Supporting Information

Platinum on Carbon–Catalyzed and Chemoselective Aqueous Oxygen Oxidation of Aromatic Acetals to Benzoic Acids.

Naoki Yasukawa, Takumi Matsuda, Eisho Shimizu,
Hironao Sajiki* and Yoshinari Sawama*

Laboratory of Organic Chemistry, Gifu Pharmaceutical University,
1-25-4 Daigaku-nishi, Gifu 501-1196, Japan

Contents

1. General Information.

10% Pt/C, 10% Pd/C, 10% Ru/C, 10% Rh/C and 10% Au/C were supplied by the N. E. Chemcat Corporation (Tokyo, Japan). Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 63–210 μm spherical, neutral). ^{1}H NMR spectrum was recorded on a JEOL EX 400, AL 400, ECZ400 or ECA 500 spectrometer at room temperature in $CDCl_3$ or DMSO-d_6 as a solvent and internal standard (^{1}H NMR: δ= 7.26 for $CDCl_3$; ^{1}H NMR: δ = 2.50 for DMSO-d_6) with tetramethylsilane as an internal standard. Substrates (**1a**–**1e**, **1g**–**1k**, **2a**, and **3a**) were prepared according to reference 1. The substrate (**1f**) was prepared according to reference 2.

2. Typical procedures.

(A) Oxidation of aromatic acetal. (Schemes 1 and 2)

Aromatic acetal (**1**; 0.25 mmol), 10% Pt/C (5–15 mol%), NaOH (22.0 mg, 0.55 mmol, 2.2 equiv.), and H_2O (1 mL) were added to the test tube, which was then sealed with a septum. The inside air was replaced with O_2 (balloon). The reaction mixture was stirred with a ChemiStation

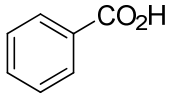
(EYELA, Tokyo Rikakikai Co., Ltd., Tokyo, Japan) and heated (80 ºC outer aluminum heating block temperature). After an adequate reaction time, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pt/C. 1N H_2SO_4 (2 mL) was added to the filtrate, and the solution was extracted with Et_2O (10 mL X 2), and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding benzoic acid derivative (**4**).

(B) Chemoselective reactions. (Scheme 3)

The substrates [aromatic acetal (**1a**; 37.5 mg, 0.25 mmol) and aliphatic acetal (**2a**; 50.0 mg, 0.25 mmol) or ketal (**3a**; 41.0 mg, 0.25 mmol)], 10% Pt/C (24.4 mg, 0.0125 mmol, 5 mol%), NaOH (22.0 mg, 0.55 mmol, 2.2 equiv.), and H_2O (1 mL) were added to the test tube, which were then sealed with a septum. The inside air was replaced with O_2 (balloon). The reaction mixture was stirred with a ChemiStation (EYELA, Tokyo Rikakikai Co., Ltd., Tokyo, Japan) and heated (80 ºC outer aluminum heating block temperature). After 6 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pt/C. The filtrate was extracted with Et_2O (10 mL X 2, and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to give the substrates (**2a** or **3a**) and the deprotected products. On the side, 1N H_2SO_4 (2 mL) was added to the aqueous layers including benzoic acid sodium salt after extraction, and the solution was extracted with Et_2O (10 mL X 2), and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to give the corresponding benzoic acid (**4a**).

3. Spectroscopic data of the synthesized products.

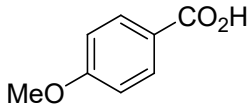
Benzoic acid (4a)



1a (37.5 mg, 0.25 mmol) was used as a substrate and **4a** (24.8 mg, 0.213 mmol) was obtained in 85% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1).

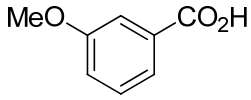
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.49 (dd, *J* = 7.2, 7.2 Hz, 1H). Spectroscopic data of ^{1}H NMR of the product was identical to that of reference 3.

4-Methoxybenzoic acid (4b)



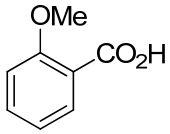
1b (45.1 mg, 0.25 mmol) was used as a substrate and **4b** (31.7 mg, 0.208 mmol) was obtained in 83% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H). Spectroscopic data of ^{1}H NMR of the product was identical to that of reference 3.

3-Methoxybenzoic acid (4c)



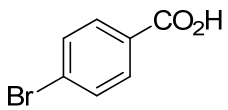
1c (45.1 mg, 0.25 mmol) was used as a substrate and **4c** (28.9 mg, 0.191 mmol) was obtained in 76% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.64 (s, 1H), 7.39 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H) 3.88 (s, 3H). Spectroscopic data of ^{1}H NMR of the product was identical to that of reference 4.

2-Methoxybenzoic acid (4d)



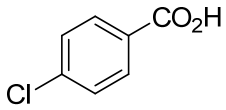
1d (45.1 mg, 0.25 mmol) was used as a substrate and **4d** (26.3 mg, 0.173 mmol) was obtained in 69% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 3/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 7.6 Hz, 1H), 7.58 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H). Spectroscopic data of ^{1}H NMR of the product was identical to that of reference 3.

4-Bromobenzoic acid (4e)



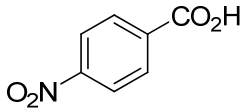
1e (57.3 mg, 0.25 mmol) was used as a substrate and **4e** (39.2 mg, 0.195 mmol) was obtained in 78% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H). Spectroscopic data of ^{1}H NMR of the product was identical to that of reference 4.

4-Chlorobenzoic acid (4f)



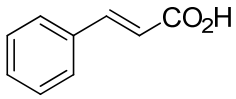
1f (46.2 mg, 0.25 mmol) was used as a substrate and **4f** (30.5 mg, 0.195 mmol) was obtained in 78% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.94 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H). Spectroscopic data of ^{1}H NMR of the product was identical to that of reference 4.

4-Nitorobenzoic acid (4g)



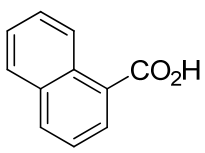
1g (48.8 mg, 0.25 mmol) was used as a substrate and **4g** (27.2 mg, 0.163 mmol) was obtained in 65% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 1/1).
^{1}H NMR (500 MHz, DMSO-d_6): δ 8.31 (d, J = 9.0 Hz, 2H), 8.16 (d, J = 9.0 Hz, 2H). Spectroscopic data of ^{1}H NMR of the product was identical to that of reference 3.

***trans*-Cinnamic acid (4h)**



1h (44.1 mg, 0.25 mmol) was used as a substrate and **4h** (27.2 mg, 0.183 mmol) was obtained in 73% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 2/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 16.0 Hz, 1H), 7.57–7.55 (m, 2H), 7.43–7.41 (m, 3H), 6.47 (d, J = 16.0 Hz, 1H). Spectroscopic data of ^{1}H NMR of the product was identical to that of reference 5.

1-Naphthoic acid (4i)



1i (50.1 mg, 0.25 mmol) was used as a substrate and **4i** (31.7 mg, 0.184 mmol) was obtained in 74% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (d, *J* = 8.8 Hz, 1H), 8.40 (d, *J* = 7.2 Hz, 1H) , 8.10 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.67 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.59–7.54 (m, 2H). Spectroscopic data of ^{1}H NMR of the product was identical to that of reference 6.

4. References.

1) N. Yasukawa, S. Asai, M. Kato, Y. Monguchi, H. Sajiki, and Y. Sawama, *Org. Lett.,* 2016, **18**, 5604.

2) T. Kawajiri, M. Kato, H. Nakata, R. Goto, S. Aibara, R. Ohta, H. Fujioka, H. Sajiki, and Y. Sawama, *J. Org. Chem.,* 2019, **84**, 3853.

3) Y. Sawama, K. Morita, S. Asai, M. Kozawa, S. Tadokoro, J. Nakajima, Y. Monguchi, and H. Sajiki, *Adv. Synth. Catal.*, 2015, **357**, 1205.

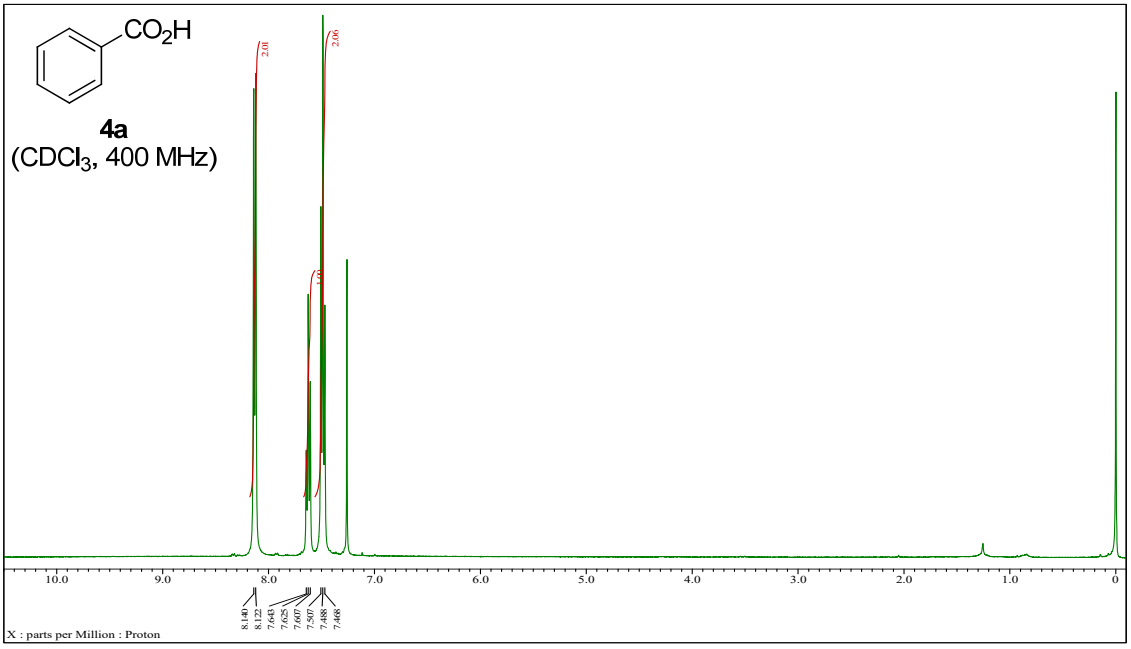
4) A. Nakamura, H. Kanou, J. Tanaka, A. Imamiya, T. Maegawa, and Y. Miki, *Org. Biomol. Chem.*, 2018, **16**, 541.

5) Y. Wang, J. Zhang, W. Zhang, and M. Zhang, *J. Org. Chem.*, 2009, **74**, 1923.

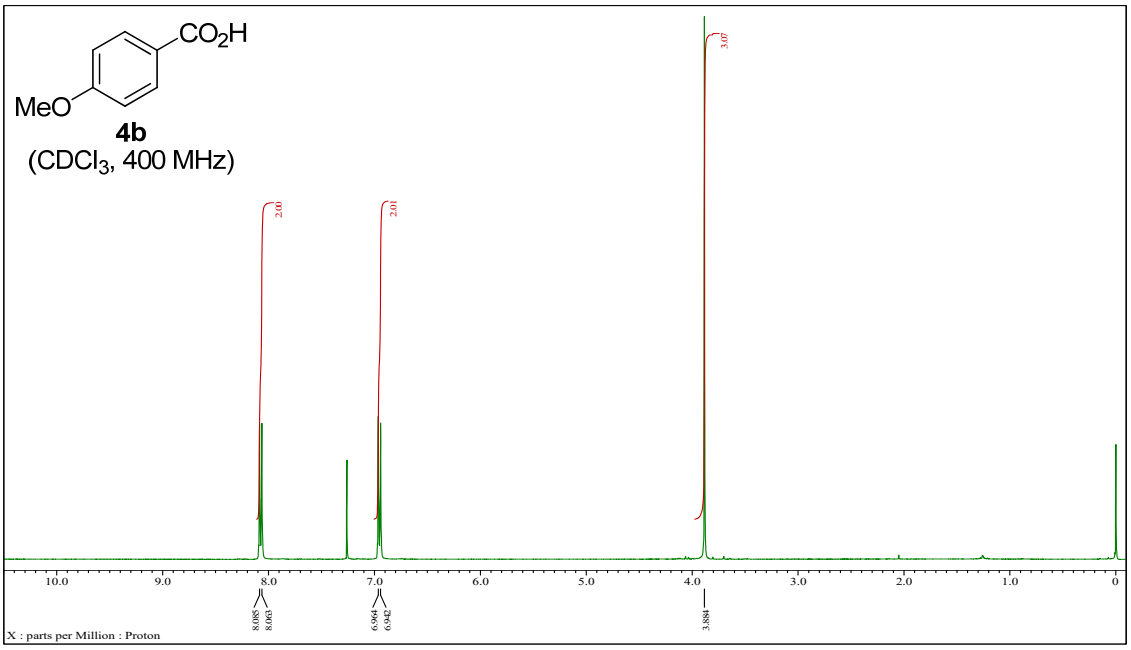
6) T. Mita, K. Suga, K. Sato, and Y. Sato, *Org. Lett.*, 2015, **17**, 5276.

5. ^{1}H NMR spectra of the synthesized products.

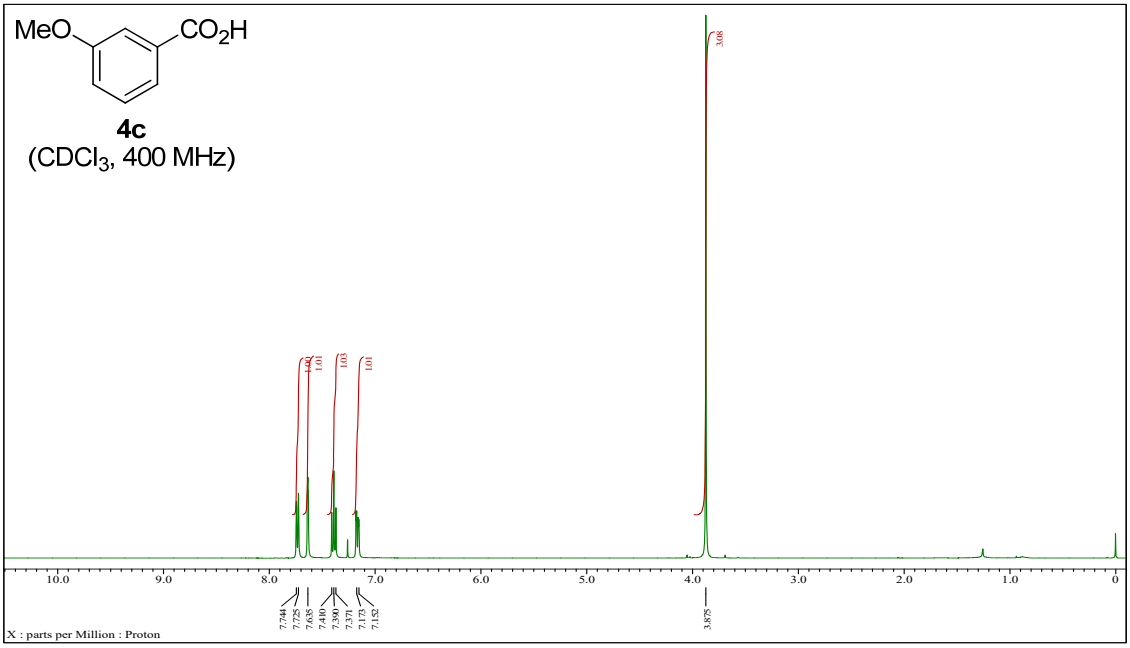
^{1}H NMR of benzoic acid (**4a**)



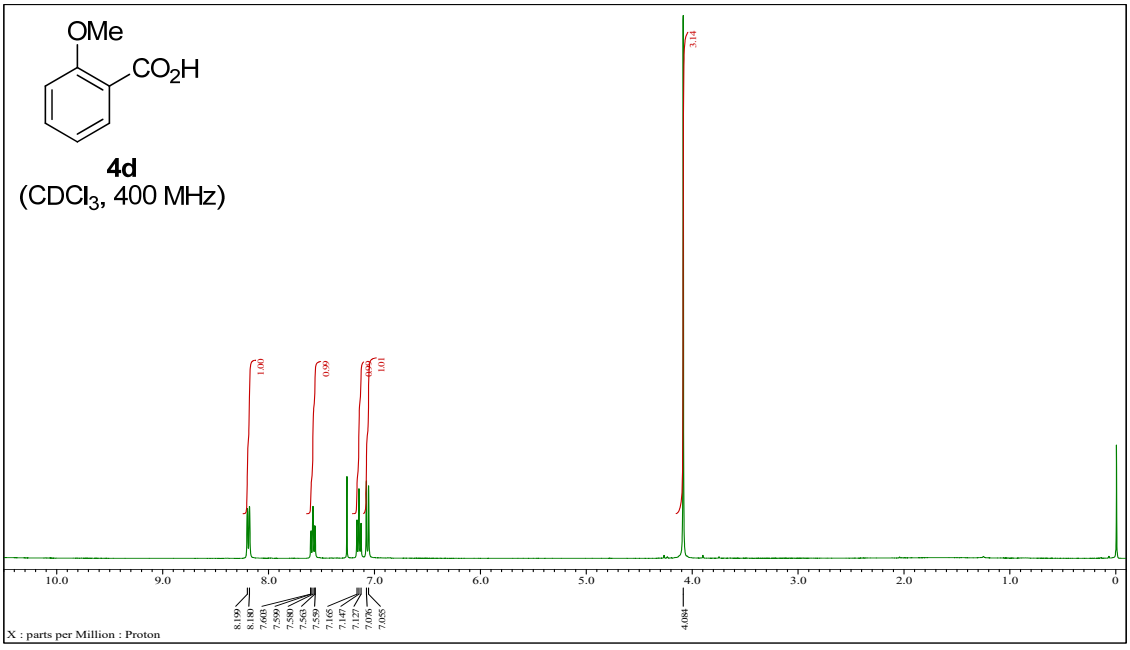
^{1}H NMR of 4-methoxybenzoic acid (**4b**)



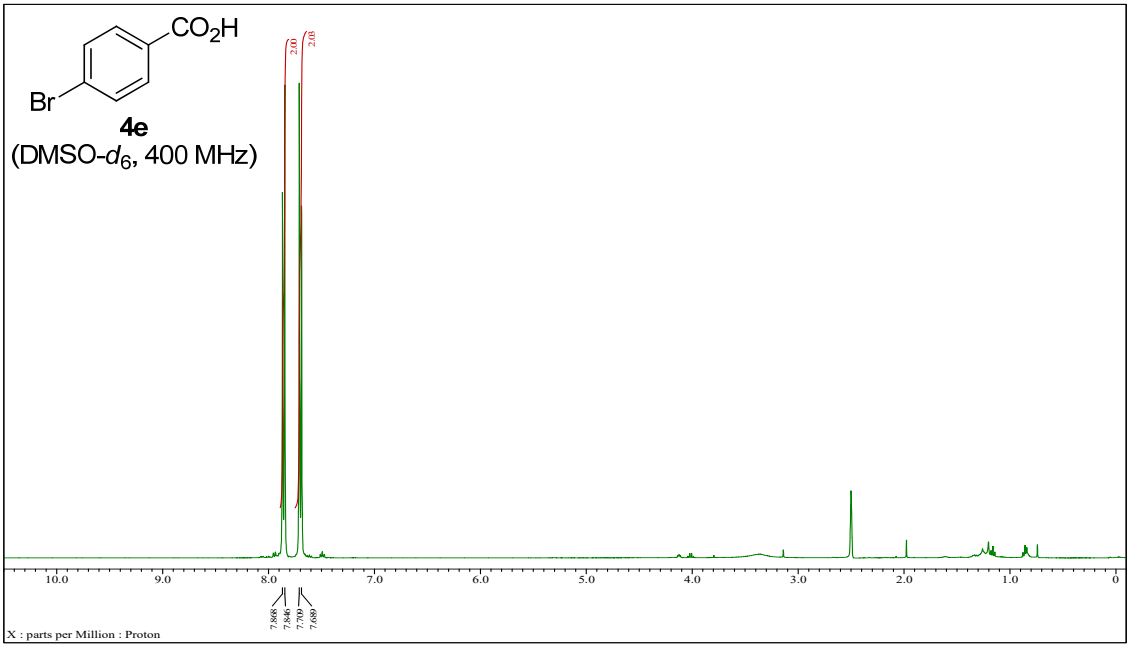
^{1}H NMR of 3-methoxybenzoic acid (**4c**)



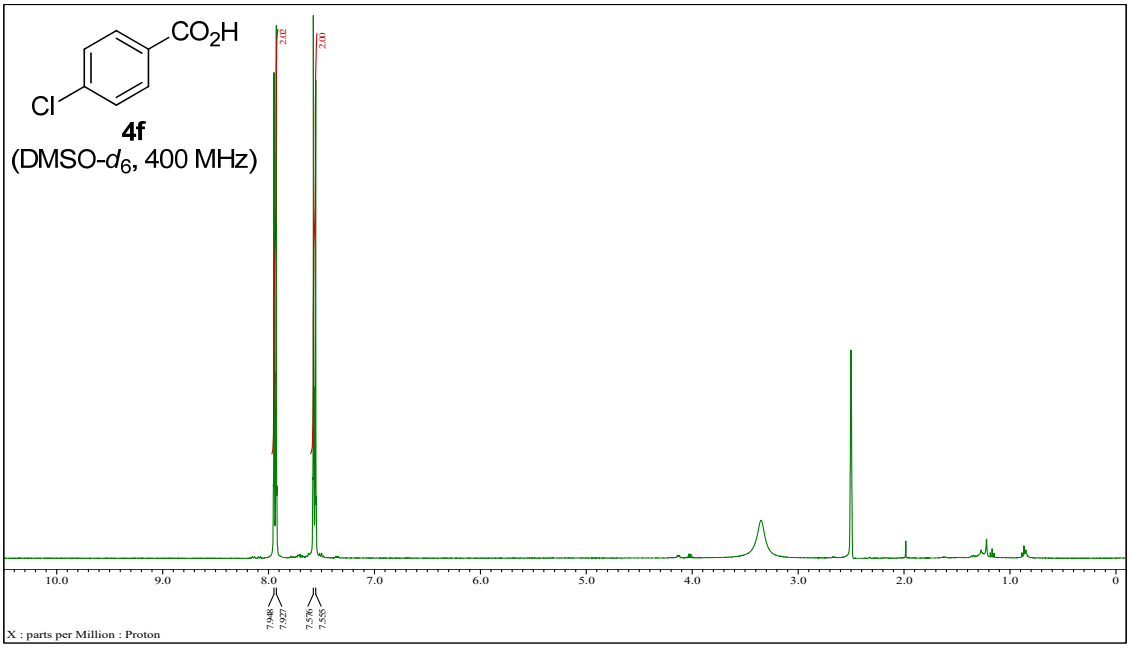
^{1}H NMR of 2-methoxybenzoic acid (**4d**)



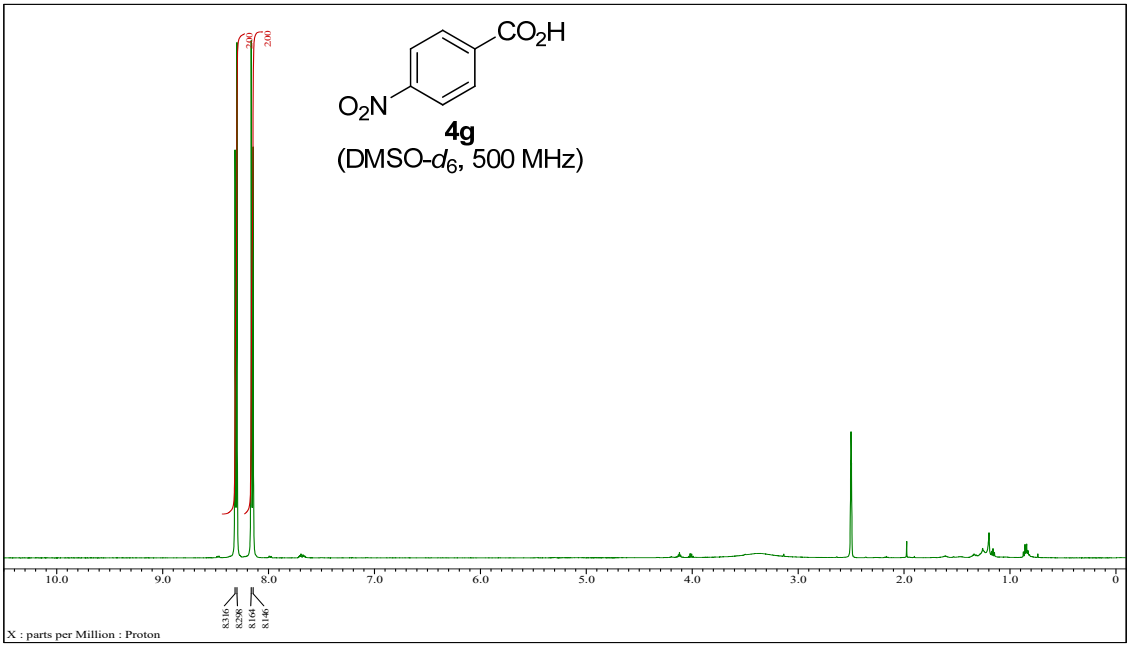
^{1}H NMR of 4-bromobenzoic acid (**4e**)



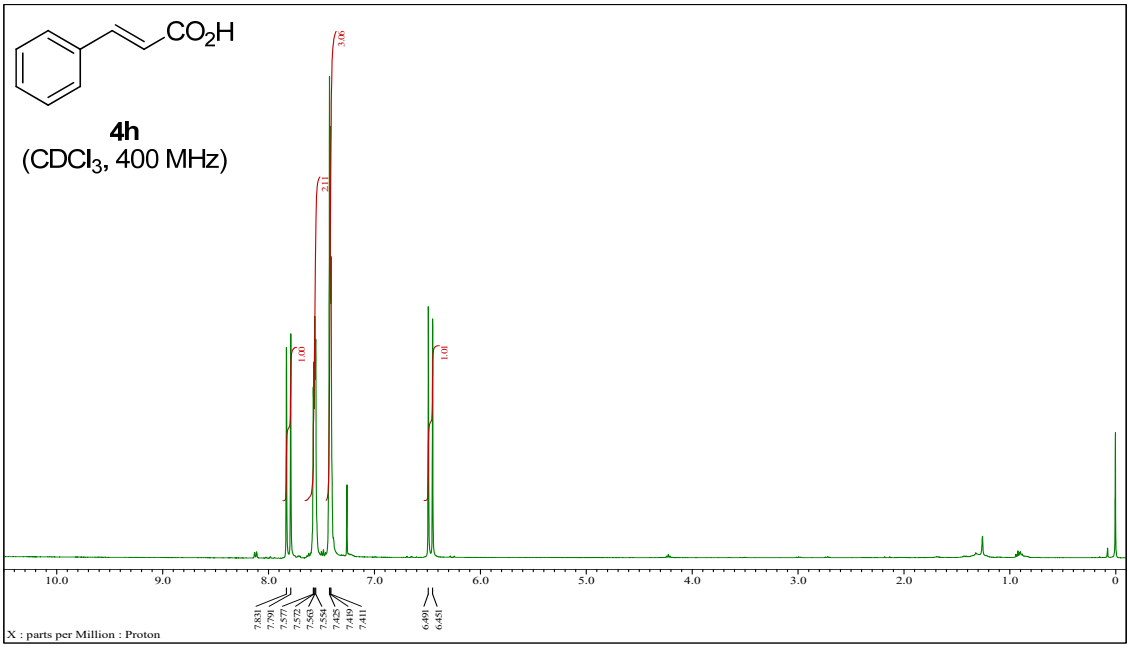
^{1}H NMR of 4-chlorobenzoic acid (**4f**)



^{1}H NMR of 4-nitorobenzoic acid (**4g**)



^{1}H NMR of *trans*-cinnamic acid (**4h**)



^{1}H NMR of 1-naphthoic acid (**4i**)