

## **Formal Intramolecular Photoredox Chemistry of Anthraquinones in Aqueous Solution: Photodeprotection for Alcohols, Aldehydes and Ketones.**

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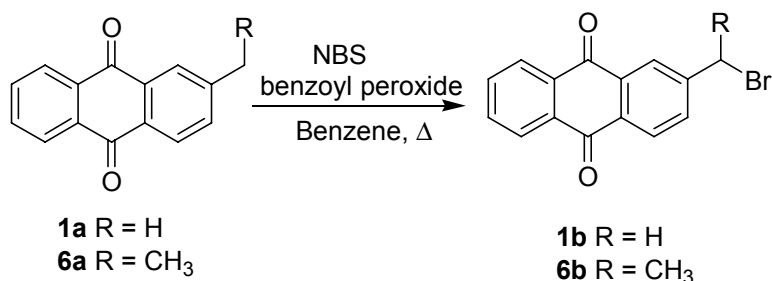
### **Experimental Procedures for the Preparation of 1- $\alpha$ D, 6-14**

#### **Preparation of $\alpha$ -D-2-(hydroxymethyl)-9,10-anthraquinone (1- $\alpha$ D)**

NaBD<sub>4</sub> (0.023g, 2.4 mmol) in 20 mL of anhydrous methanol was added dropwise to 2-(formyl)anthraquinone (**3**, 0.14 g, 0.6 mmol) in 20 mL of anhydrous methanol under N<sub>2</sub>. The mixture was stirred in an ice water bath for 2 h. After reaction, 20 ml of saturated NH<sub>4</sub>Cl was added and the resulting solution extracted by 2 × 25 mL of CH<sub>2</sub>Cl<sub>2</sub>. The collected extractions were dried over anhydrous MgSO<sub>4</sub> and the solvent removed. The residue was purified by column chromatography with silica gel using 5% EtOAc in CH<sub>2</sub>Cl<sub>2</sub> as a eluent, to give **1- $\alpha$ D** (white powder, 0.13 g, m.p 183-185°C) in 90% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  8.31-8.20 (m, 4H), 7.82-7.20 (m, 3H), 4.86 (s, 1H), 2.0 (s, broad OH peak); MS (EI), m/z 239 (M<sup>+</sup>, 100), 238 (20), 237 (32), 235 (42).

The 2-(formyl)anthraquinone (**3**) was prepared by photolysis of 2-(hydroxymethyl)anthraquinone (**1**) which was purchased from Aldrich. A solution (100 mg of **3** in 1:1 H<sub>2</sub>O-MeCN, argon purged, in 300 mL of photolysis quartz tube) was irradiated for 10 min and extracted with 3 × 50 mL CH<sub>2</sub>Cl<sub>2</sub>. The combined extractions were dried over anhydrous MgSO<sub>4</sub> and solvent was removed. The same procedure was repeated twice. The combined material was purified by column chromatography with silica gel using CH<sub>2</sub>Cl<sub>2</sub> as an eluent, to give **3** (pale yellow powder, 0.24 g) in 80% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  10.20 (s, 1H), 8.74 (s, 1H), 8.41 (d, 1H, *J* = 8.1 Hz), 8.37-8.25 (m, 2H), 8.26 (d, 1H, *J* = 8.1 Hz), 7.90-7.77 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) 191.0, 182.6, 182.3, 140.1, 137.1, 134.9, 134.8, 134.3, 133.5 (2C), 133.3, 129.7, 128.4, 127.7 (2C); MS (EI), m/z 236 (M<sup>+</sup>, 100), 237 (75), 235 (90), 207 (38).

Preparation of benzylic bromides **1b** and **6b**



A mixture of **1a** (2 g, 8 mmol), NBS (1.8 g, 10 mmol) and benzoyl peroxide (0.2 g, 0.8 mmol) in 100 mL of benzene was refluxed overnight. After reaction, the mixture was washed with distilled water (2 × 50 mL) and the collected organic solution was dried over anhydrous MgSO<sub>4</sub>. After solvent was removed, the brown crude product was purified by column chromatography with silica gel using CH<sub>2</sub>Cl<sub>2</sub> as an eluent, to give **1b** (yellow powder, 2.3 g) in 92% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.33-8.22 (m, 4H), 7.84-7.71 (m, 3H), 4.57 (s, 1H).

Compound **6b** (yellow powder, 2.1 g, 90% yield) was prepared following the same procedure as that described for **1b**. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.32-8.13 (m, 3H), 8.03 (d, 1H, *J* = 8.1 Hz), 7.78 (d, 1H, *J* = 8.1 Hz), 7.75-7.67 (m, 2H), 5.20 (q, 1H, *J* = 6.6 Hz), 2.03 (d, 3H, *J* = 6.6 Hz).

Preparation of 2-(1-hydroxyethyl)-9,10-anthraquinone (**6**)

A mixture of **6b** (2.0 g, 6.3 mmol) and CaCO<sub>3</sub> (4.5 g, 4.5 mmol) in 50 mL of 1:1 water and dioxane was refluxed for 2 days. After the reaction, 5 mL of H<sub>2</sub>SO<sub>4</sub> (0.5 M) was added to the mixture to neutralize the excess CaCO<sub>3</sub> and extracted with 2 × 50 mL CH<sub>2</sub>Cl<sub>2</sub>. The collected extractions were dried over anhydrous MgSO<sub>4</sub> and solvent was removed. The crude material was purified by column chromatography with silica gel using a mixture of hexane and EtOAc as eluent, to give **6** (yellow powder, 1.2 g, m.p 101-103°C) in 75% yield, <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>) δ 8.35-8.24 (m, 4H), 7.87-7.74 (m,

3H), 5.08 (q, 1H,  $J = 6.6$  Hz), 2.0 (s, broad OH peak), 1.56 (d, 3H,  $J = 6.6$  Hz);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 75 MHz) 183.3, 183.1, 152.9 (2C), 134.4, 134.3, 133.7, 133.6, 132.7, 131.3, 127.9, 127.4, 127.3, 124.2; MS (EI),  $m/z$  252 ( $\text{M}^+$ , 3), 237 (75), 210 (100); HRMS calculated for C<sub>16</sub>H<sub>12</sub>O<sub>3</sub> 252.0786; observed 252.0776; IR (KBr, cm<sup>-1</sup>) 3418, 2973, 1675, 1591.

#### Preparation of 2-(ethoxymethyl)-9,10-anthraquinone (7)

A mixture of **1b** (0.37 g, 1.2 mmol) and CaCO<sub>3</sub> (0.31 g, 6 mmol) in 20 mL of ethanol was refluxed overnight. After the reaction, 6 mL of H<sub>2</sub>SO<sub>4</sub> (0.5 M) was added to neutralize the excess CaCO<sub>3</sub> and extracted by 2 × 50 mL CH<sub>2</sub>Cl<sub>2</sub>. The collected extracts were dried over anhydrous MgSO<sub>4</sub> and solvent was removed to give a brown crude material which was purified by column chromatography with silica gel using CH<sub>2</sub>Cl<sub>2</sub> as an eluent, to give **7** (pale yellow powder, 0.18g, 115-117°C) in 56% yield.  $^1\text{H}$ -NMR (300MHz, CDCl<sub>3</sub>)  $\delta$  8.33-8.25 (m, 3H), 8.23 (s, 1H), 7.82-7.74 (m, 2H), 4.65 (s, 2H), 3.61 (q, 2H,  $J = 7.4$  Hz), 1.28 (t, 3H,  $J = 7.4$  Hz);  $^{13}\text{C}$ -NMR (CDCl<sub>3</sub>, 75 MHz) 183.3, 183.1, 152.9 (2C), 134.4, 134.3, 133.7, 133.6, 132.7, 131.3, 127.9, 127.4, 127.3, 124.2; MS (EI),  $m/z$  266 ( $\text{M}^+$ , 10), 237 (75), 210 (100); HRMS calculated for C<sub>17</sub>H<sub>14</sub>O<sub>3</sub> 266.0943; observed 266.0945; IR (KBr, cm<sup>-1</sup>) 2974, 2867, 1677, 1590.

#### Preparation of 2-(1-methoxyethyl)-9,10-anthraquinone (8)

A mixture of **6b** (0.27 g, 0.86 mmol) and CaCO<sub>3</sub> (0.43g, 4.3 mmol) in 30 mL of methanol was refluxed for 3 days. After the reaction, 9 mL of H<sub>2</sub>SO<sub>4</sub> (0.5 M) was added to neutralize excess CaCO<sub>3</sub>. This was followed by the addition of 200 mL of water to the mixture to give a yellow precipitate. After suction filtration, the yellow precipitate (powder) was recrystallized from ethanol to give **8** (yellow crystalline plates, 0.17g, m.p.

95-96°C) in 74% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.34-8.26 (m, 3H), 8.22 (s, 1H), 7.82-7.73 (m, 3H), 4.47(q, 1H,  $J = 6.6$  Hz), 3.28 (s, 3H), 1.47 (d, 3H,  $J = 6.6$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz) 183.4, 183.1, 150.9 (2C), 134.4, 134.3, 133.9, 133.7, 133.0, 131.8, 128.0, 127.4 (2C), 125.1, 79.3, 57.1, 23.8; MS (EI),  $m/z$  266 ( $\text{M}^+$ , 10), 251 (100), 235 (20); HRMS calculated for  $\text{C}_{17}\text{H}_{14}\text{O}_3$  266.0943; observed 266.0941; IR (KBr,  $\text{cm}^{-1}$ ) 2974, 2823, 1677, 1590.

#### Preparation of 2-(acetoxymethyl)-9,10-anthraquinone (9)

A mixture of **1** (0.20 g, 0.8 mmol) and NaOAc (0.13 g, 1.6 mmol) was refluxed in 10 mL of anhydrous EtOAc for 1 h. After the reaction, the solution was poured into 50 mL of ice-cold water and stirred to give a yellow precipitate. The precipitate was isolated by suction filtration and purified by column chromatography with silica gel using 20% EtOAc- $\text{CH}_2\text{Cl}_2$  as an eluent, to give **9** in 70% yield (pale yellow powder, 0.14 g, m.p. 149-150°C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.35-8.25 (m, 4H), 7.85-7.72 (m, 3H), 5.25 (s, 2H), 2.16 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz) 183.1, 182.9, 170.8, 142.9 (2C), 134.5, 134.4, 133.9, 133.7, 133.3, 133.1, 127.9, 127.5 (2C), 126.3, 65.3, 21.1; MS (EI),  $m/z$  280 ( $\text{M}^+$ , 3), 238 (100), 221 (10), 209 (25); HRMS calculated for  $\text{C}_{17}\text{H}_{12}\text{O}_4$  280.0736; observed 280.0740; IR (KBr,  $\text{cm}^{-1}$ ) 1741, 1677, 1590.

#### Preparation of 9-phenyl-7,11-dihydro-8,10-dioxo-cyclohepta [b]anthracene-5,13-dione (10)

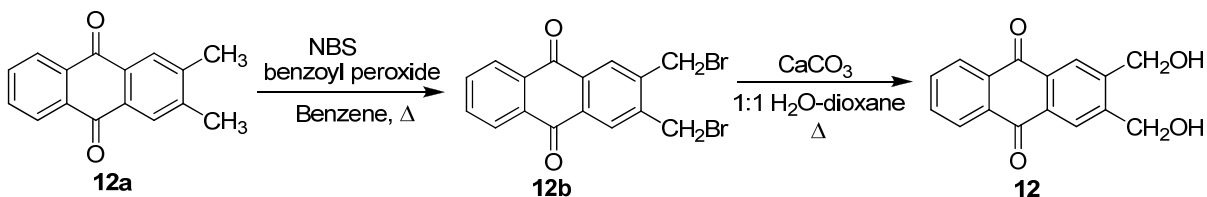
A solution of **12** (0.2 g, 0.74 mmol) and benzaldehyde (0.4 mL, 3.0 mmol) in 10 mL of toluene along with one drop of conc.  $\text{H}_2\text{SO}_4$  was refluxed for 0.5 h in a Dean-Stark apparatus, to give a brown solution. After the reaction, the solution was neutralized with 5%  $\text{NaHSO}_3$  to give a brown precipitate. The brown precipitate was isolated by suction

filtration and purified by column chromatography with silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent, to give **10** (pale yellow powder, 0.13 g, m.p. 223-225°C) in 49% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.35-8.24 (m, 2H), 8.06 (s, 2H), 7.84-7.75 (m, 2H), 7.60-7.52 (m, 2H), 7.44-7.33 (m, 3H), 6.00 (s, 1H), 5.12 (d, 2H, *J* = 14.7 Hz), 5.02 (d, 2H, *J* = 14.7 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) 183.0 (2C), 145.6 (2C), 138.0, 134.4 (2C), 133.7 (2C), 132.5 (2C), 129.1, 128.6 (2C), 127.5 (2C), 126.7 (2C), 125.8 (2C), 103.6, 68.4 (2C); MS (EI), *m/z* 356 (M<sup>+</sup>, 2), 250 (80), 234 (100); IR (KBr, cm<sup>-1</sup>) 1671, 1590.

Preparation of 9-methyl-9-phenyl-7,11-dihydro-8,10-dioxo-cyclohepta [b]anthracene-5,13-dione (**11**)

Compound **11** was prepared from **12** (0.1g, 0.37 mmol) and acetophenone (0.18 mL, 1.5 mmol) following the synthetic procedure described for **10** in 30% overall yield (**11**, white powder, 0.041 g, m.p. 209-210°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.26-8.18 (m, 2H), 7.92 (s, 2H), 7.76-7.68 (m, 2H), 7.58-7.51 (m, 2H), 7.38-7.24 (m, 3H), 5.02 (d, 2H, *J* = 15.5 Hz), 4.82 (d, 2H, *J* = 15.5 Hz), 1.64 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) 183.0 (2C), 145.4 (2C), 142.4, 134.3 (2C), 133.8 (2C), 132.3 (2C), 128.6, 128.4 (2C), 127.4 (2C), 126.2 (2C), 125.3 (2C), 104.7, 65.7 (2C), 26.1; MS (EI), *m/z* 370 (M<sup>+</sup>, 2), 355 (20), 250 (40), 105 (100); HRMS calculated for C<sub>24</sub>H<sub>18</sub>O<sub>4</sub> 370.1205; observed 370.1209; IR (KBr, cm<sup>-1</sup>) 2934, 1675, 1591.

Preparation of 2,3-di(hydroxymethyl)-9,10-anthraquinone (**12**)

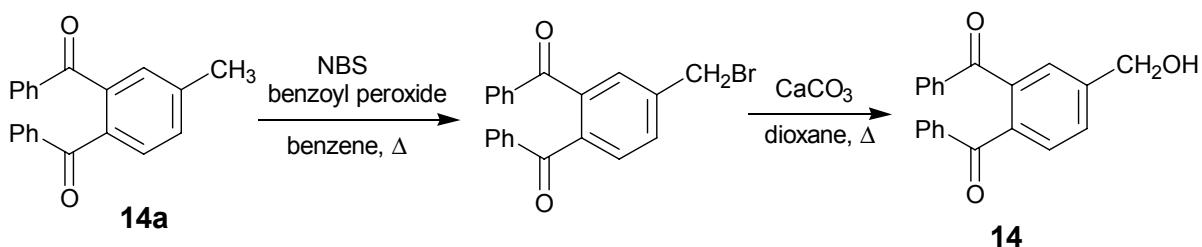


A mixture of **12a** (Aldrich, 1.0 g, 4.5 mmol), NBS (1.8 g, 10.4 mmol) and benzoyl peroxide (0.10 g, 0.04 mmol) in 50 mL of benzene was refluxed for overnight. After the reaction, the mixture was washed with distilled water ( $2 \times 50$  mL) and the collected organic solution was dried over anhydrous  $\text{MgSO}_4$ . After solvent was removed, a brown residue (**12b**, 1.8g, 90% yield) was obtained. A mixture of **12b** (1.8 g, 4.6 mmol) and  $\text{CaCO}_3$  (4.6g, 46 mmol) was refluxed in 1:1 water and dioxane for 2 days to give a brown solution. After the reaction, 50 mL of  $\text{H}_2\text{SO}_4$  (0.5 M) was added to neutralized excess  $\text{CaCO}_3$ . Upon addition of 200 mL water, a brown precipitate was formed which was collected by suction filtration. This crude material was recrystallized from toluene to give **12** (yellow brown needles, 0.34 g, m.p. 214-216°C) in 30% yield.  $^1\text{H}$  NMR (acetone- $d_6$ , 500 MHz)  $\delta$  8.42 (s, 1H), 8.30-8.26 (m, 2H), 7.94-7.90 (m, 2H), 4.88 (d, 2H,  $J = 5.5$  Hz), 4.65 (t, OH,  $J = 5.5$  Hz);  $^{13}\text{C}$  NMR (acetone- $d_6$ , 125 MHz) 183.6 (2C), 147.3 (2C), 135.1 (2C), 134.7 (2C), 133.2 (2C), 127.7 (2C), 125.8 (2C), 61.7 (2C); MS (EI),  $m/z$  267 ( $\text{M}^+ - 1$ , 3), 264 (70), 248 (65), 235 (100); IR (KBr,  $\text{cm}^{-1}$ ) 3205, 1672, 1587.

#### Preparation of 2-[1,3]dioxolan-2-yl-9,10-anthraquinone (**13**)

Compound **13** was prepared from **3** (0.3 g, 1.3 mmol) and ethylene glycol (0.08 g, 1.3 mmol) followed the procedure described for **10** with 74% overall yield (**13**, pale yellow powder, 0.27 g, m.p. 129-131°C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.34 (s, 1H), 8.28-8.19 (m, 3H), 7.84 (d, 1H,  $J = 8.1$  Hz), 7.78-7.70 (m, 2H), 5.89 (s, 1H), 4.16-4.00 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz) 183.1 (2C), 144.7 (2C), 134.4, 134.1, 133.8, 133.7, 133.6, 132.2, 127.8, 127.5, 127.4, 125.7, 102.8, 65.8 (2C); MS (EI),  $m/z$  280 ( $\text{M}^+$ , 75), 279 (100); HRMS calculated for  $\text{C}_{17}\text{H}_{12}\text{O}_4$  280.0736; observed 280.0728; IR (KBr,  $\text{cm}^{-1}$ ) 3069, 1724, 1676, 1592.

Preparation of 1,2-dibenzoyl-4-methylbenzene (**14a**)



Compound **14** was prepared from **14a** (0.8 g, 2.7 mmol) following the synthetic procedure described for **12** with 65% overall yield (**14**, pale yellow oil, 0.55 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.70-7.61 (m, 4H), 7.57 (s, 1H), 7.56 (d, 2H,  $J = 5.9$  Hz), 7.53-7.44 (tt, 2H,  $J = 8.1$  Hz), 7.53-7.43 (tt, 4H,  $J = 8.1$  Hz), 4.79 (s, 2H), 2.0 (s, broad OH peak);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz) 197.1, 196.6, 144.3, 140.7, 138.9, 137.4, 137.3, 133.3, 133.2, 130.4, 130.0 (2C), 129.9 (2C), 128.6 (2C), 128.5 (2C), 128.4, 127.7, 64.4; IR (KBr,  $\text{cm}^{-1}$ ) 3448, 3059, 2870, 1655, 1596; MS (EI),  $m/z$  316 ( $\text{M}^+$ , 10), 314 ( $\text{M}^+ - 2$ , 60), 237 (55), 105 (100).

Compound **14a** was in turn prepared following a literature procedure<sup>9</sup> with 30% overall yield (**14a**, pale yellow oil, 1.2 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.65-7.54 (m, 4H), 7.49-7.35 (m, 3H), 7.35-7.22 (m, 6H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz) 197.2, 196.5, 141.7, 140.8, 137.7, 137.6, 137.0, 133.2, 133.0, 131.0, 130.4, 130.3, 130.0 (2C), 129.9 (2C), 128.6 (2C), 128.5 (2C), 21.7; MS (EI),  $m/z$  300 ( $\text{M}^+$ , 60), 223 (100).

Photolysis procedures for 1- $\alpha$ D, 6-14 and characterization of photolysis products

Photolysis of 1- $\alpha$ D



Compound **1- $\alpha$ D** (6 mg in 50 mL MeCN and 50 mL H<sub>2</sub>O, pH 7) was irradiated for 1 min, 2 min and 4 min at 300 nm (2 lamps) under argon, to give a yellow brown solution. After work-up in air, the brown residue was characterized by <sup>1</sup>H NMR to give a mixture of **3** (8-28%) and **16** (17-57%). Further purification was obtained by prep. TLC (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) to give a mixture of **3** and **16** (yellow powder, 5 mg), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  10.2 (s, 1H), 8.77 (s, 3.1 H), 8.45 (d, 3.1 H,  $J = 8.1$  Hz), 8.40-8.23 (m, 8.8 H), 7.91-7.76 (m, 6.2 H); MS (EI),  $m/z$  237 (M<sup>+</sup>, 80), 236 (60), 235 (100).

#### Photolysis of **1** to give **17** and **19**

Compound **1** (20 mg in 50mL of MeCN and 50 mL of H<sub>2</sub>O, pH 7) was irradiated for 1 min at 300 nm (16 lamps) under argon to give a yellow brown solution. Sufficient solid NaOH was added to change the solution colour to blue. This was followed by the addition of 1 mL of Ac<sub>2</sub>O, which turned the solution to a bright yellow. After work-up in air, the material was characterized by <sup>1</sup>H NMR showing formation of **17** (50 % conversion). Separation and purification was achieved by prep. TLC (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) to give **17** in 40% yield (yellow powder, 11 mg, m.p. 175-177°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  10.16 (s, 1H), 8.43 (s, 1H), 8.05-7.91 (m, 4H), 7.66-7.05 (m, 2H), 2.69 (s, 3H), 2.65 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) 191.8, 169.5 (2C), 142.6, 140.8, 134.5 (2C), 130.4, 128.2, 127.5, 126.7, 125.7, 125.1, 123.5, 122.4 (2C), 122.2, 21.0, 20.9; MS (EI),  $m/z$  322 (M<sup>+</sup>, 3), 280 (10), 238 (100); HRMS calculated for C<sub>19</sub>H<sub>14</sub>O<sub>5</sub> 322.0841; observed 322.0845; IR (KBr, cm<sup>-1</sup>) 3067, 2918, 2849, 1757, 1689, 1626.

Followed with the above procedure, photolysis of compound **1** (20 mg, 350 nm, 16 lamps, 20 min) in neat ethanol gave **19** (75% conversion). Further purification was obtained by prep. TLC (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) to give **19** in 60% yield (pale yellow powder,

16 mg, m.p. 194-196°C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.97-7.89 (m, 3H), 7.87 (s, 1H), 7.56-7.45 (m, 3H), 4.87 (s, 2H), 2.63 (s, 3H), 2.62 (s, 3H);  $^{13}\text{C}$  NMR (acetone- $d_6$ , 125 MHz) 170.2 (2C), 142.0, 141.4, 141.3, 127.4, 127.19, 127.17, 125.4, 125.2, 124.9, 124.7, 122.94, 122.87, 122.79, 118.7, 64.4, 20.79, 20.78; MS (EI), m/z 324 ( $\text{M}^+$ , 10), 282 (15), 240 (100); HRMS calculated for  $\text{C}_{19}\text{H}_{16}\text{O}_5$  324.0998; observed 324.1000; IR (KBr,  $\text{cm}^{-1}$ ) 3449, 1751.

#### Photolysis of **6** and **8**

Photolysis of compound **6** (10 mg, 1:1  $\text{H}_2\text{O}$ -MeCN, 350 nm, 16 lamps, 1 min, argon purged) gave a yellow brown solution. After work-up in air, the brown residue was characterized by  $^1\text{H}$  NMR to give **8b** (70% conversion). Further purification was obtained by prep. TLC (silica gel,  $\text{CH}_2\text{Cl}_2$ ) to give **8b** (yellowish powder, 6 mg, 60% yield). Following the same photolysis procedure of **6**, photolysis of **8** also gave product **8b** (60% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.79 (s, 1H), 8.41-8.23 (m, 4H), 7.86-7.75 (m, 2H), 2.73 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) 196.97, 182.7, 182.6, 141.3, 136.3, 134.7 (2C), 134.0, 133.7, 133.6, 133.1, 128.1, 127.69, 127.67, 127.6, 22.3; MS (EI), m/z 322 ( $\text{M}^+$ , 3), 280 (10), 238 (100); HRMS calculated for  $\text{C}_{19}\text{H}_{14}\text{O}_5$  250.0630; observed 250.0630; IR (KBr,  $\text{cm}^{-1}$ ) 1693, 1673, 1589.

#### Photolysis of **7**

Following the same photolysis procedure as for **6**, photolysis of **7** gave product **3** (yellow powder, 60% yield).

#### Photolysis of **10** and **11**

Photolysis of **10** (5 mg, 1:3  $\text{H}_2\text{O}$ -MeCN, pH 7, 300 nm, 16 lamps, 5 min, argon purged) gave a yellow brown solution. After work-up in air, the brown residue was characterized

by  $^1\text{H}$  NMR to give **27** (30% conversion). Further purification was obtained by TLC (silica gel,  $\text{CH}_2\text{Cl}_2$ ) to give **27** (white powder, 1 mg, 25% yield). Photolysis of **11** also gave **27** by following the same photolysis procedure of **10**.  $^1\text{H}$  NMR (Acetone- $d_6$ , 500 MHz)  $\delta$  8.66 (s, 1H), 8.59 (s, 1H), 8.37-8.33 (m, 2H), 8.03-7.98 (m, 2H), 5.67 (s, 2H); MS (EI),  $m/z$  264 ( $\text{M}^+$ , 60), 248(5), 235 (100); HRMS calculated for  $\text{C}_{16}\text{H}_8\text{O}_4$  264.0432; observed 2264.0420; IR (KBr,  $\text{cm}^{-1}$ ) 1764, 1673, 1586, 1332, 1303.

### Photolysis of 12

Photolysis of **12** (5 mg, 1:3  $\text{H}_2\text{O}$ -MeCN, pH 7, 300 nm, 16 lamps, 1 min) gave a brown solution. After work-up in air, the brown residue was characterized by  $^1\text{H}$  NMR to give **25** (50% conversion). Further purification was obtained by prep. TLC (silica gel, 20% EtOAc- $\text{CH}_2\text{Cl}_2$ ) to give **25** (brown yellow powder, 2 mg, 40%).  $^1\text{H}$  NMR (Acetone- $d_6$ , 300 MHz)  $\delta$  8.40 (s, 1H), 8.36-8.28 (m, 2H), 8.23 (s, 1H), 7.85-7.77 (m, 2H), 6.63 (d, 1H,  $J = 7.3$  Hz), 5.38 (d, 1H,  $J = 14.0$  Hz), 5.17 (d, 1H,  $J = 14.0$  Hz), 3.08 (d, OH,  $J = 7.3$  Hz); MS (EI),  $m/z$  266 ( $\text{M}^+$ , 60), 248(100), 235 (45); HRMS calculated for  $\text{C}_{16}\text{H}_{10}\text{O}_4$  266.0579; observed 266.0572; IR (KBr,  $\text{cm}^{-1}$ ) 3368, 1675 1590, 1327, 1300.

### Photolysis of 13

Photolysis of **13** (10 mg, 1:1  $\text{H}_2\text{O}$ -MeCN, pH 7, 300 nm, 16 lamps, 1 min) gave a yellow solution. After work-up in air, the yellow residue was characterized by  $^1\text{H}$  NMR to give **30** in 40% yield. Separation and purification was achieved by prep. TLC (silica gel,  $\text{CH}_2\text{Cl}_2$ ) to give **30** (yellow powder, 3.5 mg, 30%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{Cl}$ , 500 MHz)  $\delta$  8.94 (d, 1H,  $J = 1.8$ ), 8.44 (dd, 1H,  $J = 1.8$ ,  $J = 8.1$ ), 8.38 (d, 1H,  $J = 8.1$ ), 8.35-8.30 (m, 2H), 7.85-7.80 (m, 2H), 4.54 (t, 2H,  $J = 4.6$  Hz), 4.02 (t, 2H,  $J = 4.6$  Hz);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{Cl}$ , 500 MHz) 182.4, 182.2, 165.2, 136.1, 134.8, 134.6, 134.44, 134.38, 133.5, 133.33, 133.3,

128.6, 127.5, 127.4, 127.3, 67.3, 61.1; MS (EI),  $m/z$  295 ( $M^+ - 1$ , 1), 253 ( $M^+ - C_2H_3O$ , 70), 235(100), 207 (25); IR (KBr,  $cm^{-1}$ ) 3358, 2956, 2884, 1726, 1680, 1591, 1273, 1247.

#### Photolysis of **14**

Photolysis of **14** (20 mg, 1:1 H<sub>2</sub>O-MeCN, pH ~ 0 (5% H<sub>2</sub>SO<sub>4</sub>), 300 nm, 16 lamps, 1.5 h, argon purged) gave a yellow solution. After work-up in air, the yellow powder was characterized by <sup>1</sup>H NMR and assigned to be a mixture of product **32** (30% conversion) and **33** (14% conversion). The mixture was separated by prep. TLC (silica gel, 20% EtOAc-CH<sub>2</sub>Cl<sub>2</sub>) to give pure **33** (colourless oil, 2 mg, 10% yield) and **32** (yellow-orange powder, 5 mg) contaminated with 10% of **33** since **32** was found to be sensitive to oxygen and light, being readily converted to **33** under such conditions. Characterization of **32**: <sup>1</sup>H NMR (CD<sub>3</sub>Cl, 300 MHz) δ 9.95 (s, 1H), 8.35 (s, 1H), 8.03-7.83 (m, 5H), 7.59-7.44 (m, 5H), 7.44-7.29 (m, 2H); MS (EI),  $m/z$  298 ( $M^+$ , 100), 269(15); HRMS calculated for C<sub>21</sub>H<sub>14</sub>O<sub>2</sub> 298.0994; observed 298.0995. Characterization of **33**: <sup>1</sup>H NMR (CD<sub>3</sub>Cl, 300 MHz) δ 10.12 (s, 1H), 8.12 (d, 1H,  $J = 8.8$  Hz), 8.10 (s, 1H), 7.75 (d, 1H,  $J = 8.8$  Hz), 7.70 (d, 4H,  $J = 7.3$  Hz), 7.59-7.50 (m, 2H), 7.45-7.35 (tt, 4H, 1H,  $J = 7.3$  Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) 196.0, 195.5, 190.9, 145.7, 140.8, 137.1, 136.7 (2C), 133.8, 133.7, 131.5, 130.7, 130.2 (2C), 130.0 (2C), 128.8 (4C); MS (EI),  $m/z$  314 ( $M^+$ , 80), 237 (70), 105 (100); HRMS calculated for C<sub>21</sub>H<sub>14</sub>O<sub>3</sub> 314.0943; observed 314.0937; IR (neat film,  $cm^{-1}$ ) 3061, 1703, 1664, 1597.