Electronic Supplementary Material (ESI) for Green Chemistry.


# Light-Promoted Oxidation of Aldehydes to Carboxylic Acids under Aerobic and Photocatalyst-free Conditions

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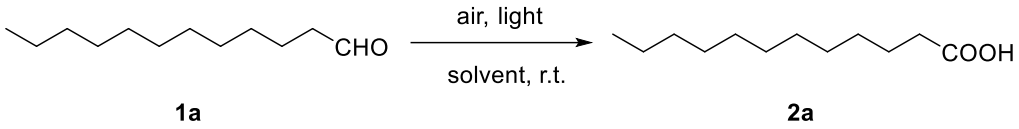
# General Remarks

Chromatographic purification of products was accomplished using forced-flow chromatography on Merck® Kieselgel 60 F254 230-400 mesh. Thin-layer chromatography (TLC) was performed on aluminum backed silica plates (0.2 mm, 60 F254). Visualization of the developed chromatogram was performed by fluorescence quenching using phosphomolybdic acid, anisaldehyde or potassium permanganate stains. Melting points were measured on a Buchi 530 apparatus. Mass spectra (ESI) were recorded on a Finningan® Surveyor MSQ LC-MS spectrometer. HRMS spectra were recorded on Bruker® Maxis Impact QTOF spectrometer. $^{1}$H-NMR and $^{13}$C-NMR spectra were recorded on Varian® Mercury (200 MHz and 50 MHz, respectively) or an Avance III HD Bruker 400 MHz (400 MHz and 100 MHz, respectively) and are internally referenced to residual solvent signals. Data for $^{1}$H-NMR are reported as follows: chemical shift ($\delta$ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad signal), coupling constant and assignment. Data for $^{13}$C-NMR are reported in terms of chemical shift ($\delta$ ppm). HPLC analyses were carried out on a Shimadzu LC-2010A HT system and a Luna C18 (150 mm × 2.0 mm, 5μm) analytical column, using $H_2O$/acetonitrile at a flow rate of 1.0 ml/min. Kessil lamps PR160L were used as the irradiation source. For all experiments, the intensity of Kessil lamps was controlled in the maximum level with power consumption: 370 nm (max 43W), 390 nm (max 52W), 427 nm & 440 nm (max 45W), 456 nm (max 50W), 467 nm (max 40W), 525 nm (max 44W).

*CAUTION: Although we did not observe any problems or acetone peroxides in our reactions, extra caution should be given, since the formation of acetone peroxides or their possible accumulation are explosive.*

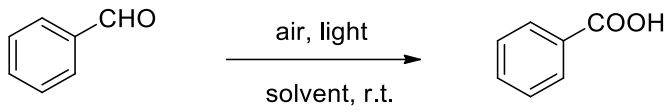
# Optimization of the Reaction Conditions for the Photochemical Aerobic Catalyst-free Oxidation of Aldehydes




**1a** **2a**

| Entry | Solvent | Light | Time (h) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | EtOAc | dark | 5 | 7 |
| 2 | EtOAc | daylight | 5 | 22 |
| 3 | EtOAc | 456 nm | 5 | traces |
| 4 | EtOAc | 370 nm | 5 | 82 (77) |
| 5 | EtOAc | 370 nm 4-AcNH-TEMPO | 5 | 0 |
| 6 | EtOAc | 370 nm under Argon | 5 | traces |
| 7 | acetone | 370 nm | 3 | 94 |
| 8 | $H_2O$ | 370 nm | 3 | 82 |
| **9** | **acetone + 10% v/v $H_2O$** | **370 nm** | **3** | **96 (94)** |
| **10** | **acetone + 3% v/v $H_2O$** | **370 nm** | **3** | **94** |
| 11 | THF + 10% v/v $H_2O$ | 370 nm | 3 | 49 |
| 12 | 2-Me-THF +10% v/v $H_2O$ | 370 nm | 3 | traces |
| 13 | γ-valerolactone + 10 % v/v $H_2O$ | 370 nm | 3 | 31 |
| 14 | EtOAc + 10% v/v $H_2O$ | 370 nm | 3 | 64 |
| 15 | acetone + 10% v/v $H_2O$ | 390 nm | 3 | 80 |
| 16 | acetone + 10% v/v $H_2O$ | 427 nm | 3 | traces |
| 17 | acetone + 10% v/v $H_2O$ | 440 nm | 3 | 14 |
| 18 | acetone + 10% v/v $H_2O$ | 456 nm | 3 | traces |
| 19 | acetone + 10% v/v $H_2O$ | 467 nm | 3 | 0 |
| 20 | acetone + 10% v/v $H_2O$ | 525 nm | 3 | 0 |
| 21 | **acetone + 10% v/v $H_2O$** | **sunlight** | **3** | **87 (82)** |

[a] Conversion determined by NMR. Yield of isolated product after base-acid wash in parenthesis.

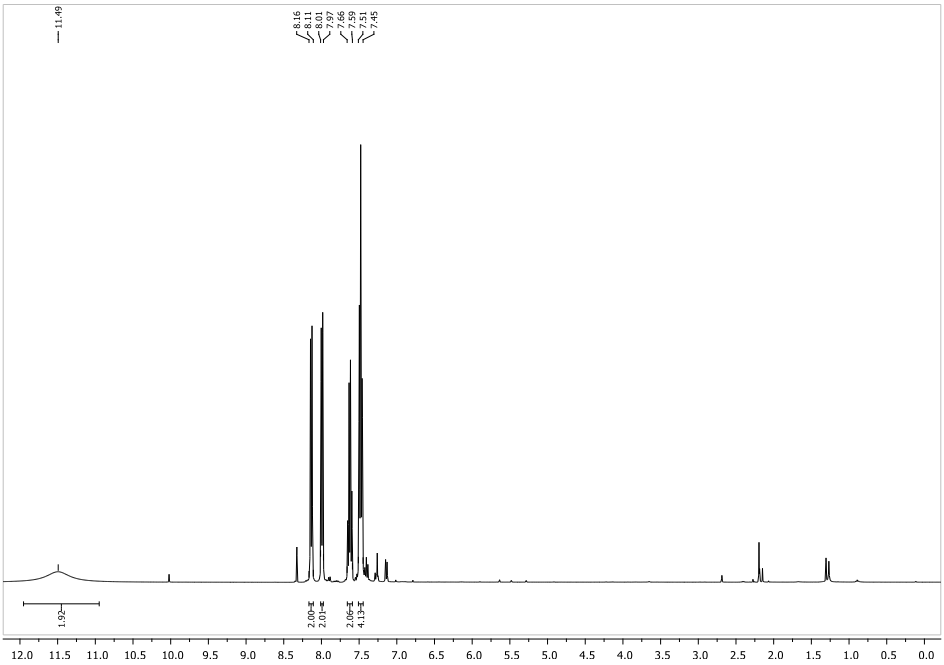



**1l** **2l**

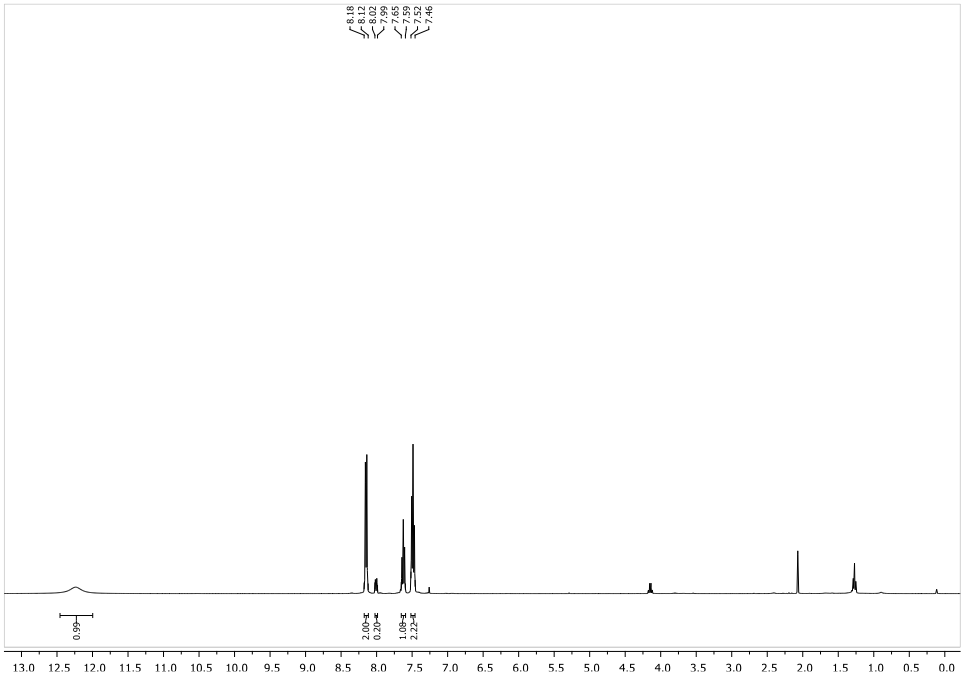
| Entry | Solvent | Light | Time (h) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | EtOAc | 370 nm | 9 | 83 |
| 2 | acetone | 370 nm | 9 | 85 |
| 3 | $H_2O$ | 370 nm | 9 | 38 |
| **4** | **acetone + 10% v/v $H_2O$** | **370 nm** | **7** | **87 (87)** |
| 5 | acetone + 10% v/v $H_2O$ | 390 nm | 9 | 86 |
| 6 | acetone + 10% v/v $H_2O$ | 427 nm | 9 | 25 |
| 7 | acetone + 10% v/v $H_2O$ | 456 nm | 9 | 28 |
| 8 | acetone + 10% v/v $H_2O$ | 525 nm | 9 | 14 |
| 9 | acetone + 10% v/v $H_2O$ | sunlight | 8 | 82[b] |
| 10 | acetone + 10% v/v $H_2O$ | dark | 9 | 0 |

[a] Conversion determined by NMR or HPLC, while the reaction was monitored by HPLC. Yield of isolated product after base-acid wash in parenthesis. [b] A 1:1 mixture of peracid:acid was received, after the work-up of the reaction. Stirring of the mixture in acetone:$H_2O$ (1:3) at 40 $^oC$ for 3 h led to the conversion of the peracid to the acid, isolating finally, the acid in a pure form.

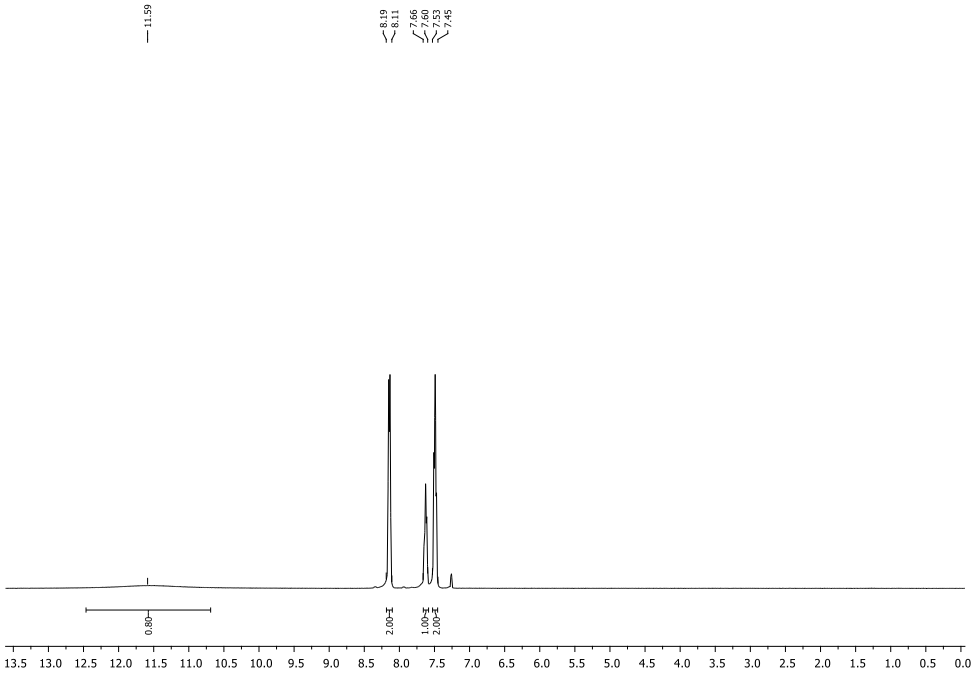
## $^1$H-NMR (400 MHz, $CDCl_3$) spectrum of the aerobic oxidation product of benzaldehyde under sunlight, immediately after the initial work-up (entry 9)



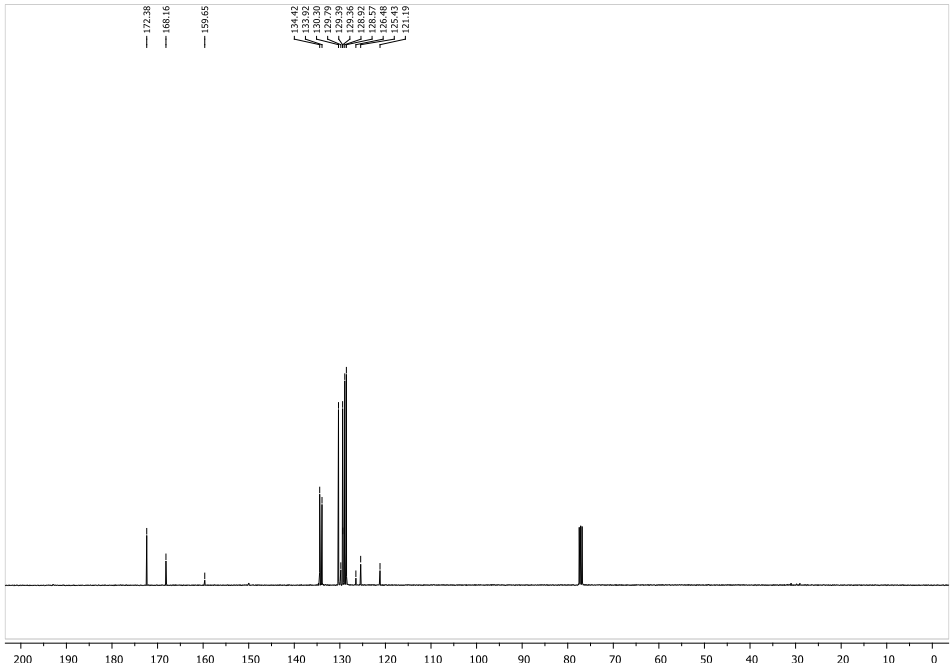
**$^1$H-NMR (400 MHz, $CDCl_3$) spectrum of the aerobic oxidation product of benzaldehyde under sunlight, after stirring in acetone:$H_2O$ at 40 $^o$C for 3 h**



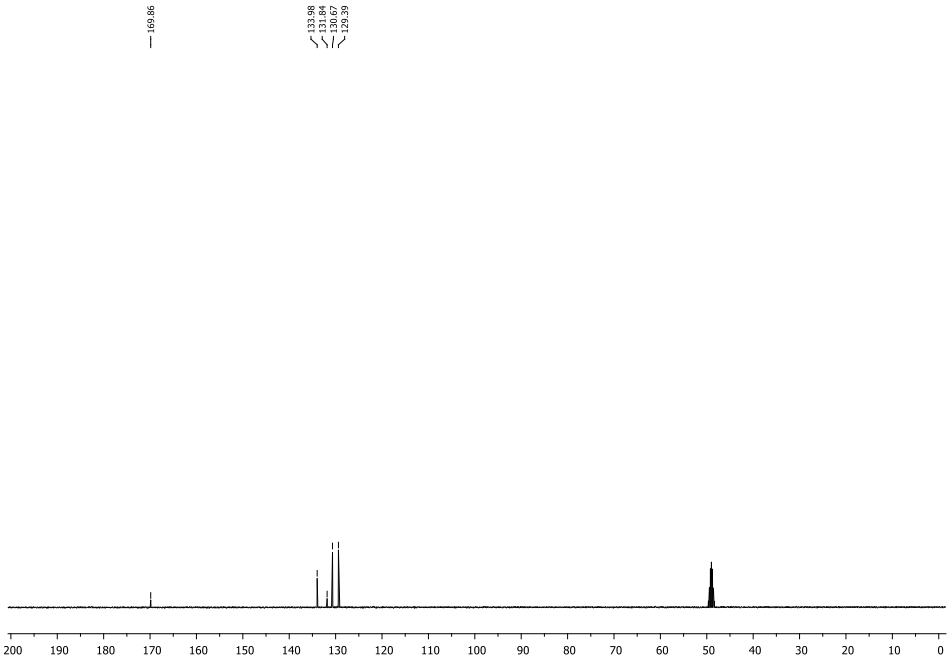

**$^1$H-NMR (400 MHz, $CDCl_3$) spectrum of the aerobic oxidation product of benzaldehyde under sunlight, after the final purification**



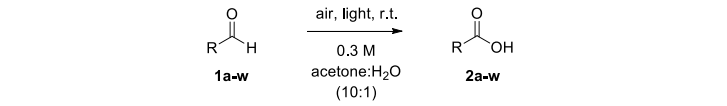
**$^{13}$C-NMR (100 MHz, $CDCl_3$) spectrum of the aerobic oxidation product of benzaldehyde under sunlight, immediately after the initial work-up (entry 9)**

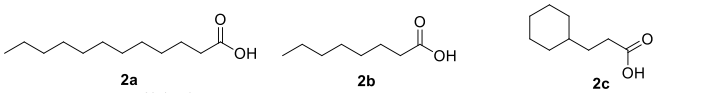



**$^{13}$C-NMR (100 MHz, $CDCl_3$) spectrum of the aerobic oxidation product of benzaldehyde under sunlight, after the final purification**



# Substrate Scope for the Photochemical Aerobic Catalyst-free Oxidation of Aldehydes



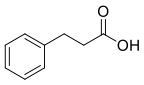
**2a**
370 nm, 94% (3 h)
sunlight, 88% (3 h)



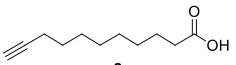
**2b**
370 nm, 85% (3 h)
sunlight, 87% (3 h)



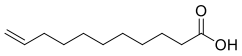
**2c**
370 nm, 85% (3 h)
sunlight, 90% (3 h)



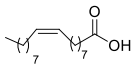
**2d**
370 nm, 85% (3 h)
sunlight, 85% (3 h)



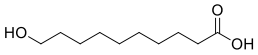
**2e**
370 nm, 85% (3 h)
sunlight, 70% (3 h)



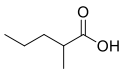
**2f**
370 nm, 91% (3 h)
sunlight, 72% (3 h)



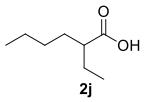
**2g**
370 nm, 36% (20 h), + 18% epoxide
sunlight, 31% (15 h), + 12% epoxide



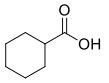
**2h**
370 nm, 81% (3 h)
sunlight, 74% (3 h)



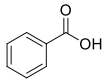
**2i**
370 nm, 70% (3 h)
sunlight, 50% (3 h)



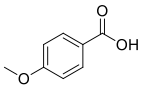
**2j**
370 nm, 66% (8 h)
sunlight, 53% (8 h)



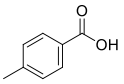
**2k**
370 nm, 75% (3 h)
sunlight, 70% (3 h)



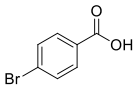
**2l**
370 nm, 87% (7 h)
sunlight, 74% (8 h)



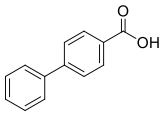
**2m**
370 nm, 87% (5 h)
sunlight, 62% (5 h)



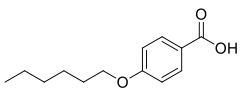
**2n**
370 nm, 90% (5 h)
sunlight, 92% (5 h)



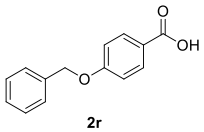
**2o**
370 nm, 95% (5 h)
sunlight, 90% (5 h)



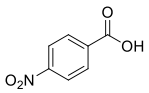
**2p**
370 nm, 83% (5 h)
sunlight, 70% (5 h)



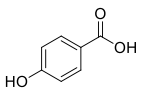
**2q**
370 nm, 86% (5 h)
sunlight, 83% (5 h)



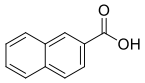
**2r**
370 nm, 79% (8 h)
sunlight, 65% (8 h)



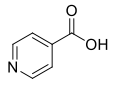
**2s**
370 nm, 87% (96 h)
sunlight, 26% (5 h)



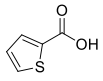
**2t**
370 nm, 44% (8 h)
sunlight, 26% (5 h)



**2u**
370 nm, 77% (26 h)
sunlight, 38% (8 h)



**2v**
370 nm, 85% (8 h)
sunlight, 80% (8 h)



**2w**
370 nm, 55% (24 h)
sunlight, 26% (5 h)

## General Procedure for the Photochemical Aerobic Catalyst-free Oxidation of Aldehydes to Carboxylic Acids

In a test tube containing acetone (3 mL) and $H_2O$ (0.3 mL, HPLC grade), aldehyde (1.00 mmol) was added and the reaction mixture was left stirring under irradiation (370 nm or sunlight) for 3-96 h. The reaction mixture was evaporated to give a crude mixture, which was diluted in EtOAc (10 mL). Then, the crude reaction mixture was treated with an aqueous solution of NaOH 1N (10 mL) and the aqueous layer was extracted with EtOAc (2 x 10 mL). The aqueous basic phase was then acidified with an aqueous solution of HCl 1N (until pH = 1) and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with $H_2O$ (20 mL) and dried over $Na_2SO_4$. The solvent was removed *in vacuo* to afford the desired carboxylic acid without the need for further purification. Carboxylic acids **2m**, **2p** and **2r** were isolated by trituration with petroleum ether (4-6 mL) (cooled with external ice bath). Compounds **2q** and **2g** were purified by flash chromatography on silica gel eluting with petroleum ether (bp 40−60 °C)/ethyl acetate 7/3.

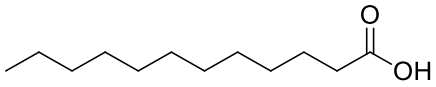
**A** **B**

**Figure S1. A.** Experimental setup of the photocatalyst-free aerobic oxidation of aldehydes to carboxylic acids using Kessil PR160L-370 nm. **B.** Experimental setup of the photocatalyst-free aerobic oxidation of aldehydes to carboxylic acids under sunlight.

## General Procedure for the Conversion of Peracid-Containing Reaction Mixture to the Corresponding Carboxylic Acid

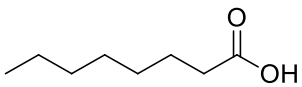
For the reactions where a mixture of peracid:acid was detected, after irradiation, the reaction mixture was diluted with acetone:$H_2O$ (3 mL:9 mL) and stirred at 40 $^oC$ (water bath) for 3 h. The solvent was evaporated to give a crude mixture, which was diluted in EtOAc (10 mL). Then, the crude reaction mixture was treated with an aqueous solution of NaOH 1N (10 mL) and the aqueous layer was extracted with EtOAc (2 x 10 mL). The aqueous basic phase was then acidified with an aqueous solution of HCl 1N (until pH = 1) and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with $H_2O$ (20 mL) and dried over $Na_2SO_4$. The solvent was removed *in vacuo* to afford the desired carboxylic acid without the need for further purification.

**Dodecanoic acid (2a)**[1]




White solid; m.p.: 41-43 $^oC$ (lit. m.p.: 42-44 $^oC$); Yield 94%; **$^1$H-NMR ($CDCl_3$, 400 MHz)**: $\delta$ 10.84 (1H, br s, COOH), 2.34 (2H, t, $J$ = 7.4 Hz, C$H_2$COOH), 1.69-1.59 (2H, m, $CH_2$), 1.38-1.21 (16H, m, 8 x $CH_2$), 0.88 (3H, t, $J$ = 6.2 Hz, $CH_3$); **$^{13}$C-NMR ($CDCl_3$, 100 MHz)**: $\delta$ 180.6, 34.3, 32.1, 29.7, 29.6, 29.5, 29.4, 29.2, 24.8, 22.8, 14.2; **MS (ESI) m/z**: 199 $[M-H]^-$.

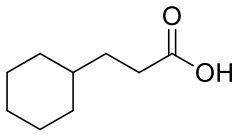
**Octanoic acid (2b)**[2]




Colorless oil; Yield 87%; **$^1$H-NMR ($CDCl_3$, 400 MHz)**: $\delta$ 11.60 (1H, br s, COOH), 2.33 (2H, t, $J$ = 6.6 Hz, C$H_2$COOH), 1.68-1.57 (2H, m, $CH_2$), 1.39-1.19 (8H, m, 4 x $CH_2$),

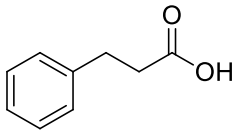
0.87 (3H, t, $J$ = 6.7 Hz, $CH_3$); **$^{13}$C-NMR ($CDCl_3$, 100 MHz)**: $\delta$ 180.7, 34.3, 31.8, 29.2, 29.0, 24.8, 22.7, 14.1; **MS (ESI) m/z**: 143 $[M-H]^-$.

**3-Cyclohexylpropanoic acid (2c)**[2]



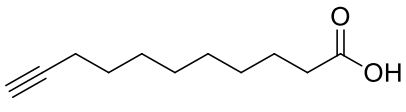

Colorless oil; Yield 90%; **$^1$H-NMR ($CDCl_3$, 400 MHz)**: $\delta$ 11.37 (1H, br s, COOH), 2.34 (2H, t, $J$ = 6.3 Hz, C$H_2$COOH), 1.79-1.58 (5H, m, 2 x $CH_2$ and CH), 1.56-1.47 (2H, m, $CH_2$), 1.30-1.06 (4H, m, 2 x $CH_2$), 0.95-0.81 (2H, m, $CH_2$); **$^{13}$C-NMR ($CDCl_3$, 100 MHz)**: $\delta$ 181.0, 37.2, 33.0, 32.1, 31.8, 26.6, 26.3; **MS (ESI) m/z**: 155 $[M-H]^-$.

**3-Phenylpropanoic acid** (**2d**)[3]




Colorless oil; Yield 85%; **$^1$H-NMR ($CDCl_3$, 400 MHz)**: $\delta$ 11.27 (1H, br s, COOH), 7.38 (2H, d, $J$ = 6.5 Hz, ArH), 7.35-7.27 (3H, m, ArH), 3.05 (2H, t, $J$ = 7.3 Hz, $CH_2$), 2.77 (2H, t, $J$ = 7.3 Hz, $CH_2$); **$^{13}$C-NMR ($CDCl_3$, 100 MHz)**: $\delta$ 179.6, 140.2, 128.6, 128.3, 126.5, 35.7, 30.6; **MS (ESI) m/z**: 149 $[M-H]^-$.

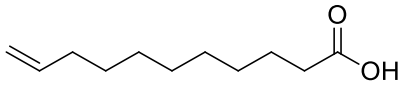
**Undec-10-ynoic acid (2e)**[4]




Colorless oil; Yield 85%; **$^1$H-NMR ($CDCl_3$, 400 MHz)**: $\delta$ 11.27 (1H, br s, COOH), 2.31 (2H, t, $J$ = 6.5 Hz, C$H_2$COOH), 2.13 (2H, t, $J$ = 6.9 Hz, $CH_2$), 1.90 (1H, s, ≡CH), 1.64-

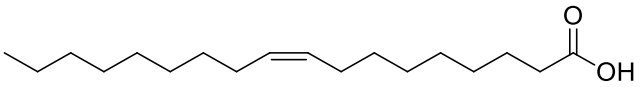
1.55 (2H, m, $CH_2$), 1.53-1.43 (2H, m, $CH_2$), 1.41-1.20 (8H, m, 4 x $CH_2$); **$^{13}$C-NMR ($CDCl_3$, 100 MHz)**: $\delta$ 180.6, 84.7, 68.2, 34.2, 29.1, 29.0, 28.9, 28.7, 28.5, 24.7, 18.4; **MS (ESI) m/z**: 181 $[M-H]^-$.

**Undec-10-enoic acid (2f)**[5]



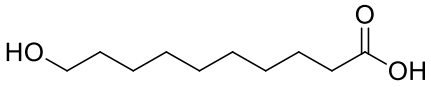

Colorless oil; Yield 91%; **$^1$H-NMR ($CDCl_3$, 400 MHz)**: $\delta$ 11.79 (1H, br s, COOH), 5.86-5.72 (1H, m, =CH), 5.02-4.87 (2H, m, $=CH_2$), 2.33 (2H, t, $J$ = 7.4 Hz, C$H_2$COOH), 2.08-1.97 (2H, m, $CH_2$), 1.69-1.56 (2H, m, $CH_2$), 1.44-1.21 (10H, m, 5 x $CH_2$); **$^{13}$C-NMR ($CDCl_3$, 100 MHz)**: $\delta$ 180.7, 139.1, 114.2, 34.2, 33.9, 29.4, 29.3, 29.1, 29.0, 24.7; **MS (ESI) m/z**: 183 $[M-H]^-$.

**Oleic acid (2g)**[6]



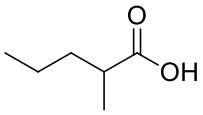

Coloreless oil; Yield 36%; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 5.42-5.29 (2H, m, 2 x =CH), 2.34 (2H, t, $J$ = 7.5 Hz, C$H_2$COOH), 2.10-1.93 (4H, m, 2 x =CHC$H_2$), 1.67-1.59 (2H, m, 2 x $CH_2$), 1.39-1.20 (20H, m, 10 x $CH_2$), 0.88 (3H, t, $J$ = 6.6 Hz, $CH_3$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 180.2, 130.2, 129.9, 34.2, 32.1, 29.9, 29.8, 29.7, 29.5, 29.3, 29.2, 27.4, 27.3, 24.8, 22.8, 14.3; HRMS calculated for $C_{18}H_{33}O_2^-$ $[M-H]^-$: 281.2486, found: 281.2480.

**10-Hydroxydecanoic acid (2h)**[7]



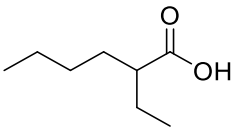

White solid; m.p.: 73-75 $^{o}$C (lit. m.p.: 74-76 $^{o}$C); Yield 81%; **$^{1}$H-NMR ($CDCl_3$, 400 MHz)**: $\delta$ 5.72 (2H, br s, OH and COOH), 3.63 (2H, t, $J$ = 6.0 Hz, C$H_2$OH), 2.32 (2H, t, $J$ = 7.1 Hz, C$H_2$COOH), 1.70-1.48 (4H, m, 2 x $CH_2$), 1.39-1.19 (10H, m, 5 x $CH_2$); **$^{13}$C-NMR ($CDCl_3$, 100 MHz)**: $\delta$ 179.3, 62.9, 34.2, 32.6, 29.4, 29.4, 29.2, 29.1, 25.7, 24.8; **MS (ESI) m/z**: 187 $[M-H]^-$.

**2-Methylpentanoic acid (2i)**[8]



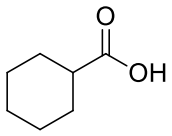

Colorless oil; Yield 70%; **$^{1}$H-NMR ($CDCl_3$, 400 MHz)**: $\delta$ 11.13 (1H, br s, COOH), 2.54-2.40 (1H, m, COCH), 1.74-1.59 (1H, m, CH$H$), 1.46-1.31 (3H, m, 3 x C$H$H), 1.17 (3H, d, $J$ = 6.9 Hz $CH_3$), 0.91 (3H, t, $J$ = 6.7 Hz, $CH_3$); **$^{13}$C-NMR ($CDCl_3$, 100 MHz)**: $\delta$ 183.7, 39.3, 35.8, 20.5, 16.9, 14.0; **MS (ESI) m/z**: 115 $[M-H]^-$.

**2-Ethylhexanoic acid (2j)**[9]



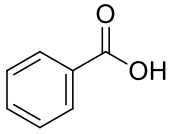

Coloreless oil; Yield 66%; $^{1}$H-NMR (400 MHz, $CDCl_3$): $\delta$ 10.99 (1H, br s, COOH), 2.32-2.24 (1H, m, COCH), 1.71-1.43 (4H, m, 2 × $CH_2$), 1.36-1.26 (4H, m, 2 × $CH_2$), 0.97-0.86 (6H, m, 2 × $CH_3$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 183.3, 47.3, 31.6, 29.7, 25.3, 22.8, 14.0, 11.9; HRMS calculated for $C_8H_{15}O_2^-$ $[M-H]^-$: 143.1078, found: 143.1076.

**Cyclohexanecarboxylic acid (2k)**[10]



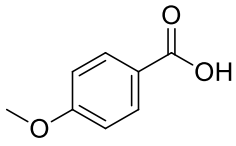

Colorless oil; Yield 75%; **$^{1}$H-NMR (CDCl$_3$, 400 MHz)**: $\delta$ 11.27 (1H, br s, COOH), 2.39-2.25 (1H, m, COCH), 1.98-1.88 (2H, m, 2 x C*H*H), 1.80-1.71 (2H, m, 2 x C*H*H), 1.67-1.59 (1H, m, CH*H*), 1.52-1.39 (2H, m, 2 x C*H*H), 1.35-1.17 (3H, m, 2 x C*H*H); **$^{13}$C-NMR (CDCl$_3$, 100 MHz)**: $\delta$ 182.9, 43.1, 28.9, 25.8, 25.5; **MS (ESI) m/z**: 127 [M-H]$^-$

**Benzoic acid (2l)**[11]



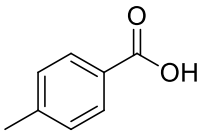

White solid; m.p.: 123-125 $^o$C (lit. m.p.: 122-124 $^o$C); Yield 87%; **$^{1}$H-NMR (CDCl$_3$, 400 MHz)**: $\delta$ 11.59 (1H, br s, COOH), 8.19-8.11 (2H, m, ArH), 7.66-7.60 (1H, m, ArH), 7.53-7.45 (2H, m, 2 x ArH); **$^{13}$C-NMR (CD$_3$OD, 100 MHz)**: $\delta$ 169.9, 134.0, 131.8, 130.7, 129.3; **MS (ESI) m/z**: 121 [M-H]$^-$.

**4-Methoxybenzoic acid (2m)**[12]



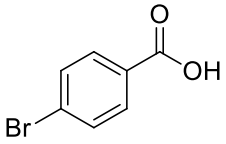

White solid; m.p.: 184-186 $^o$C (lit. m.p.: 184-186 $^o$C); Yield 87%; **$^{1}$H-NMR (CDCl$_3$, 400 MHz)**: $\delta$ 8.07 (2H, d, $J$ = 7.6 Hz, ArH), 6.95 (2H, d, $J$ = 7.6 Hz, ArH), 3.88 (3H, s, $OCH_3$); **$^{13}$C-NMR (CDCl$_3$, 100 MHz)**: $\delta$ 171.7, 164.2, 132.5, 121.8, 113.9, 55.6; **MS (ESI) m/z**: 151 [M-H]$^-$.

**4-Methylbenzoic acid** (**2n**)[13]



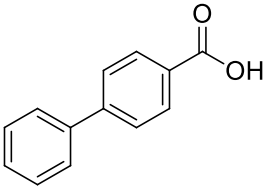

White solid; m.p.: 179-181 °C (lit. m.p.: 179-181 °C); Yield 92%; **$^1$H-NMR (DMSO-d6, 400 MHz)**: $\delta$ 12.80 (1H, s, COOH), 7.83 (2H, d, $J$ = 7.5 Hz, ArH), 7.29 (2H, d, $J$ = 7.5 Hz, ArH), 2.36 (3H, s, $CH_3$); **$^{13}$C-NMR (DMSO-d6, 100 MHz)**: $\delta$ 167.8, 143.5, 129.8, 129.6, 128.5, 21.6; **MS (ESI) m/z**: 135 $[M-H]^-$.

**4-Bromobenzoic acid** (**2o**)[14]



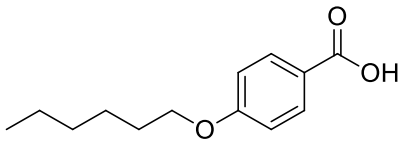

White solid; m.p.: 251-253 °C (lit. m.p.: 252-254 °C); Yield 95%; **$^1$H-NMR (DMSO-d6, 400 MHz)**: $\delta$ 13.16 (1H, s, COOH), 7.86 (2H, d, $J$ = 7.5 Hz, ArH), 7.70 (2H, d, $J$ = 7.1 Hz, ArH); **$^{13}$C-NMR (DMSO-d6, 100 MHz)**: $\delta$ 166.6, 131.7, 131.3, 130.0, 126.9; **MS (ESI) m/z**: 198 $[M-H]^-$.

**4-Biphenyl carboxylic acid (2p)**[15]



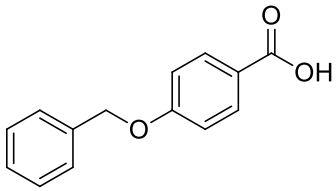

White solid; m.p.: 220-222 ºC (lit. m.p.: 222-224 ºC); Yield 83%; **$^1$H-NMR ($CDCl_3$, 400 MHz)**: $\delta$ 8.24-8.13 (2H, m, ArH), 7.76-7.68 (2H, m, ArH), 7.67-7.60 (2H, m, ArH), 7.53-7.45 (2H, m, ArH), 7.44-7.38 (1H, m, ArH); **$^{13}$C-NMR ($CD_3OD$, 100 MHz)**: $\delta$ 169.7, 147.0, 141.3, 131.3, 130.7, 130.0, 129.2, 128.2, 128.0; **MS (ESI) m/z**: 197 $[M-H]^-$.

**4-(Hexyloxy) benzoic acid (2q)**[16]



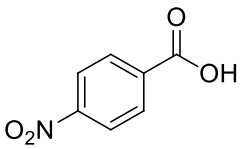
White solid; m.p.: 130-133 °C (lit. m.p.: 105-153 °C); Yield 86%; **$^{1}$H-NMR ($CDCl_3$, 400 MHz)**: $\delta$ 11.48 (1H, br s, COOH), 8.06 (2H, d, $J$ = 8.1 Hz, ArH), 6.93 (2H, d, $J$ = 8.1 Hz, ArH), 4.02 (2H, t, $J$ = 6.3 Hz, $OCH_2$), 1.85-1.76 (2H, m, $CH_2$), 1.55-1.28 (6H, m, 3 x $CH_2$), 0.98-0.85 (3H, m, $CH_3$); **$^{13}$C-NMR ($CDCl_3$, 100 MHz)**: $\delta$ 172.3, 163.9, 132.5, 121.6, 114.3, 68.4, 31.7, 29.2, 25.8, 22.7, 14.1; **MS (ESI) m/z**: 221 $[M-H]^-$.

**4-(Benzyloxy) benzoic acid (2r)**[17]



White solid; m.p.: 189-191 °C (lit. m.p.: 190-192 °C); Yield 79%; **$^{1}$H-NMR (DMSO-d6, 400 MHz)**: $\delta$ 12.61 (1H, br s, COOH), 7.91 (2H, d, $J$ = 8.0 Hz, ArH), 7.55-7.27 (5H, m, ArH), 7.09 (2H, d, $J$ = 8.0 Hz, ArH), 5.17 (2H, s, $OCH_2$); **$^{13}$C-NMR (DMSO-d6, 100 MHz)**: $\delta$ 167.0, 161.9, 136.5, 131.3, 128.5, 128.0, 127.8, 123.2, 114.6, 69.5; **MS (ESI) m/z**: 227 $[M-H]^-$.

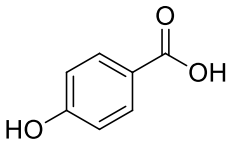
**4-Nitrobenzoic acid (2s)**[18]



White solid; m.p.: 238-240 °C (lit. m.p.: 237-240 °C); Yield 87%; $^{1}$H-NMR (400 MHz, DMSO-*d6*): $\delta$ 8.32 (2H, d, $J$ = 8.6 Hz, ArH), 8.17 (2H, d, $J$ = 8.6 Hz, ArH); $^{13}$C-NMR

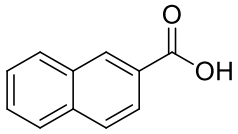
(100 MHz, DMSO-*d6*): $\delta$ 165.8, 150.1, 136.4, 130.7, 123.7; HRMS calculated for $C_7H_4NO_4^-$ [M-H]$^-$: 166.0146, found: 166.0143.

**4-Hydroxybenzoic acid (2t)**[19]



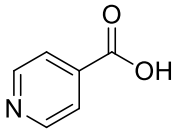

White solid; m.p.: 211-213 °C (lit. m.p.: 213-215 °C); Yield 44%; **$^1$H-NMR ($CD_3OD$, 400 MHz)**: $\delta$ 7.88 (2H, d, *J* = 8.1 Hz, ArH), 6.82 (2H, d, *J* = 8.1 Hz, ArH); **$^{13}$C-NMR ($CD_3OD$, 100 MHz)**: $\delta$ 170.1, 163.3, 133.0, 122.7, 116.0; **MS (ESI) m/z**: 137 [M-H]$^-$.

**2-Naphthoic acid (2u)**[20]




White solid; m.p.: 185-187 °C (lit. m.p.: 185-187 °C); Yield 77%; **$^1$H-NMR ($CD_3OD$, 400 MHz)**: $\delta$ 8.60 (1H, s, ArH), 8.03 (1H, d, *J* = 8.4 Hz, ArH), 7.96 (1H, d, *J* = 7.9 Hz, ArH), 7.90 (2H, d, *J* = 8.3 Hz, ArH), 7.62-7.50 (2H, m, ArH); **$^{13}$C-NMR (DMSO-d6, 100 MHz)**: $\delta$ 167.4, 134.9, 132.1, 130.5, 129.2, 128.3, 128.1, 127.6, 126.7, 125.2; **MS (ESI) m/z**: 171 [M-H]$^-$.

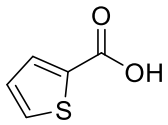
**Isonicotinic acid (2v)**[21]




Yellow solid; m.p.: > 250 °C (lit. m.p.: 308-309 °C); Yield 85%; $^1$H-NMR (400 MHz, DMSO-*d6*): $\delta$ 8.76 (2H, d, *J* = 4.2 Hz, ArH), 7.80 (2H, d, *J* = 4.2 Hz, ArH); $^{13}$C-NMR

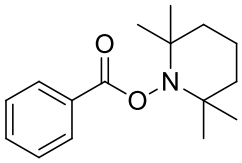
(100 MHz, DMSO-*d6*): $\delta$ 166.2, 150.6, 138.3, 122.8; HRMS calculated for $C_6H_4NO_2^-$ [M-H]$^-$: 122.0248, found: 122.0247.

**Thiophene-2-carboxylic acid (2w)**[22]




White solid; m.p.: 126-128 °C (lit. m.p.: 127-129 °C); Yield 55%; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 10.51 (1H, br s, COOH), 7.91 (1H, dd, *J* = 3.6 and 1.0 Hz, CH), 7.66 (1H, dd, *J* = 5.1 and 1.0 Hz, CH), 7.15 (1H, dd, *J* = 5.1 and 3.6 Hz, CH); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 167.9, 135.2, 134.2, 133.0, 128.2; HRMS calculated for $C_5H_3O_2S^-$ [M-H]$^-$: 126.9859, found: 126.9856.

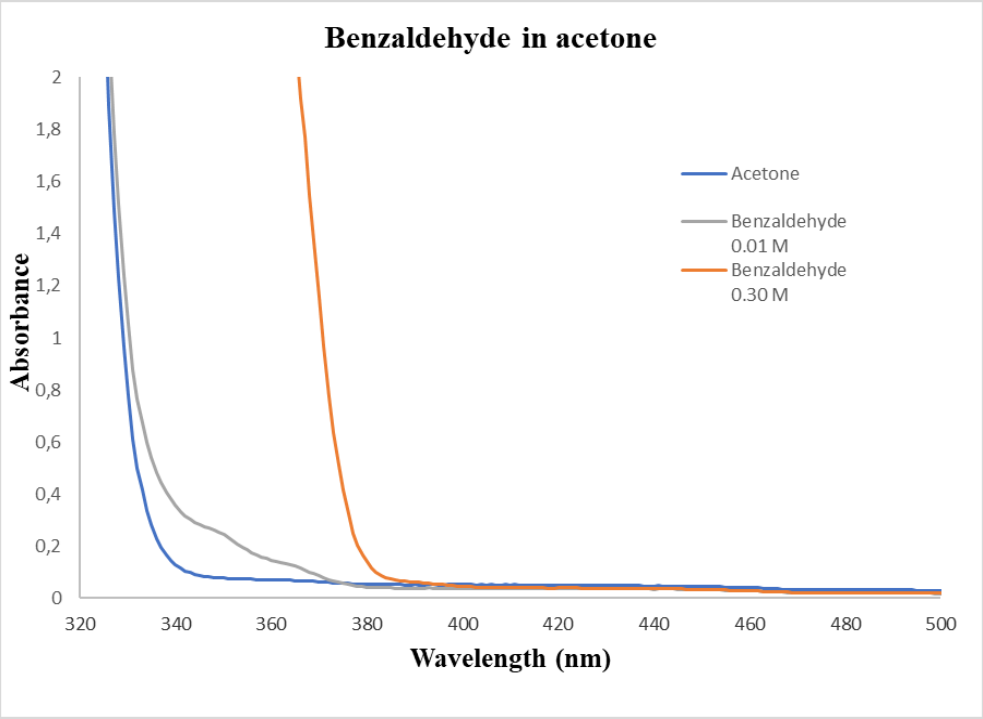
# Synthesis of 2,2,6,6-Tetramethylpiperidin-1-yl Benzoate (S1)[23]



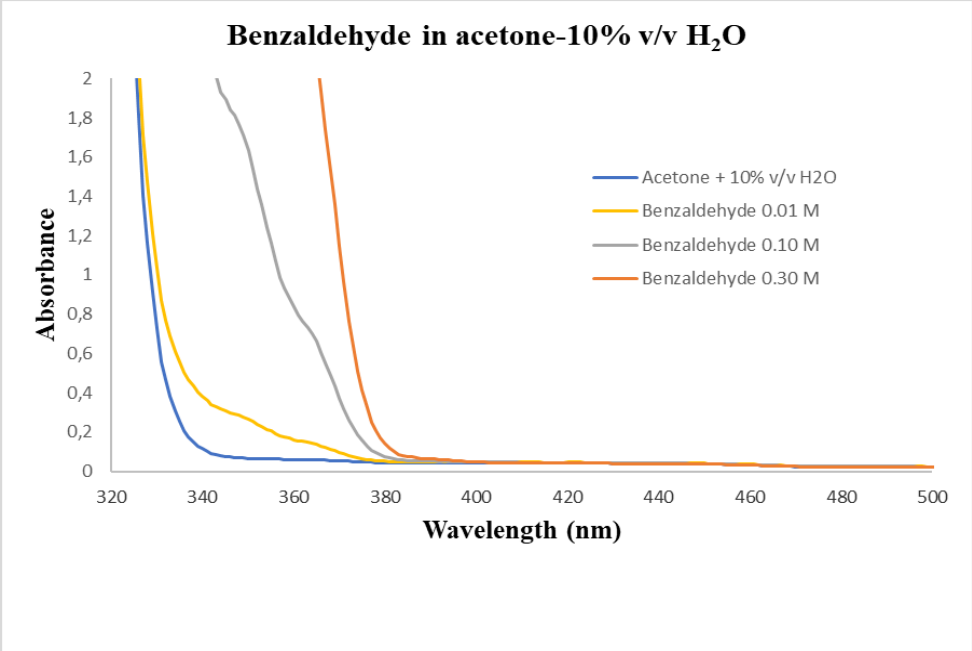

In a test tube containing acetone (3 mL) and $H_2O$ (0.3 mL, HPLC grade), benzaldehyde (106 mg, 1.00 mmol) and Tempo (156 mg, 1.00 mmol) were added and the reaction mixture was left stirring under LED 370 nm irradiation for 3 h. The reaction mixture was evaporated to give a crude mixture, which was diluted with EtOAc (10 mL). Then, the crude reaction mixture was treated with aq. NaOH 1N (10 mL) and the aqueous layer was extracted with EtOAc (2 x 10 mL). The aqueous basic phase was then acidified with aq. HCl 1N (until pH = 1) and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with $H_2O$ (20 mL) and dried over $Na_2SO_4$. The solvent was removed *in vacuo* and the desired product was purified by flash chromatography on silica gel eluting with petroleum ether (bp 40−60 °C) / ethyl acetate 7/3.

White solid; m.p.: 88-90°C; Yield 34%; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.08-8.03 (2H, m, ArH), 7.57-7.51 (1H, m, ArH), 7.46-7.40 (2H, m, ArH), 1.81-1.40 (6H, m, 3 x $CH_2$), 1.26 (6H, s, 2 x $CH_3$), 1.11 (6H, s, 2 x $CH_3$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 166.3, 132.8, 129.7, 129.5, 128.4, 60.4, 39.1, 31.9, 20.8, 17.0. HRMS calculated for $C_{16}H_{23}NO_2$ $[M+H]^+$: 261.1729, found: 261.1729.

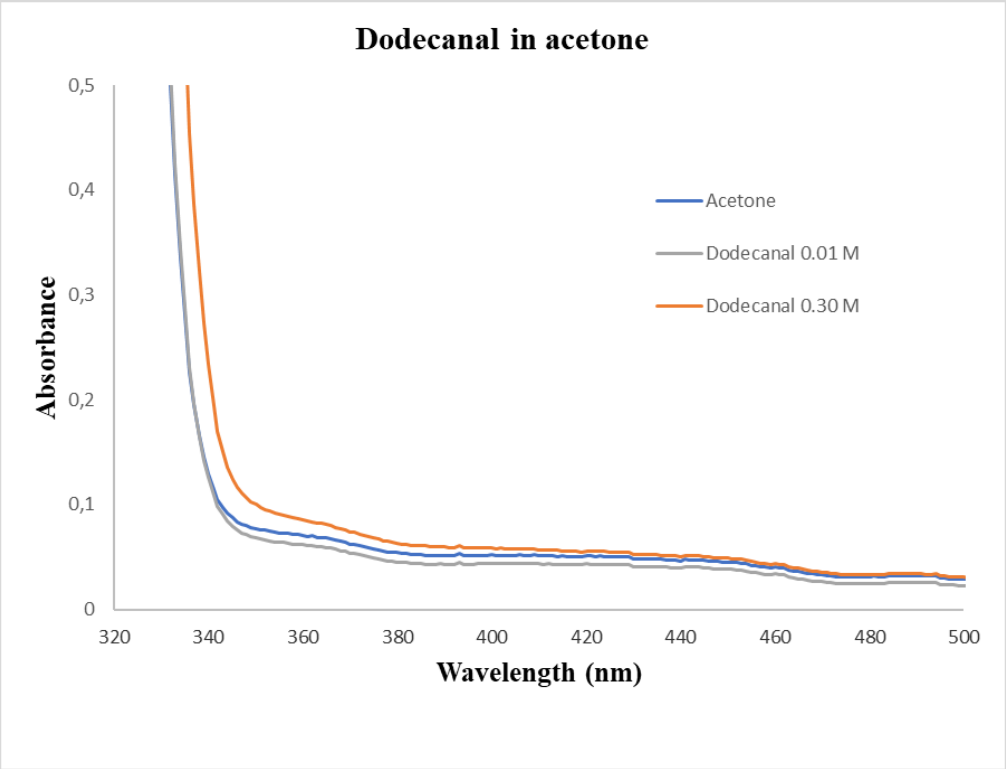
## Mechanistic Investigations with UV-Vis Absorption Spectra



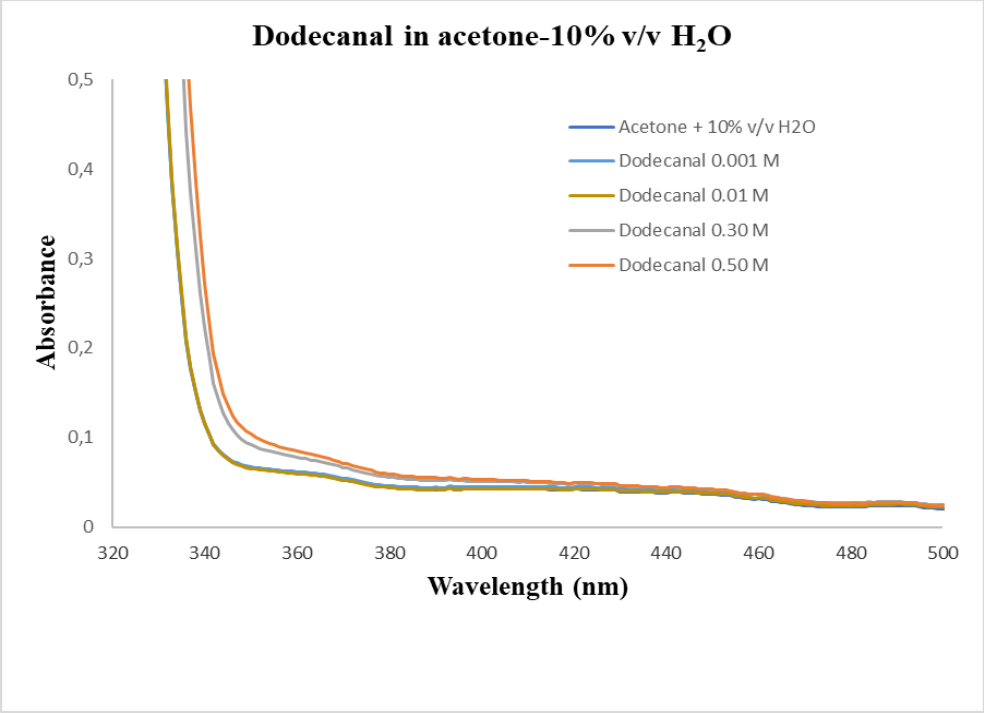

UV-Vis absorbance of benzaldehyde (0.01 or 0.30 M) in acetone.




UV-Vis absorbance of benzaldehyde (0.01 or 0.10 or 0.30 M) in acetone:$H_2O$.



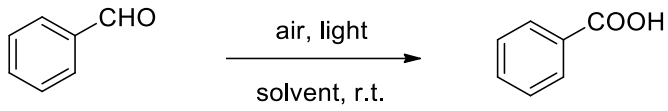

UV-Vis absorbance of dodecanal (0.01 or 0.30 M) in acetone.




UV-Vis absorbance of dodecanal (0.001 or 0.01 or 0.1 or 0.3 M) in acetone:$H_2O$.

# High Performance Liquid Chromatography (HPLC) Studies

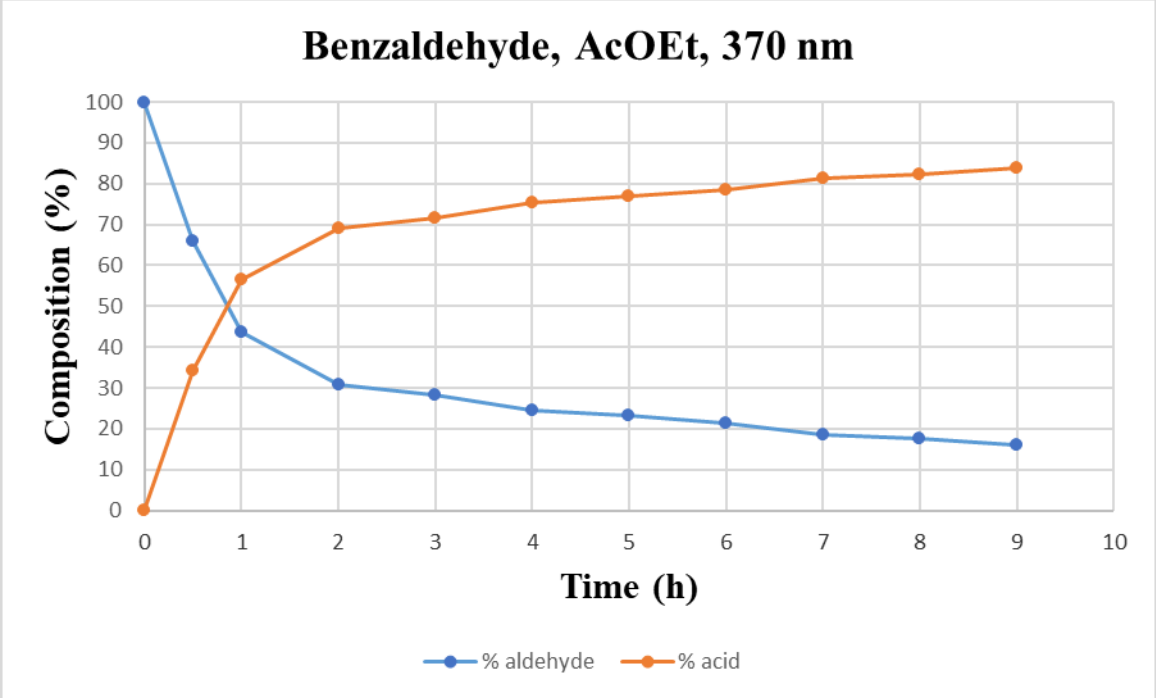
## Monitoring of the aerobic oxidation of benzaldehyde by HPLC




**1l** **2l**

The reaction was setup following the general procedure. At the specific time of study, an aliquot of 10 μL was taken from the crude reaction mixture and was diluted with 990 μL of MeOH. A sample of 10 μL from the mixture was injected for HPLC analysis. Eluting system: MeCN:$H_2O$ – 5:95 gradient to 15:85 for 15 min, 35 ºC, flow rate 1 mL/min, detector: 280 nm.

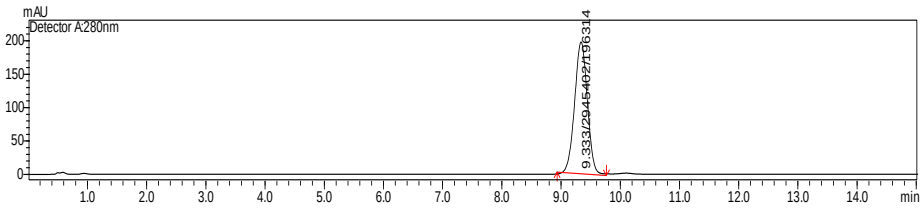
**Solvent: AcOEt. Light: LED 370 nm**




Composition of aldehyde and acid as a function of time

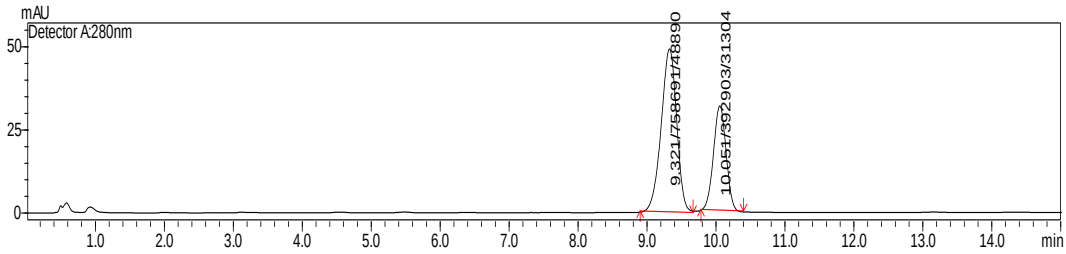
As a representative example, the chromatograms used for the construction of the above graph are shown below:

**0 hour**



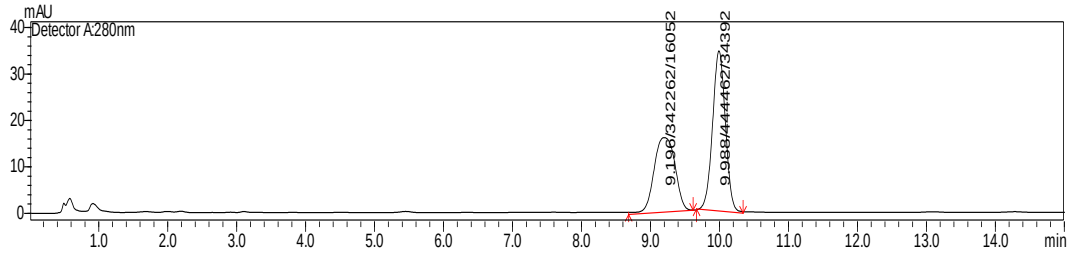

| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.333 | 2945402 | 196314 | 100.0000 | -- | 1.016 |

**30 min**



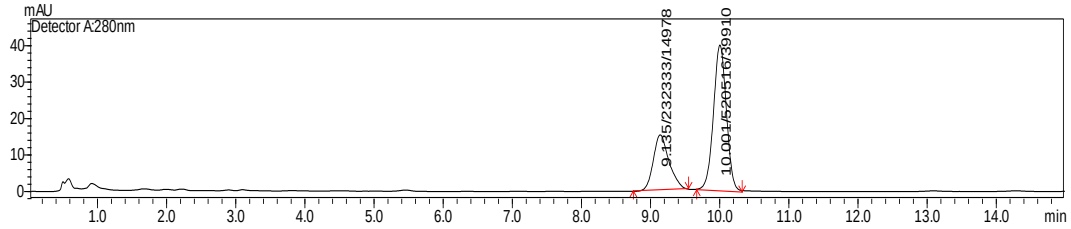

| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.321 | 758691 | 48890 | 65.8818 | -- | 0.939 |
| 2 | 10.051 | 392903 | 31304 | 34.1182 | 1.919 | 1.020 |

## 1 hour



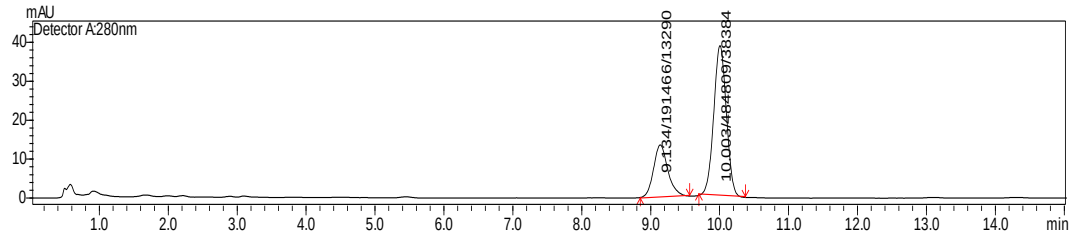

| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.196 | 342262 | 16052 | 43.5047 | -- | 1.015 |
| 2 | 9.988 | 444462 | 34392 | 56.4953 | 1.819 | 1.025 |

## 2 hours



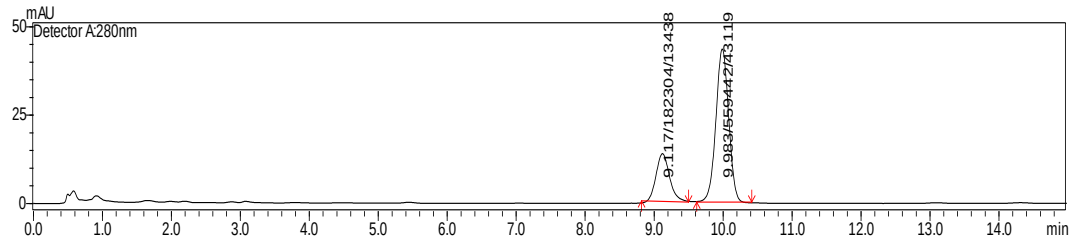

| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.135 | 232333 | 14978 | 30.8605 | -- | 1.242 |
| 2 | 10.001 | 520516 | 39910 | 69.1395 | 2.282 | 1.002 |

**3 hours**



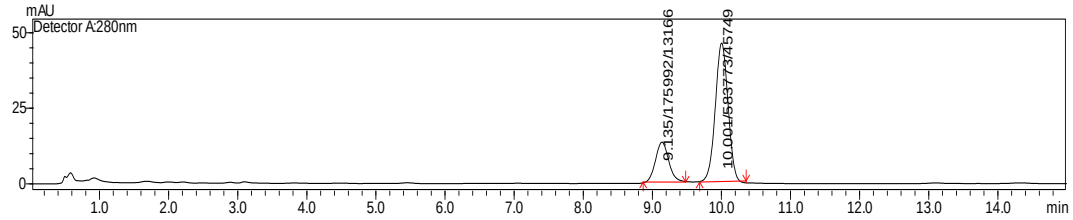

| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.135 | 191466 | 13290 | 28.3118 | -- | 1.169 |
| 2 | 10.003 | 484809 | 38384 | 71.6882 | 2.409 | 1.018 |

**4 hours**



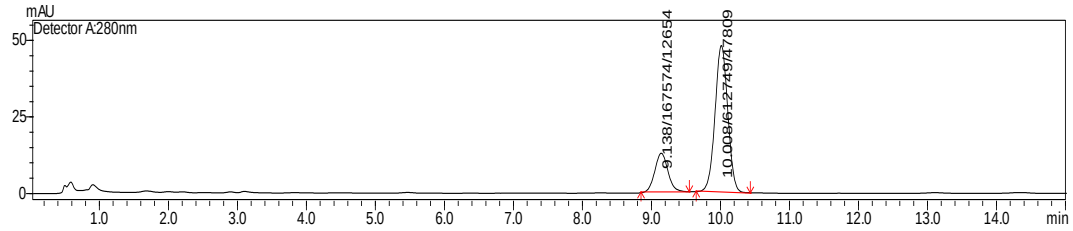

| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.117 | 182304 | 13438 | 24.5776 | -- | 1.248 |
| 2 | 9.983 | 559442 | 43119 | 75.4224 | 2.457 | 1.009 |

## 5 hours



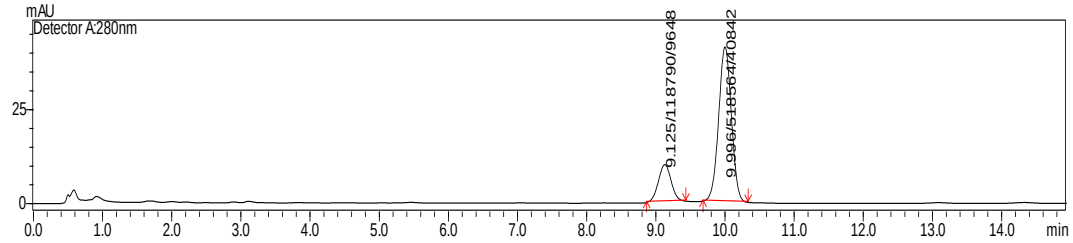

| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.135 | 175992 | 13166 | 23.1640 | -- | 1.159 |
| 2 | 10.001 | 583773 | 45749 | 76.8360 | 2.475 | 0.993 |

## 6 hours



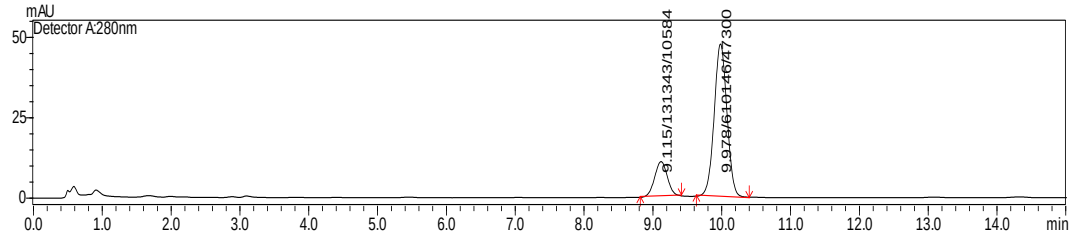

| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.138 | 167574 | 12654 | 21.4749 | -- | 1.130 |
| 2 | 10.008 | 612749 | 47809 | 78.5251 | 2.495 | 1.034 |

**7 hours**



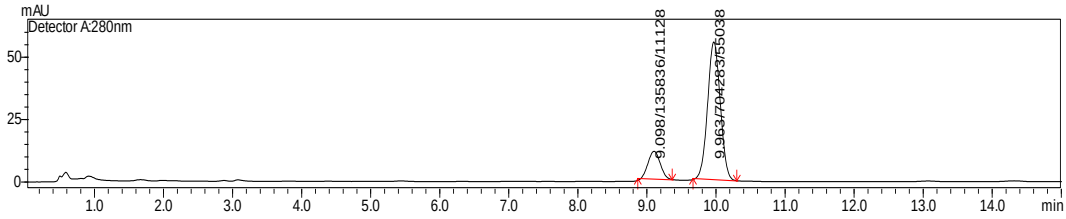

| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.125 | 118790 | 9648 | 18.6381 | -- | 1.044 |
| 2 | 9.996 | 518564 | 40842 | 81.3619 | 2.547 | 1.016 |

**8 hours**



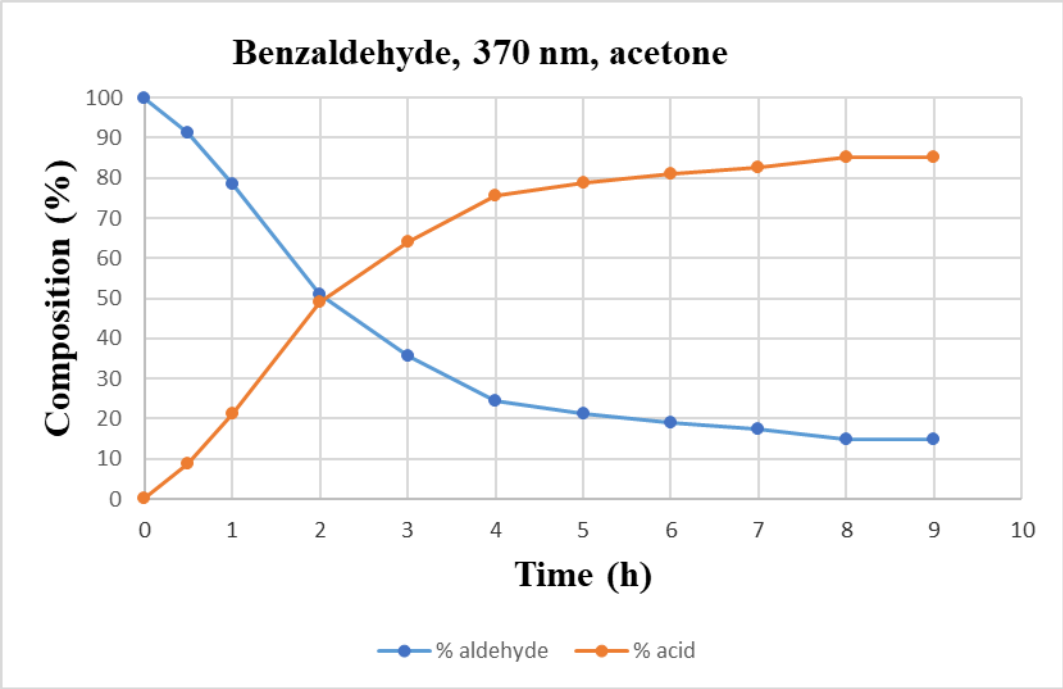

| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.115 | 131343 | 10584 | 17.7134 | -- | 1.032 |
| 2 | 9.978 | 610146 | 47300 | 82.2866 | 2.506 | 1.043 |

**9 hours**



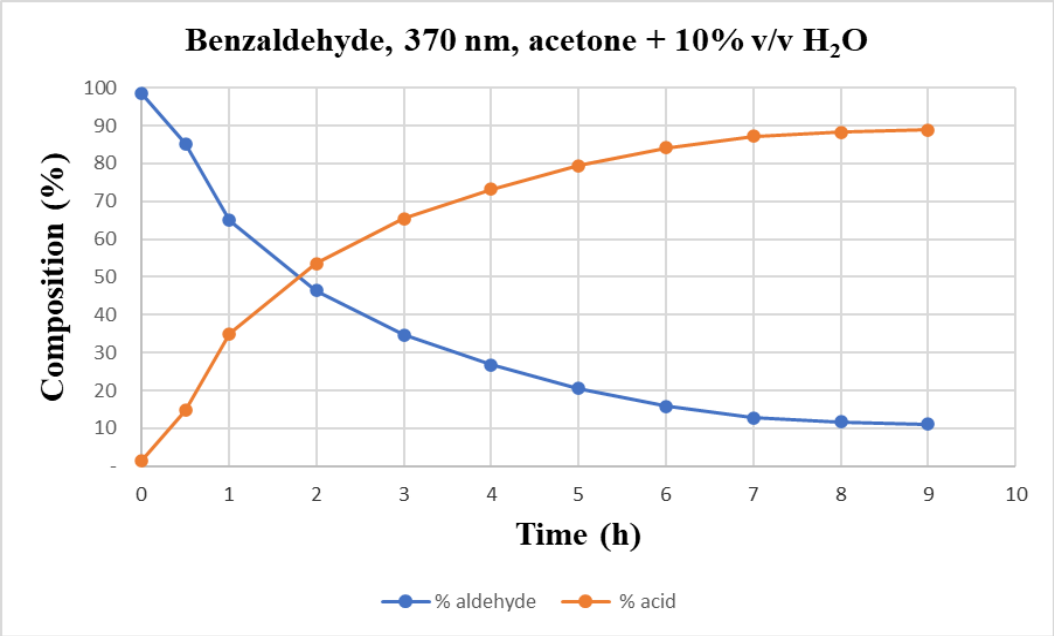

| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.098 | 135836 | 11128 | 16.1687 | -- | 1.114 |
| 2 | 9.963 | 704283 | 55038 | 83.8313 | 2.537 | 1.052 |

**Solvent: Acetone. Light: LED 370 nm**



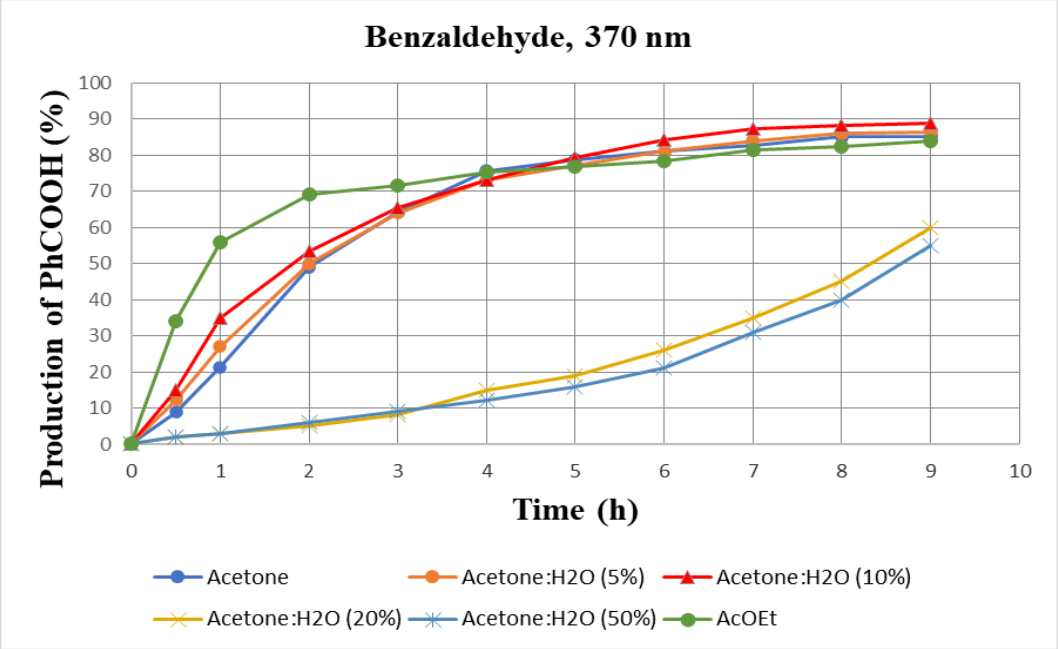

Composition of aldehyde and acid as a function of time

**Solvent: Acetone:$H_2O$. Light: LED 370 nm**

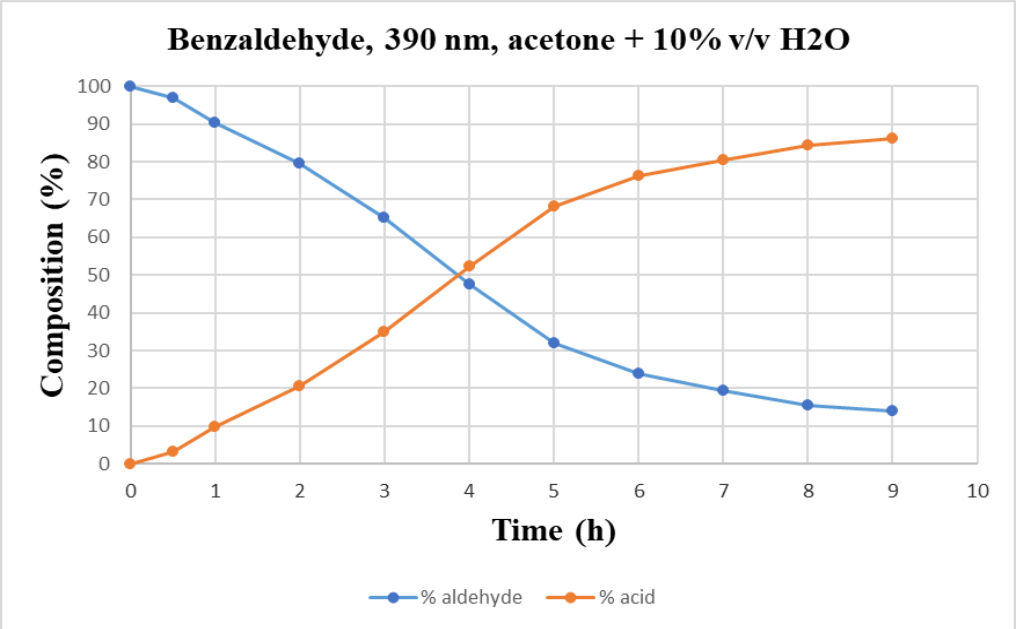



Composition of aldehyde and acid as a function of time

**Course of the production of benzoic acid in various solvents. Irradiation of benzaldehyde at 370 nm, monitoring by HPLC**

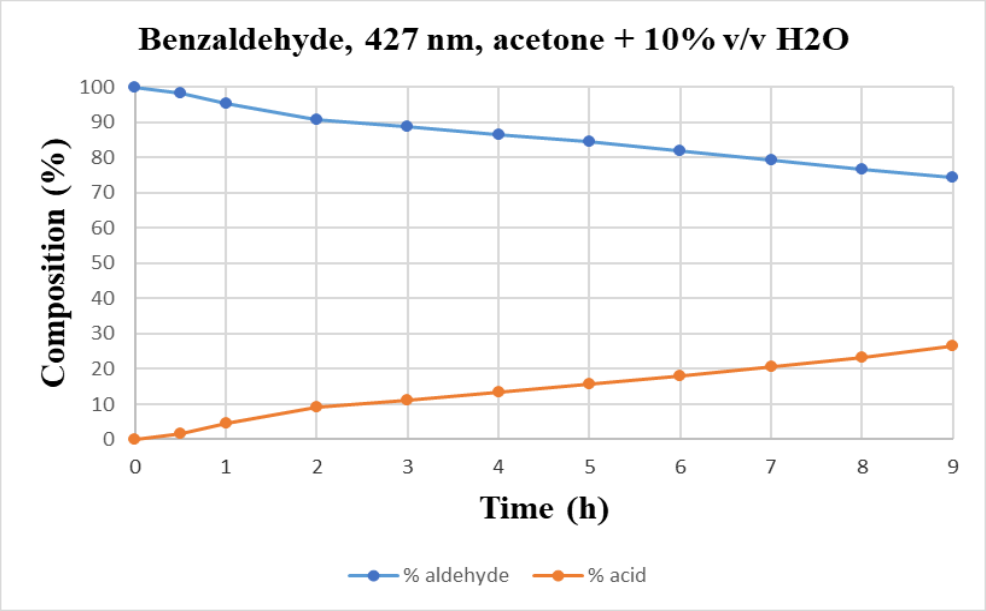


**Solvent: Acetone:$H_2O$. Light: LED 390 nm**



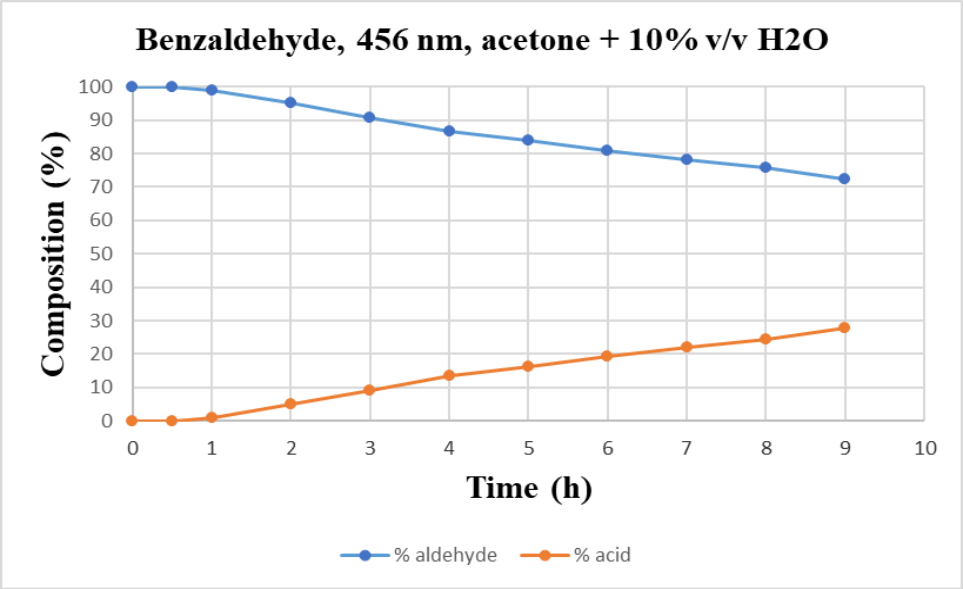

Composition of aldehyde and acid as a function of time

**Solvent: Acetone:$H_2O$. Light: LED 427 nm**



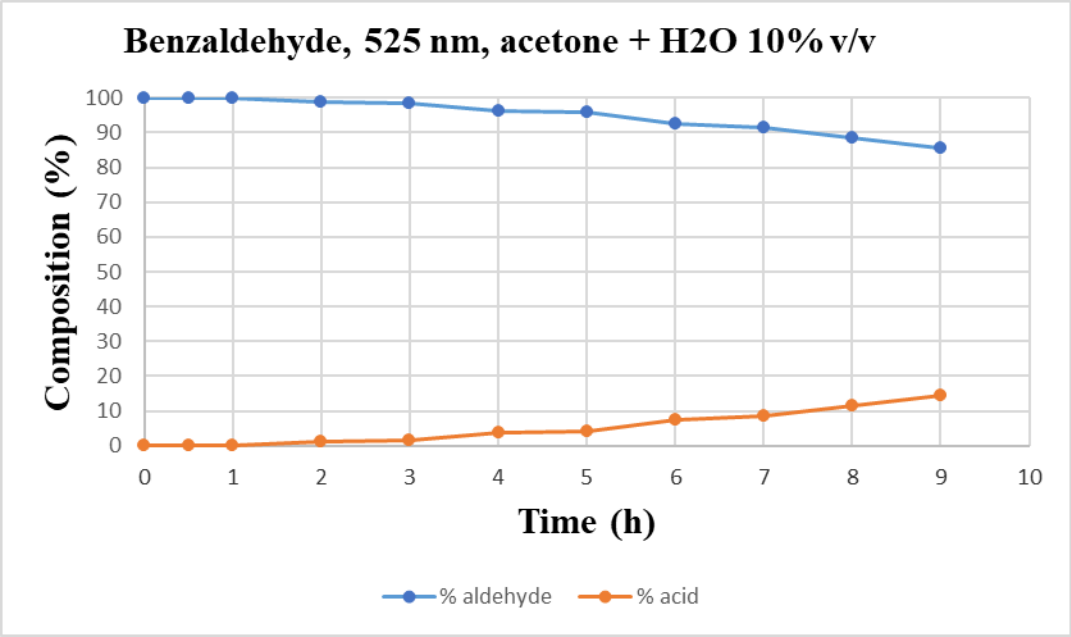

Composition of aldehyde and acid as a function of time

**Solvent: Acetone:$H_2O$. Light: LED 456 nm**



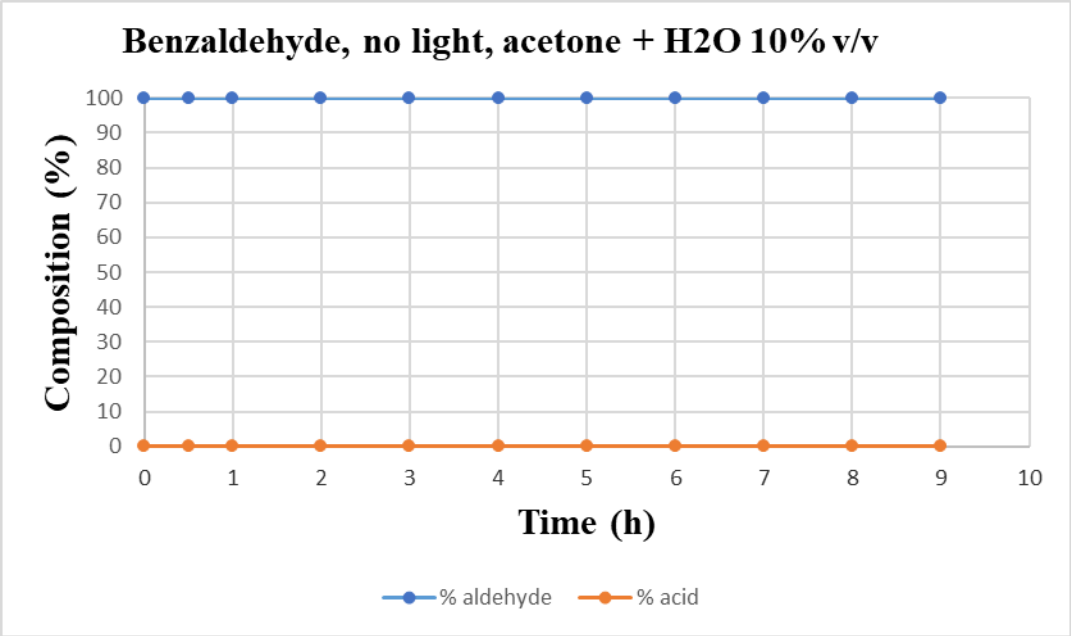

Composition of aldehyde and acid as a function of time

**Solvent: Acetone:$H_2O$. Light: LED 525 nm**




Composition of aldehyde and acid as a function of time

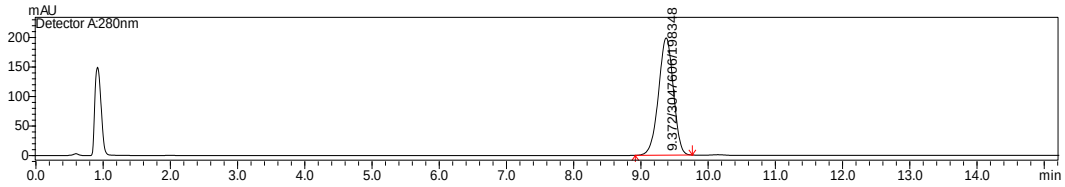
**Solvent: Acetone:$H_2O$. Light: no light**




Composition of aldehyde and acid as a function of time

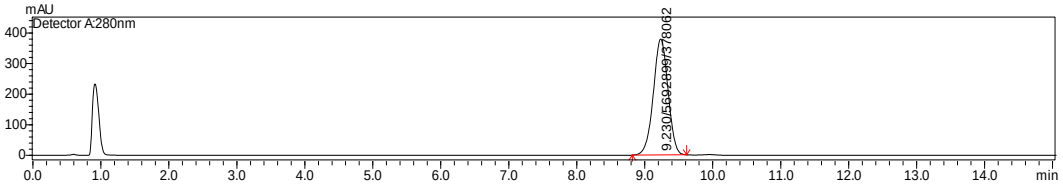
As an example, the chromatograms used for the construction of the above graph for 0 hour and 7 hours are shown below.

**0 hour**



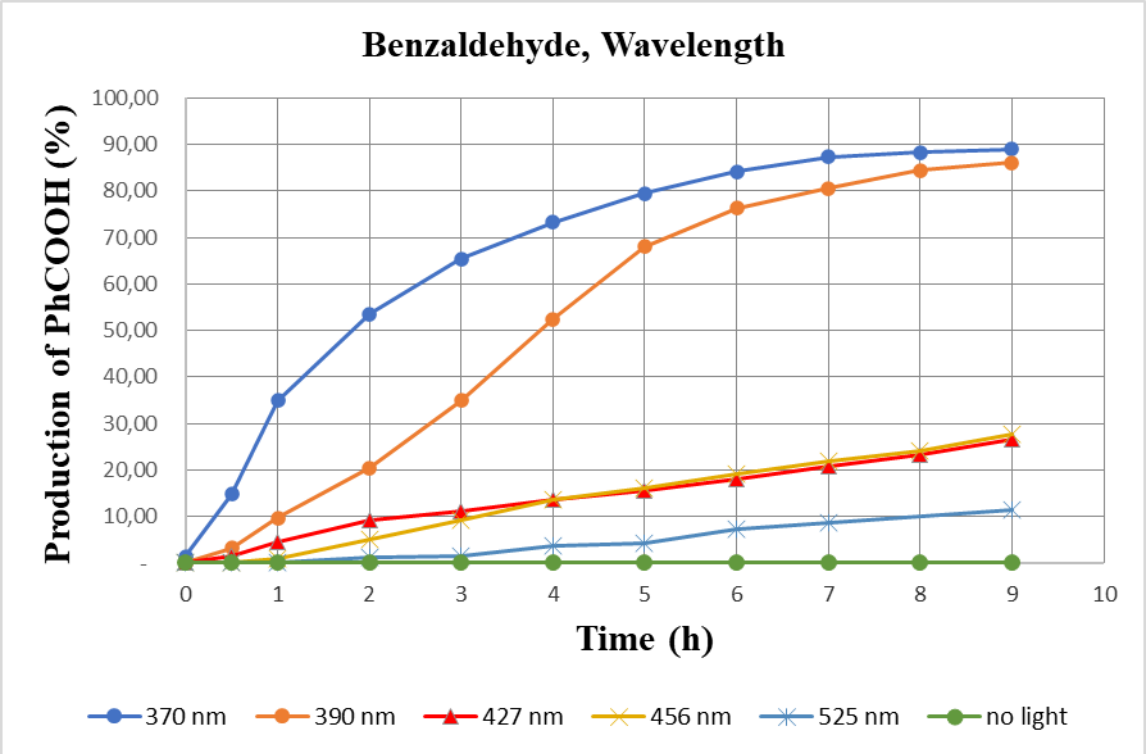

| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.372 | 3047606 | 198348 | 100.0000 | -- | 0.969 |

**7 hours**

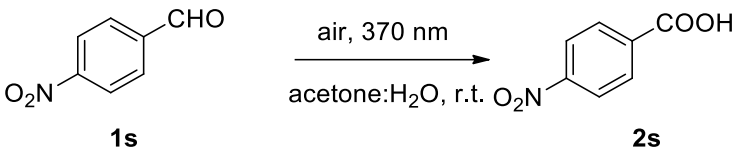



| # | Time | Area | Height | Area% | Resolution | Tailing F. |
|---|---|---|---|---|---|---|
| 1 | 9.231 | 5692899 | 378062 | 100.0000 | -- | 0.996 |

## Course of the production of benzoic acid after LED irradiation at various wavelengths, monitoring by HPLC

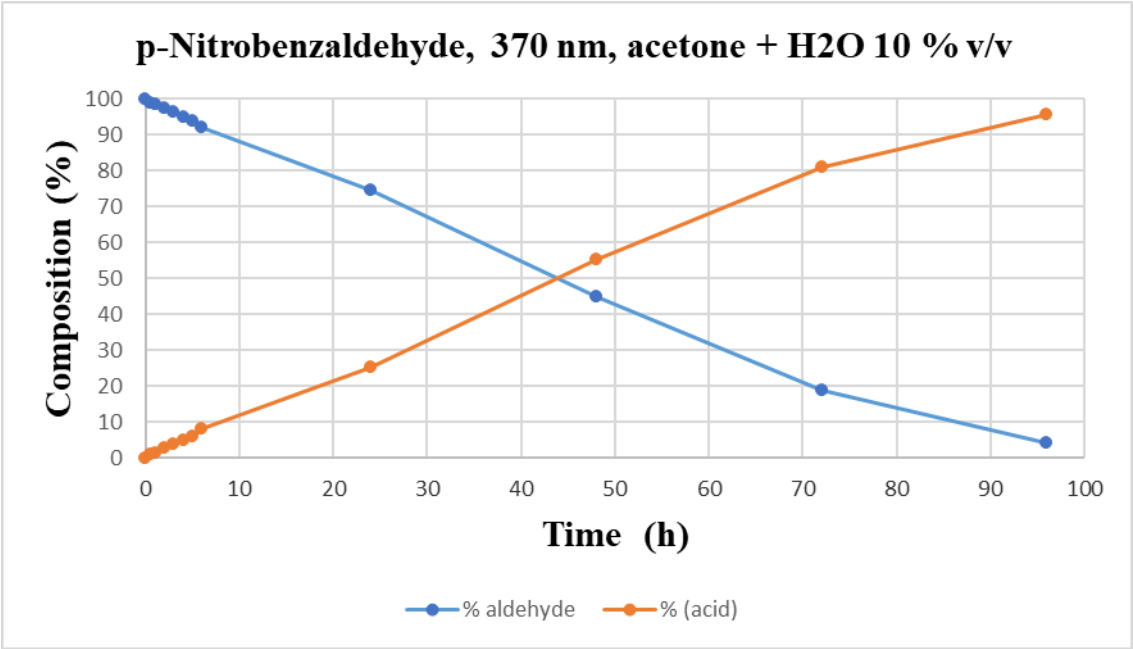


**Monitoring of the aerobic oxidation of 4-nitrobenzaldehyde in acetone:$H_2O$ irradiated at 370 nm and monitored by HPLC**

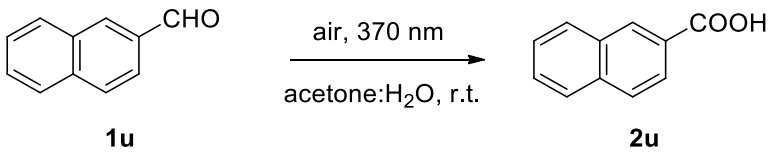



**1s** **2s**

The reaction was setup following the general procedure. At the specific time of study, an aliquot of 10 μL was taken from the crude reaction mixture and was diluted with 990 μL of MeOH. A sample of 10 μL from the mixture was injected for HPLC analysis. Eluting system: MeCN:$H_2O$ – 5:95, gradient to 10:90 for 20 min, 35 $^oC$, flow rate 1 mL/min, detector: 280 nm.

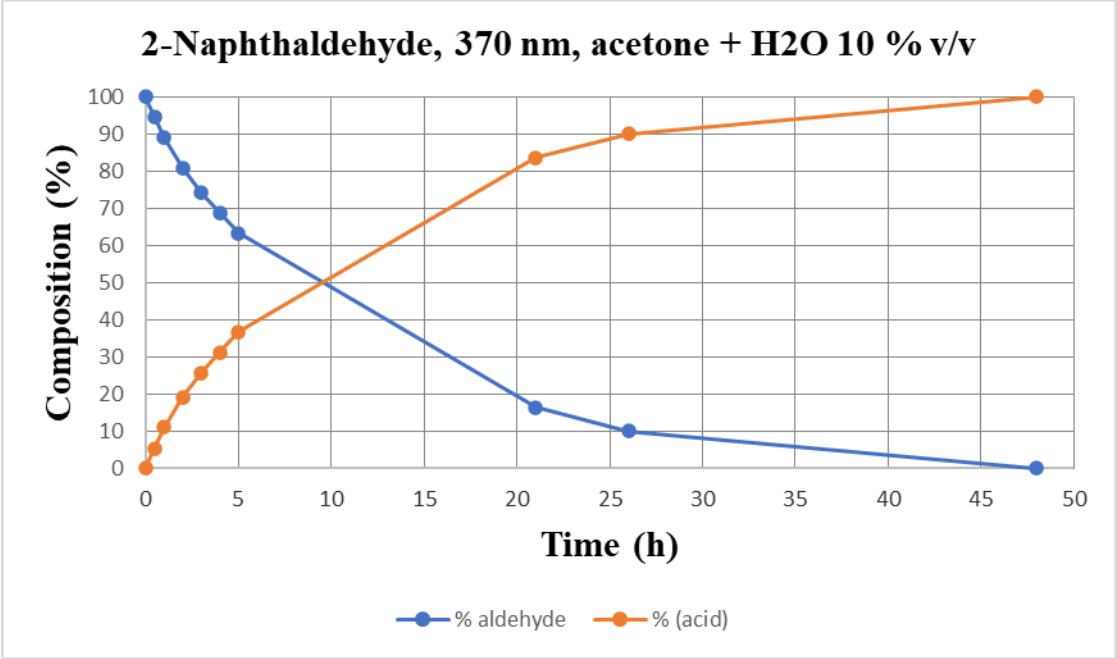


**Monitoring of the aerobic oxidation of 2-naphthaldehyde in acetone:$H_2O$ irradiated at 370 nm and monitored by HPLC**




**1u** **2u**

The reaction was setup following the general procedure. At the specific time of study, an aliquot of 10 μL was taken from the crude reaction mixture and was diluted with 990 μL of MeOH. A sample of 10 μL from the mixture was injected for HPLC analysis. Eluting system: MeCN:$H_2O$ – 20:80, gradient to 30:70 for 15 min, 35 $^oC$, flow rate 1 mL/min, detector: 280 nm.



# References


1. Y. Matsumura, Y. Yamamoto, N. Moriyama, S. Furukubo, F. Iwasaki and O. Onomura, *Tetrahedron Lett.*, 2004, **45**, 8221-8224.
2. F. Juliá-Hernández, T. Moragas, J. Cornella and R. Martin, *Nature*, 2017, **545**, 84-88.
3. Y. Monguchi, Y. Fujita, S. Hashimoto, M. Ina, T. Takahashi, R. Ito, K. Nozaki, T. Maegawa and H. Sajiki, *Tetrahedron*, 2011, **67**, 8628-8634.
4. H. Wapenaar, P. E. van der Wouden, M. R. Groves, D. Rotili, A. Mai and F. J. Dekker, *Eur. J. Med. Chem.*, 2015, **105**, 289-296.
5. V. R. Ravu, G. Y. C. Leung, C. S. Lim, S. Y. Ng, R. J. Sum and D. Y.-K. Chen, *Eur. J. Org. Chem*., 2011, 463-468.
6. M. E. Di Pietro, A. Mannu, A. Mele, *Processes*, 2020, **8**, 410-424.
7. F. A. Thesselinga, M. C. Hutter, C. Wiek, J. P. Kowalski, A. E. Rettie and M. Girhard, *Arch. Biochem. Biophys.*, 2020, **679**, 108216.
8. H. Yu, S. Ru, G. Dai, Y. Zhai, H. Lin, S. Han and Y. Wei, *Angew. Chem. Int. Ed.*, 2017, **56**, 3867-3871.
9. R. Aav, E. Shmatova, I. Reile, M. Borissova, F. Topić, K. Rissanen, *Org. Lett.*, 2013, **15**, 3786-3789.
10. C. Larpent, R. Dabard and H. Patin, *Tetrahedron Lett.*, 1987, **28**, 2507-2510.
11. J. N. Moorthy and K. N. Parida, *J. Org. Chem.*, 2014, **79**, 11431-11439.
12. M. Liu, Z. Zhang, J. Song, S. Liu, H. Liu and B. Han, *Angew. Chem. Int. Ed.*, 2019, **58**, 17393-17398.
13. D. F. Yu, P. Xing and B. Jiang, *Tetrahedron*, 2015, **71**, 4269-4273.
14. W. Wang, G. Zhang, R. Lang, C. Xia and F. Li, *Green Chem.*, 2013, **15**, 635-640.
15. A. Corma, D. Das, H. García and A. Leyva, *J. Catal*., 2005, **229**, 322-331.
16. M. Liu and C.J. Li, *Angew. Chem. Int. Ed.*, 2016, **55**, 10806-10810.
17. P. Liu, L. Huang and M. M. Faul, *Tetrahedron Lett*., 2007, **48**, 7380-7382.

18. K. Zheng, X. Yan, G. Zhang, X. Yan, X. Li and X. Xu, *Synlett*, 2020, **31**, 272-274.

19. Y. Wang, C. Zhou and R. Wang, *Green Chem.*, 2015, **17**, 3910-3915.

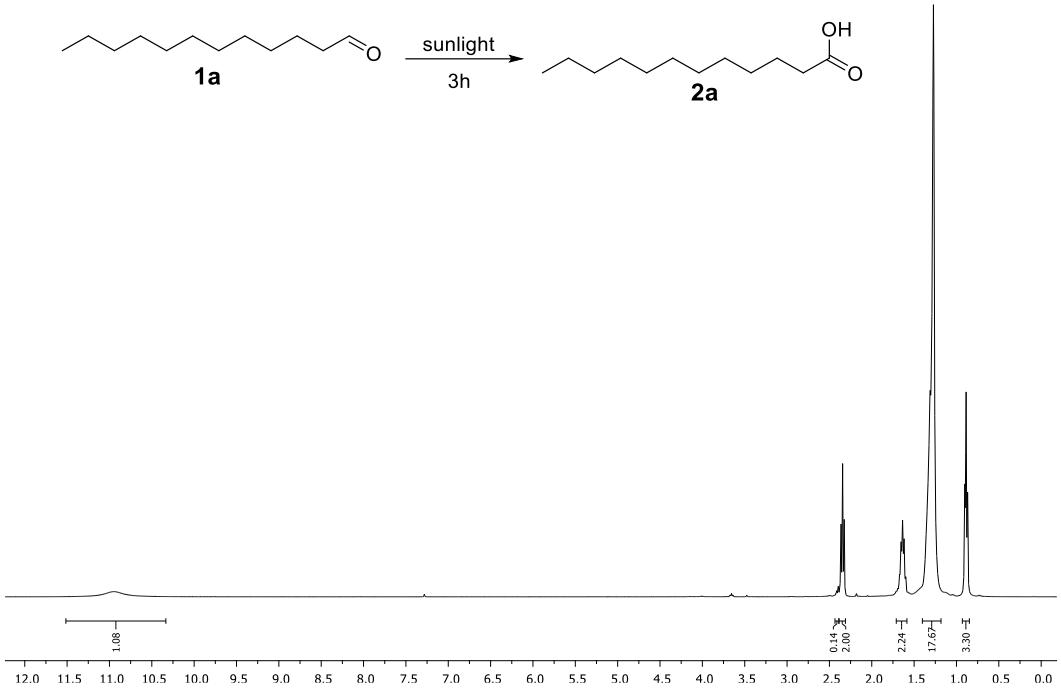
20. S. S. Shen, V. Kartika, Y. S. Tan, R. D. Webster and K. Narasaka, *Tetrahedron Lett.*, 2012, **53**, 986-990.

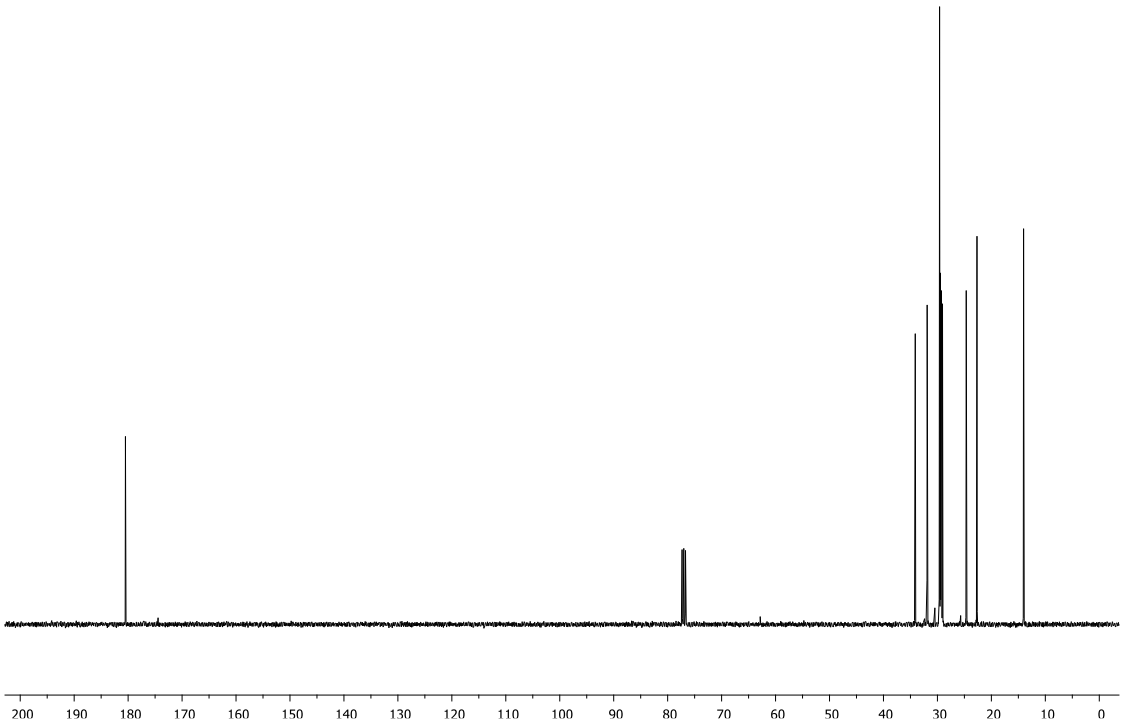
21. S. Babaee, M. Zarei and M. A. Zolfigol, *RSC Adv.*, 2021, **11**, 36230-36236.

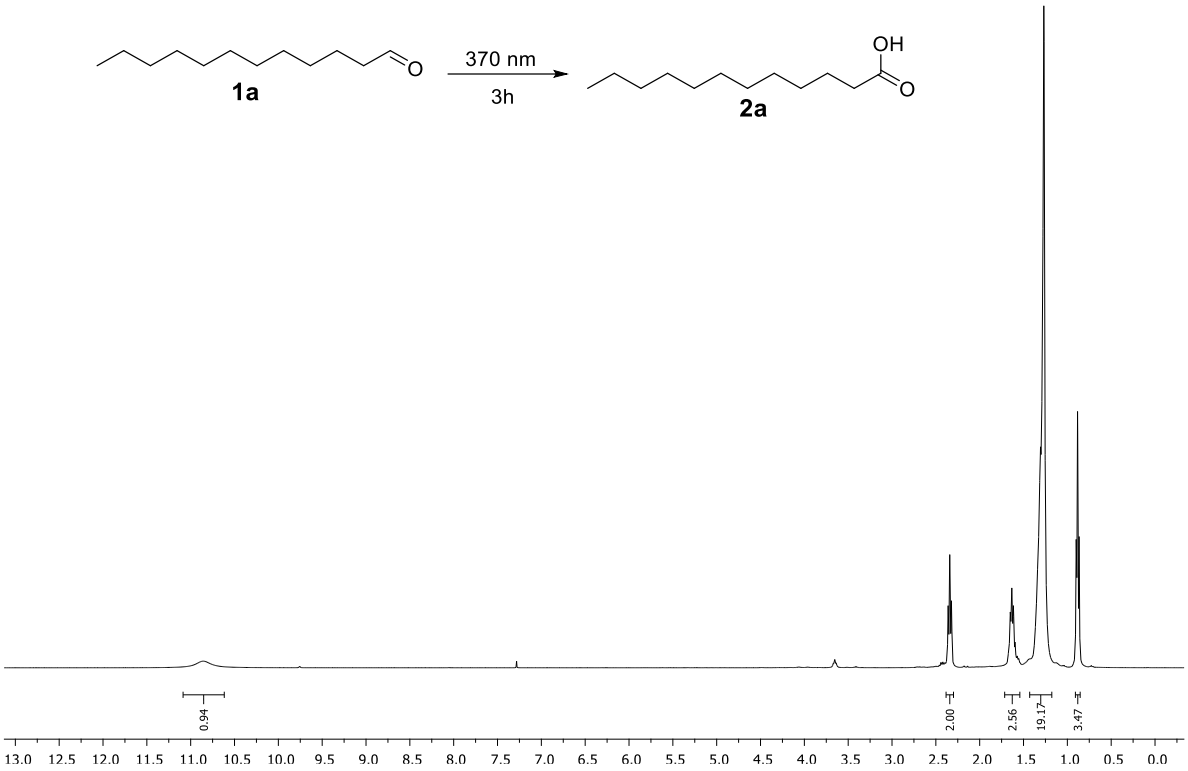
22. N. Li, Y. Gui, M. Chu, M. You, X. Qiu, H. Liu, S. Wang, M. Deng and B. Ji, *Org. Lett.*, 2021, **23**, 8460-8464.

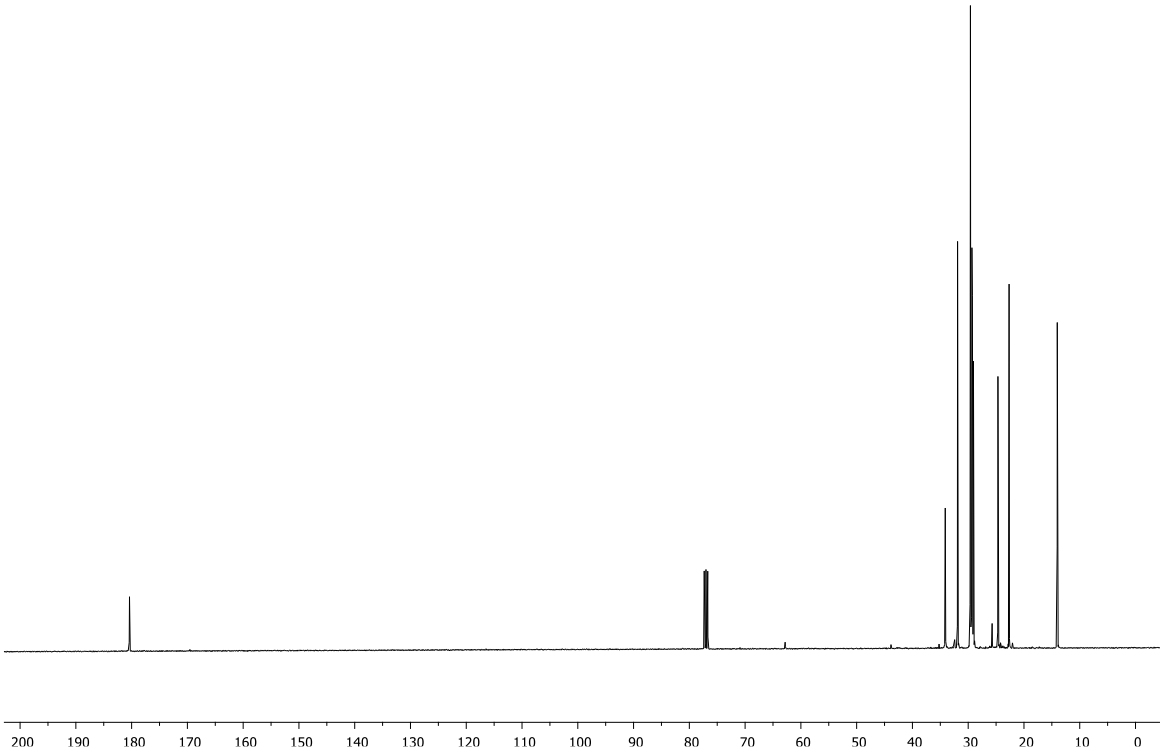
23. W. Lee, H. J. Jeon, H. Jung, D. Kim, S. Seo, S. Chang, *Chem*, 2021, **7**, 495-508.

# NMR Monitoring Studies for the Formation of Percarboxylic Acid Before Work-up




1a
370 nm
3h
OH
O
2a
0.94
2.00
2.56
19.17
3.47
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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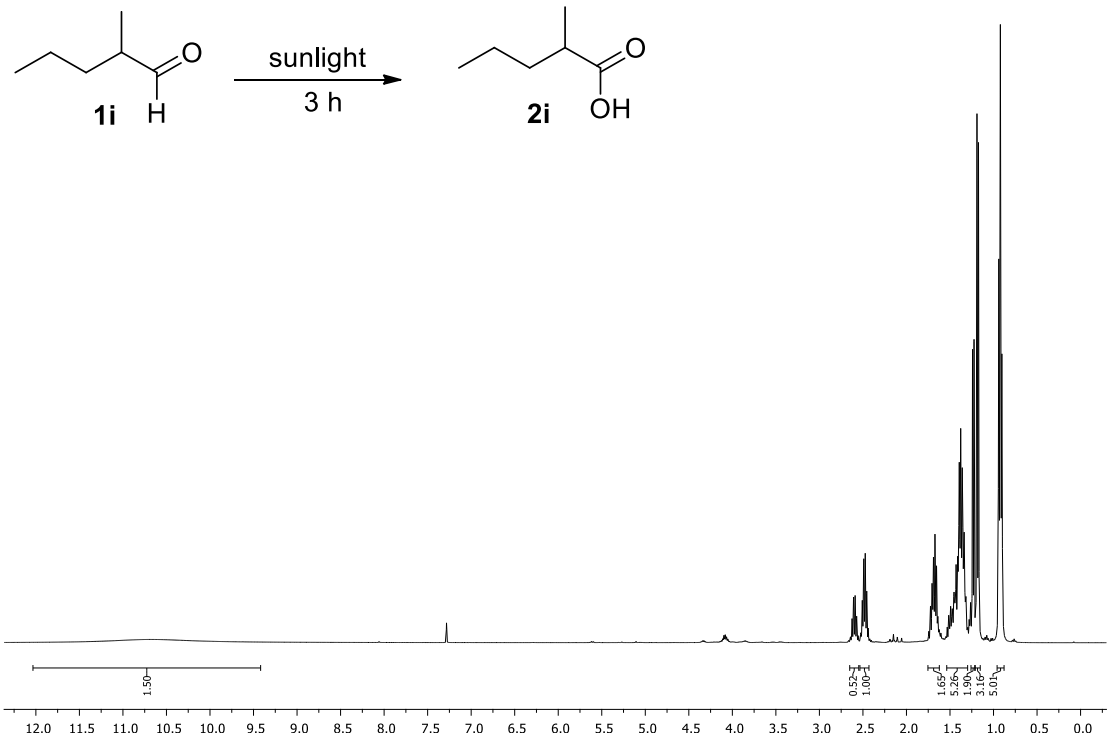
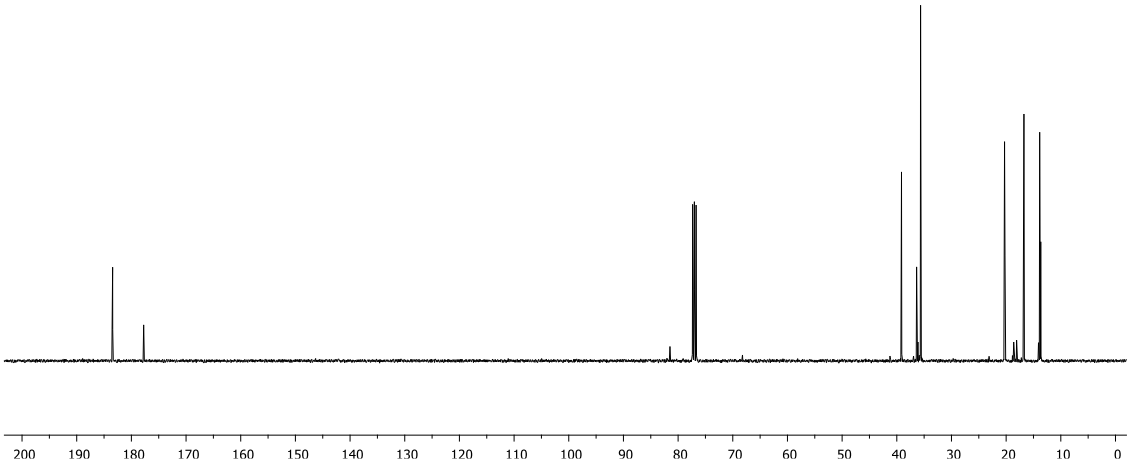

O
H
1i
sunlight
3 h
O
OH
2i
1.50
0.52
1.00
1.65
5.26
1.90
3.16
5.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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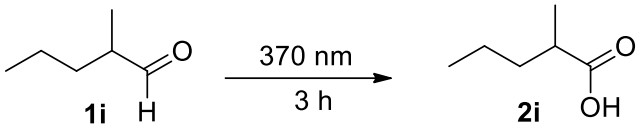
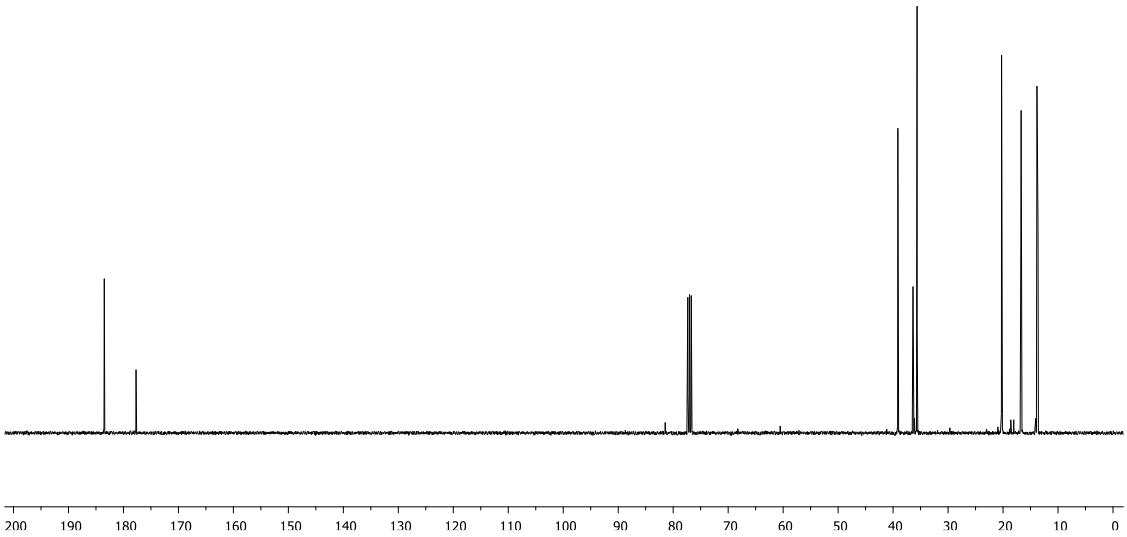

O
H
1i
370 nm
3 h
O
OH
2i


1.57
0.58
1.00
1.72
5.27
1.91
3.02
5.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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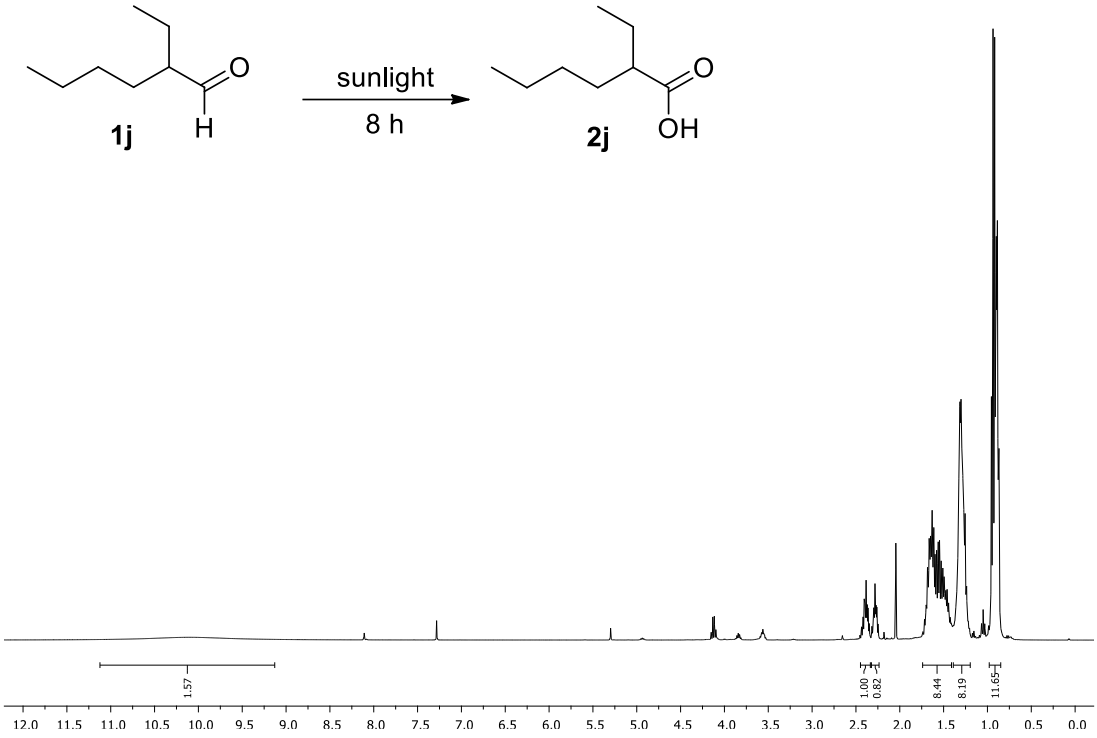
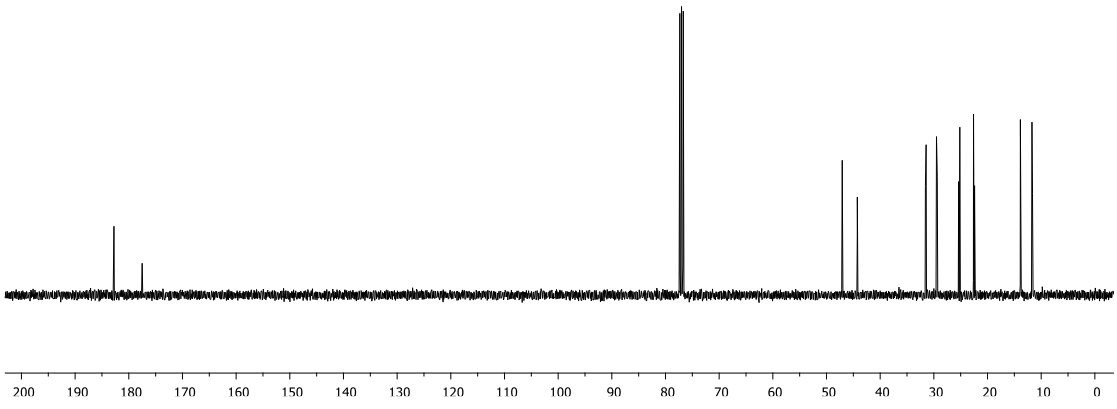

O
H
1j
sunlight
8 h
O
OH
2j
1.57
1.00
0.82
8.44
8.19
11.65
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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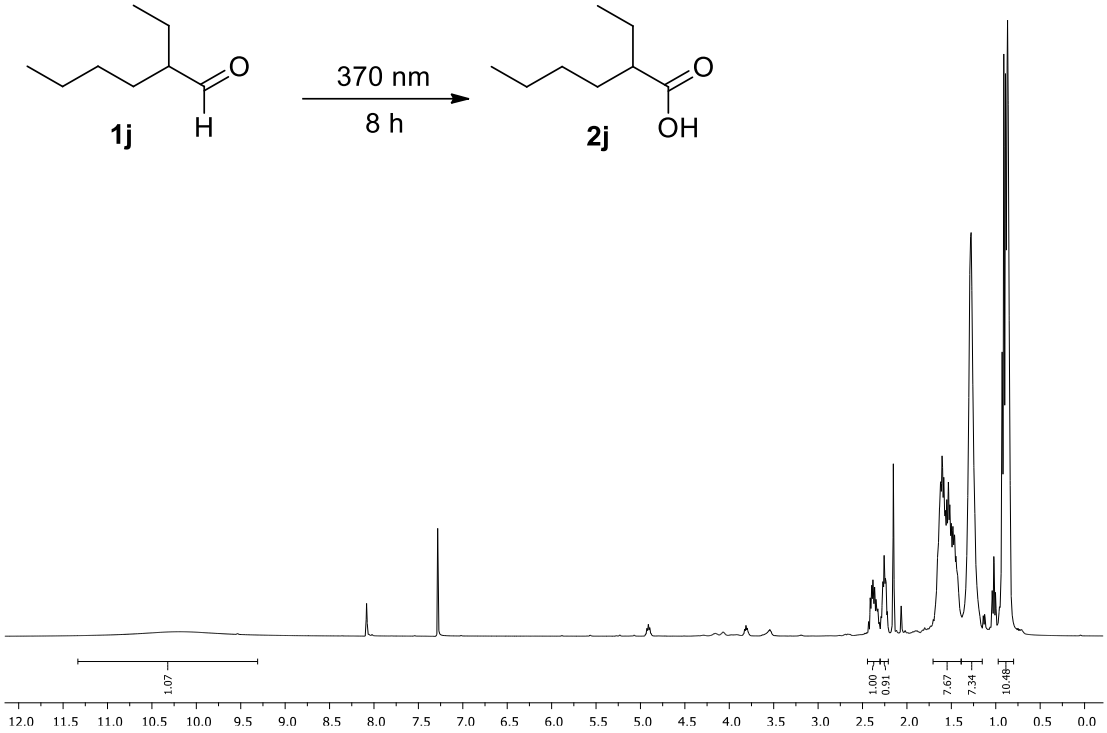
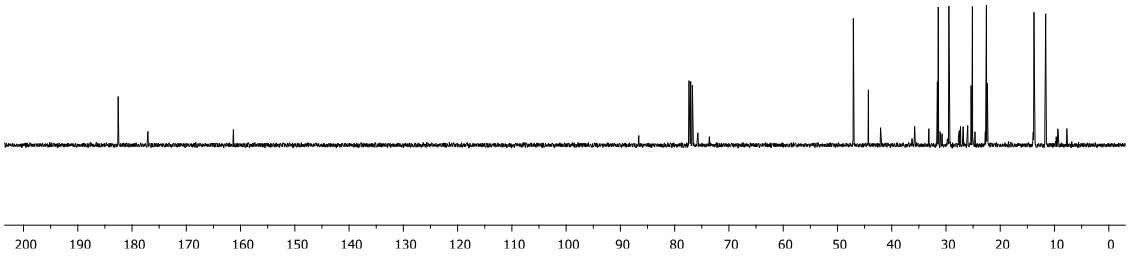

O
H
1j
370 nm
8 h
O
OH
2j
1.07
1.00
0.91
7.67
7.34
10.48
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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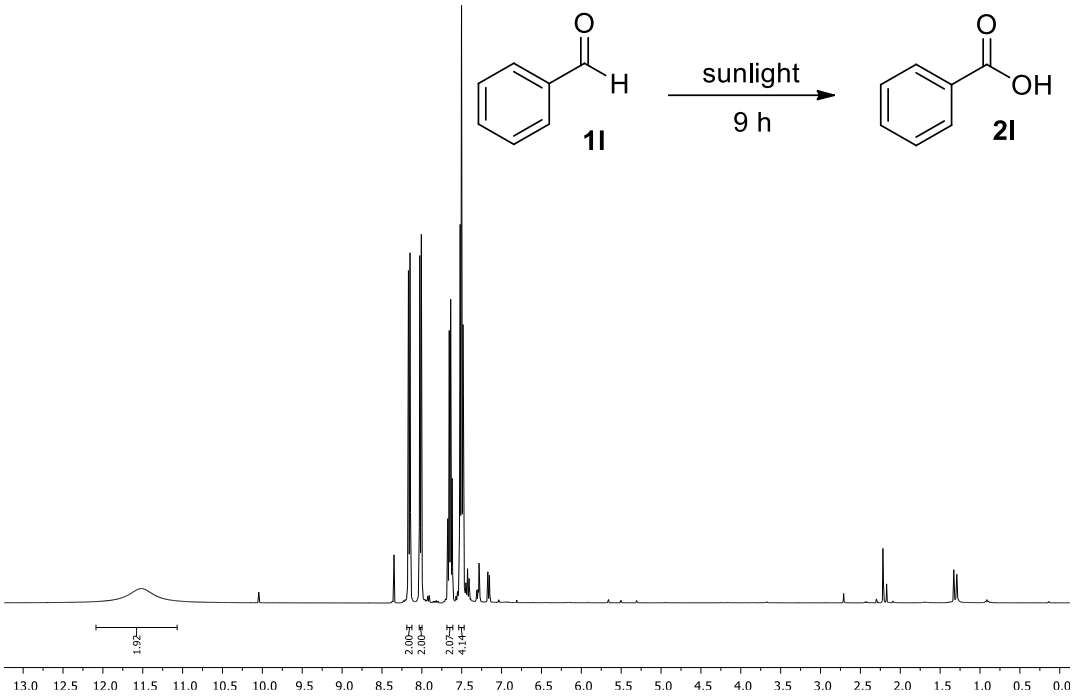
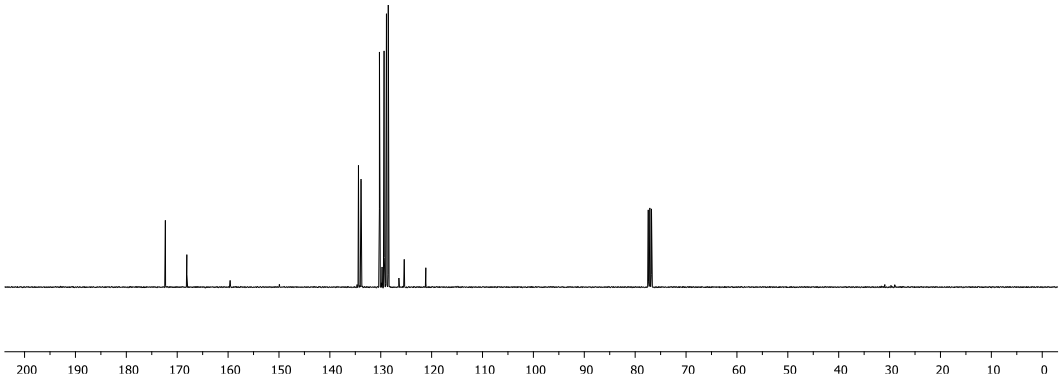

O
H
1l
sunlight
9 h
O
OH
2l
1.92
2.00
2.00
2.07
4.14
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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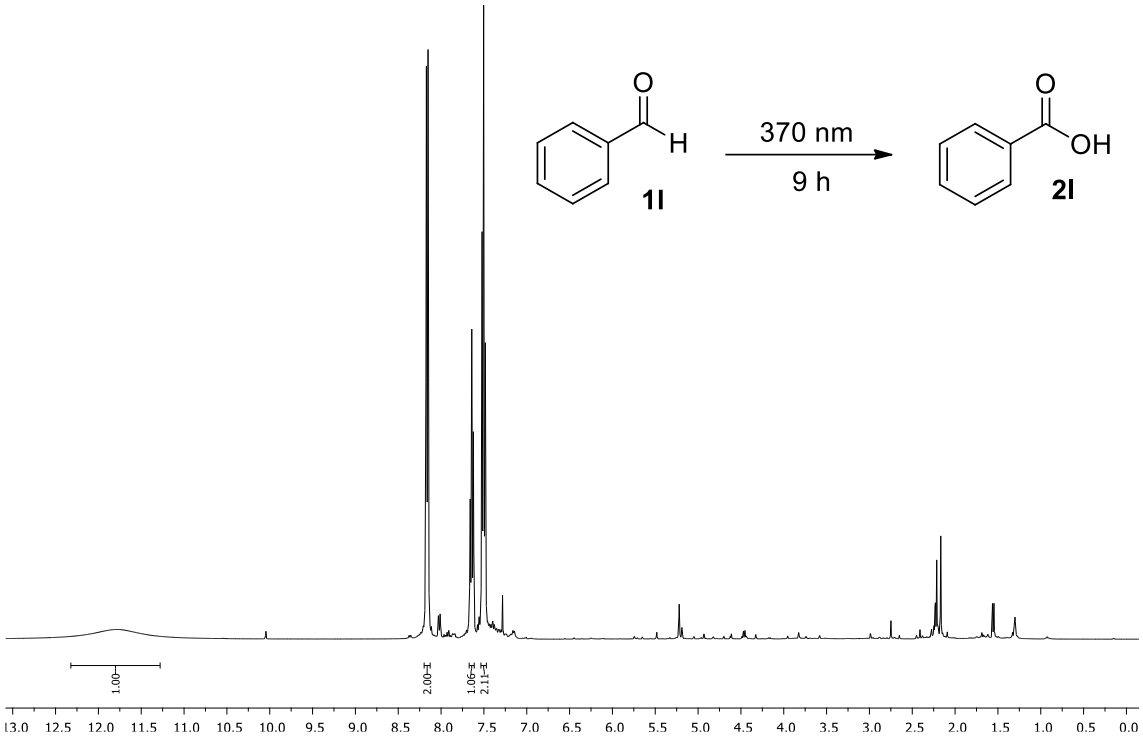
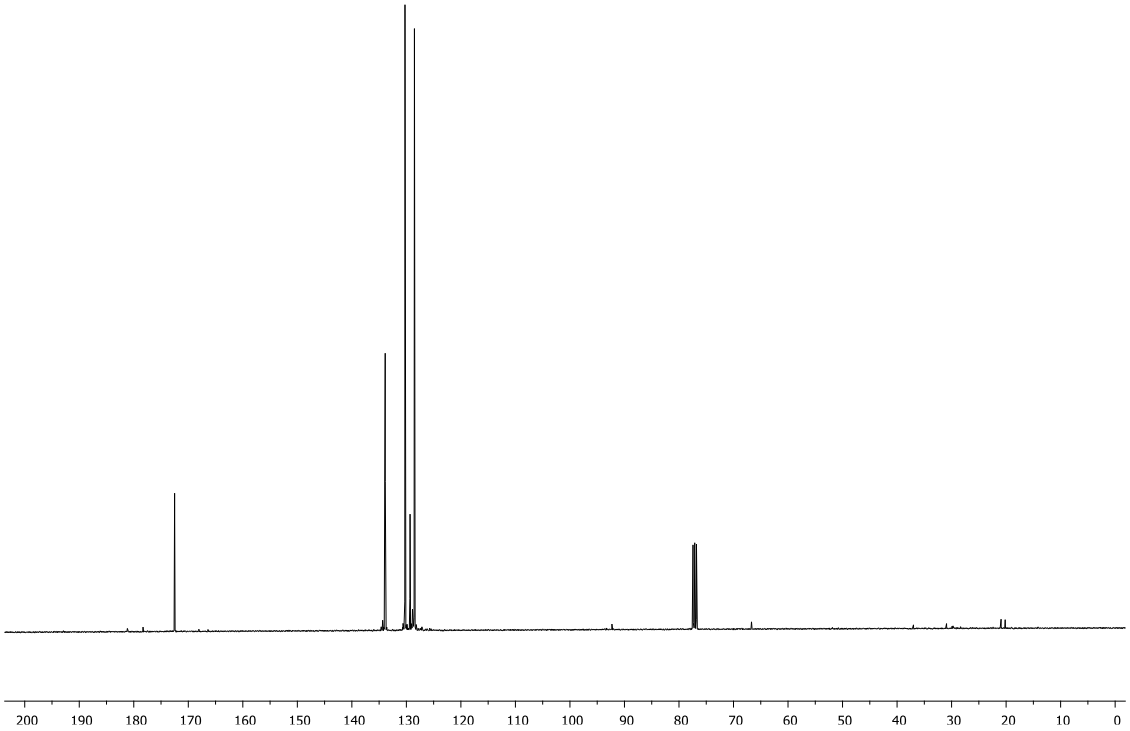

O
H
1l
370 nm
9 h
O
OH
2l
1.00
2.00
1.06
2.11
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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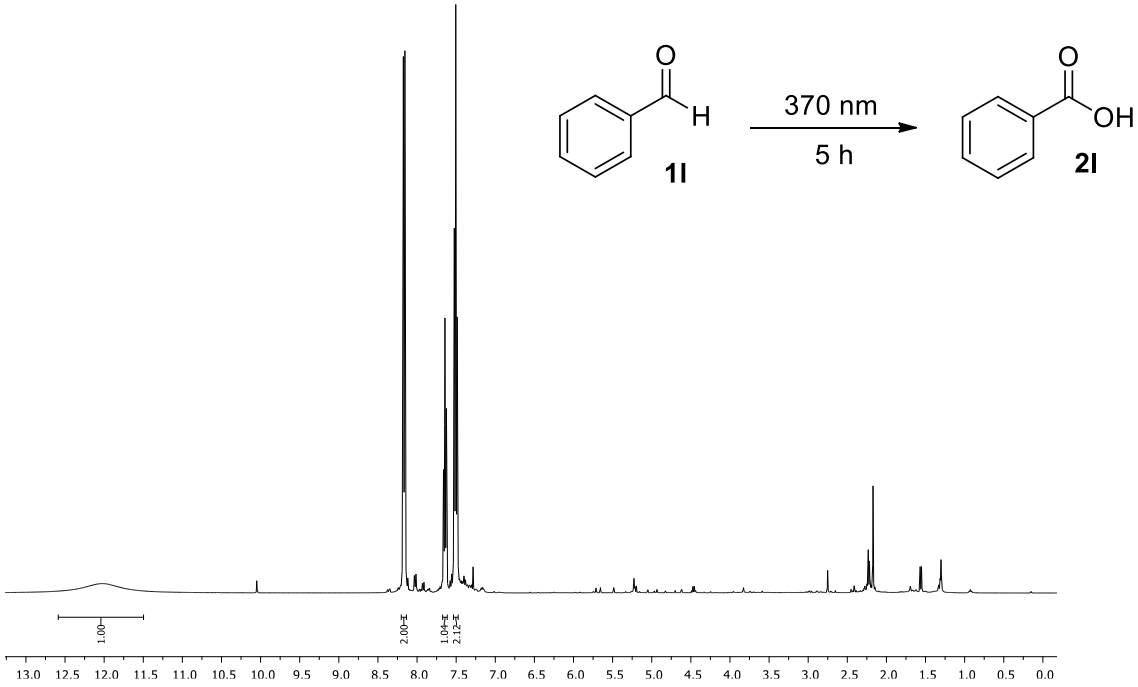
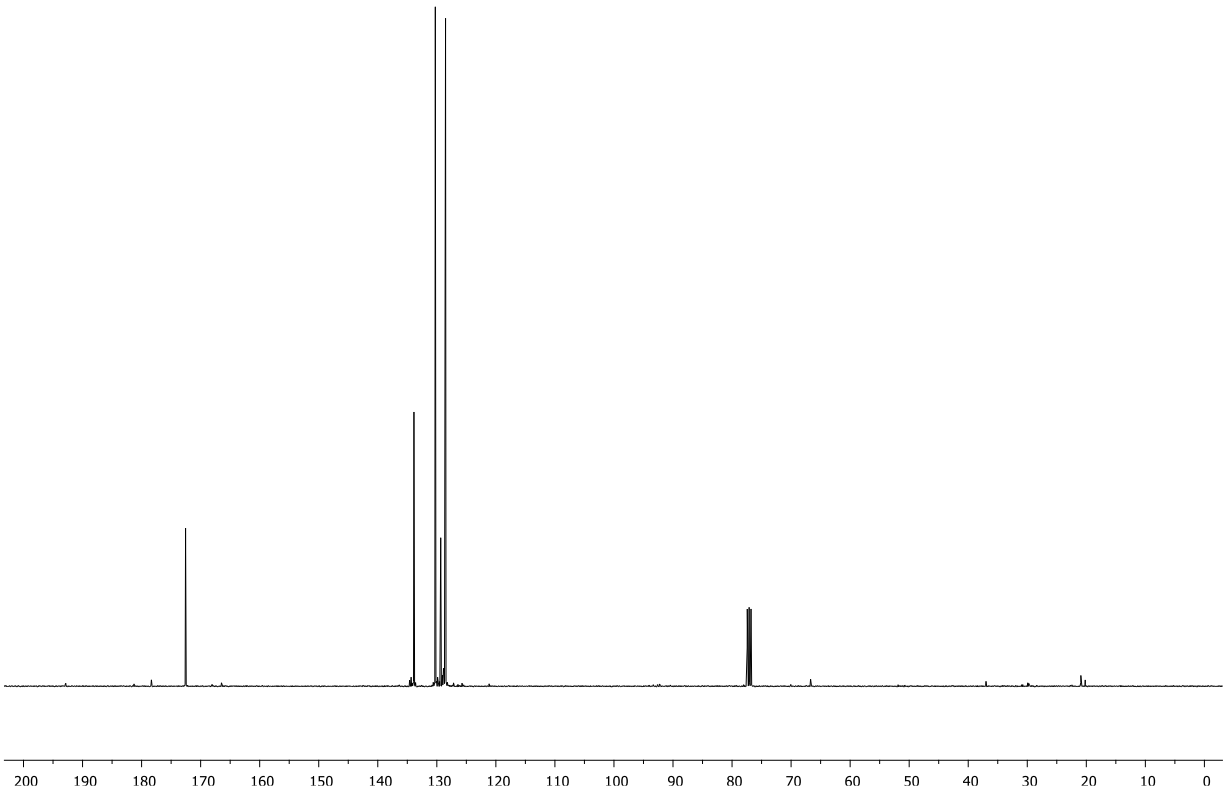

O
H
1l
370 nm
5 h
O
OH
2l
1.00
2.00
1.04
2.12
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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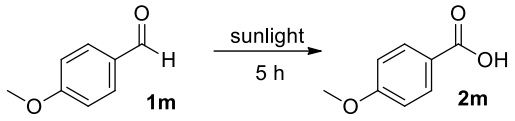
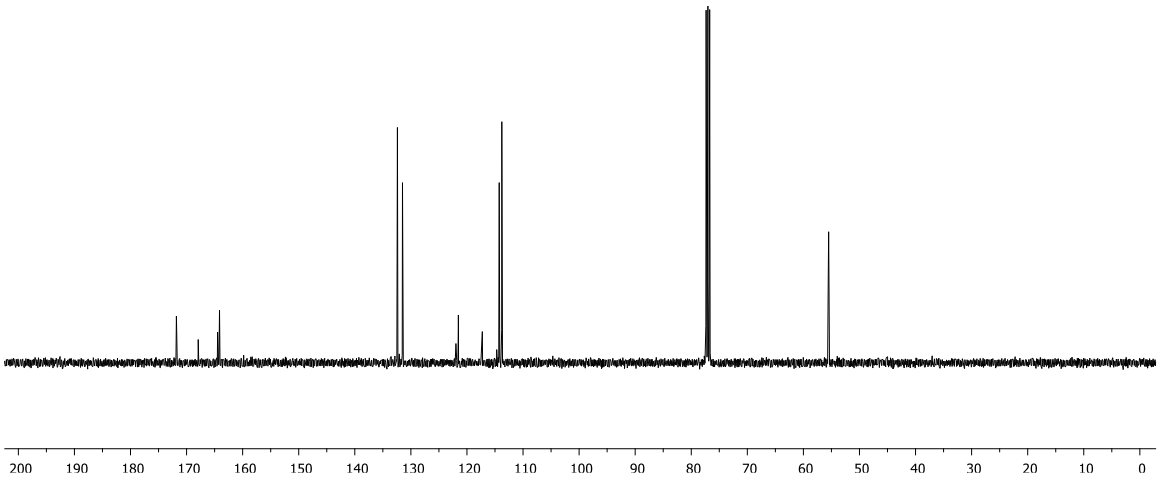

O
H
1m
sunlight
5 h
O
OH
2m


0.88
2.96
2.00
5.08
7.23
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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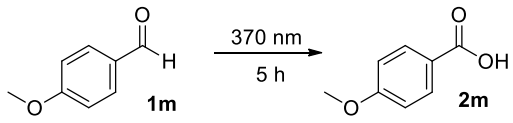
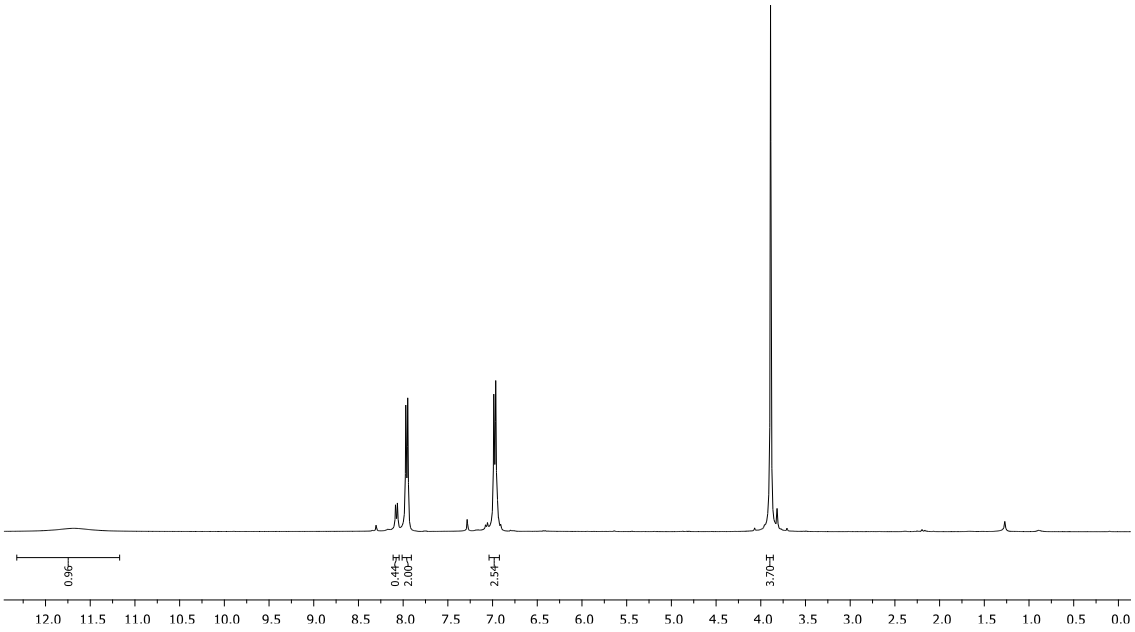
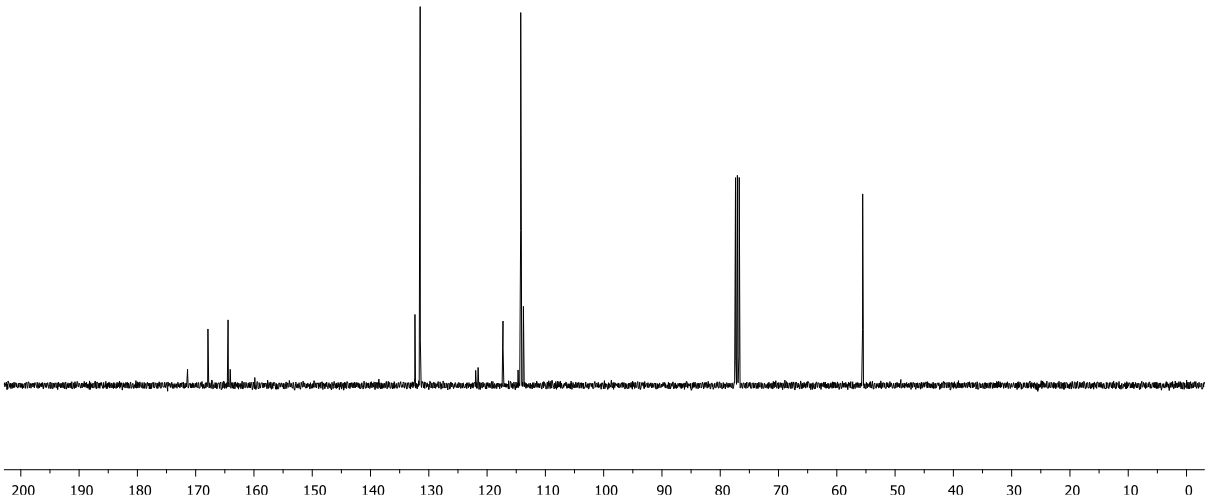

O
H
370 nm
5 h
O
OH
1m
2m


0.96
0.44
2.00
2.54
3.70
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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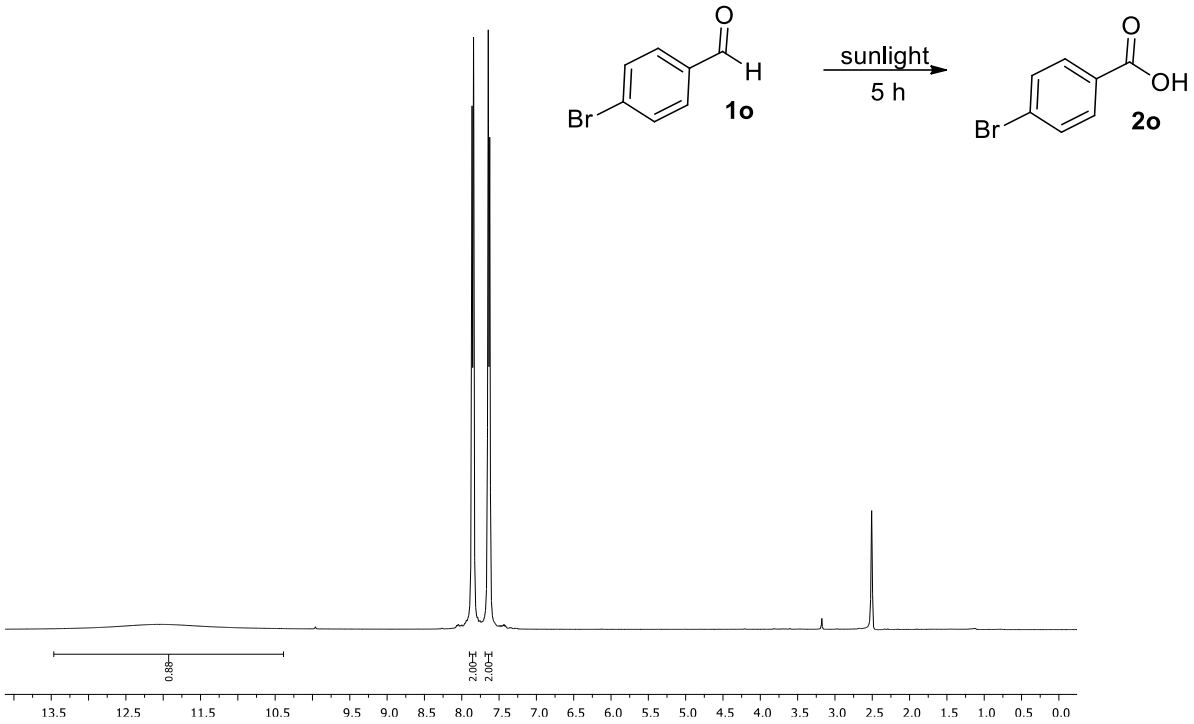
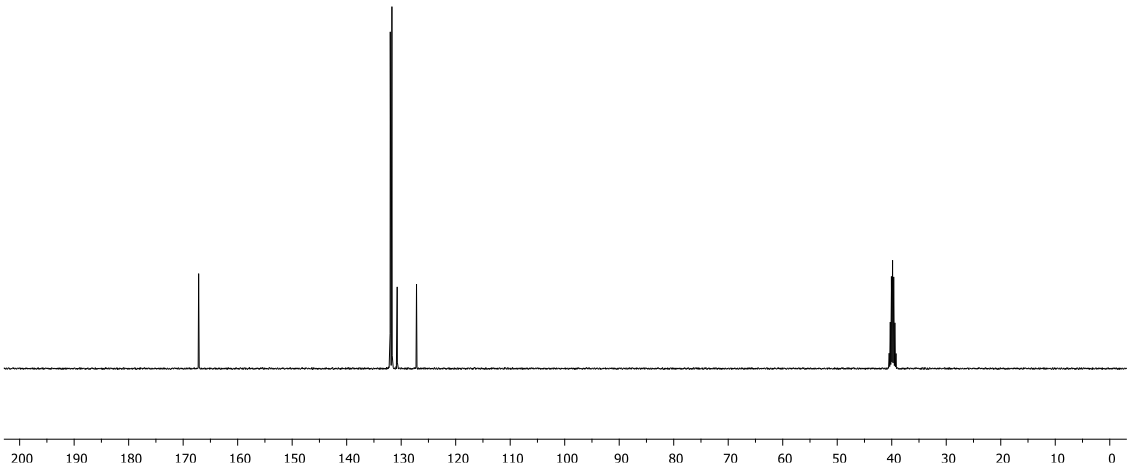

O
H
Br
1o
sunlight
5 h
O
OH
Br
2o
0.88
2.00
2.00
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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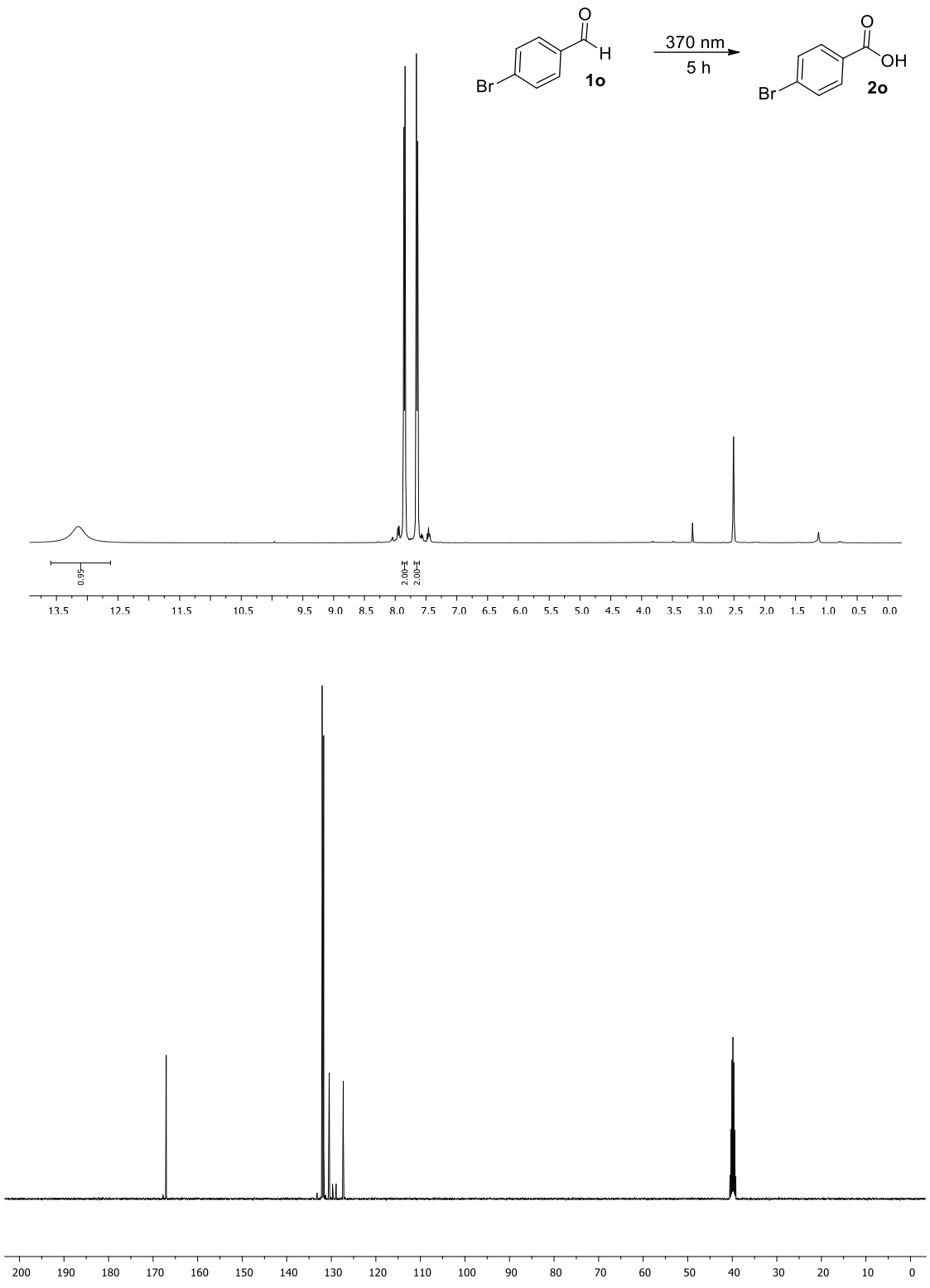
O
H
Br
1o
370 nm
5 h
O
OH
Br
2o
0.95
2.00
2.00
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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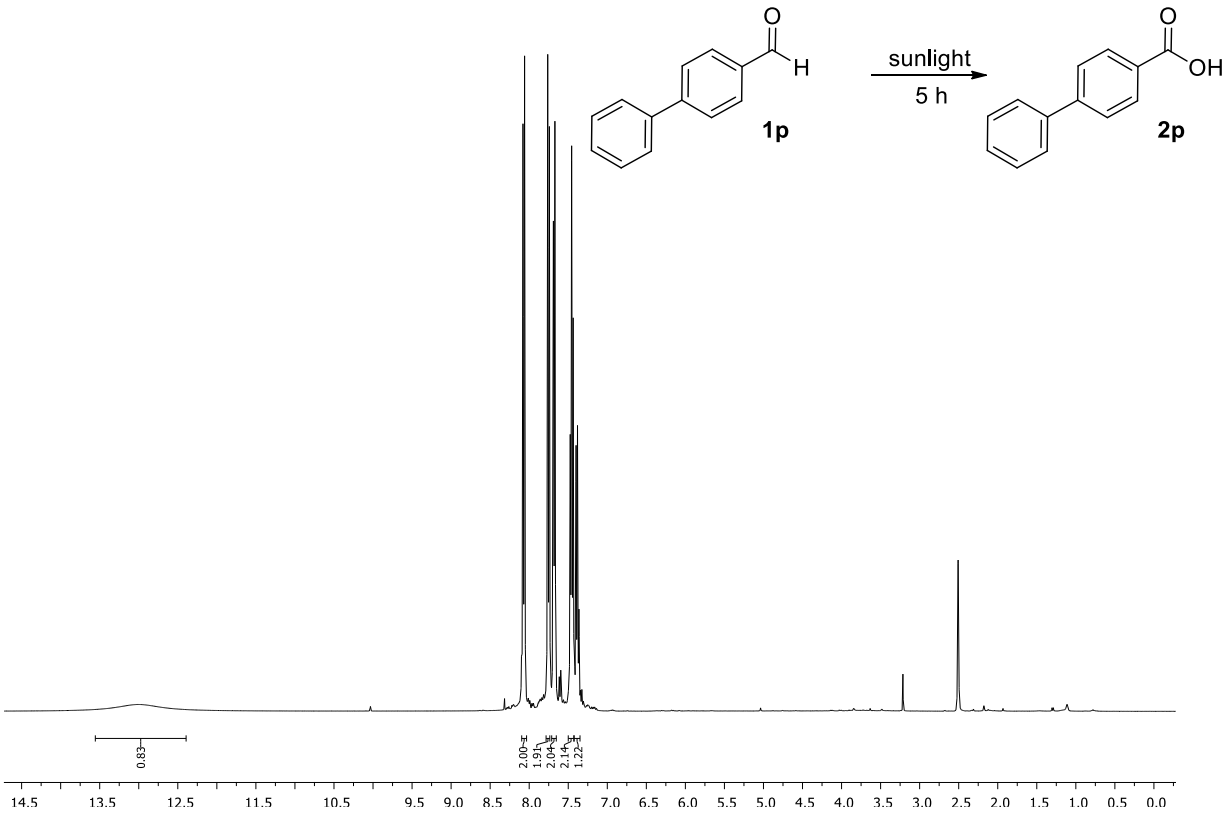
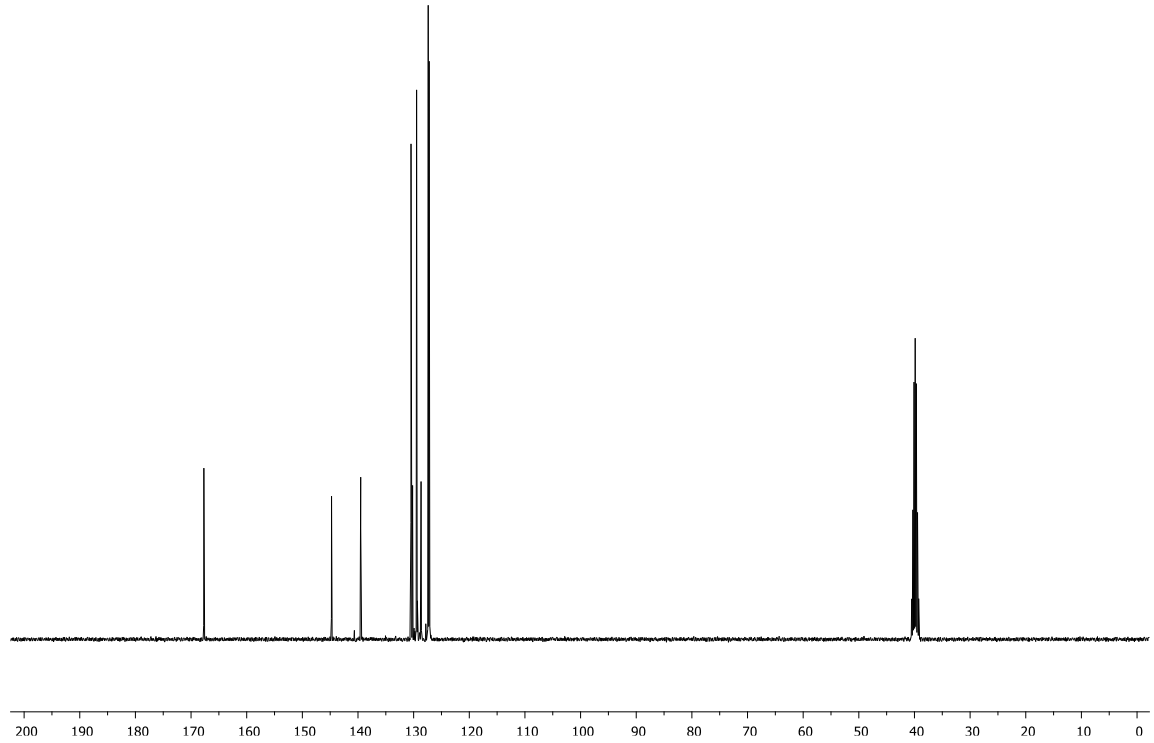

O
H
1p
sunlight
5 h
O
OH
2p
0.83
2.00
1.91
2.04
2.14
1.22
14.5 13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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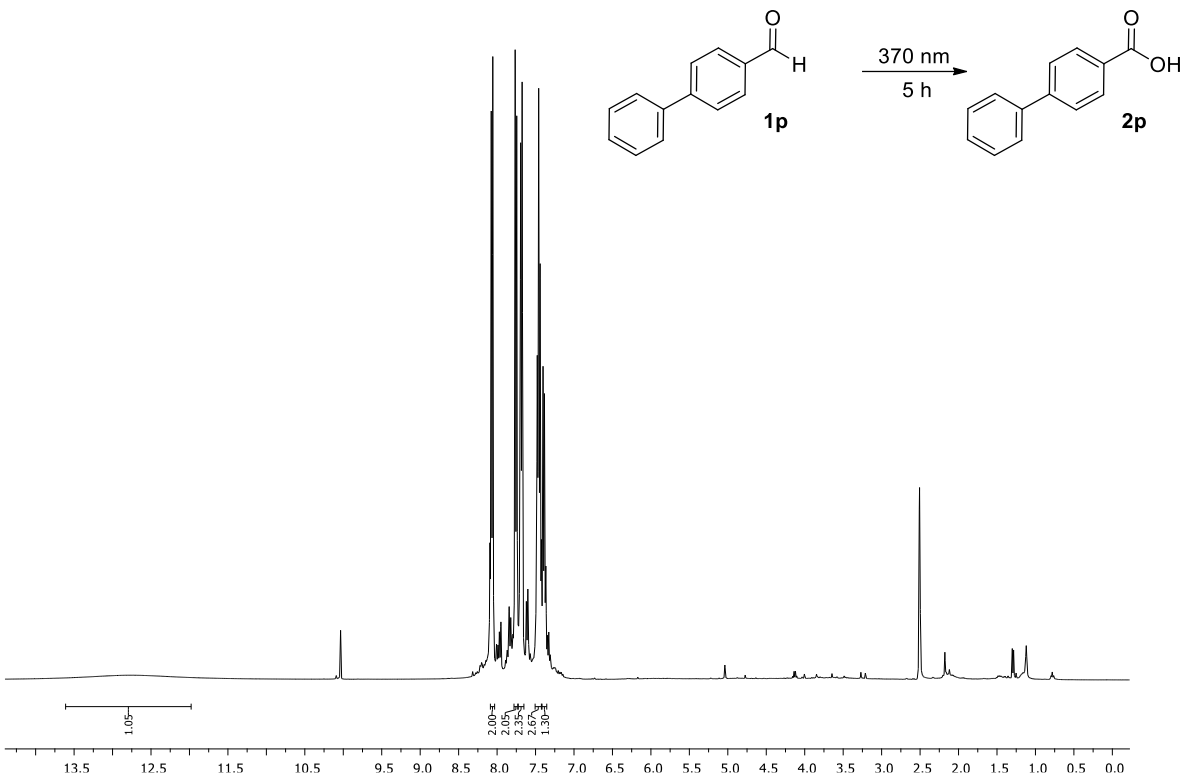
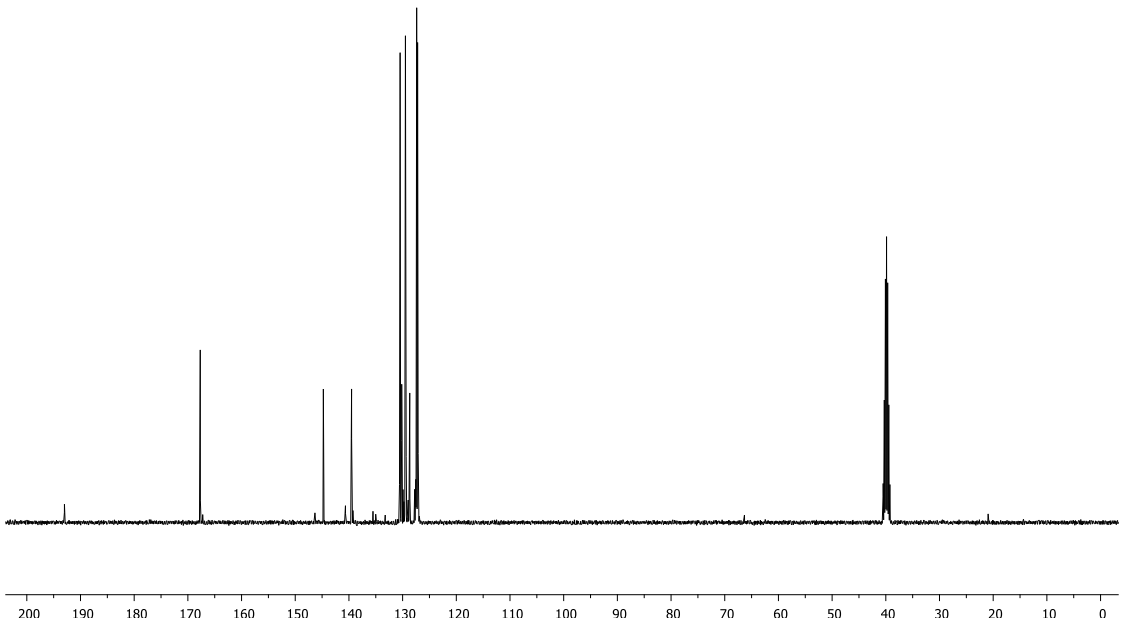

O
H
1p
370 nm
5 h
O
OH
2p
1.05
2.00
2.05
2.35
2.67
1.30
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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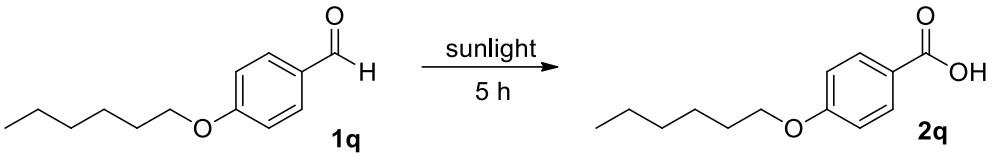
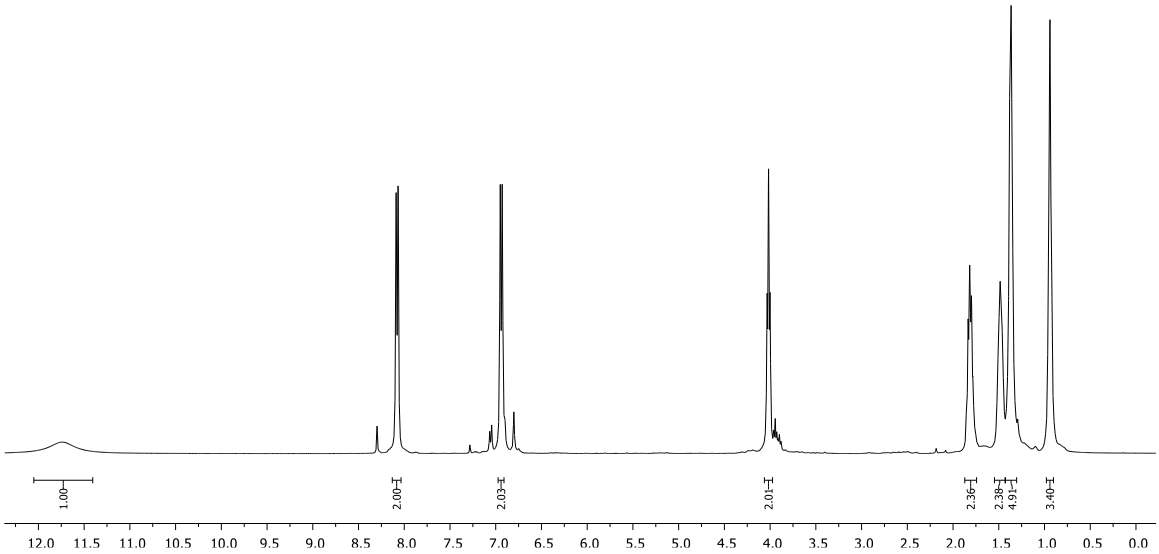
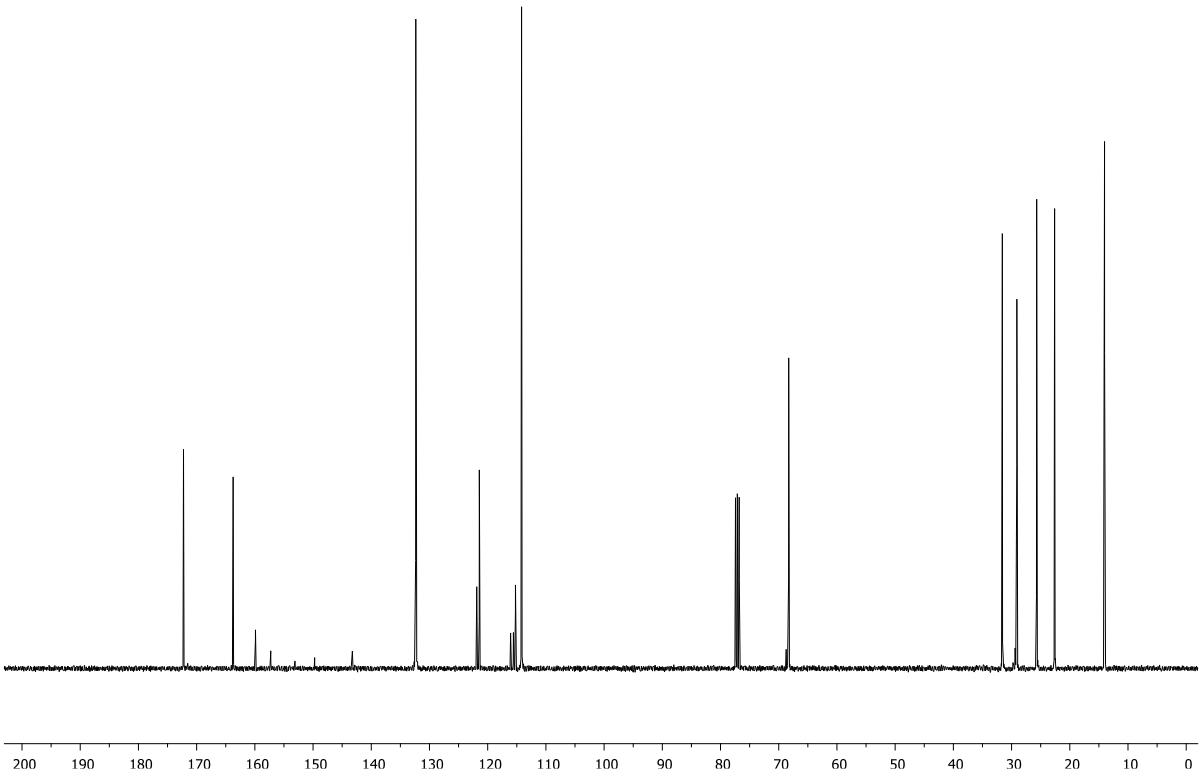

O
H
O
1q
sunlight
5 h
O
OH
O
2q


1.00
2.00
2.03
2.01
2.36
2.38
4.91
3.40
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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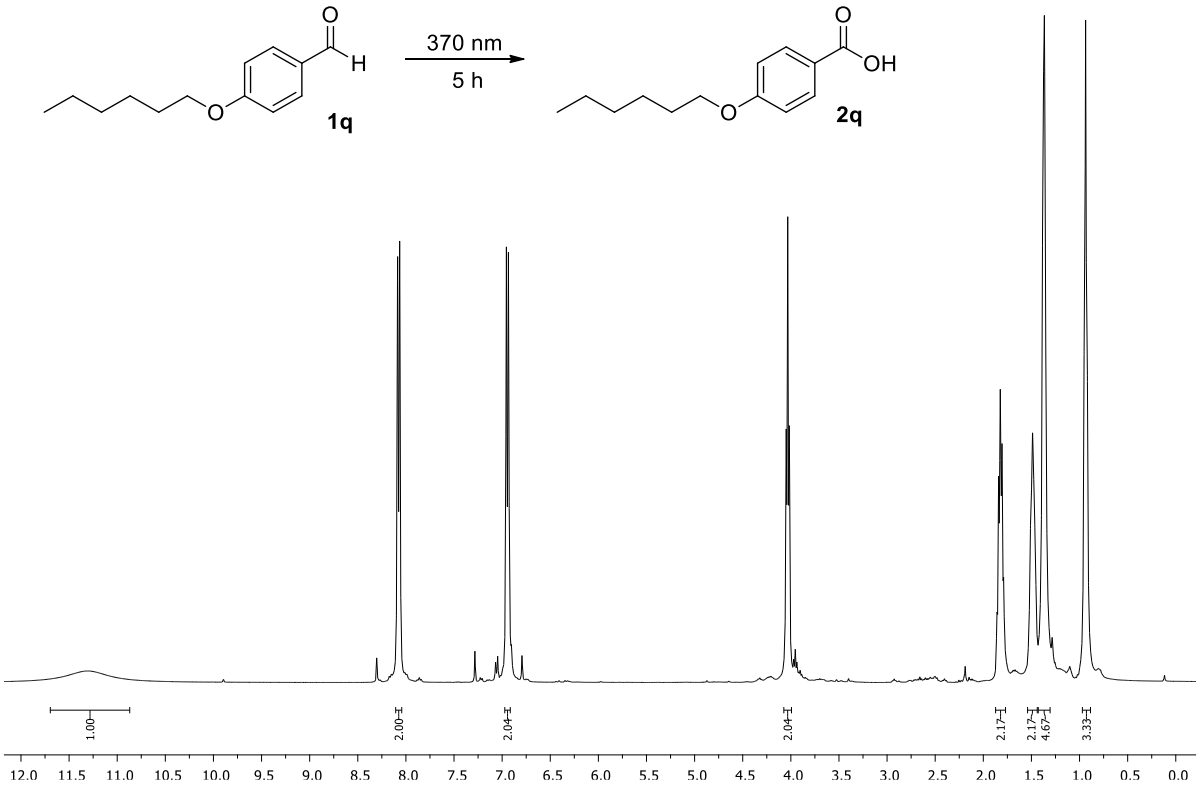
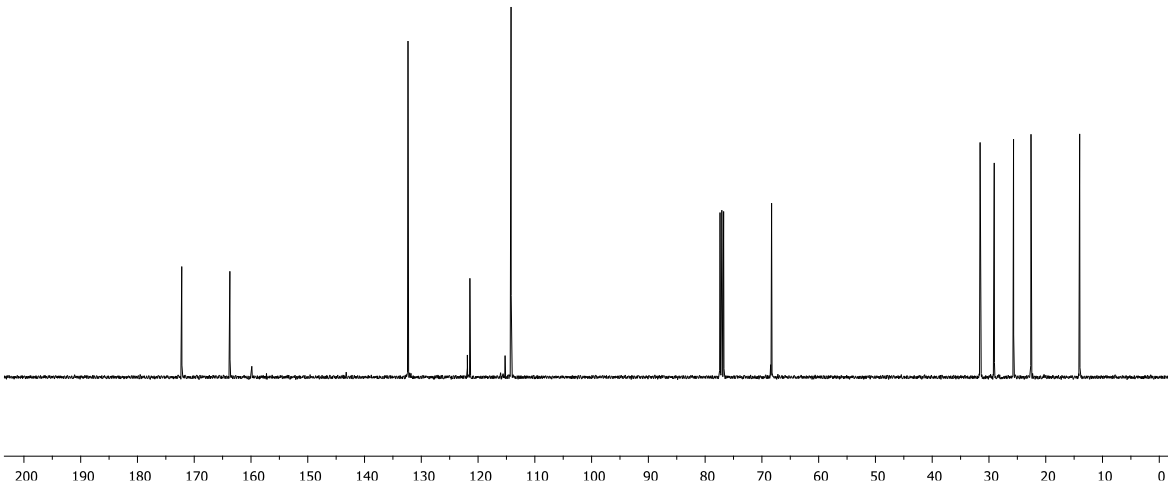

O
H
O
1q
370 nm
5 h
O
OH
O
2q
1.00
2.00
2.04
2.04
2.17
2.17
4.67
3.33
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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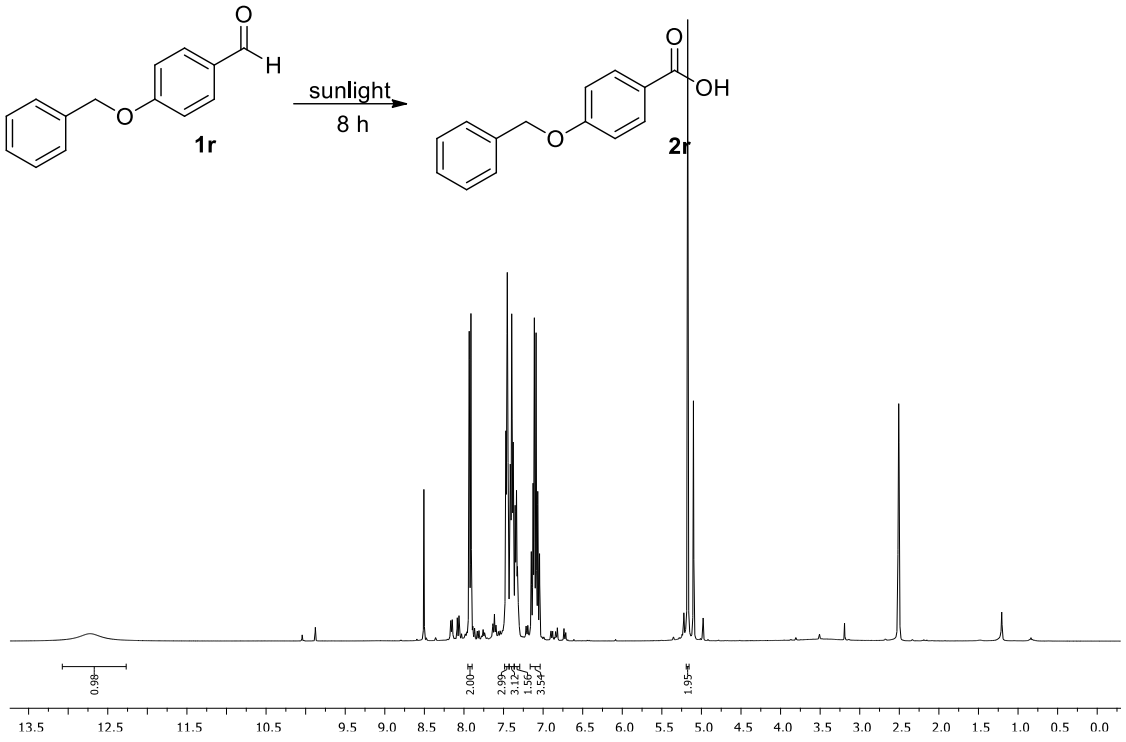
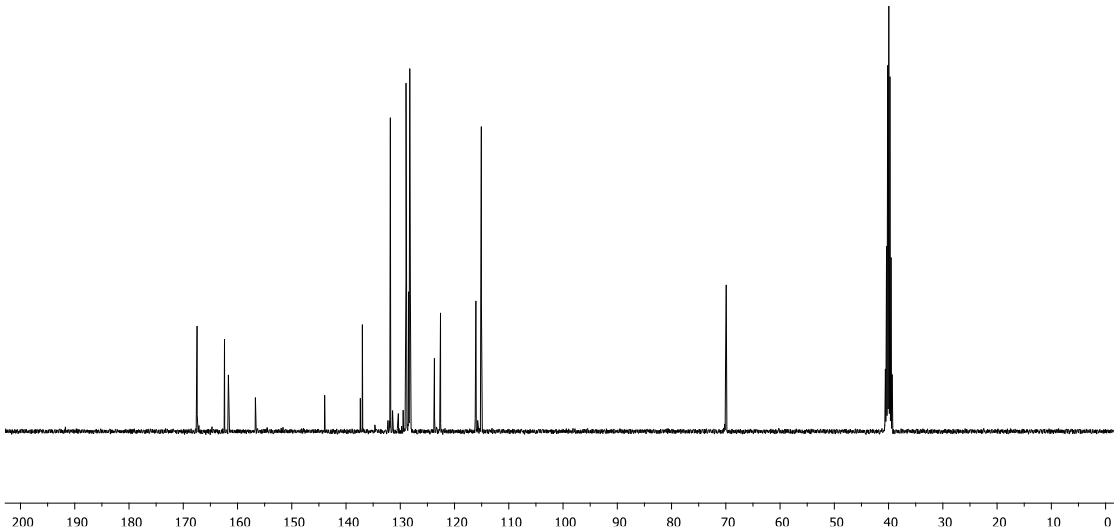

O
H
O
1r
sunlight
8 h
O
OH
O
2r
0.98
2.00
2.99
3.12
1.56
3.54
1.95
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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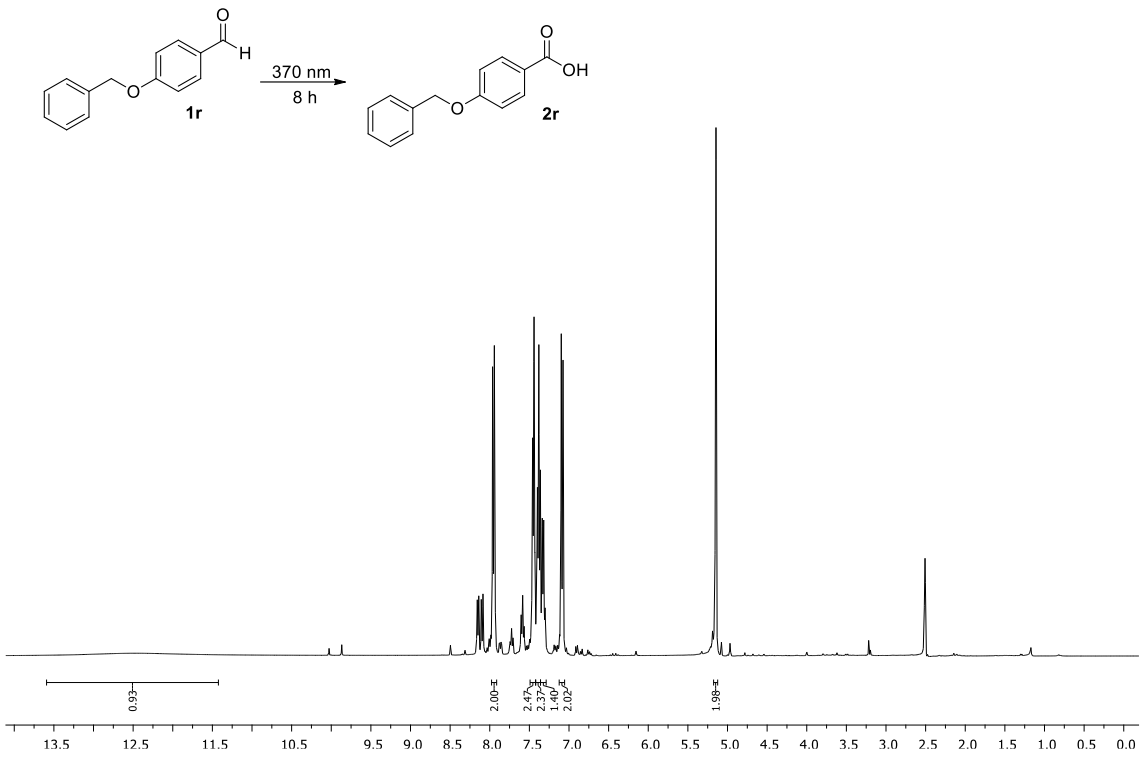
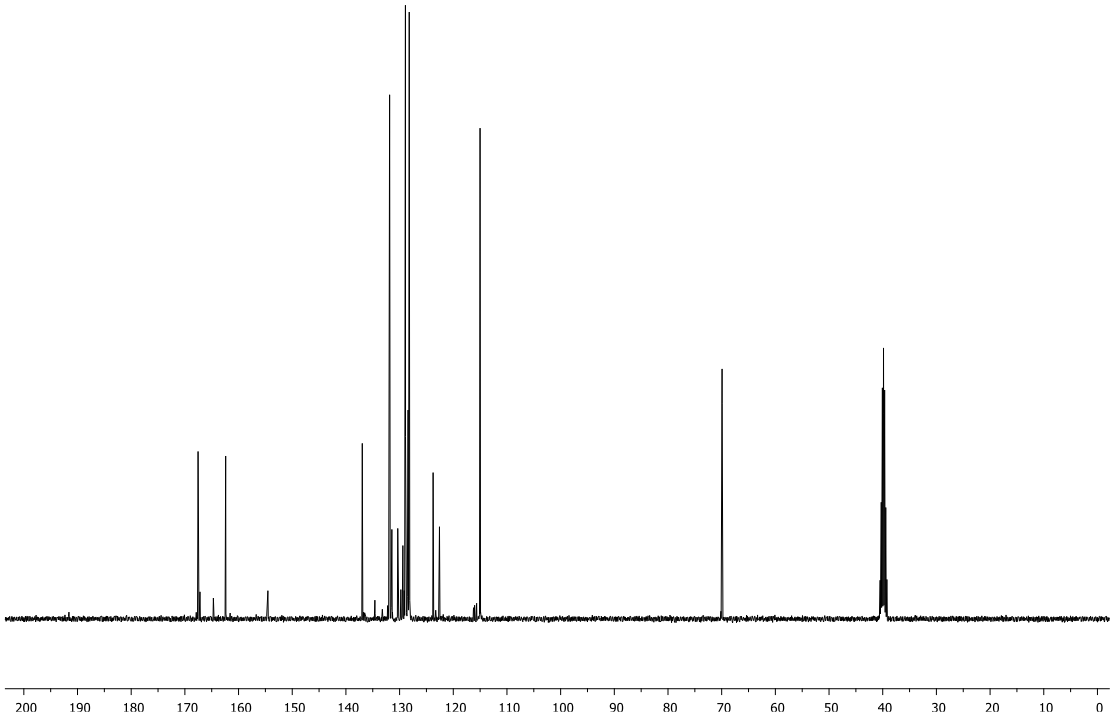

O
H
O
1r
370 nm
8 h
O
OH
O
2r
0.93
2.00
2.47
2.37
1.40
2.02
1.98
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

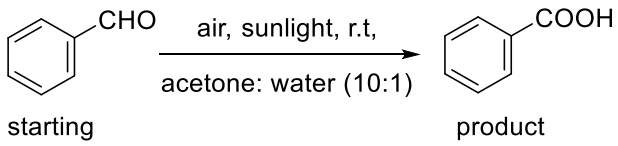

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

# Direct Infusion - High Resolution Mass Spectrometry (DI-HRMS) Studies

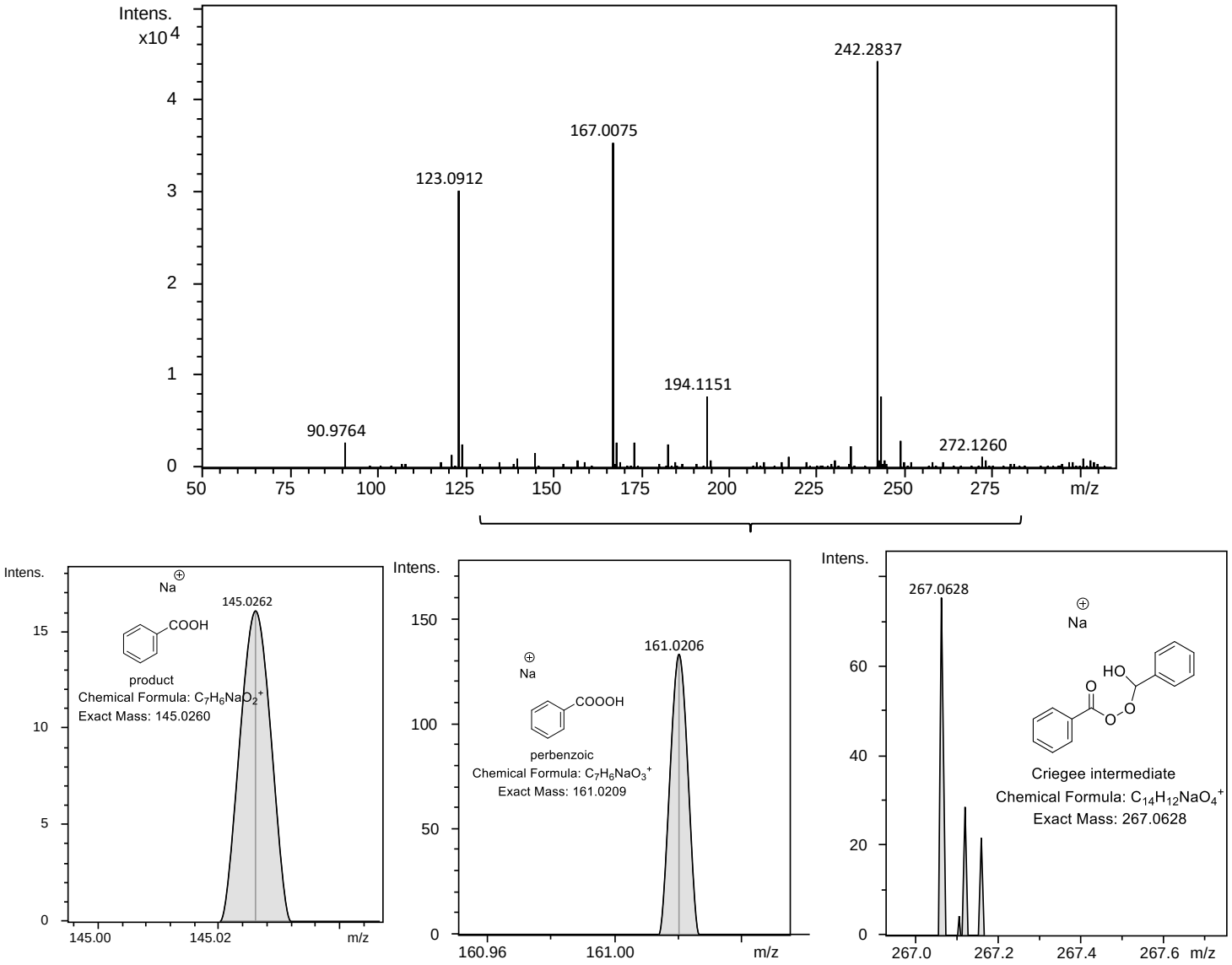
## Instrumentation

High Resolution Mass Spectra were recorded with a Q-TOF (Time of Flight Mass Spectrometer) Bruker Maxis Impact with electrospray ionization (ESI) source. $N_2$ was used as collision gas and positive ionization mode was used for all MS experiments. The data acquisition was carried out with Data Analysis from Bruker Daltonics (version 4.1). For the MS experiments, a solution approximately of 10 mg/L in acetonitrile from the reaction mixture was used. Acetonitrile LC-MS gradient was obtained from Carlo Erba Reagents (Chaussée du Vexin, France). Source conditions: End plate offset 500V, Capillary 4500V, Nebulizer 0.4 bar, dry gas 4.0 L/min, dry temperature 180 $^{o}$C and Quadrupole conditions: Ion energy 5 eV, Collision energy 10 eV, Transfer time 143 μs, Collision ion RF 3500 vpp, Pre pulse storage 1μs.

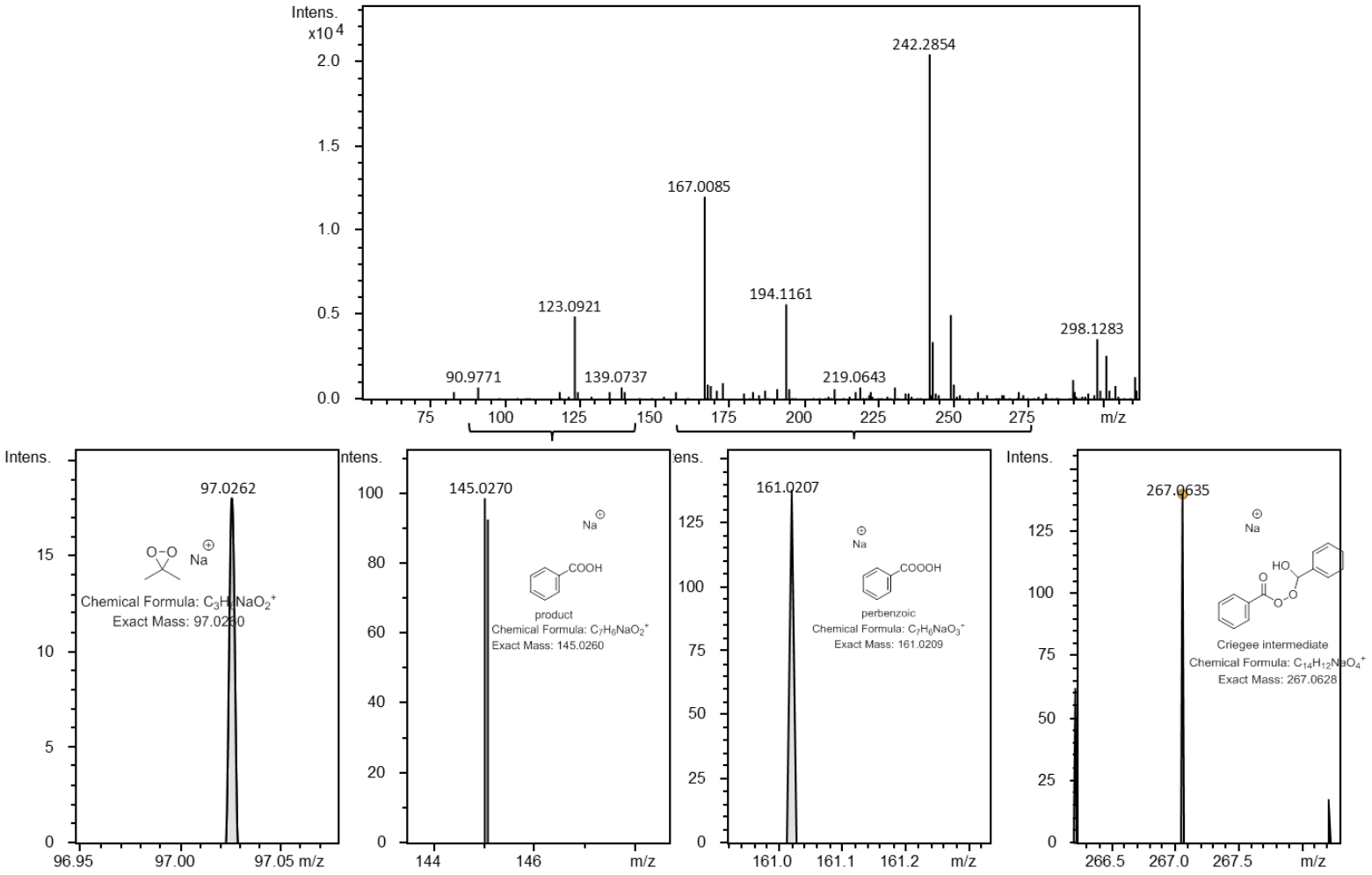
## Monitoring of the photochemical aerobic oxidation of benzaldehyde by DI-HRMS (positive ion mode)



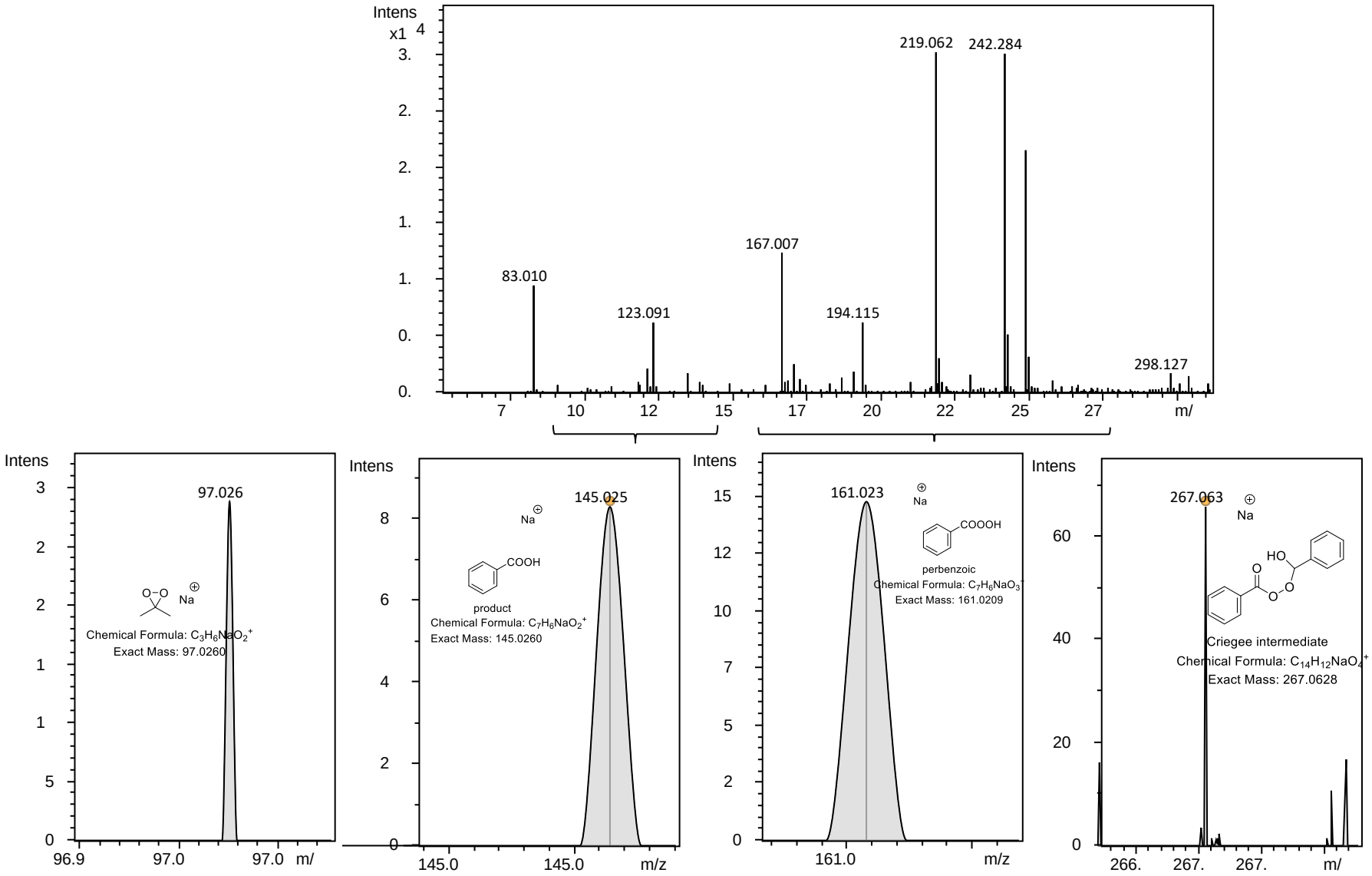
Time: 30 min


Intens.
x10 4
242.2837
167.0075
123.0912
194.1151
90.9764
272.1260
m/z
Intens.
Na
145.0262
COOH
product
Chemical Formula: C7H6NaO2+
Exact Mass: 145.0260
m/z
Intens.
161.0206
Na
COOOH
perbenzoic
Chemical Formula: C7H6NaO3+
Exact Mass: 161.0209
m/z
Intens.
267.0628
Na
HO
Criegee intermediate
Chemical Formula: C14H12NaO4+
Exact Mass: 267.0628
m/z

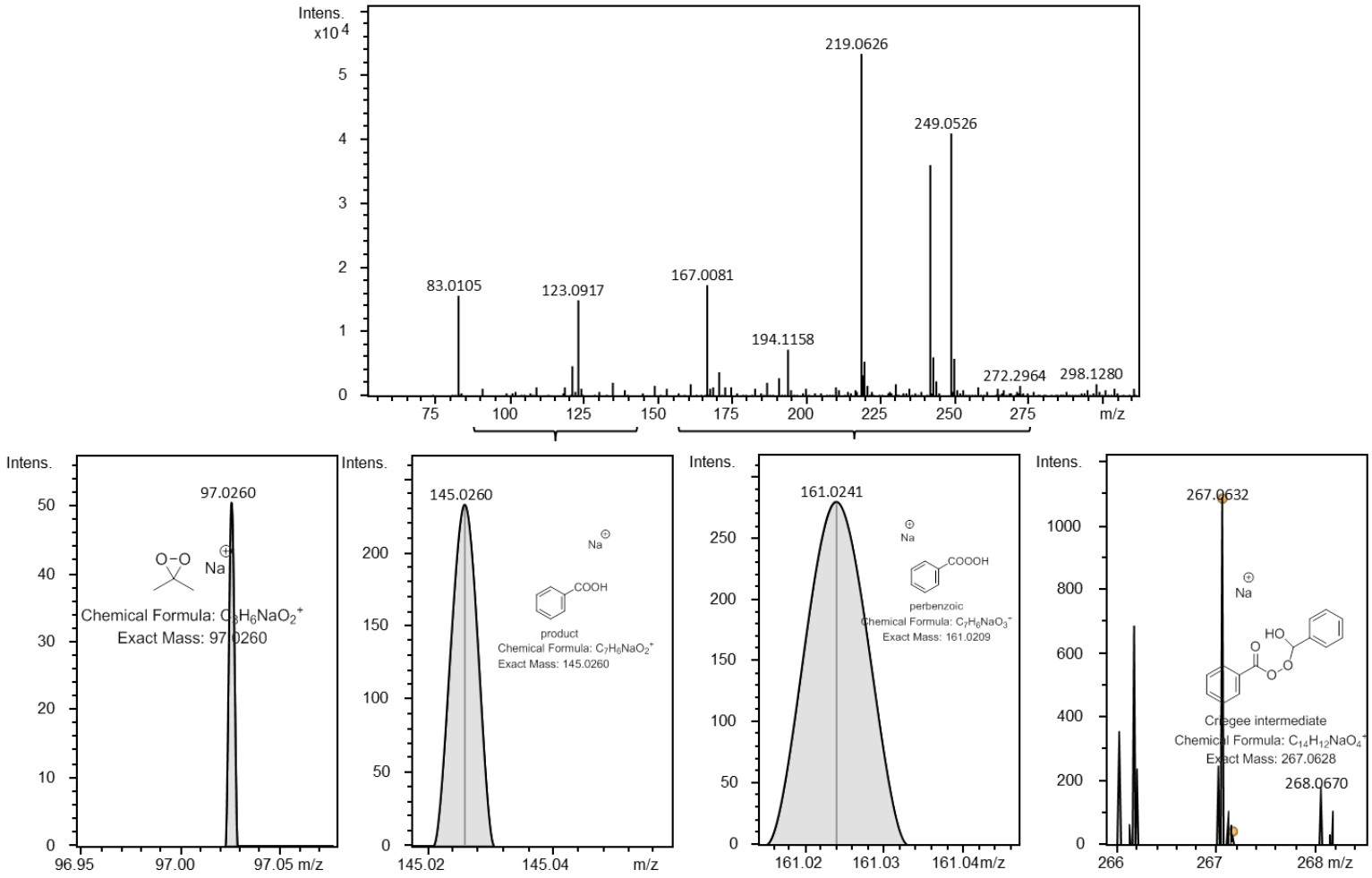
Time: 1 h

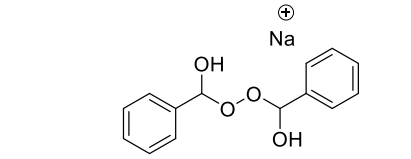

Intens.
x10 4
242.2854
167.0085
194.1161
123.0921
298.1283
90.9771
139.0737
219.0643
m/z
97.0262
Chemical Formula: C3H6NaO2+
Exact Mass: 97.0260
145.0270
product
Chemical Formula: C7H6NaO2+
Exact Mass: 145.0260
161.0207
perbenzoic
Chemical Formula: C7H6NaO3-
Exact Mass: 161.0209
267.0635
Criegee intermediate
Chemical Formula: C14H12NaO4+
Exact Mass: 267.0628

Time: 3 h

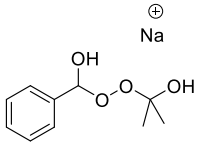

Intens
x1 4
219.062
242.284
167.007
83.010
123.091
194.115
298.127
m/
97.026
Chemical Formula: C3H6NaO2+
Exact Mass: 97.0260
145.025
product
Chemical Formula: C7H6NaO2+
Exact Mass: 145.0260
161.023
perbenzoic
Chemical Formula: C7H6NaO3+
Exact Mass: 161.0209
267.063
Criegee intermediate
Chemical Formula: C14H12NaO4+
Exact Mass: 267.0628
m/z

Time: 4 h

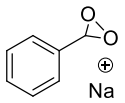

Intens.
x10 4
219.0626
249.0526
167.0081
83.0105
123.0917
194.1158
272.2964
298.1280
m/z
97.0260
Chemical Formula: C3H6NaO2+
Exact Mass: 97.0260
145.0260
product
Chemical Formula: C7H6NaO2+
Exact Mass: 145.0260
161.0241
perbenzoic
Chemical Formula: C7H6NaO3+
Exact Mass: 161.0209
267.0632
Criegee intermediate
Chemical Formula: C14H12NaO4+
Exact Mass: 267.0628
268.0670



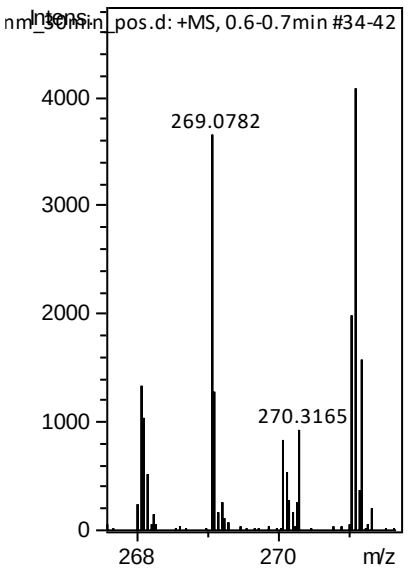

Chemical Formula: $C_{14}H_{14}NaO_4^+$
Exact Mass: 269.0784

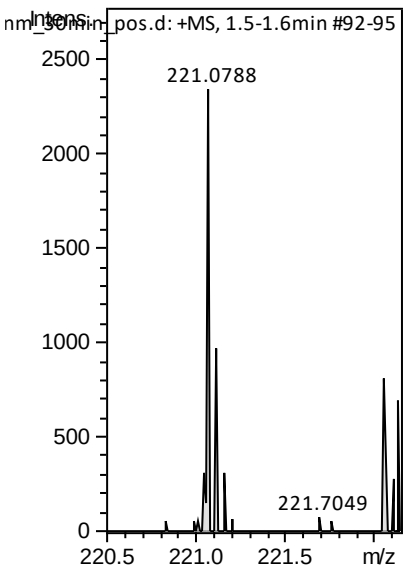



Chemical Formula: $C_{10}H_{14}NaO_4^+$
Exact Mass: 221.0784




Chemical Formula: $C_7H_6NaO_2^+$
Exact Mass: 145.0260



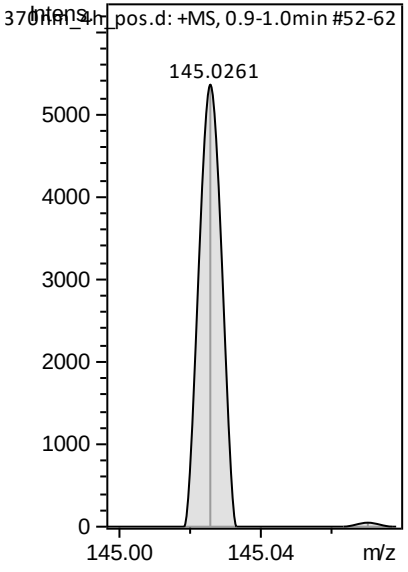
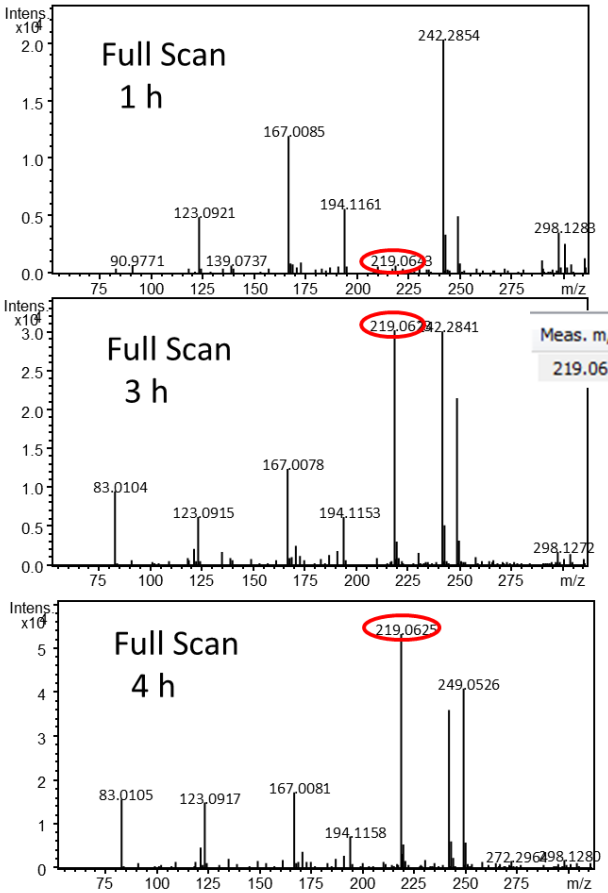



**Figure S2.** Full scan HRMS spectra taken at 1 h, 3 h and 4 h, verifying the generation of mixed Griegee intermediate with acetone (*m/z* 219.0628).

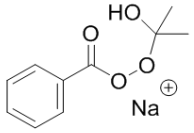



Smart Formula application
Data Analysis from Bruker Daltonics
(version 4.1)

| Meas. m/z | # | Ion Formula | m/z | err [ppm] | mSigma | # Sigma | Score | rdb | e— Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 219.0625 | 1 | C10H12NaO4 | 219.0628 | 1.1 | 8.5 | 1 | 100.00 | 4.5 | even | ok |

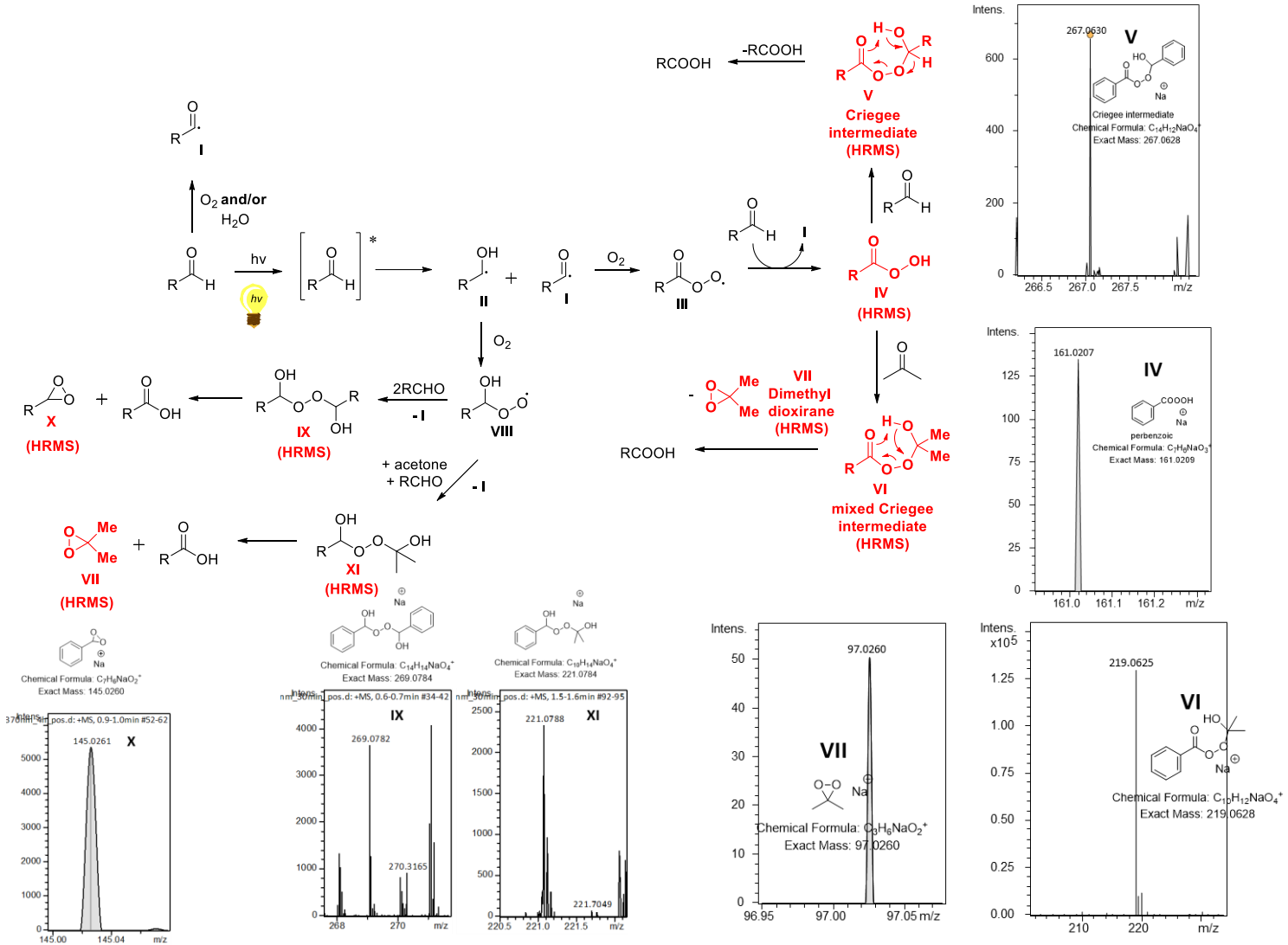
**Low mass error (ppm)**

**Perfect isotopic fit (mSigma)**

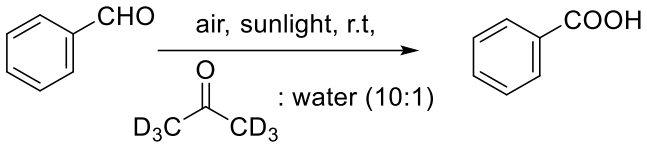



Chemical Formula: $C_{10}H_{12}NaO_4^+$
Exact Mass: 219.0628

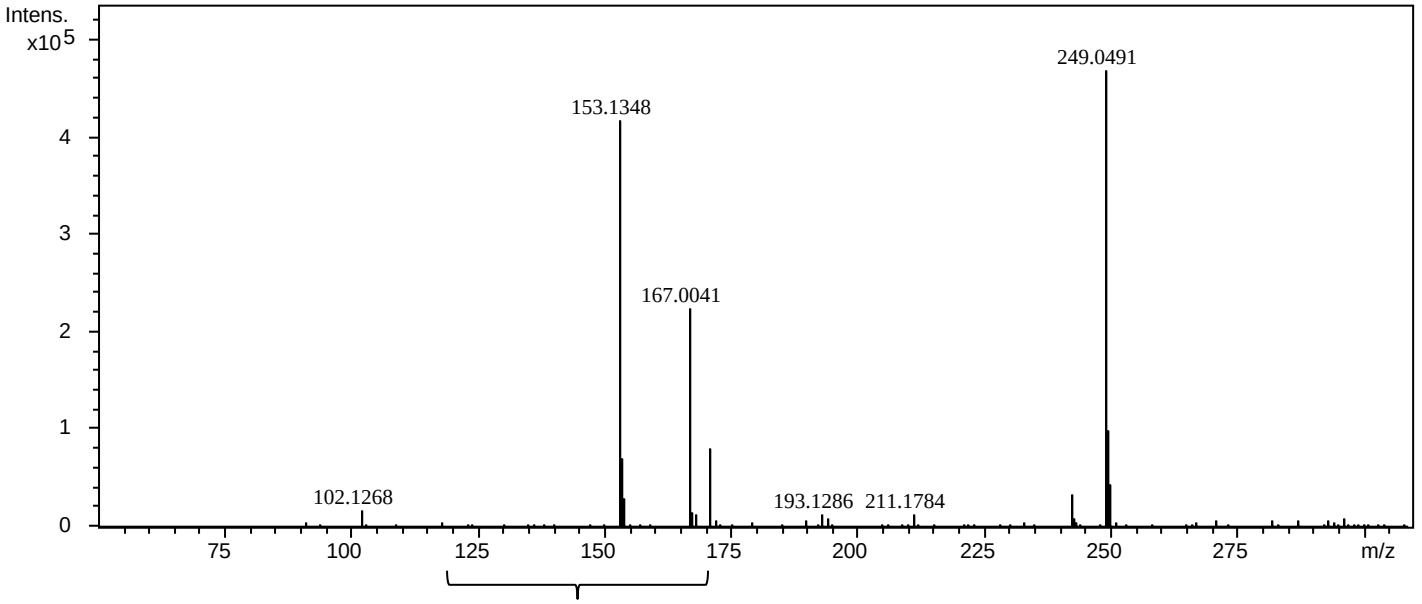
**Figure S3.** Proposed mechanism for the oxidation of aldehydes to carboxylic acids in acetone/water and selected HRMS spectra of the oxidation of benzaldehyde, verifying the generation of peracid **IV**, Griegee intermediate **V**, mixed Griegee intermediate with acetone **VI**, dimethyl dioxirane **VII** and intermediates **IX**, **X** and **XI**.

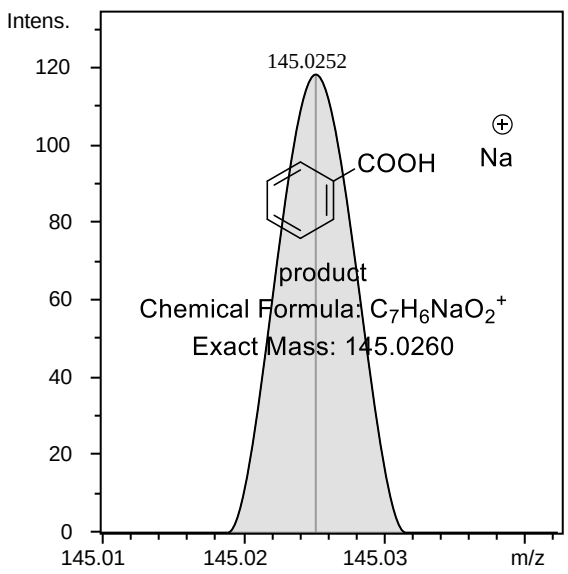


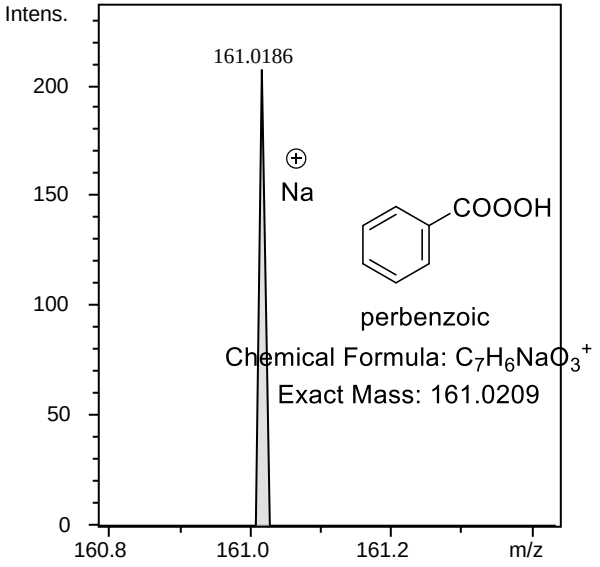
**Monitoring of the photochemical aerobic oxidation of benzaldehyde by DI-HRMS (positive ion mode) using deuterated acetone**



Time: 1 h


Intens.
x10^5
249.0491
153.1348
167.0041
102.1268
193.1286
211.1784
m/z


Intens.
145.0252
COOH
Na
product
Chemical Formula: C7H6NaO2+
Exact Mass: 145.0260
m/z


Intens.
161.0186
Na
COOOH
perbenzoic
Chemical Formula: C7H6NaO3+
Exact Mass: 161.0209
m/z

Time: 1 h

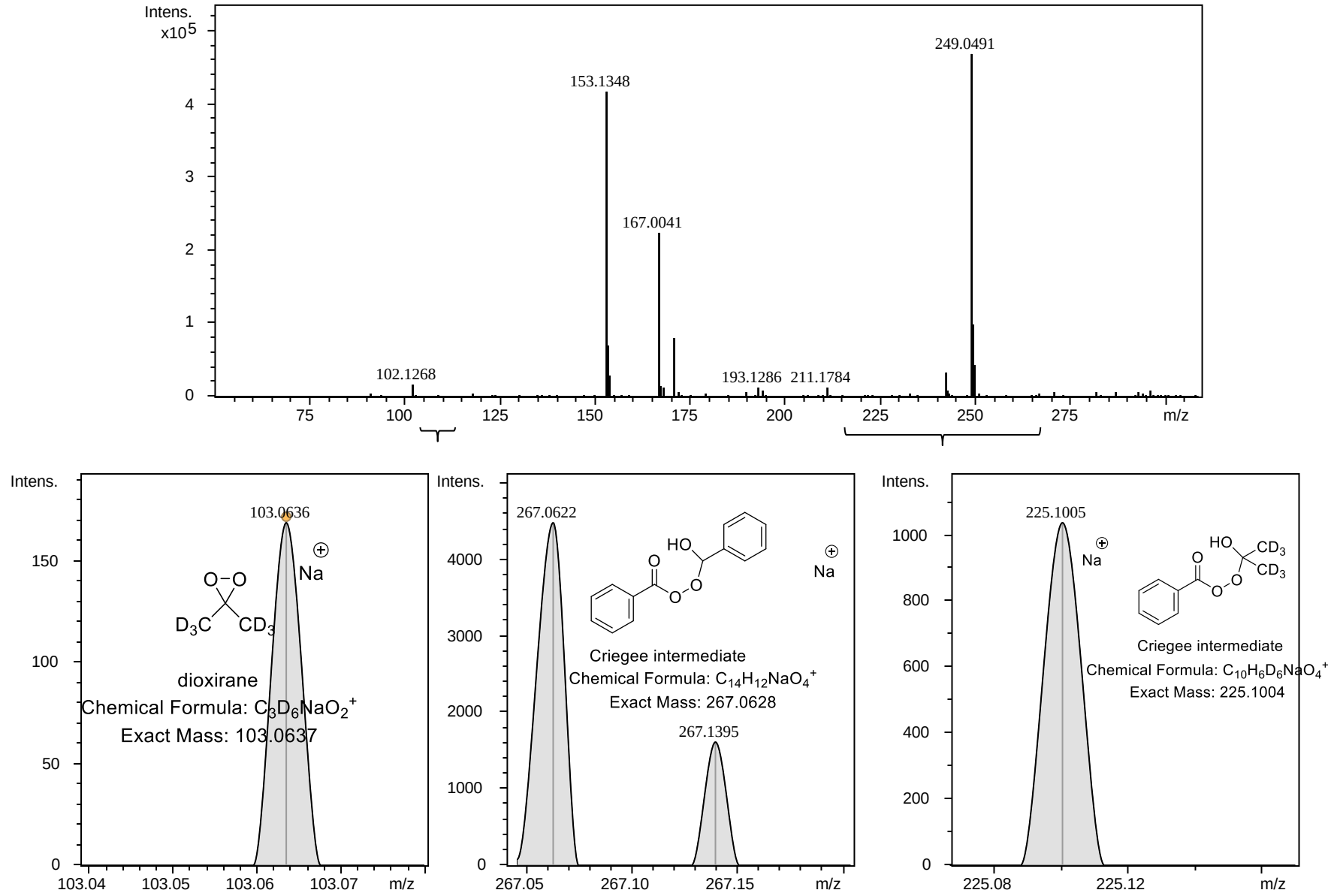
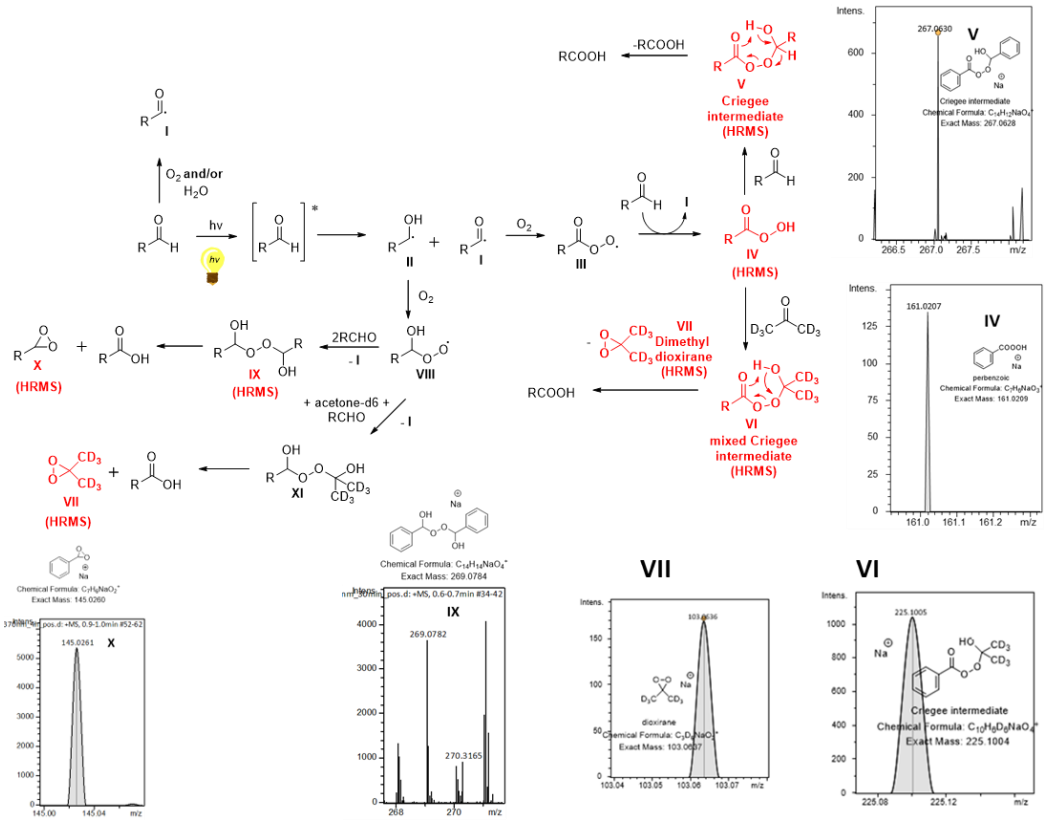

Intens.
x10^5
249.0491
153.1348
167.0041
102.1268
193.1286
211.1784
m/z
Intens.
103.0636
Na
dioxirane
Chemical Formula: C3D6NaO2+
Exact Mass: 103.0637
m/z
Intens.
267.0622
Na
Criegee intermediate
Chemical Formula: C14H12NaO4+
Exact Mass: 267.0628
267.1395
m/z
Intens.
225.1005
Na
Criegee intermediate
Chemical Formula: C10H6D6NaO4+
Exact Mass: 225.1004
m/z

**Figure S4.** Proposed mechanism for the oxidation of aldehydes to carboxylic acids in deuterated acetone/water and selected HRMS spectra of the oxidation of benzaldehyde, verifying the generation of peracid **IV**, Griegee intermediate **V**, mixed Griegee intermediate with deuterated acetone **VI** and deuterated dioxirane **VII**.



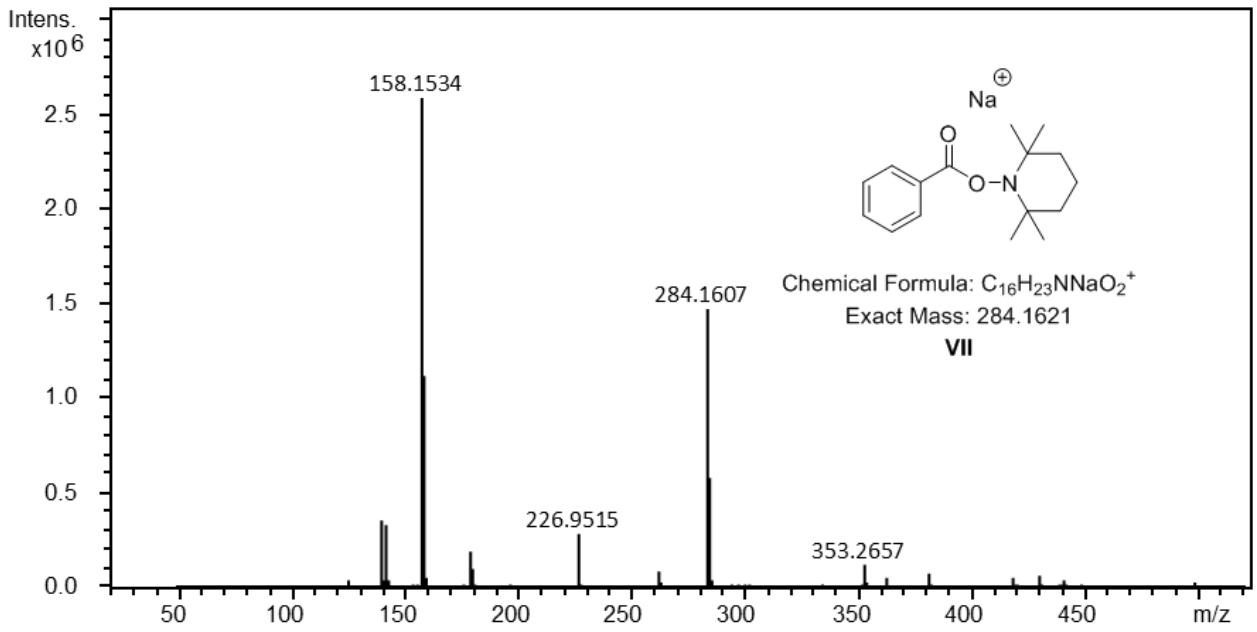
## Monitoring of the photochemical aerobic oxidation of benzaldehyde in the presence of TEMPO by DI-HRMS (positive ion mode)

### Experimental procedure

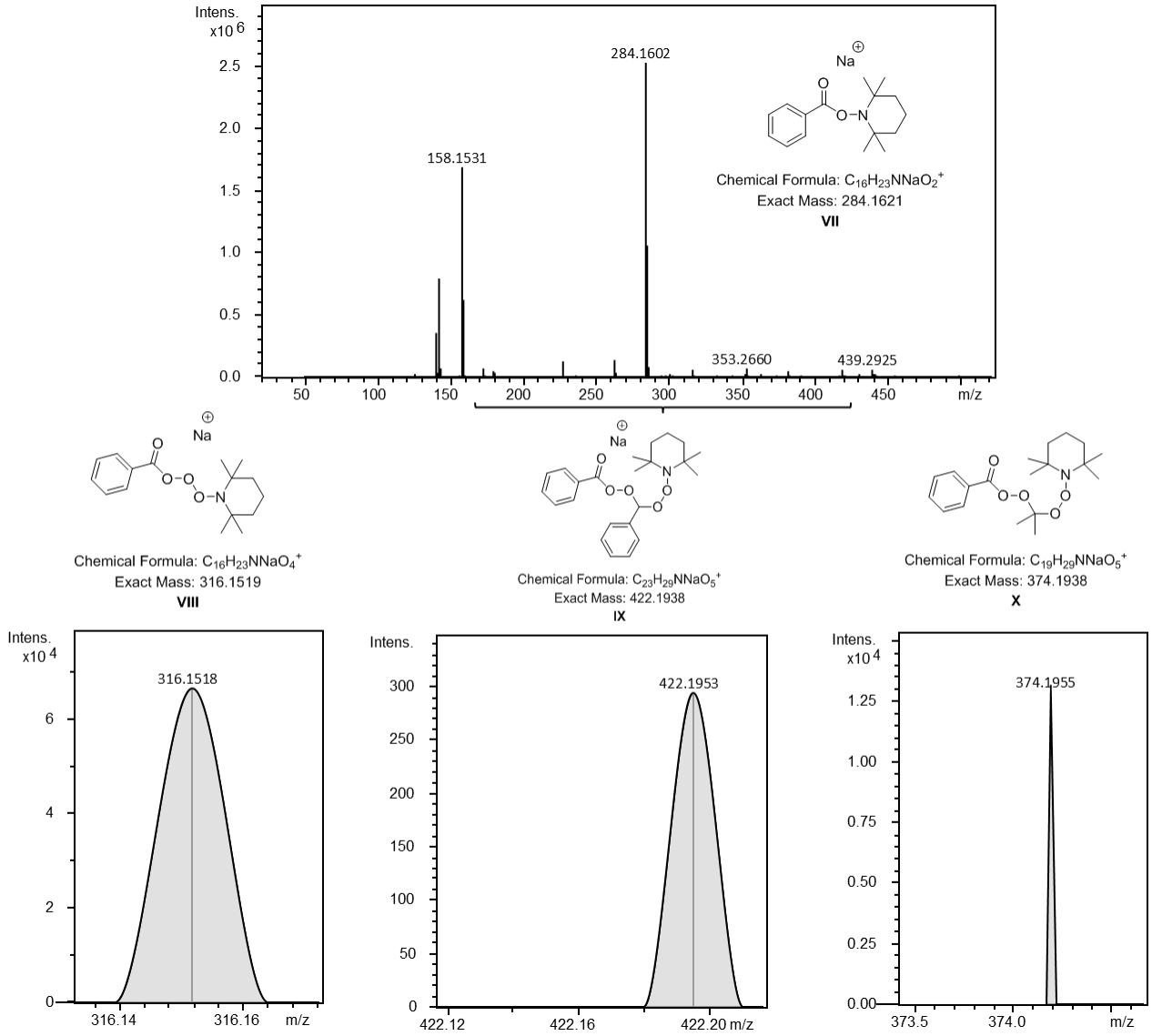
In a test tube containing acetone (3.0 mL) and $H_2O$ (0.3 mL, HPLC grade), benzaldehyde (106 mg, 1.00 mmol) and TEMPO (156 mg, 1.00 mmol) were added and the reaction mixture was left stirring under LED irradiation (370 nm) for 3 h.

At the specific time of study, an aliquot of 10 μL was taken from the reaction mixture and diluted with 990 μL MeOH. A sample of 100 μL from this mixture was further diluted with 400 μL MeOH and 500 μL $H_2O$. 10 μL of the final solution were directly injected for DI-HRMS analysis.

Full scan spectrum. Time: 1 h.



Full scan spectrum. Time: 3 h.




When the photochemical aerobic oxidation of benzaldehyde was carried out in the presence of TEMPO (irradiation by LED 370 nm), benzoic acid was not formed, but we were able to isolate and characterize the trapped by TEMPO benzoyl radical. The reaction was also monitored by DI-HRMS. In addition to a strong peak at *m/z* 284.1607, which corresponds to the trapped by TEMPO benzoyl radical **VII**, peaks at *m/z* 316.1518, 422.1953 and 374.1955, corresponding to trapped by TEMPO perbenzoyl radical **VIII** and trapped Griegee intermediates **IX** and **X**, respectively, were clearly observed.

# Liquid Chromatography-High Resolution Mass Spectrometry (LC-HRMS) Studies

## Monitoring of the photochemical aerobic oxidation of benzaldehyde in the presence of TEMPO

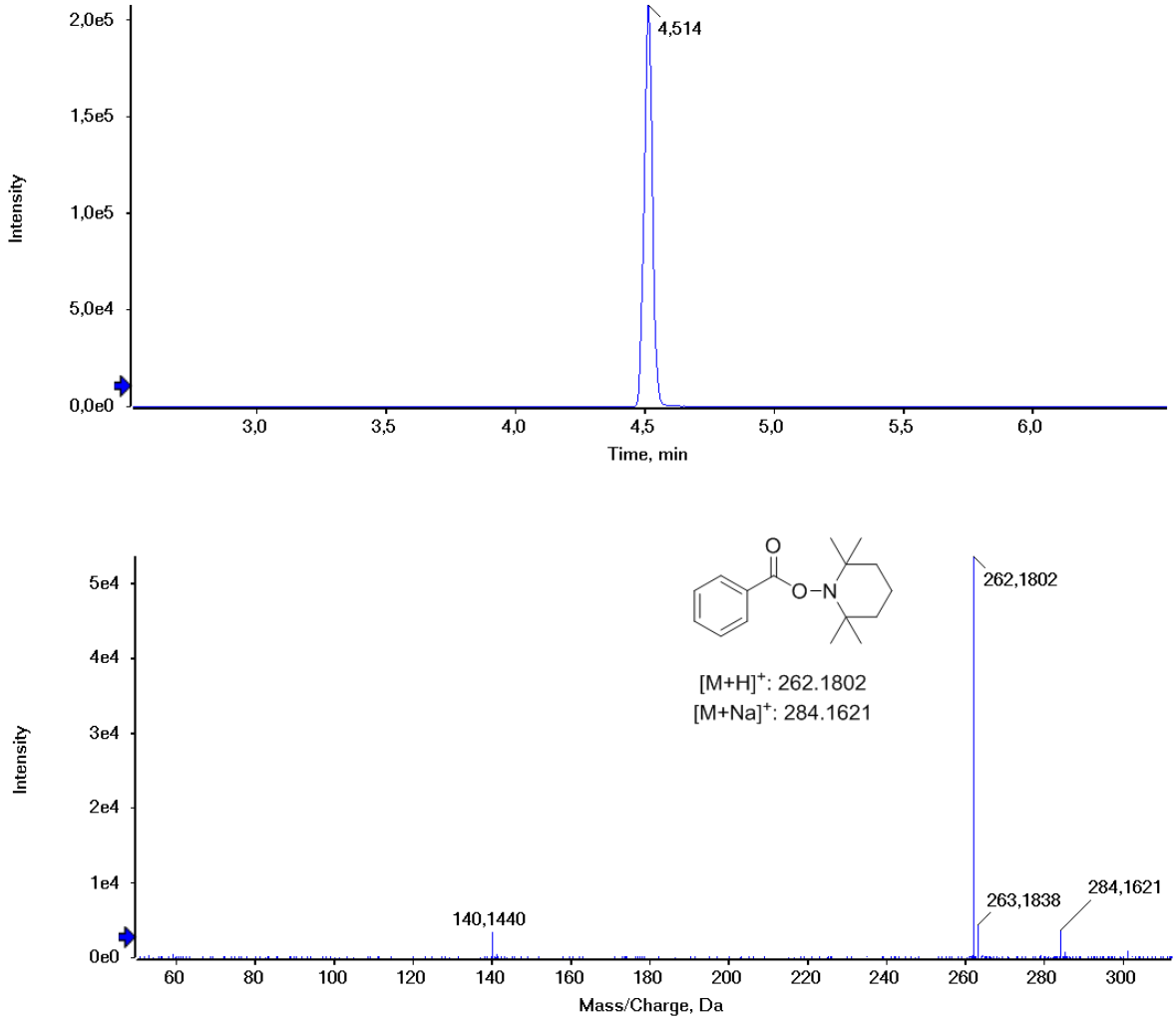
### Instrumentation

Experiments were performed using a Triple TOF 4600 ABSciex, coupled with a micro-LC Eksigent, an autosampler set at 5 $^{o}$C and a thermostated column compartment. A Halo C18 2.7 μm, 90 Å, 0.5 x 50 mm$^2$ column (Eksigent) was employed for the chromatography at a flow rate of 55 μL/min. The mobile phases A and B were acetonitrile/0.01% formic acid/isopropanol 80/20 v/v and water/0.01% formic acid, respectively. The following gradient was used: 5% of phase B for 0.5 min, gradually increasing to 98% in the next 7.5 min. These conditions were maintained for 0.5 min, and then the column was re-equilibrated (at the initial conditions) for 1.5 min. Mass spectrometry was performed with an ESI source in positive-ionization mode.

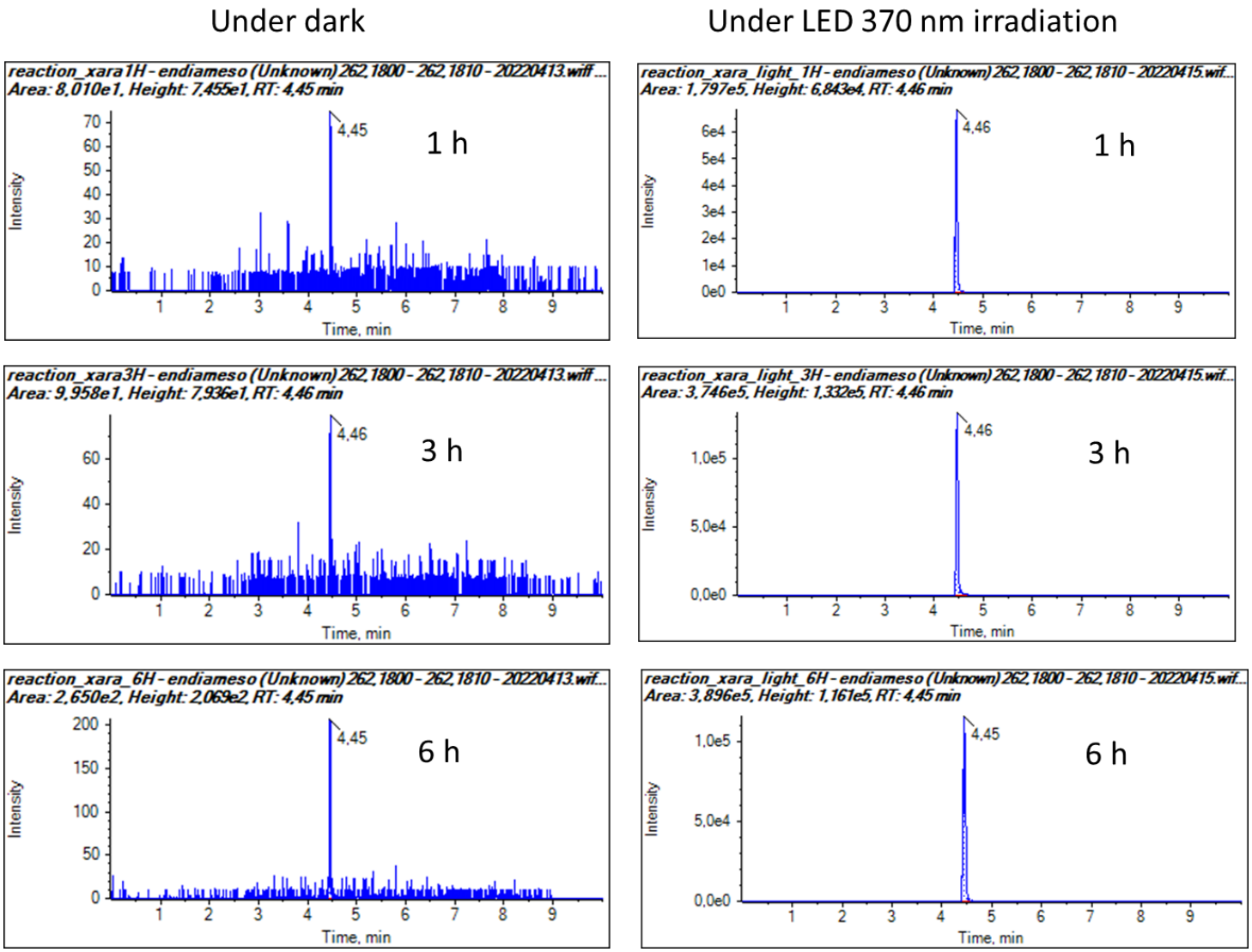
For data acquisition and processing, MultiQuant 3.0.2 and PeakView 2.1 (ABSciex) were used. Extracted ion chromatograms (EICs) were obtained with the use of MultiQuant 3.0.2, which created the base peak chromatograms for the masses that achieved a 0.01 Da mass accuracy width.

### Experimental procedure

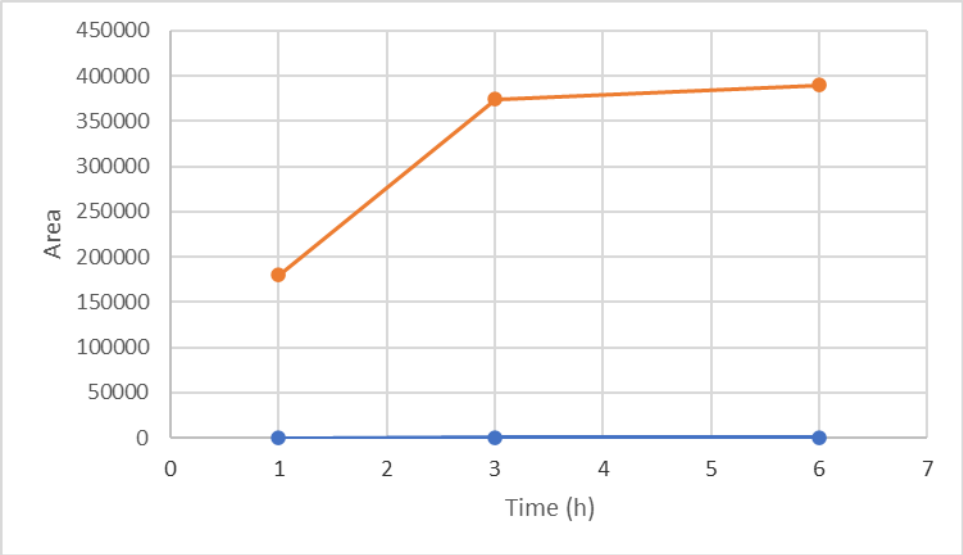
Followed the same procedure as described in page S48.




Extracted ion chromatogram of the trapped by TEMPO benzoyl radical and its mass spectrum.

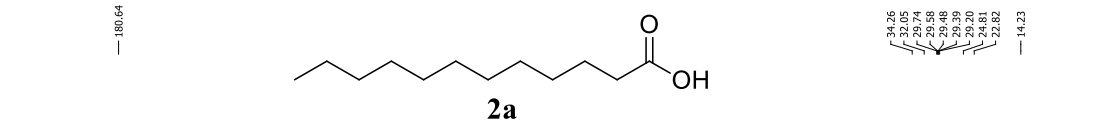



Monitoring of the photochemical aerobic oxidation of benzaldehyde in the presence of TEMPO. Extracted ion chromatograms of the trapped by TEMPO benzoyl radical either in dark or under LED 370 nm irradiation.

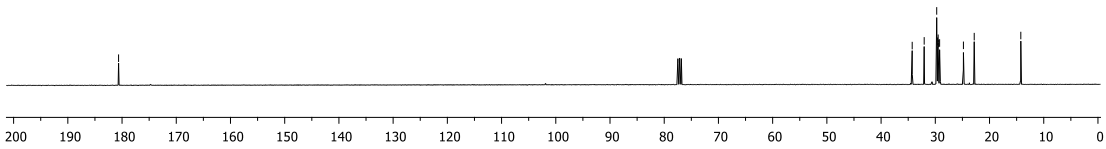



Course of the formation of the trapped by TEMPO benzoyl radical in dark (blue line) and under LED 370 nm irradiation (orange line).

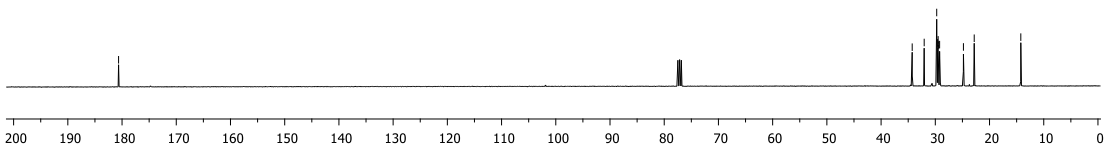
The progress of the aerobic oxidation of benzaldehyde in the presence of TEMPO, either in dark or under LED 370 nm irradiation, was monitored by LC-HRMS for 6 hours. As shown in the above Figure, traces of the trapped by TEMPO benzoyl radical were observed in dark. On the contrary, under LED 370 nm irradiation, the trapped by TEMPO benzoyl radical was detected at increasing concentrations as the time passes by, indicating once more the crucial role of light for the formation of the benzoyl radical.

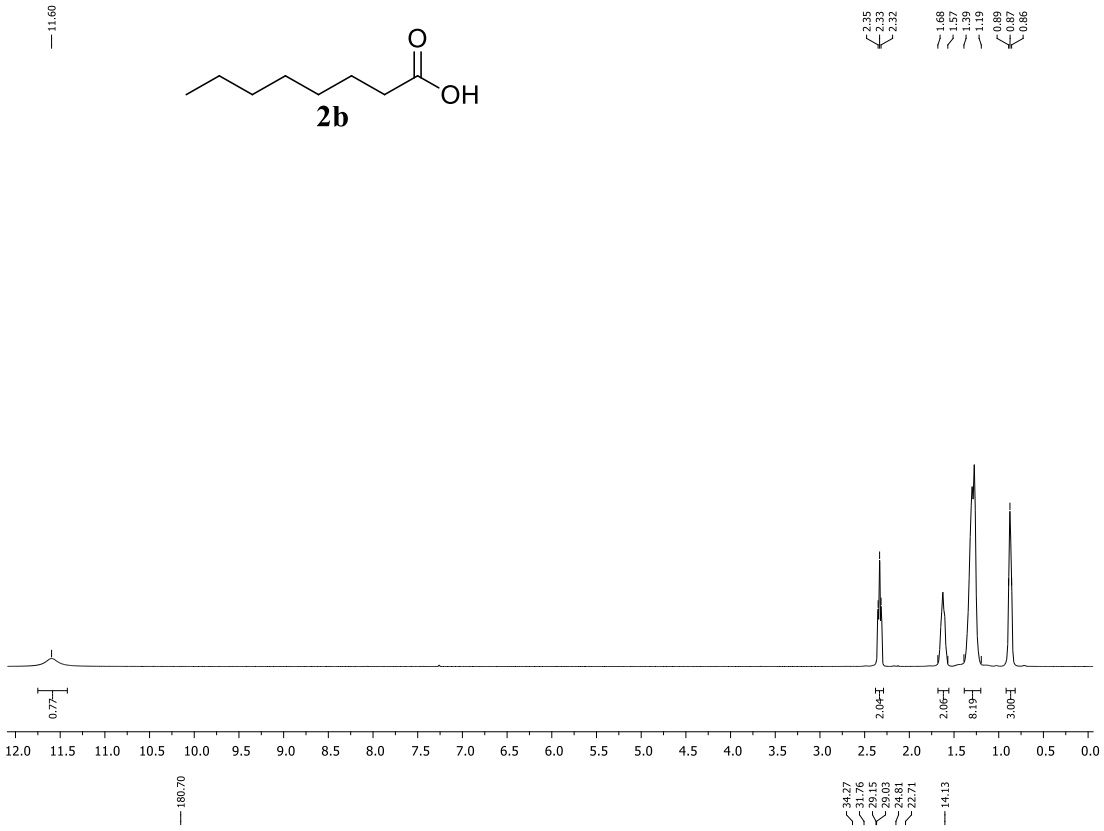

180.64
O
OH
34.26
32.05
29.74
29.58
29.48
29.39
29.20
24.81
22.82
14.23

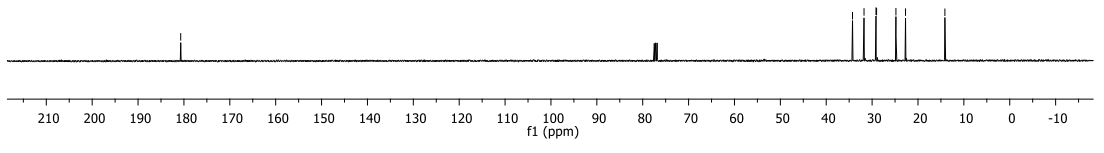
**2a**

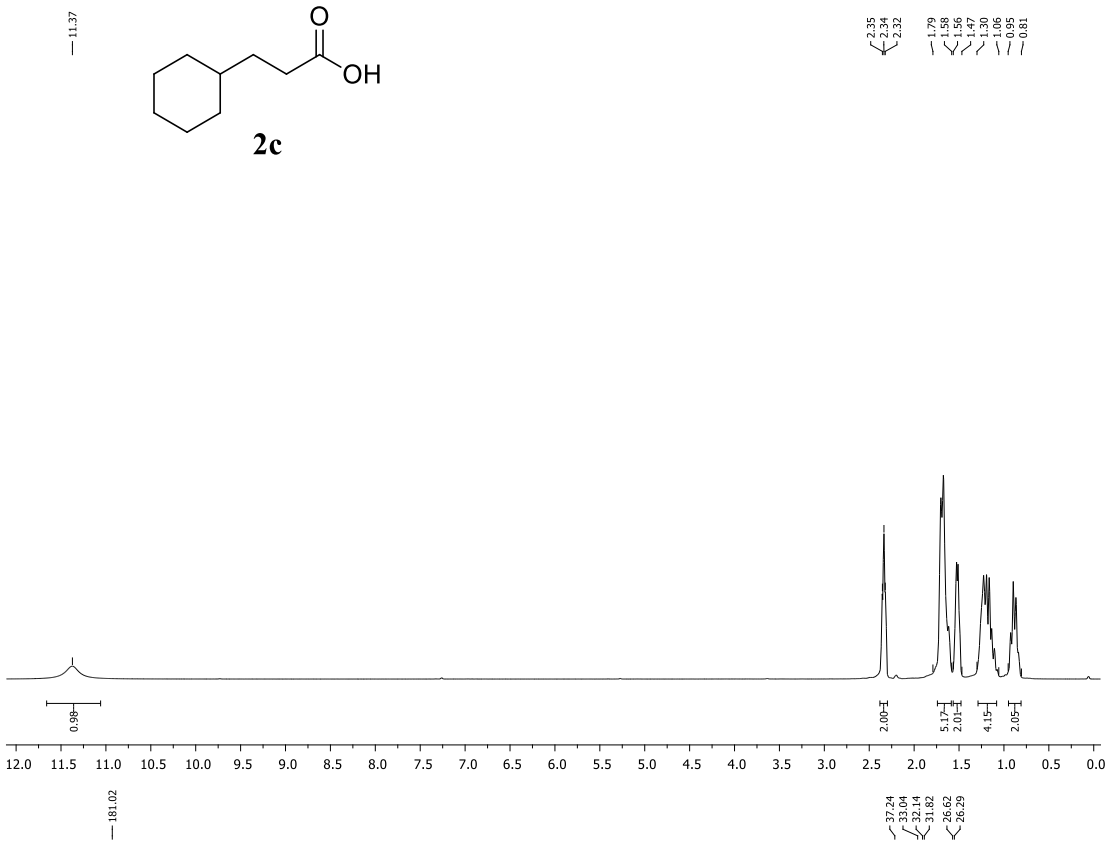

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

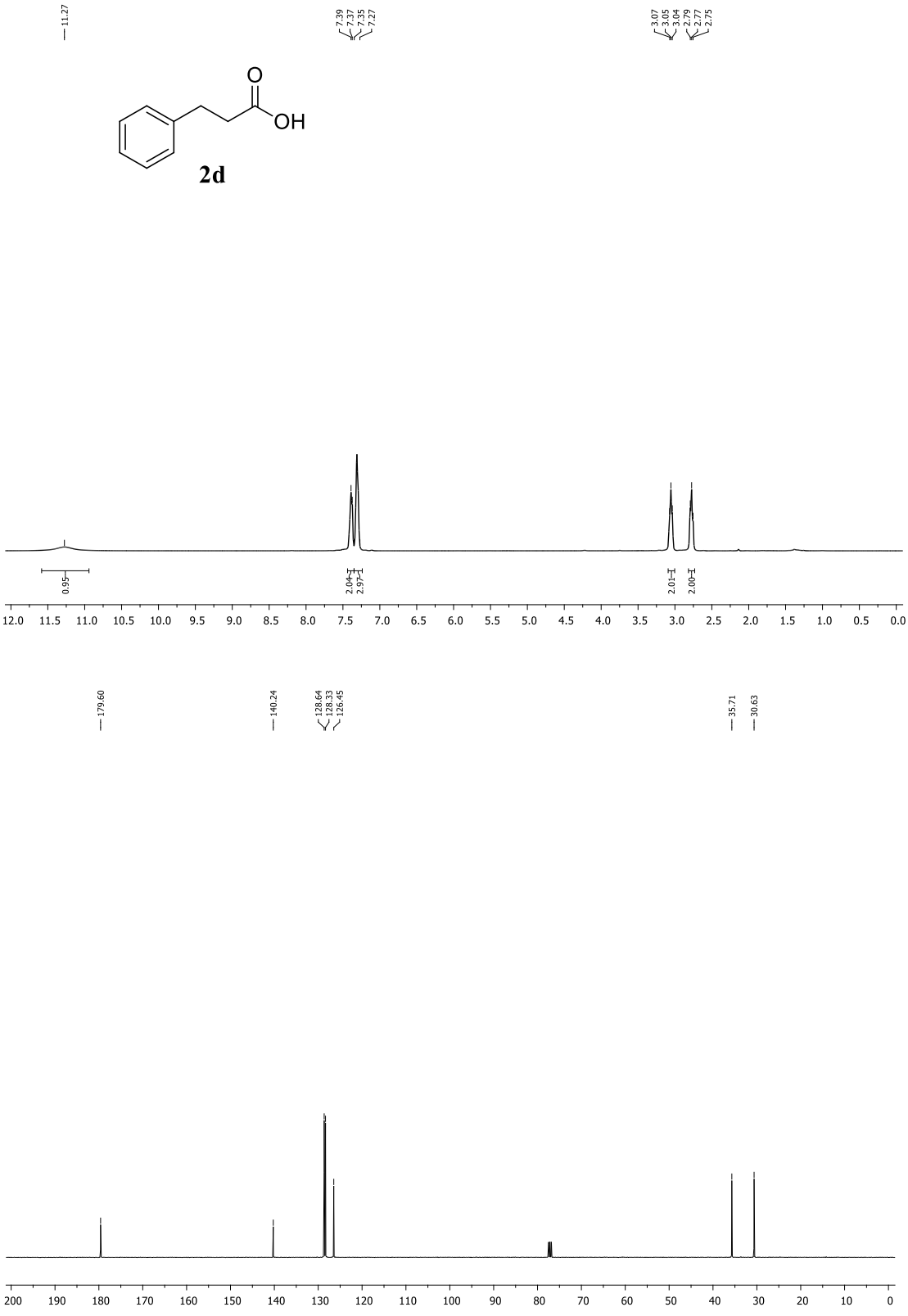

180.64
34.26
32.05
29.74
29.58
29.48
29.39
29.20
24.81
22.82
14.23

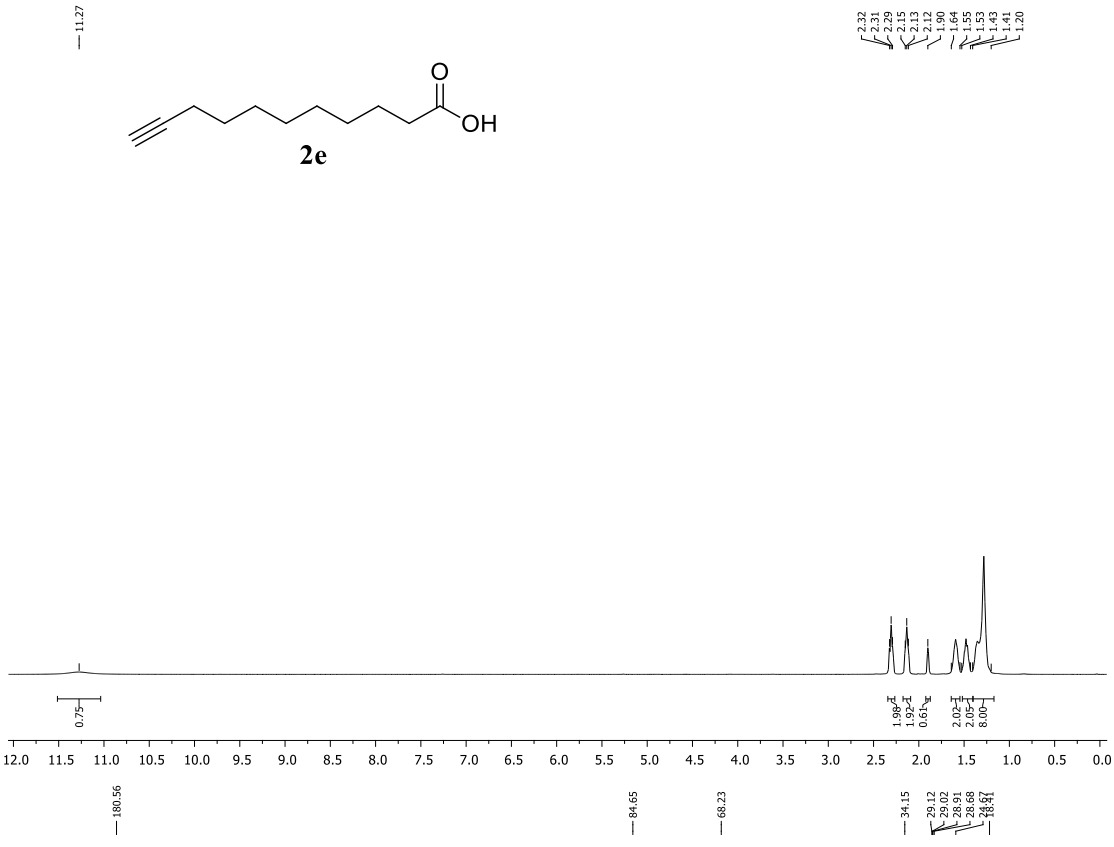

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


11.60
O
OH
2b
2.35
2.33
2.32
1.68
1.57
1.39
1.19
0.89
0.87
0.86
0.77
2.04
2.06
8.19
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
180.70
34.27
31.76
29.15
29.03
24.81
22.71
14.13

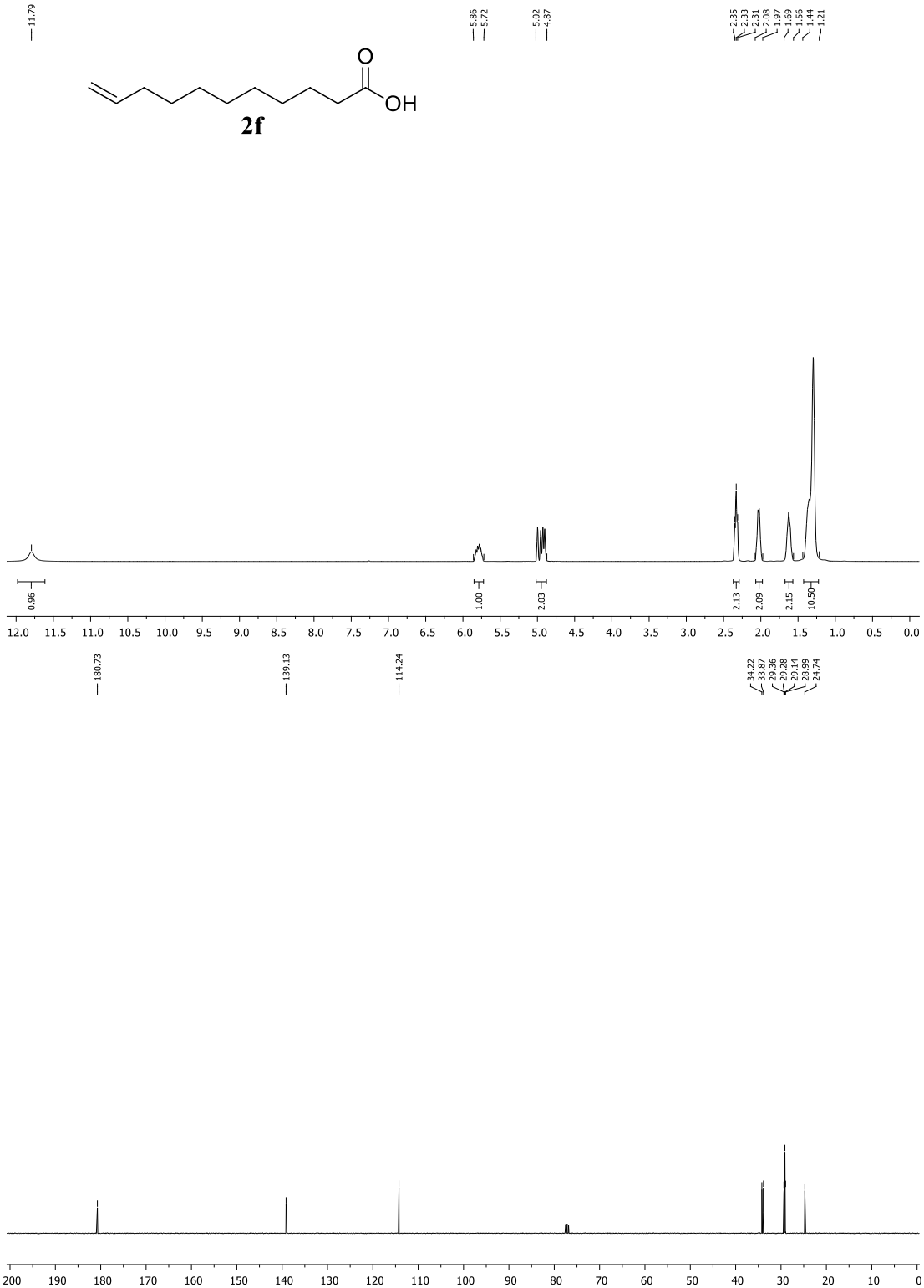

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


11.37
O
OH
2c
2.35
2.34
2.32
1.79
1.58
1.56
1.47
1.30
1.06
0.95
0.81
0.98
2.00
5.17
2.01
4.15
2.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
181.02
37.24
33.04
32.14
31.82
26.62
26.29
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


11.27
7.39
7.37
7.35
7.27
3.07
3.05
3.04
2.79
2.77
2.75
O
OH
2d
0.95
2.04
2.97
2.01
2.00
179.60
140.24
128.64
128.33
126.45
35.71
30.63


11.27
2.32
2.31
2.29
2.15
2.13
2.12
1.90
1.64
1.55
1.53
1.43
1.41
1.20
O
OH
0.75
1.98
1.92
0.61
2.02
2.05
8.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
180.56
84.65
68.23
34.15
29.12
29.02
28.91
28.68
24.67
18.41
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

**2e**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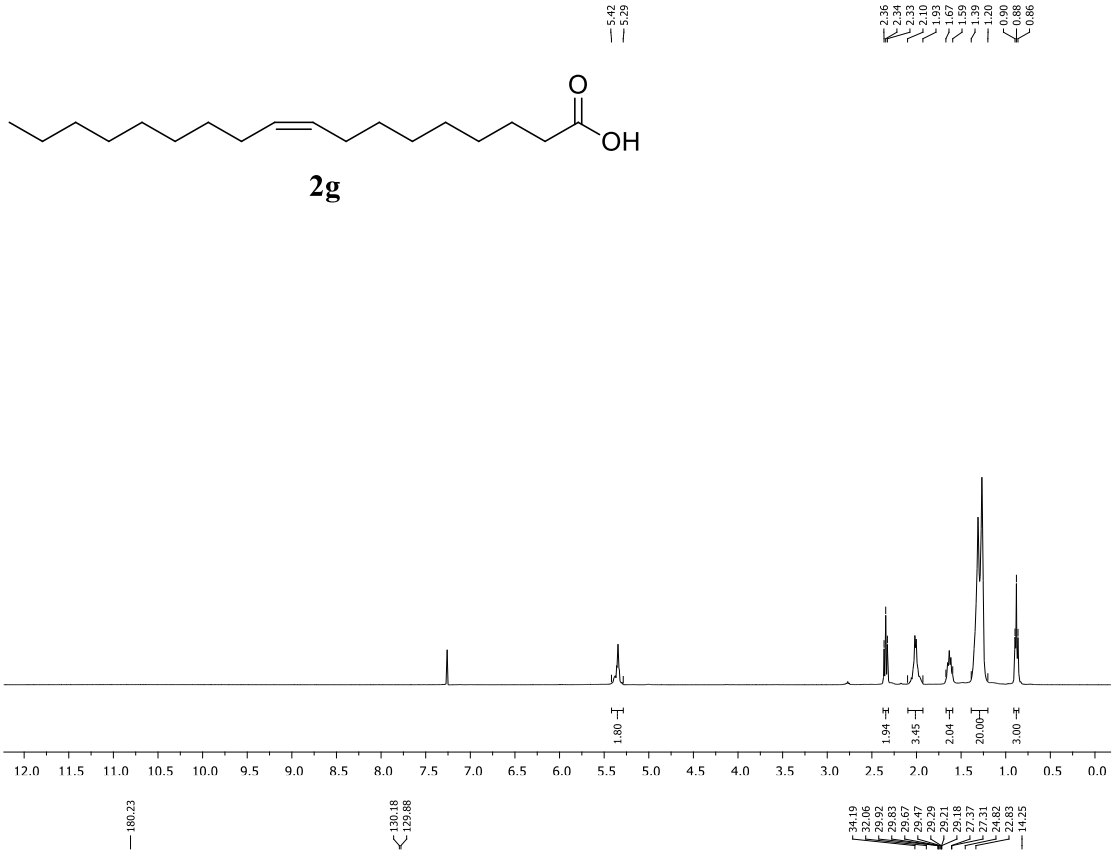
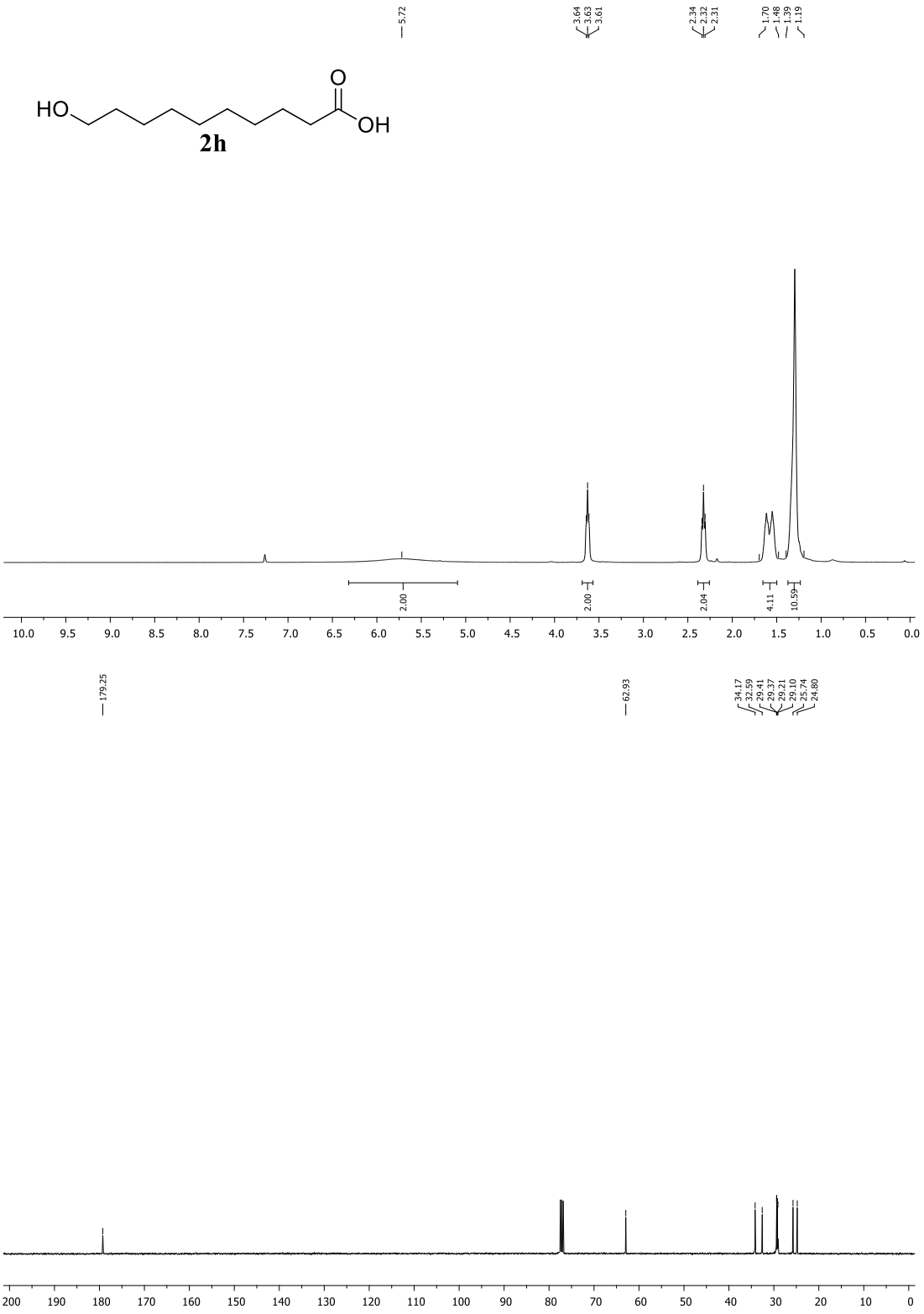
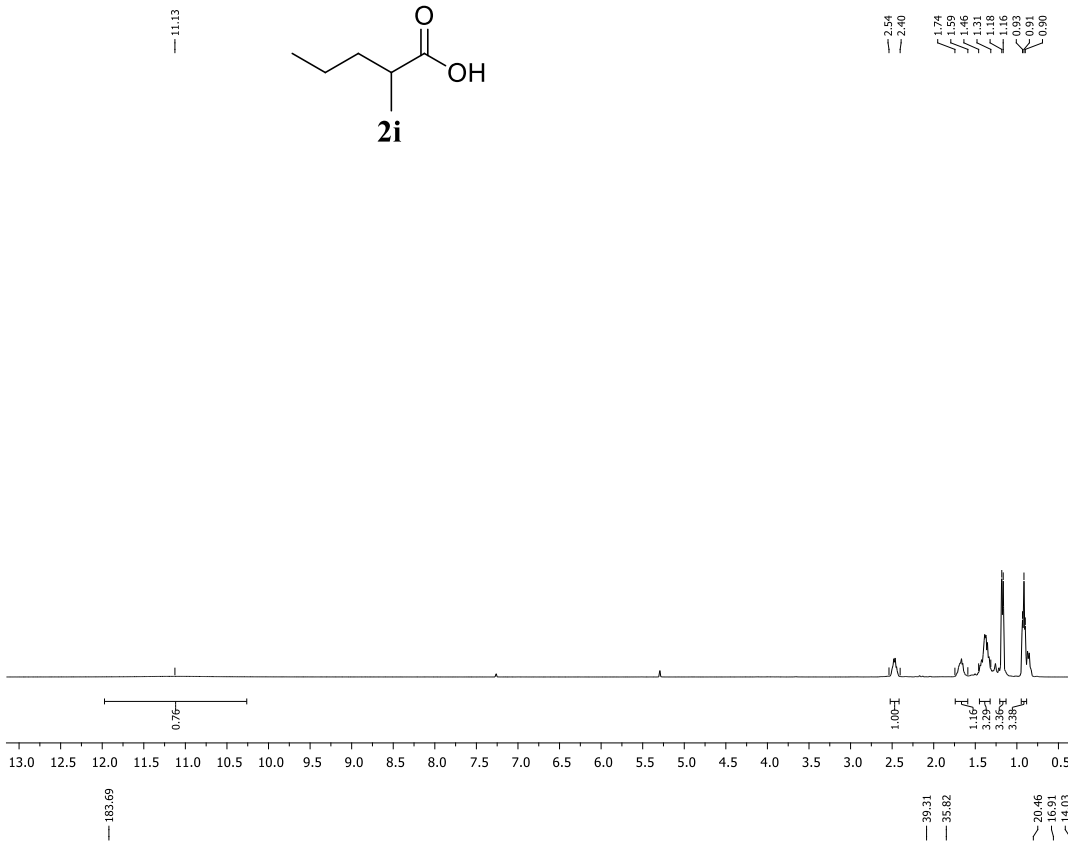
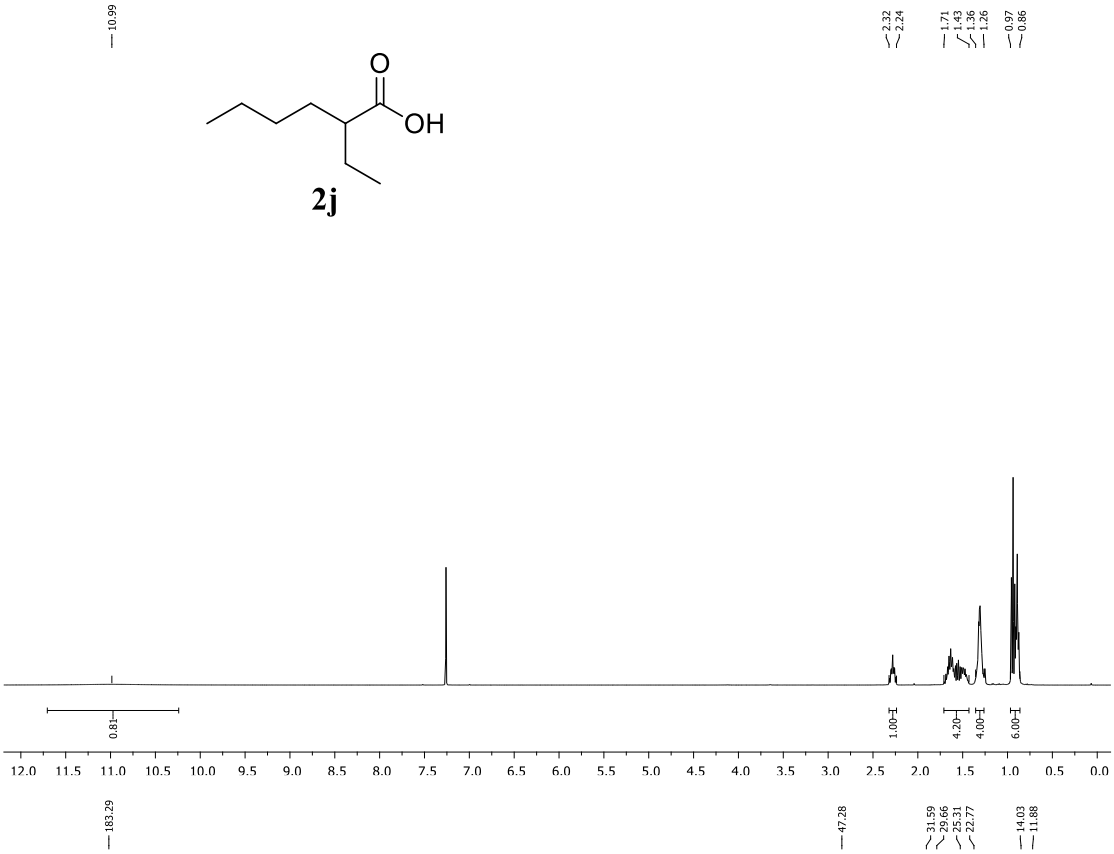
5.86
5.72
5.02
4.87
2.35
2.33
2.31
2.08
1.97
1.69
1.56
1.44
1.21
O
OH
2f
0.96
1.00
2.03
2.13
2.09
2.15
10.50
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
180.73
139.13
114.24
34.22
33.87
29.36
29.28
29.14
28.99
24.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


5.42
5.29
2.36
2.34
2.33
2.10
1.93
1.67
1.59
1.39
1.20
0.90
0.88
0.86
O
OH
1.80
1.94
3.45
2.04
20.00
3.00
180.23
130.18
129.88
34.19
32.06
29.92
29.83
29.67
29.47
29.29
29.21
29.18
27.37
27.31
24.82
22.83
14.25

**2g**


5.72
3.64
3.63
3.61
2.34
2.32
2.31
1.70
1.48
1.39
1.19
HO
O
OH
2h
2.00
2.00
2.04
4.11
10.59
179.25
62.93
34.17
32.59
29.41
29.37
29.21
29.10
25.74
24.80

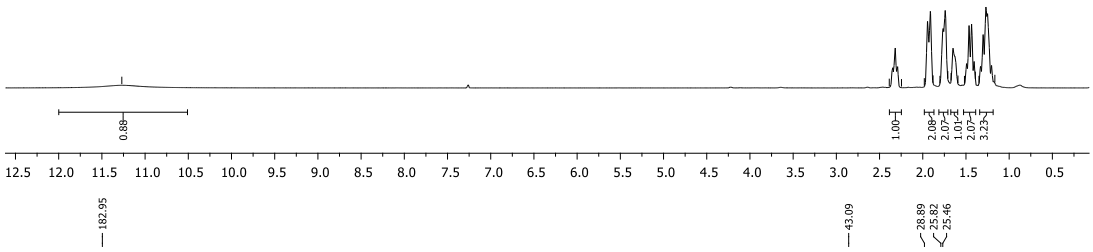

11.13
O
OH
2i
2.54
2.40
1.74
1.59
1.46
1.31
1.18
1.16
0.93
0.91
0.90
0.76
1.00
1.16
3.29
3.36
3.38
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
183.69
39.31
35.82
20.46
16.91
14.03
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


10.99
2.32
2.24
1.71
1.43
1.36
1.26
0.97
0.86
O
OH
0.81
1.00
4.20
4.00
6.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
183.29
47.28
31.59
29.66
25.31
22.77
14.03
11.88
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

**2j**


11.27
O
OH
2.39
2.25
1.98
1.88
1.80
1.71
1.67
1.59
1.52
1.39
1.35
1.17

**2k**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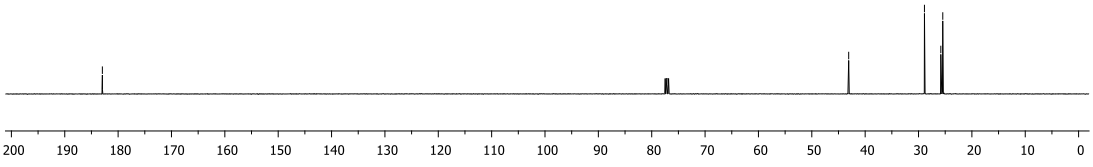
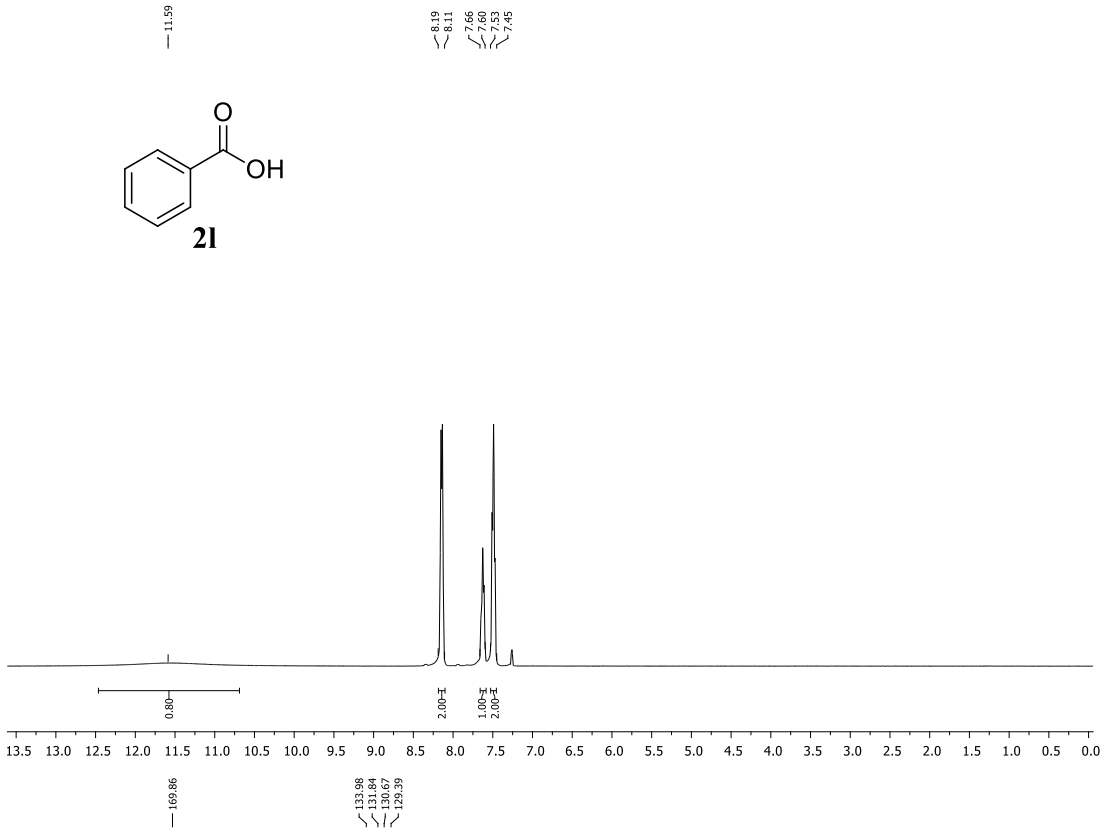
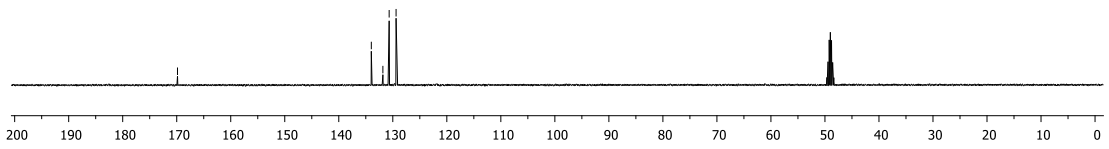
1.00
2.08
2.07
1.01
2.05
3.25
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

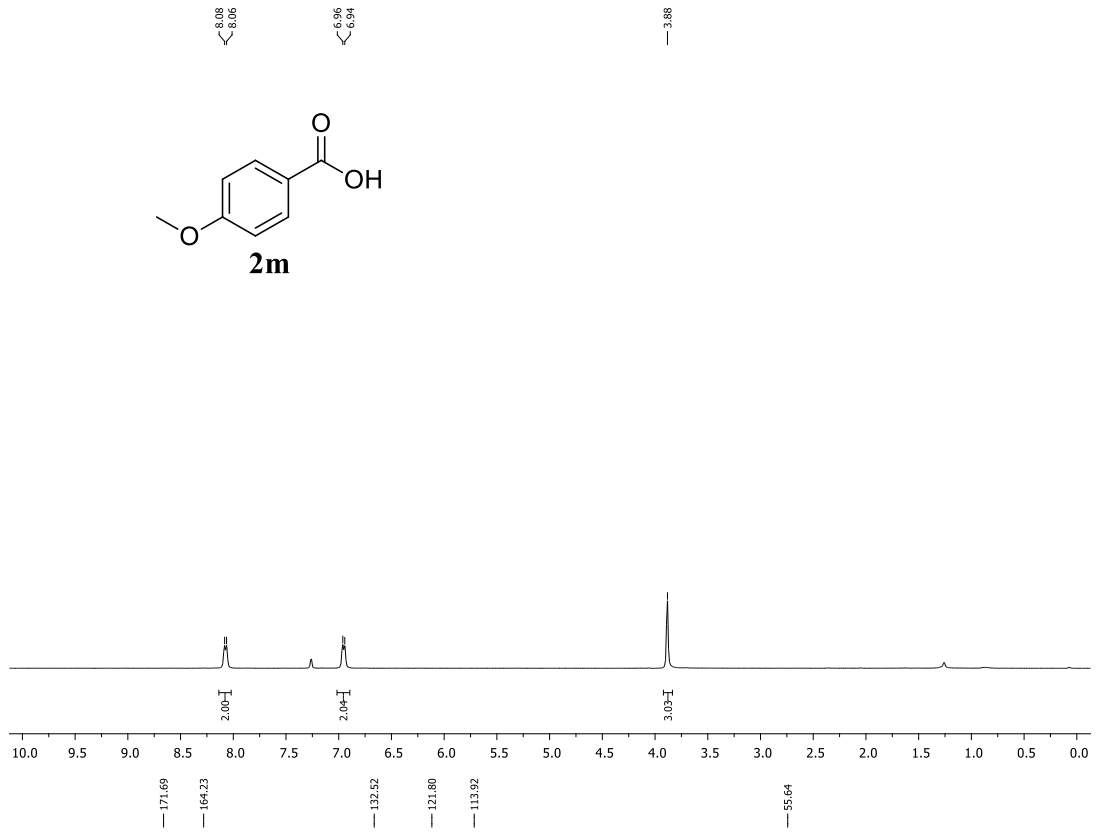

182.95
43.09
28.89
25.82
25.46

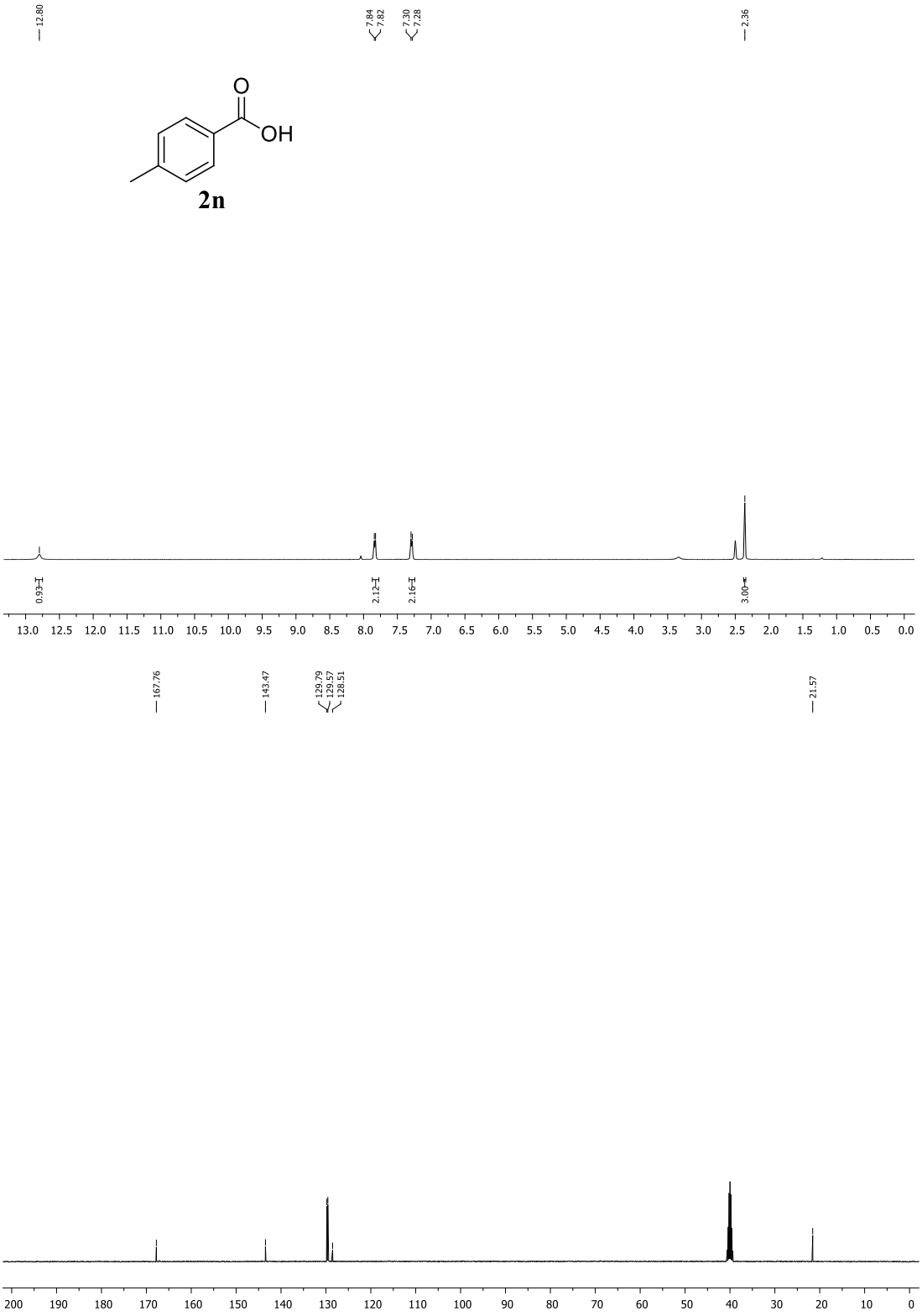

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


11.59
8.19
8.11
7.66
7.60
7.53
7.45
O
OH
0.80
2.00
1.00
2.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
169.86
133.98
131.84
130.67
129.39

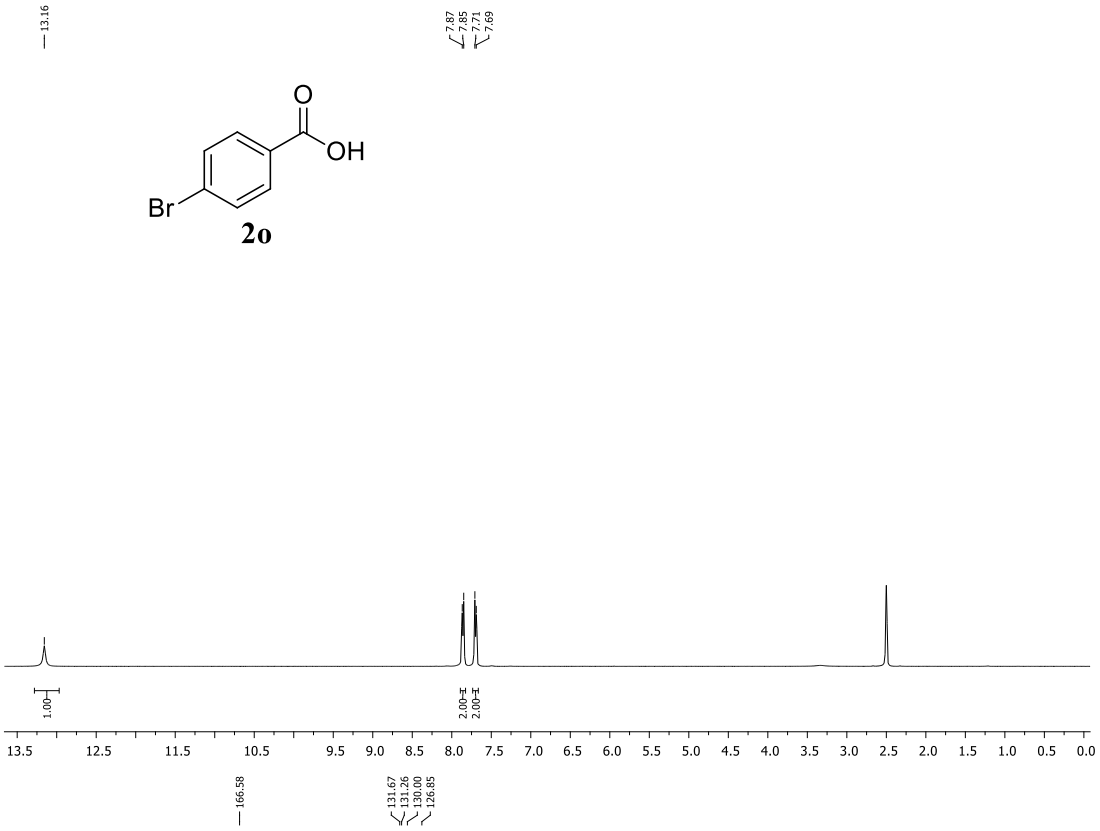
**2l**


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

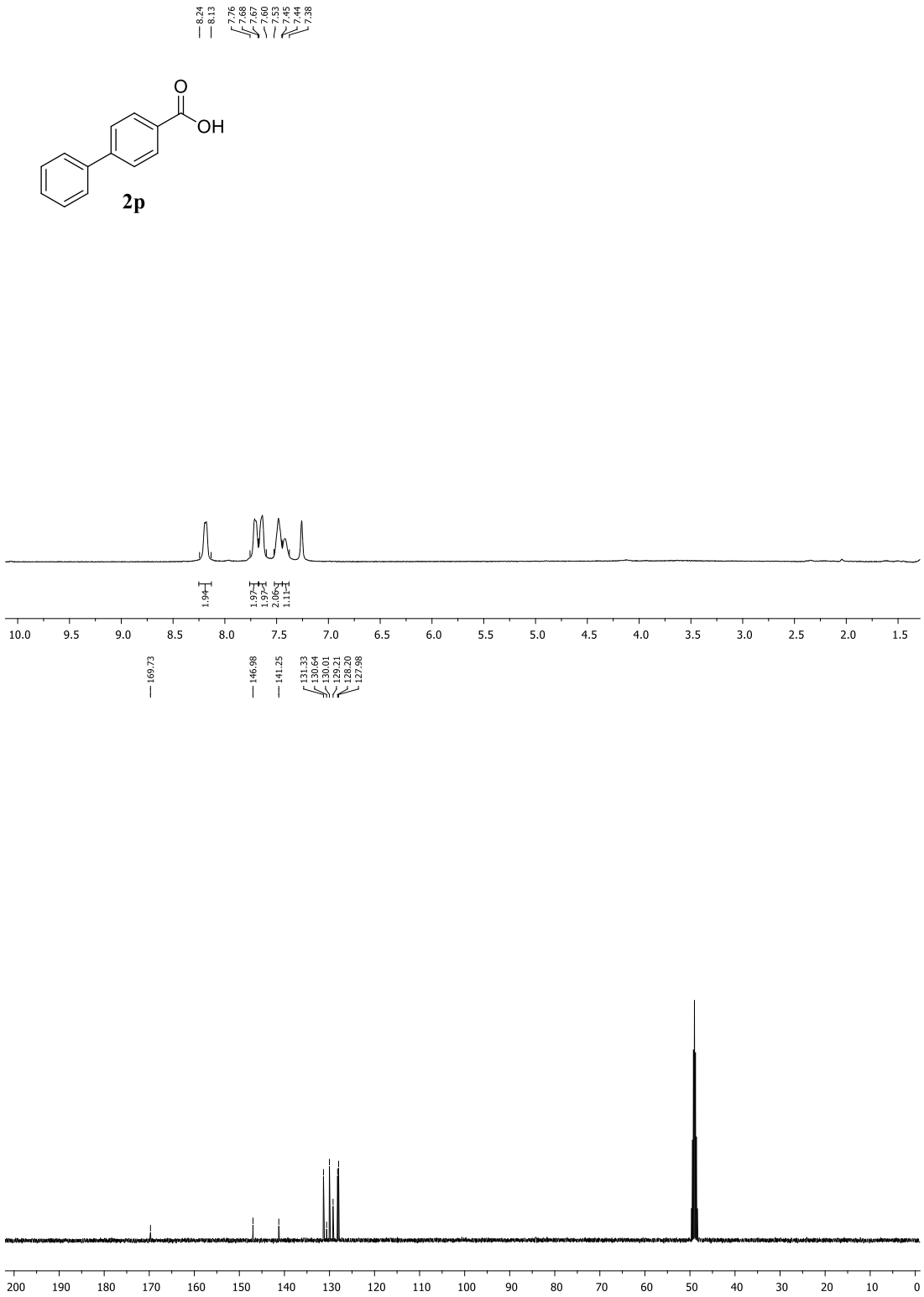

8.08
8.06
6.96
6.94
3.88
O
OH
O
2m
2.00
2.04
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
171.69
164.23
132.52
121.80
113.92
55.64
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

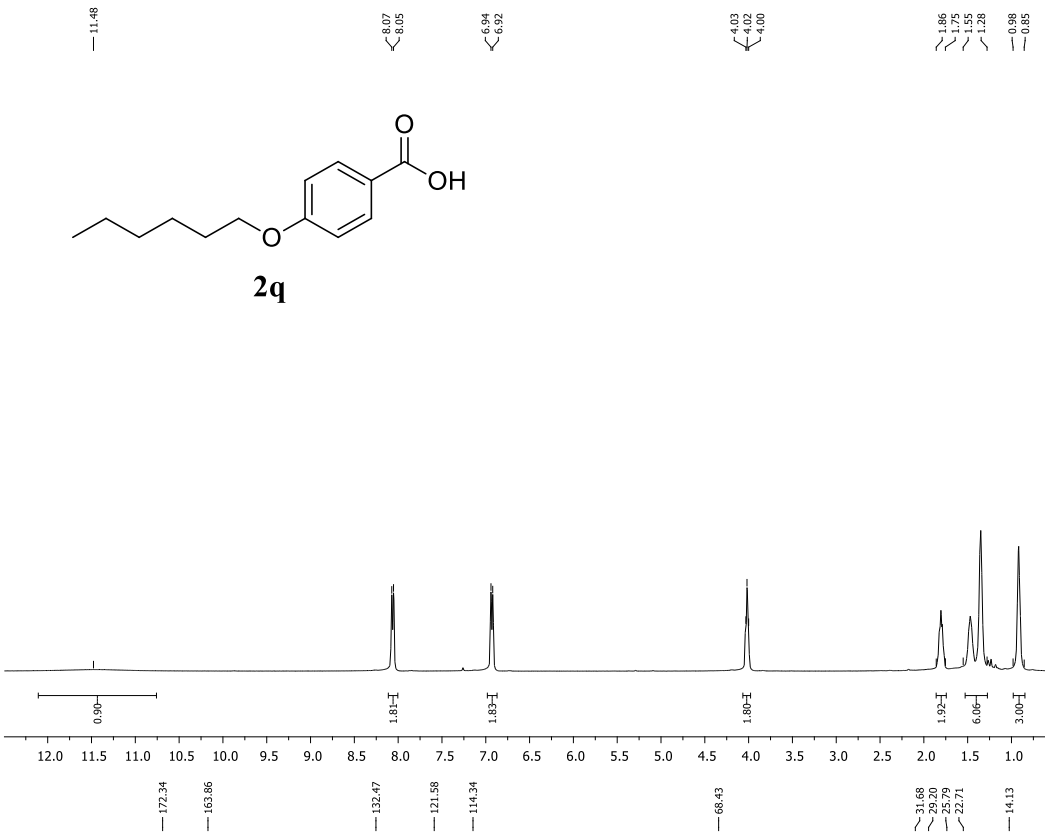

12.80
7.84
7.82
7.30
7.28
2.36
O
OH
0.93
2.12
2.16
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
167.76
143.47
129.79
129.57
128.51
21.57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

**2n**

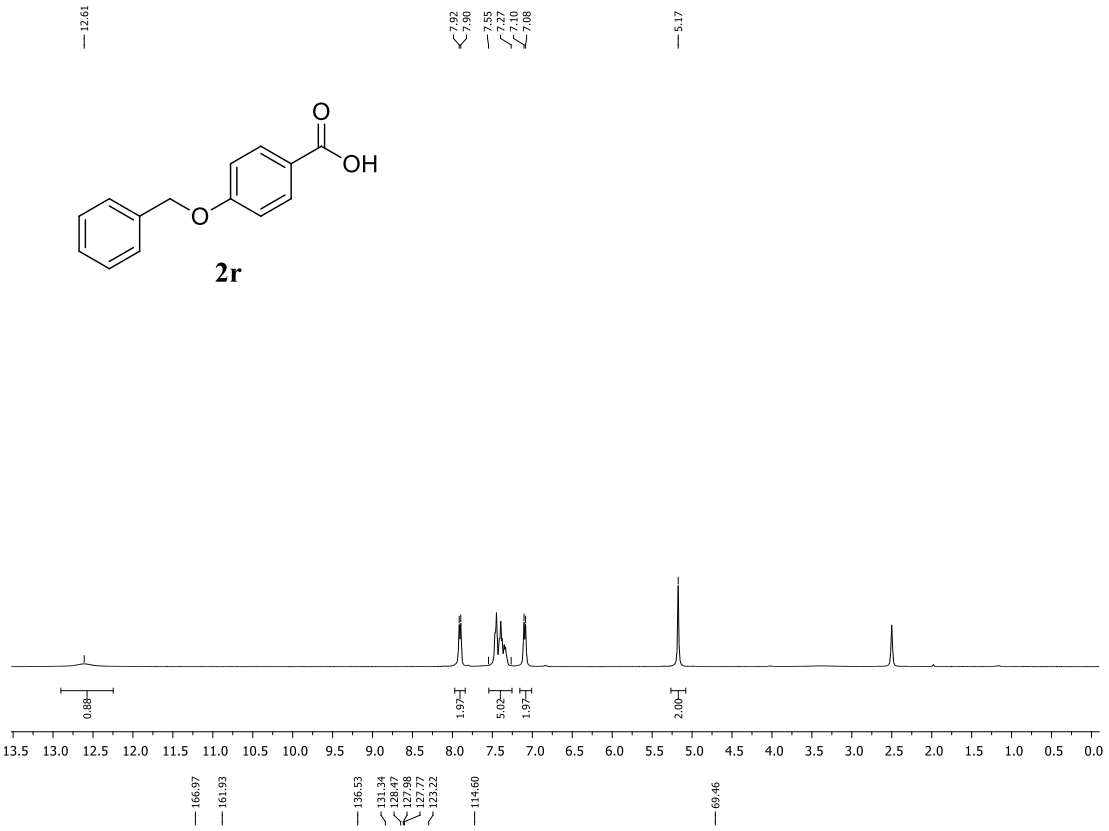

13.16
7.87
7.85
7.71
7.69
O
OH
Br
1.00
2.00
2.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
166.58
131.67
131.26
130.00
126.85
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

**2o**

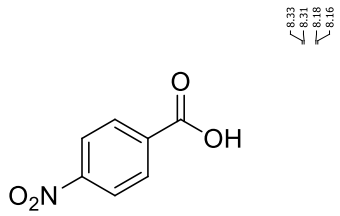

8.24
8.13
7.76
7.68
7.67
7.60
7.53
7.45
7.44
7.38
O
OH
2p
1.94
1.97
1.97
2.06
1.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
169.73
146.98
141.25
131.33
130.64
130.01
129.21
128.20
127.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


11.48
8.07
8.05
6.94
6.92
4.03
4.02
4.00
1.86
1.75
1.55
1.28
0.98
0.85
O
OH
O
0.90
1.81
1.83
1.80
1.92
6.06
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
172.34
163.86
132.47
121.58
114.34
68.43
31.68
29.20
25.79
22.71
14.13
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

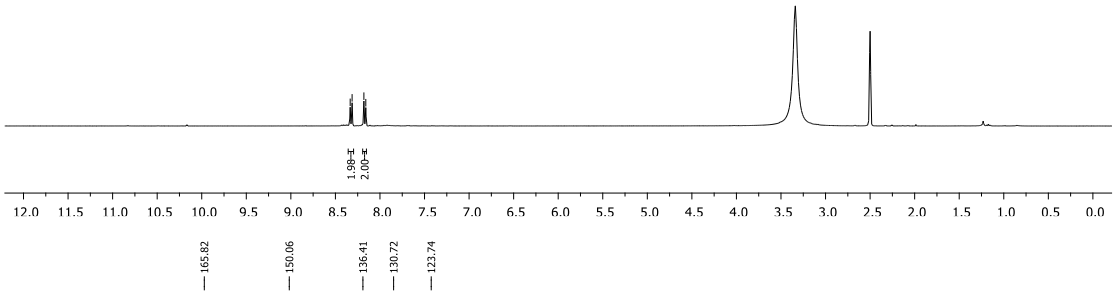
**2q**


12.61
7.92
7.90
7.55
7.27
7.10
7.08
5.17
O
OH
O
0.88
1.97
5.02
1.97
2.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
166.97
161.93
136.53
131.34
128.47
127.98
127.77
123.22
114.60
69.46
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

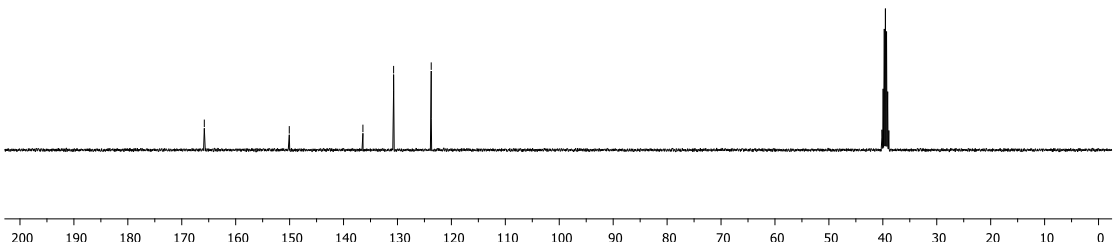
**2r**

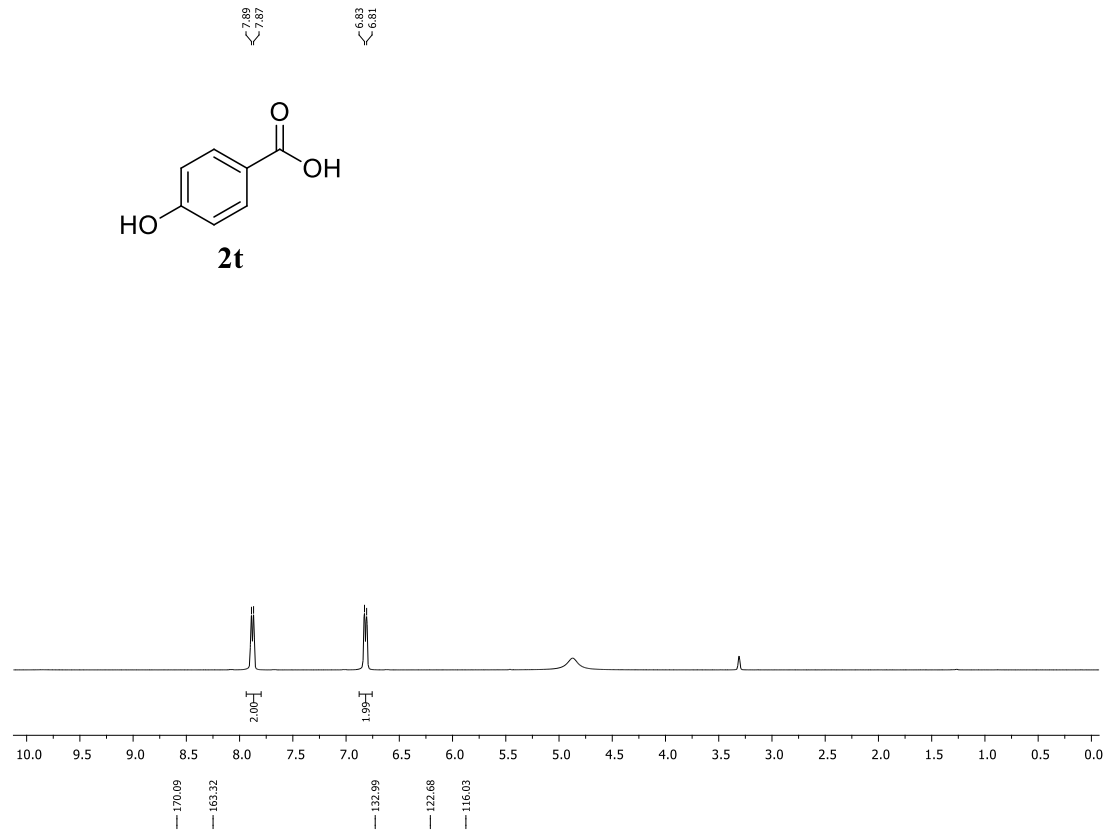

8.33
8.31
8.18
8.16
O
OH
O2N

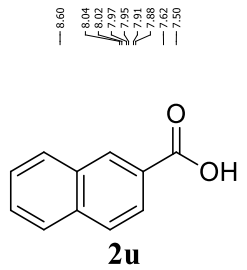
**2s**


1.98
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


165.82
150.06
136.41
130.72
123.74


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.89
7.87
6.83
6.81
O
OH
HO
2t
2.00
1.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
170.09
163.32
132.99
122.68
116.03
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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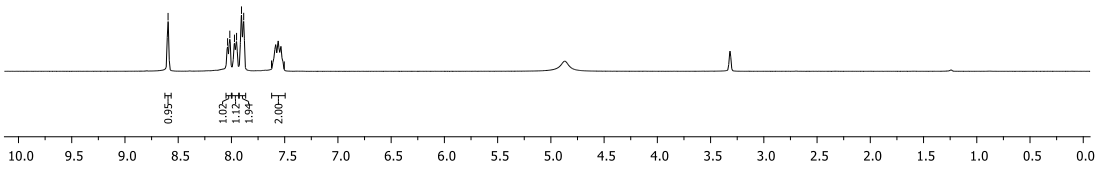
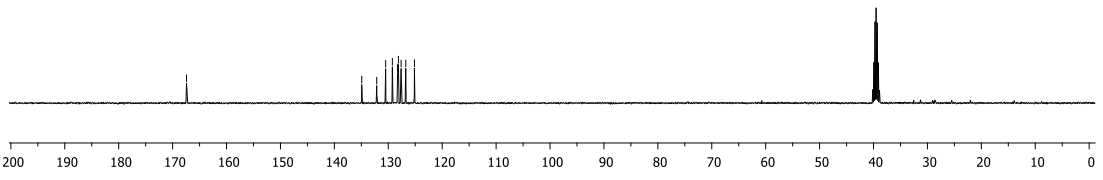
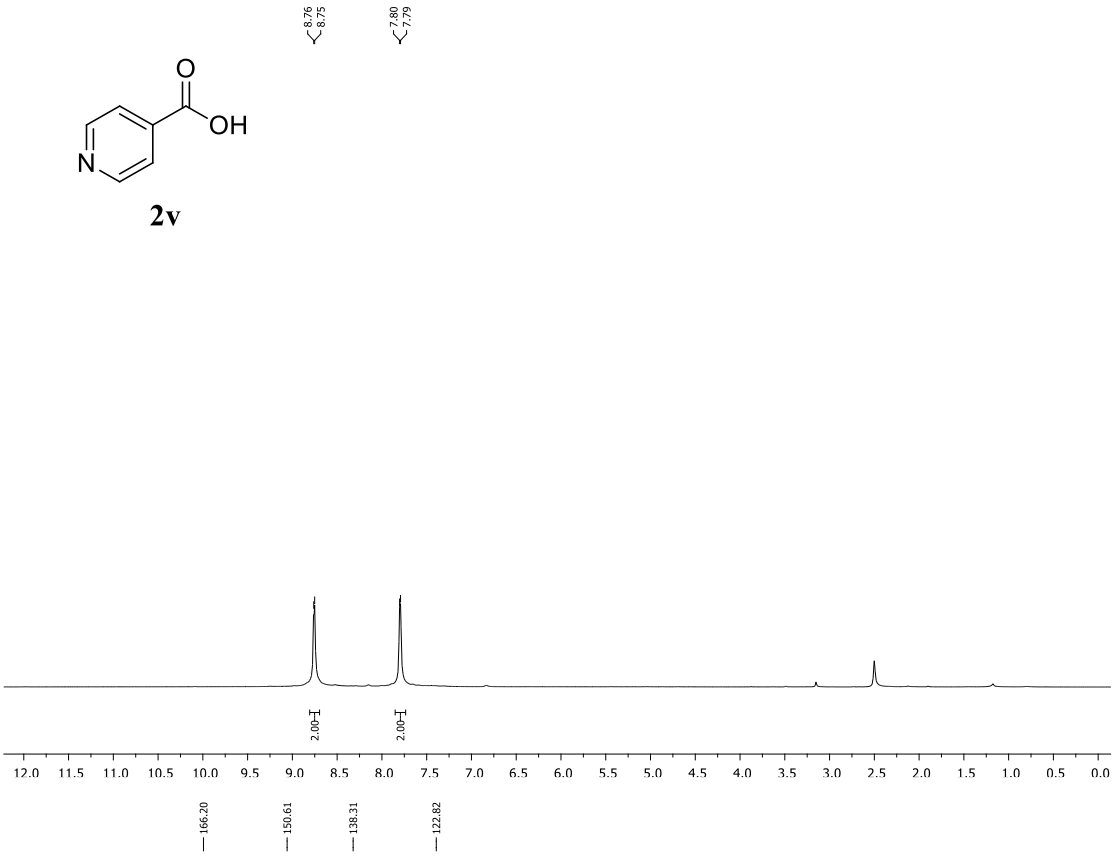
8.04
8.02
7.97
7.95
7.91
7.88
7.62
7.50
O
OH

**2u**

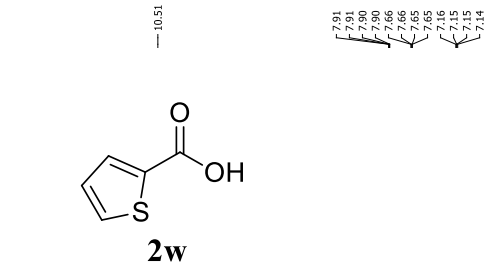

0.95
1.02
1.12
1.94
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


167.42
134.92
132.14
130.49
129.24
128.27
128.12
127.62
126.76
125.15

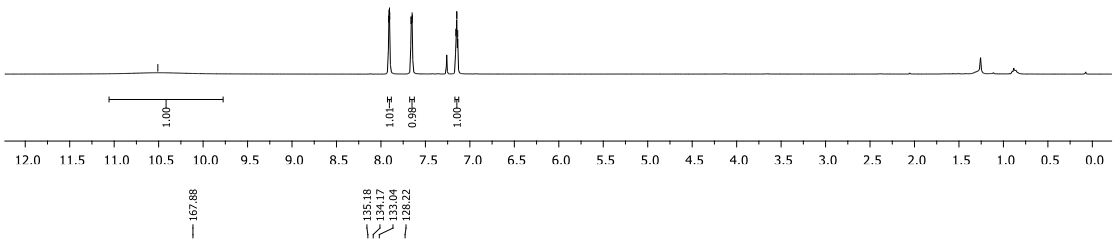

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.76
8.75
7.80
7.79
O
OH
N
2.00
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
166.20
150.61
138.31
122.82
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

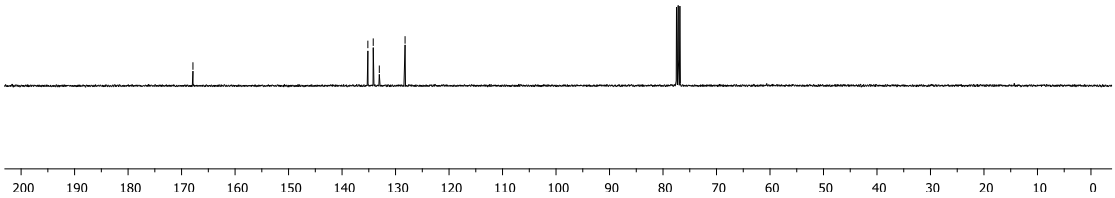
**2v**

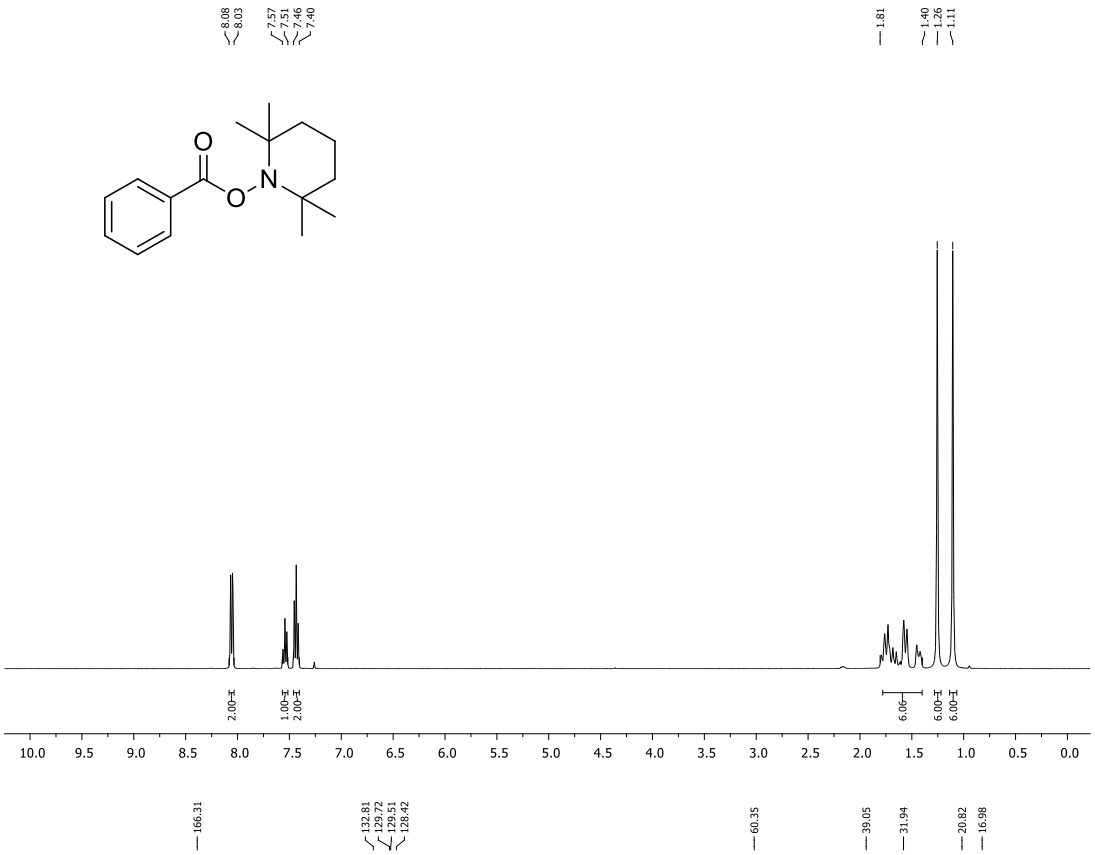

10.51
7.91
7.91
7.90
7.90
7.66
7.66
7.65
7.65
7.16
7.15
7.15
7.14
O
OH
S

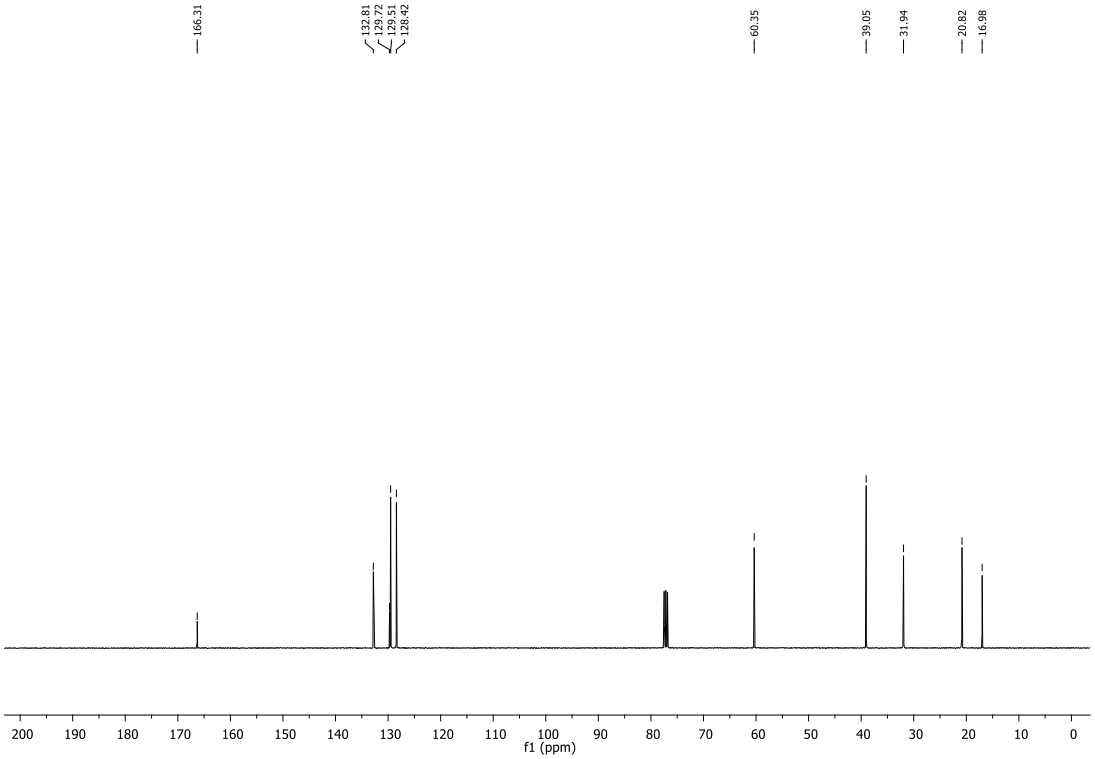
**2w**


1.00
1.01
0.98
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


167.88
135.18
134.17
133.04
128.22


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8.08
8.03
7.57
7.51
7.46
7.40
1.81
1.40
1.26
1.11
O
O
N
2.00
1.00
2.00
6.06
6.00
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


166.31
132.81
129.72
129.51
128.42
60.35
39.05
31.94
20.82
16.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)