Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Simultaneous Production of *p*-Tolualdehyde and Hydrogen Peroxide in Photocatalytic Oxygenation of *p*-Xylene and Reduction of Oxygen with 9-Mesityl-10-Methylacridinium Ion Derivatives

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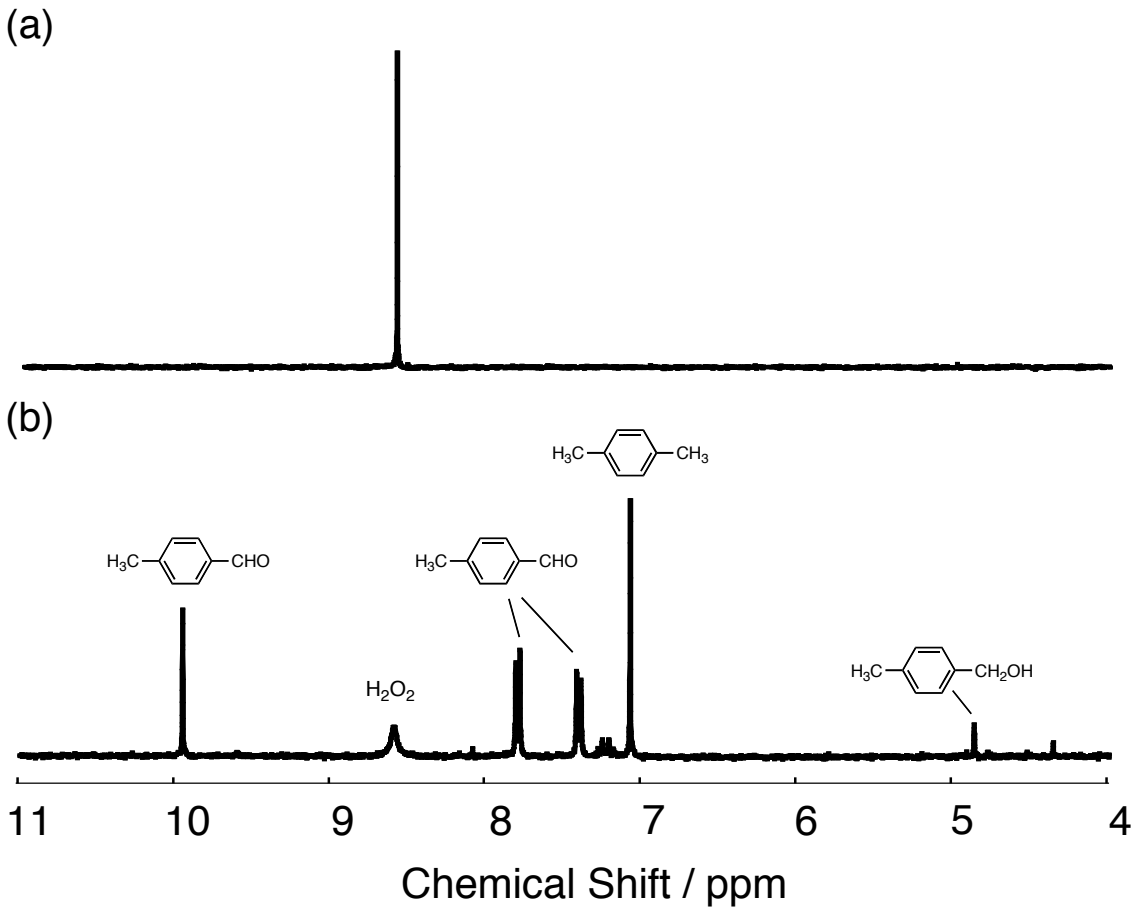

Fig. S1 ^{1}H NMR spectra of oxygen-saturated CD_3CN solutions containing (a) H_2O_2 (0.7 mM) and (b) Acr^{+}–Mes (2.0×10^{-4} M) and *p*-xylene (2.0×10^{-2} M) after photoirradiation for 60 min.

S2: Synthesis of [Me_2Acr^+–Mes]ClO_4^- and General Experimental Procedures:

Synthesis of [Me_2Acr^+–Mes]ClO_4^-: 2-Amino-5-methyl-benzoic acid (10 g, 66 mmol), K_2CO_3 (11 g, 79 mmol) and 4-bromotoluene (11 g, 66 mmol), $Pd(OAc)_2$ (300 mg, 2.0 mol%), and tri-*tert*-butylphosphine (1.08 g, 8 mol%) were dissolved in a solution of 1,4-dioxane (40 mL). The reaction mixture was stirred at 95˚C for 2 days under argon atmosphere. After being cooled room temperature, the reaction mixture was dropped into and ethyl acetate (50 mL) containing HCl (6 M, 50 mL). The organic layer was washed with three times of water (50 mL) and then was dried with Na_2SO_4. The solvent was evaporated at reduced pressure. The solvent was evaporated at reduced pressure. Recrystalization with ethanol gave 5-methyl-*N*-(4'-methyl)-phenylanthranilic acid (7.1 g, 45%). ^{1}H NMR (270 MHz; DMSO-d_6): δ 9.39 (brs, 1H), 7.70 (s, 1H), 7.20–7.06 (m, 6H), 2.27 (s, 3H), 2.20 (s, 3H) ppm. ^{13}C NMR (DMSO-d_6): δ 196.96, 145.34, 138.22, 134.95, 131.90, 131.57, 129.87, 125.61, 121.44, 113.78, 112.10, 20.38, 19.86 ppm.

5-Methyl-*N*-(4'-methyl)phenylanthranilic acid (6.9 g, 29 mmol) was dissolved in conc. H_2SO_4 (28 mL) and stirred at 90 ℃ for 1 h. After being cooled room temperature, the reaction mixture was gently dropped into distilled water (280 mL). The resulting precipitate was filtered, washed with twice of water (50 mL) and dried overnight at 60 ˚C under reduced pressure. 2,7-Dimethyl-9(10H)-acridone is obtained as yellow powder (5.71 g, 90%). ^{1}H NMR (DMSO-d_6): δ 11.41 (s, 1H), 8.03 (s, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 2.41 (s, 6H) ppm. ^{13}C NMR (DMSO-d_6): δ 176.10, 138.73, 134.31, 129.45, 124.82, 120.11, 116.93, 20.26 ppm.

2,7-Dimethyl-9(10H)-acridone (7.0 g, 34 mmol), NaOH (2.5 g, 63 mmol), methyl iodide (10 g, 70.4 mmol) and benzyltriethylammonium chloride (220 mg, 0.94 mmol) were dissolved in 2-butanone (28 mL) and water (28 mL), and stirred overnight at 60 ˚C. After being cooled room temperature, the reaction mixture was dropped into gently distilled water (480 mL). The precipitate was filtered, washed with twice of water (50 mL) and dried overnight at 60 ˚C under reduced pressure. Recrystallization with

methanol gave 2,7,10-trimethyl-9(10H)-acridone as a yellow powder (4.46 g, 72%). ^{1}H NMR (DMSO-d_6): δ 8.12 (s, 1H), 7.75 (d, J = 8.9 Hz, 2H), 7.64 (d, J = 8.9 Hz, 2H), 3.91 (s, 3H), 2.43 (s, 6H) ppm. ^{13}C NMR (DMSO-d_6): δ 176.07, 140.22, 134.97, 129.85, 125.66, 121.28, 115.83, 33.39, 20.15 ppm.

9-Mesityl-2,7,10-trimethylacridinium perchlorate ([Me_2Acr^+–Mes]ClO_4^-) was prepared by the reaction of 2,7,10-trimethyl-9(10H)-acridinone (1.0 g, 4.21 mmol) in dry THF (12.8 ml) with mesitylmagnesium bromide (8.85 mmol) stirring 63 ℃ for 4 h, followed by addition of water (12.8 mL) and 60% perchloric acid (1.45 mL) for the hydrolysis, then the precipitate was filtered and recrystallized from methanol. The yield was 1.15 g (66%). 9-Mesityl-2,7,10-trimethylacridinium perchlorate ([Me_2Acr^+–Mes]ClO_4^-): Anal. Calcd for $C_{25}H_{26}ClNO_4$: C, 68.25; H, 5.96; N, 3.18. Found: C, 67.98; H, 5.87; N, 3.29. ^{1}H NMR (CD_3CN): δ 8.57 (d, J = 9.6 Hz, 2H), 8.25 (d, J = 9.6 Hz, 2H), 7.59 (s, 2H), 7.29 (s, 2H), 4.86 (s, 3H), 2.56 (s, 6H), 2.54 (s, 3H), 1.76 (s, 6H) ppm. ^{13}C NMR (CD_3CN): δ 160.44, 141.64, 140.94, 140.87, 139.95, 136.95, 130.86, 129.65, 127.48, 127.21, 119.59, 39.45, 21.34 (2C), 19.95 ppm. MALDI-TOF-MS m/z = 340 (Me_2Acr^+–Mes Calcd for $C_{25}H_{26}N^+$, 340.2).

The photocatalytic reaction was carried out by the following procedure. Typically, an MeCN solution (0.6 mL) containing Me_2Acr^+–Mes (0.20 mM) and *p*-xylene (4.0 mM) in an NMR tube with a rubber septum was saturated with oxygen by bubbling oxygen through a stainless steel needle for 5 min. The solution was then irradiated with a 500 W xenon lamp (Ushio Optical ModelX SX-UID 500XAMQ) through a color filter glass (Asahi Techno Glass, λ = 380–500 nm) at 298 K. After photoirradiation, the corresponding aldehyde was identified and quantified by comparison of the ^{1}H NMR spectra with that of an authentic sample.

The amount of H_2O_2 was determined by titration by iodide ion; the diluted reaction mixture was treated with excess amount of NaI in MeCN. The amount of I_3^- formed was then determined from the UV-vis spectrum (λ_{max} = 361 nm, ε = 2.50 × 10^4 M^{-1}

cm^{-1} in MeCN). The yield of H_2O_2 was also determined by ^1H NMR spectroscopy when the photooxygenation was carried out in the absence of aqueous H_2SO_4. H_2O_2: ^1H NMR (CD_3CN): δ 8.67 (s, 2H).

Isolation of *p*-toluadehyde was carried out by the following procedure. Typically, Me_2Acr^+–Mes (60 mg, 0.136 mmol) and *p*-xylene (0.5 g, 4.72 mmol) were dissolved in an MeCN solution (100 mL) containing conc. H_2SO_4 (45 μg) and water (255 μL). The solution was stirred under photoirradiation with a xenon lamp attached with a colour glass filter (λ = 380–500 nm) for 12 h. The reaction mixture was neutralized by aqueous NaOH, diluted with hexane (100 mL) and distilled water (100 mL). The organic layer was washed with three times of water (50 mL x 3) and then was dried with Na_2SO_4. The isolation yield of *p*-tolualdehyde was 40%.

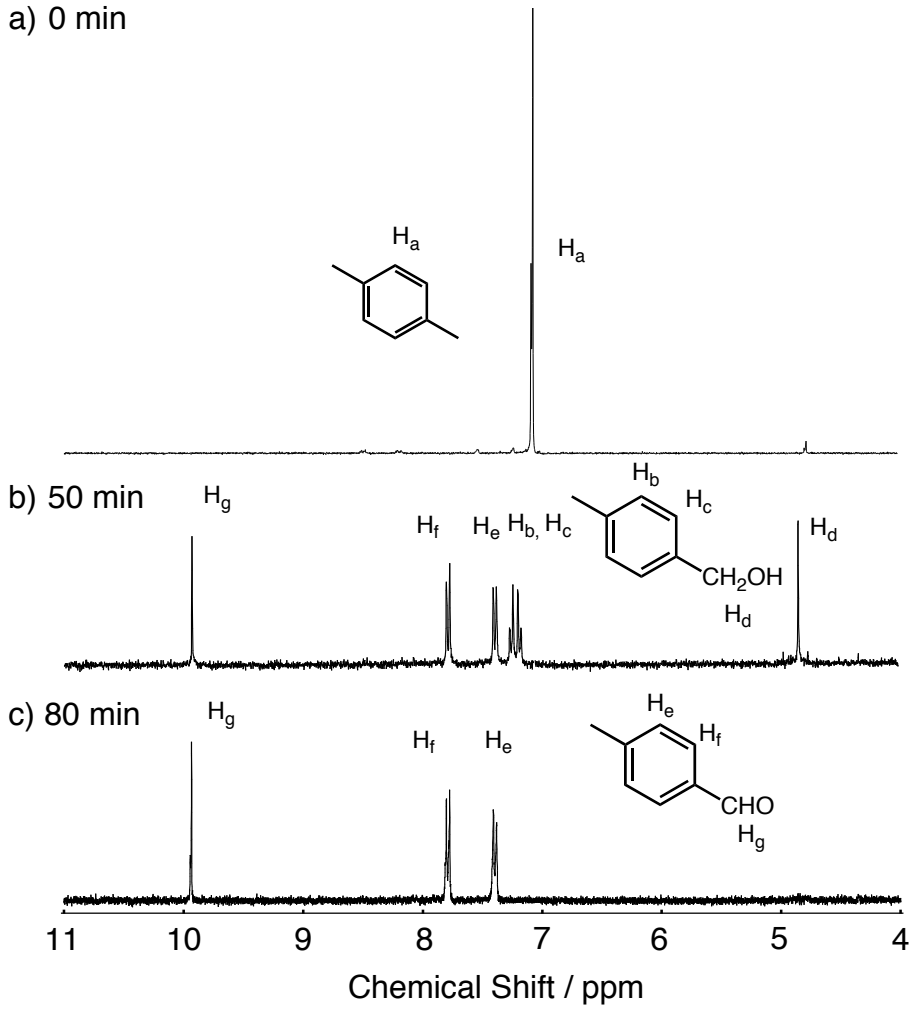

Fig. S3 ^{1}H NMR spectra of oxygen-saturated CD_3CN solutions containing Me_2Acr^+–Mes (2.0×10^{-4} M), *p*-xylene (4.0×10^{-3} M) and (a) before and (b)(c) after photoirradiation (50 min and 80 min, $\lambda > 380$ nm).

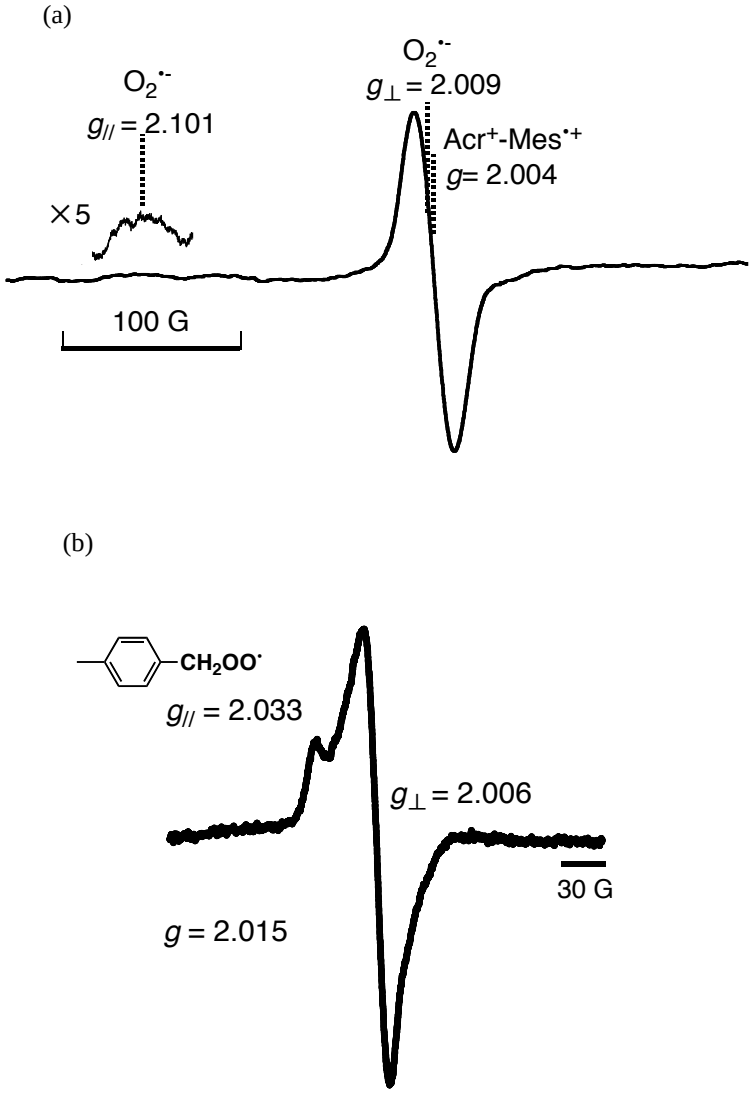

Fig. S4 ESR spectra observed under photoirradiation of an oxygen-saturated MeCN solution of Me_2Acr^+–Mes (1.0 x 10^{-3} M) (a) in the absence and (b) presence0 of *p*-xylene (4.0 x 10^{-2} M) at 198 K.

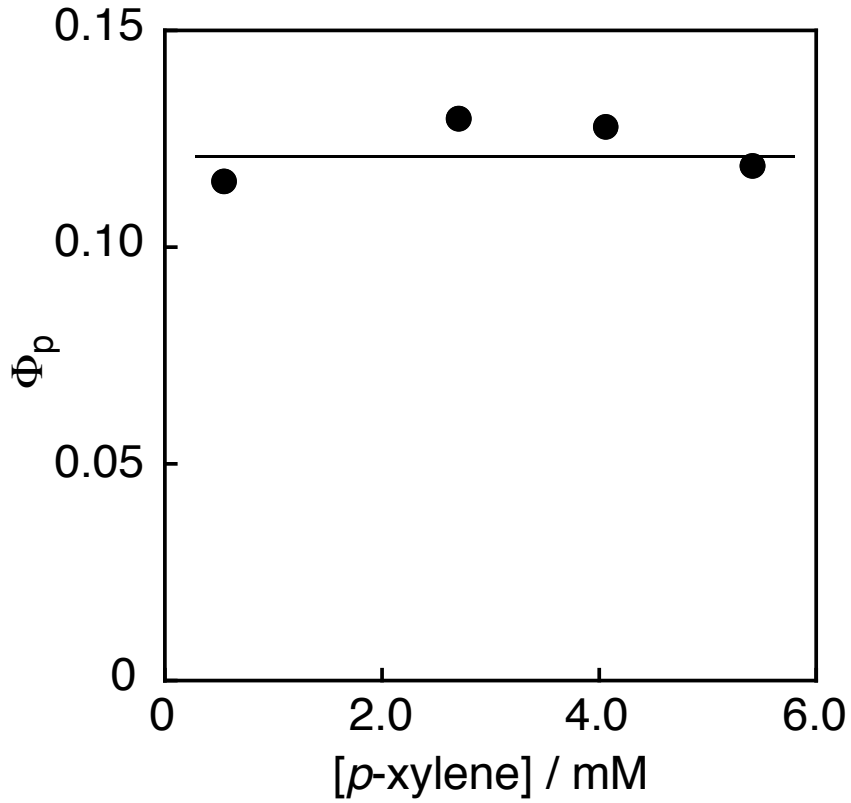

Fig. S5 Dependence of quantum yield of formation of *p*-tolualdehyde on concentration of *p*-xylene in phtocatalytic oxygenation of *p*-xylene with Me_2Acr^+–Mes (0.2 mM) in O_2-saturated MeCN.

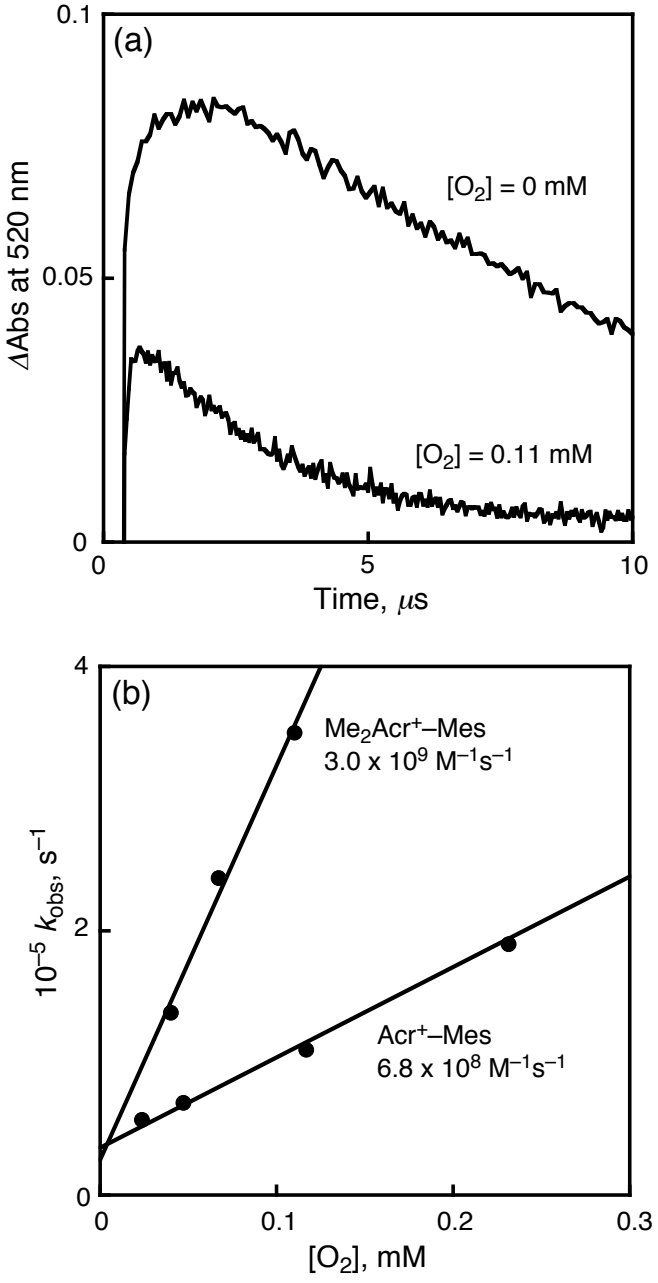

Fig. S6 (a) Absorbance time profiles at 520 nm due to $Me_2Acr^{\bullet}$–$Mes^{\bullet+}$ in the in aerated and deaerated MeCN containing Me_2Acr^{+}–Mes (1.0×10^{-4} M); (b) Plot of the pseudo-first-order rate constant (k_{obs}) for electron transfer from the $Acr^{\bullet}$ moiety of $Acr^{\bullet}$–$Mes^{\bullet+}$ and $Me_2Acr^{\bullet}$–$Mes^{\bullet+}$ to O_2 vs $[O_2]$.