Supporting Information for

Nucleophilic Ring Opening of Aziridines with Amines under Catalyst- and Solvent-free Conditions

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General methods

All reactions and manipulations involving air-sensitive compounds were performed using standard Schlenk techniques. All reactions were monitored by TLC. TLC analysis was performed by illumination with a UV lamp (254 nm). All flash chromatography was packed with silica-gel as the stationary phase. 1H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from internal TMS with the solvent resonance as the internal standard (CDCl3, δ = 7.26 ppm). 13C NMR (126 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from TMS with the solvent resonance as the internal standard (CDCl3, δ = 77.2 ppm). High resolution MS (P-ESI HRMS) were obtained on Thermo Fisher Q Exactive Mass Spectrometer.

General procedure for the ring opening reactions

Amine (1.1 equiv) and aziridine1 (1.0 equiv) were added to a 1 mL test tube, followed by stirring at 50 °C. The reaction process was monitored by TLC. After the reaction completed, the residue was directly subjected to the preparative thin layer chromatography to afford the title product.
Characterization data of the ring opening adducts

**4-methyl-N-(2-phenyl-2-(phenylamino)ethyl)benzenesulfonamide (3aa):**
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1a (27.4 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 4:1) to afford the title compound (30.4 mg, 83%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.72 (d, 7.3 Hz, 2H), 7.34 - 7.26 (m, 7H), 7.07 (t, 7.0 Hz, 2H), 6.67 (t, 6.7 Hz, 1H), 6.47 (d, 7.4 Hz, 2H), 4.92 (s, 1H), 4.44 (d, 24.3 Hz, 2H), 3.34 (d, 13.2 Hz, 1H), 3.25 - 3.14 (m, 1H), 2.42 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 146.73, 143.75, 140.09, 136.80, 129.88, 129.07 (d, 18.9 Hz), 127.88, 127.09, 126.55, 117.98, 113.75, 57.44, 49.08, 21.53.

**N-(2-phenyl-2-(phenylamino)ethyl)methanesulfonamide (3ba):**
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1b (19.7 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 4:1) to afford the title compound (20.0 mg, 69%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.41 - 7.33 (m, 4H), 7.32 - 7.27 (m, 1H), 7.10 (t, 6.9 Hz, 2H), 6.69 (t, 6.7 Hz, 1H), 6.57 (d, 7.4 Hz, 2H), 4.77 (s, 1H), 4.53 (s, 2H), 3.48 (s, 1H), 3.41 (d, 5.8 Hz, 1H), 2.87 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 146.72, 140.08, 129.25, 129.07, 127.09, 126.64, 118.10, 113.77, 57.97, 49.16, 40.61.

**4-nitro-N-(2-phenyl-2-(phenylamino)ethyl)benzenesulfonamide (3ca):**
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1c (30.4 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 4:1) to afford the title compound (15.9 mg, 40%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.30 (d, 8.5 Hz, 2H), 7.99 (d, 8.5 Hz, 2H), 7.36 - 7.26 (m, 5H), 7.09 (t, 7.7 Hz, 2H), 6.70 (t, 7.3 Hz, 1H), 6.50 (d, 7.8 Hz, 2H), 4.95 (s, 1H), 4.59 - 4.30 (m, 2H), 3.50 - 3.40 (m, 1H), 3.29 (dt, 13.0 Hz, 6.4 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 150.08, 146.26, 145.69, 139.48, 129.22 (d, 14.1 Hz), 128.19, 126.46, 124.47, 118.54, 113.76, 60.43, 57.44, 48.97, 21.06, 14.20. HRMS calcd. for [M+H]$: 398.1175$, found: 398.1162.
tert-butyl (2-phenyl-2-(phenylamino)ethyl)carbamate (3da):
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1d (21.9 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (4.4 mg, 14%). 1H NMR (500 MHz, CDCl3) δ 7.36 (dd, 14.7 Hz, 7.7 Hz, 4H), 7.31 - 7.22 (m, 1H), 7.09 (t, 6.4 Hz, 2H), 6.65 (s, 1H), 6.51 (d, 6.9 Hz, 2H), 4.90 (d, 48.6 Hz, 2H), 4.44 (d, 3.9 Hz, 1H), 3.47 (d, 15.0 Hz, 2H), 1.48 (s, 9H). 13C NMR (126 MHz, CDCl3) δ 157.15, 147.50, 141.20, 129.12, 128.83, 127.51, 126.56, 117.26, 113.28, 79.96, 60.04, 47.31, 28.39. HRMS calcd. for [M+H]+: 313.1916, found: 313.1903.

benzyl (2-phenyl-2-(phenylamino)ethyl)carbamate (3ea):
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1e (25.3 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (20.1 mg, 58%). 1H NMR (500 MHz, CDCl3) δ 7.46 - 7.29 (m, 9H), 7.16 (t, 7.5 Hz, 1H), 7.09 (t, 7.0 Hz, 2H), 6.73 - 6.61 (m, 2H), 6.51 (d, 7.1 Hz, 2H), 5.14 (s, 2H), 5.02 (s, 1H), 4.48 (s, 1H), 3.55 (t, 5.6 Hz, 2H). 13C NMR (126 MHz, CDCl3) δ 157.45, 147.18, 140.84, 136.31, 129.31, 129.13, 128.90, 128.60, 128.21 (d, 12.4 Hz), 127.65, 126.57, 118.58, 117.52, 115.13, 113.40, 67.10, 59.41, 47.61. HRMS calcd. for [M+H]+: 347.1760, found: 347.1749.

N-(2-(2-chlorophenyl)-2-(phenylamino)ethyl)-4-methylbenzenesulfonamide (3fa):
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1f (30.8 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (31.7 mg, 79%). 1H NMR (500 MHz, CDCl3) δ 7.74 (d, 7.8 Hz, 2H), 7.43 (s, 1H), 7.34 (d, 2.6 Hz, 1H), 7.31 - 7.25 (m, 2H), 7.19 (s, 2H), 7.07 (t, 7.5 Hz, 2H), 6.67 (t, 7.2 Hz, 1H), 6.42 (d, 7.8 Hz, 2H), 4.83 (s, 3H), 3.48 - 3.35 (m, 1H), 3.25 - 3.10 (m, 1H), 2.42 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 146.27, 143.81, 136.86 (d, 15.2 Hz), 132.73, 129.88, 129.09 (d, 15.9 Hz), 128.22, 127.52, 127.09, 118.04, 113.51, 54.30, 46.82, 21.53.
N-(2-(3-chlorophenyl)-2-(phenylamino)ethyl)-4-methylbenzenesulfonamide (3ga):
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1g (30.8 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (36.5 mg, 91%). ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, 7.4 Hz, 2H), 7.27 (d, 9.1 Hz, 3H), 7.22 (s, 2H), 7.18 (d, 5.8 Hz, 1H), 7.08 (t, 7.4 Hz, 2H), 6.69 (t, 7.2 Hz, 1H), 6.45 (d, 7.7 Hz, 2H), 4.98 (s, 1H), 4.80 - 4.44 (m, 1H), 4.36 (s, 1H), 3.34 - 3.28 (m, 1H), 3.20 - 3.12 (m, 1H), 2.42 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 146.44, 143.91, 136.65, 134.92, 130.28, 129.94, 129.19, 128.12, 127.05, 126.66, 124.80, 118.23, 113.72, 57.25, 48.99, 21.55. HRMS calcd. for [M+H]^+: 401.1091, found: 401.1080.

N-(2-(4-chlorophenyl)-2-(phenylamino)ethyl)-4-methylbenzenesulfonamide (3ha):
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1h (30.8 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (34.9 mg, 87%). ¹H NMR (500 MHz, CDCl₃) δ 7.70 (d, 7.4 Hz, 2H), 7.23 (dd, 19.5 Hz, 7.7 Hz, 6H), 7.07 (t, 7.2 Hz, 2H), 6.68 (t, 7.1 Hz, 1H), 6.44 (d, 7.6 Hz, 2H), 5.06 (s, 1H), 4.85 - 4.42 (m, 1H), 4.37 (s, 1H), 3.38 - 3.23 (m, 1H), 3.15 (dd, 13.2 Hz, 6.7 Hz, 1H), 2.41 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 146.47, 143.88, 138.73, 136.64, 133.55, 129.92, 129.14 (d, 6.6 Hz), 127.96, 127.03, 118.17, 113.74, 57.00, 49.00, 21.54.

N-(2-(4-bromophenyl)-2-(phenylamino)ethyl)-4-methylbenzenesulfonamide (3ia):
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1i (35.2 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 24 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (42.3 mg, 95%). ¹H NMR (500 MHz, CDCl₃) δ 7.70 (d, 7.5 Hz, 2H), 7.40 (d, 7.5 Hz, 2H), 7.25 (d, 7.1 Hz, 2H), 7.16 (d, 7.5 Hz, 2H), 7.07 (t, 7.2 Hz, 2H), 6.68 (t, 7.1 Hz, 1H), 6.43 (d, 7.7 Hz, 2H), 5.07 (s, 1H), 4.57 (s, 1H), 4.35 (s, 1H), 3.37 - 3.21 (m, 1H), 3.15 (dd, 13.3 Hz, 6.9 Hz,
1H), 2.41 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 146.45, 143.89, 139.29, 136.62, 132.06, 129.93, 129.17, 128.32, 127.03, 121.65, 118.18, 113.74, 57.07, 48.94, 21.55. HRMS calcd. for [M+H]$^+$: 445.0585, found: 445.0572.

N-(2-(4-fluorophenyl)-2-(phenylamino)ethyl)-4-methylbenzenesulfonamide (3ja):
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1j (29.1 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 24 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (36.5 mg, 95%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.72 (d, 7.2 Hz, 2H), 7.26 (t, 7.2 Hz, 4H), 7.08 (t, 7.1 Hz, 2H), 6.98 (t, 7.8 Hz, 2H), 6.69 (t, 7.1 Hz, 1H), 6.45 (d, 7.6 Hz, 2H), 5.02 (s, 1H), 4.48 (d, 91.9 Hz, 2H), 3.38 - 3.25 (m, 1H), 3.17 (dd, 13.0 Hz, 6.8 Hz, 1H), 2.42 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 163.26, 161.30, 146.55, 143.85, 136.70, 135.83 (d, 3.0 Hz), 129.91, 129.16, 128.15 (d, 8.1 Hz), 127.04, 118.12, 115.94, 115.77, 113.74, 56.91, 49.11, 21.53.

4-methyl-N-(2-phenyl-2-(phenylamino)propyl)benzenesulfonamide (3ka):
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1k (28.7 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (32.0 mg, 84%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.63 (d, 7.3 Hz, 2H), 7.39 (d, 6.8 Hz, 2H), 7.32 (t, 6.5 Hz, 2H), 7.25 (d, 7.8 Hz, 3H), 6.97 (t, 6.4 Hz, 2H), 6.64 (t, 6.4 Hz, 1H), 6.29 (d, 7.4 Hz, 2H), 4.79 (s, 1H), 3.36 - 3.28 (m, 1H), 3.25 (d, 12.2 Hz, 1H), 2.41 (s, 3H), 2.16 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 144.83, 143.53 (d, 14.7 Hz), 136.50, 129.82, 128.85 (d, 7.3 Hz), 127.22, 126.95, 125.99, 117.68, 115.48, 58.08, 52.54, 25.40, 21.50. HRMS calcd. for [M+Na]$^+$: 403.1456, found: 403.1444.

4-methyl-N-(1-(phenylamino)hexan-2-yl)benzenesulfonamide (4la):
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1l (25.3 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 24 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (31.8 mg, 92%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.75 (d, 7.5 Hz, 2H), 7.25 (d, 7.2 Hz, 2H), 7.12 (t, 7.1 Hz, 2H), 6.69 (t, 7.1 Hz, 1H), 6.46 (d, 7.5 Hz, 2H), 4.86 (d, 6.7 Hz, 1H), 3.38 (d, 5.7 Hz, 1H), 3.21 (dd, 13.7 Hz, 8.0 Hz, 1H), 2.41 (s, 3H), 2.07 (s, 3H), 1.66 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 144.83, 143.53 (d, 14.7 Hz), 136.50, 129.82, 128.85 (d, 7.3 Hz), 127.22, 126.95, 125.99, 117.68, 115.48, 58.08, 52.54, 25.40, 21.50. HRMS calcd. for [M+Na]$^+$: 403.1444, found: 403.1444.
3.14 (d, 12.8 Hz, 1H), 3.03 (dd, 12.1 Hz, 7.8 Hz, 1H), 2.41 (s, 3H), 1.56 - 1.29 (m, 4H), 1.15 (d, 4.9 Hz, 2H), 0.77 (t, 5.6 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 147.76, 143.48, 137.64, 129.69, 129.18, 127.14, 117.59, 112.92, 53.50, 48.07, 33.26, 27.56, 22.37, 21.49, 13.80.

4-methyl-N-(2-methyl-3-(phenylamino)butan-2-yl)benzenesulfonamide (4ma):
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1m (23.9 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 24 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (21.3 mg, 64%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.72 (d, 7.4 Hz, 2H), 7.25 (d, 6.1 Hz, 2H), 7.07 (t, 7.1 Hz, 2H), 6.78 (t, 6.9 Hz, 1H), 6.55 (d, 7.5 Hz, 2H), 5.09 (s, 1H), 3.40 (s, 1H), 2.42 (s, 3H), 1.21 (s, 3H), 1.17 (s, 3H), 1.09 (d, 5.8 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 129.72, 128.92, 127.24, 119.53, 118.53, 56.99, 56.45, 24.55, 23.52, 21.54, 16.13. HRMS calcd. for [M+H]$^+$: 333.1637, found: 333.1626.

4-methyl-N-(2-(phenylamino)cyclopentyl)benzenesulfonamide (3na):
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1n (23.7 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (31.4 mg, 95%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.77 (d, 7.5 Hz, 2H), 7.25 (d, 7.9 Hz, 2H), 7.12 (t, 7.1 Hz, 2H), 6.69 (t, 7.1 Hz, 1H), 6.50 (d, 7.5 Hz, 2H), 5.16 (d, 5.9 Hz, 1H), 3.47 (d, 6.3 Hz, 1H), 3.44 - 3.37 (m, 1H), 2.41 (s, 3H), 2.19 (td, 13.6 Hz, 6.7 Hz, 1H), 1.87 (dd, 13.0 Hz, 6.7 Hz, 1H), 1.69 (dd, 14.9 Hz, 7.5 Hz, 2H), 1.45 (dt, 14.1 Hz, 7.4 Hz, 1H), 1.40 - 1.33 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 147.49, 143.50, 137.46, 129.77, 129.19, 127.14, 117.58, 113.32, 60.34, 59.77, 30.63, 30.40, 21.53, 20.46.

4-methyl-N-(2-(phenylamino)cyclohexyl)benzenesulfonamide (3oa):
Aniline 2a (10.3 mg, 0.11 mmol) and aziridine 1o (25.1 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (31.0 mg, 90%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.75 (d, 7.5 Hz, 2H), 7.28 (d, 7.5 Hz, 2H), 7.14 (t, 7.2 Hz, 2H), 6.70 (t, 7.1 Hz, 1H), 6.48 (d, 7.6 Hz, 2H), 5.06 (s, 1H), 3.47 (s, 1H), 3.06 (t, 9.5 Hz, 1H), 2.93 (s, 1H), 2.44 (s, 3H), 2.17 (d, 12.9 Hz, 1H), 2.02 (d, 12.0 Hz, 1H), 1.65 (d, 11.0 Hz, 2H), 1.28 (dd, 26.1 Hz, 13.8 Hz, 3H), 1.04 (d, 11.5 Hz, 1H). $^{13}$C NMR (126
MHz, CDCl$_3$) $\delta$ 147.07, 143.44, 137.56, 129.74, 129.32, 127.18, 117.81, 113.49, 57.08, 56.52, 33.00, 32.13, 24.41, 24.13, 21.57.

4-methyl-N-(2-phenyl-2-(o-tolylamino)ethyl)benzenesulfonamide (3ab):
o-Toluidine 2b (11.8 mg, 0.11 mmol) and aziridine 1a (27.3 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 $^\circ$C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (33.5 mg, 88%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.72 (d, 7.6 Hz, 2H), 7.29 (dd, 18.2 Hz, 8.5 Hz, 7H), 7.05 (d, 7.1 Hz, 1H), 6.91 (t, 7.5 Hz, 1H), 6.62 (t, 7.2 Hz, 1H), 6.25 (d, 8.0 Hz, 1H), 4.78 (s, 1H), 4.56 (d, 17.5 Hz, 1H), 4.46 (s, 1H), 3.42 - 3.33 (m, 1H), 3.26 (dt, 13.5 Hz, 6.7 Hz, 1H), 2.41 (s, 3H), 2.25 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 144.68, 143.74, 140.15, 136.88, 130.14, 129.86, 129.02, 127.87, 127.03, 126.85, 126.51, 122.72, 117.51, 111.06, 57.37, 49.25, 21.53, 17.68. HRMS calcd. for [M+H]$^+$: 381.1637, found: 381.1628.

N-(2-((2-chlorophenyl)amino)-2-phenylethyl)-4-methylbenzenesulfonamide (3ac):
2-Chloroaniline 2c (14.0 mg, 0.11 mmol) and aziridine 1a (27.3 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 $^\circ$C for 24 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (32.9 mg, 82%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.74 (d, 7.6 Hz, 2H), 7.35 - 7.29 (m, 2H), 7.29-7.20 (m, 6H), 6.94 (t, 7.5 Hz, 1H), 6.61 (t, 7.4 Hz, 1H), 6.34 (d, 8.0 Hz, 1H), 4.96 (s, 1H), 4.82 (s, 1H), 4.49 (s, 1H), 3.51 - 3.33 (m, 1H), 3.27 (d, 6.3 Hz, 1H), 2.41 (s, 3H), $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 143.73, 142.49, 139.35, 136.84, 129.86, 129.13 (d, 5.4 Hz), 128.10, 127.61, 127.08, 126.44, 119.77, 118.09, 112.66, 57.21, 49.01, 21.53.

N-(2-((2-fluorophenyl)amino)-2-phenylethyl)-4-methylbenzenesulfonamide (3ad):
2-Fluoroaniline 2d (12.2 mg, 0.11 mmol) and aziridine 1a (27.3 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 $^\circ$C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (36.1 mg, 94%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.73 (d, 7.6 Hz, 2H), 7.35 - 7.30 (m, 2H), 7.27 (d, 6.3 Hz, 5H), 6.99 - 6.89 (m, 1H), 6.80 (d, 7.6 Hz, 1H), 6.60 (d, 5.8 Hz, 1H), 6.38 (t, 8.2 Hz, 1H), 4.77 (s, 1H), 4.55 (s, 1H), 4.45 (s, 1H), 3.43 - 3.33 (m, 1H), 3.28 - 3.18
N-(2-((3-fluorophenyl)amino)-2-phenylethyl)-4-methylbenzenesulfonamide (3ae):
3-Fluoroaniline 2e (12.2 mg, 0.11 mmol) and aziridine 1a (27.3 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 24 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (32.7 mg, 85%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, 7.9 Hz, 2H), 7.39 - 7.14 (m, 7H), 6.99 (q, 7.7 Hz, 1H), 6.34 (t, 8.3 Hz, 1H), 6.27 (d, 8.1 Hz, 1H), 6.09 (d, 11.5 Hz, 1H), 5.06 (d, 5.8 Hz, 1H), 4.36 (d, 4.2 Hz, 1H), 3.40 - 3.29 (m, 1H), 3.19 (dd, 13.6 Hz, 6.8 Hz, 1H), 2.41 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 143.91, 139.56, 136.70, 129.93, 129.07, 128.03, 127.04, 126.48, 109.61 (d, 2.0 Hz), 104.40, 104.23, 100.52, 100.32, 57.45, 48.99, 21.51. HRMS calcd. for [M+H]\(^+\): 385.1386, found: 385.1375.

4-methyl-N-(2-phenyl-2-((3-trifluoromethyl)phenyl)amino)ethyl)benzenesulfonamide (3af):
3-Aminobenzotrifluoride 2f (17.7 mg, 0.11 mmol) and aziridine 1a (27.3 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (41.2 mg, 95%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, 7.9 Hz, 2H), 7.30 (dt, 18.9 Hz, 9.3 Hz, 7H), 7.14 (t, 7.8 Hz, 1H), 6.89 (d, 7.6 Hz, 1H), 6.66 (s, 1H), 6.58 (d, 8.1 Hz, 1H), 4.76 (t, 6.2 Hz, 2H), 4.42 (s, 1H), 3.37 (dd, 12.5 Hz, 5.8 Hz, 1H), 3.23 (dd, 13.7 Hz, 6.8 Hz, 1H), 2.42 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 146.96, 143.98, 139.34, 136.68, 129.93, 129.52, 129.10, 128.09, 127.00, 126.46, 116.33, 114.18 (d, 3.8 Hz), 110.07 (d, 3.9 Hz), 57.36, 48.99, 21.47. HRMS calcd. for [M+H]\(^+\): 435.1354, found: 435.1345.

N-(2-((4-fluorophenyl)amino)-2-phenylethyl)-4-methylbenzenesulfonamide (3ag):
4-Fluoroaniline 2g (12.2 mg, 0.11 mmol) and aziridine 1a (27.3 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (35.0 mg, 91%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, 7.8 Hz, 2H), 7.36 - 7.19 (m, 7H), 6.78 (t, 8.2 Hz, 2H), 6.41 (dd, 7.2 Hz, 4.4 Hz, 2H), 4.80 (s, 1H), 4.42 - 4.29 (m, 1H), 3.38 -
3.29 (m, 1H), 3.20 (dd, 13.4 Hz, 6.6 Hz, 1H), 2.42 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 157.10, 155.22, 143.81, 142.77, 139.72, 136.74, 129.88, 129.04, 128.02, 127.07, 126.55, 115.66, 115.49, 114.81 (d, 7.4 Hz), 58.26, 49.05, 21.52. HRMS calcd. for [M+H]$^+$: 385.1386, found: 385.1376.

4-methyl-N-(2-phenyl-2-((4-(trifluoromethyl)phenyl)amino)ethyl)benzenesulfonamide (3ah):
4-Aminobenzotrifluoride 2h (17.7 mg, 0.11 mmol) and aziridine 1a (27.3 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (32.2 mg, 74%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.71 (d, 7.6 Hz, 2H), 7.39 - 7.15 (m, 9H), 6.46 (d, 7.9 Hz, 2H), 5.01 (s, 2H), 4.43 (s, 1H), 3.44 - 3.29 (m, 1H), 3.29 - 3.10 (m, 1H), 2.40 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 149.29, 143.99, 139.21, 136.62, 129.93, 129.15, 128.14, 126.99, 126.42 (d, 3.7 Hz), 112.82, 57.20, 48.97, 21.48. HRMS calcd. for [M+H]$^+$: 435.1354, found: 435.1346.

N-(2-((4-tert-butyl)phenyl)amino)-2-phenylethyl)-4-methylbenzenesulfonamide (3ai):
4-tert-Butylaniline 2i (16.4 mg, 0.11 mmol) and aziridine 1a (27.3 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 5:1) to afford the title compound (36.8 mg, 87%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.73 (d, 7.4 Hz, 2H), 7.28 (dt, 11.0 Hz, 5.6 Hz, 7H), 7.12 (d, 7.3 Hz, 2H), 6.44 (d, 7.4 Hz, 2H), 4.80 (s, 1H), 4.39 (s, 2H), 3.38 - 3.26 (m, 1H), 3.25 - 3.14 (m, 1H), 2.43 (s, 3H), 1.24 (s, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 144.31, 143.70, 140.82, 140.33, 136.82, 129.87, 128.99, 127.87, 127.12, 126.57, 125.95, 113.43, 57.72, 49.10, 33.85, 31.50, 21.55. HRMS calcd. for [M+H]$^+$: 423.2106, found: 423.2095.

N-(2-((2,4-dimethoxyphenyl)amino)-2-phenylethyl)-4-methylbenzenesulfonamide (3aj):
2,4-Dimethoxyaniline 2j (16.8 mg, 0.11 mmol) and aziridine 1a (27.3 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 4:1) to afford the title compound (37.6 mg,
88%). $^1H$ NMR (500 MHz, CDCl$_3$) $\delta$ 7.72 (d, 7.9 Hz, 2H), 7.35 - 7.19 (m, 7H), 6.42 (s, 1H), 6.22 (s, 2H), 4.93 (s, 1H), 4.74 - 4.16 (m, 2H), 3.83 (s, 3H), 3.69 (s, 3H), 3.34 (dd, 12.6 Hz, 6.0 Hz, 1H), 3.19 (dd, 12.9 Hz, 7.0 Hz, 1H), 2.42 (s, 3H). $^{13}C$ NMR (126 MHz, CDCl$_3$) $\delta$ 152.48, 148.27, 143.51, 140.36, 136.96, 130.55, 129.76, 128.89, 127.79, 127.13, 126.50, 112.01, 103.72, 99.18, 57.97, 55.63 (d, 11.9 Hz), 49.12, 21.53. HRMS calcd. for [M+H]$^+$: 427.1692, found: 427.1683.

4-methyl-N-(2-(methyl(phenyl)amino)-2-phenylethyl)benzenesulfonamide (3ak):
N-methylaniline 2k (11.8 mg, 0.11 mmol) and aziridine 1a (27.3 mg, 0.1 mmol) were added to a 1 mL test tube. The mixture was stirred at 50 °C for 6 h, then passed through a plug of silica gel (PE:EA = 4:1) to afford the title compound (35.8 mg, 94%). $^1H$ NMR (500 MHz, CDCl$_3$) $\delta$ 7.78 (d, 7.8 Hz, 2H), 7.34 (d, 7.8 Hz, 2H), 7.25 (dd, 16.8 Hz, 9.2 Hz, 5H), 7.05 (d, 6.6 Hz, 2H), 6.84 (t, 7.2 Hz, 1H), 6.78 (d, 8.0 Hz, 2H), 4.99 (dd, 9.9 Hz, 5.1 Hz, 1H), 4.75 (d, 7.5 Hz, 1H), 3.75 - 3.61 (m, 1H), 3.48 (t, 11.4 Hz, 1H), 2.52 (s, 3H), 2.47 (s, 3H). $^{13}C$ NMR (126 MHz, CDCl$_3$) $\delta$ 150.31, 143.62, 137.07, 136.78, 129.85, 129.33, 128.67, 127.86, 127.18, 126.95, 118.64, 114.68, 61.71, 43.19, 31.82, 21.58. HRMS calcd. for [M+H]$^+$: 381.1637, found: 381.1629.

Synthesis of Compound 4

N-methyl-N-phenyl-2-tosyl-1,2,3,4-tetrahydroisoquinolin-4-amine (4):
N-methylaniline 2k (406.8 mg, 3.80 mmol, 1.1 equiv) and aziridine 1a (943.5 mg, 3.45 mmol, 1.0 equiv) were added to a 5 mL test tube, followed by stirring at 50 °C for 6 h. The reaction process was monitored by TLC. After the reaction completed, the residue was directly subjected to the preparative thin layer chromatography to afford the compound 3ak as white solid in 91% yield (1.19 g).
To a 10 mL Schlenk tube equipped with a magnetic stir bar, 3ak (190.3 mg, 0.50 mmol, 1.0 equiv) and paraformaldehyde (18.0 mg, 0.6 mmol based on formaldehyde, 1.2 equiv) were added. The tube was evacuated and refilled with N$_2$ gas three times. Then trifluoroacetic acid (1.0 mL) was added, and the resulting mixture was stirred at 90 °C for 5 h. The reaction mixture was allowed to cool to room temperature and poured into H$_2$O (10 mL). The organic layer was separated, and the aqueous layer was extracted with CHCl$_3$ (3 mL × 3). Organic layers were combined, washed with sat. NaHCO$_3$ aq. (3 mL), and dried over Na$_2$SO$_4$. Solvent was removed under reduced
pressure, then the residue was purified by flash column chromatography on silica gel (PE:EA = 5:1), giving the title compound as white solid in 66% yield (129.6 mg).21H NMR (500 MHz, CDCl3) δ 7.64 (d, 7.3 Hz, 2H), 7.27 (d, 8.3 Hz, 6H), 7.13 (d, 5.9 Hz, 2H), 7.02 (d, 7.1 Hz, 1H), 6.90 (t, 8.8 Hz, 2H), 4.54 (s, 2H), 4.18 (d, 7.8 Hz, 1H), 3.56 (d, 14.3 Hz, 1H), 3.39 (dd, 13.9 Hz, 8.3 Hz, 1H), 2.59 (s, 3H), 2.42 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 148.97, 143.20, 140.09, 136.50, 129.83, 129.61 (d, 13.9 Hz), 128.56, 127.69, 127.25 (d, 7.7 Hz), 126.79, 121.79, 118.99, 66.91, 50.36, 49.88, 38.99, 21.53. HRMS calcd. for [M+H]+: 393.1637, found: 393.1618.

References

Copies of 1H and 13C NMR spectra
The image contains two NMR spectra and their respective chemical structures.

**1H NMR (CDCl₃, 500 MHz)**

- Chemical shift: 7.73, 7.71, 7.38, 7.08, 6.89, 6.86, 6.48, 6.46, 4.92, 4.46, 3.35, 3.22, 3.18

**13C NMR (CDCl₃, 126 MHz)**

- Chemical shift: 148.73, 140.09, 123.44, 126.48, 123.86, 117.98, 113.75, -57.44, -49.88, -21.53

The structures include a benzene ring attached to an amine group with a substituent labeled as NHTs.
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)
$^1$H NMR (CD$_3$OD, 600 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)
$^1$H NMR (CDCl$_3$, 600 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)