# Supporting Information

# 2-Hydroxyphenacyl ester: A new photoremovable protecting group

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# **Experimental Section**

## **Material and Methods**

NMR spectra were recorded on 200 or 300 MHz spectrometers in acetone- $d_6$ , acetonitrile- $d_3$ , benzene- $d_6$ , chloroform-d, methanol- $d_4$ , water- $d_2$ , or their mixtures, and were referenced to the residual peak of a (major) solvent except H<sub>2</sub>O. Quantitative analyses were performed on a gas chromatograph equipped with a 15-m column (5% diphenyldimethylsiloxane) or a 58-m column (DB-XLB), and a FID detector. Mass spectra were recorded on a GC-coupled (30-m DB-XLB column) spectrometer in a positive mode with EI using a direct inlet. UV spectra were obtained with matched 1.0-cm quartz cells. IR spectra were obtained on an FT spectrometer in KBr pellets. Exact masses were performed using a triple quadrupole electrospray ionization mass spectrometer in positive or negative modes. Melting points were conducted using a non-calibrated Kofler's hot stage melting point apparatus. Elementary analyses were performed using an automatic analyzer. The solution pH values were determined using a glass electrode calibrated with certified buffer solutions at pH = 4, 7 or 10. The reagents and solvents of the highest purity available were used as purchased or purified/dried by standard procedures when necessary. All column chromatography purification procedures were done on silica.

A Rayonet reactor equipped with 300-nm lamps or a light source consisting of a 40-W medium pressure mercury lamp and a 313-nm band-pass filter or a Pyrex filter ( $\lambda \ge 280$  nm) were used for irradiation of the samples.

#### Synthesis

#### 2-Bromo-1-(2-hydroxyphenyl)ethanone (5)

A solution of 2-hydroxyacetophenone (4, 2.00 g, 14.7 mmol) and copper (II) bromide (6.80 g, 30.4 mmol) in ethyl acetate/CHCl<sub>3</sub> (80 mL, 1:1, v/v) was vigorously stirred and refluxed overnight (the reaction progress was monitored by GC). Then the mixture was cooled to 20 °C, filtered through a pad of silica, and concentrated under reduced pressure. The title product was purified using column chromatography (dichloromethane/petroleum ether, 1:4, v/v); a crude mixture of 5 and the side-products (2,2-dibromo-1-(2nevertheless. hydroxyphenyl)ethanone,  $\sim 7\%$ , benzofuran-3(2H)-one, 9,  $\sim 5\%$ ) was used in the subsequent step. Yield (5): 2.56 g (81%); white crystalline powder; mp 34.3–37.4 °C (lit. 37–39 °C).<sup>1</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 4.45 (s, 2H), 6.95 (ddd, 1H,  $J_1 = 7.3$  Hz,  $J_2 = 7.3$  Hz,  $J_3 =$ 1.3 Hz), 7.04 (dd, 1H,  $J_1 = 8.3$  Hz,  $J_2 = 1.0$  Hz), 7.54 (ddd, 1H,  $J_1 = 7.3$  Hz,  $J_2 = 7.3$  Hz,  $J_3 = 7.3$  Hz,  $J_3 = 7.3$  Hz,  $J_2 = 7.3$  Hz,  $J_3 =$ 1.6 Hz), 7.76 (dd, 1H,  $J_1 = 8.3$  Hz,  $J_2 = 1.6$  Hz), 11.72 (s, 1H, -OH). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 30.1, 117.3, 119.2, 119.5, 130.6, 137.6, 163.5, 197.2. MS (EI, 70 eV): m/z =216 (13), 214 (14), 136 (4), 121 (100), 107 (12), 92 (10), 79 (16), 77 (25), 63 (10), 53 (7), 51 (7). FTIR (KBr, cm<sup>-1</sup>): 3438 (br), 3058, 3005, 2944, 1643, 1612, 1572, 1484, 1448, 1387, 1302, 1248, 1223, 1156, 989, 836, 753, 691, 635, 511. This compound has also been characterized elsewhere.<sup>2</sup>

**2,2-Dibromo-1-(2-hydroxyphenyl)ethanone.** This compound was obtained from the previous procedure and purified using column chromatography (dichloromethane/petroleum ether, 1:4). Yield: 31 mg (7%); colorless viscous liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.78 (s, 1H), 6.96 (t, 1H, J = 7.8 Hz), 7.08 (d, 1H, J = 8.2 Hz), 7.57 (t, 1H, J = 7.3 Hz), 7.87 (dd, 1H,  $J_1 = 7.8$  Hz,  $J_2 = 0.5$  Hz), 11.45 (s, 1H, -OH). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 38.3, 114.1, 119.5, 119.6, 130.2, 138.3, 164.3, 191.2. MS (EI, 70 eV): m/z = 296 (2), 294 (4), 292 (2), 216 (4), 214 (4), 181 (3), 152 (1), 134 (10), 121 (100), 105 (11), 93 (10), 77 (12), 65 (10), 51 (10). FTIR (KBr, cm<sup>-1</sup>): 3436 (br), 3044, 2924, 2853, 1645, 1574, 1486,

1452, 1302, 1248, 1162, 986, 778, 752, 642, 520. This compound has also been characterized elsewhere.<sup>3</sup>

## 2-(2-Methoxyphenyl)-2-oxoethyl Acetate (6)

**1-(2-Methoxyphenyl)ethanone (7).** A mixture of 1-(2-hydroxyphenyl) ethanone (**4**, 5.3 g, 38.9 mmol), methyl iodide (11.5 g, 78 mmol) and K<sub>2</sub>CO<sub>3</sub> (21.5 g, 156 mmol) in acetone (80 mL) was stirred overnight at 20 °C. The reaction mixture was filtered and the solvent was removed under reduced pressure. A residue was dissolved in ethyl acetate (50 mL), and the solution was washed with water ( $3 \times 50$  mL). The organic layer was dried over MgSO<sub>4</sub>, filtered, and solvent was removed under reduced pressure to give the crude product **7** (purity >98%, GC). It was used in the subsequent step without any further purification. Yield: 5.0 g (86%); slightly yellowish oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 2.62 (s, 3H), 3.92 (s, 3H), 6.96–7.02 (m, 2H), 7.44–7.49 (m, 1H), 7.73 (dd, 1H,  $J_1 = 7.7$  Hz,  $J_2 = 1.8$  Hz). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 31.6, 55.2, 111.5, 120.3, 128.0, 130.0, 133.5, 158.8, 199.3. MS (EI): m/z = 150 (25), 135 (100), 120 (1), 105 (<1), 92 (23), 77 (43), 63 (9), 51 (6), 43 (12). FTIR (KBr, cm<sup>-1</sup>): 3075, 3003, 2964, 2943, 2841, 1684, 1601, 1579, 1485, 1437, 1358, 1295, 1244, 1164, 1126, 1022, 967, 806, 763, 595, 534. This compound has also been characterized elsewhere.<sup>4,5</sup>

**2-Bromo-1-(2-methoxyphenyl)ethanone (8).** This compound was prepared according to a known procedure.<sup>6</sup> A solution of the 1-(2-methoxyphenyl) ethanone (**7**, 5.0 g, 33.3 mmol) and copper (II) bromide (18.7 g, 70 mmol) in ethyl acetate/CHCl<sub>3</sub> (80 mL, 1:1, v/v) was vigorously stirred and refluxed overnight (the reaction progress was monitored by GC). The mixture was then cooled to 20 °C, filtered through a pad of silica, and concentrated under reduced pressure. The title product was purified using column chromatography (dichloromethane/petroleum ether, 1:4, v/v); nevertheless, a crude mixture of **8** and a side-product (2,2-dibromo-1-(2-methoxyphenyl)ethanone, ~5%) was used in the subsequent step. Yield: 4.5 g (60 %); light yellow oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 3.82 (s, 3H), 4.50 (s, 2H), 6.91 (t, 2H, *J* = 7.6 Hz), 7.38–7.44 (m, 1H), 7.71 (dd, 1H, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 1.7 Hz). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 37.7, 55.5, 111.6, 120.6, 124.3, 130.9, 134.5, 158.5, 191.5. MS (EI, 70 eV): 228 (7), 148 (<1), 135 (100), 120 (3), 105 (3), 91 (10), 77 (19), 63 (4), 51 (5). FTIR (KBr, cm<sup>-1</sup>): 2930, 2843, 1740, 1682, 1597, 1485, 1437, 1366, 1298, 1243, 1163, 1021, 1109, 1021, 993, 759, 696, 618, 529. This compound has also been characterized elsewhere.<sup>7,8</sup>

**2,2-Dibromo-1-(2-methoxyphenyl)ethanone.** This compound was obtained from the previous procedure and purified using column chromatography (dichloromethane/petroleum ether, 1:4). Yield: 0.5 g (5%); white crystalline powder; mp 35.0–36.7 °C (lit. 50–51 °C).<sup>9</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 3.92 (s, 3H), 6.97 (d, 1H, J = 8.3 Hz), 7.00 (t, 1H, J = 7.6 Hz), 7.09 (s, 1H), 7.47–7.55 (m, 1H), 7.78 (dd, 1H,  $J_1 = 7.7$  Hz,  $J_2 = 2.0$  Hz). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 45.0, 56.1, 111.9, 121.4, 122.0, 132.4, 135.3, 158.3, 187.7. MS (EI, 70 eV): 310 (1), 308 (2), 306 (1), 171 (4), 169 (4), 135 (100), 120 (3), 105 (5), 92 (10), 77 (21), 63 (11), 51 (14), 39 (2). FTIR (KBr, cm<sup>-1</sup>): 3049, 2945, 2839, 1691, 1595, 1482, 1432, 1295, 1254, 1163, 1109, 1052, 1014, 981, 816, 785, 754, 699, 627, 524. This compound has also been characterized elsewhere.<sup>9</sup>

**2-(2-Methoxyphenyl)-2-oxoethyl acetate (6).** This compound was prepared according to a known procedure.<sup>6</sup> A solution of 2-bromo-1-(2-methoxyphenyl)ethanone (**8**, 4.5 g, 19.6 mmol) in acetone (5 mL) and triethylamine (2.75 mL, 19.6 mmol) was added to a solution of acetic acid (1.18 g, 1.13 mL, 19.6 mmol) in acetone (30 mL) at 20 °C. The reaction mixture was then refluxed; the reaction conversion was monitored by GC. After the starting material was consumed (~2 h), the reaction mixture was cooled to 20 °C, filtered, and the solvent was removed under reduced pressure. The remaining solid was dissolved in ethyl acetate (20 mL)

and water (20 mL) was added; the aqueous layer was washed with ethyl acetate (20 mL), and the combined organic layers were washed with water (20 mL) and brine (20 mL), dried over MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure to give the crude product. The title product was purified using column chromatography (ethyl acetate/*n*-hexane, 1:4). Yield: 1.75 g (43%); white crystals; mp 101.4–104.5 °C (lit. 55 °C).<sup>10</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 2.21 (s, 3H), 3.94 (s, 3H), 5.23 (s, 2H), 6.99 (d, 1H, *J* = 8.4 Hz), 7.05 (d, 1H, *J* = 7.3 Hz), 7.49–7.55 (m, 1H), 7.93 (dd, 1H, *J*<sub>1</sub> = 7.8 Hz, *J*<sub>2</sub> = 1.8 Hz) (Figure S21). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 20.6, 55.6, 70.0, 111.6, 121.0, 124.3, 130.9, 135.0, 159.5, 170.6, 193.0 (Figure S22). MS (EI, 70 eV): 208 (5), 149 (<1), 135 (100), 120 (2), 105 (2), 92 (5), 77 (12). FTIR (KBr, cm<sup>-1</sup>): 3340, 2954, 2030, 1741, 1680, 1596, 1376, 1230, 1116, 967, 828, 767, 671, 635, 455. UV-vis (H<sub>2</sub>O/MeCN, 9:1):  $\varepsilon_{313}$  = 4300 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>;  $\varepsilon_{366}$  = 30 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> (Figure S23). HRMS (APCI<sup>+</sup>) calcd for C<sub>11</sub>H<sub>12</sub>O<sub>4</sub> [M + H<sup>+</sup>] 209.0808, found 209.0806. This compound has also been characterized elsewhere.<sup>10</sup>

#### Laser Flash Photolysis

**Quenching of**  ${}^{3}\mathbf{3}^{-*}$ . Potassium sorbate was used as a triplet quencher ( $E_{\rm T} = 59$  kcal/ mol)<sup>11</sup> in determination of the excited state multiplicity of **3** in water. The inherent decay rate constant of  ${}^{3}\mathbf{3c}^{-*}$  in water ( $k_0$ ) and the bimolecular quenching rate constant ( $k_q$ ) of  ${}^{3}\mathbf{3c}^{-*}$  using potassium sorbate (Q) were calculated from a linear fit of the dependence of the observed rate constant of  ${}^{3}\mathbf{3c}^{*}$  decay at  $\lambda_{obs} = 460$  nm ( $k_{obs}$ ) on the Q concentration (Eq S1; Figure S1a).

$$k_{obs} = k_0 + k_q [Q]$$
Eq S1  

$$k_{obs} = (2.9 \pm 1.0) \times 10^6 \text{ s}^{-1} + (2.8 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1} [Q]$$
Eq S2

The values of  $k_0 = (2.9 \pm 1.0) \times 10^6 \text{ s}^{-1}$  and  $k_q = (2.8 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  were obtained (Eq S2). The rate  $k_q$  is near diffusion controlled, which suggests that an efficient triplet energy transfer between  ${}^3\mathbf{3c}^{-*}$  and potassium sorbate occurred. Comparison of the triplet-triplet absorption spectra of pure **3c** in an aerated aqueous solution ( $\lambda_{\text{max}} = 460 \text{ nm}$ ,  ${}^3\mathbf{3c}^{-*}$  was present) and **3c** in aq potassium sorbate (0.1 M, only **3c**<sup>-</sup> was observed) also advocated the quenching process (Figure S1b).



**Figure S1.** (a) Plot of the  ${}^{3}3c^{-*}$  decay rate constants (monitored at  $\lambda_{obs} = 460$  nm) against the concentration of potassium sorbate in an aerated aqueous solution; (b) the transient absorption spectra of **3c** without (red,  ${}^{3}3c^{-*}$  was present) and with potassium sorbate (0.1 M) (black, **3c**<sup>-</sup> was present) in aerated water solutions recorded 20 and 30 ns, respectively, following a  $\lambda_{exc} = 355$  nm flash.

Sensitized Formation of <sup>3</sup>3\*. Xanthenone was chosen as a sensitizer possessing welldetectable and relatively long-lived triplet in various organic solvents<sup>12</sup> and the triplet energy of  $E_{\rm T} = 74.6$  kcal/mol.<sup>13</sup> It was excited at  $\lambda_{\rm exc} = 355$  nm and its triplet state was monitored at 600 nm; its lifetime was 100 ns in aerated water/acetonitrile (1:1) and 4.7 µs in degassed water/acetonitrile (1:1, v/v) solutions ( $c_{\rm xanthenone} = 0.37$  mM).

Both **3b** and **3c** quenched the xanthenone triplet in degassed water/acetonitrile (1:1, v/v) solution with the rate constants of  $k_q$  (**3b**) =  $(3.8 \pm 0.2) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, and  $k_q$  (**3c**) =  $(3.5 \pm 0.2) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> calculated from the linear fit of the dependence of the observed decay rate constant  $k_{obs}$  (at  $\lambda_{obs} = 600$  nm) on the concentration of **3b** or **3c** using Eq S1 (Figure S3). The near diffusion controlled rate constants suggests that an efficient triplet energy transfer from the xanthenone triplet to **3b**, **c** occurred.

The triplet-triplet absorption spectra of xanthenone in the presence of **3c**, indicating a triplet energy transfer process, are shown in Figure S2.



**Figure S2.** Triplet-triplet transient absorption spectra of xanthenone (black), **3c**  $(3.2 \times 10^{-4} \text{ M})$  with xanthenone (blue), and **3c**  $(1.5 \times 10^{-3} \text{ M})$  with xanthenone (red). All spectra were measured in H<sub>2</sub>O/CH<sub>3</sub>CN (1:1, v/v) solutions in a 50-ns time window following 23 ± 5 ns after laser flash at  $\lambda_{\text{exc}} = 355$  nm. The concentration of xanthenone was c = 0.37 mM in all samples.





**Figure S3.** Plot of the observed rate constants of xanthenone decay (at  $\lambda_{obs} = 600$  nm) against the concentration of (a) **3b** and (b) **3c** in degassed water/acetonitrile (1:1, v/v) using a  $\lambda_{exc} = 355$  nm laser flash.



**Figure S4.** Transient absorption spectra of (a) 4 ( $2.5 \times 10^{-4}$  M) recorded 20 ns (black) and 5  $\mu$ s (red) after excitation in aerated aqueous malonate buffer (pH = 5.5, *I* = 0.1 M); and (b) 4 ( $2.5 \times 10^{-4}$  M) in aerated aqueous HCl solution (pH = 1.5) recorded 50 ns (black) and 5  $\mu$ s (red) after the laser flash. All samples were excited at  $\lambda_{exc} = 266$  nm.



**Figure S5.** Transient absorption spectra of (a) **3b**  $(3 \times 10^{-4} \text{ M})$  recorded in aerated acetonitrile (black) and aerated *n*-hexane (red), respectively in a 50-ns time window after 35 ns delay following a  $\lambda_{\text{exc}} = 266 \text{ nm flash}$ ; (b) normalized transient absorption spectra of **3c**  $(3 \times 10^{-3} \text{ M})$  recorded in aerated acetonitrile (black) and aerated *n*-hexane (red) in a 50-ns time window after a 50 ns delay following a  $\lambda_{\text{exc}} = 266 \text{ nm flash}$ ; (b) normalized transient absorption spectra of **3c**  $(3 \times 10^{-3} \text{ M})$  recorded in aerated acetonitrile (black) and aerated *n*-hexane (red) in a 50-ns time window after a 50 ns delay following a  $\lambda_{\text{exc}} = 266 \text{ nm flash}$ .





**Figure S6.** Transient absorption spectra of (a) **3b** recorded 15 ns after a  $\lambda_{exc} = 266$  nm flash, and (b) **3c** recorded 17 ns after a  $\lambda_{exc} = 355$  nm flash in aerated aqueous solutions.



**Figure S7.** Transient absorption spectrum of **3b** in  $H_2O/CH_3CN$  (95:5, v/v) with NaOH (1 mM; pH = 11.2) recorded 50 ns after a 266 nm flash.



**Figure S8.** Transient absorption spectrum of **3b** in water/acetonitrile 95:5 (v/v; pH = 2, adjusted with conc. aq HClO<sub>4</sub>) recorded in a 10-ns window following after a 17 ns delay after a  $\lambda_{\text{exc}} = 266$  nm flash.



**Figure S9.** Transient triplet-triplet absorption spectra of **3c** in aqueous acetate buffer (pH = 5.5; I = 0.01 M, red) and in aqueous HClO<sub>4</sub> (pH = 1, black) recorded 20 ns after excitation with a laser pulse at  $\lambda_{exc} = 266$  nm.



**Figure S10.** A kinetic trace obtained by laser flash photolysis of **3c** (monitored at  $\lambda_{obs}$  = 460 nm) after excitation at  $\lambda_{exc}$  = 266 nm in an aerated non-buffered aqueous solution.

### **Quantum Chemical Calculations**

Quantum chemical calculations were performed with the Gaussian 09 package (revision A.02) of programs.<sup>14</sup> Geometries were fully optimized at the BMK level of theory with the standard 6-311+G(d,p) basis set and the PCM solvation model for water environment ( $\varepsilon$  = 78.3553) with default settings of Gaussian 09. The unrestricted formalism was used in the case of the triplet state species. For all stationary points, harmonic vibrational frequencies were computed. Zero-point corrections were scaled by a factor of 0.9857<sup>15</sup> to provide energies at 0 K. Single point energies at the BMK geometries were computed at the B2PLYP level of theory with the 6-311+G(2df,2p) basis set in PCM. Electronic transitions were calculated using the time-dependent density functional theory (TD-DFT) approach employing the B3LYP/6-311+G(d,p) level of theory. Complete UV-VIS spectra were obtained using the linearized harmonic reflection principle as employed by Wirz and coworkers<sup>16</sup> where equilibrium solvation is used. Solvent water was also simulated by adding explicit water molecules to the specific sites of the solute in a polarizable continuum.

## $(U)B2PLYP/6-311+G(2df,2p)//(U)BMK/6-311+G(d,p)\ energies\ in\ kcal\ mol^{-1}\ with\ solvation\ mod$

#### PCM 2W/PCM

#### SINGLET GROUND STATE



**Figure S11.** The calculated relative energies of the singlet ground state and the triplet state of **4** and **q4**. The drawings are schematic representations of the real optimized structures.



Figure S12. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 2-(2-Hydroxyphenyl)-2-oxoethyl Benzoate (3a)





Figure S14. UV-vis (both dry and aqueous CH<sub>3</sub>CN): 2-(2-Hydroxyphenyl)-2-oxoethyl Benzoate (3a)



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Figure S17. UV-vis (both dry and aqueous CH<sub>3</sub>CN): 2-(2-Hydroxyphenyl)-2-oxoethyl Acetate (3b)



**Figure S18.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 2-(2-Hydroxyphenyl)-2-oxoethyl Methanesulfonate (**3c**)





Figure S20. UV-vis (both dry and aqueous CH<sub>3</sub>CN): 2-(2-Hydroxyphenyl)-2-oxoethyl Methanesulfonate (3c)



**Figure S21.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 2-(2-Methoxyphenyl)-2-oxoethyl Acetate (6)

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Figure S23. UV-vis (in both dry and aqueous CH<sub>3</sub>CN): 2-(2-Methoxyphenyl)-2-oxoethyl Acetate (6)







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