Supporting Information

Pd-Catalyzed [3+2] cycloaddition of cyclic ketimines with trimethylenemethanes toward *N*-fused pyrrolidines bearing a quaternary carbon

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List of Contents

1. General information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in oven-dried Schlenk tubes. Reaction temperatures are reported as the temperature of the heat transfer medium surrounding the vessel unless otherwise stated. Dry toluene was distilled from sodium prior to use. Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Alfa Aesar, and TCI and used as received unless otherwise stated.

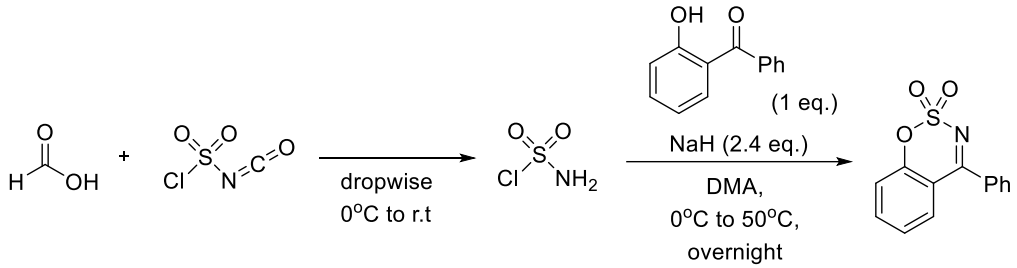
Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum plates (Merck). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 366 nm) and/or $KMnO_4$ solution. Flash chromatography was performed on Merck silica gel (40-63 mesh) by standard techniques.

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-300, Bruker DRX-500 and chemical shifts (δ) for ^1H and ^{13}C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^1H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$: δ^1H = 7.26 ppm, $\delta^{13}C$ = 77.16 ppm).

The high-resolution mass spectra were measured by electron ionization from JEOL (JMS-700) using magnetic sector mass analyzer type, or electrospray ionization from Water (Xevo G2-XS Tof) using quadrupole Time-of-flight mass analyzer type.

Phosphoramidite **L1**[1], cyclic aldimines **1**[2], cyclic ketimines **4**[3] were synthesized according to the literatures.

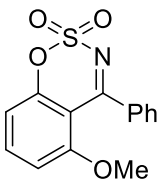
2. General procedure for the synthesis cyclic ketimines 4[3]



Ketimines **4** were synthesized according to reported methods. Anhydrous formic acid (30.0 mmol, 1.1 mL, 1 equiv.) was added dropwise to neat chlorosulfonyl isocyanate (30.0 mmol, 2.6 mL, 1 equiv.) at 0 ℃ with rapid stirring. Vigorous gas evolution was observed during the addition process. The resulting viscous suspension was stirred at room temperature until gas evolution ceased (1−2 h). The resulting white solid was used in the following step immediately. Then, hydroxybenzophenone (15 mmol, 2.97 g) was added to $ClSO_2NH_2$. To this mixture, *N*,*N*-Dimethylacetamide (30 mL) was dropwise at 0 ℃. The resulting solution was stirred for 10 min at room temperature and sodium hydride (18.0 mmol, 0.48 g) was added. After stirring for 30 min, another portion of sodium hydride (18.0 mmol, 0.48 g) and 4Å molecular sieve was added. After stirring for 1 h at room temperature, the reaction mixture was stirred for overnight at 50 ℃. The reaction was quenched with H_2O (100 mL) and the aqueous layer was extracted with ethyl acetate (20 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc/Hexane) on silica to afford corresponding imines in 40% yields.

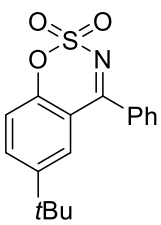
Compounds **4a**, **4c**, **4e**, **4g**-**4o**, **4r**-**4u** are known compounds and the spectra data were consistent with previously known data. The compounds below are unknown.

5-methoxy-4-phenylbenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4b)



Slightly yellow solid (0.36 g, yield: 28%); mp 179-181 ℃; purification by silica gel chromatography (EtOAc:Hexane= 1:5, Rf = 0.25); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.71 – 7.49 (m, 4H), 7.49 – 7.38 (m, 2H), 6.98 (dd, J = 8.27, 0.93 Hz, 1H), 6.85 (dd, J = 8.53, 0.91 Hz, 1H), 3.57 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-d) δ 176.6, 159.3, 155.4, 137.6, 137.1, 132.2, 129.0, 128.1, 111.3, 109.3, 108.0, 56.0;HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{14}H_{12}NO_4S^+$ 290.0487, found 290.0485.

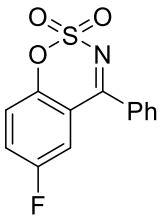
6-(tert-butyl)-4-phenylbenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4d)



White solid (0.47 g, yield: 25%); mp 183-185 ℃; purification by silica gel chromatography (EtOAc:Hexane= 1:5, R_f = 0.45); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.81 – 7.74 (m, 3H), 7.73 – 7.65 (m, 1H), 7.63 – 7.54 (m, 3H), 7.34 (d, *J* = 8.67 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ

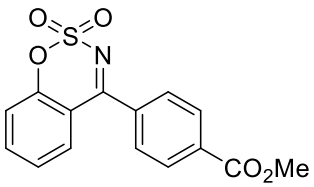
176.9, 152.6, 149.1, 134.4, 134.0, 133.3, 130.8, 128.9, 128.6, 119.0, 116.1, 35.0, 31.3; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{17}H_{18}NO_3S^+$ 316.1007, found 316.1007.

8-fluoro-4-phenylbenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (4f)



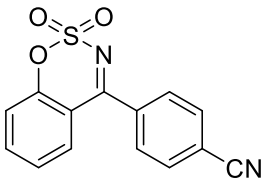
Slightly yellow solid (0.10 g, yield: 11%); mp 170-172 ℃; purification by silica gel chromatography (EtOAc:Hexane= 1:5, R_f = 0.50); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.83 – 7.33 (m, 8H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 175.5, 160.5, 157.3, 150.7, 133.7, 133.2, 130.6, 129.2, 124.3, 124.0, 121.4, 121.3, 118.0, 117.6, 117.4, 117.3; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{13}H_9FNO_3S^+$ 278.0287, found 278.0287.

methyl 4-(2,2-dioxidobenzo[*e*][1,2,3]oxathiazin-4-yl)benzoate (4p)



Slightly yellow solid (0.17 g, yield: 22%); mp 191-193 ℃; purification by silica gel chromatography (EtOAc:Hexane= 1:5, R_f = 0.30); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.27 – 8.19 (m, 2H), 7.87 – 7.75 (m, 3H), 7.59 (dd, *J* = 7.92, 1.62 Hz, 1H), 7.47 – 7.36 (m, 2H), 3.99 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 175.6, 166.0, 154.8, 137.6, 137.4, 134.2, 131.5, 130.6, 130.0, 126.0, 119.7, 116.4, 52.8; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{15}H_{12}NO_5S^+$ 318.0436, found 318.0436.

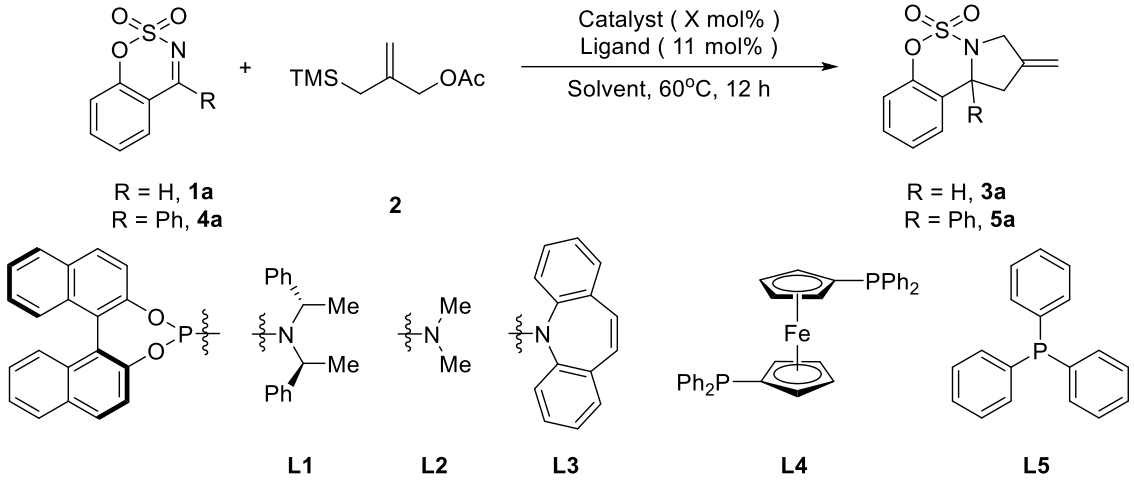
4-(2,2-dioxidobenzo[*e*][1,2,3]oxathiazin-4-yl)benzonitrile (4q)



Slightly yellow solid (0.28 g, yield: 43%); mp 235-237 ℃; purification by silica gel chromatography (EtOAc:Hexane= 1:5, R_f = 0.30); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.88 (s, 2H), 7.81 (ddd, *J* = 8.34, 7.37, 1.68 Hz, 1H), 7.55 (ddd, *J* = 7.98, 1.70, 0.46 Hz, 1H), 7.48 – 7.38 (m, 1H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 174.6, 154.8, 137.8, 137.7, 132.7, 131.1, 131.0, 126.2, 119.9, 117.6, 116.7, 116.1; HRMS (EI-MS) *m/z* calcd for C14H8N_2O_3S $[M]^+$ 284.0256, found 284.0253

3. Reaction optimization

Table S1. Reaction optimization of the Pd-catalyzed cycloaddition of sulfamate-derived cyclic imine **1a** or **4a** with 2-(trimethylsilylmethyl)allyl acetate **2**[a]

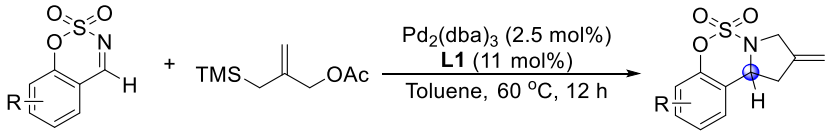


Entry	Cyclic ketimine	Catalyst (mol%)	Ligand	Solvent	Yield[b] 3a or 5a (%)
1	**1a**	$Pd_2(dba)_3$ (2.5)	**L1**	Toluene	**3a,** 98 (97)[c]
2	**1a**	$Pd_2(dba)_3$ (2.5)	**L2**	Toluene	**3a,** 54
3	**1a**	$Pd_2(dba)_3$ (2.5)	**L3**	Toluene	**3a,** 96
4	**1a**	$Pd_2(dba)_3$ (2.5)	**L4**	Toluene	**3a,** 91
5	**1a**	$Pd_2(dba)_3$ (2.5)	**L5**	Toluene	**3a,** 55
6	**1a**	$Pd(OAc)_2$ (5)	**L1**	Toluene	**3a,** 90
7	**1a**	PdCp(allyl) (5)	**L1**	Toluene	**3a,** 76
8	**1a**	$Pd(PPh_3)_4$ (5)	**-**	Toluene	**3a**, 51
9	**1a**	$Pd_2(dba)_3$ (2.5)	**L1**	THF	**3a,** 98
10[d]	**1a**	$Pd_2(dba)_3$ (2.5)	**L1**	Toluene	**3a,** 83
11[e,f]	**1a**	$Pd_2(dba)_3$ (2.5)	**L1**	Toluene	**3a,** 88
12[f]	**4a**	$Pd_2(dba)_3$ (2.5)	**L1**	Toluene	**5a,** 91[c]
13[e,f]	**4a**	$Pd_2(dba)_3$ (2.5)	**L1**	Toluene	**5a,** 95[c]
14[d,f]	**4a**	$Pd_2(dba)_3$ (2.5)	**L1**	Toluene	**5a,** 85[c]

[a]Reaction conditions: **1a or 4a** (0.1 mmol), **2** (0.15 mmol), $Pd_2(dba)_3$ (5 mol %), and ligand (11 mol %) in toluene (1.0 mL) at 60 °C for 12 h under Ar. [b]NMR yield was ^{1}H NMR using 1,2-dibromoethane as internal standard. [c]Isolated yield [d]Reaction was performed with 1 equiv of **2**. [e]Reaction was performed with 1.2 equiv of **2**. [f]Reaction was performed at 30 °C for 20 h.

4. General procedure for the synthesis of pyrrolidines

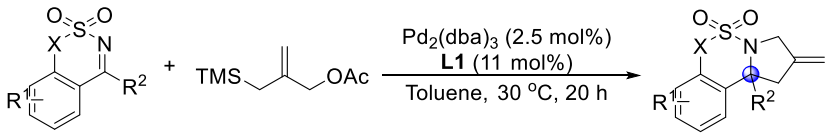
4.1 General procedure for synthesis of pyrrolidines 3



1 2 3

To a flame-dried Schlenk tube, $Pd_2(dba)_3$ (2.3 mg, 2.5 mol%), **L1** (6.0 mg, 11 mol%) were added in glove box, then aldimine **1** (0.1 mmol), 2-(trimethylsilylmethyl)allyl acetate **2** (0.15 mmol), toluene (1.0 mL) were added under argon atmosphere. The reaction mixture was stirred at 60 ℃ for 12 h. After reaction completed, the solvent was evaporated and the product was isolated by silica gel column chromatography using an appropriate eluent. The isolated yields were determined by ^{1}H NMR analysis.

4.2 General procedure for synthesis of pyrrolidines 5



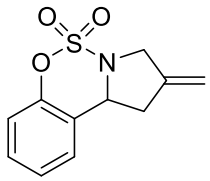
4 2 5

To a flame-dried Schlenk tube, $Pd_2(dba)_3$ (2.3 mg, 2.5 mol%), **L1** (6.0 mg, 11 mol%) were added in glove box, then ketimines **4** (0.1 mmol), 2-(trimethylsilylmethyl)allyl acetate **2** (0.12 mmol), toluene (1.0 mL) were added under argon atmosphere. The reaction mixture was stirred at 30 ℃ for 20 h. After reaction completed, the solvent was evaporated and the product was isolated by silica gel column chromatography using an appropriate eluent. The isolated yields were determined by ^{1}H NMR analysis.

5. Characterization

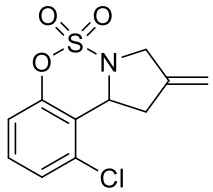
5.1 Characterization data of products 3a-3g

2-Methylene-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3a):



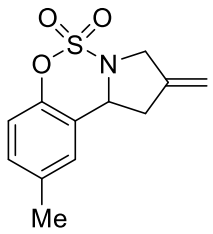
White solid (23.0 mg, yield: 97%); mp 102−104 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.5); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.45 – 7.27 (m, 8H), 7.17 – 7.09 (m, 1H), 5.02 (dp, *J* = 6.28, 2.17 Hz, 2H), 4.41 (dddd, *J* = 14.20, 3.34, 2.08, 1.16 Hz, 1H), 4.18 (dq, *J* = 14.22, 2.17 Hz, 1H), 3.52 – 3.32 (m, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.9, 142.4, 140.4, 130.1, 129.6, 128.3, 128.1, 127.1, 125.2, 122.6, 119.5, 108.8, 75.5, 55.1, 51.9; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{11}H_{12}NO_3S^+$ 238.0538, found 238.0537.

10-Chloro-2-methylene-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3b):

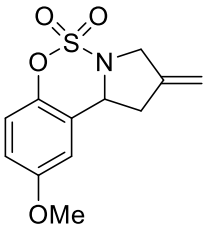


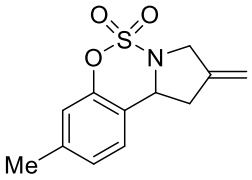
Slightly yellow solid (25.3 mg, yield: 93%); mp 69−71 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.58); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.27 – 7.23 (m, 2H), 6.97 (dd, *J* = 5.21, 4.31 Hz, 1H), 5.32 (dd, *J* = 8.56, 3.33 Hz, 1H), 5.06 (dt, *J* = 4.15, 2.10 Hz, 2H), 4.23 – 4.07 (m, 2H), 3.51 – 3.39 (m, 1H), 3.13 – 3.01 (m, 1H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 151.6, 140.7, 133.1, 129.7, 127.6, 122.0, 118.0, 109.3, 62.9, 54.7, 39.8; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{11}H_{11}ClNO_3S^+$ 272.0148, found 272.0150.

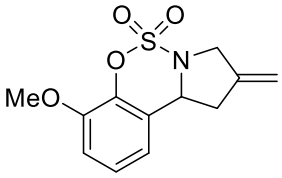
9-Methyl-2-methylene-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3c):

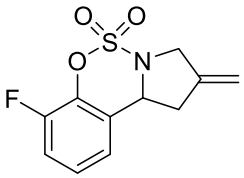


Slightly yellow solid (22.4 mg, yield: 89%); mp 109−111 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:10, R_f = 0.58); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.09 (ddt, *J* = 8.41, 2.23, 0.77 Hz, 1H), 6.95 – 6.86 (m, 2H), 5.25 (d, *J* = 7.82 Hz, 1H), 5.08 – 4.96 (m, 2H), 4.19 – 4.09 (m, 1H), 3.93 (dq, *J* = 14.17, 2.40 Hz, 1H), 3.26 (ddtd, *J* = 15.88, 7.93, 2.66, 1.37 Hz, 1H), 2.94 (dt, *J* = 15.90, 1.60 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 148.9, 141.4, 135.6, 130.2, 127.3, 120.7, 118.5, 109.3, 63.1, 53.1, 39.6, 21.0; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{12}H_{14}NO_3S^+$ 252.0694, found 252.0693.

9-Methoxy-2-methylene-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3d): 
White solid (24.6 mg, yield: 92%); mp 128−130 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.25); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.94 (d, *J* = 9.00 Hz, 1H), 6.83 (ddd, *J* = 9.01, 2.93, 0.80 Hz, 1H), 6.63 (dd, *J* = 2.96, 0.99 Hz, 1H), 5.25 (d, *J* = 7.77 Hz, 1H), 5.07 – 4.97 (m, 2H), 4.13 (ddt, *J* = 14.19, 2.19, 0.91 Hz, 1H), 3.98 – 3.88 (m, 1H), 3.79 (s, 3H), 3.26 (ddddd, *J* = 15.89, 6.69, 4.07, 2.63, 1.36 Hz, 1H), 2.92 (dt, *J* = 15.88, 1.59 Hz, 1H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 157.1, 144.7, 141.2, 122.0, 119.7, 114.9, 111.9, 109.3, 63.2, 55.9, 53.1, 39.7; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{12}H_{14}NO_4S^+$ 268.0644, found 268.0649.

8-Methyl-2-methylene-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3e): 
Colorless oil (23.6 mg, yield: 94%); purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.50); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.02 (d, *J* = 0.97 Hz, 2H), 6.81 (d, *J* = 1.28 Hz, 1H), 5.26 (d, *J* = 7.72 Hz, 1H), 5.06 – 4.96 (m, 2H), 4.19 – 4.07 (m, 1H), 3.93 (dq, *J* = 14.21, 2.40 Hz, 1H), 3.25 (dddt, *J* = 15.78, 7.84, 4.08, 2.68 Hz, 1H), 2.92 (dt, *J* = 15.86, 1.58 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.9, 141.4, 140.2, 126.8, 126.8, 119.1, 117.9, 109.3, 63.0, 53.0, 39.6, 21.1; HRMS (EI-MS) *m/z* calcd for $C_{12}H_{13}NO_3S$ $[M]^+$ 251.0610, found 251.0616.

7-Methoxy-2-methylene-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3f): 
White solid (22.5 mg, yield: 84%); mp 154-156 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.25); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.13 (t, *J* = 8.07 Hz, 1H), 6.87 (dt, *J* = 8.16, 1.03 Hz, 1H), 6.71 (dt, *J* = 7.94, 1.14 Hz, 1H), 5.29 (d, *J* = 7.82 Hz, 1H), 5.06 – 4.94 (m, 2H), 3.86 (s, 3H), 3.33 – 3.19 (m, 1H), 2.93 (dt, *J* = 15.89, 1.56 Hz, 1H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 148.7, 141.2, 140.6, 125.4, 122.1, 118.0, 111.8, 109.3, 63.2, 56.3, 53.2, 39.7; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{12}H_{14}NO_4S^+$ 268.0644, found 268.0644.

7-Fluoro-2-methylene-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3g): 
White solid (20.9 mg, yield: 82%); mp 125−127 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.25); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.19 – 7.06 (m, 2H), 6.93 (ddd, *J* = 7.54, 2.40, 1.28 Hz, 1H), 5.33 (d, *J* = 7.86 Hz, 1H), 5.04 (ddd, *J* = 6.78, 3.47, 1.85 Hz, 2H), 4.17 (dt, *J* = 14.31, 1.94 Hz, 1H), 3.98 (dq, *J* = 14.26,

2.39 Hz, 1H), 3.29 (ddq, *J* = 17.38, 7.01, 2.47 Hz, 1H), 2.94 (dt, *J* = 15.92, 1.54 Hz, 1H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.9 (d, *J* = 250.5 Hz), 140.6, 139.5 (d, *J* = 13.5 Hz), 125.3 (d, *J* = 7.5 Hz), 123.3, 121.8 (d, *J* = 3.8 Hz), 116.3(d, *J* = 17.3 Hz), 109.7, 63.2(d, *J* = 2.25 Hz), 53.0, 39.6; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -132.5 (dd, *J* = 9.54, 5.21 Hz); HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{11}H_{11}FNO_3S^+$ 256.0444, found 256.0453.

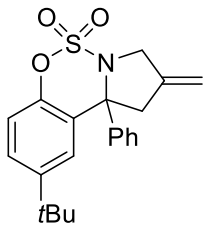
5.2 Characterization data of products 5a-5u

2-Methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2*c*][1,2,3] oxathiazine 5,5-dioxide (5a): slightly yellow solid (29.8 mg, yield: 95%); mp 138-140 ℃; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.55); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.45 – 7.27 (m, 8H), 7.17 – 7.09 (m, 1H), 5.02 (dp, *J* = 6.28, 2.17 Hz, 2H), 4.41 (dddd, *J* = 14.20, 3.34, 2.08, 1.16 Hz, 1H), 4.18 (dq, *J* = 14.22, 2.17 Hz, 1H), 3.52 – 3.32 (m, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.9, 142.4, 140.4, 130.1, 129.6, 128.3, 128.1, 127.1, 125.2, 122.6, 119.5, 108.8, 75.5, 55.1, 51.9; HRMS (EI-MS) *m/z* calcd for $C_{17}H_{15}NO_3S$ $[M]^+$ 313.0773, found 313.0772.

10-Methoxy-2-methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*] [1,2,3]oxathiazine 5,5-dioxide (5b): slightly yellow solid (28.5 mg, yield: 83%); mp 115−117 ℃; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.38); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 (t, *J* = 8.34 Hz, 1H), 7.26 (t, *J* = 1.82 Hz, 5H), 6.80 (ddd, *J* = 16.78, 8.35, 1.03 Hz, 2H), 5.08 (h, *J* = 2.12 Hz, 2H), 4.33 (dq, *J* = 13.50, 1.57 Hz, 1H), 4.18 (dt, *J* = 13.61, 1.74 Hz, 1H), 3.72 (s, 3H), 3.65 – 3.51 (m, 2H ^{13}C NMR (75 MHz, Chloroform-*d*) δ 157.5, 151.3, 142.7, 141.8, 130.2, 127.7, 127.5, 126.9, 113.3, 111.8, 108.4, 108.0, 74.3, 56.0, 55.3, 50.1; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{18}H_{18}NO_4S^+$ 344.0957, found 344.0959.

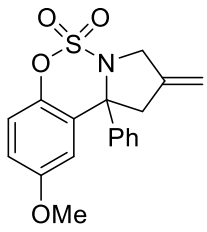
9-Methyl-2-methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3] oxathiazine 5,5-dioxide (5c): White solid (30.1 mg, yield: 92%); mp 131-133 ℃; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.55); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.27 (m, 5H), 7.19 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.08 (d, *J* = 2.1 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 5.02 (dt, *J* = 7.6, 2.1 Hz, 2H), 4.44 – 4.33 (m, 1H), 4.16 (dd, *J* = 14.4, 2.2 Hz, 1H), 3.51 – 3.32 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 148.8, 142.6, 140.6, 135.0, 130.8, 129.6, 128.3, 128.0, 127.2, 122.3, 119.2, 108.6, 55.1, 51.7, 21.2; HRMS (EI-MS) *m/z* calcd for $C_{18}H_{17}NO_3S$ $[M]^+$ 327.0929, found 327.0928.

9-(*tert*-Butyl)-2-methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*]



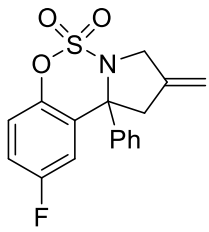
[1,2,3]oxathiazine 5,5-dioxide (5d): White solid (34.1 mg, yield: 98%); mp 132−134 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:10, R_f = 0.38); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.46 – 7.27 (m, 7H), 7.04 (d, *J* = 8.64 Hz, 1H), 5.03 (dp, *J* = 4.16, 2.15 Hz, 2H), 4.41 (dtt, *J* = 14.11, 2.20, 1.10 Hz, 1H), 4.22 – 4.12 (m, 1H), 3.55 – 3.33 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 148.6, 148.3, 142.9, 140.6, 128.3, 128.0, 127.1, 126.3, 121.7, 118.8, 108.6, 75.7, 55.2, 52.2, 34.7, 31.5; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{21}H_{24}NO_3S^+$ 370.1477, found 370.1479.

9-Methoxy-2-methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]



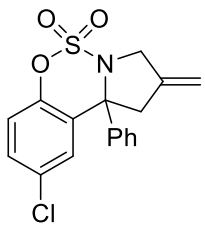
oxathiazine 5,5-dioxide (5e): White solid (32.6 mg, yield: 95%); mp 126−128 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.42); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, 5H), 7.05 (d, *J* = 9.00 Hz, 1H), 6.93 (dd, *J* = 9.03, 2.91 Hz, 1H), 6.78 (d, *J* = 2.90 Hz, 1H), 5.03 (dt, *J* = 7.93, 2.13 Hz, 2H), 4.42 – 4.33 (m, 1H), 4.15 (dq, *J* = 14.24, 2.21 Hz, 1H), 3.82 (s, 3H), 3.50 – 3.29 (m, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 156.5, 144.5, 142.3, 140.5, 128.3, 128.1, 127.1, 123.9, 120.3, 115.2, 114.5, 108.7, 75.6, 55.9, 55.1, 51.6; HRMS (EI-MS) *m/z* calcd for $C_{18}H_{17}NO_4S$ [M]$^+$ 343.0878, found 343.0886.

9-Fluoro-2-methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]



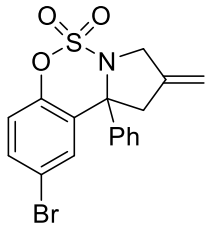
oxathiazine 5,5-dioxide (5f): White solid (29.5 mg, yield: 89%); mp 144−146 °C; purification by silica gel chromatography (Acetone:Hexane= 1:10, R_f = 0.25); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 5H), 7.15 – 7.09 (m, 2H), 7.05 – 6.99 (m, 1H), 5.04 (dp, *J* = 8.5, 2.2 Hz, 2H), 4.40 (ddt, *J* = 14.4, 2.2, 1.0 Hz, 1H), 4.21 – 4.11 (m, 1H), 3.48 (ddd, *J* = 16.1, 2.3, 1.1 Hz, 1H), 3.30 (dd, *J* = 16.0, 1.6 Hz,); ^{13}C NMR (71H5 MHz, Chloroform-*d*) δ 159.1 (d, *J*= 244.5 Hz), 146.7 (d, *J* = 2.3 Hz), 140.0, 128.5, 128.3, 127.0, 124.6 (d, *J* = 6.8 Hz) 121.0 (d, *J* = 8.3 Hz), 117.3 (d, *J* = 23.3Hz), 115.9 (d, *J* = 24 Hz), 109.1, 75.5, 55.1, 51.8; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -115.4 – -115.4 (m); HRMS (EI-MS) *m/z* calcd for $C_{17}H_{14}FNO_3S$ [M]$^+$ 331.0678, found 331.0672.

9-Chloro-2-methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]



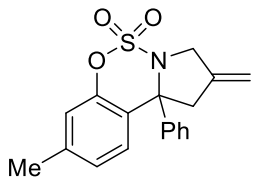
oxathiazine 5,5-dioxide (5g): White solid (35.3 mg, yield: 93%); mp 171−173 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:10, R_f = 0.28); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.41 – 7.27 (m, 7H), 7.07 (d, *J* = 8.78 Hz, 1H), 5.11 – 4.95 (m, 2H), 4.41 (dtt, *J* = 14.29, 2.22, 1.18 Hz, 1H), 4.16 (dq, *J* = 14.25, 2.17 Hz, 1H), 3.54 – 3.25 (m, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 149.4, 141.7, 139.8, 130.5, 130.3, 129.2, 128.5, 128.3, 127.0, 124.5, 120.9, 109.2, 75.4, 55.1, 51.8; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{17}H_{15}ClNO_3S^+$ 348.0461, found 348.0469.

9-Bromo-2-methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]



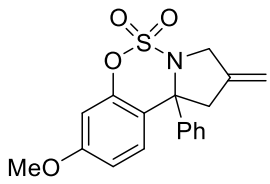
oxathiazine 5,5-dioxide (5h): White solid (36.7 mg, yield: 96%); mp 166−168 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.43); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 8.74, 2.34 Hz, 1H), 7.44 (d, *J* = 2.33 Hz, 1H), 7.38 – 7.29 (m, 5H), 7.01 (d, *J* = 8.73 Hz, 1H), 5.06 (dp, *J* = 9.57, 2.17 Hz, 2H), 4.41 (dtt, *J* = 14.25, 2.18, 1.22 Hz, 1H), 4.16 (dq, *J* = 14.30, 2.19 Hz, 1H), 3.53 – 3.43 (m, 1H), 3.37 – 3.28 (m, 1H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.0, 141.7, 139.8, 133.2, 132.2, 128.5, 128.4, 127.0, 124.9, 121.3, 117.9, 109.3, 75.4, 55.2, 51.9; HRMS (EI-MS) *m/z* calcd for $C_{17}H_{14}BrNO_3S$ [M]$^+$ 390.9878, found 390.9876.

8-Methyl-2-methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2*c*][1,2,3]



oxathiazine 5,5-dioxide (5i): White solid (28.5 mg, yield: 87%); mp 181−183 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.50); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.92 (s, 1H), 5.00 (dt, *J* = 6.1, 2.1 Hz, 2H), 4.45 – 4.35 (m, 1H), 4.15 (dd, *J* = 14.3, 2.2 Hz, 1H), 3.49 – 3.29 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.7, 142.6, 140.7, 140.6, 129.3, 128.3, 128.0, 127.1, 126.2, 119.7, 119.3, 108.6, 75.4, 55.1, 51.9, 21.2; HRMS (EI-MS) *m/z* calcd for $C_{18}H_{17}NO_3S$ [M]$^+$ 327.0929, found 327.0929.

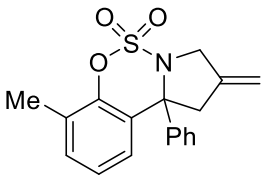
8-Methoxy-2-methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2,*c*][1,2,3]



oxathiazine 5,5-dioxide (5j): White solid (32.6 mg, yield: 95%); mp 170−173 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.37); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.27 (m, 5H), 7.20 (d, *J* = 8.8 Hz, 1H), 6.87 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.62 (d, *J* = 2.6 Hz, 1H), 5.04 – 4.97 (m, 2H), 4.42 (ddt, *J* = 14.3, 2.3, 1.0 Hz, 1H), 4.19 (s, 1H), 3.84 (s, 3H), 3.48 – 3.27 (m, 2H); ^{13}C NMR (75 MHz, Chloroform-

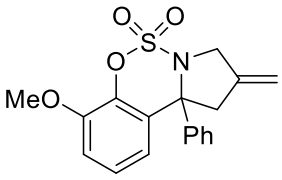
d) δ 160.6, 151.7, 142.7, 140.5, 130.2, 128.2, 128.0, 127.1, 113.8, 112.4, 108.7, 103.7, 75.3, 55.8, 55.2, 52.0; HRMS (EI-MS) *m/z* calcd for $C_{18}H_{17}NO_4S$ $[M]^+$ 343.0878, found 343.0877.

7-Methyl-2-methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]



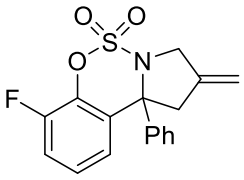
oxathiazine 5,5-dioxide (5k): White solid (31.8 mg, yield: 97%); mp 125−127 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.67); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 5H), 7.24 (dd, *J* = 2.0, 0.9 Hz, 1H), 7.21 – 7.11 (m, 2H), 5.02 (dp, *J* = 8.2, 2.2 Hz, 2H), 4.43 – 4.34 (m, 1H), 4.17 (dd, *J* = 14.3, 2.2 Hz, 1H), 3.49 – 3.33 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 149.3, 142.6, 140.6, 131.5, 128.9, 128.3, 128.0, 127.1, 126.9, 124.6, 123.0, 108.6, 75.5, 55.0, 51.6, 16.0.; HRMS (EI-MS) *m/z* calcd for $C_{18}H_{17}NO_3S[M]^+$ 327.0929, found 327.0932.

7-Methoxy-2-methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]



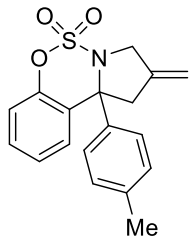
oxathiazine 5,5-dioxide (5l): White solid (34.0 mg, yield: 99%); mp 146−148 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:8, R_f = 0.12); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.42 – 7.26 (m, 5H), 7.22 (t, *J* = 8.11 Hz, 1H), 6.97 (dd, *J* = 8.21, 1.33 Hz, 1H), 6.87 (dd, *J* = 8.01, 1.36 Hz, 1H), 5.01 (dp, *J* = 6.42, 2.18 Hz, 2H), 4.39 (d, *J* = 14.45 Hz, 1H), 4.20 (dq, *J* = 14.25, 2.20 Hz, 1H), 3.90 (s, 3H), 3.50 – 3.31 (m, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 149.3, 142.4, 140.6, 140.5, 128.2, 128.0, 127.1, 124.7, 123.9, 120.5, 112.1, 108.7, 75.7, 56.3, 55.1, 51.8.; HRMS (EI-MS) *m/z* calcd for $C_{17}H_{18}NO_4S$ $[M]^+$ 343.0878, found 343.0873.

7-Fluoro-2-methylene-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]



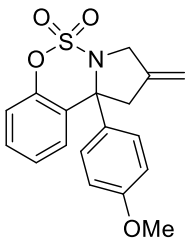
oxathiazine 5,5-dioxide (5m): White solid (29.5 mg, yield: 89%); mp 165−167 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.30); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.33 (dtt, *J* = 7.03, 5.57, 3.82 Hz, 5H), 7.26 – 7.16 (m, 2H), 7.13 – 7.06 (m, 1H), 5.07 – 5.01 (m, 2H), 4.44 (dtt, *J* = 14.32, 2.22, 1.21 Hz, 1H), 4.21 (dq, *J* = 14.30, 2.16 Hz, 1H), 3.54 – 3.29 (m, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 151.5 (d, *J* = 252.0 Hz), 141.9, 139.9, 139.8 (d, J = 13.5 Hz), 128.4, 128.3, 127.0, 124.7, 124.6, 124.5, 124.4, 116.8 (d, *J* = 18Hz), 116.7, 109.2, 75.9 (d, J = 2.25 Hz), 55.2, 52.2; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -131.3, -131.2 – -131.4 (m); HRMS (EI-MS) *m/z* calcd for $C_{17}H_{14}FNO_3S[M]^+$ 331.0678, found 331.0677.

2-Methylene-10b-(*p*-tolyl)-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine



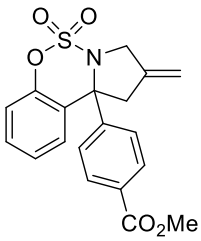
5,5-dioxide (5n): White solid (32.1 mg, yield: 98%); mp 130−132 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:5, R_f = 0.38); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40 (ddd, *J* = 8.18, 5.24, 3.80 Hz, 1H), 7.30 (dd, *J* = 4.15, 0.98 Hz, 2H), 7.24 (d, *J* = 2.10 Hz, 1H), 7.12 (ddt, *J* = 7.96, 6.14, 0.77 Hz, 3H), 5.01 (dt, *J* = 7.35, 2.10 Hz, 2H), 4.40 (dtt, *J* = 14.30, 2.22, 1.18 Hz, 1H), 4.17 (dq, *J* = 14.26, 2.17 Hz, 1H), 3.52 – 3.30 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.8, 140.4, 139.4, 137.8, 130.0, 129.5, 129.0, 127.0, 125.2, 122.9, 119.4, 108.7, 75.4, 55.1, 51.8, 21.1; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd for $C_{18}H_{18}NO_3S^+$ 328.1007, found 328.1008.

10b-(4-Methoxyphenyl)-2-methylene-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]



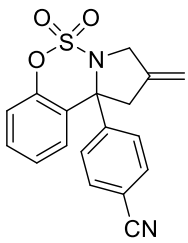
oxathiazine 5,5-dioxide (5o): Sticky oil (31.9 mg, yield: 93%); purification by silica gel chromatography (EtOAc:Hexane= 1:3, R_f = 0.50); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40 (ddd, *J* = 8.1, 5.0, 4.0 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.25 (s, 1H), 7.10 (dt, *J* = 8.0, 0.9 Hz, 1H), 6.88 – 6.80 (m, 2H), 5.02 (dq, *J* = 8.2, 2.2 Hz, 2H), 4.39 (dtt, *J* = 14.3, 2.2, 1.1 Hz, 1H), 4.16 (ddt, *J* = 14.3, 3.4, 1.7 Hz, 1H), 3.78 (s, 3H), 3.51 – 3.30 (m, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 159.2, 150.8, 140.4, 134.3, 130.0, 129.5, 128.4, 125.2, 123.0, 119.4, 113.5, 108.7, 75.3, 55.3, 55.1, 51.7; HRMS (EI-MS) *m/z* calcd for $C_{18}H_{17}NO_4S$ [M]$^+$ 343.0878, found 343.0877.

Methyl 4-(2-methylene-5,5-dioxido-2,3-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazin-



10b(1*H*)-yl)benzoate (5p): White solid (27.1 mg, yield: 73%); mp 162−164 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:10, R_f = 0.13); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.01 – 7.94 (m, 2H), 7.47 – 7.39 (m, 3H), 7.36 – 7.29 (m, 2H), 7.15 – 7.10 (m, 1H), 5.03 (dt, *J* = 3.2, 2.1 Hz, 2H), 4.47 – 4.38 (m, 1H), 4.22 – 4.11 (m, 1H), 3.89 (s, 3H), 3.48 – 3.33 (m, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.7, 150.9, 147.5, 139.9, 130.4, 129.8, 129.6, 129.5, 127.1, 125.4, 121.8, 119.7, 109.2, 75.2, 55.1, 52.3, 52.0; HRMS (EI-MS) *m/z* calcd for $C_{19}H_{17}NO_5S$ [M]$^+$ 371.0827, found 371.0828.

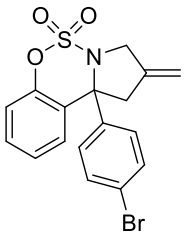
4-(2-Methylene-5,5-dioxido-2,3-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazin-10b



(1*H*)-yl)benzonitrile (5q): white solid (27.7 mg, yield: 82%); mp 184−186 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.6); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.63 – 7.57 (m, 2H), 7.52 – 7.41 (m, 3H), 7.38 – 7.27 (m, 2H), 7.13 (dd, *J* = 8.22, 1.25 Hz, 1H), 5.04 (q, *J* = 2.11 Hz, 2H), 4.48 – 4.38 (m, 1H), 4.16 (ddd, *J* = 14.21, 2.49, 1.35 Hz, 1H), 3.39 (q, *J* = 1.66

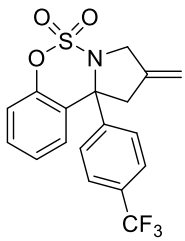
Hz, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.9, 147.8, 139.5, 132.1, 130.7, 129.4, 127.8, 125.6, 121.0, 119.8, 118.6, 111.9, 109.5, 74.9, 55.1, 52.1; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}N_2O_3S^+$ 339.0803, found 339.0800.

10b-(4-Bromophenyl)-2-methylene-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]



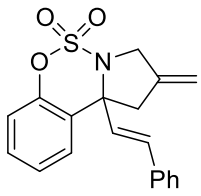
oxathiazine 5,5-dioxide (5r): White solid (35.7 mg, yield: 91%); mp 153−155 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:10, R_f = 0.12); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.47 – 7.38 (m, 3H), 7.35 – 7.27 (m, 2H), 7.25 – 7.19 (m, 2H), 7.12 (dd, *J* = 8.16, 1.20 Hz, 1H), 5.02 (dp, *J* = 4.17, 2.15 Hz, 2H), 4.40 (ddt, *J* = 14.27, 2.16, 1.00 Hz, 1H), 4.21 – 4.08 (m, 1H), 3.37 (q, *J* = 1.68 Hz, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.8, 141.7, 139.9, 131.4, 130.4, 129.4, 128.9, 125.4, 122.2, 122.0, 119.6, 109.1, 75.0, 55.1, 51.9; HRMS (EI-MS) *m/z* calcd for $C_{17}H_{14}BrNO_3S[M]^+$ 390.9878, found 390.9872.

2-Methylene-10b-(4-(trifluoromethyl)phenyl)-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*]



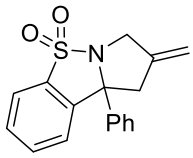
[1,2,3]oxathiazine 5,5-dioxide (5s): White solid (34.3 mg, yield: 90%); mp 160−162 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.50); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.61 – 7.41 (m, 5H), 7.38 – 7.28 (m, 2H), 7.13 (dd, *J* = 8.1, 1.1 Hz, 1H), 5.04 (q, *J* = 2.3 Hz, 2H), 4.44 (dt, *J* = 14.2, 1.2 Hz, 1H), 4.18 (dt, *J* = 14.2, 1.4 Hz, 1H), 3.41 (t, *J* = 1.7 Hz, 2H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.9, 146.5, 139.8, 130.6, 130.2 (q, *J* = 32.4 Hz), 127.5, 125.5, 125.3 (q, *J* = 3.75 Hz), 124.1 (q, *J* = 270.5 Hz), 121.7, 119.7, 75.0, 55.2, 52.1; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.6; HRMS (EI-MS) *m/z* calcd for $C_{18}H_{14}F_3NO_3S$ $[M]^+$ 381.0646, found 381.0646.

(*E*)-2-Methylene-10b-styryl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]



oxathiazine 5,5-dioxide (5t): colorless oil (24.1 mg, yield: 71%); purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f = 0.50); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.26 (m, 7H), 7.26 – 7.20 (m, 1H), 7.10 – 7.04 (m, 1H), 6.60 (d, *J* = 16.04 Hz, 1H), 6.41 (d, *J* = 16.04 Hz, 1H), 5.03 – 4.96 (m, 2H), 4.32 (dtt, *J* = 14.29, 2.22, 1.24 Hz, 1H), 4.16 (dq, *J* = 14.31, 2.11 Hz, 1H), 3.28 (ddt, *J* = 15.39, 4.18, 2.28 Hz, 1H), 3.14 (dq, *J* = 15.43, 1.45 Hz, 1H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.6, 139.7, 136.1, 131.7, 131.3, 129.9, 128.7, 128.6, 128.2, 126.9, 125.5, 122.8, 119.2, 109.1, 73.9, 55.1, 48.4; HRMS (EI-MS) *m/z* calcd for $C_{19}H_{17}NO_3S$ $[M]^+$ 339.0923, found 339.0929.

2-Methylene-9b-phenyl-1,2,3,9b-tetrahydrobenzo[*d*]pyrrolo[1,2-*b*]isothiazole 5,5-dioxide



(5u): slightly yellow solid (26.4 mg, yield: 89%); mp 119−121 °C; purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f= 0.25); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 7.78, 1.31 Hz, 1H), 7.64 – 7.45 (m, 4H), 7.41 – 7.27 (m, 4H), 5.02 (ddd, *J* = 18.59, 2.75, 1.41 Hz, 2H), 4.61 – 4.47 (m, 1H), 3.84 (dd, *J* = 15.14, 1.93 Hz, 1H), 3.48 (dd, *J* = 15.08, 1.41 Hz, 1H), 2.89 (ddt, *J* = 15.10, 2.72, 1.13 Hz, 1H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 145.6, 142.4, 141.2, 133.6, 133.5, 129.6, 129.0, 128.3, 126.1, 124.5, 121.9, 108.6, 48.6, 45.5; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{17}H_{16}NO_2S^+$ 298.0902, found 298.0916.

6. Single crystal x-ray diffraction data

Single-crystal x-ray dirffraction data were collected using an Bruker D8 VENTURE and a APEX II CCD area detector with a multilayer-monochromated Mo K_α radiation (λ = 0.71073 Å) generated by a rotating anode. Data collection, data reduction, and semiempirical absorption correction were carried out using the software package APEX2.* All of the calculations for the structure determination were carried out using the SHELXTL package.** All non-H atoms were refined anisotropically. All hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms. The ellipsoids are drawn at the 50% probability level.

* APEX2 (Version 2009.1−0) Data Collection and Processing Software; Bruker AXS Inc.: Madison, Wisconsin, U.S.A., 2008.

** SHELXTL-PC (Version 6.22) Program for Solution and Refinement of Crystal Structures; Bruker AXS Inc.: Madison, Wisconsin, U.S.A., 2001.

6.1 Recrystallization method

Product **5i** was recrystallized from a mixture ethyl acetate/*n*-hexane (v/v = 1:10). The solvent was partially evaporated over several days at room temperature (slightly opened vial for slow evaporation).

6.2 X-ray crystallographic data of 5i (CCDC 2114538)

Single-crystal sample (**5i**) was prepared in ethyl acetate and *n*-hexane.

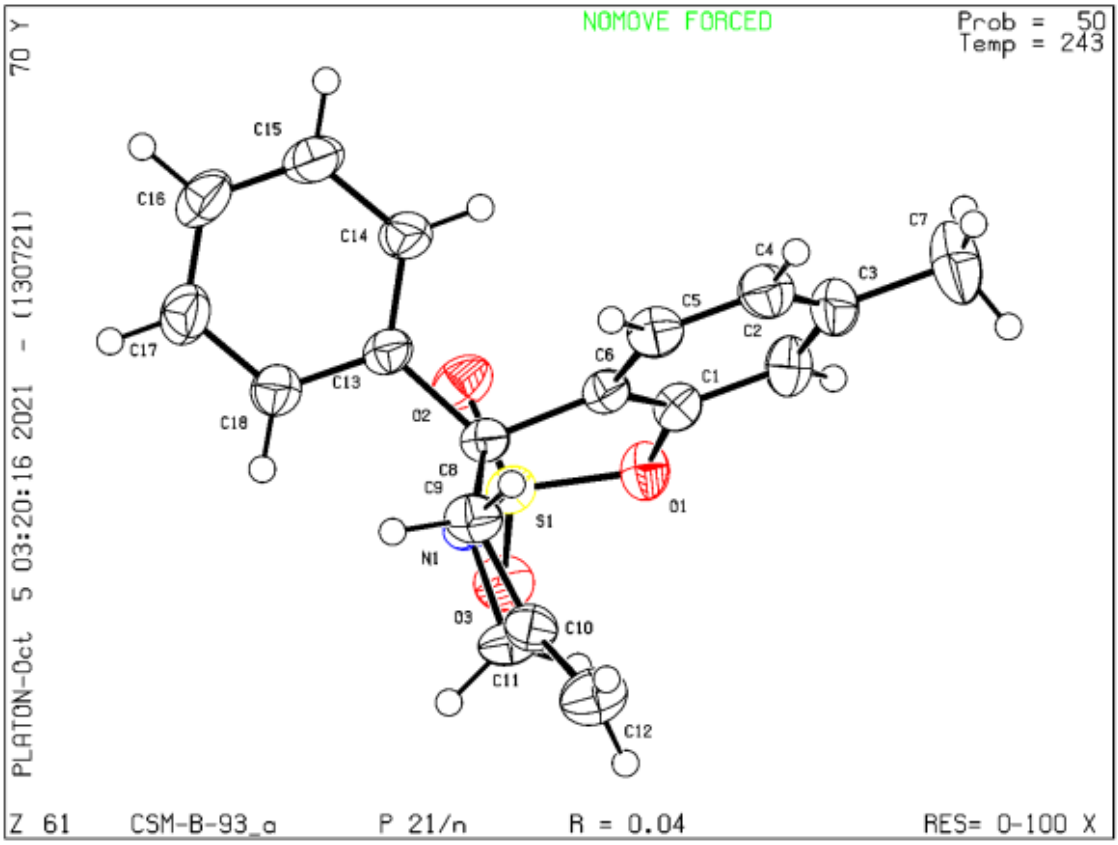


Figure S1. The ellipsoid (50% probability) plot of **5i**.

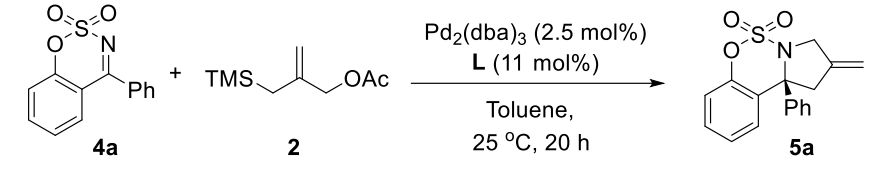
Table S2. Crystal data and structure refinement for **5i**.

Identification code	**5i**	
Empirical formula	C18 H17 N O3 S	
Formula weight	327.38	
Temperature	243(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.8132(12) Å	α= 90°.
	b = 18.052(3) Å	β= 102.448(5)°.
	c = 10.3523(16) Å	γ = 90°.
Volume	1608.3(4) $Å^3$	
Z	4	

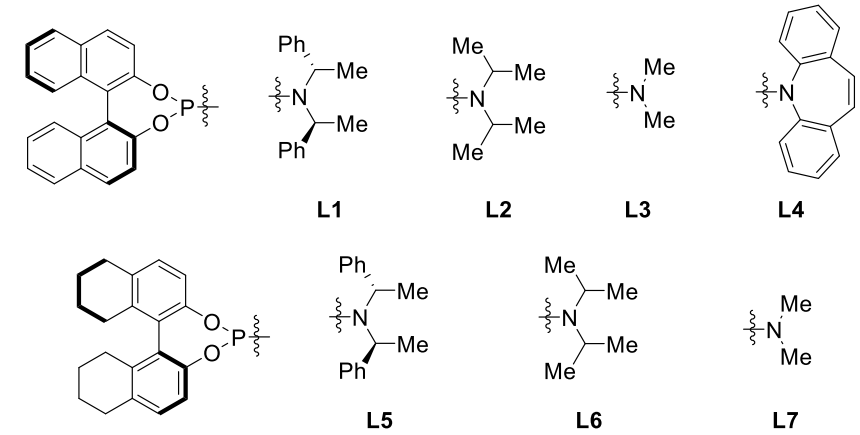
Density (calculated)	1.352 Mg/m^3
Absorption coefficient	0.216 mm^{-1}
F(000)	688
Crystal size	0.417 x 0.188 x 0.075 mm^3
Theta range for data collection	2.256 to 28.278°.
Index ranges	-11<=h<=10, -24<=k<=24, -13<=l<=13
Reflections collected	21427
Independent reflections	3979 [R(int) = 0.0464]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6586
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3979 / 0 / 208
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.1055
R indices (all data)	R1 = 0.0496, wR2 = 0.1113
Extinction coefficient	n/a
Largest diff. peak and hole	0.313 and -0.376 $e.Å^{-3}$

7. The investigation on asymmetric [3+2] cycloaddition

Table S3. The investigation on asymmetric [3+2] cycloaddition of sulfamate-derived cyclic ketimine **4a** with 2-(trimethylsilylmethyl)allyl acetate **2**[a]



4a **2** **5a**

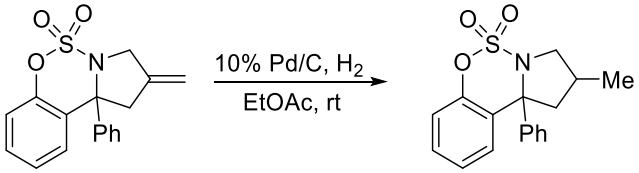


Entry	Ligand	Yield[b] (%) 5a	ee (%)[c] 5a
1	**L1**	85	20
2	**L2**	55	7
3	**L3**	40	-4
4	**L4**	72	-14
5	**L5**	85	19
6	**L6**	66	0
7	**L7**	60	5
8[d]	**L1**	63	28

[a]Reaction conditions: **4a** (0.1 mmol), **2** (0.1 mmol), $Pd_2(dba)_3$ (2.5 mol%), and ligand (11 mol%) in toluene (1.0 mL) at 25 ℃ for 20 h under Ar. [b]Isolated yield. [c]determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH=85/15, flow rate: 1.0 mL/min, λ = 220 nm, For the **5a**, t_{major}=11.59 min, t_{minor}=15.52 min. [d]Reaction was performed at 0 ℃.

8. Synthetic transformations compound 5a

8.1 Synthesis and characterization for the compound 6a[4]

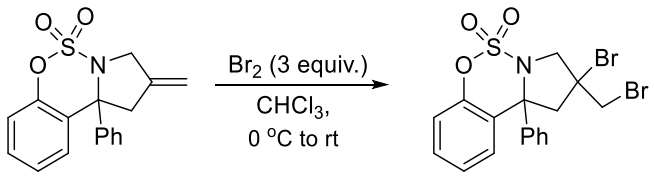


5a **6a**

To a dry tube equipped with a stirring bar added **5a** (25.9 mg, 0.1 mmol), Pd/C (10.6 mg, 0.1 mmol) and EtOAc (1 mL). The reaction mixture was stirred under an atmosphere of hydrogen at room temperature. Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was filtered celite to afford product **6a** in 85 % (26.8 mg) yield as a white sticky oil.

2-Methyl-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine 5,5-dioxide (6a): White sticky oil (26.8 mg, yield: 85%); purification by silica gel chromatography (EtOAc:Hexane= 1:7, R_f= 0.55); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.47 – 7.26 (m, 9H), 7.26 – 7.17 (m, 2H), 7.10 (dt, *J* = 7.91, 1.77 Hz, 1H), 3.90 (ddd, *J* = 9.06, 6.67, 1.19 Hz, 1H), 3.42 (dd, *J* = 10.88, 9.85 Hz, 0H), 3.17 (dd, *J* = 10.60, 9.11 Hz, 1H), 3.04 (ddd, *J* = 13.02, 6.95, 1.20 Hz, 1H), 2.72 (dddd, *J* = 21.48, 13.26, 11.76, 6.16 Hz, 1H), 2.40 (t, *J* = 12.41 Hz, 0H), 2.23 (dd, *J* = 13.00, 11.00 Hz, 1H), 1.10 (dd, *J* = 6.48, 4.14 Hz, 4H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 151.9, 149.2, 143.9, 130.0, 129.3, 128.9, 128.3, 128.2, 127.9, 127.1, 125.6, 124.9, 119.6, 119.4, 76.7, 74.9, 58.2, 58.1, 54.1, 53.6, 32.5, 31.2, 17.0, 16.9; HRMS (EI-MS) *m/z* calcd for $C_{17}H_{17}NO_3S$ $[M]^+$ 315.0929, found 315.0928.

8.2 Synthesis and characterization for the compound 6b[5]



5a **6b**

In a dry flask under argon atmosphere, **5a** (31.3 mg, 0.1 mmol) was dissolved in CHCl3 (1 mL) and cooled to 0 ℃. Br_2 (47.9 mg, 0.3 mmol) was added slowly. The mixture was kept at 0 ℃ in the ice bath for 30 min. Then, the reaction mixture was warmed to room temperature, and stirred for 6 h. After completion of the reaction by checking TLC, the solvent was evaporated, and the product was isolated by silica gel column chromatography. The desired product **6b** was obtained in 91 % (43.0 mg) yield as a pale yellow solid.

2-Bromo-2-(bromomethyl)-10b-phenyl-1,2,3,10b-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine 5,5-dioxide (6a): Pale yellow solid (15.8 mg, yield: 91%); mp : 191–193 ℃ purification by silica gel chromatography (EtOAc:Hexane= 1:7, Rf= 0.50); For the mixture of major and minor, 1H NMR (300 MHz, Chloroform-*d*) δ 7.47 – 7.40 (m, 3H), 7.37 – 7.16 (m, 17H), 7.02 (ddd, J = 8.06, 5.29, 1.21 Hz, 2H), 4.44 (d, J = 13.18 Hz, 1H), 4.24 (d, J = 13.18 Hz, 1H), 4.12 (d, J = 11.94 Hz, 1H), 3.93 – 3.80 (m, 3H), 3.72 (d, J = 2.53 Hz, 3H), 3.59 – 3.48 (m, 2H), 3.42 (dd, J = 15.74, 0.97 Hz, 1H), 3.15 (d, J = 15.37 Hz, 1H). For the mixture of major and minor 13C{1H} (75 MHz, Chloroform-*d*) δ 151.4, 149.8, 142.2, 130.5, 130.4, 130.0, 129.4, 128.5, 128.4, 128.3, 127.6, 127.2, 125.8, 12 4.9, 122.8, 122.1, 119.7, 119.5, 76.2, 76.0, 64.3, 63.9, 61.4, 59.8, 58.5, 39.6, 39.2.; HRMS (EI-MS) m/z calcd for C17H17NO3S [M]+ 315.0929, found 315.0928.

9. References

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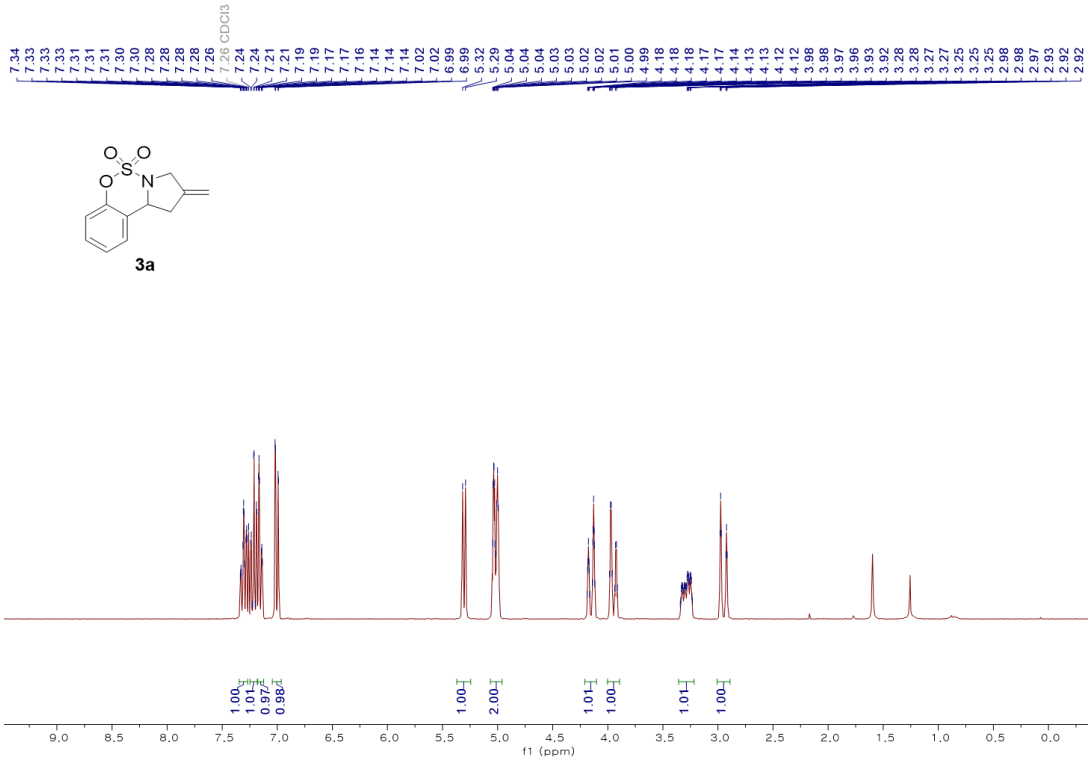
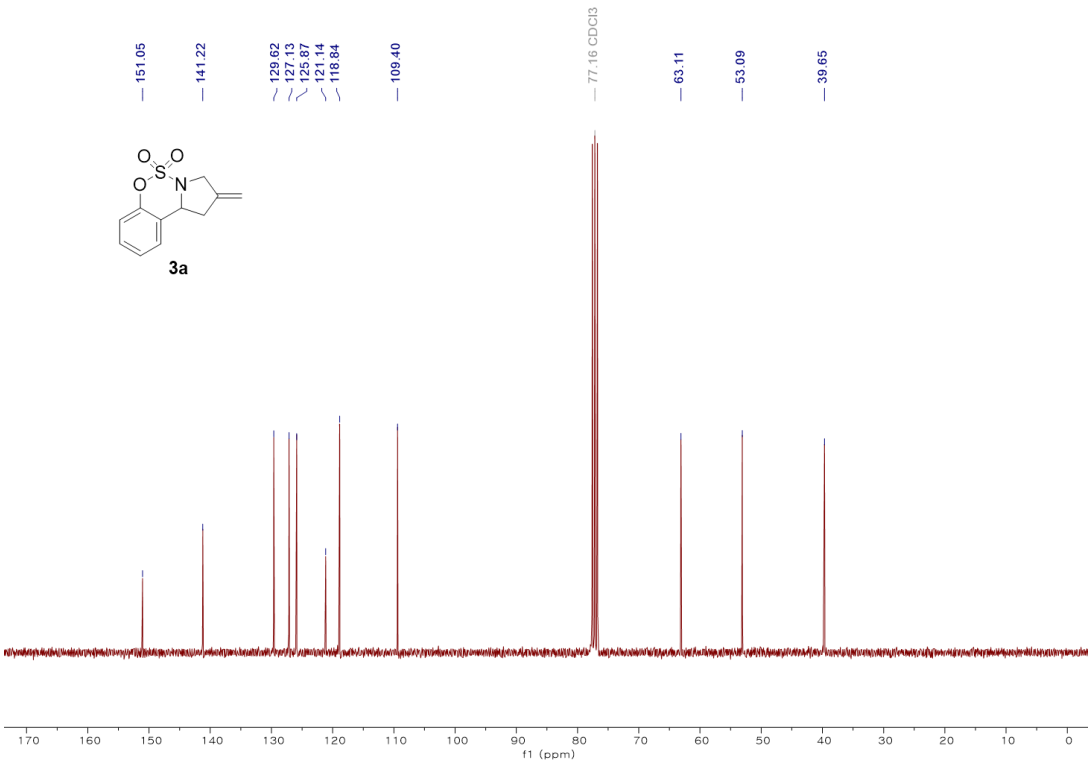
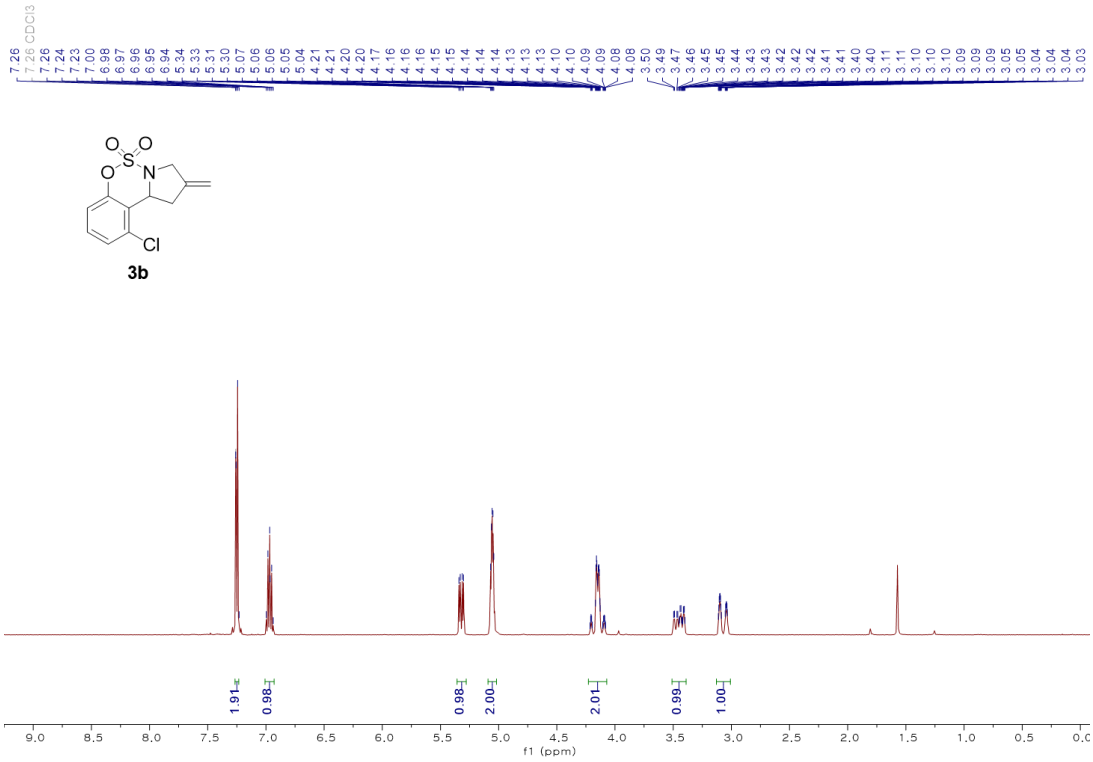
10. ^{1}H, ^{13}C and ^{19}F NMR Spectra for all compounds



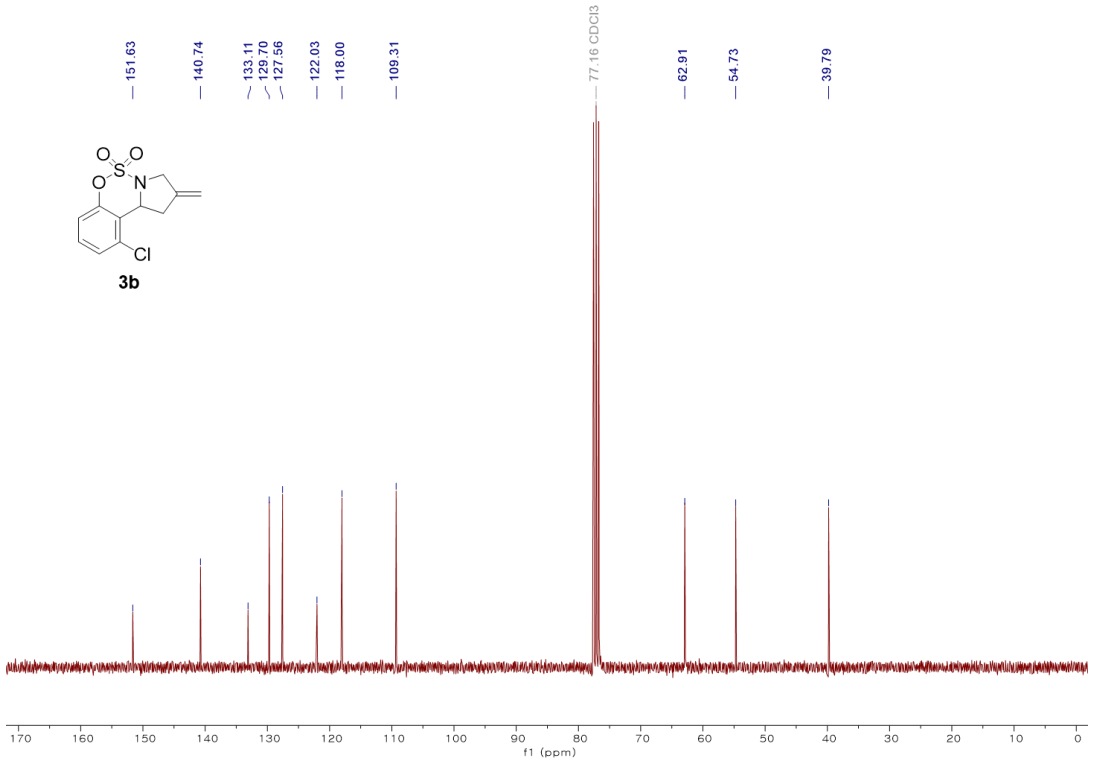
^{1}H Spectrum of **3a** in Chloroform-*d* (300 MHz)



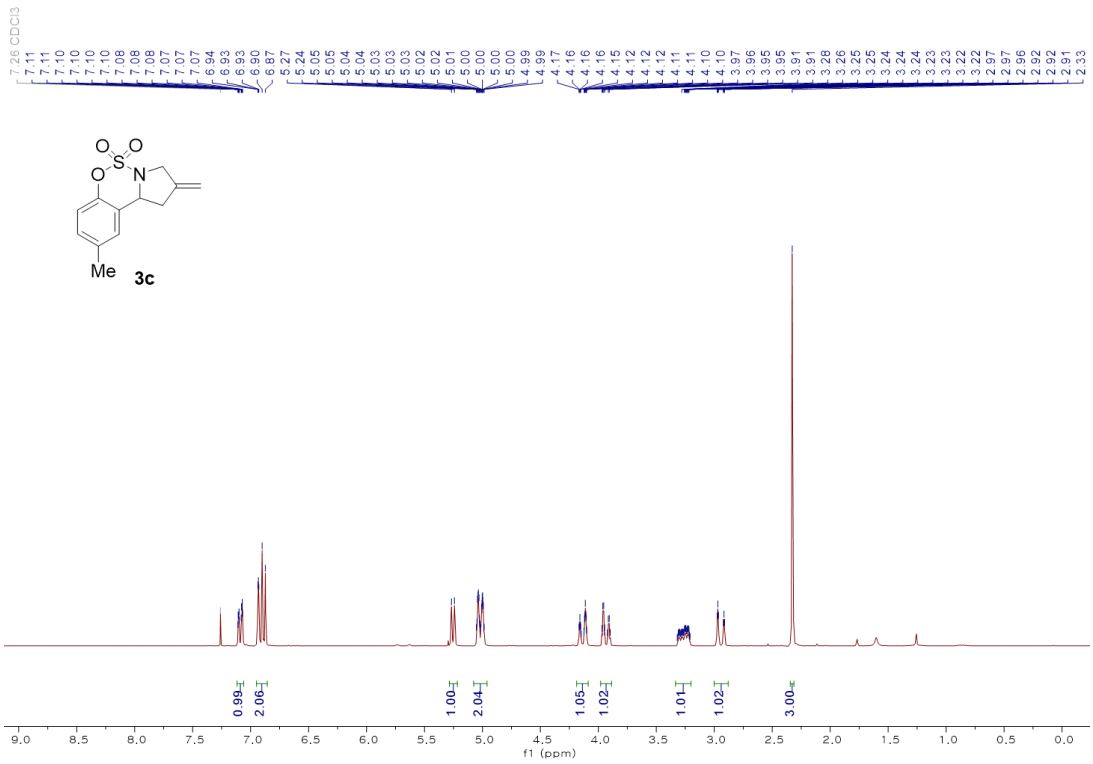
^{13}C Spectrum of **3a** in Chloroform-*d* (75 MHz)



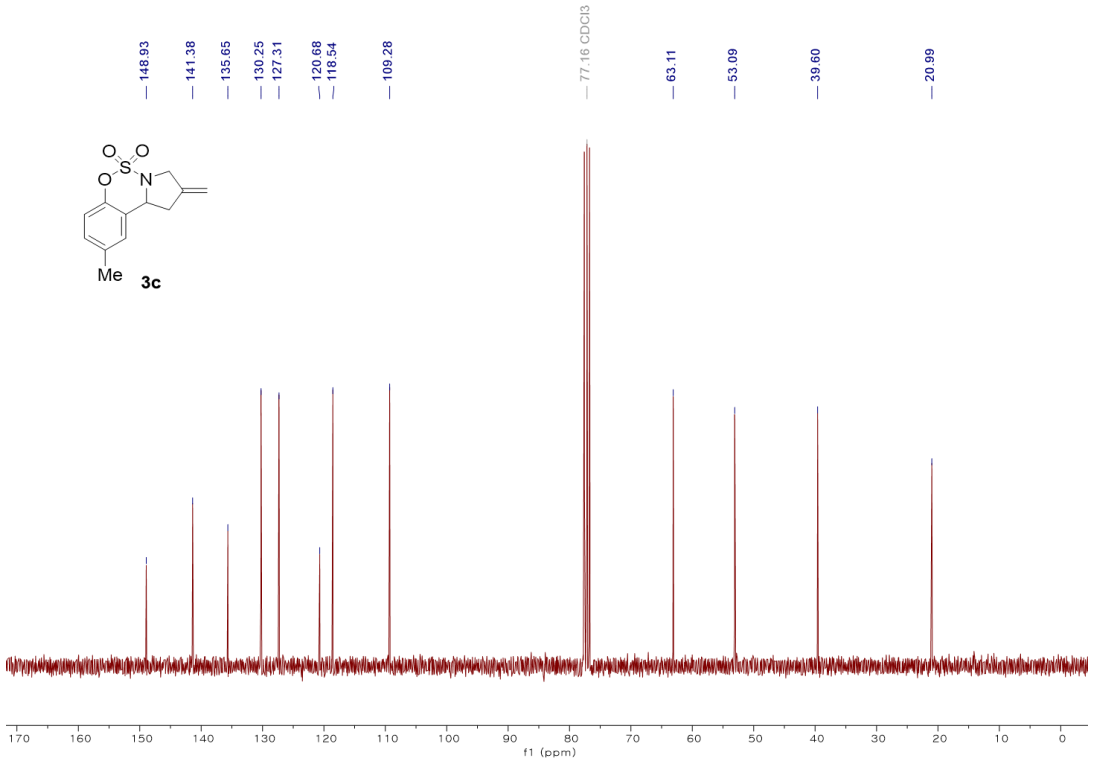
^{1}H Spectrum of **3b** in Chloroform-*d* (300 MHz)



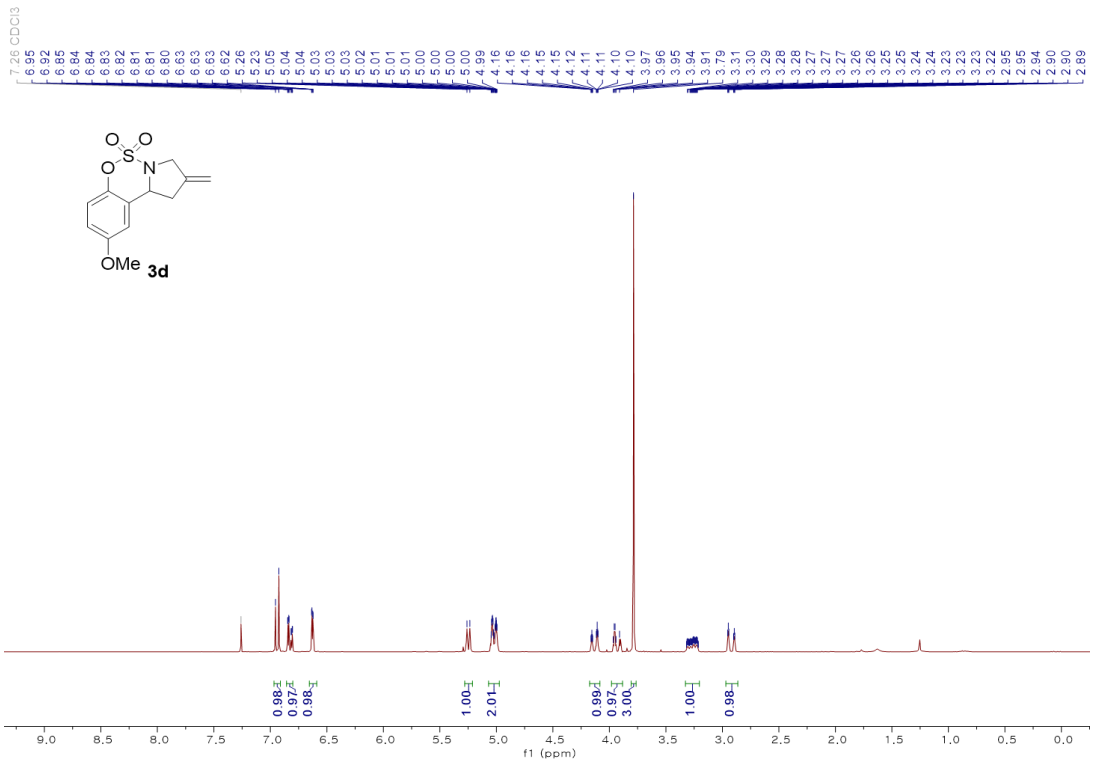
^{13}C Spectrum of **3b** in Chloroform-*d* (75 MHz)



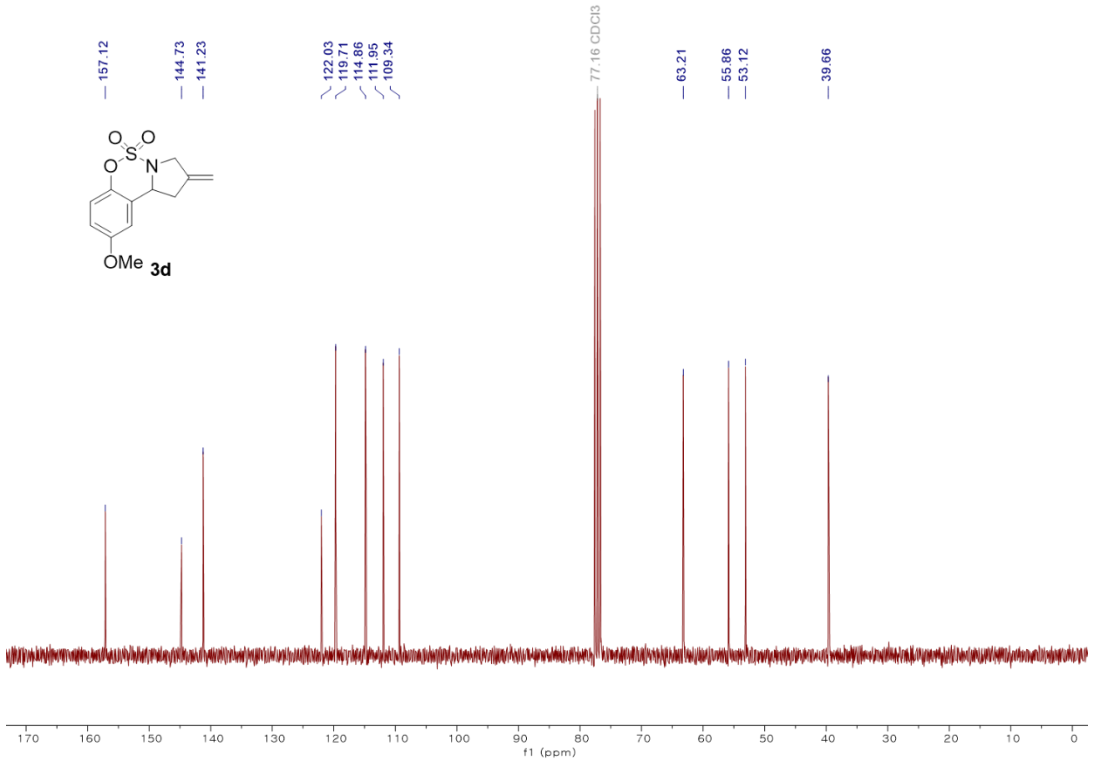
^{1}H Spectrum of **3c** in Chloroform-*d* (300 MHz)



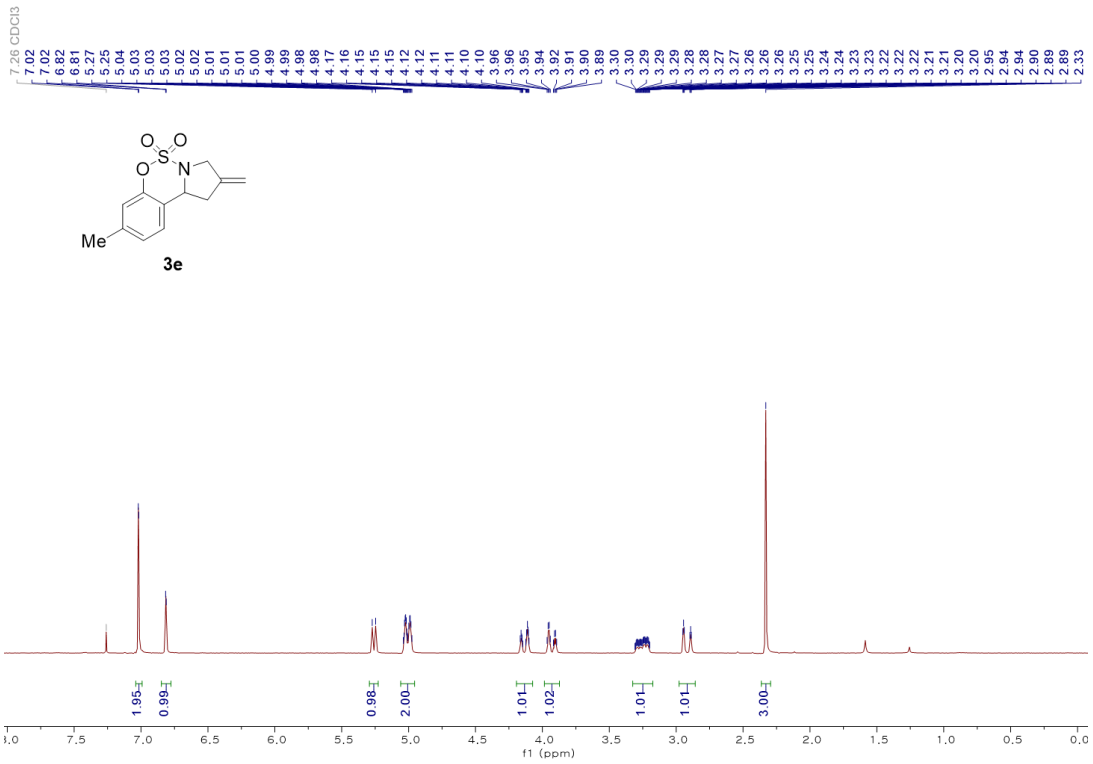
^{13}C Spectrum of **3c** in Chloroform-*d* (75 MHz)



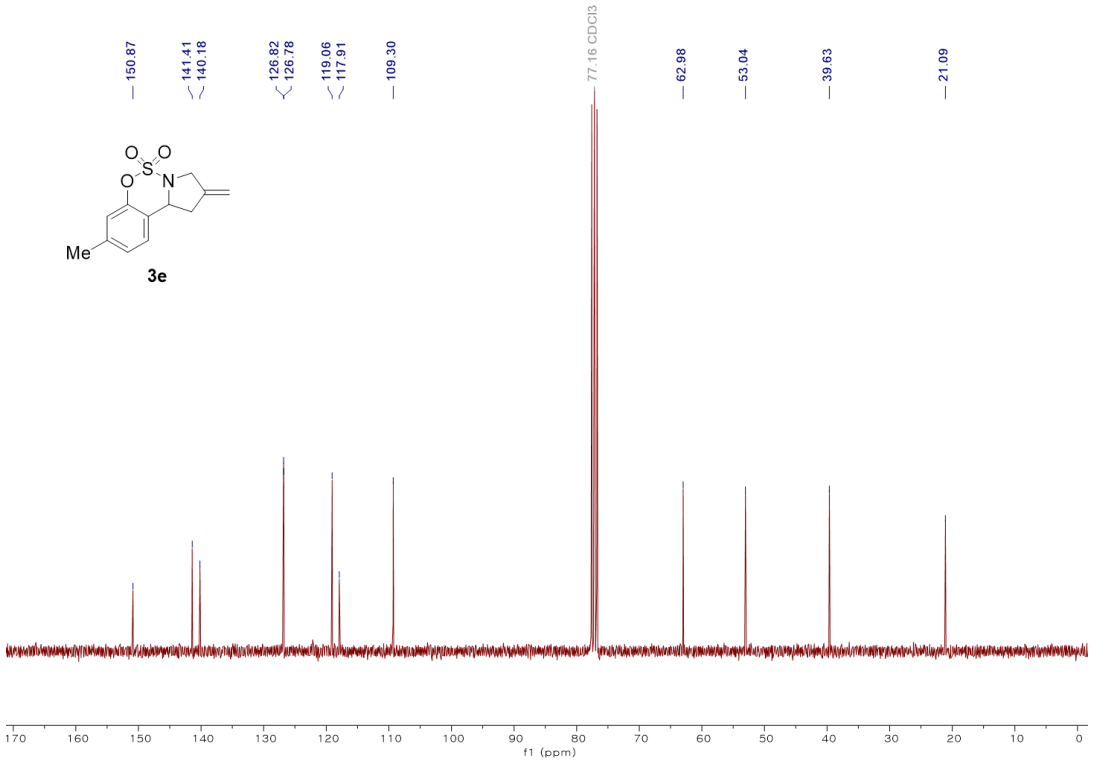
^{1}H Spectrum of **3d** in Chloroform-*d* (300 MHz)



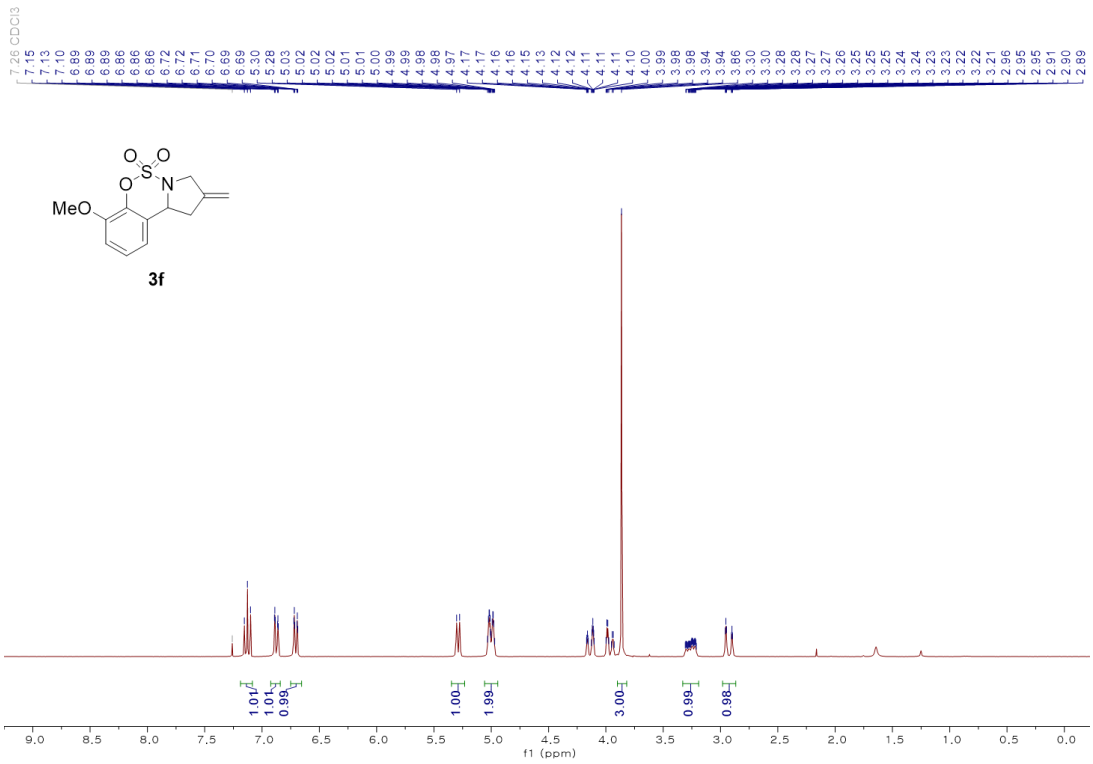
^{13}C Spectrum of **3d** in Chloroform-*d* (75 MHz)



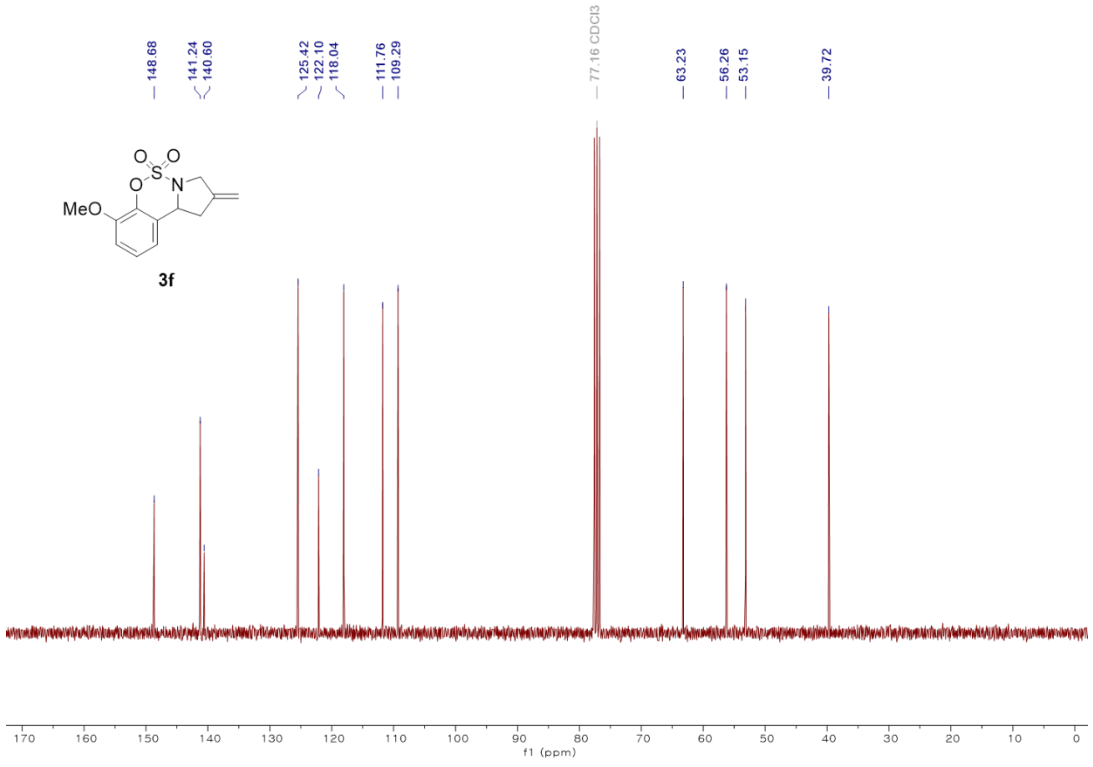
^{1}H Spectrum of **3e** in Chloroform-*d* (300 MHz)



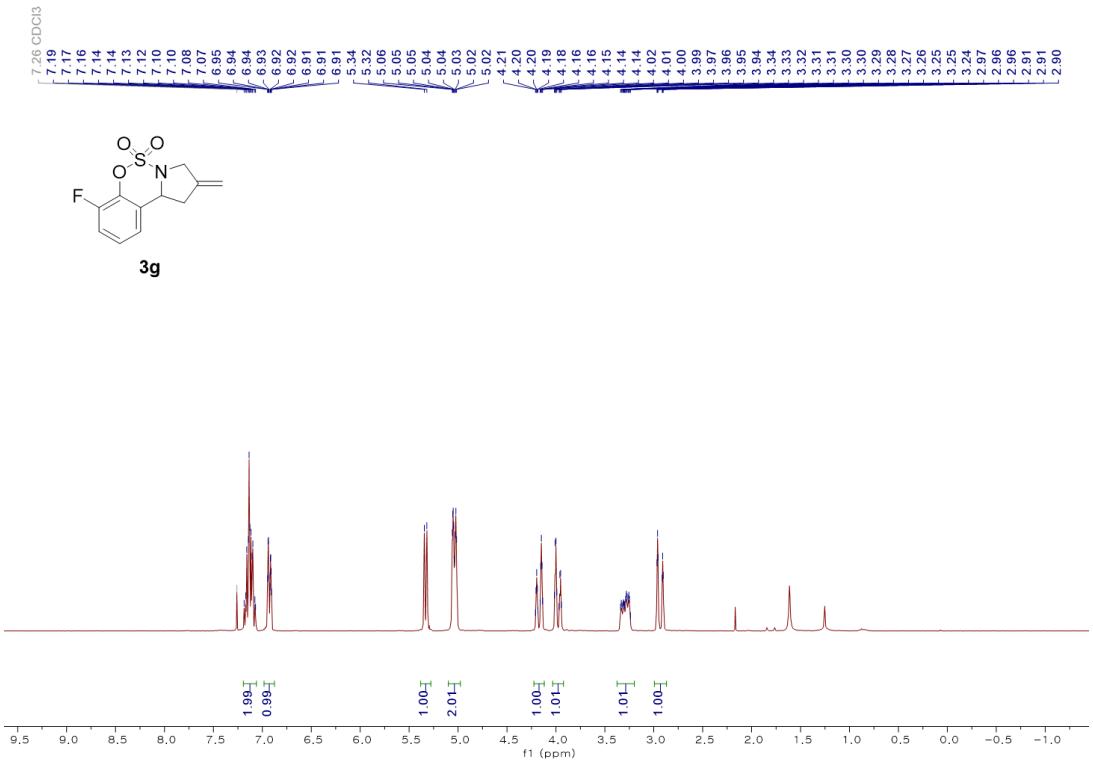
^{13}C Spectrum of **3e** in Chloroform-*d* (75 MHz)



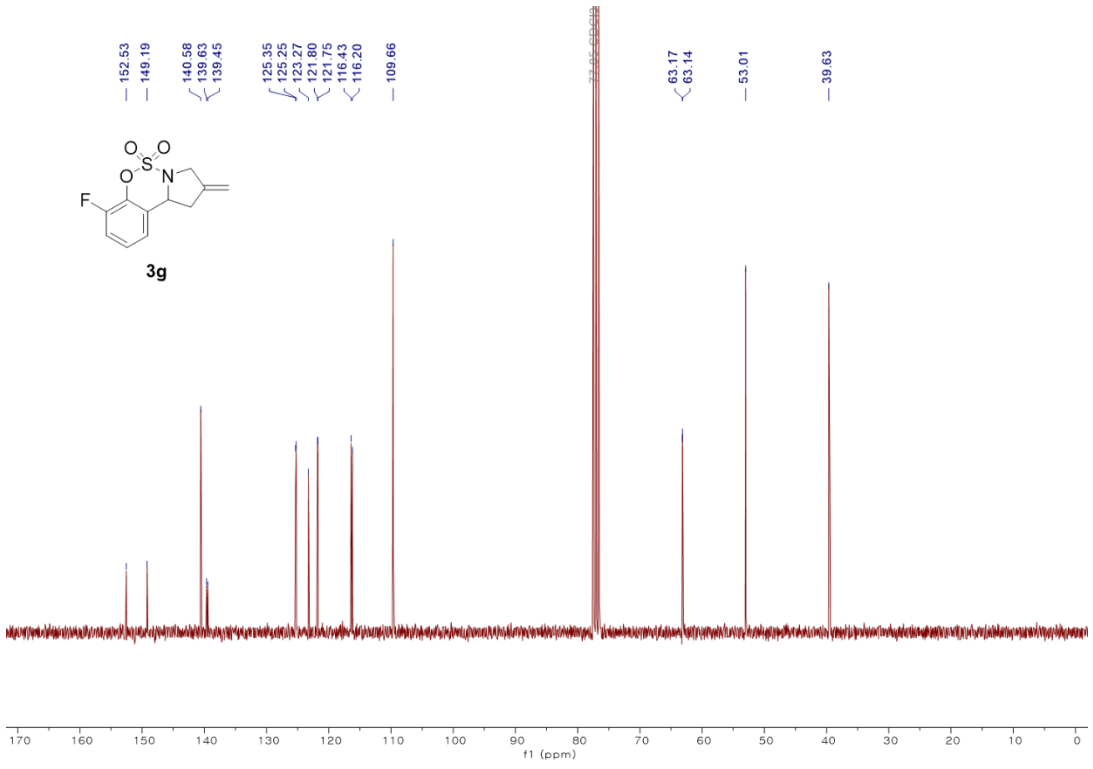
^{1}H Spectrum of **3f** in Chloroform-*d* (300 MHz)



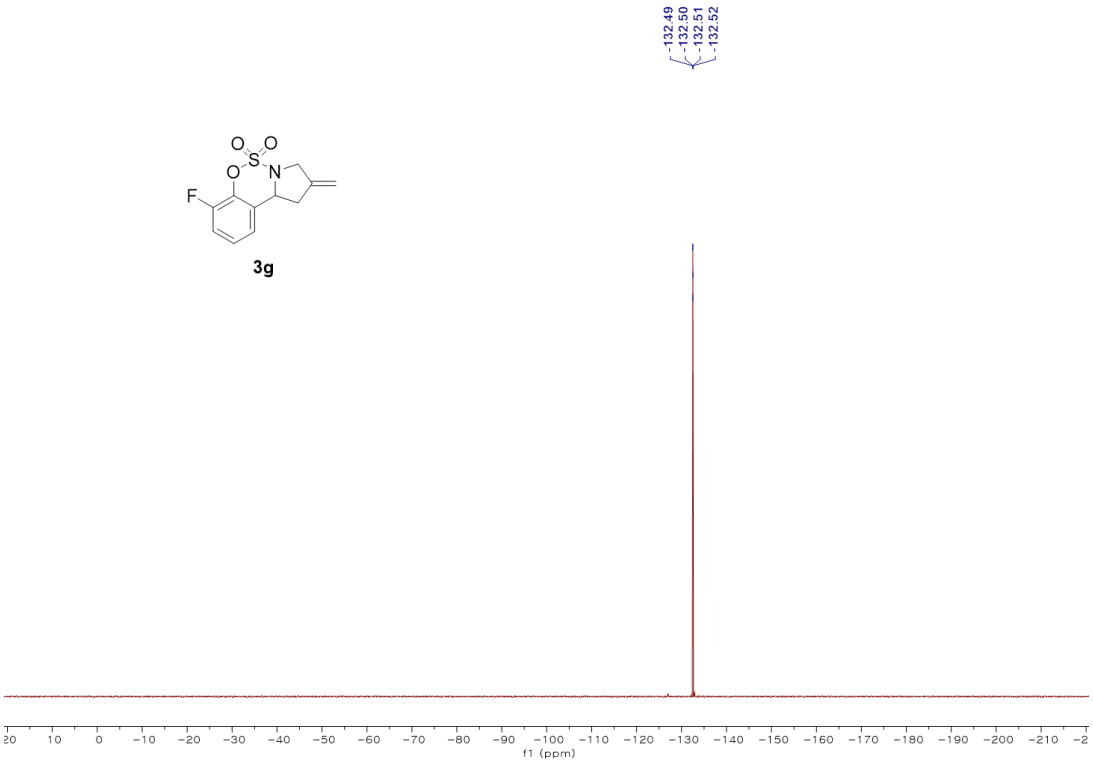
^{13}C Spectrum of **3f** in Chloroform-*d* (75 MHz)



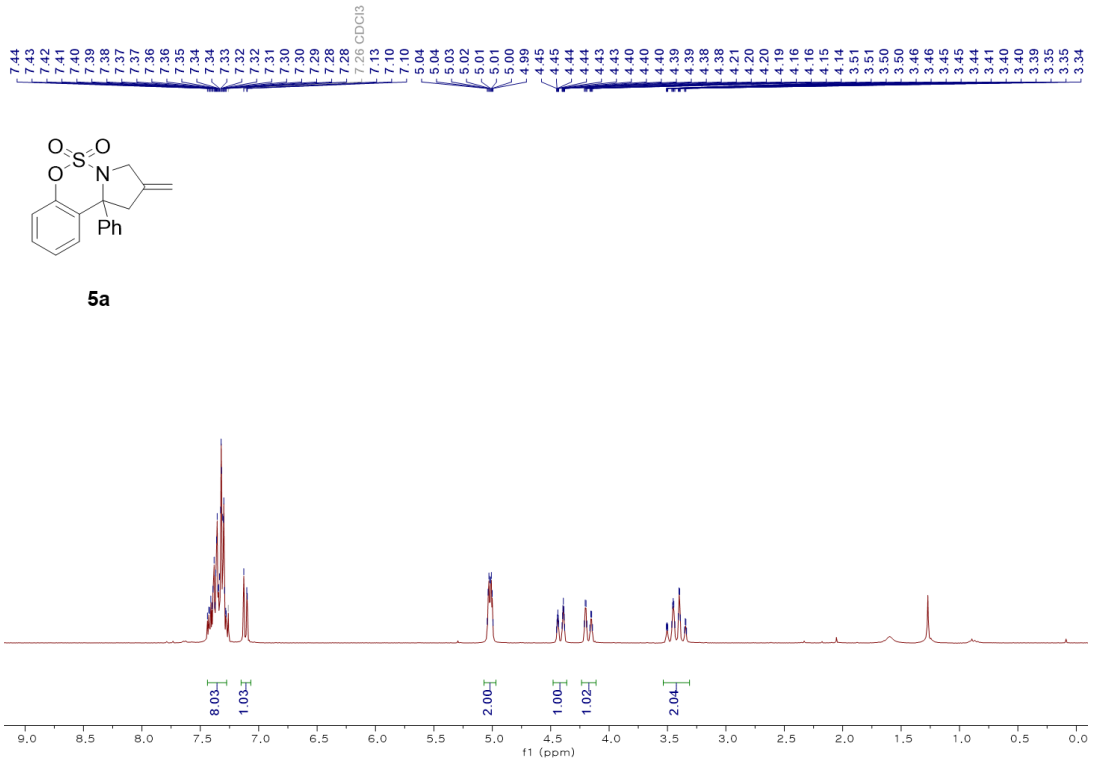
^{1}H Spectrum of **3g** in Chloroform-*d* (300 MHz)



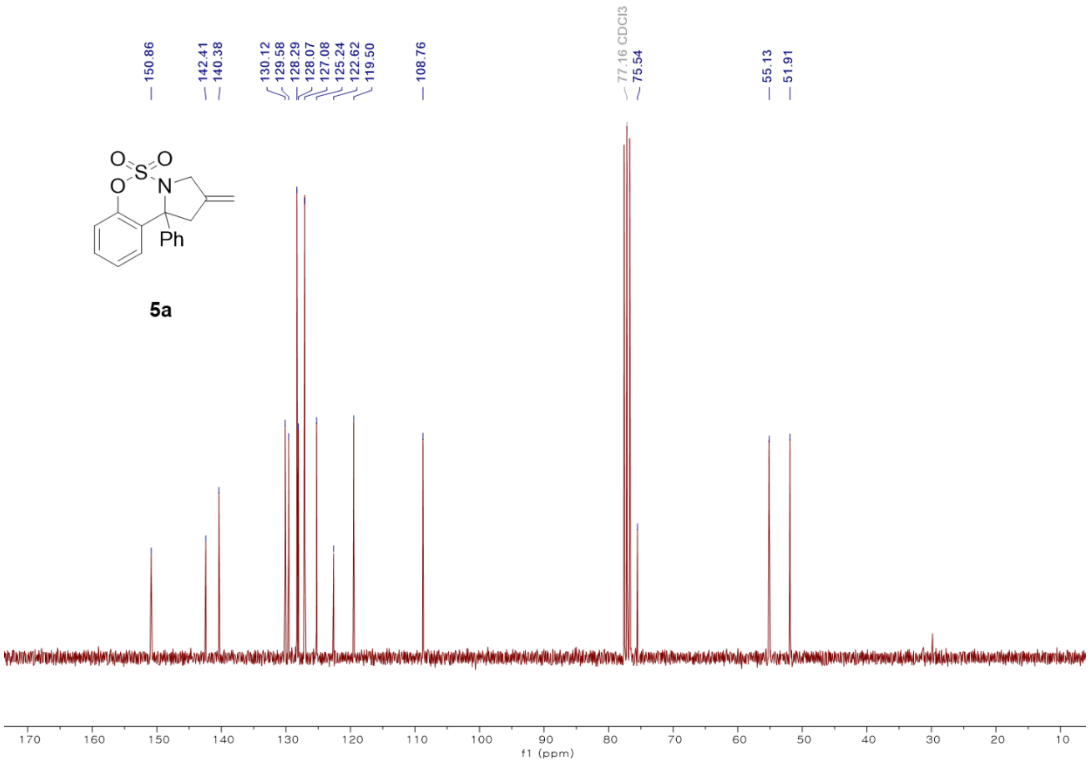
^{13}C Spectrum of **3g** in Chloroform-*d* (75 MHz)



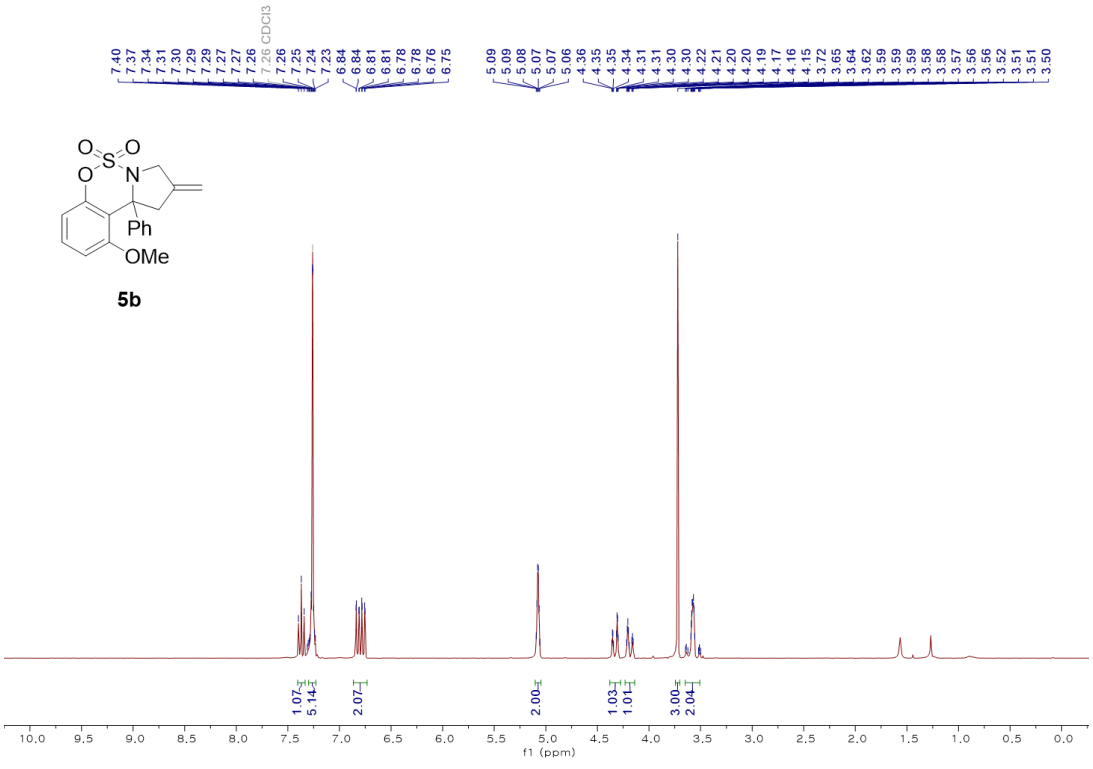
^{19}F Spectrum of **3g** in Chloroform-*d* (471 MHz)



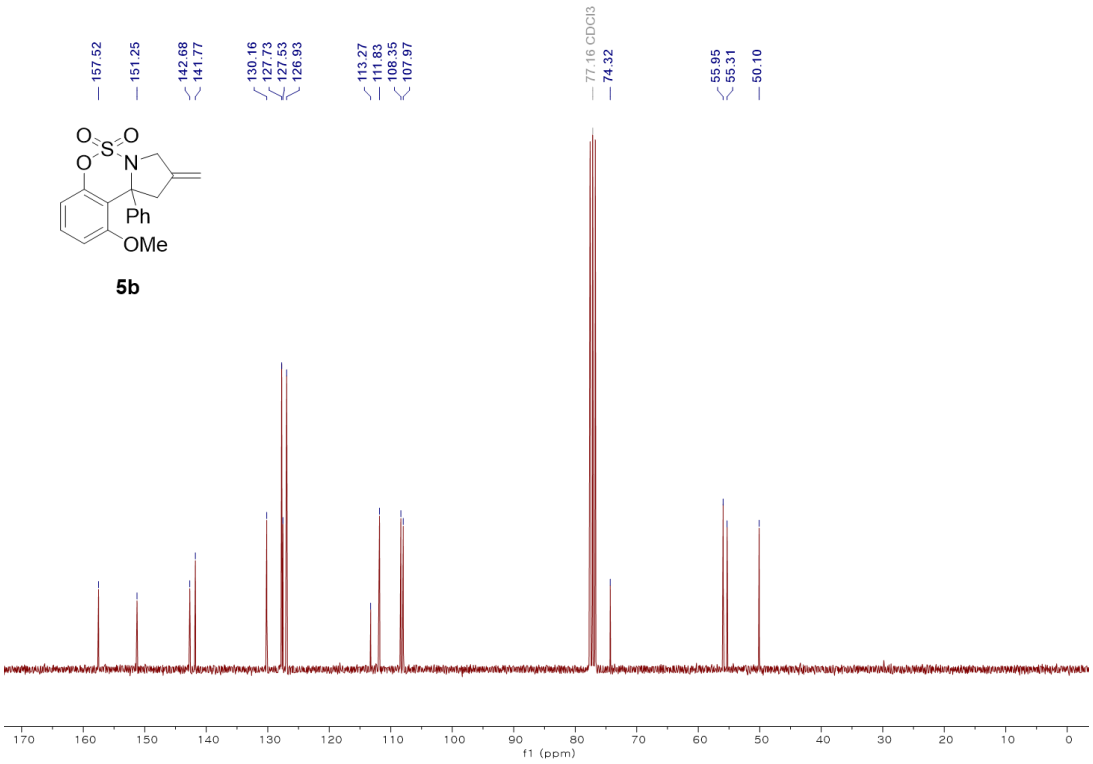
^{1}H Spectrum of **5a** in Chloroform-*d* (300 MHz)



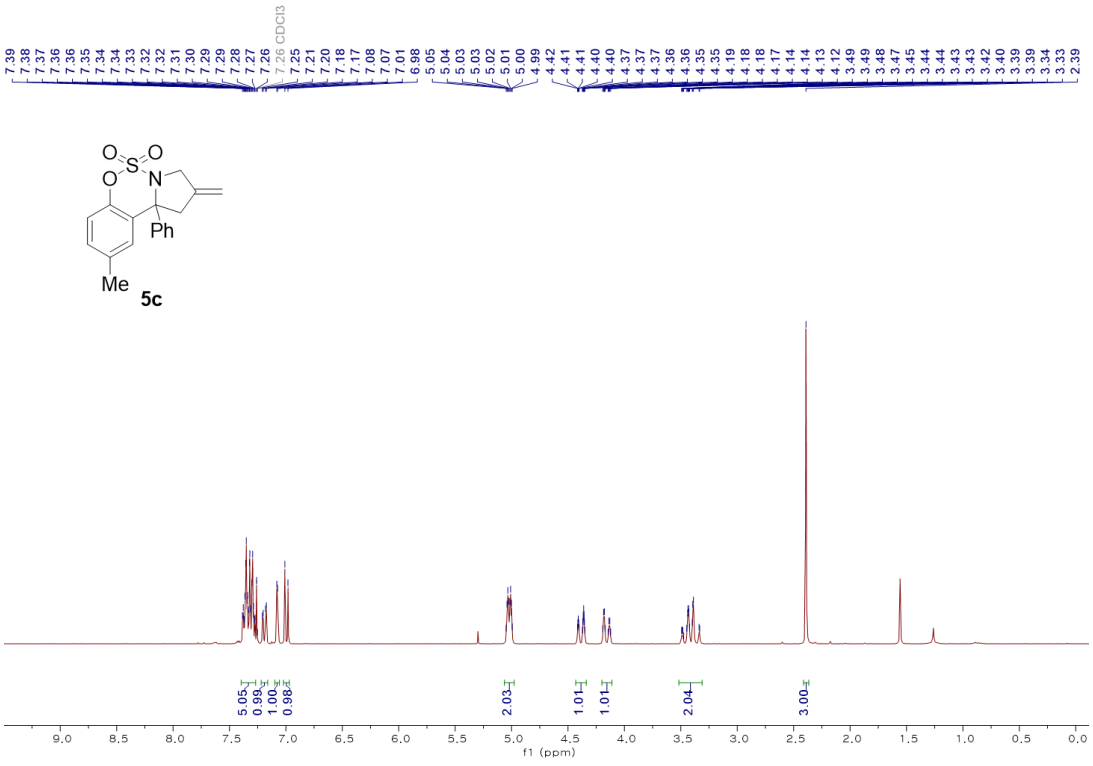
^{13}C Spectrum of **5a** in Chloroform-*d* (75 MHz)



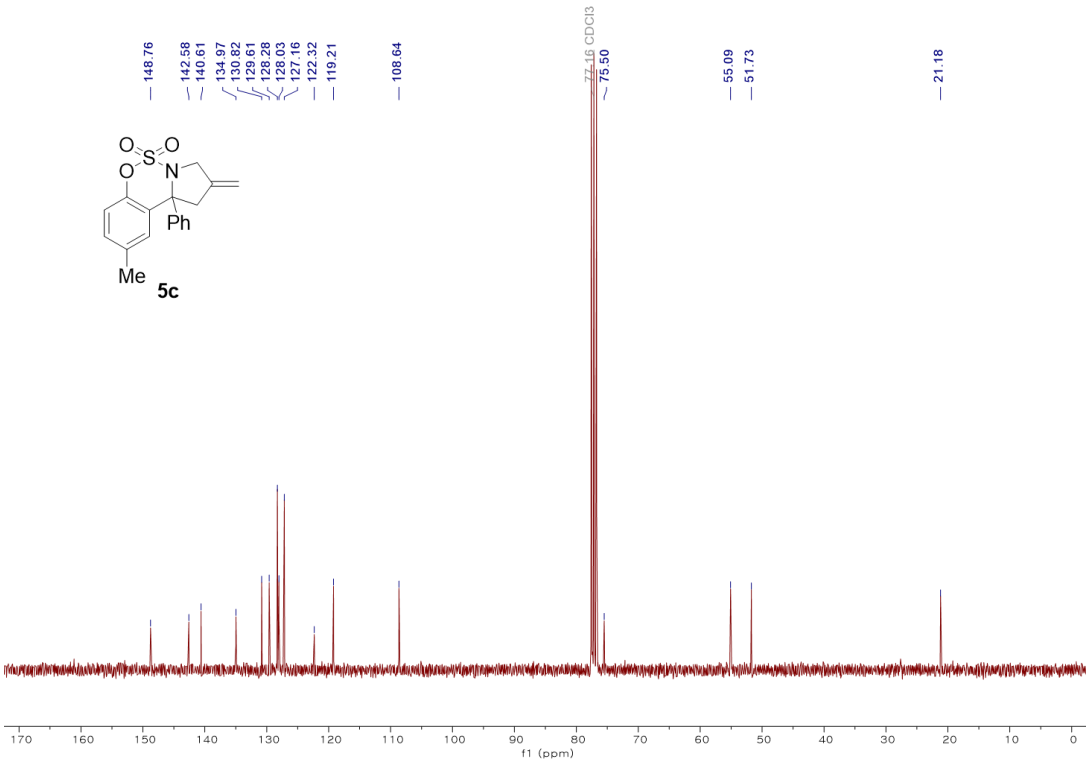
^{1}H Spectrum of **5b** in Chloroform-*d* (300 MHz)



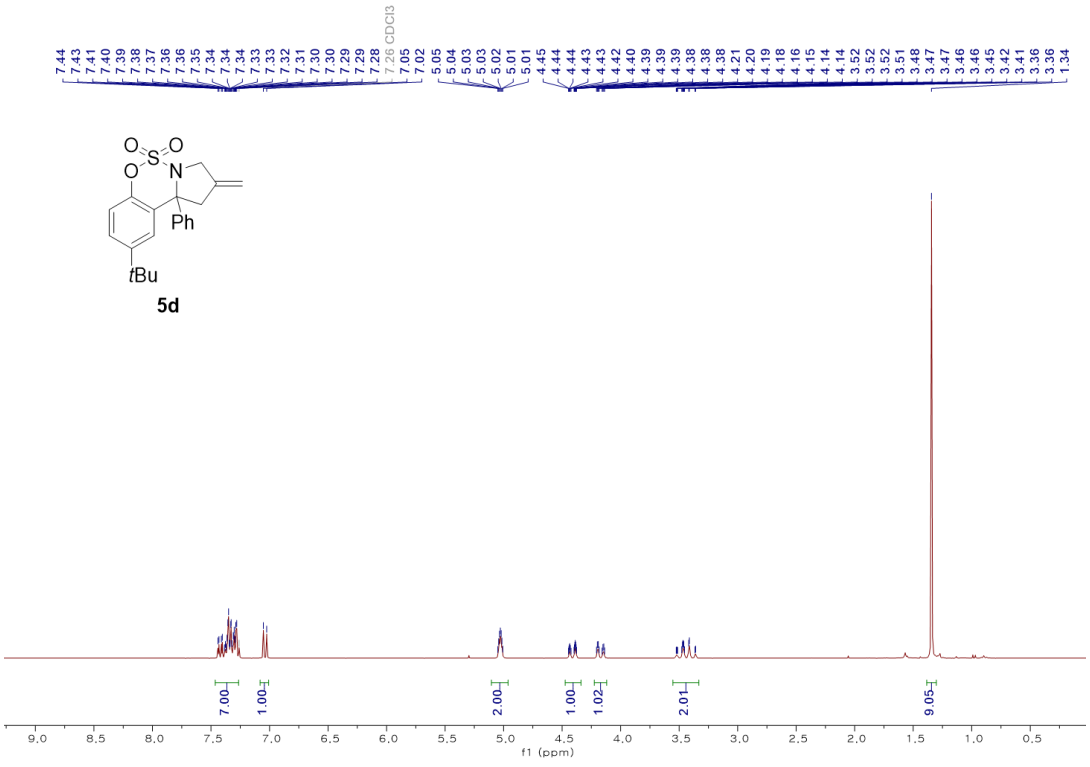
^{13}C Spectrum of **5b** in Chloroform-*d* (75 MHz)



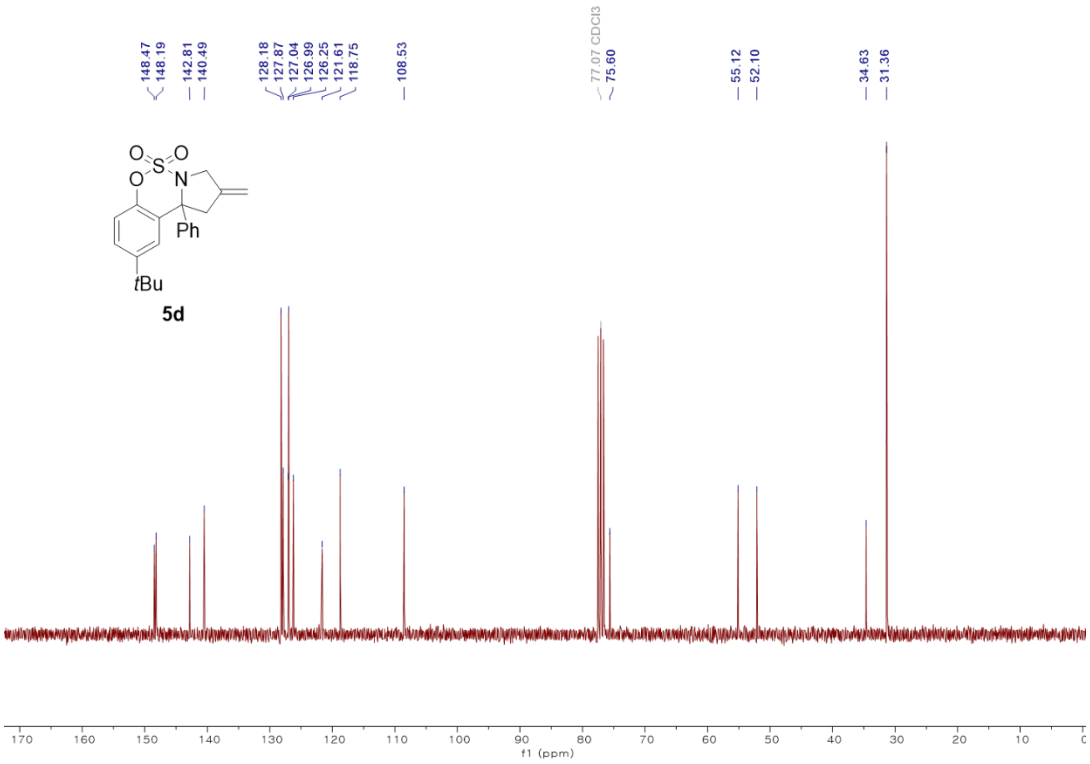
^{1}H Spectrum of **5c** in Chloroform-*d* (300 MHz)



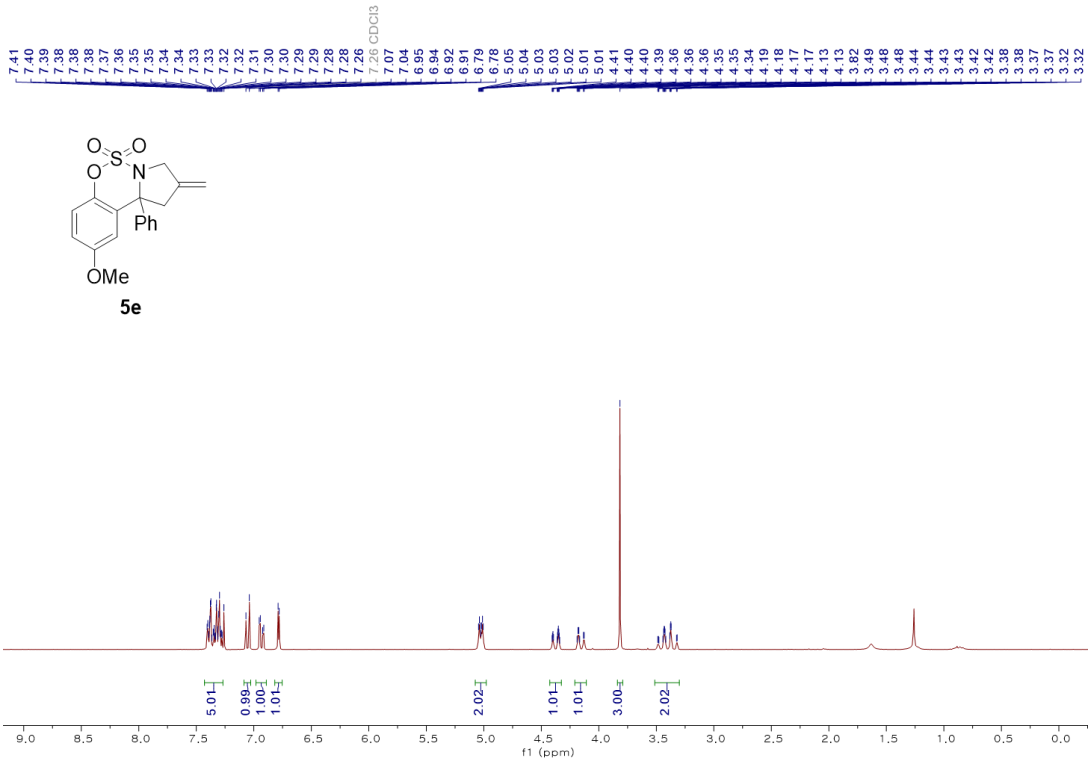
^{13}C Spectrum of **5c** in Chloroform-*d* (75 MHz)



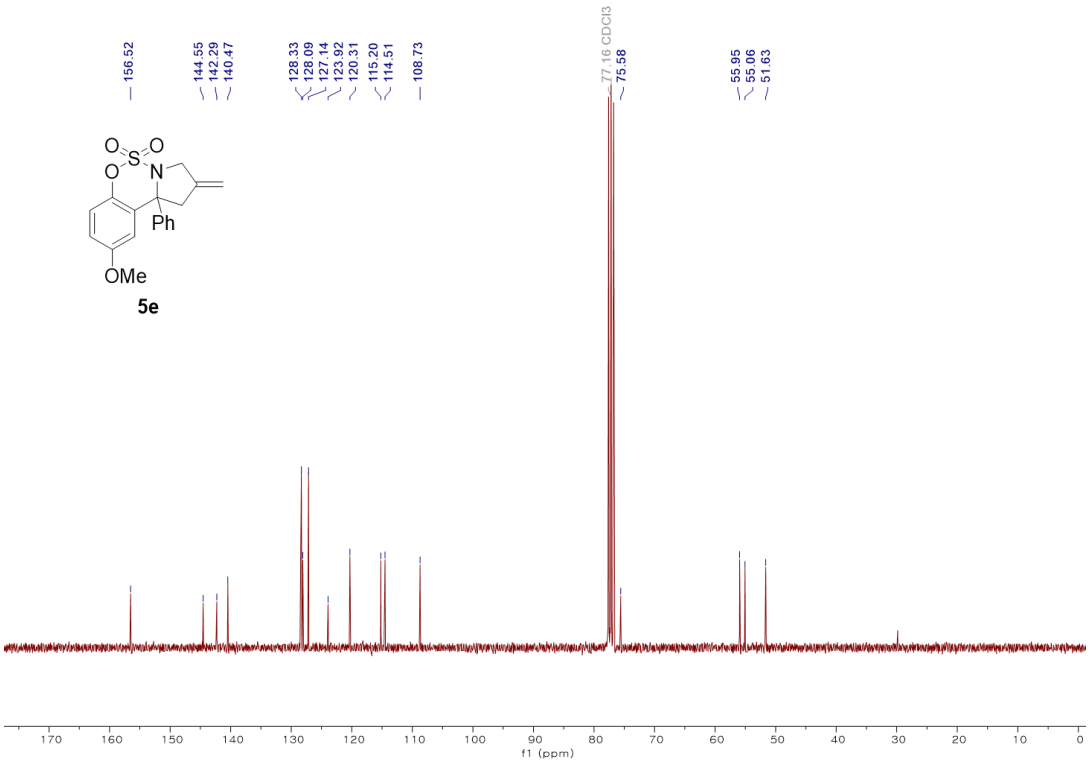
^{1}H Spectrum of **5d** in Chloroform-*d* (300 MHz)



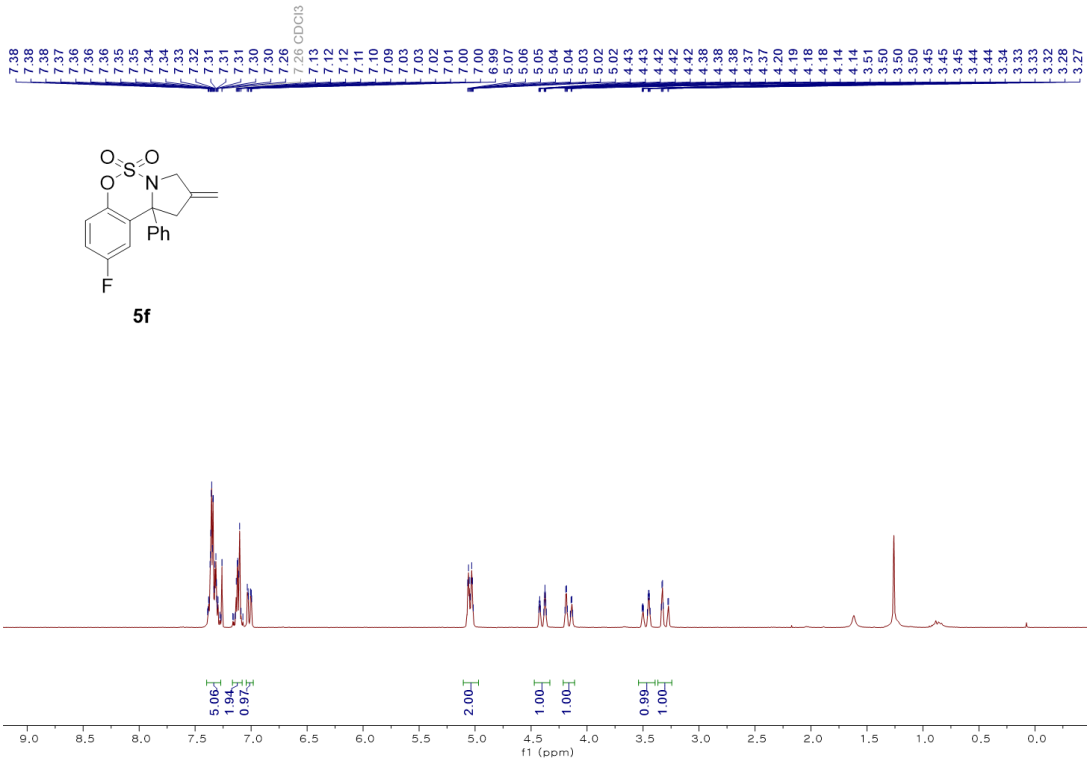
^{13}C Spectrum of **5d** in Chloroform-*d* (75 MHz)



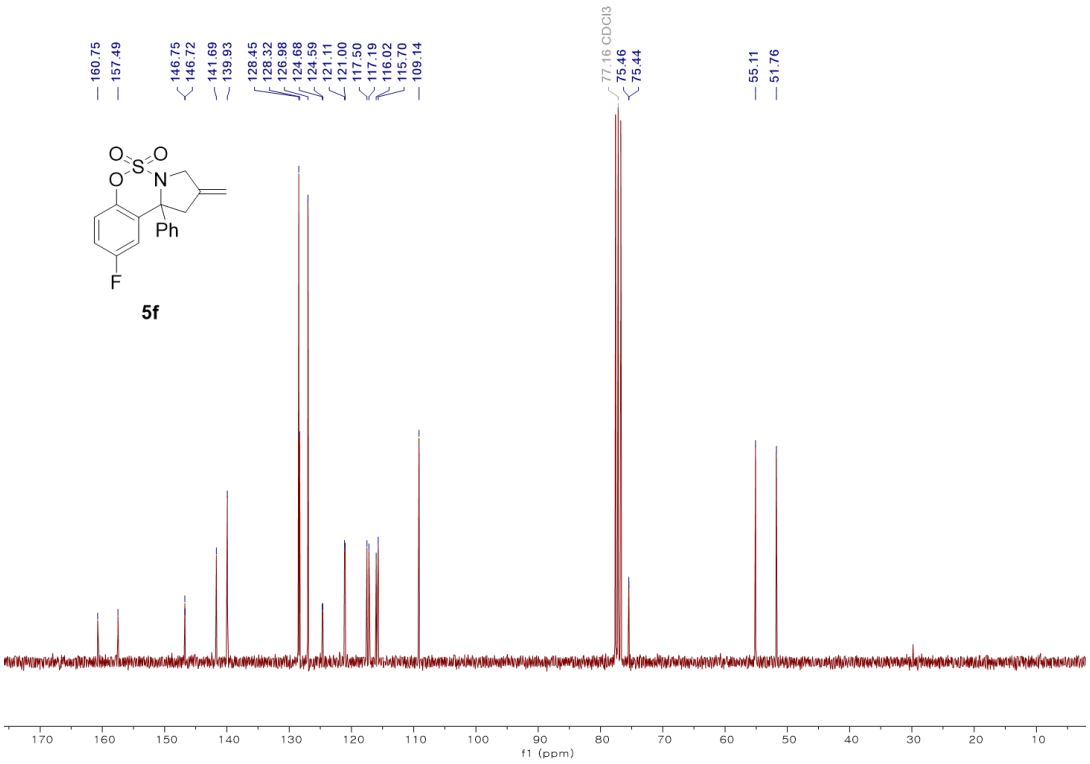
^{1}H Spectrum of **5e** in Chloroform-*d* (300 MHz)



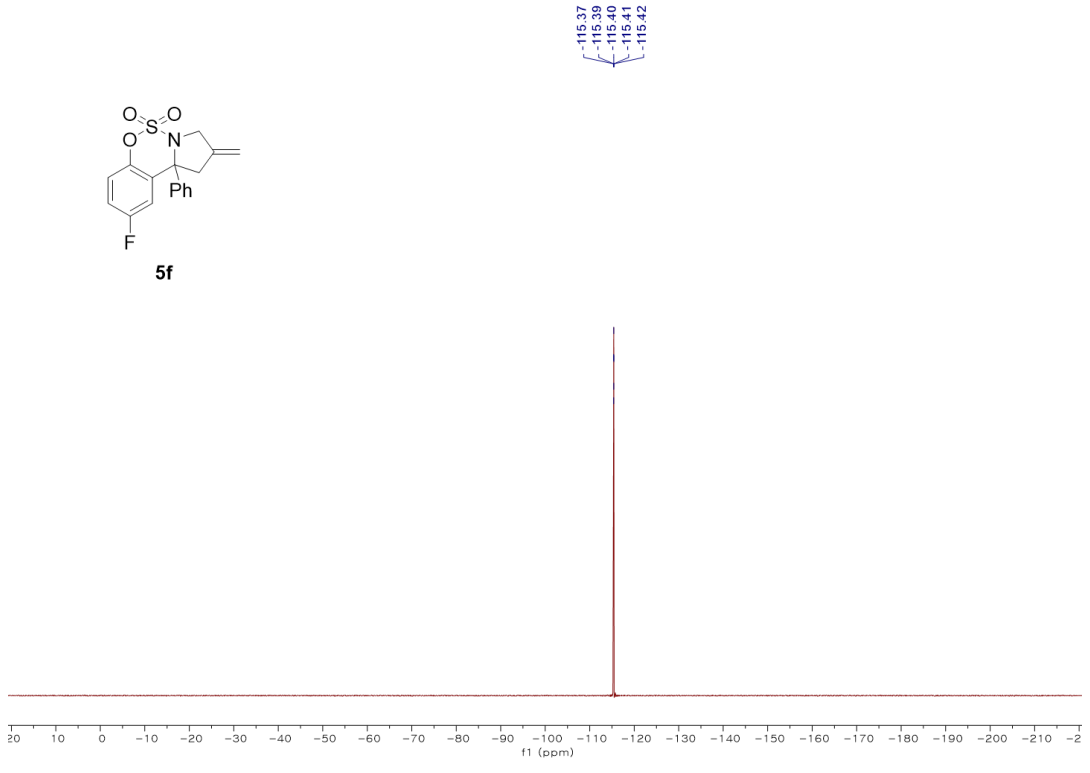
^{13}C Spectrum of **5e** in Chloroform-*d* (75 MHz)



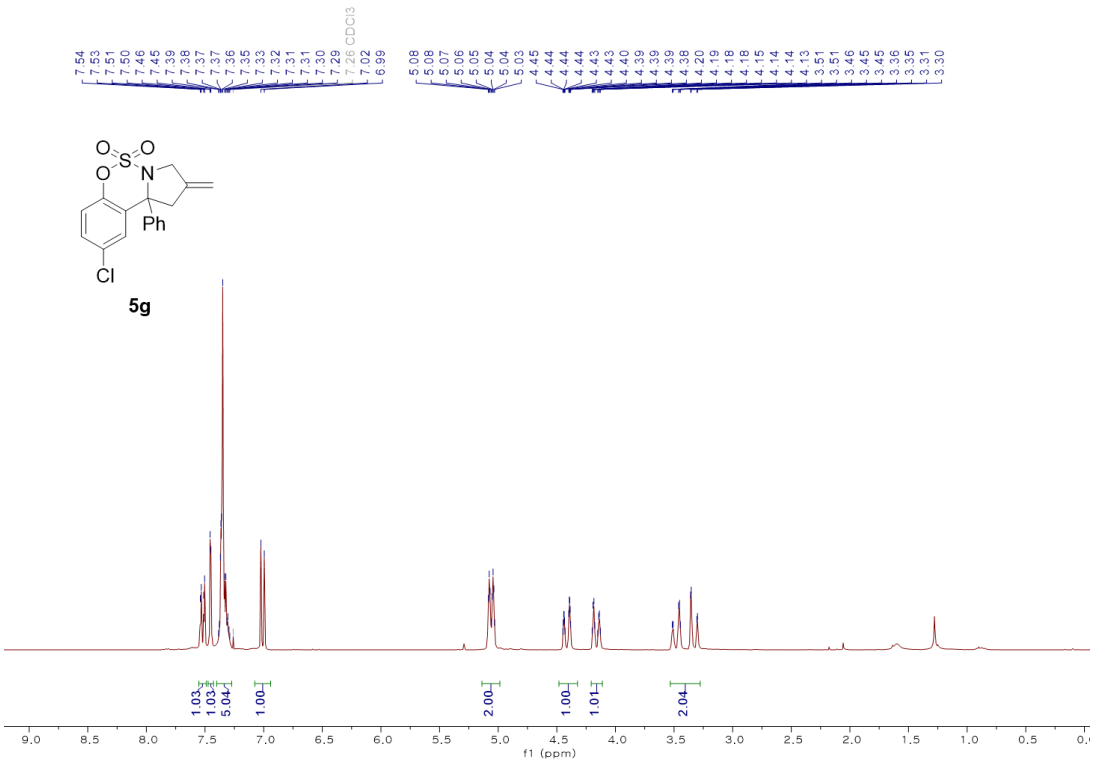
^{1}H Spectrum of **5f** in Chloroform-*d* (300 MHz)



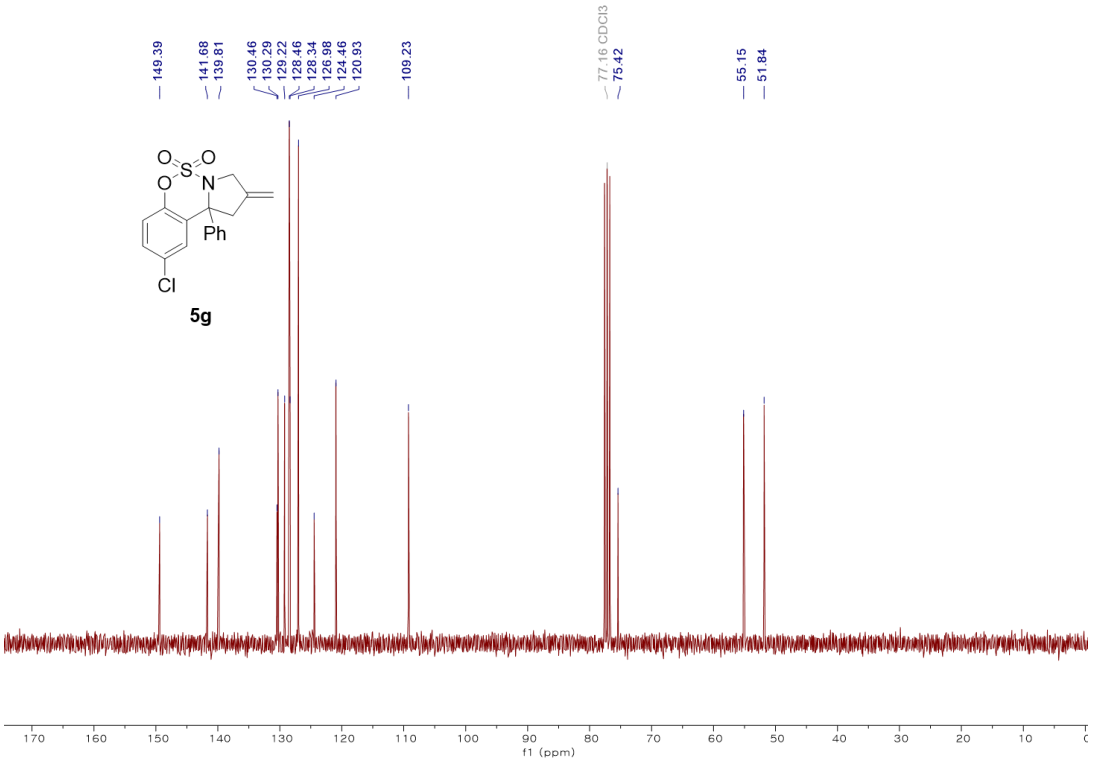
^{13}C Spectrum of **5f** in Chloroform-*d* (75 MHz)



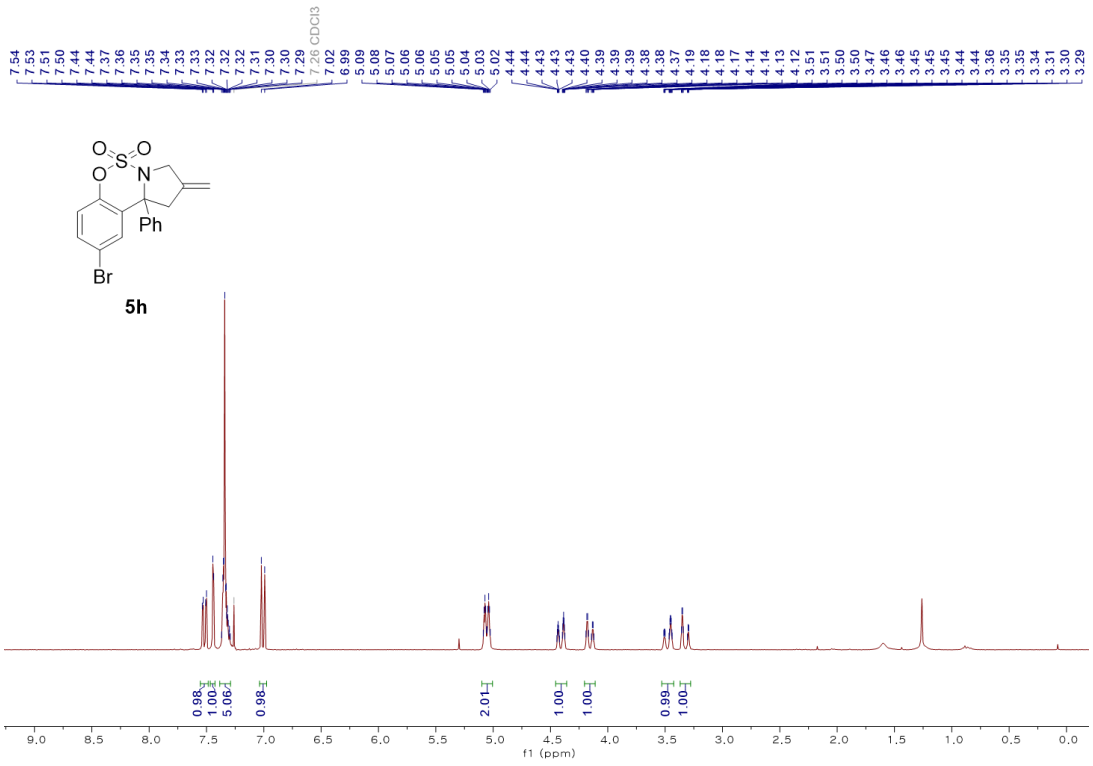
^{19}F Spectrum of **5f** in Chloroform-*d* (471 MHz)



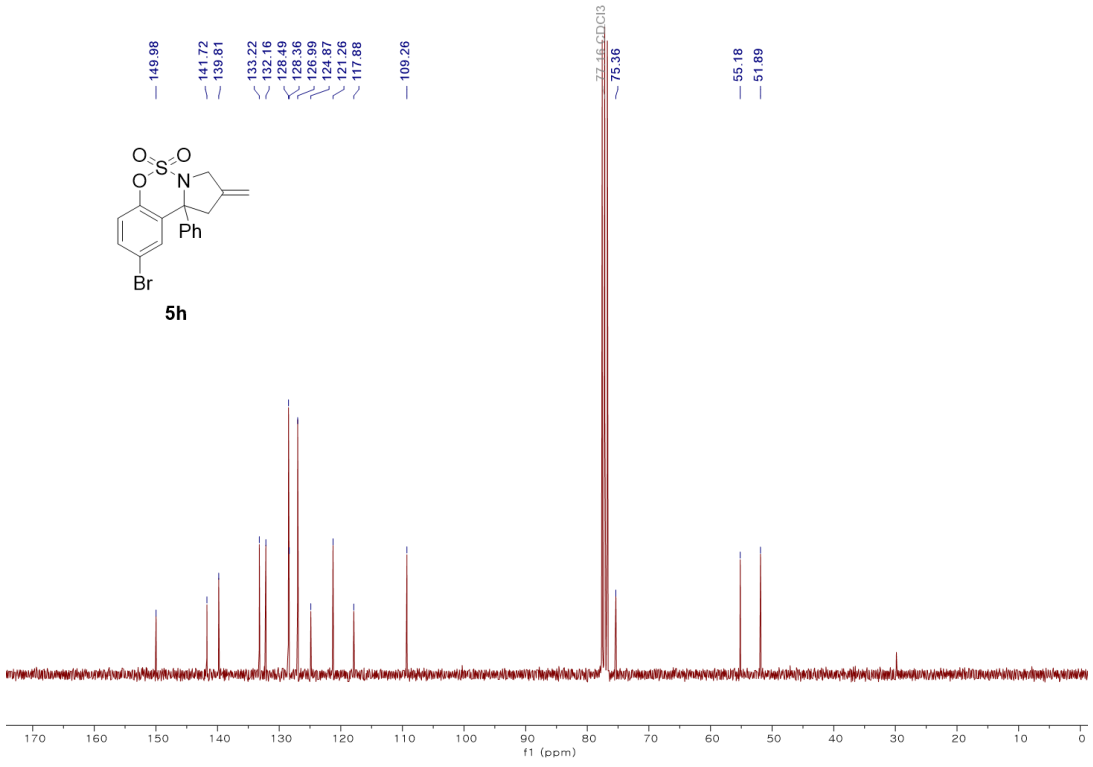
^{1}H Spectrum of **5g** in Chloroform-*d* (300 MHz)



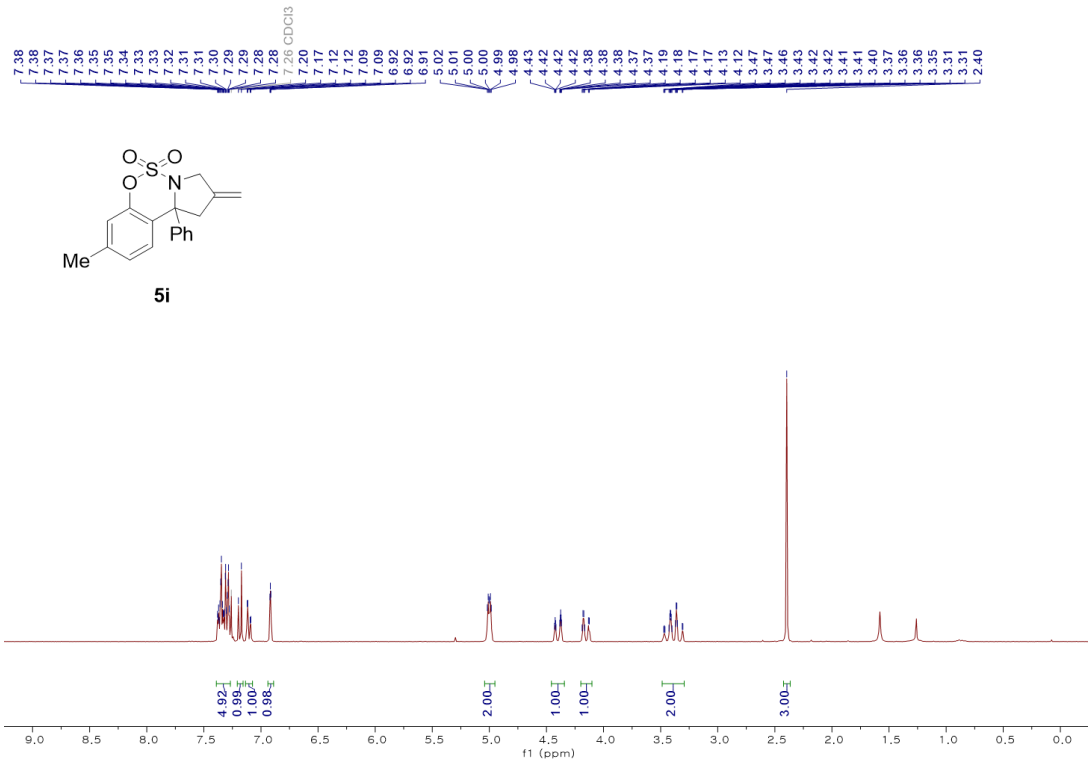
^{13}C Spectrum of **5g** in Chloroform-*d* (75 MHz)



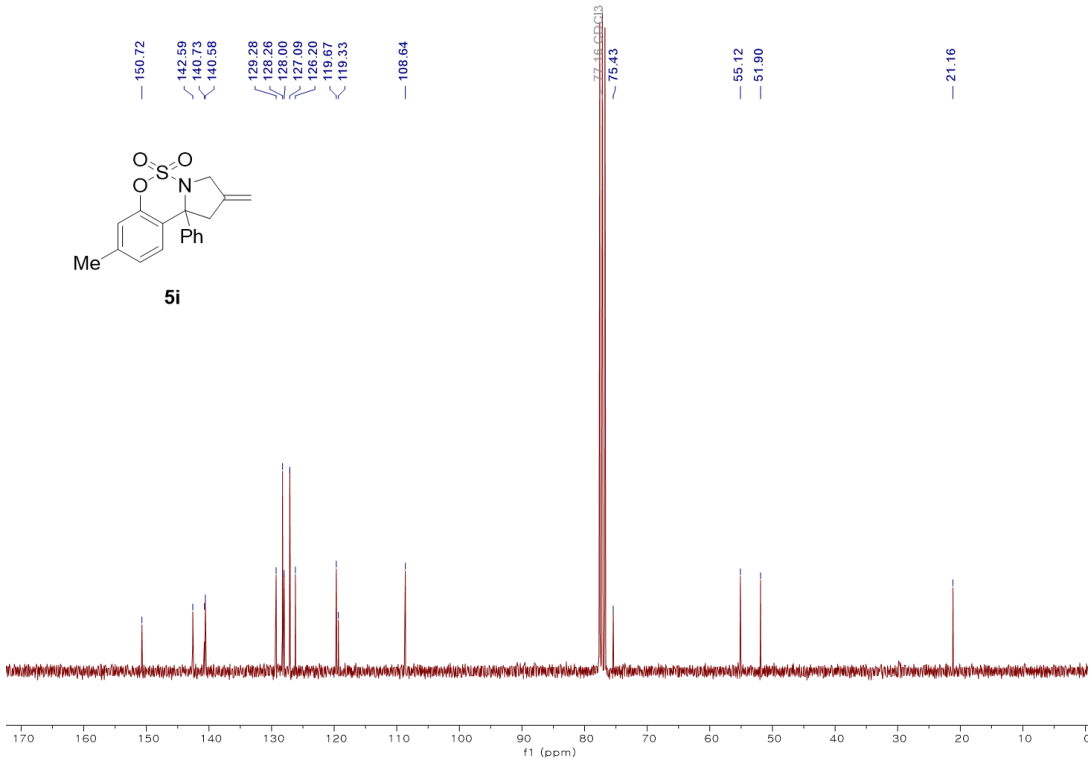
^{1}H Spectrum of **5h** in Chloroform-*d* (300 MHz)



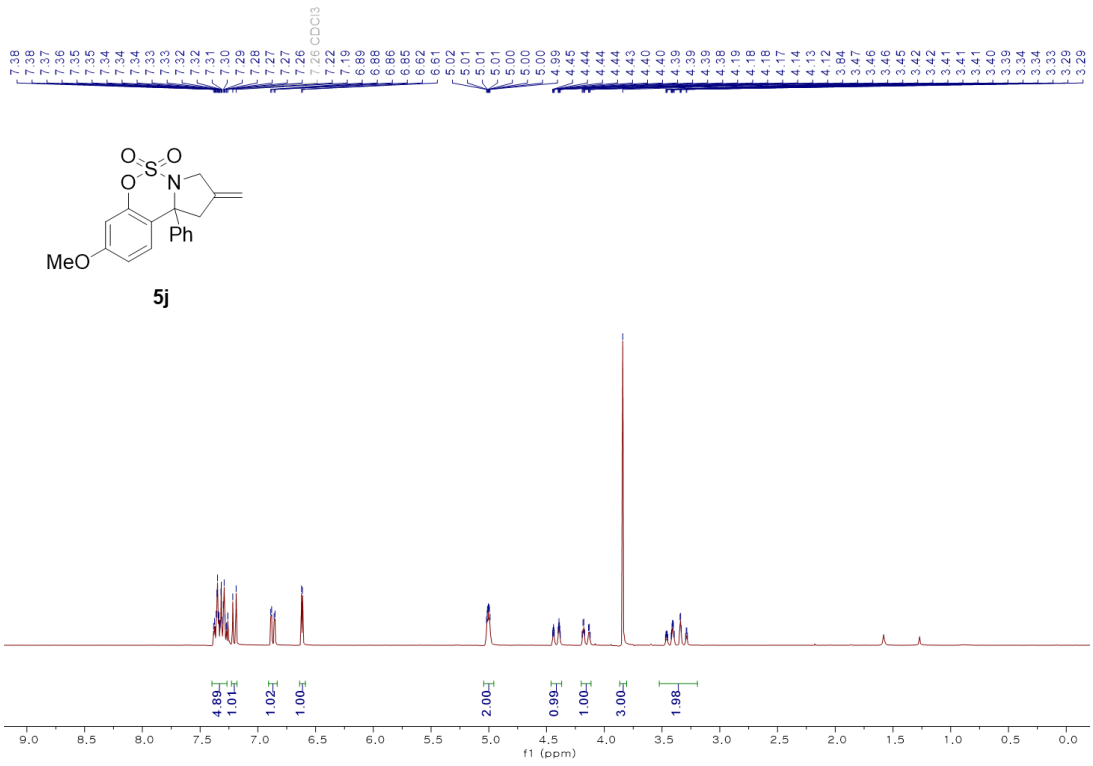
^{13}C Spectrum of **5h** in Chloroform-*d* (75 MHz)



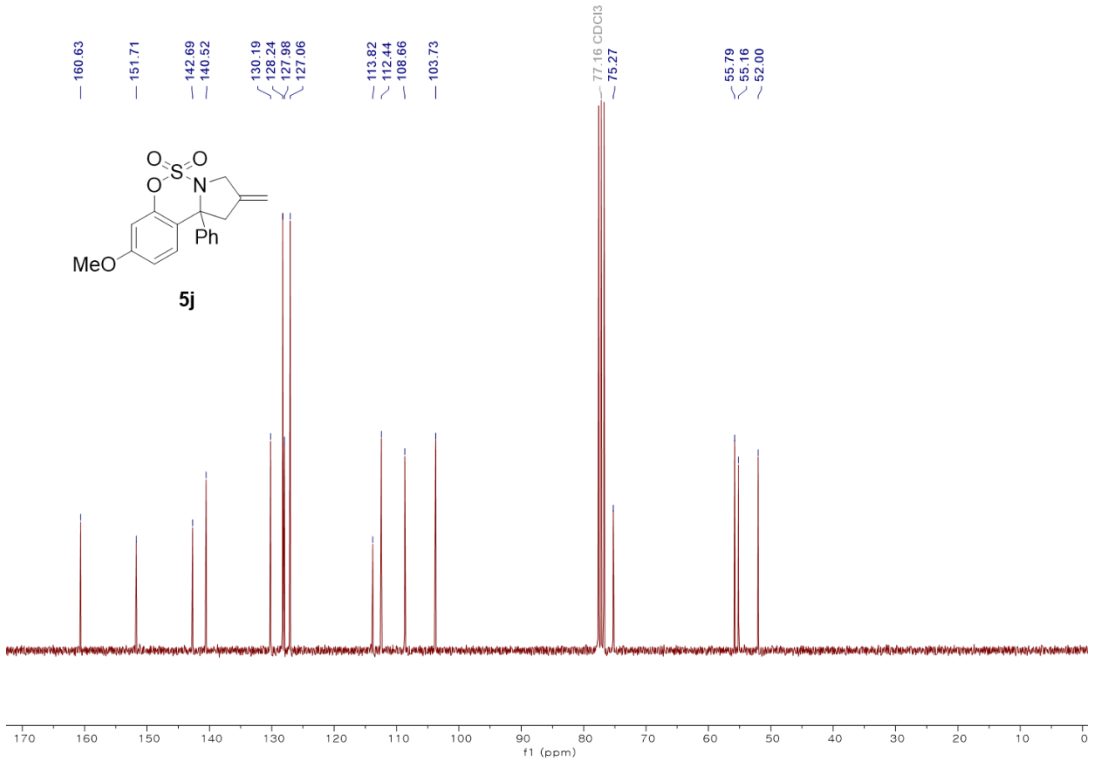
^{1}H Spectrum of **5i** in Chloroform-*d* (300 MHz)



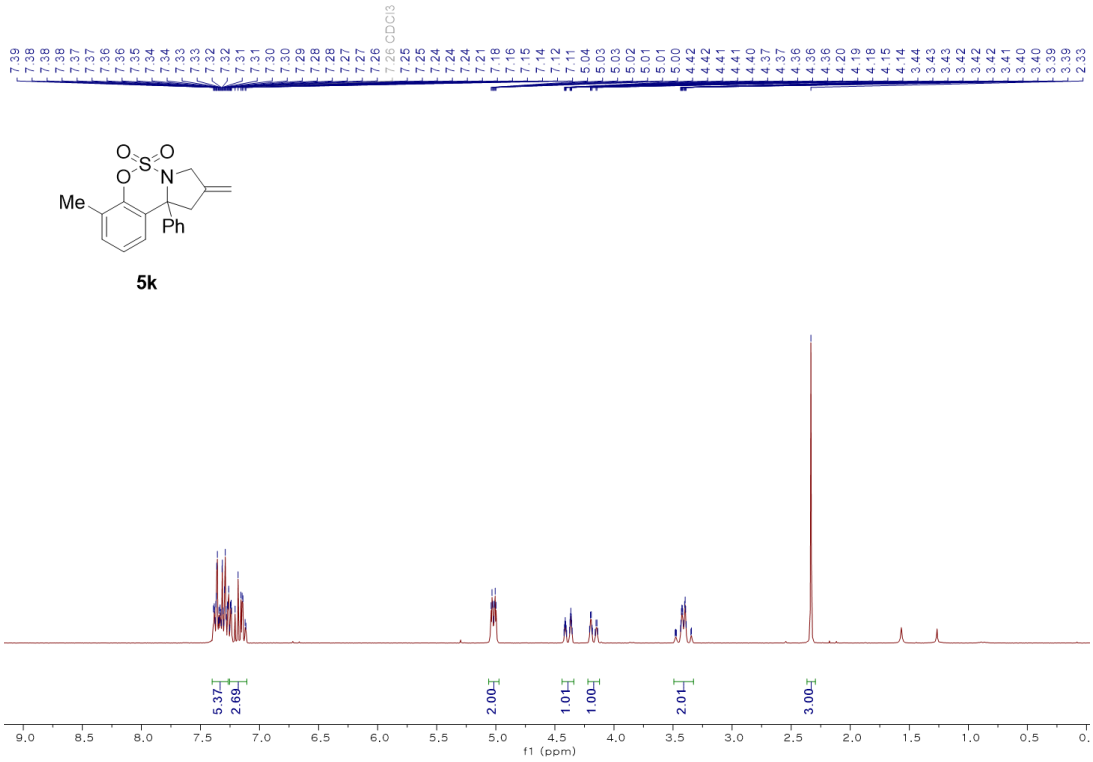
^{13}C Spectrum of **5i** in Chloroform-*d* (75 MHz)



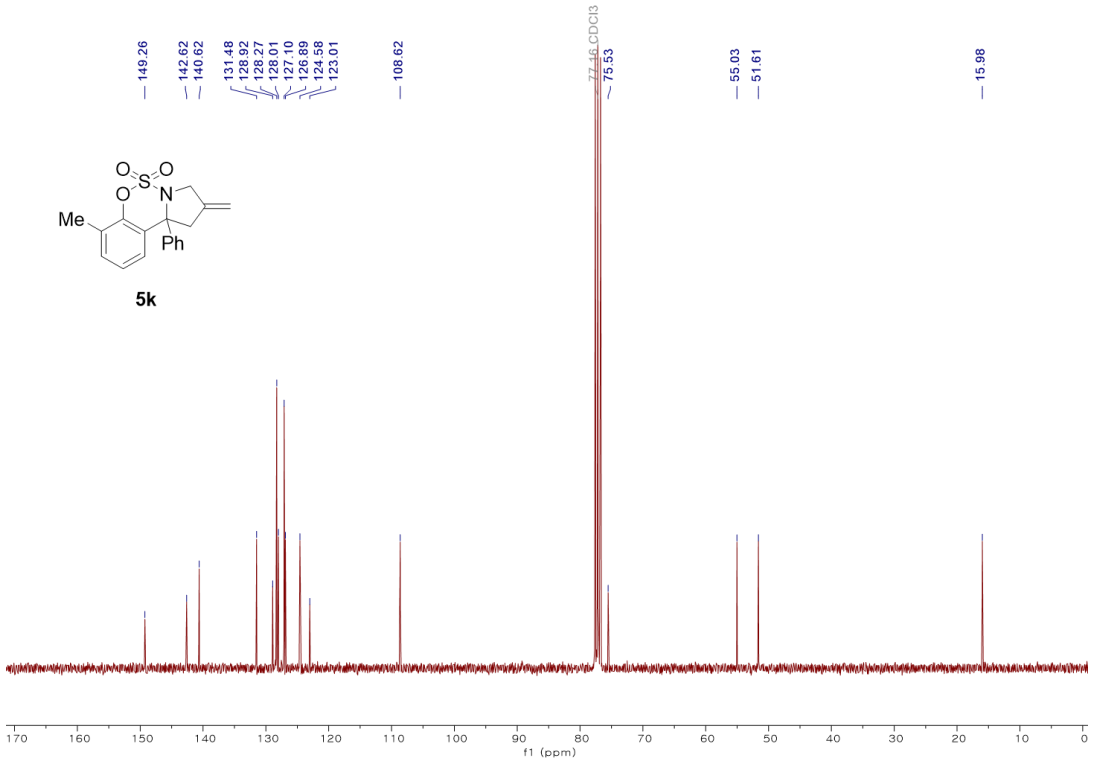
^{1}H Spectrum of **5j** in Chloroform-*d* (300 MHz)



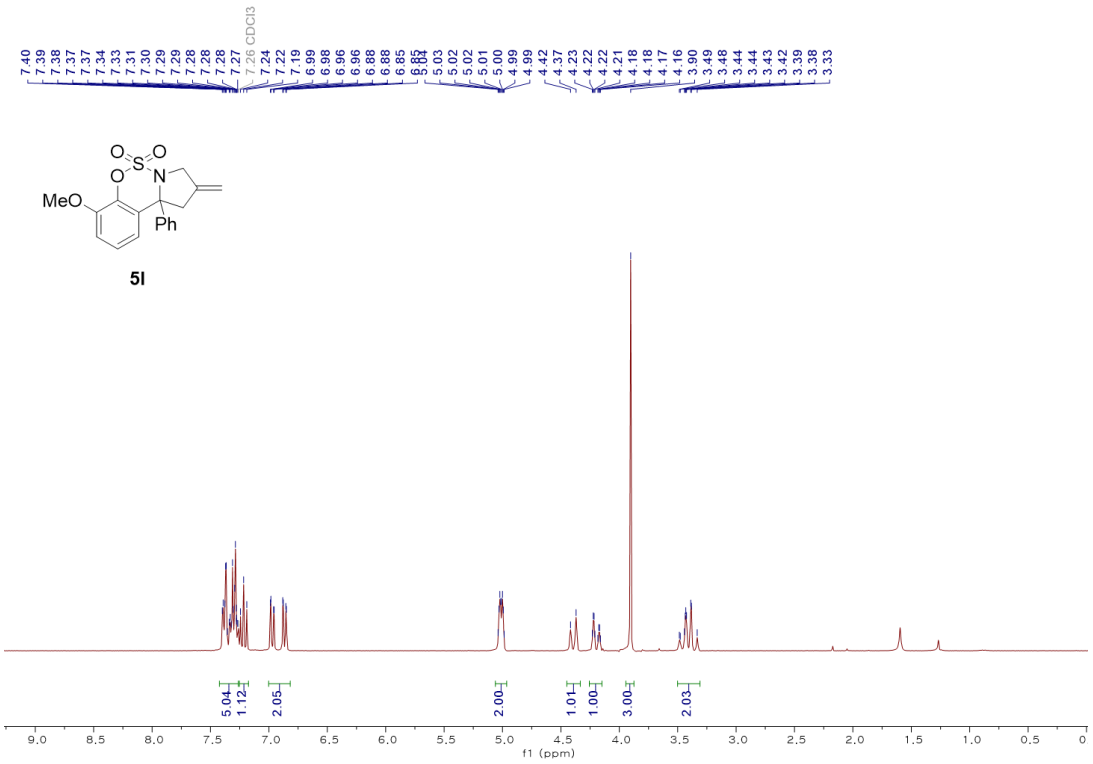
^{13}C Spectrum of **5j** in Chloroform-*d* (75 MHz)



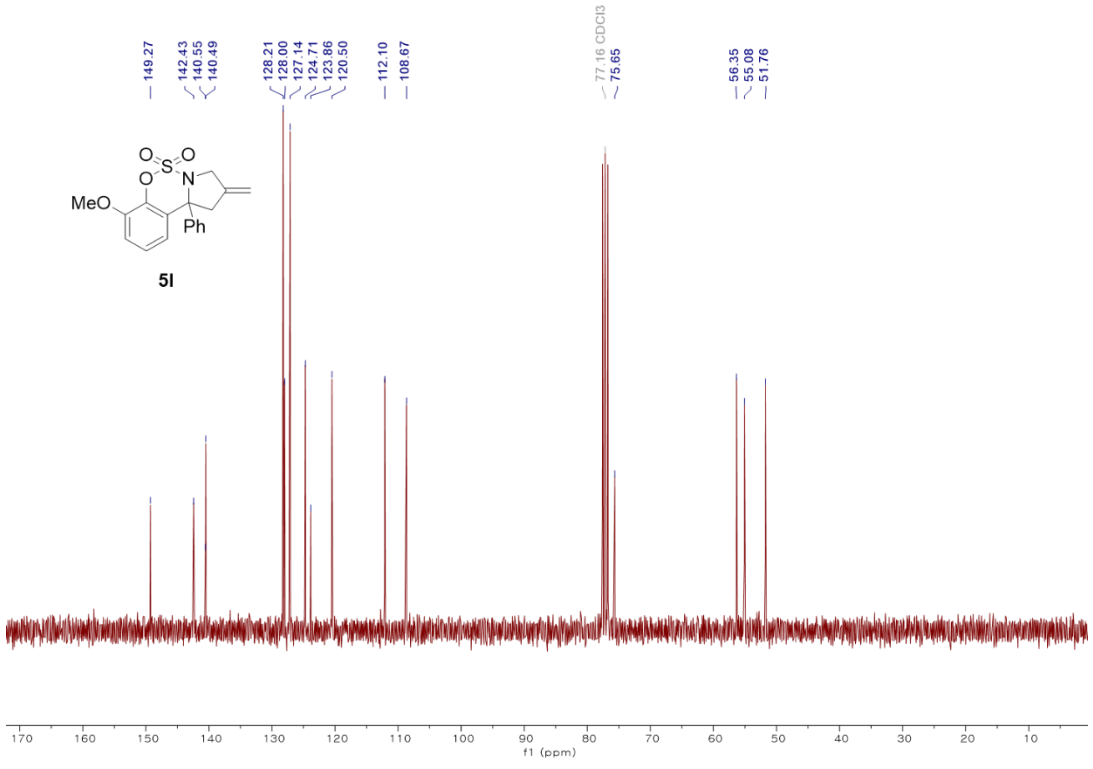
^{1}H Spectrum of **5k** in Chloroform-*d* (300 MHz)



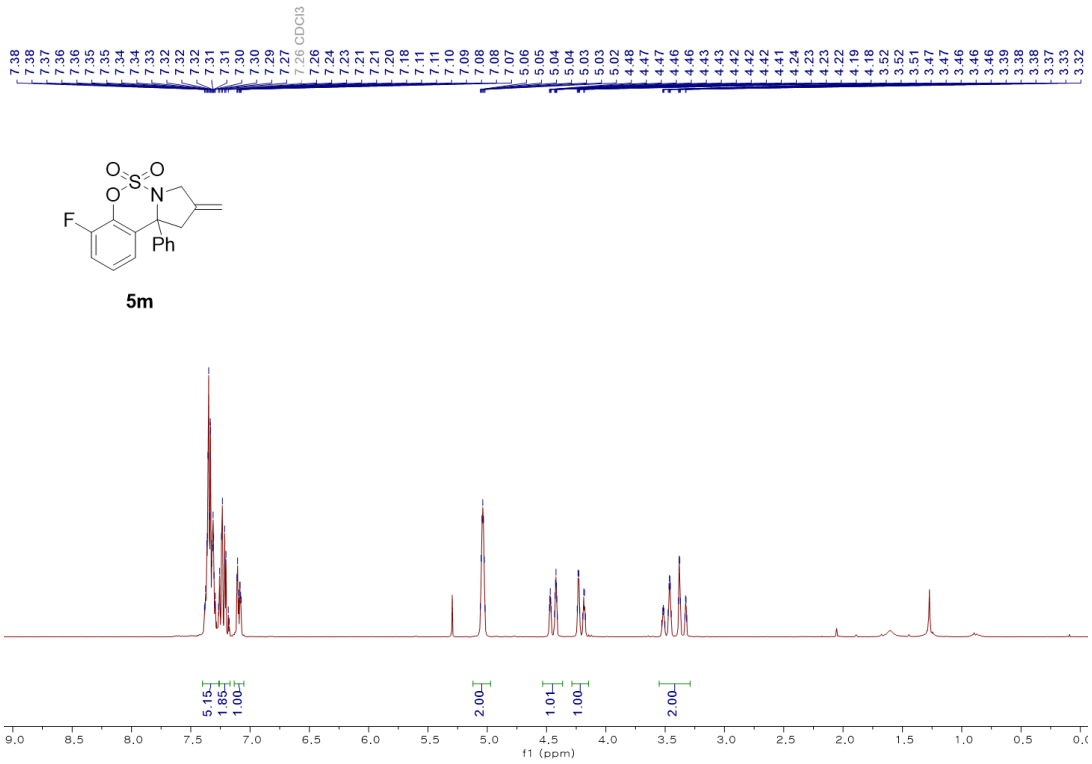
^{13}C Spectrum of **5k** in Chloroform-*d* (75 MHz)



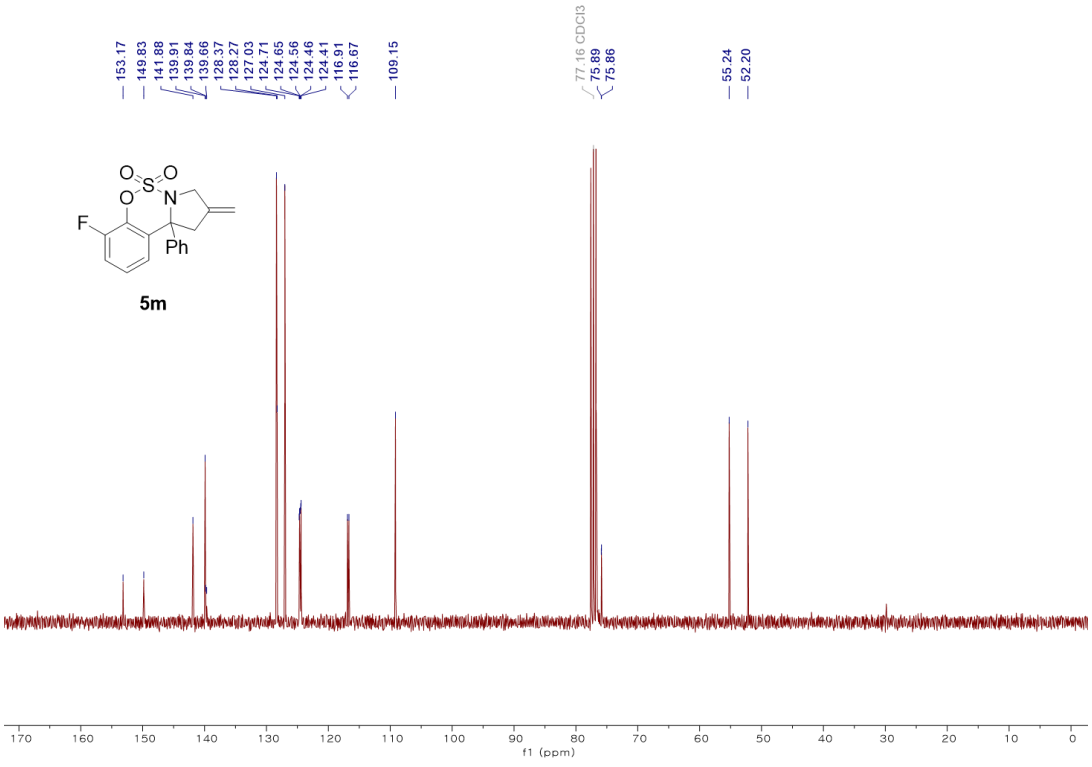
^{1}H Spectrum of **5l** in Chloroform-*d* (300 MHz)



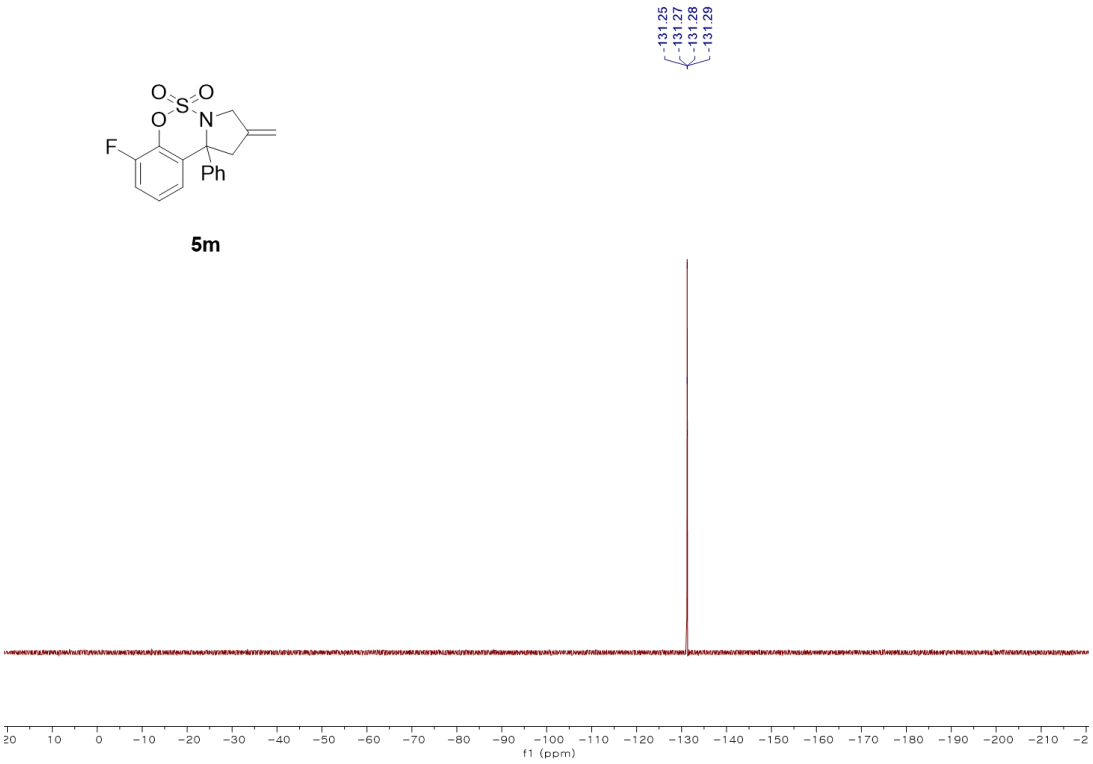
^{13}C Spectrum of **5l** in Chloroform-*d* (75 MHz)



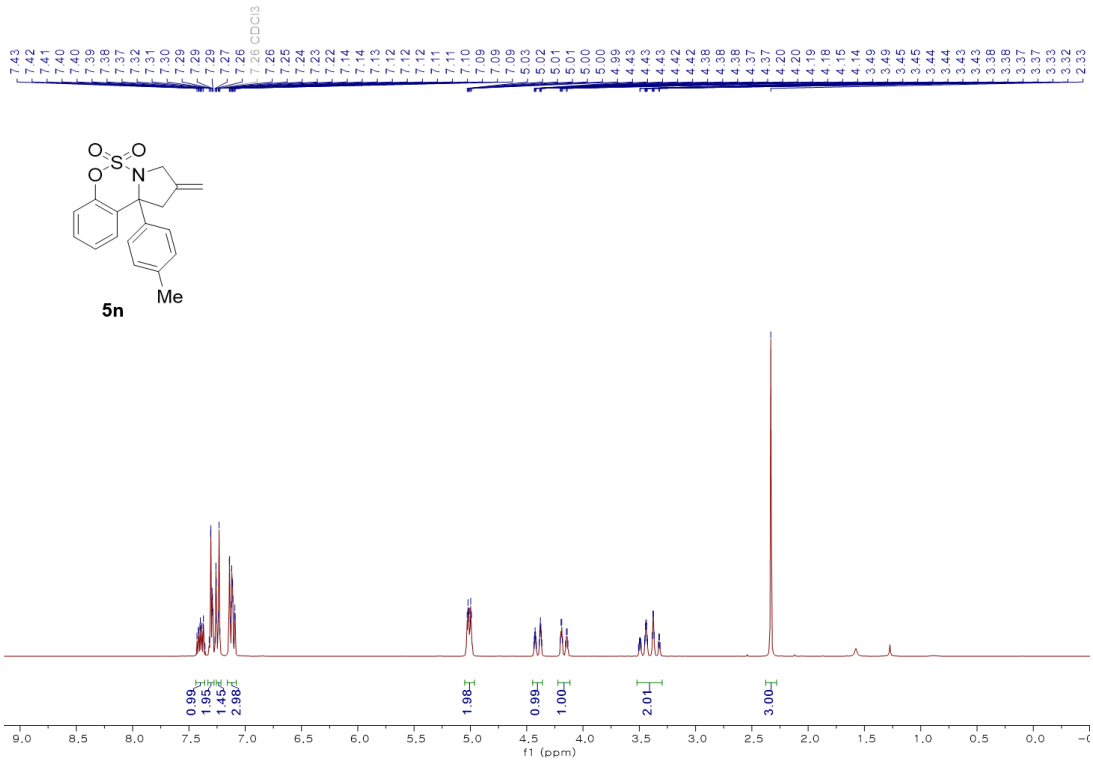
^{1}H Spectrum of **5m** in Chloroform-*d* (300 MHz)



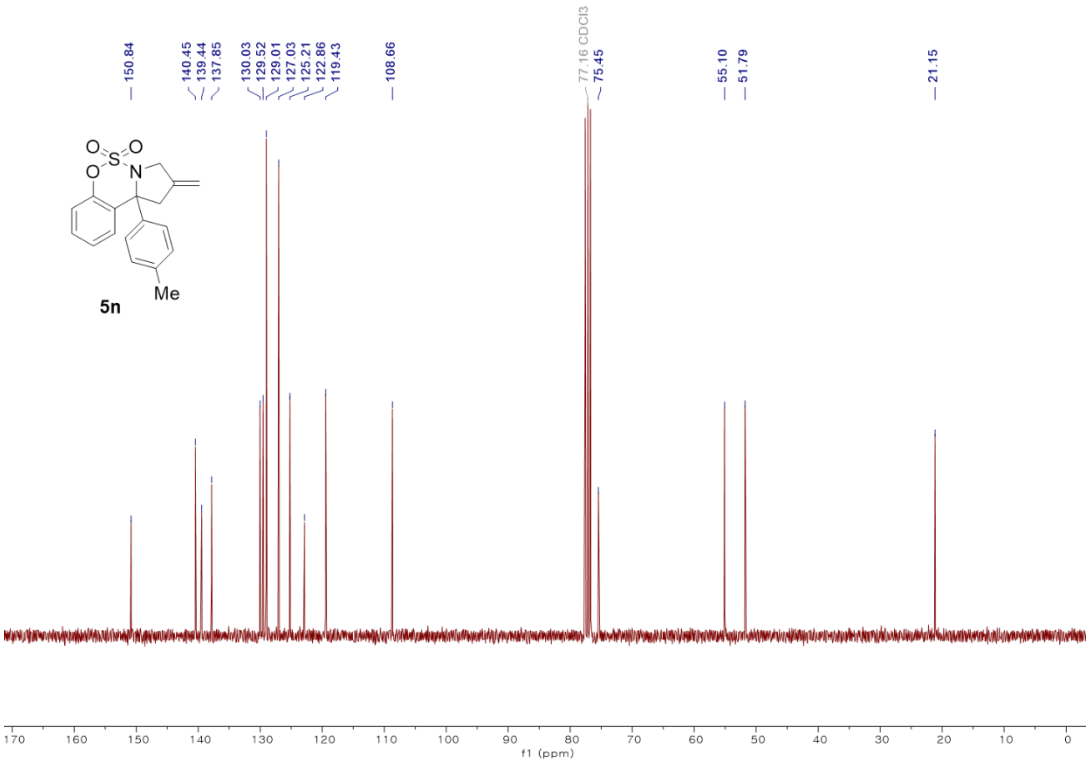
^{13}C Spectrum of **5m** in Chloroform-*d* (75 MHz)



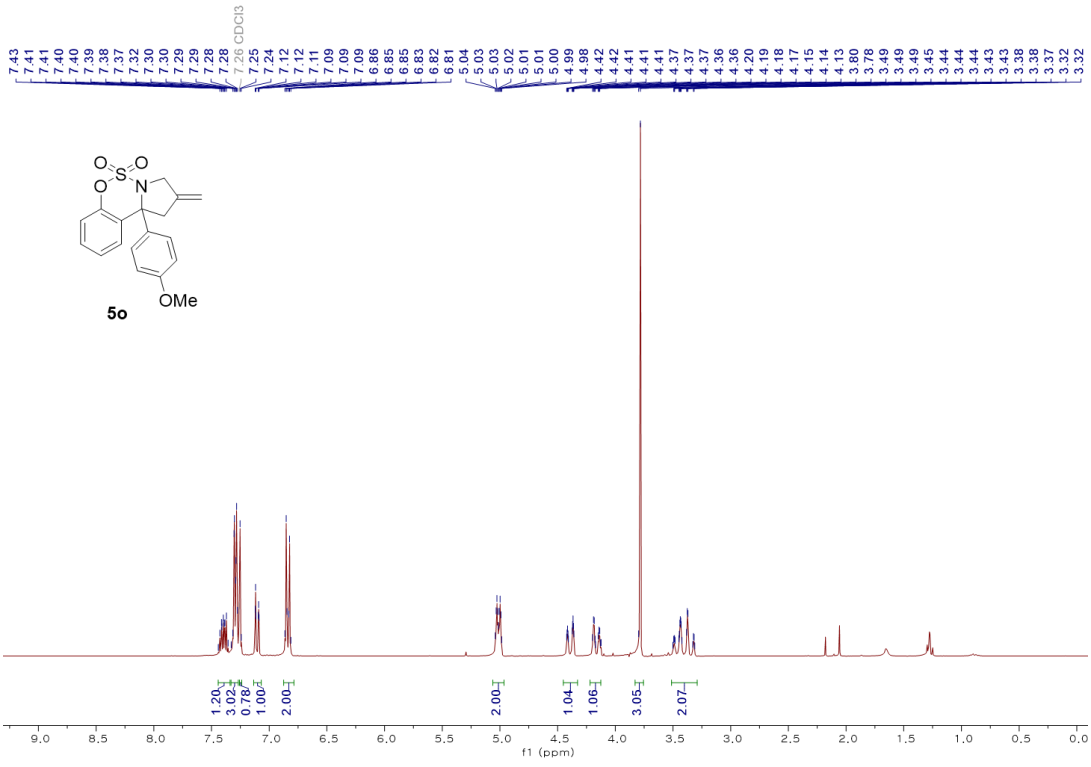
^{19}F Spectrum of **5m** in Chloroform-*d* (75 MHz)



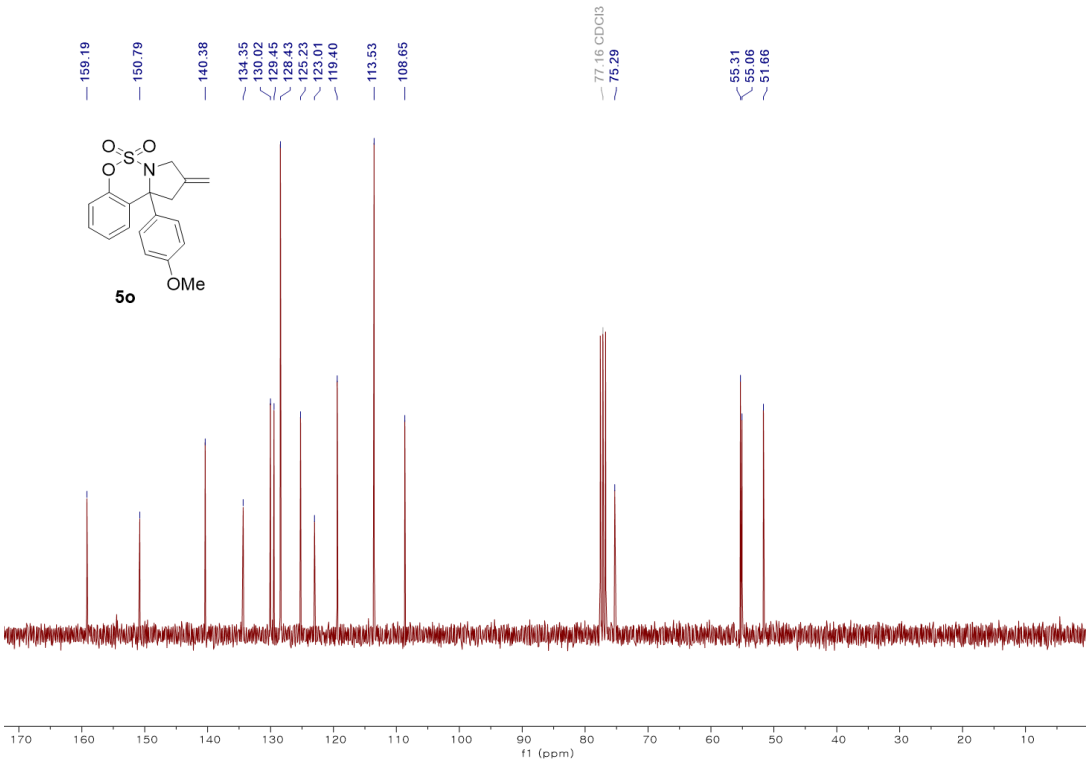
^{1}H Spectrum of **5n** in Chloroform-*d* (300 MHz)



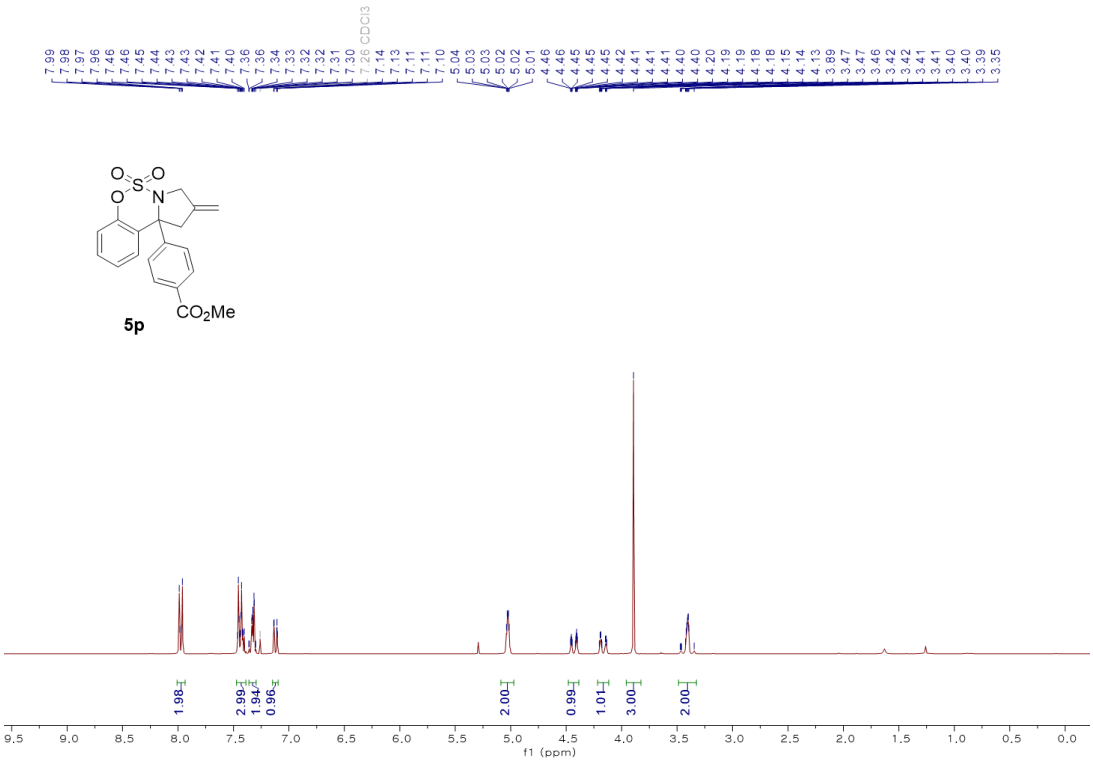
^{13}C Spectrum of **5n** in Chloroform-*d* (75 MHz)



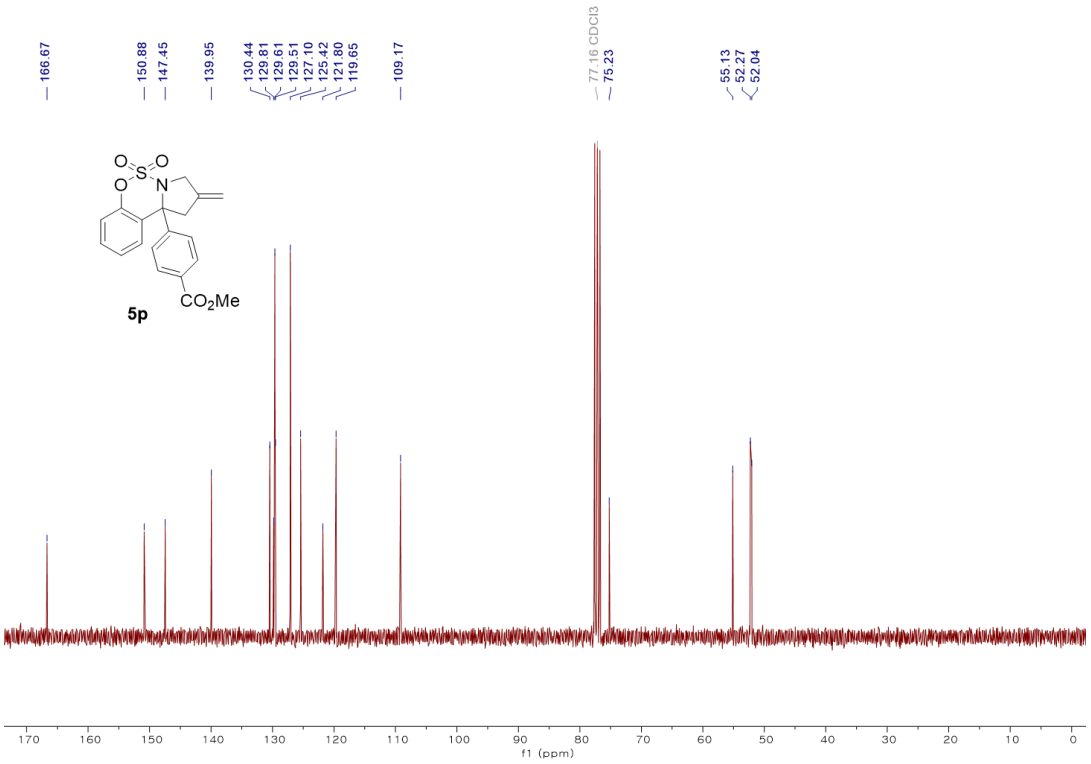
^{1}H Spectrum of **5o** in Chloroform-*d* (300 MHz)



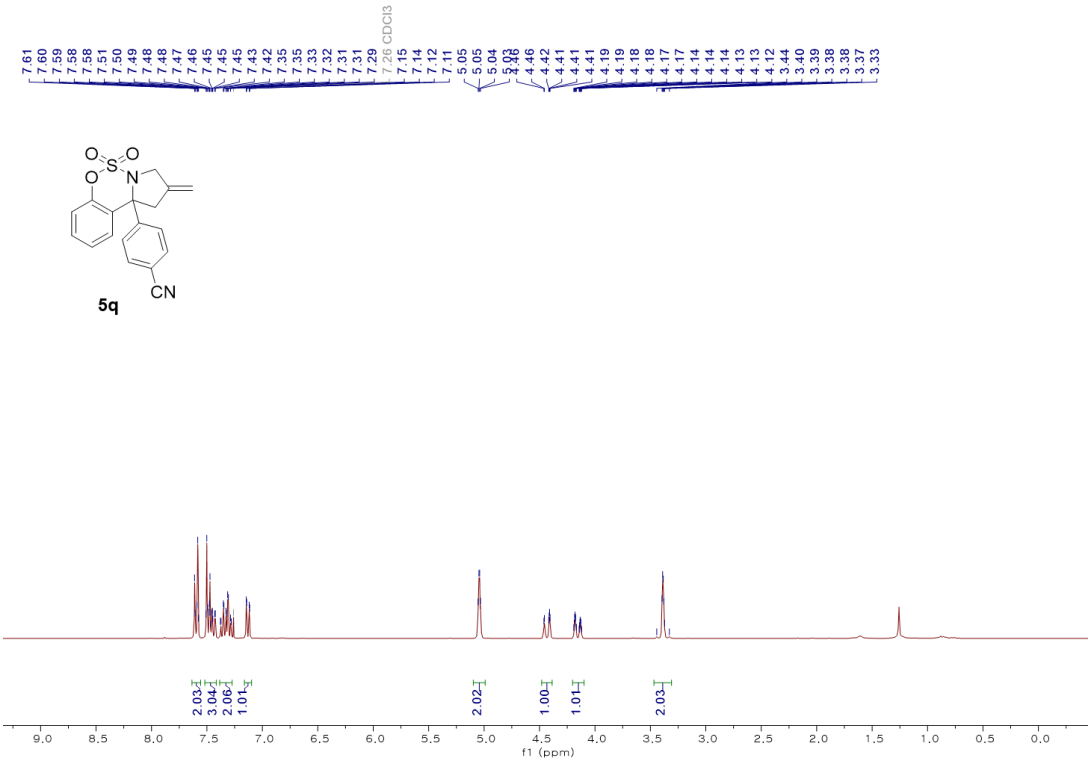
^{13}C Spectrum of **5o** in Chloroform-*d* (75 MHz)



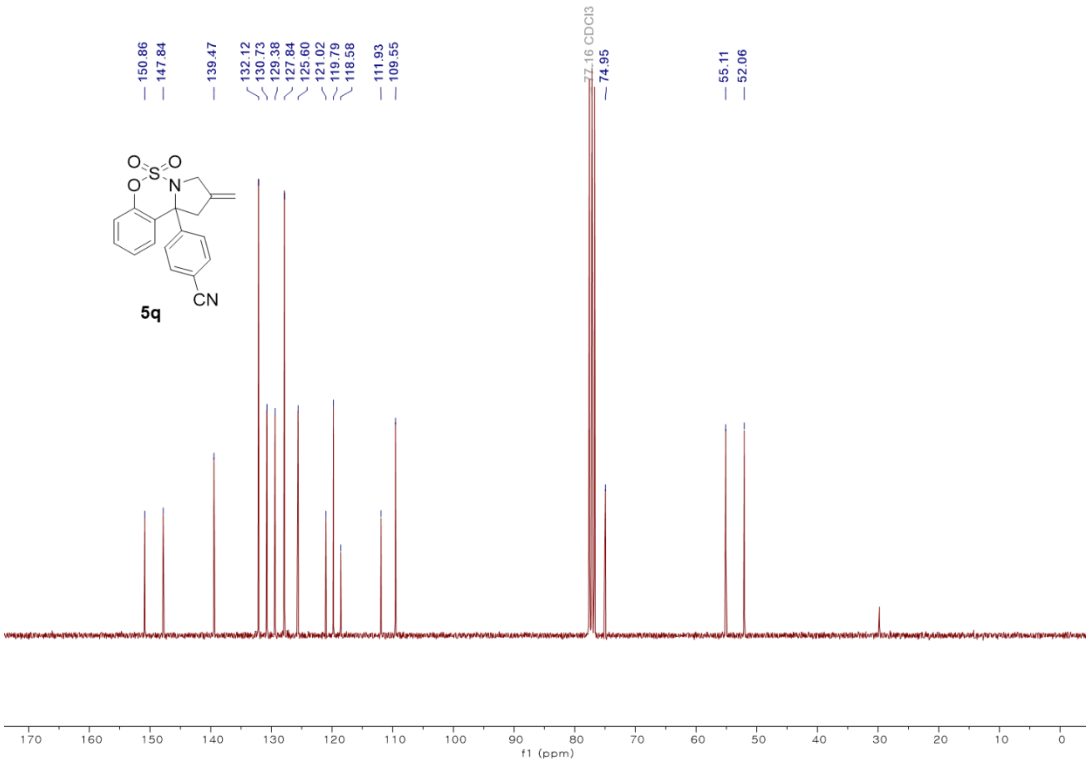
^{1}H Spectrum of **5p** in Chloroform-*d* (300 MHz)



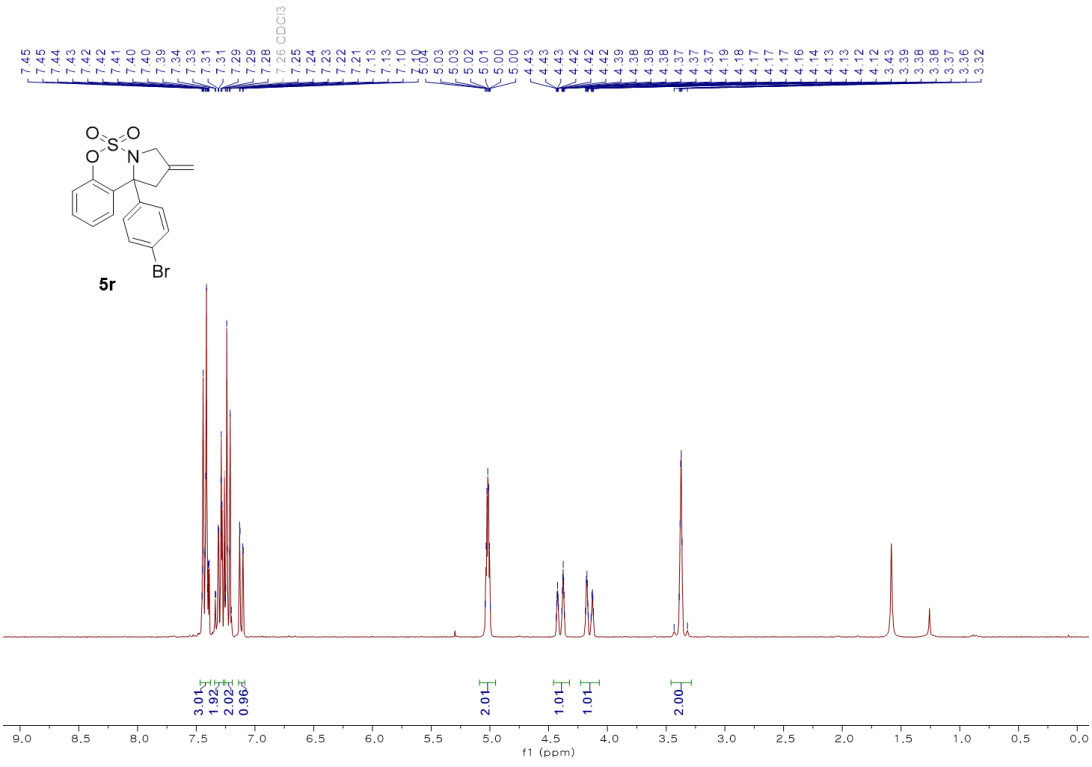
^{13}C Spectrum of **5p** in Chloroform-*d* (75 MHz)



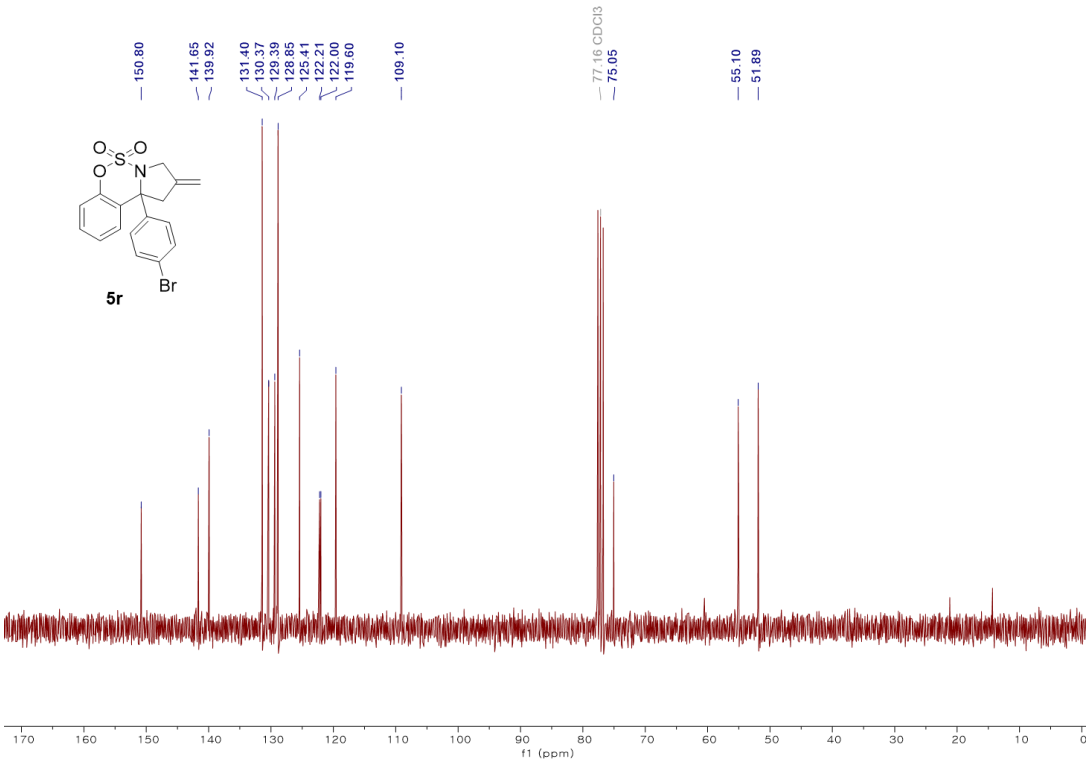
^{1}H Spectrum of **5q** in Chloroform-*d* (300 MHz)



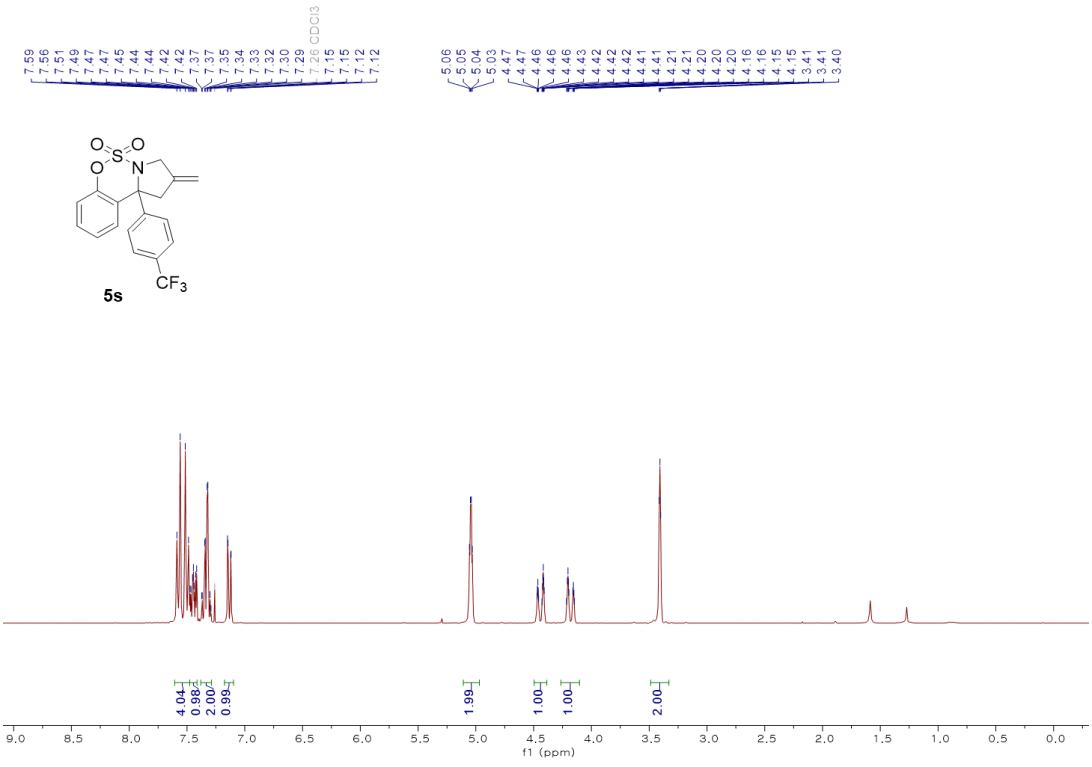
^{13}C Spectrum of **5q** in Chloroform-*d* (75 MHz)



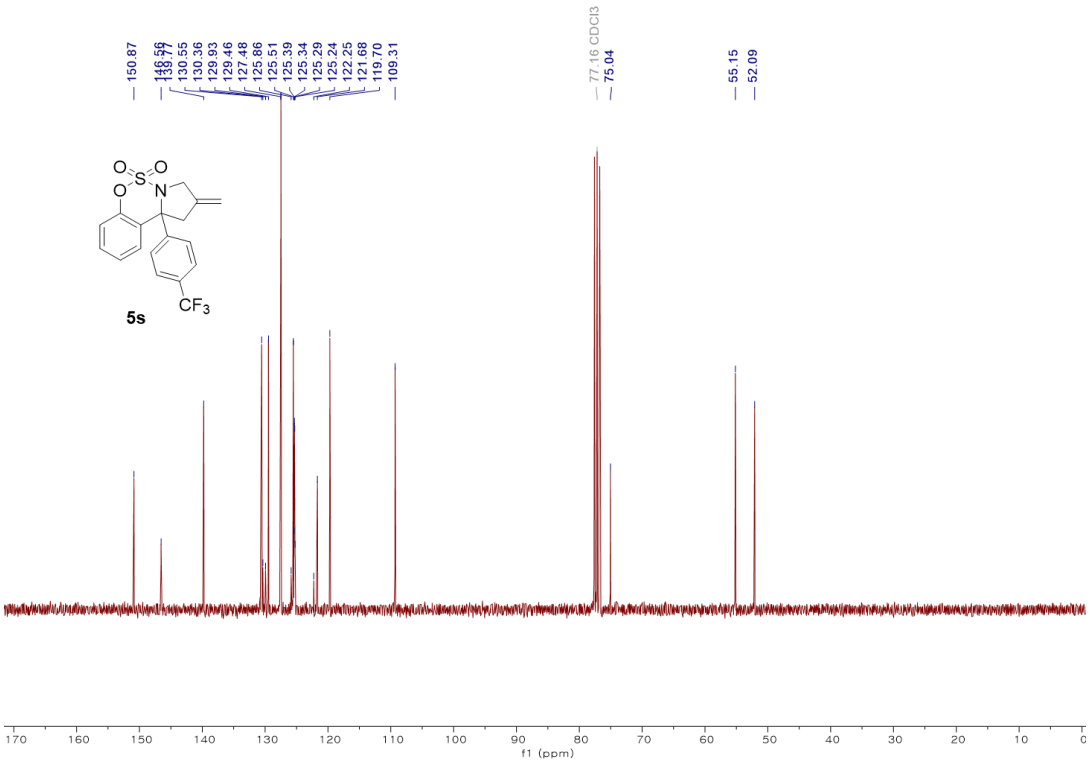
^{1}H Spectrum of **5r** in Chloroform-*d* (300 MHz)



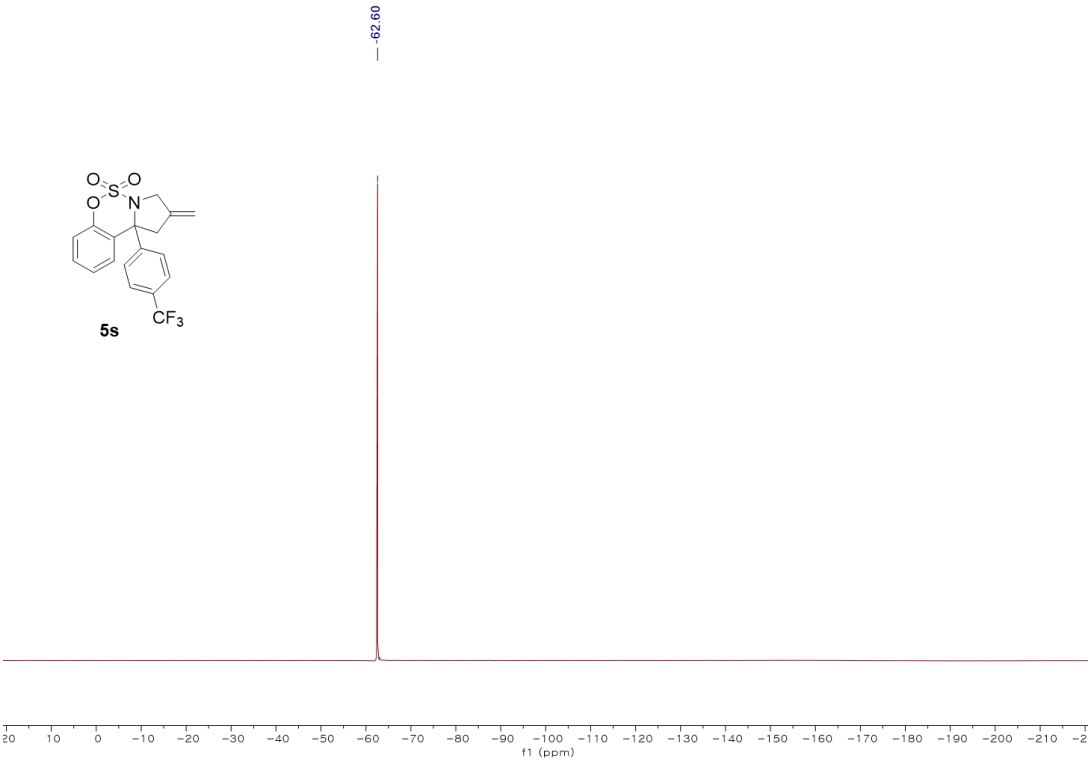
^{13}C Spectrum of **5r** in Chloroform-*d* (75 MHz)



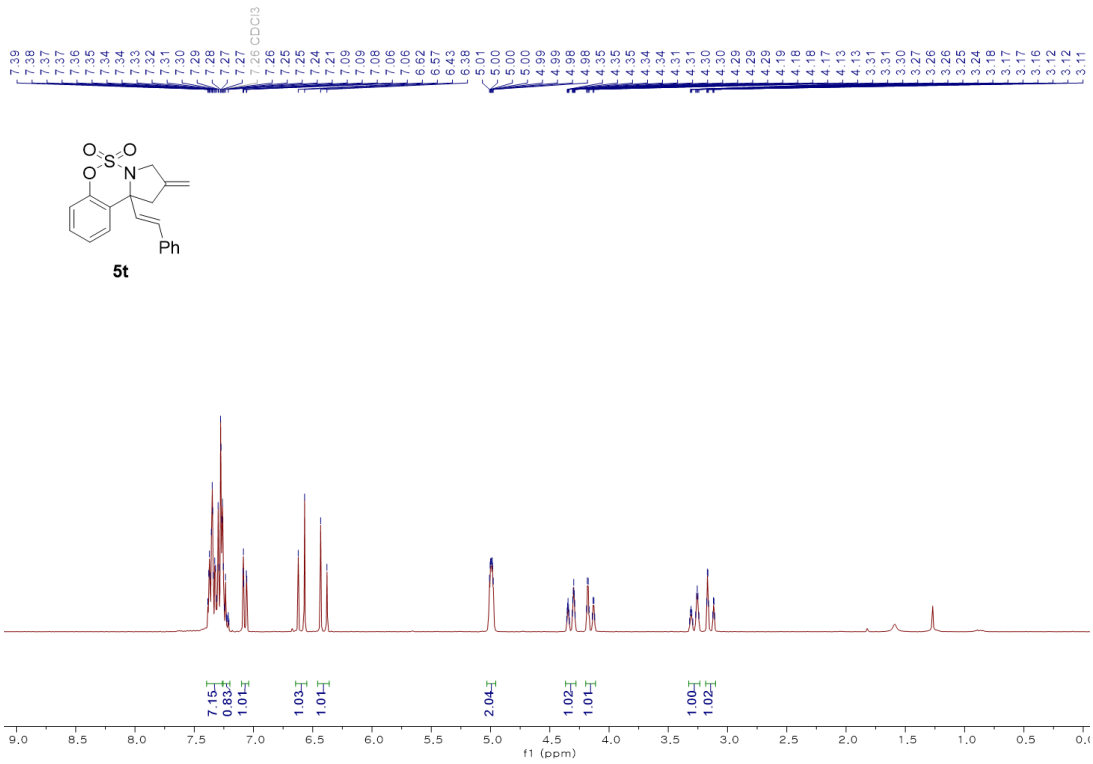
^{1}H Spectrum of **5s** in Chloroform-*d* (300 MHz)



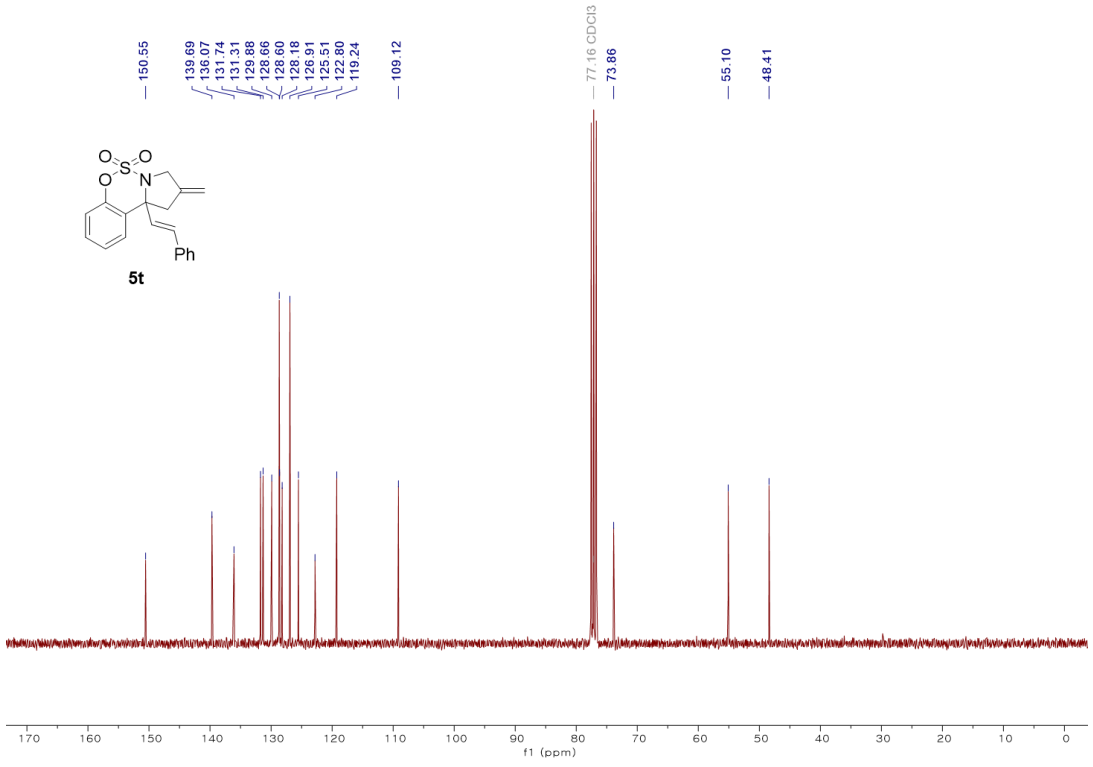
^{13}C Spectrum of **5s** in Chloroform-*d* (75 MHz)



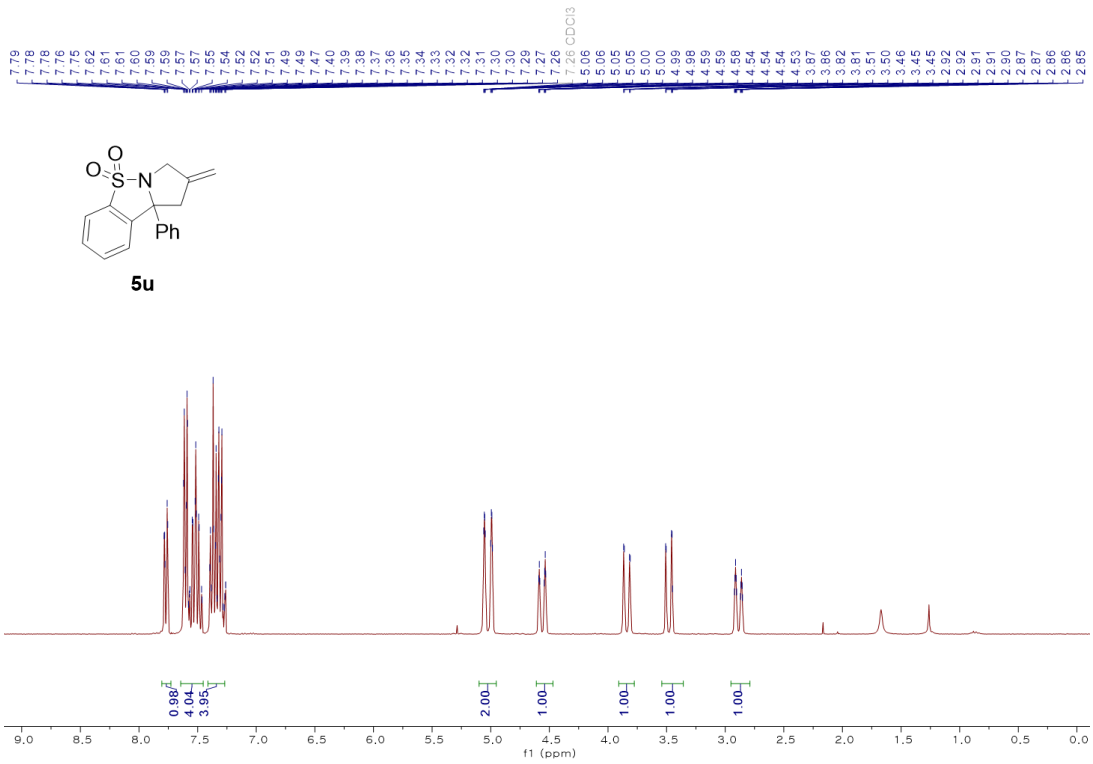
^{19}F Spectrum of **5s** in Chloroform-*d* (471 MHz)



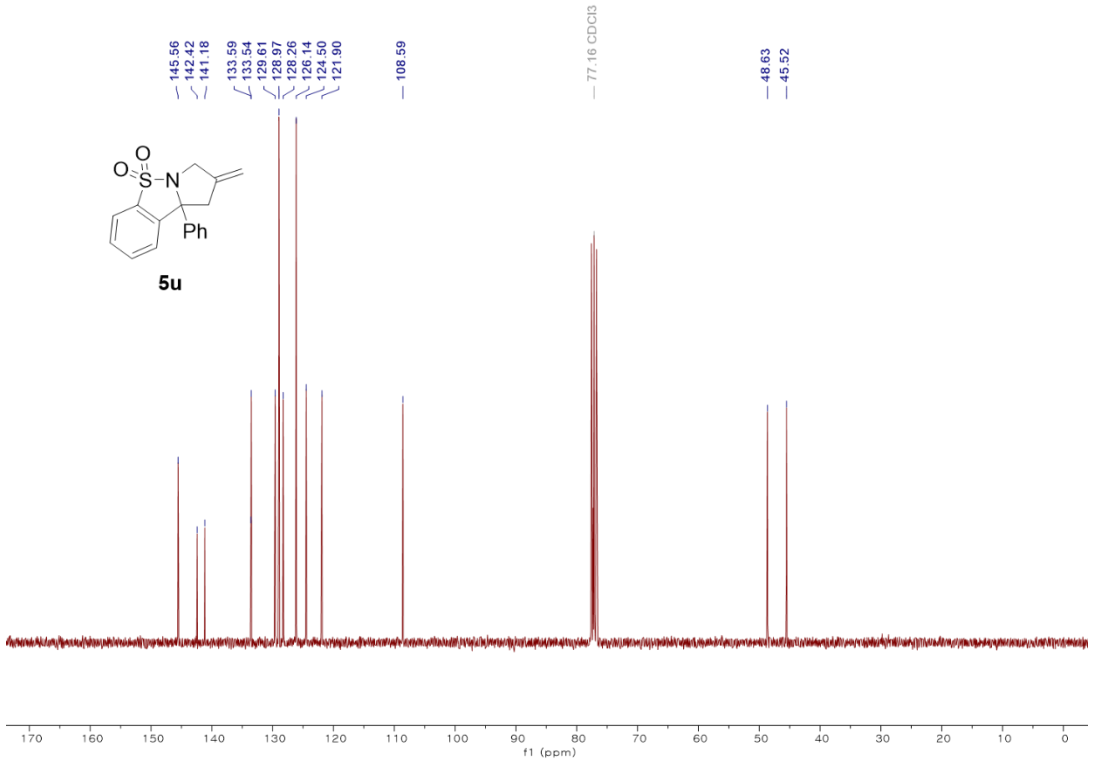
^{1}H Spectrum of **5t** in Chloroform-*d* (300 MHz)



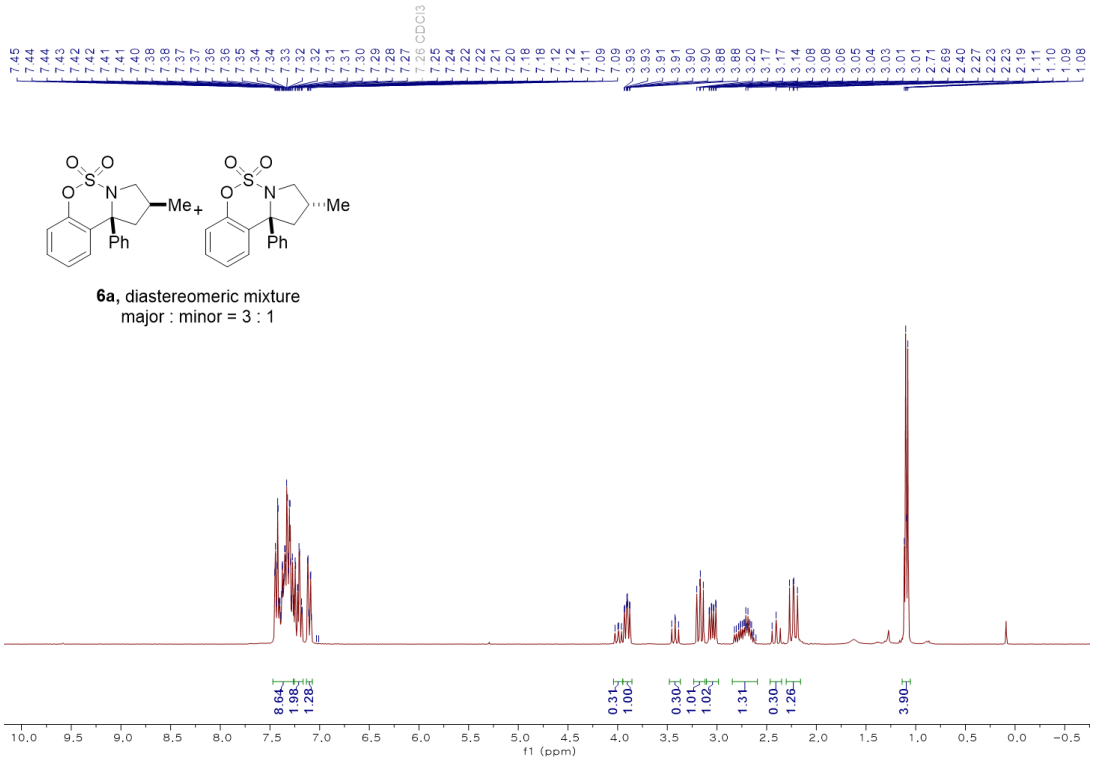
^{13}C Spectrum of **5t** in Chloroform-*d* (75 MHz)



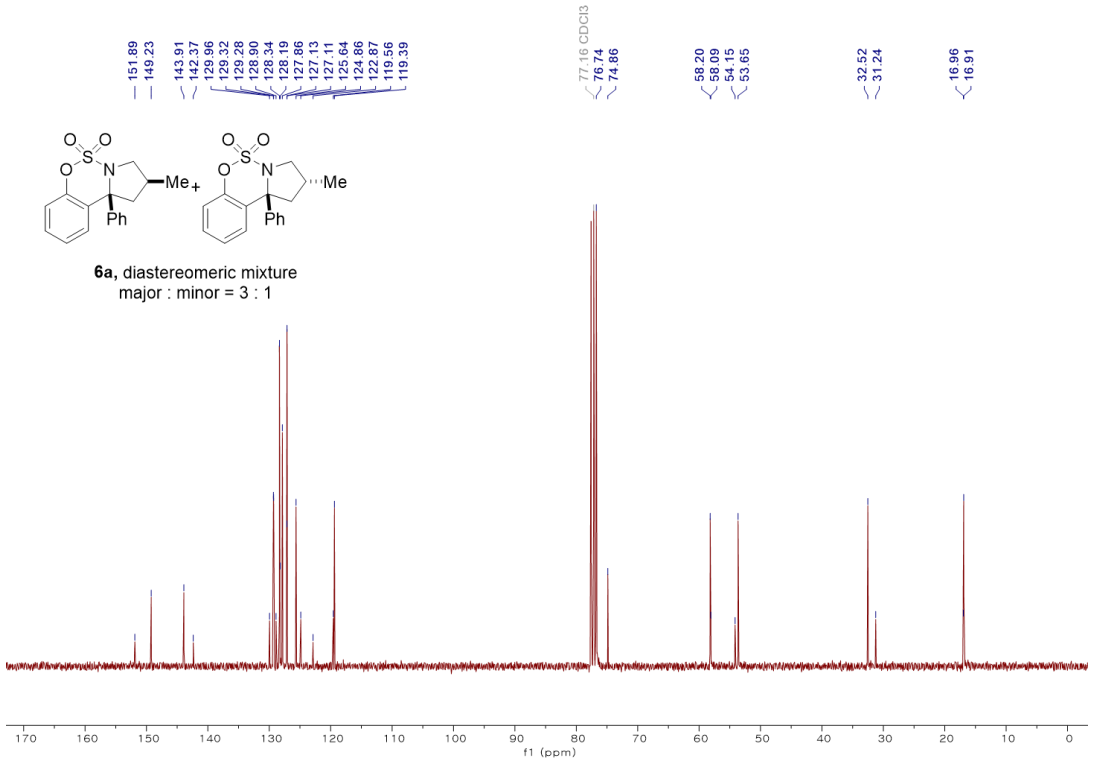
^{1}H Spectrum of **5u** in Chloroform-*d* (300 MHz)



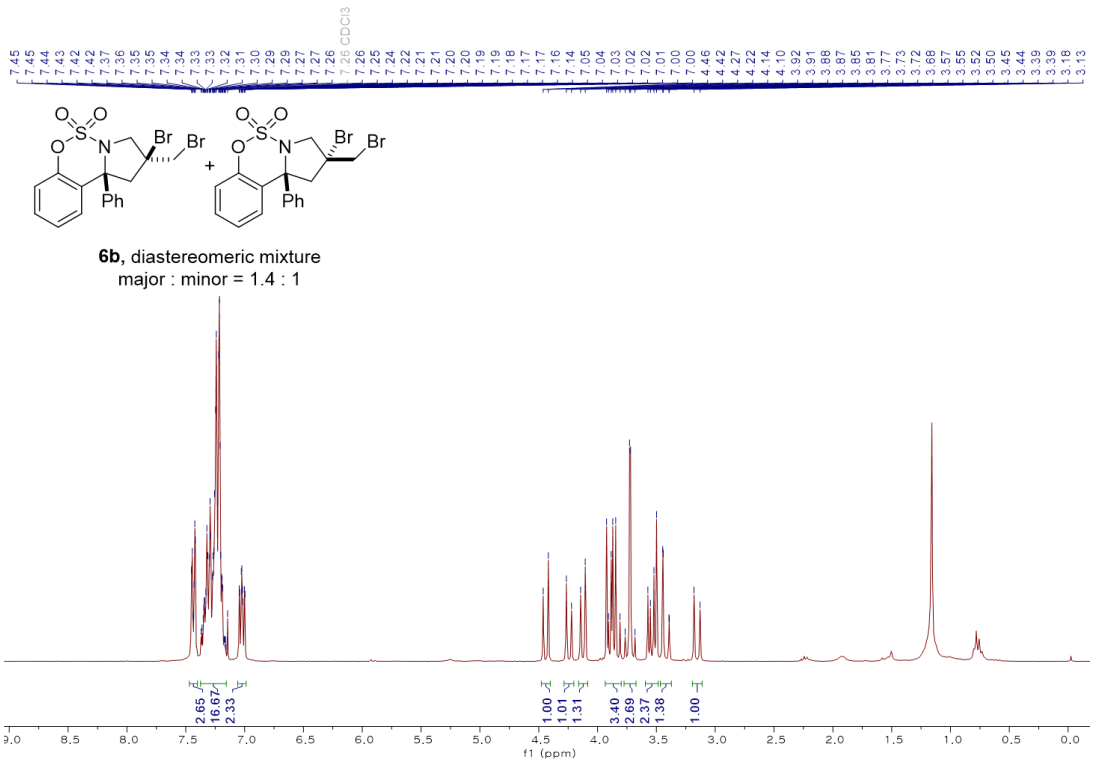
^{13}C Spectrum of **5u** in Chloroform-*d* (75 MHz)



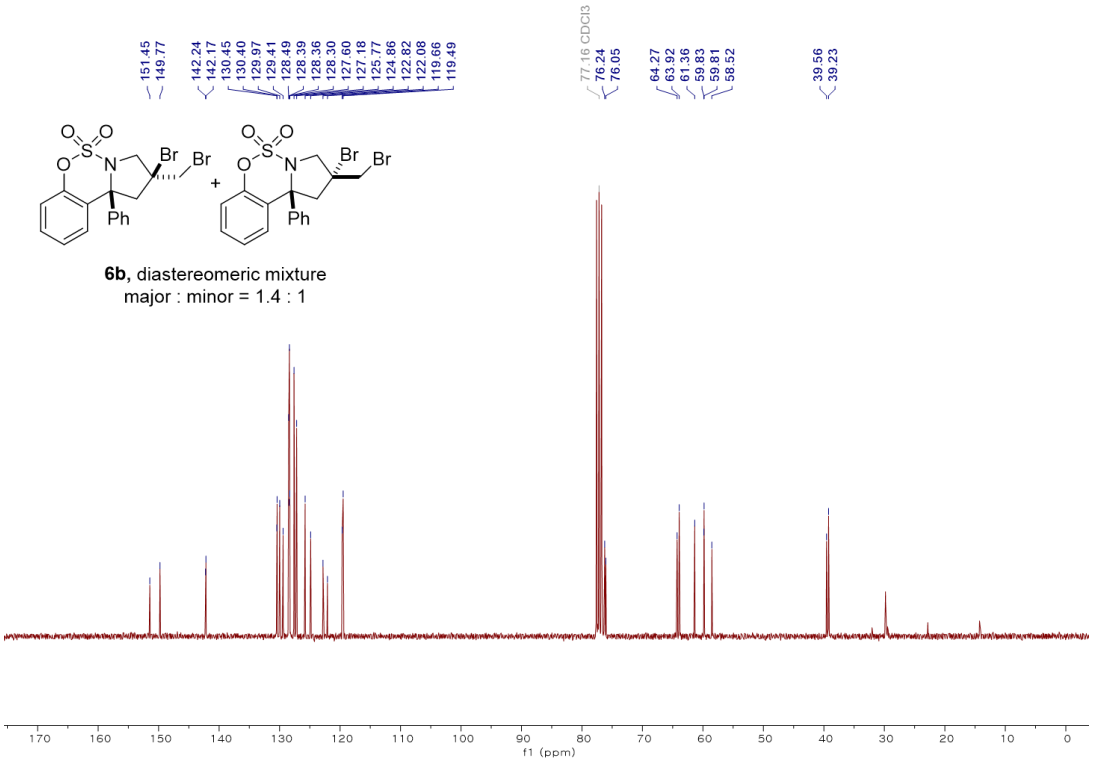
^{1}H Spectrum of **6a** in Chloroform-*d* (300 MHz)



^{13}C Spectrum of **6a** in Chloroform-*d* (75 MHz)



^{1}H Spectrum of **6b** in Chloroform-*d* (300 MHz)



^{13}C Spectrum of **6b** in Chloroform-*d* (75 MHz)