SUPPORTING INFORMATION FOR PUBLICATION

Structural Identification of Monounsaturated Branched Chain Fatty Acid Methyl Esters by Combination of Electron Ionization and Covalent Adduct Chemical Ionization Tandem Mass Spectrometry

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The Supporting Information contains the following:

Table S1. Precursor ions and collision energy applied for MS/MS analysis of tested FAME.

Figure S1. EI-MS/MS spectra of isomeric 17:0 and isomeric 19:0 FAME. (A) *n*-17:0; (B) *iso*-17:0; (C) *anteiso*-17:0; (D) *n*-19:0; (E) *iso*-19:0; (F) *anteiso*-19:0.

Figure S2. CI-MS/MS spectra at collision energies 3V and 18V of isomeric 17:0 FAME fragmented from $[MH]^+$ at *m/z* 285. (A) *n*-17:0 (3V); (B) *iso*-17:0 (3V); (C) *anteiso*-17:0 (3V); (D) *n*-17:0 (18V); (E) *iso*-17:0 (18V); (F) *anteiso*-17:0 (18V).

Figure S3. CI-MS/MS spectra at collision energies 3V, 6V and 18V of isomeric 17:1 FAME fragmented from $[MH]^+$ at *m/z* 283. (A) *n*-6*Z*-17:1 (3V); (B) *iso*-6*Z*-17:1 (3V); (C) *anteiso*-6*Z*-17:1 (3V); (D) *n*-6*Z*-17:1 (6V); (E) *iso*-6*Z*-17:1 (6V); (F) *anteiso*-6*Z*-17:1 (6V); (G) *n*-6*Z*-17:1 (18V); (H) *iso*-6*Z*-17:1 (18V); (I) *anteiso*-6*Z*-17:1 (18V).

Figure S4. *m/z* 141 is present in EI-MS/MS spectra of MUFAME and monocyclopropane FAME (A) Elaidic acid 9*E*-18:1; (B) Oleic acid 9*Z*-18:1; (C) *Cis*-vaccenic acid 11*Z*-18:1; (D) 7,8-cyclopropane-17:0; (E) 9,10-cyclopropane-19:0.

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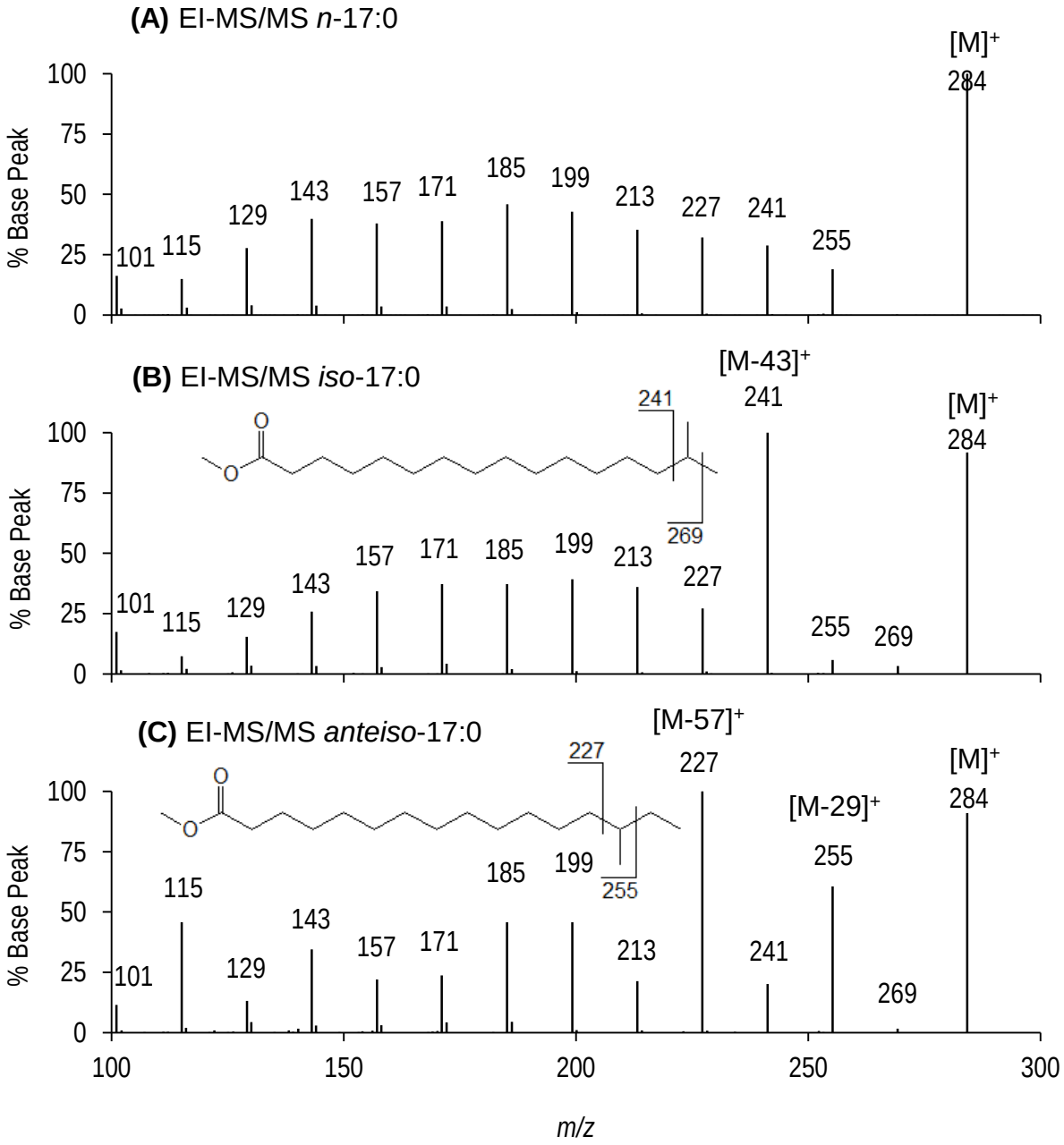
Table S1. Precursor ions and collision energy applied for MS/MS analysis of tested FAME.

FAME (*n*-, i*so*- and *anteiso*-)	Molecular Mass (*m/z*)	EI-MS/MS		CI-MS/MS	
		Precursor Ion $[M]^+$ (*m/z*)	Collision energy (V)	Precursor Ion $[M+54]^+$ (*m/z*)	Collision energy (V)
15:1	254	254	3	308	6
16:1	268	268	3	322	6
17:1	282	282	3	336	6
18:1	296	296	3	350	6
19:1	310	310	3	364	6
20:1	324	324	3	378	6


(A) EI-MS/MS n-17:0
[M]+
284
100
75
50
25
0
% Base Peak
101
115
129
143
157
171
185
199
213
227
241
255
(B) EI-MS/MS iso-17:0
[M-43]+
241
241
[M]+
284
O
O
269
100
75
50
25
0
% Base Peak
101
115
129
143
157
171
185
199
213
227
255
269
(C) EI-MS/MS anteiso-17:0
[M-57]+
227
227
[M]+
284
O
O
[M-29]+
255
100
75
50
25
0
% Base Peak
115
185
199
255
143
157
171
213
241
101
129
269
100
150
200
250
300
m/z

34

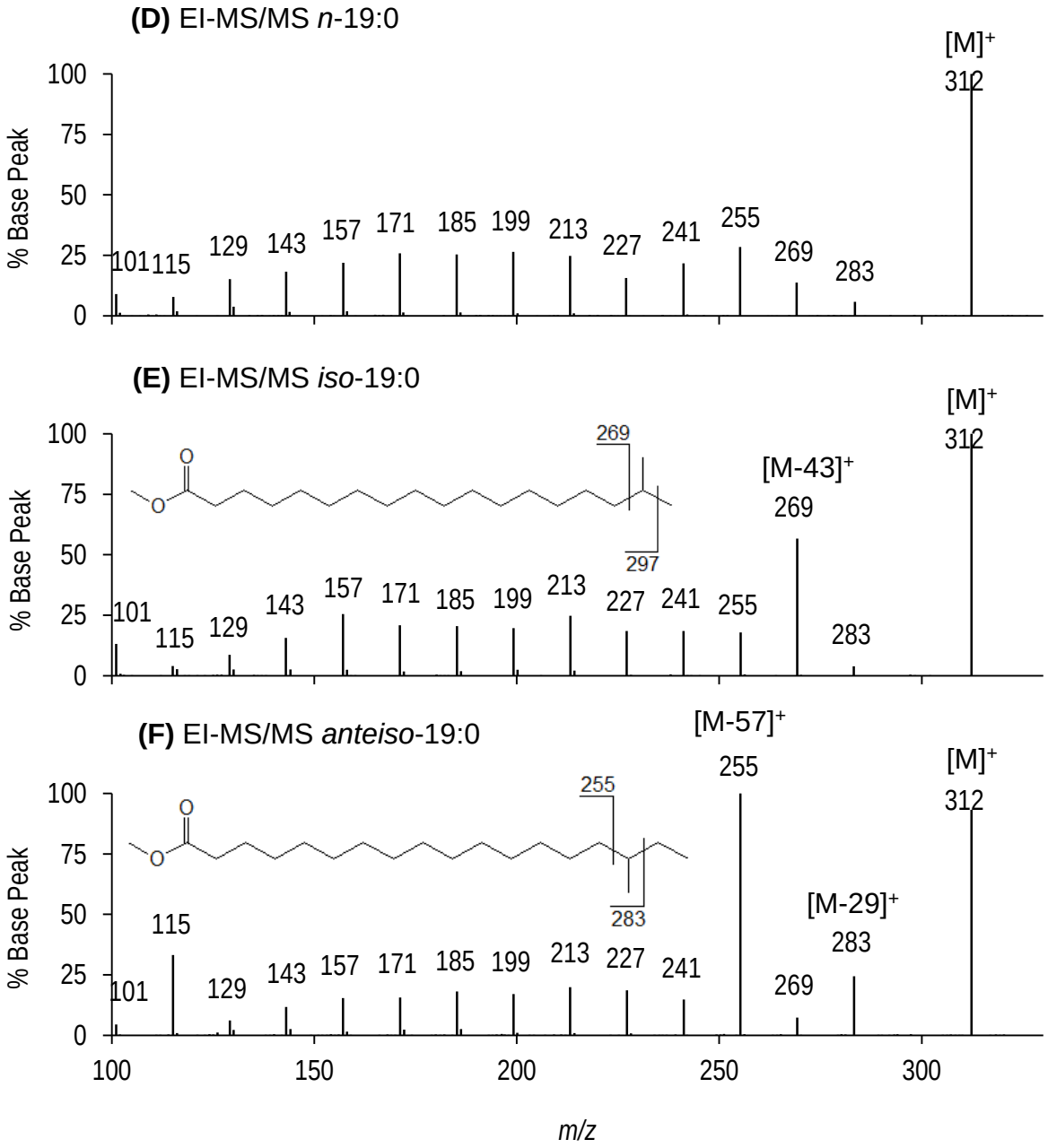
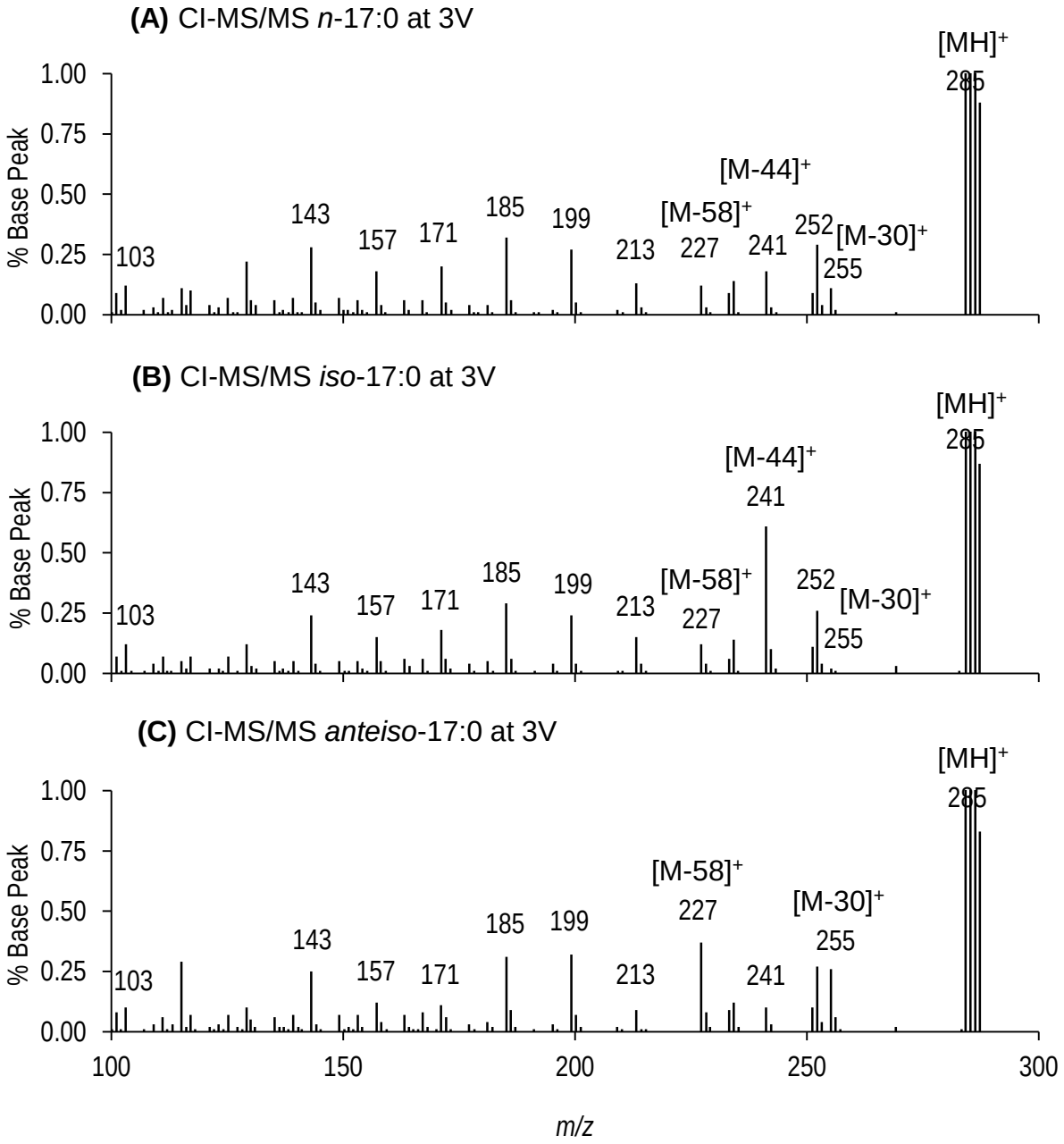


Figure S1. EI-MS/MS spectra of isomeric 17:0 and isomeric 19:0 FAME. (A) *n*-17:0; (B) *iso*-17:0; (C) *anteiso*-17:0; (D) *n*-19:0; (E) *iso*-19:0; (F) *anteiso*-19:0. $[M-43]^+$ is the only diagnostic ion of *iso*-SBCFA; while both $[M-57]^+$ and $[M-29]^+$ are diagnostic ions of *anteiso*-SBCFA, among which $[M-57]^+$ is the most prominent.


(A) CI-MS/MS n-17:0 at 3V
(B) CI-MS/MS iso-17:0 at 3V
(C) CI-MS/MS anteiso-17:0 at 3V
% Base Peak
1.00
0.75
0.50
0.25
0.00
[MH]+
285
[M-44]+
[M-58]+
[M-30]+
103
143
157
171
185
199
213
227
241
252
255
100
150
200
250
300
m/z

41

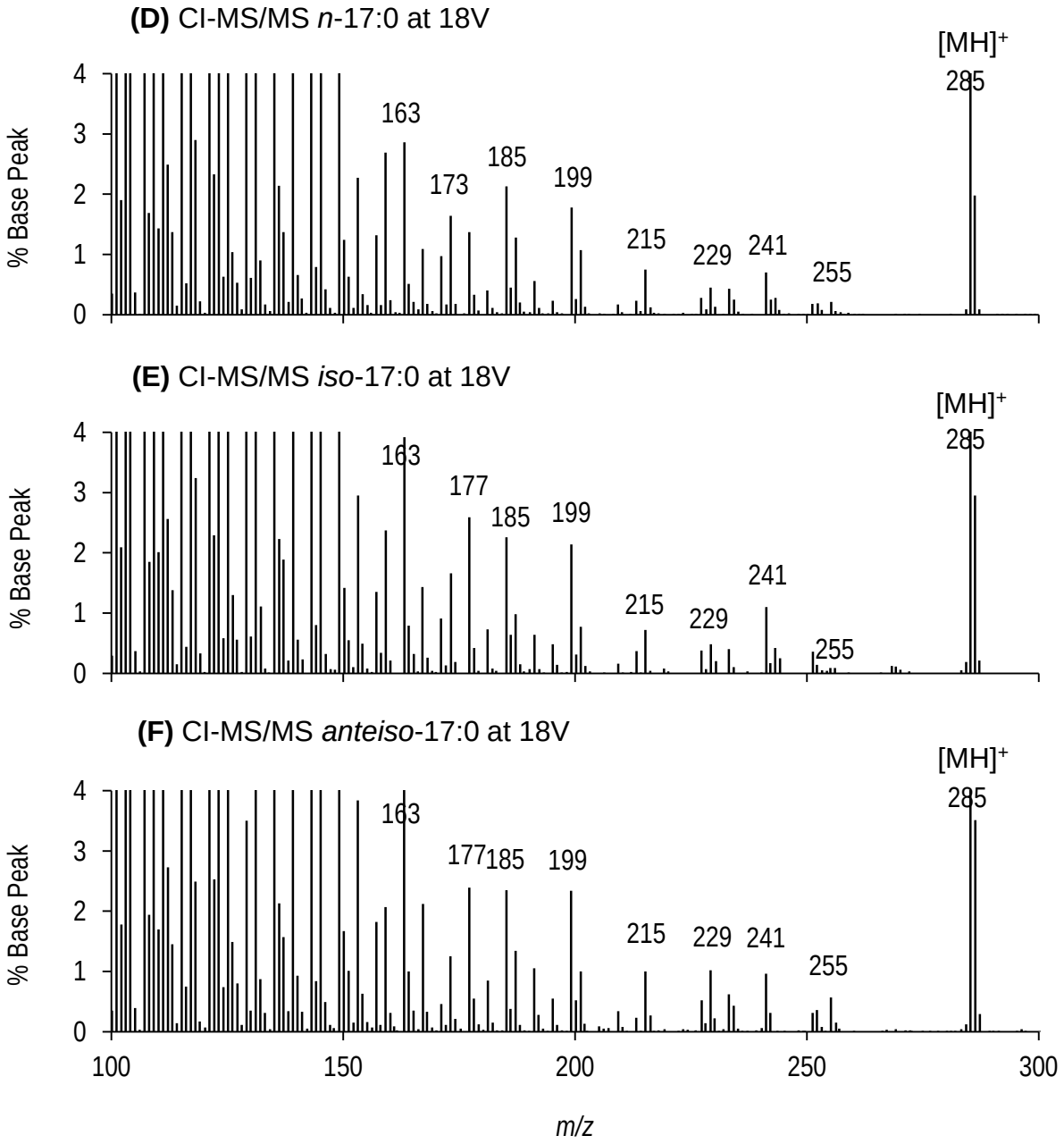
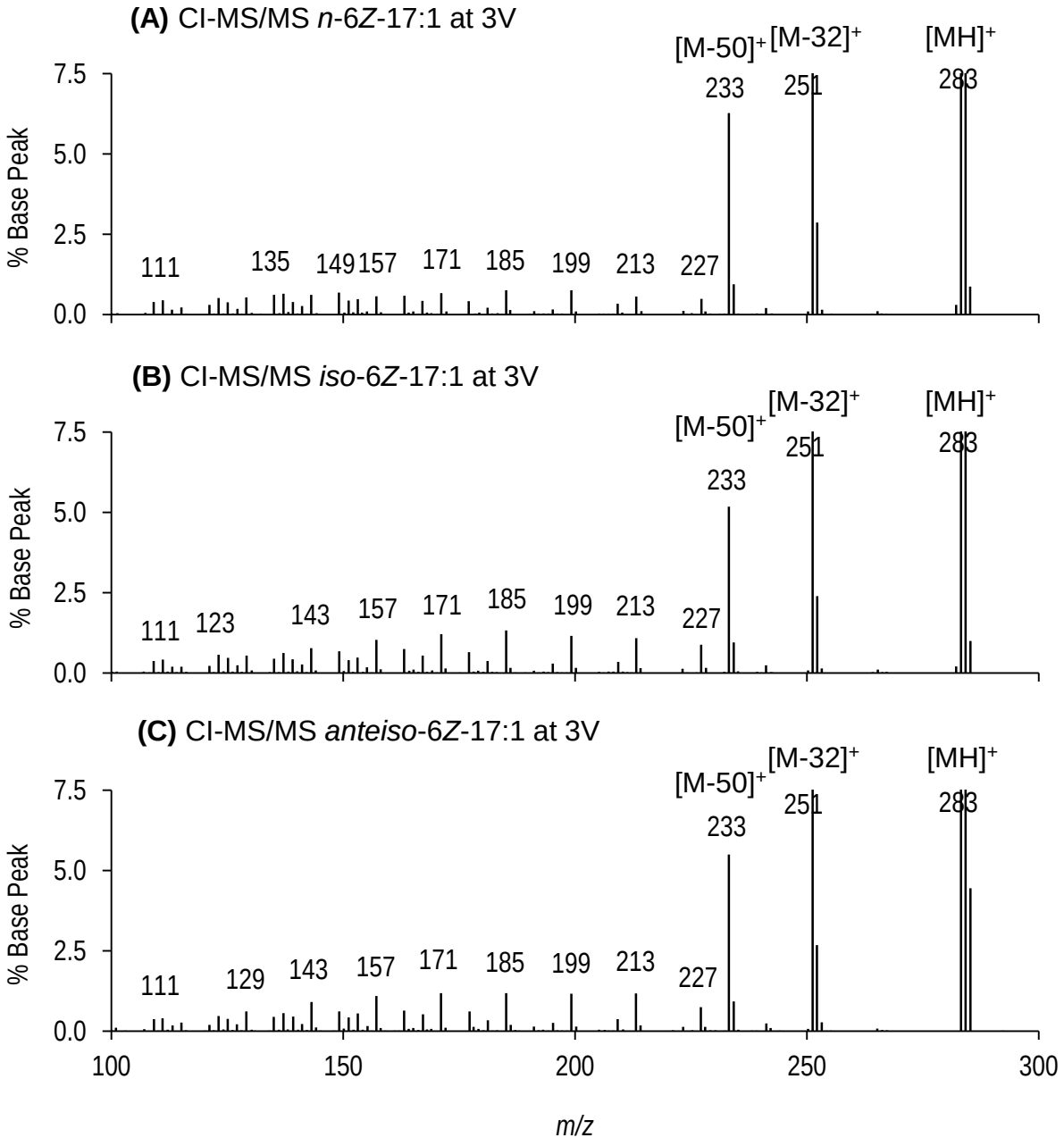
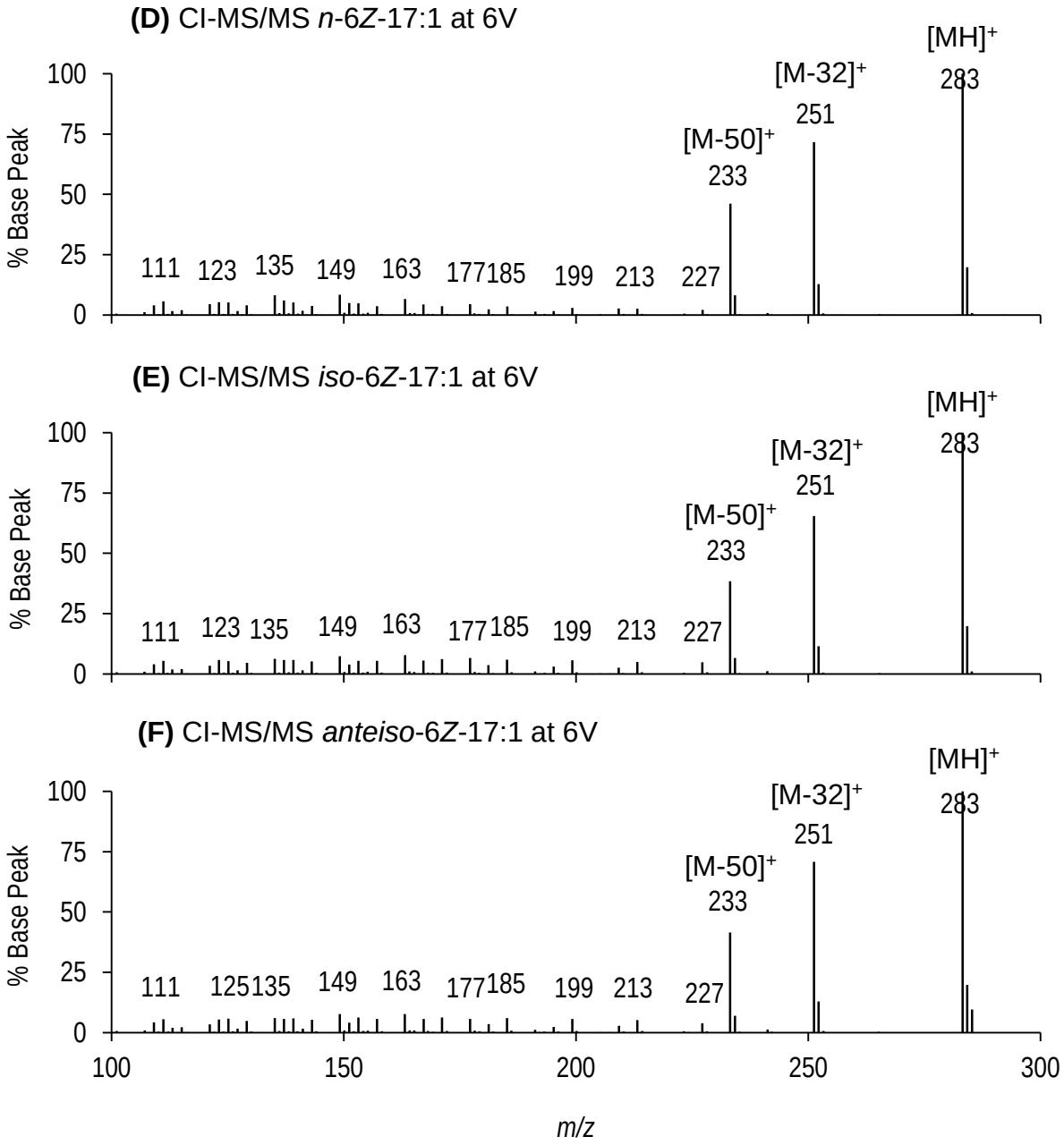


Figure S2. CI-MS/MS spectra at collision energies 3V and 18V of isomeric 17:0 FAME fragmented from $[MH]^+$ at *m/z* 285. (A) *n*-17:0 (3V); (B) *iso*-17:0 (3V); (C) *anteiso*-17:0 (3V); (D) *n*-17:0 (18V); (E) *iso*-17:0 (18V); (F) *anteiso*-17:0 (18V). Compared to collision energy at 6V presented in Figure 9, CI-MS/MS at 3V yield similar but lower abundance of characteristic ions for assigning branched ends of isomeric 17:0. 18V is too high to generate useful characteristic ions as 3V and 6V.


(A) CI-MS/MS n-6Z-17:1 at 3V
(B) CI-MS/MS iso-6Z-17:1 at 3V
(C) CI-MS/MS anteiso-6Z-17:1 at 3V
% Base Peak
7.5
5.0
2.5
0.0
[M-50]+
[M-32]+
[MH]+
233
251
283
111
123
129
135
143
149
157
171
185
199
213
227
100
150
200
250
300
m/z

50


(D) CI-MS/MS n-6Z-17:1 at 6V
(E) CI-MS/MS iso-6Z-17:1 at 6V
(F) CI-MS/MS anteiso-6Z-17:1 at 6V
% Base Peak
100
75
50
25
0
[MH]+
283
[M-32]+
251
[M-50]+
233
111
123
125
135
149
163
177
185
199
213
227
100
150
200
250
300
m/z

51

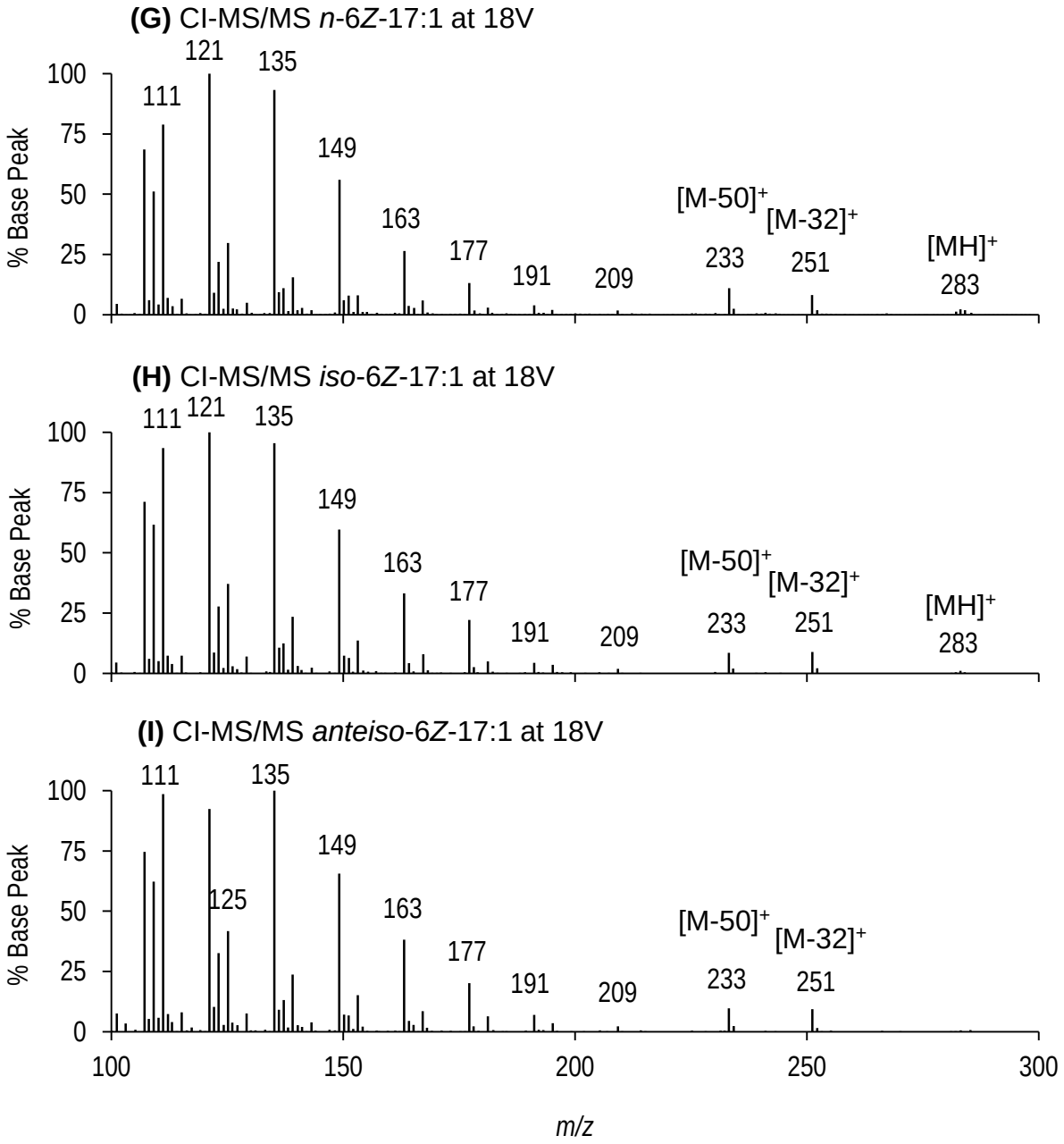
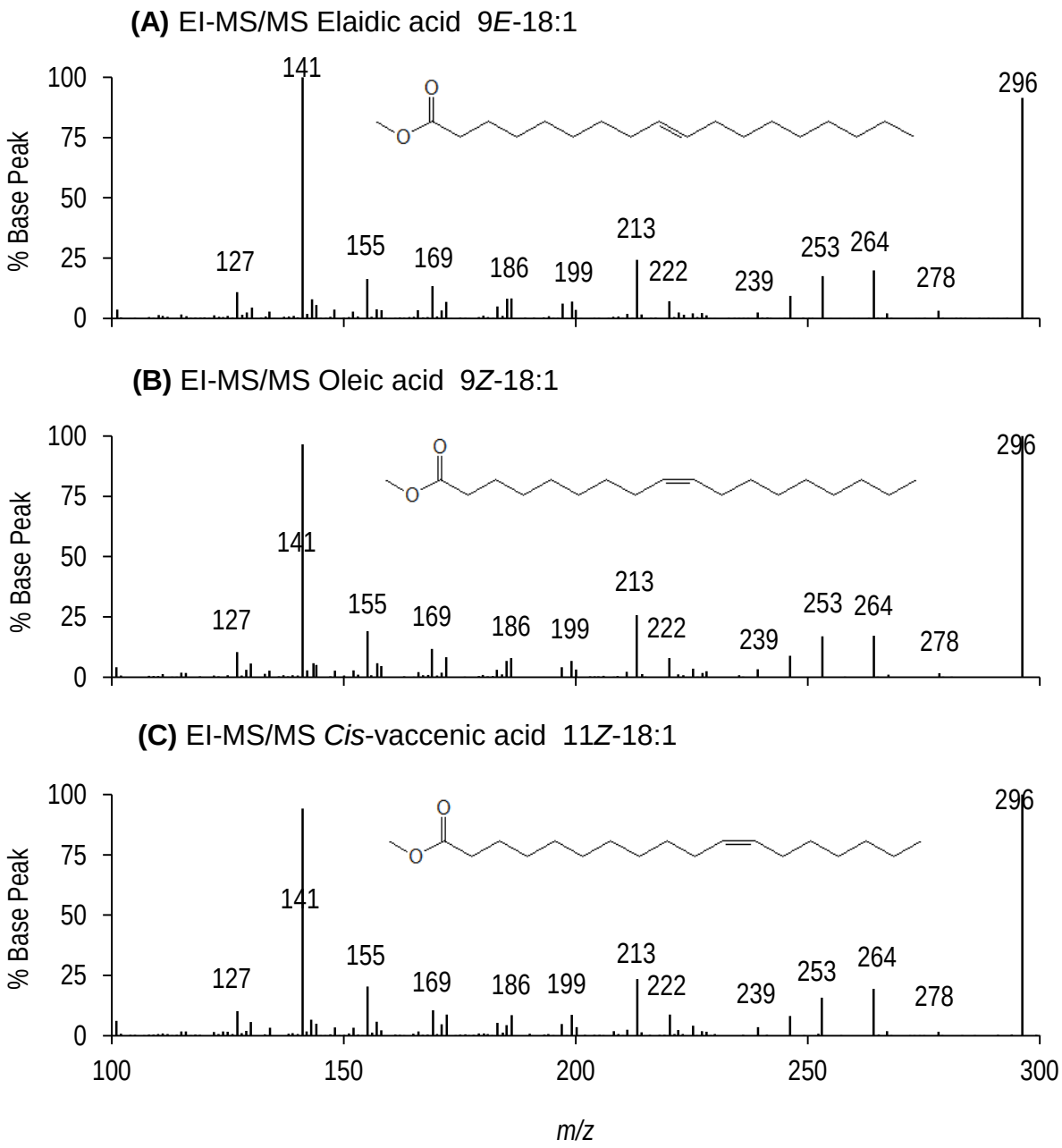


Figure S3. CI-MS/MS spectra at collision energies 3V, 6V and 18V of isomeric 17:1 FAME fragmented from $[MH]^+$ at *m/z* 283. (A) *n*-6*Z*-17:1 (3V); (B) *iso*-6*Z*-17:1 (3V); (C) *anteiso*-6*Z*-17:1 (3V); (D) *n*-6*Z*-17:1 (6V); (E) *iso*-6*Z*-17:1 (6V); (F) *anteiso*-6*Z*-17:1 (6V); (G) *n*-6*Z*-17:1 (18V); (H) *iso*-6*Z*-17:1 (18V); (I) *anteiso*-6*Z*-17:1 (18V). Isomeric 17:1 share the most abundant ions $[MH-32]^+$ and $[MH-50]^+$ at *m/z* 251 and 233 when collision energy is 3V or 6V. After careful inspection, no unique ions are found to distinguish isomeric 17:1 at either 3V, 6V or 18V.


(A) EI-MS/MS Elaidic acid 9E-18:1
(B) EI-MS/MS Oleic acid 9Z-18:1
(C) EI-MS/MS Cis-vaccenic acid 11Z-18:1
% Base Peak
m/z
100
75
50
25
0
100
150
200
250
300
141
296
127
155
169
186
199
213
222
239
253
264
278

61

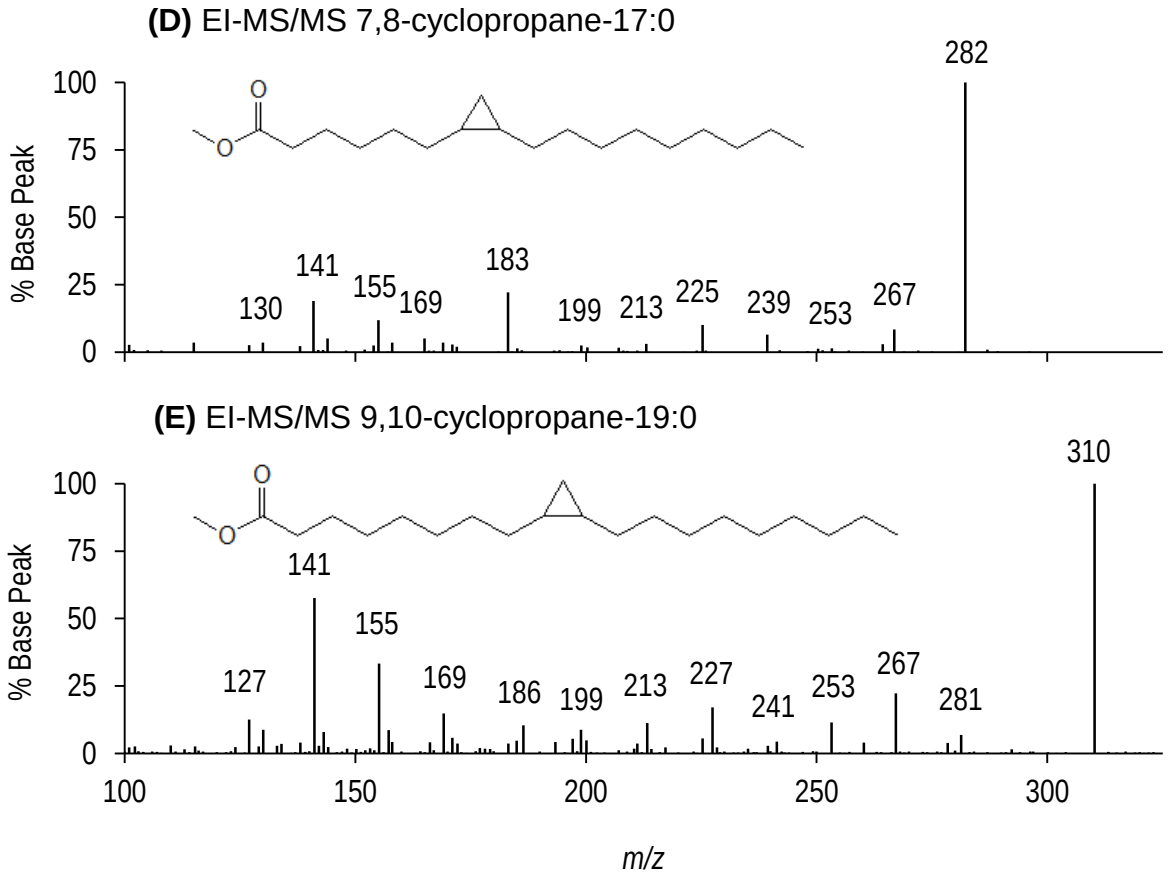


Figure S4. *m/z* 141 is present in EI-MS/MS spectra of MUFAME and monocyclopropane FAME (A) Elaidic acid 9*E*-18:1; (B) Oleic acid 9*Z*-18:1; (C) *Cis*-vaccenic acid 11*Z*-18:1; (D) 7,8-cyclopropane-17:0; (E) 9,10-cyclopropane-19:0.