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CATALYTIC ENANTIOSELECTIVE AZIRIDINATION OF ALKENES

USING CHIRAL DIRHODIUM(II) CARBOXYLATES[†]

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Abstract – The enantioselective aziridination of alkenes with [*N*-(4-nitrophenylsulfonyl)imino]phenyliodinane catalyzed by dirhodium(II) tetrakis[*N*-tetrachlorophthaloyl-(*S*)-*tert*-leucinate], Rh₂(*S*-TCPTTL)₄, is described. While such enantioselectivities are highly dependent on the properties of the alkenes, 2,2-dimethylchromene was found to be a particularly suitable substrate which can be efficiently transformed into the aziridine product in 98% yield with 94% ee.

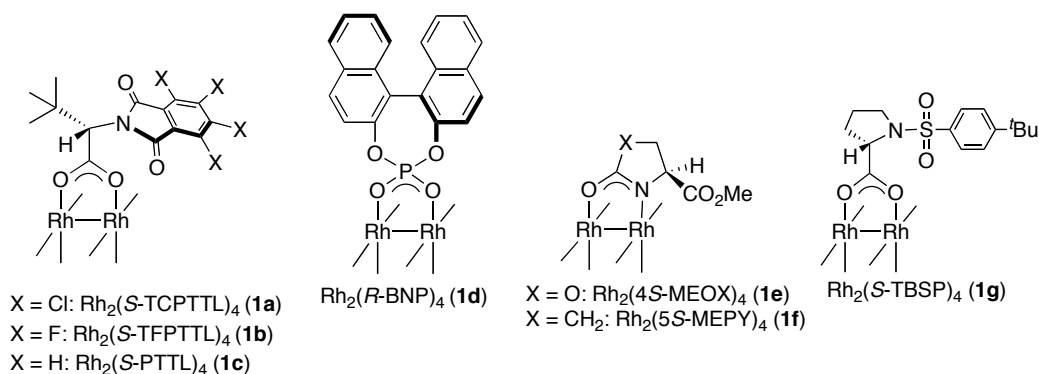
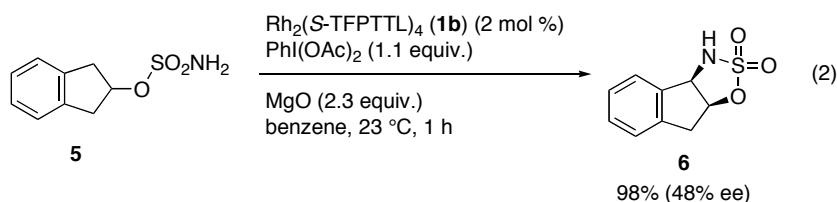
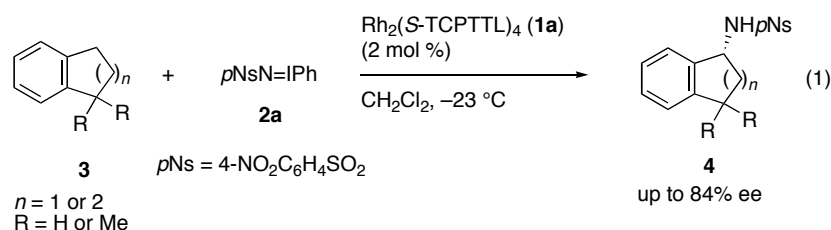
The enantioselective nitrene transfer reaction from [*N*-(arylsulfonyl)imino]phenyliodines to alkenes catalyzed by chiral transition metal complexes represents one of the most direct and powerful methods for the construction of optically active aziridines which are versatile building blocks for the synthesis of biologically important, nitrogen-containing molecules.¹ Over the past fifteen years, substantial progress has been made in the development of enantioselective variants through catalysis by copper,²⁻⁴ manganese,^{5,6} and ruthenium⁷ complexes of well-designed chiral ligands, in which excellent levels of enantioselectivity have been achieved with a limited range of alkenes.⁸

While the first use of Rh₂(OAc)₄ as a nitrene transfer catalyst was demonstrated by Breslow and Gellman in 1983,⁹ Evans and co-workers in the early 1990s reported that Cu(I) and Cu(II) triflate and perchlorate salts were far superior to Rh₂(OAc)₄ in aziridination reactions using [*N*-(4-methylphenylsulfonyl)imino]phenyliodinane.¹⁰ Thus, the application of chiral dirhodium(II) complexes to enantioselective aziridination has been less investigated. In 1996, Müller and co-workers demonstrated the first example of the dirhodium(II)-catalyzed enantioselective aziridination of styrene and *cis*- β -methylstyrene (up to 73% ee) by exploiting [*N*-(4-nitrophenylsulfonyl)imino]phenyliodinane

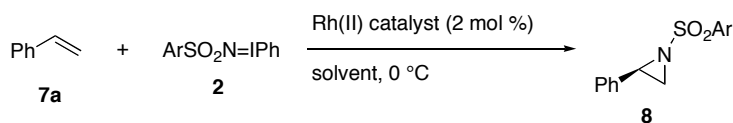
[†] Dedicated to Professor Yoshito Kishi on the occasion of his 70th birthday.

(**2a**) as a nitrene precursor and dirhodium(II) binaphtholphosphate complex $\text{Rh}_2(R\text{-BNP})_4$ (**1d**) as a chiral catalyst.¹¹ Thereafter, the Che, Müller, and Hayes groups independently reported enantioselective intramolecular aziridinations of sulfonamides, sulfamate esters, and carbamates via *in situ* generated iminoiodinanes in the presence of chiral dirhodium(II) carboxamidate catalysts, $\text{Rh}_2(4S\text{-MEOX})_4$ (**1e**) and $\text{Rh}_2(5S\text{-MEPY})_4$ (**1f**), and dirhodium(II) prolinates catalyst $\text{Rh}_2(S\text{-TBSP})_4$ (**1g**), in which cyclic sulfonamides,^{12a,b} cyclic sulfamidates,^{12c} and oxazolidinones^{12d} were obtained in up to 76%, 52%, and 23% ee, respectively.

We recently demonstrated that the enantioselective benzylic C–H amidation of aromatic hydrocarbons with [*N*-(4-nitrophenylsulfonyl)imino]phenyliodinane (**2a**) catalyzed by chiral dirhodium(II) carboxylates provides sulfonamides in up to 84% ee [eqn. (1)].¹³ In this process, $\text{Rh}_2(S\text{-TCPTTL})_4$ (**1a**), characterized by the substitution of chlorine atoms for four hydrogen atoms on the phthalimido group in the parent dirhodium(II) complex, $\text{Rh}_2(S\text{-PTTL})_4$ (**1c**),^{14,15} proved to be the catalyst of choice in terms of product yield and enantioselectivity as well as catalytic activity. Very recently, we also reported on the one-pot enantioselective intramolecular C–H amidation of sulfamate esters using $\text{Rh}_2(S\text{-TFPTTL})_4$ (**1b**) as a chiral catalyst and $\text{PhI}(\text{OAc})_2$ as an oxidant, in which cyclic sulfamidates were obtained in up to 48% ee [eqn. (2)].¹⁶ As a logical extension of our studies, we now address the issue of enantiocontrol in the intermolecular aziridination of alkenes.



At the outset, we explored the aziridination of styrene (**7a**) with 1.1 equiv. of **2a** in the presence of 2 mol % of $\text{Rh}_2(S\text{-TCPTTL})_4$ (**1a**). In dichloromethane at $0\text{ }^\circ\text{C}$, the reaction proceeded smoothly to give

Table 1. Enantioselective Aziridination of Styrene (**7a**) Catalyzed by Chiral Dirhodium(II) Carboxylates^{a)}

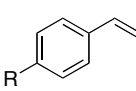
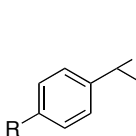
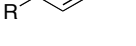
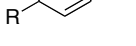
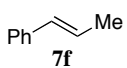
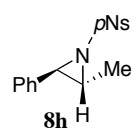
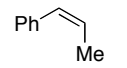
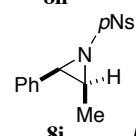
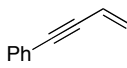
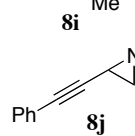
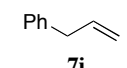
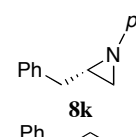
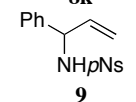
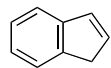
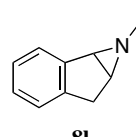
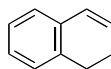
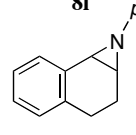
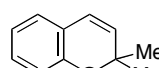
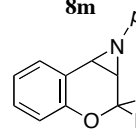
Entry	Iminoiodinane		Rh(II) catalyst	Solvent	Time (h)	Aziridine			
	Ar					Yield (%) ^{b)}	Ee (%) ^{c)}	Confign ^{d)}	
1	2a	4-NO ₂ C ₆ H ₄	Rh ₂ (<i>S</i> -TCPTTL) ₄ (1a)	CH ₂ Cl ₂	1.5	8a	98	35	<i>R</i>
2	2b	2-NO ₂ C ₆ H ₄	Rh ₂ (<i>S</i> -TCPTTL) ₄ (1a)	CH ₂ Cl ₂	0.5	8b	97	5 ^{e)}	<i>S</i>
3	2c	2,4-(NO ₂) ₂ C ₆ H ₃	Rh ₂ (<i>S</i> -TCPTTL) ₄ (1a)	CH ₂ Cl ₂	5	8c	93	9 ^{e)}	— ^{f)}
4	2a	4-NO ₂ C ₆ H ₄	Rh ₂ (<i>S</i> -TCPTTL) ₄ (1a)	EtOAc	6	8a	95	25	<i>R</i>
5	2a	4-NO ₂ C ₆ H ₄	Rh ₂ (<i>S</i> -TCPTTL) ₄ (1a)	CF ₃ C ₆ H ₅	30	8a	81	13	<i>R</i>
6	2a	4-NO ₂ C ₆ H ₄	Rh ₂ (<i>S</i> -TFPTTL) ₄ (1b)	CH ₂ Cl ₂	1	8a	88	21	<i>R</i>
7	2a	4-NO ₂ C ₆ H ₄	Rh ₂ (<i>S</i> -PTTL) ₄ (1c)	CH ₂ Cl ₂	1	8a	93	12	<i>R</i>

^{a)} All reactions were performed on a 0.2 mmol scale. ^{b)} Isolated yield. ^{c)} Determined by HPLC (Daicel Chiralpak AD-H column) unless otherwise stated. ^{d)} Determined by comparison of the sign of optical rotation with the literature value. ^{e)} Determined by HPLC (Daicel Chiralpak AD column). ^{f)} Absolute configuration was not determined.

aziridine (**8a**), $[\alpha]_D^{23} -24.2^\circ$ (*c* 1.14, CHCl₃), in 98% yield (Table 1, Entry 1). The enantioselectivity of this reaction was determined to be 35% ee by HPLC analysis (Daicel Chiralpak AD-H). The preferred absolute configuration of **8a** was established as *R* by comparing the sign of the optical rotation with the literature value [lit.,¹⁷ $[\alpha]_D +77.8^\circ$ (*c* 1.0, CHCl₃) for (*S*)-**8a**]. Although the use of [*N*-(2-nitrophenylsulfonyl)imino]phenyliodinane (**2b**) and [*N*-(2,4-dinitrophenylsulfonyl)imino]phenyliodinane (**2c**) as nitrene precursors provided the corresponding aziridines (**8b,c**) in high yield, the enantioselectivity was significantly diminished (Entries 2 and 3).¹⁸ A survey of solvents revealed that dichloromethane was the optimal solvent for this reaction. The use of ethyl acetate provided (*R*)-**8a** in 95% yield with 25% ee, but the reaction required much longer times to reach completion (Entry 4). Benzotrifluoride was found to be the least effective in terms of both reaction rate and enantioselectivity (Entry 5). We then evaluated the performance of two other chiral dirhodium(II) complexes, Rh₂(*S*-TFPTTL)₄ (**1b**)¹⁹ and Rh₂(*S*-PTTL)₄ (**1c**),^{14,15} derived from *N*-tetrafluorophthaloyl- and *N*-phthaloyl-(*S*)-*tert*-leucine, respectively. Although both catalysts (**1b,c**) afforded (*R*)-**8a** at similar reaction rates and yields as those found with **1a**, Rh₂(*S*-TCPTTL)₄ proved to be the catalyst of choice for producing a more reasonable degree of enantioselectivity (Entries 1 vs. 6 and 7).

With optimized conditions in hand, we then investigated the applicability of the present catalytic system to alkenes other than styrene. Some representative results are presented in Table 2. Styrene derivatives (**7b-d**) with electron-withdrawing groups at the *para* position on the benzene ring exhibited higher enantioselectivities than styrene (58%, 40% and 36% ee, Entries 1–3). In contrast, a sharp drop in

Table 2. Enantioselective Aziridination of Alkenes with **3a** Catalyzed by $\text{Rh}_2(\text{S-TCPTTL})_4$ (**1a**)^{a)}

Entry	Alkene	Time (h)	Product	Yield (%) ^{b)}	Ee (%)	Confign
1	7b , R = CF ₃	1.5	8d , R = CF ₃	96	58 ^{c)}	_d)
2	 7c , R = Cl	1.5	 8e , R = Cl	92	40 ^{e)}	_d)
3	 7d R = OAc	1.5	 8f , R = OAc	96	36 ^{c)}	_d)
4	7e , R = Me	1.5	8g , R = Me	82	19 ^{e)}	_d)
5	 7f	1	 8h	80	14 ^{f)}	2 <i>R</i> ,3 <i>R</i> ^{g)}
6	 7g	0.5	 8i	79	23 ^{c)}	_d)
7	 7h	2	 8j	58	14 ^{h)}	_d)
8	 7i	1	 8k	46	56 ⁱ⁾	S ^{g)}
			 9	13	20 ⁱ⁾	_d)
9	 7j	0.5	 8l	54	15 ⁱ⁾	_d)
10	 7k	1	 8m	83	32 ^{c)}	_d)
11	 7l	1	 8n	98	94 ^{h)}	_d)

^{a)} All reactions were performed at 0 °C using 2 mol % of Rh(II) catalyst and 1.1 equiv. of **2a**. ^{b)} Isolated yield. ^{c)} Determined by HPLC (Daicel Chiralpak AS-H column). ^{d)} Absolute configuration was not determined. ^{e)} Determined by HPLC (Daicel Chiralpak AS column). ^{f)} Determined by HPLC (Daicel Chiralpak AD column × 2). ^{g)} Determined by comparison of optical rotation with the literature value. ^{h)} Determined by HPLC (Daicel Chiralcel OD-H column). ⁱ⁾ Determined by HPLC (Daicel Chiralpak AD-H column).

enantioselectivity was observed when 4-methylstyrene (**7e**), which contains an electron-donating substituent, was used (19% ee, Entry 4). As expected from results for the $\text{Rh}_2(\text{OAc})_4$ -catalyzed aziridination reported by Müller,¹¹ the reactions of *trans*- and *cis*- β -methylstyrene (**7f,g**) with **2a** proceeded in a stereospecific manner to give the derived *trans*- and *cis*-2,3-disubstituted aziridines (**8h,i**)

in high yields, although the ee values were significantly lower than that found with **7a** (Entries 5 and 6). The aziridination of the alkyne-conjugated terminal alkene (**7h**) also resulted in a low enantioselectivity (Entry 7). On the other hand, the reaction with allylbenzene (**7i**) provided the aziridine (**8k**) in 46% yield with 56% ee (Entry 8). The low yield in this reaction was due to the competitive formation of the allylic C–H amidation product (**9**)²⁰ (13% yield, 20% ee). The aziridination of indene (**7j**) and 1,2-dihydronaphthalene (**7k**) resulted in 15% and 32% ee, respectively (Entries 9 and 10). It is interesting to note that no allylic or benzylic C–H amidation products were obtained in these reactions. Gratifyingly, the use of 2,2-dimethylchromene (**7l**) produced the aziridine (**8n**) in 98% yield with 94% ee (Entry 11). While exceptionally high levels of enantioselectivity (>98% ee) in the aziridination of 6-substituted 2,2-dimethylchromenes have already been achieved using the copper(I)-diimine complexes pioneered by Jacobsen,^{3a,d,g,i} the enantioselectivity of 94% ee obtained for **1a** is the highest reported to date for a chiral dirhodium(II) complex-catalyzed aziridination reaction.

In summary, we have reported the enantioselective aziridination of alkenes with [*N*-(4-nitrophenylsulfonyl)imino]phenyliodinane using Rh₂(*S*-TCPTTL)₄ as a catalyst. Only in the case of 2,2-dimethylchromene, a high level of enantioselectivity (94% ee) has been achieved. The design and synthesis of a new class of chiral dirhodium(II) catalysts to extend the scope of such enantioselective nitrene transfer reactions 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-4100 spectrometer and absorbance bands are reported in wavenumber (cm⁻¹). ¹H NMR spectra were recorded on JEOL JNM-ECX400P (400 MHz) spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane; δ_H 0.00). Data are presented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant and integration. ¹³C NMR spectra were recorded on JEOL JNM-ECX400P (100 MHz) spectrometer. Chemical shifts are reported relative to internal standard (CDCl₃; δ 77.0). 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 Wakogel[®] C-200 (75-150 μm). Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F₂₅₄ plates with visualization by ultraviolet, anisaldehyde stain solution or phosphomolybdic acid stain solution. Analytical high performance liquid chromatography (HPLC) was performed on JASCO PU-980 intelligent HPLC pump with JASCO UV-970 intelligent UV/VIS detector. Detection was performed at 254 nm. Chiralpak AD, AD-H, AS,

AS-H and Chiralcel OD-H columns (0.46 cm × 25 cm) from Daicel were used. Retention times (t_R) and peak ratio were determined with JASCO-Borwin analysis system.

All reactions were carried out in flame-dried glassware under argon atmosphere unless otherwise noted. Reagents and solvents were purified by standard means. [*N*-(arylsulfonyl)imino]phenyliodinanes (**2a-c**) were prepared from corresponding sulfonamides according to the literature procedure.²¹

General procedure for the enantioselective intermolecular aziridination reaction (Table 1, Entry 1):

(*R*)-*N*-(4-nitrophenylsulfonyl)-2-phenylaziridine (8a).^{11a,17} [*N*-(4-Nitrophenylsulfonyl)imino]phenyliodinane (**2a**) (88.9 mg, 0.22 mmol, 1.1 equiv.) was added in one portion to a solution of styrene (**7a**) (20.8 mg, 0.20 mmol) and bis(ethyl acetate) adduct of Rh₂(*S*-TCPTTL)₄ (7.9 mg, 0.004 mmol, 2 mol %) in CH₂Cl₂ (2 mL) at 0 °C. After 1.5 h of stirring at this temperature, the whole mixture was concentrated *in vacuo* and purified by column chromatography (Wakogel[®] C-200, 9:1 hexane/EtOAc) to provide (*R*)-**8a** (59.6 mg, 98%) as a white solid; R_f = 0.34 (3:1 hexane/EtOAc); mp 131.5–134.0 °C; $[\alpha]_D^{23}$ –24.2° (*c* 1.14, CHCl₃) for 35% ee [lit.,¹⁷ $[\alpha]_D$ +77.8° (*c* 1.0, CHCl₃) for (*S*)-**8a**]; ¹H NMR (400 MHz, CDCl₃) δ 2.51 (d, *J* = 4.5 Hz, 1H, NCHH), 3.12 (d, *J* = 7.2 Hz, 1H, NCHH), 3.91 (dd, *J* = 4.5, 7.2 Hz, 1H, NCHPh), 7.22-7.23 (m, 2H, *Ar*), 7.30-7.34 (m, 2H, *Ar*), 8.19 (d, *J* = 9.1 Hz, 2H, *Ar*), 8.38 (d, *J* = 9.1 Hz, 2H, *Ar*). The enantiomeric excess of **8a** was determined to be 35% by HPLC with a Chiralpak AD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (major) = 25.9 min for (*R*)-enantiomer; t_R (minor) = 29.1 min for (*S*)-enantiomer.

(*S*)-*N*-(2-Nitrophenylsulfonyl)-2-phenylaziridine (8b).²² According to the general procedure for enantioselective aziridination reaction, **8b** was prepared from **7a** (20.8 mg, 0.20 mmol) and [*N*-(2-nitrophenylsulfonyl)imino]phenyliodinane (**2b**) (88.9 mg, 0.22 mmol, 1.1 equiv.). The crude product was purified by column chromatography (Wakogel[®] C-200, 9:1 hexane/EtOAc) to provide (*S*)-**8b** (58.4 mg, 97%) as a yellow oil; R_f = 0.37 (3:1 hexane/EtOAc); $[\alpha]_D^{17}$ +4.90° (*c* 1.42, CHCl₃) for 5% ee [lit.,²² $[\alpha]_D^{25}$ –99.7° (*c* 1.0, CHCl₃) for (*R*)-**8b**]; ¹H NMR (400 MHz, CDCl₃) δ 2.63 (d, *J* = 4.8 Hz, 1H, NCHH), 3.24 (d, *J* = 7.3 Hz, 1H, NCHH), 4.03 (dd, *J* = 4.8, 7.3 Hz, NCHPh), 7.28-7.36 (m, 5H, *Ar*), 7.70-7.36 (m, 3H, *Ar*), 8.21-8.24 (m, 1H, *Ar*). The enantiomeric excess of **8b** was determined to be 5% by HPLC with a Chiralpak AD column (5:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (major) = 16.6 min for (*S*)-enantiomer; t_R (minor) = 20.3 min for (*R*)-enantiomer.

***N*-(2,4-Dinitrophenylsulfonyl)-2-phenylaziridine (8c).**^{11b} According to the general procedure for enantioselective aziridination reaction, **8c** was prepared from **7a** (20.8 mg, 0.20 mmol) and [*N*-(2,4-dinitrophenylsulfonyl)imino]phenyliodinane (**2c**) (98.8 mg, 0.22 mmol, 1.1 equiv.). The crude

product was purified by column chromatography (Wakogel[®] C-200, 5:1 hexane/EtOAc) to provide **8c** (64.6 mg, 93%) as a yellow oil; $R_f = 0.28$ (3:1 hexane/EtOAc); $[\alpha]_D^{19} +5.13^\circ$ (c 1.92, CHCl_3) for 9% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.71 (d, $J = 4.8$ Hz, 1H, NCHH), 3.32 (d, $J = 7.1$ Hz, 1H, NCHH), 4.11 (dd, $J = 4.8, 7.1$ Hz, ArCH), 7.26-7.34 (m, 5H, Ar), 8.45-8.47 (m, 1H, Ar), 8.53-8.56 (m, 2H, Ar). The enantiomeric excess of **8c** was determined to be 9% by HPLC with a Chiralpak AD column (3:1 hexane/*i*-PrOH, 2.0 mL/min): t_R (major) = 10.2 min; t_R (minor) = 20.3 min. The absolute configuration of **8c** was not determined.

***N*-(4-Nitrophenylsulfonyl)-2-[(4-trifluoromethyl)phenyl]aziridine (8d)**.²³ According to the general procedure for enantioselective aziridination reaction, **8d** was prepared from 4-(trifluoromethyl)styrene (**7b**) (34.4 mg, 0.2 mmol) and **2a** (88.9 mg, 0.22 mmol, 1.1 equiv.). The crude product was purified by column chromatography (Wakogel[®] C-200, 9:1 hexane/EtOAc) to provide **8d** (71.3 mg, 96%) as a colorless oil; $R_f = 0.35$ (3:1 hexane/EtOAc); $[\alpha]_D^{23} -30.6^\circ$ (c 1.10, CHCl_3) for 58% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.49 (d, $J = 4.6$ Hz, 1H, NCHH), 3.15 (d, $J = 7.4$ Hz, 1H, NCHH), 3.95 (dd, $J = 4.6, 7.4$ Hz, 1H, ArCH), 7.36 (d, $J = 8.2$ Hz, 2H, Ar), 7.59 (d, $J = 8.2$ Hz, 2H, Ar), 8.20 (d, $J = 9.1$ Hz, 2H, Ar), 8.41 (d, $J = 9.1$ Hz, 2H, Ar). The enantiomeric excess of **8d** was determined to be 58% by HPLC with a Chiralpak AS-H column (3:1 hexane/*i*-PrOH, 2.0 mL/min): t_R (major) = 8.9 min; t_R (minor) = 14.8 min. The absolute configuration of **8d** was not determined.

2-(4-Chlorophenyl)-*N*-(4-nitrophenylsulfonyl)aziridine (8e).²³ According to the general procedure for enantioselective aziridination reaction, **8e** was prepared from 4-chlorostyrene (**7c**) (27.7 mg, 0.2 mmol) and **2a** (88.9 mg, 0.22 mmol, 1.1 equiv.). The crude product was purified by column chromatography (Wakogel[®] C-200, 9:1 hexane/EtOAc) to provide **8e** (61.5 mg, 92%) as a colorless solid; $R_f = 0.39$ (3:1 hexane/EtOAc); mp 97.0–98.5 °C; $[\alpha]_D^{23} -25.7^\circ$ (c 1.46, CHCl_3) for 40% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.47 (d, $J = 4.5$ Hz, 1H, NCHH), 3.11 (d, $J = 7.2$ Hz, 1H, NCHH), 3.88 (dd, $J = 4.5, 7.2$ Hz, ArCH), 7.16 (d, $J = 8.9$ Hz, 2H, Ar), 7.29 (d, $J = 8.9$ Hz, 2H, Ar), 8.18 (d, $J = 9.1$ Hz, 2H, Ar), 8.39 (d, $J = 9.1$ Hz, 2H, Ar). The enantiomeric excess of **8e** was determined to be 40% by HPLC with a Chiralpak AS column (3:1 hexane/*i*-PrOH, 2.0 mL/min): t_R (major) = 13.9 min; t_R (minor) = 22.0 min. The absolute configuration of **8e** was not determined.

2-(4-Acetoxyphenyl)-*N*-(4-nitrophenylsulfonyl)aziridine (8f).^{11b} According to the general procedure for enantioselective aziridination reaction, **8f** was prepared from 4-acetoxystyrene (**7d**) (32.4 mg, 0.2 mmol) and **2a** (88.9 mg, 0.22 mmol, 1.1 equiv.). The crude product was purified by column chromatography (Wakogel[®] C-200, 4:1 hexane/EtOAc) to provide **8f** (69.4 mg, 96%) as a white solid; $R_f = 0.29$ (2:1

hexane/EtOAc); mp 143.0–144.0 °C; $[\alpha]_D^{23}$ -21.4° (c 0.91, CHCl_3) for 36% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.29 (s, 3H, CH_3CO), 2.48 (d, $J = 4.6$ Hz, 1H, NCHH), 3.11 (d, $J = 7.3$ Hz, 1H, NCHH), 3.90 (dd, $J = 4.6, 7.3$ Hz, ArCH), 7.04 (d, $J = 8.7$ Hz, 2H, Ar), 7.24 (d, $J = 8.7$ Hz, 2H, Ar), 8.19 (d, $J = 9.2$ Hz, 2H, Ar), 8.40 (d, $J = 9.2$ Hz, 2H, Ar). The enantiomeric excess of **8f** was determined to be 36% by HPLC with a Chiralpak AS-H column (1:1 hexane/*i*-PrOH, 2.0 mL/min): t_R (major) = 12.7 min; t_R (minor) = 20.0 min. The absolute configuration of **8f** was not determined.

2-(4-Methylphenyl)-N-(4-nitrophenylsulfonyl)aziridine (8g).^{11a} According to the general procedure for enantioselective aziridination reaction, **8g** was prepared from 4-methylstyrene (**7e**) (23.6 mg, 0.2 mmol) and **2a** (88.9 mg, 0.22 mmol, 1.1 equiv.). The crude product was purified by column chromatography (Wakogel[®] C-200, 9:1 hexane/EtOAc) to provide **8g** (51.7 mg, 82%) as a white solid; $R_f = 0.47$ (3:1 hexane/EtOAc); mp 139.0–140.0 °C; $[\alpha]_D^{23}$ -12.7° (c 0.83, CHCl_3) for 19% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.32 (s, 3H, ArCH₃), 2.50 (d, $J = 4.6$ Hz, 1H, NCHH), 3.10 (d, $J = 7.2$ Hz, 1H, NCHH), 3.86 (dd, $J = 4.6, 7.2$, 1H, ArCH), 7.08–7.13 (m, 4H, Ar), 8.18 (d, $J = 8.8$ Hz, 2H, Ar), 8.37 (d, $J = 8.8$ Hz, 2H, Ar). The enantiomeric excess of **8g** was determined to be 19% by HPLC with a Chiralpak AS column (3:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (major) = 19.1 min; t_R (minor) = 27.1 min. The absolute configuration of **8g** was not determined.

(2R,3R)-2-Methyl-N-(4-nitrophenylsulfonyl)-3-phenylaziridine (8h).^{2d} According to the general procedure for enantioselective aziridination reaction, **8h** was prepared from *trans*- β -methylstyrene (**7f**) (23.6 mg, 0.2 mmol) and **2a** (88.9 mg, 0.22 mmol, 1.1 equiv.). The crude product was purified by column chromatography (Wakogel[®] C-200, 9:1 hexane/EtOAc) to provide (2R,3R)-**8h** (50.7 mg, 80%) as a pale yellow oil; $R_f = 0.40$ (3:1 hexane/EtOAc); $[\alpha]_D^{23}$ -3.93° (c 0.83, CHCl_3) for 14% ee [lit.,^{2d} $[\alpha]_D^{24}$ $+60.4^\circ$ (c 1.08, CHCl_3) for 80% ee of (2S,3S)-**8h**]; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.89 (d, $J = 6.3$ Hz, 3H, CH₃), 3.05 (dq, $J = 4.5, 6.3$ Hz, 1H, CH₃CH), 3.87 (d, $J = 4.5$ Hz, PhCH), 7.12–7.15 (m, 2H, Ar), 7.26–7.29 (m, 3H, Ar), 8.12 (d, $J = 9.1$ Hz, 2H, Ar), 8.30 (d, $J = 9.1$ Hz, 2H, Ar). The enantiomeric excess of **8h** was determined to be 14% by HPLC with a Chiralpak AD ($\times 2$) columns (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (major) = 16.6 min for (2R,3R)-enantiomer; t_R (minor) = 33.4 min for (2S,3S)-enantiomer.

cis-2-Methyl-N-(4-nitrophenylsulfonyl)-3-phenylaziridine (8i).^{11a} According to the general procedure for enantioselective aziridination reaction, **8i** was prepared from *cis*- β -methylstyrene (**7g**) (23.6 mg, 0.2 mmol) and **2a** (88.9 mg, 0.22 mmol, 1.1 equiv.). The crude product was purified by column chromatography (Wakogel[®] C-200, 9:1 hexane/EtOAc) to provide **8i** (49.7 mg, 79%) as a pale yellow oil; $R_f = 0.42$ (3:1 hexane/EtOAc); $[\alpha]_D^{23}$ $+18.3^\circ$ (c 1.19, CHCl_3) for 23% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ

1.06 (d, $J = 5.9$ Hz, 3H, CH_3), 3.34 (dq, $J = 7.2, 5.9$ Hz, 1H, CH_3CH), 4.08 (d, $J = 7.2$ Hz, PhCH), 7.18-7.21 (m, 2H, Ar), 7.29-7.31 (m, 3H, Ar), 8.22 (d, $J = 8.6$ Hz, 2H, Ar), 8.39 (d, $J = 8.6$ Hz, 2H, Ar). The enantiomeric excess of **8i** was determined to be 23% by HPLC with a Chiralpak AS-H column (9:1 hexane/*i*-PrOH, 2.0 mL/min): t_{R} (major) = 18.2 min; t_{R} (minor) = 22.0 min. The absolute configuration of **8i** was not determined.

***N*-(4-Nitrophenylsulfonyl)-2-(2-phenylethynyl)aziridine (8j)**.^{8b} According to the general procedure for enantioselective aziridination reaction, **8j** was prepared from (3-buten-1-ynyl)benzene (**7h**) (25.6 mg, 0.2 mmol) and **2a** (88.9 mg, 0.22 mmol, 1.1 equiv.). The crude product was purified by column chromatography (Wakogel[®] C-200, 9:1 hexane/EtOAc) to provide **8j** (37.5 mg, 58%) as a pale yellow oil; $R_f = 0.42$ (3:1 hexane/EtOAc); $[\alpha]_{\text{D}}^{26} -5.30^\circ$ (c 0.69, CHCl_3) for 14% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.63 (d, $J = 4.5$ Hz, 1H, NCHH), 2.99 (d, $J = 7.2$ Hz, 1H, NCHH), 3.60 (dd, $J = 4.5, 7.2$ Hz, $\text{C}\equiv\text{CCH}$), 7.26-7.41 (m, 4H, Ar), 8.21 (d, $J = 9.1$ Hz, 2H, Ar), 8.42 (d, $J = 9.1$ Hz, 2H, Ar). The enantiomeric excess of **8j** was determined to be 14% by HPLC with a Chiralcel OD-H column (3:1 hexane/*i*-PrOH, 1.0 mL/min): t_{R} (major) = 28.5 min; t_{R} (minor) = 38.6 min. The absolute configuration of **8j** was not determined.

(*S*)-2-Benzyl-*N*-(4-nitrophenylsulfonyl)aziridine (8k).²⁴ According to the general procedure for enantioselective aziridination reaction, **8k** was prepared from allylbenzene (**7i**) (23.6 mg, 0.2 mmol) and **2a** (88.9 mg, 0.22 mmol, 1.1 equiv.). The crude product was purified by column chromatography (Wakogel[®] C-200, 19:1 toluene/EtOAc) to provide **8k** (29.0 mg, 46%, as a white solid) and 4-nitro-*N*-(1-phenylprop-2-enyl)benzenesulfonamide (**9**)²⁰ (8.2 mg, 13% as a pale yellow oil).

8k: $R_f = 0.44$ (9:1 toluene/EtOAc); mp 113.0–115.0 °C; $[\alpha]_{\text{D}}^{23} -4.43^\circ$ (c 0.81, acetone) for 56% ee [lit.,²⁴ $[\alpha]_{\text{D}}^{25} -10^\circ$ (c 0.25, acetone) for (*S*)-**8k**]; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.32 (d, $J = 4.5$ Hz, 1H, NCHH), 2.47 (dd, $J = 8.2, 14.2$ Hz, 1H, NCH), 2.90 (d, $J = 6.9$ Hz, PhCHH), 2.96-3.05 (m, 2H, NCHH and PhCHH), 6.96-6.98 (m, 2H, Ar), 7.06-7.14 (m, 3H, Ar), 7.88 (d, $J = 8.6$ Hz, 2H, Ar), 8.16 (d, $J = 8.6$ Hz, 2H, Ar). The enantiomeric excess of **8k** was determined to be 56% by HPLC with a Chiralpak AD-H column (3:1 hexane/*i*-PrOH, 1.0 mL/min): t_{R} (minor) = 11.7 min for (*R*)-enantiomer; t_{R} (major) = 12.8 min for (*S*)-enantiomer.

9: $R_f = 0.24$ (9:1 toluene/EtOAc); $[\alpha]_{\text{D}}^{23} -4.63^\circ$ (c 0.39, CHCl_3) for 20% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.08-5.21 (m, 4H, NH, PhCH and $=\text{CH}_2$), 5.89 (ddd, $J = 5.8, 10.5, 16.3$ Hz, 1H, $\text{CH}_2=\text{CH}$), 7.07-7.09 (m, 2H, Ar), 7.19-7.21 (m, 3H, Ar), 7.84 (dt $J = 8.7$ Hz, 2H, Ar), 8.18 (d, $J = 8.7$ Hz, 2H, Ar). The enantiomeric excess of **9** was determined to be 14% by HPLC with a Chiralpak AD-H column (3:1

hexane/*i*-PrOH, 1.0 mL/min): t_R (minor) = 7.9 min; t_R (major) = 8.9 min. The absolute configuration of **9** was not determined.

1,1a,6,6a-Tetrahydro-1-(4-nitrophenylsulfonyl)-indeno[1,2-b]azirine (8l).^{11b} According to the general procedure for enantioselective aziridination reaction, **8l** was prepared from indene (**7j**) (23.2 mg, 0.2 mmol) and **2a** (88.9 mg, 0.22 mmol, 1.1 equiv.). The crude product was purified by column chromatography (Wakogel[®] C-200, 9:1 hexane/EtOAc) to provide **8l** (34.0 mg, 54%) as a pale yellow solid; R_f = 0.43 (3:1 hexane/EtOAc); mp = 126.0-127.0 °C; $[\alpha]_D^{23}$ +4.68° (*c* 1.07, CHCl₃) for 15% ee; ¹H NMR (400 MHz, CDCl₃) δ 3.15 (dd, *J* = 0.9, 17.9 Hz, 1H, ArCHH), 3.22 (dd, *J* = 4.2, 17.9 Hz, 1H, ArCHH), 4.04 (ddd, *J* = 0.9, 4.2, 5.1 Hz, 1H, NCHCH₂), 4.41 (d, *J* = 5.1 Hz, 1H, ArCHN), 7.18-7.42 (m, 4H, Ar), 8.14 (d, *J* = 9.0 Hz, 2H, Ar), 8.36 (d, *J* = 9.0 Hz, 2H, Ar). The enantiomeric excess of **8l** was determined to be 15% by HPLC with a Chiralpak AD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (major) = 34.7 min; t_R (minor) = 37.3 min. The absolute configuration of **8l** was not determined.

1a,2,3,7,7b-Tetrahydro-1-(4-nitrophenylsulfonyl)-1H-naphth[1,2-b]azirine (8m).²⁵ According to the general procedure for enantioselective aziridination reaction, **8m** was prepared from 1,2-dihydronaphthalene (**7k**) (26.0 mg, 0.2 mmol) and **2a** (88.9 mg, 0.22 mmol, 1.1 equiv.). The crude product was purified by column chromatography (Wakogel[®] C-200, 9:1 hexane/EtOAc) to provide **8m** (53.7 mg, 83%) as a white solid; R_f = 0.46 (3:1 hexane/EtOAc); mp = 136.0-137.5 °C; $[\alpha]_D^{23}$ -22.0° (*c* 0.88, CHCl₃) for 32% ee; ¹H NMR (400 MHz, CDCl₃) δ 1.75 (m, 1H, NCHCHH), 2.31 (m, 1H, NCHCHH), 2.59 (dd, *J* = 5.5, 14.8 Hz, 1H, ArCHH), 2.73 (ddd, *J* = 6.1, 14.8, 14.8 Hz, 1H, ArCHH), 3.72 (d, *J* = 7.1 Hz, 1H, NCHCH₂), 3.93 (d, *J* = 7.1 Hz, 1H, NCHAr), 7.06-7.31 (m, 4H, Ar), 8.12 (d, *J* = 9.2 Hz, 2H, Ar), 8.35 (d, *J* = 9.2 Hz, 2H, Ar). The enantiomeric excess of **8m** was determined to be 32% by HPLC with a Chiralpak AS-H column (3:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (major) = 28.5 min; t_R (minor) = 38.6 min. The absolute configuration of **8m** was not determined.

1,1a,2,7b-Tetrahydro-2,2-dimethyl-1-(4-nitrophenylsulfonyl)-[1]benzopyrano[3,4-b]azirine (8n). According to the general procedure for enantioselective aziridination reaction, **8n** was prepared from 2,2-dimethyl-2*H*-chromene (**7l**) (16.0 mg, 0.1 mmol) and **2a** (44.5 mg, 0.11 mmol, 1.1 equiv.). The crude product was purified by column chromatography (Wakogel[®] C-200, 9:1 hexane/EtOAc) to provide **8n** (35.6 mg, 98%) as a colorless oil; R_f = 0.46 (3:1 hexane/EtOAc); $[\alpha]_D^{23}$ +13.1° (*c* 1.05, CHCl₃) for 94% ee; IR(neat) ν: 1531, 1350, 1163 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.26 (s, 3H, CH₃), 1.36 (s, 3H, CH₃), 3.51 (d, *J* = 7.5 Hz, 1H, NCH), 4.02 (d, *J* = 7.5 Hz, 1H, ArCH), 6.78 (d, *J* = 8.1 Hz, 1H, Ar), 6.92 (t, *J* = 7.4 Hz, 1H, Ar), 7.21-7.28 (m, 2H, Ar), 8.16 (d, *J* = 8.7 Hz, 2H, Ar), 8.36 (d, *J* = 8.7 Hz, 2H, Ar); ¹³C

NMR (100 MHz, CDCl₃) δ 23.22 (CH₃), 26.12 (CH₃), 41.45 (CH), 50.83 (CH), 71.58 (C), 117.11 (C), 118.43 (CH), 121.66 (CH), 124.30 (CH), 129.18 (CH), 129.22 (CH), 130.72 (CH), 143.87 (C), 150.60 (C), 152.43 (C); HRMS (EI) calcd for C₁₇H₁₆N₂O₅S (M⁺) 360.0780, found 360.0785. The enantiomeric excess of **8n** was determined to be 94% by HPLC with a Chiralcel OD-H column (9:1 hexane/*i*-PrOH, 0.5 mL/min): t_R (minor) = 28.2 min; t_R (major) = 31.4 min. The absolute configuration of **8n** was not determined.

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