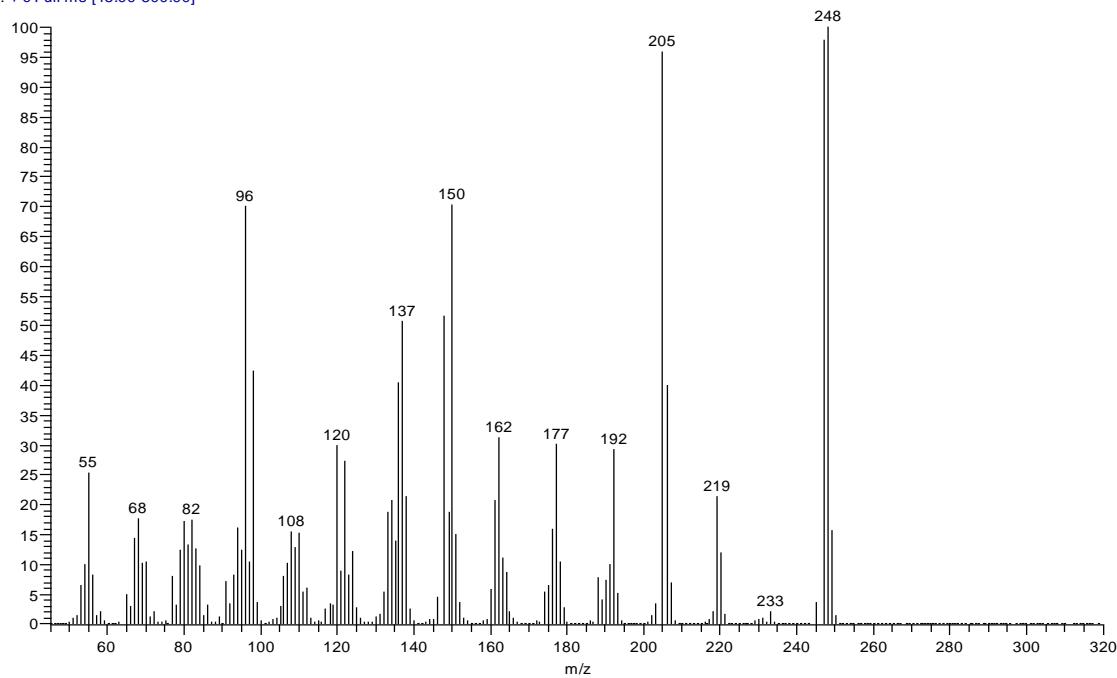
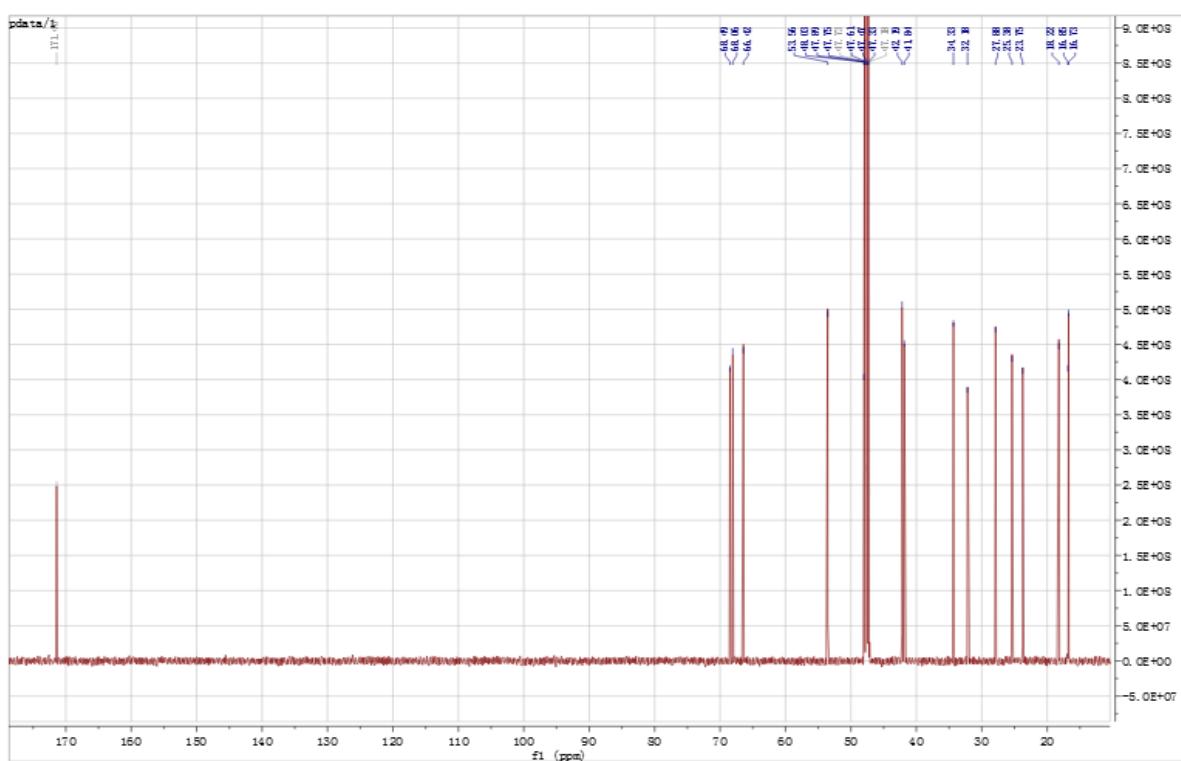
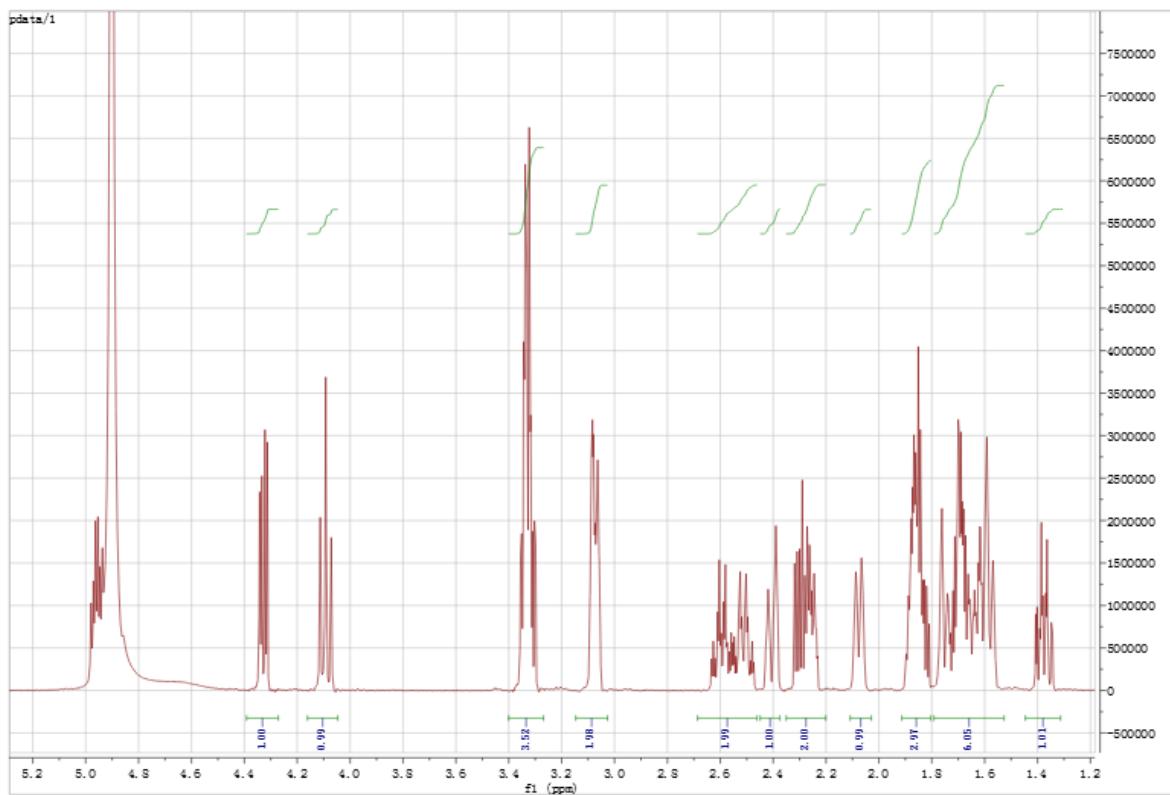


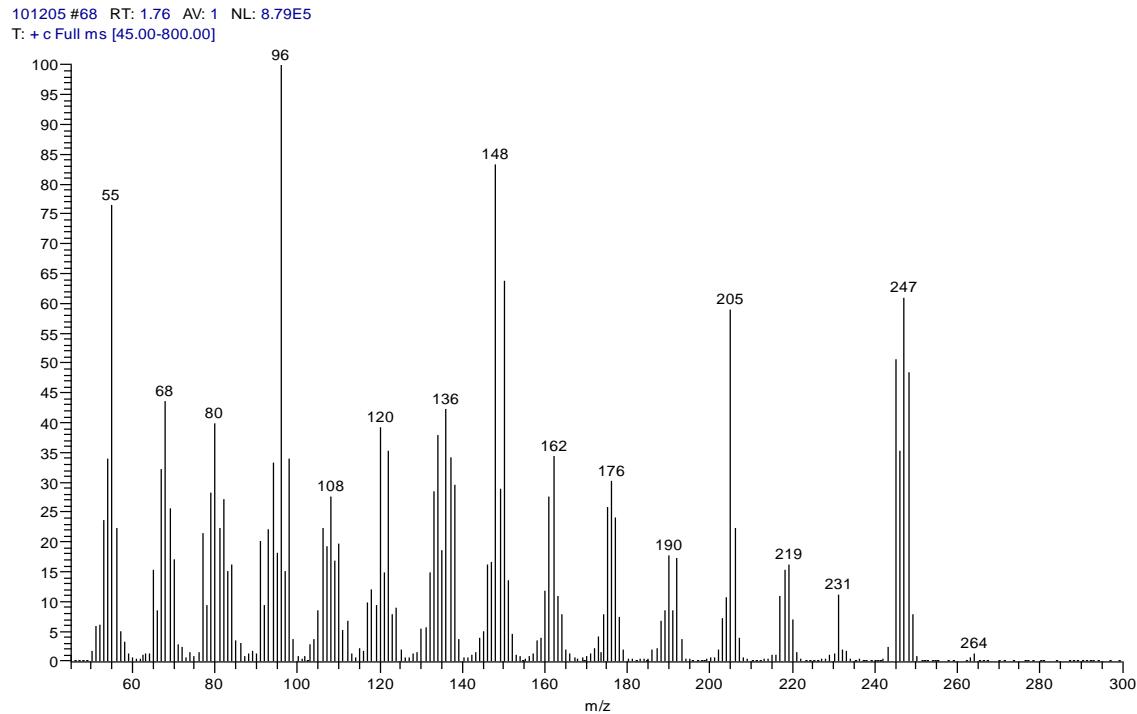
101202 #32 RT: 0.83 AV: 1 NL: 4.12E7  
 T: + c Full ms [45.00-800.00]



**Figure S1.** Analysis of compound 1.

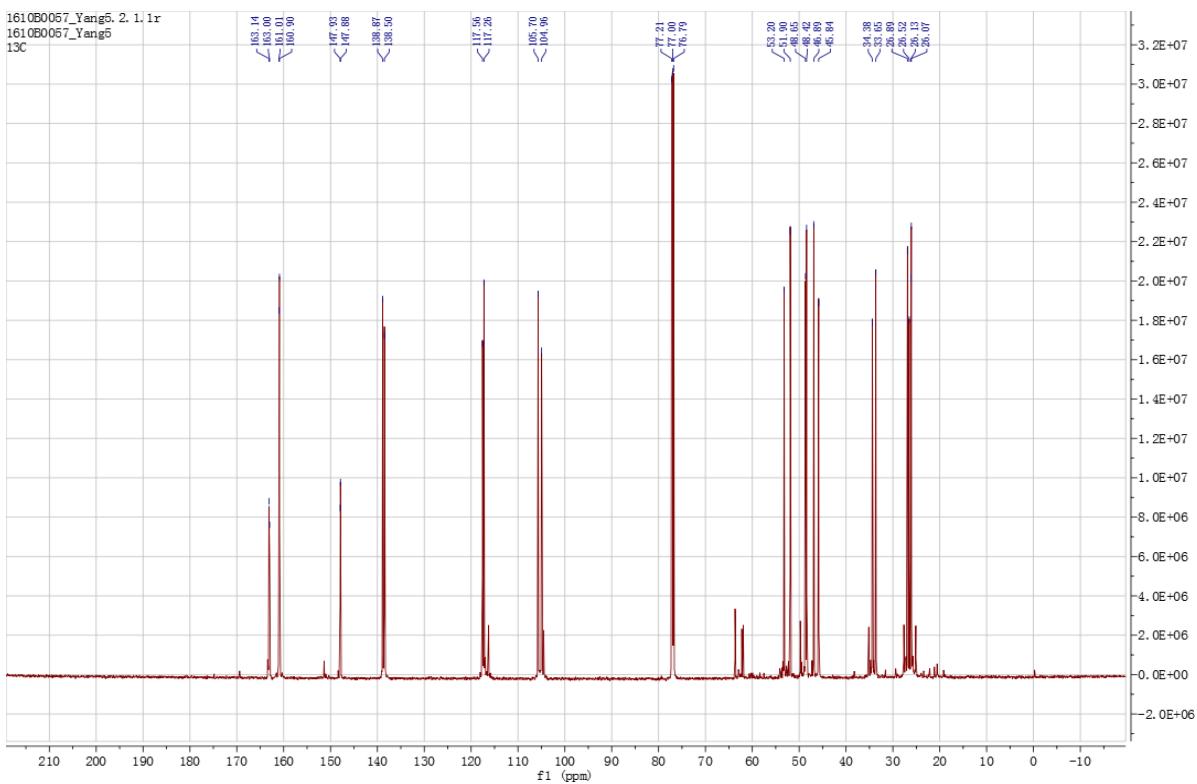
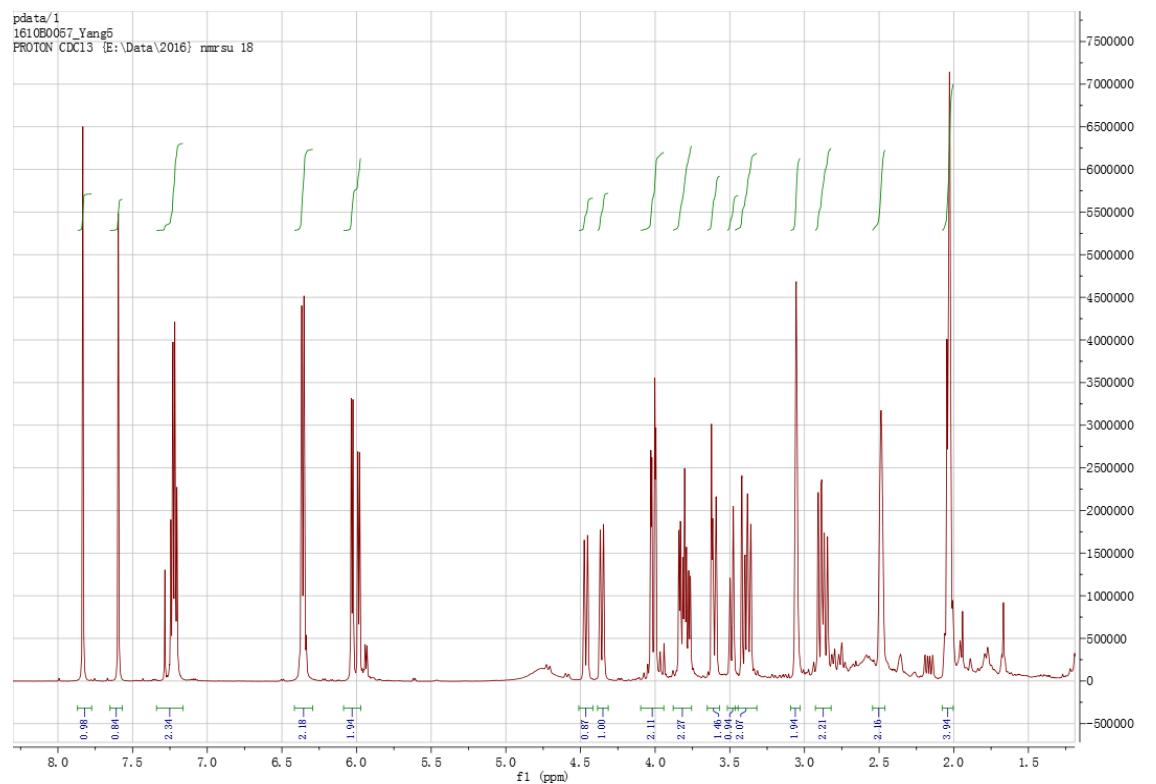
*Matrine (peak 1 in Fig. 2): EI-MS, m/z 248 [M]+; <sup>1</sup>H-NMR (600MHz, MeOD) δ: 2.91-2.85 (m, 1H, H-2), 2.05-2.00 (m, 1H, H-2'), 1.80-1.56 (m, 6H, 3, 4, 5, 8, H-12, H-13'), 1.56-1.42 (m, 5H, H-3', 4', 8', 9', H-7), 2.20 (m, 1H, H-6), 2.20-2.12 (m, 1H, H-9), 2.85-2.79 (m, 1H, H-10), 2.11-2.05 (m, 1H, H-10'), 3.84 (ddd, 1H, J=10.9, 8.9, 5.8 Hz, H-11), 1.89-1.80 (m, 1H, H-12'), 2.00-1.94 (m, 1H, H-13), 2.37 (dtd, 1H, J=17.6, 4.7, 1.5 Hz, H-14), 2.26 (ddd, 1H, J=17.0, 10.7, 5.5 Hz, H-14'), 4.32 (dd, 1H, J=12.8, 4.3 Hz, H-17), 3.08 (t, 1H, J=12.8Hz, H-17'). <sup>13</sup>C-NMR (151MHz, MeOD) δ: 56.92(N-CH<sub>2</sub>, C-2), 20.23 (CH<sub>2</sub>, C-3), 26.62 (CH<sub>2</sub>, C-4), 35.48 (CH, C-5), 63.65 (N-CH, C-6), 41.42 (CH, C-7), 25.84 (CH<sub>2</sub>, C-8), 20.72 (CH<sub>2</sub>, C-9), 56.84 (N-CH<sub>2</sub>, C-10), 53.34 (N-CH, C-11), 27.38 (CH<sub>2</sub>, C-12), 18.17 (CH<sub>2</sub>, C-13), 31.99 (CH<sub>2</sub>, C-14), 170.65 (N-C=O, C-15), 43.17 (N-CH<sub>2</sub>, C-17).*



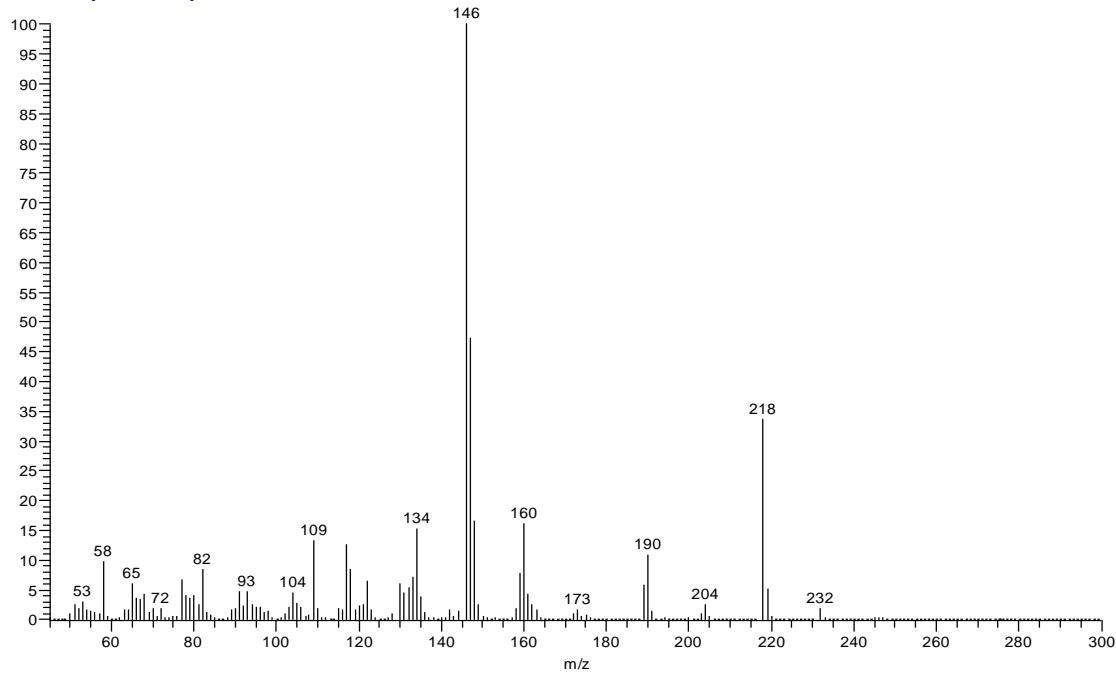


**Figure S2.** Analysis of compound 2.

*Oxymatrine (peak 2 in Fig. 2): EI-MS, m/z 264 [M]+; <sup>1</sup>H-NMR (600MHz, MeOD) δ: 3.39-3.28 (m, 3H, 2, 10, H-11), 3.07 (ddd, 2H, J=10.2, 4.4, 2.2 Hz, H-2', 10'), 2.65-2.44 (m, 2H, CH<sub>2</sub>-3), 1.91-1.80 (m, 3H, H-4, 5, 8), 1.80-1.54 (m, 4H, H-4', 7, 8, 9'), 4.96 (td, 1H, J=10.0, 5.5 Hz, H-6), 2.08 (dt, 1H, J=12.9, 4.2Hz, H-9), 2.34-2.22 (m, 2H, H-12', 14'), 1.37 (tdd, 1H, J=12.7, 9.5, 3.1Hz, H-12), 1.54 (m, 2H, CH<sub>2</sub>-13), 2.44-2.36 (m, 1H, H-14), 4.33 (dd, 1H, J=12.2, 5.0 Hz, H-17), 4.09 (t, 1H, J=12.5Hz, H-17'). <sup>13</sup>C-NMR (151MHz, MeOD) δ: 68.06 (N-CH<sub>2</sub>, C-2), 16.85 (CH<sub>2</sub>, C-3), 25.37 (CH<sub>2</sub>, C-4), 34.33 (CH, C-5), 68.50 (N-CH, C-6), 41.84 (CH, C-7), 23.75 (CH<sub>2</sub>, C-8), 18.21 (CH<sub>2</sub>, C-9), 66.42 (N-CH<sub>2</sub>, C-10), 53.56 (N-CH, C-11), 27.88 (CH<sub>2</sub>, C-12), 16.73 (CH<sub>2</sub>, C-13), 32.18 (CH<sub>2</sub>, C-14), 171.40 (N-C=O, C-15), 42.19 (N-CH<sub>2</sub>, C-17).*

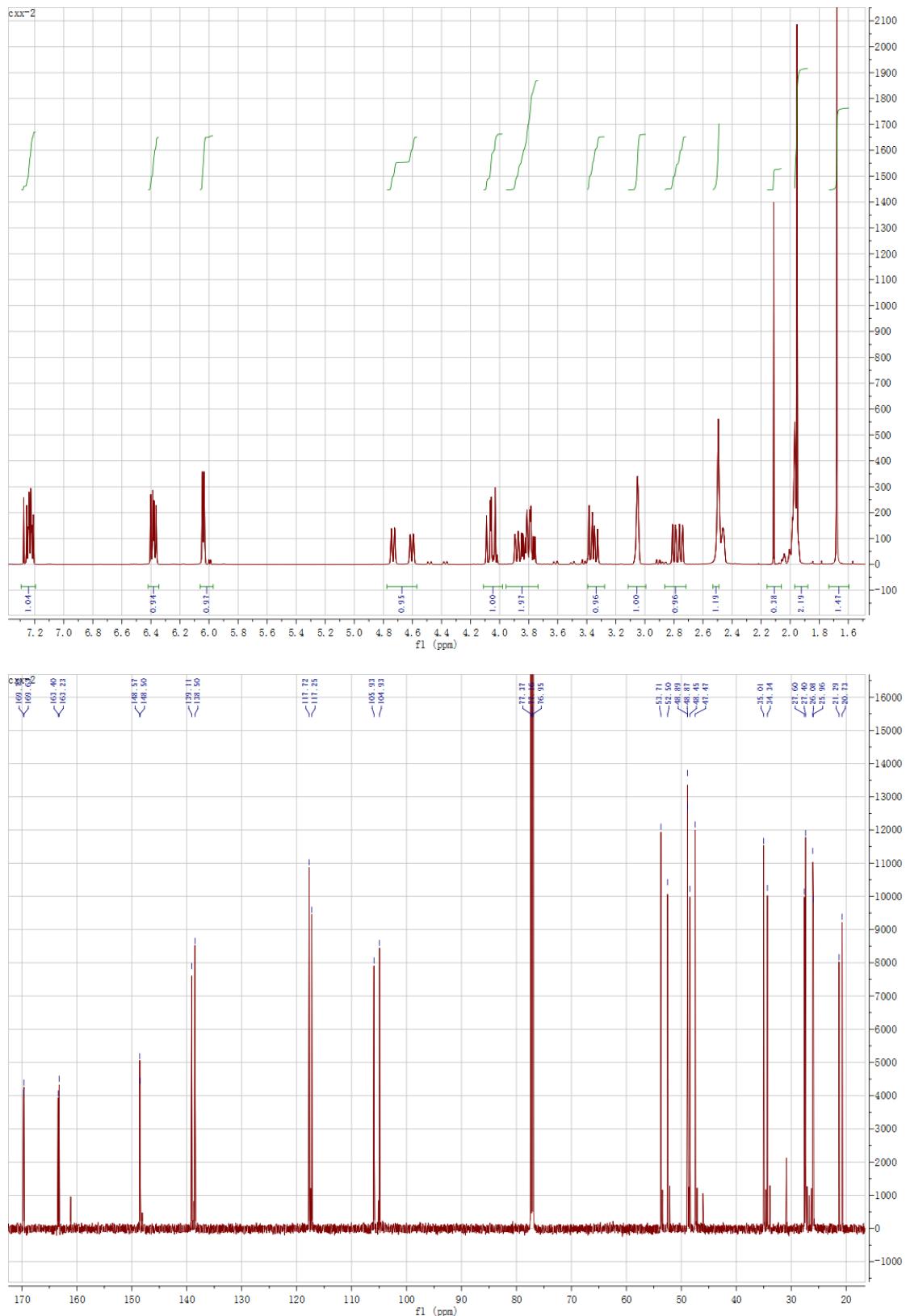


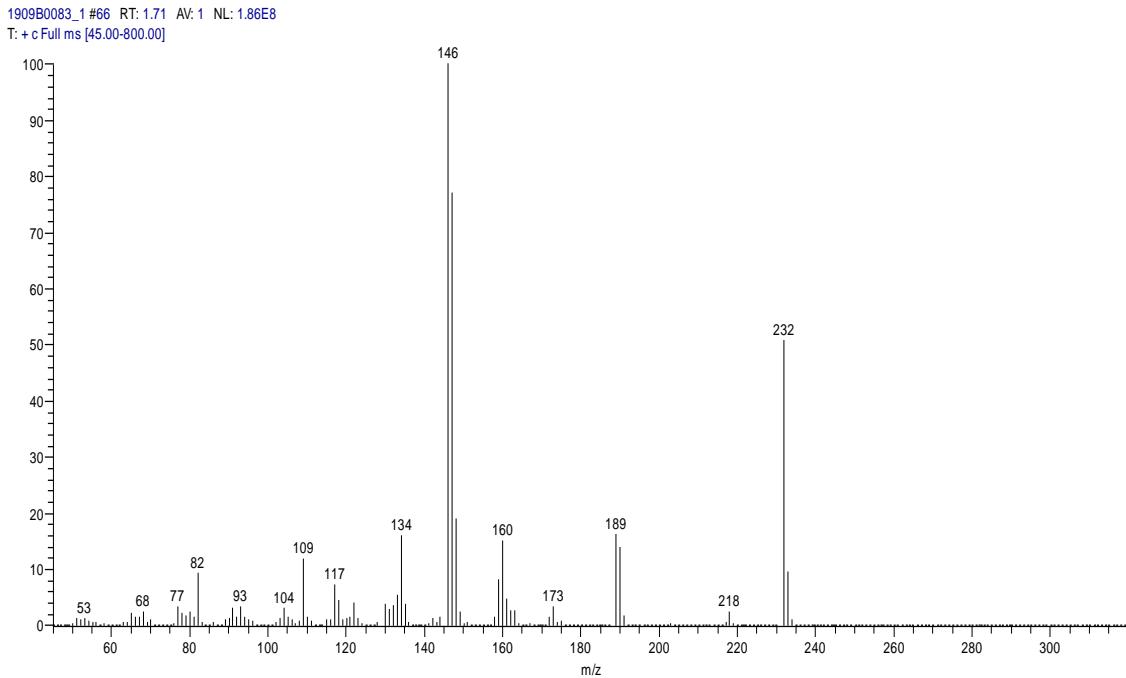
101206 #60 RT: 1.55 AV: 1 NL: 7.89E7  
T: + c Full ms [45.00-800.00]



**Figure S3.** Analysis of compound 3.

*N-formyl cytisine (peak 3 in Fig. 2): EI-MS, m/z 218 [M]+; <sup>1</sup>H-NMR (600MHz, CDCl<sub>3</sub>) δ: 3.44/ 3.42 (d/dd, 1H, J= 12.8, 2.5 Hz, H-2), 3.56/ 3.53 (d, 1H, J=1.8 Hz, H-2'), 2.55 (1H, H-3), 3.85/ 3.88 (dd, 1H, J=15.7, 6.0 Hz, H-4), 4.10/ 4.08 (d, 1H, J=15.6, 3.6 Hz, H-4'), 6.45/ 6.44 (d, 1H, J=9.0 Hz, H-7), 7.27/ 7.19 (m, 1H, H-8), 6.08/ 6.02 (d, 1H, J=6.8Hz, H-9), 3.10 (m, 1H, H-11), 4.46/ 4.36 (d, 1H, J=13.6Hz, H-12), 2.96/ 2.92 (dd/d, 1H, J=13.2, 1.2Hz, 15.0Hz, H-12'), 2.08/ 2.09 (dd, 2H, J=8.3, 4.8Hz, CH<sub>2</sub>-13), 7.83/7.60 (s, 1H, H-14). <sup>13</sup>C-NMR (151MHz, CDCl<sub>3</sub>) δ: 51.90/ 45.84 (N-CH<sub>2</sub>, C-2), 26.89/ 26.52 (CH, C-3), 48.65/ 48.42 (N-CH<sub>2</sub>, C-4), 163.14/ 163.00 (N-C=O, C-6), 117.56/ 117.26 (CH, C-7), 138.87/ 138.50 (CH, C-8), 104.96/ 105.70 (CH, C-9), 147.93/ 147.88 (C, C-10), 33.65/ 34.38 (CH, C-11), 53.20/ 46.89 (N-CH<sub>2</sub>, C-12), 26.13/ 26.07 (CH<sub>2</sub>, C-13), 160.90/ 161.01 (N-CHO, C-14).*





**Figure S4.** Analysis of compound 4.

*N-acetyl cytisine (peak 4 in Fig. 2): EI-MS, m/z 232 [M]+; <sup>1</sup>H-NMR (600MHz, CDCl<sub>3</sub>) δ: 1.68 (s, 2H, CH<sub>2</sub>-13), 1.98 (s, 3H, CH<sub>3</sub>-15), 2.48 (s, 1H, H-3), 2.84 (m, 1H, H-11), 3.05 (s, 1H, H-4), 3.34 (m, 1H, H-4), 3.72-3.89 (m, 2H, CH<sub>2</sub>-2), 4.01/ 4.07 (d, 1H, J=10.1Hz, H-12), 4.60/ 4.72 (d, 1H, J=13.1Hz, H-12), 6.03/ 6.04 (d, 1H, J=6.8Hz, H-9), 6.36 (m, 1H, H-7), 7.25 (m, 1H, H-8). <sup>13</sup>C-NMR (151MHz, CDCl<sub>3</sub>): δ: 21.29/ 20.73 (CH<sub>3</sub>, C-15), 26.08/ 25.96 (CH, C-3), 27.60/ 27.40 (CH<sub>2</sub>, C-13), 35.01/ 34.34 (CH, C-11), 48.45/ 47.47 (N-CH<sub>2</sub>, C-12), 48.88 (N-CH<sub>2</sub>, C-2), 53.71/ 52.50 (N-CH<sub>2</sub>, C-4), 105.93/ 104.93 (CH, C-9), 117.77/ 117.25 (CH, C-7), 139.11/ 138.50 (CH, C-8), 148.53 (C, C-10), 163.40/ 163.23 (N-C=O, C-6), 169.71/ 169.63 (N-C=O, C-14).*