

*Electronic Supplementary Information for*

**Ir(tri-*N*-Heterocyclic Carbene)-Catalyzed Upgrading Glycerol: C-C Bond Formation for the  
Synthesis of  $\alpha$ -Hydroxy Acids**

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## I. Experimental procedures

### General information.

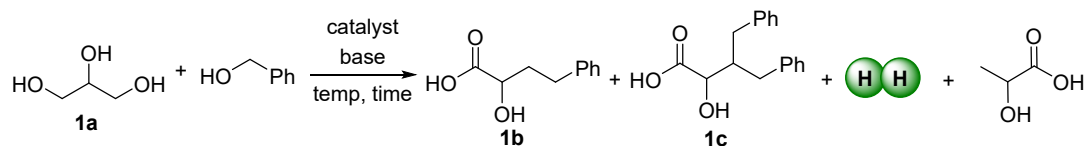
Commercially available reagents were purchased from major suppliers and used as received. All reactions carried out in two-neck round flasks. DMSO- $d_6$ ,  $CDCl_3$ ,  $CD_3OD$  were purchased from Cambridge Isotope Laboratories.  $^1H$  and  $^{13}C$  NMR spectra were acquired on JEOL Resonance ECZ600R (600 MHz) spectrometer. The  $^1H$  (600 MHz) chemical shifts( $\delta$ ) are given in parts per million (ppm) referenced to the residual DMSO or  $H_2O$  signal of the deuterated solvent. The  $^{13}C$  (151 MHz) chemical shifts( $\delta$ ) reported in parts per million (ppm) referenced from DMSO or methanol-added signal. The following abbreviations are used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet. ESI-MS spectra were recorded on a SYNAPT G2 (U.K) from Korea Basic Science Institute. Mass spectra were recorded on a JMS-700 (Jeol) from Korea Basic Science Institute.

### Catalytic procedure for hydrogen generation from glycerol

In a two-neck round bottom flask, glycerol (10 mmol), catalysts (0.00625 mol%, 0.625  $\mu$ mol), and NaOH (15 mmol, 1.5 equiv.) were dissolved in primary alcohols (70 mmol, 7 equiv.) and magnetically stirred for 2 h at 180  $^{\circ}C$ . The evolved gas was passed through a solution of 10 M sodium hydroxide aqueous solution to trap carbon dioxide and collected in a measuring cylinder. The yield of hydrogen was calculated by the ideal gas law. Then, the reaction mixture was cooled down to ambient temperature and diluted with methanol. The TOFs of products and lactic acid were calculated by  $^1H$  NMR spectroscopy in  $d_6$ -DMSO using isonicotinic acid as an internal standard.

## II. Additional catalytic reaction data

**Table S1** Optimization of dehydrogenative coupling of glycerol and benzyl alcohol



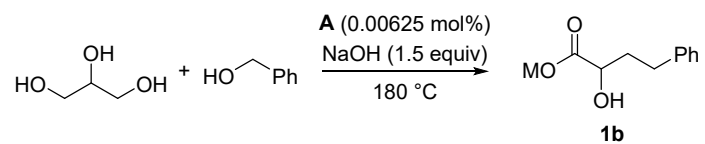
entry	catalyst (mol%)	base (equiv)	temp	time	1b TOF, yield	1c TOF, yield	H <sub>2</sub> TOF	lactic acid yield
1	A (0.00625)	LiOH (1.5)	180 °C	2 h	--	--	2500 h <sup>-1</sup>	38%
2	A (0.00625)	NaOH (1.5)	180 °C	2 h	5100 h <sup>-1</sup> , 64%	150 h <sup>-1</sup> , 1.8%	11100 h <sup>-1</sup>	0%
3	A (0.00625)	KOH (1.5)	180 °C	2 h	3000 h <sup>-1</sup> , 38%	190 h <sup>-1</sup> , 2.4%	10600 h <sup>-1</sup>	22%
4	A (0.00625)	CsOH·H <sub>2</sub> O (1.5)	180 °C	2 h	1400 h <sup>-1</sup> , 18%	310 h <sup>-1</sup> , 3.9%	10500 h <sup>-1</sup>	45%
5	A (0.00625)	Ba(OH) <sub>2</sub> (1.5)	180 °C	2 h	--	--	1600 h <sup>-1</sup>	8.3%
6	A (0.00625)	K <sub>2</sub> CO <sub>3</sub> (1.5)	180 °C	2 h	--	--	1600 h <sup>-1</sup>	4.5%
7	A (0.0125)	NaOH (1.5)	180 °C	2 h	2700 h <sup>-1</sup> , 68%	170 h <sup>-1</sup> , 4.2%	7000 h <sup>-1</sup>	0%
8	A (0.00625)	NaOH (1.5)	150 °C	2 h	680 h <sup>-1</sup> , 8.5%	--	4900 h <sup>-1</sup>	28%
9	A (0.00625)	NaOH (1.5)	180 °C	1 h	9200 h <sup>-1</sup> , 58%	--	22600 h <sup>-1</sup>	12%
10	A (0.00625)	NaOH (3.0)	180 °C	2 h	5200 h <sup>-1</sup> , 65%	240 h <sup>-1</sup> , 2.9%	30000 h <sup>-1</sup>	0%
11	A (0.00625)	NaOH (1.0)	180 °C	2 h	2200 h <sup>-1</sup> , 28%	--	8200 h <sup>-1</sup>	39%
12	A (0.00625)	--	180 °C	2 h	--	--	--	--
13 <sup>a</sup>	A (0.00625)	NaOH (1.5)	180 °C	2 h	4700 h <sup>-1</sup> , 58%	540 h <sup>-1</sup> , 6.7%	11900 h <sup>-1</sup>	0%
14	B (0.00625)	NaOH (1.5)	180 °C	2 h	5300 h <sup>-1</sup> , 66%	--	10800 h <sup>-1</sup>	2.6%
15	C (0.00625)	NaOH (1.5)	180 °C	2 h	--	--	1800 h <sup>-1</sup>	21%
16	D (0.00625)	NaOH (1.5)	180 °C	2 h	--	--	1500 h <sup>-1</sup>	15%
17	E (0.00625)	NaOH (1.5)	180 °C	2 h	--	--	1000 h <sup>-1</sup>	13%
18	F (0.00625)	NaOH (1.5)	180 °C	2 h	--	--	1100 h <sup>-1</sup>	20%
19	--	NaOH (1.5)	180 °C	2 h	--	--	2100 h <sup>-1</sup>	0%

The mixture of catalysts, glycerol (10 mmol), benzyl alcohol (7 equiv), and base (1.5 equiv) was heated. The yields and TONs were determined by <sup>1</sup>HNMR using isonicotinic acid as an internal standard. The acids exist as salts under basic conditions.<sup>a</sup>benzyl alcohol (3.5 equiv)

**Table S2** Dehydrogenation of benzyl alcohol in the absence of glycerol

entry	base (equiv)	H <sub>2</sub> volume	H <sub>2</sub> mmol	H <sub>2</sub> TOF
1	LiOH (1.5)	20 ml	0.8 mmol	650 h <sup>-1</sup>
2	NaOH (1.5)	520 ml	21 mmol	17000 h <sup>-1</sup>
3	KOH (1.5)	335 ml	14 mmol	11000 h <sup>-1</sup>
4	CsOH·H <sub>2</sub> O (1.5)	380 ml	16 mmol	12400 h <sup>-1</sup>
5	Ba(OH) <sub>2</sub> (1.5)	490 ml	20 mmol	16000 h <sup>-1</sup>
6	K <sub>2</sub> CO <sub>3</sub> (1.5)	20 ml	0.8 mmol	650 h <sup>-1</sup>

The mixture of catalyst **A** (0.00625 mol%), benzyl alcohol (70 mmol), and base (15 mmol) was heated at 180 °C for 2 h.

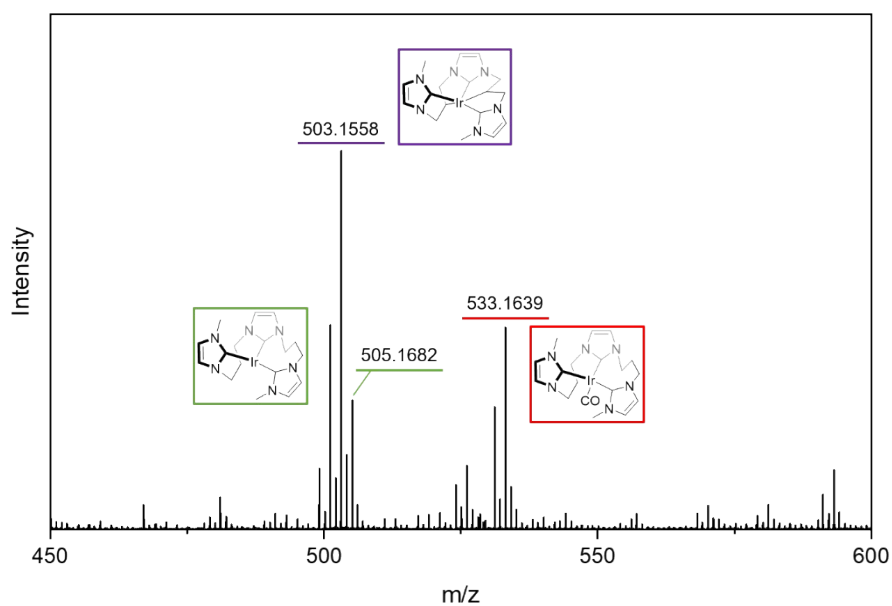


1<sup>st</sup> run: yield (1b) = 64%, TOF (H<sub>2</sub>) = 9800 h<sup>-1</sup>

2<sup>nd</sup> run: yield (1b) = 43%, TOF (H<sub>2</sub>) = 8000 h<sup>-1</sup>

**Scheme S1** Catalyst recycling experiment; glycerol (10 mmol), benzyl alcohol (70 mmol), and NaOH (15 mmol) were added in 1<sup>st</sup> run and 2<sup>nd</sup> run

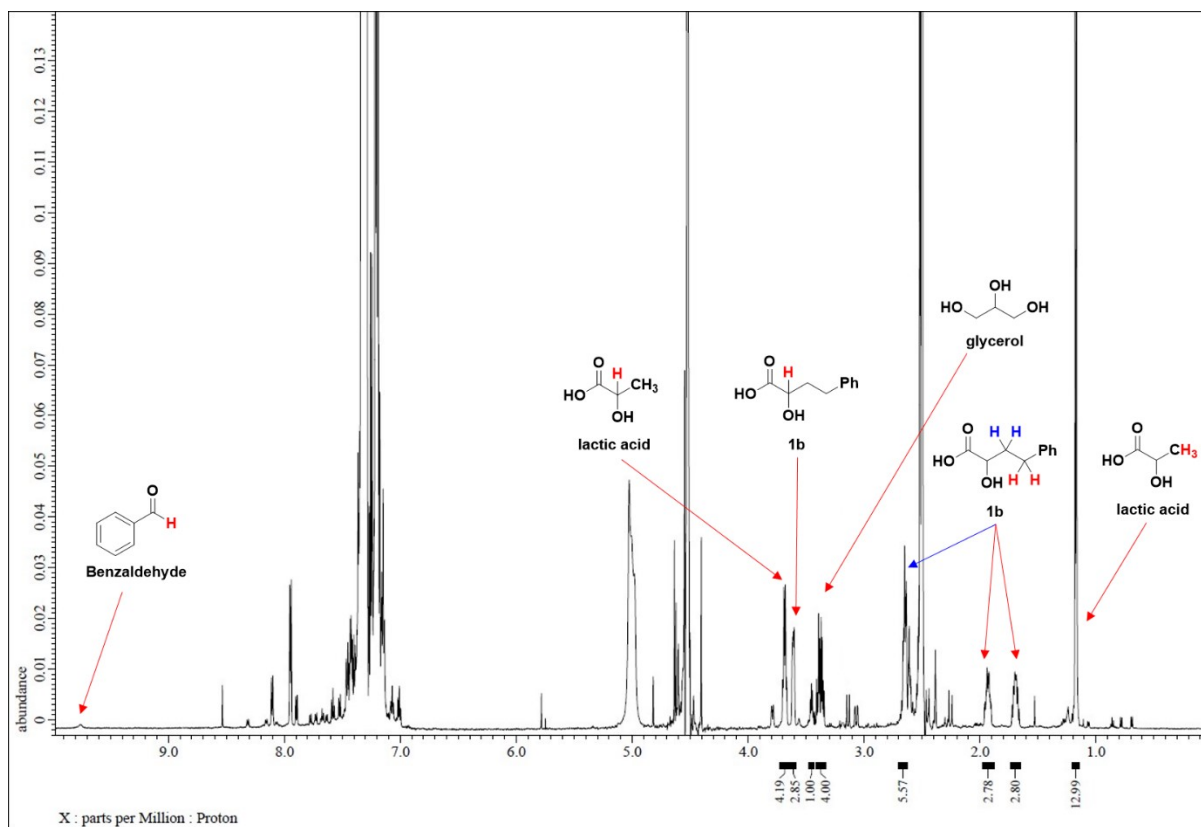
### III. Analysis of reaction mixtures



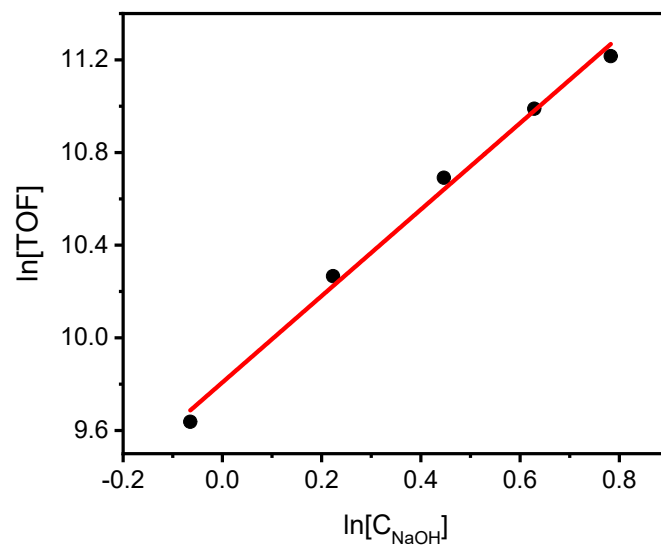
**Figure S1** ESI-MS spectrum of the reaction mixture using catalyst **B** (0.05 mmol), glycerol (5 mmol), NaOH (7.5 mmol), and benzyl alcohol (35 mmol). The mixture was heated at 180 °C for 2 min under a nitrogen atmosphere. The peak at 503 is believed to originate from the compound at 505, which undergoes C-H activation. The cleavage of C-H bond in a trimethylene-linked bis (NHC) ligand has been documented.<sup>1</sup>

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<sup>1</sup> J. A. Cabeza, M. Damonte, P. García-Álvarez, E. Pérez-Carreno, *Chem. Commun.* **2013**, *49*, 2813-2815.



**Figure S2** <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) spectrum of the reaction mixture using catalyst A (0.05 mmol), glycerol (5 mmol), NaOH (7.5 mmol), and benzyl alcohol (35 mmol). The mixture was heated at 180 °C for 7 min under a nitrogen atmosphere.



**Figure S3** Log graph displaying the relationship between the initial TOFs (10 min) and the concentration of NaOH; glycerol (10 mmol), benzyl alcohol (70 mmol), catalyst A (0.00625 mol%), and NaOH (indicated concentrations) were stirred at 180 °C.

Determination of the reaction order in [NaOH]

$$\text{Rate} = \Delta[\text{glycerol}]/\text{time} = k[\text{NaOH}]^a \times [\text{other components}]^b$$

$$\text{TOF} = \Delta[\text{glycerol}]/[\text{catalyst}] \cdot \text{time}$$

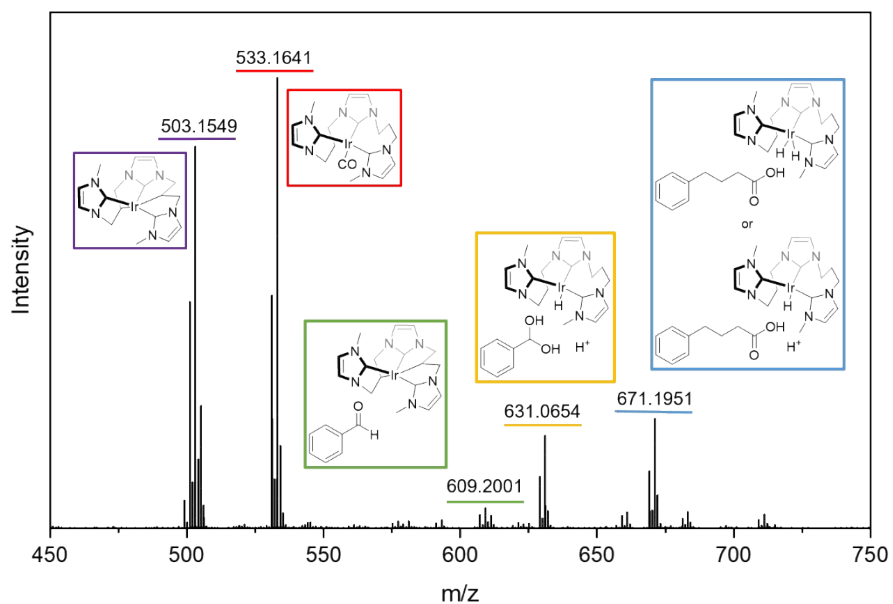
$$\text{Rate} = \text{TOF} \times [\text{catalyst}] = k[\text{NaOH}]^a \times [\text{other components}]^b$$

During the initial stage of the reaction ( $t = 10$  min), the relationship between  $\ln[\text{TOF}]$  and  $\ln[\text{NaOH}]$  was plotted to determine the reaction order concerning [NaOH], with [catalyst], [glycerol], and [benzyl alcohol] held constant.

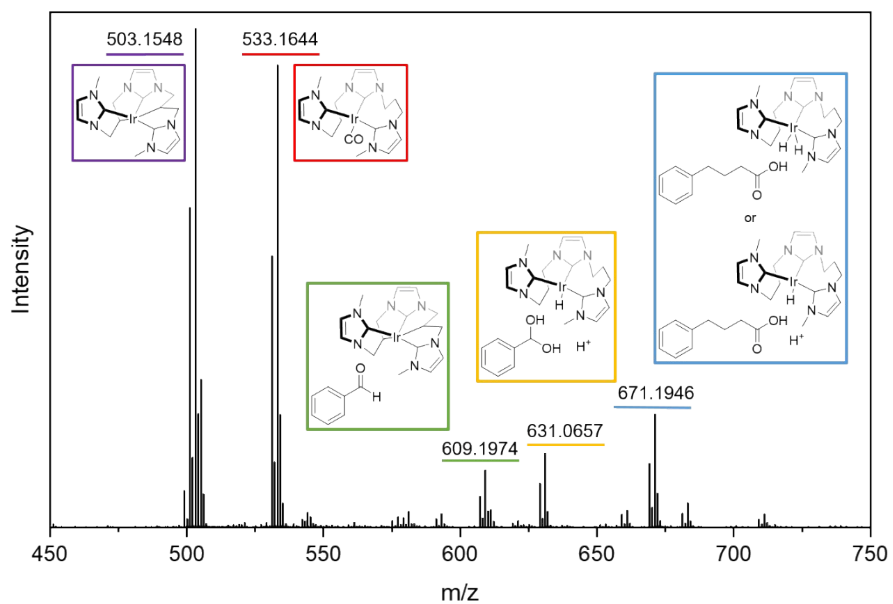
$$\ln\text{TOF} = a\ln[\text{NaOH}] + \text{const}$$

As illustrated in Figure S3, the slope of the  $\ln\text{TOF}$  versus  $\ln[\text{NaOH}]$  plot, equal to 1.9, indicates a reaction order of 1.9 in NaOH.



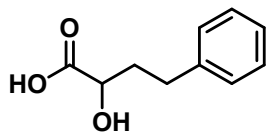


**Figure S4** ESI-MS spectrum of the reaction mixture using catalyst **A** (0.05 mmol), glycerol (0.2 mmol), NaOH (0.5 mmol), and benzyl alcohol (9.6 mmol). The mixture was heated at 180 °C for 30 min under a nitrogen atmosphere. The peak at 503 is believed to originate from the compound at 505, which undergoes C-H activation. The cleavage of C-H bond in a trimethylene-linked bis (NHC) ligand has been documented.<sup>1</sup>



**Figure S5** ESI-MS spectrum of the reaction mixture using catalyst **A** (0.05 mmol), lactic acid (0.2 mmol), NaOH (0.5 mmol), and benzyl alcohol (9.6 mmol). The mixture was heated at 180 °C for 30 min under a nitrogen atmosphere. The peak at 503 is believed to originate from the compound at 505, which undergoes C-H activation. The cleavage of C-H bond in a trimethylene-linked bis (NHC) ligand has been documented.<sup>1</sup>

#### IV. Spectral analysis of the compounds



##### 2-Hydroxy-4-phenylbutanoic acid (1b)

By adding HCl aqueous solution to the catalytic reaction mixture, the reaction mixture was acidified to pH = 1. The crude mixture was then purified using flash column chromatography on silica gel (using a gradient of dichloromethane 100% ~ dichloromethane: Acetone (5:1)). Obtained as a white solid.

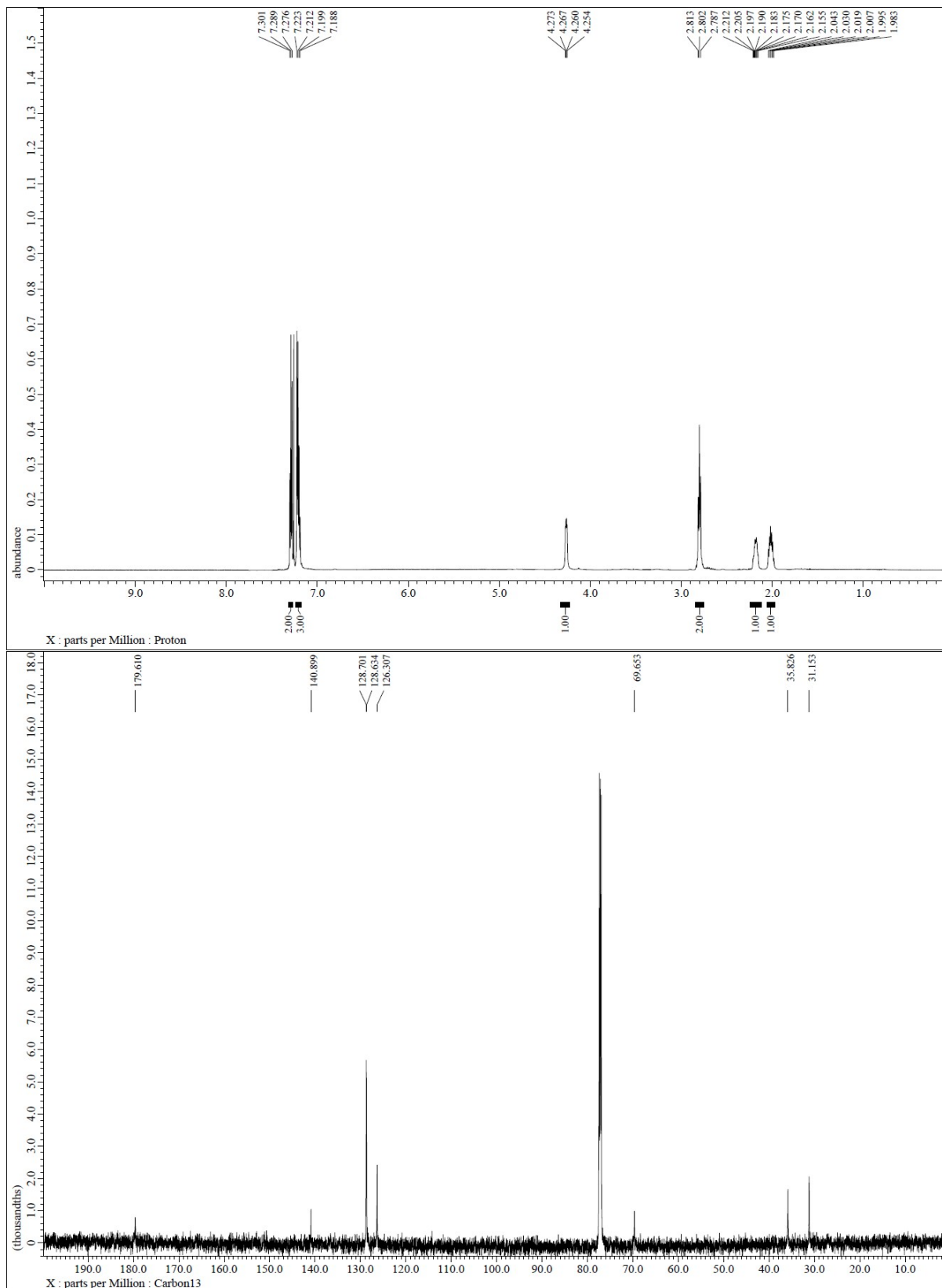
$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (t,  $J = 7.5$  Hz, 2H), 7.19-7.22 (m, 3H), 4.26 (dd,  $J = 7.8, 3.6$  Hz, 1H), 2.76-2.84 (m, 2H), 2.15-2.21 (m, 1H), 1.98-2.04 (m, 1H) ppm.

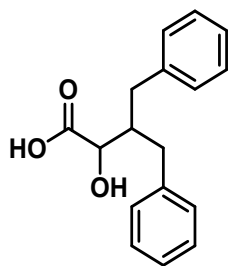
$^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  179.6, 140.9, 128.7, 128.6, 126.3, 69.7, 35.8, 31.2 ppm.

**HRMS**  $m/z$  (EI+, [M]) calculated for  $\text{C}_{10}\text{H}_{12}\text{O}_3$  180.0786, found: 180.0786.

**IR** (neat,  $\text{cm}^{-1}$ ) 3449, 2915, 2854, 1720, 1241, 1178, 1095.

**Mp** 110 °C





**3-Benzyl-2-hydroxy-4-phenylbutanoic acid (1c)**

By adding HCl aqueous solution to the catalytic reaction mixture, the reaction mixture was acidified to pH = 1. The crude mixture was then purified using flash column chromatography on silica gel (using a gradient of dichloromethane 100% ~ dichloromethane: acetone (5:1). Obtained as a white solid.

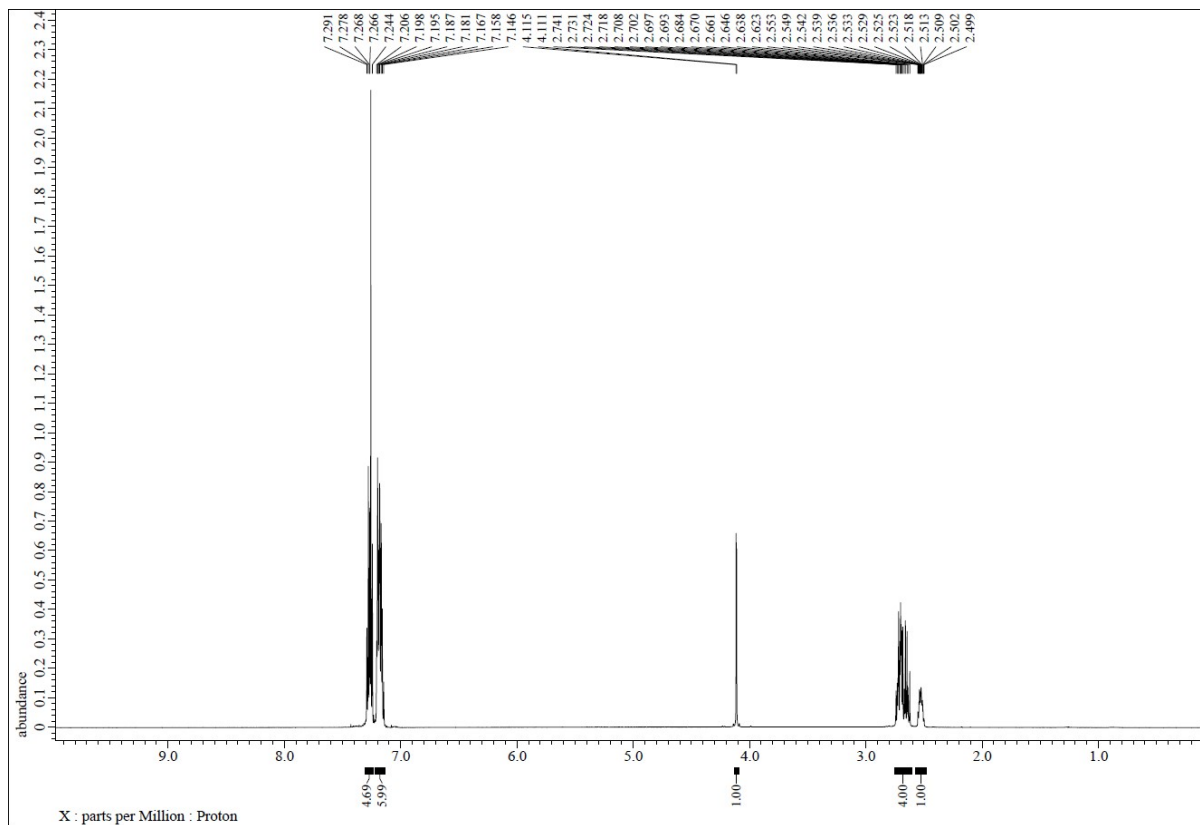
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.24-7.29 (m, 4H), 7.21-7.15 (m, 6H), 4.11 (d, *J* = 2.8 Hz, 1H), 2.74-2.62 (m, 4H), 2.55-2.50 (m, 1H) ppm.

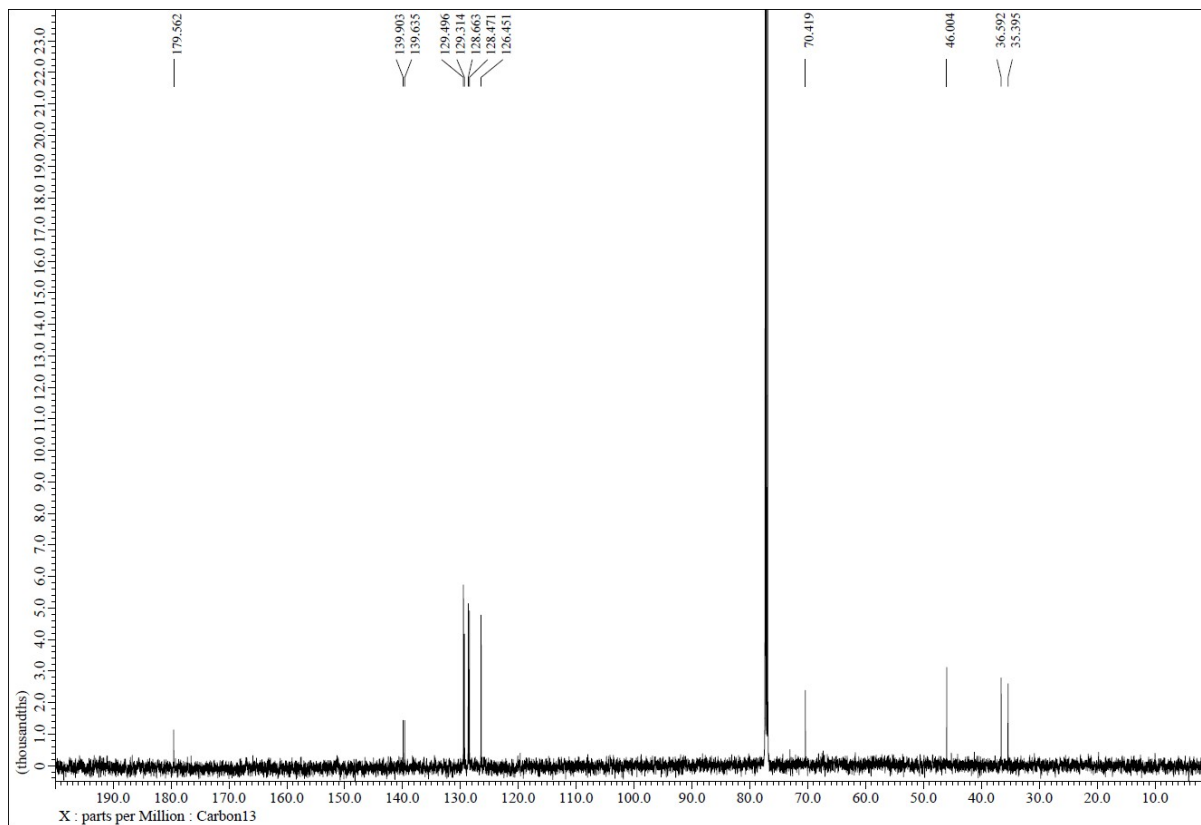
**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 179.6, 139.9, 139.6, 129.5, 129.3, 128.7, 128.5, 126.5, 70.4, 46.0, 36.6, 35.4 ppm.

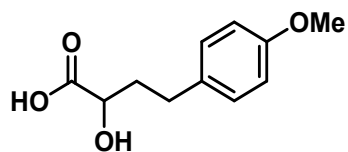
**HRMS** *m/z* (EI+, [M]) calculated for C<sub>17</sub>H<sub>18</sub>O<sub>3</sub> 270.1256, found: 270.1256.

**IR** (neat, cm<sup>-1</sup>) 3452, 3401, 3028, 2944, 1732, 1495, 1451, 1310, 1248, 1186, 1102.

**Mp** 147 °C







**2-Hydroxy-4-(4-methoxyphenyl)butanoic acid (2b)**

By adding HCl aqueous solution to the catalytic reaction mixture, the reaction mixture was acidified to pH = 1. The crude mixture was then purified using flash column chromatography on silica gel (using a gradient of dichloromethane 100% ~ dichloromethane: acetone (5:1)). Obtained as a white solid.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.13 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.25 (dd, *J* = 7.5, 3.9 Hz, 1H), 3.78 (s, 3H), 2.83-2.70 (m, 2H), 2.11-2.18 (m, 1H), 1.95-2.01 (m, 1H) ppm.

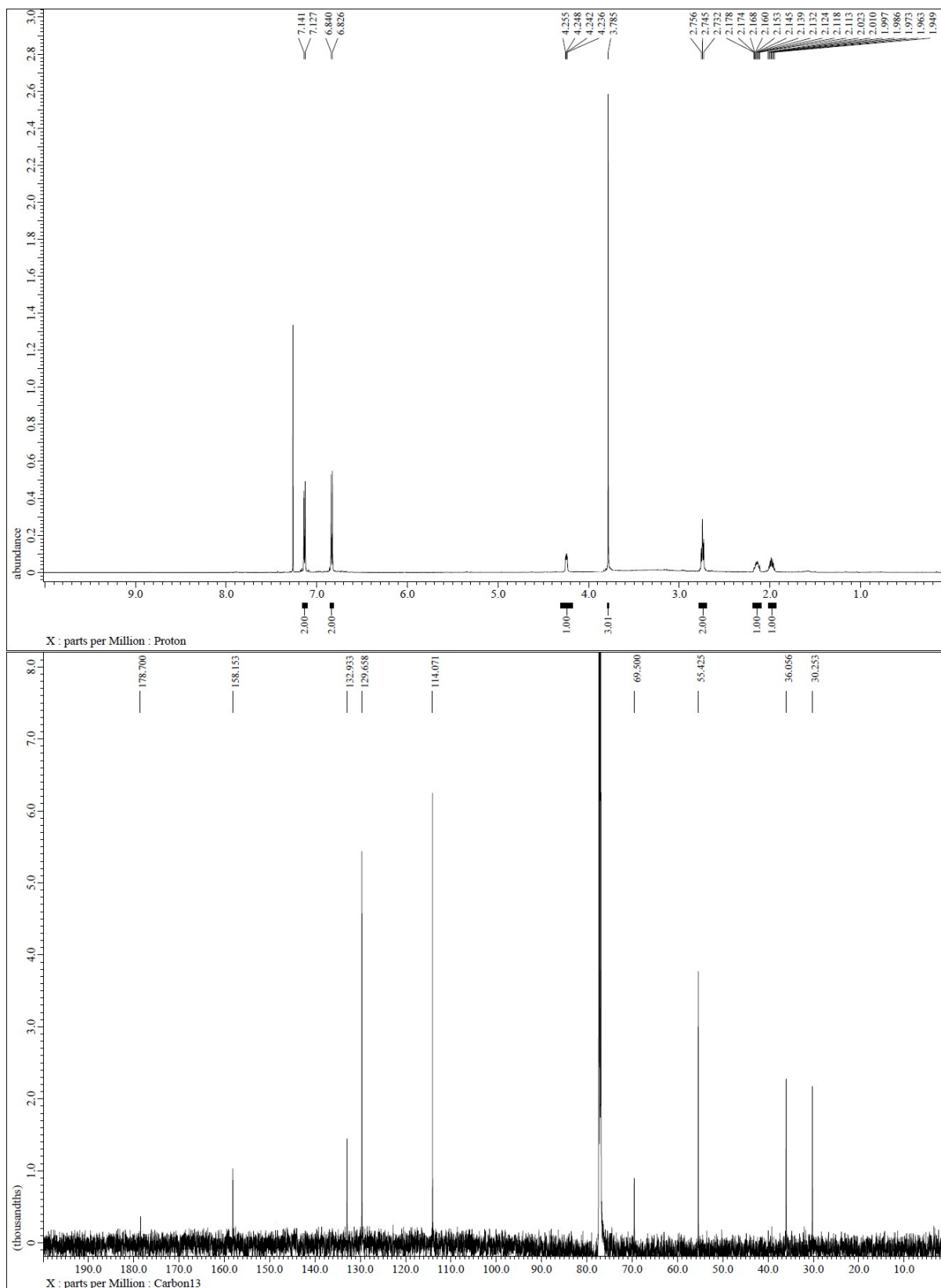
**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 178.5, 158.2, 132.9, 129.7, 114.1, 69.6, 55.4, 36.1, 30.3 ppm.

**HRMS** *m/z* (EI<sup>+</sup>, [M]) calculated for C<sub>11</sub>H<sub>14</sub>O<sub>4</sub> 210.0892, found: 210.0892.

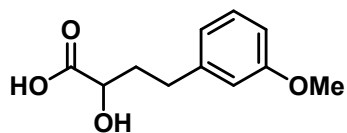
**IR** (neat, cm<sup>-1</sup>) 3452, 2909, 1716, 1513, 1244, 1177, 1094.

**Mp** 149 °C









**2-Hydroxy-4-(3-methoxyphenyl)butanoic acid (3b)**

By adding HCl aqueous solution to the catalytic reaction mixture, the reaction mixture was acidified to pH = 1. The crude mixture was then purified using flash column chromatography on silica gel (using a gradient of dichloromethane 100% ~ dichloromethane: acetone (5:1)). Obtained as a brown solid.

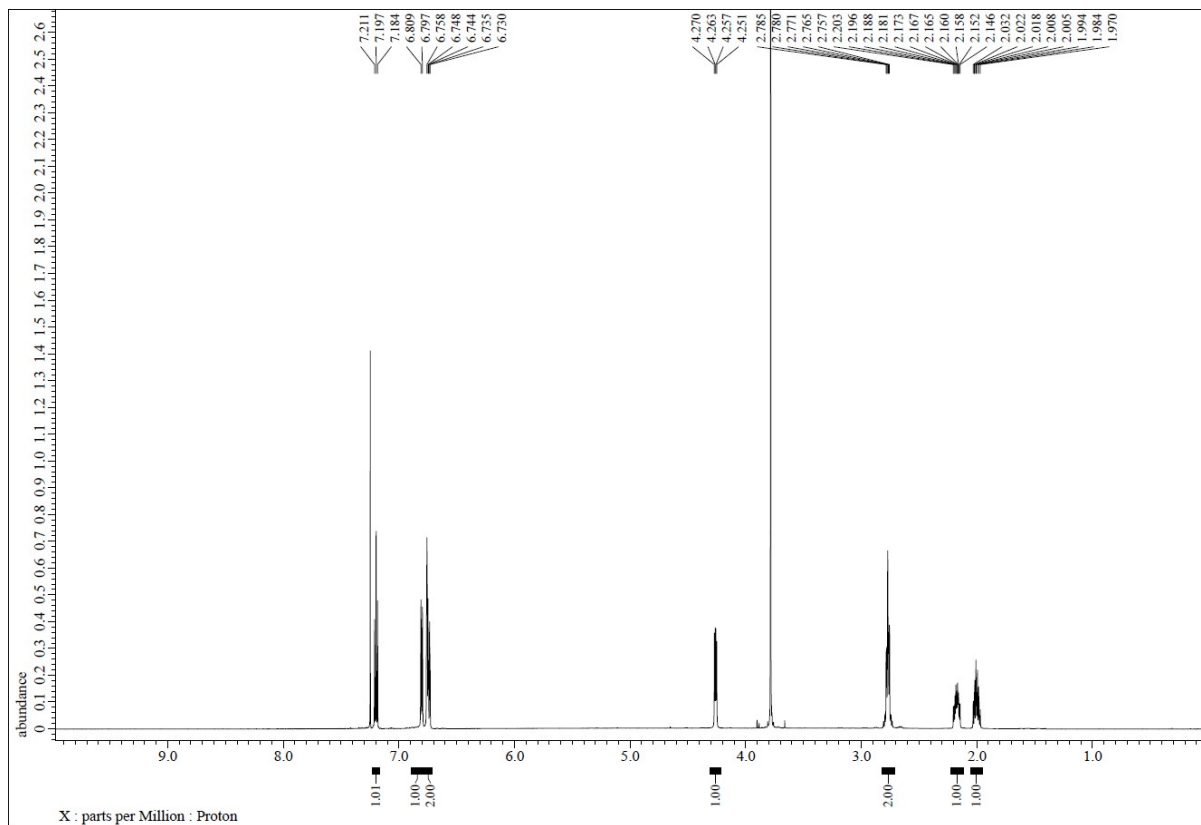
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.21 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.75-6.77 (m, 2H), 4.27 (dd, *J* = 8.1, 3.9 Hz, 1H), 2.74-2.82 (m, 2H), 2.16-2.22 (m, 1H), 1.98-2.04 (m, 1H) ppm.

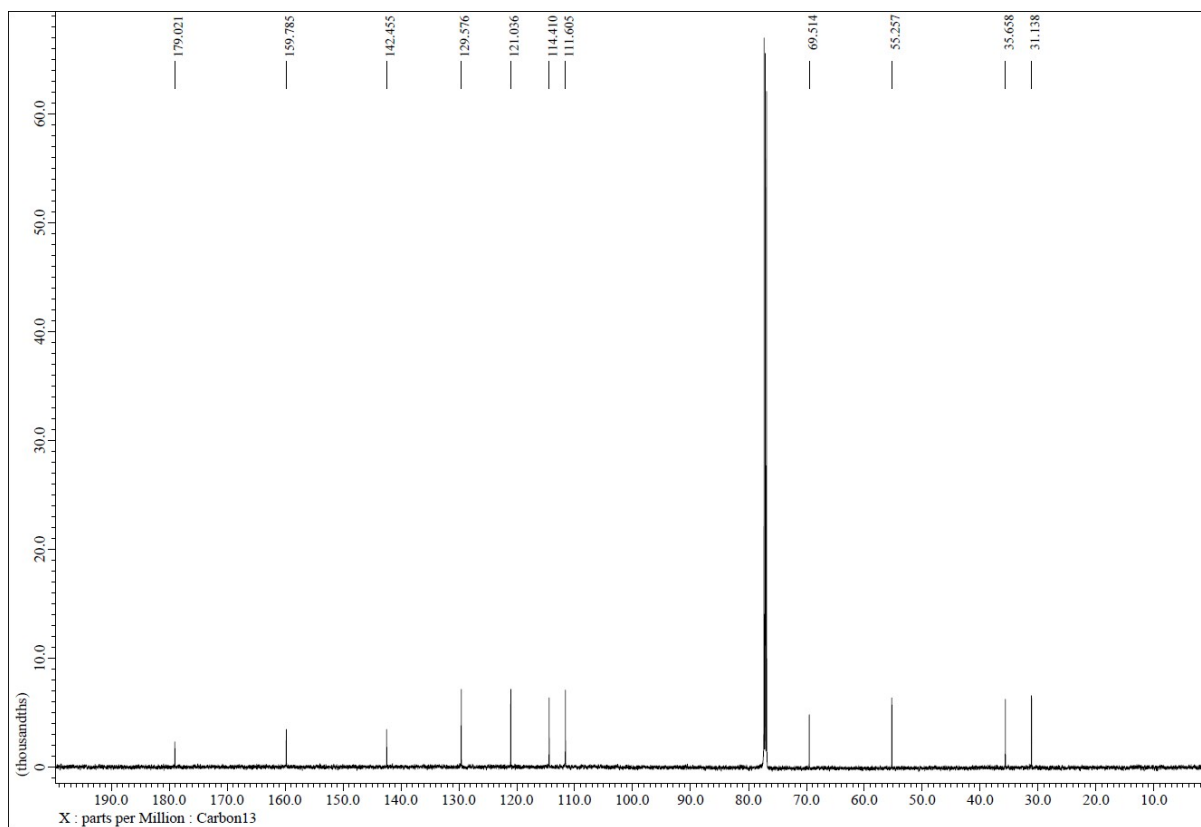
**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 179.0, 159.8, 142.4, 129.6, 121.0, 114.4, 111.6, 69.5, 55.3, 35.7, 31.1 ppm.

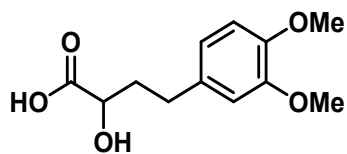
**HRMS** *m/z* (EI+, [M]) calculated for C<sub>11</sub>H<sub>14</sub>O<sub>4</sub> 210.0892, found: 210.0892.

**IR** (neat, cm<sup>-1</sup>) 3518, 2966, 2935, 1699, 1593, 1492, 1437, 1265, 1170, 1099.

**Mp** 55 °C







**4-(3,4-Dimethoxyphenyl)-2-hydroxybutanoic acid (4b)**

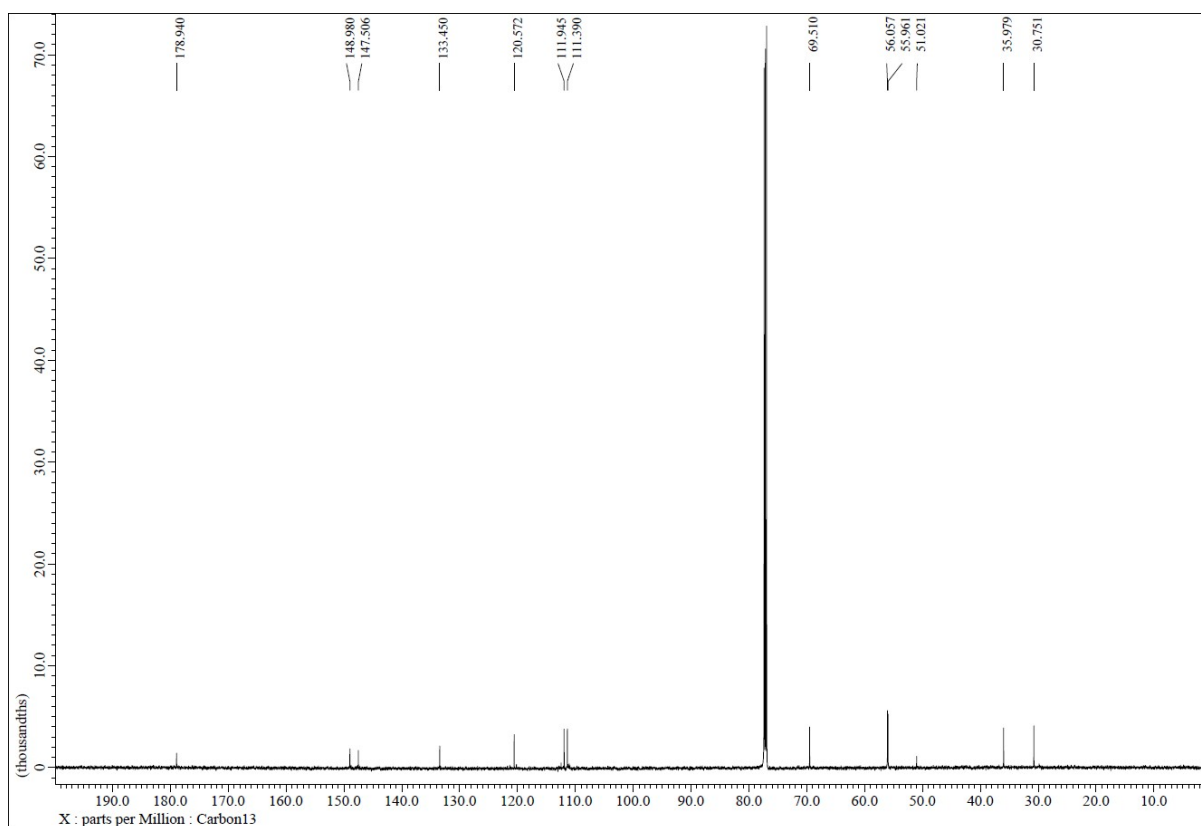
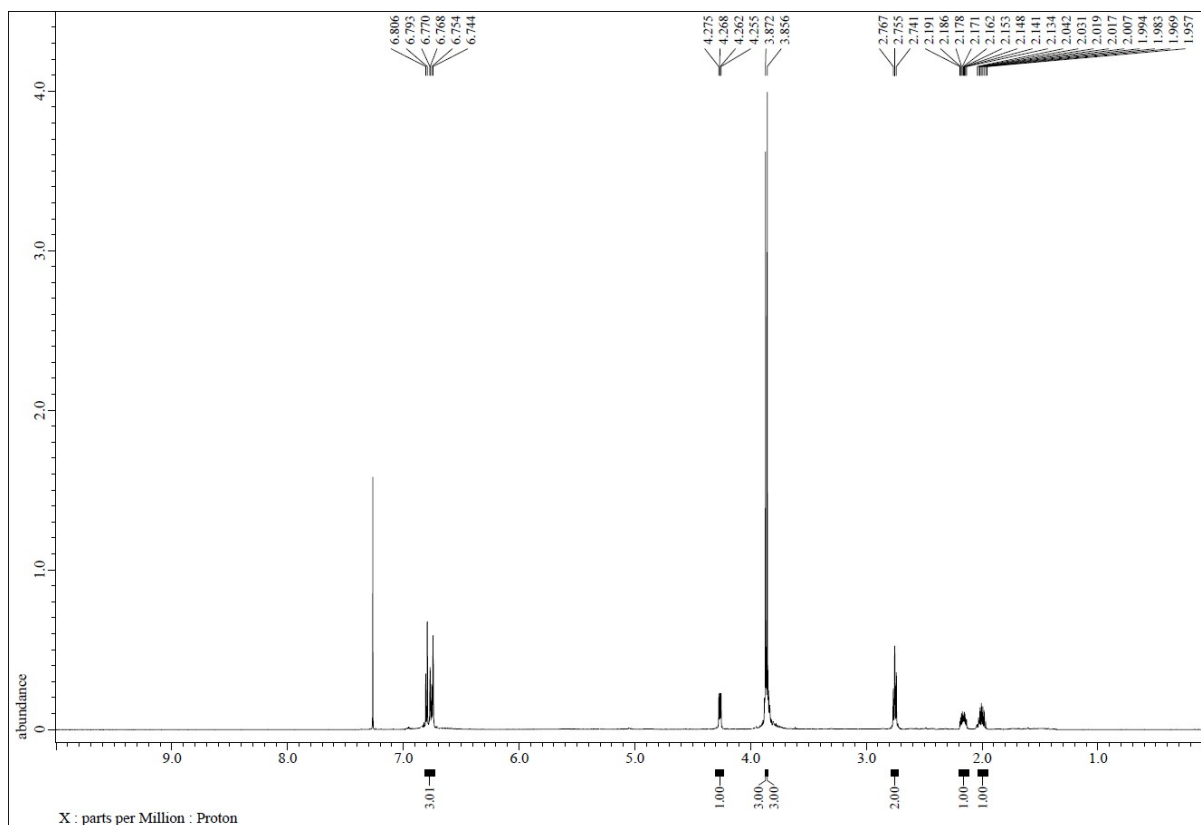
By adding HCl aqueous solution to the catalytic reaction mixture, the reaction mixture was acidified to pH = 1. The crude mixture was then purified using flash column chromatography on silica gel (using a gradient of dichloromethane 100% ~ dichloromethane: acetone (5:1)). Obtained as a brown oil.

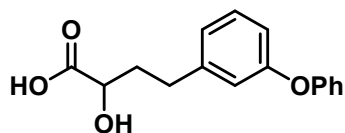
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 6.74-6.81 (m, 3H), 4.27 (dd, *J* = 7.8, 4.2 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.73-2.78 (m, 2H), 2.13-2.19 (m, 1H), 1.96-2.03 (m, 1H) ppm.

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 178.9, 149.0, 147.5, 133.5, 120.6, 112.0, 111.4, 69.5, 56.1, 56.0, 51.0, 36.0, 30.8 ppm.

**HRMS** *m/z* (EI+, [M]) calculated for C<sub>12</sub>H<sub>16</sub>O<sub>6</sub> 240.0998, found: 240.0998.

**IR** (neat, cm<sup>-1</sup>) 3463, 2929, 2842, 1725, 1517, 1263, 1133, 1025.





**2-hydroxy-4-(3-phenoxyphenyl)butanoic acid (5b)**

By adding HCl aqueous solution to the catalytic reaction mixture, the reaction mixture was acidified to pH = 1. The crude mixture was then purified using flash column chromatography on silica gel (using a gradient of dichloromethane 100% ~ dichloromethane: acetone (5:1)). Obtained as a white solid.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.33 (t, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 8.1 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.89 (s, 1H), 6.84 (dd, *J* = 8.1, 2.1 Hz, 1H), 4.27 (dd, *J* = 8.1, 3.9 Hz, 1H), 2.82-2.74 (m, 2H), 2.20-2.14 (m, 1H), 2.03-1.97 (m, 1H) ppm.

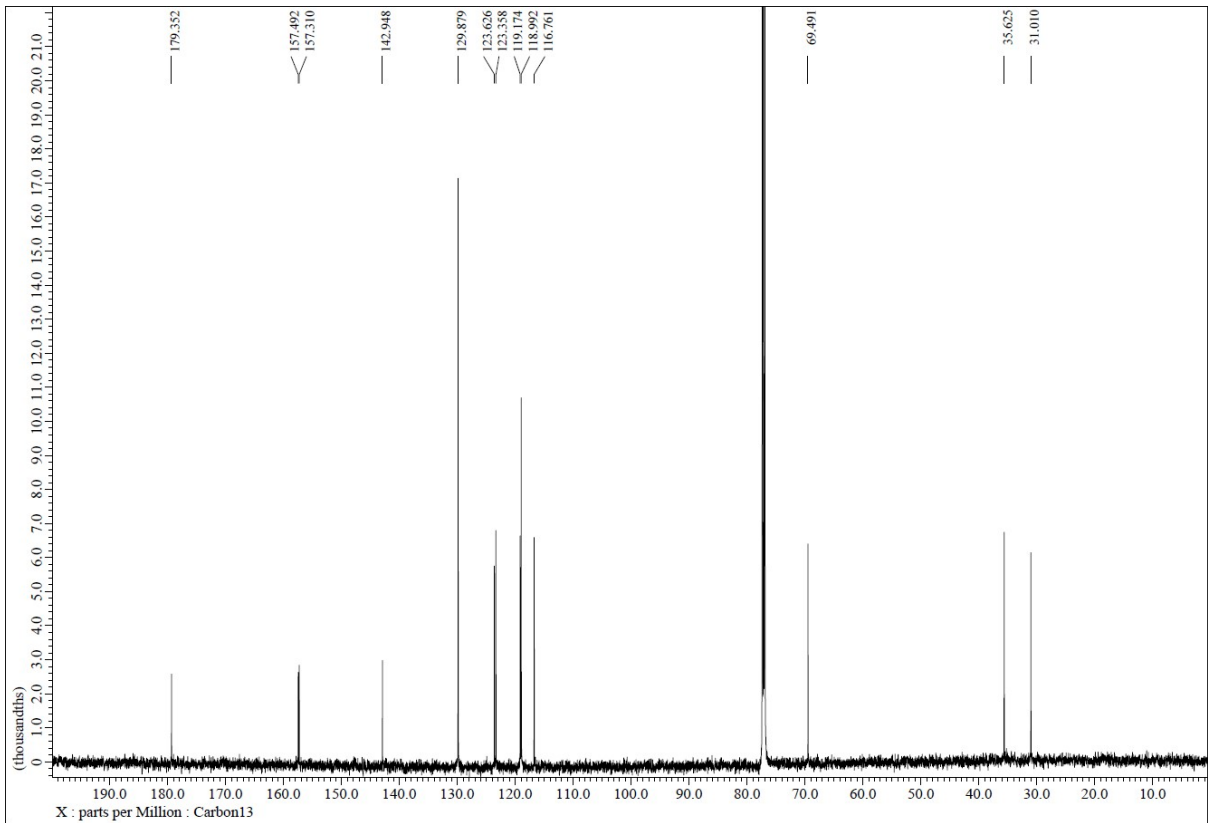
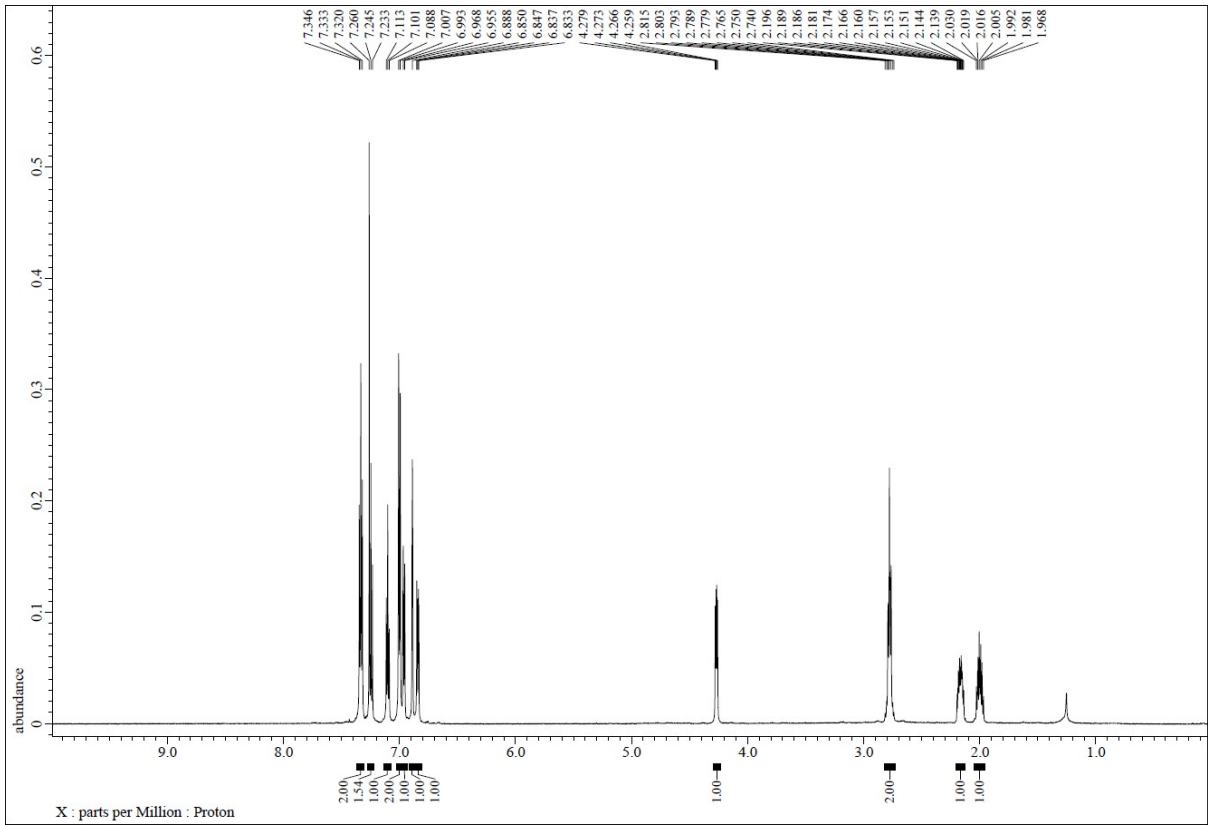
**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 179.4, 157.5, 157.3, 142.9, 129.9, 123.6, 123.4, 119.2, 119.0, 116.8, 69.5, 35.6, 31.0 ppm.

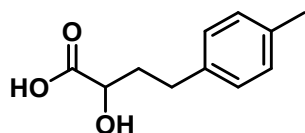
**HRMS** *m/z* (EI<sup>+</sup>, [M]) calculated for C<sub>16</sub>H<sub>16</sub>O<sub>4</sub> 272.1049, found: 272.1046

**IR** (neat, cm<sup>-1</sup>) 3508, 3308, 2942, 1690, 1585, 1484, 1449, 1257, 1178, 1081.

**Mp** 77 °C







**2-Hydroxy-4-(*p*-tolyl)butanoic acid (6b)**

By adding HCl aqueous solution to the catalytic reaction mixture, the reaction mixture was acidified to pH = 1. The crude mixture was then purified using flash column chromatography on silica gel (using a gradient of dichloromethane 100% ~ dichloromethane: acetone (5:1)). Obtained as a white solid.

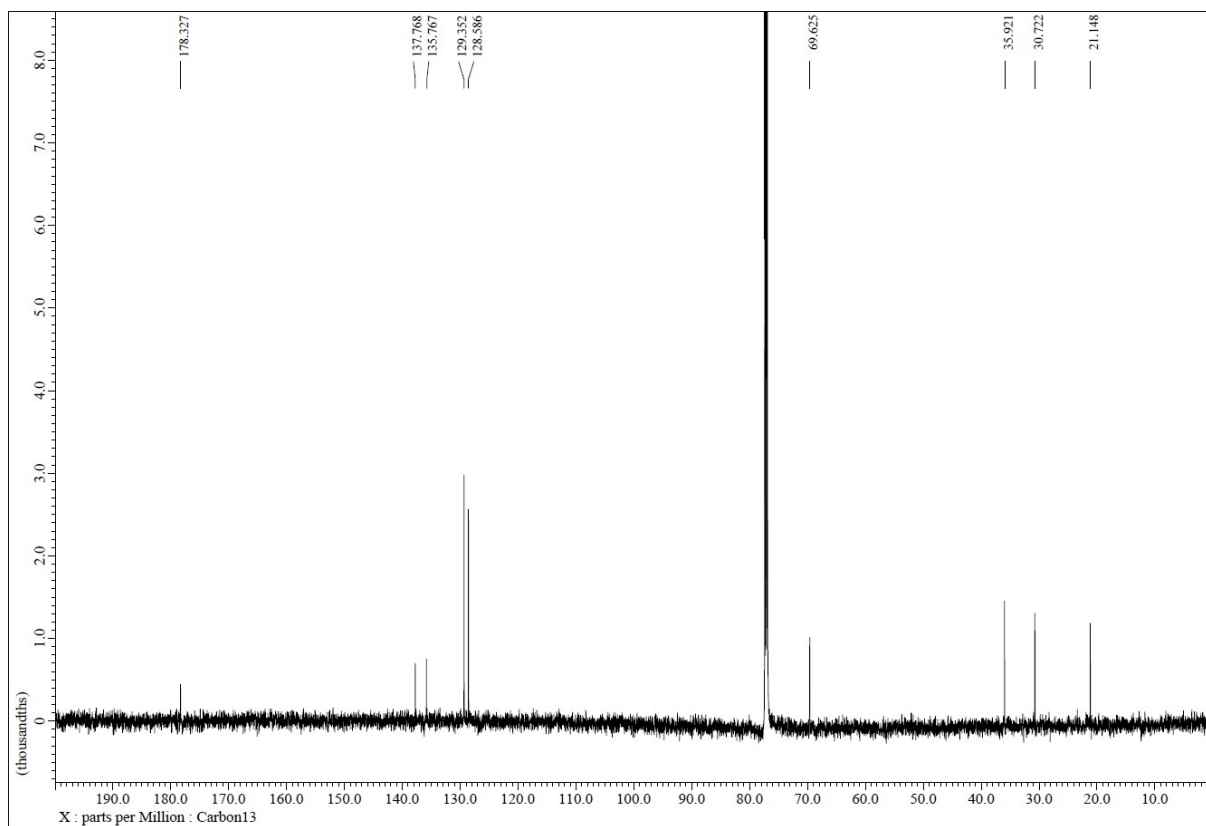
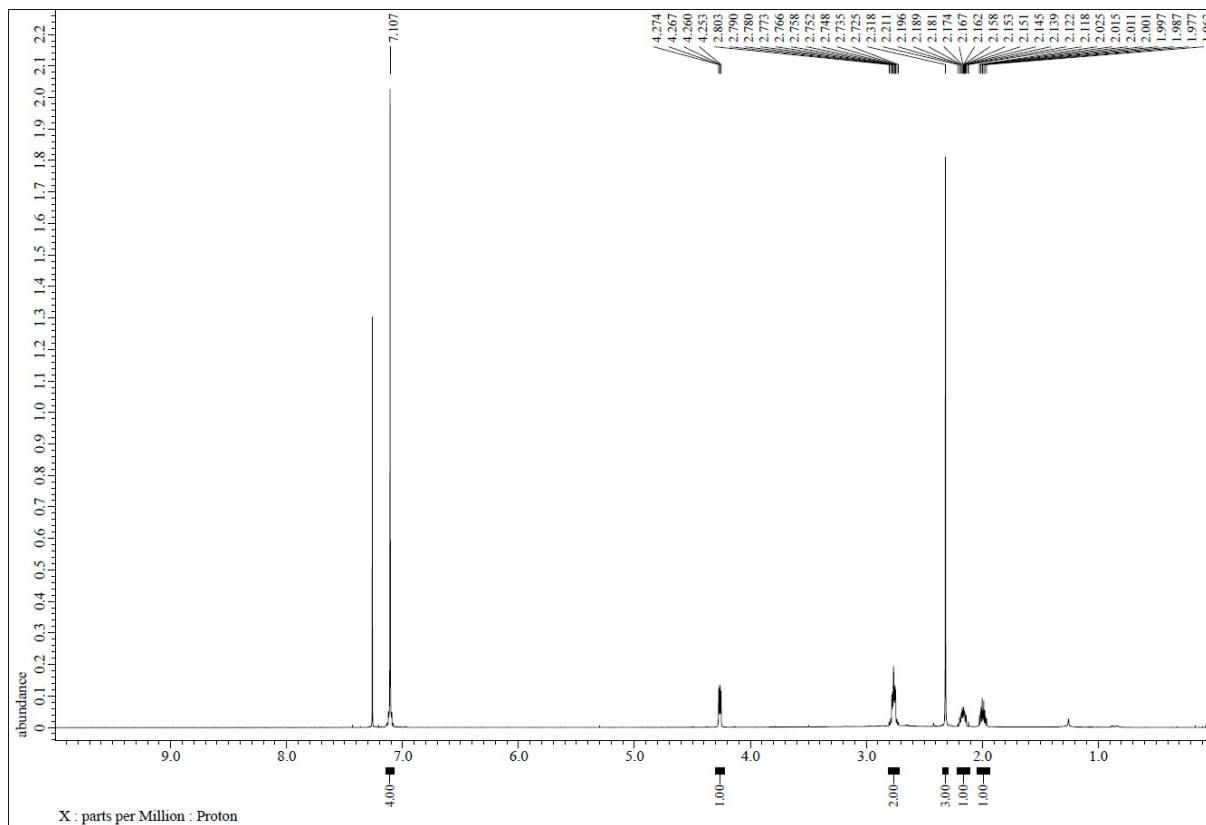
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.11 (m, 4H), 4.26 (dd, *J* = 8.4, 4.1 Hz, 1H), 2.72-2.80 (m, 2H), 2.32 (s, 3H), 2.12-2.21 (m, 1H), 1.96-2.02 (m, 1H) ppm.

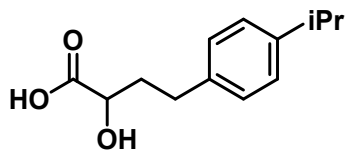
**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 178.2, 137.8, 135.8, 129.4, 128.6, 69.6, 36.0, 30.6, 21.2 ppm.

**HRMS** *m/z* (EI+, [M]) calculated for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> 194.0943, found: 194.0943.

**IR** (neat, cm<sup>-1</sup>) 3513, 2920, 2854, 1692, 1304, 11701, 1092.

**Mp** 103 °C





**2-Hydroxy-4-(4-isopropylphenyl)butanoic acid (7b)**

By adding HCl aqueous solution to the catalytic reaction mixture, the reaction mixture was acidified to pH = 1. The crude mixture was then purified using flash column chromatography on silica gel (using a gradient of dichloromethane 100% ~ dichloromethane: acetone (5:1)). Obtained as a white solid.

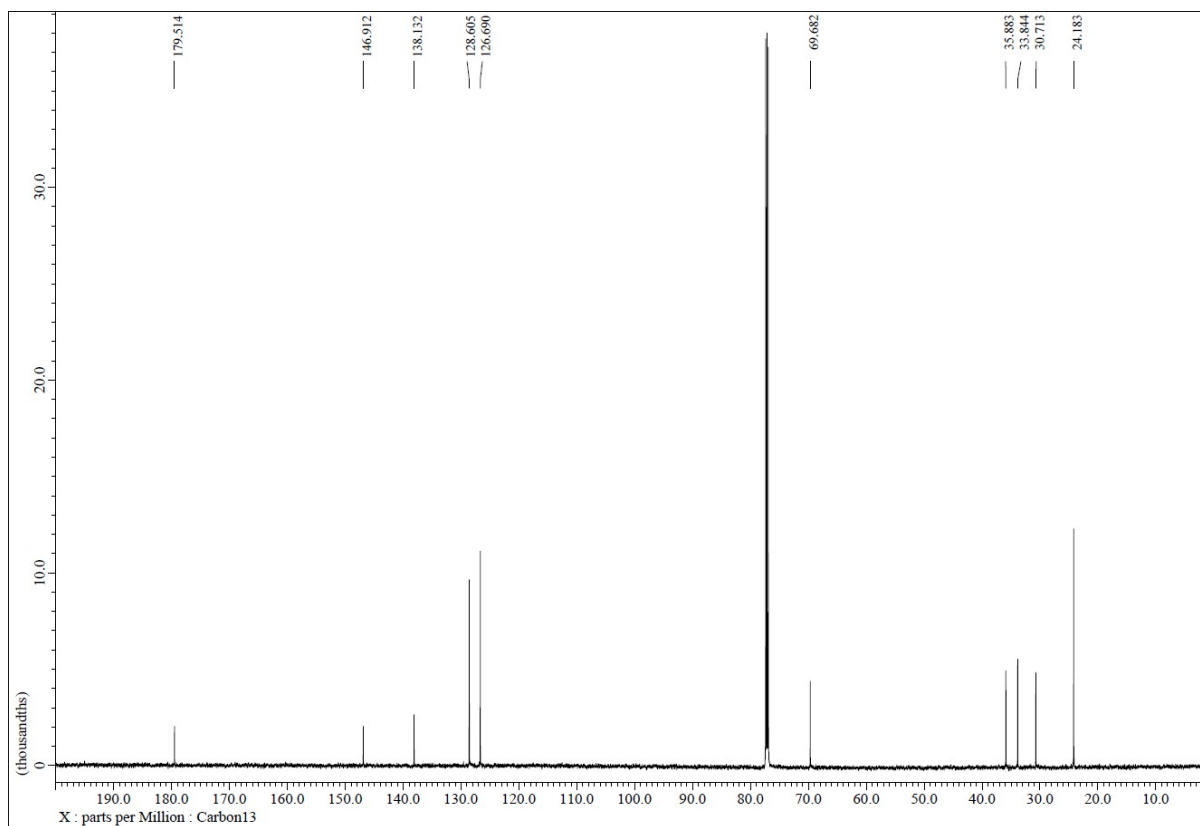
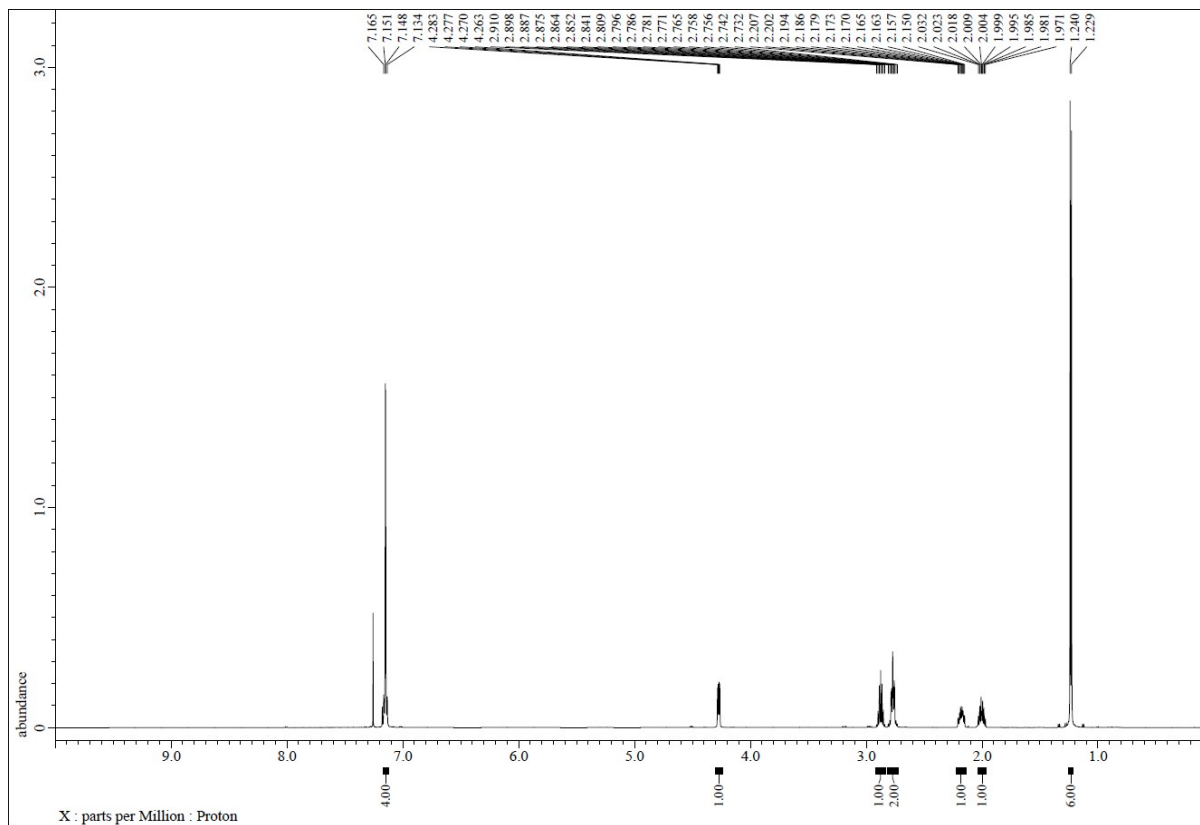
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.15 (dd, *J* = 10.3, 8.3 Hz, 4H), 4.27 (dd, *J* = 8.1, 3.9 Hz, 1H), 2.84-2.91 (sept, *J* = 6.9 Hz, 1H), 2.73-2.81 (m, 2H), 2.15-2.21 (m, 1H), 1.97-2.03 (m, 1H), 1.23 (d, *J* = 6.6 Hz, 6H) ppm.

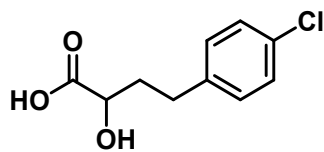
**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 179.3, 146.9, 138.0, 128.6, 126.7, 69.7, 35.9, 33.8, 30.7, 24.2 ppm.

**HRMS** *m/z* (EI<sup>+</sup>, [M]) calculated for C<sub>13</sub>H<sub>18</sub>O<sub>3</sub> 222.1256, found: 222.1259.

**IR** (neat, cm<sup>-1</sup>) 3396, 2954, 2867, 1742, 1300, 1179, 1088.

**Mp** 81 °C





**4-(4-Chlorophenyl)-2-hydroxybutanoic acid (8b)**

By adding HCl aqueous solution to the catalytic reaction mixture, the reaction mixture was acidified to pH = 1. The crude mixture was then purified using flash column chromatography on silica gel (using a gradient of dichloromethane 100% ~ dichloromethane: acetone (5:1)). Obtained as a white solid.

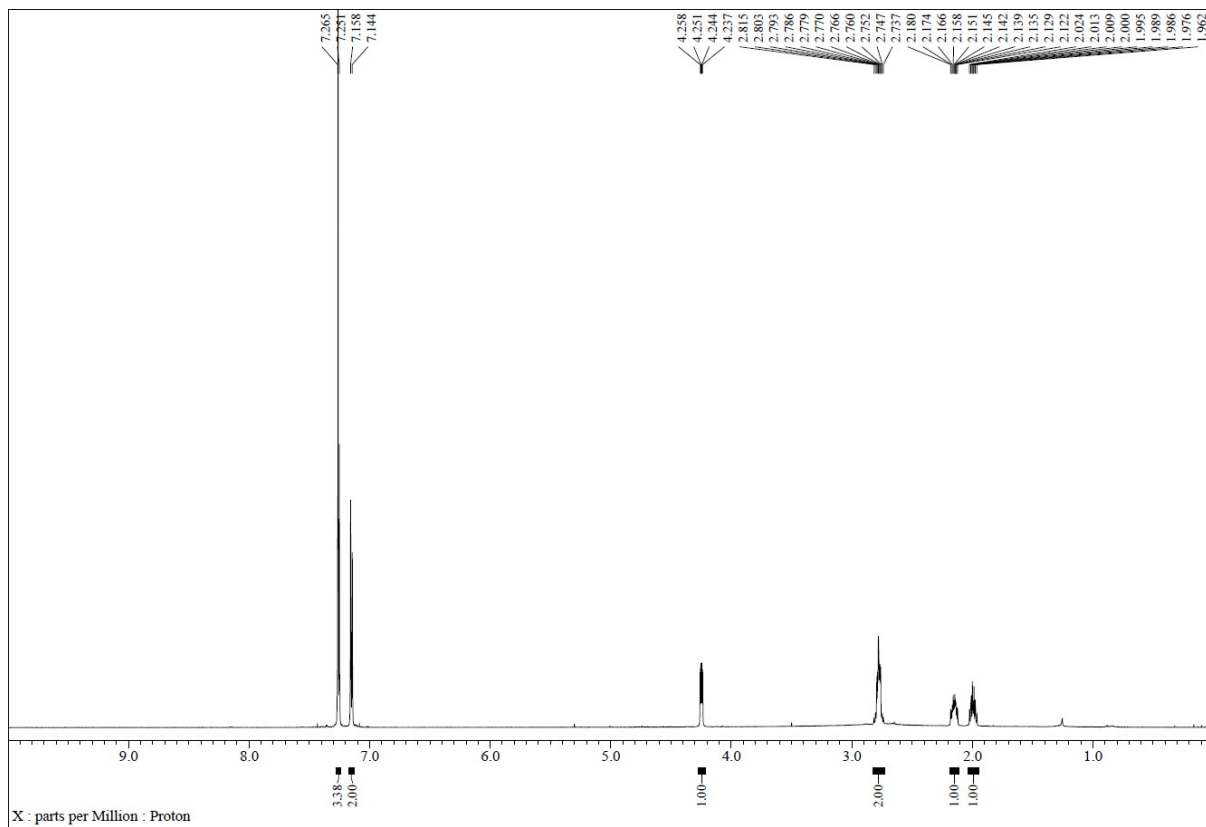
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.25 (d, *J* = 8.4 Hz, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 4.25 (dd, *J* = 8.4, 4.1 Hz, 1H), 2.74-2.82 (m, 2H), 2.12-2.18 (m, 1H), 1.96-2.02 (m, 1H) ppm.

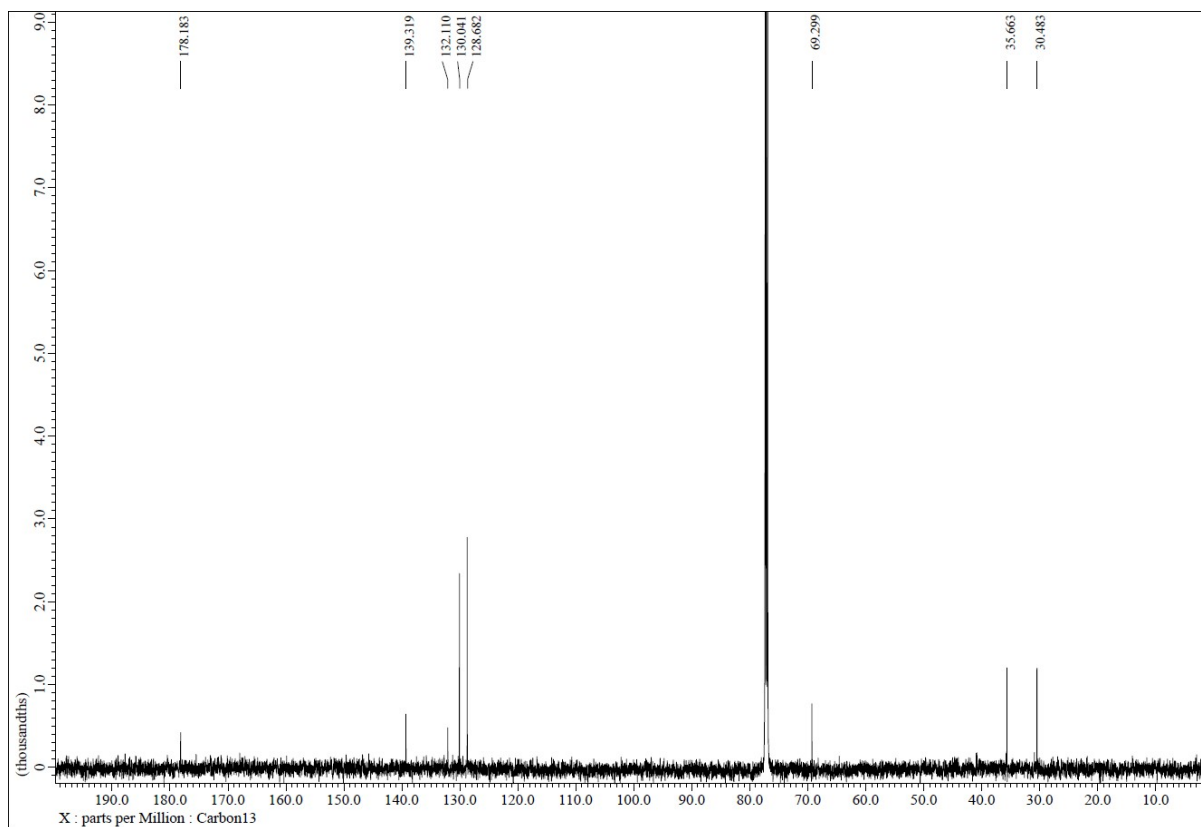
**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 178.2, 139.3, 132.1, 130.2, 128.8, 69.3, 35.7, 30.5 ppm.

**HRMS** *m/z* (EI+, [M]) calculated for C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>Cl 214.0397, found: 214.0397.

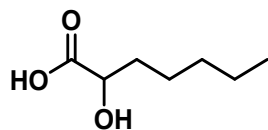
**IR** (neat, cm<sup>-1</sup>) 3421, 2917, 2854, 1708, 1262, 1083.

**Mp** 112 °C









**2-Hydroxyheptanoic acid (9b)**

By adding HCl aqueous solution to the catalytic reaction mixture, the reaction mixture was acidified to pH = 1. The crude mixture was then purified using flash column chromatography on silica gel (using a gradient of hexane: ethyl acetate (10:1) ~ hexane: ethyl acetate (1:1)). Obtained as a white solid.

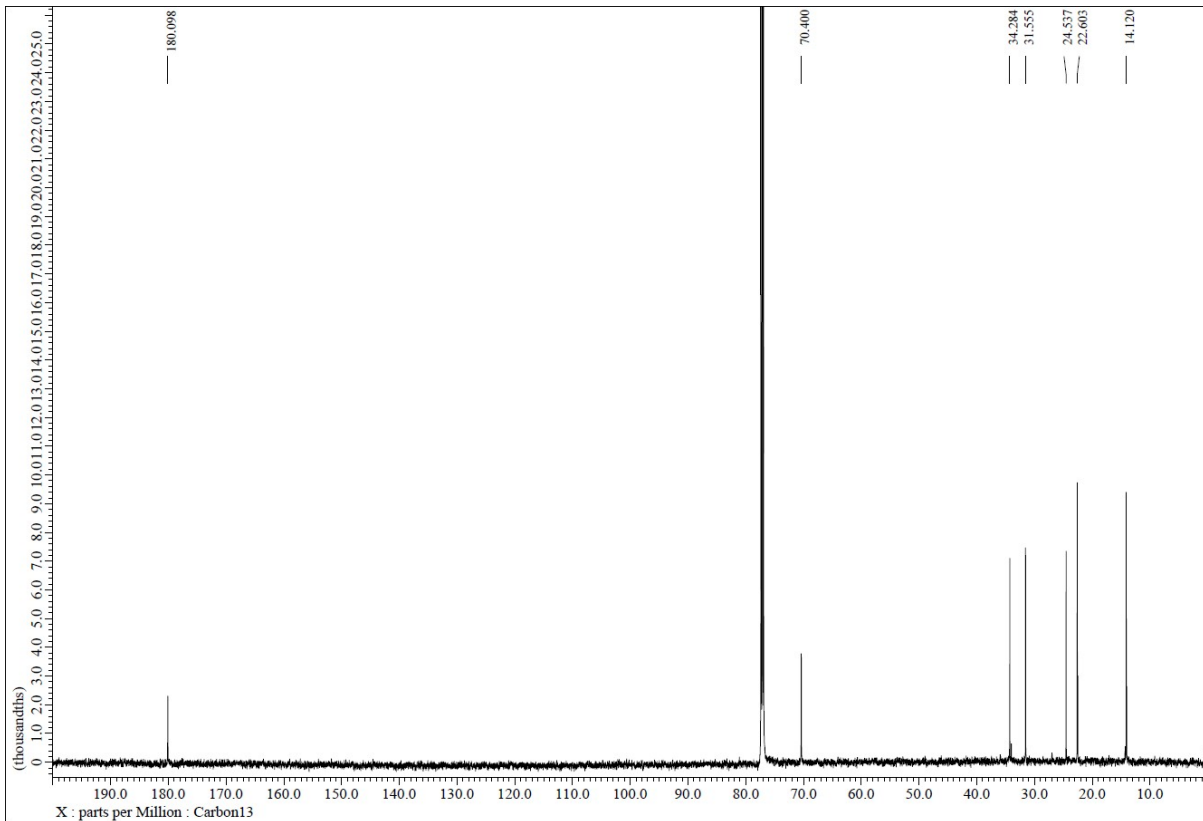
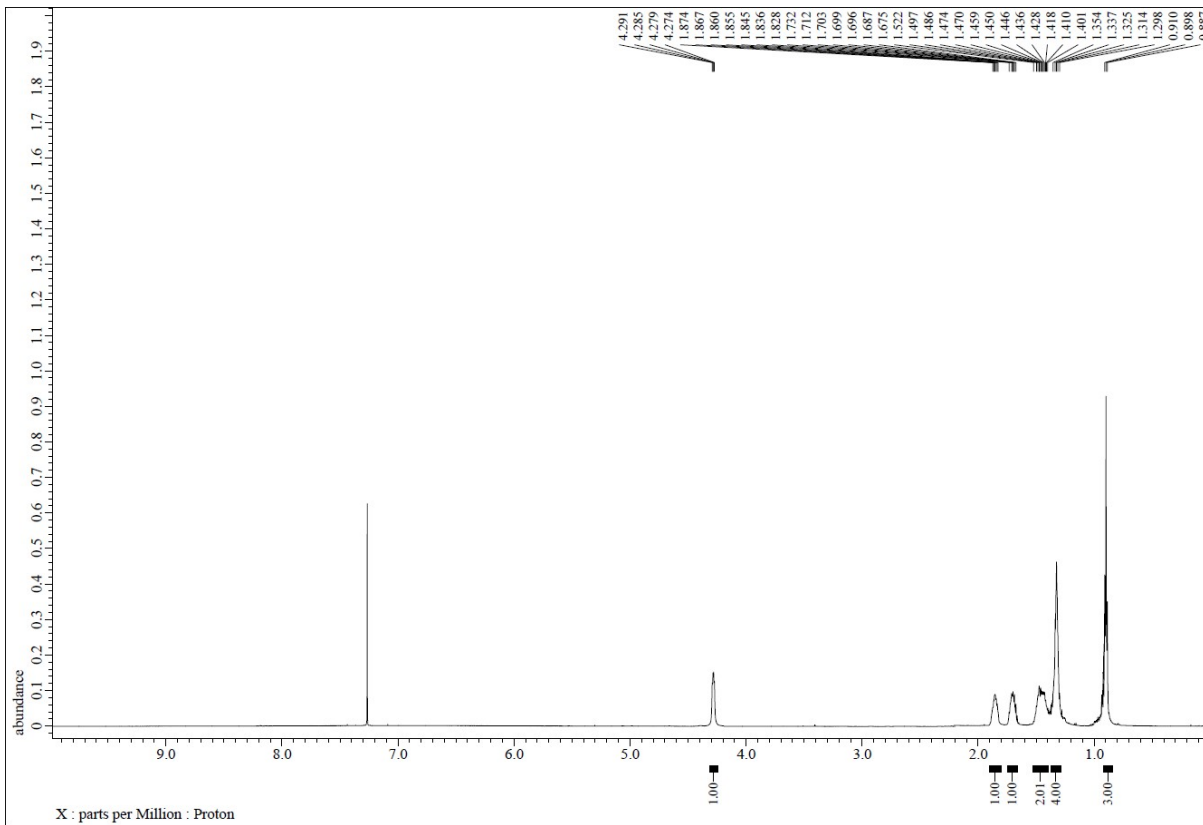
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 4.28 (dd, *J* = 6.9, 3.3 Hz, 1H), 1.87-1.83 (m, 1H), 1.73-1.68 (m, 1H), 1.52-1.40 (m, 2H), 1.35-1.30 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H) ppm.

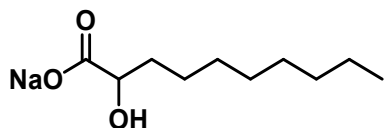
**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 180.1, 70.4, 34.3, 31.6, 24.5, 22.6, 14.1 ppm.

**HRMS** *m/z* (FAB+, [M+H]<sup>+</sup>) calculated for C<sub>7</sub>H<sub>15</sub>O<sub>3</sub> 147.1016, found: 147.1021.

**IR** (neat, cm<sup>-1</sup>) 3454, 3400, 2958, 2875, 1704, 1208, 1083.

**Mp** 48 °C





**Sodium 2-hydroxydecanoate (10b)**

By adding HCl aqueous solution to the catalytic reaction mixture, the reaction mixture was acidified to pH = 1. The crude mixture was then purified using flash column chromatography on silica gel (using a gradient of dichloromethane 100% ~ dichloromethane: acetone (5:1)). The obtained organic acid was basified by treating with a methanolic solution of NaOH to form a salt. Obtained as a white solid.

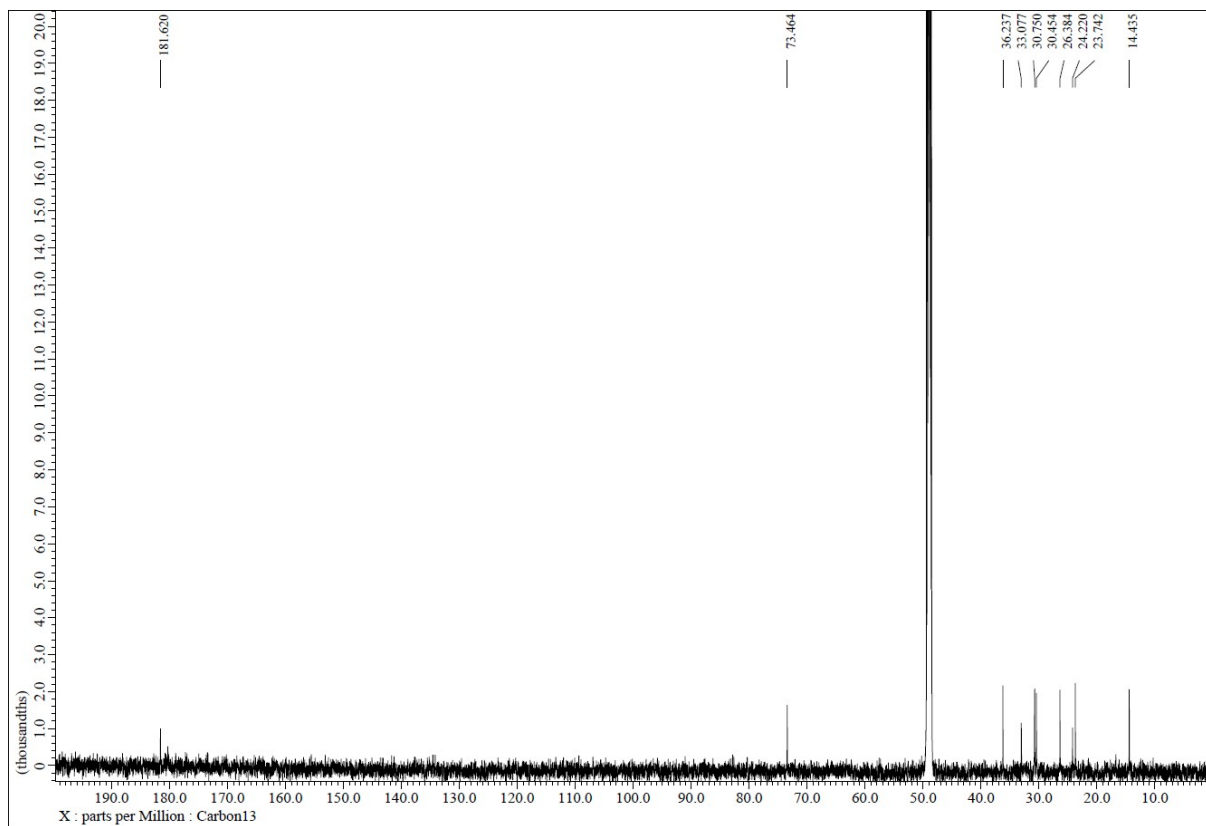
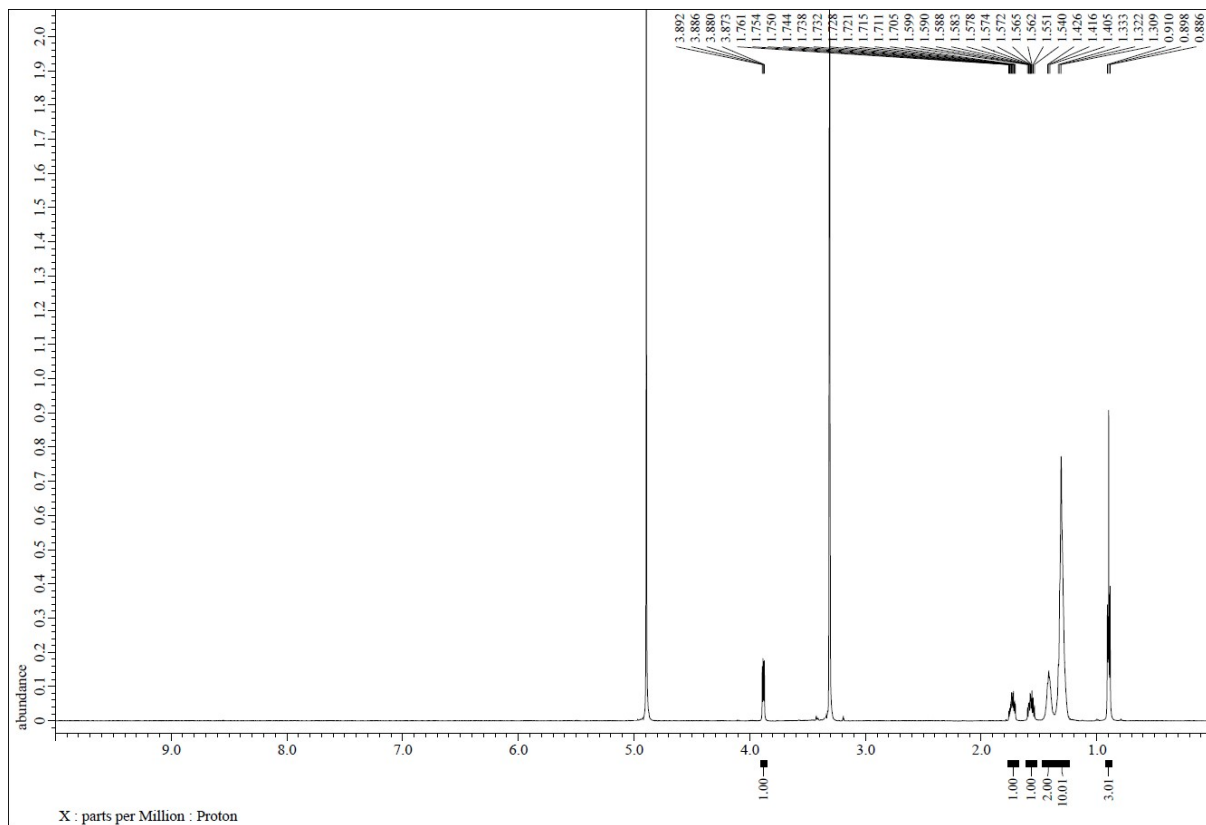
<sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD) δ 3.88 (dd, *J* = 7.5, 3.5 Hz, 1H), 1.76-1.71 (m, 1H), 1.59-1.55 (m, 1H), 1.46-1.37 (m, 2H), 1.36-1.25 (m, 10H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>OD) δ 181.6, 73.5, 36.2, 33.1, 30.8, 30.5, 26.4, 24.2, 23.7, 14.4 ppm.

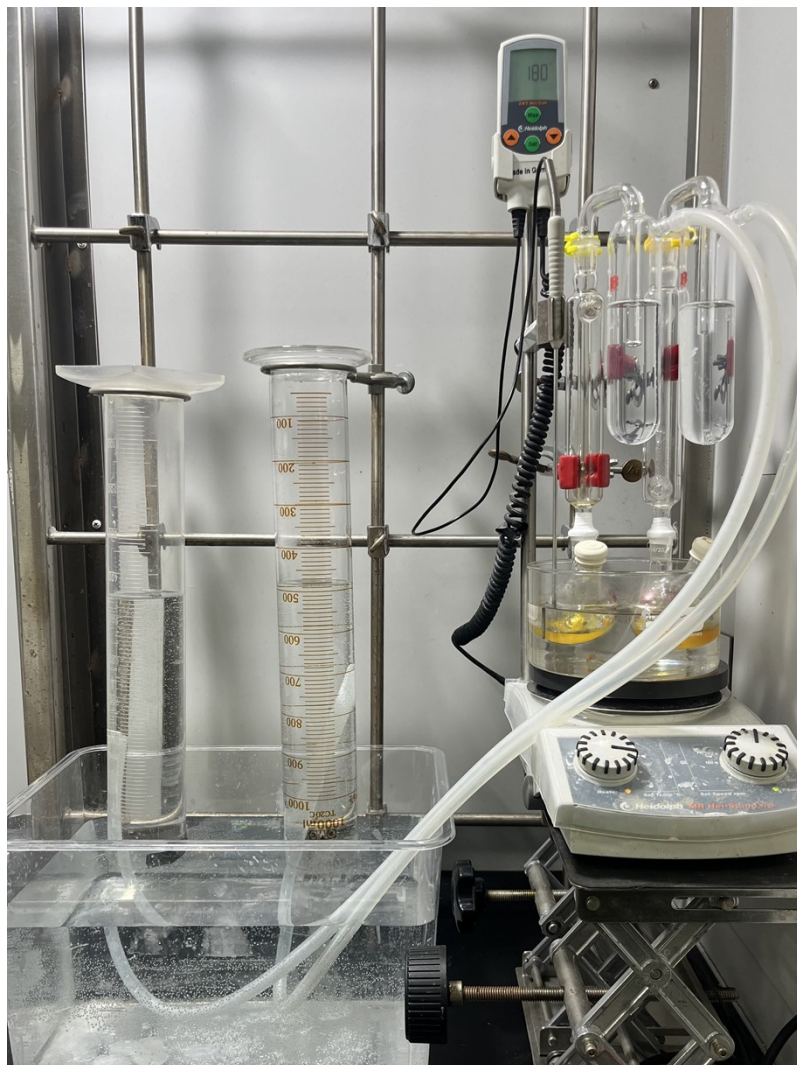
HRMS *m/z* (FAB-, [M-Na]<sup>-</sup>) calculated for C<sub>10</sub>H<sub>19</sub>O<sub>3</sub> 187.1340, found: 187.1337

IR (neat, cm<sup>-1</sup>) 3169, 2918, 2851, 1571, 1421, 1322, 1087.

Mp decomposed at 280 °C



## V. A photo of the reaction apparatus



**Figure S5** Reaction setup for the coupling of glycerol and alcohols