Supplementary Information-1

Stereoselective synthesis of 1,3-disubstituted isoindolines via Rh(III)-catalyzed tandem oxidative olefination-cyclization of 4-aryl cyclic sulfamidates

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General

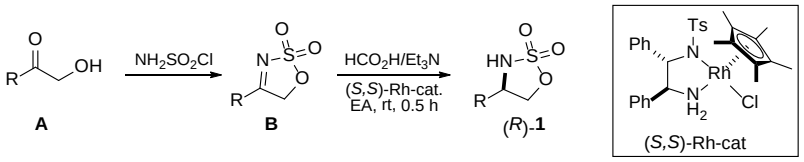
All commercial reagents were used as obtained commercially unless otherwise noted. Reactions were performed using oven dried glassware. Dichloromethane (DCM), ether, THF were dried and purified using a solvent purification system. Flash column chromatography was carried out on Fuji Chromatorex silica gel (38-75 μm). Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates. Preparative thin layer chromatography (PLC) was performed on Merck silica gel 60 F_{254} 2mm plates. Visualization of the developed chromatogram was accomplished with UV light and by staining with ethanolic phosphomolybdic acid (PMA) solution or ninhydrin solution followed by heating.

Nuclear magnetic resonance (NMR) spectra were recorded using Bruker 500 MHz NMR instrument (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz) or Bruker 300 MHz NMR instrument (^{1}H NMR at 300 MHz and ^{13}C NMR at 75 MHz). ^{1}H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constants (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High performance liquid chromatography (HPLC) was carried out on a Young Lin HPLC system (7725i Injector, SDV 30 Plus Solvent Degassor & Valve Module (Helium Sparging), SP930D Solvent Delivery Pump, UV 730D Absorbance Detector) equipped with a Chiralpak IA, IB, IC, or Chiralpak AD-H column or an Aglient 1100 Series HPLC equipped with Chiralpak IB or Chiralpak IC column. Specific rotations were measured on a Rudolph Autopol IV (Automatic polarimeter). High-resolution mass spectra and elemental analysis were obtained from the Korea Research Institute of Chemical Technology (EI) or Korea Basic Science Institute (ESI). HR-MS were measured with electron impact (EI) ionization via double focusing mass analyzer (magnetic and electric fields) or electrospray ionization (ESI) via time of flight (TOF) analyzer.

1. Synthesis of 4-aryl cyclic sufamidates (1) from imines

Enantiomerically enriched 4-aryl cyclic sulfamidates (**1**) were conveniently prepared, by employing our previous report [1], from the corresponding imines [2] via asymmetric transfer hydrogenation employing HCO_2H/Et_3N as hydrogen source and well-defined Noyori-type chiral Rh-catalyst.

Table S1. 4-Aryl cyclic sufamidates (1) from imines (B)



1	R	yield(%)[b]	e.e.(%)[c]
1a	Ph	98	99
1b	2-MeC_6H_4	98	89
1c	4-MeC_6H_4	92	99
1d	3-MeC_6H_4	98	99
1e	3-ClC_6H_4	99	98
1f	4-ClC_6H_4	99	99
1g	4-FC_6H_4	99	99
1h	4-CNC_6H_4	91	99
1i	4-$OMeC_6H_4$	94	99
1j	4-$CF_3C_6H_4$	99	99
1k	4-$MeO_2CC_6H_4$	91	99
1l	2-Thiophenyl	95	99
1m	2-Furyl	90	97
1n	2-naphthyl	99	99

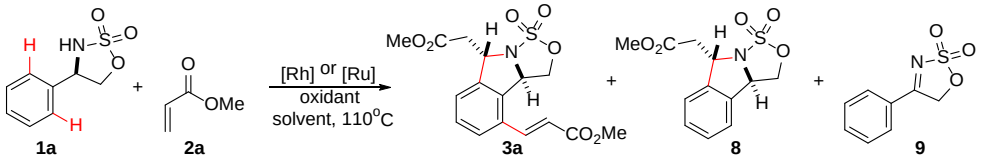
[1] S. Kang, J. Han, E. S. Lee, E. B. Choi and H.-K. Lee, *Org. Lett*. 2010, **12**, 4184.

[2] H.-K. Lee, S. Kang and E. B. Choi, *J. Org. Chem*. 2012, **77**, 5454.

2. Optimization of reaction conditions in oxidative olefination-cyclization of 1a

2-1. Optimization of catalysts and oxidants

Table S2. Optimization of catalysts and oxidants

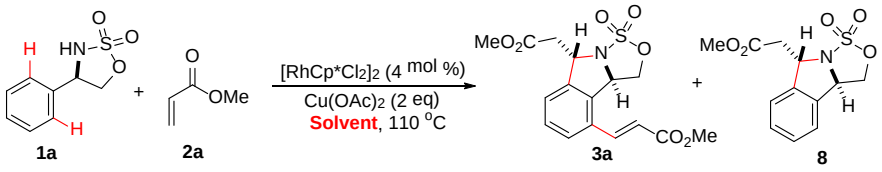


Entry	Catalyst (mol %)	Oxidant (mol %)	2a	Solvent(Time)	Yield(%)[a]			
					3a	8	9	1a
1	$[RhCp^*Cl_2]_2$ (1)	$Cu(OAc)_2$ (200)	3 eq	Toluene(20h)	11	33	5	51
2	$[RhCp^*Cl_2]_2$ (3)	$Cu(OAc)_2$ (200)	3 eq	Toluene(20h)	74	26	-	-
3	$[RhCp^*Cl_2]_2$ (3)	$Cu(OAc)_2$ (200)	2 eq	Toluene(20h)	73	27	-	-
4	$[RhCp^*Cl_2]_2$ (3)	$Cu(OAc)_2$ (200)	1 eq	Toluene(20h)	10	23	8	60
5	$[RhCp^*Cl_2]_2$ (3)	$Cu(OAc)_2 \cdot H_2O$ (200)	3 eq	Toluene(20h)	67	33	-	-
6	$[RhCp^*Cl_2]_2$ (3)	$Cu(OAc)_2$ (100)	3 eq	Toluene (20h)	60	40	-	-
7	$[RhCp^*Cl_2]_2$ (4)	$Cu(OAc)_2$ (200)	3 eq	Toluene(3h)	88	12	-	-
8	**$[RhCp^*Cl_2]_2$ (4)**	**$Cu(OAc)_2$ (200)**	**3 eq**	***t*-AmOH(6h)**	**>99**	-	-	-
9	$[RhCp^*Cl_2]_2$ (4)	$Cu(OAc)_2$ (200)	2 eq	*t*-AmOH(6h)	72	23	-	5
10	$[RhCp^*Cl_2]_2$ (4)	Air, NaOAc (100)	3 eq	Toluene (20h)	-	35	65	-
11	$[RuCl_2(p\text{-cymene})_2]_2$ (5)	$Cu(OAc)_2$ (200)	3 eq	Toluene (20h)	6	17	33	44
12	$[RuCl_2(p\text{-cymene})_2]_2$ (5)	$Cu(OAc)_2$ (200)	3 eq	DCE (8h)	14	-	70	15
13	$[RuCl_2(p\text{-cymene})_2]_2$ (5)	$Cu(OAc)_2$ (200)	3 eq	*t*-AmOH (9h)	13	-	5	81
14	$[RuCl_2(p\text{-cymene})_2]_2$ (5)	AgOAc (200)	3 eq	Toluene (9h)	6	12	38	44

[a]Product ratio was determined by ^{1}H-NMR integration.

2-2. Optimization of solvents

Table S3. Optimization of solvents[a]

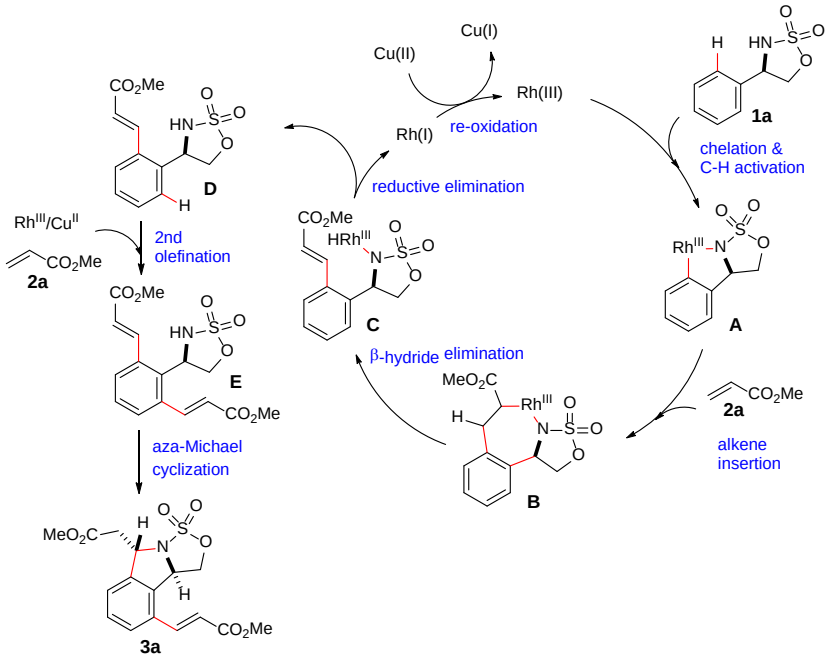


Entry	Solvent	Time(h)	Conversion[b]	Yield[c] (3a:8)[d]	% ee[e]
1	Toluene	3	>99	93(88:12)	99.0
2	DMF	3	>99	51(100:0)	>99
3	Dioxane	4	>99	93(89:11)	98.9
4	DCE	6	>99	96(73:27)	>99
5	CH_3CN	1	>99	63(100:0)	>99
6	***t*-Amyl-OH**	**5**	**>99**	**92(100:0)**	**99.5**

[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.9 mmol), $[RhCp^*Cl_2]_2$ (4 mol%), $Cu(OAc)_2$ (200 mol%), **solvent** (3 mL), 110 °C in sealed tubes. [b]Determined by ^{1}H-NMR analysis of the crude product mixtures [c]Isolated yields after silica gel chromatographic purification. [d]Product ratio was determined by ^{1}H-NMR integration. [e]ee was determined by using chiral HPLC.

3. Plausible reaction mechanism

Scheme S1. Plausible reaction mechanism[a]



[a]Modified from references 1-3

(1) Q. Ding, T. Liu, Q. Zheng, Y. Zhang, L. Long and Y. Peng, *RSC Adv*. 2014, **4**, 51309.

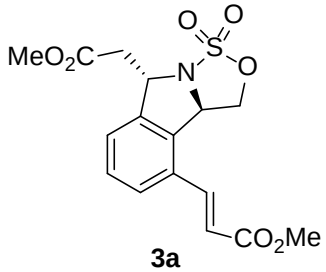
(2) X. Li, Y. Dong, F. Qu and G Liu, *J. Org. Chem*. 2015, **80**, 790.

(3) N. K. Mishra, J. Park, S. Sharma, S. Han, M. Kim. Y. Shin, J. H. Kwak, Y. H. Jung and I. S. Kim, *Chem. Commun.* 2014, **50**, 2350.

4. General procedure for the oxidative olefination-cyclization of 4-aryl cyclic sulfamidates 1

A 20 mL sealed tube equipped with a magnetic stir bar was charged with cyclic sulfamidate **1** (0.30 mmol), $[Cp^*RhCl_2]_2$ (7.4 mg, 0.012 mmol, 4.0 mol %), $Cu(OAc)_2$ (109 mg, 0.60 mmol), and 5 mL of anhydrous *t*-amyl-OH. The reaction mixture was stirred at 50 ^oC for 1min and then methyl acrylate (0.08 ml, 0.90 mmol) was added. The reaction tube was capped and stirred at 110^oC (bath temperature). When the starting material was consumed completely (monitored by TLC), the tube was cooled to room temperature. The mixture was diluted with EtOAc and filtered through a pad of Celite. The evaporation of the solvent and volatiles under reduced pressure was followed by purification through flash column chromatography on silica gel (eluent EtOAc /hexane =1/5 to 1/3, typically).

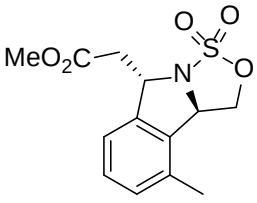
(3a): Methyl (*E*)-3-((*3aR,8S*)-8-(2-methoxy-2-oxoethyl)-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-4-yl)acrylate



3a

yield: 92% (101 mg as a white solid); mp = 104.1-107.5 ^oC; 99.5% ee (Chiralpak IC, 40% EtOH/n-hexane, 1.0 ml/min, 215nm, t_R(major) = 19.7 min, t_R(minor) = 24.6 min); $[\alpha]_D^{30}$ = -72.6 (c 0.6, $CHCl_3$).; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, 1H, *J* = 7.7 Hz), 7.49 (d, 1H, *J* = 15.9 Hz), 7.47 (t, 1H, *J* = 7.7 Hz), 7.32 (d, 1H, *J* = 7.7 Hz), 6.46 (d, 1H, *J* = 15.9 Hz), 5.70 (td, 1H, *J* = 6.3, 1.6 Hz,), 5.67 (t, *J* = 6.3 Hz, 1H), 4.94 (dd, 1H, *J* = 8.6, 7.0 Hz), 4.31 (dd, 1H, *J* = 8.6, 5.6 Hz), 3.86 (s, 3H), 3.77 (s, 3H), 2.93 (dd, 1H, *J* = 16.4, 5.9 Hz), 2.89 (dd, 1H, *J* = 16.3, 6.8 Hz).; ^{13}C NMR (125 MHz, $CDCl_3$) 170.1, 166.4, 140.4, 139.1, 136.4, 130.3, 129.4, 127.1, 124.5, 121.5, 72.0, 66.0, 64.6, 52.1, 52.1, 41.9; HRMS (EI): m/z calcd for $C_{16}H_{17}NO_7S$ 367.0726, found 367.0704.

(3b): Methyl 2-((*3aR,8S*)-4-methyl-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-8-yl)acetate

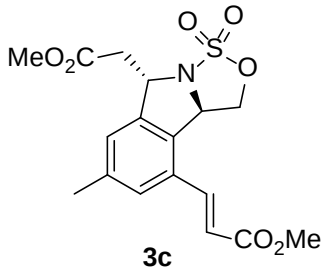


3b

yield: 96% (89 mg as a white solid); mp = 119.0-121.1 ^oC; 89.8% ee (Chiralpak IC, 10% EtOH/n-hexane, 1.0 ml/min, 215nm, t_R(minor) = 52.3 min, t_R(major) = 58.5 min); $[\alpha]_D^{31}$ = -41.0 (c 0.5, $CHCl_3$).; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, 1H, *J* = 7.6 Hz), 7.19 (d, 1H, *J* = 7.5 Hz), 7.09 (d, 1H, *J* = 7.6 Hz), 5.65 (t, 1H, *J* = 6.2 Hz), 5.53 (t, 1H, *J* = 5.9 Hz), 4.87 (dd, 1H, *J*

= 8.3, 7.1 Hz), 4.33 (dd, 1H, *J* = 8.3, 6.2 Hz), 3.78 (s, 3H), 2.91 (dd, 1H, *J* = 16.1, 5.7 Hz), 2.84 (dd, 1H, *J* = 16.0, 7.2 Hz), 2.30 (s, 3H).; ^{13}C NMR (125 MHz,) 170.3, 139.2, 135.4, 132.1, 130.1, 129.9, 120.3, 72.0. 66.4, 64.9, 52.0, 42.3, 18.8; HRMS (EI): m/z calcd for $C_{13}H_{15}NO_5S$ 297.0671, found 297.0664.

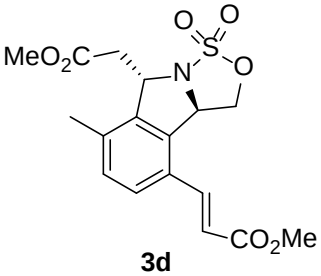
(3c): Methyl (*E*)-3-((*3aR,8S*)-8-(2-methoxy-2-oxoethyl)-6-methyl-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-4-yl)acrylate



3c

yield: 93% (106 mg as a pale yellow solid); mp = 116.8-119.8 ^{o}C; >99% ee (Chiralpak IC, 40% EtOH/n-hexane, 1.0 ml/min, 215nm, t_R(major) = 24.4 min, t_R(minor) = 32.9 min); $[\alpha]_D^{29}$ = -85.5 (c 0.5, $CHCl_3$).; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, 1H, *J* = 15.9 Hz), 7.41 (s, 1H), 7.11 (s, 1H), 6.43 (d, 1H, *J* = 15.9 Hz), 5.66 (t, 1H, *J* = 6.2 Hz), 5.61 (t, 1H, *J* = 6.2 Hz), 4.91 (dd, 1H, *J* = 8.5, 7.0 Hz), 4.28 (dd, 1H, *J* = 8.6, 5.6 Hz), 3.85 (s, 3H), 3.77 (s, 3H), 2.92 (dd, 1H, *J* = 16.3, 5.7 Hz), 2.86 (dd, 1H, *J* = 16.3, 6.9 Hz), 2.43 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 170.2, 166.5, 140.6, 139.4, 133.7, 129.0, 127.9, 125.1, 121.2, 72.2, 65.9, 64.5, 52.1, 42.0, 21.4; HRMS (EI): m/z calcd for $C_{17}H_{19}NO_7S$ 381.0882, found 381.0880.

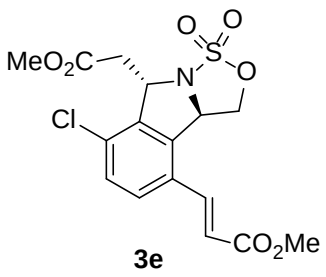
(3d): Methyl (*E*)-3-((*3aR,8S*)-8-(2-methoxy-2-oxoethyl)-7-methyl-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-4-yl)acrylate



3d

yield: 88% (101 mg as a white solid); mp = 114.1-117.3 ^{o}C; >99% ee (Chiralpak IC, 20% EtOH/n-hexane, 1.0 ml/min, 215nm, t_R (major) = 26.9 min, t_R(minor) = 36.9 min); $[\alpha]_D^{29}$ = -85.4 (c 0.4, $CHCl_3$).; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, 1H, *J* = 7.9 Hz), 7.47 (d, 1H, *J* = 15.9 Hz), 7.25 (d, 1H, *J* = 7.9 Hz), 6.42 (d, 1H, *J* = 15.9 Hz), 5.76 - 5.61 (m, 2H), 4.93 (dd, 1H, *J* = 8.8, 6.9 Hz), 4.33 (dd, 1H, *J* = 8.8, 4.9 Hz), 3.85 (s, 3H), 3.76 (s, 3H), 3.01 (dd, 1H, *J* = 16.3, 3.1 Hz), 2.65 (dd, 1H, *J* = 16.3, 9.1 Hz), 2.39 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 170.0, 166.6, 139.2, 138.8, 137.2, 135.0, 131.8, 127.5, 126.9, 120.5, 71.4. 66.5, 64.3, 52.1, 52.1, 40.4, 19.2; HRMS (EI): m/z calcd for $C_{17}H_{19}NO_7S$ 381.0882, found 381.0886..

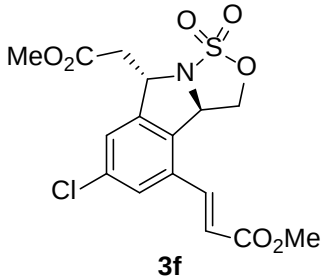
(3e): Methyl (*E*)-3-((*3aR,8S*)-7-chloro-8-(2-methoxy-2-oxoethyl)-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-4-yl)acrylate



3e

yield: 78% (94mg as a pale yellow solid); mp = 114.1-117.3 ^{o}C; 98.7% ee (Chiralpak IC, 50% EtOH/n-hexane, 1.1 ml/min, 215nm, t_R (major) = 12.7 min, t_R (minor) = 15.4 min); $[\alpha]_D^{29}$ = -137.4 (c 0.4, $CHCl_3$).; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, 1H, *J* = 8.3 Hz), 7.45 (d, 1H, *J* = 15.3 Hz), 7.42 (d, 1H, *J* = 7.8 Hz), 6.45 (d, 1H, *J* = 15.9 Hz), 5.78 - 5.68 (m, 2H), 4.94 (dd, 1H, *J* = 8.9, 7.0 Hz), 4.37 (dd, 1H, *J* = 8.9, 4.8 Hz), 3.86 (s, 3H), 3.75 (s, 3H), 3.25 (dd, 1H, *J* = 16.8, 3.4 Hz), 2.87 (dd, 1H, *J* = 16.8, 7.9 Hz).; ^{13}C NMR (125 MHz, $CDCl_3$) 169.9, 166.2, 139.2, 138.0, 130.8, 130.7, 128.7, 128.0, 122.0, 71.0. 66.9, 64.6, 52.2, 52.1, 39.0.; HRMS (EI): m/z calcd for $C_{16}H_{16}ClNO_7S$ 401.0336, found 401.0344.

(3f): Methyl (*E*)-3-((*3aR,8S*)-6-chloro-8-(2-methoxy-2-oxoethyl)-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-4-yl)acrylate



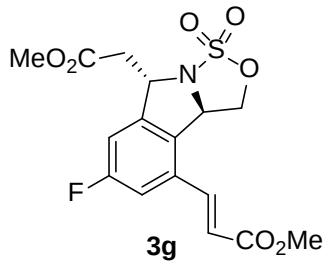
3f

yield: 89% (107 mg as a pale yellow solid); mp = 117.3-120.5 ^{o}C; >99% ee (Chiralpak IC, 40% EtOH/n-hexane, 1.0 ml/min, 215nm, t_R(major) = 20.0 min, t_R(minor) = 25.6 min); $[\alpha]_D^{30}$ = -69.7 (c 1.0, $CHCl_3$).; ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.87 (d, 1H, *J* = 1.4 Hz), 7.60 (d, 1H, *J* =2.7 Hz), 7.59 (d, 1H, *J* =15.8 Hz), 6.72 (d, 1H, *J* =15.9 Hz), 6.01 (td, 1H, *J* =1.5, 6.1 Hz), 5.64 (t, 1H, *J* = 6.2 Hz), 5.11 (dd, 1H, *J* = 7.1, 9.0 Hz), 4.56 (dd, 1H, *J* = 5.3, 9.0 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.07 (dd, 1H, *J* = 5.1, 16.5 Hz), 2.91 (dd, 1H, *J* = 7.5, 16.5 Hz).; ^{13}C NMR (125 MHz, $CDCl_3$) 169.9, 166.1, 142.3, 137.8, 136.4, 135.0, 130.7, 127.0, 124.6, 122.8, 71.8, 65.6, 64.2, 52.2, 52.1, 41.5; HRMS (EI): m/z calcd for $C_{16}H_{16}ClNO_7S$ 401.0336, found 401.0335.

(3g): Methyl (*E*)-3-((*3aR,8S*)-6-fluoro-8-(2-methoxy-2-oxoethyl)-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-4-yl)acrylate

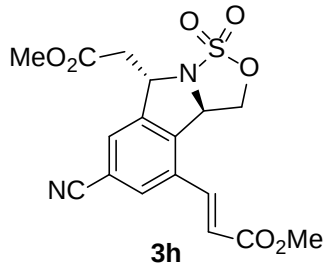
yield: 94% (109 mg as a pale brown solid); mp = 130.5-134.2 ^{o}C; >99% ee (Chiralpak IC, 40% EtOH/n-hexane, 1.0 ml/min, 215nm, t_R(major) = 20.0 min, t_R(minor) = 22.9 min); $[\alpha]_D^{30}$ = -73.0 (c 0.4, $CHCl_3$).; ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.65 (dd, 1H, *J* = 2.2, 10.1 Hz), 7.59 (dd, 1H, *J* =0.8,

16.0 Hz), 7.35 (dd, 1H, *J* =1.9, 8.3 Hz), 6.70 (d, 1H, *J* =15.8 Hz), 6.00 (t, 1H, *J* = 5.7 Hz), 5.64 (t, 1H, *J* = 6.4 Hz), 5.11 (dd, 1H, *J* = 7.0, 8.9 Hz), 4.54 (dd, 1H, *J* = 5.2, 8.9 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.04 (dd, 1H, *J* = 5.1, 16.4 Hz), 2.89 (dd, 1H, *J* =7.5, 16.4 Hz).; ^{13}C NMR (125 MHz, $CDCl_3$) 169.9, 166.1, 163.8 (d, J_{CF} = 248.3 Hz), 142.7 (d, J_{CF} = 8.7 Hz), 137.9 (d, J_{CF} = 1.9 Hz), 132.2 (d, J_{CF} = 2.1 Hz), 131.1 (d, J_{CF} = 8.7 Hz), 122.8, 113.8 (d, J_{CF} = 23.9 Hz), 112.0 (d, J_{CF} = 24.4 Hz), 72.0. 65.4, 64.3 (d, J_{CF} = 2.2 Hz), 52.2, 52.1, 41.6.; HRMS (EI): m/z calcd for $C_{16}H_{16}FNO_7S$ 385.0632, found 385.0634.



3g

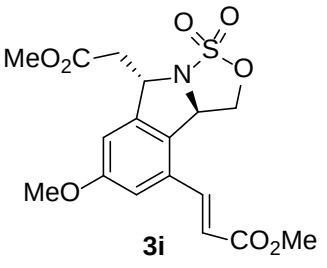
(3h): *Methyl* (*E*)-3-((*3aR,8S*)-6-cyano-8-(2-methoxy-2-oxoethyl)-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-4-yl)acrylate



3h

yield: 86% (118 mg as a pale yellow solid); mp = 162.1-163.9 ^{o}C; >99% ee (Chiralcel OD-H, 30% IPA/n-hexane, 1.0 ml/min, 215nm, t_R(major) = 36.0 min, t_R(minor) = 41.4 min); $[\alpha]_D^{29}$ = -54.4 (c 0.5, $CHCl_3$).; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.63 (s, 1H), 7.45 (d, 1H, *J* = 15.9 Hz), 6.54 (d, 1H, *J* = 15.9 Hz), 5.72 -5.70 (m, 1H), 5.66 (t, 1H, *J* = 5.9 Hz), 4.96 (dd, 1H, *J* = 8.7, 7.3 Hz), 4.33 (dd, 1H, *J* = 8.8, 5.2 Hz), 3.88 (s, 3H), 3.76 (s, 3H), 2.97 (d, 2H, *J* = 6.0 Hz).; ^{13}C NMR (125 MHz,) 169.7, 165.7, 142.1, 141.2, 136.7, 130.8, 130.7, 127.4, 124.2, 117.3, 114.8, 71.2. 65.8, 64.3, 52.4, 52.2, 41.2; HRMS (EI): m/z calcd for $C_{17}H_{16}N_2O_7S$ 392.0678, found 392.0679.

(3i): Methyl (*E*)-3-((*3aR,8S*)-6-methoxy-8-(2-methoxy-2-oxoethyl)-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-4-yl)acrylate

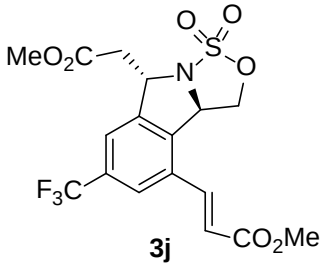


3i

yield: 94% (112 mg as a white solid); mp = 109.8-113.1 ^{o}C; 99.3% ee (Chiralcel OD-H, 30% IPA/n-hexane, 1.0 ml/min, 215nm, t_R(minor) = 15.3 min, t_R(major) = 19.6 min); $[\alpha]_D^{30}$ = -81.6 (c 0.4, $CHCl_3$).; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, 1H, *J* = 15.9 Hz), 7.09 (d, 1H, *J* = 1.9 Hz), 6.83 (d, 1H, *J* = 1.4 Hz), 6.42 (d, 1H, *J* = 15.9 Hz), 5.64-5.59 (m, 2H), 4.89 (dd, 1H, *J* = 8.5, 6.9 Hz), 4.27 (dd, 1H, *J* = 8.5, 5.6 Hz), 3.86 (s, 3H), 3.85 (s, 3H), 3.77 (s, 3H), 2.93 – 2.84 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) 170.1, 166.4, 161.4, 142.0, 139.2, 130.2, 128.5, 121.6, 112.6, 110.1, 72.3. 65.7, 64.4, 55.8, 52.1, 52.1, 42.0;

HRMS (EI): m/z calcd for $C_{17}H_{19}NO_8S$ 397.0831, found 397.0826.

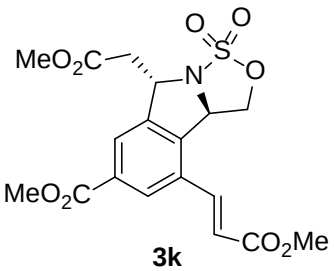
(3j): Methyl (*E*)-3-((*3aR,8S*)-8-(2-methoxy-2-oxoethyl)-1,1-dioxido-6-(trifluoromethyl)-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-4-yl)acrylate



3j

yield: 76% (99 mg as a pale brown solid); mp = 91.0-93.2 ^{o}C; 98.8% ee (Chiralcel OD-H, 30% IPA/n-hexane, 1.0 ml/min, 215nm, t_R(minor) = 11.2 min, t_R(major) = 17.3 min); $[\alpha]_D^{30}$ = -54.4 (c 0.5, $CHCl_3$).; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.58 (s, 1H), 7.49 (d, 1H, *J* = 15.9 Hz), 6.55 (d, 1H, *J* = 15.9 Hz), 5.73 -5.68 (m, 2H), 4.96 (dd, 1H, *J* = 8.7, 7.2 Hz), 4.34 (dd, 1H, *J* = 8.7, 5.3 Hz), 3.88 (s, 3H), 3.77 (s, 3H), 3.04 - 2.89 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) 169.8, 165.9, 141.7, 140.1, 137.5, 133.2 (d, J_{CF} = 33.0 Hz), 130.3, 124.1 (d, J_{CF} = 3.7 Hz), 123.5, 123.2 (d, J_{CF} = 271.6 Hz), 121.1 (d, J_{CF} = 3.5 Hz), 71.4. 65.8, 64.5, 52.3, 52.2, 41.4.; HRMS (EI): m/z calcd for $C_{17}H_{16}F_3NO_7S$ 435.0600, found 435.0592.

(3k): Methyl (3aR,8S)-8-(2-methoxy-2-oxoethyl)-4-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindole-6-carboxylate 1,1-dioxide

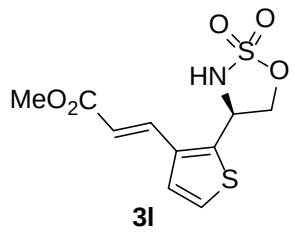


3k

yield: 94% (120 mg as a pale yellow solid); mp = 152.4-161.9 ^{o}C; 99.6% ee (Chiralpak IC, 40% EtOH/n-hexane, 1.0 ml/min, 215nm, t_R(major) = 46.3 min, t_R(minor) = 52.4 min); $[\alpha]_D^{30}$ = -62.9 (c 0.5, $CHCl_3$).; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.95 (s, 1H), 7.49 (d, 1H, *J* = 15.9 Hz), 6.58 (d, 1H, *J* = 15.9 Hz), 5.77 - 5.69 (m, 1H), 5.67 (t, 1H, *J* = 5.9 Hz), 4.96 (dd, 1H, *J* = 8.7, 7.2 Hz), 4.33 (dd, 1H, *J* = 8.7, 5.4 Hz), 3.98 (s, 3H), 3.87 (s, 3H), 3.76 (s, 3H), 3.00 (dd, 1H, *J* = 16.5, 5.5 Hz), 2.91 (dd, 1H, *J* = 16.5, 6.5 Hz).; ^{13}C NMR (125 MHz, $CDCl_3$) 169.8, 166.2, 165.5, 141.1, 140.8, 138.0, 132.7, 129.7, 128.4, 125.1, 122.8, 71.5. 66.0, 64.5, 52.7, 52.2, 52.1, 41.4; HRMS (EI): m/z calcd for $C_{18}H_{19}NO_9S$ 425.0781, found 425.0780.

(3l): Methyl (*S,E*)-3-(2-(2,2-dioxido-1,2,3-oxathiazolidin-4-yl)thiophen-3-yl)acrylate

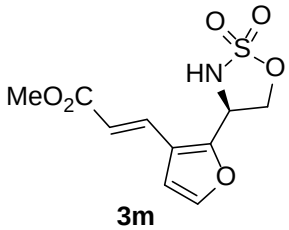
yield: 81% (70 mg as a white solid); mp = 137.6-141.4 ^{o}C; >99% ee (Chiralpak IC, 10% EtOH/n-



3l

hexane, 1.0 ml/min, 215nm, t_R(major) = 33.6 min, t_R(minor) = 37.5 min); $[\alpha]_D^{29}$ = +58.9 (c 0.5, Acetone).; ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.76 (d, 1H, *J* = 15.7 Hz), 7.60 (d, 1H, *J* = 5.4 Hz), 7.52 (d, 1H, *J* = 5.4 Hz), 6.46 (d, 1H, *J* = 15.7 Hz), 5.93 (t, 1H, *J* = 7.4 Hz), 5.18 (dd, 1H, *J* = 8.9, 7.2 Hz), 4.53 (dd, 1H, *J* = 8.8, 7.6 Hz), 3.76 (s, 3H).; ^{13}C NMR (125 MHz, Acetone-d_6) 166.7, 142.5, 135.1, 134.8, 126.6, 126.1, 119.2, 74.1. 53.2, 50.9; HRMS (EI): m/z calcd for $C_{10}H_{11}NO_5S_2$ 289.0079, found 289.0074.

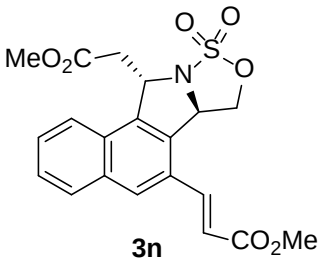
(3m): Methyl (*S,E*)-3-(2-(2,2-dioxido-1,2,3-oxathiazolidin-4-yl)furan-3-yl)acrylate



3m

yield: 31% (25 mg as a white solid); mp = 145.3-148.9 °C; 98.1% ee (Chiralpak OD-H, 30% IPA/n-hexane, 1.0 ml/min, 215nm, t_R(major) = 12.2 min, t_R(minor) = 21.5 min); $[\alpha]_D^{29}$ = +31.4 (c 0.2, $CHCl_3$).; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, 1H, *J* = 15.7 Hz), 7.52 (d, 1H, *J* = 1.9 Hz), 6.65 (d, 1H, *J* = 2.0 Hz), 6.26 (d, 1H, *J* = 15.7 Hz), 5.33 (dd, 1H, *J* = 15.6, 8.4 Hz), 4.83 (brs, 1H), 4.76 (m, 2H), 3.83 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 166.7, 145.9, 144.8, 131.8, 122.4, 120.5, 109.0, 72.1. 51.9, 51.2.; HRMS (EI): m/z calcd for $C_{10}H_{11}NO_6S$ 273.0307, found 273.0301.

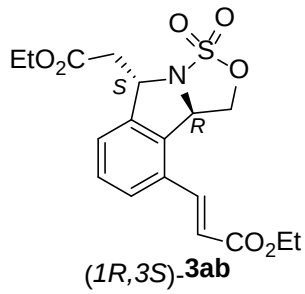
(3n): Methyl (*E*)-3-((*6bR,11S*)-11-(2-methoxy-2-oxoethyl)-9,9-dioxido-6b,11-dihydro-7H-benzo[e][1,2,3]oxathiazolo[4,3-a]isoindol-6-yl)acrylate



3n

yield: 72% (90 mg as a pale yellow solid); mp: 112.7~119.8 °C; 99.1% ee (Chiralpak IC, 50% EtOH/n-hexane, 1.0 ml/min, 215nm, t_R(major) = 21.4 min, t_R(minor) = 29.7 min); $[\alpha]_D^{22}$ = -80.7 (c 0.4, $CHCl_3$).; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.99 (d, 1H, *J* = 8.1 Hz), 7.80 (d, 1H, *J* = 8.2 Hz), 7.72-7.54 (m, 3H), 6.54 (d, 1H, *J* = 15.9 Hz), 6.18 (dt, 1H, *J* =2.4, 9.4 Hz), 5.89-5.86 (m, 1H), 4.97 (dd, 1H, *J* = 6.9, 8.9 Hz), 4.42 (dd, 1H, *J* = 4.6, 8.9 Hz), 3.88 (s, 3H), 3.81 (s, 3H), 3.26 (dd, 1H, *J* = 3.0, 16.4 Hz), 2.76 (dd, 1H, *J* = 16.4, 9.5 Hz).; ^{13}C NMR (125 MHz, $CDCl_3$) 170.2, 166.5, 140.0, 136.3, 134.1, 133.4, 129.7, 129.6, 129.0, 128.0, 127.6, 126.7, 123.6, 121.4, 71.1, 67.2, 64.8, 52.2, 52.2, 41.5.; HRMS (EI): m/z calcd for $C_{20}H_{19}NO_7S$ 417.0882, found 417.0882.

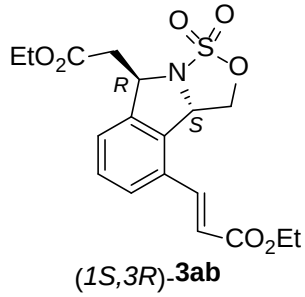
(*1R,3S*)-**3ab: Ethyl (*E*)-3-((*3aR,8S*)-8-(2-ethoxy-2-oxoethyl)-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo-[4,3-a]isoindol-4-yl)acrylate**



(*1R,3S*)-**3ab**

Yield: 86% (68mg as a brown oil); 99% ee: Chiralpak IC, 20% EtOH/n-hexane, 1.0 ml/min, 254 nm t_R(minor) = 39.9 min, t_R(major) = 50.6 min; $[\alpha]_D^{28}$= -64.6 (c 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, 1H, *J* = 7.8 Hz), 7.41-7.47 (m, 2H), 7.26-7.29 (m, 1H), 6.43 (d, 1H, *J* = 16 Hz), 5.61-5.68 (m, 2H) 4.87-4.90 (m, 1H), 4.16-4.30 (m, 5H), 2.80-2.90 (m, 2H), 1.24-1.35 (m, 6H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 160.0, 140.5, 138.9, 136.4, 130.3, 129.4, 127.1, 124.4, 122.0, 72.0, 66.0, 64.7, 61.1, 61.0, 42.2, 14.3, 14.1.; HRMS(EI): m/z calcd for $C_{18}H_{21}NO_7S$ 395.1039, found 395.1038.

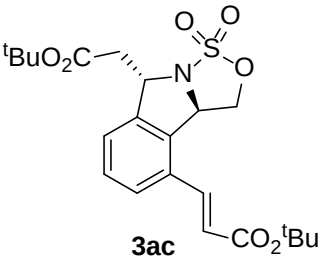
(*1S,3R*)-**3ab: Ethyl (*E*)-3-((*3aS,8R*)-8-(2-ethoxy-2-oxoethyl)-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo-[4,3-a]isoindol-4-yl)acrylate**



(*1S,3R*)-**3ab**

Yield: 84.3% (100 mg as a brown oil); >99% ee: Chiralpak IC, 20% EtOH/n-hexane, 1.0 ml/min, 254 nm t_R(major) = 38.5 min, t_R(minor) = 50.6 min; $[\alpha]_D^{23}$ = +65.6 (c 0.13, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, 1H, *J* = 7.8 Hz), 7.42-7.48 (m, 2H), 7.29-7.30 (m, 1H), 6.43 (d, 1H, *J* = 16 Hz), 5.63-5.69 (m, 2H) 4.85-4.91 (m, 1H), 4.26-4.43 (m, 3H), 4.18-4.22 (m, 2H), 2.86-2.87 (m, 2H), 1.26-1.36 (m, 6H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 160.0, 140.5, 138.9, 136.4, 130.3, 129.6, 127.1, 124.4, 121.7, 72.0, 66.0, 64.7, 61.2, 61.1, 42.2, 14.3, 14.1.; HRMS(EI): m/z calcd for $C_{18}H_{21}NO_7S$ 395.1039, found 395.1039.

(3ac): tert-Butyl (*E*)-3-((*3aR,8S*)-8-(2-(tert-butoxy)-2-oxoethyl)-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-4-yl)acrylate

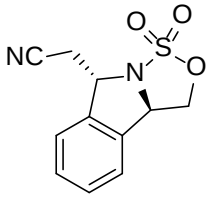


3ac

Yield : 79% (71 mg as a brown solid), mp = 33.1-36.8 °C, 99.5% ee: Chiralpak IC, 20% EtOH/n-hexane, 1.0 ml/min, 254 nm t_R(minor) = 9.0 min, t_R(major) = 9.9 min; $[\alpha]_D^{29}$= -62.5 (c 0.5, $CHCl_3$); ^{1}H NMR (500

MHz, $CDCl_3$) δ 7.6 (d, 1H, *J* = 7.7 Hz), 7.38-7.42 (m, 2H), 7.30 (d, 1H, *J* = 7.6 Hz), 6.40 (d, 1H, *J* = 16 Hz), 5.60-5.65(m, 2H), 4.88-4.91 (m, 1H), 4.29-4.32 (m, 1H), 2.77-2.78 (m, 2H), 1.54 (s, 9H), 1.45 (s, 9H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 165.3, 140.8, 137.9, 136.3, 130.1, 129.6, 126.9, 124.2, 123.7, 81.8, 81.4, 71.9, 66.0, 65.0, 43.6, 28.2, 28.0.; HRMS(EI): m/z calcd for $C_{22}H_{29}NO_7S$ 451.1665, found 451.1667

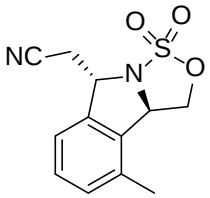
(3ad): 2-((*3aR,8S*)-1,1-Dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-8-yl)acetonitrile



3ad

Yield : 54% (27 mg as a brown oil), $[\alpha]_D^{23}$= -174.57 (c 0.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.46-7.49 (m, 2H), 7.37-7.39 (m, 1H), 7.30-7.32 (m, 1H), 5.49-5.51 (m, 2H), 4.86-4.89 (m,1H), 4.39-4.42 (m,1H), 2.91-3.01 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 136.8, 130.2, 130.1, 122.9, 122.2, 115.9, 72.9, 66.4, 64.5, 26.7.; HRMS(EI): m/z calcd for $C_{11}H_{10}N_2O_3S$ 250.0412, found 250.0422

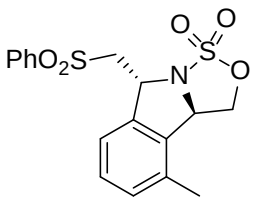
(3bd): 2-((*3aR,8S*)-4-Methyl-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-8-yl)acetonitrile



3bd

Yield : 51% (51 mg as a brown solid), mp = 51.6-57.2 °C, 90% ee , $[\alpha]_D^{24}$ = -45.8 (c 0.5, $CHCl_3$).; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.39 (m, 1H), 7.24 (d, 1H, *J* = 7.4 Hz), 7.19 (d, 1H, *J* = 7.7 Hz), 5.54-5.56 (m, 1H), 5.45-5.47 (m, 1H), 4.86-4.89 (m, 1H), 4.31-4.34 (m,1H), 2.92-3.0 (m, 2H), 2.29 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 135.9, 132.5, 131.1, 130.3, 120.2, 116.0, 72.6, 65.9, 64.5, 26.5, 18.8.; HRMS(EI): m/z calcd for $C_{12}H_{12}N_2O_3S$ 264.0569, found 264.0552.

(3be): (*3aR,8R*)-4-Methyl-8-((phenylsulfonyl)methyl)-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindole 1,1-dioxide

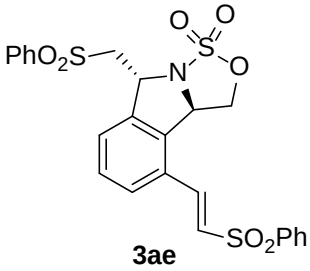


3be

Yield : 57.5 % (44 mg as a brown solid), mp = 82.3-85.2 °C, 93% ee: Chiralpak AD-H, 30% IPA/n-hexane, 0.7 ml/min, 215 nm t_R(major) = 23.7min, t_R(minor) = 27.6 min.; $[\alpha]_D^{18}$ = -78.8 (c 0.25, $CHCl_3$).; ^1H NMR

(500 MHz, $CDCl_3$) δ 7.95-7.97 (m, 2H), 7.66-7.67 (m, 1H), 7.56-7.59 (m, 2H), 7.29-7.30 (m, 1H), 7.25-7.27 (m, 1H), 7.17 (d, 1H, *J* = 7.35 Hz), 5.66-5.68 (m, 1H), 5.37-5.39 (m, 1H), 4.77-4.80 (m, 1H), 4.30-4.33 (m,1H), 3.57-3.67 (m, 2H), 2.26 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 137.4, 135.6, 134.1, 132.1, 130.7, 130.1, 129.5, 129.4, 128.3, 128.0, 121.0, 71.4, 66.1, 63.5, 62.7, 18.7.; HRMS(EI): m/z calcd for $C_{17}H_{17}NO_5S_2$ 379.0548, found 379.0522

(3ae): (*3aR,8R*)-8-((Phenylsulfonyl)methyl)-4-((*E*)-2-(phenylsulfonyl)-vinyl)-3ª,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindole 1,1-dioxide

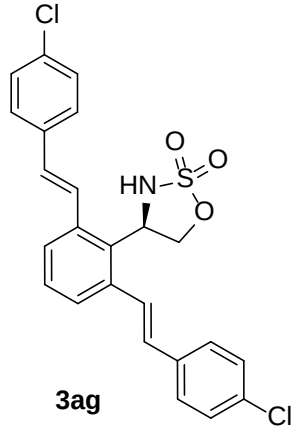


3ae

Yield : 24% (25 mg as a brown oil), ^1H NMR (500 MHz, $CDCl_3$) δ 7.93-7.95 (m, 4H), 7.66-7.69 (m, 2H), 7.59-7.60 (m, 5H), 7.53 (d, 1H, *J* = 7.65 Hz), 7.41-7.47 (m, 2H), 6.89 (d, 1H, *J* = 15.3 Hz) 5.68-5.70 (m, 1H), 5.57-5.59 (m, 1H), 4.81-4.84 (m, 1H), 4.22-4.24 (m, 1H), 3.60-3.72 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.6, 139.4, 139.0, 137.0, 136.2, 134.2, 134.0, 131.5, 130.7, 129.7, 129.5, 128.1, 128.0, 127.8, 127.4, 126.3, 71.5, 65.6, 63.3, 62.2.; HRMS(EI): m/z calcd for $C_{24}H_{21}NO_7S_3$ 531.0480, found 531.0455

(3ag): (*R*)-4-(2,6-bis((*E*)-4-chlorostyryl)phenyl)-1,2,3-oxathiazolidine 2,2-dioxide

A 20 mL sealed tube equipped with a magnetic stir bar was charged with 4-phenyl-cyclic sulfamidate **1a** (40 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (6 mg, 0.01 mmol), AgOAc (133 mg, 0.8 mmol), and 3 mL of anhydrous *t*-amyl-OH. 4-Chlorostyrene **2g** (111.3 mg, 0.8 mmol) was added and the reaction tube was capped and stirred at 120 °C (bath temp.) for 48 h. The tube was cooled to room temperature. The mixture was diluted with EtOAc and filtered through a pad of Celite. The evaporation of the solvent and volatiles under reduced pressure was followed by purification through flash column chromatography on silica gel.

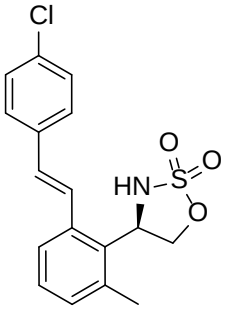


3ag

Yield : 30% (29 mg as a brown oil), ^1H NMR (500 MHz, $CDCl_3$) δ 7.6 (d, 2H, *J* = 15.9 Hz), 7.49-7.52 (m, 6H), 7.43 (d, 1H, *J* = 7.6 Hz), 7.36 (d, 4H, *J* = 8.5 Hz), 6.86 (d, 2H, *J* = 15.9 Hz) 5.70-5.72 (m, 1H), 4.96 (d, 1H, *J* = 6.6 Hz) 4.78-4.82 (m, 1H), 4.70-4.73 (m, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 134.9, 134.2, 133.2, 130.1, 129.1, 128.2, 128.1, 128.0,

125.6, 72.2, 55.6.; HRMS(EI): m/z calcd for $C_{24}H_{19}Cl_2NO_3S$ 471.0463, found 471.0430

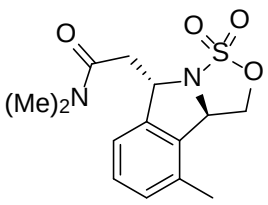
(3bg): (*R,E*)-4-(2-(4-Chlorostyryl)-6-methylphenyl)-1,2,3-oxathiazolidine 2,2-dioxide



3bg

Yield : 42.5% (29.7 mg as a brown oil), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, 1H, *J* = 16 Hz), 7.51 (d, 2H, *J* = 8.5 Hz), 7.46 (d, 1H, *J* = 7.7 Hz), 7.29-7.35 (m, 3H), 7.17 (d, 1H, *J* = 7.6 Hz), 6.85 (d, 1H, *J* = 16 Hz), 5.60-5.65 (m, 1H), 4.84 (d, 1H, *J* = 6.7 Hz), 4.70-4.77 (m, 2H), 2.48 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 137.6, 135.1, 134.0, 132.4, 131.2, 129.7, 129.0, 128.9, 128.2, 127.1, 124.7, 72.1, 55.4, 20.7.; HRMS(EI): m/z calcd for $C_{17}H_{16}NO_3S$ 349.0539, found 349.0536

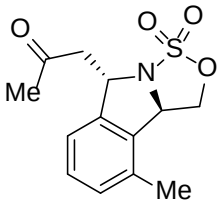
(3bf): *N,N*-Dimethyl-2-((*3aR,8S*)-4-methyl-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-8-yl)acetamide



3bf

Yield: 54% (50 mg as a pale yellow oil); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, 1H, *J* = 7.6 Hz), 7.25 (d, 1H, *J* =7.7 Hz), 7.16 (d, 1H, *J* =7.3 Hz), 5.76 (t, 1H, *J* =6.2 Hz), 5.50 (t, 1H, *J* =6.6 Hz), 4.85 (dd, 1H, *J* = 7.2, 8.1 Hz), 4.31 (dd, 1H, *J* = 6.4, 8.2 Hz), 3.04 (s, 3H), 3.02 (s, 3H), 2.99 (dd, 1H, *J* = 5.6, 15.9 Hz), 2.85 (dd, 1H, *J* = 7.2, 15.8 Hz), 2.29 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 169.2, 140.1, 135.3, 131.7, 129.8, 129.8, 121.2, 72.3, 66.0, 65.7, 41.7, 37.4, 35.5, 18.8; HRMS (EI): m/z calcd for $C_{14}H_{18}N_2O_4S$ 310.0987, found 310.0974.

(3bi): 1-((*3aR,8S*)-4-Methyl-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-8-yl)propan-2-one

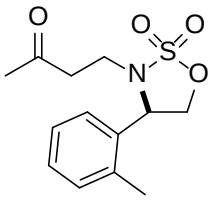


3bi

Yield : 37.2% (43.9 mg as a brown oil), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.28 (m, 1H), 7.13 (d, 1H, *J* = 7.5 Hz), 7.04 (d, 1H, *J* = 7.7 Hz), 5.62-5.65 (m, 1H), 5.45-5.48 (m, 1H), 4.81-4.84 (m, 1H), 4.27-4.30 (m, 1H), 2.95-3.07 (m, 2H), 2.26 (s, 3H), 2.20 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 139.8, 135.3, 132.0, 130.0, 129.8, 120.5, 72.1, 66.2, 64.2, 51.0, 30.6, 18.8.; HRMS(EI): m/z

calcd for $C_{13}H_{15}NO_4S$ 281.0722, found 281. 281.0706.

(3bi′): (*R*)-4-(2,2-Dioxido-4-(o-tolyl)-1,2,3-oxathiazolidin-3-yl)butan-2-one

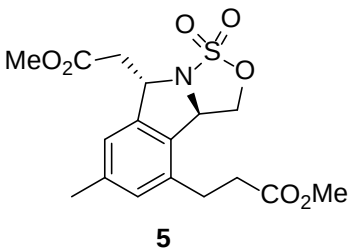


Yield : 11% (13.2 mg as a brown oil), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18-7.21 (m, 1H), 7.03-7.09 (m, 3H), 5.56-5.61 (m, 1H), 4.68-4.71 (m, 1H), 4.58-4.62 (m, 1H), 3.05-3.16 (m, 2H), 2.80-2.95 (m, 2H), 2.49 (s, 3H), 2.12 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.5, 140.4, 138.4, 130.5, 130.0, 129.4, 127.7, 72.6, 54.3, 44.5, 30.1, 25.1, 21.1.; HRMS(EI): m/z calcd for $C_{13}H_{17}NO_4S$ 283.0878, found 283.0880.

5. Synthetic applications

(5): Methyl 3-((*3aR,8S*)-8-(2-methoxy-2-oxoethyl)-6-methyl-1,1-dioxido-3a,8-dihydro-3H-[1,2,3]oxathiazolo[4,3-a]isoindol-4-yl)propanoate

To a solution of **3c** (150 mg, 0.39 mmol) in THF/MeOH (3:2, 1.5 mL) were added $NiCl_2$-$6H_2O$ (186 mg, 0.78 mmol) and $NaBH_4$ (30 mg, 0.78 mmol) at 0 ^{o}C under nitrogen atmosphere. The resulting mixture was stirred overnight at room temperature and then quenched with water (1 mL). The crude mixture was diluted with EtOAc and filtered through a pad of Celite. The filtrate was evaporated under reduced pressure and then diluted with EtOAc. The organic layer was washed with water and brine and dried over anhydrous $MgSO_4$. The solvent was evaporated and the crude mixture was purified by column chromatography on silica gel (eluent EtOAc /hexane =1/5 to 1/3) to give 150 mg (100% yield) as a colorless oil.

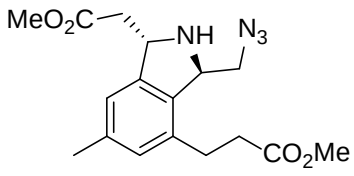


5

Yield : 100% (100 mg as a colorless oil); $[\alpha]_D^{20}$ = -73.5 (c 0.6, $CHCl_3$).; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.91 (s, 1H), 5.60 - 5.57 (m, 2H), 4.90 (dd, 1H, *J* = 8.4, 7.2 Hz), 4.32 (dd, 1H, *J* = 8.4, 6.7 Hz), 3.77 (s, 3H), 3.70 (s, 3H), 2.88 (dd, 1H, *J* = 16.0, 5.7 Hz), 2.82 (dd, 1H, *J* = 16.0, 7.1 Hz), 2.81 - 2.78 (m, 2H), 2.70 - 2.67 (m, 2H), 2.37 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 172.6, 170.3, 140.2, 139.9, 134.6, 132.5, 129.2, 121.5, 72.7. 66.2, 64.5, 52.0, 51.9, 42.3, 34.0, 27.5, 21.4.; HRMS (EI): m/z calcd for $C_{17}H_{21}NO_7S$ 383.1039, found 383.1041.

(6): Methyl 3-((*1S,3R*)-3-(azidomethyl)-1-(2-methoxy-2-oxoethyl)-6-methylisoindolin-4-yl)propanoate

To a solution of **5** (150 mg, 0.39 mmol) in anhydrous DMF (2 mL) was added NaN_3 (127 mg, 0.78 mmol) under nitrogen atmosphere. The reaction mixture was stirred at 65 ^oC for 4 h until the starting material was consumed completely (monitored by TLC) and cooled to room temperature. Subsequently, water (0.43 mL) was added and stirring was continued for 30 min. DMF was removed on a rotary evaporator under vacuum (bath temp. 60 ^0C) and the residue was re-dissolved in EtOAc. The organic layer was washed with 1/2 saturated brine and dried over anhydrous $MgSO_4$. The solvent was evaporated and the crude mixture was purified by column chromatography on silica gel (eluent DCM/MeOH =9/1) to give 125 mg (92% yield) as pale red solid.

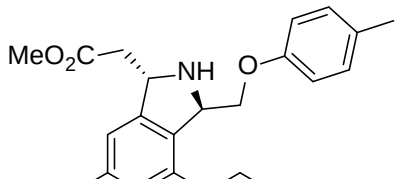


6

Yield : 92% (125 mg as a solid); mp = 96.9-100.2 ^oC; $[\alpha]_D^{20}$ = +51.0 (c 0.3, $CHCl_3$).; ^1H NMR (500 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.83 (s, 1H), 5.36 (s, 1H), 5.24 (s, 1H), 4.40 (d, 1H, *J* = 12.6 Hz), 3.71-3.61 (m, 1H), 3.65 (s, 3H), 3.58 (s, 3H), 3.28-3.25 (m, 1H), 2.98-2.93 (m, 1H), 2.91-2.83 (m, 2H), 2.62 (t, 2H, *J* = 7.8 Hz), 2.51 (brs, 1H), 2.31 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 174.2, 173.1, 142.6, 138.5, 134.4, 132.8, 128.5, 121.2, 64.3. 60.7, 53.4, 51.8, 51.7, 41.2, 34.5, 27.1, 21.4.; HRMS (EI): m/z calcd for $C_{17}H_{22}N_4O_4$ 346.1641, found 346.1650.

(7): Methyl 3-((*1S,3R*)-1-(2-methoxy-2-oxoethyl)-6-methyl-3-((p-tolyloxy)methyl)isoindolin-4-yl)propanoate

The mixture of *p*-cresol (23 mg, 0.21 mmol) and NaH (5 mg, 0.21 mmol) in anhydrous DMF (0.5mL) was stirred at rt for 5 min. A solution of **5** (38 mg, 0.1 mmol) in anhydrous DMF (0.7 mL) was added to the reaction mixture at 0 ^oC. The resulting mixture was stirred overnight at room temperature. When the starting material was consumed completely (monitored by TLC), water (0.5mL) was added and stirring was continued for 1 hr. DMF was removed on a rotary evaporator under vacuum (bath temp. 60 ^0C) and the residue was purified by preparative TLC on silica gel (eluent DCM/MeOH = 9/1) to afford 36 mg (88% yield) as a white solid.



7

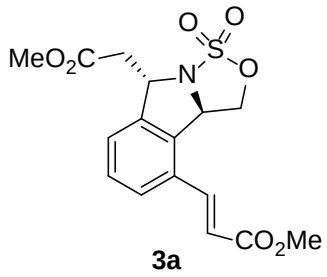
Yield : 88% (36 mg as a white solid); mp = 145.3-151.7 ^oC; $[\alpha]_D$

^{20} = +62.7 (c 0.3, $CHCl_3$).; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (d, 2H, *J* = 8.2 Hz), 6.78 (s, 1H), 6.71 (s, 1H), 6.61 (d, 2H, *J* = 8.3 Hz), 5.29 (s,1H), 5.25 (s, 1H), 4.53 (d, 1H, *J* = 8.2 Hz), 4.43 (brs, 1H), 3.60 (s, 3H), 3.46 (s, 3H), 3.16 (dd, 1H, *J* = 16.3, 4.8 Hz), 2.99-2.92(m, 2H), 2.81-2.76 (m, 1H), 2.54-2.42 (m, 3H), 2.28 (s, 3H), 2.13 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 174.4, 173.5, 156.9, 142.3, 137.6, 135.2, 134.6, 129.8, 129.5, 128.2, 120.8, 115.3, 70.5. 64.1, 60.1, 51.8, 51.6, 40.7, 34.8, 27.6, 21.4, 20.4.; HRMS (EI): m/z calcd for $C_{24}H_{29}NO_5$ 411.2046, found 411.2068.

6. X-ray crystallography analysis

6-1. X-ray crystallography analysis data of (*1R,3S*)-3a

CCDC-1435134 contains the supplementary crystallographic data for (*1R,3S*)-**3a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.



3a

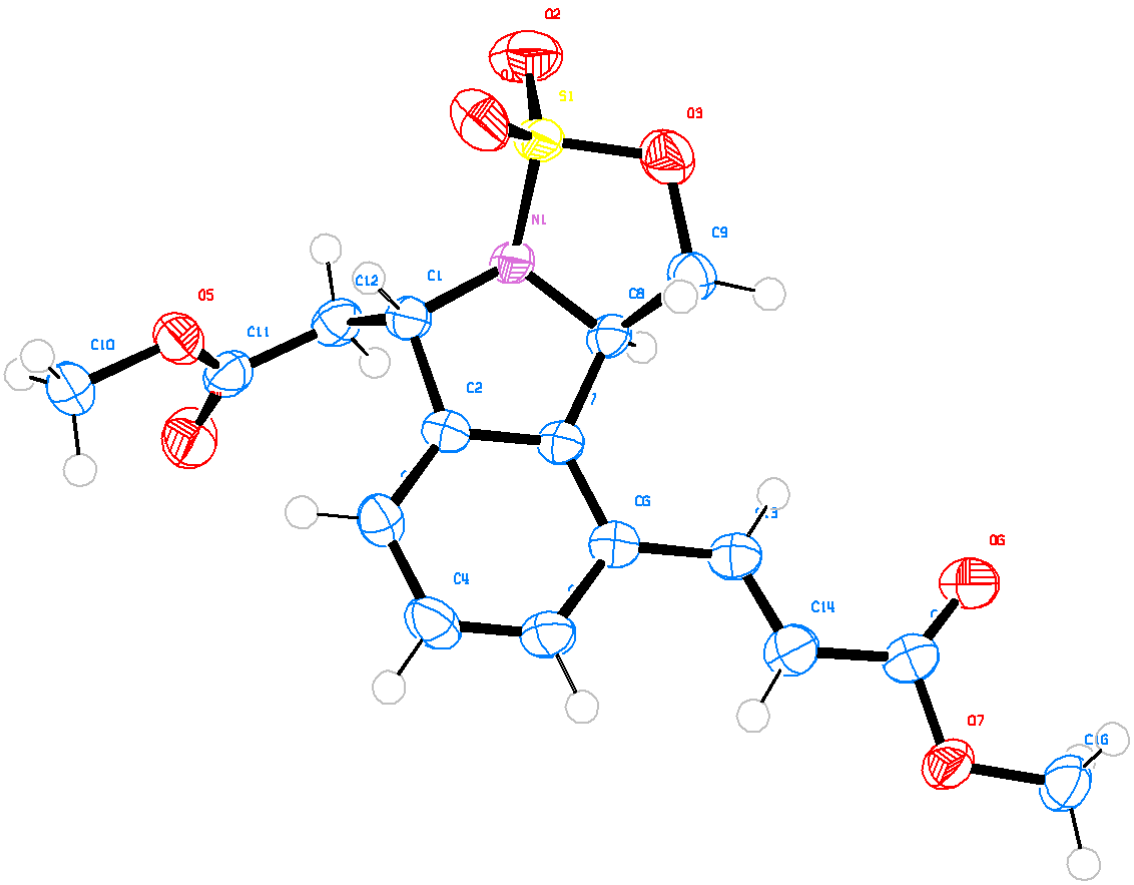
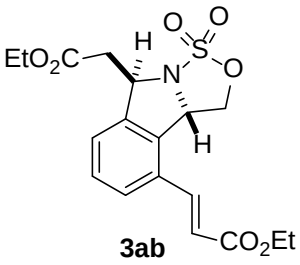


Table 1. Crystal data and structure refinement for (*1R,3S*)-3a

Identification code	20151103lt_0m	
Empirical formula	C16 H17 N O7 S	
Formula weight	367.37	
Temperature	100(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.1638(3) Å	α= 90°.
	b = 14.6526(7) Å	β= 102.564(3)°.
	c = 9.1812(4) Å	γ = 90°.
Volume	809.35(7) $Å^3$	
Z	2	
Density (calculated)	1.507 Mg/m^3	
Absorption coefficient	0.241 mm^{-1}	
F(000)	384	
Crystal size	0.32 x 0.10 x 0.08 mm^3	
Theta range for data collection	2.27 to 28.46°	
Index ranges	-8<=h<=8, -19<=k<=19, -12<=l<=12	
Reflections collected	14993	
Independent reflections	4033 [R(int) = 0.0341]	
Completeness to theta = 28.46°	98.9 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9810 and 0.9270	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4033 / 1 / 226	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0401, wR2 = 0.1037	
R indices (all data)	R1 = 0.0460, wR2 = 0.1079	
Absolute structure parameter	0.06(7)	
Largest diff. peak and hole	0.848 and -0.261 $e.Å^{-3}$	

6-2. X-ray crystallography analysis data of (*1S,3R*)-3ab

CCDC-1400877 contains the supplementary crystallographic data for (*1S,3R*)-**3ab**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.



3ab

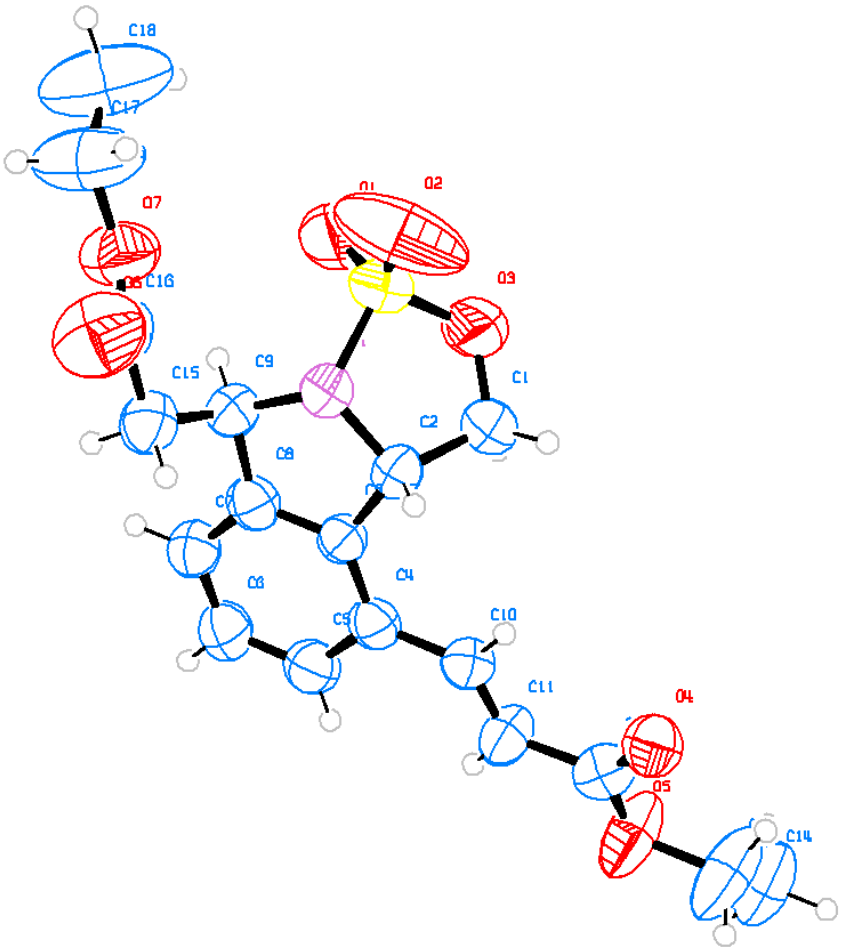
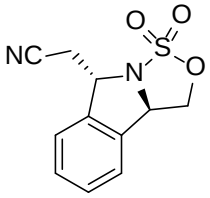


Table 2. Crystal data and structure refinement for (*1S,3R*)-3ab

Identification code	20150112_0m	
Empirical formula	C18 H21 N O7 S	
Formula weight	395.42	
Temperature	296(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 6.6015(2) Å	α= 90°.
	b = 16.8605(4) Å	β= 90°.
	c = 17.1484(4) Å	γ = 90°.
Volume	1908.70(9) $Å^3$	
Z	4	
Density (calculated)	1.376 Mg/m^3	
Absorption coefficient	0.209 mm^{-1}	
F(000)	832	
Crystal size	0.24 x 0.04 x 0.02 mm^3	
Theta range for data collection	1.69 to 28.32°	
Index ranges	-8<=h<=8, -22<=k<=22, -22<=l<=22	
Reflections collected	53487	
Independent reflections	4748 [R(int) = 0.1093]	
Completeness to theta = 28.32°	99.8 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9958 and 0.9515	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4748 / 0 / 245	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0670, wR2 = 0.1734	
R indices (all data)	R1 = 0.1579, wR2 = 0.2193	
Absolute structure parameter	-0.02(16)	
Extinction coefficient	0.008(3)	
Largest diff. peak and hole	0.301 and -0.252 $e.Å^{-3}$	

6-3. X-ray crystallography analysis data of *racemic*-3ad

CCDC-1432488 contains the supplementary crystallographic data for *racemic*-**3ad**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.



3ad

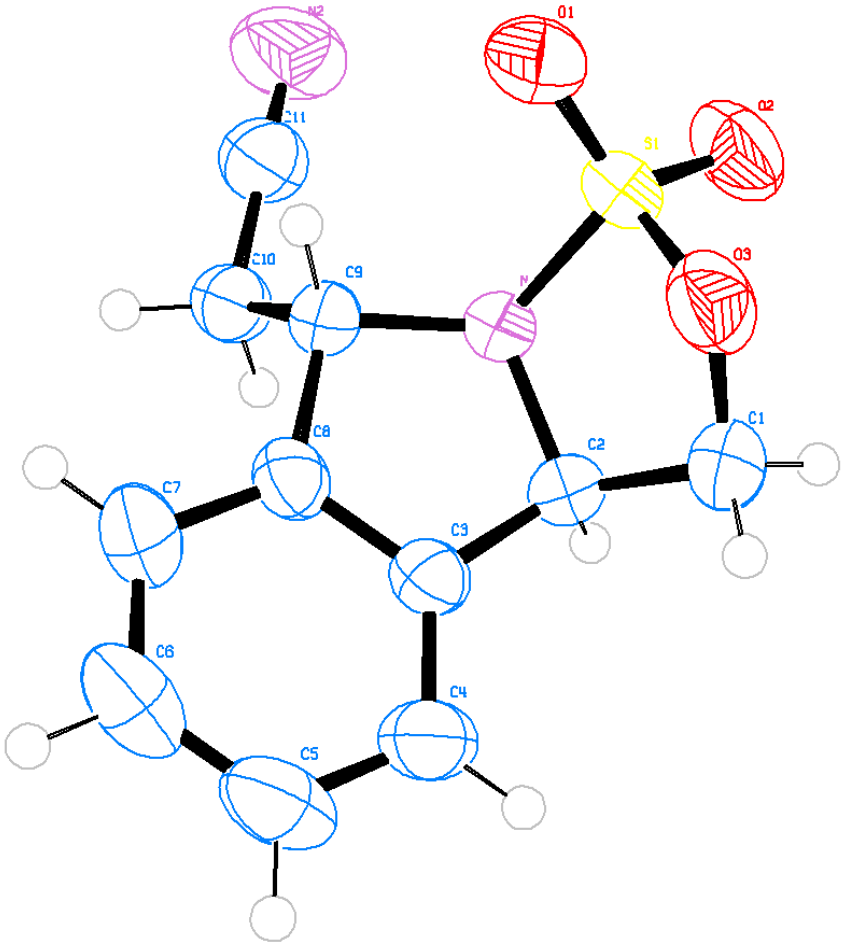
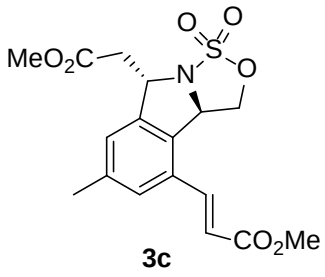


Table 3. Crystal data and structure refinement for *racemic*-3ad

Identification code	20150720_2_0m	
Empirical formula	C11 H10 N2 O3 S	
Formula weight	250.27	
Temperature	296(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.1628(2) Å	α= 90°.
	b = 8.11110(10) Å	β= 90.5330(10)°.
	c = 17.0276(3) Å	γ = 90°.
Volume	1127.34(4) $Å^3$	
Z	4	
Density (calculated)	1.475 Mg/m^3	
Absorption coefficient	0.284 mm^{-1}	
F(000)	520	
Crystal size	0.51 x 0.40 x 0.16 mm^3	
Theta range for data collection	2.39 to 28.30°	
Index ranges	-10<=h<=10, -10<=k<=10, -22<=l<=22	
Reflections collected	20136	
Independent reflections	2800 [R(int) = 0.0231]	
Completeness to theta = 28.30°	99.8 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9559 and 0.8685	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2800 / 0 / 154	
Goodness-of-fit on F^2	1.080	
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.1005	
R indices (all data)	R1 = 0.0416, wR2 = 0.1051	
Largest diff. peak and hole	0.254 and -0.404 $e.Å^{-3}$	

6-4. X-ray crystallography analysis data of (*1R,3S*)-3c

CCDC-1400887 contains the supplementary crystallographic data for *racemic*-**3ad**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.



3c

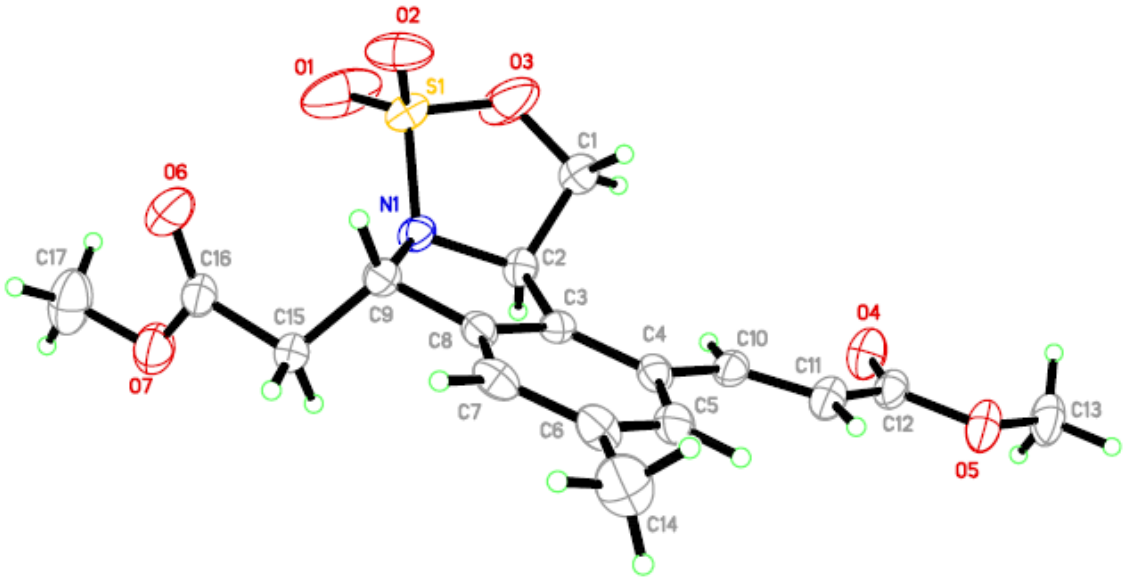


Table 4. Crystal data and structure refinement for (*1R,3S*)-3c

Identification code	20150429_0m	
Empirical formula	C17 H19 N O7 S	
Formula weight	381.39	
Temperature	296(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 6.20840(10) Å	α= 90°.
	b = 13.7420(2) Å	β= 90°.
	c = 21.5303(4) Å	γ = 90°.
Volume	1836.88(5) $Å^3$	
Z	4	
Density (calculated)	1.379 Mg/m^3	
Absorption coefficient	0.215 mm^{-1}	
F(000)	800	
Crystal size	0.28 x 0.08 x 0.02 mm^3	
Theta range for data collection	1.76 to 28.34°	
Index ranges	-8<=h<=8, -18<=k<=18, -28<=l<=28	
Reflections collected	49437	
Independent reflections	4571 [R(int) = 0.0664]	
Completeness to theta = 28.34°	99.7 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9957 and 0.9423	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4571 / 0 / 236	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0618, wR2 = 0.1407	
R indices (all data)	R1 = 0.1195, wR2 = 0.1629	
Absolute structure parameter	-0.01(13)	
Largest diff. peak and hole	0.469 and -0.538 $e.Å^{-3}$	