

## Supporting Information

### Palladium on Carbon-Catalyzed Chemoselective Oxygen Oxidation of Aromatic Acetals

Naoki Yasukawa, Shota Asai, Maho Kato, Yasunari Monguchi  
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.
2. Preparation of several substrates including literature unknown compounds.
3. Typical procedure in oxidation.
4. Spectroscopic data of the synthesized products.
5. Metal leaching test.
6. Reuse test.
7. References.
8.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the newly synthesized substrates and products.

#### 1. General Information.

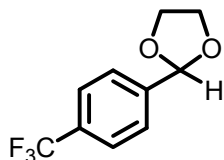
10% Pt/C, 10% Pd/C, 10% Ru/C, 10% Rh/C and 10% Au/C were supplied by the N. E. Chemcat Corporation (Tokyo, Japan). All reactions were performed in oven-dried glassware. MeOH, ethylen glycol, THF, DMF, pyridine, toluene,  $\text{CH}_2\text{Cl}_2$ , DMSO, AcOH and AcOEt as solvents were purchased from a commercial source and used without further purification. Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 63–210  $\mu\text{m}$  spherical, neutral).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL EX 400, AL 400 or ECA 500 spectrometer at room temperature in  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  as a solvent and internal standard ( $^1\text{H}$  NMR:  $\delta = 7.26$ ;  $^{13}\text{C}$  NMR:  $\delta = 77.0$  for  $\text{CDCl}_3$ ;  $^1\text{H}$  NMR:  $\delta = 2.5$  for  $\text{DMSO}-d_6$ ) with tetramethylsilane as an internal standard. IR spectra were recorded by a Bruker FT-IR ALPHA. The Pd leaching was analysed by ICP-OES using SPS5520 (SII Nano Technology, Tokyo, Japan). ESI high resolution mass spectra (HRMS) were measured by a Shimadzu hybrid IT-TOF mass spectrometer. Melting points were measured by a SANSYO

SMP-300 melting point apparatus. Substrates (**1a**, **1b**, **1e**, **1l**, **1n** and **2a**) were prepared according to reference 1. The substrate (**1o**) was prepared according to reference 2. The substrate (**3a**) was prepared according to reference 3. Synthetic procedures of other substrates were shown in Section 2.

## 2. Preparation of several substrates including literature unknown compounds.

Preparation of substrate (**1c**) in Table 2, entry 2: To a solution of 4-(trifluoromethyl)benzaldehyde (1.75 g, 10 mmol) and triethyl orthoformate (1.8 mL, 11 mmol) in ethylene glycol (2.2 mL, 40 mmol) was added tetrabutylammonium tribromide (48.2 mg, 0.10 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After 10 h, the reaction mixture was quenched with sat. NaHCO<sub>3</sub> aq. (1 mL) and extracted with Et<sub>2</sub>O (20 mL × 2). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 5/1) to give the substrate (**1c**) in Table 2, entry 2 (1.17 g, 5.36 mmol, 54%).

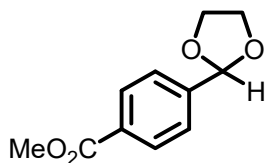
### 4-(1,3-Dioxolan-2-yl)trifluoromethylbenzene (**1c**)<sup>4</sup>



Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.66—7.59 (m, 2H), 5.83 (s, 1H), 4.13—4.10 (m, 2H), 4.08—4.05 (m, 2H). Spectroscopic data of <sup>1</sup>H NMR was identical to that of the reference 4.

Preparation of substrate (**1d**) in Table 2, entry 3: To a solution of methyl terephthalaldehyde (0.82 g, 5 mmol) and triethyl orthoformate (0.9 mL, 5.5 mmol) in ethylene glycol (1.1 mL, 20 mmol) was added tetrabutylammonium tribromide (24.1 mg, 0.05 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After 10 h, the reaction mixture was quenched with sat. NaHCO<sub>3</sub> aq. (1 mL) and extracted with Et<sub>2</sub>O (10 mL × 2). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 5/1) to give the substrate (**1d**) in Table 2, entry 3 (0.81 g, 3.91 mmol, 78%).

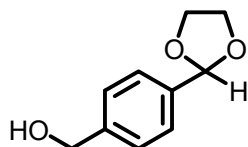
### Methyl-4-(1,3-dioxolan-2-yl)benzoate (**1d**)<sup>5</sup>



Colorless solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (d,  $J = 8.0$  Hz, 2H), 7.55 (d,  $J = 8.0$  Hz, 2H), 5.86 (s, 1H), 4.14—4.11 (m, 2H), 4.09—4.04 (m, 2H), 3.92 (s, 1H). Spectroscopic data of  $^1\text{H}$  NMR was identical to that of the reference 5.

Preparation of substrate (**1f**) in Table 2, entry 5: To a solution of methyl-4-(1,3-dioxolan-2-yl)benzoate (**1d**: 0.73 g, 3.5 mmol) in anhydrous THF (3.5 mL) was added  $\text{LiAlH}_4$  (199 mg, 5.25 mmol) at  $0^\circ\text{C}$  under argon. After stirring for 24 h at room temperature, the reaction mixture was quenched with water (0.12 mL), 15% sodium hydroxide aq (0.12 mL) and water (0.36 mL) and passed through a celite pat. The filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 1/1) to give the substrate (**1f**) in Table 2, entry 5 (0.41 g, 2.29 mmol, 52%).

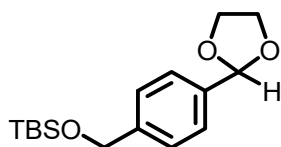
**4-(1,3-Dioxolan-2-yl)phenylmethanol (**1f**)**<sup>5</sup>



Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 (d,  $J = 7.8$  Hz, 2H), 7.38 (d,  $J = 7.8$  Hz, 2H), 5.82 (s, 1H), 4.70 (d,  $J = 6.0$  Hz, 2H), 4.15—4.09 (m, 2H), 4.08—4.02 (m, 2H), 1.71 (t,  $J = 6.0$  Hz, 1H). Spectroscopic data of  $^1\text{H}$  NMR was identical to that of the reference 8.

Preparation of substrate (**1g**) in Table 2, entry 6: To a solution of the 4-(1,3-dioxolan-2-yl)phenylmethanol (**1f**: 0.54 mg, 3.0 mmol) in anhydrous DMF (10 mL) were added imidazole (306 mg, 4.5 mmol) and TBSCl (678 mg, 4.5 mmol) at  $0^\circ\text{C}$  under argon. After stirring for 18 h at room temperature, the reaction mixture was quenched with sat.  $\text{NaHCO}_3$  aq. (1 mL) and extracted with AcOEt (10 mL  $\times$  2). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 5/1) to give the substrate (**1g**) in Table 2, entry 6 (0.88 g, 3.0 mmol, quantitative yield).

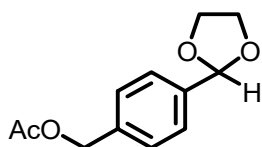
**[4-(1,3-Dioxolan-2-yl)benzyloxy]tert-butyldimethylsilane (**1g**)**



Colorless solid; M.p. 55—58 °C; IR (ATR)  $\text{cm}^{-1}$ : 2954, 2929, 2885, 2857, 1472, 1430, 1389, 1256, 1218, 1083, 1020, 1006;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.44 (d,  $J$  = 7.8 Hz, 2H), 7.34 (d,  $J$  = 7.8 Hz, 2H), 5.81 (s, 1H), 4.75 (s, 2H), 4.15—4.09 (m, 2H), 4.07—4.01 (m, 2H), 0.94 (s, 9H), 0.09 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.6, 136.5, 126.3, 126.0, 103.7, 62.3, 64.7, 25.9, 18.4, -5.3; ESI-HRMS  $m/z$ : 317.1543 ( $[\text{M}+\text{Na}]^+$ ); Calcd for  $\text{C}_{16}\text{H}_{26}\text{O}_3\text{SiNa}$ : 317.1543.

Preparation of substrate (**1h**) in Table 2, entry 7: To a solution of the 4-(1,3-dioxolan-2-yl)phenylmethanol (**1f**: 0.54 g, 3.0 mmol) in pyridine (10 mL) were added DMAP (18 mg, 0.15 mmol) and acetic anhydride (613 mg, 6.0 mmol) at room temperature under argon. After stirring for 18 h at room temperature, the reaction mixture was quenched with sat.  $\text{NaHCO}_3$  aq. and extracted with AcOEt (10 mL  $\times$  2). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 1/1) to give the substrate (**1h**) in Table 2, entry 7 (0.80 g, 3.0 mmol, quantitative yield).

#### 4-(1,3-Dioxolan-2-yl)benzylacetate (**1h**)

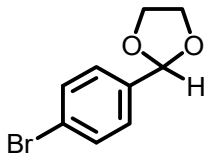


Colorless oil; IR (ATR)  $\text{cm}^{-1}$ : 2955, 2887, 1735, 1430, 1379, 1362, 1221, 1078, 1019;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 (d,  $J$  = 7.8 Hz, 2H), 7.37 (d,  $J$  = 7.8 Hz, 2H), 5.82 (s, 1H), 5.11 (s, 2H), 4.12—4.10 (m, 2H), 4.05—4.03 (m, 2H), 2.10 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.8, 138.1, 136.9, 128.2, 126.7, 103.4, 65.9, 65.3, 21.0; ESI-HRMS  $m/z$ : 245.0784 ( $[\text{M}+\text{Na}]^+$ ); Calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_4\text{Na}$ : 245.0778.

Preparation of substrate (**1i**) in Table 2, entry 8: To a solution of 4-bromobenzaldehyde (1.85 g, 10 mmol) and triethyl orthoformate (1.8 mL, 11 mmol) in ethylene glycol (2.2 mL, 40.0 mmol) was added tetrabutylammonium tribromide (48.2 mg, 0.1 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After 30 h, the reaction mixture was quenched with sat.  $\text{NaHCO}_3$  aq. (1 mL) and extracted with  $\text{Et}_2\text{O}$  (20 mL  $\times$  2). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by silica-gel column

chromatography (Hex/EtOAc = 5/1) to give the substrate (**1i**) in Table 2, entry 7 (1.49 g, 6.5 mmol, 65%).

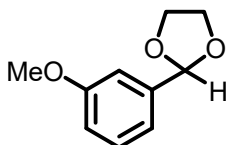
**2-(4-Bromophenyl)-1,3-dioxolane (**1i**)**<sup>6</sup>



Colorless solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.78 (s, 1H), 4.11—4.09 (m, 2H), 4.05—4.03 (m, 2H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 6.

Preparation of substrate (**1j**) in Table 2, entry 9: To a solution of *m*-anisaldehyde (1.36 g, 10 mmol) and triethyl orthoformate (1.8 mL, 11 mmol) in ethylene glycol (2.2 mL, 40 mmol) was added tetrabutylammonium tribromide (48.2 mg, 0.1 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After 5 h, the reaction mixture was quenched with sat. NaHCO<sub>3</sub> aq. (1 mL) and extracted with Et<sub>2</sub>O (20 mL × 2). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 5/1) to give the substrate (**1j**) in Table 2, entry 9 (0.91 g, 5.02 mmol, 50%).

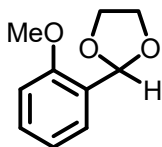
**2-(3-Methoxyphenyl)-1,3-dioxolane (**1j**)**<sup>6</sup>



Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.30 (t, *J* = 7.6 Hz, 1H), 7.10—7.03 (m, 2H), 6.92—6.91 (m, 1H), 5.81 (s, 1H), 4.15—4.08 (m, 2H), 4.05—4.02 (m, 2H), 3.83 (s, 3H). Spectroscopic date of <sup>1</sup>H NMR was identical to that of the reference 6.

Preparation of substrate (**1k**) in Table 2, entry 10: To a solution of *o*-anisaldehyde (1.36 g, 10 mmol) and triethyl orthoformate (1.8 mL, 11 mmol) in ethylene glycol (2.2 mL, 40 mmol) was added tetrabutylammonium tribromide (48.2 mg, 0.1 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After 5 h, the reaction mixture was quenched with sat. NaHCO<sub>3</sub> aq. (1 mL) and extracted with Et<sub>2</sub>O (20 mL × 2). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 3/1) to give the substrate (**1k**) in Table 2, entry 10 (0.44 g, 2.45 mmol, 25%).

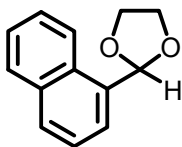
#### 2-(2-Methoxyphenyl)-1,3-dioxolane (**1k**)<sup>6</sup>



Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.53 (dd, *J* = 2.0, 7.6 Hz, 1H), 7.35—7.31 (m, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.18 (s, 1H), 4.16—4.10 (m, 2H), 4.08—4.02 (m, 2H), 3.87 (s, 3H). Spectroscopic data of <sup>1</sup>H NMR was identical to that of the reference 6.

Preparation of substrate (**1m**) in Table 2, entry 12: To a solution of 1-naphthaldehyde (0.78 g, 5 mmol) and triethyl orthoformate (1.0 mL, 1.2 mmol) in ethylene glycol (1.1 mL, 20 mmol) was added tetrabutylammonium tribromide (24.1 mg, 0.05 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After 20 h, the reaction mixture was quenched with sat. NaHCO<sub>3</sub> aq. (1 mL) and extracted with Et<sub>2</sub>O (10 mL × 2). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 5/1) to give the substrate (**1m**) in Table 2, entry 12 (0.90 g, 4.50 mmol, 90%).

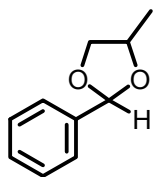
#### 2-(Naphth-1-yl)-1,3-dioxolane (**1m**)<sup>7</sup>



Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.87 (m, 2H), 7.77 (d, *J* = 6.8 Hz, 1H), 7.57—7.46 (m, 3H), 6.49 (s, 1H), 4.23—4.20 (m, 2H), 4.18—4.14 (m, 2H). Spectroscopic data of <sup>1</sup>H NMR was identical to that of the reference 7.

Preparation of substrate (**1p**) in Table 2, entry 15: To a solution of benzaldehyde (3.20 g, 30 mmol) and triethyl orthoformate (11 mL, 66 mmol) in 1,2-propanediol (8.9 mL, 120 mmol) was added tetrabutylammonium tribromide (289 mg, 0.6 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After 12 h, the reaction mixture was quenched with sat. NaHCO<sub>3</sub> aq. (1 mL) and extracted with Et<sub>2</sub>O (50 mL × 2). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 5/1) to give the substrate (**1p**) in Table 2, entry 15 (0.42 g, 2.59 mmol, 9%).

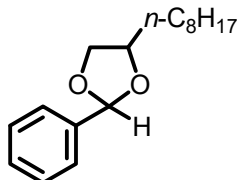
#### 4-Methyl-2-phenyl-1,3-dioxolane (4 : 6 mixture of diastereoisomers) (**1p**)<sup>8</sup>



Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.51—7.47 (m, 2H), 7.40—7.36 (m, 3H), 5.97 (s, 0.6H), 5.82 (s, 0.4H), 4.39—4.35 (m, 1H), 4.29—4.27 (m, 0.6H), 4.13 (t,  $J = 7.5$  Hz, 0.4H), 3.62 (t,  $J = 7.5$  Hz, 0.4H), 3.57 (t,  $J = 7.5$  Hz, 0.6H), 1.41 (d,  $J = 6.0$  Hz, 1.2H), 1.36 (d,  $J = 6.5$  Hz, 1.8H). Spectroscopic data of  $^1\text{H}$  NMR was identical to that of the reference 8.

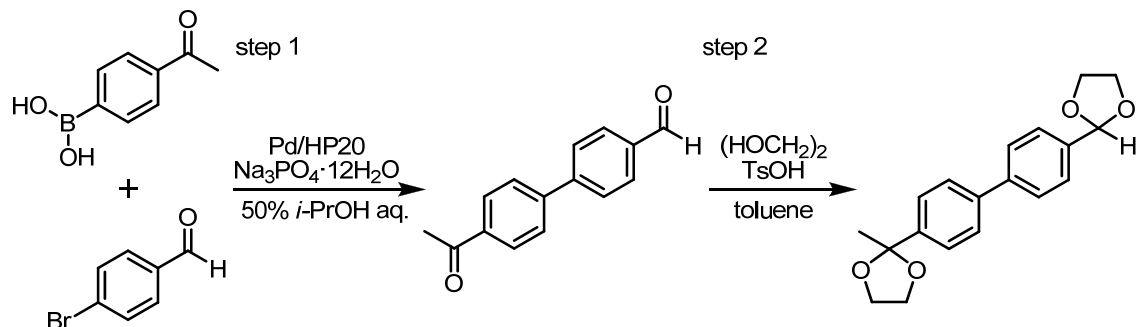
Preparation of substrate (**1q**) in Table 2, entry 16: To a solution of benzaldehyde (1.06 g, 10 mmol) in anhydrous toluene (5 mL) were added decane-1,2-diol (0.87 g, 5 mmol) and TsOH (8.6 mg, 0.05 mmol, 1.0 mol%) at room temperature under argon. Then the reaction mixture was refluxed at 130  $^\circ\text{C}$ . After stirring for 72 h at 130  $^\circ\text{C}$ , the reaction mixture was cooled to room temperature, quenched with sat.  $\text{NaHCO}_3$  aq. (1 mL), and extracted with AcOEt (10 mL  $\times$  2). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 10/1) to give the substrate (**1q**) in Table 2, entry 16 (1.14 g, 4.35 mmol, 87%).

**4-*n*-Octyl-2-phenyl-1,3-dioxolane (1 : 1 mixture of diastereoisomers) (**1q**)**



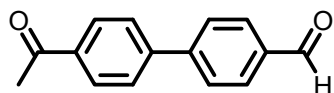
Colorless oil; IR (ATR)  $\text{cm}^{-1}$ : 2924, 2854, 1458, 1401, 1378, 1309, 1219, 1092, 1067, 1027, 1011;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.51—7.46 (m, 2H), 7.39—7.35 (m, 3H), 5.92 (s, 0.5H), 5.81 (s, 0.5H), 4.27—4.18 (m, 1.5H), 4.10 (t,  $J = 7.2$  Hz, 0.5H), 3.68 (t,  $J = 7.6$  Hz, 0.5H), 3.62 (t,  $J = 6.8$  Hz, 0.5H), 1.77—1.28 (m, 14H), 0.89 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  138.6, 137.9, 129.2, 129.0, 128.3, 126.7, 126.4, 103.9, 103.1, 77.5, 76.6, 70.8, 70.2, 33.4, 33.3, 31.9, 29.6, 29.5, 29.2, 25.8, 25.8, 22.7, 14.1; ESI-HRMS  $m/z$ : 263.2029 ( $[\text{M}+\text{H}]^+$ ); Calcd for  $\text{C}_{17}\text{H}_{26}\text{O}_2$ : 263.2006.

Preparation of substrate (**1r**) in Table 3, entry 5:



Step 1 based on reference 9: To a flask containing a stir bar were added 4-bromobenzaldehyde (0.93 g, 5 mmol), 4-acetylphenylboronic acid (0.90 g, 5.5 mmol), 10% Pd/HP20 (26.5 mg, 0.025 mmol, 0.5 mol%),  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (6.65 g, 17.5 mmol),  $\text{H}_2\text{O}$  (10 mL) and *i*-PrOH (10 mL), then the flask was sealed with a septum. The air inside was replaced with Ar (balloon) by three vacuum/argon cycles. The reaction mixture was stirred at room temperature for 30 h and then passed through a celite pat to remove the catalyst. The filtrate was extracted with AcOEt (30 mL  $\times$  3) and the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hex/EtOAc = 5/1) to give 4'-acetyl-(1,1'-biphenyl)-4-carbaldehyde (1.11 g, 4.95 mmol, 99%).

#### 4'-Acetyl-(1,1'-biphenyl)-4-carbaldehyde<sup>10</sup>

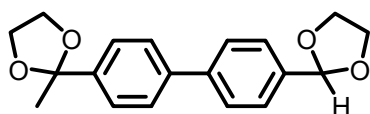


Colorless solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.09 (s, 1H), 8.08 (d,  $J$  = 8.4 Hz, 2H), 8.00 (d,  $J$  = 8.4 Hz, 2H), 7.80 (d,  $J$  = 8.4 Hz, 2H), 7.74 (d,  $J$  = 8.4 Hz, 2H), 2.66 (s, 3H). Spectroscopic data of  $^1\text{H}$  NMR was identical to that of the reference 10.

Step 2: To a solution of a 4'-acetyl-(1,1'-biphenyl)-4-carbaldehyde (112 mg, 0.5 mmol) in anhydrous toluene (1 mL) was added ethylene glycol (35  $\mu\text{L}$ , 1.2 mmol) and TsOH (1.7 mg, 0.01 mmol) at room temperature under argon. Then the reaction mixture was refluxed at 130  $^\circ\text{C}$ . After stirring for 48 h at 130  $^\circ\text{C}$ , the reaction mixture was cooled to room temperature, quenched with sat.  $\text{NaHCO}_3$  aq. (1 mL) and extracted with AcOEt (20 mL  $\times$  2). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 4/1) to give the substrate (**1r**) in Table 3, entry 5 (87.5 mg, 0.28 mmol, 56%).

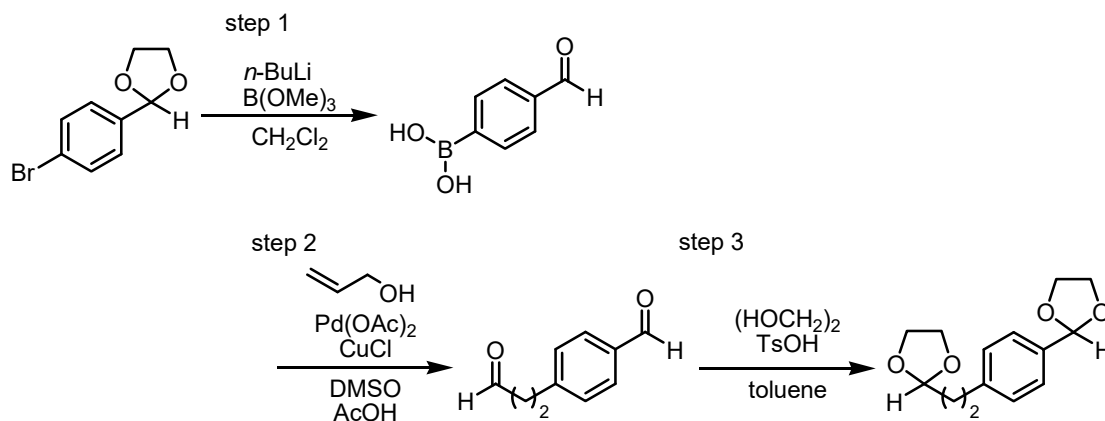
**1r**





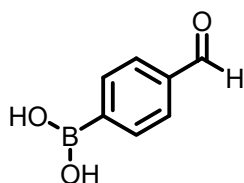
Colorless solid; M.p. 82—88 °C; IR (ATR)  $\text{cm}^{-1}$ : 2987, 2952, 2894, 1610, 1497, 1474, 1428, 1372, 1307, 1285, 1245, 1222, 1196, 1142, 1116, 1075, 1025, 1005;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ );  $\delta$  7.62—7.54 (m, 8H), 5.87 (s, 1H), 4.17—4.15 (m, 2H), 4.08—4.05 (m, 4H), 3.84—3.82 (m, 2H), 1.70 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.5, 141.7, 140.3, 136.9, 127.1, 127.0, 126.9, 125.8, 108.8, 103.6, 65.4, 64.5, 27.6; ESI-HRMS  $m/z$ : 313.1435 ( $[\text{M}+\text{H}]^+$ ); Calcd for  $\text{C}_{19}\text{H}_{21}\text{O}_4$ : 313.1434.

Preparation of substrate (**1s**) in Table 3, entry 6:



Step 1: To a solution of 2-(4-bromophenyl)-1,3-dioxolane (**1i**: 3.44g, 15 mmol) in anhydrous THF (37.5 mL) maintained at  $-78^\circ\text{C}$  under argon, *n*-butyllithium (8.6 mL, 2.09 M in hexane, 18 mmol) was added dropwise and the mixture was stirred for 2 h. Then trimethoxy borate (1.87 g, 18 mmol) was injected into this solution and the mixture was allowed to warm up gradually to room temperature and stirred for further 1 h. The reaction was quenched with 1N HCl aq (37.5 mL) and stirred for additional 24 h. Then the crude product was extracted with  $\text{Et}_2\text{O}$  (30 mL  $\times$  2). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated in vacuo. The residue was recrystallized with the mixture of ethyl acetate and hexane. The obtained product was added 25% acetone aq and stirred for 24 h. The resulting solid was filtrated to give 4-formylphenylboronic acid (1.41 g, 9.4 mmol, 63%).

#### 4-Formylphenylboronic acid<sup>11</sup>

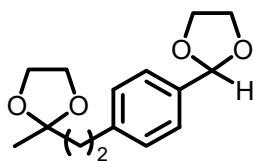


Colorless solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.02 (s, 1H), 8.34 (brs, 2H), 7.97 (d,  $J = 8.4$  Hz, 2H), 7.85 (d,  $J = 8.4$  Hz, 2H). Spectroscopic data of  $^1\text{H}$  NMR was identical to that of the reference 11.

Step 2: Synthesized according to reference 12.

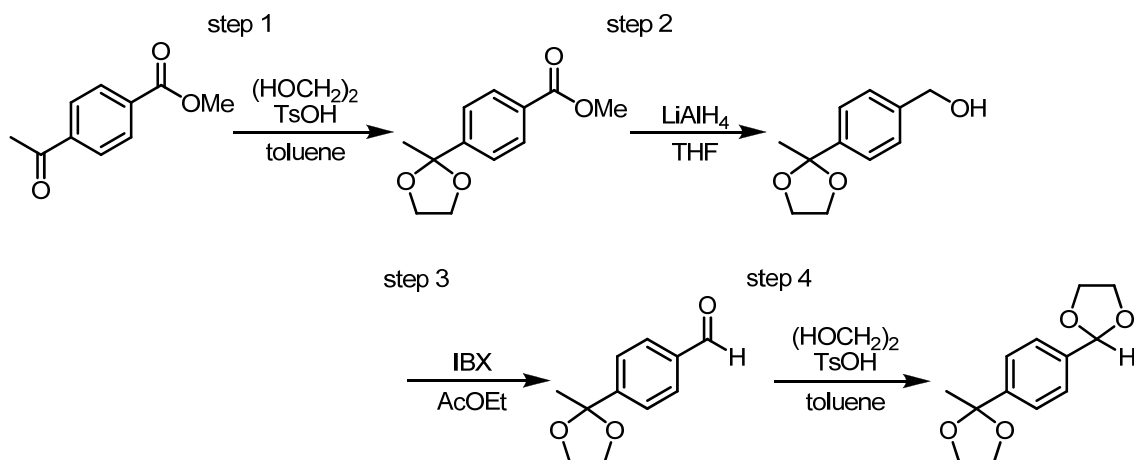
Step 3: To a solution of 4-(3-oxopropyl)benzaldehyde (172 mg, 1.1 mmol) in anhydrous toluene (5 mL) were added ethylene glycol (0.3 mL, 4.4 mmol) and TsOH (9.5 mg, 0.055 mmol, 5 mol%) at room temperature under argon. Then, the reaction mixture was refluxed at 130  $^\circ\text{C}$ . After stirring for 56 h at 130  $^\circ\text{C}$ , the reaction mixture was cooled to room temperature and quenched with sat.  $\text{NaHCO}_3$  aq. (1 mL). The solution was extracted with AcOEt (20 mL  $\times$  2), the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 3/1) to give the substrate (**1s**) in Table 3, entry 6 (204 mg, 0.82 mmol, 74%).

**2-[4-(1,3-Dioxolan-2-yl)phenethyl]-1,3-dioxolane (**1s**)**



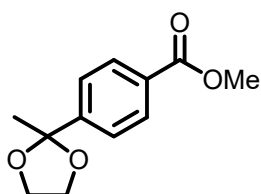
Colorless oil; IR (ATR)  $\text{cm}^{-1}$ : 2954, 2882, 1429, 1389, 1221, 1179, 1134, 1078, 1020;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39 (d,  $J = 8.0$  Hz, 2H), 7.23 (d,  $J = 8.0$  Hz, 2H), 5.79 (s, 1H), 4.88 (t,  $J = 4.5$  Hz, 1H), 4.13—4.12 (m, 2H), 4.06—3.98 (m, 4H), 3.88—3.85 (m, 2H), 2.78—2.74 (m, 2H), 1.99—1.95 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.7, 135.4, 128.4, 126.5, 103.7, 103.7, 65.3, 64.9, 35.4, 29.9; ESI-HRMS  $m/z$ : 273.1080 ( $[\text{M}+\text{Na}]^+$ ); Calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_4\text{Na}$ : 273.1097.

Preparation of substrate (**1t**) in eq 4:



Step 1: To a solution of methyl-4-acetylbenzoate (1.34 g, 7.5 mmol) in anhydrous toluene (7.5 mL) were added ethylene glycol (0.83 mL, 15 mmol) and TsOH (12.9 mg, 0.075 mmol) at room temperature under argon. Then the reaction mixture was heated up to 130 °C. After stirring for 12 h at 130 °C, the reaction mixture was cooled to room temperature and quenched with sat.  $\text{NaHCO}_3$  aq. (1 mL). The solution was extracted with AcOEt (20 mL  $\times$  2), the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 5/1) to give methyl-4-(2-methyl-1,3-dioxolan-2-yl)benzoate (1.11 g, 4.99 mmol, 67%).

**Methyl-4-(2-methyl-1,3-dioxolan-2-yl)benzoate**<sup>13</sup>

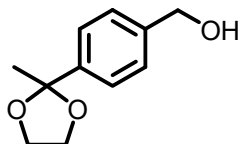


Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.01 (dd,  $J$  = 2.0, 6.5 Hz, 2H), 7.55 (dd,  $J$  = 2.0, 6.5 Hz, 2H), 4.07—4.04 (m, 2H), 3.91 (s, 1H), 3.77—3.74 (m, 2H), 1.65 (s, 3H). Spectroscopic data of  $^1\text{H}$  NMR was identical to that of the reference 13.

Step 2: To a solution of the methyl-4-(2-methyl-1,3-dioxolan-2-yl)benzoate (0.89 g, 4 mmol) in anhydrous THF (12 mL) was added  $\text{LiAlH}_4$  (380 mg, 10 mmol) at 0 °C. After being stirred for 12 h at room temperature, the reaction mixture was quenched with water (0.4 mL) and 15% sodium hydroxide aq (0.4 mL) and water (1.2 mL) were added. The residue was extracted with AcOEt (30 mL  $\times$  2), the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 1/1) to

give 4-(2-methyl-1,3-dioxolan-2-yl)phenylmethanol (0.80 g, 4 mmol, quantitative yield).

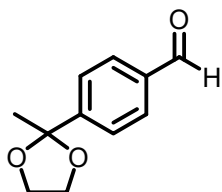
#### 4-(2-Methyl-1,3-dioxolan-2-yl)phenylmethanol



Colorless oil; IR (ATR)  $\text{cm}^{-1}$ : 3396, 2987, 2934, 2887, 1509, 1443, 1412, 1373, 1197, 1079, 1036;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 (d,  $J = 8.3$  Hz, 2H), 7.35 (d,  $J = 8.3$  Hz, 2H), 4.69 (d,  $J = 5.0$  Hz, 2H), 4.04—4.02 (m, 2H), 3.78—3.76 (m, 2H), 1.74 (brs, 1H), 1.65 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.7, 140.4, 126.9, 125.5, 108.7, 65.1, 64.4, 27.6; ESI-HRMS  $m/z$ : 195.1018 ( $[\text{M}+\text{H}]^+$ ); Calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_3$ : 195.1016.

Step 3: To a solution of the [4-(2-methyl-1,3-dioxolan-2-yl)phenyl]methanol (194 mg, 1 mmol) in anhydrous AcOEt (7 mL) was added *o*-iodoxybenzoic acid (0.84 g, 3 mmol, 33% oil suspension) at room temperature. Then the reaction mixture was heated up to 80 °C. After being stirred for 2 h open to the atmosphere, the reaction mixture was cooled to room temperature and filtered through a celite pat. The filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 3/1) to give 2-(4-formylphenyl)-2-methyl-1,3-dioxolane (125 mg, 0.65 mmol, 65%).

#### 2-(4-Formylphenyl)-2-methyl-1,3-dioxolane<sup>13</sup>

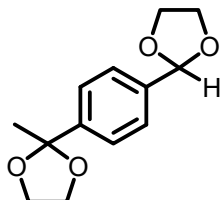


Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.02 (s, 1H), 7.87 (d,  $J = 8.8$  Hz, 2H), 7.66 (d,  $J = 8.8$  Hz, 2H), 4.08—4.06 (m, 2H), 3.78—3.76 (m, 2H), 1.66 (s, 3H). Spectroscopic data of  $^1\text{H}$  NMR was identical to that of the reference 13.

Step 4: To a solution of 2-(4-formylphenyl)-2-methyl-1,3-dioxolane (96.1 mg, 0.5 mmol) in anhydrous toluene (1 mL) were added ethylene glycol (55.4  $\mu\text{L}$ , 1 mmol) and TsOH (0.86 mg, 0.005 mmol) at room temperature. Then, the reaction mixture was heated up to 130 °C. After being stirred for 3 h, the reaction mixture was cooled to room temperature and quenched with sat.  $\text{NaHCO}_3$  aq. (1 mL). The solution was extracted with AcOEt (20 mL  $\times$  2), the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by

silica-gel column chromatography using (Hex/EtOAc = 5/1) to give the substrate (**1t**) in eq 4 (60.5 mg, 0.26 mmol, 51%).

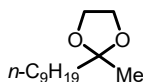
**2-[4-(1,3-Dioxolan-2-yl)phenyl]-2-methyl-1,3-dioxolane (**1t**)**



Colorless solid; M.p. 69—75 °C; IR (ATR)  $\text{cm}^{-1}$ : 2994, 2961, 2902, 2891, 1427, 1370, 1244, 1224, 1199, 1099, 1077, 1027;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.50 (d,  $J = 7.5$  Hz, 2H), 7.46 (d,  $J = 7.5$  Hz, 2H), 5.81 (s, 1H), 4.16—4.11 (m, 2H), 4.08—4.02 (m, 4H), 3.76—3.73 (m, 2H), 1.64 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.3, 137.4, 126.4, 125.4, 108.7, 103.5, 65.4, 64.4, 27.6; ESI-HRMS  $m/z$ : 237.1111 ( $[\text{M}+\text{H}]^+$ );  $\text{C}_{13}\text{H}_{17}\text{O}_4$ : 237.1121.

Preparation of substrate (**2b**) in Table 3, entry 2: To a solution of 2-undecanone (0.43 g, 2.5 mmol) in anhydrous toluene (2 mL) were added ethylene glycol (0.3 mL, 5 mmol) and TsOH (21.5 mg, 0.125 mmol) at room temperature. Then the reaction mixture was heated up to 130 °C. After being stirred for 16 h, the reaction mixture was cooled to room temperature and quenched with sat.  $\text{NaHCO}_3$  aq. (1 mL). The solution was extracted with  $\text{Et}_2\text{O}$  (20 mL  $\times$  2), the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 10/1) to give the substrate (**2b**) in Table 3, entry 2 (0.20 g, 0.95 mmol, 38%).

**2-Methyl-2-nonyl-1,3-dioxolane (**2b**)**

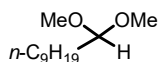


Colorless oil; IR (ATR)  $\text{cm}^{-1}$ : 2981, 2923, 2854, 1466, 1376, 1251, 1218, 1146, 1105, 1058;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.95—3.90 (m, 4H), 1.63—1.60 (m, 2H), 1.39—1.36 (m, 2H), 1.31 (s, 3H), 1.29—1.26 (m, 12H), 0.87 (t,  $J = 6.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 110.0, 64.6, 39.2, 31.9, 29.9, 29.6, 29.5, 29.3, 24.1, 23.7, 22.7, 14.1; ESI-HRMS  $m/z$ : ( $[\text{M}+\text{Na}]^+$ ); 237.1797 ( $[\text{M}+\text{Na}]^+$ );  $\text{C}_{13}\text{H}_{26}\text{O}_2\text{Na}$ : 237.1825.

Preparation of substrate (**3b**) in Table 3, entry 4: To a solution of decanal (0.78 g, 5 mmol) in anhydrous methanol (0.8 mL, 20 mmol) was added palladium acetate (112.3 mg, 0.5 mmol). After being stirred for 48 h at room temperature, the reaction mixture was quenched with sat.  $\text{NaHCO}_3$  aq. (1 mL). The solution was extracted with  $\text{Et}_2\text{O}$  (20 mL  $\times$  2), the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by silica-gel

column chromatography (Hex/EtOAc = 10/1) to give the substrate (**3b**) in Table 3, entry 4 (0.83 g, 4.1 mmol, 82%).

**Decanal dimethylacetal (**3b**)**<sup>14</sup>



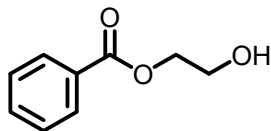
Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.35 (t, *J* = 6.0 Hz, 1H), 3.31 (s, 6H), 1.60—1.55 (m, 2H), 1.30—1.27 (m, 14H), 0.88 (t, *J* = 6.0 Hz, 1H). Spectroscopic data of <sup>1</sup>H NMR was identical to that of the reference 14.

**3. Typical procedure in oxidation.**

To a test tube were added aromatic acetals (**1**: 0.25 mmol), 10% Pd/C, and ethylene glycol (1 mL), then the system was sealed with a septum. The air inside was replaced with O<sub>2</sub> (balloon) by five vacuum/oxygen cycles. The test tube was placed on an organic reactor, Chemi Station (EYELA, Tokyo Rikakikai Co., Ltd., Tokyo, Japan), and the mixture was refluxed [80 °C outer (aluminum heating black) 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 Pd/C. The filtrate was extracted with Et<sub>2</sub>O (20 mL × 2) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding ester derivative (**4**).

**4. Spectroscopic data of synthesized products**

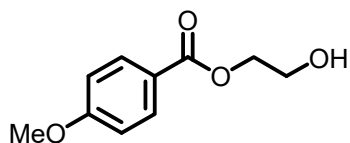
**2-Hydroxyethyl benzoate (**4a**)**<sup>15</sup>



When using substrate (**1a**: 37.5 mg, 0.25 mmol) in Table 1, entry 6 according to typical procedure, 2-hydroxyethyl benzoate (**4a**: 35.3 mg, 0.21 mmol) was obtained in 85% yield for 6 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 4.47 (t, *J* = 4.2 Hz, 2H), 3.96 (t, *J* = 4.2 Hz, 2H), 2.13 (brs, 1H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 15.

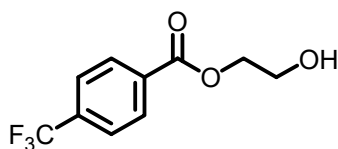
**2-Hydroxyethyl 4-methoxybenzoate (**4b**)**<sup>15</sup>



When using substrate (**1b**: 45.1 mg, 0.25 mmol) in Table 2, entry 1 according to typical procedure, 2-hydroxyethyl 4-methoxybenzoate (**4b**: 49.0 mg, 0.25 mmol) was obtained in quantitative yield for 6 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

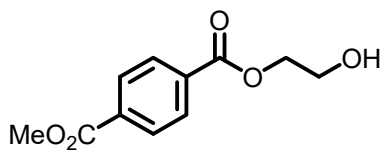
Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.01 (d,  $J = 9.2$  Hz, 2H), 6.92 (d,  $J = 9.2$  Hz, 2H), 4.44 (t,  $J = 4.8$  Hz, 2H), 3.95 (t,  $J = 4.8$  Hz, 2H), 3.87 (s, 3H), 2.11 (brs, 1H). Spectroscopic data of  $^1\text{H}$  NMR of the product was identical to that of the reference 15.

#### 2-Hydroxyethyl 4-(trifluoromethyl)benzoate (**4c**)<sup>15</sup>



When using substrate (**1c**: 54.5 mg, 0.25 mmol) in Table 2, entry 2 according to typical procedure, 2-hydroxyethyl 4-(trifluoromethyl)benzoate (**4c**: 49.7 mg, 0.21 mmol) was obtained in 85% yield for 9 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1). Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.18 (d,  $J = 8.2$  Hz, 2H), 7.71 (d,  $J = 8.2$  Hz, 2H), 4.51 (t,  $J = 4.6$  Hz, 2H), 3.99 (t,  $J = 4.6$  Hz, 2H), 1.96 (brs, 1H). Spectroscopic data of  $^1\text{H}$  NMR of the product was identical to that of the reference 15.

#### Terephthalic acid-(2-hydroxyethyl ester)-methyl ester (**4d**)

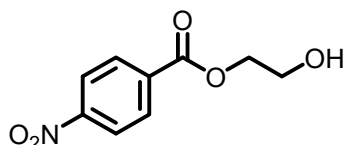


When using substrate (**1d**: 52.1 mg, 0.25 mmol) in Table 2, entry 3 according to typical procedure, terephthalic acid-(2-hydroxyethyl ester)-methyl ester (**4d**: 51.6 mg, 0.23 mmol) was obtained in 92% yield for 6 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

Colorless oil; IR (ATR)  $\text{cm}^{-1}$ : 3454, 2960, 2880, 1713, 1696, 1578, 1435, 1409, 1377, 1276, 1192, 1103, 1071, 1016;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.11—8.06 (m, 4H), 4.49—4.47 (m, 2H), 3.99—3.95 (m, 2H), 3.93 (s, 3H), 2.25 (t,  $J = 5.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$

166.2, 166.0, 134.1, 133.6, 129.6, 129.5, 67.0, 61.2, 52.4; ESI-HRMS  $m/z$ : 247.0581 ( $[M+Na]^+$ ); Calcd for  $C_{11}H_{12}O_5Na$ : 247.0577.

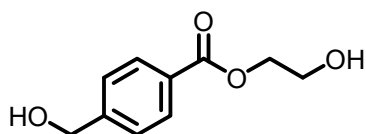
#### 2-Hydroxyethyl 4-nitrobenzoate (**4e**)<sup>15</sup>



When using substrate (**1e**: 48.8 mg, 0.25 mmol) in Table 2, entry 4 according to typical procedure, 2-hydroxyethyl 4-nitrobenzoate (**4e**: 28.3 mg, 0.13 mmol) was obtained in 54% yield, and substrate (**1e**: 20 mg, 0.10 mmol) was recovered in 42% yield for 24 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

Colorless solid;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.28 (d,  $J$  = 8.8 Hz, 2H), 8.23 (d,  $J$  = 8.8 Hz, 2H), 4.52 (t,  $J$  = 4.6 Hz, 2H), 3.99 (t,  $J$  = 4.6 Hz, 2H), 2.11 (brs, 1H). Spectroscopic data of  $^1H$  NMR of the product was identical to that of the reference 15.

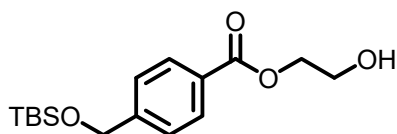
#### Benzoic acid 4-(hydroxymethyl)-2-hydroxyethyl ester (**4f**)



When using substrate (**1f**: 45.1 mg, 0.25 mmol) in Table 2, entry 5 according to typical procedure, benzoic acid 4-(hydroxymethyl)-2-hydroxyethyl ester (**4f**: 26.0 mg, 0.13 mmol) was obtained in 53% yield for 6 h after purification by silica-gel column chromatography (Hex/EtOAc = 1/1).

Colorless solid; M.p. 75–78 °C; IR (ATR)  $cm^{-1}$ : 3357, 2920, 2850, 1700, 1613, 1578, 1455, 1416, 1374, 1276, 1176, 1124, 1074, 1050, 1017;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.05 (d,  $J$  = 8.0 Hz, 2H), 7.44 (d,  $J$  = 8.0 Hz, 2H), 4.78 (s, 2H), 4.47 (t,  $J$  = 4.8 Hz, 2H), 3.97 (t,  $J$  = 4.8 Hz, 2H), 2.05 (brs, 2H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  166.8, 146.3, 129.9, 128.9, 126.5, 66.7, 64.6, 61.4; ESI-HRMS  $m/z$ : 197.0786 ( $[M+H]^+$ ); Calcd for  $C_{10}H_{12}O_4$ : 197.0808.

#### 2-Hydroxyethyl 4-(*tert*-butyldimethylsilyloxymethyl)benzoate (**4g**)



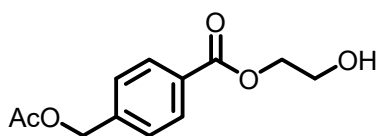
When using substrate (**1g**: 73.6 mg, 0.25 mmol) in Table 2, entry 6 according to typical procedure, 2-hydroxyethyl 4-(*tert*-butyldimethylsilyloxymethyl)benzoate (**4g**: 45.1 mg, 0.15



mmol) was obtained in 58% yield for 3 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

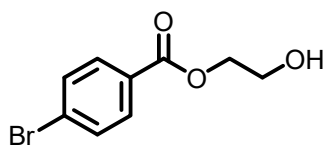
Colorless oil; IR (ATR)  $\text{cm}^{-1}$ : 3435, 2953, 2929, 2885, 2857, 1718, 1613, 1462, 1415, 1373, 1271, 1119, 1081, 1019;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.02 (d,  $J$  = 8.4 Hz, 2H), 7.39 (d,  $J$  = 8.4 Hz, 2H), 4.79 (s, 2H), 4.45 (t,  $J$  = 4.6 Hz, 2H), 3.95 (t,  $J$  = 4.6 Hz, 2H), 2.25 (brs, 1H), 0.94 (s, 9H), 0.10 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.9, 147.1, 129.7, 128.4, 125.7, 66.5, 64.5, 61.4, 25.9, 18.3, -5.3; ESI-HRMS  $m/z$ : 333.1497 ( $[\text{M}+\text{Na}]^+$ ); Calcd for  $\text{C}_{16}\text{H}_{26}\text{O}_4\text{SiNa}$ : 333.1493.

#### 2-Hydroxyethyl 4-(acetoxymethyl)benzoate (**4h**)



When using substrate (**1h**: 55.6 mg, 0.25 mmol) in Table 2, entry 7 according to typical procedure, 2-hydroxyethyl 4-(acetoxymethyl)benzoate (**4h**: 36.4 mg, 0.15 mmol) was obtained in 61% yield for 6 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1). Colorless oil; IR (ATR)  $\text{cm}^{-1}$ : 3467, 2954, 1716, 1615, 1418, 1379, 1274, 1228, 1180, 1124, 1075, 1020;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.04 (d,  $J$  = 8.6 Hz, 2H), 7.40 (d,  $J$  = 8.6 Hz, 2H), 5.14 (s, 2H), 4.45 (t,  $J$  = 4.8 Hz, 2H), 3.94 (t,  $J$  = 4.8 Hz, 2H), 2.36 (brs, 1H), 2.12 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.7, 166.5, 141.3, 129.9, 129.6, 127.7, 66.7, 65.4, 61.3, 20.9; ESI-HRMS  $m/z$ : 261.0736 ( $[\text{M}+\text{Na}]^+$ ); Calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_5\text{Na}$ : 261.0733.

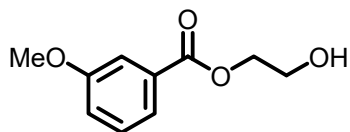
#### 2-Hydroxyethyl 4-bromobenzoate (**4i**)<sup>15</sup>



When using substrate (**1i**: 57.3 mg, 0.25 mmol) in Table 2, entry 8 according to typical procedure at 120 °C, 2-hydroxyethyl 4-bromobenzoate (**4i**: 31.2 mg, 0.13 mmol) was obtained in 51% yield, 2-hydroxyethyl benzoate (**4a**: 2.5 mg, 0.01 mmol) was obtained as a side-product in 6% yield, and substrate (**1e**: 14 mg, 0.06 mmol) was recovered in 24% yield for 6 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.92 (dd,  $J$  = 2.0, 8.0 Hz, 2H), 7.59 (dd,  $J$  = 2.0, 8.0 Hz, 2H), 4.47 (t,  $J$  = 4.4 Hz, 2H), 3.97 (s, 2H), 1.96 (brs, 1H). Spectroscopic data of  $^1\text{H}$  NMR of the product was identical to that of the reference 15.

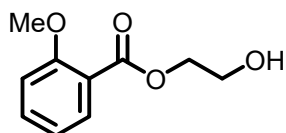
### 2-Hydroxyethyl 3-methoxybenzoate (**4j**)<sup>16</sup>



When using substrate (**1j**: 45.1 mg, 0.25 mmol) in Table 2, entry 9 according to typical procedure, 2-hydroxyethyl 3-methoxybenzoate (**4j**: 44.6 mg, 0.23 mmol) was obtained in 91% yield for 9 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 2.8, 8.4 Hz, 1H), 4.45 (t, *J* = 4.2 Hz, 1H), 3.95 (t, *J* = 4.2 Hz, 1H), 3.84 (s, 3H), 2.21 (brs, 1H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 16.

### 2-Hydroxyethyl 2-methoxybenzoate (**4k**)



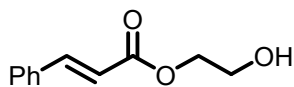
When using substrate (**1k**: 45.1 mg, 0.25 mmol) in Table 2, entry 10 according to typical procedure, 2-hydroxyethyl 2-methoxybenzoate (**4k**: 37.4 mg, 0.19 mmol) was obtained in 77% yield for 12 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

Colorless oil; IR (ATR) cm<sup>-1</sup>: 3468, 2947, 1709, 1600, 1492, 1464, 1437, 1301, 1249, 1138, 1072, 1022; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.81 (d, *J* = 8.4 Hz, 1H), 7.51—7.46 (m, 1H), 7.02—6.98 (m, 2H), 4.45 (t, *J* = 4.4 Hz, 2H), 3.93 (t, *J* = 4.4 Hz, 2H), 3.91 (s, 3H), 2.28 (t, *J* = 6.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.6, 159.0, 133.7, 131.7, 120.3, 120.0, 112.0, 66.4, 61.2, 56.0; ESI-HRMS *m/z*: 219.0621 ([M+Na]<sup>+</sup>); C<sub>10</sub>H<sub>12</sub>O<sub>4</sub>Na: 219.0628.

### 2-Hydroxyethyl cinnamate (**4l**)<sup>15</sup> and 2-Hydroxyethyl 3-phenylpropanoate<sup>15</sup>

When using substrate (**1l**: 45.1 mg, 0.25 mmol) in Table 2, entry 11 according to typical procedure, 2-hydroxyethyl cinnamate (**4l**: 39.6 mg, 0.21 mmol) and inseparable reduced product (2-hydroxyethyl 3-phenylpropanoate: 4.8 mg, 0.03 mmol) were respectively obtained in 82% yield and 10% yield as inseparable mixtures for 12 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

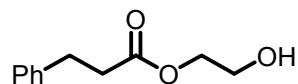
### 2-Hydroxyethyl cinnamate (**4l**)<sup>15</sup>



Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.73 (d, *J* = 15.8 Hz, 1H), 7.53—7.51 (m, 2H), 7.40—7.36 (m, 3H), 6.48 (d, *J* = 15.8 Hz, 1H), 4.35 (t, *J* = 4.5 Hz, 2H), 3.91 (t, *J* = 4.5 Hz, 2H),

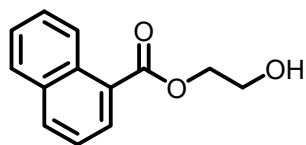
2.25 (brs, 1H). Spectroscopic data of  $^1\text{H}$  NMR of the product was identical to that of the reference 15.

**2-Hydroxyethyl 3-phenylpropanoate**<sup>15</sup>



Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.31—7.28 (m, 2H), 7.23—7.20 (m, 3H), 4.20—4.18 (m, 2H), 3.76 (t,  $J = 5.0$  Hz, 2H), 2.97 (t,  $J = 7.5$  Hz, 2H), 2.69 (t,  $J = 7.5$  Hz, 2H), 2.25 (brs, 1H). Spectroscopic data of  $^1\text{H}$  NMR of the product was identical to that of the reference 15.

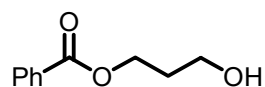
**2-Hydroxyethyl 1-naphthoate (4m)**<sup>17</sup>



When using substrate (**1m**: 50.1 mg, 0.25 mmol) in Table 2, entry 12 according to typical procedure, 2-hydroxyethyl 1-naphthoate (**4m**: 42.3 mg, 0.20 mmol) was obtained in 79% yield for 12 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.90 (d,  $J = 8.8$  Hz, 1H), 8.21 (dd,  $J = 1.6, 7.2$  Hz, 1H), 8.04 (d,  $J = 8.4$  Hz, 1H), 7.89 (d,  $J = 8.4$  Hz, 1H), 7.65—7.60 (m, 1H), 7.56—7.48 (m, 2H), 4.56 (t,  $J = 4.8$  Hz, 2H), 4.02 (t,  $J = 4.8$  Hz, 2H), 2.13 (brs, 1H). Spectroscopic data of  $^1\text{H}$  NMR of the product was identical to that of the reference 17.

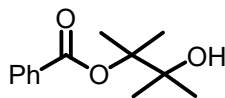
**3-Hydroxypropyl benzoate (4n)**<sup>15</sup>



When using substrate (**1n**: 41.1 mg, 0.25 mmol) in Table 2, entry 13 according to typical procedure, 3-hydroxypropyl benzoate (**4n**: 26.9 mg, 0.15 mmol) was obtained in 60% yield for 6 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.04 (d,  $J = 7.2$  Hz, 2H), 7.56 (t,  $J = 7.2$  Hz, 1H), 7.44 (t,  $J = 7.2$  Hz, 2H), 4.49 (t,  $J = 5.8$  Hz, 2H), 3.78 (t,  $J = 5.8$  Hz, 2H), 2.09 (brs, 1H), 2.04—1.98 (m, 2H). Spectroscopic data of  $^1\text{H}$  NMR of the product was identical to that of the reference 15.

**3-Hydroxy-2,3-dimethylbutan-2-yl benzoate (4o)**<sup>18</sup>

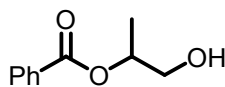


When using substrate (**1o**: 51.6 mg, 0.25 mmol) in Table 2, entry 14 according to typical procedure, 3-hydroxy-2,3-dimethylbutan-2-yl benzoate (**4n**: 4.36 mg, 0.20 mmol) was obtained in 79% yield for 6 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1). Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.99 (d,  $J$  = 7.4 Hz, 2H), 7.56 (t,  $J$  = 7.4 Hz, 1H), 7.44 (t,  $J$  = 7.4 Hz, 2H), 3.69 (brs, 1H), 1.63 (s, 6H), 1.30 (s, 6H). Spectroscopic data of  $^1\text{H}$  NMR of the product was identical to that of the reference 18.

**2-Hydroxy-1-methylethyl benzoate (4pa)<sup>17</sup> and 2-hydroxy-2-methylethyl benzoate (4pb)<sup>17</sup>**

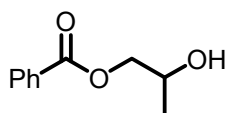
When using substrate (**1p**: 41.1 mg, 0.25 mmol) in Table 2, entry 15 according to typical procedure, 2-hydroxy-1-methylethyl benzoate (**4pa**: 18.5 mg, 0.1 mmol) and 2-hydroxy-2-methylethyl benzoate (**4pb**: 22.1 mg, 0.12 mmol) were respectively obtained in 41% yield and 49% yield for 6 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

**2-Hydroxy-1-methylethyl benzoate (4pa)<sup>17</sup>**



Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05—8.02 (m, 2H), 7.56—7.52 (m, 1H), 7.44—7.40 (m, 2H), 5.24—5.20 (m, 1H), 3.76 (m, 2H), 2.56 (brs, 1H), 1.34 (d,  $J$  = 6.8 Hz, 3H). Spectroscopic data of  $^1\text{H}$  NMR of the product was identical to that of the reference 17.

**2-Hydroxy-2-methylethyl benzoate (4pb)<sup>17</sup>**

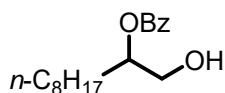


Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05—8.02 (m, 2H), 7.56—7.52 (m, 1H), 7.44—7.40 (m, 2H), 4.32—4.28 (m, 1H), 4.22—4.17 (m, 2H), 2.56 (brs, 1H), 1.27 (t,  $J$  = 6.0 Hz, 3H). Spectroscopic data of  $^1\text{H}$  NMR of the product was identical to that of the reference 17.

**1-Hydroxydecan-2-yl benzoate (4qa) and 2-hydroxydecan-2-yl benzoate (4qb)**

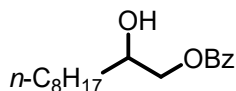
When using substrate (**1q**: 65.6 mg, 0.25 mmol) in Table 2, entry 16 according to typical procedure, 1-hydroxydecan-2-yl benzoate (**4qa**: 41.8 mg, 0.15 mmol) and 2-hydroxydecan-2-yl benzoate (**4qb**: 19.7 mg, 0.07 mmol) were respectively obtained in 60% yield and 28% yield for 6 h after purification by silica-gel column chromatography (Hex/EtOAc = 5/1).

**1-Hydroxydecan-2-yl benzoate (4qa)**



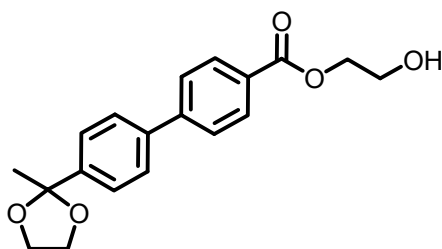
Colorless oil; IR (ATR)  $\text{cm}^{-1}$ : 3433, 2924, 2855, 1716, 1602, 1585, 1451, 1359, 1315, 1270, 1176, 1114, 1098, 1069, 1026;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06 (d,  $J = 8.6$  Hz, 2H), 7.57 (t,  $J = 8.6$  Hz, 1H), 7.45 (t,  $J = 8.6$  Hz, 2H), 5.19—5.13 (m, 1H), 3.85—3.74 (m, 2H), 2.19 (brs, 1H), 1.77—1.68 (m, 2H), 1.43—1.25 (m, 12H), 0.86 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.9, 133.1, 130.2, 129.6, 128.4, 76.4, 65.0, 31.8, 30.7, 29.4, 29.4, 29.2, 25.3, 22.6, 14.1; ESI-HRMS  $m/z$ : 301.1793 ( $[\text{M}+\text{Na}]^+$ );  $\text{C}_{17}\text{H}_{26}\text{O}_3\text{Na}$ : 301.1774.

#### 2-Hydroxydecyl benzoate (4qb)



Colorless oil; IR (ATR)  $\text{cm}^{-1}$ : 3470, 2924, 2854, 1720, 1602, 1584, 1452, 1378, 1315, 1271, 1177, 1116, 1070, 1027;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (d,  $J = 7.6$  Hz, 1H), 7.57 (t,  $J = 7.6$  Hz, 1H), 7.45 (dd,  $J = 7.6, 7.6$  Hz, 2H), 4.39 (dd,  $J = 7.2, 11.5$  Hz, 1H), 4.22 (dd,  $J = 7.2, 11.5$  Hz, 1H), 3.98 (m, 1H), 2.18 (brs, 1H), 1.58—1.27 (m, 14H), 0.88 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.7, 133.1, 129.9, 129.6, 128.4, 70.2, 69.2, 33.5, 31.8, 29.6, 29.5, 29.2, 25.4, 22.6, 14.1; ESI-HRMS  $m/z$ : 301.1789 ( $[\text{M}+\text{Na}]^+$ );  $\text{C}_{17}\text{H}_{26}\text{O}_3\text{Na}$ : 301.1774.

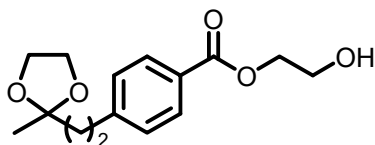
#### 4r



When using substrate (**1r** 31.2 mg, 0.1 mmol) in Table 3, entry 5 according to typical procedure, **4r** (28.8 mg, 0.088 mmol) was obtained in 88% yield for 24 h after purification by silica-gel column chromatography (Hex/EtOAc = 1/1).

Colorless solid; M.p. 95—99 °C; IR (ATR)  $\text{cm}^{-1}$ : 3489, 2986, 2887, 1716, 1608, 1374, 1275, 1199, 1180, 1121, 1082, 1038, 1006;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.12 (d,  $J = 8.2$  Hz, 2H), 7.66 (d,  $J = 8.2$  Hz, 2H), 7.62—7.57 (m, 4H), 4.49 (t,  $J = 4.4$  Hz, 2H), 4.09—4.05 (m, 2H), 3.98 (brs, 2H), 3.84—3.80 (m, 2H), 2.13 (brs, 1H), 1.70 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.8, 145.5, 143.4, 139.4, 130.2, 128.6, 127.2, 127.0, 125.9, 108.7, 66.7, 64.5, 61.5, 27.6; ESI-HRMS  $m/z$ : 351.1200 ( $[\text{M}+\text{Na}]^+$ );  $\text{C}_{19}\text{H}_{20}\text{O}_5\text{Na}$ : 351.1203.

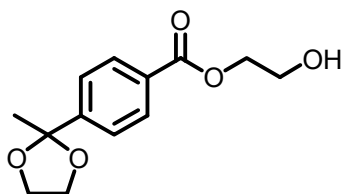
#### 2-Hydroxyethyl 4-[2-(1,3-dioxolan-2-yl)ethyl]benzoate (4s)



When using substrate (**1s**: 62.6 mg, 0.25 mmol) in Table 3, entry 6 according to typical procedure, 2-hydroxyethyl 4-[2-(1,3-dioxolan-2-yl)ethyl]benzoate (**4s**: 43.3 mg, 0.16 mmol) was obtained in 65% yield for 36 h after purification by silica-gel column chromatography (Hex/EtOAc = 2/1).

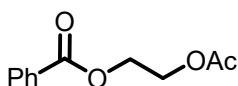
Colorless oil; IR (ATR)  $\text{cm}^{-1}$ : 3464, 2955, 2884, 1713, 1611, 1415, 1271, 1179, 1123, 1070, 1020;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (d,  $J$  = 8.2 Hz, 2H), 7.27 (d,  $J$  = 8.2 Hz, 2H), 4.88 (t,  $J$  = 4.4 Hz, 1H), 4.44 (t,  $J$  = 4.4 Hz, 2H), 3.99—3.86 (m, 6H), 2.82—2.78 (m, 2H), 2.30 (brs, 1H), 2.01—1.95 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.9, 147.5, 129.8, 128.4, 127.6, 103.5, 66.5, 65.0, 61.4, 35.0, 30.1; ESI-HRMS  $m/z$ : 289.1042 ( $[\text{M}+\text{Na}]^+$ );  $\text{C}_{14}\text{H}_{18}\text{O}_5\text{Na}$ : 289.1046.

#### 2-Hydroxyethyl 4-(2-methyl-1,3-dioxolan-2-yl)benzoate (**4t**)



When using substrate (**1t**: 29.5 mg, 0.125 mmol) in eq 4 according to typical procedure, 2-hydroxyethyl 4-(2-methyl-1,3-dioxolan-2-yl)benzoate (**4t**: 27.1 mg, 0.11 mmol) was obtained in 86% yield for 9 h after purification by silica-gel column chromatography (Hex/EtOAc = 1/1). Colorless oil; IR (ATR)  $\text{cm}^{-1}$ : 3466, 2988, 2889, 1719, 1406, 1374, 1275, 1123, 1094, 1037;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.04 (d,  $J$  = 8.0 Hz, 2H), 7.57 (d,  $J$  = 8.0 Hz, 2H), 4.48—4.46 (m, 2H), 4.07—4.03 (m, 2H), 3.98—3.96 (m, 2H), 3.77—3.74 (m, 2H), 2.01 (t,  $J$  = 5.5 Hz, 1H), 1.65 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 166.7, 148.7, 129.7, 129.4, 125.4, 108.5, 66.7, 64.5, 61.5, 27.4; ESI-HRMS  $m/z$ : 275.0874 ( $[\text{M}+\text{Na}]^+$ );  $\text{C}_{13}\text{H}_{16}\text{O}_5\text{Na}$ : 275.0890.

#### 2-(Acetyloxy)ethyl benzoate (**5**)<sup>19</sup>

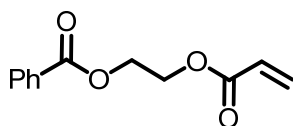


To a solution of the 2-hydroxyethyl benzoate (**4a**: 42 mg, 0.25 mmol) in pyridine (1 mL) were added DMAP (2 mg, 0.0125 mmol) and acetic anhydride (51 mg, 0.5 mmol) at room temperature under argon. After stirring for 6 h at room temperature, the reaction mixture was

quenched with water and extracted with AcOEt (20 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 5/1) to give 2-(acetyloxy)ethyl benzoate (**5**: 49 mg, 0.24 mmol, 94%) in eq 3.

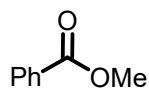
Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.05 (d,  $J$  = 7.3 Hz, 2H), 7.58 (d,  $J$  = 7.3 Hz, 1H), 7.45 (d,  $J$  = 7.3 Hz, 2H), 4.54—4.51 (m, 2H), 4.43—4.41 (m, 2H), 2.10 (s, 3H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 19.

#### 2-(Acryloyloxy)ethyl benzoate (**6**)<sup>20</sup>



To a solution of the 2-hydroxyethyl benzoate (**4a**: 42 mg, 0.25 mmol) in AcOEt (1.5 mL) were added Et<sub>3</sub>N (34.8  $\mu$ L, 0.25 mmol) and acryloyl chloride (20.2  $\mu$ L, 0.25 mmol) at 0 °C under argon. After stirring for 4 h, the reaction mixture was quenched with 1N HCl aq. (2 mL) and extracted with AcOEt (10 mL  $\times$  3). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 10/1) to give 2-(acryloyloxy)ethyl benzoate (**6**: 41 mg, 0.20 mmol, 80%) in eq 3. Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.05 (d,  $J$  = 7.3 Hz, 2H), 7.57 (t,  $J$  = 7.3 Hz, 1H), 7.44 (t,  $J$  = 7.3 Hz, 2H), 6.45 (dd,  $J$  = 1.4, 17.6 Hz, 1H), 6.15 (dd,  $J$  = 10.6, 17.4 Hz, 1H), 5.86 (dd,  $J$  = 1.4, 10.6 Hz, 1H), 4.57—4.55 (m, 2H), 4.52—4.50 (m, 2H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 20.

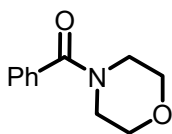
#### Methyl benzoate (**7**)<sup>21</sup>



To a solution of the 2-hydroxyethyl benzoate (**4a**: 42 mg, 0.25 mmol) in methanol (1 mL) was added sodium hydroxide (12 mg, 0.3 mmol) at room temperature. After stirring for 15 min at room temperature, the reaction mixture was quenched with 1N H<sub>2</sub>SO<sub>4</sub> aq. (0.3 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo to give methyl benzoate (**7**: 34 mg, 0.25 mmol, 99%) in eq 3.

Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.04 (dd,  $J$  = 1.0, 7.8 Hz, 2H), 7.56 (d,  $J$  = 7.5 Hz, 1H), 7.44 (d,  $J$  = 7.5 Hz, 1H), 3.92 (s, 3H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 21.

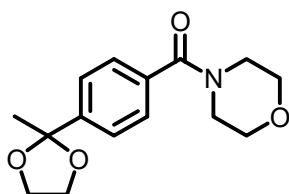
#### N-Benzoylmorpholine (**8**)<sup>22</sup>



To a solution of morpholine (87 mg, 1.0 mmol) in anhydrous THF (0.5 mL) was added sodium hydride (26 mg, 1.1 mmol, 60% oil suspension) at 0 °C under argon. After stirring for 1 h, a solution of 2-hydroxyethyl benzoate (**4a**: 42 mg, 0.25 mmol) in dry THF (0.5 mL) was added at 0 °C. After further stirring for 12 h, the reaction mixture was quenched with 1N H<sub>2</sub>SO<sub>4</sub> aq. (1.0 mL) and extracted with AcOEt (20 mL × 2). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 1/1) to give *N*-benzoylmorpholine (**8**: 41 mg, 0.22 mmol, 86%) in eq 3.

Colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.46—7.40 (m, 5H), 3.77—3.44 (m, 8H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 22.

#### [4-(2-Methyl-1,3-dioxolan-2-yl)phenyl] (morpholino)methanone

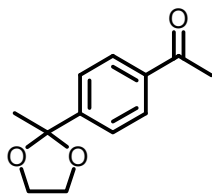


To a solution of morpholine (17 mg, 0.2 mmol) in anhydrous THF (0.1 mL) was added sodium hydride (5 mg, 0.22 mmol, 60% oil suspension) at 0 °C under argon. After stirring for 1 h, a solution of 2-hydroxyethyl 4-(2-methyl-1,3-dioxolan-2-yl)benzoate (**4t**: 13 mg, 0.05 mmol) in dry THF (0.1 mL) was added at 0 °C. After further stirring for 12 h, the reaction mixture was quenched with 1N H<sub>2</sub>SO<sub>4</sub> aq. (1.0 mL) and extracted with AcOEt (20 mL × 2). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 1/1) to give [4-(2-methyl-1,3-dioxolan-2-yl)phenyl] (morpholino)methanone (11 mg, 0.04 mmol, 79%) in eq 4.

Colorless solid; M.p. 126-127 °C; IR (ATR) cm<sup>-1</sup>: 2986, 2893, 1634, 1429, 1373, 1301, 1278, 1257, 1199, 1156, 1114, 1076, 1037, 1013; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 4.06—4.03 (m, 2H), 3.79—3.46 (m, 10H), 1.64 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 170.3, 145.2, 134.8, 127.0, 125.6, 108.5, 66.9, 64.5, 27.5; ESI-HRMS *m/z*: 300.1210 ([M+Na]<sup>+</sup>); C<sub>15</sub>H<sub>19</sub>NO<sub>4</sub>Na: 300.1206.

#### 1-[4-(2-methyl-1,3-dioxolan-2-yl)phenyl]ethanone (**9**)<sup>23</sup>





To a solution of [4-(2-methyl-1,3-dioxolan-2-yl)phenyl](morpholino)methanone (8.2 mg, 0.03 mmol) in anhydrous THF (0.3 mL) was added dropwise methylmagnesium chloride solution (0.1 mL, 3.0 M in THF, 0.3 mmol) at 0 °C under argon. After further stirring for 6 h, the reaction mixture was quenched with water and extracted with AcOEt (20 mL  $\times$  2). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 5/1) to give 1-[4-(2-methyl-1,3-dioxolan-2-yl)phenyl]ethanone (**9**: 3.7 mg, 0.02 mmol, 60%) in eq 3.

Colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.94 (d,  $J$  = 8.5 Hz, 2H), 7.58 (d,  $J$  = 8.5 Hz, 2H), 4.08—4.03 (m, 2H), 3.79—3.75 (m, 2H), 2.61 (s, 3H), 1.66 (s, 3H). Spectroscopic data of <sup>1</sup>H NMR of the product was identical to that of the reference 23.

## 5. Metal leaching test.

2-Phenyl-1,3-dioxolane (**1a**: 751 mg, 5 mmol), 10% Pd/C (266 mg, 0.25 mmol), and ethylene glycol (20 mL) were mixed in a flask (100 mL). The air inside was replaced with O<sub>2</sub> (balloon) by five vacuum/oxygen cycles and the reaction mixture was stirred at 80 °C for 6 h. After 6 h, the reaction mixture was cooled to room temperature. The reaction mixture was passed through a filter paper [Kiriya, No. 5C (1  $\mu$ m), diameter = 40 mm] and the catalyst was washed with H<sub>2</sub>O (20 mL  $\times$  5) and Et<sub>2</sub>O (20 mL  $\times$  5). The filtrate was extracted with Et<sub>2</sub>O (20 mL  $\times$  2) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was dissolved in Et<sub>2</sub>O, and the aqueous layer was diluted with H<sub>2</sub>O to 100 mL, respectively. The Pd leaching in each layer was measured by ICP-OES. Consequently, metal leaching was observed 0.1 ppm in water layers.

## 6. Reuse test.

To a test tube were added 2-phenyl-1,3-dioxolane (**1a**: 0.25 mmol), 10% Pd/C, and ethylene glycol (1 mL), then the system was sealed with a septum. The air inside was replaced with O<sub>2</sub> (balloon) by five vacuum/oxygen cycles. The test tube was placed on an organic reactor, Chemi Station (EYELA, Tokyo Rikakikai Co., Ltd., Tokyo, Japan), and the mixture was refluxed (80 °C outer temperature). After 6 h, the reaction mixture was cooled to room temperature. The

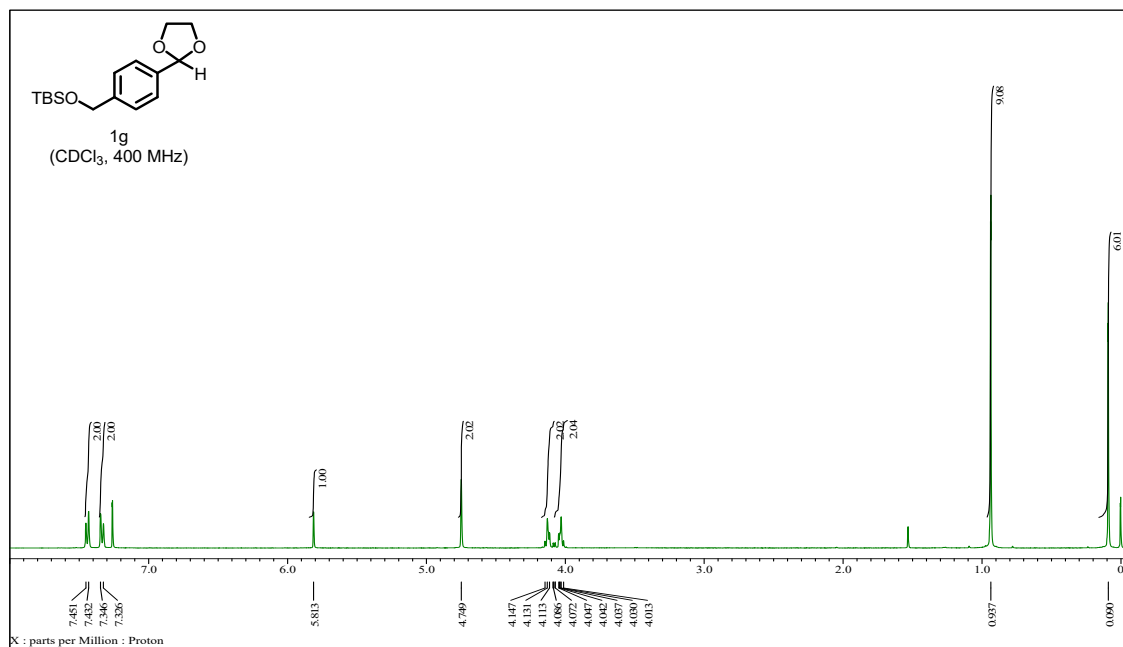
reaction mixture was passed through a filter paper [Kiriya, No. 5C (1  $\mu$ m), diameter = 40 mm] and the catalyst was washed with H<sub>2</sub>O (10 mL  $\times$  5) and MeOH (10 mL  $\times$  5). The filtrate was extracted with Et<sub>2</sub>O (20 mL  $\times$  2) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The filtrated catalysts was further washed with MeOH (50 mL) and water (50 mL) and dried in a desiccator under vacuum overnight, then the recovered catalyst was used for the next run.

## 7. References.

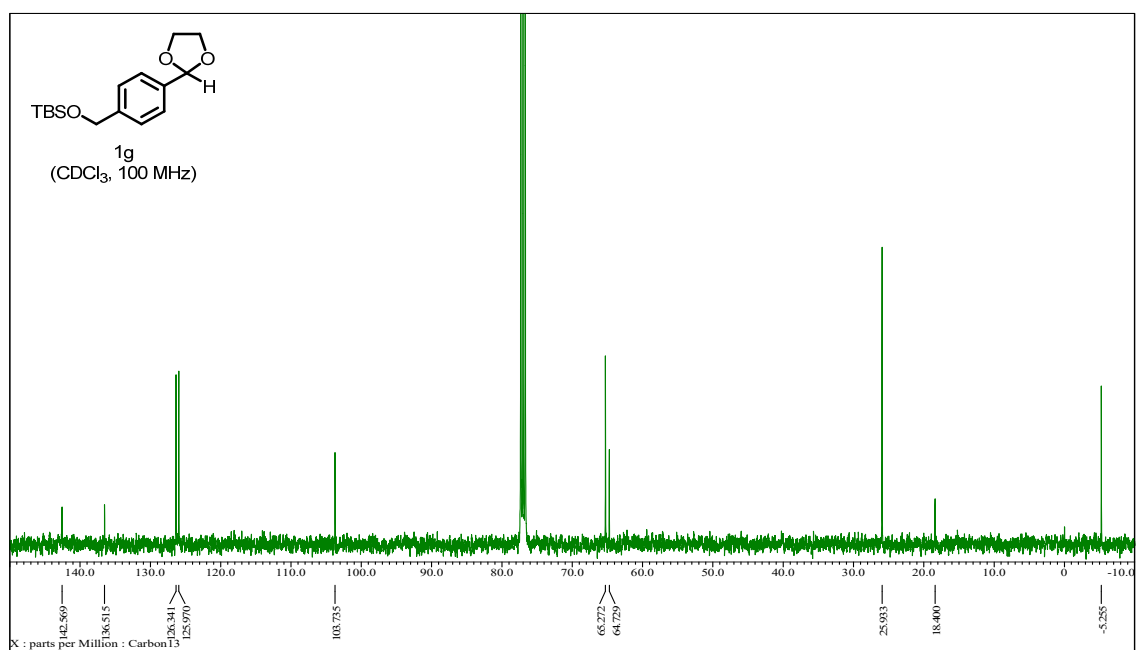
- 1) R. Gopinath, S. J. Haque, and B. K. Patel. *J. Org. Chem.* **2002**, 67, 5842–5845.
- 2) Y. Seeleob, G. Nemecek, D. Pfaff, B. D. Suveges, and J. Podlech. *Synth. Commun.* **2014**, 44, 2966–2973.
- 3) D. M. Podgorski, S. W. Krabbe, L. N. Le, P. R. Sierszulski, and R. S. Mohan. *Synthesis.* **2010**, 16, 2771–2775.
- 4) T. Knauber, F. Arian, Gerd-Volker Roschenthaler, and L. J. Gooben. *Chem. Eur. J.* **2011**, 17, 2689–2697.
- 5) U. Azzena, M. Carraro, A. D. Mamuye, I. Murgia, L. Pisano, and G. Zedde. *Green Chem.* **2015**, 17, 3281–3284.
- 6) M. Barbasiewicz, and M. Makosza. *Org. Lett.* **2006**, 17, 3745–3748.
- 7) P. Muller, P. Nury, and G. Bernardinelli. *Eur. J. Org. Chem.* **2001**, 21, 4137–4147.
- 8) P. J. Garegg, and C. G. Swahn. *Acta Chemica Scandinavica* **1972**, 26, 3895–3901.
- 9) Y. Monguchi, Y. Fujita, K. Endo, S. Takao, M. Yoshimura, Y. Takagi, T. Maegawa, and H. Sajiki. *Chem. Eur. J.* **2009**, 15, 834–837.
- 10) G. A. Edwards, M. A. Trafford, A. E. Hamilton, A. M. Buxton, M. C. Bardeaux, and J. M. Chalker. *J. Org. Chem.* **2014**, 79, 2094–2104.
- 11) J. H. Klein, D. Schmidt, U. E. Steiner, and C. Lambert. *J. Am. Chem. Soc.* **2015**, 137, 11011–11021.
- 12) M. Chen, J. Wang, Z. Chai, C. You, and A. Lei. *Adv. Synth. Catal.* **2012**, 354, 341–346.
- 13) I. Kondolff, H. Doucet, and M. Santelli. *Chem. Eur. J.* **2006**, 3, 765–774.
- 14) H. Fujioka, T. Okitsu, Y. Sawama, N. Murata, R. Li, and Y. Kita. *J. Am. Chem. Soc.* **2006**, 128, 5930–5938.
- 15) T. Yasukawa, H. Miyamura, and S. Kobayashi. *Chem. Asian. J.* **2011**, 6, 621–627.
- 16) B. Karimi, and J. Rajabi. *J. Mol. Catal.* **2005**, 226, 165–169.
- 17) N. Wakita, and S. Hara. *Tetrahedron* **2010**, 66, 7939–7945.
- 18) H. Sharghi, and M. H. Sarvari. *J. Org. Chem.* **2003**, 68, 4096–4099.
- 19) A. Coskun, M. Guney, A. Dastan, and M. Balci. *Tetrahedron.* **2007**, 63, 4944–4950.
- 20) B. Zhu, G. Qian, Y. Xiao, S. Deng, M. Wang, and A. Hu. *J. Polym. Sci. A. Polym. Chem.* **2011**, 49, 5330–5338.
- 21) S. Seo, J. B. Taylor, and M. F. Greaney. *Chem. Commun.* **2012**, 48, 8270–8272.
- 22) K. Xu, Y. Hu, S. Zhang, Z. Zha, and Z. Wang. *Chem. Eur. J.* **2012**, 18, 9793–9797.
- 23) Z. Hyder, J. Ruan, and J. Xiao. *Chem. Eur. J.* **2008**, 14, 5555–5566.

## 6. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of the newly synthesized substrates and products.

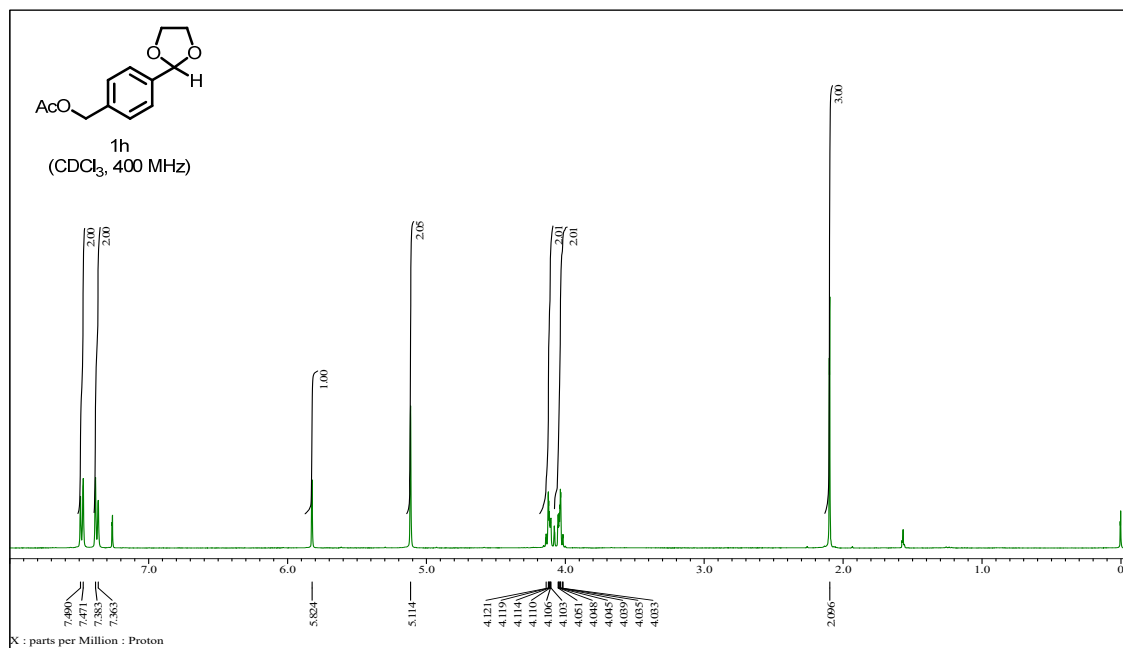
$^1\text{H}$  NMR of [4-(1,3-dioxolan-2-yl)benzyloxy]tert-butyldimethylsilane (**1g**)



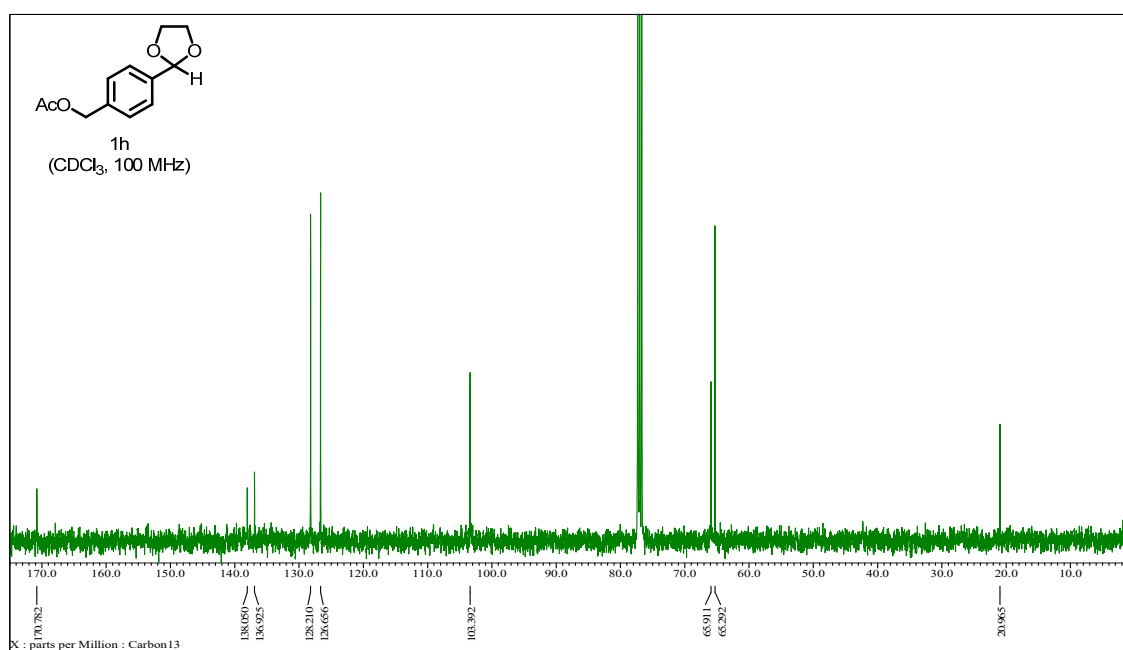
$^{13}\text{C}$  NMR of [4-(1,3-dioxolan-2-yl)benzyloxy]tert-butyldimethylsilane (**1g**)



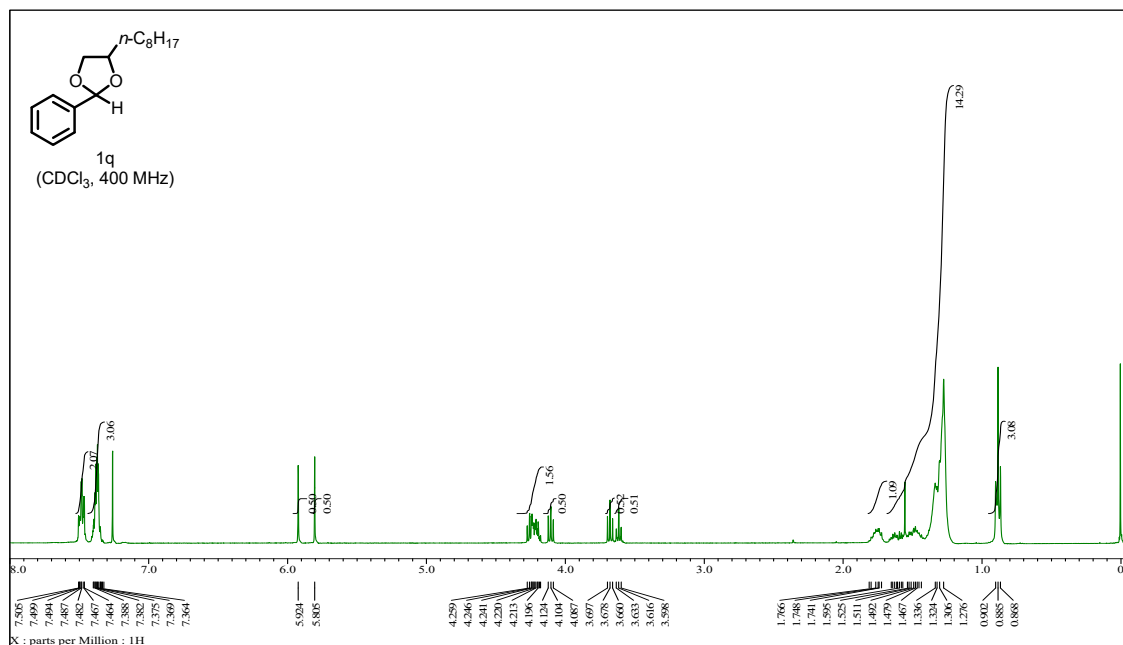
$^1\text{H}$  NMR of 4-(1,3-dioxolan-2-yl)benzylacetate (**1h**)



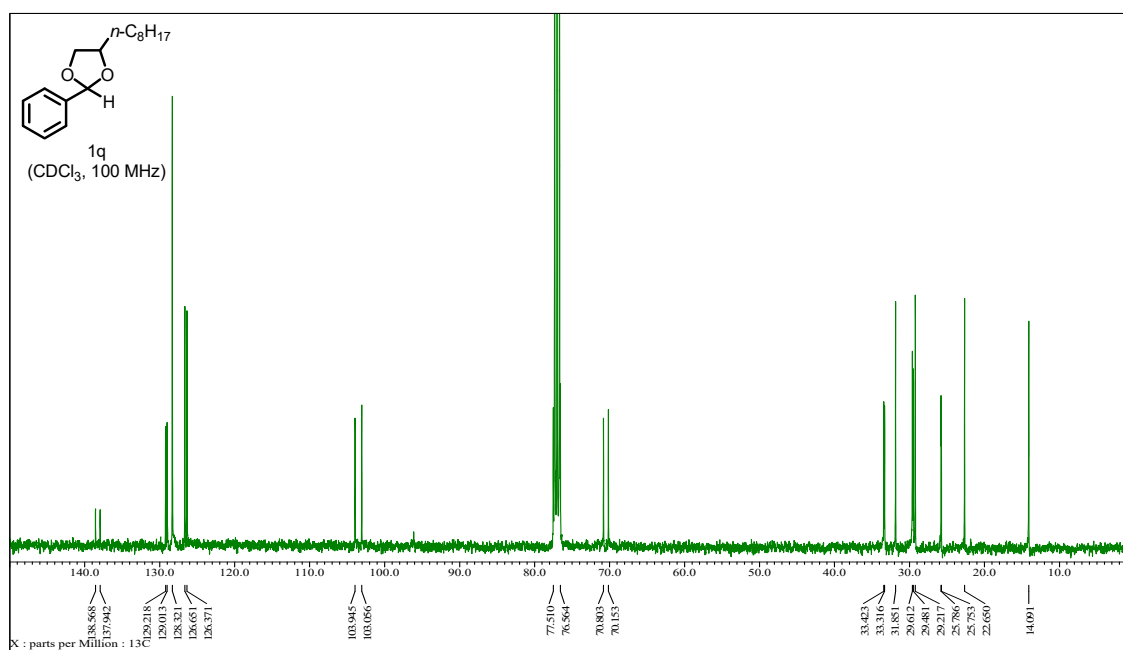
$^{13}\text{C}$  NMR of 4-(1,3-dioxolan-2-yl)benzylacetate (**1h**)



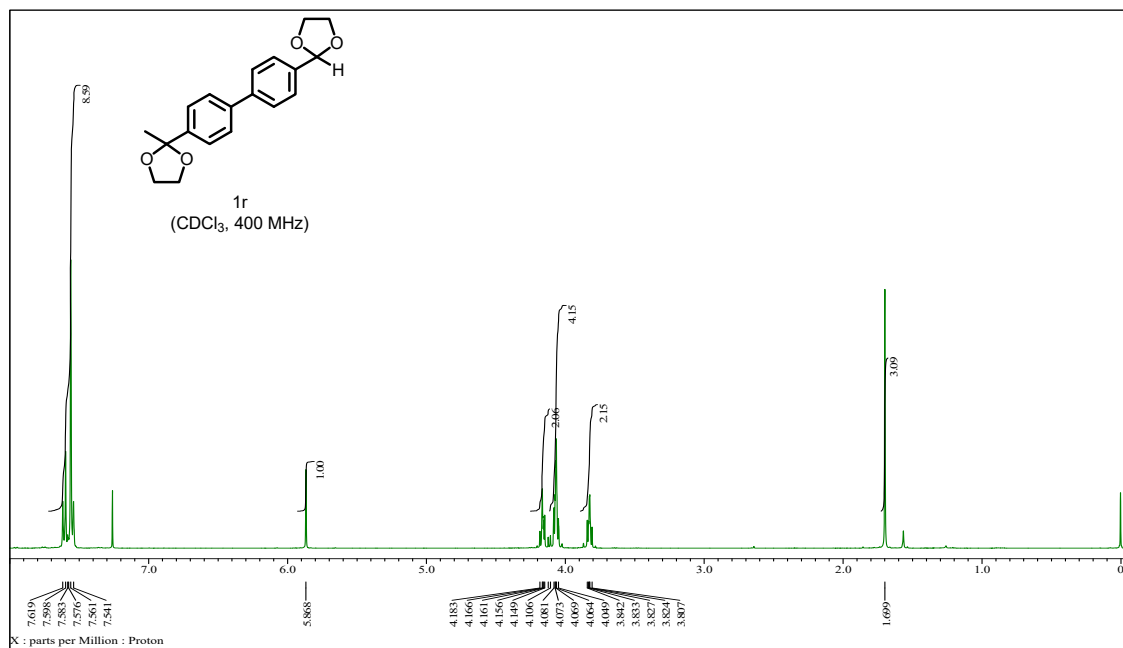
$^1\text{H}$  NMR of 4-octyl-2-phenyl-1,3-dioxolane (1:1 mixture of diastereoisomers) (**1q**)



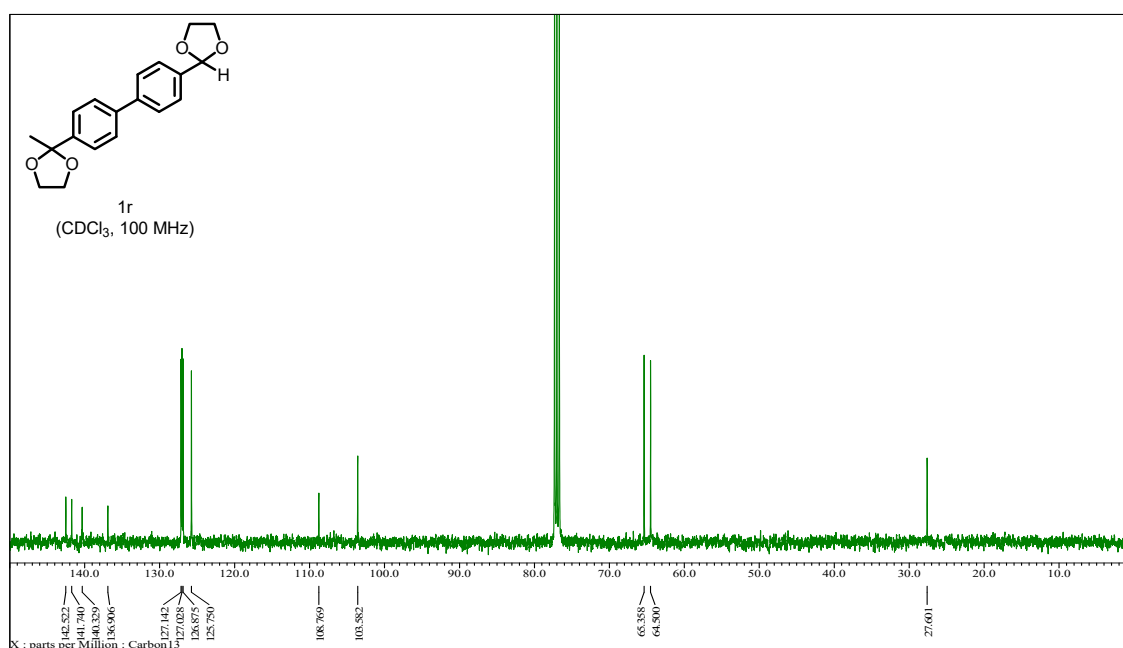
$^{13}\text{C}$  NMR of 4-octyl-2-phenyl-1,3-dioxolane (1:1 mixture of diastereoisomers) (**1q**)



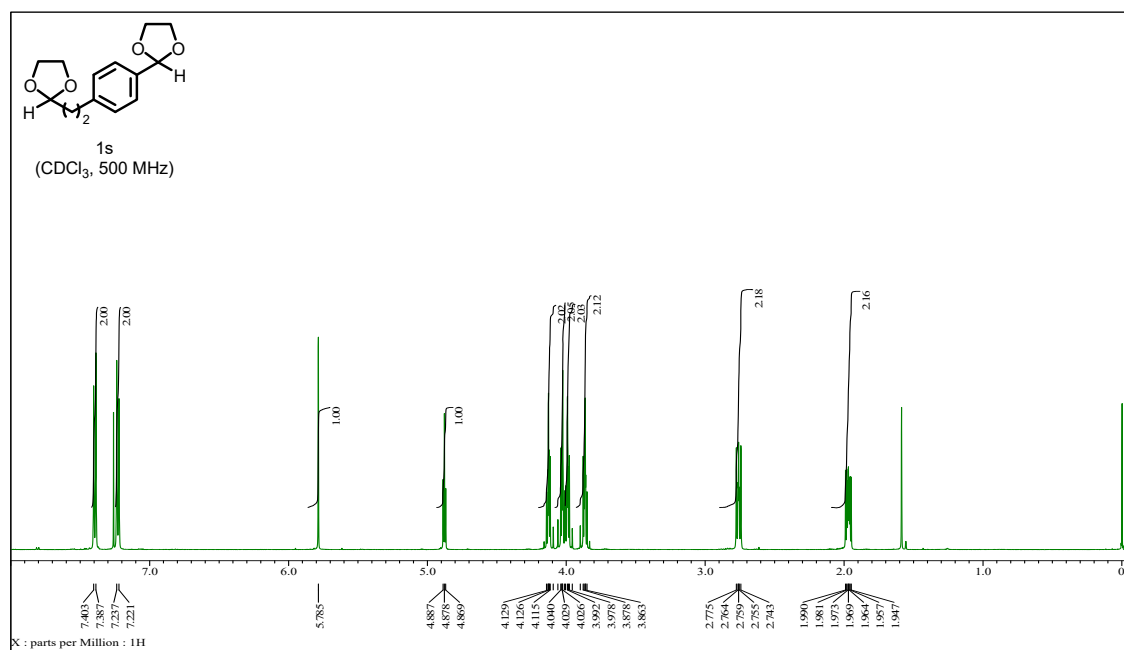
$^1\text{H}$  NMR of **1r**



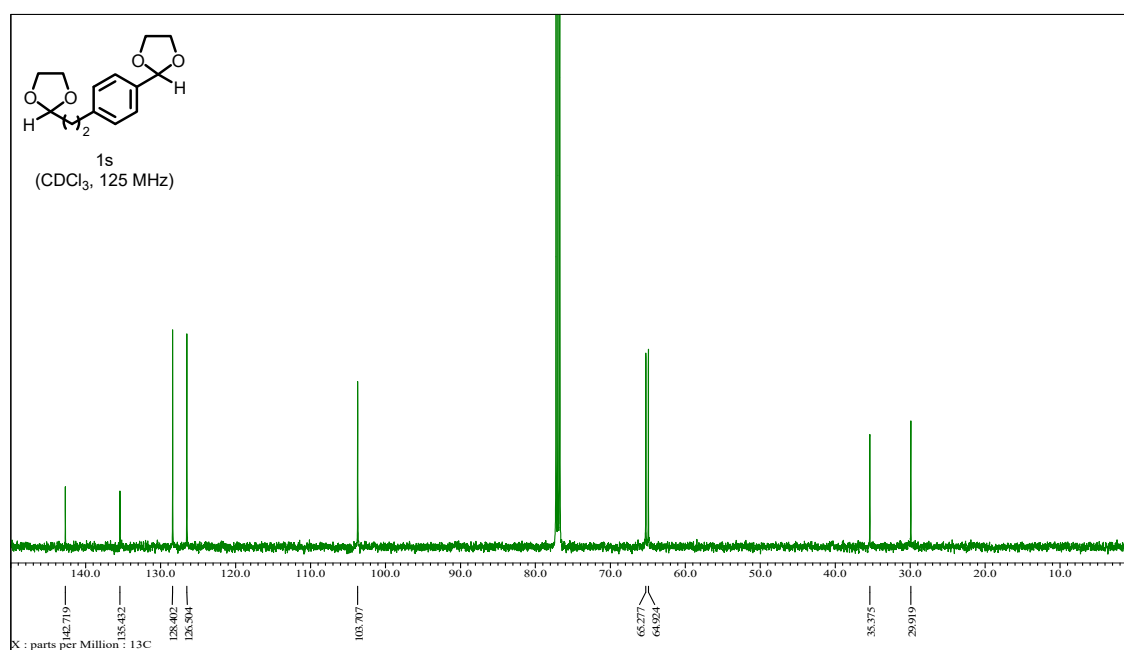
$^{13}\text{C}$  NMR of **1r**



$^1\text{H}$  NMR of 2-[4-(1,3-dioxolan-2-yl)phenethyl]-1,3-dioxolane (**1s**)

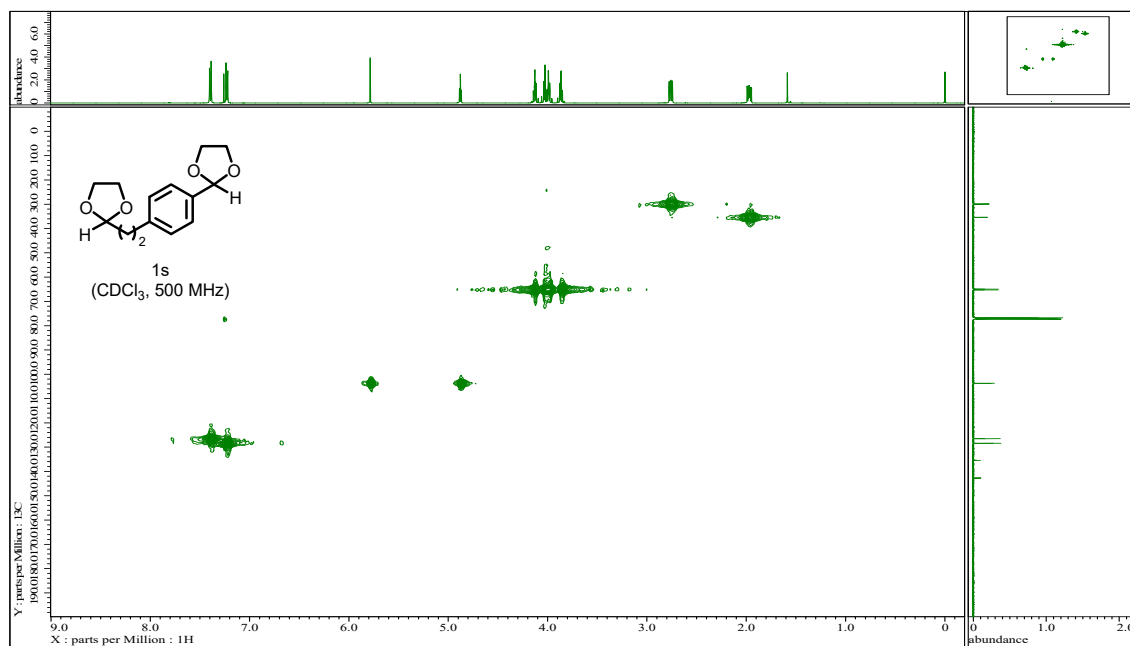


$^{13}\text{C}$  NMR of 2-[4-(1,3-dioxolan-2-yl)phenethyl]-1,3-dioxolane (**1s**)

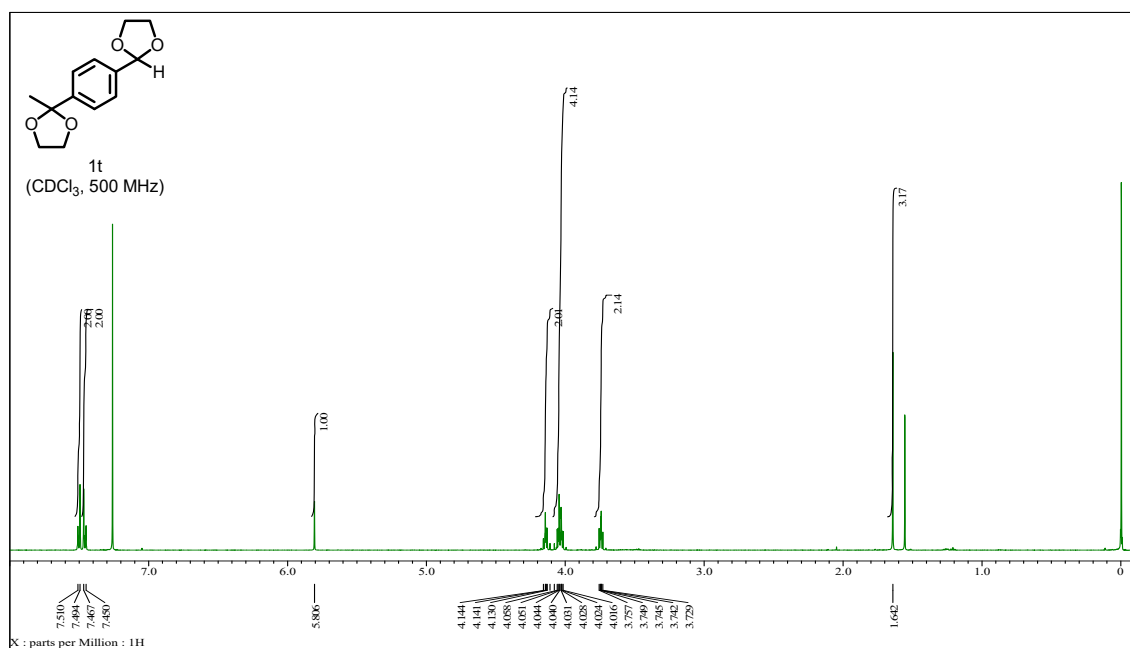




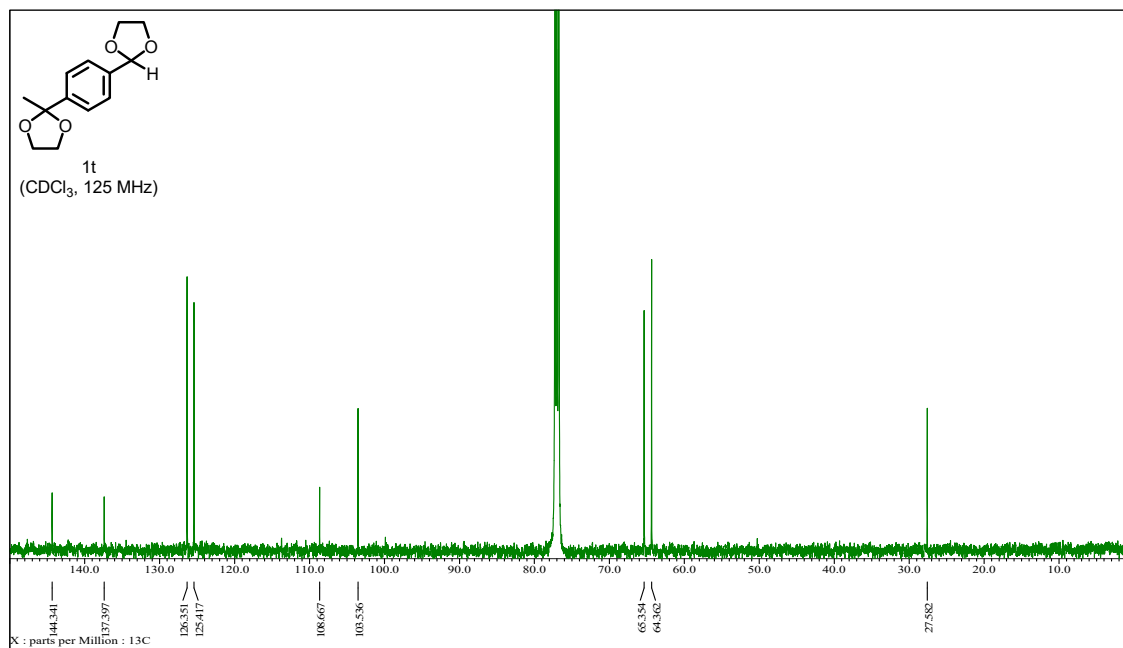
HMBC NMR of 2-[4-(1,3-dioxolan-2-yl)phenethyl]-1,3-dioxolane (**1s**)



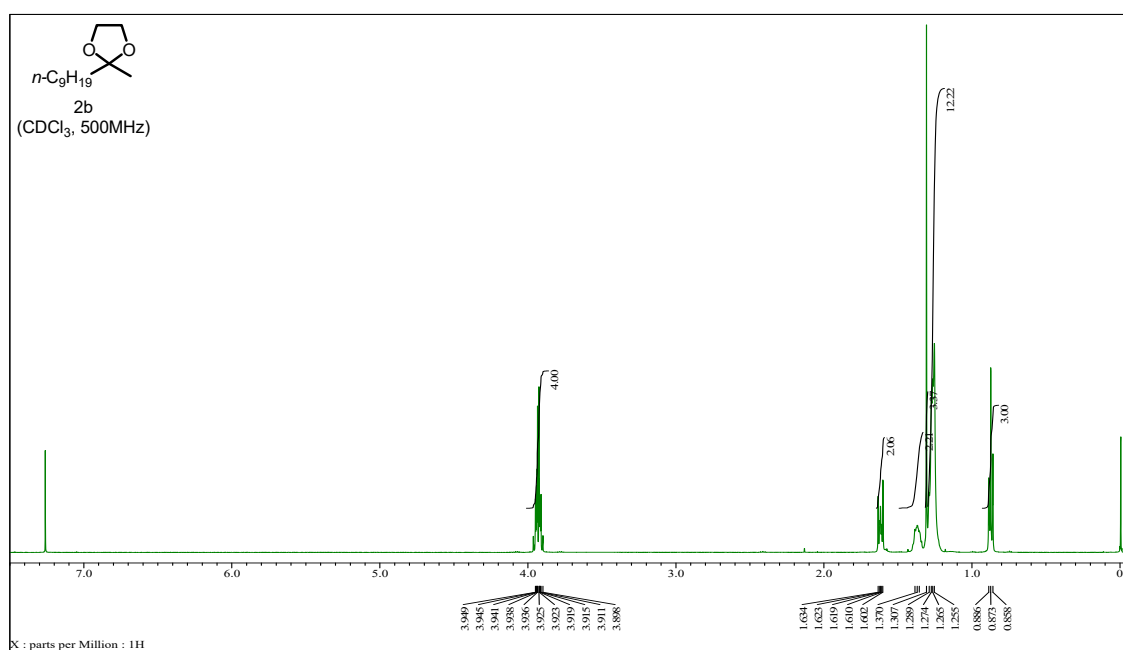
<sup>1</sup>H NMR of 2-[4-(1,3-dioxolan-2-yl)phenyl]-2-methyl-1,3-dioxolane (**1t**)



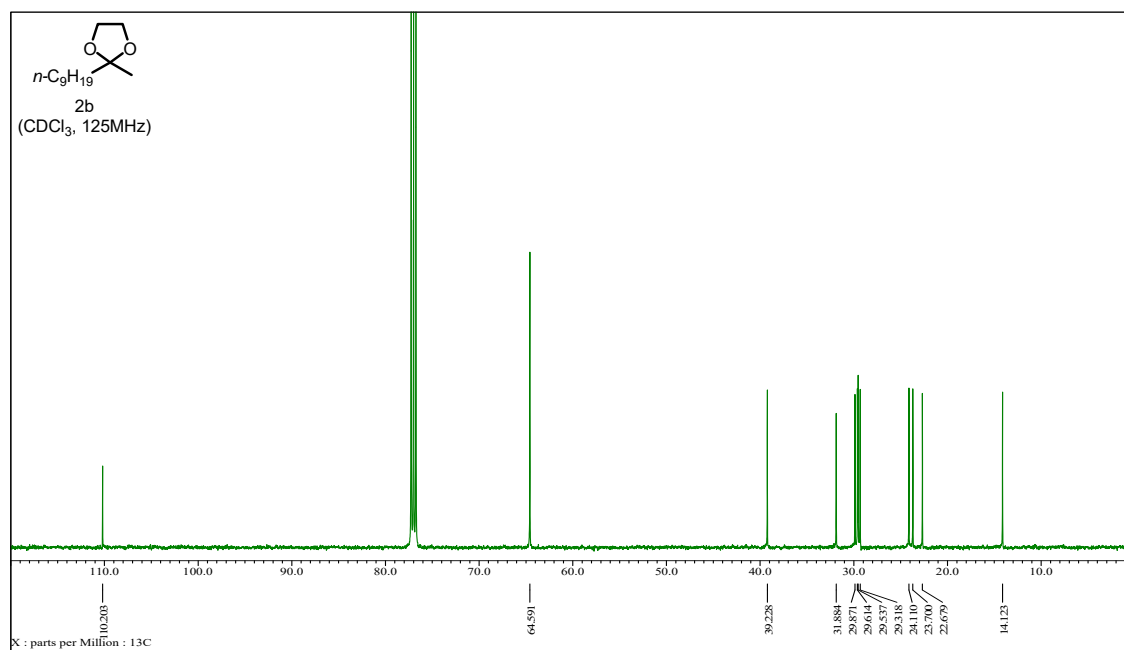
$^{13}\text{C}$  NMR of 2-[4-(1,3-dioxolan-2-yl)phenyl]-2-methyl-1,3-dioxolane (**1t**)



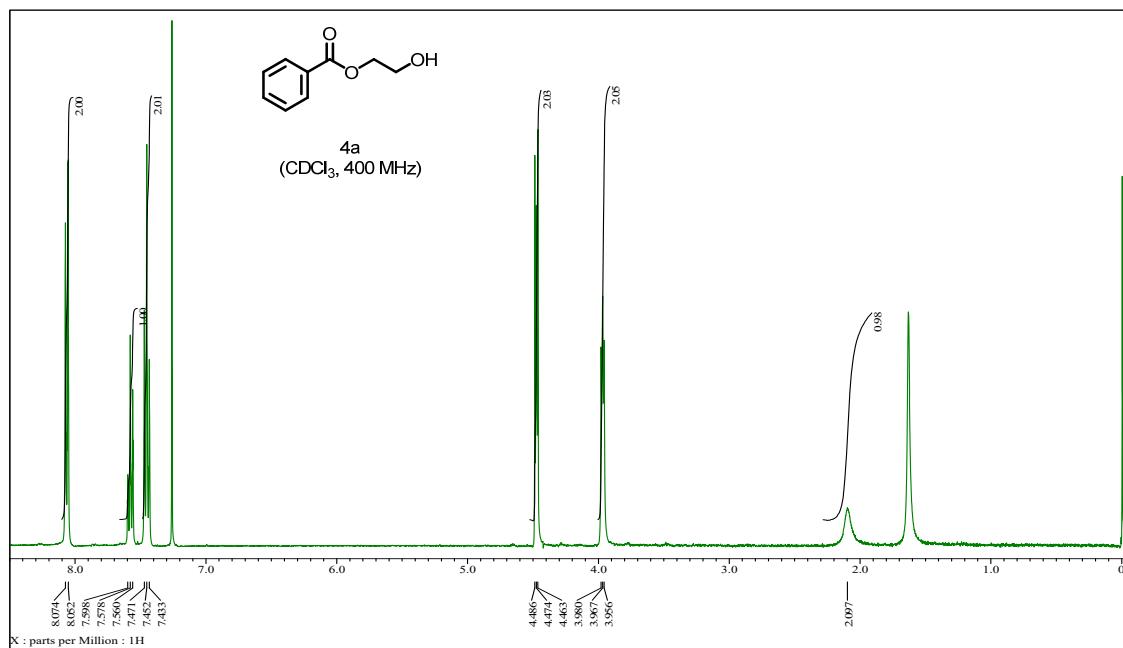
$^1\text{H}$  NMR of 2-methyl-2-nonyl-1,3-dioxolane (**2b**)



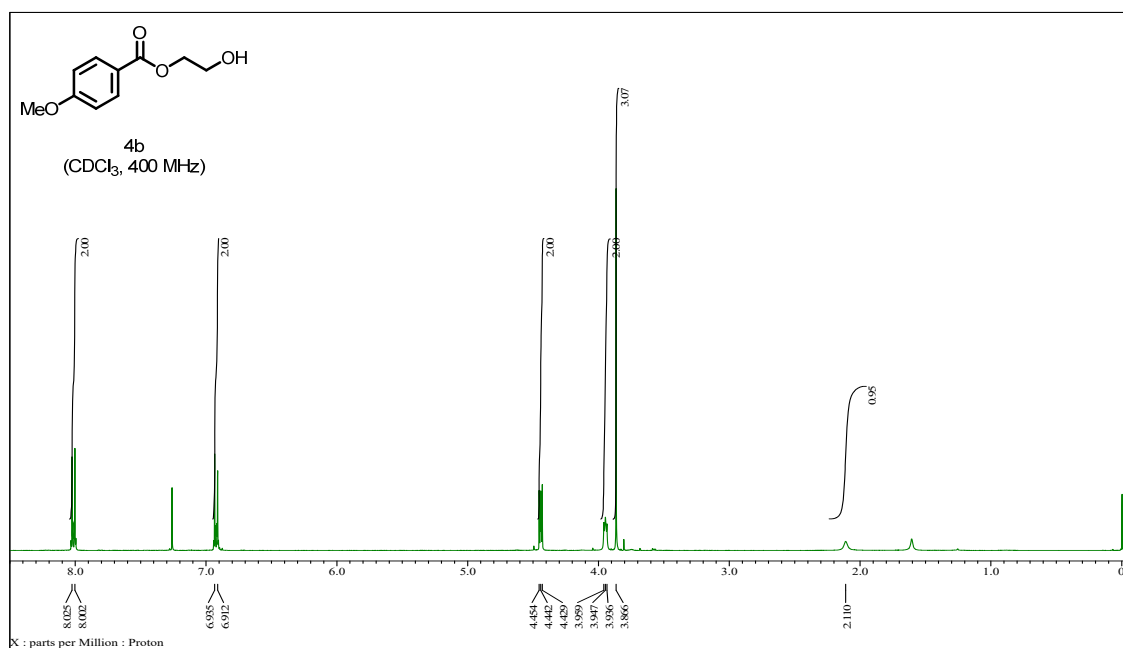
$^{13}\text{C}$  NMR of 2-methyl-2-nonyl-1,3-dioxolane (**2b**)



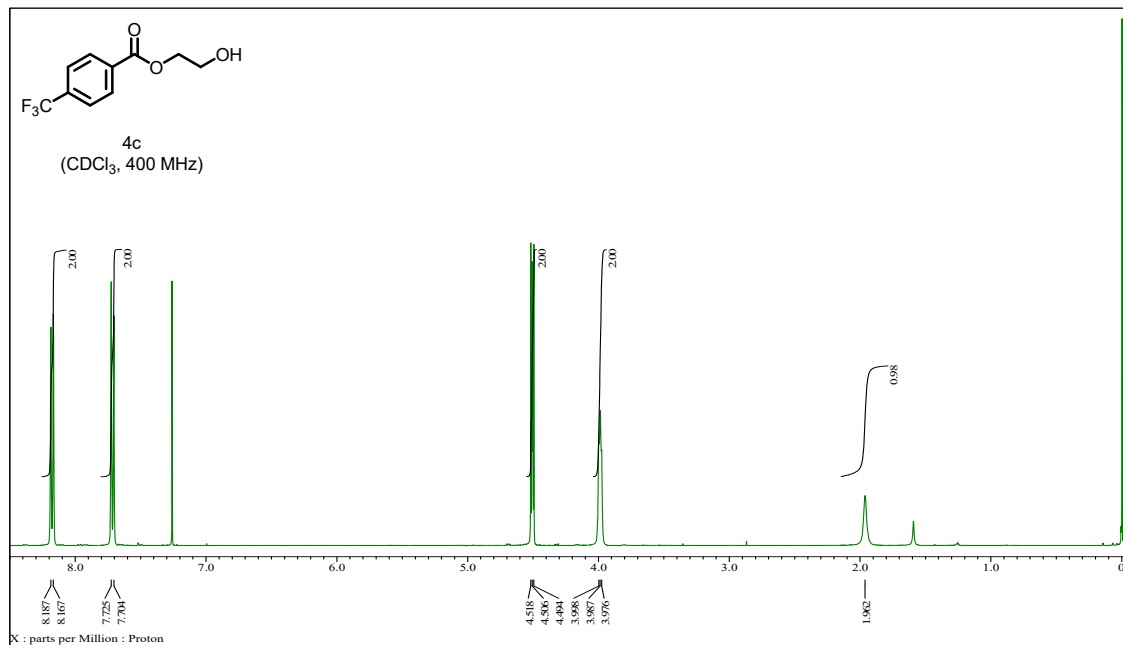
<sup>1</sup>H NMR of 2-hydroxyethyl benzoate (**4a**)



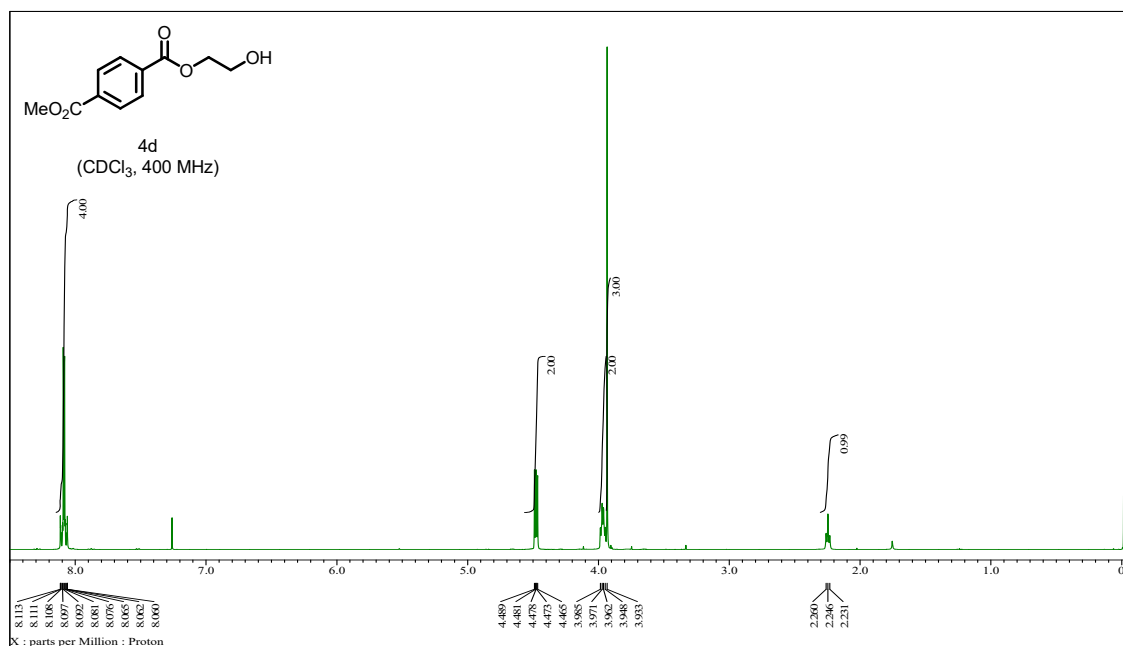
<sup>1</sup>H NMR of 2-hydroxyethyl 4-methoxybenzoate (**4b**)



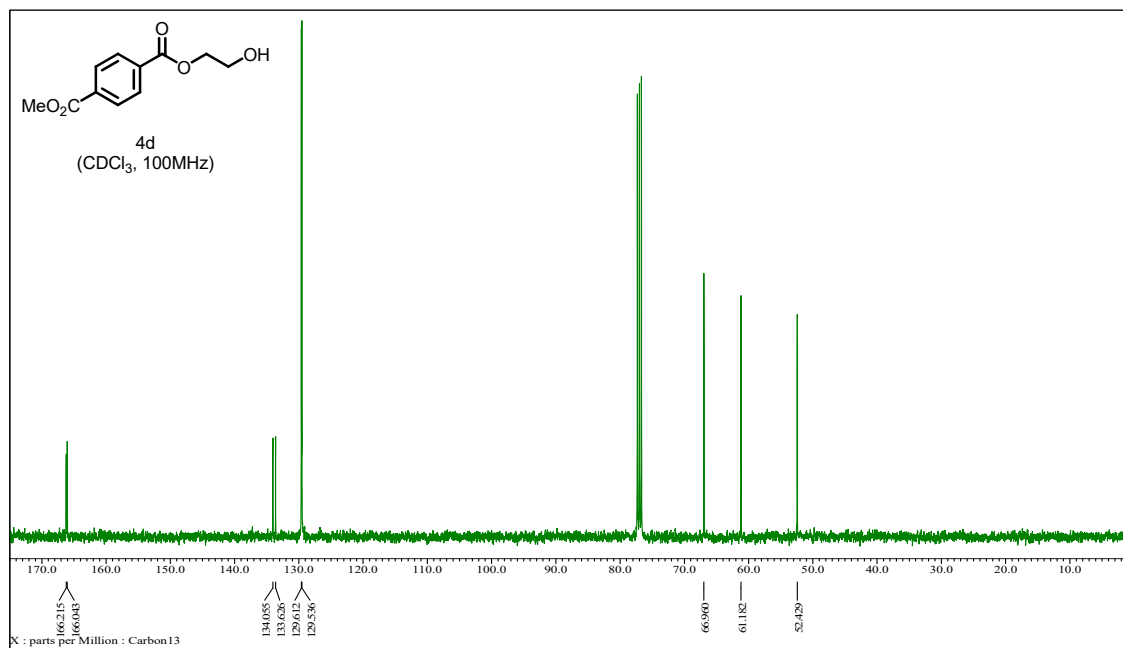
<sup>1</sup>H NMR of 2-hydroxyethyl 4-(trifluoromethyl)benzoate (**4c**)



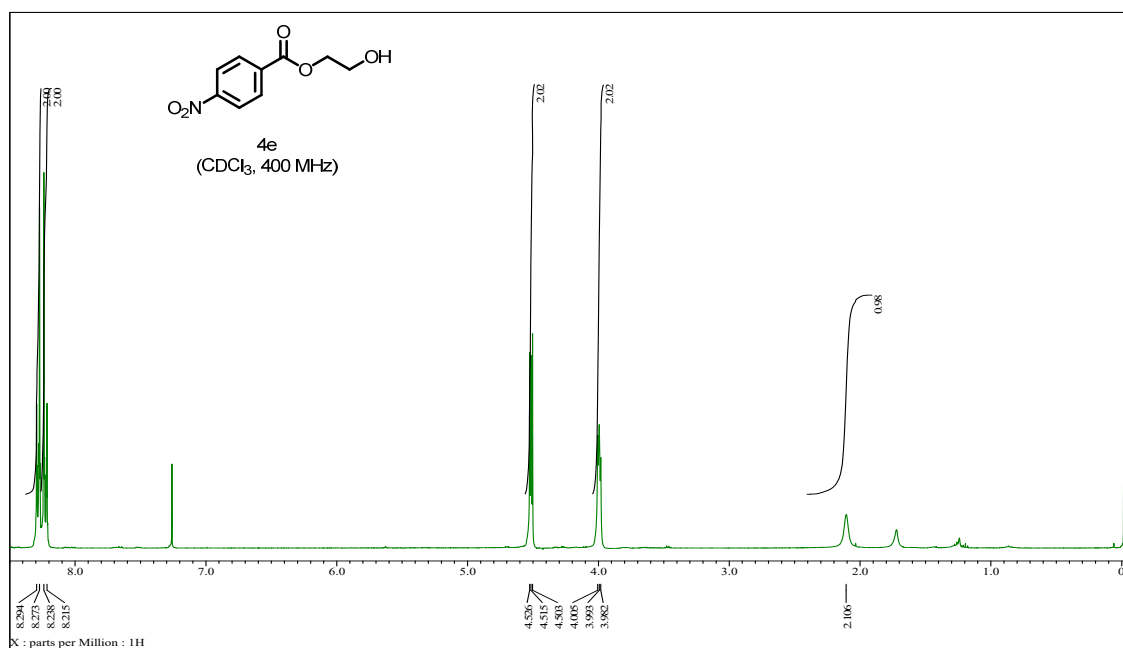
<sup>1</sup>H NMR of terephthalic acid-(2-hydroxyethyl ester)-methyl ester (**4d**)



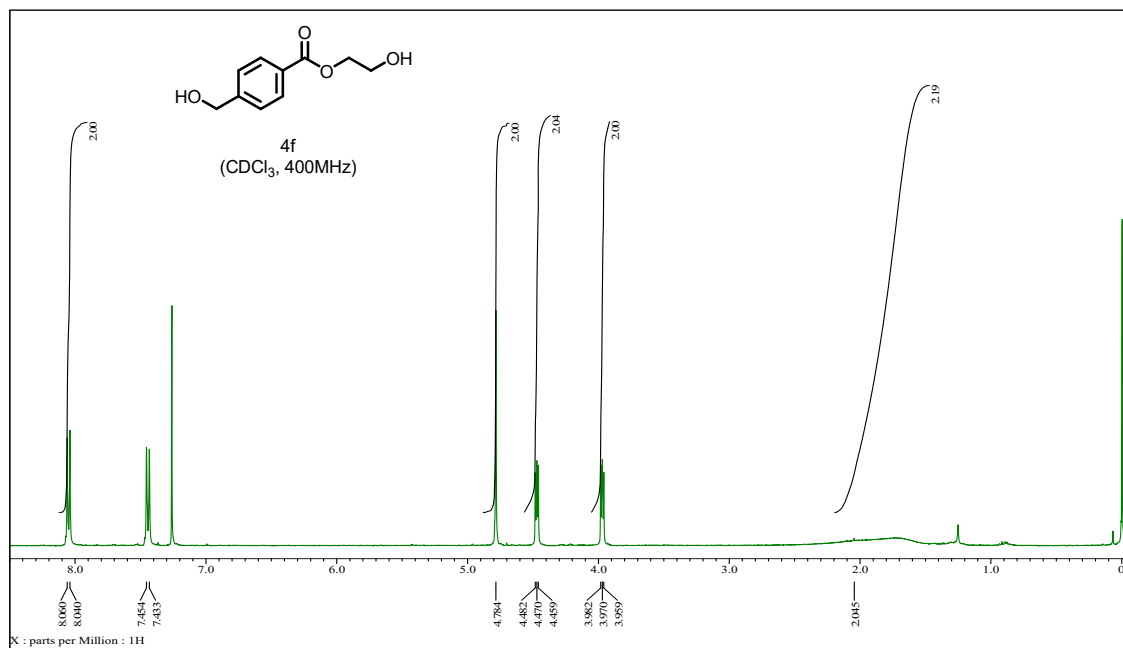
$^{13}\text{C}$  NMR of terephthalic acid-(2-hydroxy-ethyl ester)-methyl ester (**4d**)



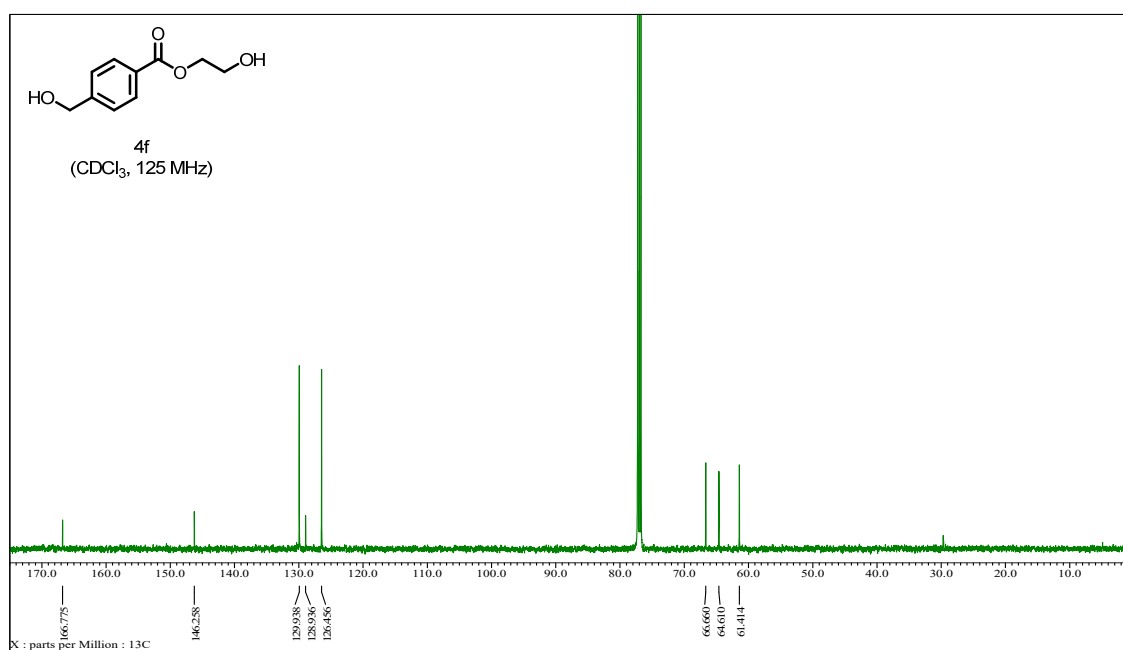
$^1\text{H}$  NMR of 2-hydroxyethyl 4-nitrobenzoate (**4e**)



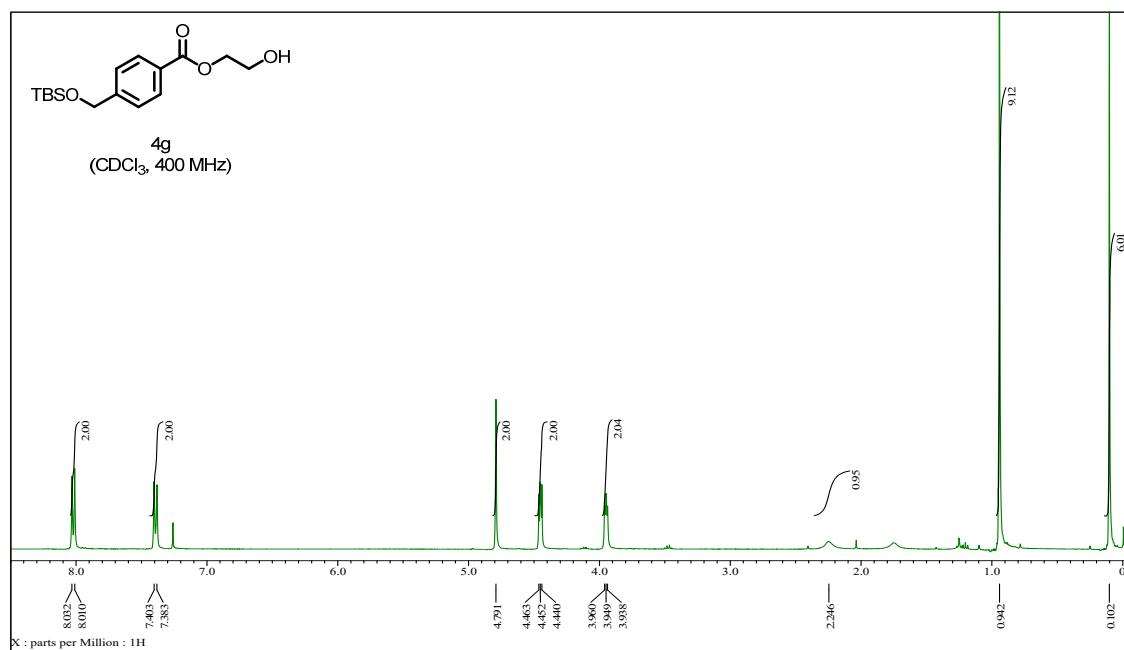
<sup>1</sup>H NMR of benzoic acid 4-(hydroxymethyl)-2-hydroxyethyl ester (**4f**)



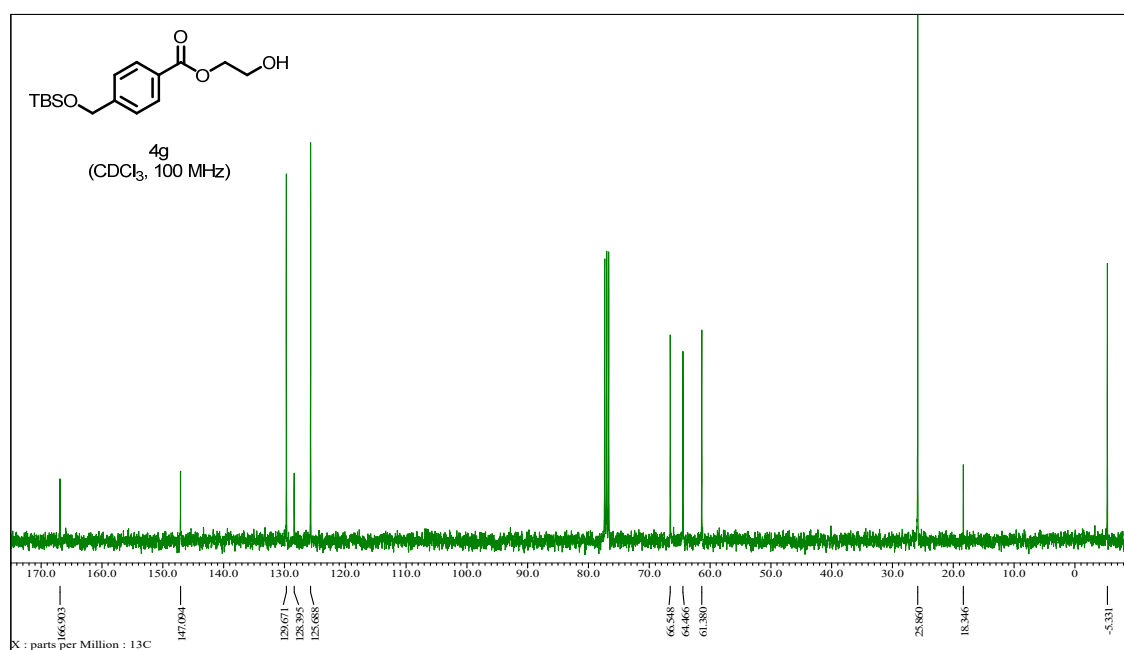
<sup>13</sup>C NMR of benzoic acid 4-(hydroxymethyl)-2-hydroxyethyl ester (**4f**)



<sup>1</sup>H NMR of 2-hydroxyethyl 4-(*tert*-butyldimethylsilyloxymethyl)benzoate (**4g**)

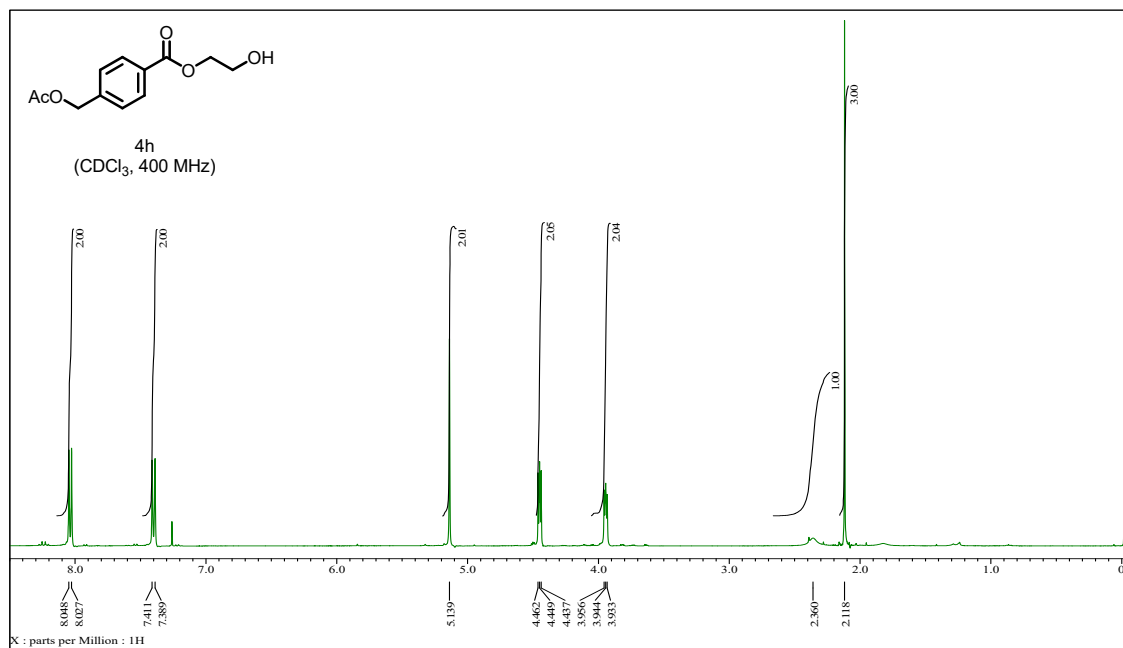


<sup>13</sup>C NMR of 2-hydroxyethyl 4-(*tert*-butyldimethylsilyloxymethyl)benzoate (**4g**)

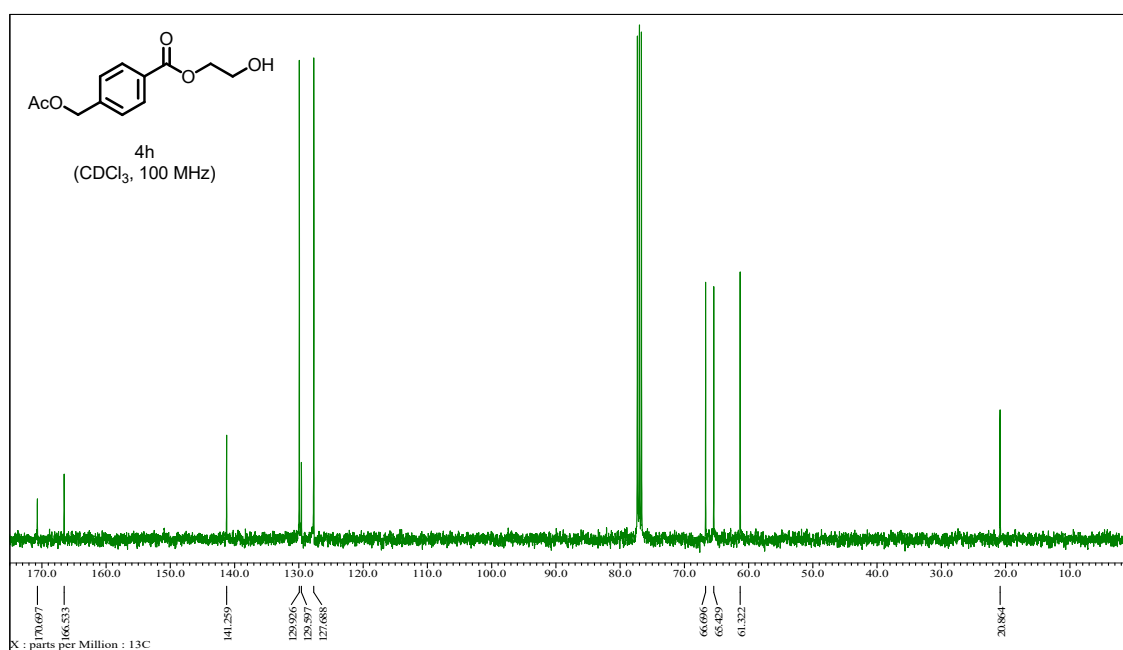




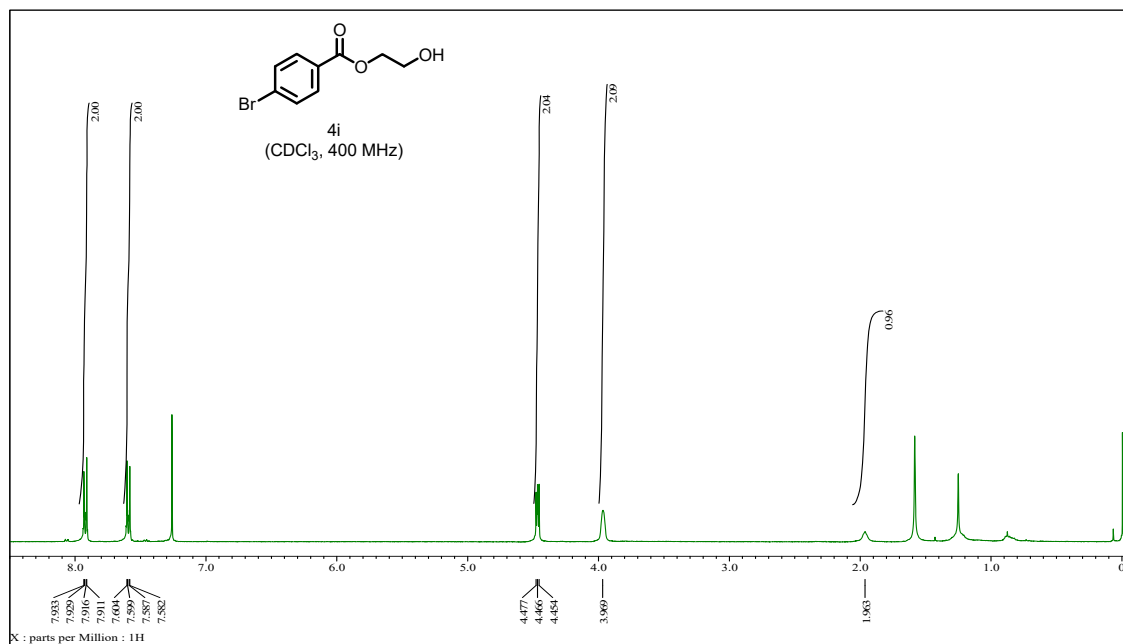
<sup>1</sup>H NMR of 2-hydroxyethyl 4-(acetoxymethyl)benzoate (**4h**)



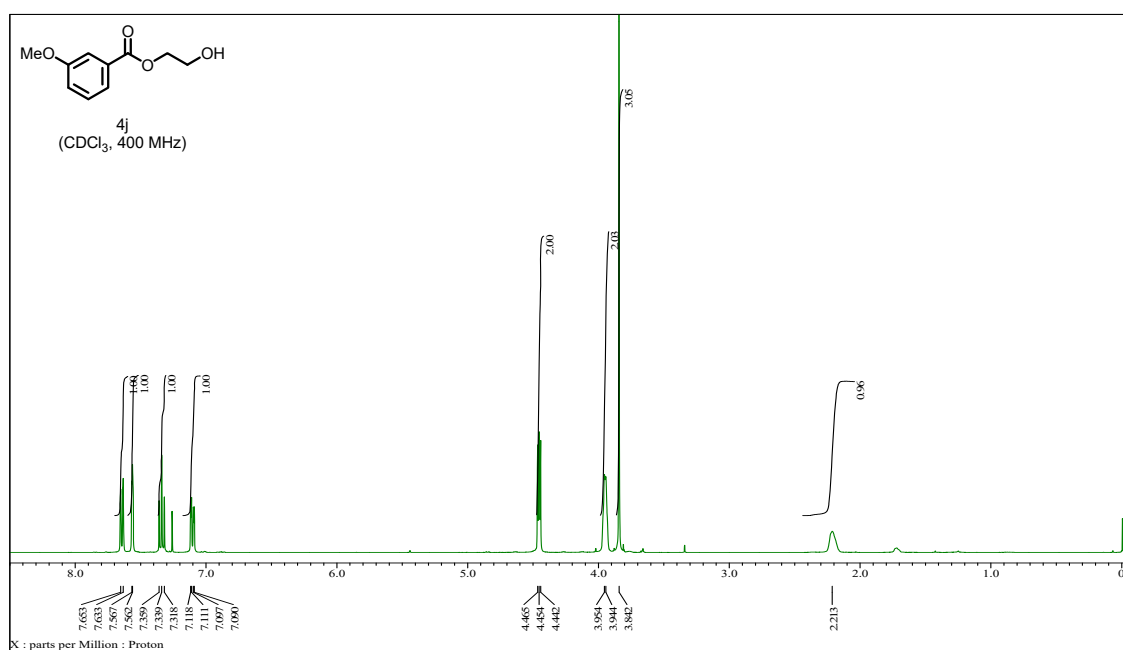
<sup>13</sup>C NMR of 2-hydroxyethyl 4-(acetoxymethyl)benzoate (**4h**)



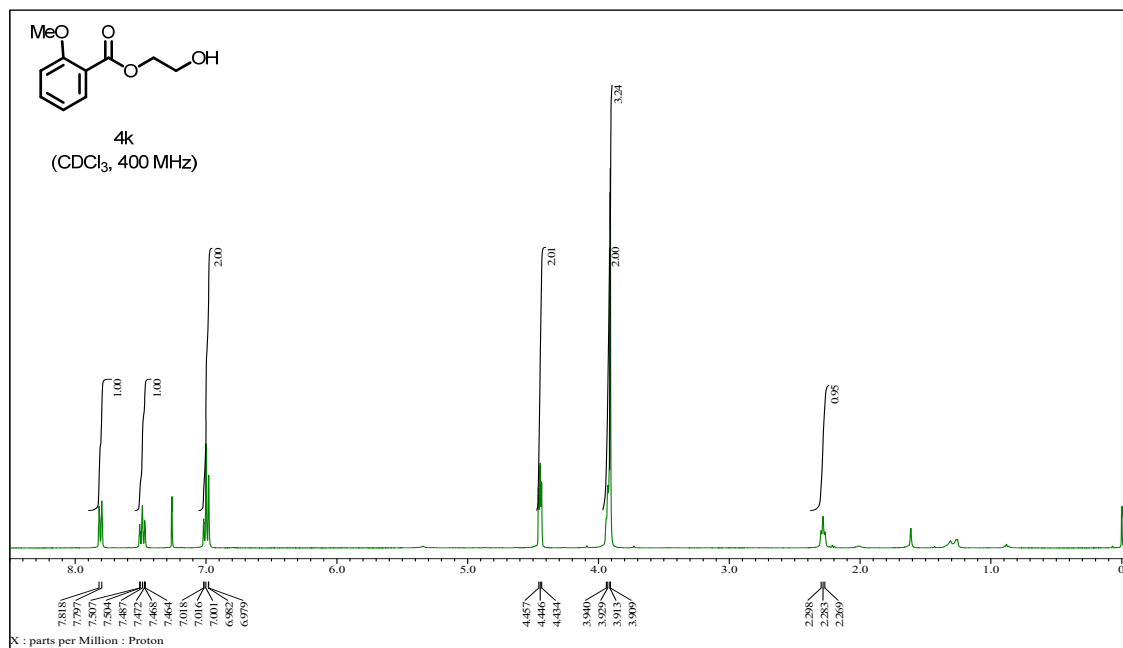
<sup>1</sup>H NMR of 2-hydroxyethyl 4-bromobenzoate (**4i**)



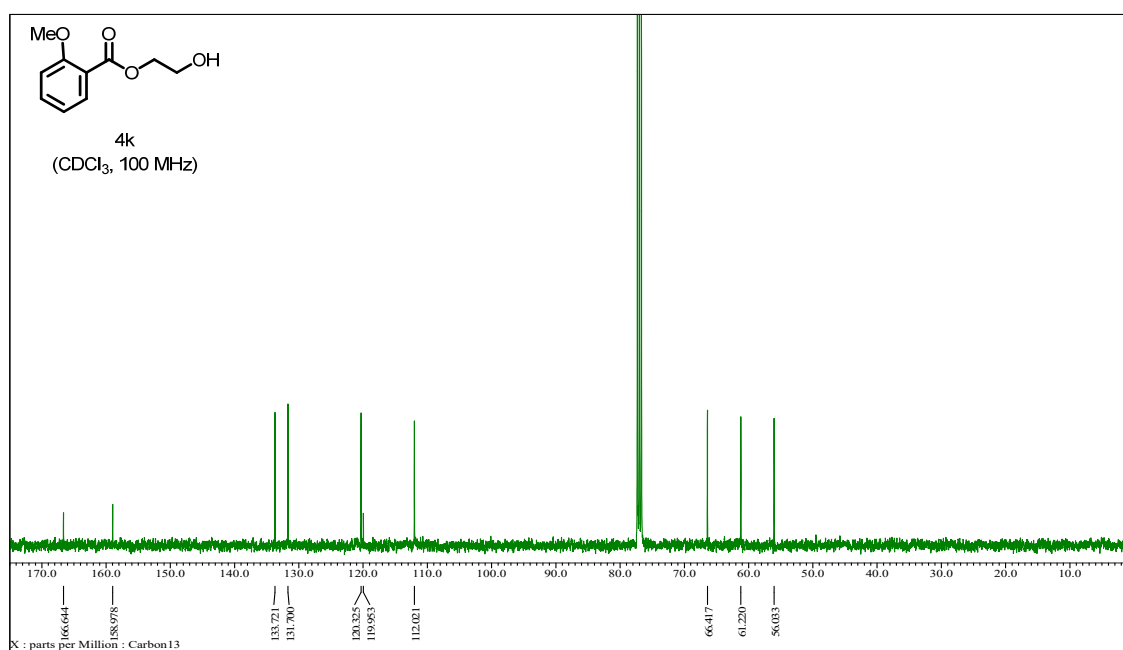
<sup>1</sup>H NMR of 2-hydroxyethyl 3-methoxybenzoate (**4j**)



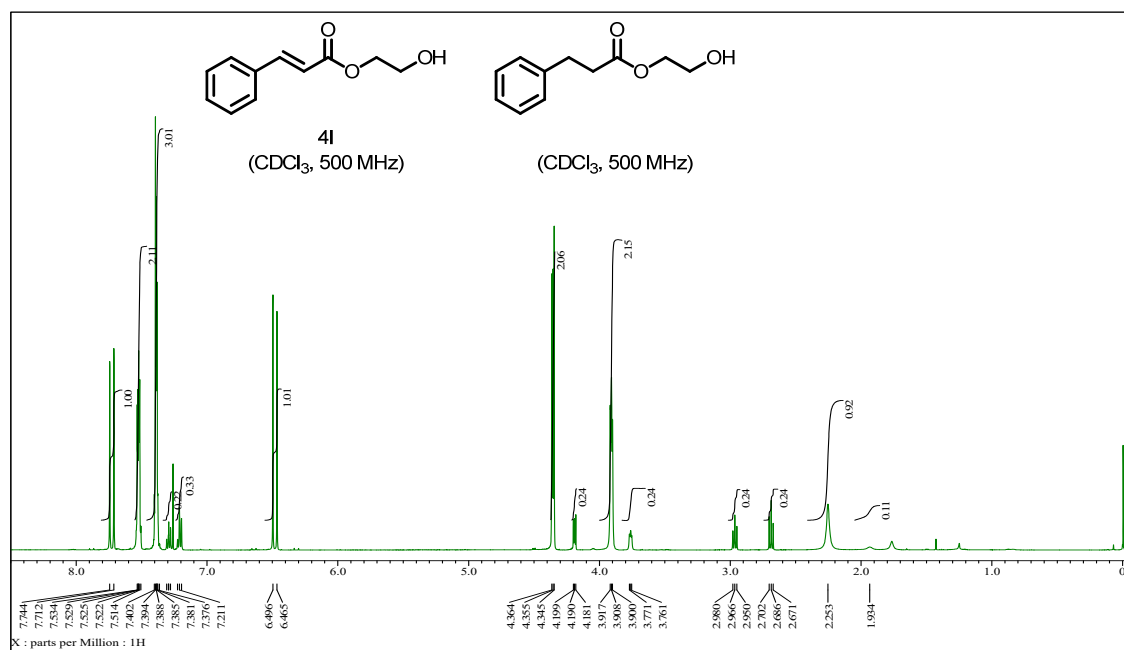
$^1\text{H}$  NMR of 2-hydroxyethyl 2-methoxybenzoate (**4k**)



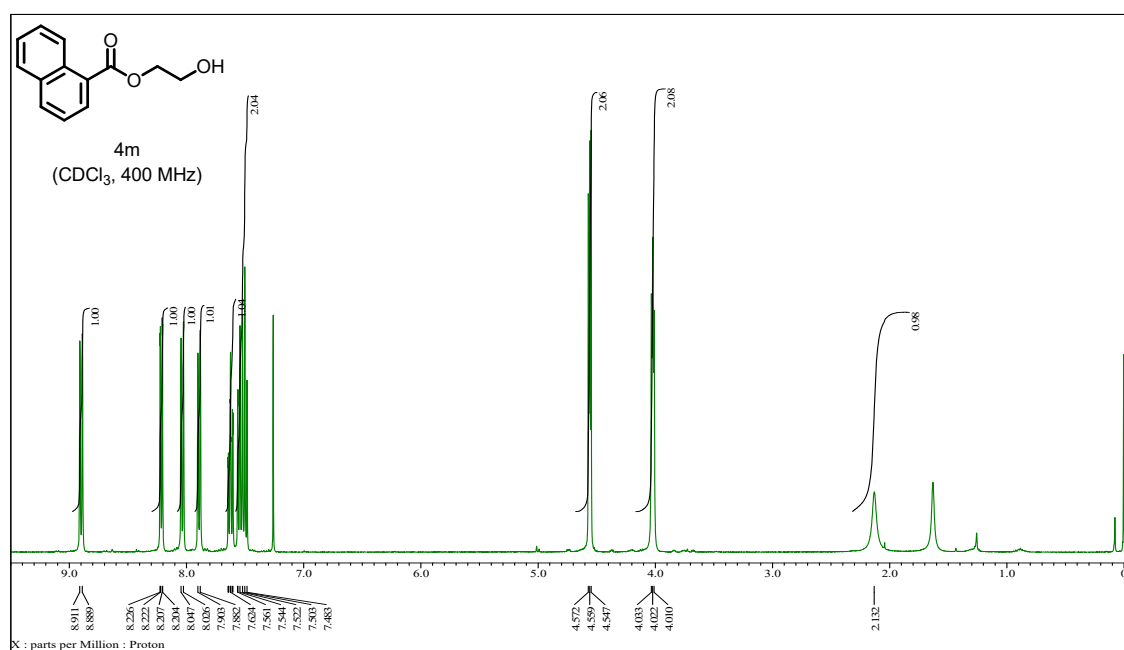
$^{13}\text{C}$  NMR of 2-hydroxyethyl 2-methoxybenzoate (**4k**)



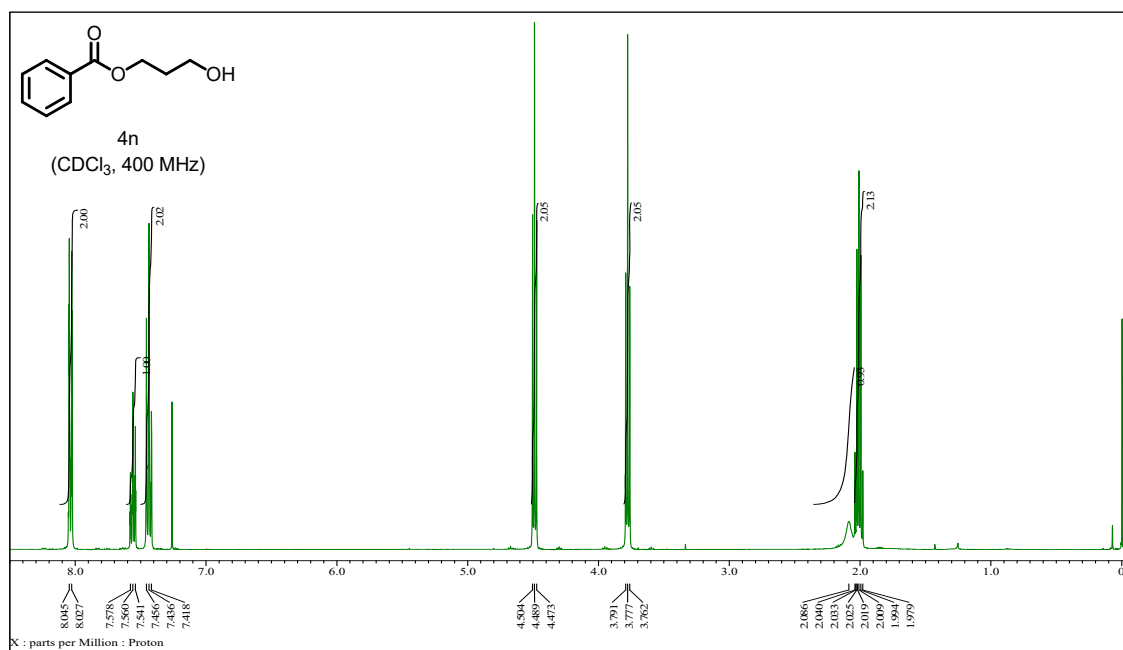
$^1\text{H}$  NMR of 2-hydroxyethyl cinnamate (**4l**) and 2-hydroxyethyl 3-phenylpropanoate



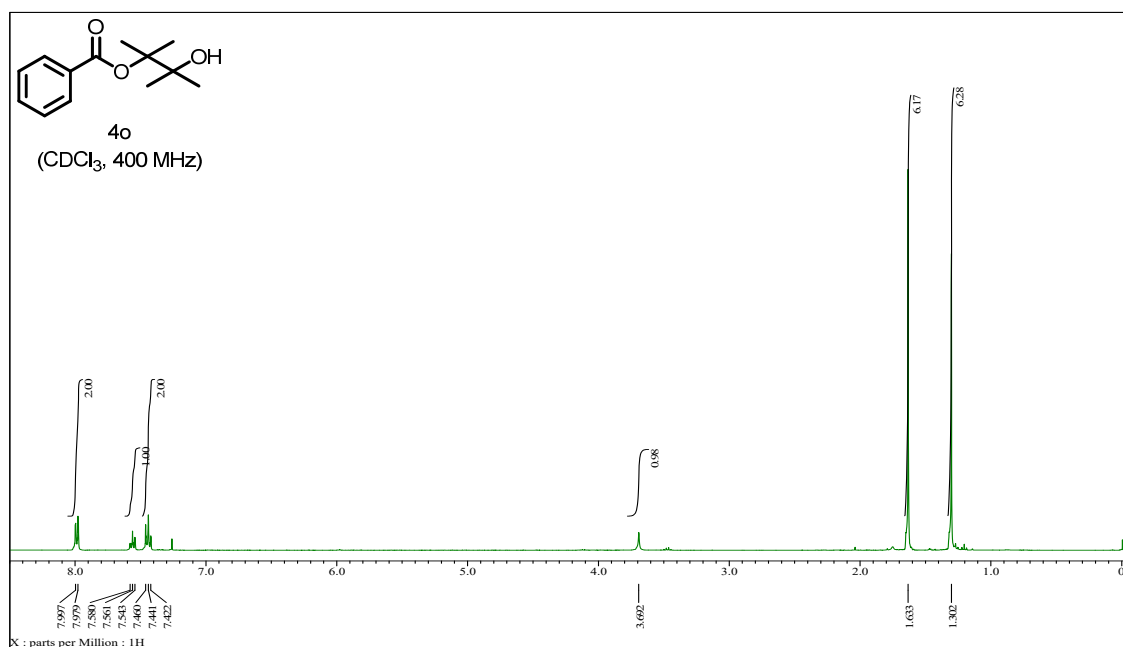
$^1\text{H}$  NMR of 2-hydroxyethyl 1-naphthoate (**4m**)



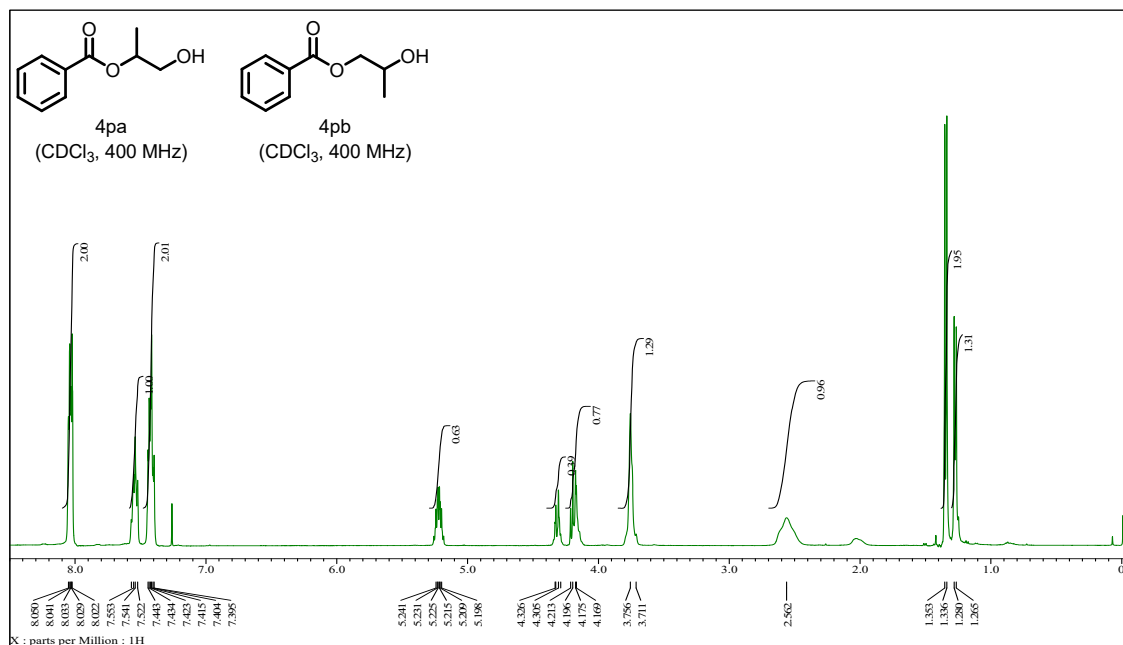
<sup>1</sup>H NMR of 3-hydroxypropan-1-yl benzoate (**4n**)



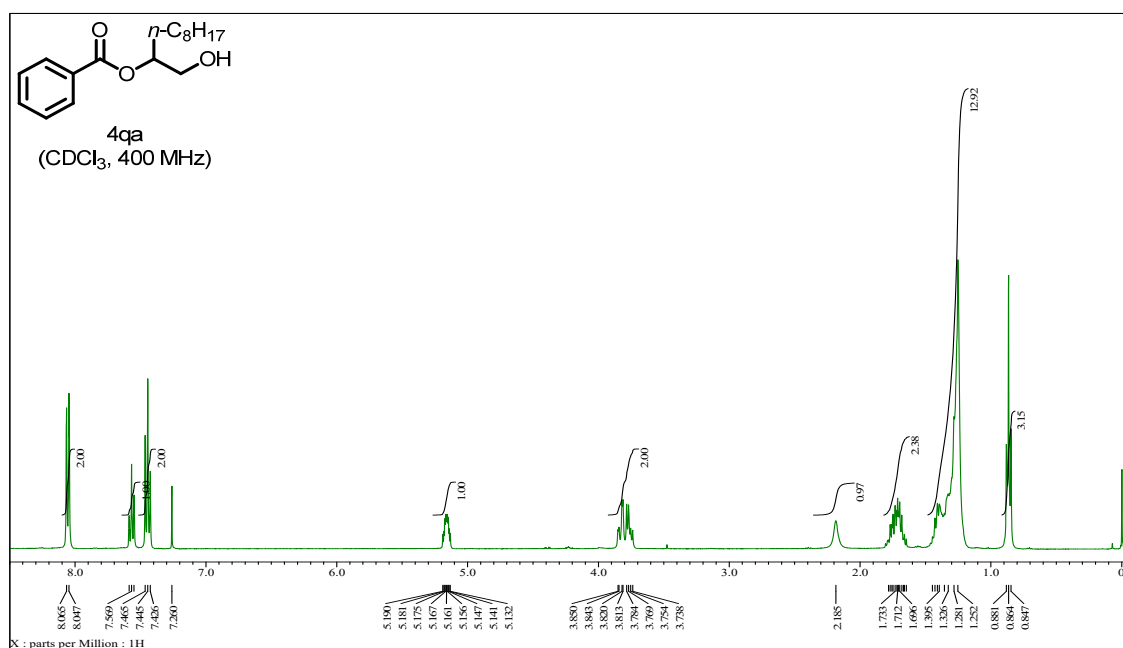
<sup>1</sup>H NMR of 3-hydroxy-2,3-dimethylbutan-2-yl benzoate (**4o**)



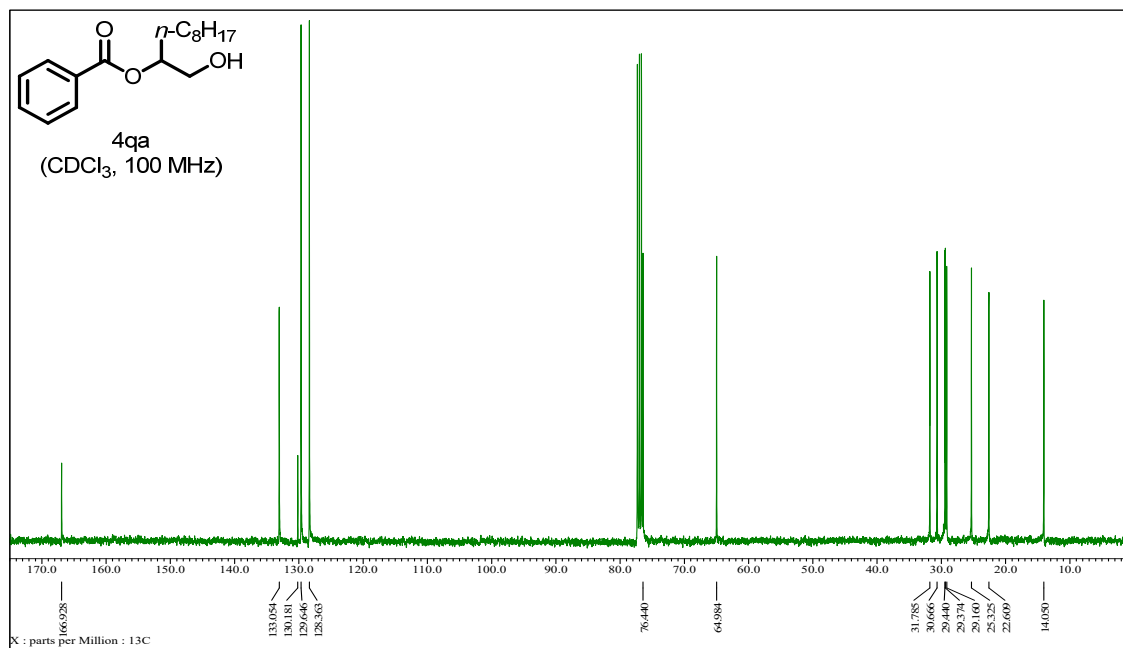
$^1\text{H}$  NMR of 2-hydroxy-1-methylethyl benzoate (**4pa**) and 2-hydroxy-2-methylethyl benzoate (**4pb**)



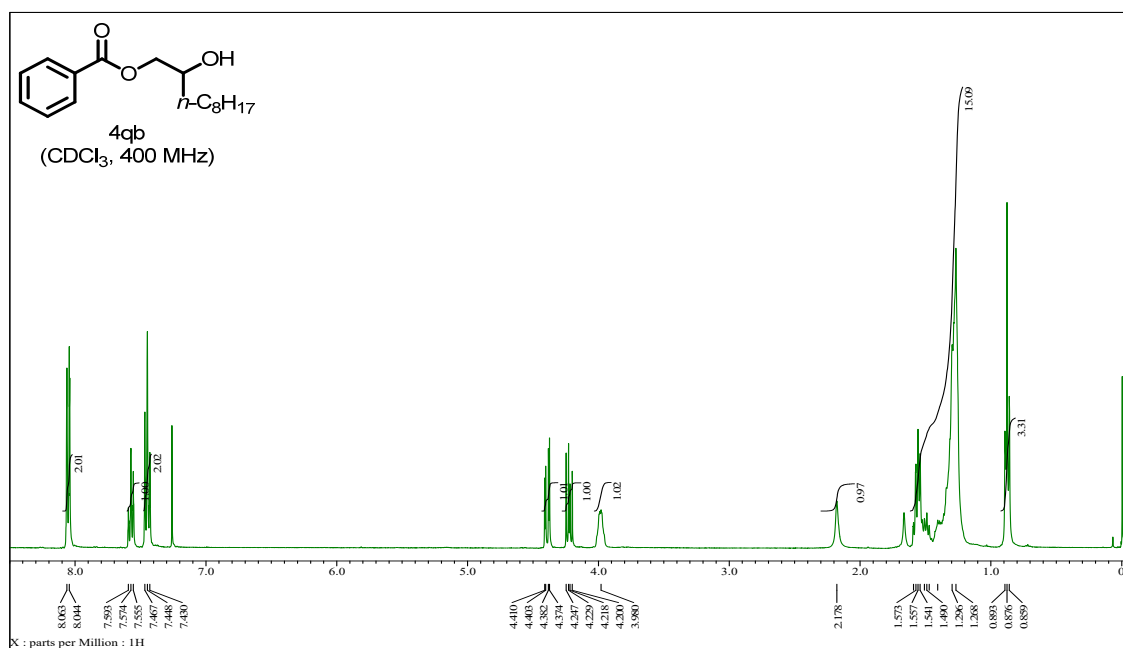
$^1\text{H}$  NMR of 1-hydroxydecan-2-yl benzoate (**4qa**)



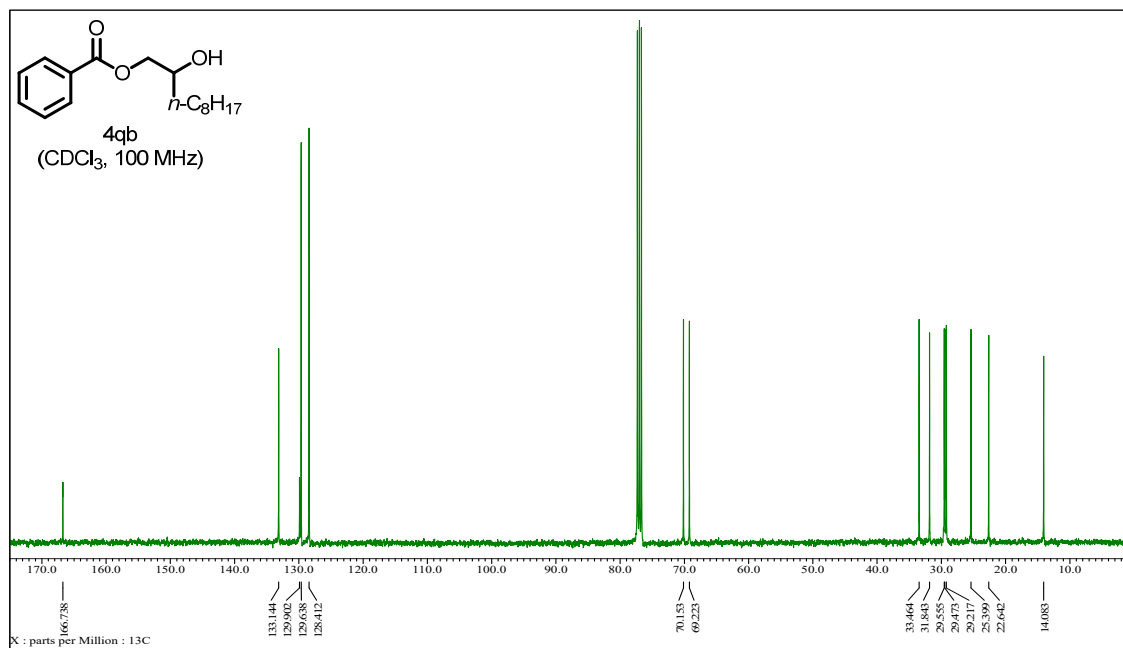
$^{13}\text{C}$  NMR of 1-hydroxydecan-2-yl benzoate (**4qa**)



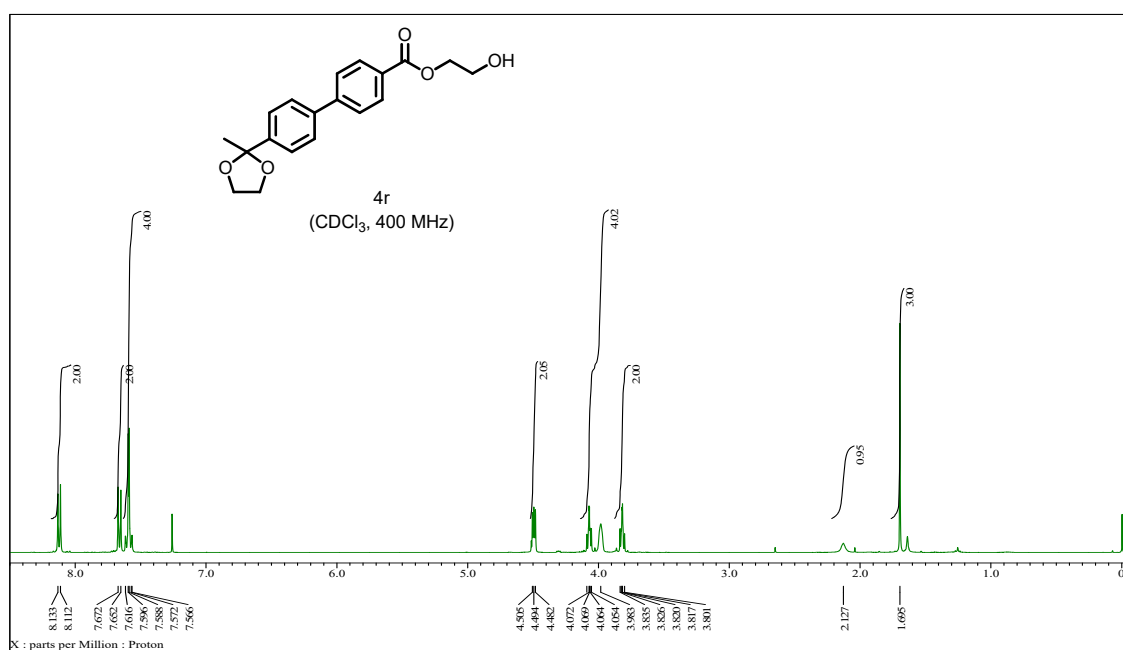
$^1\text{H}$  NMR of 2-hydroxydecyl benzoate (**4qb**)



<sup>13</sup>C NMR of 2-hydroxydecyl benzoate (**4qb**)

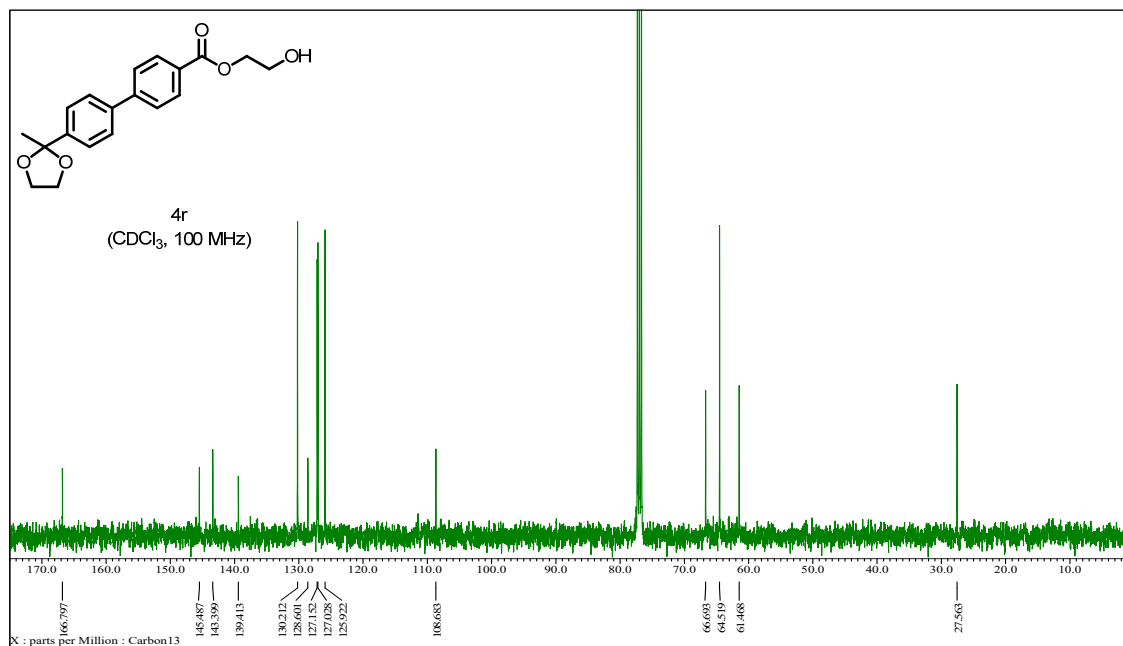


<sup>1</sup>H NMR of **4r**

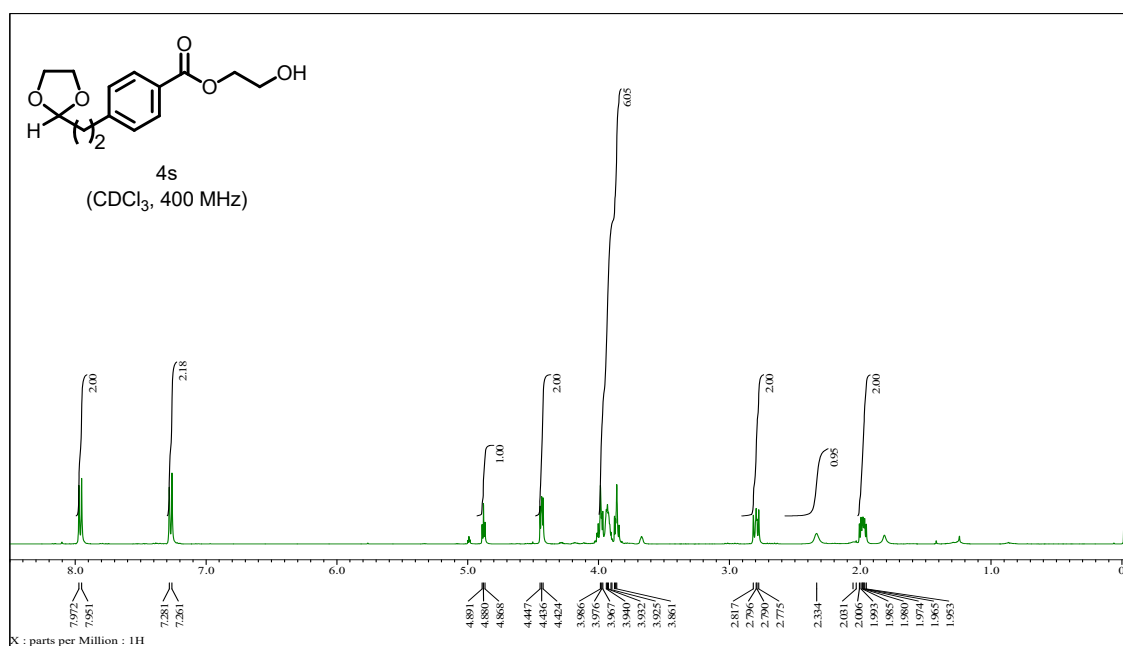




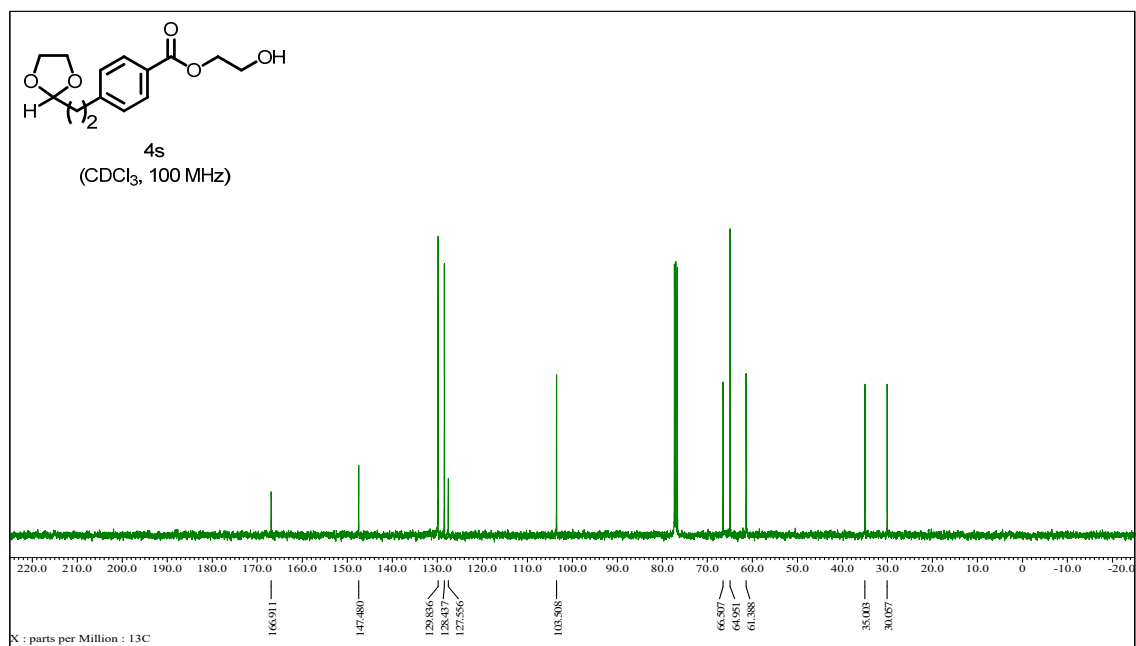
$^{13}\text{C}$  NMR of **4r**



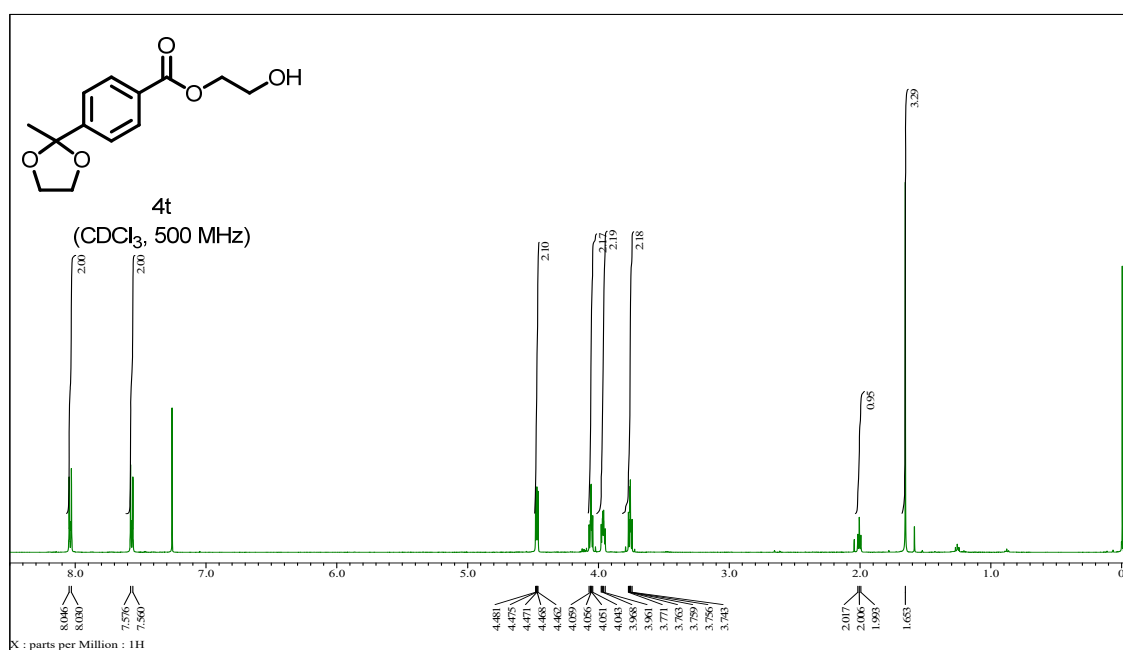
$^1\text{H}$  NMR of 2-hydroxyethyl 4-[2-(1,3-dioxolan-2-yl)ethyl]benzoate (**4s**)



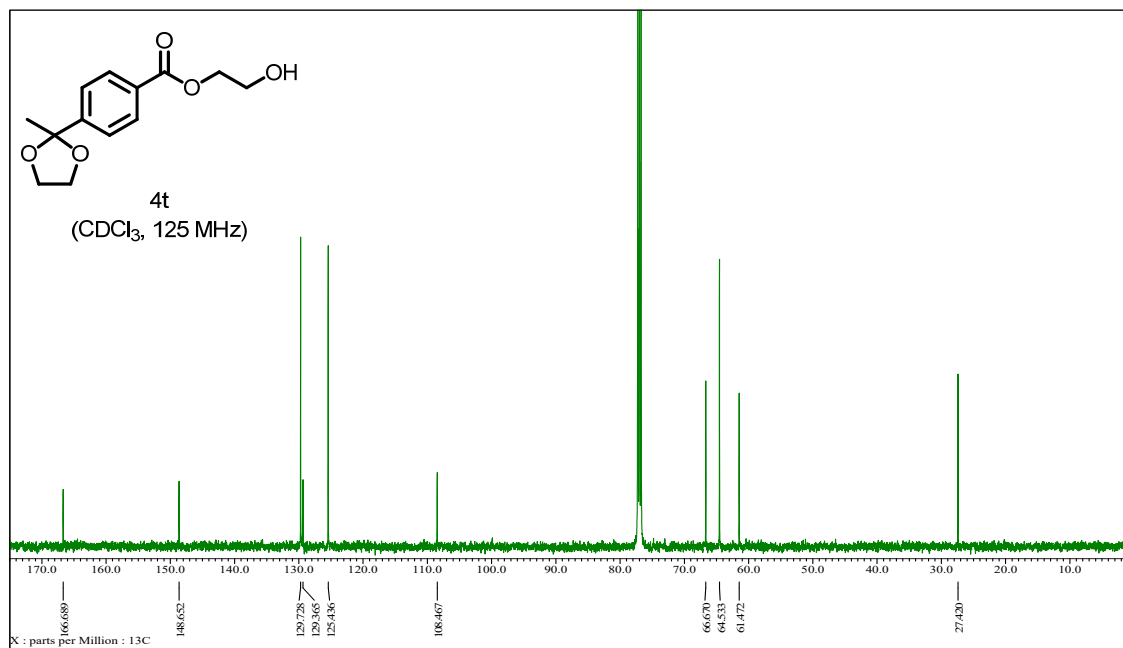
$^{13}\text{C}$  NMR of 2-hydroxyethyl 4-[2-(1,3-dioxolan-2-yl)ethyl]benzoate (**4s**)



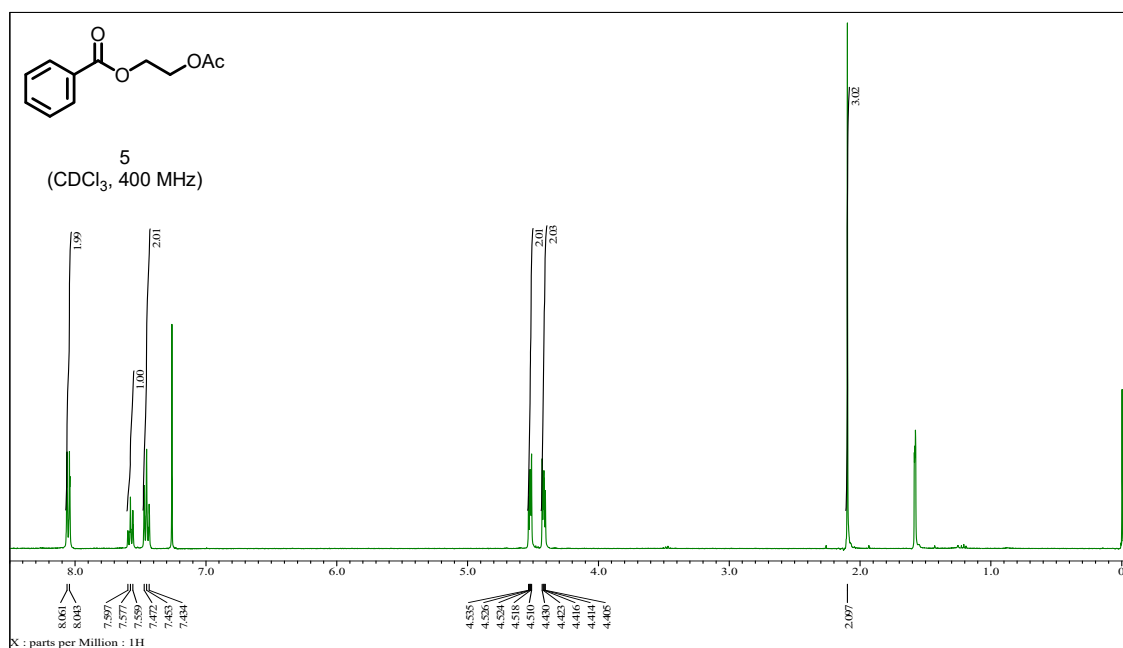
$^1\text{H}$  NMR of 2-hydroxyethyl 4-(2-methyl-1,3-dioxolan-2-yl)benzoate (**4t**)



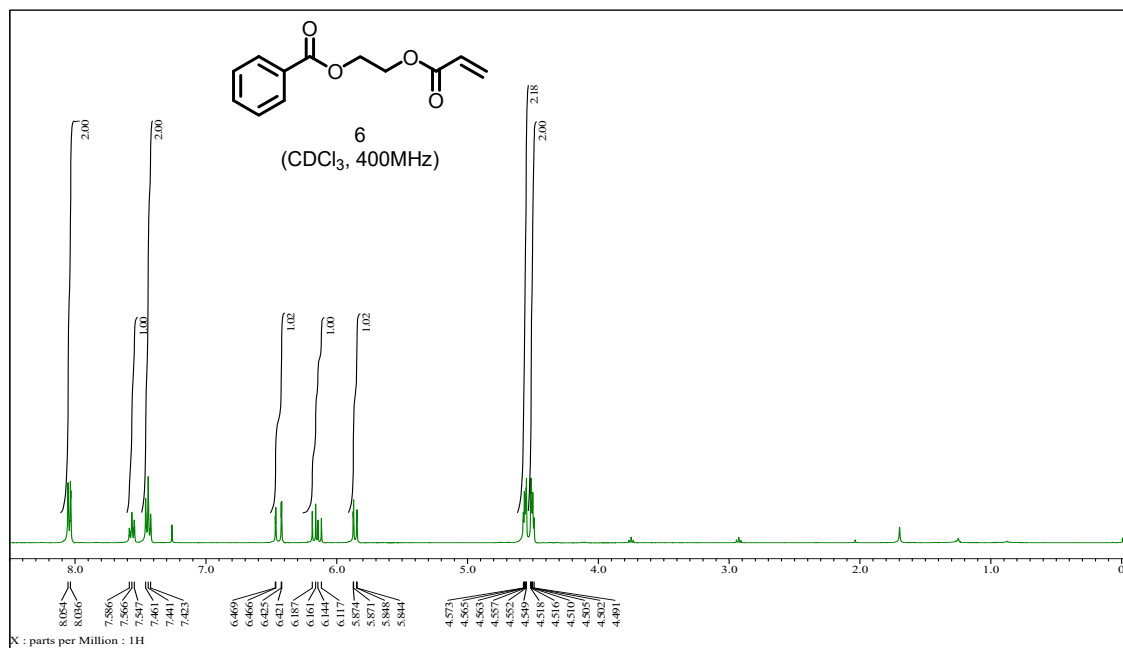
$^{13}\text{C}$  NMR of 2-hydroxyethyl 4-(2-methyl-1,3-dioxolan-2-yl)benzoate (**4t**)



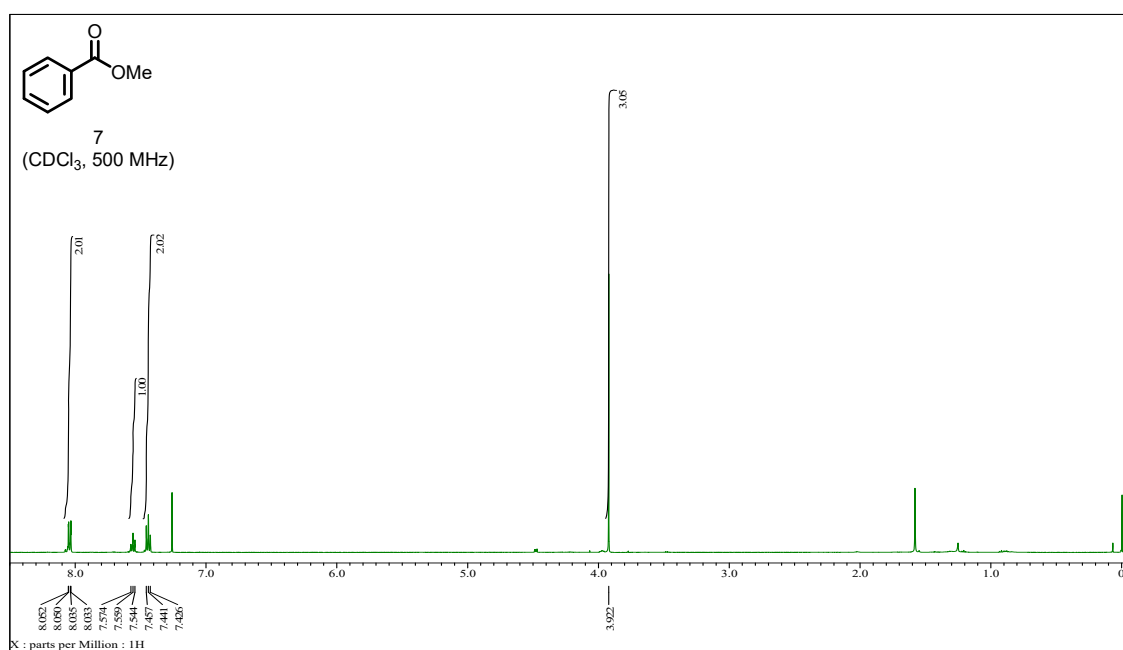
$^1\text{H}$  NMR of 2-(acetyloxy)ethyl benzoate (**5**)

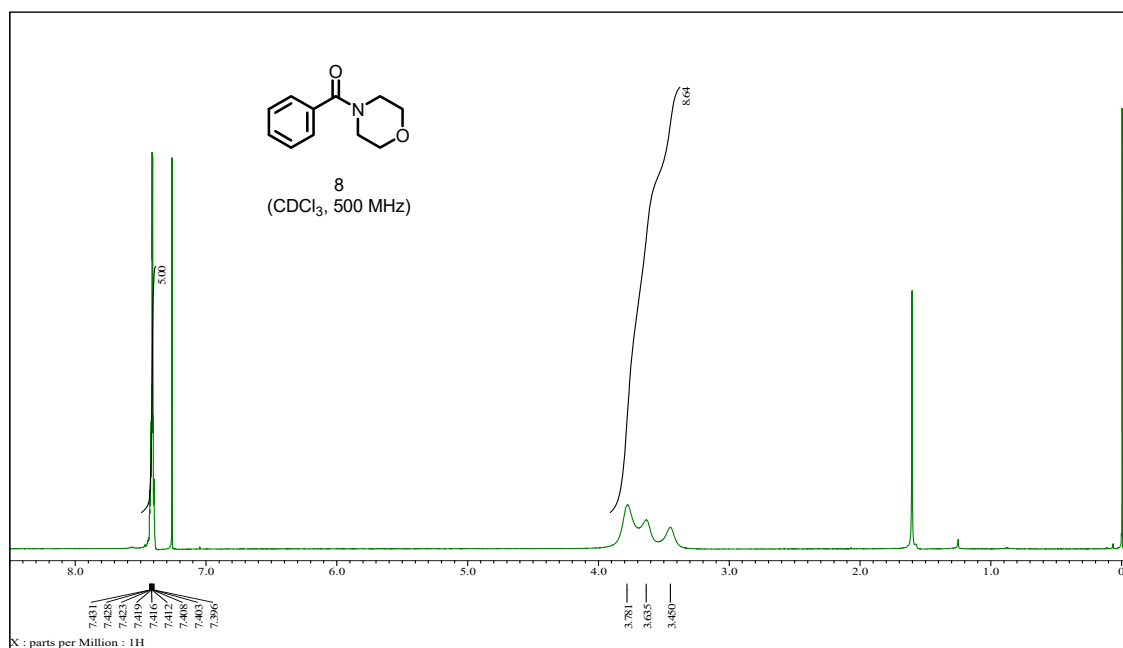
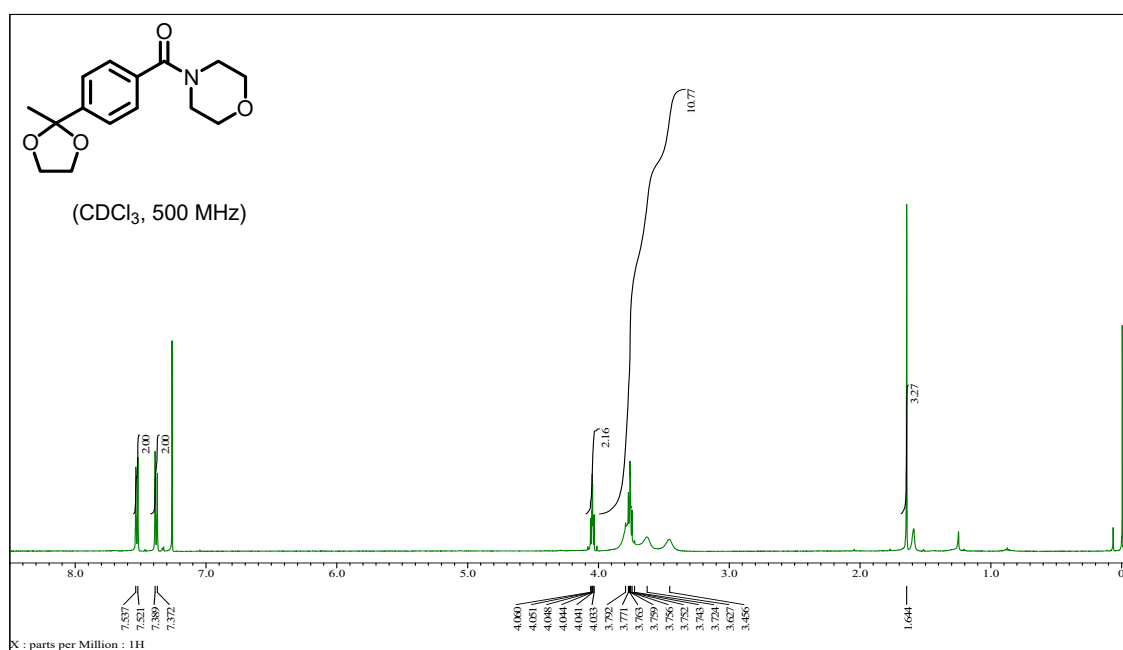


$^1\text{H}$  NMR of 2-(acryloyloxy)ethyl benzoate (**6**)

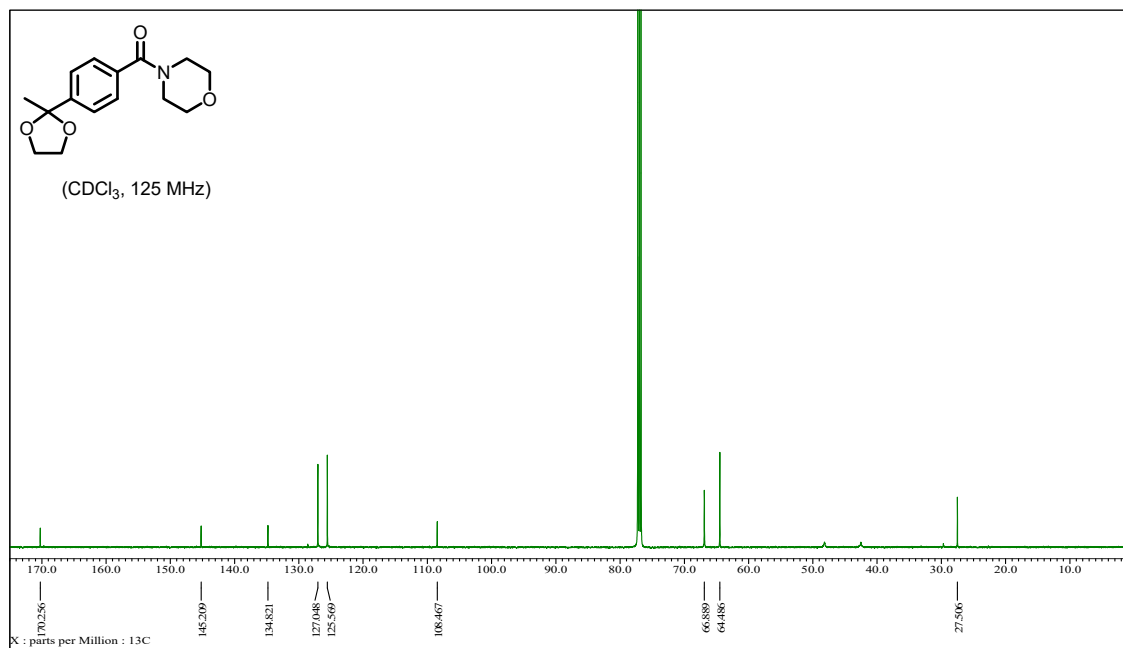


$^1\text{H}$  NMR of methyl benzoate (**7**)



<sup>1</sup>H NMR of *N*-benzoylmorpholine (**8**)<sup>1</sup>H NMR of [4-(2-methyl-1,3-dioxolan-2-yl)phenyl] (morpholino)methanone

$^{13}\text{C}$  NMR of [4-(2-methyl-1,3-dioxolan-2-yl)phenyl] (morpholino)methanone



$^1\text{H}$  NMR of 1-[4-(2-methyl-1,3-dioxolan-2-yl)phenyl]ethanone (**9**)

