Supporting Information

Pd-Catalyzed Asymmetric [5+2] Cycloaddition of Vinylethylene Carbonates and Cyclic Imines: Access to N-Fused 1,3-Oxazepines

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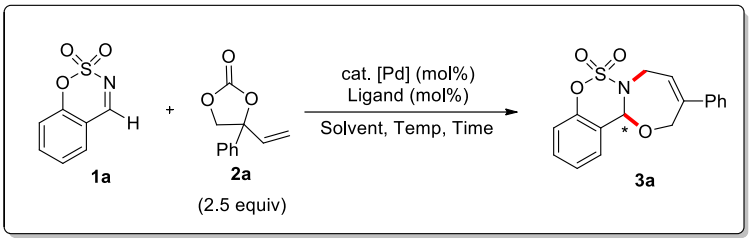
1. General informations

All reactions and manipulations were carried out under an argon atmosphere using oven-dried Schlenk techniques. The reaction flasks were flamed dried and solvents were transferred by oven-dried syringe. Dichloromethane were distilled over calcium hydride, toluene and THF were distilled over sodium. The 1,3-dioxolane was placed in the dry 4Å molecular sieve and was degassed under argon atmosphere. Commercially available chemical reagents and other anhydrous solvents from Acros Organics, Aldrich Chemical Co., Alfa Aesar, and TCI were directly used without further purification. All catalytic reactions were stirred in a pre-heated heating mantle. Thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum plates (Merck). TLC plates were visualized by short-wave ultraviolet light (254 and 366 nm) and/or $KMnO_4$ solution. Flash chromatography was performed on Merck silica gel (40–63 mesh) by standard techniques. The $[\alpha]_D$ was recorded using KRUSS P8000-T Polarimeter. Infrared (IR) spectra were obtained using a Nicolet iS5 FT-IR spectrometer. The ^1H NMR spectra were recorded by 300 MHz or 500MHz, and ^{13}C NMR spectra were recorded by 75.5 MHz or 126 MHz. The chemical shifts (δ) are given in ppm relative to TMS ($CDCl_3$: δ ^1H = 7.26 ppm, δ ^{13}C = 77.16 ppm). The HRMS data (high resolution mass spectra) were obtained by electrospray ionization (ESI) from SYNAPT G2 (Waters, U.K.). Enantiomeric ratios (er) were determined by HPLC analysis (high performance liquid chromatography) (YL9100) using chiral column (Daicel Chiralpak, AD-H, 250X 4.6 mm ID). Diastereomeric ratio (dr) of **3x** was determined by ^1H NMR. The sulfamate-derived cyclic imines **1**[1], vinylethylene carbonates (VECs) **2**[2], CpPd(allyl)[3] and CpPd(cinnamyl)[3] were prepared according to the literature procedures.

2. Reaction optimization



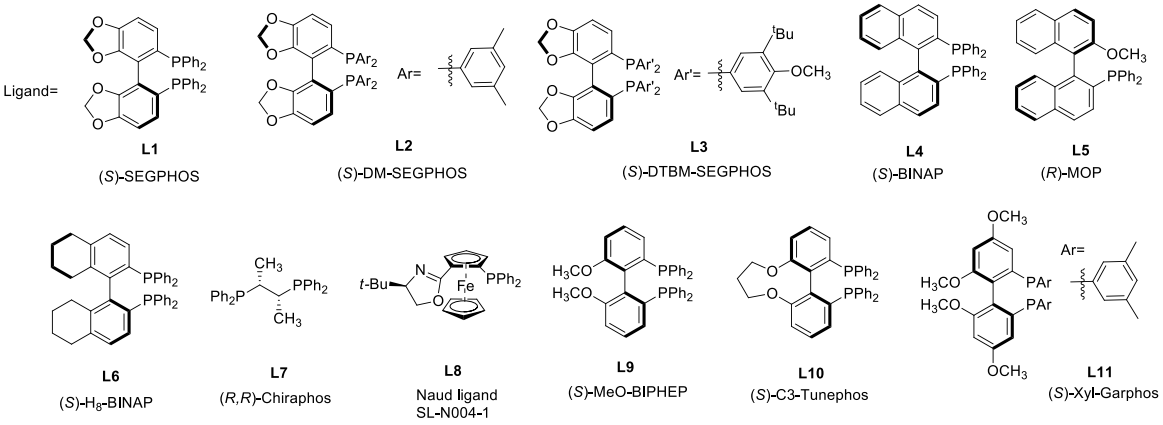


Table S1.

Entry	Pd catalyst (mol%)	Ligand (mol%)	Solvent (M)	Temp. (°C)	Time (h)	Yield (%) (er)
1	PdCp(allyl) (5)	**L1** (5.5)	tolune (0.1)	80	8	51 (80:20)
2	PdCp(allyl) (5)	**L1** (5.5)	THF (0.2)	50	16	34 (80:20)
3	PdCp(cinnamyl) (5)	**L1** (5.5)	THF (0.2)	50	16	60 (80:20)
4	$Pd_2(dba)_3$ (2.5)	**L1** (5.5)	THF (0.2)	50	16	21 (80:20)
5	PdCp(cinnamyl) (5)	**L2** (5.5)	THF (0.2)	50	16	<5 (68:32)
6	PdCp(cinnamyl) (5)	**L3** (5.5)	THF (0.2)	50	16	6 (58:42)
7	PdCp(cinnamyl) (5)	**L4** (5.5)	THF (0.2)	50	16	54 (73:27)
8	PdCp(cinnamyl) (5)	**L5** (11)	THF (0.2)	50	16	ND[a]
9	PdCp(cinnamyl) (5)	**L6** (5.5)	THF (0.2)	50	16	26 (70:30)
10	PdCp(cinnamyl) (5)	**L7** (5.5)	THF (0.2)	50	16	0
11	PdCp(cinnamyl) (5)	**L8** (5.5)	THF (0.2)	50	16	0
12	PdCp(cinnamyl) (5)	**L9** (5.5)	THF (0.2)	50	16	<5 (70:30)
13	PdCp(cinnamyl) (5)	**L10** (5.5)	THF (0.2)	50	16	21 (80:20)
14	PdCp(cinnamyl) (5)	**L11** (5.5)	THF (0.2)	50	16	0
15	PdCp(cinnamyl) (5)	**L1** (5.5)	toluene (0.2)	50	16	30 (79:21)
16	PdCp(cinnamyl) (5)	**L1** (5.5)	DCM (0.2)	50	16	38 (70:30)
17	PdCp(cinnamyl) (5)	**L1** (5.5)	THF/DCM =1/1, (v/v) (0.2)	50	16	36 (78:22)
18	PdCp(cinnamyl) (5)	**L1** (5.5)	1,4-dixoane (0.2)	50	16	0
19	PdCp(cinnamyl) (5)	**L1** (5.5)	diethyl ether (0.2)	50	16	21 (78:22)

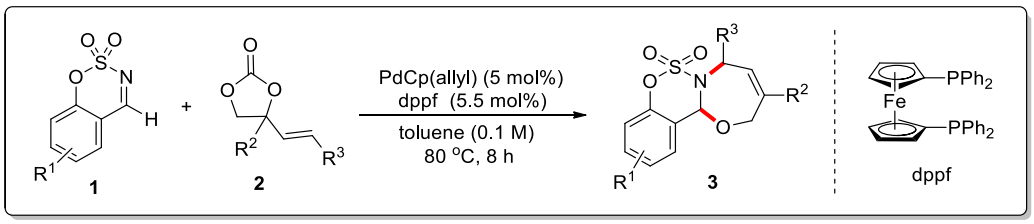
20	PdCp(cinnamyl) (5)	**L1** (5.5)	1,3-dioxolane (0.2)	50	16	78 (79:21)
21	PdCp(cinnamyl) (5)	**L1** (5.5)	1,3-dioxolane (0.1)	50	16	92 (80:20)
22	PdCp(cinnamyl) (10)	**L1** (11)	1,3-dioxolane (0.2)	50	16	84 (79:21)
23	PdCp(cinnamyl) (10)	**L1** (11)	1,3-dioxolane (0.1)	50	16	98 (80:20)
24	PdCp(cinnamyl) (10)	**L1** (11)	1,3-dioxolane (0.1)	30	16	79 (80:20)
25	PdCp(cinnamyl) (10)	**L1** (11)	THF (0.2)	50	16	74 (81:19)
26	PdCp(cinnamyl) (10)	**L1** (11)	THF (0.2)	30	24	55 (83:17)
27	PdCp(allyl) (10)	**L1** (11)	THF (0.2)	30	16	21 (81:19)
28	$Pd(OAc)_2$ (10)	**L1** (11)	THF (0.2)	30	16	0
29	$PdCl_2$ (10)	**L1** (11)	THF (0.2)	30	16	0
30	$[(cinnnamylPdCl]_2$ (5)	**L1** (11)	THF (0.2)	30	16	70 (85:15)
31	$[(cinnnamylPdCl]_2$ (5)	**L1** (11)	THF (0.2)	30	24	76 (85:15)

[a]ND : No detection.

To a flame-dried Schlenk tube, palladium catalyst, chiral phosphine ligand and solvent were added under Ar atmosphere, and stirred for 15 minutes at room temperature. Then sulfamate-derived cyclic imines **1a** (0.2 mmol, 1.0 equiv), then 4-phenyl-4-vinyl-1,3-dioxolan-2-one (**2a**) (0.5 mmol, 2.5 equiv) were added under Ar atmosphere. The reaction mixture was stirred at corresponding reaction temperature and reaction time. After the reaction completed as determined by TLC analysis, the reaction solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: acetone/*n*-hexane =1/15) to afford **3a**. The enantiomeric ratio (er) of **3a** was recorded by HPLC (Daicel Chiralpak AD-H), eluent: *n*-hexane/*i*-PrOH = 85/15.

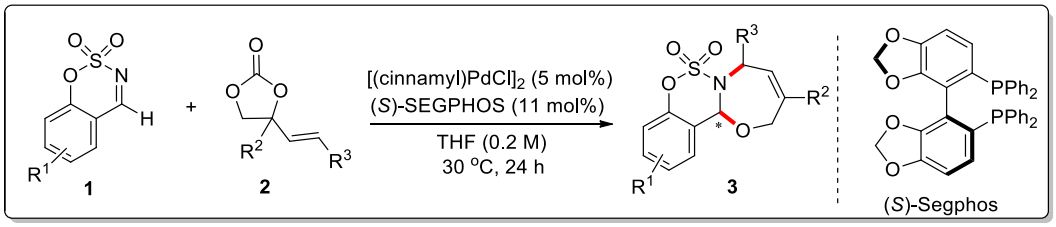
3. General procedure

3.1 Procedure for the preparation of the racemic compounds 3



To a flame-dried Schlenk tube, sulfamate-derived cyclic imines **1** (0.2 mmol, 1.0 equiv), PdCp(allyl) (2.13 mg, 5 mol%), 1,1'-Bis(diphenylphosphino)ferrocene (6.10 mg, 5.5 mol%) were added under Ar atmosphere, then vinyl ethylene carbonate **2** (0.5 mmol, 2.5 equiv) and toluene (2.0 mL) were added under Ar atmosphere. The reaction mixture was stirred at 80 °C for 8 h. After the reaction completed as determined by TLC analysis, the reaction solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography to afford racemic **3**. The racemic spectra of compounds **3** were recorded by HPLC (Daicel Chiralpak AD-H).

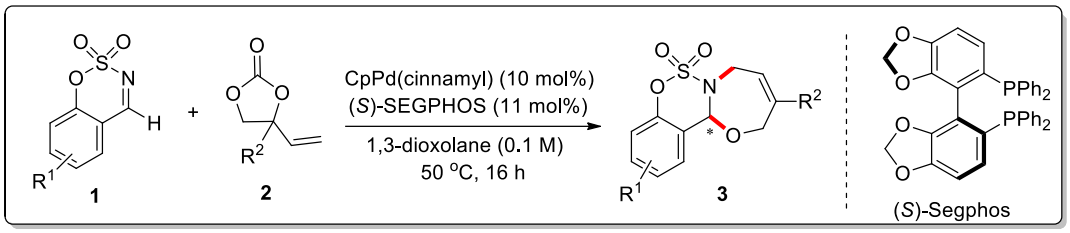
3.2 General procedure for asymmetric synthesis of compounds 3



To a flame-dried Schlenk tube, [(cinnamyl)PdCl]$_2$ (5.18 mg, 5 mol%), (*S*)-SEGPHOS (13.40 mg, 11 mol%) and THF (1.0 mL) were added under Ar atmosphere, and stirred for 15 minutes at room temperature. Then sulfamate-derived cyclic imines **1** (0.2 mmol, 1.0 equiv), vinyl ethylene carbonate **2** (0.5 mmol, 2.5 equiv) were added under Ar atmosphere. The reaction mixture was stirred at 30 °C for 24 h. After the reaction completed as determined by TLC analysis, the reaction solvent was evaporated under reduced pressure. The residue

was purified by silica gel column chromatography to afford **3**. The enantiomeric ratios of compunds **3** were recorded by HPLC (Daicel Chiralpak AD-H).

3.3 Typical procedure for asymmetric synthesis of compounds 3d, 3i, 3k, 3l

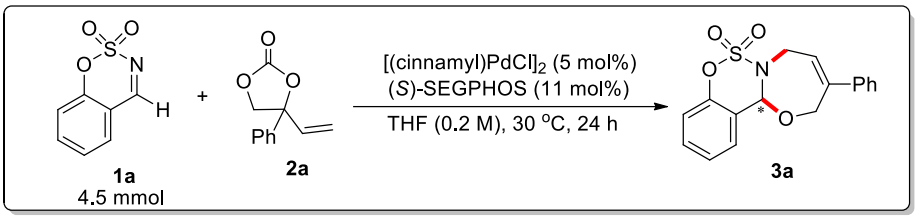


The compounds **3d**, **3i**, **3k** and **3l** were synthesized through the typical procedure (Table S1, entry 23) since the reaction efficiencies were higher than the general reaction conditions.

To a flame-dried Schlenk tube, CpPd(cinnamyl) (5.59 mg, 10 mol%), (*S*)-SEGPHOS (13.40 mg, 11 mol%) and 1,3-dioxolane (2.0 mL) were added under Ar atmosphere, and stirred for 15 minutes at room temperature. Then sulfamate-derived cyclic imines **1** (0.2 mmol, 1.0 equiv), vinyl ethylene carbonate **2** (0.5 mmol, 2.5 equiv) were added under Ar atmosphere. The reaction mixture was stirred at 50 °C for 16 h. After the reaction completed as determined by TLC analysis, the reaction solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography affording **3d, 3i, 3k** and **3l**. The enantiomeric ratios were recorded by HPLC (Daicel Chiralpak AD-H).

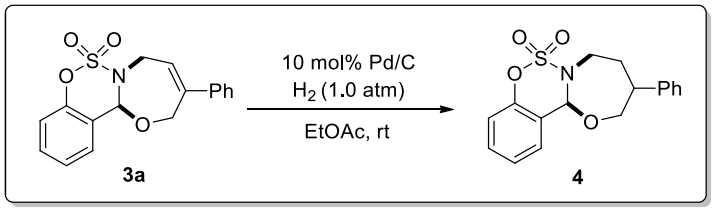
4. Procedure for the synthetic transformations of compounds 3

4.1 Procedure for the gram-scale synthesis of 3a



To a flame-dried Schlenk tube, $[(cinnamyl)PdCl]_2$ (116.6 mg, 5 mol%), (*S*)-SEGPHOS (302.2 mg, 11 mol%) and THF (22.5 mL) were added under Ar atmosphere, and stirred for 15 minutes at room temperature. Then sulfamate-derived cyclic imine **1a** (4.5 mmol, 1.0 equiv) and vinyl ethylene carbonate **2a** (11.25 mmol, 2.5 equiv) were added under Ar atmosphere and stirred at 30 °C for 24 h. After the reaction completed, the solvent was evaporated, and **3a** was isolated by silica gel column chromatography (eluent: acetone/*n*-hexane =1/15). The desired product **3a** was formed in 77% isolated yield as a white solid, 84:16 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm).

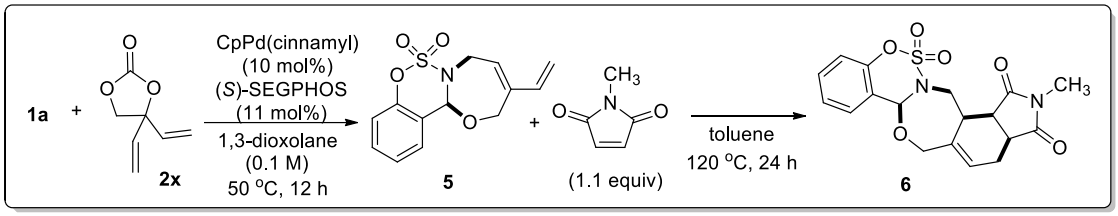
4.2 Procedure for the synthesis of 4



Compound **3a** (0.2 mmol, 65.8mg) was added into flame-dried tube, Pd/C (10 wt%, 21.2 mg, 10 mol% based on Pd contents) and etheyl acetate (2.0 mL) wcere added at Ar atmosphere. The reaction mixture was degassed followed by hydrogen gas was charged and stirred under room temperature for 24 h. After reaction completed, the reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (eluent: acetone/*n*-hexane = 1/20), affording **4** in 70 % combined yield with 3.3:1 dr (82:18 er for the major diastereomer of **4**, 82:18 er for

the minor diastereomer of **4**). (Note: Diastereomers of **4** were separated by column chromatography)

4.3 Procedure for the synthesis of 5 and 6

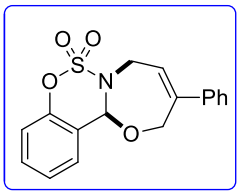


To a flame-dried Schlenk tube, CpPd(cinnamyl) (5.59 mg, 10 mol%), (*S*)-SEGPHOS (13.40 mg, 11 mol%) and 1,3-dioxolane (2.0 mL) were added under Ar atmosphere, and stirred for 15 minutes at room temperature. Then sulfamate-derived cyclic imines **1** (0.2 mmol, 1.0 equiv), vinyl ethylene carbonates **2x** (0.5 mmol, 2.5 equiv) were added under Ar atmesphere. The reaction mixture was stirred at 50 °C for 16 h. After the reaction completed as determined by TLC analysis, the reaction solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography to afford compound **5** in 60% isolated yield (eluent: acetone/*n*-hexane = 1/20) with 77:23 er.

Compound **5** (0.1 mmol, 29.7mg) was added in a round flask followed by the addition of *N*-methylmaleimide (0.11 mmol, 12.2mg) with toluene (0.5 mL), and stirred at room temperature for 24 h. After the reaction completed as determined by TLC analysis, the reaction solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/*n*-hexane = 1/1), affording compound **6** in 57% yield.

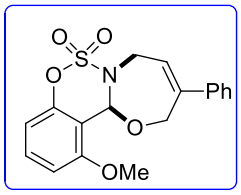
5. Characterization data of all compounds

3-phenyl-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3a) (CAS: 2153466-34-1).



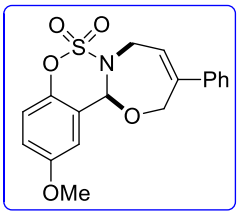
white solid (50.1 mg, yield: 76%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 85:15 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 10.21 min, t_{minor} = 15.06 min; $[\alpha]_D^{25}$ = +38.1 (c = 0.46, $CHCl_3$); mp: 112-114 ℃; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.62 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.47 – 7.27 (m, 7H), 7.06 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.28 (s, 1H), 5.94 (m, 1H), 5.06 – 4.88 (m, 2H), 4.18 (dd, *J* = 16.3, 7.3 Hz, 1H), 3.92 (dq, *J* = 16.5, 2.9 Hz, 1H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 149.8, 142.0, 138.7, 131.2, 128.7, 128.5, 128.2, 126.2, 125.7, 122.9, 118.7, 118.0, 90.3, 71.5, 43.4 ppm. These data were similar to those reported in the literature.[4]

12-methoxy-3-phenyl-5,12b,-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3b)



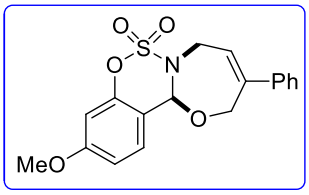
white solid (61.8 mg, yield: 86%); purification by silica gel chromatography (ethyl acetate:*n*-hexane = 1:8, R_f: 0.3); 82:18 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 9.80 min, t_{minor} = 13.77 min; $[\alpha]_D^{25}$ = -29.7 (c = 0.12, $CHCl_3$); mp: 126-128 ℃; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.41 – 7.27 (m, 6H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 6.28 (s, 1H), 6.02 (t, *J* = 5.4 Hz, 1H), 4.95 – 4.72 (m, 2H), 4.38 (m, 1H), 4.23 (dd, *J* = 16.4, 5.9 Hz, 1H), 3.91 (s, 3H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 158.9, 151.3, 142.9, 138.9, 131.7, 128.7, 128.1, 126.3, 123.2, 110.8, 109.2, 108.5, 88.8, 71.2, 56.5, 44.7 ppm; IR (ATR) ν_{max} 2922, 2857, 1440, 1380, 1272, 1184, 1131, 1012, 836; **HRMS (ESI-MS)** calcd for $C_{18}H_{17}NO_5SNa$ $(M + Na)^+$: 359.0827, Found: 359.0813.

11-methoxy-3-phenyl-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3c) (CAS:2153466-38-5).



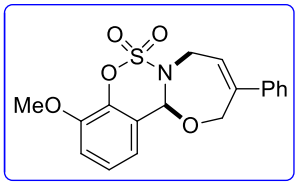
white solid (51.8 mg, yield: 72%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 85:15 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 14.49 min, t_{minor} = 23.00 min; $[\alpha]_D^{25}$ = +23.7 (c = 0.22, $CHCl_3$); mp: 116-118 ℃; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.39 – 7.27 (m, 5H), 7.10 (d, *J* = 2.6 Hz, 1H), 7.02 – 6.92 (m, 2H), 6.22 (s, 1H), 5.93 (dt, *J* = 7.3, 2.5 Hz, 1H), 5.07 – 4.85 (m, 2H), 4.17 (dd, *J* = 16.4, 7.3 Hz, 1H), 3.97 – 3.86 (m, 1H), 3.83 (s, 3H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 157.1, 143.5, 141.9, 138.7, 128.7, 128.1, 126.2, 123.0, 119.3, 119.0, 117.5, 112.1, 90.3, 71.4, 55.9, 43.4 ppm. These data were similar to those reported in the literature.[4]

10-methoxy-3-phenyl-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3d) (CAS:2153466-39-6)



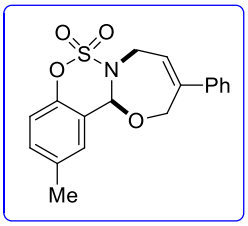
3d was synthesized through the typical procedure (Table S1, entry 23). white solid (47.4 mg, yield: 66%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 82:18 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 13.34 min, t_{minor} = 18.16 min; $[\alpha]_D^{25}$ = +66.9 (c = 0.42, $CHCl_3$); mp: 191-193 ℃; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.49 (d, *J* = 8.7 Hz, 1H), 7.39 – 7.26 (m, 5H), 6.83 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.56 (d, *J* = 2.5 Hz, 1H), 6.21 (s, 1H), 5.93 (dt, *J* = 7.2, 2.5 Hz, 1H), 5.05 – 4.85 (m, 2H), 4.15 (dd, *J* = 16.3, 7.3 Hz, 1H), 3.91 (m, 1H), 3.82 (s, 3H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 161.7, 150.7, 142.1, 138.8, 129.2, 128.7, 128.2, 126.3, 123.0, 112.6, 110.6, 102.8, 90.3, 71.3, 55.8, 43.4 ppm. These data were similar to those reported in the literature.[4]

9-methoxy-3-phenyl-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide) (3e) (CAS:2153466-40-9).



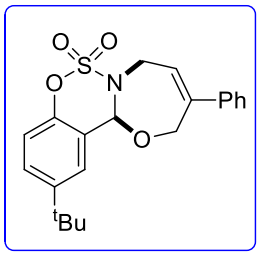
white solid (64.0 mg, yield: 89%); purification by silica gel chromatography (ethyl acetate:*n*-hexane = 1:8, R_f: 0.3); 80:20 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 16.58 min, t_{minor} = 22.37 min; $[\alpha]_D^{25}$ = +20.7 (c = 0.80, $CHCl_3$); mp: 136-138 °C; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.39 – 7.27 (m, 5H), 7.25 – 7.15 (m, 2H), 7.00 (dd, *J* = 7.4, 2.3 Hz, 1H), 6.27 (s, 1H), 5.98 – 5.89 (m, 1H), 5.04 – 4.87 (m, 2H), 4.19 (dd, *J* = 16.4, 7.3 Hz, 1H), 3.98 (m, 1H), 3.90 (s, 3H) ppm; **^{13}C NMR (75 MHz, Chloroform-*d*)** δ 148.2, 142.0, 139.6, 138.8, 128.7, 128.2, 126.3, 125.3, 123.0, 119.6, 119.3, 113.4, 90.4, 71.5, 56.4, 43.5 ppm. These data were similar to those reported in the literature.[4]

11-methyl-3-phenyl-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3f) (CAS:2153466-35-2).



white solid (55.6 mg, yield: 81%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 83:17 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 9.47 min, t_{minor} = 17.79 min; $[\alpha]_D^{25}$ = +40.2 (c = 0.76, $CHCl_3$); mp: 126-128 °C; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.44 – 7.27 (m, 6H), 7.21 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.24 (s, 1H), 5.98 – 5.89 (m, 1H), 5.05 – 4.87 (m, 2H), 4.17 (dd, *J* = 16.3, 7.3 Hz, 1H), 3.91 (m, 1H), 2.38 (s, 3H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 147.8, 142.0, 138.8, 135.6, 131.8, 128.7, 128.5, 128.1, 126.2, 123.0, 118.2, 117.8, 90.4, 71.4, 43.4, 20.9 ppm. These data were similar to those reported in the literature.[4]

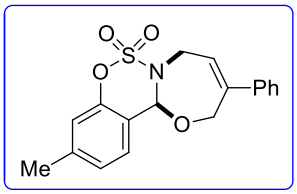
11-(tert-butyl)-3-phenyl-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3g) (CAS:2153466-42-1).



white solid (47.8 mg, yield: 62%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 82:18 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 5.96 min, t_{minor} = 8.19 min; $[\alpha]_D^{25}$ = -1.1 (c = 0.25, $CHCl_3$); mp: 191-

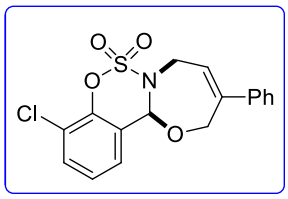
193 ℃; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.59 (d, *J* = 2.5 Hz, 1H), 7.47 – 7.27 (m, 7H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.26 (s, 1H), 5.94 (dt, *J* = 7.3, 2.5 Hz, 1H), 5.09 – 4.87 (m, 2H), 4.18 (dd, *J* = 16.3, 7.4 Hz, 1H), 3.93 (m, 1H), 1.34 (s, 9H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 148.9, 147.6, 142.1, 138.9, 128.8, 128.4, 128.2, 126.3, 125.0, 123.1, 117.8, 117.5, 90.6, 71.5, 43.4, 34.8, 31.5 ppm. These data were similar to those reported in the literature.[4]

10-methyl-3-phenyl-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3h) (CAS:2153466-36-3).



white solid (44.0 mg, yield: 64%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 85:15 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 10.54 min, t_{minor} = 12.60 min; $[\alpha]_D^{25}$ = -15.8 (c = 0.50, $CHCl_3$); mp: 178-180 ℃; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.48 (d, *J* = 7.9 Hz, 1H), 7.31 (m, 6H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.86 (s, 1H), 6.23 (s, 1H), 5.93 (m, 1H), 4.97 (m, 2H), 4.16 (dd, *J* = 16.3, 7.3 Hz, 1H), 3.98 – 3.83 (m, 1H), 2.38 (s, 3H) ppm; **^{13}C NMR (75 MHz, Chloroform-*d*)** δ 149.7, 142.1, 142.0, 138.8, 128.7, 128.1, 126.6, 126.2, 123.0, 118.2, 115.7, 90.3, 71.4, 43.4, 21.3 ppm. These data were similar to those reported in the literature.[4]

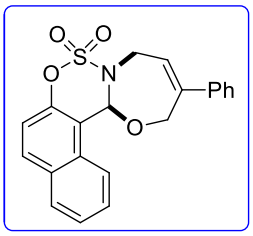
9-chloro-3-phenyl-2,5,8,12b-tetrahydrobenzo[4,5][1,2]thiazino[3,2-b][1,3]oxazepine 7,7-dioxide (3i) (CAS:2153466-51-2).



3i was synthesized through the typical procedure (Table S1, entry 23). white solid (9.5 mg, yield: 13%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 71:29 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} =9.81min, t_{minor} =16.72 min; $[\alpha]_D^{25}$ = -22.0 (c = 0.18, $CHCl_3$); mp: 121-123 ℃; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.52 (m, 2H), 7.33 (m, 5H), 7.21 (t, *J* = 7.9 Hz, 1H), 6.28 (s, 1H), 5.99 – 5.91 (m, 1H), 5.07 – 4.88 (m, 2H), 4.20 (dd, *J* = 16.3, 7.3 Hz, 1H), 3.98 – 3.85 (m, 1H) ppm; **^{13}C NMR (75 MHz, Chloroform-*d*)** δ 145.9, 142.0, 138.6, 132.0, 128.8, 128.3, 126.8, 126.2, 125.6, 123.1,

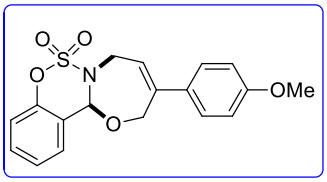
122.7, 120.4, 90.2, 71.7, 43.5 ppm. These data were similar to those reported in the literature.[4]

3-phenyl-5,14c-dihydro-2H-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3j) (CAS:2153466-53-4).



white solid (68.0 mg, yield: 89%); purification by silica gel chromatography (acetone:*n*-hexane = 1:6, R_f: 0.3); 87:13 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 15.57 min, t_{minor} = 33.22 min; $[\alpha]_D^{25}$ = -72.6 (c = 0.37, $CHCl_3$); mp: 112-114 ℃; **^{1}H NMR (300 MHz, Chloroform-d)** δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.83 – 7.72 (m, 2H), 7.54 – 7.37 (m, 2H), 7.18 (m, 6H), 7.05 (d, *J* = 9.0 Hz, 1H), 6.58 (s, 1H), 5.91 (t, *J* = 5.3 Hz, 1H), 4.86 (m, 2H), 4.17 (dd, *J* = 5.1, 2.1 Hz, 2H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 148.7, 142.1, 138.6, 132.6, 131.8, 131.3, 129.0, 128.7, 128.2, 127.8, 126.2, 126.0, 124.9, 123.4, 117.9, 112.7, 91.1, 71.1, 44.5 ppm. These data were similar to those reported in the literature.[4]

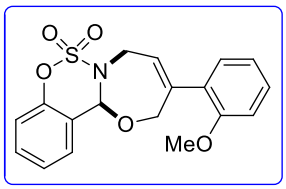
3-(4-methoxyphenyl)-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3k).



3k was synthesized through the typical procedure (Table S1, entry 23). white solid (44.6 mg, yield: 62%); purification by silica gel chromatography (ethyl acetate:*n*-hexane = 1:10, R_f: 0.3); 83:17 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 15.49 min, t_{minor} = 23.44 min; $[\alpha]_D^{25}$ = +4.4 (c = 0.38, $CHCl_3$); mp: 119-121 ℃; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.65 – 7.58 (m, 1H), 7.42 (td, *J* = 7.8, 1.7 Hz, 1H), 7.29 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.05 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.93 – 6.84 (m, 2H), 6.26 (s, 1H), 5.86 (dt, *J* = 7.5, 2.7 Hz, 1H), 5.05 – 4.83 (m, 2H), 4.15 (dd, *J* = 16.3, 7.4 Hz, 1H), 3.90 (m, 1H), 3.82 (s, 3H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 159.6, 149.8, 141.4, 131.2, 131.1, 128.5, 127.4, 125.7, 121.5, 118.7, 118.0, 114.1, 90.3, 71.5, 55.4, 43.4 ppm; IR

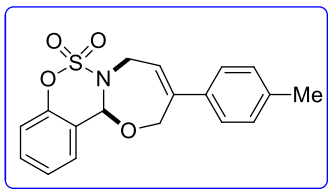
(ATR) ν_{max} 2922, 2844, 1435, 1400, 1265, 1168, 1142, 1014, 832; **HRMS (ESI-MS)** calcd for $C_{18}H_{17}NO_5SNa$ $(M + Na)^+$: 359.0827, Found: 359.0823.

3-(2-methoxyphenyl)-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3l).



3l was synthesized through the typical procedure (Table S1, entry 23). white solid (43.1 mg, yield: 60%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 78:22 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 21.93 min, t_{minor} = 39.29 min; $[\alpha]_D^{25}$ = +13.0 (c = 0.58, $CHCl_3$); mp: 108-110 °C; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.67 – 7.59 (m, 1H), 7.46 – 7.37 (m, 1H), 7.30 (m, 2H), 7.17 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.05 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.00 – 6.85 (m, 2H), 6.28 (s, 1H), 5.77 (dt, *J* = 7.2, 2.6 Hz, 1H), 5.04 – 4.77 (m, 2H), 4.17 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.91 (m, 1H), 3.85 (s, 3H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 156.7, 149.8, 142.1, 131.1, 130.0, 129.5, 128.8, 128.5, 125.6, 124.1, 120.9, 118.8, 117.9, 110.8, 90.4, 71.7, 55.5, 43.6 ppm; IR (ATR) ν_{max} 2921, 2844, 1435, 1391, 1251, 1156, 1144, 1013, 833; **HRMS (ESI-MS)** calcd for $C_{18}H_{17}NO_5SNa$ $(M + Na)^+$: 359.0827, Found: 359.0827.

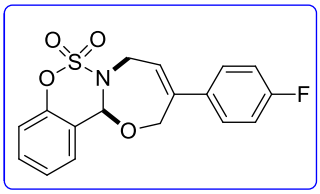
3-(p-tolyl)-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3m).



white solid (48.8 mg, yield: 71%); purification by silica gel chromatography (acetone:*n*-hexane=1:10, R_f: 0.3); 85:15 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 10.21 min, t_{minor} = 12.47 min; $[\alpha]_D^{25}$ = +57.3 (c = 0.63, $CHCl_3$); mp: 99-101 °C; **^{1}H NMR (300 MHz, Chloroform-d)** δ 7.62 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.42 (td, *J* = 7.8, 1.8 Hz, 1H), 7.30 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.23 – 7.13 (m, 4H), 7.05 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.27 (s, 1H), 5.91 (dt, *J* = 7.4, 2.5 Hz, 1H), 5.06 – 4.85 (m, 2H), 4.17 (dd, *J* = 16.3, 7.3 Hz, 1H), 3.91 (m, 1H), 2.36 (s, 3H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 149.8, 141.8, 138.0, 135.8, 131.2, 129.4, 128.5, 126.1, 125.7, 122.1, 118.7, 118.0, 90.3, 71.5, 43.4, 21.2 ppm; IR

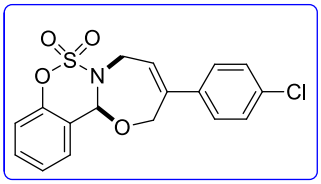
(ATR) ν_{max} 2921, 2850, 1399, 1283, 1120, 1143, 1014, 831; **HRMS (ESI-MS)** calcd for $C_{18}H_{17}NO_4SNa$ $(M + Na)^+$: 343.0878, Found: 343.0878.

3-(4-fluorophenyl)-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3n) (CAS: 2153466-57-8).



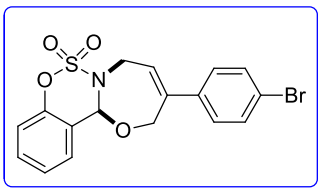
white solid (49.3 mg, yield: 71%); purification by silica gel chromatography (acetone:*n*-hexane = 1:15, R_f: 0.3); 82:18 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 14.77 min, t_{minor} = 19.35 min; $[\alpha]_D^{25}$ = +42.2 (c = 0.23, $CHCl_3$); mp: 130-132 °C; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.61 (m, 1H), 7.43 (m, 1H), 7.31 (m, 3H), 7.25 – 7.18 (m, 2H), 7.05 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.26 (s, 1H), 5.98 – 5.89 (m, 1H), 5.00 – 4.84 (m, 2H), 4.17 (dd, *J* = 16.4, 7.3 Hz, 1H), 3.90 (m, 1H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 162.7 (d, *J* = 252.0 Hz), 149.8, 141.1, 134.8 (d, *J* = 3.8 Hz), 131.3, 128.4, 128.0, 127.9, 125.8, 123.1, 118.6, 118.1, 115.7 (d, *J* = 21.4 Hz), 90.3, 71.4, 43.4 ppm; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -113.8 ppm. These data were similar to those reported in the literature.[4]

3-(4-chlorophenyl)-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3o) (CAS: 2153466-59-0).



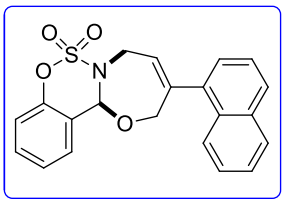
white solid (50.2 mg, yield: 69%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 84:16 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 12.45 min, t_{minor} = 18.68 min; $[\alpha]_D^{25}$ = +57.2 (c = 0.42, $CHCl_3$); mp: 124-126 °C; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.61 (m, 1H), 7.42 (m, 1H), 7.31 (m, 3H), 7.25 – 7.15 (m, 2H), 7.05 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.26 (s, 1H), 5.99 – 5.88 (m, 1H), 5.01 – 4.84 (m, 2H), 4.17 (dd, *J* = 16.4, 7.3 Hz, 1H), 3.90 (m, 1H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 149.8, 141.0, 137.1, 134.1, 131.3, 128.9, 128.4, 127.5, 125.8, 123.6, 118.6, 118.1, 90.3, 71.1, 43.4 ppm. These data were similar to those reported in the literature.[4]

3-phenyl-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3p) (CAS: 2153466-60-3).



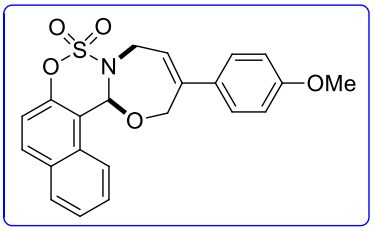
white solid (53.9 mg, yield: 66%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 83:17 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 17.36 min, t_{minor} = 23.48 min; $[\alpha]_D^{25}$ = +51.2 (c = 0.60, $CHCl_3$); mp: 151-153 ℃; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.61 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.51 – 7.38 (m, 3H), 7.30 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.20 – 7.12 (m, 2H), 7.05 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.26 (s, 1H), 5.93 (m, 1H), 5.00 – 4.84 (m, 2H), 4.17 (dd, *J* = 16.4, 7.3 Hz, 1H), 3.89 (m, 1H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 149.8, 141.0, 137.6, 131.9, 131.3, 128.4, 127.8, 125.8, 123.6, 122.2, 118.5, 118.0, 90.3, 71.0, 43.4 ppm. These data were similar to those reported in the literature.[4]

3-(naphthalen-1-yl)-5,12b-dihydro-2H-benzo[5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3q).



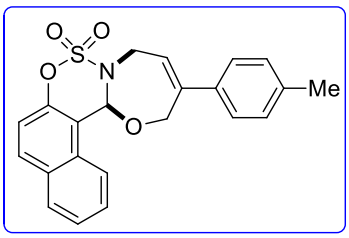
white solid (56.2 mg, yield: 74%); purification by silica gel chromatography (ethyl acetate:*n*-hexane = 1:10, R_f: 0.3); 81:19 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 18.28 min, t_{minor} = 31.29 min; $[\alpha]_D^{25}$ = +62.2 (c = 0.98, $CHCl_3$); mp: 129-131 ℃; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.83 (dd, *J* = 9.0, 3.2 Hz, 3H), 7.73 – 7.62 (m, 2H), 7.55 – 7.39 (m, 4H), 7.30 (td, *J* = 7.6, 1.3 Hz, 1H), 7.07 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.31 (s, 1H), 6.07 (dt, *J* = 7.3, 2.6 Hz, 1H), 5.19 – 4.95 (m, 2H), 4.23 (dd, *J* = 16.4, 7.3 Hz, 1H), 3.96 (m, 1H) ppm; **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 149.8, 141.8, 135.9, 133.3, 133.0, 131.2, 128.5, 128.4, 128.2, 127.7, 126.6, 126.4, 125.7, 124.9, 124.3, 123.4, 118.7, 118.0, 90.3, 71.4, 43.5 ppm; IR (ATR) ν_{max} 2922, 2843, 1453, 1398, 1279, 1170, 1144, 1013, 839; **HRMS (ESI-MS)** calcd for $C_{21}H_{17}NO_4SNa$ $(M + Na)^+$: 379.0878, Found: 379.0873.

3-(4-methoxyphenyl)-5,14c-dihydro-2H-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3r).



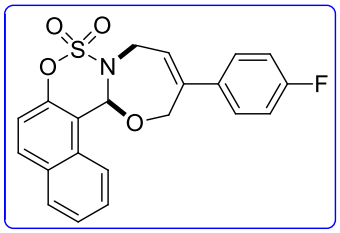
white solid (60.0 mg, yield: 73%); purification by silica gel chromatography (ethyl acetate:*n*-hexane = 1:10, R_f: 0.3); 90:10 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 12.87 min, t_{minor} = 20.31 min; $[\alpha]_D^{25}$ = -88.1 (c = 0.89, $CHCl_3$); mp: 136-138 ℃; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 8.26 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.89 (m, 2H), 7.58 (m, 2H), 7.32 (m, 1H), 7.22 – 7.11 (m, 4H), 6.70 (s, 1H), 6.08 – 5.96 (m, 1H), 5.12 – 4.86 (m, 2H), 4.37 – 4.21 (m, 2H), 2.36 (s, 3H) ppm; **^{13}C NMR (75 MHz, Chloroform-*d*)** δ 148.6, 141.8, 138.0, 135.6, 132.5, 131.7, 131.3, 129.4, 128.9, 128.7, 127.8, 126.1, 126.0, 124.8, 122.5, 117.8, 112.6, 91.1, 71.2, 44.5, 21.2 ppm; IR (ATR) ν_{max} 2919, 2850, 1440, 1402, 1339, 1281, 1175, 1138, 1070, 817; **HRMS (ESI-MS)** calcd for $C_{22}H_{19}NO_5SNa$ $(M + Na)^+$: 409.0984, Found: 409.0981.

3-(p-tolyl)-5,14c-dihydro-2H-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3s).



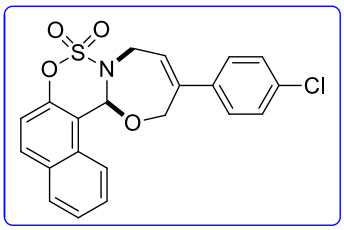
white solid (51.1 mg, yield: 65%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 83:17 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 19.92 min, t_{minor} = 60.53 min; $[\alpha]_D^{25}$ = -69.0 (c = 0.26, $CHCl_3$); mp: 98-100 ℃; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 8.26 (d, *J* = 8.5 Hz, 1H), 7.89 (dd, *J* = 12.2, 8.5 Hz, 2H), 7.57 (m, 2H), 7.25 – 7.15 (m, 3H), 6.91 – 6.83 (m, 2H), 6.69 (s, 1H), 5.96 (t, *J* = 5.4 Hz, 1H), 5.08 – 4.86 (m, 2H), 4.28 (d, *J* = 5.3 Hz, 2H), 3.81 (s, 3H) ppm; **^{13}C NMR (75 MHz, Chloroform-*d*)** δ 148.7, 141.9, 138.1, 135.6, 132.5, 131.8, 131.3, 129.4, 129.0, 127.8, 126.0, 124.9, 122.5, 117.9, 112.7, 91.1, 71.2, 44.5, 21.2 ppm; IR (ATR) ν_{max} 2921, 2864, 1454, 1379, 1279, 1176, 1137, 1013, 812; **HRMS (ESI-MS)** calcd for $C_{22}H_{19}NO_4SNa$ $(M + Na)^+$: 393.1035, Found: 393.1037.

3-(4-fluorophenyl)-5,14c-dihydro-2H-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3t).



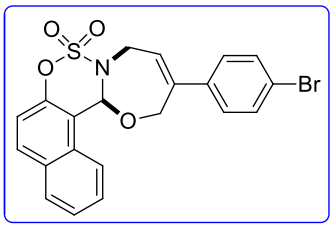
white solid (56.4 mg, yield: 71%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 88:12 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 14.69 min, t_{minor} = 27.57 min; $[\alpha]_D^{25}$ = -66.9 (c = 0.37, $CHCl_3$); mp: 91-93 °C; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 8.25 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.94 – 7.83 (m, 2H), 7.57 (m, 2H), 7.25 – 7.21 (m, 2H), 7.17 (d, *J* = 9.0 Hz, 1H), 7.07 – 6.98 (m, 2H), 6.69 (s, 1H), 5.98 (m, 1H), 4.94 (m, 2H), 4.28 (m, 2H) ppm; **^{13}C NMR (75 MHz, Chloroform-*d*)** δ 162.7 (d, *J* = 247.5 Hz), 148.7, 141.2, 134.6 (d, *J* = 3.0 Hz), 132.6, 131.8, 131.2, 129.0, 127.9, 127.8, 126.1, 124.8, 123.5, 117.8, 115.6 (d, *J* = 21.8 Hz), 112.6, 91.0, 71.0, 44.5 ppm; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -113.8 ppm; IR (ATR) ν_{max} 2922, 2864, 1454, 1379, 1279, 1177, 1136, 1012, 811; **HRMS (ESI-MS)** calcd for $C_{21}H_{16}FNO_4SNa$ $(M + Na)^+$: 397.0784, Found: 397.0786.

3-(4-chlorophenyl)-5,14c-dihydro-2H-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3u).



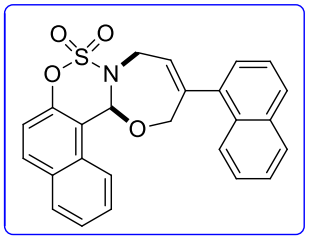
white solid (56.3 mg, yield: 68%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 89:11 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 16.39 min, t_{minor} = 29.57 min; $[\alpha]_D^{25}$ = -65.9 (c = 0.04, $CHCl_3$); mp: 78-80 °C; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 8.25 (m, 1H), 7.95 – 7.84 (m, 2H), 7.58 (m, 2H), 7.33 – 7.27 (m, 3H), 7.23 – 7.15 (m, 3H), 6.69 (s, 1H), 6.03 (m, 1H), 5.05 – 4.83 (m, 2H), 4.34 – 4.24 (m, 2H) ppm; **^{13}C NMR (75 MHz, Chloroform-*d*)** δ 148.7, 141.1, 137.0, 134.1, 132.7, 131.8, 131.3, 129.0, 128.9, 128.7, 127.9, 127.5, 126.2, 126.1, 124.8, 124.0, 117.9, 112.6, 91.1, 70.7, 44.5 ppm; IR (ATR) ν_{max} 2922, 2843, 1399, 1331, 1176, 1158, 1032, 812; **HRMS (ESI-MS)** calcd for $C_{21}H_{16}ClNO_4SNa$ $(M + Na)^+$: 413.0489, Found: 413.0486.

3-(4-bromophenyl)-5,14c-dihydro-2H-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3v).



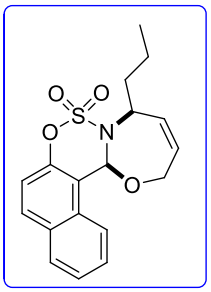
white solid (67.8 mg, yield: 74%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 85:15 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 17.83 min, t_{minor} = 32.13 min; $[\alpha]_D^{25}$ = -55.5 (c = 0.65, $CHCl_3$); mp: 147-149 °C; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 8.24 (d, *J* = 8.5 Hz, 1H), 7.95 – 7.82 (m, 2H), 7.57 (m, 2H), 7.49 – 7.42 (m, 2H), 7.22 – 7.10 (m, 3H), 6.69 (s, 1H), 6.03 (t, *J* = 5.3 Hz, 1H), 5.04 – 4.82 (m, 2H), 4.35 – 4.22 (m, 2H) ppm; **^{13}C NMR (75 MHz, Chloroform-*d*)** δ 148.7, 141.1, 137.4, 132.7, 131.8, 131.2, 129.0, 127.9, 127.8, 126.1, 124.8, 124.1, 122.2, 117.8, 112.5, 91.0, 70.6, 44.5 ppm; IR (ATR) ν_{max} 2922, 2864, 1451, 1379, 1278, 1175, 1137, 1007, 813; **HRMS (ESI-MS)** calcd for $C_{21}H_{16}BrNO_4SNa$ $(M + Na)^+$: 456.9983, Found: 456.9980.

3-(naphthalen-1-yl)-5,14c-dihydro-2H-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3w).



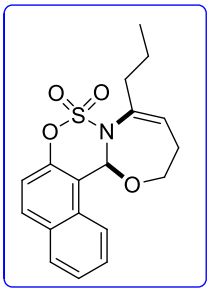
white solid (75.6 mg, yield: 88%); purification by silica gel chromatography (ethyl acetate:*n*-hexane= 1:10, R_f: 0.3); 85:15 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 18.07 min, t_{minor} = 36.01 min; $[\alpha]_D^{25}$ = -66.1 (c = 1.00, $CHCl_3$); mp: 142-143 °C; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 8.29 (d, *J* = 8.6 Hz, 1H), 7.93 – 7.76 (m, 5H), 7.72 – 7.60 (m, 2H), 7.60 – 7.47 (m, 3H), 7.43 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.18 (d, *J* = 9.0 Hz, 1H), 6.73 (s, 1H), 6.16 (t, *J* = 5.4 Hz, 1H), 5.23 – 4.91 (m, 2H), 4.39 – 4.25 (m, 2H) ppm; **^{13}C NMR (75 MHz, Chloroform-*d*)** δ 148.6, 141.8, 135.7, 133.3, 133.0, 132.5, 131.7, 131.2, 128.9, 128.4, 128.2, 127.8, 127.7, 126.6, 126.4, 126.0, 124.9, 124.8, 124.2, 123.8, 117.8, 112.6, 91.1, 71.0, 44.5 ppm; IR (ATR) ν_{max} 2921, 2864, 1463, 1377, 1273, 1179, 1134, 1012, 832; **HRMS (ESI-MS)** calcd for $C_{25}H_{19}NO_4SNa$ $(M + Na)^+$: 429.1035, Found: 429.1038.

5-propyl-5,14c-dihydro-2H-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3x).



white solid (40.8 mg, yield: 59%); purification by silica gel chromatography (acetone:*n*-hexane = 1:15, R_f: 0.3); dr = 9.1:1; **major diastereomer**: 55:45 er, **minor diastereomer**: 72:28 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, λ = 220 nm, **major diastereomer**: t_{major} = 7.54 min, t_{minor} = 14.41 min; **minor diastereomer**: t_{major} = 6.75 min, t_{minor} = 4.69 min; $[\alpha]_D^{25}$ = -45.0 (c = 0.01, $CHCl_3$); mp: 83-85 °C; **mixture of diastereomers 3x and 3x'**, **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.15 (d, *J* = 8.6 Hz, 1H), 7.88 (dd, *J* = 17.4, 8.6 Hz, 2H), 7.57 (dt, *J* = 42.6, 7.5 Hz, 2H), 7.17 (d, *J* = 8.9 Hz, 1H), 6.87 (s, 1H), 6.70 (s, 1H), 5.88 (dt, *J* = 14.3, 6.8 Hz, 1H), 5.71 (dt, *J* = 11.2, 7.5 Hz, 1H), 5.65 – 5.55 (m, 1H), 5.47 (dd, *J* = 15.3, 9.6 Hz, 1H), 4.87 (dt, *J* = 8.9, 6.0 Hz, 1H), 4.52 (td, *J* = 7.2, 4.6 Hz, 1H), 4.34 (dd, *J* = 8.3, 4.9 Hz, 1H), 4.15 – 4.06 (m, 1H), 3.92 (dd, *J* = 9.0, 4.6 Hz, 1H), 3.87 (dd, *J* = 8.8, 5.3 Hz, 1H), 2.21 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.09 (q, *J* = 7.2 Hz, 2H), 1.98 (q, *J* = 7.3 Hz, 2H), 1.46 (m, 2H), 1.36 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 7.5 Hz, 3H); **mixture of diastereomers 3x and 3x'**, **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 149.1, 138.8, 136.1, 135.1, 132.4, 132.1, 131.7, 131.5, 130.9, 128.9, 128.8, 128.0, 128.0, 127.9, 126.6, 126.2, 126.2, 126.1, 124.5, 124.2, 118.2, 118.0, 117.9, 114.6, 113.3, 113.1, 90.8, 90.7, 89.2, 73.2, 71.4, 71.2, 63.9, 62.6, 57.8, 34.3, 29.9, 29.8, 22.7, 22.1, 22.0, 13.8 ppm; IR (ATR) ν_{max} 2922, 2844, 1411, 1322, 1186, 1159, 1017, 863; **HRMS (ESI-MS)** calcd for $C_{18}H_{19}NO_4SNa$ $(M + Na)^+$: 345.1035, Found: 345.1032.

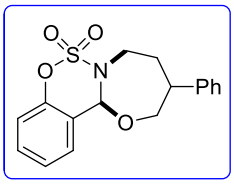
5-propyl-3,14c-dihydro-2H-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (3x').



white solid (2.8 mg, yield: 4%); purification by silica gel chromatography (acetone:*n*-hexane = 1:15, R_f: 0.3); 74:26 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, λ = 220 nm, **isomer**: t_{major} = 5.16 min, t_{minor} = 12.79 min; $[\alpha]_D^{25}$ = -45.0 (c = 0.01, $CHCl_3$); mp: 83-85 °C; **mixture of diastereomers 3x and 3x'**, **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.15 (d, *J* = 8.6 Hz, 1H), 7.88 (dd, *J* = 17.4, 8.6 Hz, 2H), 7.57 (dt, *J* = 42.6, 7.5 Hz, 2H), 7.17 (d, *J* = 8.9 Hz, 1H), 6.87 (s, 1H), 6.70 (s, 1H), 5.88 (dt, *J* = 14.3, 6.8 Hz, 1H), 5.71 (dt, *J* = 11.2, 7.5 Hz, 1H), 5.65 – 5.55

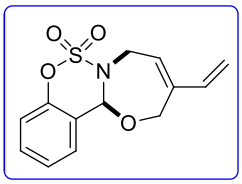
(m, 1H), 5.47 (dd, *J* = 15.3, 9.6 Hz, 1H), 4.87 (dt, *J* = 8.9, 6.0 Hz, 1H), 4.52 (td, *J* = 7.2, 4.6 Hz, 1H), 4.34 (dd, *J* = 8.3, 4.9 Hz, 1H), 4.15 – 4.06 (m, 1H), 3.92 (dd, *J* = 9.0, 4.6 Hz, 1H), 3.87 (dd, *J* = 8.8, 5.3 Hz, 1H), 2.21 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.09 (q, *J* = 7.2 Hz, 2H), 1.98 (q, *J* = 7.3 Hz, 2H), 1.46 (m, 2H), 1.36 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 7.5 Hz, 3H); **mixture of diastereomers 3x and 3x'**, **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 149.1, 138.8, 136.1, 135.1, 132.4, 132.1, 131.7, 131.5, 130.9, 128.9, 128.8, 128.0, 128.0, 127.9, 126.6, 126.2, 126.2, 126.1, 124.5, 124.2, 118.2, 118.0, 117.9, 114.6, 113.3, 113.1, 90.8, 90.7, 89.2, 73.2, 71.4, 71.2, 63.9, 62.6, 57.8, 34.3, 29.9, 29.8, 22.7, 22.1, 22.0, 13.8 ppm; IR (ATR) ν_{max} 2922, 2844, 1411, 1322, 1186, 1159, 1017, 863; **HRMS (ESI-MS)** calcd for $C_{18}H_{19}NO_4SNa$ $(M + Na)^+$: 345.1035, Found: 345.1032.

3-(naphthalen-1-yl)-5,14c-dihydro-2H-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (4).



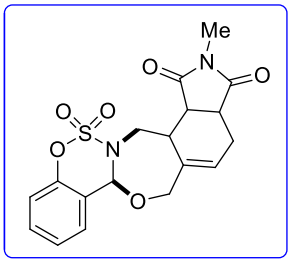
white oil (46.4 mg, yield: 70%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); dr = 3.3:1; **major diastereomer**: 82:18 er, **minor diastereomer**: 82:18 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 99/1, flow rate: 1.0 mL/min, λ = 220 nm, **major diastereomer**: t_{major} = 21.02 min, t_{minor} = 22.47 min, **minor diastereomer**: t_{major} = 20.05 min, t_{minor} = 24.81 min; **major 4,** $[\alpha]_D^{25}$ = -55.5 (c = 0.27, $CHCl_3$); **major 4, ^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.5 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.4 (td, *J* = 7.8, 1.7 Hz, 1H), 7.3 – 7.3 (m, 2H), 7.3 – 7.2 (m, 4H), 7.1 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.1 (s, 1H), 4.0 (dd, *J* = 12.1, 8.3 Hz, 1H), 4.0 – 3.9 (m, 2H), 3.6 (ddd, *J* = 14.2, 8.2, 3.9 Hz, 1H), 3.2 (qd, *J* = 4.9, 2.1 Hz, 1H), 2.2 – 2.1 (m, 2H) ppm; **major 4, ^{13}C NMR (75 MHz, Chloroform-*d*)** δ 149.8, 141.8, 131.1, 128.8, 128.1, 127.7, 127.0, 125.9, 121.1, 118.1, 88.1, 70.7, 45.0, 44.1, 35.6 ppm; **major 4, IR** (ATR) ν_{max} 2922, 2843, 1378, 1271, 1169, 1059, 910, 753; **minor 4, IR** (ATR) ν_{max} 2922, 2844, 1391, 1249, 1169, 1137, 1022, 906, 762; **HRMS (ESI-MS)** calcd for $C_{17}H_{17}NO_4SNa$ $(M + Na)^+$: 331.0878, Found: 331.0882.

3-(naphthalen-1-yl)-5,14c-dihydro-2H-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (5).



5 was synthesized through the typical procedure (Table S1, entry 23). white oil (33.5 mg, yield: 60%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); 77:23 er (determined by HPLC analysis Daicel Chiralpak AD-H, eluent: *n*-hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, λ = 220 nm, t_{major} = 7.52 min, t_{minor} = 9.14 min; $[\alpha]_D^{25}$ = -22.5 (c = 0.02, $CHCl_3$); **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.6 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.4 (td, *J* = 7.8, 1.7 Hz, 1H), 7.3 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.0 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.3 (dd, *J* = 17.8, 11.2 Hz, 1H), 6.2 (s, 1H), 5.8 (dd, *J* = 6.7, 3.3 Hz, 1H), 5.1 – 5.0 (m, 2H), 4.9 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.7 – 4.6 (m, 1H), 4.1 (dd, *J* = 16.6, 7.3 Hz, 1H), 3.8 (dd, *J* = 17.0, 3.7 Hz, 1H) ppm; **^{13}C NMR (75 MHz, Chloroform-*d*)** δ 149.8, 139.6, 136.1, 131.2, 128.5, 126.2, 125.7, 118.7, 118.0, 113.6, 90.2, 68.6, 43.2 ppm; IR (ATR) ν_{max} 2921, 2851, 1454, 1398, 1264, 1202, 1170, 1033, 757, 562; **HRMS (ESI-MS)** calcd for $C_{13}H_{13}NO_4SNa$ $(M + Na)^+$: 279.0565, Found: 279.0566.

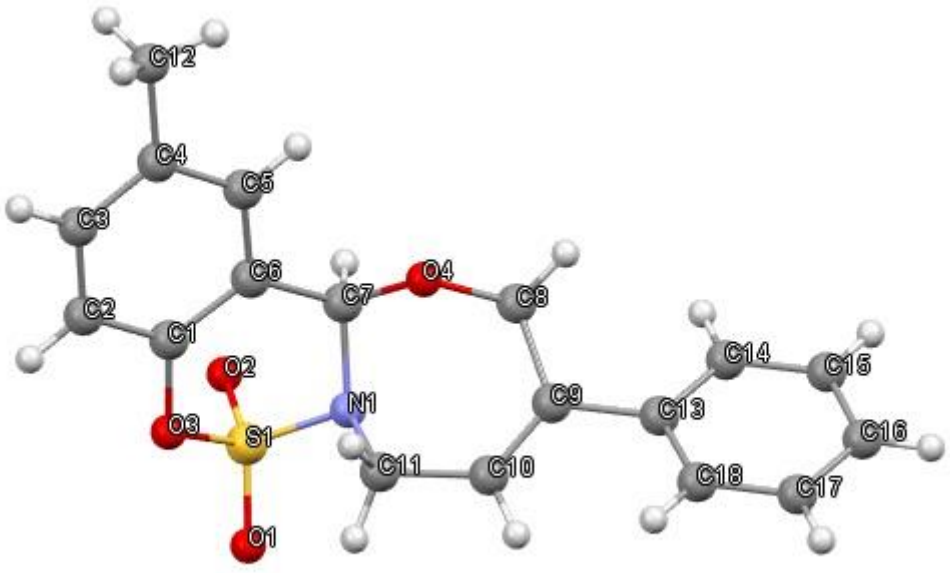
3-(naphthalen-1-yl)-5,14c-dihydro-2H-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-b][1,3]oxazepine 7,7-dioxide (6).



light yellow solid (22.1 mg, yield: 57%); purification by silica gel chromatography (acetone:*n*-hexane = 1:10, R_f: 0.3); mp: 233-235 °C; **^{1}H NMR (300 MHz, Chloroform-*d*)** δ 7.5 – 7.4 (m, 2H), 7.3 – 7.3 (m, 1H), 7.1 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.0 – 5.9 (m, 1H), 5.7 (s, 1H), 4.5 – 4.4 (m, 4H), 3.3 – 3.2 (m, 2H), 3.1 – 3.0 (m, 1H), 2.9 (s, 3H), 2.8 – 2.7 (m, 1H), 2.4 – 2.2 (m, 1H) ppm; **^{13}C NMR (75 MHz, Chloroform-*d*)** δ 179.2, 178.0, 149.0, 139.3, 131.2, 129.4, 127.2, 125.9, 120.6, 118.4, 92.4, 74.3, 49.9, 43.3, 40.4, 39.9, 25.1, 25.0 ppm; IR (ATR) ν_{max} 2922, 2843, 1691, 1436, 1372, 1168, 1052, 1032, 1011, 855, 762; **HRMS (ESI-MS)** calcd for $C_{18}H_{18}N_2O_6SNa$ $(M + Na)^+$: 390.0886, Found: 390.0886.

6. X-ray crystallographic data of 3f

Crystallographic data for **3f** have been deposited with the Cambridge Crystallographic Data Centre as deposition numbers CCDC 2045193 respectively.



Empirical formula	C18 H17 N O4 S	
Formula weight	343.38	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 13.738(13) Å	α= 90°.
	b = 15.885(13) Å	β= 111.13(4)°.
	c = 7.706(6) Å	γ = 90°.
Volume	1569(2) $Å^3$	
Z	4	
Density (calculated)	1.454 Mg/m^3	
Absorption coefficient	0.229 mm^{-1}	
F(000)	720	
Crystal size	0.182 x 0.175 x 0.103 mm^3	
Theta range for data collection	2.564 to 28.409°.	

Index ranges	-18<=h<=18, -21<=k<=21, -9<=l<=10
Reflections collected	10297
Independent reflections	3782 [R(int) = 0.0245]
Completeness to theta = 25.242°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6691
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3782 / 2 / 218
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0317, wR2 = 0.0732
R indices (all data)	R1 = 0.0361, wR2 = 0.0761
Absolute structure parameter	0.07(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.179 and -0.319 e.$Å^{-3}$

7. References

[1] B. Mao, W. Shi, J. Liao, H. Liu, C. Zhang, H. Guo, *Org. Lett*., 2017, **19**, 6340−6343.

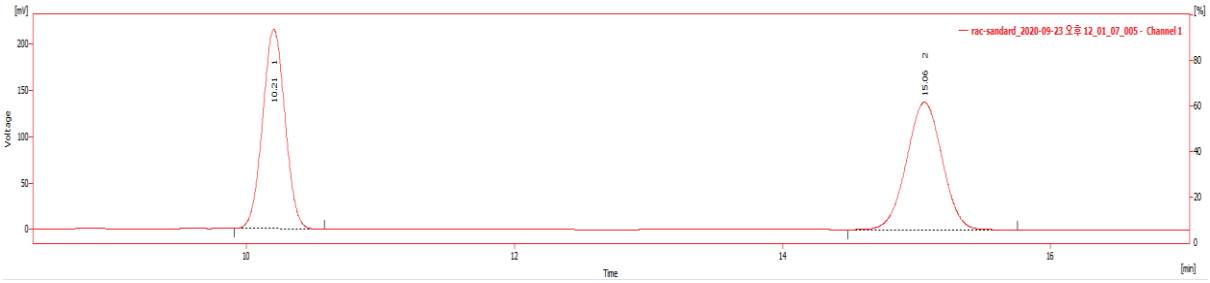
[2] A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing, Y. J. Zhang, *Angew. Chem. Int. Ed*., 2014, **53**, 6439−6442.

[3] Y. Tatsuno, T. Yoshida, Seiotsuka, N. Al-Salem, B. L. Shaw, *Inorganic Synthesis*, 1979**, 19**, 220−223.

[4] Y. Wu, C. Yuan, C. Wang, B. Mao, H. Jia, X. Gao, J. Liao, F. Jiang, L. Zhou, Q. Wang, H. Guo, *Org. Lett*., 2017, **19**, 6268−6271.

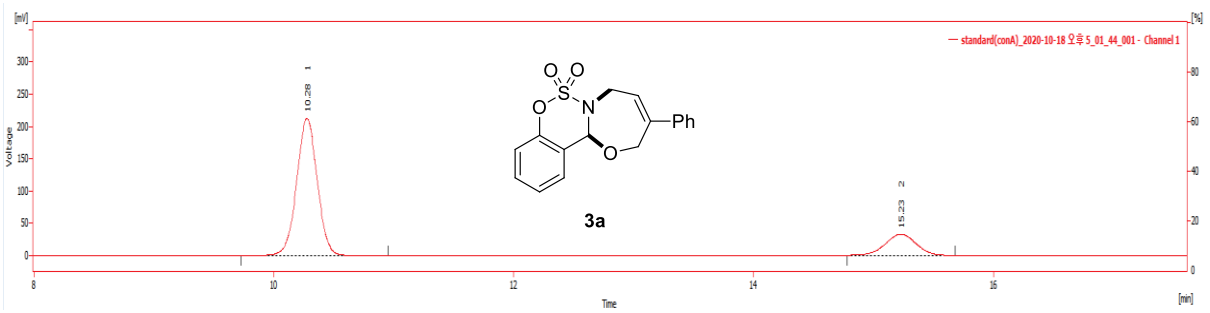
8. HPLC chromatograms of all compounds

For racemic **3a**



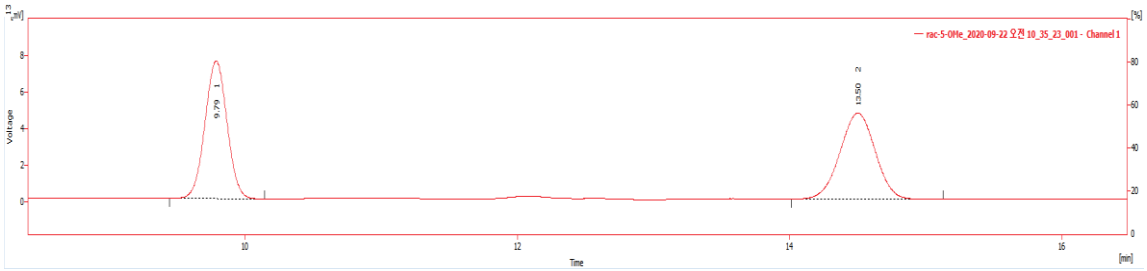
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	10.205	2502.025	215.606	50.0	61.2
2	15.060	2500.220	136.942	50.0	38.8
	All Signals	5002.245	352.548	100.0	100.0

For chiral **3a**



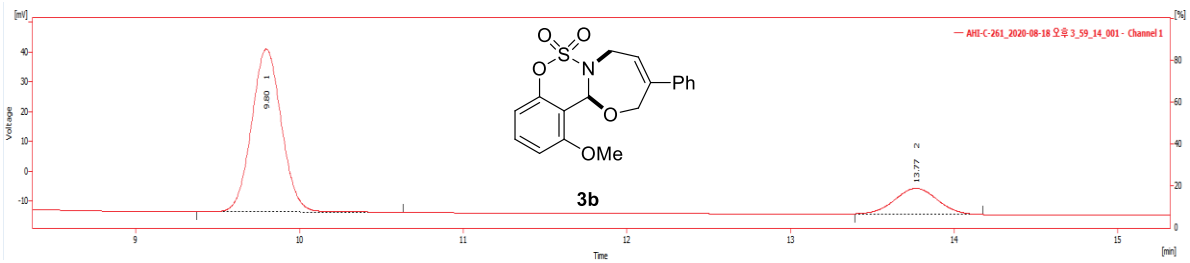
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	10,278	2535,610	212,153	85,0	88,0
2	15,230	448,833	28,976	15,0	12,0
	Total	2984,444	241,129	100,0	100,0

For racemic **3b**



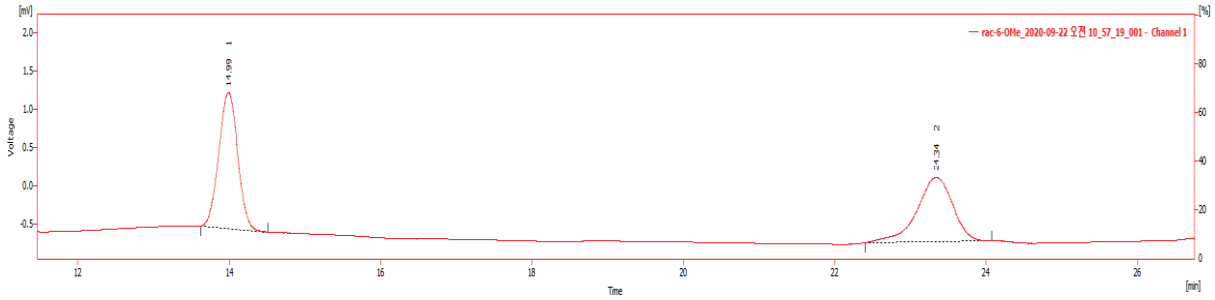
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	9,788	84,477	7,504	50,0	61,5
2	13,502	84,429	4,693	50,0	38,5
	Total	168,907	12,197	100,0	100,0

For chiral **3b**



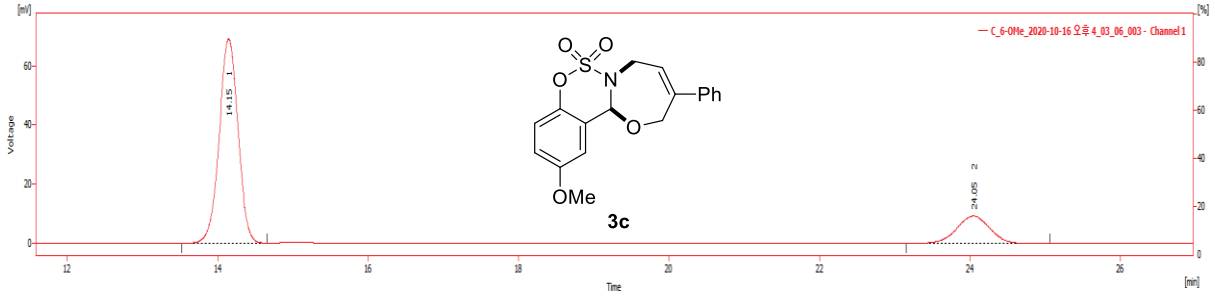
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	9,797	698,290	54,730	81,6	86,3
2	13,767	157,427	8,667	18,4	13,7
	Total	855,717	63,397	100,0	100,0

For racemic **3c**



	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	14,988	27,839	1,706	50,1	67,0
2	24,343	27,770	0,842	49,9	33,0
	Total	55,609	2,548	100,0	100,0

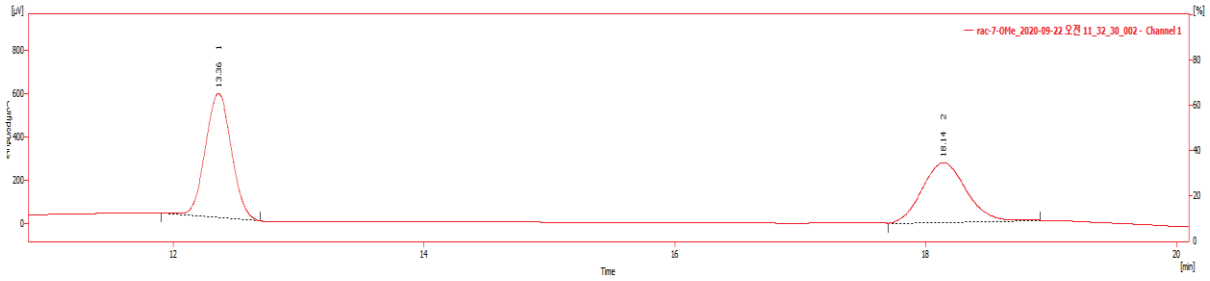
For chiral **3c**



3c

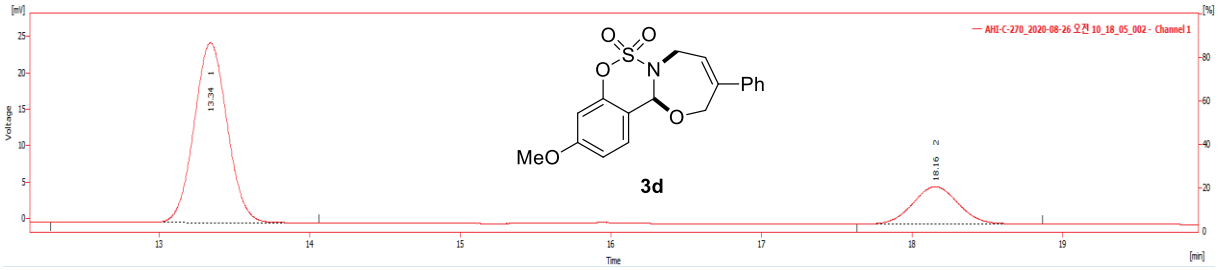
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	14,150	1201,842	69,238	85,1	89,7
2	24,048	209,909	7,976	14,9	10,3
	Total	1411,751	77,213	100,0	100,0

For racemic **3d**



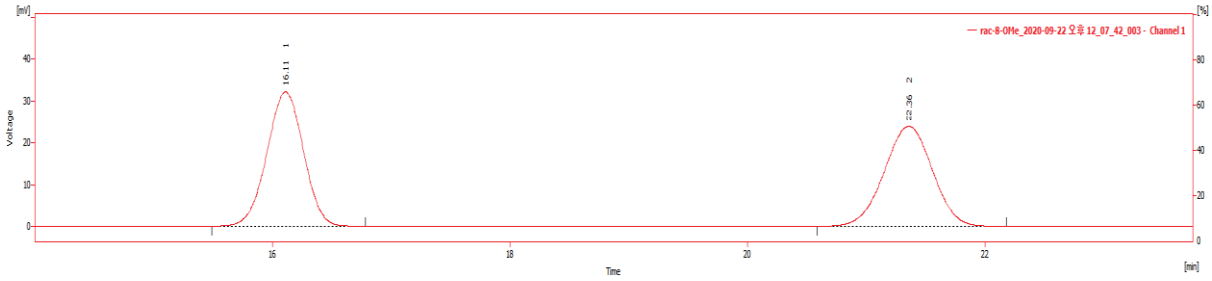
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	13,360	7,327	0,546	50,0	65,9
2	18,138	7,315	0,283	50,0	34,1
	Total	14,642	0,829	100,0	100,0

For chiral **3d**



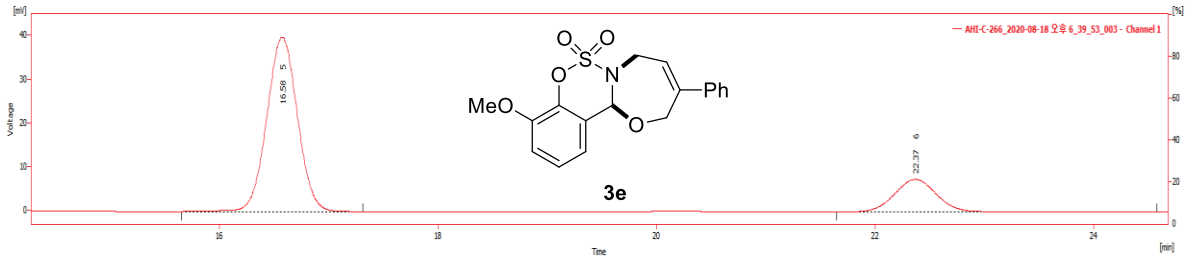
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	13,343	377,643	24,687	82,0	84,5
2	18,157	82,709	4,545	18,0	15,5
	Total	460,352	29,232	100,0	100,0

For racemic **3e**



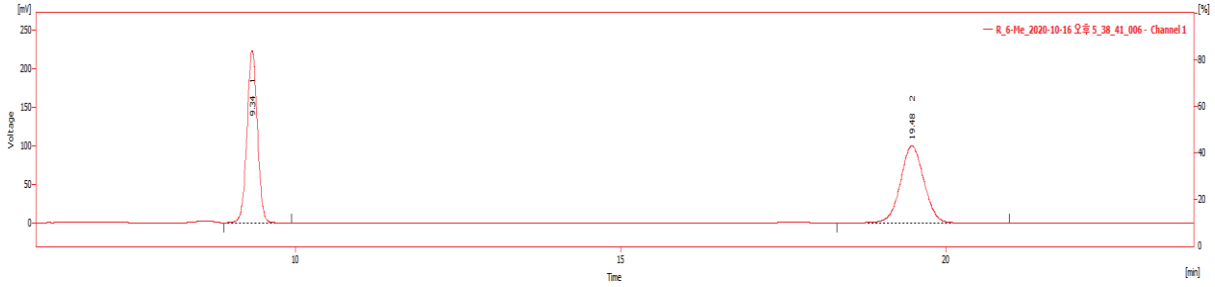
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	16,108	675,363	31,863	50,0	57,1
2	22,360	674,827	23,910	50,0	42,9
	Total	1350,190	55,773	100,0	100,0

For chiral **3e**



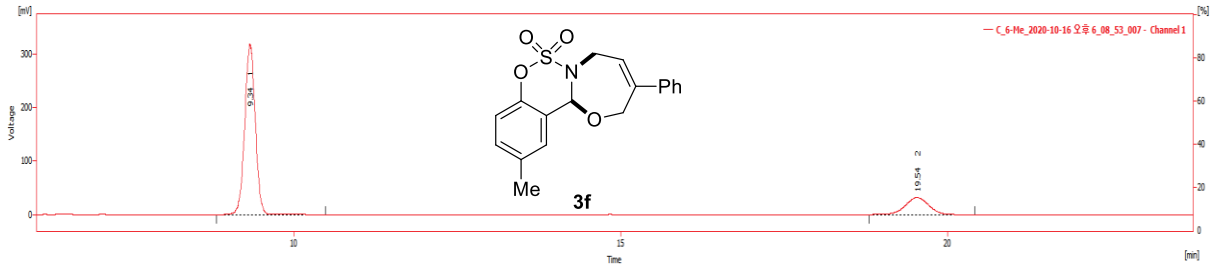
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	16,578	775,228	39,875	79,7	84,3
2	22,370	197,744	7,447	20,3	15,7
	Total	972,972	47,322	100,0	100,0

For racemic **3f**



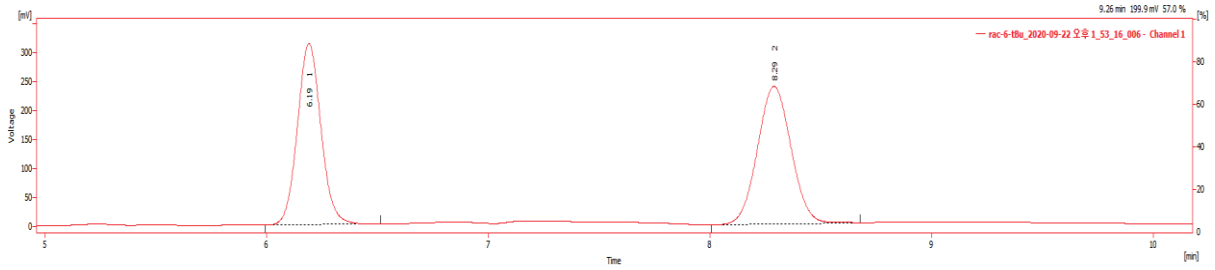
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	9.335	2484.385	223.665	49.8	69.1
2	19.475	2501.003	99.932	50.2	30.9
	Total	4985.388	323.596	100.0	100.0

For chiral **3f**



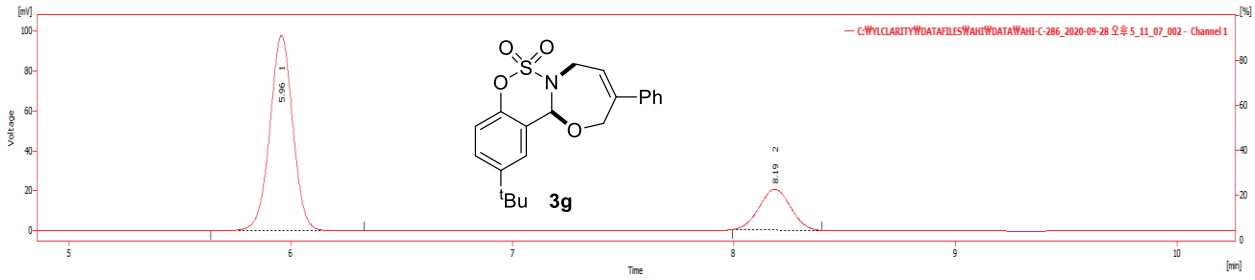
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	9.335	3560.570	318.618	83.3	91.0
2	19.535	782.533	31.555	16.7	9.0
	Total	4343.103	350.174	100.0	100.0

For racemic **3g**



	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	6,192	2326,792	313,465	49,9	57,5
2	8,290	2335,876	231,481	50,1	42,5
	Total	4662,668	544,947	100,0	100,0

For chiral **3g**

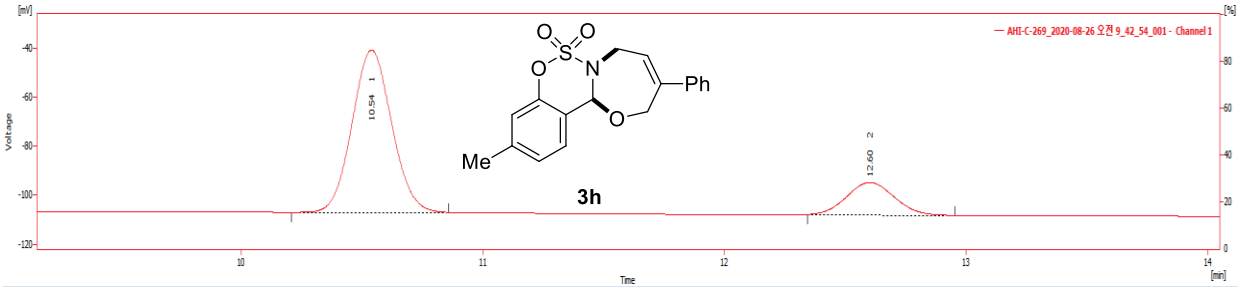


	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	5,958	704,670	97,887	81,9	84,5
2	8,185	155,872	18,020	18,1	15,5
	Total	860,542	115,907	100,0	100,0

For racemic **3h**

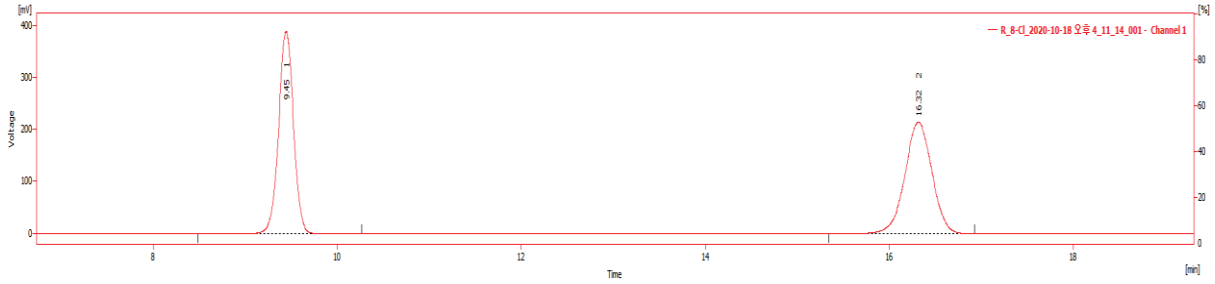
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	10,912	941,546	81,334	50,0	57,5
2	12,707	939,860	60,126	50,0	42,5
	Total	1881,406	141,460	100,0	100,0

For chiral **3h**



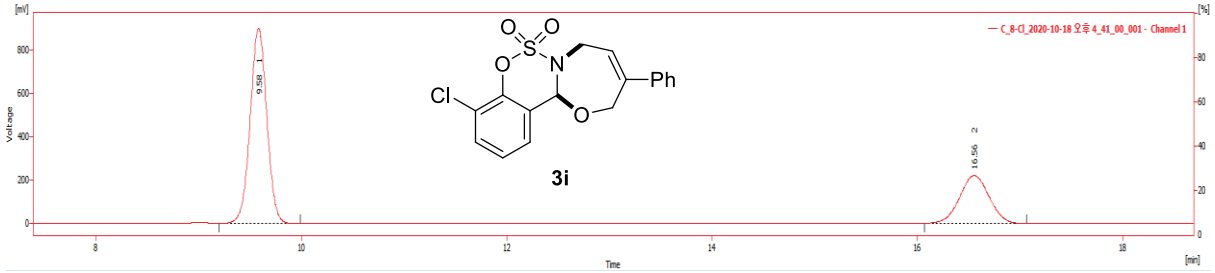
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	10,538	766,921	66,160	84,9	85,1
2	12,602	136,885	11,582	15,1	14,9
	Total	903,806	77,742	100,0	100,0

For racemic **3i**



	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	9,448	4385,768	390,696	50,0	64,5
2	16,317	4389,104	215,117	50,0	35,5
	Total	8774,872	605,813	100,0	100,0

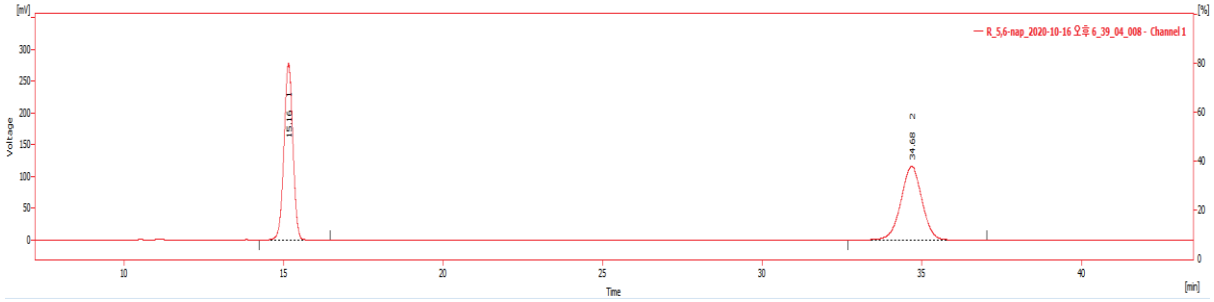
For chiral **3i**



3i

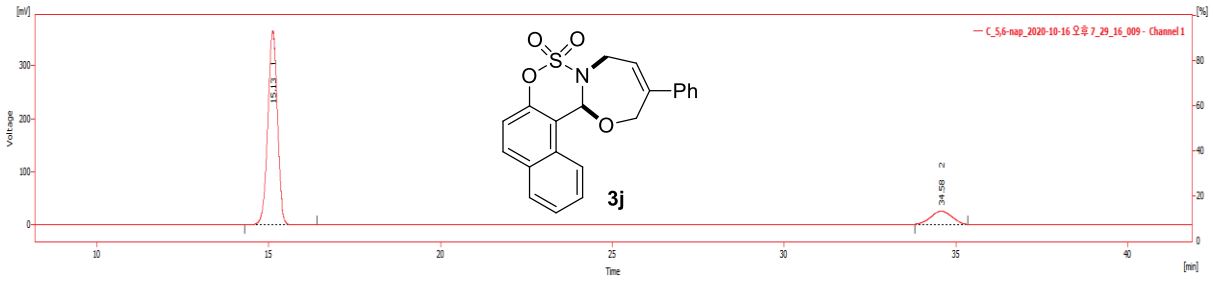
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	9,583	10145,920	897,011	71,0	80,7
2	16,555	4153,955	214,421	29,0	19,3
	Total	14299,875	1111,432	100,0	100,0

For racemic **3j**



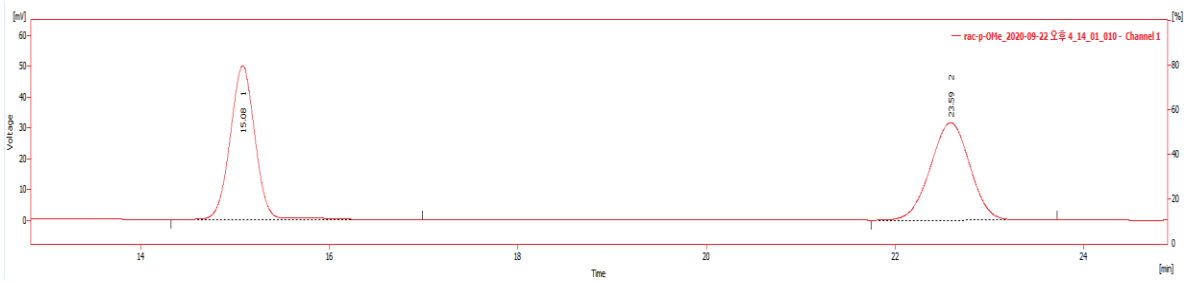
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	15,160	5347,616	278,088	49,9	70,5
2	34,682	5362,679	116,101	50,1	29,5
	Total	10710,295	394,189	100,0	100,0

For chiral **3j**



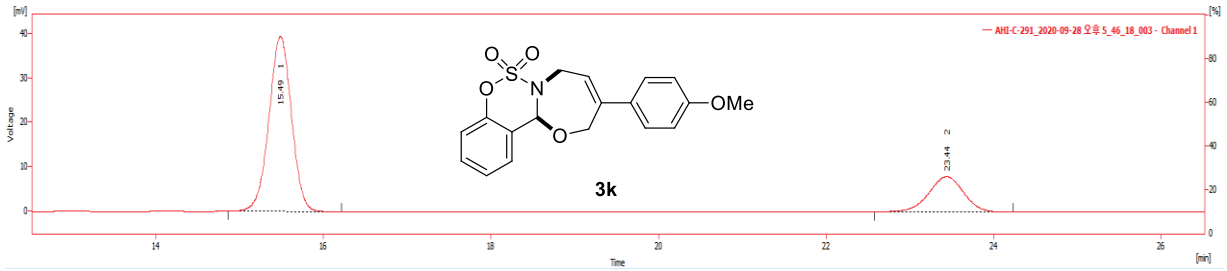
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	15,127	7008,031	365,989	87,0	93,7
2	34,582	1043,750	24,488	13,0	6,3
	Total	8051,780	390,477	100,0	100,0

For racemic **3k**



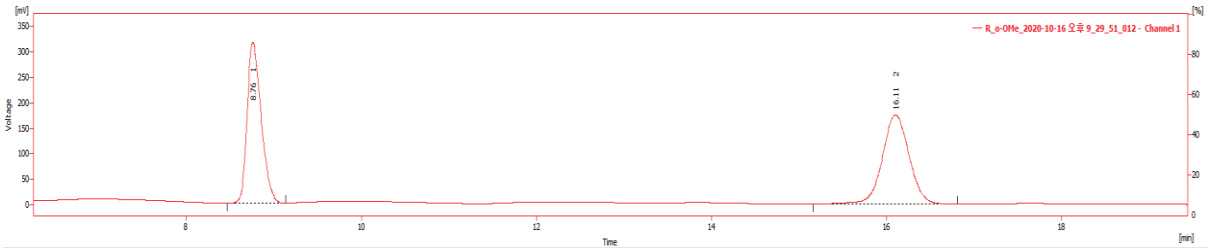
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	15,082	922,362	49,760	50,1	61,1
2	23,592	917,305	31,661	49,9	38,9
	Total	1839,667	81,420	100,0	100,0

For chiral **3k**



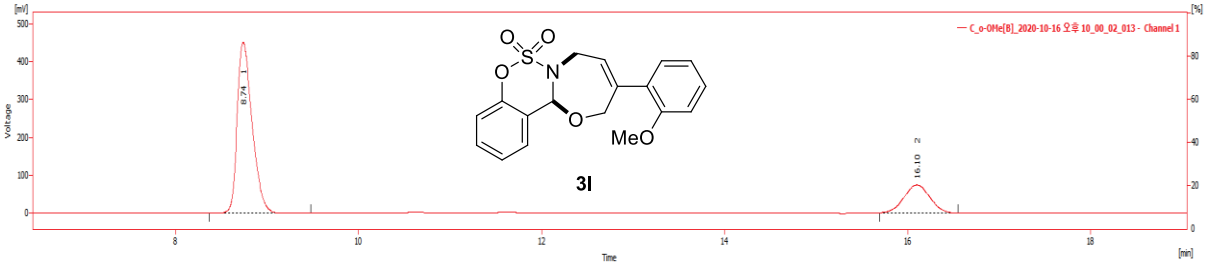
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	15,488	737,507	39,436	83,2	86,1
2	23,440	149,032	6,362	16,8	13,9
	Total	886,540	45,798	100,0	100,0

For racemic **3l**



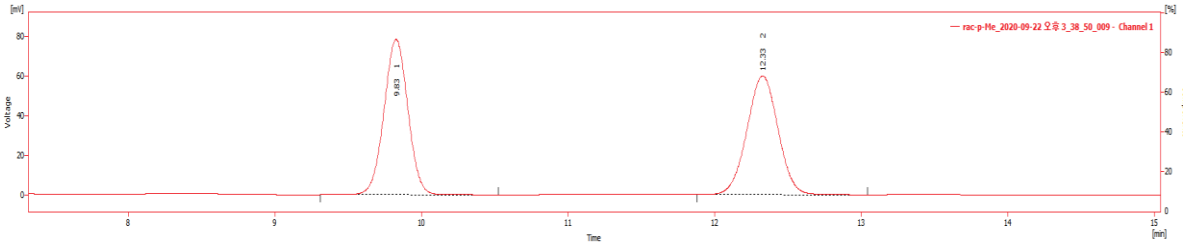
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	8,763	3537,662	316,327	49,9	64,4
2	16,105	3680,515	175,010	50,1	35,6
	Total	7218,177	491,337	100,0	100,0

For chiral **3l**



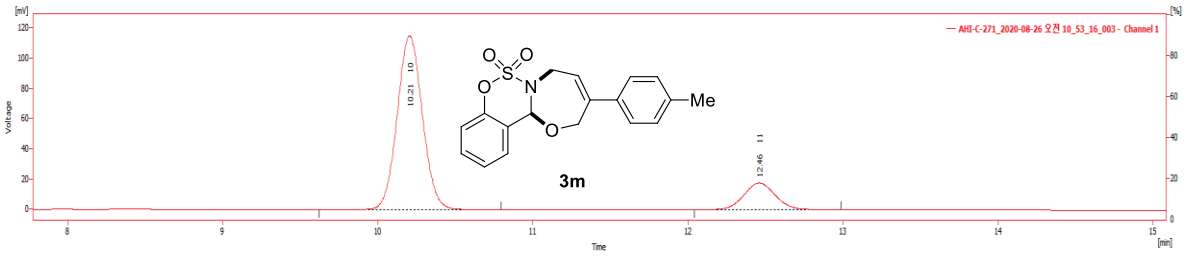
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	8,742	5100,983	450,797	77,8	85,9
2	16,102	1458,100	73,926	22,2	14,1
	Total	6559,083	524,723	100,0	100,0

For racemic **3m**



	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	9,827	893,012	78,698	50,1	56,7
2	12,328	889,880	60,164	49,9	43,3
	Total	1782,892	138,862	100,0	100,0

For chiral **3m**

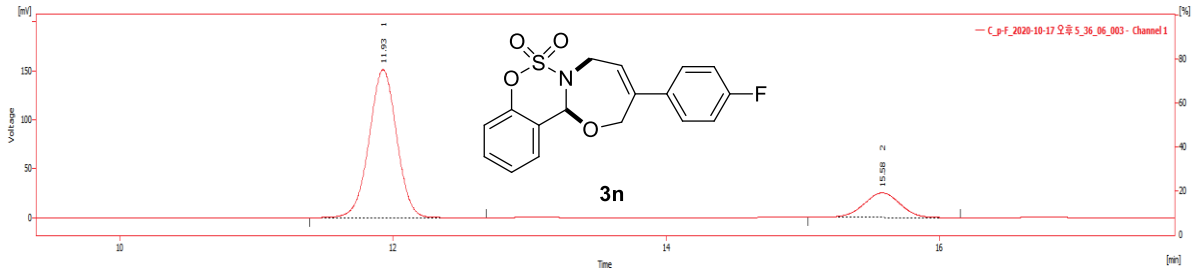


	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	10,207	1293,958	114,966	84,7	87,0
2	12,460	233,934	17,220	15,3	13,0
	Total	1527,892	132,186	100,0	100,0

For racemic **3n**

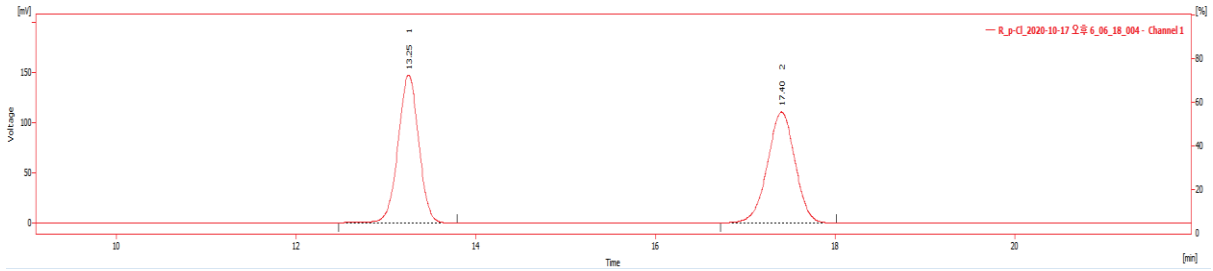
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	11,923	2483,336	177,903	50,0	57,0
2	15,565	2482,978	134,184	50,0	43,0
	Total	4966,314	312,087	100,0	100,0

For chiral **3n**



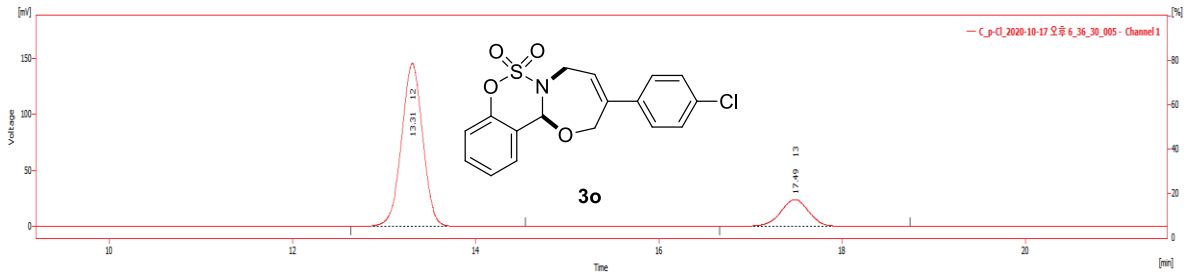
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	11,928	2122,064	151,288	82,0	85,7
2	15,580	465,553	25,197	18,0	14,3
	Total	2587,618	176,486	100,0	100,0

For racemic **3o**



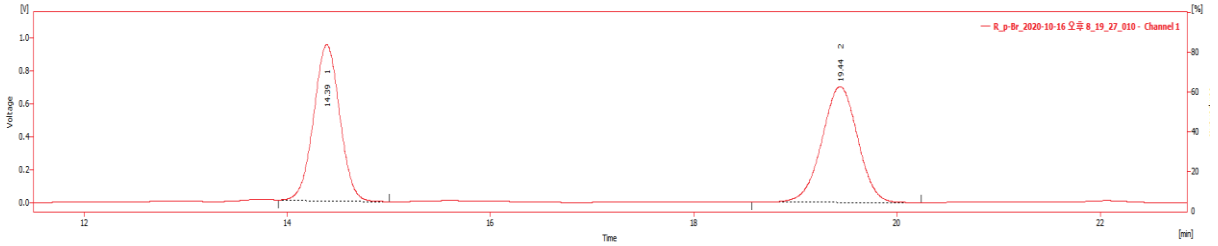
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	13.252	2351.829	147.146	50.0	57.1
2	17.403	2353.284	110.401	50.0	42.9
	Total	4705.112	257.547	100.0	100.0

For chiral **3o**



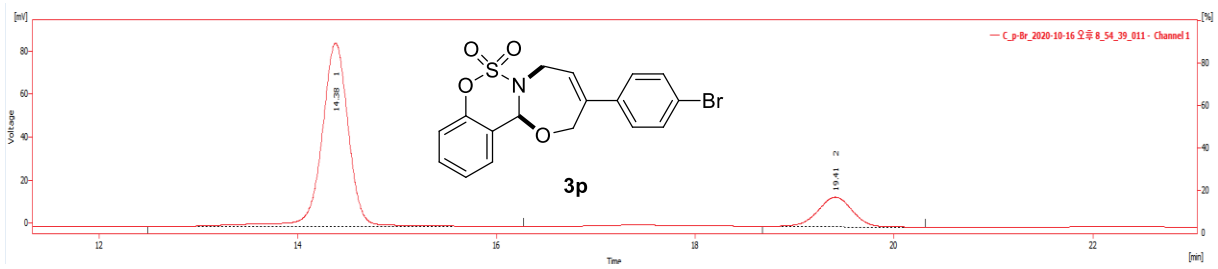
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	13.310	2337.382	145.703	84.0	86.6
2	17.487	443.976	22.541	16.0	13.4
	Total	2781.358	168.243	100.0	100.0

For racemic **3p**



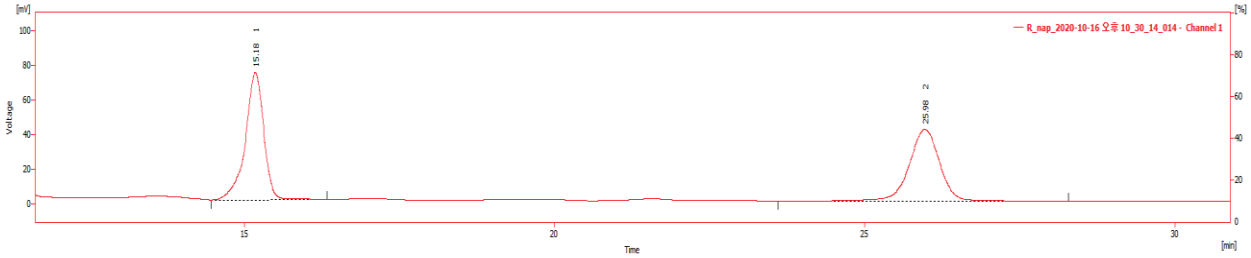
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	14.390	16860.058	946.666	49.9	57.4
2	19.440	17237.369	703.454	50.1	42.6
	Total	34097.427	1650.120	100.0	100.0

For chiral **3p**



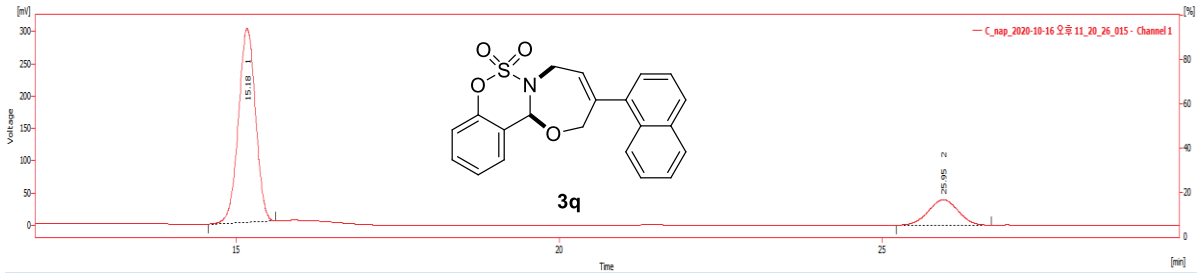
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	14.383	1600.691	85.242	83.0	86.2
2	19.412	327.128	13.695	17.0	13.8
	Total	1927.819	98.938	100.0	100.0

For racemic **3q**



	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	15,183	1457,401	72,828	50,1	63,7
2	25,975	1454,067	41,543	49,9	36,3
	Total	2911,468	114,370	100,0	100,0

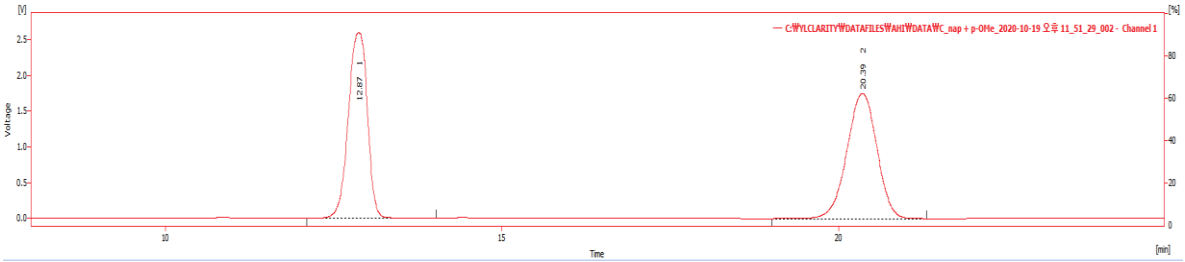
For chiral **3q**



3q

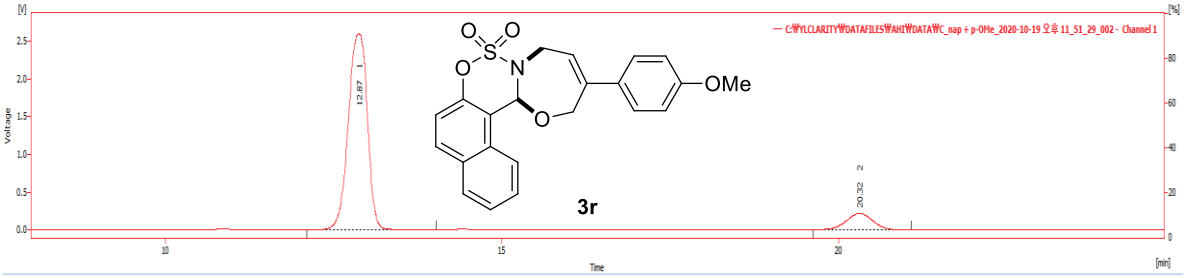
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	15,175	5505,174	300,310	81,3	88,4
2	25,948	1263,301	39,343	18,7	11,6
	Total	6768,475	339,653	100,0	100,0

For racemic **3r**



	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	12,873	51135,011	2600,880	50,0	60,3
2	20,392	5829,040	216,221	50,0	39,7
	Total	56965,051	2817,101	100,0	100,0

For chiral **3r**

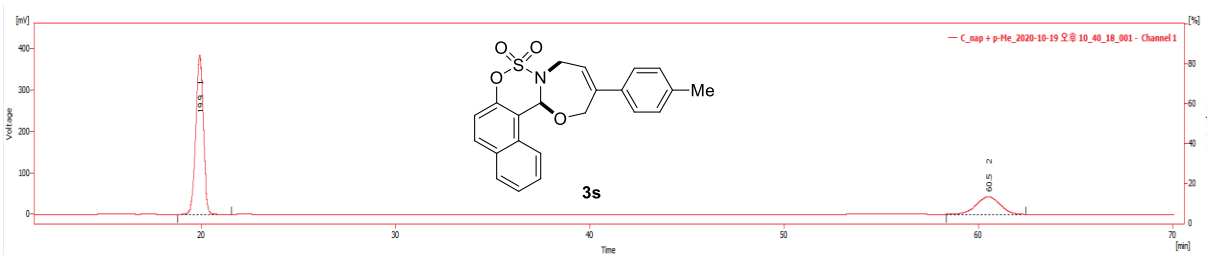


	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	12,873	51135,839	2600,880	89,8	92,3
2	20,315	5829,427	216,221	10,2	7,7
	Total	56965,267	2817,101	100,0	100,0

For racemic **3s**

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	19,915	10218,983	383,960	50,3	90,0
2	60,045	3614,317	42,651	49,7	10,0
	Total	13832,244	426,610	100,0	100,0

For chiral **3s**

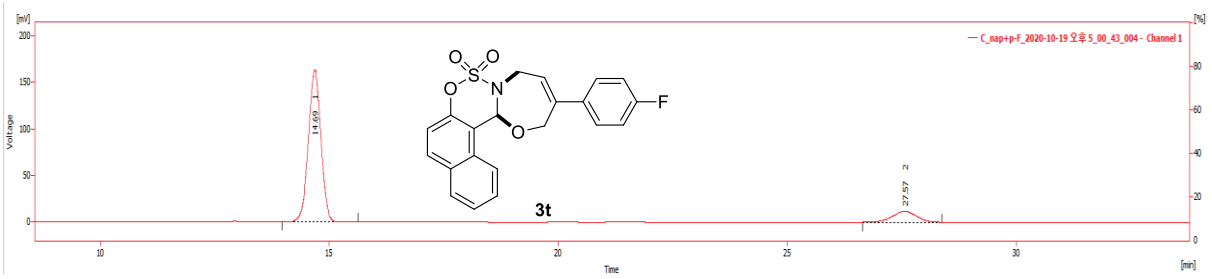


	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	19,915	10218,389	383,962	83,3	92,3
2	60,527	2051,207	32,032	16,7	7,7
	Total	12269,596	415,993	100,0	100,0

For racemic **3t**

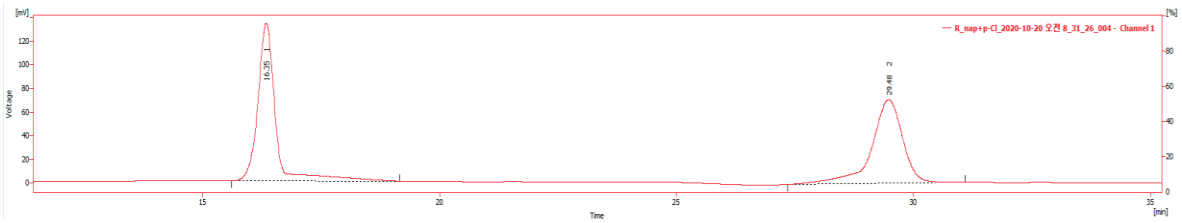
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	14,885	19044,183	947,983	50,3	66,0
2	27,045	18813,677	489,317	49,7	34,0
	Total	37857,859	1437,300	100,0	100,0

For chiral **3t**



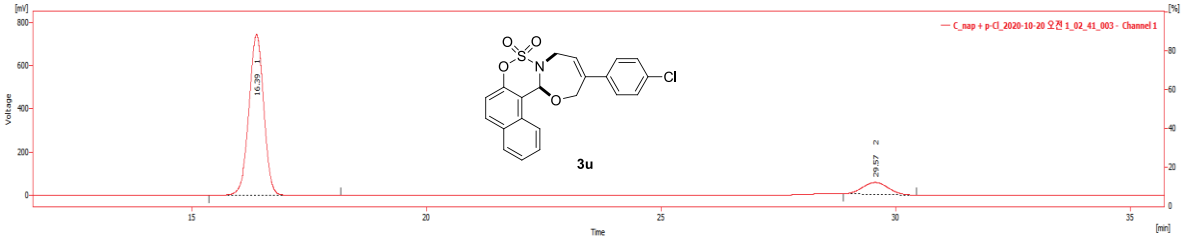
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	14,690	3125,945	163,881	88,0	93,4
2	27,570	425,058	11,534	12,0	6,6
	Total	3551,003	175,415	100,0	100,0

For racemic **3u**



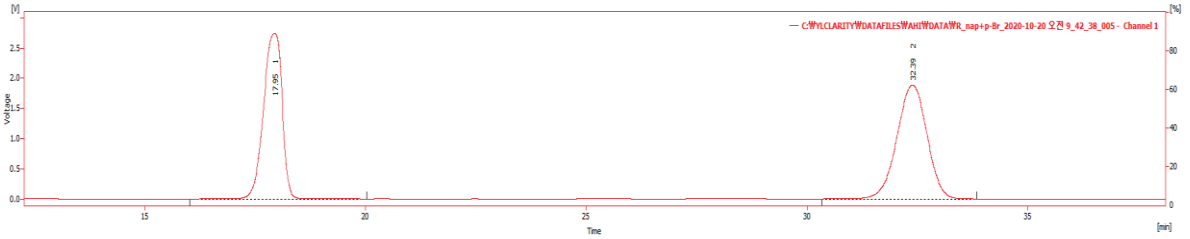
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	16,348	2403,584	121,012	49,9	65,1
2	29,478	2413,449	64,833	50,1	34,9
	Total	4817,034	185,845	100,0	100,0

For chiral **3u**



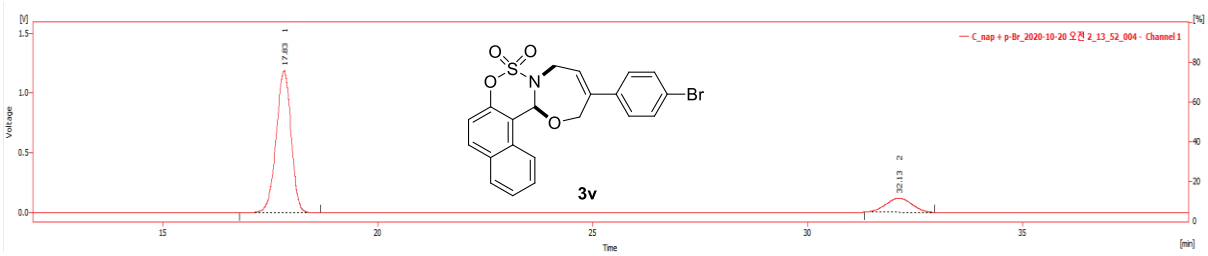
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	16,387	16290,086	743,675	88,7	93,1
2	29,570	2078,006	55,267	11,3	6,9
	Total	18368,092	798,942	100,0	100,0

For racemic **3v**



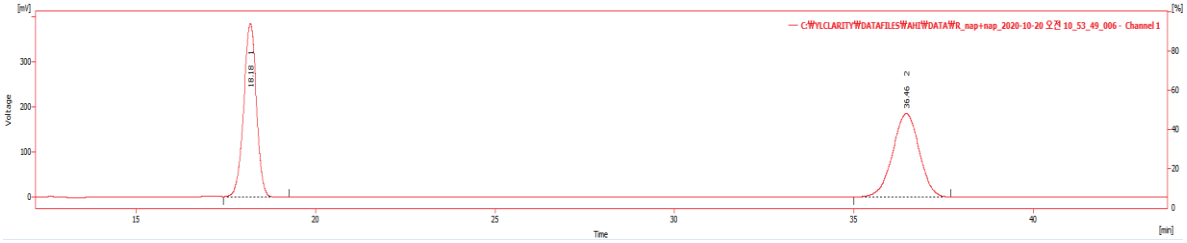
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	17,948	80289,630	2740,870	50,0	60,3
2	32,392	80312,321	1807,975	50,0	39,7
	Total	160601,951	4548,844	100,0	100,0

For chiral **3v**



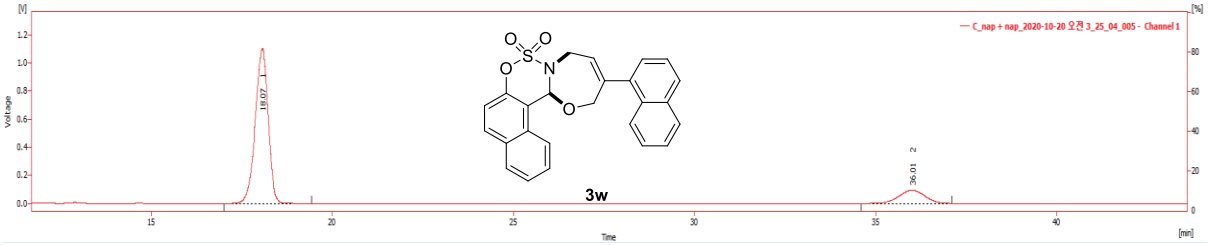
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	17,828	28709,612	1188,442	85,1	91,0
2	32,128	5010,886	118,101	14,9	9,0
	Total	33720,498	1306,543	100,0	100,0

For racemic **3w**



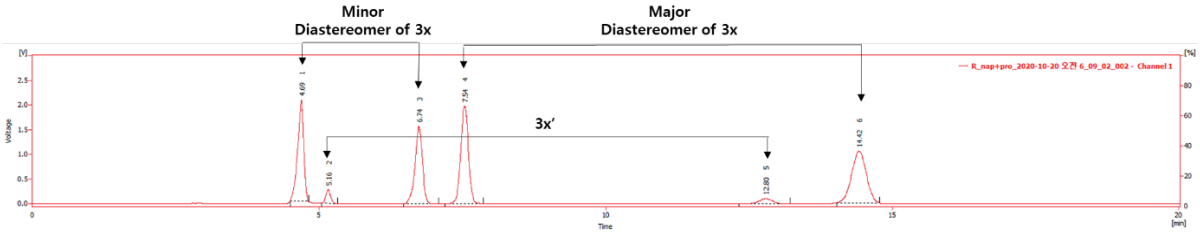
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	18,185	9497,011	384,155	50,0	67,5
2	36,463	9513,040	185,346	50,0	32,5
	Total	19010,051	569,501	100,0	100,0

For chiral **3w**



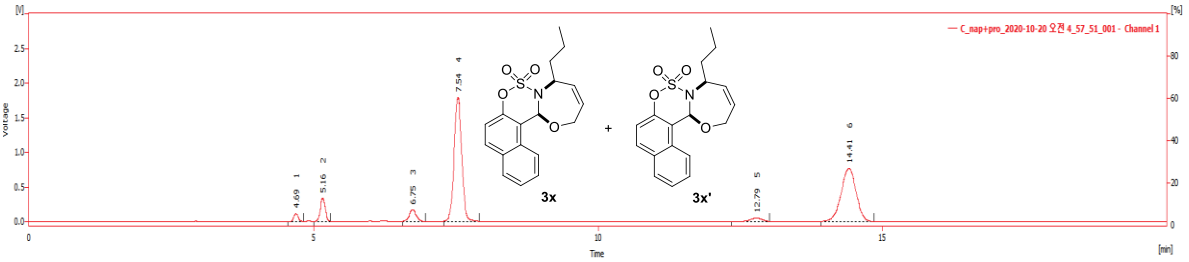
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	18,073	27410,431	1102,803	85,3	92,2
2	36,012	4712,242	93,658	14,7	7,8
	Total	32122,672	1196,461	100,0	100,0

For racemic compounds of diastereomers **3x** and **3x'**



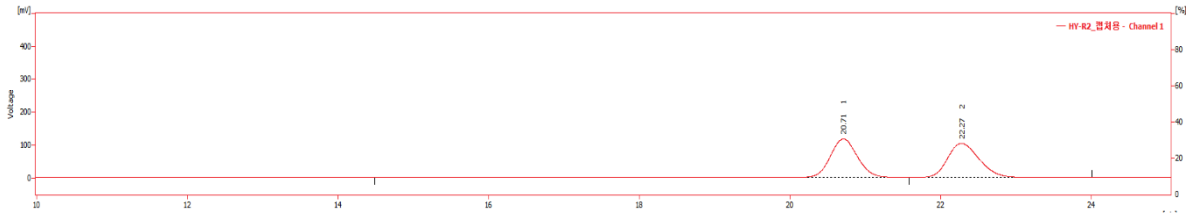
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	4,692	15018,582	2050,299	21,6	29,2
2	5,160	1604,222	274,839	2,3	3,9
3	6,743	14130,288	1573,378	20,3	22,4
4	7,540	18558,222	1976,641	26,7	28,2
5	12,797	1600,760	100,661	2,3	1,4
6	14,422	18651,451	1044,708	26,8	14,9
	Total	69563,526	7020,527	100,0	100,0

For chiral compounds of diastereomers **3x** and **3x'**



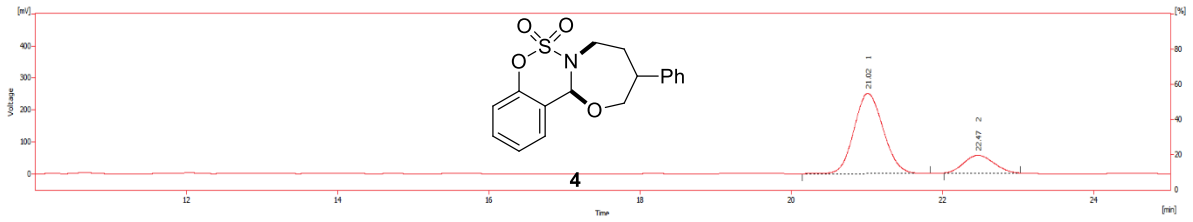
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	4,692	600,599	111,273	1,7	3,4
2	5,162	2003,345	339,267	5,6	10,5
3	6,745	1455,019	171,592	4,1	5,3
4	7,540	16732,054	1792,040	47,1	55,5
5	12,785	715,142	48,721	2,0	1,5
6	14,412	14034,165	768,908	39,5	23,8
	Total	35540,324	3231,800	100,0	100,0

For racemic compound of major diastereomer **4**



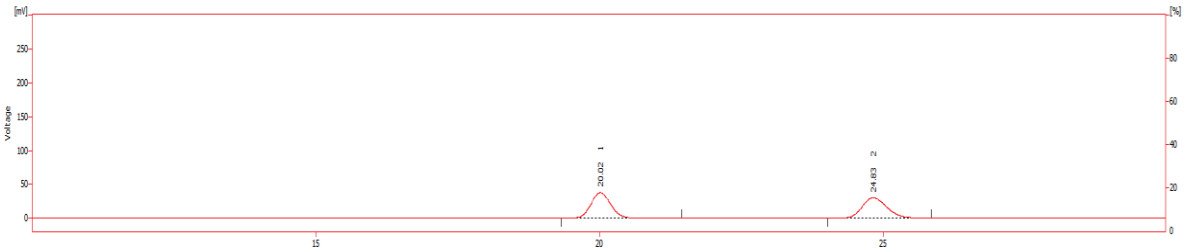
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	20,707	2965,733	116,738	49,9	53,0
2	22,275	2977,650	103,463	50,1	47,0
	Total	5943,383	220,201	100,0	100,0

For chiral compound of major diastereomer **4**



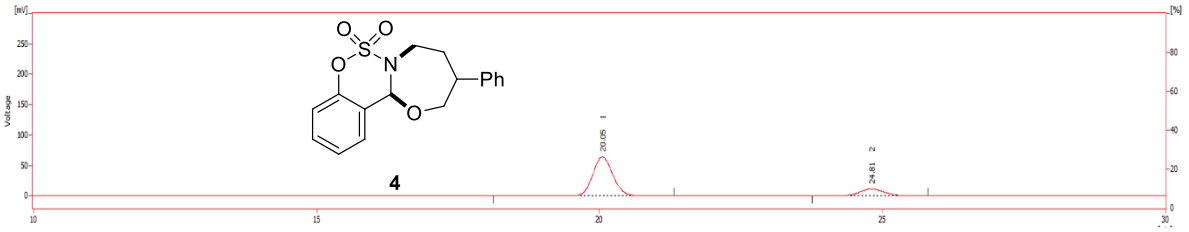
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	21,015	6804,620	250,699	81,8	81,9
2	22,467	1509,171	55,384	18,2	18,1
	Total	8313,791	306,083	100,0	100,0

For racemic compound of minor diastereomer **4**



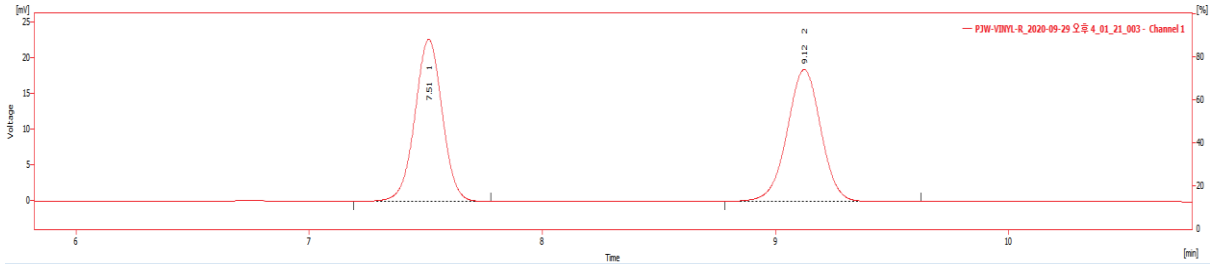
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	20,015	906,785	37,662	49,9	55,6
2	24,830	909,577	30,103	50,1	44,4
	Total	1816,362	67,765	100,0	100,0

For chiral compound of minor diastereomer **4**



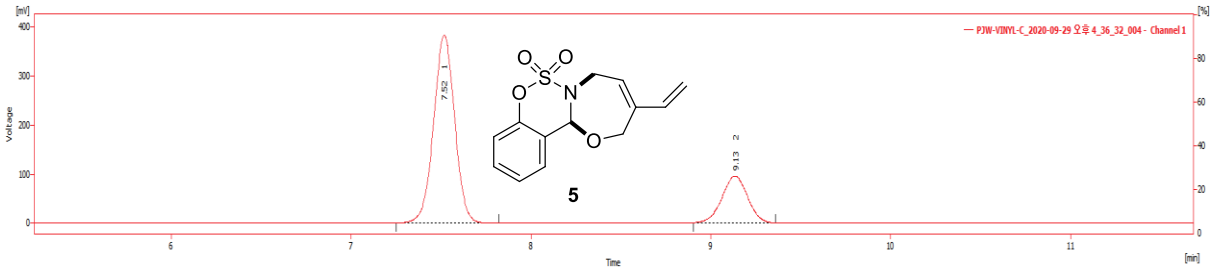
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	20,053	1576,695	64,000	82,0	84,8
2	24,807	345,677	11,487	18,0	15,2
	Total	1922,373	75,488	100,0	100,0

For racemic **5**



	Signal Name	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	Channel 1	7.513	184.820	22.683	49.9	55.1
2	Channel 1	9.123	185.506	18.462	50.1	44.9
		All Signals	370.327	41.145	100.0	100.0

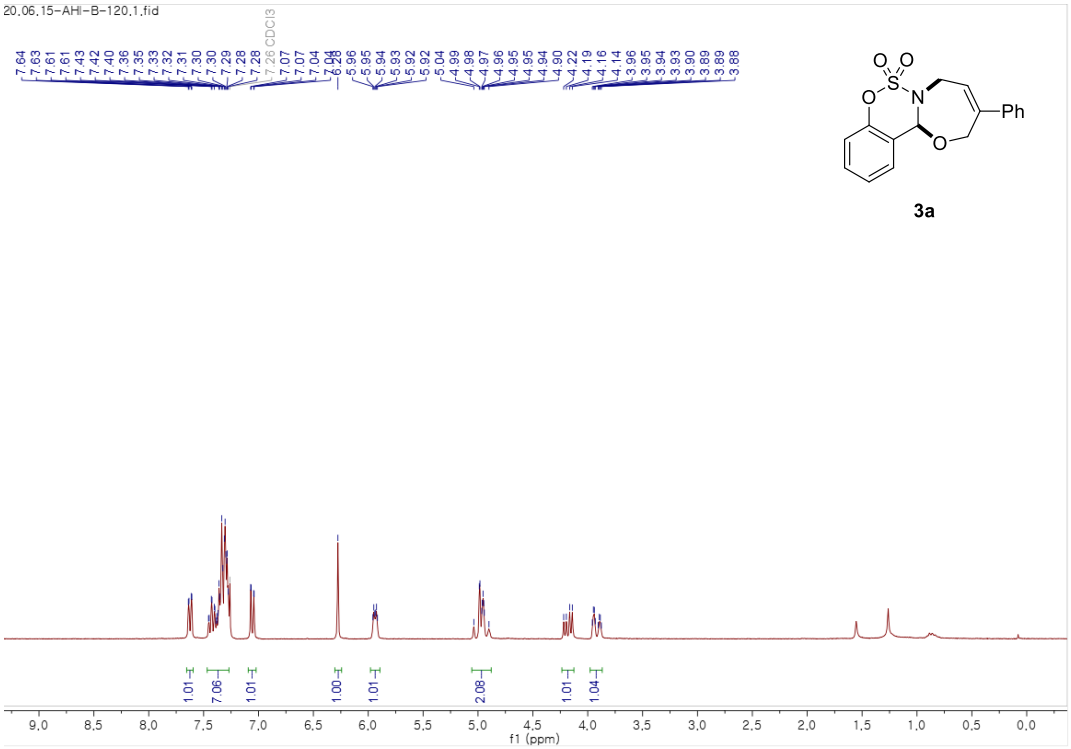
For chiral **5**



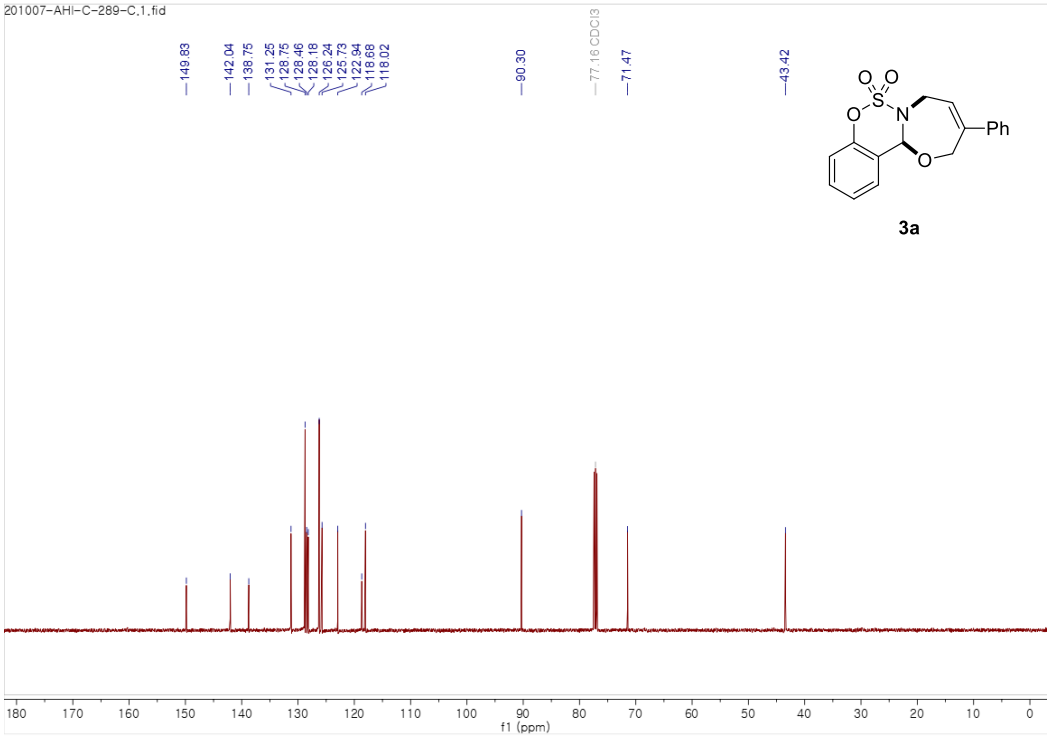
	Signal Name	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	Channel 1	7.518	3114.004	382.500	76.8	80.1
2	Channel 1	9.135	940.612	95.303	23.2	19.9
		All Signals	4054.616	477.802	100.0	100.0

9. NMR spectra of all compounds

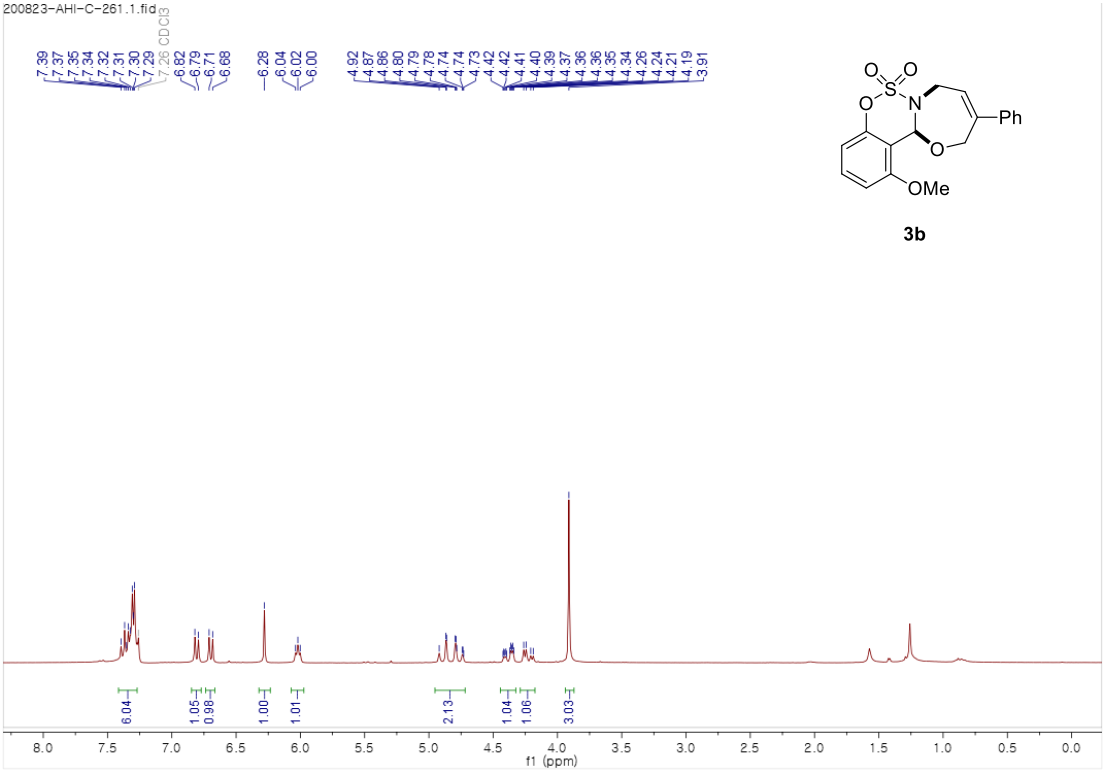
^{1}H NMR spectrum of **3a**



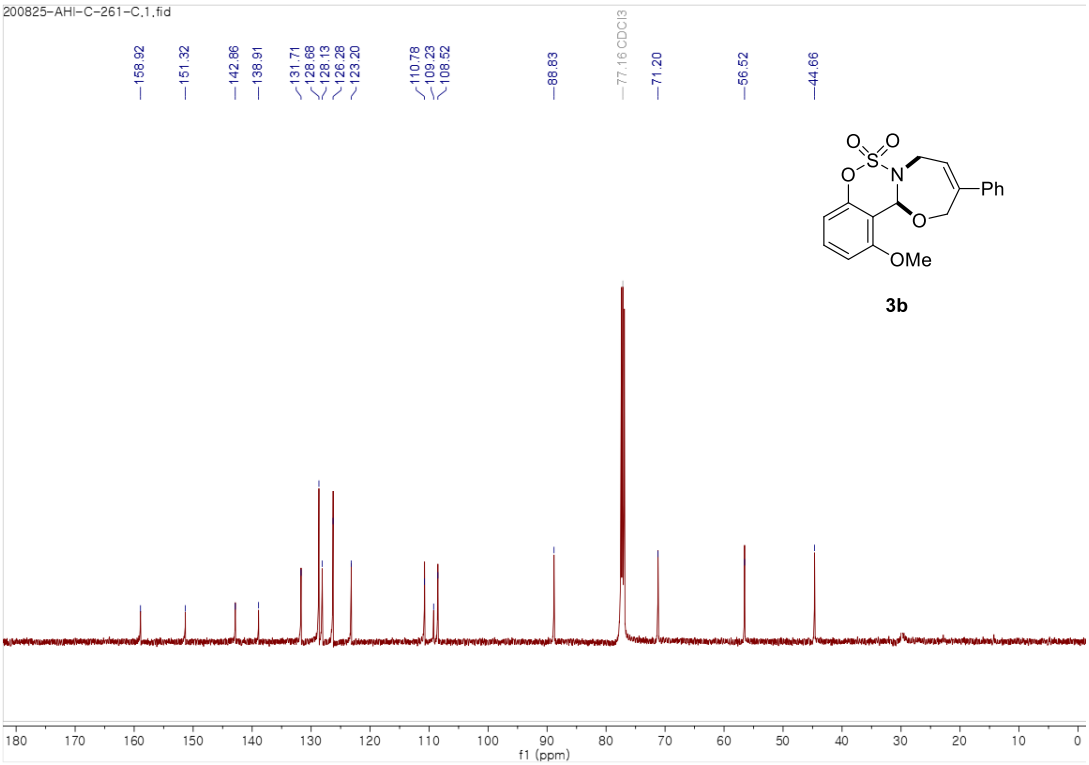
^{13}C NMR spectrum of **3a**



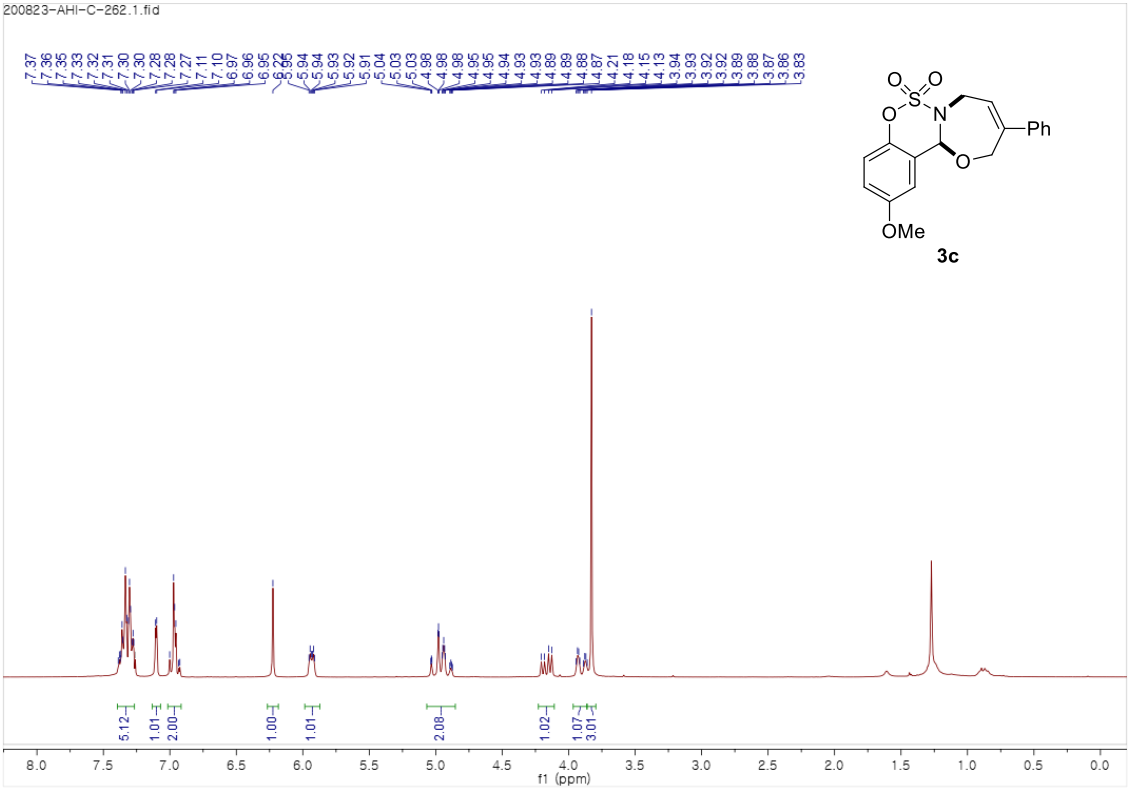
^{1}H NMR spectrum of **3b**



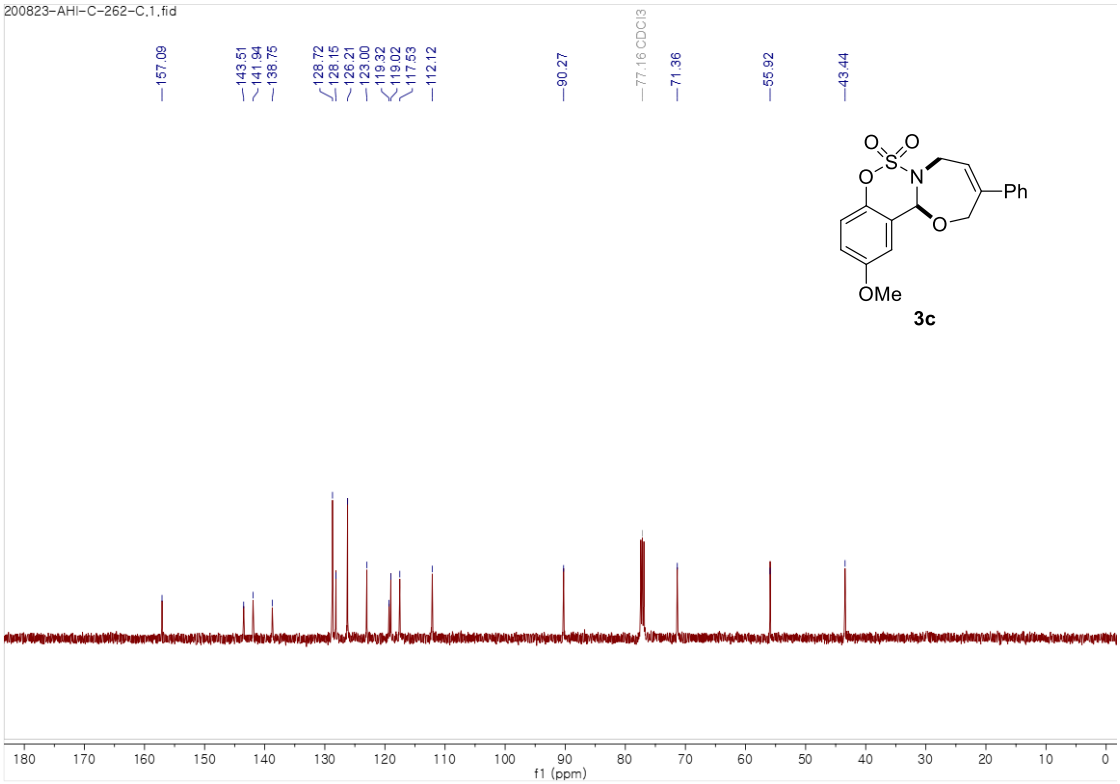
^{13}C NMR spectrum of **3b**



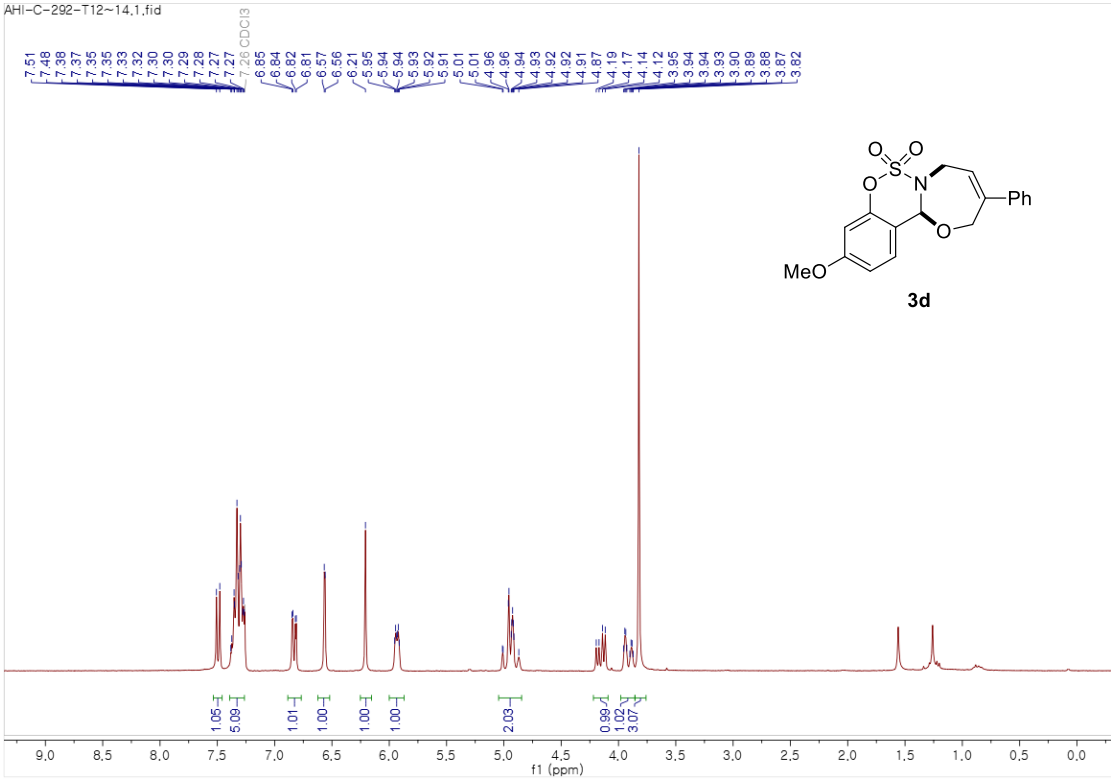
^{1}H NMR spectrum of **3c**



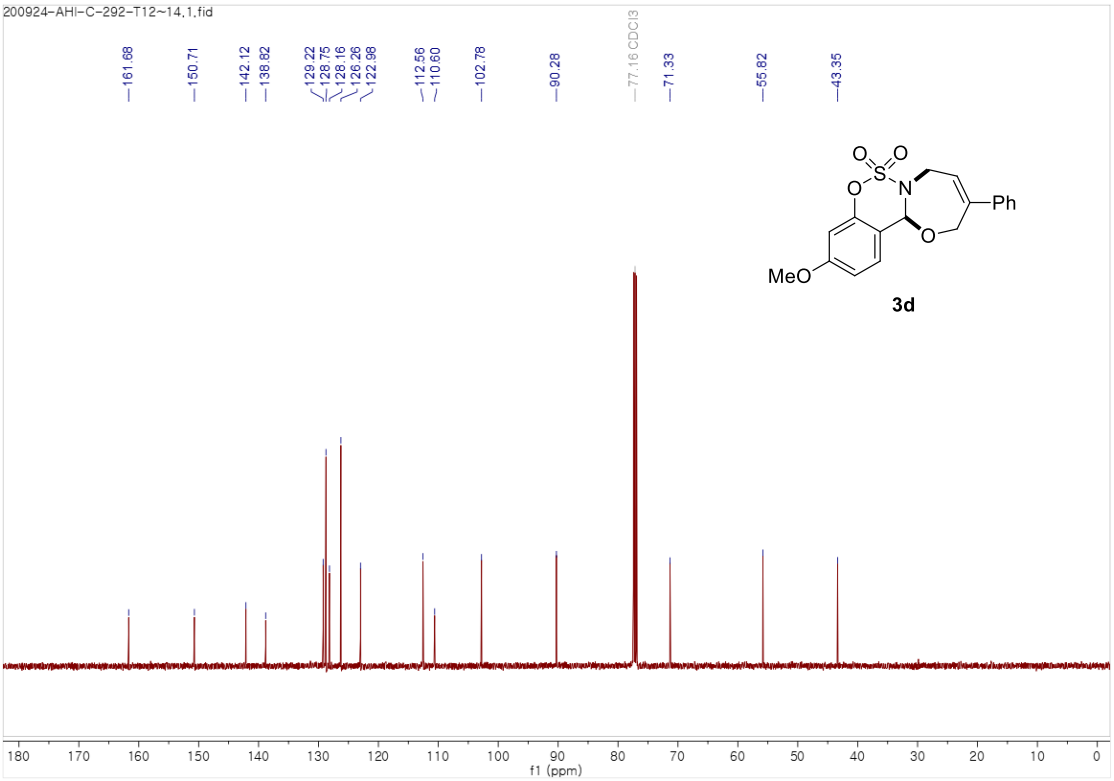
^{13}C NMR spectrum of **3c**



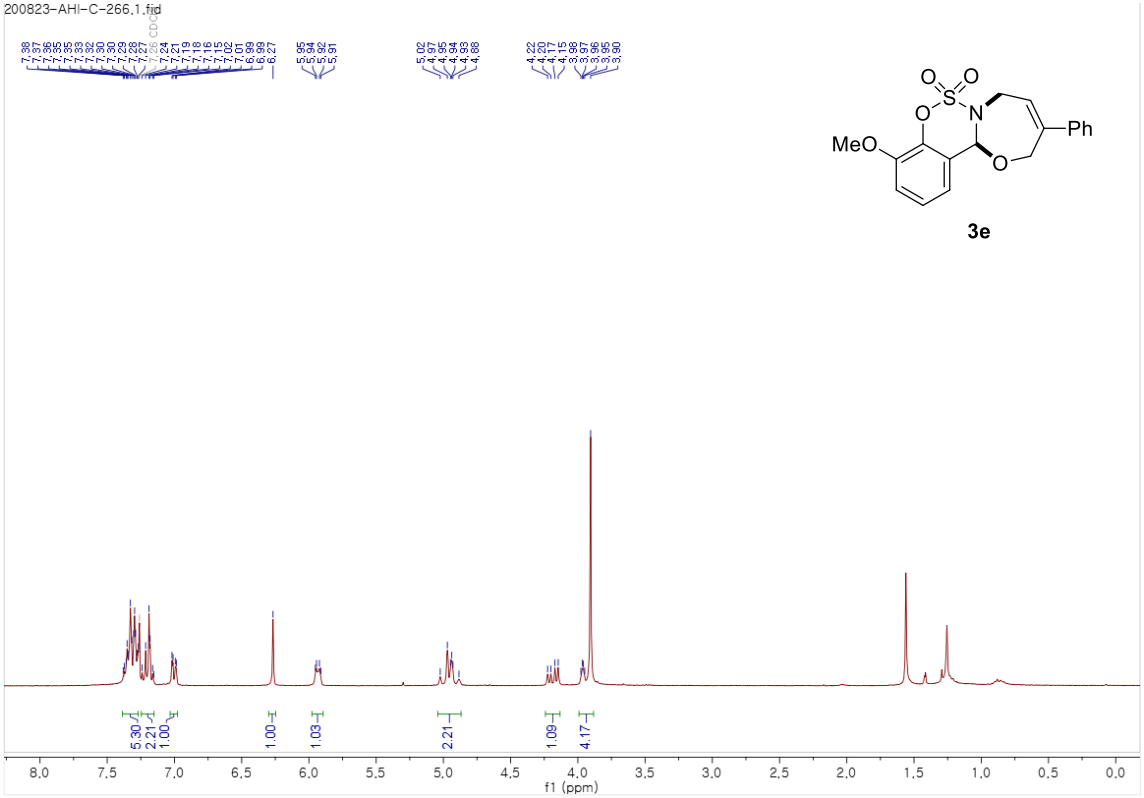
^{1}H NMR spectrum of **3d**



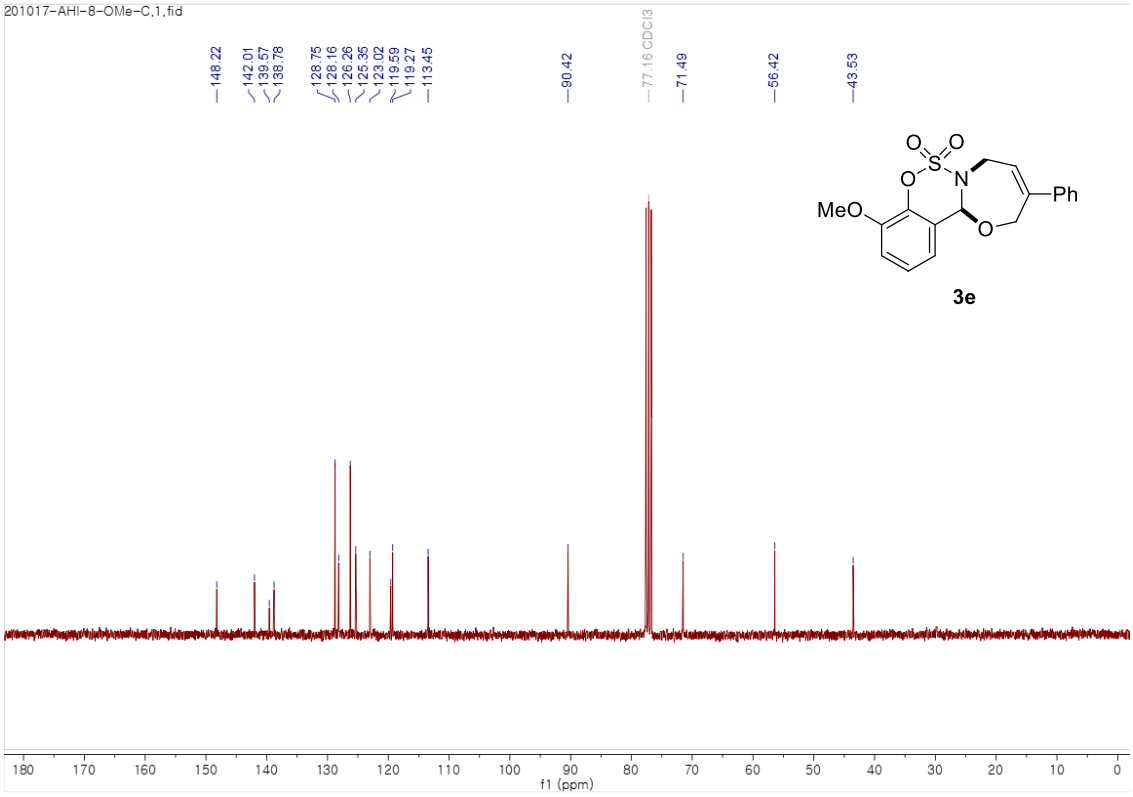
^{13}C NMR spectrum of **3d**



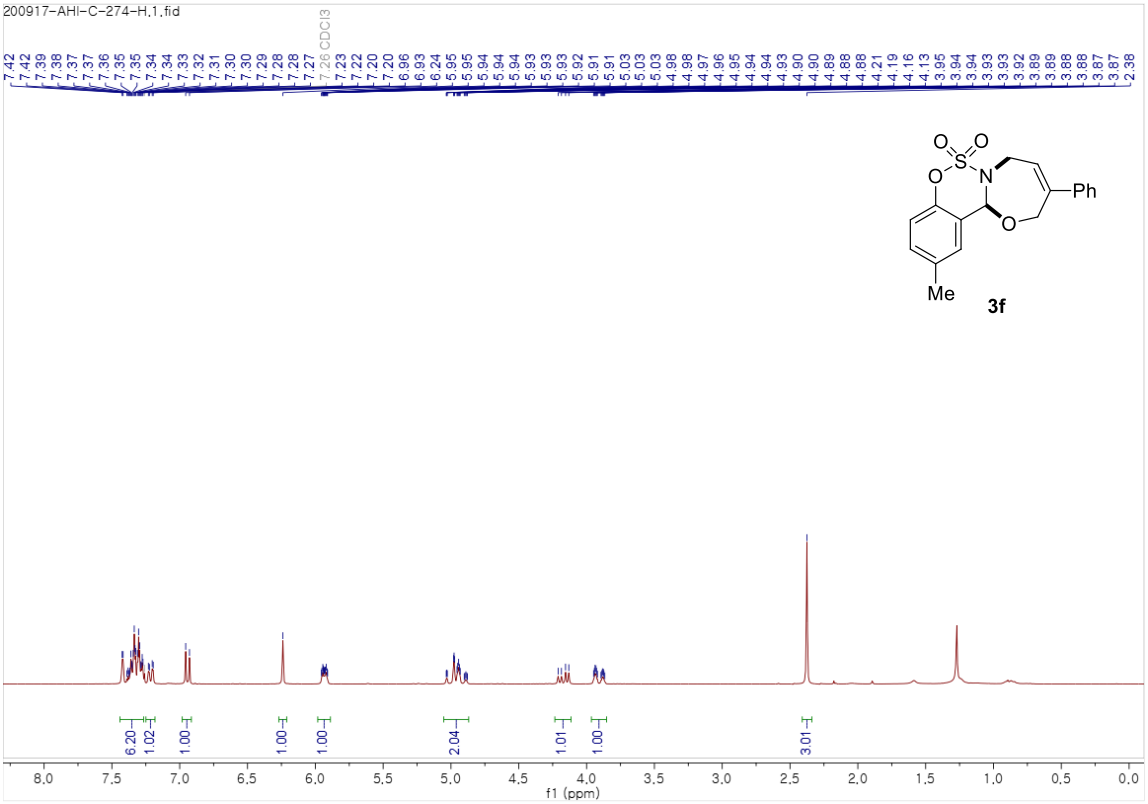
^{1}H NMR spectrum of **3e**



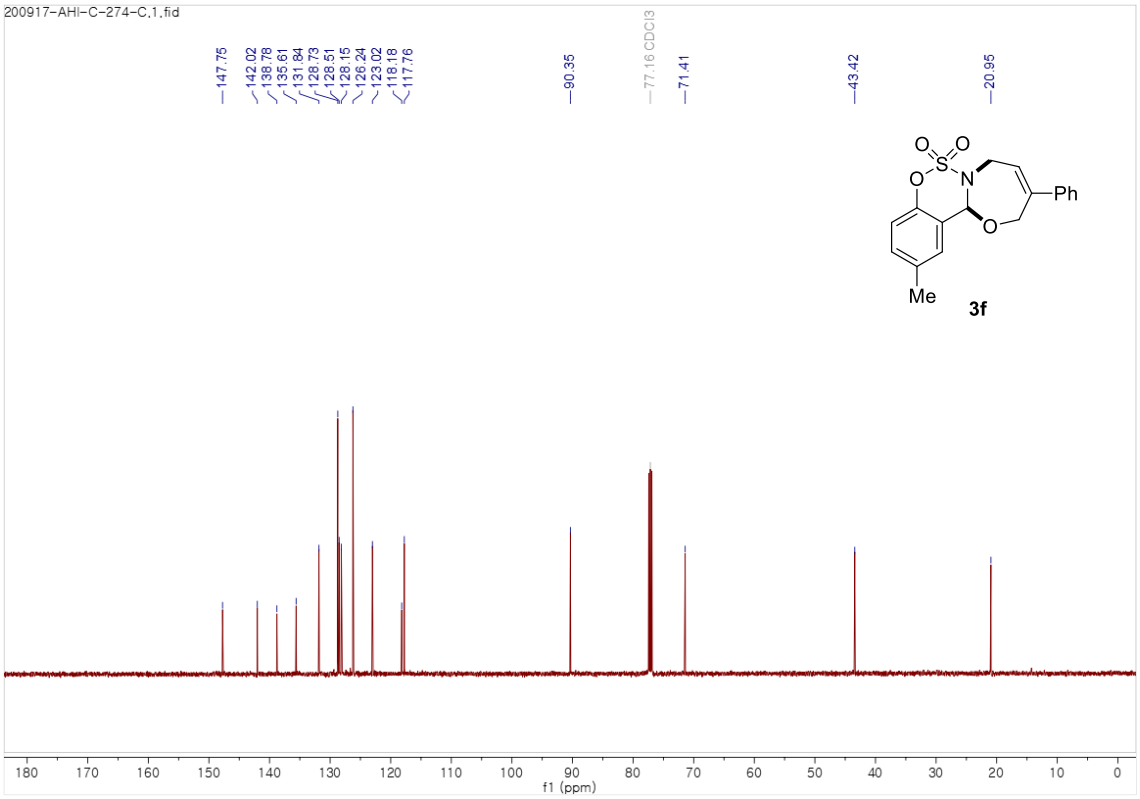
^{13}C NMR spectrum of **3e**



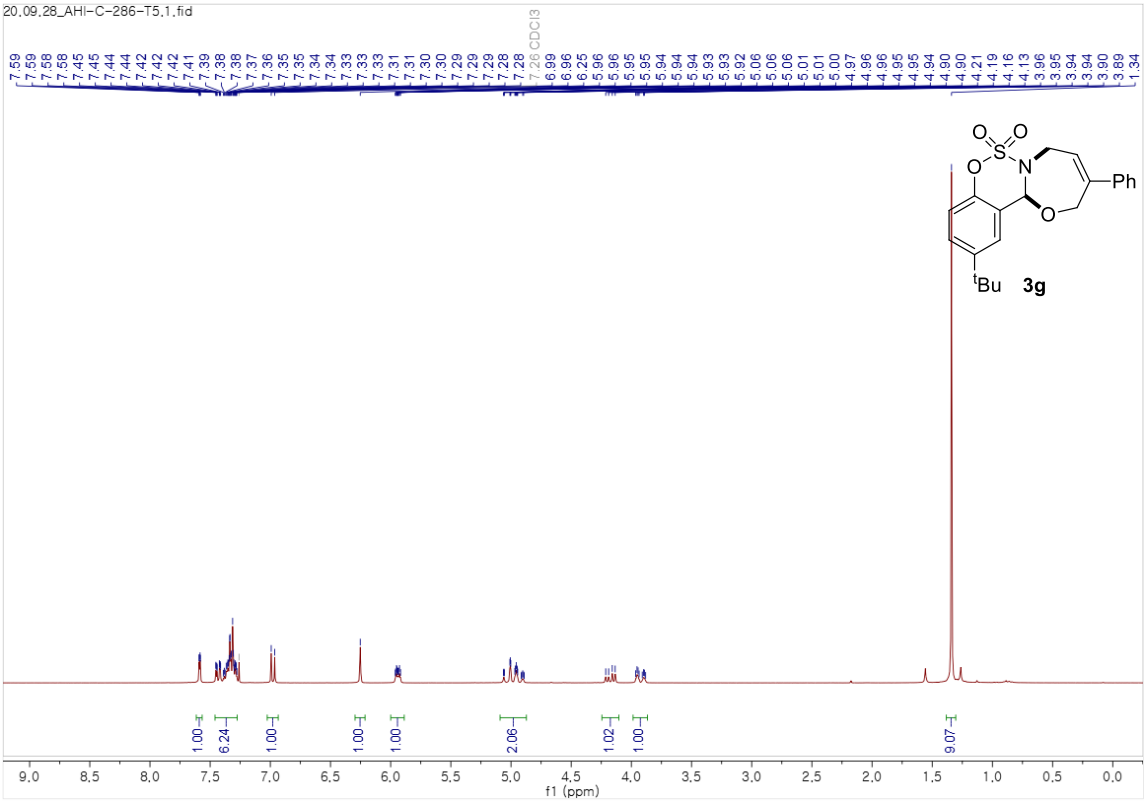
^{1}H NMR spectrum of **3f**



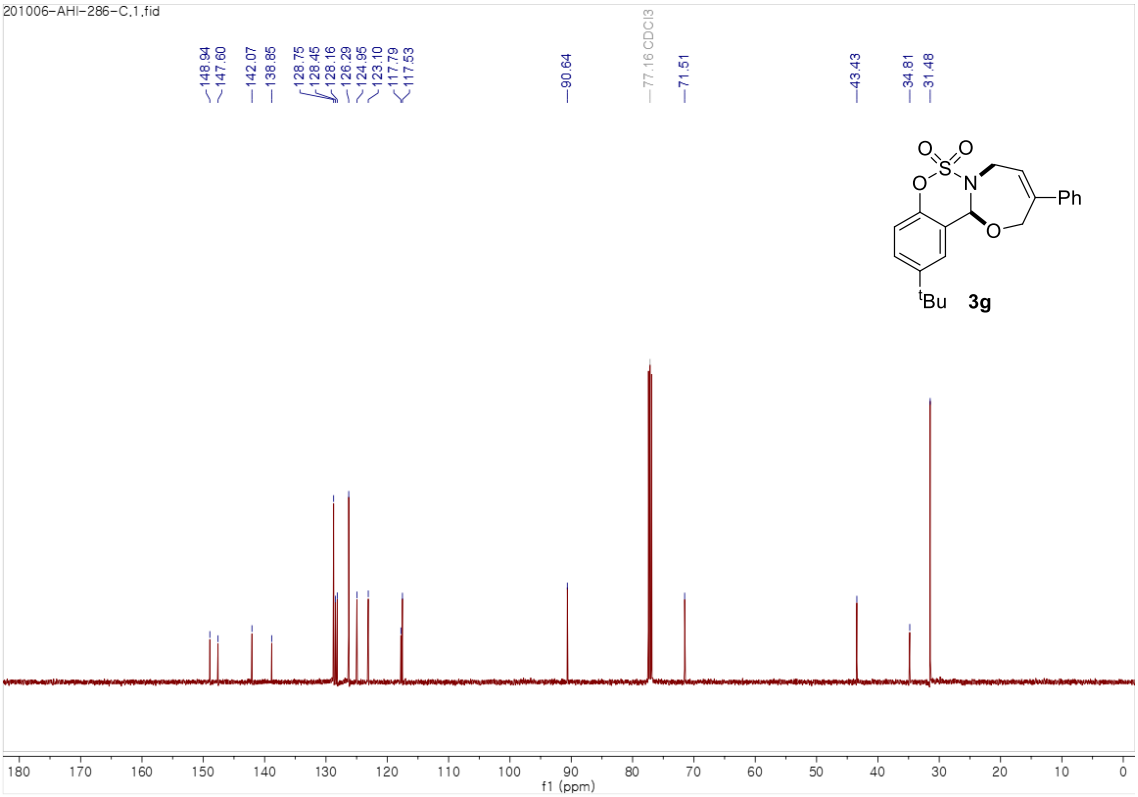
^{13}C NMR spectrum of **3f**



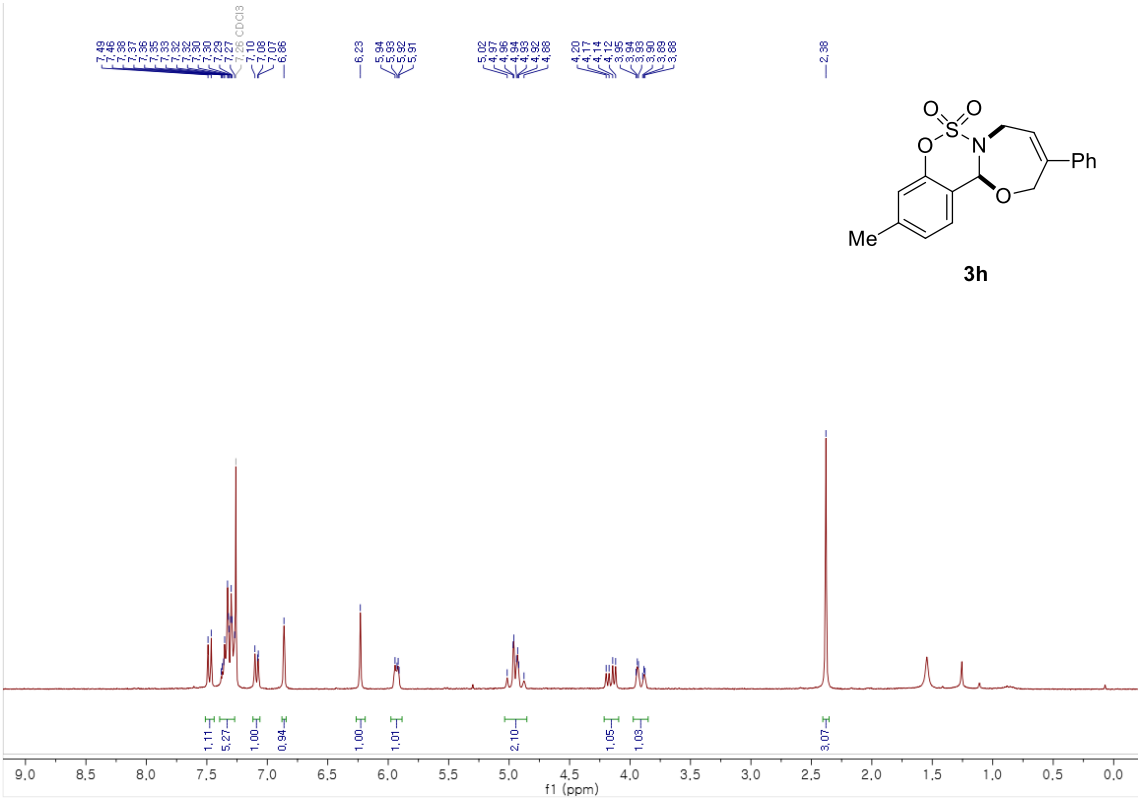
^{1}H NMR spectrum of **3g**



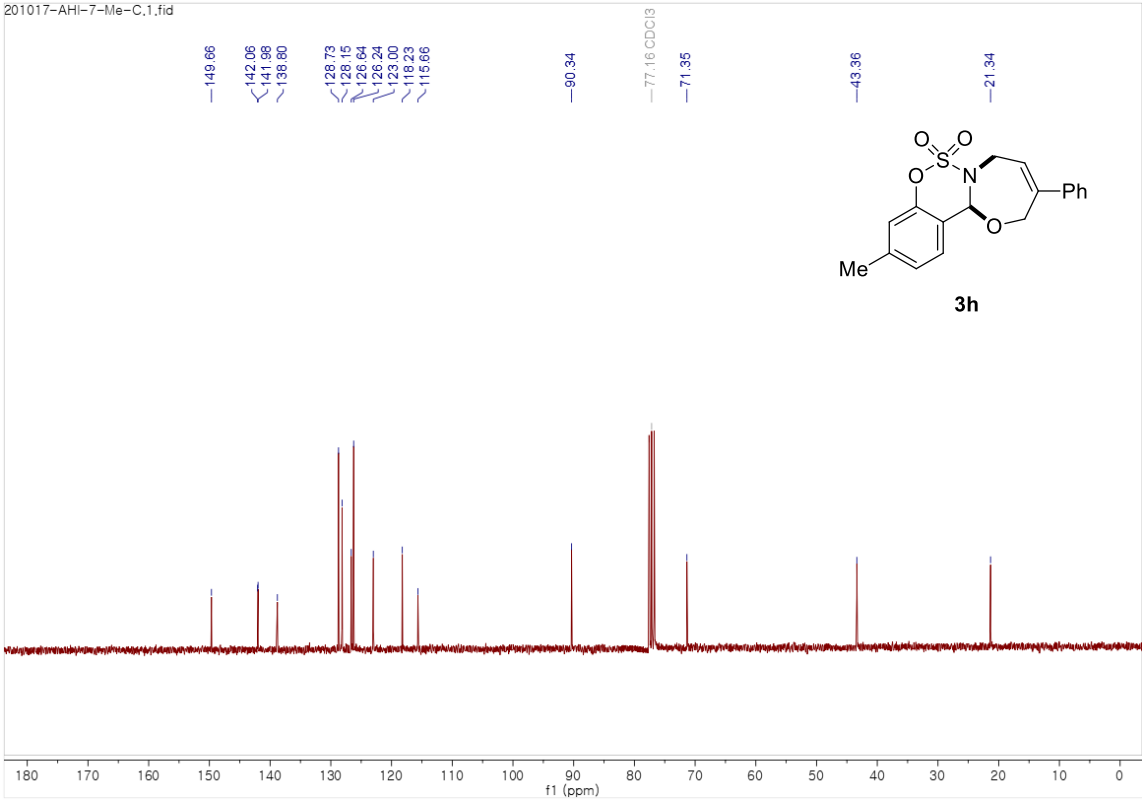
^{13}C NMR spectrum of **3g**



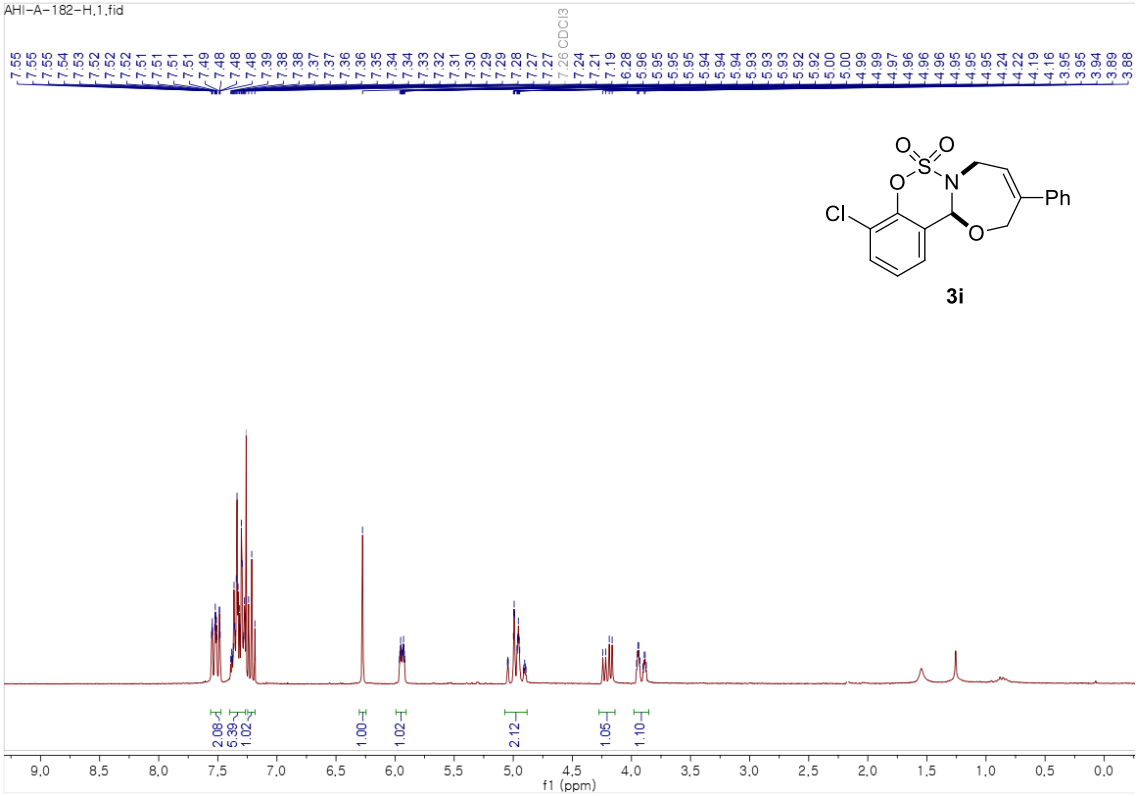
^{1}H NMR spectrum of **3h**



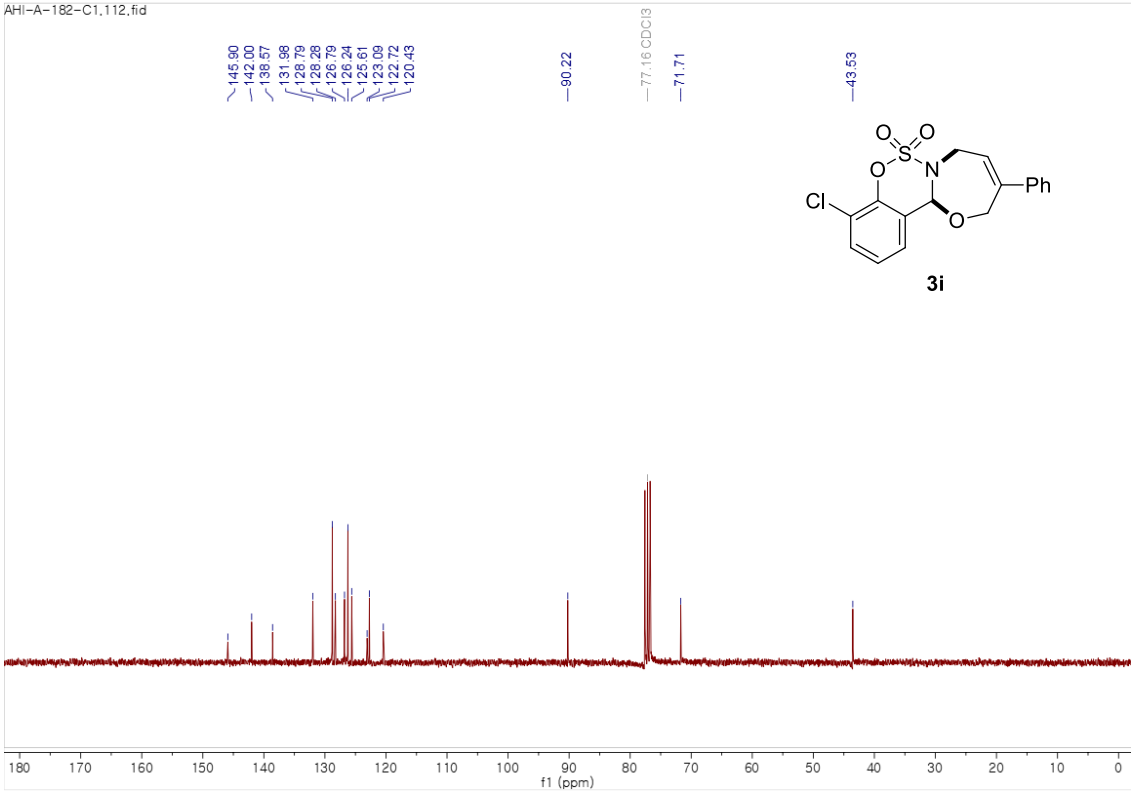
^{13}C NMR spectrum of **3h**



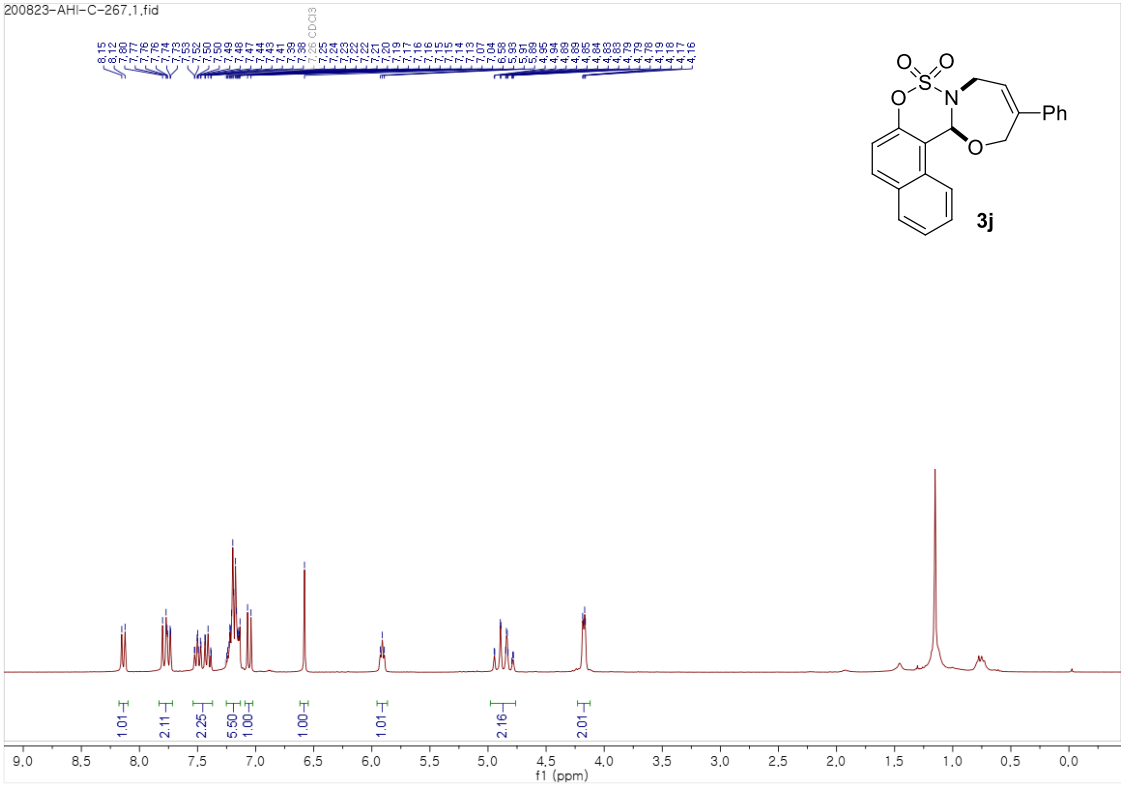
^{1}H NMR spectrum of **3i**



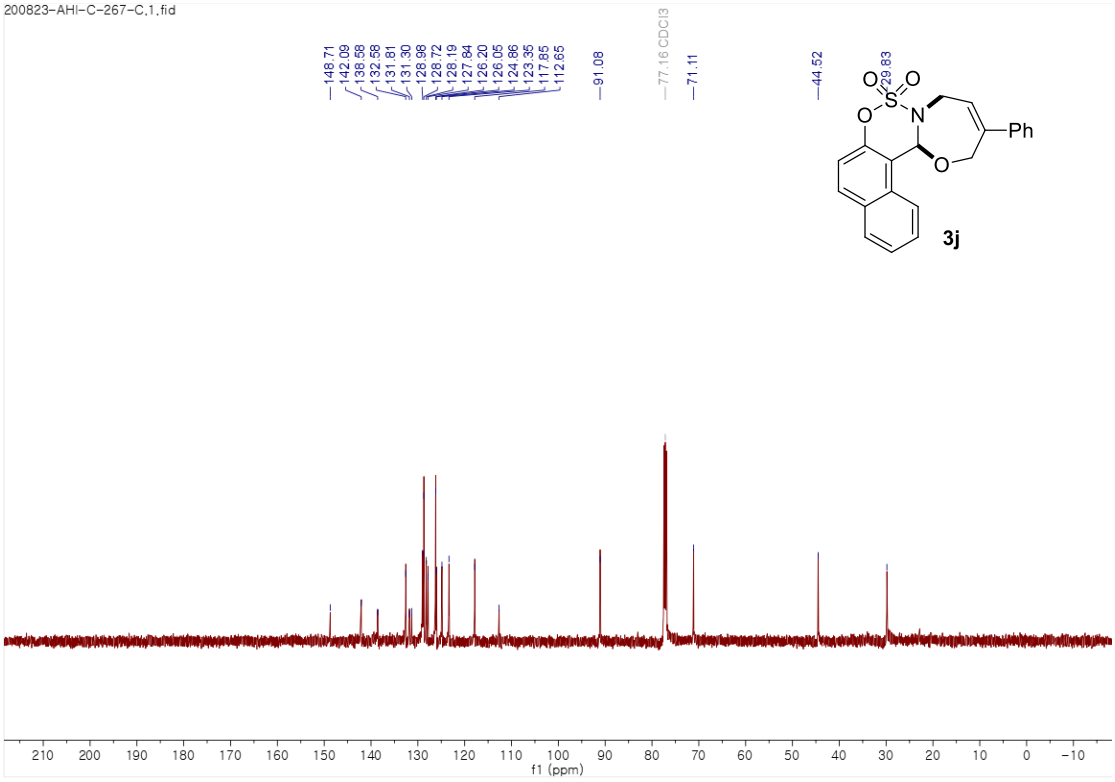
^{13}C NMR spectrum of **3i**



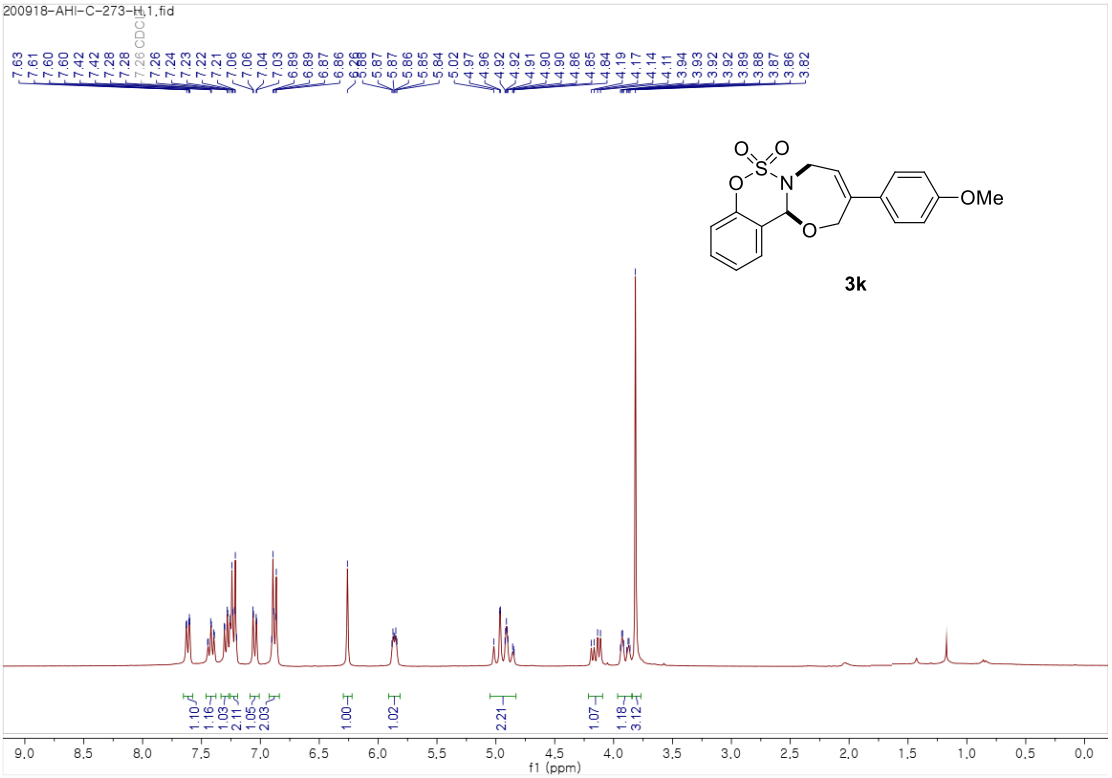
^{1}H NMR spectrum of **3j**



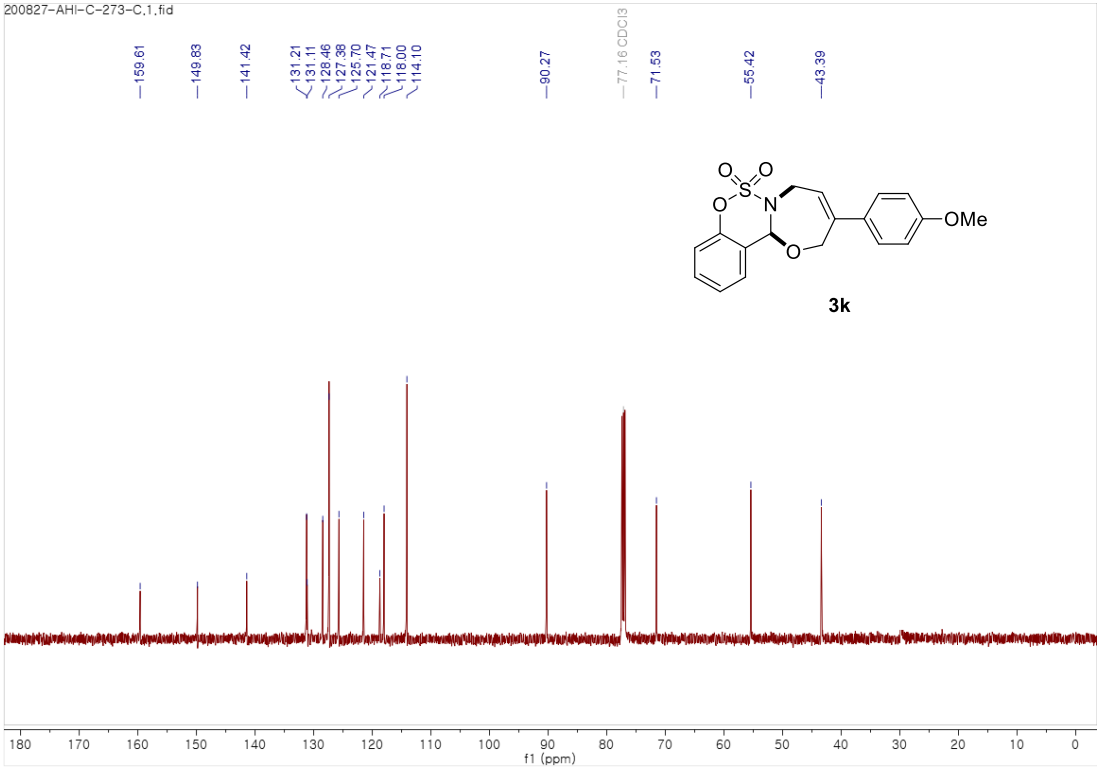
^{13}C NMR spectrum of **3j**



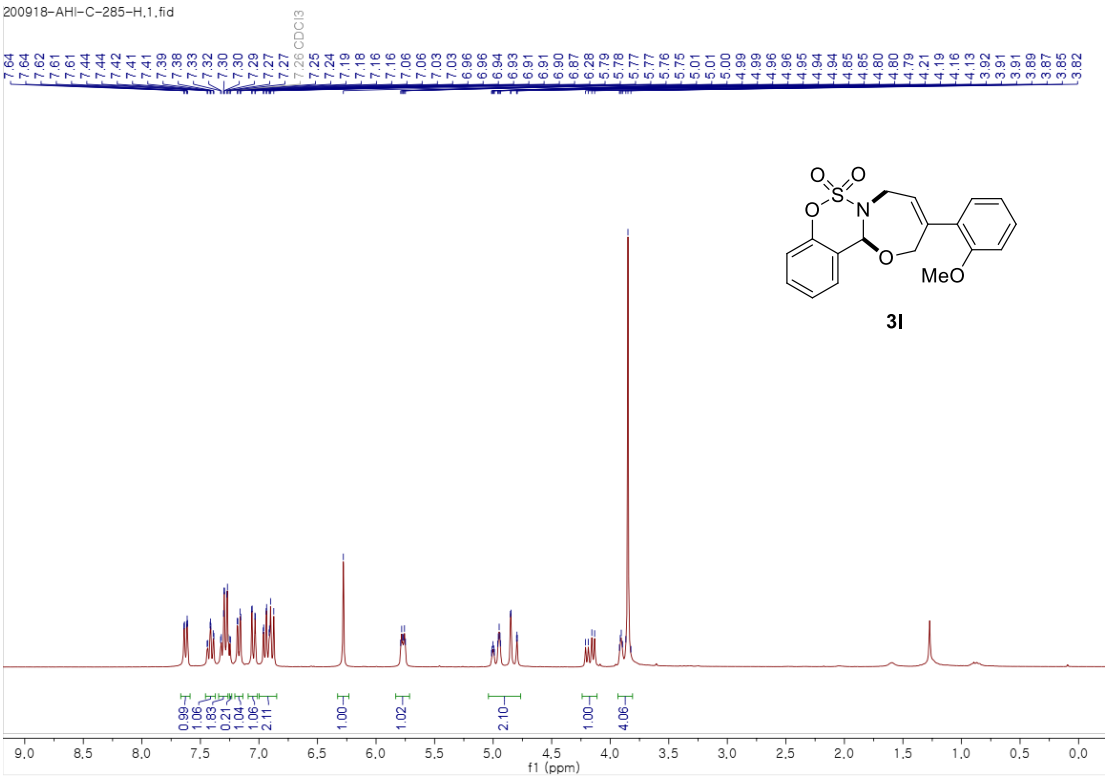
^{1}H NMR spectrum of **3k**



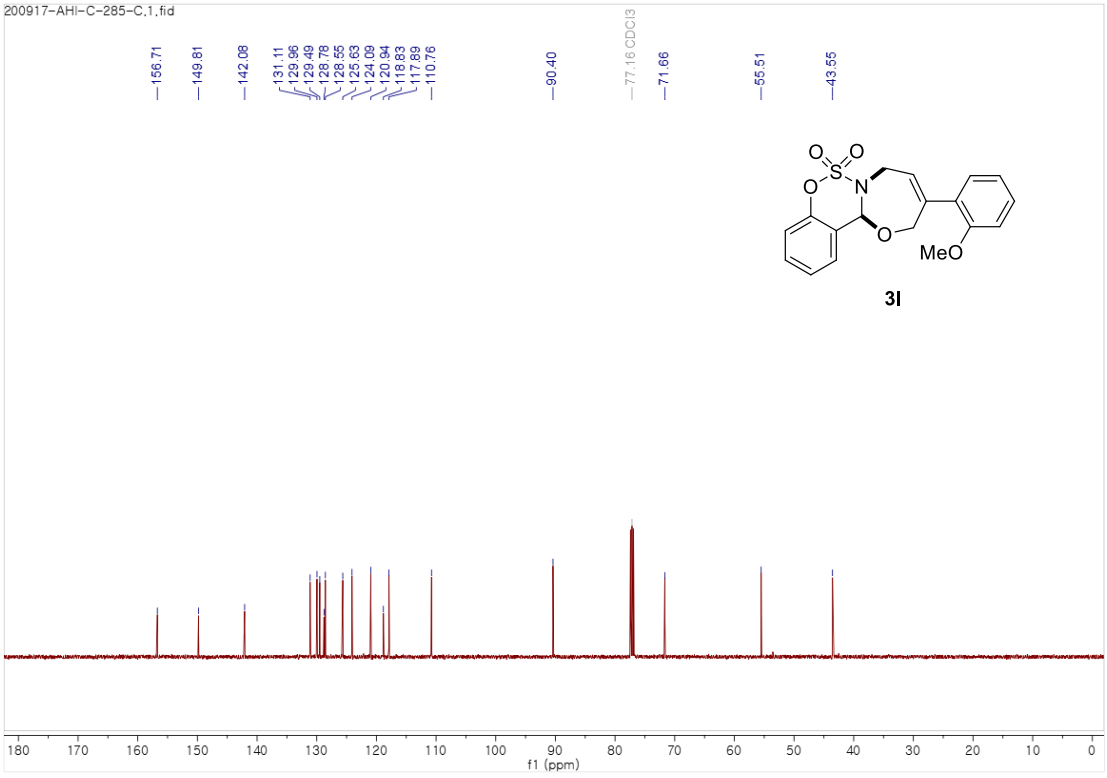
^{13}C NMR spectrum of **3k**



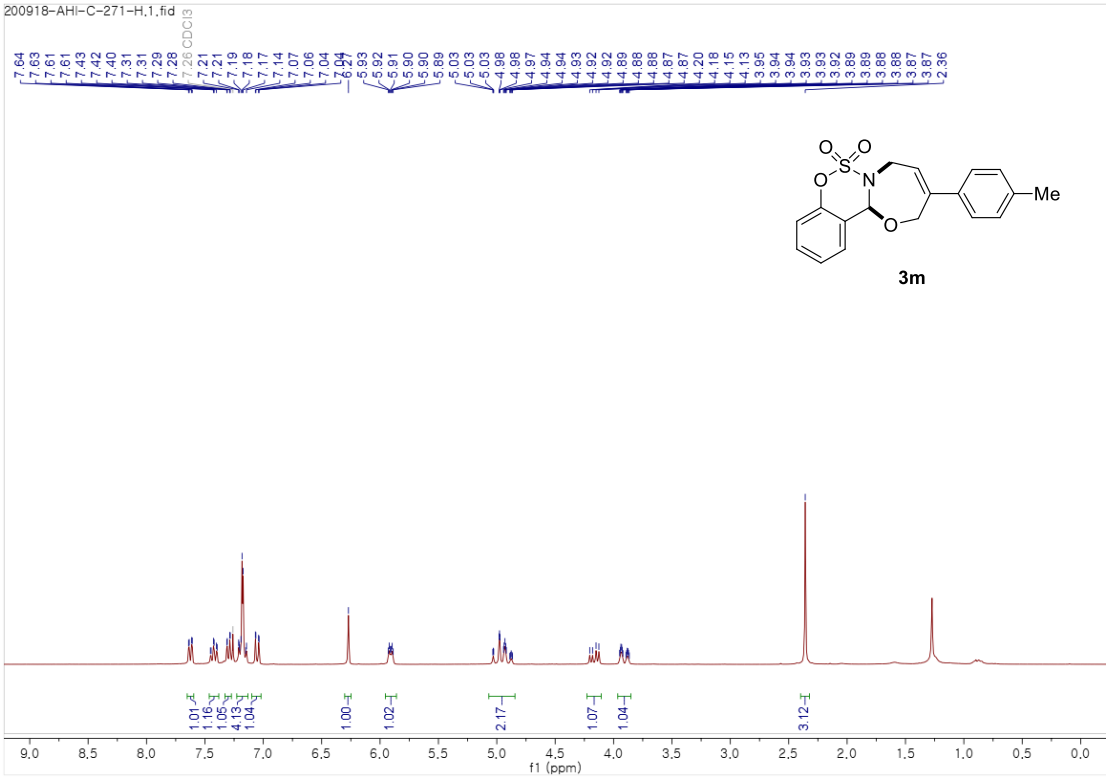
^{1}H NMR spectrum of **3l**



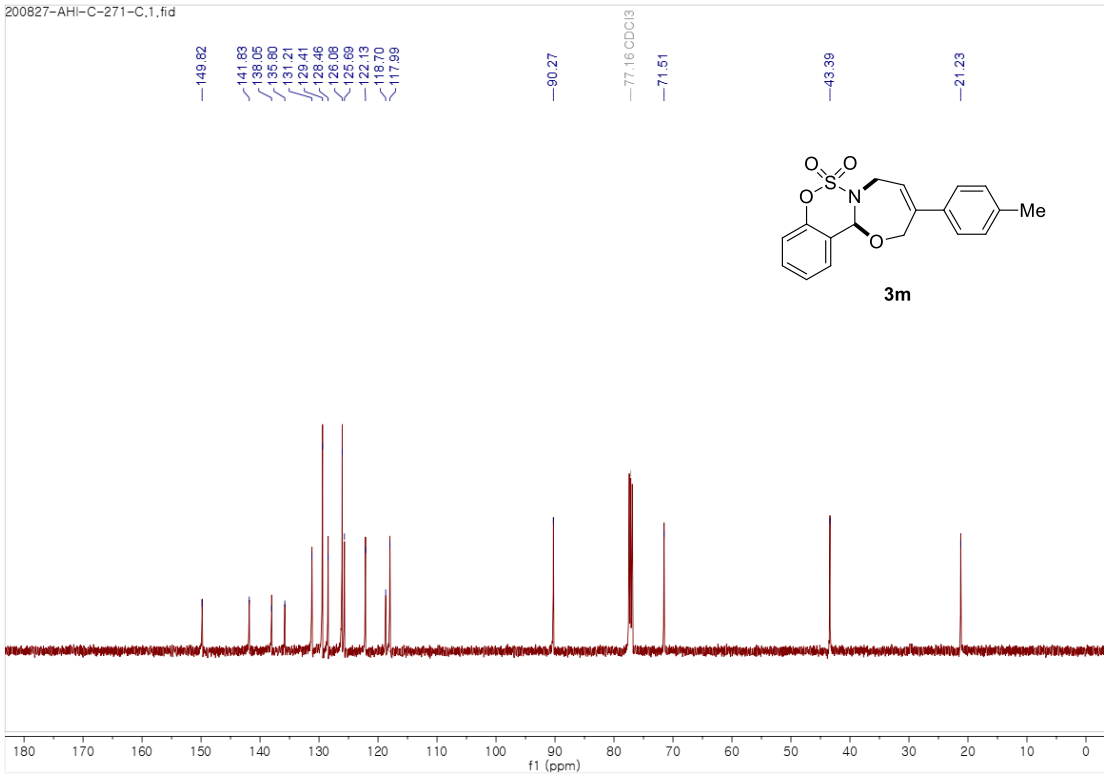
^{13}C NMR spectrum of **3l**



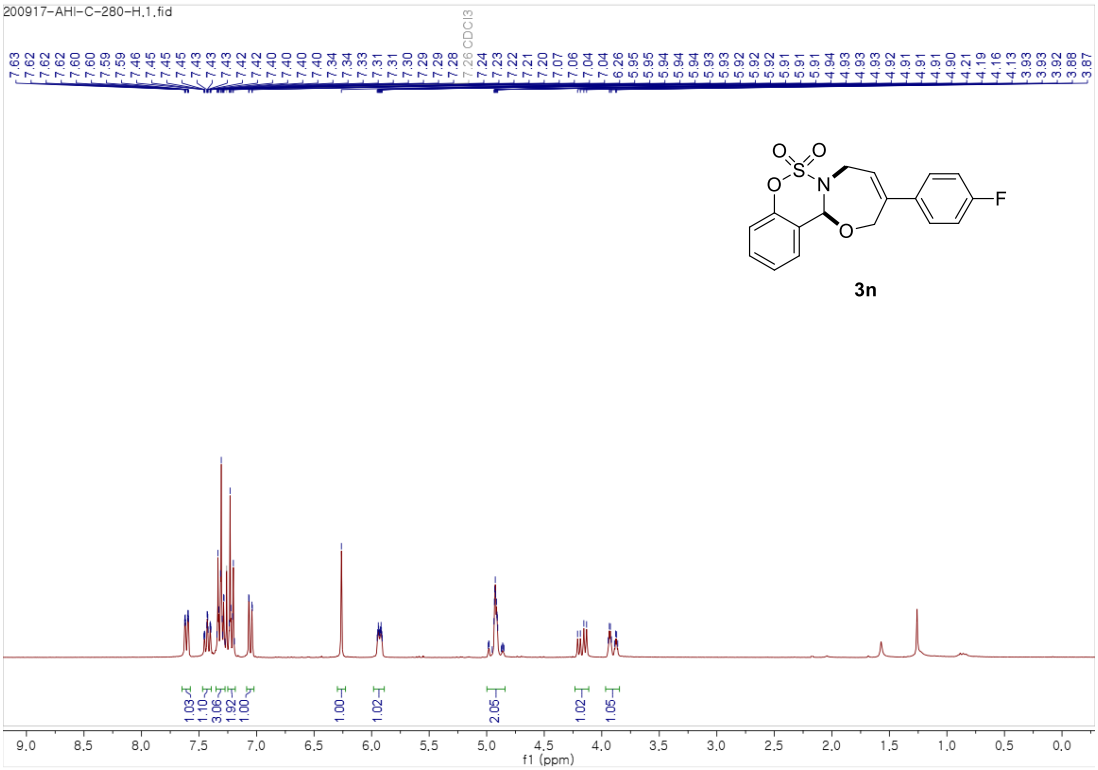
^{1}H NMR spectrum of **3m**



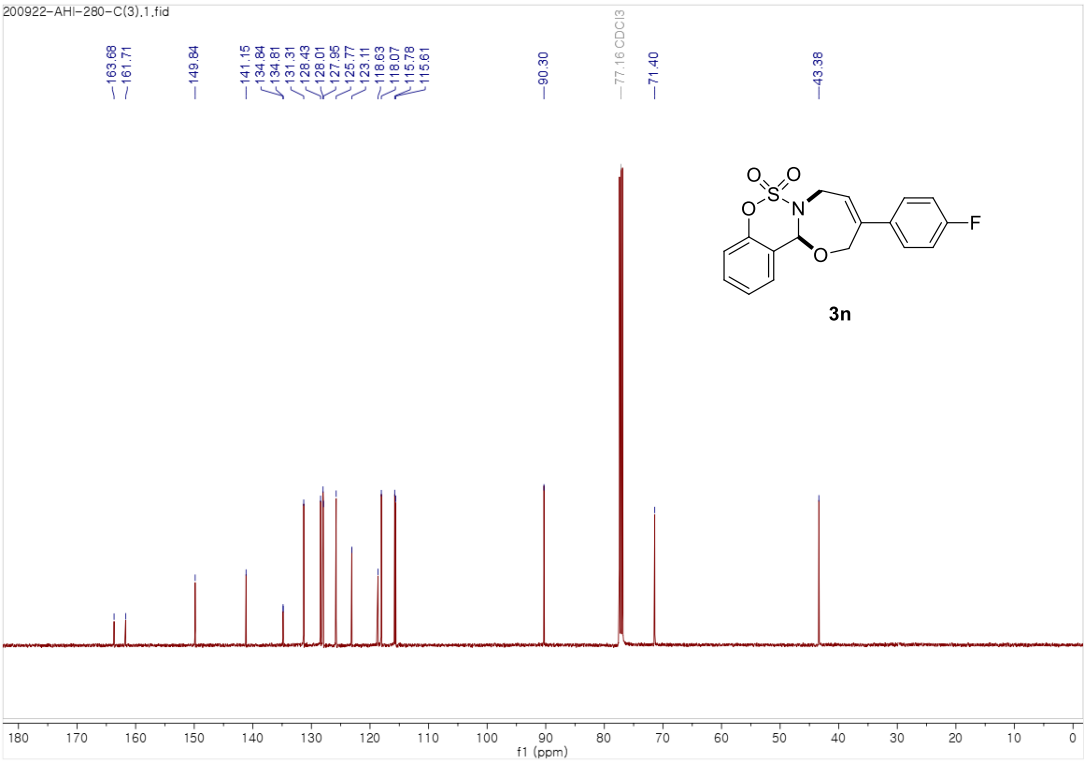
^{13}C NMR spectrum of **3m**



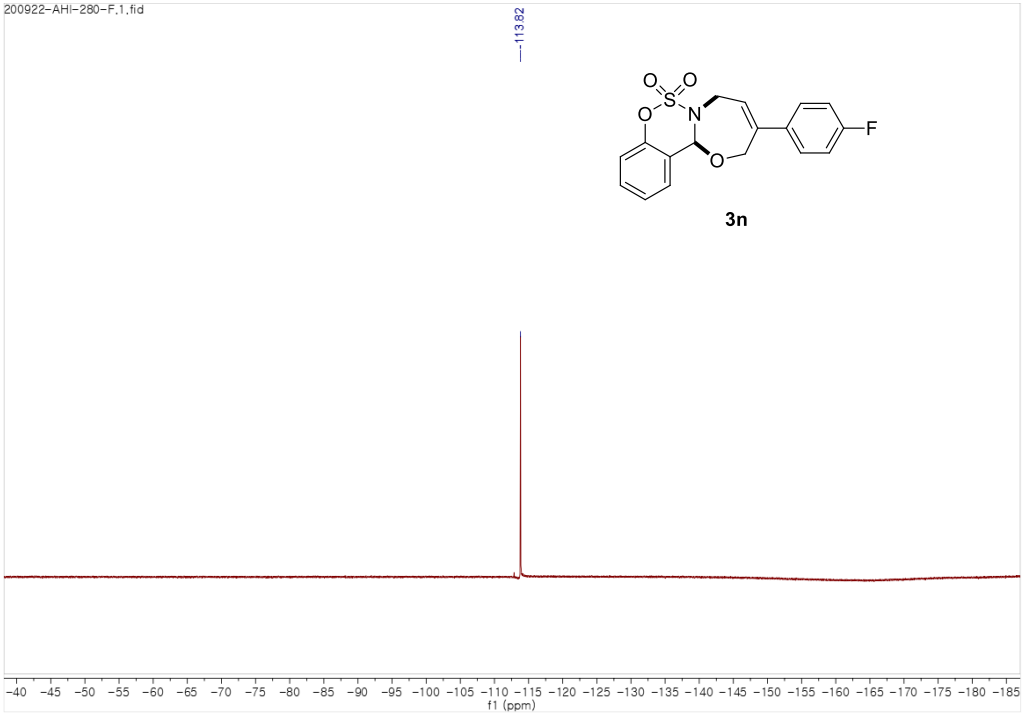
^{1}H NMR spectrum of **3n**



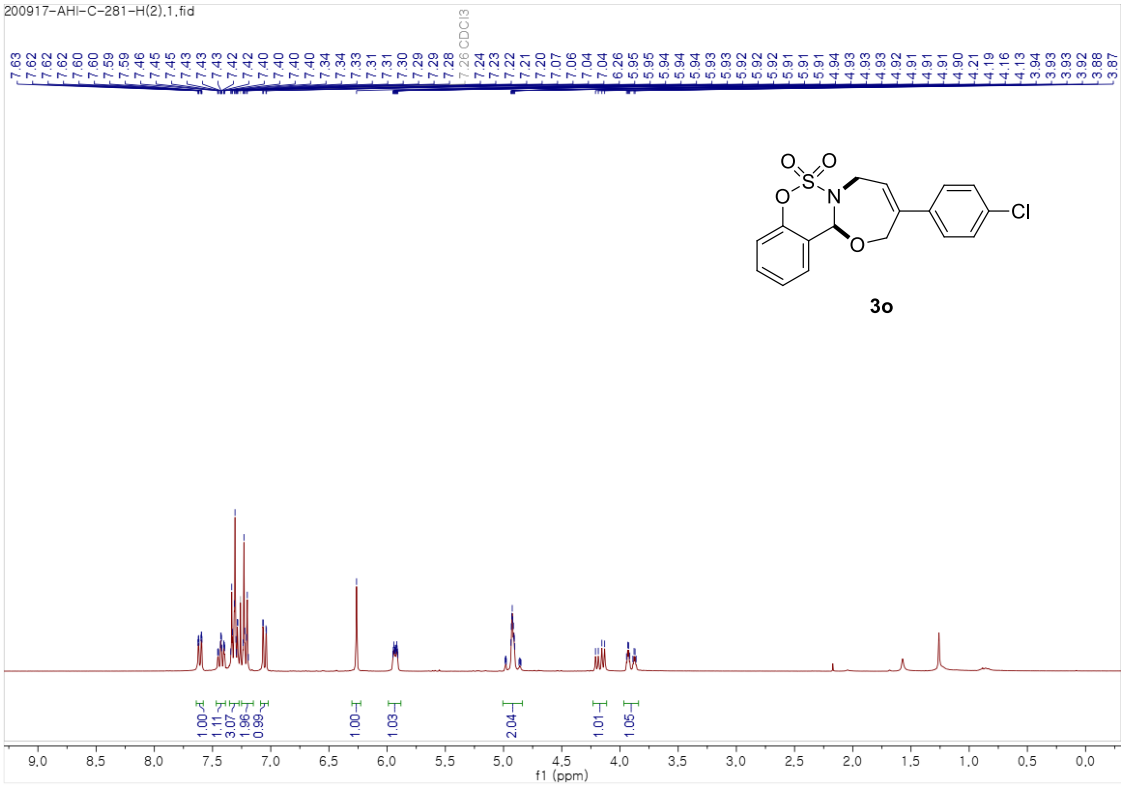
^{13}C NMR spectrum of **3n**



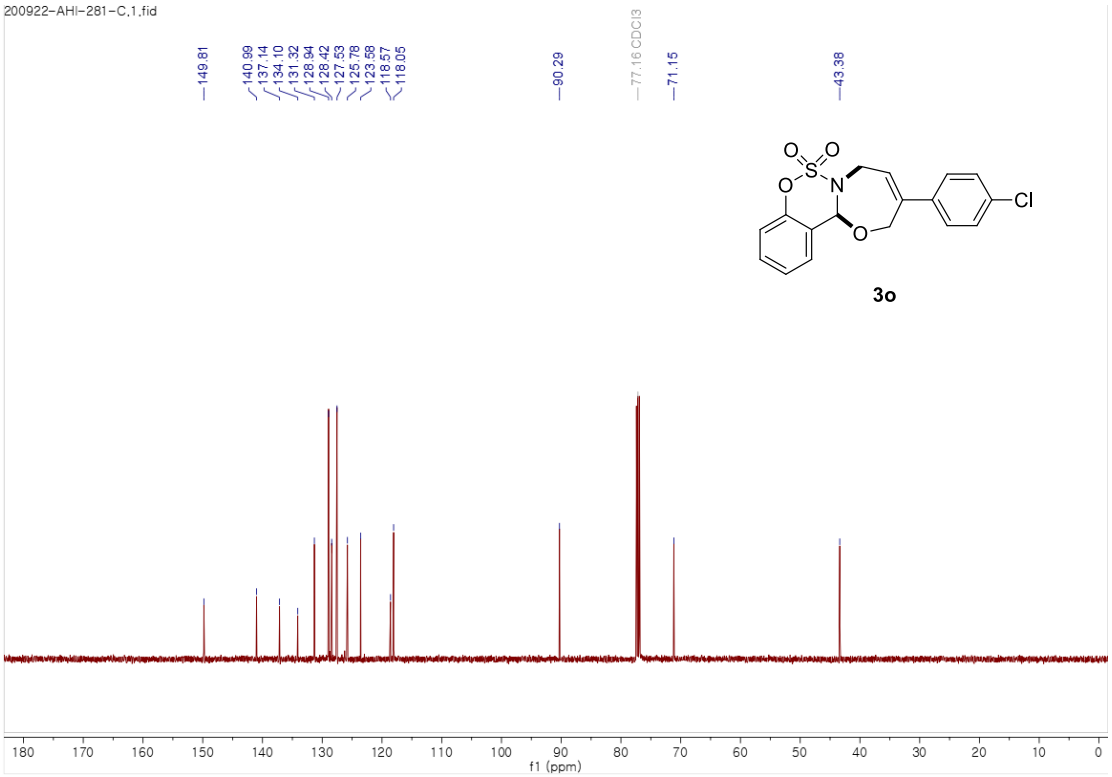
^{19}F NMR spectrum of **3n**



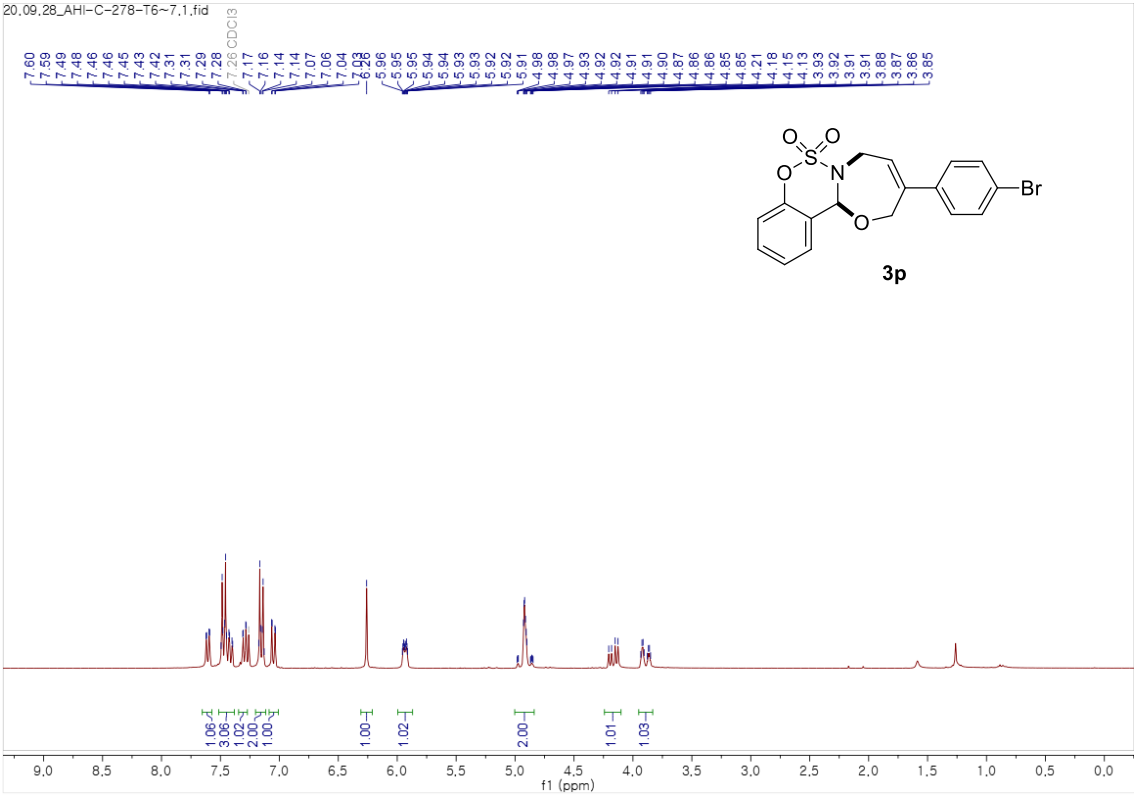
^{1}H NMR spectrum of **3o**



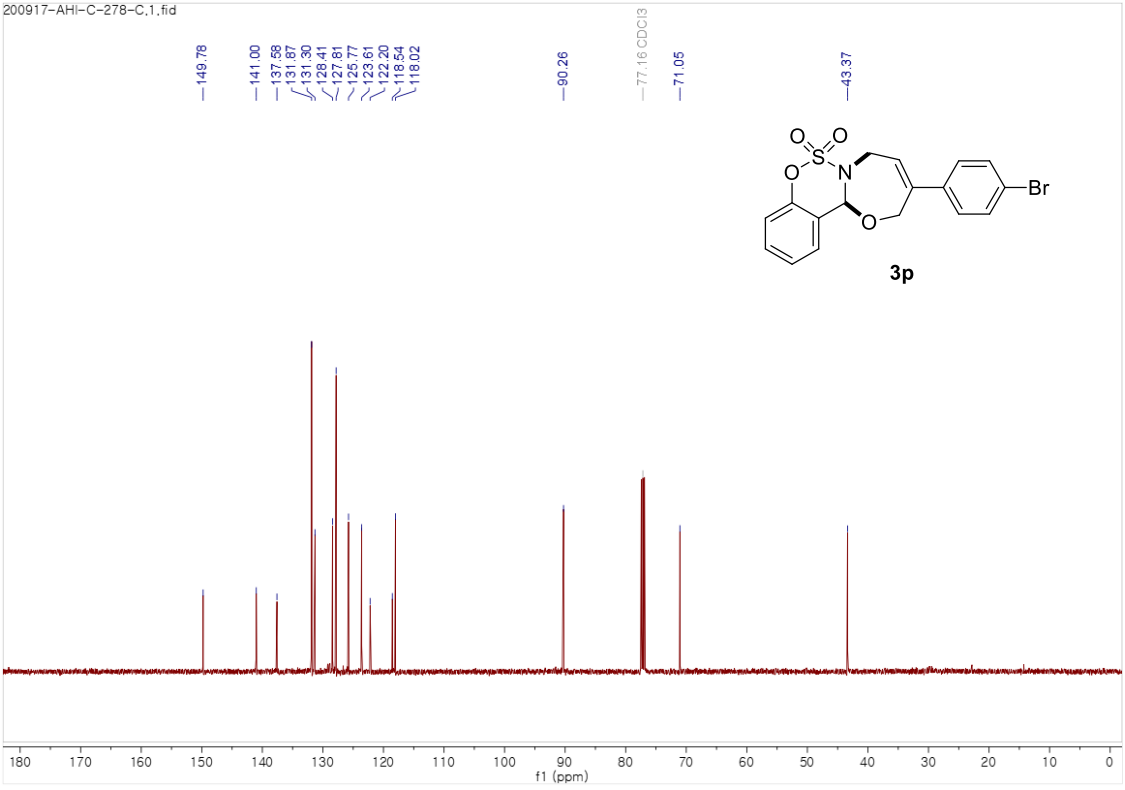
^{13}C NMR spectrum of **3o**



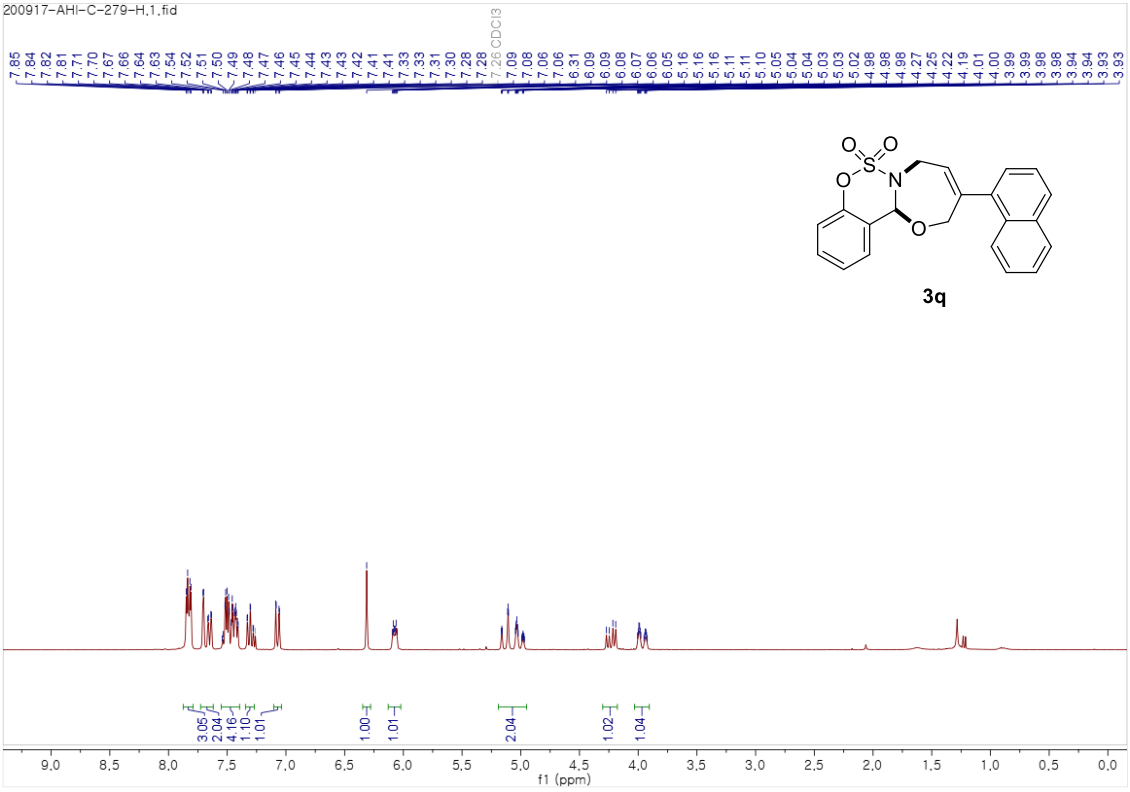
^{1}H NMR spectrum of **3p**



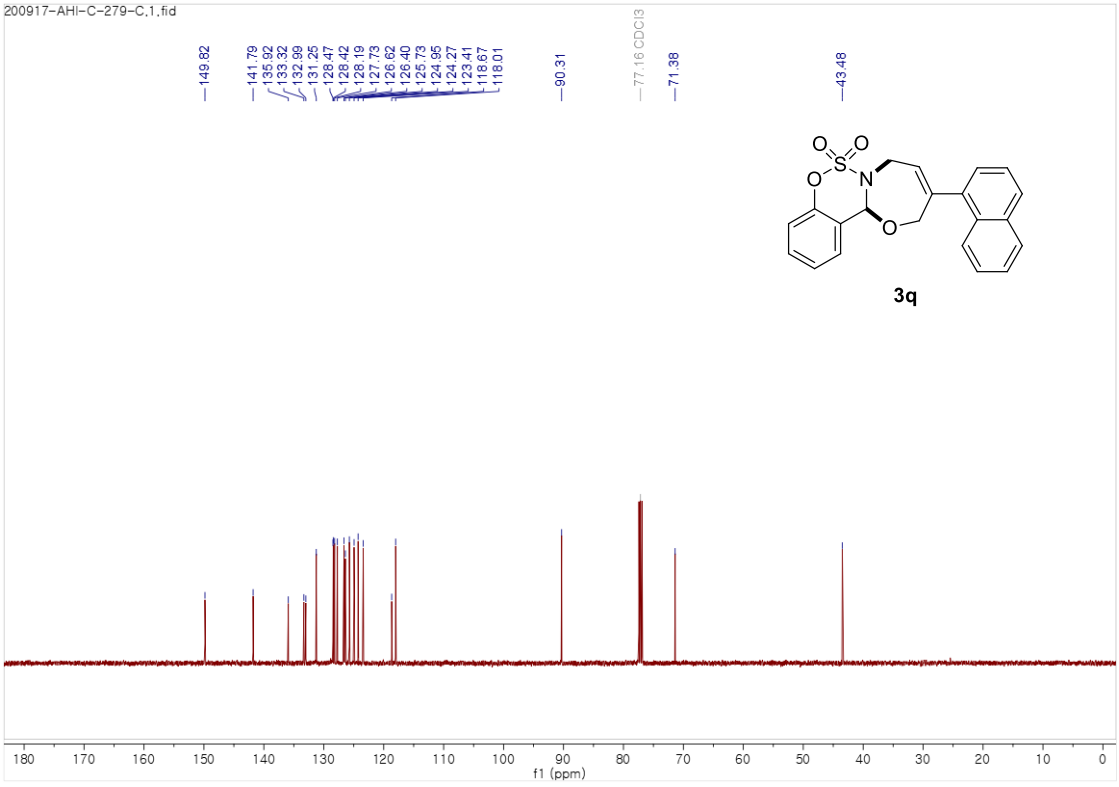
^{13}C NMR spectrum of **3p**



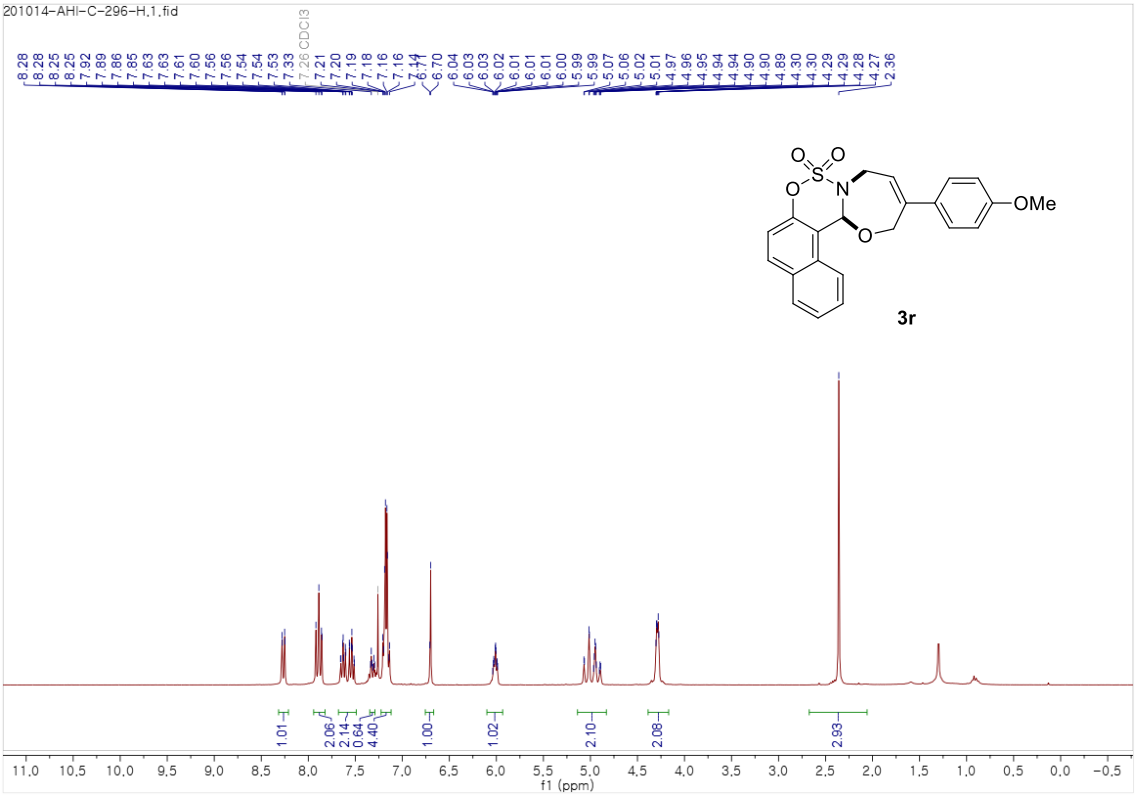
^{1}H NMR spectrum of **3q**



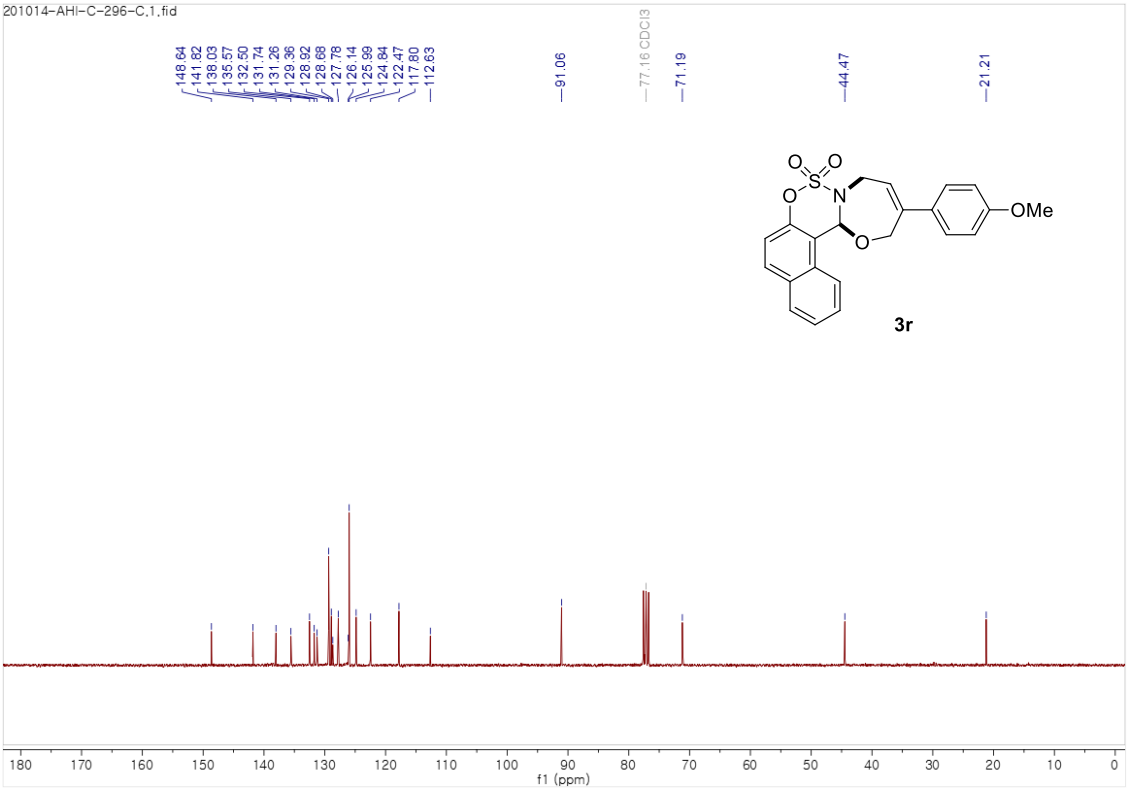
^{13}C NMR spectrum of **3q**



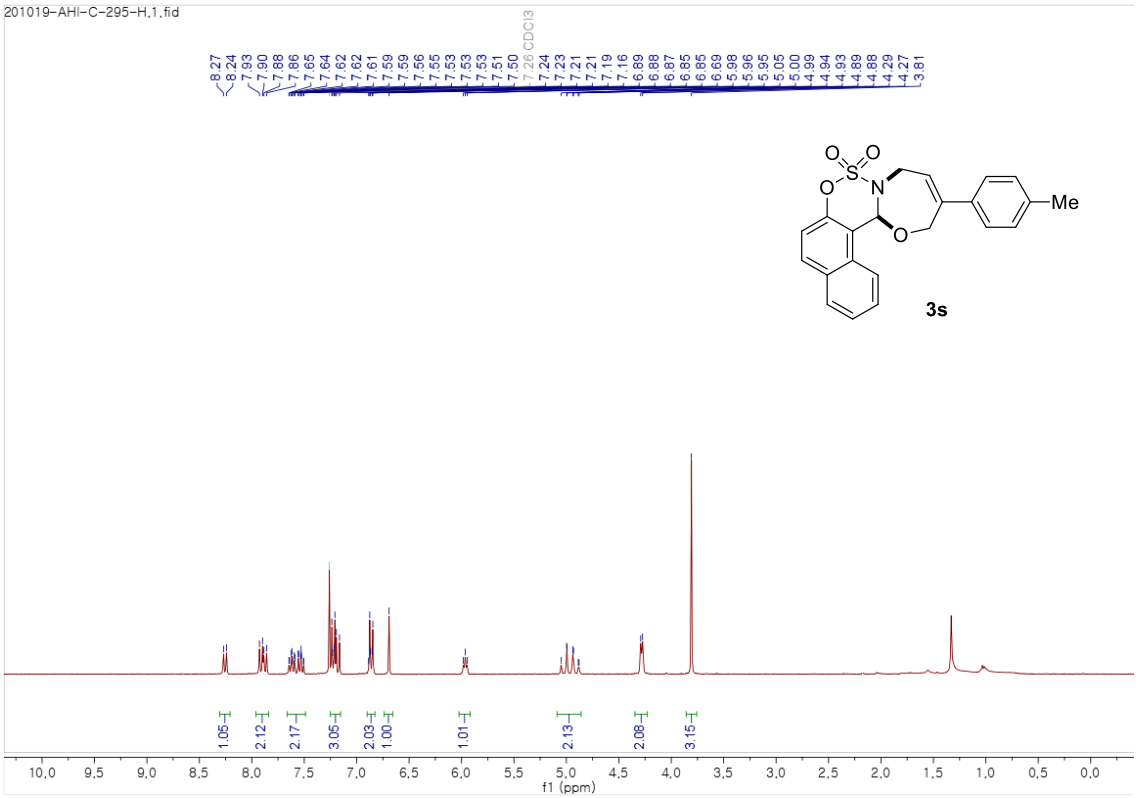
^{1}H NMR spectrum of **3r**



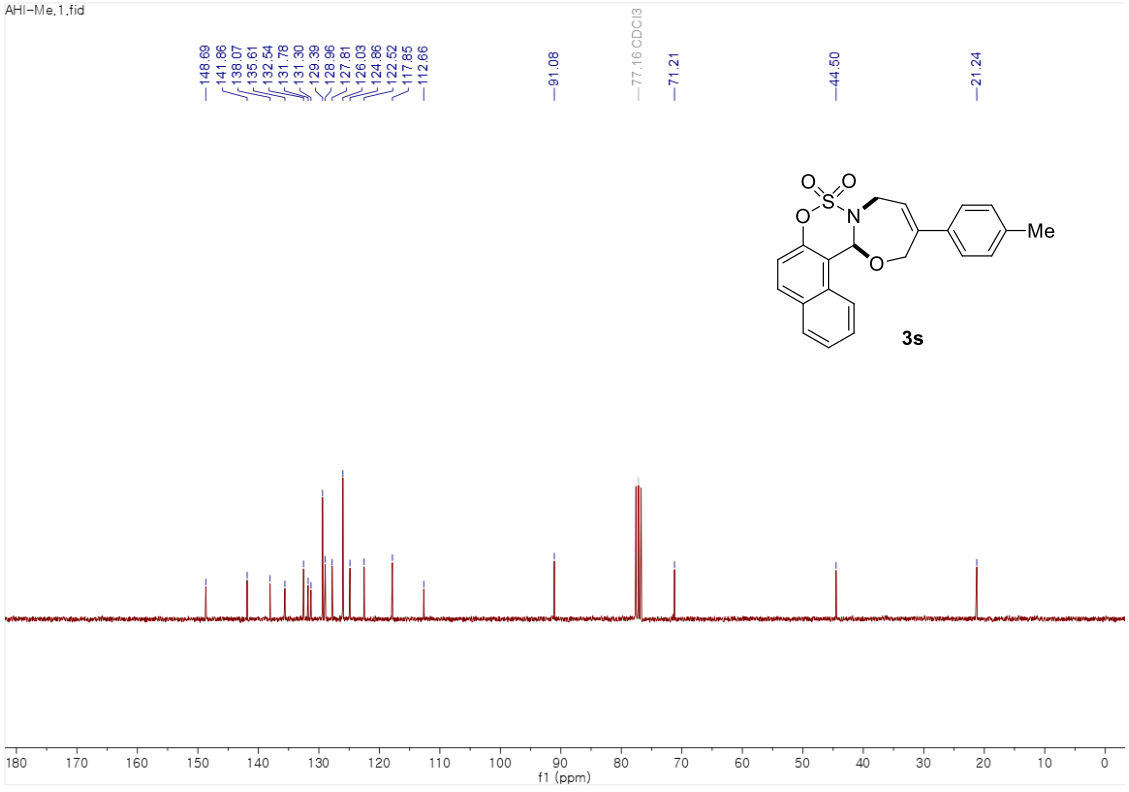
^{13}C NMR spectrum of **3r**



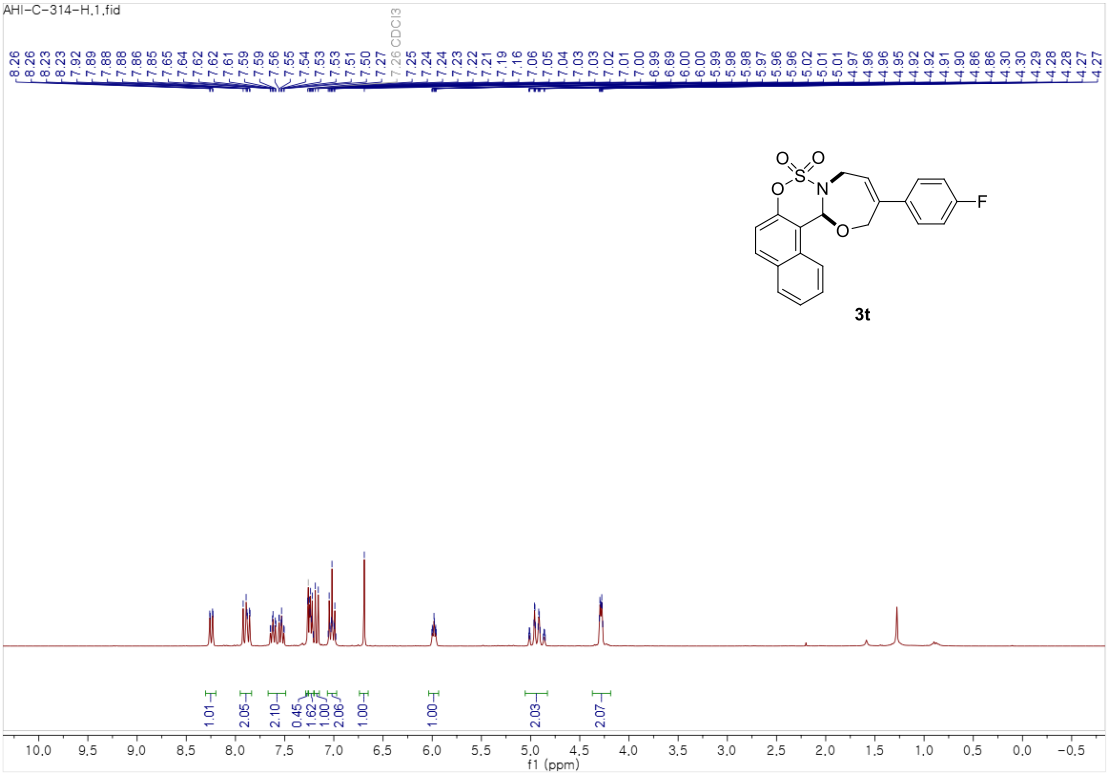
^{1}H NMR spectrum of **3s**



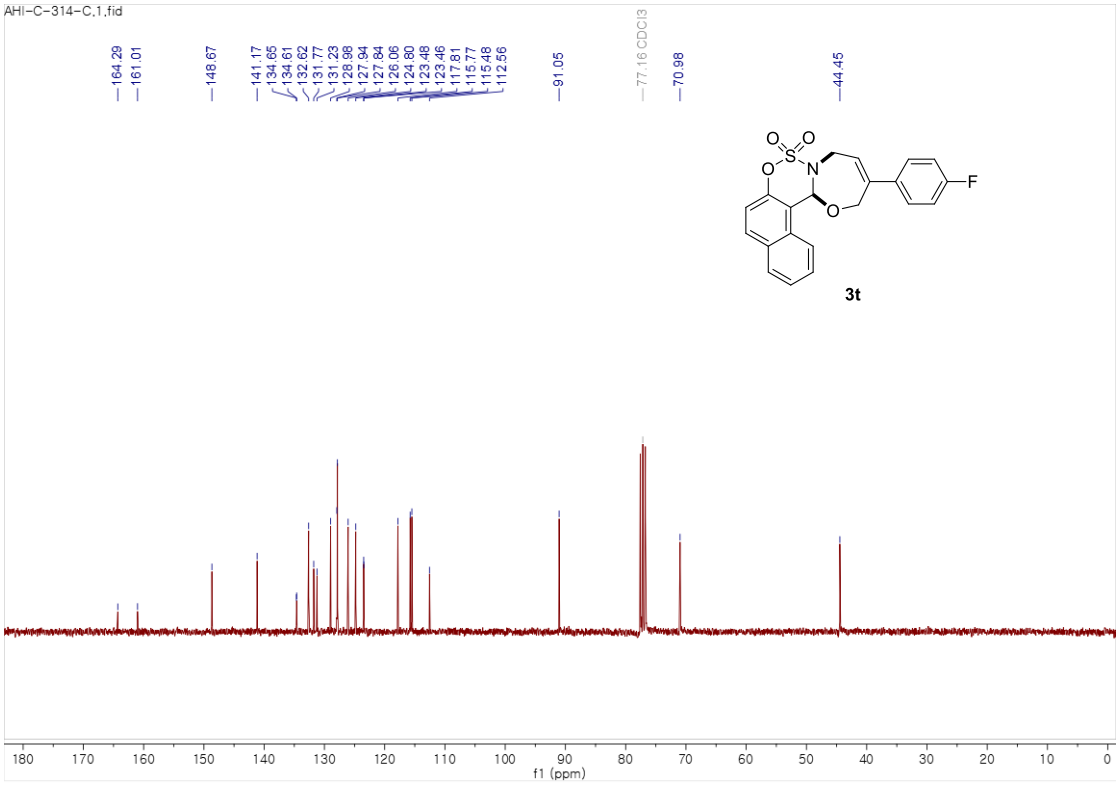
^{13}C NMR spectrum of **3r**



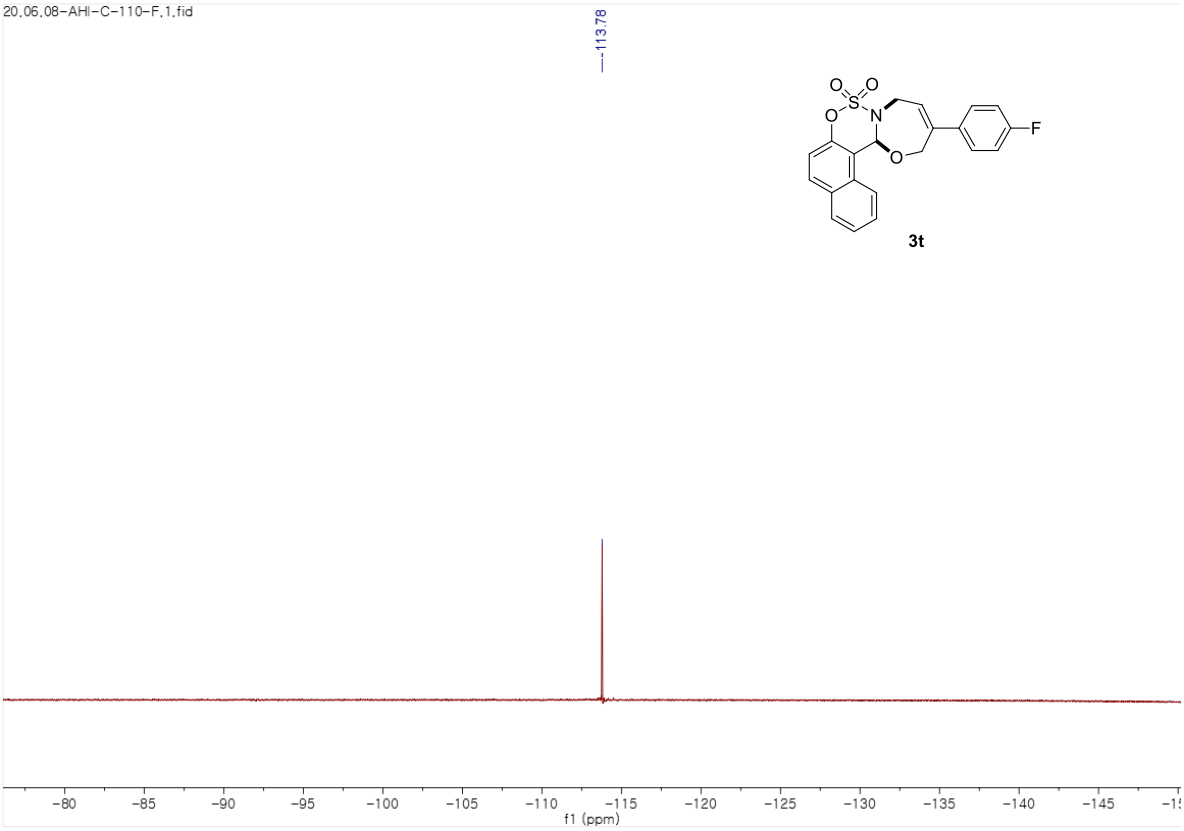
^{1}H NMR spectrum of **3t**



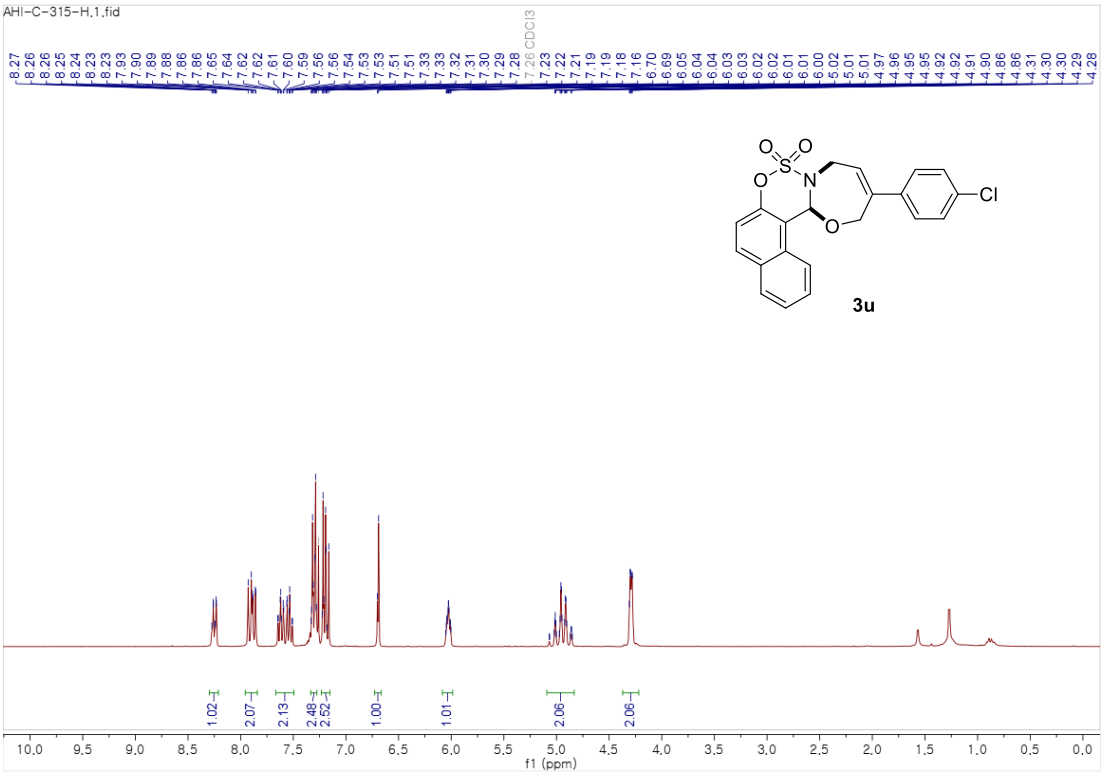
^{13}C NMR spectrum of **3t**



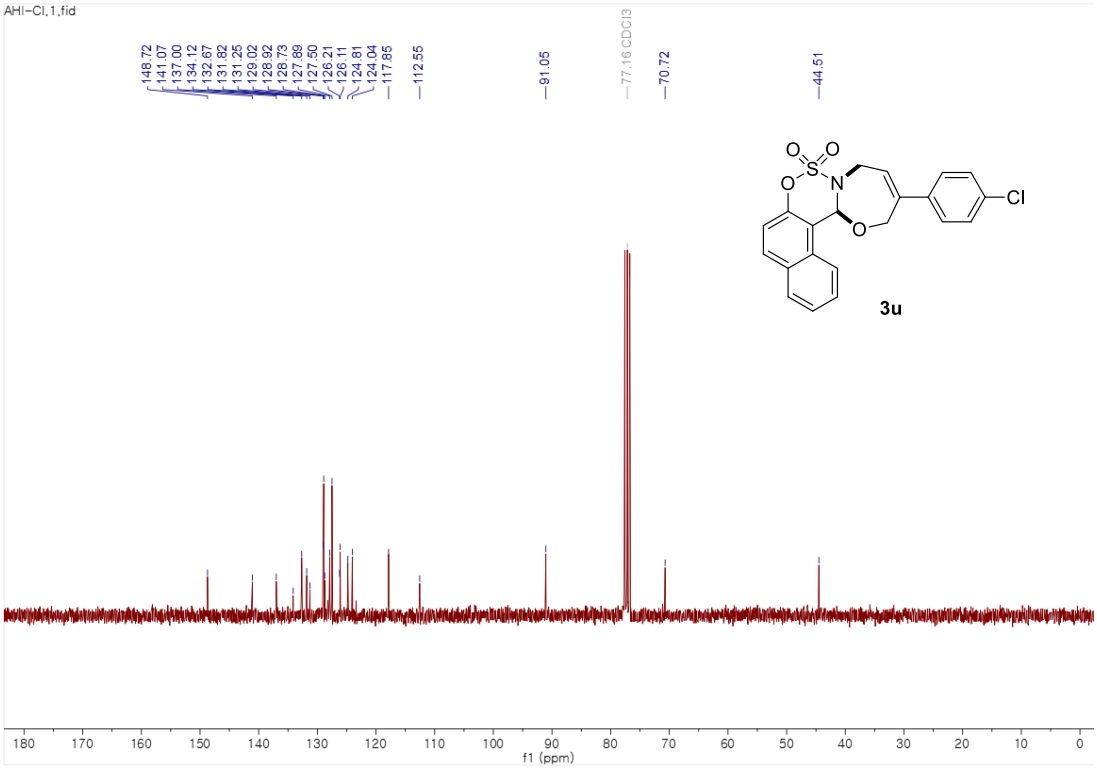
^{19}F NMR spectrum of **3t**



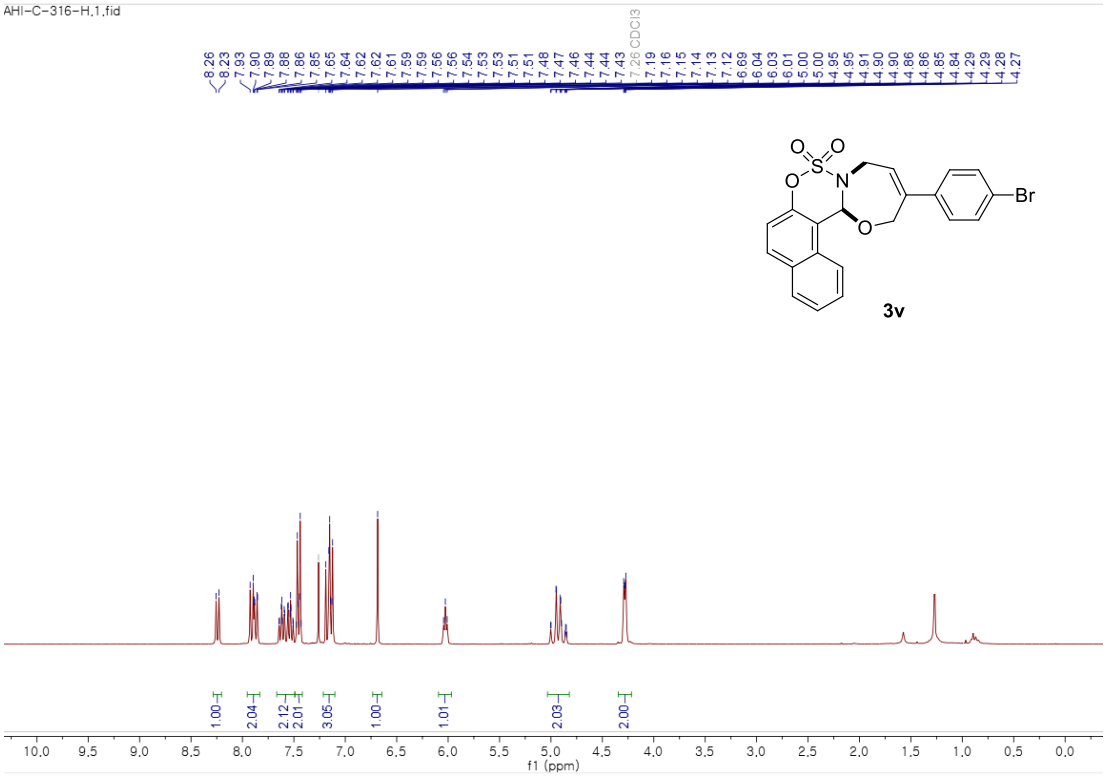
^{1}H NMR spectrum of **3u**



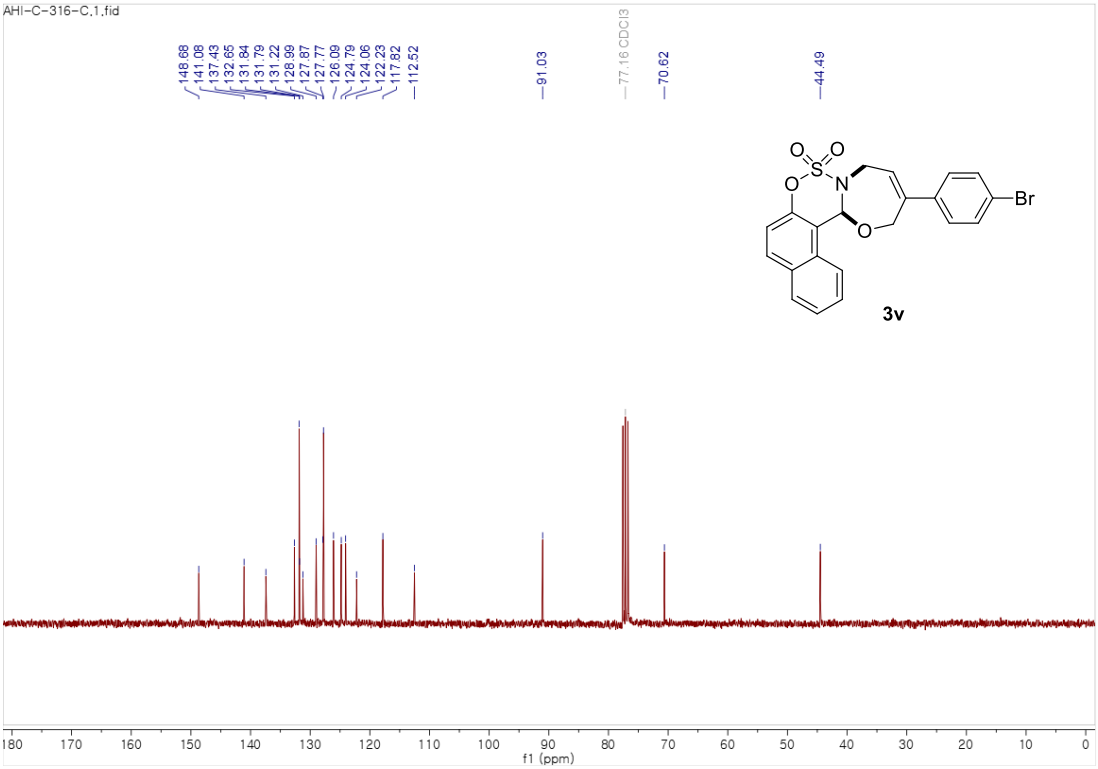
^{13}C NMR spectrum of **3u**



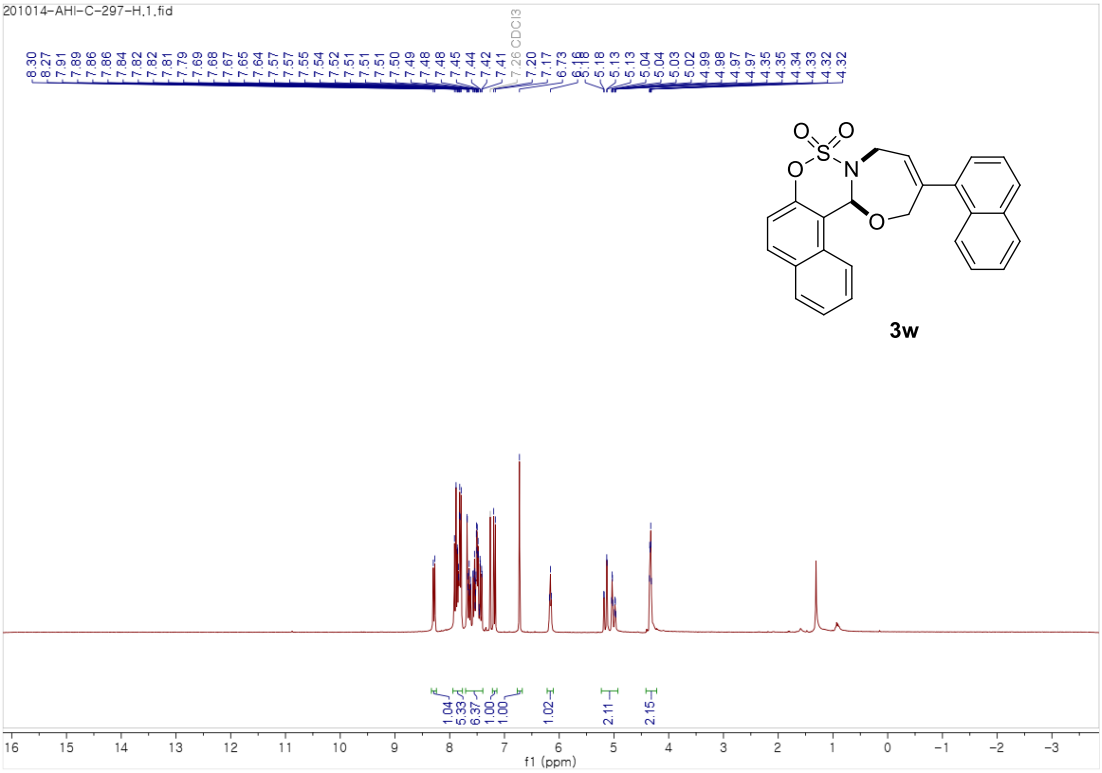
^{1}H NMR spectrum of **3v**



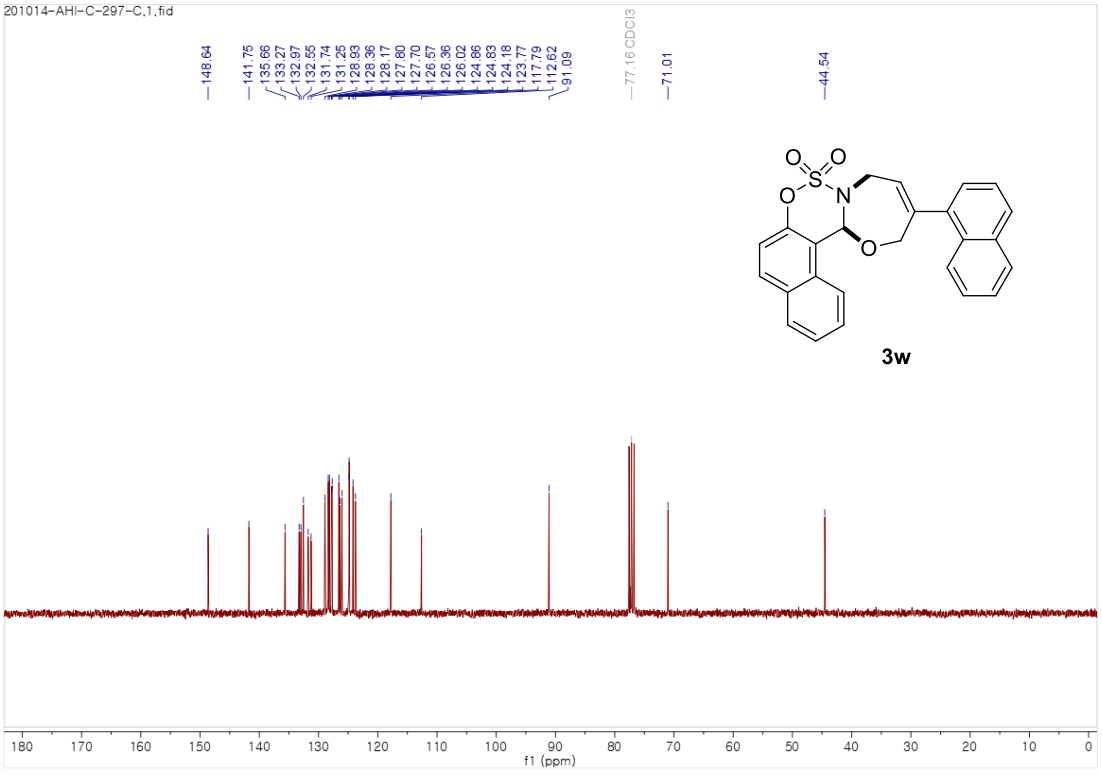
^{13}C NMR spectrum of **3v**



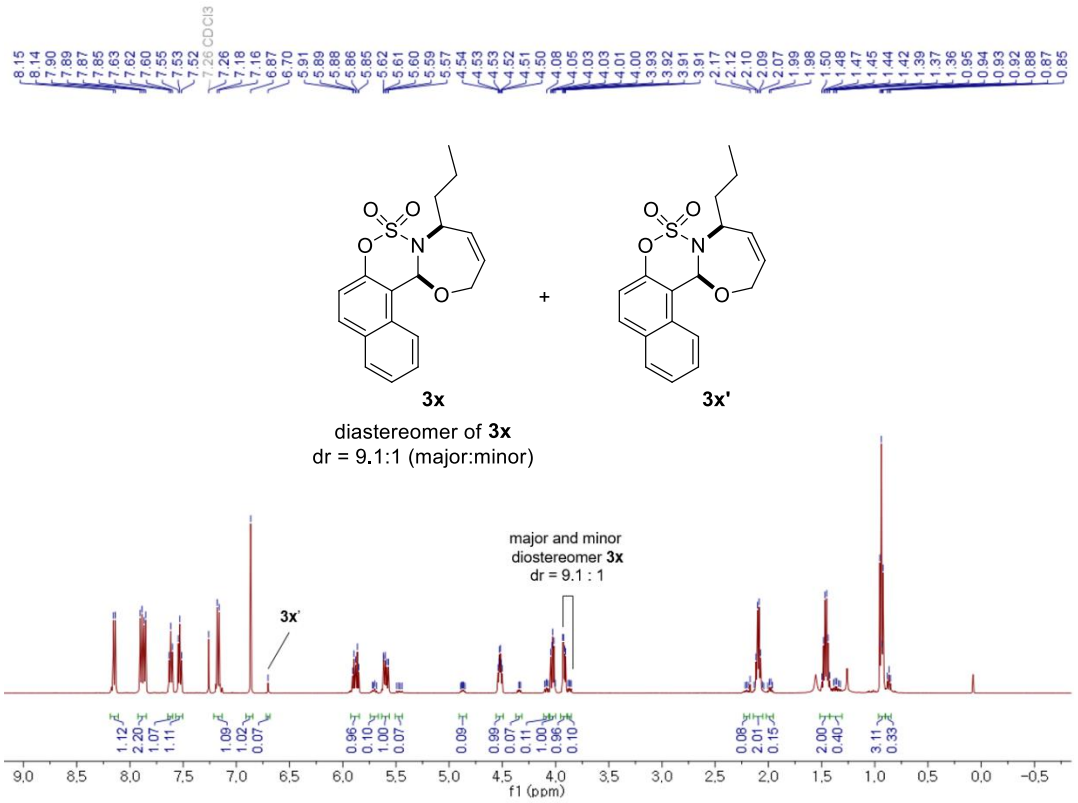
^{1}H NMR spectrum of **3w**



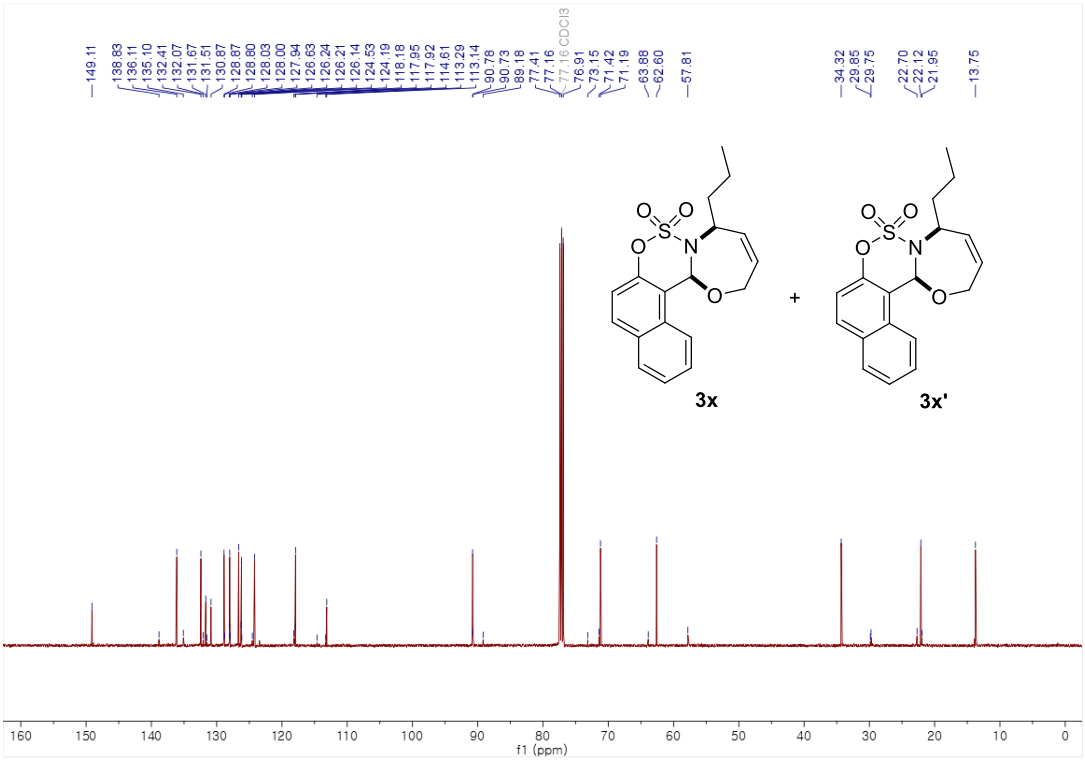
^{13}C NMR spectrum of **3w**



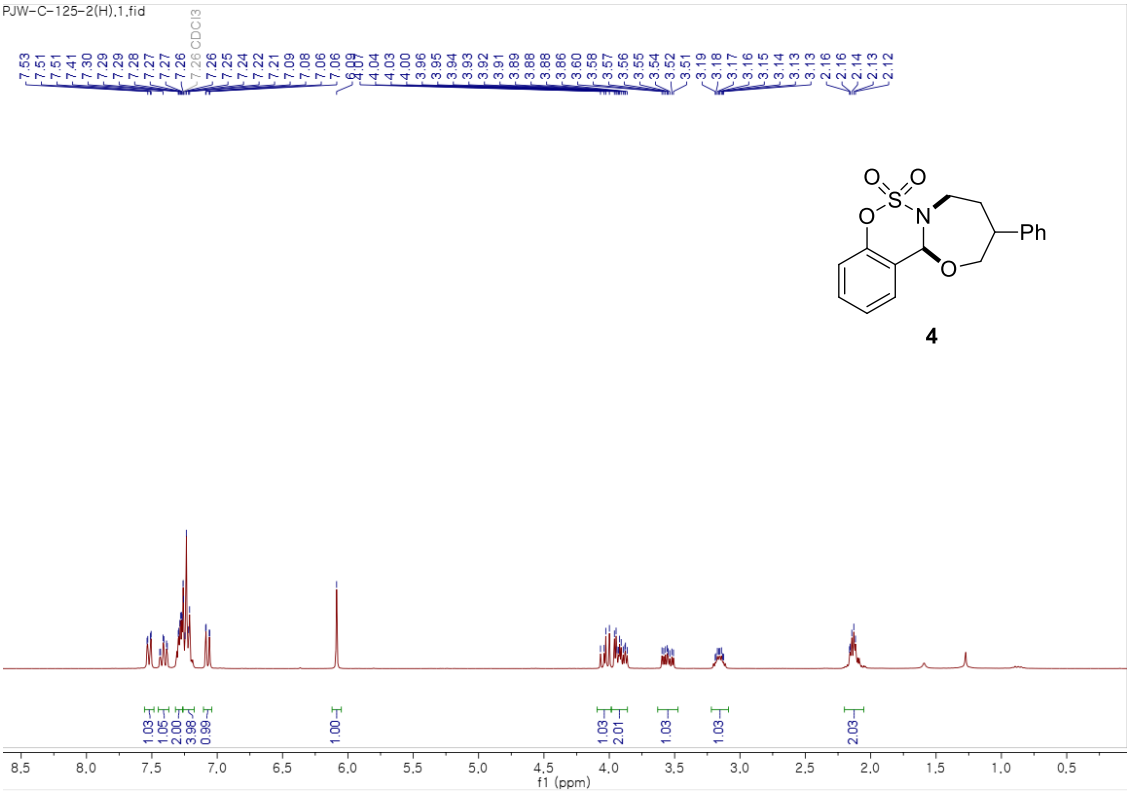
^{1}H NMR spectrum of **3x** and **3x'**



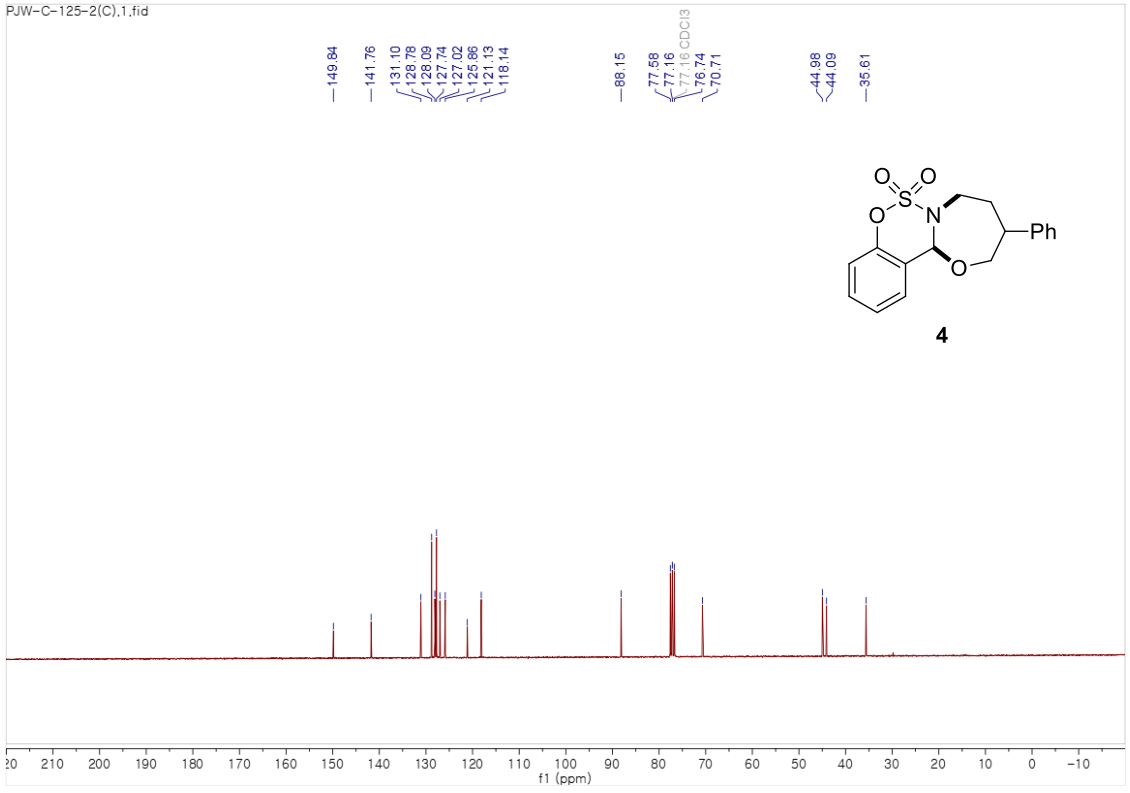
^{13}C NMR spectrum of **3x** and **3x'**



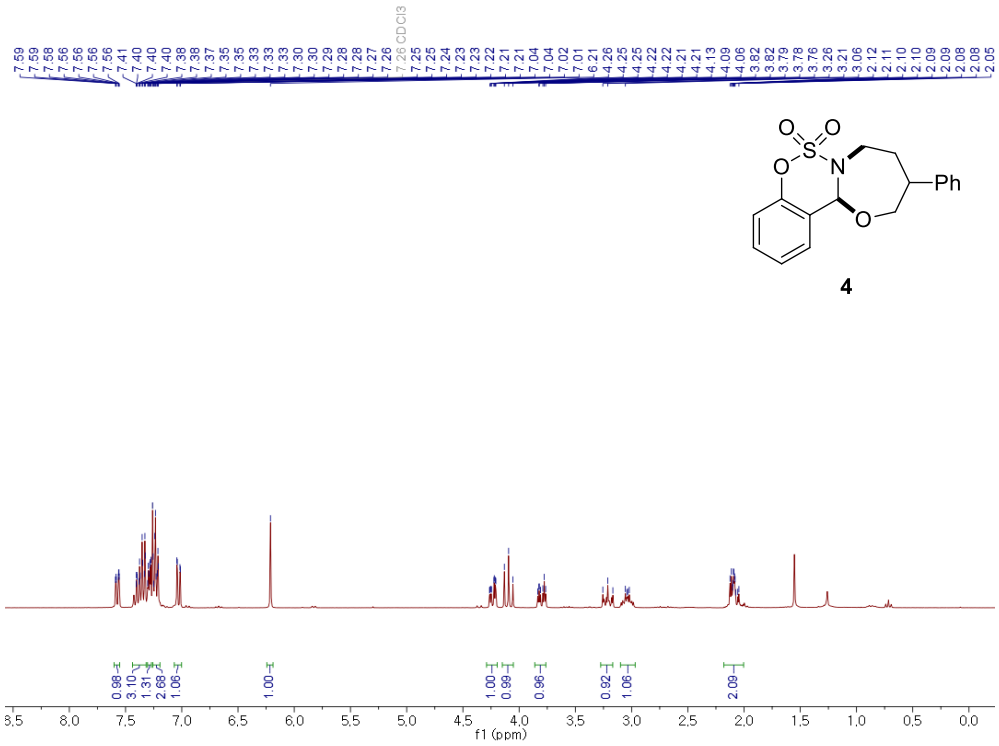
^{1}H NMR spectrum for major diasteromer of **4**



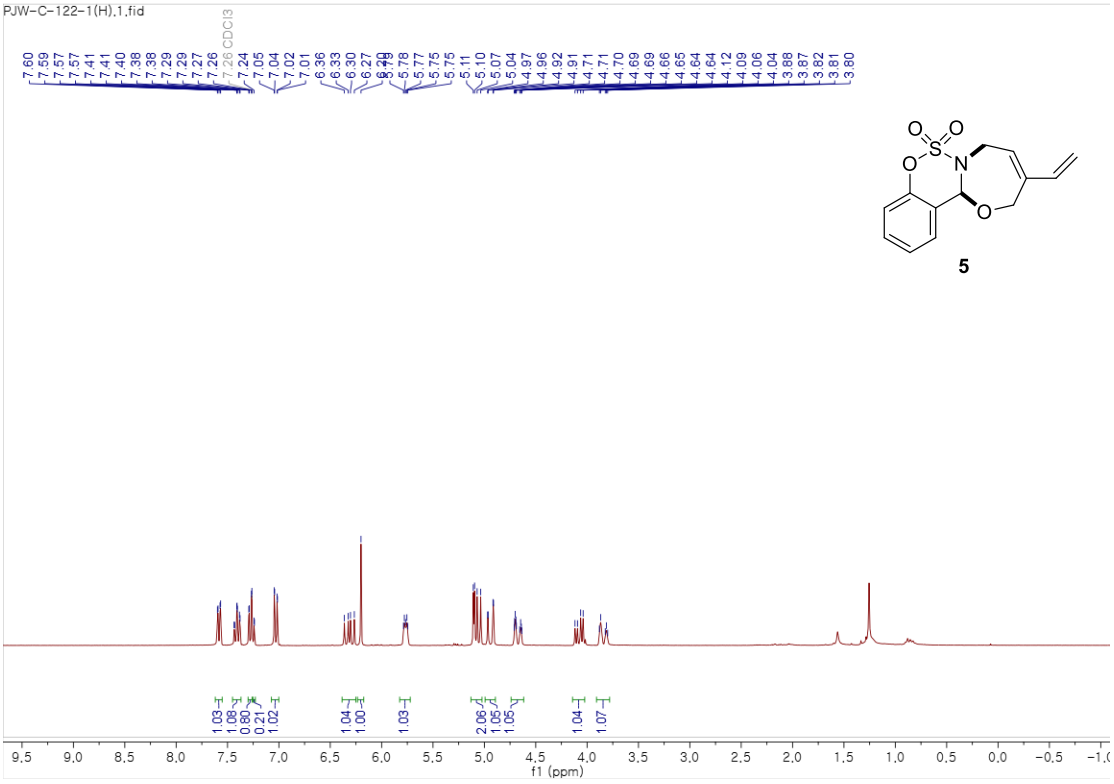
^{13}C NMR spectrum for major diasteromer of **4**



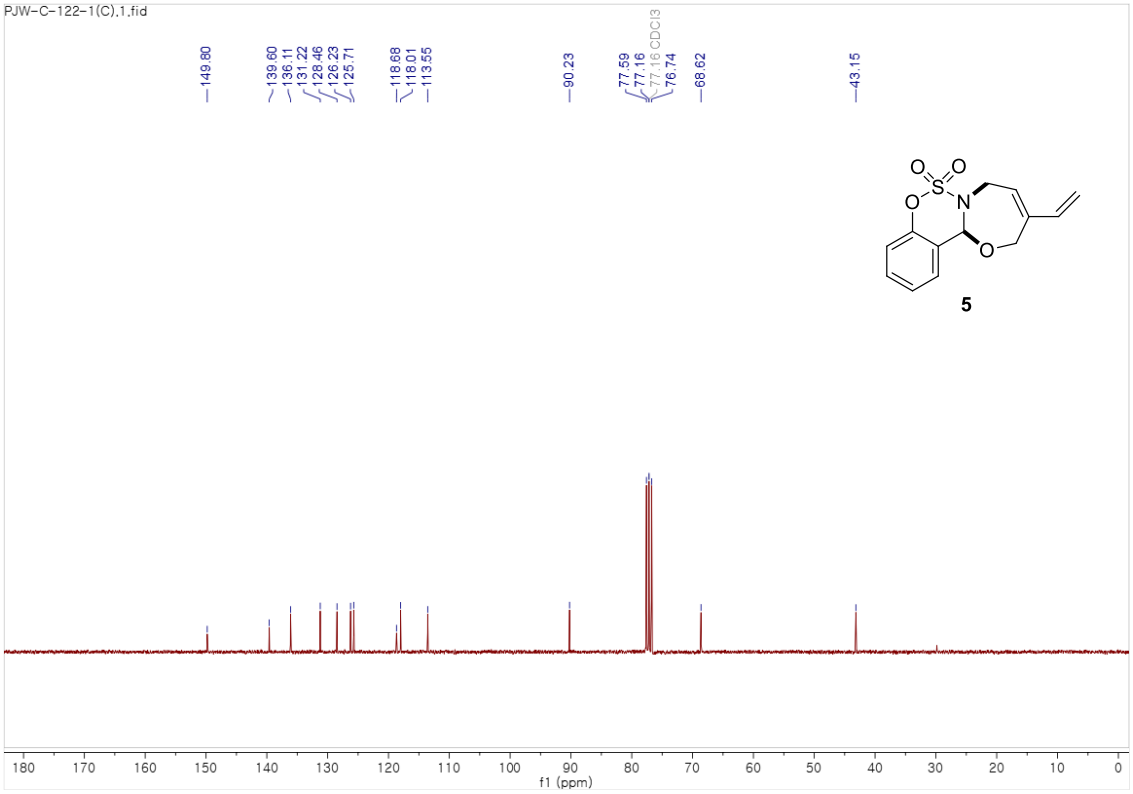
^{1}H NMR spectrum for minor diasteromer of **4**



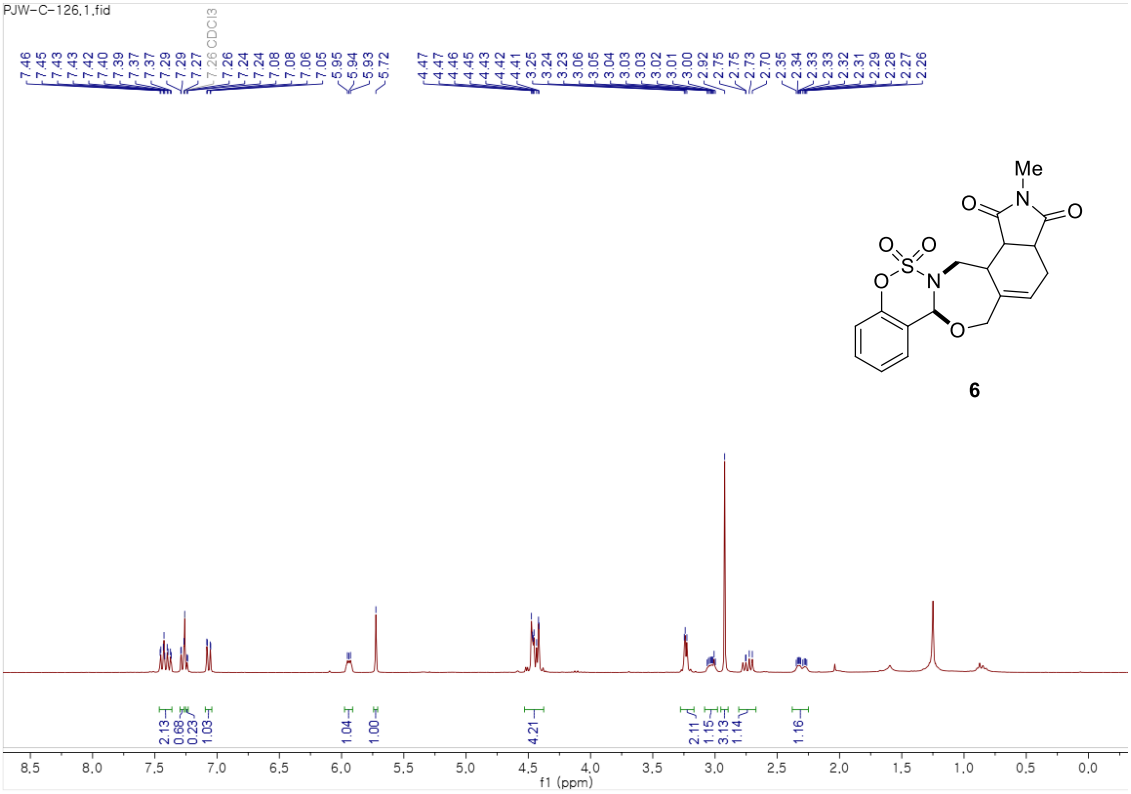
^{1}H NMR spectrum of **5**



^{13}C NMR spectrum of **5**



^{1}H NMR spectrum of **6**



^{13}C NMR spectrum of **6**