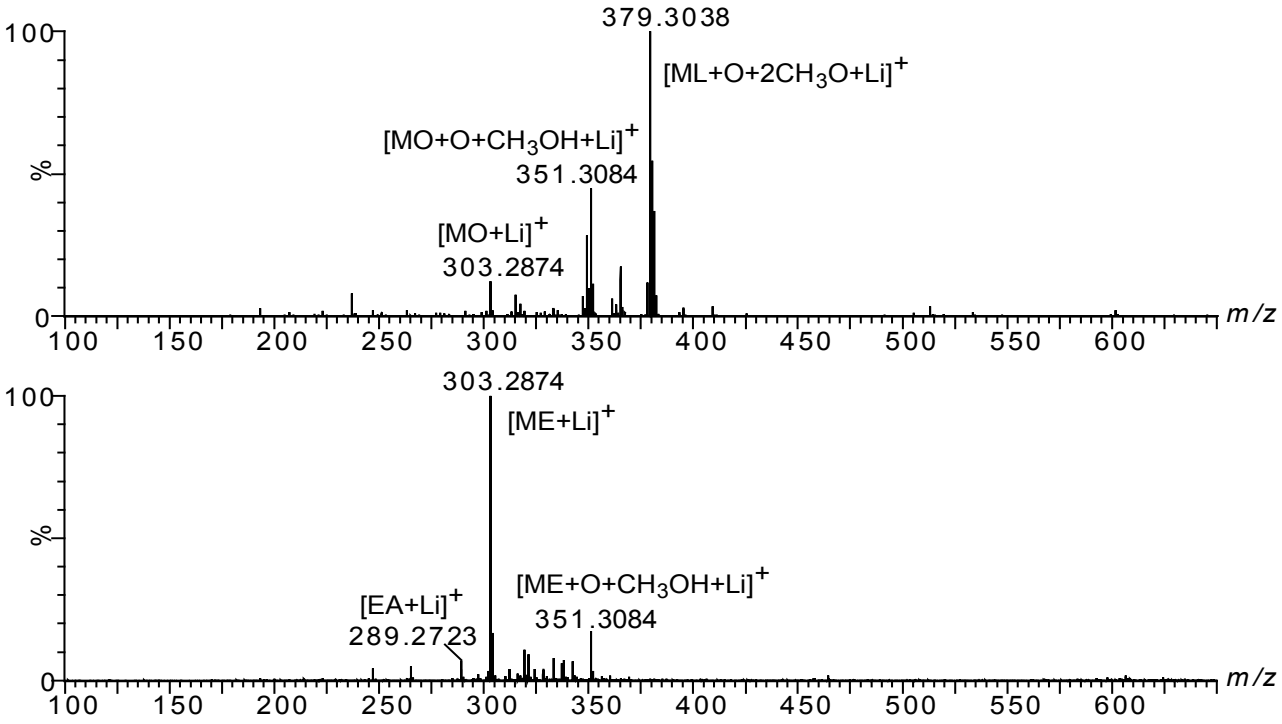
Supplementary Information

Figure SI.1. (a) ESI mass spectrum of methyl esters obtained after fatty acid methylation and (b) interpretation of *m/z* 351.3 and *m/z* 379.3 as $[ME+O+CH_3OH+Li]^+$ and $[ME+O+2CH_3OH+Li]^+$, respectively, corresponding to side-products of methylation reaction using H_2SO_4 catalyst. The reported structures are putative ones among various isomeric possibilities.

(a)



(b)

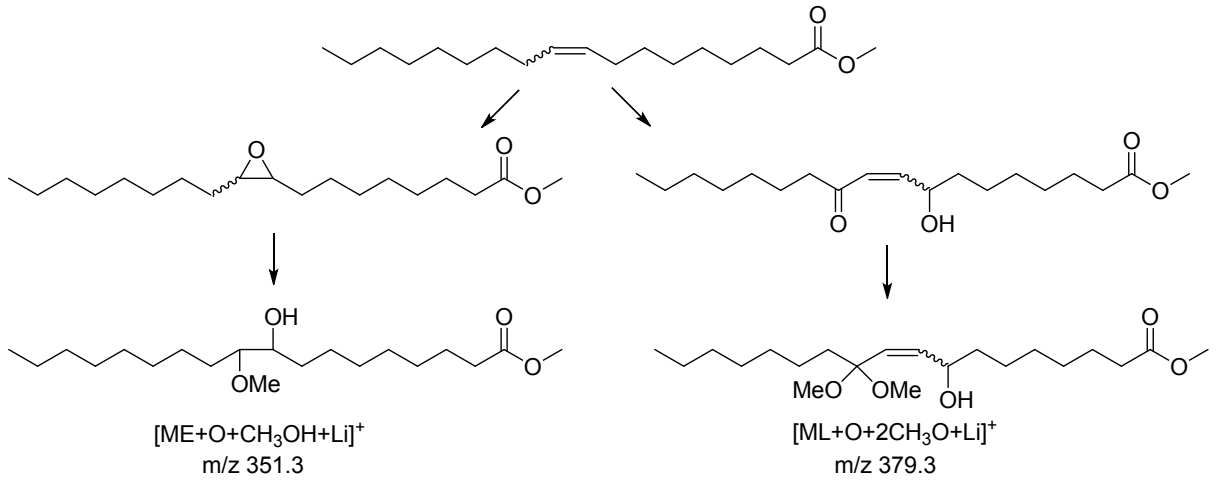


Figure SI.2. Photo-oxidation kinetic study of methyl elaidate: evolution of (a) double bond conversion and (b) OH absorbance variation – T = 30°C, polychromatic light (I_0 = 120 mW.cm^{-2} at 365 nm)

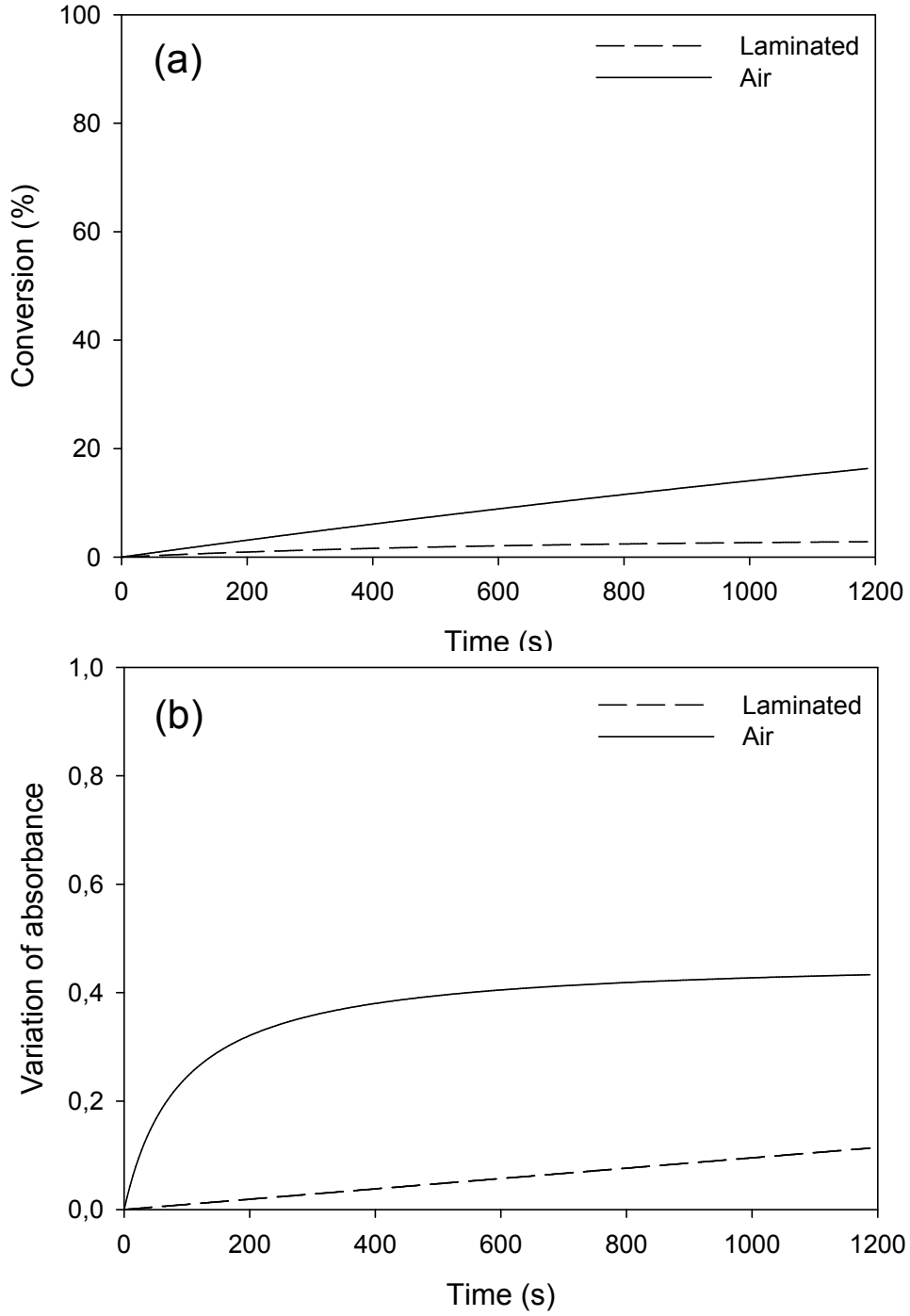


Figure SI.3. HRMS spectra of methyl oleate after different UV irradiation times under air

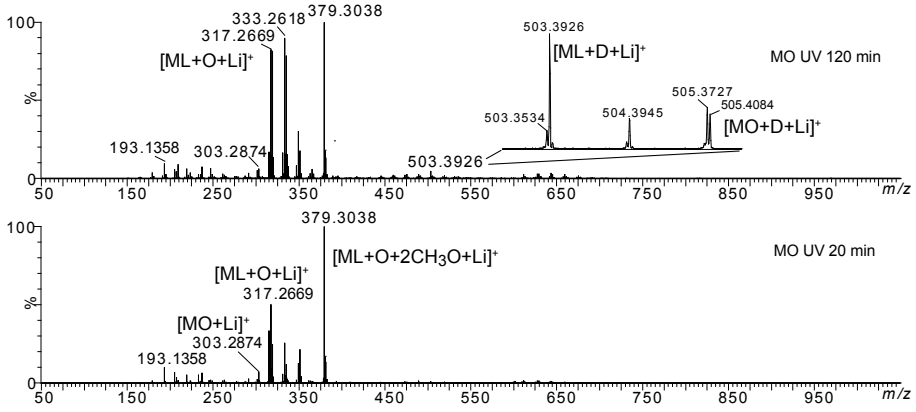
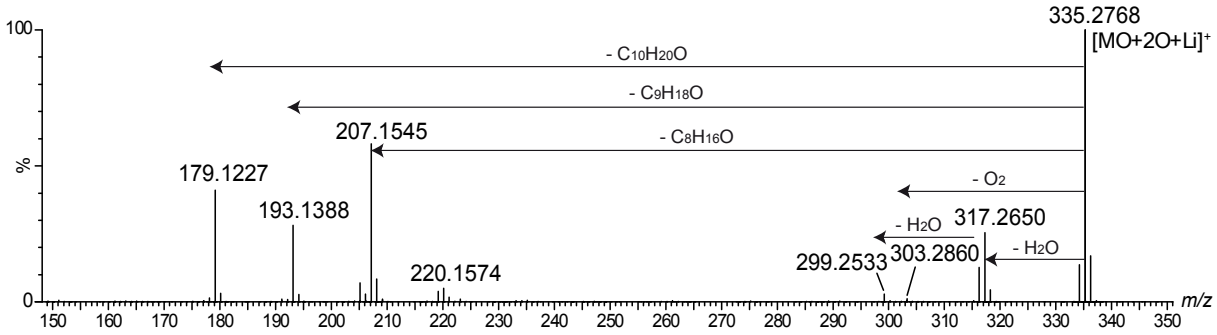


Figure SI.4. (a) MS^2 spectrum and (b) possible fragmentation mechanisms of $[MO+2O+Li]^+$ ion at *m/z* 335.2768

(a)



(b)

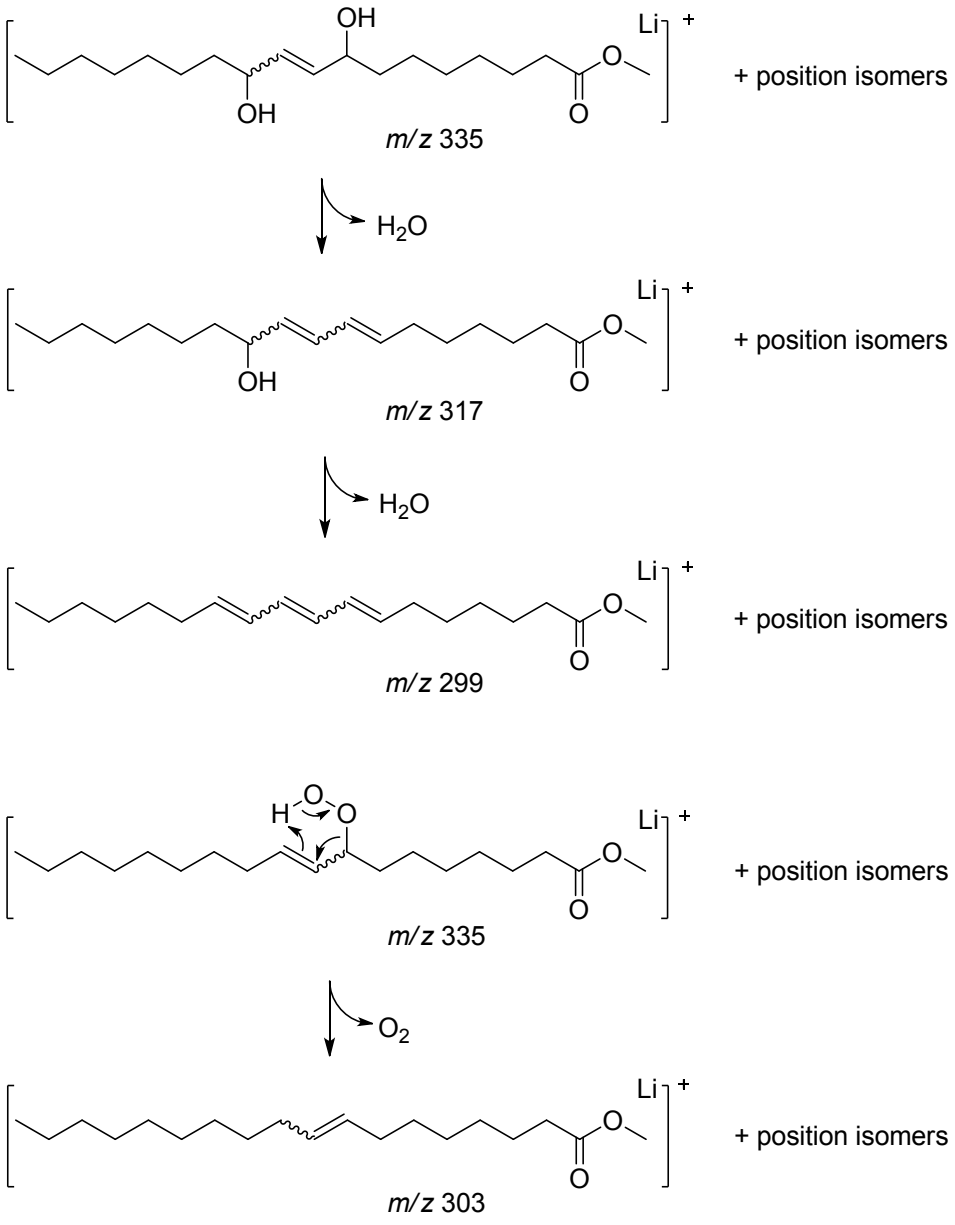
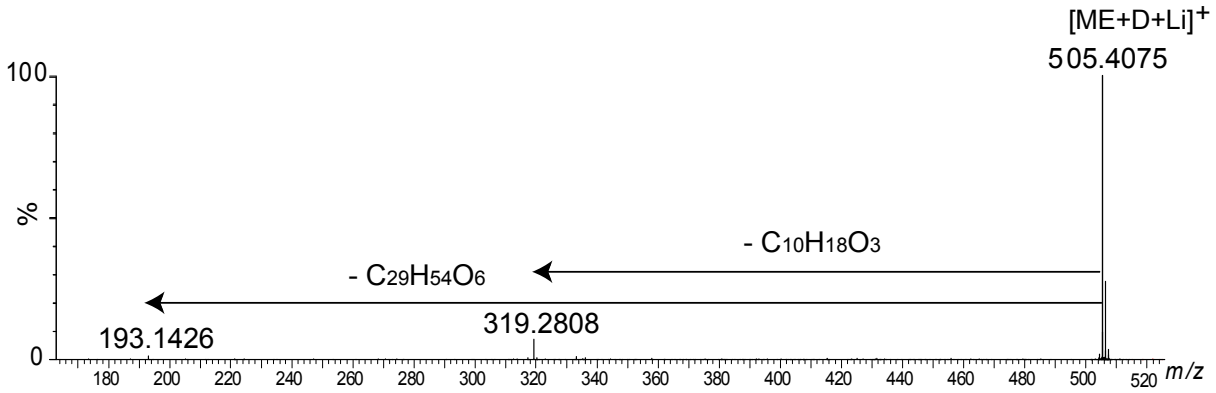


Figure SI.5. (a) MS^2 spectrum and (b) possible fragmentation mechanisms of $[ME+D+Li]^+$ ion at *m/z* 505.4075 (putative structure)

(a)



(b)

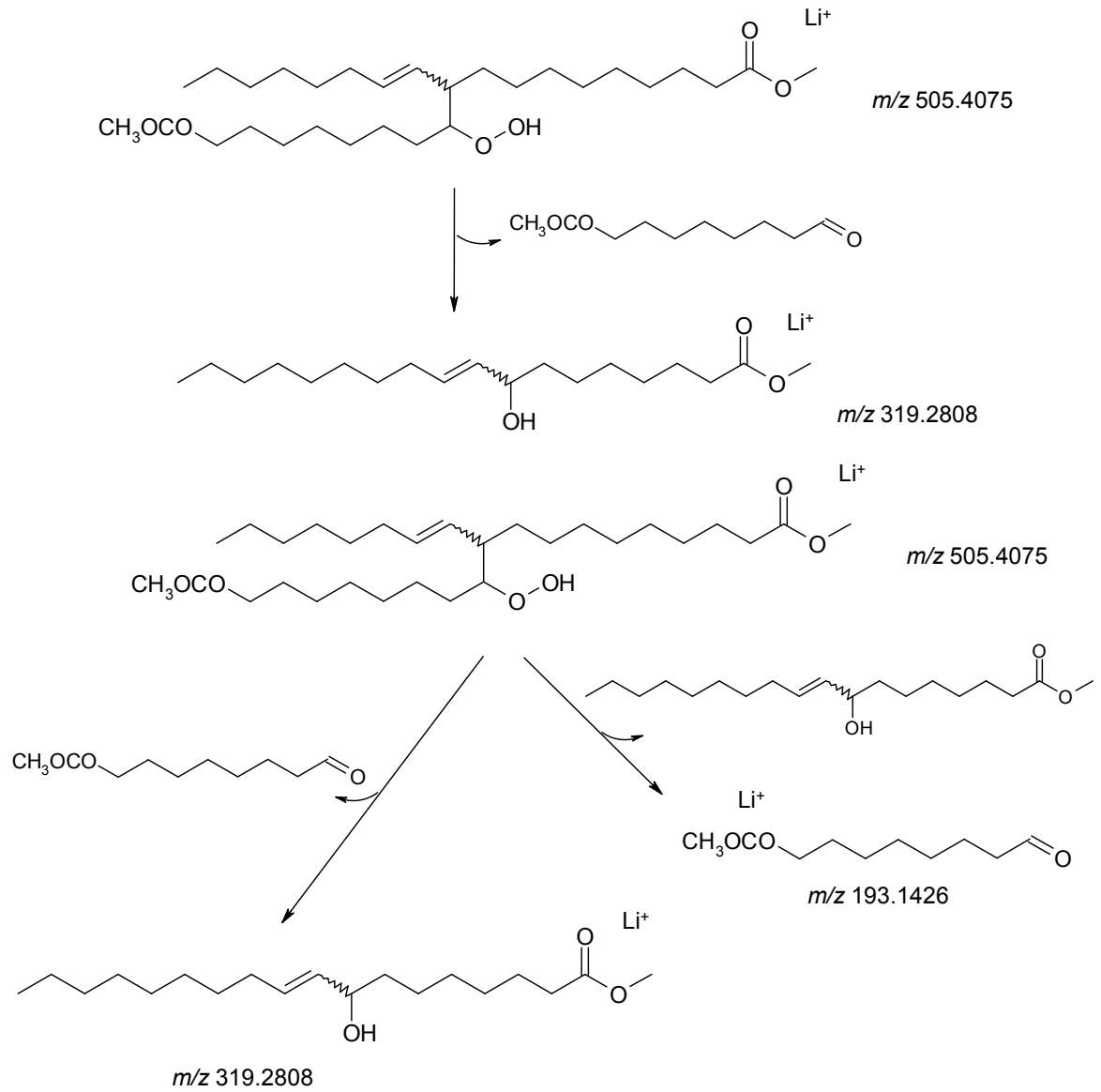


Figure SI.6. Comparison of photoinitiated thiol-ene kinetics of methyl elaidate in the presence or not of 0.5 equivalent SH: evolution of (a) double bond conversion and (b) OH absorbance variation – T = 30°C, polychromatic light (I_0 = 120 mW.cm^{-2} at 365 nm)

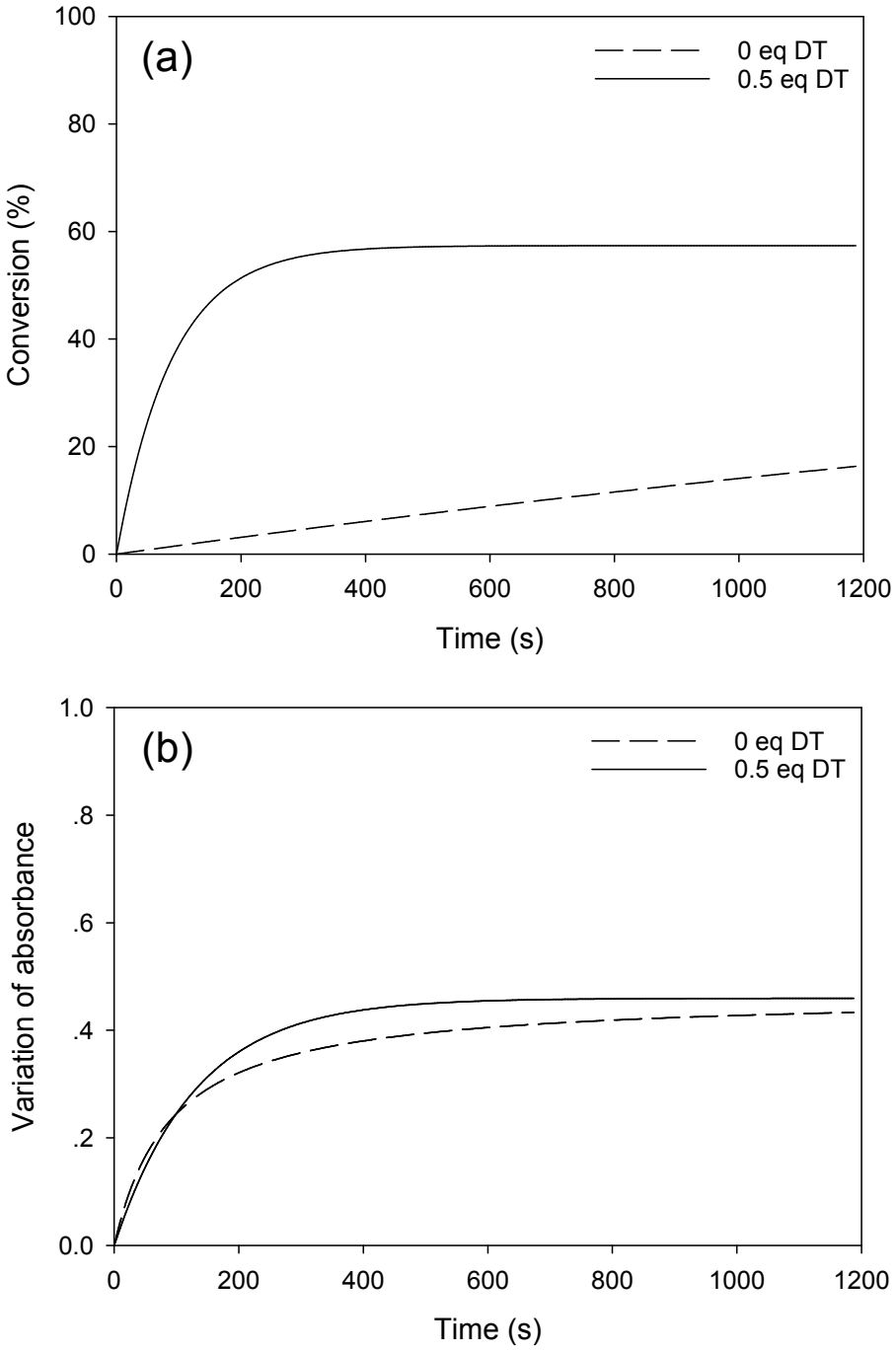
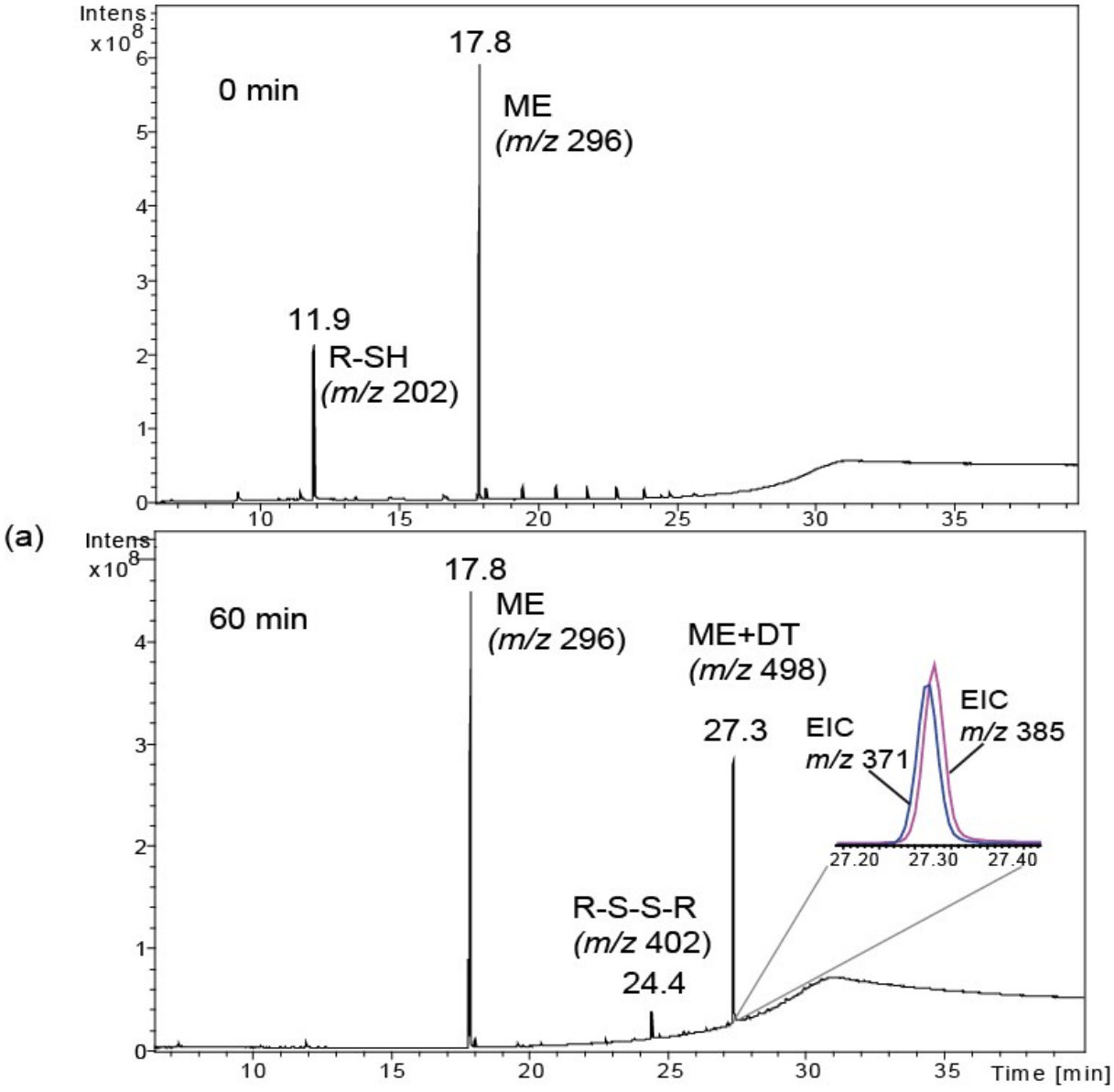


Figure SI.7. GC-MS spectra for the mixture of methyl elaidate + 0.5 eq dodecanethiol as a function of irradiation time: (a) TICC of irradiated reaction media at 0 min and 60 min and (b) EI mass spectra of the two region-isomers of thiol-ene adduct at *m/z* 498.4 (first mass spectra is extracted at the beginning of the chromatographic peak while the second mass spectra is extracted at the end of the chromatographic peak). The *m/z* values of the molecular ions are reported into brackets)



(b)

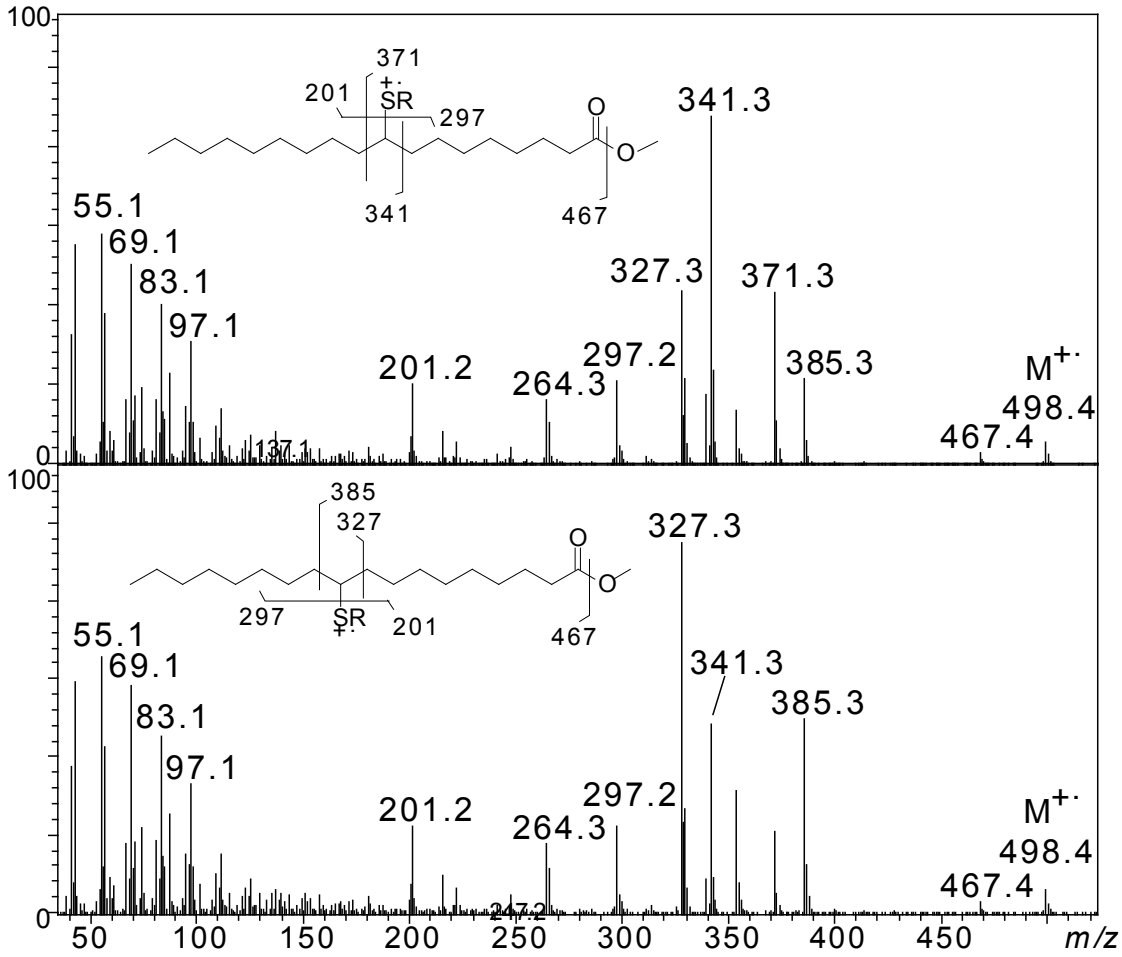

100
0
371
+·
201
SR
297
341
467
O
O
341.3
55.1
69.1
83.1
97.1
327.3
371.3
201.2
264.3
297.2
385.3
M+·
498.4
467.4
137.1
100
0
385
327
297
SR
+·
201
467
O
O
327.3
55.1
69.1
83.1
97.1
341.3
385.3
201.2
264.3
297.2
M+·
498.4
467.4
247.2
50
100
150
200
250
300
350
400
450
m/z

Figure SI.8. ESI-MS spectra of methyl oleate + 0.5 eq dodecanethiol as a function of irradiation time

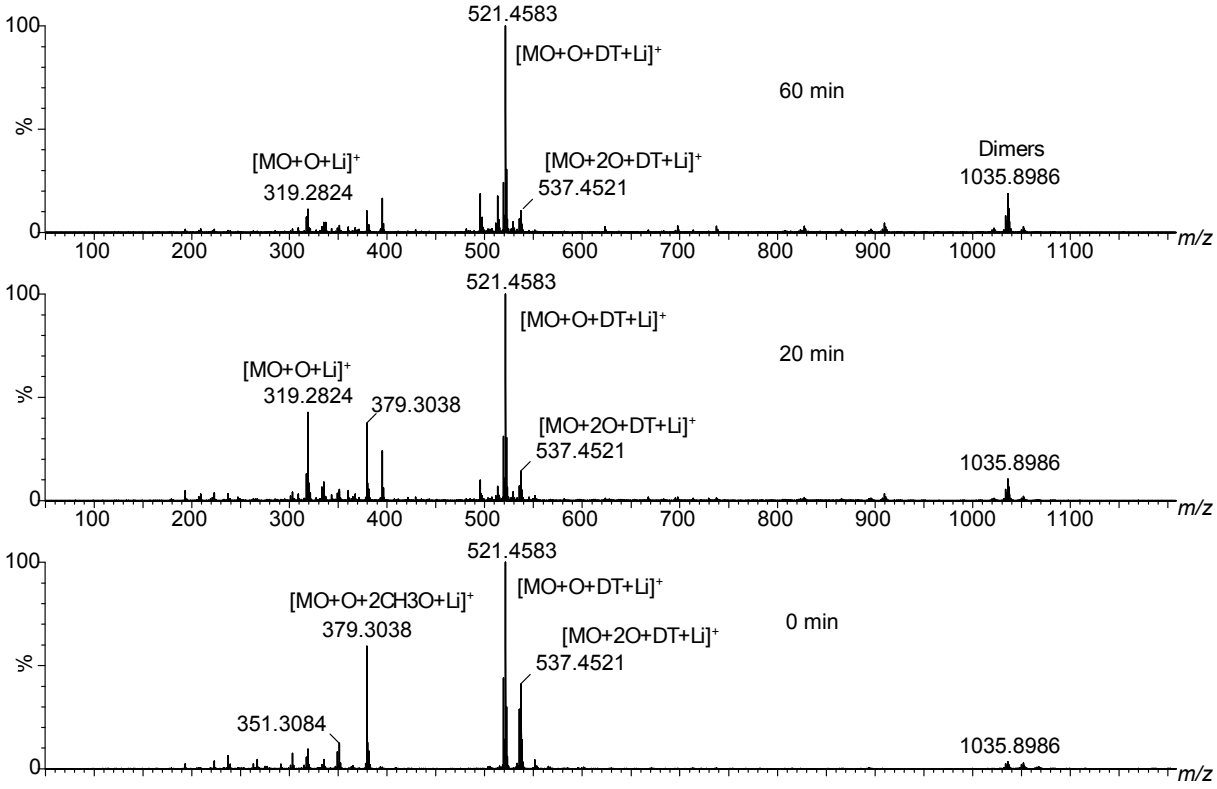


Figure SI.9. ESI-IMS-MS/MS spectra of the thiol-ene adduct ions at (a) *m/z* 505.4623, (b) *m/z* 521.4583 and (c) *m/z* 537.4521