Supplementary Information

Olefin Epoxidation using Electricity as Renewable Power in a Bromide-Mediated Electrochemical Process

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1. General Information

Sample preparation for chromatography: 150 µl product mixture, 1350 µl ethanol, and 20 µl octane as the internal standard.

Preparation of reference epoxide products: To a 0.022 M solution of the substrate in 6 mL CH_2Cl_2, 0.022 M meta-chloroperoxybenzoic acid (mCPBA) was added. After stirring for 60 minutes at room temperature, the epoxide is formed in large yield.

Gas chromatography (GC) yields were determined using a Shimadzu GC-2014 equipped with a CP-SIL 8 CB column (Agilent, 60 m, 0.25 µm film thickness, 0.32 mm ID). Samples of 1 µl were injected automatically with an AOC-20s auto sampler and AOC-20i auto-injector aided by the GCsolution software bundle (version 2.44.00). Products were identified on an Agilent 6890 gas chromatograph equipped with a HP 1 MS column and coupled to a 5973 MSD mass spectrometer. The hydrogen was identified on a Shimadzu GC-2014 equipped with INJ-MTN column.

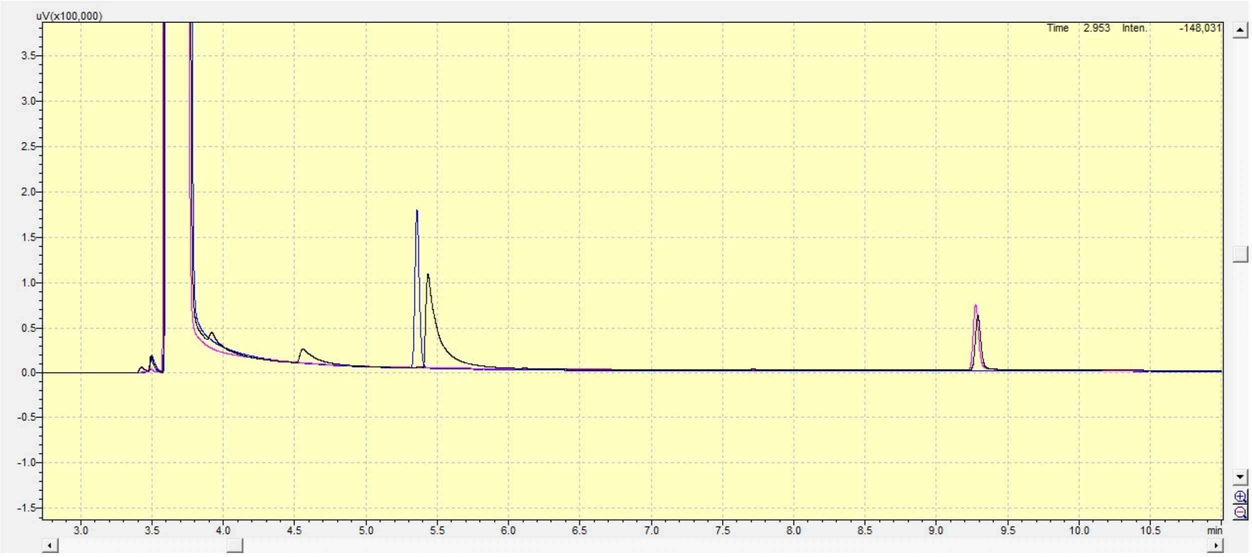
Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) curves were obtained on a Princeton Applied Research VersaSTAT 3 electrochemical workstation and VersaStudio software. Solutions of **1a** (0.1 mmol) in $MeCN/H_2O$ = 6:4 (10 ml), NaBr (0.5 mmol), Et_4NBF_4 (0.67 mmol) as electrolyte were recorded at room temperature with a scan rate of 200 mV/s using a glassy carbon disk or a platinum disk anode (diameter 1 mm), a platinum wire cathode and SCE reference electrode.

^{1}H and ^{13}C NMR were recorded at room temperature, using a Bruker Avance III HD 400 (400 MHz) equipped with a 5 mm PABBO BB/^{19}F-^{1}H/D probe. As solvent, $CDCl_3$ was used in all cases.

Potential of hydrogen (pH) was measured to follow pH changes by using a VWR Symphony SB70P pH meter or VWR Dosatest pH test strips.

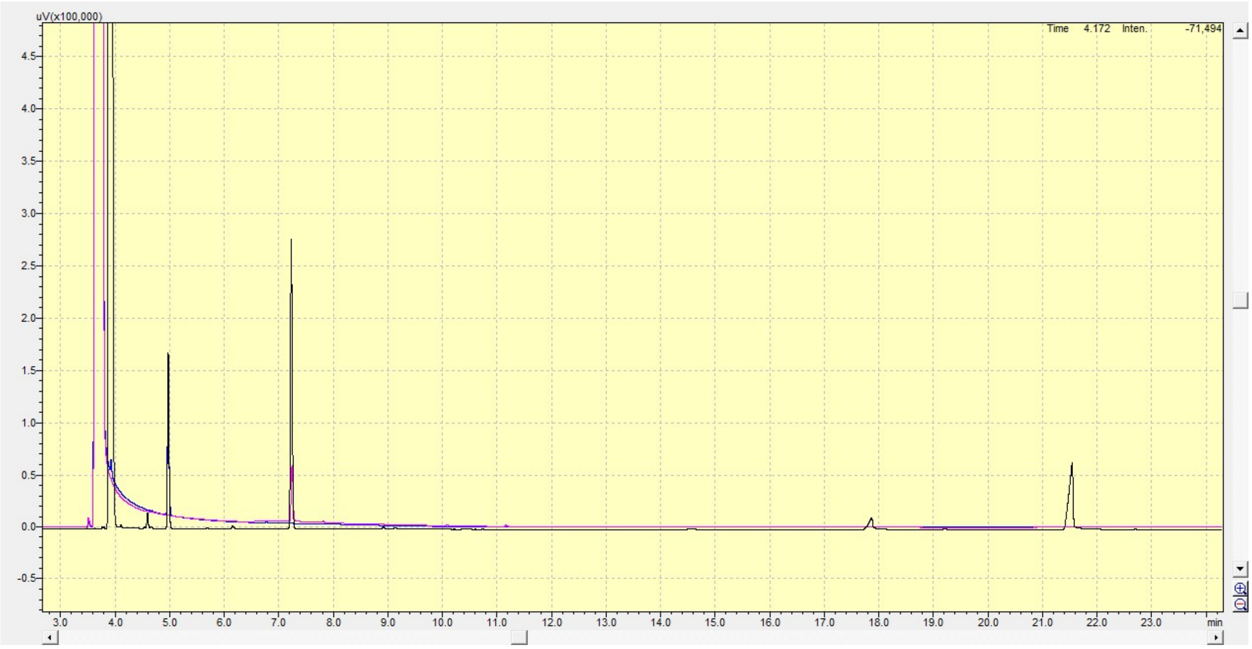
Exemplary chromatogram for cyclohexene:

Blue trace: solution of cyclohexene (reference at 5.35 min); Pink trace: solution of cyclohexene oxide (reference, 9.28 min); Black trace: reaction mixture, with cyclohexene oxide (at 9.29 min) and octane (at 5.44 min).



Exemplary chromatogram for 1-methyl-1-cyclopentene:

Blue trace: solution of 1-methyl-1-cyclopentene (reference at 4.98 min); Pink trace: electrocatalysis of 1-methyl-1-cyclopentene reaction, with 1-methyl-1-cyclopentene oxide (reference at 7.24 min); Black trace: mCPBA reaction mixture, with 1-methyl-1-cyclopentene (at 4.98 min), 1-methyl-1-cyclopentene oxide (at 7.24 min), and mCPBA (at 21.54 min).



The reaction mixture was analyzed by GC and GC-MS to identify the product compounds, and to determine conversion and selectivity. The conversion, yield, selectivity and Faradaic efficiency values were calculated as follows:

$$Conversion\ (\%) = \frac{N_{con}}{N_{ini}}\ x\ 100\%$$

where N_{con} and N_{ini} are the consumed and initial substrate moles, respectively.

The yield of cyclohexene oxide was calculated as follows:

$$Yield\ (\%) = \frac{N_{desired\ epoxide}N_{yield}}{N_{initial\ olefin}}\ x\ 100\%$$

where $N_{desired\ epoxide}$ and $N_{initial\ olefin}$ are the moles of epoxide obtained and of initial olefin, respectively.

The selectivity for an epoxide like cyclohexene oxide was calculated as follows:

$$Selectivity\ (\%) = \frac{Yield_{epoxide}}{Conversion_{olefin}}\ x\ 100\%$$

The Faradaic efficiency of cyclohexene oxide was calculated as follows:

$$FE\ (\%) = \frac{N_i\ n\ F}{Q}\ x\ 100\%$$

where N_i is the moles of the product i; n is the number of electrons transferred per mole of product generated (2 electrons in this system); F is the Faradaic constant of 96487 C mol^{-1}; Q is the total passed charge.

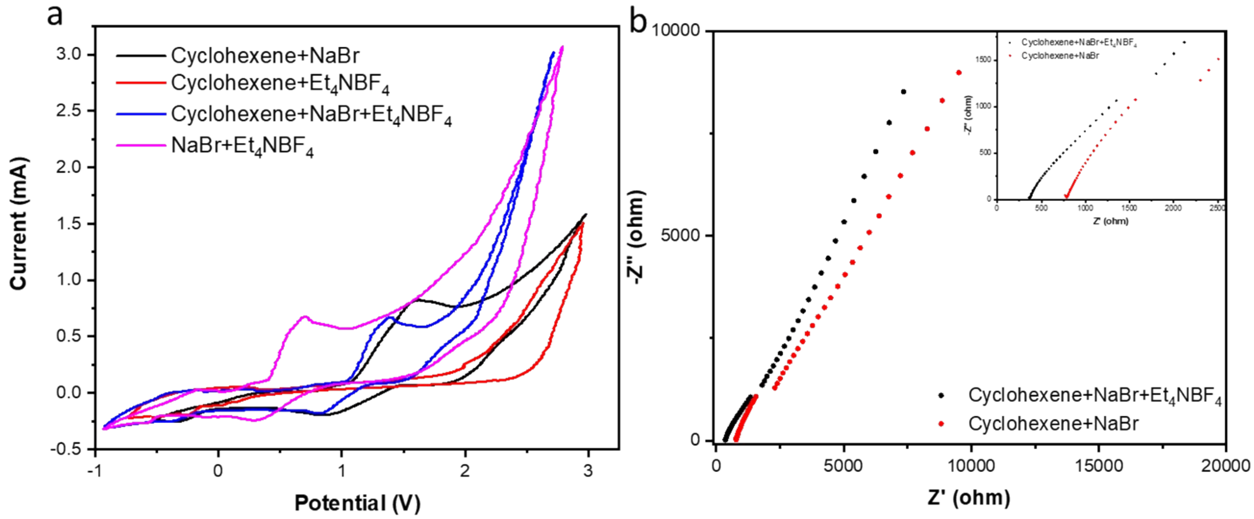


Figure S1 Cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS) on a platinum plate cathode, and a SCE reference electrode at 200 mV/s under nitrogen, MeCN:H_2O (3:2, 6 ml). a) with a platinum wire as anode (1 mm diameter); b) EIS data with a platinum wire as anode (1 mm diameter).

Discussion of the cyclic voltammetry and EIS measurements: For various compositions of the reaction mixture, i.e. the solvent plus added

- NaBr and cyclohexene,
- NaBr, Et_4NBF_4 and cyclohexene,

the voltammograms show an anodic bromide oxidation peak; this peak is not observed when only Et_4NBF_4 and cyclohexene are present.

Additionally, one remarks in the CV of the reaction mixture containing both NaBr and Et_4NBF_4 (blue curve in Figure S1, a) that the current increases steeply when the voltage is further increased. This indicates that particularly under these conditions, the oxidized Br-species (e.g. HOBr) eventually react with the olefin, regenerating in the process the bromide (Br^-) which is then available to be oxidized again at the anode. This catalytic process gives rise to the clearly enhanced anodic current in Figure S1, a.

In addition we also studied the system by electrical impedance spectroscopy (Figure S1, b). The Nyquist plot clearly shows the effect of the addition of Et_4NBF_4: in its presence, the resistance of the system decreases. As an electrolyte, Et_4NBF_4 dissolves very well in the aqueous-organic solvent CH_3CN-H_2O, resulting in a lower resistance, which makes the reaction easier.

2 Procedures for the epoxide formation

For the optimal reactions, the reactor was equipped with two platinum foils as anode and cathode, respectively. In a glass reactor, cyclohexene (**1a**, 0.45 mmol, 1 equiv.) as the model substrate, sodium bromide (NaBr, 1.5 equiv.) and tetraethylammonium tetrafluoroborate

(Et_4NBF_4, 2 equiv.) as the electrolyte, acetonitrile (MeCN) and deionized water (H_2O) as solvent (6 ml, 3:2) were added. The starting pH was 7.02.

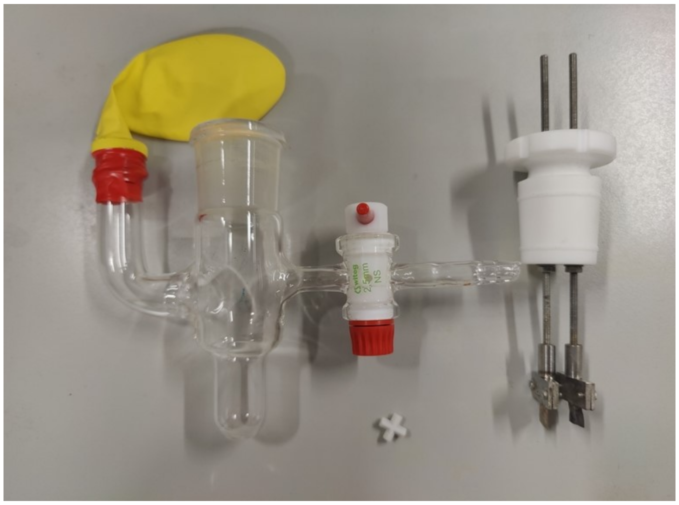
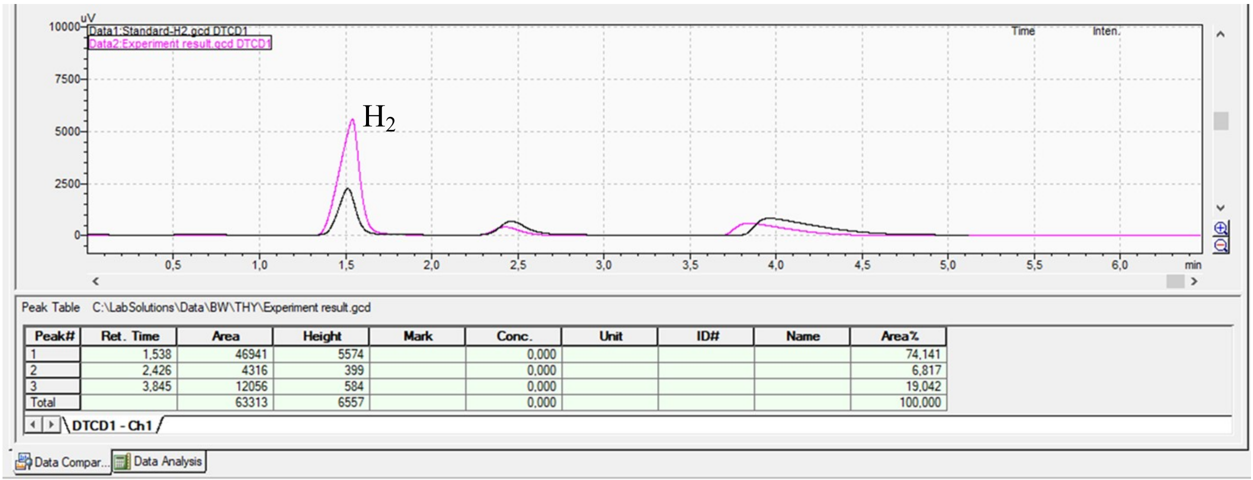


Figure S2. Glass reactors for the electrocatalytic formation of epoxides.

Figure S3. pH changes measured over the course of a typical reaction.



Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Name	Area%
1	1,538	46941	5574		0,000				74,141
2	2,426	4316	399		0,000				6,817
3	3,845	12056	584		0,000				19,042
Total		63313	6557		0,000				100,000

Figure S4. Detection of hydrogen evolution with gas chromatography. (Black trace is the H_2 standard-H_2 (reference at 1.53 min); the pink trace results from injection of the gas atmosphere in the headspace of the electrochemical reactor.

H_2 was identified on a Shimadzu GC-2014 equipped with INJ-MTN column.

3. Gram-scale experiment:

1) Electrocatalytic epoxidation protocol: For the gram-scale experiment, the reactor was equipped with two platinum foils as anode and cathode, respectively. In a round bottom flask, cyclohexene (**1a**, 10 mmol, 1 equiv.), sodium bromide (NaBr, 1.5 equiv.) and tetraethylammonium tetrafluoroborate (Et_4NBF_4, 2 equiv.) as the electrolyte were added, together with acetonitrile (MeCN) and deionized water (H_2O) as solvent (133.4 ml, 3:2). The electrocatalytic experiments were controlled by a power supply at 7.5 mA cm^{-1}, and the total passed charge was 2.02 faraday per mole, over a period of 72 h (Figure S5).

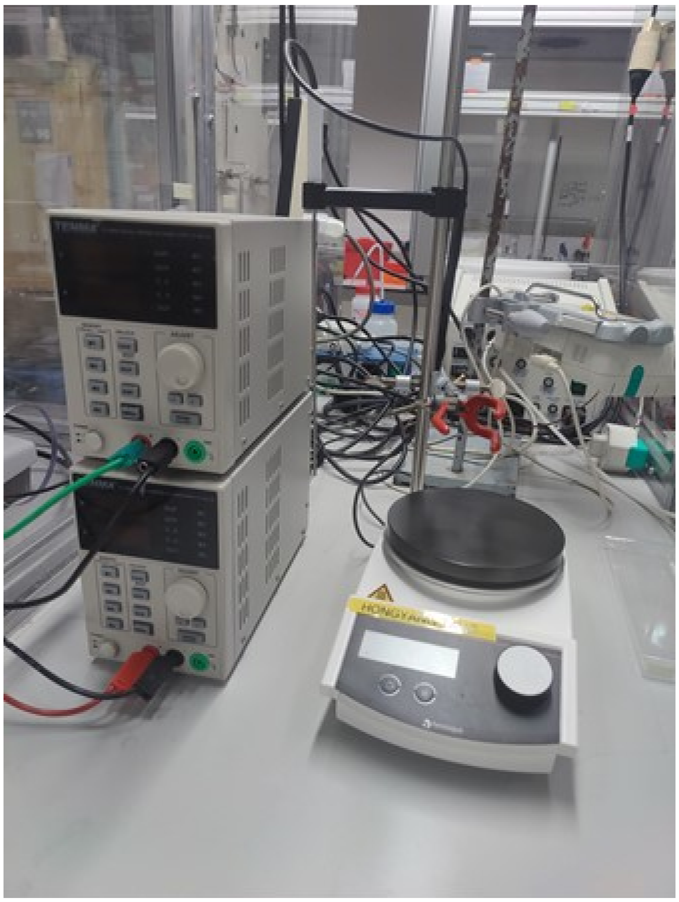
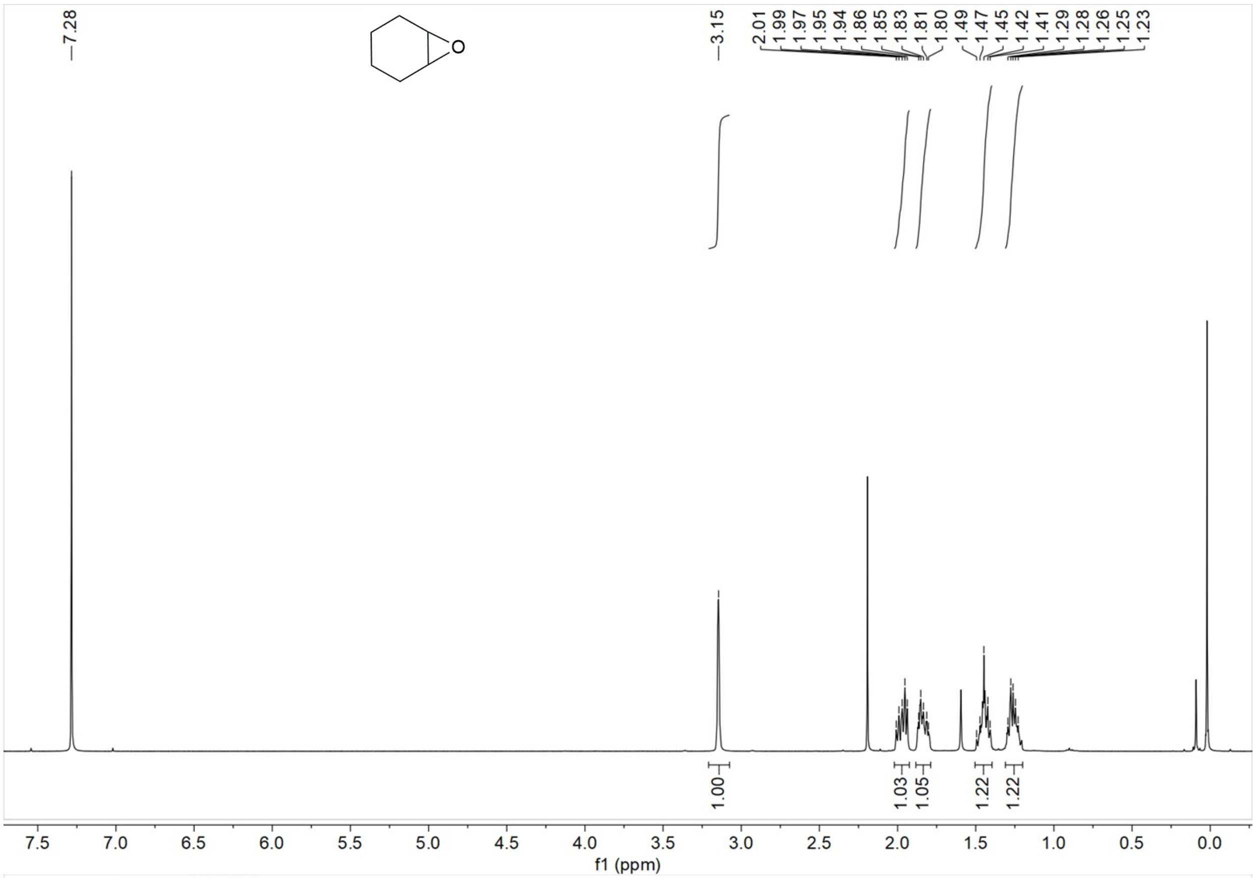


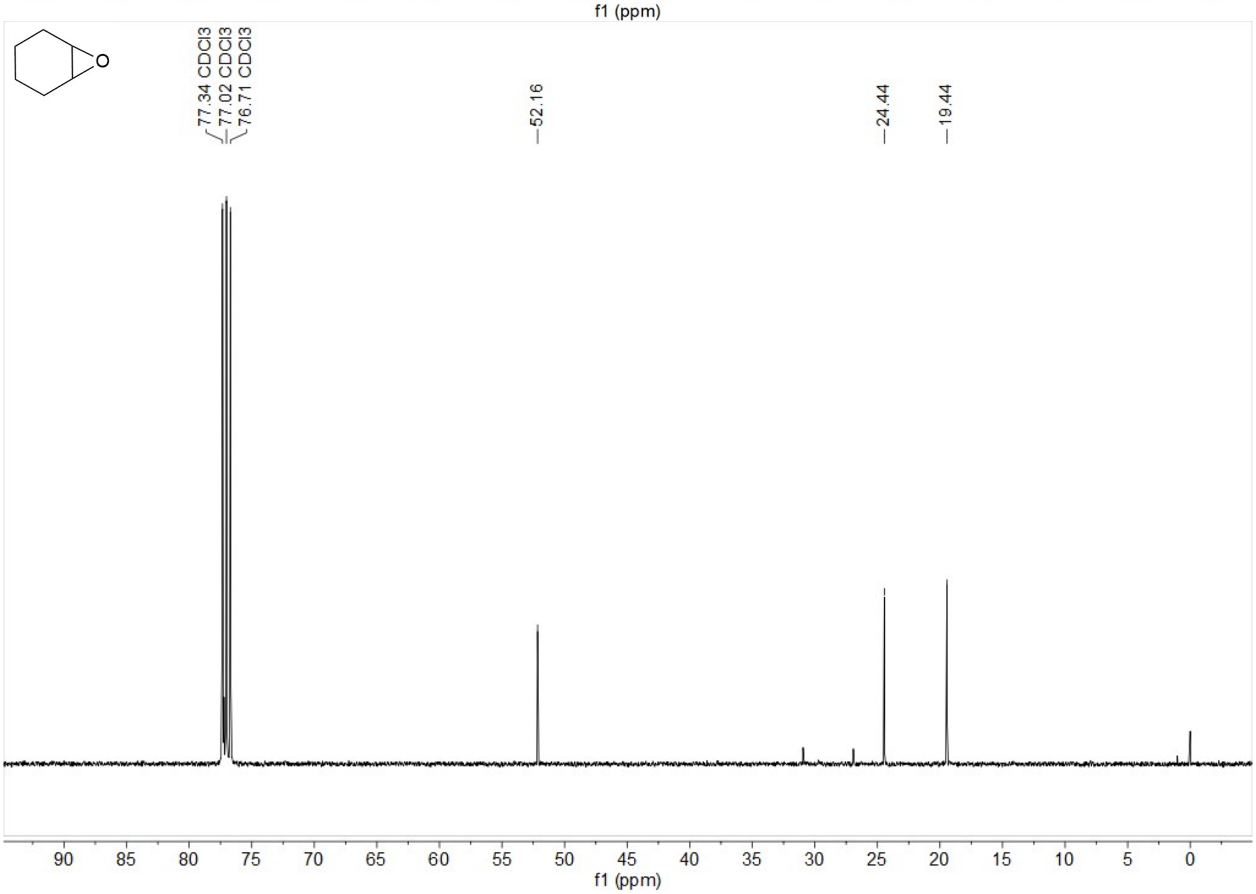
Figure S5. Power supply and magnetic stirrer for the electrocatalytic formation of epoxides.

2) Work-up: A work-up procedure was designed to obtain pure epoxides. After the gram-scale experiment under standard conditions, the product solution was transferred to a separatory funnel. Then, cyclohexane was added and the polar layer, containing mainly H_2O and acetonitrile was removed by extraction. Next, the apolar cyclohexane layer was dried with $MgSO_4$. Finally , the cyclohexane solvent was removed with the rotary evaporator (40°C).

3) Analysis by NMR: The resulting oily product was analyzed with ^{1}H NMR and ^{13}C NMR in $CDCl_3$.



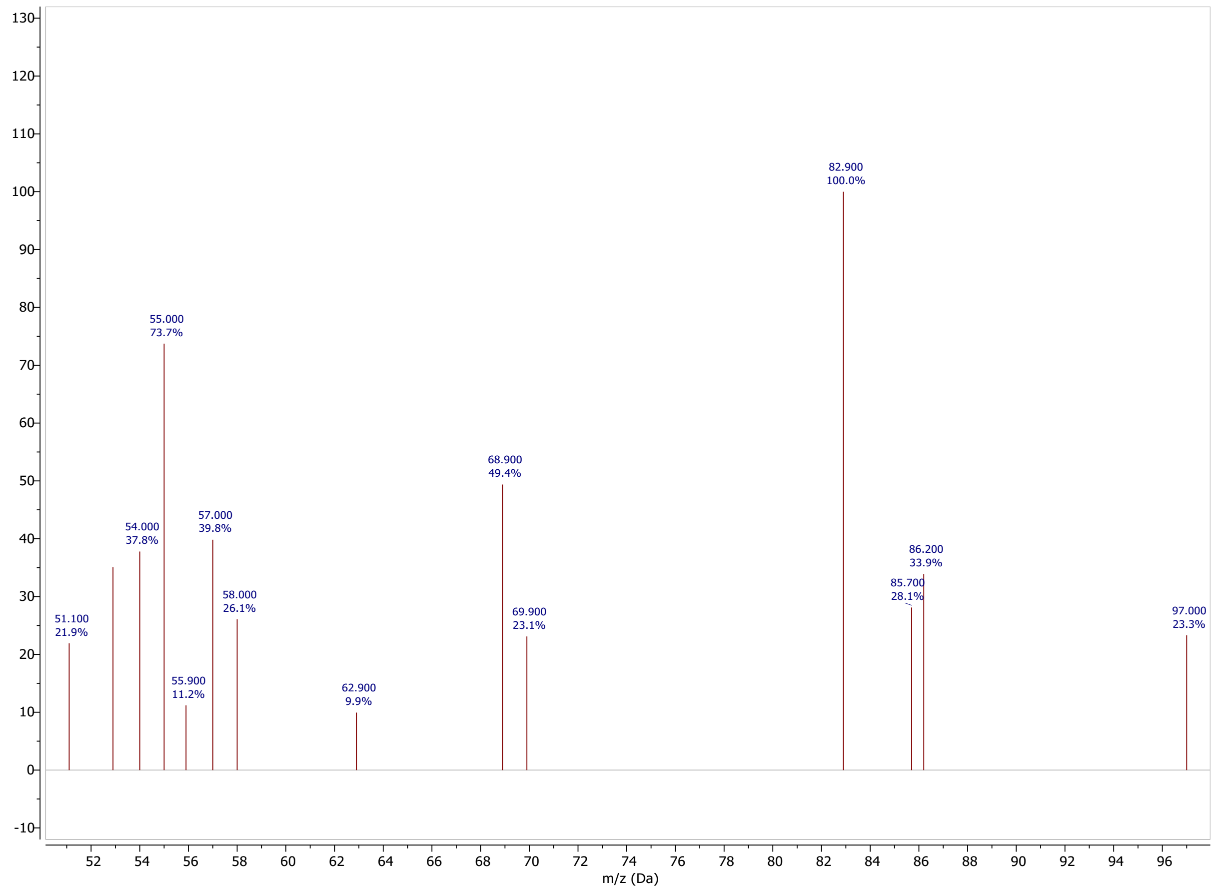
7.28
3.15
2.01
1.99
1.97
1.95
1.94
1.86
1.85
1.83
1.81
1.80
1.49
1.47
1.45
1.42
1.41
1.29
1.28
1.26
1.25
1.23
O
1.00
1.03
1.05
1.22
1.22
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



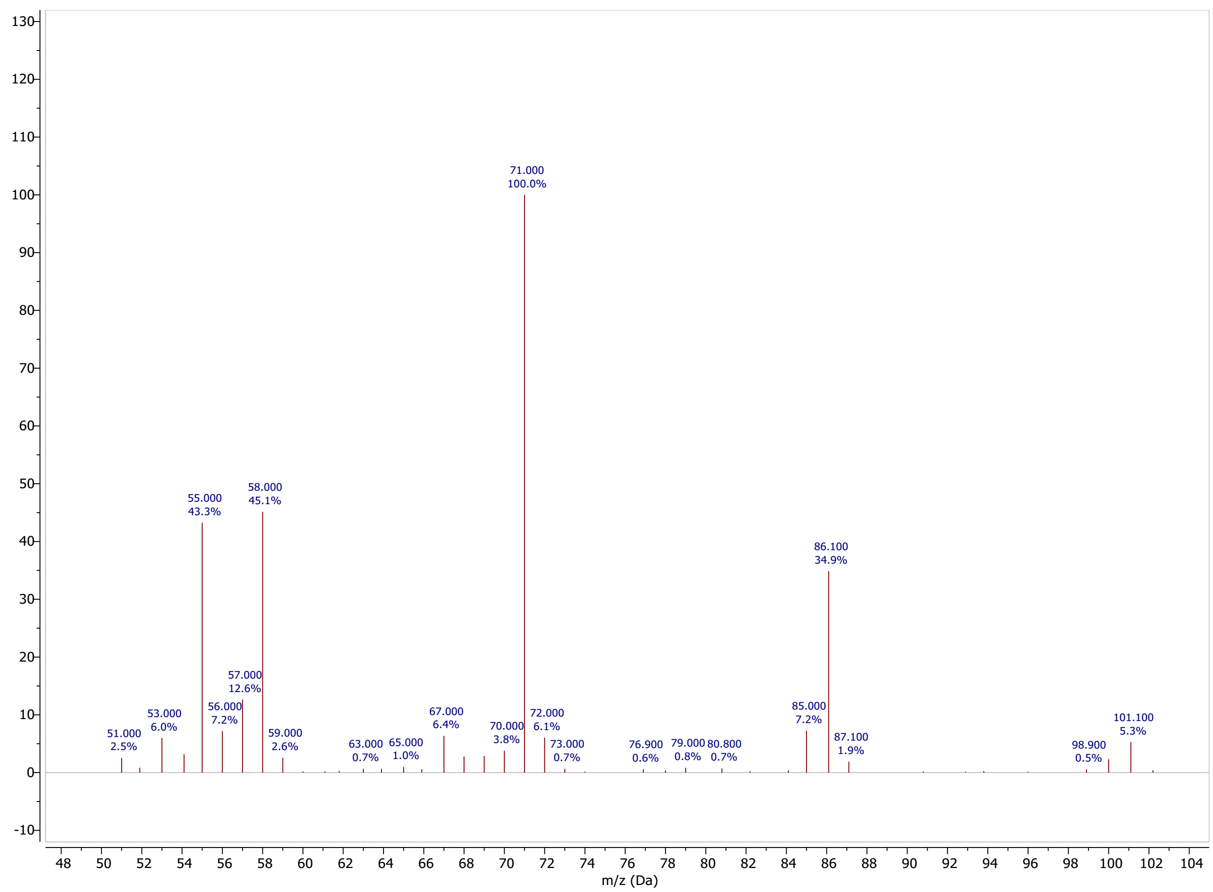
O
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
52.16
24.44
19.44
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

Cyclohexene oxide (1b): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (400 MHz, Chloroform-*d*) = 3.15 (2 H, m), 1.97 (m, 2 H), 1.88 – 1.79 (m, 2H), 1.50 – 1.40 (m, 2H), 1.26 (m, 2H). δ_C (101 MHz, Chloroform-*d*) = 52.16, 24.44, 19.44.

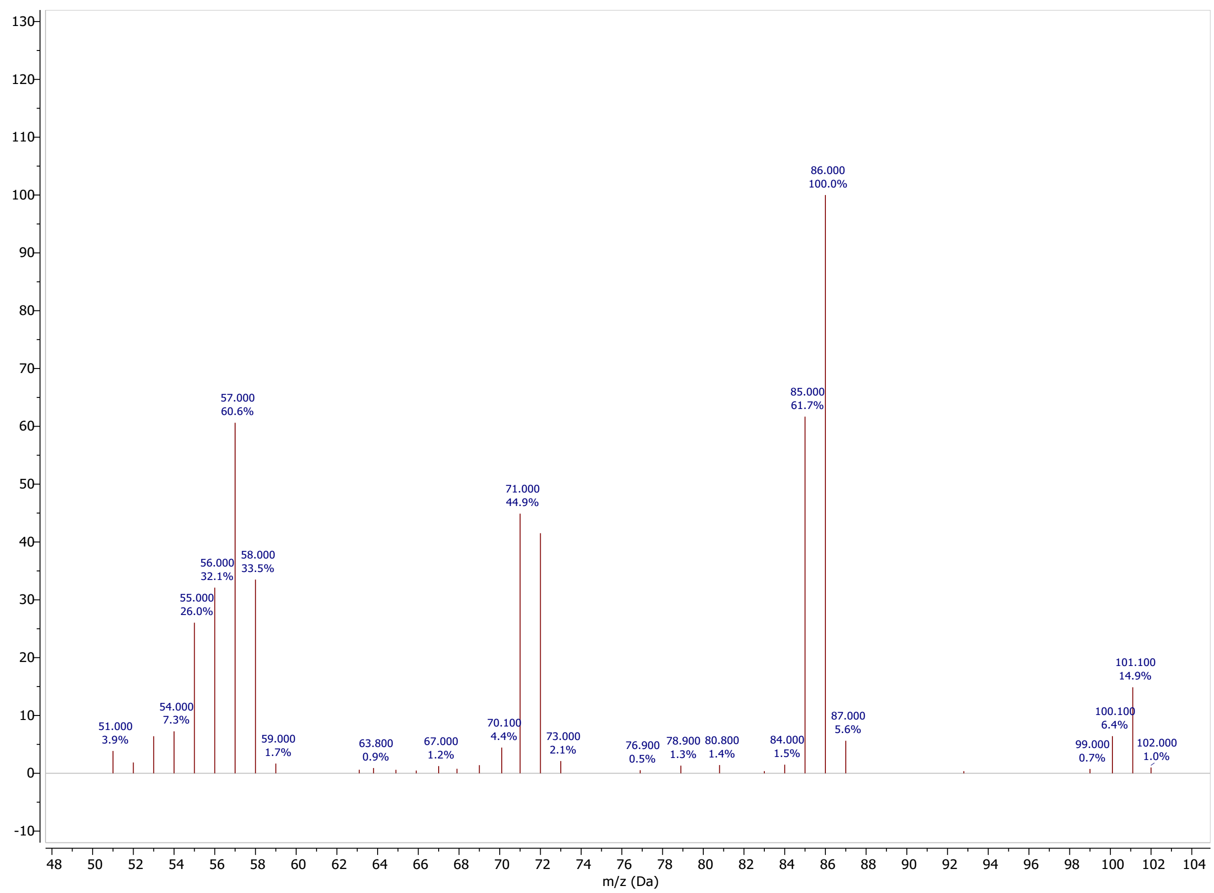
4. Characterization Data of Products



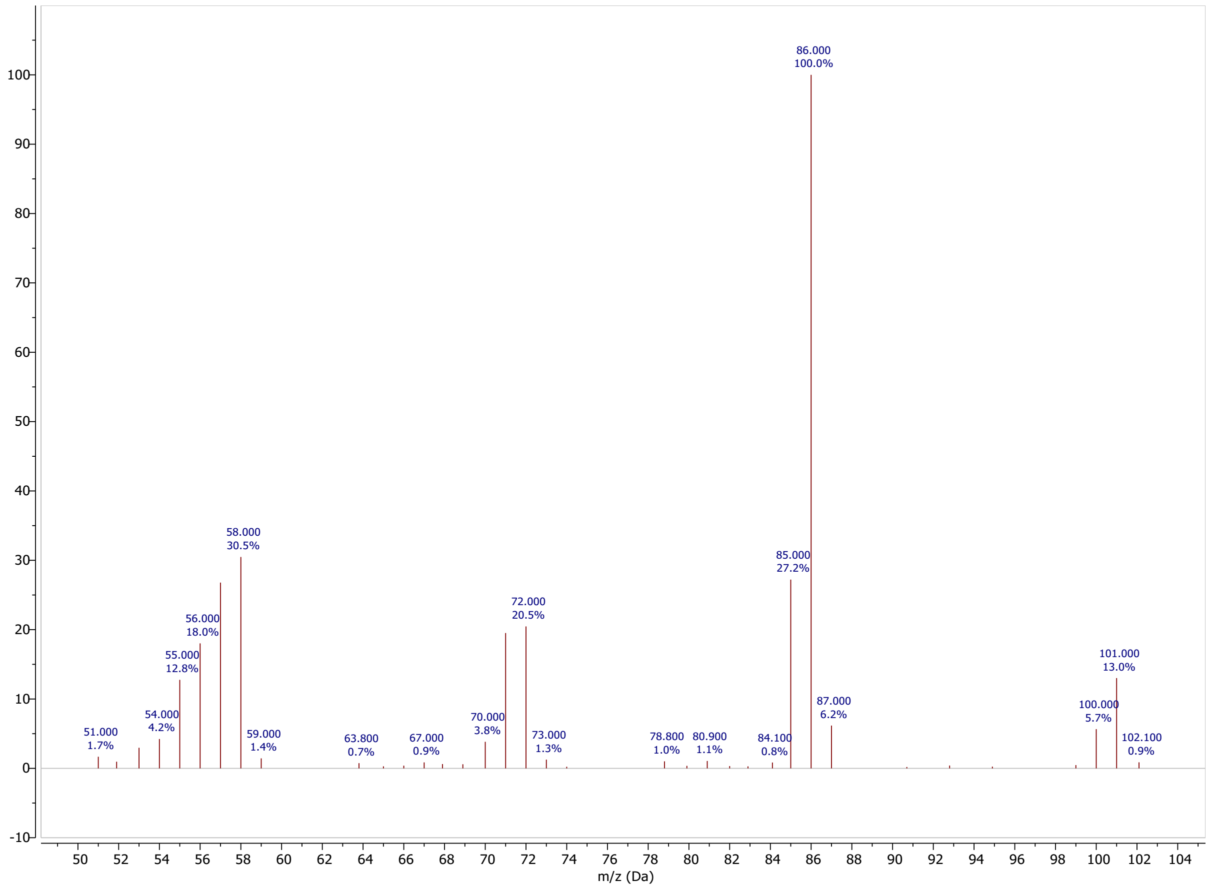
1,2-epoxycyclohexane (1b): GC-MS (EI, 70 eV): *m/z* (rel int., %): 51.1 (21.9), 52.9 (35.1), 54.0 (37.8), 55.0 (73.7), 55.9 (11.2), 57.0 (39.8), 58.0 (26.1), 62.9 (9.9), 68.9 (49.4), 69.9 (23.1), 82.9 (100.0), 85.7 (28.1), 86.2 (33.9), 97.0 (23.3).



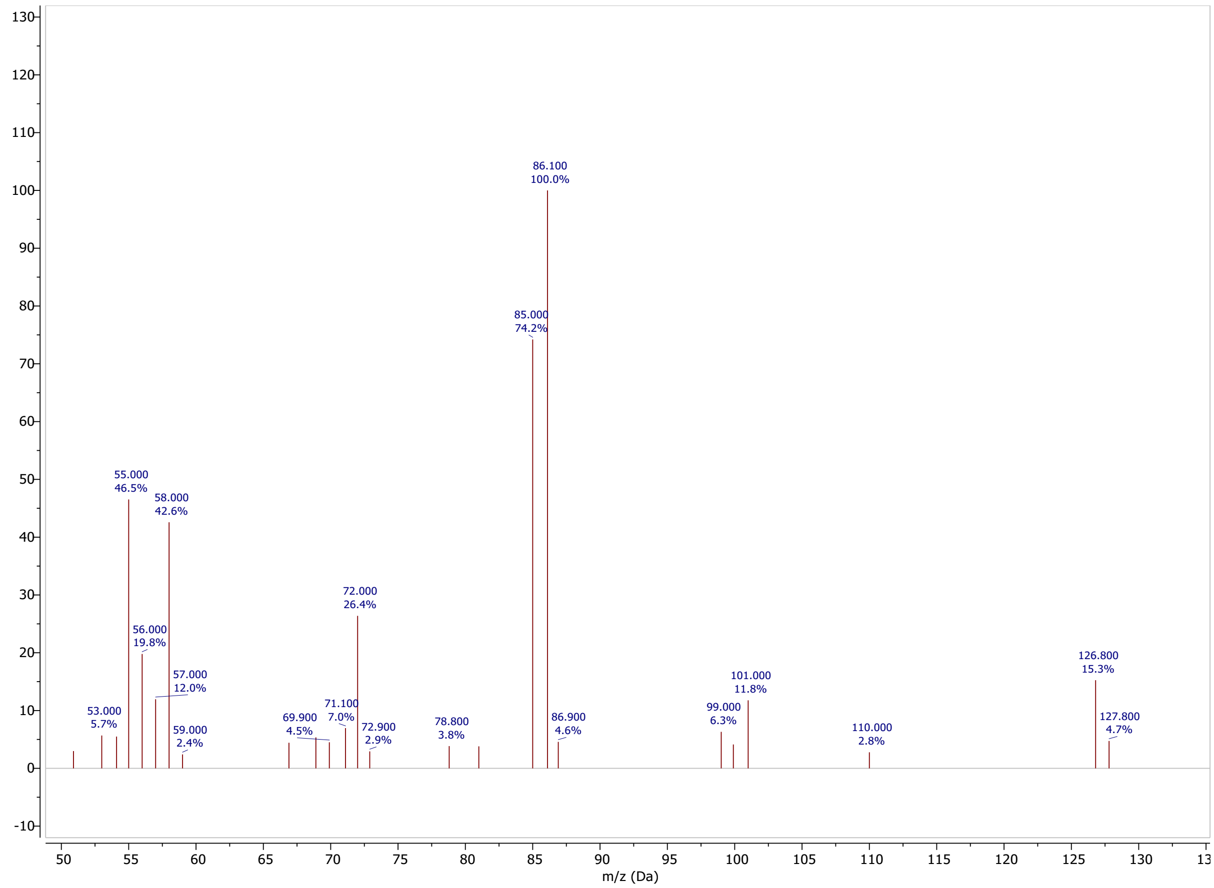
1,2-epoxyhexane (1): GC-MS (EI, 70 eV): *m/z* (rel int., %): 53.0 (6.0), 55.0 (43.3), 56.0 (7.2), 57.0 (12.6), 58.0 (45.1), 67.0 (6.4), 71.0 (100.0), 72.0 (6.1), 85.0 (7.2), 86.1 (34.9), 101.1 (5.3).



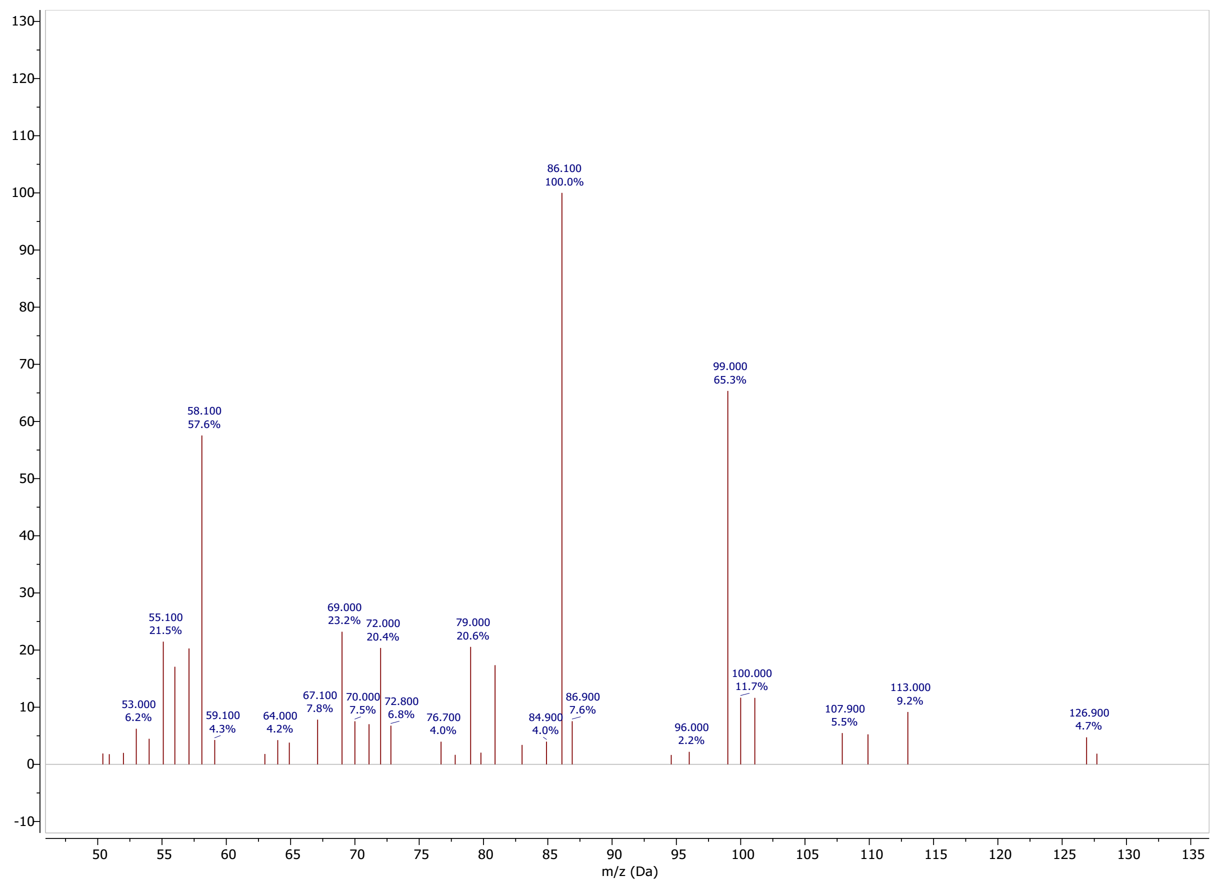
***Cis*-2,3-epoxyhexane (2)**: GC-MS (EI, 70 eV): *m/z* (rel int., %): 53.0 (6.4), 54.0 (7.3), 55.0 (26.0), 56.0 (32.1), 57.0 (60.6), 58.0 (33.5), 71.0 (44.9), 72.0 (41.5), 85.0 (61.7), 86.0 (100.0), 87.0 (5.6), 100.1 (6.4), 101.1 (14.9).



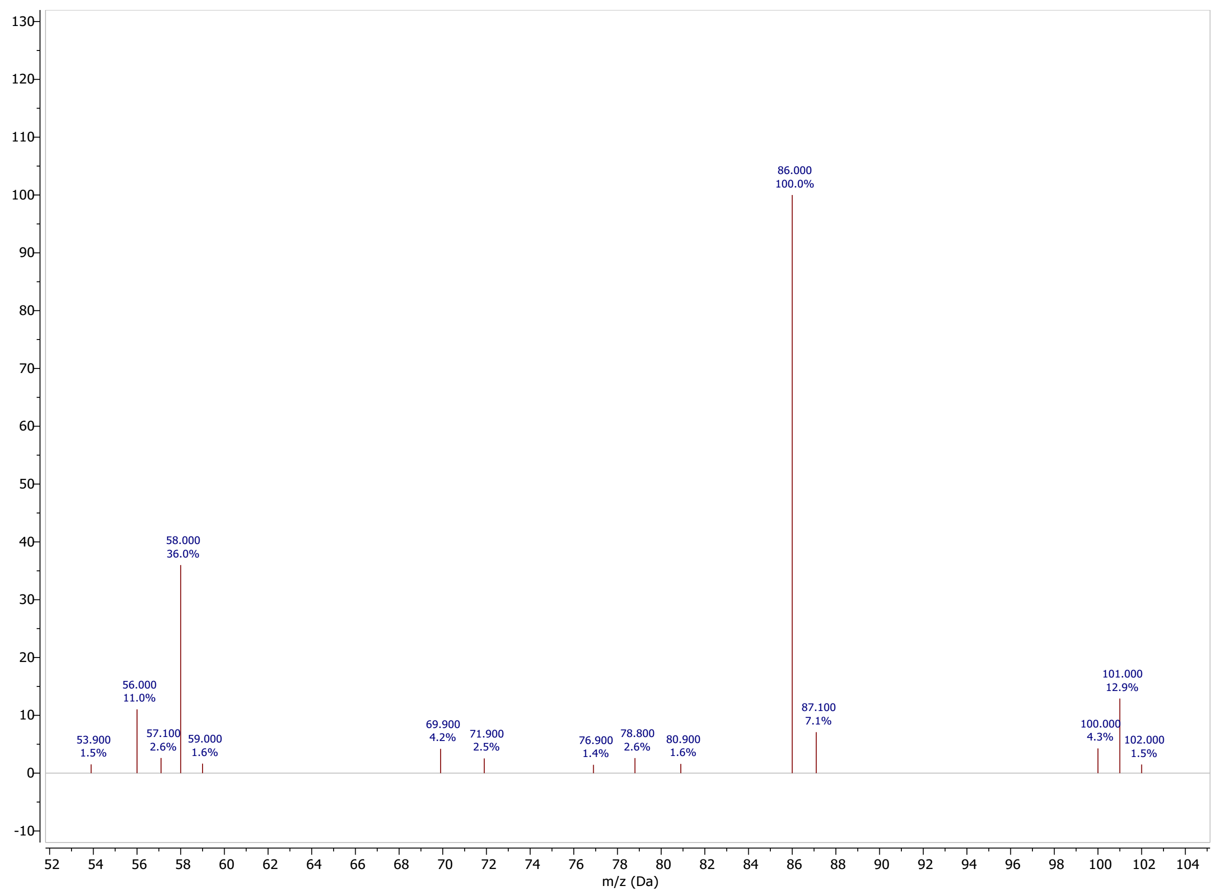
***Trans*-2,3-epoxyhexane (3)**: GC-MS (EI, 70 eV): *m/z* (rel int., %): 55.0 (12.8), 56.0 (18.0), 57.0 (26.8), 58.0 (30.5), 71.0 (19.5), 72.0 (20.5), 85.0 (27.2), 86.0 (100.0), 87.0 (6.2), 100.1, (5.7), 101.1 (13.0).



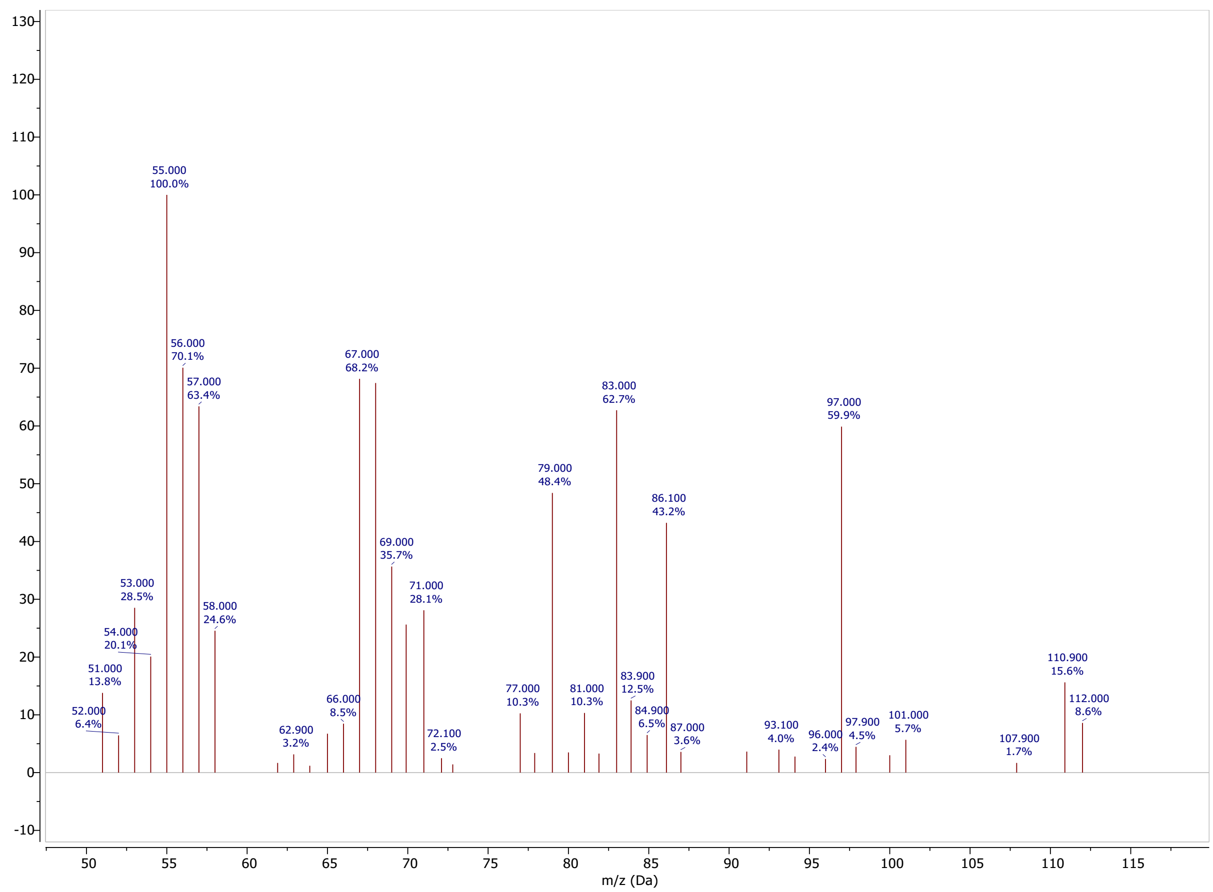
2-methyl-1,2-epoxyhexane (4): GC-MS (EI, 70 eV): *m/z* (rel int., %): 53.0 (5.7), 54.1 (5.5), 55.0 (46.5), 56.0 (19.8), 57.0 (12.0), 58.0 (42.6), 68.9 (5.4), 71.1 (7.0), 72.0 (26.4), 85.0 (74.2), 86.1 (100.0), 99.0 (6.3), 101.0 (11.8), 126.8 (15.3).



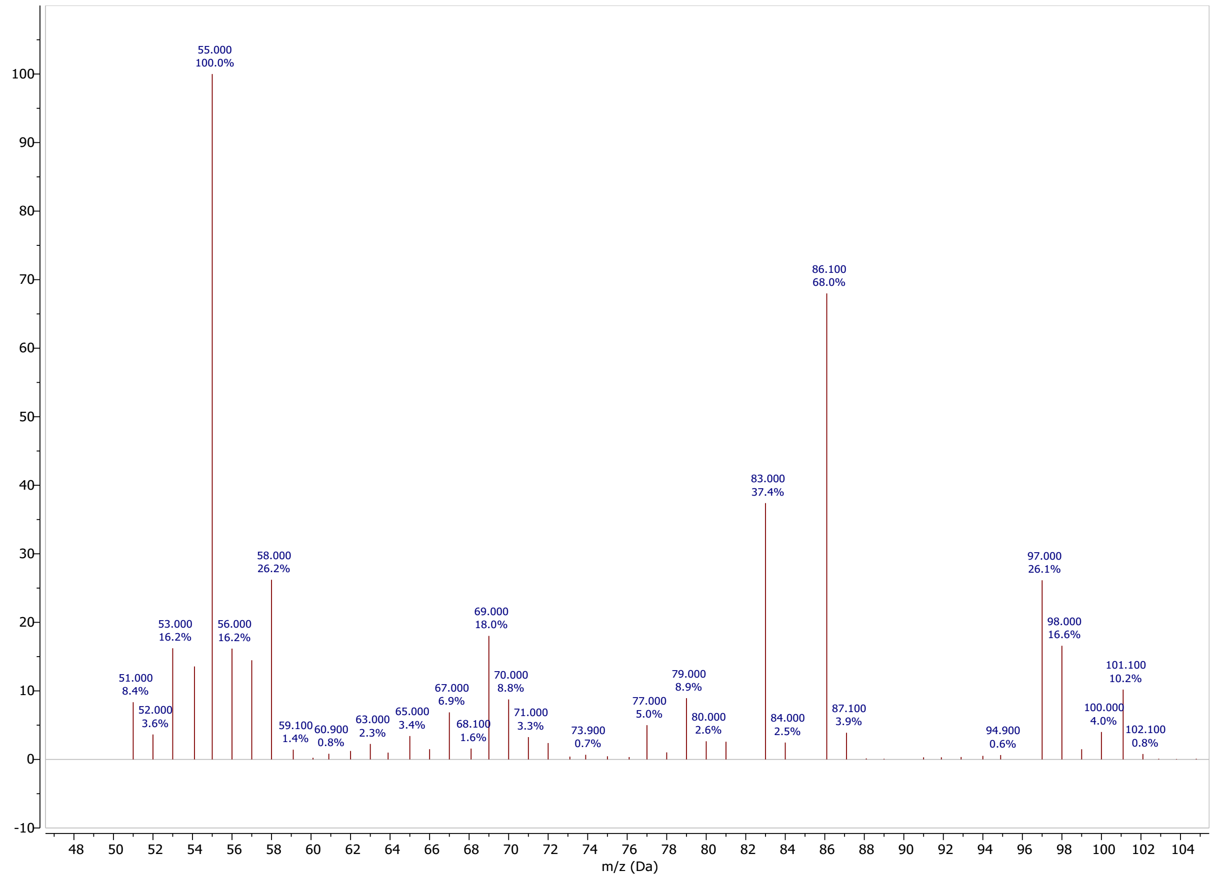
2,4-dimethyl-1,2-epoxyhexane (5): GC-MS (EI, 70 eV): *m/z* (rel int., %): 53.0 (6.2), 54.0 (4.5), 55.1 (21.5), 56.0 (17.1), 57.1 (20.3), 58.1 (57.6), 59.1 (4.3), 64.0 (4.2), 67.1 (7.8), 69.0 (23.2), 70.0 (7.5), 71.1 (7.0), 72.0 (20.4), 72.8 (6.8), 76.7 (4.0), 79.0 (20.6), 80.9 (17.4), 84.9 (4.0), 86.1 (100.0), 86.9 (7.6), 99.0 (65.3), 100.0 (11.7), 101.1 (11.6), 107.9 (5.5), 109.9 (5.3), 113.0 (9.2), 126.9 (4.7).



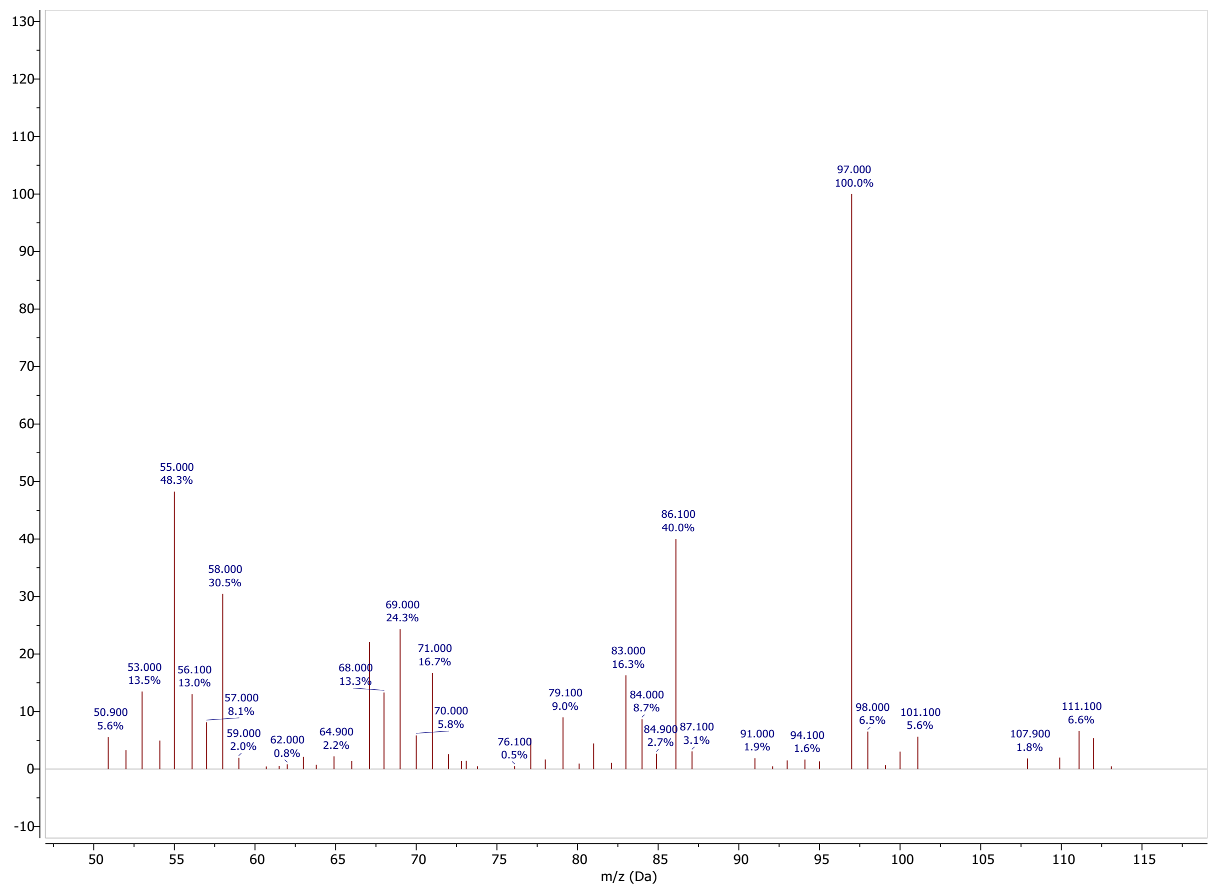
1,2-epoxycyclopentane (6): GC-MS (EI, 70 eV): *m/z* (rel int., %): 56.0 (11.0), 58.0 (36.0), 86.0 (100.0), 87.1 (7.1), 101.0 (12.9).



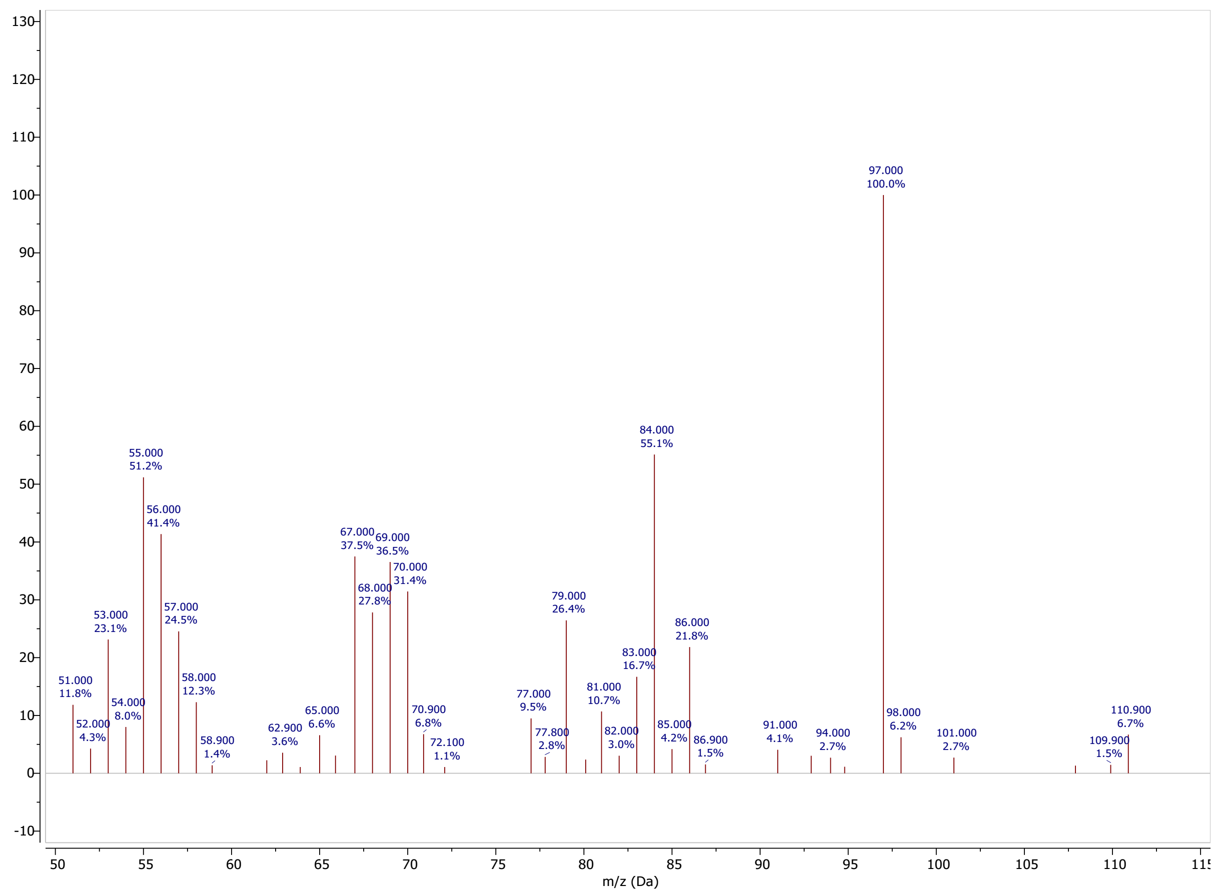
1,2-epoxycycloheptane (7): GC-MS (EI, 70 eV): *m/z* (rel int., %): 51.0 (13.8), 52.0 (6.4), 53.0 (28.5), 54.0 (20.1), 55.0 (100.0), 56.0 (70.1), 57.0 (63.4), 58.0 (24.6), 65.0 (6.7), 66.0 (8.5), 67.0 (68.2), 68.0 (67.4), 69.0 (35.7), 69.9 (25.6), 71.0 (28.1), 77.0 (10.3), 79.0 (48.4), 81.0 (10.3), 83.0 (62.7), 83.9 (12.5), 84.9 (6.5), 86.1 (43.2), 97.0 (59.9), 101.0 (5.7), 110.9 (15.6), 112.0 (8.6).



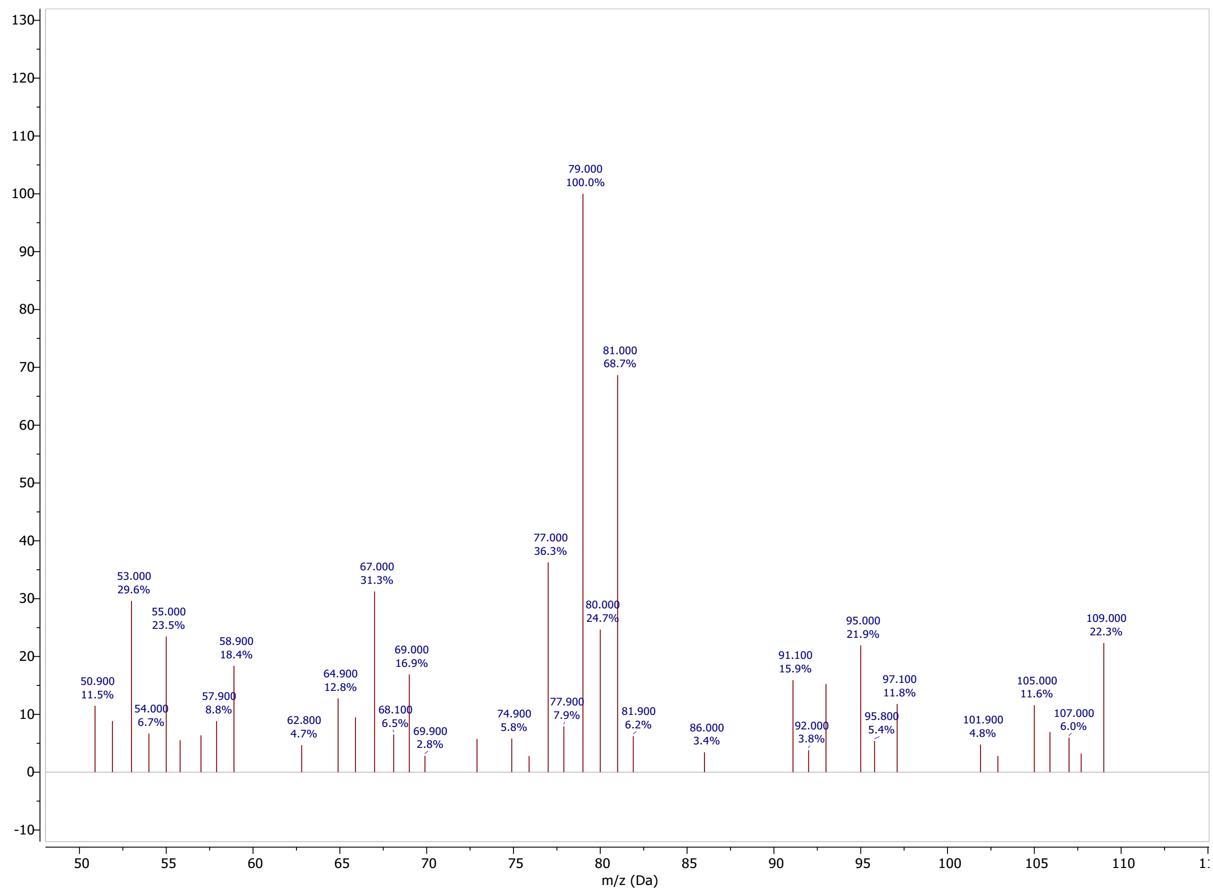
1-methyl-1,2-epoxycyclopentane (8): GC-MS (EI, 70 eV): *m/z* (rel int., %): 51.0 (8.4), 53.0 (16.2), 54.1 (13.6), 55.0 (100.0), 56.0 (16.2), 57.0 (14.5), 58.0 (26.2), 67.0 (6.9), 69.9 (18.0), 70.0 (8.8), 77.0 (5.0), 79.0 (8.9), 83.0 (37.4), 86.1 (68.0), 97.0 (26.1), 98.0 (16.6), 101.1 (10.2).



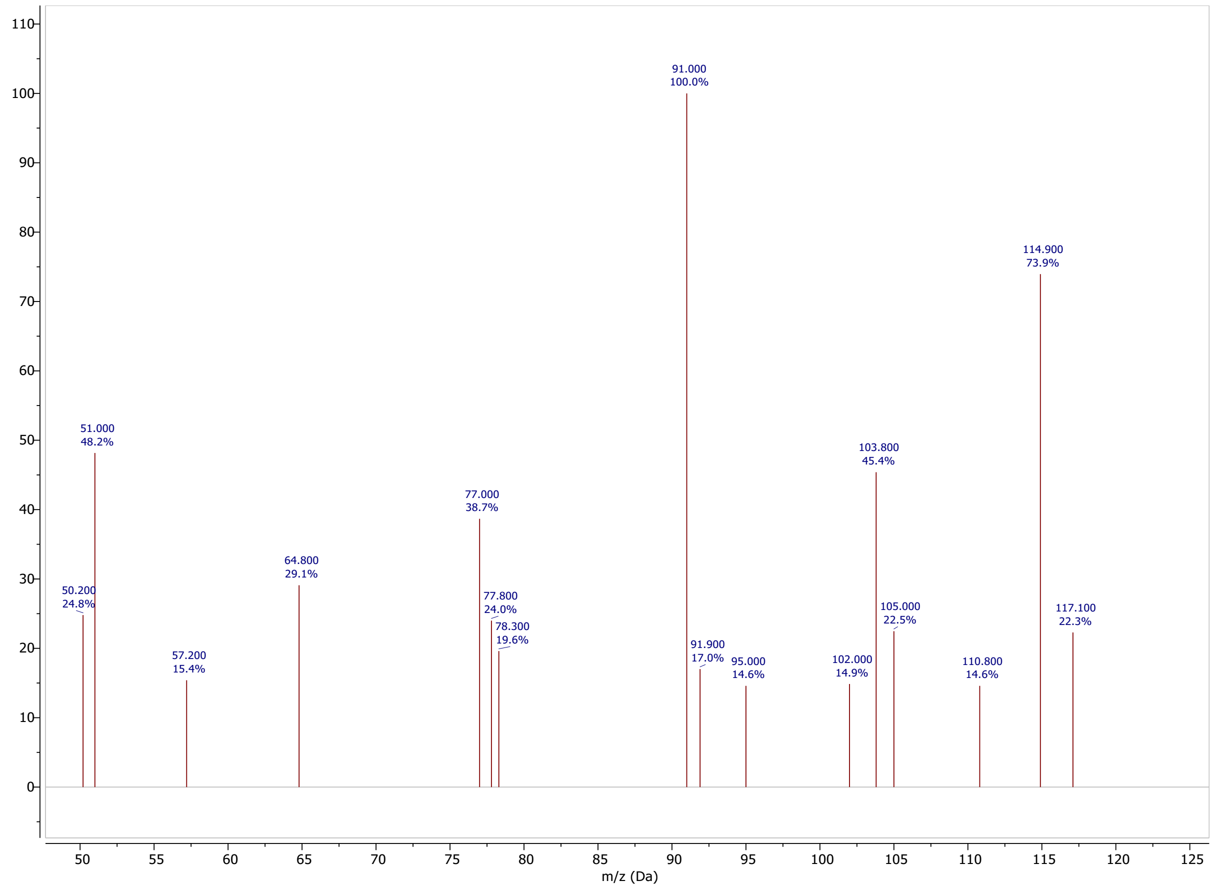
1-methyl-1,2-epoxycyclohexane (9): GC-MS (EI, 70 eV): *m/z* (rel int., %): 50.9 (5.6), 53.0 (13.5), 54.1 (4.9), 55.0 (48.3), 56.1 (13.0), 57.0 (8.1), 58.0 (30.5), 67.0 (22.1), 68.0 (13.3), 69.0 (24.3), 70.0 (5.8), 71.0 (16.7), 77.1 (5.3), 79.1 (9.0), 83.0 (16.3), 84.0 (8.7), 86.1 (40.0), 97.0 (100.0), 98.0 (6.5), 101.1 (5.6), 111.1 (6.6).



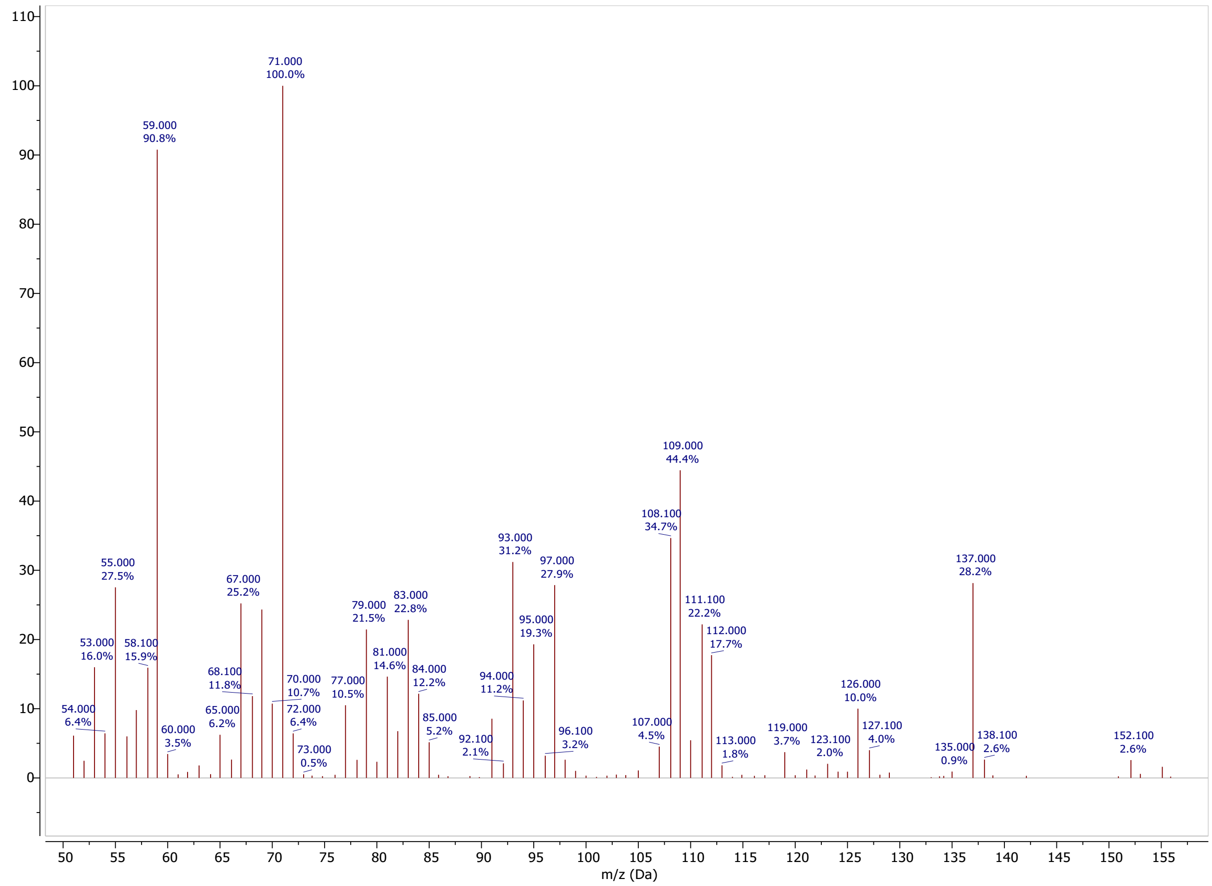
4-methyl-1,2-epoxycyclohexane (10): GC-MS (EI, 70 eV): *m/z* (rel int., %): 51.0 (11.8), 53.0 (23.1), 54.0 (8.0), 55.0 (51.2), 56.0 (41.4), 57.0 (24.5), 58.0 (12.3), 65.0 (6.6), 67.0 (37.5), 68.0 (27.8), 69.0 (36.5), 70.0 (31.4), 70.9 (6.8), 77.0 (9.5), 79.0 (26.4), 81.0 (10.7), 83.0 (16.7), 84.0 (55.1), 86.0 (21.8), 97.0 (100.0), 98.0 (6.2), 110.9 (6.7).



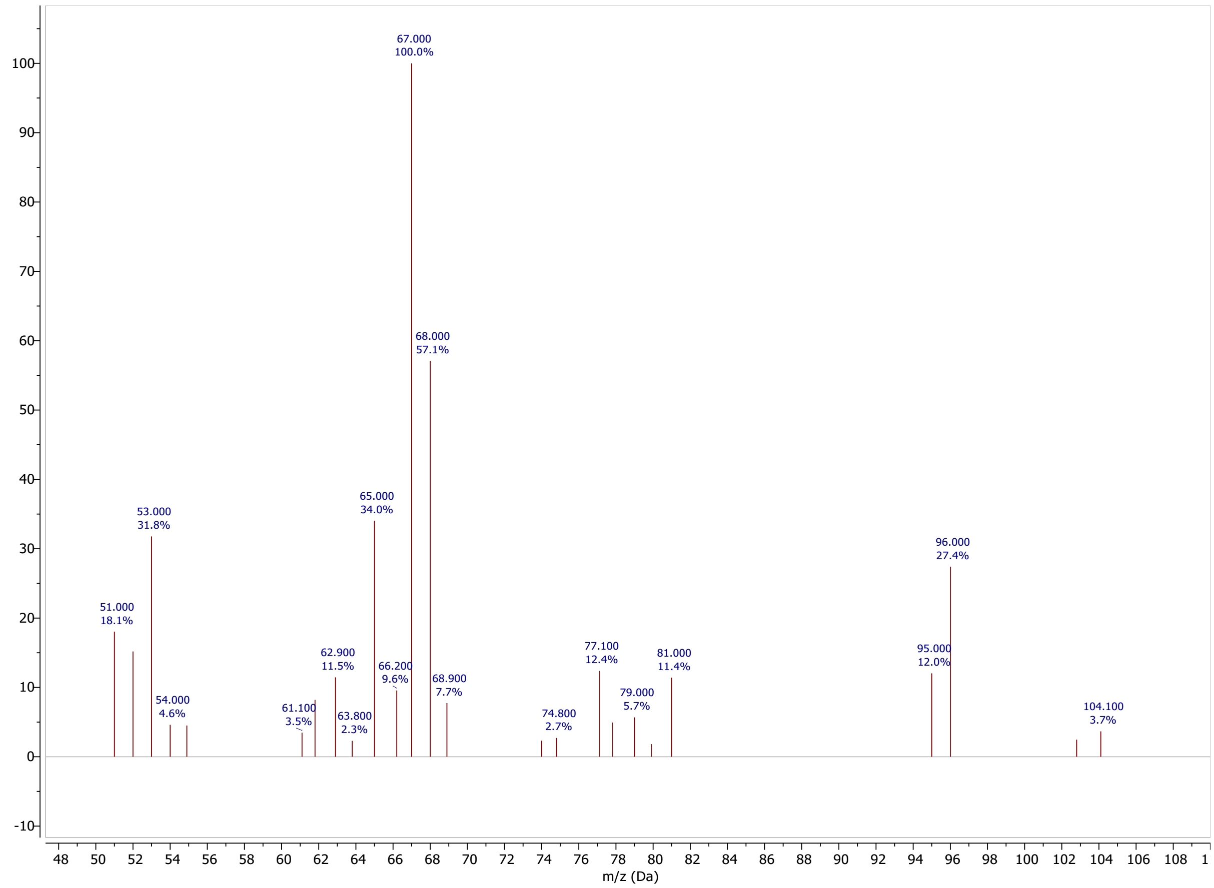
4-vinyl-cyclohexene dioxide (11): GC-MS (EI, 70 eV): *m/z* (rel int., %): 50.9 (11.5), 51.9 (8.8), 53.0 (29.6), 54.0 (6.7), 55.0 (23.5), 55.8 (5.5), 57.0 (6.4), 57.9 (8.8), 58.9 (18.4), 64.9 (12.8), 65.9 (9.5), 67.0 (31.3), 68.1 (6.5), 69.0 (16.9), 72.9 (5.7), 74.9 (5.8), 77.0 (36.3), 77.9 (7.9), 79.0 (100.0), 80.0 (24.7), 81.0 (68.7), 81.9 (6.2), 91.1 (15.9), 93.0 (15.2), 95.0 (21.9), 95.8 (5.4), 97.1 (11.8), 105.0 (11.6), 105.9 (6.9), 107.0 (6.0), 109.0 (22.3).



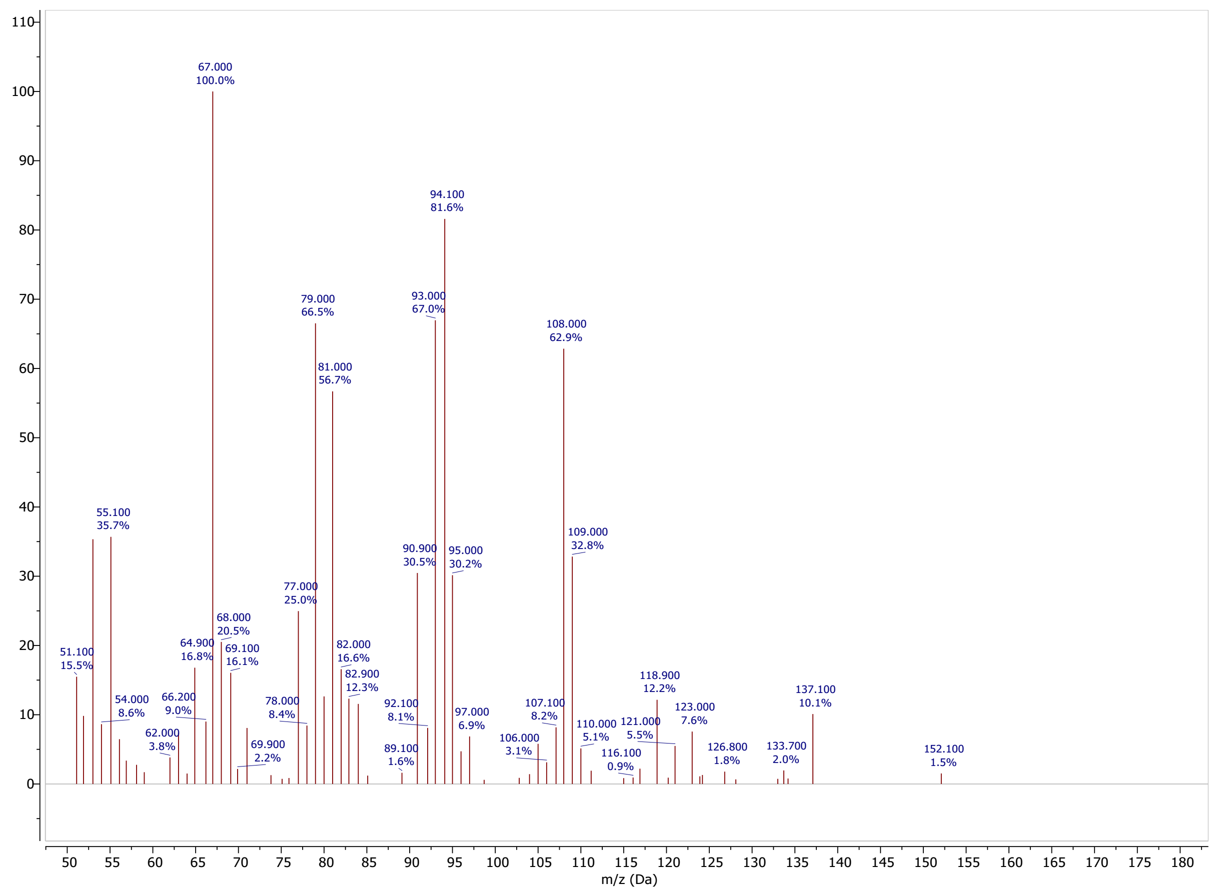
2,2'-dimethyl-2,2'-bioxirane (12): GC-MS (EI, 70 eV): *m/z* (rel int., %): 50.2 (24.8), 51.0 (48.2), 57.2 (15.4), 64.8 (29.1), 77.0 (38.7), 77.8 (24.0), 78.3 (19.6), 91.0 (100.0). 91.9 (17.0), 95 (14.6), 102.0 (14.9), 103.8 (45.4), 105.0 (22.5), 110.8 (14.6), 114.9 (73.9), 117.1 (22.3).



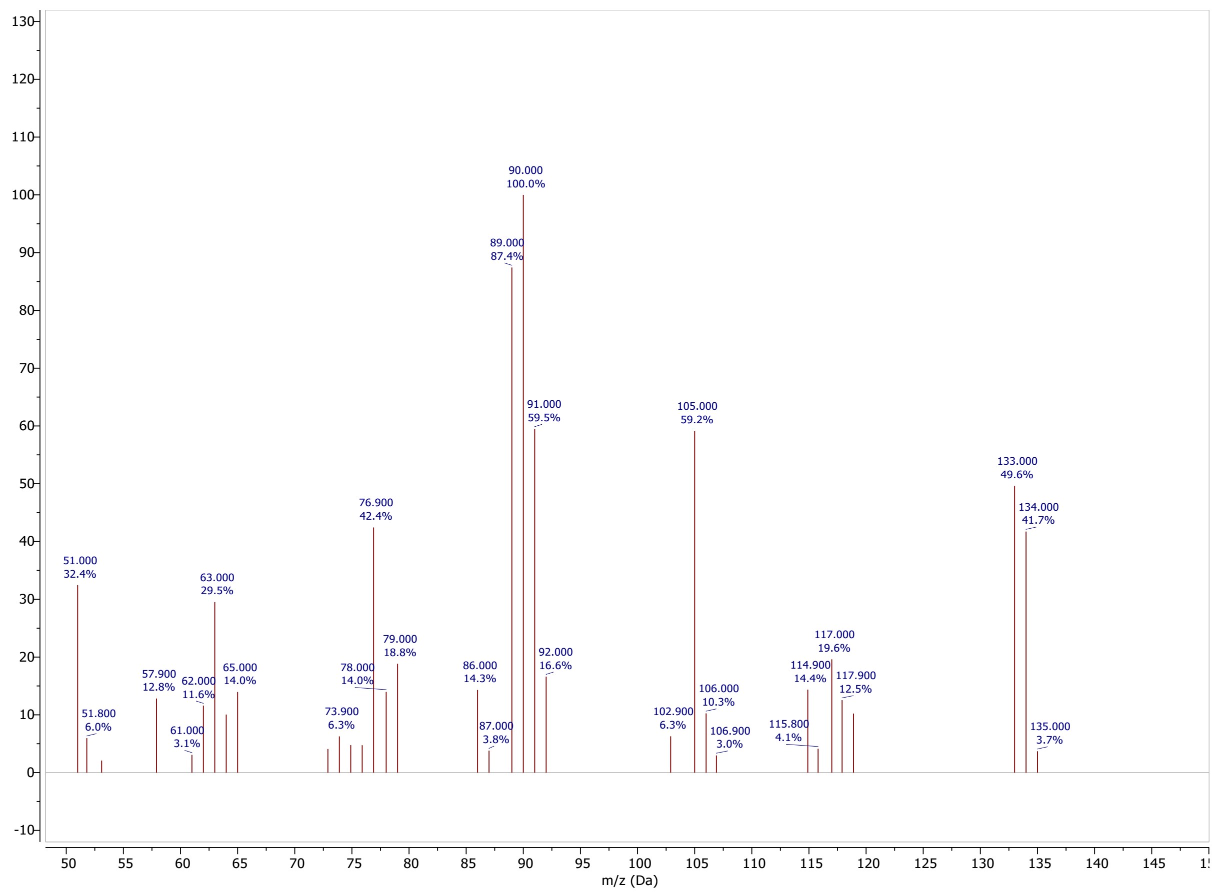
4-isopropyl-1-methyl-7-oxabicyclo[4.1.0]hept-3-ene (13): GC-MS (EI, 70 eV): *m/z* (rel int., %): 51.0 (6.1), 53.0 (16.0), 55.0 (27.5), 56.1 (6.0), 57.0 (9.8), 58.1 (15.9), 59.0 (90.8), 57.0 (6.4), 67.0 (25.2), 68.1 (11.8), 69.0 (24.3), 70.0 (10.7), 71.0 (100.0), 72.0 (6.4), 77.0 (10.5), 79.0 (21.5), 81.0 (14.6), 82.0 (6.8), 83.0 (22.8), 84 (12.2), 85.0 (5.2), 91.0 (8.6), 93.0 (31.2), 94.0 (11.2), 95.0 (19.3), 97.0 (27.9), 108.1 (34.7), 109.0 (44.4), 110.0 (5.4), 111.1 (22.2), 112.0 (17.7), 126.0 (10.0), 137.0 (28.2).



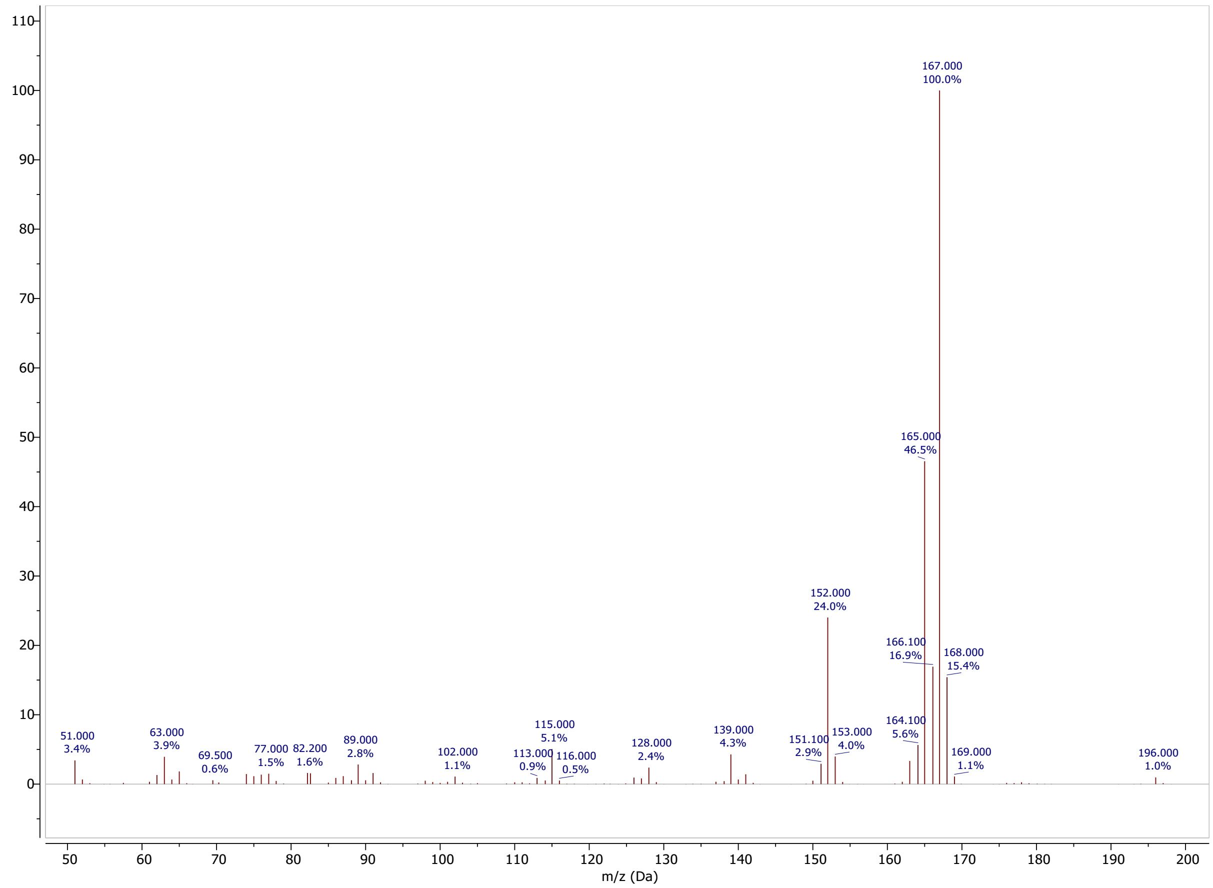
7-oxabicyclo[4.1.0]hept-3-ene (14): GC-MS (EI, 70 eV): *m/z* (rel int., %): 51.0 (18.1), 52.0 (15.2), 53.0 (31.8), 54.0 (4.6), 54.9 (4.5), 62.9 (11.5), 65.0 (34.0), 66.2 (9.6), 68.9 (7.7), 77.1 (12.4), 77.8 (4.9), 79.0 (5.7), 81.0 (11.4), 95.0 (12.0), 96.0 (27.4).



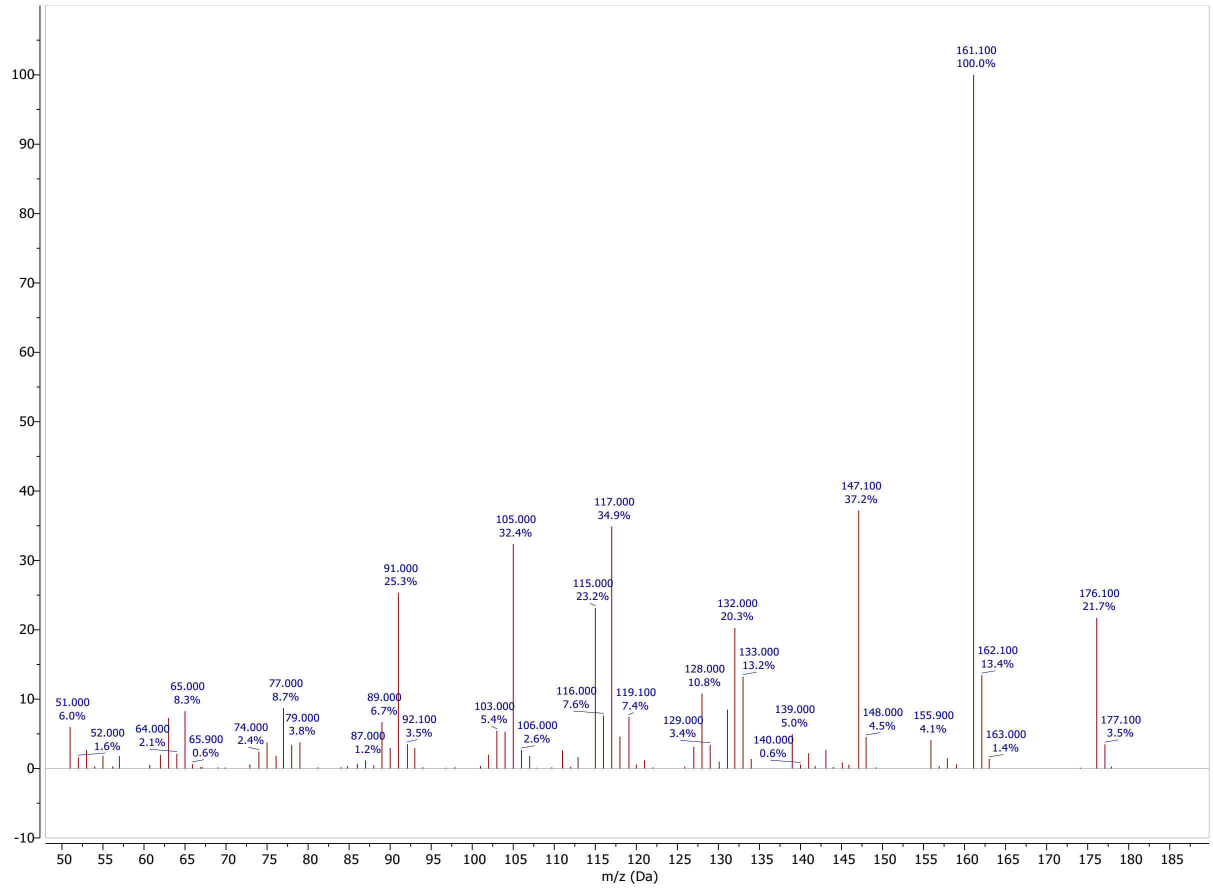
2,2-dimethyl-3-(3-methylenepent-4-en-1-yl)oxirane (15): GC-MS (EI, 70 eV): *m/z* (rel int., %): 51.1 (15.5), 51.9 (9.8), 53.0 (35.3), 54.0 (8.6), 55.1 (35.7), 56.1 (6.5), 63.0 (7.4), 64.9 (16.8), 66.2 (9.0), 67.0 (100.0), 68.0 (20.5), 69.1 (16.1), 71.0 (8.1), 77.0 (25.0), 78.0 (8.4), 79.0 (66.5), 80.0 (12.6), 81.0 (56.7), 82.0 (16.6), 82.9 (12.3), 84.0 (11.6), 90.9 (30.5), 92.1 (8.1), 93.0 (67.0), 94.1 (81.6), 95.0 (30.2), 97.0 (6.9), 108.0 (62.9), 109.0 (32.8), 110.0 (5.1), 118.9 (12.2), 121.0 (5.5), 123.0 (7.6), 137.1 (10.1).



***Trans*-β-methylstyrene epoxide (16)**: GC-MS (EI, 70 eV): *m/z* (rel int., %): 51.0 (32.4), 51.8 (6.0), 57.9 (12.8), 62.0 (11.6), 63.0 (29.5), 64.0 (10.1), 65.0 (14.0), 73.9 (6.3), 76.9 (42.4), 78.0 (14.0), 79.0 (18.8), 86.0 (14.3), 89.0 (87.4), 90.0 (100.0), 91.0 (59.5), 92.0 (16.6), 102.9 (6.3), 105.0 (59.2), 106.0 (10.3), 114.9 (14.4), 117.0 (19.6), 117.9 (12.5), 118.9 (10.2), 133.0 (49.6), 134.0 (41.7).



2,2-diphenyloxirane (17): GC-MS (EI, 70 eV): *m/z* (rel int., %): 115.0 (5.1), 152.0 (24.0), 164.1 (5.6), 165.0 (46.5), 166.0 (16.9), 167.0 (100.0), 168.0 (15.4).



2-(4-(tert-butyl)phenyl)oxirane (18): GC-MS (EI, 70 eV): *m/z* (rel int., %): 51.0 (6.0), 63.0 (7.3), 65.0 (8.3), 77.0 (8.7), 89.0 (6.7), 91 (25.3), 103.0 (5.4), 104.0 (5.3), 105.0 (32.4), 115.0 (23.2), 116.0 (7.6), 117.0 (34.9), 118.0 (4.6), 119.1 (7.4), 128 (10.8), 131.1 (8.5), 132.0 (20.3), 133.0 (13.2), 139.0 (5), 147.1 (37.2), 148.0 (4.5), 161.1 (100.0), 162.1 (13.4), 176.1 (21.7).