Asymmetric Synthesis of Cyclopropylamines Starting from *N*-Sulfinyl α -Chloro Ketimines

Bram Denolf,[§] Sven Mangelinckx,^{§,‡} Karl W. Törnroos[‡]
and Norbert De Kimpe^{*,§}

[§] Department of Organic Chemistry, Faculty of Bioscience Engineering, Ghent
University, Coupure Links 653, B-9000 Ghent, Belgium

[‡] University of Bergen, Department of Chemistry, Allegaten 41, N-5007
Bergen, Norway

^{*} *E-mail: norbert.dekimpe@UGent.be*

Supporting Information

Table of Contents

General methods.....	S2
General procedure for synthesis of <i>N</i> -sulfinyl α -chloro ketimines (<i>R_S</i>)- 2	S2
General procedure for the synthesis of <i>N</i> -sulfinyl 1-alkyl or 1-arylcyclopropylamines 5,8,10	S3
General procedure for the synthesis of <i>N</i> -sulfinyl 2-allyl-2-methylaziridine 7,9,11	S6
Treatment of <i>N</i> -sulfinyl cyclopropylamines 5,8,10 and <i>N</i> -sulfinyl aziridines (<i>R_S</i> , <i>R</i>)- 9,11 with HCl toward the corresponding deprotected ammonium chlorides	S7
X-ray crystallography of (<i>R_S</i> , <i>S</i>)- <i>N</i> -(2,2-dimethyl-1-vinylcyclopropyl)- <i>tert</i> -butanesulfinamide [(<i>R_S</i> , <i>S</i>)- 5c]	S8
¹ H and ¹³ C NMR spectra of compounds 2,5,7-11,16-20	S9

General methods

α -Chlorinated ketones **1** were prepared as previously described.^{S1} The α -chlorinated ketones were distilled. Boiling point, ¹H and ¹³C NMR spectra are identical to literature.^{S1}

R-(+)-*tert*-Butanesulfinamide was obtained from commercial sources (Advanced Asymmetrics) in $\geq 98\%$ purity and $\geq 98\%$ ee.

General procedure for synthesis of *N*-sulfinyl α -chloro ketimines (*R_S*)-**2**

In a flame-dried 50 mL round-bottom flask was made a 0.5 M THF solution of **1a,b** (**1c** in isooctane) (11 mmol) under nitrogen atmosphere. 0.9 Equiv of *R*-(+)-*tert*-butanesulfinamide (10 mmol) and 2 equiv Ti(OEt)₄ were 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), filtrated and concentrated. The excess of ketones **1** was removed via high vacuum destillation affording the pure *N*-sulfinyl α -chloro ketimines **2**.

(*R_S*)-(-)-*N*-(2-Chloro-1,2-dimethyl-1-propylidene)-*tert*-butanesulfinamide [(*R_S*)-**2a**]

Viscous colorless oil, 91%. [α]_D -187° (c 0.15, CHCl₃). IR: 1081, 1364, 1458, 1627. MS: m/z = [M+H] 224.2/226.2 (100%). δ_{H} (300 MHz, CDCl₃) 1.25 (9H, s); 1.75 (6H, s); 2.52 (3H, s). δ_{C} (75 MHz, CDCl₃) 18.2, 22.1, 22.4, 29.8, 30.1, 57.5, 71.9, 181.1. Anal. calcd. for C₈H₁₆ClNOS: C, 48.31; H, 8.11; N, 6.26. Found: C, 48.70; H, 8.01; N, 6.47.

^{S1} De Kimpe, N.; Verhé, R. In *The chemistry of α -haloketones, α -haloaldehydes and α -haloimines*; Patai, S.; Rappoport, Z. Eds.; Wiley: New York, 1988.

(*R_S*)-(-)-*N*-(2-Chloro-2-ethyl-1-methyl-1-butylidene)-*tert*-butanesulfinamide [(*R_S*)-**2b**]

Yellow oil, 82%. [α]_D -213° (c 0.5, CHCl₃). IR: 1082, 1364, 1619. MS: *m/z* = [M+H] 251.7/253.8 (100%). δ_{H} (300 MHz, CDCl₃) 0.94 (3H, t, *J* 7.4 Hz), 0.96 (3H, t, *J* 7.4 Hz), 1.27 (9H, s), 1.93-2.15 (4H, m), 2.94 (3H, s). δ_{C} (75 MHz, CDCl₃) 9.0, 19.5, 22.4, 31.5, 32.3, 57.3, 81.1, 182.5. Anal. calcd. for C₈H₁₆ClNOS: C, 52.47; H, 8.81; N, 5.56. Found: C, 52.35; H, 9.00; N, 5.33.

(*R_S*)-(-)-*N*-(1-Chlorocyclohexyl)ethylidene)-*tert*-butanesulfinamide [(*R_S*)-**2c**]

Colorless viscous oil, 89%. [α]_D -113° (c 0.2, CHCl₃). IR: 1082, 1448, 1363, 1623, 2936. MS: *m/z* = [M+H] 264.0/266.1 (100%). δ_{H} (300 MHz, CDCl₃) 1.26 (9H, s), 1.55-1.85 (6H, m), 1.85-2.15 (4H, m), 2.49 (3H, s). δ_{C} (75 MHz, CDCl₃) 18.2, 22.1, 22.2, 22.4, 25.0, 36.5, 36.7, 57.5, 76.7, 182.3. Anal. calcd. for C₈H₁₆ClNOS: C, 54.63; H, 8.40; N, 5.31. Found: C, 54.33; H, 8.27; N, 5.16.

General procedure for the synthesis of N-sulfinyl 1-alkyl or 1-arylcyclopropylamines 5,8,10

In a flame-dried round-bottom flask was made a solution of (*R_S*)-**2** (5 mmol) in dry CH₂Cl₂ (20 mL) under nitrogen atmosphere. The stirred solution was cooled down to -78 °C before 2.2 equiv of Grignard reagent (2 M in THF) was added dropwise. The reaction mixture was stirred for 2 hours at this temperature. The temperature was raised to -40 °C and then the reaction was prolonged at this temperature for 4 hours. Then the reaction was quenched by the addition of aq NH₄Cl (5 mL) and diluted with saturated aqueous KHCO₃ (20 mL) and EtOAc (20 mL) at room temperature. The aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over MgSO₄/K₂CO₃ (10/1), filtered and concentrated to afford the *N*-sulfinyl 1-alkyl or 1-arylcyclopropylamine. The compounds were purified by flash chromatography. Compound (*R_{S,R}*)-**5a** was purified by recrystallisation (Et₂O).

(*R_{S,R}*)-*N*-(2,2-Dimethyl-1-phenylcyclopropyl)-*tert*-butanesulfinamide [(*R_{S,R}*)-**5a**]

Petroleum ether/EtOAc (80/20) + 2 % Et₃N, *R_f* 0.10. Colorless crystals (mp 91.1±0.3 °C), 57% [α]_D -115 (c 0.35, MeOH). IR: 1038, 1161, 1449, 1636, 2953, 3067, 3160. MS: *m/z* = [M+H] 266.2 (100%). δ_{H} (300 MHz, CDCl₃) 0.80 (3H, s), 0.93 (1H, d, *J*

5.2 Hz), 1.14 (9H, s), 1.19 (1H, dd, J 5.2 Hz, 4.1 Hz), 1.35 (3H, s), 3.85 (1H, s (broad)), 7.17-7.32 (5H, m). δ_{C} (75 MHz, CDCl_3) 21.1, 22.6, 24.0, 24.7, 25.8, 49.1, 55.9, 127.3, 128.6, 129.2, 141.5. Anal. calcd. for $\text{C}_{15}\text{H}_{23}\text{NOS}$: C, 67.88; H, 8.73; N, 5.28. Found: C, 67.69; H, 8.88; N, 5.16.

(R_S,R)-*N*-(1-Ethyl-2,2-dimethylcyclopropyl)-*tert*-butanesulfinamide [(*R_S,R*)-**5b**]

Petroleum ether/EtOAc (80/20) + 2 % Et_3N , R_{f} 0.08. Colorless oil, 41% $[\alpha]_{\text{D}}^{-62^\circ}$ (c 0.10, MeOH). IR: 1072, 1365, 1462, 2960, 3295. MS: m/z = $[\text{M}+\text{H}]$ 218.2 (100%). δ_{H} (300 MHz, CDCl_3) 0.49 (1H, d, J 5.1 Hz), 0.62 (1H, d, J 5.1 Hz), 1.02 (3H, t, J 7.4 Hz), 1.13 (3H, s), 1.14 (3H, s), 1.19 (9H, s), 1.43 (1H, dq, J 14.6 Hz, 7.4 Hz), 2.23 (1H, dq, J 14.6 Hz, 7.4 Hz), 3.75 (1H, s (broad)). δ_{C} (75 MHz, CDCl_3) 10.3, 21.7, 21.9, 22.7, 23.4, 26.9, 28.6, 46.5, 55.8. Anal. calcd. for $\text{C}_{11}\text{H}_{23}\text{NOS}$: C, 60.78; H, 10.66; N, 6.44. Found: C, 60.94; H, 10.80; N, 6.59.

(R_S,S)-*N*-(1-Ethyl-2,2-dimethylcyclopropyl)-*tert*-butanesulfinamide [(*R_S,S*)-**5b**]

Petroleum ether/EtOAc (80/20) + 2 % Et_3N , R_{f} 0.10. Colorless oil, 10% $[\alpha]_{\text{D}}^{-100^\circ}$ (c 0.25, MeOH). IR: 1058, 1363, 1459, 2958, 3230. MS: m/z = $[\text{M}+\text{H}]$ 218.2 (100%). δ_{H} (300 MHz, CDCl_3) 0.36 (1H, d, J 5.0 Hz), 0.91 (1H, d, J 5.0 Hz), 1.01 (3H, t, J 7.4 Hz), 1.16 (3H, s), 1.20 (3H, s), 1.22 (9H, s), 1.56 (1H, dq, J 14.1 Hz, 7.4 Hz), 1.71 (1H, dq, J 14.1 Hz, 7.4 Hz), 3.69 (1H, s (broad)). δ_{C} (75 MHz, CDCl_3) 10.3, 21.8, 22.6, 22.7, 22.9, 26.7, 29.2, 46.3, 55.8. Anal. calcd. for $\text{C}_{11}\text{H}_{23}\text{NOS}$: C, 60.78; H, 10.66; N, 6.44. Found: C, 60.64; H, 10.74; N, 6.32.

(R_S,S)-*N*-(2,2-Dimethyl-1-vinylcyclopropyl)-*tert*-butanesulfinamide [(*R_S,S*)-**5c**]

Petroleum ether/EtOAc (80/20) + 2 % Et_3N , R_{f} 0.10. Colorless crystals (mp $106.6^\circ\text{C} \pm 0.2^\circ\text{C}$), 62% $[\alpha]_{\text{D}}^{-73^\circ}$ (c 0.4, MeOH). IR: 1057, 1364, 1458, 1636, 2953, 3215. MS: m/z = $[\text{M}+\text{H}]$ 216.2 (100%). δ_{H} (300 MHz, CDCl_3) 0.86 (1H, d, J 5.5 Hz), 0.97 (1H, dd, J 5.5 Hz, 1.1 Hz), 1.08 (3H, s), 1.20 (3H, s), 1.21 (9H, s), 3.82 (1H, s (broad)), 5.20 (1H, dd, J 10.7 Hz, 1.1 Hz), 5.35 (1H, dd, J 17.2 Hz, 1.1 Hz), 5.92 (1H, dd, J 17.2 Hz, 10.7 Hz). δ_{C} (75 MHz, CDCl_3) 21.2, 22.0, 22.7, 25.9, 26.6, 47.0, 55.9, 115.0, 139.0. Anal. calcd. for $\text{C}_{11}\text{H}_{21}\text{NOS}$: C, 61.35; H, 9.83; N, 6.50. Found: C, 61.49; H, 9.66; N, 6.47.

(R_S,R)-*N*-(2,2-Diethyl-1-phenylcyclopropyl)-*tert*-butanesulfinamide [(*R_S,R*)-**8a**]

Petroleum ether/EtOAc (80/20) + 2 % Et_3N , R_{f} 0.12. Pale white highly viscous oil, 38% $[\alpha]_{\text{D}}^{-78^\circ}$ (c 0.3, MeOH). IR: 1054, 1363, 1458, 1496, 2963, 3064, 3176. MS: m/z = $[\text{M}+\text{H}]$ 294.2 (100%). δ_{H} (300 MHz, CDCl_3) 0.44 (1H, dq, J 14.5 Hz, 7.4 Hz), 0.79 (3H, t, J 7.4 Hz), 0.93 (1H, d, J 5.2 Hz), 1.03 (3H, t, J 7.4 Hz), 1.14 (9H, s), 1.19 (1H, d, J 5.2 Hz), 1.37-1.90 (3H, m), 3.78 (1H, s (broad)), 7.20-7.36 (5H, m). δ_{C} (75 MHz, CDCl_3) 10.6, 11.3, 22.6, 22.8, 24.0, 25.4, 34.7, 50.4, 55.8, 127.2, 128.6, 129.1, 141.4. Anal. calcd. for $\text{C}_{17}\text{H}_{27}\text{NOS}$: C, 69.58; H, 9.27; N, 5.45. Found: C, 69.44; H, 9.19; N, 5.56. ESI-HRMS: Calcd. for $\text{C}_{17}\text{H}_{27}\text{NOS}-\text{H}^+$: 294.18861. Found 294.18873.

(R_S,R)-*N*-(2,2,3-Triethylcyclopropyl)-*tert*-butanesulfinamide [(*R_S,R*)-**8b**]

Petroleum ether/EtOAc (80/20) + 2 % Et₃N, R_f 0.11. Pale white highly viscous oil, 30% [α]_D -58° (c 0.3, MeOH). IR: 1061, 1364, 1461, 2963, 3235. MS: m/z = [M+H] 246.3 (100%). δ_{H} (300 MHz, CDCl₃) 0.45 (1H, d, *J* 5.2 Hz), 0.62 (1H, d, *J* 5.2 Hz), 0.86 (3H, t, *J* 7.4 Hz), 0.91 (3H, t, *J* 7.2 Hz), 1.01 (3H, t, *J* 7.4 Hz), 1.19 (9H, s), 1.06-2.27 (6H, m), 3.75 (1H, s (broad)). δ_{C} (75 MHz, CDCl₃) 10.2, 11.1, 11.2, 22.7, 22.8, 23.3, 25.1, 28.1, 33.8, 47.7, 55.7. Anal. calcd. for C₁₃H₂₇NOS: C, 63.62; H, 11.09; N, 5.71. Found: C, 63.42; H, 10.87; N, 5.54.

(R_S,S)-*N*-(2,2-Diethyl-1-vinylcyclopropyl)-*tert*-butanesulfinamide [(*R_S,S*)-**8c**]

Petroleum ether/EtOAc (80/20) + 2 % Et₃N, R_f 0.10. Yellow oil, 37% [α]_D -79° (c 0.3, MeOH). IR: 1062, 1363, 1459, 1635, 2965, 3207. MS: m/z = [M+H] 244.5 (100%). δ_{H} (300 MHz, CDCl₃) 0.80 (1H, d, *J* 5.2 Hz), 0.85 (3H, t, *J* 7.4 Hz), 0.91 (3H, t, *J* 7.4 Hz), 0.93 (1H, d, *J* 5.2 Hz), 1.20 (9H, s), 1.21-1.65 (4H, m), 3.77 (1H, s (broad)), 5.19 (1H, dd, *J* 10.7 Hz, 1.1 Hz), 5.31 (1H, dd, *J* 17.1 Hz, 1.1 Hz), 5.99 (1H, dd, *J* 17.1 Hz, 10.7 Hz). δ_{C} (75 MHz, CDCl₃) 10.7, 10.9, 22.7, 22.8, 23.7, 24.9, 35.9, 48.0, 55.9, 115.1, 139.0. Anal. calcd. for C₁₃H₂₅NOS: C, 64.15; H, 10.35; N, 5.75. Found: C, 64.01; H, 10.54; N, 5.62.

(R_S,R)-*N*-(1-Phenylspiro[2.5]oct-1-yl)-*tert*-butanesulfinamide [(*R_S,R*)-**10a**]

Petroleum ether/EtOAc (75/25) + 2 % Et₃N, R_f 0.17. White highly viscous oil, 31% [α]_D -80° (c 0.1, MeOH). IR: 1055, 1362, 1447, 1604, 2925, 3061, 3161. MS: m/z = [M+H] 306.3 (100%). δ_{H} (300 MHz, CDCl₃) 0.72 (1H, d, *J* 5.5 Hz), 0.88 (1H, d, *J* 5.5 Hz), 1.13 (9H, s), 1.19-1.76 (10H, m), 3.83 (1H, s (broad)), 7.19-7.34 (5H, m). δ_{C} (75 MHz, CDCl₃) 22.6, 24.1, 25.1, 26.0, 26.2, 31.1, 31.9, 33.5, 49.6, 55.8, 127.2, 128.4, 129.1, 141.2. Anal. calcd. for C₁₈H₂₇NOS: C, 70.77; H, 8.91; N, 4.59. Found: C, 70.59; H, 8.99; N, 4.45.

(R_S,R)-*N*-(1-Ethylspiro[2.5]oct-1-yl)-*tert*-butanesulfinamide [(*R_S,R*)-**10b**]

Petroleum ether/EtOAc (75/25) + 2 % Et₃N, R_f 0.15. Colorless viscous oil, 23% [α]_D -81° (c 0.1, MeOH). IR: 1059, 1364, 1446, 2927, 3247. MS: m/z = [M+H] 258.2 (100%). δ_{H} (300 MHz, CDCl₃) 0.44 (1H, d, *J* 5.1 Hz), 0.59 (1H, d, *J* 5.1 Hz), 1.03 (3H, t, *J* 7.4 Hz), 1.19 (9H, s), 1.14-1.69 (11H, m), 2.18 (1H, dq, 14.7 Hz, 7.4 Hz), 3.11 (1H, s (broad)). δ_{C} (75 MHz, CDCl₃) 10.4, 22.8, 24.9, 25.7, 25.9, 26.4, 27.9, 31.0, 31.6, 46.9, 55.7. Anal. calcd. for C₁₄H₂₇NOS: C, 65.32; H, 10.57; N, 5.44. Found: C, 65.11; H, 10.41; N, 5.59.

(R_S,R)-(-)-*N*-(1-Allylspiro[2.5]oct-1-yl)-*tert*-butanesulfinamide [(*R_S,R*)-**10d**]

Petroleum ether/EtOAc (85/15) + 2 % Et₃N, R_f 0.11. Colorless highly viscous oil, 2% [α]_D -87° (c 0.4, MeOH). IR: 1061, 1364, 1447, 1638, 2927, 3076, 3293. MS: m/z = [M+H] 270.2 (100%). δ_{H} (300 MHz, CDCl₃) 0.52 (1H, d, *J* 5.2 Hz), 0.74 (1H, d, *J* 5.2 Hz), 1.18 (9H, s), 1.13-1.65 (10H, m), 2.16 (1H, m), 2.95 (1H, dd, *J* 14.9 Hz, *J* 8.8 Hz), 3.92 (1H, s (broad)), 5.17-5.26 (2H, m), 5.76-5.90 (1H, m). δ_{C} (75 MHz, CDCl₃) 22.9, 23.8, 25.7, 25.8, 26.4, 31.1, 31.5, 32.1, 39.8, 45.0, 55.9, 119.2, 134.8.

General procedure for the synthesis of N-sulfinyl 2-allyl-2-methylaziridine 7,9,11

In a flame-dried round-bottom flask was prepared a solution of (*R_S*)-**2** (5 mmol) in dry CH₂Cl₂ (20 mL) under nitrogen atmosphere. The stirred solution was cooled to – 78 °C before 1.05 equiv of AllylMgCl (1 M in THF) was added drop wise. The reaction mixture was stirred 5-6 hours at this temperature. Then the reaction was quenched by the addition of aq NH₄Cl (5 mL) and diluted with saturated aqueous KHCO₃ (20 mL) and EtOAc (20 mL) at room temperature. The aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were dried over MgSO₄/K₂CO₃ (10/1), filtered and concentrated to afford the *N*-sulfinyl 2-allyl-2-methylaziridine **7,9,11**. *N*-Sulfinyl aziridines **9,11** were purified by flash chromatography.

(R_S,R)-(-)-N-(tert-Butylsulfinyl)-2-allyl-2,3,3-trimethylaziridine [(R_S,R)-7]

Colorless oil, 95% [α]_D -85° (c 1.5, MeOH). IR: 1074, 1362, 1457, 1640, 2959, 3077. MS: m/z = [M+H] 230.2 (100%). δ _H (300 MHz, CDCl₃) 1.21 (12H, s), 1.43 (6H, s), 2.48 (2H, d, *J* 5.2 Hz), 5.06-5.16 (2H, m), 5.83-5.95 (1H, m). δ _C (75 MHz, CDCl₃ (45 °C)) 17.3, 21.5, 22.8, 40.3, 48.9, 50.6, 56.1, 117.7, 134.5. Anal. calcd. for C₁₂H₂₃NOS: C, 62.83; H, 10.11; N, 6.11. Found: C, 62.62; H, 9.93; N, 6.30.

(R_S,R)-(-)-N-(tert-Butylsulfinyl)-2-allyl-3,3-diethyl-2-methylaziridine [(R_S,R)-9]

Petroleum ether/EtOAc (75/25) + 2 % Et₃N, R_f 0.20. Colorless highly viscous oil, 84% [α]_D -73° (c 0.3, MeOH). IR: 1077, 1360, 1459, 1477, 1640, 2977, 3078. MS: m/z = [M+H] 258.5 (100%). δ _H (300 MHz, CDCl₃) 0.98 (3H, t, *J* 7.4 Hz), 1.00 (3H, t, *J* 7.4 Hz), 1.24 (9H, s), 1.47 (1H, dq, *J* 14.3 Hz, 7.4 Hz), 1.53 (1H, dq, *J* 14.3 Hz, 7.4 Hz), 1.53 (3H, s), 1.85-2.03 (2H, m), 2.30 (1H, dd, *J* 14.5 Hz, 5.8 Hz), 2.47 (1H, dd, *J* 14.5 Hz, 7.8 Hz), 5.09-5.16 (2H, m), 5.66-5.80 (1H, m). δ _C (75 MHz, CDCl₃) 9.7, 10.4, 16.4, 21.6, 22.9, 23.0, 41.9, 53.6, 54.1, 56.7, 118.0, 133.9. Anal. calcd. for C₁₄H₂₇NOS: C, 65.32; H, 10.57; N, 5.44. Found: C, 65.47; H, 10.69; N, 5.29.

(R_S,R)-(-)-N-(tert-Butylsulfinyl)-2-allyl-2-methyl-1-azaspiro[2.5]octane [(R_S,R)-11]

Petroleum ether/EtOAc (85/15) + 2 % Et₃N, R_f 0.15. Colorless highly viscous oil, 65% [α]_D -107° (c 0.3, MeOH). IR: 1077, 1360, 1455, 1476, 1640, 2927, 3076. MS: m/z = [M+H] 270.0 (100%). δ _H (300 MHz, CDCl₃) 1.23 (9H, s), 1.48 (3H, s), 1.40-1.84 (10H, m), 2.41 (1H, dd, *J* 14.4 Hz, 6.9 Hz), 2.50 (1H, dd, *J* 14.4 Hz, 7.4 Hz), 5.08-

5.17 (2H, m), 5.76-5.94 (1H, m). δ_C (75 MHz, $CDCl_3$) 16.6, 22.7, 25.5, 25.6, 25.9, 31.1, 31.7, 40.7, 52.0, 53.3, 56.3, 117.1, 134.4. Anal. calcd. for $C_{15}H_{27}NOS$: C, 66.86; H, 10.10; N, 5.20. Found: C, 66.60; H, 10.18; N, 5.42.

Treatment of N-sulfinyl cyclopropylamines 5,8,10 and N-sulfinyl aziridines (R_s,R)-9,11 with HCl toward the corresponding deprotected ammonium chlorides

In a 50 mL round-bottom flask equipped with a magnetic stirring bar was prepared a solution (5 mmol) of compound **5,8,10** or (R_s,R)-**9,11** in dry diethylether (20 mL). The flask was placed in a water bath before the dry, freshly prepared saturated dioxane.HCl was added (dropwise). The mixture was allowed to stir for several minutes (15 min). Then the reaction mixture was filtered. The crystals were washed with Et₂O (5 mL) and placed under vacuo for a few minutes.

(2R)-2-Allyl-3,3-diethyl-2-methylaziridinium chloride [(R)-16]

White crystals (mp 136.9±0.5 °C), 84%. $[\alpha]_D +6.0^\circ$ (c 0.2, MeOH). IR: 1403, 1461, 1643, 2577, 2977, 3118. MS: m/z = [M+H] 154.3 (100%). δ_H (300 MHz, CD_3OD) 0.97 (3H, t, *J* 7.4 Hz), 1.00 (3H, t, *J* 7.4 Hz), 1.31 (3H, s), 1.40-1.84 (4H, m), 2.30-2.48 (2H, m), 5.10-5.17 (2H, m), 5.76-5.90 (1H, m). δ_C (75 MHz, CD_3OD) 10.0, 10.1, 18.2, 23.3, 24.0, 39.8, 48.4, 53.2, 118.8, 134.9.

(2R)-2-Allyl-2-methyl-1-azoniaspiro[2.5]octane chloride [(R)-17]

White crystals (mp 144.4±0.3 °C), 86%. $[\alpha]_D +2.7^\circ$ (c 0.2, MeOH). IR: 937, 1445, 1644, 2088, 2574, 2932, 3436. MS: m/z = [M+H] 166.0 (100%). δ_H (300 MHz, CD_3OD) 1.53 (3H, s), 1.42-1.95 (10H, m), 2.56 (1H, dd, *J* 14.9 Hz, 6.9 Hz), 2.64 (1H, dd, *J* 14.9 Hz, 6.6 Hz), 5.24-5.31 (2H, m), 5.78-5.91 (1H, m). δ_C (75 MHz, CD_3OD) 15.8, 25.3, 25.4, 25.8, 29.1, 29.4, 37.1, 53.8, 56.1, 120.8, 132.4.

(1R)-2,2-Dimethyl-1-phenylcyclopropanaminium chloride [(R)-18a]

White crystals (mp 216.7±0.3 °C), 93%. $[\alpha]_D +7.1^\circ$ (c 0.3, MeOH). IR: 699, 1448, 2235, 2980, 3435. MS: m/z = 162.2 [M+H] (100%). δ_H (300 MHz, CD_3OD) 0.82 (3H, s), 1.18 (1H, d, *J* 6.6 Hz), 1.36 (1H, d, *J* 6.6 Hz), 1.47 (3H, s), 7.37-7.50 (5H, m). δ_C (75 MHz, CD_3OD) 20.2, 22.8, 23.0, 23.7, 46.0, 130.3, 130.6, 136.7

(1*R*)-1-Ethyl-2,2-dimethylcyclopropanaminium chloride [(*R*)-**18b**]

White crystals (carbonization when heated >115 °C), 96%. [α]_D +5.9° (c 0.1, MeOH). IR: 1183, 1465, 1520, 2179, 2974, 3401. MS: m/z = [M+H] 114.1 (100%). δ_H (300 MHz, CD₃OD) 0.62 (1H, d, J 6.3 Hz), 0.79 (1H, d, J 6.3 Hz), 1.08 (3H, t, J 7.4 Hz), 1.21 (3H, s), 1.27 (3H, s), 1.61 (1H, dq, J 15.6 Hz, 7.4 Hz), 1.97 (1H, dq, J 15.6 Hz, 7.4 Hz). δ_C (75 MHz, CD₃OD) 9.1, 19.6, 20.1, 20.3, 22.8, 25.4, 42.3.

(1*S*)-2,2-Diethyl-1-phenylcyclopropanaminium chloride [(*R*)-**19a**]

White crystals (carbonization when heated > 110 °C), 91%. [α]_D +6.3° (c 0.2, MeOH). IR: 1130, 1451, 1528, 2664, 2969, 3369. MS: m/z = [M+H] 190.3 (100%). δ_H (300 MHz, CD₃OD) 0.80 (3H, t, J 7.4 Hz), 1.07 (1H, d, J 6.9 Hz), 1.14 (3H, t, J 7.4 Hz), 1.36 (1H, d, J 6.9 Hz), 1.64-1.86 (4H, m), 7.39-7.49 (5H, m). δ_C (75 MHz, CD₃OD) 10.1, 11.0, 21.3, 23.0, 26.0, 32.9, 47.4, 130.1, 130.2, 130.6, 136.4.

(1*R*)-1-phenylspiro[2.5]octan-1-aminium chloride [(*R*)-**20a**]

White crystals (carbonization when heated > 50 °C), 90%. [α]_D +5.7° (c 0.1, MeOH). IR: 1195, 1449, 1534, 2676, 1929, 3411. MS: m/z = [M+H] 202.2 (100%). δ_H (300 MHz, CD₃OD) 0.62 (1H, d, J 6.6 Hz), 1.35 (1H, d, J 6.6 Hz), 1.26-1.94 (10H, m), 7.38-7.50 (5H, m). δ_C (75 MHz, CD₃OD) 21.3, 21.6, 26.4, 26.8, 29.9, 30.9, 34.2, 46.4, 130.0, 130.5, 136.4.

X-ray crystallography of (R_S,S)-N-(2,2-dimethyl-1-vinylcyclopropyl)-tert-butanesulfinamide [(R_S,S)-5c]

¹H and ¹³C NMR spectra of compounds 2,5,7-11,16-20

¹H and ¹³C NMR spectra of compounds 2,5,7-11,16-20

^1H and ^{13}C NMR spectra of compounds 2,5,7-11,16-20

¹H and ¹³C NMR spectra of compounds 2,5,7-11,16-20

^1H and ^{13}C NMR spectra of compounds 2,5,7-11,16-20

^1H and ^{13}C NMR spectra of compounds 2,5,7-11,16-20

^1H and ^{13}C NMR spectra of compounds 2,5,7-11,16-20

^1H and ^{13}C NMR spectra of compounds 2,5,7-11,16-20

^1H and ^{13}C NMR spectra of compounds 2,5,7-11,16-20

¹H and ¹³C NMR spectra of compounds 2,5,7-11,16-20

¹H and ¹³C NMR spectra of compounds 2,5,7-11,16-20

¹H and ¹³C NMR spectra of compounds 2,5,7-11,16-20

^1H and ^{13}C NMR spectra of compounds 2,5,7-11,16-20

¹H and ¹³C NMR spectra of compounds 2,5,7-11,16-20

¹H and ¹³C NMR spectra of compounds 2,5,7-11,16-20

¹H and ¹³C NMR spectra of compounds 2,5,7-11,16-20

^1H and ^{13}C NMR spectra of compounds 2,5,7-11,16-20

¹H and ¹³C NMR spectra of compounds 2,5,7-11,16-20

^1H and ^{13}C NMR spectra of compounds 2,5,7-11,16-20

¹H and ¹³C NMR spectra of compounds 2,5,7-11,16-20

¹H and ¹³C NMR spectra of compounds 2,5,7-11,16-20

^1H and ^{13}C NMR spectra of compounds 2,5,7-11,16-20