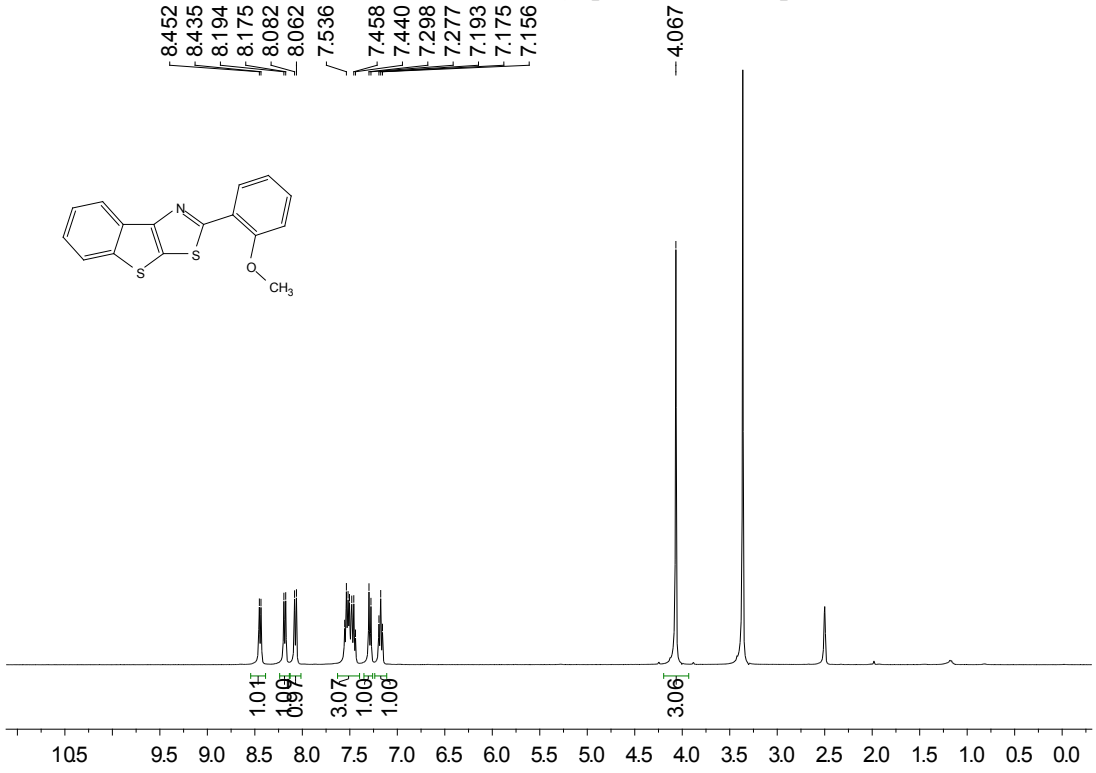


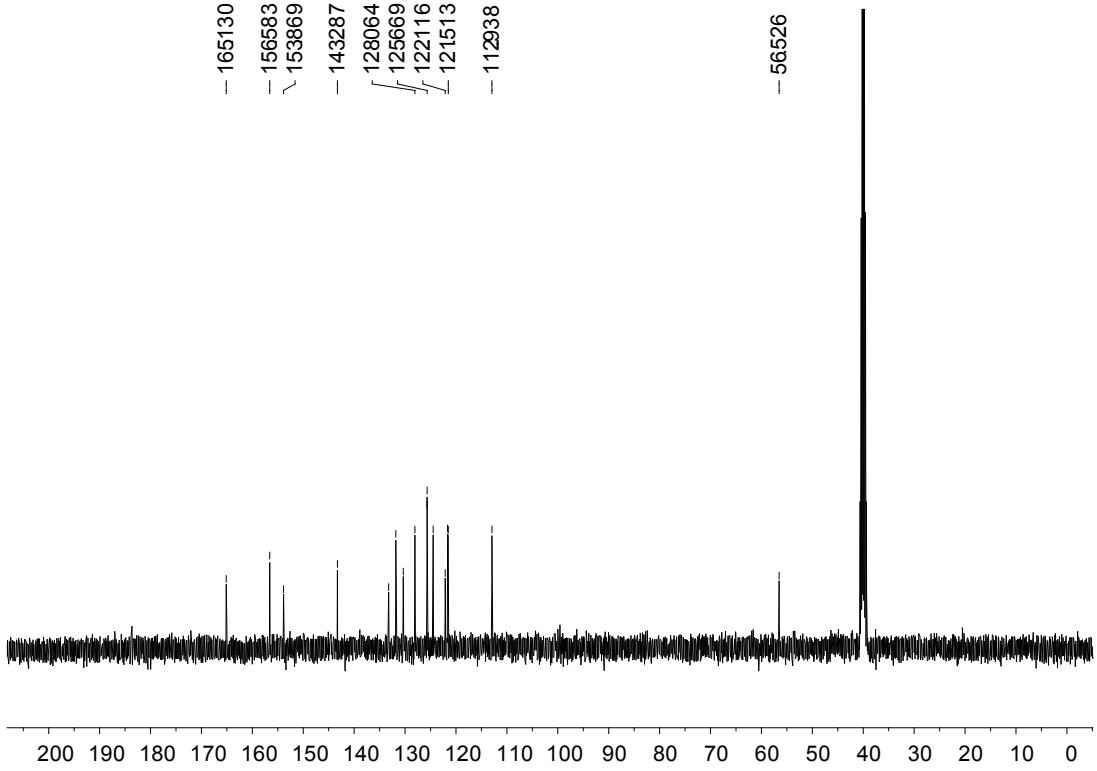
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ak



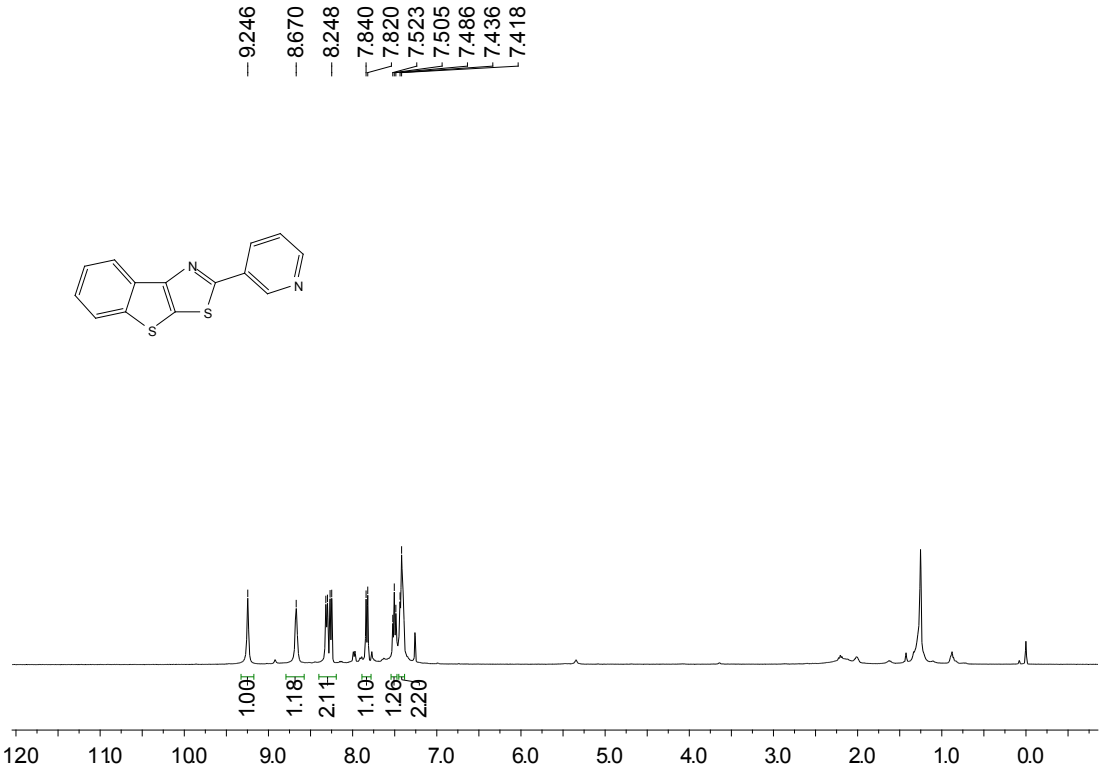
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3al



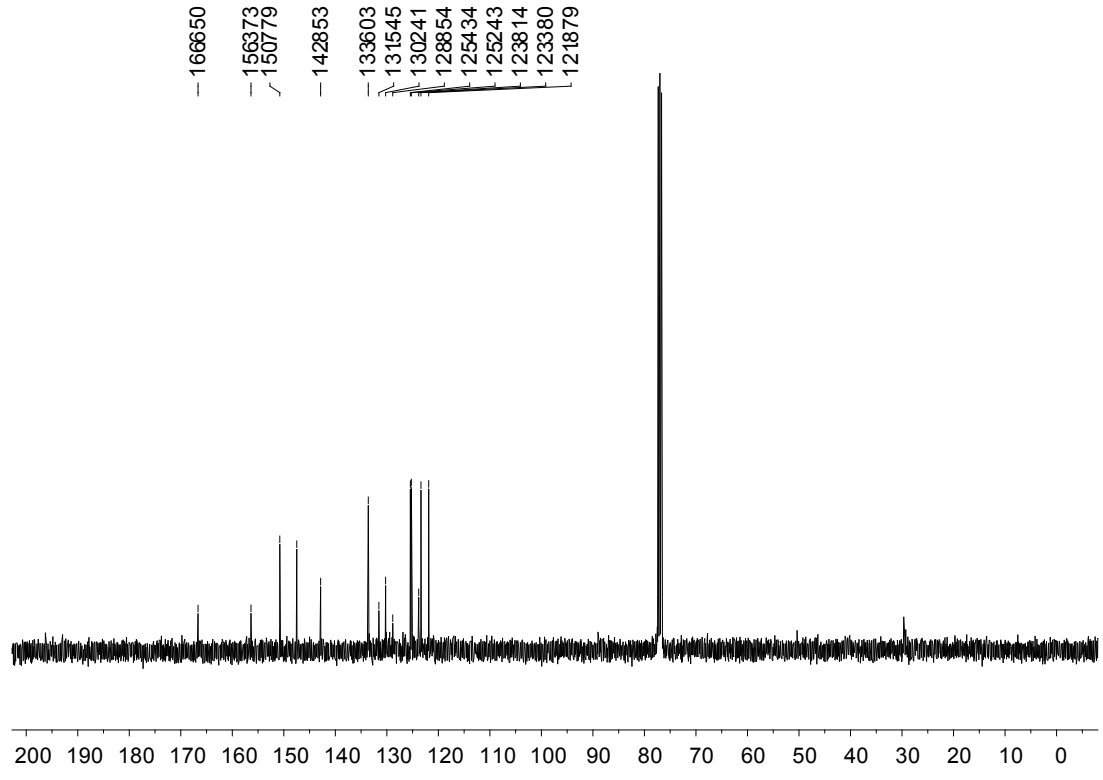
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3al



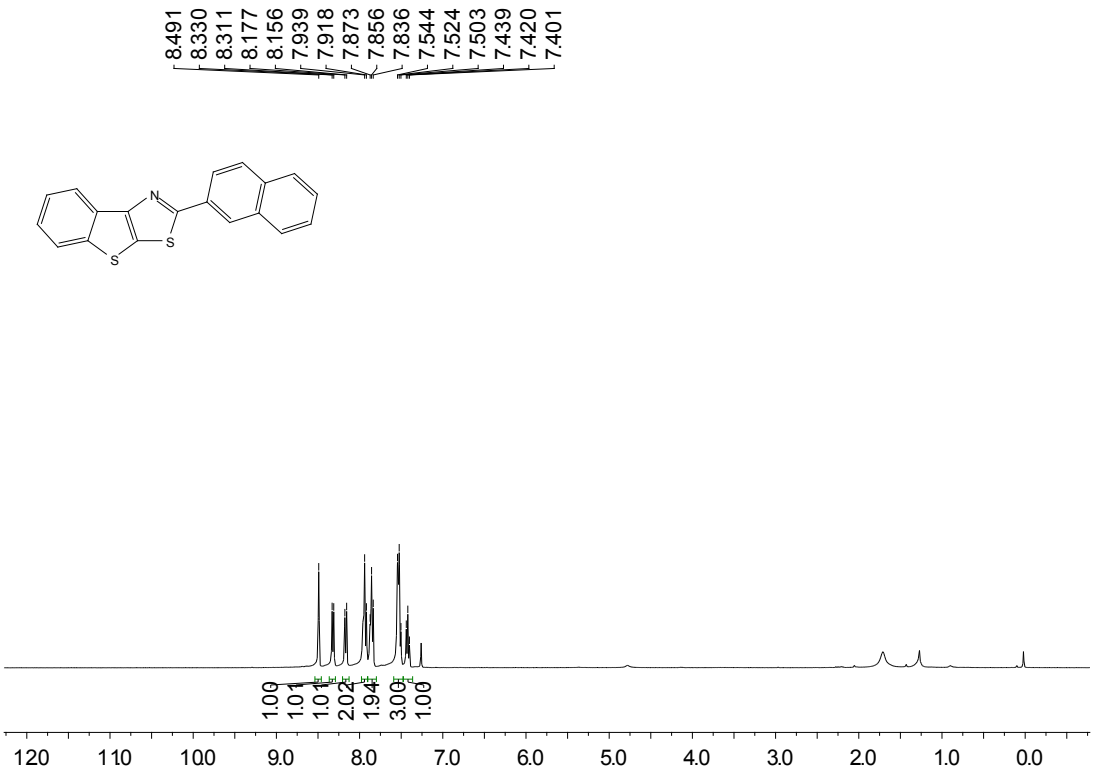
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3ao



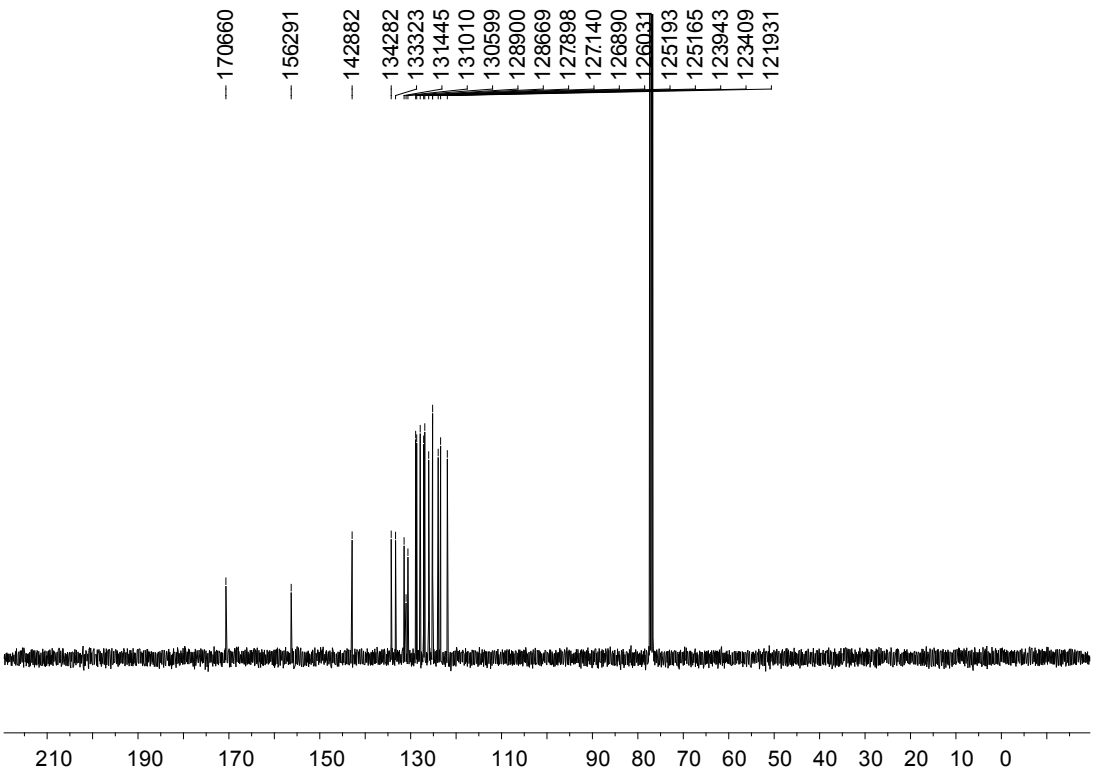
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3ao



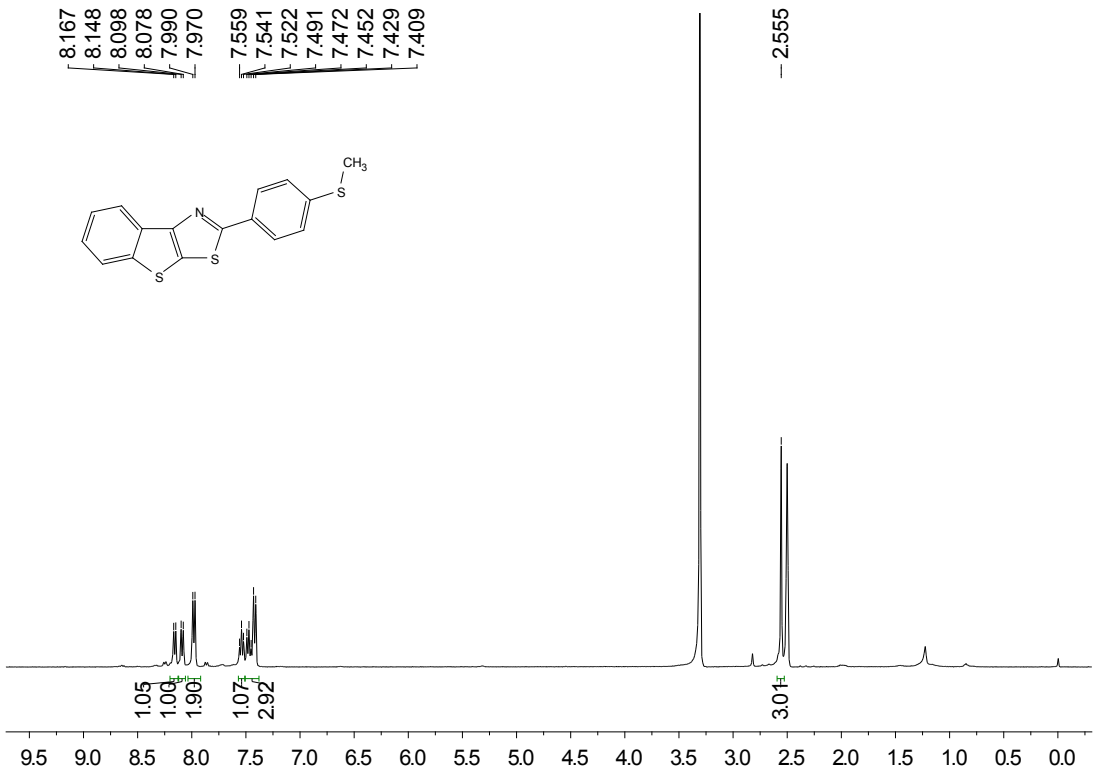
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3ap



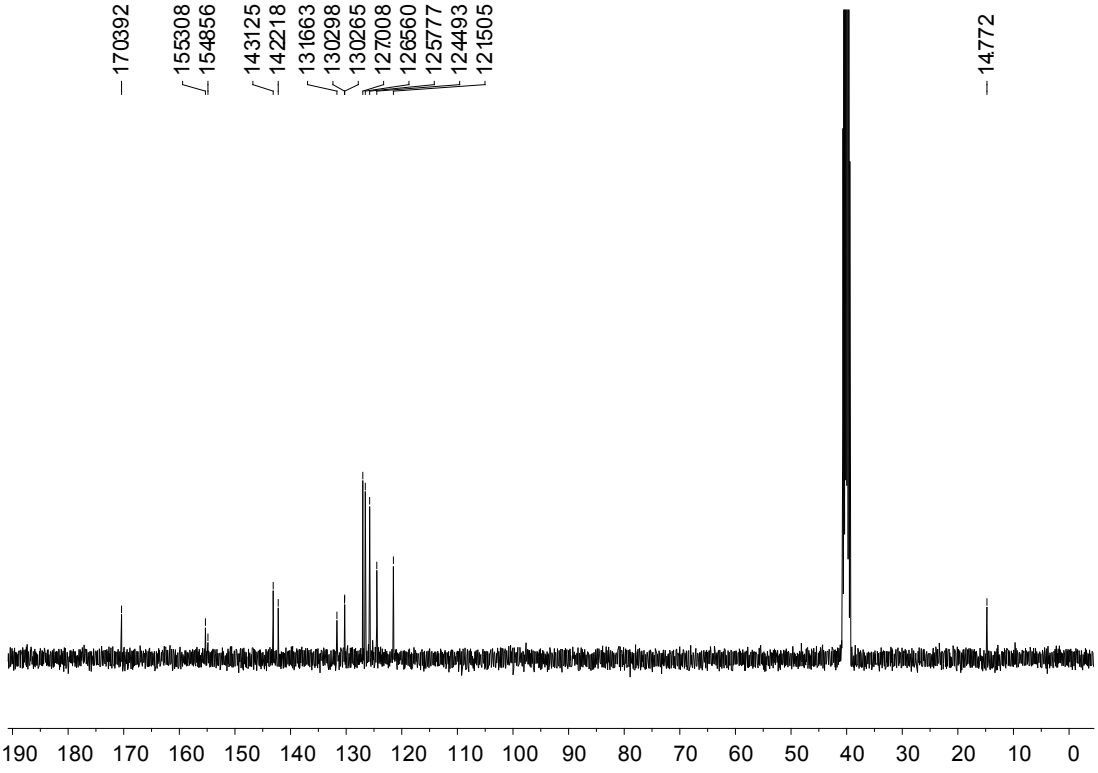
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3ap



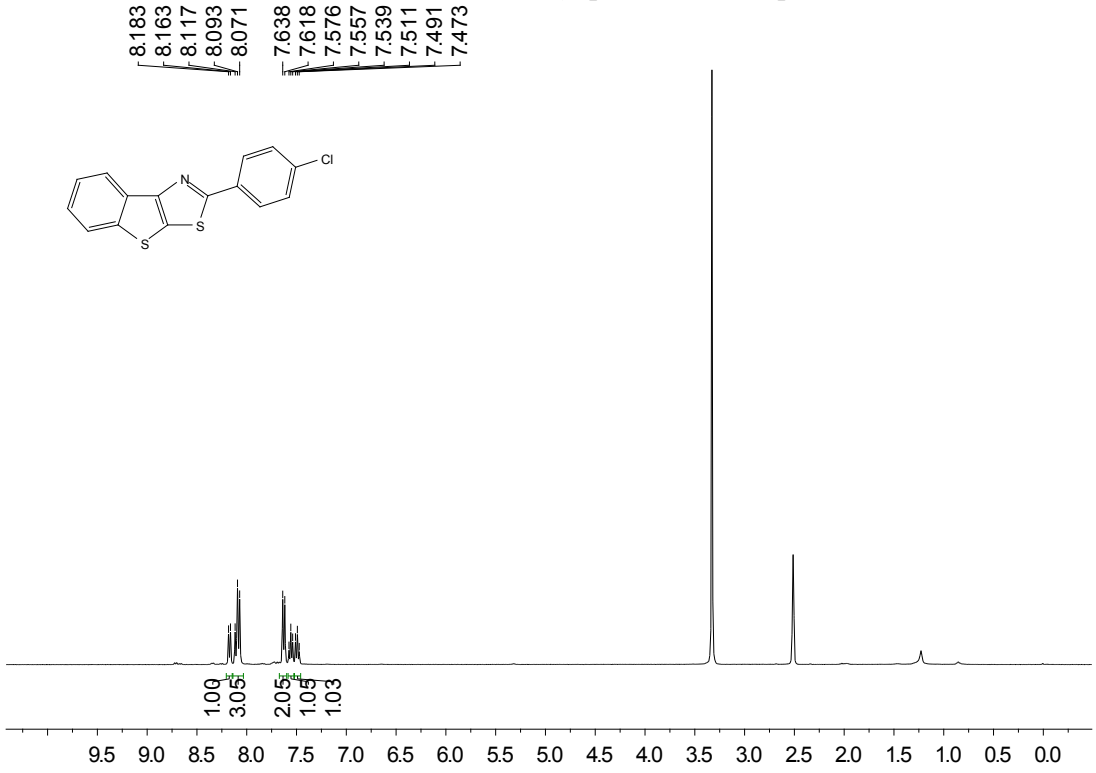
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3aq



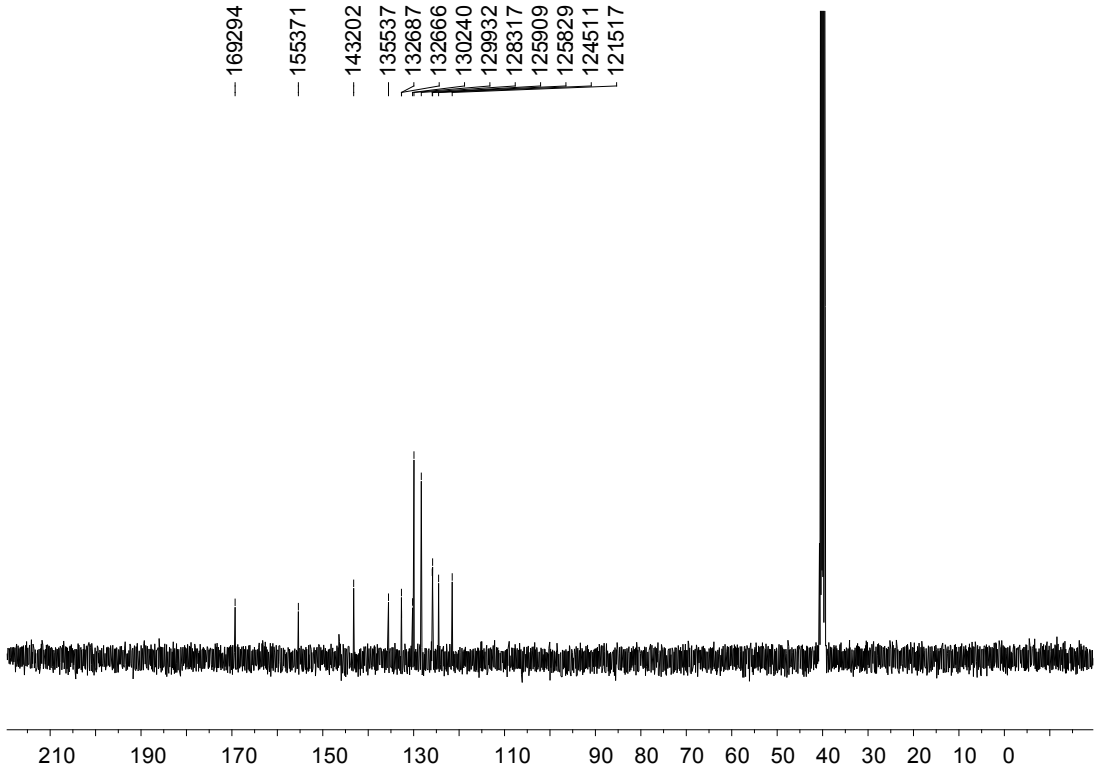
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3aq



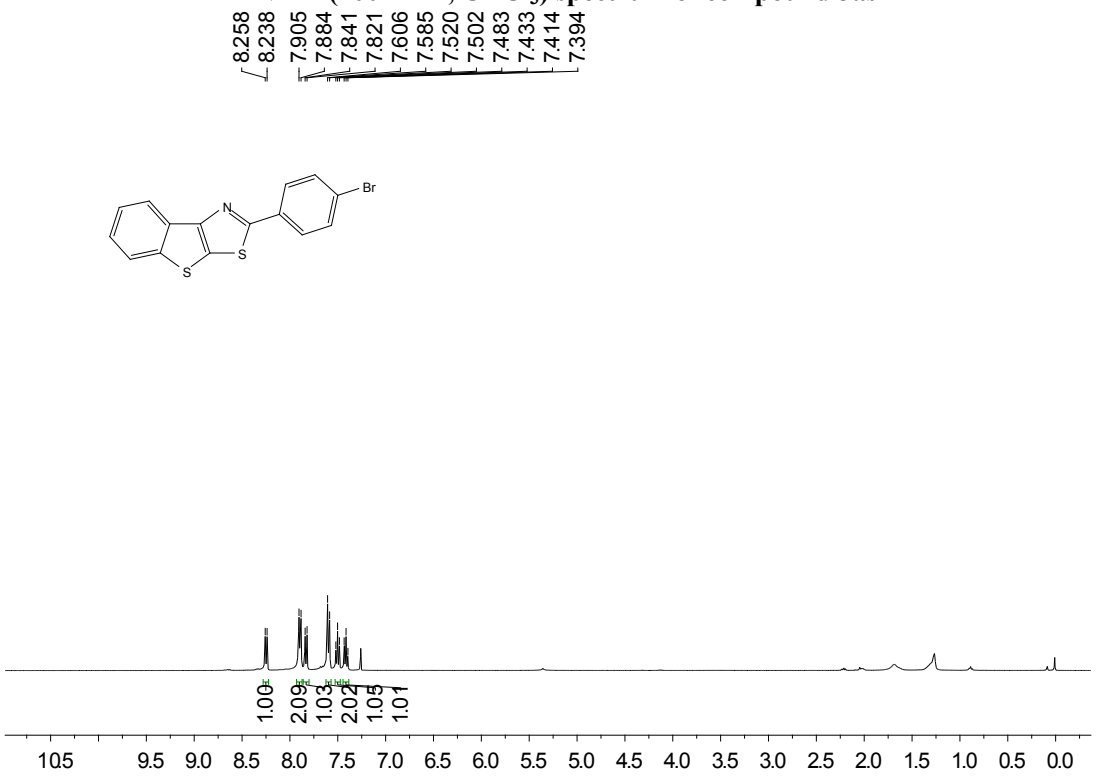
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3ar



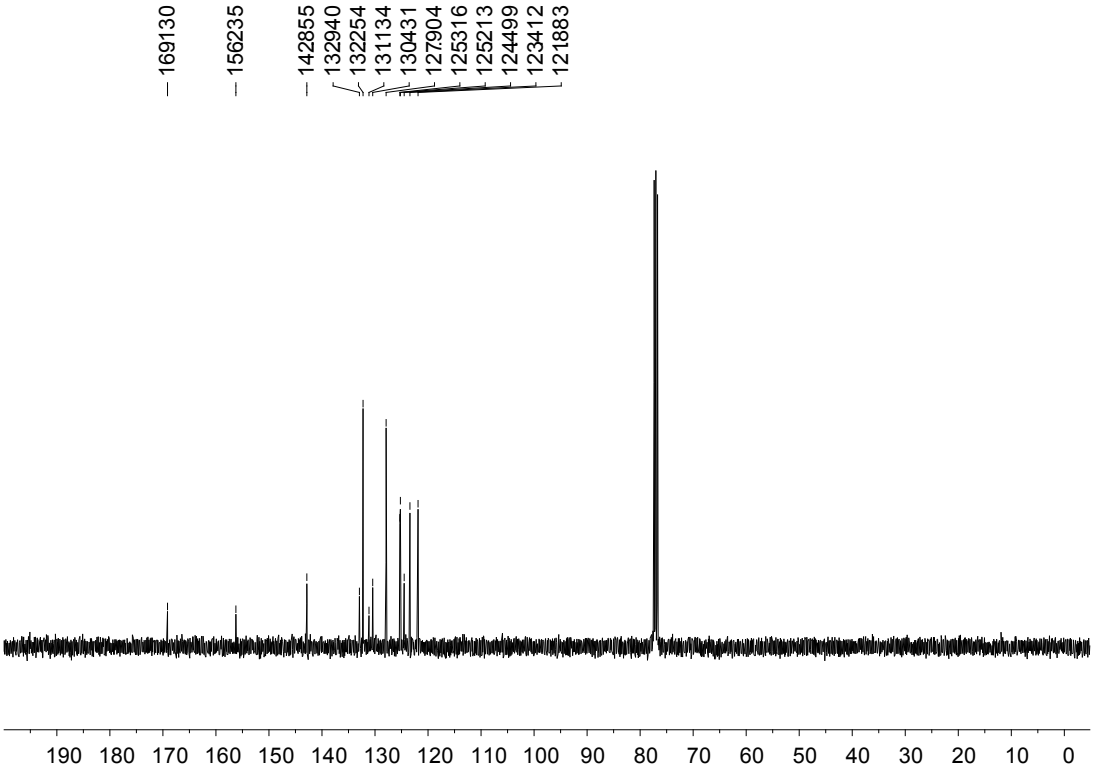
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ar



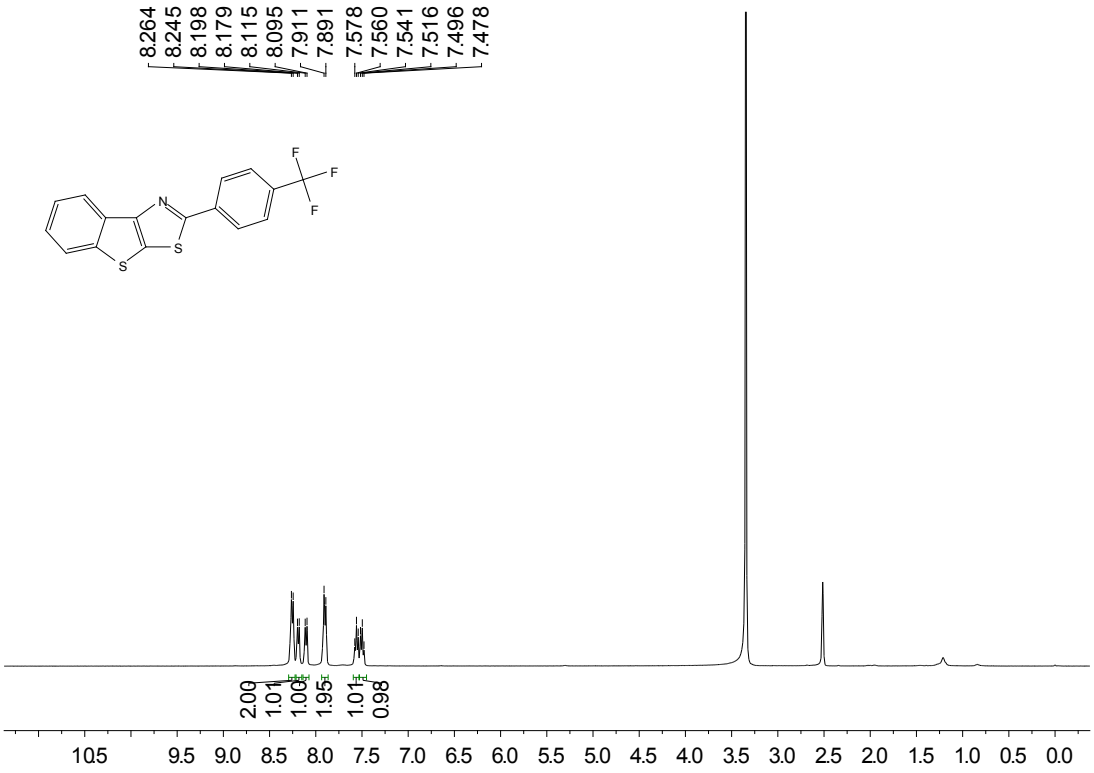
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3as



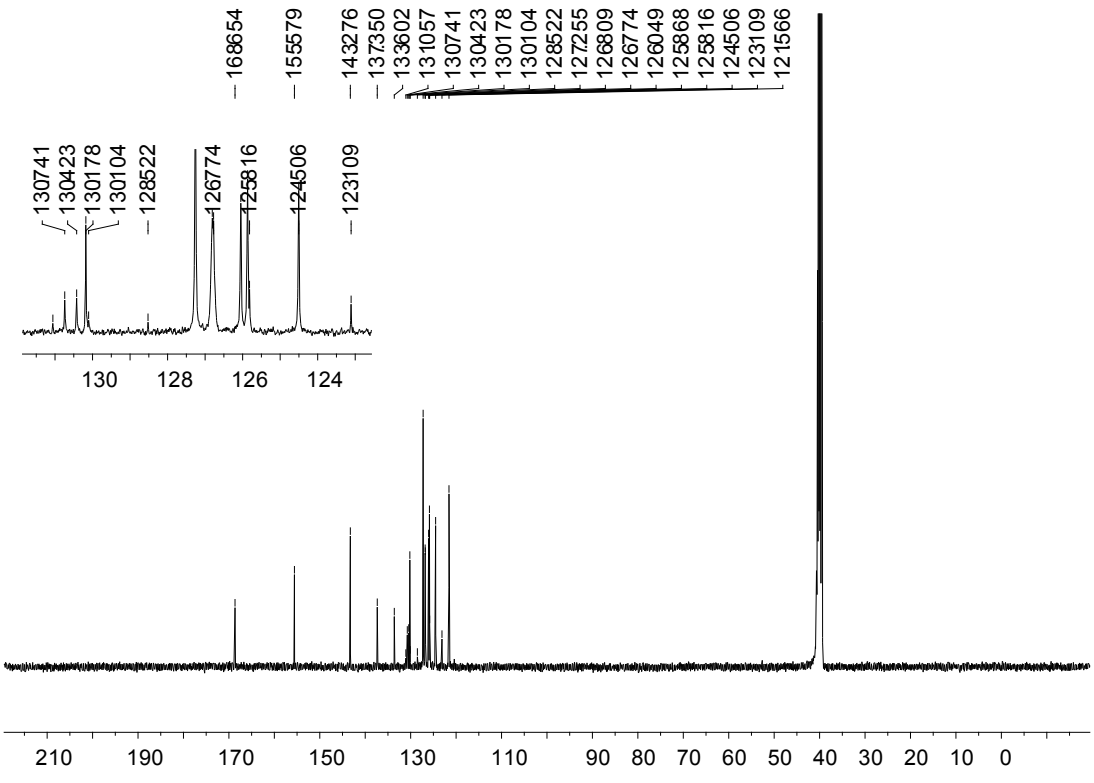
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3as



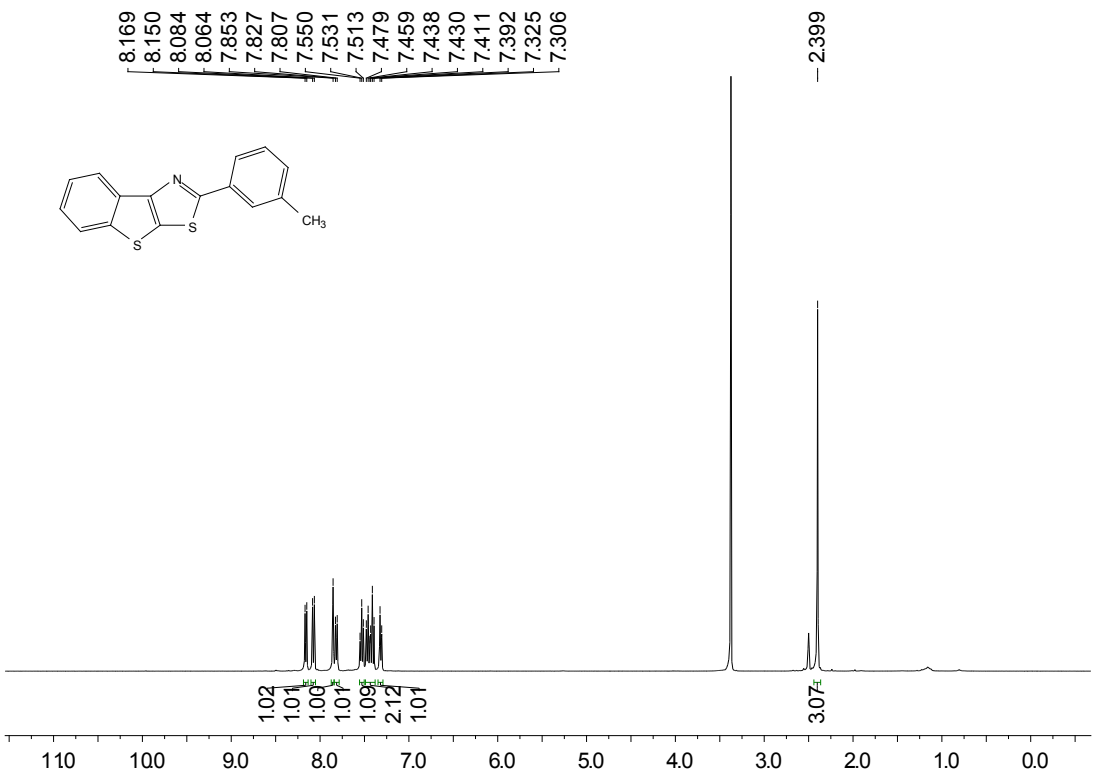
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3at



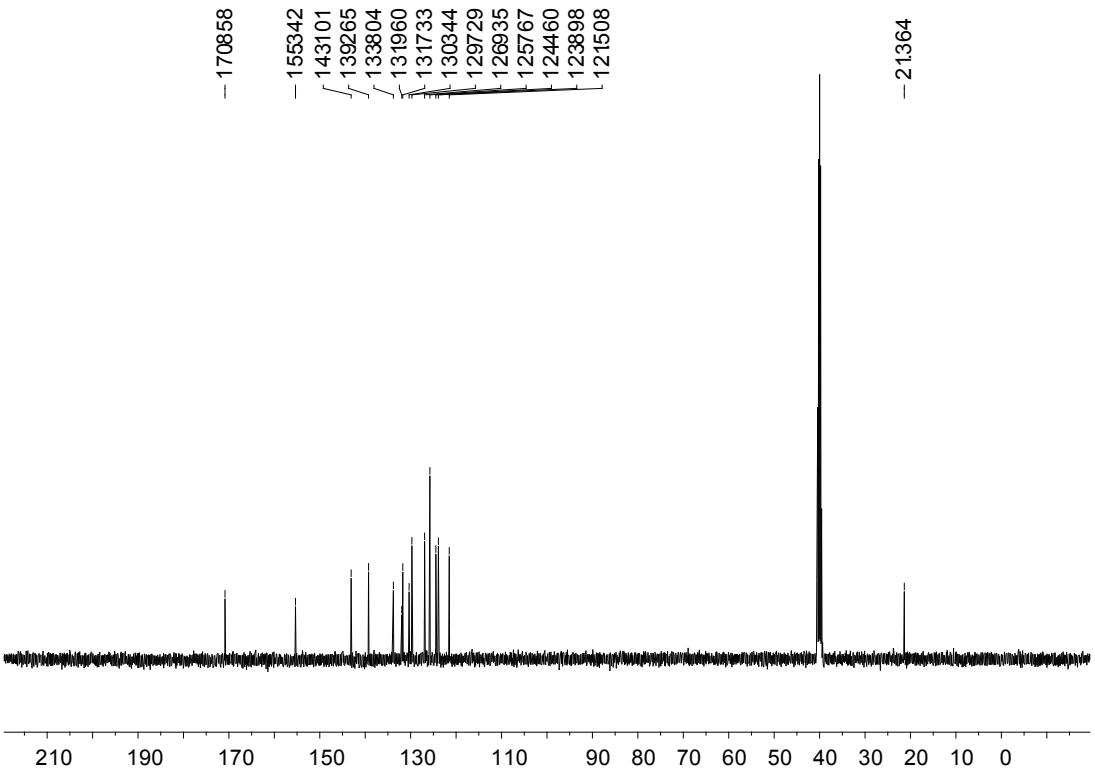
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3at



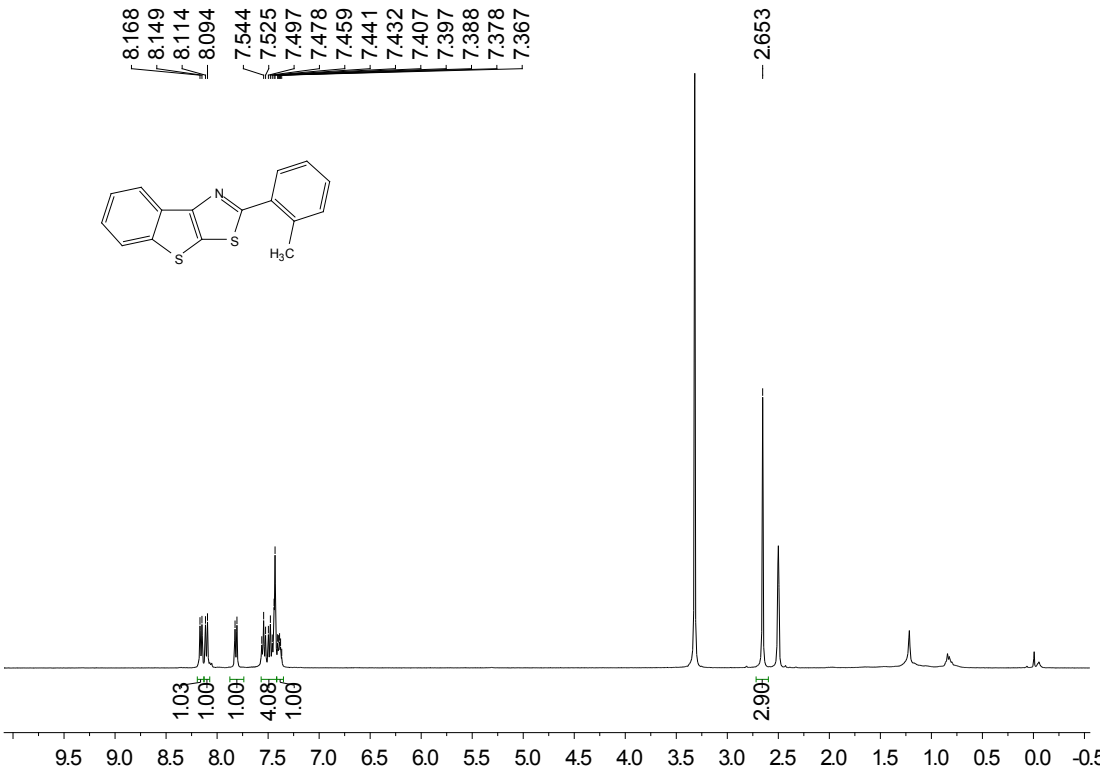
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3au



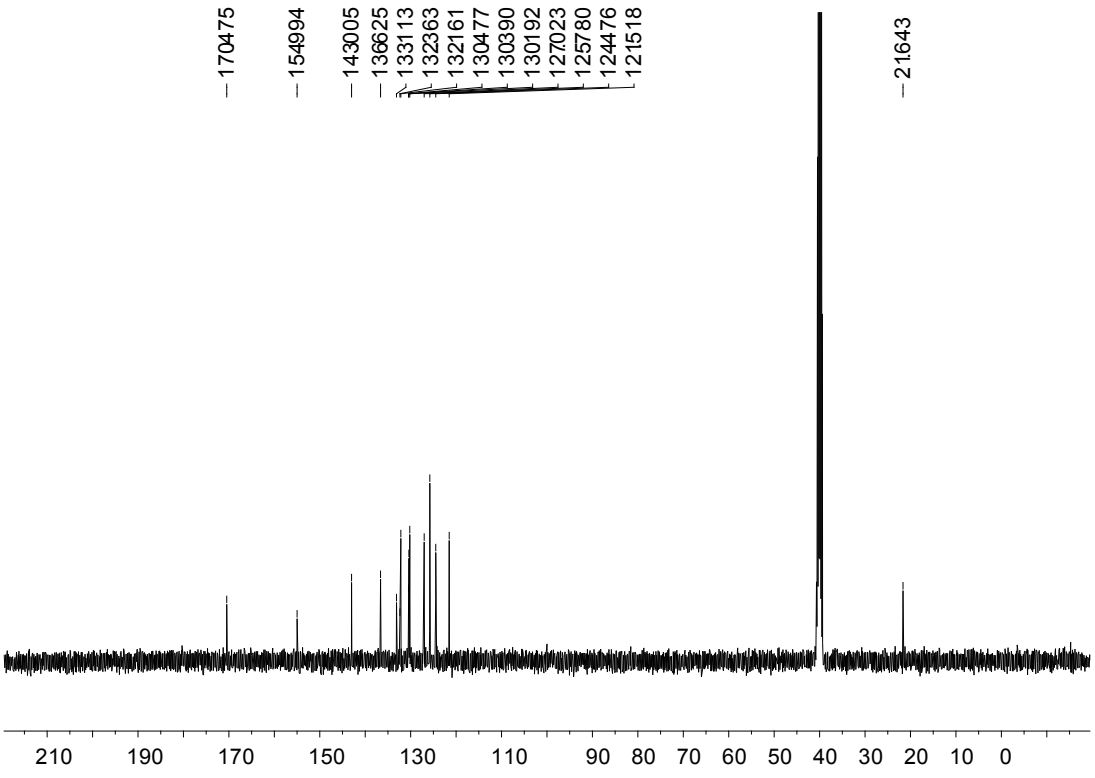
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3au



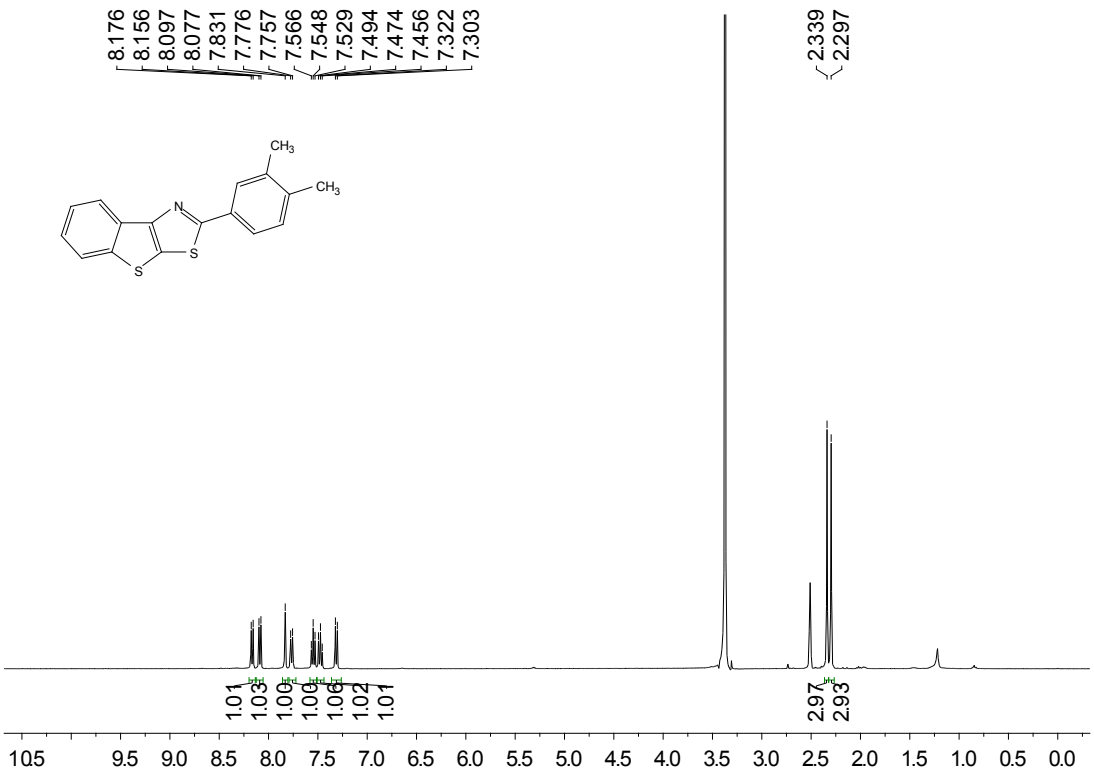
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3av



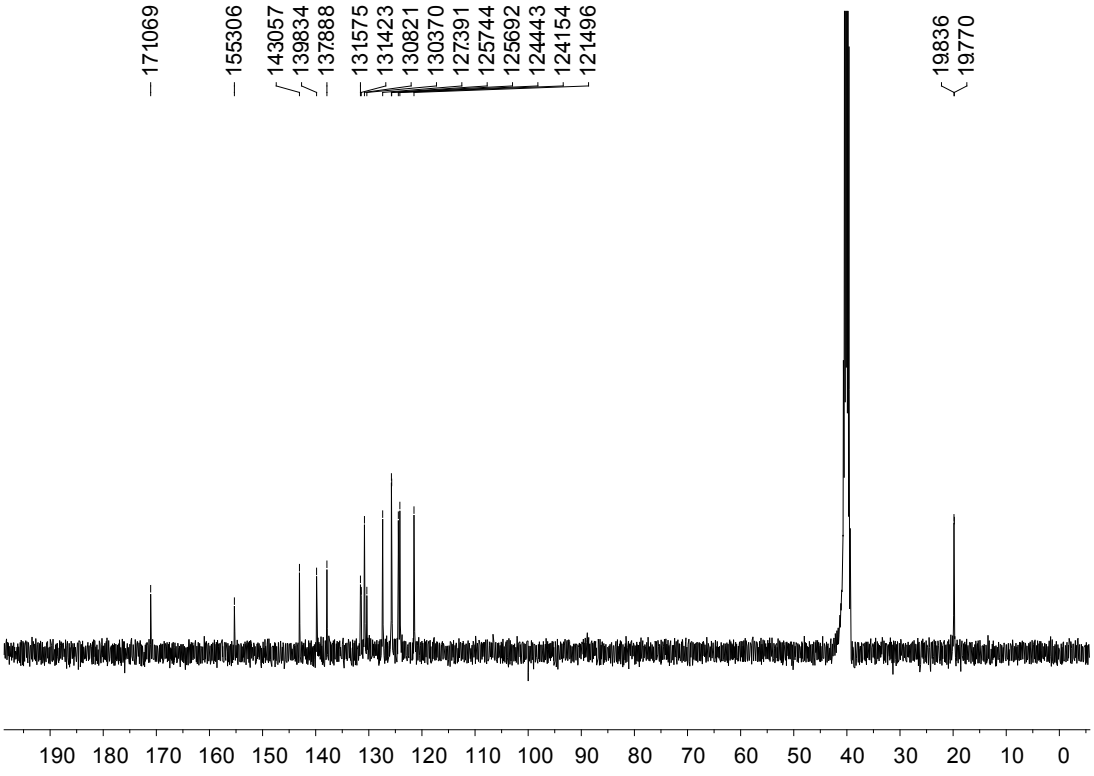
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3av



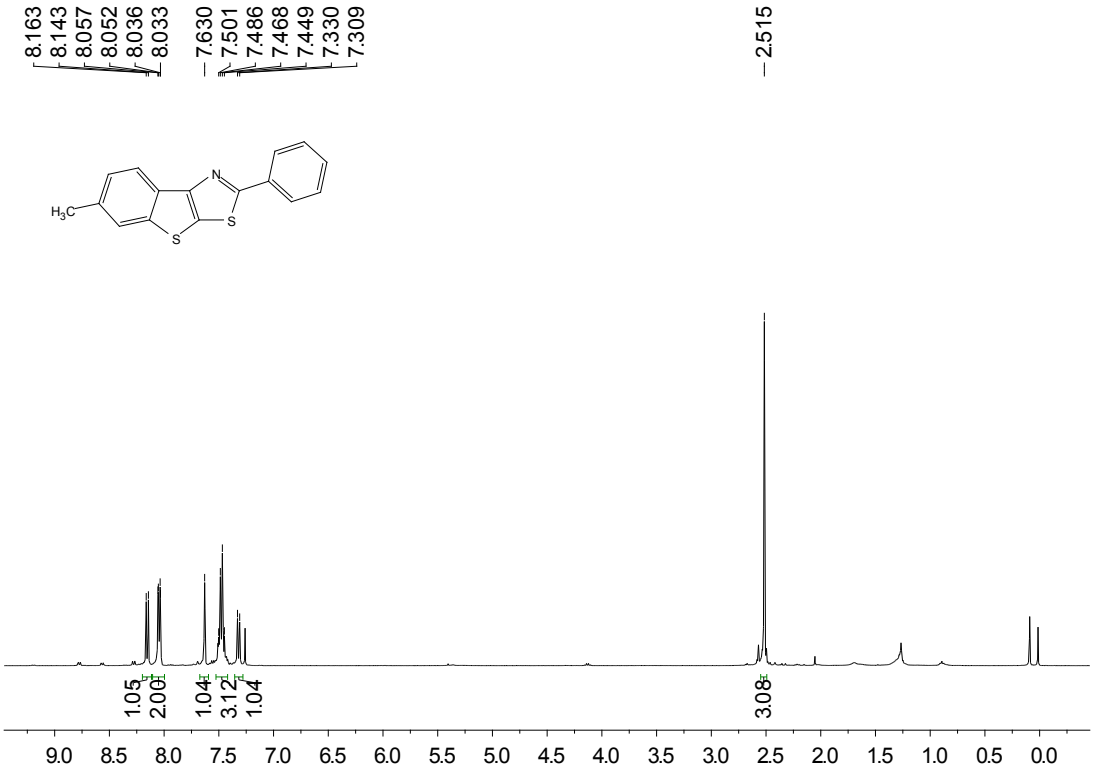
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3aw



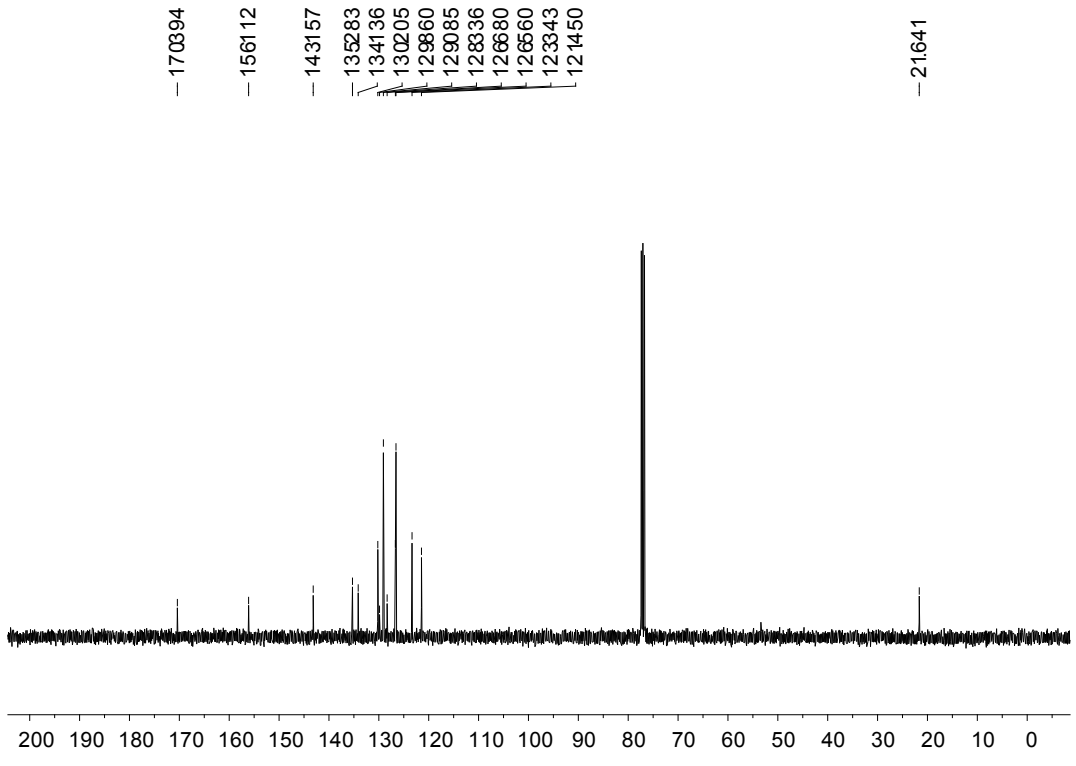
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3aw



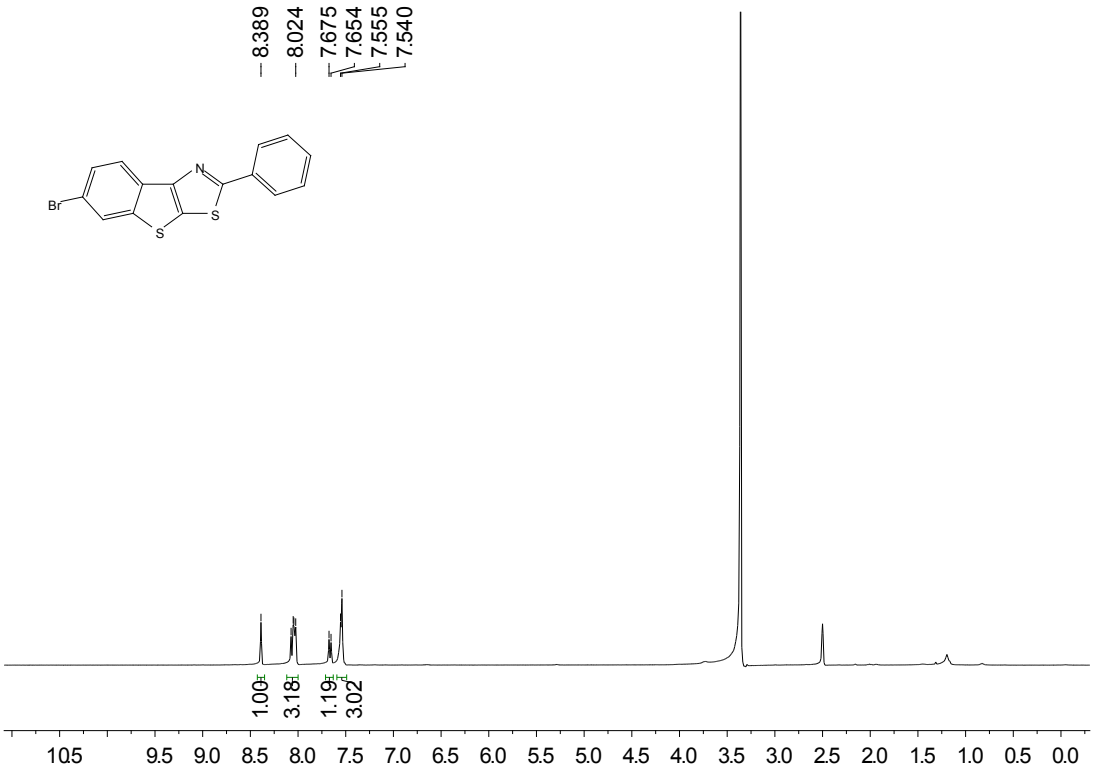
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3ba



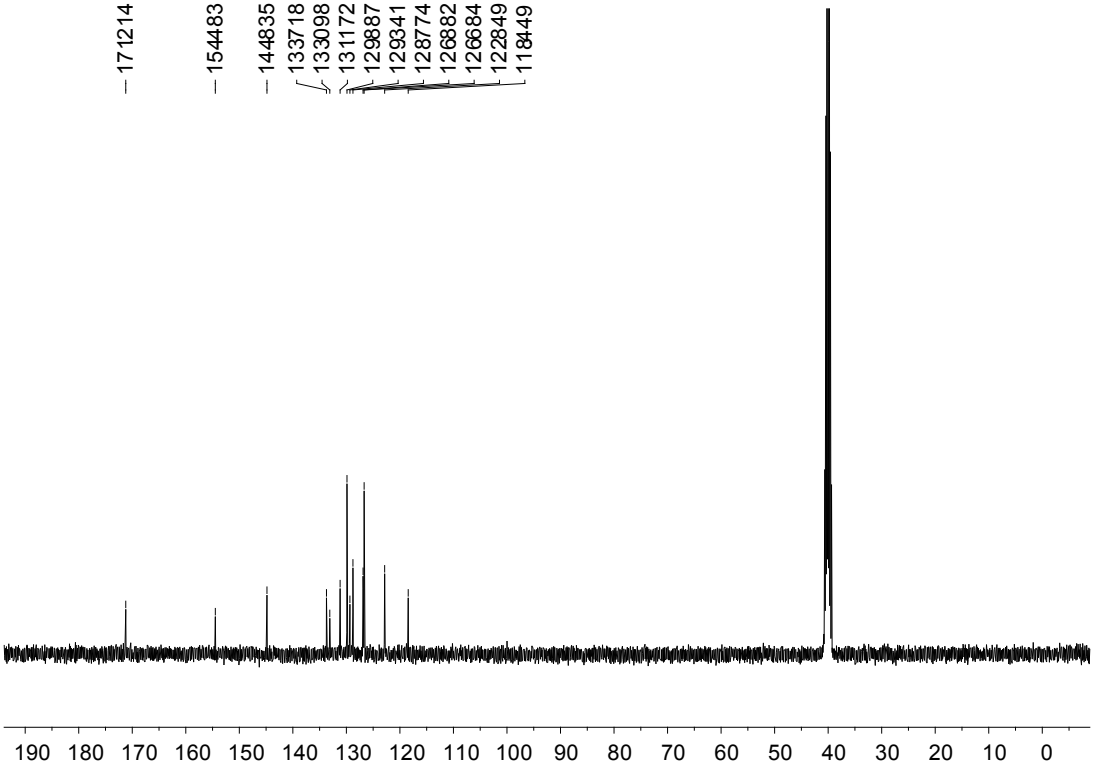
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3ba



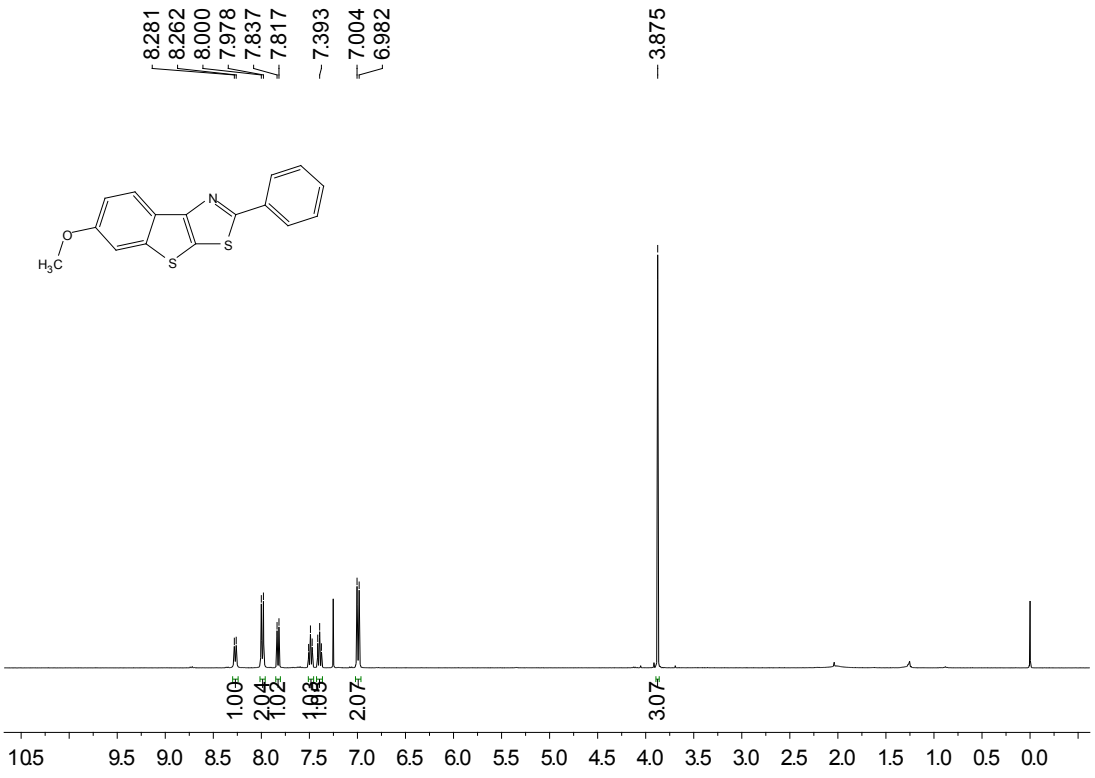
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3ca



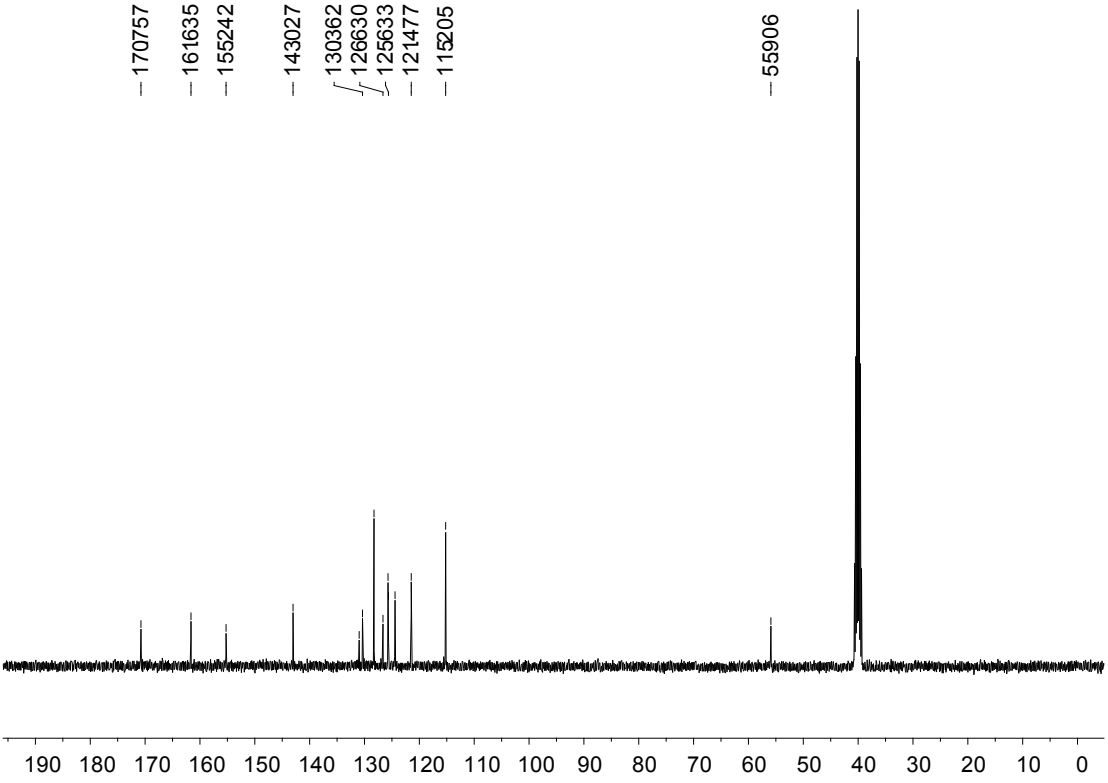
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ca



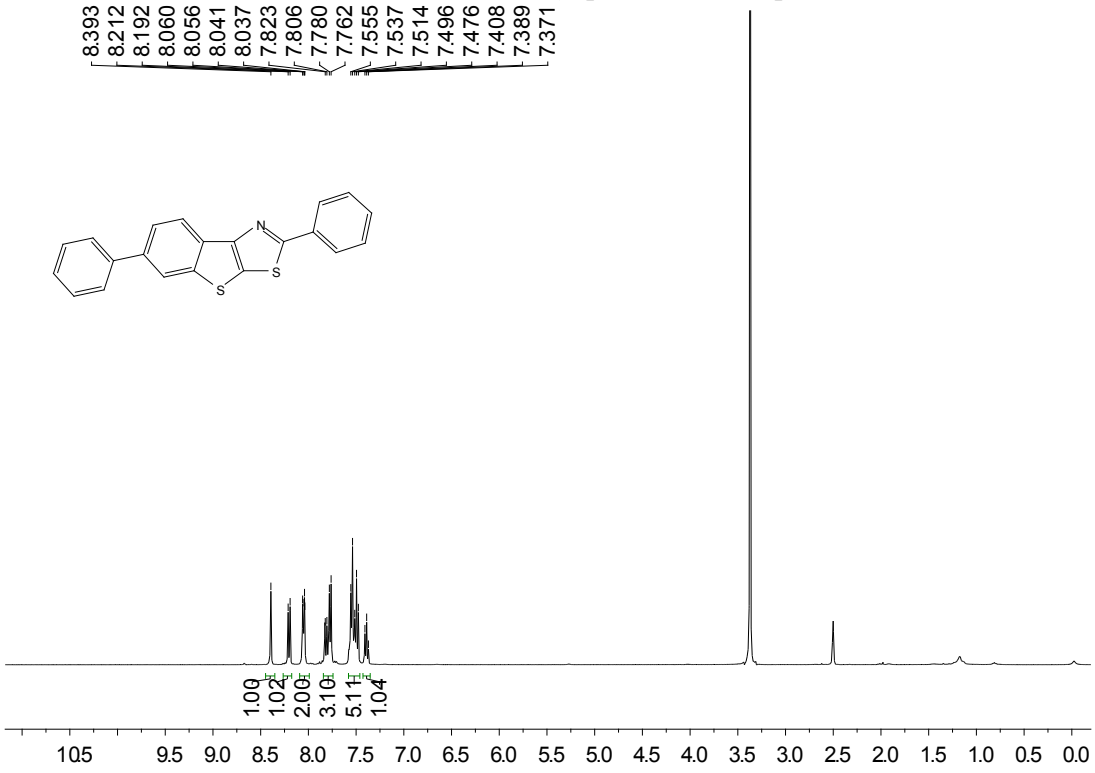
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3da



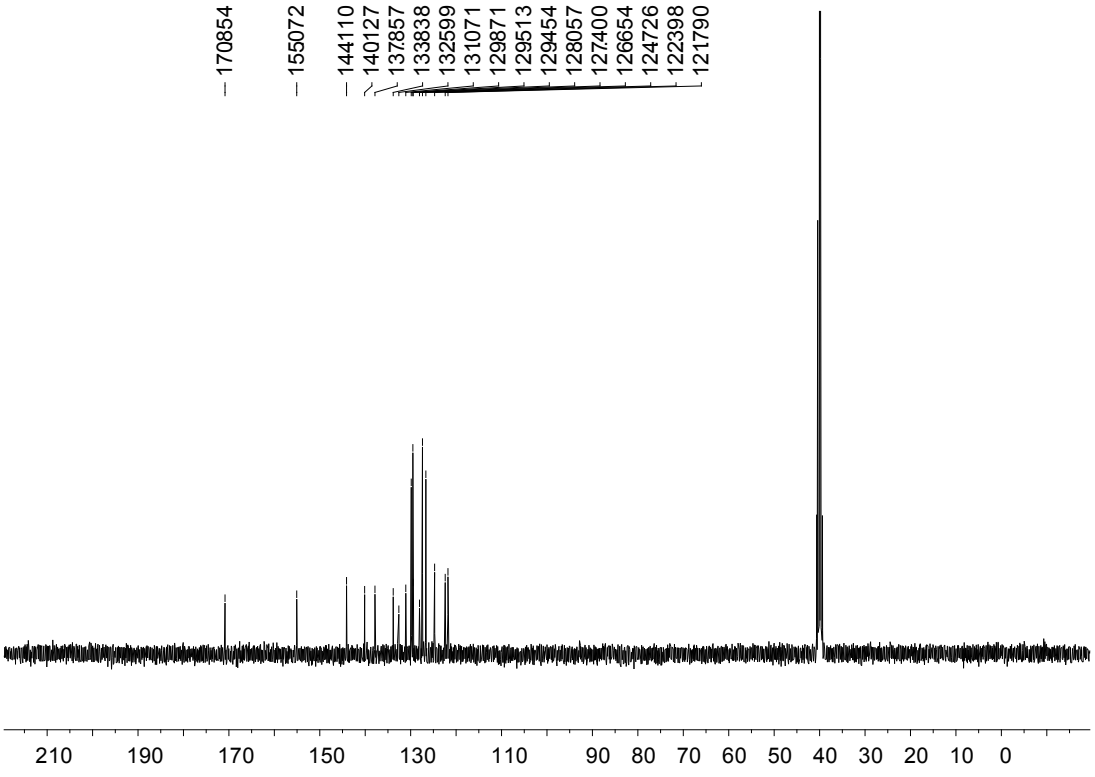
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3da



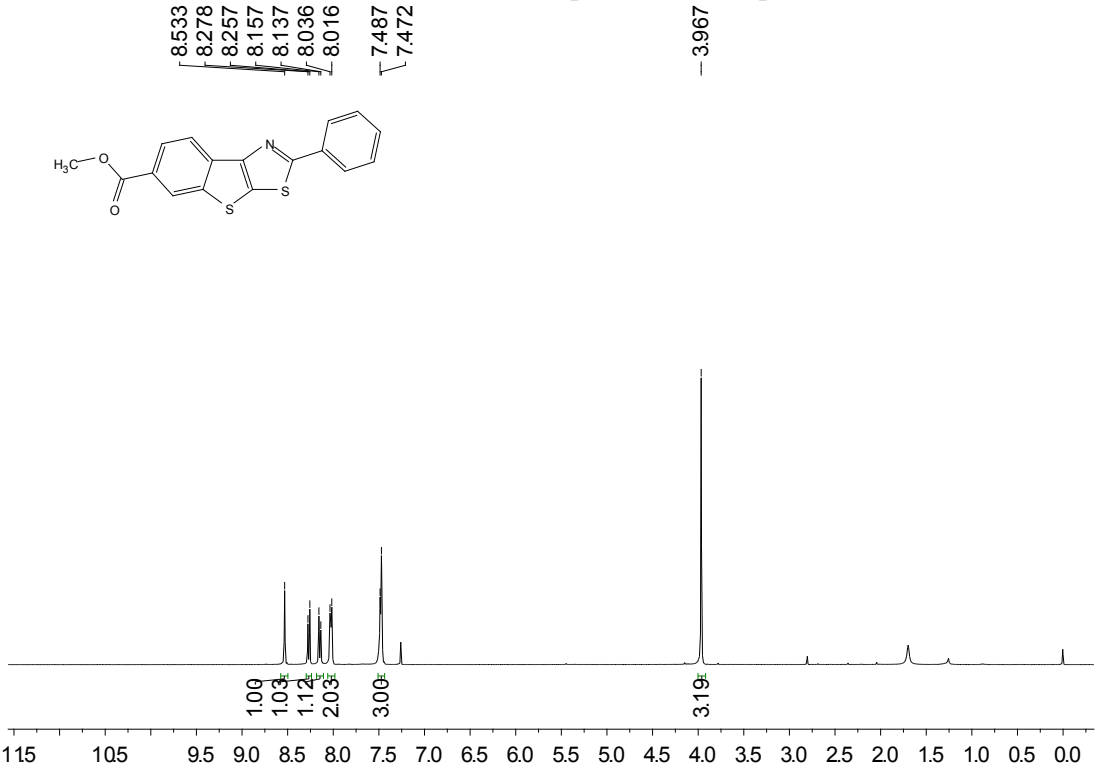
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3ea



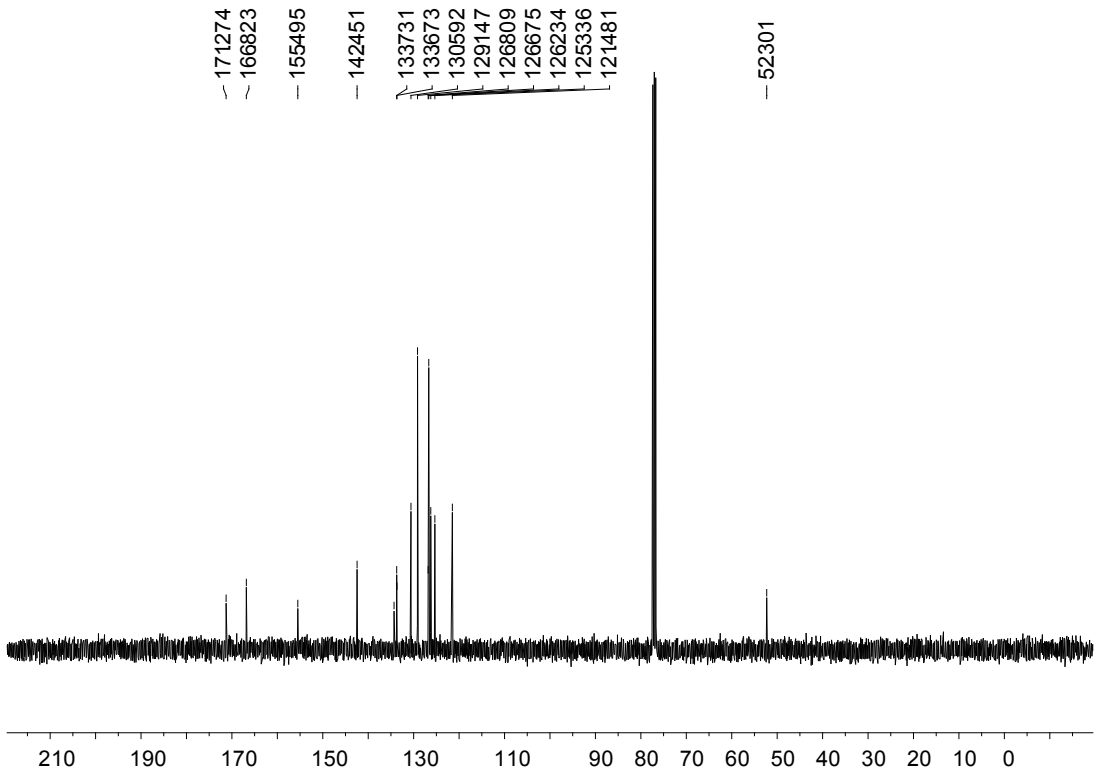
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ea



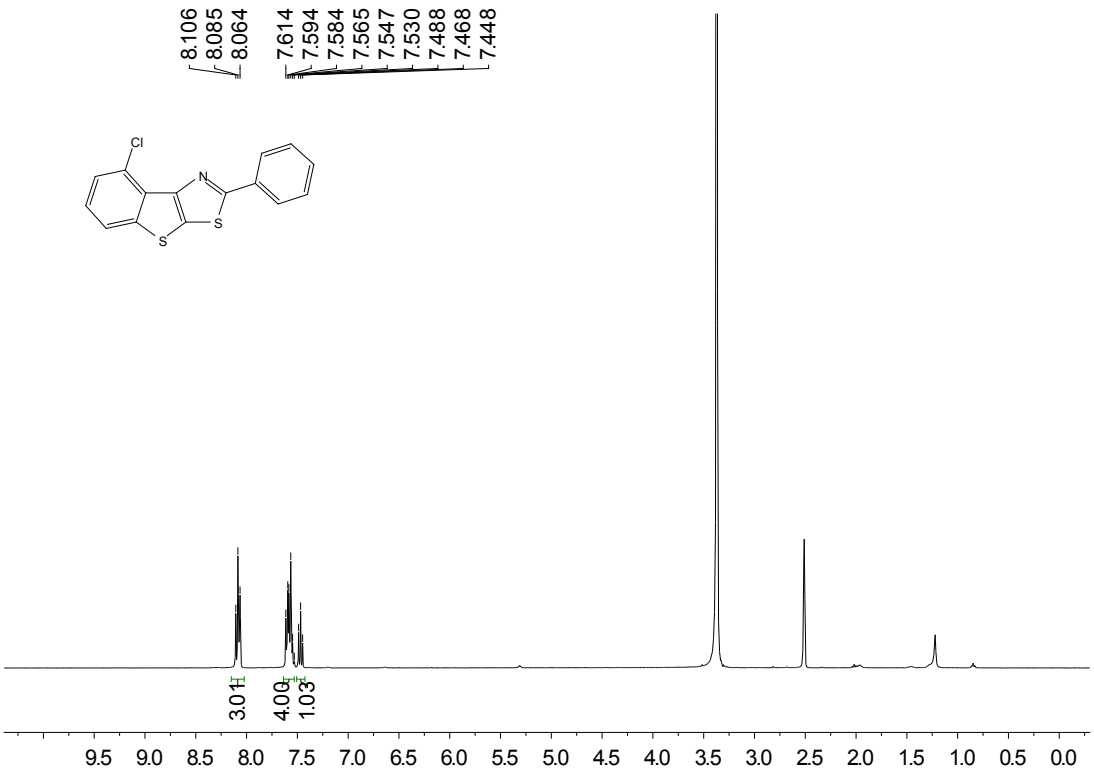
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3fa



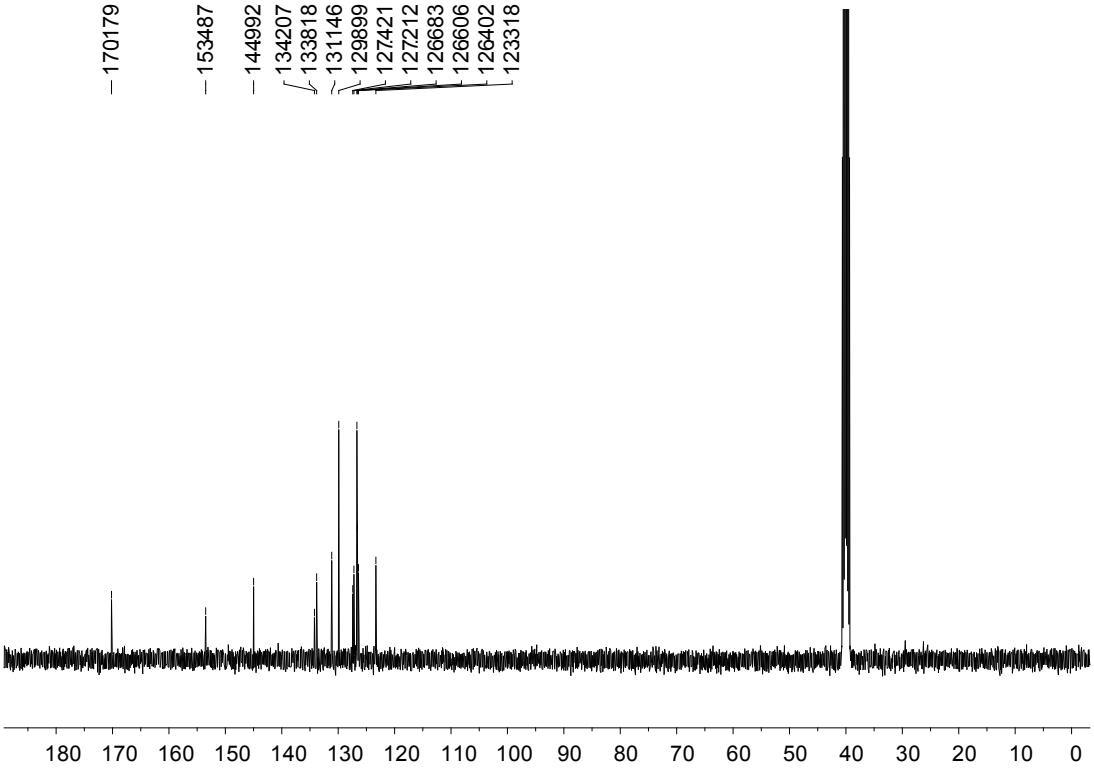
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3fa



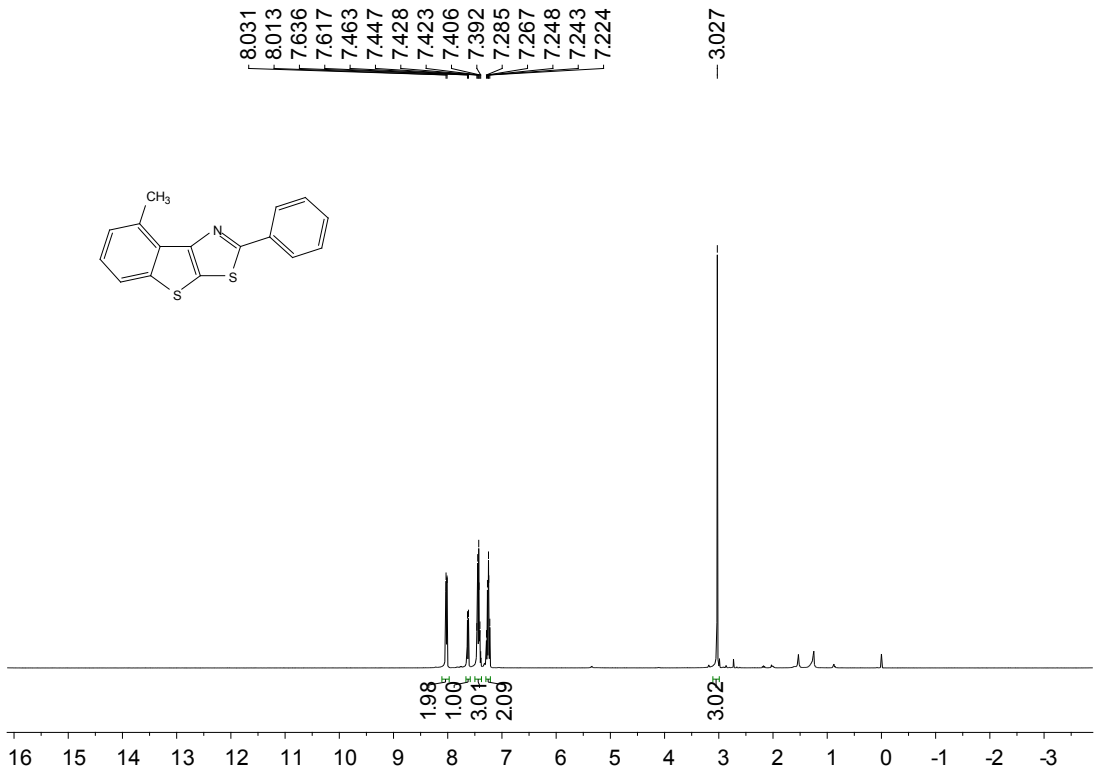
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3ga



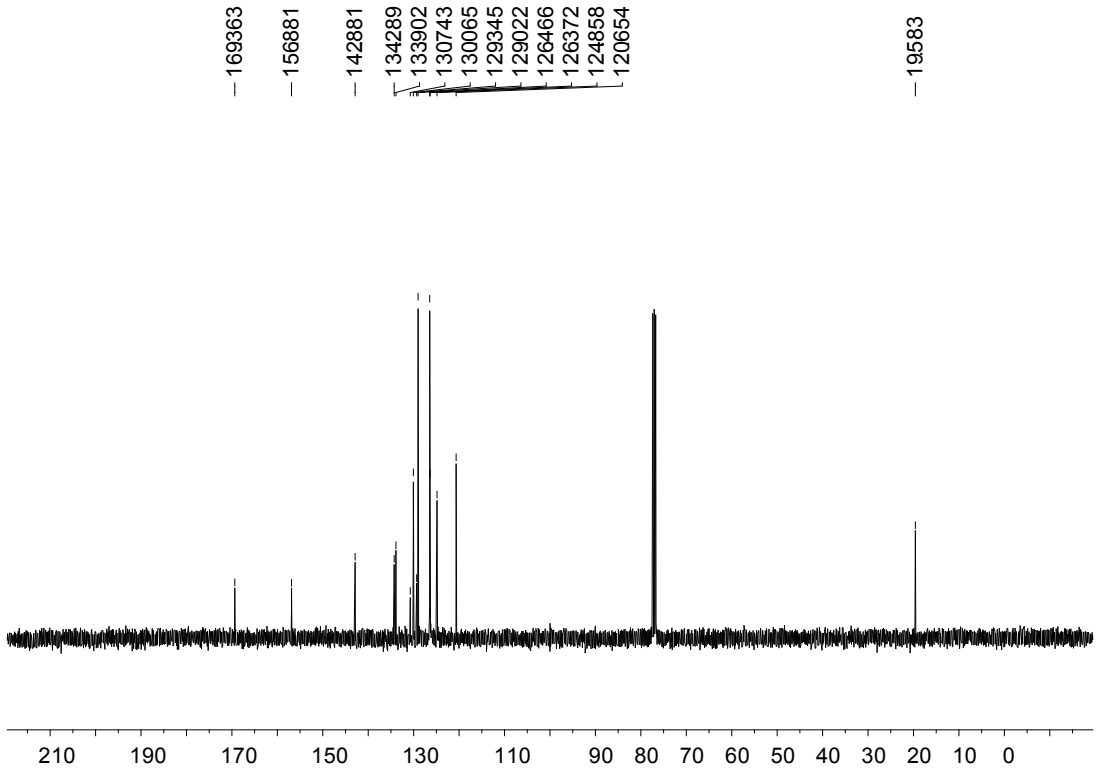
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ga



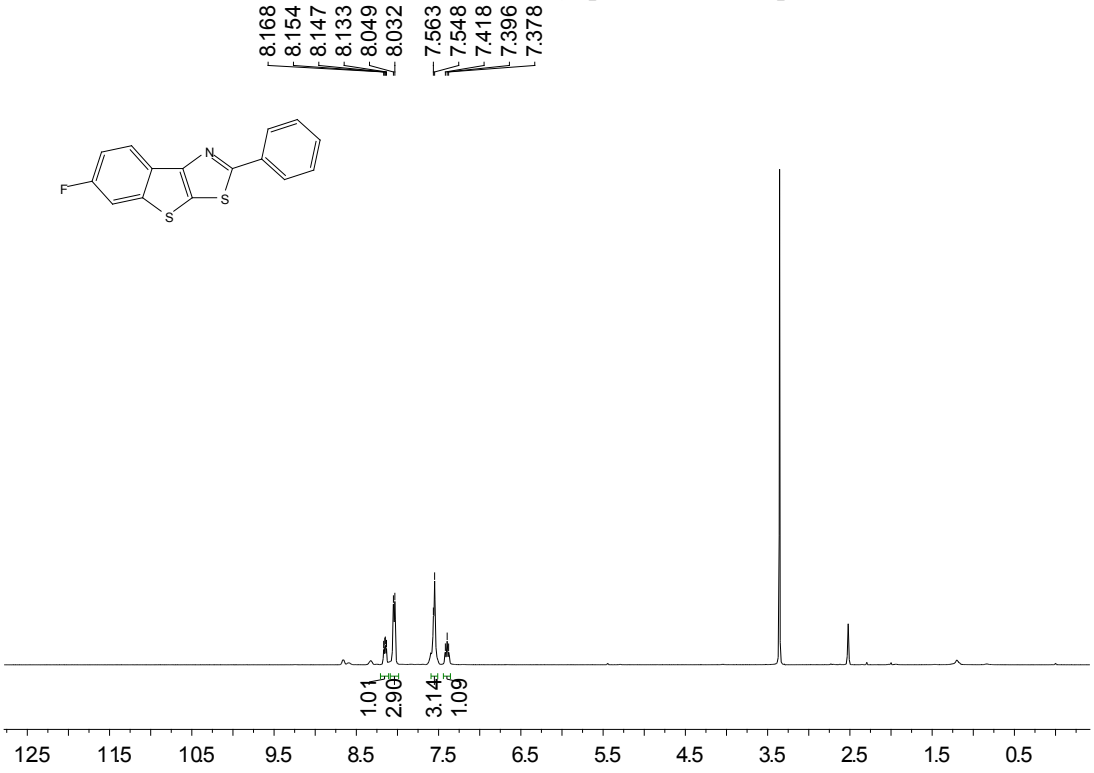
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3ha



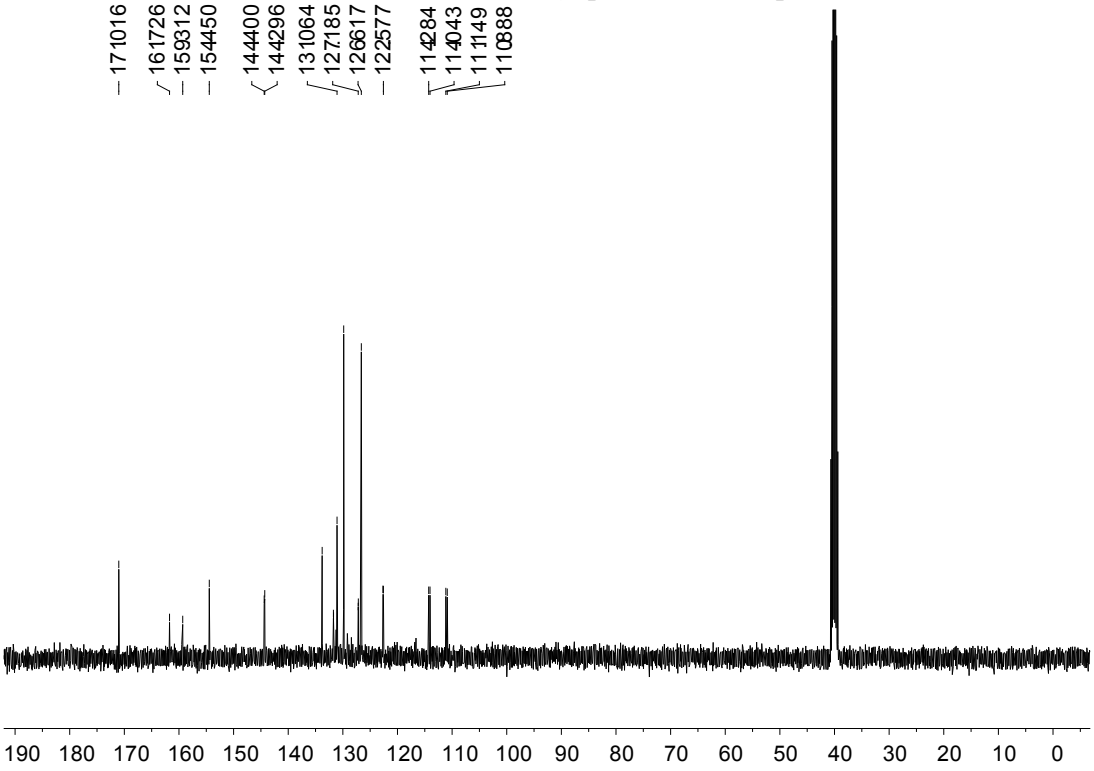
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3ha



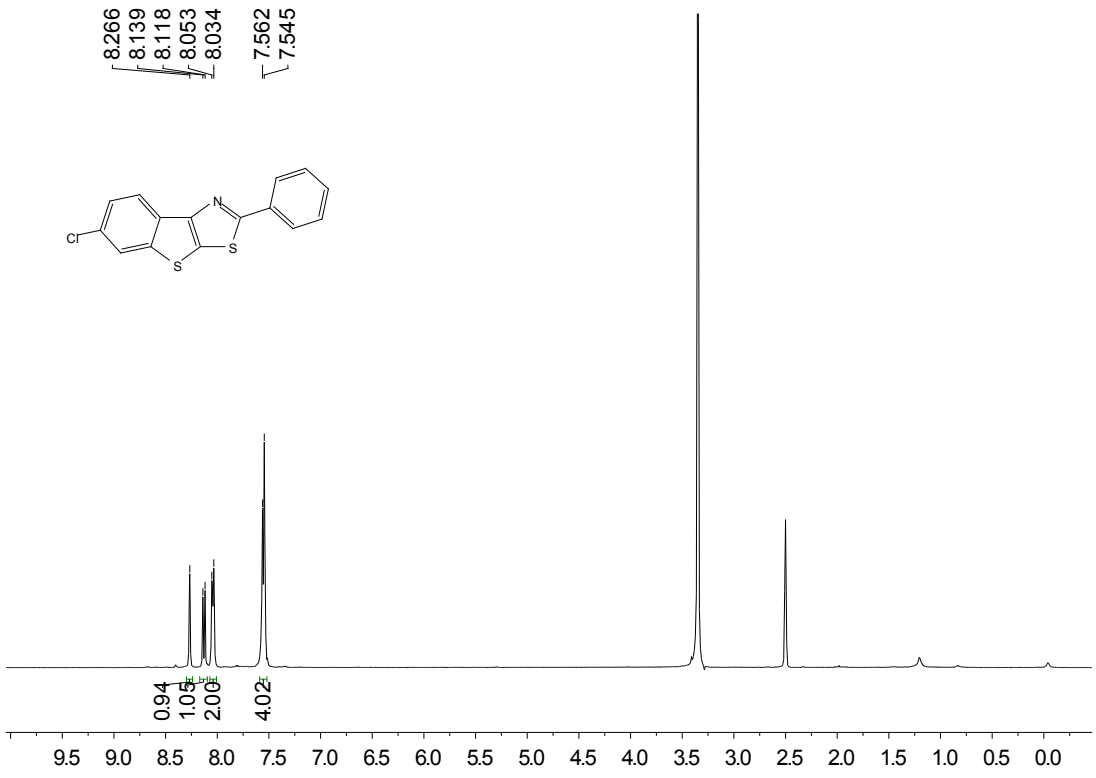
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3ia



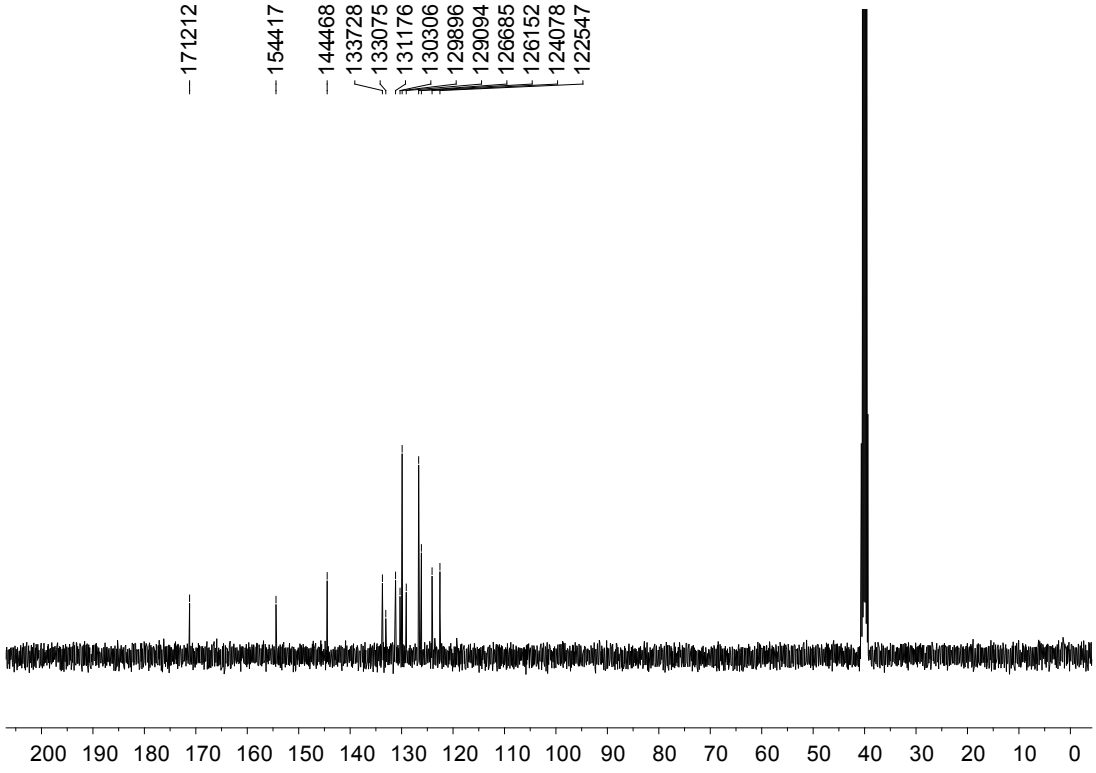
^{1}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ia



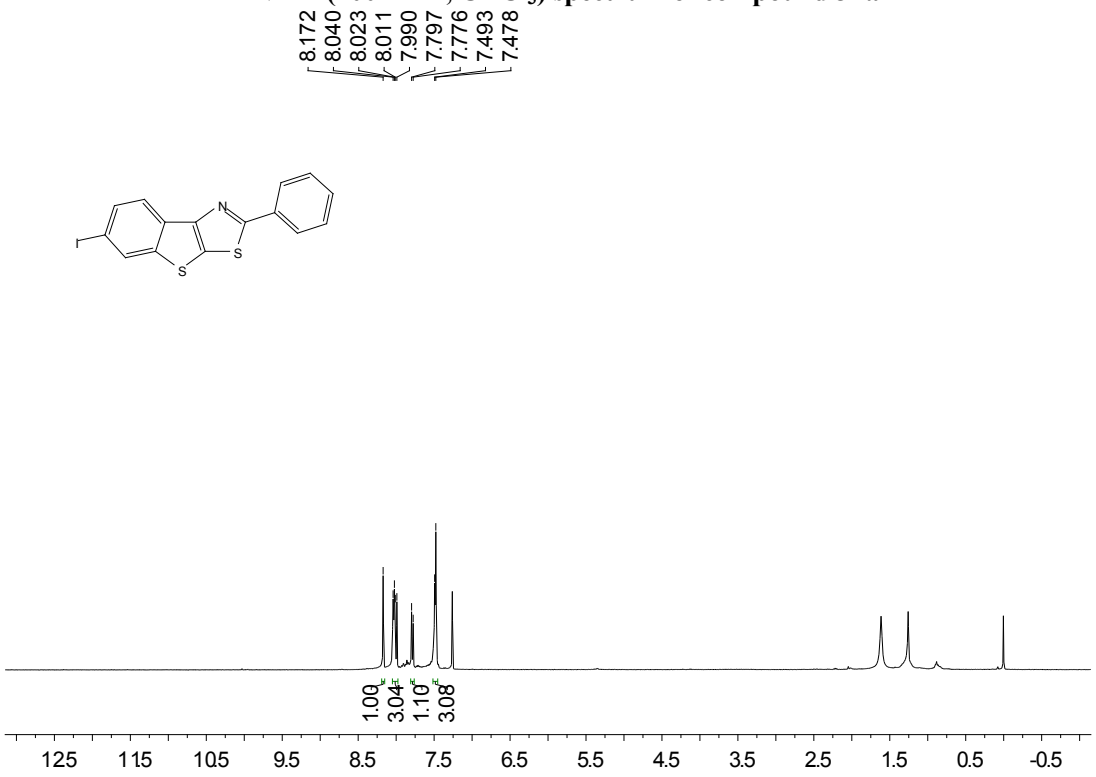
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3ja



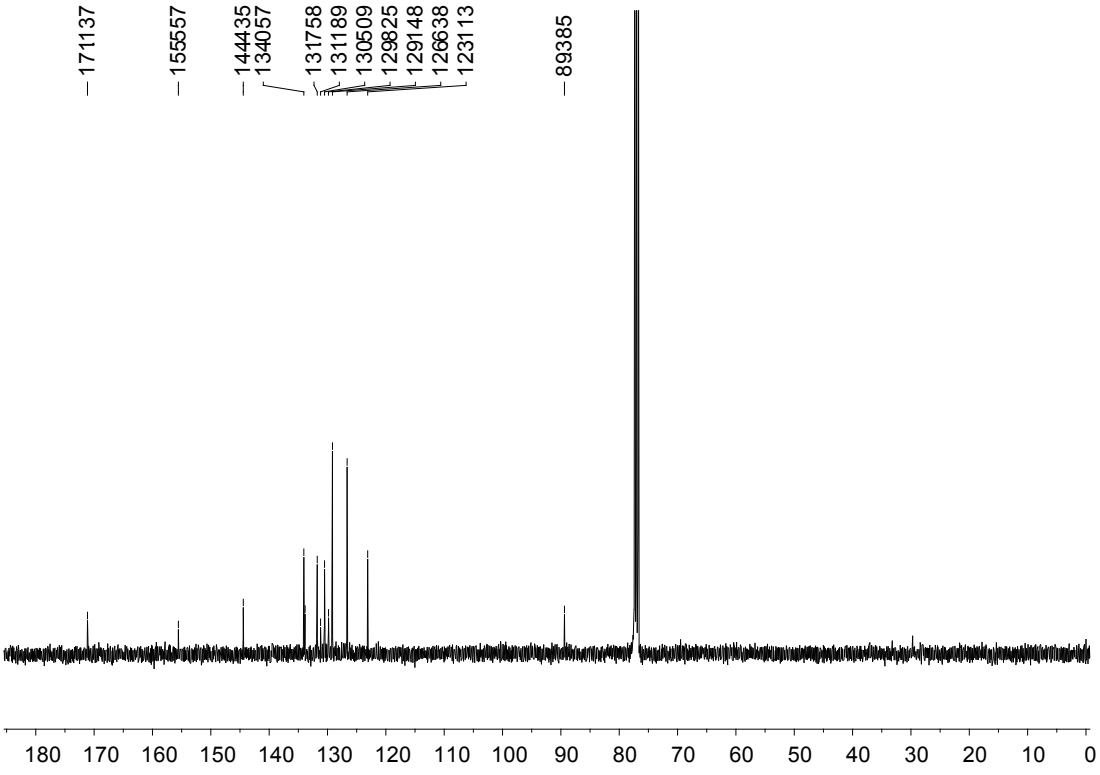
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ja



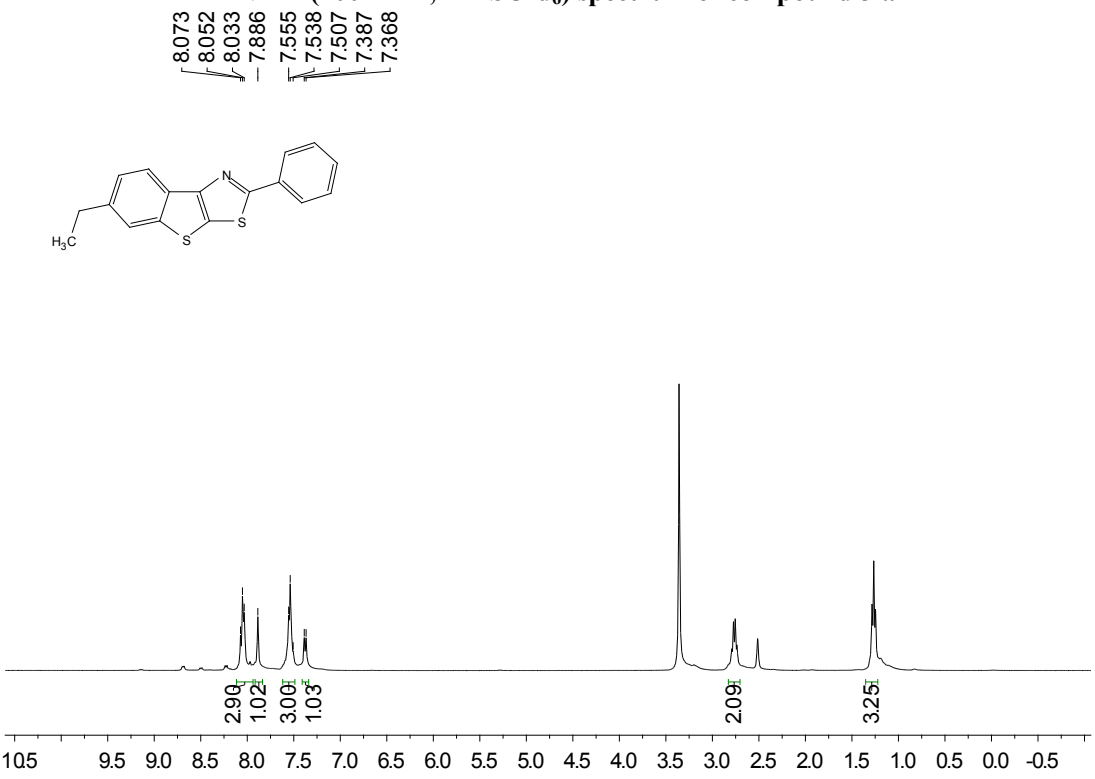
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3ka



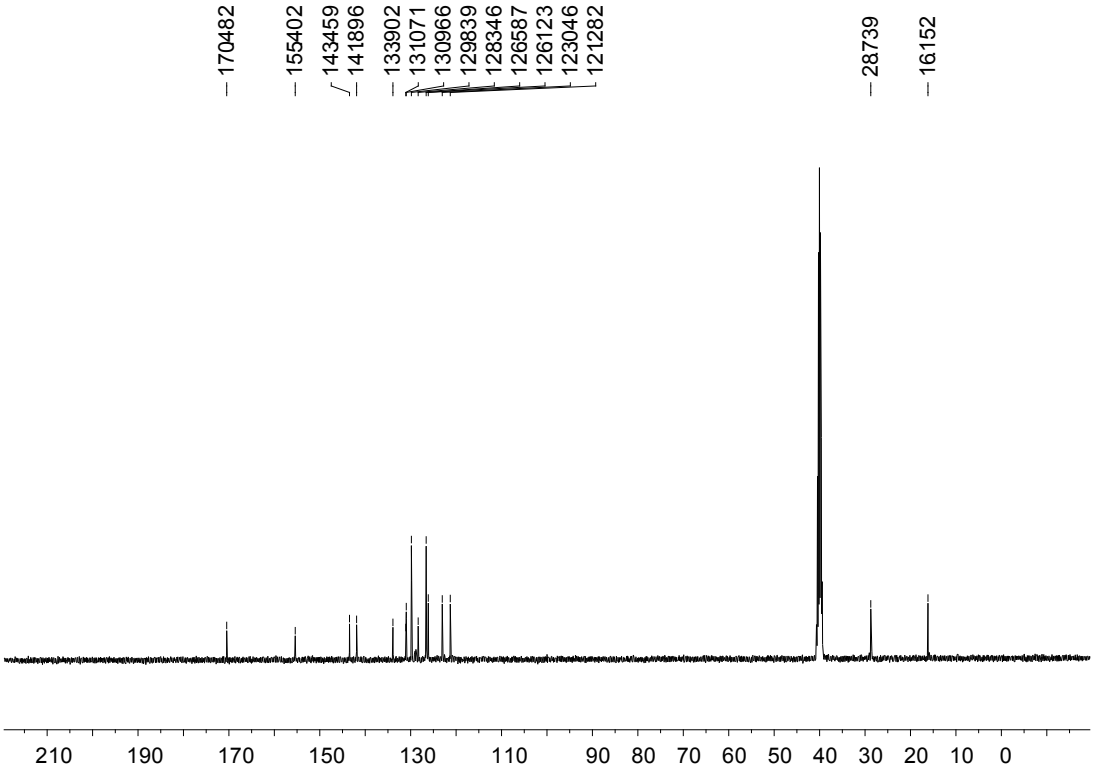
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3ka



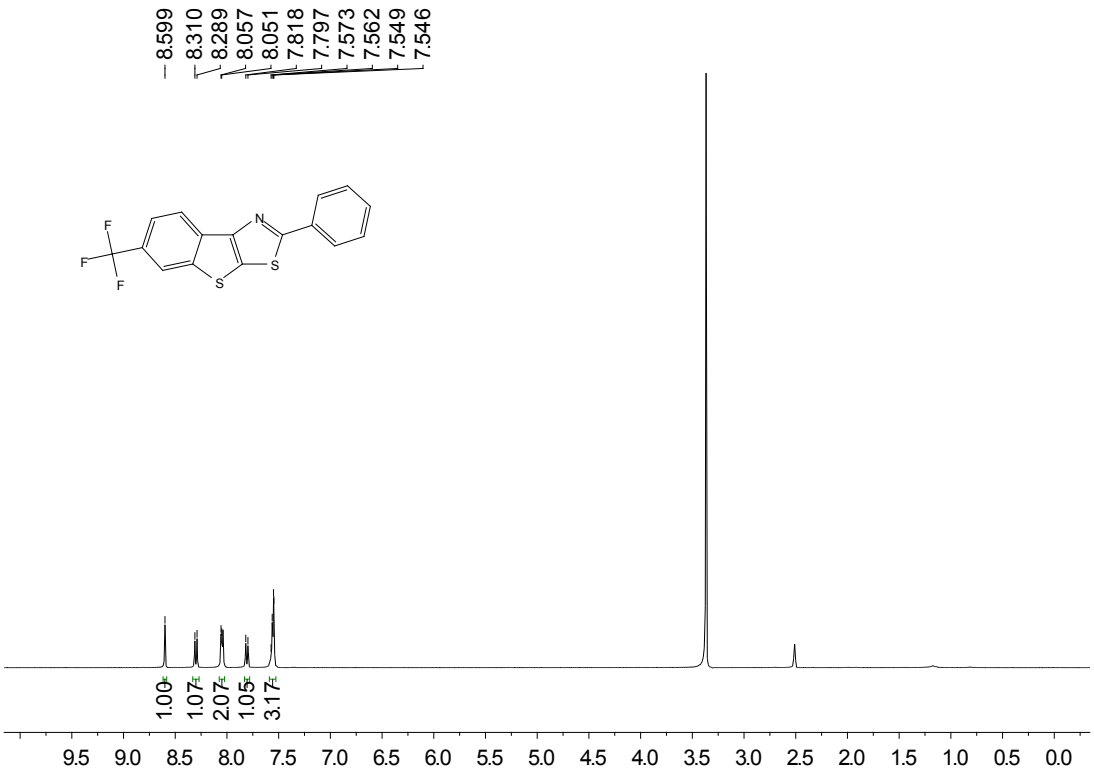
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3la



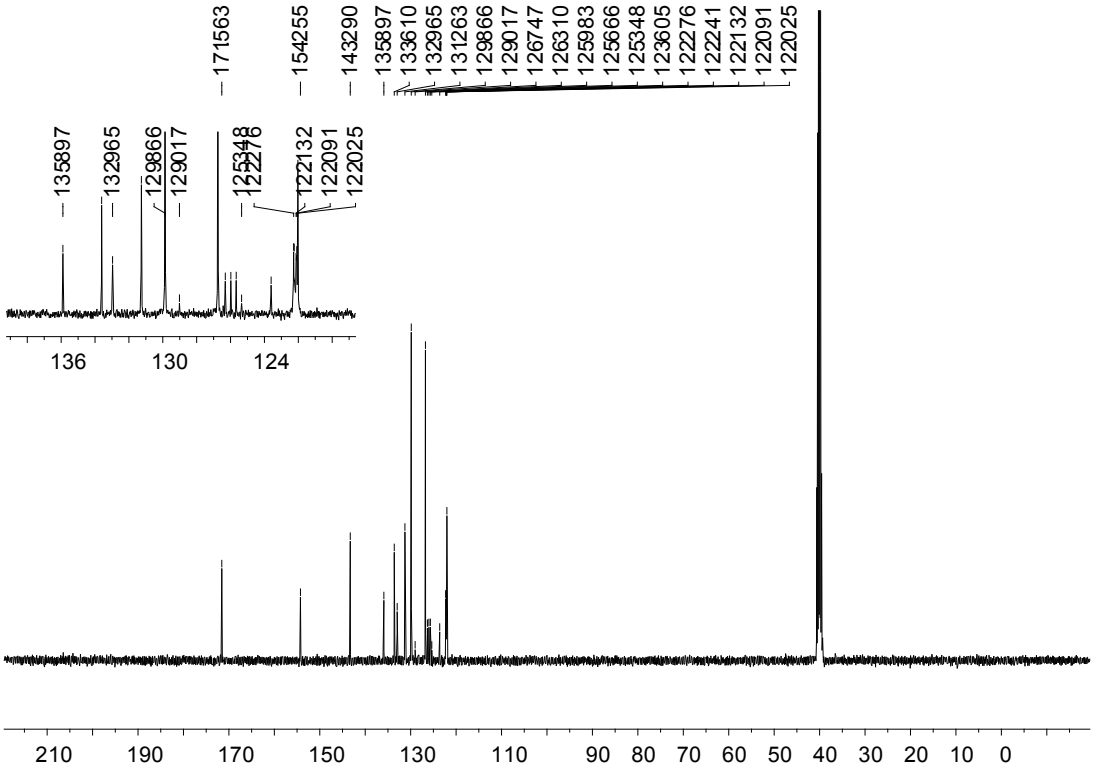
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3la



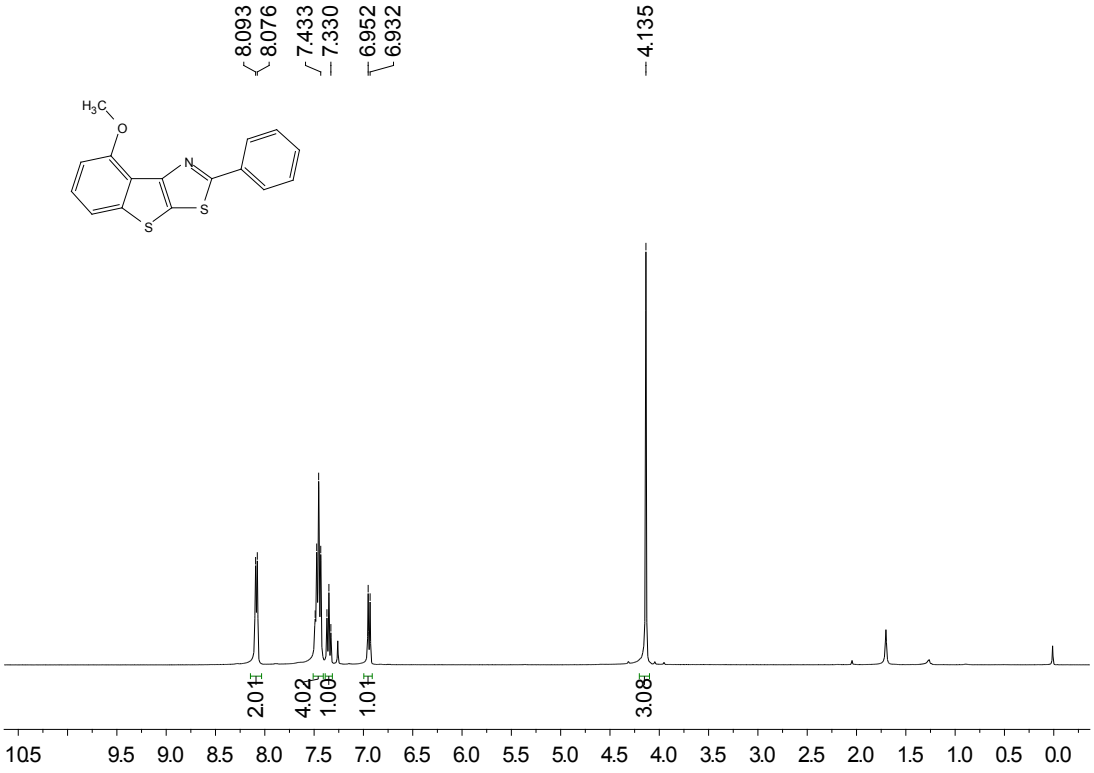
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 3ma



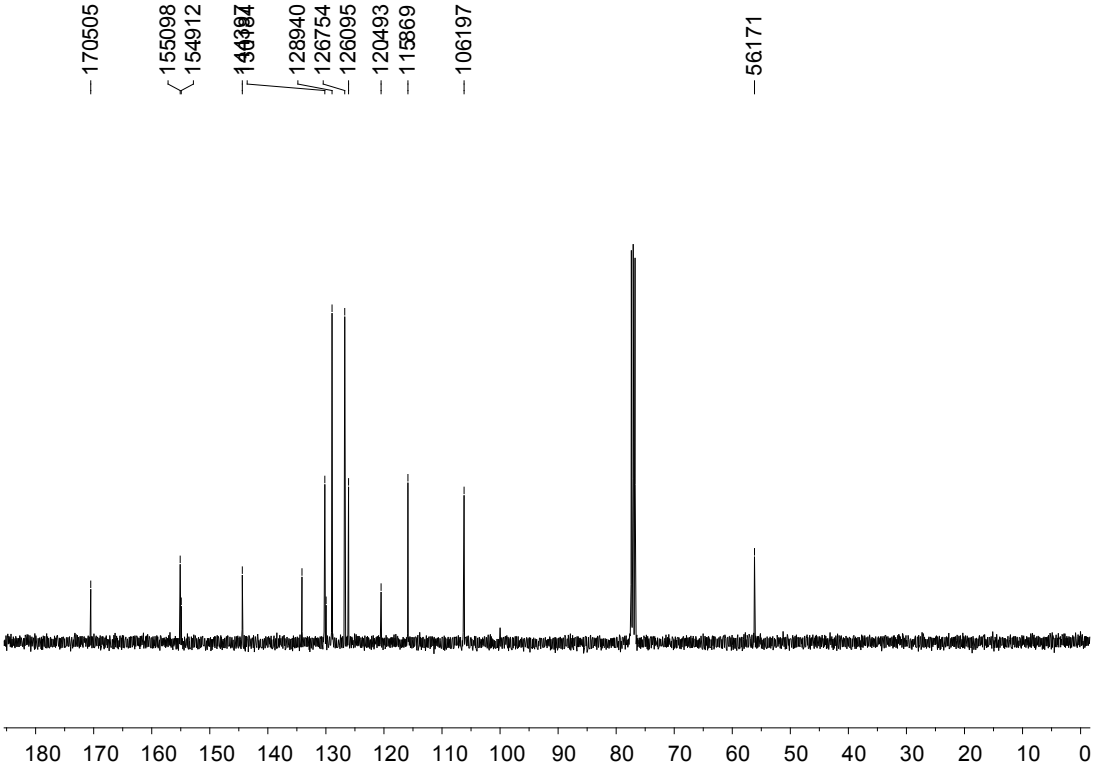
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 3ma



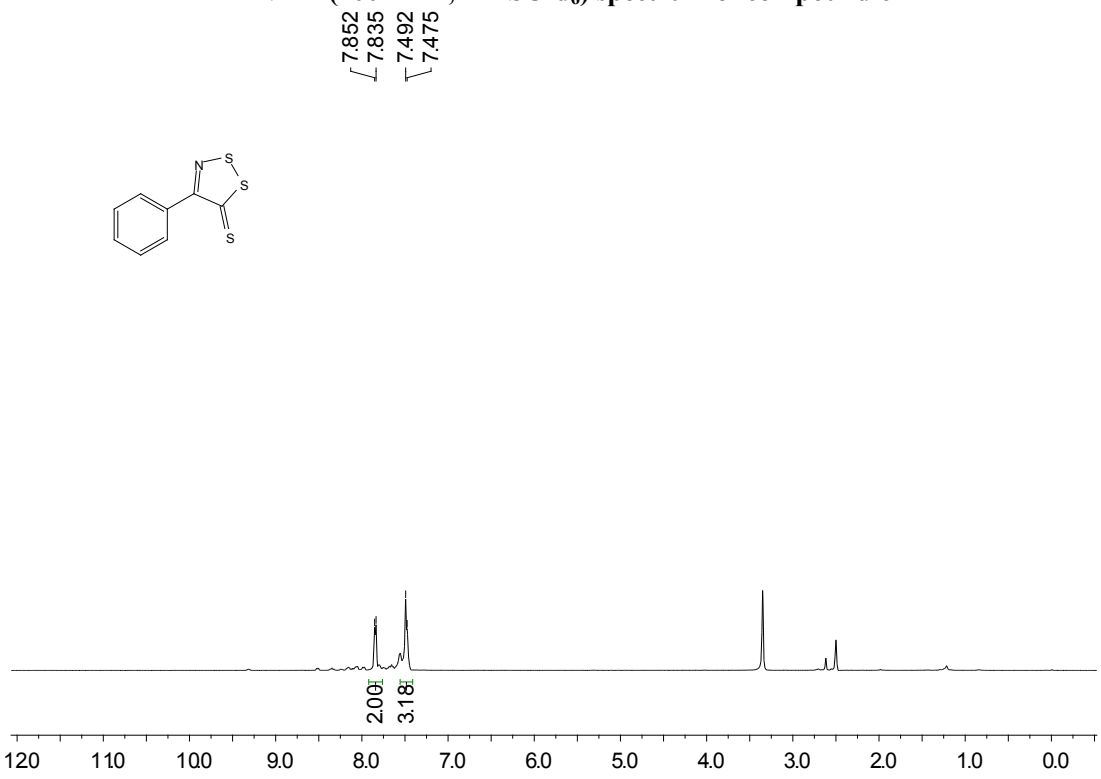
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3na



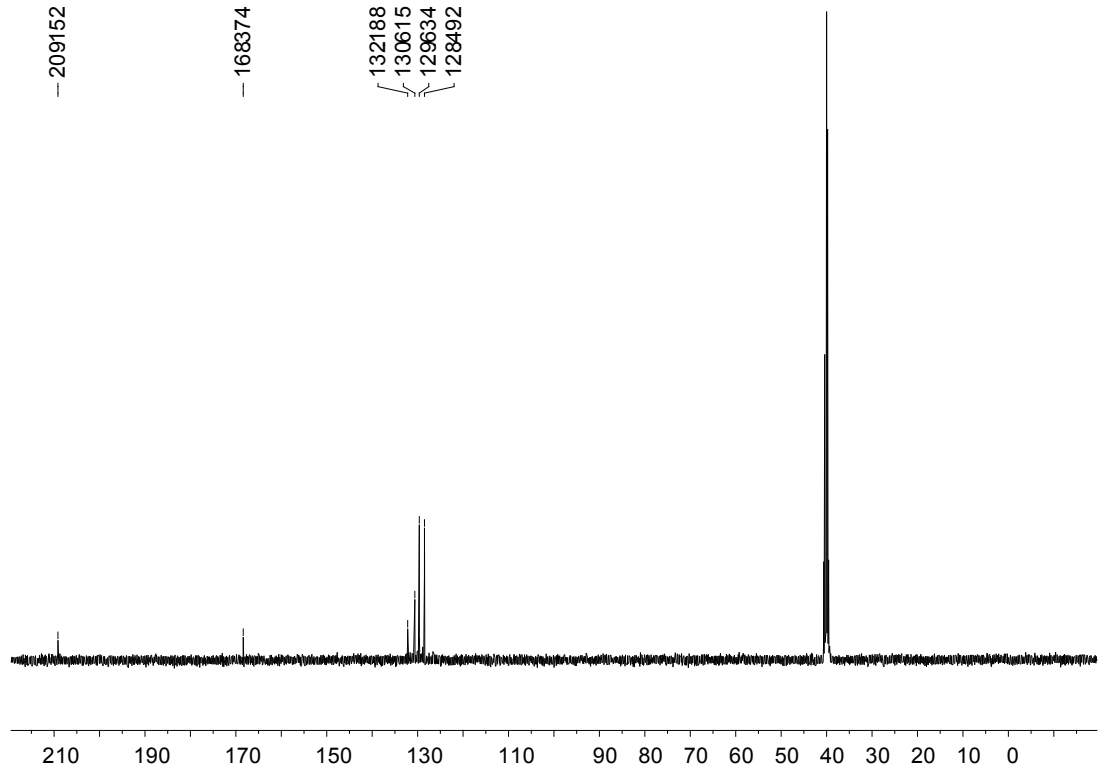
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3na



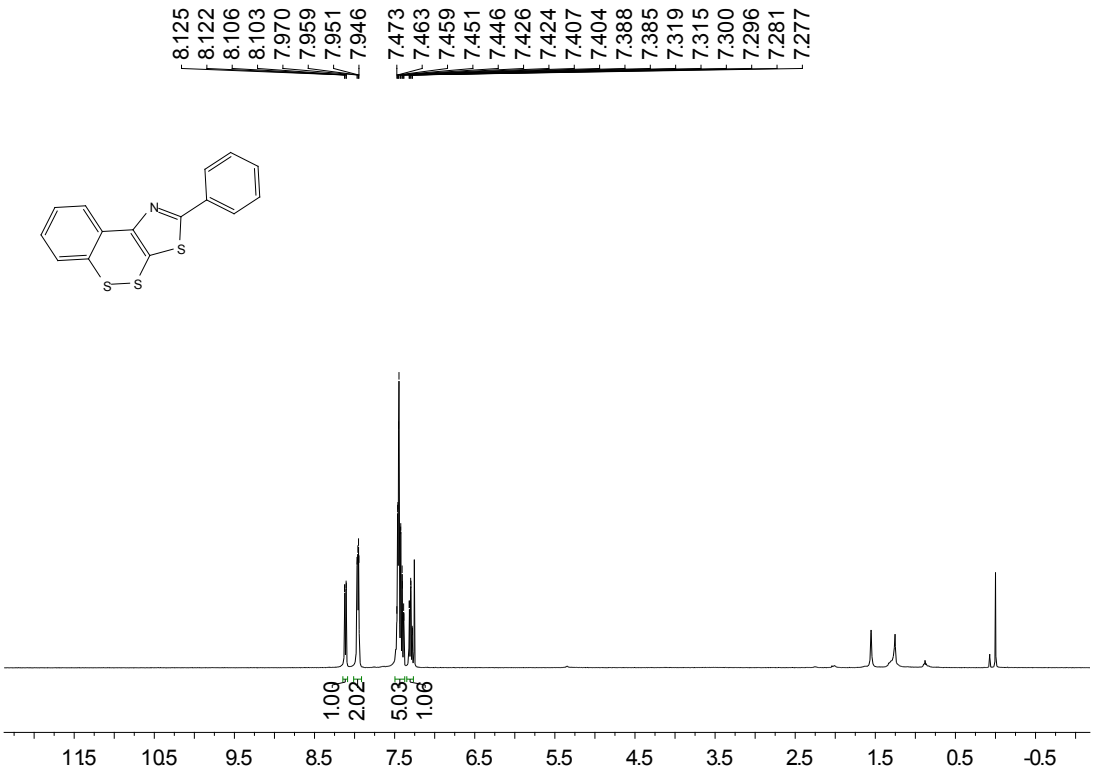
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 6



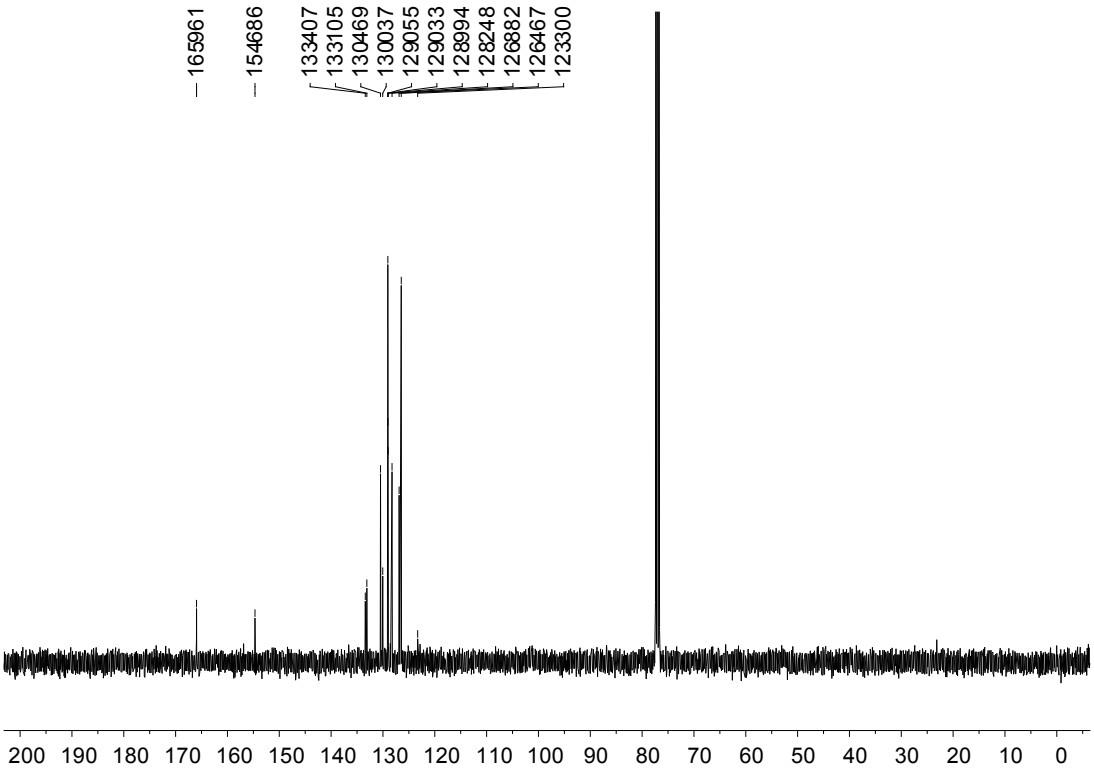
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 6



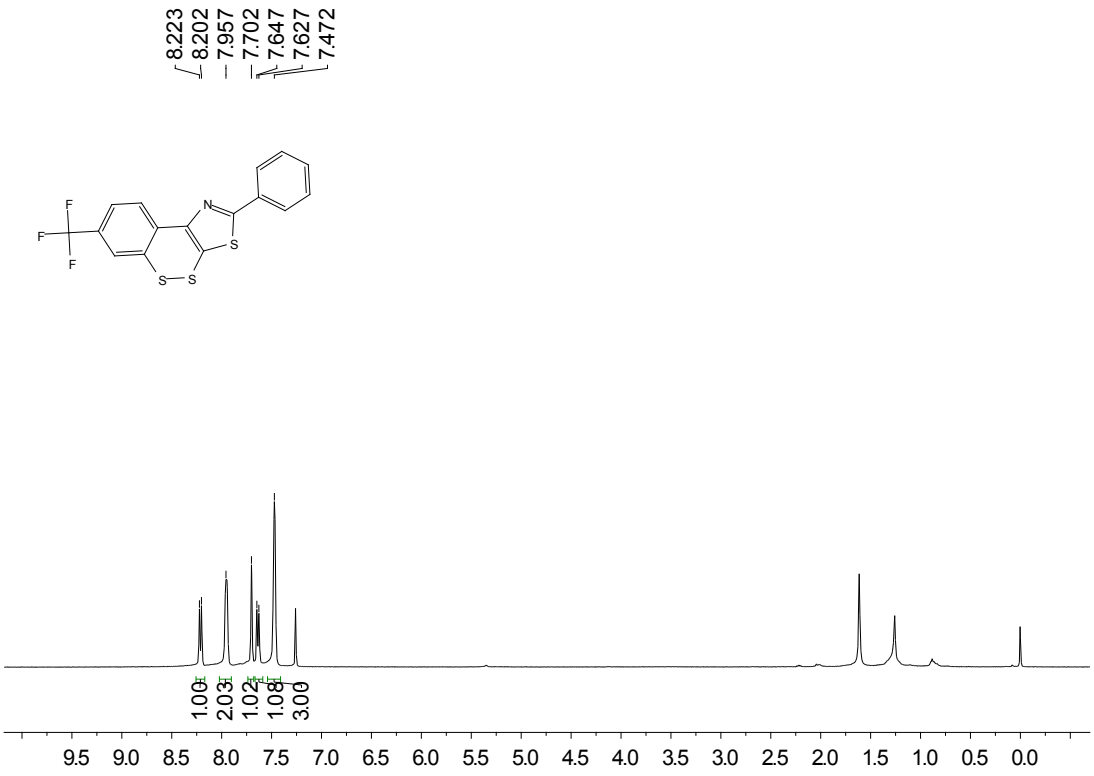
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 10aa



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 10aa



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 10ma



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 10ma