Identification and classification of cathinone unknowns by statistical analysis processing of direct analysis in real time-high resolution mass spectrometry-derived "neutral loss" spectra.

SUPPLEMENTARY MATERIAL

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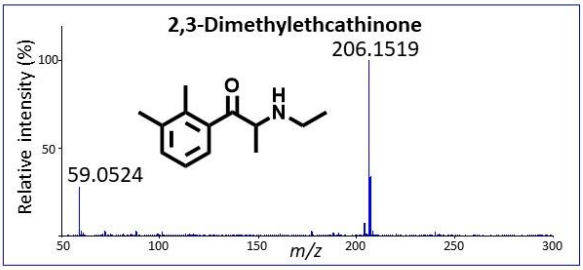
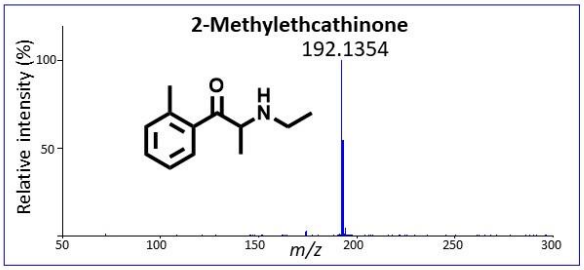
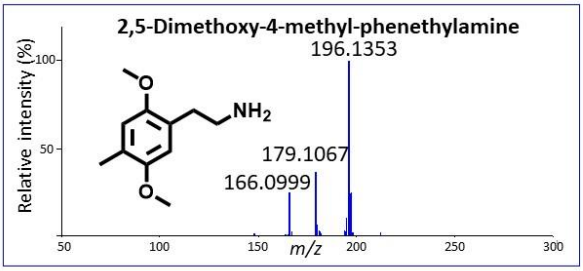
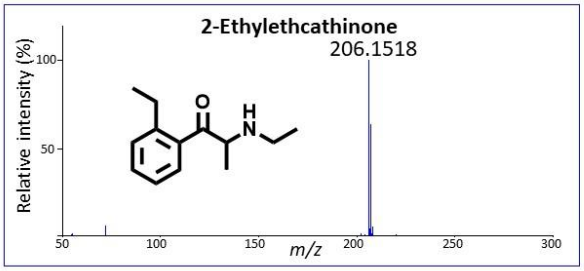
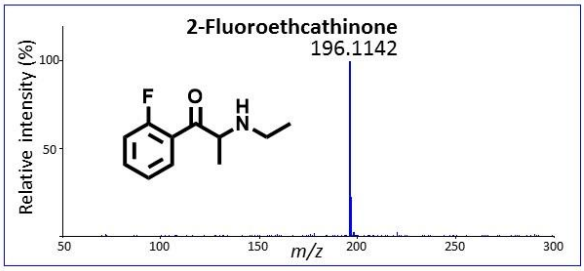
*Corresponding author: E-mail address: rmusah@albany.edu


2,3-Dimethylethcathinone
206.1519
59.0524
Relative intensity (%)
m/z


2-Methylethcathinone
192.1354
Relative intensity (%)
m/z


2,5-Dimethoxy-4-methyl-phenethylamine
196.1353
179.1067
166.0999
Relative intensity (%)
m/z


2-Ethylethcathinone
206.1518
Relative intensity (%)
m/z


2-Fluoroethcathinone
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Relative intensity (%)
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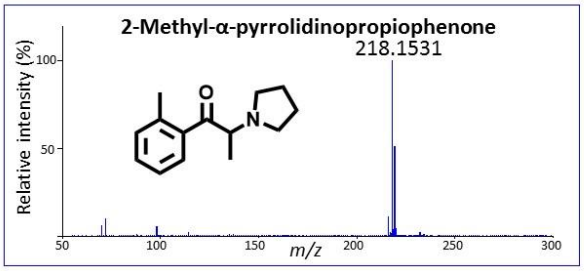
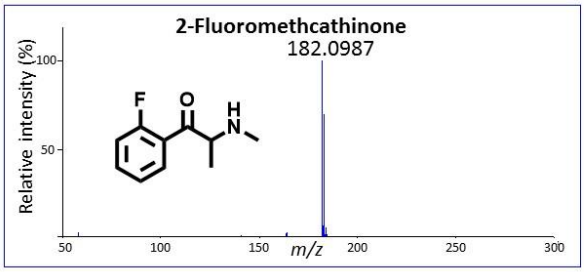
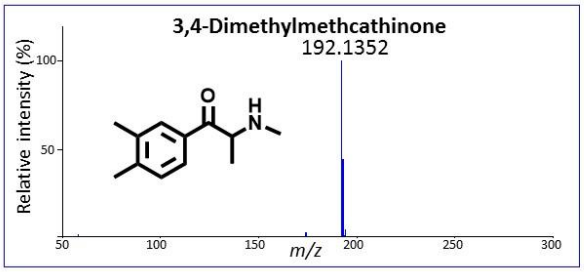

2-Methyl-α-pyrrolidinopropiophenone
218.1531
Relative intensity (%)
m/z


2-Fluoromethcathinone
182.0987
Relative intensity (%)
m/z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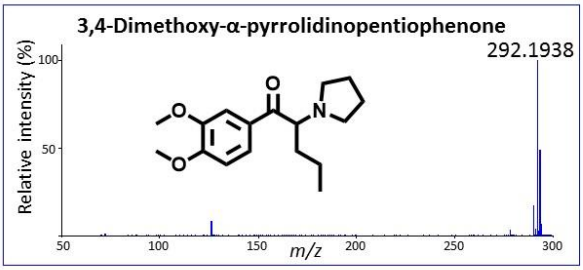
Relative intensity (%)
m/z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292.1938
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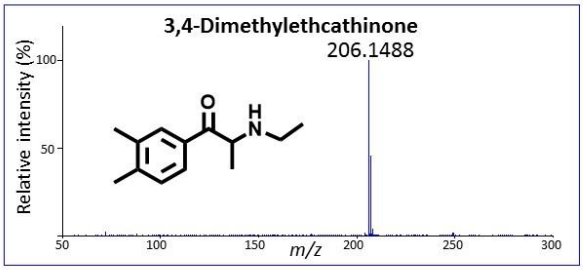
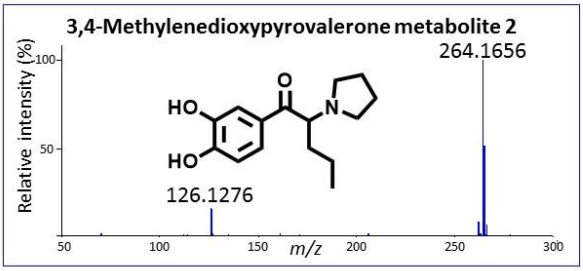
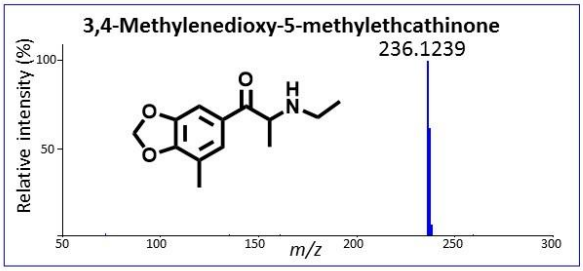
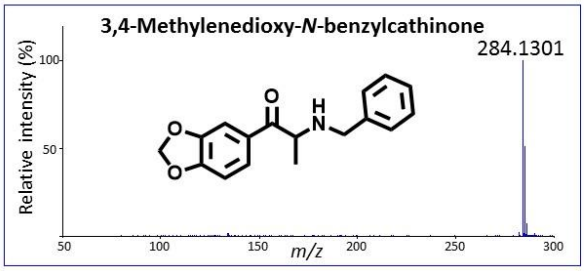
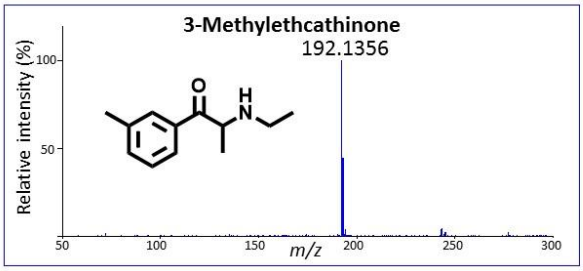
m/z

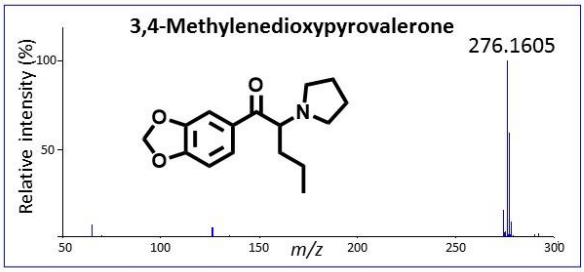

3,4-Dimethylethcathinone
206.1488
Relative intensity (%)
m/z


3,4-Methylenedioxypyrovalerone metabolite 2
264.1656
126.1276
Relative intensity (%)
m/z


3,4-Methylenedioxy-5-methylethcathinone
236.1239
Relative intensity (%)
m/z


3,4-Methylenedioxy-N-benzylcathinone
284.1301
Relative intensity (%)
m/z


3-Methylethcathinone
192.1356
Relative intensity (%)
m/z


3,4-Methylenedioxypyrovalerone
276.1605
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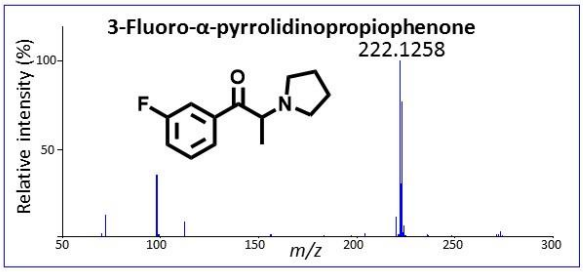
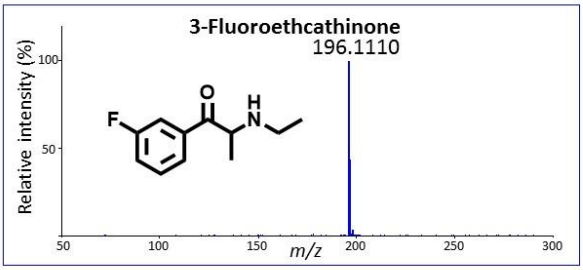
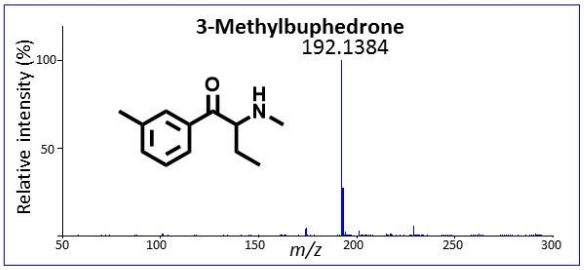
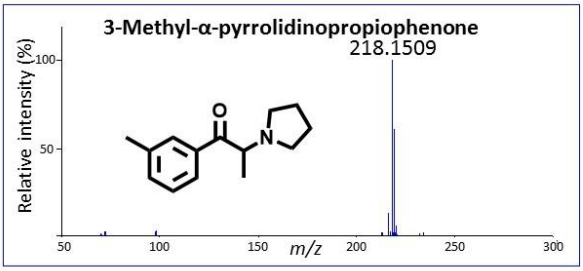
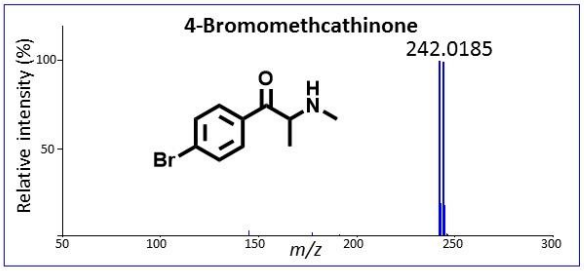
m/z


3-Fluoro-α-pyrrolidinopropiophenone
222.1258
Relative intensity (%)
m/z


3-Fluoroethcathinone
196.1110
Relative intensity (%)
m/z
F
O
H
N


3-Methylbuphedrone
192.1384
Relative intensity (%)
m/z
O
H
N


3-Methyl-α-pyrrolidinopropiophenone
218.1509
Relative intensity (%)
m/z
O
N


4-Bromomethcathinone
242.0185
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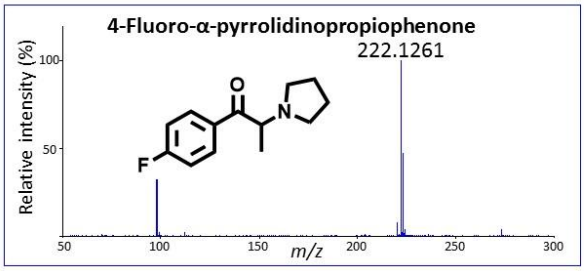
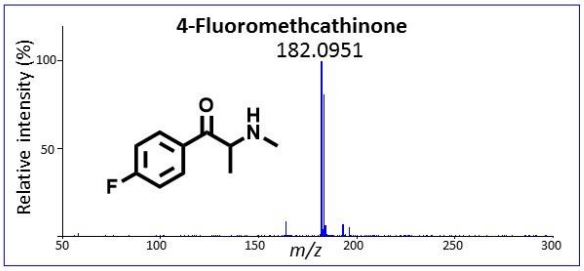
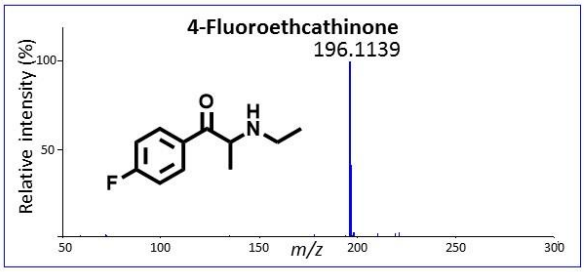
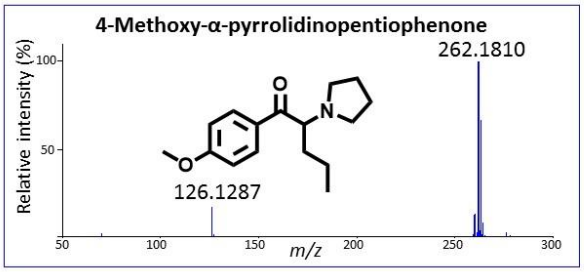
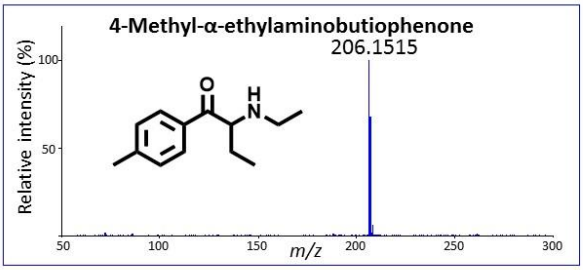
m/z
Br
O
H
N

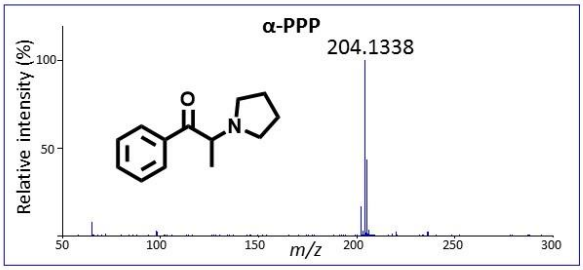

4-Fluoro-α-pyrrolidinopropiophenone
222.1261
Relative intensity (%)
m/z
F
O
N

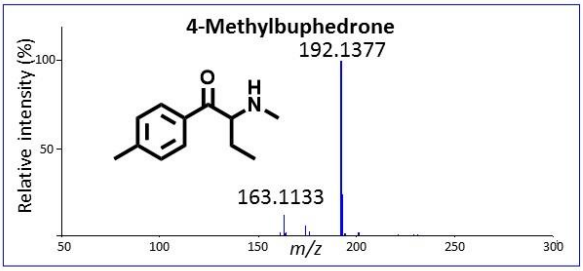

4-Fluoromethcathinone
182.0951
Relative intensity (%)
m/z
F
O
H
N

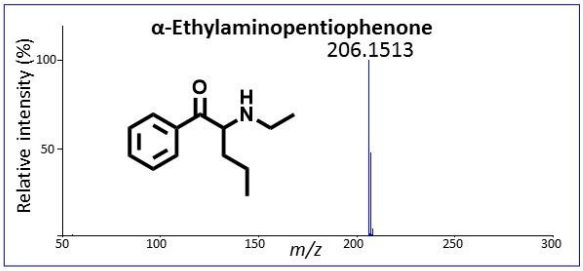

4-Fluoroethcathinone
196.1139
Relative intensity (%)
m/z
F
O
H
N

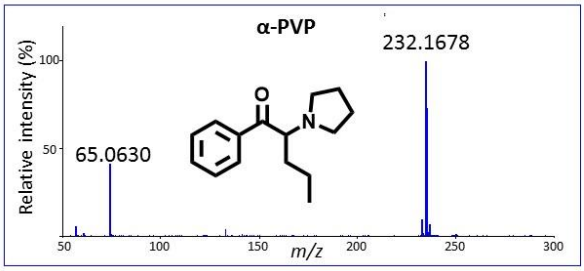

4-Methoxy-α-pyrrolidinopentiophenone
262.1810
126.1287
Relative intensity (%)
m/z
O
N


4-Methyl-α-ethylaminobutiophenone
206.1515
Relative intensity (%)
m/z


α-PPP
204.1338
Relative intensity (%)
m/z


4-Methylbuphedrone
192.1377
163.1133
Relative intensity (%)
m/z


α-Ethylaminopentiophenone
206.1513
Relative intensity (%)
m/z


α-PVP
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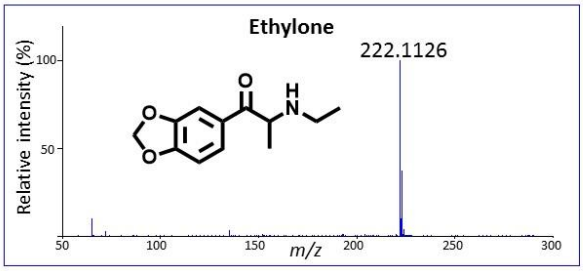
65.0630
Relative intensity (%)
m/z


Ethylone
222.1126
Relative intensity (%)
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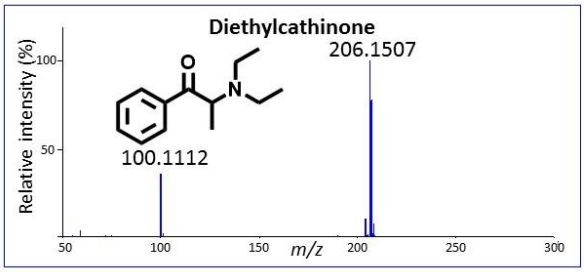
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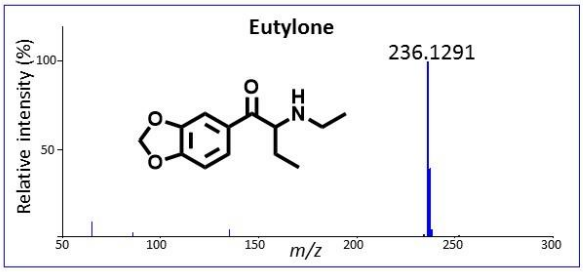
Eutylone
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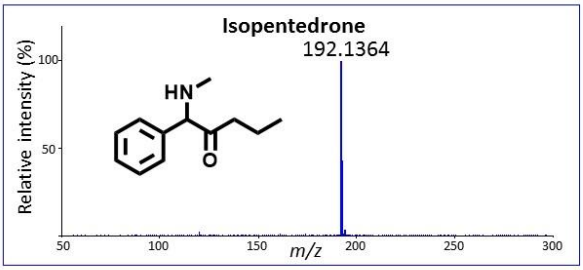
Relative intensity (%)
m/z


Isopentedrone
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HN
O
Relative intensity (%)
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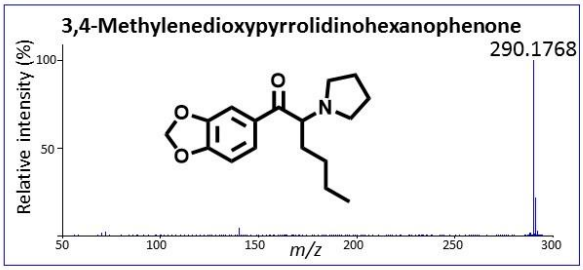
50
50
100
150
200
250
300
m/z


3,4-Methylenedioxypyrrolidinohexanophenone
290.1768
O
O
O
N
Relative intensity (%)
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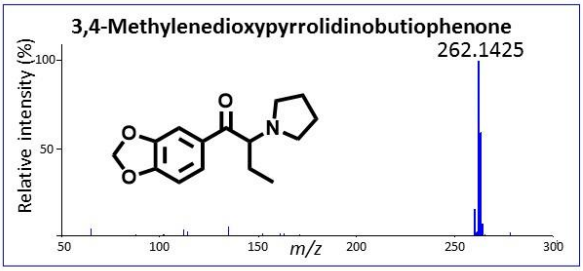
50
100
150
200
250
300
m/z


3,4-Methylenedioxypyrrolidinobutiophenone
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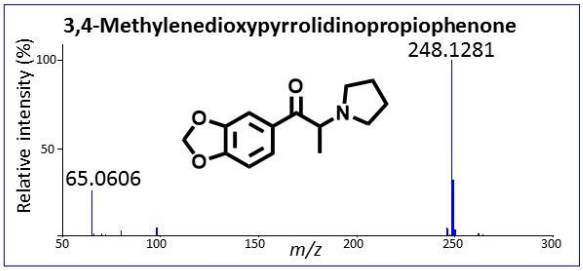
O
O
O
N
Relative intensity (%)
100
50
50
100
150
200
250
300
m/z


3,4-Methylenedioxypyrrolidinopropiophenone
248.1281
65.0606
O
O
O
N
Relative intensity (%)
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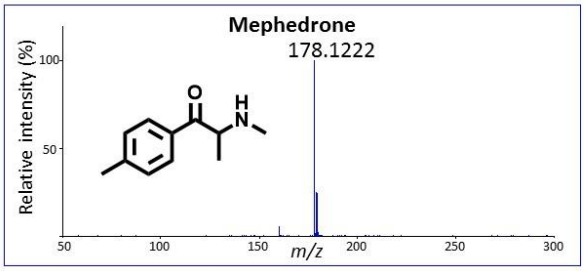
50
100
150
200
250
300
m/z


Mephedrone
178.1222
O
H
N
Relative intensity (%)
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50
50
100
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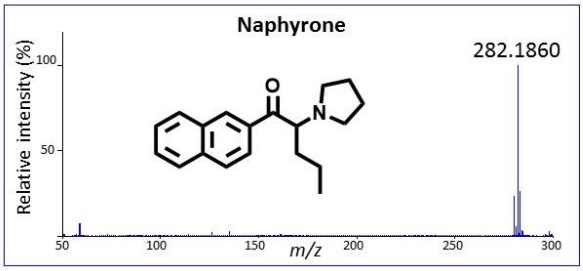
250
300
m/z


Naphyrone
282.1860
O
N
Relative intensity (%)
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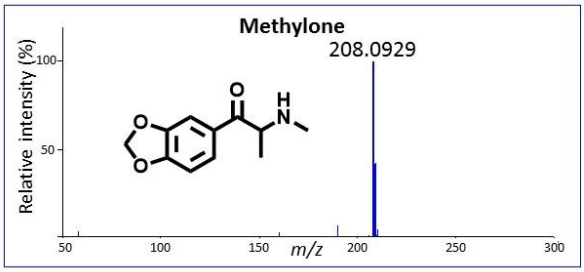
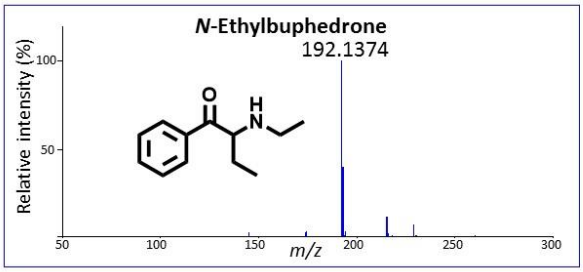
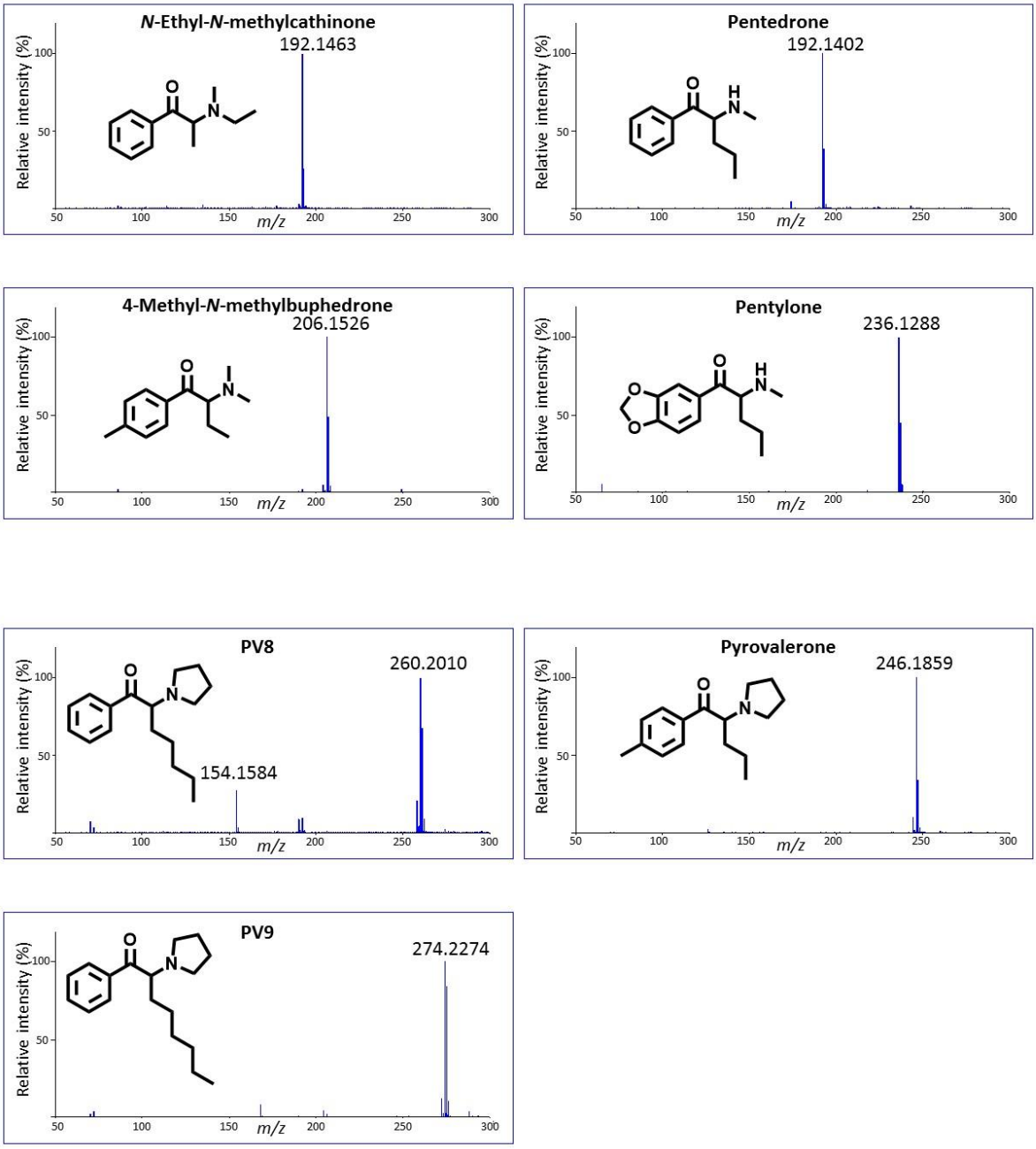
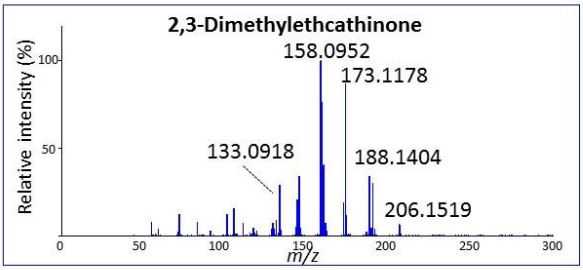
50
50
100
150
200
250
300
m/z

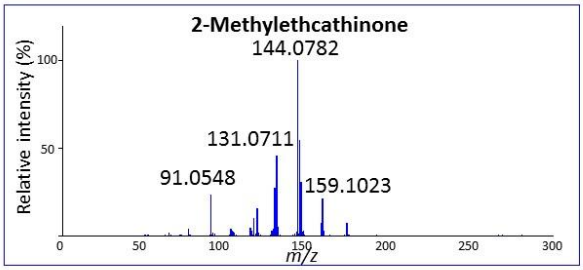

Methylone
208.0929
O
O
O
H
N
Relative intensity (%)
100
50
50
100
150
200
250
300
m/z

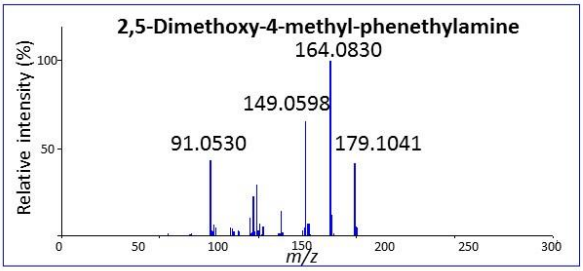

N-Ethylbuphedrone
192.1374
O
H
N
Relative intensity (%)
100
50
50
100
150
200
250
300
m/z

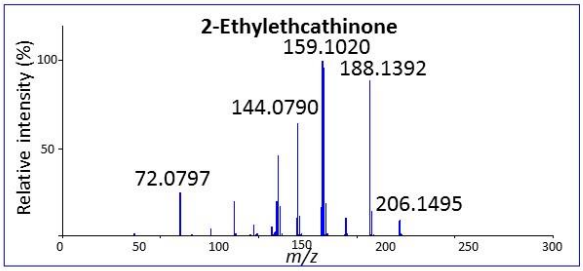


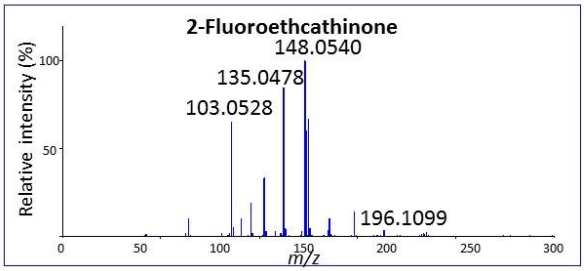
Supplementary Figure S1. The 20 V soft ionization spectra for the 47 cathinones analyzed in this study. The structures of the indicated cathinones are also shown.

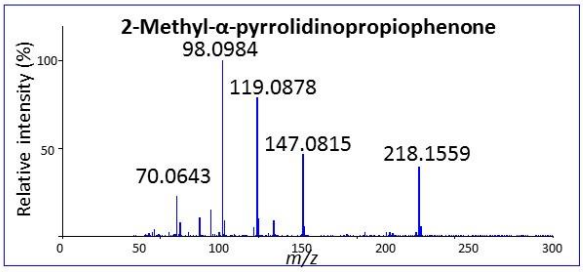

2,3-Dimethylethcathinone
158.0952
173.1178
133.0918
188.1404
206.1519
Relative intensity (%)
m/z

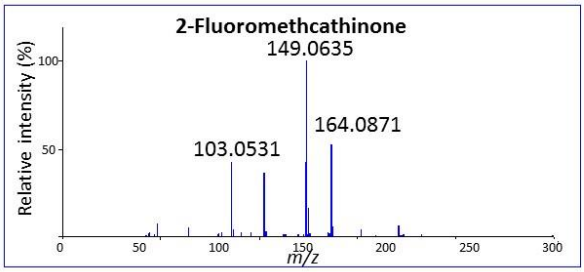

2-Methylethcathinone
144.0782
131.0711
91.0548
159.1023
Relative intensity (%)
m/z

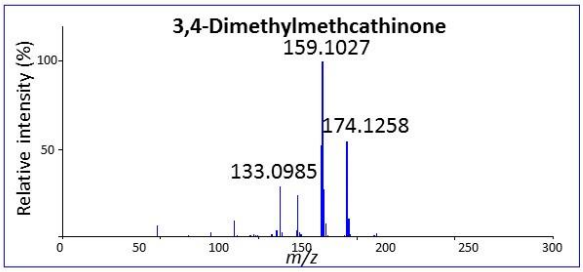

2,5-Dimethoxy-4-methyl-phenethylamine
164.0830
149.0598
91.0530
179.1041
Relative intensity (%)
m/z

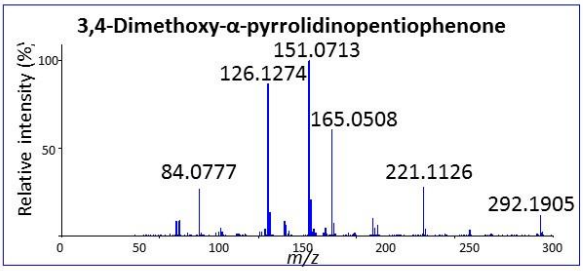

2-Ethylethcathinone
159.1020
188.1392
144.0790
72.0797
206.1495
Relative intensity (%)
m/z

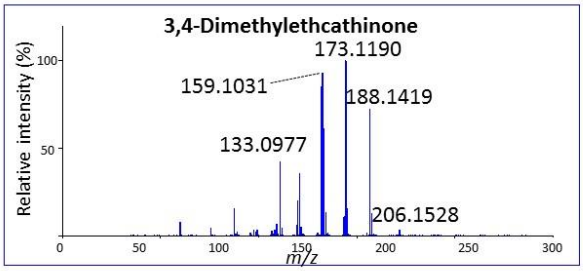

2-Fluoroethcathinone
148.0540
135.0478
103.0528
196.1099
Relative intensity (%)
m/z

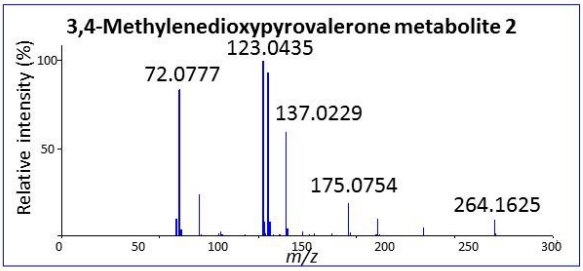

2-Methyl-α-pyrrolidinopropiophenone
98.0984
119.0878
147.0815
218.1559
70.0643
Relative intensity (%)
m/z

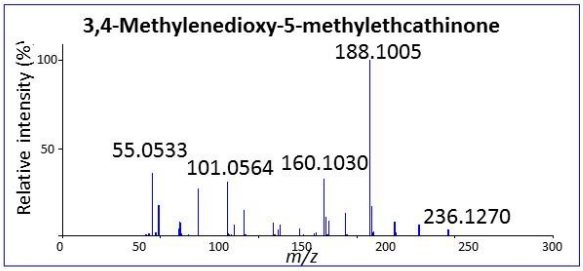

2-Fluoromethcathinone
149.0635
164.0871
103.0531
Relative intensity (%)
m/z

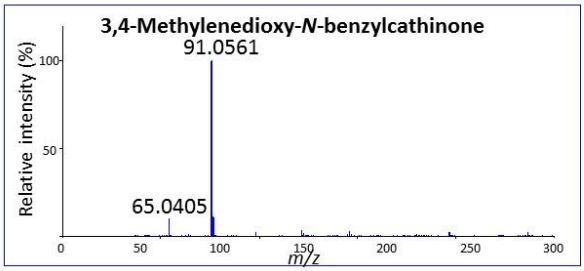

3,4-Dimethylmethcathinone
159.1027
174.1258
133.0985
Relative intensity (%)
m/z

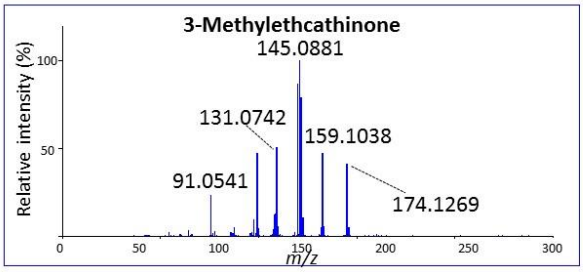

3,4-Dimethoxy-α-pyrrolidinopentiophenone
151.0713
126.1274
165.0508
84.0777
221.1126
292.1905
Relative intensity (%)
m/z

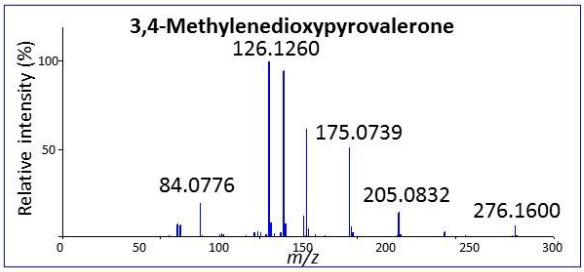

3,4-Dimethylethcathinone
173.1190
159.1031
188.1419
133.0977
206.1528
Relative intensity (%)
m/z

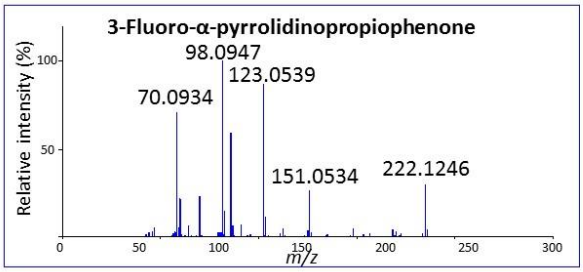

3,4-Methylenedioxypyrovalerone metabolite 2
123.0435
72.0777
137.0229
175.0754
264.1625
Relative intensity (%)
m/z

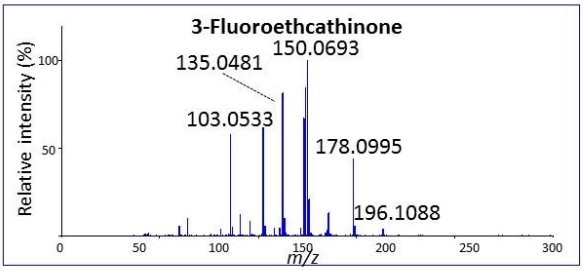

3,4-Methylenedioxy-5-methylethcathinone
188.1005
55.0533
101.0564
160.1030
236.1270
Relative intensity (%)
m/z

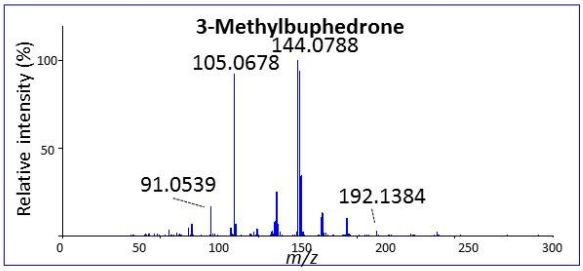

3,4-Methylenedioxy-N-benzylcathinone
91.0561
65.0405
Relative intensity (%)
m/z

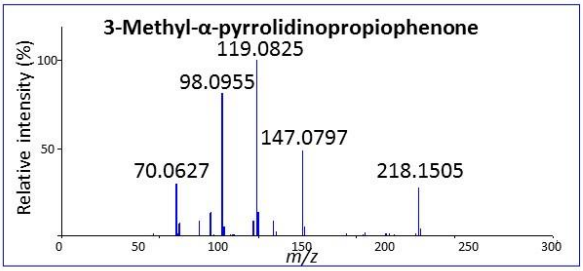

3-Methylethcathinone
145.0881
131.0742
159.1038
91.0541
174.1269
Relative intensity (%)
m/z

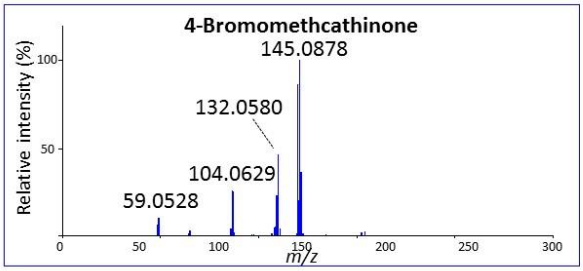

3,4-Methylenedioxypyrovalerone
126.1260
175.0739
84.0776
205.0832
276.1600
Relative intensity (%)
m/z

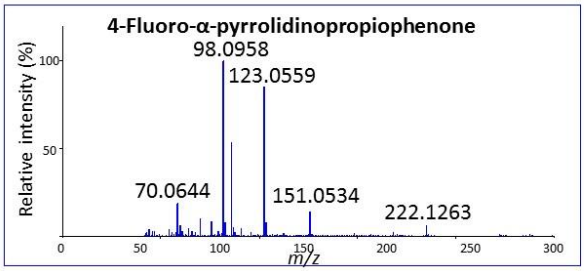

3-Fluoro-α-pyrrolidinopropiophenone
98.0947
123.0539
70.0934
151.0534
222.1246
Relative intensity (%)
m/z

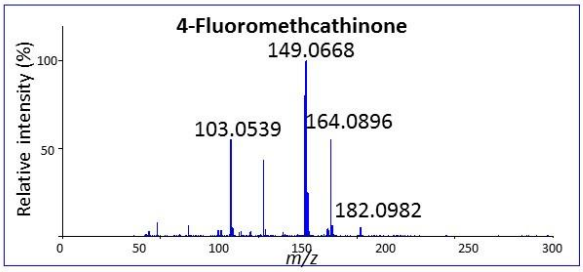

3-Fluoroethcathinone
135.0481
150.0693
103.0533
178.0995
196.1088
Relative intensity (%)
m/z

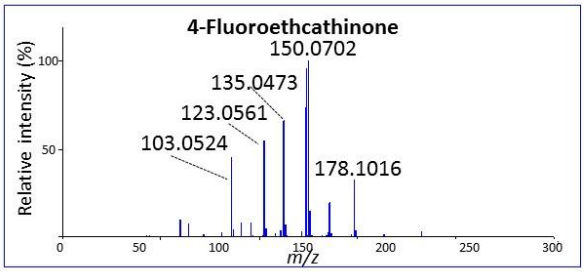

3-Methylbuphedrone
105.0678
144.0788
91.0539
192.1384
Relative intensity (%)
m/z

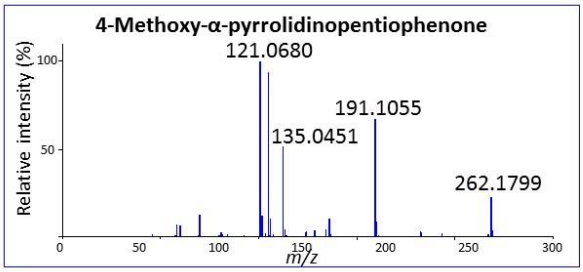

3-Methyl-α-pyrrolidinopropiophenone
119.0825
98.0955
147.0797
70.0627
218.1505
Relative intensity (%)
m/z

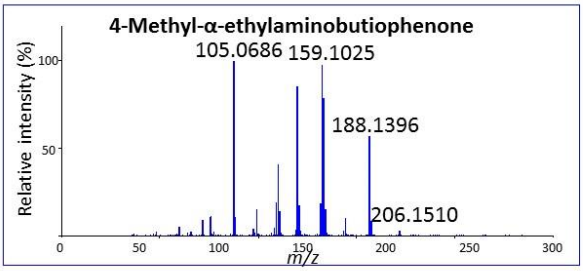

4-Bromomethcathinone
145.0878
132.0580
104.0629
59.0528
Relative intensity (%)
m/z

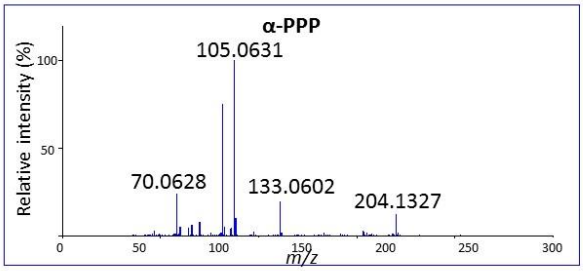

4-Fluoro-α-pyrrolidinopropiophenone
98.0958
123.0559
70.0644
151.0534
222.1263
Relative intensity (%)
m/z

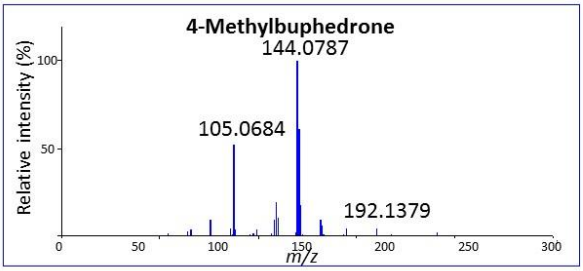

4-Fluoromethcathinone
149.0668
103.0539
164.0896
182.0982
Relative intensity (%)
m/z

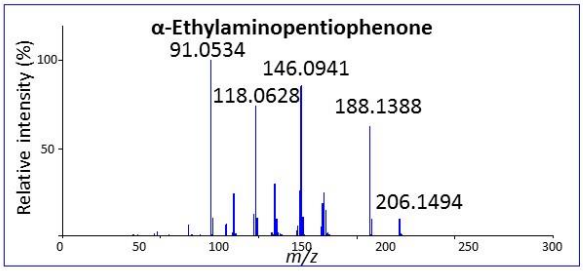

4-Fluoroethcathinone
150.0702
135.0473
123.0561
103.0524
178.1016
Relative intensity (%)
m/z

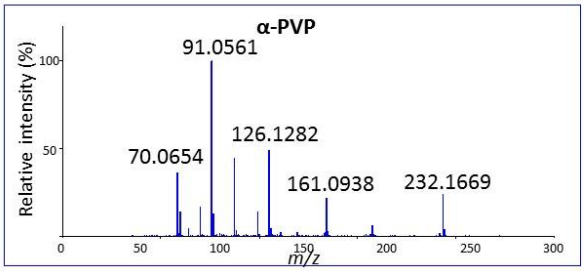

4-Methoxy-α-pyrrolidinopentiophenone
121.0680
191.1055
135.0451
262.1799
Relative intensity (%)
m/z

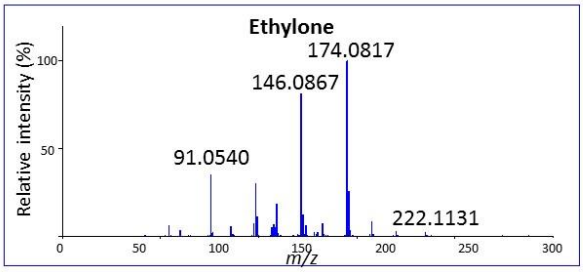

4-Methyl-α-ethylaminobutiophenone
105.0686
159.1025
188.1396
206.1510
Relative intensity (%)
m/z

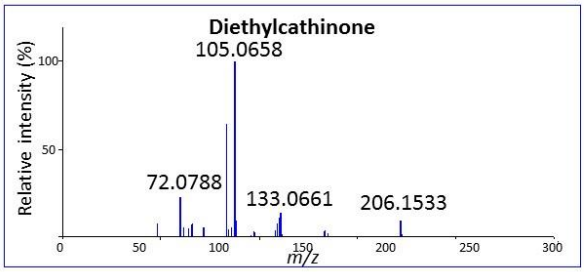

α-PPP
105.0631
70.0628
133.0602
204.1327
Relative intensity (%)
m/z

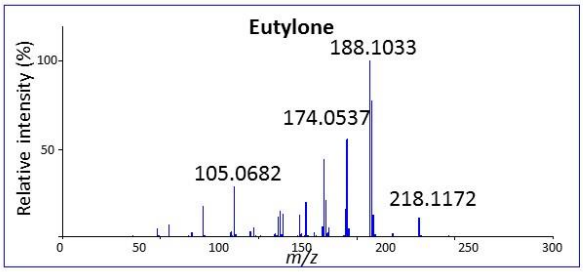

4-Methylbuphedrone
144.0787
105.0684
192.1379
Relative intensity (%)
m/z

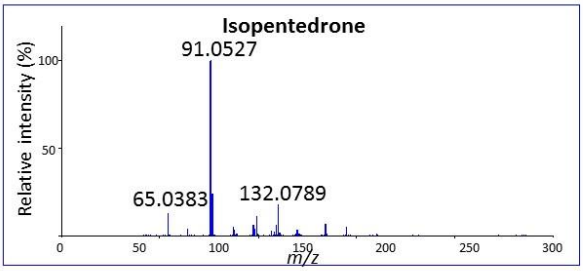

α-Ethylaminopentiophenone
91.0534
146.0941
118.0628
188.1388
206.1494
Relative intensity (%)
m/z

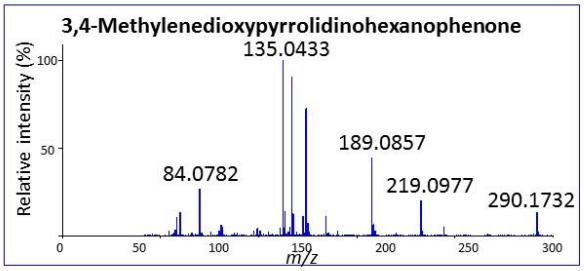

α-PVP
91.0561
126.1282
70.0654
161.0938
232.1669
Relative intensity (%)
m/z

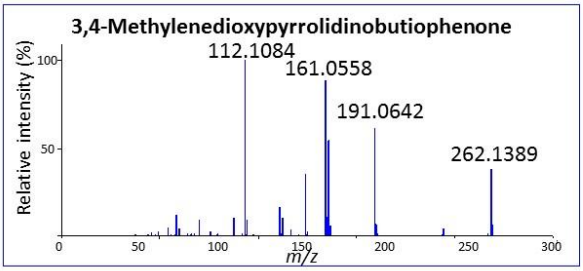

Ethylone
174.0817
146.0867
91.0540
222.1131
Relative intensity (%)
m/z

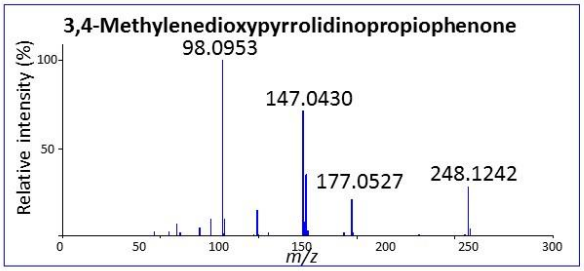

Diethylcathinone
105.0658
72.0788
133.0661
206.1533
Relative intensity (%)
m/z

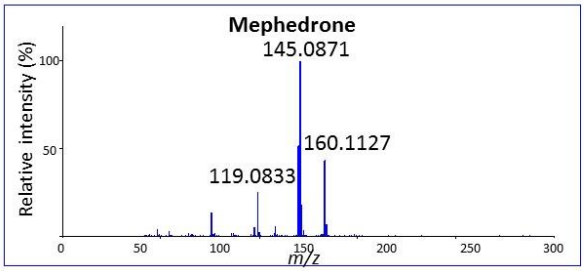

Eutylone
188.1033
174.0537
105.0682
218.1172
Relative intensity (%)
m/z

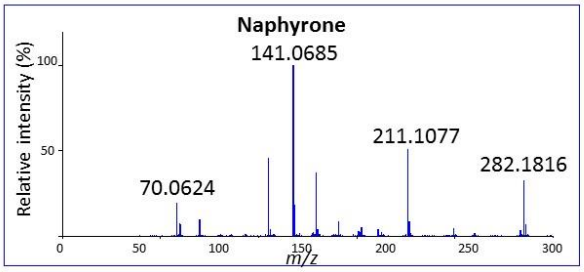

Isopentedrone
91.0527
65.0383
132.0789
Relative intensity (%)
m/z

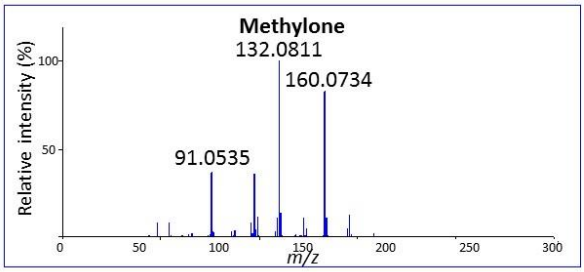

3,4-Methylenedioxypyrrolidinohexanophenone
135.0433
189.0857
84.0782
219.0977
290.1732
Relative intensity (%)
m/z

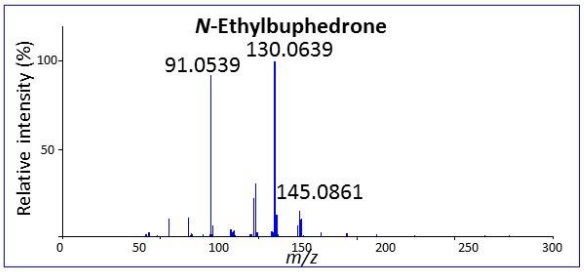

3,4-Methylenedioxypyrrolidinobutiophenone
112.1084
161.0558
191.0642
262.1389
Relative intensity (%)
m/z

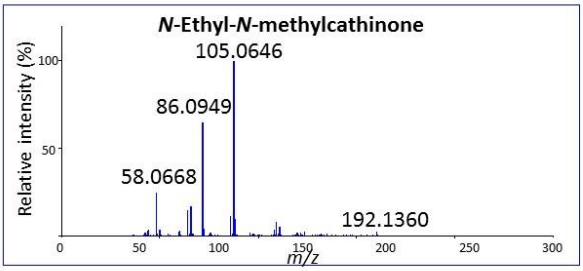

3,4-Methylenedioxypyrrolidinopropiophenone
98.0953
147.0430
177.0527
248.1242
Relative intensity (%)
m/z

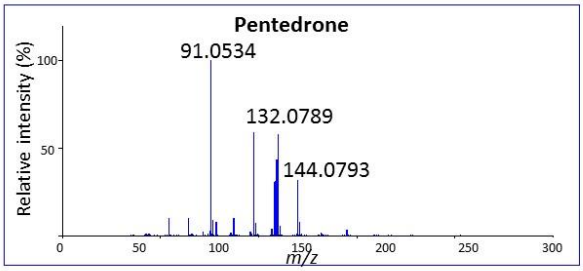

Mephedrone
145.0871
160.1127
119.0833
Relative intensity (%)
m/z

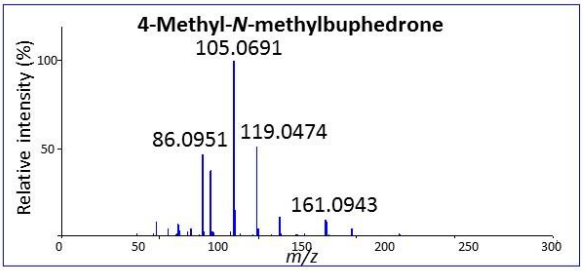

Naphyrone
141.0685
211.1077
282.1816
70.0624
Relative intensity (%)
m/z

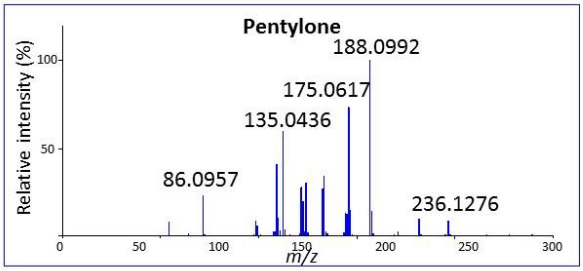

Methylone
132.0811
160.0734
91.0535
Relative intensity (%)
m/z

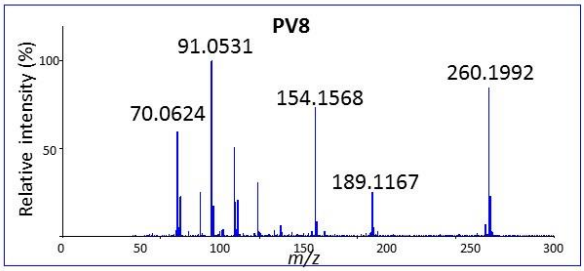

N-Ethylbuphedrone
130.0639
91.0539
145.0861
Relative intensity (%)
m/z

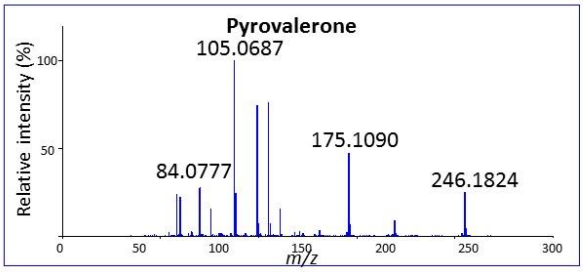


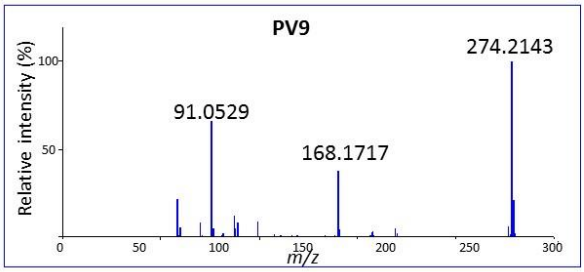




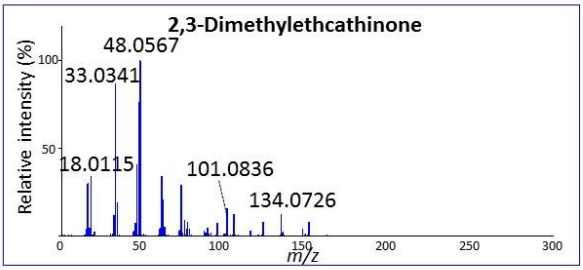


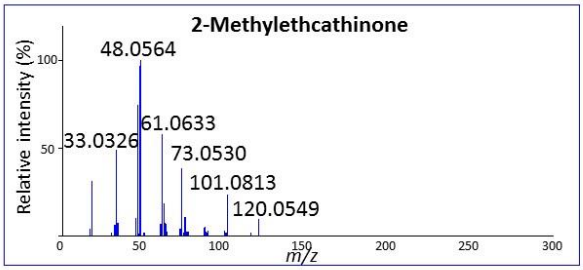


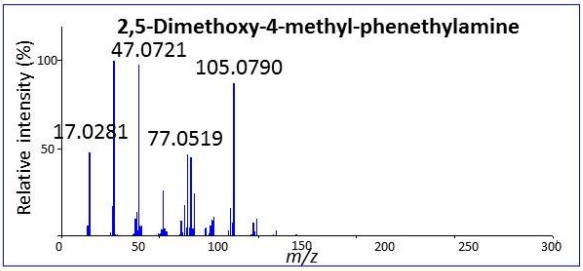


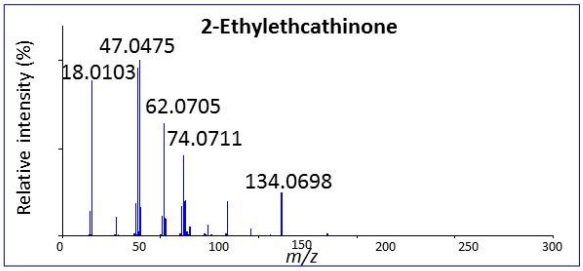


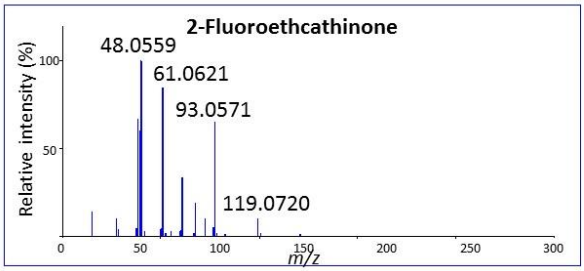
Supplementary Figure S2. The 90 V fragmentation spectra of the 47 cathinones analyzed in this study. Their structures are shown in Supplementary Figure S1.

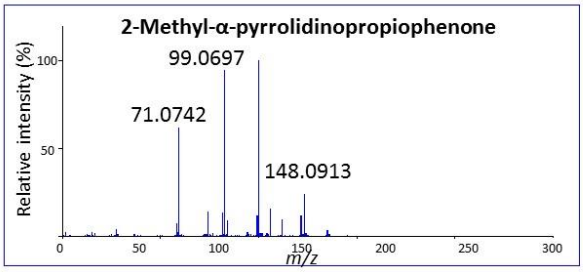

2,3-Dimethylethcathinone
48.0567
33.0341
18.0115
101.0836
134.0726
Relative intensity (%)
m/z

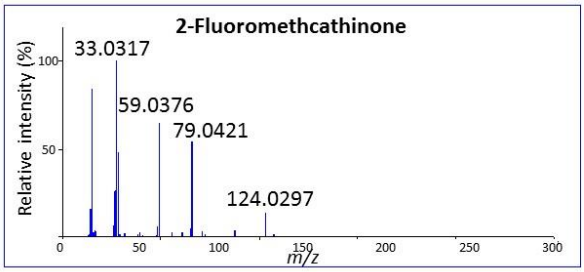

2-Methylethcathinone
48.0564
61.0633
33.0326
73.0530
101.0813
120.0549
Relative intensity (%)
m/z

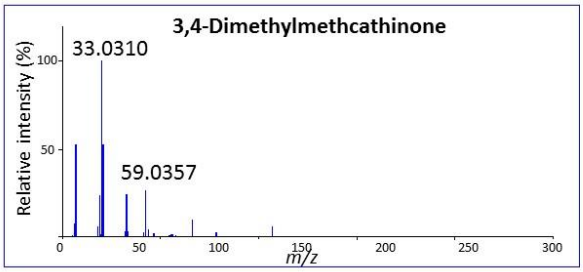

2,5-Dimethoxy-4-methyl-phenethylamine
47.0721
105.0790
17.0281
77.0519
Relative intensity (%)
m/z

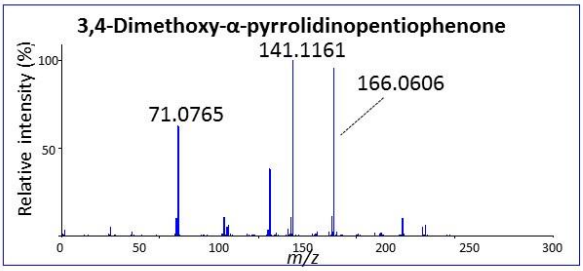

2-Ethylethcathinone
47.0475
18.0103
62.0705
74.0711
134.0698
Relative intensity (%)
m/z

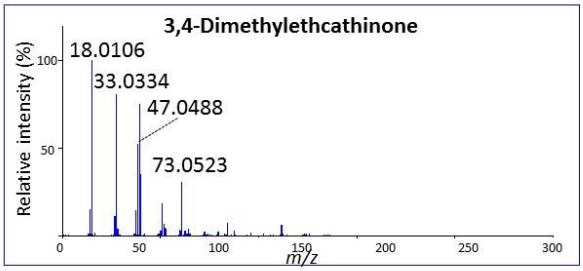

2-Fluoroethcathinone
48.0559
61.0621
93.0571
119.0720
Relative intensity (%)
m/z

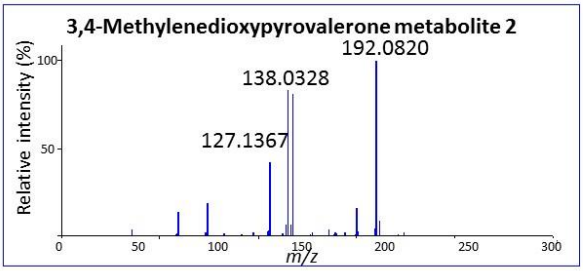

2-Methyl-α-pyrrolidinopropiophenone
99.0697
71.0742
148.0913
Relative intensity (%)
m/z

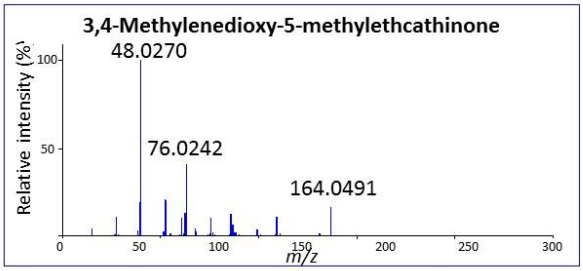

2-Fluoromethcathinone
33.0317
59.0376
79.0421
124.0297
Relative intensity (%)
m/z

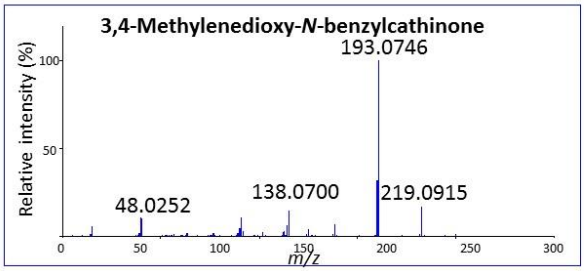

3,4-Dimethylmethcathinone
33.0310
59.0357
Relative intensity (%)
m/z

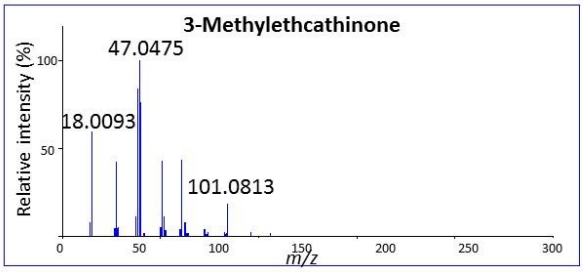

3,4-Dimethoxy-α-pyrrolidinopentiophenone
141.1161
166.0606
71.0765
Relative intensity (%)
m/z

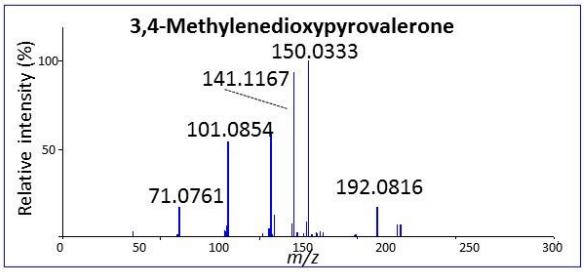

3,4-Dimethylethcathinone
18.0106
33.0334
47.0488
73.0523
Relative intensity (%)
m/z

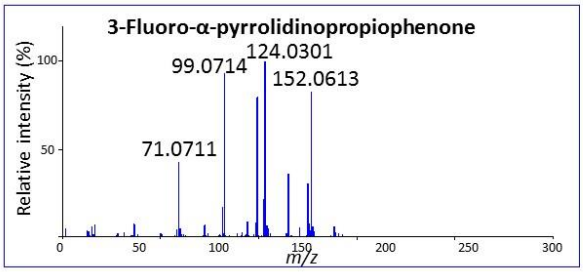

3,4-Methylenedioxypyrovalerone metabolite 2
192.0820
138.0328
127.1367
Relative intensity (%)
m/z

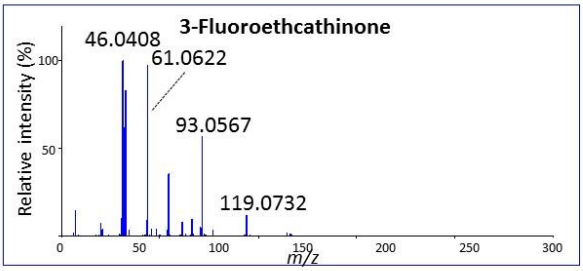

3,4-Methylenedioxy-5-methylethcathinone
48.0270
76.0242
164.0491
Relative intensity (%)
m/z

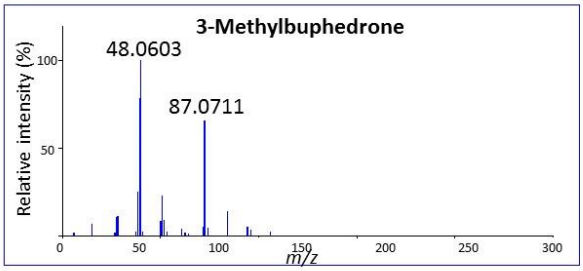

3,4-Methylenedioxy-N-benzylcathinone
193.0746
48.0252
138.0700
219.0915
Relative intensity (%)
m/z

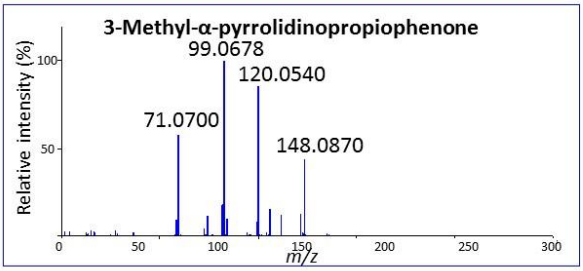

3-Methylethcathinone
47.0475
18.0093
101.0813
Relative intensity (%)
m/z

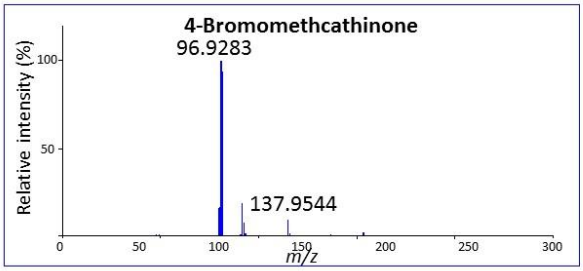

3,4-Methylenedioxypyrovalerone
150.0333
141.1167
101.0854
71.0761
192.0816
Relative intensity (%)
m/z

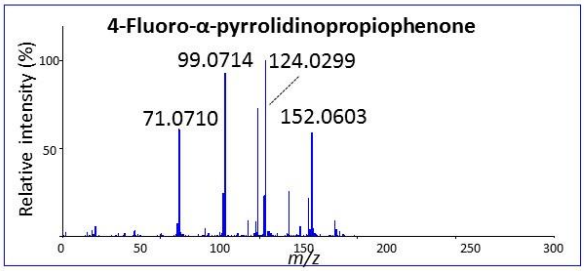

3-Fluoro-α-pyrrolidinopropiophenone
124.0301
99.0714
152.0613
71.0711
Relative intensity (%)
m/z

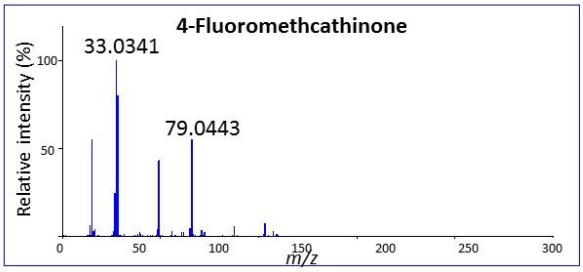

3-Fluoroethcathinone
46.0408
61.0622
93.0567
119.0732
Relative intensity (%)
m/z

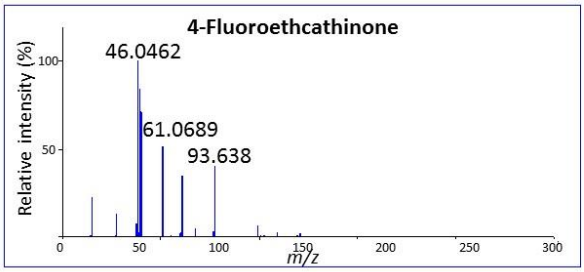

3-Methylbuphedrone
48.0603
87.0711
Relative intensity (%)
m/z

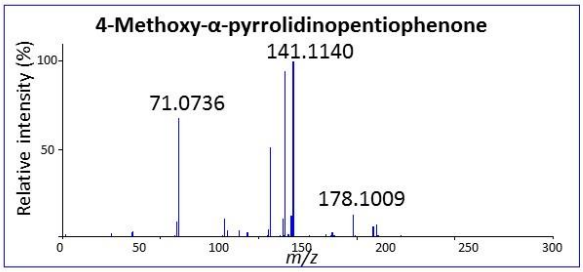

3-Methyl-α-pyrrolidinopropiophenone
99.0678
120.0540
71.0700
148.0870
Relative intensity (%)
m/z

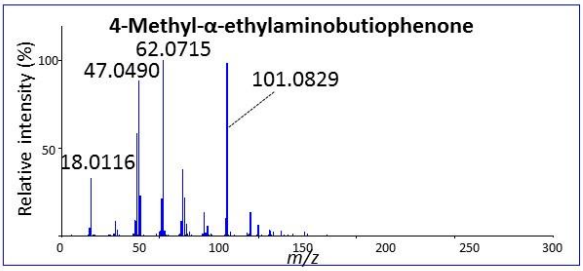

4-Bromomethcathinone
96.9283
137.9544
Relative intensity (%)
m/z

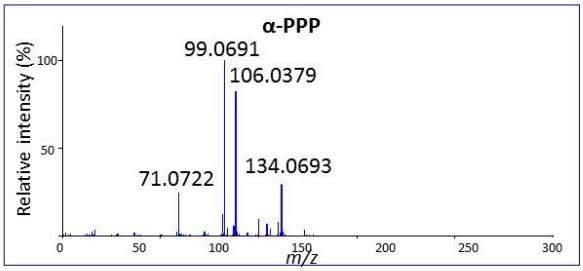

4-Fluoro-α-pyrrolidinopropiophenone
99.0714
124.0299
71.0710
152.0603
Relative intensity (%)
m/z

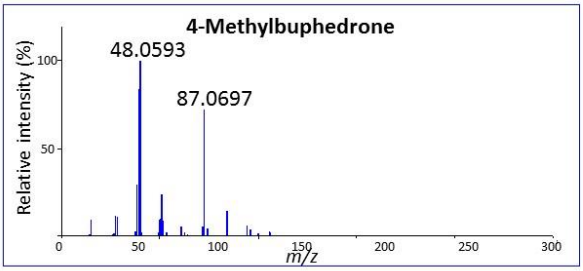

4-Fluoromethcathinone
33.0341
79.0443
Relative intensity (%)
m/z

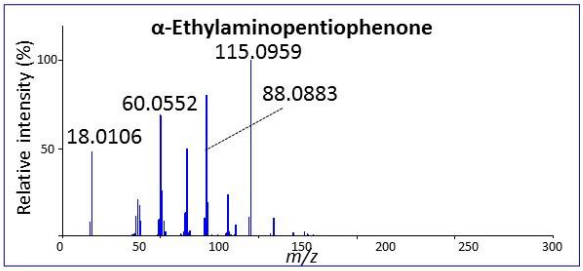

4-Fluoroethcathinone
46.0462
61.0689
93.638
Relative intensity (%)
m/z

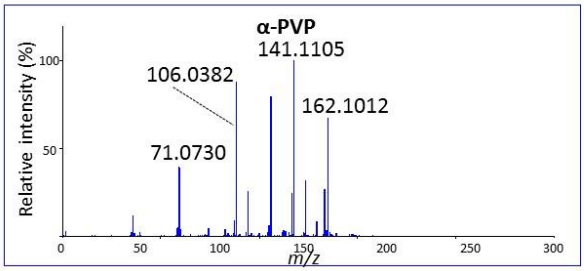

4-Methoxy-α-pyrrolidinopentiophenone
141.1140
71.0736
178.1009
Relative intensity (%)
m/z

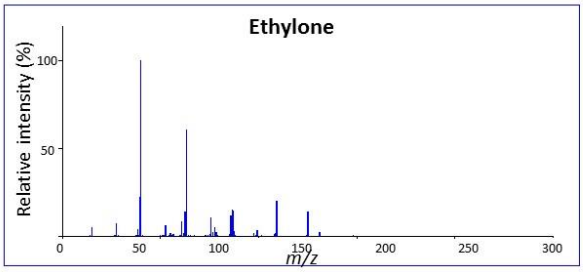

4-Methyl-α-ethylaminobutiophenone
62.0715
47.0490
101.0829
18.0116
Relative intensity (%)
m/z

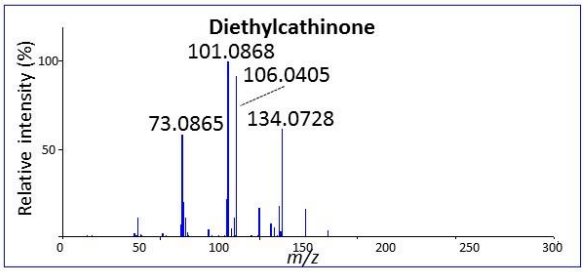

α-PPP
99.0691
106.0379
71.0722
134.0693
Relative intensity (%)
m/z

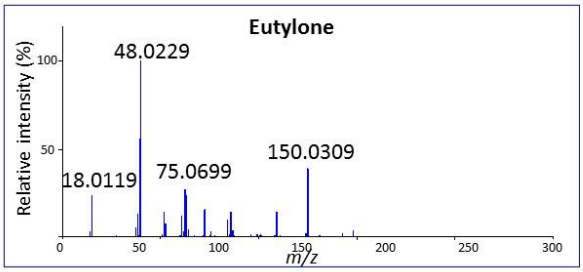

4-Methylbuphedrone
48.0593
87.0697
Relative intensity (%)
m/z

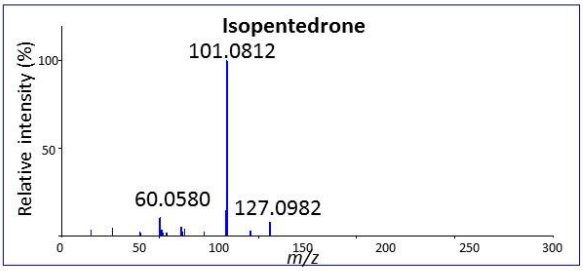

α-Ethylaminopentiophenone
115.0959
60.0552
88.0883
18.0106
Relative intensity (%)
m/z

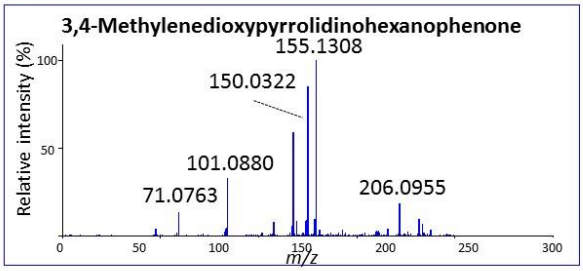

α-PVP
141.1105
106.0382
162.1012
71.0730
Relative intensity (%)
m/z

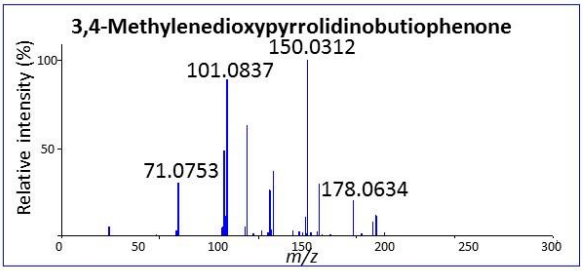

Ethylone
Relative intensity (%)
m/z

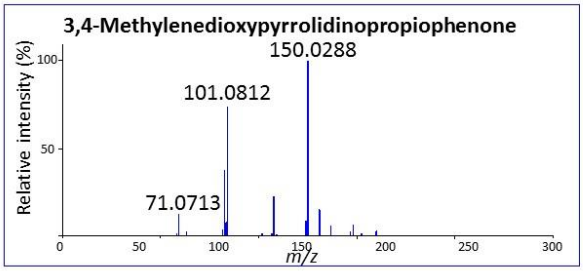

Diethylcathinone
101.0868
106.0405
73.0865
134.0728
Relative intensity (%)
m/z

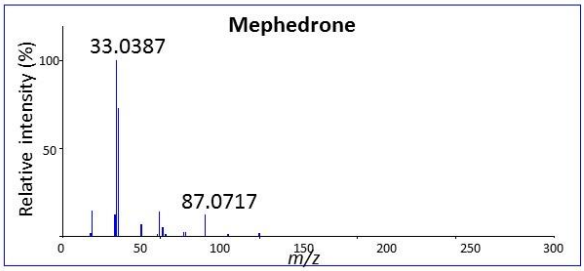

Eutylone
48.0229
150.0309
75.0699
18.0119
Relative intensity (%)
m/z

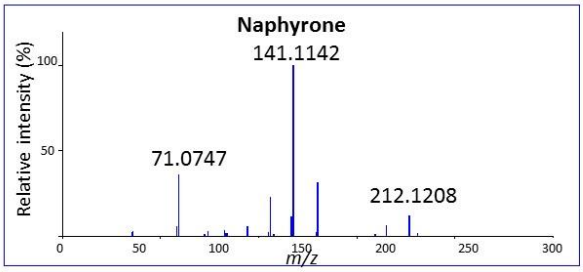

Isopentedrone
101.0812
60.0580
127.0982
Relative intensity (%)
m/z

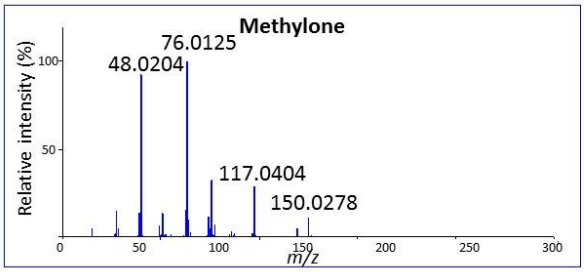

3,4-Methylenedioxypyrrolidinohexanophenone
155.1308
150.0322
101.0880
71.0763
206.0955
Relative intensity (%)
m/z

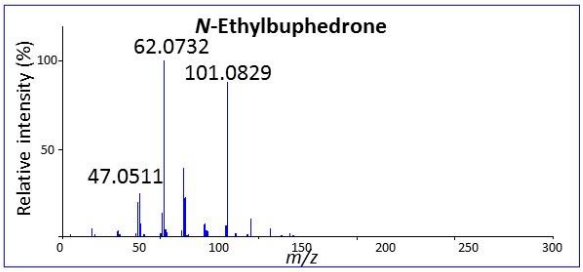

3,4-Methylenedioxypyrrolidinobutiophenone
150.0312
101.0837
71.0753
178.0634
Relative intensity (%)
m/z

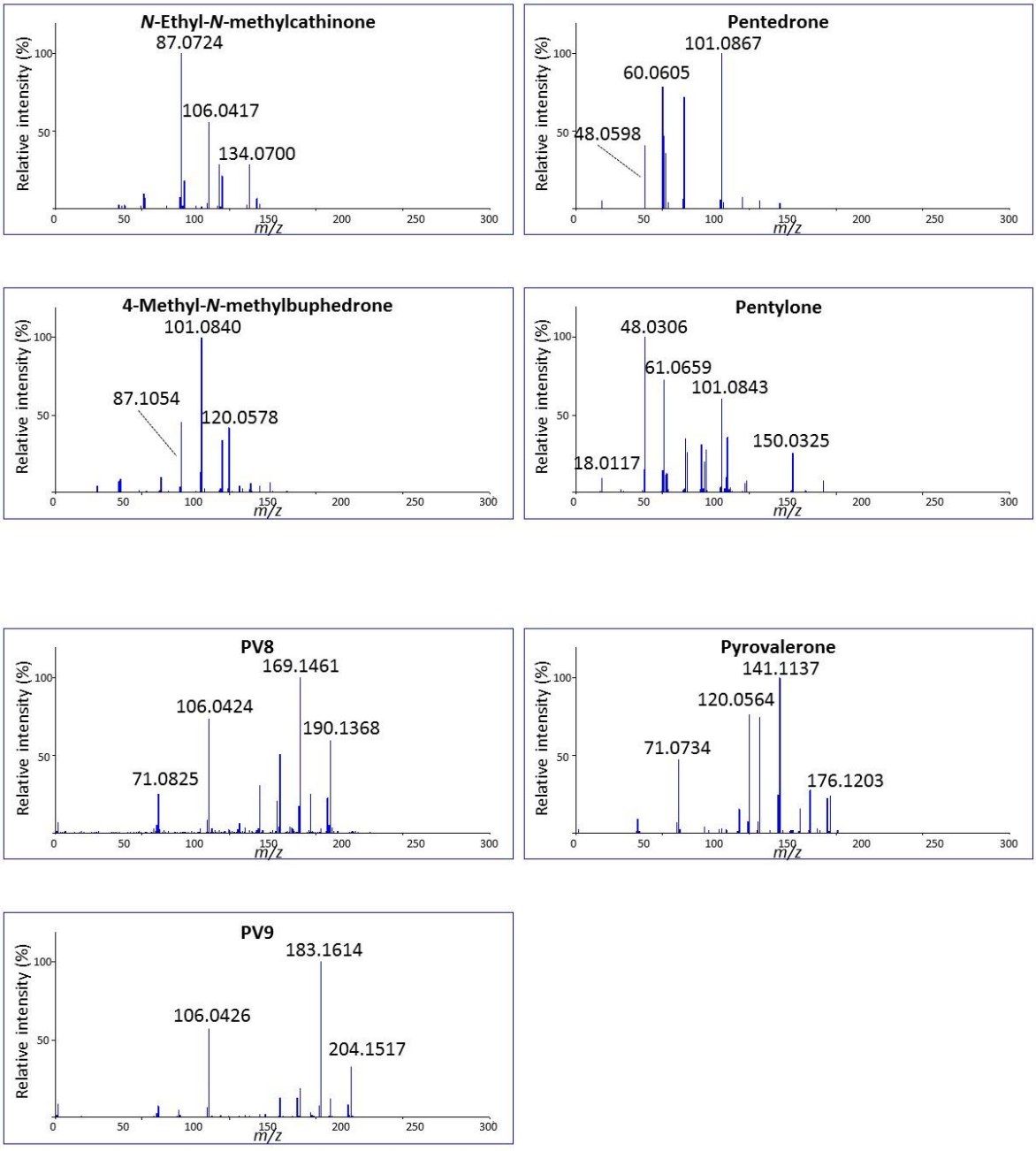

3,4-Methylenedioxypyrrolidinopropiophenone
150.0288
101.0812
71.0713
Relative intensity (%)
m/z


Mephedrone
33.0387
87.0717
Relative intensity (%)
m/z

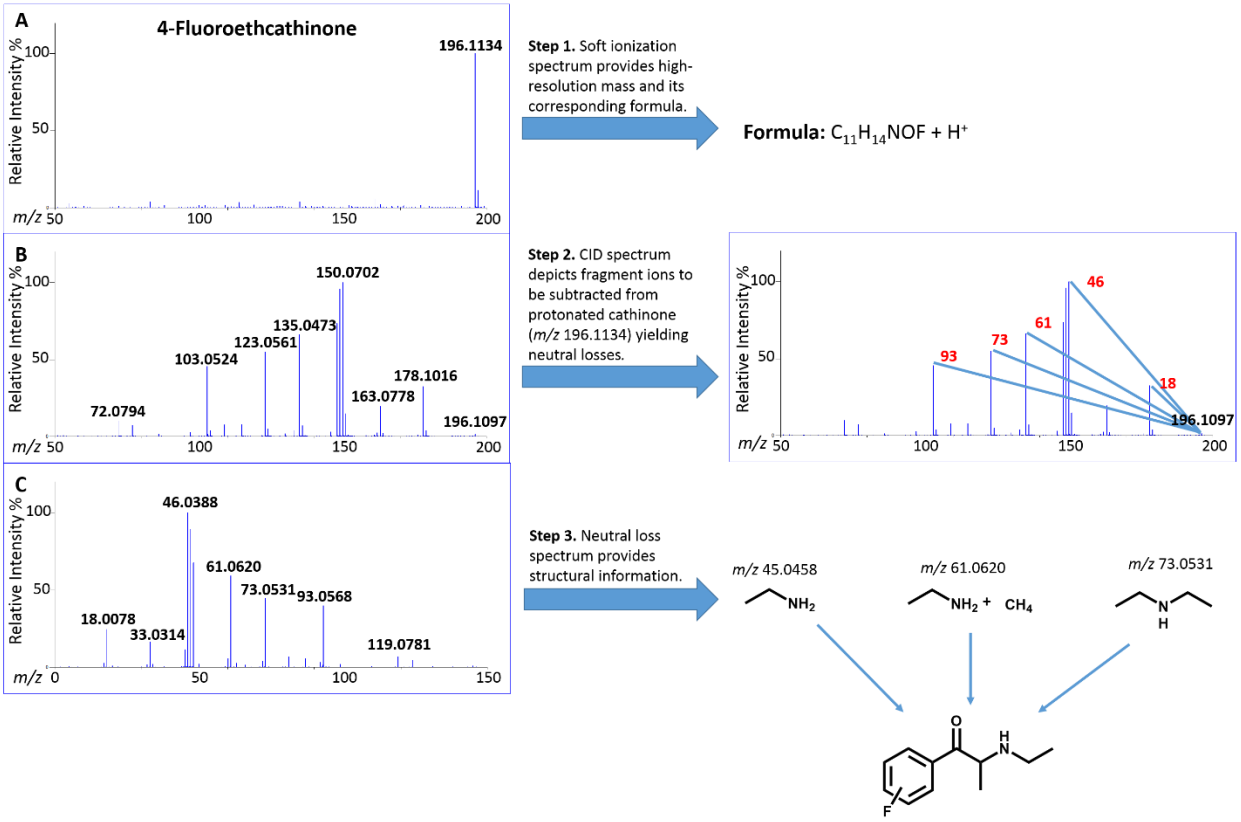

Naphyrone
141.1142
71.0747
212.1208
Relative intensity (%)
m/z


Methylone
76.0125
48.0204
117.0404
150.0278
Relative intensity (%)
m/z

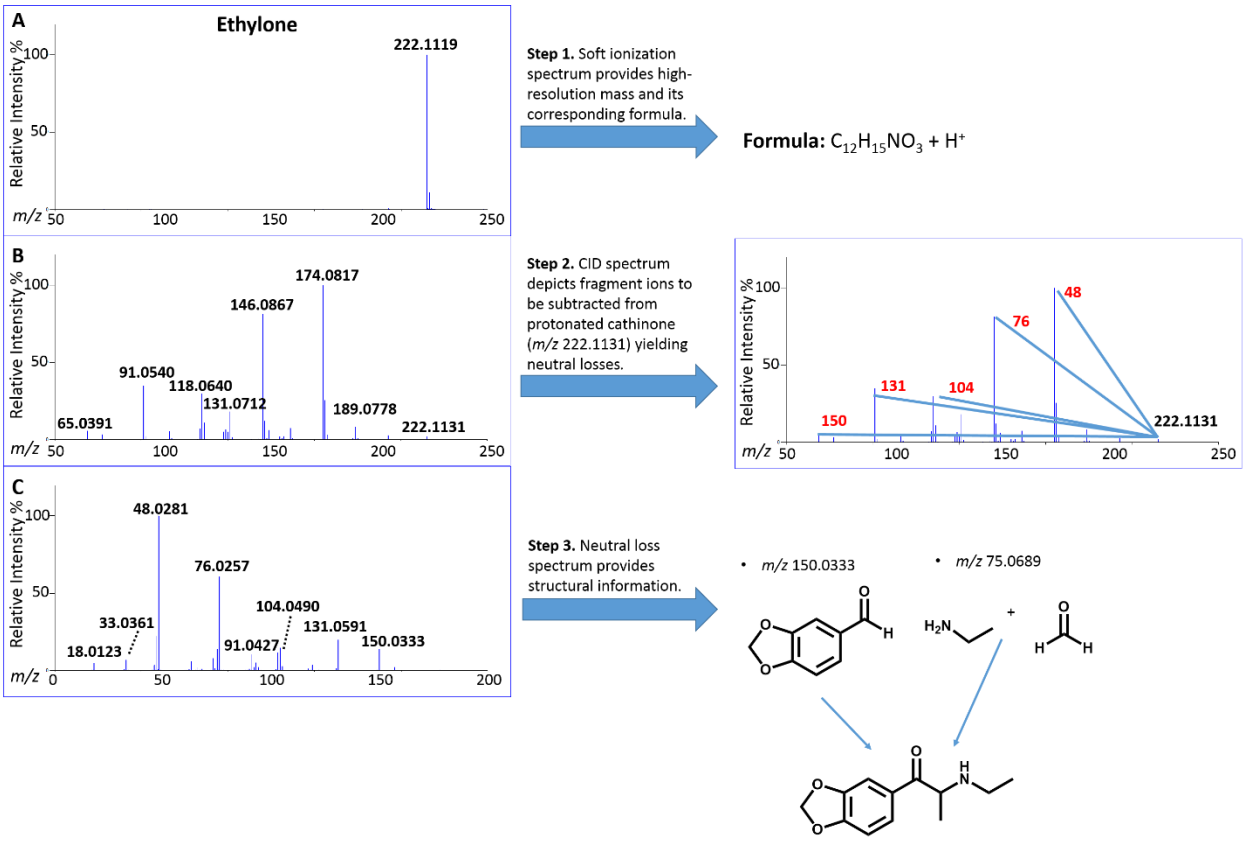

N-Ethylbuphedrone
62.0732
101.0829
47.0511
Relative intensity (%)
m/z



Supplementary Figure S3. Neutral loss spectra for the 47 cathinones analyzed in this study. The structures of the cathinones are shown in Supplementary Figure S1. Cathinones with similar structures exhibit common neutral losses corresponding to diagnostic structural features.



Supplementary Figure S4. Steps taken to deduce the structure of the "unknown" 4-fluoroethcathinone. The soft ionization spectrum (Panel A) shows the protonated cathinone *m/z* 196.1134 leading to the formula $[C_{11}H_{14}NOF + H]^+$. The CID spectrum (Panel B) containing the protonated cathinone and fragment ions was used to calculate the neutral masses lost during fragmentation. Panel C, the neutral loss spectrum, allows for the determination of structural characteristics of the unknown.



Supplementary Figure S5. Steps taken to deduce the structure of the "unknown" ethylone. The soft ionization spectrum (Panel A) shows the protonated cathinone *m/z* 222.1119 leading to the formula $[C_{12}H_{15}NO_3 + H]^+$. The CID spectrum (Panel B) was used to calculate the neutral masses lost during fragmentation. Panel C, the neutral loss spectrum, allows for the determination of structural characteristics of the unknown including the methylenedioxy moiety.