

Environmental Processing of Lipids Driven by Aqueous Photochemistry of α -Keto Acids

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Supporting Information

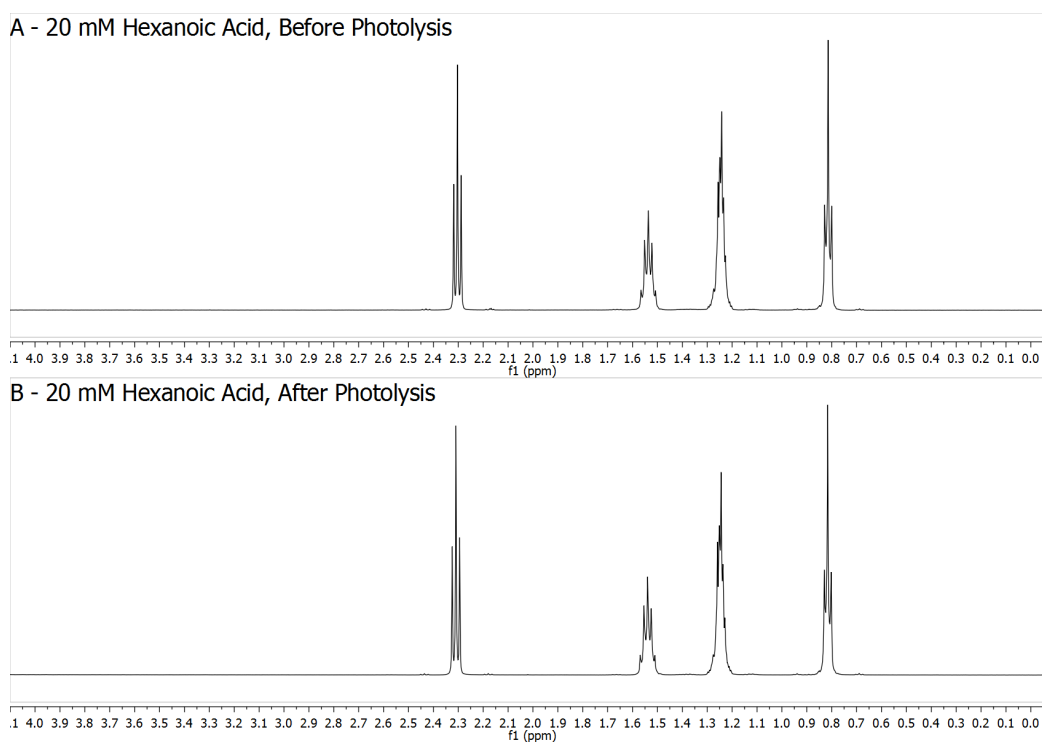


Figure S1. Representative NMR spectra of 20 mM hexanoic acid before (A) and after (B) 5 hours of photolysis. No observable differences are present between the two solutions.

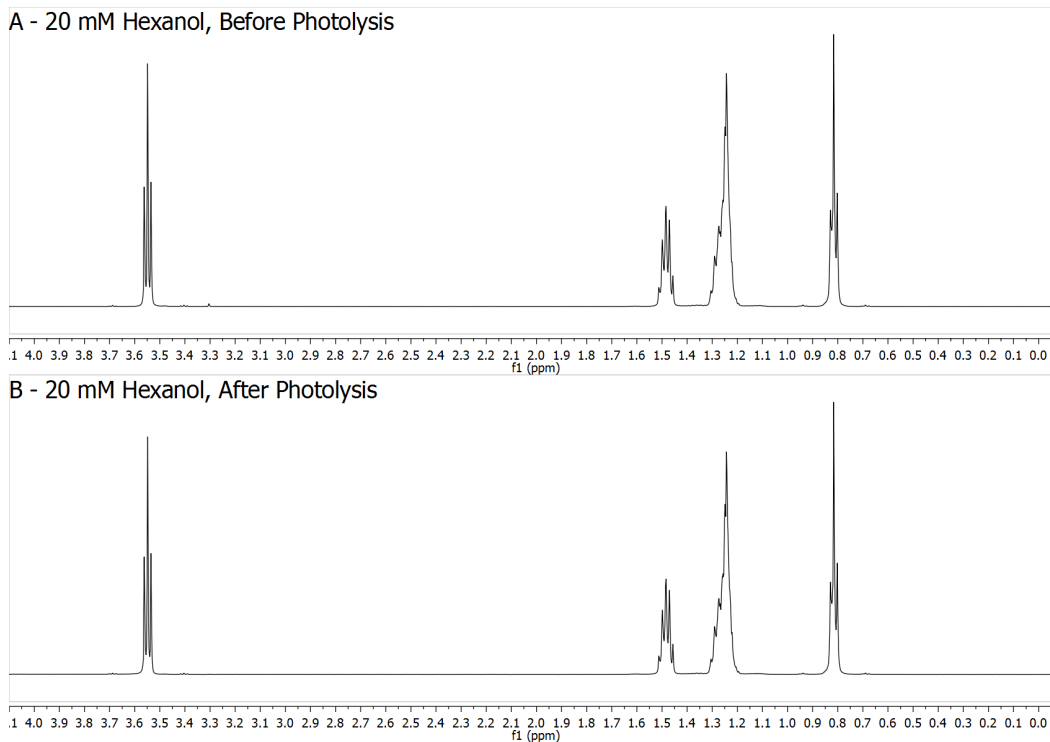


Figure S2. NMR spectra of 20 mM hexanol before (A) and after (B) 5 hours of photolysis. No observable differences are present between the two solutions.

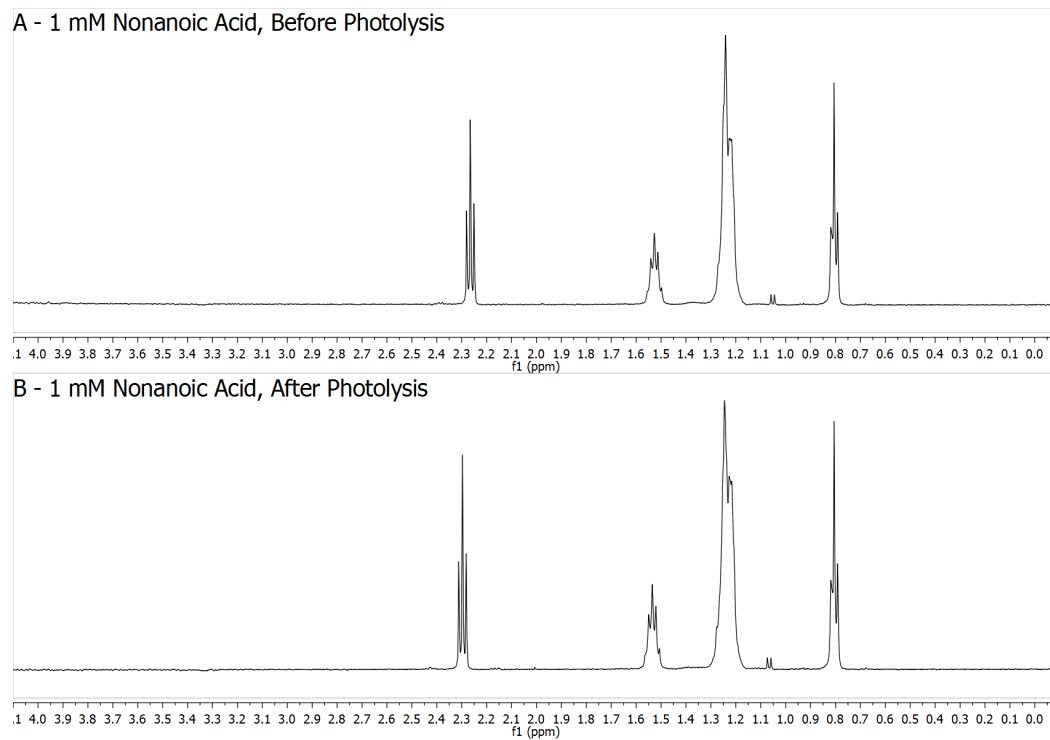


Figure S3. Representative NMR spectra of 1 mM nonanoic acid before (A) and after (B) 5 hours of photolysis. No observable differences are present between the two solutions.

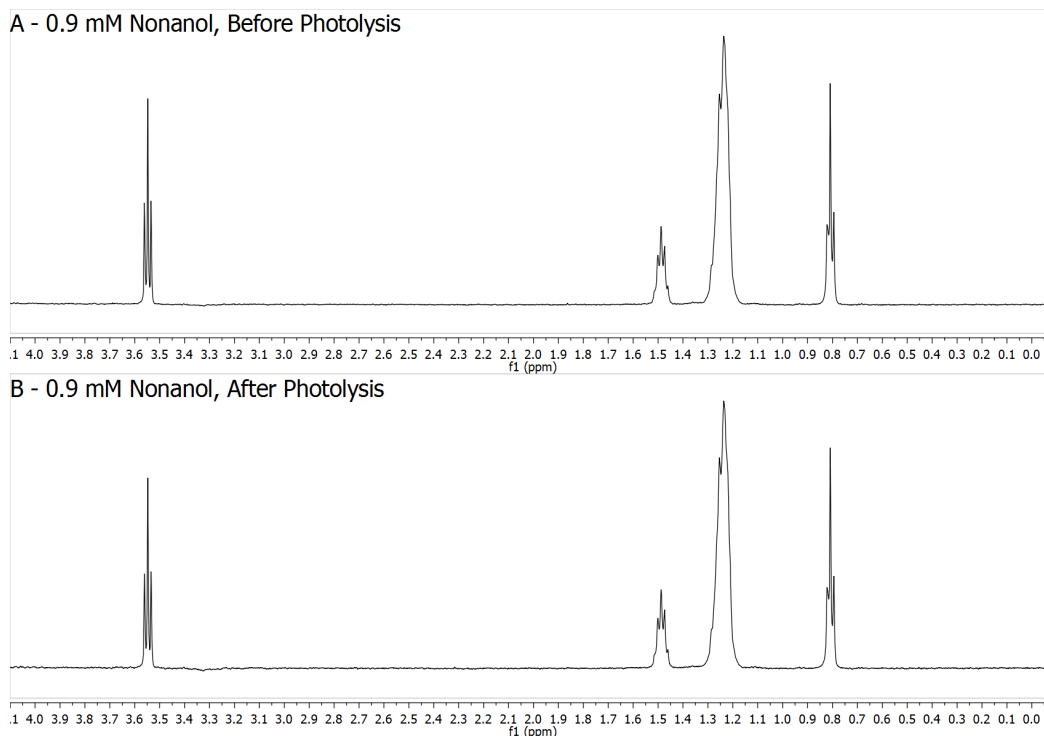


Figure S4. Representative NMR spectra of 0.9 mM nonanol before (A) and after (B) 5 hours of photolysis. No observable differences are present between the two solutions.

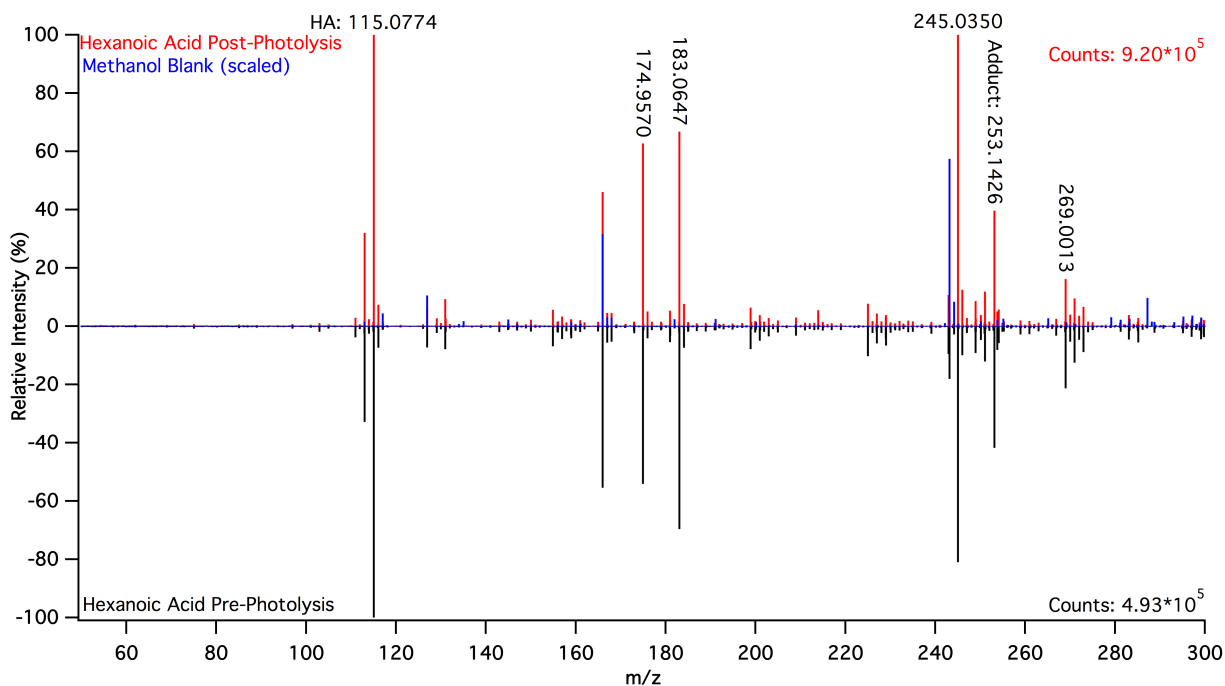


Figure S5. Representative ESI⁻ MS of 20 mM hexanoic acid solutions before (black, multiplied by -1 for ease of presentation), after 5 hours of photolysis (red), and the corresponding methanol blank (blue). There is essentially no difference between the pre- and post-photolysis solutions.

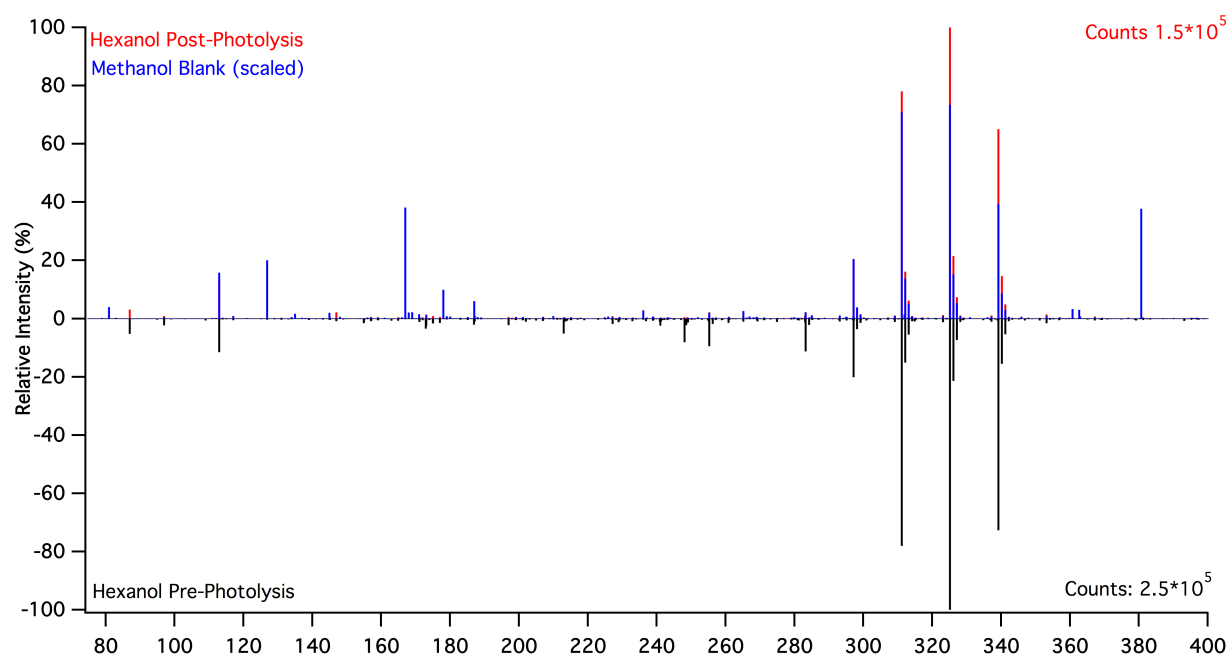


Figure S6. Representative ESI⁻ MS of 20 mM hexanol solutions before (black, multiplied by -1 for ease of presentation), after 5 hours of photolysis (red), and the corresponding methanol blank (blue). Essentially all the observed signal is due to species also present in the methanol blank.

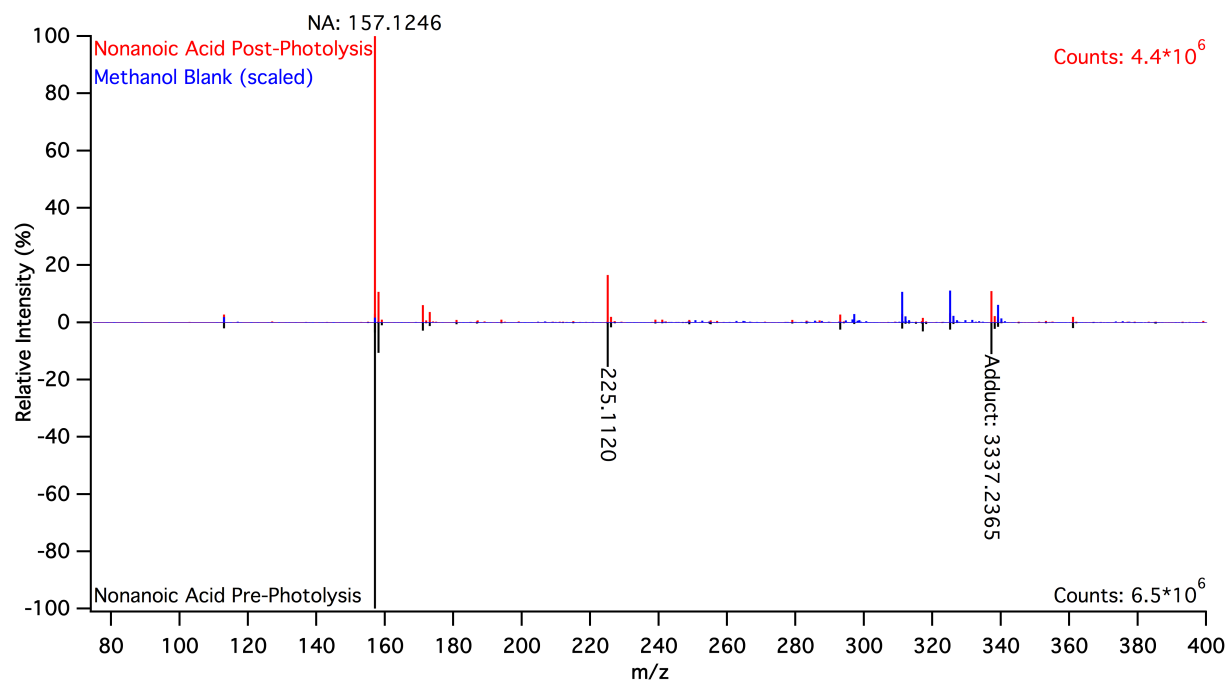


Figure S7. Representative ESI⁻ MS of 1 mM nonanoic acid solutions before (black, multiplied by -1 for ease of presentation), after 5 hours of photolysis (red), and the corresponding methanol blank (blue). There is essentially no difference between the two samples.

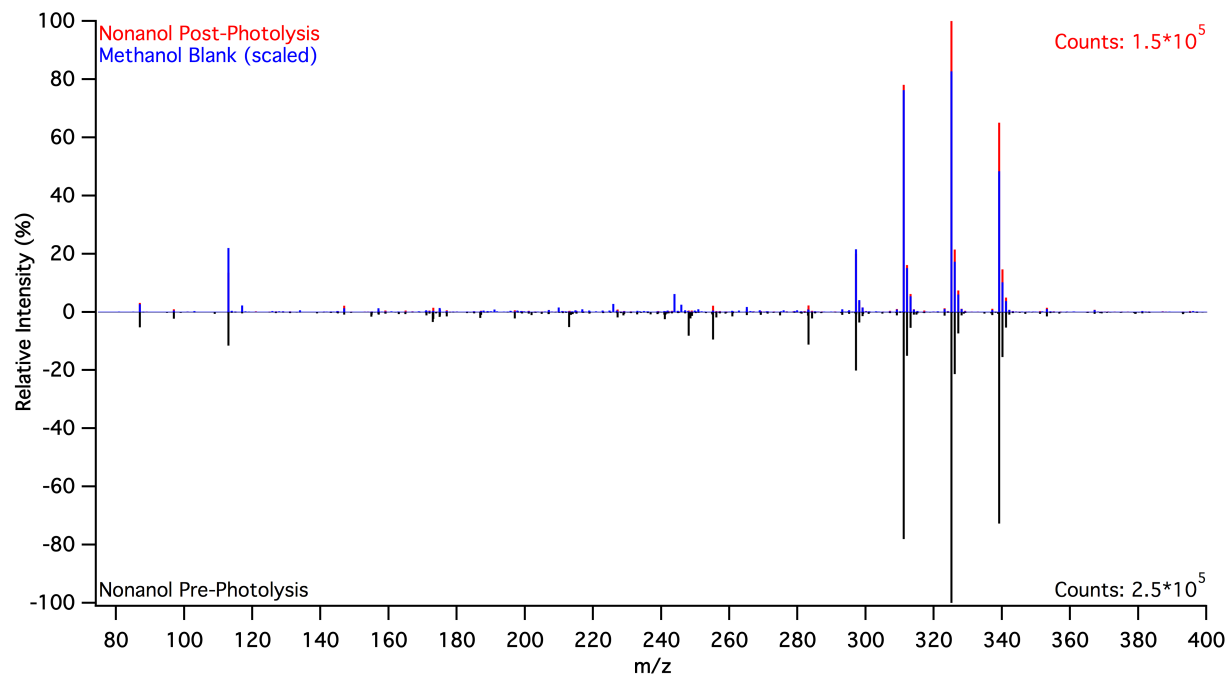


Figure S8. Representative ESI⁻ MS of 0.9 mM nonanol solutions before (black, multiplied by -1 for ease of presentation), after 5 hours of photolysis (red), and the corresponding methanol blank (blue). Essentially all of the signal observed is due to species that are also present in the methanol blank.

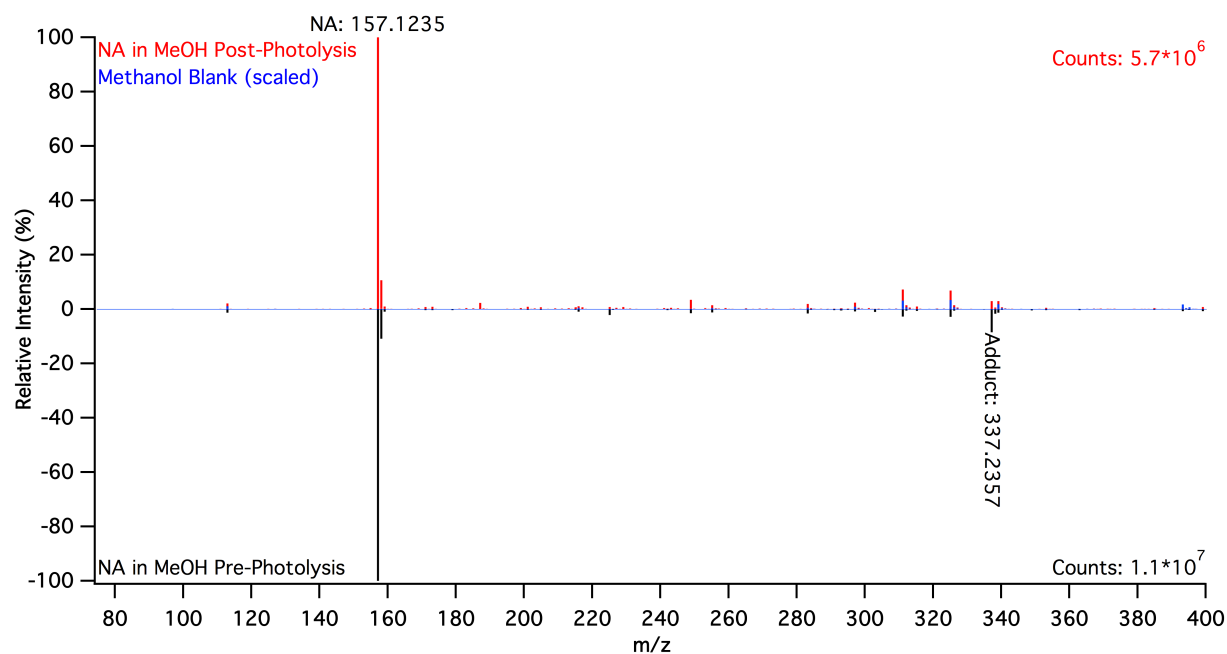


Figure S9. Representative ESI⁻ MS of 100 mM nonanoic acid dissolved in methanol before (black, multiplied by -1 for ease of presentation), after 5 hours of photolysis (red), and the corresponding methanol blank (blue). There is essentially no difference between the two samples.

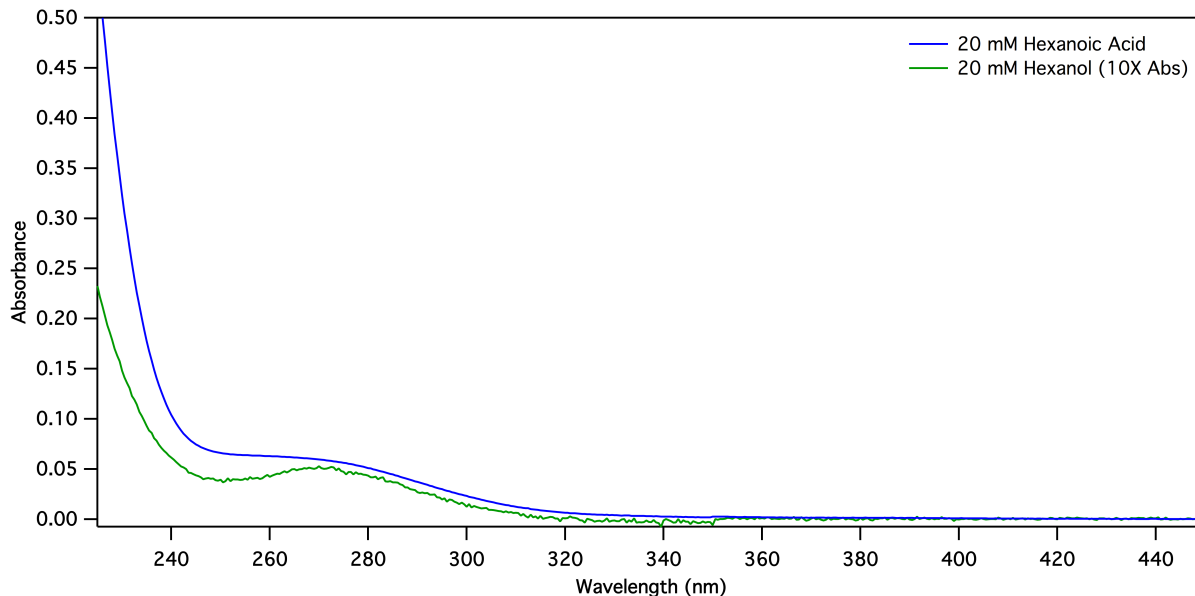


Figure S10. Representative UV-vis absorption spectra of 20 mM hexanoic acid (blue) and 20 mM hexanol (green). The absorbance of hexanol has been multiplied by 10 for clarity.

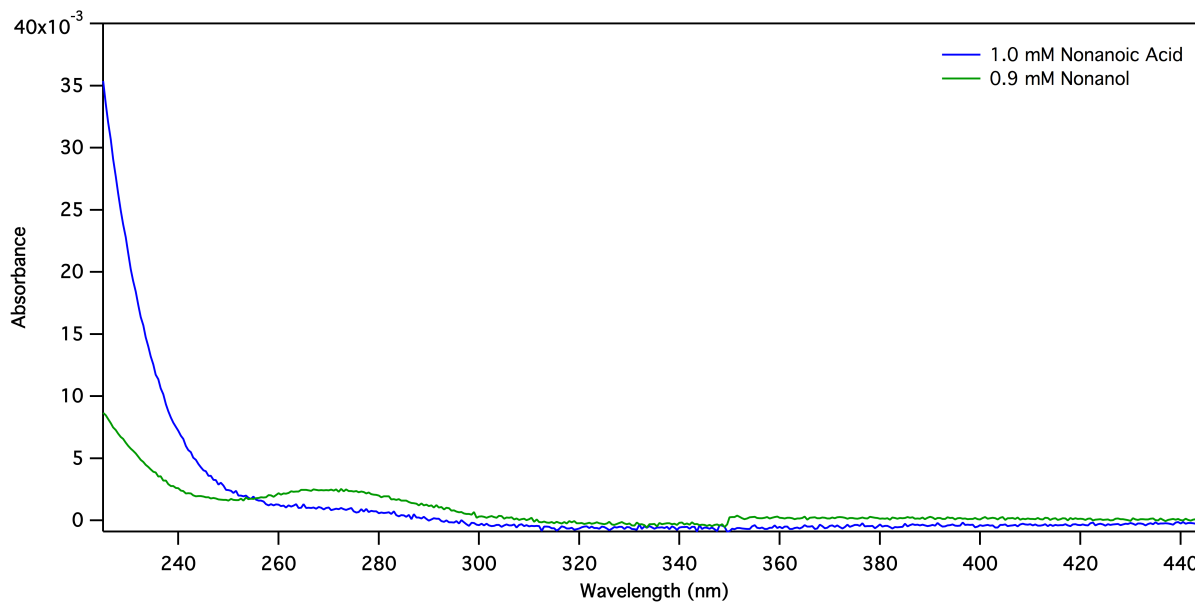


Figure S11. Representative UV-vis absorption spectra of 1 mM nonanoic acid (blue) and 0.9 mM nonanol (green).



Figure S12. Representative UV-vis absorption spectra of 10 mM nonanoic acid dissolved in methanol before (purple) and after (black) distillation.

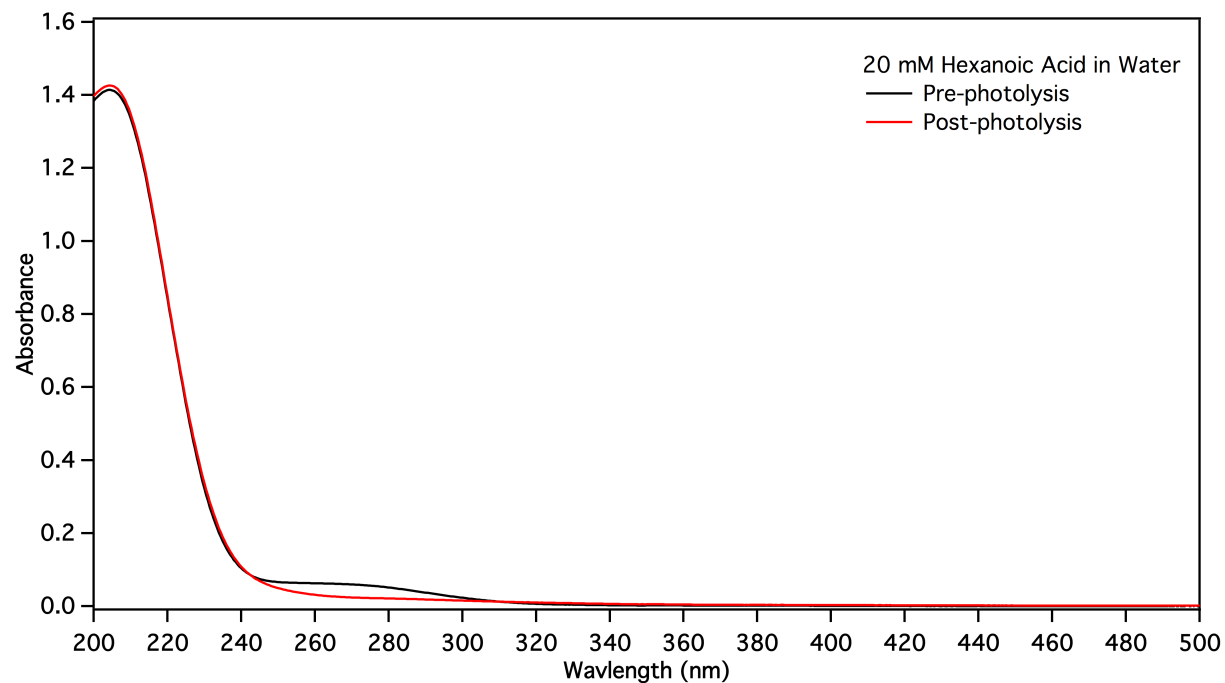


Figure S13. UV-vis spectra of distilled 20 mM hexanoic acid before (black) and after (red) 5 hours photolysis.

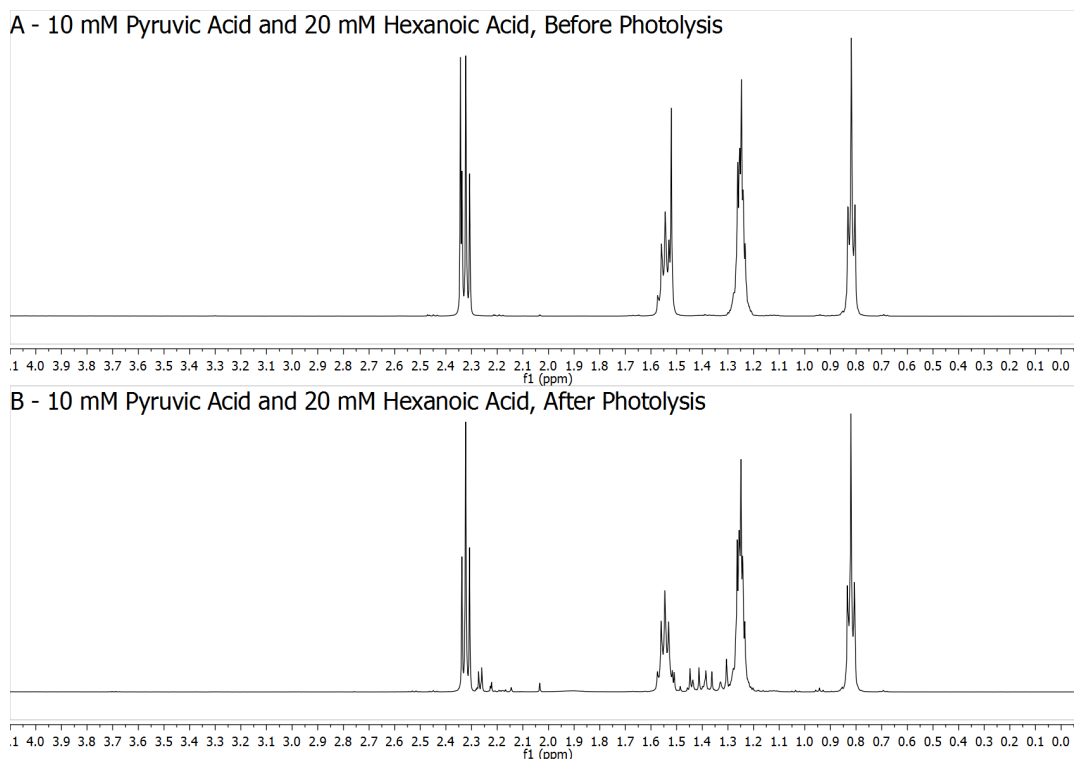


Figure S14. Representative NMR spectra of 10 mM pyruvic acid and 20 mM hexanoic acid before (A) and after (B) 5 hours of photolysis.

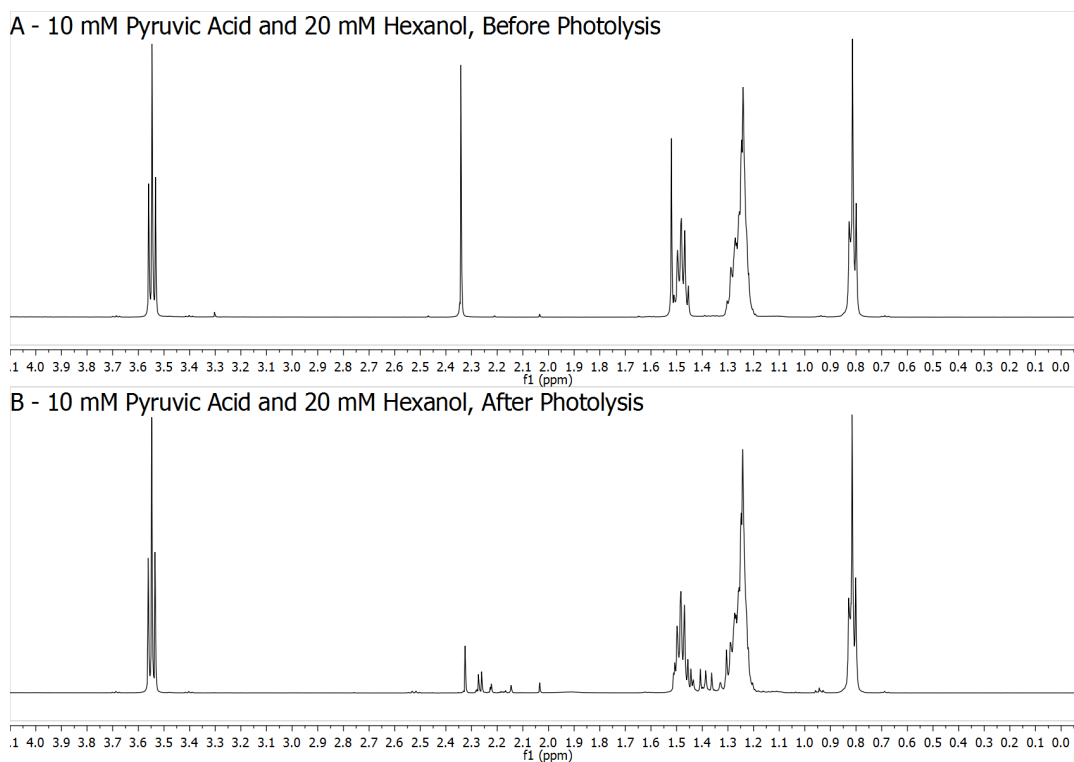


Figure S15. Representative NMR spectra of 10 mM pyruvic acid and 20 mM hexanol before (A) and after (B) 5 hours of photolysis.

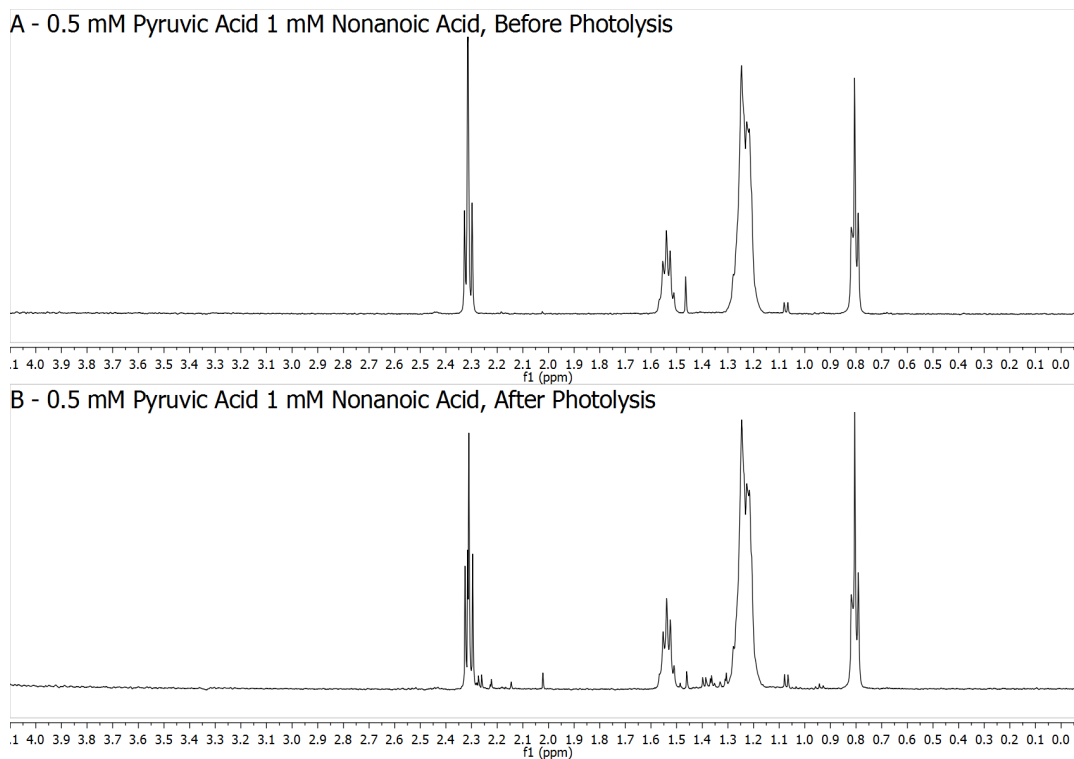


Figure S16. Representative NMR spectra of 0.5 mM pyruvic acid and 1 mM nonanoic acid before (A) and after (B) 5 hours of photolysis.

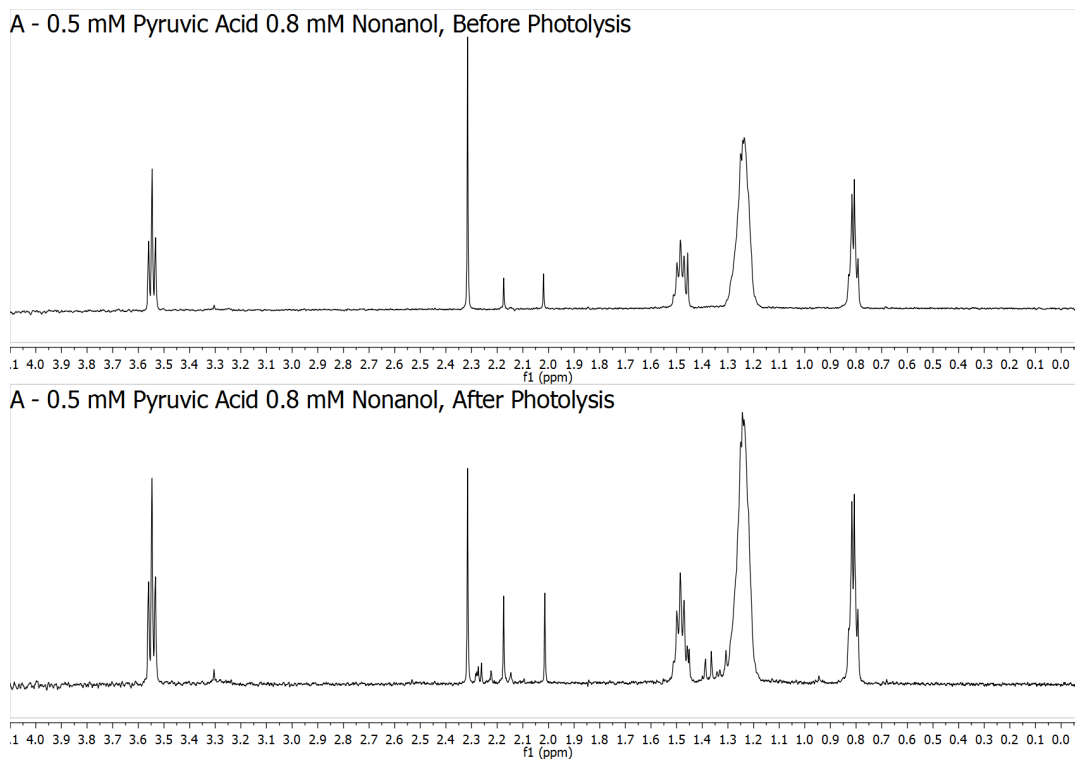


Figure S17. Representative NMR spectra of 0.5 mM pyruvic acid and 0.8 mM nonanol before (A) and after (B) 5 hours of photolysis.

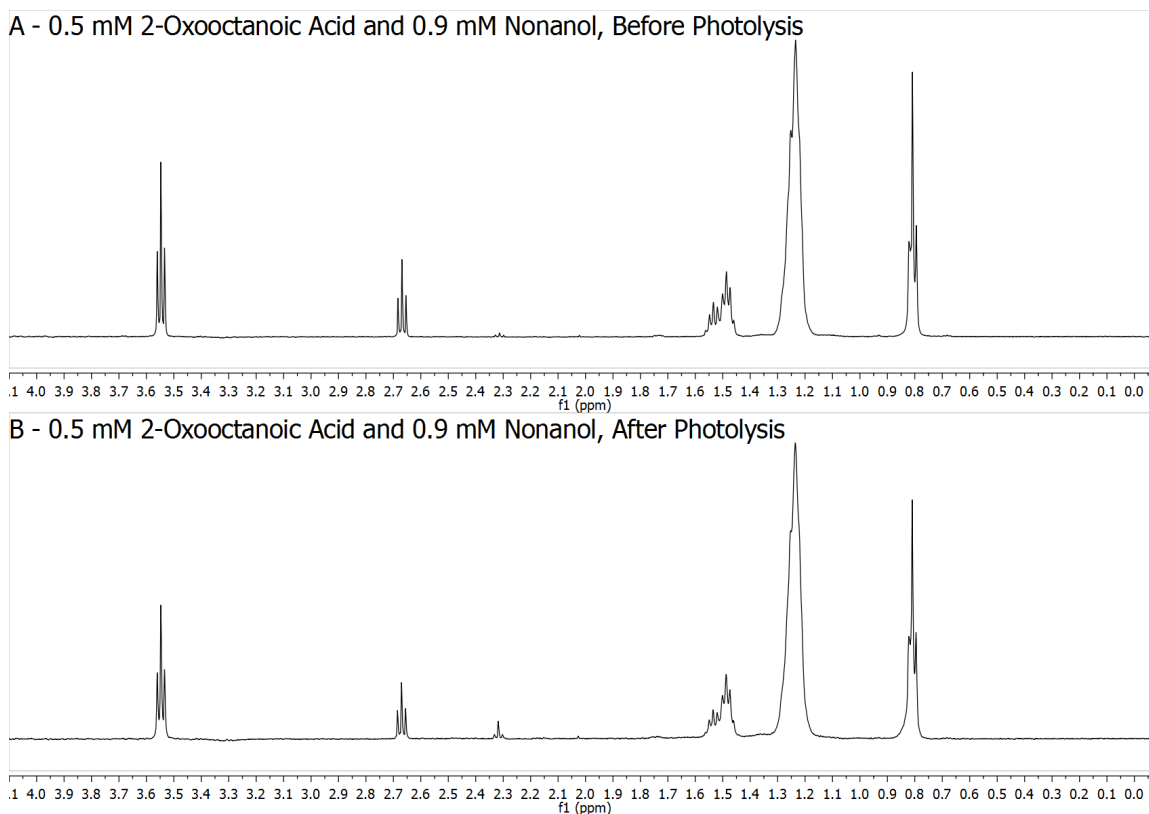


Figure S18. Representative NMR spectra of 0.5 mM 2-oxooctanoic acid and 0.9 mM nonanol before (A) and after (B) 5 hours of photolysis.

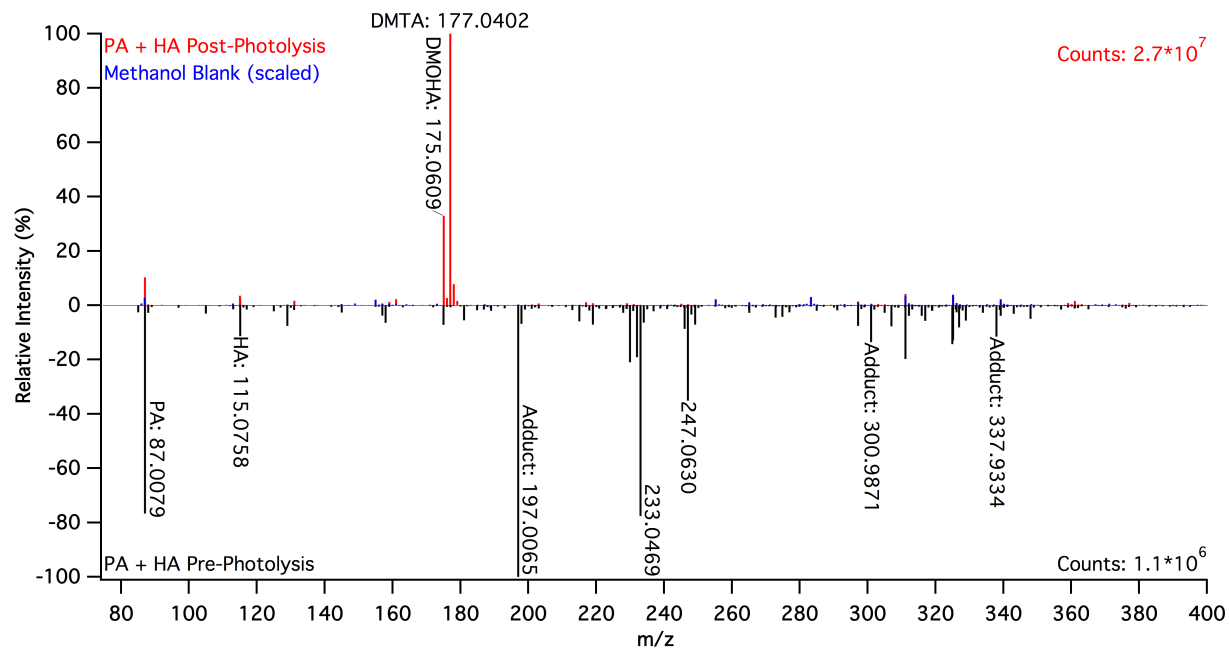


Figure S19. Representative ESI⁻ MS of a solution of 10 mM pyruvic acid and 20 mM hexanoic acid before (black, multiplied by -1 for ease of presentation), after 5 hours of photolysis (red), and the corresponding methanol blank (blue).

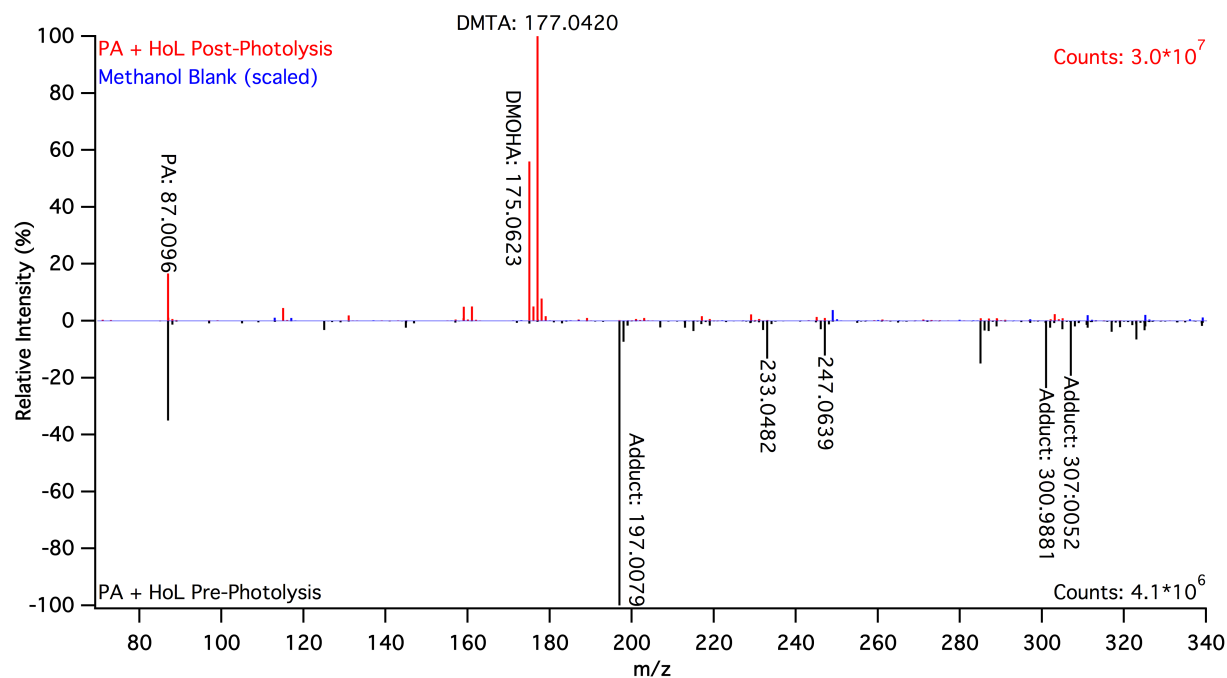


Figure S20. Representative ESI⁻ MS of a solution of 10 mM pyruvic acid and 20 mM hexanol before (black, multiplied by -1 for ease of presentation), after 5 hours of photolysis (red), and the corresponding methanol blank (blue).

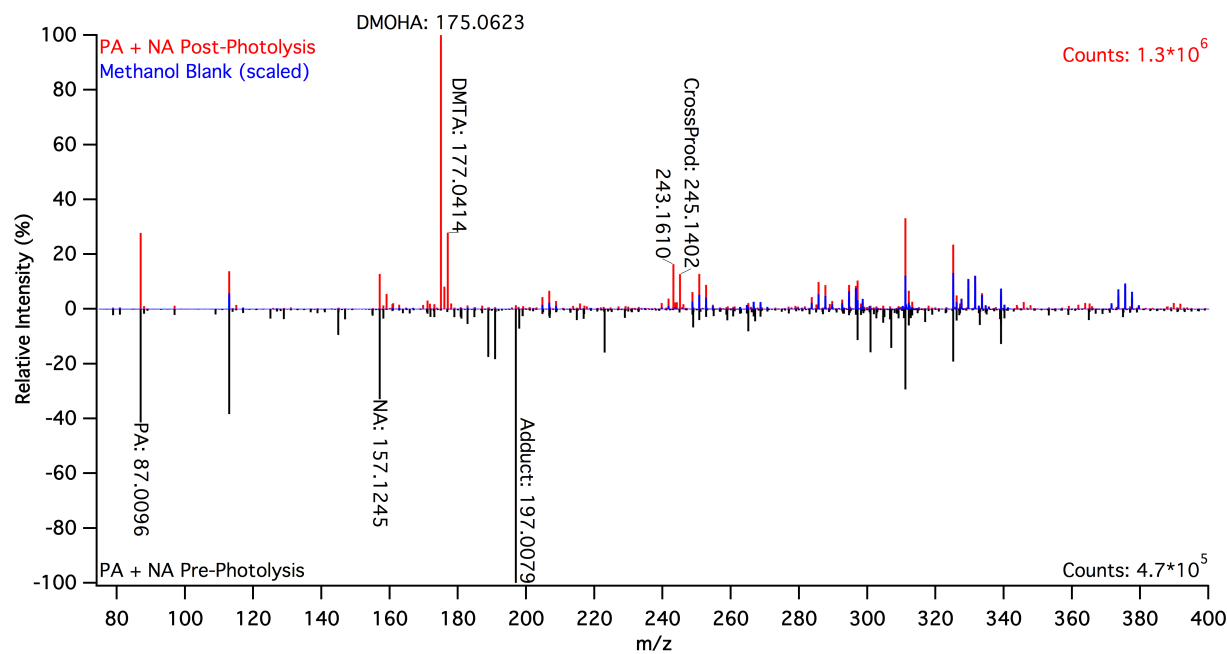


Figure S21. Representative ESI⁻ MS of a solution of 0.5 mM pyruvic acid and 1 mM nonanoic acid before (black, multiplied by -1 for ease of presentation), after 5 hours of photolysis (red), and the corresponding methanol blank (blue).

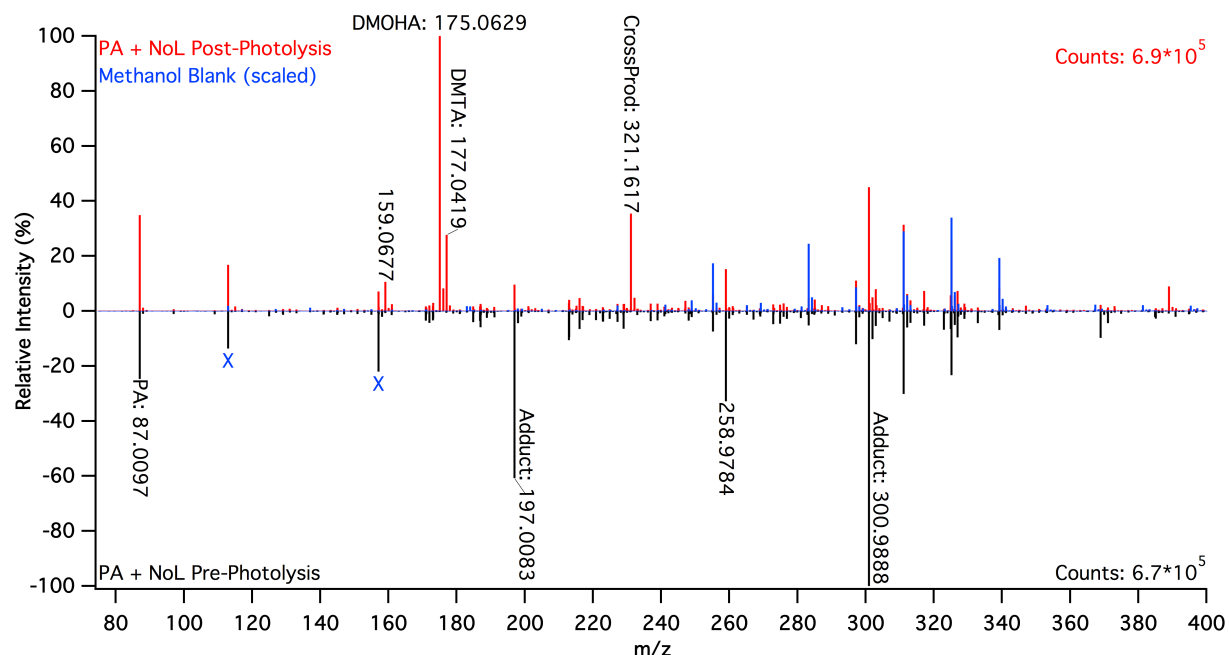


Figure S22. Representative ESI⁻ MS of a solution of 0.5 mM pyruvic acid and 0.8 mM nonanol before (black, multiplied by -1 for ease of presentation), after 5 hours of photolysis (red), and the corresponding methanol blank (blue). Blue X's indicate signal due to carry-over of material from previous experimental samples.

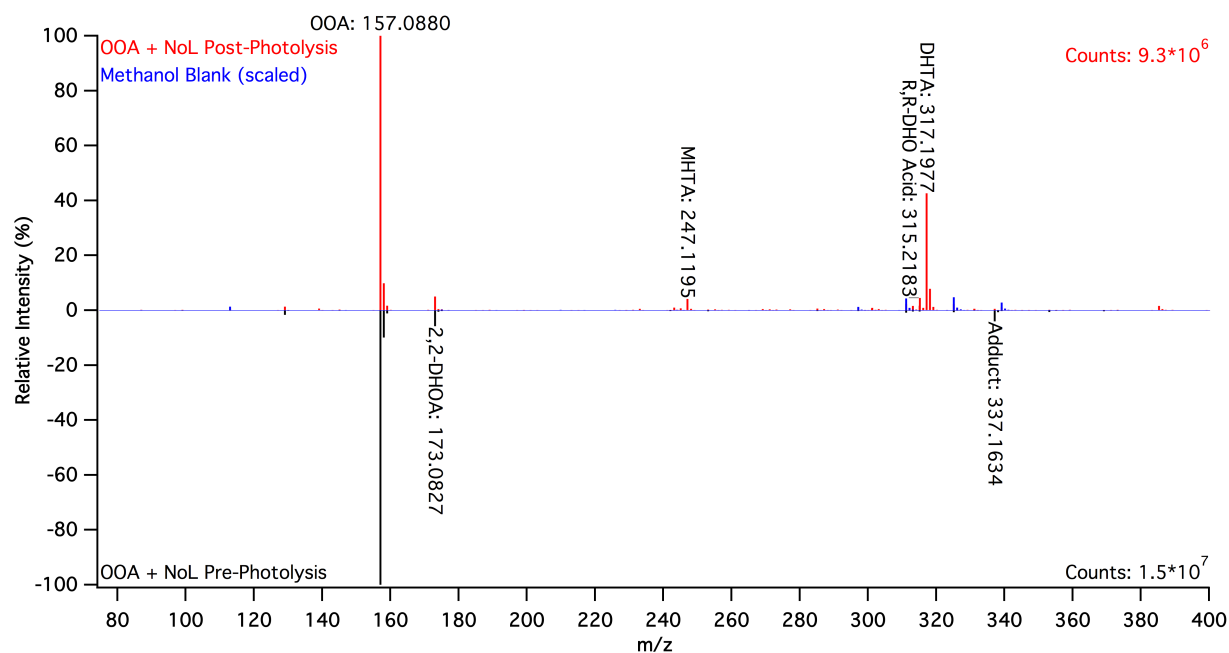


Figure S23. Representative ESI⁻ MS of a solution of 0.5 mM 2-oxooctanoic acid and 0.9 mM nonanol before (black, multiplied by -1 for ease of presentation) and after 5 hours of photolysis (red).

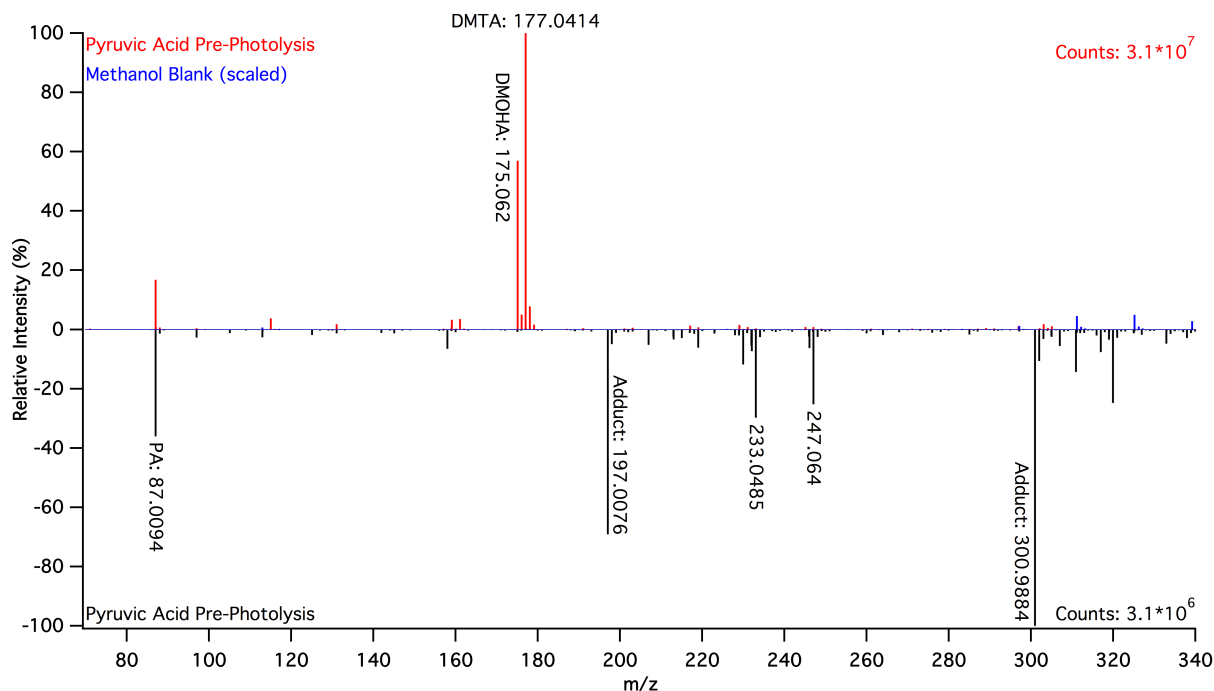


Figure S24. Representative ESI⁻ MS of a solution of 10 mM pyruvic acid before (black, multiplied by -1 for ease of presentation), after 5 hours of photolysis (red), and the corresponding methanol blank (blue).

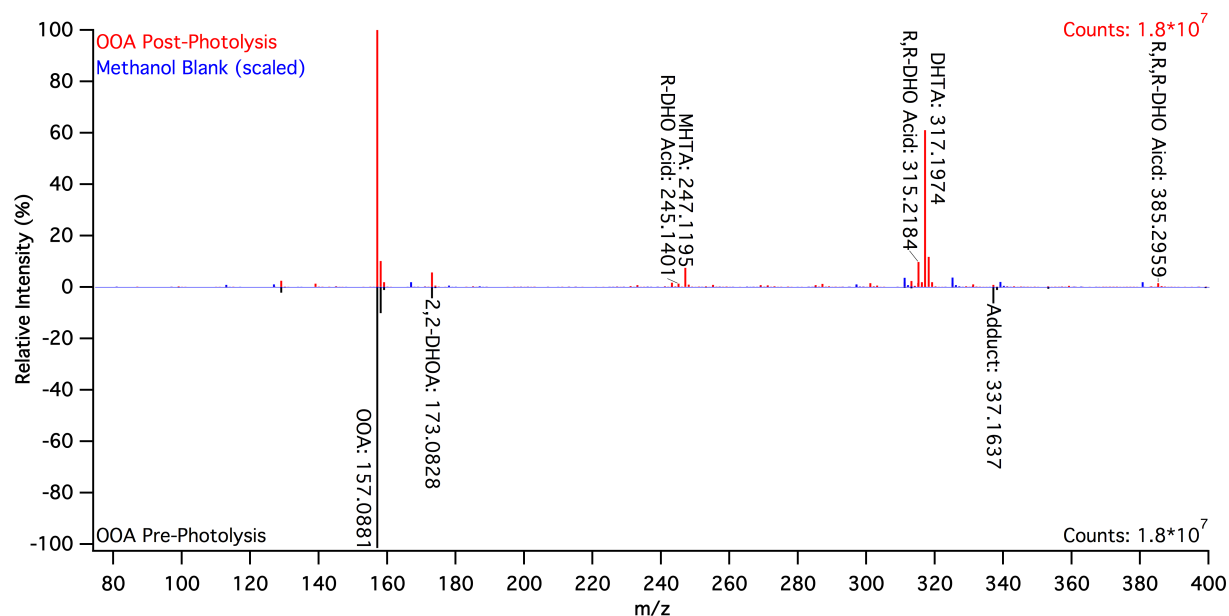


Figure S25. Representative ESI⁻ MS of a solution of 0.5 mM 2-oxocotanoic acid before (black, multiplied by -1 for ease of presentation), after 5 hours of photolysis (red), and the corresponding methanol blank (blue). Product species are labeled following the conventions of Rapf, et al. 2017¹ and consist of two tartaric acid derivatives, dihexyltartaric acid (DHTA) and methylhexyltartaric acid (MHTA), as well as three dihydroxyoxoalkanoic acid species with between one and three alkyl tails (R-DHO acid, R,R-DHO acid, and R,R,R-DHO acid).

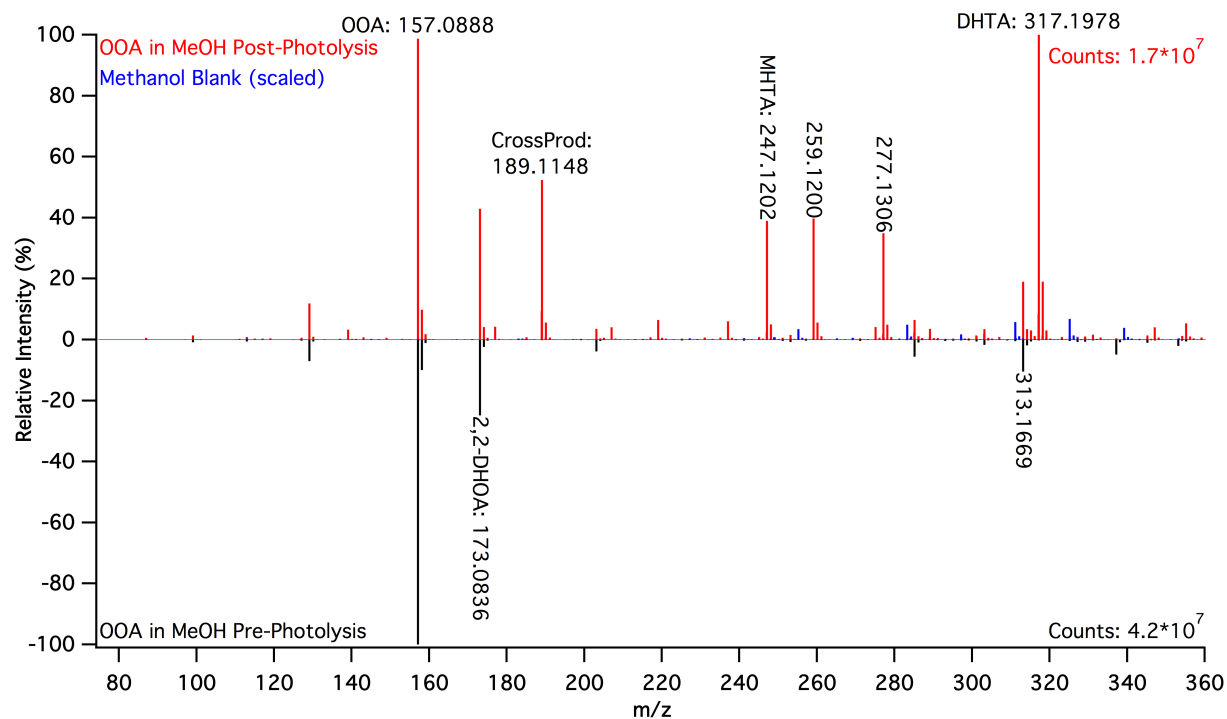


Figure S26. Representative ESI⁻ MS of 6 mM 2-oxooctanoic acid dissolved in methanol before (black, multiplied by -1 for ease of presentation), after 5 hours of photolysis (red), and the corresponding methanol blank (blue).

Analytical Techniques and Instrument Parameters:

UV-Vis Spectroscopy: A Varian (Agilent) Cary 5000 spectrometer with a 0.1 s average time, 0.5 nm data interval, and a spectral bandwidth of either 0.5 nm or 1 nm was used for both pre- and post-photolysis solutions of the α -keto acids.

NMR Analysis: ¹H NMR experiments were obtained using a Varian INOVA-500 NMR spectrometer operating at 499.60 MHz at 23 °C. In aqueous solution, experiments were performed using an optimized WET solvent suppression pulse sequence to eliminate >99% of the H₂O signal.²

Mass Spectrometry: A Waters Synapt G2 HDMS mass spectrometer was used to collect high resolution mass spectrometry data using electrospray ionization operated in negative mode. Instrument parameters were as follows: analyzer, resolution mode; capillary voltage, 1.5 kV; source temperature, 80 °C; sampling cone, 30 V; extraction cone, 5 V; source gas flow, 0.00 mL/min; desolvation temperature, 150 °C; cone gas flow, 0.0 L/h; desolvation gas flow, 500.0 L/h. These parameters were chosen to minimize the potential for in-source fragmentation and reactions due to ionization and were held constant for all experiments.

Analyte intensities may not correlate directly to absolute concentrations and are used only for relative comparison. A conservative intensity threshold of 10⁴ counts was applied for analyte identification to avoid incorrect ion assignments to noise peaks; the noise threshold is about 1000 counts. For comparative purposes, categories of signal intensity are defined as follows: “strong” ions display intensities greater than 10⁶ counts, “medium” ions display intensities greater than 10⁵ counts, and “weak” ions display intensities greater than 10⁴ counts for the monoisotopic ion in all cases.

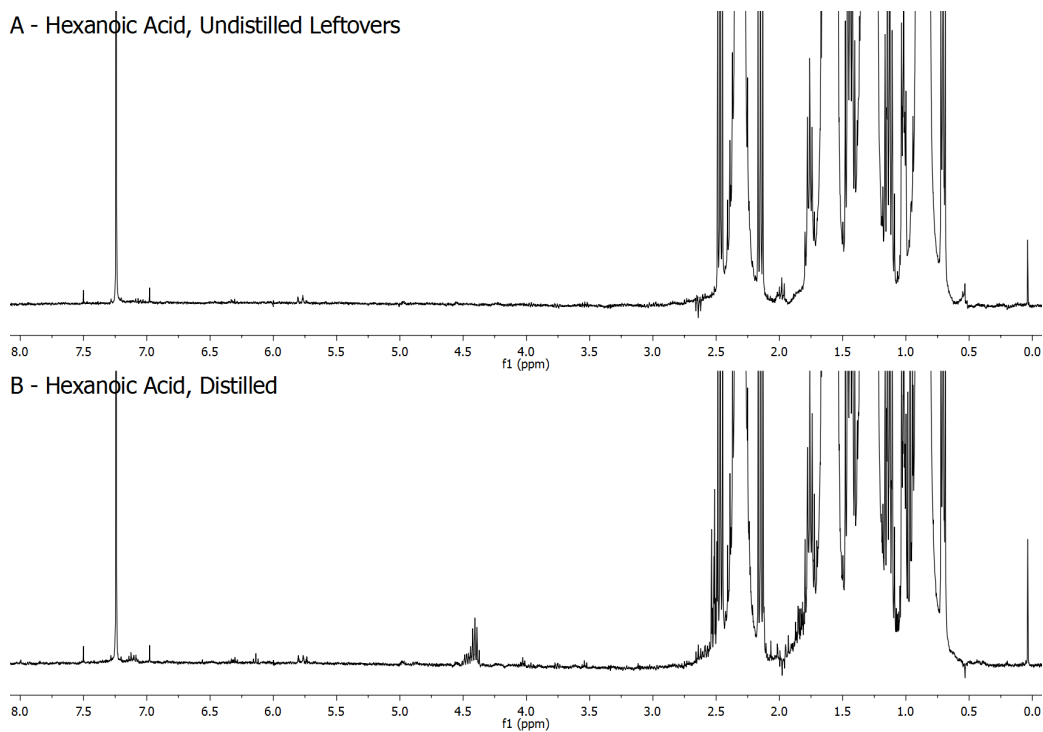


Figure S27. Representative NMR spectra of hexanoic acid after (B) distillation compared to the remnant material that was left over following distillation (A). Little change was observed upon distillation due to the starting purity of $>99.5\%$ for hexanoic acid.

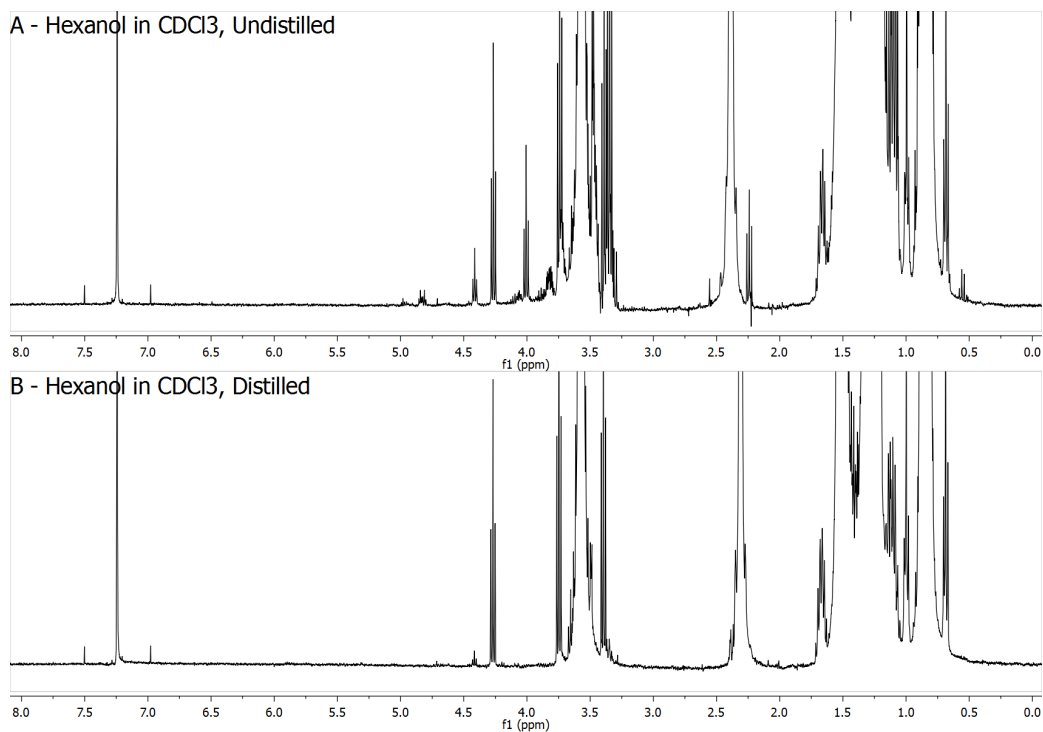


Figure S28. Representative NMR spectra of 1-hexanol before (A) and after (B) distillation.

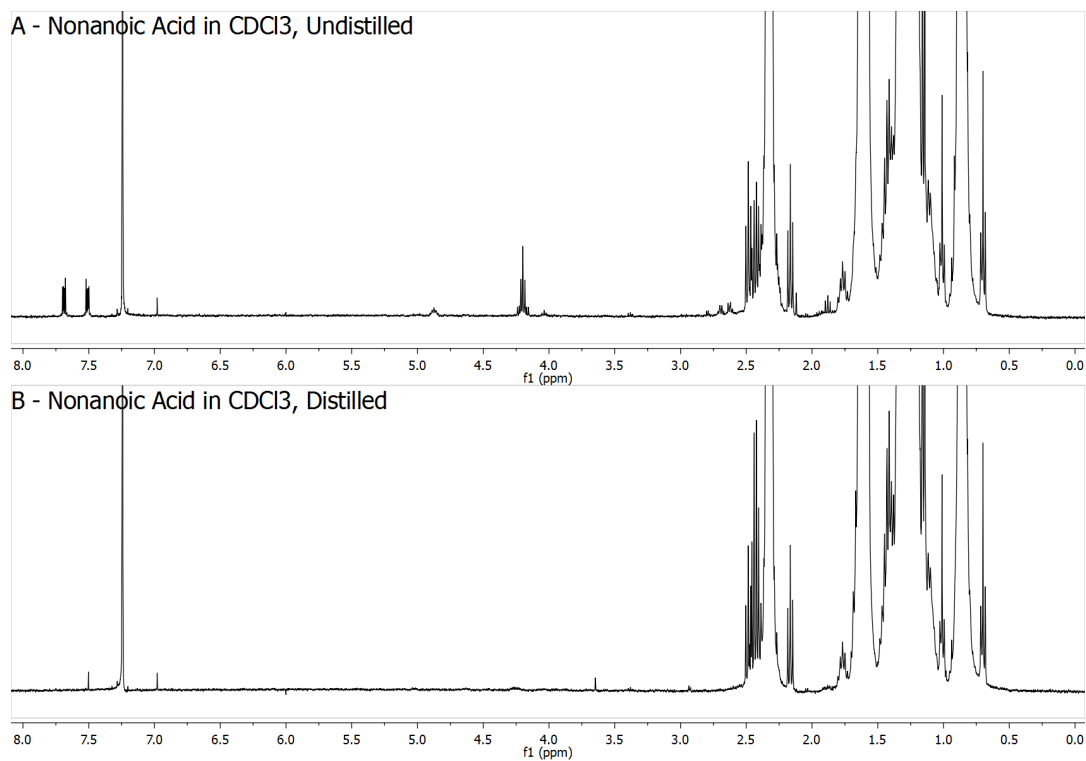


Figure S29. Representative NMR spectra of nonanoic acid before (A) and after (B) distillation.

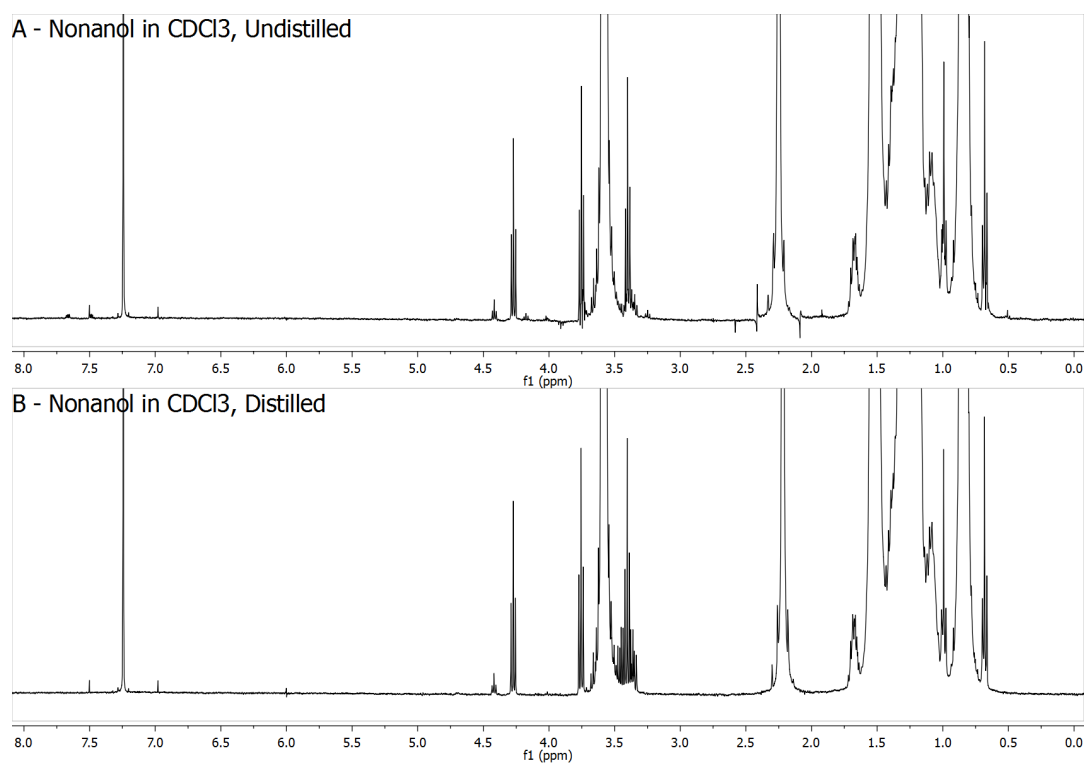


Figure S30. Representative NMR spectra of nonanol before (A) and after (B) distillation.

Table S1. Compiled ESI⁻ MS Data for Pyruvic Acid and Hexanoic Acid

Assigned Formula [M-H] ⁻	Assigned Structure	Theor. m/z	Avg. Exp. m/z (ppm)	Pyruvic Acid		Hexanoic Acid		Mixed PA + HA	
				Pre-hv	Post-hv	Pre-hv	Post-hv	Pre-hv	Post-hv
C ₃ H ₃ O ₃ ⁻	Pyruvic Acid	87.0088	87.0088 (0.4)	S	S			S	S
C ₄ H ₇ O ₂ ⁻	Acetoin	87.0452	87.0452 (0.4)		M				M
C ₃ H ₅ O ₃ ⁻	Lactic Acid	89.0244	89.0239 (-5.6)		W				W
C ₃ H ₅ O ₄ ⁻	2,2-DHPA	105.0193	105.0192 (-1.3)	W				W	
C ₅ H ₇ O ₃ ⁻	Unassigned	115.0401	115.0403 (1.6)		M				M
C ₆ H ₁₁ O ₂ ⁻	Hexanoic Acid	115.0765	115.0768 (3.4)			M	M	M	M
C ₅ H ₇ O ₄ ⁻	Acetolactic Acid	131.0350	131.0353 (2.7)		M				M
C ₈ H ₁₃ O ₃ ⁻	Unassigned	157.0870	157.0876 (3.5)						W
C ₇ H ₁₁ O ₄ ⁻	Unassigned	159.0663	159.0665 (3.4)		M				M
C ₆ H ₉ O ₅ ⁻	Unassigned	161.0455	161.0461 (3.4)		M				M
Unidentified			174.9569 ± 0.0001			M	M		
C ₆ H ₇ O ₆ ⁻	Parapyruvic Acid*	175.0248	175.0239 (-5.4)	W					
C ₇ H ₁₁ O ₅ ⁻	DMOHA	175.0612	175.0614 (1.1)		S				S
C ₆ H ₉ O ₆ ⁻	Dimethyltartaric Acid	177.0405	177.0408 (2.2)		S				S
Unidentified			183.0647 ± 0.0001			M	M		W
Unidentified			185.1189 ± 0.0005						W
C ₆ H ₆ O ₆ Na ⁻	Na Adduct of 2 PA-	197.0068	197.0073 (2.6)	S	W			S	W
C ₉ H ₁₅ O ₅ ⁻	Cross-product of PA and HA	203.0925	203.0926 (0.5)		W				M
Unidentified			217.0719 ± 0.0006		M				M
C ₈ H ₁₁ O ₇ ⁻	CDMOHA	219.0510	219.0517 (3.1)		M				M
C ₉ H ₁₄ O ₅ Na ⁻	Na Adduct of PA- and HA-	225.0744	225.0752 (3.4)					W	W
C ₁₀ H ₁₃ O ₆ ⁻	Unassigned	229.0718	229.0721 (1.6)		M				M
C ₉ H ₁₁ O ₇ ⁻	Unassigned	231.0510	231.0518 (3.1)		M				M

$C_{10}H_{15}O_6^-$	Unassigned	231.0874	231.0876 (0.9)		M					M
Unidentified			233.0473 ± 0.0007	M					M	
Unidentified			245.0350 ± 0.0000			M	M			W
Unidentified			247.0632 ± 0.0004	S					M	
$C_{12}H_{22}O_4Na^-$	Na Adduct of HA-	253.1421	253.1430 (3.4)			M	M		W	W
Unidentified			269.0014 ± 0.0001			M	M			
$C_{10}H_{14}O_8Na^-$	Na Adduct of PA- and DMOHA-	285.0592	285.0598 (2.0)		M					W
$C_9H_{12}O_9Na^-$	Na Adduct of PA- and DMTA-	287.0384	287.0385 (0.2)		W					W
$C_9H_9O_9Ca^-$	Ca Adduct of 3 PA-	300.9878	300.9877 (-0.2)	M					M	
$C_9H_9O_9Na_2^-$	Na Adduct of 3 PA-	307.0047	307.0048 (0.1)	M					M	
Unidentified			313.0218 ± 0.0001			M	M			
$C_{12}H_{20}O_8Na^-$	Na Adduct of DMTA- and HA-	315.1061	315.1073 (3.5)						W	W
Unidentified			315.1124 ± 0.0001			M	M			
Unidentified			383.0997 ± 0.0001			M	M			
$C_{18}H_{33}O_6Ca^-$	Ca Adduct of 3 HA-	385.1908	385.1906 (-0.6)			M	M			
$C_{18}H_{33}O_6Na_2^-$	Na Adduct of 3 HA-	391.2078	391.2077 (-0.3)			W	W			

Notes: Chemical formulas are assigned as the ionized $[M-H]^-$ species, structures are assigned as the neutral species. The theoretical m/z for each species is given, where known. The experimental mass differences from this value were <15 ppm for each species assigned for each experiment, with typical values of <8 ppm. The experimental m/z and mass differences reported are average values combined across all experiments in which the analyte was detected. Where the peak has not been assigned, the average m/z value across experiments is given, with uncertainties given as a 95% confidence interval.

S = Strong, M = Medium, W = Weak

Blank entries indicate that the species was not observed with an intensity above the cut-off threshold, which was set conservatively at 10^4 counts.

2,2-DHPA = 2,2-Dihydroxypropanoic Acid, diol of pyruvic acid

DMOHA = 2,4-dihydroxy-2-methyl-5-oxohexanoic acid

CDMOHA = 4-carboxy-2,4-dihydroxy 2-methyl-5-oxohexanoic acid

*The peak assigned to parapyruvic acid likely also has contributions from the closed ring form of the zymonic acid diol as well.

Table S2. Compiled ESI⁻ MS Data for Pyruvic Acid and Hexanol

Assigned Formula [M-H] ⁻	Assigned Structure	Theor. m/z	Avg. Exp. m/z (ppm)	Pyruvic Acid		Hexanol		Mixed PA+HoL	
				Pre-hv	Post-hv	Pre-hv	Post-hv	Pre-hv	Post-hv
C ₃ H ₃ O ₃ ⁻	Pyruvic Acid	87.0088	87.0095 (8.7)	S	S			S	S
C ₄ H ₇ O ₂ ⁻	Acetoin	87.0452	87.0454 (2.7)		M				M
C ₃ H ₅ O ₃ ⁻	Lactic Acid	89.0244	89.0240 (-4.7)		W				
C ₃ H ₅ O ₄ ⁻	2,2-DHPA	105.0193	105.0197 (3.7)	W				W	
C ₅ H ₇ O ₃ ⁻	Unassigned	115.0401	115.0404 (3.1)		M				M
C ₅ H ₇ O ₄ ⁻	Acetolactic Acid	131.0350	131.0352 (2.0)		M				M
C ₇ H ₁₁ O ₄ ⁻	Unassigned	159.0663	159.0668 (2.9)		M				M
C ₆ H ₉ O ₆ ⁻	Unassigned	161.0455	161.0466 (6.3)		M				M
C ₆ H ₇ O ₆ ⁻	Parapyruvic Acid*	175.0248	175.0253 (3.0)	W					
C ₇ H ₁₁ O ₅ ⁻	DMOHA	175.0612	175.0618 (3.4)		S				S
C ₆ H ₉ O ₆ ⁻	Dimethyltartaric Acid	177.0405	177.0411 (3.6)		S				S
C ₉ H ₁₇ O ₄ ⁻	Cross-product of PA and HoL	189.1132	189.1143 (5.6)						M
C ₆ H ₆ O ₆ Na ⁻	Na Adduct of 2 PA-	197.0068	197.0075 (3.8)	S	W			S	W
Unidentified			217.0719 ± 0.0006		M				M
C ₈ H ₁₁ O ₇ ⁻	CDMOHA	219.0510	219.0515 (2.2)		M				M
C ₁₀ H ₁₃ O ₆ ⁻	Unassigned	229.0718	229.0726 (3.5)		M				M
C ₉ H ₁₁ O ₇ ⁻	Unassigned	231.0510	231.0516 (2.4)		M				M
C ₁₀ H ₁₅ O ₆ ⁻	Unassigned	231.0874	231.0876 (0.8)		M				M
Unidentified			233.0473 ± 0.0007	M				M	
Unidentified			247.0632 ± 0.0004	S				M	
C ₁₀ H ₁₄ O ₈ Na ⁻	Na Adduct of PA- and DMOHA-	285.0592	285.0597 (1.7)		M				W
C ₉ H ₁₂ O ₉ Na ⁻	Na Adduct of PA- and DMTA-	287.0384	287.0393 (2.9)		W				W

$C_9H_9O_9Ca^-$	Ca Adduct of 3 PA-	300.9878	300.9881 (1.1)	M				M	W
$C_9H_9O_9Na_2^-$	Na Adduct of 3 PA-	307.0047	307.0052 (1.5)	M				M	

Table S3. Compiled ESI⁻ MS Data for Pyruvic Acid and Nonanoic Acid

				Pyruvic Acid		Nonanoic Acid		Mixed PA + NA	
Assigned Formula [M-H] ⁻	Assigned Structure	Theor. m/z	Avg. Exp. m/z (ppm)	Pre-hv	Post-hv	Pre-hv	Post-hv	Pre-hv	Post-hv
$C_3H_3O_3^-$	Pyruvic Acid	87.0088	87.0092 (5.0)	M	M			M	M
$C_4H_7O_2^-$	Acetoin	87.0452	87.0451 (-0.1)		W				W
$C_5H_7O_3^-$	Unassigned	115.0401	115.0404 (2.5)		W				W
$C_5H_7O_4^-$	Acetolactic Acid	131.0350	131.0350 (0.0)		W				
$C_9H_{17}O_2^-$	Nonanoic Acid	157.1234	157.1241 (4.4)			S	S		
$C_7H_{11}O_4^-$	Unassigned	159.0663	159.0665 (1.2)		W				W
$C_6H_9O_6^-$	Unassigned	161.0455	161.0465 (5.8)						W
$C_6H_7O_6^-$	Parapyruvic Acid*	175.0248	175.0250 (1.0)	W					
$C_7H_{11}O_5^-$	DMOHA	175.0612	175.0618 (3.4)		S				S
$C_6H_9O_6^-$	Dimethyltartaric Acid	177.0405	177.0410 (3.0)		M				M
$C_8H_6O_6Na^-$	Na Adduct of 2 PA-	197.0068	197.0074 (3.1)	M	M			M	M
Unidentified			217.0719 ± 0.0006		W				W
Unidentified			225.1115 ± 0.0004			M	M		
$C_{10}H_{13}O_6^-$	Unassigned	229.0718	229.0722 (2.1)						W
$C_{10}H_{15}O_6^-$	Unassigned	231.0874	231.0876 (0.8)						W
Unidentified			243.1607						M
$C_{12}H_{21}O_5^-$	Cross-Product of PA + NA	245.1394	245.1400 (2.3)						M
$C_{10}H_{14}O_8Na^-$	Na Adduct of PA- and DMOHA-	285.0592	285.0598 (2.2)		W				W
$C_9H_{12}O_9Na^-$	Na Adduct of PA- and DMTA-	287.0384	287.0391 (2.3)		W				W

Unidentified			293.0985 ± 0.0004			W	W		
C ₉ H ₉ O ₉ Ca ⁻	Ca Adduct of 3 PA-	300.9877	300.9881 (1.0)	M	M			W	W
C ₉ H ₉ O ₉ Na ₂ ⁻	Na Adduct of 3 PA-	307.0047	307.0052 (1.4)	W	W			W	
C ₁₈ H ₃₄ O ₄ Na ⁻	Na Adduct of 2 NA-	337.2360	337.2360 (-0.1)			M	M	W	
Unidentified			403.2355 ± 0.0004			M	M		
Unidentified			473.2107 ± 0.0004			M	M		
C ₂₇ H ₅₁ O ₆ Ca ⁻	Ca Adduct of 3 NA-	511.3317	511.3310 (-1.4)			W	W		
C ₂₇ H ₅₁ O ₆ Na ₂ ⁻	Na Adduct of 3 NA-	517.3487	517.3482 (-0.9)			M	M		

Table S4. Compiled ESI⁻ MS Data for Pyruvic Acid and Nonanol

				Pyruvic Acid		Nonanol		Mixed PA + NoL	
Assigned Formula [M-H] ⁻	Assigned Structure	Theor. m/z	Avg. Exp. m/z (ppm)	Pre-hv	Post-hv	Pre-hv	Post-hv	Pre-hv	Post-hv
C ₃ H ₃ O ₃ ⁻	Pyruvic Acid	87.0088	87.0093 (5.8)	M	M			M	M
C ₄ H ₇ O ₂ ⁻	Acetoin	87.0452	87.0454 (3.0)		W				
C ₅ H ₇ O ₃ ⁻	Unassigned	115.0401	115.0405 (4.0)		W				W
C ₅ H ₇ O ₄ ⁻	Acetolactic Acid	131.0350	131.0352 (2.0)		W				
C ₇ H ₁₁ O ₄ ⁻	Unassigned	159.0663	159.0668 (3.3)		W				W
C ₆ H ₉ O ₆ ⁻	Unassigned	161.0450	161.0466 (6.8)						W
C ₆ H ₇ O ₆ ⁻	Parapyruvic Acid*	175.0248	175.0250 (1.0)	W					
C ₇ H ₁₁ O ₅ ⁻	DMOHA	175.0612	175.0620 (4.5)		S				S
C ₆ H ₉ O ₆ ⁻	Dimethyltartaric Acid	177.0405	177.0411 (3.8)		M				M
C ₆ H ₆ O ₆ Na ⁻	Na Adduct of 2 PA-	197.0068	197.0075 (3.8)	M	M			M	W
Unidentified			217.0719 ± 0.0006		W				W
C ₁₂ H ₂₃ O ₄ ⁻	Cross Product of PA and NoL	231.1602	231.1607 (2.2)						M
Unidentified			258.9780					W	W

$C_{10}H_{14}O_8Na^-$	Na Adduct of PA- and DMOHA-	285.0592	285.0598 (2.2)		W				W
$C_9H_{12}O_9Na^-$	Na Adduct of PA- and DMTA-	287.0384	287.0391 (2.3)		W				W
$C_9H_9O_9Ca^-$	Ca Adduct of 3 PA-	300.9878	300.9884 (2.0)	M	M			M	W
$C_9H_9O_9Na_2^-$	Na Adduct of 3 PA-	307.0047	307.0053 (1.8)	W	W			W	

Table S5. Compiled ESI⁻ MS Data for OOA and Nonanol

Assigned Formula [M-H] ⁻	Assigned Structure	Theor. m/z	Avg. Exp. m/z (ppm)	2-Oxooctanoic Acid		Nonanol		Mixed OOA + NoL	
				Pre-hv	Post-hv	Pre-hv	Post-hv	Pre-hv	Post-hv
$C_3H_3O_3^-$	Pyruvic Acid	87.0088	87.0093 (5.8)		W				W
$C_7H_{13}O_2^-$	Heptanoic Acid	129.0921	129.0930 (6.9)	M	M			M	M
$C_8H_{11}O_2^-$	Unassigned	139.0765	139.0775 (7.5)		M				W
$C_8H_{13}O_3^-$	2-Oxooctanoic Acid	157.0870	157.0880 (6.3)	S	S			S	S
$C_9H_{17}O_2^-$	Nonanoic Acid	157.1234	157.1240 (3.8)	W	W				
$C_8H_{13}O_4^-$	2,2-DHOA	173.0819	173.0828 (4.7)	M	M			M	M
$C_6H_9O_6^-$	Dimethyltartaric Acid	177.0405	177.0405 (0.2)		W				
$C_{14}H_{27}O_2^-$	8-hydroxy-tetradecan-7-one	227.2017	227.2017 (0.1)		W				
$C_{11}H_{17}O_6^-$	R-PPA	245.1031	245.1400 (2.3)		W				
$C_{12}H_{21}O_5^-$	R-DHO Acid	245.1394	245.1400 (2.3)		M				W
$C_{11}H_{19}O_6^-$	Methylhexyl-tartaric Acid	247.1187	247.1193 (2.2)		S				M
$C_{15}H_{27}O_3^-$	Unassigned	255.1966	255.1968 (0.7)		M				W
Unidentified			269.1763 ± 0.0004		M				W
$C_{15}H_{27}O_4^-$	8-C-8-H-tetradecan-7-one	271.1915	271.1920 (1.9)		M				W
$C_{15}H_{29}O_4^-$	Unassigned	273.2071	273.2070 (-0.5)		W				W
$C_{13}H_{28}O_5Na^+$	Unassigned	287.1840	287.1868 (9.6)		W				W

$C_{13}H_{21}O_7^-$	R-DHO Diacid	289.1293	289.1295 (0.8)		W				
$C_{17}H_{33}O_4^-$	Cross Product of OOA and NoL	301.2384	301.2390 (1.7)						M
$C_{16}H_{25}O_6^-$	R,R-DODA	313.1657	313.1661 (1.5)	M	M			W	M
$C_{16}H_{27}O_6^-$	R,R-PPA	315.1813	315.1802 (-3.5)	W	W			W	W
$C_{17}H_{31}O_5^-$	R,R-DHO Acid	315.2177	315.2180 (1.0)		S				M
$C_{16}H_{29}O_6^-$	Dihexyltartaric Acid	317.1970	317.1975 (1.7)		S				S
$C_{16}H_{26}O_6Na^-$	Na Adduct of 2 OOA-	337.1633	337.1635 (0.7)	S	M			M	M
$C_{16}H_{26}O_7Na^-$	Na Adduct of OOA- and OOA Diol-	353.1582	353.1573 (-2.6)	M	W			W	
$C_{18}H_{31}O_7^-$	R,R-DHO Diacid	359.2075	359.2073 (-0.8)		W				W
$C_{22}H_{41}O_5^-$	R,R,R-DHO Acid	385.2959	385.2957 (-0.7)		M				W
$C_{23}H_{41}O_7^-$	R,R,R-DHO Diacid	429.2858	429.2850 (-1.8)		W				
$C_{26}H_{41}O_9^-$	Unassigned	497.2756	497.2720 (-7.3)		W				W
$C_{24}H_{39}O_9Ca^-$	Ca Adduct of 3 OOA-	511.2225	511.2221 (-0.8)	M	W			M	M
$C_{24}H_{39}O_9Na_2^-$	Na Adduct of 3 OOA-	517.2395	517.2390 (-1.0)	M				W	W

Notes: Chemical formulas are assigned as the ionized $[M-H]^-$ species, structures are assigned as the neutral species. The theoretical m/z for each species is given, where known. The experimental mass differences from this value were <15 ppm for each species assigned for each experiment, with typical values of <8 ppm. The experimental m/z and mass differences reported are average values combined across all experiments in which the analyte was detected. Where the peak has not been assigned, the average m/z value across experiments is given, with uncertainties given as a 95% confidence interval.

S = Strong, M = Medium, W = Weak

Blank entries indicate that the species was not observed with an intensity above the cut-off threshold, which was set conservatively at 10^4 counts.

2,2-DHOA = 2,2-Dihydroxyoctanoic Acid, Diol of OOA

DMOHA = 2,4-dihydroxy-2-methyl-5-oxohexanoic acid

8-C-8-H-tetradecan-7-one = 8-carboxy-8-hydroxy-tetradecan-7-one

† Assignment is tentative

Table S6. Compiled ESI⁻ MS Data for OOA Dissolved in Methanol

				OOA in MeOH	
Assigned Formula [M-H] ⁻	Assigned Structure	Theor. m/z	Avg. Exp. m/z (ppm)	Pre-hv	Post-hv
$C_3H_3O_3^-$	Pyruvic Acid	87.0088	87.0089 (1.5)		M
$C_7H_{13}O_2^-$	Heptanoic Acid	129.0921	129.0926 (3.7)	S	S

$C_8H_{11}O_2^-$	Unassigned	139.0765	139.0771 (4.7)		M
$C_8H_{13}O_3^-$	2-Oxooctanoic Acid	157.0870	157.0876 (3.9)	S	S
$C_9H_{17}O_2^-$	Nonanoic Acid	157.1234	157.1237 (2.1)	W	W
$C_8H_{13}O_4^-$	2,2-DHOA	173.0819	173.0825 (3.3)	S	S
$C_7H_{11}O_5^-$	DMOHA	175.0614	175.0606 (-3.4)		W
$C_6H_9O_6^-$	Dimethyltartaric Acid	177.0405	177.0411 (3.3)		M
$C_9H_{17}O_4^-$	Cross Product of OOA and MeOH	189.1132	189.1139 (3.5)	W	S
$C_{10}H_{19}O_4^-$	Unassigned	203.1288	203.1295 (3.2)	M	M
Unidentified			207.0517		M
Unidentified			219.0517		M
$C_{14}H_{27}O_2^-$	8-hydroxy-tetradecan-7-one	227.2017	227.2018 (0.6)		W
Unidentified			237.0622		M
$C_{11}H_{17}O_6^-$	R-PPA	245.1031	245.1037 (2.4)		W
$C_{12}H_{21}O_5^-$	R-DHO Acid	245.1394	245.1403 (3.5)		M
$C_{11}H_{19}O_6^-$	Methylhexyl-tartaric Acid	247.1187	247.1191 (1.6)		S
$C_{15}H_{27}O_3^-$	Unassigned	255.1966	255.1960 (-2.4)		M
$C_{12}H_{19}O_6^-$	Unassigned	259.1187	259.1190 (1.1)		S
Unidentified			269.1757		M
Unidentified			275.1501		M
Unidentified			277.1297		S
Unidentified			285.1709	M	M
$C_{16}H_{25}O_6^-$	R,R-DODA	313.1657	313.1659 (0.8)	M	M
$C_{16}H_{29}O_6^-$	Dihexyltartaric Acid	317.1970	317.1970 (0.0)		S
$C_{16}H_{26}O_6Na^-$	Na Adduct of 2 OOA-	337.1633	337.1641 (2.4)	S	M
$C_{16}H_{26}O_7Na^-$	Na Adduct of OOA- and OOA Diol-	353.1582	353.1578 (-1.1)	M	W
$C_{18}H_{31}O_7^-$	R,R-DHO Diacid	359.2075	359.2073 (-0.8)		W
Unidentified			387.2197	S	
$C_{24}H_{39}O_9Ca^-$	Ca Adduct of 3 OOA-	511.2225	511.2229 (0.6)	M	W

Table S7. Electronic Structure Calculation Data: Propionic Acid

Cartesian Coordinates (Å):			
C	0.563733	0.106791	-0.000036
C	-0.691126	-0.736027	-0.000195
C	-1.971125	0.094583	0.000159
O	1.678078	-0.667168	0.000139
O	0.612669	1.309880	-0.000089
H	-0.639855	-1.397729	0.870832
H	-2.019862	0.738689	0.879973
H	-2.848173	-0.556441	0.000183
H	-2.020172	0.739015	-0.879396
H	2.433125	-0.060270	0.000212
Harmonic Vibration Frequencies (cm ⁻¹):			
54.0838	194.3315	250.4081	466.9120
520.1678	616.3077	663.1325	815.9129
818.0480	1011.1317	1082.6862	1112.4933
1168.1050	1283.1439	1311.8993	1407.3020
1422.5820	1464.1958	1494.7021	1504.0592
1829.6991	3038.5034	3044.4414	3064.2989
3110.1123	3115.6713	3759.1615	
Energetics:			
CBS-QB3 Energy =		-267.985656 hartree	
CBS-QB3 Enthalpy =		-267.984712 hartree	
CBS-QB3 Free Energy =		-268.020784 hartree	

Table S8. Electronic Structure Calculation Data: Alpha-Propionyl Radical

Cartesian Coordinates (Å):			
C	0.545234	0.086340	-0.000011
C	-0.693180	-0.662576	-0.000022
C	-2.006560	0.021627	0.000019
O	1.643298	-0.721583	0.000015
O	0.635169	1.300776	-0.000014
H	-0.630683	-1.744400	-0.000096
H	-1.878397	1.103919	0.000141
H	-2.600934	-0.266901	-0.876779
H	2.410211	-0.131413	0.000070
Harmonic Vibration Frequencies (cm ⁻¹):			
92.8094	151.2975	259.7703	482.0871
523.8215	609.0210	623.3863	740.4152
835.6772	991.3542	1060.7819	1112.1891
1173.9460	1306.4940	1396.7702	1439.7262
1474.0438	1499.5985	1714.1527	2994.9754
3026.9234	3125.7182	3189.8983	3774.9722
Energetics:			
CBS-QB3 Energy =		-267.338318 hartree	
CBS-QB3 Enthalpy =		-267.337374 hartree	
CBS-QB3 Free Energy =		-267.373755 hartree	

Table S9. Electronic Structure Calculation Data: Pyruvic acid $^3(n,\pi^*)$ state

Cartesian Coordinates (Å):			
C	-1.798715	-0.741322	0.004418
C	-0.654931	0.236256	0.002499
C	0.721080	-0.233310	-0.002630
O	1.614247	0.790849	-0.003678
O	1.048941	-1.409516	-0.005760
O	-0.898972	1.493174	0.005299
H	-1.362585	-1.741604	0.000230
H	-2.428809	-0.604848	-0.879273
H	-2.421961	-0.609388	0.893655
H	2.495018	0.390041	-0.007221
Harmonic Vibration Frequencies (cm ⁻¹):			
121.2752	137.9882	237.3834	304.6244
349.4645	494.9044	510.4565	551.6879
672.1335	760.7918	997.8989	1023.5836
1096.9460	1193.7874	1312.8923	1366.9864
1404.5718	1456.4856	1484.4932	1687.3367
3020.7945	3080.0122	3122.4437	3779.1842
Energetics:			
CBS-QB3 Energy =		-341.826975 hartree	
CBS-QB3 Enthalpy =		-341.826031 hartree	
CBS-QB3 Free Energy =		-341.864614 hartree	

Table S10. Electronic Structure Calculation Data: Alpha-hydroxy-alpha-propionyl radical

Cartesian Coordinates (Å):			
C	0.775447	0.009761	0.000010
C	-0.658021	0.084842	-0.000560
C	-1.627560	-1.035742	0.000190
O	-1.161277	1.330208	-0.000116
O	1.291728	-1.246777	-0.000158
O	1.476755	1.019372	0.000310
H	-1.108547	-1.992226	-0.008774
H	-2.283738	-0.978190	-0.875898
H	-2.271117	-0.988768	0.886391
H	-0.386519	1.924292	0.000305
H	2.253079	-1.140695	-0.000146
Harmonic Vibration Frequencies (cm ⁻¹):			
100.5276	142.9462	249.6052	312.5716
376.3218	512.8432	516.2796	585.4922
686.2913	701.4101	767.5449	1008.3421
1022.4657	1130.1845	1192.1805	1342.2861
1393.1006	1447.4320	1469.5232	1471.2538
1543.9159	1698.2366	3010.5211	3048.8812
3146.4547	3619.5396	3785.1392	
Energetics:			
CBS-QB3 Energy =		-342.501262 hartree	
CBS-QB3 Enthalpy =		-342.500317 hartree	
CBS-QB3 Free Energy =		-342.538671 hartree	

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