

Supporting Information

Synthesis of Benzo[*f*][1,2]thiazepine 1,1-Dioxides Based on the Visible-Light Mediated Aza Paternò-Büchi Reaction of Benzo[*d*]isothiazole 1,1-dioxides with Alkenes

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1. General Information

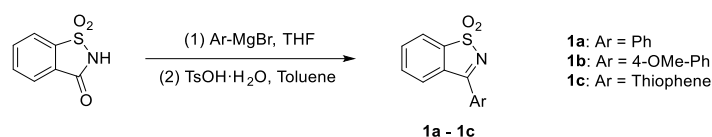
All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200 – 300 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on 400 MHz and 600 MHz spectrometer. The spectra were recorded in deuteriochloroform (CDCl_3) as solvent at room temperature, and ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references, and the chemical shifts were converted to the TMS scale (CDCl_3 : $\delta\text{H} = 7.26$ ppm, $\delta\text{C} = 77.0$ ppm). Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet doublet, br = broad), integration, coupling constant (Hz), and assignment. Data for ^{13}C NMR are reported as chemical shift. HRMS analysis was performed on a Bruker Apex II mass instrument (ESI).

2. Preparation of Substrates

2.1 General Procedures for the Preparation of the Cyclic Sulfonyl Ketimines.

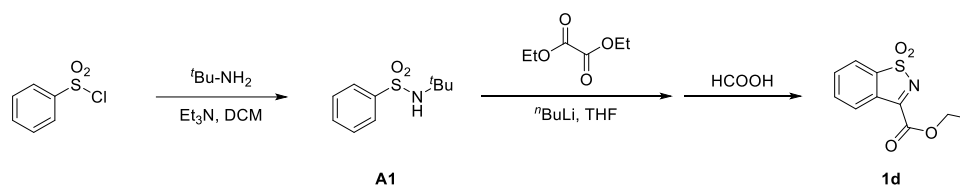
The ketimines were prepared according to modified literature procedures, **1a** – **1e** are known compounds.

Method A



To a Schlenk flask with saccharin (10 mmol) in anhydrous THF (40 mL) under an argon atmosphere at 0 °C, the corresponding Grignard reagent (22 mmol) was slowly added. The resulting mixture was stirred overnight at room temperature and then poured into HCl (30 mL, 1 M) solution. The aqueous layer was extracted twice with CH₂Cl₂ and the combined organic layers were dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography using petroleum ether and EtOAc to afford the pure product.

Method B



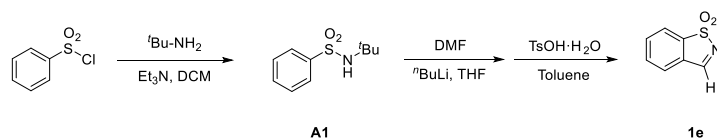
To a solution of tert-butylamine (75 mmol) and triethylamine (100 mmol) in dichloromethane in an ice bath was added arylsulfonyl chloride (50 mmol) dropwise. The mixture was stirred at room temperature overnight. It was washed with saturated sodium carbonate and brine. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na₂SO₄. The solvent was evaporated in vacuo to give the aryl sulfonamide **A1** as a white solid without further purification.

Butyllithium (44 mmol) was added dropwise over a 20 minute period to a cold (-78 °C), mechanically stirred solution of **A1** (20 mmol) in anhydrous THF (50 mL) under a dry nitrogen

atmosphere. After stirring an additional 30 min at 0 °C a precipitate formed. The suspension was cooled to -78 °C again and diethyl oxalate (60 mmol) was added. After stirring an additional 4 h at -78 °C, the cooling bath was removed and the mixture was stirred at room temperature over night. The reaction was quenched with 5% HCl (40 ml) and added to water (200 mL). The organics were extracted with EtOAc. The organic phase was washed with brine. The solvent was removed and the crude product was obtained used directly in the next step.

To the crude product obtained above, formic acid (60 mL) was added and the suspension was stirred at room temperature under a dry nitrogen atmosphere. After 20 h the solution was concentrated and the resultant solid was dissolved in CH₂Cl₂ and concentrated (three times) to remove traces of formic acid. This afforded **1d** as a solid which was further purified by flash chromatography.

Method C

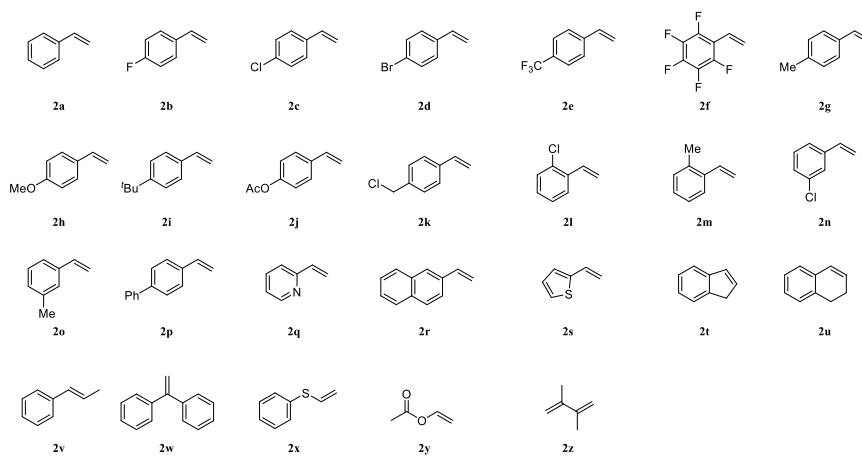


The preparation method for A1 is identical to that in **Method B**. Butyllithium (44 mmol) was added dropwise over a 20 minute period to a cold (-78 °C), mechanically stirred solution of **A1** (20 mmol) in anhydrous THF (50 mL) under a dry nitrogen atmosphere. After stirring an additional 30 min at 0 °C a precipitate formed. The suspension was cooled to -78 °C again and DMF (30 mmol) was added. After stirring an additional 4 h at -78 °C, the cooling bath was removed and the mixture was stirred at room temperature over night. The reaction was quenched with saturated aqueous solution of ammonium chloride. The organics were extracted with EtOAc. The organic phase was washed with brine. The solvent was removed and the crude product was obtained used directly in the next step.

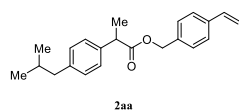
Subsequently, to a solution of the above crude product in toluene, *p*-toluenesulfonic acid (20 mg) was added. The mixture was stirred at 120 °C for 5 h. The yellow oil was purified by a silica gel column to give pure product **1e**.

2.2 Sources of olefin substrates

Commercially available alkenes

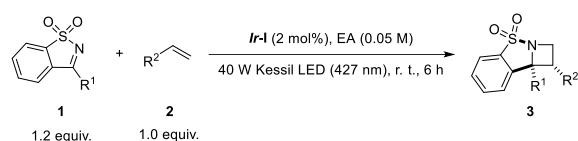


Synthesized literature-known alkenes



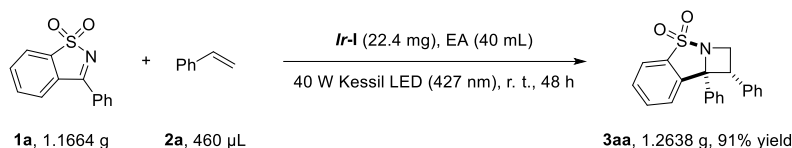
Commercially available alkenes were used as received, if not quoted differently. **2aa** was literature known and was synthesized according to literature procedures¹.

3. General Procedure for the [2 + 2]-Photocycloaddition Reactions



An oven-dried Schlenk tube equipped with a magnetic stir bar was added the substrate **1a** (0.24 mmol) and [Ir(dF-CF₃-ppy)₂(dtbbpy)]·PF₆ (0.004 mmol). Dry EtOAc (4 mL, 0.05 M) was added, after which styrene (0.2 mmol) were added at room temperature. The heterogeneous mixture was degassed by three cycles of freeze – pump – thaw under argon and then placed in the irradiation apparatus equipped with 40 W kessil light ($\lambda = 427$ nm). The resulting mixture was stirred at room temperature until the starting material was completely consumed as monitored by TLC. Subsequently, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1), which furnished the title compounds **3aa** (65.2 mg, 94%) as described.

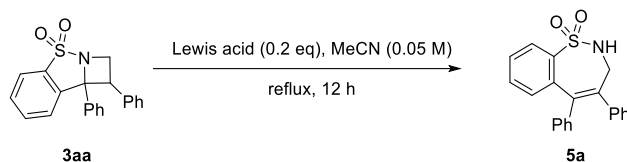
4. Procedure for Gram-Scale Preparation of 1,8b-diphenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide



To a 100 mL round-bottom flask equipped with a magnetic stir bar was added the substrate **1a** (1.1664 g, 4.8 mmol) and [Ir(dF-CF₃-ppy)₂(dtbbpy)]·PF₆ (22.4 mg, 0.02 mmol). Dry EtOAc (40 mL, 0.1 M) was added, after which the styrene (460 μ L, 4.0 mmol) were added at room temperature. The heterogeneous mixture was degassed by three cycles of freeze – pump – thaw under argon and then placed in the irradiation apparatus equipped with two 40 W kessil lights ($\lambda = 427$ nm). The mixture was stirred at room temperature for 48 h. Subsequently, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1), which furnished the title compounds **3aa** (1.2638 g, 91%) as described.

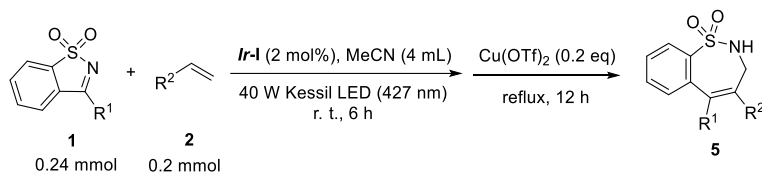
5. General Procedure for the screening of Lewis acid of the ring-expansion

Reactions



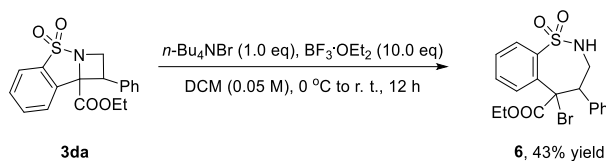
An oven-dried Schlenk tube equipped with a magnetic stir bar was added the purified **3aa** (0.2 mmol) and Lewis acid (0.04 mmol) under N₂ atmosphere. After that 4 mL of MeCN was injected using a syringe. The mixture was stirred at refluxing for 12 hours. After completion, the reaction mixture was cooled to room temperature, the solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford the product **5a**.

6. General Procedure for the one-pot ring-expansion Reactions

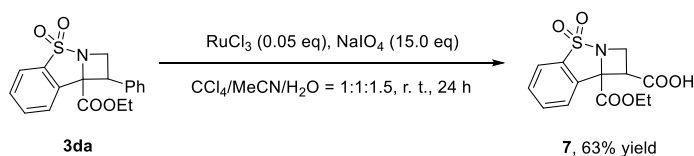


After the photochemical reaction using general procedure for the [2 + 2]-photocycloaddition reactions (0.2 mmol scale, in MeCN), Cu(OTf)₂ (14.5 mg, 0.04 mmol) was added under N₂ atmosphere to the untreated reaction mixture. The mixture was stirred at refluxing for 12 hours. After completion, the reaction mixture was cooled to room temperature, the solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford the product **5**.

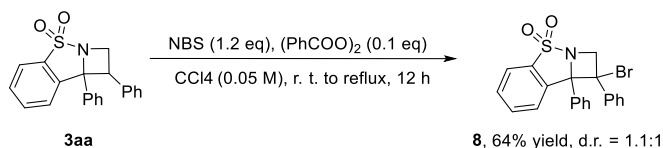
7. Procedure of Divergent Transformations



To a 10 mL oven-dried sealed tube charging with **3da** (34.3 mg, 0.1 mmol, 1.0 equiv.) and *n*-Bu₄NBr (32.3 mg, 0.1 mmol, 1.0 equiv.), DCM (2 mL) was added under N₂ atmosphere. BF₃·OEt₂ was partly added every 30 minutes for more transformation of **3da**. Then the mixture was stirred for another 6 hours at room temperature. After completion, the reaction was quenched with water. The aqueous layers were extracted with DCM and the combine organic phase was washed with brine. The solvent was removed and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford the product **6** (18.3 mg, 43% yield).



To a 10 mL oven-dried sealed tube charging with **3da** (171.5 mg, 0.5 mmol, 1.0 equiv.) and NaIO₄ (1.62 g, 7.5 mmol, 15.0 equiv.), CCl₄ (2 mL), MeCN (2 mL) and water (3 mL) was added. The mixture was stirred at room temperature until fully dissolved, then RuCl₃ (37 ww%, 20.8 mg, 0.05 equiv.) was added and stirring continued for 24 hours. The mixture was diluted with DCM, filtered through a pad of Celite, and the residue was washed three times with DCM. The organic phase was then treated with a saturated sodium carbonate solution and extracted with water three times. The aqueous phase is acidified (pH = 1) with hydrochloric acid, followed by extraction with DCM three times. The organic phases were combined, dried with MgSO₄, and the solvent is removed under vacuum to obtain the product **7** (98.3 mg, 63% yield).



To a 10 mL oven-dried sealed tube charging with **3aa** (34.7 mg, 0.1 mmol, 1.0 equiv.) and *N*-Bromosuccinimide (22.0 mg, 0.12 mmol, 1.2 equiv.), CCl₄ (2 mL) was added under N₂ atmosphere. The mixture was stirred at room temperature and then benzoyl peroxide (2.4 mg, 0.01

mmol, 0.1 equiv.) was added. After that the mixture was heated to 80 °C and continued to stirring for 12 h. After completion, the reaction mixture was cooled to room temperature, the solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford the product **8** (12.6 mg, 30% yield) and **8'** (14.4 mg, 34% yield).

8. Stern-Volmer Fluorescence Quenching Experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 1×10^{-4} M $[\text{Ir}(\text{dF-CF}_3\text{-ppy})_2(\text{dtbbpy})] \cdot \text{PF}_6$ and varying concentrations of quencher in acetonitrile at room temperature. The solutions were irradiated at 420 nm and fluorescence was measured from 440 nm to 600 nm. The Stern–Volmer equation, $I_0/I = 1 + k_q\tau_0[\text{Q}]$, where I_0 and I are the emission intensity in the absence and presence of quencher, respectively, k_{sv} is the quenching rate constant, and $[\text{Q}]$ is the concentration of quencher.

Rates of quenching (k_q) were determined using Stern-Volmer kinetics²

$$I_0/I = 1 + k_q\tau_0[\text{Q}]$$

Where I_0 is the luminescence intensity without the quencher, I is the intensity with the quencher, and τ_0 is the lifetime of the photocatalyst (2300 ns for $[\text{Ir}(\text{dF-CF}_3\text{-ppy})_2(\text{dtbbpy})(\text{PF}_6)]$ in acetonitrile)³, and $[\text{Q}]$ is the concentration of quencher.

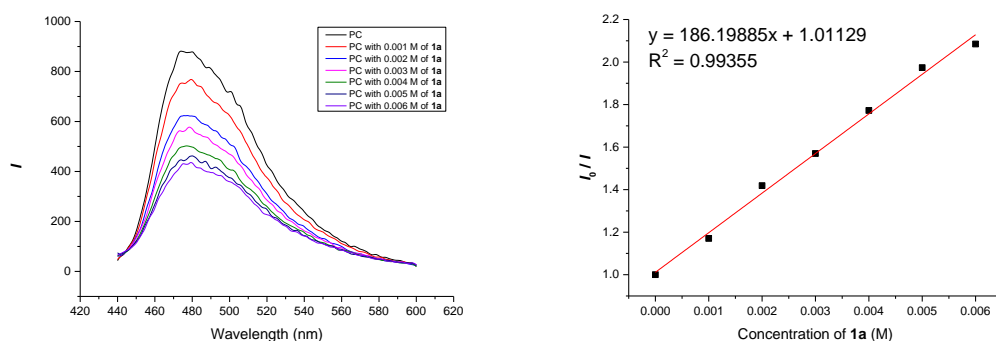


Figure S1. 1a as a quencher

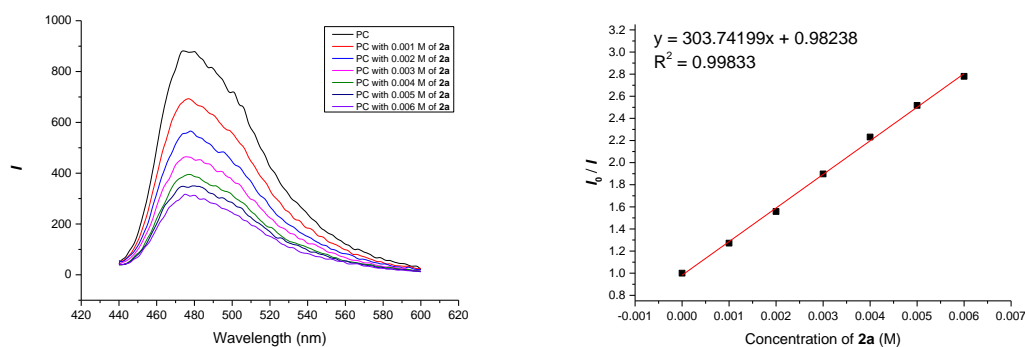


Figure S2. 2a as a quencher

Table S1. Quencher **1a/2a** Stern-Volmer constant (k_{sv}) and quenching rate constant (k_q)

	1a	2a
k_{sv} (L·mol ⁻¹)	186.2	303.7
k_q (L·mol ⁻¹ ·s ⁻¹)	8.096×10 ⁷	1.320×10 ⁸

Reference

1. (a) Gonzalez-de-Castro, A., Xiao, J. *J. Am. Chem. Soc.* **2015**, *137*, 8206-8218. (b) Jiang, Y. S., Liu, F., Huang, M. S., Luo, X. L., Xia, P. J. *Org. Lett.* **2022**, *24*, 8019-8024. (c) Zhu, Y., Colomer, I., Thompson, A. L., Donohoe, T. J. *J. Am. Chem. Soc.* **2019**, *141*, 6489-6493. (d) Aratikatla, E. K., Valkute, T. R., Puri, S. K., Srivastava, K., Bhattacharya, A. K. *Eur. J. med. Chem.* **2017**, *138*, 1089-1105.
2. Mukherjee, S., Maji, B., Tlahuext-Aca A., and Glorius, F., *J. Am. Chem. Soc.*, **2016**, *138*, 16200–16203.
3. Lowry, M. S., Goldsmith, J. I., Slinker, J. D., Rohl, R., Pascal, R. A., Malliaras, G. G., and Bernhard, S. *Chem. Mater.*, **2005**, *17*, 5712–5719.

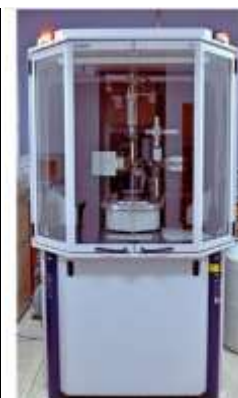
9. X-ray Crystallographic Data

9.1. Preparation of crystal

The pure compound (about 60 mg) was dissolved in a centrifuge tube containing solvent and covered with a lid. Then put the centrifuge tube in the room temperature for about a week, during which the crystal was formed. The X-ray was detected after the crystal was formed. The X-ray data was detected by Smart APEX II which was purchased from Bruker.

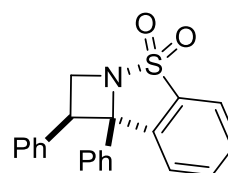
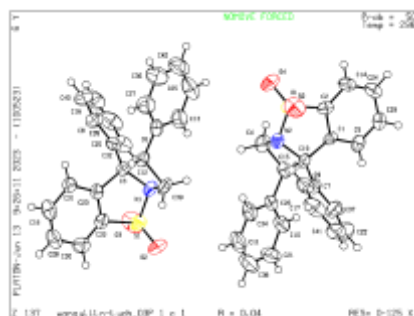
Table S2. Information about the X-ray single crystal diffractometer

Name	X-Ray crystal	diffractometer	Model Smart APEX II
Serial number	010301990904001	Manufacturer	Bruker
Main Specifications	X-ray generating power: 3.0 kw, 4k 62mm CCD Overall light transmittance: 70% Light source yield: >170 e/Mo Photon Temperature range: 100 K- 298K		
Main accessories	Mo		



9.2 Crystallographic data of compound 3aa

The crystals of compound **3aa** were obtained in a mixed solvent of toluene and ethyl acetate.



3aa

Figure S3. The crystal structure of compound **3aa** (CCDC = 2269490)

Table S3. Crystal parameters of compound **3aa** (CCDC = 2269490)

Bond precision:	C-C = 0.0086 Å	Wavelength=1.54184	
Cell:	a=15.7591(3)	b=7.2376(1)	c=17.3492(3)
	alpha=90	beta=116.140(2)	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	1776.42(6)	1776.42(6)	
Space group	P c	P 1 c 1	
Hall group	P -2yc	P -2yc	

Moiety formula	C ₂₁ H ₁₇ N O ₂ S	2(C ₂₁ H ₁₇ N O ₂ S)
Sum formula	C ₂₁ H ₁₇ N O ₂ S	C ₄₂ H ₃₄ N ₂ O ₄ S ₂
Mr	347.42	694.83
Dx,g cm ⁻³	1.299	1.299
Z	4	2
Mu (mm ⁻¹)	1.723	1.723
F000	728	728
F000'	731.28	
h,k,lmax	19,9,21	19,8,21
Nref	7419[3714]	5123
Tmin,Tmax	0.783,0.813	0.457,1.000
Tmin'	0.711	
Correction method= # Reported T Limits: Tmin=0.457 Tmax=1.000 AbsCorr = MULTI-SCAN		
Data completeness= 1.38/0.69 Theta(max)= 76.265		
R(reflections)= 0.0412(4779)		wR2(reflections)= 0.1181(5123)
S = 1.066		Npar= 451
Displacement ellipsoids are drawn at 50% probability level		

9.3 Crystallographic data of compound 5a

The crystals of compound **5a** were obtained in MeCN.

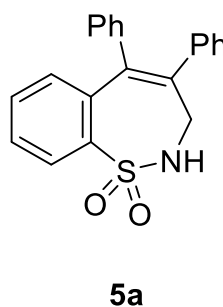
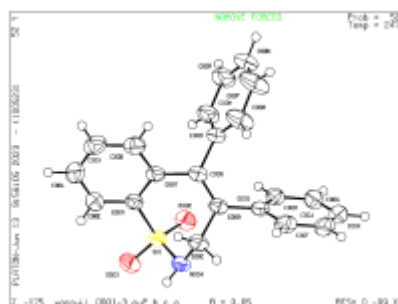


Figure S4. The crystal structure of compound **5a** (CCDC = 2269492)

Table S4. Crystal parameters of compound **5a** (CCDC = 2269492)

Bond precision:	C-C = 0.0024 Å	Wavelength=0.71073	
Cell:	a=6.9772(3)	b=19.6390(11)	c=25.1001(11)
	alpha=90	beta=90	gamma=90
Temperature:	247 K		
	Calculated	Reported	
Volume	3439.4(3)	3439.3(3)	
Space group	P b c a	P b c a	
Hall group	-P 2ac 2ab	-P 2ac 2ab	
Moiety formula	C ₂₁ H ₁₇ N O ₂ S	C ₂₁ H ₁₇ N O ₂ S	
Sum formula	C ₂₁ H ₁₇ N O ₂ S	C ₂₁ H ₁₇ N O ₂ S	
Mr	347.42	347.42	
Dx,g cm ⁻³	1.342	1.342	
Z	8	8	
Mu (mm ⁻¹)	0.202	0.202	
F000	1456	1456	

F000'	1457.57	
h,k,lmax	10,28,36	9,27,35
Nref	5459	4525
Tmin,Tmax	0.964,0.972	0.269,1.000
Tmin'	0.958	
Correction method= # Reported T Limits: Tmin=0.269 Tmax=1.000 AbsCorr = MULTI-SCAN		
Data completeness= 0.829 Theta(max)= 30.950		
R(reflections)= 0.0474(3581)		wR2(reflections)= 0.1324(4525)
S = 1.054	Npar= 230	
Displacement ellipsoids are drawn at 50% probability level		

9.4 Crystallographic data of compound 3av

The crystals of compound **3av** were obtained in a mixed solvent of toluene and ethyl acetate.

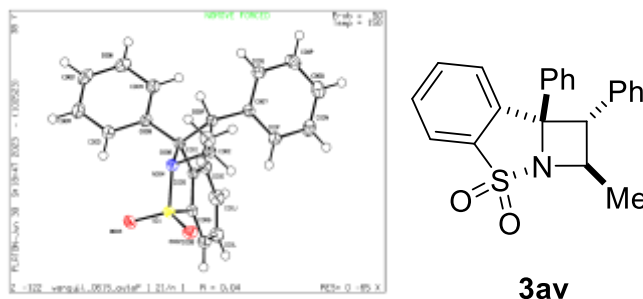


Figure S5. The crystal structure of compound **3av** (CCDC = 2278125)

Table S5. Crystal parameters of compound **3av** (CCDC = 2278125)

Bond precision:	C-C = 0.0019 Å	Wavelength=0.71073	
Cell:	a=8.6492(2)	b=17.3276(5)	c=12.0342(3)
	alpha=90	beta=95.352(2)	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	1795.70(8)	1795.71(9)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C ₂₂ H ₁₉ N O ₂ S	C ₂₂ H ₁₉ N O ₂ S	
Sum formula	C ₂₂ H ₁₉ N O ₂ S	C ₂₂ H ₁₉ N O ₂ P S _{0.25}	
Mr	361.44	368.37	
Dx,g cm ⁻³	1.337	1.363	
Z	4	4	
Mu (mm ⁻¹)	0.196	0.199	
F000	760	772	
F000'	760.8		
h,k,lmax	12,24,17	11,22,16	
Nref	5616	4511	
Tmin,Tmax	0.983,0.990	0.753,1.000	
Tmin'	0.978		
Correction method= # Reported T Limits: Tmin=0.753 Tmax=1.000 AbsCorr = MULTI-SCAN			
Data completeness= 0.803 Theta(max)= 30.766			

R(reflections)= 0.0366(3806)	wR2(reflections)= 0.0941(4511)
S = 1.068	Npar= 236
Displacement ellipsoids are drawn at 50% probability level	

9.5 Crystallographic data of compound 3av'

The crystals of compound **3av'** were obtained in a mixed solvent of toluene and ethyl acetate.

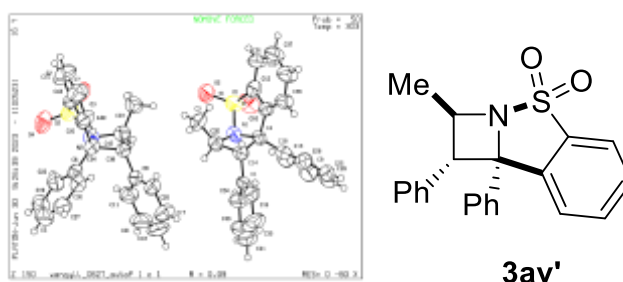


Figure S6. The crystal structure of compound **3av'** (CCDC = 2278127)

Table S6. Crystal parameters of compound **3av'** (CCDC = 2278127)

Bond precision:	C-C = 0.0156 Å	Wavelength=0.71073	
Cell:	a=15.2972(15)	b=7.4805(5)	c=17.3374(16)
	alpha=90	beta=107.376(10)	gamma=90
Temperature:	303 K		
	Calculated	Reported	
Volume	1893.4(3)	1893.4(3)	
Space group	P c	P 1 c 1	
Hall group	P -2yc	P -2yc	
Moiety formula	C ₂₂ H ₁₉ N O ₂ S	2(C ₂₂ H ₁₉ N O ₂ S)	
Sum formula	C ₂₂ H ₁₉ N O ₂ S	C ₄₄ H ₃₈ N ₂ O ₄ S ₂	
Mr	361.44	722.88	
Dx, g cm ⁻³	1.268	1.268	
Z	4	2	
Mu (mm ⁻¹)	0.186	0.186	
F000	760	760	
F000'	760.8		
h,k,lmax	22,10,24	22,10,23	
Nref	11830[5920]	7899	
Tmin,Tmax	0.971,0.978	0.292,1.000	
Tmin'	0.971		
Correction method= # Reported T Limits: Tmin=0.292 Tmax=1.000 AbsCorr = MULTI-SCAN			
Data completeness= 1.33/0.67	Theta(max)= 30.778		
R(reflections)= 0.0949(4330)	wR2(reflections)= 0.2786(7899)		
S = 1.000	Npar= 471		
Displacement ellipsoids are drawn at 50% probability level			

9.6 Crystallographic data of compound 3ea

The crystals of compound **3ea** were obtained in a mixed solvent of toluene and ethyl acetate.

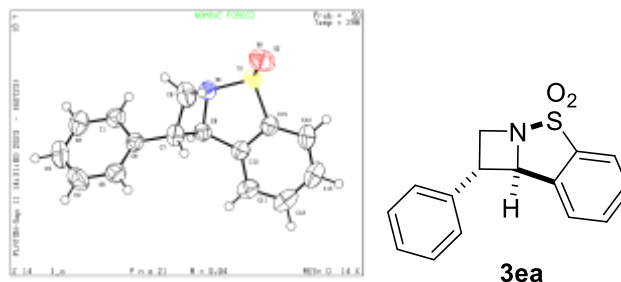


Figure S7. The crystal structure of compound **3ea** (CCDC = 2294249)

Table S7. Crystal parameters of compound **3ea** (CCDC = 2294249)

Bond precision:	C-C = 0.0036 Å	Wavelength=0.71073	
Cell:	a=11.6930(16)	b=12.6184(17)	c=8.9005(12)
	alpha=90	beta=90	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	1313.2(3)	1313.2(3)	
Space group	P n a 21	P n a 21	
Hall group	P 2c -2n	P 2c -2n	
Moiety formula	C15 H13 N O2 S	?	
Sum formula	C15 H13 N O2 S	C15 H13 N O2 S	
Mr	271.32	271.32	
Dx, g cm ⁻³	1.372	1.372	
Z	4	4	
Mu (mm ⁻¹)	0.243	0.243	
F000	568	568	
F000'	568.73		
h,k,lmax	17,18,12	16,17,12	
Nref	4252[2249]	3333	
Tmin,Tmax	0.943,0.953	0.662,0.746	
Tmin'	0.93		
Correction method= # Reported T Limits: Tmin=0.662 Tmax=0.746 AbsCorr = MULTI-SCAN			
Data completeness= 1.48/0.78 Theta(max)= 31.202			
R(reflections)= 0.0353(2797)		wR2(reflections)= 0.0955(3333)	
S = 1.003	Npar= 172		
Displacement ellipsoids are drawn at 50% probability level			

9.7 Crystallographic data of compound 7

The crystals of compound **7** were obtained in a mixed solvent of toluene and ethyl acetate.

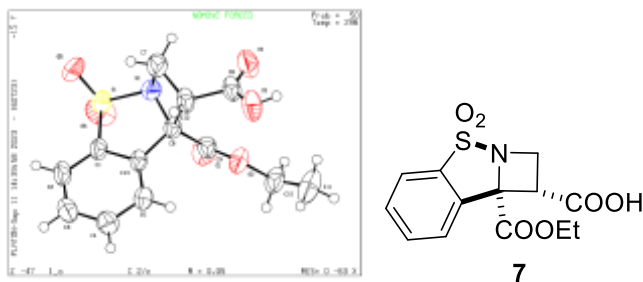


Figure S8. The crystal structure of compound **7** (CCDC = 2294248)

Table S8. Crystal parameters of compound **7** (CCDC = 2294248)

Bond precision:	C-C = 0.0032 Å	Wavelength=0.71073	
Cell:	a=29.787(5)	b=7.0172(12)	c=13.601(2)
	alpha=90	beta=103.886(3)	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	2759.8(8)	2759.9(8)	
Space group	C 2/c	C 2/c	
Hall group	-C 2yc	-C 2yc	
Moiety formula	C13 H13 N O6 S	?	
Sum formula	C13 H13 N O6 S	C13 H13 N O6 S	
Mr	311.3	311.3	
Dx, g cm ⁻³	1.498	1.498	
Z	8	8	
Mu (mm ⁻¹)	0.262	0.262	
F000	1296	1296	
F000'	1297.74		
h,k,lmax	43,10,19	42,10,19	
Nref	4501	3981	
Tmin,Tmax	0.939,0.949	0.595,0.746	
Tmin'	0.924		
Correction method= # Reported T Limits:	Tmin=0.595 Tmax=0.746	AbsCorr = MULTI-SCAN	
Data completeness= 0.884	Theta(max)= 31.255		
R(reflections)= 0.0510(2258)		wR2(reflections)= 0.1631(3981)	
S = 1.003	Npar= 192		
Displacement ellipsoids are drawn at 50% probability level			

10. The detail data of HRMS.

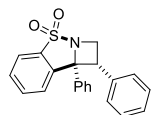
The HRMS data were detected by LTQ(Velos Pro)/Orbitrap Elite/ETD which was purchased from Thermo Scientific. The detail data are listed as follows.

Table S9. Information about the high resolution quadrupole time-of-flight mass spectrometer

Name	High resolution quadrupole time-of-flight mass spectrometer	Model	Bruker micrOTOF Q II
Serial number	0102019911815	Manufacturer	Bruker Daltonics
Main Specifications	Ion funnel type ESI source, high molecular weight quadrupole mass filter, collision cell Time-of-flight mass analyzer and peristaltic injection pump with temperature intelligent compensation ESI applicable flow rate range 1 μ l/min~1 ml/min TOF mass range: 50~20000 m/z Focus resolution >17500 FWHM (positive and negative ions, within the range of m/z 900~1000) Quality accuracy: internal standard method \leq 2 ppm, external standard method \leq 5 ppm (detection at 622.02896 m/z)		

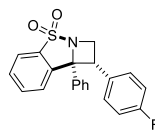
11. Characterization of Products

1,8b-diphenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3aa)



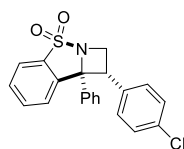
White solid; 65.2 mg, 94% yield, reaction time 6 h; m.p. : 228 – 231 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.77 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 4.0 Hz, 2H), 7.53 (dt, J = 8.0, 4.1 Hz, 1H), 7.31 – 7.30 (m, 2H), 7.25 – 7.24 (m, 3H), 7.20 – 7.14 (m, 3H), 7.12 – 7.02 (m, 3H), 4.49 (t, J = 8.8 Hz, 1H), 4.08 – 4.02 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm) = 145.6, 138.5, 138.1, 134.3, 134.1, 129.9, 129.1, 128.5, 128.0, 127.6, 127.2, 125.6, 124.4, 122.6, 81.8, 56.1, 42.3; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{17}\text{NO}_2\text{SNa}$ [$\text{M}+\text{Na}$] $^+$: 370.0872, found: 370.0880.

1-(4-fluorophenyl)-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ab)



White solid; 64.7 mg, 89% yield, reaction time 6 h; m.p. : 256 – 258 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.79 (d, J = 7.8 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.57 – 7.53 (m, 1H), 7.30 – 7.28 (m, 2H), 7.24 – 7.19 (m, 2H), 7.15 – 7.05 (m, 3H), 6.91 – 6.85 (m, 2H), 4.49 (t, J = 7.76 Hz, 1H), 4.04 – 4.00 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm) = 162.0 (d, J = 246.9 Hz), 145.3, 138.2, 134.3, 134.1, 134.0 (d, J = 3.4 Hz), 130.6 (d, J = 8.1 Hz), 129.9, 128.1, 127.2, 125.5, 124.3, 122.6, 115.4 (d, J = 21.4 Hz), 81.7, 56.2, 47.5; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ (ppm) = -114.30; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{16}\text{FNO}_2\text{SNa}$ [$\text{M}+\text{Na}$] $^+$: 388.0778, found: 388.0775.

1-(4-chlorophenyl)-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ac)

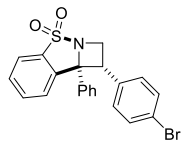


White solid; 62.5 mg, 82% yield, reaction time 6 h; m.p. : 270 – 272 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.79 (d, J = 7.7 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.55 (ddd, J = 8.1, 6.1, 2.1 Hz, 1H), 7.31 – 7.29 (m, 2H), 7.20 – 7.06 (m, 7H), 4.48 (t, J = 10.7 Hz, 1H), 4.02 – 3.98 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm) = 145.23, 138.10, 136.77, 134.26, 134.10, 133.39, 130.31, 129.97, 128.60, 128.17, 127.34, 125.44,

124.34, 122.64, 81.52, 56.04, 47.55.; HRMS (ESI) calcd for C₂₁H₁₆ClNO₂SNa [M+Na]⁺:

404.0482, found: 404.0480.

1-(4-bromophenyl)-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ad)



White solid; 67.2 mg, 82% yield, reaction time 6 h; m.p. : 263 – 265 °C; ¹H

NMR (400 MHz, CDCl₃) δ (ppm) = 7.79 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.62 (m, 2H),

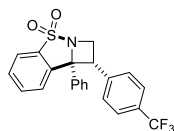
7.57 – 7.53 (m, 1H), 7.33 – 7.28 (m, 4H), 7.16 – 7.06 (m, 5H), 4.48 (t, *J* = 10.5 Hz,

1H), 4.01 – 3.97 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 145.2, 138.1, 137.3, 134.2,

134.1, 131.6, 130.7, 130.0, 128.2, 127.4, 125.4, 124.3, 122.7, 121.5, 81.4, 56.0, 47.6; HRMS (ESI)

calcd for C₂₁H₁₆BrNO₂SNa [M+Na]⁺: 447.9977, found: 447.9975.

8b-phenyl-1-(4-(trifluoromethyl)phenyl)-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ae)



White solid; 77.8 mg, 94% yield, reaction time 6 h; m.p. : 255 – 257 °C; ¹H

NMR (400 MHz, CDCl₃) δ (ppm) = 7.81 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.65 (m, 2H),

7.60 – 7.56 (m, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.30 – 7.27

(m, 2H), 7.15 – 7.05 (m, 3H), 4.51 (t, *J* = 9.2 Hz, 1H), 4.09 (dd, *J* = 9.0, 4.0 Hz, 1H), 4.03 (dd, *J* = 9.7,

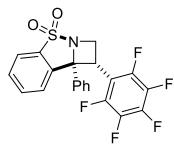
4.0 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) = 145.0, 142.4, 137.9, 134.3, 134.2, 130.1,

129.7 (q, *J* = 32.4 Hz), 129.4, 128.2, 127.5, 125.4, 125.3 (q, *J* = 3.4 Hz), 124.4, 123.9 (q, *J* = 270.7

Hz), 122.7, 121.2, 81.4, 55.9, 47.8; ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) = -62.61; HRMS (ESI)

calcd for C₂₂H₁₆F₃NO₂SNa [M+Na]⁺: 438.0746, found: 438.0742.

1-(perfluorophenyl)-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3af)



White solid; 88.2 mg, 98% yield, reaction time 6 h; m.p. : 245 – 247 °C; ¹H

NMR (400 MHz, CDCl₃) δ (ppm) = 7.78 (d, *J* = 7.7 Hz, 1H), 7.72 – 7.67 (m, 2H),

7.60 – 7.56 (m, 1H), 7.43 – 7.41 (m, 2H), 7.26 – 7.15 (m, 3H), 4.52 – 4.40 (m, 3H);

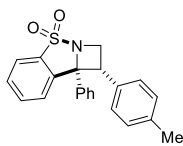
¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 144.2, 137.5, 134.5, 134.3, 130.4, 128.4, 128.1, 124.5,

124.2, 122.5, 80.4, 51.0, 38.0; ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) = -152.86 (t, *J* = 21.1 Hz), -

161-35 (td, *J* = 21.4, 7.0 Hz); HRMS (ESI) calcd for C₂₁H₁₂F₅NO₂SNa [M+Na]⁺: 460.0401, found:

460.0397.

8b-phenyl-1-(p-tolyl)-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ag)



White solid; 39.4 mg, 79% yield, reaction time 6 h; m.p. : 259 – 262 °C; ¹H

NMR (400 MHz, CDCl₃) δ (ppm) = 7.78 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.61 (m, 2H),

7.54 – 7.50 (m, 1H), 7.32 – 7.30 (m, 2H), 7.13 – 7.09 (m, 4H), 7.07 – 7.03 (m, 1H),

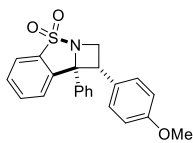
6.99 (d, *J* = 7.9 Hz, 2H), 4.48 (t, *J* = 9.1 Hz, 1H), 4.05 – 3.98 (m, 2H), 2.24 (s, 3H); ¹³C **NMR (100**

MHz, CDCl₃) δ (ppm) = 145.7, 138.5, 137.2, 135.0, 134.3, 134.0, 129.8, 129.1, 128.9, 127.9,

127.0, 125.5, 124.3, 122.5, 81.8, 56.2, 47.9, 21.0; HRMS (ESI) calcd for C₂₂H₁₉NO₂SNa [M+Na]⁺:

384.1029, found: 384.1025.

1-(4-methoxyphenyl)-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ah)



Yellow solid; 47.2 mg, 66% yield, reaction time 6 h; m.p. : 249 – 251 °C; ¹H

NMR (400 MHz, CDCl₃) δ (ppm) = 7.79 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.61 (m,

2H), 7.56 – 7.52 (m, 1H), 7.32 – 7.29 (m, 2H), 7.16 – 7.04 (m, 5H), 6.74 –

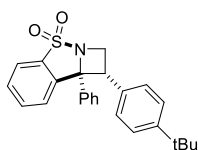
6.70 (m, 2H), 4.49 (t, *J* = 8.9 Hz, 1H), 4.05 – 3.98 (m, 2H), 3.73 (s, 3H); ¹³C **NMR (100 MHz,**

CDCl₃) δ (ppm) = 158.9, 145.7, 138.5, 134.3, 134.0, 130.1, 129.8, 128.0, 127.1, 125.6, 124.3,

122.6, 113.8, 81.9, 56.3, 55.2, 47.7; HRMS (ESI) calcd for C₂₂H₁₉NO₃SNa [M+Na]⁺: 400.0978,

found: 400.0974.

1-(4-(tert-butyl)phenyl)-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ai)



White solid; 62.4 mg, 77% yield, reaction time 6 h; m.p. : 229 – 231 °C; ¹H

NMR (400 MHz, CDCl₃) δ (ppm) = 7.76 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.60 (m,

2H), 7.53 – 7.49 (m, 1H), 7.30 – 7.28 (m, 2H), 7.21 – 7.18 (m, 2H), 7.15 –

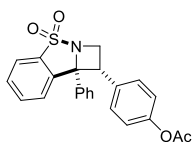
7.13 (m, 2H), 7.10 – 7.06 (m, 2H), 7.05 – 7.01 (m, 1H), 4.48 (t, *J* = 9.2 Hz, 1H), 4.08 – 4.01 (m,

2H), 1.22 (s, 9H); ¹³C **NMR (100 MHz, CDCl₃)** δ (ppm) = 150.6, 145.7, 138.4, 134.9, 134.3,

134.0, 129.7, 128.7, 127.8, 127.0, 125.5, 125.2, 124.3, 122.5, 81.8, 55.9, 47.9, 34.4, 31.2; HRMS

(ESI) calcd for C₂₅H₂₆NO₂S [M+H]⁺: 404.1679, found: 404.1677.

4-(4,4-dioxido-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazol-1-yl)phenyl acetate (3aj)

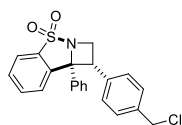


White solid; 63.1mg, 78% yield, reaction time 6 h; m.p. : 228 – 230 °C; ¹H

NMR (400 MHz, CDCl₃) δ (ppm) = 7.78 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.62 (m,

2H), 7.54 (ddd, $J = 8.1, 5.8, 2.4$ Hz, 1H), 7.31 – 7.29 (m, 2H), 7.27 – 7.23 (m, 2H), 7.14 – 7.11 (m, 2H), 7.08 – 7.04 (m, 1H), 6.94 – 6.91 (m, 2H), 4.49 (t, $J = 10.6$ Hz, 1H), 4.04 (tt, $J = 7.3, 3.3$ Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 169.2, 149.9, 145.3, 138.2, 135.7, 134.2, 134.1, 130.0, 129.9, 128.1, 127.2, 125.5, 124.3, 122.6, 121.5, 81.6, 56.0, 47.6, 21.0; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_4\text{SNa}$ $[\text{M}+\text{Na}]^+$: 428.0927, found: 428.0925.

1-(4-(chloromethyl)phenyl)-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-*b*]benzo[*d*]isothiazole 4,4-dioxide (3ak)

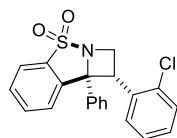


White solid; 59.3 mg, 75% yield, reaction time 6 h; m.p. : 248 – 251 °C; ^1H

NMR (400 MHz, CDCl_3) δ (ppm) = 7.77 (d, $J = 7.7$ Hz, 1H), 7.67 – 7.62 (m, 2H), 7.56 – 7.50 (m, 1H), 7.31 – 7.29 (m, 2H), 7.22 (q, $J = 8.2$ Hz, 4H), 7.12 –

7.09 (m, 2H), 7.06 – 7.03 (m, 1H), 4.50 – 4.45 (m, 3H), 4.06 – 4.00 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 145.4, 138.5, 138.3, 136.8, 134.3, 134.2, 123.0, 129.5, 128.7, 128.1, 127.3, 125.5, 124.4, 122.6, 81.7, 56.1, 47.9, 45.8; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{18}\text{ClNO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 418.0639, found: 418.0636.

1-(2-chlorophenyl)-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-*b*]benzo[*d*]isothiazole 4,4-dioxide (3al)

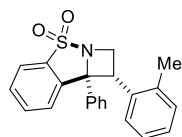


White solid; 68.1 mg, 89% yield, reaction time 6 h; m.p. : 222 – 224 °C; ^1H

NMR (400 MHz, CDCl_3) δ (ppm) = 7.82 – 7.77 (m, 2H), 7.69 (t, $J = 7.4$ Hz, 1H), 7.55 (t, $J = 7.7$ Hz, 1H), 7.43 (dd, $J = 5.9, 3.6$ Hz, 1H), 7.40 – 7.38 (m, 2H),

7.33 – 7.29 (m, 1H), 7.12 – 7.00 (m, 5H), 4.71 (dd, $J = 9.4, 4.1$ Hz, 1H), 4.47 (t, $J = 9.7$ Hz, 1H), 4.12 (dd, $J = 9.9, 4.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 145.1, 138.0, 135.4, 134.7, 134.4, 134.1, 130.0, 129.4, 129.0, 128.7, 128.0, 127.3, 127.2, 125.2, 124.8, 122.5, 81.7, 54.4, 43.3; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{16}\text{ClNO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 404.0482, found: 404.0480.

8b-phenyl-1-(*o*-tolyl)-1,8b-dihydro-2H-azeto[1,2-*b*]benzo[*d*]isothiazole 4,4-dioxide (3am)

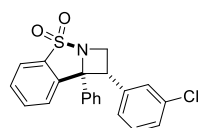


Yellow solid; 28.1 mg, 39% yield, reaction time 6 h; m.p. : 245 – 247 °C; ^1H

NMR (400 MHz, CDCl_3) δ (ppm) = 7.80 (d, $J = 7.8$ Hz, 1H), 7.69 – 7.63 (m, 2H), 7.55 (ddd, $J = 8.1, 6.5, 1.7$ Hz, 1H), 7.31 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.27 –

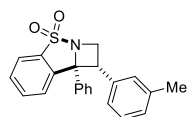
7.24 (m, 2H), 7.11 – 7.08 (m, 3H), 7.06 – 7.01 (m, 2H), 7.00 – 6.97 (m, 1H), 4.49 (t, $J = 9.5$ Hz, 1H), 4.37 (dd, $J = 9.5, 4.3$ Hz, 1H), 4.12 (dd, $J = 9.6, 4.3$ Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 145.6, 138.3, 135.9, 136.0, 134.5, 134.1, 130.0, 129.8, 128.4, 128.0, 127.3, 127.2, 126.5, 125.3, 124.2, 122.7, 81.9, 55.4, 43.0, 20.3; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 384.1029, found: 384.1026.

1-(3-chlorophenyl)-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-*b*]benzo[*d*]isothiazole 4,4-dioxide (3an)



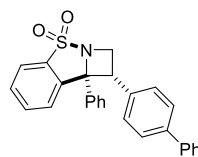
Yellow solid; 64.1 mg, 84% yield, reaction time 6 h; m.p. : 260 – 262 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.80 (d, $J = 7.7$ Hz, 1H), 7.69 – 7.64 (m, 2H), 7.56 (ddd, $J = 8.0, 5.4, 2.7$ Hz, 1H), 7.33 – 7.30 (m, 2H), 7.25 (m, 1H), 7.16 – 7.06 (m, 6H), 4.48 (t, $J = 9.0$ Hz, 1H), 4.04 – 3.98 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 145.1, 140.3, 138.0, 134.3, 134.2, 134.1, 130.0, 129.7, 129.3, 128.1, 127.7, 127.4, 127.0, 125.4, 124.4, 122.7, 81.5, 55.8, 47.8.; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{16}\text{ClNO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 404.0482, found: 404.0484.

8b-phenyl-1-(*m*-tolyl)-1,8b-dihydro-2H-azeto[1,2-*b*]benzo[*d*]isothiazole 4,4-dioxide (3ao)



Yellow solid; 36.1 mg, 50% yield, reaction time 6 h; m.p. : 219 – 221 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.77 (d, $J = 7.7$, 1H), 7.65 – 7.61 (m, 2H), 7.52 (ddd, $J = 8.0, 4.8, 3.4$ Hz, 1H), 7.32 – 7.29 (m, 2H), 7.13 – 7.09 (m, 2H), 7.07 – 7.02 (m, 4H), 6.96 – 6.94 (m, 1H), 4.47 (t, $J = 9.5$ Hz, 1H), 4.06 (dd, $J = 9.7, 4.3$ Hz, 1H), 3.99 (dd, $J = 9.3, 4.3$ Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 145.6, 138.4, 138.0, 137.9, 134.3, 134.0, 129.8, 129.8, 128.2, 128.2, 127.9, 127.0, 126.0, 125.4, 124.3, 122.5, 81.7, 56.0, 48.1, 21.2; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 384.1029, found: 384.1025.

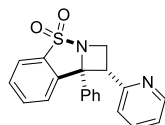
1-([1,1'-biphenyl]-4-yl)-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-*b*]benzo[*d*]isothiazole 4,4-dioxide (3ap)



Yellow solid; 40.4 mg, 48% yield, reaction time 6 h; m.p. : 232 – 234 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.80 (d, $J = 7.7$ Hz, 1H), 7.66 – 7.65 (m, 2H), 7.57 – 7.50 (m, 3H), 7.44 – 7.38 (m, 4H), 7.35 – 7.29 (m, 5H), 7.13 – 7.09 (m, 2H), 7.06 – 7.02 (m, 1H), 4.55 – 4.49 (m, 1H), 4.11 – 4.06 (m, 2H); ^{13}C NMR (100 MHz,

CDCl_3) δ (ppm) = 145.6, 140.3, 140.2, 138.4, 137.2, 134.3, 134.1, 129.9, 129.5, 128.7, 128.0, 127.4, 127.2, 127.0, 126.9, 125.5, 124.4, 122.6, 81.7, 56.0, 48.0; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{21}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 446.1185, found: 446.1187.

8b-phenyl-1-(pyridin-2-yl)-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3aq)



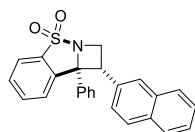
White solid; 42.3 mg, 61% yield, reaction time 6 h; m.p. : 230 – 233 °C; ^1H

NMR (400 MHz, CDCl_3) δ (ppm) = 8.48 – 8.47 (m, 1H), 7.79 (d, J = 7.7 Hz,

1H), 7.73 (d, J = 7.9 Hz, 1H), 7.66 (td, J = 7.6, 1.1 Hz, 1H), 7.57 – 7.53 (m, 1H),

7.49 (td, J = 7.7, 1.8 Hz, 1H), 7.36 – 7.33 (m, 3H), 7.11 – 7.01 (m, 4H), 4.50 – 4.45 (m, 1H), 4.30 – 4.24 (m, 2H); ^{13}C **NMR (100 MHz, CDCl_3)** δ (ppm) = 157.9, 149.0, 145.0, 138.4, 136.4, 134.3, 134.0, 123.0, 128.0, 127.1, 125.3, 124.7, 123.5, 122.5, 122.3, 81.3, 54.3, 49.8; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 349.1005, found: 349.1002.

1-(naphthalen-2-yl)-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ar)



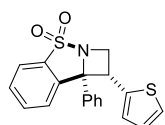
White solid; 23.9 mg, 28% yield, reaction time 6 h; m.p. : 278 – 280 °C; ^1H

NMR (400 MHz, CDCl_3) δ (ppm) = 7.82 (d, J = 7.8 Hz, 1H), 7.76 – 7.71 (m,

3H), 7.68 – 7.67 (m, 2H), 7.62 (d, J = 8.5 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.48 –

7.41 (m, 2H), 7.38 – 7.34 (m, 3H), 7.07 – 7.03 (m, 2H), 7.01 – 6.96 (m, 1H), 4.57 (t, J = 9.4 Hz, 1H), 4.21 (dd, J = 9.1, 4.2 Hz, 1H), 4.15 (dd, J = 9.6, 4.2 Hz, 1H); ^{13}C **NMR (100 MHz, CDCl_3)** δ (ppm) = 145.6, 138.4, 135.7, 134.3, 134.1, 133.0, 132.6, 129.9, 128.5, 128.4, 128.1, 127.7, 127.6, 127.2, 126.2, 126.1, 126.1, 125.4, 124.4, 122.7, 81.7, 56.1, 48.5; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{19}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 420.1029, found: 420.1025.

8b-phenyl-1-(thiophen-2-yl)-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3as)



White solid; 67.7 mg, 96% yield, reaction time 6 h; m.p. : 230 – 232 °C; ^1H

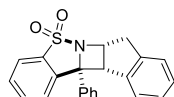
NMR (400 MHz, CDCl_3) δ (ppm) = 7.76 (d, J = 7.7 Hz, 1H), 7.70 – 7.68 (m,

1H), 7.65 (td, J = 6.9, 0.9 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.44 – 7.41 (m, 2H), 7.19

– 7.15 (m, 2H), 7.14 – 7.11 (m, 2H), 6.90 (dd, J = 3.5, 1.1 Hz, 1H), 6.83 (dd, J = 5.1, 3.5 Hz, 1H),

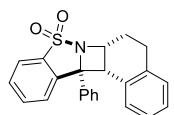
4.52 (t, $J = 9.6$ Hz, 1H), 4.35 (dd, $J = 9.4, 4.4$ Hz, 1H), 4.11 (dd, $J = 9.8, 4.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 144.8, 140.8, 138.1, 134.5, 134.0, 123.0, 128.0, 127.4, 127.2, 126.9, 125.7, 125.3, 124.3, 122.6, 82.0, 56.9, 43.5; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{16}\text{NO}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 354.0617, found: 354.0613.

11c-phenyl-6a,7,11b,11c-tetrahydrobenzo[*d*]indeno[1',2':3,4]azeto[1,2-*b*]isothiazole 5,5-dioxide (3at)



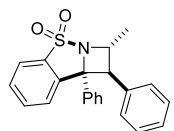
White solid; 33.0 mg, 46% yield, reaction time 6 h; m.p. : 320 – 324 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.99 (d, $J = 7.8$ Hz, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.76 (td, $J = 7.6, 1.1$ Hz, 1H), 7.60 (td, $J = 7.5, 0.9$ Hz, 1H), 7.47 – 7.44 (m, 2H), 7.29 (d, $J = 7.6$ Hz, 1H), 7.22 – 7.11 (m, 4H), 6.95 (t, $J = 7.4$, 1H), 6.86 (d, $J = 7.6$ Hz, 1H), 4.88 (t, $J = 6.3$ Hz, 1H), 4.26 (d, $J = 6.3$ Hz, 1H), 3.45 (d, $J = 17.3$ Hz, 1H), 3.26 (dd, $J = 17.4, 6.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 145.0, 143.4, 138.2, 137.4, 136.0, 133.6, 129.9, 128.2, 128.1, 127.7, 127.3, 126.4, 125.6, 125.5, 125.5, 122.8, 81.7, 65.6, 53.8, 40.0; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{18}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 360.1053, found: 360.1051.

12b-phenyl-6,6a,12b,12c-tetrahydro-5*H*-benzo[*d*]naphtho[1',2':3,4]azeto[1,2-*b*]isothiazole 8,8-dioxide (3au)



Yellow solid; 30.4 mg, 41% yield, reaction time 6 h; m.p. : 288 – 290 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.79 (d, $J = 8.7$ Hz, 2H), 7.71 – 7.67 (m, 1H), 7.58 – 7.54 (m, 1H), 7.42 – 7.39 (m, 2H), 7.18 – 7.12 (m, 2H), 7.10 – 7.07 (m, 3H), 7.05 – 7.01 (m, 1H), 7.00 – 6.98 (m, 1H), 4.84 (d, $J = 8.7$ Hz, 1H), 4.13 (d, $J = 8.7$ Hz, 1H), 3.05 (ddd, $J = 16.5, 13.3, 4.3$ Hz, 1H), 2.64 (d, $J = 15.6$ Hz, 1H), 2.30 (ddt, $J = 14.2, 4.5, 2.5$ Hz, 1H), 1.56 – 1.47 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 145.9, 139.1, 137.4, 135.2, 133.9, 131.7, 131.2, 129.7, 128.8, 127.8, 127.4, 127.2, 126.0, 125.6, 124.5, 122.4, 79.8, 60.0, 46.5, 28.0, 25.7; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 396.1029, found: 396.1030.

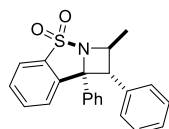
2-methyl-1,8b-diphenyl-1,8b-dihydro-2*H*-azeto[1,2-*b*]benzo[*d*]isothiazole 4,4-dioxide (3av)



White solid; 7.0 mg, 10% yield, reaction time 6 h; m.p. : 211 – 214 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.83 (d, $J = 7.8$ Hz, 1H), 7.64 – 7.61 (m, 2H), 7.50

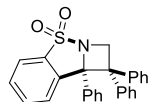
- 7.46 (m, 1H), 7.40 – 7.36 (m, 2H), 7.31 – 7.22 (m, 5H), 6.89 – 6.87 (m, 2H), 6.51 (d, $J = 8.0$ Hz, 1H), 4.41 (dq, $J = 8.9, 6.2$ Hz, 1H), 4.02 (d, $J = 8.9$ Hz, 1H), 1.56 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 143.3, 140.1, 136.4, 134.8, 132.3, 129.8, 129.3, 128.8, 128.5, 128.2, 127.8, 127.5, 124.6, 122.4, 79.2, 63.0, 55.0, 22.1; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 384.1029, found: 384.1025.

2-methyl-1,8b-diphenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3av')



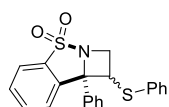
White solid; 27.9 mg, 39% yield, reaction time 6 h; m.p. : 206 – 209 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.71 (dd, $J = 16.5, 7.8$ Hz, 2H), 7.64 – 7.60 (m, 1H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.36 (d, $J = 7.1$ Hz, 2H), 7.19 – 7.07 (m, 7H), 7.05 – 7.01 (m, 1H), 4.65 (qd, $J = 6.8, 5.1$ Hz, 1H), 3.73 (d, $J = 5.2$ Hz, 1H), 1.49 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 147.6, 138.1, 137.3, 137.1, 133.6, 129.4, 129.3, 128.3, 127.8, 127.5, 127.0, 125.9, 123.6, 121.2, 78.7, 67.6, 57.3, 19.9; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 384.1029, found: 384.1028.

1,1,8b-triphenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3aw)



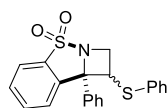
White thick oil; 52.9 mg, 59% yield, reaction time 6 h; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.66 – 7.61 (m, 3H), 7.38 – 7.36 (m, 4H), 7.30 – 7.26 (m, 4H), 7.22 – 7.16 (m, 4H), 7.13 – 7.09 (m, 1H), 7.08 – 7.04 (m, 3H), 4.96 (d, $J = 9.1$ Hz, 1H), 4.31 (d, $J = 9.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 142.7, 141.8, 139.6, 138.7, 134.3, 132.5, 129.4, 129.2, 129.1, 128.5, 128.4, 128.3, 127.6, 127.4, 127.2, 126.8, 125.8, 122.3, 87.5, 61.1, 56.8; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{22}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 424.1366, found: 424.1362.

8b-phenyl-1-(phenylthio)-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ax)



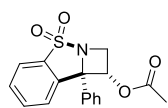
Yellow thick oil; 18.0 mg, 24% yield, reaction time 6 h; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.83 (d, $J = 7.5$ Hz, 1H), 7.66 (td, $J = 7.5, 1.3$ Hz, 1H), 7.60 (td, $J = 7.5, 1.2$ Hz, 1H), 7.55 – 7.52 (m, 3H), 7.36 – 7.26 (m, 8H), 4.65 (t, $J = 8.3$ Hz, 1H), 4.42 (dd, $J = 9.5, 8.1$ Hz, 1H), 3.96 (dd, $J = 9.5, 8.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 141.7, 139.1, 135.4, 133.5, 132.9, 131.0, 130.5, 129.5, 128.9, 128.2, 127.8, 127.5, 124.3, 122.7, 82.6, 57.3, 47.7; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{17}\text{NO}_2\text{S}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 402.0593, found: 402.0589.

8b-phenyl-1-(phenylthio)-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ax')



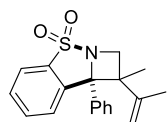
Yellow thick oil; 39.7 mg, 45% yield, reaction time 6 h; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.75 (d, $J = 7.8$ Hz, 1H), 7.70 – 7.66 (m, 4H), 7.55 (ddd, $J = 8.1, 4.7, 3.6$ Hz, 1H), 7.41 – 7.32 (m, 3H), 7.27 – 7.20 (m, 3H), 7.13 – 7.11 (m, 2H), 4.43 – 4.37 (m, 2H), 3.98 – 3.93 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm) = 143.8, 136.9, 134.8, 134.0, 133.3, 130.8, 130.3, 129.2, 128.4, 128.2, 127.4, 126.1, 124.6, 122.7, 80.6, 55.6, 48.3; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{17}\text{NO}_2\text{S}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 402.0593, found: 402.0588.

4,4-dioxido-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazol-1-yl acetate (3ay)



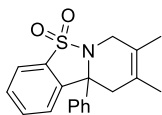
White solid; 27.0 mg, 41% yield, reaction time 6 h; m.p. : 177 – 179 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.84 (d, $J = 7.9$ Hz, 1H), 7.78 (d, $J = 7.7$ Hz, 1H), 7.72 (td, $J = 7.7, 1.2$ Hz, 1H), 7.66 – 7.63 (m, 2H), 7.61 (td, $J = 7.6, 1.0$ Hz, 1H), 7.41 – 7.36 (m, 2H), 7.34 – 7.30 (m, 1H), 5.57 (dd, $J = 7.4, 3.3$ Hz, 1H), 4.37 (dd, $J = 11.4, 7.4$ Hz, 1H), 4.09 (dd, $J = 11.4, 3.4$ Hz, 1H), 1.86 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm) = 170.4, 141.3, 135.4, 135.4, 134.0, 130.6, 128.4, 126.3, 125.5, 122.7, 82.6, 71.4, 54.4, 20.5; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_4\text{SNa}$ $[\text{M}+\text{Na}]^+$: 352.0614, found: 352.0611.

1-methyl-8b-phenyl-1-(prop-1-en-2-yl)-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3az)



White solid; 11.3 mg, 17% yield, reaction time 6 h; m.p. : 208 – 210 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.78 (d, $J = 7.7$ Hz, 1H), 7.60 – 7.53 (m, 3H), 7.52 – 7.46 (m, 2H), 7.30 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 5.14 (s, 1H), 5.00 (s, 1H), 4.10 (d, $J = 9.3$ Hz, 1H), 3.74 (d, $J = 9.3$ Hz, 1H), 1.60 (d, $J = 1.2$ Hz, 3H), 1.30 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm) = 145.8, 142.8, 140.4, 135.0, 133.1, 129.7, 128.1, 127.4, 126.8, 124.7, 122.9, 115.6, 83.8, 59.2, 47.6, 24.4, 20.4; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 326.1209, found: 326.1207.

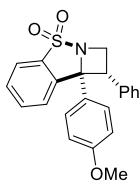
1-methyl-8b-phenyl-1-(prop-1-en-2-yl)-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3az')



White solid; 20.2 mg, 31% yield, reaction time 6 h; m.p. : 214 – 216 °C; ¹H

NMR (400 MHz, CDCl₃) δ (ppm) = 7.89 – 7.84 (m, 1H), 7.49 (dd, *J* = 5.8, 3.1 Hz, 2H), 7.37 – 7.27 (m, 5H), 7.09 – 7.05 (m, 1H), 4.04 (d, *J* = 17.6 Hz, 1H), 3.27 (d, *J* = 17.7 Hz, 1H), 3.01 (d, *J* = 16.8 Hz, 1H), 2.56 (d, *J* = 16.8 Hz, 1H), 1.78 (s, 3H), 1.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 144.1, 139.1, 133.0, 132.9, 129.0, 128.9, 128.1, 126.7, 123.9, 122.8, 122.3, 121.5, 64.6, 60.4, 40.5, 38.4, 21.1, 19.3, 15.7, 14.2; HRMS (ESI) calcd for C₁₉H₂₀NO₂S [M+H]⁺: 326.1209, found: 326.1208.

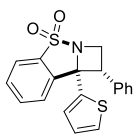
8b-(4-methoxyphenyl)-1-phenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ba)



White solid; 49.7 mg, 66% yield, reaction time 6 h; m.p. : 260 – 261 °C; ¹H NMR

(400 MHz, CDCl₃) δ (ppm) = 7.76 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.52 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.26 – 7.13 (m, 7H), 6.64 – 6.60 (m, 2H), 4.47 (t, *J* = 9.4 Hz, 1H), 4.06 (dd, *J* = 9.7, 4.3 Hz, 1H), 4.01 (dd, *J* = 9.2, 4.3 Hz, 1H), 3.64 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 158.6, 146.1, 138.2, 134.2, 134.1, 130.6, 129.8, 129.1, 128.5, 127.6, 126.8, 124.3, 122.6, 113.5, 81.6, 56.0, 55.1, 48.1; HRMS (ESI) calcd for C₂₂H₂₀NO₃S [M+H]⁺: 378.1158, found: 378.1156.

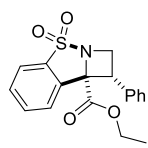
1-phenyl-8b-(thiophen-2-yl)-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ca)



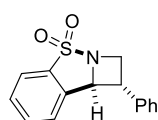
Yellow solid; 28.9 mg, 41% yield, reaction time 6 h; m.p. : 247 – 251 °C; ¹H NMR

(400 MHz, CDCl₃) δ (ppm) = 7.80 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.59 (ddd, *J* = 8.1, 6.3, 2.0 Hz, 1H), 7.35 – 7.33 (m, 2H), 7.28 – 7.20 (m, 3H), 7.03 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.97 (dd, *J* = 3.7, 1.3 Hz, 1H), 6.72 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.40 (t, *J* = 9.7 Hz, 1H), 4.21 (dd, *J* = 10.0, 4.5 Hz, 1H), 4.01 (dd, *J* = 9.3, 4.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 144.7, 140.7, 136.9, 134.7, 134.1, 130.1, 128.8, 128.4, 127.9, 126.5, 126.0, 126.0, 124.5, 122.6, 79.4, 54.6, 48.8; HRMS (ESI) calcd for C₁₉H₁₆NO₂S₂ [M+H]⁺: 354.0617, found: 354.0622.

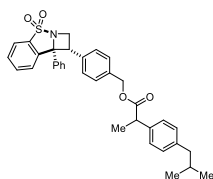
ethyl 1-phenyl-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide

(3da)

White solid; 63.0 mg, 91% yield, reaction time 6 h; m.p. : 178 – 180 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.87 (d, *J* = 7.8 Hz, 1H), 7.82 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.76 (td, *J* = 7.6, 1.2 Hz, 1H), 7.67 (td, *J* = 7.5, 1.0 Hz, 1H), 7.57 – 7.55 (m, 2H), 7.43 – 7.39 (m, 2H), 7.37 – 7.33 (m, 1H), 4.33 (t, *J* = 9.4 Hz, 1H), 4.10 (dd, *J* = 9.7, 4.1 Hz, 1H), 3.87 – 3.80 (m, 3H), 0.86 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 166.2, 138.5, 137.1, 135.5, 134.0, 130.9, 128.8, 128.3, 128.0, 125.6, 122.3, 79.2, 62.0, 55.0, 47.1, 13.4; HRMS (ESI) calcd for C₁₈H₁₈NO₄S [M+H]⁺: 344.0951, found: 344.0949.

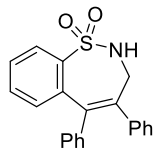
1-phenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (3ea)

White solid; 49.0 mg, 90% yield, reaction time 6 h; m.p. : 174 – 176 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.85 (d, *J* = 7.7 Hz, 1H), 7.71 (td, *J* = 7.6, 1.1 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.48 – 7.44 (m, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.35 (m, 1H), 5.36 (d, *J* = 3.7 Hz, 1H), 4.48 (t, *J* = 9.6 Hz, 1H), 4.10 (dd, *J* = 9.9, 4.7 Hz, 1H), 3.55 (dt, *J* = 8.9, 4.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 140.6, 140.3, 136.0, 133.9, 130.2, 129.3, 128.0, 127.1, 124.4, 122.6, 73.5, 57.9, 43.0; HRMS (ESI) calcd for C₁₅H₁₃NO₂SNa [M+Na]⁺: 294.0559, found: 294.0555.

4-(4,4-dioxido-8b-phenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazol-1-yl)benzyl 2-(4-isobutylphenyl)propanoate (4)

Yellow solid; 76.5 mg, 68% yield, reaction time 6 h; m.p. : 170 – 172 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.75 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 3.9 Hz, 2H), 7.51 (dq, *J* = 8.0, 4.3 Hz, 1H), 7.30 – 7.28 (m, 2H), 7.18 – 7.14 (m, 4H), 7.11 – 7.02 (m, 7H), 4.99 (s, 2H), 4.46 (t, *J* = 10.5 Hz, 1H), 4.03 – 3.99 (m, 2H), 3.71 (q, *J* = 7.1 Hz, 1H), 2.45 (d, *J* = 7.1 Hz, 2H), 1.84 (dh, *J* = 13.5, 6.7 Hz, 1H), 1.47 (dd, *J* = 7.2, 2.1 Hz, 3H), 0.91 (s, 3H), 0.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 174.2, 174.2, 145.4, 140.5, 138.2, 138.2, 137.8, 137.4, 137.4, 135.4, 135.4, 134.2, 134.0, 129.8, 129.2, 129.0, 127.9, 127.7, 127.1, 127.1, 125.4, 124.3, 122.5, 81.5, 65.6, 55.9, 47.8, 45.0, 44.9, 44.9, 30.1, 22.3, 18.3, 18.2; HRMS (ESI) calcd for C₃₅H₃₅NO₄SNa [M+Na]⁺: 588.2179, found: 588.2180.

4,5-diphenyl-2,3-dihydrobenzo[f][1,2]thiazepine 1,1-dioxide (5a)



White solid; 56.5 mg, 81% yield; m.p. : 270 – 272 °C; ¹H NMR (400 MHz,

CDCl₃) δ (ppm) = 8.09 – 8.07 (m, 1H), 7.53 – 7.51 (m, 2H), 7.23 – 7.11 (m, 9H),

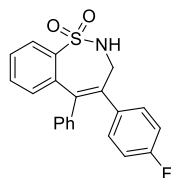
7.00 – 6.98 (m, 2H), 5.06 (s, 1H), 3.89 (d, *J* = 2.5 Hz, 2H); ¹³C NMR (100 MHz,

CDCl₃) δ (ppm) = 143.6, 141.1, 140.6, 140.1, 137.1, 134.3, 132.5, 131.1, 130.8, 129.5, 128.5,

128.1, 127.8, 127.3, 127.2, 125.9, 49.4; HRMS (ESI) calcd for C₂₁H₁₇NO₂SNa [M+Na]⁺:

370.0872, found: 370.0874.

4-(4-fluorophenyl)-5-phenyl-2,3-dihydrobenzo[f][1,2]thiazepine 1,1-dioxide (5b)



White solid; 49.4 mg, 68% yield; m.p. : 269 – 271 °C; ¹H NMR (600 MHz,

CDCl₃) δ (ppm) = 8.08 – 8.06 (m, 1H), 7.54 – 7.50 (m, 2H), 7.20 – 7.18 (m, 2H),

7.15 – 7.11 (m, 4H), 6.98 – 6.97 (m, 2H), 6.88 (t, *J* = 8.7 Hz, 2H), 5.10 (s, 1H),

3.86 (d, *J* = 2.1 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) = 161.9 (d, *J* =

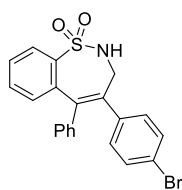
247.4 Hz), 144.1, 131.0, 139.9, 137.1, 136.6 (d, *J* = 3.4 Hz), 133.3, 132.6, 131.3 (d, *J* = 8.4 Hz),

131.1, 130.7, 128.6, 128.0, 127.5, 126.0, 115.2 (d, *J* = 21.6 Hz), 49.4; ¹⁹F NMR (376 MHz,

CDCl₃) δ (ppm) = -114.30; HRMS (ESI) calcd for C₂₁H₁₇FNO₂S [M+H]⁺: 366.0959, found:

366.0940.

4-(4-bromophenyl)-5-phenyl-2,3-dihydrobenzo[f][1,2]thiazepine 1,1-dioxide (5c)



White solid; 45.2 mg, 53% yield; m.p. : 265 – 267 °C; ¹H NMR (400 MHz,

CDCl₃) δ (ppm) = 8.09 – 8.07 (m, 1H), 7.54 – 7.52 (m, 2H), 7.33 – 7.31 (m,

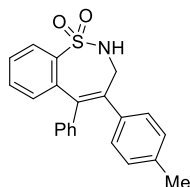
2H), 7.16 – 7.09 (m, 6H), 6.99 – 6.97 (m, 2H), 5.03 (s, 1H), 3.85 (d, *J* = 2.0 Hz,

2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 144.4, 140.8, 139.7, 139.6, 137.1,

133.0, 132.6, 131.4, 131.3, 131.1, 128.7, 128.1, 127.7, 121.5, 49.2; HRMS (ESI) calcd for

C₂₁H₁₆BrNO₂SNa [M+Na]⁺: 447.9977, found: 447.9977.

5-phenyl-4-(p-tolyl)-2,3-dihydrobenzo[f][1,2]thiazepine 1,1-dioxide (5d)

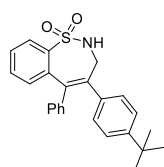


White solid; 54.2 mg, 75% yield; m.p. : 277 – 279 °C; ¹H NMR (400 MHz,

CDCl₃) δ (ppm) = 8.08 – 8.06 (m, 1H), 7.51 – 7.50 (m, 2H), 7.14 – 7.09 (m,

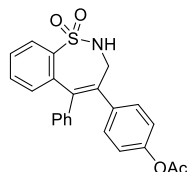
6H), 7.00 – 6.99 (m, 4H), 5.02 (s, 1H), 3.87 (s, 2H), 2.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 143.1, 141.3, 140.3, 137.6, 137.1, 137.0, 134.4, 132.5, 131.1, 130.8, 129.4, 128.9, 128.4, 127.9, 127.3, 125.9, 49.5, 21.2; HRMS (ESI) calcd for C₂₂H₁₉NO₂SNa [M+Na]⁺: 384.1029, found: 384.1031.

4-(4-(tert-butyl)phenyl)-5-phenyl-2,3-dihydrobenzo[f][1,2]thiazepine 1,1-dioxide (5e)



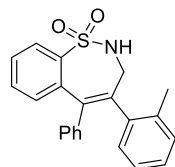
White solid; 51.2 mg, 64% yield; m.p. : 245 – 247 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) = 8.07 – 8.06 (m, 1H), 7.52 – 7.48 (m, 2H), 7.20 – 7.19 (m, 2H), 7.14 – 7.10 (m, 6H), 7.00 – 6.99 (m, 2H), 5.05 (s, 1H), 3.88 (d, *J* = 2.5 Hz, 2H), 1.25 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) = 150.2, 143.1, 141.4, 140.3, 137.5, 137.2, 134.3, 132.5, 131.1, 130.8, 129.2, 128.3, 127.8, 127.3, 125.9, 125.1, 49.5, 34.5, 31.2; HRMS (ESI) calcd for C₂₅H₂₅NO₂SNa [M+Na]⁺: 426.1498, found: 426.1474.

4-(1,1-dioxido-5-phenyl-2,3-dihydrobenzo[f][1,2]thiazepin-4-yl)phenyl acetate (5f)



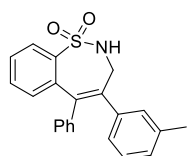
White solid; 55.6 mg, 67% yield; m.p. : 253 – 256 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.08 – 8.06 (m, 1H), 7.52 – 7.51 (m, 2H), 7.23 – 7.21 (m, 2H), 7.16 – 7.11 (m, 4H), 7.00 – 6.98 (m, 2H), 6.94 – 6.92 (m, 2H), 5.10 (s, 1H), 3.87 (s, 2H), 2.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 169.2, 149.7, 144.1, 141.0, 139.9, 138.2, 137.1, 133.4, 132.5, 131.1, 130.74, 130.67, 128.6, 128.0, 127.5, 126.0, 121.3, 49.3, 21.2; HRMS (ESI) calcd for C₂₃H₁₉NO₄SNa [M+Na]⁺: 428.0927, found: 428.0930.

5-phenyl-4-(*o*-tolyl)-2,3-dihydrobenzo[f][1,2]thiazepine 1,1-dioxide (5g)



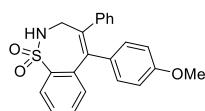
White solid; 22.2 mg, 31% yield; m.p. : 250 – 253 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) = 8.09 – 8.08 (m, 1H), 7.54 – 7.50 (m, 2H), 7.17 – 7.13 (m, 3H), 7.11 – 7.07 (m, 4H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.93 – 6.92 (m, 2H), 5.05 (s, 1H), 3.78 (ddd, *J* = 70.2, 11.5, 2.4 Hz, 2H), 2.32 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) = 144.0, 140.7, 140.5, 140.0, 137.2, 135.2, 134.5, 132.5, 131.2, 130.2, 129.9, 129.8, 128.4, 127.7, 127.44, 127.36, 125.9, 125.8, 48.4, 19.9; HRMS (ESI) calcd for C₂₂H₁₉NO₂SNa [M+Na]⁺: 384.1029, found: 384.1003.

5-phenyl-4-(*m*-tolyl)-2,3-dihydrobenzo[f][1,2]thiazepine 1,1-dioxide (5h)



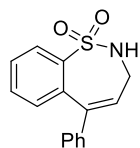
White solid; 41.5 mg, 57% yield; m.p. : 255 – 256 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) = 8.08 – 8.06 (m, 1H), 7.51 (td, *J* = 7.6, 6.6, 3.8 Hz, 2H), 7.15 – 7.10 (m, 4H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.02 (s, 1H), 7.00 – 6.98 (m, 3H), 6.96 (d, *J* = 7.6 Hz, 1H), 5.06 (s, 1H), 3.88 (d, *J* = 2.4 Hz, 2H), 2.21 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) = 143.3, 141.2, 140.5, 140.2, 137.7, 137.1, 134.5, 132.5, 131.1, 130.8, 130.0, 128.4, 128.04, 128.00, 127.8, 127.3, 126.7, 125.9, 49.4, 21.4; HRMS (ESI) calcd for C₂₂H₁₉NO₂SNa [M+Na]⁺: 384.1029, found: 384.1006.

5-(4-methoxyphenyl)-4-phenyl-2,3-dihydrobenzo[f][1,2]thiazepine 1,1-dioxide (5i)



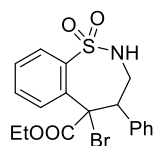
White solid; 53.2 mg, 71% yield; m.p. : 267 – 270 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.08 – 8.04 (m, 1H), 7.54 – 7.48 (m, 2H), 7.24 – 7.19 (m, 4H), 7.18 – 7.15 (m, 2H), 6.90 – 6.87 (m, 2H), 6.66 – 6.62 (m, 2H), 5.05 (s, 1H), 3.86 (d, *J* = 2.4 Hz, 2H), 3.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 158.8, 143.2, 141.5, 141.0, 137.1, 133.4, 132.5, 132.4, 132.1, 131.2, 129.6, 128.4, 128.2, 127.1, 125.9, 113.3, 55.1, 49.5; HRMS (ESI) calcd for C₂₂H₁₉NO₃SNa [M+Na]⁺: 400.0980, found: 400.0978.

5-phenyl-2,3-dihydrobenzo[f][1,2]thiazepine 1,1-dioxide (5j)



White solid; 29.8 mg, 55% yield; m.p. : 237 – 240 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) = 8.04 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.48 (dtd, *J* = 22.4, 7.5, 1.5 Hz, 2H), 7.33 – 7.32 (m, 3H), 7.26 – 7.23 (m, 2H), 7.16 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.25 (t, *J* = 6.8 Hz, 1H), 5.23 (s, 1H), 3.70 (dd, *J* = 6.8, 2.9 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) = 147.3, 141.4, 139.5, 137.5, 132.4, 131.3, 128.5, 128.4, 128.2, 126.2, 124.5, 42.0; HRMS (ESI) calcd for C₁₅H₁₃NO₂SNa [M+Na]⁺: 294.0559, found: 294.0552.

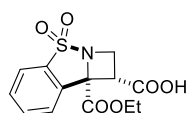
ethyl 5-bromo-4-phenyl-2,3,4,5-tetrahydrobenzo[f][1,2]thiazepine-5-carboxylate 1,1-dioxide (6)



White thick oil; 16.2 mg, 43% yield; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.98 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.69 (td, *J* = 7.6, 1.0 Hz, 1H), 7.42 – 7.34 (m, 5H), 5.72 (s, 1H), 4.11 – 3.98 (m, 2H), 3.95 (dd, *J* = 11.3, 3.7 Hz, 1H), 3.74 (t, *J* = 10.9 Hz, 1H), 3.17 (dd, *J* = 10.6, 3.7 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz,

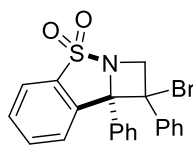
CDCl_3) δ (ppm) = 168.3, 136.1, 135.6, 135.3, 134.2, 131.3, 129.0, 128.7, 125.3, 131.9, 72.2, 63.9, 55.9, 31.4, 13.9; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{BrNO}_4\text{SNa}$ $[\text{M}+\text{Na}]^+$: 446.0032, found: 446.0036.

8b-(ethoxycarbonyl)-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole-1-carboxylic acid 4,4-dioxide (7)



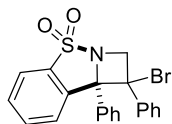
White solid; 98.3 mg, 63% yield; m.p. : 220 – 222 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.86 (d, J = 7.6 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.70 (ddd, J = 7.6, 5.9, 2.6 Hz, 1H), 6.51 (s, 1H), 4.36 – 4.22 (m, 2H), 4.20 (dd, J = 9.8, 4.7 Hz, 1H), 4.12 (t, J = 9.5 Hz, 1H), 3.55 (dd, J = 9.1, 4.7 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 175.0, 167.1, 136.9, 135.8, 134.4, 131.6, 125.3, 122.7, 74.8, 63.2, 50.2, 44.6, 13.8; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_6\text{SNa}$ $[\text{M}+\text{Na}]^+$: 344.0356, found: 344.0356.

1-bromo-1,8b-diphenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (8)



White solid; 12.6 mg, 30% yield; m.p. : 243 – 247 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.82 (t, J = 8.7 Hz, 2H), 7.72 – 7.66 (m, 3H), 7.59 (td, J = 7.5, 1.0 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.18 – 7.14 (m, 2H), 7.13 – 7.09 (m, 1H), 7.07 – 7.03 (m, 2H), 7.01 – 6.97 (m, 1H), 4.78 (d, J = 10.3 Hz, 1H), 4.72 (d, J = 10.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 142.3, 138.2, 138.1, 134.1, 132.9, 130.4, 128.6, 128.4, 128.3, 127.9, 127.9, 127.5, 125.1, 122.5, 88.1, 66.3, 63.1; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{17}\text{BrNO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 426.0158, found: 426.0154.

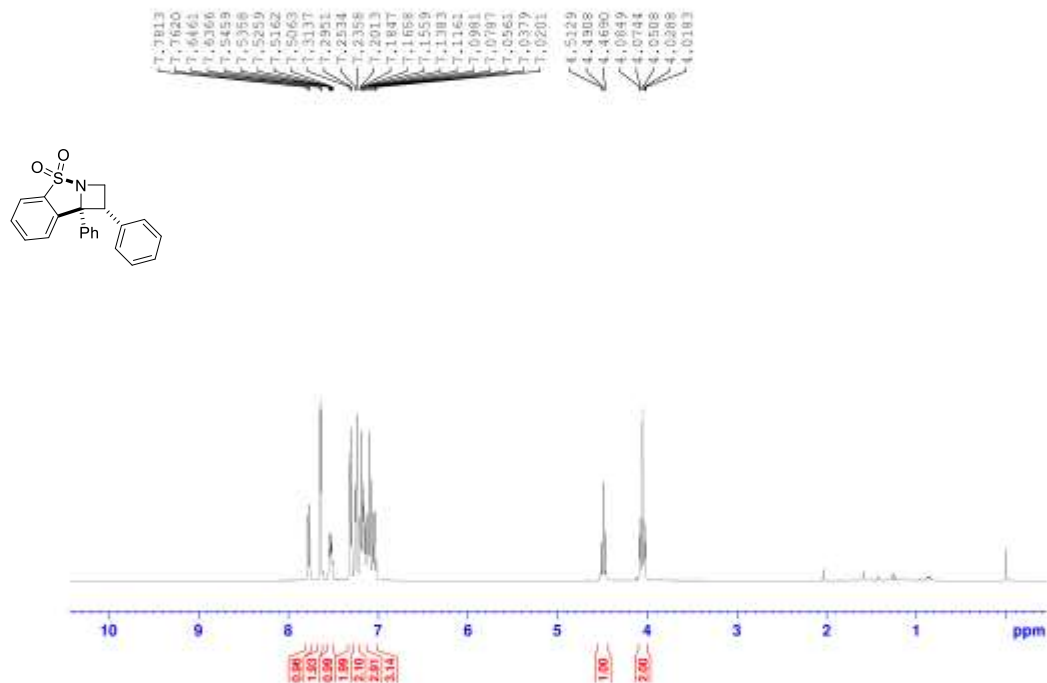
1-bromo-1,8b-diphenyl-1,8b-dihydro-2H-azeto[1,2-b]benzo[d]isothiazole 4,4-dioxide (8')



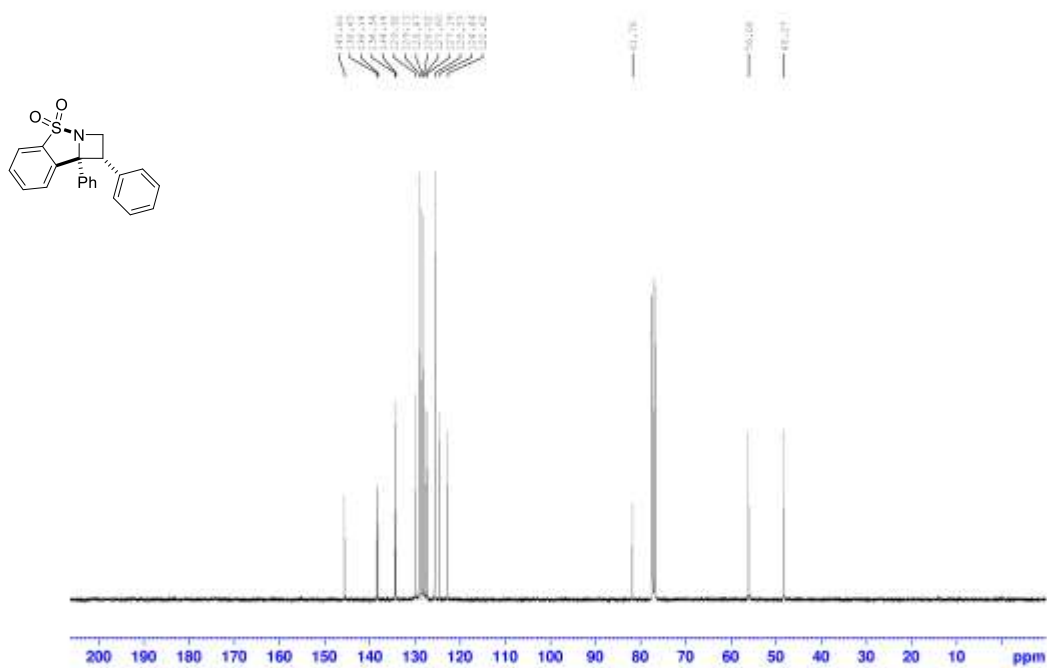
White solid; 14.4 mg, 34% yield; m.p. : 248 – 251 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.83 – 7.81 (m, 2H), 7.69 (d, J = 7.8 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.41 – 7.32 (m, 7H), 7.18 (ddd, J = 8.3, 7.3, 1.2 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 4.99 (d, J = 10.9 Hz, 1H), 4.51 (d, J = 10.9 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 140.0, 139.5, 138.1, 135.0, 132.7, 130.2, 129.1, 128.7, 128.5, 128.4, 127.7, 127.0, 125.8, 111.7, 87.4, 66.2, 62.4; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{17}\text{BrNO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 426.0158, found: 426.0165.

12. Copy of ^1H NMR and ^{13}C NMR spectra of the compounds

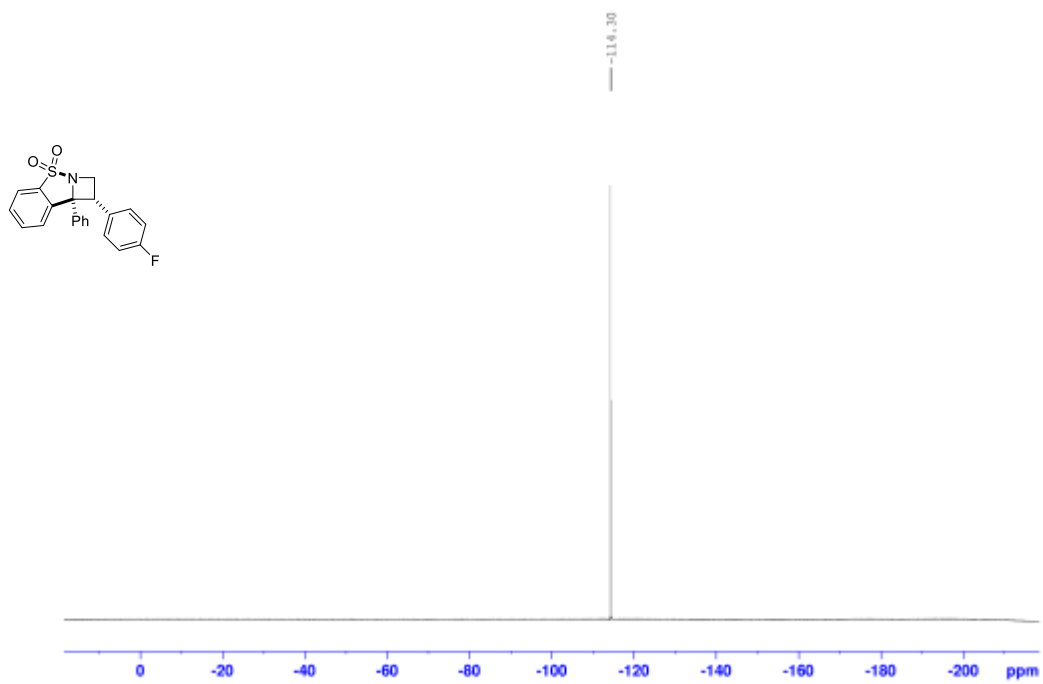
^1H NMR (400 MHz, CDCl_3) spectra of **3aa**



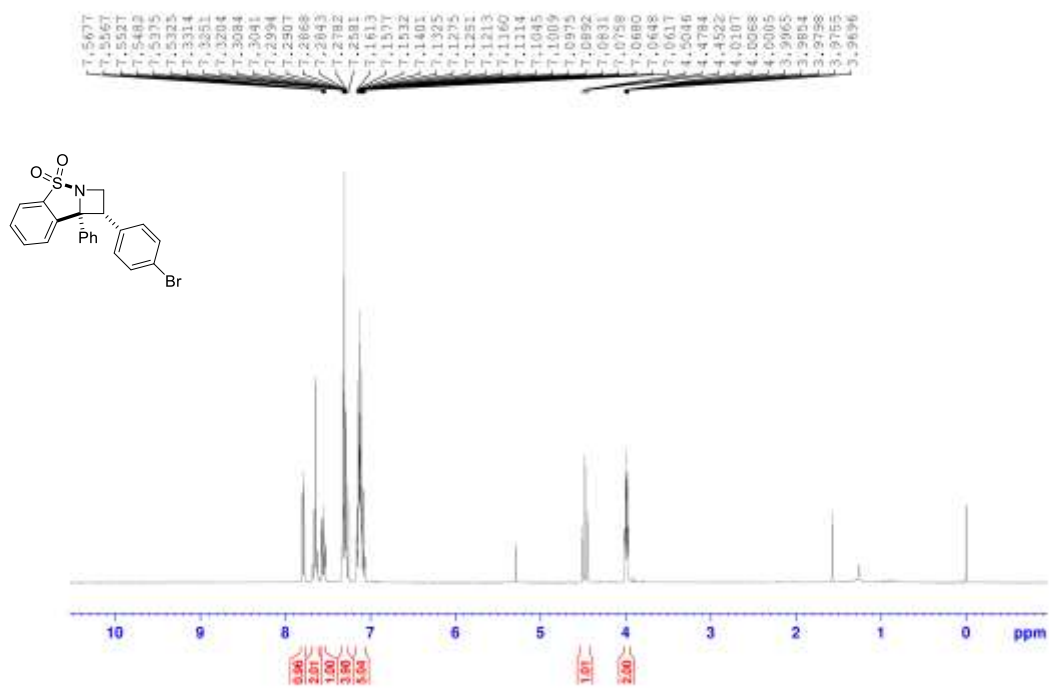
^{13}C NMR (100 MHz, CDCl_3) spectra of **3aa**



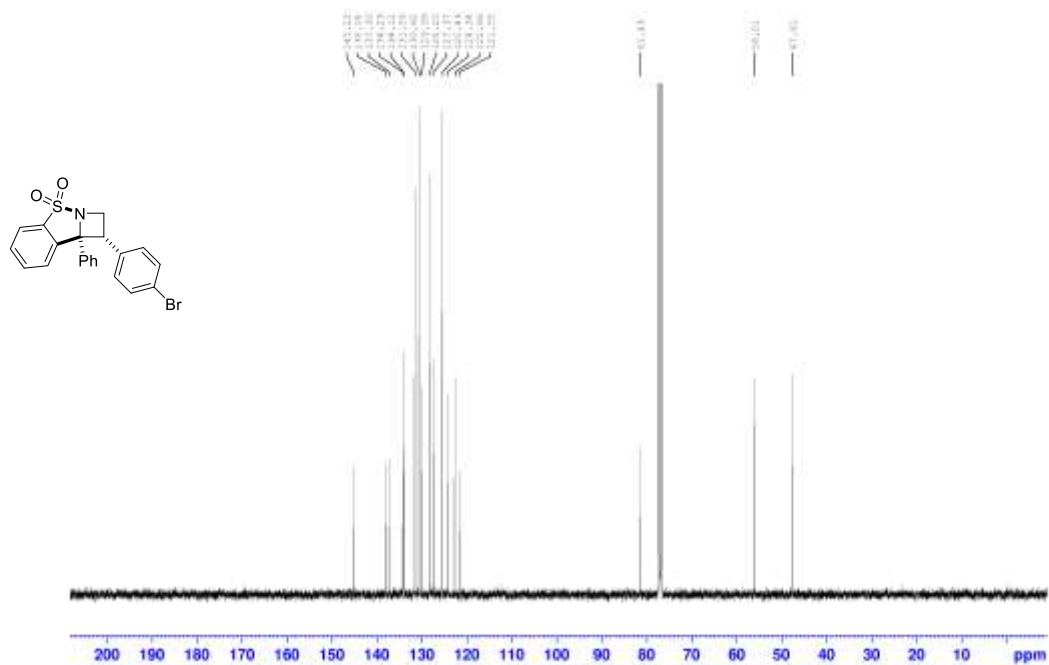
^{19}F NMR (376 MHz, CDCl_3) spectra of **3ab**



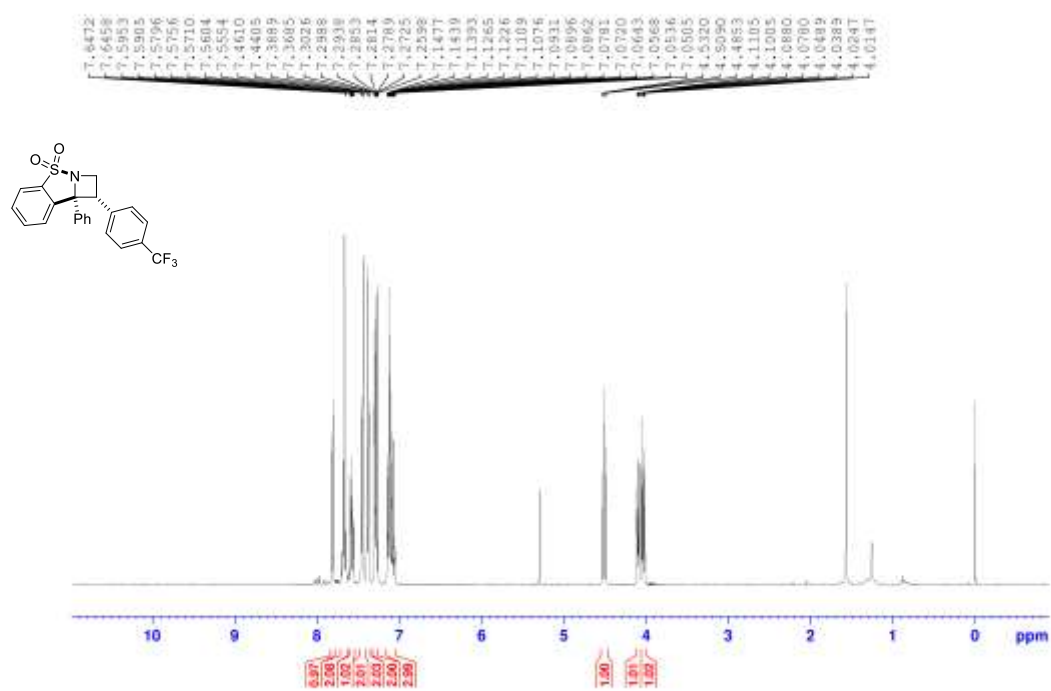
^1H NMR (400 MHz, CDCl_3) spectra of **3ad**



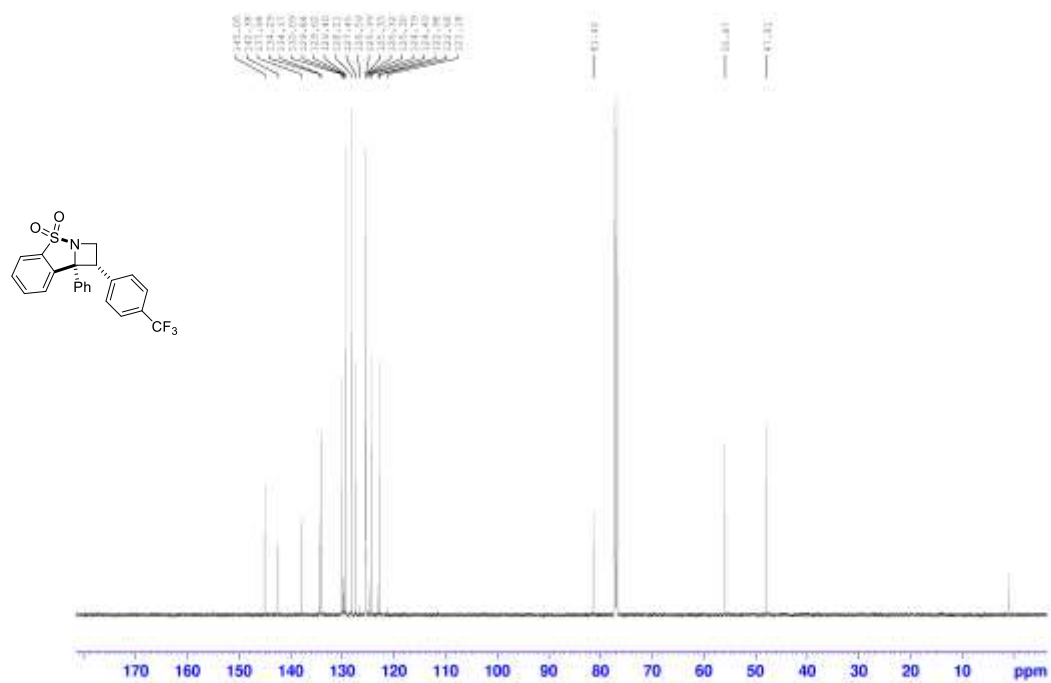
^{13}C NMR (100 MHz, CDCl_3) spectra of **3ad**



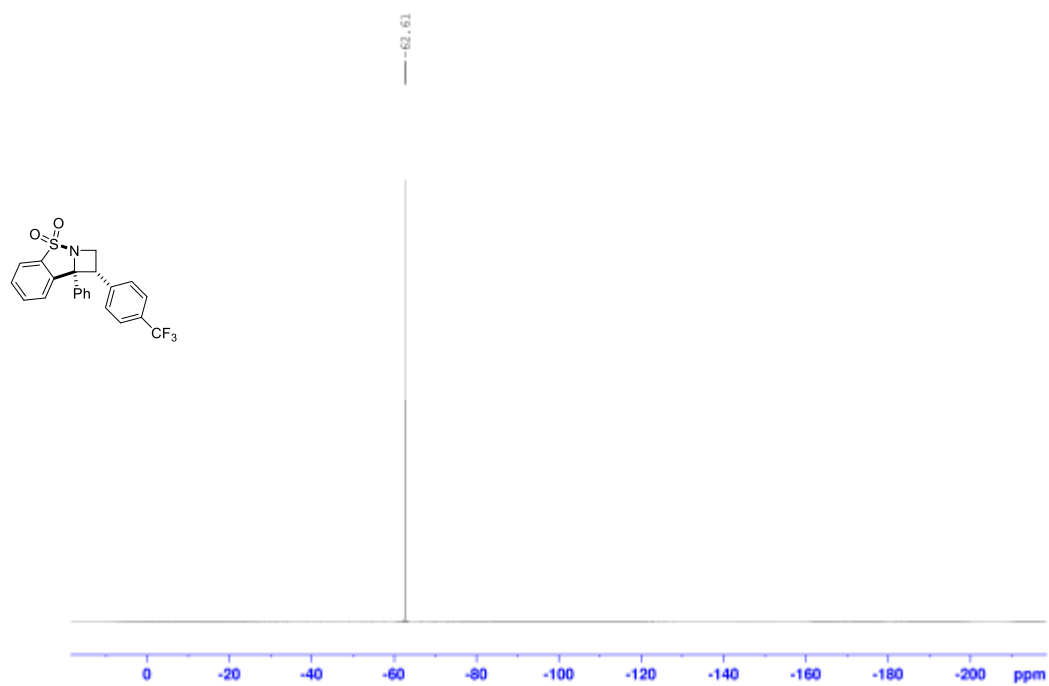
^1H NMR (400 MHz, CDCl_3) spectra of **3ae**



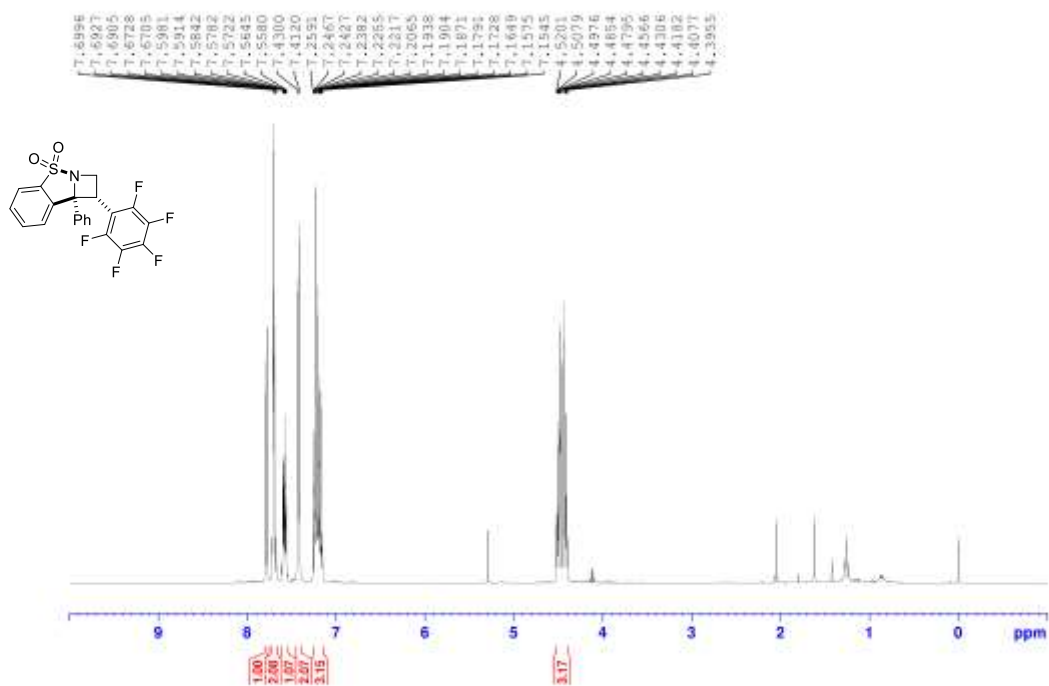
^{13}C NMR (100 MHz, CDCl_3) spectra of **3ae**



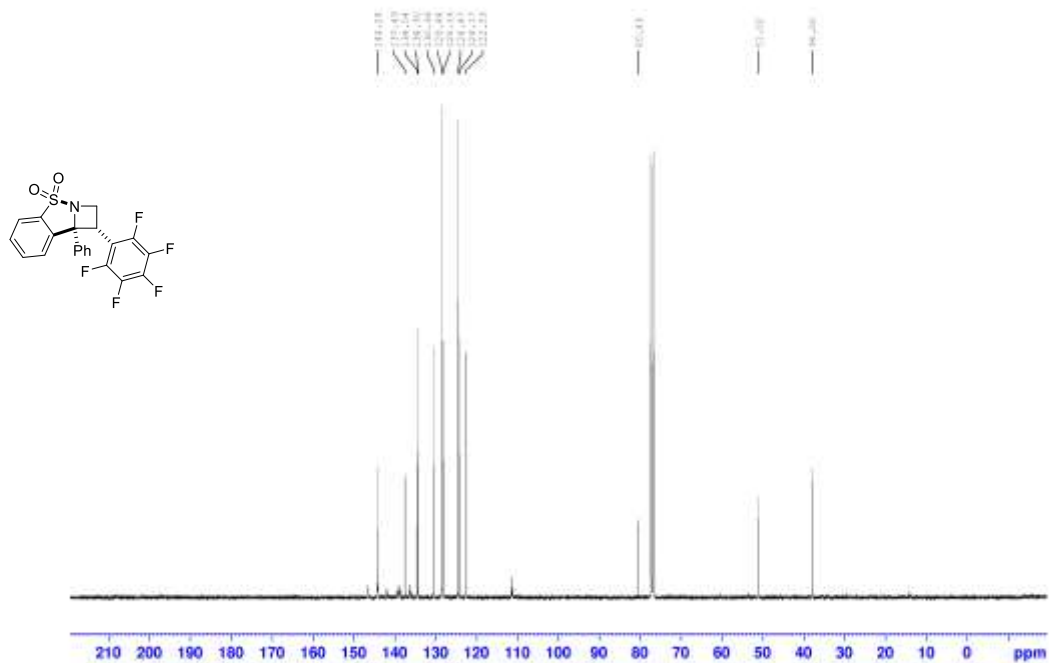
^{19}F NMR (376 MHz, CDCl_3) spectra of **3ae**



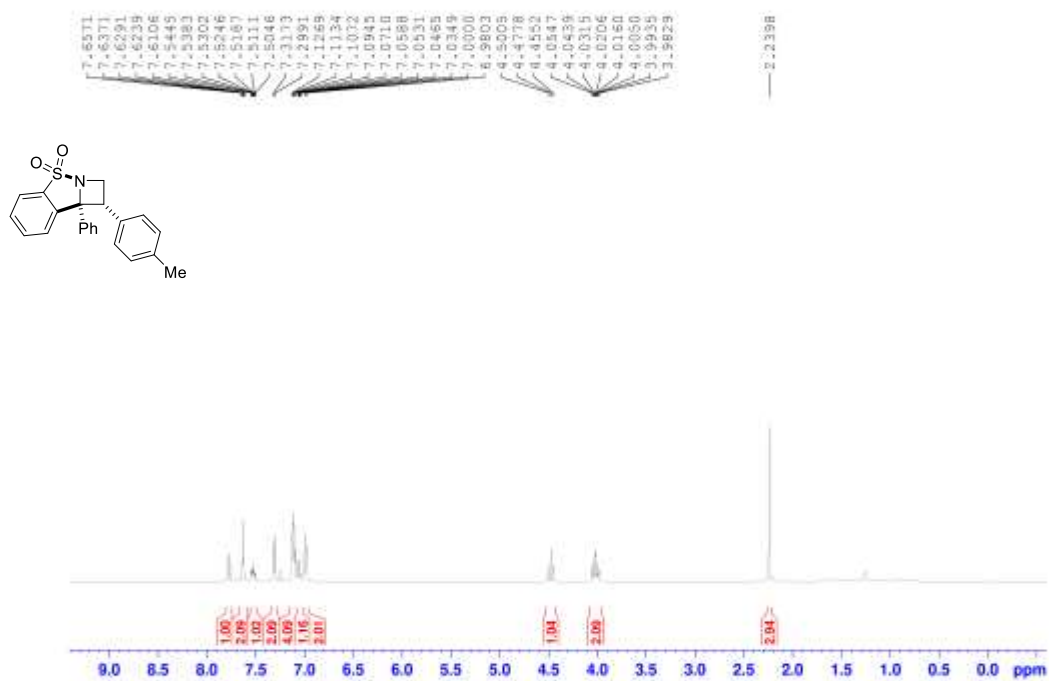
¹H NMR (400 MHz, CDCl₃) spectra of **3af**



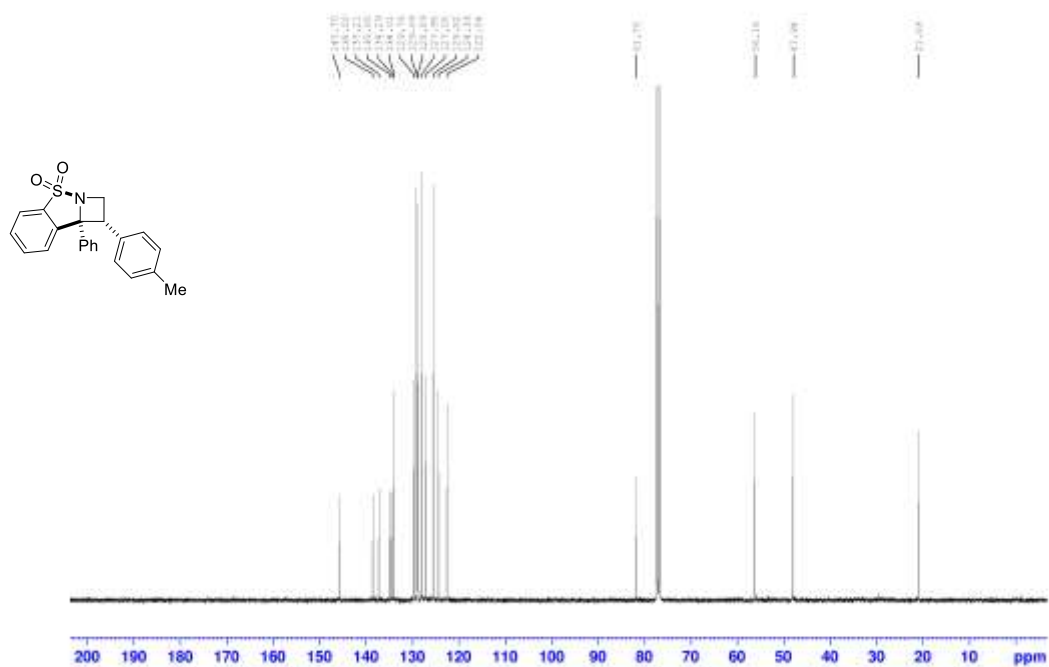
¹³C NMR (100 MHz, CDCl₃) spectra of **3af**



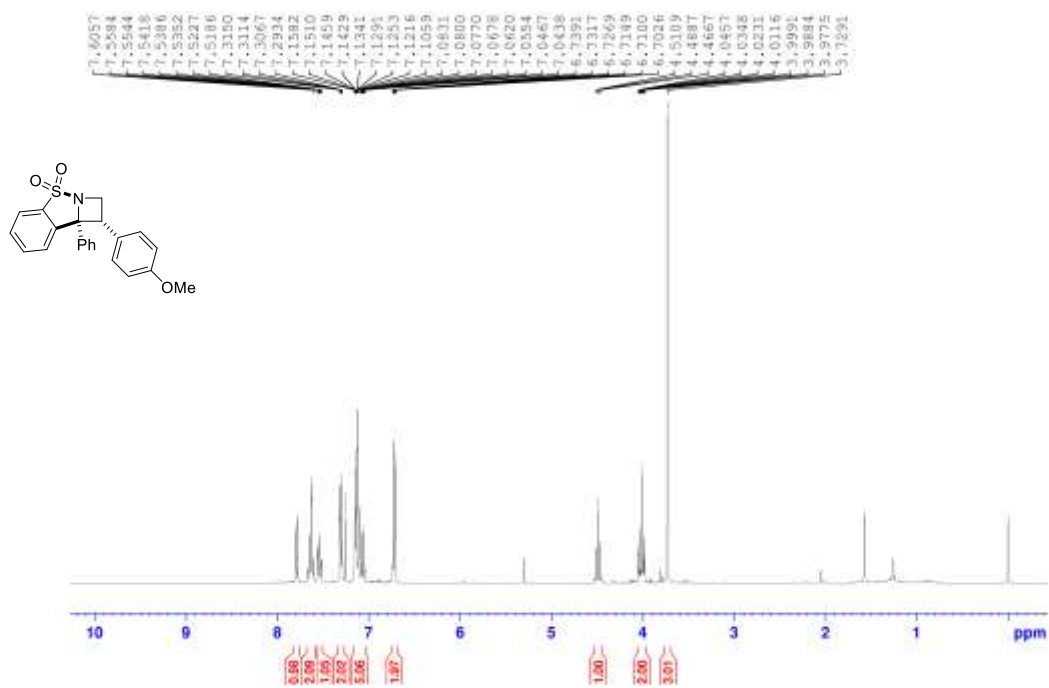
^1H NMR (400 MHz, CDCl_3) spectra of **3ag**



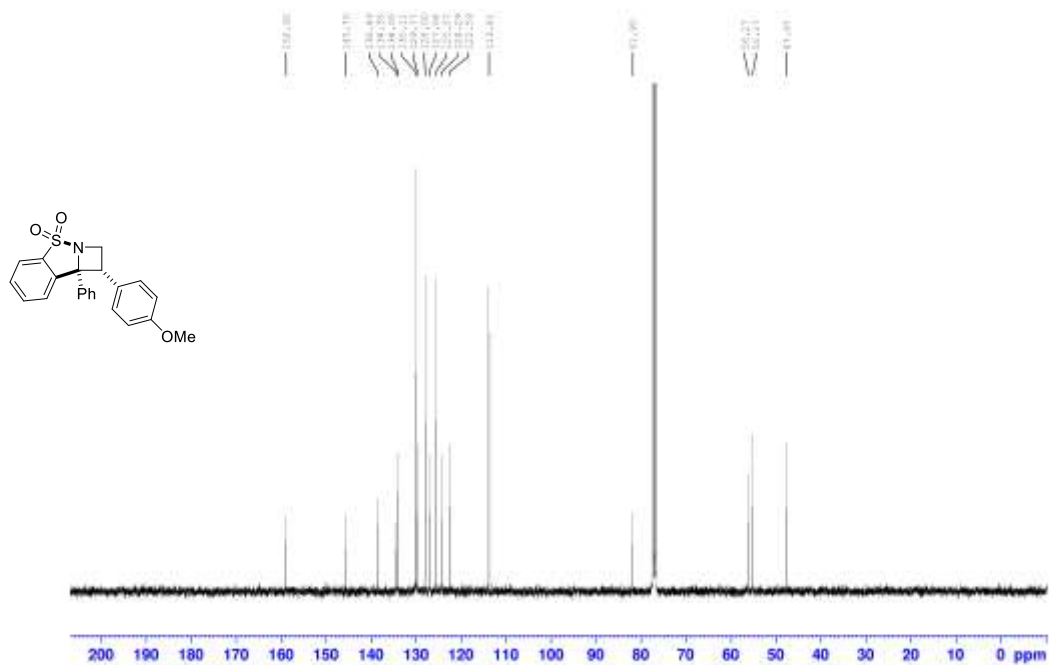
^{13}C NMR (100 MHz, CDCl_3) spectra of **3ag**



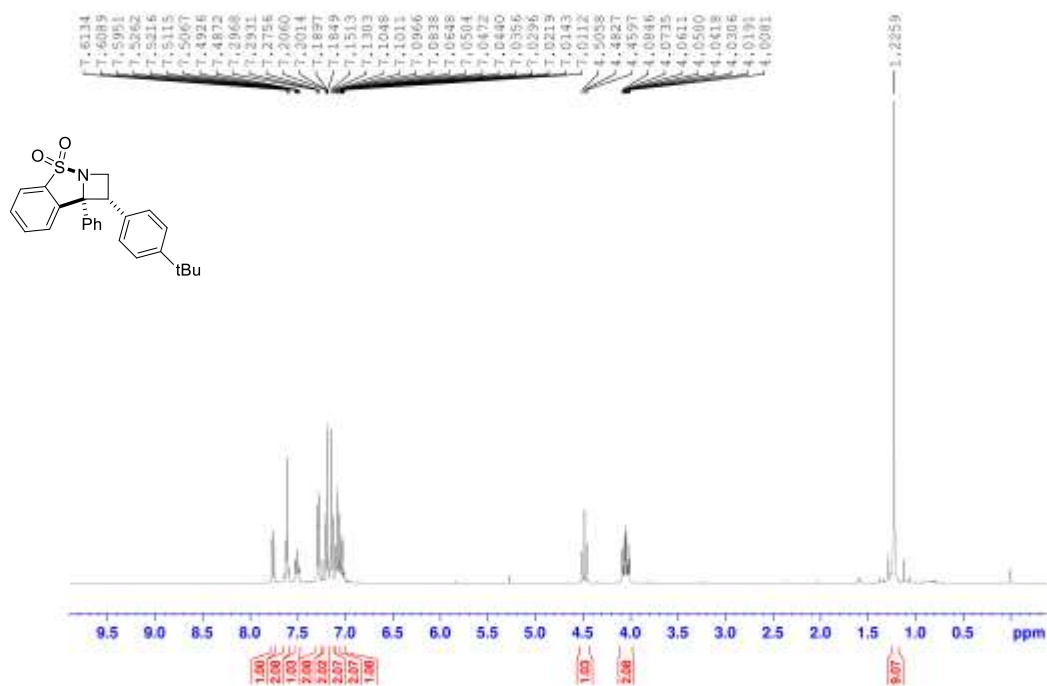
^1H NMR (400 MHz, CDCl_3) spectra of **3ah**



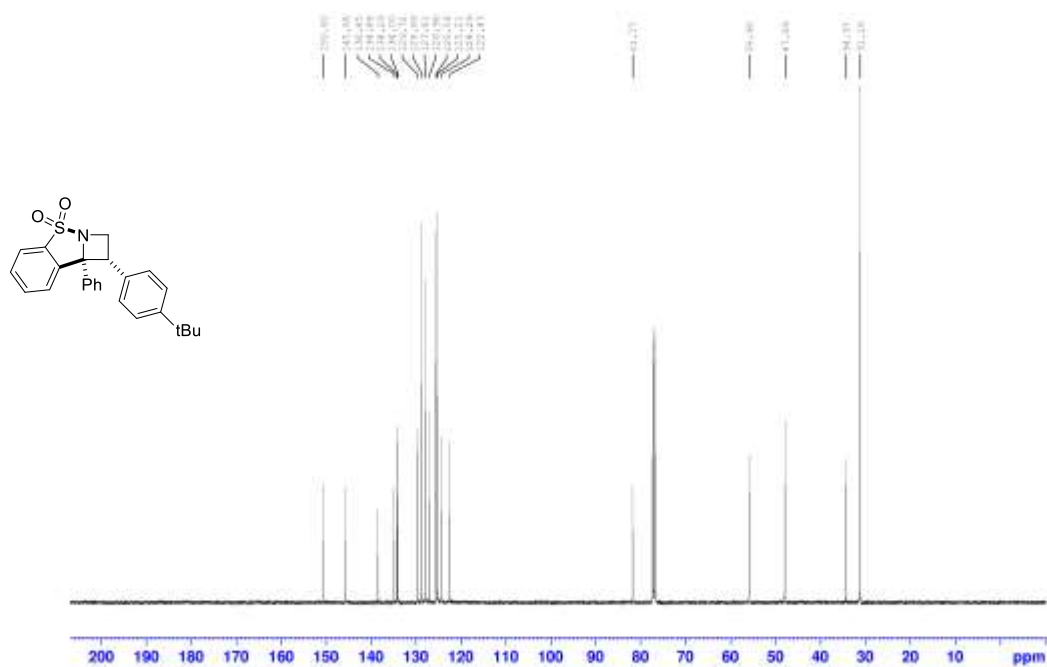
^{13}C NMR (100 MHz, CDCl_3) spectra of **3ah**



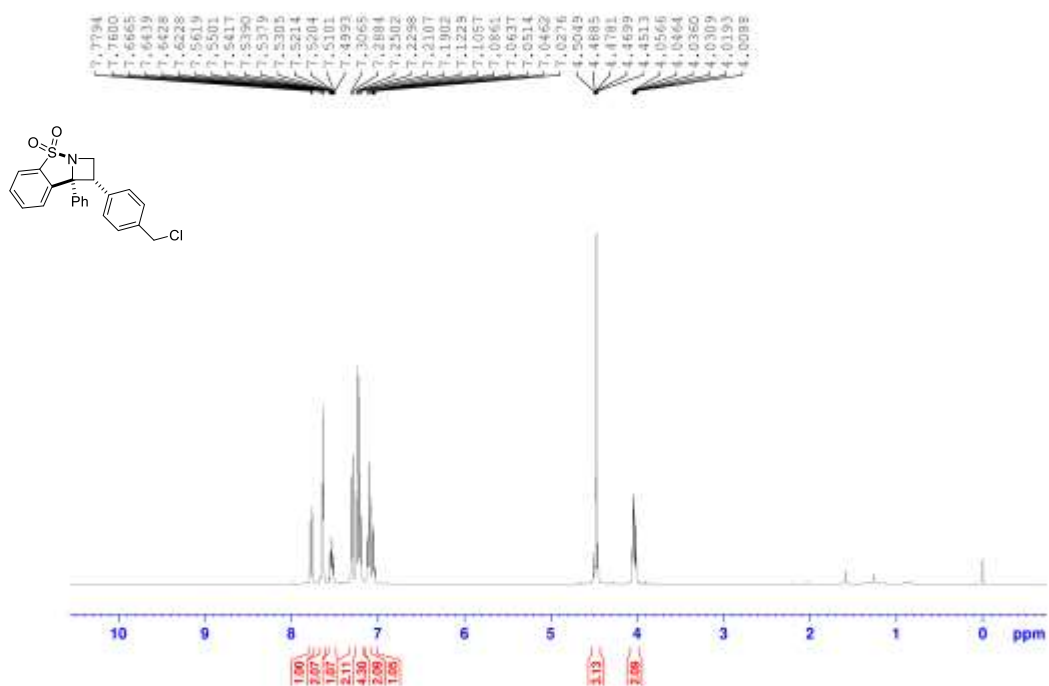
¹H NMR (400 MHz, CDCl₃) spectra of **3ai**



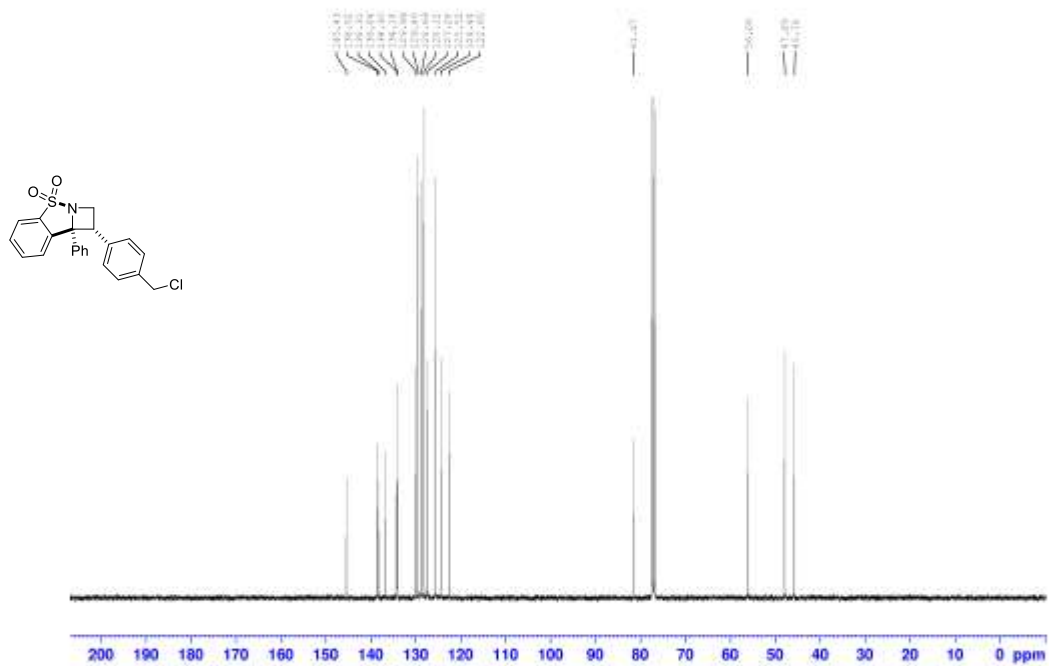
¹³C NMR (100 MHz, CDCl₃) spectra of **3ai**



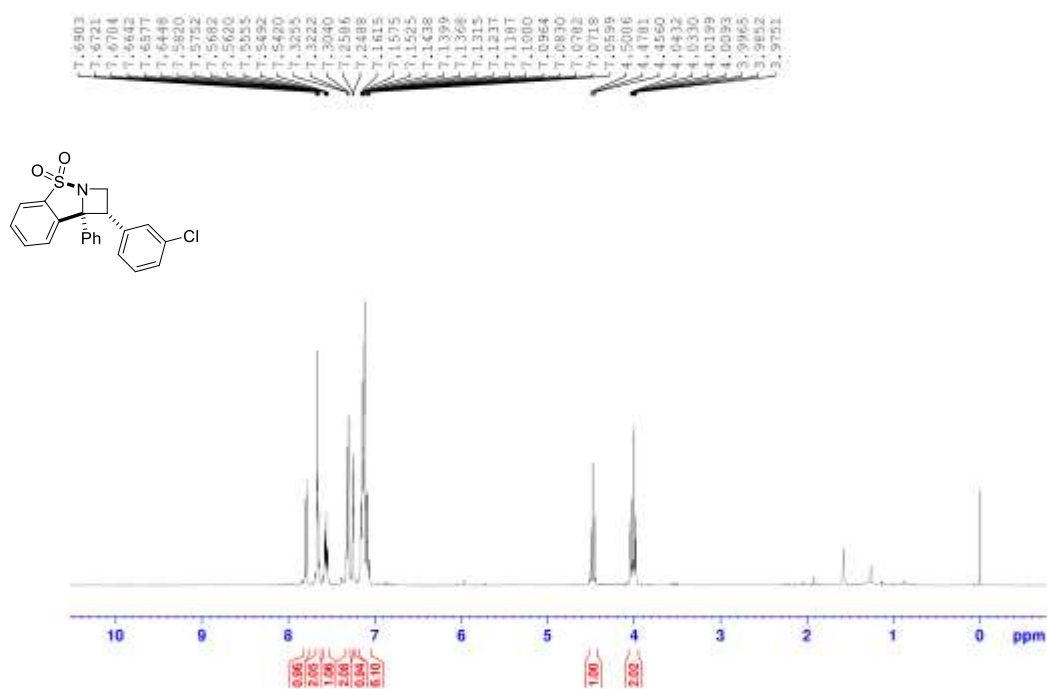
¹H NMR (400 MHz, CDCl₃) spectra of **3ak**



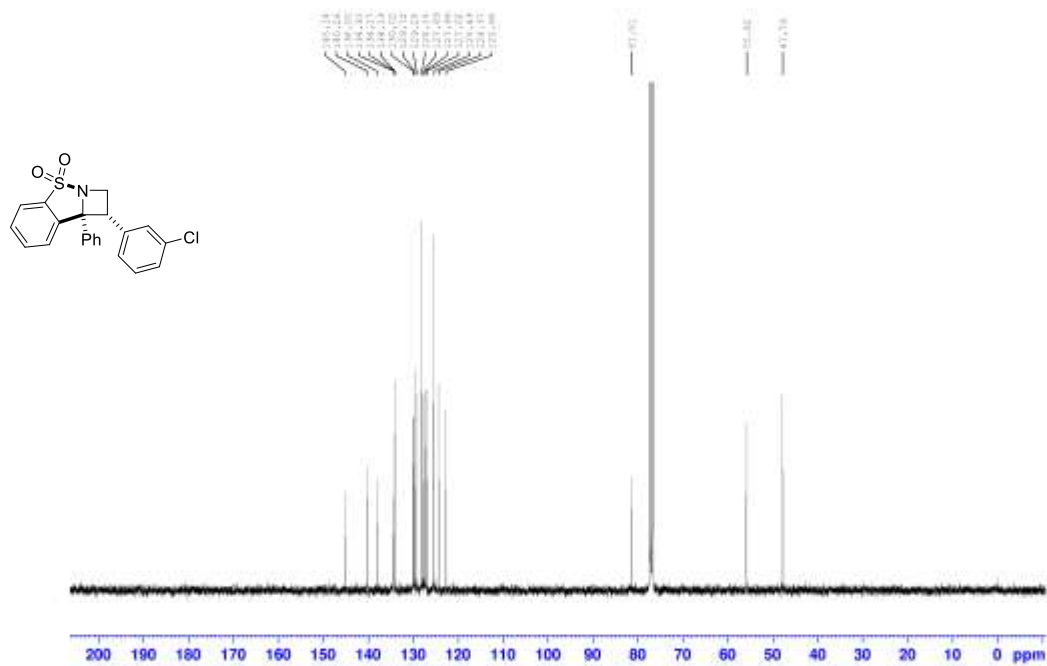
¹³C NMR (100 MHz, CDCl₃) spectra of **3ak**



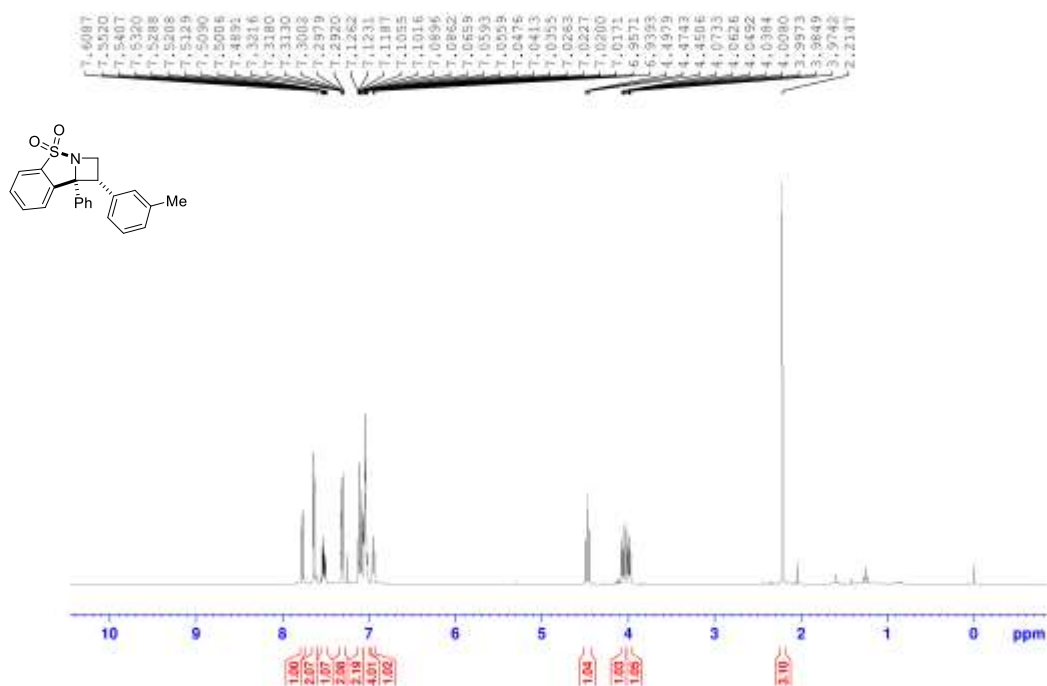
^1H NMR (400 MHz, CDCl_3) spectra of **3an**



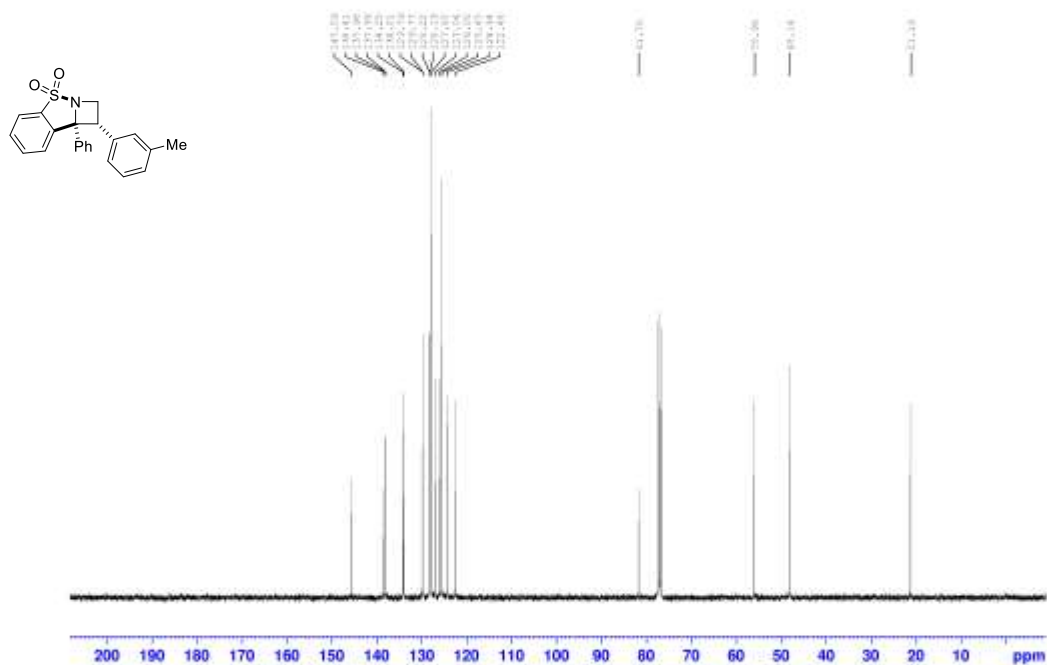
^{13}C NMR (100 MHz, CDCl_3) spectra of **3an**



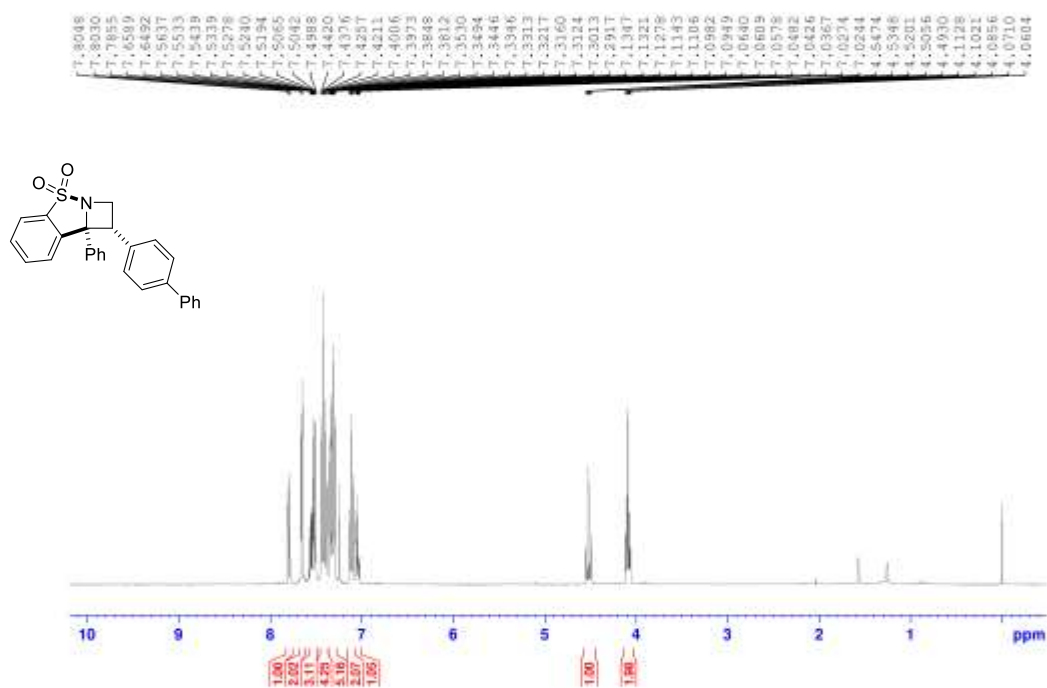
^1H NMR (400 MHz, CDCl_3) spectra of **3ao**



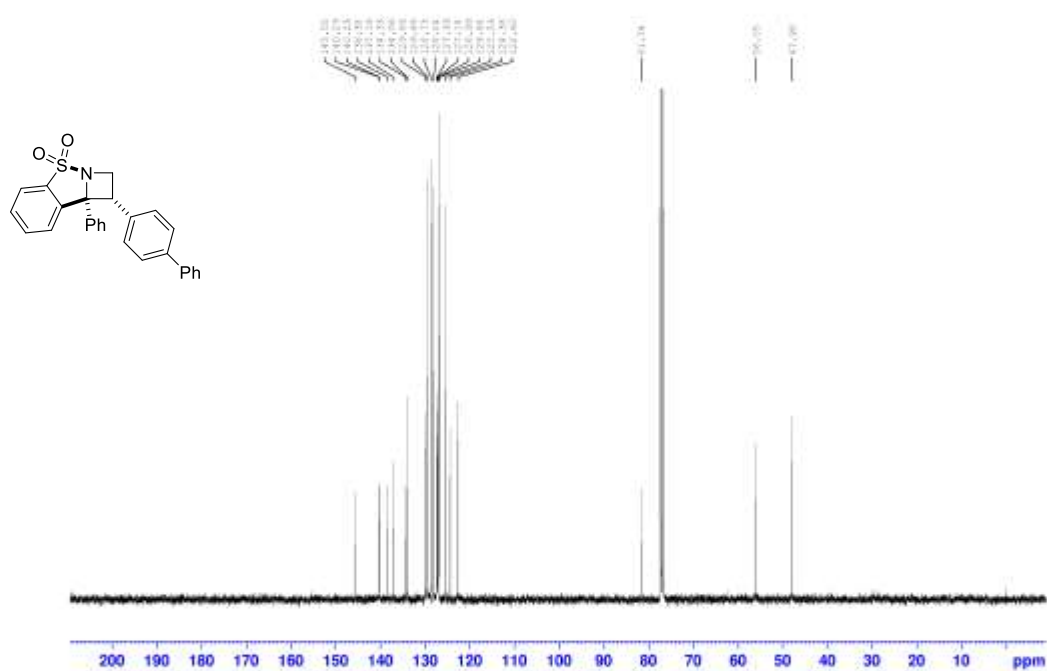
^{13}C NMR (100 MHz, CDCl_3) spectra of **3ao**



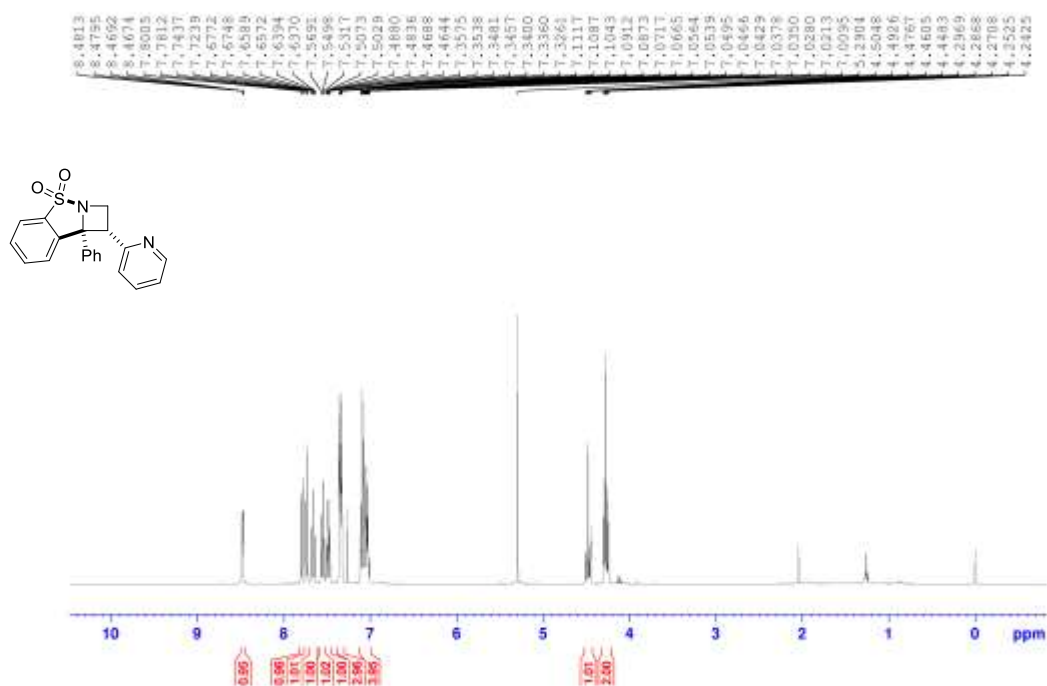
^1H NMR (400 MHz, CDCl_3) spectra of **3ap**



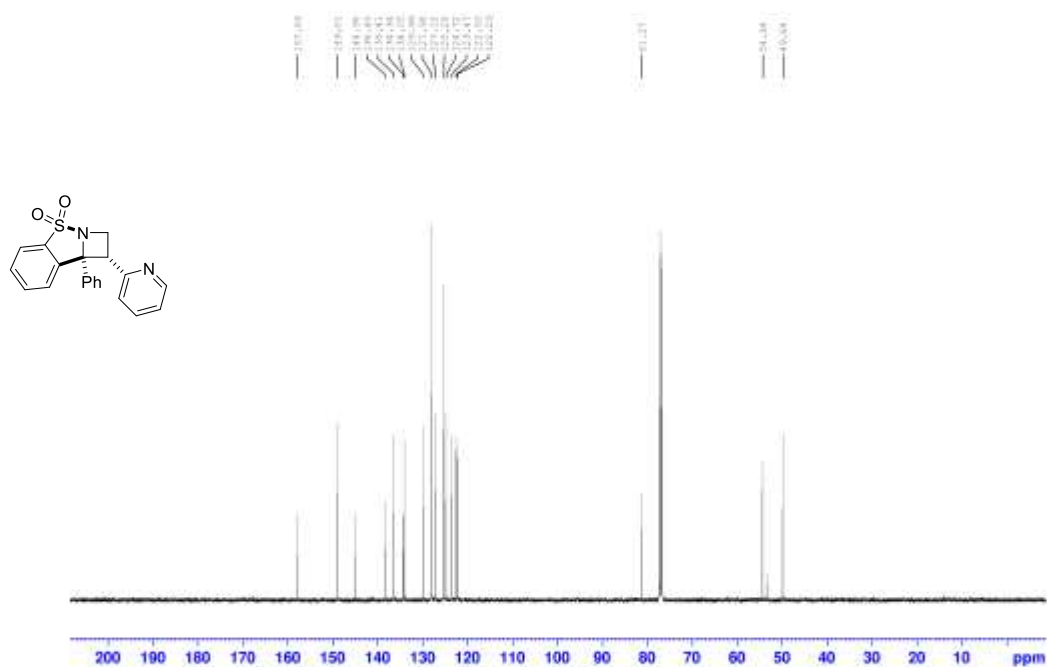
^{13}C NMR (100 MHz, CDCl_3) spectra of **3ap**



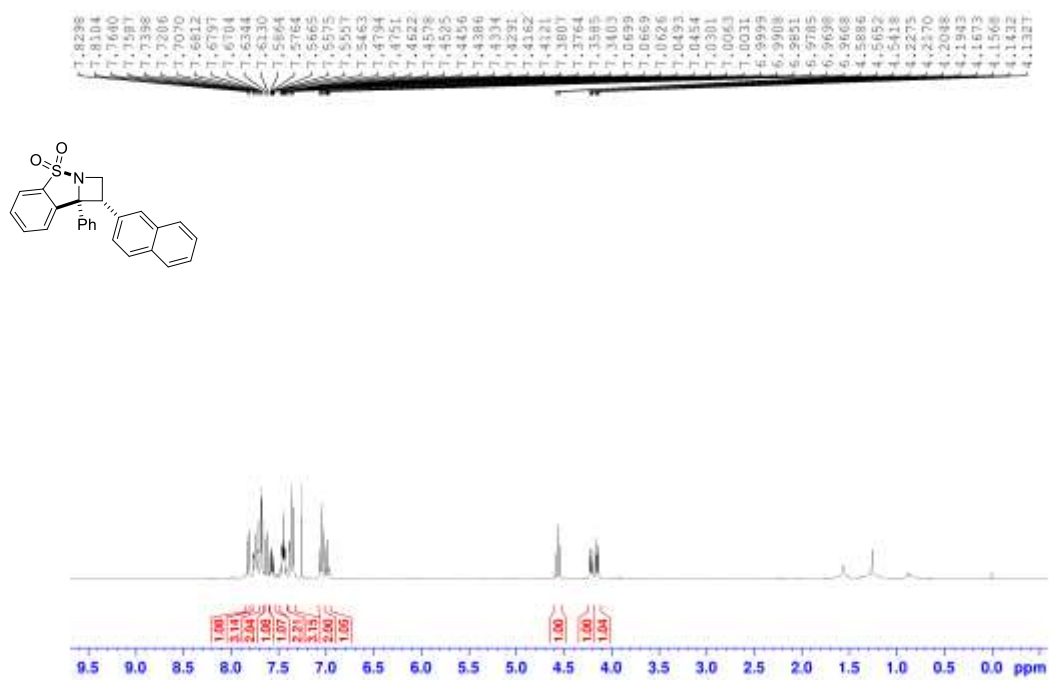
^1H NMR (400 MHz, CDCl_3) spectra of **3aq**



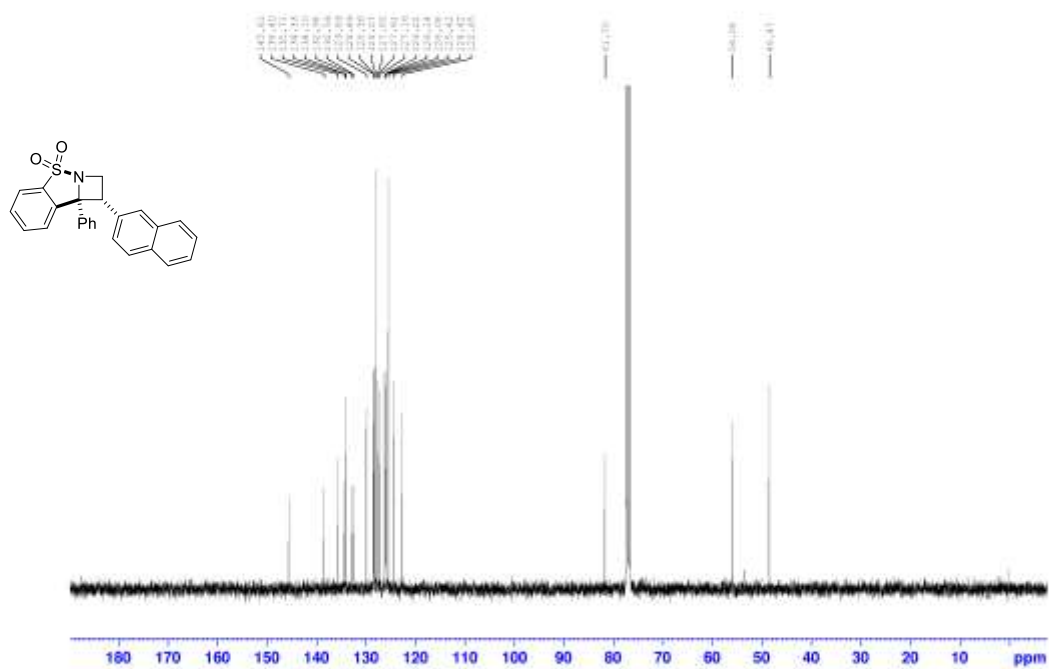
^{13}C NMR (100 MHz, CDCl_3) spectra of **3aq**



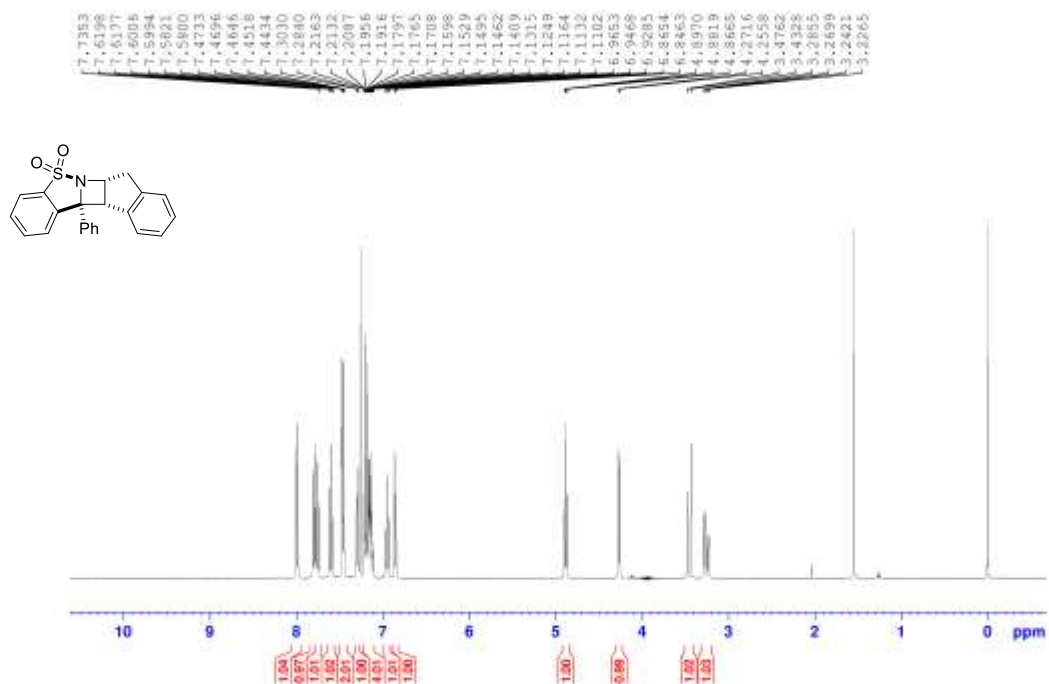
^1H NMR (400 MHz, CDCl_3) spectra of **3ar**



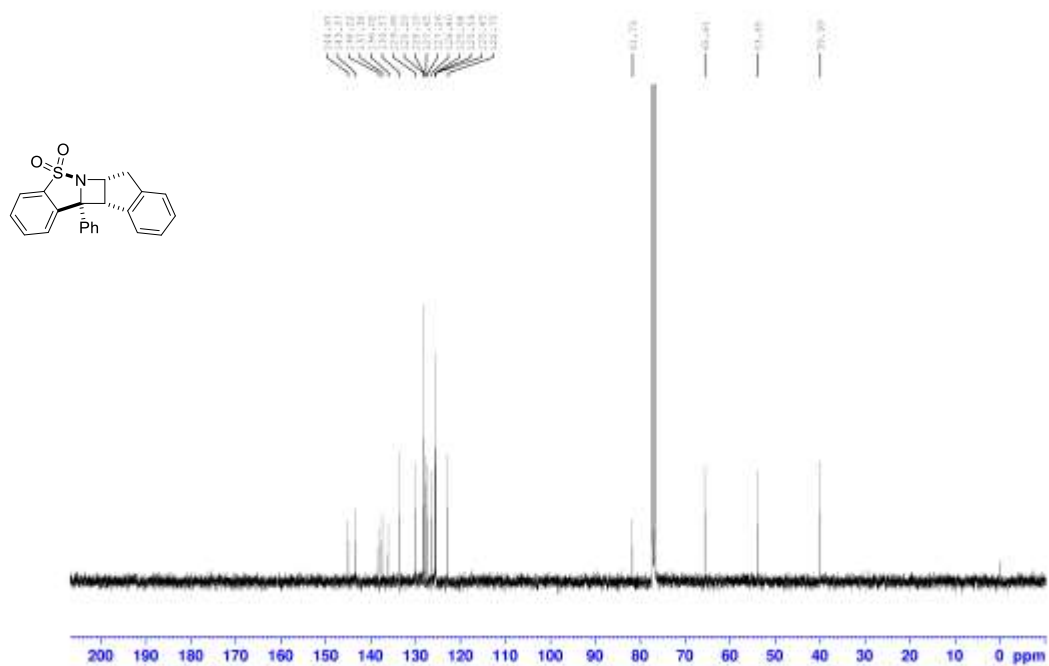
^{13}C NMR (100 MHz, CDCl_3) spectra of **3ar**



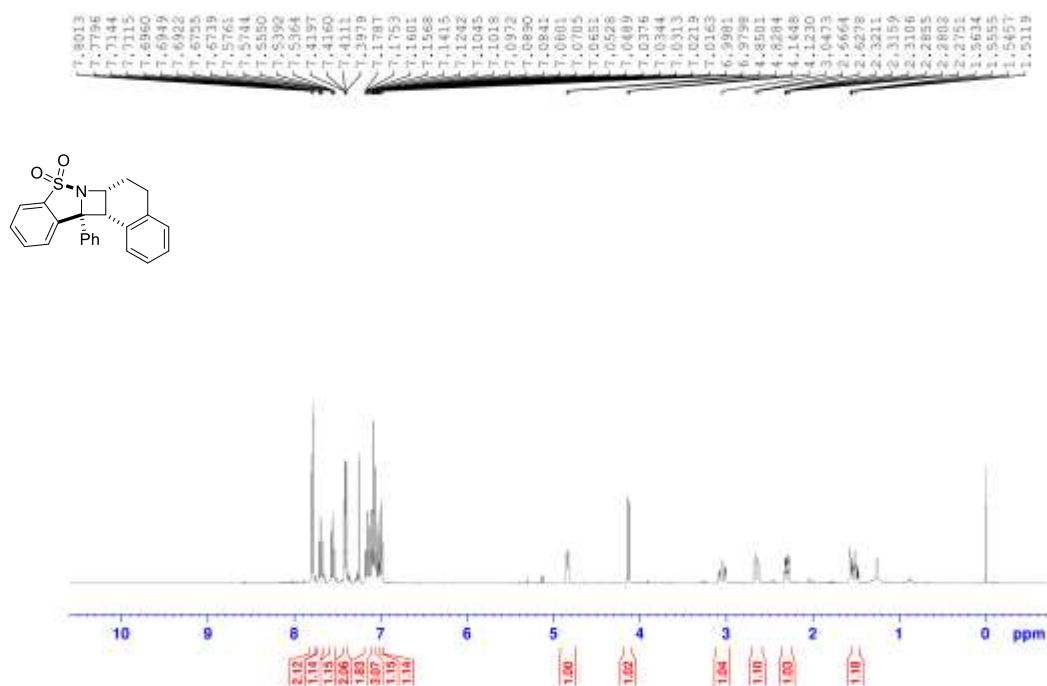
¹H NMR (400 MHz, CDCl₃) spectra of **3at**



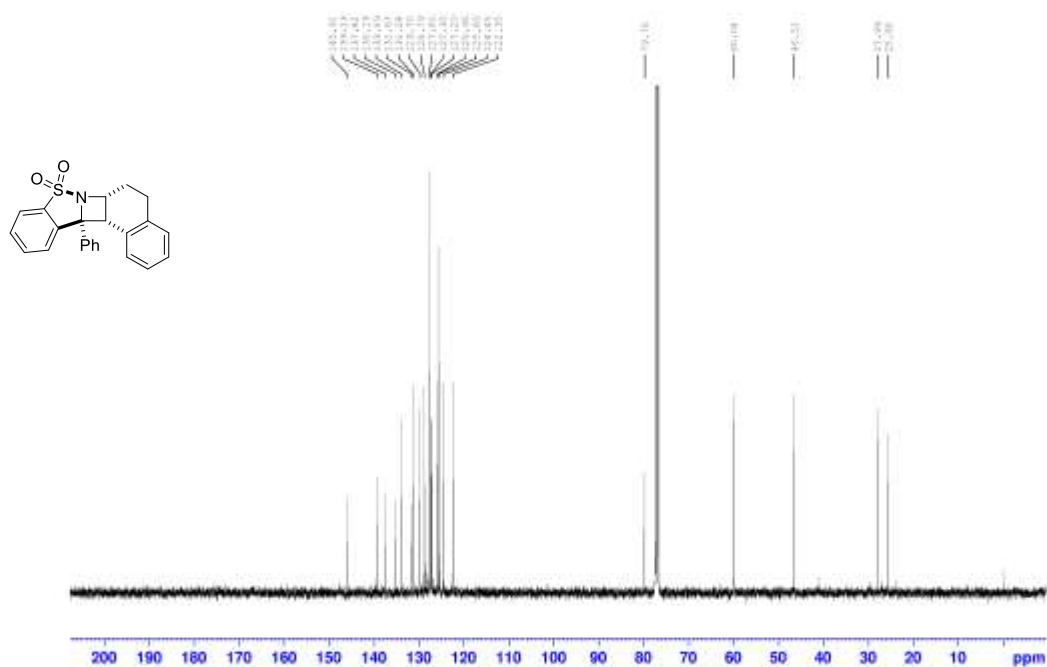
¹³C NMR (100 MHz, CDCl₃) spectra of **3at**



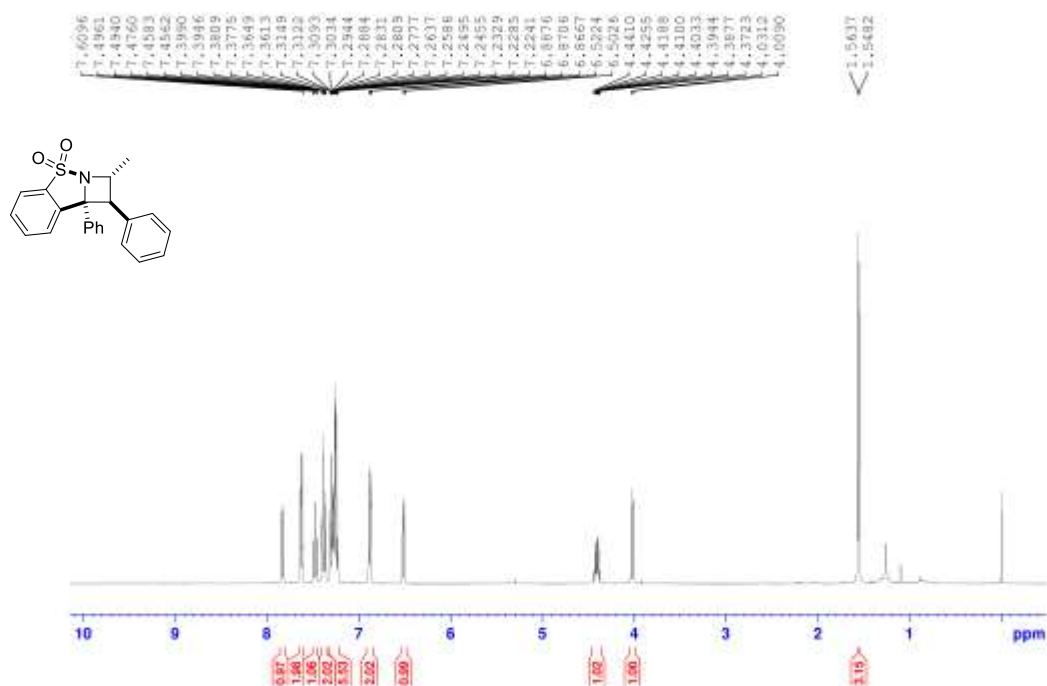
¹H NMR (400 MHz, CDCl₃) spectra of **3au**



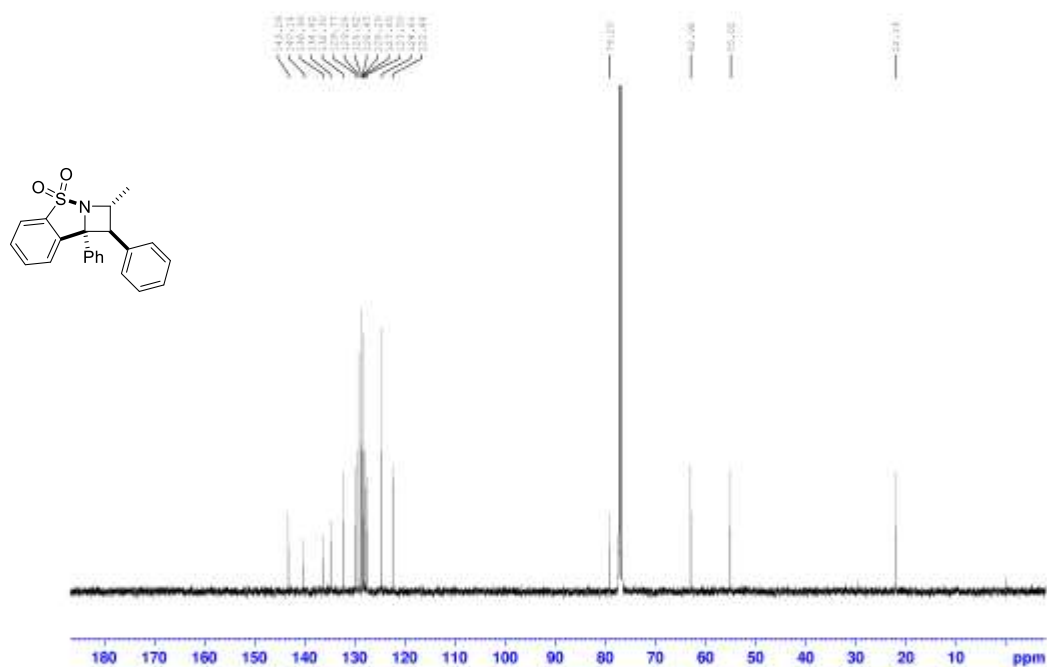
¹³C NMR (100 MHz, CDCl₃) spectra of **3au**



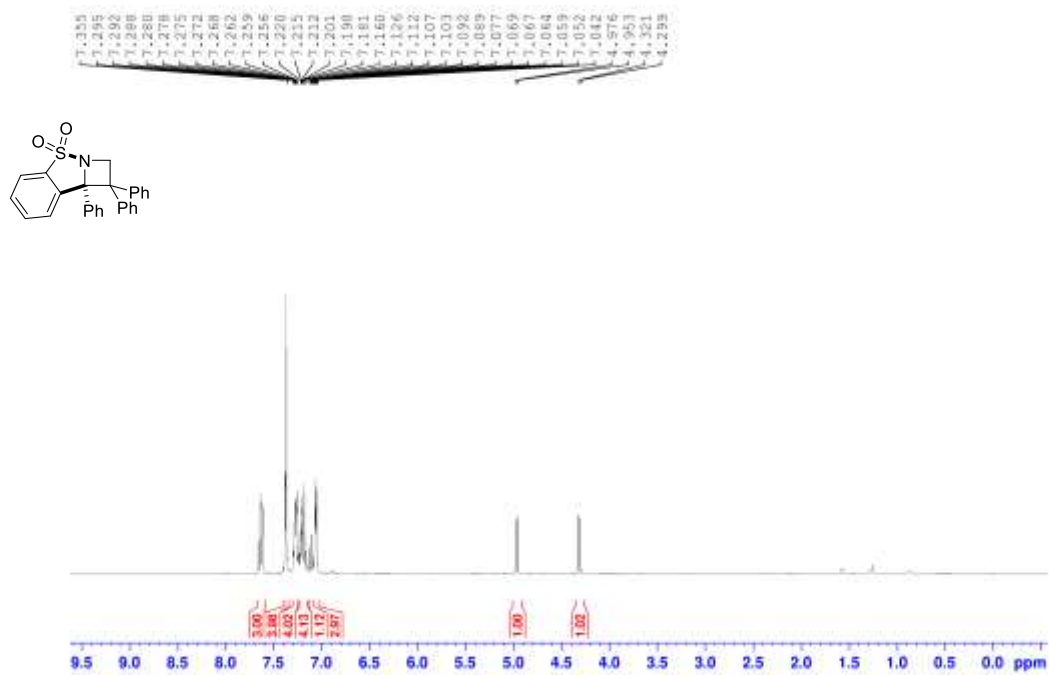
^1H NMR (400 MHz, CDCl_3) spectra of **3av**



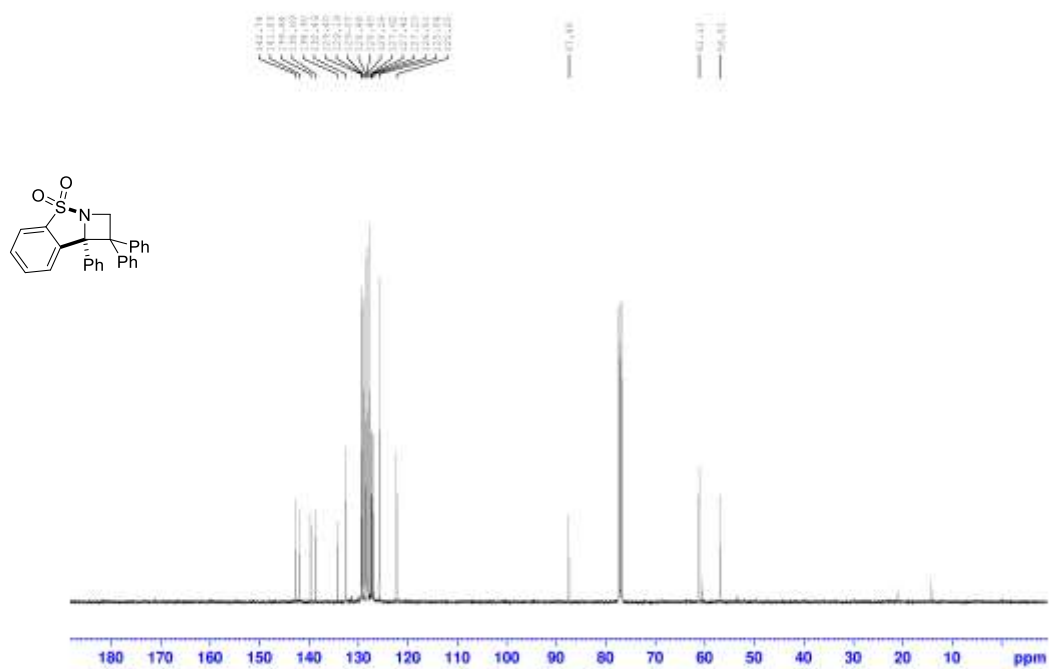
^{13}C NMR (100 MHz, CDCl_3) spectra of **3av**



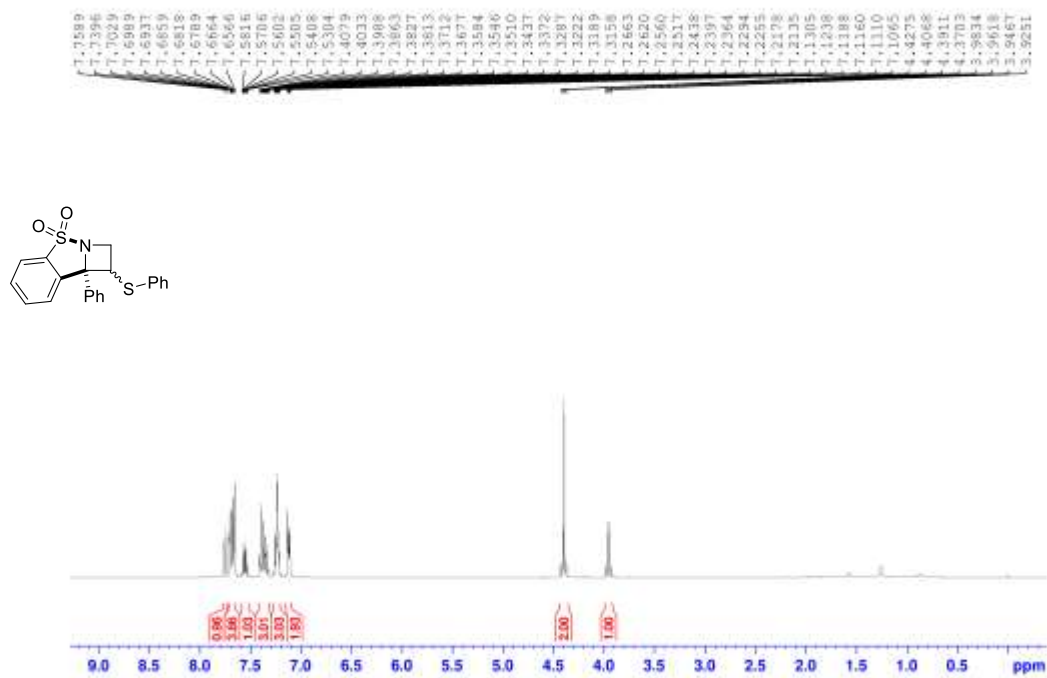
^1H NMR (400 MHz, CDCl_3) spectra of **3aw**



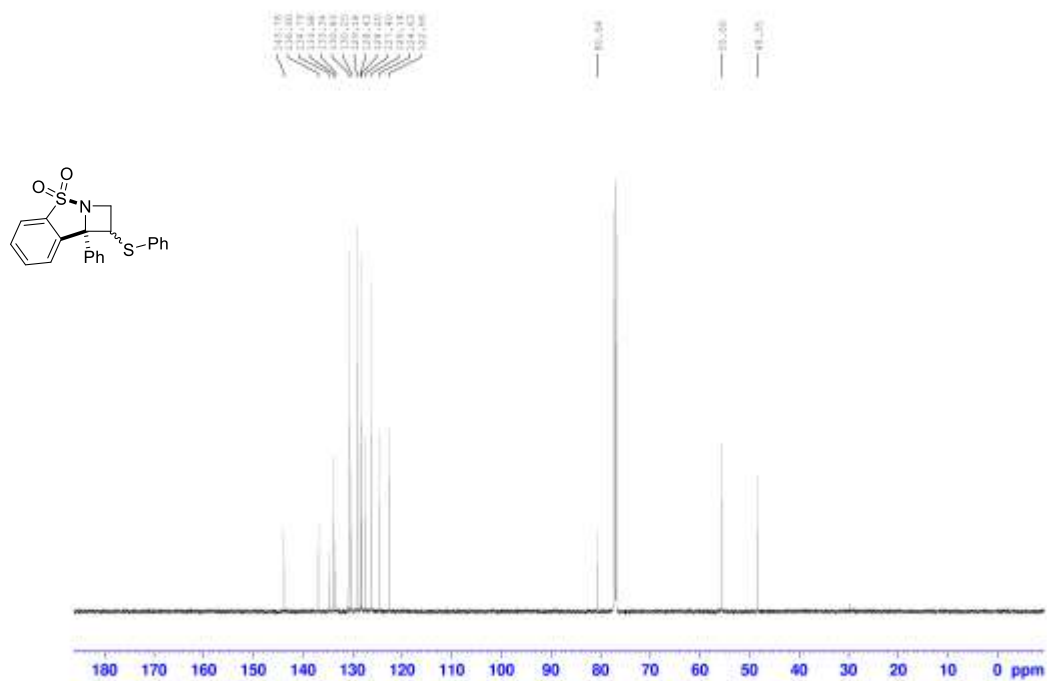
^{13}C NMR (100 MHz, CDCl_3) spectra of **3aw**



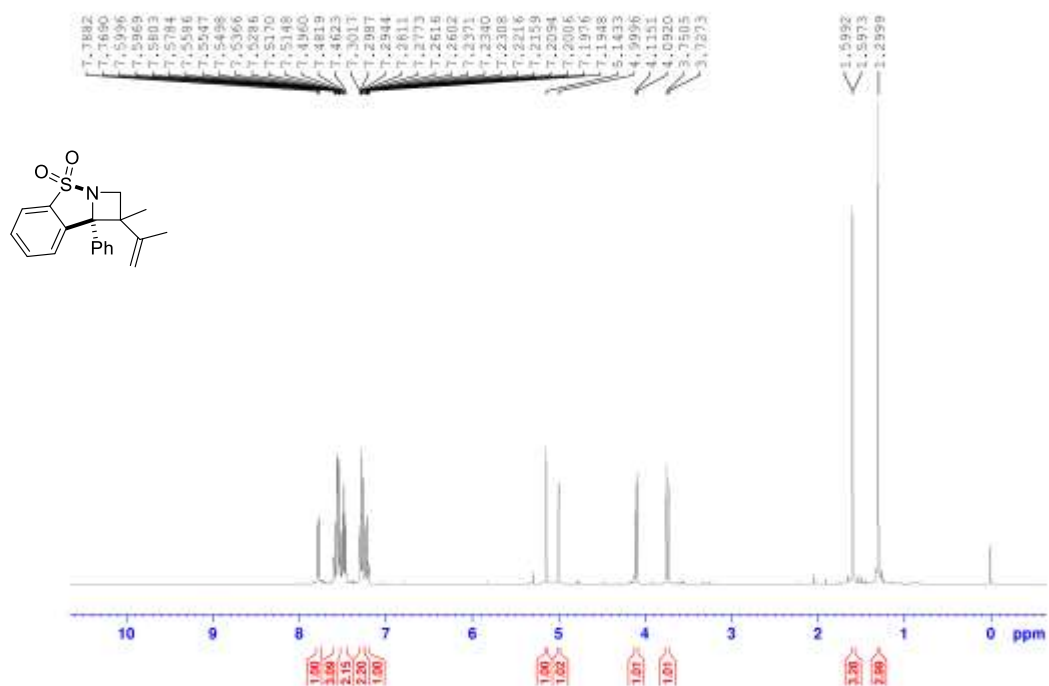
^1H NMR (400 MHz, CDCl_3) spectra of **3ax'**



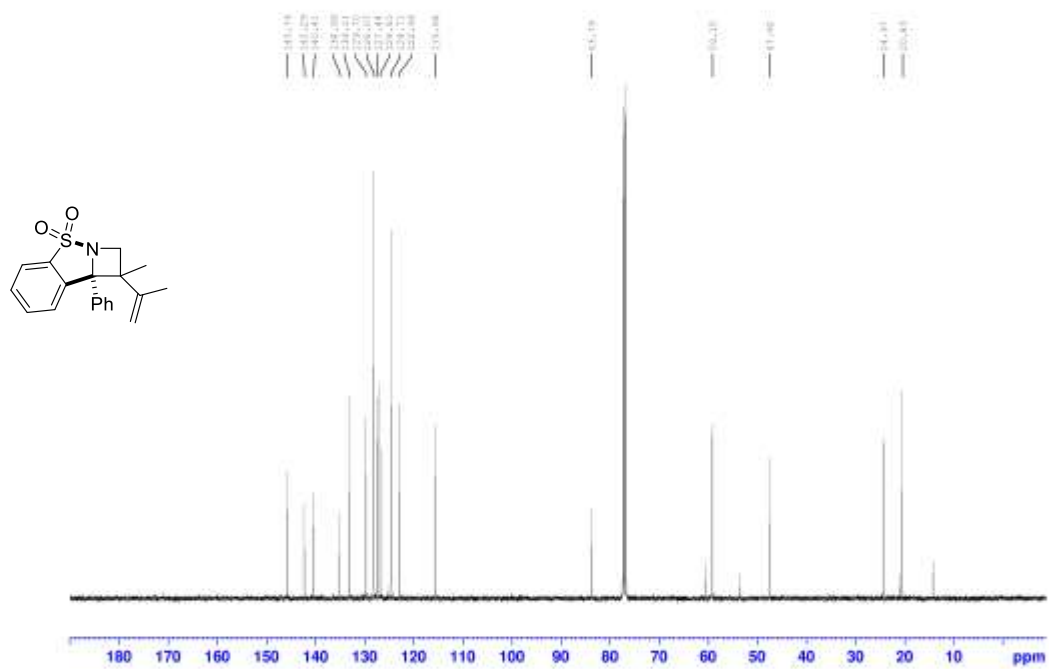
^{13}C NMR (100 MHz, CDCl_3) spectra of **3ax'**



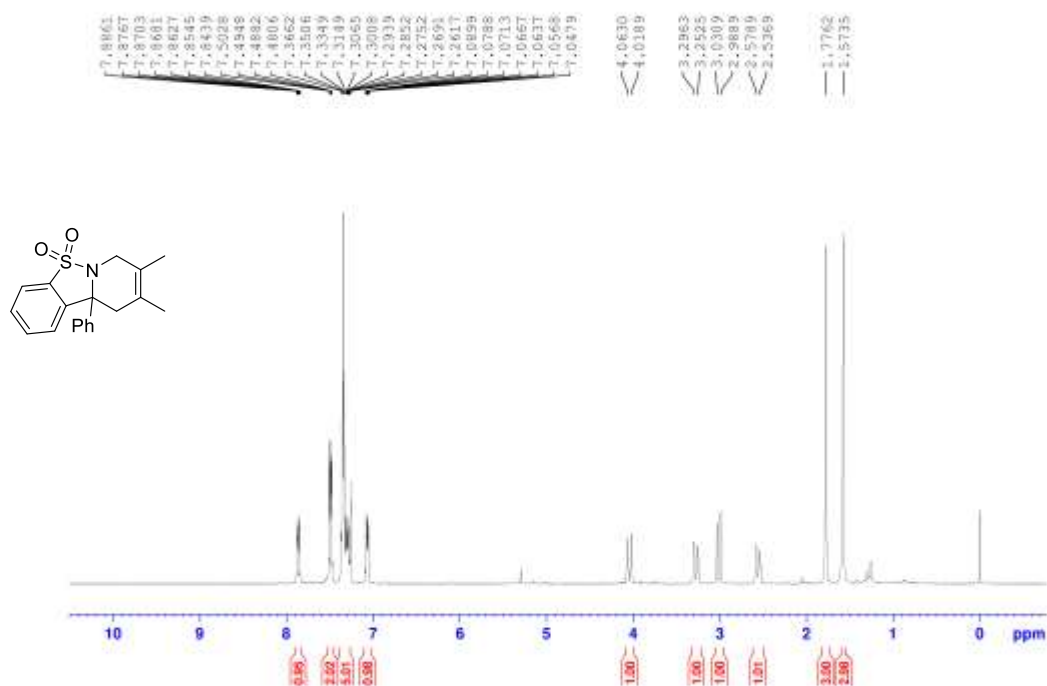
^1H NMR (400 MHz, CDCl_3) spectra of **3az**



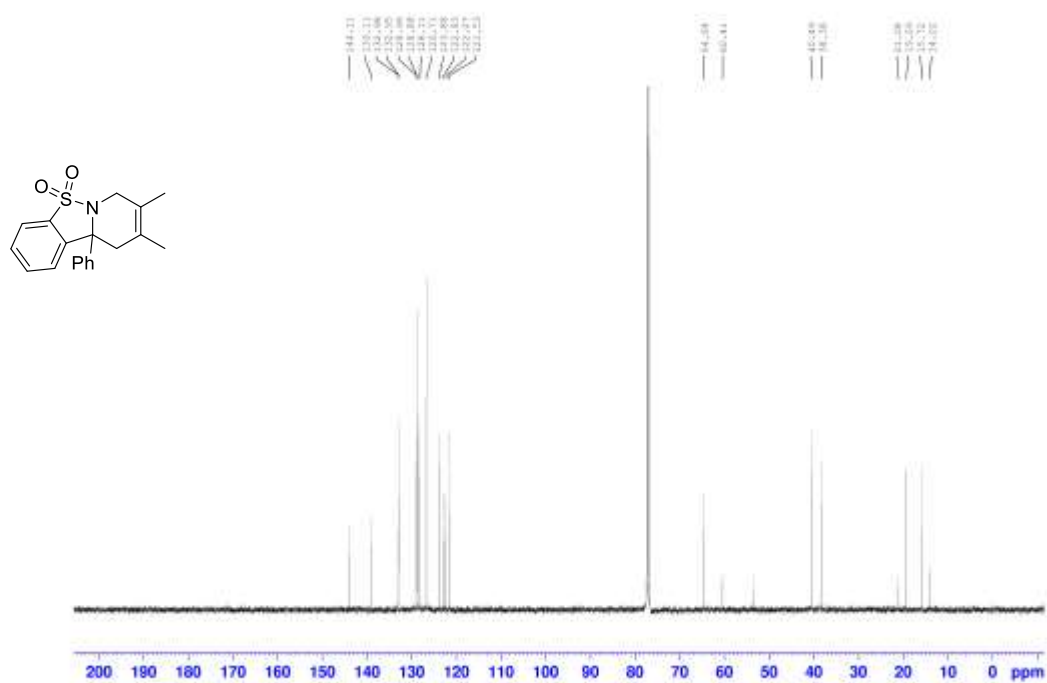
^{13}C NMR (100 MHz, CDCl_3) spectra of **3az**



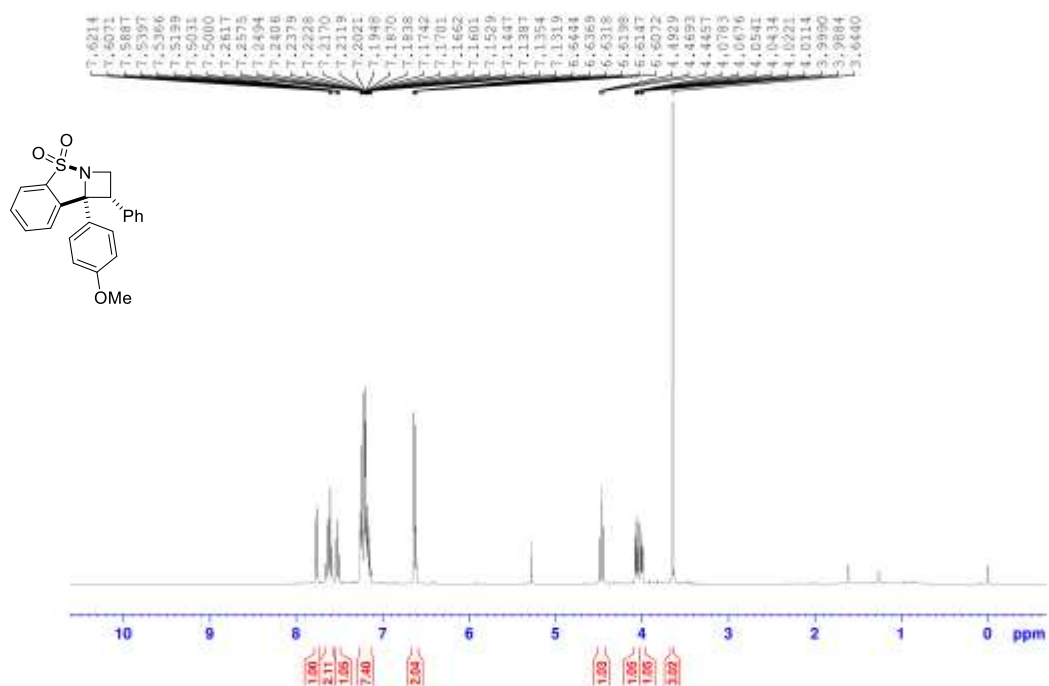
^1H NMR (400 MHz, CDCl_3) spectra of **3az'**



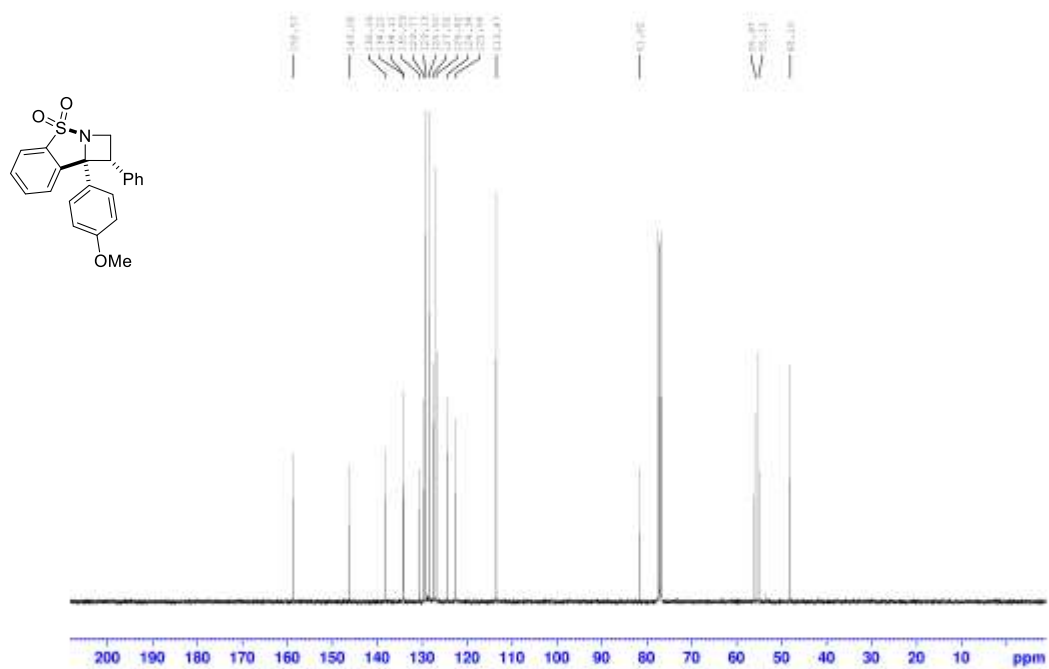
^{13}C NMR (100 MHz, CDCl_3) spectra of **3az'**



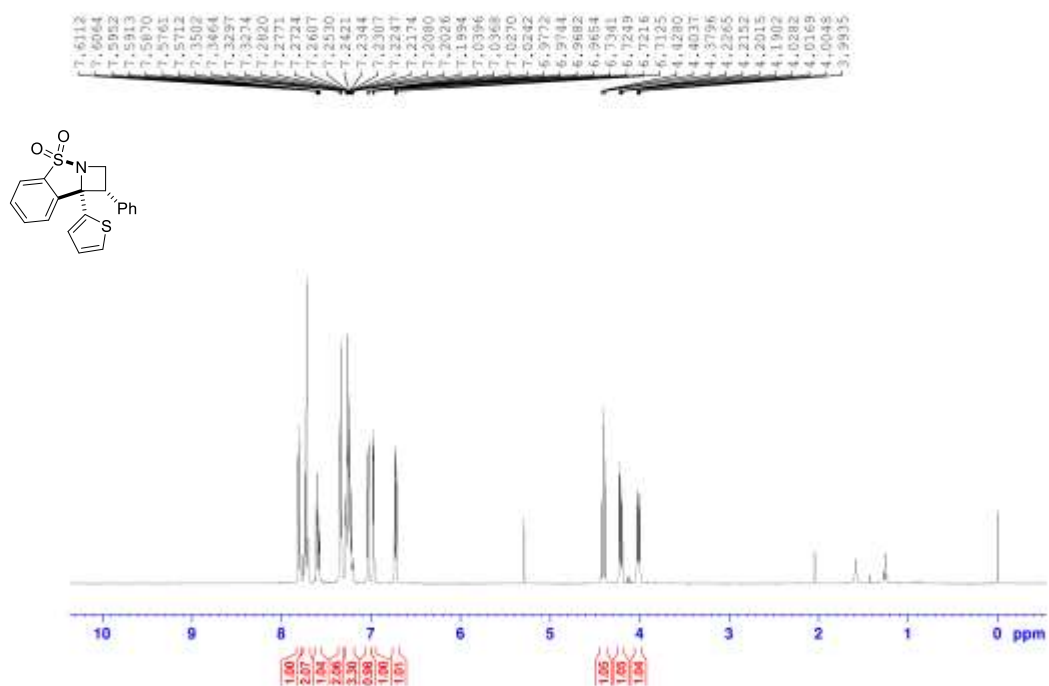
¹H NMR (400 MHz, CDCl₃) spectra of **3ba**



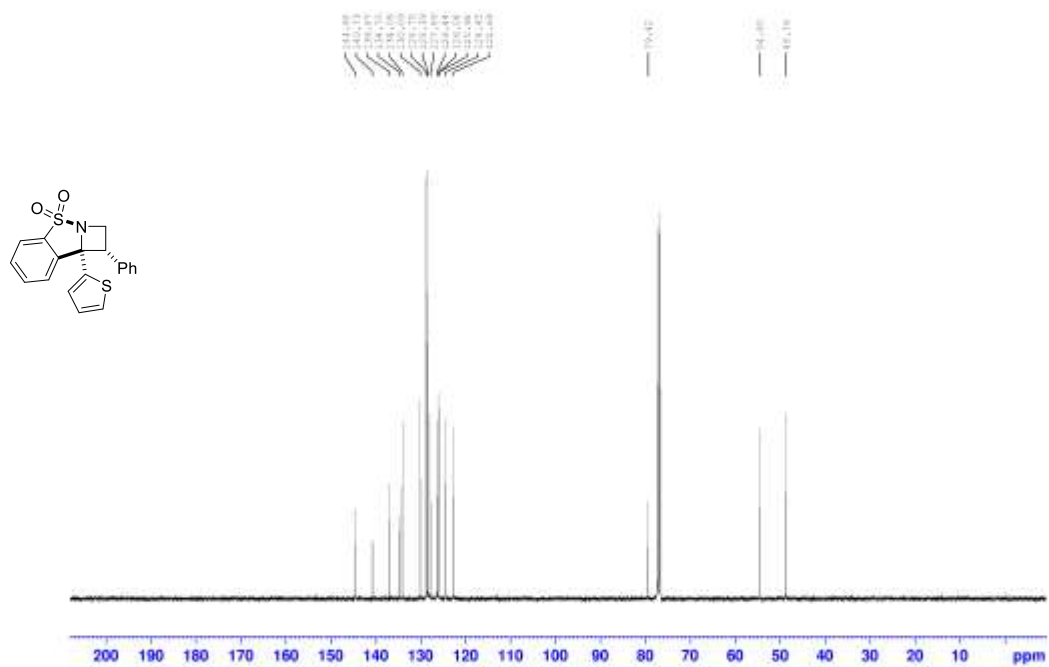
¹³C NMR (100 MHz, CDCl₃) spectra of **3ba**



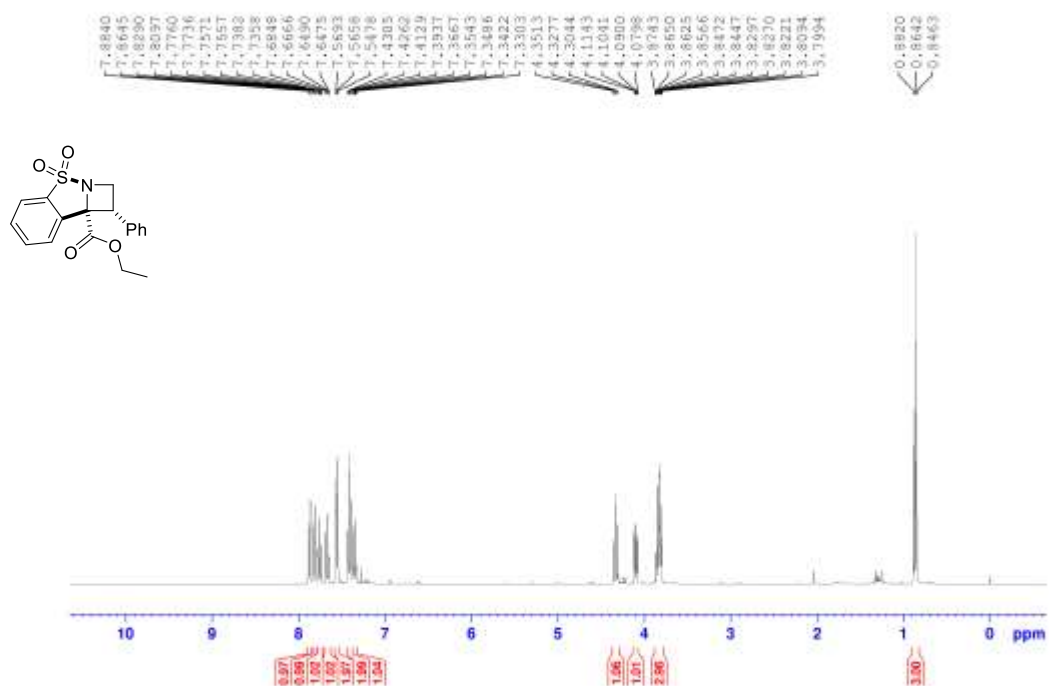
^1H NMR (400 MHz, CDCl_3) spectra of **3ca**



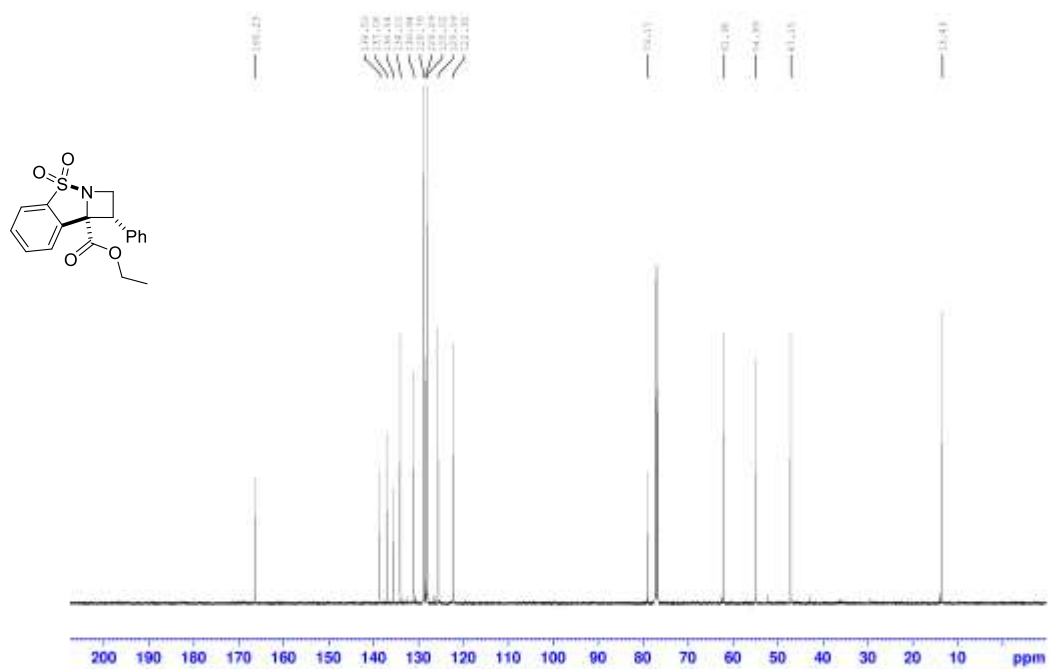
^{13}C NMR (100 MHz, CDCl_3) spectra of **3ca**



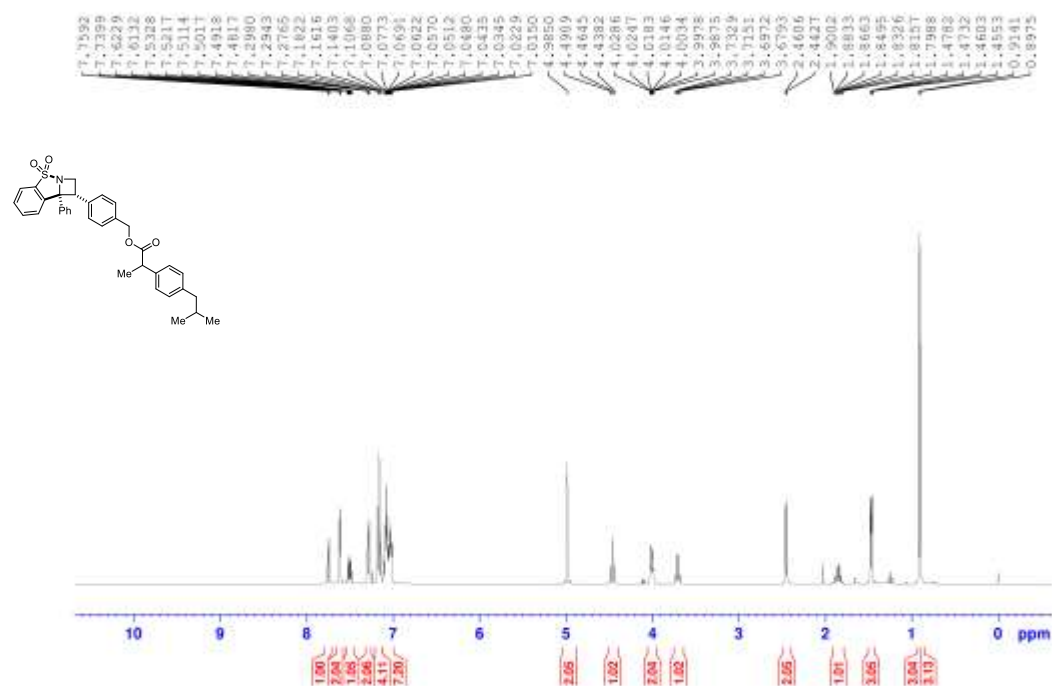
^1H NMR (400 MHz, CDCl_3) spectra of **3da**



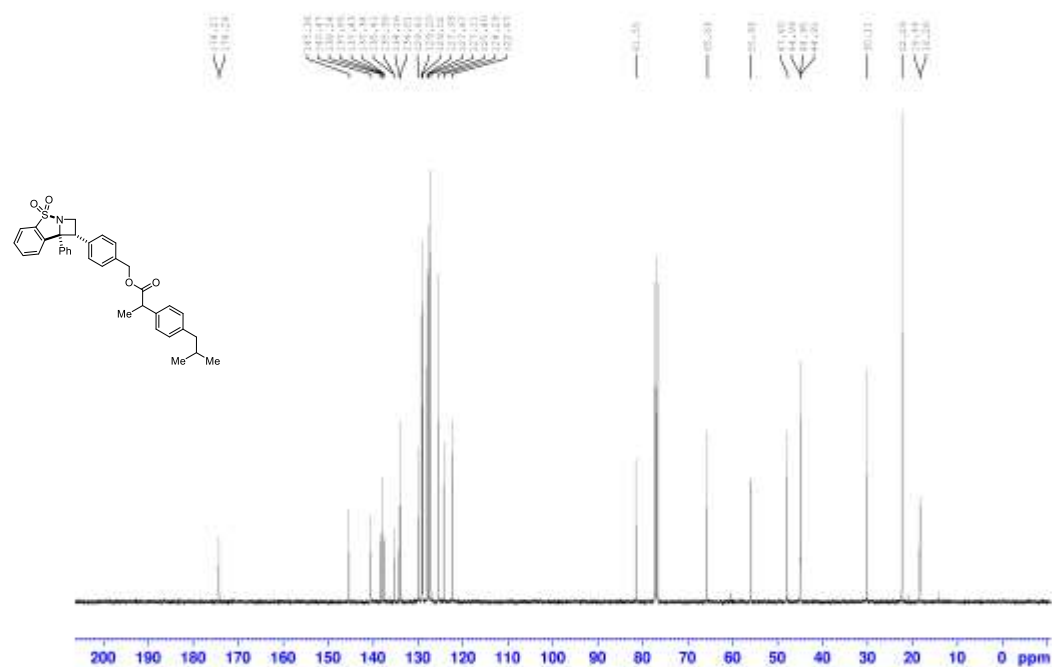
^{13}C NMR (100 MHz, CDCl_3) spectra of **3da**



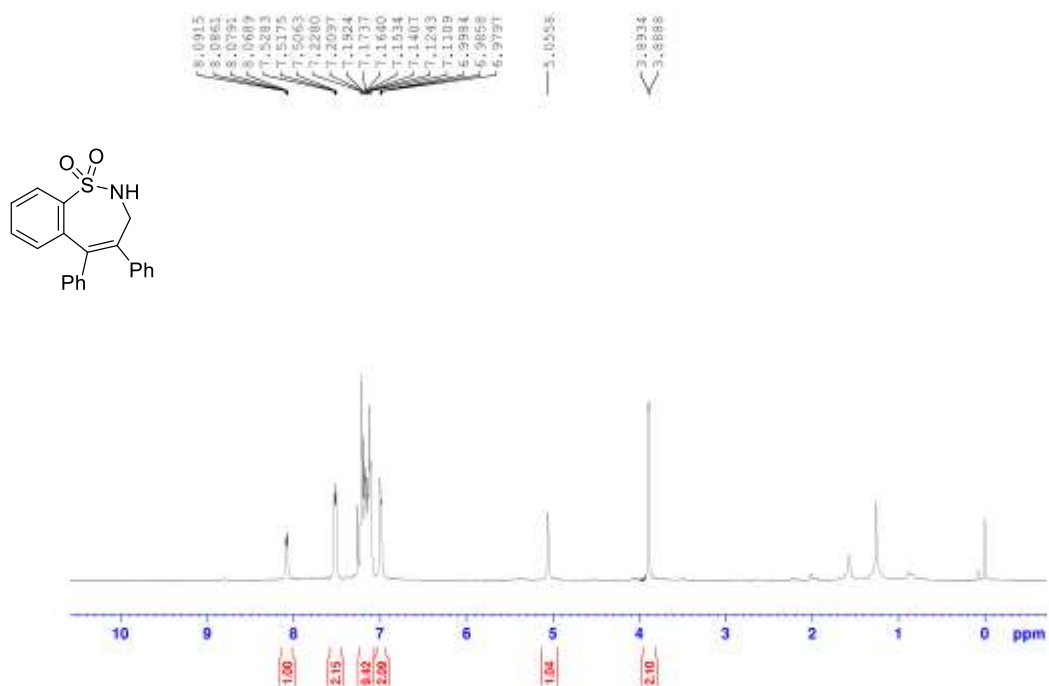
¹H NMR (400 MHz, CDCl₃) spectra of **4**



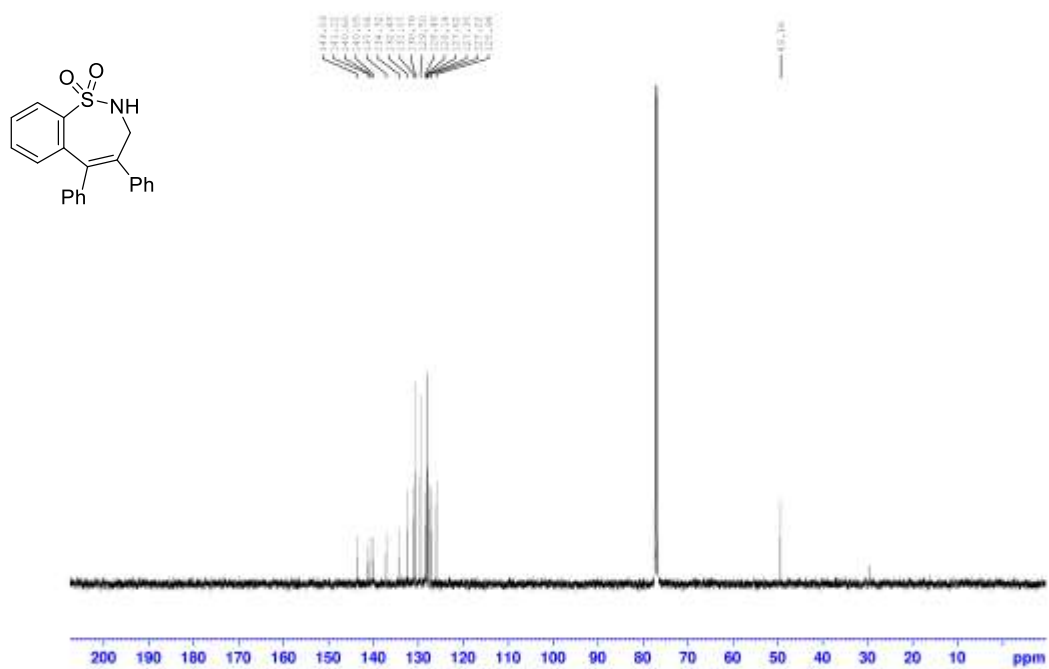
¹³C NMR (100 MHz, CDCl₃) spectra of **4**



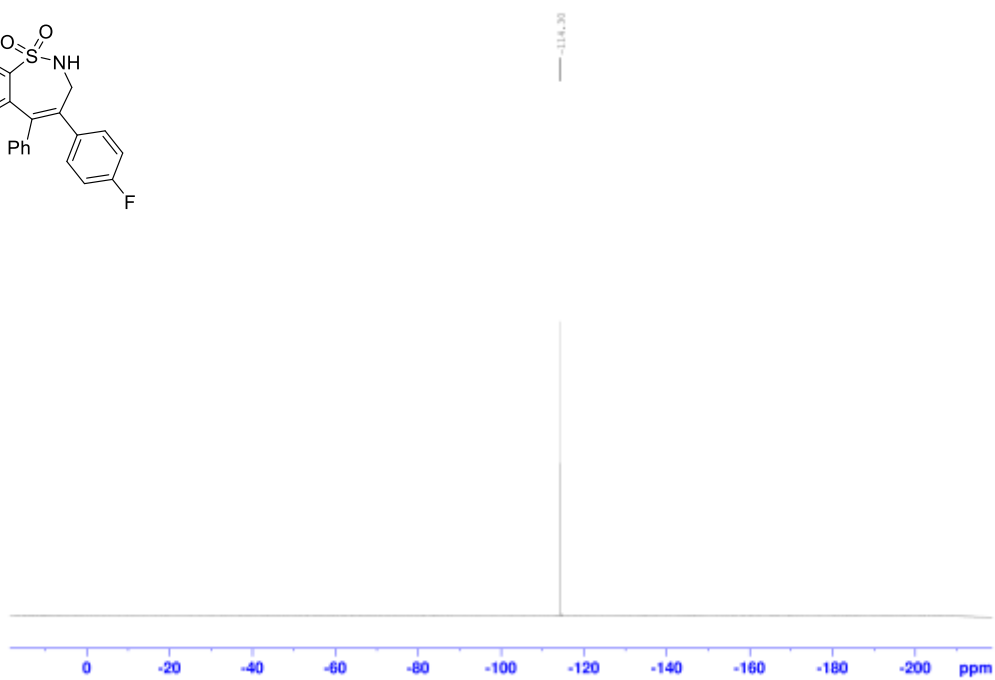
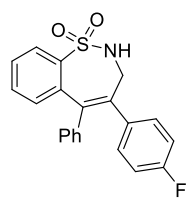
^1H NMR (400 MHz, CDCl_3) spectra of **5a**



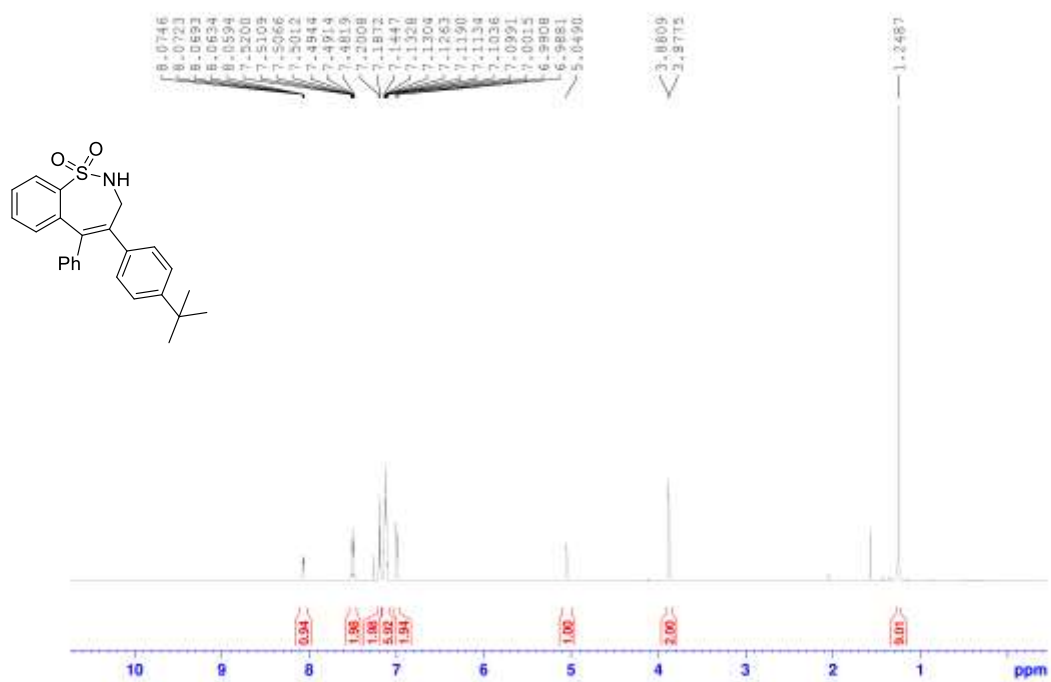
^{13}C NMR (100 MHz, CDCl_3) spectra of **5a**



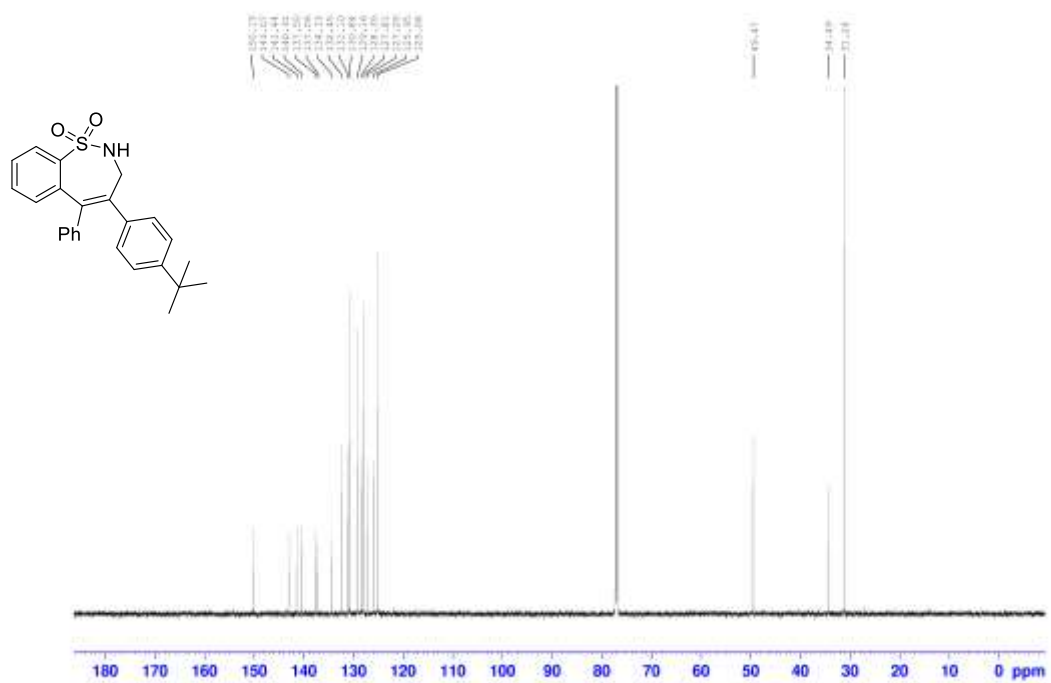
^{19}F NMR (376 MHz, CDCl_3) spectra of **5b**



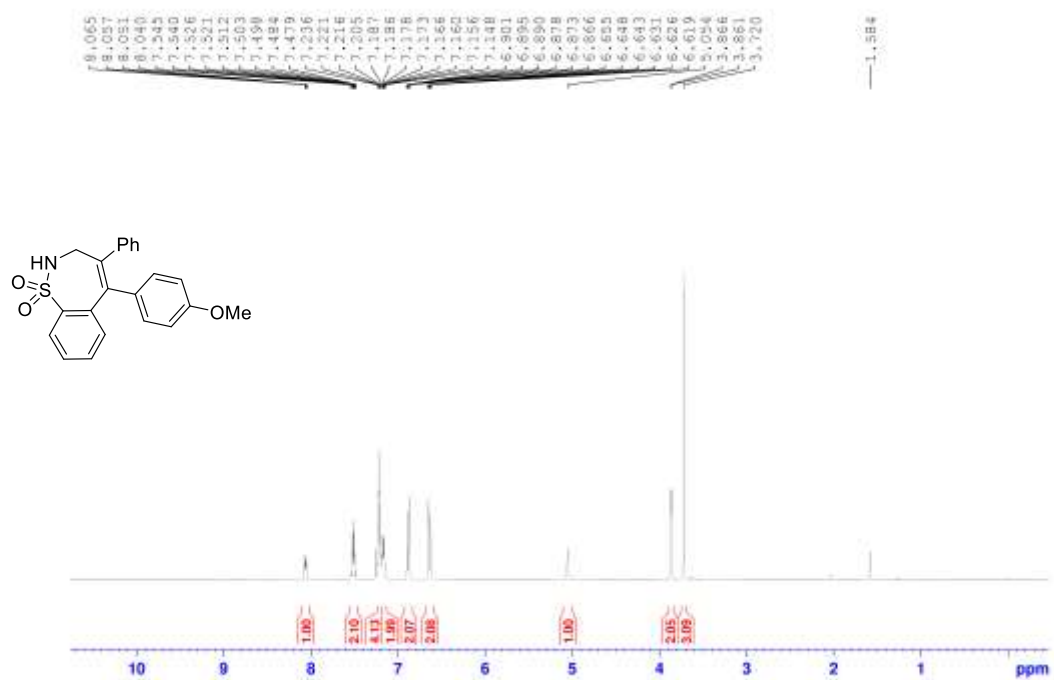
^1H NMR (600 MHz, CDCl_3) spectra of **5e**



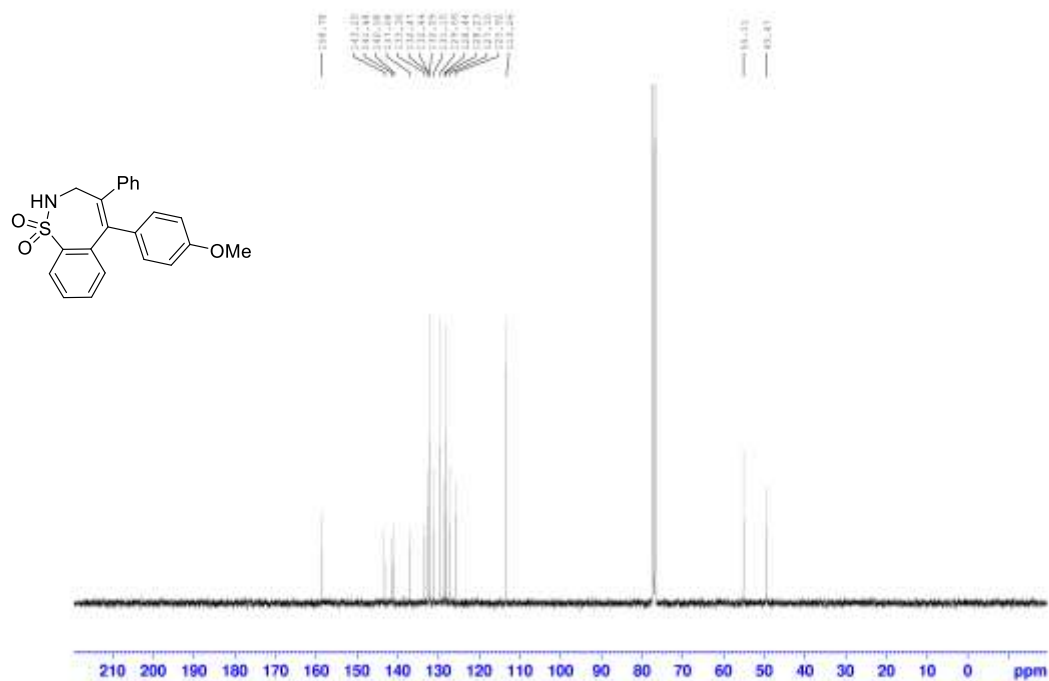
^{13}C NMR (150 MHz, CDCl_3) spectra of **5e**



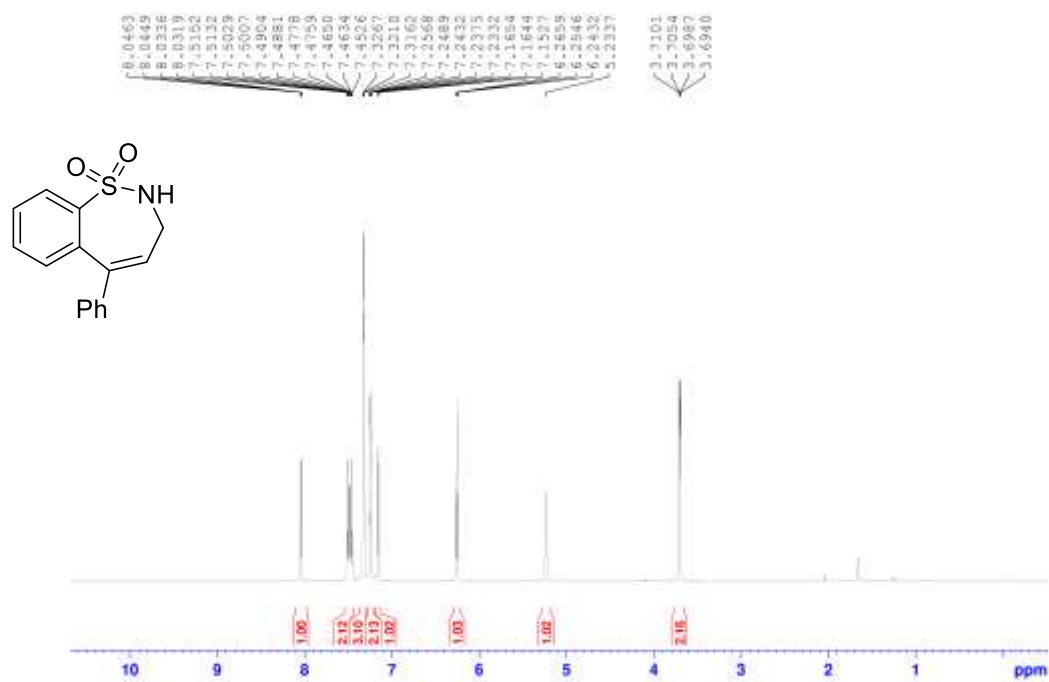
^1H NMR (400 MHz, CDCl_3) spectra of **5i**



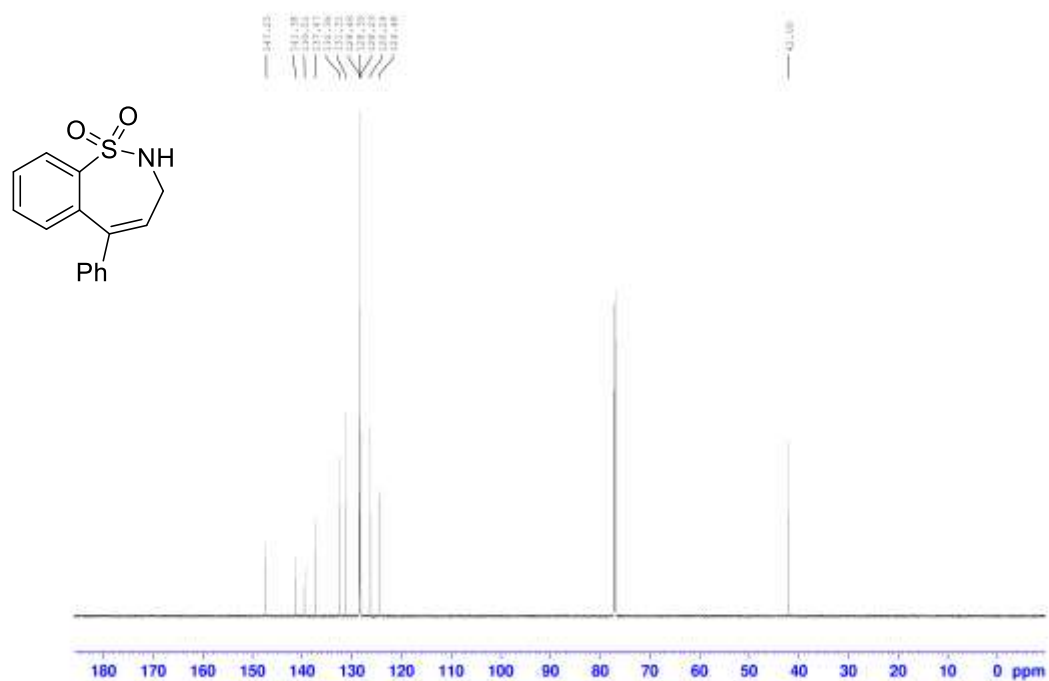
^{13}C NMR (100 MHz, CDCl_3) spectra of **5i**



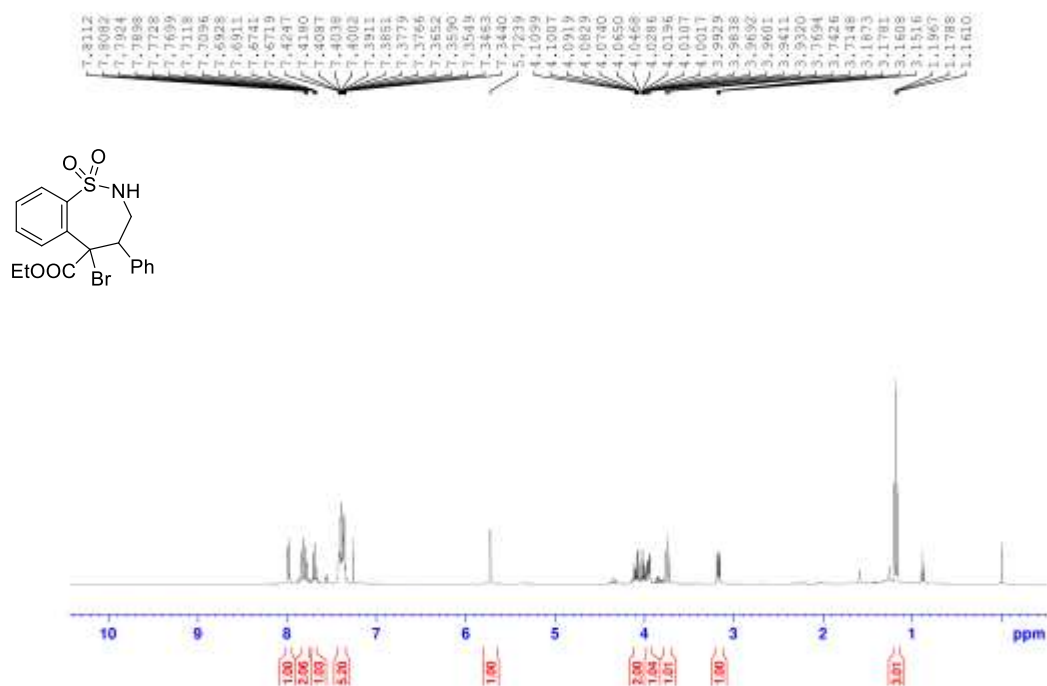
^1H NMR (600 MHz, CDCl_3) spectra of **5j**



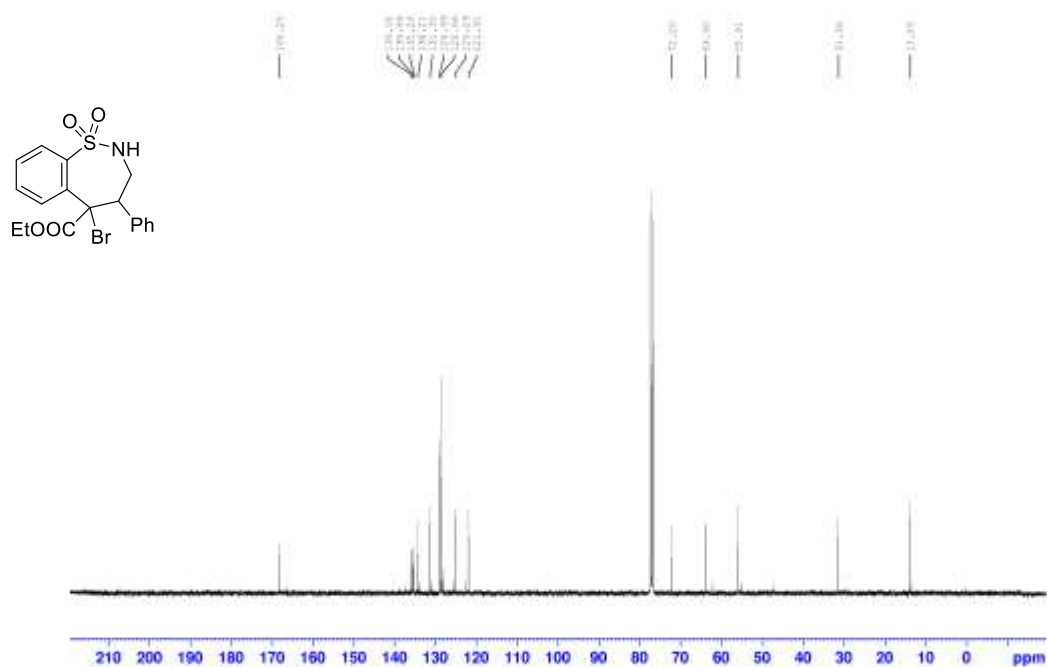
^{13}C NMR (150 MHz, CDCl_3) spectra of **5j**



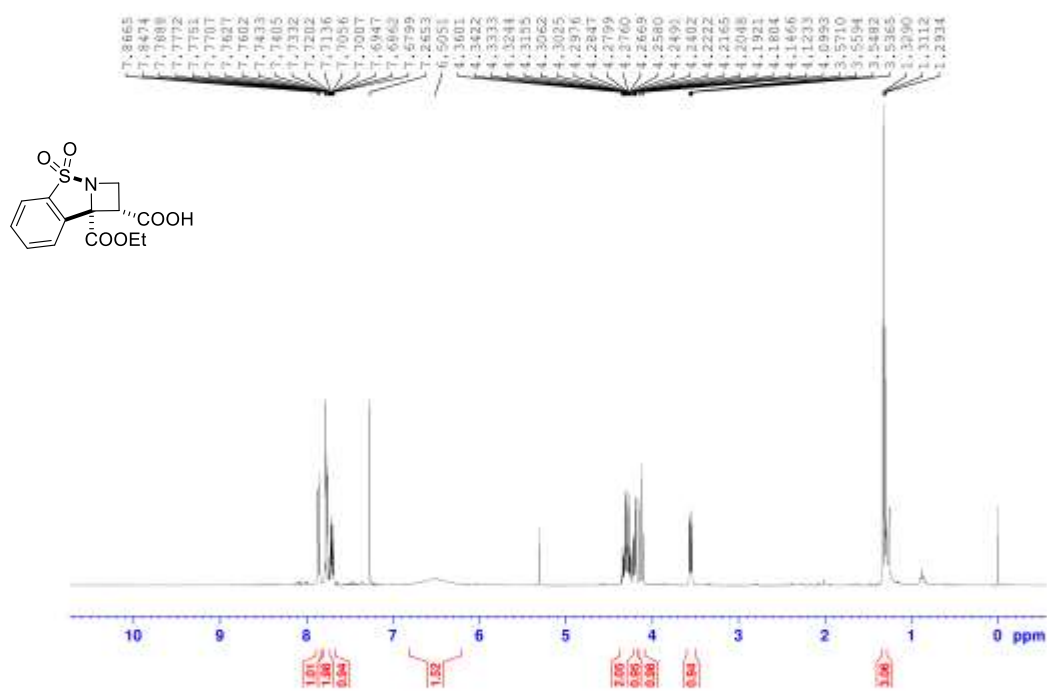
^1H NMR (400 MHz, CDCl_3) spectra of **6**



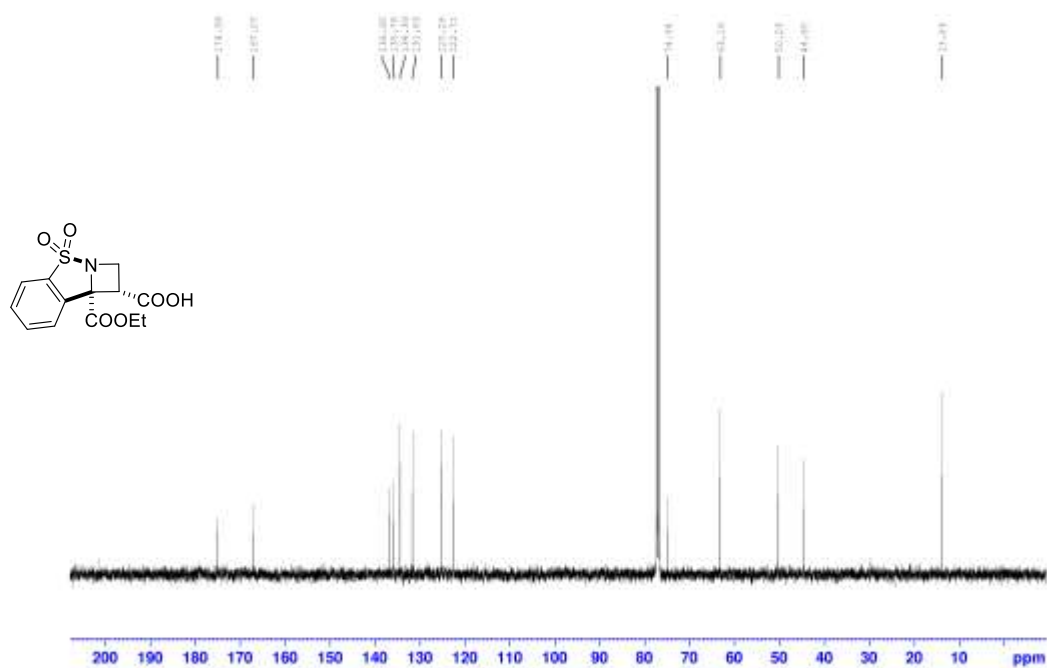
^{13}C NMR (100 MHz, CDCl_3) spectra of **6**



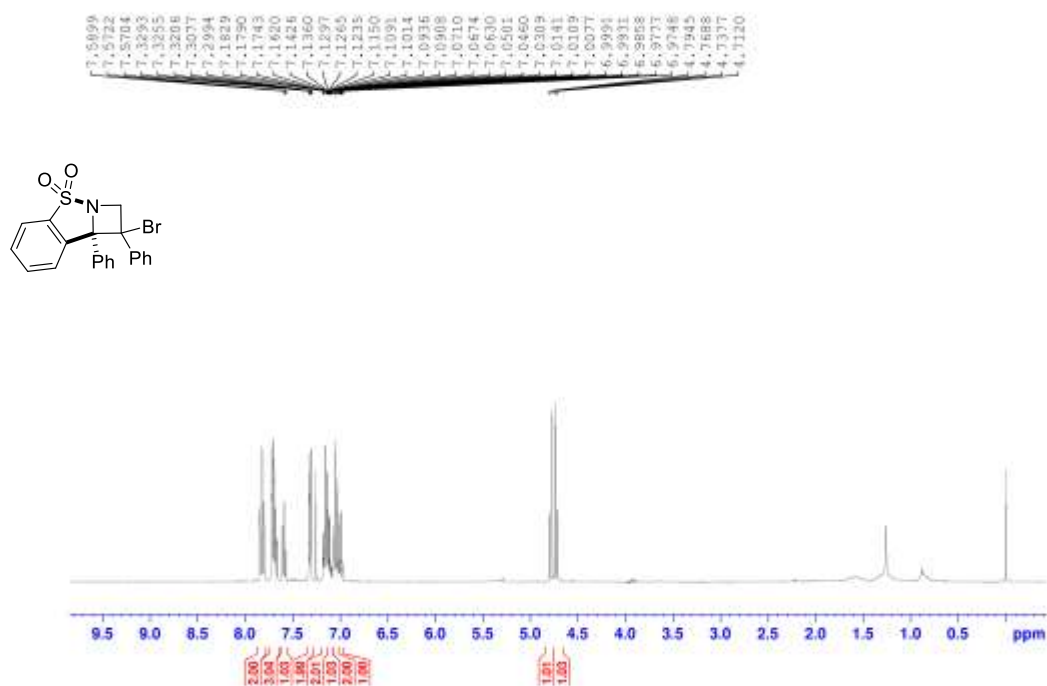
^1H NMR (400 MHz, CDCl_3) spectra of **7**



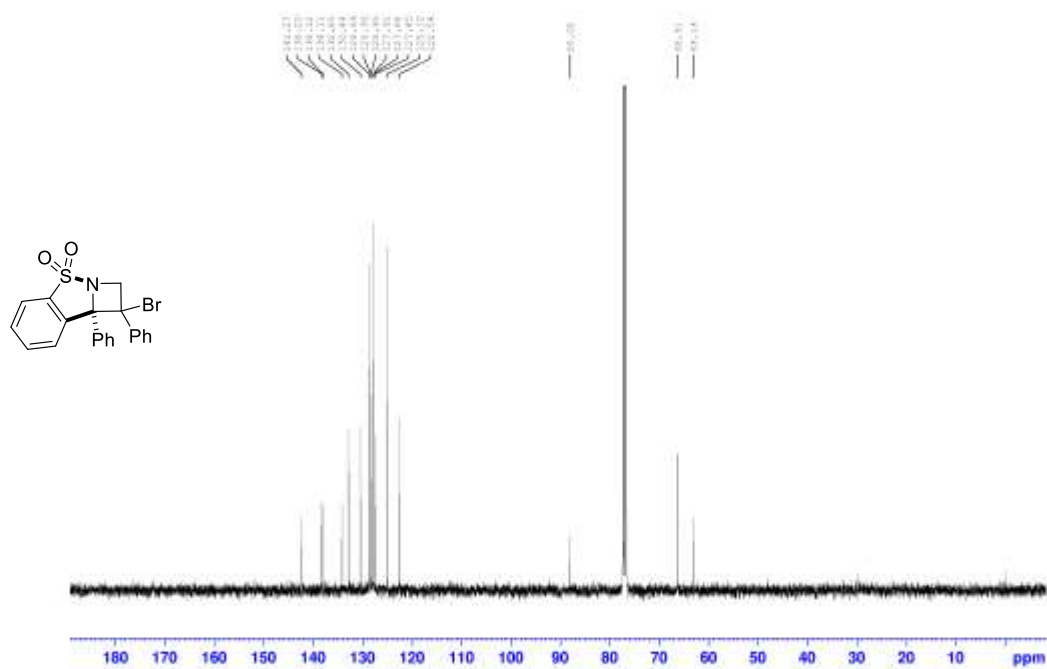
^{13}C NMR (100 MHz, CDCl_3) spectra of **7**



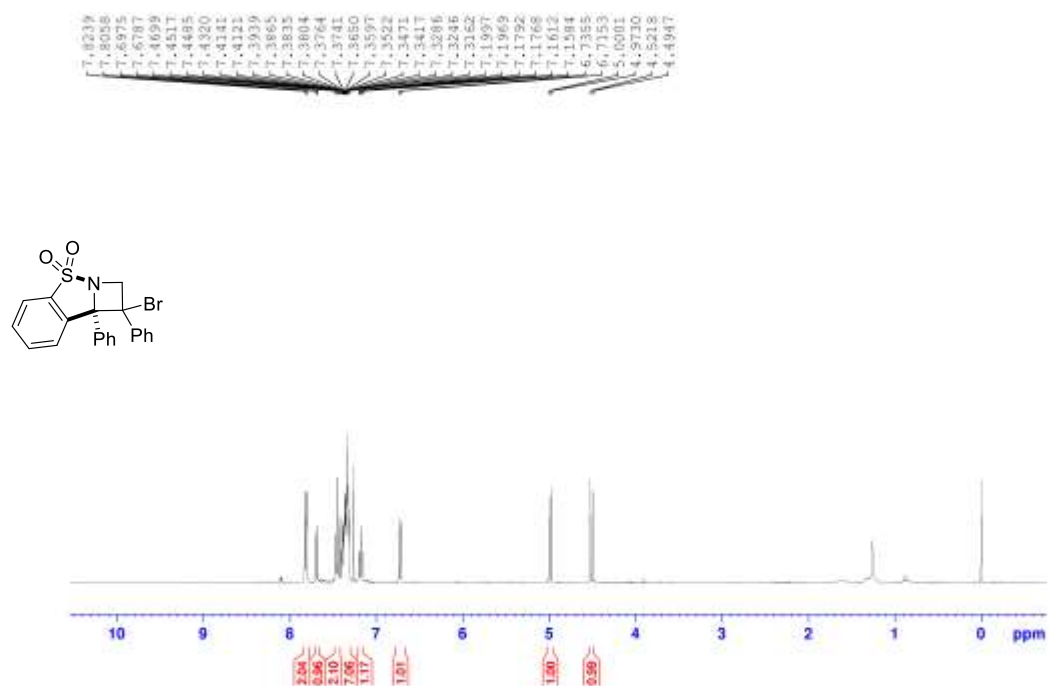
¹H NMR (400 MHz, CDCl₃) spectra of **8**



¹³C NMR (100 MHz, CDCl₃) spectra of **8**



^1H NMR (400 MHz, CDCl_3) spectra of **8'**



^{13}C NMR (100 MHz, CDCl_3) spectra of **8'**

