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ENANTIOSELECTIVE INTRAMOLECULAR C–H AMIDATION OF SULFAMATE ESTERS CATALYZED BY CHIRAL DIRHODIUM(II) CARBOXYLATES†

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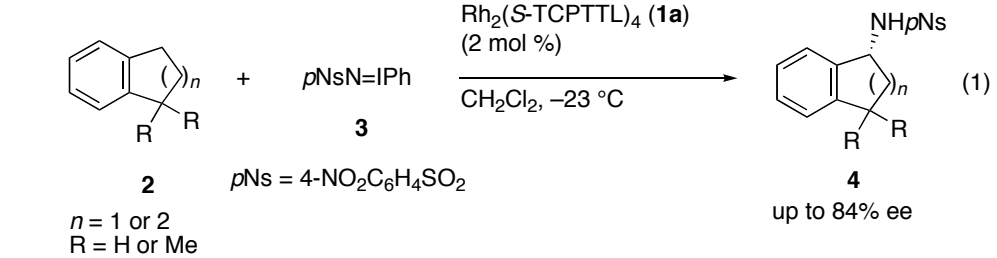
Abstract – The chiral dirhodium(II) carboxylate-catalyzed enantioselective intramolecular C–H amidation reaction of sulfamate esters via *in situ* generated iminoiodinanes is described. The use of dirhodium(II) tetrakis[*N*-tetrafluorophthaloyl-(*S*)-*tert*-leucinate], Rh_2(*S*-TFPTTL)$_4$, as a catalyst and PhI(OAc)$_2$ as an oxidant provides cyclic sulfamidates in up to 48% ee.

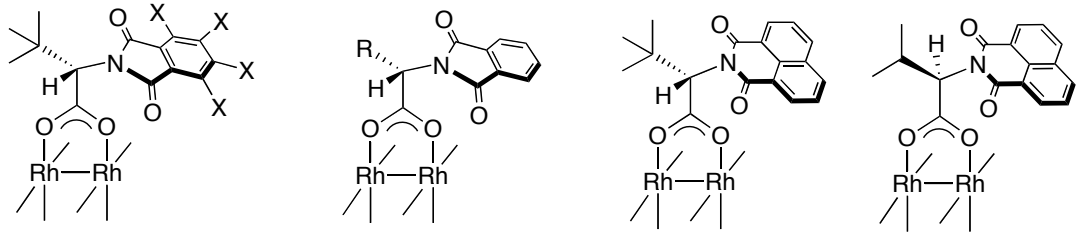
The transition metal-catalyzed intramolecular C–H amidation of iminoiodinanes, which features C–N bond formation at an unactivated carbon atom, offers a potentially powerful strategy for the synthesis of heterocycles.[1] While the pioneering work of Breslow and Gellman in 1983 demonstrated that the $Rh_2(OAc)_4$-catalyzed intramolecular C–H amidation of [(2,5-diisopropyl)phenylsulfonylimino]phenyliodinane provided cyclic sulfonamide in high yield,[2] it was not until several years ago that an efficient and general intramolecular C–H amidation procedure with *in situ* generated iminoiodinanes was developed.[3-5] Du Bois and co-workers demonstrated that the oxidation of carbamates and sulfamate esters by PhI(OAc)$_2$ in the presence of MgO gives only low concentrations of iminoiodinanes, which undergo rapid C-H insertion under the influence of a dirhodium(II) catalyst to produce oxazolidinones and cyclic sulfamidates, respectively, with high regioselectivity and good to excellent diastereoselectivity.[3,4] Since then, remarkable progress has been achieved in the development of intramolecular C–H amidations with effective metal catalysts derived from Ru(II),[6] Mn(III),[7] and Ag(I).[8] Consequently, a great deal of effort has been directed toward the development of an enantioselective version of these catalytic processes. Che and co-workers demonstrated the first successful examples of

† Dedicated to Professor Satoshi Ōmura on the occasion of his 70th birthday.

the enantioselective intramolecular C–H amidation of sulfamate esters (up to 88% ee), using a chiral ruthenium(II) porphyrin-catalyst.[6] Thereafter, Fruit and Müller reported enantioselective intramolecular C–H amidation reactions of sulfamate esters and sulfonamides catalyzed by chiral dirhodium(II) carboxylates, Rh_2(*S*-NTTL)$_4$ (**1g**) and Rh_2(*R*-NTV)$_4$ (**1h**), in up to 52% ee and 66% ee, respectively.[9] More recently, the Che group explored the intramolecular C–H amidation of sulfamate esters in the presence of chiral manganese(III)-salen-catalysts, in which moderate to good enantioselectivities (up to 79% ee) were obtained.[7] Recently, Che and co-workers reported enantioselective intramolecular aziridination of sulfonamides via *in situ* generated iminoiodinanes (up to 76% ee), using a chiral dirhodium(II) carboxamidate catalyst Rh_2(4*S*-MEOX)$_4$.

We recently reported that the enantioselective intermolecular benzylic C–H amidation of aromatic hydrocarbons (**2**) with [(4-nitrophenyl)sulfonylimino]phenyliodinane (**3**) catalyzed by chiral dirhodium(II) carboxylates provides sulfonamides in up to 84% ee [eqn. (1)].[10] In this process, Rh_2(*S*-TCPTTL)$_4$ (**1a**), characterized by the substitution of chlorine atoms for four hydrogen atoms on the phthalimido group in the parent dirhodium(II) complex, Rh_2(*S*-PTTL)$_4$ (**1c**),[11,12] proved to be the catalyst of choice in terms of product yield and enantioselectivity as well as catalyst activity. As a logical extension of our studies, we now address the issue of enantiocontrol in the intramolecular C–H amidation of sulfamate esters.





X = Cl: Rh_2(*S*-TCPTTL)$_4$ (**1a**)
X = F: Rh_2(*S*-TFPTTL)$_4$ (**1b**)
X = H: Rh_2(*S*-PTTL)$_4$ (**1c**)

R = Me: Rh_2(*S*-PTA)$_4$ (**1d**)
R = Bn: Rh_2(*S*-PTPA)$_4$ (**1e**)
R = ^{i}Pr: Rh_2(*S*-PTV)$_4$ (**1f**)

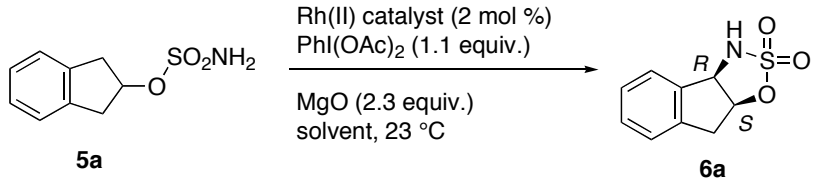
Rh_2(*S*-NTTL)$_4$ (**1g**)

Rh_2(*R*-NTV)$_4$ (**1h**)

In an extension of our previous work, we initially explored the C–H amidation of indan-2-yl sulfamate (**5a**) using 2 mol % of Rh_2(*S*-TCPTTL)$_4$ (**1a**), in the presence of 1.1 equiv. of PhI(OAc)$_2$ and 2.3 equiv. of MgO. The reaction in dichloromethane at 23 °C proceeded smoothly to give the cyclic sulfamidate (**6a**), $[\alpha]_D^{25}$ +31.3° (*c* 0.87, THF), in 81% yield with complete *cis* selectivity (Table 1, Entry 1). The

enantioselectivity of this reaction was determined to be 22% ee by HPLC analysis (Daicel Chiralcel OD-H). The preferred absolute stereochemistry of **6a** was established as (3a*R*,8a*S*) by comparing the sign

Table 1. Enantioselective Intramolecular C–H Amidation of Indan-2-yl Sulfamate (**5a**) Catalyzed by Chiral Dirhodium(II) Carboxylates[a)]



5a **6a**

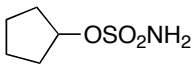
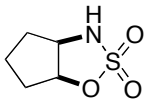
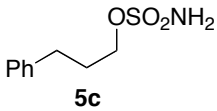
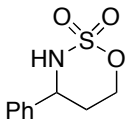
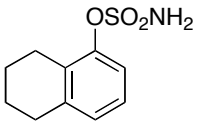
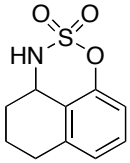
Entry	Rh(II) catalyst	Solvent	Time (h)	Cyclic sulfamidate **6a** Yield (%)[b)]	$[\alpha]_D$ (*c*, THF)	Ee (%)[c)]
1	Rh_2(*S*-TCPTTL)$_4$ (**1a**)	CH_2Cl_2	3	81	+31.3° (0.87)	22
2	Rh_2(*S*-TCPTTL)$_4$ (**1a**)	benzene	1	79	+48.9° (1.05)	35
3	Rh_2(*S*-TCPTTL)$_4$ (**1a**)	toluene	1	37	+30.0° (0.63)	23
4	Rh_2(*S*-TFPTTL)$_4$ (**1b**)	benzene	1	98	+68.3° (1.03)	48
5	Rh_2(*S*-PTTL)$_4$ (**1c**)	benzene	2	75	+52.0° (1.13)	43
6	Rh_2(*S*-PTA)$_4$ (**1d**)	benzene	1	61	+15.7° (1.01)	15
7	Rh_2(*S*-PTPA)$_4$ (**1e**)	benzene	1.5	70	+21.5° (0.86)	18
8	Rh_2(*S*-PTV)$_4$ (**1f**)	benzene	2	79	+16.8° (1.20)	19
9[d)]	Rh_2(*S*-TFPTTL)$_4$ (**1b**)	benzene	1	98	+64.2° (0.93)	45
10[d)]	Rh_2(*S*-PTTL)$_4$ (**1c**)	benzene	0.5	51	+56.3° (0.75)	38

[a)] All reactions were performed on a 0.2 mmol scale. [b)] Isolated yield. [c)] Determined by HPLC (Daicel Chiralcel OD-H column). [d)] The reaction was carried out in the absence of MgO.

of the optical rotation with (3a*R*,8a*S*)-**6a** [$[\alpha]_D^{24}$ +141° (*c* 0.82, THF)], prepared from (1*R*,2*S*)-1-aminoindan-2-ol according to the procedure of Harwood (SO_2Cl_2, Et_3N, CH_2Cl_2, 0 °C, 1 h, 67%).[13] A survey of solvents revealed that benzene was the optimal solvent for this transformation, improving the enantioselectivity to 35% ee (Entry 2). Toluene was inferior to benzene in terms of both product yield and enantioselectivity (Entry 3).[14] Using benzene as the solvent, we next evaluated the performance of other chiral dirhodium(II) carboxylate catalysts. While a uniform sense of asymmetric induction was observed in all cases, the ee values were dependent on the catalyst. As might be expected from the results for the enantioselective intermolecular amidation of indan, chiral dirhodium(II) carboxylate catalysts, Rh_2(*S*-PTA)$_4$ (**1d**), Rh_2(*S*-PTPA)$_4$ (**1e**), and Rh_2(*S*-PTV)$_4$ (**1f**) were less effective than Rh_2(*S*-TCPTTL)$_4$ (Entries 6–8).[15] Somewhat surprisingly, Rh_2(*S*-TFPTTL)$_4$ (**1b**)[16] and Rh_2(*S*-PTTL)$_4$ (**1c**) proved to be the catalysts of choice for this process, displaying higher enantioselectivities than Rh_2(*S*-TCPTTL)$_4$ (48% and 43% ee, Entries 4 and 5). Although the enantioselectivities are modest, these ee values exceed those (22% and 30% ee)[9b] reported previously by Fruit and Müller, using Rh_2(*S*-NTTL)$_4$ (**1g**) and Rh_2(*R*-NTV)$_4$ (**1h**). It is noteworthy that the isolated yield (98%) obtained using Rh_2(*S*-TFPTTL)$_4$ is the highest ever reported for the intramolecular C–H amidation of **5a**. In this respect,

it is interesting to note that the reaction with Rh_2(*S*-TFPTTL)$_4$ in the absence of MgO as an AcOH scavenger gave nearly the same result as that in the presence of MgO (Entry 4 vs. 9), which is in marked

Table 2. Enantioselective Intramolecular C–H Amidation of Sulfamate Esters (**5b-d**)[a)]

Entry	Sulfamate ester	Rh(II) catalyst	Time (h)	Product	Yield (%)[b)]	Ee (%)
1	 **5b**	Rh_2(*S*-TFPTTL)$_4$ (**1b**)	1	 **6b**	30	27[c)]
2		Rh_2(*S*-PTTL)$_4$ (**1c**)	1		34	14[c)]
3	 **5c**	Rh_2(*S*-TFPTTL)$_4$ (**1b**)	10	 **6c**	87	10[d)]
4		Rh_2(*S*-PTTL)$_4$ (**1c**)	30		67	21[d)]
5	 **5d**	Rh_2(*S*-TFPTTL)$_4$ (**1b**)	2	 **6d**	49(39)[e)]	14[f)]
6		Rh_2(*S*-PTTL)$_4$ (**1c**)	2		9(45)[e)]	–16[f)]

[a)] All reactions were performed on a 0.2 mmol scale with 2 mol % of Rh(II) catalyst, 1.1 equiv. of $PhI(OAc)_2$ and 2.3 equiv. of MgO in benzene at 23 °C. [b)] Isolated yield. [c)] Determined by HPLC (Daicel Chiralpak AD column) after conversion to the corresponding benzyl carbamate. [d)] Determined by HPLC (Daicel Chiralcel OD column). [e)] Values in parentheses refer to the yields of sulfamate esters recovered. [f)] Determined by HPLC (Daicel Chiralpak IA column).

contrast with the results for Rh_2(*S*-PTTL)$_4$ (Entry 5 vs. 10). These results demonstrate the robust nature and high reactivity of Rh_2(*S*-TFPTTL)$_4$.

We then investigated the applicability of the present catalytic system to sulfamate esters other than **5a**. Some representative results are presented in Table 2. To our disappointment, the method was found to be highly sensitive to the structure of the substrate. The reaction of cyclopentyl sulfamate ester (**5b**) under the influence of Rh_2(*S*-TFPTTL)$_4$ or Rh_2(*S*-PTTL)$_4$ gave the cyclic sulfamidate (**6b**) in low yields with complete *cis* selectivity, wherein ee values were significantly lower than those in the case of **5a** (Entries 1 and 2). These results strongly suggest that the presence of a phenyl ring is required for both product yield and enantioselectivity in the five-membered ring insertion process. It was also found that the formation of the six-membered cyclic sulfamidate (**6c**), the preferred pathway in the C–H amidation of acyclic, conformationally mobile sulfamate esters, resulted in disappointing enantioselectivities (Entries 3 and 4). In this reaction, Rh_2(*S*-PTTL)$_4$ exhibited a higher enantioselectivity than Rh_2(*S*-TFPTTL)$_4$. The intramolecular insertion of aromatic sulfamate ester (**5d**) into a benzylic C–H bond provided the tricyclic sulfamidate (**6d**) in low to moderate yields with *ca*. 60% substrate conversion and only a poor enantioselectivity (Entries 5 and 6).

In summary, we have reported one-pot enantioselective C–H amidation of sulfamate esters with the use of chiral dirhodium(II) carboxylate catalysts and $PhI(OAc)_2$ as an oxidant. Rh_2(*S*-TFPTTL)$_4$ is the most effective catalyst for this process (up to 48% ee). In contrast to the enantioselective intermolecular amidation of benzylic C–H bonds, there is considerable room for improvement in the intramolecular amidation of sulfamate esters catalyzed by chiral dirhodium(II) complexes. The design and synthesis of a new class of chiral bridging ligands to further enhance enantioselectivity is currently in progress.

EXPERIMENTAL

General. Melting points were determined on a Büchi 535 digital melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer and absorbance bands are reported in wavenumber (cm^{-1}). ^{1}H NMR spectra were recorded on JEOL JNM-AL 400 (400 MHz) spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane; δ_H 0.00 or acetone-d_6; δ_H 2.04). Data are presented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant and integration. ^{13}C NMR spectra were recorded on JEOL JNM-AL 400 (100 MHz) spectrometer. Chemical shifts are reported relative to internal standard ($CDCl_3$; δ 77.0, acetone-d_6; δ 29.8). Optical rotations were measured on a JASCO P-1030 digital polarimeter at the sodium D line (589 nm). EI-MS spectra were obtained on a JEOL JMS-HX 110 spectrometer. Column chromatography was carried out on Kanto silica gel 60 N (63-210 mesh). Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F_{254} plates with visualization by ultraviolet, anisaldehyde stain solution or phosphomolybdic acid stain solution. Analytical high performance liquid chromatography (HPLC) was performed on JASCO PU-1580 intelligent HPLC pump with JASCO UV-1575 intelligent UV/VIS detector. Detection was performed at 254 nm. Chiralcel OD, OD-H, Chiralpak IA and AD columns (0.46 cm × 25 cm) from Daicel were used. Retention times (t_R) and peak ratio were determined with Shimadzu C-R8A chromatopac integrator or JASCO-Borwin analysis system.

All non-aqueous reactions were carried out in flame-dried glassware under argon atmosphere. Reagents and solvents were purified by standard means. Dehydrated THF, CH_2Cl_2 and toluene were purchased from Kanto Chemical Co., Inc. Benzene was distilled from Na/benzophenone ketyl. Sulfamoyl chloride was prepared according to the procedure of Appel and Berger.[17]

General procedure for sulfamate ester preparation: indan-2-yl sulfamate (5a).[3b,9b] The sulfamate ester (**5a**) was prepared according to the procedure of Okada.[18] Sulfamoyl chloride (2.25 g, 15.0 mmol, 1.5 equiv) was added to a solution of 2-indanol (1.3 g, 10 mmol) in *N*,*N*-dimethylacetamide (40 mL, 0.25 M) at 0 °C. The mixture was stirred at 23 °C for 1 h and poured into cold brine (100 mL). The whole

mixture was extracted with EtOAc (2 × 100 mL), and the combined organic layers were washed with H_2O (50 mL) and brine (2 × 50 mL), and dried over Na_2SO_4. Filtration and evaporation gave the crude product (2.4 g), which was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) followed by recrystallization from benzene to provide **5a** (1.8 g, 84%) as colorless needles; R_f = 0.54 (5:1 CH_2Cl_2/EtOAc); mp 99.5-100.5 °C (lit.,[9b] mp 89 °C); IR (KBr) ν 3370, 3281, 1346, 1179 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.26 (dd, *J* = 3.6, 17.0 Hz, 2H, C1-*H* and C3-*H*), 3.33 (dd, *J* = 5.8, 17.0 Hz, 2H, C1-*H* and C3-*H*), 4.94 (br-s, 2H, NH_2), 5.40 (tt, *J* = 3.6, 5.8 Hz, 1H, C2-*H*), 7.17-7.24 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.81 (CH_2), 83.58 (CH), 124.54 (CH), 127.04 (CH), 139.14 (C); HRMS (EI) calcd for $C_9H_{11}NO_3S$ (M^+) 213.0460, found 213.0445; Anal. Calcd for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20; N, 6.57; S, 15.04. Found: C, 50.60; H, 5.15; N, 6.64; S, 15.20.

Cyclopentyl sulfamate (5b).[19] The sulfamate ester (**5b**) was prepared according to the general procedure, using cyclopentanol (861.4 mg, 10 mmol) and sulfamoyl chloride (4.50 g, 30 mmol). The crude product (1.9 g) was purified by column chromatography (3:1 hexane/EtOAc) followed by recrystallization from 1:1 ^{i}PrOH/hexane to afford **5b** (1.51 g, 67%) as colorless plates; R_f = 0.60 (1:1 hexane/EtOAc); mp 181.5-182.5 °C (dec.) (lit.,[19] mp 58-60 °C); IR (KBr) ν 3360, 3264, 1345, 1181, 1155 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.60-1.68 (m, 2H, CH_2), 1.77-1.81 (m, 2H, CH_2), 1.84-1.94 (m, 2H, CH_2), 1.99-2.03 (m, 2H, CH_2), 4.68 (br-s, 2H, NH_2), 5.10 (quintet, *J* = 2.8 Hz, 1H, C*H*OSO_2NH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.24 (CH_2), 33.11 (CH_2), 86.45 (CH); HRMS (EI) calcd for $C_5H_{12}NO_3S$ (MH^+) 166.0538, found 166.0534.

3-Phenylpropyl sulfamate (5c).[3b] According to the general procedure, **5c** was prepared from 3-phenylpropanol (1 g, 7.3 mmol) and sulfamoyl chloride (1.64 g, 11 mmol). The crude product (1.5 g) was purified by column chromatography (silica gel, 3:1 hexane/EtOAc) followed by recrystallization from 3:1 ether/hexane to afford **5c** (1.3 g, 82%) as colorless needles; R_f = 0.53 (1:1 hexane/EtOAc); mp 56.5-57.0 °C; IR (KBr) ν 3370, 3285, 1350, 1184 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.02-2.19 (m, 2H, $CH_2CH_2CH_2$), 2.74 (t, *J* = 7.5 Hz, 2H, PhCH_2), 4.20 (t, *J* = 6.4 Hz, 2H, OCH_2), 4.92 (br-s, 2H, NH_2), 7.17-7.31 (m, 5H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.28 (CH_2), 31.55 (CH_2), 70.52 (CH_2), 126.14 (CH), 128.37 (CH), 128.44 (CH), 140.32 (C); HRMS (EI) calcd for $C_9H_{13}NO_3S$ (M^+) 215.0616, found 215.0609; Anal. Calcd for $C_9H_{13}NO_3S$: C, 50.21; H, 6.09; N, 6.51; S, 14.90. Found: C, 50.15; H, 5.98; N, 6.47; S, 15.19.

1,2,3,4-Tetrahydronaphthalen-8-yl sulfamate (5d).[3e] According to the general procedure, **5d** was prepared from 1,2,3,4-tetrahydronaphthalen-8-ol (1.5 g, 10 mmol) and sulfamoyl chloride (2.25 g, 15

mmol). The crude product (3.0 g) was purified by column chromatography (silica gel, 5:1 hexane/EtOAc) followed by recrystallization from benzene to afford **5d** (2.2 g, 98%) as colorless needles; R_f = 0.50 (2:1 hexane/EtOAc); mp 87.5-88 °C; IR (KBr) ν 3387, 3279, 1346, 1175 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.77-1.80 (m, 4H, C1-*H*, C4-*H*), 2.79-2.81 (m, 4H, C2-*H*, C3-*H*), 5.03 (br-s, 2H, NH_2), 7.02 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.11 (dd, *J* = 7.8, 7.8 Hz, 1H, Ar*H*), 7.18 (d, *J* = 7.8 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.36 (CH_2), 22.55 (CH_2), 23.70 (CH_2), 29.44 (CH_2), 118.35 (CH), 125.95 (CH), 127.94 (CH), 130.56 (C), 139.98 (C), 148.45 (C); HRMS (EI) calcd for $C_{10}H_{13}NO_3S$ (M^+) 227.0616, found 227.0612; Anal. Calcd for $C_{10}H_{13}NO_3S$: C, 52.85; H, 5.77; N, 6.16; S, 14.11. Found: C, 52.93; H, 5.66; N, 6.06; S, 14.16.

General procedure for the enantioselective intramolecular C–H amidation reaction (Table 1, Entry 4): (3a*R*,8a*S*)-3,3a,8,8a-tetrahydroindeno[1,2-*d*]-1,2,3-oxathiazole 2,2-dioxide (6a).[3b,6a,9b] To a suspension of **5a** (42.6 mg, 0.2 mmol), MgO (18.5 mg, 0.46 mmol, 2.3 equiv.) and Rh_2(*S*-TFPTTL)$_4$·2EtOAc (6.8 mg, 0.004 mmol, 2 mol %) in benzene (5 mL) was added $PhI(OAc)_2$ (70.9 mg, 0.22 mmol, 1.1 equiv.) in one portion at 23 °C. After stirring at this temperature for 1 h, the whole mixture was filtered through a pad of Celite. The filter cake was rinsed with EtOAc and the combined filtrates were evaporated under reduced pressure. The residue (113 mg) was purified by column chromatography (silica gel, 5:1 hexane/EtOAc) to provide (3a*R*,8a*S*)-**6a** (40.9 mg, 98%) as a white solid; R_f = 0.32 (2:1 hexane/EtOAc); mp 169-170 °C; $[\alpha]_D^{22}$ +68.3° (*c* 1.03, THF) for 48% ee; IR (KBr) ν 3283, 1350, 1187 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 3.29 (d, *J* = 18.1 Hz, 1H, C8-C*H*), 3.46 (dd, *J* = 6.2, 18.1 Hz, 1H, C8-C*H*), 5.44 (t, *J* = 6.2 Hz, 1H, C3a-C*H*), 5.61 (m, 1H, C8a-C*H*), 7.03 (br-d, *J* = 6.2 Hz, 1H, N*H*), 7.29-7.32 (m, 3H, Ar*H*), 7.39-7.41 (m, 1H, Ar*H*); ^{13}C NMR (100 MHz, acetone-d_6) δ 38.07 (CH_2), 65.12 (CH), 86.95 (CH), 125.77 (CH), 126.29 (CH), 128.19 (CH), 129.90 (CH), 139.56 (C), 140.63 (C); HRMS (EI) calcd for $C_9H_9NO_3S$ (M^+) 211.0303, found 211.0294. The enantiomeric excess of **6a** was determined to be 48% by HPLC with a Chiralcel OD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (minor) = 26.5 min for (3a*S*,8a*R*)-enantiomer; t_R (major) = 31.5 min for (3a*R*,8a*S*)-enantiomer. The absolute configuration of **6a** was determined to be 3a*R*, 8a*S* by chemical correlation (*vide infra*).

Determination of absolute configuration of 6a: (3a*R*,8a*S*)-3,3a,8,8a-tetrahydroindeno[1,2-*d*]-1,2,3-oxathiazole 2,2-dioxide (6a) from (1*R*,2*S*)-1-aminoindan-2-ol. The cyclic sulfamidate (**6a**) was prepared according to the procedure of Harwood.[13] To a solution of (1*R*,2*S*)-1-amino-2-indanol (>99% ee, purchased from Aldrich, 100 mg, 0.67 mmol) and Et_3N (102 mg, 1.0 mmol) in CH_2Cl_2 (3 mL) was added SO_2Cl_2 (136 mg, 1.0 mmol) at 0 °C. After stirring at this temperature for 1 h, the reaction mixture was poured into cold water (10 mL), and the whole was extracted with EtOAc (3 × 10 mL). The combined

organic layers were washed with saturated $NaHCO_3$ solution (10 mL), water (10 mL) and brine (2 × 10 mL), and dried over Na_2SO_4. Filtration and evaporation gave the crude product (118.7 mg), which was purified by column chromatography (silica gel, 3:1 hexane/EtOAc) followed by recrystallizations from 1:1 ^{i}PrOH/hexane to furnish (3a*R*,8a*S*)-**6a** (94.5 mg, 67%) as colorless needles; mp 187–188 °C (dec); $[\alpha]_D^{24}$ +141.2° (*c* 0.82, THF) for >99% ee of (3a*R*,8a*S*)-**6a**; Anal. Calcd for $C_9H_9NO_3S$: C, 51.17; H, 4.29; N, 6.63; S, 15.18. Found: C, 51.15; H, 4.33; N, 6.53; S, 15.29. The enantiomeric excess was determined to be >99% by HPLC.

Tetrahydro-3(3aH)-cyclopent-1,2,3-oxathiazole (6b). According to the general procedure for C–H amidation, **6b** was prepared from **5b** (33.0 mg, 0.20 mmol), $PhI(OAc)_2$ (70.9 mg, 0.22 mmol), MgO (18.5 mg, 0.46 mmol), and Rh_2(*S*-TFPTTL)$_4$·2EtOAc (6.8 mg, 0.004 mmol, 2 mol %). The crude product (76 mg) was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) to provide **6b** (9.7 mg, 30%) as a colorless oil; R_f = 0.38 (2:1 hexane/EtOAc); $[\alpha]_D^{24}$ +1.21° (*c* 0.58, $CHCl_3$) for 27% ee; IR (neat) ν 3268, 1354, 1188 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (m, 1H), 1.83-2.05 (m, 4H), 2.17 (m, 1H), 4.28 (ddt *J* = 3.2, 9.6, 6.4 Hz, 1H, C3a-*H*), 4.40 (br-s, 1H, N*H*), 5.17 (dt, *J* = 1.9, 6.4 Hz, 1H, C6a-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.58 (CH_2), 32.70 (CH_2), 33.15 (CH_2), 59.77 (CH), 86.84 (CH); HRMS (EI) calcd for $C_5H_9NO_3S$ (M^+) 163.0303, found 163.0299. The enantiomeric excess of **6b** was determined to be 27% by HPLC after conversion to the corresponding benzyl carbamate (*vide infla*). The absolute stereochemistry of **6b** was not determined.

Benzyl tetrahydro-3(3aH)-cyclopent-1,2,3-oxathiazole-3-carboxylate. A solution of **6b** (8.1 mg, 0.05 mmol) in THF (0.4 mL) was added to a solution of sodium *tert*-butoxide (10 mg, 0.1 mmol) in THF (0.6 mL) at 0 °C. After 0.5 h of stirring at this temperature, benzyl chloroformate (34 mg, 0.2 mmol) was added to the mixture. After 5 min of stirring at the same temperature, the reaction was quenched by crushed ice, and the whole mixture was extracted with EtOAc (20 mL). The organic layer was washed with water (5 mL) and brine (2 × 5 mL), and dried over Na_2SO_4. Filtration and evaporation in vacuo followed by column chromatography (silica gel, 20:1 toluene/EtOAc) provided benzyl tetrahydro-3(3aH)-cyclopent-1,2,3-oxathiazole-3-carboxylate (10.3 mg, 70%) as a colorless oil; R_f = 0.60 (1:1 hexane/EtOAc); $[\alpha]_D^{23}$ +6.51° (*c* 0.85, $CHCl_3$); IR (neat) ν 1740, 1380, 1335,1305,1196 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83-1.90 (m, 2H), 1.96-2.06 (m, 3H), 2.21 (m, 1H), 4.60 (dt *J* = 2.7, 5.4 Hz, 1H, C6a-*H*), 5.21 (t, *J* = 5.4 Hz, 1H, C3a-*H*), 5.30 (d, *J* = 12.4 Hz, 1H, PhC*H*), 5.34 (d, *J* = 12.4 Hz, PhC*H*), 7.32-7.41 (m, 5H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.69 (CH_2), 32.31 (CH_2), 32.63 (CH_2), 61.52 (CH), 69.26 (CH_2), 84.13 (CH), 127.83 (CH), 128.51 (CH), 128.59 (CH), 134.40 (C), 150.05 (C=O); HRMS (EI) calcd for $C_{13}H_{15}NO_5S$ (M^+) 297.0671, found 297.0681. The enantiomeric excess was

determined to be 27% by HPLC [Daicel Chiralpak AD column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (major) = 17.9 min; t_R (minor) = 21.0 min].

Tetrahydro-4-phenyl-1,2,3-oxathiazine 2,2-dioxide (6c).[3b] According to the general procedure for C–H amidation, **6c** was prepared from **5c** (43.1 mg, 0.20 mmol), $PhI(OAc)_2$ (70.9 mg, 0.22 mmol), MgO (18.5 mg, 0.46 mmol), and Rh_2(*S*-PTTL)$_4$·2EtOAc (5.69 mg, 0.004 mmol, 2 mol %). The crude product (70 mg) was purified by column chromatography (silica gel, 6:1 hexane/EtOAc) to provide **6c** (28.4 mg, 67%) as a white solid; R_f = 0.44 (2:1 hexane/EtOAc); mp 120–120.5 °C; $[\alpha]_D^{23}$ +1.09° (*c* 0.99, THF) for 21% ee; IR (KBr) ν 3212, 1355, 1180 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (dq *J* = 14.7, 1.8 Hz, 1H, C5$_{eq}$-*H*), 2.25 (ddt, *J* = 4.9, 14.7, 12.8 Hz, 1H, C5$_{ax}$-*H*), 4.50 (br-d, *J* = 9.1 Hz, 1H, N*H*), 4.64 (ddd, *J* = 1.8, 4.9, 11.8 Hz, 1H, C6$_{eq}$-*H*), 4.81-4.88 (m, 2H, C4-*H* and C6$_{ax}$-*H*), 7.33-7.41 (m, 5H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.13 (CH_2), 58.94 (CH), 71.91 (CH_2), 126.17 (CH), 128.76 (CH), 129.02 (CH), 137.84 (C); HRMS (EI) calcd for $C_9H_{11}NO_3S$ (M^+) 213.0459, found 213.0462. The enantiomeric excess of **6c** was determined to be 21% by HPLC with a Chiralcel OD column (3:1 hexane/*i*-PrOH, 0.5 mL/min): t_R (major) = 26.4 min; t_R (minor) = 30.1 min. The absolute stereochemistry of **6c** was not determined.

3a,4,5,6-Tetrahydro-3*H*-naphth[1,8-*de*]-1,2,3-oxathiazine 2,2-dioxide (6d).[3e] According to the general procedure for C–H amidation, **6d** was prepared from **5d** (45.5 mg, 0.20 mmol), $PhI(OAc)_2$ (70.9 mg, 0.22 mmol), MgO (18.5 mg, 0.46 mmol), and Rh_2(*S*-TFPTTL)$_4$·2EtOAc (6.8 mg, 0.004 mmol, 2 mol %). The crude product (102 mg) was purified by column chromatography (silica gel, 3:1 hexane/EtOAc) to provide **6d** (22.2 mg, 49%) as an orange solid, along with recovered **5d** (17.6 mg, 39%). **6d**: R_f = 0.47 (2:1 hexane/EtOAc); mp 123-124 °C; $[\alpha]_D^{24}$ +5.28° (*c* 0.90, MeOH) for 14% ee; IR (KBr) ν 3259, 1370, 1174 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (dq, *J* = 3.6, 12.4 Hz, 1H, C4-*H*), 1.87 (m, 1H, C5-*H*), 2.11 (m, 1H, C5-*H*), 2.34 (m, 1H, C4-*H*), 2.82 (ddd, J = 6.2, 11.3, 17.5 Hz, 1H, C6-*H*), 2.91 (ddd, J = 2.4, 7.0, 17.5 Hz, 1H, C6-*H*), 4.52 (br-s, 1H, N*H*), 4.71 (dt, *J* = 5.1, 11.5, 1H, C3a-*H*), 6.78 (d, *J* = 7.9 Hz, 1H, Ar*H*), 6.95 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.20 (t, *J* = 7.9 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.29 (CH_2), 27.97 (CH_2), 28.06 (CH_2), 53.39 (CH), 114.86 (CH), 119.87 (C), 125.04 (CH), 128.97 (CH), 137.51 (C), 151.80 (C); HRMS (EI) calcd for $C_{10}H_{11}NO_3S$ (M^+) 225.0460, found 225.0461. The enantiomeric excess of **6d** was determined to be 14% by HPLC with a Chiralpak IA column (3:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (major) = 17.2 min; t_R (minor) = 19.0 min. The absolute stereochemistry of **6d** was not determined.

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