Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

Continuous Flow Telescopic Oxidation of Alcohols via Generation of Chlorine and Hypochlorite

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S1: Continuous synthesis of Sodium hypochlorite: The commercially available bleach requires storage temperature of 2 to 8 ^{0}C, and its strength decrease over the time as it slowly evolves Cl_2 gas. NaOCl decomposes to NaCl and $NaClO_3$ because of its highly unstable nature. So each time before using it, one has to check the strength of this commercially available hypochlorite, which changes over the time and results will be non-reproducible. To overcome this reapeatative titration at each stage and for reproducibility of results, insitu generated hypochlorite is the best alternative. For a fixed flow rate of chlorine, the flow rate of NaOH and its concentration in water was varied to obtain hypochlorite of various strengths. Homogeneous oxidations needed low strength hypochlorite however for bi-phasic oxidation reactions solution of relatively higher strength was needed to reduce the diffusion limitations. Initially NaOH of different concentrations (5 – 20%) was used, of which 10% solution resulted in gives maximum strength of NaOCl for a fixed residence time. It required pH of 13 for the stability.

Table 1: Effect of NaOH % on pH and strength of hypochlorite at 2 ^{0}C at a fixed residence time

NaOH %	pH	strength %
5	5.11	5.83
10	13.04	7.20
15	13.05	2.06
20	13.47	0.75

In another set of experiments, in order to maintain identical flow regime during these experiments, flow rates of chlorine and NaOH solution were maintained constant while the residence time was varied by changing reactor volume.

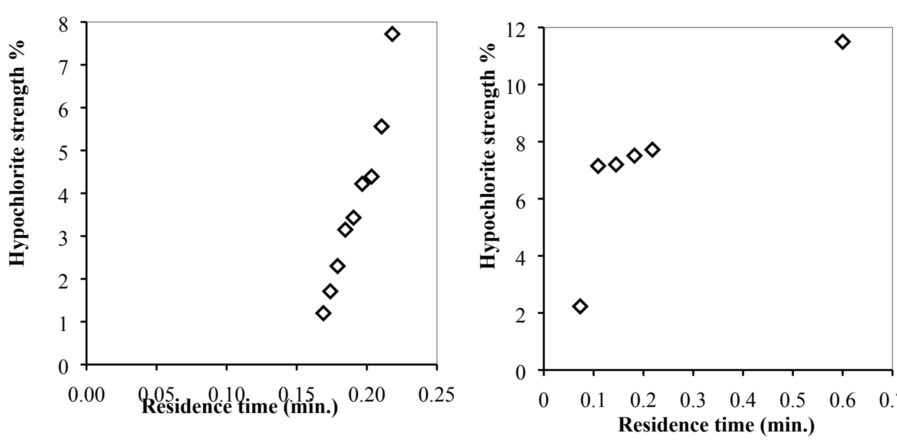


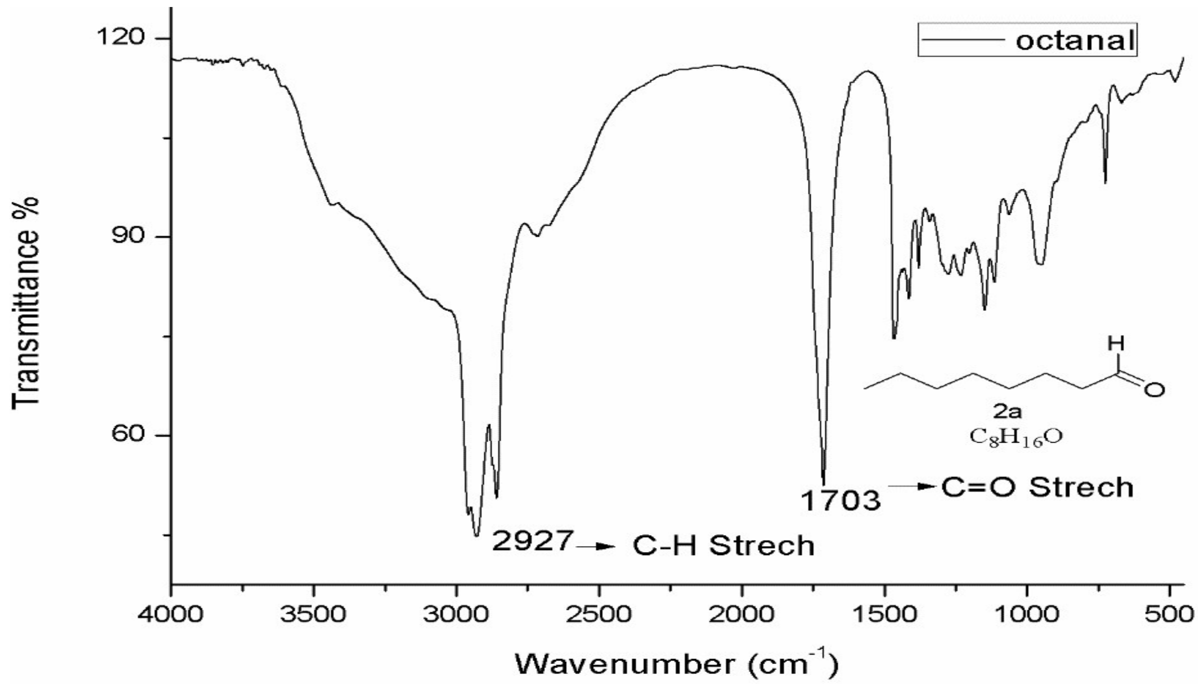
Figure 1: Effect of residence time on hypochlorite strength: (A) For a fixed reactor volume (12 mL) NaOH flow rate was varied in range of 4 to 20 mL/min, (B) Reactor volume was changed from 4 ml to 38 mL at a constant flow rate of NaOH 4mL/min. (flow rate of Cl_2 was 51 mL/min, ice cold condition for both cases),

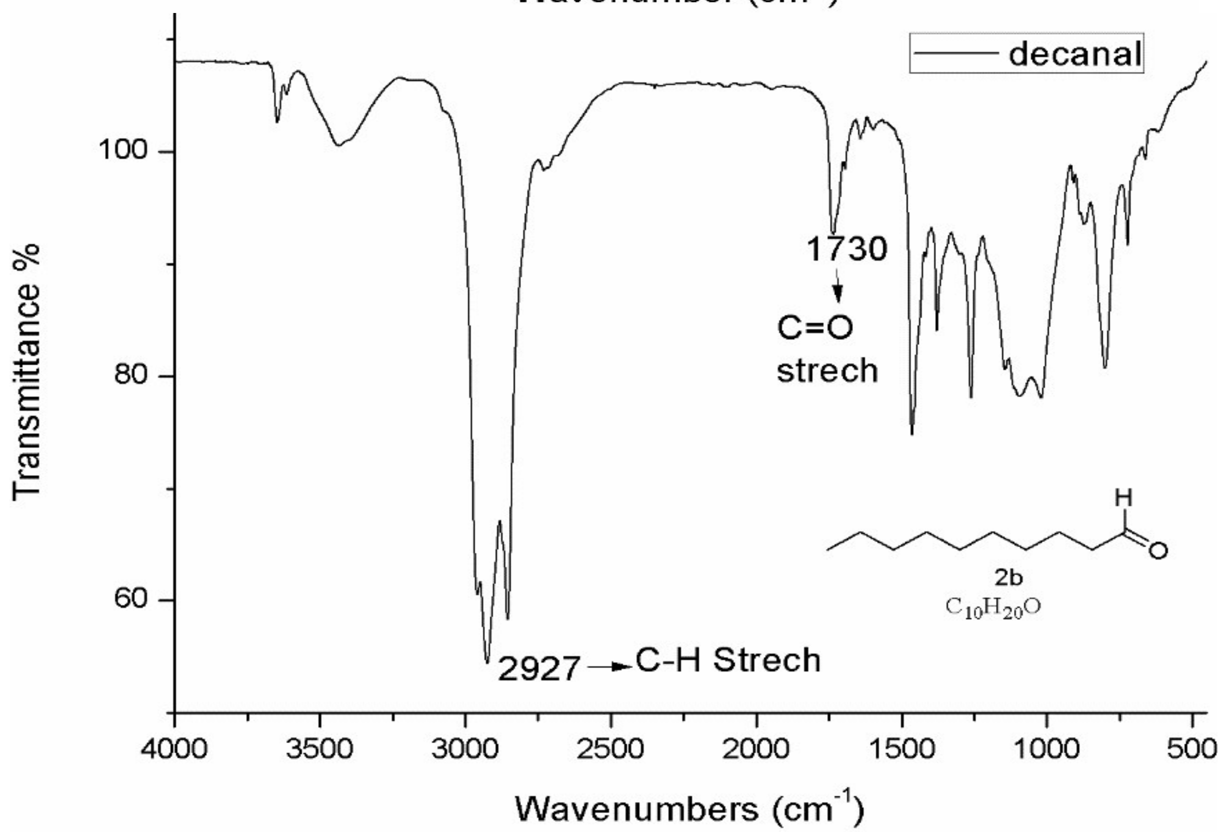
Longer residence time was seen to result in higher strength hypochlorite as it helped reduce the extent in rise in local temperature due to this exothermic reaction. A 4 ml reactor resulted in only 2% strength solution of hypochlorite in 5 s while in a 38 ml reactor that the solution strength is 11.52% with a residence time of 36 s. Thus longer residence time can help to achieve high strength hypochlorite. However the stability of the solution also depends on pH. It was observed that while one can use higher strengths of NaOH solutions for this reaction depending upon pH the strength of solution may decrease rapidly. In our experiments we had observed that for TEMPO mediated oxidation of alcohols pH of the solution should be in range of 9 to 9.8. For acidic pH, over-oxidation happens and acid forms as major product while at higher pH no reaction takes place. For pH adjustment, saturated sodium-bicarbonate solution was used which decreases hypochlorite

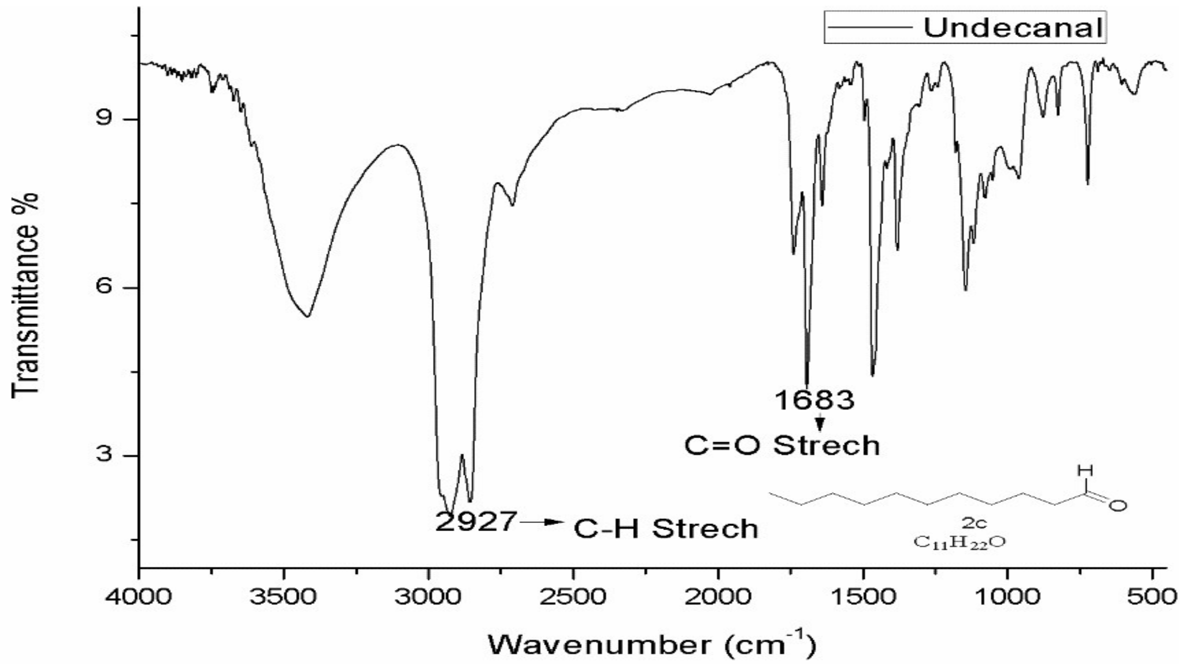
S2: IR spectra, NMR and GCMS spectra for various substrates and products are reported here.

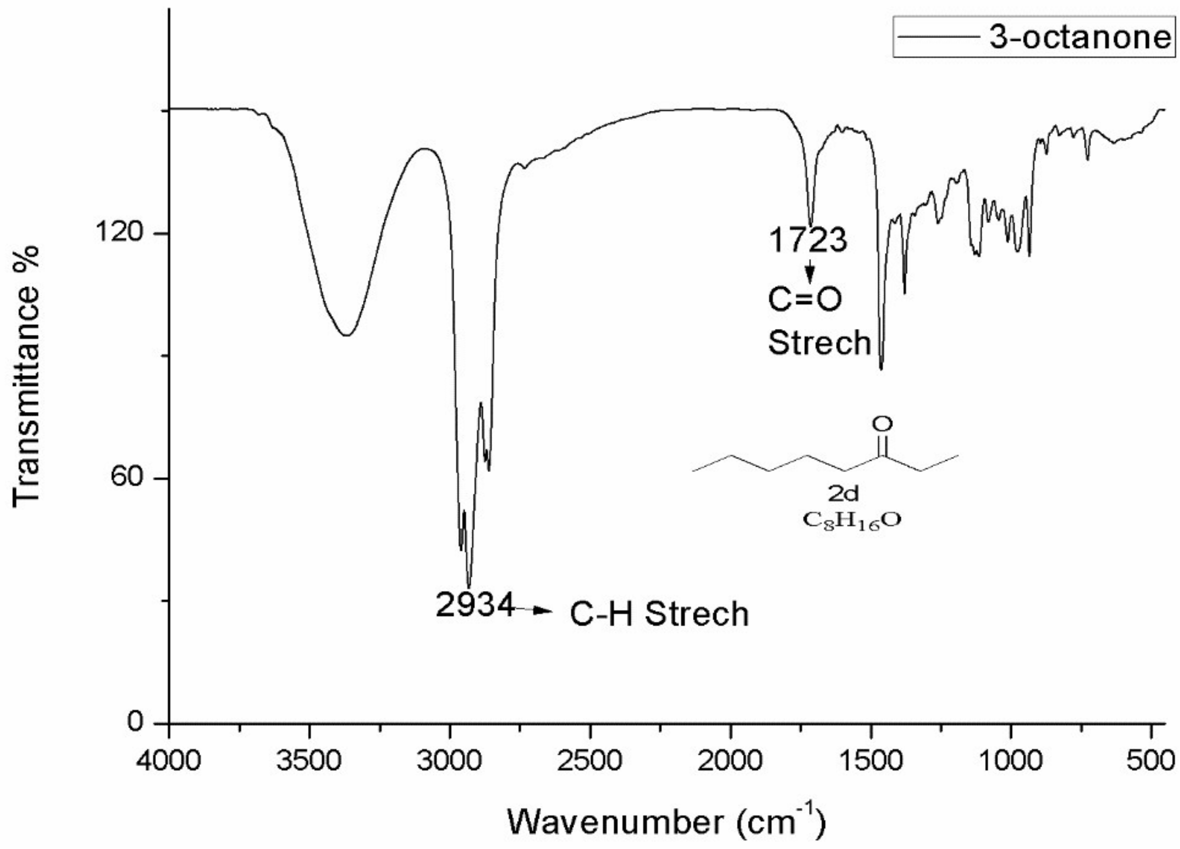
1) Octanal (2a)
2) Decanal (2b)
3) Undecanal (2c)
4) 3-octanone (2d)
5) P-methoxy benzeldehyde (2e)
6) Citral (geranial 2f and neral 2f')
7) Benzeldehyde (2g)
8) 2-bromobenzeldehyde (2h)

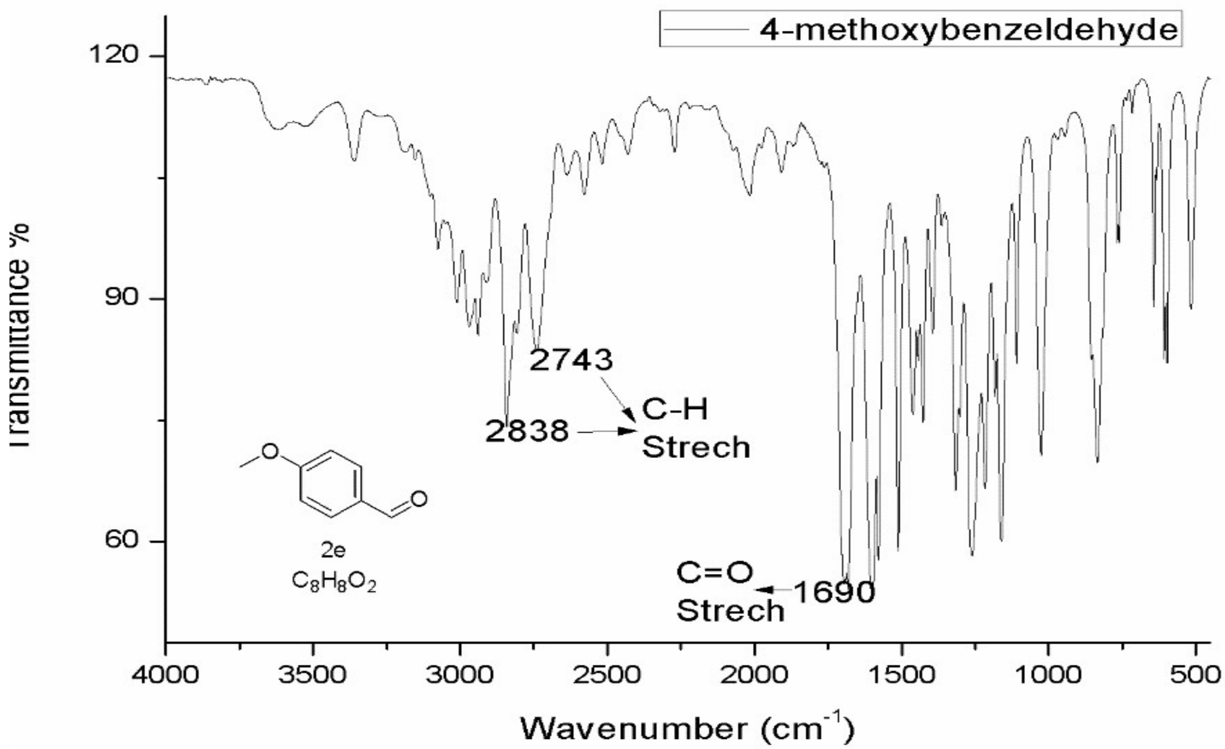
IR spectra

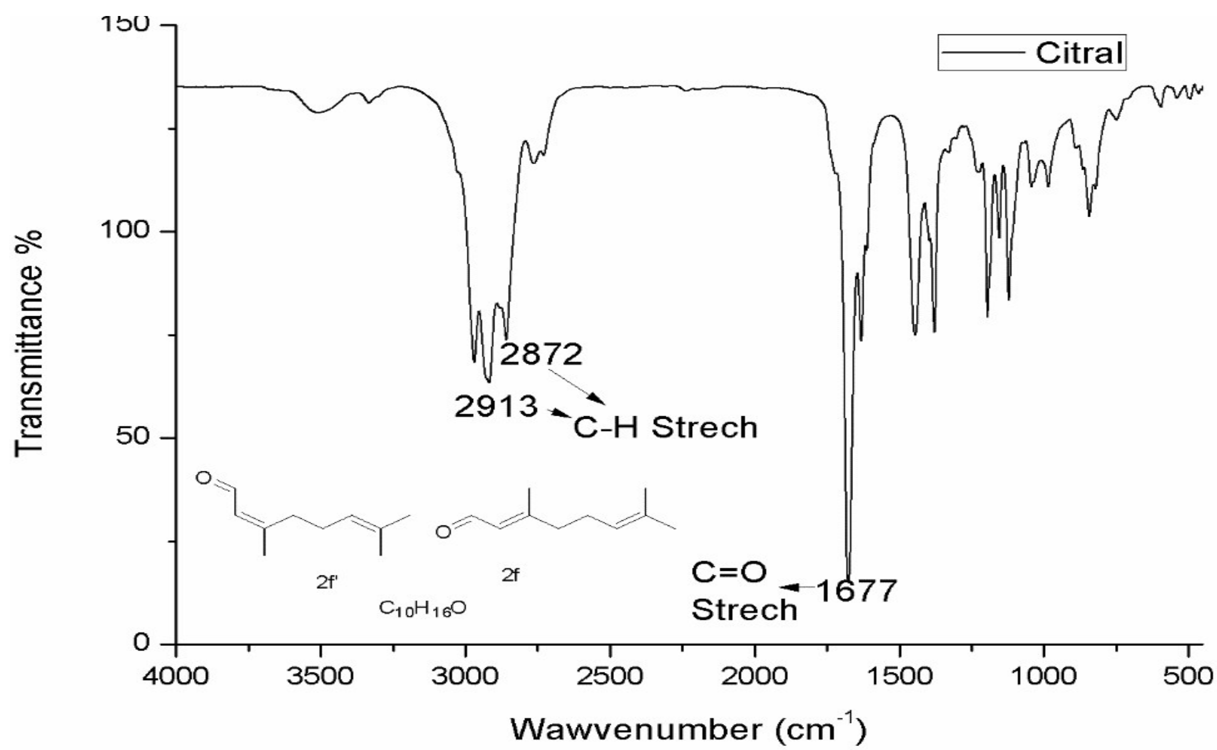

octanal
Transmittance %
120
90
60
2927 → C-H Strech
1703 → C=O Strech
2a
$C_8H_{16}O$
H
O
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm^{-1})


decanal
Transmittance %
100
80
60
1730
C=O
strech
2927 → C-H Strech
2b
$C_{10}H_{20}O$
H
O
4000 3500 3000 2500 2000 1500 1000 500
Wavenumbers (cm^{-1})

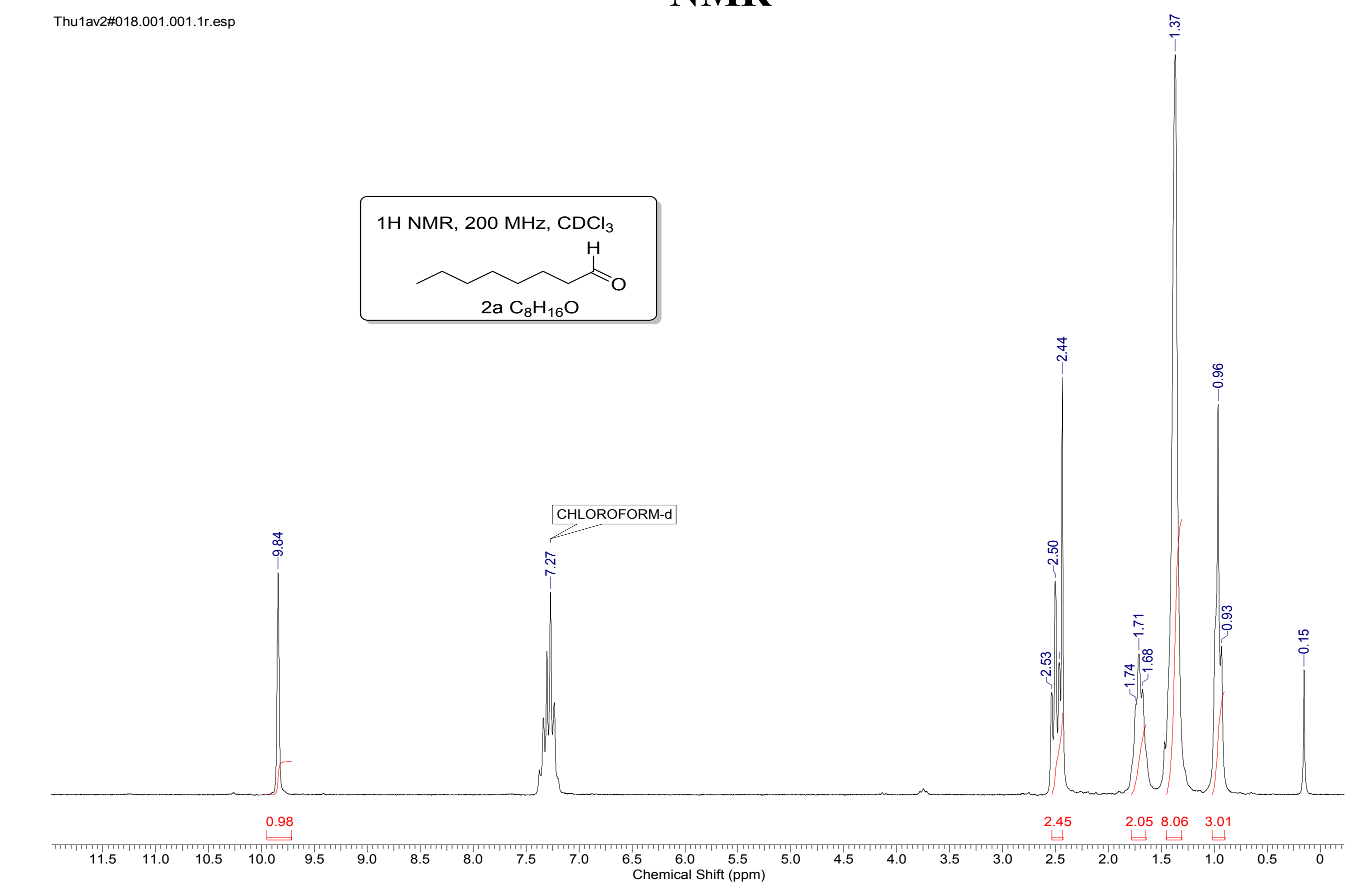

Undecanal
Transmittance %
9
6
3
1683
C=O Strech
2927
C-H Strech
2c
$C_{11}H_{22}O$
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

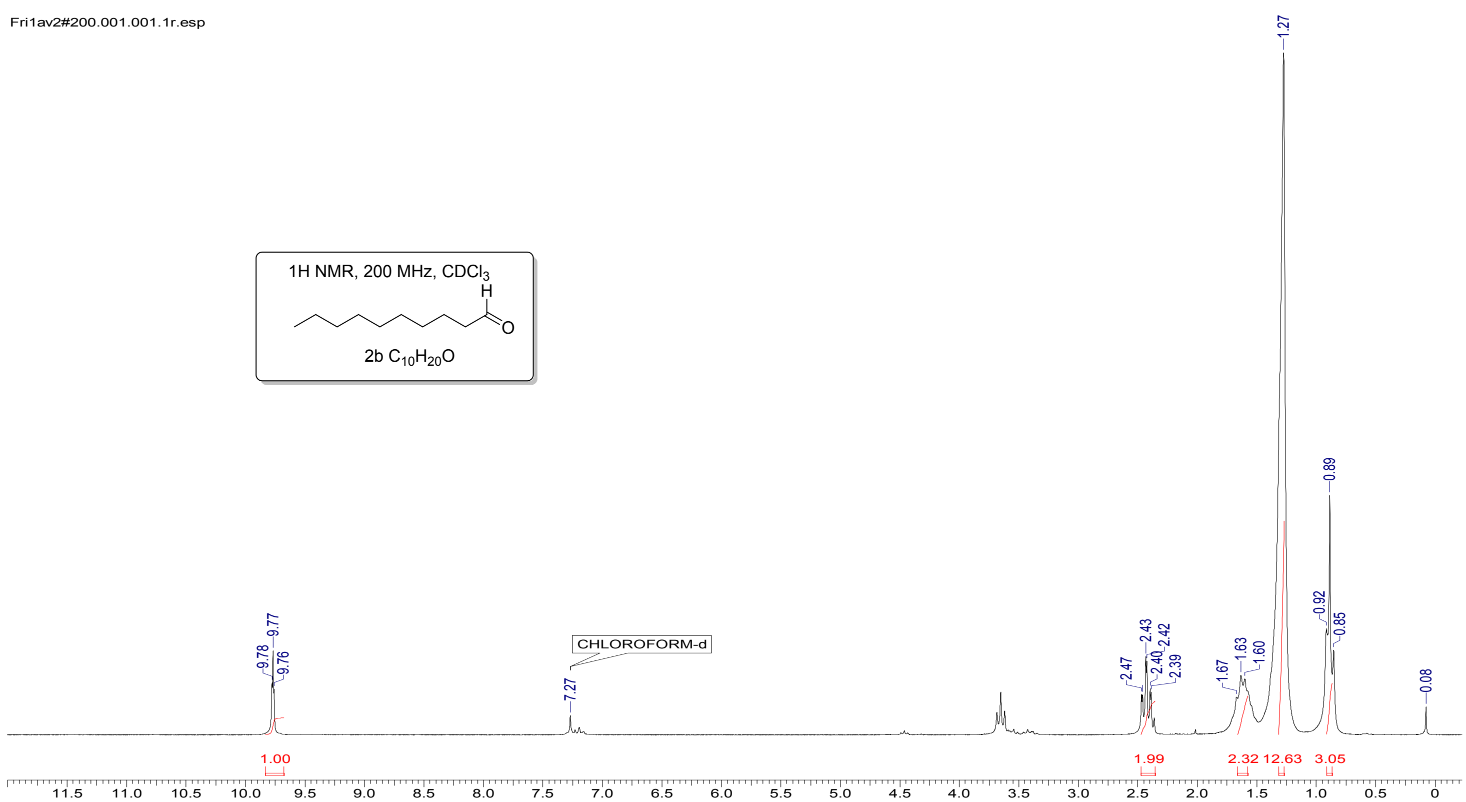

3-octanone
Transmittance %
120
60
0
1723
C=O
Strech
2d
$C_8H_{16}O$
2934
C-H Strech
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})


4-methoxybenzeldehyde
Transmittance %
120
90
60
2743
2838
C-H
Strech
2e
$C_8H_8O_2$
C=O
Strech
1690
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

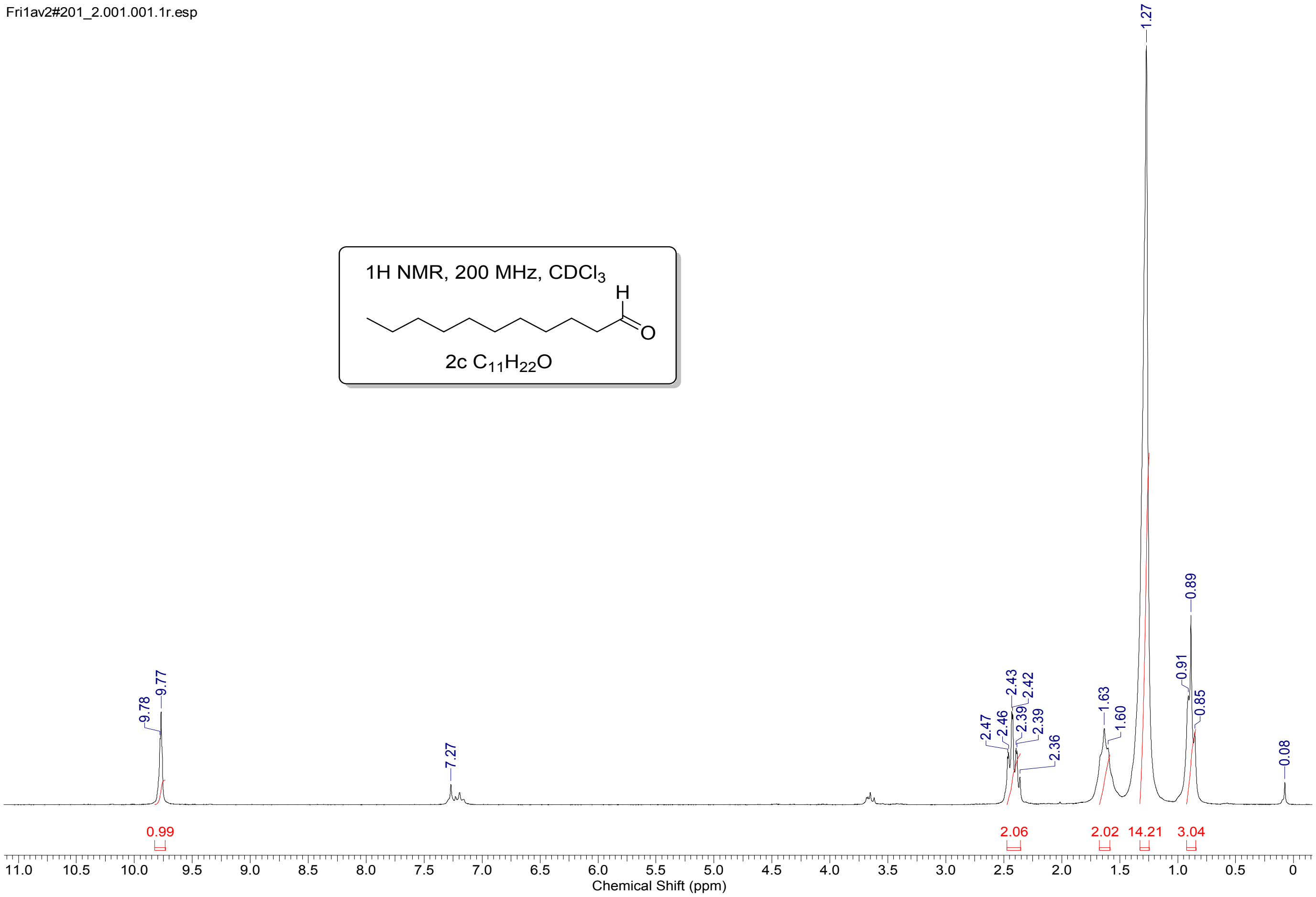

Citral
Transmittance %
150
100
50
0
2872
2913
C-H Strech
2f'
2f
$C_{10}H_{16}O$
C=O
Strech
1677
4000
3500
3000
2500
2000
1500
1000
500
Wawvenumber (cm^{-1})

NMR

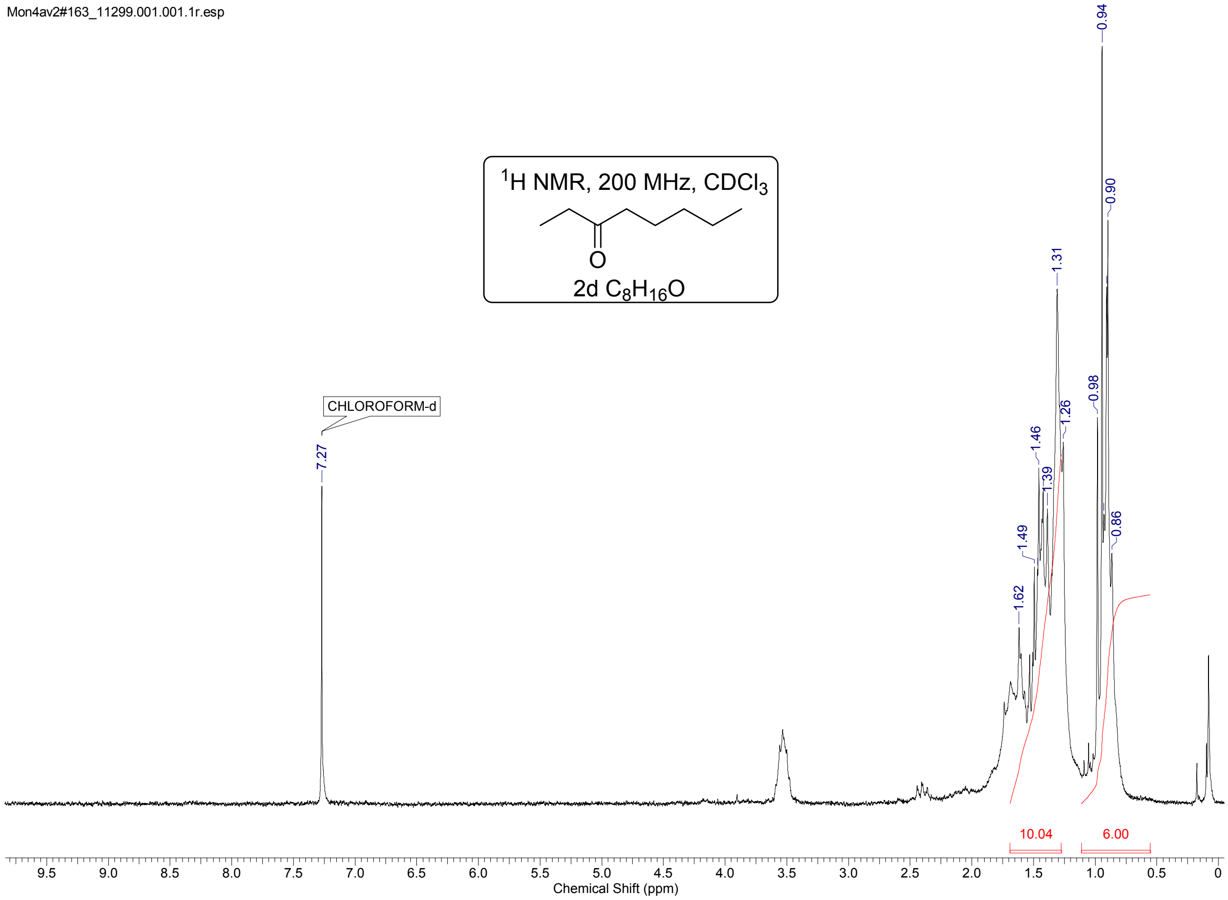

Thu1av2#018.001.001.1r.esp
1H NMR, 200 MHz, $CDCl_3$
H
O
2a $C_8H_{16}O$
CHLOROFORM-d
9.84
7.27
2.53
2.50
2.44
1.74
1.71
1.68
1.37
0.96
0.93
0.15
0.98
2.45
2.05
8.06
3.01
Chemical Shift (ppm)


Fri1av2#200.001.001.1r.esp
1H NMR, 200 MHz, $CDCl_3$
H
O
2b $C_{10}H_{20}O$
CHLOROFORM-d
9.78
9.77
9.76
7.27
2.47
2.43
2.42
2.40
2.39
1.67
1.63
1.60
1.27
0.92
0.89
0.85
0.08
1.00
1.99
2.32
12.63
3.05
Chemical Shift (ppm)

Fri1av2#201_2.001.001.1r.esp



Mon4av2#163_11299.001.001.1r.esp



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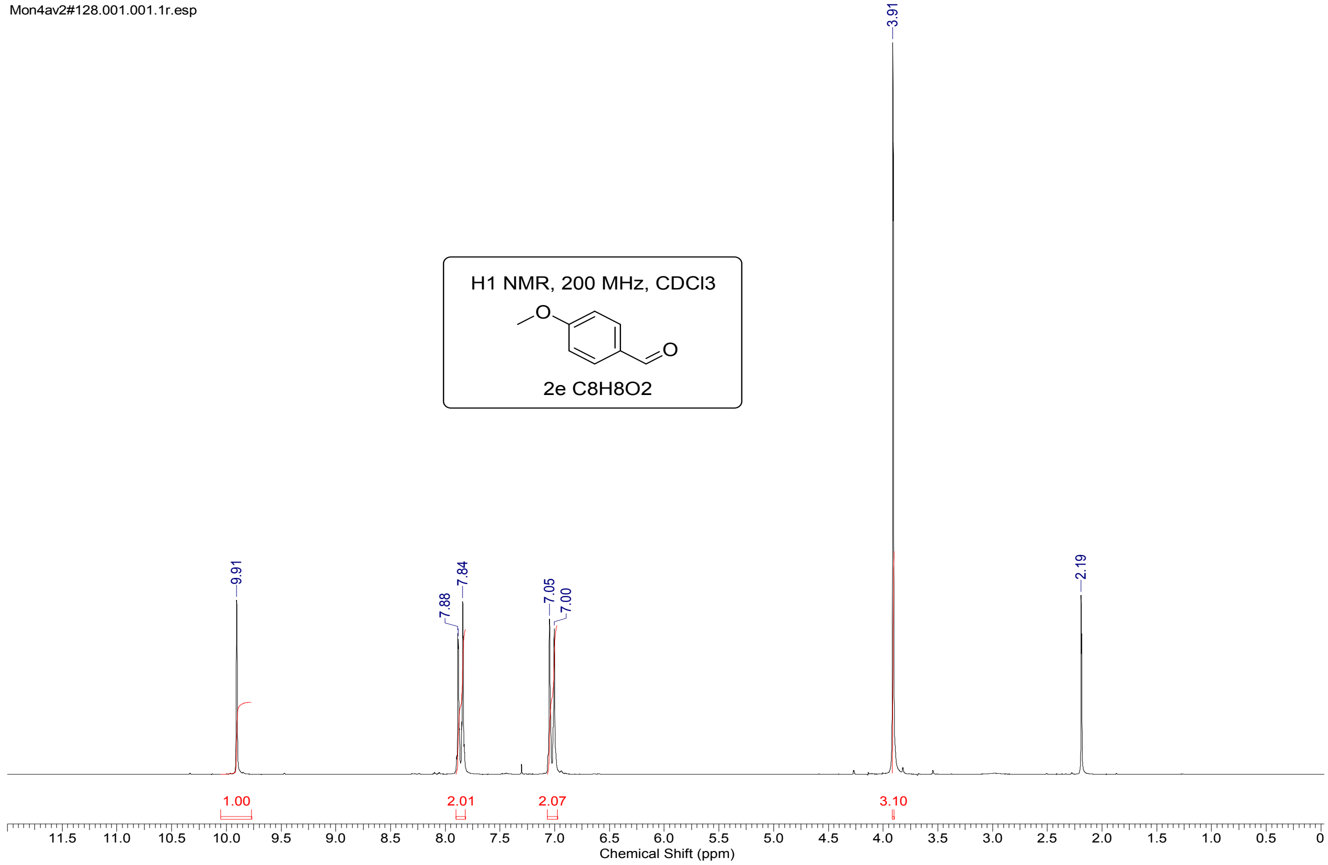
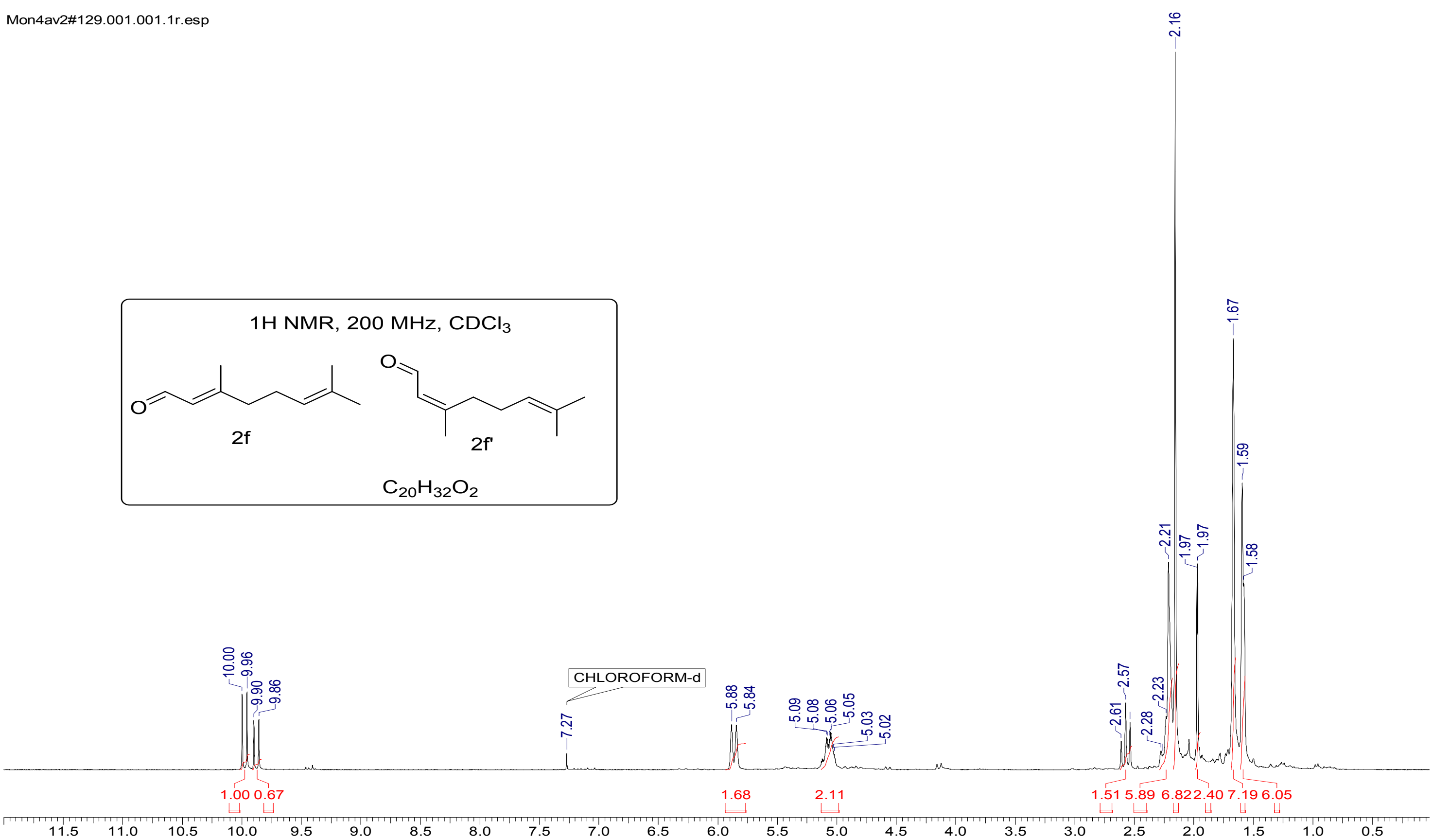
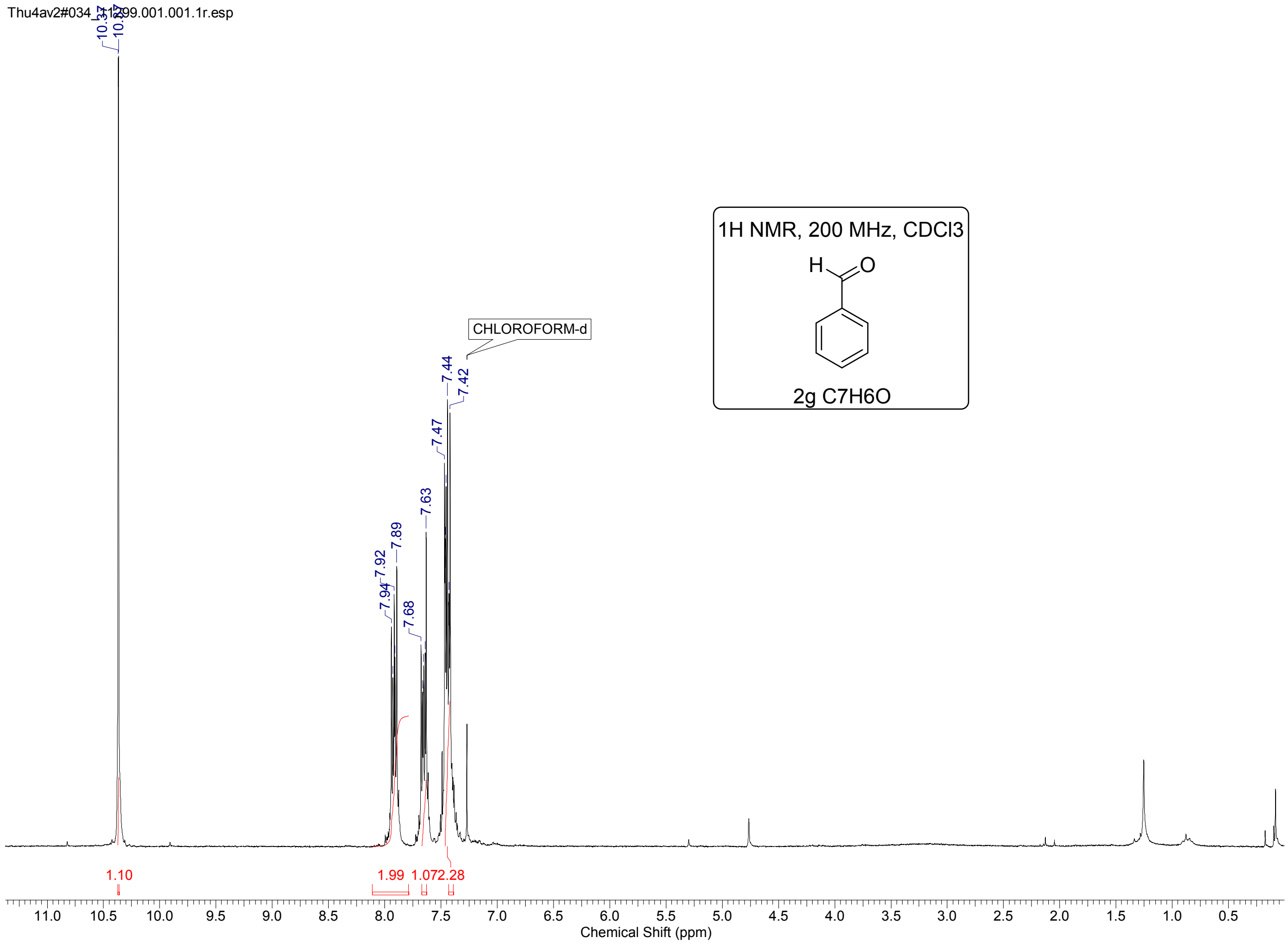
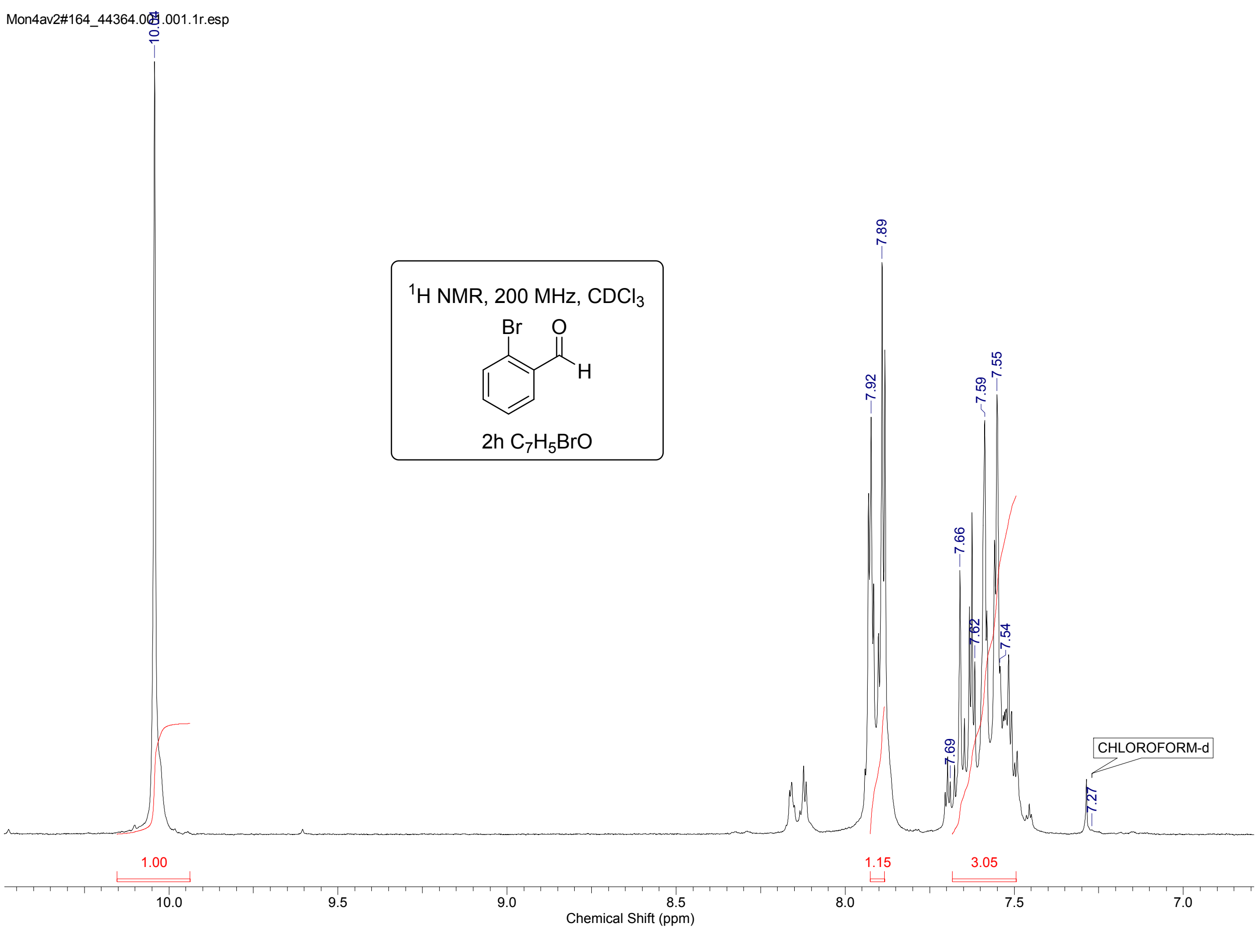


Mon4av2#129.001.001.1r.esp





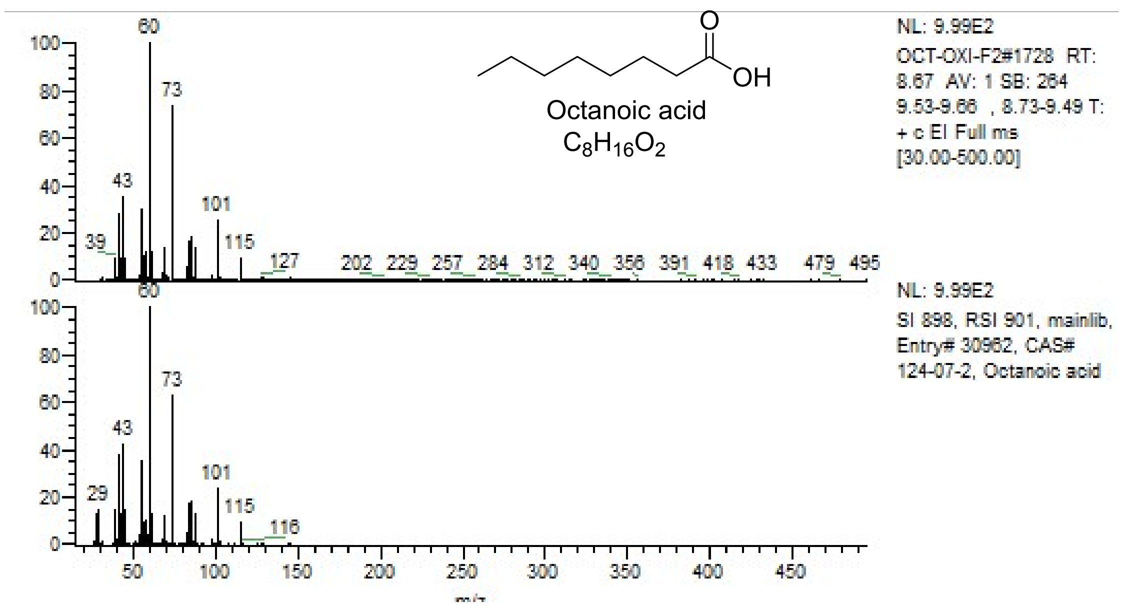
Thu4av2#034_11299.001.001.1r.esp
1H NMR, 200 MHz, CDCl3
2g C7H6O
CHLOROFORM-d
7.94
7.92
7.89
7.68
7.63
7.47
7.44
7.42
1.10
1.99
1.07
2.28
Chemical Shift (ppm)

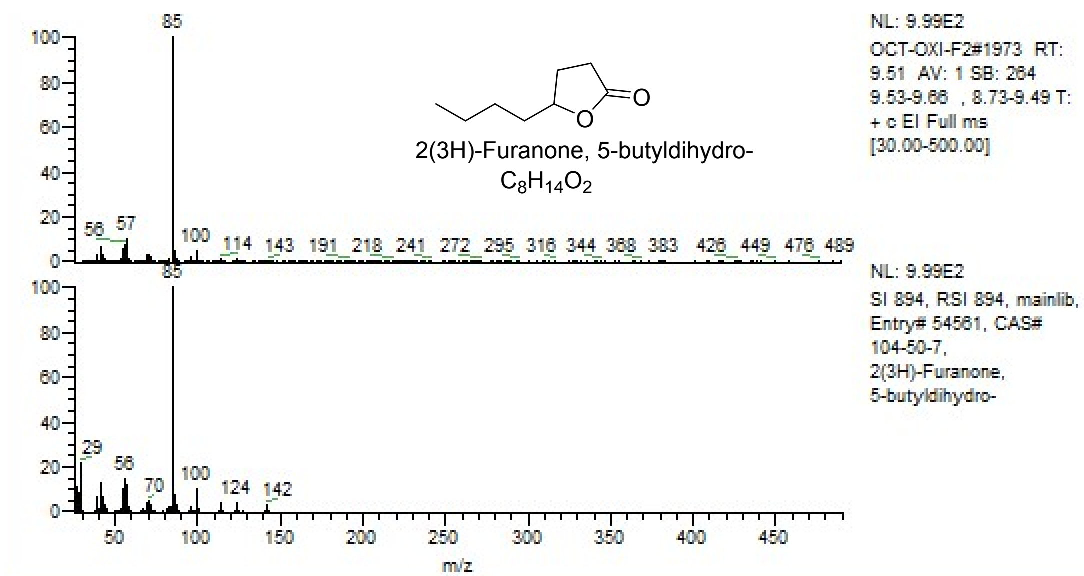


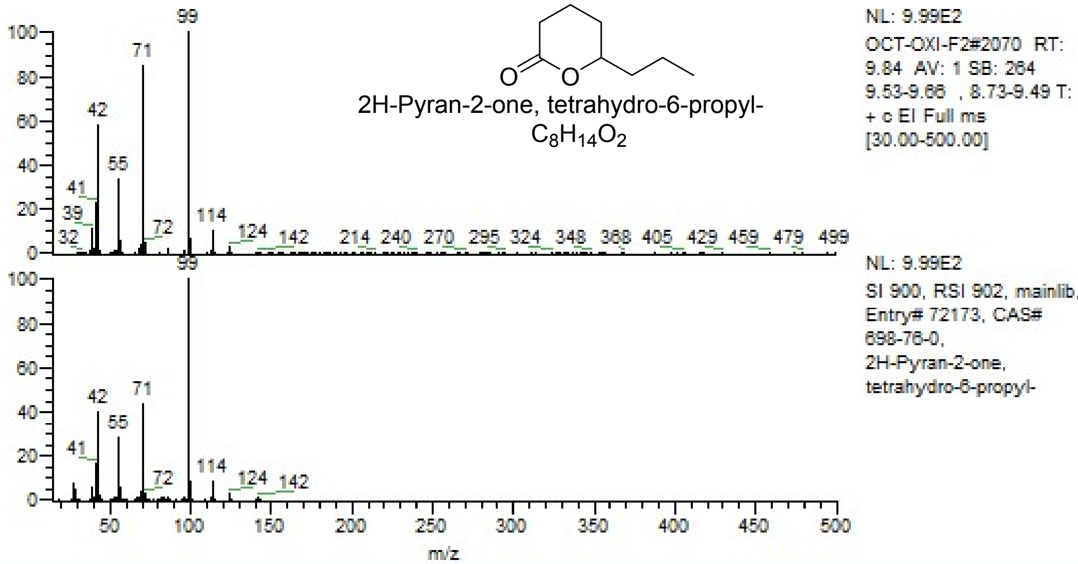
Mon4av2#164_44364.001.001.1r.esp
1H NMR, 200 MHz, CDCl3
Br
O
H
2h C7H5BrO
CHLOROFORM-d
7.92
7.89
7.69
7.66
7.62
7.59
7.55
7.54
7.27
1.00
1.15
3.05
Chemical Shift (ppm)

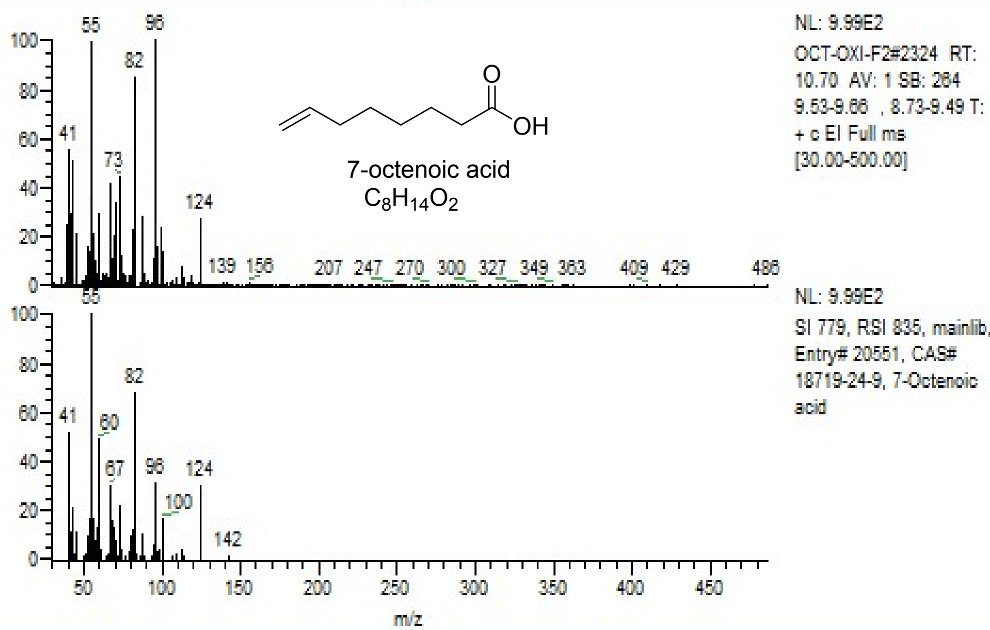
GCMS of Impurity:

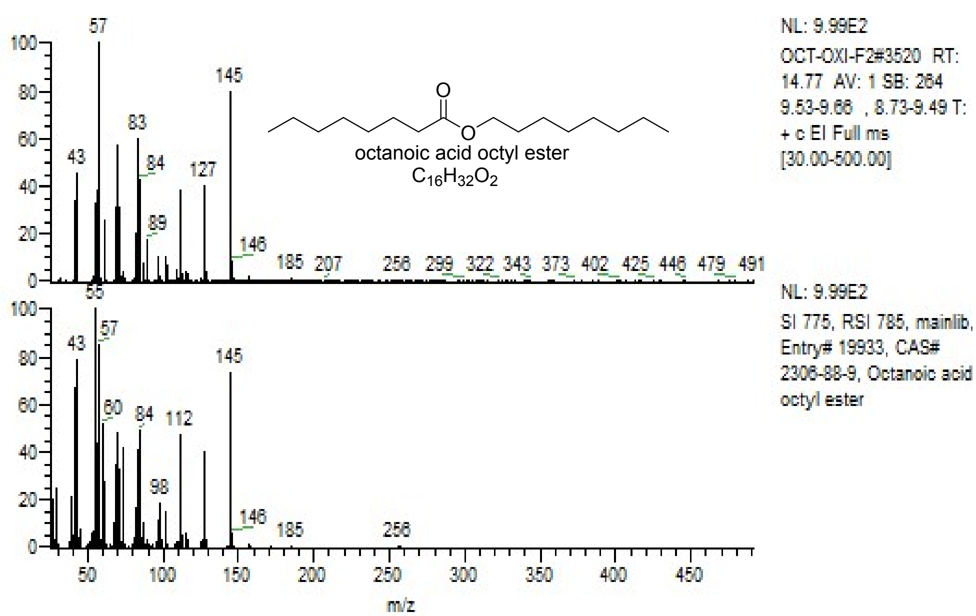
Impurity formed during octanol oxidation






2H-Pyran-2-one, tetrahydro-6-propyl-
$C_8H_{14}O_2$
NL: 9.99E2
OCT-OXI-F2#2070 RT: 9.84 AV: 1 SB: 264 9.53-9.66 , 8.73-9.49 T: + c EI Full ms [30.00-500.00]
NL: 9.99E2
SI 900, RSI 902, mainlib, Entry# 72173, CAS# 698-76-0, 2H-Pyran-2-one, tetrahydro-6-propyl-
m/z


7-octenoic acid
$C_8H_{14}O_2$
NL: 9.99E2
OCT-OXI-F2#2324 RT: 10.70 AV: 1 SB: 264 9.53-9.66 , 8.73-9.49 T: + c EI Full ms [30.00-500.00]
NL: 9.99E2
SI 779, RSI 835, mainlib, Entry# 20551, CAS# 18719-24-9, 7-Octenoic acid
m/z


octanoic acid octyl ester
$C_{16}H_{32}O_2$
NL: 9.99E2
OCT-OXI-F2#3520 RT: 14.77 AV: 1 SB: 264 9.53-9.66 , 8.73-9.49 T: + c EI Full ms [30.00-500.00]
NL: 9.99E2
SI 775, RSI 785, mainlib, Entry# 19933, CAS# 2306-88-9, Octanoic acid octyl ester
m/z