Highly cis-Selective Synthesis of Iodo-Aziridines using Diiodomethylithium and in situ Generated N-Boc-Imines.

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Table of Contents
S1
General Experimental Conditions .................................................................
S2
Further Discussion on the Origin of cis-Selectivity .............................................. S3
Synthesis of Imine-Toluene Sulfonic Acid Adducts 1a-1m .................................... S4-S7
Synthesis of Diiodides 2a and 2m .................................................................. S8
Synthesis of Iodoaziridines 3a to 3l ............................................................. S9-S13
Synthesis of Bromoaziridine 5 ....................................................................... S14
Reaction Sampling ......................................................................................... S15
1H and 13C NMR spectra for novel compounds .............................................. S16-S31
General Experimental Conditions

All non-aqueous reactions were run under an inert atmosphere (argon) with flame-dried glassware using standard techniques. Anhydrous solvents were obtained by filtration through drying columns (THF, diethyl ether, CH₂Cl₂).

Flash column chromatography was performed using 230-400 mesh silica with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm), or aqueous potassium permanganate stain.

Infrared spectra (FTIR) were recorded in reciprocal centimeters (cm⁻¹).

Nuclear magnetic resonance spectra were recorded on a 400 MHz spectrometer. Chemical shifts for ¹H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ = 7.27 ppm). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant in Hz, integration]. ¹³C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard (¹³CDCl₃: 77.0 ppm and ¹³CD₃OD: 49.00 ppm). ¹⁹F NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million referenced to the standard monofluorobenzene: −113.5 ppm.

Melting points are uncorrected.

Reagents: Commercial reagents were used as supplied or purified by standard techniques where necessary.

Compound Handling/Purification/Storage:

During all handling, exposure of iodoaziridines to light should be minimized. Iodoaziridines can be stored at −20 °C, as a solution in CH₂Cl₂ or CHCl₃ to prevent decomposition. For example, compound 3a was stored in a CH₂Cl₂ solution for >4 weeks without displaying noticeable decomposition.

Note on Assignment of Stereochemistry:

Iodoaziridines were assigned as cis-iodoaziridines on the basis of the magnitude of the coupling constant between the coupling of the CHAr and CHI protons (J = 5.4 Hz). trans-Iodoaziridines were observed in small amounts, where stated, with coupling constants of 2.3 Hz. These assignments are consistent with the coupling constants observed for cis- and trans-bromoaziridines by Ziegler and co-workers.¹,²,³

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Further Discussion on the Origin of cis-Selectivity

Our initial proposal for the stereoselectivity in the cyclisation to iodoaziridines 3 is based on subtle steric effects, illustrated below by consideration of the possible Newman projections of the intermediate anionic diiodide.

The aryl and Boc groups are likely to adopt an anti-periplanar orientation preferentially thus providing two potential reactive conformations, with N and I in an anti-periplanar arrangement appropriate for cyclisation (conformations A and B). We propose that an unfavourable interaction between the non-displaced iodide with the Boc group is dominant. Hence in the cyclisation TS, as the N-atom becomes sp³ hybridised, the non-displaced iodine prefers to adopt a position away from the bulk of the Boc group and so gauche to the Ph group, resulting in the cis-aziridine configuration.

\[
\begin{array}{c}
\text{A - cis} \\
\text{B - trans}
\end{array}
\]

In considering the steric bias for cyclisation it is important to consider the hybridisation at nitrogen in the transition state of the cyclisation. The geometry at nitrogen in aziridines is pyramidal (sp³ hybridisation). In the transition state, the N-hybridisation will approach sp³ as required for the bond formation and for progression to the product. This places the electron density on N, rather than conjugated into the carbonyl.

Given the large size of the iodine atom (radius I = 1.33 Å) a cis-substituent on N would provide a steric conflict. Furthermore, it is likely that the tBu group will be oriented into space, which will orient the C=O towards the relevant CHI₂ centre. It is on this basis that we propose the trans-aziridine would be dis-favoured.

\[
\begin{array}{c}
\text{A - cis} \\
\text{B - trans}
\end{array}
\]

We thank a referee for suggesting a dipole minimisation argument, due to a dipole in the CHI₂ unit, that could reinforce the above stereochemical outcome.
Synthesis of N-Boc Imine-\(p\)-Toluenesulfinic Acid Adducts 1a to 1m

**General Procedure**

Benzaldehyde (3.91 mL, 38.4 mmol, 1.50 equiv) was added to a suspension of tert-butyl carbamate (3.00 g, 25.6 mmol, 1.00 equiv) and sodium \(p\)-toluenesulfinate (9.11 g, 51.2 mmol, 2.0 equiv) in methanol and water (1:2, 75 mL), followed by formic acid (98%, 2.0 mL). The resulting mixture was stirred for \(rt\) for 2-4 days, during which time the product precipitated as a white solid. The precipitate was collected by filtration, then purified by trituration with diethyl ether and dried *in vacuo* to afford N-Boc imine-\(p\)-toluenesulfinic acid adduct 1a as a white solid (8.38 g, 91%).

<table>
<thead>
<tr>
<th>Compound Number</th>
<th>Structure</th>
<th>Yield (%)</th>
<th>NMR Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>![structure_1a]</td>
<td>91</td>
<td>(^1H) NMR (400 MHz, CDCl(_3)) (\delta) 7.81 (d, (J = 8.1) Hz, 2 H, 2 × SO(_2)-Tol-H), 7.47–7.42 (m, 5 H, 5 × Ph-H), 7.35 (d, (J = 8.1) Hz, 2 H, 2 × SO(_2)-Tol-H), 5.90 (d, (J = 10.8) Hz, 1 H, NH), 5.73 (d, (J = 10.8) Hz, 1 H, CHN), 2.45 (s, 3 H, SO(_2)-Tol-CH(_3)), 1.29 (s, 9 H, C(CH(_3))(_3)).</td>
</tr>
<tr>
<td>1b</td>
<td>![structure_1b]</td>
<td>79</td>
<td>(^{13}C) NMR (101 MHz, CDCl(_3)) (\delta) 153.5 (C=O), 145.0 (TolC-SO(_2) quat.), 133.7 (SO(_2)-TolC-CH(_3) quat.), 130.0 (PhC-CH quat.), 129.7 (2 × Ph-C), 129.6 (2 × SO(_2)-Tol-C), 129.5 (2 × SO(_2)-Tol-C), 128.9 (Ph-C), 128.7 (2 × Ph-C), 81.1 (C(CH(_3))(_3)), 73.8 (HC-NH), 27.9 (C(CH(_3))(_3)), 21.6 (SO(_2)-Tol-CH(_3)).</td>
</tr>
<tr>
<td>1c</td>
<td>![structure_1c]</td>
<td>25</td>
<td>(^1H) NMR (400 MHz, CDCl(_3)) (\delta) 7.80 (d, (J = 7.9) Hz, 2 H, 2 × SO(_2)-Tol-H), 7.48–7.41 (m, 1 H, Tol-H), 7.37–7.29 (m, 5 H, 3 × Tol-H and 2 × SO(_2)-Tol-H), 6.20 (d, 1 H, (J = 10.8) Hz, NH), 5.75 (d, (J = 10.8) Hz, 1 H, CHN), 2.44 (s, 3 H, SO(_2)-Tol-CH(_3)), 2.43 (s, 3 H, Tol-CH(_3)), 1.26 (s, 9 H, C(CH(_3))(_3)).</td>
</tr>
</tbody>
</table>

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$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, $J = 8.4$ Hz, 1 H, napthyl-H), 7.94 (d, $J = 8.1$ Hz, 1 H, napthyl-H), 7.91–7.84 (m, 3 H, napthyl-H and 2 $\times$ SO$_2$ Tol-H), 7.77 (d, $J = 7.3$ Hz, 1 H, napthyl-H), 7.61–7.49 (m, 3 H, 3 $\times$ napthyl-H), 7.34 (d, $J = 8.0$ Hz, 2 H, 2 $\times$ SO$_2$ Tol-H), 6.82 (d, $J = 10.5$ Hz, 1 H, NH), 5.87 (d, $J = 10.5$ Hz, 1 H, CHN), 2.43 (s, 3 H, SO$_2$ Tol-CH$_3$), 1.28 (s, 9 H, C(CH$_3$)$_3$).

1d

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.6 (C=O), 145.0 (TolC-SO$_2$ quat.), 134.2 (napthyl-C-CH quat.), 133.6 (SO$_2$ TolC-CH$_3$ quat.), 131.7 (napthyl-C quat.), 130.4 (napthyl-C), 129.7 (2 $\times$ SO$_2$ Tol-C), 129.4 (2 $\times$ SO$_2$ Tol-C), 128.8 (napthyl-C), 127.1 (napthyl-C), 126.5 (napthyl-C), 126.0 (napthyl-C), 125.0 (napthyl-C), 122.9 (napthyl-C), 81.1 (C(CH$_3$)$_3$ quat.), 69.0 (HC-NH), 27.9 (C(CH$_3$)$_3$), 21.6 (SO$_2$ Tol-CH$_3$).

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$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 8.2$ Hz, 2 H, 2 $\times$ SO$_2$ Tol-H), 7.45 (d, $J = 8.5$ Hz, 2 H, 2 $\times$ BuAr-H), 7.39 (d, $J = 8.5$ Hz, 2 H, 2 $\times$ BuAr-H), 7.34 (d, $J = 8.2$ Hz, 2 H, 2 $\times$ SO$_2$ Tol-H), 5.87 (d, $J = 10.8$ Hz, 1 H, NH), 5.71 (d, $J = 10.8$ Hz, 1 H, CHN), 2.43 (s, 3 H, SO$_2$ Tol-CH$_3$), 1.33 (s, 9 H, OC(CH$_3$)$_3$), 1.25 (s, 9 H, C(CH$_3$)$_3$).

1e

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.4 (C=O), 152.9 (ArC-Buquat.), 144.8 (TolC-SO$_2$ quat.), 133.9 (SO$_2$ TolC-CH$_3$ quat.), 129.6 (2 $\times$ SO$_2$ Tol-C), 129.5 (2 $\times$ SO$_2$ Tol-C), 128.6 (BuArC-CH quat.), 125.7 (BuArC-CH), 80.9 (OC(CH$_3$)$_3$), 73.6 (HC-NH), 34.7 (ArC-C(CH$_3$)$_3$), 31.2 (ArC-C(CH$_3$)$_3$), 27.9 (OC(CH$_3$)$_3$), 21.6 (SO$_2$ Tol-CH$_3$).

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$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 7.8$ Hz, 2 H, 2 $\times$ SO$_2$ Tol-H), 7.40–7.37 (m, 4 H, 4 $\times$ ClAr-H), 7.34 (d, $J = 8.0$ Hz, 2 H, 2 $\times$ SO$_2$ Tol-H), 5.89 (d, $J = 10.6$ Hz, 1 H, NH), 5.81 (d, $J = 10.6$ Hz, 1 H, CHN), 2.44 (s, 3 H, SO$_2$ Tol-CH$_3$), 1.26 (s, 9 H, C(CH$_3$)$_3$).

1f

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.4 (C=O), 145.2 (TolC-SO$_2$ quat.), 135.9 (ArC-Cl quat.), 133.5 (SO$_2$ TolC-CH$_3$ quat.), 130.2 (2 $\times$ ClAr-C), 129.7 (2 $\times$ SO$_2$ Tol-C), 129.5 (2 $\times$ SO$_2$ Tol-C), 128.9 (2 $\times$ ClAr-C), 128.6 (ClArC-CH quat.), 81.3 (C(CH$_3$)$_3$), 73.1 (HC-NH), 27.9 (C(CH$_3$)$_3$), 21.6 (SO$_2$ Tol-CH$_3$).

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$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 8.0$ Hz, 2 H, SO$_2$ Tol-H), 7.59–7.53 (m, 1 H, ClAr-H), 7.40–7.31 (m, 5 H, 3 $\times$ ClAr-H and 2 $\times$ SO$_2$ Tol-H), 6.57 (d, $J = 10.9$ Hz, 1 H, NH), 5.82 (d, 1 H, $J = 10.8$ Hz, CHN), 2.44 (s, 3 H, SO$_2$ Tol-CH$_3$), 1.30 (s, 9 H, C(CH$_3$)$_3$).

1g

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.5 (C=O), 145.3 (TolC-SO$_2$ quat.), 135.3 (ClArC-C quat.), 133.9 (SO$_2$ TolC-CH$_3$ quat.), 130.8 (ClAr-C), 129.8 (ClAr-C), 129.7 (2 $\times$ SO$_2$ Tol-C), 129.3 (2 $\times$ SO$_2$ Tol-C and ClAr-C), 129.0 (ClArC-CH quat.), 127.2 (ClAr-C), 81.2 (C(CH$_3$)$_3$), 70.0 (HC-NH), 27.9 (C(CH$_3$)$_3$), 21.6 (SO$_2$ Tol-CH$_3$).

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$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J = 8.1$ Hz, 2 H, 2 $\times$ SO$_2$ Tol-H), 7.56 (d, $J = 8.5$ Hz, 2 H, 2 $\times$ BrAr-H), 7.35 (d, $J = 8.1$ Hz, 2 H, 2 $\times$ SO$_2$ Tol-H), 7.32 (d, $J = 8.5$ Hz, 2 H, 2 $\times$ BrAr-H), 5.85 (d, $J = 10.5$ Hz, 1 H, NH), 5.66 (d, $J = 10.5$ Hz, 1 H, CHN), 2.44 (s, 3 H, SO$_2$ Tol-CH$_3$), 1.27 (s, 9 H, C(CH$_3$)$_3$).

1h

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.4 (C=O), 145.3 (TolC-SO$_2$ quat.), 133.4 (SO$_2$ TolC-CH$_3$ quat.), 131.9 (2 $\times$ BrAr-C), 130.4 (2 $\times$ BrAr-C), 129.8 (2 $\times$ SO$_2$ Tol-C), 129.5 (2 $\times$ SO$_2$ Tol-C), 129.1 (BrArC-CH quat.), 124.1 (ArC-Br quat.), 81.3 (C(CH$_3$)$_3$), 73.1 (HC-NH), 27.9 (C(CH$_3$)$_3$), 21.6 (SO$_2$ Tol-CH$_3$).
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S6

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J = 8.1$ Hz, 2 H, 2 $\times$ SO$_2$Tol-H), 7.47-7.39 (m, 2 H, FAr-H), 7.35 (d, $J = 8.1$ Hz, 2 H, SO$_2$Tol-H), 7.16-7.07 (m, 2 H, 2 $\times$ FAr-H), 5.87 (d, $J = 10.8$ Hz, 1 H, CHN), 5.67 (d, $J = 10.8$ Hz, 1 H, CHN), 2.44 (s, 3 H, SO$_2$Tol-CH$_3$), 1.27 (s, 9 H, C(CH$_3$)$_3$).

1i

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.5 (d, $J = 249.5$ Hz, Ar-CH quat.), 153.5 (C=O), 145.1 (TolC-SO$_2$), 133.5 (SO$_2$Tol-CH$_3$ quat.), 130.8 (d, $J = 8.2$ Hz, 2 $\times$ FAr-C), 129.7 (2 $\times$ SO$_2$Tol-C), 129.4 (2 $\times$ SO$_2$Tol-C), 125.9 (d, $J = 3.0$ Hz, FAr-C-CH quat.), 115.8 (d, $J = 21.7$ Hz, 2 $\times$ FAr-C), 81.2 (C(CH$_3$)$_3$ quat.), 73.1 (CHN), 27.9 (C(CH$_3$)$_3$), 21.6 (SO$_2$Tol-CH$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 8.2$ Hz, 2 H, 2 $\times$ SO$_2$Tol-H), 7.33 (m, 3 H, 2 $\times$ SO$_2$Tol-H and MeOAr-H), 7.02 (d, $J = 7.7$ Hz, 1 H, MeOAr-H), 6.97 (m, 2 H, 2 $\times$ FAr-H), 5.85 (d, $J = 10.5$ Hz, 1 H, NH), 5.69 (d, $J = 10.7$ Hz, 1 H, CHN), 3.82 (s, 3 H, Ar-OCH$_3$), 2.44 (s, 3 H, SO$_2$Tol-CH$_3$), 1.28 (s, 9 H, C(CH$_3$)$_3$).

1j

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.6 (Ar-C-OCH$_3$ quat.), 153.5 (C=O), 145.0 (TolC-SO$_2$ quat.), 133.8 (SO$_2$Tol-CH$_3$ quat.), 131.4 (MeOArC-CH), 129.7 (MeOAr-C), 129.6 (2 $\times$ SO$_2$Tol-C), 129.5 (2 $\times$ SO$_2$Tol-C), 121.1 (MeOAr-C), 115.5 (MeOAr-C), 114.4 (MeOAr-C), 81.1 (C(CH$_3$)$_3$), 73.8 (HC-NH), 55.3 (Ar-C-OCH$_3$), 27.9 (C(CH$_3$)$_3$), 21.6 (SO$_2$Tol-CH$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 8.2$ Hz, 2 H, 2 $\times$ SO$_2$Tol-H), 7.68 (d, $J = 8.3$ Hz, 2 H, 2 $\times$ FAr-C), 7.59 (d, $J = 8.3$ Hz, 2 H, 2 $\times$ FAr-C), 7.36 (d, $J = 8.2$ Hz, 2 H, 2 $\times$ SO$_2$Tol-H), 5.96 (d, $J = 10.8$ Hz, 1 H, NH), 5.83 (d, $J = 10.8$ Hz, 1 H, CHN), 2.45 (s, 3 H, SO$_2$Tol-CH$_3$), 1.27 (s, 9 H, C(CH$_3$)$_3$).

1k

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.4 (C=O), 145.5 (TolC-SO$_2$ quat.), 134.0 (F$_3$CArC-CH quat.), 133.4 (SO$_2$Tol-CH$_3$ quat.), 131.8 (q, $J = 32.8$ Hz, F$_3$C-CH), 129.8 (2 $\times$ F$_3$CAr-C), 129.5 (2 $\times$ SO$_2$Tol-C), 129.4 (2 $\times$ SO$_2$Tol-C), 125.6 (q, $J = 3.1$ Hz, 2 $\times$ F$_3$CAr-C), 124.8 (q, $J = 272.7$ Hz, F$_3$C-CH), 81.5 (C(CH$_3$)$_3$), 73.2 (HC-NH), 27.9 (C(CH$_3$)$_3$), 21.7 (SO$_2$Tol-CH$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.68 (dd, $J = 4.8$, 1.4 Hz, 1 H, pyr-H), 8.67-8.63 (m, 1 H, pyr-H), 7.89-7.83 (m, 1 H, pyr-H), 7.80 (d, $J = 8.2$ Hz, 2 H, 2 $\times$ SO$_2$Tol-H), 7.43-7.32 (m, 3 H, pyr-H and 2 $\times$ SO$_2$Tol-H), 6.02-5.79 (m, 2 H, NH and CHN), 2.45 (s, 3 H, SO$_2$Tol-CH$_3$), 1.28 (s, 9 H, C(CH$_3$)$_3$).

1l

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.6 (C=O), 150.6 (pyr-C), 149.9 (pyr-C), 145.5 (TolC-SO$_2$ quat.), 136.3 (pyr-C-CH quat.), 133.2 (SO$_2$Tol-CH$_3$ quat.), 129.8 (2 $\times$ SO$_2$Tol-C), 129.5 (2 $\times$ SO$_2$Tol-C), 126.6 (pyr-C), 123.5 (pyr-C), 81.4 (C(CH$_3$)$_3$), 71.9 (HC-NH), 27.9 (C(CH$_3$)$_3$), 21.6 (SO$_2$Tol-CH$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 8.2$ Hz, 2 H, 2 $\times$ SO$_2$Tol-H), 7.31 (d, $J = 8.2$ Hz, 2 H, 2 $\times$ SO$_2$Tol-H), 5.18 (d, 1 H, CHN), 4.67 (dd, $J = 11.2$, 3.6 Hz, 1 H, CHN), 2.40 (s, 3 H, SO$_2$Tol-CH$_3$), 2.13 (d, $J = 12.4$ Hz, 1 H, Cy-H), 1.82-1.64 (m, 5 H, 5 $\times$ Cy-H), 1.41-1.32 (m, 2 H, 2 $\times$ Cy-H), 1.23 (s, 9 H, C(CH$_3$)$_3$), 1.14 (m, 3 H, 3 $\times$ Cy-H).

1m

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.0 (C=O), 144.5 (TolC-SO$_2$ quat.), 134.9 (SO$_2$Tol-CH$_3$ quat.), 129.5 (2 $\times$ SO$_2$Tol-C), 128.9 (2 $\times$ SO$_2$Tol-C), 80.4 (C(CH$_3$)$_3$), 74.3 (HC-NH), 36.2 (Cy-C-CH), 30.5 (Cy-C), 27.8 (C(CH$_3$)$_3$), 27.4 (Cy-C), 27.2 (Cy-C), 25.9 (Cy-C), 25.6 (Cy-C), 25.5 (Cy-C), 21.4 (SO$_2$Tol-CH$_3$).
Compounds 1a, 1b, 1f, 1j, and 1m are previously reported without NMR characterisation data. Compound 1c is previously reported and the above data is consistent with that in the literature.


Synthesis of amino-gem-diiodides

(2,2-Diiodo-1-phenyl-ethyl)-tert-butylcarbamate (2a)

Diiodomethane (145 μL, 1.80 mmol, 3.0 equiv.) in THF (1.6 mL) was added dropwise to a solution of LiHMDS (1 M solution in THF, 1.56 mL, 1.56 mmol, 2.6 equiv.) in THF (6.0 mL) and diethyl ether (3.0 mL) at −78 °C in the dark. After 20 minutes at −78 °C, a solution of the imine-toluene sulfonic acid adduct 1a (217 mg, 0.60 mmol, 1.0 equiv.) in THF (3 mL) was added dropwise to the reaction mixture. After a further 10 minutes at −78 °C, the reaction was quenched by the addition of saturated aqueous sodium bicarbonate solution (40 mL). The aqueous solution was extracted with CH₂Cl₂ (3 × 30 mL) and the organic extracts were combined, dried (Na₂SO₄), filtered and solvent removed in vacuo. Purification by flash chromatography (10% diethyl ether/hexanes) afforded amino-gem-diiodide 2a (232 mg, 80%) as a white solid. Rᵣ(0.10 (10% diethyl ether/hexanes). νₑₛₑ (film)/cm⁻¹: 2980, 1699 (C=O), 1490, 1366, 1244, 1160, 1047. ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.35 (m, 5 H, Ph-H), 5.46 (br s, 1 H, CH₂), 5.37 (br s, 1 H, NH), 4.90 (br s, 1 H, CHPh), 1.51 (s, 9 H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 154.8 (C=O), 138.7 (Ph-C quat.), 128.6 (Ph-C), 128.3 (2 x Ph-C), 126.7 (2 x Ph-C), 80.5 (C(CH₃)₃), 62.2 (CHN), 28.3 (C(CH₃)₃), −14.7 (CHI₂). HRMS (ES) m/z Calculated for C₉H₁₀I₂NO₂⁺ [M+Bu⁺/2H]⁺: 417.8795; Found: 417.8794.

(2,2-Diiodo-1-cyclohexyl-ethyl)-tert-butylcarbamate (2m)

Diiodomethane (145 μL, 1.80 mmol, 3.0 equiv.) in THF (1.6 mL) was added dropwise to a solution of LiHMDS (1 M solution in THF, 1.56 mL, 1.56 mmol, 2.6 equiv.) in THF (6.0 mL) and diethyl ether (3.0 mL) at −78 °C in the dark. After 20 minutes at −78 °C, a solution of the imine-toluene sulfonic acid adduct 1m (222 mg, 0.60 mmol, 1.0 equiv.) in THF (3 mL) was added dropwise to the reaction mixture. After 10 minutes at −78 °C, the reaction was then transferred to warm in a water bath at 30 °C for 30 minutes and then was then quenched by the addition of saturated aqueous sodium bicarbonate solution (40 mL). The aqueous mixture was extracted with CH₂Cl₂ (3 × 40 mL). The organic extracts were then combined, dried (Na₂SO₄), filtered and solvent removed in vacuo. Purification by flash chromatography (10% ethyl acetate/hexane) afforded amino-gem-diiodide 2m (83 mg, 29%) as a colourless oil. Rᵣ(0.33 (10% ethyl acetate/hexane). νₑₛₑ (film)/cm⁻¹: 2979, 2925, 2853, 1706 (C=O), 1495, 1366, 1240, 1163, 1056, 1017. ¹H NMR (400 MHz, CDCl₃) δ 5.50 (1 H, d, J = 2.7 Hz, CHI), 4.76 (1 H, d, J = 10.3 Hz, NH), 3.20 (1 H, ddd, J = 10.3, 8.9, 2.7 Hz, CHN), 1.88–1.61 (4 H, m, 4 × Cy-H), 1.49 (9 H, s, C(CH₃)₃), 1.33–0.86 (6 H, m, 6 × Cy-H). ¹³C NMR (101 MHz, CDCl₃) δ 155.6 (C=O), 79.7 (C(CH₃)₃ quat.), 63.1 (CHN), 43.8 (CyC-CH), 29.7 (Cy-C), 28.9, 28.4 (C(CH₃)₃), 25.8(3) (Cy-C), 25.7(9) (Cy-C), 25.6 (Cy-C), −15.1 (CHI₂).

**Note:** Rotamers observed for CHN, NH and CHI₂ protons. Peaks given for major rotamer.
Synthesis of Iodoaziridines 3a-l

General Procedures:

**General Procedure A**

Diiodomethane (145 μL, 1.80 mmol, 3.0 equiv.) in THF (1.6 mL) was added dropwise to a solution of LiHMDS (1 M solution in THF, 1.56 mL, 1.56 mmol, 2.6 equiv.) in THF (6.0 mL) and diethyl ether (3.0 mL) at −78 °C in the dark. After 20 minutes at −78 °C, a solution of the imine-toluene sulfinic acid adduct (0.60 mmol, 1.0 equiv.) in THF (2.0 mL) was added dropwise to the reaction mixture. After 10 minutes at −78 °C, the reaction flask was transferred to a water bath at 30 °C for 10 minutes and then quenched by the addition of saturated aqueous sodium bicarbonate solution (30 mL). The aqueous mixture was extracted with CH₂Cl₂ (3 × 30 mL). The organic extracts were combined, dried (Na₂SO₄), filtered and solvent removed in vacuo. Purification by flash chromatography (10% diethyl ether/hexane) afforded the cis-iodoaziridine.

**General Procedure B**

Same as **General Procedure A**, but the reaction was warmed to 30 °C for 30 minutes.
cis-(±)-2-ido-3-phenyl-1-tert-butoxycarbonylaziridine (3a)

Prepared according to the General Procedure A described above starting from imine-HO₂STol adduct 1a (217 mg, 0.60 mmol). Purification by flash chromatography (10% diethyl ether/hexane) afforded cis-iodoaziridine 3a (172 mg, 83%) as a colourless oil. Rf 0.37 (20% diethyl ether/hexane). \( \nu_{\text{max}} \) (film)/cm⁻¹ 2981, 1724 (C=O), 1610, 1496, 1478, 1458, 1399, 1372, 1320, 1306, 1285, 1258, 1230, 1147, 1078, 1029. \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.43–7.34 (m, 5 H, Ph-H), 4.72 (d, \( J = 5.4 \) Hz, 1 H, CH), 3.59 (d, \( J = 5.4 \) Hz, 1 H, CH₂), 1.51 (s, 9 H, C(CH₃)₃). \(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta \) 159.7 (C=O), 134.8 (Ph-C quat.), 128.4 (Ph-C), 128.0 (2 × Ph-C), 127.5 (2 × Ph-C), 82.9 (C(CH₃)₃), 43.1 (PhCH₂), 27.9 (C(CH₃)₃), 18.2 (CH₃). HRMS (ESI) m/z Calculated for C₁₃H₁₇INO₂⁺ [M+H]⁺: 346.0298; Found: 346.0295.

Alternative procedure from diiodide (2a)

Ceasium carbonate (299 mg, 0.85 mmol, 2.0 equiv.) was added to a solution of diiodide 2a (200 mg, 0.42 mmol) in N,N-dimethylformamide (10 mL) at rt, monitoring reaction progress via thin layer chromatography. After 15 h at rt, diethyl ether (50 mL) was added to the reaction mixture. The reaction mixture was then washed with water (50 mL) and brine (50 mL). The organic layer was then dried (Na₂SO₄), filtered and the solvent removed in vacuo. Purification by flash chromatography (10% ethyl acetate/hexanes) afforded cis-iodoaziridine 3a (83 mg, 54%) as a colourless oil.

 cis-(±)-2-ido-3-(4-toly)-1-tert-butoxycarbonylaziridine (3b)

Prepared according to the General Procedure A described above starting from imine-HO₂STol adduct 1b (226 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded cis-iodoaziridine 3b (208 mg, 96%) as a colourless oil. Rf 0.45 (20% ethyl acetate/hexane). \( \nu_{\text{max}} \) (film)/cm⁻¹ 2981, 1724 (C=O), 1525, 1455, 1391, 1368, 1315, 1298, 1280, 1253, 1149, 1082, 974, 862. \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.24 (d, \( J = 8.3 \) Hz, 2 H, 2 × Tol-H), 7.20 (d, \( J = 8.3 \) Hz, 2 H, 2 × Tol-H), 4.71 (d, \( J = 5.4 \) Hz, 1 H, CH), 3.55 (d, \( J = 5.4 \) Hz, 1 H, CH₂), 2.38 (s, 3 H, Tol-CH₃), 1.51 (s, 9 H, C(CH₃)₃). \(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta \) 159.7 (C=O), 138.3 (Tol-C quat.), 131.8 (Tol-C quat.), 128.8 (2 × Tol-C), 127.4 (2 × Tol-C), 82.9 (C(CH₃)₃), 43.2 (TolCH₂), 27.9 (C(CH₃)₃), 21.3 (Tol-CH₃), 18.7 (CH₃). HRMS (ESI) m/z Calculated for C₁₇H₁₇NO₂⁺ [M-I+H]⁺: 233.1410; Found: 233.1435.

 cis-(±)-2-ido-3-(2-toly)-1-tert-butoxycarbonylaziridine (3c)

Prepared according to the General Procedure B described above starting from imine-HO₂STol adduct 1c (226 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded cis-iodoaziridine 3c (192 mg, 89%) as a colourless oil. Rf 0.14 (10% ethyl acetate/hexane). \( \nu_{\text{max}} \) (film)/cm⁻¹ 2981, 1723 (C=O), 1494, 1480, 1462, 1392, 1304, 1282, 1252, 1235, 1204, 1148, 1082, 970, 788. \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.37 (d, 1 H, \( J = 7.6 \) Hz, Tol-H), 7.33–7.20 (m, 3 H, 3 × Tol-H), 4.76 (d, \( J = 5.3 \) Hz, 1 H, CH), 3.59 (d, \( J = 5.3 \) Hz, 1 H, CH₂), 2.36 (s, 3 H, Tol-CH₃), 1.54 (s, 9 H, C(CH₃)₃). \(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta \) 159.7 (C=O), 136.0 (Tol-C quat.), 133.6 (Tol-C quat.), 129.6 (Tol-C), 128.2 (Tol-C), 127.7 (Tol-C), 125.7 (Tol-C), 82.8 (C(CH₃)₃), 42.5 (TolCH₂), 27.9 (C(CH₃)₃), 18.9 (Tol-CH₃), 17.0 (CH₃). HRMS (ESI) m/z Calculated for C₁₄H₁₉INO₂⁺ [M+H]⁺: 360.0455; Found: 360.0471.
cis-(±)-2-iodo-3-(2-naphthyl)-1-tert-butoxycarbonylaziridine (3d)
Prepared according to the General Procedure A described above starting from imine-HO₂STol adduct 1d (247 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded cis-iodoaziridine 3d (219 mg, 92%) as a colourless oil. Rf 0.46 (20% ethyl acetate/hexane). νmax (film)/cm⁻¹ 2981, 1722 (C=O), 1511, 1483, 1369, 1347, 1291, 1249, 1205, 1149, 1092, 1047, 967, 802. ¹H NMR (400 MHz, CDCl₃) δ 8.03–8.01 (1 H, m, napthyl-H), 7.96–7.94 (1 H, m, napthyl-H), 7.91 (1 H, d, J = 8.3 Hz, napthyl-H), 7.65–7.50 (m, 4 H, 4 x napthyl-H), 4.93 (d, J = 5.4 Hz, 1 H, CHI), 4.09 (d, J = 5.4 Hz, 1 H, CHAr), 1.57 (s, 9 H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.8 (C=O), 133.2 (napthyl-C quat.), 131.2 (napthyl-C quat.), 131.0 (napthyl-C quat.), 128.8 (napthyl-C), 128.7 (napthyl-C), 126.8 (napthyl-C), 126.1 (napthyl-C), 126.0 (napthyl-C), 125.3 (napthyl-C), 122.7 (napthyl-C), 83.0 (OC(CH₃)₃), 42.4 (ArCHN), 28.0 (C(CH₃)₃), 16.8 (CHI). HRMS (ESI) m/z Calculated for C₁₇H₁₉NO₂⁺ [M-I⁺H]⁺: 269.1410; Found: 269.1423.

cis-(±)-2-iodo-3-(4-tert-butylbenzene)-1-tert-butoxycarbonylaziridine (3e)
Prepared according to the General Procedure A described above starting from imine-HO₂STol adduct 1e (251 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded cis-iodoaziridine 3e (160 mg, 67%) as a colourless oil. Rf 0.34 (10% ethyl acetate/hexane). νmax (film)/cm⁻¹ 2985, 1725 (C=O), 1391, 1368, 1280, 1253, 1148, 844. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 8.3 Hz, 2 H, tBuAr-H), 7.29 (d, J = 8.3 Hz, 2 H, 2 x tBuAr-H), 4.73 (d, J = 5.4 Hz, 1 H, CHI), 3.56 (d, J = 5.4 Hz, 1 H, CHAr), 1.51 (s, 9 H, C(CH₃)₃), 1.36 (s, 9 H, ArC(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.7 (C=O), 151.3 (tBuAr-C(CH₃)₃ quat.), 131.7 (tBuAr-C-CH quat.), 127.1 (2 x tBuAr-C), 124.9 (2 x tBuAr-C), 82.7 (OC(CH₃)₃), 43.1 (ArCHN), 34.6 (Ar-C(CH₃)₃), 31.3 (Ar-C(CH₃)₃), 27.9 (OC(CH₃)₃), 18.6 (CHI). HRMS (ESI) m/z Calculated for C₁₇H₂₇NO₂⁺ [M-I⁺H]⁺: 275.1879; Found: 275.1879.

cis-(±)-2-iodo-3-(4-chlorobenzene)-1-tert-butoxycarbonylaziridine (3f)
Prepared according to the General Procedure A described above starting from imine-HO₂STol adduct 1f (237 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded cis-iodoaziridine 3f (117 mg, 51%) as a colourless oil. Rf 0.20 (10% ethyl acetate/hexane). νmax (film)/cm⁻¹ 2984, 1724 (C=O), 1494, 1598, 1420, 1392, 1369, 1308, 1289, 1276, 1252, 1146, 1089, 1015, 970, 842. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, J = 8.4 Hz, 2 H, 2 x ClAr-H), 7.28 (d, J = 8.4 Hz, 2 H, 2 x ClAr-H), 4.70 (d, J = 5.4 Hz, 1 H, CHI), 3.55 (d, J = 5.4 Hz, 1 H, CHAr), 1.51 (s, 9 H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.3 (C=O), 134.2 (ClAr-C quat.), 133.4 (ClAr-C quat.), 128.8 (2 x ClAr-C), 128.3 (2 x ClAr-C), 83.1 (ClCH=CH₂), 42.4 (ArCHN), 27.9 (C(CH₃)₃), 17.8 (CHI). HRMS (ESI) m/z Calculated for C₁₃H₁₆ClINO₂⁺ [M+H]⁺: 379.9909; Found: 379.9923.

cis-(±)-2-iodo-3-(2-chlorobenzene)-1-tert-butoxycarbonylaziridine and trans-(±)-2-iodo-3-(2-chlorobenzene)-1-tert-butoxycarbonylaziridine (3g)
Prepared according to the General Procedure B described above starting from imine-HO₂STol adduct 1g (238 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/petroleum ether) afforded a 88:12 mixture of cis-iodoaziridine cis-3g and transiodoaziridine trans-3g (118 mg, 52%) as a colourless oil. Rf 0.31 (10% ethyl acetate/petroleum ether). νmax (film)/cm⁻¹ 2984, 1726 (C=O), 1483, 1441, 1396, 1369, 1301, 1290, 1276, 1253, 1224, 1147, 1054, 967, 851, 750.
cis-aziridine 1H NMR (400 MHz, CDCl₃) δ 7.44–7.34 (m, 4 H, 4 × ClAr-H), 4.77 (d, J = 5.4 Hz, 1 H, CHI), 3.80 (d, J = 5.4 Hz, 1 H, CHAr), 1.54 (s, 9 H, C(CH₃)₃). ¹³C NMR (400 MHz, CDCl₃) δ 159.4 (C=O), 133.4 (ClAr-C quat.), 133.3 (ClAr-C quat.), 130.0 (ClAr-C), 129.5 (ClAr-C), 129.0 (ClAr-C), 126.5 (ClAr-C), 83.0 (C(CH₃)₃), 42.2 (ArCHN), 27.9 (C(CH₃)₃), 16.3 (CHI).

trans-aziridine 1H NMR (400 MHz, CDCl₃) δ 7.36–7.27 (m, 4 H, 4 × Ar-H), 4.01 (d, J = 2.3 Hz, 1 H, CHI), 3.84 (d, J = 2.3 Hz, 1 H, CHAr), 1.56 (s, 9 H, C(CH₃)₃). ¹³C NMR (400 MHz, CDCl₃) δ 157.2 (C=O), 134.3 (ClAr-C quat.), 133.8 (ClAr-C quat.), 129.3 (ClAr-C), 129.2 (5) (ClAr-C), 127.0 (ClAr-C), 126.9 (ClAr-C), 83.3 (C(CH₃)₃), 46.1 (ArCHN), 28.0 (C(CH₃)₃), 10.2 (CHI).

HRMS (ESI) m/z Calculated for C₁₁H₁₆ClINO₂⁺ [M+H⁺]: 379.9909; Found: 379.9907.

cis-(±)-2-iodo-3-(4-bromobenzene)-1-tert-butoxycarbonylaziridine (3h)
Prepared according to the General Procedure A described above starting from imine-HO₂STol adduct 1h (264 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded cis-iodoaziridine 3h (100 mg, 42%) as a colourless oil. Rᶠ 0.39 (20% ethyl acetate/hexane). vₘₐₓ (film)/cm⁻¹ 2984, 1725 (C=O), 1490, 1424, 1369, 1307, 1290, 1276, 1253, 1149, 1069, 1011, 974, 842. ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.4 Hz, 2 H, 2 × BrAr-H), 7.22 (d, J = 8.4 Hz, 2 H, 2 × BrAr-H), 4.69 (d, J = 5.4 Hz, 1 H, CHI), 3.53 (d, J = 5.4 Hz, 1 H, CHAr), 1.50 (s, 9 H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.3 (C=O), 134.0 (Br-C=O quat.), 131.2 (2 × BrAr-C), 129.2 (2 × BrAr-C), 122.5 (BrArC-CH quat.), 83.1 (C(CH₃)₃), 42.5 (ArCHN), 27.9 (C(CH₃)₃), 17.7 (CHI). HRMS (ESI) m/z Calculated for C₁₃H₁₆⁺BrINO₂⁺ [M⁺]: 423.9404; Found: 423.9420.

cis-(±)-2-iodo-3-(4-fluorobenzene)-1-tert-butoxycarbonylaziridine (3i)
Prepared according to the General Procedure A described above starting from imine-HO₂STol adduct 1i (228 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded cis-iodoaziridine 3i (165 mg, 76%) as a colourless oil. Rᶠ 0.14 (10% ethyl acetate/hexane). vₘₐₓ (film)/cm⁻¹ 2984, 1724 (C=O), 1609, 1512, 1483, 1462, 1427, 1396, 1369, 1308, 1281, 1254, 1146, 1099, 1078, 1015, 970. ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.28 (m, 2 H, 2 × FAr-H), 7.13–7.03 (m, 2 H, 2 × FAr-H), 4.70 (d, J = 5.2 Hz, 1 H, CHI), 3.56 (d, J = 5.2 Hz, 1 H, CHAr), 1.51 (s, 9 H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 162.7 (d, J = 247.1 Hz, Ar-CHF quat.), 159.4 (C=O), 130.6 (d, J = 3.1 Hz, FAr-C quat.), 129.2 (d, J = 8.4 Hz, 2 × FAr-C), 115.0 (d, J = 21.9 Hz, 2 × FAr-C), 83.0 (C(CH₃)₃), 42.4 (ArCHN), 27.8 (C(CH₃)₃), 18.2 (CHI). ¹⁹F NMR (377 MHz, CDCl₃) δ -113.3 (C-F). HRMS (ESI) m/z Calculated for C₁₃H₁₆FINO₂⁺ [M⁺]: 364.0228; Found: 364.0228.

cis-(±)-2-iodo-3-(3-methoxybenzene)-1-tert-butoxycarbonylaziridine (3j)
Prepared according to the General Procedure A described above starting from imine-HO₂STol adduct 1j (235 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) on neutral alumina afforded cis-iodoaziridine 3j (174 mg, 77%) as a colourless oil. Rᶠ 0.45 (10% ethyl acetate/hexane). vₘₐₓ (film)/cm⁻¹ 2980, 1723 (C=O), 1392, 1369, 1279, 1252, 1145, 1043, 840. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (t, J = 7.4 Hz, 1 H, MeOAr-H), 6.96–6.88 (m, 3 H, 3 × MeOAr-H), 4.71 (d, J = 5.4 Hz, 1 H, CHI), 3.84 (s, 3 H, OMe), 3.57 (d, J = 5.4 Hz, 1 H, CHAr), 1.51 (s, 9 H, C(CH₃)₃). ¹³C NMR (400 MHz, CDCl₃) δ 159.5 (C=O), 159.3 (ArC-OCH₃ quat.), 136.3 (ArC-CH quat.), 129.1 (MeOAr-C), 119.8 (MeOAr-C), 114.2 (MeOAr-C), 112.6 (MeOAr-C), 82.8 (C(CH₃)₃), 55.2 (Ar-OCH₃), 43.0 (ArCHN), 27.8 (C(CH₃)₃), 18.0 (CHI). HRMS (ESI) m/z Calculated for C₁₃H₁₉INO₂⁺ [M⁺]: 376.0404; Found: 376.0415.
**cis-(±)-2-iodo-3-(4-trifluoromethylbenzene)-1-tert-butoxycarbonylaziridine (3k)**

Prepared according to the General Procedure A described above starting from imine-HO2STol adduct 1k (258 mg, 0.60 mmol). Purification by flash chromatography (5% ethyl acetate/hexane) afforded *cis*-idoaziridine 3k (30 mg, 13%) as a colourless oil. Rf 0.19 (10% ethyl acetate/hexane). ν_max (film)/cm⁻¹ 2984, 1729 (C=O), 1323, 1285, 1151, 1128, 1066, 855. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.3 Hz, 2 H, 2 × F₃CAr-H), 7.47 (d, J = 8.4 Hz, 2 H, 2 × F₃CAr-H), 4.72 (d, J = 5.4 Hz, 1 H, CHI), 3.63 (d, J = 5.4 Hz, 1 H, CHAr), 1.52 (s, 9 H, C(CH₃)₃). ¹³C NMR (500 MHz, CDCl₃) δ 159.2 (C=O), 138.8 (F₃CAr-C, CHN quat.), 130.5 (q, J = 32.5 Hz, 2 × F₃Car-C), 127.9 (2 × F₃Car-C), 125.1 (q, J = 3.6 Hz, 2 × F₃Car-C), 124.1 (q, J = 272.2 Hz, F₃Car-C), 83.3 (C(CH₃)₃ quat.), 42.5 (F₃Car-CHN), 27.9 (C(CH₃)₃), 17.0 (CHI). ¹⁹F NMR (470 MHz, CDCl₃) δ −62.7 (ArC-F₃). HRMS (ESI) m/z Calculated for C₁₄H₁₆F₃INO₂⁺ [M+H]^+ : 414.0172; Found: 414.0183.

**cis-(±)-2-iodo-3-(3-pyridyl)-1-tert-butoxycarbonylaziridine (3l)**

Prepared according to the General Procedure A described above starting from imine-HO2STol adduct 1l (219 mg, 0.60 mmol). Purification by flash chromatography (40% ethyl acetate/hexane) afforded *cis*-idoaziridine 3l (101 mg, 49%) as a yellow oil. Rf 0.16 (40% ethyl acetate/hexane). ν_max (film)/cm⁻¹ 2981, 1729 (C=O), 1370, 1293, 1252, 1152, 755. ¹H NMR (400 MHz, CDCl₃) δ 8.64 (br s, 2 H, 2 × pyr-H), 7.66 (d, J = 7.7 Hz, 1 H, pyr-H), 7.35 (br s, 1 H, pyr-H), 4.72 (d, J = 5.4 Hz, 1 H, CHI), 3.61 (d, J = 5.4 Hz, 1 H, CHAr), 1.49 (s, 9 H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.1 (C=O), 149.3 (pyr-C), 148.8 (pyr-C), 135.4 (pyr-C, CH quat.), 131.0, (pyr-C) 123.0 (pyr-C), 83.3 (C(CH₃)₃ quat.), 40.8 (pyr-CHN), 27.8 (C(CH₃)₃), 17.1 (CHI). HRMS (ESI) m/z Calculated for C₁₂H₁₆INO₂⁺ [M+H]^+ : 374.0251; Found: 347.0261.
Synthesis of Bromoaziridine

cis-(±)-2-Bromo-3-phenyl-1-tert-butoxycarbonylaziridine (5)

Dibromomethane (126 µL, 1.80 mmol, 3.0 equiv.) in THF (1.6 mL) was added dropwise to a solution of LiHMDS (1 M solution in THF, 1.56 mL, 1.56 mmol, 2.6 equiv.) in THF (6.0 mL) and diethyl ether (3.0 mL) at −78 °C in the dark. After 20 minutes at −78 °C, a solution of imine-toluene sulfinic acid adduct 1a (0.60 mmol, 1.0 equiv.) in THF (2.0 mL) was added dropwise to the reaction mixture. After 10 minutes at −78 °C, the reaction flask was transferred to a water bath at 30 °C for 10 minutes and then quenched by the addition of saturated aqueous sodium bicarbonate solution (30 mL). The aqueous mixture was extracted with CH₂Cl₂ (3 × 30 mL). The organic extracts were combined, dried (Na₂SO₄), filtered and solvent removed in vacuo. Purification by flash chromatography (10% diethyl ether/hexane) afforded cis-bromoaziridine 5 (53 mg, 30%) as a colourless oil. R₁ 0.25 (10% ethyl acetate/hexane). νmax (film)/cm⁻¹ 2982, 1726 (C=O), 1303, 1279, 1257, 1233, 1156, 907, 730, 698. ¹H NMR (400 MHz, CDCl₃) δ 7.43–7.35 (m, 5 H, Ph-H), 4.87 (d, J = 5.1 Hz, 1 H, CHBr), 3.75 (d, J = 5.1 Hz, 1 H, CHPh), 1.52 (s, 9 H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 159.3 (C=O), 133.2 (Ph-C quat.), 128.4 (Ph-C), 128.0 (2 × Ph-C), 127.8 (2 × Ph-C), 83.0 (C(CH₃)₃ quat.), 44.7 (CHBr), 44.1 (CHPh), 27.9 (C(CH₃)₃). HRMS (Cl) m/z Calculated for C₁₃H₁₇NO₂⁷⁹Br⁺ [M+H]⁺: 298.0437; Found: 298.0450.
Sampling was carried out at low temperature (−78 °C) and at the elevated temperature (30 °C) after the addition of the imine toluene sulfonic acid adduct to the reaction mixture. Aliquots of the reaction mixture were quenched by addition to a saturated aqueous sodium bicarbonate solution. The aqueous layer was then extracted with diethyl ether to give a sample for $^1$H NMR analysis.

After 30 min at −78 °C, it is evident from the $^1$H NMR spectra that the amino gem-diiodoide was the only product obtained from the low temperature quench. According to the general procedure, the reaction vessel was transferred to a warm water bath at 30 °C. Sampling the reaction mixture after 5 min at 30 °C, it was evident that the cis-iodoaziridine was the only product from the elevated temperature quench. The cis-iodoaziridine was stable at 30 min at 30 °C, with the sample showing no degradation products.

This further supports our mechanistic hypothesis of addition followed by cyclisation at elevated temperatures, rather than an alternative via diiodocarbene. Low temperature is required for the initial addition for the stability of LiCHI$_2$. 
$^1$H and $^{13}$C NMR spectra of selected compounds
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
2m

$^1$H NMR (400 MHz, CDCl$_3$)

**NB:** Rotamers present (87:13)

2m

$^{13}$C NMR (101 MHz, CDCl$_3$)
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$\begin{align*}
3a \\
^1H \text{ NMR (400 MHz, CDCl}_3) \\
^13C \text{ NMR (101 MHz, CDCl}_3)
\end{align*}$
$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{3g}$

$^1$H NMR (400 MHz, CDCl$_3$)

$(cis:trans = 88:12)$

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
3i

$^1$H NMR (400 MHz, CDCl$_3$)

3i

$^{13}$C NMR (101 MHz, CDCl$_3$)
J. A. Bull, T. Boulton and T. A. Taylor

1H NMR (400 MHz, CDCl₃)

13C NMR (101 MHz, CDCl₃)
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**3k**

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
\[ 3 \text{I} \]

\(^{1}H\) NMR (400 MHz, CDCl\(_3\))

\[ 3 \text{I} \]

\(^{13}C\) NMR (101 MHz, CDCl\(_3\))
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)