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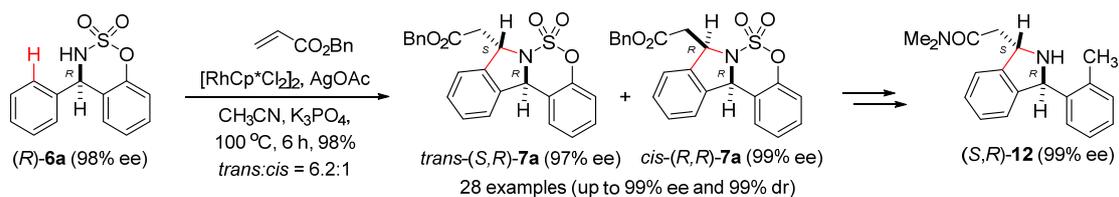
Tandem Rh-catalyzed oxidative C-H olefination and cyclization of enantiomerically enriched benzo-1,3-sulfamidates: Stereoselective synthesis of *trans*-1,3-disubstituted isoindolines

Raghavendra Achary,[†] In-A Jung^{†‡} and Hyeon-Kyu Lee^{†**}

[†]Korea Chemical Bank, Korea Research Institute of Chemical Technology, PO Box 107, Yuseong, Daejeon 305-600, Korea; [‡]Department of Medicinal Chemistry and Pharmacology, University of Science and Technology, 113 Gwahango, Yuseong, Daejeon 305-333, Korea.

leehk@kriict.re.kr

ABSTRACT



A tandem process, involving Rh(III)-catalyzed oxidative C-H olefination of enantiomerically enriched 4-aryl-benzo-1,3-sulfamidates and subsequent intramolecular aza-Michael cyclization has been developed. The reaction produces *trans*-benzosulfamidate-fused-1,3-disubstituted isoindolines as major products, in which the configurational integrity of the stereogenic center in the starting material is preserved. Further transformations of the benzosulfamidate-fused-1,3-disubstituted isoindolines are described.

INTRODUCTION

Owing to their atom- and step-economic nature, direct catalytic activation of unreactive C-H bonds and subsequent C-C bond formation reactions have become increasingly important in routes for the synthesis of organic substances. Among transformations of this type, site-selective, transition metal-catalyzed, C-H bond functionalization reactions of arenes bearing directing groups have emerged as powerful and straightforward methods for the preparation of structurally diverse molecules.¹ In earlier

studies, Pd(II)² complexes were extensively explored and widely used to promote C-H activation processes. However, more recently, Ru(II)^{1f,3} and Rh(III)^{1a,4} complexes have been found to exhibit high catalytic activities, lower catalyst loadings and broader functional group compatibilities, which in some cases are superior to those of Pd(II) catalysts.

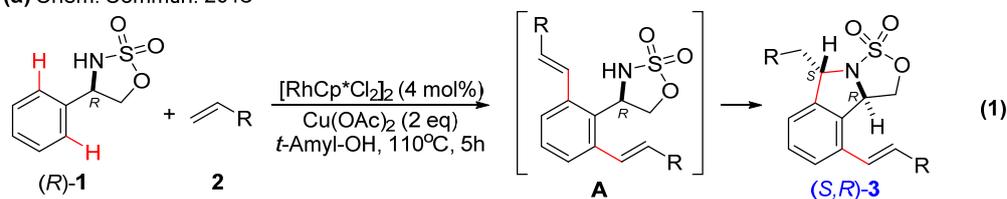
In these catalytic C-H bond functionalization processes, pre-coordination of transition metal catalysts to directing groups and subsequent selective activation of proximal *ortho* C-H bonds are fundamentally important steps.⁵ Therefore, a large effort has been devoted to site-selective functionalization of C(sp²)-H bonds of arenes bearing various directing groups⁵ such as amides, anilides, carbamates, sulfonamides, ketones, acids, esters and hydroxyls. In addition to these monodentate groups, bidentate directing groups, most typically 8-aminoquinoline amides,^{2b,6} have also been observed to promote activation of C-H bonds effectively. These types of directing groups not only enhance the activities of the transition metal catalysts but also confer site-selectivity on the reactions.

In this regard, we recently demonstrated that enantiomerically enriched 5-membered cyclic sulfamidates serve as a novel chiral directing groups⁷ (Scheme 1).

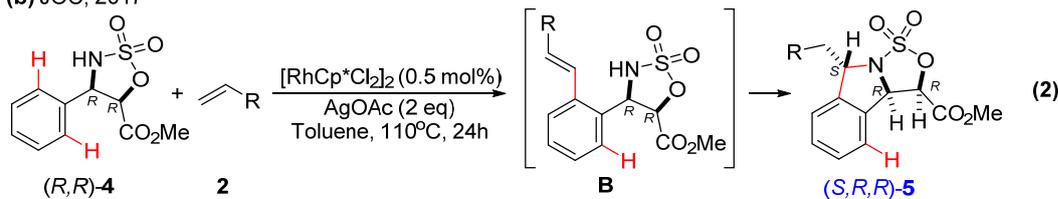
Scheme 1.

Our Previous Studies

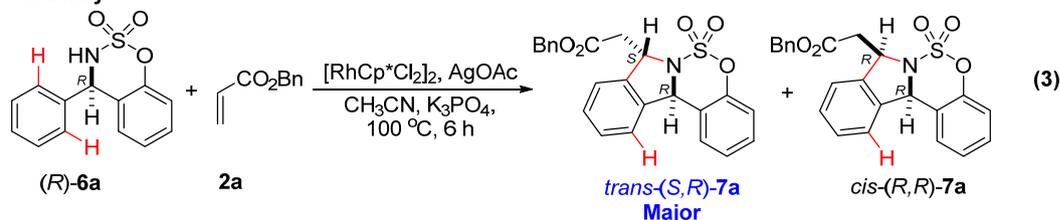
(a) Chem. Commun. 2016^{7a}



(b) JOC, 2017^{7b}



This Study



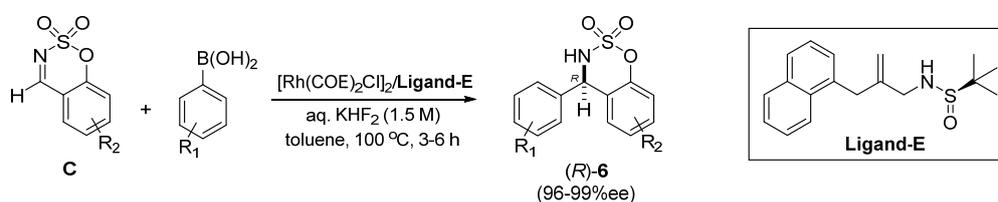
In those efforts, we showed that 5-membered cyclic 4-aryl-sulfamidates (*R*)-**1** and (*R,R*)-**4** undergo oxidative C-H olefination with alkenes **2**, in the presence of Rh(III) to generate the respective styrene and bis-styrene intermediates **A** or **B**, which spontaneously cyclize to produce the corresponding 1,3-disubstituted isoindolines (*S,R*)-**3** or (*S,R,R*)-**5** as exclusive products. In these processes, the configurational integrities of the stereogenic centers in the starting sulfamidates (*R*)-**1** and (*R,R*)-**4** are completely retained and *trans*-1,3-disubstituted isoindolines are formed exclusively (Scheme 1). Moreover, we found that the cyclic sulfamidate moieties in the isoindoline products **3** and **5** produced in the process are reactive with a variety of nucleophiles.⁷⁻⁸ Consequently, this moiety serves as a versatile synthetic handle for further functionalization of the isoindoline ring system.

RESULTS AND DISCUSSION

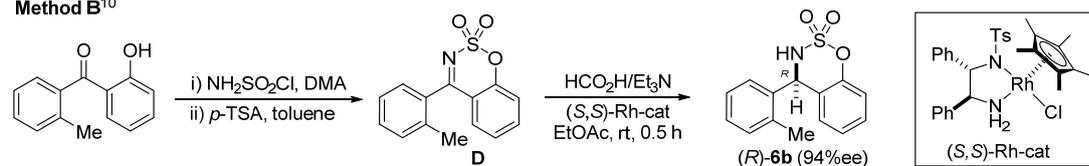
In continuation of this efforts, we explored C(sp²)-H functionalization reaction of enantiomerically enriched, 6-membered 4-aryl-benzo-1,3-sulfamidates **6** to determine if they would serve as effective substrates for processes that form enantiomerically enriched chiral benzo-1,3-sulfamidate-fused-isoindolines **7**. Most of the requisite chiral 4-aryl-benzo-1,3-sulfamidates **6** employed in this study were prepared using a slight modification of previously described methods⁹ involving asymmetric addition of arylboronic acids to cyclic sulfamidate imines **C** (Scheme 2, Method A). These processes take place in most cases with excellent levels of enantioselectivity (96-99%ee). The exception of this trend is (*R*)-**6b**, which is produced in low enantiomeric purity of 88%ee. Consequently this sulfamidate was prepared by using asymmetric transfer hydrogenation¹⁰ of corresponding imine **D**, a process that occurs with a high level of enantioselectivity (94%ee) (Scheme 2, Method B).

Scheme 2. Stereoselective synthesis of 4-aryl-benzo-1,3-sulfamidates **6**

Method A⁹



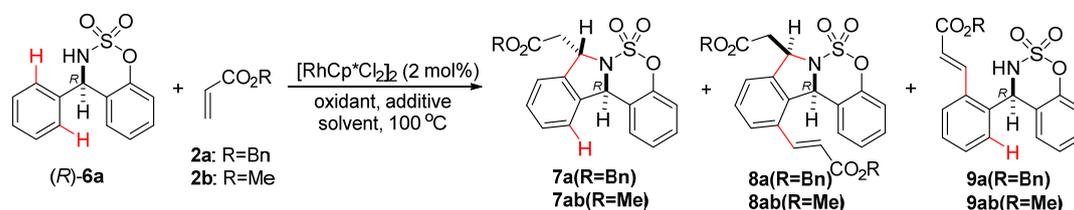
Method B¹⁰



In the initial studies aimed at optimizing the reaction conditions, (*R*)-4-phenyl-benzo-1,3-sulfamidate

((*R*)-**6a**) and methyl acrylate (**2b**) were chosen as model substrates and subjected to selected oxidants and additives in various solvents in the presence of rhodium catalyst, [RhCp*Cl₂]₂, at 100 °C (Table 1).

Table 1. Optimization of the reaction conditions ^a



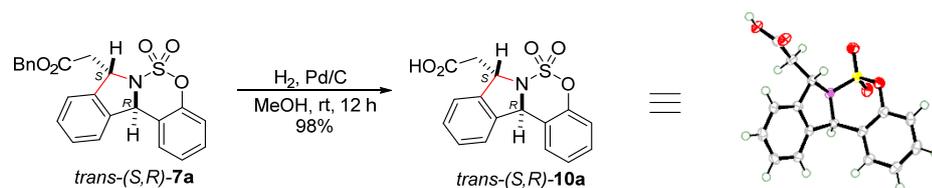
Entry	Oxidant (equiv.)	Additive (equiv.)	R (equiv.)	Solvent	Time (h)	Conversion (7:8:9) ^b %
1	AgOAc (2.0)	--	Me (2)	toluene	12	>99 (21:72:7)
2	AgOAc (2.0)	--	Me (2)	<i>t</i> -amyl-OH	12	>99 (22:24:54)
3	AgOAc (2.0)	--	Me (2)	CH ₃ CN	12	>99 (52:35:13)
4	AgOAc (2.0)	--	Me (2)	acetone	12	>20 (0:0:20)
5	AgOAc (2.0)	--	Me (1.5)	CH ₃ CN	12	>99 (58:30:12)
6	AgOAc (2.0)	--	Me (1.1)	CH ₃ CN	12	>99 (60:30:10)
7	AgOAc (2.0)	K ₃ PO ₄ (1.0)	Me (1.1)	CH ₃ CN	6	>99 (90:10:0)
8	AgOAc (2.0)	K ₃ PO ₄ (0.5)	Me (1.1)	CH ₃ CN	6	>99 ^c (92:8:0)
9	Cu(OAc) ₂ (2.0)	K ₃ PO ₄ (0.5)	Me (1.1)	CH ₃ CN	12	>99 (57:33:10)
10	Cu(OAc) ₂ ·H ₂ O (2.0)	K ₃ PO ₄ (0.5)	Me (1.1)	CH ₃ CN	12	>99 (65:30:5)
11	AgOAc (2.0)	K₃PO₄ (0.5)	Bn (1.1)	CH₃CN	6	>99^d (100:0:0)
12	AgOAc (1.0)	K ₃ PO ₄ (0.5)	Bn (1.1)	CH ₃ CN	24	85 ^d (51:0:34)
13	AgOAc (2.0)	K ₃ PO ₄ (0.5)	Bn (1.1)	CH ₃ CN	24	75 ^c (23:0:52)
14	Cu(OAc) ₂ (2.0)	K ₃ PO ₄ (0.5)	Bn (1.1)	CH ₃ CN	12	>99 (74:21:5)

^a Reaction conditions: **6a** (0.34 mmol), **2a** or **2b** (1.1-2.0 equiv.), [RhCp*Cl₂]₂ (2.0 mol%), Oxidant (2 equiv.), K₃PO₄ (0-1.0 equiv.), solvent (3 mL), 100 °C in sealed tube. ^b Product ratios were determined by using ¹H-NMR analysis of crude reaction mixtures, **7** & **8** are mixtures of *cis* and *trans* diastereomers. ^c isolated yield = 80%. ^d isolated yield = 98%. ^e The reaction was carried out at 60 °C.

The results show that reaction of **6a** with 2 equiv. of methyl acrylate (**2b**) in the presence of [RhCp*Cl₂]₂, and AgOAc as oxidant produces a mixture of **7ab** (mono-olefinated and cyclized product) and **8ab** (di-olefinated and cyclized product) along with small amounts of uncyclized product **9ab**. Moreover, the ratio of **7ab**:**8ab**:**9ab** are highly dependent on solvent. In toluene, **8ab** is the major product (Table 1, entry 1) while **7ab** is generated as the major product in CH₃CN solvent (Table 1, entry 3). The results

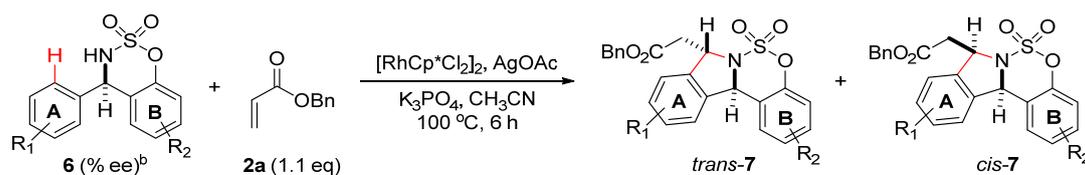
of additional screening demonstrated that presence of the base, K_3PO_4 , leads to a significant improvement in the yield of mono-olefinated and cyclized product **7ab** and a reduction in the amounts of bis-olefinated and cyclized product **8ab** (Table 1, entries 7 and 8). It is believed that K_3PO_4 facilitates intramolecular cyclization of mono-olefinated intermediate **9ab** to form **7ab** and, hence, reduces bis-olefination leading to **8ab** (see discussion of mechanism below). Moreover, when sterically more bulky benzyl acrylate (**2a**, 1.1 equiv.) is employed as the olefin substrate, the mono-olefinated and cyclized product **7a** is formed exclusively in excellent yield (98%, Table 1, entry 11). Interestingly, in contrast to reactions of the 5-membered cyclic sulfamates **1** and **4** (Scheme 1), which produce only *trans*-1,3-disubstituted isoindolines **3** and **5**, respectively, oxidative olefination of the 6-membered cyclic sulfamidate **6a** generates a small amount of the *cis*-1,3-disubstituted isoindoline along with the *trans*-1,3-isomer as a major product (*trans*-**7a**(97% ee):*cis*-**7a**(99% ee) = 6.2:1, Table 2, entry 1). The decreased diastereoselectivity of the latter process is likely a consequence of the increased structural flexibility of the 6-membered ring system in **7a** compared to the structurally more rigid 5-membered counterpart in **3** and **5**. In addition, the diastereoselectivity of **7** (*trans*:*cis* ratio) might be resulted from the thermodynamic stability of *trans*-**7a** and *cis*-**7a** isomers. Actually, a small amount of pure *cis*-**7a** was isolated and subjected to heating conditions in the presence of base (DBU, toluene, 110 °C) and, after 6 h, **7a** was recovered quantitatively with *trans*-**7a** (*trans*:*cis*=6.6:1) as a major product. The absolute stereochemistry of **7a** was assigned by using X-ray crystallographic analysis of the carboxylic acid derivative **10a** (CCDC 1523356) generated from **7a** by hydrogenolysis (Scheme 3). In addition, the structures and stereochemistries of **7f** (CCDC 1523015) and **7j** (CCDC 1526196) were unambiguously determined by using X-ray crystallographic analysis (see Table 2, entries 7 and 11, and SI).

Scheme 3. X-ray crystal structure of *trans*-(*S,R*)-**10a**

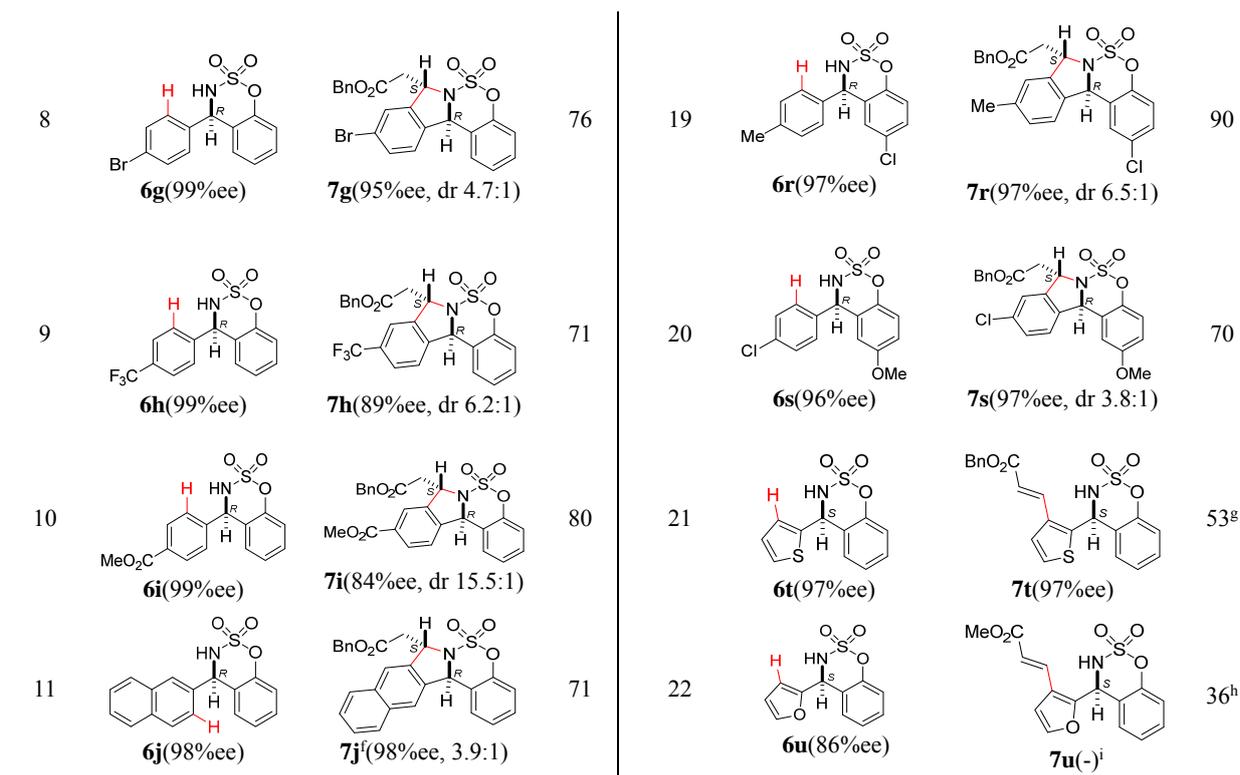


Using the optimized reaction conditions, the sulfamidate scope of the oxidative tandem C-H olefination-cyclization reactions with benzyl acrylate (**2a**) was investigated.

Table 2. Cyclic sulfamidate substrate scope of reactions with benzyl acrylate (**2a**)^a



entry	substrate 6 (% ee) ^b	product 7 (% ee, ^b dr ^c)	yield (%) ^d	entry	substrate 6 (% ee) ^b	product 7 (% ee, ^b dr ^c)	yield (%) ^d
1	 6a (98.0%ee)	 7a (97%ee, dr 6.2:1)	98	12	 6k (98%ee)	 7k (98%ee, dr 6:1)	86
2	 <i>ent-6a</i> (99%ee)	 <i>ent-7a</i> (97%ee, dr 5:1)	98	13	 6l (97%ee)	 7l (97%ee, dr 27.9:1)	90
3	 6b (94%ee)	 7b (94%ee, dr 3.4:1)	90	14	 6m (97%ee)	 7m (96%ee, dr 5.4:1)	87
4	 6c (98%ee)	 7c ^e (98%ee, dr 17:1)	92	15	 6n (99%ee)	 7n (96%ee, dr 14.4:1)	82
5	 6d (97%ee)	 7d (97%ee, 8:1)	92	16	 6o (98%ee)	 7o (97%ee, dr 3.9:1)	84
6	 6e (97%ee)	 7e (96%ee, dr 7.9:1)	82	17	 6p (98%ee)	 7p (99%ee, dr 12.2:1)	80
7	 6f (99%ee)	 7f ^f (99%ee, dr >30:1)	90	18	 6q (98%ee)	 7q (79%ee, dr 7.9:1)	81

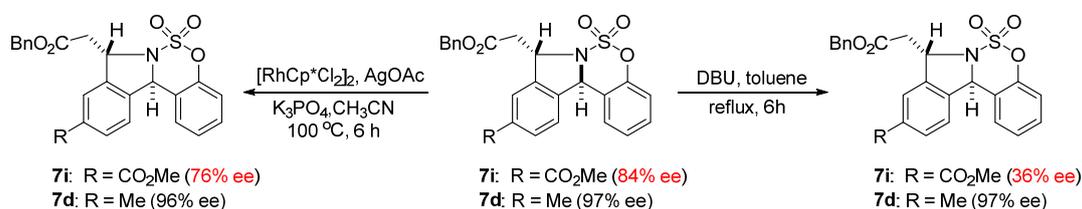


^a Reaction conditions: **6a** (0.38 mmol), **2a** (0.42 mmol), [RhCp*Cl₂]₂ (2.0 mol%), AgOAc (0.76 mmol), K₃PO₄ (0.19 mmol), CH₃CN, 100 °C in a sealed tube for 6-7 h. ^b *ee* and *dr* were determined by using chiral HPLC. ^c *dr* = *trans*-**7**:*cis*-**7**. ^d Isolated yields of diastereomers after silica-gel chromatography. ^e Regiochemistry was identified by using 2D-NOESY analysis (see, SI). ^f Structure and stereochemistry were determined by X-ray crystallography analysis. **7f** (CCDC 1523015), **7j** (CCDC 1526196). ^g 3.0 equiv. of benzyl acrylate without K₃PO₄ was used. ^h 3.0 equiv. of methyl acrylate was used. ⁱ Enantiomers are inseparable

Inspection of the results displayed in Table 2 show that 6-membered cyclic sulfamidates **6** containing various substituents, such as Cl, Br, F, Me, OMe, CF₃, and CO₂Me on either or both of the aryl rings (**A** & **B** rings) undergo the process to produce the corresponding olefinated and cyclized products **7** in high yields and with excellent levels of *ee* and good diastereoselectivities. Because halogen substituents (F, Cl, Br) on the substrates **6** (**6e-g**, **6n-o**, and **6r-s**) are tolerated in this reaction, the corresponding products can be further functionalized by using conventional metal-catalyzed cross coupling reactions (for example, see Scheme 6, eq. 2). As exemplified by reactions of **6b**, **6c** and **6d**, with respective *ortho*, *meta*, *para*-Me on the **A** ring, and **6k**, **6l** and **6m** (with respective *ortho*, *meta*, *para*-OMe on the **B** ring), positions of the substituents on both aromatic rings of **6** have little effect on the reaction efficiencies and enantiomeric excess of the products. However, cyclic sulfamidates having substituents on *meta* position of **A** or **B** ring (**6c** and **6l**) provided corresponding **7c** and **7l** with better diastereoselectivities (for **7c**, *trans*:*cis* = 17:1, for **7l**, *trans*:*cis* = 14.4:1) than those of having *ortho* or *para*-substituents. It is noteworthy that **6c** and **6f**, which possess *meta*-substituents on the **A** ring, react to generate **7c** and **7f**

as exclusive products arising by regioselective activation of the sterically less hindered *ortho* C-H position (Table 2, entries 4 and 7). The structure of **7c** was determined by using 2D-NOE spectroscopy and that of **7f** utilizing X-ray crystallography (see SI). Reaction of **6j**, which possesses a 2-naphthyl ring also successfully produces **7j** as a consequence of activation of the less hindered C(3)-H of naphthyl ring (Table 2, entry 11). The structure of **7j** was also determined by using X-ray crystallographic analyses (see SI). In contrast, **6h**, **6i** and **6q**, which contain strong electron-withdrawing groups such as CF₃ (**6h**, **6q**) or CO₂M (**6i**) at *para*-positions of the **A** or **B** rings react to form the corresponding products **7h**, **7i** and **7q** with decreased levels of ee (**7h**: 99→89% ee, **7i**: 99→84% ee, **7q**: 98→79% ee, Table 2, entries 9, 10 and 18). We assume that the decreased enantioselectivities of these processes might be caused by base-promoted partial racemization of bridgehead protons in **7h**, **7i** and **7q**. To examine this proposal, **7i** (84% ee), which has an electron withdrawing CO₂Me group on *para*-position of ring **A**, was re-subjected to the optimized reaction conditions in the absence of benzyl acrylate (**2a**). After 6 h, **7i**, recovered almost quantitatively, was found to have a 76% ee. Moreover, treatment of **7i** (84% ee) with DBU in refluxing toluene for 6 h led to recovered **7i** with a 36% ee. In contrast, the ee of **7d** (97% ee), which contains a *para*-methyl substituent, is unchanged under the same conditions (97% ee, DBU, toluene, reflux, 6 h) (Scheme 4).

Scheme 4. Base-promoted partial racemization of **7i** and comparison with **7d**^a



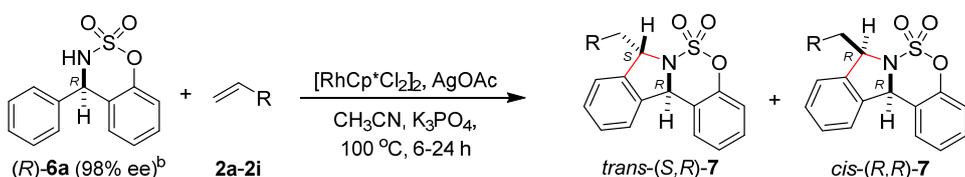
^a Reaction conditions: **6i** (0.1 mmol), [RhCp*Cl₂]₂ (2.0 mol%), AgOAc (0.2 mmol), K₃PO₄ (0.05 mmol), CH₃CN, 100 °C in sealed tube for 6 h. ee and dr were determined by using chiral HPLC.

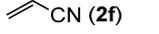
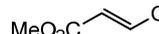
Finally, 6-membered cyclic sulfamidate derivatives possessing heterocyclic substituents such as thiophene (**6t**) and furan (**6u**) react under the standard reaction conditions to form the respective oxidative olefination products **7t** (53%) and **7u** (36%) exclusively, which do not undergo cyclization even when excess amounts of benzyl or methyl acrylate (3 equiv.) are used (Table 2, entries 21 and 22).

The alkene substrate scope of the process was investigated next using reactions of **2b-2g** with (*R*)-**6a** under the optimized reaction conditions. As shown in Table 3, not only benzyl but also methyl and *tert*-

butyl acrylates serve as substrates for this transformation generating the corresponding adducts **7ab-7ac** with high efficiencies and stereoselectivities. Reaction of **6a** with other activated olefins such as phenyl vinyl sulfone (**2d**), methyl vinyl ketone (**2e**) and acrylonitrile (**2f**) also take place to form the corresponding adducts **7ad-7af** in good yields and high stereoselectivities. However, *N,N*-dimethyl acrylamide **2g**, branched acrylate **2h** and internal olefin **2i** does not undergo oxidative olefinations with **6a** under the standard reaction conditions.

Table 3. Alkene substrate scope of reactions with (*R*)-**6a**^a

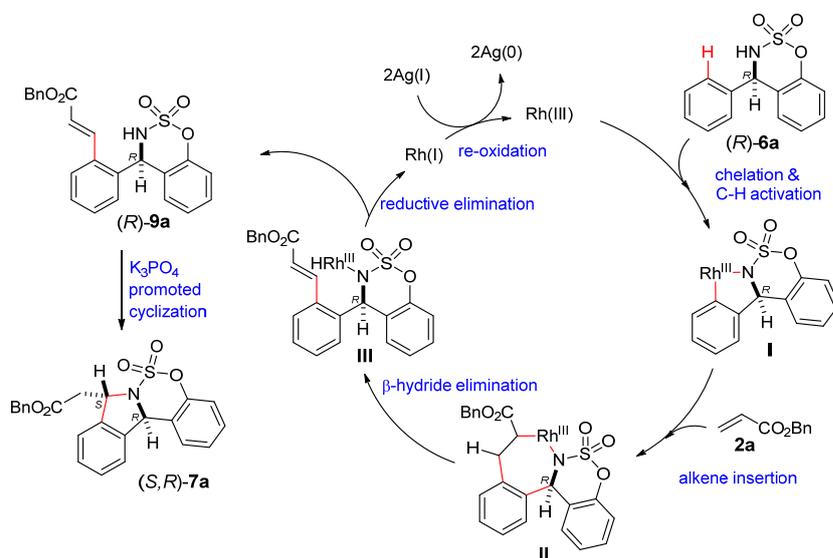


entry	2a-2i	time (h)	product 7	yield (%) ^b	dr ^c (<i>trans</i> -7: <i>cis</i> -7)	%ee ^c (for <i>trans</i> -7)
1	 2a	6	7a	98	6.2:1	98
2	 2b	24	7ab	80	4.6:1	99
3	 2c	24	7ac	70	9.9:1	98
4	 2d	24	7ad	73	10.5:1	97
5	 2e	24	7ae	64	16.5:1	98
6	 2f	6	7af	85	8.8:1	98
7 ^d	 2g	24	7ag	-	-	-
8 ^d	 2h	24	7ah	-	-	-
9	 2i	24	7ai	-	-	-

^a Reaction conditions: **6a** (0.19 mmol), **2** (0.21 mmol), [RhCp*Cl₂]₂ (2.0 mol%), AgOAc (200 mol%), K₃PO₄ (0.1 mmol), CH₃CN, 100 °C in sealed tube for 6-24 h. ^b Isolated yields of diastereomers after silica-gel chromatography. ^c ee and dr were determined by using chiral HPLC. ^d 2 equiv. of olefins were used.

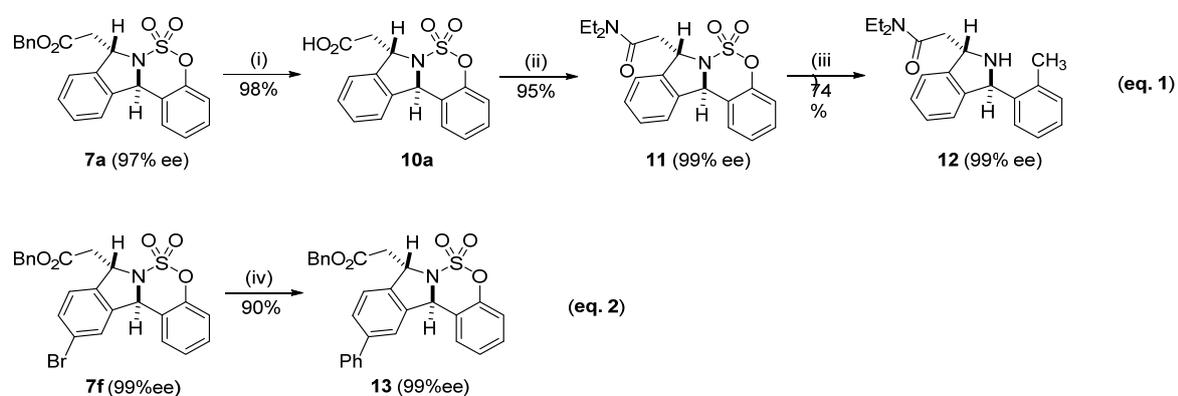
The mechanism displayed in Scheme 5, which is based on the previously reported C-H functionalization reactions of 5-membered cyclic sulfamidate⁷ and related C-H functionalization processes,^{4c,4e,11} is proposed for the reaction forming (*S,R*)-**7a**.

Scheme 5. Plausible mechanism



The pathway is initiated by coordination of Rh(III) to the sulfamidate nitrogen of **6a** and subsequent C-H activation at the *ortho*-position leading to the 5-membered rhodacycle **I**. Coordination and migratory insertion of alkene **2a** to **I** then generates **II** and subsequent β -hydride elimination of **II** forms olefinated product (*R*)-**9a** via intermediate **III** with concomitant release of a Rh(I) species that is reoxidized to the Rh(III) by the action of AgOAc. The formed intermediate (*R*)-**9a** undergoes K_3PO_4 promoted cyclization to generate the thermodynamically more stable *trans*-(*S,R*)-**7a** as the major product accompanied by a different amount of *cis*-(*R,R*)-**7a** (*trans*-**7a**:*cis*-**7a** = 6.2:1, Table 3, entry 1). Actually, treatment of independently synthesized (*R*)-**9a** with K_3PO_4 in CH_3CN results in formation of cyclized product (*S,R*)-**7a** in 80% yield (*trans*:*cis*=5.9:1). But, when (*R*)-**9a** is subjected to the same reaction conditions in the absence of K_3PO_4 , the yield of (*S,R*)-**7a** is only 33% (*trans*:*cis* = 4.5:1).

The isoindoline-fused-1,3-sulfamidates **7**, produced in the process described above can be transformed to more complex substances. For example, **7a** is converted to the 1,3-disubstituted isoindoline **12** via Ni-catalyzed Kumada coupling with $MeMgBr$ (Scheme 6, eq. 1).^{9b} In addition, **7f** is transformed to the biphenyl derivative **13** via Pd-catalyzed Suzuki coupling with phenyl boronic acid (Scheme 6, eq. 2).

Scheme 6. Transformations of **7**^a

^a Reaction conditions: (i) 10% Pd/C (10% wt/wt), H₂ (g), MeOH, rt, 12 h. (ii) diethyl amine, EDCI·HCl, HOBT, DCM, rt, 12 h. (iii) MeMgBr, cat. Ni(dppp)Cl₂ (5 mol%), ether, 55 °C, 16 h; HCl in MeOH, 55 °C, 6 h. (iv) PhB(OH)₂, Pd(PPh₃)₂Cl₂ (4 mol%), Na₂CO₃, dioxane/H₂O (3:1)

CONCLUSION

In the effort described above, we developed a tandem Rh(III)-catalyzed oxidative C-H olefination and intramolecular aza-Michael cyclization reaction that transforms 4-aryl-benzo-1,3-sulfamidates **6** to benzosulfamidate-fused-*trans*-1,3-isoindolines **7**. The process serves as a direct and stereoselective method for synthesis of highly functionalized benzosulfamidate-fused *trans*-1,3-isoindolines from enantiomerically enriched 4-aryl-benzo-1,3-sulfamidates. A wide number of sulfamidates, containing a variety of functional groups on both aryl rings, and activated olefins participate in this process. The configurational integrity of the chiral center in the starting cyclic sulfamidates **6** is retained in the product and the process generates the *trans*-isomers as major products. Finally, examples are provided that show the isoindoline-fused-1,3-sulfamidates **7** produced in this process can be further transformed to more complex substances.

EXPERIMENTAL SECTION

General

All commercial reagents were used as obtained unless otherwise noted. Reactions were performed using oven dried glassware. Flash column chromatography was carried out on silica gel (38-75 μm). Analytical thin layer chromatography (TLC) was performed on silica gel 60 F₂₅₄ plates. Preparative thin layer chromatography (PLC) was performed on silica gel 60 F₂₅₄ 2 mm plates. Visualization of the

developed chromatogram was accomplished with UV light and by staining with Potassium Permanganate (KMnO₄) solution followed by heating. Nuclear magnetic resonance (NMR) spectra were recorded using 500 MHz NMR instrument (¹H NMR at 500 MHz and ¹³C NMR at 125 MHz) or 300 MHz NMR instrument (¹H NMR at 300 MHz and ¹³C NMR at 75 MHz). ¹H 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 ¹³C NMR are reported in terms of chemical shift (δ, ppm). High performance liquid chromatography (HPLC) was carried out on a HPLC system (7725i Injector, SDV 30 Plus Solvent Degassor & Valve Module (Helium Sparging), SP930D Solvent Delivery Pump, UV 730D Absorbance Detector) equipped with Chiralpak (IA, IB, IC, ID, OD, AD-H and OD-H) columns. Specific rotations were measured on a Rudolph Autopol IV (Automatic polarimeter). High-resolution mass spectra and elemental analysis were obtained from the Center for Chemical Analysis of Korea Research Institute of Chemical Technology. HR-MS were measured with electron impact (EI) ionization or fast atom bombardment (FAB) ionization via double focusing mass analyzer (magnetic and electric fields).

Representative Procedure for the Stereoselective Synthesis of benzo-1,3-sulfamidate **6**

Method A: **6a** and **6c**–**6u** (modified from reported procedure)⁹

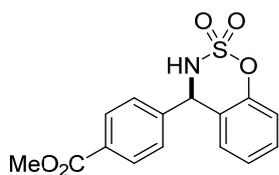
To a solution of cyclic aldimine (50 mg, 0.27 mmol), [Rh(COE)₂Cl₂] (3.0 mg, 1.5 mol%), chiral ligand-**E** (2.7 mg, 3.3 mol%), and ArB(OH)₂ (111 mg, 0.82 mmol) in toluene was stirred at rt for 30 min then 1.5 M aqueous KHF₂ (0.55 mL, 0.82 mmol) was added. The mixture was stirred at 100 °C for 4 h, quenched with water, and extracted with EtOAc. The organic layer was dried over Na₂SO₄, evaporated under vacuum, and purified on silica gel column chromatography using EA/hexanes (1/1 to 2/1) as eluent to afford title compound.

Method B¹⁰: **6b**

To a solution of cyclic sulfamidate imine (100 mg, 0.37 mmol) in EtOAc (3.7 mL) was added (*S,S*)-ClRhCp*[TsDPEN] (1.2 mg, 0.5 mol%) followed by the dropwise addition of HCOOH:Et₃N (1:1 mixture, 0.37 mL) under nitrogen atmosphere. The reaction mixture was stirred at rt for 4 h and quenched with NaHCO₃ (aq). The mixture was extracted with EtOAc and washed with H₂O followed by saturated NaCl (aq). The organic layer was dried over MgSO₄ and evaporated under vacuum. The crude residue was purified on silica gel column chromatography using EA/hexane (1/1 to 2/1) as an eluent to afford title compound as a white solid.

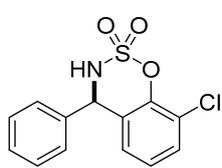
6a–**6h**, **6j**–**6m**, **6o** are known compounds.⁹

6i: Methyl (*R*)-4-(2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)benzoate



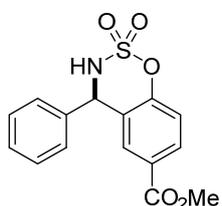
Yield: 95% (145.0 mg as a white solid); mp: 185.5~190.8 °C; 99% ee (Chiralpak AD-H, 20% IPA/*n*-hexanes, 1.0 ml/min, 215nm, $t_R(\text{major}) = 12.6$ min, $t_R(\text{minor}) = 11.9$ min); $[\alpha]_D^{21} = -5.50$ (*c* 0.2, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, *J* = 8.1 Hz, 2H), 7.47-7.45 (m, 2H), 7.38-7.36 (m, 1H), 7.14 (t, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.7 Hz, 1H), 5.99 (d, *J* = 8.4 Hz, 1H), 4.90 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.2, 151.5, 142.4, 131.3, 130.7, 130.0, 128.9, 128.4, 125.4, 121.3, 119.1, 61.5, 52.4; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₁₅H₁₃NO₅S 319.0514; found 319.0517.

6n: (*R*)-8-chloro-4-phenyl-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide



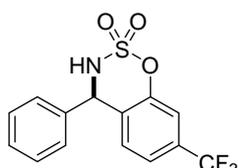
Yield: 88% (120 mg as a white solid); mp: 149.3-151.8 °C; 99% ee (Chiralpak IB, 10% EtOH/*n*-hexanes, 1.1 ml/min, 215nm, $t_R(\text{major}) = 9.5$ min, $t_R(\text{minor}) = 8.5$ min); $[\alpha]_D^{27} = +2.33$ (*c* 0.1, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.54-7.42 (m, 3H), 7.43-7.28 (m, 3H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.92 (d, *J* = 8.7 Hz, 1H), 5.10 (d, *J* = 8.7 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 147.4, 137.4, 130.4, 129.8, 129.6, 128.8, 126.9, 125.1, 124.0, 123.8, 62.1; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₁₃H₁₀ClNO₃S 295.0070; found 295.0080.

6p: Methyl (*R*)-4-phenyl-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine-6-carboxylate-2,2-dioxide

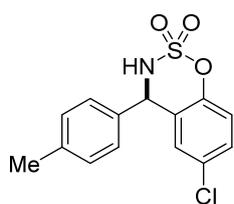


Yield: 80% (105.0 mg as a white solid); mp: 113.0-115.3 °C; 98% ee (Chiralpak AD-H, 30% EtOH/*n*-hexanes, 1.0 ml/min, 215nm, $t_R(\text{major}) = 9.50$ min, $t_R(\text{minor}) = 6.42$ min); $[\alpha]_D^{20} = -4.40$ (*c* 0.5, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.01 (dd, *J* = 2.0, 8.7 Hz, 1H), 7.55 (t, *J* = 1.4 Hz, 1H), 7.46-7.44 (m, 3H), 7.34-7.32 (m, 2H), 7.14 (d, *J* = 8.7 Hz, 1H), 5.93 (d, *J* = 8.6 Hz, 1H), 4.77 (d, *J* = 8.5 Hz, 1H), 3.83 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.5, 154.7, 137.2, 131.1, 130.4, 129.9, 129.7, 128.8, 127.3, 122.1, 119.2, 61.9, 52.4; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₁₅H₁₃NO₅S 319.0514; found 319.0511.

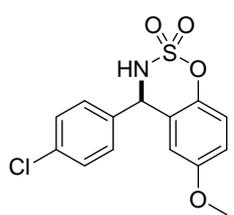
6q: (*R*)-4-phenyl-7-(trifluoromethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide



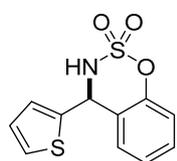
Yield: 77% (50.0 mg as a yellow oil); 98% ee (Chiralpak AD-H, 30% IPA/*n*-hexanes, 0.8 ml/min, 215nm, $t_R(\text{major}) = 5.78$ min, $t_R(\text{minor}) = 6.93$ min); $[\alpha]_D^{29} = +5.55$ (*c* 0.2, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.49 (s, 3H), 7.39-7.37 (m, 4H), 7.01 (d, *J* = 7.6 Hz, 1H), 5.97 (s, 1H), 4.83 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 151.5, 137.0, 132.3 (q, *J*_{CF} = 35.5 Hz), 130.0, 129.8, 129.5, 128.7, 125.9, 124.1, 121.8 (d, *J*_{CF} = 6.9 Hz), 116.5 (q, *J*_{CF} = 3.9 Hz), 61.9; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₁₄H₁₀F₃NO₃S 329.0333; found 329.0306.

6r: (*R*)-6-chloro-4-(*p*-tolyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide

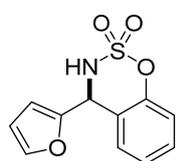
Yield: 88% (100 mg as a colorless oil); 97% ee (Chiralpak AD-H, 30% EtOH/*n*-hexanes, 1.0 ml/min, 215nm, t_R (major) = 6.61 min, t_R (minor) = 5.45 min); $[\alpha]_D^{21} = +59.8$ (*c* 0.5, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.28 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.84 (d, *J* = 1.8 Hz, 1H), 5.85 (d, *J* = 8.6 Hz, 1H), 4.68 (d, *J* = 8.8 Hz, 1H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 150.0, 140.1, 134.1, 130.5, 130.4, 129.9, 128.6, 128.3, 123.8, 120.3, 61.6, 21.3; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₁₄H₁₂ClNO₃S 309.0226; found 309.0212.

6s: (*R*)-4-(4-chlorophenyl)-6-methoxy-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine-2,2-dioxide

Yield: 92% (140.0 mg as a colorless oil); 96% ee (Chiralpak AD-H, 30% EtOH/*n*-hexanes, 1.0 ml/min, 215nm, t_R (major) = 9.63 min, t_R (minor) = 7.48 min); $[\alpha]_D^{21} = +48.8$ (*c* 0.5, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 1H), 6.87 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.27 (d, *J* = 2.8 Hz, 1H), 5.83 (d, *J* = 8.5 Hz, 1H), 4.68 (d, *J* = 8.5 Hz, 1H), 3.67 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 156.6, 145.3, 136.2, 135.7, 130.2, 129.7, 122.2, 120.0, 115.4, 113.1, 61.4, 55.7; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₁₄H₁₂ClNO₄S 325.0176; found 325.0155.

6t: (*S*)-4-(thiophen-2-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide

Yield: 84% (122.0 mg as a white solid); mp: 117.5-120.7 °C; 97% ee (Chiralpak IC, 10% IPA/*n*-hexanes, 0.8 ml/min, 215nm, t_R (major) = 17.9 min, t_R (minor) = 19.8 min); $[\alpha]_D^{20} = +92.4$ (*c* 0.2, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.44-7.38 (m, 2H), 7.20-7.16 (m, 2H), 7.12-7.08 (m, 3H), 6.25 (d, *J* = 8.6 Hz, 1H), 4.75 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 150.9, 140.1, 130.2, 128.8, 128.5, 127.6, 127.3, 125.3, 121.6, 118.9, 57.0; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₁₁H₉NO₃S₂ 267.0024; found 267.0015.

6u: (*S*)-4-(furan-2-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide

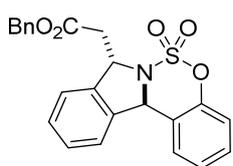
Yield: 89% (122.0 mg as a yellow solid); mp: 94.4-98.1 °C; 86% ee (Chiralpak IC, 10% IPA/*n*-hexanes, 0.8 ml/min, 215nm, t_R (major) = 21.5 min, t_R (minor) = 20.6 min); $[\alpha]_D^{20} = +15.5$ (*c* 0.5, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.48 (d, *J* = 1.5 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.48 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.05 (d, *J* = 9.5 Hz, 1H), 4.96 (d, *J* = 9.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 151.0, 140.2, 130.3, 128.9, 128.6, 127.7, 127.4, 125.4, 121.7, 119.0, 57.1; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₁₁H₉NO₄S 251.0252; found 251.0246.

General procedure for the oxidative olefination-cyclization of **6** to **7**

A 20 mL sealed tube equipped with a magnetic stirring bar was charged with benzo-1,3-sulfamidate **6a** (100 mg, 0.34 mmol), [RhCp*Cl₂]₂ (4.2 mg, 2.0 mol%), AgOAc (115 mg, 0.69 mmol), benzyl acrylate (61 mg, 0.38 mmol), K₃PO₄ (36 mg, 0.17 mmol) and 3 mL of anhydrous MeCN. The reaction tube was capped and stirred at 100 °C (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 celite pad. The solvents and the volatiles were evaporated under reduced pressure followed by the purification through flash column chromatography using EtOAc /hexanes (1/5 to 1/3) as an eluent to afford title compounds as diastereomeric mixture (determined by chiral HPLC chromatography).

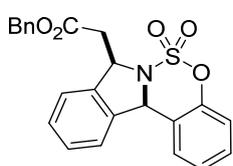
7a: Yield 98% (158 mg as a colorless oil, *trans*:*cis*=6.2:1).

trans-(S,R)-7a: Benzyl-2-((8*S*,12*bR*)-6,6-dioxido-8,12*b*-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-*a*]isoindol-8-yl)acetate



White solid, mp: 87.1-89.2 °C; 97% ee (Chiralpak AD-H, 20% IPA/*n*-hexanes, 1.0 ml/min, 215nm, *t*_R(major) = 20.8 min, *t*_R(minor) = 23.5 min); [α]_D²² = +68.9 (*c* 0.7, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.43-7.30 (m, 7H), 7.27-7.19 (m, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.04 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.26 (s, 1H), 5.54 (d, *J* = 7.5 Hz, 1H), 5.19 (s, 2H), 3.43 (dd, *J* = 16.6, 3.3 Hz, 1H), 3.06 (dd, *J* = 16.6, 7.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 170.1, 149.8, 138.6, 135.5, 129.2, 129.2, 128.9, 128.6, 128.5, 128.4, 126.5, 125.8, 123.0, 122.2, 119.3, 67.3, 63.1, 41.2; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₃H₁₉NO₅S 421.0984; found 421.0966.

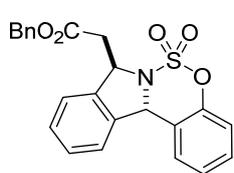
cis-(R,R)-7a: Benzyl-2-((8*R*,12*bR*)-6,6-dioxido-8,12*b*-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-*a*]isoindol-8-yl)acetate



Colorless oil, >99% ee (Chiralpak AD-H, 20% IPA/*n*-hexanes, 1.0 ml/min, 215nm, *t*_R(major) = 13.1 min); [α]_D²² = -86.3 (*c* 0.3, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.69 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.39-7.30 (m, 7H), 7.24-7.17 (m, 2H), 7.03 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.24 (s, 1H), 5.58 (dd, *J* = 10.8, 3.4 Hz, 1H), 5.14 (s, 2H), 3.64 (dd, *J* = 15.6, 3.5 Hz, 1H), 2.35 (dd, *J* = 15.6, 10.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.8, 150.4, 139.7, 137.2, 135.2, 129.6, 129.1, 128.8, 128.6, 128.5, 126.0, 125.5, 123.8, 123.7, 121.4, 119.1, 66.8, 65.3, 62.9, 38.1; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₃H₁₉NO₅S 421.0984; found 421.0956.

ent-7a: Yield 98% (78.0 mg as a colorless oil, *trans*:*cis*=5:1).

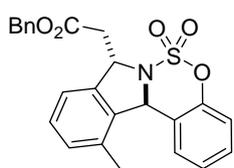
trans-(R,S)-7a: Benzyl-2-((8R,12bS)-6,6-dioxido-8,12b-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate



Colorless oil, 97% ee (Chiralpak AD-H, 20% IPA/*n*-hexanes, 1.0 ml/min, 215nm, $t_R(\text{major}) = 23.8$ min, $t_R(\text{minor}) = 21.1$ min); $[\alpha]_D^{25} = 62.2$ (*c* 0.2, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.41-7.36 (m, 9H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 8.1, 1H), 6.26 (s, 1H), 5.54 (d, *J* = 7.4 Hz, 1H), 5.19 (s, 2H), 3.43 (dd, *J* = 16.6, 3.2 Hz, 1H), 3.06 (dd, *J* = 16.6, 7.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 170.1, 149.8, 138.6, 137.7, 135.5, 129.2, 129.1, 128.5, 128.4, 126.4, 125.8, 122.9, 122.8, 122.2, 119.3, 67.2, 66.7, 63.1, 41.2.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₃H₁₉NO₅S 421.0984; found 421.0981.

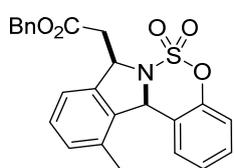
7b: Yield 90% (142 mg as a colorless oil, *trans:cis*=3.4:1).

trans-(S,R)-7b: Benzyl-2-((8S,12bR)-12-methyl-6,6-dioxido-8,12b-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate



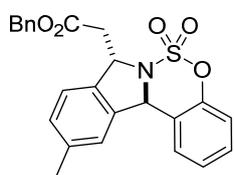
Colorless oil, 94% ee (Chiralpak AD-H, 10% EtOH/*n*-hexanes, 0.5 ml/min, 215nm, $t_R(\text{major}) = 29.9$ min, $t_R(\text{minor}) = 22.8$ min); $[\alpha]_D^{22} = -52.2$ (*c* 0.5, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.41-7.30 (m, 5H), 7.25-7.20 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 6.9 Hz, 1H), 6.35 (s, 1H), 5.32 (dd, *J* = 7.8, 2.8 Hz, 1H), 5.24-5.18 (m, 2H), 3.54 (dd, *J* = 17.0, 3.2 Hz, 1H), 2.95 (dd, *J* = 17.0, 8.0 Hz, 1H), 2.66 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.4, 149.9, 140.2, 136.6, 135.5, 131.8, 130.6, 129.5, 129.2, 128.6, 128.4, 128.3, 127.2, 125.7, 121.3, 120.4, 118.9, 66.7, 66.2, 62.0, 40.0, 20.5.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₄H₂₁NO₅S 435.1140; found 435.1128.

cis-(R,R)-7b: Benzyl-2-((8R,12bR)-12-methyl-6,6-dioxido-8,12b-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate

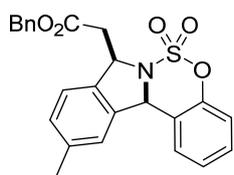


Colorless oil, 94% ee (Chiralpak AD-H, 10% EtOH/*n*-hexanes, 0.5 ml/min, 215nm, $t_R(\text{major}) = 16.9$ min, $t_R(\text{minor}) = 21.3$ min); $[\alpha]_D^{22} = -98.9$ (*c* 0.2, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.30 (m, 6H), 7.25-7.03 (m, 6H), 6.26 (s, 1H), 5.51 (dd, *J* = 11.0, 3.4 Hz, 1H), 5.32-5.01 (m, 2H), 3.46 (dd, *J* = 15.6, 3.4 Hz, 1H), 2.64 (s, 3H), 2.19 (dd, *J* = 15.5, 11.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.8, 150.8, 140.3, 136.5, 135.2, 132.8, 130.6, 129.9, 129.2, 128.7, 128.6, 128.5, 126.5, 125.3, 122.0, 121.4, 118.8, 66.8, 63.9, 63.0, 37.5, 20.5.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₄H₂₁NO₅S 435.1140; found 435.1120.

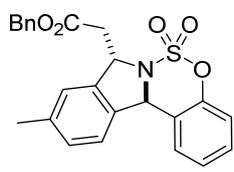
7c: Yield 92% (145 mg as a colorless oil, *trans:cis*=17:1).

trans-(S,R)-7c:*Benzyl-2-((8S,12bR)-11-methyl-6,6-dioxido-8,12b-**dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*

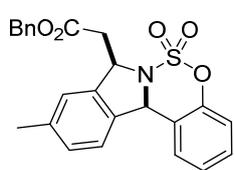
Colorless oil, 98% ee (Chiralpak IC, 5% EtOH/*n*-hexanes, 0.8 ml/min, 215nm, $t_R(\text{major}) = 38.4$ min, $t_R(\text{minor}) = 24.1$ min); $[\alpha]_D^{21} = +12.6$ (*c* 0.8, CHCl₃).; ¹H NMR (500 MHz, CDCl₃) δ 7.49 (d, *J* = 7.7 Hz, 1H), 7.41-7.28 (m, 7H), 7.28-7.22 (m, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.05-7.02 (m, 2H), 6.21 (s, 1H), 5.50 (d, *J* = 7.5 Hz, 1H), 5.19 (d, *J* = 1.4 Hz, 2H), 3.40 (dd, *J* = 16.5, 3.3 Hz, 1H), 3.03 (dd, *J* = 16.5, 7.8 Hz, 1H), 2.42 (s, 3H).; ¹³C NMR (125 MHz, CDCl₃) δ 170.1, 149.8, 138.9, 137.8, 135.7, 135.5, 130.1, 129.1, 128.6, 128.5, 128.3, 126.5, 125.8, 123.3, 122.7, 122.4, 119.2, 67.2, 66.7, 63.0, 41.2, 21.5.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₄H₂₁NO₅S 435.1140; found 435.1130.

cis-(R,R)-7c:*Benzyl-2-((8R,12bR)-11-methyl-6,6-dioxido-8,12b-**dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*

Colorless oil, 91% ee (Chiralpak IC, 5% EtOH/*n*-hexanes, 0.8 ml/min, 215nm, $t_R(\text{major}) = 22.4$ min, $t_R(\text{minor}) = 19.7$ min); $[\alpha]_D^{21} = +4.50$ (*c* 1.2, CHCl₃).; ¹H NMR (300 MHz, CDCl₃) δ 7.55-7.52 (m, 1H), 7.48 (s, 1H), 7.39-7.32 (m, 6H), 7.23-7.18 (m, 1H), 7.10 (s, 2H), 7.03 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.18 (s, 1H), 5.53 (dd, *J* = 10.8, 3.5 Hz, 1H), 5.18-5.08 (m, 2H), 3.62 (dd, *J* = 15.5, 3.5 Hz, 1H), 2.47 (s, 3H), 2.33 (dd, *J* = 15.5, 10.8 Hz, 1H).; ¹³C NMR (125 MHz, CDCl₃) δ 170.1, 149.8, 138.9, 137.8, 135.7, 135.5, 130.1, 129.1, 128.6, 128.5, 128.3, 126.5, 125.8, 123.3, 122.7, 122.4, 119.2, 67.2, 66.7, 63.0, 41.3, 21.5.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₄H₂₁NO₅S 435.1140; found 435.1134.

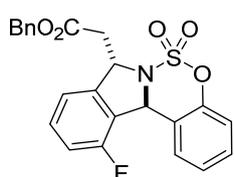
7d: Yield 92% (145 mg as a colorless oil, *trans:cis*=8:1).**trans-(S,R)-7d:***Benzyl-2-((8S,12bR)-10-methyl-6,6-dioxido-8,12b-**dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*

Colorless oil, 97% ee (Chiralpak IC, 20% IPA/*n*-hexanes, 1.0 ml/min, 215nm, $t_R(\text{major}) = 38.6$ min, $t_R(\text{minor}) = 16.9$ min); $[\alpha]_D^{22} = +39.2$ (*c* 0.4, CHCl₃).; ¹H NMR (300 MHz, CDCl₃) δ 7.49-7.42 (m, 2H), 7.38 (s, 5H), 7.31-7.23 (m, 1H), 7.21-7.17 (m, 1H), 7.03 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.93 (s, 1H), 6.23 (s, 1H), 5.51 (d, *J* = 7.8 Hz, 1H), 5.21 (s, 2H), 3.43 (dd, *J* = 16.6, 3.2 Hz, 1H), 3.03 (dd, *J* = 16.6, 7.9 Hz, 1H), 2.29 (s, 3H).; ¹³C NMR (125 MHz, CDCl₃) δ 170.1, 149.8, 139.4, 138.7, 135.6, 134.9, 129.7, 129.1, 128.6, 128.4, 126.4, 125.8, 123.4, 122.5, 119.2, 67.1, 66.7, 63.1, 41.3, 21.3.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₄H₂₁NO₅S 435.1140; found 435.1124.

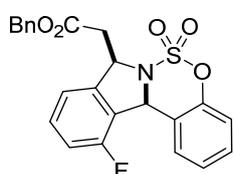
cis-(R,R)-7d:*Benzyl-2-((8R,12bR)-10-methyl-6,6-dioxido-8,12b-**dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*

Colorless oil, 96% ee (Chiralpak IC, 20% IPA/*n*-hexanes, 1.0 ml/min, 215nm, $t_R(\text{major}) = 21.5$ min, $t_R(\text{minor}) = 14.9$ min); $[\alpha]_D^{22} = -113.8$ (*c* 0.2, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.40-7.30 (m, 6H), 7.26-7.16 (m, 2H), 7.04-7.01 (m, 2H), 6.19 (s, 1H), 5.54 (dd, *J* = 10.9, 3.4 Hz, 1H), 5.15 (s, 1H), 3.63 (dd, *J* = 15.6, 3.5 Hz, 1H), 2.38-2.33 (m, 1H), 2.29 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.8, 150.4, 139.8, 139.2, 135.3, 134.3, 129.6, 129.5, 128.6, 128.5, 126.0, 125.4, 124.1, 123.5, 121.7, 119.1, 66.7, 65.1, 62.8, 38.2, 21.4.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₄H₂₁NO₅S 435.1140; found 435.1121.

7e: Yield 82% (128 mg as a colorless oil, *trans:cis*=7.9:1).

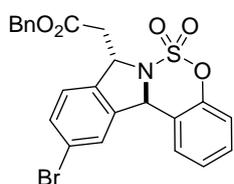
trans-(S,S)-7e:*Benzyl-2-((8S,12bS)-12-fluoro-6,6-dioxido-8,12b-**dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*

White solid, mp: 128.1-130.3 °C; 96% ee (Chiralpak AD-H, 10% IPA/*n*-hexanes, 0.8 ml/min, 215nm, $t_R(\text{major}) = 12.0$ min, $t_R(\text{minor}) = 14.6$ min); $[\alpha]_D^{21} = +309.9$ (*c* 0.7, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.43-7.33 (m, 5H), 7.31-7.19 (m, 3H), 7.13-7.04 (m, 2H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.51 (s, 1H), 5.48 (d, *J* = 7.4 Hz, 1H), 5.20 (s, 2H), 3.48 (dd, *J* = 16.8, 3.0 Hz, 1H), 3.04 (dd, *J* = 16.8, 8.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 157.9, 155.9, 149.6, 142.33, 142.30, 135.4, 131.4, 131.3, 129.5, 128.6, 128.5, 128.4, 127.5, 127.4, 126.2, 124.9, 124.7, 121.5, 119.1, 118.9, 118.8, 116.1, 115.9, 66.8, 65.6, 62.8, 40.6.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₃H₁₈FNO₅S 439.0890; found 439.0880.

cis-(R,S)-7e:*Benzyl-2-((8R,12bS)-12-fluoro-6,6-dioxido-8,12b-**dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*

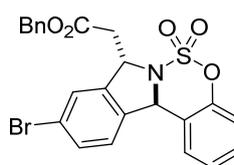
Colorless oil, 99% ee (Chiralpak AD-H, 10% IPA/*n*-hexanes, 0.8 ml/min, 215nm, $t_R(\text{major}) = 10.1$ min, $t_R(\text{minor}) = 10.9$ min); $[\alpha]_D^{20} = -121.9$ (*c* 0.1, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.39-7.29 (m, 7H), 7.27-7.14 (m, 2H), 7.05-7.02 (m, 2H), 6.47 (s, 1H), 5.56 (dd, *J* = 11.1, 3.4 Hz, 1H), 5.14 (d, *J* = 2.4 Hz, 2H), 3.63 (dd, *J* = 15.7, 3.4 Hz, 1H), 2.36 (dd, *J* = 15.7, 11.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.6, 158.4, 156.5, 150.3, 143.0, 135.1, 131.4, 131.3, 129.9, 128.7, 128.64, 128.60, 127.1, 127.0, 126.0, 124.6, 124.4, 121.3, 119.8, 119.7, 119.0, 116.1, 116.0, 66.9, 63.8, 63.0, 37.7, 29.7.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₃H₁₈FNO₅S 439.0890; found 439.0860.

7f: Yield 90% (113 mg as a colorless oil, *trans:cis*=99.8:0.2).

trans-(S,R)-7f:*Benzyl-2-((8S,12bR)-11-bromo-6,6-dioxido-8,12b-**dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*

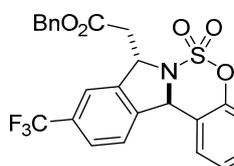
White solid, mp: 133.2-135.5 °C; 99% ee (Chiralpak AD-H, 40% IPA/*n*-hexanes, 0.8 ml/min, 215nm, t_R (major) = 11.6 min, t_R (minor) = 14.8 min); $[\alpha]_D^{22} = -118.9$ (c 0.1, CHCl₃).; ¹H NMR (300 MHz, CDCl₃) δ 7.64 (s, 1H), 7.43-7.29 (m, 7H), 7.25 (dd, $J = 7.4, 1.5$ Hz, 1H), 7.07-7.00 (m, 2H), 6.19 (s, 1H), 5.45 (d, $J = 7.7$ Hz, 1H), 5.17 (s, 2H), 3.39 (dd, $J = 16.7, 3.1$ Hz, 1H), 3.05 (dd, $J = 16.7, 7.7$ Hz, 1H).; ¹³C NMR (125 MHz, CDCl₃) δ 169.8, 149.8, 139.8, 137.6, 135.4, 132.4, 129.5, 128.6, 128.5, 128.4, 126.3, 126.1, 126.0, 124.6, 122.6, 121.6, 119.4, 66.84, 66.80, 62.8, 40.9.; HRMS (EI, double focusing) m/z: [M]⁺ Calcd for C₂₃H₁₈ BrNO₅S 499.0089; found 499.0091.

7g: Yield 76% (100 mg as a colorless oil, *trans:cis*=4.7:1).

trans-(S,R)-7g:*Benzyl-2-((8S,12bR)-10-bromo-6,6-dioxido-8,12b-**dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*

Orange oil, 95% ee (Chiralpak IA, 5% IPA/*n*-hexanes, 0.7 ml/min, 215nm, t_R (major) = 65.1 min, t_R (minor) = 52.1 min); $[\alpha]_D^{19} = +13.7$ (c 0.1, CHCl₃).; ¹H NMR (500 MHz, CDCl₃) δ 7.51 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.43-7.35 (m, 8H), 7.33-7.30 (m, 1H), 7.25-7.22 (m, 1H), 7.05 (dd, $J = 8.2, 1.3$ Hz, 1H), 6.20 (s, 1H), 5.50 (d, $J = 7.7$ Hz, 1H), 5.20 (s, 2H), 3.41 (dd, $J = 16.9, 3.0$ Hz, 1H), 3.07 (dd, $J = 16.9, 7.9$ Hz, 1H).; ¹³C NMR (125 MHz, CDCl₃) δ 169.8, 149.7, 140.8, 136.8, 135.3, 132.1, 129.4, 128.7, 128.5, 126.3, 126.2, 126.0, 124.3, 123.2, 121.7, 119.4, 66.9, 66.8, 62.7, 40.9.; HRMS (EI, double focusing) m/z: [M]⁺ Calcd for C₂₃H₁₈ BrNO₅S 499.0089; found 499.0099.

7h: Yield 71% (106 mg as a colorless oil, *trans:cis*=6.2:1).

trans-(S,R)-7h:*Benzyl-2-((8S,12bR)-6,6-dioxido-10-(trifluoromethyl)-8,12b-**dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*

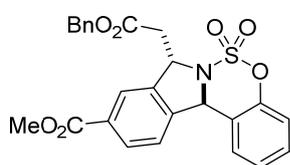
Brown oil, 89% ee (Chiralcel OD-H, 5% IPA/*n*-hexanes, 1.0 ml/min, 215nm, t_R (major) = 25.3 min, t_R (minor) = 22.9 min); $[\alpha]_D^{19} = +235.0$ (c 0.2, CHCl₃).; ¹H NMR (500 MHz, CDCl₃) δ 7.68-7.65 (m, 2H), 7.51 (s, 1H), 7.47 (d, $J = 7.7$ Hz, 1H), 7.41-7.32 (m, 5H), 7.27-7.24 (m, 1H), 7.07 (d, $J = 8.2$ Hz, 1H), 6.31 (s, 1H), 5.57 (d, $J = 7.7$ Hz, 1H), 5.22-5.16 (m, 2H), 3.45 (dd, $J = 16.9, 3.0$ Hz, 1H), 3.12 (dd, $J = 16.9, 7.8$ Hz, 1H).; ¹³C NMR (125 MHz, CDCl₃) δ 169.8, 149.9, 141.6, 139.7, 135.3, 131.8 (q, $J_{CF} = 32.7$ Hz), 128.7, 128.5, 128.4, 126.3, 126.2 (d, $J_{CF} = 3.8$ Hz), 126.1, 123.5, 123.1 (q, $J_{CF} = 270.0$ Hz), 121.3, 120.3 (q, $J_{CF} = 3.8$ Hz), 119.5, 67.1, 66.9, 62.9, 40.8.; HRMS (EI, double focusing) m/z: [M]⁺ Calcd for C₂₄H₁₈ F₃NO₅S 489.0858; found 489.0834.

7i: Yield 80% (120 mg as a colorless oil, *trans:cis*=15.5:1).

***trans*-(S,R)-7i:**

Methyl-(8S,12bR)-8-(2-(benzyloxy-2-oxoethyl)-8,12b-

dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindole-10-carboxylate 6,6 dioxide



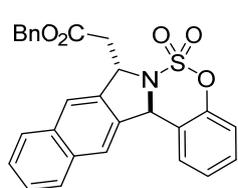
yellow oil, 84% ee (Chiralpak AD-H, 30% EtOH/*n*-hexanes, 1.0 ml/min, 215nm, t_R (major) = 42.9 min, t_R (minor) = 24.7 min); $[\alpha]_D^{20} = +2.67$ (*c* 0.3, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.91 (s, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H) 7.39-7.30 (m, 6H), 7.26-7.23 (m, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.27 (s, 1H), 5.54 (d, *J* = 6.9 Hz, 1H), 5.17 (s, 2H), 3.93 (s, 3H), 3.40 (dd, *J* = 16.8, 3.1 Hz, 1H), 3.17 (dd, *J* = 16.8, 7.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.7, 165.9, 149.9, 142.5, 139.1, 135.4, 131.4, 130.4, 129.5, 128.6, 128.4, 128.3, 126.3, 126.0, 124.2, 122.9, 121.4, 119.5, 67.2, 66.8, 62.9, 52.4, 40.6.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₅H₂₁NO₇S 479.1039; found 479.1039.

7j: Yield 71% (150 mg as a white solid, *trans:cis*=3.9:1).

***trans*-(S,R)-7j:**

Benzyl-2-((8S,14bR)-6,6-dioxido-8,14b-

*dihydrobenzo[*f*][benzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*



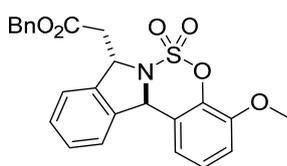
white solid, mp: 148.3-150.2°C; 98% ee (chiralpak AD-H, 20% IPA/*n*-hexanes, 1.0ml/min, 215nm, t_R (major) = 25.4 min, t_R (minor) = 19.6 min); $[\alpha]_D^{20} = -30.7$ (*c* 0.3, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.01(s, 1H) 7.92 (d, *J*=8.0, 1H), 7.70(d, *J* = 7.8, 1H), 7.61-7.58 (m, 2H), 7.56-7.49 (m, 2H), 7.37-7.28 (m, 7H), 7.05 (d, *J* = 8.1, 1H), 6.42 (s, 1H), 5.64 (d, *J* = 5.5 Hz, 1H), 5.22 (d, *J* = 4.9, 2H), 3.57 (dd, *J* = 16.9, 3.1, 1H), 3.15 (dd, *J* = 16.9, 7.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 170.2, 149.9, 137.1, 136.2, 135.5, 133.6, 133.3, 129.3, 128.6, 128.5, 128.4, 128.2, 128.1, 126.8, 126.73, 126.71, 125.9, 122.0, 121.9, 119.2, 66.9, 66.7, 62.4, 41.3.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₇H₂₁NO₅S 471.1140; found 471.1142.

7k: Yield 86% (134 mg as a colorless oil, *trans:cis*=6:1).

***trans*-(S,R)-7k:**

Benzyl-2-((8S,12bR)-4-methoxy-6,6-dioxido-8,12b-

dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate

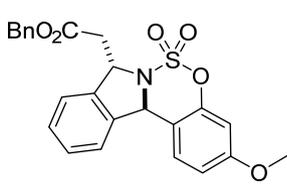


Colorless oil, 98% ee (Chiralcel OD-H, 20% IPA/*n*-hexanes, 1.0 ml/min, 215nm, t_R (major) = 15.7 min, t_R (minor) = 21.4 min); $[\alpha]_D^{21} = +49.3$ (*c* 0.3, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.39-7.30 (m, 7H), 7.16-7.14 (m, 2H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.25 (s, 1H), 5.55 (d, *J* = 7.8 Hz, 1H), 5.18 (s, 2H), 3.88 (s, 3H), 3.43 (dd, *J* = 16.6, 3.2 Hz, 1H), 3.06 (dd, *J* = 16.6, 8.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 170.0, 149.0, 139.4, 138.6, 137.7, 135.5,

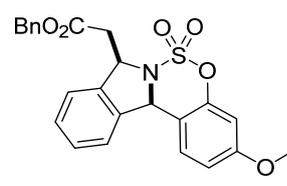
129.2, 128.8, 128.6, 128.5, 128.3, 125.5, 123.3, 123.0, 122.9, 117.4, 111.5, 67.4, 66.7, 63.2, 56.2, 41.2.; HRMS (EI, double focusing) m/z: [M]⁺ Calcd for C₂₄H₂₁NO₆S 451.1090; found 451.1092.

7l: Yield 90% (140 mg as a colorless oil, *trans:cis*=27.9:1).

***trans*-(S,R)-7l:** *Benzyl-2-((8S,12bR)-3-methoxy-6,6-dioxido-8,12b-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*

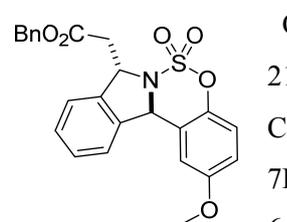
 Colorless oil, 97% ee (Chiralpak AD-H, 30% EtOH/*n*-hexanes, 0.8 ml/min, 215nm, *t_R*(major) = 26.6 min, *t_R*(minor) = 24.3 min); [α]_D²² = +47.9 (*c* 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.43-7.30 (m, 7H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.78 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.56 (d, *J* = 2.5 Hz, 1H), 6.20 (s, 1H), 5.53 (d, *J* = 7.5 Hz, 1H), 5.19 (s, 2H), 3.78 (s, 3H), 3.43 (dd, *J* = 16.6, 3.2 Hz, 1H), 3.05 (dd, *J* = 16.6, 7.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 170.1, 160.0, 150.5, 138.5, 138.1, 135.5, 129.1, 128.8, 128.6, 128.5, 128.4, 127.1, 123.0, 122.7, 113.9, 112.8, 103.9, 66.9, 66.7, 63.1, 55.6, 41.2.; HRMS (EI, double focusing) m/z: [M]⁺ Calcd for C₂₄H₂₁NO₆S 451.1090; found 451.1061.

***cis*-(R,R)-7l:** *Benzyl-2-((8R,12bR)-3-methoxy-6,6-dioxido-8,12b-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*

 Colorless oil, 99% ee (Chiralpak AD-H, 30% EtOH/*n*-hexanes, 0.8 ml/min, 215nm, *t_R*(major) = 15.5 min, *t_R*(minor) = 17.3 min); [α]_D²² = -81.7 (*c* 0.3, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.53-7.21 (m, 9H), 6.75 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.55 (d, *J* = 2.6 Hz, 1H), 6.16 (s, 1H), 5.57 (dd, *J* = 10.9, 3.5 Hz, 1H), 5.19 – 5.10 (m, 2H), 3.79 (s, 3H), 3.63 (dd, *J* = 15.6, 3.5 Hz, 1H), 2.36 (dd, *J* = 15.6, 10.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.8, 160.3, 151.1, 139.6, 137.5, 135.2, 128.9, 128.8, 128.6, 128.5, 126.7, 123.7, 123.6, 113.1, 112.4, 103.7, 66.8, 64.9, 62.9, 55.6, 38.1.; HRMS (EI, double focusing) m/z: [M]⁺ Calcd for C₂₄H₂₁NO₆S 451.1090; found 451.1088.

7m: Yield 87% (135 mg as a colorless oil, *trans:cis*=5.4:1).

***trans*-(S,R)-7m:** *Benzyl-2-((8S,12bR)-2-methoxy-6,6-dioxido-8,12b-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*

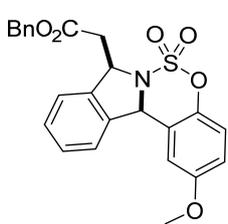
 Colorless oil, 96% ee (Chiralpak AD-H, 20% IPA/*n*-hexanes, 0.8 ml/min, 215nm, *t_R*(major) = 28.7 min, *t_R*(minor) = 30.4 min); [α]_D²¹ = +161.8 (*c* 0.3, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 7.7 Hz, 1H), 7.41-7.30 (m, 7H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.99-6.97 (m, 2H), 6.82 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.20 (s, 1H), 5.52 (d, *J* = 7.7 Hz, 1H), 5.19 (s, 2H), 3.81 (s, 3H), 3.42 (dd, *J* = 16.6, 3.3 Hz, 1H), 3.05 (dd, *J* = 16.6, 7.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 170.1, 157.0, 143.5, 138.7, 137.6, 135.5, 129.2, 128.9, 128.6, 128.5, 128.3, 123.1, 123.0, 122.9, 120.1, 114.0, 111.9, 67.3,

66.7, 63.1, 55.7, 41.2.; HRMS (EI, double focusing) m/z: $[M]^+$ Calcd for $C_{24}H_{21}NO_6S$ 451.1090; found 451.1089.

cis-(R,R)-7m:

Benzyl-2-((8R,12bR)-2-methoxy-6,6-dioxido-8,12b-

dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate



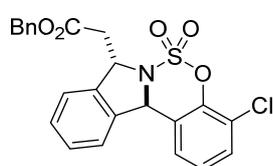
Colorless oil, 95% ee (Chiralpak AD-H, 20% IPA/*n*-hexanes, 0.8 ml/min, 215nm, t_R (major) = 18.6 min, t_R (minor) = 25.1 min); $[\alpha]_D^{22} = -20.1$ (c 0.3, $CHCl_3$).; 1H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, $J = 7.7$ Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.39-7.30 (m, 9H), 7.23 (d, $J = 7.7$ Hz, 1H), 7.01-6.97 (m, 2H), 6.84 (dd, $J = 9.1, 2.8$ Hz, 1H), 6.18 (s, 1H), 5.56 (dd, $J = 10.9, 3.4$ Hz, 1H), 5.15 (s, 2H), 3.80 (s, 3H), 3.64 (dd, $J = 15.5, 3.5$ Hz, 1H), 2.36 (dd, $J = 15.6, 10.9$ Hz, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 156.7, 144.1, 139.8, 137.1, 135.2, 129.1, 128.9, 128.6, 128.5, 123.8, 123.7, 122.2, 119.9, 114.4, 111.4, 66.8, 65.4, 62.8, 55.7, 38.1.; HRMS (EI, double focusing) m/z: $[M]^+$ Calcd for $C_{24}H_{21}NO_6S$ 451.1090; found 451.1089.

7n: Yield 82% (63 mg as a colorless oil, *trans:cis*=14.4:1).

trans-(S,R)-7n:

Benzyl-2-((8S,12bR)-4-chloro-6,6-dioxido-8,12b-

dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate



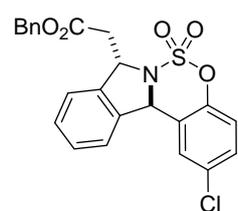
Colorless oil, 96% ee (Chiralpak IC, 20% EtOH/*n*-hexanes, 0.8 ml/min, 215nm, t_R (major) = 16.1 min, t_R (minor) = 8.5 min); $[\alpha]_D^{22} = +22.1$ (c 0.7, $CHCl_3$).; 1H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, $J = 7.7$ Hz, 1H), 7.41-7.31 (m, 8H), 7.16 (t, $J = 8.0$ Hz, 2H), 6.25 (s, 1H), 5.57 (d, $J = 7.6$ Hz, 1H), 5.19 (s, 2H), 3.41 (dd, $J = 16.6, 3.2$ Hz, 1H), 3.08 (dd, $J = 16.6, 7.8$ Hz, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 145.8, 138.4, 137.2, 135.4, 129.9, 129.4, 128.9, 128.6, 128.5, 128.4, 125.8, 124.7, 124.2, 123.0, 122.9, 67.4, 66.7, 63.4, 41.1.; HRMS (EI, double focusing) m/z: $[M]^+$ Calcd for $C_{23}H_{18}ClNO_5S$ 455.0594; found 455.0573.

7o: Yield 84% (130 mg as a colorless oil, *trans:cis*=3.9:1).

trans-(S,R)-7o:

Benzyl-2-((8S,12bR)-2-chloro-6,6-dioxido-8,12b-

dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate

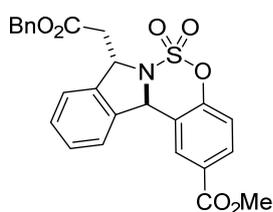


Colorless oil, 97% ee (Chiralpak AD-H, 30% EtOH/*n*-hexanes, 1.0 ml/min, 215nm, t_R (major) = 15.7 min, t_R (minor) = 18.6 min); $[\alpha]_D^{19} = +94.4$ (c 0.3, $CHCl_3$).; 1H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, $J = 7.7$ Hz, 1H), 7.45-7.33 (m, 8H), 7.26 (dd, $J = 8.8, 2.5$ Hz, 1H), 7.17 (d, $J = 7.7$ Hz, 1H), 7.00 (d, $J = 8.8$ Hz, 1H), 6.20 (s, 1H), 5.52 (d, $J = 7.7$ Hz, 1H), 5.19 (s, 2H), 3.42 (dd, $J = 16.6, 3.2$ Hz, 1H), 3.05 (dd, $J = 16.7, 7.8$ Hz, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 148.4, 138.6, 137.0, 135.4,

131.0, 129.5, 129.3, 129.1, 128.6, 128.5, 128.4, 126.4, 123.8, 123.1, 122.8, 120.7, 67.0, 66.8, 63.2, 41.0.; HRMS (EI, double focusing) m/z: $[M]^+$ Calcd for $C_{23}H_{18}ClNO_5S$ 455.0594; found 455.0592.

7p: Yield 80% (96 mg as a colorless oil, *trans:cis*=12.2:1).

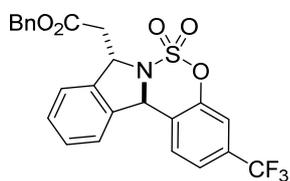
***trans*-(S,R)-7p:** *Methyl-(8S,12bR)-8-(2-(benzyloxy)-2-oxoethyl)-8,12b-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindole-2-carboxylate 6,6-dioxide*



Colorless oil, 99% ee (Chiralpak AD-H, 10% IPA/*n*-hexanes, 1.0 ml/min, 215nm, t_R (major) = 64.3 min, t_R (minor) = 57.4 min); $[\alpha]_D^{20} = +83.5$ (*c* 0.2, $CHCl_3$).; 1H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.96 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.44-7.32 (m, 7H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 6.29 (s, 1H), 5.55 (d, *J* = 7.7, 1H), 5.19 (s, 2H), 3.95 (s, 3H), 3.42 (dd, *J* = 16.6, 3.3 Hz, 1H), 3.07 (dd, *J* = 16.6, 3.32 Hz, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 165.5, 153.1, 138.4, 137.2, 135.4, 130.5, 129.5, 129.2, 128.6, 128.5, 128.44, 128.41, 127.8, 123.0, 122.9, 122.4, 119.5, 67.1, 66.8, 63.3, 52.5, 41.1, 25.4.; HRMS (EI, double focusing) m/z: $[M]^+$ calcd for $C_{25}H_{21}NO_7S$ 479.1039; found 479.1039.

7q: Yield 81% (60 mg as a colorless oil, *trans:cis*=7.9:1).

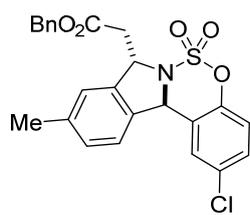
***trans*-(S,R)-7q:** *Benzyl-2-((8S,12bR)-6,6-dioxido-3-(trifluoromethyl)-8,12b-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*



Brown oil, 79% ee (Chiralpak IA, 10%EtOH/*n*-hexanes, 0.7 ml/min, 215nm, t_R (major) = 18.6 min, t_R (minor) = 16.7 min); $[\alpha]_D^{28} = -1.998$ (*c* 0.3, $CHCl_3$).; 1H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.44 – 7.31 (m, 11H), 7.18 (d, *J* = 7.7 Hz, 1H), 6.29 (s, 1H), 5.55 (d, *J* = 7.5 Hz, 1H), 5.19 (s, 2H), 3.41 (dd, *J* = 16.6, 3.2 Hz, 1H), 3.08 (dd, *J* = 16.7, 7.7 Hz, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 150.0, 138.5, 136.7, 135.4, 131.8, 131.6, 129.6, 129.1, 128.6, 128.5, 128.4, 127.3, 126.2, 123.1, 122.8, 122.4 (t, $J_{CF} = 3.7$ Hz), 116.8 (q, $J_{CF} = 3.7$ Hz), 67.2, 66.8, 63.3, 41.0.; HRMS (EI, double focusing) m/z: $[M]^+$ Calcd for $C_{24}H_{18}F_3NO_5S$ 489.0858; found 489.0855.

7r: Yield 90% (150 mg as a colorless oil, *trans:cis*=6.5:1).

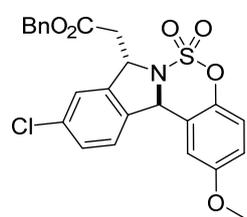
***trans*-(S,R)-7r:** *Benzyl-2-((8S,12bR)-2-chloro-10-methyl-6,6-dioxido-8,12b-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate*



Colorless oil, 97% ee (Chiralcel OD-H, 5% IPA/*n*-hexanes, 1.0 ml/min, 215nm, $t_R(\text{major}) = 18.5$ min, $t_R(\text{minor}) = 16.3$ min); $[\alpha]_D^{20} = +113.7$ (*c* 0.3, CHCl_3).; ^1H NMR (500 MHz, CDCl_3) δ 7.43-7.35 (m, 7H), 7.26-7.21 (m, 2H), 6.99 (d, $J = 8.7$ Hz, 1H), 6.94 (s, 1H), 6.16 (s, 1H), 5.48 (d, $J = 7.7$ Hz, 1H), 5.21 (d, $J = 2.2$ Hz, 2H), 3.41 (dd, $J = 16.6, 3.2$ Hz, 1H), 3.03 (dd, $J = 16.6, 7.9$ Hz, 1H), 2.30 (s, 3H).; ^{13}C NMR (125 MHz, CDCl_3) δ 170.0, 148.3, 139.7, 138.7, 135.5, 134.1, 130.1, 130.0, 129.2, 128.6, 128.5, 128.4, 126.4, 124.1, 123.5, 122.5, 120.6, 66.8, 66.7, 63.1, 41.1, 21.4.; HRMS (EI, double focusing) *m/z*: $[\text{M}]^+$ Calcd for $\text{C}_{24}\text{H}_{20}\text{ClNO}_5\text{S}$ 469.0751; found 469.0743.

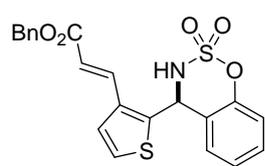
7s: Yield 70% (145 mg as a colorless oil, *trans:cis*=3.8:1).

***trans*-(*S,R*)-7s:** Benzyl 2-((8*S*,12*bR*)-10-chloro-2-methoxy-6,6-dioxido-8,12*b*-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-*a*]isoindol-8-yl)acetate



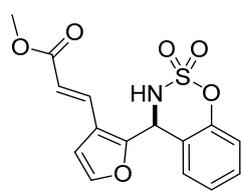
Brown oil, 97% ee (Chiralpak IC, 50% IPA/*n*-hexanes, 0.6 ml/min, 215nm, $t_R(\text{major}) = 28.1$ min, $t_R(\text{minor}) = 16.2$ min); $[\alpha]_D^{20} = +124.6$ (*c* 0.4, CHCl_3).; ^1H NMR (500 MHz, CDCl_3) δ 7.46-7.34 (m, 7H), 7.42-7.35 (m, 6H), 7.20 (s, 1H), 6.99 (d, $J = 9.0$ Hz, 1H), 6.90 (d, $J = 2.7$ Hz, 1H), 6.83 (dd, $J = 9.0, 2.8$ Hz, 1H), 6.15 (s, 1H), 5.48 (d, $J = 7.8$ Hz, 1H), 5.20 (s, 2H), 3.81 (s, 3H), 3.41 (dd, $J = 16.9, 3.0$ Hz, 1H), 3.06 (dd, $J = 16.9, 8.0$ Hz, 1H).; ^{13}C NMR (125 MHz, CDCl_3) δ 169.9, 157.1, 143.4, 140.7, 136.2, 135.4, 129.3, 128.7, 128.5, 123.9, 123.4, 122.7, 120.2, 114.1, 111.8, 66.9, 66.8, 62.8, 55.8, 40.9.; HRMS (EI, double focusing) *m/z*: $[\text{M}]^+$ Calcd for $\text{C}_{24}\text{H}_{20}\text{ClNO}_6\text{S}$ 485.0700; found 485.0699.

7t: Benzyl (*S,E*)-3-(2-(2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)thiophen-3-yl)acrylate



Yield: 56% (45 mg as a colorless oil); 97% ee (chiralpak ID, 30% EtOH/*n*-hexane, 1.0ml/min, 215nm, $t_R(\text{major}) = 6.88$ min, $t_R(\text{minor}) = 9.48$ min); $[\alpha]_D^{20} = +24.3$ (*c* 0.5, CHCl_3).; ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, $J = 15.7$ Hz, 1H), 7.41-7.35 (m, 7H), 7.31 (d, $J = 5.4$ Hz, 1H), 7.16 (t, $J = 7.6$ Hz, 1H), 7.08 (d, $J = 8.3$ Hz, 1H), 7.00 (d, $J = 7.8$ Hz, 1H), 6.46-6.42 (m, 2H), 5.23 (s, 3H).; ^{13}C NMR (125 MHz, CDCl_3) δ 166.6, 150.8, 141.1, 136.7, 135.7, 134.8, 130.4, 128.6, 128.4, 127.3, 127.0, 125.9, 125.5, 121.2, 120.5, 119.1, 66.7, 54.6.; HRMS (EI, double focusing) *m/z*: $[\text{M}]^+$ Calcd for $\text{C}_{21}\text{H}_{17}\text{NO}_5\text{S}_2$ 427.0548; found 427.0546.

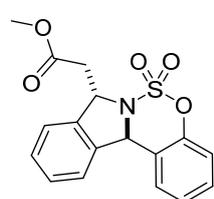
7u: Methyl (*S,E*)-3-(2-(2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)furan-3-yl)acetate



Yield: 36% (24.0 mg as a yellow solid); mp: 229.0-232.2 °C; $[\alpha]_D^{20} = +5.50$ (c 0.2, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.32 (d, 1H, $J = 16.1$ Hz), 8.20 (d, $J = 8.0$ Hz, 1H), 7.80-7.76 (m, 2H), 7.47-7.39 (m, 2H), 6.98 (s, 1H), 6.48 (d, $J = 16.1$ Hz, 1H), 3.86 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 166.2, 163.1, 154.6, 147.7, 146.0, 136.9, 133.8, 132.2, 131.1, 125.8, 124.4, 119.5, 115.8, 111.8, 52.0; HRMS (EI, double focusing) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_6\text{S}$ 335.0464; found 335.0459.

7ab: Yield 80% (53 mg as a colorless oil, *trans:cis*=4.6:1).

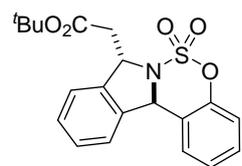
***trans*-(S,R)-7ab:** Methyl-2-((8*S*,12*bR*)-6,6-dioxido-8,12*b*-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-*a*]isoindol-8-yl)acetate



Colorless oil, 99% ee (Chiralpak AD-H, 20% EtOH/*n*-hexanes, 1.0 ml/min, 215nm, $t_R(\text{major}) = 21.4$ min, $t_R(\text{minor}) = 16.1$ min); $[\alpha]_D^{23} = +128.9$ (c 0.2, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.61 (d, $J = 7.5$ Hz, 1H), 7.52 (d, $J = 7.7$ Hz, 1H), 7.43-7.37 (m, 2H), 7.32-7.17 (m, 3H), 7.05 (d, $J = 8.1$ Hz, 1H), 6.34 (s, 1H), 5.54 (d, $J = 7.9$ Hz, 1H), 3.77 (s, 3H), 3.41 (dd, $J = 16.8, 3.2$ Hz, 1H), 2.99 (dd, $J = 16.8, 8.1$ Hz, 1H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 170.8, 149.8, 138.8, 137.7, 129.3, 129.2, 128.9, 126.5, 125.8, 123.0, 122.9, 122.2, 119.3, 67.3, 63.0, 51.9, 41.0; HRMS (EI, double focusing) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_5\text{S}$ 345.0671; found 345.0677.

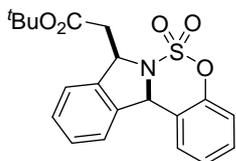
7ac: Yield 70% (52 mg as a colorless oil, *trans:cis*=9.9:1).

***trans*-(S,R)-7ac:** *tert*-Butyl-2-((8*S*,12*bR*)-6,6-dioxido-8,12*b*-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-*a*]isoindol-8-yl)acetate



Colorless oil, 98% ee (Chiralpak IA, 5% EtOH/*n*-hexanes, 0.7 ml/min, 215nm, $t_R(\text{major}) = 21.2$ min, $t_R(\text{minor}) = 18.0$ min); $[\alpha]_D^{27} = +22.2$ (c 0.5, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.60 (d, $J = 7.3$ Hz, 1H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.42-7.36 (m, 2H), 7.31-7.28 (m, 2H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.05 (d, $J = 8.2$ Hz, 1H), 6.31 (s, 1H), 5.48 (d, $J = 8.0$ Hz, 1H), 3.32 (dd, $J = 16.4, 3.0$ Hz, 1H), 2.92 (dd, $J = 16.4, 8.0$ Hz, 1H), 1.46 (s, 9H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 169.5, 149.9, 139.1, 137.7, 129.2, 129.1, 128.7, 126.5, 125.8, 123.1, 122.8, 122.2, 119.2, 81.3, 67.2, 63.3, 42.2, 28.0; HRMS (EI, double focusing) m/z : $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_5\text{S}$ 387.1140; found 387.1138.

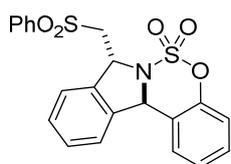
cis-(R,R)-7ac: *tert*-Butyl-2-((8*R*,12*bR*)-6,6-dioxido-8,12*b*-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-*a*]isoindol-8-yl)acetate Colorless oil, >99% ee (Chiralpak IA, 5% EtOH/*n*-hexanes, 0.7 ml/min, 215nm, t_{R} (major) = 13.2 min, t_{R} (minor) = 14.2 min);



$[\alpha]_{\text{D}}^{27} = -28.4$ (*c* 0.4, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.49–7.32 (m, 3H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.24 (s, 1H), 5.55 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.56 (dd, *J* = 15.6, 3.3 Hz, 1H), 2.19 (dd, *J* = 15.6, 11.2 Hz, 1H), 1.46 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 169.2, 150.5, 140.2, 137.2, 129.5, 129.0, 128.7, 126.0, 125.4, 123.9, 123.8, 121.5, 119.1, 81.7, 65.3, 63.1, 39.0, 28.1; HRMS (EI, double focusing) *m/z*: [M]⁺ calcd for C₂₀H₂₁NO₅S 387.1140; found 387.1137.

7ad: Yield 73% (60 mg as a colorless oil, *trans*:*cis*=10.5:1).

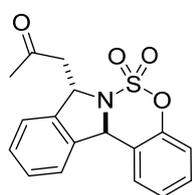
***trans*-(R,R)-7ad:** (8*R*,12*bR*)-8-((phenylsulfonyl)methyl)-8,12*b*-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-*a*]isoindole 6,6-dioxide



Colorless oil, 97% ee (Chiralpak IA, 30% EtOH/*n*-hexanes, 1.0 ml/min, 215nm, t_{R} (major) = 26.9 min, t_{R} (minor) = 24.4 min); $[\alpha]_{\text{D}}^{22} = +171.6$ (*c* 0.3, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.96 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.84–7.80 (m, 1H), 7.73–7.70 (m, 1H), 7.63–7.60 (m, 3H), 7.50–7.43 (m, 3H), 7.30–7.21 (m, 2H), 6.99 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.21 (s, 1H), 5.53 (d, *J* = 7.7 Hz, 1H), 4.16 (dd, *J* = 15.0, 1.5 Hz, 1H), 3.89 (dd, *J* = 15.0, 7.7 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 149.5, 139.7, 137.5, 136.9, 134.1, 129.6, 129.4, 129.3, 128.2, 126.6, 126.1, 124.4, 122.7, 121.9, 119.2, 67.2, 61.5, 61.2; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₁H₁₇NO₅S₂ 427.0548; found 427.0533.

7ae: Yield 64% (40 mg as a colorless oil, *trans*:*cis*=16.5:1).

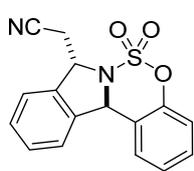
***trans*-(S,R)-7ae:** 1-((8*S*,12*bR*)-6,6-dioxido-8,12*b*-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-*a*]isoindol-8-yl)propan-2-one



Colorless oil, 98% ee (Chiralpak AD-H, 5% EtOH/*n*-hexanes, 1.0 ml/min, 215nm, t_{R} (major) = 34.0 min, t_{R} (minor) = 26.7 min); $[\alpha]_{\text{D}}^{22} = +40.1$ (*c* 0.2, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.42–7.29 (m, 4H), 7.23–7.19 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 5.57 (d, *J* = 8.1 Hz, 1H), 3.62–3.58 (m, 1H), 3.10 (dd, *J* = 18.2, 8.4 Hz, 1H), 2.28 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 205.8, 149.8, 139.6, 137.5, 129.3, 128.7, 126.5, 125.8, 123.3, 122.8, 121.9, 119.2, 67.2, 62.2, 50.4, 30.7; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₁₇H₁₅NO₄S 329.0722; found 329.0719.

7af: Yield 82% (51 mg as a colorless oil, *trans*:*cis*=8.8:1).

trans-(S,R)-7af: 2-((8*S*,12*bR*)-6,6-dioxido-8,12*b*-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-*a*]isoindol-8-yl)acetonitrile

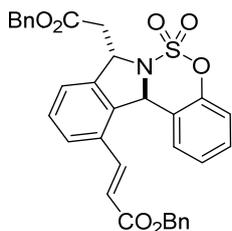


Colorless oil, 98% ee (Chiralpak AD-H, 30% EtOH/*n*-hexanes, 1.0 ml/min, 215nm, $t_R(\text{major}) = 14.0$ min, $t_R(\text{minor}) = 18.1$ min); $[\alpha]_D^{25} = +16.5$ (*c* 0.4, CHCl₃).; ¹H NMR (500 MHz, CDCl₃) δ 7.68-7.66 (m, 1H), 7.55-7.46 (m, 3H), 7.44-7.42 (m, 1H), 7.34-7.25 (m, 1H), 7.06 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.43 (s, 1H), 5.34-5.33 (m, 1H), 3.35-3.23 (m, 2H).; ¹³C NMR (125 MHz, CDCl₃) δ 149.6, 138.1, 135.8, 130.0, 129.8, 129.4, 126.4, 126.2, 123.4, 122.8, 122.0, 119.4, 115.9, 67.5, 62.4, 25.4.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₁₆H₁₂N₂O₃S 312.0569; found 312.0550.

8a: Benzyl (*E*)-3-((8*S*,12*bR*)-8-(2-(benzyloxy)-2-oxoethyl)-6,6-dioxido-8,12-*b*dihydrobenzo[5,6][1,2,3]oxathiazino [4,3-*a*]isoindol-12-yl)acrylate

A 20 mL sealed tube equipped with a magnetic stirring bar was charged with benzo-1,3-sulfamidate **6a** (30 mg, 0.16 mmol), [RhCp*Cl₂]₂ (1.4 mg, 2.0 mol%), AgOAc (38 mg, 0.23 mmol), benzyl acrylate (56 mg, 0.35 mmol), K₃PO₄ (12 mg, 0.06 mmol) and 2 mL of anhydrous MeCN. The reaction tube was capped and stirred at 100 °C for 12 h. 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 celite pad. The solvents and the volatiles were evaporated under reduced pressure followed by the purification through flash column chromatography using EtOAc /hexanes as an eluent to afford title compounds as diastereomeric mixture. Yield 31% (21 mg as a colorless oil). *trans:cis*=5.7:1 (determined by chiral HPLC chromatography).

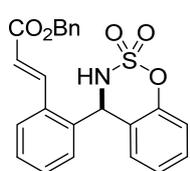
trans-(S,R)-8a:



Colorless viscous oil, 98% ee (Chiralpak ID, 50% IPA/*n*-hexanes, 1.0 ml/min, 215 nm, $t_R(\text{major}) = 58.5$ min, $t_R(\text{minor}) = 35.3$ min); $[\alpha]_D^{17} = -118.5$ (*c* 0.3, CHCl₃).; ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 15.9 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.30 (m, 8H), 7.15 (d, *J* = 6.9 Hz, 3H), 7.12 – 7.05 (m, 2H), 6.69 (d, *J* = 15.9 Hz, 1H), 6.54 (s, 1H), 5.33 (d, *J* = 3.2 Hz, 2H), 5.20 (d, *J* = 2.2 Hz, 2H), 3.54 (dd, *J* = 17.0, 3.1 Hz, 1H), 3.00 (dd, *J* = 17.0, 8.0 Hz, 1H).; ¹³C NMR (125 MHz, CDCl₃) δ 170.2, 165.9, 149.8, 141.1, 140.9, 137.6, 135.7, 135.4, 129.8, 129.6, 128.7, 128.6, 128.5, 128.5, 128.4, 127.5, 126.5, 125.9, 124.7, 120.9, 120.4, 119.0, 77.3, 66.8, 66.8, 65.9, 61.8, 39.9.; HRMS (FAB, double focusing) *m/z*: [M+H]⁺ Calcd for C₃₃H₂₇NO₇S 582.1586; found 582.1592 (M+H⁺).

9a: Benzyl (*R,E*)-3-(2-(2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phenyl)acrylate

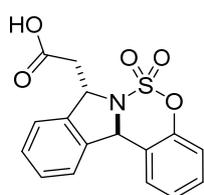
A 20 mL sealed tube equipped with a magnetic stirring bar was charged with benzo-1,3-sulfamidate **6a** (30 mg, 0.12 mmol), [RhCp*Cl₂]₂ (1.4 mg, 2.0 mol%), AgOAc (38 mg, 0.23 mmol), benzyl acrylate (20 mg, 0.13 mmol), and 2 mL of anhydrous acetone. The reaction tube was capped and stirred at 100 °C (bath 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 celite pad. The solvents and the volatiles were evaporated under reduced pressure followed by the purification through flash column chromatography using EtOAc /hexanes as an eluent to afford title compounds as colorless liquid.



Yield: 39% (19 mg as a colorless viscous oil); 98% ee (Chiralpak AD-H, 30% EtOH/*n*-hexanes, 1.0 ml/min, 215 nm, *t_R*(major) = 12.1 min, *t_R*(minor) = 20.0 min); [α]_D¹⁷ = 27.9 (*c* 0.15, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, *J* = 15.7 Hz, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.56 – 7.31 (m, 7H), 7.26 (d, *J* = 8.8 Hz, 1H), 7.12 (t, *J* = 7.0 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.29 (d, *J* = 8.5 Hz, 1H), 5.27 (s, 2H), 4.73 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 165.8, 151.6, 140.5, 136.4, 135.7, 134.6, 130.6, 129.9, 129.9, 129.7, 128.6, 128.4, 128.2, 128.1, 125.5, 122.7, 121.5, 119.2, 66.7, 58.6.; HRMS (FAB, double focusing) *m/z*: [M+H⁺] Calcd for C₂₃H₁₉NO₅S 422.1062; found 422.1048 (M+H⁺).

trans-(S,R)-10a: 2-((8*S*,12*bR*)-6,6-dioxido-8,12*b*-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-*a*]isoindol-8-yl)acetic acid

To a solution of (*S,R*)-**7a** (50 mg, 0.24 mmol) in MeOH (5.0 mL) was added 10% Pd/C (5 mg, 10% wt/wt) and the reaction mixture was stirred under H₂ (g) for 12 h. The mixture was filtered through a celite pad and the filtrate was evaporated under vacuum to get (*S,R*)-**10a** as a white solid.

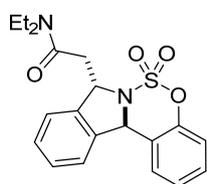


Yield: 98% (38.5 mg as a white solid); mp: 212.5-215.1 °C; 99% ee (Chiralpak IA, 10% IPA/*n*-hexanes/TFA, 1.1 ml/min, 215 nm, *t_R*(major) = 16.2 min, *t_R*(minor) = 18.8 min); [α]_D¹² = +92.4 (*c* 0.1, acetone); ¹H NMR (500 MHz, CDCl₃) ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.35 (m, 3H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.46 (s, 1H), 5.51 (d, *J* = 8.0 Hz, 1H), 3.41 (dd, *J* = 17.0, 2.8 Hz, 1H), 3.00 (dd, *J* = 17.0, 8.1 Hz, 1H); ¹³C NMR (125 MHz, Acetone-*d*₆) δ 170.8, 149.7, 138.9, 138.0, 129.2, 129.1, 128.8, 127.2, 125.9, 123.4, 122.8, 122.6, 118.7, 67.2, 63.1, 40.3.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₁₆H₁₃NO₅S 331.0514; found 331.0510.

(S,R)-11: 2-((8*S*,12*bR*)-6,6-dioxido-8,12*b*-dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-*a*]isoindol-8-yl)-*N,N*-diethylacetamide

To a solution of (*S,R*)-**10a** (35 mg, 0.11 mmol) in DCM (2.0 mL) was added EDCI·HCl (30 mg, 0.16

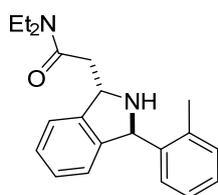
mmol) and HOBt (24 mg, 0.16 mmol) followed by diethylamine (9.3 mg, 0.13 mmol). The reaction mixture was stirred at rt for 12 h. The mixture was diluted with water and extracted with DCM (2 x 25 mL). The combined organic layer was dried over Na₂SO₄ and evaporated under reduced pressure. The crude mixture was purified on silica gel column chromatography using EtOAc/hexanes as an eluent to give (*S,R*)-**11** as a white solid.



Yield: 95% (39 mg as a white solid); mp: 158.2-161.3 °C; >99% ee (Chiralpak IC, 15% EtOH/*n*-hexanes, 1.0 ml/min, 215 nm, *t_R*(major) = 16.0 min, *t_R*(minor) = 18.1 min); [α]_D²⁸ = +83.2 (*c* 0.35, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.59 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.40-7.33 (m, 2H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.32 (s, 1H), 5.70 (d, *J* = 9.2 Hz, 1H), 3.53-3.45 (m, 3H), 3.35 (sept, *J* = 7.6 Hz, 2H), 2.85 (dd, *J* = 16.3, 9.3 Hz, 1H), 1.21-1.18 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 168.8, 149.8, 140.2, 137.4, 129.2, 129.1, 128.5, 126.5, 125.7, 124.1, 122.5, 122.1, 119.2, 67.2, 63.8, 42.1, 40.8, 40.3, 14.2, 13.1.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₀H₂₂N₂O₄S 386.1300; found 386.1297.

(*S,S*)-12: *N,N*-diethyl-2-((1*S*,3*S*)-3-(*o*-tolyl)isoindolin-1-yl)acetamide

A solution of (*S,R*)-**11** (30 mg, 0.07 mmol) in THF/Et₂O (0.2/2.0 mL) was degassed for 5 min and added Ni(dppf)Cl₂ (5 mol%) followed by the addition of 3 M MeMgBr (0.078 mL, 0.23 mmol). The mixture was heated to 55 °C for 12 h. The reaction mixture was allowed to cool to rt and quenched with MeOH. The solvents were evaporated under vacuum, treated with 2 M HCl in methanol, and heated to 55 °C for 6 h. The reaction mixture was evaporated again and washed with EtOAc. The resulting aqueous layer was basified with NaHCO₃ and extracted with DCM. The organic layer was evaporated under vacuum and the crude mixture was purified on silica gel column chromatography using DCM/MeOH as an eluent to afford (*S,S*)-**12** as a white solid.



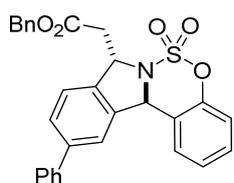
Yield: 74% (18.5 mg as a white solid); mp: 246.4-248.0 °C; >99% ee (Chiralpak OD-H, 5% IPA/*n*-hexanes, 0.8 ml/min, 215nm, *t_R*(major) = 15.3 min, *t_R*(minor) = 25.4 min); [α]_D²⁰ = -8.9 (*c* 0.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.48-7.41 (m, 2H), 7.33-7.32 (m, 3H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.13-7.10 (m, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.43 (s, 1H), 5.39 (dd, *J* = 9.3, 3.7 Hz, 1H), 3.72 (dd, *J* = 16.8, 9.2 Hz, 1H), 3.49-3.31 (m, 4H), 3.17 (dd, *J* = 17.0, 3.7 Hz, 1H), 2.63 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 168.4, 137.9, 137.6, 137.3, 133.4, 131.4, 130.0, 129.7, 129.4, 128.1, 126.7, 124.5, 122.1, 62.7, 60.5, 42.3, 40.6, 34.9, 19.9, 14.1, 12.9.; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₁H₂₆N₂O 322.2045; found 322.2032.

(*S,R*)-13:

Benzyl-2-((8*S*,12*B**R*)-6,6-dioxido-11-phenyl-8,12*b*-

dihydrobenzo[5,6][1,2,3]oxathiazino[4,3-a]isoindol-8-yl)acetate

A sealed tube containing Na₂CO₃ (19.6 mg, 0.18 mmol) was added PhB(OH)₂ (11 mg, 0.11 mmol) and PdCl₂(PPh₃)₂ (2.1 mg, 4 mol%). The tube was evacuated and backfilled with nitrogen three times, before a solution of (*S,R*)-**7f** (37 mg, 0.07 mmol) in dioxane/H₂O (1.5/0.5 mL) was added, and the resulting mixture was then stirred at reflux for 8 h. The reaction mixture was cooled to room temperature and concentrated under *vacuo* and the crude mixture was purified on silica gel column chromatography using EtOAc/hexanes as an eluent to afford desired product as a white solid.



Yield: 90% (33 mg as a colorless viscous oil); 99% ee (Chiralpak AD-H, 30% EtOH/*n*-hexanes, 1.1 ml/min, 215nm, *t_R*(major) = 16.4 min, *t_R*(minor) = 25.4 min); $[\alpha]_{\text{D}}^{28} = -94.3$ (*c* 0.55, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.72 (s, 1H), 7.59-7.50 (m, 6H), 7.45-7.42 (m, 1H), 7.39-7.35 (m, 5H), 7.31 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.25-7.21 (m, 2H), 7.06 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.31 (s, 1H), 5.58 (d, *J* = 7.9 Hz, 1H), 5.22 (s, 2H), 3.47 (dd, *J* = 16.6, 3.2 Hz, 1H), 3.10 (dd, *J* = 16.6, 7.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 170.1, 149.9, 142.4, 140.3, 138.4, 137.6, 135.5, 129.3, 129.0, 128.6, 128.5, 128.4, 128.3, 127.9, 127.3, 126.4, 125.9, 123.3, 122.2, 121.6, 119.3, 67.3, 66.7, 63.0, 41.2; HRMS (EI, double focusing) *m/z*: [M]⁺ Calcd for C₂₉H₂₃NO₅S 497.1297; found 497.1298.

ACKNOWLEDGMENTS

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Supporting Information. Copies of ¹H-, ¹³C-NMR, chiral HPLC chromatograms for all new compounds, X-ray crystallographic data in CIF for **10a**(CCDC-1523356), **7f**(CCDC-1523015), **7j**(CCDC-1526196) and 2D-NOESY spectrum of **7c**.

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