Table S1. Main SOA constituents identified by UPLC/ESI-HR-Q-TOFMS in MACR/ NO_x photooxidation experiments

Oligoester Series	$[M-H]^-$	Measured Mass	Suggested Formula	Diff (mDa)	# of MAE monomer units
1	119	119.03498	$C_4H_7O_4^-$	0.18	1
	221	221.06668	$C_8H_{13}O_7^-$	0.34	2
	323	323.09837	$C_{12}H_{19}O_{10}^-$	0.14	3
	425	425.10036	$C_{16}H_{25}O_{13}^-$	-0.13	4
	527	527.16176	$C_{20}H_{32}O_{16}^-$	-0.02	5
	629	629.19276	$C_{24}H_{37}O_{19}^-$	0.70	6
2	164	164.02006	$C_4H_6NO_6^-$	-0.17	1
	266	266.05175	$C_8H_{12}NO_9^-$	0.30	2
	368	368.08345	$C_{12}H_{18}NO_{12}^-$	0.08	3
	470	470.11514	$C_{16}H_{24}NO_{15}^-$	-0.19	4
	572	572.14684	$C_{20}H_{30}NO_{18}^-$	-0.47	5
3	147	147.02990	$C_5H_7O_5^-$	0.34	1
	249	249.06159	$C_9H_{13}O_8^-$	0.62	2
	351	351.09329	$C_{13}H_{19}O_{11}^-$	0.37	3
	453	453.12498	$C_{17}H_{25}O_{14}^-$	0.04	4
	555	555.15667	$C_{21}H_{31}O_{17}^-$	-0.08	5
4	161	161.04555	$C_6H_9O_5^-$	0.50	1
	263	263.07724	$C_{10}H_{15}O_8^-$	0.30	2
	365	365.10894	$C_{14}H_{21}O_{11}^-$	-0.18	3
	467	467.14063	$C_{18}H_{27}O_{14}^-$	-0.51	4
	569	569.17232	$C_{22}H_{34}O_{17}^-$	0.63	5

Oligoester series 1: H_2O involved in oligoesters formation
Oligoester series 2: HNO_3 involved in oligoesters formation
Oligoester series 3: HCOOH involved in oligoesters formation
Oligoester series 4: CH_3COOH involved in oligoesters formation

Table S2. Summary of experimental conditions for indoor chamber dark reactive uptake experiments

exp. #	date	precursor	mixing ratio (ppbv)	seed aerosol	MAE injected ($\mu g\ m^{-3}$)	SOA formed* ($\mu g\ m^{-3}$)
1	10/30/2011	MAE	300	none	1110	0
2	11/18/2011	MAE	300	acidic	1100	14.0
3	11//21/2011	MAE	300	acidic	1181	16.6
4	1/26/2012	MAE	300	acidic	1151	16.3
5	11/14/2011	MAE	300	neutral	1160	0
6	11/16/2011	MAE	300	neutral	1271	0

*Assuming a density of 1.35 g cm^{-3} for isoprene high-NO_x SOA (19).

Table S3. Summary of field measurements taken in Chapel Hill, NC to detect gaseous MAE

Date	Start time	End time	Day or Night	Sampling Flow Rate (LPM)	Sampling Volume (m^3)	MAE detected ($\mu g/m^3$)
7/18/2012	9:30	19:30	Day	1.30	0.78	0.75
7/18/2012	20:30	6:30	Night	1.30	0.78	0.34
7/30/2012	13:00	19:30	Day	1.21	0.47	0.24
7/30/2012	20:30	6:30	Night	1.21	0.73	0.12
7/31/2012	9:30	19:30	Day	1.24	0.74	0.27
7/31/2012	20:30	6:30	Night	1.29	0.77	0.14
8/1/2012	9:30	19:30	Day	1.25	0.75	0.31
8/1/2012	20:30	6:30	Night	1.29	0.77	0.14
8/2/2012	9:30	19:30	Day	1.29	0.77	0.27
8/2/2012	20:30	6:30	Night	1.27	0.76	0.13
8/3/2012	9:30	19:30	Day	1.29	0.77	0.21
8/3/2012	20:30	6:30	Night	1.33	0.80	0.07

Table S4. Species Added to CMAQ Simulations

Species	Description	Molecular weight (g/mol)	Dry Deposition Surrogate	Wet Deposition Surrogate	Transport?
IMACO3	peroxyacyl radicals formed from methacrolein	101.08	NA	NA	no
IMPAA	methacrylicperoxy acid	102.08	PAA	Peroxyacetic acid	yes
IMAPAN	methacryloyl peroxy nitrate	147.09	PAN	MPAN	yes
IMAE	methacrylic acid epoxide	102.00	ORA	Propanoic acid	yes
IHMML	hydroxymethyl-methyl-α-lactone	102.00	ORA	Propanoic acid	yes

Table S5. Reactions Removed from CMAQ Simulations

Label	Reaction	Rate Constant[a]	Original Implementation
BP56	MACR + NO3 = 0.5*MACO3 + 0.5*RO2C + 0.5*HNO3 + 0.5*xHO2 + 0.5*xCO + 0.5*yROOH + 1.5*XC + 0.5*XN	# 1.50e-12@1815;	Base SAPRC07TC (11, 12)
BP58	MACR = 0.33*OH + 0.67*HO2 + 0.34*MECO3 + 0.33*MACO3 + 0.33*RO2C + 0.67*CO + 0.34*HCHO + 0.33*xMECO3 + 0.33*xHCHO + 0.33*yROOH	Photolysis	Base SAPRC07TC (11, 12)
CP16	MACR + CL = 0.25*HCL + 0.165*MACO3 + 0.802*RO2C + 0.033*RO2XC + 0.033*zRNO3 + 0.802*xHO2 + 0.541*xCO + 0.082*xIPRD + 0.18*xCLCCHO + 0.541*xCLACET + 0.835*yROOH + 0.208*XC;	# 3.85e-10	Base SAPRC07TC (17, 18)
IS00	MACR + OH = 0.47*MACROO + 0.53*MACO3	# 8.00e-12@-380	Updated isoprene (5)

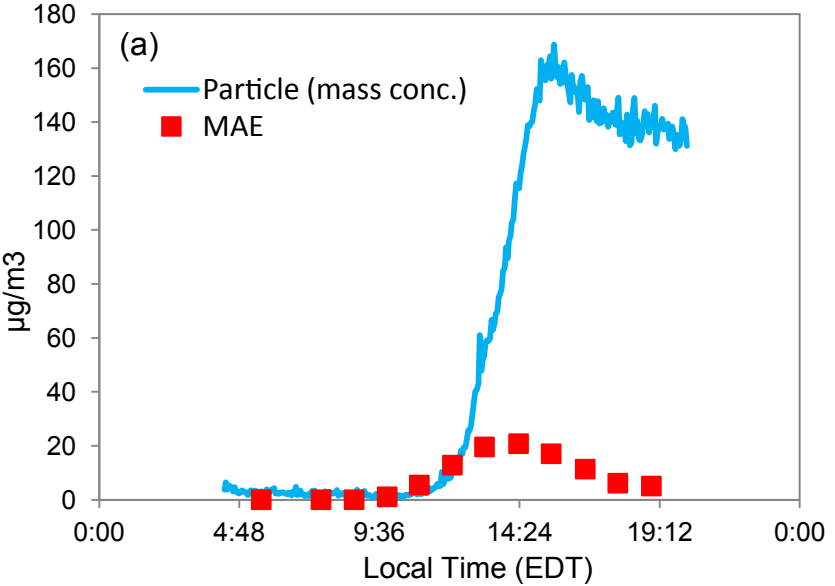
[a] Rate constant k(T) = A · (T/300)^B · exp(-Ea/RT); formatted as #A^B@Ea/R

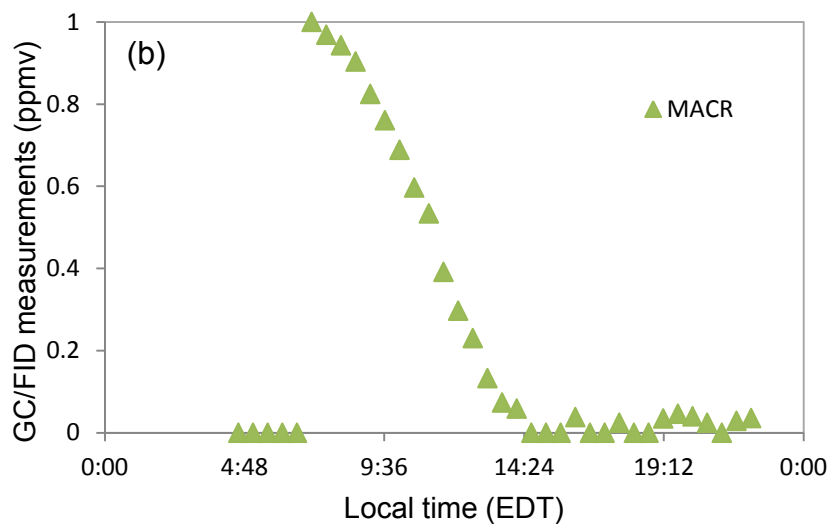
Table S6. Reactions Added to CMAQ Simulations

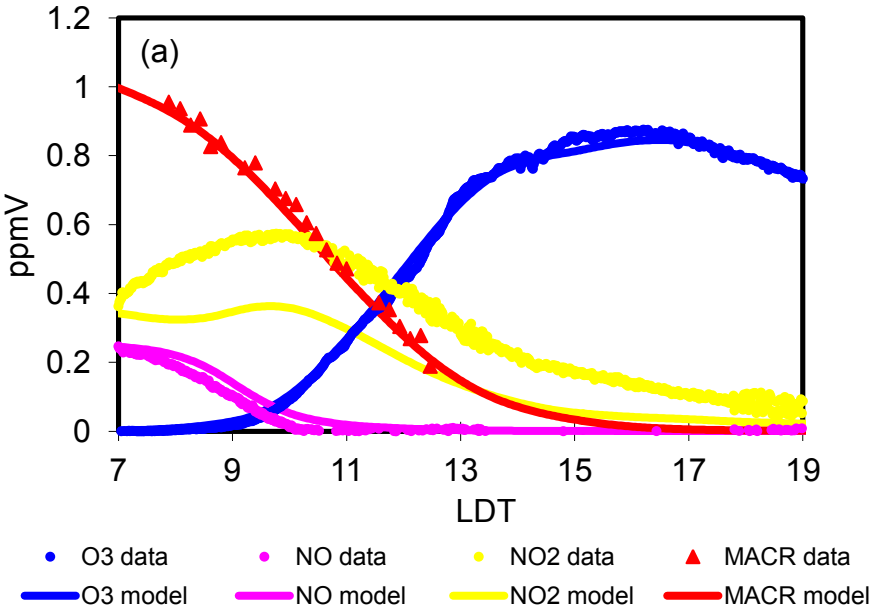
Label	Reaction	Rate Constant[a]	Notes
	IMACO3 Production		
BP56	MACR + NO3 = 0.5*IMACO3 + 0.5*RO2C + 0.5*HNO3 + 0.5*xHO2 + 0.5*xCO + 0.5*yROOH + 1.5*XC + 0.5*XN	# 1.50e-12@1815;	Generic MACO3 replaced with specific IMACO3
BP58	MACR = 0.33*OH + 0.67*HO2 + 0.34*MECO3 + 0.33*IMACO3 + 0.33*RO2C + 0.67*CO + 0.34*HCHO + 0.33*xMECO3 + 0.33*xHCHO + 0.33*yROOH	Photolysis	Generic MACO3 replaced with specific IMACO3
CP16	MACR + CL = 0.25*HCL + 0.165*IMACO3 + 0.802*RO2C + 0.033*RO2XC + 0.033*zRNO3 + 0.802*xHO2 + 0.541*xCO + 0.082*xIPRD + 0.18*xCLCCHO + 0.541*xCLACET + 0.835*yROOH + 0.208*XC	# 3.85e-10;	Generic MACO3 replaced with specific IMACO3
IS00	MACR + OH = 0.47*MACROO + 0.53*IMACO3	# 8.00e-12@-380;	Generic MACO3 replaced with specific IMACO3
	MAPAN Reactions		
IA51	IMACO3 + NO2 = IMAPAN	# 1.21e-11^-1.07@0;	MAPAN formation, rate constant based on peroxypropionyl nitrate
IA52	IMAPAN = IMACO3 + NO2	#1.60e+16@13486;	MAPAN decomposition
IA53	IMAPAN = 0.6*IMACO3 + 0.6*NO2 + 0.4*CO2 + 0.4*HCHO + 0.4*MECO3 + 0.4*NO3	Photolysis	MAPAN photolysis
IA108	IMAPAN + OH = 0.03*HACET + 0.03*CO + 0.81*NO3 + 0.21*IMAE + 0.57*IHMML + 0.19*PAN + 0.19*HCHO + 0.19*HO2	3.00e-11 cm^3 $molecule^{-1}$ s^{-1}	Four product channels (HOMAPAN, MAE, HMML, HACET) with yields based on computational chemistry (19%, 21%, 57%, 3%). For the HOMPAN channel, assume the hydroxyperoxy radical formed from OH addition to MAPAN reacts with NO and forms a carbonyl peroxyacylnitrate along with HCHO and HO2. Given that the peroxyacylnitrate would thermally decompose to a product similar to PAN photolysis products (20) represent the carbonylperoxyacylnitrate as PAN. The rate constant is modified from its original value of 2.9e-11 to 3.0e-11 according to computational chemistry (this work)
	Additional MAE and HMML Reactions		
IA90	IMAE + OH =	1.E-12 cm^3 $molecule^{-1}$ s^{-1}	Rate from structure reactivity relationships (6)
IA91	IHMML + OH =	4.4E-12 cm^3 $molecule^{-1}$ s^{-1}	Rate from structure reactivity relationships (6)
IA70	IMACO3 + HO2 = 0.75*IMPAA + 0.25*RCOOH + 0.25*O3 + XC	# 1.0*K<BR22>; # 5.20e-13@-980;	Replace generic hydroperoxide (RCOOOH) from MACO3 with MPAA from IMACO3
IA92	IMPAA + OH = 0.83*IMACO3 + 0.17*IHMML	1.66E-11 cm^3 $molecule^{-1}$ s^{-1}	Rate from MCM (species MACO3H) and yield of HMML from (14)
	Other IMACO3 Reactions		
IA69	IMACO3 + NO = NO2 + CO + CO2 + HCHO + MEO2	# 6.70e-12@-340;	following MACO3
IA71	IMACO3 + NO3 = NO2 + CO + CO2 + HCHO + MEO2	# 4.00e-12;	following MACO3
IA72	IMACO3 + MEO2 = HCHO + HO2 + CO + CO2 + HCHO + MEO2	# 1.0*K<BR24>;	following MACO3
IA73	IMACO3 + RO2C = CO + CO2 + HCHO + MEO2	# 1.0*K<BR25>;	following MACO3
IA74	IMACO3 + RO2XC = CO + CO2 + HCHO + MEO2	# 1.0*K<BR25>;	following MACO3
IA75	IMACO3 + MECO3 = CO2 + MEO2 + CO + CO2 + HCHO + MEO2	# 1.0*K<BR27>;	following MACO3
IA76	IMACO3 + RCO3 = CO +CO2 + HCHO + MEO2 + RO2C + xHO2 + yROOH + xCCHO + CO2	# 1.0*K<BR27>;	following MACO3
IA77	IMACO3 + BZCO3 = CO + CO2 + HCHO + MEO2 + BZO + RO2C + CO2	# 1.0*K<BR27>;	following MACO3
IA78	IMACO3 + MACO3 = 2*CO + 2*CO2 + 2*HCHO + 2*MEO2	# 1.0*K<BR27>;	following MACO3

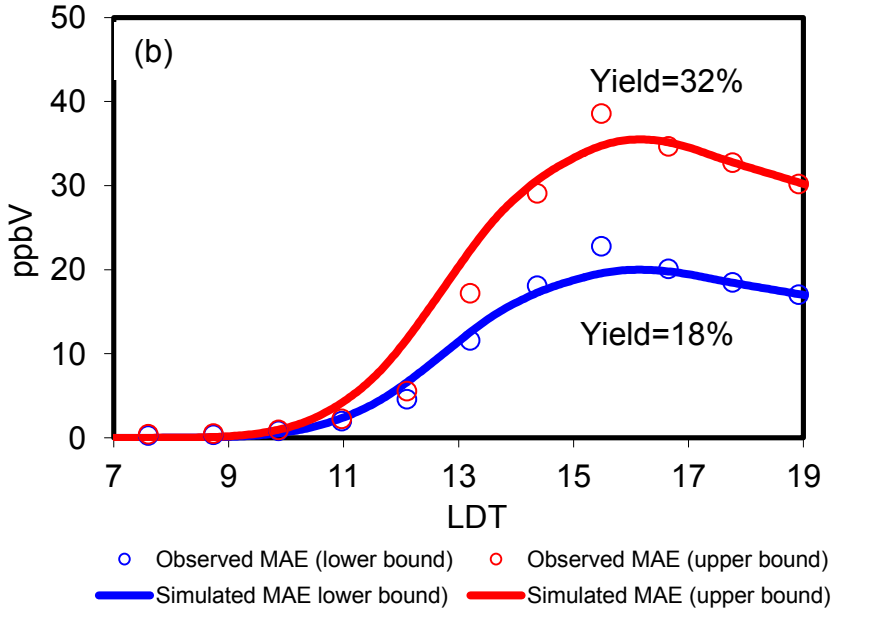
IA79	IMACO3 + IMACO3 = 2*CO + 2*CO2 + 2*HCHO + 2*MEO2	# 1.0*K<BR27>;	following MACO3
IC01	xCO + IMACO3 = IMACO3 + CO	# 1.0*K<BR25>;	following MACO3
IC02	xTBUO + IMACO3 = IMACO3 + TBUO	# 1.0*K<BR25>;	following MACO3
IC03	xMACO3 + IMACO3 = IMACO3 + MACO3	# 1.0*K<BR25>;	following MACO3
IC04	xRCO3 + IMACO3 = IMACO3 + RCO3	# 1.0*K<BR25>;	following MACO3
IC05	xMECO3 + IMACO3 = IMACO3 + MECO3	# 1.0*K<BR25>;	following MACO3
IC06	xMEO2 + IMACO3 = IMACO3 + MEO2	# 1.0*K<BR25>;	following MACO3
IC07	xNO2 + IMACO3 = IMACO3 + NO2	# 1.0*K<BR25>;	following MACO3
IC08	xOH + IMACO3 = IMACO3 + OH	# 1.0*K<BR25>;	following MACO3
IC09	xHO2 + IMACO3 = IMACO3 + HO2	# 1.0*K<BR25>;	following MACO3
IC10	xACROLEIN + IMACO3 = IMACO3 + ACROLEIN	# 1.0*K<BR25>;	following MACO3
IC11	xHOCCHO + IMACO3 = IMACO3 + HOCCHO	# 1.0*K<BR25>;	following MACO3
IC12	zRNO3 + IMACO3 = IMACO3 + PRD2 + HO2	# 1.0*K<BR25>;	following MACO3
IC13	yRAOOH + IMACO3 = IMACO3	# 1.0*K<BR25>;	following MACO3
IC14	yR6OOH + IMACO3 = IMACO3	# 1.0*K<BR25>;	following MACO3
IC15	yROOH + IMACO3 = IMACO3	# 1.0*K<BR25>;	following MACO3
IC16	xRNO3 + IMACO3 = IMACO3 + RNO3	# 1.0*K<BR25>;	following MACO3
IC17	xIPRD + IMACO3 = IMACO3 + IPRD	# 1.0*K<BR25>;	following MACO3
IC18	xMVK + IMACO3 = IMACO3 + MVK	# 1.0*K<BR25>;	following MACO3
IC19	xMACR + IMACO3 = IMACO3 + MACR	# 1.0*K<BR25>;	following MACO3
IC20	xAFG3 + IMACO3 = IMACO3 + AFG3	# 1.0*K<BR25>;	following MACO3
IC21	xAFG2 + IMACO3 = IMACO3 + AFG2	# 1.0*K<BR25>;	following MACO3
IC22	xAFG1 + IMACO3 = IMACO3 + AFG1	# 1.0*K<BR25>;	following MACO3
IC23	xBALD + IMACO3 = IMACO3 + BALD	# 1.0*K<BR25>;	following MACO3
IC24	xBACL + IMACO3 = IMACO3 + BACL	# 1.0*K<BR25>;	following MACO3
IC25	xMGLY + IMACO3 = IMACO3 + MGLY	# 1.0*K<BR25>;	following MACO3
IC26	xGLY + IMACO3 = IMACO3 + GLY	# 1.0*K<BR25>;	following MACO3
IC27	xPROD2 + IMACO3 = IMACO3 + PRD2	# 1.0*K<BR25>;	following MACO3
IC28	xMEK + IMACO3 = IMACO3 + MEK	# 1.0*K<BR25>;	following MACO3
IC29	xACETONE + IMACO3 = IMACO3 + ACETONE	# 1.0*K<BR25>;	following MACO3
IC30	xRCHO + IMACO3 = IMACO3 + RCHO	# 1.0*K<BR25>;	following MACO3
IC31	xCCHO + IMACO3 = IMACO3 + CCHO	# 1.0*K<BR25>;	following MACO3
IC32	xHCHO + IMACO3 = IMACO3 + HCHO	# 1.0*K<BR25>;	following MACO3
IC33	xCL + IMACO3 = IMACO3 + CL	# 1.0*K<BR25>;	following MACO3
IC34	xCLACET + IMACO3 = IMACO3 + CLACET	# 1.0*K<BR25>;	following MACO3
IC35	xCLCCHO + IMACO3 = IMACO3 + CLCCHO	# 1.0*K<BR25>;	following MACO3

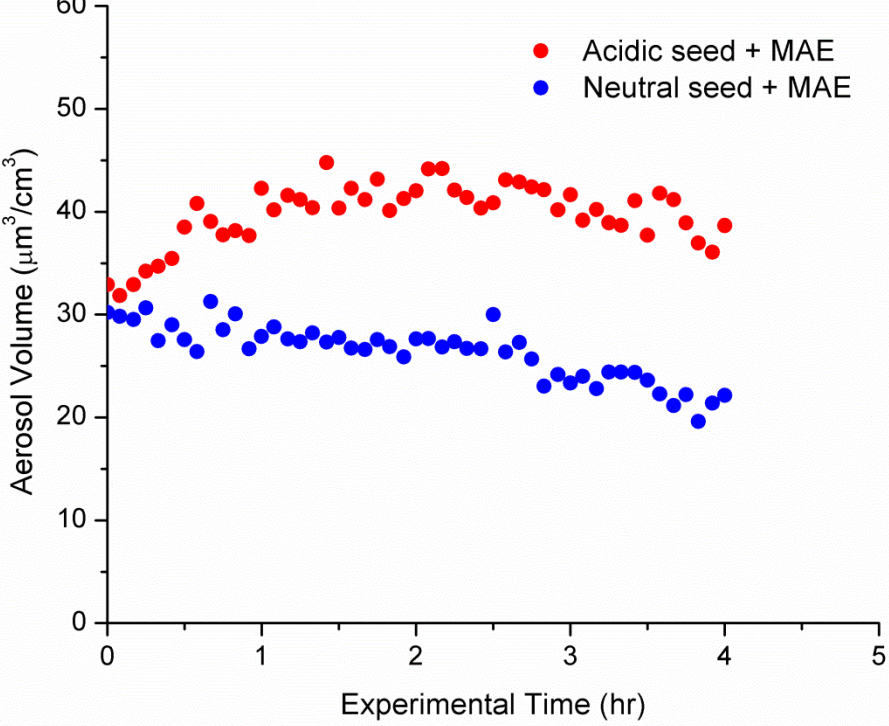
[a] Rate constant k(T) = A · (T/300)^B · exp(-Ea/RT); formatted as #A^B@Ea/R, some reactions use existing SAPRC07 Rate constants (e.g. <BR25>)

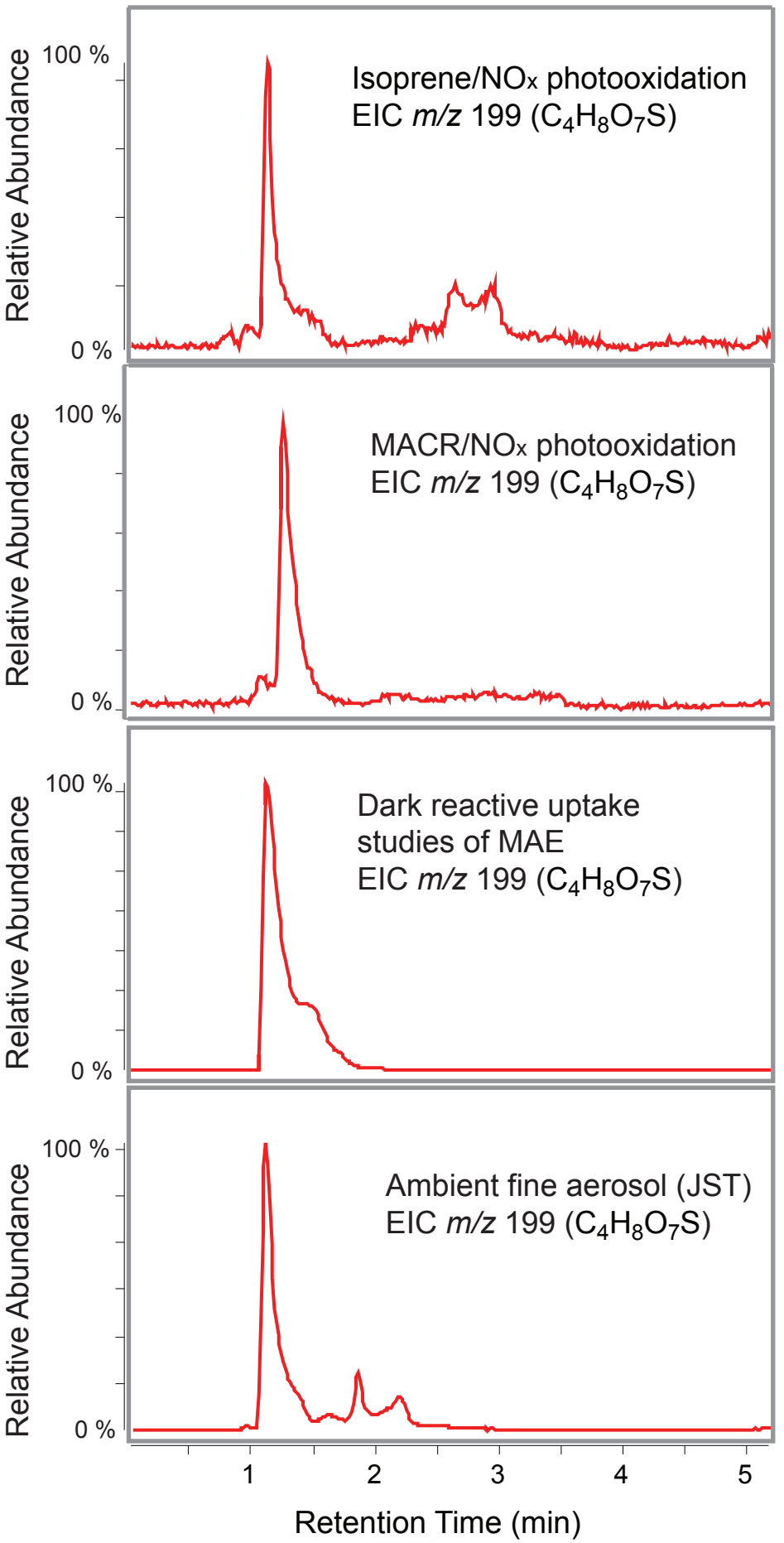

(a)
Particle (mass conc.)
MAE
µg/m3
180
160
140
120
100
80
60
40
20
0
0:00
4:48
9:36
14:24
19:12
0:00
Local Time (EDT)

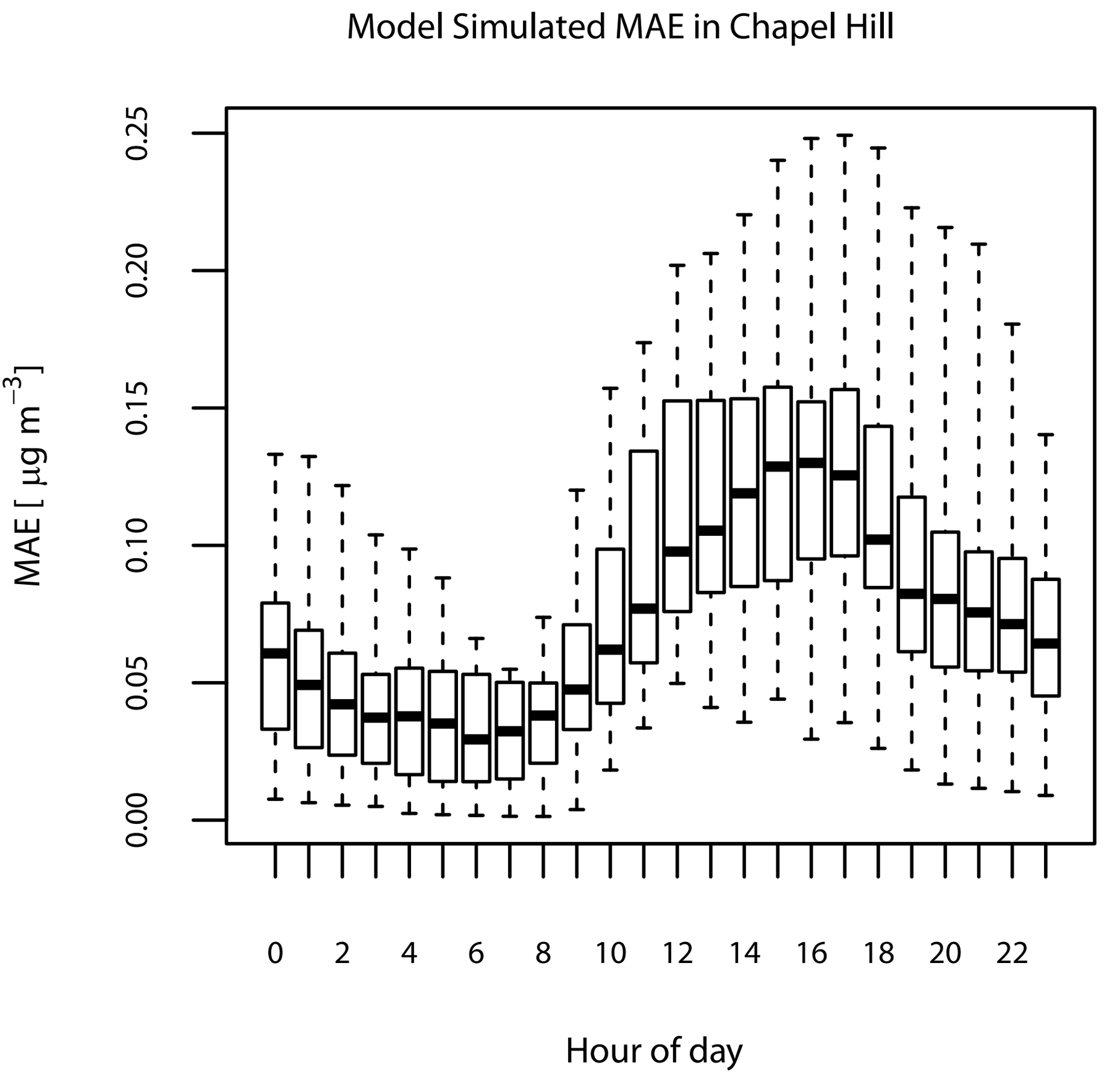

(b)
MACR
GC/FID measurements (ppmv)
1
0.8
0.6
0.4
0.2
0
0:00
4:48
9:36
14:24
19:12
0:00
Local time (EDT)

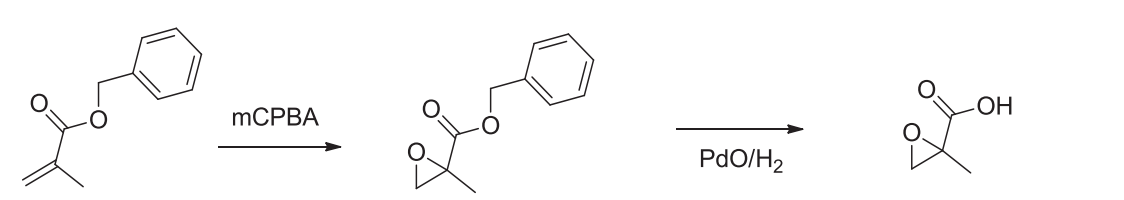

(a)
1.2
1
0.8
0.6
0.4
0.2
0
ppmV
7
9
11
13
15
17
19
LDT
O3 data
NO data
NO2 data
MACR data
O3 model
NO model
NO2 model
MACR model


(b)
Yield=32%
Yield=18%
50
40
30
20
10
0
ppbV
7
9
11
13
15
17
19
LDT
Observed MAE (lower bound)
Observed MAE (upper bound)
Simulated MAE lower bound)
Simulated MAE (upper bound)


Acidic seed + MAE
Neutral seed + MAE
Aerosol Volume (μm³/cm³)
Experimental Time (hr)
0
10
20
30
40
50
60
0
1
2
3
4
5


Relative Abundance
100 %
0 %
Isoprene/NOx photooxidation
EIC m/z 199 (C4H8O7S)
MACR/NOx photooxidation
EIC m/z 199 (C4H8O7S)
Dark reactive uptake
studies of MAE
EIC m/z 199 (C4H8O7S)
Ambient fine aerosol (JST)
EIC m/z 199 (C4H8O7S)
1
2
3
4
5
Retention Time (min)

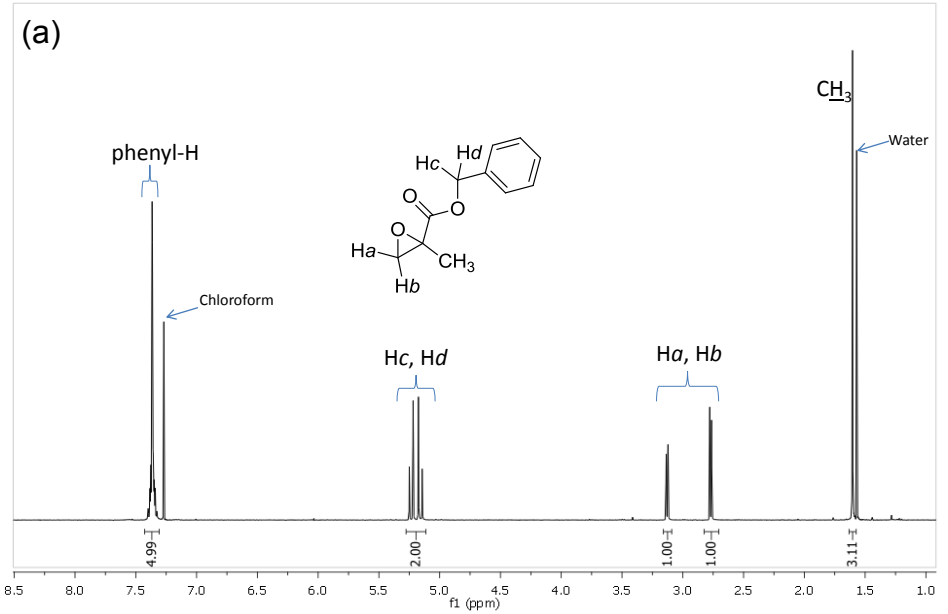

Model Simulated MAE in Chapel Hill
MAE [µg m^{-3}]
0.00
0.05
0.10
0.15
0.20
0.25
0
2
4
6
8
10
12
14
16
18
20
22
Hour of day



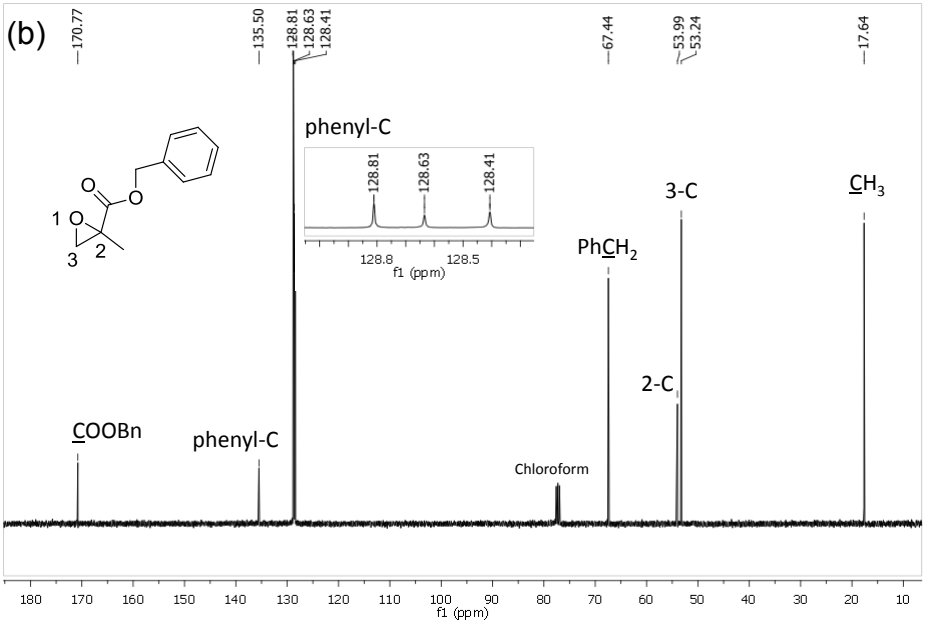
benzyl methacrylate

benzyl 2-methyloxirane-2-carboxylate

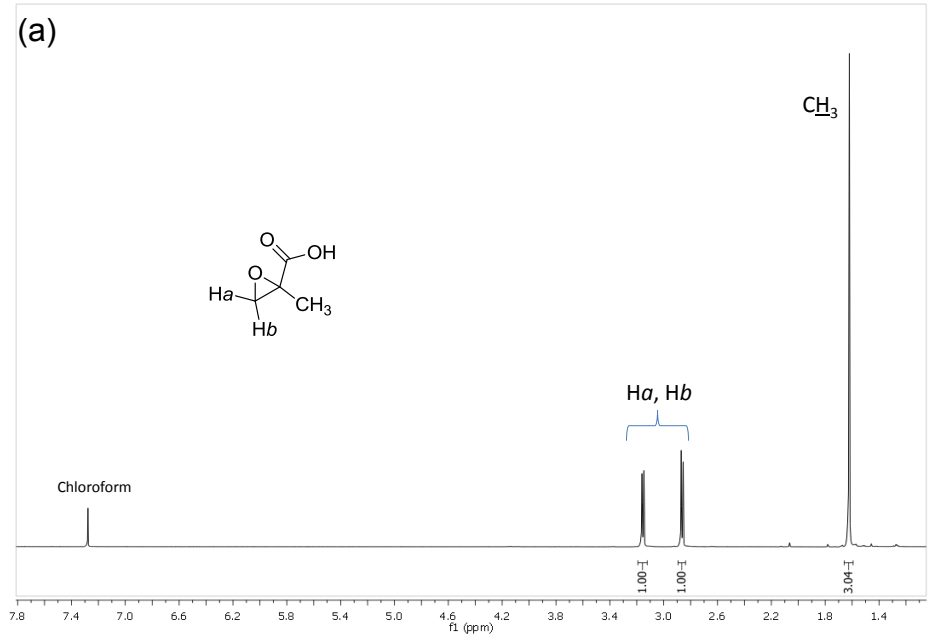
methacrylic acid epoxide



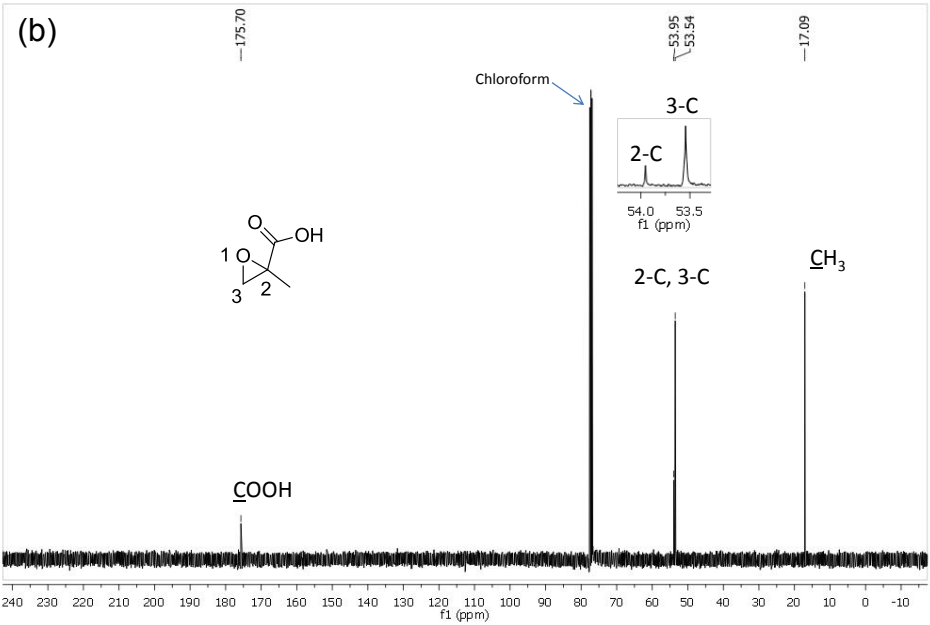
^{1}H NMR (400 MHz, $CDCl_3$) of benzyl 2-methyloxirane-2-carboxylate



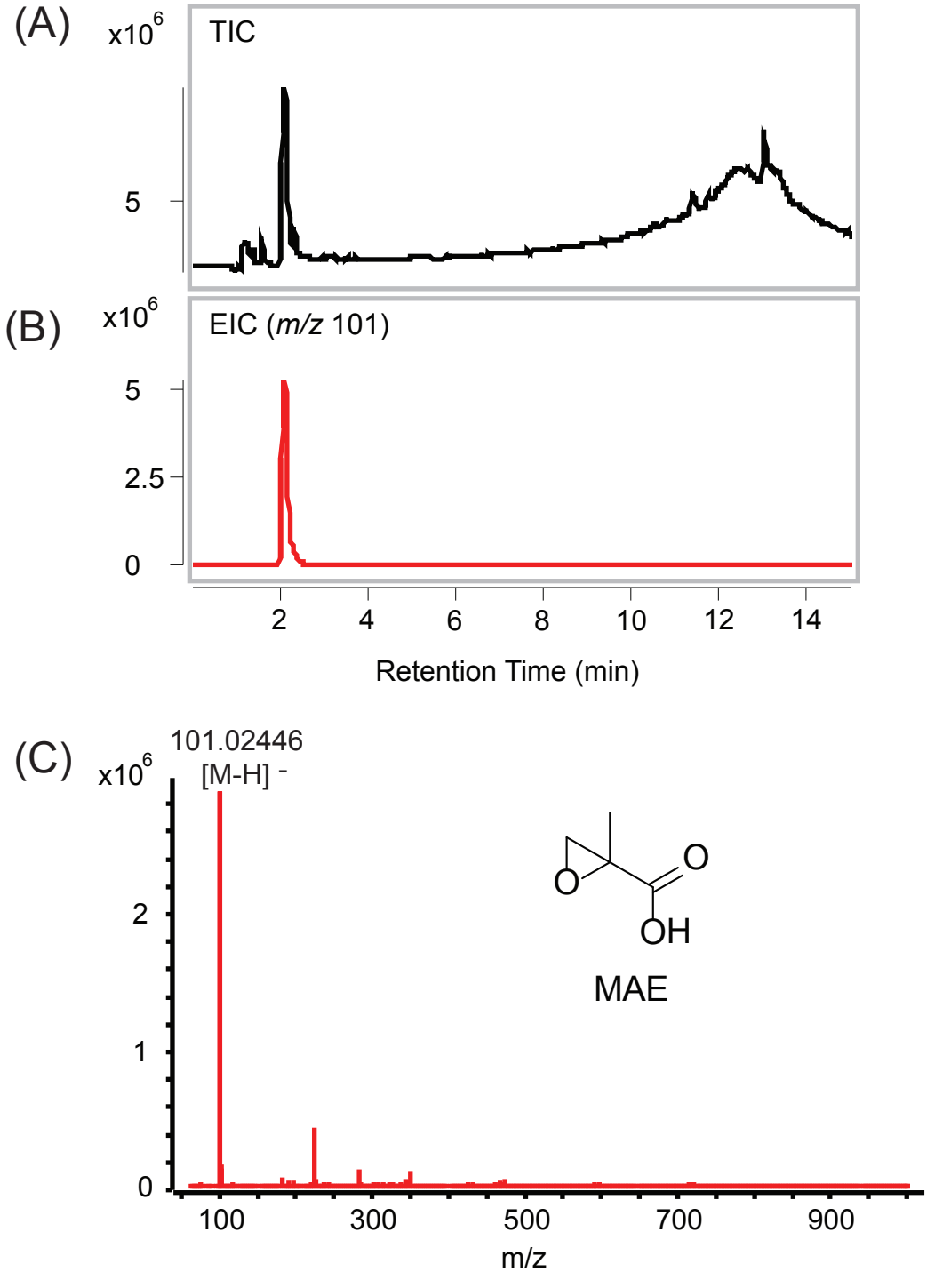
^{13}C NMR (100 MHz, $CDCl_3$) of benzyl 2-methyloxirane-2-carboxylate

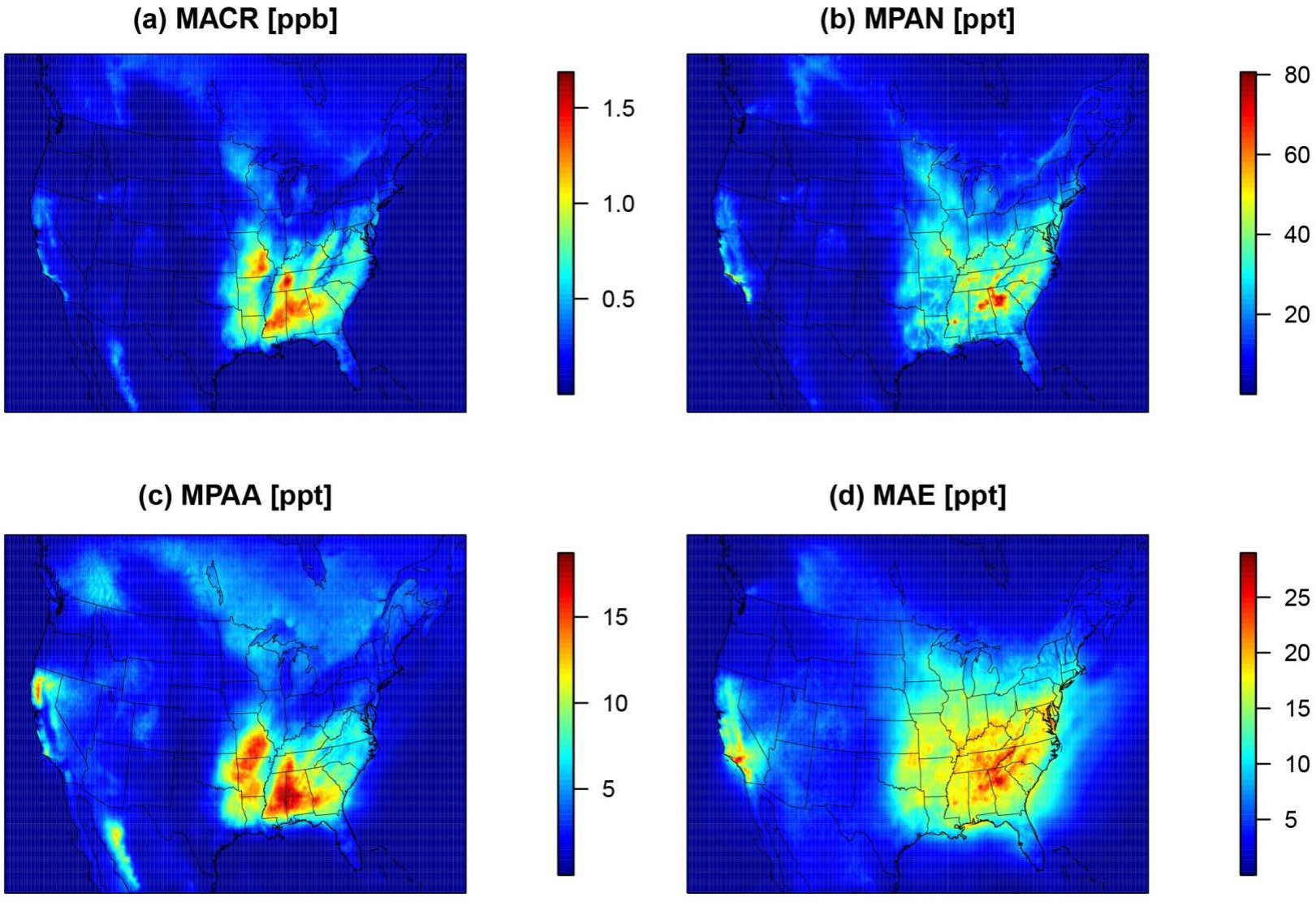


^{1}H NMR (400 MHz, $CDCl_3$) of 2-methyloxirane-2-carboxylic acid



^{13}C NMR (100 MHz, $CDCl_3$) of 2-methyloxirane-2-carboxylic acid


(A)
x10^6
TIC
5
(B)
x10^6
EIC (m/z 101)
5
2.5
0
2
4
6
8
10
12
14
Retention Time (min)
(C)
101.02446
[M-H] -
x10^6
2
1
0
100
300
500
700
900
m/z
O
O
OH
MAE


(a) MACR [ppb]
1.5
1.0
0.5
(b) MPAN [ppt]
80
60
40
20
(c) MPAA [ppt]
15
10
5
(d) MAE [ppt]
25
20
15
10
5