Supporting information for

Factors affecting chlorinated product formation from sodium hypochlorite bleach and limonene reactions in the gas phase

Callee M. Walsh*, Notashia N. Baughman, Jason E. Ham, J.R. Wells

Health Effects Laboratory Division, NIOSH, Morgantown, WV 26505

* To whom correspondence should be addressed: qqf2@cdc.gov

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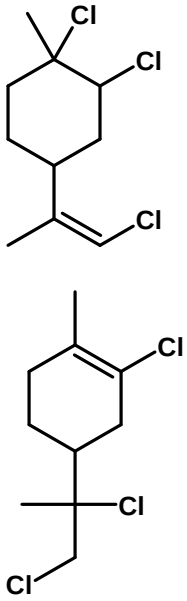
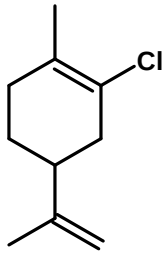
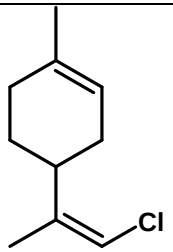
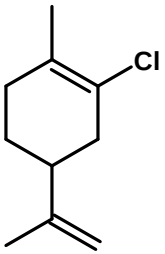
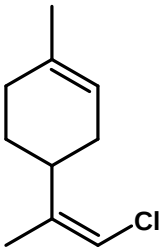
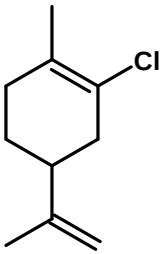
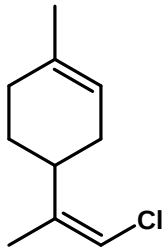
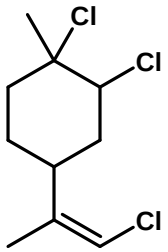
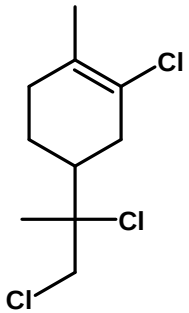
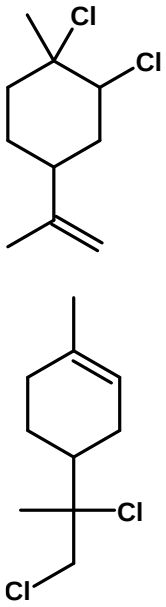
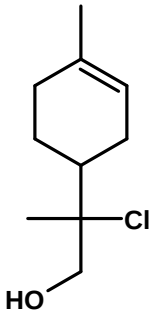
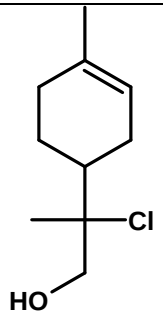
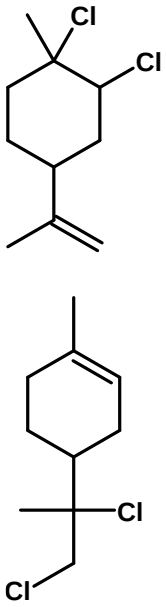
Table S1. Detailed description of chlorinated products detected in gas-phase reactions between limonene and $HOCl/Cl_2$

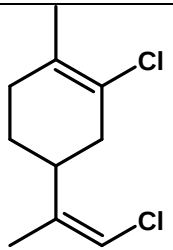
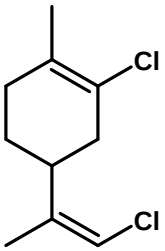
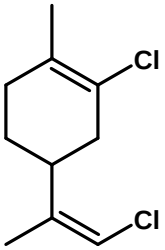
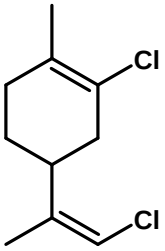
Structure ID	Structure	RT	Formula	Theoretical Monoisotopic (m/z)	Experimental Monoisotopic (m/z)	EI fragments observed (m/z)	Formula of fragments	ppb[1]	Yield (%)
4		**18.37**	**$C_{10}H_{15}Cl_3$**	**240.0234**	**240.0238**	**205.0547** **171.0749** **169.0779** **133.1013** **119.0856** **105.0700** **91.0543**	**$C_{10}H_{15}{}^{35}Cl_2$** **$C_{10}H_{14}{}^{37}Cl$** **$C_{10}H_{14}{}^{35}Cl$** **$C_{10}H_{13}$** **C_9H_{11}** **C_8H_9** **C_7H_7**		
1		**21.13**	**$C_{10}H_{15}Cl$**	**170.0857**	**170.0855**	**135.1167** **127.0308** **119.0855** **91.0542** **79.0542**	**$C_{10}H_{15}$** **$C_7H_8{}^{35}Cl$** **C_9H_{11}** **C_7H_7** **C_6H_7**		

									
1	 	**21.59**	**$C_{10}H_{15}Cl$**	**170.0857**	**170.0854**	**135.1167** **127.0308** **119.0855** **93.0699** **91.0542** **79.0542**	**$C_{10}H_{15}$** **$C_7H_8{}^{35}Cl$** **C_9H_{11}** **C_8H_9** **C_7H_7** **C_6H_7**	**46 ± 11**	**57 ± 8.7**
1		**21.80**	**$C_{10}H_{15}Cl$**	**170.0857**	**170.0856**	**135.1168** **134.1089** **119.0855** **105.0699** **93.0699** **91.0543** **77.0386**	**$C_{10}H_{15}$** **$C_{10}H_{14}$** **C_9H_{11}** **C_8H_9** **C_7H_9** **C_7H_7** **C_6H_5**		

							
4	 	**21.96**	**$C_{10}H_{15}Cl_3$**	**240.0234**	**240.0235**	**205.0547** **171.0748** **169.0778** **155.0622** **133.1012** **127.0309** **105.0700** **89.0153**	**$C_{10}H_{15}{}^{35}Cl_2$** **$C_{10}H_{14}{}^{37}Cl$** **$C_{10}H_{14}{}^{35}Cl$** **$C_9H_{12}{}^{35}Cl$** **$C_{10}H_{13}$** **$C_7H_8{}^{35}Cl$** **C_8H_9** **$C_4H_6{}^{35}Cl$**

2		**22.94**	**$C_{10}H_{16}Cl_2$**	**206.0624**	**206.0621**	**171.0932** **170.0855** **135.1167** **119.0855** **107.0855** **93.0699** **91.0542** **79.0542**	**$C_{10}H_{16}{}^{35}Cl$** **$C_{10}H_{15}{}^{35}Cl$** **$C_{10}H_{15}$** **C_9H_{11}** **C_8H_{11}** **C_7H_9** **C_7H_7** **C_6H_7**
5		**23.56**	**$C_{10}H_{17}OCl$**	**188.0962**	**188.0962**	**173.0726** **153.1272** **137.0960** **111.0804** **93.0698** **83.0491**	**$C_9H_{14}O^{35}Cl$** **$C_{10}H_{17}O$** **$C_9H_{13}O$** **$C_7H_{11}O$** **C_7H_9** **C_5H_7O**

5		**23.63**	**$C_{10}H_{17}OCl$**	**188.0962**	**188.0961**	**173.0726** **171.0570** **153.1272** **137.0960** **111.0804** **93.0698**	**$C_9H_{14}O^{35}Cl$** **$C_9H_{12}O^{35}Cl$** **$C_{10}H_{17}O$** **$C_9H_{13}O$** **$C_7H_{11}O$** **C_7H_9**
2		**24.27**	**$C_{10}H_{16}Cl_2$**	**206.0624**	**206.0622**	**171.0932** **135.1167** **107.0854** **93.0698** **91.0542** **79.0542**	**$C_{10}H_{16}{}^{35}Cl$** **$C_{10}H_{15}$** **C_8H_{11}** **C_7H_9** **C_7H_7** **C_6H_7**

3		**24.49**	**$C_{10}H_{14}Cl_2$**	**204.0467**	**204.0462**	**171.0748** **167.0621** **153.0464** **133.1011** **115.0542** **105.0699** **91.0542** **79.0542**	**$C_{10}H_{14}{}^{37}Cl$** **$C_{10}H_{12}{}^{35}Cl$** **$C_9H_{10}{}^{35}Cl$** **$C_{10}H_{13}$** **C_9H_7** **C_8H_9** **C_7H_7** **C_6H_7**		
3		**24.70**	**$C_{10}H_{14}Cl_2$**	**204.0467**	**204.0465**	**169.0777** **155.0621** **133.1011** **127.0309** **91.0543** **79.0542**	**$C_{10}H_{14}{}^{35}Cl$** **$C_9H_{12}{}^{35}Cl$** **$C_{10}H_{13}$** **$C_7H_8{}^{35}Cl$** **C_7H_7** **C_6H_7**	**2 ± 0.5**	**2 ± 0.5**
3		**25.10**	**$C_{10}H_{14}Cl_2$**	**204.0467**	**204.0466**	**169.0777** **155.0621** **133.111** **119.0855** **91.0543** **79.0542**	**$C_{10}H_{14}{}^{35}Cl$** **$C_9H_{12}{}^{35}Cl$** **$C_{10}H_{13}$** **C_9H_{11}** **C_7H_7** **C_6H_7**		
3		**25.15**	**$C_{10}H_{14}Cl_2$**	**204.0467**	**204.0466**	**169.0777** **133.1011** **127.0308** **105.0699** **91.0542** **79.0542**	**$C_{10}H_{14}{}^{35}Cl$** **$C_{10}H_{13}$** **$C_7H_8{}^{35}Cl$** **C_8H_9** **C_7H_7** **C_6H_7**	**21 ± 5.9**	**26 ± 6.0**

[1]Number of molecules of chlorinated product per billion air molecules within 80 L chambers

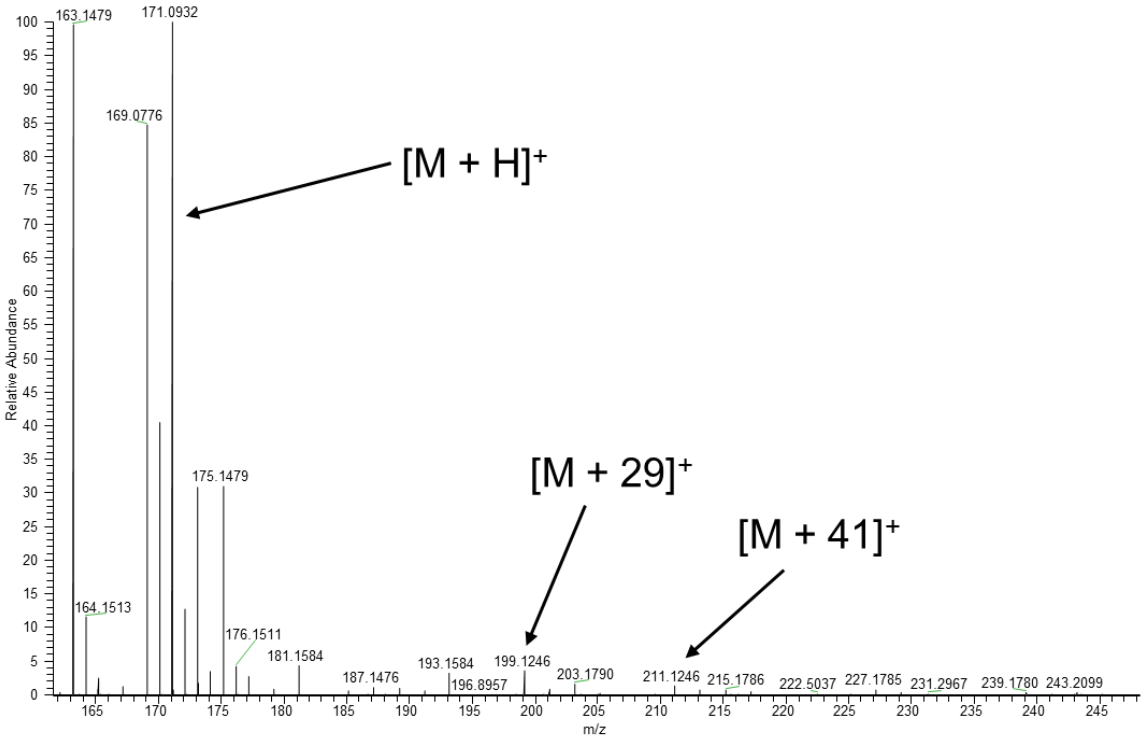


Figure S1. Representative mass spectrum from peak at RT 21.13 min collected in PCI mode, showing the expected adducts and confirming the parent species detected in EI mode, m/z 170.0857 ($M^{+\cdot}$).

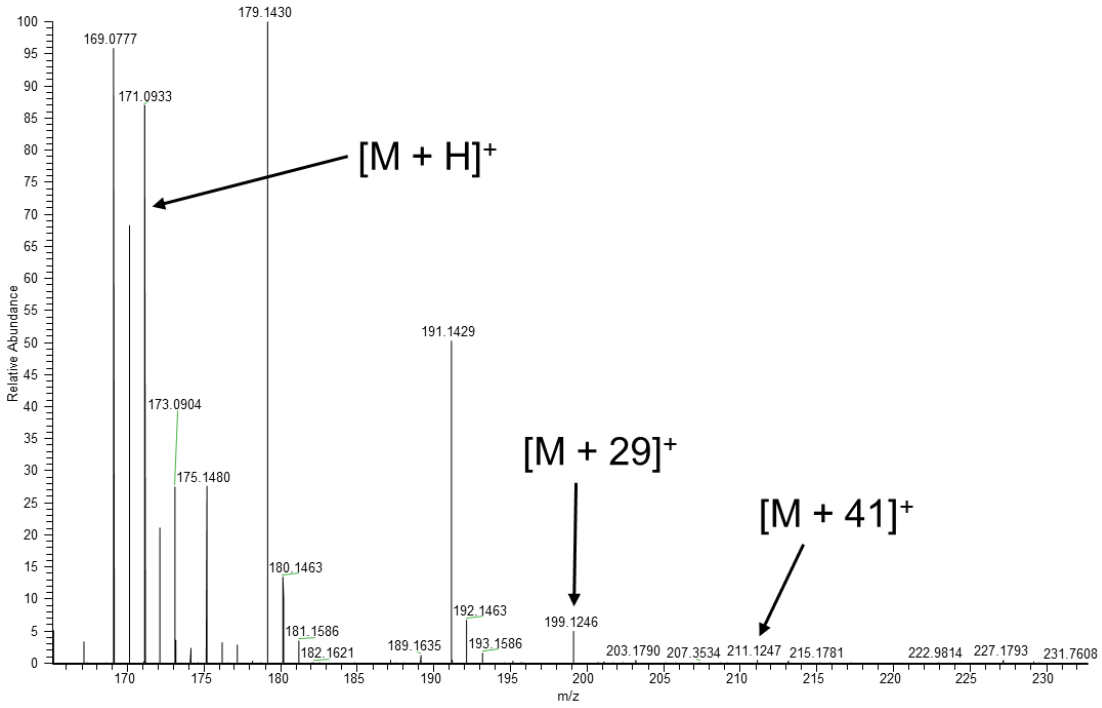


Figure S2. Representative mass spectrum from peak at RT 21.59 min collected in PCI mode, showing the expected adducts and confirming the parent species detected in EI mode, m/z 170.0857 ($M^{+\cdot}$).

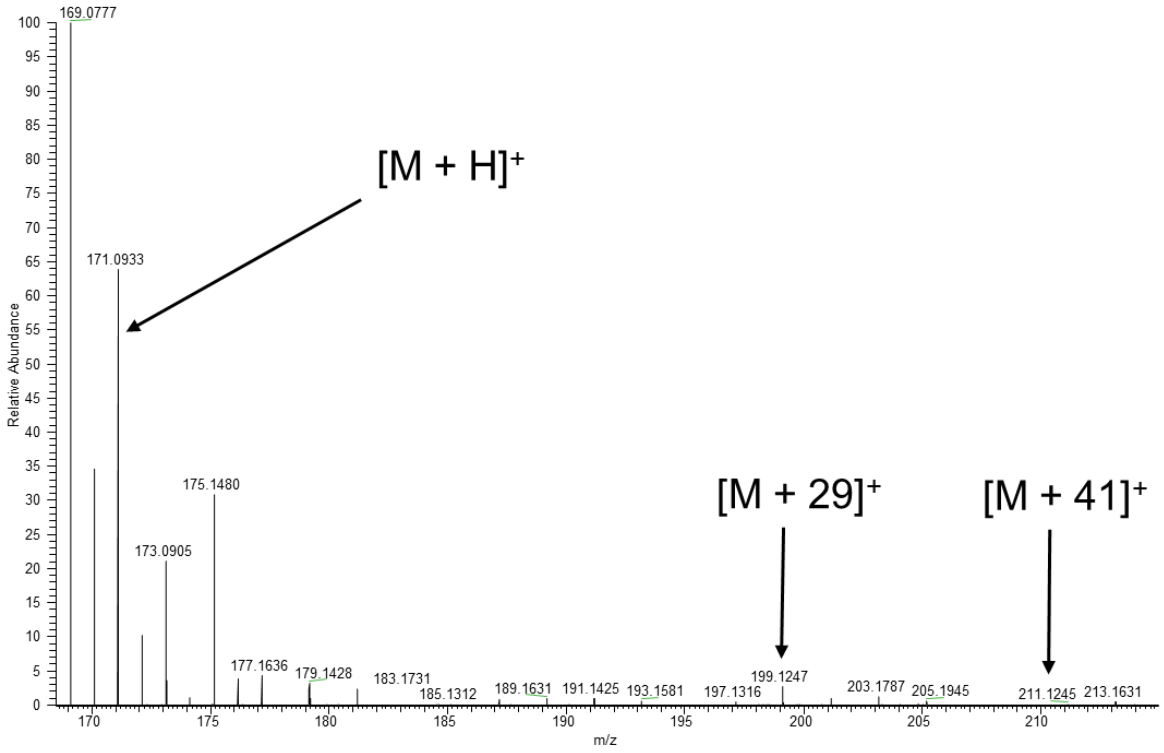


Figure S3. Representative mass spectrum from peak at RT 21.8 min collected in PCI mode, showing the expected adducts and confirming the parent species detected in EI mode, m/z 170.0857 ($M^{+\cdot}$).

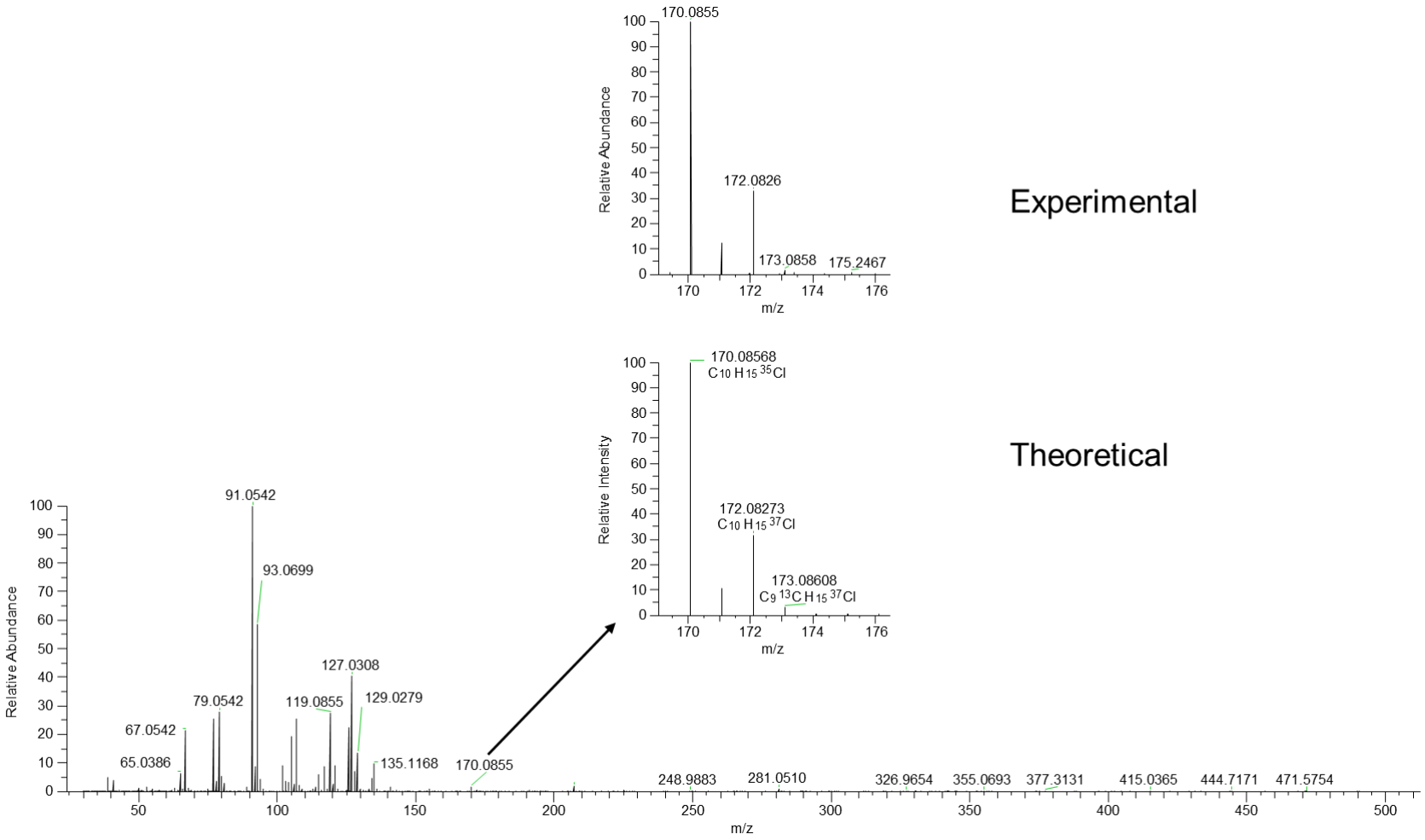


Figure S4. Representative GC-MS chromatogram from singly chlorinated limonene species (1, Table 1) detected at RT 21.13, 21.59, and 21.80 min from the reaction of limonene with $HOCl/Cl_2$ in the gas phase. The parent ion for this molecule was detected at m/z 170.0855 (EI mode, $M^{+\cdot}$), and the inset shows the expected isotopic pattern.

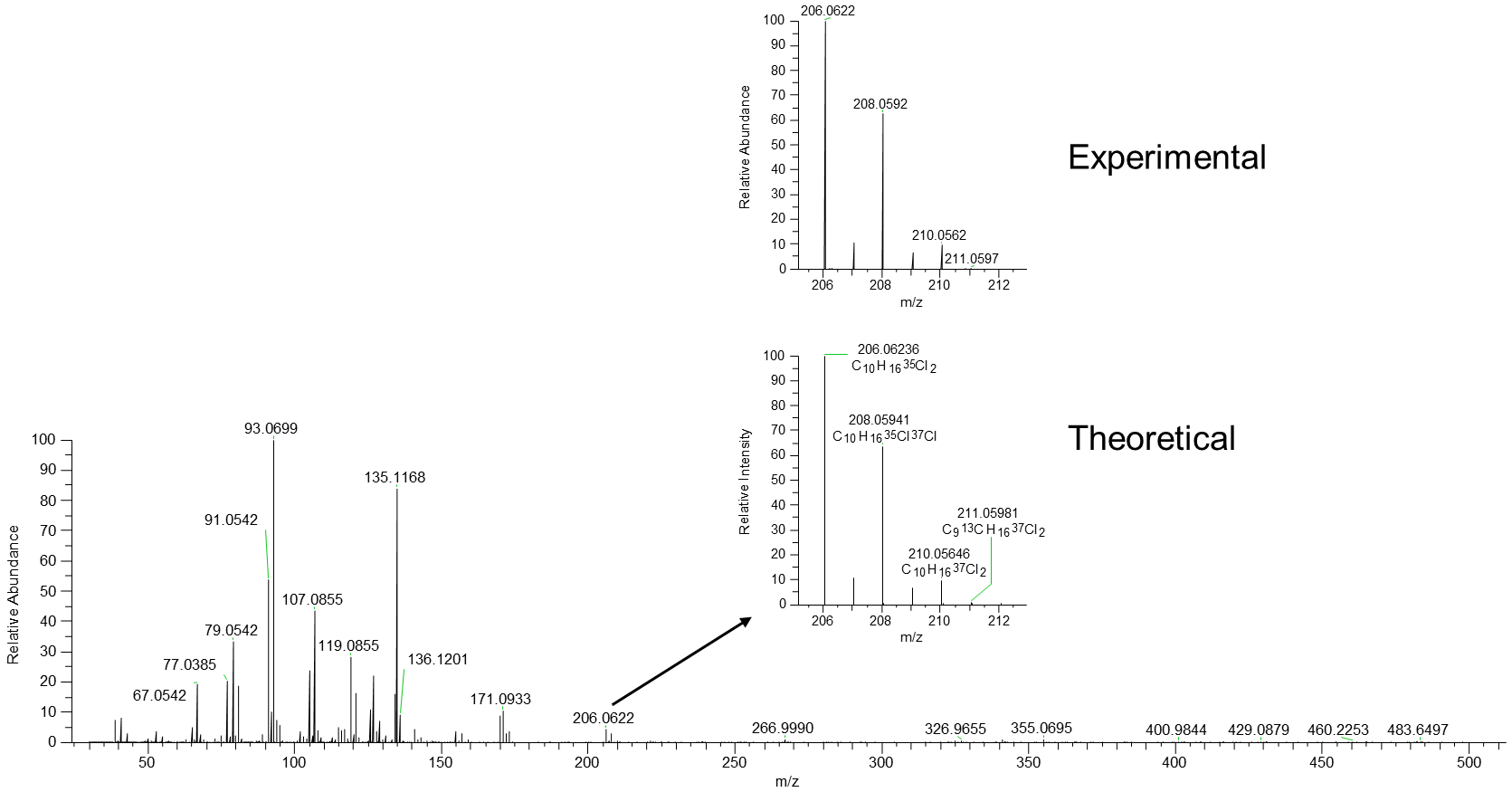


Figure S5. Representative GC-MS chromatogram from dichlorinated limonene species (2, Table 1) detected at RT 22.94 and 24.27 min from the reaction of limonene with HOCl/Cl_2 in the gas phase. The parent ion for this molecule was detected at m/z 206.0622 (EI mode, $M^{+\cdot}$), and the inset shows the expected isotopic pattern.

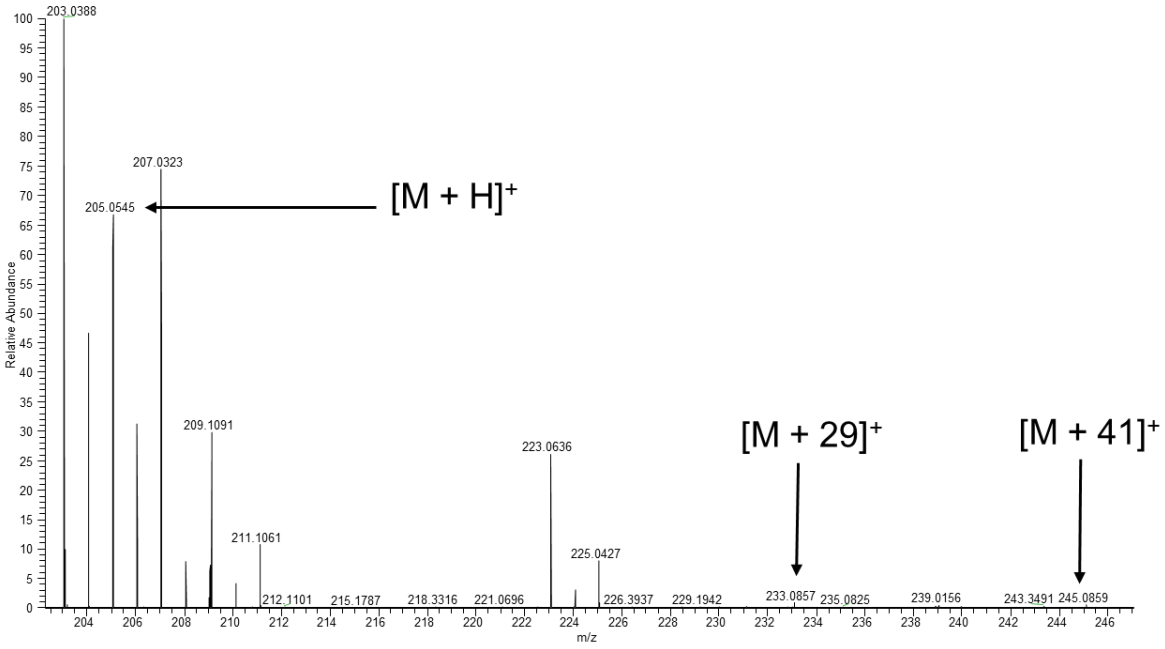


Figure S6. Representative mass spectrum from peak at RT 24.70 min collected in PCI mode, showing the expected adducts and confirming the parent species detected in EI mode,m/z 204.0467 ($M^{+\cdot}$).

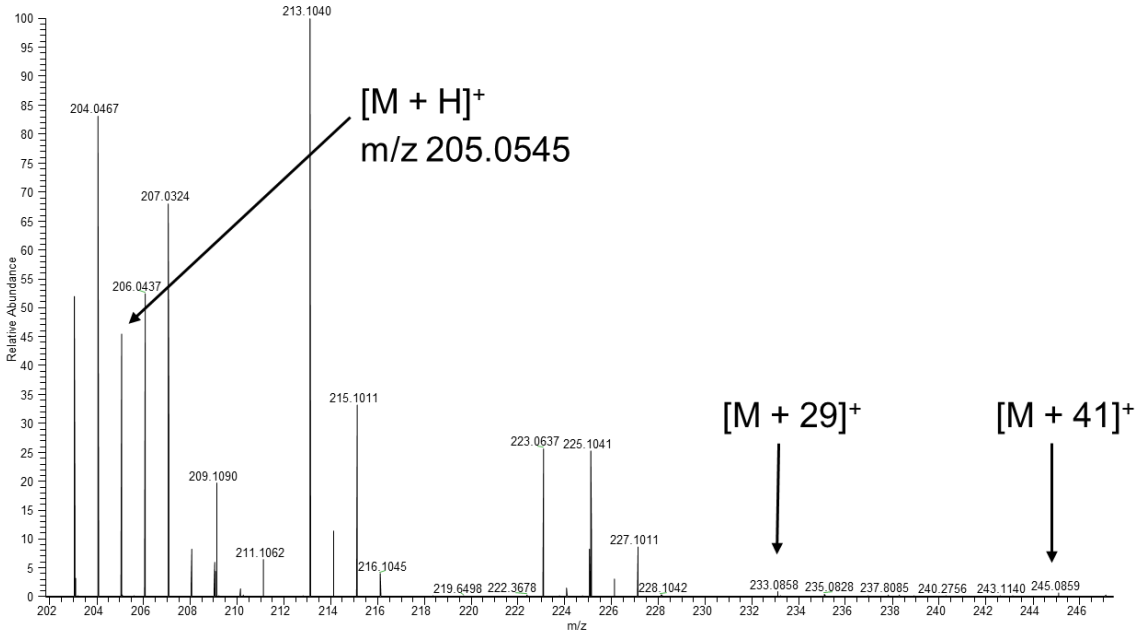


Figure S7. Representative mass spectrum from peak at RT 25.10 min collected in PCI mode, showing the expected adducts and confirming the parent species detected in EI mode, m/z 204.0467 ($M^{+\cdot}$).

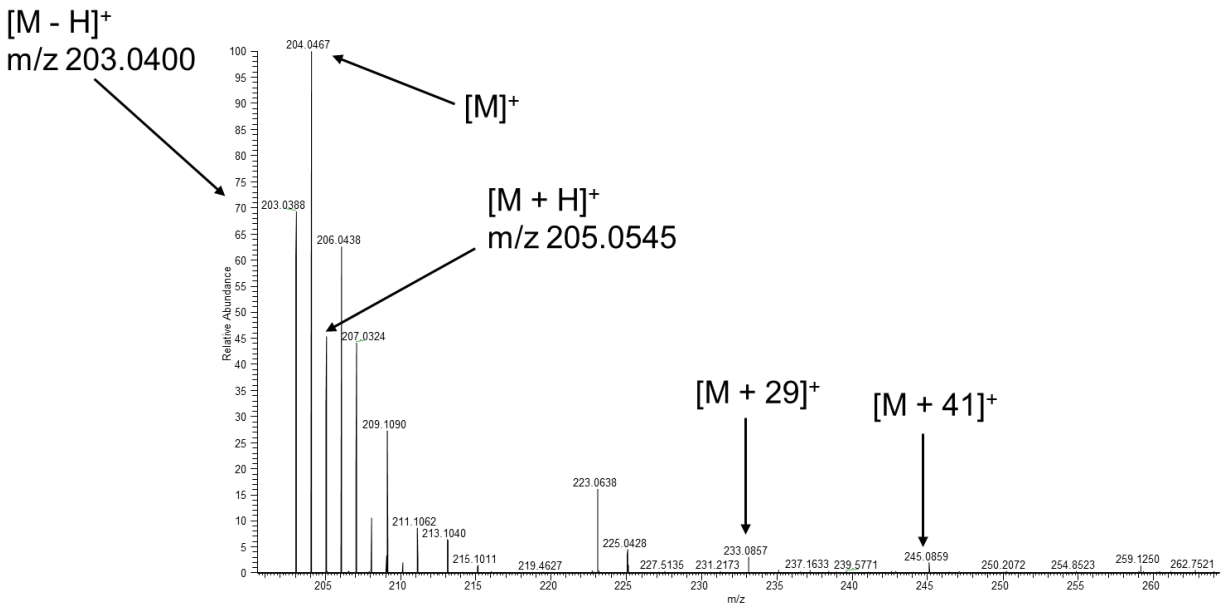


Figure S8. Representative mass spectrum from peak at RT 25.15 min collected in PCI mode, showing the expected adducts and confirming the parent species detected in EI mode, m/z 204.0467 ($M^{+\cdot}$).

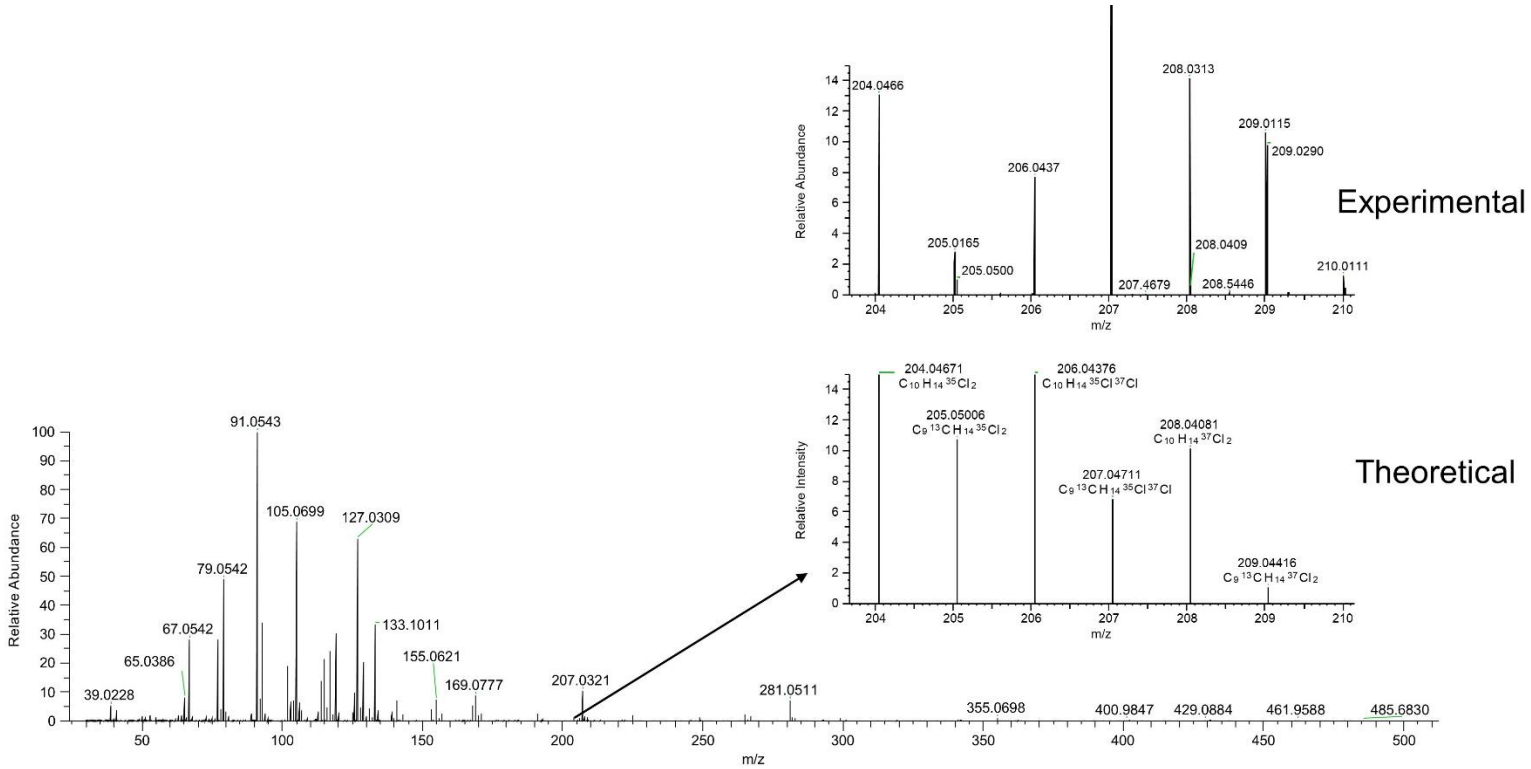


Figure S9. Representative GC-MS chromatogram from dichlorinated limonene species (3, Table 1) detected at 24.49, 24.70, 25.10, and 25.12 min from the reaction of limonene with $HOCl/Cl_2$ in the gas phase. The parent ion for this molecule was detected at m/z 204.0466 (EI mode, $M^{+\cdot}$), and the inset shows the expected isotopic pattern.

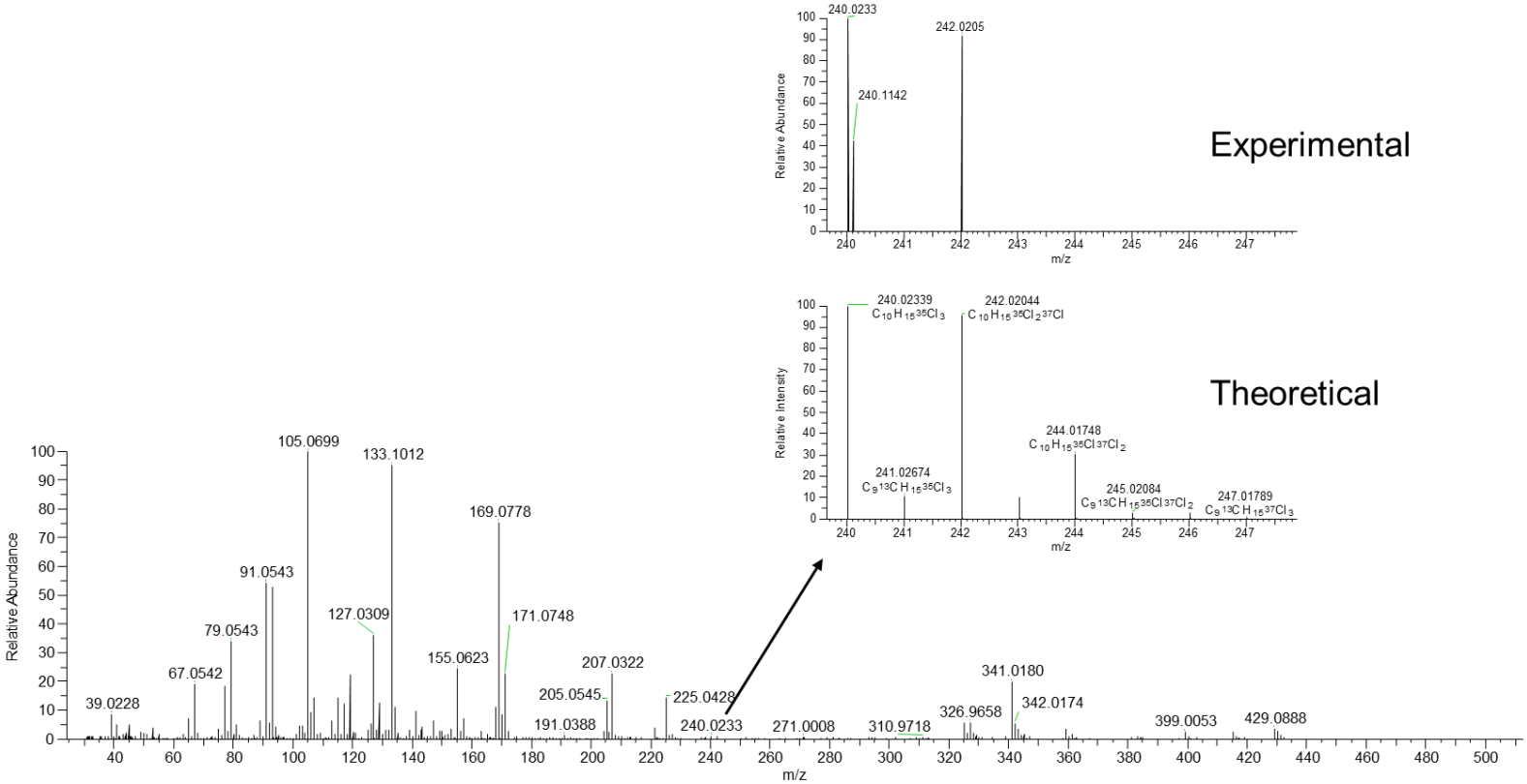


Figure S10. Representative GC-MS chromatogram from tri-chlorinated limonene species (4, Table 1) detected at RT 18.4 and 21.96 min from the reaction of limonene with $HOCl/Cl_2$ in the gas phase. The parent ion for this molecule was detected at m/z 240.0233 (EI mode, $M^{+\cdot}$), and the inset shows detection of the two most abundant isotopes.

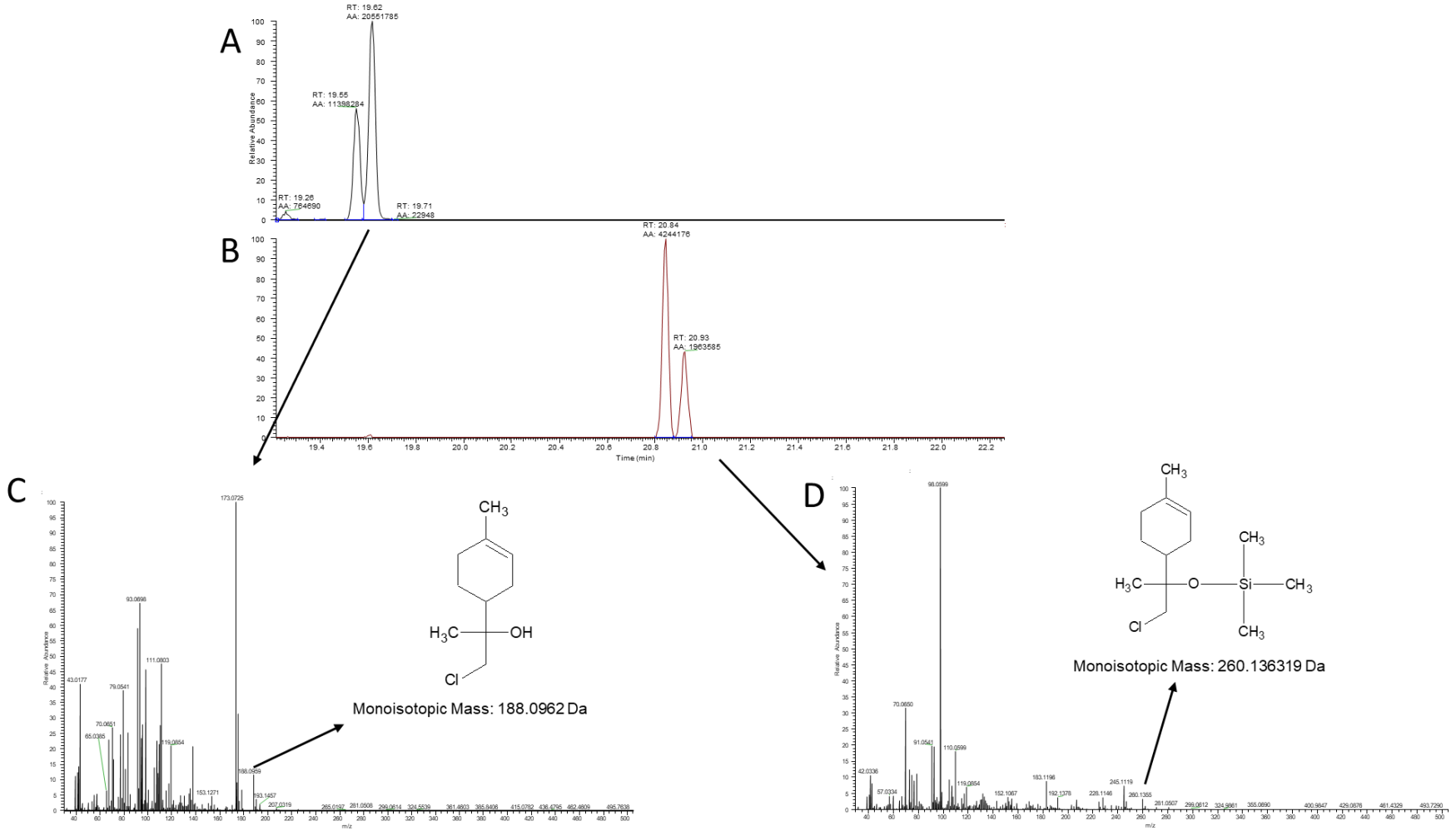


Figure S11. GC-MS extracted ion chromatograms for limonene chlorohydrin (Panel A) and BSTFA-derivatized limonene chlorohydrin (Panel B) and corresponding mass spectra (C and D).

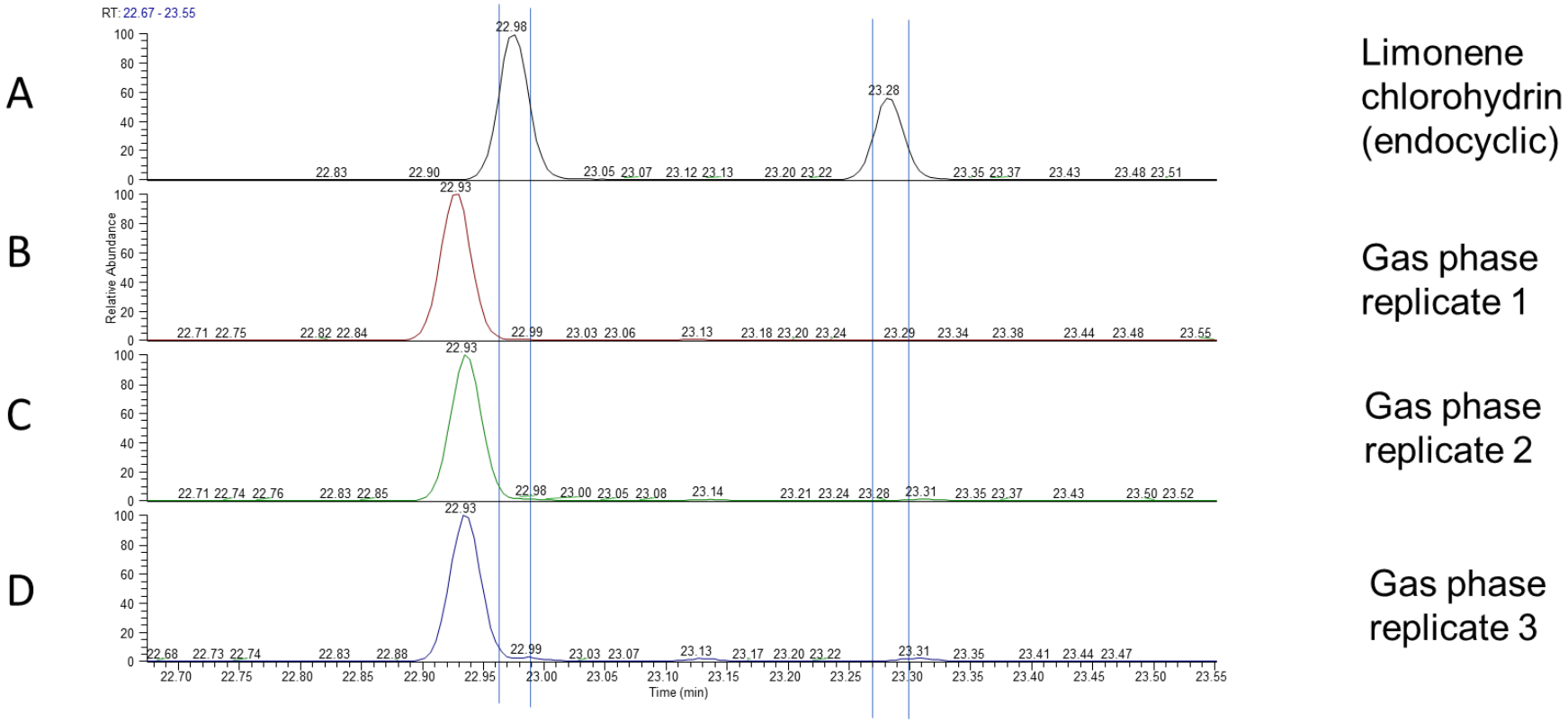


Figure S12. GC-MS extracted ion chromatogram (m/z 135.1171) for synthesized endocyclic limonene chlorohydrin (Panel A) with its two corresponding peaks at RT 22.98 and 23.28 min highlighted with vertical lines. Extracted ion chromatograms (m/z 135.1171) for products generated from the reaction between HOCl/Cl_2 + limonene are shown in panels B-D. As highlighted by the vertical lines, the endocyclic limonene chlorohydrin is not produced at appreciable levels in the gas phase reactions. The peak at RT 22.93 in the gas phase reaction pertains to the dichlorinated limonene (**2;** m/z 206.0625).

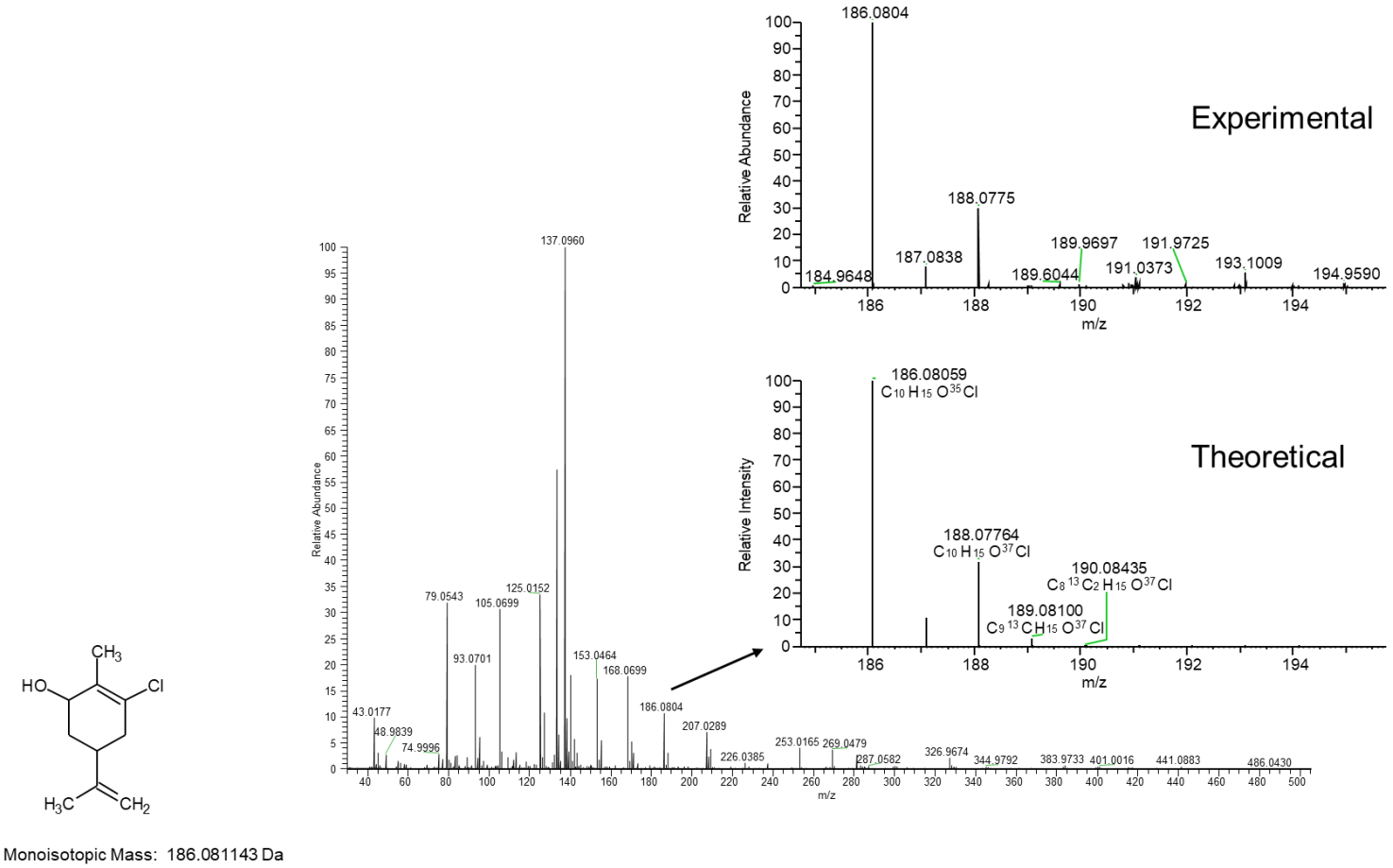


Figure S13. Representative GC-MS chromatogram from chlorinated, oxygenated limonene species detected at RT 22.31 min from the reaction of limonene with HOCl/Cl_2 in the gas phase. The parent ion for this molecule was detected at m/z 186.0804 (EI mode, $M^{+\cdot}$), and the inset shows the expected isotopic pattern.

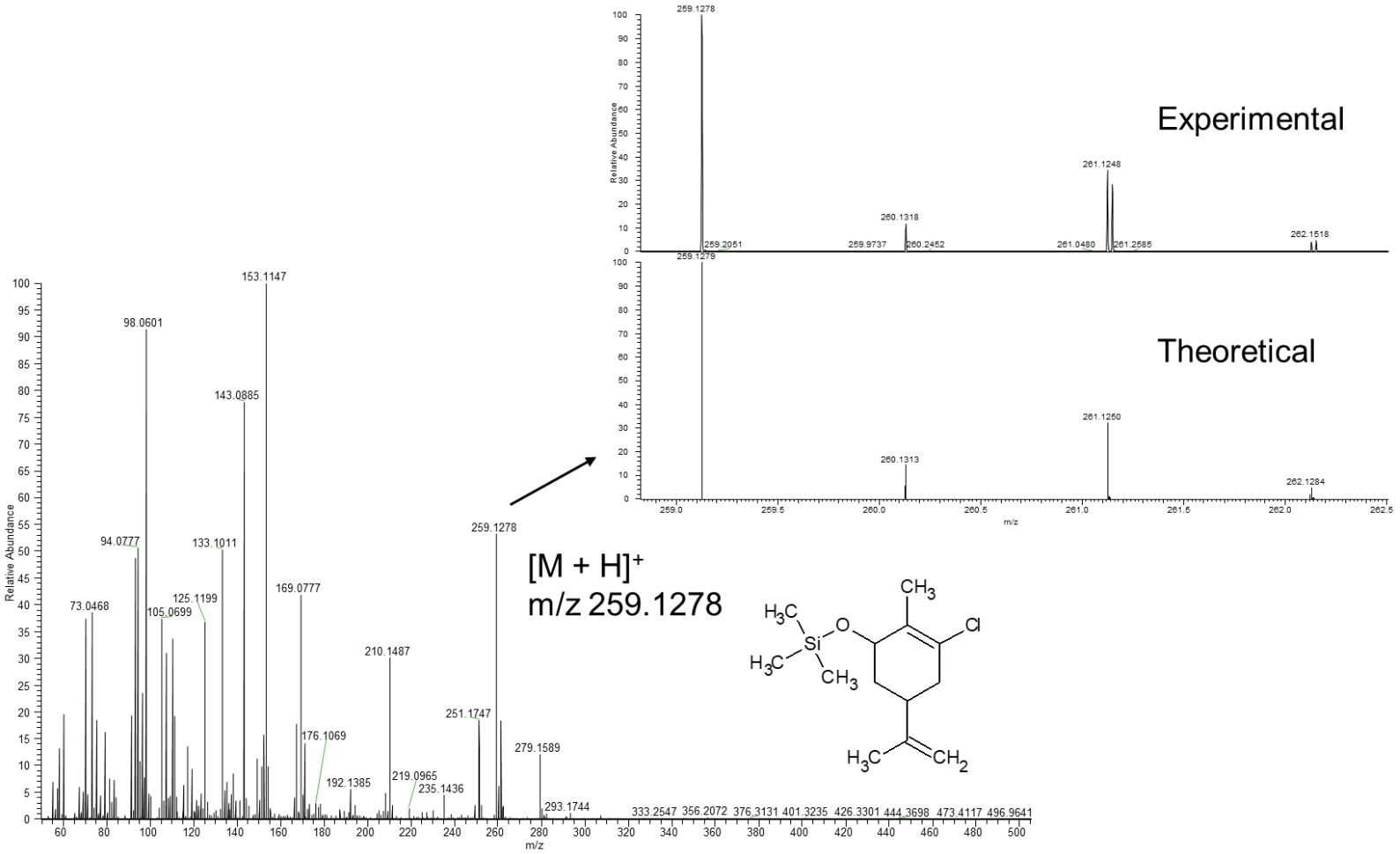


Figure S14. Representative PCI GC-MS spectrum from chlorinated, oxygenated limonene species after derivatization with BSTFA. The species was generated from the reaction of limonene with $HOCl/Cl_2$ in the gas phase followed by collection by impinger and derivatization by BSTFA. The parent ion for this molecule was detected at m/z 186.0804 (EI mode, $M^{+\cdot}$). The derivatized m/z value 259.1278 $[M + H]^+$ was detected, and the inset shows the expected isotopic pattern.

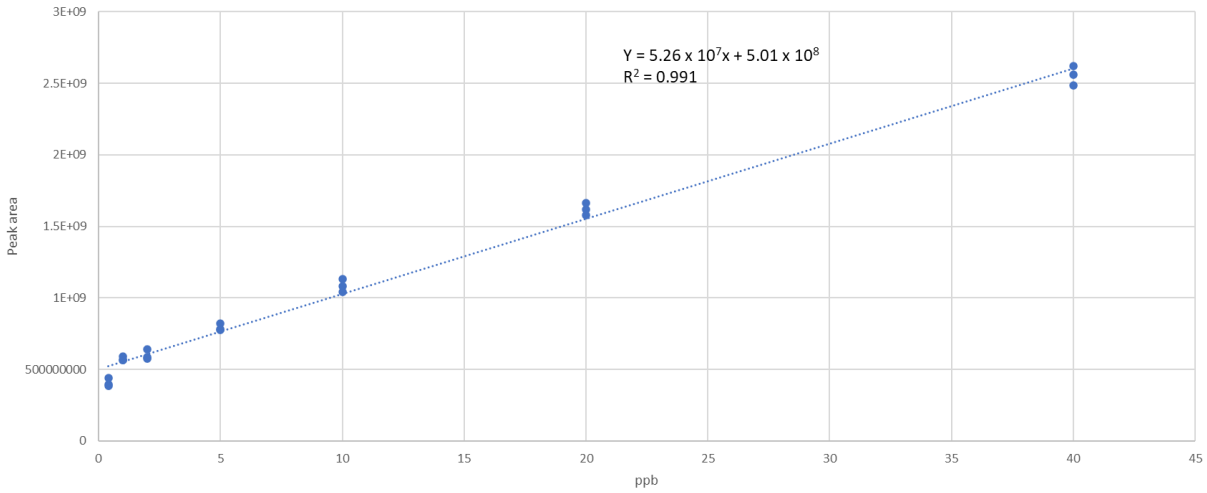


Figure S15. Calibration curve for limonene created from standard canister sampling using a gas preconcentrator with detection by GC-MS. The calibration curve was used to determine concentrations and yields of some chlorinated limonene species.

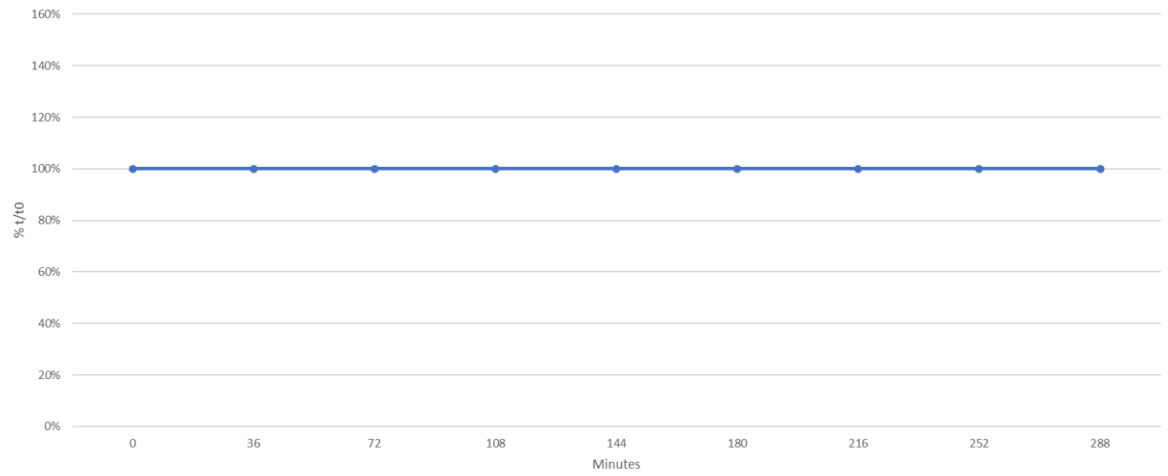


Figure S16. Stability of exocyclic limonene chlorohydrin within a Teflon chamber (50% RH, n=1).

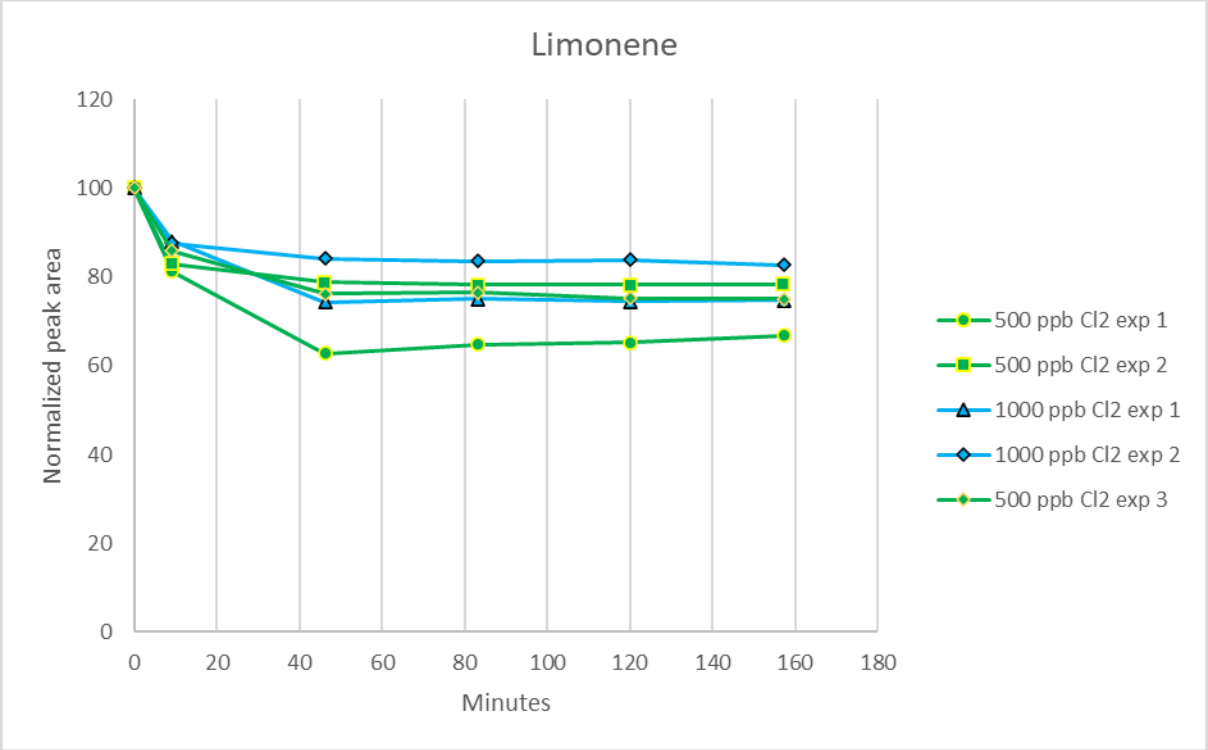


Figure S17. Loss of limonene in several experiments due to treatment with 500 ppb (green traces) and 1000 ppb (blue traces) Cl_2.

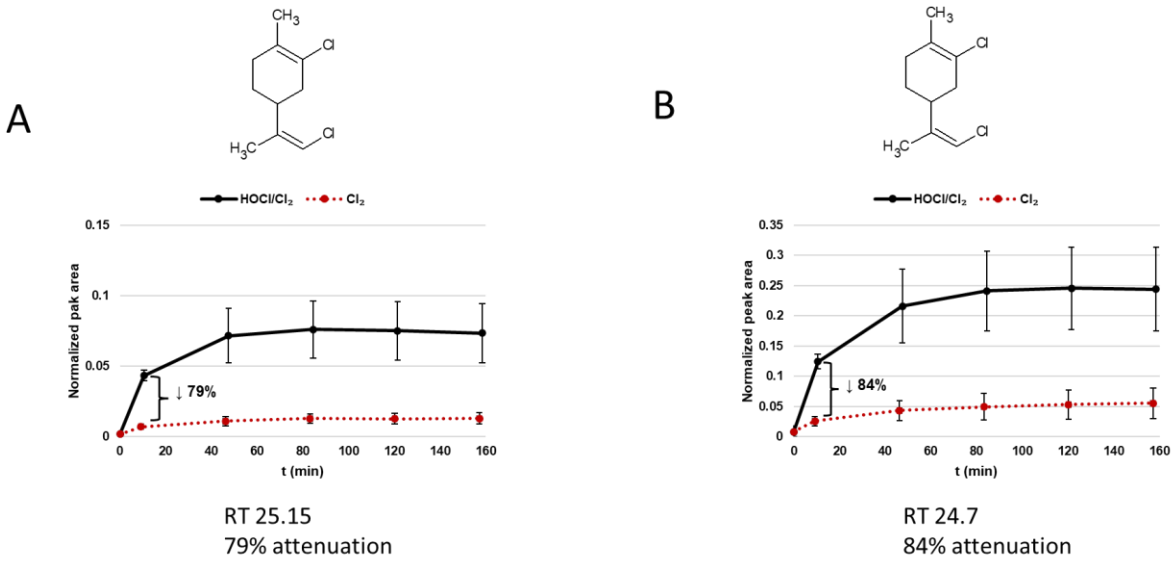


Figure S18. Effect of Cl_2 (red trace) and $HOCl/Cl_2$ (black trace) on limonene products in gas phase reactions. A) Comparison between effect of Cl_2 and $HOCl/Cl_2$ on dichlorinated limonene at RT 24.7 min (structure **3** in Table 1). B) Comparison between effect of Cl_2 and $HOCl/Cl_2$ on dichlorinated limonene at RT 25.15 min (structure **3,** Table 1). The normalized peak area pertains to peak area of each species divided by peak area of limonene at time zero. Error bars represent standard deviation with n=3 for limonene + $HOCl/Cl_2$ and n=7 for limonene + Cl_2.

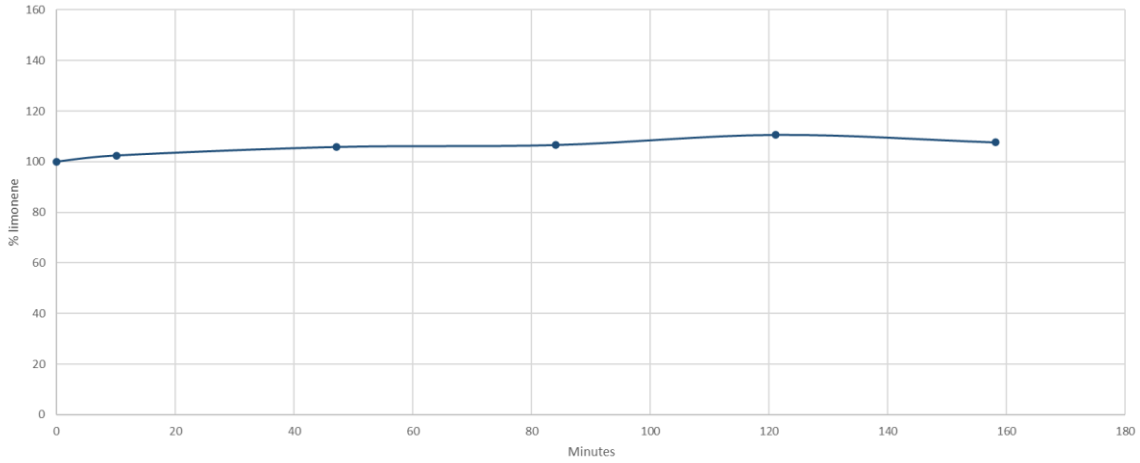


Figure S19. Stability of limonene in low humidity conditions (5% RH, n=1).