

## Supporting Information

# Direct Aerobic Photo-oxidative Syntheses of Aromatic Methyl Esters from Methyl Aromatics Using Anthraquinone-2,3-dicarboxylic Acid as Organophotocatalyst

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## 1. General Information.

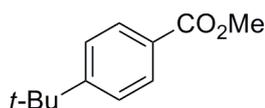
Dry methanol was obtained from Kanto Kagaku Co., Ltd. Other chemicals used were of reagent grade and were obtained from Aldrich Chemical Co., Tokyo Kasei Kogyo Co., Ltd. and Wako Pure Chemical Industries, Ltd.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained on a JEOL AL 400 spectrometer, JEOL EX 400 spectrometer (400 MHz for  $^1\text{H}$  NMR and 100 MHz for  $^{13}\text{C}$  NMR) or ECA 500 spectrometer (500 MHz for  $^1\text{H}$  NMR and 125 MHz for  $^{13}\text{C}$  NMR). Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) downfield from internal  $\text{Me}_4\text{Si}$ . Mass spectra (MS) were obtained on a JEOL JMS-SX102A instrument, JEOL JMS-T100GC instrument or JEOL JMS-T00TD instrument. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (MERCK, silica gel F-254).

## 2. Direct Aerobic Photooxidative Synthesis of Methyl Esters **2** from Methyl Aromatics **1**

### General Procedure

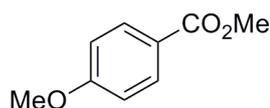
**Synthesis of Methyl 4-*tert*-butylbenzoate (2a)** (Table 2, entry 2): a solution of 4-*tert*-butyltoluene (**1a**, 0.3 mmol) and anthraquinone-2,3-dicarboxylic acid (0.03 mmol) in dry MeOH (5 mL) in a pyrex test tube, purged with an  $\text{O}_2$  balloon, was stirred and irradiated externally with a 500 W Xenon lamp for 24 h. The reaction mixture was concentrated *in vacuo*, and purification of the crude product by PTLC (toluene) provided Methyl 4-*tert*-butylbenzoate (51.4 mg, 89%).

**Methyl 4-*tert*-butylbenzoate (2a)**<sup>1)</sup> (Table 2, entry 2):

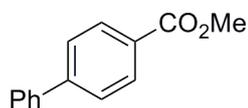


$^1\text{H}$  NMR spectrum of **2a** was identical with that in the literature.<sup>1)</sup>

**Methyl 4-methoxybenzoate (2b)**<sup>2)</sup> (Table 2, entry 1): colorless solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 9.0$  Hz, 2H), 6.92 (d,  $J = 9.0$  Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 163.5, 131.6, 122.6, 113.6, 55.4, 51.8; MS  $m/z$  166 ( $\text{M}^+$ ), 135, 107.

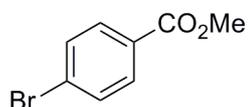


**Methyl 4-phenylbenzoate (2c)**<sup>1)</sup> (Table 2, entry 3):



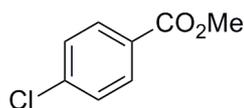
$^1\text{H}$  NMR spectrum of **2c** was identical with that in the literature.<sup>1)</sup>

**Methyl 4-bromobenzoate (2d)**<sup>1)</sup> (Table 2, entry 4):



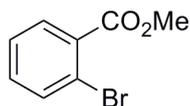
$^1\text{H}$  NMR spectrum of **2a** was identical with that in the literature.<sup>1)</sup>

**Methyl 4-chlorobenzoate (2e)<sup>1</sup> (Table 2, entry 5):**



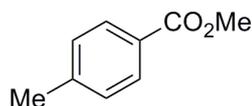
<sup>1</sup>H NMR spectrum of **2a** was identical with that in the literature.<sup>1)</sup>

**Methyl 2-bromobenzoate (2g)<sup>1</sup> (Table 2, entry 7):**

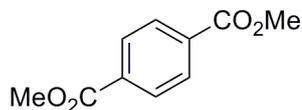


<sup>1</sup>H NMR spectrum of **2g** was identical with that in the literature.<sup>1)</sup>

**Methyl 4-methylbenzoate (2ha)<sup>2</sup> (Table 2, entry 8):** pale yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 2.40 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.3, 143.7, 129.7, 129.2, 127.5, 52.1, 21.8; MS *m/z* 150 (M<sup>+</sup>), 119, 91.

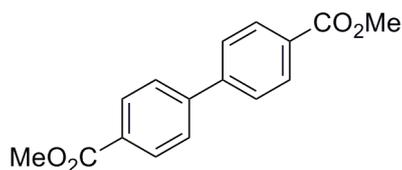


**Dimethyl terephthalate (2hb)<sup>1</sup> (Table 2, entry 9):**



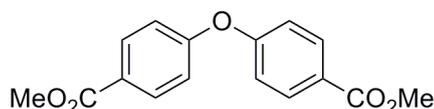
<sup>1</sup>H NMR spectrum of **2hb** was identical with that in the literature.<sup>1)</sup>

**Dimethyl biphenyl-4,4'-dicarboxylate (2i)<sup>1</sup> (Table 2, entry 10):**



<sup>1</sup>H NMR spectrum of **2i** was identical with that in the literature.<sup>1)</sup>

**Dimethyl biphenylether-4,4'-dicarboxylate (2j)<sup>3</sup> (Table 2, entry 11):** colorless solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.06 (d, *J* = 9.2 Hz, 4H), 7.06 (d, *J* = 9.2 Hz, 4H), 3.92 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.5, 160.3, 132.0, 125.8, 118.7, 52.3; MS (EI) *m/z* 286 (M<sup>+</sup>), 255, 168.

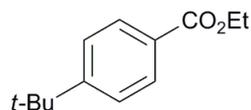


### 3. Direct Aerobic Photooxidative Synthesis of Alkyl Esters 2 from Methyl Aromatics 1

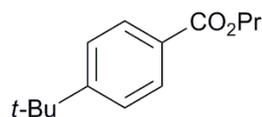
### General Procedure

**Synthesis of Ethyl 4-*tert*-butylbenzoate (2k) (Scheme 1):** 4-*tert*-butyltoluene (**1a**, 0.3 mmol), Anthraquinone-2,3-dicarboxylic acid (0.03 mmol) and trifluoroacetic acid (0.09 mmol) in dry EtOH (2 mL) in a pyrex test tube, purged with an O<sub>2</sub> balloon, was stirred and irradiated externally with four 22 W fluorescent lamps for 24 h. The reaction mixture was concentrated *in vacuo*, and purification of the crude product by PTLC (toluene) provided Ethyl 4-*tert*-butylbenzoate (51.6 mg, 75%).

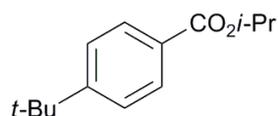
**Ethyl 4-*tert*-butylbenzoate (2k)<sup>4</sup> (Scheme 1):** colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.34 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.8, 156.5, 129.5, 127.8, 125.4, 60.8, 35.1, 31.2, 14.5; MS (EI) *m/z* 207 (M<sup>+</sup>), 169, 83.



**Propyl 4-*tert*-butylbenzoate (2l)<sup>5</sup> (Scheme 1):** colorless oil ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 4.28 (t, *J* = 6.6 Hz, 2H), 1.80 (m, 2H), 1.35 (s, 9H), 1.04 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.8, 156.5, 129.5, 127.8, 125.4, 66.4, 35.2, 31.2, 22.2, 10.6; HRMS (DART) Calcd. for C<sub>14</sub>H<sub>21</sub>O<sub>2</sub> [(M+H)<sup>+</sup>]: 221.1542. Found: 221.1542.



***iso*-Propyl 4-*tert*-butylbenzoate (2m)<sup>6</sup> (Scheme 1):** colorless oil ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 5.25 (sept, *J* = 6.3 Hz, 1H), 1.36 (d, *J* = 6.3 Hz, 6H), 1.34 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.2, 156.4, 129.5, 128.2, 125.3, 68.1, 35.1, 31.2, 22.1; HRMS (DART) Calcd. for C<sub>14</sub>H<sub>21</sub>O<sub>2</sub> [(M+H)<sup>+</sup>]: 221.1542. Found: 221.1548.



## 4. References

- 1) S. Hirashima, T. Nobuta, N. Tada, T. Miura, A. Itoh, *Org. Lett.*, **2010**, *12*, 3645-3647.
- 2) AIST: Integrated Spectral Database System of Organic Compounds. (Data were obtained from the National Institute of Advanced Industrial Science and Technology (Japan))
- 3) WSS: Spectral data were obtained from Wiley Subscription Services, Inc. (US)
- 4) A. Joshi-Pangu, C-Y. Wang, M. R. Biscoe, *J. Am. Chem. Soc.*, **2011**, *133*, 8478-8481
- 5) CAS Registry Number: 6282-27-5
- 6) CAS Registry Number: 67952-56-1

## 5. UV-vis spectra of anthraquinone derivatives in MeOH

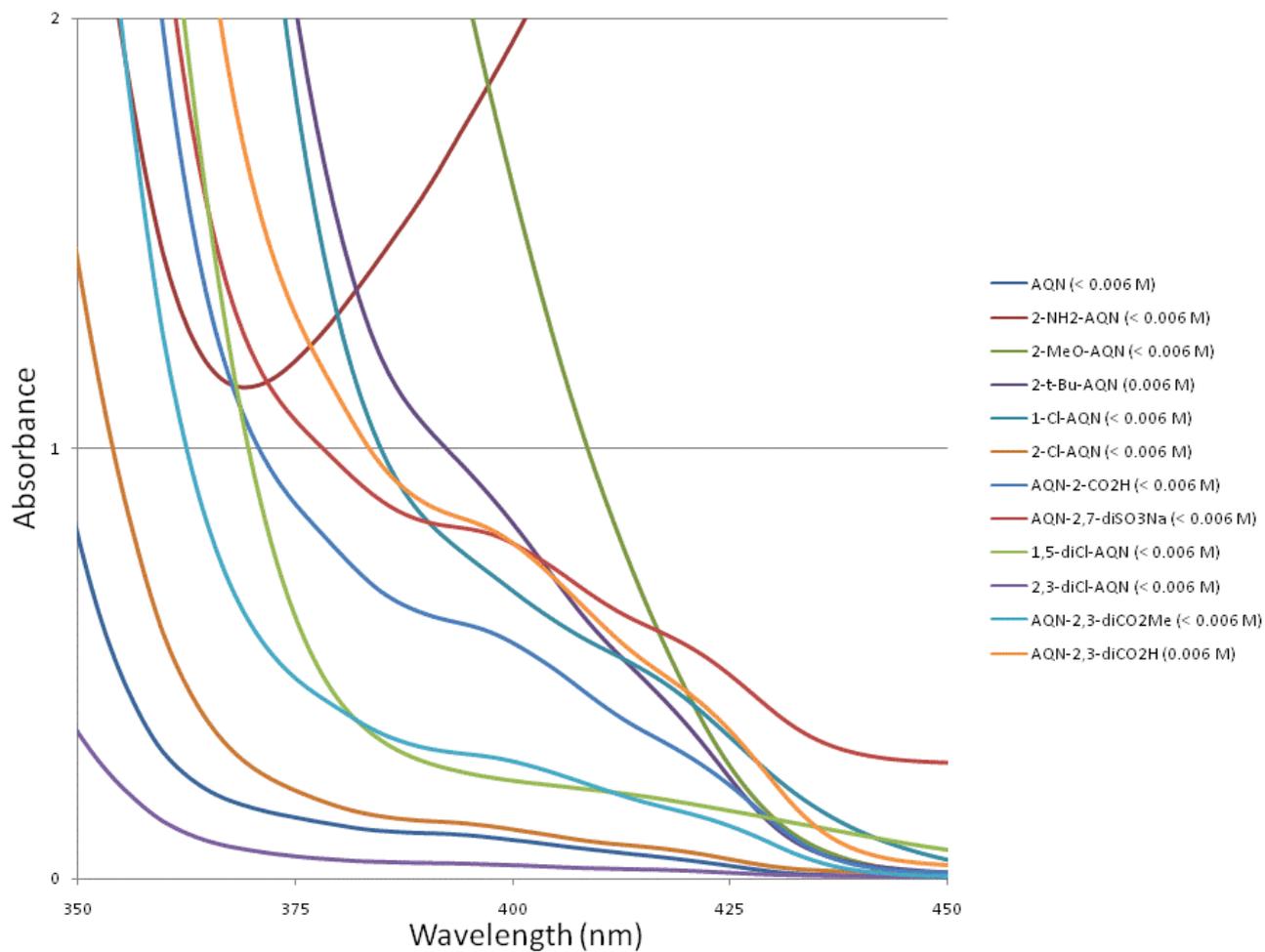


Figure 1. UV-vis spectra of anthraquinone derivatives in MeOH.

