Supporting Information

for

Switching the reaction pathways of electrochemically generated β-haloalkoxysulfonium ions – synthesis of halohydrins and epoxides

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Experimental and analytical data

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1. General

$^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ using a Varian MERCURY plus-400 ($^1$H 400 MHz, $^{13}$C 100 MHz) spectrometer, or a JEOL ECA-600P spectrometer ($^1$H 600 MHz, $^{13}$C 150 MHz) with tetramethylsilane as an internal standard unless otherwise noted. Mass spectra were obtained on JEOL EXACTIVE (ESI and APCI) mass spectrometer, and JEOL JMS-SX102A mass spectrometer (EI). GC analysis was performed on a SHIMADZU GC-2014 gas chromatograph equipped with a flame ionization detector using a fused silica capillary column (column, CBP1; 0.22 mm x 25 m). Merck precoated silica gel F254 plates (thickness 0.25 mm) were used for thin layer chromatography (TLC) analysis. Flash chromatography was carried out on a silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40–100 μm) unless otherwise noted. All reactions were carried out under argon atmosphere unless otherwise noted. The anodic oxidation was carried out using an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon GF-20-P21E, ca. 160 mg for 0.25 mmol scale, dried at 300 °C/1 mmHg for 3 h before use) and a platinum plate cathode (10 mm x 10 mm). Bu$_4$NBF$_4$ was purchased from TCI and dried at 25 °C/1 mmHg for 12 h. Dichloromethane was washed with water, distilled from P$_2$O$_5$, redistilled from dry K$_2$CO$_3$ to remove trace amounts of acid, and stored over molecular sieves 4 Å. Dimethyl sulfoxide (DMSO) and triethylamine were dried over molecular sieves 4 Å before use. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification.

2. Reaction of 3a-X (X = Br, I) with bases

Generation of 1-Br and 1-I was conducted in a similar manner to a procedure from reference$^1$.

Typical procedure for generation of 1-Br and 3a-Br and reaction of 3a-Br with bases

In the anodic chamber were placed Bu$_4$NBr (80.7 mg, 0.251 mmol), Bu$_4$NBF$_4$ (100 mg, 0.3 mmol), DMSO (1 mL), and 0.3 M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ (9 mL). In the cathodic chamber were placed TfOH (60 μL, 0.68 mmol) and 0.3 M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ (10 mL). The constant current electrolysis (8.0 mA) was carried out at −78 °C with magnetic stirring until 2.1 F mol$^{-1}$ of electricity was consumed. To the anodic chamber was added a solution of (Z)-5-decene (2a) (27.7 mg, 0.197 mmol) in CH$_2$Cl$_2$ (0.5 mL), and to the cathodic chamber 0.5 mL of CH$_2$Cl$_2$ was added at −78 °C. The solution was stirred for 30 min at −78 °C then stirring was continued for 30 min at 0 °C. Et$_3$N (100 μL) was added to both the anodic and the cathodic chambers, and the resulting mixture was warmed to 25 °C and stirred for 1 h. The solution in the anodic
chamber was collected and the solvent was removed under reduced pressure. The residue was filtered through a short column (2 x 4 cm) of silica gel to remove Bu₄NBF₄ by using hexane/EtOAc (1:1) as an eluent. The GC analysis using hexadecane as an internal standard indicated that 6-bromodecan-5-one (4a-Br) was obtained in 83% yield (38.6 mg, 0.164 mmol). The ¹H NMR data was reported previously. Addition of NaOH (2.5 M in H₂O, 0.16 mL) instead of Et₃N gave (5R*,6R*)-6-bromodecan-5-ol (5a-Br) in 89% yield (0.174 mmol). TLC Rf 0.19 (hexane/EtOAc 20:1); ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, J = 7.2 Hz, 6 H), 1.25–1.61 (m, 10 H), 1.84 (d, J = 8.0 Hz, 1 H), 1.86–2.00 (m, 2 H), 3.20–3.57 (m, 1 H), 4.07 (ddd, J = 3.2, 5.2, 8.4 Hz, 1 H); The ¹H NMR spectrum is in agreement with that of an authentic sample synthesized using NBS according to the literature (vide infra). Addition of NaOMe (5.0 M in MeOH, 0.2 mL) instead of Et₃N gave (5R*,6S*)-5,6-epoxydecane (6a) in 95% yield (0.187 mmol). TLC Rf 0.83 (hexane/EtOAc 5:1); ¹H NMR (400 MHz, CDCl₃) δ 0.93 (t, J = 7.2 Hz, 6 H), 1.37–1.55 (m, 12 H), 2.88–2.94 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 22.6, 27.5, 28.3, 57.2; HRMS (APCI) calcd for C₁₀H₂₁O (M+H⁺): 157.1587, found: 157.1587. Stereochemistry was determined by comparison of the ¹H NMR spectrum with that in the literature³.

**Typical procedure for the generation of 1-I and 3a-I and reaction of 3a-I with bases**

![Diagram](image)

In the anodic chamber were placed Bu₄NI (91.6 mg, 0.248 mmol), Bu₄NBF₄ (102 mg, 0.3 mmol), DMSO (1 mL), and 0.3 M Bu₄NBF₄/CH₂Cl₂ (9 mL). In the cathodic chamber were placed TfOH (60 μL, 0.68 mmol) and 0.3 M Bu₄NBF₄/CH₂Cl₂ (10 mL). The constant current electrolysis (8.0 mA) was carried out at −78 °C with magnetic stirring until 2.1 F mol⁻¹ of electricity was consumed. To the anodic chamber was added a solution of (Z)-5-decene (2a) (28.7 mg, 0.205 mmol) in CH₂Cl₂ (0.5 mL), and to the cathodic chamber was added 0.5 mL of CH₂Cl₂ at −78 °C. The solution was stirred for 30 min at −78 °C then stirring was continued for 30 min at 0 °C. Et₃N (100 μL) was added to both the anodic and the cathodic chambers, and the resulting mixture was warmed to 25 °C and stirred for 1 h. The solution in the anodic chamber was collected and the solvent was removed under reduced pressure. The residue was filtered through a short column (2 x 4 cm) of silica gel to remove Bu₄NBF₄ by using hexane/EtOAc (1:1 v/v) as an eluent. The GC analysis using hexadecane as an internal standard indicated that 6-iododecan-5-one (4a-I) was obtained in 85% yield (49.2 mg, 0.174 mmol). The ¹H NMR data was reported previously. Addition of NaOH (2.5 M in H₂O, 0.16 mL) instead of Et₃N gave (5R*,6R*)-6-iododecan-5-ol (5a-I) in 84% yield (0.169 mmol). TLC Rf 0.19 (hexane/EtOAc 20:1); ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, J = 7.2 Hz, 6 H), 1.25–1.61 (m, 10 H), 1.84 (d,
J = 8.0 Hz, 1 H), 1.86−2.00 (m, 2 H), 3.20−3.57 (m, 1 H), 4.07 (ddd, J = 3.2, 5.2, 8.4 Hz, 1 H); The $^1$H NMR spectrum is in agreement with that of an authentic sample synthesized using I$_2$ and H$_2$O$_2$ according to the literature$^4$ (vide infra). Addition of NaOMe (5.0 M in MeOH, 0.2 mL) instead of Et$_3$N gave (5R*,6S*)-5,6-epoxydecane (6a) in 96% yield (0.191 mmol). TLC $R_f$ 0.83 (hexane/EtOAc 5:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 0.92 (t, $J$ = 7.2 Hz, 6 H), 1.25−1.61 (m, 10 H), 1.84 (d, $J$ = 8.0 Hz, 1 H), 1.86−2.00 (m, 2 H), 3.20−3.57 (m, 1 H), 4.07 (ddd, $J$ = 3.2, 5.2, 8.4 Hz, 1 H); The $^1$H NMR spectrum is in agreement with that of an authentic sample synthesized using I$_2$ and H$_2$O$_2$ according to the literature$^3$.

3. Synthesis of halohydrins

Generation of 1-Br and 1-I was conducted in a similar manner to a procedure from ref. 1.

Typical procedure for generation of 1-Br and synthesis of bromohydrins

In the anodic chamber were placed Bu$_4$NBr (81.0 mg, 0.252 mmol), Bu$_4$NBF$_4$ (101 mg, 0.3 mmol), DMSO (1 mL), and 0.3 M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ (9 mL). In the cathodic chamber were placed TfOH (60 μL, 0.68 mmol) and 0.3 M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ (10 mL). The constant current electrolysis (8.0 mA) was carried out at −78 °C with magnetic stirring until 2.1 F mol$^{-1}$ of electricity was consumed. To the anodic chamber was added a solution of (Z)-5-decene (2a) (27.0 mg, 0.193 mmol) in CH$_2$Cl$_2$ (0.5 mL), and to the cathodic chamber 0.5 mL of CH$_2$Cl$_2$ was added at −78 °C. The solution was stirred for 30 min at −78 °C then stirring was continued for 30 min at 0 °C. NaOH (2.5 M in H$_2$O, 0.16 mL) was added to both the anodic and the cathodic chambers, and the resulting mixture was warmed to 25 °C and was stirred for 1 h. The solution in the anodic chamber was collected and the solvent was removed under reduced pressure. The residue was filtered through a short column (2 x 4 cm) of silica gel to remove Bu$_4$NBF$_4$ by using hexane/EtOAc (1:1) as an eluent. After removal of the solvent under reduced pressure, the crude product was purified by flash chromatography (hexane/EtOAc 20:1) to obtain (5R*,6R*)-6-bromodecan-5-ol (5a-Br) in 87% yield (40.0 mg, 0.169 mmol). TLC $R_f$ 0.19 (hexane/EtOAc 20:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 0.92 (t, $J$ = 7.2 Hz, 6 H), 1.25−1.61 (m, 10 H), 1.84 (d, $J$ = 8.0 Hz, 1 H), 1.86−2.00 (m, 2 H), 3.20−3.57 (m, 1 H), 4.07 (ddd, $J$ = 3.2, 5.2, 8.4 Hz, 1 H); The $^1$H NMR spectrum is in agreement with that of an authentic sample synthesized using NBS according to the literature$^2$ (vide infra).
**2-Bromocyclododecan-1-ol (5b-Br).** Electrochemical oxidation (2.1 F mol\(^{-1}\)) of Bu\(_2\)NBr (82 mg, 0.25 mmol), subsequent addition of the solution of cyclododecene (2b) (Z/E = 72:28, 31.6 mg, 0.190 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 20:1) gave the title compound (32.2 mg, 0.150 mmol, 74\%, trans/cis = 79:21). TLC R\(_f\) 0.42 and 0.48 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.24–1.82 (m, 18 H), 1.85–1.96 (m, 1 H), 2.01–2.16 (m, 2 H), 2.23 (d, \(J = 5.2\) Hz, 1 H), 3.80 (td, \(J = 5.2, 12.0\) Hz, trans 1 H), 3.90 (br, cis 1 H), 4.32–4.41 (m, 1 H); The \(^1\)H NMR spectrum is in agreement with that in the literature\(^5\).

**1-Bromododecan-2-ol (5c-Br).** Electrochemical oxidation (2.1 F mol\(^{-1}\)) of Bu\(_2\)NBr (81 mg, 0.25 mmol), subsequent addition of the solution of 1-dodecene (2c) (32.5 mg, 0.193 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 100:0 to 50:1) gave the title compound (29.3 mg, 0.110 mmol, 57\%). TLC R\(_f\) 0.48 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.91 (t, \(J = 6.8\) Hz, 3 H), 1.23–1.61 (m, 20 H), 2.10–2.14 (m, 1 H), 3.39 (dd, \(J = 7.2, 10.4\) Hz, 1 H), 3.55 (dd, \(J = 2.8, 10.4\) Hz, 1 H), 3.74–3.82 (m, 1 H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.1, 22.7, 25.6, 29.3, 29.47, 29.48, 29.54, 29.6, 31.9, 35.1, 40.7, 71.1; HRMS (EI) calecd for C\(_{12}\)H\(_{22}\)OBr (M+: 263.1016, found: 263.1016, 263.1013. The \(^1\)H NMR spectrum is in agreement with that in the literature\(^6\).

**1R*,2S*)-2-Bromo-1-phenyl-1-propanol (5d-Br).** Electrochemical oxidation (2.1 F mol\(^{-1}\)) of Bu\(_2\)NBr (81.2 mg, 0.252 mmol), subsequent addition of the solution of (E)-\(\beta\)-methylstylylene ((E)-2d) (22.8 mg, 0.193 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 100:0 to 20:1) gave the title compound (30.2 mg, 0.140 mmol, 73\%). TLC R\(_f\) 0.33 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.54 (d, \(J = 6.8\) Hz, 3 H), 2.51 (m, 1 H), 4.43 (dq, \(J = 3.6, 6.8\) Hz, 1 H), 5.01 (t, \(J = 3.6\) Hz, 1 H), 7.27–7.40 (m, 5 H). The \(^1\)H NMR spectrum is in agreement with that in the literature\(^1\).

**1R*,2R*)-2-Bromo-1-phenyl-1-propanol (5d*-Br).** Electrochemical oxidation (2.1 F mol\(^{-1}\)) of Bu\(_2\)NBr (81.9 mg, 0.254 mmol), subsequent addition of the solution of (Z)-\(\beta\)-methylstylylene ((Z)-2d) (23.5 mg, 0.199 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 100:0 to 20:1) gave the title compound (32.2 mg, 0.150 mmol, 75\%). TLC R\(_f\) 0.38 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.57 (d, \(J = 6.8\) Hz, 3 H), 2.77 (m, 1 H), 4.34 (dq, \(J = 6.8, 7.6\) Hz, 1 H), 4.62 (dd, \(J = 3.6, 7.6\) Hz, 1 H), 7.30–7.40 (m, 5 H). The \(^1\)H NMR spectrum is in agreement with that in the literature\(^1\).
Synthesis of \((5R^*,6R^*)\)-6-bromodecan-5-ol (5a-Br)

To a round-bottom flask were added NBS (640 mg, 3.59 mmol), (Z)-5-decene (417 mg, 2.97 mmol), DMSO (10 mL), and H₂O (0.1 mL) and the mixture was stirred for 4 h. After the addition of NBS (600 mg, 3.37 mmol), the mixture was stirred at room temperature for 1 d. The solution was diluted with EtOAc (30 mL), washed with sat aq NaHCO₃ (10 mL x 2), H₂O (10 mL x 2), and brine (10 mL) and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the crude product was purified by flash chromatography (hexane/EtOAc 100:0 to 20:1) to obtain \((5R^*,6R^*)\)-6-bromodecan-5-ol (5a-Br) in 60% yield (420 mg, 1.77 mmol). TLC Rₐ 0.19 (hexane/EtOAc 20:1); \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 0.92 (t, \(J\) = 7.2 Hz, 6 H), 1.25−1.61 (m, 10 H), 1.84 (d, \(J\) = 8.0 Hz, 1 H), 1.86−2.00 (m, 2 H), 3.20−3.57 (m, 1 H), 4.07 (ddd, \(J\) = 3.2, 5.2, 8.4 Hz, 1 H); \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 13.9, 14.0, 22.1, 22.6, 27.8, 30.0, 35.48, 35.52, 65.5, 73.8; HRMS (EI) calcd for C₁₀H₂₀OBr (M−H⁺): 235.0703, found: 235.0702.

Typical procedure for the generation of 1-I and the synthesis of iodohydrins

In the anodic chamber were placed Bu₄NI (93 mg, 0.25 mmol), Bu₄NBF₄ (980 mg, 3.0 mmol), DMSO (1 mL), and CH₂Cl₂ (9 mL). In the cathodic chamber were placed TfOH (60 μL, 0.68 mmol) and 0.3 M Bu₄NBF₄/CH₂Cl₂ (10 mL). The constant current electrolysis (8.0 mA) was carried out at −78 °C with magnetic stirring until 2.1 F mol⁻¹ of electricity was consumed. To the anodic chamber was added a solution of (Z)-5-decene (2a) (27.0 mg, 0.193 mmol) in CH₂Cl₂ (0.5 mL), and to the cathodic chamber was added 0.5 mL of CH₂Cl₂ at −78 °C. The solution was stirred for 30 min at −78 °C then stirring was continued for 30 min at 0 °C. NaOH (2.5 M in H₂O, 0.16 mL) was added to both the anodic and the cathodic chambers, and the resulting mixture was warmed to 25 °C and stirred for 1 h. The solution in the anodic chamber was collected and the solvent was removed under reduced pressure. The residue was filtered through a short column (2 x 4 cm) of silica gel to remove Bu₄NBF₄ by using hexane/EtOAc (1:1 v/v) as an eluent. The GC analysis using hexadecane as an internal standard indicated that \((5R^*,6R^*)\)-6-iododecan-5-ol (5a-I) was obtained in 84% yield (0.169 mmol). TLC Rₜ 0.56 (hexane/ EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 0.92 (t, \(J\) = 7.2 Hz, 6 H), 1.25−1.46 (m, 6 H), 1.47−1.60 (m, 4 H), 1.62 (d, \(J\) = 8.4 Hz, 1 H), 1.78−1.88 (m, 1 H), 1.98−2.09 (m, 1 H), 2.85−2.90 (m, 1 H), 4.19 (ddd, \(J\) = 2.8, 4.8, 9.2 Hz, 1 H); The \(^1\)H NMR spectrum is in agreement with that of an authentic sample synthesized using I₂ and H₂O₂ according to the literature⁴ (vide infra).
2-Iodocyclododecan-1-ol (5b-I). Electrochemical oxidation (2.1 F mol\(^{-1}\)) of Bu\(_4\)NI (90.8 mg, 0.246 mmol), subsequent addition of the solution of cyclododecene (2b) (z/e = 72:28, 31.4 mg, 0.189 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 20:1) gave the title compound (55.0 mg, 0.177 mmol, 94%, trans:cis = 71:29). TLC R\(_f\) 0.42 and 0.50 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.20–1.80 (m, 18 H), 1.91–2.08 (m, 3 H), 3.39 (m, trans 1 H), 4.51 (dt, \(J = 6.0, 6.0\) Hz, 1 H); The \(^1\)H NMR spectrum is in agreement with that of an authentic sample synthesized using I\(_2\) and H\(_2\)O\(_2\) according to the literature\(^4\) (vide infra).

1-Iodododecan-2-ol (5c-I). Electrochemical oxidation (2.1 F mol\(^{-1}\)) of Bu\(_4\)NI (93 mg, 0.25 mmol), subsequent addition of the solution of 1-dodecene (2c) (33.9 mg, 0.201 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 10:1) gave the title compound (27.0 mg, 0.098 mmol, 51%). TLC R\(_f\) 0.42 and 0.50 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.88 (t, \(J = 6.8\) Hz, 3 H), 1.10–1.50 (m, 16 H), 1.52–1.58 (m, 2 H), 1.98 (d, \(J = 5.2\) Hz, 1 H), 3.23 (dd, \(J = 6.8, 10.0\) Hz, 1 H), 3.40 (dd, \(J = 3.6, 10.4\) Hz, 1 H), 3.45–3.60 (m, 1 H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.1, 16.9, 22.7, 25.6, 29.3, 29.43, 29.47, 29.53, 29.6, 31.9, 36.6, 71.0; HRMS (EI) calcd for C\(_{13}\)H\(_{26}\)OBr (M\(^+\)) 312.0951, found: 312.0958. The \(^1\)H NMR spectrum is in agreement with that in the literature\(^7\).

(1R\(^*\),2S\(^*\))-2-Iodo-1-phenyl-1-propanol (5d-I). Electrochemical oxidation (2.1 F mol\(^{-1}\)) of Bu\(_4\)NI (87.4 mg, 0.236 mmol), subsequent addition of the solution of (E)-\(\beta\)-methylstyrene ((E)-2d\(^+\)) (21.8 mg, 0.185 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 50:1) gave the title compound (22.18 mg, 0.061 mmol, 35%). TLC R\(_f\) 0.35 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.74 (d, \(J = 6.8\) Hz, 3 H), 2.37 (s, 1 H), 4.52 (dq, \(J = 3.6, 7.2\) Hz, 1 H), 4.96 (t, \(J = 3.6\) Hz, 1 H), 7.29–7.40 (m, 5 H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 21.2, 35.9, 78.5, 126.4, 128.0, 128.4, 139.7; HRMS (EI) calcd for C\(_9\)H\(_{14}\)O (M\(^+\)) 261.9855, found: 261.9860. Stereochemistry was determined by comparison of the \(^1\)H NMR spectrum with that in the literature\(^8\).

(1R\(^*\),2R\(^*\))-2-Iodo-1-phenyl-1-propanol (5d\(^+\)-I). Electrochemical oxidation (2.1 F mol\(^{-1}\)) of Bu\(_4\)NI (93.1 mg, 0.252 mmol), subsequent addition of the solution of (Z)-\(\beta\)-methylstyrene ((Z)-2d) (22.4 mg, 0.190 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 10:1) gave the title compound (27.0 mg, 0.098 mmol, 51%). TLC R\(_f\) 0.13 (hexane/EtOAc 10:1);
\[ ^1 \text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 1.81 \text{ (d, } J = 6.8 \text{ Hz, 3 H)}, 2.51 \text{ (d, } J = 4.0 \text{ Hz, 1 H)}, 4.39–4.47 \text{ (m, 2 H)}, 7.31–7.41 \text{ (m, 5 H)}; ^{13} \text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 25.4, 39.1, 79.6, 126.3, 128.4, 128.6, 139.9; \text{ HRMS (EI) calsd for C}_{10}H_{21}O\text{I} (M^+): 261.9855, \text{ found: 261.9856}. \text{ Stereochemistry was determined by comparison of the } ^1 \text{H NMR spectrum with that in the literature}^8. 

**Synthesis of (5R*,6R*)-6-iododecan-5-ol (5a-I)**

\[
\begin{array}{c}
\text{nBu} \quad \text{nBu} \\
\text{I} \quad \text{H}_2\text{O} \\
\text{acetone} \\
\text{nBu} \quad \text{nBu}
\end{array}
\]

To a round-bottom flask were added iodine (1.07 g, 4.22 mmol), (Z)-5-decene (271 mg, 1.94 mmol), H\(_2\)O (10 mL) and stirred for 30 min. Then acetone (10 mL), H\(_2\)O\(_2\) (31\% in H\(_2\)O, 400 \mu\text{L}, 3.64 mmol) were added and the mixture was stirred at room temperature for 3 d. Afterwards, the solution was extracted with CH\(_2\)Cl\(_2\) (20 mL \times 3), dried over Na\(_2\)SO\(_4\) and the solvent removed under reduced pressure. The crude product was purified by flash chromatography (hexane/EtOAc 100:0 to 20:1) to obtain (5R*,6R*)-6-iododecan-5-ol (5a-I) in 91\% yield (500 mg, 1.76 mmol). TLC R\(_f\) 0.56 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.92 (t, \(J = 7.2 \text{ Hz, 6 H}\)), 1.25–1.46 (m, 6 H), 1.47–1.60 (m, 4 H), 1.62 (d, \(J = 8.4 \text{ Hz, 1 H}\)), 1.78–1.88 (m, 1 H), 1.98–2.09 (m, 1 H), 2.85–2.90 (m, 1 H), 4.19 (ddd, \(J = 2.8, 4.8, 9.2 \text{ Hz, 1 H}\)) \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 13.9, 14.0, 22.0, 22.6, 27.7, 32.0, 37.4, 37.7, 50.5, 74.1; HRMS (ESI) calsd for C\(_{10}\)H\(_{21}\)O\text{I} (M+Cl\(^-\)): 319.0331, found: 319.0331.

**Synthesis of 2-iodocyclododecan-1-ol (5b-I)**

\[
\begin{array}{c}
\text{Z/E} = 72:28 \\
\text{I}_2 \quad \text{H}_2\text{O} \\
\text{acetone} \\
\text{47%} \quad \text{14%} \quad \text{23%} \quad \text{10%}
\end{array}
\]

To a round-bottom flask were added iodine (550 mg, 2.16 mmol), cyclododecene (Z/E = 72:28, 174 mg, 1.05 mmol), and H\(_2\)O (5 mL). The mixture was stirred for 30 min at room temperature. After the addition of acetone (5 mL) and H\(_2\)O\(_2\) (31\% in H\(_2\)O, 200 \mu\text{L}, 1.82 mmol), the mixture was stirred at room temperature for 3 d. The solution was extracted with CH\(_2\)Cl\(_2\) (20 mL \times 3), dried over Na\(_2\)SO\(_4\) and the solvent removed under reduced pressure. NMR analysis of the crude product indicated that (Z)- and (E)-cyclododecenes were recovered in 47\%, 14\% yield, respectively and that (1S*,2S*)-2-iodocyclododecan-1-ol and (1S*,2R*)-2-iodocyclododecan-1-ol were obtained in 23\%, and 10\% yield, respectively. (1S*,2S*)-2-Iodocyclododecan-1-ol and (1S*,2R*)-2-iodocyclododecan-1-ol were isolated by column chromatography. (1R*,2R*)-2-Iodocyclododecan-1-ol (trans-5b-I): TLC R\(_f\) 0.57 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.15–1.31 (m, 20 H), 1.37–1.46 (m, 20 H), 1.62 (d, \(J = 6.8 \text{ Hz, 1 H}\)), 1.78–1.88 (m, 18 H), 1.98–2.09 (m, 18 H), 2.09–2.85 (m, 18 H), 3.60 (dd, \(J = 8.8, 13.2 \text{ Hz, 1 H}\)), 3.78 (d, \(J = 8.8 \text{ Hz, 1 H}\)), 7.31–7.41 (m, 5 H); HRMS (ESI) calsd for C\(_{10}\)H\(_{21}\)O\text{I} (M+Cl\(^-\)): 319.0331, found: 319.0331.
(CDCl$_3$) δ 1.20–1.80 (m, 18 H), 1.88 (d, $J = 6.4$ Hz, 1 H), 1.91–2.01 (m, 1 H), 2.08–2.18 (m, 1 H), 3.39 (m, 1 H), 4.52 (dt, $J = 6.0, 6.0$ Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 20.9, 23.0, 23.3, 23.4, 23.8, 23.9, 24.0, 24.4, 32.1, 34.9, 47.3, 70.8; HRMS (ESI) calcd for C$_{12}$H$_{23}$IONa$^+$ (M+Na$^+$): 333.0686, found: 333.0685.

(1R*,2S*)-2-iodocyclododecan-1-ol (cis-5b-I): TLC R$_f$ 0.45 (hexane/EtOAc 5:1); $^1$H NMR (600 MHz, CDCl$_3$, 50 °C) δ 1.25–1.56 (m, 17 H), 1.71–1.80 (m, 1 H), 1.88 (s, br, 1 H), 2.02 (dt, $J = 7.2, 7.2$ Hz, 2 H), 3.59 (s, br, 1 H), 4.50 (t, $J = 7.2$ Hz, 1 H); $^{13}$C NMR (150 MHz, pyridine-d$_5$, 100 °C) δ 22.8, 22.9, 24.91, 24.98, 25.01, 25.4, 25.9, 32.5, 33.8, 45.5, 73.5; HRMS (ESI) calcd for C$_{12}$H$_{23}$IOCl$^-$ (M+Cl$^-$): 345.0488, found: 345.0490.

4. Synthesis of epoxides

Generation of 1-Br and 1-I was conducted in a similar manner to a procedure from ref. 1.

Preparation of 4-pentenyl benzoate

\[
\begin{align*}
\text{OH} & \quad \text{O} \\
\text{H} & \quad \text{O} \\
\text{CH}_2\text{Cl}_2 & \quad \text{EDCI} \\
& \quad \text{DMAP}
\end{align*}
\]

To a round-bottom flask were added 4-pentenol (430 mg, 5.0 mmol), benzoic acid (630 mg, 5.2 mmol), EDCI (1.15 g, 6.0 mmol), DMAP (120 mg, 0.98 mmol), and CH$_2$Cl$_2$ (15 mL). The mixture was stirred at room temperature for 2 d. After the addition of water, the solution was extracted with CH$_2$Cl$_2$ (20 mL x 3). The solvent was removed under reduced pressure, and the residue was purified through a short column (2 x 4 cm) of silica gel by using hexane/EtOAc (1:1) as an eluent. After removal of the solvent under reduced pressure, the crude product was further purified by flash chromatography (hexane/EtOAc 20:1) to obtain 4-pentenyl benzoate (2e) in 96% yield (910 mg, 4.78 mmol). TLC R$_f$ 0.59 (hexane/EtOAc 1:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 1.88 (tt, $J = 6.4, 7.6$ Hz, 2 H), 2.23 (td, $J = 6.8, 8.0$ Hz, 2 H), 4.34 (t, $J = 6.4$ Hz, 2 H), 5.02 (dd, $J = 2.0, 10.0$ Hz, 1 H), 5.08 (dd, $J = 2.0, 16.8$ Hz, 1 H), 5.86 (tdd, $J = 6.4, 10.4, 17.2$ Hz, 1 H), 7.44 (t, $J = 7.2$ Hz, 2 H), 7.56 (t, $J = 7.6$ Hz, 1 H), 8.05 (d, $J = 7.6$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 27.9, 30.2, 64.3, 115.4, 128.3, 129.5, 130.4, 132.8, 137.5, 166.6; HRMS (EI) calcd for C$_{12}$H$_{14}$OICl$^-$ (M+Na$^+$): 213.088, found: 213.0883. The $^1$H NMR spectrum is in agreement with that in the literature.

Typical procedure for the generation of 1-Br and the synthesis of epoxides

\[
\begin{align*}
\text{Bu}_4\text{NBr} & \quad \text{DMSO/CH}_2\text{Cl}_2 \quad \text{Bu}_4\text{NBF}_4, -78 \text{ °C} \\
\text{Br} & \quad \text{2a} \\
\text{NaOMe} \quad \text{NaOMe} \quad \text{nBu} \quad \text{nBu} \quad \text{nBu} \quad \text{nBu}
\end{align*}
\]

In the anodic chamber were placed Bu$_4$NBr (80.6 mg, 0.250 mmol), Bu$_4$NBF$_4$ (97 mg, 0.29 mmol), DMSO (1 mL), and 0.3 M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ (9 mL). In the cathodic chamber were placed TfOH (60 μL,
0.68 mmol) and 0.3 M Bu₄NBF₄/CH₂Cl₂ (10 mL). The constant current electrolysis (8.0 mA) was carried out at −78 °C with magnetic stirring until 2.1 F mol⁻¹ of electricity was consumed. To the anodic chamber was added a solution of (Z)-5-decene (2a) (27.7 mg, 0.197 mmol) in CH₂Cl₂ (0.5 mL), and to the cathodic chamber 0.5 mL of CH₂Cl₂ was added at −78 °C. The solution was stirred for 30 min at −78 °C then stirring was continued for 30 min at 0 °C. NaOMe (5.0 M in MeOH, 0.2 mL) was added to both the anodic and the cathodic chambers, and the resulting mixture was warmed to 25 °C and stirred for 5 min. The solution in the anodic chamber was filtered through a short column (2 x 4 cm) of silica gel to remove Bu₄NBF₄ by using Et₂O as an eluent. The GC analysis using hexadecane as an internal standard indicated that (5R*,6S*)-5,6-epoxydecane (6a) was obtained in 95% yield (0.187 mmol). TLC Rf 0.83 (hexane/EtOAc 5:1); ¹H NMR (400 MHz, CDCl₃) δ 0.93 (t, J = 7.2 Hz, 6 H), 1.37–1.55 (m, 12 H), 2.88–2.94 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 22.6, 27.5, 28.3, 57.2; HRMS (APCI) calcd for C₁₀H₂₀O (M+H⁺): 157.1587, found: 157.1587. Stereochemistry was determined by comparison of the ¹H NMR spectrum with that in the literature³.

1,2-Epoxycyclododecane (6b). Electrochemical oxidation (2.1 F mol⁻¹) of Bu₄NBr (81.7 mg, 0.254 mmol), subsequent addition of the solution of cyclododecane (2b) (Z/E = 72:28, 32.7 mg, 0.196 mmol) in CH₂Cl₂ (0.5 mL), and treatment with NaOMe followed by flash chromatography (hexane) gave the title compound (22.3 mg, 0.134 mmol, 68%, cis:trans = 74:26). TLC Rf 0.54 (hexane/EtOAc 5:1); ¹H NMR (400 MHz, CDCl₃) δ 1.20–1.61 (m, 20 H), 1.70–1.87 (m, cis 2 H), 2.15–2.23 (m, trans 2 H), 2.71 (m, trans 2 H), 2.90 (td, J = 1.6, 10.0 Hz, cis 2 H). The ¹H NMR spectrum is in agreement with the literature¹⁰.

1,2-Epoxydodecane (6c). Electrochemical oxidation (2.1 F mol⁻¹) of Bu₄NBr (80.5 mg, 0.250 mmol), subsequent addition of the solution of 1-dodecene (2c) (31.8 mg, 0.189 mmol) in CH₂Cl₂ (0.5 mL), and treatment with NaOMe gave the title compound (0.138 mmol, 73%). The yield was determined by GC analysis using hexadecane as internal standard. TLC Rf 0.63 (hexane/EtOAc 5:1); ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, J = 6.8 Hz, 3 H), 1.20–1.38 (m, 14 H), 1.40–1.56 (m, 4 H), 2.46 (dd, J = 2.8, 4.8 Hz, 1 H), 2.75 (dd, J = 3.6, 4.0 Hz, 1 H), 2.88–2.94 (m, 1 H). The ¹H NMR spectrum is in agreement with the literature¹¹.

(1R*,2R*)-1-Phenyl-1,2-epoxypropane (6d). Electrochemical oxidation (2.1 F mol⁻¹) of Bu₄NBr (82.4 mg, 0.256 mmol), subsequent addition of the solution of (E)-β-methylstyrene ((E)-2d) (22.9 mg, 0.194 mmol) in CH₂Cl₂ (0.5 mL), and treatment with NaOMe followed by flash chromatography¹² (hexane) gave
the title compound (13.7 mg, 0.102 mmol, 53%). TLC Rf 0.58 (hexane/EtOAc 5:1); 1H NMR (400 MHz, CDCl3) δ 1.46 (d, J = 5.2 Hz, 3 H), 3.04 (dq, J = 2.0, 5.2 Hz, 1 H), 3.58 (d, J = 1.6 Hz, 2 H), 7.24–7.39 (m, 5 H). The 1H NMR spectrum is in agreement with the literature13.

(1R*,2S*)-1-Phenyl-1,2-epoxypropane (6d*). Electrochemical oxidation (2.1 F mol−1) of Bu4NBr (81.7 mg, 0.254 mmol), subsequent addition of the solution of (Z)-β-methylstyylene ((Z)-2d) (22.9 mg, 0.194 mmol) in CH2Cl2 (0.5 mL), and treatment with NaOMe followed by flash chromatography12 (hexane) gave the title compound (15.7 mg, 0.117 mmol, 60%). TLC Rf 0.56 (hexane/EtOAc 5:1); 1H NMR (400 MHz, CDCl3) δ 1.09 (d, J = 5.6 Hz, 3 H), 3.34 (dq, J = 4.4, 5.2 Hz, 1 H), 4.07 (d, J = 4.4 Hz, 1 H) 7.26–7.40 (m, 5 H). The 1H NMR spectrum is in agreement with the literature13.

4,5-Epoxypentenyl benzoate (6e). Electrochemical oxidation (2.1 F mol−1) of Bu4NBr (81.6 mg, 0.253 mmol), subsequent addition of the solution of 4-pentenyl benzoate (2f) (37.2 mg, 0.196 mmol) in CH2Cl2 (0.5 mL), and treatment with NaOMe followed by flash chromatography12 (hexane/EtOAc 100:0 to 20:1) gave the title compound (21.0 mg, 0.102 mmol, 52%). TLC Rf 0.29 (hexane/EtOAc 5:1); 1H NMR (400 MHz, CDCl3) δ 1.62–1.82 (m, 2 H), 1.88–2.04 (m, 2 H), 2.52 (dd, J = 2.8, 5.2 Hz, 1 H), 2.78 (dd, J = 4.0, 5.2 Hz, 1 H), 2.98–3.02 (m, 1 H), 4.38 (dt, J = 2.8, 6.4 Hz, 2 H), 7.44 (t, J = 8.0 Hz, 2 H), 7.56 (t, J = 7.6 Hz, 1 H), 8.04 (d, J = 8.4 Hz, 2 H); 13C NMR (100 MHz, CDCl3) δ 25.3, 29.1, 47.0, 51.7, 64.4, 128.3, 129.5, 130.2, 132.9, 166.5; HRMS (ESI) calcd for C17H16O2 (M+H+): 207.1016, found: 207.1012. The 1H NMR spectrum is in agreement with the literature14.

6,7-Epoxyneryl acetate (6f). Electrochemical oxidation (2.1 F mol−1) of Bu4NBr (80.7 mg, 0.251 mmol), subsequent addition of the solution of neryl acetate (2f) (357.3 mg, 0.190 mmol) in CH2Cl2 (0.5 mL), and treatment with NaOMe followed by flash chromatography12 (hexane/EtOAc 100:0 to 50:1) gave the title compound (19.7 mg, 0.093 mmol, 49%). TLC Rf 0.30 (hexane/EtOAc 5:1); 1H NMR (400 MHz, CDCl3) δ 1.27 (s, 3 H), 1.31 (s, 3 H), 1.56–1.71 (m, 2 H), 1.79 (s, 3 H), 2.05 (s, 3 H) 2.23–2.29 (m, 2 H), 2.71 (t, J = 6.0 Hz, 1 H), 4.59 (d, J = 7.6 Hz, 2 H), 5.41 (t, J = 7.2 Hz, 1 H); 13C NMR (100 MHz, CDCl3) δ 18.7, 21.0, 23.4, 24.8, 27.5, 28.8, 58.4, 60.8, 63.7, 119.7, 141.7, 171.0; HRMS (ESI) calcd for C12H20O3Na (M+Na+): 235.1305, found: 235,1299. The 1H NMR spectrum is in agreement with the literature15.
(1S,3R,4S,6R)-3,4-Epoxycarane (6g). Electrochemical oxidation (2.1 F mol⁻¹) of Bu₄NBr (80.4 mg, 0.250 mmol), subsequent addition of the solution of (+)-3-carene (2g) (26.1 mg, 0.192 mmol) in CH₂Cl₂ (0.5 mL), and treatment with NaOMe followed by flash chromatography<sup>12</sup> (hexane) gave the title compound. (20.1 mg, 0.132 mmol, 69%). TLC R<sub>f</sub> 0.50 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl₃) δ 0.52 (dt, J = 2.0, 9.2 Hz, 1 H), 0.57 (dt, J = 2.0, 9.2 Hz, 1 H), 0.92 (s, 3 H), 0.96 (s, 3 H), 1.30 (s, 3 H), 1.78 (d, J = 15.6 Hz, 2 H), 2.06 (dd, J = 9.2, 16.4 Hz, 1 H) 2.28 (ddd, J = 5.6, 9.2, 16.4 Hz, 1 H) 2.88 (d, 5.6 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl₃) δ 14.7, 17.3, 17.5, 18.3, 19.4, 23.9, 24.7, 29.1, 55.9, 58.2; HRMS (ESI) calcd for C₁₀H₁₇O (M+H<sup>+</sup>): 153.1274, found: 153.1270. Stereochemistry was determined by comparison of the <sup>1</sup>H NMR spectrum with that in the literature<sup>16</sup>.

Typical procedure for the generation of 1-I and the synthesis of epoxides

In the anodic chamber were placed Bu₄NI (91.7 mg, 0.248 mmol), Bu₄NBF₄ (102 mg, 0.3 mmol), DMSO (1 mL), and 0.3 M Bu₄NBF₄/CH₂Cl₂ (9 mL). In the cathodic chamber were placed TfOH (60 μL, 0.68 mmol) and 0.3 M Bu₄NBF₄/CH₂Cl₂ (10 mL). The constant current electrolysis (8.0 mA) was carried out at −78 °C with magnetic stirring until 2.1 F mol⁻¹ of electricity was consumed. To the anodic chamber was added a solution of (Z)-5-decene (2a) (27.9 mg, 0.199 mmol) in CH₂Cl₂ (0.5 mL), and to the cathodic chamber 0.5 mL of CH₂Cl₂ was added at −78 °C. The solution was stirred for 30 min at −78 °C then stirring was continued for 30 min at 0 °C. NaOMe (5.0 M in MeOH, 0.2 mL) was added to both the anodic and the cathodic chambers, and the resulting mixture was warmed to 25 °C and stirred for 5 min. The solution in the anodic chamber was filtered through a short column (2 x 4 cm) of silica gel to remove Bu₄NBF₄ by using Et₂O as an eluent. The GC analysis using hexadecane as an internal standard indicated that (5R*,6S*)-5,6-epoxydecane (6a) was obtained in 96% yield (0.191 mmol). TLC R<sub>f</sub> 0.83 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl₃) δ 0.93 (t, J = 7.2 Hz, 6 H), 1.37–1.55 (m, 12 H), 2.88–2.94 (m, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl₃) δ14.0, 22.6, 27.5, 28.3, 57.2; HRMS (APCI) calcd for C₁₀H₁₇O (M+H<sup>+</sup>): 157.1587, found: 157.1587. Stereochemistry was determined by comparison of the <sup>1</sup>H NMR spectrum with that in the literature<sup>3</sup>.
1,2-Epoxydodecane (6b). Electrochemical oxidation (2.1 F mol\(^{-1}\)) of Bu\(_4\)NI (92.5 mg, 0.250 mmol), subsequent addition of the solution of cyclododecene (2b) (\(Z/E = 72.28\), 33.3 mg, 0.200 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL), and treatment with NaOMe followed by flash chromatography (hexane/EtOAc 50:1) gave the title compound (32.6 mg, 0.179 mmol, 89\%, cis:trans = 74:26). TLC \(R_f\) 0.54 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.20−1.61 (m, 20 H), 1.70−1.87 (m, cis 2 H), 2.15−2.23 (m, trans 2 H), 2.71 (m, trans 2 H), 2.90 (td, \(J = 1.6, 10.0\) Hz, cis 2 H). The \(^1\)H NMR spectrum is in agreement with the literature\(^{10}\).

1,2-Epoxydodecane (6c). Electrochemical oxidation (2.1 F mol\(^{-1}\)) of Bu\(_4\)NI (91.5 mg, 0.248 mmol), subsequent addition of the solution of 1-dodecene (2c) (31.8 mg, 0.189 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL), and treatment with NaOMe gave the title compound (0.162 mmol, 86\%). The yield was determined by GC analysis using hexadecane as internal standard. TLC \(R_f\) 0.63 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.88 (t, \(J = 6.8\) Hz, 3 H), 1.20−1.38 (m, 14 H), 1.40−1.56 (m, 4 H), 2.46 (dd, \(J = 2.8, 4.8\) Hz, 1 H), 2.75 (dd, \(J = 3.6, 4.0\) Hz, 1 H), 2.88−2.94 (m, 1 H). The \(^1\)H NMR spectrum is in agreement with the literature\(^{11}\).

(1R\(^*,2R\(^*)\))-1-Phenyl-1,2-epoxypropane (6d). Electrochemical oxidation (2.1 F mol\(^{-1}\)) of Bu\(_4\)NI (148 mg, 0.401 mmol), subsequent addition of the solution of (E)-\(\beta\)-methylstylene ((E)-2d) (22.8 mg, 0.193 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL), and treatment with NaOMe followed by flash chromatography\(^ {12} \) (hexane) gave the title compound (10.0 mg, 0.074 mmol, 38\%). TLC \(R_f\) 0.58 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.46 (d, \(J = 5.2\) Hz, 3 H), 3.04 (dq, \(J = 4.4, 5.2\) Hz, 1 H), 3.58 (d, \(J = 1.6\) Hz, 2 H), 7.24−7.39 (m, 5 H); The \(^1\)H NMR spectrum is in agreement with the literature\(^ {13} \).

(1R\(^*,2S\(^*)\))-1-Phenyl-1,2-epoxypropane (6d\(^*\)). Electrochemical oxidation (2.1 F mol\(^{-1}\)) of Bu\(_4\)NI (149 mg, 0.403 mmol), subsequent addition of the solution of (Z)-\(\beta\)-methylstylene ((Z)-2d) (23.6 mg, 0.200 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL), and treatment with NaOMe followed by flash chromatography\(^ {9} \) (hexane) gave the title compound (134 mg, 0.134 mmol, 67\%). TLC \(R_f\) 0.56 (hexane/EtOAc 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.09 (d, \(J = 5.6\) Hz, 3 H), 3.34 (dq, \(J = 4.4, 5.2\) Hz, 1 H), 4.07 (d, \(J = 4.4\) Hz, 1 H) 7.26−7.40 (m, 5 H). The \(^1\)H NMR spectrum is in agreement with the literature\(^ {13} \).
4,5-Epoxypentenyl benzoate (6e). Electrochemical oxidation (2.1 F mol$^{-1}$) of Bu$_4$NI (91.0 mg, 0.246 mmol), subsequent addition of the solution of 4-pentenyl benzoate (2f) (39.0 mg, 0.205 mmol) in CH$_2$Cl$_2$ (0.5 mL), and treatment with NaOMe followed by flash chromatography$^{12}$ (hexane/EtOAc 100:0 to 20:1) gave the title compound (24.0 mg, 0.116 mmol, 57%). TLC $R_f$ 0.29 (hexane/EtOAc 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.62–1.82 (m, 2 H), 1.88–2.04 (m, 2 H), 2.52 (dd, $J$ = 2.8, 5.2 Hz, 1 H), 2.78 (dd, $J$ = 4.0, 5.2 Hz, 1 H), 2.98–3.02 (m, 1 H), 4.38 (dt, $J$ = 2.4, 6.4 Hz, 2 H), 7.44 (t, $J$ = 8.0 Hz, 2 H), 7.56 (t, $J$ = 7.6 Hz, 1 H), 8.04 (d, $J$ = 8.4 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 25.3, 29.1, 47.0, 51.7, 64.4, 128.3, 129.5, 130.2, 132.9, 166.5; HRMS (ESI) calcd for C$_7$H$_7$O$_2$ (M+H$^+$): 207.1016, found: 207.1012. The $^1$H NMR spectrum is in agreement with the literature$^{14}$.

6,7-Epoxyneryl acetate (6f). Electrochemical oxidation (2.1 F mol$^{-1}$) of Bu$_4$NI (92.8 mg, 0.251 mmol), subsequent addition of the solution of neryl acetate (2f) (35.6 mg, 0.182 mmol) in CH$_2$Cl$_2$ (0.5 mL), and treatment with NaOMe followed by flash chromatography$^{12}$ (hexane/EtOAc 100:0 to 20:1) gave the title compound (18.2 mg, 0.086 mmol, 47%). TLC $R_f$ 0.30 (hexane/EtOAc 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.27 (s, 3 H), 1.31 (s, 3 H), 1.56–1.71 (m, 2 H), 1.79 (s, 3 H), 2.05 (s, 3 H) 2.23–2.29 (m, 2 H), 2.71 (t, $J$ = 6.0 Hz, 1 H), 4.59 (d, $J$ = 7.6 Hz, 2 H), 5.41 (t, $J$ = 7.2 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 18.7, 21.0, 23.4, 24.8, 27.5, 28.8, 58.4, 60.8, 63.7, 119.7, 141.7, 171.0; HRMS (ESI) calcd for C$_{12}$H$_{20}$O$_3$Na (M+Na$^+$): 235.1305, found: 235.1299. The $^1$H NMR spectrum is in agreement with the literature$^{15}$. 

S14
5. Synthesis of $^{18}$O-labelled epoxide

**Synthesis of $^{18}$O-labelled DMSO**$^{17}$

![Chemical reaction](image)

To a round-bottom flask were added dimethylsulfide (2.6 mL, 33 mmol) and CH$_2$Cl$_2$ (10 mL). Bromine (1.8 mL, 33 mmol) was added dropwise to the solution at 0 °C over a period of 30 min. The mixture was stirred at 0 °C for 30 min to precipitate a yellow solid material. The liquid phase was removed by syringe and the solid material washed with dry CH$_2$Cl$_2$ under an Ar atmosphere. THF (10 mL) was added, followed by the dropwise addition of H$_2$O$_{^{18}}$ (242 mg, 12.1 mmol) at 0 °C over a period of 5 min. After stirring at 0 °C for 1 h, Et$_3$N (6.4 mL) was added to the mixture. The precipitate of triethylamine hydrobromide was separated by filtration and was washed twice with CH$_2$Cl$_2$. The combined yellow filtrate and washings were evaporated under reduced pressure to remove the solvents. The residue was purified by flash chromatography (hexane/EtOAc 1:1 to 0:100 to EtOAc/MeOH 10:1). THF (10 mL) was added, followed by the dropwise addition of H$_2$O$_{^{18}}$ (242 mg, 12.1 mmol) at 0 °C over a period of 5 min. After stirring at 0 °C for 1 h, Et$_3$N (6.4 mL) was added to the mixture. The precipitate of triethylamine hydrobromide was separated by filtration and was washed twice with CH$_2$Cl$_2$. The combined yellow filtrate and washings were evaporated under reduced pressure to remove the solvents. The residue was purified by flash chromatography (hexane/EtOAc 1:1 to 0:100 to EtOAc/MeOH 10:1). After Kugelrohr distillation (20 mmHg, 80 °C), $^{18}$O-labelled DMSO was obtained in 34% yield (332 mg, 4.14 mmol). TLC R$_f$ 0.05 (EtOAc); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.62 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 40.5; HRMS (ESI) calcd for C$_4$H$_{12}$O$_2$S (2M+H$^+$): 161.0436, found: 161.0433.

**Synthesis of $^{18}$O-labelled epoxide 6c**

![Chemical reaction](image)

In the anodic chamber were placed Bu$_4$NI (91.8 mg, 0.248 mmol), DMSO (96% $^{18}$O, 0.2 mL), and 0.3 M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ (10 mL). In the cathodic chamber were placed TfOH (60 μL, 0.68 mmol) and 0.3 M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ (10 mL). The constant current electrolysis (8.0 mA) was carried out at −78 °C with magnetic stirring until 2.1 F mol$^{-1}$ of electricity was consumed. To the anodic chamber was added a solution of 1-dodecene (2c) (32.5 mg, 0.193 mmol) in CH$_2$Cl$_2$ (0.5 mL), and to the cathodic chamber was added 0.5 mL of CH$_2$Cl$_2$ at −78 °C. The solution was stirred for 30 min at −78 °C then stirring was continued for 30 min at 0 °C. NaOMe (5.0 M in MeOH, 0.2 mL) was added to both the anodic and cathodic chambers, and the resulting mixture was warmed to 25 °C and stirred for 5 min. The solution in the anodic chamber was filtered through a short column (2 x 4 cm) of silica gel to remove Bu$_4$NBF$_4$ by using Et$_2$O as an eluent. After removal of the solvent under reduced pressure the crude product was purified by flash chromatography$^9$ (hexane) to obtain $^{18}$O-labelled 1,2-epoxydodecane (6c) in 81% yield (29.0 mg, 0.155 mmol). TLC R$_f$ 0.67 (hexane/EtOAc 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, $J = 6.8$ Hz, 6 H), 1.22–1.56 (m, 18 H), 2.46 (dd, $J = 2.8$, 5.2 Hz, 1 H), 2.74 (dd, $J = 4.0$, 5.2 Hz, 1 H), 2.88–2.93 (m, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 22.7, 26.0, 29.3, 29.4, 29.54, 29.57, 31.9, 32.5, 47.1, 52.4; HRMS (APCI) calcd for C$_{12}$H$_{25}$O$_2$(M+H$^+$): 187.1942, found: 187.1940.
6. References

(12) Flash chromatography was carried out on a silica gel (Fuji Silysia Chemical Ltd., CHROMATOREX
    FL100DX, spherical, pH = 8.7, 100 μm)
7. NMR spectra
8. Mass spectra of $^{18}$O-labelled DMSO and 6c