Electronic Supplementary Information

Palladium-Catalyzed Stereoselective (3+2) Cycloaddition of Vinylethylene Carbonates with Cyclic N-Sulfonyl Ketimines

Xing Gao,[a] Dongyu Zhu,[a] Feng Jiang,[a] Jianning Liao,[a] Wei Wang,[b] Yongjun Wu,[b] Lufei Zheng,*[c] and Hongchao Guo*[ad]

[a]Department of Chemistry and Innovation Center of Pesticide Research, China Agricultural University, Beijing 100193, P. R. China

[b]College of Public Health, Zhengzhou University, Zhengzhou 450001, P. R. China

[c]Institute of Quality Standards & Testing Technology for Agro-Products, Chinese Academy of Agricultural Sciences, Beijing 100081, China

[d]Department of Nutrition and Health, China Agricultural University, Beijing 100193, P. R. China

E-mail: hchguo@cau.edu.cn; 13522807385@163.com

Contents

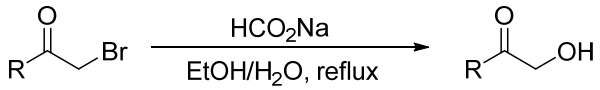
General Information

All reactions were performed under an Argon atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure using a rotary evaporator or oil pump. Reactions were monitored through thin-layer chromatography (TLC) on silica gel–precoated glass plates. Visualization on TLC was achieved by use of UV light (254 nm), iodine or basic $KMnO_4$ indicator. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker 300 MHz or 400 MHz NMR instrument (referenced internally to Me_4Si). Chemical shifts (δ, ppm) are relative to tetramethylsilane (TMS) with the resonance of the non-deuterated solvent or TMS as the internal standard. ^1H NMR data are reported as follows: chemical shift, multiplicity (s =singlet; d = doublet; t = triplet; q = quartet; p = pentet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. HRMS analyses were carried out on a Thermo Q-Exactive high resolution mass spectrometer (Thermo Scientific, Waltham, MA, USA) apparatus. Data were analyzed using instrument-supplied software Xcalibur Qual Browser. HPLC analysis was performed on Agilent 1100 or 1220 series, UV detection monitored at 254 or 225 nm, using a DAICEL CHIRALPAK IE, and IA column with hexane and *i*-PrOH as solvents. X-ray crystallographic data were collected using a Bruker SMART CCD-based diffractometer equipped with a low-temperature apparatus operated at 173.15 K.

General Procedure for Preparation of Substituted VECs[1]

VECs were prepared from ketols, which were prepared using Method A, or Method B

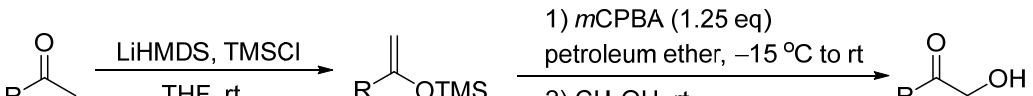
Method A



S1 **S2**

A solution of α-bromo ketone **S1** (10.0 mmol) and 5.0 g (73.5 mmol) of sodium formate in 50 mL 85% ethanol was heated to reflux for 12 h. After the reaction was completed, the mixture was cooled to ambient temperature, and ethanol was removed in vacuo, diluted with water (20 mL), aqueous layer was extracted with ethyl acetate (3 × 40 mL), and the combined organic phases were dried over Na_2SO_4, filtered and concentrated. The ketols **S2** were used without further purification.

Method B



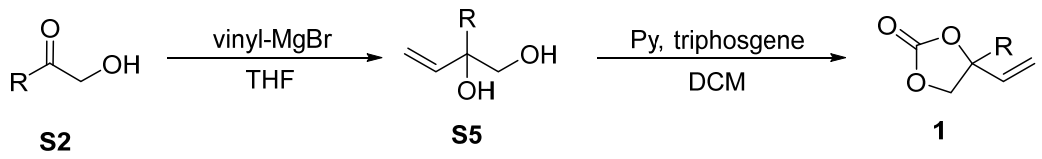
S3 **S4** **S2**

To a stirred solution of aromatic ketone **S3** (20 mmol) in THF (80 mL), LiHMDS (25 mmol, 1M in THF) was added dropwise over a period of 15 min at room temperature. After 20 min, the mixture was quenched with chlorotrimethylsilane (22 mmol). and was stirred for another 2h. The solvent was removed and the mixture was diluted with petroleum ether. The resulting precipitate was filtered through the Celite (washing with petroleum ether), and the filtrate was concentrated in vacuo to afford the crude enol silyl ether **S4**.

To a slurry of *m*CPBA (2.15 g, 12.5 mmol) in petroleum ether (20 mL) was added a solution of the crude product in petroleum ether (10 mL) at –15 °C under Ar atmosphere. The reaction mixture was stirred for over 2 h at room temperature and filtered through a glass filter. The filtrate was evaporated and methanol was added to the reaction mixture. With additional 2 h stirring at room temperature, the solvent was evaporated. The ketols **S2** was used without further purification.

[1] (a) A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing and Y. J. Zhang, *Angew. Chem. Int. Ed.*, 2014, **53**, 6439; (b) S. Singha, T. Patra, C. G. Daniliuc and F. Glorius, *J. Am. Chem. Soc.*, 2018, **140**, 3551.

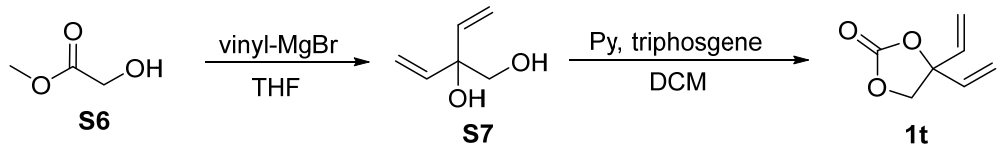
VECs were prepared from ketol



S2 **S5** **1**

To a solution of **S2** (1 equiv.) in THF (20 mL) was added vinylmagnesium bromide (1.0 M in THF, 2.5 equiv.) at 0 °C. The reaction was stirred under Ar atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica to afford corresponding diols **S5**. To a solution of diol **S5** (1 equiv.) and pyridine (4 equiv.) in CH_2Cl_2 (20 mL) was added triphosgene (0.5 equiv., 1.0 M in CH_2Cl_2) at 0 °C. The reaction was stirred under Ar atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl, and extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica to afford corresponding VECs **1**.

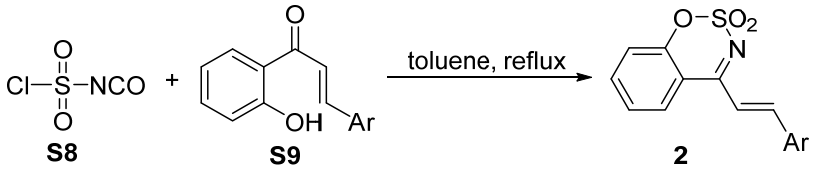
VEC 1t was prepared from 2-hydroxyacetate



S6 **S7** **1t**

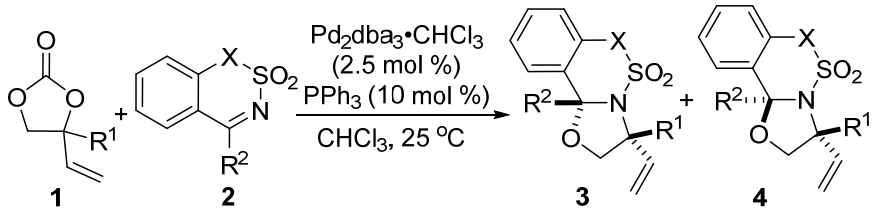
To a solution of **S6** (1 equiv.) in THF (20 mL) was added vinylmagnesium bromide (1.0 M in THF, 5.0 equiv.) at 0 °C. The reaction was stirred under Ar atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica to afford corresponding diols **S7**. To a solution of diol **S7** (1 equiv.) and pyridine (4 equiv.) in CH_2Cl_2 (20 mL) was added triphosgene (0.5 equiv., 1.0 M in CH_2Cl_2) at 0 °C. The reaction was stirred under Ar atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica to afford vinyl VEC **1t**.

General Procedure for Preparation of Substituted Ketimines[2]



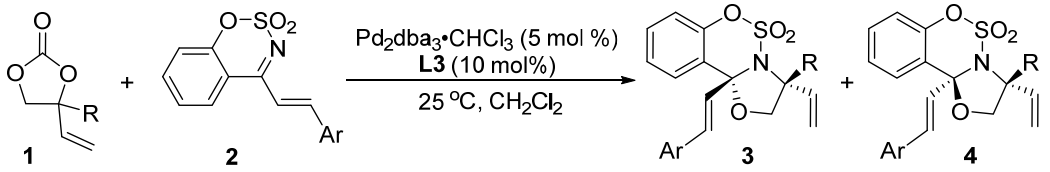
Chlorosulphonyl isocyanate **S8** (2.83g, 20mmol) in toluene (20 ml) was added over a period of 20 minutes to a stirred solution of 2'-hydroxychalcone **S9** (20mmol) in toluene (20 ml) at 100 ^{o}C. Stirring was continued for 3 hours at this temperature. The toluene was distilled off in vacuo and the residue was added to cold water (50 ml). The solid thus obtained was filtered, washed with water and recrystallized from ethanol to yield the desired ketimines **2**.

General Procedure for Nonasymmetric Annulation Reaction of VECs 1 with Ketimines 2



An oven-dried 10 mL of Schlenk tube was charged with VECs **1** (0.15 mmol), ketimines **2** (0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.025 equiv, 2.6 mg), PPh_3 (0.10 equiv, 2.6 mg) in 1 mL of $CHCl_3$ under Ar atmosphere at 25 °C. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography to afford the product **3**/**4**.

General Procedure for Asymmetric Annulation Reaction of VECs 1 with Ketimines 2

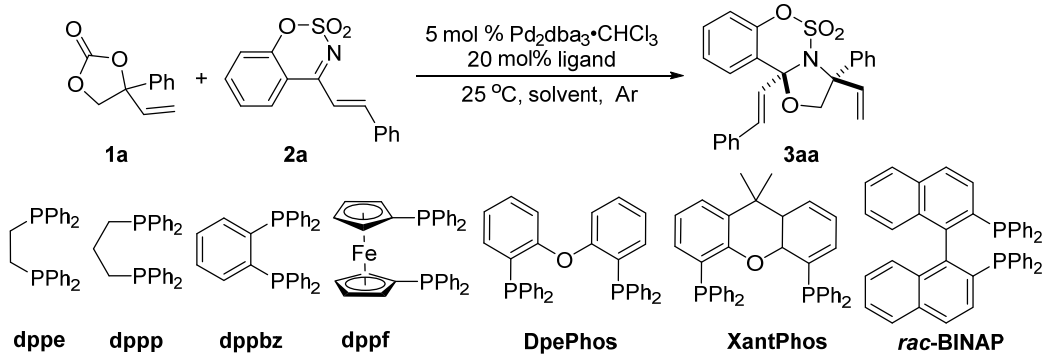


An oven-dried 10 mL of Schlenk tube was charged with VECs **1** (0.075 mmol), ketimines **2** (0.05 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.05 equiv, 2.6 mg), **L3** (0.10 equiv, 3.3 mg) in 1 mL of $CHCl_3$ under Ar atmosphere at 25 °C. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography to afford the product **3**/**4**.

[2] M. Tripathi and D. N. Dhar, *J. Heterocycl. Chem.*, 1988, **25**, 1191.

Optimization of Reaction Conditions for Nonasymmetric Annulation of VEC 1a with Ketimine 2a

Table S1. Optimization of Reaction Conditions for Nonasymmetric Annulation of VEC **1a** with Ketimine **2a**

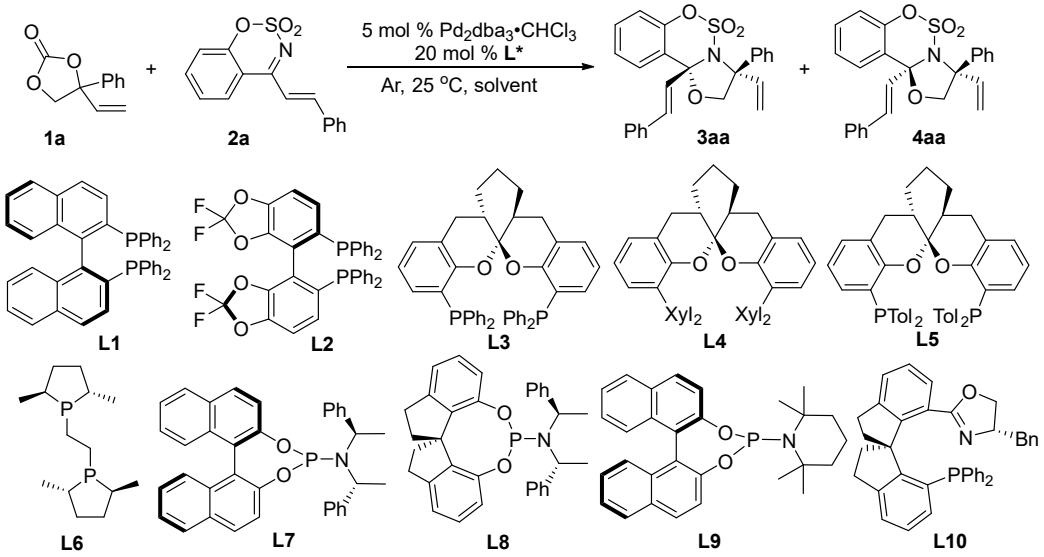


entry	ligand	solvent	time (h)	yield (%)[b]	dr[c]
1	\	CH_2Cl_2	48	NR[d]	\
2	dppe	CH_2Cl_2	23	NR	\
3	dppp	CH_2Cl_2	48	trace	ND[c]
4	PPh_3	CH_2Cl_2	23	96	80:20
5	dppf	CH_2Cl_2	72	CC[d]	\
6	dppbz	CH_2Cl_2	48	trace	ND
7	*rac*-Binap	CH_2Cl_2	48	trace	ND
8	DpePhos	CH_2Cl_2	23	NR	\
9	XantPhos	CH_2Cl_2	7.5	44	ND
10	(*o*-tol)$_3$P	CH_2Cl_2	48	trace	ND
11	(*p*-tol)$_3$P	CH_2Cl_2	20	79	90:10
12	(*m*-tol)$_3$P	CH_2Cl_2	20	77	85:15
13	PPh_3	DCE	20	89	88:12
14	PPh_3	$CHCl_3$	20	99	86:14
15	PPh_3	toluene	20	90	85:15
16	PPh_3	$PhCF_3$	20	80	86:14
17	PPh_3	THF	5	87	88:12
18	PPh_3	1,4-dioxane	20	86	85:15
19	PPh_3	CH_3CN	20	22	ND
20	PPh_3	CH_3OH	20	NR	\
21[e]	PPh_3	THF	48	50	ND
22[e]	PPh_3	$CHCl_3$	20	99	80:20

[a]Unless noted otherwise, the reaction of **1a** (0.15 mmol), **2a** (0.10 mmol), Pd_2dba_3•$CHCl_3$ (5 mol%) and ligand (10 mol% for diphosphines, 20 mol% for phosphoramidites) was performed at 25 °C in 1 mL of solvent under indicated reaction conditions. [b]Isolated yield. [c]dr is determined by ^{1}H NMR analysis of the product. [d] NR: no reaction; ND: no detection; CC: complex compounds. [e]The reaction was carried out with 2.5 mol% Pd and 10 mol % of ligand.

Optimization of Reaction Conditions for Asymmetric Annulation of VEC 1a with Ketimine 2a

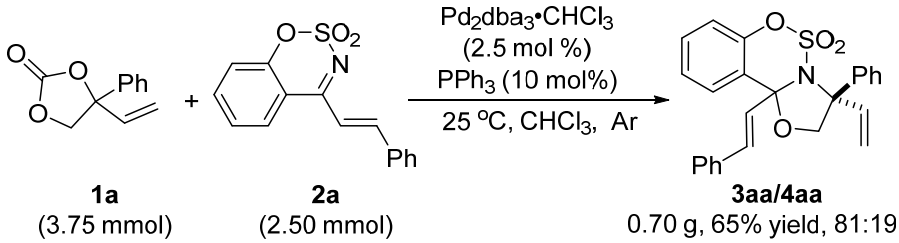
Table S2. Optimization of Reaction Conditions for Asymmetric Annulation of VEC **1a** with Ketimine **2a**



entry	ligand	temp.	solvent	time/h	yield (%)[b]	dr[c]	ee (%)[d]
1	**L1**	25	CH_2Cl_2	48	NR[e]	-	-
2	**L2**	25	CH_2Cl_2	48	NR	-	-
3	**L3**	25	CH_2Cl_2	12	79	78:22	98/96
4	**L4**	25	CH_2Cl_2	48	49	71:29	90/96
5	**L5**	25	CH_2Cl_2	9	63	72:28	99/99
6	**L6**	25	CH_2Cl_2	48	NR	-	-
7	**L7**	25	CH_2Cl_2	72	trace	-	-
8	**L8**	25	CH_2Cl_2	48	trace	-	-
9	**L9**	25	CH_2Cl_2	48	NR	-	-
10	**L10**	25	CH_2Cl_2	48	NR	-	-
11	**L3**	25	DCE	40	55	66:34	99/98
12	**L3**	25	$CHCl_3$	48	59	54:46	99/99
13	**L3**	25	THF	48	36	55:45	95/99
14	**L3**	25	toluene	15	41	52:48	98/96
15	**L3**	40	CH_2Cl_2	12	75	69:31	98/96
16	**L3**	0	CH_2Cl_2	72	trace	-	-

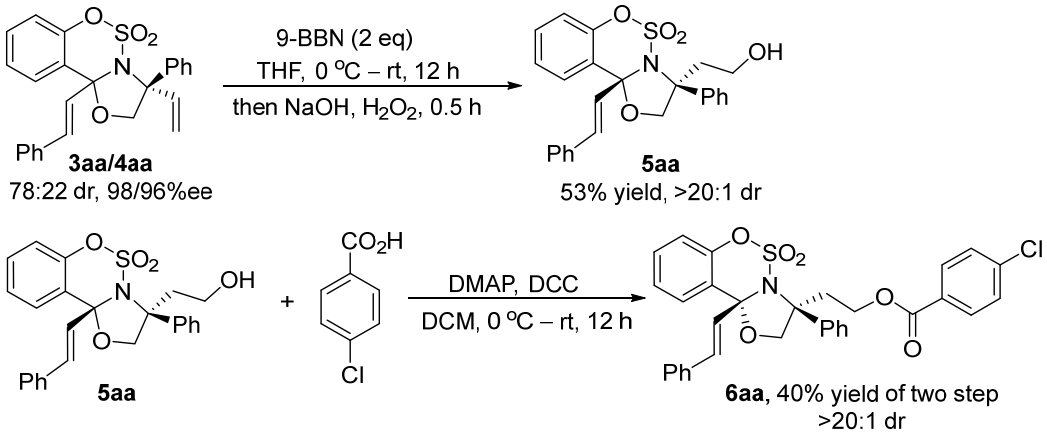
[a]Unless noted otherwise, the reaction of **1a** (0.075 mmol), **2a** (0.050 mmol), Pd_2dba_3•$CHCl_3$ (5 mol%) and ligand (10 mol% for diphosphines, 20 mol% for phosphoramidites) was performed in 1 mL of solvent under indicated reaction conditions. [b]Isolated yield. [c]dr is determined by ^1H NMR analysis of the product. [d]Determined by chiral HPLC analysis. [e]NR: no reaction.

The Scaled-up Annulation Reaction



An oven-dried 100 mL of Schlenk tube was charged with VEC **1a** (0.71 g 3.75 mmol), ketimines **2a** (0.72 g, 2.5 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.025 equiv, 0.0647 g, 0.0625 mmol), PPh_3 (0.10 equiv, 0.0655 g, 0.25 mmol) in 20 mL of $CHCl_3$ for 48 h under Ar atmosphere at 25 °C. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column to afford the product **3aa/4aa** (0.70 g, 65% yield, 81:19 dr).

Further Transformation of the Product

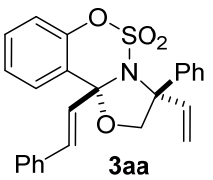


To 3 mL of 9-BBN (0.5 M in THF) solution at 0 °C under Ar atmosphere, a solution of the cycloaddition product **3aa/4aa** (0.2 M in THF, 0.1 mmol, 43.1 mg) was added dropwise. The resulting mixture was stirred at room temperature for 48 h and quenched with 2.0 mL of 2 N aqueous NaOH solution and 0.60 mL of 30% aqueous H_2O_2 solution. After stirring for 30 min, the aqueous layer was extracted with 5 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by flash column on silica gel to afford a colorless oil **5aa**.

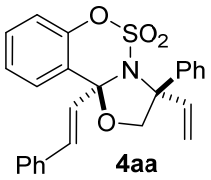
To a solution of 4-chlorobenzoic acid (1.5 equiv.), DMAP (0.2 equiv.) and DCC (1.5 eq) in CH_2Cl_2 (0.5 mL) was added **5aa** (1.0 equiv., 1.0 M in CH_2Cl_2) at 0 °C. The reaction was stirred at room temperature for 12 h. The mixture was concentrated to dryness. The residue was purified by flash chromatography on silica to afford oxazolidine benzoate ester **6aa**.

Characterization Data of All Products

3-phenyl-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]-oxa-thiazine 5,5-dioxide (3aa/4aa)



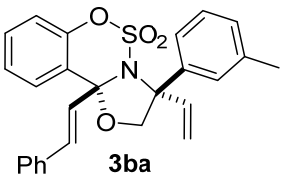
3aa



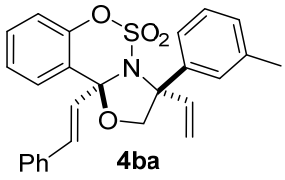
4aa

Yellow solid (42.7 mg, 99% yield); **3aa**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.27 (m, 13H), 7.08 – 7.05 (m, 1H), 6.95 (d, *J* = 16.0 Hz, 1H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.52 (ddd, *J* = 17.6, 10.9, 1.1 Hz, 1H), 5.48 (d, *J* = 10.9 Hz, 1H), 5.42 (d, *J* = 17.6 Hz, 1H), 4.48 (d, *J* = 9.2 Hz, 1H), 4.10 (dd, *J* = 9.2, 1.1 Hz, 1H); **3aa** + **4aa**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.6, 148.9, 143.0, 138.5, 135.2, 134.3, 130.5, 130.2, 129.7, 128.7, 128.4, 128.3, 128.26, 128.22, 128.1, 127.8, 126.9, 126.5, 126.2, 125.2, 122.6, 119.1, 118.1, 98.8, 74.0; IR (film) ν_{max} 550, 576, 630, 699, 750, 760,788, 859, 969, 1012, 1030, 1061, 1112, 1177, 1206, 1280, 1404, 1449, 1485 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{22}NO_4S^+$ $[M+H]^+$ 432.1270, found 432.1261.

10b-((*E*)-styryl)-3-(m-tolyl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxa-thiazine 5,5-dioxide (3ba/4ba)



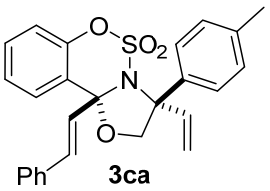
3ba



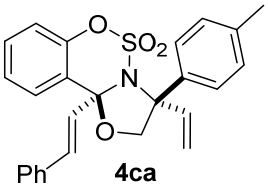
4ba

Yellow solid (43.1 mg, 97% yield); **3ba**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.02 (m, 13H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.52 (ddd, *J* = 17.6, 10.9, 1.1 Hz, 1H), 5.48 (d, *J* = 11.0 Hz, 1H), 5.42 (d, *J* = 17.5 Hz, 1H), 4.48 (d, *J* = 9.1 Hz, 1H), 4.10 (dd, *J* = 9.1, 1.2 Hz, 1H), 2.38 (s, 3H); **4ba**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.02 (m, 13H), 7.00 (d, *J* = 16.0 Hz, 1H), 6.72 (d, *J* = 15.9 Hz, 1H), 6.40 (dd, *J* = 17.2, 10.9 Hz, 1H), 5.68 – 5.51 (m, 2H), 4.58 (d, *J* = 8.7 Hz, 1H), 4.32 (d, *J* = 8.7 Hz, 1H) , 2.07 (s, 3H); **3ba** + **4ba**: ^{13}C NMR (75 MHz, CDCl3) δ 148.9, 137.9, 134.4, 130.4, 129.7, 128.6, 128.4, 128.20, 128.18, 126.9, 126.7, 126.6, 125.2, 123.2, 118.9, 118.1, 98.8, 76.1, 73.9; IR (film) ν_{max} 443, 550, 561, 575, 629, 691, 703, 736, 788, 858, 1017, 1175, 1208, 1260, 1402, 1450, 1633, 2921, 2961 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{24}NO_4S^+$ $[M+H]^+$ 446.1426, found 446.1418.

10b-((*E*)-styryl)-3-(p-tolyl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ca/4ca)



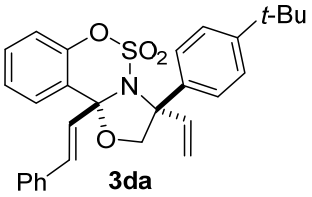
3ca



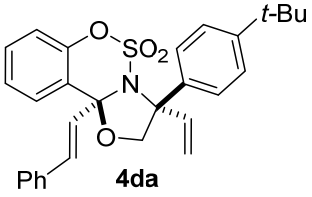
4ca

Semisolid (36.9 mg, 83% yield); **3ca**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.02 (m, 13H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.52 (ddd, *J* = 17.6, 10.9, 1.0 Hz, 1H), 5.47 (d, *J* = 10.9 Hz, 1H), 5.42 (d, *J* = 17.5 Hz, 1H), 4.48 (d, *J* = 9.1 Hz, 1H), 4.09 (dd, *J* = 9.1, 1.2 Hz, 1H), 2.36 (s, 3H); **4ca**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.02 (m, 13H), 7.01 (d, *J* = 16.0 Hz, 1H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.38 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.67 – 5.50 (m, 2H), 4.57 (d, *J* = 8.7 Hz, 1H), 4.30 (d, *J* = 8.7 Hz, 1H), 2.33 (s, 3H); **3ca** + **4ca**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 137.5, 134.4, 130.4, 129.6, 129.0, 128.4, 128.2, 126.9, 126.1, 125.2, 122.7, 118.9, 118.1, 98.7, 76.1, 73.9; IR (film) ν_{max} 549, 629, 660, 692, 736, 748, 787, 859, 968, 1013, 1059, 1176, 1206, 1261, 1402, 1450, 1483, 1652, 2920 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{24}NO_4S^+$ $[M+H]^+$ 446.1426, found 446.1417.

3-(4-(tert-butyl)phenyl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3da/4da)



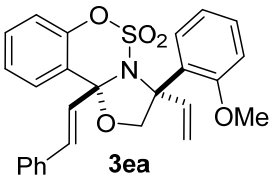
3da



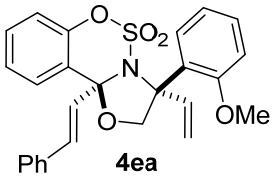
4da

Yellow solid (48.2 mg, 99% yield); **3da**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.04 (m, 13H), 6.99 (d, *J* = 16.0 Hz, 1H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.60 – 6.49 (m, 1H), 5.53 – 5.41 (m, 2H), 4.50 (d, *J* = 9.2 Hz, 1H), 4.12 (dd, *J* = 9.2, 1.1 Hz, 1H), 1.35 (s, 9H); **4da**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.04 (m, 13H), 7.02 (d, *J* = 15.9 Hz, 1H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.42 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.68 – 5.56 (m, 2H), 4.60 (d, *J* = 8.7 Hz, 1H), 4.32 (d, *J* = 8.7 Hz, 1H), 1.32 (s, 9H); **3da** + **4da**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 148.9, 134.5, 130.4, 129.6, 128.4, 126.9, 125.8, 125.2, 124.4, 122.7, 118.9, 118.1, 98.8, 76.2, 73.9, 31.0; IR (film) ν_{max} 441, 574, 630, 693, 750, 788, 861, 1061, 1112, 1179, 1209, 1262, 1406, 1450, 1507, 1653, 2159, 2360, 2961 cm^{-1}; HRMS (ESI) calculated for $C_{29}H_{29}NNaO_4S^+$ $[M+Na]^+$ 510.1715, found 510.1708.

3-(2-methoxyphenyl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ea/4ea)



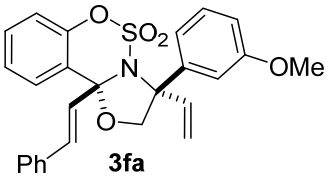
3ea



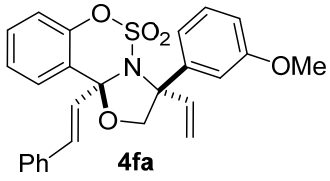
4ea

Yellow solid (26.4 mg, 57% yield); **3ea**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.24 (m, 13H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.39 – 5.09 (m, 2H), 4.62 (d, *J* = 9.2 Hz, 1H), 4.38 (d, *J* = 9.2 Hz, 1H), 3.77 (s, 3H); **4ea**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.12 (m, 13H) 6.93 (d, *J* = 11.4 Hz, 1H), 6.73 (d, *J* = 16.1 Hz, 1H), 6.38 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.69 – 5.53 (m, 2H), 4.59 (d, *J* = 8.7 Hz, 1H), 4.33 (d, *J* = 8.7 Hz, 1H), 3.89 (s, 3H); **3ea** + **4ea**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 149.4, 135.2, 134.9, 130.5, 129.1, 128.5, 128.34, 128.28, 128.1, 126.8, 126.7, 125.2, 122.9, 120.5, 118.2, 117.6, 111.1, 98.8, 75.6, 73.6, 54.9; IR (film) ν_{max} 544, 609, 627, 657, 693, 750, 790, 859, 968, 1025, 1064, 1113, 1177, 1204, 1245, 1401, 1450, 1487, 1583 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{24}NO_5S^+$ $[M+H]^+$ 462.1375, found 462.1365.

3-(3-methoxyphenyl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3fa/4fa)



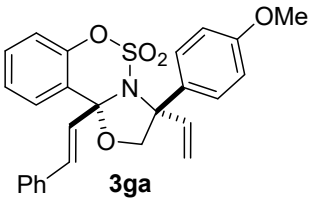
3fa



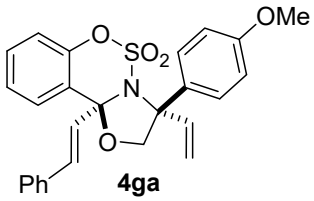
4fa

Yellow oil (42.6 mg, 92% yield); **3fa**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.01 (m, 13H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.52 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.50 – 5.39 (m, 2H), 4.48 (d, *J* = 9.2 Hz, 1H), 4.11 (d, *J* = 9.2 Hz, 1H), 3.80 (s, 3H); **4fa**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.01 (m, 13H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.72 (d, *J* = 15.9 Hz, 1H), 6.41 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.67 – 5.54 (m, 2H), 4.58 (d, *J* = 8.7 Hz, 1H), 4.32 (d, *J* = 8.7 Hz, 1H), 3.52 (s, 3H); **3fa** + **4fa**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 140.3, 134.2, 130.5, 129.7, 129.3, 128.37, 128.35, 128.2, 126.9, 126.5, 125.2, 122.6, 119.1, 118.4, 118.1, 112.8, 112.5, 98.8, 76.1, 73.8, 54.9; IR (film) ν_{max} 404, 421, 450, 692, 750, 796, 860, 1017, 1175, 1260, 1402, 1449, 1653, 2342, 2360, 2923, 2962 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{24}NO_5S^+$ $[M+H]^+$ 462.1375, found 462.1368.

3-(4-methoxyphenyl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ga/4ga)



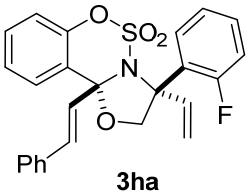
3ga



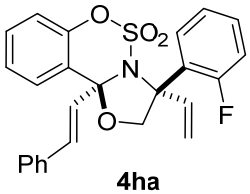
4ga

Yellow oil (39.0 mg, 86% yield); **3ga**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.01 (m, 13H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.51 (ddd, *J* = 17.6, 10.9, 1.1 Hz, 1H), 5.47 (d, *J* = 10.9 Hz, 1H), 5.41 (d, *J* = 17.5 Hz, 1H), 4.46 (d, *J* = 9.2 Hz, 1H), 4.09 (dd, *J* = 9.2, 1.1 Hz, 1H), 3.81 (s, 3H); **4ga**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.01 (m, 13H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.70 (d, *J* = 15.9 Hz, 1H), 6.36 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.65 – 5.49 (m, 2H), 4.56 (d, *J* = 8.7 Hz, 1H), 4.28 (d, *J* = 8.7 Hz, 1H), 3.79 (s, 3H); **3ga** + **4ga**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 148.9, 135.2, 134.4, 130.42, 130.38, 129.7, 129.6, 128.4, 128.2, 127.4, 126.9, 126.6, 125.2, 118.9, 118.1, 113.6, 112.8, 98.7, 76.1, 73.7, 55.0; IR (film) ν_{max} 421, 550, 629, 691, 749, 788, 1029, 1110, 1175, 1205, 1259, 1401, 1450, 1511, 1633, 2360, 2850, 2920 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{24}NO_5S^+$ $[M+H]^+$ 462.1375, found 462.1367.

3-(2-fluorophenyl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]-oxathiazine 5,5-dioxide (3ha/4ha)



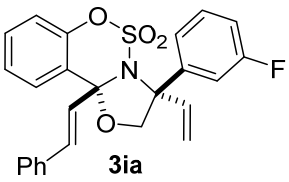
3ha



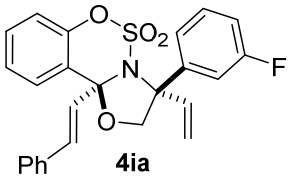
4ha

Yellow solid (36.7 mg, 82% yield); **3ha**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.04 (m, 13H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.28 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.47 (d, *J* = 10.6 Hz, 1H), 5.21 (dd, *J* = 17.3, 1.4 Hz, 1H), 4.53 (dd, *J* = 9.2, 2.3 Hz, 1H), 4.35 (d, *J* = 9.2 Hz, 1H); **3ha** + **4ha**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 135.1, 133.4, 130.8, 130.7, 128.4, 128.3, 126.9, 126.3, 125.4, 124.63, 124.59, 124.09, 124.05, 122.6, 118.2, 115.84, 115.78, 115.57, 115.48, 99.1, 75.5, 72.6, 72.54, 72.50; IR (film) ν_{max} 497, 554, 609, 627, 657, 692, 736, 758, 791, 858, 1016, 1063, 1176, 1208, 1260, 1404, 1450, 1487, 1581, 2920 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{21}FNO_4S^+$ $[M+H]^+$ 450.1175, found 450.1172.

3-(3-fluorophenyl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ia/4ia)



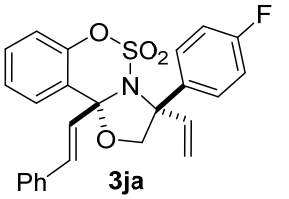
3ia



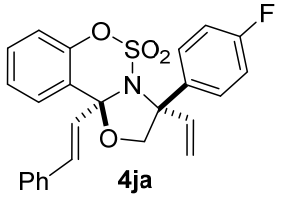
4ia

Yellow solid (42.1 mg, 94% yield); **3ia**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.03 (m, 13H), 6.99 (d, *J* = 16.1 Hz, 1H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.52 (ddd, *J* = 17.6, 10.9, 1.0 Hz, 1H), 5.56 – 5.41 (m, 2H), 4.51 (d, *J* = 9.2 Hz, 1H), 4.11 (dd, *J* = 9.2, 1.1 Hz, 1H); **4ia**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.03 (m, 13H), 6.99 (d, *J* = 16.1 Hz, 1H), 6.72 (d, *J* = 15.9 Hz, 1H), 6.39 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.69 – 5.57 (m, 2H), 4.58 (d, *J* = 8.9 Hz, 1H), 4.34 (d, *J* = 8.8 Hz, 1H); **3ia** + **4ia**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 160.9, 148.8, 135.1, 133.7, 130.6, 129.8, 128.4, 127.0, 126.3, 125.3, 122.5, 121.9, 121.85, 121.81, 119.6, 118.1, 114.9, 114.7, 113.7, 113.4, 99.0, 75.9, 73.4; IR (film) ν_{max} 551, 631, 694, 737, 788, 859, 967, 1021, 1060, 1175, 1207, 1261, 1403, 1449, 1485, 1590, 2920 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{21}FNO_4S^+$ $[M+H]^+$ 450.1175, found 450.1175.

3-(4-fluorophenyl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ja/4ja)



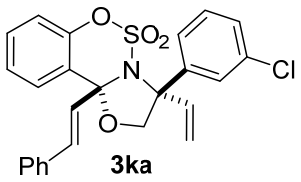
3ja



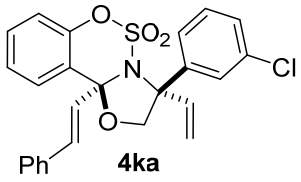
4ja

Yellow solid (29.4 mg, 65% yield); **3ja**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.04 (m, 13H), 6.98 (d, *J* = 16.0 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.52 (ddd, *J* = 17.6, 10.9, 1.1 Hz, 1H), 5.54 – 5.39 (m, 2H), 4.49 (d, *J* = 9.2 Hz, 1H), 4.09 (dd, *J* = 9.2, 1.1 Hz, 1H); **4ja**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.04 (m, 13H), 6.96 (d, *J* = 15.9 Hz, 1H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.37 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.66 – 5.56 (m, 2H), 4.59 (d, *J* = 8.8 Hz, 1H), 4.32 (d, *J* = 8.8 Hz, 1H); **3ja** + **4ja**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 160.5, 148.8, 142.9, 135.1, 134.0, 130.5, 130.2, 129.7, 129.3, 128.6, 128.5, 128.4, 128.3, 128.10, 128.06, 128.01, 127.99, 127.95, 126.9, 126.4, 125.3, 125.1, 122.6, 119.3, 118.1, 115.3, 115.0, 98.9, 76.0, 73.5; IR (film) ν_{max} 408, 420, 429, 454, 550, 630, 693, 749, 789, 860, 1061, 1177, 1206, 1261, 1405, 1450, 1508, 1653, 2362, 2920 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{21}FNO_4S^+$ $[M+H]^+$ 450.1175, found 450.1173.

3-(3-chlorophenyl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ka/4ka)



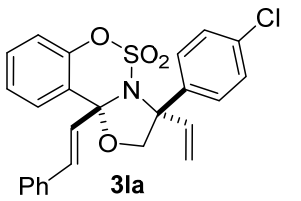
3ka



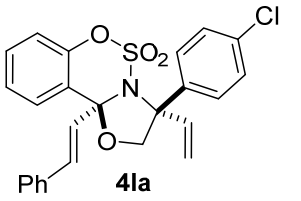
4ka

Yellow solid (36.8 mg, 79% yield); **3ka**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.02 (m, 13H), 6.96 (d, *J* = 16.0 Hz, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.48 (ddd, *J* = 17.5, 10.9, 1.0 Hz, 1H), 5.54 – 5.38 (m, 2H), 4.48 (d, *J* = 9.2 Hz, 1H), 4.07 (dd, *J* = 9.2, 1.1 Hz, 1H); **4ka**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.02 (m, 13H), 7.00 (d, *J* = 15.9 Hz, 1H), 6.69 (d, *J* = 15.9 Hz, 1H), 6.36 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.66 – 5.53 (m, 2H), 4.55 (d, *J* = 8.8 Hz, 1H), 4.13 (d, *J* = 7.2 Hz, 1H); **3ka** + **4ka**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 140.7, 135.1, 134.2, 133.7, 130.6, 129.9, 129.6, 128.4, 128.39, 128.36, 128.30, 128.1, 127.0, 126.5, 126.2, 125.3, 124.4, 122.5, 119.7, 118.1, 99.0, 75.9, 73.4; IR (film) ν_{max} 410, 420, 450, 552, 629, 693, 750, 790, 859, 1060, 1176, 1204, 1261, 1276, 1403, 1450, 1653, 2341, 2361, 2923 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{21}ClNO_4S^+$ $[M+H]^+$ 466.0880, found 466.0872.

3-(4-chlorophenyl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3la/4la)



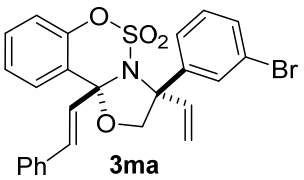
3la



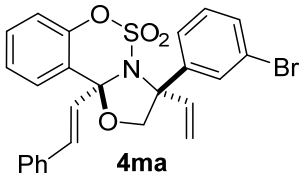
4la

Yellow solid (25.9 mg, 56% yield); **3la**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.03 (m, 13H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.70 (d, *J* = 15.9 Hz, 1H), 6.48 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.52 – 5.36 (m, 2H), 4.46 (d, *J* = 9.2 Hz, 1H), 4.06 (d, *J* = 9.2 Hz, 1H); **4la**:^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.03 (m, 13H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.34 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.64 – 5.54 (m, 2H), 4.54 (d, *J* = 8.8 Hz, 1H), 4.30 (d, *J* = 8.9 Hz, 1H); **3la** + **4la**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 161.1, 148.9, 138.4, 137.5 134.2, 130.6, 130.5, 129.9, 129.8, 128.8, 128.7, 128.45, 128.39, 128.36, 128.30, 128.2, 128.1, 128.0, 127.8, 127.6, 126.1, 125.3, 125.2, 122.8, 122.4, 119.2, 118.1, 115.2, 114.9, 113.6, 113.3, 98.6, 78.0, 76.1, 74.0, 73.5; IR (film) ν_{max} 533, 549, 628, 691, 736, 788, 859, 1011, 1060, 1094, 1175, 1206, 1261, 1404, 1450, 1633, 2850, 2920 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{21}ClNO_4S^+$ $[M+H]^+$ 466.0880, found 466.0872.

3-(3-bromophenyl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ma/4ma)



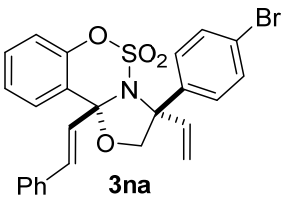
3ma



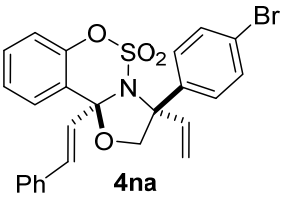
4ma

Yellow solid (41.9 mg, 82% yield); **3ma**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.24 (m, 13H), 6.98 (d, *J* = 16.0 Hz, 1H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.50 (ddd, *J* = 17.6, 10.9, 1.1 Hz, 1H), 5.55 – 5.40 (m, 2H), 4.49 (d, *J* = 9.2 Hz, 1H), 4.09 (dd, *J* = 9.2, 1.1 Hz, 1H); **4ma**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.24 (m, 13H) 7.02 (d, *J* = 16.1 Hz, 1H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.43 – 6.32 (m, 1H), 5.68 – 5.55 (m, 2H), 4.57 (d, *J* = 8.8 Hz, 1H), 4.33 (d, *J* = 8.8 Hz, 1H); **3ma** + **4ma**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 141.0, 133.6, 131.0, 130.6, 129.94, 129.91, 129.4, 128.40, 128.36, 128.30, 127.0, 126.2, 125.4, 124.9, 122.4, 119.7, 118.1, 99.0, 75.9, 73.3; IR (film) ν_{max} 561, 629, 694, 738, 789, 859, 967, 1061, 1176, 1205, 1262, 1404, 1450, 1472, 1633, 2850, 2920 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{24}BrN_2O_4S^+$ $[M+H]^+$ 527.0640, found 527.0634.

3-(4-bromophenyl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3na/4na)



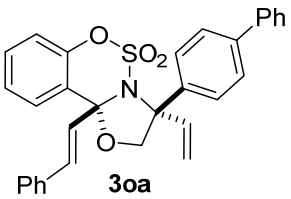
3na



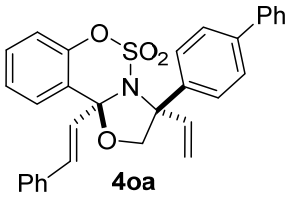
4na

Yellow solid (44.3 mg, 87% yield); **3na**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.00 (m, 13H), 6.95 (d, *J* = 15.8 Hz, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 6.54 – 6.41 (m, 1H), 5.53 – 5.35 (m, 2H), 4.46 (d, *J* = 9.2 Hz, 1H), 4.06 (dd, *J* = 9.2, 1.1 Hz, 1H); **4na**: ^{1}H NMR (300 MHz, $CDCl_3$) δ.69 – 7.00 (m, 13H), 7.00 (d, *J* = 15.9 Hz, 1H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.33 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.65 – 5.54 (m, 2H), 4.54 (d, *J* = 8.8 Hz, 1H), 4.30 (d, *J* = 8.8 Hz, 1H); **3na** + **4na**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 137.7, 135.0, 133.8, 131.4, 130.6, 129.8, 128.40, 128.37, 128.31, 128.0, 126.9, 126.3, 125.3, 122.5, 122.0, 119.6, 118.1, 98.9, 75.9, 73.5; IR (film) ν_{max} 528, 549, 628, 658, 691, 748, 790, 859, 1008, 1174, 1205, 1260, 1403, 1450, 1485, 1581, 2921, 2961 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{21}BrNO_4S^+$ $[M+H]^+$ 510.0375, found 510.0366.

3-([1,1'-biphenyl]-4-yl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3oa/4oa)



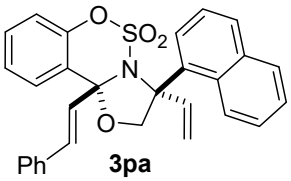
3oa



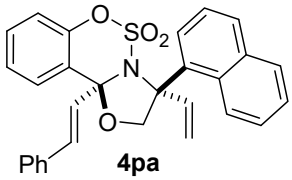
4oa

Yellow solid (33.7 mg, 66% yield); **3oa**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.06 (m, 18H), 7.01 (d, *J* = 15.9 Hz, 1H), 6.79 (d, *J* = 15.9 Hz, 1H), 6.58 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.57 – 5.45 (m, 2H), 4.54 (d, *J* = 9.2 Hz, 1H), 4.18 (dd, *J* = 9.2, 1.1 Hz, 1H); **4oa**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.06 (m, 18H), 7.05 (d, *J* = 16.0 Hz, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.47 – 6.39 (m, 1H), 5.72 – 5.59 (m, 2H), 4.65 (d, *J* = 8.8 Hz, 1H), 4.37 (d, *J* = 8.7 Hz, 1H); **3oa** + **4oa**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 140.7, 140.2, 137.5, 135.2, 134.3, 130.5, 129.8, 128.7, 128.49, 128.45, 128.41, 128.4, 127.01, 126.98, 126.8, 126.7, 126.5, 125.3, 122.7, 119.3, 118.1, 98.9, 76.1, 73.9; IR (film) ν_{max} 404, 410, 417, 424, 573, 630, 695, 764, 788, 860, 1061, 1177, 1208, 1261, 1405, 1450, 1486, 1653, 2359 cm^{-1}; HRMS (ESI) calculated for $C_{31}H_{25}NNaO_4S^+$ $[M+Na]^+$ 508.1402, found 508.1397.

3-(naphthalen-1-yl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3pa/4pa)



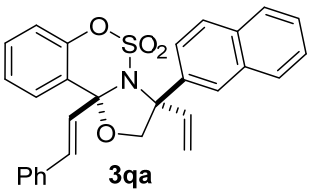
3pa



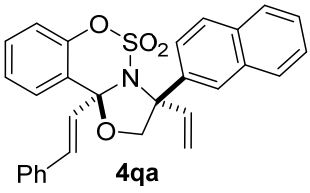
4pa

Yellow oil (14.9 mg, 31% yield); **3pa**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.04 (m, 16H), 6.78 (d, J = 16.0 Hz, 1H), 6.64 (d, J = 16.0 Hz, 1H), 6.40 (dd, J = 17.7, 10.8 Hz, 1H), 5.46 (d, J = 10.8 Hz, 1H), 5.25 (d, J = 17.6 Hz, 1H), 4.76 (d, J = 9.1 Hz, 1H), 4.37 (d, J = 9.1 Hz, 1H); **3pa** + **4pa**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 136.2, 135.2, 134.3, 130.7, 130.66, 130.61, 130.2, 129.1, 129.06, 129.01, 128.6, 128.36, 128.30, 128.2, 128.1, 126.9, 126.6, 125.6, 125.4, 125.2, 125.1, 124.9, 120.4, 118.2, 98.6, 76.1, 74.5; IR (film) ν_{max} 554, 627, 692, 791, 859, 1015, 1176, 1259, 1403, 1450, 1633, 2360, 2850, 2920, 2959, 3360 cm^{-1}; HRMS (ESI) calculated for $C_{29}H_{24}NO_4S^+$ $[M+H]^+$ 482.1426, found 482.1414.

3-(naphthalen-2-yl)-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1, 2,3]oxathiazine 5,5-dioxide (3qa/4qa)



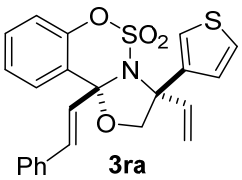
3qa



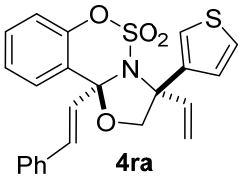
4qa

Yellow oil (44.1 mg, 92% yield); **3qa**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.25 (m, 16H), 7.02 (d, *J* = 16.1 Hz, 1H), 6.82 (d, *J* = 16.0 Hz, 1H), 6.66 (ddd, *J* = 17.6, 10.9, 1.0 Hz, 1H), 5.61 – 5.46 (m, 2H), 4.58 (d, *J* = 9.2 Hz, 1H), 4.24 (dd, *J* = 9.2, 1.1 Hz, 1H); **4qa**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.25 (m, 16H), 7.02 (d, *J* = 16.1 Hz, 1H), 6.78 (d, *J* = 16.0 Hz, 1H), 6.55 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.78 – 5.64 (m, 2H), 4.71 (d, *J* = 8.7 Hz, 1H), 4.43 (d, *J* = 8.8 Hz, 1H); **3qa** + **4qa**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 135.8, 135.2, 134.3, 132.69, 132.65, 130.5, 129.8, 128.41, 128.39, 128.26, 128.24, 127.0, 126.1, 125.7, 125.3, 123.7, 119.4, 118.1, 99.0, 75.9, 74.1; IR (film) ν_{max} 478, 549, 628, 692, 747, 789, 858, 1016, 1175, 1205, 1260, 1402, 1450, 1581, 2921, 2961 cm^{-1}; HRMS (ESI) calculated for $C_{29}H_{24}NO_4S^+$ $[M+H]^+$ 482.1426, found 482.1421.

10b-((*E*)-styryl)-3-(thiophen-3-yl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2, 3]oxathiazine 5,5-dioxide (3ra/4ra)



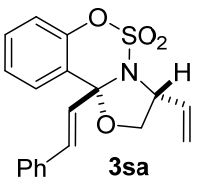
3ra



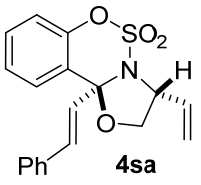
4ra

Yellow semisolid (43.2 mg, 99% yield); **3ra**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.01 (m, 12H), 6.95 (d, *J* = 16.0 Hz, 1H), 6.69 (dd, *J* = 16.0, 0.8 Hz, 1H), 6.54 – 6.43 (m, 1H), 5.48 – 5.35 (m, 2H), 4.39 (d, *J* = 9.1 Hz, 1H), 4.17 (dd, *J* = 9.1, 0.9 Hz, 1H); **4ra**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.01 (m, 11H), 7.00 (d, *J* = 15.9 Hz, 2H), 6.81 (d, *J* = 9.3 Hz, 1H), 6.51 (dd, *J* = 10.8, 0.8 Hz, 1H), 5.57 – 5.49 (m, 2H), 4.51 (d, *J* = 8.7 Hz, 1H), 4.25 (d, *J* = 8.7 Hz, 1H); **3ra** + **4ra**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 148.8, 143.0, 140.1, 138.0, 136.7, 135.2, 134.2, 130.5, 130.0, 128.4, 128.37, 128.33, 126.9, 126.6, 126.2, 126.1, 125.3, 122.9, 119.1, 118.1, 98.7, 98.4, 75.7, 71.8 70.8; IR (film) ν_{max} 406, 422, 445, 669, 691, 750, 794, 1020, 1176, 1207, 1260, 1403, 1449, 1507, 1559, 1653, 2342, 2360, 2962, 3735 cm^{-1}; HRMS (ESI) calculated for $C_{23}H_{20}NO_4S_2^+$ $[M+H]^+$ 438.0834, found 438.0826.

10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3sa/4sa)



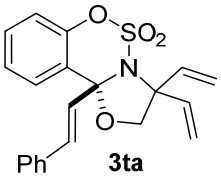
3sa



4sa

Yellow solid (35.1 mg, 99% yield); **3sa**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.22 (m, 9H), 7.08 (d, *J* = 1.2 Hz, 1H), 6.90 (d, *J* = 5.6 Hz, 1H), 6.61 (s, 1H), 5.89 (q, *J* = 10.0 Hz, 1H), 5.47 (d, *J* = 17.0 Hz, 1H), 5.34 (t, *J* = 9.9 Hz, 1H), 4.64 – 4.49 (m, 1H), 4.05 – 3.91 (m, 1H); **3sa** + **4sa**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 148.7, 135.2, 134.7, 131.9, 131.8, 130.8, 130.5, 129.7, 128.7, 128.5, 128.3, 128.2, 126.9, 126.5, 126.4, 125.5, 125.3, 121.1, 118.4, 98.8, 71.1, 69.3, 65.0, 63.0; IR (film) ν_{max} 562, 599, 631, 692, 736, 789, 855, 925, 1029, 1066, 1175, 1205, 1262, 1402, 1450, 1633, 2920 cm^{-1}; HRMS (ESI) calculated for $C_{19}H_{18}NO_4S^+$ $[M+H]^+$ 356.0957, found 356.0949.

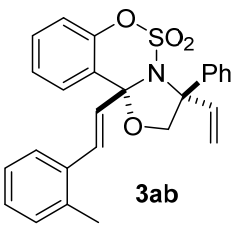
10b-styryl-3,3-divinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ta/4ta)



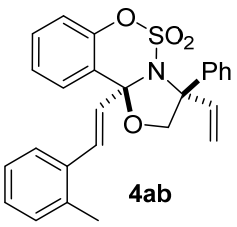
3ta

Yellow solid (33.7 mg, 88% yield); **3ta**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.03 (m, 9H), 6.93 (d, *J* = 15.9 Hz, 1H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.20 (ddd, *J* = 17.5, 13.2, 10.8 Hz, 2H), 5.46 – 5.35 (m, 4H), 4.17 (d, *J* = 8.9 Hz, 1H), 4.08 (d, *J* = 9.0 Hz, 1H); **3ta**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 135.7, 133.7, 130.5, 130.0, 128.3, 128.2, 126.9, 126.6, 125.2, 122.5, 119.0, 118.2, 117.8, 98.4, 74.2; IR (film) ν_{max} 564, 597, 630, 692, 737, 787, 857, 935, 1015, 1058, 1175, 1208, 1260, 1402, 1450, 1633, 2920 cm^{-1}; HRMS (ESI) calculated for $C_{21}H_{20}NO_4S^+$ $[M+H]^+$ 382.1113, found 382.1104.

10b-((*E*)-2-methylstyryl)-3-phenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ab/4ab)



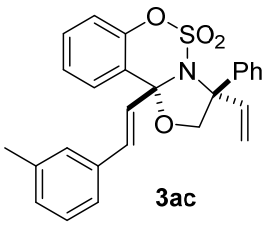
3ab



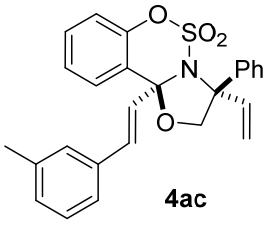
4ab

Yellow solid (36.0 mg, 81% yield); **3ab**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.19 (m, 14H), 6.61 (d, *J* = 15.8 Hz, 1H), 6.57 – 6.48 (m, 1H), 5.55 – 5.39 (m, 2H), 4.50 (d, *J* = 9.2 Hz, 1H), 4.14 (d, *J* = 10.3 Hz, 1H), 2.39 (s, 3H); **3ab** + **4ab**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 138.6, 135.9, 134.43, 134.39, 130.5, 130.1, 128.7, 128.31, 128.26, 128.07, 128.03, 128.0, 127.8, 127.7, 126.2, 125.9, 125.2, 122.7, 119.1, 118.2, 98.9, 76.0, 74.0; IR (film) ν_{max} 403, 419, 444, 669, 699, 751, 858, 1059, 1177, 1205, 1261, 1404, 1449, 1653, 2342, 2360, 2922 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{24}NO_4S^+$ $[M+H]^+$ 446.1426, found 1419.

10b-((*E*)-3-methylstyryl)-3-phenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ac/4ac)



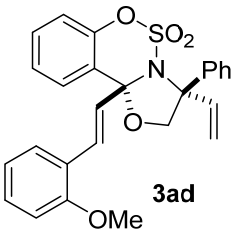
3ac



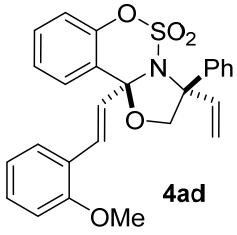
4ac

Semisolid (40.0 mg, 90% yield); **3ac**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.02 (m, 13H), 6.96 (d, *J* = 16.0 Hz, 1H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.61 – 6.53 (m, 1H), 5.54 – 5.41 (m, 2H), 4.52 (d, *J* = 9.2 Hz, 1H), 4.13 (dd, *J* = 9.2, 1.1 Hz, 1H), 2.40 (s, 3H); **3ac** + **4ac**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 138.0, 134.3, 130.4, 129.7, 129.0, 128.4, 128.28, 128.26, 127.8, 127.5, 126.2, 125.2, 124.2, 119.1, 118.1, 98.9, 76.1, 73.9; IR (film) ν_{max} 549, 630, 699, 733, 759, 858, 970, 1060, 1113, 1177, 1205, 1265, 1403, 1450 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{24}NO_4S^+$ $[M+H]^+$ 446.1426, found 446.1422.

10b-((*E*)-2-methoxystyryl)-3-phenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1, 2,3]oxathiazine 5,5-dioxide (3ad/4ad)



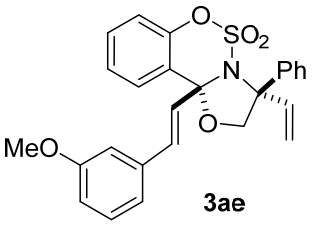
3ad



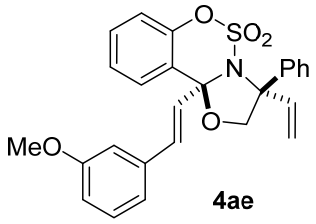
4ad

Oil (30.4 mg, 66% yield); **3ad**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 6.89 (m, 14H), 6.78 (d, *J* = 16.1 Hz, 1H), 6.56 (ddd, *J* = 17.5, 10.9, 1.1 Hz, 1H), 5.54 – 5.42 (m, 2H), 4.52 (d, *J* = 9.2 Hz, 1H), 4.13 (dd, *J* = 9.2, 1.2 Hz, 1H), 3.88 (s, 3H); **3ad** + **4ad**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 148.8, 138.5, 134.4, 130.29, 130.27, 129.3, 128.5, 128.2, 127.7, 127.2, 126.2, 125.2, 124.5, 123.0, 120.3, 118.1, 110.7, 99.1, 76.1, 74.0, 55.2; IR (film) ν_{max} 421, 450, 669, 700, 751, 854, 1025, 1177, 1260, 1403, 1457, 1489, 1559, 1653, 2342, 2361, 2922, 3735 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{24}NO_5S^+$ $[M+H]^+$ 462.1375, found 462.1363.

10b-((*E*)-3-methoxystyryl)-3-phenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1, 2,3]oxathiazine 5,5-dioxide (3ae/4ae)



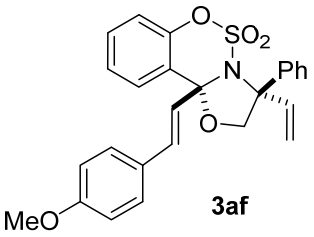
3ae



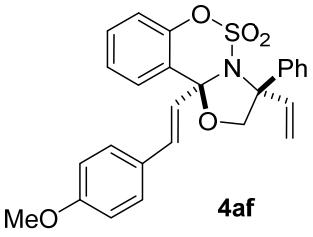
4ae

Semisolid (31.3 mg, 68% yield); **3ae**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.22 (m, 13H), 6.95 (d, *J* = 16.0 Hz, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.60 – 6.48 (m, 1H), 5.53 – 5.40 (m, 2H), 4.51 (d, *J* = 9.2 Hz, 1H), 4.12 (d, *J* = 9.2 Hz, 1H), 3.85 (s, 3H); **3ae** + **4ae**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 148.9, 142.9, 138.4, 136.6, 134.3, 130.5, 129.4, 128.4, 128.3, 126.7, 126.1, 125.2, 122.6, 119.6, 119.1, 118.1, 114.1, 112.0, 98.8, 76.1, 74.0, 55.0; IR (film) ν_{max} 550, 631, 700, 736, 759, 792, 857, 977, 1058, 1176, 1205, 1259, 1402, 1450, 1484, 1580 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{24}NO_5S^+$ $[M+H]^+$ 462.1375, found 462.1365.

10b-((*E*)-4-methoxystyryl)-3-phenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1, 2,3]oxathiazine 5,5-dioxide (3af/4af)



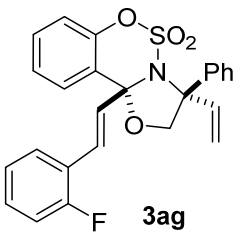
3af



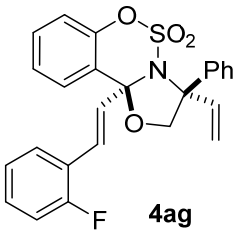
4af

Oil (36.0 mg, 78% yield); **3af**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.22 (m, 13H), 6.91 (d, *J* = 15.6 Hz, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.56 – 6.47 (m, 1H), 5.53 – 5.38 (m, 2H), 4.49 (d, *J* = 9.2 Hz, 1H), 4.12 (d, *J* = 9.2 Hz, 1H), 3.85 (s, 3H); **3af** + **4af**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 148.9, 134.4, 130.4, 129.2, 128.4, 128.2, 127.7, 126.2, 125.2, 124.3, 119.1, 118.1, 113.8, 99.0, 76.1, 73.9, 55.0; IR (film) ν_{max} 549, 627, 699, 736, 759, 800, 858, 1030, 1058, 1109, 1174, 1205, 1250, 1401, 1449, 1512, 1606, 1805 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{24}NO_5S^+$ $[M+H]^+$ 462.1375, found 462.1364.

10b-((*E*)-2-fluorostyryl)-3-phenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2, 3]oxathiazine 5,5-dioxide (3ag/4ag)



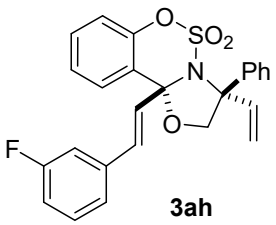
3ag



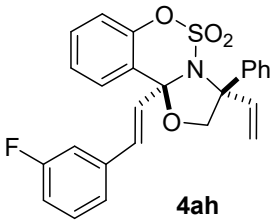
4ag

Semisolid (22.4 mg, 63% yield); **3ag**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.03 (m, 13H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.54 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.53 – 5.40 (m, 2H), 4.52 (d, *J* = 9.2 Hz, 1H), 4.12 (d, *J* = 9.2 Hz, 1H); **3ag** + **4ag**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 148.9, 138.4, 136.5, 134.3, 130.5, 128.3, 127.6, 126.1, 123.92, 123.87, 122.1, 119.1, 118.1, 115.7, 115.4, 98.7, 76.2, 74.0; IR (film) ν_{max} 550, 564, 584, 629, 700, 737, 755, 787, 856, 970, 1058, 1094, 1176, 1205, 1231, 1262, 1403, 1449, 1486, 1581 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{21}FNO_4S^+$ $[M+H]^+$ 450.1175, found 450.1169.

10b-((*E*)-3-fluorostyryl)-3-phenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ah/4ah)



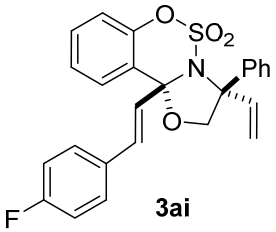
3ah



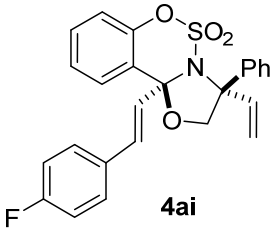
4ah

Yellow oil (31.9 mg, 71% yield); **3ah**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.24 (m, 13H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.53 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.53 – 5.38 (m, 2H), 4.50 (d, *J* = 9.2 Hz, 1H), 4.12 (d, *J* = 9.2 Hz, 1H); **3ah** + **4ah**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 134.2, 130.6, 128.3, 127.9, 127.8, 126.1, 125.3, 122.79, 122.75, 119.2, 118.1, 113.6, 113.3, 98.6, 76.1, 74.0; IR (film) ν_{max} 550, 578, 631, 699, 760, 858, 977, 1059, 1177, 1205, 1261, 1339, 1404, 1449, 1485, 1584, 1613, 1653 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{21}FNO_4S^+$ $[M+H]^+$ 450.1175, found 450.1170.

10b-((*E*)-4-fluorostyryl)-3-phenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ai/4ai)



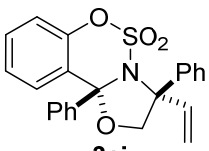
3ai



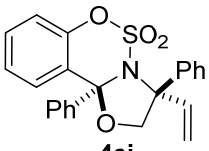
4ai

Yellow oil (25.6 mg, 57% yield); **3ai**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.24 (m, 13H), 6.94 (d, *J* = 15.8 Hz, 1H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.53 (ddd, *J* = 17.6, 11.0, 1.0 Hz, 1H), 5.53 – 5.38 (m, 2H), 4.50 (d, *J* = 9.2 Hz, 1H), 4.13 (dd, *J* = 9.2, 1.1 Hz, 1H); **3ai** + **4ai**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 160.9, 148.9, 138.5, 134.3, 130.5, 128.6, 128.5, 128.30, 128.26, 126.2, 125.3, 122.6, 119.2, 118.1, 115.5, 115.2, 98.8, 76.3, 76.1, 74.0; IR (film) ν_{max} 495, 550, 566, 626, 699, 735, 758, 784, 858, 1012, 1058, 1176, 1206, 1261, 1402, 1450, 1509, 1602 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{21}FNO_4S^+$ $[M+H]^+$ 450.1175, found 450.1167.

3,10b-diphenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3aj/4aj)



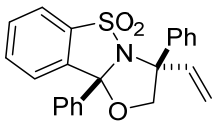
3aj



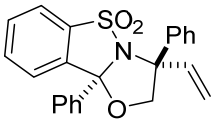
4aj

Oil (40.1 mg, 99% yield); **3aj**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.11 (m, 14H), 6.43 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.45 (d, *J* = 10.8 Hz, 1H), 5.13 (d, *J* = 17.4 Hz, 1H), 4.46 (d, *J* = 9.4 Hz, 1H), 4.27 (d, *J* = 9.5 Hz, 1H); **3aj** + **4aj**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 135.7, 130.9, 129.0, 128.9, 128.1, 127.8, 127.6, 127.5, 126.8, 125.1, 119.8, 118.2, 101.0, 75.8, 74.2; IR (film) ν_{max} 564, 663, 697, 758, 781, 847, 941, 975, 1029, 1076, 1097, 1121, 1158, 1176, 1207, 1261, 1403, 1449 cm^{-1}; HRMS (ESI) calculated for $C_{23}H_{23}N_2O_4S^+$ $[M+NH_4]^+$ 423.1379, found 423.1364.

3,9b-diphenyl-3-vinyl-2,3-dihydro-9b*H*-benzo[4,5]isothiazolo[3,2-*b*]oxazole 5,5-dioxide (3am/4am)



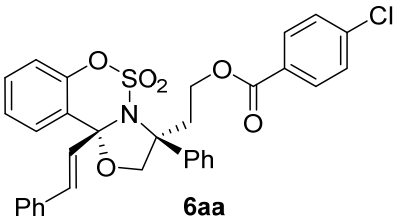
3am



4am

Yellow solid (38.5 mg, 99% yield); **3am**/**4am**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.31 (m, 14H), 5.98 (dd, *J* = 17.0, 10.5 Hz, 1H), 5.29 – 5.11 (m, 2H), 4.62 (d, *J* = 8.6 Hz, 1H), 4.44 (d, *J* = 8.3 Hz, 1H); **3am** + **4am**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 139.8, 139.6, 139.2, 139.0, 138.9, 138.6, 138.1, 137.8, 136.3, 136.2, 135.8, 133.2, 133.15, 133.11, 130.3, 130.2, 128.67, 128.65, 128.58, 128.4, 128.2, 128.1, 128.0, 127.9, 127.6, 127.3, 126.9, 126.6, 125.7, 125.6, 124.5, 124.2, 120.4, 120.3, 117.2, 116.5, 115.6, 101.8, 101.7, 85.2, 78.9, 77.9, 76.9, 75.2, 74.4, 74.2; IR (film) ν_{max} 457, 515, 564, 606, 649, 699, 733, 761, 801, 943, 998, 1025, 1064, 1135, 1160, 1178, 1206 cm^{-1}; HRMS (ESI) calculated for $C_{23}H_{20}NO_3S^+$ $[M+H]^+$ 390.1164, found 390.1149.

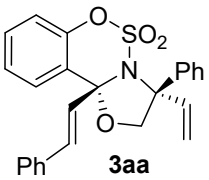
2-((3*S*,10b*R*)-5,5-dioxido-3-phenyl-10b-((*E*)-styryl)-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazin-3-yl)ethyl 4-chlorobenzoate (6aa)



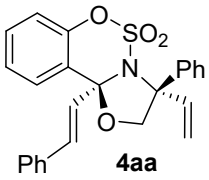
6aa

White solid (23.4 mg, 40 % yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 2H), 7.67 – 7.57 (m, 2H), 7.54 – 7.42 (m, 7H), 7.40 – 7.23 (m, 6H), 7.16 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.85 (d, *J* = 16.0 Hz, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 4.59 – 4.49 (m, 2H), 4.36 – 4.24 (m, 2H), 3.14 (ddd, *J* = 13.9, 7.6, 5.8 Hz, 1H), 2.83 (dt, *J* = 14.5, 7.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 149.5, 139.6, 139.2, 135.1, 130.91, 130.86, 130.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 126.9, 126.5, 125.9, 125.5, 122.2, 118.3, 98.9, 75.9, 72.3, 61.1, 34.0; IR (film) ν_{max} 629, 697, 759, 788, 855, 965, 1015, 1092, 1181, 1208, 1273, 1405, 1449, 1489, 1559, 1595, 1653, 1718, 2923 cm^{-1}; HRMS (ESI) calculated for $C_{32}H_{30}ClN_2O_6S^+$ $[M+NH_4]^+$ 605.1513, found 605.1498.

(3*S*,10b*R*)-3-phenyl-10b-((*E*)-styryl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3aa), (3*S*,10b*S*)-(4aa)



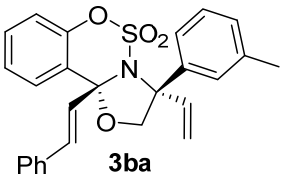
3aa



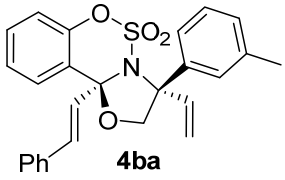
4aa

3aa/4aa, yellow oil. 34.0 mg, 79% yield, 78:22 dr, >99%, 95% ee [Daicel Chiralpak IE (0.46 cm x 25 cm)], *n*-hexane/isopropanol = 99/1, *v* = 0.15 mL•min^{-1}, λ = 254 nm, t (major) = 106.4, 111.8 min, t (minor) = 99.2, 125.7 min.

(3*S*,10b*R*)-10b-((*E*)-styryl)-3-(m-tolyl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ba), (3*S*,10b*S*)-(4ba)



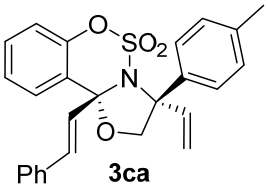
3ba



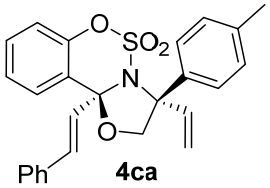
4ba

3ba/4ba, yellow oil. 28.2 mg, 63% yield, 61:39 dr, >99%, >99% ee [Daicel Chiralpak IA (0.46 cm x 25 cm)], *n*-hexane/isopropanol = 95/5, *v* = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 10.6, 13.4 min, t (minor) = 11.9, 16.2 min.

(3*S*,10b*R*)-10b-((*E*)-styryl)-3-(p-tolyl)-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ca), (3*S*,10b*S*)-(4ca)



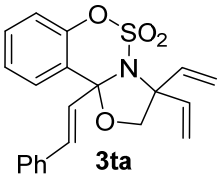
3ca



4ca

3ca/4ca, yellow oil. 31.2 mg, 70% yield, 65:35 dr, >99%, >99% ee [Daicel Chiralpak IE (0.46 cm x 25 cm)], *n*-hexane/isopropanol = 98/2, *v* = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 22.1, 23.6 min, t (minor) = 26.5, 31.5 min.

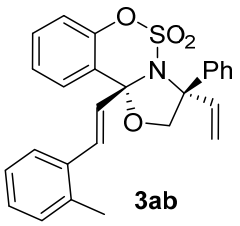
10b-styryl-3,3-divinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ta)



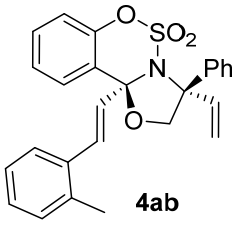
3ta

3ta, White soild. 17.2 mg, 45% yield, 27% ee [Daicel Chiralpak IE (0.46 cm x 25 cm)], *n*-hexane/isopropanol = 98/2, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 19.3min, t (minor) = 22.6 min.

(3*S*,10b*R*)-10b-((*E*)-2-methylstyryl)-3-phenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ab), (3*S*,10b*S*)-(4ab)



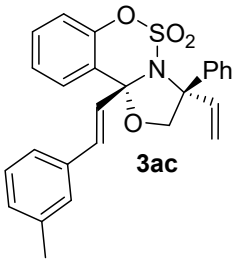
3ab



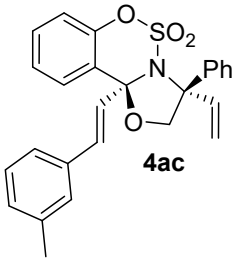
4ab

3ab/4ab, yellow soild. 31.8 mg, 71% yield, 58:42 dr, 99%, 96% ee [Daicel Chiralpak IE (0.46 cm x 25 cm)], *n*-hexane/isopropanol = 98/2, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 21.5, 23.7 min, t (minor) = 20.8, 26.4 min.

(3*S*,10b*R*)-10b-((*E*)-3-methylstyryl)-3-phenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ac), (3*S*,10b*S*)-(4ac)



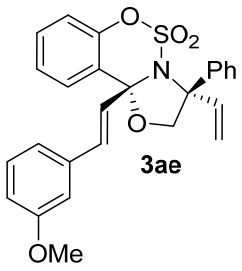
3ac



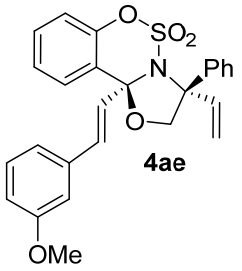
4ac

3ac/4ac, yellow oil. 28.4 mg, 64% yield, 55:45 dr, 99%, 97% ee [Daicel Chiralpak IE (0.46 cm x 25 cm)], *n*-hexane/isopropanol = 98/2, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 20.8, 22.1 min, t (minor) = 19.0, 24.7 min.

(3*S*,10b*R*)-10b-((*E*)-3-methoxystyryl)-3-phenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3ae), (3*S*,10b*S*)-(4ae)



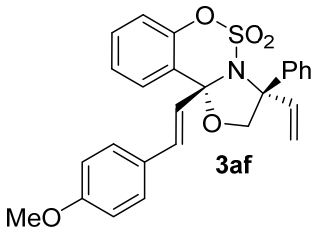
3ae



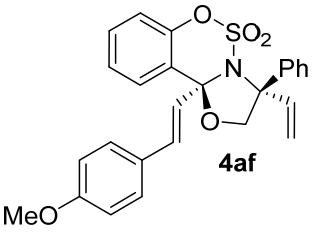
4ae

3ae/4ae, semisoild. 13.6 mg, 30% yield, 59:41 dr, 94%, 88% ee [Daicel Chiralpak IE (0.46 cm x 25 cm)], *n*-hexane/isopropanol = 98/2, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 27.0, 28.7 min, t (minor) = 25.5, 31.4 min.

(3*S*,10b*R*)-10b-((*E*)-4-methoxystyryl)-3-phenyl-3-vinyl-2,3-dihydro-10b*H*-benzo[*e*]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (3af), (3*S*,10b*S*)-(4af)



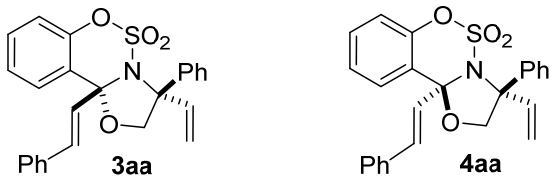
3af

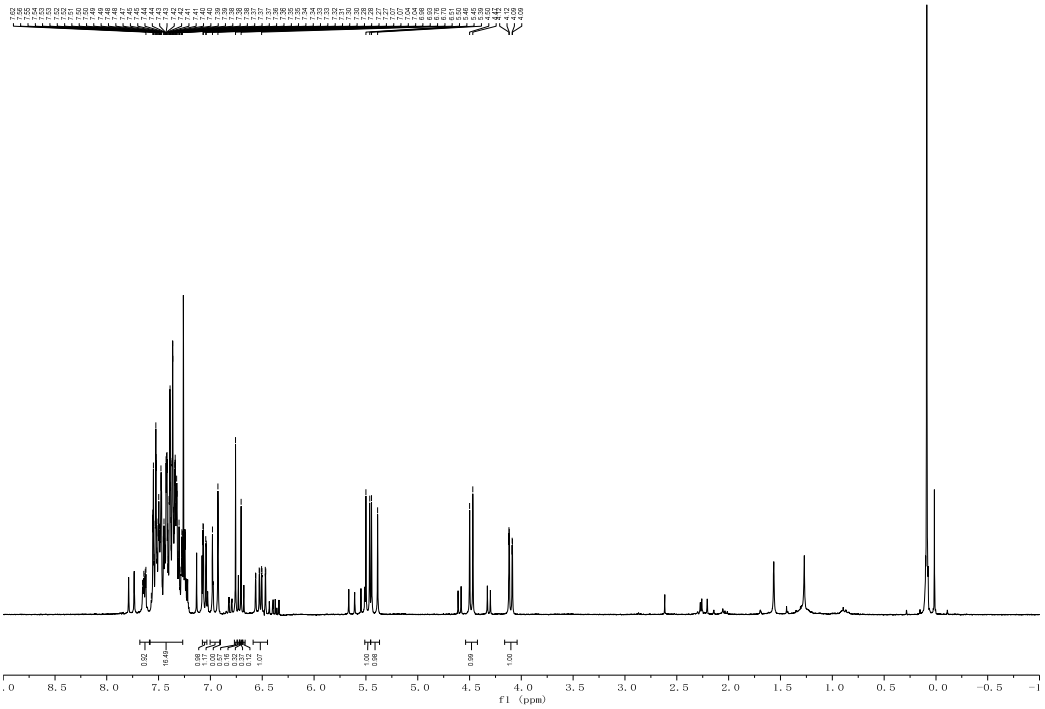


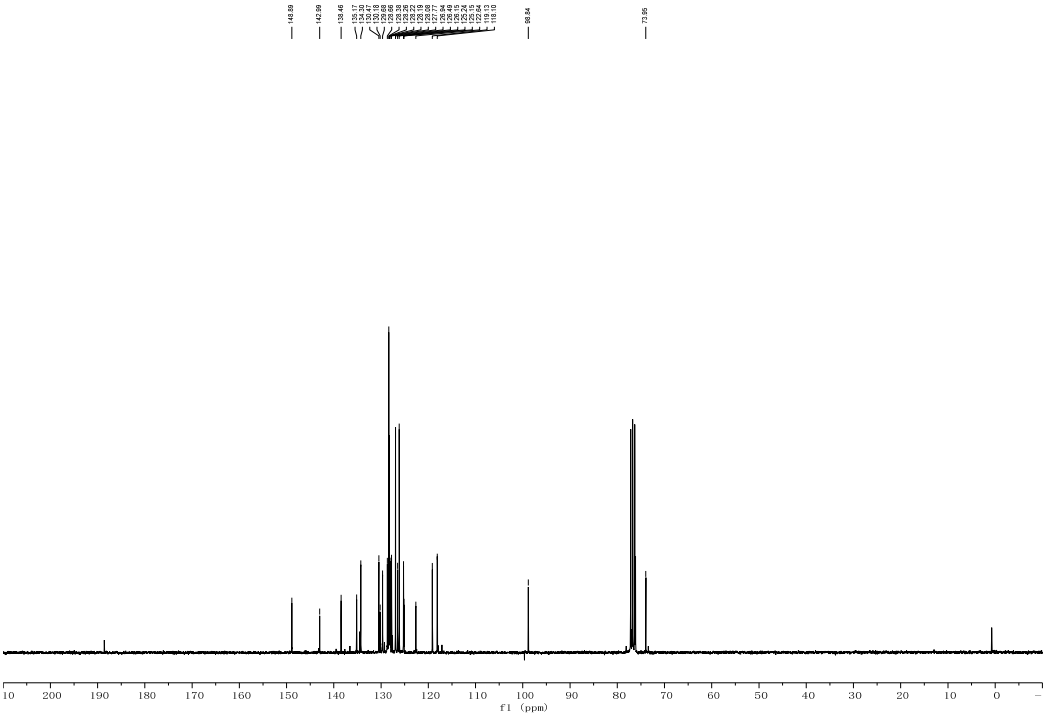
4af

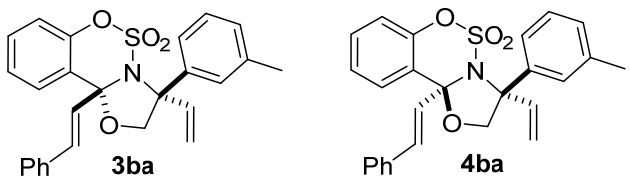
3af/4af, yellow oil. 14.6 mg, 32% yield, 48:52 dr, 83%, 97% ee [Daicel Chiralpak IE (0.46 cm x 25 cm)], *n*-hexane/isopropanol = 98/2, v = 1.0 mL•min^{-1}, λ = 254 nm, t (major) = 13.1, 14.3 min, t (minor) = 12.3, 15.4 min.

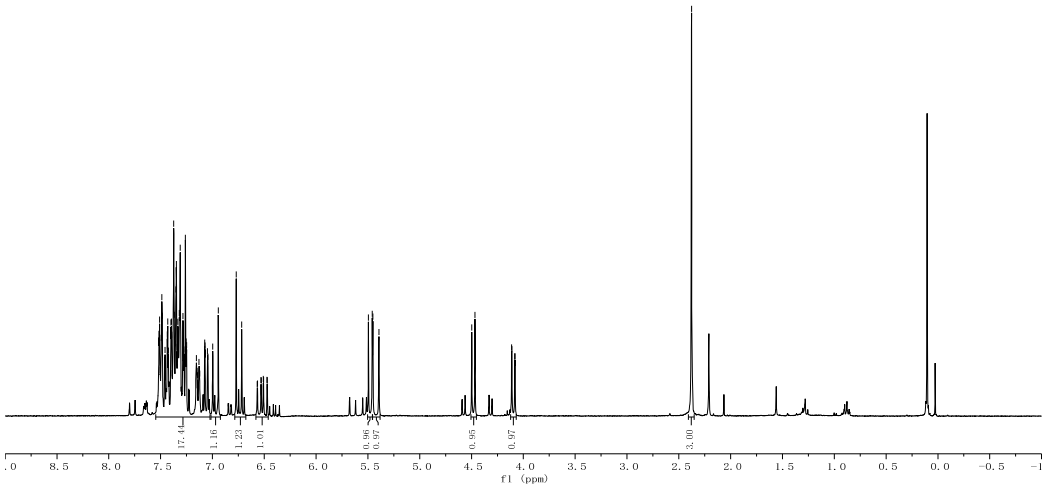
^{1}H and ^{13}C NMR Spectra of All Products

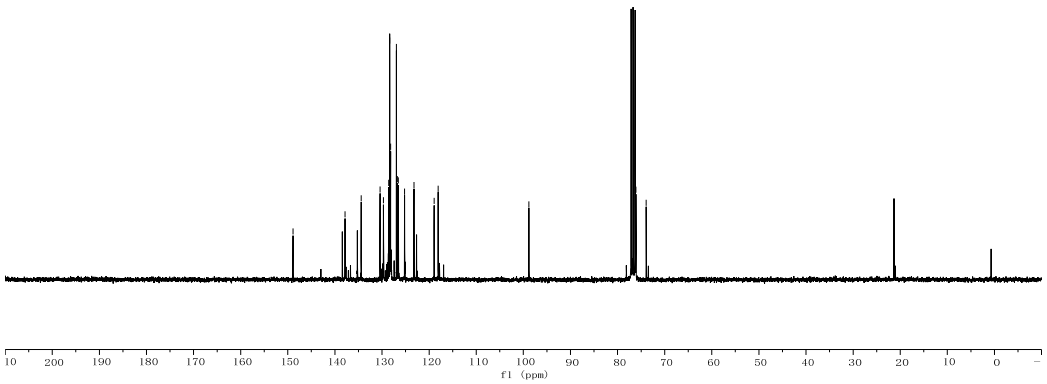


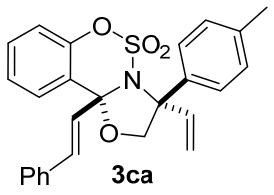




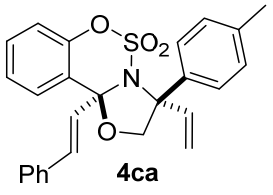

O
SO2
N
O
Ph
3ba
O
SO2
N
O
Ph
4ba


17.44
1.16
1.23
1.01
0.96
0.97
0.95
0.97
3.00
f1 (ppm)

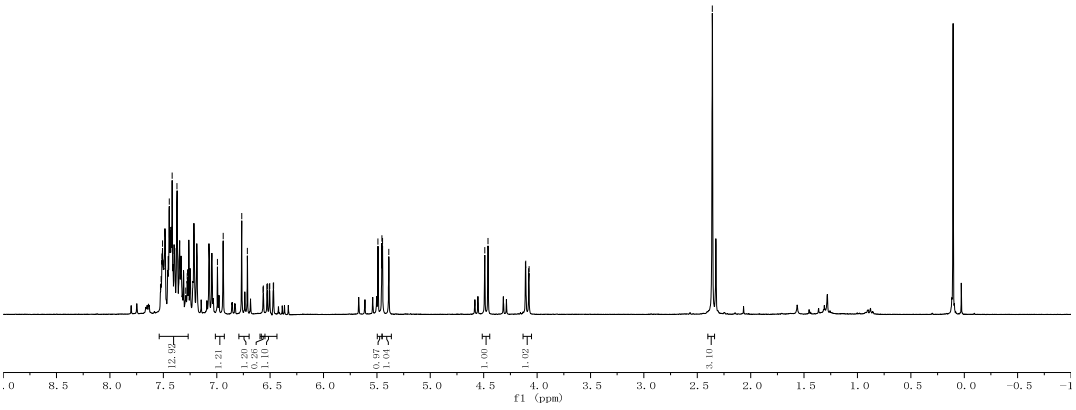

f1 (ppm)

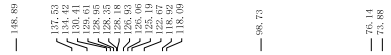

O
SO2
N
O
Ph

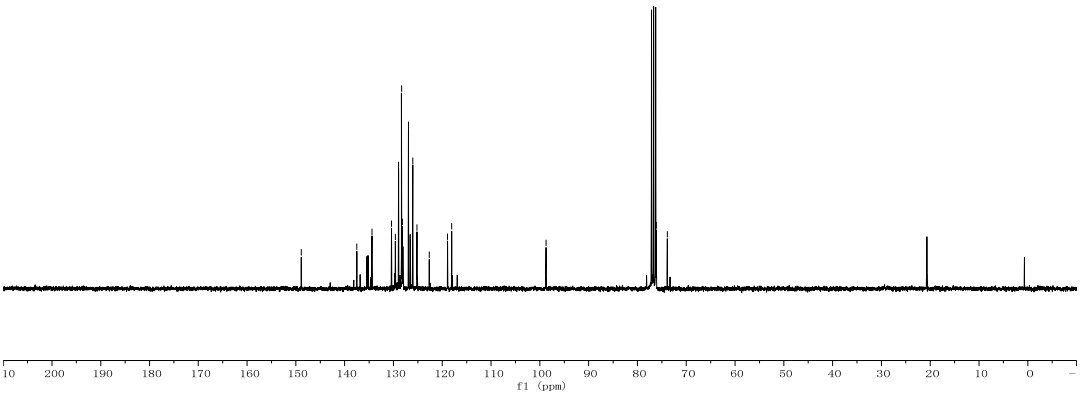
3ca

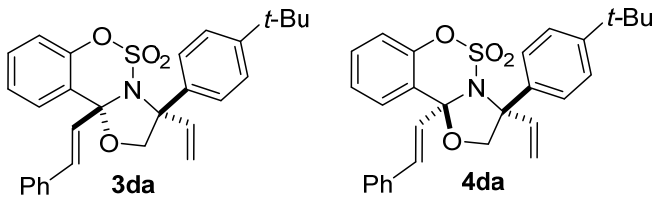

O
SO2
N
O
Ph

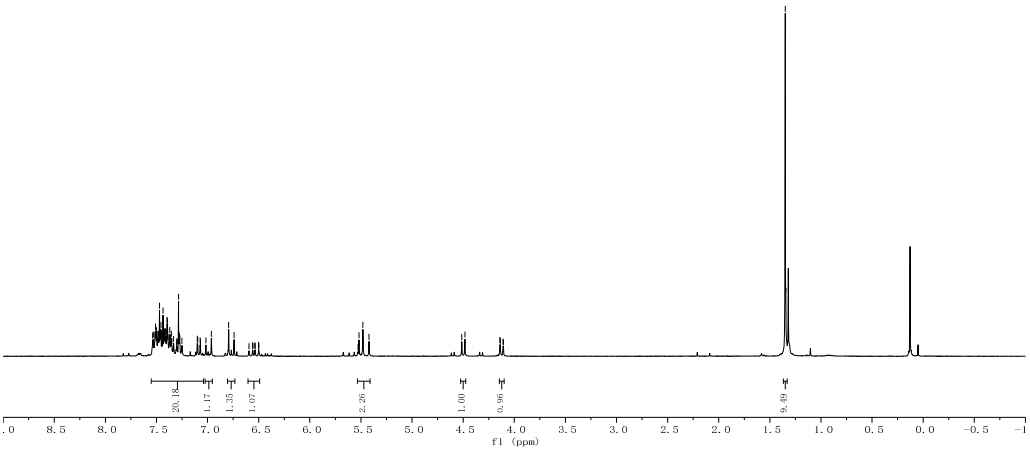
4ca

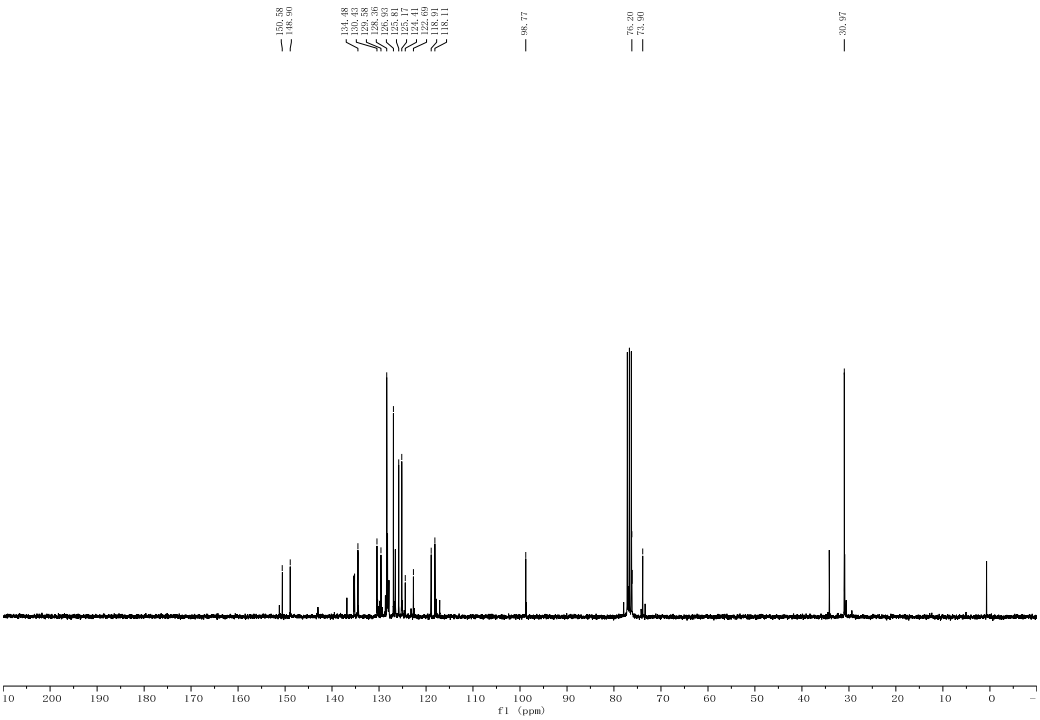

12.98
1.21
1.20
0.95
1.10
0.97
1.04
1.00
1.02
3.10
f1 (ppm)

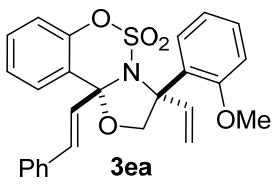



f1 (ppm)

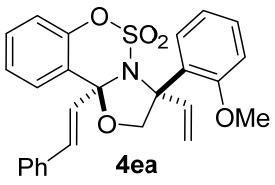

t-Bu
O
SO2
N
O
Ph
3da
t-Bu
O
SO2
N
O
Ph
4da


20.18
1.17
1.35
1.07
2.26
1.00
0.96
9.49
f1 (ppm)

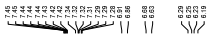

f1 (ppm)

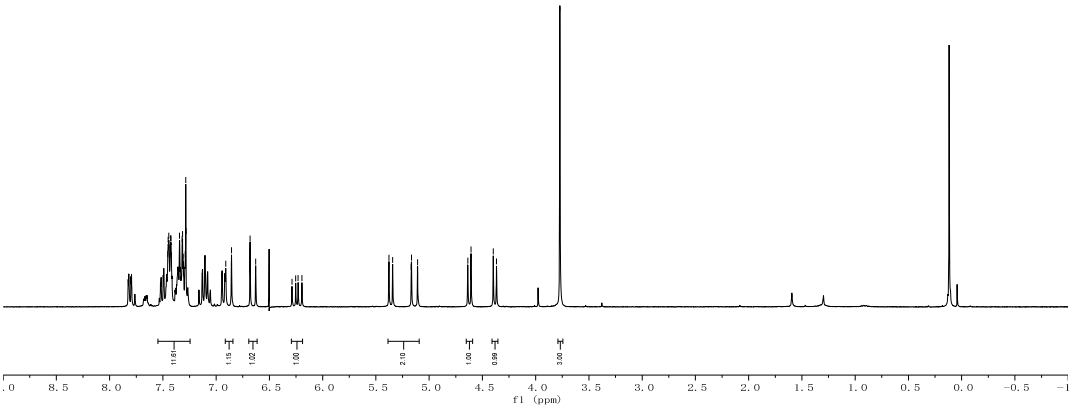

O
SO2
N
O
OMe
Ph

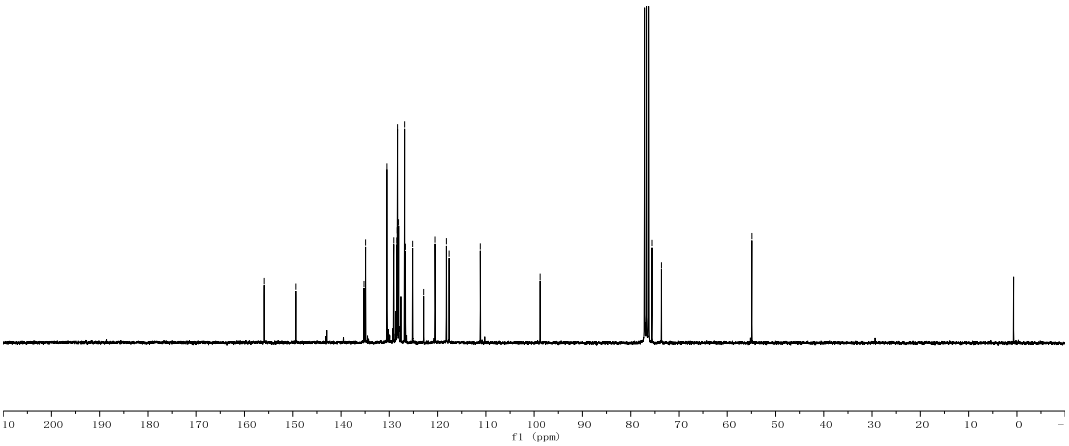
3ea

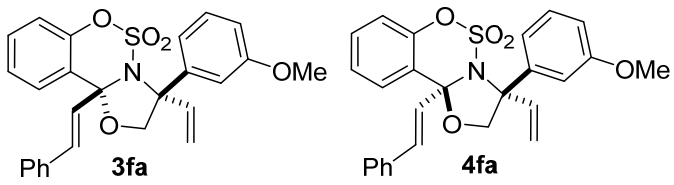

O
SO2
N
O
OMe
Ph

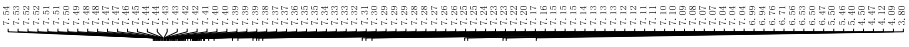
4ea

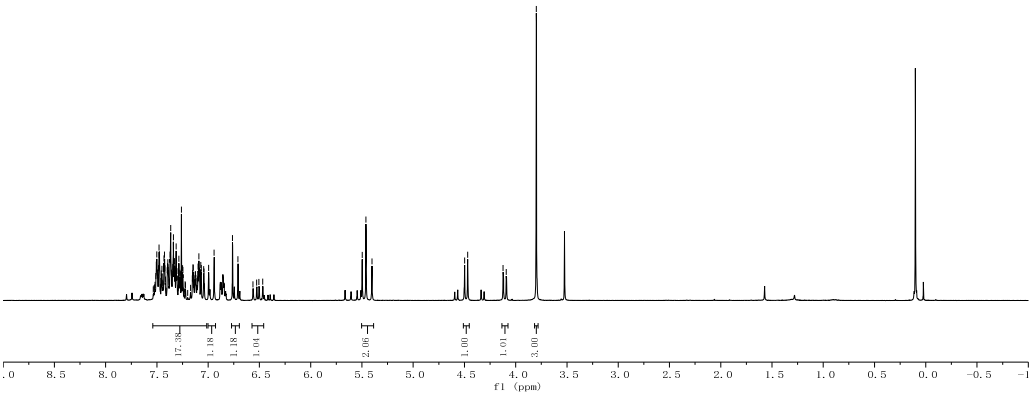


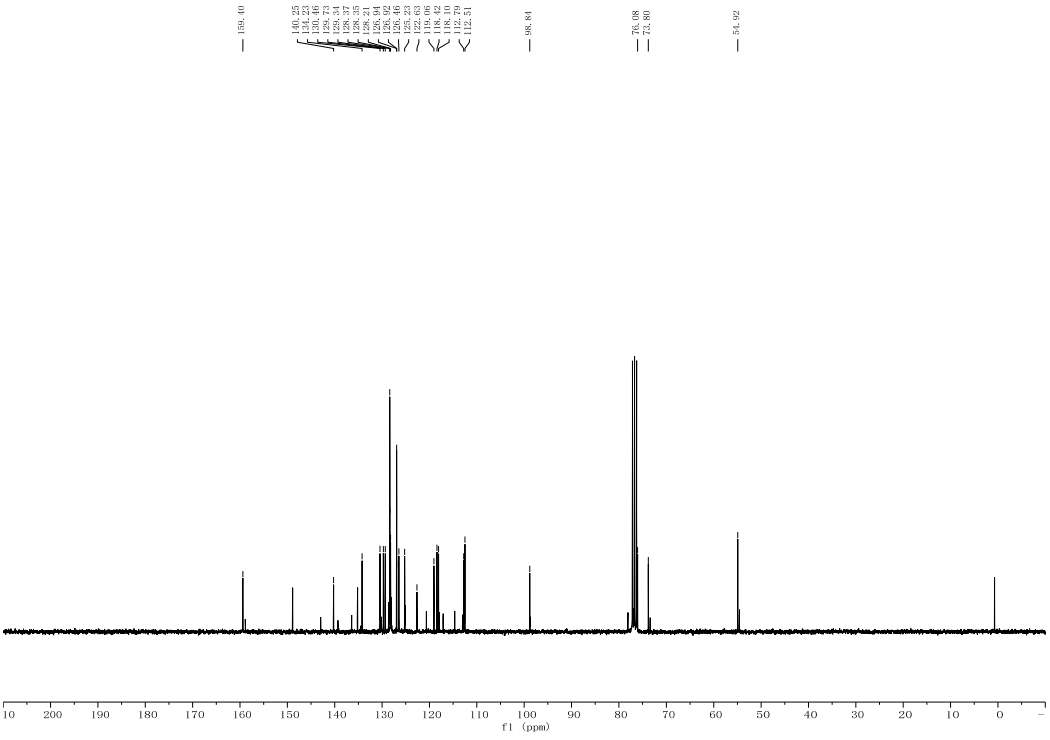

11.61
1.15
1.02
1.00
2.10
1.00
0.99
3.00
f1 (ppm)

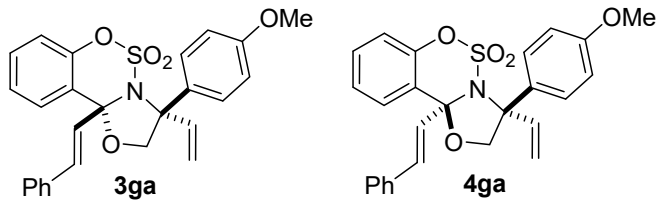

f1 (ppm)

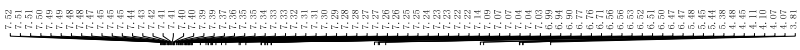

O
SO2
N
OMe
O
Ph
3fa
O
SO2
N
OMe
O
Ph
4fa

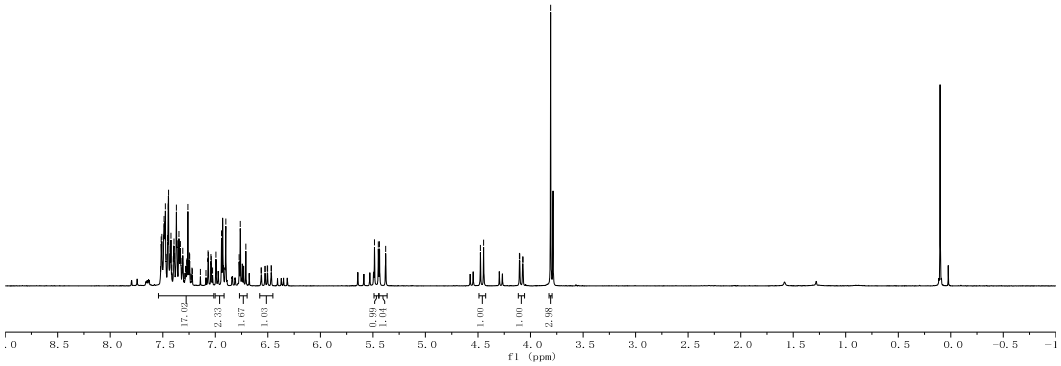


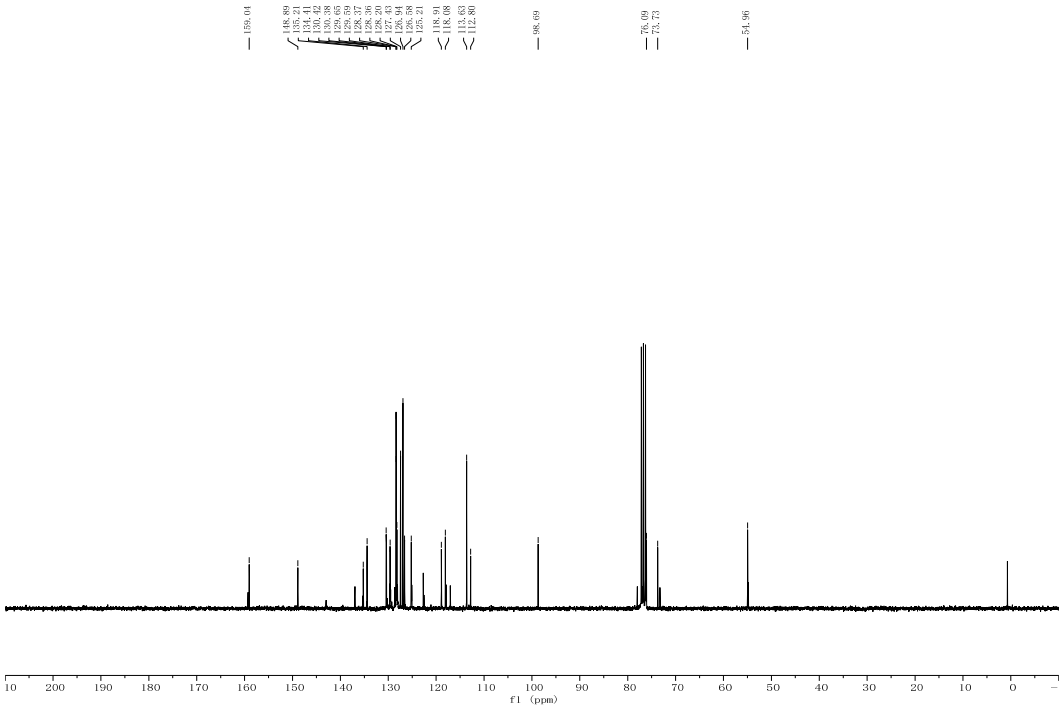

17.38
1.18
1.18
1.04
2.06
1.00
1.01
3.00
f1 (ppm)

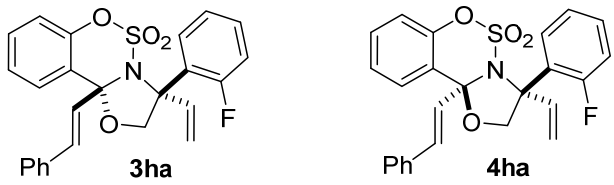

159.40
140.95
134.23
130.46
129.73
129.34
128.37
128.35
128.31
126.94
126.46
125.33
122.63
119.06
118.42
114.10
112.79
112.51
98.84
76.08
75.80
54.92
f1 (ppm)


OMe
O
SO2
N
O
Ph
3ga
OMe
O
SO2
N
O
Ph
4ga




17.02
2.33
1.67
1.03
0.99
1.04
1.00
1.00
2.98
f1 (ppm)

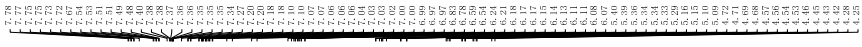

159.04
148.89
135.71
134.41
130.42
130.08
129.65
129.59
128.37
128.36
128.20
127.43
126.94
126.58
125.21
118.91
118.08
113.63
112.80
98.69
76.09
73.73
54.96
f1 (ppm)

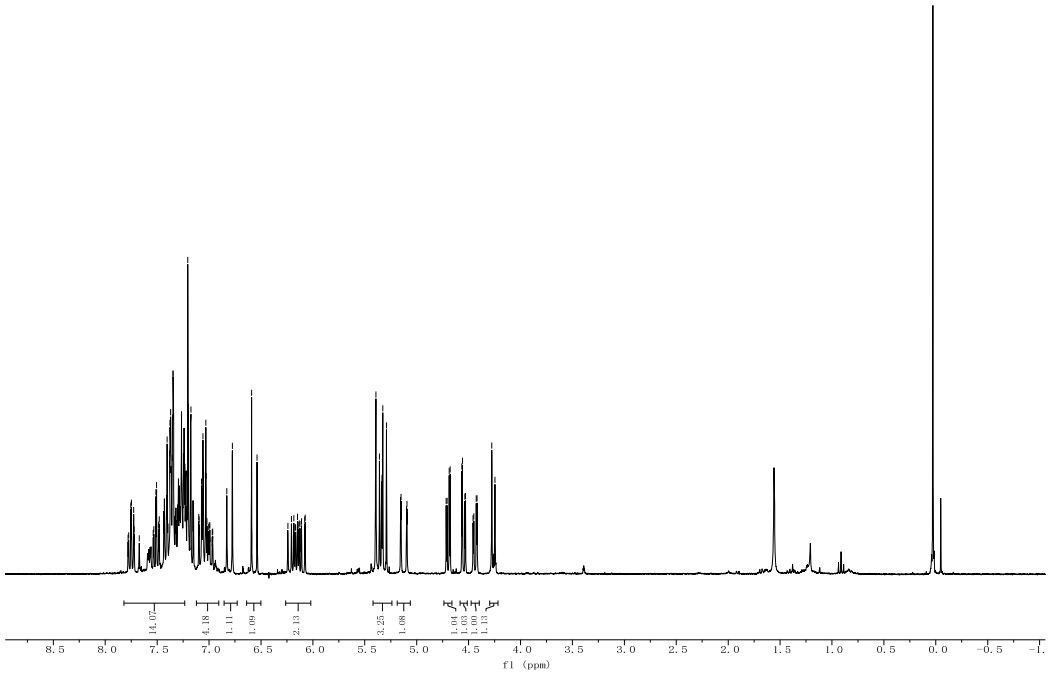

O
SO2
N
O
F
Ph

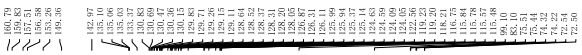
3ha

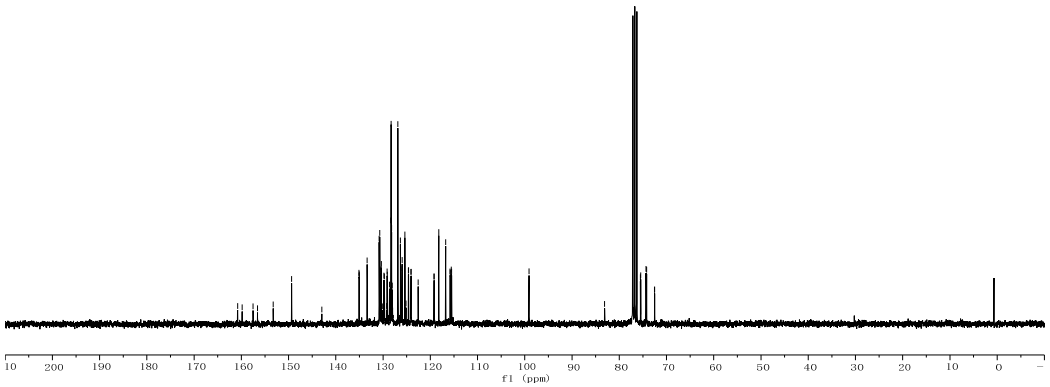
O
SO2
N
O
F
Ph

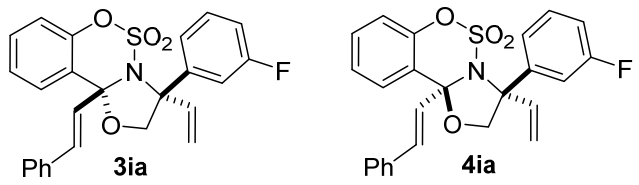
4ha

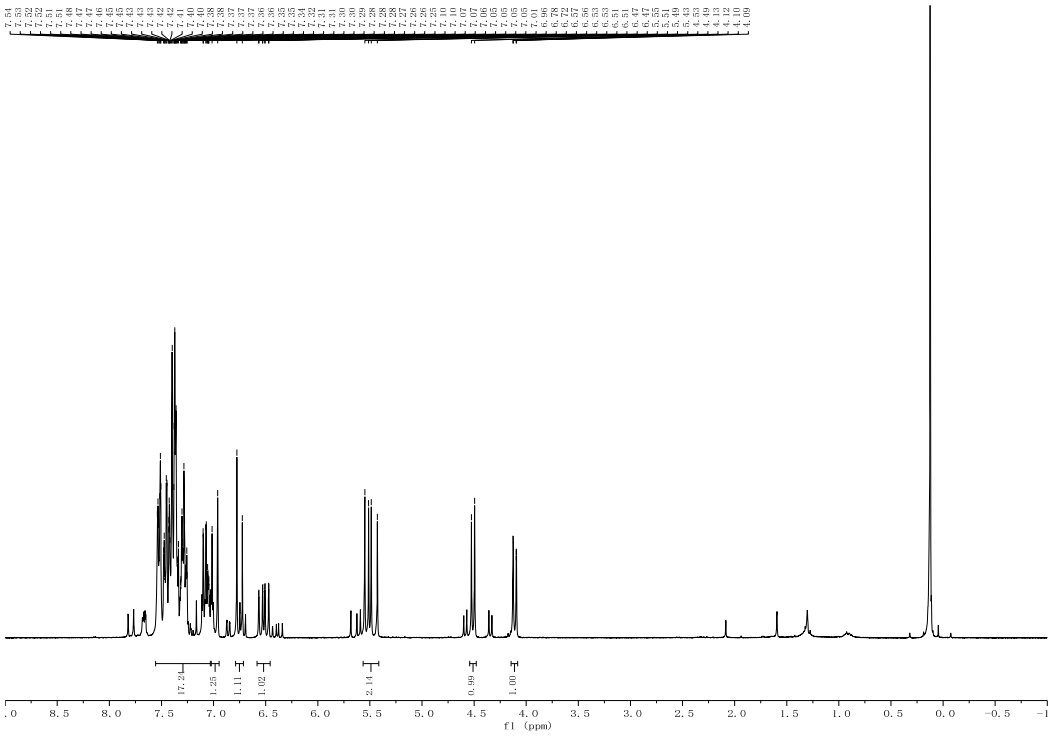


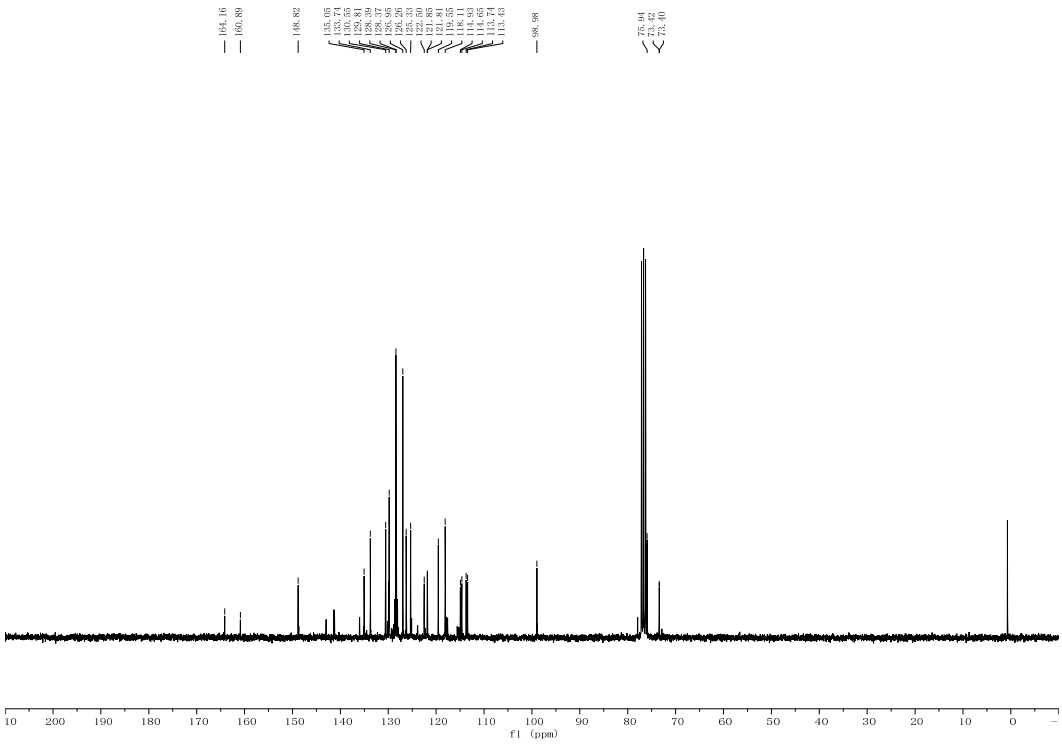

14.07
4.18
1.11
1.09
2.13
3.25
1.08
1.04
1.05
1.00
1.13
f1 (ppm)

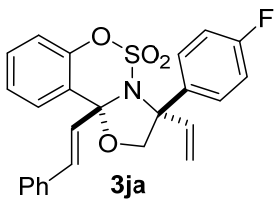



f1 (ppm)

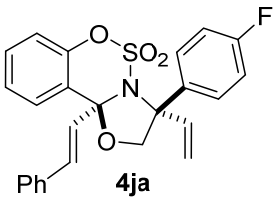

O
SO2
N
O
F
Ph
3ia
4ia


17.24
1.25
1.11
1.02
2.14
0.99
1.00
f1 (ppm)

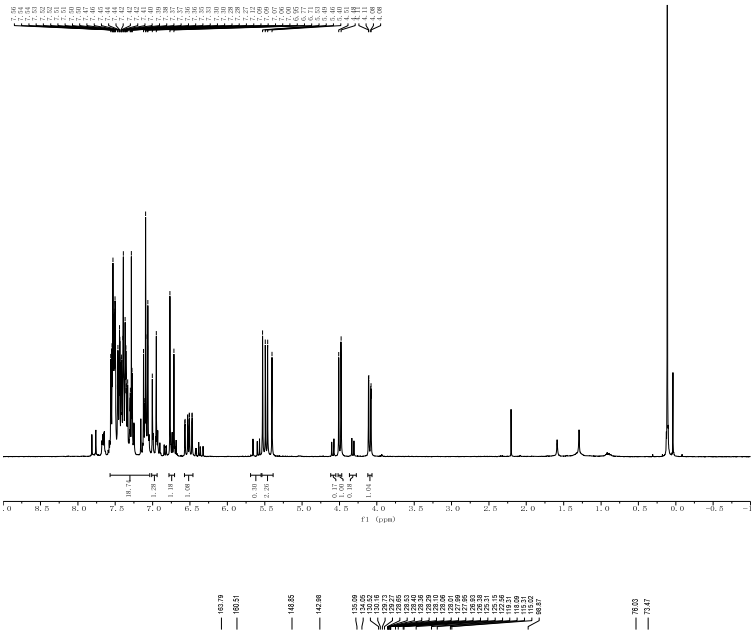

f1 (ppm)

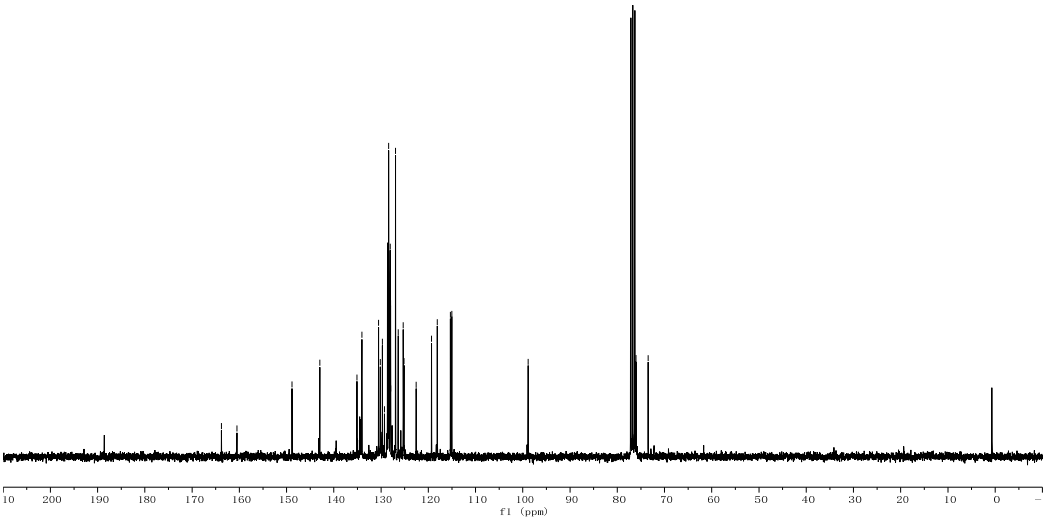


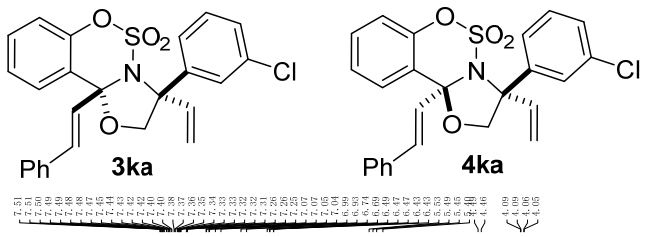
3ja

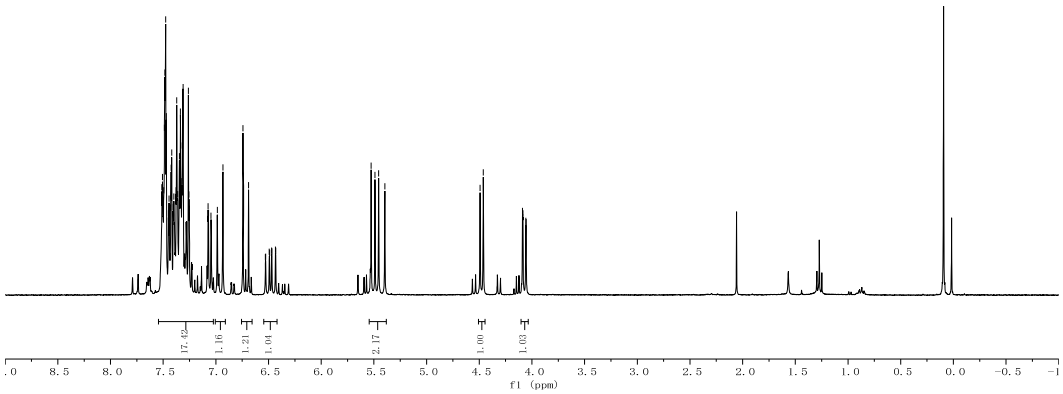


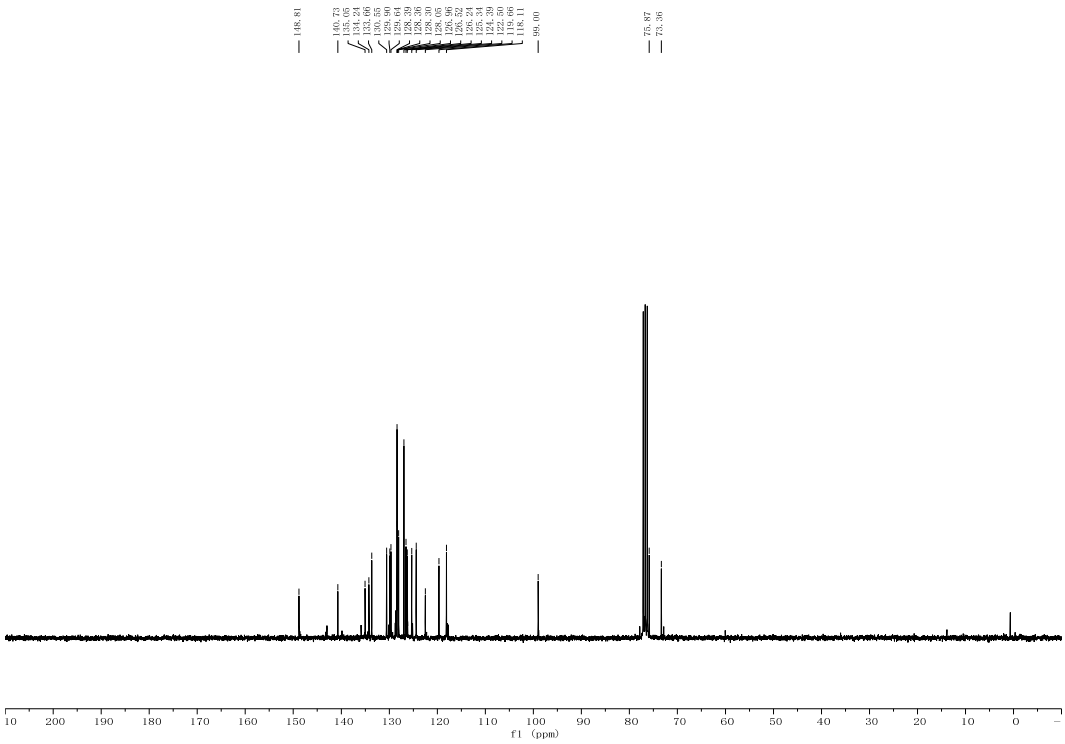
4ja

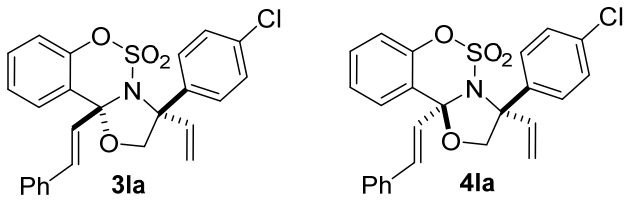


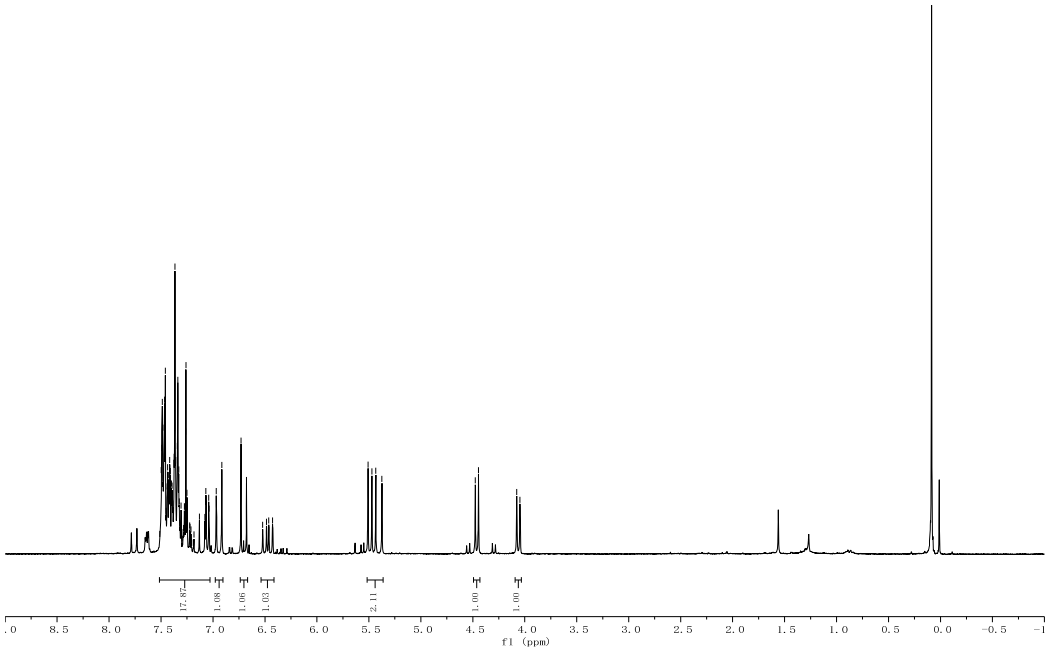


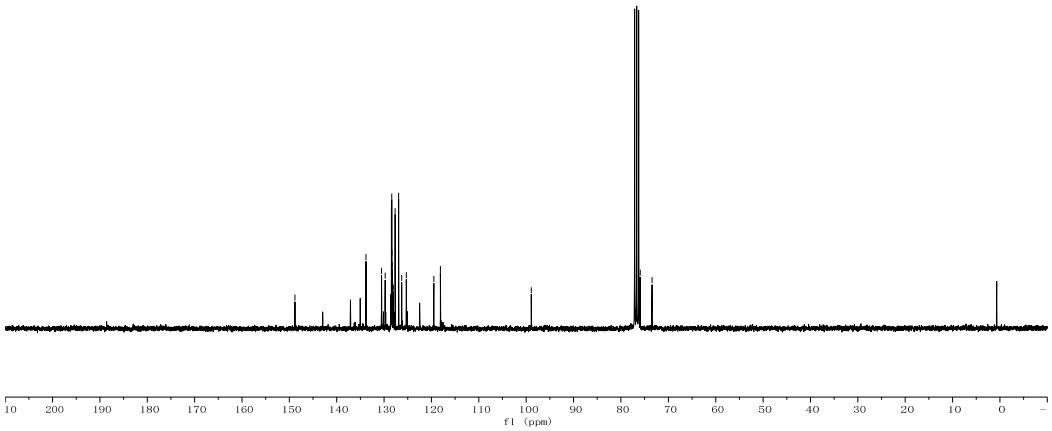

O
SO2
N
Cl
O
Ph
3ka
O
SO2
N
Cl
O
Ph
4ka

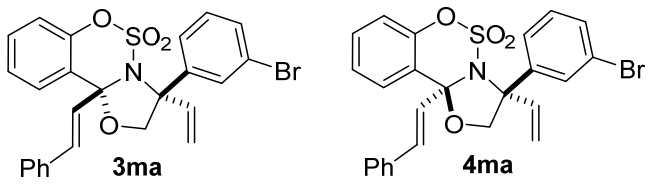

17.62
1.16
1.21
1.04
2.17
1.00
1.03
f1 (ppm)

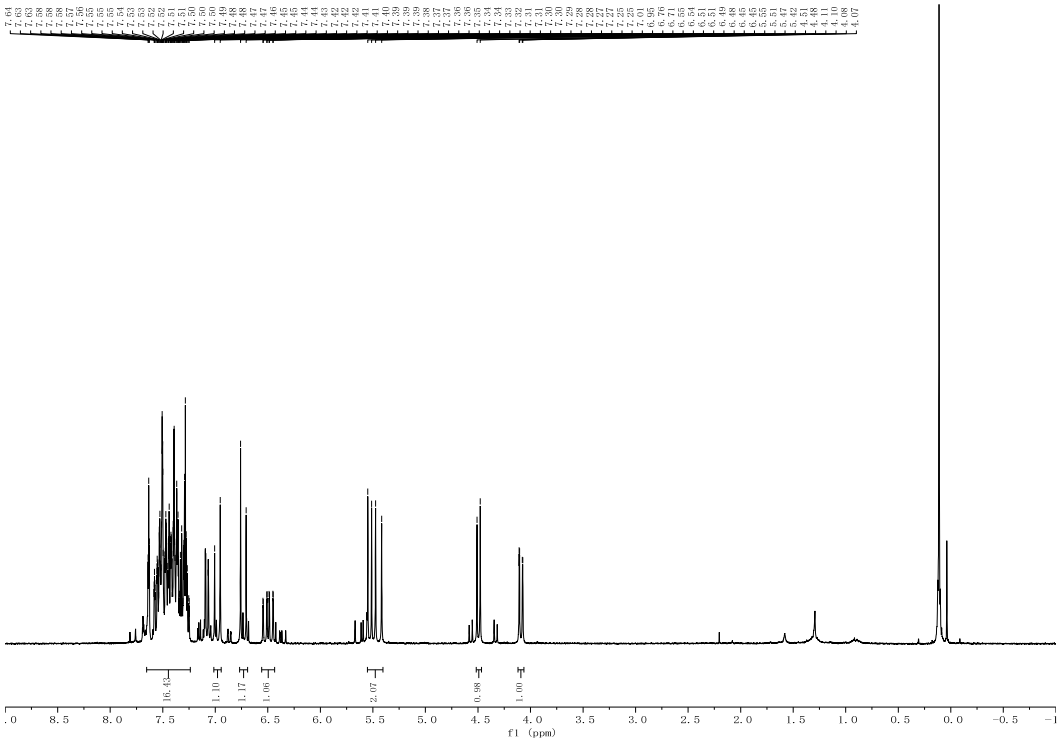

148.81
140.73
135.05
134.24
133.66
130.55
129.90
128.64
128.39
128.36
128.30
126.65
126.96
126.52
126.24
125.74
124.39
122.50
119.66
118.11
99.00
75.87
73.96
f1 (ppm)

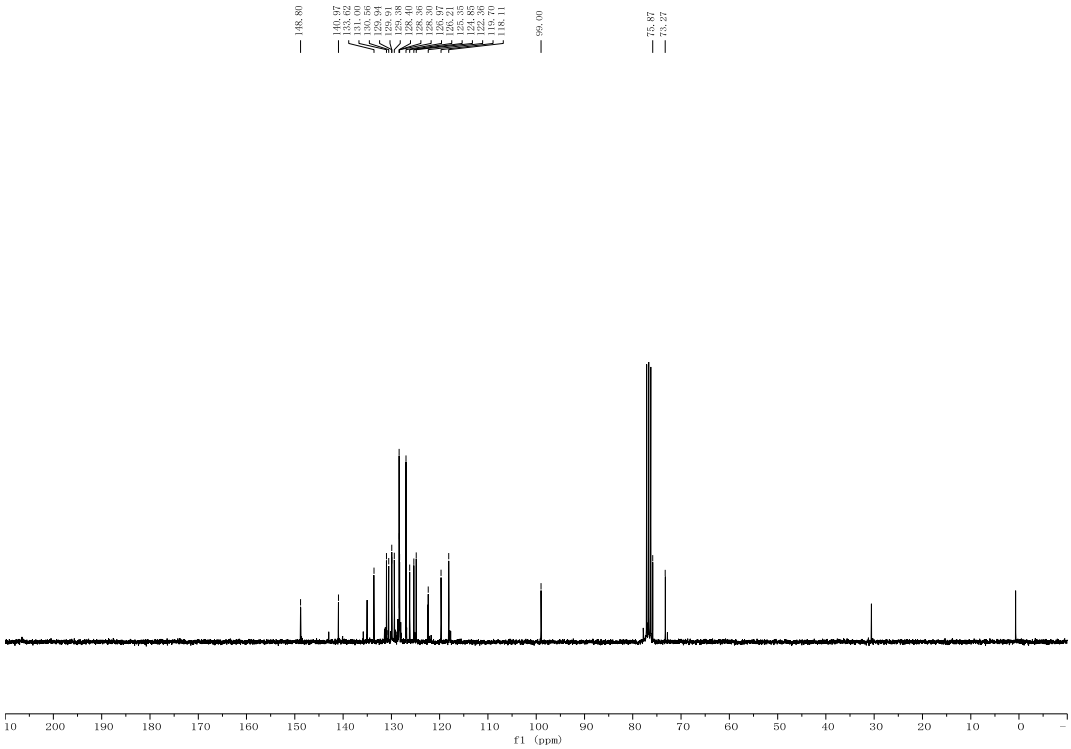

Cl
O
SO2
N
O
Ph
3la
Cl
O
SO2
N
O
Ph
4la

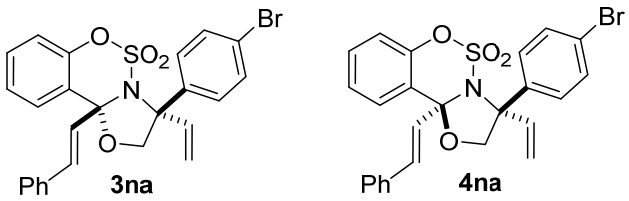

17.87
1.08
1.06
1.03
2.11
1.00
1.00
f1 (ppm)


f1 (ppm)


O
SO2
N
Br
O
Ph
3ma
O
SO2
N
Br
O
Ph
4ma


16.43
1.10
1.17
1.06
2.07
0.98
1.00
f1 (ppm)

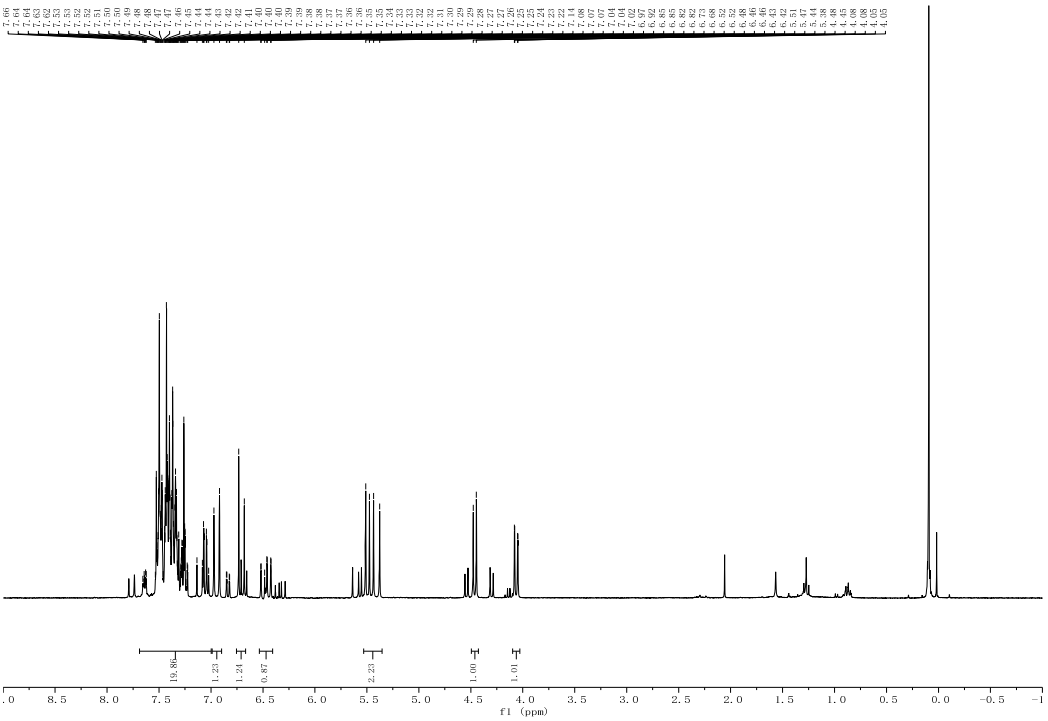

148.80
140.97
133.62
131.90
130.56
129.94
129.91
128.38
128.40
128.36
128.30
126.97
126.71
125.35
124.85
122.36
121.70
118.11
99.00
76.87
75.27
f1 (ppm)


Br
O
SO2
N
O
Ph

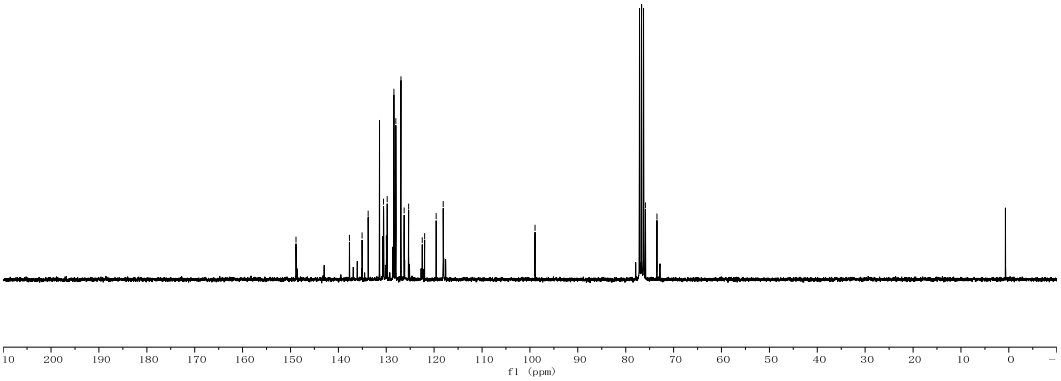
3na

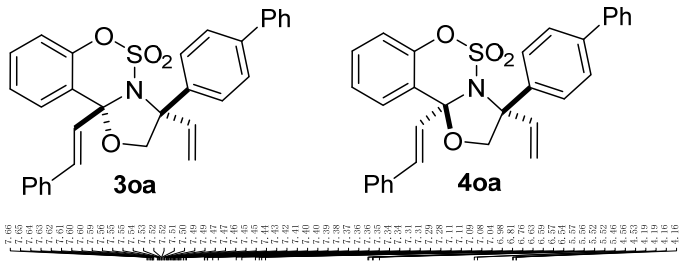
Br
O
SO2
N
O
Ph

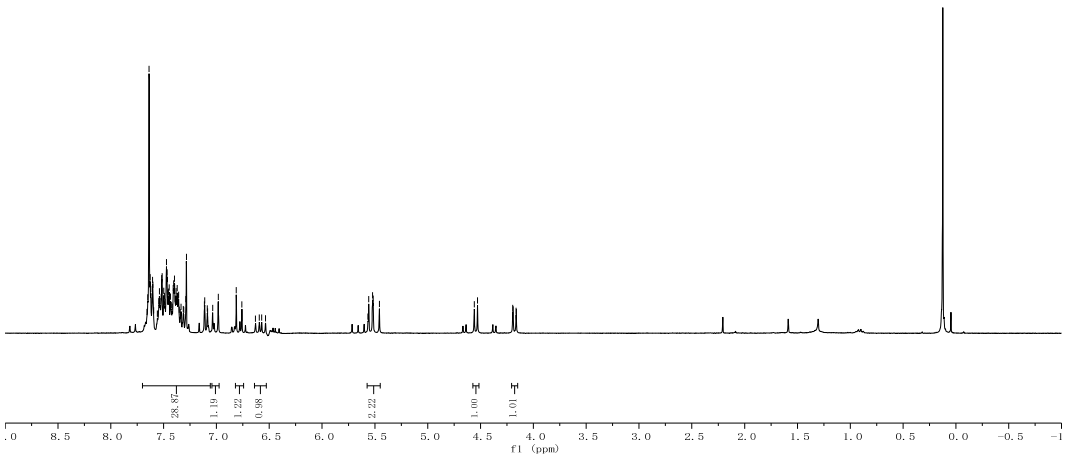
4na

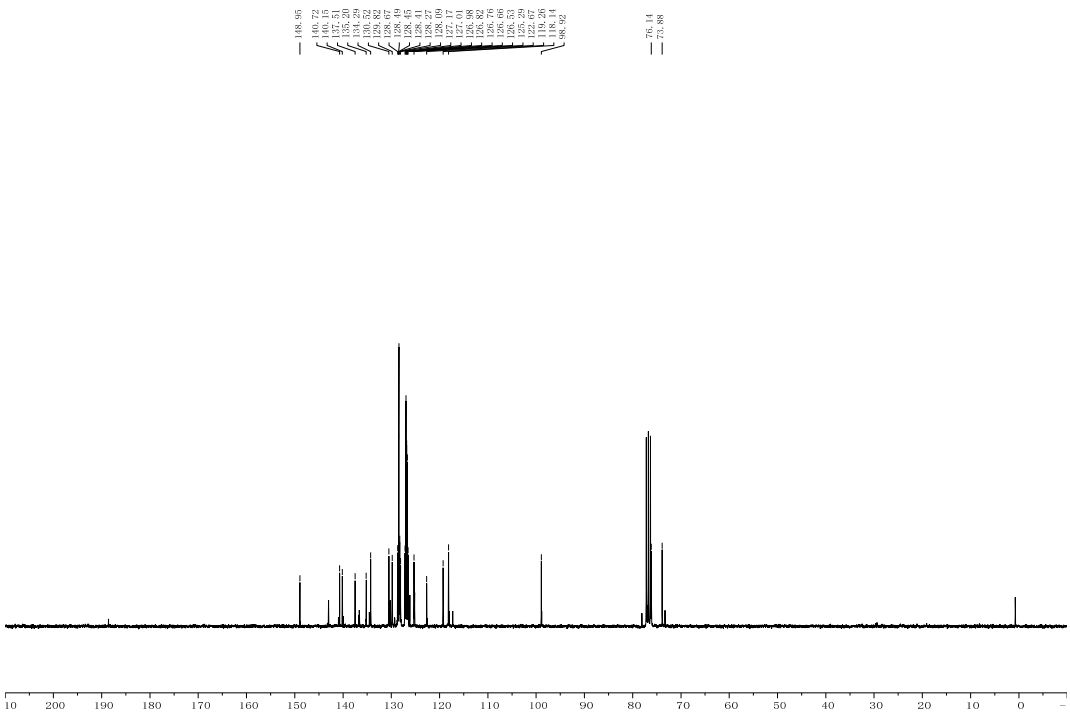

19.86
1.23
1.24
0.87
2.23
1.00
1.01
f1 (ppm)

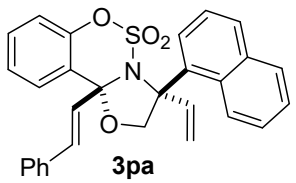

148.84
137.68
135.40
133.76
131.42
130.56
129.80
128.40
128.37
128.31
128.00
126.94
126.27
125.34
122.49
122.00
119.58
118.11
98.94
75.89
73.49


f1 (ppm)

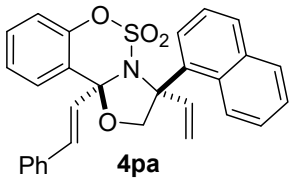

Ph
O
SO2
N
O
Ph
3oa
Ph
O
SO2
N
O
Ph
4oa


28.87
1.19
1.22
0.98
2.22
1.00
1.01
f1 (ppm)

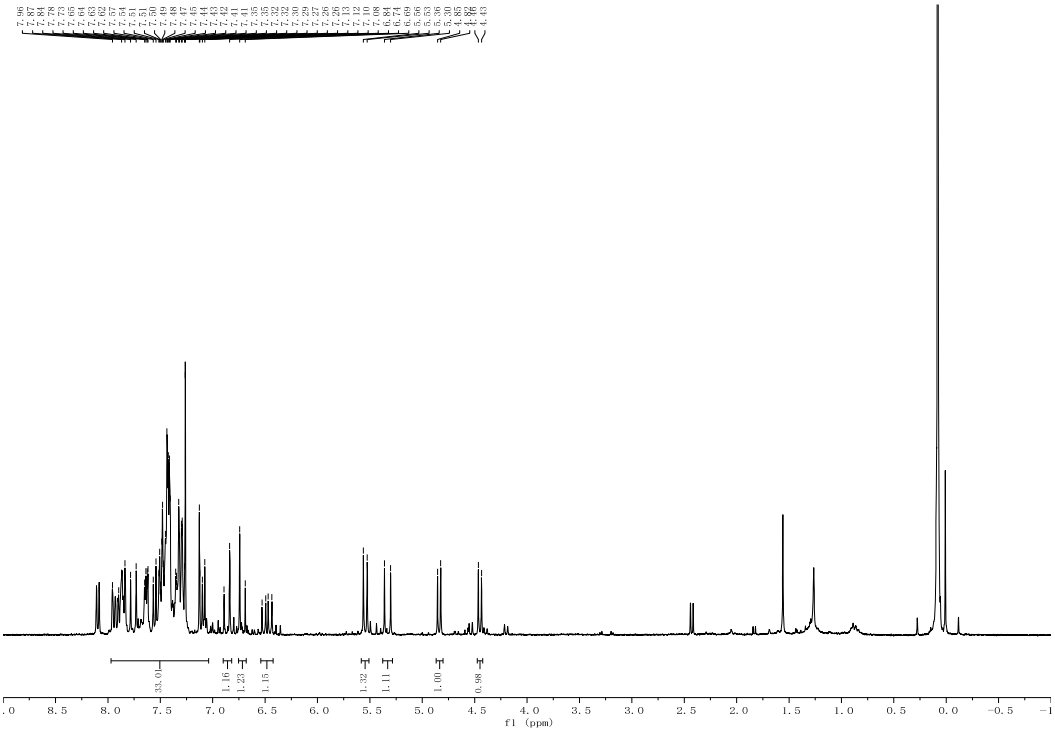

f1 (ppm)

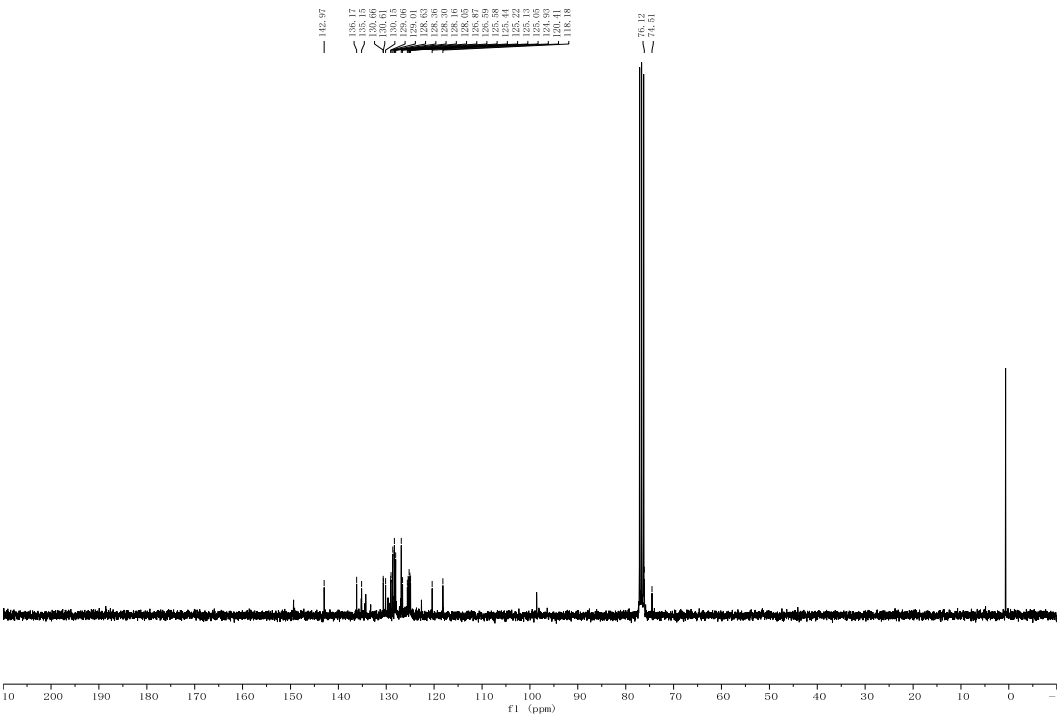

O
SO2
N
O
Ph

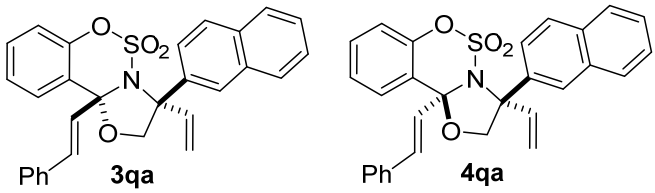
3pa

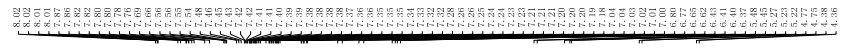

O
SO2
N
O
Ph

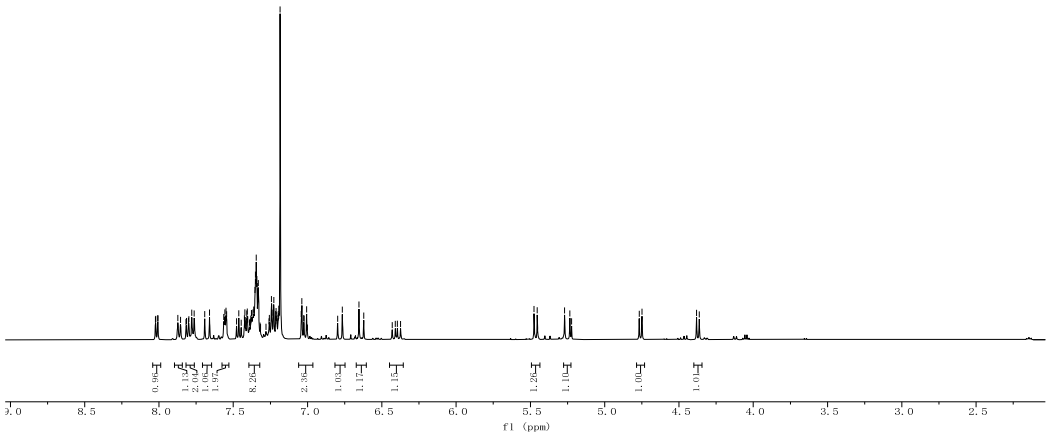
4pa

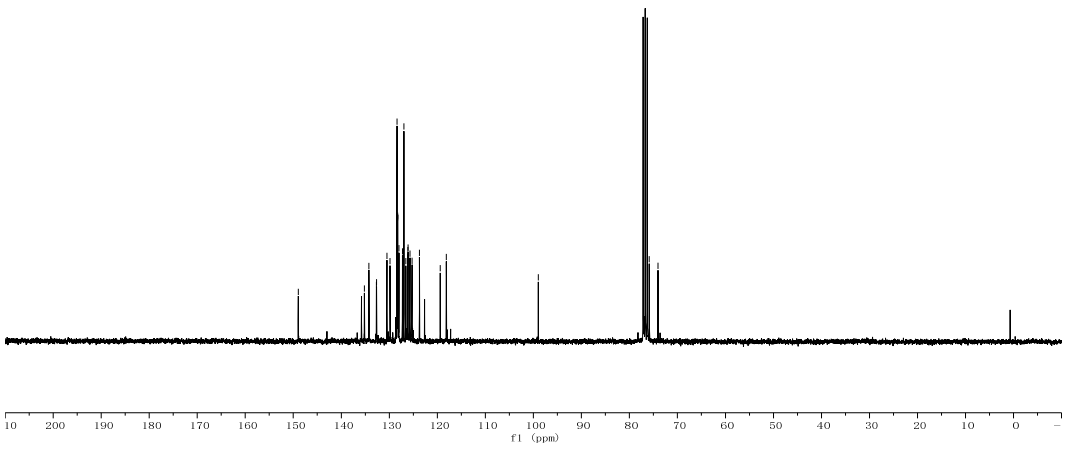

33.01
1.16
1.23
1.15
1.32
1.11
1.00
0.58
f1 (ppm)

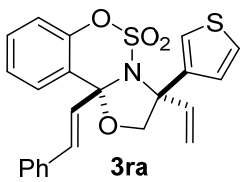

142.97
136.17
135.15
130.66
130.61
130.15
129.06
129.01
128.63
128.36
128.30
128.16
128.05
126.87
126.59
125.88
125.44
125.22
125.13
125.05
124.58
120.41
118.18
76.12
74.51
f1 (ppm)


O
SO2
N
O
Ph
3qa
O
SO2
N
O
Ph
4qa

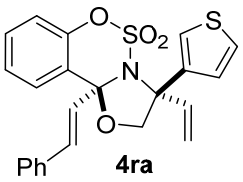



0.96
1.12
2.04
1.06
1.95
8.20
2.36
1.03
1.17
1.15
1.20
1.10
1.00
1.01
f1 (ppm)

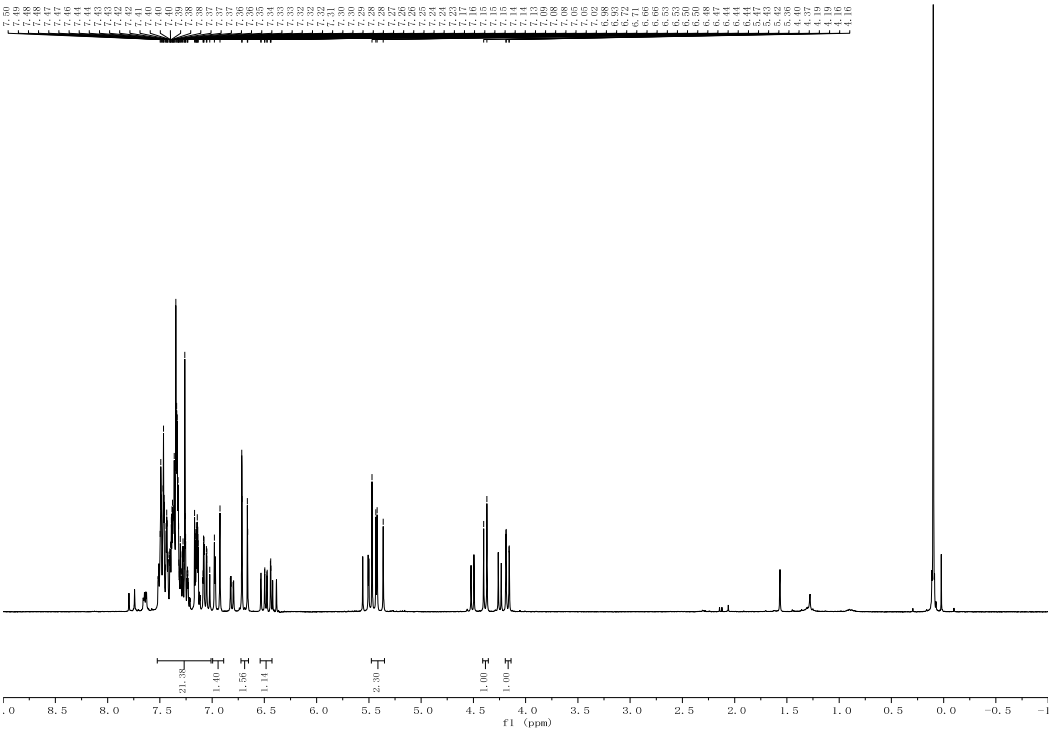

f1 (ppm)

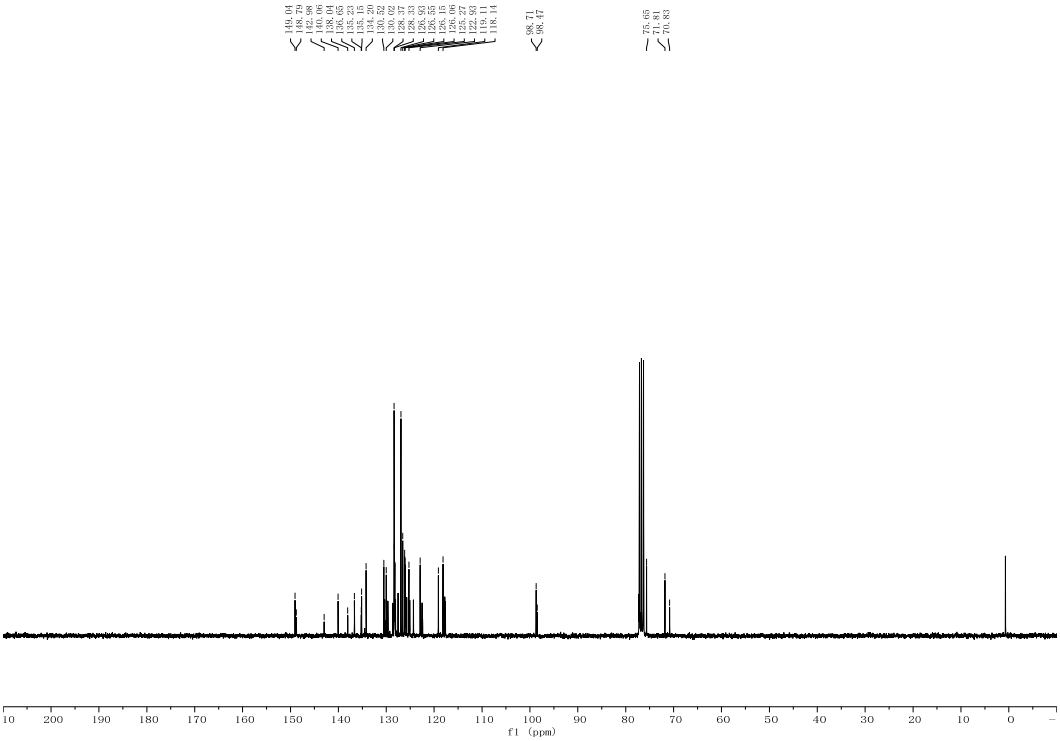

O
SO2
S
N
O
Ph

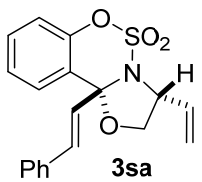
3ra


O
SO2
S
N
O
Ph

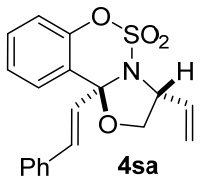
4ra


21.38
1.40
1.56
1.14
2.30
1.00
1.60
f1 (ppm)

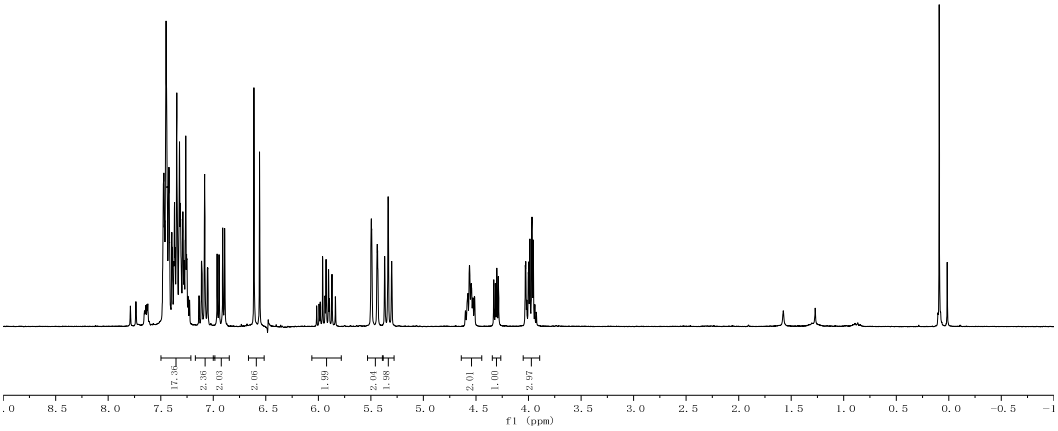

f1 (ppm)


O
SO2
N
H
O
Ph

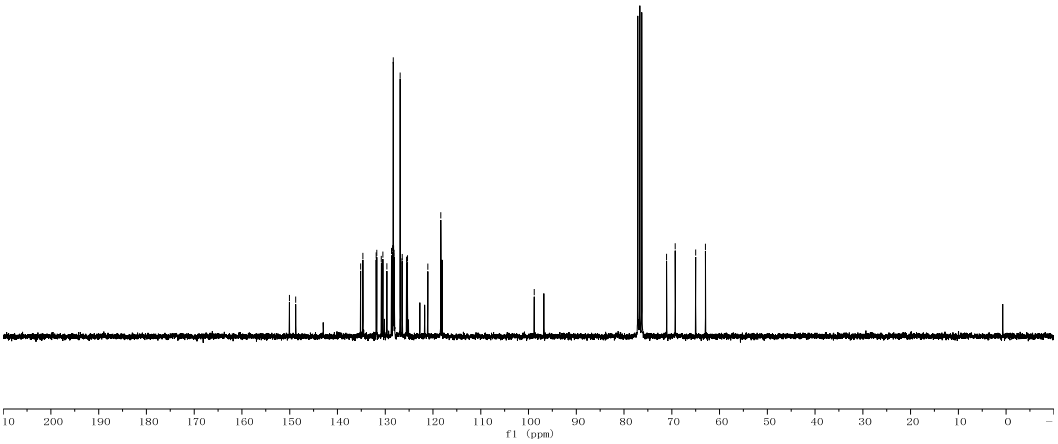
3sa

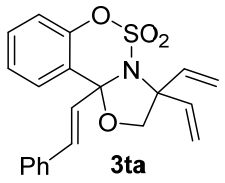

O
SO2
N
H
O
Ph

4sa

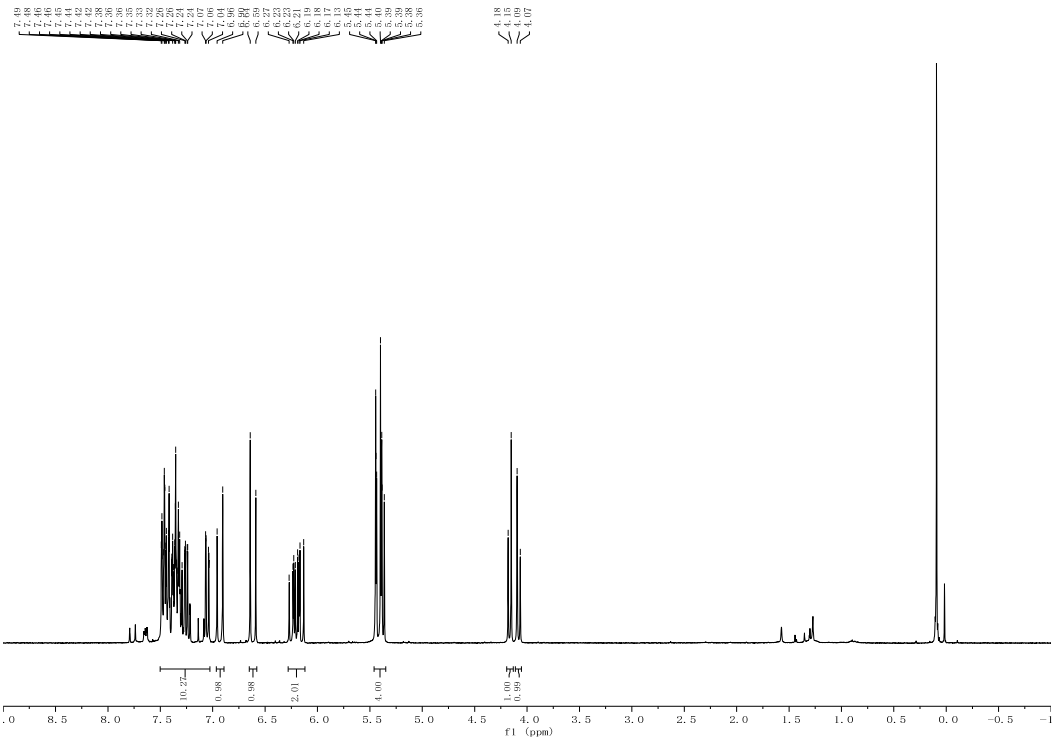

17.36
2.36
2.03
2.06
1.89
2.04
1.98
2.01
1.00
2.97
f1 (ppm)

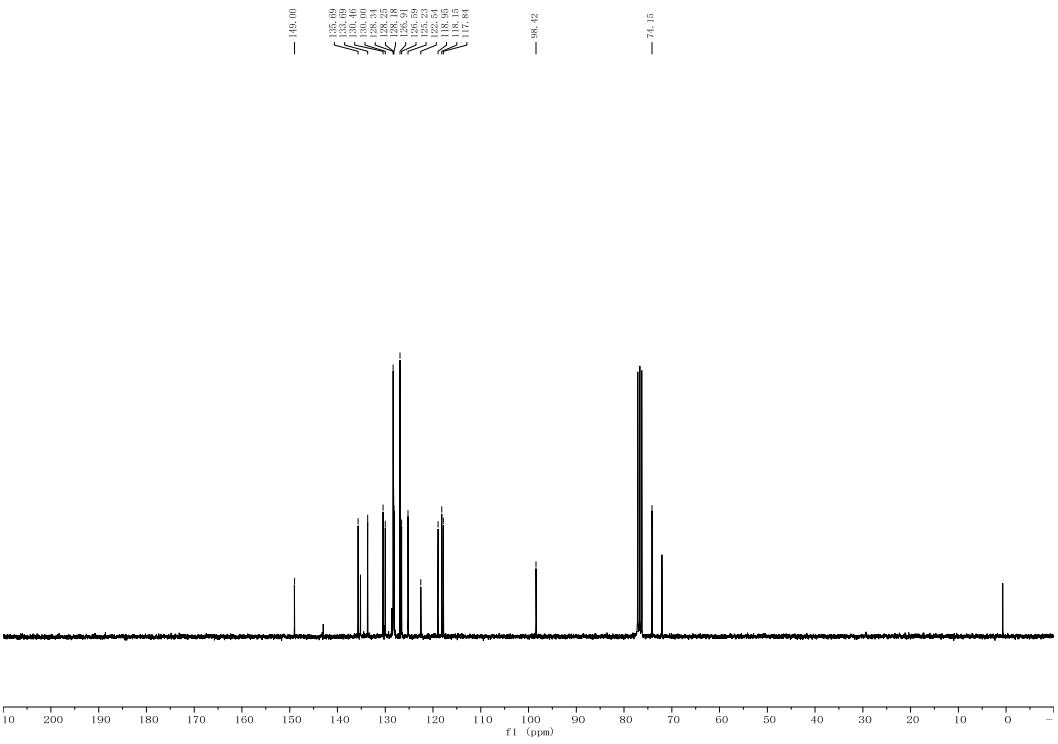

150.07
134.74
133.16
131.89
131.78
130.81
130.48
129.66
128.68
128.45
128.33
126.25
125.15
125.88
125.50
125.44
125.34
125.33
123.09
118.36
98.81
71.08
69.28
65.01
62.96

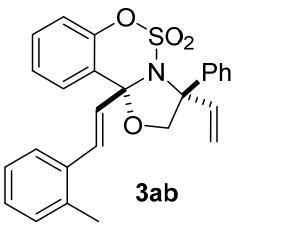

f1 (ppm)


O
SO2
N
O
Ph

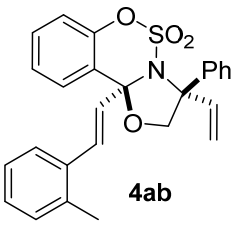
3ta


10.27
0.98
0.98
2.01
4.00
1.00
0.49
f1 (ppm)

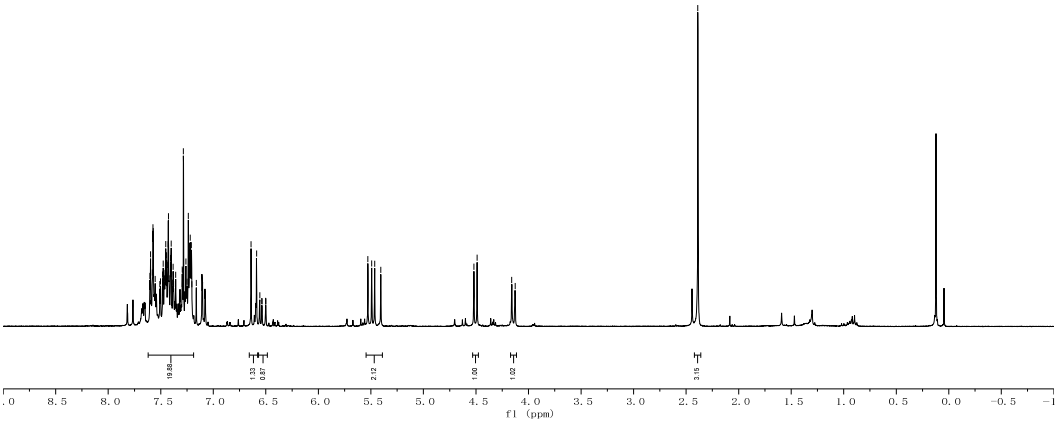

149.00
135.69
133.69
130.46
130.00
128.34
128.25
128.08
126.91
126.59
125.23
122.54
118.95
118.15
117.84
98.82
74.15
f1 (ppm)

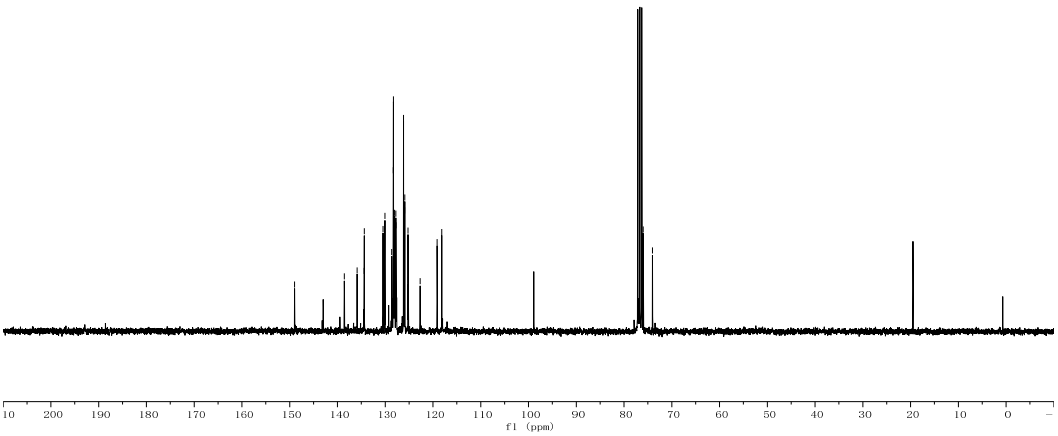


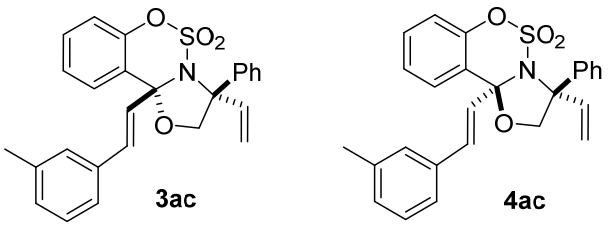
3ab

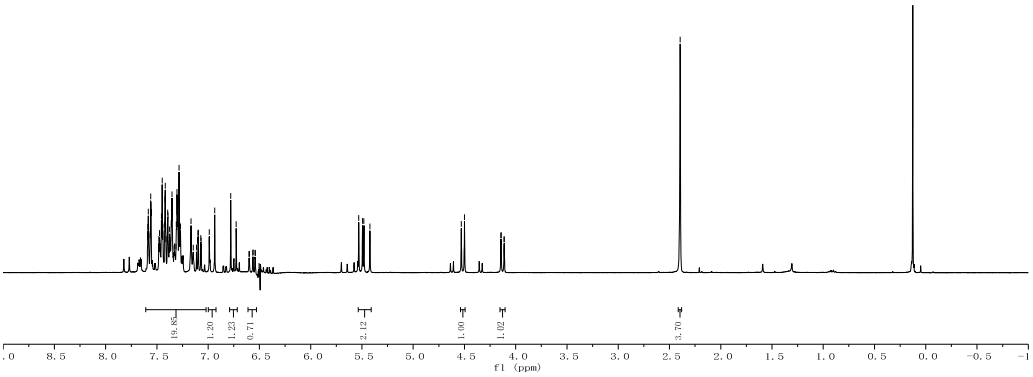


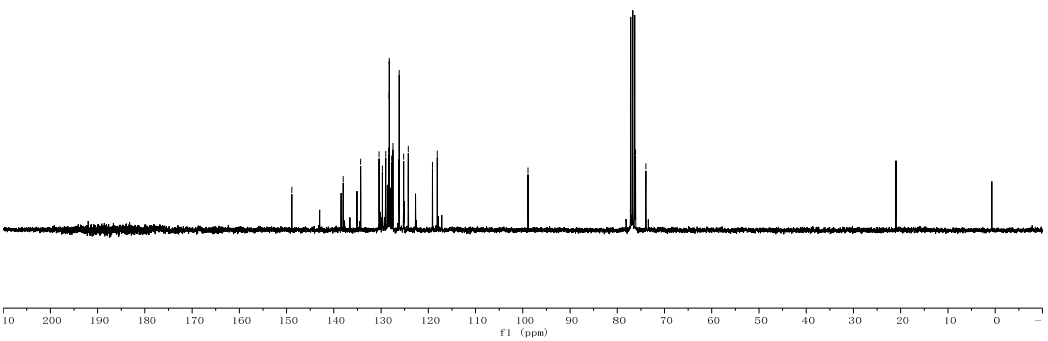
4ab

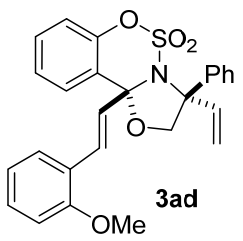




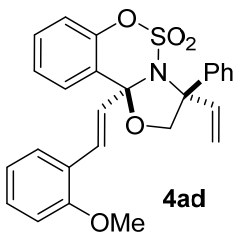

O
SO2
N
Ph
O
3ac
4ac


19.85
1.20
1.23
0.71
2.12
1.00
1.02
3.70
f1 (ppm)

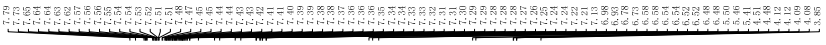

f1 (ppm)

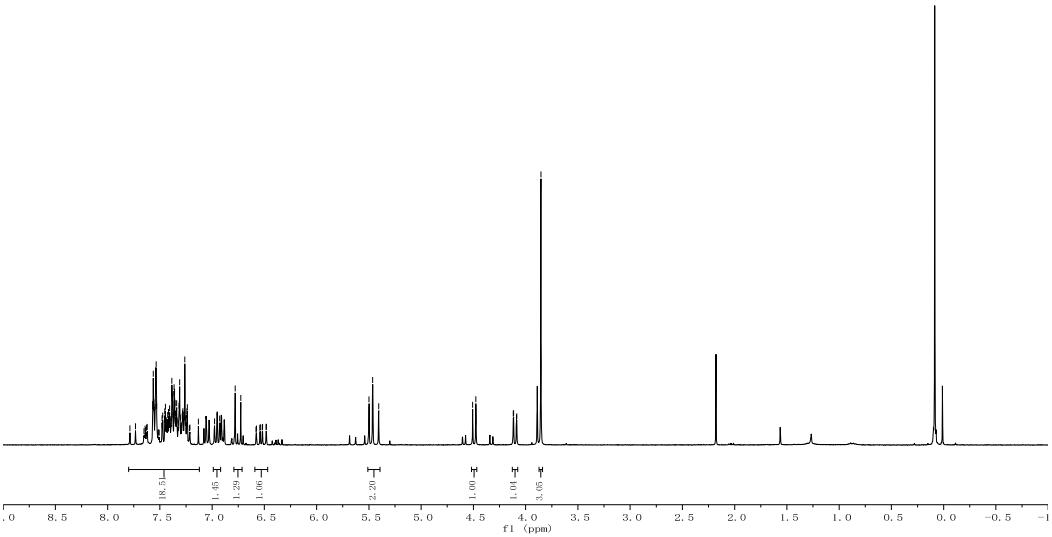

O
SO2
N
Ph
O
OMe

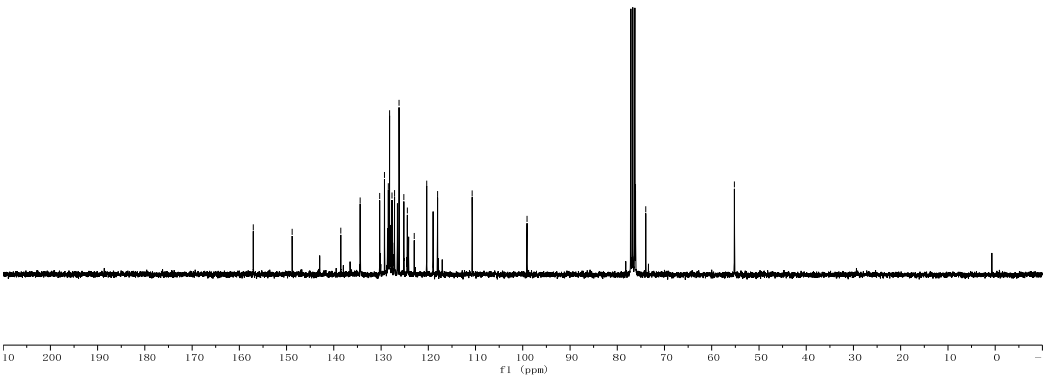
3ad

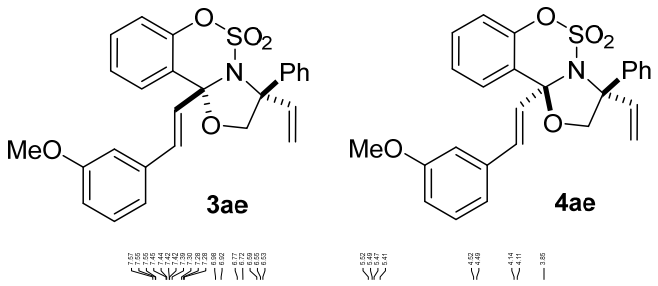

O
SO2
N
Ph
O
OMe

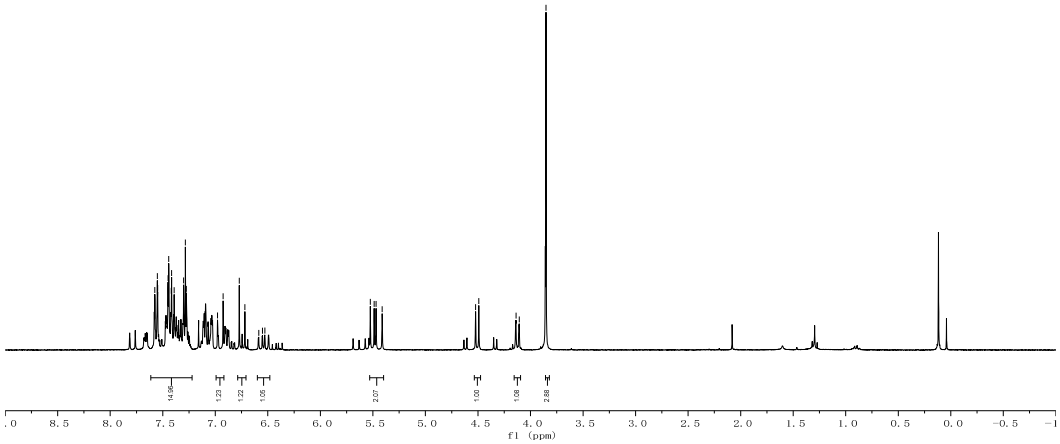
4ad

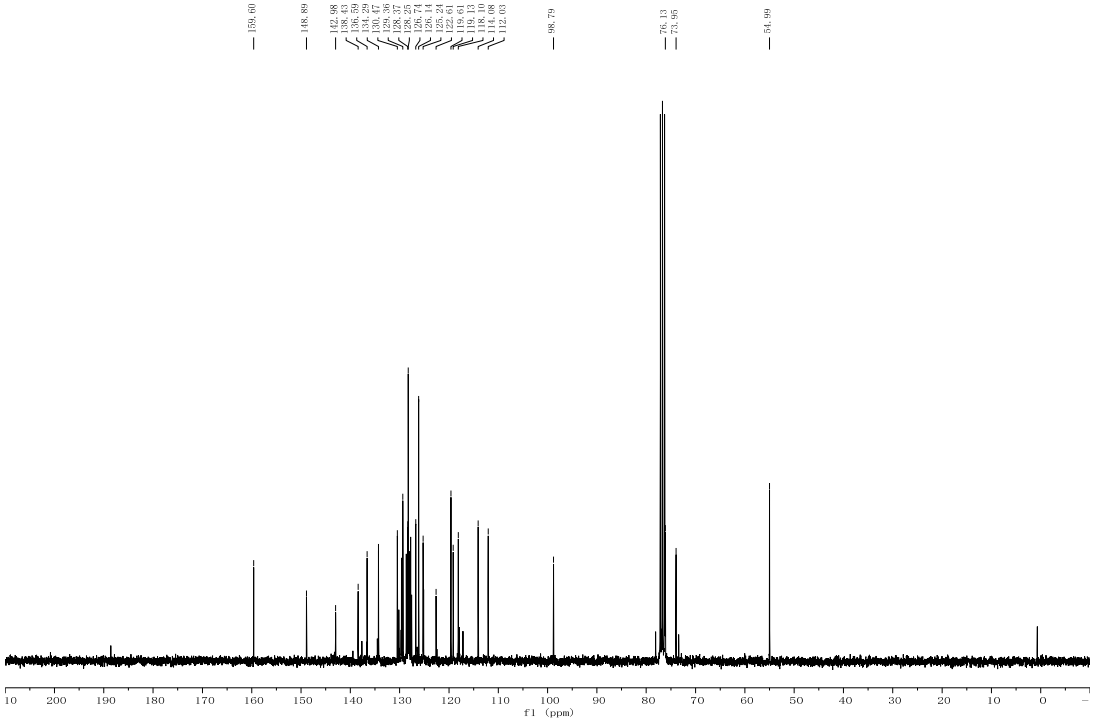


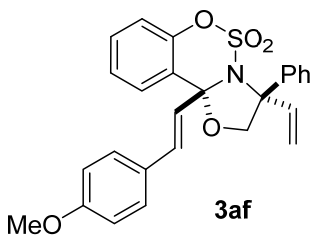

18.51
1.45
1.29
1.06
2.20
1.00
1.04
3.05
f1 (ppm)


f1 (ppm)

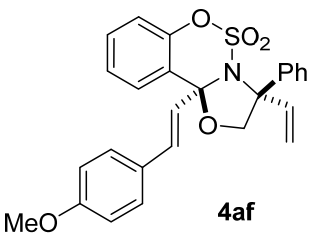

O
SO2
N
Ph
O
MeO
3ae
O
SO2
N
Ph
O
MeO
4ae


f1 (ppm)

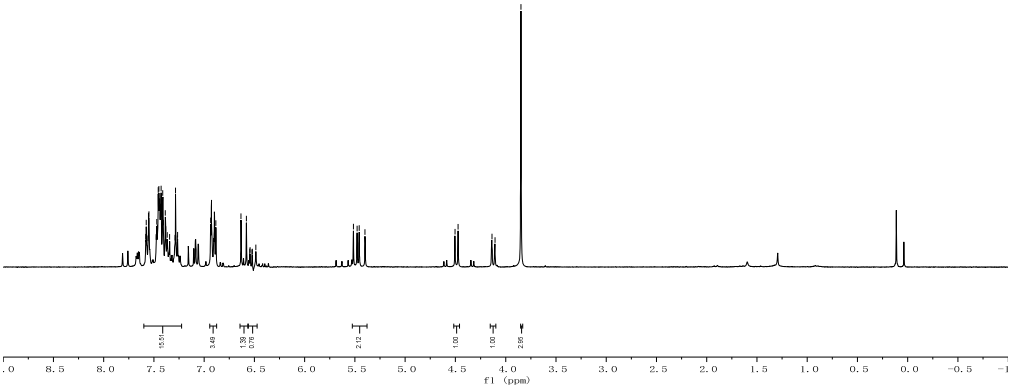

159.60
148.89
142.98
138.43
136.39
134.29
130.47
129.36
128.57
126.55
126.74
126.14
125.24
122.61
119.61
119.13
118.10
114.08
112.03
98.79
76.13
73.85
54.99
f1 (ppm)

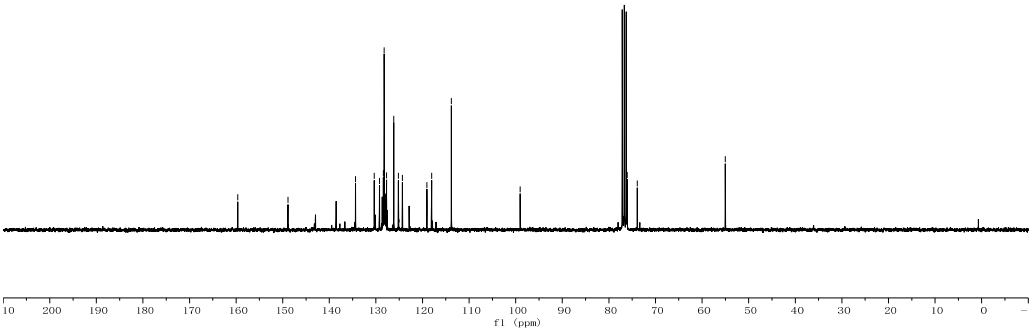


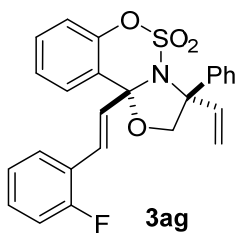
3af



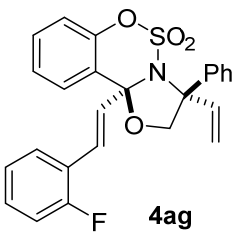
4af



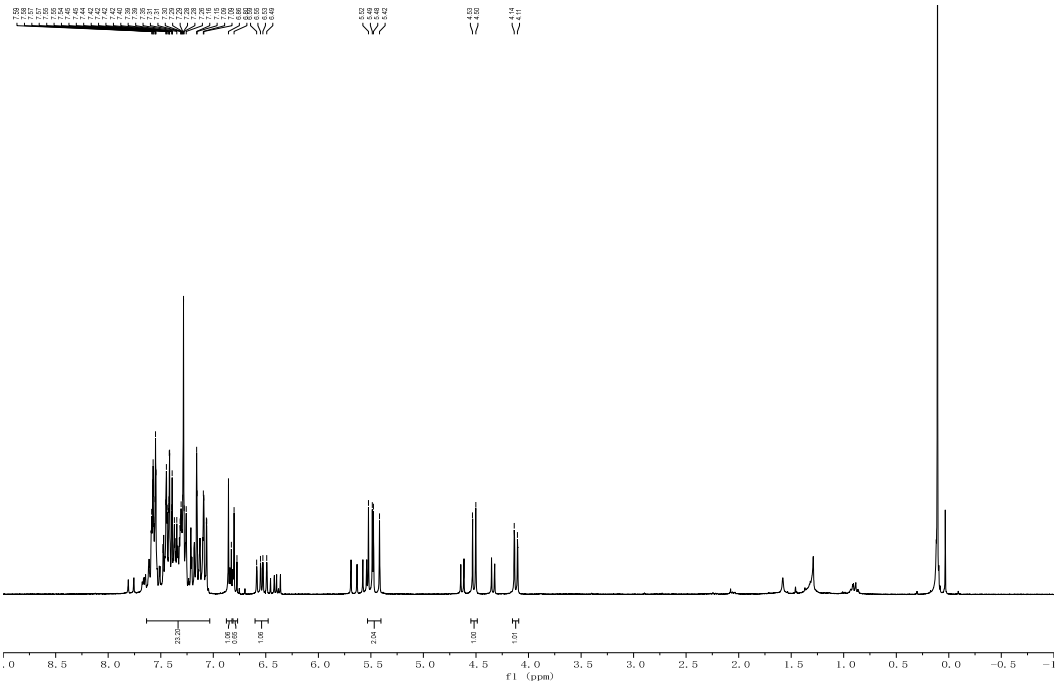


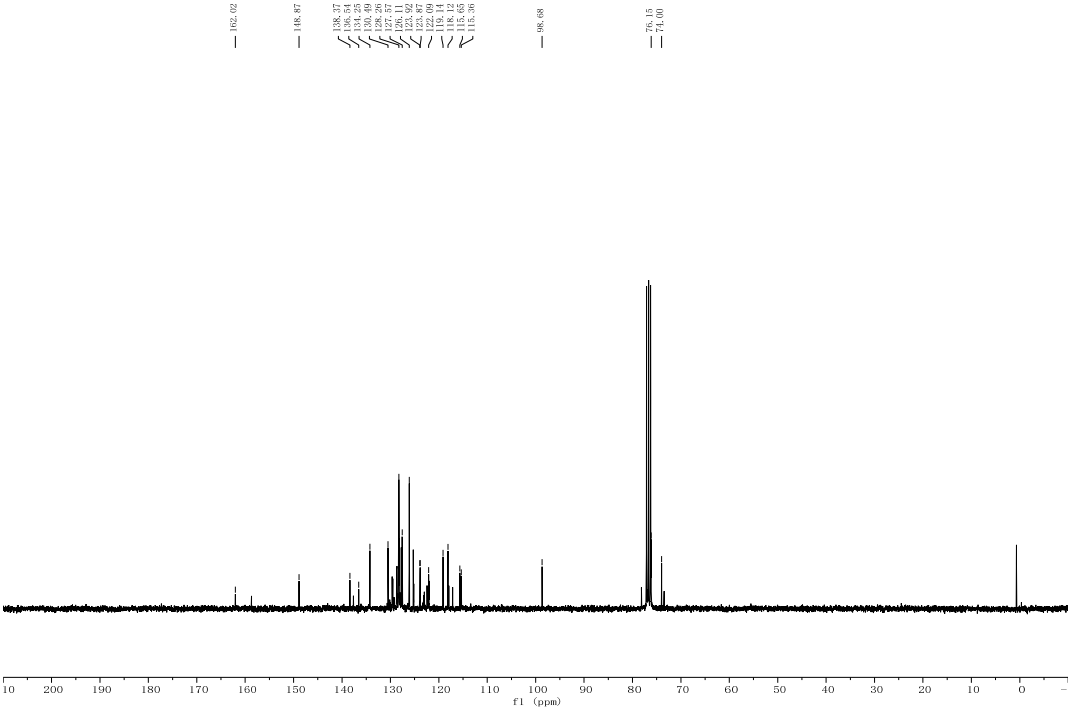


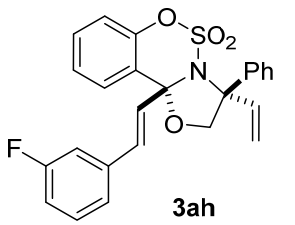
3ag



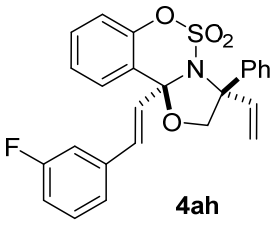
4ag



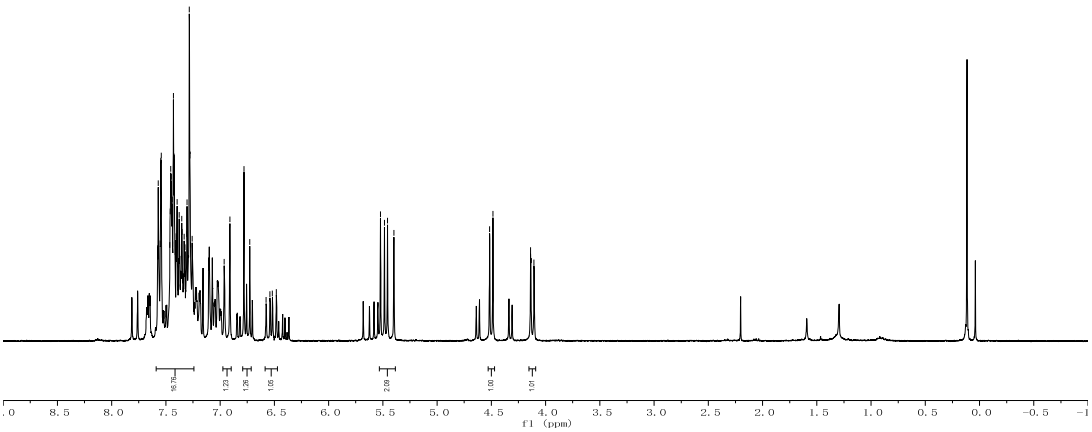


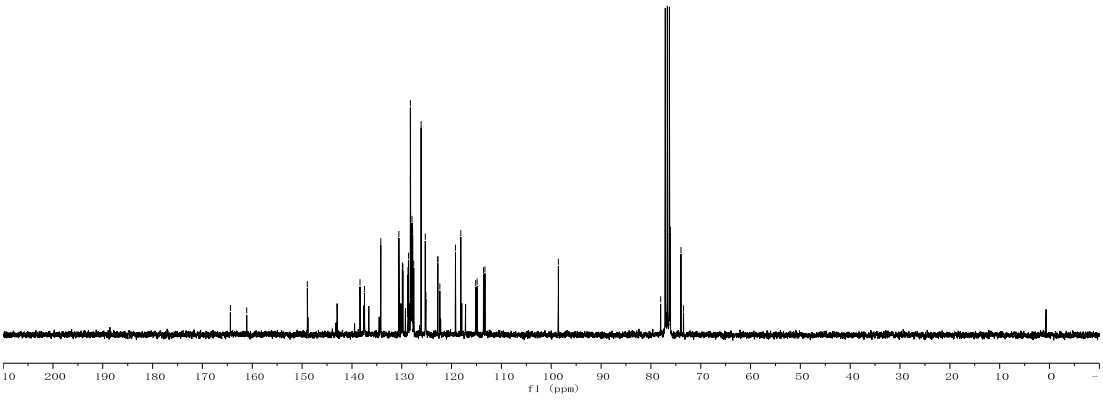


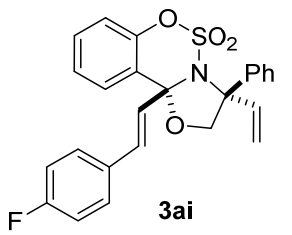
3ah



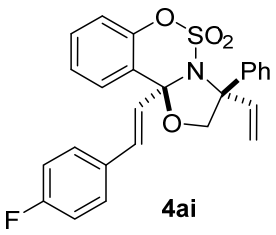
4ah



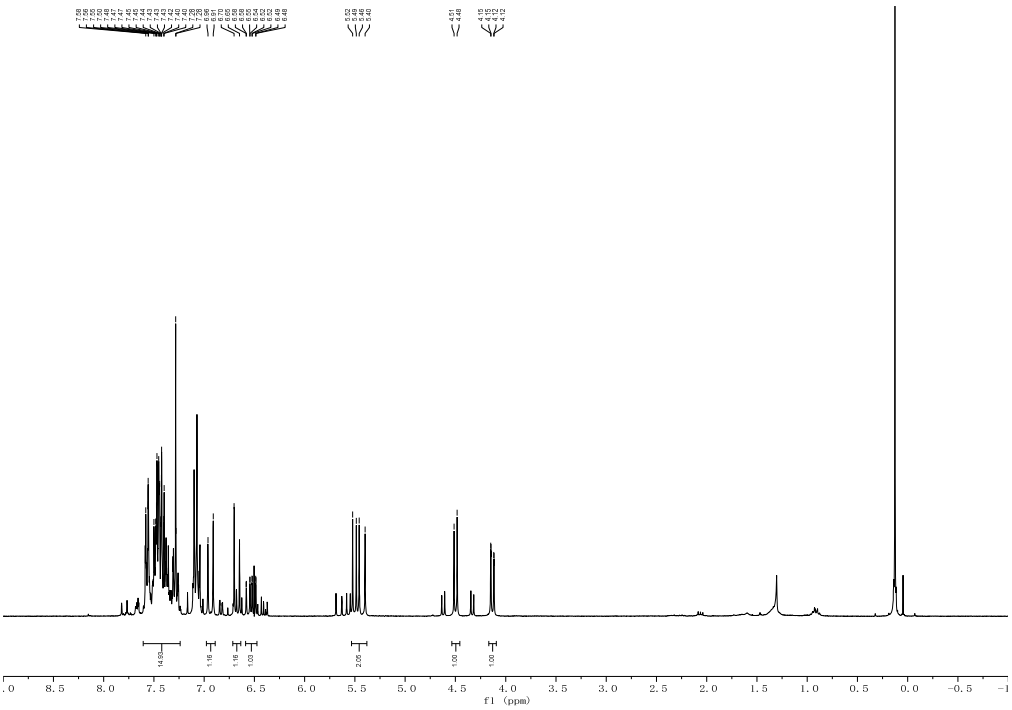


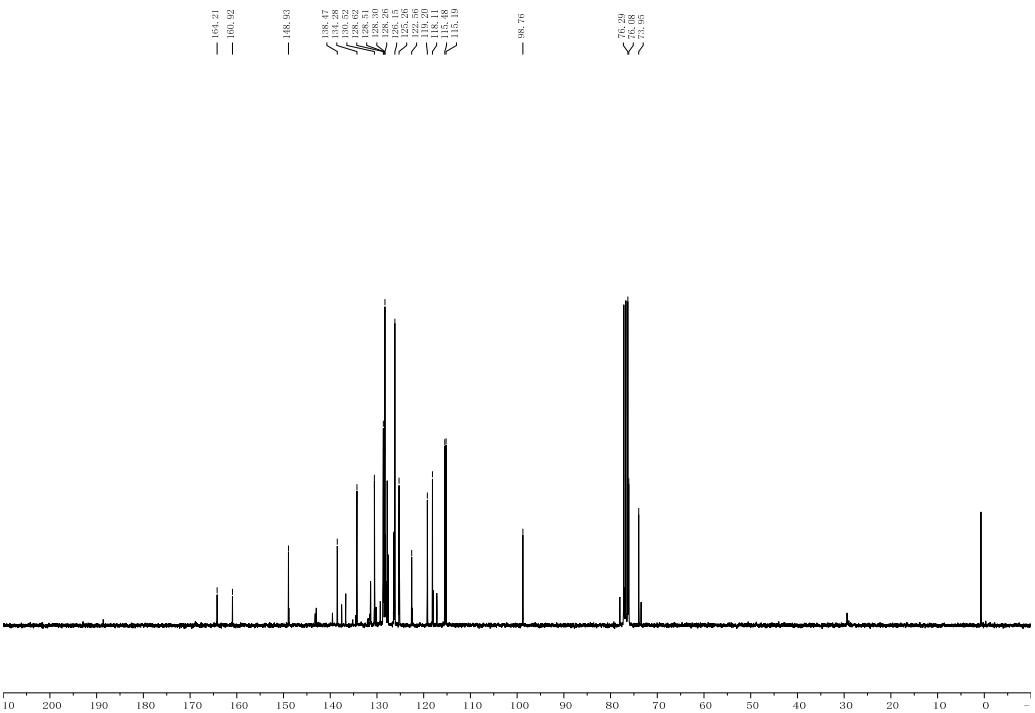


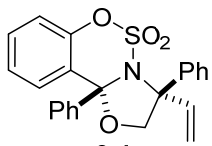
3ai



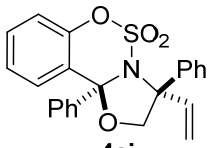
4ai



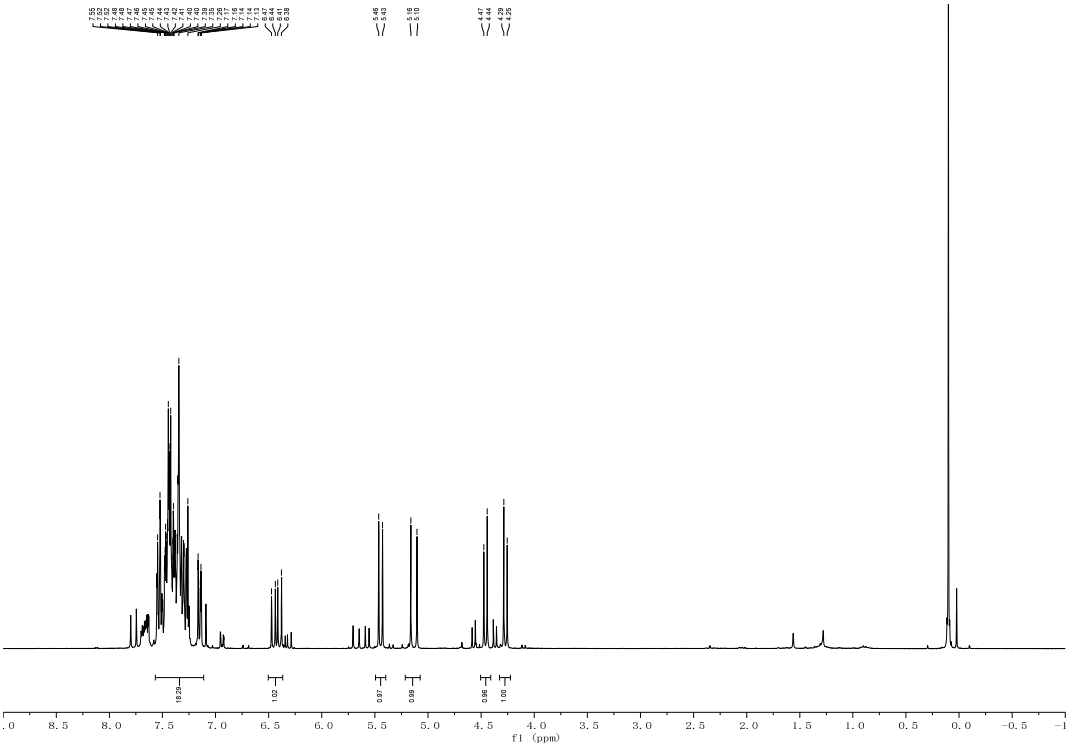


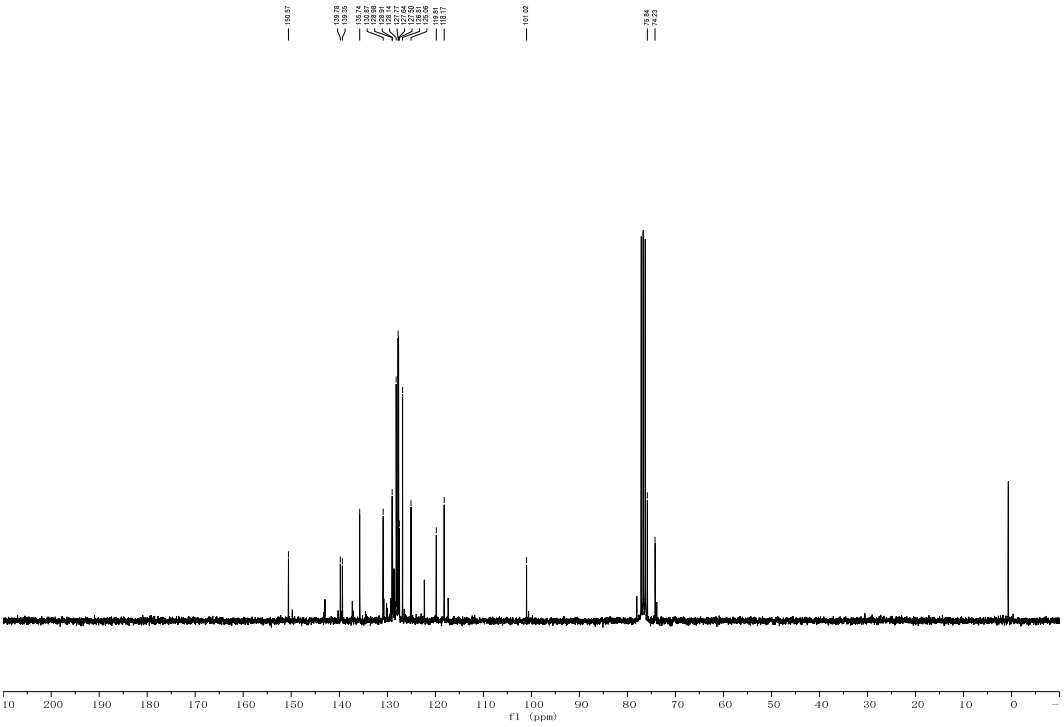


3aj

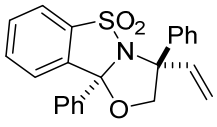


4aj

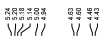


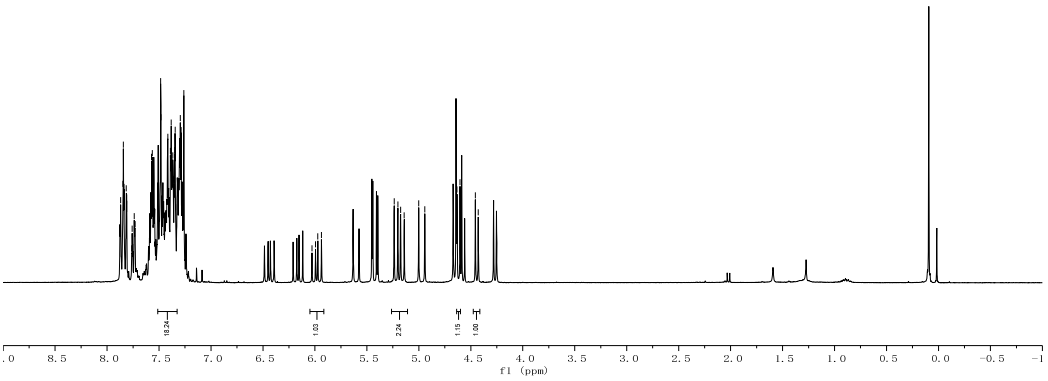


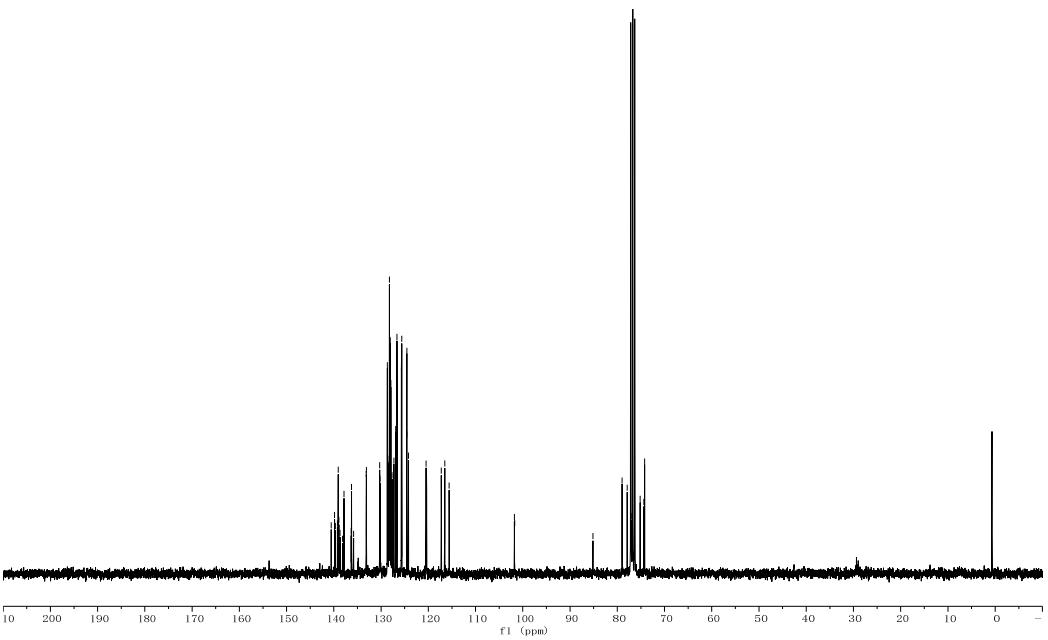
3am

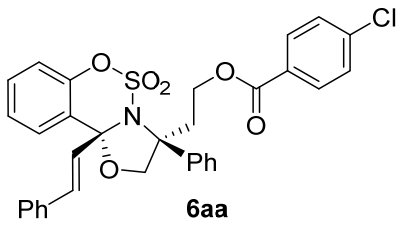


4am

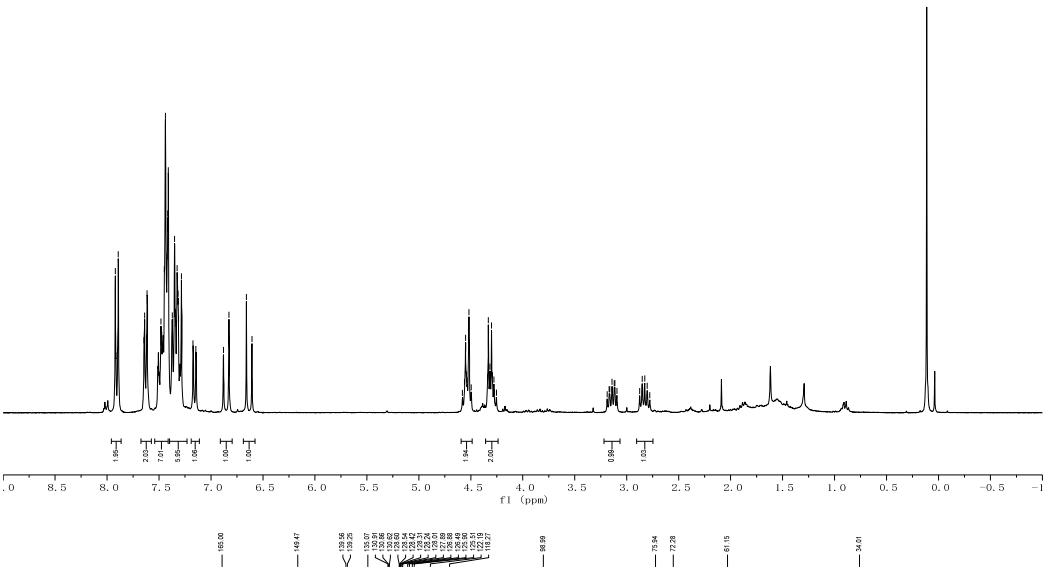


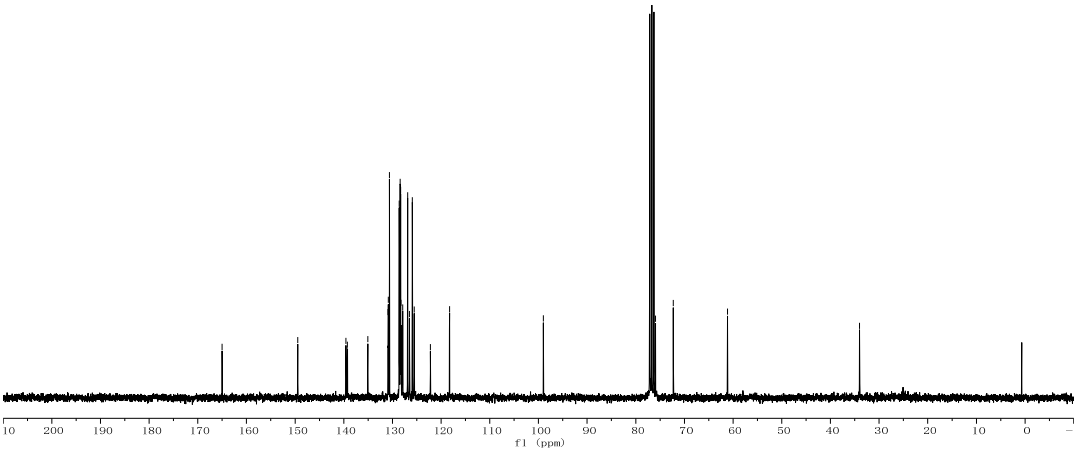






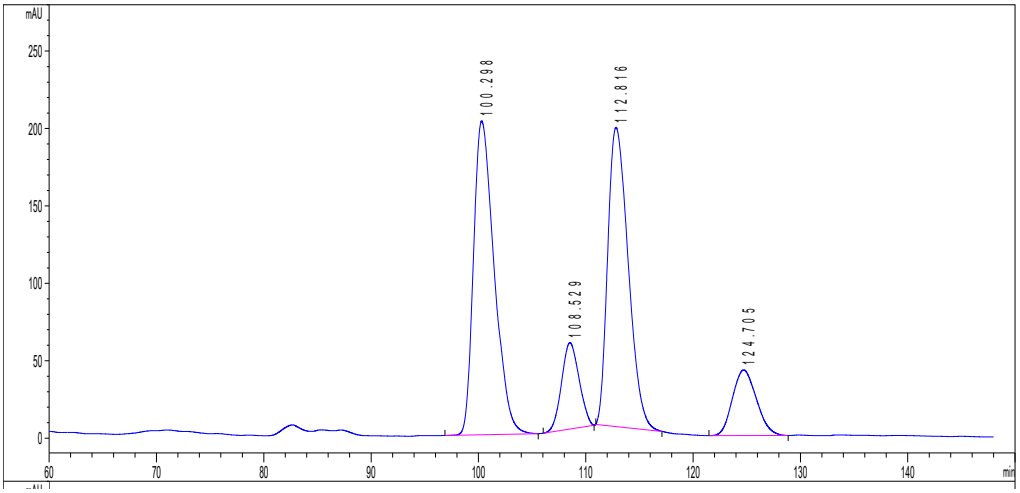
6aa





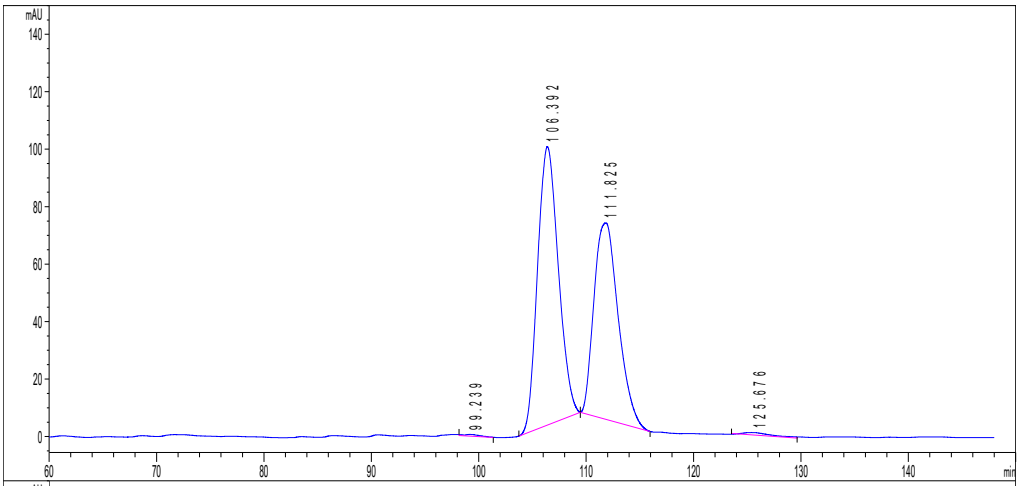
HPLC Chromatograms of Chiral Products

HPLC chromatogram of racemic product 3aa/4aa



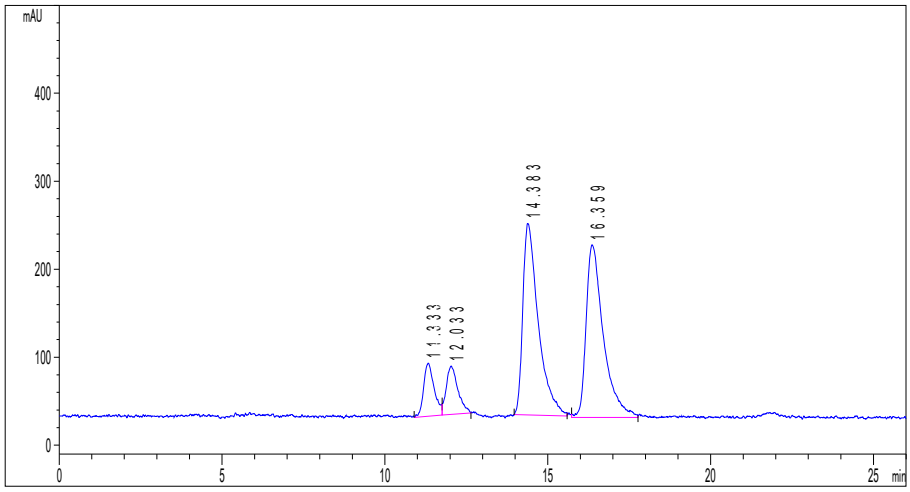
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	100.298	BB	1.7781	2.71460e4	202.61336	41.3486
2	108.529	BB	1.5388	6328.89258	55.77676	9.6401
3	112.816	MM	2.2092	2.56138e4	193.23625	39.0148
4	124.705	BB	2.0176	6562.81787	42.42738	9.9965

HPLC chromatogram of chiral product 3aa/4aa



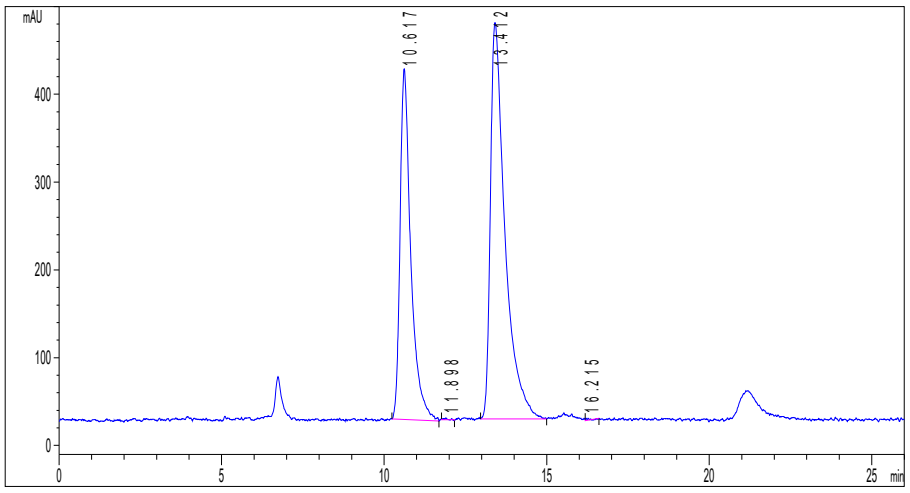
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	99.239	MM	1.7039	61.32920	5.99888e-1	0.2556
2	106.392	BB	1.7810	1.30444e4	96.93005	54.3677
3	111.825	BB	2.0031	1.07252e4	68.37218	44.7015
4	125.676	MM	3.1006	162.01898	8.70909e-1	0.6753

HPLC chromatogram of racemic product 3ba/4ba



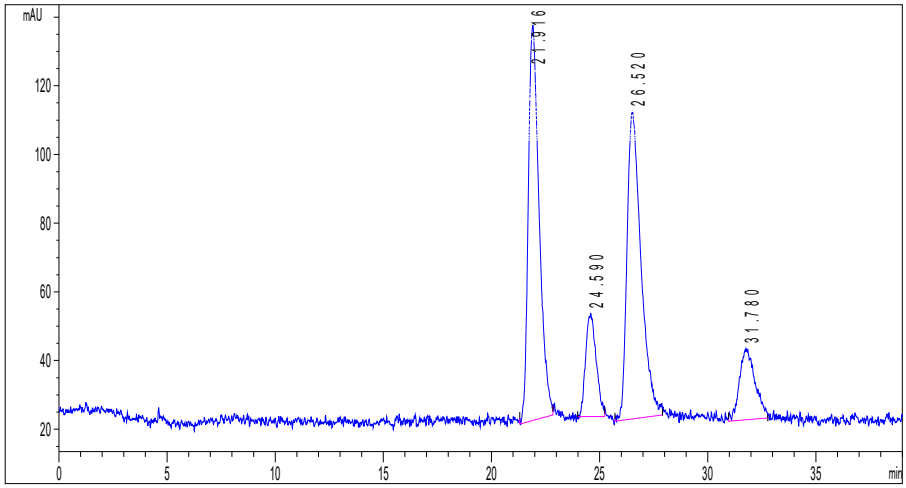
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.333	MF	0.3756	1359.37292	60.32086	7.9436
2	12.033	FM	0.4123	1358.48340	54.91198	7.9384
3	14.383	MM	0.5503	7178.85205	217.42143	41.9504
4	16.359	MM	0.6131	7215.99707	196.17076	42.1675

HPLC chromatogram of chiral product 3ba/4ba



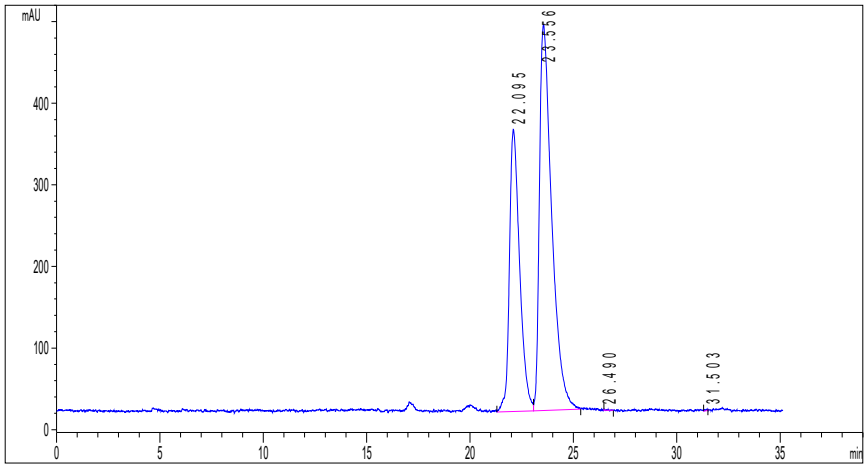
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.617	BB	0.3388	9207.27539	399.43372	39.5130
2	11.898	MM	0.1366	16.48657	2.01195	0.0708
3	13.412	BB	0.4420	1.40649e4	451.55917	60.3595
4	16.215	MM	0.0873	13.23342	2.52653	0.0568

HPLC chromatogram of racemic product 3ca/4ca



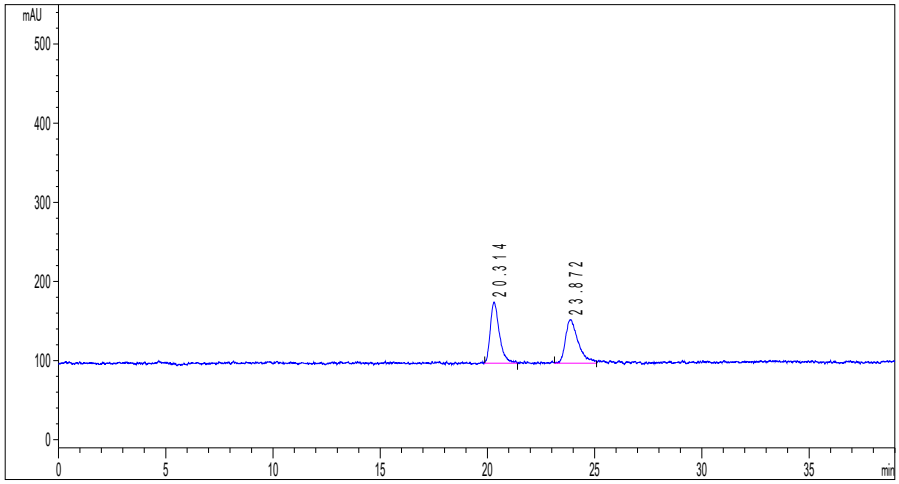
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.916	MM	0.5802	4010.97461	115.22775	39.7626
2	24.590	MM	0.5633	1016.74945	30.08115	10.0795
3	26.520	MM	0.7482	4020.45020	89.55573	39.8566
4	31.780	MM	0.8352	1039.12341	20.73482	10.3013

HPLC chromatogram of chiral product 3ca/4ca



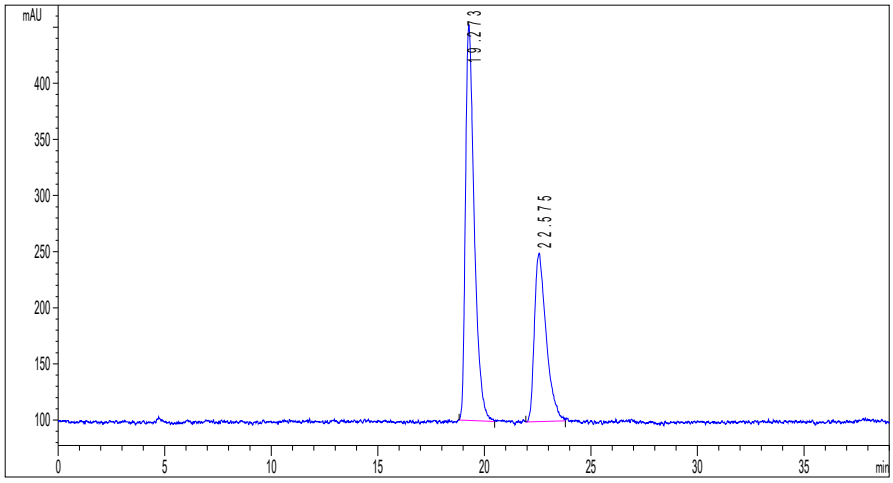
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.095	BV	0.4963	1.18530e4	345.50513	37.7203
2	23.556	VB	0.5958	1.95473e4	472.91193	62.2064
3	26.490	MM	0.0898	8.58268	1.59240	0.0273
4	31.503	MM	0.1471	14.43083	1.63474	0.0459

HPLC chromatogram of racemic product 3ta



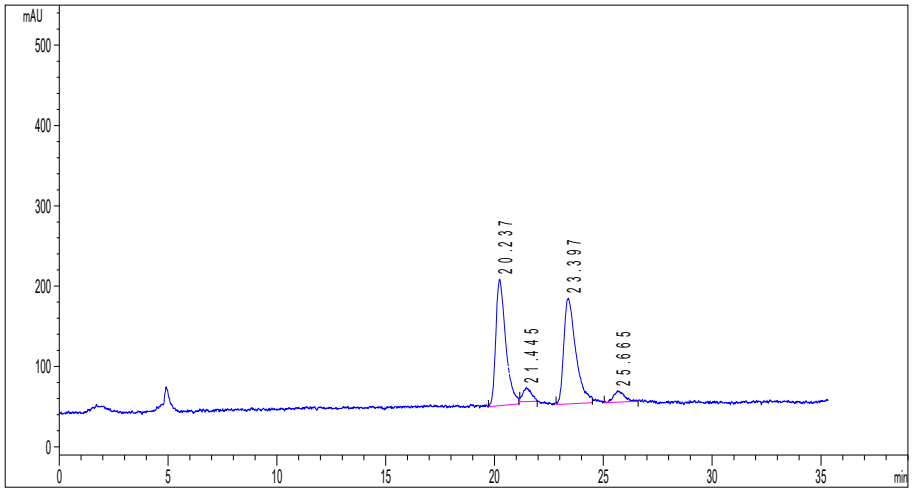
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.314	BB	0.3799	2251.06274	77.43117	52.3786
2	23.875	BB	0.4807	2046.61243	53.56918	47.6214

HPLC chromatogram of chiral product 3ta



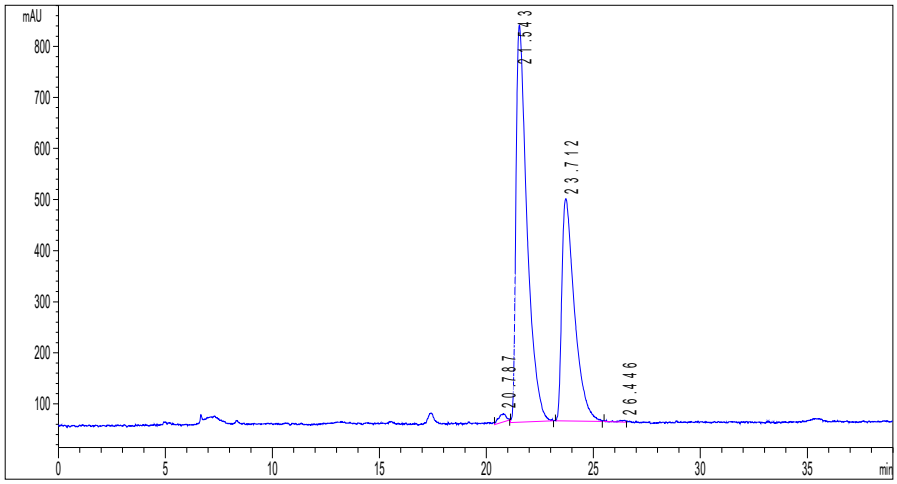
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.273	BB	0.4375	1.01342e4	352.32736	63.6886
2	22.575	BB	0.4783	5777.88867	150.08334	36.3114

HPLC chromatogram of racemic product 3ab/4ab



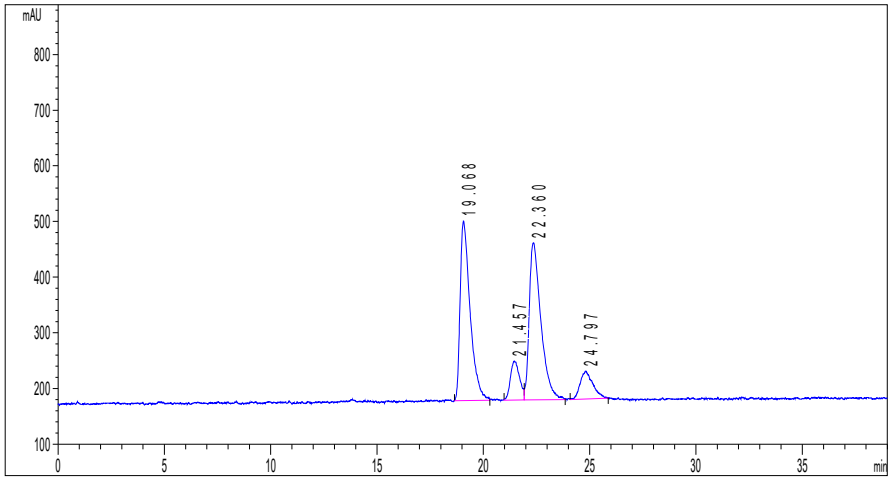
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.237	MF	0.5301	5008.47607	157.45973	45.6536
2	21.445	MM	0.4657	462.97946	16.57078	4.2202
3	23.397	MM	0.6371	5017.96729	131.27850	45.7401
4	25.665	MM	0.5596	481.17493	14.33189	4.3860

HPLC chromatogram of chiral product 3ab/4ab



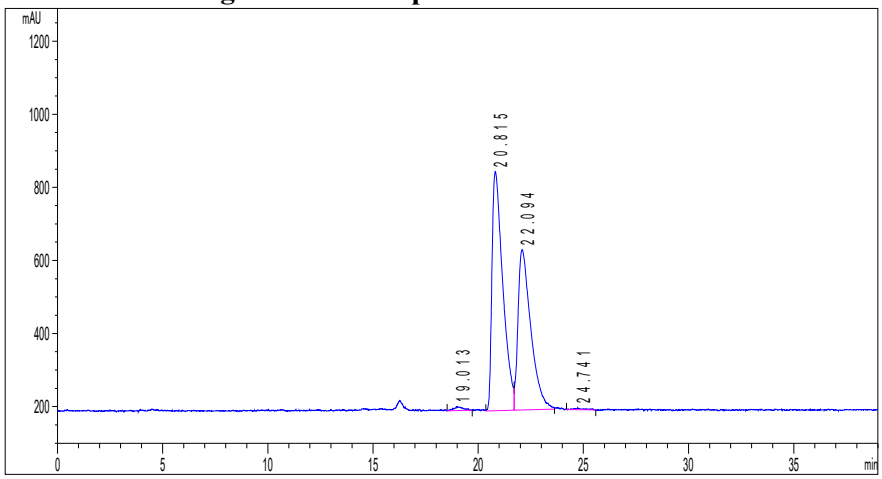
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.787	MM	0.4101	399.08279	16.21980	0.8605
2	21.543	VB	0.5186	2.79636e4	777.50293	60.2947
3	23.712	BB	0.5735	1.79307e4	435.54614	38.6619
4	26.446	MM	0.3603	84.84118	3.92435	0.1829

HPLC chromatogram of racemic product 3ac/4ac



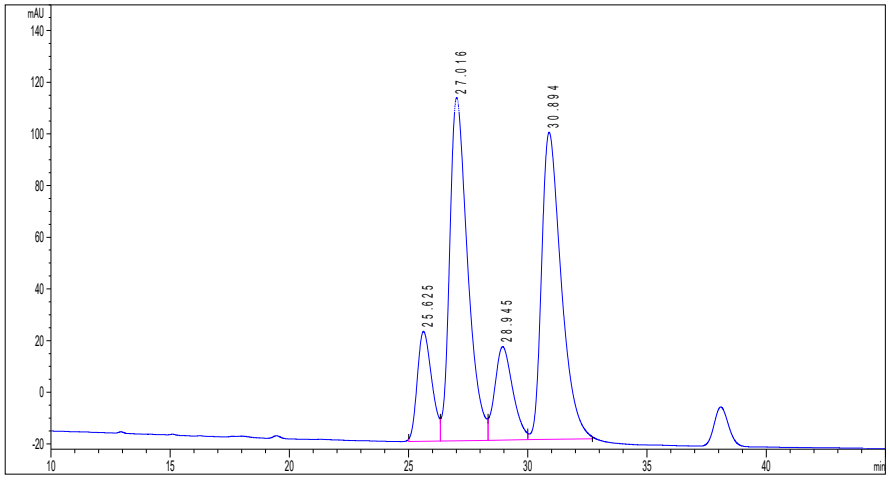
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.068	MM	0.5425	1.04973e4	322.50360	41.2892
2	21.457	MF	0.5019	2101.33350	69.78432	8.2652
3	22.360	FM	0.6353	1.07544e4	282.13275	42.3003
4	24.797	MM	0.6913	2070.84521	49.92407	8.1453

HPLC chromatogram of chiral product 3ac/4ac



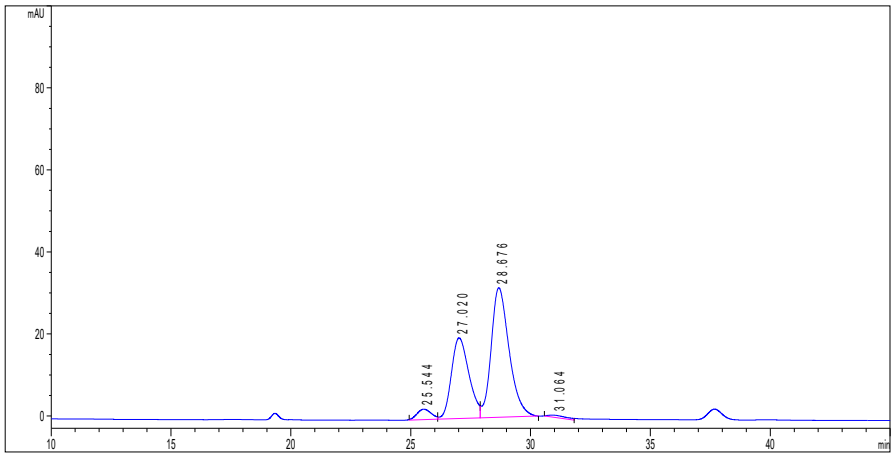
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.013	MM	0.5295	314.36743	9.89570	0.7405
2	20.815	MF	0.5968	2.34415e4	654.68854	55.2145
3	22.094	FM	0.7056	1.85540e4	438.27191	43.7025
4	24.741	MM	0.5433	145.43018	4.46119	0.3425

HPLC chromatogram of racemic product 3ae/4ae



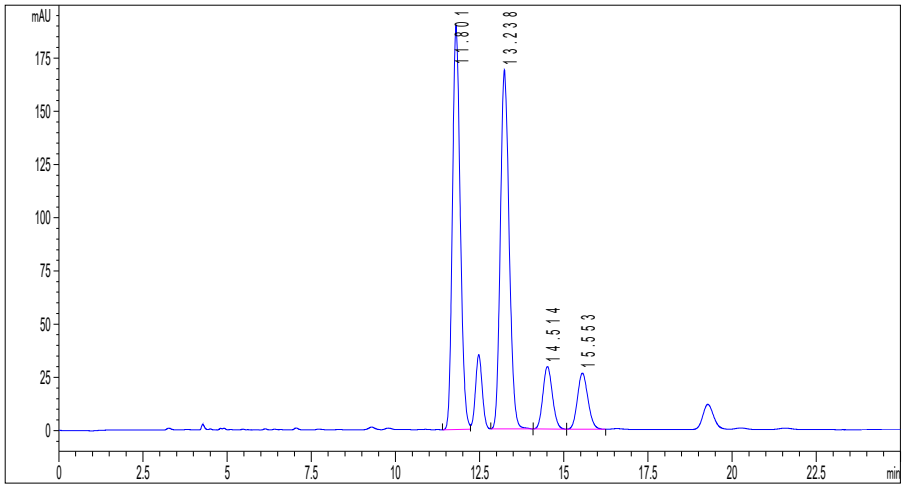
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.625	MF	0.7042	1795.85510	42.50170	10.2922
2	27.016	MF	0.8724	6954.01270	132.85303	39.8542
3	28.945	MF	0.8728	1893.88379	36.16375	10.8540
4	30.894	FM	0.9540	6804.90137	118.88712	38.9996

HPLC chromatogram of chiral product 3ae/4ae



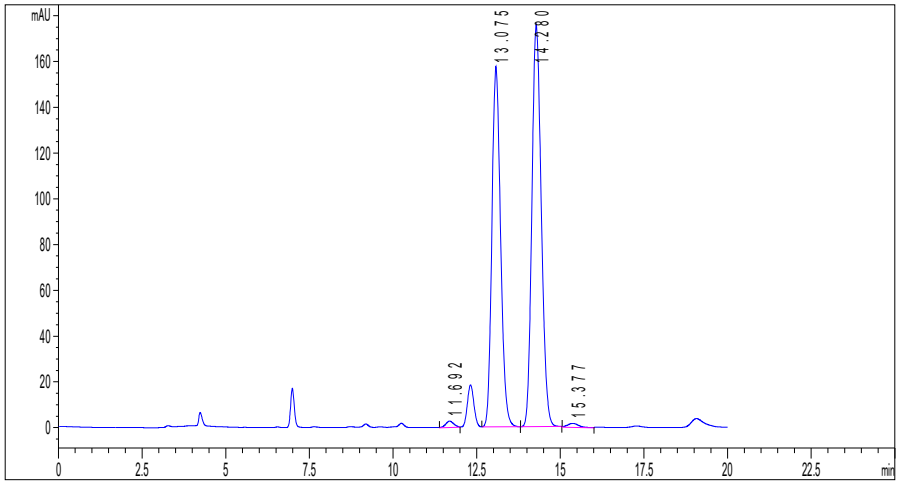
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.544	MF	0.6853	105.58092	2.56778	3.7898
2	27.020	MF	0.8488	1002.38708	19.68298	35.9804
3	28.676	FM	0.8685	1646.56836	31.59737	59.1031
4	31.064	MM	0.9352	31.38754	5.59347e-1	1.1266

HPLC chromatogram of racemic product 3af/4af



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.801	BV	0.2504	3065.61987	189.87392	42.1032
2	13.238	BB	0.2842	3068.18530	168.66493	42.1384
3	14.514	BB	0.3072	577.28870	29.39074	7.9285
4	15.553	BB	0.3367	570.11768	26.32134	7.8300

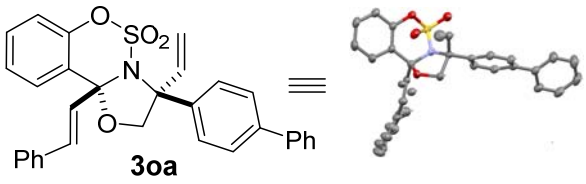
HPLC chromatogram of chiral product 3af/4af



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.317	MM	0.2318	265.00836	19.05628	4.0170
2	13.075	BB	0.2810	2848.29395	157.45146	43.1742
3	14.280	BB	0.3055	3424.86475	175.61397	51.9139
4	15.444	MM	0.3386	59.03835	2.90611	0.8949

X-Ray Crystallographic Data

Crystallographic data for **3oa**, **4ba** and **6aa** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 1891975, 1916284 and 1916285. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



3oa

Table S3. Crystal data and structure refinement for **3oa**.

Identification code	**3oa**
Empirical formula	$C_{31}H_{25}NO_4S$
Formula weight	507.58
Temperature/K	153.15
Crystal system	triclinic
Space group	P-1
a/Å	7.6699(15)
b/Å	11.185(2)
c/Å	14.839(3)
α/°	97.37(3)
β/°	95.12(3)
γ/°	94.17(3)
Volume/Å^3	1252.9(4)
Z	2
ρ_{calc}g/cm^3	1.345
μ/mm^{-1}	0.168
F(000)	532.0
Crystal size/mm^3	0.23 × 0.21 × 0.19
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.782 to 54.982
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 14, -19 ≤ l ≤ 18
Reflections collected	11494
Independent reflections	5668 [R_{int} = 0.0307, R_{sigma} = 0.0422]
Data/restraints/parameters	5668/310/407
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.1092
Final R indexes [all data]	R_1 = 0.0610, wR_2 = 0.1138
Largest diff. peak/hole / e Å^{-3}	0.27/-0.42

Table S4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3oa**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	3282.1(6)	905.3(4)	2098.7(3)	28.08(12)
O1	3734.6(17)	-444.7(11)	2226.4(9)	28.8(3)
O2	4575.2(17)	1698.8(12)	2671.6(10)	35.8(3)
O3	3064.0(18)	921.1(13)	1144.7(10)	35.4(3)
O4	-325.0(17)	267.6(13)	3524.2(9)	33.0(3)
N1	1431.1(19)	1024.7(14)	2524.7(10)	25.2(3)
C1	3669(2)	-738.4(16)	3120.0(13)	26.4(4)
C2	4671(3)	-1659.4(17)	3339.4(14)	31.9(4)
C3	4645(3)	-2016.3(19)	4197.6(15)	36.9(5)
C4	3660(3)	-1432(2)	4831.9(15)	39.9(5)
C5	2682(3)	-503(2)	4599.7(14)	36.2(5)
C6	2638(2)	-158.6(17)	3732.1(13)	27.6(4)
C7	1414(2)	793.1(18)	3494.2(12)	28.1(4)
C8	1864(4)	2021(3)	4080.3(19)	25.1(6)
C9	904(3)	2428(2)	4739.7(17)	29.8(6)
C10	1313(4)	3543(3)	5386(3)	30.7(7)
C11	2462(5)	4498(3)	5232(3)	40.3(8)
C12	2871(9)	5503(5)	5903(4)	46.6(12)
C13	2146(10)	5560(6)	6719(4)	45.3(11)
C14	970(6)	4644(4)	6863(3)	51.8(10)
C15	550(5)	3638(3)	6207(2)	43.2(8)
C16	-1412(2)	681.1(19)	2815.9(13)	30.0(4)
C17	-324(2)	609.0(16)	1993.3(12)	24.6(4)
C18	-941(3)	-1670(2)	1737.7(18)	47.3(6)
C19	-324(2)	-655.0(16)	1482.5(13)	28.5(4)
C20	-896(2)	1514.2(16)	1367.7(12)	24.0(4)
C21	-200(2)	2714.5(17)	1515.7(13)	28.0(4)
C22	-784(2)	3531.6(17)	957.2(13)	27.9(4)
C23	-2091(2)	3189.1(17)	239.0(13)	27.1(4)
C24	-2808(3)	1989.5(17)	104.0(14)	30.9(4)

C25	-2212(2)	1165.4(17)	657.6(13)	28.5(4)
C26	-2690(2)	4077.9(17)	-356.9(14)	29.6(4)
C27	-2838(3)	5277.0(17)	3.7(15)	33.7(4)
C28	-3434(3)	6101.2(19)	-547.8(17)	40.6(5)
C29	-3901(3)	5749(2)	-1466.1(18)	46.3(6)
C30	-3746(3)	4572(2)	-1839.5(18)	50.5(6)
C31	-3131(3)	3739.9(19)	-1289.2(15)	41.2(5)
C8A	1447(15)	1689(11)	4333(7)	26(2)
C9A	1576(13)	2819(10)	4245(7)	33(2)
C10A	1722(17)	3786(12)	5063(9)	31(2)
C15A	983(19)	3589(12)	5839(11)	39(2)
C14A	1300(20)	4447(16)	6619(11)	47(2)
C13A	2370(40)	5520(30)	6570(20)	45(3)
C12A	3110(40)	5670(20)	5769(16)	43(3)
C11A	2730(20)	4822(14)	5021(11)	42(3)

Table S5. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3oa**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	20.9(2)	27.4(2)	37.5(3)	8.67(19)	4.12(18)	3.78(17)
O1	29.6(7)	27.7(7)	31.1(7)	6.0(5)	6.6(5)	8.9(5)
O2	22.5(7)	31.9(7)	52.0(9)	7.1(6)	-1.7(6)	-0.5(6)
O3	31.2(7)	43.2(8)	36.2(8)	15.7(6)	9.0(6)	7.9(6)
O4	22.8(6)	52.2(9)	26.7(7)	11.7(6)	3.2(5)	9.1(6)
N1	19.4(7)	26.8(7)	28.9(8)	3.2(6)	-0.1(6)	3.4(6)
C1	23.6(9)	26.7(9)	28.4(9)	4.6(7)	-1.6(7)	2.0(7)
C2	27.0(9)	27.3(9)	40.3(11)	3.5(8)	-1.7(8)	3.6(8)
C3	31.2(10)	35.2(11)	43.8(12)	12.0(9)	-9.6(9)	4.3(9)
C4	35.2(11)	51.8(13)	34.2(11)	16.3(10)	-3.4(9)	4.1(10)
C5	29.5(10)	50.9(13)	29.1(10)	7.9(9)	0.7(8)	8.2(9)
C6	23.5(9)	30.6(9)	27.9(9)	3.5(8)	-2.8(7)	4.3(7)
C7	22.8(9)	36.5(10)	24.8(9)	1.2(8)	0.6(7)	7.2(8)
C8	25.9(13)	26.3(14)	24.2(13)	6.8(10)	1.4(10)	4.8(10)

C9	26.4(12)	30.5(12)	31.7(13)	0.4(10)	3.8(10)	3.2(10)
C10	27.8(15)	29.7(14)	34.8(18)	1.6(13)	3.2(13)	7.4(11)
C11	43.4(18)	32.8(18)	46.1(19)	2.8(14)	12.9(14)	6.9(15)
C12	50(3)	30(2)	59(3)	0.8(17)	9.1(19)	2.9(16)
C13	50(3)	35.0(16)	47(3)	-8.7(17)	-1.1(17)	10.1(16)
C14	62(2)	49(2)	40.5(19)	-12.0(15)	10.1(16)	3.4(16)
C15	44.8(17)	43.8(16)	38.6(18)	-5.2(14)	10.9(14)	-1.9(13)
C16	21.5(9)	41.2(11)	28.3(10)	7.9(8)	0.7(7)	6.3(8)
C17	20.1(8)	27.2(9)	26.5(9)	4.5(7)	1.2(7)	2.7(7)
C18	56.0(15)	29.1(11)	55.6(15)	4.4(10)	5.3(12)	-2.4(10)
C19	26.6(9)	27.3(9)	30.5(10)	1.5(8)	-0.8(7)	3.5(7)
C20	21.8(8)	25.7(9)	25.2(9)	4.5(7)	3.3(7)	4.8(7)
C21	25.9(9)	28.0(9)	28.8(10)	3.1(7)	-0.9(7)	0.3(7)
C22	26.8(9)	24.0(9)	32.8(10)	2.9(7)	3.3(8)	1.6(7)
C23	25.0(9)	27.6(9)	30.1(10)	5.3(7)	5.2(7)	6.5(7)
C24	28.3(9)	28.2(9)	34.9(10)	3.4(8)	-5.1(8)	4.1(8)
C25	26.7(9)	24.1(9)	33.6(10)	3.0(7)	-1.6(8)	1.9(7)
C26	24.4(9)	27.5(9)	37.8(11)	7.9(8)	1.7(8)	4.3(7)
C27	26.7(9)	28.1(10)	47.7(12)	8.4(9)	6.1(9)	3.7(8)
C28	29.9(10)	27.6(10)	68.0(16)	17.0(10)	7.3(10)	5.0(8)
C29	34.1(11)	38.9(12)	68.4(17)	27.6(12)	-7.8(11)	0.4(9)
C30	58.4(15)	43.5(13)	48.1(14)	16.8(11)	-14.4(12)	-1.0(11)
C31	48.4(13)	31.8(11)	42.2(12)	7.9(9)	-7.2(10)	4.6(10)
C8A	21(4)	35(4)	25(4)	6(3)	7(3)	6(3)
C9A	31(4)	36(4)	32(4)	2(3)	4(3)	9(3)
C10A	28(4)	28(4)	36(4)	4(4)	2(4)	3(3)
C15A	39(4)	36(4)	40(5)	0(4)	13(4)	-7(4)
C14A	52(4)	45(4)	43(4)	-4(4)	16(4)	3(4)
C13A	51(4)	35(4)	46(5)	-9(4)	3(4)	5(4)
C12A	47(4)	33(4)	48(4)	0(4)	9(4)	1(4)
C11A	44(4)	37(5)	45(4)	4(4)	8(4)	3(4)

Table S6. Bond Lengths for **3oa**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.6045(14)	C16	C17	1.536(3)
S1	O2	1.4219(15)	C17	C19	1.516(2)
S1	O3	1.4130(15)	C17	C20	1.521(2)
S1	N1	1.6123(16)	C18	C19	1.312(3)
O1	C1	1.411(2)	C20	C21	1.391(2)
O4	C7	1.425(2)	C20	C25	1.389(3)
O4	C16	1.427(2)	C21	C22	1.382(3)
N1	C7	1.495(2)	C22	C23	1.391(3)
N1	C17	1.509(2)	C23	C24	1.395(3)
C1	C2	1.384(3)	C23	C26	1.484(3)
C1	C6	1.386(3)	C24	C25	1.387(3)
C2	C3	1.384(3)	C26	C27	1.395(3)
C3	C4	1.388(3)	C26	C31	1.391(3)
C4	C5	1.385(3)	C27	C28	1.384(3)
C5	C6	1.389(3)	C28	C29	1.377(3)
C6	C7	1.524(3)	C29	C30	1.379(3)
C7	C8	1.527(3)	C30	C31	1.394(3)
C7	C8A	1.491(10)	C8A	C9A	1.284(17)
C8	C9	1.330(4)	C9A	C10A	1.508(13)
C9	C10	1.469(4)	C10A	C15A	1.364(13)
C10	C11	1.389(4)	C10A	C11A	1.357(13)
C10	C15	1.393(4)	C15A	C14A	1.397(15)
C11	C12	1.400(5)	C14A	C13A	1.423(18)
C12	C13	1.373(6)	C13A	C12A	1.379(18)
C13	C14	1.365(6)	C12A	C11A	1.360(17)
C14	C15	1.388(4)			

Table S7. Bond Angles for **3oa**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	N1	103.65(8)	C13	C14	C15	120.7(4)
O2	S1	O1	106.51(8)	C14	C15	C10	120.8(3)
O2	S1	N1	107.90(9)	O4	C16	C17	104.98(14)
O3	S1	O1	105.34(9)	N1	C17	C16	96.73(14)
O3	S1	O2	121.40(9)	N1	C17	C19	111.45(14)
O3	S1	N1	110.53(9)	N1	C17	C20	111.49(14)
C1	O1	S1	115.01(11)	C19	C17	C16	114.16(16)
C7	O4	C16	107.12(14)	C19	C17	C20	112.24(15)
C7	N1	S1	115.72(12)	C20	C17	C16	109.84(14)
C7	N1	C17	110.52(14)	C18	C19	C17	127.0(2)
C17	N1	S1	123.52(12)	C21	C20	C17	121.64(16)
C2	C1	O1	115.67(17)	C25	C20	C17	119.91(16)
C2	C1	C6	122.18(18)	C25	C20	C21	118.36(17)
C6	C1	O1	122.14(16)	C22	C21	C20	120.65(17)
C1	C2	C3	119.04(19)	C21	C22	C23	121.45(17)
C2	C3	C4	120.01(19)	C22	C23	C24	117.70(17)
C5	C4	C3	119.9(2)	C22	C23	C26	120.63(17)
C4	C5	C6	121.1(2)	C24	C23	C26	121.67(17)
C1	C6	C5	117.72(17)	C25	C24	C23	120.93(18)
C1	C6	C7	123.75(17)	C24	C25	C20	120.91(17)
C5	C6	C7	118.48(17)	C27	C26	C23	120.88(18)
O4	C7	N1	103.28(14)	C31	C26	C23	121.06(18)
O4	C7	C6	106.13(15)	C31	C26	C27	118.06(19)
O4	C7	C8	115.03(18)	C28	C27	C26	121.0(2)
O4	C7	C8A	96.3(5)	C29	C28	C27	120.4(2)
N1	C7	C6	112.62(15)	C28	C29	C30	119.6(2)
N1	C7	C8	106.04(18)	C29	C30	C31	120.2(2)
C6	C7	C8	113.42(17)	C26	C31	C30	120.7(2)
C8A	C7	N1	128.4(5)	C9A	C8A	C7	118.1(10)
C8A	C7	C6	106.7(5)	C8A	C9A	C10A	121.6(10)
C9	C8	C7	122.4(3)	C15A	C10A	C9A	121.2(12)

C8	C9	C10	126.3(3)	C11A	C10A	C9A	117.3(12)
C11	C10	C9	123.3(3)	C11A	C10A	C15A	121.2(12)
C11	C10	C15	118.2(3)	C10A	C15A	C14A	120.0(12)
C15	C10	C9	118.5(3)	C15A	C14A	C13A	118.0(17)
C10	C11	C12	120.1(3)	C12A	C13A	C14A	120(2)
C13	C12	C11	120.7(4)	C11A	C12A	C13A	120(2)
C14	C13	C12	119.5(5)	C10A	C11A	C12A	120.8(15)

Table S8. Torsion Angles for **3oa**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	O1	C1	C2	-155.72(14)	C8	C9	C10	C15	-158.3(3)
S1	O1	C1	C6	25.6(2)	C9	C10	C11	C12	-176.1(4)
S1	N1	C7	O4	-147.28(12)	C9	C10	C15	C14	176.4(3)
S1	N1	C7	C6	-33.23(19)	C10	C11	C12	C13	0.0(9)
S1	N1	C7	C8	91.37(17)	C11	C10	C15	C14	-1.9(5)
S1	N1	C7	C8A	103.4(6)	C11	C12	C13	C14	-2.2(11)
S1	N1	C17	C16	166.96(13)	C12	C13	C14	C15	2.4(10)
S1	N1	C17	C19	47.7(2)	C13	C14	C15	C10	-0.3(7)
S1	N1	C17	C20	-78.60(17)	C15	C10	C11	C12	2.1(6)
O1	S1	N1	C7	56.78(14)	C16	O4	C7	N1	-25.28(18)
O1	S1	N1	C17	-85.02(15)	C16	O4	C7	C6	-143.94(15)
O1	C1	C2	C3	-178.66(17)	C16	O4	C7	C8	89.8(2)
O1	C1	C6	C5	-179.20(17)	C16	O4	C7	C8A	106.7(5)
O1	C1	C6	C7	3.3(3)	C16	C17	C19	C18	-9.6(3)
O2	S1	O1	C1	61.75(14)	C16	C17	C20	C21	85.4(2)
O2	S1	N1	C7	-55.91(15)	C16	C17	C20	C25	-91.0(2)
O2	S1	N1	C17	162.29(14)	C17	N1	C7	O4	-0.68(18)
O3	S1	O1	C1	-168.10(12)	C17	N1	C7	C6	113.37(16)
O3	S1	N1	C7	169.21(13)	C17	N1	C7	C8	-122.03(17)
O3	S1	N1	C17	27.41(16)	C17	N1	C7	C8A	-110.0(6)

O4	C7	C8	C9	16.5(3)	C17	C20	C21	C22	-177.72(16)
O4	C7	C8A	C9A	-115.6(9)	C17	C20	C25	C24	177.09(17)
O4	C16	C17	N1	-38.48(17)	C19	C17	C20	C21	-146.42(17)
O4	C16	C17	C19	78.68(19)	C19	C17	C20	C25	37.2(2)
O4	C16	C17	C20	-154.25(15)	C20	C17	C19	C18	-135.4(2)
N1	S1	O1	C1	-51.95(14)	C20	C21	C22	C23	0.7(3)
N1	C7	C8	C9	129.9(2)	C21	C20	C25	C24	0.6(3)
N1	C7	C8A	C9A	-3.1(13)	C21	C22	C23	C24	0.5(3)
N1	C17	C19	C18	98.8(2)	C21	C22	C23	C26	-179.58(17)
N1	C17	C20	C21	-20.6(2)	C22	C23	C24	C25	-1.2(3)
N1	C17	C20	C25	163.02(16)	C22	C23	C26	C27	-37.5(3)
C1	C2	C3	C4	-1.7(3)	C22	C23	C26	C31	142.8(2)
C1	C6	C7	O4	112.90(19)	C23	C24	C25	C20	0.7(3)
C1	C6	C7	N1	0.6(3)	C23	C26	C27	C28	-178.56(18)
C1	C6	C7	C8	-119.8(2)	C23	C26	C31	C30	178.0(2)
C1	C6	C7	C8A	-145.2(6)	C24	C23	C26	C27	142.4(2)
C2	C1	C6	C5	2.2(3)	C24	C23	C26	C31	-37.3(3)
C2	C1	C6	C7	-175.30(18)	C25	C20	C21	C22	-1.3(3)
C2	C3	C4	C5	1.0(3)	C26	C23	C24	C25	178.89(18)
C3	C4	C5	C6	1.3(3)	C26	C27	C28	C29	0.2(3)
C4	C5	C6	C1	-2.9(3)	C27	C26	C31	C30	-1.7(3)
C4	C5	C6	C7	174.75(19)	C27	C28	C29	C30	-1.0(3)
C5	C6	C7	O4	-64.5(2)	C28	C29	C30	C31	0.4(4)
C5	C6	C7	N1	-176.85(17)	C29	C30	C31	C26	0.9(4)
C5	C6	C7	C8	62.7(3)	C31	C26	C27	C28	1.1(3)
C5	C6	C7	C8A	37.3(6)	C8A	C9A	C10A	C15A	-29.4(18)
C6	C1	C2	C3	0.1(3)	C8A	C9A	C10A	C11A	145.7(13)
C6	C7	C8	C9	-106.0(3)	C9A	C10A	C15A	C14A	173.0(13)
C6	C7	C8A	C9A	135.5(9)	C9A	C10A	C11A	C12A	-172(2)

C7	O4	C16	C17	42.12(19)	C10A	C15A	C14A	C13A	1(3)
C7	N1	C17	C16	23.46(17)	C15A	C10A	C11A	C12A	3(3)
C7	N1	C17	C19	-95.82(17)	C15A	C14A	C13A	C12A	-2(4)
C7	N1	C17	C20	137.90(15)	C14A	C13A	C12A	C11A	4(5)
C7	C8	C9	C10	174.5(2)	C13A	C12A	C11A	C10A	-4(4)
C7	C8A	C9A	C10A	-176.4(9)	C11A	C10A	C15A	C14A	-2(2)
C8	C9	C10	C11	19.9(5)					

Table S9. Hydrogen Atom Coordinates (Å × 10^4) and Isotropic Displacement Parameters (Å^2 × 10^3) for **3oa**.

Atom	*x*	*y*	*z*	U(eq)
H2	5366.32	-2041.3	2907.22	38
H3	5301.43	-2661.7	4352.55	44
H4	3655.62	-1667.82	5424.31	48
H5	2030.06	-94.91	5041.38	43
H8	2865.86	2511.91	3970	30
H9	-146.01	1951.33	4798.05	36
H11	2970.75	4468.9	4670.04	48
H12	3657.44	6151.81	5793.22	56
H13	2461.49	6230.72	7180.59	54
H14	432.53	4696.01	7417.66	62
H15	-266.54	3007.66	6319.76	52
H16A	-1688.75	1522.97	3000.16	36
H16B	-2524.54	157.73	2668.94	36
H18A	-1455.9	-1658.55	2297.32	57
H18B	-872.54	-2417.23	1362.81	57
H19	177.32	-718.61	917.2	34
H21	684.09	2975.27	2005.67	34
H22	-281.05	4345.02	1065.95	34

H24	-3718.52	1733.9	-373.98	37
H25	-2709.9	350.97	549.64	34
H27	-2524.31	5531.64	636.77	40
H28	-3521.73	6914.73	-290.81	49
H29	-4327.26	6313.79	-1840.68	56
H30	-4058.99	4326.52	-2473.77	61
H31	-3012	2934.11	-1553.77	49
H8A	817.31	1437.48	4808.27	31
H9A	1966.59	3037.73	3694.39	39
H15A	252.86	2868.5	5849.32	46
H14A	812.21	4316.59	7168.62	56
H13A	2578.75	6138.46	7076.92	54
H12A	3885.29	6365.39	5742.47	51
H11A	3176.95	4956.27	4461.99	50

Table S10. Atomic Occupancy for **3oa**.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
C8	0.799(5)	H8	0.799(5)	C9	0.799(5)
H9	0.799(5)	C10	0.799(5)	C11	0.799(5)
H11	0.799(5)	C12	0.799(5)	H12	0.799(5)
C13	0.799(5)	H13	0.799(5)	C14	0.799(5)
H14	0.799(5)	C15	0.799(5)	H15	0.799(5)
C8A	0.201(5)	H8A	0.201(5)	C9A	0.201(5)
H9A	0.201(5)	C10A	0.201(5)	C15A	0.201(5)
H15A	0.201(5)	C14A	0.201(5)	H14A	0.201(5)
C13A	0.201(5)	H13A	0.201(5)	C12A	0.201(5)
H12A	0.201(5)	C11A	0.201(5)	H11A	0.201(5)

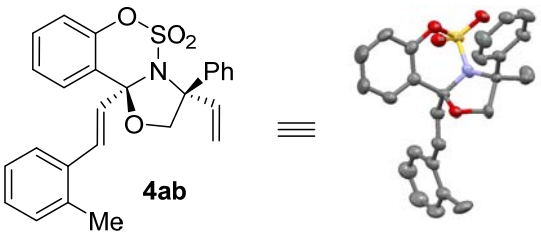


Table S11. Crystal data and structure refinement for **4ab**.

Identification code	**4ab**
Empirical formula	$C_{26}H_{23}NO_4S$
Formula weight	445.51
Temperature/K	153.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.5652(15)
b/Å	9.5590(19)
c/Å	32.515(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2351.4(8)
Z	4
ρ_{calc}g/cm^3	1.258
μ/mm^{-1}	0.169
F(000)	936.0
Crystal size/mm^3	0.16 × 0.14 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.442 to 55.424
Index ranges	$-8 \le h \le 9$, $-12 \le k \le 12$, $-42 \le l \le 40$
Reflections collected	14656
Independent reflections	5288 [R_{int} = 0.1851, R_{sigma} = 0.1415]
Data/restraints/parameters	5288/0/290
Goodness-of-fit on F^2	1.142
Final R indexes [I>=2σ (I)]	R_1 = 0.1261, wR_2 = 0.2985
Final R indexes [all data]	R_1 = 0.1505, wR_2 = 0.3277
Largest diff. peak/hole / e Å^{-3}	0.74/-0.98
Flack parameter	-0.24(16)

Table S12. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4ab**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	6934(2)	5222(2)	5929.1(6)	35.5(5)
O1	6674(8)	3553(6)	5902.8(17)	40.6(14)
O2	7550(7)	5499(7)	6338.2(16)	42.3(15)
O3	7954(8)	5593(8)	5577.7(16)	42.5(14)
O4	1987(7)	5208(6)	5957.1(15)	35.4(12)
N1	4934(8)	5814(8)	5888(2)	36.2(15)
C1	5425(12)	2992(9)	6171(3)	39.0(18)
C2	5674(15)	1561(11)	6271(3)	51(2)
C3	4453(17)	947(11)	6534(4)	67(3)
C4	2990(16)	1683(10)	6689(3)	57(3)
C5	2780(12)	3084(11)	6583(3)	45(2)
C6	3968(11)	3751(10)	6323(2)	35.0(17)
C7	3583(9)	5263(9)	6189(2)	31.5(16)
C8	2112(11)	6280(9)	5646(2)	36.3(17)
C9	4068(10)	6224(9)	5489(2)	32.0(16)
C10	4582(11)	7698(10)	5354(3)	41.4(19)
C11	5674(14)	8582(11)	5551(3)	51(2)
C12	4339(10)	5103(10)	5151(2)	36.4(17)
C13	3551(12)	3804(11)	5171(2)	46(2)
C14	3774(15)	2852(13)	4852(3)	55(3)
C15	4806(11)	3142(11)	4512(3)	43(2)
C16	5638(12)	4429(13)	4491(3)	52(3)
C17	5380(12)	5419(11)	4805(2)	43(2)
C18	3441(10)	6266(9)	6554(2)	36.2(17)
C19	1935(11)	6839(9)	6681(2)	38.1(18)
C20	1739(12)	7788(9)	7043(2)	40.2(19)
C21	2992(14)	7795(10)	7356(3)	47(2)
C22	2795(16)	8648(15)	7700(3)	66(3)
C23	1385(15)	9519(12)	7726(3)	56(3)
C24	99(15)	9525(11)	7424(3)	54(2)
C25	251(12)	8687(10)	7077(2)	41.4(19)
C26	-1159(14)	8774(12)	6744(4)	59(3)

Table S13. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4ab**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	22.3(8)	52.4(11)	31.9(9)	-0.3(8)	0.4(7)	0.6(8)
O1	40(3)	43(3)	39(3)	0(3)	7(3)	4(3)
O2	33(3)	63(4)	31(3)	-4(3)	-6(2)	2(3)
O3	29(3)	63(4)	35(3)	3(3)	5(2)	-1(3)
O4	27(2)	51(3)	28(2)	1(2)	1.1(19)	3(3)
N1	28(3)	50(4)	31(3)	5(3)	-2(3)	-9(3)
C1	41(5)	36(4)	40(4)	-3(3)	-10(4)	3(4)
C2	54(6)	47(5)	53(5)	-5(4)	-4(4)	25(5)
C3	69(7)	45(6)	87(8)	25(5)	-1(6)	-2(6)
C4	60(6)	44(5)	67(6)	23(5)	6(5)	0(5)
C5	34(4)	58(5)	43(4)	3(4)	6(4)	3(4)
C6	33(4)	42(4)	31(3)	-3(3)	-9(3)	1(3)
C7	19(3)	42(4)	33(3)	1(3)	4(3)	1(3)
C8	34(4)	39(4)	36(4)	13(3)	1(3)	-4(4)
C9	28(4)	32(4)	36(4)	6(3)	4(3)	5(3)
C10	31(4)	53(5)	40(4)	12(4)	4(3)	7(4)
C11	57(6)	52(6)	44(5)	-3(4)	2(4)	-14(5)
C12	25(3)	49(5)	35(4)	1(4)	4(3)	-2(4)
C13	38(4)	72(6)	29(4)	-3(4)	4(3)	-17(5)
C14	54(6)	65(6)	45(5)	-11(5)	0(4)	-20(5)
C15	32(4)	57(5)	40(4)	-8(4)	1(3)	1(4)
C16	35(5)	89(8)	33(4)	-11(5)	7(3)	-5(5)
C17	41(4)	55(5)	35(4)	-4(4)	9(3)	-4(4)
C18	29(4)	48(4)	31(3)	-6(3)	-2(3)	0(4)
C19	32(4)	52(5)	31(3)	-5(3)	-1(3)	-5(4)
C20	41(5)	45(5)	35(4)	-4(3)	9(3)	-9(4)
C21	46(5)	51(5)	44(4)	-7(4)	2(4)	3(5)
C22	66(7)	98(9)	33(4)	-13(5)	-9(5)	6(7)
C23	61(6)	63(6)	43(4)	-26(5)	-1(4)	-4(5)
C24	60(6)	54(6)	48(5)	-20(5)	7(4)	12(5)
C25	41(4)	50(5)	33(4)	-4(4)	2(3)	5(4)
C26	44(5)	56(6)	77(7)	-17(5)	-11(5)	22(5)

Table S14. Bond Lengths for **4ab**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.610(7)	C9	C10	1.526(12)
S1	O2	1.434(5)	C9	C12	1.548(12)
S1	O3	1.424(6)	C10	C11	1.343(13)
S1	N1	1.620(7)	C12	C13	1.379(13)
O1	C1	1.394(11)	C12	C17	1.405(10)
O4	C7	1.424(9)	C13	C14	1.388(14)
O4	C8	1.444(9)	C14	C15	1.384(13)
N1	C7	1.510(9)	C15	C16	1.384(15)
N1	C9	1.506(10)	C16	C17	1.406(13)
C1	C2	1.419(13)	C18	C19	1.330(12)
C1	C6	1.408(12)	C19	C20	1.493(11)
C2	C3	1.389(16)	C20	C21	1.392(12)
C3	C4	1.406(16)	C20	C25	1.421(12)
C4	C5	1.392(14)	C21	C22	1.392(14)
C5	C6	1.389(12)	C22	C23	1.355(16)
C6	C7	1.538(12)	C23	C24	1.381(14)
C7	C18	1.530(11)	C24	C25	1.391(12)
C8	C9	1.567(11)	C25	C26	1.521(13)

Table S15. Bond Angles for **4ab**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	N1	103.1(4)	N1	C9	C8	98.0(5)
O2	S1	O1	105.8(4)	N1	C9	C10	112.1(7)
O2	S1	N1	108.4(4)	N1	C9	C12	112.0(6)
O3	S1	O1	105.7(4)	C10	C9	C8	107.6(7)
O3	S1	O2	121.5(4)	C10	C9	C12	113.7(6)
O3	S1	N1	110.7(4)	C12	C9	C8	112.3(7)
C1	O1	S1	115.5(5)	C11	C10	C9	127.0(8)
C7	O4	C8	106.8(6)	C13	C12	C9	122.2(7)
C7	N1	S1	117.2(5)	C13	C12	C17	118.3(8)
C9	N1	S1	124.6(5)	C17	C12	C9	119.6(8)
C9	N1	C7	110.8(6)	C12	C13	C14	120.2(8)

O1	C1	C2	115.1(8)	C15	C14	C13	122.3(10)
O1	C1	C6	123.5(8)	C14	C15	C16	118.2(9)
C6	C1	C2	121.4(9)	C15	C16	C17	120.0(8)
C3	C2	C1	117.4(9)	C12	C17	C16	121.0(9)
C2	C3	C4	122.2(9)	C19	C18	C7	124.0(7)
C5	C4	C3	118.8(10)	C18	C19	C20	125.4(8)
C6	C5	C4	121.2(9)	C21	C20	C19	120.8(8)
C1	C6	C7	122.2(8)	C21	C20	C25	118.7(8)
C5	C6	C1	118.9(8)	C25	C20	C19	120.5(8)
C5	C6	C7	118.8(8)	C22	C21	C20	121.2(9)
O4	C7	N1	104.1(6)	C23	C22	C21	119.6(10)
O4	C7	C6	106.0(6)	C22	C23	C24	120.9(9)
O4	C7	C18	112.0(6)	C23	C24	C25	121.1(9)
N1	C7	C6	112.5(6)	C20	C25	C26	122.3(8)
N1	C7	C18	109.4(7)	C24	C25	C20	118.5(8)
C18	C7	C6	112.5(6)	C24	C25	C26	119.2(9)
O4	C8	C9	105.4(6)				

Table S16. Torsion Angles for **4ab**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
S1	O1	C1	C2	-155.7(7)	C6	C1	C2	C3	-1.9(14)
S1	O1	C1	C6	26.9(10)	C6	C7	C18	C19	-108.9(9)
S1	N1	C7	O4	-145.5(5)	C7	O4	C8	C9	40.2(8)
S1	N1	C7	C6	-31.1(8)	C7	N1	C9	C8	16.4(8)
S1	N1	C7	C18	94.7(7)	C7	N1	C9	C10	129.1(7)
S1	N1	C9	C8	165.2(6)	C7	N1	C9	C12	-101.7(7)
S1	N1	C9	C10	-82.1(8)	C7	C18	C19	C20	178.1(8)
S1	N1	C9	C12	47.2(9)	C8	O4	C7	N1	-28.3(8)
O1	S1	N1	C7	54.9(6)	C8	O4	C7	C6	-147.2(6)
O1	S1	N1	C9	-92.1(7)	C8	O4	C7	C18	89.8(8)
O1	C1	C2	C3	-179.3(9)	C8	C9	C10	C11	107.0(10)
O1	C1	C6	C5	178.8(7)	C8	C9	C12	C13	-40.5(10)

O1	C1	C6	C7	2.7(12)	C8	C9	C12	C17	137.7(7)
O2	S1	O1	C1	62.1(6)	C9	N1	C7	O4	5.9(8)
O2	S1	N1	C7	-56.9(7)	C9	N1	C7	C6	120.3(7)
O2	S1	N1	C9	156.1(6)	C9	N1	C7	C18	-114.0(7)
O3	S1	O1	C1	-167.9(5)	C9	C12	C13	C14	177.4(9)
O3	S1	N1	C7	167.5(6)	C9	C12	C17	C16	-179.4(8)
O3	S1	N1	C9	20.5(8)	C10	C9	C12	C13	-163.0(8)
O4	C7	C18	C19	10.4(12)	C10	C9	C12	C17	15.2(10)
O4	C8	C9	N1	-33.3(8)	C12	C9	C10	C11	-127.9(10)
O4	C8	C9	C10	-149.6(7)	C12	C13	C14	C15	1.4(16)
O4	C8	C9	C12	84.5(7)	C13	C12	C17	C16	-1.1(13)
N1	S1	O1	C1	-51.7(6)	C13	C14	C15	C16	0.0(16)
N1	C7	C18	C19	125.3(9)	C14	C15	C16	C17	-1.9(14)
N1	C9	C10	C11	0.4(12)	C15	C16	C17	C12	2.5(14)
N1	C9	C12	C13	68.6(10)	C17	C12	C13	C14	-0.8(14)
N1	C9	C12	C17	-113.1(8)	C18	C19	C20	C21	-21.4(14)
C1	C2	C3	C4	1.8(17)	C18	C19	C20	C25	159.6(9)
C1	C6	C7	O4	112.6(8)	C19	C20	C21	C22	-178.2(10)
C1	C6	C7	N1	-0.7(10)	C19	C20	C25	C24	178.3(9)
C1	C6	C7	C18	-124.7(8)	C19	C20	C25	C26	-2.5(14)
C2	C1	C6	C5	1.5(12)	C20	C21	C22	C23	-1.9(18)
C2	C1	C6	C7	-174.5(8)	C21	C20	C25	C24	-0.7(14)
C2	C3	C4	C5	-1.4(18)	C21	C20	C25	C26	178.5(9)
C3	C4	C5	C6	1.0(16)	C21	C22	C23	C24	3.0(19)
C4	C5	C6	C1	-1.1(13)	C22	C23	C24	C25	-3.0(18)
C4	C5	C6	C7	175.1(9)	C23	C24	C25	C20	1.8(16)
C5	C6	C7	O4	-63.5(9)	C23	C24	C25	C26	-177.4(11)
C5	C6	C7	N1	-176.7(7)	C25	C20	C21	C22	0.8(15)
C5	C6	C7	C18	59.2(9)					

Table S17. Hydrogen Atom Coordinates (Å × 10^4) and Isotropic Displacement Parameters (Å^2 × 10^3) for **4ab**.

Atom	*x*	*y*	*z*	U(eq)
H2	6637.2	1042.45	6161.61	61
H3	4612.6	-3.02	6611.23	80
H4	2159.73	1232.96	6863.75	68
H5	1806.19	3593.83	6690.36	54
H8A	1840.25	7210.64	5763.13	44
H8B	1277.16	6089.47	5417.77	44
H10	4075.24	8026.58	5105.04	50
H11A	6216.35	8306.99	5801.75	61
H11B	5902.95	9482.46	5439.32	61
H13	2853.5	3560.36	5402.78	56
H14	3197.94	1971.31	4869.38	66
H15	4940.47	2474.03	4297.45	52
H16	6382.96	4644.65	4264.44	63
H17	5917.47	6314.35	4783.4	52
H18	4492.84	6492.23	6699.21	43
H19	898.05	6627.18	6528.38	46
H21	3999.62	7206.41	7335.05	57
H22	3642.82	8620.24	7915.22	79
H23	1280.86	10133.42	7953.97	67
H24	-906.73	10110.97	7455.34	65
H26A	-592.26	8878.74	6474.91	88
H26B	-1923.37	9582.7	6796.61	88
H26C	-1871.2	7917.68	6746.69	88

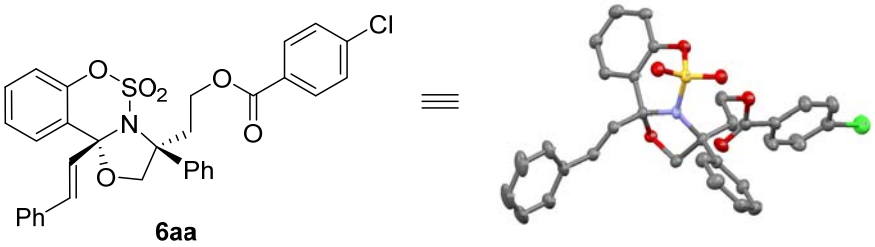


Table S18. Crystal data and structure refinement for **6aa**.

Identification code	**6aa**
Empirical formula	$C_{32}H_{26}ClNO_6S$
Formula weight	588.05
Temperature/K	153.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.7340(19)
b/Å	11.144(2)
c/Å	25.686(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2786.3(10)
Z	4
ρ_{calc}g/cm^3	1.402
μ/mm^{-1}	0.260
F(000)	1224.0
Crystal size/mm^3	0.21 × 0.2 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6 to 54.972
Index ranges	$-11 \le h \le 12$, $-9 \le k \le 14$, $-33 \le l \le 27$
Reflections collected	17291
Independent reflections	6358 [R_{int} = 0.0492, R_{sigma} = 0.0603]
Data/restraints/parameters	6358/0/370
Goodness-of-fit on F^2	1.111
Final R indexes [I>=2σ (I)]	R_1 = 0.0593, wR_2 = 0.1026
Final R indexes [all data]	R_1 = 0.0663, wR_2 = 0.1063
Largest diff. peak/hole / e Å^{-3}	0.25/-0.43
Flack parameter	0.01(4)

Table S19. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **6aa**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	1410.8(14)	8982.7(11)	1489.6(5)	47.7(3)
S1	7935.2(11)	766.1(10)	295.0(4)	25.1(2)
O1	7273(3)	1205(3)	-158.3(10)	33.2(7)
O2	8869(3)	-211(3)	268.5(11)	30.3(7)
O3	8770(3)	1887(3)	520.8(11)	27.2(6)
O4	4174(3)	3508(3)	1732.9(13)	39.8(8)
O5	5287(3)	4209(3)	1026.9(11)	28.7(6)
O6	6280(3)	694(3)	1603.3(9)	22.6(6)
N1	6831(3)	493(3)	743.2(11)	20.6(7)
C1	2298(5)	7629(4)	1465.2(18)	31.0(10)
C2	2261(5)	6884(4)	1887(2)	45.8(13)
C3	2950(5)	5798(5)	1862.8(18)	43.4(12)
C4	3679(4)	5480(3)	1422.8(16)	26.6(9)
C5	3713(5)	6253(4)	1003.4(16)	32.6(10)
C6	3006(5)	7338(4)	1017.7(17)	34.7(10)
C7	4386(4)	4296(4)	1419.6(16)	27.1(9)
C8	5994(4)	3061(4)	987.8(17)	29.3(9)
C9	5144(5)	2215(4)	646.9(17)	29.5(10)
C10	5364(4)	865(4)	746.9(15)	22.8(8)
C11	4507(4)	106(4)	367.3(15)	24.5(9)
C12	3122(4)	386(4)	290.8(17)	31.9(10)
C13	2321(5)	-313(4)	-34.6(18)	37.5(11)
C14	2865(5)	-1300(4)	-286.1(18)	37.9(11)
C15	4223(5)	-1591(5)	-208.7(18)	39.2(12)
C16	5040(5)	-890(4)	117.5(17)	34.3(10)
C17	5026(4)	518(4)	1316.3(15)	26.2(9)
C18	7359(4)	262(3)	1283.6(14)	21.1(8)
C19	8634(4)	1009(3)	1394.0(14)	21.5(8)
C20	9211(4)	970(4)	1892.3(15)	24.3(8)
C21	10348(5)	1655(4)	2020.7(17)	31.0(10)
C22	10948(5)	2385(4)	1652.0(18)	32.0(10)

C23	10417(4)	2439(4)	1152.8(17)	27.5(9)
C24	9269(4)	1751(4)	1035.4(15)	23.9(9)
C25	7622(4)	-1060(3)	1362.7(14)	22.6(8)
C26	7091(4)	-1700(4)	1749.8(15)	25.4(8)
C27	7347(5)	-2982(4)	1850.7(16)	29.9(10)
C28	8419(5)	-3611(4)	1611.7(17)	38.1(12)
C29	8618(7)	-4814(5)	1705(2)	56.4(17)
C30	7766(8)	-5420(4)	2050(2)	62.6(19)
C31	6727(6)	-4806(5)	2299(2)	52.0(16)
C32	6512(5)	-3597(4)	2204.4(18)	40.1(12)

Table S20. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **6aa**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	48.5(7)	32.1(6)	62.6(8)	-1.9(6)	11.5(6)	16.2(6)
S1	28.8(5)	28.6(5)	17.9(4)	1.0(4)	1.5(4)	0.9(5)
O1	35.6(17)	46.6(19)	17.3(13)	7.6(13)	-3.4(12)	-1.2(16)
O2	33.2(16)	29.7(16)	28.1(15)	-4.4(13)	5.7(14)	7.2(14)
O3	32.8(16)	26.0(15)	22.8(13)	3.1(12)	-0.8(13)	-4.0(14)
O4	40.5(19)	28.7(17)	50(2)	13.4(15)	7.9(16)	1.1(15)
O5	33.5(15)	19.2(14)	33.5(15)	-0.8(13)	3.9(13)	6.8(14)
O6	22.2(13)	27.6(14)	18.1(12)	-3.4(11)	3.4(11)	2.2(13)
N1	22.1(17)	25.3(17)	14.4(14)	1.3(12)	-0.2(12)	6.2(14)
C1	31(2)	23(2)	39(2)	-4.4(18)	5(2)	5.0(19)
C2	51(3)	41(3)	46(3)	4(2)	25(3)	15(3)
C3	50(3)	40(3)	40(2)	15(2)	21(2)	15(3)
C4	30(2)	21(2)	30(2)	2.0(17)	2.5(18)	0.5(18)
C5	42(3)	31(2)	25(2)	-1.6(18)	3.9(19)	8(2)
C6	47(3)	28(2)	29(2)	3.8(18)	2(2)	8(2)
C7	26(2)	22(2)	33(2)	0.1(18)	0.0(17)	-0.6(18)
C8	30(2)	19(2)	39(2)	-2.7(18)	-3.5(19)	8.3(19)
C9	35(2)	24(2)	30(2)	0.0(18)	-7.6(19)	5.8(19)
C10	20.1(18)	24(2)	23.8(18)	-0.5(16)	-3.1(15)	4.7(17)
C11	26(2)	25(2)	22.9(19)	-0.1(16)	-1.9(17)	2.5(18)

C12	28(2)	35(2)	33(2)	-1(2)	-4(2)	4.5(19)
C13	30(2)	43(3)	40(3)	3(2)	-8(2)	-4(2)
C14	38(2)	45(3)	31(2)	-4(2)	-5(2)	-15(2)
C15	39(3)	46(3)	33(2)	-13(2)	3(2)	-3(2)
C16	34(2)	34(2)	35(2)	-6(2)	-1.7(19)	2(2)
C17	22(2)	32(2)	25(2)	-1.6(17)	-0.5(16)	3.4(18)
C18	21.5(19)	23.7(19)	18.1(17)	1.5(15)	-1.3(15)	1.1(17)
C19	20.1(18)	21.7(19)	22.6(18)	-0.5(16)	-1.3(15)	4.7(17)
C20	27(2)	23(2)	23.0(18)	-0.5(16)	-2.5(16)	1.1(18)
C21	30(2)	36(2)	28(2)	-5.0(19)	-7.6(19)	0(2)
C22	30(2)	30(2)	36(2)	-9(2)	-2(2)	-1(2)
C23	25(2)	26(2)	31(2)	-2.3(18)	3.5(18)	-2.2(19)
C24	27(2)	25(2)	19.6(18)	0.9(16)	-1.4(16)	0.4(18)
C25	25(2)	20.4(19)	21.9(17)	-1.1(15)	-0.7(16)	2.9(17)
C26	26(2)	26(2)	24.2(18)	0.2(16)	-2.9(17)	0.6(18)
C27	43(3)	22(2)	24(2)	1.3(16)	-12.0(19)	-5(2)
C28	59(3)	26(2)	29(2)	4.3(19)	-4(2)	7(2)
C29	99(5)	33(3)	37(3)	-7(2)	-22(3)	22(3)
C30	113(6)	22(2)	53(3)	4(2)	-42(4)	-3(3)
C31	75(4)	30(3)	51(3)	16(2)	-27(3)	-22(3)
C32	45(3)	36(3)	40(3)	11(2)	-13(2)	-8(2)

Table S21. Bond Lengths for **6aa**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C1	1.739(4)	C10	C17	1.548(5)
S1	O1	1.418(3)	C11	C12	1.398(5)
S1	O2	1.420(3)	C11	C16	1.384(6)
S1	O3	1.599(3)	C12	C13	1.383(6)
S1	N1	1.604(3)	C13	C14	1.382(6)
O3	C24	1.416(4)	C14	C15	1.375(7)
O4	C7	1.209(5)	C15	C16	1.394(6)

O5	C7	1.340(5)	C18	C19	1.520(5)
O5	C8	1.456(5)	C18	C25	1.509(5)
O6	C17	1.439(4)	C19	C20	1.399(5)
O6	C18	1.417(4)	C19	C24	1.384(5)
N1	C10	1.487(5)	C20	C21	1.384(6)
N1	C18	1.502(4)	C21	C22	1.378(6)
C1	C2	1.367(6)	C22	C23	1.384(6)
C1	C6	1.379(6)	C23	C24	1.388(6)
C2	C3	1.385(6)	C25	C26	1.328(5)
C3	C4	1.380(6)	C26	C27	1.474(5)
C4	C5	1.380(5)	C27	C28	1.399(6)
C4	C7	1.488(5)	C27	C32	1.398(6)
C5	C6	1.392(6)	C28	C29	1.376(6)
C8	C9	1.529(6)	C29	C30	1.389(9)
C9	C10	1.542(6)	C30	C31	1.378(8)
C10	C11	1.537(5)	C31	C32	1.384(6)

Table S22. Bond Angles for **6aa**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	O2	121.07(18)	C16	C11	C10	122.2(4)
O1	S1	O3	105.02(17)	C16	C11	C12	118.4(4)
O1	S1	N1	110.52(17)	C13	C12	C11	120.2(4)
O2	S1	O3	106.93(17)	C14	C13	C12	121.0(4)
O2	S1	N1	108.51(17)	C15	C14	C13	119.2(4)
O3	S1	N1	103.22(16)	C14	C15	C16	120.2(5)
C24	O3	S1	115.4(2)	C11	C16	C15	121.0(4)

C7	O5	C8	115.1(3)	O6	C17	C10	105.6(3)
C18	O6	C17	106.6(3)	O6	C18	N1	102.9(3)
C10	N1	S1	126.5(3)	O6	C18	C19	108.1(3)
C10	N1	C18	111.7(3)	O6	C18	C25	112.3(3)
C18	N1	S1	117.8(3)	N1	C18	C19	111.0(3)
C2	C1	Cl1	119.1(4)	N1	C18	C25	110.4(3)
C2	C1	C6	122.1(4)	C25	C18	C19	111.8(3)
C6	C1	Cl1	118.8(4)	C20	C19	C18	118.8(3)
C1	C2	C3	118.8(4)	C24	C19	C18	124.6(3)
C4	C3	C2	120.7(4)	C24	C19	C20	116.6(4)
C3	C4	C7	118.0(4)	C21	C20	C19	121.5(4)
C5	C4	C3	119.4(4)	C22	C21	C20	120.0(4)
C5	C4	C7	122.6(4)	C21	C22	C23	120.3(4)
C4	C5	C6	120.7(4)	C22	C23	C24	118.6(4)
C1	C6	C5	118.3(4)	C19	C24	O3	122.1(4)
O4	C7	O5	124.1(4)	C19	C24	C23	123.0(4)
O4	C7	C4	124.2(4)	C23	C24	O3	114.8(4)
O5	C7	C4	111.8(3)	C26	C25	C18	124.0(4)
O5	C8	C9	109.0(3)	C25	C26	C27	125.9(4)
C8	C9	C10	115.5(3)	C28	C27	C26	122.4(4)
N1	C10	C9	113.9(3)	C32	C27	C26	119.4(4)
N1	C10	C11	111.3(3)	C32	C27	C28	118.2(4)
N1	C10	C17	98.1(3)	C29	C28	C27	121.1(5)
C9	C10	C17	111.8(3)	C28	C29	C30	120.0(6)
C11	C10	C9	110.9(3)	C31	C30	C29	119.5(5)
C11	C10	C17	110.3(3)	C30	C31	C32	120.9(5)
C12	C11	C10	119.4(4)	C31	C32	C27	120.2(5)

Table S23. Torsion Angles for **6aa**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C1	C2	C3	179.0(4)	C9	C10	C11	C16	136.0(4)
Cl1	C1	C6	C5	179.9(4)	C9	C10	C17	O6	-88.1(4)
S1	O3	C24	C19	-27.1(5)	C10	N1	C18	O6	-9.5(4)
S1	O3	C24	C23	154.3(3)	C10	N1	C18	C19	-125.0(3)
S1	N1	C10	C9	-52.0(4)	C10	N1	C18	C25	110.5(4)
S1	N1	C10	C11	74.2(4)	C10	C11	C12	C13	-177.6(4)
S1	N1	C10	C17	-170.2(3)	C10	C11	C16	C15	177.4(4)
S1	N1	C18	O6	149.6(2)	C11	C10	C17	O6	148.1(3)
S1	N1	C18	C19	34.1(4)	C11	C12	C13	C14	0.5(7)
S1	N1	C18	C25	-90.4(4)	C12	C11	C16	C15	0.9(7)
O1	S1	O3	C24	166.4(3)	C12	C13	C14	C15	0.2(7)
O1	S1	N1	C10	-12.2(4)	C13	C14	C15	C16	-0.4(7)
O1	S1	N1	C18	-167.8(3)	C14	C15	C16	C11	-0.2(7)
O2	S1	O3	C24	-63.8(3)	C16	C11	C12	C13	-1.1(6)
O2	S1	N1	C10	-147.1(3)	C17	O6	C18	N1	30.6(4)
O2	S1	N1	C18	57.3(3)	C17	O6	C18	C19	148.1(3)
O3	S1	N1	C10	99.7(3)	C17	O6	C18	C25	-88.2(4)
O3	S1	N1	C18	-56.0(3)	C17	C10	C11	C12	76.8(5)
O5	C8	C9	C10	-154.7(3)	C17	C10	C11	C16	-99.6(5)
O6	C18	C19	C20	63.5(4)	C18	O6	C17	C10	-41.0(4)
O6	C18	C19	C24	-115.5(4)	C18	N1	C10	C9	104.9(4)
O6	C18	C25	C26	-11.6(5)	C18	N1	C10	C11	-128.9(3)
N1	S1	O3	C24	50.6(3)	C18	N1	C10	C17	-13.3(4)
N1	C10	C11	C12	-175.4(4)	C18	C19	C20	C21	-178.1(4)
N1	C10	C11	C16	8.1(6)	C18	C19	C24	O3	0.3(6)
N1	C10	C17	O6	31.7(4)	C18	C19	C24	C23	178.7(4)

N1	C18	C19	C20	175.7(3)	C18	C25	C26	C27	-178.2(4)
N1	C18	C19	C24	-3.4(5)	C19	C18	C25	C26	110.1(4)
N1	C18	C25	C26	-125.9(4)	C19	C20	C21	C22	-0.9(6)
C1	C2	C3	C4	0.9(8)	C20	C19	C24	O3	-178.8(3)
C2	C1	C6	C5	-0.7(7)	C20	C19	C24	C23	-0.4(6)
C2	C3	C4	C5	-0.2(8)	C20	C21	C22	C23	0.1(7)
C2	C3	C4	C7	-179.4(5)	C21	C22	C23	C24	0.5(7)
C3	C4	C5	C6	-0.9(7)	C22	C23	C24	O3	178.2(4)
C3	C4	C7	O4	13.7(7)	C22	C23	C24	C19	-0.3(6)
C3	C4	C7	O5	-166.3(4)	C24	C19	C20	C21	1.0(6)
C4	C5	C6	C1	1.4(7)	C25	C18	C19	C20	-60.5(5)
C5	C4	C7	O4	-165.5(5)	C25	C18	C19	C24	120.4(4)
C5	C4	C7	O5	14.5(6)	C25	C26	C27	C28	14.2(7)
C6	C1	C2	C3	-0.4(8)	C25	C26	C27	C32	-167.0(4)
C7	O5	C8	C9	88.9(4)	C26	C27	C28	C29	-178.7(4)
C7	C4	C5	C6	178.2(4)	C26	C27	C32	C31	179.1(4)
C8	O5	C7	O4	1.7(6)	C27	C28	C29	C30	-1.3(8)
C8	O5	C7	C4	-178.3(3)	C28	C27	C32	C31	-2.0(7)
C8	C9	C10	N1	-51.1(5)	C28	C29	C30	C31	-0.3(8)
C8	C9	C10	C11	-177.6(4)	C29	C30	C31	C32	0.8(8)
C8	C9	C10	C17	58.9(5)	C30	C31	C32	C27	0.4(8)
C9	C10	C11	C12	-47.6(5)	C32	C27	C28	C29	2.4(7)

Table S24. Hydrogen Atom Coordinates (Å × 10^4) and Isotropic Displacement Parameters (Å^2 × 10^3) for **6aa**.

Atom	*x*	*y*	*z*	U(eq)
H2	1770.6	7106.18	2192.39	55
H3	2921.83	5266.55	2151.77	52

H5	4224.05	6042.57	701.87	39
H6	3010.89	7864.08	726.66	42
H8A	6111.98	2709.34	1338.85	35
H8B	6914.89	3178.05	832.43	35
H9A	5361.59	2384.43	277.64	35
H9B	4159.47	2401.01	700.29	35
H12	2729.7	1057.92	462.85	38
H13	1382.63	-111.06	-85.87	45
H14	2307.86	-1773.41	-509.91	45
H15	4606.04	-2270.45	-378.22	47
H16	5975.68	-1100.75	169.12	41
H17A	4286.44	1035.63	1456.16	31
H17B	4726.73	-329.12	1337.29	31
H20	8814.84	461.3	2148.36	29
H21	10714.69	1621.96	2363.18	37
H22	11728.8	2853.22	1741.02	38
H23	10829.35	2935.38	896.03	33
H25	8201.82	-1458.5	1120.82	27
H26	6491.72	-1293.79	1982.7	30
H28	9018.79	-3201.08	1380.66	46
H29	9340	-5231.12	1534.03	68
H30	7897.85	-6251.45	2114.4	75
H31	6150.41	-5217.17	2537.7	62
H32	5795.82	-3184.35	2380.55	48