

Supplementary Information

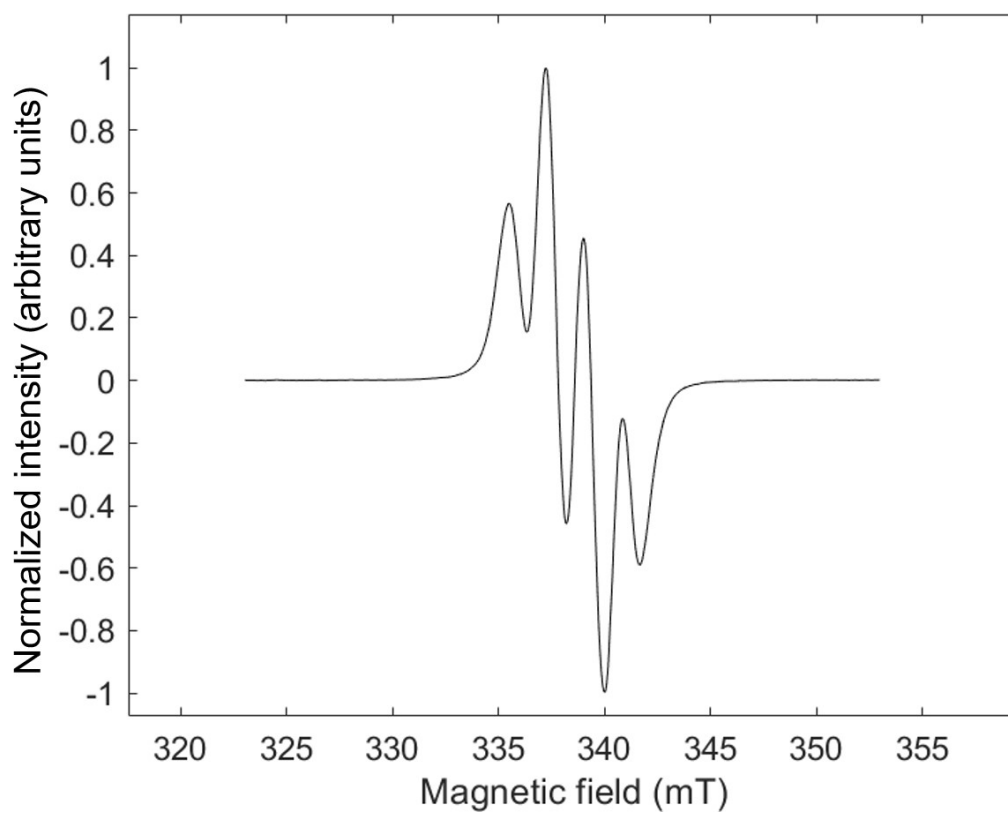


Fig. S1 X-band ESR spectrum measured at 77 K in photo-irradiated supercooled 300 mM aqueous pyruvic acid solution.

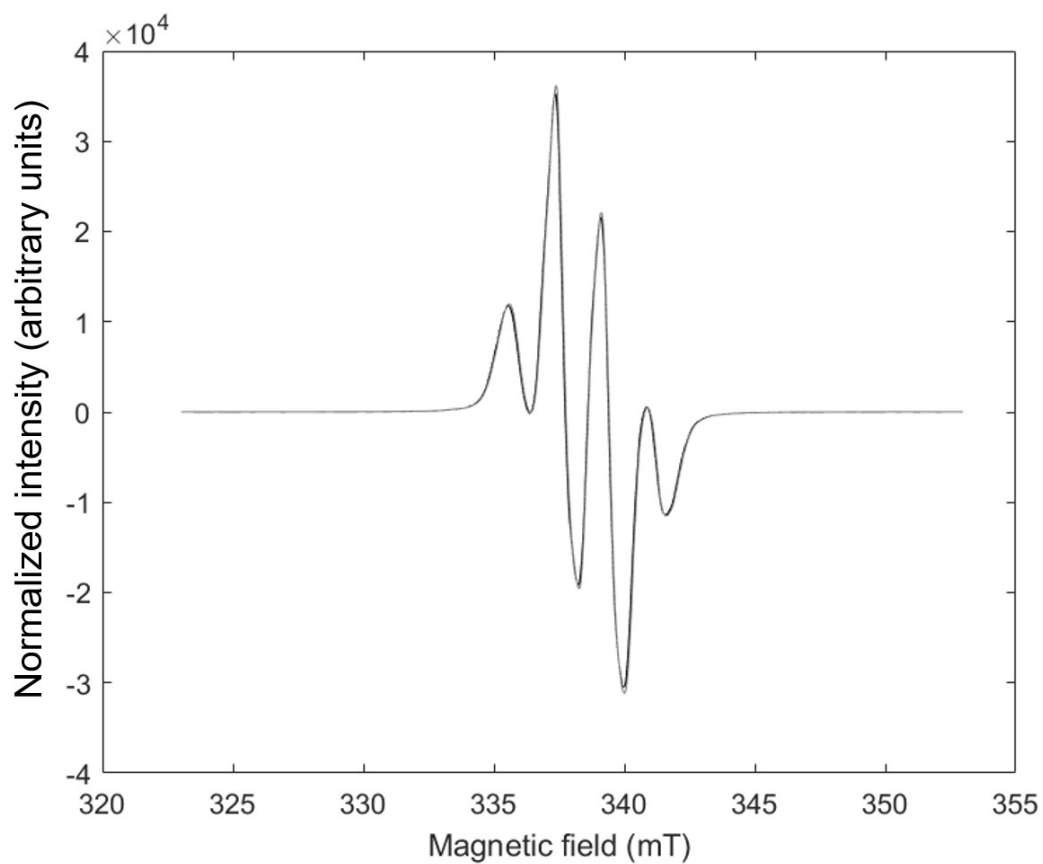


Fig. S2 X-band ESR spectra measured at 77 K in photo-irradiated supercooled neat pyruvic acid prepared with (black) and without (grey) sparging argon gas prior to snap freezing pyruvic acid. The radical concentration was 60 ± 4 mM in both samples.

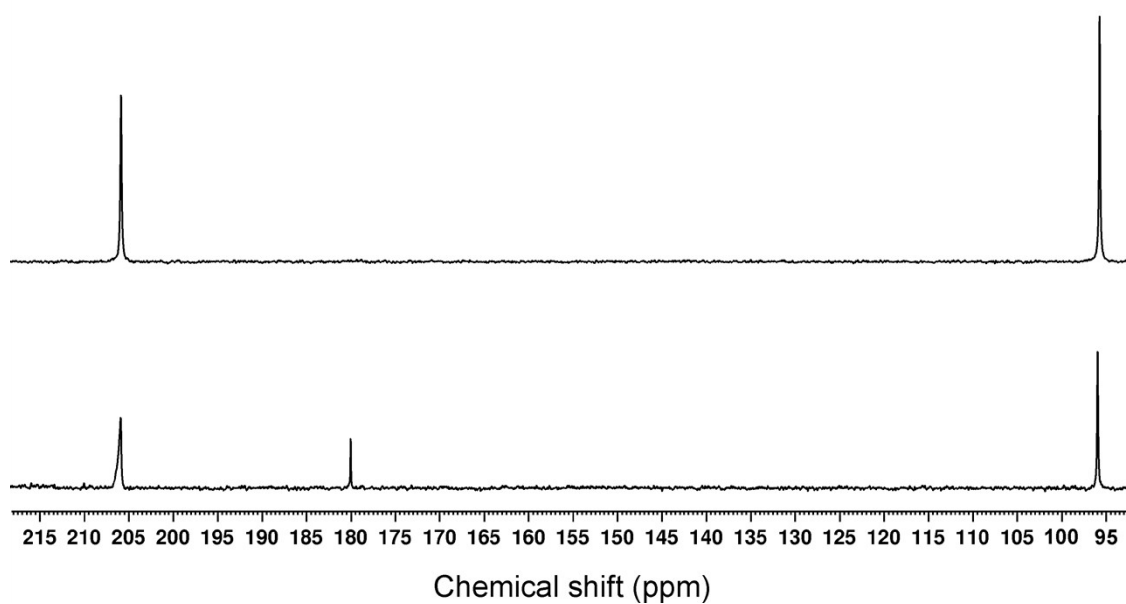


Fig. S3 Room-temperature liquid-state ^{13}C NMR spectra of dissolved photo-irradiated (bottom) and non-photo-irradiated (top) supercooled 300 mM aqueous $[2-^{13}\text{C}]$ PA sample (24 μL) dissolved in 500 μL D_2O . The singlet peaks from the keto form (205.3 ppm) and the hydrated form (95.2 ppm) are visible. The singlet peak from the breakdown product $[1-^{13}\text{C}]$ acetic acid appears on the photo-irradiated spectrum at 179.7 ppm.

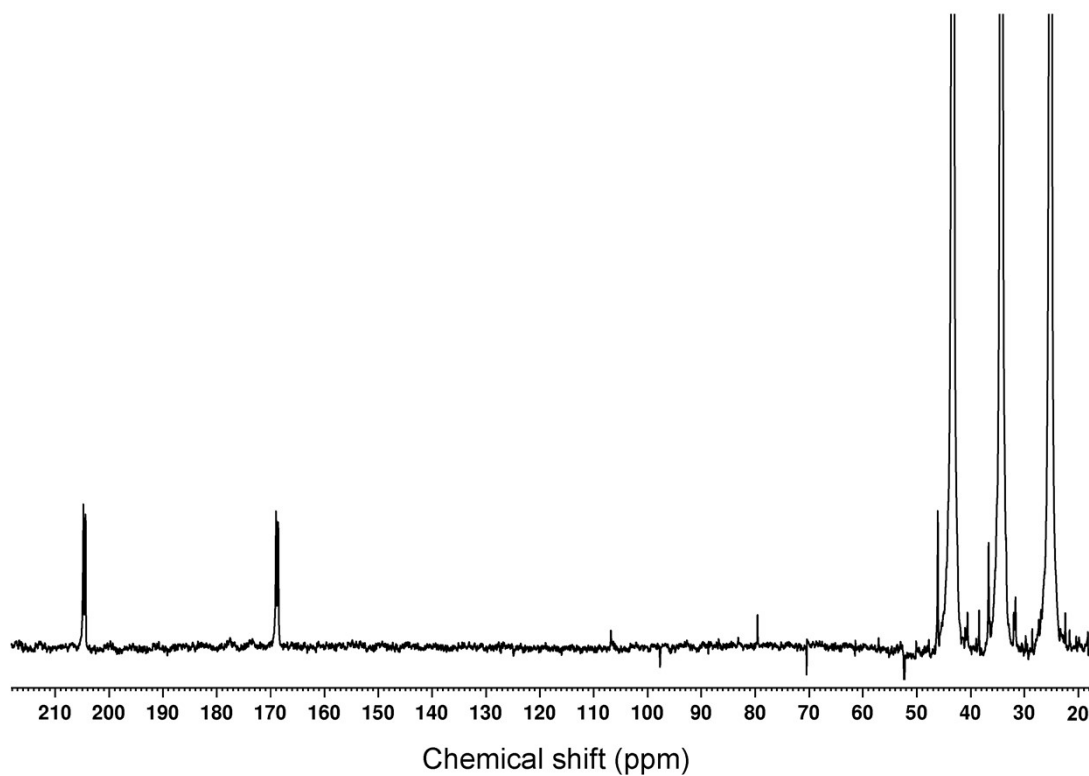


Fig. S4 Room-temperature liquid-state ^{13}C NMR spectrum (600 MHz) of photo-irradiated supercooled 300 mM $[1,2-^{13}\text{C}_2]$ PA solution in hexane (24 μL) dissolved in 500 μL D_2O . The natural abundance ^{13}C hexane peaks (25 ppm, 34 ppm, and 43 ppm) were observed along with the keto form of $[1,2-^{13}\text{C}_2]$ pyruvic acid (C1 at 169 ppm, and C2 at 205 ppm). No $^{13}\text{CO}_2$ was detected.