

• *Electronic Supplementary Information*

## **Epoxidation of Cyclic Enones with Hydrogen Peroxide Catalysed by Alkylcarboxylate Anion-Intercalated Ni-Zn Mixed Basic Salts**

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### **Materials**

Ni(OCOCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and Zn(OCOCH<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O were obtained from Wako Pure Chemical Ind. Co. Ltd. All organic reagents and solvents were purchased from Wako Pure Chemical Ind. Co. Ltd., Tokyo Kasei, and Aldrich. All chemical compounds were purified by standard procedures before use.<sup>1S</sup>

### **General**

Analytical gas chromatography (GC) was performed by a Shimadzu GC-2010 with a flame ionization detector equipped with a RESTEK Rtx®-5MS capillary column (30 m, 0.25 mmID, 0.25 μm) or a Shimadzu GC-8A with a flame ionization detector equipped a Silicon OV-17 packed column (2 m). Gas chromatograph-mass spectroscopy (GC-MS) was performed by Shimadzu GCMS-QP2010 Plus with a thermal conductivity detector equipped with a RESTEK Rtx®-5MS capillary column (30 m, 0.25 mmID, 0.25 μm), and ionizing by electron impact. Products were confirmed by use of GC-MS, FT-IR, and <sup>1</sup>H and <sup>13</sup>C NMR. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy were performed using a JNM-AL400 spectrometer at 400 MHz in CDCl<sub>3</sub> with TMS as an internal standard. Powder X-ray diffraction (XRD) was conducted using a Bruker AXS MXP<sup>3</sup>V with Cu Kα radiation. UV-Visible spectra were recorded on a Shimadzu UV-2101PC. Ion chromatography was performed by a DIONEX ICS-1100 equipped with a Thermo

Science IonPac AS18 (mobile phase: 32 mM of aqueous NaOH). Flame atomic absorption spectroscopy (AAS) was performed using a Thermo Elemental SOLARR AA series equipped with a Hamamatsu Photonics K. K. hollow cathode lamp, and atomizing by air-acetylene flame.

#### **Preparation of CH<sub>3</sub>COO<sup>-</sup>/NiZn**

Acetate anion-intercalated Ni-Zn hydroxy double salt (CH<sub>3</sub>COO<sup>-</sup>/NiZn) was prepared according to the literature procedures.<sup>28</sup> Ni(OCOCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (134 mmol) and Zn(OCOCH<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (66 mmol) were dissolved in deionized water (200 mL). The solution was hydrolyzed by heating in a Teflon-lined pressure bottle at 200 °C for 24 h. The resulting precipitates were filtered, washed with deionized water, and dried under vacuum, yielding *ca.* 5 g of Ni<sub>0.63</sub>Zn<sub>0.37</sub>(OAc)<sub>0.37</sub>(OH)<sub>2</sub>·1.93H<sub>2</sub>O (Ni/Zn = 2.20; CH<sub>3</sub>COO<sup>-</sup>/NiZn) as a light green powder.

#### **Preparation of Alkylcarboxylate Anion-exchanged NiZn Catalyst (X/NiZn)**

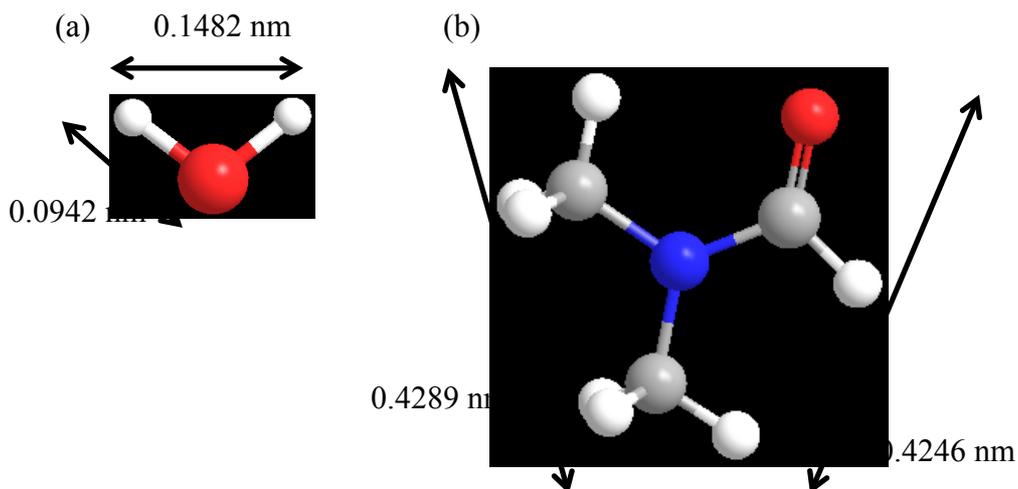
X/NiZn catalyst was prepared by a simple intercalation technique.<sup>35</sup> Treatment of CH<sub>3</sub>COO<sup>-</sup>/NiZn (0.5 g) with 1 M of various sodium alkyl carboxylates solution (50 mL) at 60 °C for 24 h yielded the anion-exchanged NiZn catalysts as a green powder.

#### **Typical procedure for the epoxidation of 2-cyclohexen-1-one with aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%) catalyzed by C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn**

2-Cyclohexen-1-one (0.5 mmol, 0.0481 g), C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn (0.05 g), 30 % aq H<sub>2</sub>O<sub>2</sub> (2 mmol), and DMF (2 mL) were added in a Shrenk tube at 60 °C under 1 atm of air and stirred for 6 h. 2-Cyclohexen-1-one conversion and 2,3-epoxycyclohexanone yield were determined by GC analysis using chlorobenzene as an internal standard. Isolation procedure was follows: After 6 h, the C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>/NiZn catalyst was separated from the reaction mixture by a centrifugation. The remained H<sub>2</sub>O<sub>2</sub> was completely decomposed by the addition of MnO<sub>2</sub>, followed by extraction with diethyl ether (15 mL×5). The clear supernatant liquid was concentrated and subjected to column chromatography on silica gel (Wako gel HG-300) with a mixture of *n*-hexane and ethyl acetate (3:1) to afford 0.1009 g (90 % isolated yield) of analytically pure 2,3-epoxycyclohexanone as a colorless liquid.

### Procedure for the reuse experiment

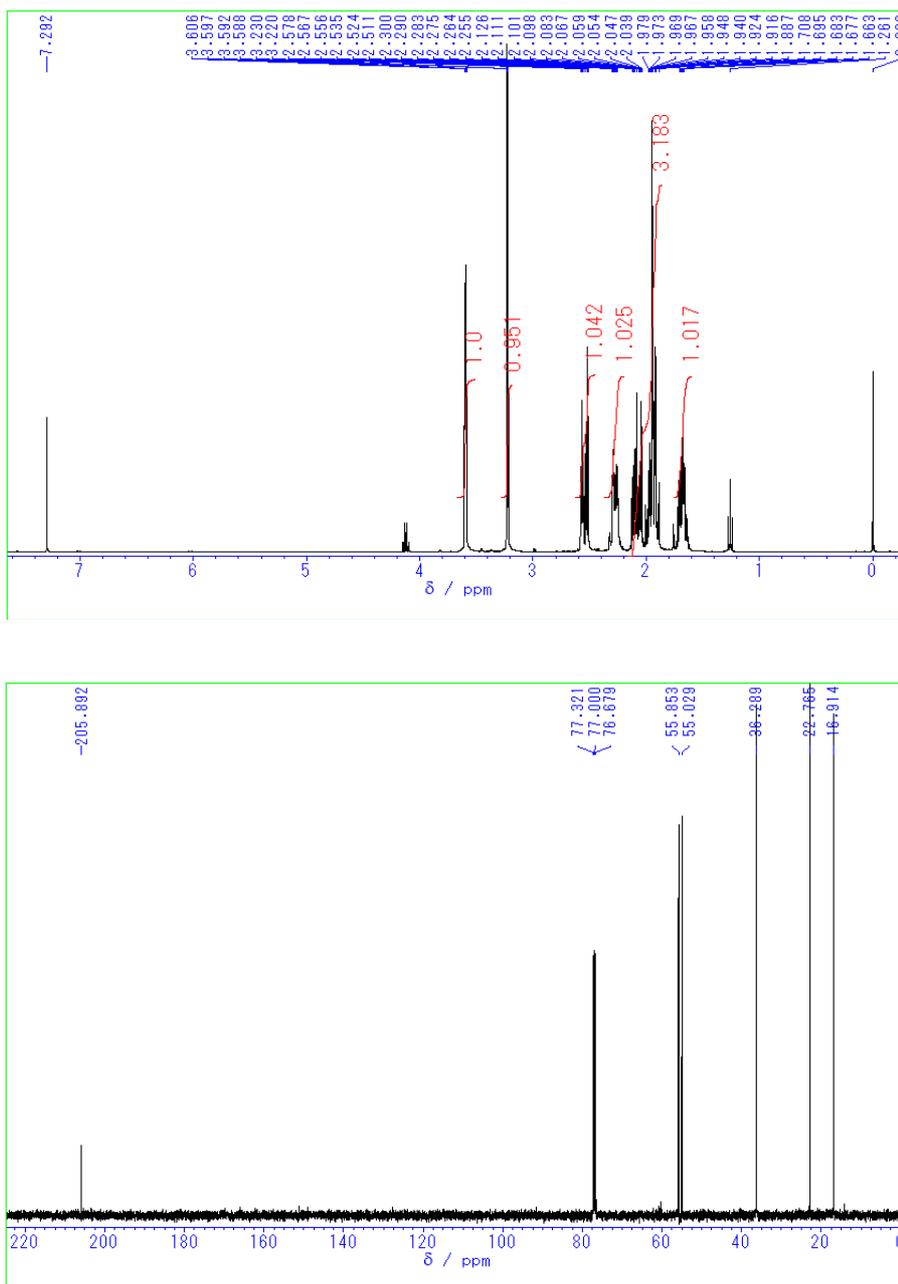
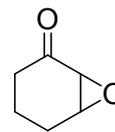
After the catalytic epoxidation of **1** (Table 1, entry 3), the spent  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$  catalyst was separated by centrifugation and filtration. The recovered  $\text{C}_3\text{H}_7\text{COO}^-/\text{NiZn}$  catalyst was washed with water ( $20 \text{ mL} \times 5$ ) and dried under vacuum at room temperature before recycling for the next run.



**Fig. S1.** (a) water and (b) DMF in its energy-minimized conformations, determined using molecular mechanics.

**2,3-epoxycyclohexanone**<sup>4S, 5S</sup>

Colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.62-1.72 (m, 1H, CH<sub>2</sub>), 1.88-2.14 (m, 3H, CH<sub>2</sub>), 2.20-2.34 (m, 1H, CH<sub>2</sub>), 2.51-2.58 (m, 1H, CH<sub>2</sub>), 3.22 (d, *J*=3.91 Hz, 1H, CH), 3.59-3.61 (m, 1H, CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 16.9 (CH<sub>2</sub>), 22.8 (CH<sub>2</sub>), 36.3 (CH<sub>2</sub>), 55.0 (CH), 55.9 (CH), 205.9 (CO). EI-MS (*m/z*, %) 112 (M<sup>+</sup>, 23), 83 (11), 57 (21), 56 (16), 55 (100).



**Fig. S2.** 2,3-epoxycyclohexanone (a) <sup>1</sup>H NMR and (b) <sup>13</sup>C NMR spectrum.

### 2,3-Epoxy-cyclopentanone<sup>4S</sup>

Colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.0-2.5 (m, 4H, CH<sub>2</sub>), 3.17 (d, *J* = 2.4 Hz, 1H, CH), 3.81 (d, *J* = 1.9 Hz, 1H, CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 23.1 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 54.8 (CH), 57.8 (CH), 210.0 (CO); IR (Neat) 1745 (s, CO) cm<sup>-1</sup>; EI-MS (*m/z*, %) 98 (M<sup>+</sup>, 29), 69 (19), 55 (18), 43 (18), 42 (100), 41 (70).

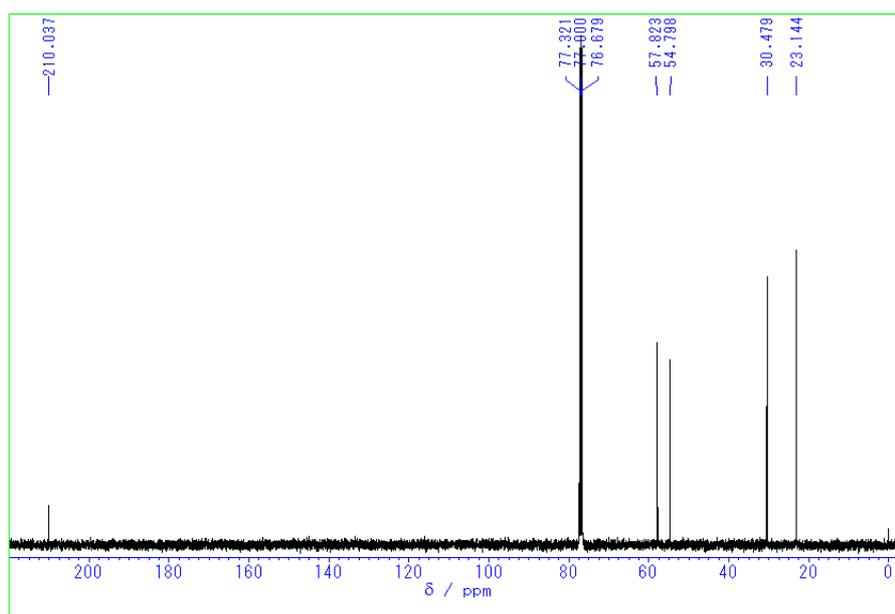
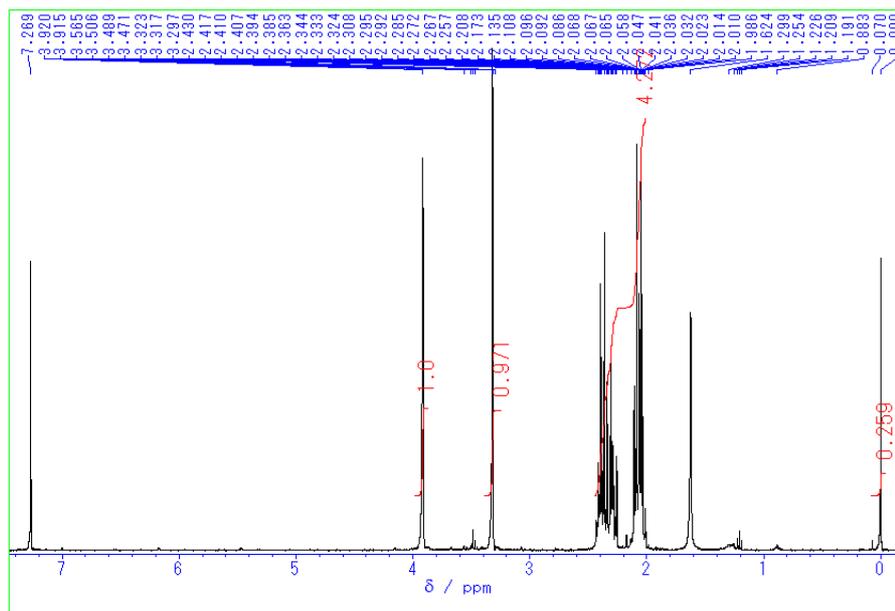
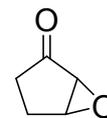
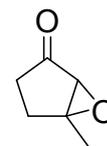
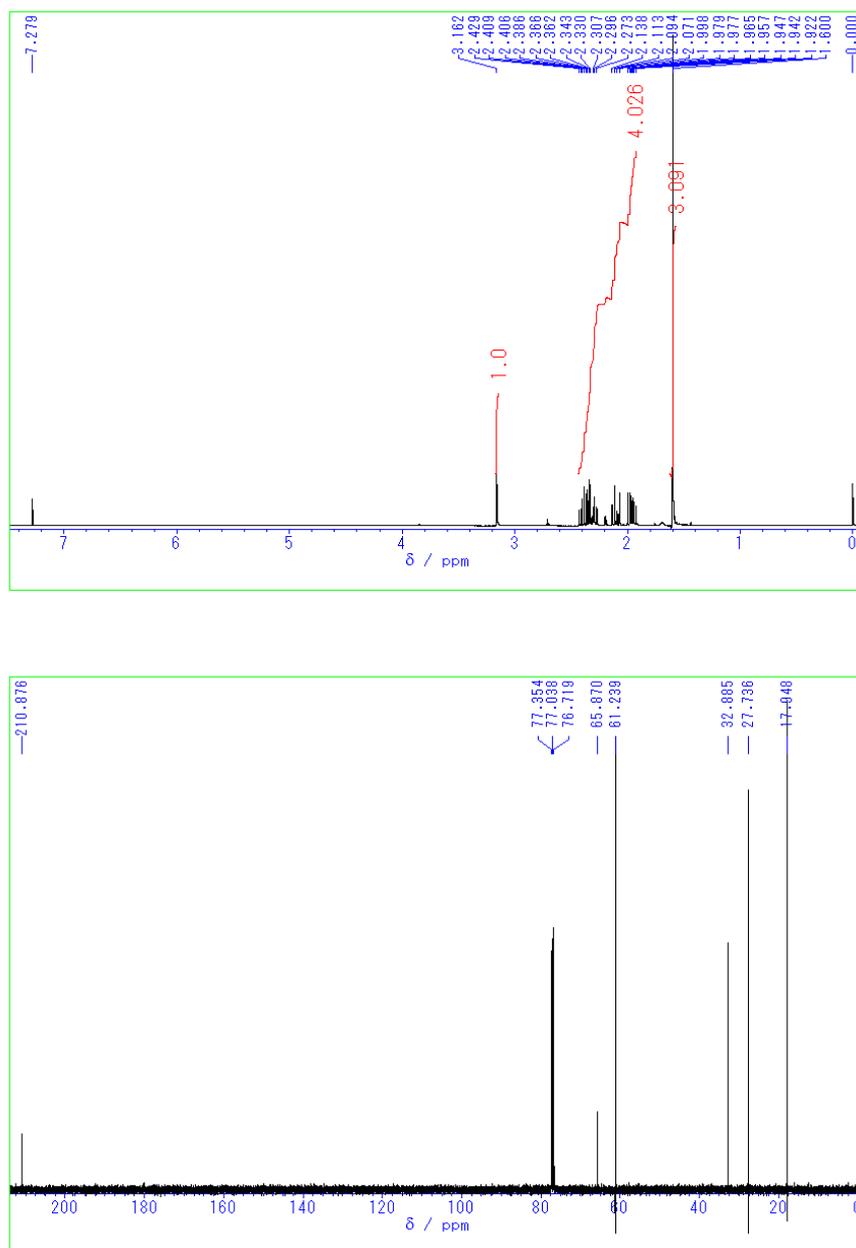


Fig. S3. <sup>1</sup>H NMR spectrum of 2,3-epoxycyclopentanone.

### 3-Methyl-2,3-epoxycyclopentanone<sup>4S</sup>



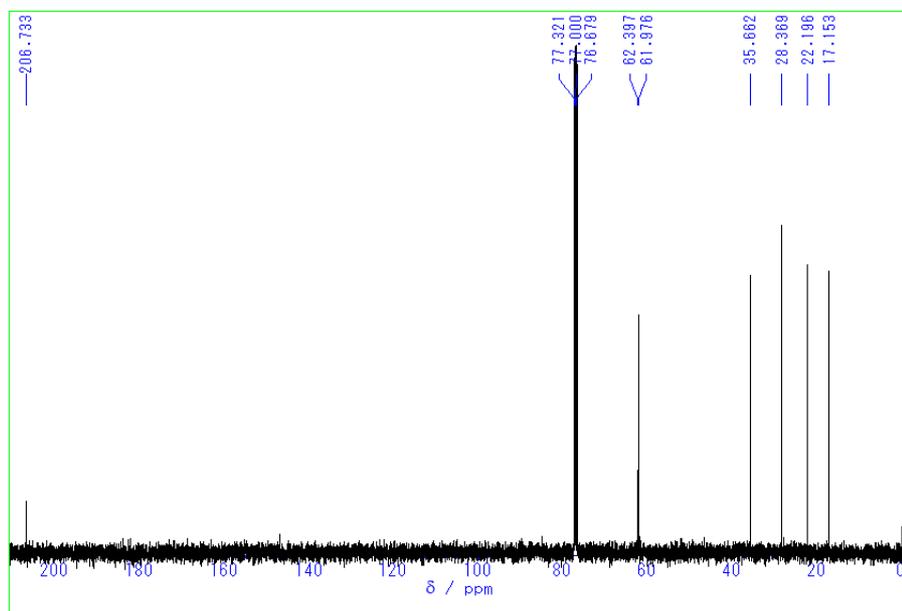
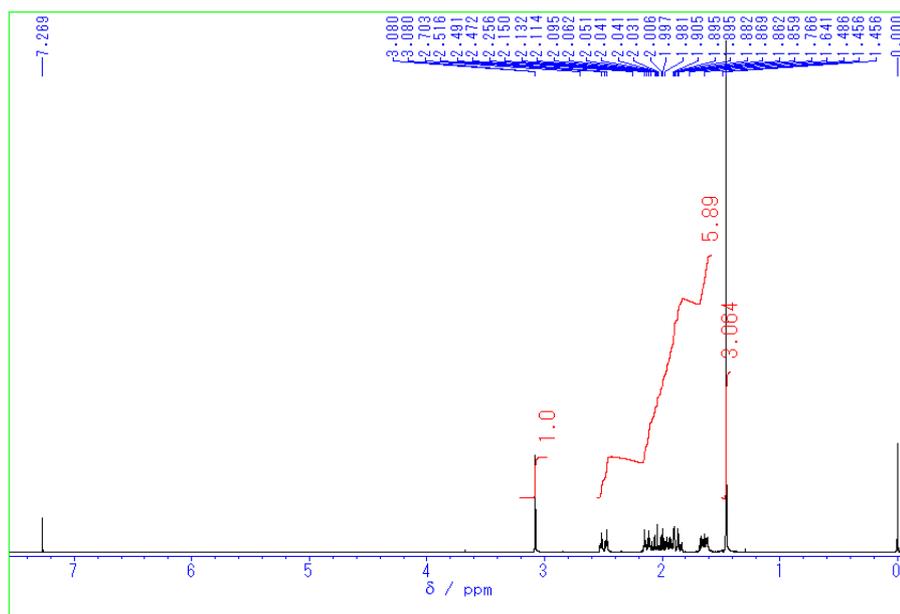
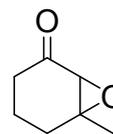
Colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.60 (s, 3H, CH<sub>3</sub>), 1.92-2.43 (m, 4H, CH<sub>2</sub>), 3.16 (s, 1H, CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 18.0 (CH<sub>3</sub>), 27.7 (CH<sub>2</sub>), 32.9 (CH<sub>2</sub>), 61.2 (C), 65.9 (CH), 210.9 (CO); IR (Neat) 1747 (s, CO) cm<sup>-1</sup>; EI-MS (*m/z*, %) 112 (M<sup>+</sup>, 35), 69 (30), 56 (23), 55 (63), 53 (13), 43 (87), 42 (100), 41 (86).



**Fig. S4.** <sup>1</sup>H NMR spectrum of 3-methyl-2,3-epoxycyclopentanone.

**3-Methyl-2,3-epoxycyclohexanone**<sup>4S, 6S-7S</sup>

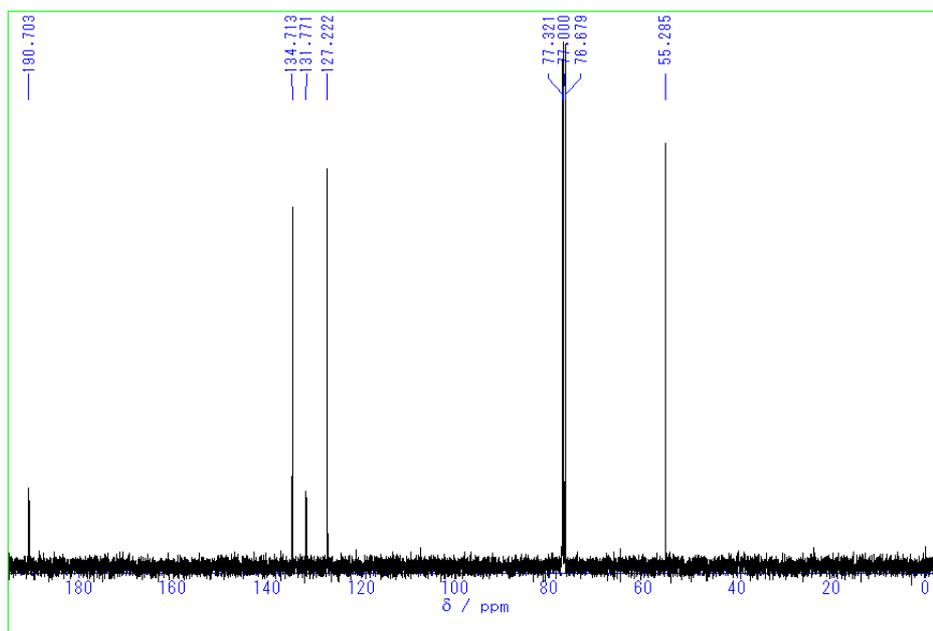
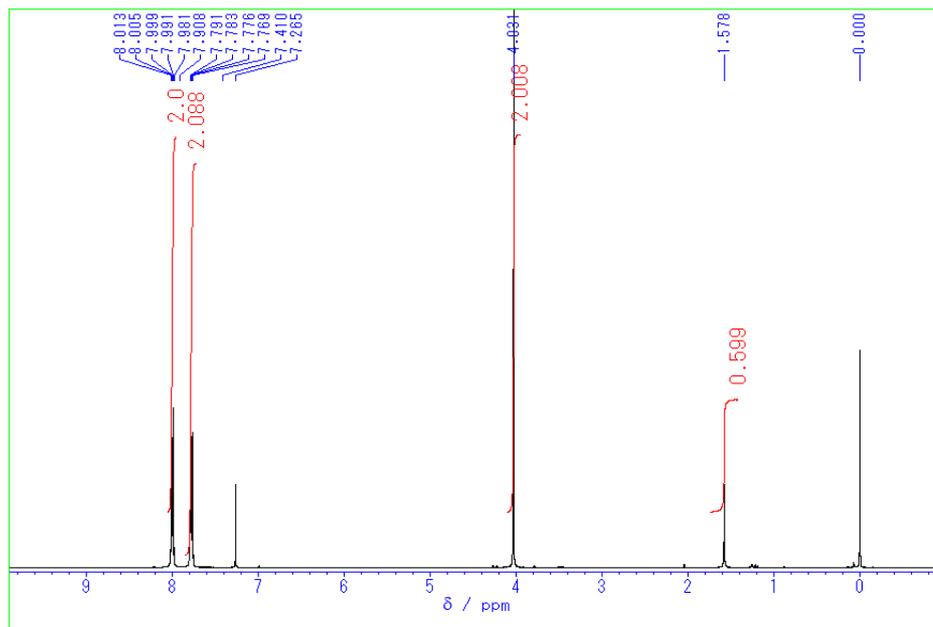
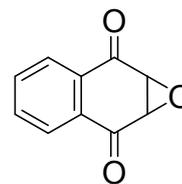
Colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.46 (s, 3H, CH<sub>3</sub>), 1.58-2.55 (m, 6H, CH<sub>2</sub>), 3.08 (s, 1H, CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 17.2 (CH<sub>2</sub>), 22.2 (CH<sub>3</sub>), 28.4 (CH<sub>3</sub>), 35.7 (CH<sub>2</sub>), 62.0 (CH), 62.4 (C), 206.7 (CO); IR (Neat) 1709 (s, CO) cm<sup>-1</sup>; EI-MS (*m/z*, %) 126 (M<sup>+</sup>, 19), 97 (15), 83 (13), 71 (39), 69 (20), 56 (17), 55 (63), 41 (100).



**Fig. S5.** <sup>1</sup>H NMR spectrum of 3-methyl-2,3-epoxycyclohexanone.

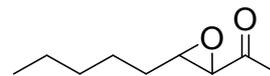
**2,3-Epoxy-2,3-dihydro-1,4-naphthoquinone**<sup>7S, 8S</sup>

Light yellow solid. Mp 134-136 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.03 (s, 2H, CH), 7.75-7.80 (m, 2H, Ar-CH), 7.97-8.03 (m, 2H, Ar-CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 55.3 (CH), 127.2 (Ar-CH), 131.8 (Ar-CH), 134.7 (Ar-C), 190.7 (CO); IR (KBr) 1693 (s, CO) cm<sup>-1</sup>; EI-MS (*m/z*, %) 174 (M<sup>+</sup>, 66), 173 (23), 146 (44), 105 (100)



**Fig. S6.** <sup>1</sup>H NMR spectrum of 2,3-epoxy-2,3-dihydro-1,4-naphthoquinone.

### 3,4-Epoxy-nonan-2-one<sup>9S</sup>



Colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.90 (m, 3H, CH<sub>3</sub>), 1.27-1.71 (m, 8H, CH<sub>2</sub>), 2.06 (s, 3H, CH<sub>3</sub>), 3.05-3.10 (dt, *J*=2.0, 5.0 Hz, H, CH), 3.18-3.19 (d, *J*=2.0 Hz, 1H, CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 13.9 (CH<sub>3</sub>), 22.5 (CH<sub>2</sub>), 24.4 (CH<sub>3</sub>), 25.5 (CH<sub>3</sub>), 31.4 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 58.1 (CH), 59.0 (CH), 206.2 (CO); IR (Neat) 1712 (s, CO) cm<sup>-1</sup>; EI-MS (*m/z*, %) 155 (M<sup>+</sup>-1, 1), 144 (1), 100 (2), 85 (39), 71 (3), 69 (5), 57 (19), 43 (100), 41 (24).

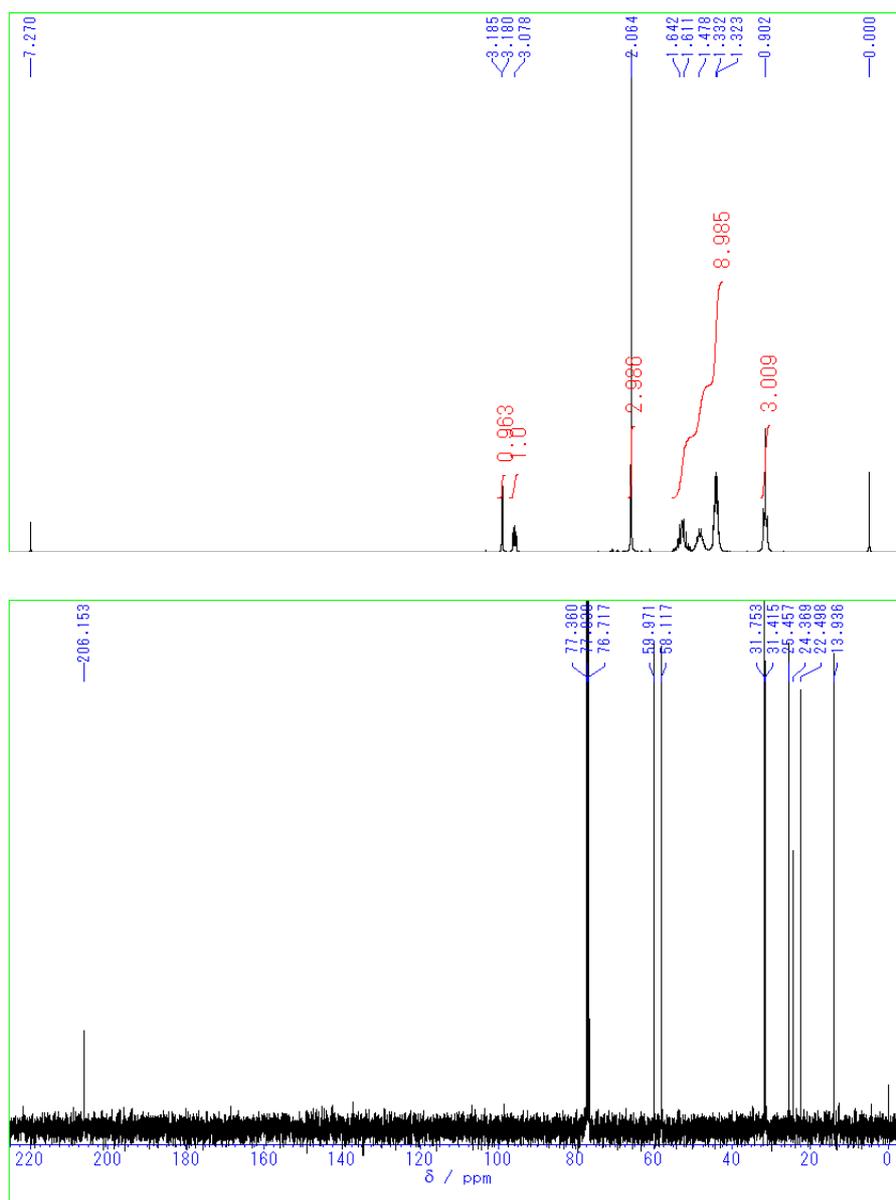
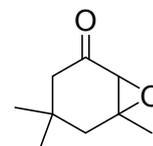


Fig. S7. <sup>1</sup>H NMR spectrum of 3,4-epoxy-nonan-2-one.

### Isophorone oxide<sup>10S</sup>



Colorless liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.91(s, 3H,  $\text{CH}_3$ ), 1.02 (s, 3H,  $\text{CH}_3$ ), 1.42 (s, 3H,  $\text{CH}_3$ ), 1.66-1.72 (m, 1H,  $\text{CH}_2$ ), 1.79-1.83 (m, 1H,  $\text{CH}_2$ ), 2.06-2.10 (d, 1H,  $\text{CH}_2$ ,  $J=15.0$  Hz), 2.60-2.64 (d, 1H,  $\text{CH}_2$ ,  $J=13.4$  Hz) 3.06 (s, 1H, CH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  24.0 ( $\text{CH}_3$ ), 27.8 ( $\text{CH}_3$ ), 30.8 ( $\text{CH}_3$ ), 36.2 (Ar-C), 42.8 (Ar- $\text{CH}_2$ ), 48.0 (Ar- $\text{CH}_2$ ), 61.4 (Ar- $\text{CH}_2$ ), 64.3 (Ar-C), 208.0 (CO).

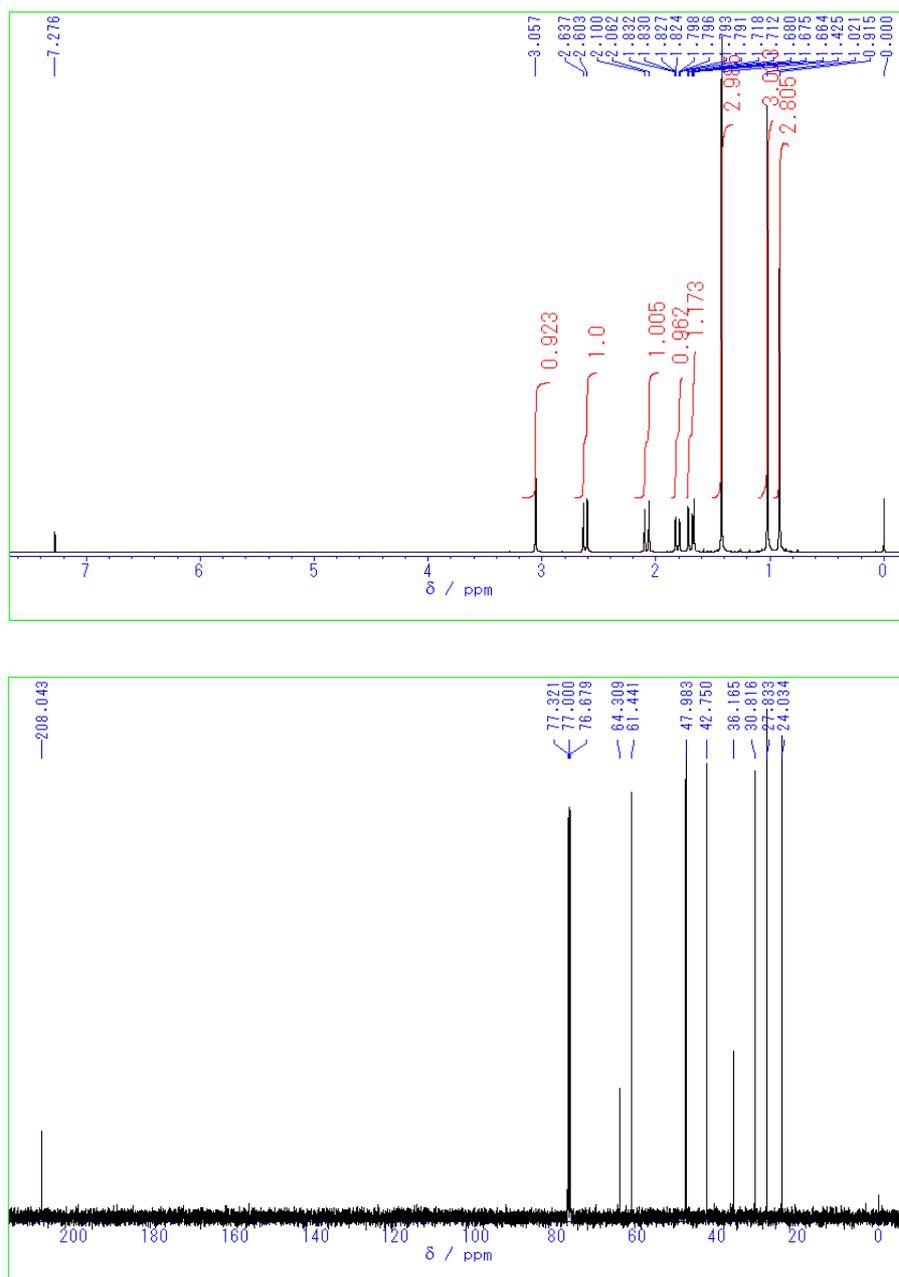
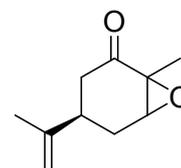


Fig. S8.  $^1\text{H}$  NMR spectrum of isophorone oxide.

**(4*S*)-1-Methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptan-2-one<sup>11S</sup>**



Colorless liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.42 (s, 3H,  $\text{CH}_3$ ,  $J=5.0$  Hz), 1.72 (s, 3H,  $\text{CH}_3$ ,  $J=5.9$  Hz), 1.87-2.07 (m, 2H,  $\text{CH}_2$ ), 2.30-2.44 (m, 1H,  $\text{CH}_2$ ), 2.56-2.62 (m, 1H,  $\text{CH}_2$ ), 2.68-2.84 (m, 1H, CH), 3.44-3.46 (m, 1H, CH), 4.68-4.84 (d, 2H,  $\text{CH}_2$ ,  $J=28.4$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  15.3 ( $\text{CH}_3$ ), 20.6 ( $\text{CH}_3$ ), 28.7 ( $\text{CH}_2$ ), 35.0 (CH), 41.8 ( $\text{CH}_2$ ), 58.8 (CH), 61.3 (C), 110.5 ( $\text{CH}_2$ ), 146.3 (C), 205.5 (CO).

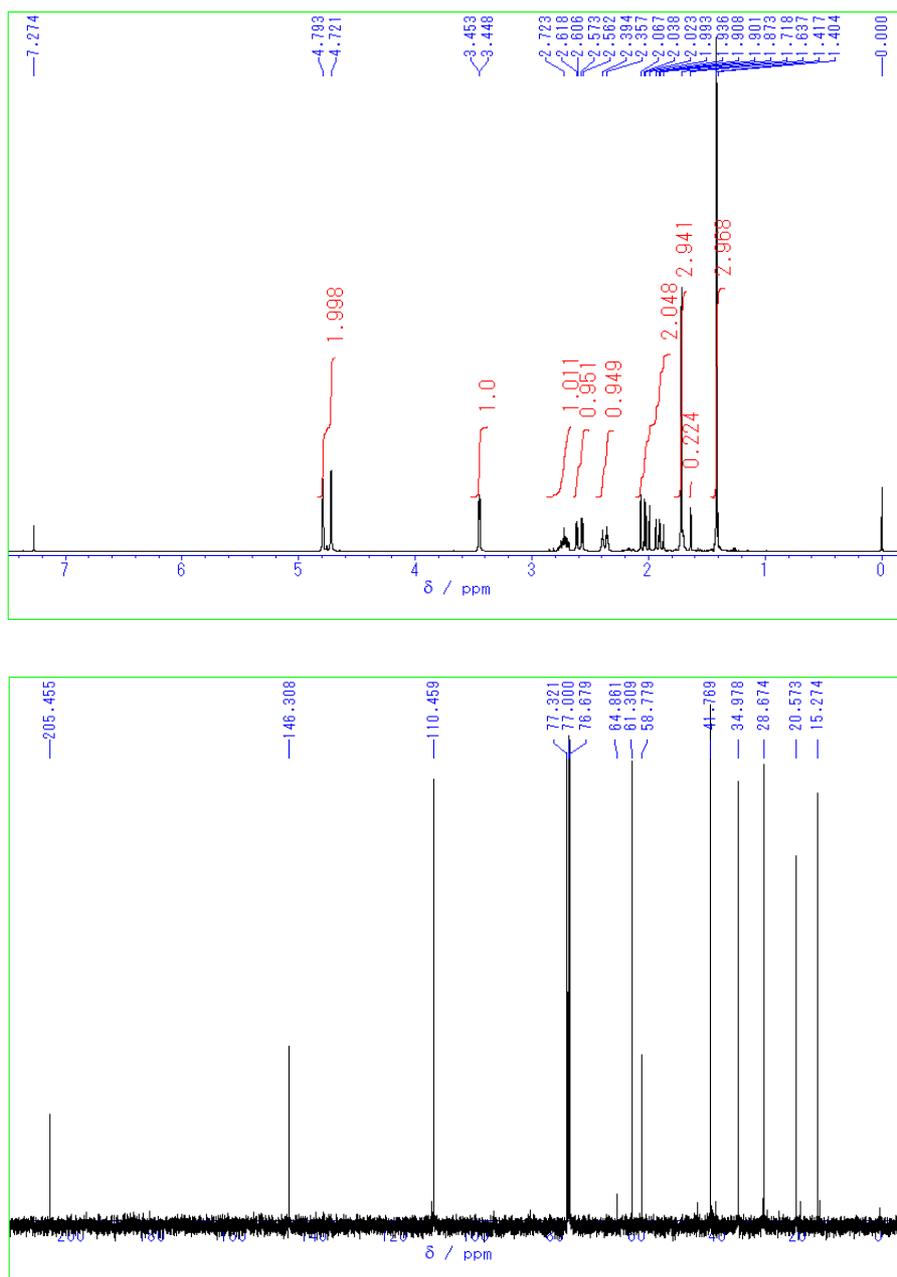
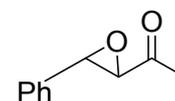


Fig. S9.  $^1\text{H}$  NMR spectrum of (4S)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptan-2-one.

3,4-Epoxy-4-phenyl-2-butanone<sup>12S</sup>



White plate. Mp 53-54 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.20 (s, 3H,  $\text{CH}_3$ ), 3.49 (d,  $J=1.8$  Hz, 1H, CH), 4.00 (d,  $J=1.8$  Hz, 1H, CH), 7.27-7.39 (m, 5H, Ar-CH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  24.8 ( $\text{CH}_3$ ), 57.8 (CH), 63.5 (CH), 125.7 (Ar-CH), 128.7 (Ar-CH), 129.0 (Ar-CH), 135.0 (Ar-C), 204.1 (CO); IR (KBr) 1711 (s, CO)  $\text{cm}^{-1}$ ; EI-MS ( $m/z$ , %) 162 ( $\text{M}^+$ , 21), 120, (41), 119 (21), 105 (12), 91 (100), 90 (28), 89 (33), 77 ( $\text{C}_6\text{H}_5^+$ , 17), 51 ( $\text{C}_4\text{H}_3^+$ , 12), 43 (56).

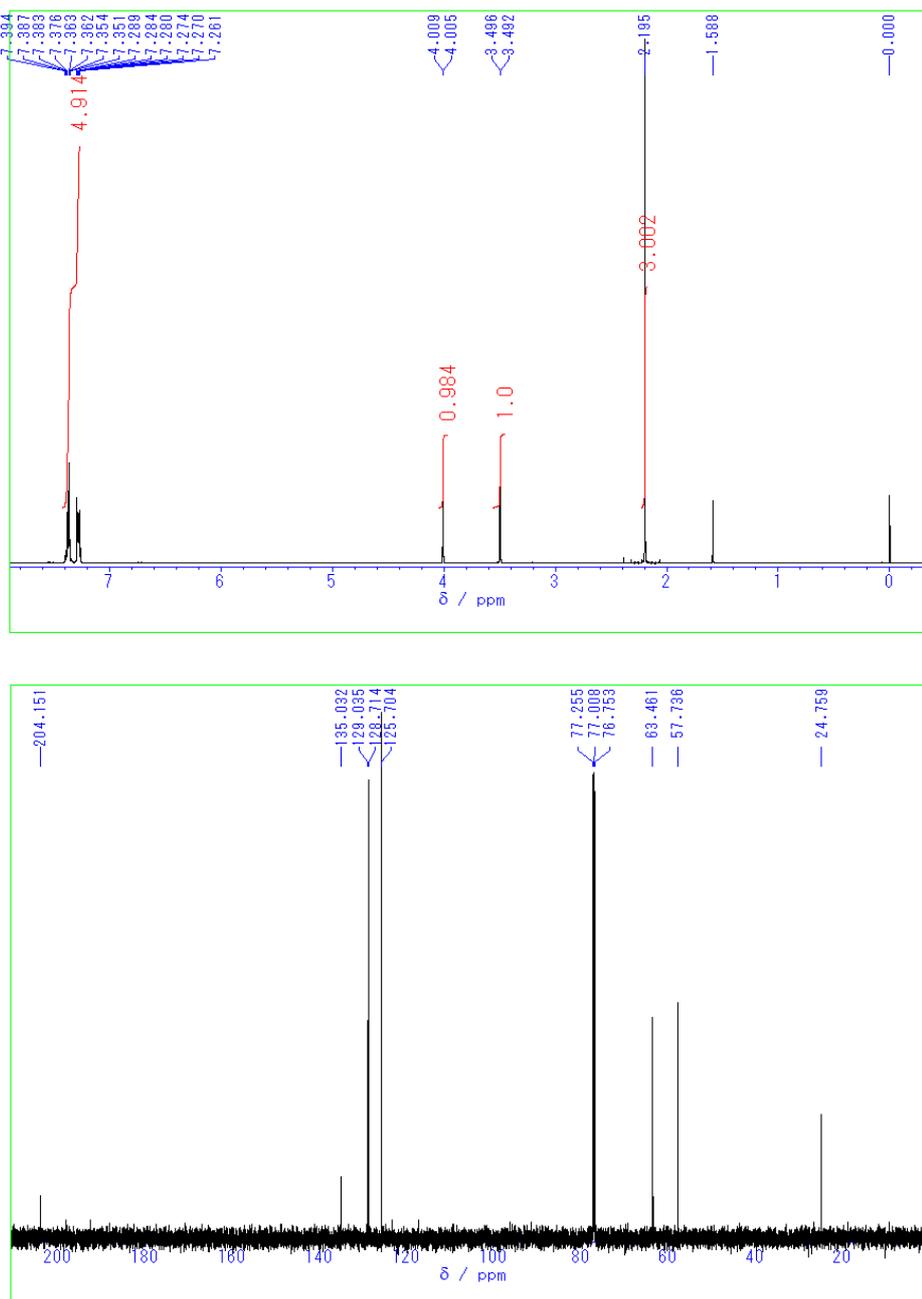
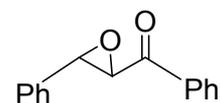


Fig. S10.  $^1\text{H}$  NMR spectrum of 3,4-epoxy-4-phenyl-2-butanone.

2,3-Epoxy-1,3-diphenylpropanone<sup>13S, 14S</sup>



White crystalline solid. Mp 90-91 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.08 (d, 1H, CH,  $J= 1.9$  Hz), 4.31 (d, 1H, CH,  $J= 1.9$  Hz), 7.33-7.67 (m, 8H, Ar-CH), 7.98-8.06 (m, 2H, Ar-CH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  59.4 (CH), 61.0 (CH), 125.8 (Ar-CH), 128.3 (Ar-CH), 128.8 (Ar-CH), 128.9 (Ar-CH), 134.0 (Ar-CH), 135.5 (Ar-CH), 193.1 (CO); IR (KBr) 1687 (s, CO)  $\text{cm}^{-1}$ ; EI-MS ( $m/z$ , %) 224 ( $\text{M}^+$ , 3), 105 (100), 90 (13), 89 (17), 77 (13), 51 (24).

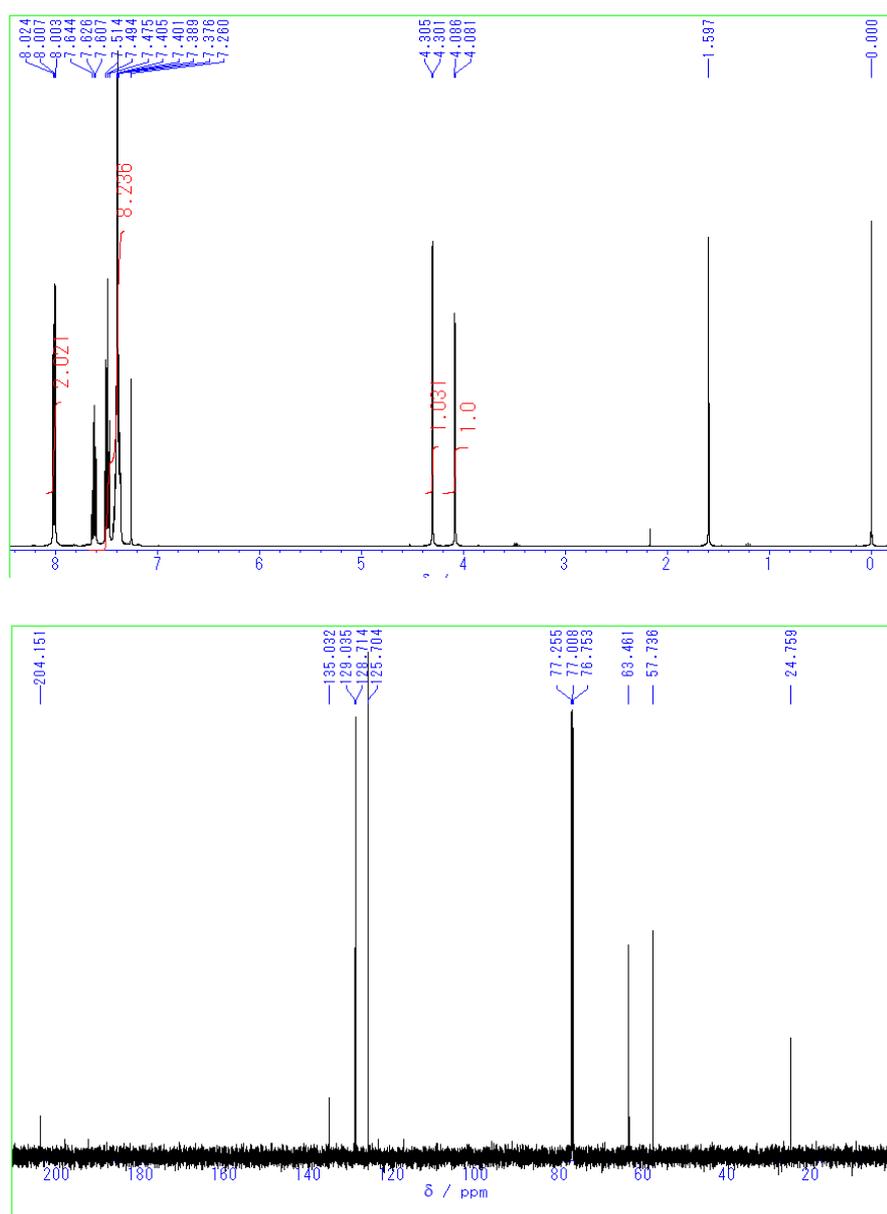


Fig. S11.  $^1\text{H}$  NMR spectrum of 2,3-epoxy-1,3-diphenylpropanone.

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