Supporting Information


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Contents

1. General information S2
2. Cyclic voltammetry studies S3
3. General procedure for electrochemical semi-pinacol rearrangement S4
4. Preparation of simulated solutions and applications S16
5. Using wastewaters to synthesize bioactive natural products S19
6. X-ray structure of compound 2i S20
7. Preliminary mechanistic studies S21
8. Reference S22
9. NMR spectra for products S24
1. General information

Reagents: All commercial materials were used as received from Energy Chemical or Adamas-beta, Alfa Aesar, TCI and Acros unless otherwise noted. MgCl₂ (99%, Energy), MgBr₂·6H₂O (98+, Alfa Aesar) were used in the electrochemical reactions.

Reactions: All reactions were carried out in undivided electrochemical cells (30 mL) using pre-dried glassware, if not noted otherwise. The electrochemical cells were fitted with a threaded Teflon cap with electrical feed-throughs. Electrocatalysis was conducted using an DC-power supplier HY3005ET in constant current mode, CV studies were performed using a CHI660E workstation.

Chromatography: Thin layer chromatography (TLC) was carried out on silica gel 60 F254 pre-coated glass plates. Visualization was detected by irradiation with UV light (254 nm), or by treatment with a solution of phosphomolybdic acid in ethanol followed by heating. Flash chromatography was carried out on 200 – 300 mesh silica gel, eluting with a mixture of petroleum ether (b.p. 60 – 90 °C) and ethyl acetate.

NMR Spectroscope: ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE III HD 400 or 500 spectrometer, operating at 400 (or 500) MHz and 100 (or 125) MHz respectively. Chemical shifts (δ) were given in parts per million (ppm), and referenced relative to residual solvent CHCl₃ (7.26 ppm) in CDCl₃, or tetramethylsilane (0.00 ppm) as an internal standard for ¹H NMR spectra and deuterated solvent CDCl₃ (77.0 ppm) for ¹³C NMR spectra. Coupling constants (J) were reported in hertz (Hz). The following abbreviations are used to indicate the multiplicity of the signals: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and associated combinations, e.g. dd = doublet of doublets.

Mass Spectrometry: High-resolution mass spectra (HRMS) were obtained on a Waters ACQUITYTM UPLC & Q-TOF MS Premier using the electrospray ionization (ESI) technique.

X-Ray: X-ray diffraction data were collected on a Bruker APEX-II CCD diffractometer.

Preparation of substrates: The allylic alcohols and alkenyl bromides were prepared
according to the related references.[1-7]

2. Cyclic voltammetry studies

**General information:** Cyclic voltammetry (CV) experiments were conducted in a 30 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter, BASi), a saturated calomel electrode as reference electrode, and a platinum wire counter electrode. The solution of interest was sparged with nitrogen for 3-5 minutes before data collection. The diagrams were made using OriginLab 8.0.

![Cyclic voltammogram](image)

**Fig. S1.** Cyclic voltammogram of 1a, MgBr₂·6H₂O, and their mixture in MeCN/MeOH. Conditions: LiClO₄ (1 mmol) in MeCN/MeOH (6/3 mL), and with (a) none, (b) 1a (0.04mmol), (c) MgBr₂·6H₂O (0.08 mmol) and (d) MgBr₂·6H₂O (0.08 mmol) and 1a (0.04mmol). **Scan rate:** 50 mV/s.
**Fig. S2.** Cyclic voltammogram of halide salt and their mixture in MeCN/MeOH. Conditions: LiClO$_4$ (1 mmol) in MeCN/MeOH (6/3 mL), and with (a) MgBr$_2$·6H$_2$O (0.08 mmol), (b) MgCl$_2$ (0.08 mmol), (c) KI (0.16 mmol) and (d) MgBr$_2$·6H$_2$O (0.08 mmol) and MgCl$_2$ (0.08 mmol). **Scan rate: 50 mV/s.**

**Fig. S3.** Cyclic voltammogram of halide salt and their mixture in MeCN/MeOH. Conditions: LiClO$_4$ (1 mmol) in MeCN/MeOH (6/3 mL), KF (0.16 mmol). **Scan rate: 50 mV/s.**

3. **General procedure for electrochemical semi-pinacol rearrangement**
**General procedure:** To an oven-dried, undivided electrochemical cell equipped with a magnetic stir bar, a carbon anode (10.0 mm * 10.0 mm), and a Pt plate cathode (10.0 mm * 10.0 mm) were added MgCl₂ or MgBr₂·6H₂O (4.0 equiv., 1.6 mmol), allylic alcohol (1.0 equiv., 0.4 mmol) and followed by the addition of 6 mL MeCN and 3 mL H₂O. The mixture was stirred for 5 min. The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h, electricity = 2.3 F. Ethyl acetate (10 mL) and water (10 mL) was added, the aqueous layer was separated and extracted with ethyl acetate (3×10 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2a as colorless oil in 81% yield (82.5 mg).

**¹H NMR** (400 MHz, CDCl₃) δ 7.45 – 7.39 (m, 2H), 7.38 – 7.35 (m, 2H), 7.33 – 7.27 (m, 1H), 3.77 (d, J = 10.3 Hz, 1H), 3.57 (d, J = 10.3 Hz, 1H), 2.71 – 2.65 (m, 1H), 2.53 – 2.19 (m, 3H), 2.07 – 1.93 (m, 1H), 1.86 – 1.66 (m, 1H).

**¹³C NMR** (101 MHz, CDCl₃) δ 216.1, 136.9, 128.9, 127.9, 126.8, 57.8, 39.1, 37.6, 32.8, 18.3.

**HRMS (ESI) m/z** calculated for C₁₂H₁₄BrO⁺ [M+H⁺] 255.0202, found 255.0218.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2b as pale yellow oil in 83% yield (88.8 mg).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 – 7.15 (m, 2H), 7.15 – 7.06 (m, 2H), 3.85 (m, 2H), 2.68 – 2.52 (m, 2H), 2.52 – 2.38 (m, 4H), 2.36 – 2.27 (m, 1H), 2.04 – 1.94 (m, 1H), 1.82 – 1.71 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 217.7, 137.3, 136.1, 133.3, 127.8, 127.6, 126.2, 58.5, 37.9, 36.3, 34.2, 21.8, 18.8.

HRMS (ESI) $m/z$ calculated for C$_{13}$H$_{16}$BrO [M+H$^+$] 267.0379, found 267.0382.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2c as colorless oil in 72% yield (52.3 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 – 7.17 (m, 1H), 7.15 – 7.07 (m, 1H), 3.76 (d, $J$ = 10.3 Hz, 1H), 3.56 (d, $J$ = 10.3 Hz, 1H), 2.69 – 2.63 (m, 1H), 2.50 – 2.30 (m, 2H), 2.35 (s, 3H), 2.31 – 2.21 (m, 1H), 2.06 – 1.94 (m, 1H), 1.86 – 1.69 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 216.3, 138.6, 136.8, 128.8, 128.7, 127.5, 123.8, 57.8, 39.1, 37.6, 32.8, 21.6, 18.3.

HRMS (ESI) $m/z$ calculated for C$_{13}$H$_{16}$BrO [M+H$^+$] 267.0379, found 267.0381.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2d as colorless oil in 92% yield (98.2 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.27 (m, 2H), 7.18 – 7.16 (m, 2H), 3.76 (d, $J$ = 10.3 Hz, 1H), 3.55 (d, $J$ = 10.3 Hz, 1H), 2.69 – 2.63 (m, 1H), 2.51 – 2.16 (m, 6H), 2.07 – 1.93 (m, 1H), 1.89 – 1.68 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 216.4, 137.8, 133.7, 129.7, 126.7, 57.6, 39.3, 37.6, 32.7, 21.0, 18.3.

HRMS (ESI) $m/z$ calculated for C$_{13}$H$_{16}$BrO [M+H$^+$] 267.0379, found 267.0391.
Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2e as white solid in 79% yield (85.7 mg).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.44 – 7.35 (m, 2H), 7.07 – 7.02 (m, 2H), 3.71 (d, $J = 10.3$ Hz, 1H), 3.53 (d, $J = 10.4$ Hz, 1H), 2.67 – 2.62 (m, 1H), 2.47 – 2.22 (m, 3H), 2.05 – 1.98 (m, 1H), 1.83 – 1.68 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 216.0, 162.3 (d, $J = 248.3$ Hz), 132.5 (d, $J = 3.2$ Hz), 128.7 (d, $J = 8.0$ Hz), 115.8 (d, $J = 21.4$ Hz), 57.1, 39.3 (d, $J = 1.6$ Hz), 37.6, 33.0, 18.3.

HRMS (ESI) $m/z$ calculated for C$_{12}$H$_{12}$BrFNaO [M+Na$^+$] 292.9948, found 292.9956.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2f as pale yellow oil in 98% yield (111.0 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.29 (m, 2H), 6.92 – 6.83 (m, 2H), 3.80 (s, 3H), 3.75 (d, $J = 10.3$ Hz, 1H), 3.52 (d, $J = 10.3$ Hz, 1H), 2.67 – 2.61 (m, 1H), 2.48 – 2.17 (m, 3H), 2.04 – 1.95 (m, 1H), 1.85 – 1.67 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 216.4, 159.2, 128.4, 128.1, 114.3, 57.2, 55.2, 39.4, 37.6, 32.7, 18.3.

HRMS (ESI) $m/z$ calculated for C$_{13}$H$_{16}$BrO$_2$ [M+H$^+$] 285.0308, found 285.0320.

Purification of the crude product by flash column chromatography afforded the
semi-pinacol rearrangement product 2g as white solid in 92% yield (109.3 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.91 (d, $J = 2.0$ Hz, 1H), 6.85 (dd, $J = 8.2$, 2.0 Hz, 1H), 6.76 (d, $J = 8.2$ Hz, 1H), 5.94 (d, $J = 1.1$ Hz, 2H), 3.70 (d, $J = 10.3$ Hz, 1H), 3.50 (d, $J = 10.3$ Hz, 1H), 2.60 – 2.54 (m, 1H), 2.46 – 2.15 (m, 3H), 2.02 – 1.94 (m, 1H), 1.88 – 1.65 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 215.9, 148.2, 147.2, 130.3, 120.4, 108.4, 107.3, 101.3, 57.4, 39.3, 37.5, 33.0, 18.2.

HRMS (ESI) m/z calculated for C$_{13}$H$_{14}$BrO$_3$ [M+H$^+$] 299.0100, found 299.0106.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2h as white solid in 93% yield (113.2 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 – 7.76 (m, 4H), 7.56 (dd, $J = 8.7$, 2.0 Hz, 1H), 7.53 – 7.48 (m, 2H), 3.85 (d, $J = 10.3$ Hz, 1H), 3.69 (d, $J = 10.4$ Hz, 1H), 2.85 – 2.79 (m, 1H), 2.61 – 2.24 (m, 3H), 2.09 – 2.01 (m, 1H), 1.89 – 1.76 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 216.2, 134.1, 133.2, 132.6, 128.8, 128.1, 127.4, 126.5, 126.4, 126.3, 124.2, 58.0, 39.0, 37.7, 32.8, 18.4.

HRMS (ESI) m/z calculated for C$_{16}$H$_{16}$BrO$_3$ [M+H$^+$] 305.0359, found 305.0351.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2i as white solid in 79% yield (84.2 mg).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.58 – 7.51 (m, 2H), 7.40 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 4.78 (q, $J = 6.9$ Hz, 1H), 2.75 – 2.66 (m, 1H), 2.63 – 2.57 (m, 1H), 2.31 – 2.21 (m, 2H), 2.11 – 2.01 (m, 1H), 1.86 – 1.68 (m, 1H), 1.35 (d, $J = 6.9$ Hz, 3H).
13C NMR (126 MHz, CDCl3) δ 216.1, 134.8, 129.0, 127.9, 127.4, 61.8, 54.9, 37.5, 27.7, 21.5, 18.6.

HRMS (ESI) m/z calculated for C13H18BrO [M+H+] 267.0379, found 267.0388.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2j as white solid in 45% yield (47.8 mg).

1H NMR (400 MHz, CDCl3) δ 7.30 – 7.13 (m, 3H), 7.13 – 7.03 (m, 1H), 4.36 (dd, J = 10.2, 7.7 Hz, 1H), 3.66 (dd, J = 15.3, 10.2 Hz, 1H), 3.31 (dd, J = 15.3, 7.7 Hz, 1H), 2.56 – 2.41 (m, 2H), 2.41 – 2.23 (m, 3H), 2.21 – 2.00 (m, 1H).

13C NMR (101 MHz, CDCl3) δ 215.6, 143.8, 141.8, 128.0, 127.3, 124.5, 122.2, 63.5, 54.0, 41.2, 38.6, 34.7, 20.2.

HRMS (ESI) m/z calculated for C13H14BrO [M+H+] 265.0223, found 265.0215.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2k as colorless oil in 66% yield (50.4 mg).

1H NMR (500 MHz, CDCl3) δ 3.48 (d, J = 10.1 Hz, 1H), 3.31 (d, J = 10.1 Hz, 1H), 2.42 – 2.33 (m, 1H), 2.29 – 2.16 (m, 2H), 2.04 – 1.92 (m, 1H), 1.92 – 1.77 (m, 2H), 1.13 (s, 3H).

13C NMR (126 MHz, CDCl3) δ 219.5, 49.7, 39.0, 38.0, 34.7, 21.7, 18.5.

HRMS (ESI) m/z calculated for C7H12BrO [M+H+] 191.0066, found 191.0072.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2l as pale yellow oil in 55% yield (51.0 mg).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.99 (dd, \(J = 12.0, 4.8\) Hz, 1H), 2.70 (qd, \(J = 12.8, 4.1\) Hz, 1H), 2.52 – 2.44 (m, 1H), 2.38 – 2.18 (m, 2H), 2.18 – 2.06 (m, 1H), 2.04 – 1.94 (m, 2H), 1.92 – 1.75 (m, 2H), 1.74 – 1.62 (m, 2H), 1.54 – 1.39 (m, 1H), 1.39 – 1.19 (m, 2H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 218.2, 58.4, 52.2, 39.6, 37.9, 34.6, 33.4, 27.1, 20.4, 18.7.

HRMS (ESI) \(m/z\) calculated for C\(_{10}\)H\(_{16}\)BrO [M+H\(^+\)] 233.0359, found 233.0368.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2m as pale yellow oil in 42% yield (34 mg).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.37 (m, 2H), 7.34 – 7.28 (m, 1H), 7.25 – 7.14 (m, 2H), 3.80 (d, \(J = 10.5\) Hz, 1H), 3.50 (d, \(J = 10.5\) Hz, 1H), 2.90 – 2.84 (m, 1H), 2.38 – 2.22 (m, 2H), 2.04 – 1.89 (m, 2H), 1.86 – 1.63 (m, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 210.8, 137.7, 129.1, 127.8, 127.0, 57.2, 42.9, 40.0, 33.9, 27.7, 21.4.

HRMS (ESI) \(m/z\) calculated for C\(_{13}\)H\(_{16}\)BrO [M+H\(^+\)] 267.0379, found 267.0385.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2n as white solid in 81% yield (116.7 mg).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.11 (dd, \(J = 7.5, 1.9\) Hz, 1H), 8.07 (dd, \(J = 7.8, 1.5\) Hz, 1H), 8.00 (d, \(J = 8.1\) Hz, 1H), 7.63 – 7.60 (m, 1H), 7.54 – 7.48 (m, 2H), 7.42 (dd, \(J = 7.3, 1.9\) Hz, 1H), 7.37 – 7.34 (m, 1H), 7.24 – 7.15 (m, 3H), 7.14 – 7.04 (m, 2H), 4.96 (d, \(J = 10.1\) Hz, 1H), 4.02 (d, \(J = 10.1\) Hz, 1H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 196.6, 140.0, 137.8, 136.8, 134.7, 131.3, 129.1, 129.1, 128.8, 128.7, 128.3, 128.2, 128.2, 128.0, 127.2, 124.2, 123.0, 60.5, 36.2.
HRMS (ESI) m/z calculated for C_{21}H_{16}BrO [M+H^+] 363.0379, found 363.0386.

![Diagram of 2o]

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2o as white solid in 79% yield (116.1 mg).

^{1}H NMR (500 MHz, CDCl_{3}) δ 7.61 – 7.56 (m, 2H), 7.50 – 7.44 (m, 4H), 7.41 – 7.30 (m, 7H), 7.23 – 7.19 (m, 2H), 4.32 (s, 2H).

^{13}C NMR (126 MHz, CDCl_{3}) δ 198.9, 139.3, 136.9, 132.0, 129.9, 129.6, 128.5, 127.9, 127.8, 65.0, 42.1.

HRMS (ESI) m/z calculated for C_{21}H_{18}BrO [M+H^+] 365.0536, found 365.0533.

![Diagram of 2p]

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2p as white solid in 74% yield (90 mg).

^{1}H NMR (500 MHz, CDCl_{3}) δ 7.44 – 7.30 (m, 10H), 4.21 (s, 2H), 2.13 (s, 3H).

^{13}C NMR (126 MHz, CDCl_{3}) δ 206.0, 138.8, 129.4, 128.4, 127.8, 66.6, 40.2, 27.5.

HRMS (ESI) m/z calculated for C_{16}H_{18}BrO [M+H^+] 303.0379, found 303.0385.

![Diagram of 2q]

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2q as pale yellow oil in 56% yield (66.8 mg).

^{1}H NMR (400 MHz, CDCl_{3}) δ 7.36 (dd, J = 8.3, 6.6 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.20 (dd, J = 7.5, 1.8 Hz, 2H), 4.03 (d, J = 10.9 Hz, 1H), 3.86 (dd, J = 10.9, 1.1 Hz, 1H), 2.34 – 2.27 (m, 1H), 2.23 – 2.11 (m, 2H), 2.12 – 2.03 (m, 1H), 1.52 – 1.42 (m, 2H), 1.34 – 1.15 (m, 1H), 1.13 – 0.94 (m, 4H), 0.73 (t, J = 7.4 Hz, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 210.2, 139.7, 128.8, 127.5, 126.5, 59.4, 39.8, 38.9, 33.9, 17.3, 16.9, 14.5, 13.5.

HRMS (ESI) $m/z$ calculated for C$_{15}$H$_{22}$BrO [M+H$^+$] 297.0849, found 297.0856.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2r as white solid in 73% yield (89.1 mg).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.83 (s, 1H), 7.44 – 7.31 (m, 6H), 7.25 – 7.22 (m, 4H), 4.17 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 196.2, 137.5, 129.1, 128.8, 128.0, 63.9, 36.2.

HRMS (ESI) $m/z$ calculated for C$_{15}$H$_{14}$BrO [M+H$^+$] 289.0223, found 289.0256.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2s as pale yellow oil in 58% yield (74.5 mg).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.79 (s, 1H), 7.48 – 7.31 (m, 5H), 7.25 – 7.13 (m, 4H), 4.21 – 4.06 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 195.8, 137.0, 136.1, 134.2, 130.5, 129.0, 129.0, 128.3, 63.5, 35.9.

HRMS (ESI) $m/z$ calculated for C$_{15}$H$_{13}$BrClO [M+H$^+$] 322.9833, found 322.9851.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2t as pale yellow oil in 76% yield (96.9 mg).
**1H NMR** (500 MHz, CDCl$_3$) δ 9.79 (s, 1H), 7.43 – 7.31 (m, 3H), 7.25 – 7.20 (m, 2H), 7.17 – 7.11 (m, 2H), 6.95 – 6.86 (m, 2H), 4.16 – 4.12 (m, 2H), 3.81 (s, 3H).

**13C NMR** (126 MHz, CDCl$_3$) δ 196.2, 159.2, 137.8, 130.3, 129.1, 128.7, 128.0, 114.2, 63.2, 55.2, 36.5.

**HRMS (ESI)** m/z calculated for C$_{16}$H$_{16}$BrO$_2$ [M+H$^+$] 319.0328, found 319.0331.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2u as white solid in 52% yield (64.9 mg).

**1H NMR** (400 MHz, CDCl$_3$) δ 9.47 (s, 1H), 6.84 – 6.82 (m, 2H), 6.76 (dd, J = 8.1, 2.0 Hz, 1H), 5.98 (q, J = 1.4 Hz, 2H), 5.00 (dd, J = 6.7, 3.3 Hz, 1H), 2.35 – 2.28 (m, 1H), 2.20 – 1.93 (m, 3H), 1.89 – 1.78 (m, 1H), 1.70 – 1.61 (m, 1H), 1.54 – 1.41 (m, 2H).

**13C NMR** (101 MHz, CDCl$_3$) δ 199.0, 148.6, 147.0, 130.6, 121.1, 108.7, 107.7, 101.4, 57.4, 55.4, 31.9, 28.5, 22.9, 21.2.

**HRMS (ESI)** m/z calculated for C$_{14}$H$_{16}$BrO$_3$ [M+H$^+$] 311.0277, found 311.0290.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 3a as colorless oil in 64% yield (53.5 mg).

**1H NMR** (400 MHz, CDCl$_3$) δ 7.46 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 3.91 (d, J = 11.1 Hz, 1H), 3.67 (d, J = 11.1 Hz, 1H), 2.68 – 2.62 (m, 1H), 2.52 – 2.44 (m, 1H), 2.42 – 2.33 (m, 1H), 2.31 – 2.22 (m, 1H), 2.08 – 1.96 (m, 1H), 1.86 – 1.70 (m, 1H).

**13C NMR** (101 MHz, CDCl$_3$) δ 216.5, 136.8, 128.9, 127.9, 126.8, 58.4, 49.7, 37.7, 31.6, 18.4.

**HRMS (ESI)** m/z calculated for C$_{12}$H$_{13}$ClNaO [M+Na$^+$] 231.0547, found 231.0553.
Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 3d as colorless oil in 75% yield (66.9 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.27 (m, 2H), 7.17 (d, J = 8.2 Hz, 2H), 3.89 (d, J = 11.1 Hz, 1H), 3.64 (d, J = 11.1 Hz, 1H), 2.65 – 2.61 (m, 1H), 2.49 – 2.43 (m, 1H), 2.40 – 2.30 (m, 4H), 2.29 – 2.21 (m, 1H), 2.04 – 1.97 (m, 1H), 1.84 – 1.71 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 216.6, 137.7, 133.6, 129.6, 126.7, 58.2, 49.8, 37.6, 31.5, 20.9, 18.4.

HRMS (ESI) m/z calculated for C$_{13}$H$_{16}$ClO [M+H$^+$] 223.0884, found 223.0883.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 3e as pale yellow solid in 61% yield (60 mg).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.31 (m, 2H), 7.11 – 6.95 (m, 2H), 3.85 (d, J = 11.1 Hz, 1H), 3.63 (d, J = 11.1 Hz, 1H), 7.44 – 7.31 (m, 1H), 2.52 – 2.22 (m, 3H), 2.09 – 1.95 (m, 1H), 1.83 – 1.71 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 216.4, 162.3 (d, J = 248.7 Hz), 132.4 (d, J = 3.2 Hz), 128.8 (d, J = 8.1 Hz), 115.8 (d, J = 21.4 Hz), 57.8, 49.9 (d, J = 1.5 Hz), 37.7, 31.8, 18.4.

HRMS (ESI) m/z calculated for C$_{12}$H$_{13}$ClFO [M+H$^+$] 227.0633, found 227.0636.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 3h as white solid in 64% yield (66.7 mg).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 – 7.81 (m, 4H), 7.55 (dd, $J$ = 8.7, 2.0 Hz, 1H), 7.53 – 7.44 (m, 2H), 3.99 (d, $J$ = 11.1 Hz, 1H), 3.78 (d, $J$ = 11.2 Hz, 1H), 2.82 – 2.76 (m, 1H), 2.60 – 2.52 (m, 1H), 2.47 – 2.24 (m, 2H), 2.10 – 2.02 (m, 1H), 1.92 – 1.73 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 216.5, 134.0, 133.2, 132.6, 128.8, 128.1, 127.4, 126.5, 126.4, 126.3, 124.2, 58.7, 49.6, 37.8, 31.7, 18.5.

HRMS (ESI) $m/z$ calculated for C$_{16}$H$_{16}$ClO $[\text{M+H}^+]$ 259.0884, found 259.0880.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 3l as colorless oil in 48% yield (35.9 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.85 (dd, $J$ = 11.6, 4.7 Hz, 1H), 2.62 – 2.42 (m, 2H), 2.42 – 2.18 (m, 2H), 2.07 – 1.92 (m, 3H), 1.92 – 1.75 (m, 2H), 1.75 – 1.54 (m, 2H), 1.54 – 1.38 (m, 1H), 1.38 – 1.19 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 218.3, 64.7, 52.2, 39.9, 36.8, 34.2, 32.3, 25.8, 20.4, 18.7.

HRMS (ESI) $m/z$ calculated for C$_{10}$H$_{16}$ClO $[\text{M+H}^+]$ 187.0884, found 187.0887.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 3m as colorless oil in 40% yield (35.6 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.36 (m, 2H), 7.34 – 7.27 (m, 1H), 7.25 – 7.18 (m, 2H), 3.90 (d, $J$ = 11.2 Hz, 1H), 3.61 (d, $J$ = 11.2 Hz, 1H), 2.90 – 2.85 (m, 1H), 2.40 – 2.20 (m, 2H), 2.01 – 1.90 (m, 2H), 1.86 – 1.61 (m, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 211.0, 137.5, 129.0, 127.7, 127.0, 57.9, 52.7, 40.0, 32.7, 27.6, 21.2.

HRMS (ESI) $m/z$ calculated for C$_{13}$H$_{16}$ClO $[\text{M+H}^+]$ 223.0884, found 223.0890.
Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 3p as white solid in 58% yield (59.6 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.50 – 7.31 (m, 10H), 4.36 (s, 2H), 2.14 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 206.3, 138.5, 129.4, 128.4, 127.7, 67.2, 50.2, 27.5.

HRMS (ESI) m/z calculated for C$_{16}$H$_{16}$ClO[$\text{M+H}^+$] 259.0884, found 259.0885.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 3t as colorless oil in 40% yield (35.6 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 9.81 (s, 1H), 7.41 – 7.38 (m, 2H), 7.37 – 7.31 (m, 1H), 7.26 – 7.20 (m, 2H), 7.17 – 7.11 (m, 2H), 6.96 – 6.89 (m, 2H), 4.29 (s, 2H), 3.81 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 196.5, 159.2, 137.5, 130.3, 129.1, 128.9, 128.0, 114.2, 63.9, 55.2, 47.3.

HRMS (ESI) m/z calculated for C$_{16}$H$_{15}$ClNaO$_2$ [M+Na$^+$] 297.0653, found 297.0642.

4. Preparation of simulated solutions and applications

Simulated solution $A$ (Bittern after making salt with seawater), $B$ (Dead sea water), $C$ (Industrial effluent (producing Na$_2$CO$_3$)), $D$ (sea water) were prepared according to relative literature[8-11] by adding calculated inorganic salt (NaCl, MgCl$_2$, MgSO$_4$, CaSO$_4$, K$_2$SO$_4$, CaCO$_3$, MgBr$_2$, et al) into water.
For simulated solution A (Bittern after making salt with seawater), the concentration of bromine was 6 g/L (75 mmol/L). 3 mL simulated solution A (containing 0.225 mmol Br) was added into undivided electrochemical cells (30 mL), followed by the addition of allyl alcohol 1a (calculation basis, 1 equiv., 0.055 mmol or 0.11 mmol) which is dissolved in acetonitrile (6 mL). The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h. Ethyl acetate (10 mL) and water (10 mL) was added, the aqueous layer was separated and extracted with ethyl acetate (3×10 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo and column chromatography, NMR yields and ratio of 2a/3a were obtained by dissolving the crude residue in CDCl3 using CH2Br2 as the internal standard.

For simulated solution B (Dead sea water), the concentration of bromine and chlorine was 4.2 g/L (52.5 mmol/L) and 181.4 g/L (5.11 mol/L), respectively. When calculation standard was amount of substance of Cl, 315 μL simulated solution B (containing 1.6 mmol Cl, 4 equiv.), allyl alcohol 1a (0.4 mmol, 1 equiv.) which is
dissolved in MeCN (6 mL) and additional water (2.685 mL to ensure that the total volume is 9 mL) were added into undivided electrochemical cells (30 mL). The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h. After extraction, concentration and column chromatography, NMR yields and ratio of 2a/3a were obtained by dissolving the crude residue in CDCl₃ using CH₂Br₂ as the internal standard. When calculation standard was amount of substance of Br, 3 mL simulated solution B (containing 0.1575 mmol Br, 2 equiv.) and allyl alcohol 1a (0.07875 mmol) which is dissolved in MeCN (6 mL) were added into undivided electrochemical cells (30 mL). The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h. After extraction, concentration and column chromatography, NMR yields and ratio of 2a/3a were obtained by dissolving the crude residue in CDCl₃ using CH₂Br₂ as the internal standard.

For simulated solution C (Industrial effluent (producing Na₂CO₃)), the concentration of chlorine was 116 g/L (3.2676 mol/L). When calculation standard was amount of substance of Cl, 490 μL simulated solution C (containing 1.6 mmol Cl, 4 equiv.), allyl alcohol 1a (0.4 mmol, 1 equiv.) which is dissolved in MeCN (6 mL) and additional water (2.51 mL to ensure that the total volume is 9 mL) was added into undivided electrochemical cells (30 mL). The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h. After extraction, concentration and column chromatography, NMR yields of 3a were obtained by dissolving the crude residue in CDCl₃ using CH₂Br₂ as the internal standard.

For simulated solution D (sea water), the concentration of chlorine was 19.891 g/L (560.34 mol/L). When calculation standard was amount of substance of Cl, 3 mL simulated solution D (containing 1.681 mmol Cl, 8 equiv.), allyl alcohol 1a (0.21 mmol, 1 equiv.) which is dissolved in MeCN (6 mL) was added into undivided electrochemical cells (30 mL). The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h. After extraction, concentration and column chromatography, NMR yields and ratio of 2a/3a were obtained by dissolving the crude residue in CDCl₃ using CH₂Br₂ as the internal standard.
5. Using wastewaters to synthesize bioactive natural products

Allyl alcohol 1w or 1x (0.055 mmol) which is dissolved in MeCN (6 mL) and 3 mL simulated solution A (containing 0.225 mmol Br) were added into undivided electrochemical cells (30 mL). The electrolysis was controlled at a constant current 3 mA and was terminated after 2.5 h. After extraction and concentration, the crude residue was purified by column chromatography and product 2w and 2x were isolated in 35% and 42% yield respectively. No aldehyde containing chlorine was detected in NMR spectra.

When allyl alcohol 1x (0.02375 mmol) was added into water (9 mL) directly, following by the addition of MgBr\textsubscript{2}·6H\textsubscript{2}O (0.095 mmol), 2x was obtained in 41% isolated yield under the electrochemical reaction condition. Br-concentration of water is consistant with Br-concentration of produced water from shale gas extraction (Br: 1.7 g/L).\textsuperscript{12}
Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product $2w$ as colorless oil in 35% yield (7.3 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.94 (s, 1H), 6.82 – 6.74 (m, 2H), 6.64 (dd, $J = 8.2$, 2.0 Hz, 1H), 6.02 – 5.93 (m, 2H), 4.72 (dd, $J = 12.5$, 4.2 Hz, 1H), 4.03 – 3.87 (m, 4H), 2.53 – 2.47 (m, 1H), 2.36 – 2.30 (m, 1H), 2.23 (t, $J = 13.0$ Hz, 1H), 1.90 – 1.77 (m, 2H), 1.74 – 1.63 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 202.2, 148.4, 147.1, 132.2, 120.4, 108.5, 108.0, 107.0, 101.3, 64.7, 64.4, 56.6, 51.0, 43.7, 32.2, 31.8.

HRMS (ESI) $m/z$ calculated for C$_{16}$H$_{18}$BrO$_5$ [M+H$^+$] 369.0332, found 369.0341.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product $2x$ as pale yellow solid in 42% yield (11.2 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.73 (d, $J = 1.9$ Hz, 1H), 7.03 – 6.90 (m, 2H), 6.89 – 6.75 (m, 1H), 4.79 (t, $J = 8.6$ Hz, 1H), 4.05 – 3.83 (m, 4H), 3.78 (s, 3H), 2.67 – 2.48 (m, 2H), 2.48 – 2.30 (m, 2H), 1.73 – 1.47 (m, 3H), 0.94 (s, 9H), 0.24 (s, 3H), 0.20 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 202.8, 149.2, 142.8, 130.9, 120.9, 118.6, 110.4, 108.6, 64.6, 64.3, 54.3, 53.4, 49.9, 42.4, 31.5, 30.9, 26.7, 19.7, -2.0, -2.3.

HRMS (ESI) $m/z$ calculated for C$_{22}$H$_{34}$BrO$_5$Si [M+H$^+$] 485.1353, found 485.1362.

6. X-ray structure of compound 2i
A colorless block shaped crystal of 2i (C_{13}H_{15}BrO) was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 173(2) K, on a Bruker D8 VENTURE CMOS photon 100 diffractometer with helios mx multilayer monochromator Cu-Kα radiation (λ = 1.54178 Å). The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1904039 for 2i. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

7. Preliminary mechanistic studies

a) Radical trapping experiments

To an oven-dried, undivided electrochemical cell equipped with a magnetic stir bar, a carbon anode (10.0 mm * 10.0 mm), and a Pt plate cathode (10.0 mm * 10.0 mm) were added MgBr₂·6H₂O (4.0 equiv., 1.6 mmol), allylic alcohol (1.0 equiv., 0.4 mmol), radical scavenger (tempo or BHT, 10 equiv.) and followed by the addition of 6 mL MeCN and 3 mL MeOH. The mixture was stirred for 5 min. The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h. Trace 2a was detected by thin layer chromatography.

b) The study on the migration process

Allyl alcohol 1v was tested under the standard condition, and 2v was obtained in 95% isolated yield. To further confirm the structure of 2v, N-Bromosuccinimide (0.8
equiv.) and allyl alcohol (1v) were reacted in MeCN/MeOH (2:1) for 1 hour, and NMR $^1$H and $^{13}$C spectrum of product were consistent with that of product obtained from electrochemical semi-pinacol rearrangement.

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product 2v as colorless oil in 95% yield (176 mg).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.62 (d, $J = 8.7$ Hz, 2H), 7.46 (d, $J = 8.3$ Hz, 2H), 7.42 – 7.29 (m, 7H), 6.93 – 6.85 (m, 2H), 4.25 – 4.20 (m, 2H), 3.81 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.2, 159.0, 139.9, 138.9, 133.1 (d, $J = 32.7$ Hz), 130.7, 130.2, 130.1, 129.5, 128.5, 128.0, 124.9 (q, $J = 3.7$ Hz), 122.1, 114.0, 64.5, 55.2, 41.9.

HRMS (ESI) $m/z$ calculated for C$_{23}$H$_{19}$BrF$_3$O$_2$ [M+H$^+$] 463.0515, found 463.0523.

8. Reference

China.


The image contains a chemical structure labeled as 2b, along with a spectrum graph. The spectrum graph shows peaks at various ppm values, indicating chemical shifts. The peaks are labeled with chemical shifts ranging from 0 ppm to 5 ppm, with intensity values ranging from 0 to 40,000.
2k
2o
cc-E20f-3.5_TiO2

![NMR Spectrum](image)

**Chemical Shifts:**
- 196.22
- 137.33
- 132.10
- 128.79
- 128.65
- 77.32
- 77.00
- 76.69
- 63.88
- 36.16

**Structural Formula:**

![Chemical Structure](image)
Cl-gc-20181009.2.fid

cc-Cl-gc-20181009.2.fid

18.39 31.57 37.72 49.74 58.44 76.69 77.00 77.32 126.84 127.86 128.91 136.78 216.49 67

18.39 31.57 37.72 49.74 58.44 76.69 77.00 77.32 126.84 127.86 128.91 136.78 216.49 67