Electronic Supplementary Information

Asymmetric Olefin Aziridination Using a Newly Designed Ru(CO)(salen) Complex as Catalyst

Chungsik Kim, Tatsuya Uchida and Tsutomu Katsuki*

Department of Chemistry, Faculty of Science, Graduate School, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.
International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan.
1. General

$^1$H and $^{13}$C NMR spectra were recorded at JEOL JNM–AL–400 spectrometer at 400 and 270 MHz, respectively. All signals were expressed as ppm downfield from tetramethylsilane used as an internal standard ($\delta$–value in CDCl$_3$). Optical rotations were measured with a JASCO P–1020 polarimeter. Enantiomeric excesses were determined by HPLC analysis using SHIMADZU LC–10AT–VP equipped with a chiral stationary phase. Column chromatography was conducted on a silica gel 60N (spherical, neutral), 63–210 mm, available from Kanto Chemical Co., Inc., or a Chromatorex® NH (spherical, basic), 100–200 mm, available from Fuji Silysia Chemical LTD.

Ru(CO)(salen) complex 3,$^1$ and 2-(trimethylsilyl)ethanesulfonyl azide (SESN)$_3$$^{1,2}$) were prepared according to the literatures.

1.1. Scheme for the synthesis of Ru(CO)(salen) complexes$^1$

\[
\begin{align*}
\text{Ar} &= 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3 \\
\text{OH} \quad \text{OH} &\quad \text{aR} \quad \text{OH} \quad \text{OMOM} \quad \text{CH} = \text{CHO} \quad \text{OP(O)(OEt)}_2 \\
\text{OMOM} \quad \text{OMOM} &\quad \text{OH} \quad \text{Ar} \quad \text{Ar} \\
\end{align*}
\]

a) diisopropylethylamine, MOMCl, CH$_2$Cl$_2$, 0°C, 82%; b) n-BuLi, THF, -78°C; ClP(O)(OEt)$_2$, 76%; c) Li/naphthalene, THF, -78°C, 1,2-dibromoethane, THF, -78°C to r.t., 60%; d) Pd(PPh$_3$)$_4$ (5 mol %), 3,5-bis(trifluoromethyl)phenylboronic acid, 1M Na$_2$CO$_3$, toluene, reflux, 70%; e) TMEDA, n-BuLi, -78°C, DMF, THF, 65%; f) HCl/iPrOH (20%, w/w), THF, 99%; g) (1R, 2R)-diphenyl-1,2-diamine, EtOH, reflux, 95%; h) Ru$_3$(CO)$_{12}$, EtOH, N$_2$, 65%.

1.2 Synthesis of (aR, R)-Ru(CO)(salen) complex 3 $^{1b}$

A solution of salen ligand (170 mg, 0.14 mmol) and triruthenium dodecacarbonyl (Ru$_3$(CO)$_{12}$, 180 mg, 2 eq) in dehydrated EtOH (6 mL) was refluxed under argon atmosphere for 48 h. The mixture was evaporated and subjected to chromatography on silica gel (hexanes/ethyl acetate = 4:1) to give 3 as a reddish-brown solid (122 mg, 65 % yield); IR (KBr) 3423, 3055, 1944, 1658, 1608, 1577,
1546, 1494, 1479, 1425, 1384, 1324, 1278, 1180, 1132, 1091, 954, 894, 815, 748, 705, 680, 536 cm⁻¹; HRMS (ESI-TOF): Ru(CO)(salen) m/z [M+H⁺] Calcd for [C₇₃H₄₃F₁₂N₂O₃Ru]⁺: 1324.2062; Found: 1324.2046; elemental analysis: Calcd (%) for C₇₃H₄₂F₁₂N₂O₃Ru•1.5H₂O: C 64.04, H 3.46, N 2.05; Found: C 64.00, H 3.59, N 1.97

2. Solvent screening

\[
\text{condition: M.S. 4A (50 mg), solvent (0.4 mL), r.t. to 40°C, 3 mol\% catalyst loading}
\]

<table>
<thead>
<tr>
<th>solvents</th>
<th>yield</th>
<th>ee</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃</td>
<td>54 %</td>
<td>88%</td>
</tr>
<tr>
<td>EtOAc</td>
<td>51 %</td>
<td>88%</td>
</tr>
<tr>
<td>Toluene</td>
<td>54 %</td>
<td>90%</td>
</tr>
<tr>
<td>DCM</td>
<td>81 %</td>
<td>90%</td>
</tr>
</tbody>
</table>

3. Ru(CO)(salen) 3 – catalyst loading

\[
\text{condition: M.S. 4A (30 mg), DCM (0.2 mL), r.t., 6 hr}
\]

<table>
<thead>
<tr>
<th>catalyst amount</th>
<th>yield</th>
<th>ee</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 mol %</td>
<td>99 %</td>
<td>90%</td>
</tr>
<tr>
<td>2 mol %</td>
<td>99 %</td>
<td>90%</td>
</tr>
<tr>
<td>1 mol %</td>
<td>99 %</td>
<td>90%</td>
</tr>
<tr>
<td>0.5 mol %</td>
<td>99 %</td>
<td>90%</td>
</tr>
<tr>
<td>0.1 mol %</td>
<td>57 %</td>
<td>90%</td>
</tr>
</tbody>
</table>

\(^a\) Isolated yield.
4. Asymmetric aziridination of alkenes

4.1. Typical experiment for asymmetric aziridination of alkenes using a combination of Ru(CO)(salen) complex 3 with SESN3.

A dried Schlenk tube was charged with 4Å MS (50 mg) and then additionally dried with a heat gun for 10 min. The Schlenk tube was then evacuated, backfilled with nitrogen and equipped with a magnetic stir bar. To the Schlenk tube, were added Ru(CO)(salen) complex 3 (0.5 ~ 3 mol%) and 0.4 ml of solvent, followed by olefins (0.36 ~ 0.9 mmol) and the azide (0.3 mmol) at room temperature. After stirred for another 6 ~ 24 h, the mixture was filtered through a Celite pad. Evaporation of the resulting solution and chromatographic separation on silica gel (Hexane/AcOEt=10/1 ~ 5/1) gave the corresponding aziridination compounds.

4.2. (2S)-2-(Phenyl)-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 1, entry 2)

![Chemical Structure]

Colorless oil (99%); 90% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/i-PrOH=97/03, 1.0mL/min), tR (Major)=15.0 min, tR (Minor)=21.4 min]; [α]D27.1 = +124.1 (c = 1.35, CDCl3); {[α]D25 = +115 (c = 1.3, CDCl3)}1a) 1H NMR (CDCl3, 400 MHz): δ 7.21-7.32 (m, 5H), 3.65 (dd, J = 4.4, 4.4 Hz, 1H), 3.05-3.10 (m, 2H), 2.92 (d, J = 6.8 Hz, 1H), 2.37 (d, J = 4.4 Hz, 1H), 1.06-1.11 (m, 2H), -0.017 (s, 9H); 13C NMR (CDCl3, 100 MHz): δ 135.2, 128.7, 128.4, 126.5, 49.1, 40.5, 35.1, 9.7, -2.1 ppm.; HRMS [ESI-TOF] ([M + Na]+) Calcd for C13H21NO2SSi: 306.0954; Found: 306.0960.

4.3. 2-Butyl-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 2, entry 1)

![Chemical Structure]

Colorless oil (74%); >99% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL WHELK-O1 (Hexane/i-PrOH=97/03, 1.0 mL/min), tR (Major)=10.6]; [α]D23 = +20.0 (c 0.83, CHCl3); 1H NMR (CDCl3, 400 MHz): δ 3.03-3.08 (m, 2H), 2.70-2.72 (m, 1H), 2.58 (d, J = 6.8 Hz, 1H), 2.05 (d, J = 5.2 Hz, 1H), 1.33-1.57 (m, 6H), 1.11-1.14 (m,
2H), 0.91 (t, J=6.8 Hz, 3H), 0.05 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 45.8, 39.1, 33.6, 31.2, 28.9, 22.8, 14.0, 9.7, -2.1 ppm.; HRMS [ESI-TOF] ([M + Na]$^+$) Calcd for C$_{11}$H$_{25}$NO$_2$SSi: 286.1267; Found: 286.1266.

4.4. 2-Cyclohexyl-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 2, entry 2)

![Chemical Structure Image]

Colorless oil (45%); >99% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL WHELK-O1 (Hexane/i-PrOH=99/01, 1.0 mL/min), t$_r$ (Major)=13.8 min]; $[\alpha]_D^{22} = +18.47$ (c 1.12, CHCl$_3$); $^1$H NMR (CDCl$_3$, 400 MHz): δ 3.00-3.06 (m, 2H), 2.50-2.54 (m, 2H), 2.21 (d, J=4.4 Hz, 1H), 1.63-1.80 (m, 5H), 1.11-1.23 (m, 8H), 0.04 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 48.6, 43.8, 39.4, 32.3, 30.4, 29.7, 26.0, 25.6, 25.4, 9.7, -2.0 ppm.; HRMS [ESI-TOF] ([M + Na]$^+$) Calcd for C$_{13}$H$_{27}$NO$_2$SSi: 312.1426; Found: 312.1460.

4.5. 2-(5-Methylhex-4-en-1-yl)-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 2, entry 3)

![Chemical Structure Image]

Colorless oil (54%); 89% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/i-PrOH=97/03, 1.0 mL/min), t$_r$ (Major)=6.3 min, t$_r$ (Minor)=7.4 min]; $[\alpha]_D^{22} = +8.94$ (c 0.96, CHCl$_3$); $^1$H NMR (CDCl$_3$, 400 MHz): δ 4.99-5.05 (m, 1H), 2.96-3.03 (m, 2H), 2.63-2.67 (m, 1H), 2.52 (d, J=10.4 Hz, 1H), 2.00 (d, J=4.28 Hz, 1H), 1.61 (s, 3H), 1.53 (s, 3H), 1.38-1.51 (m, 6H), 1.04-1.11 (m, 2H), 0.00 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 132.2, 123.8, 48.4, 39.0, 33.4, 30.9, 27.4, 26.9, 25.7, 17.7, 9.8, -2.1 ppm.; HRMS [ESI-TOF] ([M + Na]$^+$) Calcd for C$_{14}$H$_{29}$NO$_2$SSi: 325.1580; Found: 326.1238.

4.6. 2-Butyl-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 2, entry 4)

![Chemical Structure Image]
Colorless oil (58%); 91% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/i-PrOH=97/03, 1.0 mL/min), t_r (Major)=6.41 min, t_r (Minor)=7.1 min]; [α]_D^{24} = +25.8 (c 1.72, CHCl_3); ^1H NMR (CDCl_3, 400 MHz): δ 5.56-5.62 (m, 1H), 5.40-5.46 (m, 1H), 3.03-3.08 (m, 2H), 2.71-2.76 (m, 1H), 2.60 (d, J=8.0 Hz, 1H), 2.18-2.28 (m, 2H), 2.10 (d, J=4 Hz, 1H), 1.68 (dd, J=8.0 Hz, 3H), 1.11-1.15 (m, 2H), 0.07 (s, 9H); ^13C NMR (CDCl_3, 100 MHz): δ 128.8, 125.4, 48.3, 39.2, 34.3, 32.3, 18.0, 9.6, -2.1 ppm.; HRMS [ESI-TOF] ([M + Na]^+) Calcd for C_{11}H_{23}NO_2SiS: 284.1111; Found: 284.1164.

4.7. 2-Benzyl-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 2, entry 6)

\[
\begin{align*}
\text{O} & \quad \text{SiMe}_3 \\
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{S} \\
\text{O} & \quad \text{SiMe}_3 \\
\end{align*}
\]

Colorless oil (91%); 90% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/i-PrOH=97/03, 1.0 mL/min), t_r (Major)=16.9 min, t_r (Minor)=24.1 min]; [α]_D^{22} = +19.2 (c 0.76, CHCl_3); ^1H NMR (CDCl_3, 400 MHz): δ 7.22-7.30 (m, 5H), 2.70-2.98 (m, 3H), 2.60-2.68 (m, 3H), 2.17 (d, J=4.4 Hz, 1H), 0.85-1.02 (m, 2H), -0.05 (s, 9H); ^13C NMR (CDCl_3, 100 MHz): δ 137.2, 128.9, 128.7, 127.1, 48.4, 40.9, 37.7, 32.3, 8.9, -2.1 ppm.; HRMS [ESI-TOF] ([M + Na]^+) Calcd for C_{14}H_{23}NO_2Si: 320.1111; Found: 320.1122.

4.8. 2-(4-Bromobutyl)-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 2, entry 6)

\[
\begin{align*}
\text{Br} & \quad \text{N} \\
\text{O} & \quad \text{S} \\
\text{O} & \quad \text{SiMe}_3 \\
\end{align*}
\]

Colorless oil (95%); 91% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL WHELK-O1 (Hexane/i-PrOH=97/03, 1.0 mL/min), t_r (Major)=35.5 min, t_r (Minor)=42.4 min]; [α]_D^{22} = +14.7 (c 0.68, CHCl_3); ^1H NMR (CDCl_3, 400 MHz): δ 3.42 (t, J=8.0 Hz, 3H), 3.04-3.09 (m, 2H), 2.73 (m, 1H), 2.59 (d, J=8.0 Hz, 1H), 2.10 (d, J=4.4 Hz, 1H), 1.91-1.93 (m, 2H), 1.61-1.65 (m, 4H), 1.11-1.16 (m, 2H), 0.07 (s, 9H); ^13C NMR (CDCl_3, 100 MHz): δ 48.9, 38.3, 33.6, 33.2, 31.9, 30.5, 25.4, 9.7, -2.04 ppm.; HRMS [ESI-TOF] ([M + Na]^+) Calcd for C_{14}H_{24}BrNO_2SiS: 364.0373; Found: 364.0384.
4.9. 2-[3-(Benzyloxy)propyl]-1-[2-(trimethylsilyl)ethane sulfonyl]aziridine (Table 2, entry 7)

![Chemical Structure]

Colorless oil (65%); 87% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/i-PrOH=75/95, 1.0 mL/min), \( t_r (\text{Major}) = 25.8 \) min, \( t_r (\text{Minor}) = 29.3 \) min]; \([\alpha]_D^{22} = +17.64 (c 0.8, \text{CHCl}_3); 1^H \text{NMR (CDCl}_3, 270 \text{ MHz)}: \delta 7.23-7.32 (m, 5H), 4.46 (s, 2H), 3.45 (t, \( J = 6.0 \) Hz, 2H), 2.99-3.06 (m, 2H), 2.67 (m, 1H), 2.55 (d, \( J = 6.8 \) Hz, 1H), 2.04 (d, \( J = 4.3 \) Hz, 1H), 2.00-2.05 (m, 6H), 1.07-1.14 (m, 2H), 0.03 (s, 9H).; 13C \text{NMR (CDCl}_3, 100 \text{ MHz)}: \delta 138.5, 128.4, 127.6, 127.5, 72.9, 69.9, 48.8, 38.8, 33.5, 31.2, 29.3, 23.6, 9.7 -2.1 ppm.; HRMS [ESI-TOF] ([M + Na]^+) Calcd for C\text{18}H\text{31}NO\text{3}SSi: 392.1686; Found: 392.1714.

4.10. 2-(\(o\)-Tolyl)-1-[2-(trimethylsilyl)ethane sulfonyl]aziridine (Table 3, entry 1)

![Chemical Structure]

Colorless oil (99%); 97% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/i-PrOH=97/3, 1.0 mL/min), \( t_r (\text{Major}) = 10.1 \) min, \( t_r (\text{Minor}) = 11.3 \) min]; \([\alpha]_D^{20.0} = +126.2 (c 0.9, \text{CDCl}_3); 1^H \text{NMR (CDCl}_3, 400 \text{ MHz)}: \delta 7.13 -7.22 (m, 4H), 3.77 (dd, \( J = 4.4, 5.2 \) Hz, 1H), 3.09-3.14 (m, 2H), 2.93 (d, \( J = 7.2 \) Hz, 1H), 2.40 (s, 3H), 2.29 (d, \( J = 4.4 \) Hz, 1H), 1.11-1.16 (m, 2H), 0.03 (s, 9H); 13C \text{NMR (CDCl}_3, 100 \text{ MHz)}: \delta 136.8, 111.4, 130.1, 128.1, 126.2, 125.5, 49.1, 38.3, 34.9, 19.1, 9.7, -2.1 ppm.; HRMS [ESI-TOF] ([M + Na]^+) Calcd for C\text{14}H\text{23}NO\text{3}SSi: 320.1111; Found: 320.1271.

4.11. 2-(\(m\)-Tolyl)-1-[2-(trimethylsilyl)ethane sulfonyl]aziridine (Table 3, entry 2)

![Chemical Structure]

Colorless oil (99%); >90% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/i-PrOH=97/3, 1.0 mL/min), \( t_r (\text{Major}) = 11.6 \) min, \( t_r (\text{Minor}) = 13.8 \) min]; \([\alpha]_D^{20.0} = +131.0 (c 0.8, \text{CDCl}_3); 1^H \text{NMR (CDCl}_3, 270 \text{ MHz)}: \delta 7.23-7.32 (m, 5H), 4.46 (s, 2H), 3.45 (t, \( J = 6.0 \) Hz, 2H), 2.99-3.06 (m, 2H), 2.67 (m, 1H), 2.55 (d, \( J = 6.8 \) Hz, 1H), 2.04 (d, \( J = 4.3 \) Hz, 1H), 2.00-2.05 (m, 6H), 1.07-1.14 (m, 2H), 0.03 (s, 9H).; 13C \text{NMR (CDCl}_3, 100 \text{ MHz)}: \delta 138.5, 128.4, 127.6, 127.5, 72.9, 69.9, 48.8, 38.8, 33.5, 31.2, 29.3, 23.6, 9.7 -2.1 ppm.; HRMS [ESI-TOF] ([M + Na]^+) Calcd for C\text{18}H\text{31}NO\text{3}SSi: 392.1686; Found: 392.1714.
(Minor)=16.9 min.; [α]D \text{20} = +115.8 (c = 1.17, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.05-7.22 (m, 4H), 3.62 (dd, J=4.4, 4.4 Hz, 1H), 3.05-3.10 (m, 2H), 2.91 (d, J=7.2 Hz, 1H), 2.37 (d, J=5.2 Hz, 1H), 2.3 (s, 3H), 1.07-1.12 (m, 2H), -0.01 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz): δ 138.4, 135.0, 129.2, 128.6, 127.1, 123.6, 49.1, 40.5, 35.0, 21.3, 9.6, -2.1 ppm.; HRMS [ESI-TOF] ([M + Na⁺]) Calcd for C₁₄H₂₃NO₂SSi: 320.1111; Found: 320.1117.

4.12. (2S)-2-(p-Toly)-1-[[2-(trimethylsilyl)ethane]sulfonyl]azidine (Table 3, entry 3)

![Structure of (2S)-2-(p-Toly)-1-[[2-(trimethylsilyl)ethane]sulfonyl]azidine](image)

White solid (99%); 89% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/PrOH=90/10, 1.0 mL/min), t₁ (Major)=12.3 min, t₂ (Minor)=19.4 min]; [α]D \text{20} = +125.1 (c = 0.96, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.11-7.23 (m, 4H), 3.64 (dd, J=6.8, 6.8 Hz, 1H), 3.05-3.11 (m, 2H), 2.92 (d, J=10.8 Hz, 1H), 2.37 (d, J=6.8 Hz, 1H), 2.32 (s, 3H), 1.07-1.14 (m, 2H), 0.00 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz): δ 138.3, 129.3, 126.4, 49.1, 40.5, 34.9 21.2, 9.6, -2.1 ppm.; HRMS [ESI-TOF] ([M + Na⁺]) Calcd for C₁₄H₂₃NO₂SSi: 320.1111 Found: 320.1113.


Single crystals of the aziridine product [Table 3 (entry 3)] for X-ray diffraction experiments were obtained by recrystallization from Et₂O. The data were collected at 100 K on a Bruker SMART APEX II diffractometer equipped with APEX II 4K CCD area detector, a graphite monochromator and a rotating-anode X-ray tube (Mo-Kα radiation, λ = 0.71073) focused with Helios multilayer optics for Mo-Kα radiation operating at 50 kV and 24 mA. The data collection was performed by APEX2 software program.⁴ The cell refinement and the data reduction were carried out using SAINT-NT.⁵ The absorption correction was carried out using SADABES.⁶ The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F² with SHELXXLTL.⁷ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed from the difference map and refined with geometrical and isotropic displacement parameters. Molecular plot was obtained with ORTEP-3.⁸ Crystallographic data for Table 3 (entry 3): C₁₇H₂₃NO₂SSi, colorless block, 0.15x0.08x0.08 mm³, monoclinic, P2₁, a = 10.8858(17), b = 5.9432(9), c = 12.636(2) Å, V = 808.8(2) Å³, Z = 2, Flack = 0.04(6), R = 0.0325 and Rw = 0.0735.
CCDC 870579 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure S1. ORTEP view (50% probability) of (2S)-2-(p-Tolyl)-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine.

4.13. 2-(3-Bromophenyl)-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 3, entry 4)

Colorless oil (95 %); 90% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/i-PrOH=97/03, 1.0 mL/min), \( t_r \) (Major)=23.1 min, \( t_r \) (Minor)=29.7 min]; [\( \alpha \)]D \text{21}^\text{[1]} = +115.4 (c = 0.94, CHCl\text{3}); \( ^1\)H NMR (CDCl\text{3}, 400 MHz): \( \delta \) 7.15-7.42 (m, 4H), 3.62 (dd, \( J \)=4.4, 4.4 Hz, 1H), 3.06-3.11 (m, 2H), 2.91 (d, \( J \)=7.2 Hz, 1H), 2.32 (d, \( J \)=5.2 Hz, 1H), 1.02-1.16 (m, 2H), 0.00 (s, 9H).; \( ^{13}\)C NMR (CDCl\text{3}, 100 MHz): \( \delta \) 137.6, 131.6, 130.2, 129.4, 125.4, 122.8, 49.2, 39.3, 34.5, 9.7, -2.1 ppm.; HRMS [ESI-TOF] ([M + Na]\text{+}) Calcd for C\text{13}H\text{20}BrNO\text{2}Si: 384.0060; Found: 384.0082.
4.14. 2-(4-chlorophenyl)-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 3, entry 5)

![Aziridine structure]

Colorless oil (96%); 90% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/i-PrOH=97/03, 1 mL/min), \( t_r \) (Major)=15.8 min, \( t_r \) (Minor)=24.8 min]; \( [\alpha]_D^{21} = +121.2 \) (c = 1.12, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) 7.28 (d, \( J = 8.8 \) Hz, 2H), 7.19 (d, \( J = 8.79 \) Hz, 2H), 3.62 (dd, \( J = 4.4, 4.4 \) Hz, 1H), 3.04-3.10 (m, 2H), 2.91 (d, \( J = 7.6 \) Hz 2H), 2.32 (d, \( J = 8.4 \) Hz, 1H), 1.05-1.10 (m, 2H), -0.01 (s, 9H); \(^13\)C NMR (CDCl\(_3\), 100 MHz): \( \delta \) 134.4, 133.8, 128.9, 127.9, 49.1, 39.4, 9.7, -2.1 ppm.; HRMS [ESI-TOF] ([M + Na\(^+\])

Calcd for C\(_{13}\)H\(_{23}\)ClNO\(_2\)SSi: 340.0565; Found: 340.0573.

4.15. (2S)-2-(naphthalen-2-yl)-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 3, entry 6)

![Aziridine structure]

White solid (99%); 91% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/i-PrOH=97/03, 1.0 mL/min), \( t_r \) (Major)=54.8 min, \( t_r \) (Minor)=126.3 min]; \( [\alpha]_D^{21} = +125.1 \) (c = 1.17, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) 7.81 (m, 4H), 7.22-7.49 (m, 3H), 3.84-3.87 (dd, \( J = 4.4, 4.4 \) Hz, 1H), 3.11-3.16 (m, 2H), 3.02 (d, \( J = 6.8 \) Hz, 1H), 1.12-1.16 (m, 2H), 0.00 (s, 9H); \(^13\)C NMR (CDCl\(_3\), 100 MHz): \( \delta \) 133.2, 132.5, 128.6, 127.8, 126.6, 126.2, 123.6, 49.1, 40.7 35.2, 9.7, -2.0 ppm.; HRMS [ESI-TOF] ([M + Na\(^+\])

Calcd for C\(_{17}\)H\(_{25}\)NO\(_2\)SSi: 356.1111; Found: 356.1127.

4.15.1. Crystal structure analysis of (2S)-2-(Naphthalen-2-yl)-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 3, entry 6)

Single crystals of the aziridine product [Table 3 (entry 6)] for X-ray diffraction experiments were obtained by recrystallization from CH\(_2\)Cl\(_2\)/Hexane. The data were collected at 100 K on a Bruker SMART APEX II diffractometer equipped with APEX II 4K CCD area detector, a graphite monochromator and a rotating-anode X-ray tube (Mo-K\(\alpha\) radiation, \( l = 0.71073 \)) focused with Helios multilayer optics for Mo-K\(\alpha\) radiation operating at 50 kV and 24 mA. The data collection
was performed by APEX2 software program. The cell refinement and the data reduction were carried out using SAINT-NT. The absorption correction was carried out using SADABS. The structure was solved by direct methods and refined by full-matrix least-squares based on all data using $\mathcal{F}^2$ with SHELXLTL. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed from the difference map and refined with geometrical and isotropic displacement parameters. Molecular plot was obtained with ORTEP-3. Crystallographic data for Table 3 (entry 6): C$_{17}$H$_{23}$NO$_2$SSi, colorless block, 0.15x0.10x0.05 mm$^3$, orthorhombic, $P2_12_12_1$, $a = 6.0186(10)$, $b = 11.5512(18)$, $c = 24.941(4)$ Å, $V = 1733.9(5)$ Å$^3$, $Z = 4$, Flack = 0.05(6), $R = 0.0281$ and $R_w = 0.0682$. CCDC 870052 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Figure S2.** ORTEP view (50% probability) of (2S)-2-(naphthalen-2-yl)-1-{{2-(trimethylsilyl)ethan}sulfonyl}aziridine.

**4.16. 2-Methyl-3-phenyl-1-{{2-(trimethylsilyl)ethane}sulfonyl}aziridine (Table 3, entry 7)**

Colorless oil (72%); 99% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/i-PrOH=97/03, 1.0 mL/min), $t_r$ (Major)=8.4 min, $t_r$ (Minor)=12.2 min]; $[\alpha]_D^{22} = +124.1$ (c = 1.00, CHCl$_3$); $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.26-7.38 (m, 4H), 3.90 (d, $J$=8.0 Hz, 1H), 3.10-3.17 (m, 3H), 1.13-1.19 (m, 2H), 1.10 (d, $J$=8.0 Hz, 3H), 0.05 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 128.4, 127.9, 127.5, 49.1, 45.7, 40.9, 11.8, 9.8, -2.1 ppm.; HRMS [ESI-TOF] ([M + Na]$^+$) Calcd for C$_{14}$H$_{23}$NO$_2$SSi: 320.1111; Found: 320.1118.
4.16.1 Deprotection of the 2-Methyl-3-phenyl-1-\{[2-(trimethylsilyl)ethane]sulfonyl\}aziridine and determination of its configuration

A solution of 2-methyl-3-phenyl-1-\{[2-(trimethylsilyl)ethane]sulfonyl\}aziridine (38 mg, 0.12 mmol) and TASF (150 mg, 4 equiv.) in DMF (0.5 mL) was stirred at room temperature overnight, and chromatographed on silica gel (hexanes : ethyl acetate = 1:2) to obtain the deprotected aziridine product (11.4 mg, 67%) as a white solid. Its spectroscopic data were identical to those previously reported: \([\alpha]_D^{24} = +68.5\) (c = 0.7, CHCl\(_3\)), \([\alpha]_D^{22} = +69.1\) (c 4.43 × 10\(^{-3}\), CHCl\(_3\)) for \((2R,3S)-2\)-methyl-3-phenylaziridine. \(^{1}\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.17-7.30 (m, 3H), 3.21 (d, \(J = 8.0\) Hz, 1H), 2.37 (m, 1H), 0.87 (d, \(J = 8.0\) Hz, 3H) HRMS [ESI-TOF] \([\text{M} + \text{H}]^+\) Calcd for C\(_9\)H\(_{12}\)N: 134.0964; Found: 134.1082.

4.17. 1-\{[2-(Trimethylsilyl)ethane]sulfonyl\}-1,1a,6,6a-tetrahydroindenophenolate[1,2-b]aziridine (Table 3, entry 8)

Colorless oil (66%); 97% ee [determined by HPLC analysis using a chiral stationary phase column, DICEK CHIRALCEL OJ-H (Hexane/i-PrOH=97/03, 1.0 mL/min), \(t_r\) (Major)=15.2 min, \(t_r\) (Minor)=18.1 min]; \([\alpha]_D^{22} = +26.5\) (c = 2.1, CHCl\(_3\)); \(^{1}\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.46 (d, \(J = 6.8\) Hz, 1H), 7.21-7.26 (m, 3H), 4.20 (d, \(J = 4.8\) Hz, 1H), 3.88 (m, 1H), 3.21 (m, 1H), 3.05-3.09 (m, 2H), 1.07-1.12 (m, 2H), 0.02 (s, 9H).\(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 143.5, 127.8, 126.8, 125.7, 124.9, 49.6, 49.5, 43.5, 34.8, 9.7, -2.1 ppm.; HRMS [ESI-TOF] \([\text{M} + \text{Na}]^+\) Calcd for C\(_{14}\)H\(_{21}\)NO\(_2\)SSi: 318.0954; Found: 318.0963.

References
1) a) H. Kawabata, K. Omura and T. Katsuki, Tetrahedron Lett., 2006, 47, 1571; (b) H. Kawabata,


3) Bruker APEX2, Version 2008.5-0; Bruker AXS Inc.: Madison, WI (USA), 2005.

4) Bruker SAINT-NT (includes XPREP and SADABS), Version 6.0; Madison, WI (USA), 2005.

5) G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen (Germany), 1996.


5. $^1$H and $^{13}$C NMR spectra

5.1. (2S)-2-(Phenyl)-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 1, entry 2)
5.2. 2-Butyl-1-\{[2-(trimethylsilyl)ethane)sulfonyl]aziridine (Table 2, entry1)
5.3. 2-Cyclohexyl-1-[[2-(trimethylsilyl)ethane|sulfonyl]aziridine (Table 2, entry 2)
5.4. 2-(5-Methylhex-4-en-1-yl)-1-[[2-(trimethylsilyl)ethane sulfonyle]aziridine (Table 2, entry 3)
5.5. 2-Butyl-1-[(2-(trimethylsilyl)ethane)sulfonyl]aziridine (Table 2, entry 4)
5.6. 2-Benzyl-1-[(2-(trimethylsilyl)ethane)sulfonyl]aziridine (Table 2, entry 5)
5.7. 2-(4-Bromobutyl)-1-[[2-(trimethylsilyl)ethane]sulfonyl]aziridine (Table 2, entry 6)
5.8. 2-[(3-Benzoyloxy)propyl]-1-[[2-(trimethylsilyl)ethane)sulfonyl]aziridine (Table 2, entry 7)
5.9. 2-(o-Tolyl)-1-[[2-(trimethylsilyl)ethane)sulfonyl]aziridine (Table 3, entry 1)
5.10. 2-(m-Tolyl)-1-[[2-(trimethylsilyl)ethyl]sulfonyl]aziridine (Table 3, entry 2)
5.11. (2S)-2-(p-Tolyl)-1-[[2-(trimethylsilyl)ethane)sulfonyl]aziridine (Table 3, entry 3)
5.12. 2-(3-Bromophenyl)-1-[[2-(trimethylsilyl)ethane sulfonyl]aziridine (Table 3, entry 4)
5.13. 2-(4-Chlorophenyl)-1-[[2-(trimethylsilyl)ethanesulfonyl]aziridine (Table 3, entry 5)
5.14. (2S)-2-(Naphthalen-2-yl)-1-[(2-(trimethylsilyl)ethane)sulfonyl]aziridine (Table 3, entry 6)
5.15. 2-Methyl-3-phenyl-1-\{[2-(trimethylsilyl)ethane-sulfonyl]aziridine (Table 3, entry 7)
5.16. 1-[[2-(Trimethylsilyl)ethane)sulfonyl]-1,1a,6,6a-tetrahydroindeno[1,2-b]aziridine (Table 3, entry 8)