

## Supporting Information

### Direct Conversion of Glycerol into Formic Acid via Water Stable Pd(II) Catalyzed Oxidative Carbon-Carbon Bond Cleavage

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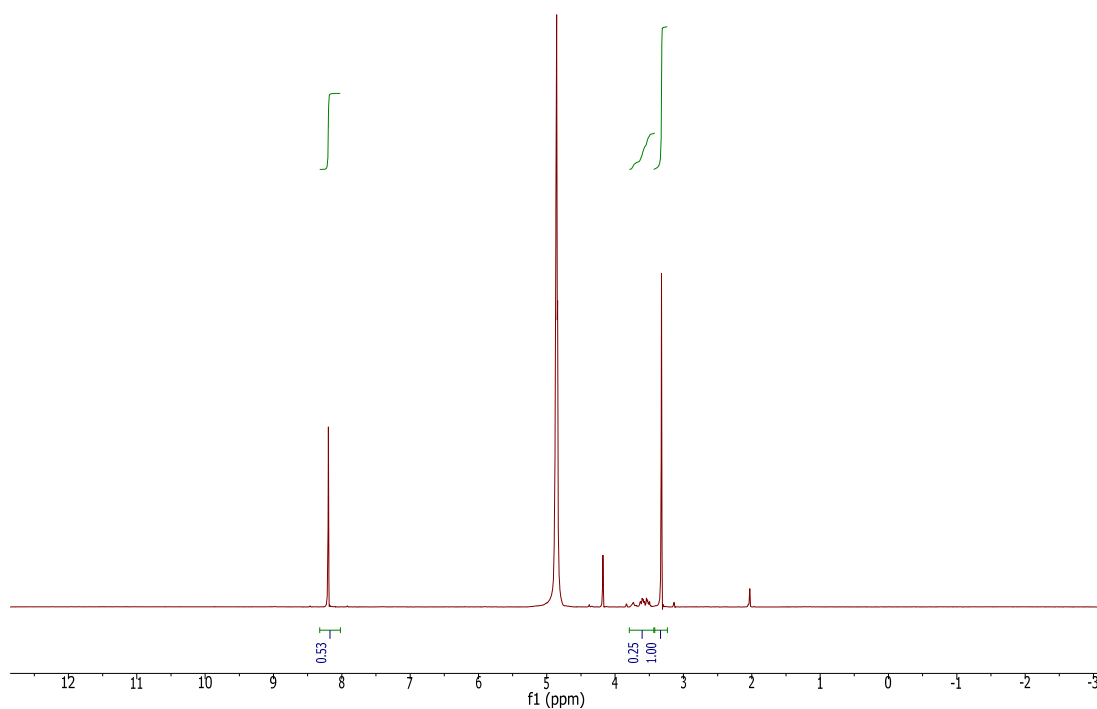
## 1. General information

All commercially available reagents and solvents were used as received from Aldrich, Acros chemical and Mallinckrodt Chemicals without further purification. 2-<sup>13</sup>C and 1,3-<sup>13</sup>C glycerol were purchased from Isotope Lab. 1-<sup>13</sup>C glycolic acid and Pd complex **4** were prepared through the methods described in previous literatures.<sup>1,2</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 400MHz Varian instrument. Chemical shifts were reported in ppm relative to TMS for <sup>1</sup>H- and <sup>13</sup>C-NMR spectra while CDCl<sub>3</sub> and D<sub>2</sub>O were used as the NMR solvents. All the experiments were run in vials and stirred using magnetic stir bars. To collect NMR data for reaction mixtures in H<sub>2</sub>O solutions, the wet1D parameter was used. In addition, 1 or 2 μL methanol was added into the reaction mixture as an internal reference after the reaction.

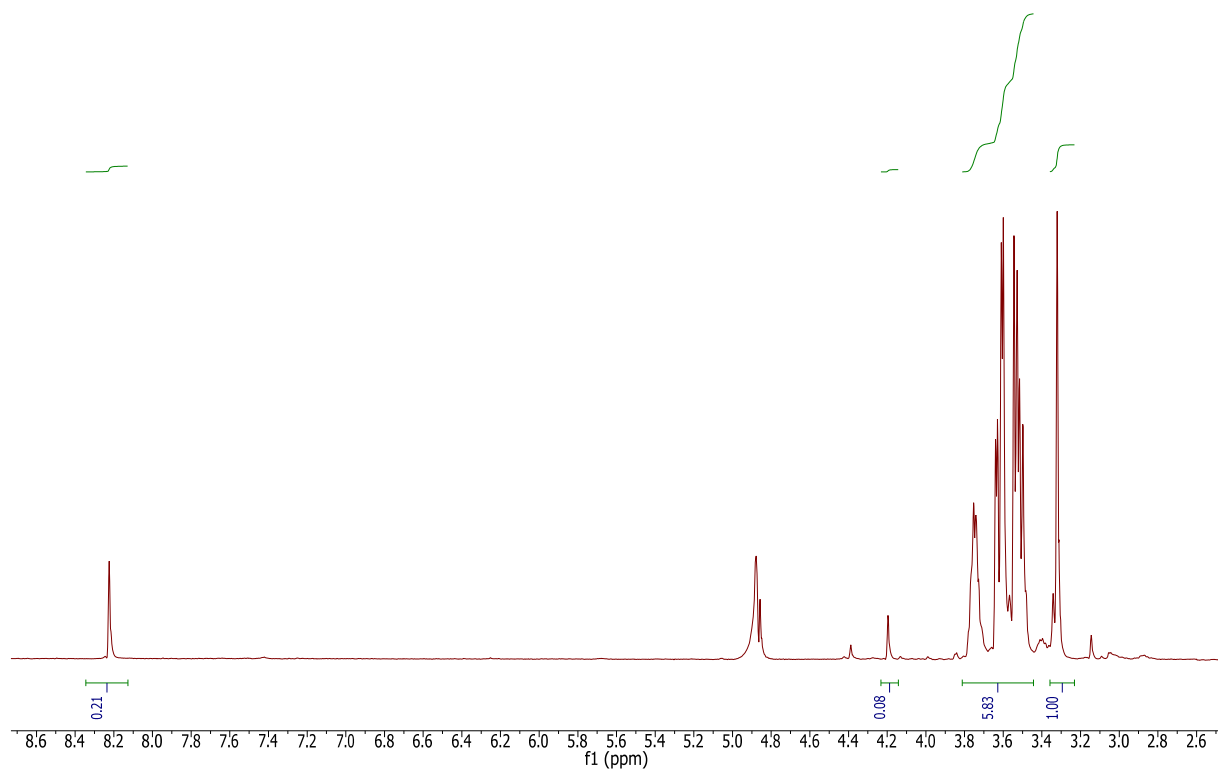
## 2. Catalytic oxidative carbon-carbon bond cleavage of glycerol with various oxidizing agents in the presence of Pd catalysts at room temperature (table 1).

Entries 1~3: Glycerol (10 mg, 10.8 x 10<sup>-5</sup> mol) and 5 mol% of Pd catalyst (entry 1: PdCl<sub>2</sub>, entry 2: Pd(OAc)<sub>2</sub>, and entry 3: **4**) were placed in a 1 dram vial with a stir bar. After the addition of 30% H<sub>2</sub>O<sub>2</sub> (0.4 mL) and H<sub>2</sub>O (0.1 mL), the reaction vial was closed and the reaction mixture was stirred for 6 hours at ambient temperatures. For the NMR study, D<sub>2</sub>O (0.2 mL) and 1 μL of methanol were added into the reaction mixture. In the entry 4, *t*BuOOH (70% in H<sub>2</sub>O, 0.4 mL) was used instead of H<sub>2</sub>O<sub>2</sub>. Entries 5~6: 10.8 x 10<sup>-5</sup> mol of oxidant (entry 5: oxone, entry 6: K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) in 0.3 mL of H<sub>2</sub>O was used instead of H<sub>2</sub>O<sub>2</sub>. Entry 7: O<sub>2</sub> was bubbled in 0.3 mL of H<sub>2</sub>O solution of catalyst and glycerol.

### <sup>1</sup>H wet1D NMR of table 1, entry 3



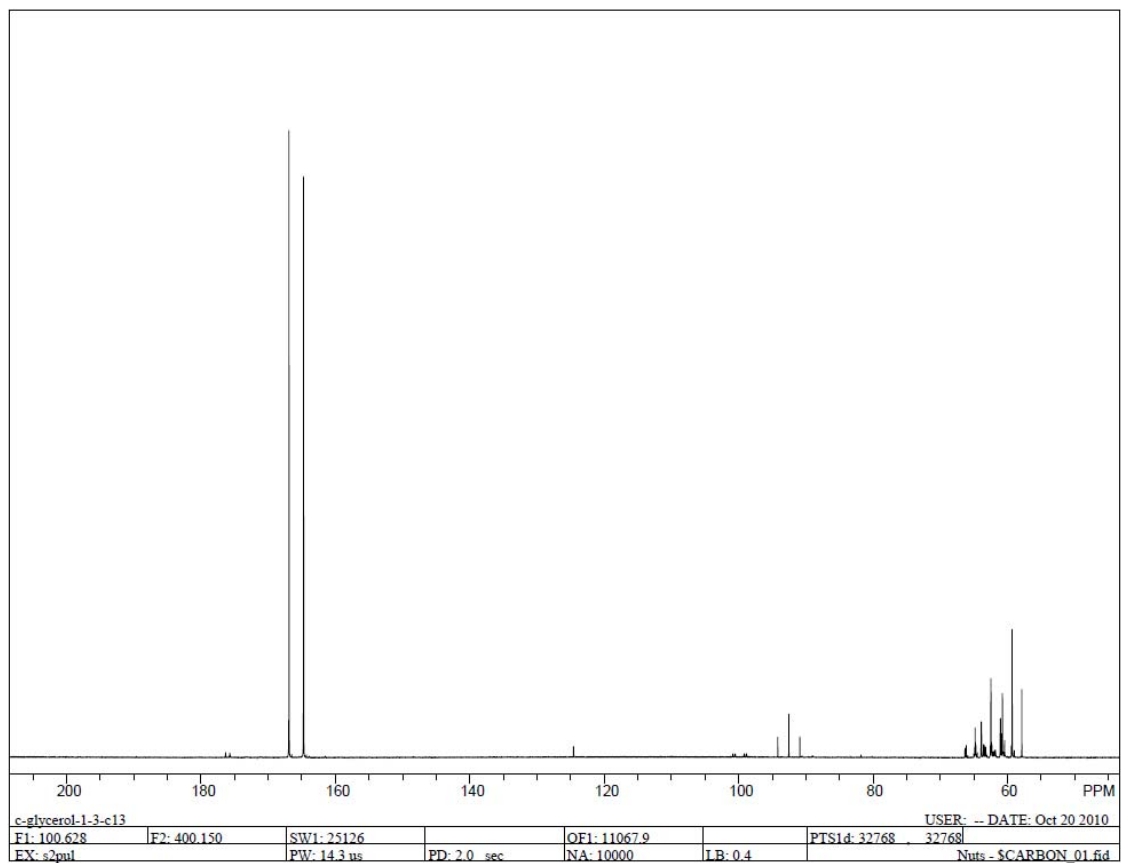
**<sup>1</sup>H wet1D NMR of table 1, entry 5**



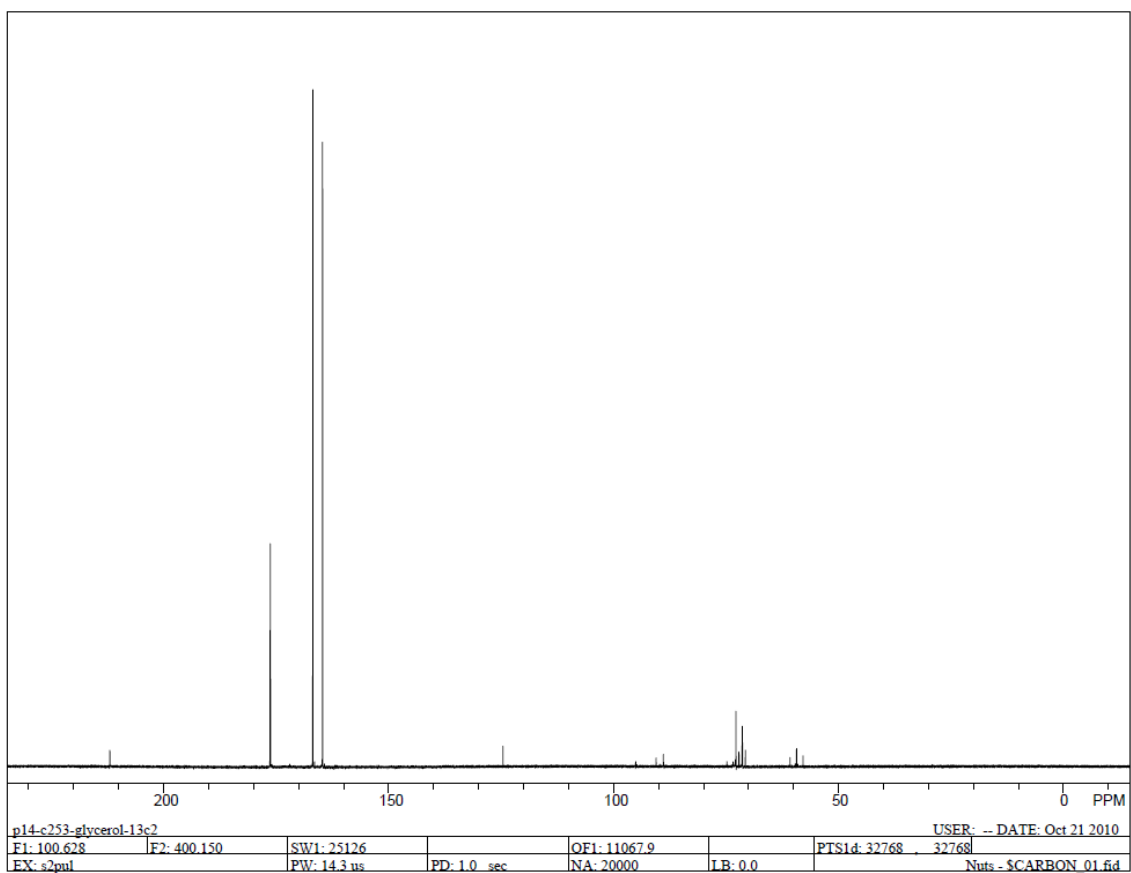
### 3. Isotope labeled study of glycerol

10 mg of  $^{13}\text{C}$ -labeled glycerol (1,3- $^{13}\text{C}$  (**5**) or 2- $^{13}\text{C}$  (**8**)) was placed in a one dram reaction vial with 4 mg of **4**. 0.4 mL of  $\text{H}_2\text{O}_2$  was added into the reaction mixture, which was placed on a 60 °C heating block for 6 hours. After the reaction, 0.2 mL of  $\text{D}_2\text{O}$  and 1  $\mu\text{L}$  of methanol were added and wet1D NMR spectra of the product were collected. The ratio of  $\text{H}^{13}\text{CO}_2\text{H}$  ( $J_{\text{C-H}} = 218 \text{ Hz}$ , 8.2 ppm) and  $\text{HCO}_2\text{H}$  (8.03 ppm) was 2 to 1 with 1,3- $^{13}\text{C}$  glycerol and 1 to 2.5 with 2- $^{13}\text{C}$  glycerol.

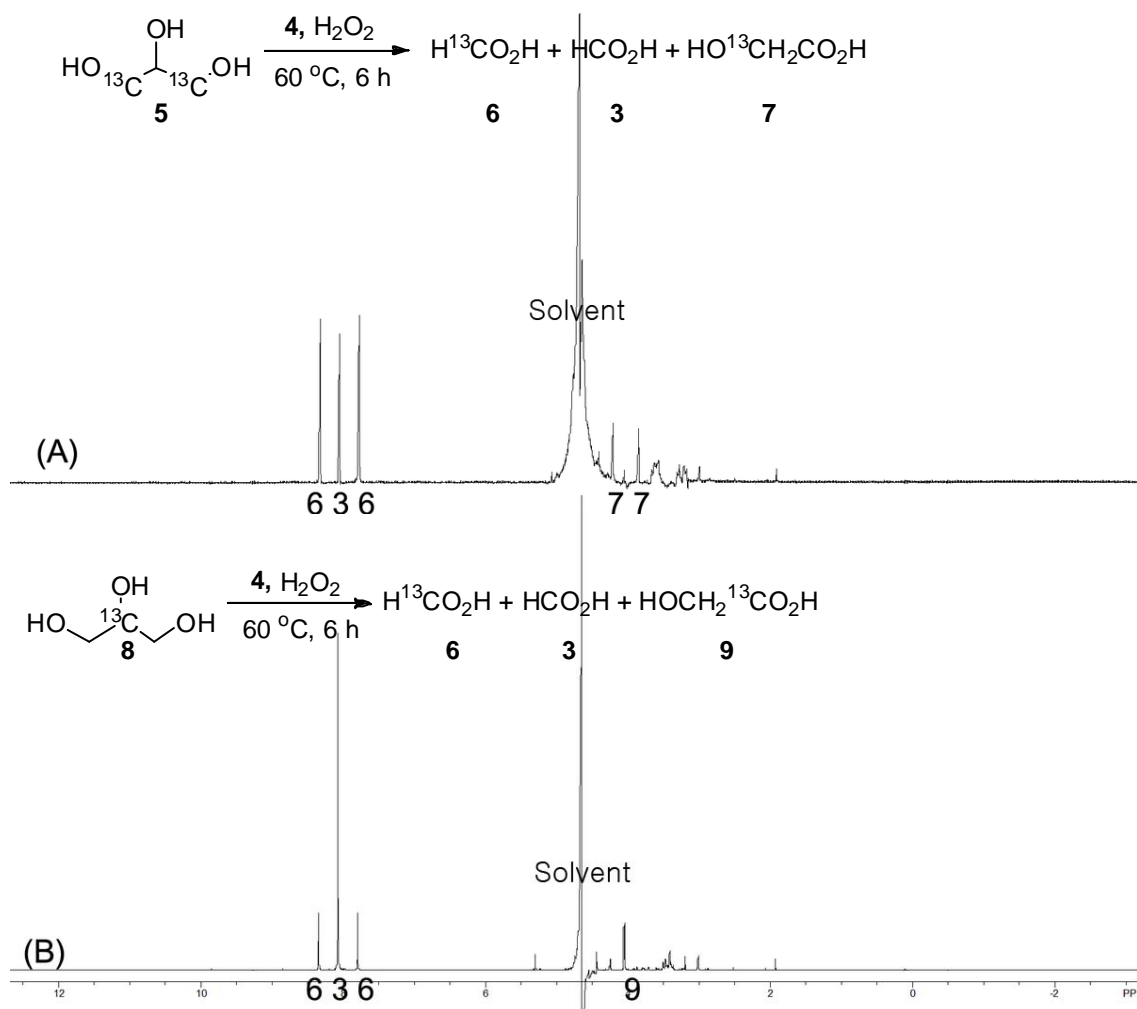
### Isotope labeled study of glycerol $^{13}\text{C}$ NMR with **5**



# Isotope labeled study of glycerol $^{13}\text{C}$ NMR with 8



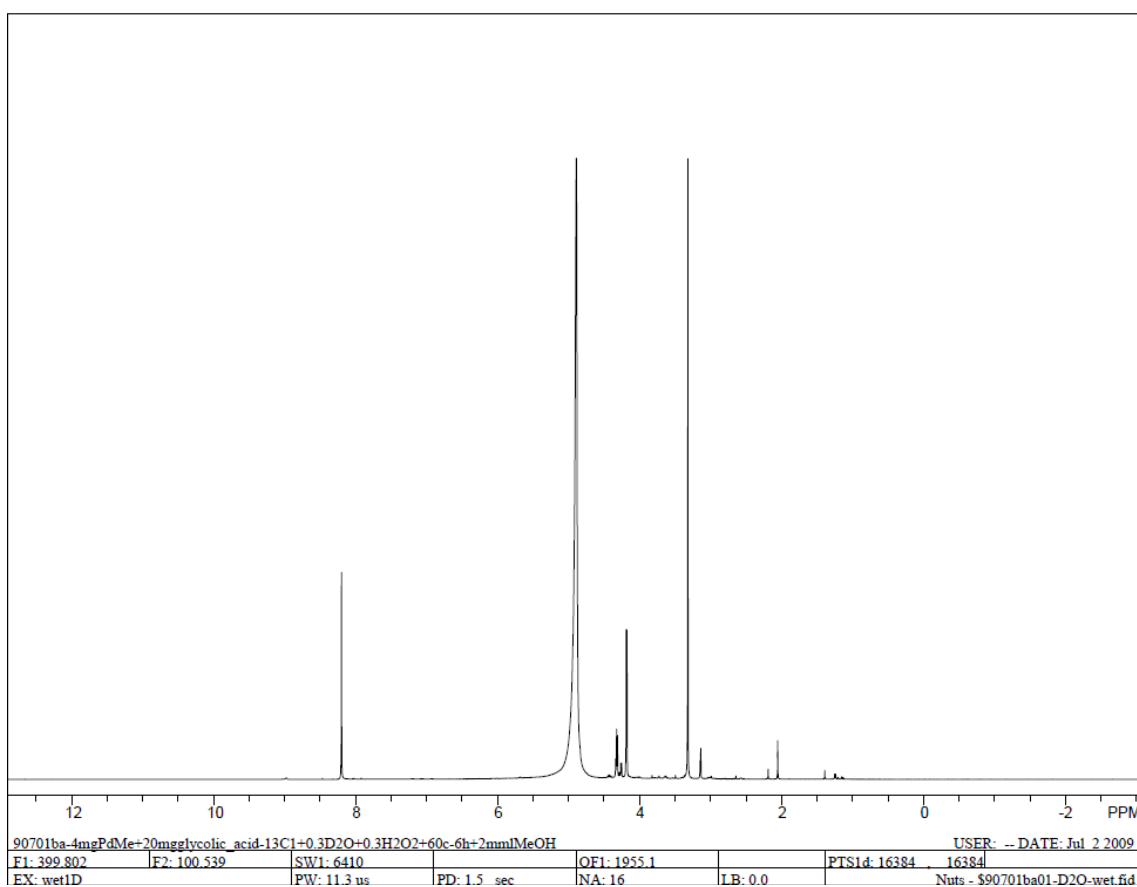
**Figure 1.**  $^1\text{H-NMR}$  spectra for the oxidative degradation reactions of 1,3- $^{13}\text{C}$ -glycerol (A) and 2- $^{13}\text{C}$ -glycerol (B).



#### 4. Isotope labeled study of glycolic acid

4mg of **4** and 20 mg of 1-<sup>13</sup>C-labeled glycolic acid (**9**) were placed into a one dram reaction vial. Then 0.3 mL of H<sub>2</sub>O<sub>2</sub> was added into the reaction mixture, which was placed on a 60 °C heating block for 6 hours. After the reaction, 0.2 mL of D<sub>2</sub>O and 2 μL of methanol were added and wet1D NMR spectra of the product were collected. Conversion yield of formic acid (HCO<sub>2</sub>H at 8.2 ppm): 10% based on glycolic acid. No formation of H<sup>13</sup>CO<sub>2</sub>H was observed.

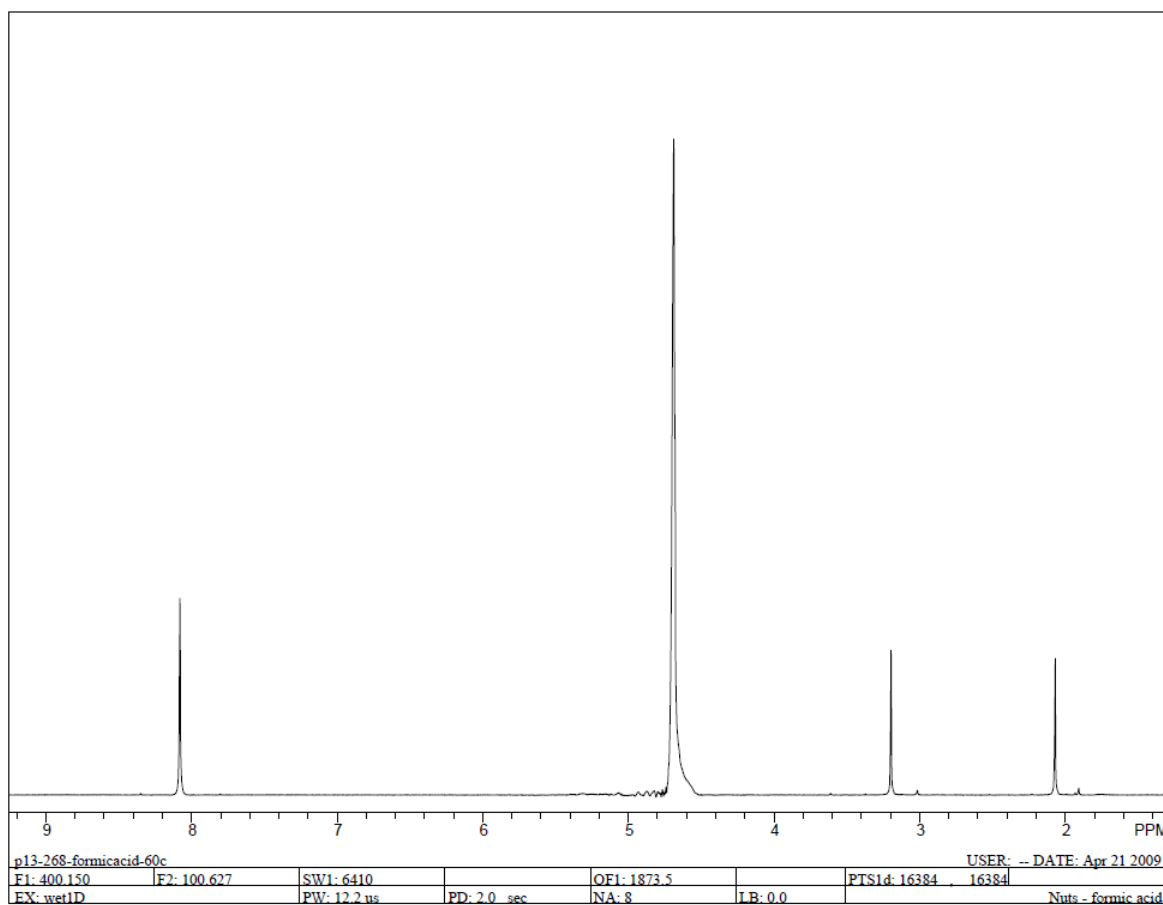
#### Isotope labeled study of glycolic acid wet1D



## 5. Degradation of formic acid.

1 mg of Pd catalyst **4** was added to 16.4 mg of formic acid in a 1 dram vial. After the addition of 0.2 mL of H<sub>2</sub>O<sub>2</sub> and 0.2 mL of H<sub>2</sub>O, the reaction mixture was stirred for 5 hours on a 60 °C heating block. Then 0.2 mL of D<sub>2</sub>O and 1 μL of methanol were added, and wet1D NMR spectra of the product were collected. 3% of formic acid (8.2 ppm) remained.

### Degradation of formic acid





## 6. Optimization of reaction conditions

### Concentration changes vs. volume of H<sub>2</sub>O<sub>2</sub> (A), reaction temperature (B), and time (C) for the oxidative carbon-carbon bond cleavage of glycerol (figure 2).

Glycerol (10 mg,  $10.8 \times 10^{-5}$  mol) and 5 mol% of Pd catalyst (**4**) were placed in a 1 dram vial with a stir bar: (A) after the addition of 30% H<sub>2</sub>O<sub>2</sub> (0.1 mL ~ 0.4 mL) with H<sub>2</sub>O (0.1 mL) to the vial, the reaction vial was closed and the reaction mixture was stirred for 1 hour at 40 °C. (B) 0.4 mL of H<sub>2</sub>O<sub>2</sub> and 0.1 mL of H<sub>2</sub>O were added to the mixture of glycerol and Pd catalyst. Reactions were conducted at various temperatures (25, 40, 50, or 60 °C) for 1 hour. (C) after the addition of 30% H<sub>2</sub>O<sub>2</sub> (0.4 mL) with H<sub>2</sub>O (0.1 mL) to the vial, reaction mixtures were stirred for 1, 3, or 6 hours at 40 °C.

#### (A) Various amount of H<sub>2</sub>O<sub>2</sub>

H <sub>2</sub> O <sub>2</sub> (mL)	Glycerol ( $\times 10^{-5}$ mol)	Formic acid ( $\times 10^{-5}$ mol)	Glycolic acid ( $\times 10^{-5}$ mol)
0.1	8.2	3.8	1
0.2	5.3	6.4	1.4
0.3	3.5	9.4	1.9
0.4	2.4	10.7	1.3

#### (B) Temperature

Temp (°C)	Glycerol ( $\times 10^{-5}$ mol)	Formic acid ( $\times 10^{-5}$ mol)	Glycolic acid ( $\times 10^{-5}$ mol)
25	5.1	8.2	1.8
40	2.4	10.7	1.3
50	1.8	10.1	1.9
60	0.4	10.3	1.6

#### (C) Time

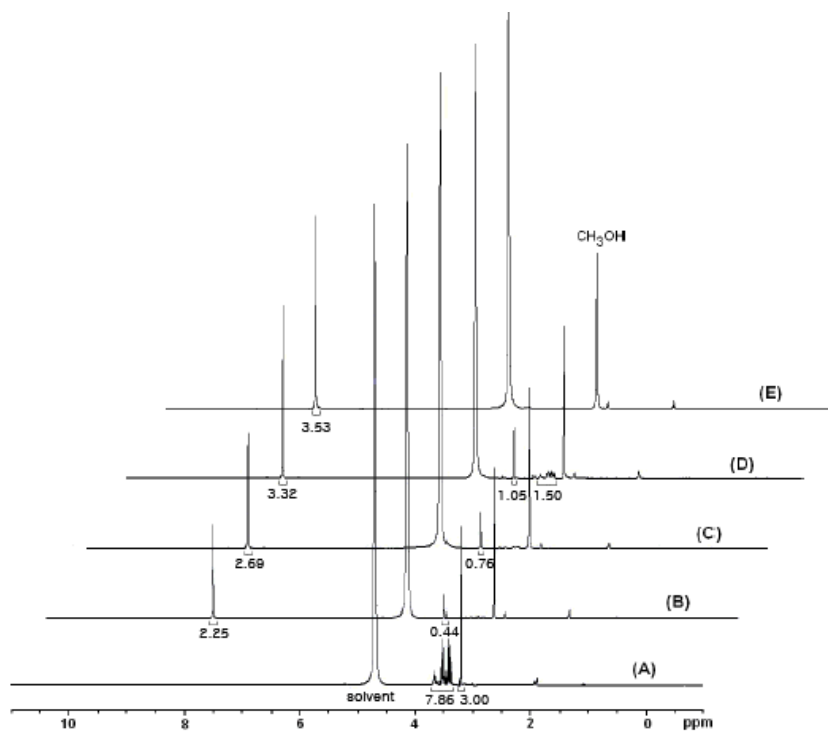
Time (hour)	Glycerol ( $\times 10^{-5}$ mol)	Formic acid ( $\times 10^{-5}$ mol)	Glycolic acid ( $\times 10^{-5}$ mol)
1	2.4	10.7	1.3
3	1.6	10.8	2.2
6	0.8	10.5	2

#### Various amount of Pd catalyst (**4**)

Glycerol (10 mg,  $10.8 \times 10^{-5}$  mol) and corresponded mol% of Pd catalyst (**4**) (2.5 %, 5, 10, and 15) were placed in a 1 dram vial with a stir bar. After the addition of 30% H<sub>2</sub>O<sub>2</sub> (0.3 mL) with H<sub>2</sub>O (0.1 mL) to reaction mixture, the mixture was placed heating bock (60 °C). After 3 hour, 0.2 mL of D<sub>2</sub>O and 2  $\mu$ L of methanol were added and wet1D NMR spectra of the product were collected.

Catalyst (mol %)	Glycerol ( $\times 10^{-5}$ mol)	Formic acid ( $\times 10^{-5}$ mol)	Glycolic acid ( $\times 10^{-5}$ mol)
2.5	3.9	9.3	2.5
5	3.1	14.7	2.1
10	7.4	6.7	1.0
15	7.7	6.1	0.5

7. Figure 3.  $^1\text{H}$ -NMR study for the degradation pathway of glycerol



## 8. References

- [1] H. Hao, J. Sieler, D. Sicker, *J. Nat. Prod.* **2002**, *65*, 466-469.
- [2] J. H. Lee, K. S. Yoo, C. P. Park, J. M. Olsen, S. Sakaguchi, G. K. S. Prakash, T. Mathew, K. W. Jung, *Adv. Synth. Catal.* **2009**, *351*, 563-568.