Asymmetric Synthesis of Aziridines by Reduction of *N*-(*tert*-Butanesulfinyl) α -Chloro Imines.

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General methods

α -Chlorinated ketones **18a,b** and α -chlorinated aldehydes **19a,b** were prepared as previously described.^{S1} The α -chlorinated ketones and aldehydes were distilled. Boiling points, ¹H and ¹³C NMR spectras were identical to literature.^{S1}

R-(+)-*tert*-Butanesulfinamide was obtained from Commercial Sources in $\geq 98\%$ purity and $\geq 98\%$ ee. α -Halo ketones **18c-g** were obtained from Commercial Sources and *N*-sulfinyl α -chloro imines **5a,b** and **12a,b** were prepared as previously described.^{S2}

General procedure for the synthesis of *N*-*tert*-butanesulfinyl α -halo imines (*R_S*)-**5,12**

All imines (*R_S*)-**5,12** were synthesized when stirring the starting materials for 4-48 h at reflux in dry THF. *N*-*tert*-Butanesulfinyl α -chloro imines (*R_S*)-**5,12** were isolated after removal of the titanium species via aqueous workup, followed by high vacuum distillation of the excess of ketones **18** or aldehydes **19** used. The synthesized *N*-*tert*-butanesulfinyl α -chloro imines (*R_S*)-**5a,b,12a,b** were obtained as single *E*-isomers and were used without further purification,^{S2} whereas *N*-*tert*-butanesulfinyl α -halo ketimines (*R_S*)-**12c-e** were purified by recrystallisation from Et₂O. The carbonyl precursors **18,19** were either commercially available ($R^2 = \text{Ar}$) or were synthesized in 60-95% yield in high purity ($>98\%$) according to literature procedures ($R^2 = \text{H, Me}$).^{S1} All *N*-*tert*-butanesulfinyl α -halo imines (*R_S*)-**5,12** could be stored for longer periods of time at -40°C .

^{S1} De Kimpe, N.; Verhé, R.; De Buyck, L.; Moëns, N.; Schamp, N. *Synthesis* **1982**, 43.

^{S2} a) Denolf, B.; Mangelinckx, S.; Törnroos, K.W.; De Kimpe, N. *Org. Lett.* **2006**, 8, 3129. b) Denolf, B.; Mangelinckx, S.; Törnroos, K.W.; De Kimpe, N. *Org. Lett.* **2007**, 2, 187.

Table S1. Synthesis of *N*-*tert*-Butanesulfinyl α -Halo Imines (*R_S*)-**5**,**12**.

18 $R^2 \neq H$
19 $R^2 = H$

1-1.1 equiv
 $Ti(OEt)_4$
THF
4-48 h, Δ

12 $R^2 \neq H$
5 $R^2 = H$

entry	R^1	R^2	temp	time (h)	product	yield %
1	Me	Me	Δ	6	12a	91
2	Et	Me	Δ	6	12b	82
3	H	Ph	Δ	48	12c	89
4	H	4-ClC ₆ H ₄	Δ	48	12d	88
5	H	4-BrC ₆ H ₄	Δ	48	12e	85
8	Me	H	Δ	4	5a	92
9	Et	H	Δ	4	5b	87

General procedure for the synthesis of N-(2-halo-1-arylethylidene)-tert-butanesulfinamides (*R_S*)-12c-g

In a flame-dried 100 mL round-bottom flask was made a 0.5 M-solution of 2-halo acetophenones **18c-e** (10 mmol) and Ti(OEt)₄ (tech. grade, ~20% Ti; 2.0 equiv) in dry THF under nitrogen atmosphere. (*R_S*)-*tert*-Butanesulfinamide (10 mmol) was added in one portion and allowed to stir for 48 hours at reflux temperature. After completion the reaction mixture was cooled to 0 °C and poured in an equal volume of brine and EtOAc (1:1-mixture), while rapidly stirring. The suspension was filtered over Celite and the solids were washed with EtOAc (2 x 10 mL) and extracted with EtOAc (3 x 20 mL). The combined organic fractions were dried (MgSO₄), filtered and concentrated. Analytically pure material was obtained after single recrystallisation from Et₂O.

(R_S)-N-[2-Chloro-1-phenylethylidene]-tert-butanefinamide (R_S)-12c

Colorless crystals (mp: 68.3 ± 0.2 °C), 89 %. [α]_D -31 (*c* 0.2, CHCl₃). IR (KBr, cm⁻¹) $\nu_{\max}$: 1062, 1364, 1574, 1604, 2925. MS: *m/z* (M⁺+H): 258.2/260.2 (100). δ_{H} (300 MHz, CDCl₃): 1.37 (9H, s), 5.01 (1H, d, *J* 10.7 Hz), 5.18 (1H, d, *J* 10.7 Hz), 7.40-7.90 (5H, m). δ_{C} (75 MHz, CDCl₃): 23.3, 35.5, 59.7, 127.6, 128.8, 132.0, 136.0, 169.6. Anal. Calcd. for C₁₂H₁₆ClNOS: C, 55.91; H, 6.26; N, 5.44. Found: C, 55.53; H, 6.01; N, 5.67.

(R_S)-N-[2-Chloro-1-(4-chlorophenyl)ethylidene]-tert-butanefinamide (R_S)-12d

White crystals (mp: 81.1 ± 0.2 °C), 88 %. [α]_D -15 (*c* 0.72, CHCl₃). IR (KBr, cm⁻¹) $\nu_{\max}$: 1071, 1362, 1561, 1587, 1601, 2980. MS: *m/z* (M⁺+H): 292.3/294.2/296.3 (100), 236.2/238.3/240.0 (20). δ_{H} (300 MHz, CDCl₃): 1.36 (9H, s) 5.00 (1H, d, *J* 11.1 Hz); 5.14 (1H, d, *J* 11.1 Hz); 7.43 and 7.81 (2 x 2H, 2 x d, *J* 8.5 Hz). δ_{C} (75 MHz, CDCl₃): 23.2, 35.2, 59.9, 128.9, 129.0, 134.3, 138.3, 168.2. Anal. Calcd. for C₁₂H₁₅Cl₂NOS: C, 49.32; H, 5.17; N, 4.79. Found: C, 49.51; H, 5.30; N, 4.66.

(R_S)-N-[2-Chloro-1-(4-bromophenyl)ethylidene]-tert-butanefinamide (R_S)-12e

White crystals (mp: 79.2 ± 0.2 °C), 85 %. [α]_D -23 (*c* 1.3, CHCl₃). IR (KBr, cm⁻¹) $\nu_{\max}$: 1073, 1362, 1560, 1587, 1598, 2981. MS: *m/z* (M⁺+H): 336.7/338.5/340.7 (100), 280.5/282.5/284.5 (37). δ_{H} (300 MHz, CDCl₃): 1.37 (9H, s), 4.84 (1H, d, *J* 9.8 Hz), 5.07 (1H, d, *J* 9.8 Hz), 7.43 and 7.82 (2 x 2H, 2 x d, *J* 8.6 Hz). δ_{C} (75 MHz, CDCl₃): 21.2, 23.3, 59.9, 128.7, 129.0, 134.4, 138.3, 168.3. Anal. Calcd. for C₁₂H₁₅BrClNOS: C, 42.81; H, 4.49; N, 4.16. Found: C, 42.90; H, 4.31; N, 4.29.

General procedure for the synthesis of N-(tert-butane)sulfinamides (R_S)-10 starting from the corresponding N-sulfinyl imines (R_S)-5

In a flame-dried 50 mL round-bottom flask was made a 10%-solution of *N-tert*-butanesulfinyl 2-chloro aldimine **5** (10 mmol) in THF under nitrogen atmosphere. 2 equiv of NaBH₄ (20 mmol) were added at room temperature to the stirred solution. Then the reaction was stirred for 12 hours before quenching with NH₄Cl (5 mL) and diluted with

saturated aqueous KHCO_3 (20 mL) and EtOAc (20 mL). The aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated to afford pure β -chloro *N*-sulfinamide **10**.

(R_S)-(-)-N-(2-Chloro-2-ethylbutyl)-tert-butan sulfinamide (R_S)-10b

Colorless oil, 97%. $[\alpha]_D -9$ (c 0.1, MeOH). (NaCl, cm^{-1}): 1060, 1364, 1458, 2975, 3216. MS: m/z ($M+H$): 240.3/242.3 (100). δ_H (300 MHz, CDCl_3): 0.93 (3H, t, J 7.4 Hz), 1.00 (3H, t, J 7.4 Hz), 1.25 (9H, s), 1.78-1.94 (4H, m), 3.24 (1H, dd, J 13.5 Hz, 5.2 Hz), 3.47 (1H, dd, J 13.5 Hz, 9.4 Hz), 3.63 (1H, m). δ_C (75 MHz, CDCl_3): 8.4, 8.6, 22.7, 30.8, 31.3, 53.4, 56.3, 78.4. Anal. Calcd for $\text{C}_{10}\text{H}_{22}\text{ClNOS}$: C, 50.08; H, 9.25; N, 5.85. Found: C, 49.81; H, 9.18; N, 5.54.

General procedure for the synthesis of N-(tert-butane)sulfinamides (R_S,S)-13 starting from the corresponding N-sulfinyl imines (R_S)-12.

In a flame-dried 50 mL round-bottom flask was made a 5%-solution of *N*-tert-butan sulfinyl 2-halo ketimine **12** (10 mmol) in THF under nitrogen atmosphere. The stirred solution was cooled to $-78\text{ }^\circ\text{C}$ before 10 equiv of MeOH (4.6 mL) and 2 equiv of NaBH_4 (20 mmol) were added. Then the reaction was stirred for 1 hour at this temperature before quenching with NH_4Cl (5 mL) and diluted with saturated aqueous KHCO_3 (20 mL) and EtOAc (20 mL). The aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated to afford pure β -halo *N*-sulfinamide **13**.

Table S2. Optimization of the Reduction of *N-tert*-Butanesulfinyl α -Chloro Imine (R_S)-**12a** with NaBH₄ in THF to β -Chloro Sulfinamide (R_S,S)-**13a**.

entry	equiv NaBH ₄	equiv MeOH	temp (°C)	time (h)	yield (%) ^a	dr ^b
1	2	-	rt	12	99 ^d	58:42
2	2	-	rt	1	97 ^d	59:41
3	2	-	-10	4	99 ^d	64:36
4	2	-	-50	5	74	91:9
5	2	-	-78	7	68	99:1
6	2	0.5	-78	1	36	90:10
7	2	1	-78	1	59	96:4
8	2	100	-78	1	98 ^d	61:39
9	2 ^c	-	-78	1	97 ^d	51:49
10	0.5	10	-78	1	86	95:5
11	1	10	-78	1	96 ^d	97:3
12	2	10	-78	1	98 ^d	98:2

^a Determined by conversion of *N*-Sulfinyl α -Chloro Imine (R_S)-**12a**, measured by H NMR analysis.

^b Determined by NMR analysis of the reaction mixture.

^c The reaction was performed in methanol.

^d Determined by a mass balance of the reaction mixture.

(R_S,S)-*N*-(2-Chloro-2-ethyl-1-methylbutyl)-*tert*-butanesulfinamide (R_S,S)-13b****

Colorless oil, 92 %. [α]_D -72 (c 0.05, MeOH). IR (NaCl, cm⁻¹) $\nu_{\max}$: 1059, 1365, 1462, 2975, 3281. MS: m/z (M^+ +H): 254.2/256.2 (100). δ_H (300 MHz, CDCl₃): 0.97 (3H, t, *J* 7.4 Hz), 0.99 (3H, t, *J* 7.2 Hz), 1.23 (9H, s), 1.26 (3H, d, *J* 6.3 Hz), 1.65-2.03 (4H, m), 3.60 (1H, dq, *J* 6.3 Hz, 5.8 Hz), 3.83 (1H, d (broad), *J* 5.8 Hz). δ_C (75 MHz, CDCl₃): 8.6, 8.7, 17.2, 22.8, 29.7, 30.4, 55.9, 56.9, 83.3. Anal. Calcd. for C₁₁H₂₄ClNOS: C, 52.05; H, 9.53; N, 5.52. Found: C, 51.88; H, 9.61; N, 5.39.

(R_S,S)-*N*-(2-Chloro-1-phenylethyl)-*tert*-butanesulfinamide (*R_S,S*)-**13c**

Yellowish viscous oil, 95%. $[\alpha]_D -10$ (c 1.1, MeOH). IR (NaCl, cm^{-1}) ν_{max} : 1060, 1364, 1455, 1603, 2954, 3206. MS: m/z ($M^+ + H$): 260.2/262.2 (100). δ_H (300 MHz, CDCl_3): 1.25 (9H, s), 3.76 (1H, d (broad), J 4.3 Hz), 3.86 (2H, d, J 5.8 Hz), 4.69 (1H, td, J 5.8 Hz, 4.3 Hz), 7.30-7.40 (5H, m, Ph). δ_C (75 MHz, CDCl_3): 22.6, 48.5, 56.5, 59.51, 127.3, 128.6, 128.9, 139.0. Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{ClNOS}$: C, 55.48; H, 6.98; N, 5.39. Found: C, 55.37; H, 7.07; N, 5.47.

(R_S,S)-*N*-[2-Chloro-1-(4-chlorophenyl)ethyl]-*tert*-butanesulfinamide (*R_S,S*)-**13d**

Yellowish viscous oil, 94%. $[\alpha]_D -24$ (c 0.8, MeOH). IR (NaCl, cm^{-1}) ν_{max} : 1065, 1362, 1597, 2957, 3152. MS: m/z ($M^+ + H$): 294.2/296.3/298.3 (100). δ_H (300 MHz, CDCl_3): 1.24 (9H, s), 3.83 (2H, d, J 5.6 Hz), 3.93 (1H, d (broad), J 5.6 Hz), 4.67 (1H, q, J 5.6 Hz), 7.31-7.39 (4H, m). δ_C (75 MHz, CDCl_3): 22.6, 48.3, 56.6, 58.8, 128.8, 129.1, 134.5, 137.4. Anal. Calcd. for $\text{C}_{12}\text{H}_{17}\text{Cl}_2\text{NOS}$: C, 48.98; H, 5.82; N, 4.76. Found: C, 48.74; H, 5.72; N, 4.63.

(R_S,S)-*N*-[2-Chloro-1-(4-bromophenyl)ethyl]-*tert*-butanesulfinamide (*R_S,S*)-**13e**

Yellowish viscous oil, 98%. $[\alpha]_D -24$ (c 0.5, MeOH). IR (NaCl, cm^{-1}) ν_{max} : 1054, 1090, 1364, 1493, 2961, 3212. MS: m/z ($M^+ + H$): 338.0/340.0/342.0 (100). δ_H (300 MHz, CDCl_3): 1.25 (9H, s), 3.70 (2H, d, J 5.6 Hz), 3.79 (1H, d (broad), J 5.6 Hz), 4.67 (1H, q, J 5.6 Hz), 7.26-7.38 (4H, m). δ_C (75 MHz, CDCl_3): 22.6, 37.2, 56.6, 58.5, 128.7, 129.0, 134.5, 137.8. Anal. Calcd. for $\text{C}_{12}\text{H}_{17}\text{BrClNOS}$: C, 42.55; H, 5.06; N, 4.14. Found: C, 42.49; H, 4.84; N, 4.02.

General procedure for the ring closure of chiral β -halo *N*-(*tert*-butane)-sulfinamides (*R_S,S*)-10,13 to the corresponding *N*-sulfinyl aziridines (*R_S,S*)-11,14.

In a 50 mL round-bottom flask was made a solution (5 mmol) of β -halo *N*-sulfinamide **10,13** in a 1:1-mixture $\text{H}_2\text{O}/\text{THF}$ (20 mL). 3 Equivalents of KOH (0.84 g) were added to the stirred solution. The stirred mixture was warmed to reflux temperature. When

complete (16 h for **14b**; 12 h for **11a,b,14c-e**), the reaction mixture was cooled to 0 °C. The organic layer was separated and the aqueous layer was extracted with Et₂O (3 x 10 mL). The combined organic layers were dried over MgSO₄/K₂CO₃ (10:1), filtered and concentrated. Aziridines (*R_S,S*)-**11** were purified by flash chromatography. Aziridine **14b** was obtained as a pure product. All other aziridines were purified by recrystallisation from Et₂O.

(R_S)-N-(tert-Butanesulfinyl)-2,2-dimethylaziridine (R_S)-11a

Colorless oil, 95%. *R_f* 0.25 [Petroleum ether/Ethyl acetate (80:20)]. [α]_D -14 (c 0.1, MeOH). (NaCl, cm⁻¹): 1073, 1117, 1362, 1460, 2981. MS: *m/z* (*M*+*H*): 176.1 (100). δ _H (300 MHz, CDCl₃): 1.21 (9H, s), 1.28 (3H, s), 1.41 (3H, s), 1.74 (1H, s), 2.44 (1H, s). δ _C (75 MHz, CDCl₃): 19.4, 22.6, 25.8, 32.1, 39.1, 57.1. Anal. Calcd. for C₈H₁₇NOS: C, 54.81; H, 9.78; N, 7.99. Found: C, 54.70; H, 9.83; N, 8.09.

(R_S)-N-(tert-Butanesulfinyl)-2,2-diethylaziridine (R_S)-11b

Colorless oil, 95%. *R_f* 0.2 [Petroleum ether/Ethyl acetate (87:23)]. [α]_D -44 (c 0.7, MeOH). (NaCl, cm⁻¹): 1071, 1081, 1361, 1459, 2976. MS: *m/z* (*M*+*H*): 204.2 (100). δ _H (300 MHz, CDCl₃): 0.90 (3H, t, *J* 7.4 Hz), 1.03 (3H, t, *J* 7.4 Hz), 1.21 (9H, s), 1.38-1.84 (4H, m), 1.75 (1H, s), 2.39 (1H, s). δ _C (75 MHz, CDCl₃): 8.8, 10.9, 22.6, 23.3, 27.3, 30.7, 46.5, 57.5. Anal. Calcd. for C₁₀H₂₁NOS: C, 59.07; H, 10.41; N, 6.89. Found: C, 59.20; H, 10.54; N, 7.08.

(R_{S,S})-N-(tert-Butylsulfinyl)-2,2-diethyl-3-methylaziridine (R_{S,S})-14b

Colorless oil, 92%. [α]_D -80 (c 0.7, MeOH). IR (NaCl, cm⁻¹) *v*_{max}: 1071, 1362, 1463, 2988. MS: *m/z* (*M*⁺+*H*): 218.1 (100), 162.1 (30). δ _H (300 MHz, CDCl₃): 1.00 (3H, t, *J* 7.4 Hz), 1.05 (3H, d, *J* 7.4 Hz), 1.22 (9H, s), 1.23 (3H, d, *J* 5.8 Hz), 1.39 (1H, dq, *J* 14.5 Hz, *J* 7.4 Hz), 1.55-1.71 (4H, m), 2.03 (1H, dq, *J* 14.3 Hz, 7.4 Hz), 2.29 (1H, q, *J* 5.8 Hz). δ _C (75 MHz, CDCl₃): 9.4, 11.0, 13.3, 22.2, 22.9, 25.1, 45.8, 53.2, 55.8. Anal. Calcd. for C₁₁H₂₃NOS: C, 60.78; H, 10.66; N, 6.44. Found: C, 60.55; H, 10.61; N, 6.36.

(R_S,S)-*N*-(*tert*-Butylsulfinyl)-2-phenylaziridine (*R_S,S*)-**14c**

Colorless crystals (mp 104.6±0.2 °C), 90%. [α]_D +310 (c 0.6, CHCl₃). IR (KBr, cm⁻¹) ν_{max} : 1074, 1363, 1584, 2982, 3063. MS: m/z (M⁺+H): 224.2 (100). δ_{H} (300 MHz, CDCl₃): 1.18 (9H, s), 2.17 (1H, d, *J* 4.1 Hz), 2.45 (1H, d, *J* 6.9 Hz), 3.61 (1H, dd, *J* 6.9 Hz, 4.1 Hz), 7.26-7.37 (5H, m). δ_{C} (75 MHz, CDCl₃): 22.9, 31.5, 32.0, 57.0, 127.0, 128.0, 128.8, 137.3.

(R_S,S)-*N*-(*tert*-Butylsulfinyl)-2-(4-chlorophenyl)aziridine (*R_S,S*)-**14d**

Colorless crystals (mp 104.6 ± 0.2 °C), 89%. [α]_D +120 (c 0.6, MeOH). IR (KBr, cm⁻¹) ν_{max} : 1082, 1361, 1493, 1599, 2963, 3056. MS: m/z (M⁺+H): 258.2/260.2 (100), 202.2/204.2 (8). δ_{H} (300 MHz, CDCl₃): 1.17 (9H, s), 2.15 (1H, d, *J* 3.8 Hz), 2.46 (1H, d, *J* 6.9 Hz), 3.58 (1H, dd, *J* 3.8 Hz, 6.9 Hz), 7.21 and 7.31 (2 x 2H, 2 x d, *J* 8.4 Hz). δ_{C} (75 MHz, CDCl₃): 22.8, 30.8, 32.0, 57.0, 128.0, 128.9, 133.6, 135.6. Anal. Calcd. for C₁₂H₁₆ClNOS: C, 55.91; H, 6.26; N, 5.43. Found: C, 56.12; H, 6.33; N, 5.31.

(R_S,S)-*N*-(*tert*-Butylsulfinyl)-2-(4-bromophenyl)aziridine (*R_S,S*)-**14e**

Orange crystals (mp 105.3 ± 0.3 °C), 91%. [α]_D +112 (c 0.9, MeOH). IR (KBr, cm⁻¹) ν_{max} : 1081, 1361, 1476, 1587, 2961, 3054. MS: m/z (M⁺+H): 301.3/304.3 (100), 246.0/248.0 (30). δ_{H} (300 MHz, CDCl₃): 1.17 (9H, s), 2.14 (1H, d, *J* 4.0 Hz), 2.46 (1H, d, *J* 7.0 Hz), 3.56 (1H, dd, *J* 4.0 Hz, 7.0 Hz), 7.15 and 7.46 (2 x 2H, 2 x d, *J* 8.5 Hz). δ_{C} (75 MHz, CDCl₃): 22.8, 30.9, 31.9, 57.0, 121.7, 128.3, 131.8, 136.2. Anal. Calcd. for C₁₂H₁₆BrNOS: C, 47.69; H, 5.34; N, 4.63. Found: C, 47.50; H, 5.45; N, 4.72.

General procedure for the synthesis of chiral N-sulfinyl aziridines (R_S,R)-14 starting from the corresponding N-sulfinyl imines (R_S)-12.

In a flame-dried 50 mL round-bottom flask was made a 5%-solution of *N-tert*-butanesulfinyl α -halo ketimine **12** (10 mmol) in THF under nitrogen atmosphere. The stirred solution was cooled to -78 °C before 1.1 equiv of LiBHEt₃ (1 M in THF) was added dropwise. Then the reaction mixture was stirred for 1 hour at this temperature

before quenching with NH_4Cl (5 mL) and diluted with saturated aqueous KHCO_3 (20 mL) and EtOAc (20 mL). The aqueous layer was extracted with EtOAc (2 x 20 mL) and the combined organic layers were concentrated in vacuum. A 0.5 M solution in a 1:1-mixture $\text{H}_2\text{O}/\text{THF}$ (40 mL) was made of (*R_S,R*)-**13** and (*R_S,R*)-**14**. 3 Equivalents of KOH (1.68 g) were added to the stirred solution. The stirred mixture was warmed to reflux temperature. When complete (16 h for **14b**; 12 h for **11a,b,14c-e**), the reaction mixture was cooled to 0 °C. The organic layer was removed and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were dried over $\text{MgSO}_4/\text{K}_2\text{CO}_3$ (10:1), filtered and concentrated. Aziridine (*R_S,R*)-**14b** was purified by flash chromatography. All other aziridines were purified by recrystallisation from Et_2O .

(R_S,R)-*N*-(*tert*-Butylsulfinyl)-2,2-diethyl-3-methylaziridine (*R_S,R*)-**14b**

Colorless oil, 57%. R_f 0.18 [Petroleum ether/Ethyl acetate (87:23)] $[\alpha]_D$ -167 (c 0.7, MeOH). IR (NaCl, cm^{-1}) ν_{max} : 1091, 1361, 1461, 2978, 2969. MS: m/z ($\text{M}^+ + \text{H}$): 218.2 (100), 162.1 (20). δ_{H} (300 MHz, CDCl_3): 0.88 (3H, t, J 7.4 Hz), 0.89 (3H, d, J 5.8 Hz), 0.98 (3H, t, J 7.4 Hz), 1.14 (9H, s), 1.23 (1H, dq, J 14.0 Hz, J 7.4 Hz), 1.44 (1H, dq, 14.0 Hz, J 7.4 Hz), 1.56 (1H, dq, J 14.6 Hz, 7.4 Hz), 1.88 (1H, q, J 5.8 Hz), 2.10 (1H, dq, J 14.6 Hz, 7.4 Hz). δ_{C} (75 MHz, CDCl_3): 9.2, 10.9, 13.3, 22.1, 22.9, 25.0, 45.7, 53.1, 55.7. Anal. Calcd. for $\text{C}_{11}\text{H}_{23}\text{NOS}$: C, 60.78; H, 10.66; N, 6.44. Found: C, 60.99; H, 10.79; N, 6.71.

(R_S,R)-*N*-(*tert*-Butylsulfinyl)-2-phenylaziridine (*R_S,R*)-**14c**

Colorless crystals (mp 84.0 ± 0.3 °C), 62%. $[\alpha]_D$ -335 (c 0.6, CHCl_3). IR (KBr, cm^{-1}) ν_{max} : 1080, 1362, 1589, 2923, 3061. MS: m/z ($\text{M}^+ + \text{H}$): 224.2 (100). δ_{H} (300 MHz, CDCl_3): 1.30 (9H, s), 2.01 (1H, d, J 4.0 Hz), 2.99 (1H, d, J 6.9 Hz), 3.12 (1H, dd, J 6.9 Hz, 3.9 Hz), 7.24-7.30 (5H, m). δ_{C} (75 MHz, CDCl_3): 22.8, 28.6, 34.8, 57.5, 126.6, 127.7, 128.4, 137.7.

(R_S,R)-*N*-(*tert*-Butylsulfinyl)-2-(4-chlorophenyl)aziridine (*R_S,R*)-**14d**

Colorless crystals (mp 103.0 ± 0.3 °C), 66%. [α]_D -141 (c 0.6, MeOH). IR (KBr, cm⁻¹) ν_{max} : 1084, 1363, 1491, 1598, 2930. MS: m/z (M⁺+H): 258.2/260.2 (100), 202.2/204.2 (20). δ_{H} (300 MHz, CDCl₃): 1.29 (9H, s), 1.96 (1H, d, *J* 3.9 Hz), 2.99 (1H, d, *J* 6.9 Hz), 3.08 (1H, dd, *J* 3.9 Hz, 6.9 Hz), 7.22 and 7.31 (2 x 2H, 2 x d, *J* 8.7 Hz). δ_{C} (75 MHz, CDCl₃): 22.8, 28.7, 34.2, 57.5, 127.7, 128.8, 133.5, 136.2. Anal. Calcd. for C₁₂H₁₆ClNOS: C, 55.91; H, 6.26; N, 5.43. Found: C, 56.01; H, 6.39; N, 5.32.

(R_S,R)-*N*-(*tert*-Butylsulfinyl)-2-(4-bromophenyl)aziridine (*R_S,R*)-**14e**

White crystals (mp 124.2 ± 0.3 °C), 71%. [α]_D -248 (c 1.1, MeOH). IR (KBr, cm⁻¹) ν_{max} : 1064, 1082, 1362, 1487, 2981. MS: m/z (M⁺+H): 302.3/304.3 (100), 246.3/248.3 (15). δ_{H} (300 MHz, CDCl₃): 1.29 (9H, s), 1.96 (1H, d, *J* 3.7 Hz), 2.99 (1H, d, *J* 6.9 Hz), 3.07 (1H, dd, *J* 3.7 Hz, 6.9 Hz), 7.16 and 7.46 (2 x 2H, 2 x d, *J* 8.4 Hz). δ_{C} (75 MHz, CDCl₃): 22.8, 28.7, 34.2, 57.5, 121.6, 128.1, 131.6, 136.8. Anal. Calcd. for C₁₂H₁₆BrNOS: C, 47.69; H, 5.34; N, 4.63. Found: C, 47.91; H, 5.43; N, 4.58.

***N*-Deprotection of *N*-sulfinyl aziridines (*R_S,S*)-**14** and (*R_S,R*)-**14** with HCl to the corresponding *N*-deprotected aziridinium chlorides (*S*)-**17** and (*R*)-**17**, respectively**

N-*tert*-Butanesulfinyl aziridine (*R_S,S*)-**14** (5 mmol) was dissolved in dry diethyl ether (20 mL) before the flask was placed in a water bath. To the stirred solution was then added dropwise 5 mL of freshly prepared saturated dioxane.HCl. The mixture was allowed to stir for 15 minutes at room temperature before the solution was concentrated in vacuo (10 mL). The crystals were filtered and washed with Et₂O (5 mL) before drying in vacuo. Recrystallisation from Et₂O afforded analytically pure white crystals.

(*S*)-2-(4-Chlorophenyl)aziridinium chloride (*S*)-**17c**

White crystals (mp 186.8 ± 0.2 °C), 90%. [α]_D -42 (c 0.7, MeOH). IR (KBr, cm⁻¹) ν_{max} : 1408, 1490, 1589, 2210, 2953. MS: m/z (M⁺+H): 234.2/236.2/238.0 (100). δ_{H} (300 MHz,

CD₃OD): 3.52 (1H, d, *J* 6.1 Hz), 3.52 (1H, d, *J* 8.4 Hz), 5.26 (1H, dd, *J* 6.1 Hz, 8.4 Hz), 7.44 and 7.61 (2 x 2H, 2 x d, *J* 8.5 Hz). δ_{C} (75 MHz, CD₃OD): 47.2, 59.5, 124.5, 130.4, 133.3, 137.8.

(R)-2-(4-Chlorophenyl)aziridinium chloride (*R*)-**17b**

White crystals (mp 199.8 $\pm$ 0.2 °C), 86%. [α]_D +46 (c 0.8, MeOH). IR (KBr, cm⁻¹) ν_{max} : 1493, 1603, 1996, 2957. MS: *m/z* (*M*⁺+H): 190.2/192.3/194.2 (100). δ_{H} (300 MHz, CD₃OD): 3.52 (1H, d, *J* 6.0 Hz), 3.53 (1H, d, *J* 8.6 Hz), 5.27 (1H, dd, *J* 8.6 Hz, 6.0 Hz), 7.45 and 7.52 (2 x 2H, 2 x d, *J* 8.7 Hz). δ_{C} (75 MHz, CD₃OD): 47.2, 59.6, 130.1, 130.3, 136.5, 137.4.

(R)-2-(4-Chlorophenyl)aziridinium chloride (*R*)-**17c**

White crystals (mp 187.1 $\pm$ 0.2 °C), 94%. [α]_D +45 (c 0.6, MeOH). IR (KBr, cm⁻¹) ν_{max} : 1408, 1491, 1593, 2118, 2953. MS: *m/z* (*M*⁺+H): 234.2/236.2/238.0 (100). δ_{H} (300 MHz, CD₃OD): 3.52 (1H, d, *J* 6.2 Hz), 3.52 (1H, d, *J* 8.4 Hz), 5.26 (1H, dd, *J* 6.2 Hz, 8.4 Hz), 7.45 and 7.60 (2 x 2H, 2 x d, *J* 8.5 Hz). δ_{C} (75 MHz, CD₃OD): 47.2, 59.6, 124.5, 130.4, 133.4, 137.9.