Synthesis of functionalized amino epoxides by a three-component coupling involving aziridines, arynes and aldehydes

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1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. 30 °C corresponds to the room temperature of the lab when the experiments were carried out. THF was freshly purified by distillation over Na-benzophenone and was transferred under argon. [18]-Crown-6 was recrystallized from dry CH₃CN and KF was dried by heating at 110 °C for 12 h and left to cool under argon and stored in argon filled glove box. The aldehydes were purchased from either Sigma Aldrich, Acros Organics or from other commercial sources and were purified either by distillation or washing with NaHCO₃ solution, prior to use. All the aziridines were prepared following the literature procedure. The 2(trimethylsilyl)phenyl trifluoromethanesulfonate and the other symmetric and unsymmetric aryne precursors were synthesized following literature procedure.

Analytical thin layer chromatography was performed on TLC Silica gel 60 F₂₅₄. Visualization was accomplished with short wave UV light. Chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with solvents as indicated.

All compounds were fully characterized. ¹H and ¹³C NMR spectra were recorded on Bruker AV 400, 500 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: δH = 7.26 ppm, δC = 77.16 ppm). Gas Chromatography was recorded on Agilent 7890 B GC. Infrared spectra were recorded on a Bruker Alpha-E Infrared Spectrophotometer. The wave numbers (ν) of recorded IR-signals are quoted in cm⁻¹. HRMS data were recorded on either Thermo Scientific Q-Exactive, Accela 1250 pump or Waters SYNAPT G2 High Definition Mass Spectroscopy System. X-ray intensity data measurements of compound 4r was carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoKα= 0.71073Å) radiation at room temperature.

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2. General Procedure for the Reaction Involving Aziridines, Arynes and Aldehydes

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added KF (87 mg, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) inside a glove-box. Aldehyde 3 (0.50 mmol) followed by THF (2.0 mL) was added outside the glove-box under argon atmosphere (solid aldehydes were weighed in air and transferred to the screw-capped test tube by closing the argon flow and liquid aldehydes were transferred via syringe with argon flow). To this solution was added aziridine 1 (0.60 mmol) and continued stirring for five minutes at 30 °C. After five minutes of stirring, aryne precursor 2 (0.75 mmol) was added. Then the reaction mixture was kept stirring for 12 h at 30 °C. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 98/02) on silica gel to afford the corresponding amino epoxides 4 in moderate to good yields. It may be mentioned that the reaction works well without glove-box techniques maintaining the isolated yield of 4.

3. General Procedure for the Reaction Involving Aziridines, Arynes and Isatins
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added KF (87 mg, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) inside a glove-box. Isatin 5 (0.50 mmol) followed by THF (2.0 mL) was added outside the glove-box under argon atmosphere. To this solution was added aziridine 1 (0.60 mmol) and continued stirring for five minutes at 30 °C. After five minutes of stirring, aryne precursor 2 (0.75 mmol) was added. Then the reaction mixture was kept stirring for 12 h at 30 °C. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 90/10) on silica gel to afford the corresponding spiro amino epoxides 6 in moderate to good yields.

4. X-ray data of 4r and 4r’

X-ray intensity data measurements of compound 4r and 4r’ were carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoKα = 0.71073Å) radiation at room temperature. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 10 secs keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on F². All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. An ORTEP III view of both compounds were drawn with 30% probability displacement ellipsoids and H atoms are shown as small spheres of arbitrary radii.

Crystal data and structure refinement for Compound 4r

Crystal data of 4r C$_{23}$H$_{19}$ClN$_2$O, M = 374.85, colorless block, 0.40 x 0.31 x 0.17 mm$^3$, monoclinic, space group $P_2_1/c$, $a = 11.925(6)$ Å, $b = 23.667(12)$ Å, $c = 7.039(4)$ Å, $\beta = 99.498(6)^\circ$, $V = 1959.4(17)$ Å$^3$, $Z = 4$, $T = 296(2)$ K, $2\theta_{\text{max}}=50.00^\circ$, $D_{\text{calc}}$ (g cm$^{-3}$) = 1.271, $F(000) = 784$, $\mu$ (mm$^{-1}$) = 0.209, 12071 reflections collected, 3345 unique reflections ($R_{\text{int}}=0.0601$), 2627 observed ($I > 2\sigma (I)$) reflections, multi-scan absorption correction, $T_{\text{min}} = 0.921$, $T_{\text{max}} = 0.965$, 334 refined parameters, $S = 1.416$, $R1 = 0.0559$, $wR2 = 0.1374$ (all data $R = 0.0722$, $wR2 = 0.1448$), maximum and minimum residual electron densities; $\Delta\rho_{\text{max}} = 0.17$, $\Delta\rho_{\text{min}} = -0.31$ (eÅ$^{-3}$).

Crystal structure of 4r (thermal ellipsoids are shown with 30% probability).

CCDC 1444745 (4r) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Crystal data and structure refinement for Compound 4r’

Crystal data of 4r’  C_{23}H_{19}ClN_{2}O, M = 374.85, colorless block, 0.45 x 0.32 x 0.26 mm^3, triclinic, space group P-1, a = 9.859(2) Å, b = 9.973(2) Å, c = 11.943(3) Å, α = 103.759(14)°, β = 101.793(14)°, γ = 114.317(12)°, V = 976.9(4) Å^3, Z = 2, T = 296(2) K, 2θ_{max} = 50.00°, D_{calc} (g cm^{-3}) = 1.274, F(000) = 392, μ (mm^{-1}) = 0.210, 9717 reflections collected, 3288 unique reflections (R_{int}=0.0910), 1556 observed (I > 2σ (I)) reflections, multi-scan absorption correction, T_{min} = 0.911, T_{max} = 0.947, 244 refined parameters, S = 1.295, R1 = 0.0923, wR2 = 0.2626 (all data R = 0.3420, wR2 = 0.4100), maximum and minimum residual electron densities; Δρ_{max} = 0.50, Δρ_{min} = -0.57 (eÅ^{-3}).

Crystal structure of 4r’ (thermal ellipsoids are shown with 30% probability).

CCDC 1444746 (4r’) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
5. Synthesis and Characterization of N-Aryl Amino Epoxides

3-(4-Chlorophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4a)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulphonate 2a (0.223 g, 182 μL, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4a (0.123 g, 72% yield). [the dr of crude reaction mixture determined using GC analysis is 90:10]

\[ R_f \text{(Pet. ether /EtOAc = 90/10): 0.53; } \]
\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 7.36 - 7.30 \text{ (m, 4H), 7.15} \]
\( d, J = 7.2 \text{ Hz, 2H}) 6.85 \text{ (t, } J = 7.2 \text{ Hz, 1H), 6.78 \text{ (d, } J = 8.2 \text{ Hz, 2H), 4.06 \text{ (d, } J = 16.0 \text{ Hz, 1H), 3.96 \text{ (d, } J = 16.1 \text{ Hz, 1H), 3.91 \text{ (s, 1H), 3.34 \text{ (dd, } J = 14.8 \text{ Hz, 6.1 Hz, 1H), 3.13 \text{ (dd, } J = 14.8 \text{ Hz, 8.5 Hz, 1H), 2.16 - 2.06 \text{ (m, 1H), 0.96 \text{ (dd, } J = 9.4 \text{ Hz, 6.8 Hz, 6H). }} \]
\[ ^13C \text{ NMR (100 MHz, CDCl}_3) \delta 147.51, 135.57, 130.37, 129.68, 128.97, 127.58, 118.36, 115.99, 113.47, 61.60, 60.46, 56.64, 53.75, 27.12, 20.54, 20.37. \]
\[ \text{HRMS (ESI) calculated [M+H]^+ for C}_20\text{H}_{22}\text{ClN}_2\text{O: 341.1415, found: 341.1413. FTIR (cm}^{-1}) 3022, 2963, 2403, 1599, 1501, 1373, 1217, 1045, 764, 672. \]

((Isobutyl(phenyl)amino)methyl)-3-(p-tolyl)oxirane-2-carbonitrile (4b)

Following the general procedure, treatment of 1-isobutylaziridin-2-carbonitrile 1a (0.075 g, 0.60 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulphonate 2a (0.223 g, 182 μL, 0.75 mmol) with p-tolualdehyde 3b (0.60 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded ((isobutyl(phenyl)amino)methyl)-3-(p-tolyl)oxirane-2-carbonitrile as a yellow oil 4b (0.96 g, 60% yield). [the dr of crude reaction mixture determined using GC analysis is 90:10]
**2-((Iso-Butyl(phenyl)amino)methyl)-3-phenyloxirane-2-carbonitrile (4c)**

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with benzaldehyde 3c (0.053 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 2-((iso-butyl(phenyl)amino)methyl)-3-phenyloxirane-2-carbonitrile as a yellow oil 4c (0.090 g, 59% yield). [the *dr* of crude reaction mixture determined using GC analysis is 88:12]

*Rf* (Pet. ether /EtOAc = 90/10): 0.53; **1H NMR** (400 MHz, CDCl₃) δ 7.42 - 7.40 (m, 3H), 7.37-7.33 (m, 2H), 7.28 - 7.25 (m, 2H), 6.90 - 6.86 (m, 1H), 6.83 (d, *J* = 8.2 Hz, 2H), 4.12 - 3.98 (m, 3H) 3.41 (dd, *J* = 6.2 Hz, 14.9 Hz, 1H), 3.21 (dd, *J* = 8.4 Hz, 14.8 Hz, 1H), 2.18 - 2.11 (m, 1H), 1.02 (dd, *J* = 6.6 Hz, 10.1 Hz, 6H). **13C NMR** (100 MHz, CDCl₃) δ 147.56, 131.77, 129.63, 129.55, 128.64, 126.19, 118.17, 116.19, 113.37, 62.16, 60.35, 56.65, 53.87, 27.08, 20.55, 20.38. **HRMS (ESI)** calculated [M+H]⁺ for C₂₀H₂₃N₂O: 307.1805, found: 307.1801. **FTIR (cm⁻¹)** 2404, 1733, 1599, 1502, 1464, 1374, 1217, 1129, 938, 864, 678.

**3-(4-Bromophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4d)**

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.60 mmol) and 2-(trimethylsilyl)phenyl...
trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 4-bromobenzaldehyde 3d (0.93 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(4-bromophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4d (0.112 g, 58% yield).

[the dr of crude reaction mixture determined using GC analysis is 89:11]

\[ R_f (\text{Pet. ether /EtOAc} = 90/10): 0.55; \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 7.66 (d, J = 8.3 \text{ Hz}, 2H), 7.34 - 7.30 (m, 4H), 6.87 (t, J = 7.3 \text{ Hz}, 1H), 6.77 (d, J = 8.3 \text{ Hz}, 2H), 4.10 (d, J = 16.3 \text{ Hz}, 1H), 3.99 (d, J = 15.5 \text{ Hz}, 1H), 3.99 (s, 1H), 3.35 (dd, J = 14.9 \text{ Hz}, 6.2 \text{ Hz}, 1H), 3.12 (dd, J = 14.8 \text{ Hz}, 8.5 \text{ Hz}, 1H), 2.13 - 2.05 (m, 1H), 0.96 (dd, J = 9.2 \text{ Hz}, 6.6 \text{ Hz}, 6H). \]

\[ ^13C \text{ NMR (100 MHz, CDCl}_3) \delta 147.31, 137.09, 132.44, 129.74, 126.97, 118.52, 118.30, 115.56, 113.44, 61.17, 60.49, 56.67, 53.53, 27.09, 20.49, 20.32. \]

HRMS (ESI) calculated [M+H] + for C_{20}H_{22}BrN_{2}O: 385.0910, found: 385.0904.

FTIR (cm⁻¹) 3022, 2965, 2235, 1645, 1599, 1218, 1036, 927, 767.

3-(4-Cyanophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4e)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.60 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 4-cyanobenzaldehyde 3e (0.66 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(4-cyanophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4e (0.111 g, 67% yield). [the dr of crude reaction mixture determined using GC analysis is 87:13]

\[ R_f (\text{Pet. ether /EtOAc} = 90/10): 0.41; \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 7.51 (d, J = 8.4 \text{ Hz}, 2H), 7.32 (t, J = 8.4 \text{ Hz}, 2H), 7.09 (d, J = 8.4 \text{ Hz}, 2H), 6.86 (t, J = 7.3 \text{ Hz}, 1H), 6.78 (d, J = 8.2 \text{ Hz}, 2H), 4.01 (dd, J = 42.8 \text{ Hz}, 16.1 \text{ Hz}, 2H), 3.90 (s, 1H), 3.35 (dd, J = 14.8 \text{ Hz}, 6.1 \text{ Hz}, 1H), 3.14 (dd, J = 14.8 \text{ Hz}, 8.5 \text{ Hz}, 1H), 2.15 - 2.06 (m, 1H), 0.97 (dd, J = 9.4 \text{ Hz}, 6.7 \text{ Hz}, 6H). \]

\[ ^13C \text{ NMR (100 MHz, CDCl}_3) \delta 147.45, 131.88, 130.87, 129.66, 127.82, 123.76, 118.33, 115.95, 113.41, 61.62, 60.42, 56.56, 53.69, 27.08, 20.52, 20.36. \]

HRMS (ESI) calculated [M+H] + for
C_{21}H_{22}N_{3}O: 332.1757, found: 332.1750. FTIR (cm\(^{-1}\)) 3021, 2962, 2404, 1599, 1500, 1372, 1217, 1125, 926, 763.

**Methyl 4-(3-cyano-3-((isobutyl(phenyl)amino)methyl)oxiran-2-yl)benzoate (4f)**

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile \(1a\) (0.075 g, 0.60 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate \(2a\) (0.223 g, 182 \(\mu\)L, 0.75 mmol) with methyl 4-formylbenzoate \(3f\) (0.82 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 98/02) of the crude reaction mixture using silica gel afforded methyl 4-(3-cyano-3-((isobutyl(phenyl)amino)methyl)oxiran-2-yl)benzoate as a yellow oil \(4f\) (0.126 g, 69% yield). [the \(d_r\) of crude reaction mixture determined using GC analysis is 87:13]

\(R_f\) (Pet. ether/EtOAc = 90/10): 0.40; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.04 (d, \(J = 8.1\) Hz, 2H), 7.33 - 7.26 (m, 7.4 Hz, 4H), 6.86 (t, \(J = 7.2\) Hz, 1H), 6.78 (d, \(J = 8.2\) Hz, 2H), 4.08 (d, \(J = 16.2\) Hz, 1H), 3.99 d, \(J = 16.0\) Hz, 1H), 3.98 (s, 1H), 3.91 (s, 3H), 3.35 (dd, \(J = 14.8\) Hz, 6.1 Hz, 1H), 3.13 (dd, \(J = 14.8\) Hz, 8.5 Hz, 1H), 2.18 - 2.00 (m, 1H), 0.96 (dd, \(J = 12.6\) Hz, 6.6 Hz, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 166.56, 147.41, 136.72, 131.23, 129.90, 129.70, 126.23, 118.35, 115.82, 113.38, 61.59, 60.42, 56.64, 53.70, 52.38, 27.09, 20.53, 20.35. HRMS (ESI) calculated [M+H]\(^+\) for C\(_{22}\)H\(_{25}\)N\(_2\)O\(_3\): 365.1860, found: 365.1854. FTIR (cm\(^{-1}\)) 3022, 2963, 2404, 1720, 1601, 1599, 1500, 1433, 1373, 1283, 1217, 1113, 1035, 769.

\(\text{2-((Isobutyl(phenyl)amino)methyl)-3-(3-methoxyphenyl)oxirane-2-carbonitrile (4g)}\)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile \(1a\) (0.075 g, 0.60 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate \(2a\) (0.223 g, 182 \(\mu\)L, 0.75 mmol) with 3-methoxybenzaldehyde \(3g\) (0.68 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 98/02) of the crude reaction mixture using silica gel
afforded 2-((isobutyl(phenyl)amino)methyl)-3-(3-methoxyphenyl)oxirane-2-carbonitrile as a yellow oil 4g (0.93 g, 55% yield). [the $dr$ of crude reaction mixture determined using GC analysis is 87:13]

$R_f$ (Pet. ether /EtOAc = 90/10): 0.50; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 - 7.19 (m, 3H), 6.91 (dd, $J = 8.2$ Hz, 2.2 Hz, 1H), 6.88 - 6.72 (m, 5H), 4.01 (dd, $J = 39.3$ Hz, 16.1 Hz, 2H), 3.93 (s, 1H), 3.80 (s, 3H), 3.35 (dd, $J = 14.8$ Hz, 6.2 Hz, 1H), 3.16 (dd, $J = 14.8$ Hz, 8.4 Hz, 1H), 2.15 - 2.07 (m, 1H), 0.97 (dd, $J = 9.5$ Hz, 6.7 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.81, 147.59, 133.33, 129.78, 129.62, 118.57, 118.24, 116.17, 115.54, 113.49, 111.17, 62.42, 60.40, 56.56, 55.37, 53.93, 27.11, 20.54, 20.38. HRMS (ESI) calculated [M+H]$^+$ for C$_{21}$H$_{25}$N$_2$O$_2$: 337.1911, found: 337.1903. FTIR (cm$^{-1}$) 3021, 2962, 2404, 1600, 1500, 1466, 1218, 1044, 871, 770.

3-(3-Bromophenyl)-2-((iso-butyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4h)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 $\mu$L, 0.75 mmol) with 3-bromobenzaldehyde 3h (0.093 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(3-bromophenyl)-2-((iso-butyl(phenyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4h (0.118 g, 61% yield). [the $dr$ of crude reaction mixture determined using GC analysis is 85:15]

$R_f$ (Pet. ether /EtOAc = 90/10): 0.53; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 7.9$ Hz, 1H), 7.37-7.33 (m, 3H), 7.29-7.25 (m, 1H), 7.19 (d, $J = 7.6$ Hz, 1H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.82 (d, $J = 8.3$ Hz, 2H), 4.11 (d, $J = 15.9$ Hz, 1H), 4.01 (d, $J = 16.6$ Hz, 1H), 3.92 (s, 1H), 3.99 (dd, $J = 6.2$ Hz, 14.9 Hz, 1H), 3.18 (dd, $J = 8.6$ Hz, 14.8 Hz, 1H), 2.18 - 2.08 (m, 1H), 1.01 (dd, $J = 6.6$ Hz, 9.2 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.45, 134.17, 132.68, 130.25, 129.69, 129.33, 124.69, 122.74, 118.43, 113.49, 61.18, 60.43, 56.57, 53.74, 27.08, 20.53, 20.36. HRMS (ESI) calculated [M+H]$^+$ for C$_{21}$H$_{25}$BrN$_2$O: 385.0910, found: 385.0912. FTIR (cm$^{-1}$) 2404, 1599, 1502, 1433, 1372, 1217, 1129, 1039, 920, 767, 678.
Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 2-fluorobenzaldehyde 3i (0.062 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(2-fluorophenyl)-2-((iso-butyl(phenyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4i (0.097 g, 60% yield). [the dr of crude reaction mixture determined using GC analysis is 87:13]

Rf(Pet. ether /EtOAc = 90/10): 0.57; \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.41 - 7.31 (m, 4H), 7.23 (t, J = 7.4 Hz, 1H), 7.11 (t, J = 8.9 Hz, 1H), 6.88-6.84 (m, 3H), 4.31 (s, 1H), 4.11 (d, J = 16.1 Hz, 1H), 4.05 (d, J = 16.1 Hz, 1H), 3.38 (dd, J = 6.7 Hz, 14.9 Hz, 1H), 3.27 (dd, J = 8.0 Hz, 14.9 Hz, 1H), 2.19 - 2.14 (m, 1H), 1.03 (dd, J = 6.8 Hz, 9.8 Hz, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 161.42 (d, J = 248.8 Hz), 147.56, 131.06 (d, J = 8.1 Hz), 129.50, 127.01 (d, J = 2.7 Hz), 124.48 (d, J = 3.4 Hz), 119.69 (d, J = 13.0 Hz), 118.19, 115.89, 115.39 (d, J = 20.4 Hz), 113.53, 60.04, 57.24 (d, J = 5.6 Hz), 56.46, 53.87, 26.87, 20.51, 20.38. HRMS (ESI) calculated [M+H]\(^+\) for C\(_{20}\)H\(_{22}\)FN\(_2\)O: 325.1711, found: 325.1705. FTIR (cm\(^{-1}\)) 2404, 1599, 1501, 1462, 1373, 1218, 1132, 1039, 981, 925, 869, 767, 675.

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 2-nitrobenzaldehyde 3j (0.76 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 2-((iso-butyl(phenyl)amino)methyl)-3-(2-nitrophenyl)oxirane-2-carbonitrile as a yellow solid 4j (0.117 g, 67% yield). [the dr of crude reaction mixture determined using GC analysis is 70:30]
R<sub>f</sub> (Pet. ether/EtOAc = 90/10): 0.37; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32 (d, J = 8.3 Hz, 1H), 7.80 - 7.61 (m, 3H), 7.34-7.28 (m, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.86-6.83 (m, 1H), 4.63 (s, 1H), 4.40 (d, J = 16.3 Hz, 1H), 3.98 (d, J = 16.3 Hz, 1H), 3.47 (dd, J<sub>1</sub> = 7.0 Hz, J<sub>2</sub> = 14.9 Hz, 1H), 3.35 (dd, J<sub>1</sub> = 7.5, J<sub>2</sub> = 15.1 Hz, 1H), 2.25 - 2.20 (m, 1H), 1.04 (d, J = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.65, 146.98, 134.90, 130.29, 129.53, 129.32, 128.53, 125.27, 118.16, 115.64, 113.94, 59.94, 59.08, 57.20, 54.20, 26.53, 20.49, 20.43. HRMS (ESI) calculated [M+H]<sup>+</sup> for C<sub>20</sub>H<sub>22</sub>N<sub>3</sub>O<sub>3</sub>: 352.1656, found: 352.1651. FTIR (cm<sup>-1</sup>) 2405, 1600, 1520, 1352, 1304, 1216, 1132, 1038, 977, 923, 854, 750, 679.

3-(3,4-Dichlorophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4k)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 3,4-dichlorobenzaldehyde 3k (0.88 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(3,4-dichlorophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4k (0.132 g, 70% yield). [the <em>dr</em> of crude reaction mixture determined using GC analysis is 87:13]

R<sub>f</sub> (Pet. ether/EtOAc = 90/10): 0.56; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 (d, J = 8.3 Hz, 1H), 7.32 (t, J = 3.0 Hz, 1H), 7.27 (t, J = 8.2 Hz, 2H), 7.04 (dd, J = 8.3 Hz, 1.8 Hz, 1H), 6.87 (t, J = 7.3 Hz, 1H), 6.77 (d, J = 8.2 Hz, 2H), 4.01 (dd, J = 45.5 Hz, 16.1 Hz, 2H), 3.87 (s, 1H), 3.33 (dd, J = 14.8 Hz, 6.1 Hz, 1H), 3.11 (dd, J = 14.8, 8.5 Hz, 1H), 2.21 - 2.01 (m, 1H), 0.96 (dd, J = 9.0 Hz, 6.7 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.42, 133.87, 133.15, 132.16, 130.83, 129.74, 128.30, 125.35, 118.57, 115.71, 113.57, 60.86, 60.53, 56.56, 53.66, 27.12, 20.53, 20.36. HRMS (ESI) calculated [M+H]<sup>+</sup> for C<sub>20</sub>H<sub>21</sub>Cl<sub>2</sub>N<sub>2</sub>O: 375.1025, found: 375.1025. FTIR (cm<sup>-1</sup>) 3022, 2967, 2403, 1599, 1528, 1427, 1247, 1217, 1043, 977, 772.
2-((iso-Butyl(phenyl)amino)methyl)-3-(naphthalen-1-yl)oxirane-2-carbonitrile (4l)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 2-naphthaldehyde 3l (0.78 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 2-((iso-butyl(phenyl)amino)methyl)-3-(naphthalen-1-yl)oxirane-2-carbonitrile as a yellow solid 4l (0.132 g, 74% yield). [the dr of crude reaction mixture determined using GC analysis is 88:12]

\[ R_f (\text{Pet. ether } /\text{EtOAc} = 90/10): 0.53; \quad ^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.90 - 7.88 (m, 3H), 7.77 (s, 1H), 7.56-7.54 (m, 2H), 7.42-7.34 (m, 3H), 6.95-6.87 (m, 3H), 4.16-4.03 (m, 3H), 3.43 (dd, \[ J = 6.2 \text{ Hz}, 15.0\text{Hz}, 1H), 3.23 (dd, \[ J = 8.3 \text{ Hz} \quad 14.7 \text{ Hz}, 1H), \quad 2.21 - 2.15 (m, 1H), 1.05 (dd, \[ J = 6.7 \text{ Hz}, 10.36 \text{ Hz}, 6H). \quad ^{13}\text{C NMR (100 MHz, CDCl}_3) \delta 147.61, 133.85, 132.92, 129.66, 129.25, 128.58, 128.24, 127.94, 126.83, 126.70, 125.97, 123.10, 118.24, 116.23, 113.48, 62.34, 60.38, 56.85, 53.96, 27.08, 20.55, 20.38. \quad \text{HRMS (ESI)} \text{ calculated } [\text{M+H}]^{+} \text{ for C}_{24}\text{H}_{25}\text{N}_{2}\text{O}: 357.1961, \text{found 357.1953.} \quad \text{FTIR (cm}^{-1}) 2404, 1692, 1599, 1504, 1469, 1374, 1217, 1129, 1041, 977, 916, 863, 786.

2-((iso-Butyl(phenyl)amino)methyl)-3-phenethyloxirane-2-carbonitrile (4m)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 3-phenylpropanal 3m (0.067 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 2-((iso-butyl(phenyl)amino)methyl)-3-phenethyloxirane-2-carbonitrile as a yellow oil 4m (0.094 g, 56% yield). [the dr of crude reaction mixture determined using GC analysis is >95:5]

\[ R_f (\text{Pet. ether } /\text{EtOAc} = 90/10): 0.57; \quad ^1\text{H NMR (400 MHz, CDCl}_3) \delta 7.34 - 7.25 (m, 5H), 7.19 (d, \[ J = 7.4 \text{ Hz}, 2H), 6.83 (t, \[ J = 6.9 \text{ Hz}, 1H), 6.76 (d, \[ J = 7.8 \text{ Hz}, 2H), 3.89-3.81 (m, 2H), 3.28
(dd, $J = 6.4\text{Hz}$, $14.4\text{Hz}$, $1\text{H}$), 3.13 (dd, $J = 8.2\text{Hz}$, $14.7\text{Hz}$, $1\text{H}$), 3.02 (t, $J = 6.0\text{Hz}$, $1\text{H}$), 2.78 (t, $J = 7.8\text{Hz}$, $2\text{H}$), 2.15-2.04 (m, $3\text{H}$), 0.97-0.94 (m, $6\text{H}$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.63, 140.03, 129.50, 128.71, 128.46, 126.51, 118.04, 116.92, 113.46, 61.13, 60.09, 53.83, 53.75, 31.79, 31.58, 26.86, 20.49, 20.38. HRMS (ESI) calculated [M+H]$^+$ for C$_{22}$H$_{27}$N$_2$O: 335.2118, found: 335.2114. FTIR (cm$^{-1}$) 2247, 1599, 1502, 1459, 1373, 1217, 1132, 1038, 984, 920, 870, 770, 677.

3-Ethyl-2-((iso-butyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4n)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 $\mu$L, 0.75 mmol) with propionaldehyde 3n (0.029 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-ethyl-2-((iso-butyl(phenyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4n (0.074 g, 57% yield). [the $d_r$ of crude reaction mixture determined using GC analysis is >95:5]

$R_f$ (Pet. ether /EtOAc = 90/10): 0.60; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 - 7.27 (m, $2\text{H}$), 6.83-6.75 (m, $3\text{H}$), 3.95 (d, $J = 16.1\text{Hz}$, $1\text{H}$), 3.88 (d, $J = 16.0\text{Hz}$, $1\text{H}$), 3.31 (dd, $J = 6.4\text{Hz}$, 14.7 Hz, $1\text{H}$), 3.16 (dd, $J_1 = 8.1\text{Hz}$, 14.8 Hz, $1\text{H}$), 2.95 (t, $J = 6.7\text{Hz}$, $1\text{H}$), 2.13-2.09 (m, $1\text{H}$), 1.87-1.82 (m, $1\text{H}$), 1.75-1.68 (m, $1\text{H}$), 1.07 (t, $J = 7.5\text{Hz}$, $3\text{H}$), 0.99-0.95 (m, $6\text{H}$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.62, 129.44, 117.93, 117.03, 113.36, 63.03, 60.10, 53.73, 53.42, 26.89, 23.35, 20.47, 20.35, 9.72. HRMS (ESI) calculated [M+H]$^+$ for C$_{16}$H$_{23}$N$_2$O: 259.1805, found: 259.1803. FTIR (cm$^{-1}$) 2405, 1631, 1600, 1502, 1463, 1375, 1218, 1037, 917, 767, 674.

3-Cyclohexyl-2-((iso-butyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4o)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 $\mu$L, 0.75 mmol) with cyclohexanecarbaldehyde 3o (0.056 g, 0.50 mmol) in the presence of
KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-cyclohexyl-2-((iso-butyl(phenyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4o (0.090 g, 58% yield). [the dr of crude reaction mixture determined using GC analysis is >95:5]

**Rf** (Pet. ether /EtOAc = 90/10): 0.70; **1H NMR (400 MHz, CDCl3)** δ 7.29 - 7.25 (m, 2H), 6.82-6.72 (m, 3H), 3.95 (d, J = 16.1 Hz, 1H), 3.85 (d, J = 16.0 Hz, 1H), 3.31 (dd, J = 6.4 Hz, 14.7 Hz, 1H), 3.14 (dd, J = 8.2 Hz, 14.8 Hz, 1H), 2.71 (d, J = 9.2 Hz, 1H), 2.15-2.05 (m, 1H), 1.92-1.90 (m, 1H), 1.73-1.67 (m, 5H), 1.46-1.11 (m, 5H), 0.97-0.94 (m, 6H). **13C NMR (100 MHz, CDCl3)** δ 205.13, 147.51, 129.41, 117.84, 117.16, 113.28, 66.13, 60.06, 53.66, 52.97, 38.91, 29.81, 28.26, 26.91, 25.94, 25.14, 25.01, 20.47, 20.34. **HRMS (ESI)** calculated [M+H] + for C20H29N2O: 313.2274, found: 313.2271. **FTIR (cm⁻¹)** 2405, 1599, 1504, 1455, 1357, 1218, 1127, 1037, 982, 921, 767, 674.

2-((Butyl(phenyl)amino)methyl)-3-(4-chlorophenyl)oxirane-2-carbonitrile (4p)

Following the general procedure, treatment of 1-butylaziridine-2-carbonitrile 1p (0.075 g, 0.60 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 2-((butyl(phenyl)amino)methyl)-3-(4-chlorophenyl)oxirane-2-carbonitrile as a yellow oil 4p (0.121 g, 71% yield). [the dr of crude reaction mixture determined using GC analysis is 87:13]

**Rf** (Pet. ether /EtOAc = 90/10): 0.57; **1H NMR (400 MHz, CDCl3)** δ 7.38 - 7.29 (m, 4H), 7.20 (d, J = 8.5 Hz, 2H), 6.84 (t, J = 7.3 Hz, 1H), 6.74 (d, J = 8.1 Hz, 2H), 4.03 - 3.87 (m, 3H), 3.39 (dd, J = 9.0 Hz, 6.7 Hz, 2H), 1.66 - 1.57 (m, 2H), 1.45 - 1.33 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H). **13C NMR (100 MHz, CDCl3)** δ 147.34, 135.61, 130.40, 129.74, 129.01, 127.64, 118.16, 115.98, 112.82, 61.26, 56.76, 53.06, 52.28, 28.95, 20.29, 14.07. **HRMS (ESI)** calculated [M+H] + for C20H22ClN2O: 341.1415, found: 341.1410. **FTIR (cm⁻¹)** 3021, 2962, 2452, 1598, 1501, 1455, 1357, 1218, 1127, 1037, 982, 921, 767, 674.
3-(4-Chlorophenyl)-2-((dodecyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4q)

Following the general procedure, treatment of 1-dodecylaziridine-2-carbonitrile 1q (0.142 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-2-((dodecyl(phenyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4q (0.136 g, 60% yield). [the dr of crude reaction mixture determined using GC analysis is 88:12]

Rf (Pet. ether/EtOAc = 90/10): 0.60; $^1$H NMR (400 MHz, CDCl₃) $\delta$ 7.36 (d, $J = 8.4$ Hz, 2H), 7.31 (t, $J = 7.9$ Hz, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 6.84 (t, $J = 7.3$ Hz, 1H), 6.73 (d, $J = 8.3$ Hz, 2H), 4.00 - 3.91 (m, 3H), 3.38 (dd, $J = 9.0$ Hz, 6.6 Hz, 2H), 1.64 - 1.60 (m, 2H), 1.33 - 1.27 (m, 18H), 0.89 (t, $J = 6.7$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ 147.33, 135.62, 130.40, 129.75, 129.01, 127.65, 118.12, 115.99, 112.76, 61.25, 56.75, 53.03, 52.55, 32.05, 29.77, 29.72, 29.59, 29.48, 27.10, 26.82, 22.83, 14.27. HRMS (ESI) calculated [M+H]$^+$ for C₂₈H₃₈ClN₂O: 453.2667, found: 453.2665. FTIR (cm⁻¹) 3021, 2962, 2404, 1737, 1599, 1500, 1430, 1372, 1219, 1094, 1045, 977, 769.

2-((Benzyl(phenyl)amino)methyl)-3-(4-chlorophenyl)oxirane-2-carbonitrile (4r)

Following the general procedure, treatment of 1-benzylaziridine-2-carbonitrile 1r (0.095 g, 0.60 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 2-((benzyl(phenyl)amino)methyl)-3-(4-chlorophenyl)oxirane-2-carbonitrile as a yellow oil 4r (0.141 g, 75% yield). [the dr of crude reaction mixture determined using GC analysis is 88:12]

Rf (Pet. ether/ EtOAc = 95/05): 0.58; $^1$H NMR (400 MHz, CDCl₃) $\delta$ 7.39 - 7.21 (m, 11H), 6.90 - 6.83 (m, 3H), 4.71 (dd, $J = 38.8$ Hz, 17.2 Hz, 2H), 4.12 - 3.99 (m, 3H). $^{13}$C NMR (100 MHz,
3-(4-Chlorophenyl)-2-(((isopropyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4s)

Following the general procedure, treatment of 1-isopropylaziridine-2-carbonitrile 1s (0.066 g, 0.60 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 µL, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-2-(((isopropyl(phenyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4s (0.100 g, 61% yield).

[the dr of crude reaction mixture determined using GC analysis is 87:13]

Rf (Pet. ether /EtOAc = 90/10): 0.58; 1H NMR (400 MHz, CDCl3) δ 7.33 (t, J = 7.8 Hz, 4H), 7.13 (d, J = 8.4 Hz, 2H), 6.92 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 8.1 Hz, 2H), 4.08 - 4.02 (m, 1H), 3.92 (s, 1H), 3.86 (d, J = 16.0 Hz, 1H), 3.72 (d, J = 16.0 Hz, 1H), 1.24 (d, J = 6.6 Hz, 3H), 1.19 (d, J = 6.6 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 148.11, 135.48, 130.55, 129.67, 128.94, 127.59, 119.61, 116.20, 115.73, 61.65, 57.01, 49.78, 46.94, 21.02, 19.61. HRMS (ESI) calculated [M+H] + for C19H20ClN2O: 327.1259, found: 327.1257. FTIR (cm⁻¹) 3021, 2964, 2405, 1737, 1600, 1500, 1374, 1220, 1121, 1022, 929, 768.

3-(4-Chlorophenyl)-2-((cyclohexyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4t)

Following the general procedure, treatment of 1-cyclohexyl aziridine-2-carbonitrile 1t (0.090 g, 0.60 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 µL, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet.
ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-2-((cyclohexyl(phenyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4t (0.134 g, 73% yield). [the dr of crude reaction mixture determined using GC analysis is 85:15] 

**R**f (Pet. ether /EtOAc = 90/10): 0.53; **1H NMR (400 MHz, CDCl3)** δ 7.35 - 7.26 (m, 4H), 7.12 (d, J = 8.5 Hz, 2H), 6.91 (t, J = 7.3 Hz, 1H), 6.85 (d, J = 8.2 Hz, 2H), 3.94 - 3.90 (m, 2H), 3.76 (d, J = 16.1 Hz, 1H), 3.58 - 3.52 (m, 1H), 1.89 (m, 4H), 1.71 (d, J = 12.8 Hz, 1H), 1.44 - 1.28 (m, 4H), 1.23 - 1.09 (m, 1H). **13C NMR (100 MHz, CDCl3)** δ 148.05, 135.47, 130.57, 129.66, 128.94, 127.58, 119.48, 116.23, 115.59, 61.63, 58.49, 57.12, 47.74, 31.67, 30.39, 26.20, 26.09, 25.87. **HRMS (ESI)** calculated [M+H] + for C22H24ClN2O: 367.1572, found: 367.1570. **FTIR (cm⁻¹)** 3021, 2935, 2859, 2404, 1597, 1499, 1351, 1218, 1092, 935, 767.

### Ethyl 3-(4-Chlorophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carboxylate (4u)

Following the general procedure, treatment of ethyl 1-isobutylaziridine-2-carboxylate 1u (0.103 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded ethyl 3-(4-chlorophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carboxylate as a yellow oil 4u (0.130 g, 67% yield). [the dr of crude reaction mixture determined using GC analysis is 89:11] 

**R**f (Pet. ether /EtOAc = 90/10): 0.56; **1H NMR (400 MHz, CDCl3)** δ 7.32 - 7.24 (m, 4H), 7.14 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.3 Hz, 2H), 6.77 (t, J = 7.2 Hz, 1H), 4.18 (d, J = 16.1 Hz, 1H), 4.04 - 3.94 (m, 3H), 3.86 (s, 1H), 3.39 (dd, J = 14.9 Hz, 5.7 Hz, 1H), 3.11 (dd, J = 14.9 Hz, 8.9 Hz, 1H), 2.26 - 2.03 (m, 1H), 1.00 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.2 Hz, 6H). **13C NMR (100 MHz, CDCl3)** δ 167.55, 148.24, 134.21, 132.05, 129.46, 128.31, 127.68, 117.09, 112.68, 65.82, 61.64, 60.39, 59.83, 52.34, 27.02, 20.59, 20.37, 13.99. **HRMS (ESI)** calculated [M+H] + for C22H27ClNO3: 388.1674, found: 388.1673. **FTIR (cm⁻¹)** 3021, 2964, 2404, 1737, 1599, 1501, 1376, 1305, 1219, 1120, 1022, 930, 767.
3-(4-Chlorophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4v)

Following the general procedure, treatment of methyl 1-isobutylaziridine-2-carboxylate 1v (0.094 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/2) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4v (0.103 g, 55% yield). [the dr of crude reaction mixture determined using GC analysis is 87:13]

Rf (Pet. ether /EtOAc = 90/10): 0.58; ¹H NMR (400 MHz, CDCl3) δ 7.30 (t, J = 8.4, 7.5 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.3 Hz, 2H), 6.78 (t, J = 7.2 Hz, 1H), 4.18 (d, J = 16.2 Hz, 1H), 3.98 (d, J = 16.2 Hz, 1H), 3.86 (s, 1H), 3.52 (s, 3H), 3.38 (dd, J = 14.8 Hz, 5.7 Hz, 1H), 3.10 (dd, J = 14.9 Hz, 9.0 Hz, 1H), 2.16 - 2.10 (m, 1H), 0.94 (dd, J = 8.9 Hz, 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl3) δ 167.98, 148.17, 134.27, 131.93, 129.48, 128.41, 127.57, 117.14, 112.67, 66.03, 60.46, 59.84, 52.38, 52.35, 27.00, 20.58, 20.37. HRMS (ESI) calculated [M+H]⁺ for C21H25ClNO3: 374.1517, found: 374.1514. FTIR (cm⁻¹) 3021, 2964, 2404, 1602, 1507, 1429, 1374, 1217, 1046, 926, 768.

Ethyl -2-((benzyl(phenyl)amino)methyl)-3-(4-chlorophenyl)oxirane-2-carboxylate (4w)

Following the general procedure, treatment of ethyl 1-benzylaziridine-2-carboxylate 1w (0.123 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/2) of the crude reaction mixture using silica gel afforded Ethyl -2-((benzyl(phenyl)amino)methyl)-3-(4-chlorophenyl)oxirane-2-carboxylate as a white solid 4w (0.152 g, 72% yield). [the dr of crude reaction mixture determined using GC analysis is 89:11]

Rf (Pet. ether /EtOAc = 90/10): 0.49; ¹H NMR (400 MHz, CDCl3) δ 7.36 - 7.23 (m, 11H), 6.91 (d, J = 8.5 Hz, 2H), 6.83 (t, J = 7.1 Hz, 1H), 4.75 (q, J = 17.4 Hz, 2H), 4.17 (dd, J = 44.4, 16.2
3-(4-Chlorophenyl)-2-(((3,4-dimethylphenyl)(isobutyl)amino)methyl)oxirane-2-carbonitrile (4x)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 2b (0.245 g, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-2-(((3,4-dimethylphenyl)(isobutyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4x (0.101 g, 55% yield). [the dr of crude reaction mixture determined using GC analysis is 78:22]

$R_f$ (Pet. ether /EtOAc = 90/10): 0.57; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, $J = 8.2$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.2$ Hz, 1H), 6.63-6.57 (m, 2H), 4.05-3.89 (m, 3H), 3.32 (dd, $J = 6.2$ Hz, 14.5 Hz, 1H), 3.16 (dd, $J = 8.3$ Hz, 14.2 Hz, 1H), 2.30 (s, 3H), 2.26 (s, 3H), 2.15 – 2.08 (m, 1H) 1.0-0.96 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.91, 137.69, 135.48, 130.67, 129.57, 128.93, 127.56, 116.11, 115.74, 111.61, 61.62, 60.73, 56.81, 54.33, 27.14, 20.53, 20.41, 18.76. HRMS (ESI) calculated [M+H]$^+$ for C$_{25}$H$_{25}$ClNO$_3$: 422.1517, found: 422.1516. FTIR (cm$^{-1}$) 3020, 2968, 2401, 1745, 1601, 1506, 1495, 1389, 1217, 1123, 1016, 773.

3-(4-Chlorophenyl)-2-(((2,3-dihydro-1H-inden-5-yl)(isobutyl)amino)methyl)oxirane-2-carbonitrile (4y)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 3-
(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate 2c (0.261 g, 182 μL, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-2-(((2,3-dihydro-1H-inden-5-yl)(isobutyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4y (0.112 g, 59% yield). [the dr of crude reaction mixture determined using GC analysis is 87:13]

\[ R_f (\text{Pet. ether /EtOAc = 90/10}): 0.56; \] ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J = 8.5 Hz, 2H), 7.19 (dd, J = 8.6 Hz, 2.4 Hz, 3H), 6.73 (s, 1H), 6.63 (dd, J = 8.2, 2.3 Hz, 1H), 4.04 (d, J = 15.9 Hz, 1H), 3.95 (s, 1H), 3.91 (d, J = 15.9 Hz, 1H), 3.30 (dd, J = 14.5 Hz, 6.3 Hz, 1H), 3.14 (dd, J = 14.6 Hz, 8.3 Hz, 1H), 2.92 (dd, J = 16.6, 7.7 Hz, 4H), 2.16 - 2.10 (m, 3H), 0.99 (dd, J = 9.5 Hz, 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 146.64, 145.91, 135.48, 134.61, 130.54, 128.92, 127.56, 125.11, 116.14, 112.63, 110.74, 61.69, 61.09, 56.81, 54.79, 33.51, 32.04, 27.08, 25.84, 20.56, 20.43. HRMS (ESI) calculated [M+H]⁺ for C₂₃H₂₆ClN₂O: 381.1728, found: 381.1727.

FTIR (cm⁻¹) 3020, 2960, 2403, 1609, 1499, 1429, 1217, 1094, 926, 766.

2-((Benzo[d][1,3]dioxol-5-yl(isobutyl)amino)methyl)-3-(4-chlorophenyl)oxirane-2-carbonitrile (4z)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 6-(trimethylsilyl)benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate 2d (0.257 g, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.70 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded inseparable diastereomeric mixture of 2-((benzo[d][1,3]dioxol-5-yl(iso-butyl) amino)methyl)-3-(4-chlorophenyl)oxirane-2-carbonitrile as a yellow oil 4z (0.105 g, 55% yield). [the dr of crude reaction mixture determined using GC analysis is 72:28]

\[ R_f (\text{Pet. ether /EtOAc = 90/10}): 0.40; \] Data for Major isomer (4z): ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.5 Hz, 1H), 6.53 (d, J = 2.4 Hz, 1H), 6.31 (m, 1H), 5.96 (s, 2H), 3.92-3.73 (m, 3H), 3.19 (dd, J = 6.0 Hz, 13.9 Hz, 1H), 3.07 (dd,
Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2e (0.251 g, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-2-(((3,4-difluorophenyl)(isobutyl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4aa (0.109 g, 58% yield). [the dr of crude reaction mixture determined using GC analysis is 82:18]

\[ R_f \text{ (Pet. ether /EtOAc = 90/10): } 0.52; \]  
\[ {^1}H\text{ NMR (400 MHz, CDCl}_3\] \(\delta\) 7.40 (d, \(J = 8.4\) Hz, 2H), 7.10 (q, \(J = 9.3\) Hz, 1H), 6.61 (ddd, \(J = 13.4, 6.5, 3.0\) Hz, 1H), 6.47 - 6.45 (m, 1H), 4.04 - 3.84 (m, 3H), 3.28 (dd, \(J = 14.8\) Hz, 6.4 Hz, 1H), 3.13 (dd, \(J = 14.8\) Hz, 8.2 Hz, 1H), 2.11 - 2.07 (m, 1H), 0.97 (dd, \(J = 9.0, 6.7\) Hz, 6H). \[ {^{13}}C\text{ NMR (100 MHz, CDCl}_3\] \(\delta\) \(\delta\) 144.82 (d, \(J = 11.1\) Hz), 135.87, 129.98, 129.15, 127.59, 117.88 (d, \(J = 71.3\) Hz), 115.67, 109.00, 103.00, (d, \(J = 21.2\) Hz), 61.51, 60.79, 56.54, 54.53, 26.95, 20.47, 20.35. \[ \text{HRMS (ESI)}\\text{ calculated [M+H]}^+ \text{ for C}_{20}\text{H}_{20}\text{ClF}_2\text{N}_2\text{O: } 377.1227, \text{ found: } 377.1223. \]  
\[ \text{FTIR (cm}^{-1}\) 3022, 2963, 2403, 1599, 1502, 1472, 1420, 1370, 1216, 1132, 1038, 976, 927, 763.}
3-(4-Chlorophenyl)-2-((isobutyl(naphthalen-2-yl)amino)methyl)oxirane-2-carbonitrile (4ab)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2f (0.261 g, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded 3-(4-Chlorophenyl)-2-((isobutyl(naphthalen-2-yl)amino)methyl)oxirane-2-carbonitrile as a yellow oil 4ab (0.113 g, 58% yield). [the dr of crude reaction mixture determined using GC analysis is 82:18]

Rf (Pet. ether /EtOAc = 90/10): 0.52; 1H NMR (400 MHz, CDCl3) δ 7.77 (dd, J = 15.0 Hz, 8.6 Hz, 2H), 7.68 (d, J = 8.2 Hz, 1H), 7.42 (t, J = 7.3 Hz, 1H), 7.30 (d, J = 6.7 Hz, 3H), 7.15 (dd, J = 9.1 Hz, 2.5 Hz, 1H), 7.09 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 2.2 Hz, 1H), 4.18 (d, J = 16.1 Hz, 1H), 4.05 (d, J = 16.1 Hz, 1H), 3.95 (s, 1H), 3.47 (dd, J = 14.8 Hz, 6.3 Hz, 1H), 3.23 (dd, J = 14.8 Hz, 8.4 Hz, 1H), 2.25 - 2.10 (m, 1H), 0.99 (t, J = 6.9 Hz, 6H). 13C NMR (100 MHz, CDCl3) δ 145.29, 135.59, 134.90, 130.28, 129.59, 128.99, 127.65, 127.53, 126.91, 126.43, 123.17, 116.13, 116.01, 107.97, 61.65, 60.56, 56.61, 53.85, 27.31, 20.55, 20.41. HRMS (ESI) calculated [M+H]+ for C24H24ClN2O: 391.1572, found: 391.1570. FTIR (cm⁻¹) 3022, 2962, 2404, 1731, 1602, 1496, 1355, 1265, 1217, 1164, 1122, 1040, 984, 770.

3-(4-Chlorophenyl)-2-((isobutyl(p-tolyl)amino)methyl)oxirane-2-carbonitrile (4ac) and 3-(4-chlorophenyl)-2-((isobutyl(m-tolyl)amino)methyl)oxirane-2-carbonitrile (4ac′)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 4-fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 2g (0.237 g, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded
inseparable mixture of 3-(4-chlorophenyl)-2-((isobutyl(p-tolyl)amino)methyl)oxirane-2-carbonitrile (4ac) and 3-(4-chlorophenyl)-2-((isobutyl(m-tolyl)amino)methyl)oxirane-2-carbonitrile (4ac') as a yellow oil (0.114 g, 64% yield). [the dr of crude reaction mixture determined using GC analysis is 85:15]

\[ R_f \text{ (Pet. ether /EtOAc = 90/10): 0.56; } ^1H \text{ NMR of 4ac (400 MHz, CDCl}_3 \delta 7.36 \text{ (d, } J = 8.5 \text{ Hz, 2H), 7.23 - 7.12 \text{ (m, 4H) 6.70 (t, } J = 8.1 \text{ Hz, 2H), 4.06 (d, } J = 16.7 \text{ Hz, 1H), 3.94 (d, } J = 17.2 \text{ Hz, 1H), 3.92 (s, 1H), 3.35 - 3.25 (m, 1H), 3.15 - 3.08 (m, 1H), 2.36 (s, 3H) 2.14 - 2.04 (m, 1H), 0.98 - 0.94 (m, 6H).} ^13C \text{ NMR of 4ac (100 MHz, CDCl}_3 \delta 147.58, 139.39, 135.52, 130.44, 130.16, 129.50, 128.95, 127.88, 127.53, 119.28, 116.02, 114.09, 110.69, 61.63, 60.46, 56.67, 54.28, 53.75, 27.10, 22.09, 20.53, 20.38. } ^1H \text{ NMR of 4ac' (400 MHz, CDCl}_3 \delta 7.36 \text{ (d, } J = 8.5 \text{ Hz, 2H), 7.23 - 7.12 \text{ (m, 3H) 6.70 (t, } J = 8.1 \text{ Hz, 1H), 6.59 - 6.58 (m, 2H), 4.01 (d, } J = 16.8 \text{ Hz, 1H), 3.92 (s, 1H), 3.90 (d, } J = 17.1 \text{ Hz, 1H), 3.35 - 3.25 (m, 1H), 3.15 - 3.08 (m, 1H), 2.32 (s, 3H) 2.14 - 2.04 (m, 1H), 0.98 - 0.94 (m, 6H).} ^13C \text{ NMR of 4ac' (100 MHz, CDCl}_3 \delta 145.46, 139.39, 135.52, 130.44, 130.16, 129.50, 127.88, 127.53, 119.28, 116.07, 114.24, 110.69, 61.57, 60.73, 56.75, 54.28, 53.75, 27.09, 22.10, 20.53, 20.38. \text{ HRMS (ESI) calculated [M+H}^+] \text{ for C}_{21}\text{H}_{24}\text{ClN}_2\text{O: 355.1572, found: 355.1568. FTIR (cm}^{-1}\text{) 3021, 2962, 2404, 1601, 1506, 1374, 1217, 1095, 1046, 927, 767.}

3-(4-Chlorophenyl)-2-(((4-fluorophenyl)(isobutyl)amino)methyl)oxirane-2-carbonitrile (4ad) and -3-(4-Chlorophenyl)-2-(((3-fluorophenyl)(isobutyl)amino)methyl)oxirane-2-carbonitrile (4ad’)

Following the general procedure, treatment of 1-isobutylaziridine-2-carbonitrile 1a (0.075 g, 0.6 mmol) and 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 2h (0.234 g, 0.75 mmol) with 4-chlorobenzaldehyde 3a (0.070 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 98/02) of the crude reaction mixture using silica gel afforded inseparable 2:1 regioisomeric mixture of 3-(4-chlorophenyl)-2-(((4-fluorophenyl)(isobutyl)amino)methyl)oxirane-2-carbonitrile
(4ad) and -3-(4-chlorophenyl)-2-(((3-fluorophenyl)(isobutyl)amino)methyl)oxirane-2-carbonitrile (4ad’) as a yellow oil (0.116 g, 65% yield). [the dr of crude reaction mixture determined using GC analysis is 78:22]

$R_f$(Pet. ether/EtOAc = 90/10): 0.51; $^1$H NMR of 4ad (400 MHz, CDCl$_3$) δ 7.43 - 7.29 (m, 2H), 7.29 - 7.10 (m, 2H), 7.10 - 6.91 (m, 2H), 6.87 - 6.62 (m, 1H), 6.52 - 6.44 (m, 1H), 3.93 (d, $J$ = 15.9 Hz, 1H), 3.89 (s, 1H) 3.85 (d, $J$ = 15.9 Hz, 1H), 3.23 (dd, $J$ = 14.5 Hz, 6.4 Hz, 1H), 3.09 (dd, $J$ = 14.5 Hz, 8.2 Hz, 1H), 2.04 - 1.97 (m, 1H), 0.97 - 0.92 (m, 6H).

$^{13}$C NMR of 4ad (100 MHz, CDCl$_3$) δ 157.66 (d, $J$ = 239.6 Hz), 149.24 (d, $J$ = 10.6 Hz), 144.36, 135.69, 130.22, 129.04, 127.58, 116.26, 116.03, 108.58, 104.70 (d, $J$ = 21.4 Hz), 100.32 (d, $J$ = 26.4 Hz), 61.62, 61.27, 56.71, 55.17, 27.02, 20.52, 20.40.

$^1$H NMR of 4ad’ (400 MHz, CDCl$_3$) δ 7.43 - 7.29 (m, 2H), 7.29 - 7.10 (m, 2H), 7.10 - 6.91 (m, 1H), 6.87 - 6.62 (m, 2H), 6.64 - 6.28 (m, 1H), 4.00 (q, $J$ = 16.7 Hz, 1H), 3.91 (s, 1H), 3.33 (dd, $J$ = 15.0, 6.3 Hz, 1H), 3.13 (dd, $J$ = 15.2, 8.5 Hz, 1H), 2.16 - 2.06 (m, 1H), 0.97 - 0.92 (m, 6H).

$^{13}$C NMR of 4ad’ (100 MHz, CDCl$_3$) δ 164.29 (d, $J$ = 243.5 Hz), 149.18, 144.36, 135.69, 130.79 (d, $J$ = 10.1 Hz), 130.11, 129.04, 127.58, 116.26, 116.03, 115.95, 104.70 (d, $J$ = 21.4 Hz), 100.32 (d, $J$ = 26.4 Hz), 61.57, 61.27, 60.35, 56.44, 53.53, 27.02, 20.47, 20.32. HRMS (ESI) calculated [M+H]$^+$ for C$_{20}$H$_{21}$FClN$_2$O: 359.1321, found: 359.1318. FTIR (cm$^{-1}$) 3021, 2925, 1725, 1601, 1503, 1452, 1371, 1279, 1107, 977, 765.

3’-((Benzyl(phenyl)amino)methyl)-1-methyl-2-oxospiro[indoline-3,2'-oxirane]-3’-carbonitrile (6a)

Following the general procedure, treatment of 1-benzylaziridine-2-carbonitrile 1r (0.095 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonyl 2a (0.223 g, 182 μL, 0.75 mmol) with 1-methylindoline-2,3-dione 5a (0.081 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 3’-((benzyl(phenyl)amino)methyl)-1-methyl-2-oxospiro[indoline-3,2'-oxirane]-3’-carbonitrile 6a (0.119 g, 60% yield). [the dr of crude reaction mixture determined using GC analysis is >95:5]

Rf (Pet. ether /EtOAc = 70/30): 0.40; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.50 - 7.44 (m, 2H), 7.28 – 7.14 (m, 8H), 7.00 (d, \(J = 8.2\) Hz, 2H), 6.89 - 6.82 (m, 2H), 4.80 - 4.70 (m, 2H), 4.65 (d, \(J = 16.3\) Hz, 1H), 4.21 (d, \(J = 16.3\) Hz, 1H), 3.19 (s, 3H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.33, 148.29, 144.96, 137.83, 131.83, 129.44, 128.66, 127.14, 126.75, 123.53, 118.91, 118.72, 115.76, 114.40, 109.15, 63.37, 59.62, 55.92, 49.91, 26.94. HRMS (ESI) calculated [M+H] \(^+\) for C\(_{25}\)H\(_{22}\)N\(_3\)O\(_2\): 396.1707, found: 396.1703. FTIR (cm\(^{-1}\)) 3018, 2921, 2404, 1952, 1815, 1599, 1501, 1450, 1356, 1216, 1036, 763.

3’-((Benzyl(phenyl)amino)methyl)-5-bromo-1-methyl-2-oxospiro[indoline-3,2'-oxirane]-3’-carbonitrile (6b)

Following the general procedure, treatment of 1-benzylaziridine-2-carbonitrile 1r (0.095 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonyl 2a (0.223 g, 182 μL, 0.75 mmol) with 5-bromo-1-methylindoline-2,3-dione 5b (0.120 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 3’-((benzyl(phenyl)amino)methyl)-5-bromo-1-methyl-2-oxospiro[indoline-3,2'-oxirane]-3’-carbonitrile 6b (0.147 g, 62% yield). [the dr of crude reaction mixture determined using GC analysis is >95:5]
$R_f$ (Pet. ether/EtOAc = 70/30): 0.42; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J = 6.1$ Hz, 2H), 7.38 – 7.09 (m, 7H), 7.00 (d, $J = 8.3$ Hz, 2H), 6.86 (t, $J = 7.2$ Hz, 1H), 6.76 (d, $J = 8.8$ Hz, 1H), 4.73 (q, $J = 17.0$ Hz, 2H), 4.63 (d, $J = 16.3$ Hz, 1H), 4.21 (d, $J = 16.2$ Hz, 1H), 3.17 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.78, 148.28, 143.94, 137.82, 134.71, 129.48, 128.68, 127.61, 127.19, 126.91, 120.70, 119.17, 116.23, 115.45, 114.58, 110.56, 62.77, 59.69, 56.09, 49.79, 27.07. HRMS (ESI) calculated [M+H]$^+$ for C$_{25}$H$_{21}$BrN$_3$O$_2$: 474.0812, found: 474.0811. FTIR (cm$^{-1}$) 3018, 2958, 2404, 1598, 1501, 1459, 1361, 1288, 1216, 929, 770.

3'-((Benzyl(phenyl)amino)methyl)-5-fluoro-1-methyl-2-oxospiro[indoline-3,2'-oxirane]-3'-carbonitrile (6c)

Following the general procedure, treatment of 1-benzylaziridine-2-carbonitrile 1r (0.095 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 $\mu$L, 0.75 mmol) with 5-fluoro-1-methylindoline-2,3-dione 5c (0.090 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 3'-((benzyl(phenyl)amino)methyl)-5-fluoro-1-methyl-2-oxospiro[indoline-3,2'-oxirane]-3'-carbonitrile 6c (0.112 g, 54% yield). [the $dr$ of crude reaction mixture determined using GC analysis is >95:5]

$R_f$ (Pet. ether/EtOAc = 70/30): 0.39; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 - 7.23 (m, 7H), 7.20 – 7.15 (m, 2H), 7.02 (d, $J = 8.2$ Hz, 2H), 6.88 (t, $J = 7.2$ Hz, 1H), 6.82 (dd, $J = 8.6$ Hz, 3.9 Hz, 1H), 4.80 (d, $J = 17.0$ Hz, 1H), 4.71 (d, $J = 17.5$ Hz, 1H), 4.66 (d, $J = 16.4$ Hz, 1H), 4.24 (d, $J = 16.2$ Hz, 1H), 3.19 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.98, 160.47, 158.05, 148.22, 140.86, 137.77, 129.44, 128.62, 127.14, 126.84, 120.26 (d, $J = 8.3$ Hz), 119.03, 118.24 (d, $J = 23.6$ Hz), 115.51, 114.41, 112.80 (d, $J = 26.5$ Hz), 109.88 (d, $J = 7.7$ Hz), 59.63, 55.96, 49.72, 27.05. HRMS (ESI) calculated [M+H]$^+$ for C$_{25}$H$_{21}$FN$_3$O$_2$: 414.1612, found: 414.1609. FTIR (cm$^{-1}$) 3021, 2966, 2929, 2873, 2596, 1498, 1454, 1374, 1276, 1219, 1030, 991, 764.
1-Benzyl-3’-((benzyl(phenyl)amino)methyl)-2-oxospiro[indoline-3,2'-oxirane]-3’-carbonitrile (6d)

Following the general procedure, treatment of 1-benzylaziridine-2-carbonitrile 1r (0.095 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 1-benzylindoline-2,3-dione 5d (0.119 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 1-benzyl-3’-((benzyl(phenyl)amino)methyl)-2-oxospiro[indoline-3,2'-oxirane]-3’-carbonitrile 6d (0.139 g, 59% yield). [the dr of crude reaction mixture determined using GC analysis is >95:5]

Rf (Pet. ether /EtOAc = 70/30): 0.38; H NMR (400 MHz, CDCl3) δ 7.51 (d, J = 7.5 Hz, 1H), 7.37 - 7.28 (m, 6H), 7.28 - 7.18 (m, 7H), 7.13 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 8.3 Hz, 2H), 6.83 (dd, J = 7.5 Hz, 4.0 Hz, 2H), 4.90 (dd, J = 34.8 Hz, 15.6 Hz, 2H), 4.79 (s, 2H), 4.67 (d, J = 16.4 Hz, 1H), 4.28 (d, J = 16.4 Hz, 1H). C NMR (100 MHz, CDCl3) δ 168.60, 148.12, 144.21, 137.69, 134.78, 131.83, 129.48, 129.16, 128.76, 128.25, 127.56, 127.19, 126.88, 124.71, 123.63, 118.80, 118.72, 115.67, 114.24, 110.21, 63.42, 59.88, 55.75, 50.02, 44.72. HRMS (ESI) calculated [M+H]⁺ for C31H26N3O2: 472.2020, found: 472.2018. FTIR (cm⁻¹) 3019, 2928, 2404, 1956, 1604, 1501, 1452, 1324, 1217, 1121, 914, 763.

1-Allyl-3’-((benzyl(phenyl)amino)methyl)-2-oxospiro[indoline-3,2'-oxirane]-3’-carbonitrile (6e)

Following the general procedure, treatment of 1-benzylaziridine-2-carbonitrile 1r (0.095 g, 0.6 mmol) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate 2a (0.223 g, 182 μL, 0.75 mmol) with 1-allylindoline-2,3-dione 5e (0.081 g, 0.50 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 90/10) of the crude reaction mixture using silica gel afforded 1-allyl-3’-((benzyl(phenyl)amino)methyl)-2-oxospiro[indoline-3,2'-oxirane]-3’-carbonitrile 6e (0.119 g, 56% yield). [the dr of crude reaction mixture determined using GC analysis is >95:5]
$R_f$ (Pet. ether /EtOAc = 70/30): 0.43; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 8.0$ Hz, 1H), 7.46 (t, $J = 7.8$, 1H), 7.31 - 7.26 (m, 6H), 7.24 - 7.17 (m, 2H), 7.01 (d, $J = 8.1$ Hz, 2H), 6.94 (d, $J = 7.9$ Hz, 1H), 6.86 (t, $J = 7.3$ Hz, 1H), 5.90 - 5.80 (m, 1H), 5.34 (d, $J = 4.2$ Hz, 1H), 5.31 (d, $J = 1.4$ Hz, 1H), 4.81 (s, 2H), 4.68 (d, $J = 16.3$ Hz, 1H), 4.36 (d, $J = 5.5$ Hz, 2H), 4.27 (d, $J = 16.3$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.13, 148.09, 144.20, 137.67, 131.79, 130.50, 129.42, 128.71, 127.14, 126.81, 124.62, 123.51, 118.75, 118.64, 115.66, 114.18, 110.06, 63.32, 59.74, 55.71, 49.90, 43.21. HRMS (ESI) calculated [M+H]$^+$ for C$_{27}$H$_{24}$N$_3$O$_2$: 422.1863, found: 422.1859. FTIR (cm$^{-1}$) 3019, 2970, 2404, 1596, 1499, 1450, 1376, 1218, 1033, 937, 769.
7. $^1$H and $^{13}$C NMR Spectra of N-Aryl Amino Epoxides

3-(4-Chlorophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4a)
((Isobutyl(phenyl)amino)methyl)-3-(p-tolyl)oxirane-2-carbonitrile (4b)
2-((iso-Butyl(phenyl)amino)methyl)-3-phenyloxirane-2-carbonitrile (4c)
3-(4-Bromophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4d)
3-(4-Cyanophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4e)
Methyl 4-(3-cyano-3-((isobutyl(phenyl)amino)methyl)oxiran-2-yl)benzoate (4f)
2-((Isobutyl(phenyl)amino)methyl)-3-(3-methoxyphenyl)oxirane-2-carbonitrile (4g)
3-(3-Bromophenyl)-2-((iso-butyrl(phenyl)amino)methyl)oxirane-2-carbonitrile (4h)
3-(2-Fluorophenyl)-2-((iso-butyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4i)
2-((iso-Butyl(phenyl)amino)methyl)-3-(2-nitrophenyl)oxirane-2-carbonitrile (4j)
3-(3,4-Dichlorophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4k)
2-((iso-Butyl(phenyl)amino)methyl)-3-(naphthalen-1-yl)oxirane-2-carbonitrile (4l)
2-((iso-Butyl(phenyl)amino)methyl)-3-phenethyloxirane-2-carbonitrile (4m)
3-Ethyl-2-((iso-butyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4n)
3-Cyclohexyl-2-((iso-butyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4o)
2-((Butyl(phenyl)amino)methyl)-3-(4-chlorophenyl)oxirane-2-carbonitrile (4p)
3-(4-Chlorophenyl)-2-((dodecyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4q)
2-((Benzyl(phenyl)amino)methyl)-3-(4-chlorophenyl)oxirane-2-carbonitrile (4r)
3-(4-Chlorophenyl)-2-((isopropyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4s)
3-(4-Chlorophenyl)-2-((cyclohexyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4t)
Ethyl 3-(4-chlorophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carboxylate (4u)
3-(4-Chlorophenyl)-2-((isobutyl(phenyl)amino)methyl)oxirane-2-carbonitrile (4v)
Ethyl -2-((benzyl(phenyl)amino)methyl)-3-(4-chlorophenyl)oxirane-2-carboxylate (4w)
3-(4-Chlorophenyl)-2-(((3,4-dimethylphenyl)(isobutyl)amino)methyl)oxirane-2-carbonitrile (4x)
3-(4-Chlorophenyl)-2-(((2,3-dihydro-1H-inden-5-yl)(isobutyl)amino)methyl)oxirane-2-carbonitrile (4y)
(2S,3R)-2-((Benzo[d][1,3]dioxol-5-yl(isobutyl)amino)methyl)-3-(4-chlorophenyl)oxirane-2-carbonitrile (4z) and (2S,3S)-2-((Benzo[d][1,3]dioxol-5-yl(isobutyl)amino)methyl)-3-(4-chlorophenyl)oxirane-2-carbonitrile (4z')
3-(4-Chlorophenyl)-2-(((3,4-difluorophenyl)(isobutyl)amino)methyl)oxirane-2-carbonitrile (4aa)
3-(4-Chlorophenyl)-2-((isobutyl(naphthalen-2-yl)amino)methyl)oxirane-2-carbonitrile (4ab)
3-(4-Chlorophenyl)-2-((isobutyl(p-tolyl)amino)methyl)oxirane-2-carbonitrile (4ac) and 3-(4-chlorophenyl)-2-((isobutyl(m-tolyl)amino)methyl)oxirane-2-carbonitrile (4ac')
-(4-Chlorophenyl)-2-(((4-fluorophenyl)(isobutyl)amino)methyl)oxirane-2-carbonitrile (4ad) and -3-(4-Chlorophenyl)-2-(((3-fluorophenyl)(isobutyl)amino)methyl)oxirane-2-carbonitrile (4ad')
8. $^1$H and $^{13}$C NMR Spectra of $N$-Aryl Spiro Amino Epoxides 6

3'-((Benzyl(phenyl)amino)methyl)-1-methyl-2-oxospiro[indoline-3,2'-oxirane]-3'-carbonitrile (6a)
3'-((Benzyl(phenyl)amino)methyl)-5-bromo-1-methyl-2-oxospiro[indoline-3,2'-oxirane]-3'-carbonitrile (6b)
3’-((Benzyl(phenyl)amino)methyl)-5-fluoro-1-methyl-2-oxospiro[indoline-3,2’-oxirane]-3’-carbonitrile (6c)
1-Benzyl-3'-(benzyl(phenyl)amino)methyl)-2-oxo[indoline-3,2'-oxirane]-3'-carbonitrile (6d)
1-Allyl-3'-(benzyl(phenyl)amino)methyl)-2-oxospiro[indoline-3,2'-oxirane]-3'-carbonitrile (6e)