General comments

$^1$H and $^{13}$C spectra were recorded on a Bruker Avance 300 spectrometer at 300 and 75 MHz respectively; chemical shifts are reported in ppm from TMS. Optical rotations were determined with a Perkin Elmer 141 instrument. All the reactions were carried out under argon. Column chromatography was performed on a silica gel 230-400 mesh. The TLCs were run on Merck Kieselgel 60F 254 plates. The melting points are uncorrected. THF and ether were distilled from sodium/benzophenone ketyl. Dichloromethane was distilled from calcium hydride.

2-[2-(Benzyl-methyl-amino)-ethyl]-3-phenyl-oxirane-2-carbonitrile, $4a$

A 50 mL flask was charged with 148 mg of azetidinium salt (0.41 mmol, M = 358.47), 25 mL of dry THF were added. After complete dissolution, the mixture was cool to -78°C with acetone/dry ice. At this temperature benzaldehyde (42 μL, 1 equiv., 0.41 mmol, M = 106.12, d = 1.044) was added immediately followed by LiHMDS in THF (620 μL, 1.5 equiv., 0.62 mmol, c = 1 mol.L$^{-1}$). The reaction was completed after a period of 15 min, at which point 20 mL of a saturated solution of ammonium chloride were added (the temperature was still of -78°C). The mixture was partitioned between water and dichloromethane, the organic phases were dried over MgSO$_4$ and the solvent evaporated under vacuum. The brown residue was rapidly purified by chromatography over silica gel (eluent Et$_2$O/PE : 1/1, $R_f$ 0.3) to give epoxide $4a$ as a colourless oil (119 mg, 98 %, M = 292.37). $\nu_{\text{max}}$(KBr)/cm$^{-1}$ 3405, 3352, 2238. $\delta$H (300 MHz; CDCl$_3$) 2.11-2.24 (2H, m), 2.29 (3H, s), 2.73-2.90 (2H, m), 3.55-3.66 (2H, m), 4.12 (1H, s), 7.31-7.35 (6H, m), 7.39-7.47 (4H, m). $\delta$C (75 MHz; CDCl$_3$) 32.59, 41.82, 52.80, 63.59, 116.54, 126.40, 127.22, 127.88, 128.30, 129.06, 129.45, 132.26, 138.50.

2-[2-(Benzyl-methyl-amino)-ethyl]-3-(3-nitro-phenyl)-oxirane-2-carbonitrile, $4b$

The procedure employed for compound $4a$ was reproduced using 3-nitrobenzaldehyde with azetidinium salt $3$. The residue was purified by chromatography over silica gel (eluent Et$_2$O/PE : 1/1, $R_f$ 0.1) to give epoxide $4b$ as a colourless oil (177 mg, 77 %, M = 337.37). $\nu_{\text{max}}$(KBr)/cm$^{-1}$ 3411, 3348, 2242. $\delta$H (300 MHz; CDCl$_3$) 2.00-2.07 (1H, m), 2.12-2.20 (1H, m), 2.17 (3H, s), 2.61-2.73 (2H, m), 3.43 (1H, d, $J$ 13 Hz), 3.52 (1H, d, $J$ 13 Hz), 4.10 (1H, s), 7.17-7.20 (5H, m), 7.50-7.63 (2H, m), 8.17-8.20 ( 2H, m). $\delta$C (75 MHz; CDCl$_3$) 32.22, 41.85, 52.66, 56.74, 62.23, 62.71, 115.97, 121.90, 124.35, 127.34, 128.40, 129.05, 129.84, 132.10, 134.73, 138.38, 148.34.

2-[2-(Benzyl-methyl-amino)-ethyl]-3-ethyl-oxirane-2-carbonitrile, $4e$

The procedure employed for compound $4a$ was reproduced using propanal with azetidinium salt $3$. The residue was purified by chromatography over silica gel (eluent Et$_2$O/PE : 1/1, $R_f$ 0.2) to give epoxide $4e$ as a colourless oil (115 mg, 94 %, M = 244.3). $\nu_{\text{max}}$(KBr)/cm$^{-1}$ 3405, 3345, 2239. $\delta$H (300 MHz; CDCl$_3$) 1.02 (3H, t, $J$ 7.5 Hz), 1.65-1.72 (2H, m), 1.74-1.98 (2H, m), 2.10 (3H, s), 2.53-2.65 (2H, m), 2.86 (1H, t, $J$ 6.1 Hz), 3.38 (1H, d, $J$ 13 Hz), 3.49 (1H, d, $J$ 13 Hz), 7.16-7.24 (5H, m). $\delta$C (75 MHz; CDCl$_3$) 9.84, 23.59, 32.10, 41.84, 52.86, 53.04, 62.55, 64.38, 117.48, 127.19, 128.33, 129.01, 138.59.

2-[2-(Benzyl-methyl-amino)-ethyl]-3-methyl-3-phenyl-oxirane-2-carbonitrile, $4f$

The procedure employed for compound $4a$ was reproduced using acetophenone with azetidinium salt $3$. The residue was purified by chromatography over silica gel (eluent Et$_2$O/PE : 1/1, $R_f$ 0.4 ) to give epoxide $4f$ as a colourless oil (179 mg, 99 %, M = 306.40). $\nu_{\text{max}}$(KBr)/cm$^{-1}$ 3419, 3355, 2245. $\delta$H (300 MHz; CDCl$_3$) 1.40-1.59 (2H, m), 1.80 (3H, s), 1.92, (3H, s), 2.35-2.52 (2H, m), 3.22 (1H, d, $J$ 13 Hz), 3.36 (1H, d, $J$ 13 Hz), 7.07-7.25 (10H, m). $\delta$C (75 MHz; CDCl$_3$) 22.69, 28.77, 41.89, 52.55, 58.13, 62.40, 67.33, 118.06, 126.39, 127.16, 128.34, 128.52, 128.54, 129.07, 136.61, 138.86.

2-[2-(Benzyl-methyl-amino)-ethyl]-3,3-dimethyl-oxirane-2-carbonitrile, $4g$

The procedure employed for compound $4a$ was reproduced using acetone with azetidinium salt $3$. The residue was purified by chromatography over silica gel (eluent Et$_2$O/PE : 1/1, $R_f$ 0.4 ) to give epoxide
2-[2-(Benzyl-methyl-amino)-1-phenyl-ethyl]-3-methyl-3-phenyl-oxirane-2-carbonitrile, \(8\)

The procedure employed for compound \(4a\) was reproduced using acetophenone with azetidinium salt \(7\). The residue was purified by chromatography over silica gel (eluent \(\text{Et}_2\text{O}/\text{PE}: 3/7, R_f 0.3\)) to give \(epoxide 8\) as a colourless oil (83 mg, 61%, \(M = 382.49\)).  
\[\begin{align*}
\delta_H & (300 MHz; \text{CDCl}_3) 1.56 (3H, s), 1.92 (3H, s), 2.47 (1H, dd, \ J = 6.7\text{ and } 9.2Hz), 2.55-2.61 (1H, m), 2.91 (1H, dd, \ J = 9.2\text{ and } 12.7Hz), 3.14 (1H, d, \ J = 13Hz), 3.40 (1H, d, \ J = 13Hz), 7.13-7.29 (15H, m). \\
\delta_C & (75 MHz; \text{CDCl}_3) 22.56, 41.99, 42.79, 59.77, 63.01, 69.33, 117.48, 127.11, 127.24, 127.80, 128.34, 128.37, 128.45, 128.77, 128.82, 129.04, 136.61, 137.48, 138.90.
\end{align*}\]

2-[2-(Benzyl-methyl-amino)-1-phenyl-ethyl]-3-phenyl-oxirane-2-carboxylic acid ethyl ester, \(10\)

The procedure employed for compound \(4a\) was reproduced using benzaldehyde with azetidinium salt \(9\). The residue was purified by chromatography over silica gel (eluent \(\text{Et}_2\text{O}/\text{PE}: 3/7, R_f 0.3\)) to give \(epoxide 10\) as a colourless oil (125 mg, 85%, \(M = 415.52\)).  
\[\begin{align*}
\alpha_D^{25} & +26.3 (c 1.35 \text{ in } \text{CHCl}_3). \\
\nu_{max} & (\text{KBr})/\text{cm}^{-1} 3425, 3356, 1745. \\
\delta_H & (300 MHz; \text{CDCl}_3) 1.06 (3H, t, \ J = 7.1Hz), 1.37 (3H, s), 2.33 (1H, dd, \ J = 4\text{ and } 12.5Hz), 2.74 (1H, dd, \ J = 4\text{ and } 10.5Hz), 2.91 (1H, d, \ J = 13.1Hz), 3.09 (1H, d, \ J = 13.1Hz), 3.35 (1H, dd, \ J = 10.5\text{ and } 12.5Hz), 4.31 (1H, s), 6.96-7.21 (15H, m). \\
\delta_C & (75 MHz; \text{CDCl}_3) 13.94, 41.30, 42.02, 57.04, 61.53, 62.45, 62.88, 65.45, 126.82, 127.04, 128.02, 128.14, 128.41, 128.56, 128.58, 128.94, 130.00, 133.61, 137.96, 138.63, 169.19.
\end{align*}\]

2-Benzyl-1-methyl-2-phenyl-pyrrolidin-3-one \(13a\)

The crude epoxide \(4a\), prepared as describe above is heated without solvent under reduced pressure for a period of 4 hours (Precautions should be taken due to the formation of hydrogen cyanide!) The yellow oil was purified by chromatography on silica gel (eluent \(\text{Et}_2\text{O}/\text{PE}: 1/1, R_f 0.6\)) to give \(pyrrolidinone 13a\) as a colourless oil (89 mg, 81%, \(M = 265.35\)).  
\[\begin{align*}
\nu_{max} & (\text{KBr})/\text{cm}^{-1} 3057, 2924, 1746. \\
\delta_H & (300 MHz; \text{CDCl}_3) 1.81-1.92 (1H, m), 2.23-2.26 (1H, m), 2.31 (3H, s), 2.69-2.82 (2H, m), 3.22 (1H, d, \ J = 11.6Hz), 3.30 (1H, d, \ J = 11.6Hz), 4.31 (1H, s), 6.96-7.21 (15H, m). \\
\delta_C & (75 MHz; \text{CDCl}_3) 35.49, 37.88, 39.11, 48.36, 73.81, 126.43, 127.42, 127.51, 127.90, 128.32, 131.18, 137.34, 139.45, 217.89. \text{HRMS (TOF MS ES+)} [\text{MH}^+] \text{ C}_{18}\text{H}_{20}\text{NO} \text{ requires } 266.1545, \text{found } 266.1551.
\end{align*}\]

2-Benzyl-1-methyl-2-(3-nitro-phenyl)-pyrrolidin-3-one, \(13b\)

The crude epoxide \(4b\), prepared as describe above is heated without solvent under reduced pressure for a period of 12 hours (Precautions should be taken due to the formation of hydrogen cyanide!) The yellow oil was purified by chromatography on silica gel (eluent \(\text{Et}_2\text{O}/\text{PE}: 1/1, R_f 0.4\)) to give \(pyrrolidinone 13b\) as a colourless oil (76 mg, 71%, \(M = 310.34\)).  
\[\begin{align*}
\delta_H & (300 MHz; \text{CDCl}_3) 2.02 (1H, ddd, \ J = 4.6\text{ and } 7.7\text{ and } 18.7Hz), 2.38 (1H, ddd, \ J = 6.5\text{ and } 8.3\text{ and } 18.7Hz), 2.49 (3H, s), 2.54-2.61 (1H, m), 2.93-3.00 (1H, m), 3.20 (1H, d, \ J = 13.6Hz), 3.47 (1H, d, \ J = 13.6Hz), 7.15-7.19 (5H, m), 7.47 (1H, t, \ J = 8.1Hz), 7.67-7.70 (1H, m), 8.05-8.09 (1H, m), 8.24 (1H, br s). \\
\delta_C & (75 MHz; \text{CDCl}_3) 35.29, 37.44, 39.73, 48.35, 73.52, 122.47, 122.53, 127.07, 128.37, 129.40, 130.97, 133.80, 136.44, 143.08, 148.07, 216.30. \text{HRMS (TOF MS ES+)} [\text{MH}^+] \text{ C}_{18}\text{H}_{19}\text{N}_{2}\text{O}_{3} \text{ requires } 311.1396, \text{found } 311.1402.
\end{align*}\]

2-Benzyl-2-(4-methoxy-phenyl)-1-methyl-pyrrolidin-3-one, \(13c\)

The crude epoxide \(4c\), prepared as describe above is heated without solvent under reduced pressure for a period of 2 hours (Precautions should be taken due to the formation of hydrogen cyanide!) The yellow oil was purified by chromatography on silica gel (eluent \(\text{Et}_2\text{O}/\text{PE}: 1/1, R_f 0.5\)) to give \(pyrrolidinone 13c\) as a colourless oil (117 mg, 58%, \(M = 295.37\)).  
\[\begin{align*}
\delta_H & (300 MHz; \text{CDCl}_3) 1.82-1.93 (1H, m), 2.23-2.33 (1H, m), 2.32 (3H, s), 2.71-2.79 (2H, m), 3.20
\end{align*}\]
2-Benzyl-2-ethyl-1-methyl-pyrrolidin-3-one, 13d
The crude epoxide 4d, prepared as described above, is heated without solvent under reduced pressure for a period of 8 hours (Precautions should be taken due to the formation of hydrogen cyanide!) The yellow oil was purified by chromatography on silica gel (eluent Et₂O/PE : 1/1, Rf 0.5) to give pyrrolidinone 13c as a colourless oil (17 mg, 20%, M = 217.30). ν max (KBr)/cm⁻¹ 3057, 3027, 2924, 1746. δH (300 MHz; CDCl₃) 0.72 (3H, t, J 7.3 Hz), 1.48-1.68 (2H, m), 1.89-1.97 (1H, m), 2.10-2.19 (1H, m), 2.46 (3H, s), 2.62-2.75 (3H, m), 2.82-2.90 (1H, m), 6.99-7.02 (2H, m), 7.08-7.18 (3H, m). δC (75 MHz; CDCl₃) 9.08, 26.12, 34.19, 37.29, 39.01, 48.26, 71.05, 126.19, 127.84, 130.59, 137.62, 218.41. HRMS (TOF MS ES+) [MH⁺] C₁₄H₂₀NO requires 218.1545, found 218.1555

2-Benzyl-1-methyl-2-((E)-styryl)-pyrrolidin-3-one, 13e
The crude epoxide 4e, prepared as described above, is heated without solvent under reduced pressure for a period of 8 hours (Precautions should be taken due to the formation of hydrogen cyanide!) The yellow oil was purified by chromatography on silica gel (eluent Et₂O/PE : 1/1, Rf 0.5) to give pyrrolidinone 13e as a colourless oil (38 mg, 20%, M = 277.36). δH (300 MHz; CDCl₃) 2.02-2.15 (1H, m), 2.30-2.44 (1H, m), 2.57 (3H, s), 2.77-2.90 (1H, m), 2.95-3.06 (1H, m), 3.04 and 3.23 (2 x 1H, AB system, J 13.8 Hz), 6.26 (1H, d, J 16.2), 6.57 (1H, d, J 16.2), 7.21-7.39 (10H, m). δC (75 MHz; CDCl₃) 35.28, 36.82, 39.30, 48.34, 72.30, 125.38, 126.24, 126.40, 127.78, 128.53, 130.71, 132.60, 136.50, 136.88, 215.39. MS (ESI) [MNa⁺] C₂₀H₂₁NNaO requires 314.15, found 314.20

Aziridination of phenyl-N-tosylimine.
A 50 mL flask was charged with 359 mg of azetidinium salt 3 (1.0 mmol, M = 358.47), 25 mL of dry THF were added. After complete dissolution, the mixture was cooled to -78°C with acetone/dry ice. At this temperature tosylimine (311 mg, 1.2 equiv., 1.2 mmol, M = 259.32) was added immediately followed by LiHMDS in THF (2.2 mL, 2.2 equiv., 2.2 mmol, c = 1 mol.L⁻¹). The reaction was completed after a period of 50 min, at which point 20 mL of a saturated solution of ammonium chloride were added (the temperature was still of -78°C). The mixture was partitioned between water and dichloromethane, the organic phases were dried over MgSO₄ and the solvent evaporated under vacuum. The TLC (eluent Et₂O/PE : 1/1) showed the presence of two products 18a and 18b, with Rf 18a 0.22 and Rf 18b 0.33. Heating at 50°C for 30 min performed the conversion of compound 18b into product 19 with Rf 19 0.46, while compound 18a were still present as indicated by the spot with Rf 18a 0.22. Chromatographic separation using silica gel allowed the isolation of 19 as a pale yellow solid (134 mg, 30 %, M = 418.55) followed by 18a as a pale yellow oil (144 mg, 30 %, M = 445.57).

2-[2-(Benzyl-methyl-amino)-ethyl]-3-phenyl-1-(toluene-4-sulfonyl)-aziridine-2-carbonitrile, 18a
ν max (KBr)/cm⁻¹ 3078, 3027, 1634, 1593. δH (300 MHz; CDCl₃) 1.33-1.44 (1H, m), 1.54-1.64 (1H, m), 1.79 (3H, s), 2.24-2.38 (2H, m), 2.33 (3H, s), 3.15 (1H, d, J 13.8 Hz), 3.22 (1H, d, J 13.8 Hz), 4.43 (1H, s), 7.05-7.24 (12H, m), 7.83 (2H, d, J 8.28 Hz). δC (75 MHz; CDCl₃) 21.81, 28.32, 40.37, 41.55, 51.01, 53.14, 62.26, 116.21, 127.13, 127.60, 128.29, 128.54, 128.80, 128.97, 129.28, 128.84, 130.04, 134.32, 138.45, 145.72.

N-[2-Benzyl-1-methyl-2-phenyl-pyrrolidin-(3E)-ylidene]-4-methyl-benzenesulfonamide, 19
ν max (KBr)/cm⁻¹ 3283, 3062, 2238. δH (300 MHz; CDCl₃) 2.19 (3H, s), 2.35 (3H, s), 2.39-2.51 (1H, m), 2.60-2.68 (1H, m), 2.83-2.89 (1H, m), 3.06-3.18 (1H, m), 3.16 (1H, d, J 13.7 Hz), 3.40 (1H, d, J 13.7 Hz), 6.98-7.08 (7H, m), 7.17-7.28 (5H, m), 7.66 (2H, d, J 8.3 Hz). δC (75 MHz; CDCl₃) 21.67, 34.72, 34.96, 39.62, 50.39, 75.01, 126.31, 127.46, 127.50, 127.58, 127.65, 128.44, 129.47, 131.32, 136.92, 137.23, 139.27, 143.97, 198.70.
# Supplementary Material (ESI) for Chemical Communications
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![NMR spectra images with chemical structures and peaks labeled with ppm values.](image-url)
N
O

N
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ORTEP diagram of compound 19