Electronic Supplementary Information

Diastereoselective Synthesis of Functionalized Pyrrolidines through N-Bromosuccinimide-Induced Aziridine Ring Expansion Cascade of Cinnamylaziridine

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(A) General. All reactions that required anhydrous conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents were used as received. The solvents were dried over a solvent purification system from Innovative Technology. Infrared spectra were recorded on a BIO-RAD FTS 165 FT-IR spectrophotometer and reported in wave numbers (cm⁻¹). Melting points were determined on a BÜCHI B-540b melting point apparatus. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker ACF300 (300 MHz), Bruker DPX300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00) for the ¹H NMR and to chloroform (δ 77.0) for the ¹³C NMR measurements. Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode. High resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. Analytical thin layer chromatography (TLC) was performed with Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.
(B) Representative procedure for the preparation of 3

Compound 7 was readily available from L-aspartic acid using the literature procedures.\textsuperscript{1,2} Aziridine 6 was synthesized from 7 using the literature method\textsuperscript{3}: to a solution of 7 in anhydrous diethyl ether (100 mL) was added TsCl (12 mmol) and KOH powder (40 mmol) at 25 °C. The resultant mixture was refluxed until complete consumption of starting material as indicated by TLC. The solution was then poured into a beaker containing crushed ice (c.a. 10 g). The organic phase was separated, washed with brine (20 mL), dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated under reduced pressure. The residue was loaded onto the surface of a thin plug of silica gel and eluted with n-hexane/EtOAC (4:1, 50 mL) to give 6 as colorless oil.

Under N\textsubscript{2} protection, Grubbs catalyst 2\textsuperscript{nd} generation\textsuperscript{4} (20 mg, 0.025 mmol) was added to the mixture of compound 6 (92 mg, 0.5 mmol) and styrene (580 \(\mu\)L, 5 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (5 mL) at 25 °C. The reaction was refluxed till complete conversion of the starting material as indicated on TLC. After evaporating the solvent, the residue was purified by column chromatography to give 3a as the exclusive isomer (white solid, 118 mg, 91%).

\begin{align*}
\text{Aziridine 3a. White solid (91%). m.p.} & \text{ 65 – 66 °C; } [\alpha]_D^{25} + 50.8 \text{ (c 1.0, CHCl}_3); \text{ }^1\text{H NMR (500 MHz, CDCl}_3) \delta 7.37 – 7.20 \text{ (m, 5H), 6.53 (d, } J = 16.0 \text{ Hz, 1H), 6.26 (dt, } J = 15.9, 6.6 \text{ Hz, 1H), 2.56 – 2.44 \text{ (m, 2H), 2.41 – 2.32 \text{ (m, 1H), 2.30 (d, } J = 5.9 \text{ Hz, 1H), 2.01 (d, } J = 3.4 \text{ Hz, 1H), 1.46 (s, 9H); } ^{13}\text{C NMR (125 MHz, CDCl}_3) \delta 162.43, 137.30, 132.08, 128.47, 127.21, 126.09, 125.59, 81.09, 37.24, 35.44, 31.17, 27.92; \text{ HRMS (ESI) calcd for C}_16\text{H}_21\text{NNaO}_2 \text{ [M+Na]}^{+}: 282.1465, \text{ found: 282.1469; IR (KBr): 2926, 1717, 1310, 1160 cm}^{-1}.}
\end{align*}
Aziridine 3b. Colorless oil (90%). \([\alpha]_D^{25} + 16.9 \text{ (c 0.5, CHCl}_3)\); \(^1\text{H NMR (500 MHz, CDCl}_3\) \(\delta 7.29 \text{ (d, } J = 8.7 \text{ Hz, 2H), 6.84 \text{ (d, } J = 8.8 \text{ Hz, 2H), 6.47 \text{ (d, } J = 16.0 \text{ Hz, 1H), 6.11 \text{ (dt, } J = 15.9, 6.7 \text{ Hz, 1H), 3.80 \text{ (s, 3H), 2.54} - 2.43 \text{ (m, 2H), 2.35} - 2.28 \text{ (m, 2H), 2.00 \text{ (d, } J = 3.5 \text{ Hz, 1H), 1.46 \text{ (s, 9H); 13C NMR (125 MHz, CDCl}_3\) \(\delta 162.46, 158.92, 131.47, 130.15, 127.21, 123.32, 113.90, 81.05, 55.26, 37.41, 35.44, 31.18, 27.93; HRMS (ESI) calcd for C\text{\_17}H\text{\_23}NNaO\text{\_3 \[M+Na\]^+}: 312.1570, found: 312.1585; IR (KBr): 2977, 2931, 1717, 1512, 1308, 1249, 1160 \text{ cm}^{-1}.\)

Aziridine 3c. Colorless oil (87%). \([\alpha]_D^{25} + 49.9 \text{ (c 1.0, CHCl}_3\) \(^1\text{H NMR (500 MHz, CDCl}_3\) \(\delta 7.26 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.11 \text{ (d, } J = 7.9 \text{ Hz, 2H), 6.49 \text{ (d, } J = 16.0 \text{ Hz, 1H), 6.20 \text{ (dt, } J = 15.9, 6.6 \text{ Hz, 1H), 2.59} - 2.43 \text{ (m, 2H), 2.38} - 2.31 \text{ (m, 4H), 2.29 \text{ (d, } J = 5.9 \text{ Hz, 1H), 2.00 \text{ (d, } J = 3.4 \text{ Hz, 1H), 1.46 \text{ (s, 9H); 13C NMR (125 MHz, CDCl}_3\) \(\delta 162.44, 136.95, 134.52, 131.92, 129.17, 125.98, 124.49, 81.05, 37.33, 35.45, 31.17, 27.92, 21.12; HRMS (ESI) calcd for C\text{\_17}H\text{\_23}NNaO\text{\_2 \[M+Na\]^+}: 296.1621, found: 296.1630; IR (KBr): 2977, 2926, 1718, 1510, 1310, 1226, 1160 \text{ cm}^{-1}.\)

Aziridine 3d. Colorless oil (81%). \([\alpha]_D^{25} + 41.0 \text{ (c 1.0, CHCl}_3\) \(^1\text{H NMR (500 MHz, CDCl}_3\) \(\delta 7.49} - 7.38 \text{ (m, 1H), 7.17} - 7.04 \text{ (m, 3H), 6.72 \text{ (d, } J = 15.7 \text{ Hz, 1H), 6.22} - 6.07 \text{ (m, 1H), 2.57} - 2.48 \text{ (m, 2H), 2.40} - 2.35 \text{ (m, 1H), 2.34 \text{ (s, 3H), 2.30 \text{ (d, } J = 6.1 \text{ Hz, 1H), 2.02 \text{ (d, } J = 3.4 \text{ Hz, 1H), 1.47 \text{ (s, 9H); 13C NMR (125 MHz, CDCl}_3\) \(\delta 162.43, 136.43, 135.04, 130.13, 130.05, 127.13, 126.87, 125.97, 125.56, 81.06, 37.29, 35.73, 31.21, 27.90, 19.77; HRMS (ESI) calcd for C\text{\_17}H\text{\_23}NNaO\text{\_2 \[M+Na\]^+}: 296.1621, found: 296.1624; IR (KBr): 2926, 1719, 1310, 1161 \text{ cm}^{-1}.\)

Aziridine 3e. Colorless oil (82%). \([\alpha]_D^{25} + 39.0 \text{ (c 1.0, CHCl}_3\) \(^1\text{H NMR (500 MHz, CDCl}_3\) \(\delta 7.34} -
7.29 (m, 4H), 6.50 (d, J = 15.8 Hz, 1H), 6.21 (dt, J = 15.9, 6.6 Hz, 1H), 2.57 – 2.46 (m, 2H), 2.36 – 2.30 (m, 1H), 2.29 (d, J = 6.0 Hz, 1H), 2.00 (d, J = 3.4 Hz, 1H), 1.47 (s, 8H), 1.31 (s, 8H); 13C NMR (125 MHz, CDCl3) δ 162.45, 150.30, 134.55, 131.86, 125.81, 125.41, 124.74, 81.07, 37.35, 35.49, 31.28, 31.17, 27.95; HRMS (ESI) calcd for C20H29NNaO2 [M+Na]+: 383.2091, found:383.2093; IR (KBr): 2966, 1719, 1310, 1163 cm⁻¹.

Aziridine 3f. Colorless oil (80%). [α]D25 + 41.1 (c 1.0, CHCl3); 1H NMR (300 MHz, CDCl3) δ 7.37 – 7.27 (m, 2H), 7.04 – 6.91 (m, 2H), 6.49 (d, J = 16.0 Hz, 1H), 6.16 (dt, J = 15.9, 6.6 Hz, 1H), 2.56 – 2.33 (m, 3H), 2.30 (d, J = 5.9 Hz, 1H), 2.00 (d, J = 3.5 Hz, 1H), 1.46 (s, 9H); 13C NMR (75 MHz, CDCl3) δ 163.67, 162.38, 160.41, 133.43, 130.85, 127.56, 127.46, 125.36, 115.45, 115.17, 81.09, 37.14, 35.34, 31.15, 27.88; HRMS (ESI) calcd for C16H20FNNaO2 [M+Na]+: 300.1370, found: 300.1383; IR (KBr): 2979, 2930, 1719, 1310, 1163 cm⁻¹.

Aziridine 3g. Whiel solid (84%). m.p. 57 – 59 °C; [α]D25 + 46.8 (c 1.0, CHCl3); 1H NMR (500 MHz, CDCl3) δ 7.29 – 6.85 (m, 4H), 6.50 (d, J = 16.0 Hz, 1H), 6.27 (dt, J = 15.9, 6.7 Hz, 1H), 2.51 (qd, J = 5.9, 3.7 Hz, 1H), 2.48 – 2.35 (m, 2H), 2.30 (d, J = 5.9 Hz, 1H), 2.00 (d, J = 3.7 Hz, 1H), 1.46 (s, 9H); 13C NMR (125 MHz, CDCl3) δ 164.04, 162.34, 162.09, 139.73, 139.66, 131.01, 130.99, 129.90, 129.83, 127.17, 121.98, 121.96, 114.04, 113.87, 112.59, 112.41, 81.10, 37.00, 35.31, 31.14, 27.89; HRMS (ESI) calcd for C16H20FNNaO2 [M+Na]+: 300.1370, found: 300.1382; IR (KBr): 2978, 2928, 1716, 1310, 1160 cm⁻¹.

Aziridine 3h. Colorless oil (73%). [α]D25 + 22.3 (c 1.0, CHCl3); 1H NMR (500 MHz, CDCl3) δ 7.33 – 7.14 (m, 4H), 6.46 (d, J = 15.9 Hz, 1H), 6.26 (dt, J = 15.9, 6.7 Hz, 1H), 2.55 – 2.46 (m, 1H), 2.46 – 2.33 (m, 2H), 2.29 (d, J = 6.0 Hz, 1H), 1.99 (d, J = 3.6 Hz, 1H), 1.45 (s, 9H); 13C NMR (125 MHz, CDCl3) δ 162.30, 139.15, 134.35, 130.70, 129.63, 127.29, 127.07, 125.94, 124.29, 81.07, 36.94, 35.29, 31.09, 27.85;
HRMS (ESI) calcd for C_{16}H_{20}ClNNaO_{2} [M+Na]^+: 316.1075, found: 316.1088; IR (KBr): 2978, 2926, 1719, 1312, 1160 cm\(^{-1}\).

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**Aziridine 3i.** White solid (78%). m.p. 53 – 55°C; \([\alpha]_D^{25} + 78.3\) (c 2.0, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.41 (d, \(J = 8.5\) Hz, 2H), 7.22 (d, \(J = 8.5\) Hz, 2H), 6.48 (d, \(J = 16.0\) Hz, 1H), 6.25 (dt, \(J = 15.9, 6.7\) Hz, 1H), 2.51 (qd, \(J = 5.9, 3.7\) Hz, 1H), 2.47 – 2.33 (m, 2H), 2.30 (d, \(J = 6.0\) Hz, 1H), 2.00 (d, \(J = 3.7\) Hz, 1H), 1.46 (s, 9H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 162.39, 136.29, 131.58, 130.94, 127.65, 126.59, 120.92, 81.15, 37.03, 35.42, 31.20, 27.93; HRMS (ESI) calcd for C_{16}H_{20}BrNNaO_{2} [M+Na]^+: 360.0570, found: 360.0563; IR (KBr): 2976, 2926, 1717, 1311, 1160 cm\(^{-1}\).

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**Aziridine 3j.** Colorless oil (72%). \([\alpha]_D^{25} + 30.4\) (c 0.5, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.94 (d, \(J = 8.3\) Hz, 2H), 7.39 (d, \(J = 8.3\) Hz, 2H), 6.55 (d, \(J = 16.0\) Hz, 1H), 6.37 (dt, \(J = 15.9, 6.7\) Hz, 1H), 3.88 (s, 3H), 2.55 – 2.47 (m, 1H), 2.41 (t, \(J = 6.2\) Hz, 2H), 2.29 (d, \(J = 6.0\) Hz, 1H), 1.99 (d, \(J = 3.6\) Hz, 1H), 1.44 (s, 9H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 166.79, 162.27, 141.73, 131.16, 129.79, 128.60, 125.89, 81.07, 51.91, 36.86, 35.42, 31.11, 27.83; HRMS (ESI) calcd for C_{18}H_{23}NNaO_{4} [M+Na]^+: 340.1519, found: 340.1525; IR (KBr): 2930, 1719, 1511, 1310, 1224, 1160 cm\(^{-1}\).

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**Aziridine 3k.** Pale yellow oil (58%). \([\alpha]_D^{25} + 38.2\) (c 1.0, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.21 (s, 1H), 8.06 (dd, \(J = 8.2, 1.3\) Hz, 1H), 7.65 (d, \(J = 7.7\) Hz, 1H), 7.46 (t, \(J = 8.0\) Hz, 1H), 6.62 (d, \(J = 16.0\) Hz, 1H), 6.42 (dt, \(J = 15.9, 6.6\) Hz, 1H), 2.60 – 2.39 (m, 3H), 2.33 (d, \(J = 5.9\) Hz, 1H), 2.02 (d, \(J = 3.6\) Hz, 1H), 1.46 (s, 9H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 162.33, 148.60, 139.13, 131.98, 129.91, 129.37, 129.33, 121.82, 120.66, 81.28, 36.77, 35.35, 31.21, 27.92; HRMS (ESI) calcd for C_{16}H_{20}N_{2}NaO_{4} [M+Na]^+: 327.1315, found: 327.1319; IR (KBr): 2930, 1717, 1309, 1159 cm\(^{-1}\).
(C) Representative procedure for the aminocyclization-ring expansion cascade of 3

\[
\begin{align*}
\text{3a} & \quad \overset{\text{NsNH}_2, \text{NBS}}{\text{CH}_3\text{CN}, -20 \degree \text{C}} \quad \text{4a} \quad + \quad \text{5a}
\end{align*}
\]

To a solution of 3a (26 mg, 0.1 mmol) in MeCN (1 mL) was added NsNH\textsubscript{2} (30 mg, 0.15 mmol) and NBS (27 mg, 0.15 mmol) at –20 °C. After stirring at the same temperature for 8 h, the reaction was quenched by saturated Na\textsubscript{2}SO\textsubscript{3} solution. Purification of the residue by column chromatography gave pyrrolidine 4a (33.5 mg) and piperidine 5a (10.5 mg) (overall yield 82%). (Note: 4 and 5 were not readily separable. However, sufficient amount of pure 4 could be isolated through column chromatography for physical analysis.)

**Pyrrolidine 4a.** Colorless oil. \([\alpha]_D^{25} + 38.4 \; (c \; 1.0, \; \text{CHCl}_3)\); \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.35 (d, \(J = 8.7\) Hz, 2H), 8.09 (d, \(J = 8.8\) Hz, 2H), 7.40 – 6.97 (m, 5H), 5.07 (s, 1H), 4.44 – 4.33 (m, 1H), 4.19 (d, \(J = 5.4\) Hz, 1H), 3.73 – 3.57 (m, 1H), 3.55 – 3.44 (m, 1H), 2.89 – 2.83 (m, 1H), 2.21 (d, \(J = 15.3\) Hz, 1H), 1.10 (s, 9H); \(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 155.77, 149.92, 146.08, 140.87, 128.83, 128.30, 127.93, 124.96, 124.27, 81.39, 73.49, 58.88, 51.54, 49.69, 37.57, 27.76; HRMS (ESI) calcd for C\textsubscript{22}H\textsubscript{26}BrN\textsubscript{3}NaO\textsubscript{6}S [M+Na]\(^+\): 562.0618, found: 562.0617; IR (KBr): 3279, 2970, 1688, 1532, 1391, 1164, 1095, 803, 744 cm\(^{-1}\).

**Pyrrolidine 4b.** Colorless oil. \([\alpha]_D^{25} + 18.8 \; (c \; 1.0, \; \text{CHCl}_3)\); \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.36 (d, \(J = 8.7\) Hz, 2H), 8.09 (d, \(J = 8.6\) Hz, 2H), 7.09 (brd, 1H), 6.96 (d, \(J = 5.2\) Hz, 1H), 3.79 (s, 3H), 3.67 – 3.58 (m, 1H), 3.53 – 3.42 (m, 1H), 2.90 – 2.84 (m, 1H), 2.22 – 2.12 (m, 1H), 1.14 (s, 9H); \(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 159.22, 155.99, 149.93, 146.12, 132.92, 128.31, 126.15, 124.30, 114.14, 81.41, 73.00, 58.79, 55.32, 51.89, 50.16, 37.76, 27.86; HRMS (ESI) calcd for C\textsubscript{23}H\textsubscript{28}BrN\textsubscript{3}NaO\textsubscript{7}S [M+Na]\(^+\): 592.0724, found: 592.0738; IR (KBr):
3281, 2965, 1690, 1532, 1393, 1258, 1095, 804 cm⁻¹.

**Pyrrolidine 4c.** Colorless oil. [α]₀^25 + 24.9 (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.36 (d, J = 8.6 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 7.12 – 7.09 (m, 3H), 6.92 (d, J = 7.9 Hz, 2H), 5.05 (s, 1H), 4.41 – 4.32 (m, 1H), 4.17 (d, J = 5.3 Hz, 1H), 3.70 – 3.60 (m, 1H), 3.53 – 3.44 (m, 1H), 2.89 – 2.83 (m, 1H), 2.32 (s, 3H), 2.17 (d, J = 15.2 Hz, 1H), 1.13 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 156.04, 149.96, 146.18, 137.76, 129.47, 128.32, 124.87, 124.29, 81.42, 73.33, 58.86, 51.82, 50.22, 37.84, 27.85, 21.04; HRMS (ESI) calcd for C₂₃H₂₈BrN₃NaO₆S [M+Na]⁺: 576.0774, found: 576.0795; IR (KBr): 3281, 2966, 1689, 1532, 1391, 1163, 1096, 804 cm⁻¹.

**Pyrrolidine 4d.** Colorless oil. [α]₀^25 + 25.2 (c 2.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.36 (d, J = 8.6 Hz, 2H), 8.10 (d, J = 8.5 Hz, 2H), 7.21 – 6.76 (m, 5H), 5.23 (s, 1H), 4.43 – 4.42 (m, 1H), 4.12 (m, 1H), 3.71 – 3.66 (m, 1H), 3.56 – 3.41 (m, 1H), 2.91 – 2.85 (m, 1H), 2.32 (s, 3H), 2.22 (d, J = 15.5 Hz, 1H), 1.09 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 155.75, 149.93, 146.09, 139.11, 134.62, 130.75, 128.32, 127.80, 126.34, 124.28, 123.12, 81.28, 70.64, 58.95, 50.49, 50.07, 37.51, 27.73, 19.44; HRMS (ESI) calcd for C₂₃H₂₈BrN₃NaO₆S [M+Na]⁺: 576.0774, found: 576.0781; IR (KBr): 3280, 2969, 1688, 1533, 1391, 1164, 1096, 804, 744 cm⁻¹.

**Pyrrolidine 4e.** Colorless oil. [α]₀^25 + 46.3 (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.36 (d, J = 8.7 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.09 (brd, J = 7.4 Hz, 1H), 6.95 (d, J = 8.3 Hz, 2H), 5.04 (s, 1H), 4.39 – 4.35 (m, 1H), 4.20 (d, J = 5.3 Hz, 1H), 3.65 – 3.62 (m, 1H), 3.50 – 3.45 (m, 1H), 2.91 – 2.85 (m, 1H), 2.18 (d, J = 15.1 Hz, 1H), 1.29 (s, 9H), 1.09 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 156.03, 151.16, 149.95, 146.15, 137.79, 128.32, 125.63, 124.78, 124.28, 81.34, 73.31, 58.79, 51.68, 50.06, 37.83, 34.53, 31.24, 27.77; HRMS (ESI) calcd for C₂₆H₃₄BrN₃NaO₆S [M+Na]⁺: 618.1244, found:
618.1253; IR (KBr): 3361, 3194, 2965, 1689, 1527, 1376, 1165, 824, 770, 611 cm⁻¹.

**Pyrrolidine 4f.** Colorless oil. \([\alpha]_D^{25} + 31.3 \text{ (c 1.0, CHCl}_3\); \(^1\)H NMR (500 MHz, CDCl₃) \(\delta 8.36 \text{ (d, } J = 8.5 \text{ Hz, 2H)}, \ 8.09 \text{ (d, } J = 8.7 \text{ Hz, 2H}), \ 7.06 – 6.95 \text{ (m, 4H)}, \ 5.05 \text{ (s, 1H)}, \ 4.42 – 4.32 \text{ (m, 1H)}, \ 4.15 \text{ (d, } J = 5.2 \text{ Hz, 1H)}, \ 3.65 – 3.57 \text{ (m, 1H)}, \ 3.54 – 3.47 \text{ (m, 1H)}, \ 2.87 – 2.81 \text{ (m, 1H)}, \ 2.22 \text{ (d, } J = 15.2 \text{ Hz, 1H)}, \ 1.13 \text{ (s, 9H)}; \ ^{13}\)C NMR (125 MHz, CDCl₃) \(\delta 163.19, 161.23, 155.57, 149.97, 146.05, 136.71, 128.30, 126.71, 126.64, 124.31, 115.91, 115.74, 81.61, 72.75, 58.97, 51.25, 49.71, 37.69, 27.83; HRMS (ESI) calcd for \(\text{C}_{22}\text{H}_{25}\text{BrFN}_3\text{NaO}_6\text{S}[\text{M+Na}^+]\): 580.0524, found: 580.0549; IR (KBr): 3277, 2978, 1694, 1532, 1371, 1163, 826, 738, 612 cm⁻¹.

**Pyrrolidine 4g.** Colorless oil. \([\alpha]_D^{25} + 29.5 \text{ (c 1.0, CHCl}_3\); \(^1\)H NMR (500 MHz, CDCl₃) \(\delta 8.37 \text{ (d, } J = 8.7 \text{ Hz, 2H)}, \ 8.09 \text{ (d, } J = 8.8 \text{ Hz, 2H}), \ 7.31 \text{ (t, } J = 8.0, 5.8 \text{ Hz, 1H)}, \ 6.99 \text{ (t, } J = 8.3 \text{ Hz, 1H)}, \ 6.95 \text{ (d, } J = 7.1 \text{ Hz, 1H)}, \ 6.86 \text{ (d, } J = 7.6 \text{ Hz, 1H)}, \ 6.77 \text{ (d, } J = 9.4 \text{ Hz, 1H)}, \ 5.05 \text{ (s, 1H)}, \ 4.39 – 4.34 \text{ (m, 1H)}, \ 4.18 \text{ (d, } J = 5.4 \text{ Hz, 1H)}, \ 3.66 – 3.58 \text{ (m, 1H)}, \ 3.57 – 3.42 \text{ (m, 1H)}, \ 2.88 – 2.82 \text{ (m, 1H)}, \ 2.22 \text{ (d, } J = 15.3 \text{ Hz, 1H)}, \ 1.14 \text{ (s, 9H)}; \ ^{13}\)C NMR (125 MHz, CDCl₃) \(\delta 164.09, 162.12, 155.57, 150.03, 146.15, 143.50, 130.58, 128.33, 124.34, 120.63, 115.08, 114.91, 112.32, 112.15, 111.90, 81.81, 72.93, 59.11, 50.86, 49.86, 37.97, 27.86; HRMS (ESI) calcd for \(\text{C}_{22}\text{H}_{25}\text{BrFN}_3\text{NaO}_6\text{S}[\text{M+Na}^+]\): 580.0524, found: 580.0540; IR (KBr): 3277, 2978, 1694, 1532, 1371, 1164 cm⁻¹.

**Pyrrolidine 4h.** Colorless oil. \([\alpha]_D^{25} + 27.7 \text{ (c 1.0, CHCl}_3\); \(^1\)H NMR (500 MHz, CDCl₃) \(\delta 8.36 \text{ (d, } J = 8.6 \text{ Hz, 2H)}, \ 8.09 \text{ (d, } J = 8.6 \text{ Hz, 2H}), \ 7.31 – 6.91 \text{ (m, 5H)}, \ 5.02 \text{ (s, 1H)}, \ 4.43 – 4.30 \text{ (m, 1H)}, \ 4.17 \text{ (d, } J = 5.4 \text{ Hz, 1H)}, \ 3.66 – 3.56 \text{ (m, 1H)}, \ 3.55 – 3.44 \text{ (m, 1H)}, \ 2.87 – 2.81 \text{ (m, 1H)}, \ 2.23 \text{ (d, } J = 15.8 \text{ Hz, 1H)}, \ 1.14 \text{ (s, 9H)}; \ ^{13}\)C NMR (125 MHz, CDCl₃) \(\delta 155.43, 149.97, 146.05, 142.89, 134.91, 130.22, 128.30, 128.18, 125.28, 124.32, 123.20, 81.81, 72.81, 59.04, 50.81, 49.59, 37.80, 27.83; HRMS (ESI) calcd for \(\text{C}_{22}\text{H}_{25}\text{BrClN}_3\text{NaO}_6\text{S}[\text{M+Na}^+]\): 596.0228, found: 596.0229; IR (KBr): 3322, 2976, 1694, 1531, 1370,
1164, 853, 737, 610 cm$^{-1}$.

**Pyrrolidine 4i.** Pale yellow oil. [$\alpha$]$_D^{25}$ + 28.0 (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.38 (d, $J$ = 8.5 Hz, 2H), 8.11 (d, $J$ = 8.7 Hz, 2H), 7.49 (d, $J$ = 8.3 Hz, 2H), 6.97 (d, $J$ = 8.2 Hz, 3H), 5.04 (s, 1H), 4.37 (t, $J$ = 8.1 Hz, 1H), 4.15 (d, $J$ = 5.0 Hz, 1H), 3.70 – 3.59 (m, 1H), 3.58 – 3.47 (m, 1H), 2.93 – 2.75 (m, 1H), 2.23 (d, $J$ = 15.2 Hz, 1H), 1.17 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 149.99, 146.09, 145.55, 139.91, 132.03, 128.30, 126.71, 124.32, 121.84, 81.80, 72.82, 59.10, 50.89, 49.82, 37.87, 27.88; HRMS (ESI) calcd for C$_{22}$H$_{25}$Br$_2$N$_3$NaO$_6$S [M+Na]$^+$: 639.9723, found: 639.9734; IR (KBr): 3261, 2977, 1693, 1532, 1348, 1163, 854, 737, 610 cm$^{-1}$.

**Pyrrolidine 4j.** Colorless oil. [$\alpha$]$_D^{25}$ + 21.8 (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.37 (d, $J$ = 8.7 Hz, 2H), 8.09 (d, $J$ = 8.8 Hz, 2H), 8.01 (d, $J$ = 8.3 Hz, 2H), 7.15 (d, $J$ = 8.3 Hz, 2H), 6.95 (d, $J$ = 6.9 Hz, 1H), 5.11 (s, 1H), 4.42 – 4.37 (m, 1H), 4.16 (d, $J$ = 5.3 Hz, 1H), 3.92 (s, 3H), 3.67 – 3.60 (m, 1H), 3.56 – 3.45 (m, 1H), 2.87 – 2.81 (m, 1H), 2.23 (d, $J$ = 15.2 Hz, 1H), 1.11 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.42, 155.47, 149.99, 146.08, 145.80, 130.47, 130.24, 128.31, 125.10, 124.33, 81.85, 73.11, 59.16, 52.26, 50.67, 49.73, 37.95, 27.83; HRMS (ESI) calcd for C$_{24}$H$_{28}$Br$_3$N$_3$NaO$_8$S [M+Na]$^+$: 620.0673, found: 620.0686; IR (KBr): 3255, 2976, 1698, 1532, 1349, 1164, 1096, 894, 743, 610 cm$^{-1}$.

**Piperidine 5a.** Colorless oil. [$\alpha$]$_D^{25}$ – 22.3 (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.38 (d, $J$ = 8.7 Hz, 2H), 8.07 (d, $J$ = 8.7 Hz, 2H), 7.38 – 7.12 (m, 5H), 5.61 (s, 1H), 5.05 (d, $J$ = 2.3 Hz, 1H), 4.44 (d, $J$ = 8.5 Hz, 1H), 4.26 (dd, $J$ = 13.4, 4.4 Hz, 1H), 4.01 – 3.94 (m, 1H), 2.55 – 2.43 (m, 1H), 2.14 (d, $J$ = 13.5 Hz, 1H), 1.78 (ddd, $J$ = 14.3, 11.6, 3.1 Hz, 1H), 1.47 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 155.11, 150.22, 146.56, 136.32, 129.28, 128.19, 127.78, 126.00, 124.61, 81.22, 59.28, 49.21, 46.46, 44.43, 35.83, 28.27; HRMS (ESI) calcd for C$_{22}$H$_{26}$Br$_3$N$_3$NaO$_6$S [M+Na]$^+$: 562.0618, found: 562.0626; IR (KBr): 3276, 2970, 1689, 1533, 1392, 1164, 1095, 803 cm$^{-1}$.
Pyrrolidine 5a-Ts. Colorless crystal (recrystallized from a solution of dichloromethane and n-hexane)
m.p. 187 – 188 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.32 (d, $J$ = 8.8 Hz, 2H), 7.93 (d, $J$ = 8.9 Hz, 2H), 7.75 (d, $J$ = 8.3 Hz, 2H), 7.38 – 7.27 (m, 5H), 7.20 (d, $J$ = 7.9 Hz, 2H), 5.49 (s, 1H), 4.91 (d, $J$ = 2.3 Hz, 1H), 4.62 (d, $J$ = 8.0 Hz, 1H), 3.91 (dd, $J$ = 13.6, 4.5 Hz, 1H), 3.77 – 3.61 (m, 1H), 2.90 (dd, $J$ = 13.6, 11.1 Hz, 1H), 2.48 (s, 3H), 1.89 (d, $J$ = 14.0 Hz, 1H), 1.74 – 1.65 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 150.18, 145.91, 143.86, 136.86, 129.53, 129.26, 128.17, 128.08, 127.74, 126.54, 124.52, 62.04, 48.97, 46.43, 46.06, 35.10, 21.60; HRMS (ESI) calcd for C$_{24}$H$_{24}$BrN$_3$NaO$_6$S$_2$ [M+Na]$^+$: 616.0182, found: 616.0192; IR (KBr): 3318, 3101, 2957, 1532, 1447, 1343, 1160, 1094 cm$^{-1}$.

References
5a-Ts
Figure S1. X-ray structure of 5a-Ts (CCDC: 970435)