Supporting information

Suzuki Cross-Coupling on Enantiomerically Pure Epoxides: Efficient Synthesis of Diverse, Modular Amino Alcohols from Single Enantiopure Precursors

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General. NMR spectra were recorded in CDCl₃ at 298 K. ¹H and ¹³C chemical shifts are reported in ppm relative to Me₄Si, and ¹⁹F chemical shifts are reported in ppm relative to CFCl₃. Dry, oxygen-free solvents were employed. Microwave reactions were carried out in sealed tubes using a CEM Discover Microwave Reactor equipped with an infrared temperature sensor. 3,5-dibromobenzaldehyde¹ and 4-bromophenylglycidol **1**² were synthesized following reported procedures. The optical purity of epoxide **1** was determined by HPLC (Chiralcel OD-H column, 1mL/min, H/IPA 98/2, 215nm). t_R (minor) 35.4 (2R, 3R) and t_R (major) 40.7 min(2S, 3S).

¹ Laughrey, Z. R.; Gibb, C. L. D.; Senechal, T.; Gibb, B. C. *Chem. Eur. J.* **2003**, 9, 130.

² Gao, Y.; Hanson, R. H.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, 109, 5765.

Synthesis of epoxyethers 2b and 2c, following the general procedure for the synthesis of epoxyethers 2a-2c

Epoxyether 2b: This epoxyether was synthesized using benzyl bromide as the alkylating agent. It was obtained as a colorless oil (90%). ^1H NMR (500 MHz): δ =3.21 (m, 1 H); 3.66 (dd, J = 5.2 and 11.5 Hz, 1 H); 3.79 (d, J = 2.1 Hz, 1 H); 3.85 (dd, J = 11.5 and 3.1 Hz, 1 H); 4.64 (m, 2 H); 7.16 (d, J = 8.5 Hz, 2 H); 7.33 (m, 1 H); 7.38 (m, 4 H); 7.48 (d, J = 8.5 Hz, 2 H). ^{13}C NMR (125 MHz): δ =55.3 (CH); 61.3 (CH); 69.6 (CH₂); 73.5 (CH₂); 122.2 (C); 127.4 (CH); 127.8 (CH); 127.9 (CH); 128.5 (CH); 131.6 (CH); 136.0 (C); 137.7 (C). $[\alpha]_{\text{D}}^{20}$: -38.1 (c 1.28, CHCl₃). HRMS (ES⁺): calcd for C₁₆H₁₆O₂Br (M+H): 321.0313; found 321.0322.

Epoxyether 2c: This epoxyether was synthesized using bromodiphenylmethane as the alkylating agent. It was obtained as a white solid (80%). ^1H NMR (400 MHz): δ =3.24 (m, 1 H); 3.67 (dd, J = 5.1 and 11.6 Hz, 1 H); 3.78 (d, J = 2.1 Hz, 1 H); 3.84 (dd, J = 11.6 and 3.1 Hz, 1 H); 5.51 (s, 1 H); 7.16 (d, J = 8.3 Hz, 2 H); 7.25-7.35 (m, 2 H); 7.35-7.45 (m, 8 H); 7.49 (d, J = 8.3 Hz, 2 H). ^{13}C NMR (100 MHz): δ =55.4 (CH); 61.3 (CH); 68.4 (CH₂); 84.1 (CH); 122.1 (C); 127.0 (CH); 127.1 (2 CH); 127.4 (CH); 127.6 (CH); 127.7 (CH); 128.5 (CH); 131.7 (CH); 136.1 (C); 141.7 (2 C). M.P.: 52-53°C; $[\alpha]_{\text{D}}^{20}$: -23.2 (c 1.36, CHCl₃). HRMS (ES⁺): calcd for C₂₂H₂₀O₂Br (M+H): 395.0647; found 395.0636.

Synthesis of epoxyethers 3ba-3ag following the general procedure for the Suzuki cross-coupling on epoxides 2:

Epoxyether 3ba: Reaction time: 3 h. Yield: 83%. ^1H NMR (400 MHz): δ =3.35 (m, 1 H); 3.70 (dd, J = 5.3 and 11.5 Hz, 1 H); 3.90 (d, J = 2.0 Hz, 1 H); 3.93 (dd, J = 3.0 and 11.5 Hz, 1 H); 4.70 (m, 2 H); 7.30-7.50 (m, 10 H); 7.63 (m, 4 H). ^{13}C NMR (100 MHz): δ =55.8 (CH); 61.3 (CH); 69.9 (CH₂); 73.5 (CH₂); 126.3 (CH); 127.1 (CH); 127.3 (CH); 127.5 (CH); 127.8 (CH); 127.9 (CH); 128.5 (CH); 128.9 (CH); 136.0 (C); 137.9 (C); 140.7 (C); 141.3 (C). M.P.: 69-70°C; $[\alpha]_D^{20}$: -33.8 (c 1.04, CHCl₃). HRMS (ES⁺): calcd for C₂₂H₂₀O₂Na (M+Na): 339.1361; found 339.1349.

Epoxyether 3ca: Reaction time: 3 h. Yield: 70%. ^1H NMR (400 MHz): δ =3.35 (m, 1 H); 3.69 (dd, J = 5.2 and 11.5 Hz, 1 H); 3.84 (d, J = 2.1 Hz, 1 H); 3.88 (dd, J = 3.1 and 11.5 Hz, 1 H); 5.54 (s, 1 H); 7.28 (m, 2 H); 7.30-7.40 (m, 7 H); 7.40-7.50 (m, 6 H); 7.55-7.65 (m, 4 H). ^{13}C NMR (100 MHz): δ =55.8 (CH); 61.3 (CH); 68.7 (CH₂); 84.0 (CH); 126.2 (CH); 127.0 (CH); 127.09 (CH); 127.11 (CH); 127.3 (CH); 127.4 (CH); 127.6 (CH); 127.7 (CH); 128.5 (CH); 128.8 (CH); 136.0 (C); 140.7 (C); 141.3 (C); 141.8 (C) 1CH and 1C not seen. M.P.: 69-70°C; $[\alpha]_D^{20}$: -36.7 (c 0.45, CHCl₃). HRMS (ES⁺): calcd for C₂₈H₂₅O₂ (M+H): 393.1855; found 393.1856.

Epoxyether 3da: Reaction time: 3 h. Yield: 73%. ^1H NMR (400 MHz): δ =3.30-3.35 (m, 2 H); 3.50 (m, 1 H); 3.86 (m, 1 H); 7.25-7.40 (m, 13 H); 7.45-7.50 (m, 2 H); 7.50-7.55 (m, 6 H); 7.60 (m, 3 H). ^{13}C NMR (100 MHz): δ =55.0 (CH); 61.4 (CH); 64.2 (CH₂); 86.9 (C); 126.2 (CH); 127.09 (CH); 127.14 (CH); 127.3 (CH); 127.4 (CH); 127.9 (CH); 128.7 (CH); 128.8 (CH); 136.2 (C); 140.7 (C); 141.2 (C); 143.8 (C). M.P.: 160-162°C; $[\alpha]_D^{20}$: -37.3 (c 1.00, CHCl₃). HRMS (ES⁺): calcd for C₃₄H₂₈O₂Na (M+Na): 491.1987; found 491.2005.

Epoxyether 3ab: Reaction time: 30 min. Yield: 84%. ^1H NMR (400 MHz): δ =3.27 (m, 1 H); 3.49 (s, 3 H); 3.62 (dd, J = 5.1 and 11.5 Hz, 1 H); 3.83 (dd, J = 3.0 and 11.5 Hz, 1 H); 3.90 (d, J = 2.1 Hz, 1 H); 7.44 (d, J = 8.4 Hz, 2 H); 7.62 (d, J = 8.4 Hz, 2 H); 7.88 (br, 1 H); 8.02 (br, 2 H). ^{13}C NMR (100 MHz): δ =55.3 (CH); 59.3 (CH₃); 61.2 (CH); 72.0 (CH₂); 121.0 (sept, J = 3.9 Hz, CH); 123.3 (q, J = 273 Hz, CF₃); 126.6 (CH); 127.1 (m, CH); 127.4 (CH); 132.2 (q, J = 33 Hz, C-CF₃); 137.9 (C); 138.1 (C); 142.7 (C). ^{19}F NMR (471 MHz): δ =-64.01. M.P.: 47°C; $[\alpha]_{\text{D}}^{20}$: -21.1 (c 1.85, CHCl₃). HRMS (ES⁺): calcd for C₁₈H₁₄O₂F₆Na (M+Na): 399.0796; found 399.0780.

Epoxyether 3ac: Reaction time: 60 min. Yield: 83%. ^1H NMR (400 MHz): δ =2.41 (s, 6 H); 3.28 (m, 1 H); 3.49 (s, 3 H); 3.59 (dd, J = 5.2 and 11.5 Hz, 1 H); 3.83 (dd, J = 3.0 and 11.5 Hz, 1 H); 3.87 (d, J = 2.1 Hz, 1 H); 7.03 (br, 1 H); 7.22 (br, 2 H); 7.36 (d, J = 8.2 Hz, 2 H); 7.59 (d, J = 8.2 Hz, 2 H). ^{13}C NMR (100 MHz): δ =21.4 (CH₃); 55.6 (CH); 59.3 (CH₃); 61.0 (CH); 72.2 (CH₂); 125.0 (CH); 126.1 (CH); 127.3 (CH); 129.1 (CH); 135.7 (C); 138.3 (C); 140.7 (C); 141.5 (C). $[\alpha]_{\text{D}}^{20}$: -29.8 (c 0.97, CHCl₃). HRMS (ES⁺): calcd for C₁₈H₂₀O₂Na (M+Na): 291.1361; found 291.1365.

Epoxyether 3ad: Reaction time: 100 min. Yield: 80%. ^1H NMR (400 MHz): δ =3.27 (m, 1 H); 3.40 (s, 3 H); 3.58 (dd, J = 5.2 and 11.5 Hz, 1 H); 3.82 (dd, J = 3.0 and 11.5 Hz, 1 H); 3.85 (d, J = 2.0 Hz, 1 H); 3.87 (s, 3 H); 6.99 (d, J = 8.8 Hz, 2 H); 7.35 (d, J = 8.2 Hz, 2 H); 7.55 (m, 4 H). ^{13}C NMR (100 MHz): δ =55.4 (CH₃); 55.6 (CH); 59.3 (CH₃); 61.0 (CH); 72.2 (CH₂); 114.3 (CH); 126.2 (CH); 126.8 (CH); 128.1 (CH); 133.2 (C); 135.2 (C); 140.9 (C); 159.3 (C). M.P.: 122-123°C; $[\alpha]_{\text{D}}^{20}$: -32.1 (c 1.38, CHCl₃). HRMS (ES⁺): calcd for C₁₇H₁₈O₃Na (M+Na): 293.1154; found 293.1157.

Epoxyether 3ae: Reaction time: 45 min. Yield: 84%. ^1H NMR (400 MHz): δ =2.30 (s, 3 H); 3.32 (m, 1 H); 3.51 (s, 3 H); 3.61 (dd, J = 5.2 and 11.5 Hz, 1 H); 3.84 (dd, J = 3.2 and 11.5 Hz, 1 H); 3.89 (d, J = 2.1 Hz, 1 H); 7.20-7.45 (m, 8 H). ^{13}C NMR (100 MHz):

δ =20.5 (CH₃); 55.7 (CH); 59.3 (CH₃); 61.0 (CH); 72.3 (CH₂); 125.6 (CH); 126.8 (CH); 127.4 (CH); 129.4 (CH); 129.7 (CH); 135.3 (C); 135.4 (C); 141.4 (C); 142.1 (C). $[\alpha]^{20}_{\text{D}}$: -34.0 (*c* 0.31, CHCl₃). HRMS (ES⁺): calcd for C₁₇H₁₈O₂Na (M+Na): 277.1204; found 277.1195.

Epoxyether 3af: Reaction time: 60 min. Yield: 70%. ¹H NMR (400 MHz): δ =2.04 (s, 6 H); 3.32 (m, 1 H); 3.49 (s, 3 H); 3.61 (dd, *J* = 5.3 and 11.4 Hz, 1 H); 3.83 (dd, *J* = 3.2 and 11.4 Hz, 1 H); 3.86 (d, *J* = 2.1 Hz, 1 H); 7.10-7.20 (m, 5 H); 7.36 (m, 2 H). ¹³C NMR (100 MHz): δ =20.8 (CH₃); 55.9 (CH); 59.4 (CH₃); 61.0 (CH); 72.3 (CH₂); 124.0 (CH); 127.1 (CH); 127.3 (CH); 129.3 (CH); 135.1 (C); 136.0 (C); 141.2 (C); 141.3 (C). $[\alpha]^{20}_{\text{D}}$: -27.6 (*c* 0.68, CHCl₃). HRMS (ES⁺): calcd for C₁₈H₂₀O₂Na (M+Na): 291.1361; found 291.1375.

Epoxyether 3ag: Reaction time: 75 min. Yield: 97%. ¹H NMR (400 MHz): δ =3.30 (m, 1 H); 3.48 (s, 3 H); 3.57 (dd, *J* = 5.4 and 11.5 Hz, 1 H); 3.76 (s, 6 H); 3.82 (dd, *J* = 3.0 and 11.6 Hz, 1 H); 3.85 (d, *J* = 2.1 Hz, 1 H); 6.67 (d, *J* = 8.4 Hz, 2 H); 7.31 (t, *J* = 8.4 Hz, 1 H); 7.36 (m, 4 H). ¹³C NMR (100 MHz): δ =55.9 (CH₃); 55.9 (CH); 59.3 (CH₃); 60.9 (CH); 72.3 (CH₂); 104.2 (CH); 119.0 (C); 125.1 (CH); 128.8 (CH); 131.1 (CH); 134.3 (C); 135.1 (C); 157.7 (C). M.P.: 77-78°C; $[\alpha]^{20}_{\text{D}}$: -22.7 (*c* 1.22, CHCl₃). HRMS (ES⁺): calcd for C₁₈H₂₀O₄Na (M+Na): 323.1259; found 323.1263.

Synthesis of aminoalcohols 3ba-3ag following the general procedure for the microwave ring opening of epoxides with ammonia:

Amino alcohol 5ba: Yield: 76%. ^1H NMR (400 MHz): δ =2.35 (br, 3 H); 3.52 (m, 2 H); 4.04 (q, J = 5.1 Hz, 1 H); 4.23 (d, J = 5.1 Hz, 1 H); 4.53 (m, 2 H); 7.30-7.40 (m, 6 H); 7.42-7.49 (m, 4 H); 7.57-7.63 (m, 4 H). ^{13}C NMR (100 MHz): δ =57.7 (CH); 71.5 (CH₂); 73.5 (CH₂); 73.6 (CH); 127.1 (CH); 127.2 (CH); 127.3 (CH); 127.7 (CH); 127.81 (CH); 127.83 (CH); 128.5 (CH); 128.8 (CH); 138.0 (C); 140.3 (C); 140.8 (C); 141.0 (C). M.P.: 102-103°C; $[\alpha]_{\text{D}}^{20}$: -11.7 (c 0.98, CHCl₃). HRMS (ES⁺): calcd for C₂₂H₂₄NO₂ (M+H): 334.1807; found 334.1808.

Aminoalcohol 5ca: Yield: 92%. ^1H NMR (400 MHz): δ =2.25 (br, 3 H); 3.53 (m, 2 H); 4.08 (q, J = 5.0 Hz, 1 H); 4.22 (d, J = 5.0 Hz, 1 H); 5.36 (s, 1 H); 7.28-7.40 (m, 11 H); 7.42 (d, J = 8.0 Hz, 2 H); 7.49 (m, 2 H); 7.58 (d, J = 8.0 Hz, 2 H); 7.64 (m, 2 H). ^{13}C NMR (100 MHz): δ =57.8 (CH); 70.4 (CH₂); 73.8 (CH); 84.4 (CH); 126.9 (CH); 127.0 (CH); 127.09 (CH); 127.13 (CH); 127.3 (CH); 127.6 (CH); 127.65 (CH); 127.68 (CH); 128.46 (CH); 128.50 (CH); 128.82 (CH); 140.3 (C); 140.9 (C); 141.3 (C); 141.91 (C); 141.93 (C). M.P.: 78-79°C; $[\alpha]_{\text{D}}^{20}$: -15.9 (c 2.48, CHCl₃). HRMS (ES⁺): calcd for C₂₈H₂₈NO₂ (M+H): 410.2120; found 410.2119.

Aminoalcohol 5da: Yield: 87%. ^1H NMR (400 MHz): δ =2.12 (br, 3 H); 3.19 (m, 2 H); 4.00 (m, 1 H); 4.26 (m, 1 H); 7.23-7.35 (m, 11 H); 7.39 (m, 1 H); 7.47 (m, 10 H); 7.57 (m, 2 H). ^{13}C NMR (100 MHz): δ =57.9 (CH); 64.5 (CH₂); 73.9 (CH); 87.0 (C); 125.3 (CH); 127.0 (CH); 127.1 (CH); 127.2 (CH); 127.6 (CH); 127.9 (CH); 128.6 (CH); 128.8 (CH); 140.2 (C); 141.0 (C); 143.7 (C); 143.8 (C). M.P.: 78-79°C; $[\alpha]_{\text{D}}^{20}$: -14.2 (c 0.75, CHCl₃). HRMS (ES⁺): calcd for C₃₄H₃₁NO₂Na (M+Na): 508.2252; found 508.2275.

Aminoalcohol 5ab: Yield 83%. ^1H NMR (400 MHz): δ =2.36 (br, 3 H); 3.36 (s, 3 H); 3.36 (m, 2H); 4.02 (q, J = 4.9 Hz, 1 H); 4.23 (d, J = 4.9 Hz, 1 H); 7.53 (d, J = 8.4 Hz, 2 H); 7.62 (d, J = 8.4 Hz, 2 H); 7.87 (br, 1 H); 8.02 (br, 2 H). ^{13}C NMR (100 MHz): δ =57.5 (CH); 59.2 (CH₃); 73.4 (CH); 73.6 (CH₂); 120.9 (sept, J = 3.4 Hz, CH); 122.9 (q, J = 272 Hz, CF₃); 127.1 (m, CH); 127.3 (CH); 128.2 (CH); 132.1 (q, J = 33 Hz, C-CF₃); 137.3 (C); 142.3 (C); 143.0 (C). ^{19}F NMR (471 MHz): δ =-64.00. M.P.: 123-124°C; $[\alpha]_{\text{D}}^{20}$: -12.1 (c 1.40, CHCl₃). HRMS (ES⁺): calcd for C₁₈H₁₈F₆NO₂Na (M+Na): 394.1242; found 394.1235.

Aminoalcohol 5ac: Yield 68%. ^1H NMR (400 MHz): δ =2.40 (br, 3 H); 2.40 (s, 6 H); 3.37 (s, 3 H); 3.38 (m, 2 H); 4.00 (q, J = 5.1 Hz, 1 H); 4.17 (d, J = 5.1 Hz, 1 H); 7.02 (s, 1 H); 7.23 (s, 2 H); 7.42 (d, J = 8.2 Hz, 2 H); 7.58 (d, J = 8.2 Hz, 2 H). ^{13}C NMR (100 MHz): δ =21.4 (CH₃); 57.6 (CH); 59.1 (CH₃); 73.5 (CH); 73.8 (CH₂); 125.0 (CH); 127.2 (CH); 127.5 (CH); 129.0 (CH); 138.3 (C); 140.6 (C); 140.77 (C); 140.80 (C). $[\alpha]_{\text{D}}^{20}$: -22.4 (c 2.55, CHCl₃). HRMS (ES⁺): calcd for C₁₈H₂₃NO₂Na (M+Na): 308.1626; found 308.1614.

Aminoalcohol 5ad: Yield 91%. ^1H NMR (400 MHz): δ =2.13 (br, 3 H); 3.37 (s, 3 H); 3.40 (m, 2 H); 3.87 (s, 3 H); 3.99 (q, J = 5.1 Hz, 1 H); 4.18 (d, J = 5.1 Hz, 1 H); 6.99 (d, J = 8.7 Hz, 2 H); 7.42 (d, J = 8.1 Hz, 2 H); 7.55 (m, 4 H). ^{13}C NMR (100 MHz): δ =55.4 (CH₃); 57.6 (CH); 59.2 (CH₃); 73.6 (CH); 73.7 (CH₂); 114.2 (CH); 126.7 (CH); 127.5 (CH); 128.1 (CH); 133.3 (C); 140.0 (C); 140.4 (C); 159.2 (C). M.P.: 132-133°C; $[\alpha]_{\text{D}}^{20}$: -20.5 (c 0.79, CHCl₃). HRMS (ES⁺): calcd for C₁₇H₂₁NO₃Na (M+Na): 310.1419; found 310.1417.

Aminoalcohol 5ae: Yield 96%. ^1H NMR (400 MHz): δ =2.30 (s, 3 H); 2.47 (br, 3 H); 3.38 (s, 3 H); 3.42 (m, 2 H); 4.03 (q, J = 5.2 Hz, 1 H); 4.19 (d, J = 5.2 Hz, 1 H); 7.20-7.30 (m, 4 H); 7.33 (d, J = 8.3 Hz, 2 H); 7.43 (d, J = 8.3 Hz, 2 H). ^{13}C NMR (100

MHz): δ =20.5 (CH₃); 57.7 (CH); 59.2 (CH₃); 73.5 (CH); 73.8 (CH₂); 125.8 (CH); 127.0 (CH); 127.3 (CH); 129.3 (CH); 129.8 (CH); 130.4 (CH); 135.3 (C); 140.4 (C); 141.1 (C); 141.5 (C). M.P.: 120-121°C; $[\alpha]_D^{20}$: -24.5 (*c* 4.10, CHCl₃). HRMS (ES⁺): calcd for C₁₇H₂₁NO₂Na (M+Na): 294.1470; found 294.1469.

Aminoalcohol 5af: Yield 68%. ¹H NMR (400 MHz): δ =2.06 (s, 6 H); 2.36 (br, 3 H); 3.37 (s, 3 H); 3.39 (m, 2 H); 4.03 (q, *J* = 5.0 Hz, 1 H); 4.21 (d, *J* = 5.0 Hz, 1 H); 7.15 (m, 5 H); 7.44 (d, *J* = 8.0 Hz, 2 H). ¹³C NMR (100 MHz): δ =20.9 (CH₃); 57.8 (CH); 59.2 (CH₃); 73.5 (CH); 78.0 (CH₂); 127.1 (CH); 127.2 (CH); 127.3 (CH); 129.1 (CH); 136.1 (C); 140.19 (C); 140.21 (C); 141.5 (C). $[\alpha]_D^{20}$: -28.7 (*c* 2.10, CHCl₃). HRMS (ES⁺): calcd for C₁₈H₂₄NO₂ (M+H): 286.1807; found 286.1798.

Aminoalcohol 5ag: Yield 97%. ¹H NMR (400 MHz): δ =2.13 (br, 3 H); 3.39 (s, 3 H); 3.47 (m, 2 H); 3.75 (s, 6 H); 4.00 (q, *J* = 5.1 Hz, 1 H); 4.17 (d, *J* = 5.1 Hz, 1 H); 6.67 (d, *J* = 8.4 Hz, 2 H); 7.30 (t, *J* = 8.4 Hz, 1 H); 7.35 (d, *J* = 8.1 Hz, 2 H); 7.40 (d, *J* = 8.1 Hz, 2 H). ¹³C NMR (100 MHz): δ =55.9 (CH₃); 57.9 (CH); 59.2 (CH₃); 73.7 (CH); 73.8 (CH₂); 114.2 (CH); 119.1 (C); 126.5 (CH); 128.7 (CH); 131.1 (CH); 133.3 (C); 140.2 (C); 157.6 (C). M.P.: 132-133°C; $[\alpha]_D^{20}$: -30.6 (*c* 1.80, CHCl₃). HRMS (ES⁺): calcd for C₁₈H₂₃NO₄Na (M+Na): 340.1525; found 340.1511.

Synthesis of epoxiethers 7a-7c following the general procedure for the synthesis of epoxyethers 2a-2c:

Epoxyether 7a: Following the general procedure, the epoxide was methylated using methyl iodide. It was then purified by flash chromatography (hexanes, then hexanes/ethyl acetate 95/5). A white solid was finally obtained (87%). ¹H NMR (400 MHz): δ=3.13 (m, 1 H); 3.44 (s, 3 H); 3.57 (dd, *J* = 4.8 and 11.5 Hz, 1 H); 3.75 (dd, *J* = 3.0 and 11.5 Hz, 1 H); 3.77 (d, *J* = 2.0 Hz, 1 H); 7.37 (d, *J* = 1.8 Hz, 2 H); 7.61 (t, *J* = 1.8 Hz, 1 H). ¹³C NMR (100 MHz): δ=54.2 (CH); 59.4 (CH₃); 61.2 (CH); 71.5 (CH₂); 123.1 (C); 127.5 (CH); 133.8 (CH); 141.2 (C). M.P.: 63-65°C; [α]_D²⁰: -30.0 (*c* 0.86, CHCl₃). HRMS: calculated for C₁₀H₁₀O₂Br₂Na: 342.8945, found 342.8953.

Epoxyether 7b: This epoxyether was synthesized using benzyl bromide as the alkylating agent. It was obtained as a white solid (93%). ¹H NMR (400 MHz): δ=3.17 (m, 1 H); 3.67 (dd, *J* = 4.8 and 11.6 Hz, 1 H); 3.77 (d, *J* = 2.0 Hz, 1 H); 3.83 (dd, *J* = 3.1 and 11.5 Hz, 1 H); 4.63 (m, 2 H); 7.30-7.40 (m, 7 H); 7.61 (t, *J* = 1.7 Hz, 1 H). ¹³C NMR (100 MHz): δ=54.4 (CH); 61.4 (CH); 69.1 (CH₂); 73.6 (CH₂); 123.1 (C); 127.5 (CH); 127.8 (CH); 128.0 (CH); 128.5 (CH); 133.8 (CH); 137.6 (C); 141.2 (C). [α]_D²⁰: -31.4 (*c* 8.8, CHCl₃). HRMS (ES⁺): calcd for C₁₆H₁₄O₂Br₂Na (M+Na): 418.9258; found 418.9275.

Epoxyether 7c: This epoxyether was synthesized using bromodiphenylmethane as the alkylating agent. It was obtained as a white solid (76%). ¹H NMR (400 MHz): δ=3.20 (m, 1 H); 3.69 (dd, *J* = 4.8 and 11.6 Hz, 1 H); 3.76 (d, *J* = 2.0 Hz, 1 H); 3.82 (dd, *J* = 3.2 and 11.6 Hz, 1 H); 5.50 (s, 1 H); 7.25-7.42 (m, 10 H); 7.52 (m, 1 H); 7.61 (m, 1 H); 7.84

(m, 1 H). ^{13}C NMR (100 MHz): δ =54.5 (CH); 61.5 (CH); 68.0 (CH₂); 84.2 (CH); 123.1 (C); 126.96 (CH); 127.04 (CH); 127.5 (CH); 127.7 (CH); 128.3 (CH); 128.5 (CH); 130.1 (CH); 133.8 (CH); 141.3 (C); 141.60 (C); 141.64 (C). $[\alpha]_{\text{D}}^{20}$: -26.7 (*c* 2.00, CHCl₃). HRMS (ES⁺): calcd for C₂₂H₁₈O₂Br₂Na (M+Na): 494.9571; found 4943.9594.

Epoxyether 7d: Following the procedure described for **2d**, epoxyalcohol **6** was reacted with trityl chloride yielding epoxyether **7d** as a white powder (80 %). ^1H NMR (400 MHz): δ =3.14 (m, 1 H); 3.31 (dd, *J* = 4.8 and 11.2 Hz, 1 H); 3.47 (dd, *J* = 3.3 and 11.2 Hz, 1 H); 3.76 (d, *J* = 2.1 Hz, 1 H); 7.25-7.28 (m, 11 H); 7.47-7.52 (m, 6 H); 7.61 (t, *J* = 1.8 Hz, 1 H). ^{13}C NMR (100 MHz): δ =54.6 (CH); 61.6 (CH); 63.5 (CH₂); 87.0 (C); 123.1 (C); 127.2 (CH); 127.5 (CH); 128.0 (CH); 128.6 (CH); 133.7 (CH); 141.4 (C); 143.6 (C). M.P.: 126-127°C; $[\alpha]_{\text{D}}^{20}$: -24.7 (*c* 1.34, CHCl₃). HRMS (ES⁺): calcd for C₂₈H₂₂O₂Br₂Na (M+Na): 570.9884; found 570.9908.

*Synthesis of epoxyethers **8ba-8ag** following the general procedure for the Suzuki cross-coupling on epoxides **7**:*

Epoxyether 8ba: Reaction time: 3 h. Yield: 94%. ¹H NMR (400 MHz): δ=3.37 (m, 1 H); 3.72 (dd, *J* = 5.2 and 11.6 Hz, 1 H); 3.93 (dd, *J* = 2.0 and 11.6 Hz, 1 H); 3.97 (d, *J* = 2.0 Hz, 1 H); 4.69 (m, 2 H); 7.27-7.50 (m, 13 H); 7.67 (m, 4 H); 7.77 (m, 1 H). ¹³C NMR (100 MHz): δ=56.0 (CH); 61.3 (CH); 69.8 (CH₂); 73.5 (CH₂); 123.4 (CH); 126.1 (CH); 127.3 (CH); 127.6 (CH); 127.8 (CH); 128.5 (CH); 128.9 (CH); 137.8 (C); 138.1 (C); 140.7 (C); 142.2 (C) 1 CH missing. [α]_D²⁰: -41.7 (*c* 1.67, CHCl₃). HRMS (ES⁺): calcd for C₂₈H₂₄O₂Na (M+Na): 415.1674; found 415.1678.

Epoxyether 8ca: Reaction time: 3 h. Yield: 68%. ¹H NMR (400 MHz): δ=3.40 (m, 1 H, CH); 3.72 (dd, *J* = 5.1 and 11.5 Hz, 1 H, CH₂); 3.91 (dd, *J* = 3.1 and 11.5 Hz, 1 H); 3.96 (d, *J* = 2.1 Hz, 1 H); 5.56 (s, 1 H); 7.26-7.32 (m, 2 H); 7.35-7.46 (m, 10 H); 7.47-7.53 (m, 6 H); 7.67 (m, 4 H), 7.78 (t, *J* = 1.7 Hz, 1 H). ¹³C NMR (100 MHz): δ=56.0 (CH); 61.4 (CH); 68.6 (CH₂); 84.1 (CH); 123.4 (CH); 126.1 (CH); 127.0 (CH); 127.1 (CH); 127.3 (CH); 127.65 (CH); 127.67 (CH); 128.5 (CH); 128.9 (CH); 138.2 (C); 140.7 (C); 141.76 (C); 141.82 (C) 2 CH and 1 C missing. M.P.: 57-58°C; [α]_D²⁰: -36.6 (*c* 3.83, CHCl₃). HRMS (ES⁺): calcd for C₃₄H₂₈O₂Na (M+Na): 491.1987; found 491.1982.

Epoxyether 8da: Reaction time: 3 h. Yield: 95%. ¹H NMR (400 MHz): δ=3.35 (m, 2 H); 3.52 (m, 1 H); 3.95 (d, *J* = 1.7 Hz, 1 H); 7.25-7.45 (m, 23 H); 7.65-7.70 (m, 4 H); 7.77 (t, *J* = 1.7 Hz, 1 H). ¹³C NMR (100 MHz): δ=56.2 (CH); 61.5 (CH); 64.1 (CH₂); 86.9 (C); 123.4 (CH); 126.0 (CH); 127.1 (CH); 127.3 (CH); 127.6 (CH); 127.9 (CH); 128.7 (CH); 128.8 (CH); 138.3 (C); 140.7 (C); 142.2 (C); 143.8 (C). M.P.: 62-63°C; [α]_D²⁰: -34.4 (*c* 1.57, CHCl₃). HRMS (ES⁺): calcd for C₄₀H₃₂O₂Na (M+Na): 567.2300; found 567.2321.

Epoxyether 8ab: Reaction time: 2 h. Yield: 81%. ^1H NMR (400 MHz): δ =3.31 (m, 1 H); 3.51 (s, 3 H); 3.67 (dd, J = 4.8 and 11.5 Hz, 1 H); 3.85 (dd, J = 2.9 and 11.5 Hz, 1 H); 4.06 (br, 1 H); 7.60 (br, 2 H); 7.71 (m, 1 H); 7.95 (br, 2 H); 8.06 (br, 4 H). ^{13}C NMR (100 MHz): δ =55.2 (CH); 59.3 (CH₃); 61.5 (CH); 71.7 (CH₂); 121.6 (sept, J = 3.4 Hz, CH); 123.3 (q, J = 273 Hz, CF₃); 124.9 (CH); 126.0 (CH); 127.4 (q, J = 2.8 Hz, CH); 132.4 (q, J = 33 Hz, C-CF₃); 139.9 (C); 140.0 (C); 142.3 (C). ^{19}F NMR (376 MHz): δ =-62.9. $[\alpha]_{\text{D}}^{20}$: -25.8 (c 2.50, CHCl₃). HRMS (ES⁺): calcd for C₂₆H₁₅O₂F₁₂ (M+H): 587.0880; found 587.0907.

Epoxyether 8ag: Reaction time: 20 h. Yield: 70%. ^1H NMR (400 MHz): δ =3.34 (m, 1 H); 3.47 (s, 3 H); 3.52 (dd, J = 5.6 and 11.5 Hz, 1 H); 3.76 (s, 6 H); 3.83 (m, 2 H); 6.67 (d, J = 8.3 Hz, 2 H); 7.26 (d, J = 1.3 Hz, 1 H); 7.28 (t, J = 8.3 Hz, 1 H); 7.35 (t, J = 1.3 Hz, 1 H). ^{13}C NMR (100 MHz): δ =55.9 (C, CH₃); 56.3 (CH); 59.3 (CH₃); 60.9 (CH); 72.6 (CH₂); 104.2 (CH); 119.4 (C); 127.1 (CH); 128.5 (CH); 133.2 (C); 134.0 (CH); 134.9 (C); 157.8 (C). $[\alpha]_{\text{D}}^{20}$: -17.9 (c 1.50, CHCl₃). HRMS (ES⁺): calcd for C₂₆H₂₈O₆Na (M+Na): 459.1784; found 459.1799.

Synthesis of aminoalcohols 9ba-9ca following the general procedure for the autoclave ring opening of epoxides with ammonia (method B):

Amino alcohol 9ba: Method B; Yield: 66%. ^1H NMR (400 MHz): δ =2.07 (br, 3 H); 3.57 (m, 2 H); 4.09 (m, 1 H); 4.33 (d, J = 5.3 Hz, 1 H); 4.52 (m, 2 H); 7.25-7.35 (m, 5 H); 7.35-7.43 (m, 2 H); 7.46-7.52 (m, 4 H); 7.60 (d, J = 1.7 Hz, 2 H); 7.64-7.68 (m, 4 H); 7.75 (t, J = 1.7 Hz, 1 H). ^{13}C NMR (100 MHz): δ =58.1 (CH); 71.4 (CH_2); 73.6 (CH_2); 73.7 (CH); 125.0 (CH); 125.3 (CH); 127.3 (CH); 127.5 (CH); 127.8 (CH); 128.4 (CH); 128.8 (CH); 137.9 (C); 141.0 (C); 142.0 (C); 143.2 (C). M.P.: 102-103°C; $[\alpha]_{\text{D}}^{20}$: -13.1 (c 1.21, CHCl_3). HRMS (ES+): calcd for $\text{C}_{28}\text{H}_{27}\text{NO}_2\text{Na}$ (M+Na): 432.1939; found 432.1949.

Aminoalcohol 9ca: Method B; Yield: 71%. ^1H NMR (400 MHz): δ =2.05 (br, 3 H); 3.54 (m, 2 H); 4.10 (m, 1 H); 4.34 (d, J = 5.3 Hz, 1 H); 5.32 (s, 1 H); 7.20-7.35 (m, 10 H); 7.35-7.50 (m, 6 H); 7.57 (d, J = 1.7 Hz, 2 H); 7.60-7.65 (m, 4 H); 7.74 (t, J = 1.7 Hz, 1 H). ^{13}C NMR (100 MHz): δ =58.3 (CH); 70.3 (CH_2); 73.8 (CH); 84.4 (CH); 125.0 (CH); 125.2 (CH); 126.8 (CH); 126.9 (CH); 127.3 (CH); 127.48 (CH); 127.51 (CH); 127.6 (CH); 128.4 (CH); 128.5 (CH); 128.8 (CH); 141.0 (C); 141.8 (C); 141.9 (C); 143.3 (C) 1 C missing. M.P.: 99-100°C; $[\alpha]_{\text{D}}^{20}$: -17.2 (c 2.90, CHCl_3). HRMS (ES+): calcd for $\text{C}_{34}\text{H}_{32}\text{NO}_2$ (M+H): 486.2433; found 486.2455.

Synthesis of aminoalcohols 9da-9ag following the general procedure for the microwave ring opening of epoxides with ammonia (method A):

Aminoalcohol 9da: Method A; time: 2.5 h. Yield: 37%. Epoxide **7d** can be recovered by flash chromatography (DCM/EA 9/1, then DCM/MeOH 9/1). ^1H NMR (400 MHz): δ =2.07 (br, 3 H); 3.22 (m, 2 H); 4.04 (m, 1 H); 4.36 (d, J = 5.1 Hz, 1 H); 7.20 (m, 9 H); 7.40 (m, 8 H); 7.45 (m, 6 H); 7.58 (m, 4 H); 7.69 (t, J = 1.7 Hz, 1 H). ^{13}C NMR (100 MHz): δ =58.3 (CH); 64.8 (CH₂); 74.0 (CH); 87.0 (C); 125.09 (CH); 125.15 (CH); 127.0 (CH); 127.3 (CH); 127.4 (CH); 127.8 (CH); 128.6 (CH); 128.8 (CH); 141.0 (C); 141.8 (C); 143.0 (C); 143.8 (C). $[\alpha]_{\text{D}}^{20}$: -10.4 (c 2.47, CHCl₃). HRMS (ES⁺): calcd for C₄₀H₃₅NO₂Na (M+Na): 584.2565; found 584.2571.

Aminoalcohol 9ab: Method A; Yield 96%. ^1H NMR (400 MHz): δ =2.19 (br, 3 H); 3.40 (s, 3 H); 3.45 (m, 2H); 4.06 (m, 1 H); 4.35 (d, J = 5.4 Hz, 1 H); 7.70-7.72 (m, 3 H); 7.94 (br, 2 H); 8.07 (br, 4 H). ^{13}C NMR (100 MHz): δ =57.8 (CH); 59.2 (CH₃); 73.5 (CH); 73.6 (CH₂); 121.6 (sept, J = 3.7 Hz, CH); 123.3 (q, J = 273 Hz, CF₃); 125.4 (CH); 125.8 (CH); 126.9 (CH); 127.5 (CH); 132.4 (q, J = 33 Hz, C-CF₃); 139.7 (C); 142.7 (C); 144.9 (C). ^{19}F NMR (376 MHz): δ =-62.9. $[\alpha]_{\text{D}}^{20}$: -6.3 (c 1.60, CHCl₃). HRMS (ES⁺): calcd for C₂₆H₁₈F₁₂NO₂ (M+H): 604.1146; found 604.1172.

Aminoalcohol 9ag: Method A; Yield 74%. ^1H NMR (400 MHz): δ =2.15 (br, 3 H); 3.40 (s, 3 H); 3.54 (m, 2 H); 3.77 (s, 6 H); 3.97 (m, 1 H); 4.23 (d, J = 5.2 Hz, 1 H); 6.67 (d, J = 8.4 Hz, 4 H); 7.25-7.35 (m, 5 H). ^{13}C NMR (100 MHz): δ =55.9 (CH₃); 58.1 (CH); 59.1 (CH₃); 73.8 (CH₂); 74.1 (CH); 104.4 (CH); 119.6 (C); 128.4 (CH); 128.5 (CH); 130.0 (CH); 130.1 (C); 139.6 (C); 157.7 (C). $[\alpha]_{\text{D}}^{20}$: -18 (c 2.06, CHCl₃). HRMS (ES⁺): calcd for C₂₆H₃₂NO₆ (M+H): 454.2230; found 454.2248.