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Asymmetric transfer of nitrenes catalyzed by chiral dirhodium(II) using aromatic sulfamate esters

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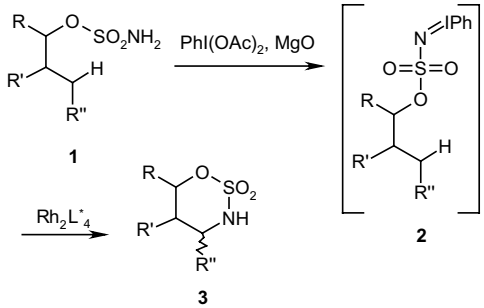
Abstract—Enantioselective intra- and intermolecular insertions of aromatic sulfamate esters into activated C–H bonds have been achieved via in situ generated phenyliodinanes in the presence of $PhI(OAc)_2$, MgO, and chiral Rh(II) catalysts. The optimal results were obtained with $[Rh_2\{(S)\text{-nttl}\}_4]$ and $[Rh_2\{(R)\text{-ntv}\}_4]$ as catalysts with up to 52% ee. In contrast, phenylsulfamates with allylic *ortho*-substituents reacted via intramolecular aziridination rather than insertion. The intermolecular amidation of indane proceeded with up to 97% yield when the reaction was carried out with the sulfamate in excess.

1. Introduction

Insertion into C–H bonds is a reaction characteristic for carbenes and has found numerous applications in asymmetric catalysis.[1] Nitrenes may insert into saturated CH bonds by analogy. Nitrene transfer reactions, usually based on transition metal-catalyzed decomposition of sulfonylimino phenyliodinanes, constitute powerful methodologies for C–N bond formation[2] and, consequently, for the synthesis of amines derivatives. The catalytic nitrene transfer became feasible once the appropriate nitrogen precursors became available. Originally, only sulfonyliminoiodinanes derived from aromatic sulfonamides were available.[3] More recently, through a variety of aliphatic and functionalized sulfonyliminoiodinanes have been synthesized and used for catalyzed nitrene transfer reactions.[4] The Rh(II)-catalyzed intermolecular insertion[5] or aziridination[6] with sulfonyl iminoiodinanes has been investigated in some detail by our group. Intermolecular amidation of C–H bonds was also realized recently by Che and Hashimoto, respectively, using chiral dirhodium catalysts.[7]

A breakthrough occurred recently, when Dauban and Du Bois independently found that iminophenyliodinanes could be generated and catalytically decomposed in situ, so that their isolation became unnecessary. Sulfonamides, carbamates, or sulfamates in conjunction with $PhI(OAc)_2$ could be used directly as nitrene sources in Cu(I)-[8] and Rh(II)-[9,10]catalyzed nitrene transfer. The decomposition of phenyliodonium ylides **2** derived from sulfamates **1** in the presence of catalysts results in the synthesis of cyclic sulfamidates **3**, which are versatile reagents in organic synthesis (Scheme 1).[11] This class of compound is of interest for the synthesis of various products possessing heteroatomic functional groups. They are useful precursors for the preparation of amino-acid derivatives,[12] piperazines or thiomorpholines,[13] amino alcohols,[14] oligosaccharides,[15] glyco-peptides,[16] or indolizidine derivatives.[17]



Scheme 1.

Recently, Che described a one pot process for intramolecular amidation of sulfamates esters, using iodobenzene diacetate/Al_2O_3, catalyzed by chiral ruthenium(II) porphyrins.[18] Sulfamidates were obtained

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in a highly diastereoselective manner, and with enantiomeric excesses in the range of 46–87% with a catalyst load of 10 mol%. Asymmetric nitrene transfer using sulfamates with chiral dirhodium(II) catalysts has not been systematically investigated so far, although these reactions appear to have substantial potential.

2. Results and discussion

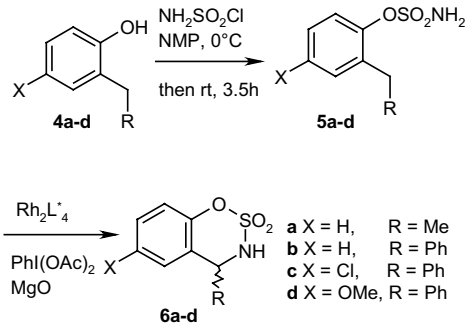
2.1. Intramolecular amidation catalyzed by chiral dirhodium(II) complexes

Following the pioneering work of Du Bois and co-workers,[9,10] we explored the in situ generation and Rh(II)-catalyzed decomposition of imino phenyliodinanes derived from aromatic sulfamates esters. The sulfamate precursors were synthesized from the corresponding phenols using in situ generated sulfamoyl chloride,[19] and obtained with yields in the range of 67–87% (see Experimental). Treatment of the sulfamates **5a–d** with $PhI(OAc)_2$ (1.5 equiv)/MgO (2.5 equiv) in dichloromethane in the presence of $[Rh_2(OAc)_4]$ afforded the cyclic sulfamidates **6a–d** with yields in the range of 24–79%. Insertion into **5a** proceeded with a slightly lower yield than with the benzyl derivatives **5b** and **5c**, but the methoxy compound **5d** afforded only a low yield of 24% of **6d** (Table 1, Scheme 2).

Table 1. Intramolecular nitrene insertion with **5a–d**[a]

Compound	Catalyst	Solvent	*t* (h)	Yield (%)	Ee (%)
5a	$[Rh_2(OAc)_4]$	CH_2Cl_2	6	61	—
5b	$[Rh_2(OAc)_4]$	CH_2Cl_2	2	77	—
5c	$[Rh_2(OAc)_4]$	CH_2Cl_2	2	79	—
5d	$[Rh_2(OAc)_4]$	CH_2Cl_2	3	24	—
5a	$[Rh_2\{(R)\text{-ntv}\}_4]$, 3.5%	CH_2Cl_2	6	75	<5
5a	$[Rh_2\{(R)\text{-ntv}\}_4]$, 2%	CH_2Cl_2	6	62	<5
5a	$[Rh_2\{(R)\text{-ntv}\}_4]$, 0.5%	CH_2Cl_2	6	45	<5
5a	$[Rh_2\{(R)\text{-ntv}\}_4]$	PhCl	21	45	<5
5a	$[Rh_2\{(R)\text{-ntv}\}_4]$	MeCN	6	32	<5
5a	$[Rh_2\{(R)\text{-ntv}\}_4]$	C_5H_{12}	6	38	<5

[a] With 3.5% of catalyst, at 40 °C, unless indicated otherwise.



Scheme 2.

The enantioselective amidation was first examined with sulfamate ester **5a** as the substrate and $[Rh_2\{(R)\text{-ntv}\}_4]$ as catalyst. Reaction of **5a** in the presence of 3.5 mol% of catalyst, afforded cyclic sulfamidate **6a** in 75% yield. With 2.0 and 0.5 mol% of $[Rh_2\{(R)\text{-ntv}\}_4]$, the yield of **6a** dropped to 62% and 45%, respectively. CH_2Cl_2 was superior to PhCl, MeCN, and pentane. In these latter three solvents, the yield of **6a** decreased significantly to 45%, 32%, and 38%, respectively. No significant enantioselectivity was induced by $[Rh_2\{(R)\text{-ntv}\}_4]$ (Table 1).

Several dirhodium(II) catalysts were then examined in the intramolecular amidation, mostly with **5b** and **5c** (Table 2). The rhodium carboxamidates, $[Rh_2\{(5S)\text{-mepy}\}_4]$ or $Rh_2\{4S)\text{-meox}\}_4]$ were less efficient than rhodium carboxylate catalysts for nitrene transfer and longer reaction times were required. In addition, rhodium carboxamidates led to no enantioselectivity. The proline-derived rhodium carboxylate $(Rh_2\{(S)\text{-dosp}\}_4]$ produced a slight induction (around 20% for compounds **6b** and **6c**), while the Hashimoto-type catalyst $[Rh_2\{(S)\text{-ptpa}\}_4]$ was unselective. However, encouraging results were obtained with $[(Rh_2\{(S)\text{-nttl}\}_4]$, a catalyst recently introduced by our group, which uses the 1,8-naphthalimide of L-*tert*-leucine as a bridging ligand.[20] With this catalyst, substrate **5c** was the most effective and afforded ee's of 49% at 40 °C and 52% at −78 °C.

Table 2. Intramolecular amidation catalyzed by Rh(II) complexes[a]

Compound	Catalyst	*T* (°C)	*t* (h)	Yield (%)	Ee (%)
5b	$[Rh_2\{(5S)\text{-mepy}\}_4]$	40	7.5	57	<5
5c	$[Rh_2\{(5S)\text{-mepy}\}_4]$	40	7.5	29	11
5a	$[Rh_2\{(4S)\text{-meox}\}_4]$	40	6	38	<5
5b	$[Rh_2\{(4S)\text{-meox}\}_4]$	40	3.5	70	<5
5a	$[Rh_2\{(S)\text{-ptpa}\}_4]$	40	6	60	<5
5b	$[Rh_2\{(S)\text{-ptpa}\}_4]$	40	2	68	<5
5c	$[Rh_2\{(S)\text{-ptpa}\}_4]$	40	2	80	<5
5a	$[Rh_2\{(S)\text{-nttl}\}_4]$	−78	13	38	32
5b	$[Rh_2\{(S)\text{-nttl}\}_4]$	40	2	82	31
5b	$[Rh_2\{(S)\text{-nttl}\}_4]$	−20	4	77	38
5c	$[Rh_2\{(S)\text{-nttl}\}_4]$	40	2	90	49
5c	$[Rh_2\{(S)\text{-nttl}\}_4]$	40	2	84[b]	42
5c	$[Rh_2\{(S)\text{-nttl}\}_4]$	−78	8	68	52
5b	$[Rh_2\{(R)\text{-ntv}\}_4]$	40	2	77	13
5c	$[Rh_2\{(R)\text{-ntv}\}_4]$	40	2	76	28
5b	$[Rh_2\{(S)\text{-dosp}\}_4]$	40	2	74	20
5c	$[Rh_2\{(S)\text{-dosp}\}_4]$	40	2	78	18

[a] Standard conditions, 3.5 mol% of catalyst; see Experimental.
[b] Reaction performed with 2% of catalyst.

The positive results with $[(Rh_2\{(S)\text{-nttl}\}_4]$ contrast markedly from those obtained with $[Rh_2\{(R)\text{-ntv}\}_4]$, which uses the 1,8-naphthalimide of D-valine as the ligand. These catalysts, which differ only by an additional methyl group adjacent to the stereogenic center, produce enantiomeric products with practically the same degree of enantioselectivity in intermolecular carbene transfer reactions.[21] Replacement of the *para*-chloro substituent of **5c** by H, that is **5b**, resulted in a decrease in selectivity from 49–31% (at 40 °C) (Chart 1).

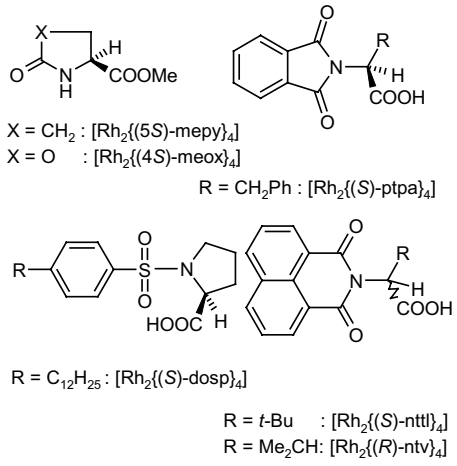


Chart 1. Ligands and abbreviations of Rh(II) catalysts.

2.2. Intramolecular aziridination catalyzed by chiral dirhodium complexes

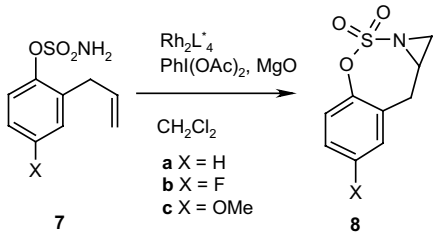
The 2-allyl substituted sulfamates **7a**–**c** failed to undergo insertion, but reacted exclusively via intramolecular aziridination instead. The same chiral Rh(II) catalysts were screened for the aziridination under standard conditions. Chiral Rh(II) catalysts were screened under standard condition with aromatic sulfamate esters **7a**–**c** as substrates (Table 3, Scheme 3).

Table 3. Enantioselective intramolecular aziridination by dirhodium(II) complexes[a]

Compound	Catalyst	*t* (h)	Yield (%)	Ee (%)
7a	$[Rh_2(OAc)_4]$[b]	1.5	62	—
7b	$[Rh_2(OAc)_4]$[b]	2	60	—
7c	$[Rh_2(OAc)_4]$[b]	3	58	—
7a	$[Rh_2\{(5S)\text{-mepy}\}_4]$	5.5	32	50
7a	$[Rh_2\{(5S)\text{-mepy}\}_4]$[c]	9.5	10	52
7b	$[Rh_2\{(5S)\text{-mepy}\}_4]$	4	63	17
7c	$[Rh_2\{(5S)\text{-mepy}\}_4]$	7	18	39
7a	$[Rh_2\{(4S)\text{-meox}\}_4]$	5.5	55	18
7b	$[Rh_2\{(4S)\text{-meox}\}_4]$	4	51	21
7c	$[Rh_2\{(4S)\text{-meox}\}_4]$	7	23	24
7a	$[Rh_2\{(S)\text{-ptpa}\}_4]$	2	79	30
7b	$[Rh_2\{(S)\text{-ptpa}\}_4]$	1.5	70	19
7c	$[Rh_2\{(S)\text{-ptpa}\}_4]$	3	53	27
7a	$[Rh_2\{(S)\text{-nttl}\}_4]$	1.5	68	19
7b	$[Rh_2\{(S)\text{-nttl}\}_4]$	1.5	72	15
7c	$[Rh_2\{(S)\text{-nttl}\}_4]$	3	36	22
7a	$[Rh_2\{(R)\text{-ntv}\}_4]$	2	63	15
7b	$[Rh_2\{(R)\text{-ntv}\}_4]$	1.5	75	7
7c	$[Rh_2\{(R)\text{-ntv}\}_4]$	3	64	15
7b	$[Rh_2\{(S)\text{-dosp}\}_4]$	1.5	80	<5

[a] Reactions carried out in CH_2Cl_2 with 3.5 mol% of catalyst (see Experimental part).
[b] 5% of catalyst.
[c] −20 °C.

Although rhodium carboxylates were efficient for aziridination, the catalysts showed only modest enantioselectivities. Hashimoto's tetrakis[*N*-phthaloyl-(*S*)-phenylalaninate], $[Rh_2\{(S)\text{-ptpa}\}_4]$, gave the optimal



Scheme 3.

result with 30% ee. Surprisingly, the dirhodium carboxamidates, such as $[Rh_2\{(4S)\text{-meox}\}_4]$ or $[Rh_2\{(5S)\text{-mepy}\}_4]$ resulted in the highest enantioselectivities, although the yields of the aziridines were slightly lower than with carboxylate catalysts. This result is consistent with those reported by Che, who found enantioselectivities of up to 49% and 76% using, respectively, $[Rh_2\{(5S)\text{-mepy}\}_4]$[7a] and $[Rh_2\{(4S)\text{-meox}\}_4]$[7c] as catalysts in intramolecular aziridinations using *N*-arylsulfonyliminoiodinane $PhINSO_2Ar$ as the nitrene precursor. The *para*-methoxy derivative **7c** afforded higher enantioselectivity than the *para*-fluoro derivative **7b**, but afforded a lower yield of aziridine **8**.

2.3. Intermolecular amidation

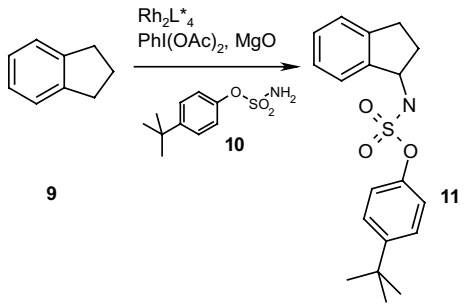
While intermolecular catalytic aziridination of olefins with sulfonamide precursors is well known, the analogous intermolecular nitrene insertions with sulfamate precursors have not yet been reported.[22] We have carried out some exploratory reactions with indane **9** as substrate and **10** in the presence of $[Rh_2(OAc)_4]$ in different solvents and with changing the indane/sulfamate ratio (Table 4). When the reagents were used in a 1:1 ratio, the reaction proceeded with 46% yield in CH_2Cl_2 (Scheme 4).

Table 4. Optimization of intermolecular amidation of indane **9**[a]

Entry	**9/10**	Solvent	*t* (h)	Yield (%)[b]
1	1/1	CH_2Cl_2	6.5	46
2	1/1	CH_2Cl_2/5% sulfolane	10	54
3	1/1	Pentane	10	—
4	1/1	CH_3 CN	8.5	12
5	1/1	$PhCH_3$	8.5	12
6	1/1	$PhCF_3$	8.5	13
7	5/1	CH_2Cl_2	6.5	70
8	10/1	CH_2Cl_2	6.5	68
9	1/2	CH_2Cl_2	9.5	75
10	1/1.5	CH_2Cl_2	8	56
11	1/1.2	CH_2Cl_2	8	46
12	1/1.2	CH_2Cl_2/5% sulfolane	8	52

[a] Conditions: at 40 °C, with 5 mol% of $[Rh_2(OAc)_4]$.
[b] Yield calculated with respect to limiting reagent.

Addition of 5% of sulfolane resulted in an increase to 54%. Other solvents, such as pentane and toluene were inappropriate. The yield of insertion product **11** increased to 70% and 68%, respectively, with a five- or tenfold excess of indane. Interestingly, the yield of **11** increased to 75% when reagent **10** was used in twofold



Scheme 4.

excess over **9**. This observation is of interest in view of synthetic applications of the reaction, and contrasts with that made in Rh(II)-catalyzed CH insertions with phenyliodinanes derived from aromatic sulfonamides, where an excess of reagent does not lead to higher yields.[5]

So far, the enantioselectivities reached in these reactions are modest and do not exceed 30% (Table 5). On the other hand, the yields of isolated insertion product **11** are encouraging.

Table 5. Enantioselective amidation of indane with sulfamate **10** catalyzed by dirhodium(II) complexes[a]

Entry	$Rh_2L^*_4$	t (h)	Yield (%)	Ee (%)
1	$[Rh_2\{(S)\text{-ptpa}\}_4]$	9.5	79[b]	18
2	$[Rh_2\{(S)\text{-nttl}\}_4]$	9.5	82[b]	27
3	$[Rh_2\{(S)\text{-ptpa}\}_4]$	9.5	97	30

[a] In refluxing CH_2Cl_2 with twofold excess of **10** and 2.5 mol% of catalyst.
[b] With 5% of sulfolane as co-solvent.

3. Conclusion

In summary, we have reported the first intra- and intermolecular amidation reaction using aromatic sulfamate ester and chiral rhodium catalyst. We have demonstrated that $[Rh_2\{(S)\text{-nttl}\}_4]$ developed in our group is the most effective catalyst for enantioselective amidation of C–H bonds (ee up to 52%). Selective intramolecular aziridination of a 2-allyl arylsulfamate **7** has been achieved using chiral dirhodium complexes without observing competitive C–H bond insertion. These aziridinations proceeded with up to 52% ee with carboxamidate ligands such as $[Rh_2(S\text{-mepy})_4]$. Finally, the intermolecular CH insertion of indane with an aryl sulfamate in twofold excess has been realized in high yield, albeit with modest enantioselectivity with Rh(II)-carboxylate catalysts.

4. Experimental part

4.1. General[23]

All reactions were carried out under an inert atmosphere (argon). CH_2Cl_2, MeCN, toluene, and chlorobenzene were dried over CaH_2 and distilled. The other solvents were purchased from Fluka or Acros and used without purification. Flash chromatography (FC): silica gel 32-63 60 Å Merck 9385. TLC: Macherey-Nagel Polygram Sil/UV_{254}; detection by UV light. The enantiomeric excess of the products was determined by GC (β-Dex columns) or by HPLC (chiracel OD-H or AD-H); t_R in minutes. IR spectra: Mattson instruments Polaris FT-IR instrument, NaCl cells, in cm^{-1}; NMR spectra: Bruker AMX-300, chemical shifts δ in ppm with respect to $SiMe_4$ ($=0$ ppm), coupling constants in Hz. MS: Varian CH4 or SM1 spectrometer with electron impact or electrospray; m/z (rel %). High resolution (HR) MS: VG-7070 analytical spectrometer (data system 11 250, resolution 7000).

4.2. Preparation of aryl sulfamate esters. Typical procedure

A 100 mL two necked round bottom flask fitted with a reflux condenser, dropping funnel, and under argon atmosphere, was charged with chlorosulfonyl isocyanate (3.5 mL, 40 mmol, 2.0 equiv) at 0 °C. Anhydrous formic acid (1.5 mL, 40 mmol, 2.0 equiv) was added dropwise with rapid stirring. The mixture was stirred at room temperature until gas evolution ceased (from 1 to 4 h). To the resulting sulfamoyl chloride was added a solution of alcohol (20 mmol) in 30 mL of 1-methyl-2-pyrrolidone under ice-cooling over 30 min dropwise. The reaction mixture was stirred at room temperature for 3 h (yellow-orange solution). The resulting mixture was poured into cold brine (100 mL) and washed twice with ethyl acetate (150 mL). The combined organic extracts were dried over magnesium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel using pentane/ethyl acetate as eluent afforded the desired sulfamate ester.

4.2.1. 2-Ethylphenylsulfamate 5a. Prepared from 2-ethylphenol **4a** (2.37 mL) according to the general method and purified by flash chromatography on silica gel (pentane/EtOAc, 3:1). Colorless solid (3.50 g, 87%): mp 67 °C; TLC $R_f = 0.50$. IR (neat): 3267, 2969, 1647, 1371, 1186, 1157, 1108, 864, 777 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 1.27 (t, 3H, $J = 7.5$ Hz), 2.80 (q, 2H, $J = 7.5$ Hz), 5.36 (br, 2H), 7.23–7.38 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 14.2 (CH_3), 23.0 (CH_2), 121.7 (CH), 127.1 (CH), 127.4 (CH), 130.1 (CH), 137.1 (C), 148.3 (C). HR MS: 201.04724 ($C_8H_{11}NO_3S^+$; calcd 201.04597).

4.2.2. 2-Benzylphenylsulfamate 5b. Prepared from 2-hydroxydiphenylmethane **4b** (3.68 g) according to the general method and purified by flash chromatography on silica gel (pentane/EtOAc, 3:1). Colorless solid (3.67 g, 70%). Mp 110 °C; TLC $R_f = 0.50$. IR (neat): 3391, 3278, 1450, 1348, 1157, 1090, 931, 886, 862, 776 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 4.11 (s, 2H), 4.34 (br, 2H), 7.26–7.37 (m, 8H), 7.51 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 36.6 (CH_2), 121.6 (CH), 126.6 (CH), 127.2 (CH), 128.1 (CH), 128.7 (CH), 129.2 (CH),

131.7 (CH), 133.8 (C), 140.2 (C), 148.9 (C). HR MS: 263.06212 ($C_{13}H_{13}NO_3S^+$; calcd 263.06162).

4.2.3. 2-Benzyl-4-chlorophenylsulfamate 5c. Prepared from 2-benzyl-4-chlorophenol (5.66 g) according to the general method and purified by flash chromatography on silica gel (pentane/EtOAc, 3:1). Colorless solid (4.16 g, 70%). Mp 77 °C; TLC $R_f = 0.44$. IR (neat): 3396, 3283, 3029, 1738, 1494, 1475, 1374, 1193, 1155, 1105, 911, 828, 740, 699 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 4.06 (s, 2H), 5.09 (br, 2H), 7.21–7.41 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz): 36.1 (CH_2), 123.1 (CH), 126.8 (CH), 127.9 (CH), 128.8 (CH), 129.2 (CH), 131.3 (CH), 132.6 (C), 136.1 (C), 139.1 (C), 141.1 (C). HR MS: 297.02264 ($C_{13}H_{12}ClNO_3S^+$; calcd 297.02272).

4.2.4. 2-Benzyl-4-methoxyphenyl sulfamate 5d. *2-Benzyl-4-methoxyphenol* **4d**.[24] 4-Methoxy-phenol (12.41 g, 100 mmol) was added gradually to a stirred suspension of sodium hydride (60%, 4.0 g, 100 mmol) in toluene (150 mL) under nitrogen. To the resulting suspension, stirred and maintained at gentle reflux, was added benzyl chloride (12.6 mL, 110 mmol) dropwise. After 5 h of vigorous refluxing, the reaction mixture was cooled and hydrolyzed with dilute hydrochloric acid. The aqueous layer was separated and the toluene washed with water and then sodium hydrogen carbonate. The toluene solution was then extracted several times with aq sodium hydroxide. The basic extracts were acidified with hydrochloric acid and the liberated phenolic material taken up in ether. Concentration under reduced pressure gave 2-benzyl-4-methoxy-phenol (9.77 g, 45%) as a pale brown solid, mp 104 °C. IR (neat): 3309, 3029, 2959, 2830, 1599, 1505, 1435, 1209, 1035, 798, 723, 693 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 3.82 (s, 3H), 4.07 (s, 2H), 5.43 (br, 1H), 6.76–6.87 (m, 3H), 7.30–7.39 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): 36.5 (CH_2), 55.9 (OCH_3), 112.6 (CH), 115.1 (CH), 116.3 (CH), 116.5 (CH), 116.8 (CH), 126.4 (CH), 128.7 (CH), 128.7 (C), 128.9 (CH), 140.1 (C), 147.9 (C), 153.6 (C). HR MS: 214.10013 ($C_{14}H_{14}O_2^+$; calcd 214.09938).

2-Benzyl-4-methoxyphenyl sulfamate **5d**. Prepared from 2-benzyl-4-methoxyphenol **4d** (4.28 g) according to the general method and purified by flash chromatography on silica gel (pentane/EtOAc, 2:1), was obtained as a pale yellow solid (3.86 g, 66%), mp 67 °C; TLC $R_f = 0.55$. IR (neat): 3390, 3277, 2932, 1736, 1594, 1489, 1349, 1164, 1932, 922, 844, 707 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 3.74 (s, 3H), 4.11 (s, 2H), 5.23 (br, 2H), 6.76 (m, 2H), 7.28–7.40 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): 36.4 (CH_2), 55.6 (OCH_3), 112.4 (CH), 116.9 (CH), 122.9 (CH), 126.6 (CH), 128.7 (CH), 129.3 (CH), 135.7 (C), 139.8 (C), 142.3 (C), 158.1 (C). HR MS: 293.06938 ($C_{14}H_{15}NO_4S^+$; calcd 293.07218).

4.2.5. 2-Allylphenylsulfamate 7a. Prepared from 2-allylphenol[25] (1.81 g, 13.5 mmol) according to the general method (chlorosulfonyl isocyanate (2.4 mL, 27 mmol, 2.0 equiv) and formic acid (1.0 mL, 27 mmol, 2.0 equiv)) and purified by flash chromatography on silica gel (pentane/EtOAc, 3:1) and was obtained as a beige solid (2.24 g, 78%), mp 64 °C; TLC $R_f = 0.50$. IR (neat): 3013, 2921, 1739, 1435, 1366, 1217 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 3.53 (d, 2H, $J = 6.4$ Hz), 5.11 (m, 1H), 5.17 (m, 1H), 5.28 (br, 2H), 5.92–6.06 (m, 1H), 7.28 (m, 3H), 7.43 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 34.2 (CH_2), 116.8 (CH_2), 121.9 (CH), 127.3 (CH), 127.8 (CH), 131.1 (CH), 133.0 (C), 136.2 (CH), 148.4 (C). MS (EI): 213 (M^+, 39), 133 (100), 105 (87), 77 (51), 51 (25). HR MS 213.04466 ($C_9H_{11}NO_3S^+$; calcd 213.04597).

4.2.6. 2-Allyl-4-fluorophenylsulfamate 7b. Prepared from 2-allyl-4-fluorophenol[26] (3.04 g) according to the general method and purified by flash chromatography on silica gel (pentane/EtOAc, 3:1), was obtained as a cream solid (3.49 g, 75%), mp 78 °C; TLC $R_f = 0.60$. IR (neat): 3013, 2970, 1739, 1438, 1366, 1217 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 3.50 (d, 2H, $J = 6.6$ Hz), 5.13–5.20 (m, 2H), 5.35 (br, 2H), 5.87–6.01 (m, 1H), 6.92–7.03 (m, 2H), 7.38 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 34.1 (CH_2), 114.2 (CH), 114.5 (CH), 117.3 (CH), 117.5 (CH_2), 123.4 (CH), 123.5 (CH), 135.1 (CH), 135.6 (C), 144.1 (C), 158.3 (C). ^{19}F NMR ($CDCl_3$, 282 MHz): −114.2 ($CFCl_3$). MS: 231 (M^+, 100), 151 (100), 123 (75), 103 (78), 77 (39), 51 (18). HR MS: 231.03448 ($C_9H_{10}FNO_3S^+$; calcd 231.03654).

4.2.7. 2-Allyl-4-methoxyphenylsulfamate 7c. Prepared from 2-allyl-4-methoxyphenol[27] (1.39 g, 8.5 mmol) according to the general method (chlorosulfonyl isocyanate (1.5 mL, 17 mmol, 2.0 equiv) and formic acid (0.64 mL, 17 mmol, 2.0 equiv)) and purified by flash chromatography on silica gel (pentane/EtOAc, 2.5:1) and was obtained as a pale yellow oil (1.54 g, 75%); TLC $R_f = 0.54$. IR (neat): 3380. 3277, 2938, 1744, 1491, 1370, 1190, 1161, 1029, 911, 841, 728 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 3.48 (d, 2H, $J = 6.4$ Hz), 3.80 (s, 3H), 5.13 (m, 1H), 5.16 (m, 1H), 5.34 (br, 2H), 5.91–6.01 (m, 1H), 7.76 (m, 1H), 6.80 (m, 1H), 7.30 (d, 1H, $J = 8.7$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): 34.3 (CH_2), 55.6 (OCH_3), 112.5 (CH), 115.9 (CH), 116.9 (CH_2), 123.0 (CH), 134.5 (C), 135.9 (CH), 142.0 (C), 158.1 (C). HR MS: 243.05780 ($C_{10}H_{13}NO_4S^+$; calcd 243.05653).

4.2.8. 4-*tert*-Butylphenylsulfamate 10. Prepared from 4-*tert*-butylphenol (3.00 g) according to the general method and purified by flash chromatography on silica gel (pentane/EtOAc, 3:1) and was obtained as colorless solid (4.24 g, 92%), mp 108 °C; TLC $R_f = 0.60$. IR (neat): 2972, 1740, 1360, 1229, 1215 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 1.34 (s, 9H), 5.21 (br, 2H), 7.27 (d, 2H, $J = 8.8$ Hz), 7.44 (d, 2H, $J = 8.8$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): 31.4 (CH_3), 34.3 (C), 121.5 (CH), 126.8 (CH), 147.7 (C), 150.5 (C). HR MS: 229.07872 ($C_{10}H_{15}NO_3S^+$; calcd 229.07727).

4.3. General procedure for the intramolecular amidation and aziridination catalyzed by dirhodium(II) complexes

Dichloromethane (3.0–5.0 mL) was added through syringe into a flask containing sulfamate ester (0.3–0.5 mmol), $PhI(OAc)_2$ (1.5 equiv), MgO (2.5 equiv), activated 4 Å molecular sieves, and rhodium catalyst (0.5–5 mol %) under an argon atmosphere. The resulting suspension was stirred vigorously at reflux until complete consumption of starting material was indicated by

thin layer chromatography. The mixture was diluted with dichloromethane (5.0 mL) and filtered through a pad of Celite. The filter cake was washed with dichloromethane and the filtrate concentrated under reduced pressure. The residue was purified by chromatography on silica gel using pentane/ethyl acetate as eluant to afford the desired cyclic compound.

4.3.1. 4-Methyl-3,4-dihydro-benzo[*e*][1,2,3]oxathiazane-2,2-dioxyde 6a. Flash chromatography on silica gel (pentane/EtOAc, 2:1) afforded a yellow oil (61%). TLC $R_f = 0.60$. IR (neat): 3266, 2987, 1738, 1484, 1423, 1364, 1201, 1167, 1115, 864, 798, 753 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 1.74 (d, 3H, $J = 6.8$ Hz), 4.76 (d, 1H, $J = 9.2$ Hz), 4.87–4.97 (m, 1H, $J = 6.8$ Hz, $J = 9.2$ Hz), 7.00 (d, 1H, $J = 8.1$ Hz), 7.24 (m, 2H), 7.32 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 20.1 (CH_3), 53.0 (CH), 118.7 (CH), 123.6 (C), 125.4 (CH), 126.3 (CH), 129.5 (CH), 151.0 (C). HR MS: 199.03249 ($C_8H_9NO_3S^+$; calcd 199.03032). Enantiomer separation: GC (γ-dex, 170 °C): $\tau_1 = 51.2$ min, $\tau_2 = 55.2$ min.

4.3.2. 4-Phenyl-3,4-dihydro-benzo[*e*][1,2,3]oxathiazane-2,2-dioxyde 6b. Flash chromatography on silica gel (pentane/EtOAc, 3:1) afforded a yellow solid (77%), mp 132 °C. TLC $R_f = 0.70$. IR (neat): 3285, 2924, 2352, 1737, 1480, 1449, 1402, 1361, 1194, 1162, 1098, 1021, 885, 839, 763, 753 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 4.93 (d, 1H, $J = 8.6$ Hz), 5.93 (d, 1H, $J = 8.6$ Hz), 6.86 (d, 1H, $J = 8.1$ Hz), 7.07–7.15 (m, 2H), 7.38 (m, 3H), 7.47 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): 62.0 (CH), 118.8 (CH), 122.1 (C), 125.3 (CH), 128.6 (CH), 128.9 (CH), 129.5 (CH), 129.6 (CH), 129.7 (CH), 137.9 (C), 151.5 (C). HR MS: 261.04541 ($C_{13}H_{11}NO_3S^+$; calcd 261.04597). Enantiomer separation: HPLC (OD-H, 23 °C, hexane/*i*-PrOH 90/10, 0.5 mL min^{-1}), $\tau_1 = 29.5$ min, $\tau_2 = 46.3$ min.

4.3.3. 6-Chloro-4-phenyl-3,4-dihydro-benzo[*e*][1,2,3]oxathiazane-2,2-dioxyde 6c. Flash chromatography on silica gel (pentane/EtOAc, 4:1) afforded a beige solid (90%), mp 159 °C. TLC $R_f = 0.38$. ^1H NMR ($CDCl_3$, 300 MHz): 5.11 (d, 1H, $J = 8.6$ Hz), 5.87 (d, 1H, $J = 8.6$ Hz), 6.83 (d, 1H, $J = 8.1$ Hz), 7.03 (d, 1H, $J = 8.9$ Hz), 7.30–7.39 (m, 3H), 7.49 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): 61.8 (CH), 120.3 (CH), 123.8 (C), 128.3 (CH), 128.8 (CH), 129.6 (CH), 129.9 (CH), 130.5 (C), 137.0 (C), 150.0 (C). MS: 295 (46), 215 (100), 181 (13), 152 (15), 104 (16), 77 (33), 51 (24). HR MS: 295.00507 ($C_{13}H_{10}ClNO_3S^+$; calcd 295.00699). Enantiomer separation: HPLC (AD-H, 23 °C, hexane/*i*-PrOH 90/10, 0.2 mL min^{-1}): $\tau_1 = 62.6$ min, $\tau_2 = 72.8$ min.

4.3.4. 6-Methoxy-4-phenyl-3,4-dihydro-benzo[*e*][1,2,3]oxathiazane-2,2-dioxyde 6d. Flash chromatography on silica gel (pentane/EtOAc, 4:1) afforded an orange oil (24%). TLC $R_f = 0.25$. IR (neat): 3283, 2927, 1739, 1491, 1427, 1365, 1196, 1166, 1029, 844 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 3.68 (s, 3H), 4.77 (d, 1H, $J = 8.5$ Hz), 5.89 (d, 1H, $J = 8.5$ Hz), 6.33 (d, 1H), 6.89 (dd, 1H), 7.05 (d, 1H, $J = 8.9$ Hz), 7.38 (m, 2H), 7.46 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): 55.7 (OCH_3), 62.1 (CH), 113.3 (CH), 115.2 (C), 119.8 (CH), 122.8 (CH), 128.8 (CH), 129.5 (CH), 129.6 (CH), 137.8 (C), 145.4 (C), 156.5 (C). HR MS: 291.05707 ($C_{14}H_{13}NO_4S^+$; calcd 291.05653).

4.3.5. 1a,2-Dihydro-1*H*-7-oxa-8-thia-8a-aza-benzo[*a*]cyclopropa[*d*]cycloheptene-8,8-dioxide 8a. Flash chromatography on silica gel (pentane/EtOAc, 3:1) afforded an orange oil, which was recrystallized from hexane to give a white solid (62%), mp 84 °C; TLC $R_f = 0.24$. IR (neat): 3536, 3288, 2932, 1731, 1368, 1182, 1153, 1096, 868, 779 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 2.46 (d, 1H, $J = 4.3$ Hz), 2.64 (d, 1H, $J = 4.3$ Hz), 3.31–3.41 (m, 2H), 3.95 (dd, 1H, $J = 13$ Hz), 7.24–7.38 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 30.6 (CH_2), 35.1 (NCH_2), 44.2 (CH), 122.4 (CH), 126.9 (C), 127.9 (CH), 129.8 (CH), 131.0 (CH), 148.5 (C). MS: 211 (10), 130 (25), 118 (100), 91 (86), 78 (23), 65 (19), 51 (25). HR MS: 211.02989 ($C_9H_9NO_3S^+$; calcd 211.03032). Enantiomer separation: HPLC (OD-H, hexane/*i*-PrOH 90/10, 0.5 mL min^{-1}): $\tau_1 = 28.7$ min, $\tau_2 = 32.4$ min.

4.3.6. 4-Fluoro-1a,2-dihydro-1*H*-7-oxa-8-thia-8a-aza-benzo[*a*]cyclopropa[*d*]cycloheptene-8,8-dioxide 8b. Flash chromatography on silica gel (pentane/EtOAc, 3:1), afforded **8b** as a pale yellow solid (60%), mp 93 °C; TLC $R_f = 0.23$. IR (neat): 3283, 2964, 1728, 1486, 1368, 1260, 1153, 830, 771 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 2.49 (d, 1H, $J = 4.5$ Hz), 2.67 (d, 1H, $J = 4.5$ Hz,), 3.28–3.35 (dd, 1H, $J = 5.3$ Hz, $J = 15$ Hz), 3.40 (m, 1H), 3.89–3.95 (dd, 1H, $J = 2.8$ Hz, $J = 15$ Hz), 6.95 (dd, 1H, $J = 2.8$ Hz, $J = 8.1$ Hz), 7.03–7.10 (td, 1H), 7.23–7.30 (dd, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 30.5 (CH_2), 35.1 (NCH_2), 44.0 (CH), 116.5 (CH), 117.6 (CH), 124.1 (CH), 129.1 (C), 144.5 (C), 162.7 (C–F). ^{19}F NMR ($CDCl_3$, 282 MHz): −113.2 ($CFCl_3$). MS (EI): 229 (19), 149 (46), 136 (100), 109 (71), 96 (21), 84 (48), 70 (13), 49 (77). HR MS: 229.02007 ($C_9H_8FNO_3S^+$; calcd 229.02089). Enantiomer separation: HPLC (OD-H, hexane/*i*-PrOH 90/10, 0.5 mL min^{-1}): $\tau_1 = 33.2$ min, $\tau_2 = 38.6$ min.

4.3.7. 4-Methoxy-1a,2-Dihydro-1*H*-7-oxa-8-thia-8a-aza-benzo[*a*]cyclopropa [*d*]cyclo-heptene-8,8-dioxide 8c. Flash chromatography on silica gel (pentane/EtOAc, 3:1), afforded **8c** (58%) as a pale yellow solid, mp 119 °C; TLC $R_f = 0.20$. IR (neat): 3013, 2921, 1739, 1596, 1491, 1360, 1161, 1024, 836, 779 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 2.44 (d, 1H, $J = 4.5$ Hz), 2.61 (d, 1H, $J = 4.5$ Hz), 3.21–3.28 (dd, 1H, $J = 4.9$ Hz, $J = 15.5$ Hz), 3.40 (m, 1H), 3.83 (s, 3H), 3.90–3.96 (dd, 1H, $J = 3.0$ Hz, $J = 15.5$ Hz), 6.72 (dd, 1H, $J = 3.0$ Hz, $J = 8.1$ Hz), 6.85 (dd, 1H, $J = 3.0$ Hz, $J = 8.9$ Hz), 7.19 (d, 1H, $J = 8.9$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): 30.5 (CH_2), 34.8 (NCH_2), 44.6 (CH), 55.7 (OCH_3), 114.0 (CH), 116.2 (CH), 123.3 (CH), 128.2 (C), 141.9 (C), 158.7 (C). MS: 241 (57), 206 (5), 161 (63), 148 (100), 133 (61), 121 (34), 105 (19), 91 (49), 77 (44). HR MS:

241.03969 ($C_{10}H_{11}NO_4S^+$; calcd 241.04088). Enantiomer separation: HPLC (OD-H, hexane/*i*-PrOH: 90/10, 0.5 mL min^{-1}). $\tau_1 = 46.1$ min, $\tau_2 = 50.4$ min.

4.4. Intermolecular amidation of indane 9. Indan-1-yl-sulfamic acid 4-*tert*-butyl-phenyl ester (11). General procedure

Dichloromethane (5.0 mL) was added through syringe into a flask containing sulfamate ester **10** (0.229 g, 1 mmol, 2 equiv), freshly distilled indane **9** (0.06 mL, 0.5 mmol), $PhI(OAc)_2$ (0.482 g, 1.5 mmol, 3 equiv), MgO (0.100 g, 2.5 mmol, 5 equiv), activated 4 Å molecular sieves, and rhodium catalyst (5 mol%) under argon atmosphere at room temperature. The resulting suspension was stirred vigorously at reflux until complete consumption of starting material was indicated by thin layer chromatography. The mixture was diluted with dichloromethane (5 mL) and filtered through a pad of Celite. The filter cake was washed with dichloromethane and the filtrate concentrated under reduced pressure. The residue was purified by chromatography on silica gel using pentane/AcOEt 6:1 as eluent to afford the sulfamidate **11** as a yellow solid, mp 84 °C; TLC $R_f = 0.70$. IR (neat): 3250, 2959, 1715, 1502, 1354, 1204, 1182, 1150, 1061, 862, 846, 760, 750 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.38 (s, 9H, CH_3), 2.01–2.13 (m, 1H), 2.61–2.72 (m, 1H), 2.84–2.94 (m, 1H), 3.00–3.10 (m, 1H), 4.96 (d, 1H, $J = 8.3$ Hz, NH), 5.12 (m, 1H), 7.29 (m, 6H), 7.45 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): 30.0 (CH_2), 31.4 (CH_3), 34.4 (CH_2), 34.6 (C), 60.1 (CH), 121.3 (CH), 124.5 (CH), 125.0 (CH), 126.7 (CH), 127.0 (CH), 128.7 (CH), 141.3 (C), 143.2 (C), 148.0 (C), 150.0 (C). MS: 345 (12), 150 (85), 135 (89), 117 (100), 91 (25), 77 (13); HR MS: 344.14221 ($C_{19}H_{23}NO_3S^+$; calcd 344.13987). Enantiomer separation: HPLC (OD-H, hexane/*i*-PrOH 90/10, 0.5 mL min^{-1}): $\tau_1 = 13.9$ min, $\tau_2 = 15.7$ min.

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