

**Electronic Supplementary Material**

**Method development for the certification of a ginsenoside calibration solution via liquid chromatography with ultraviolet/visible absorbance and mass spectrometric detection**

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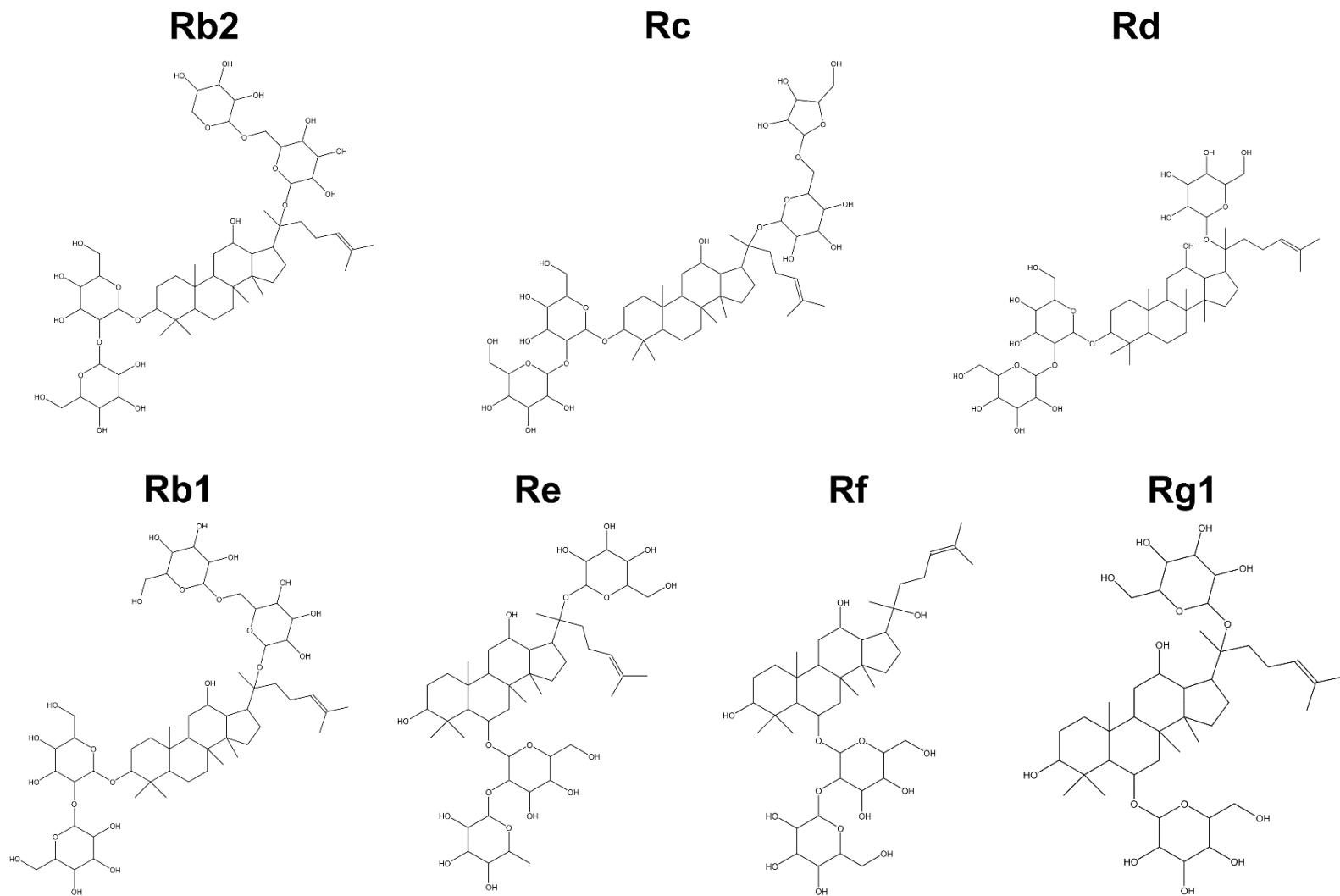
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**Table S1.** Mobile phase gradient for the preliminary LC/UV separations of 8 ginsenosides.

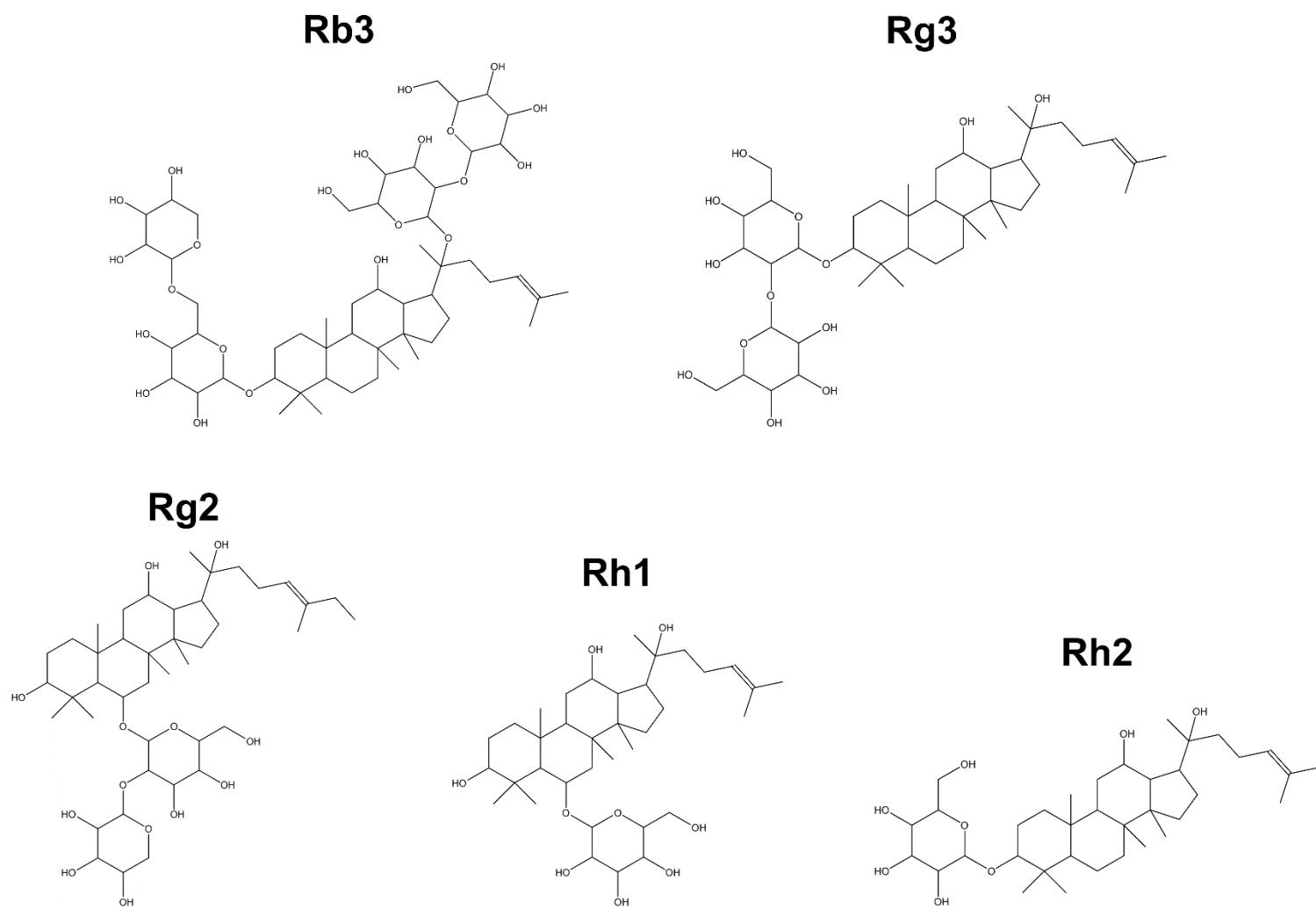
Gradient A			Gradient B		
Time	H <sub>2</sub> O (%)	ACN (%)	Time	H <sub>2</sub> O (%)	ACN (%)
-3.0	80	20	-3.0	80	20
0.0	80	20	0.0	80	20
10.0	77	23	10.0	77	20
29.0	58	42	30.0	50	50
30.0	0	100	31.0	0	100

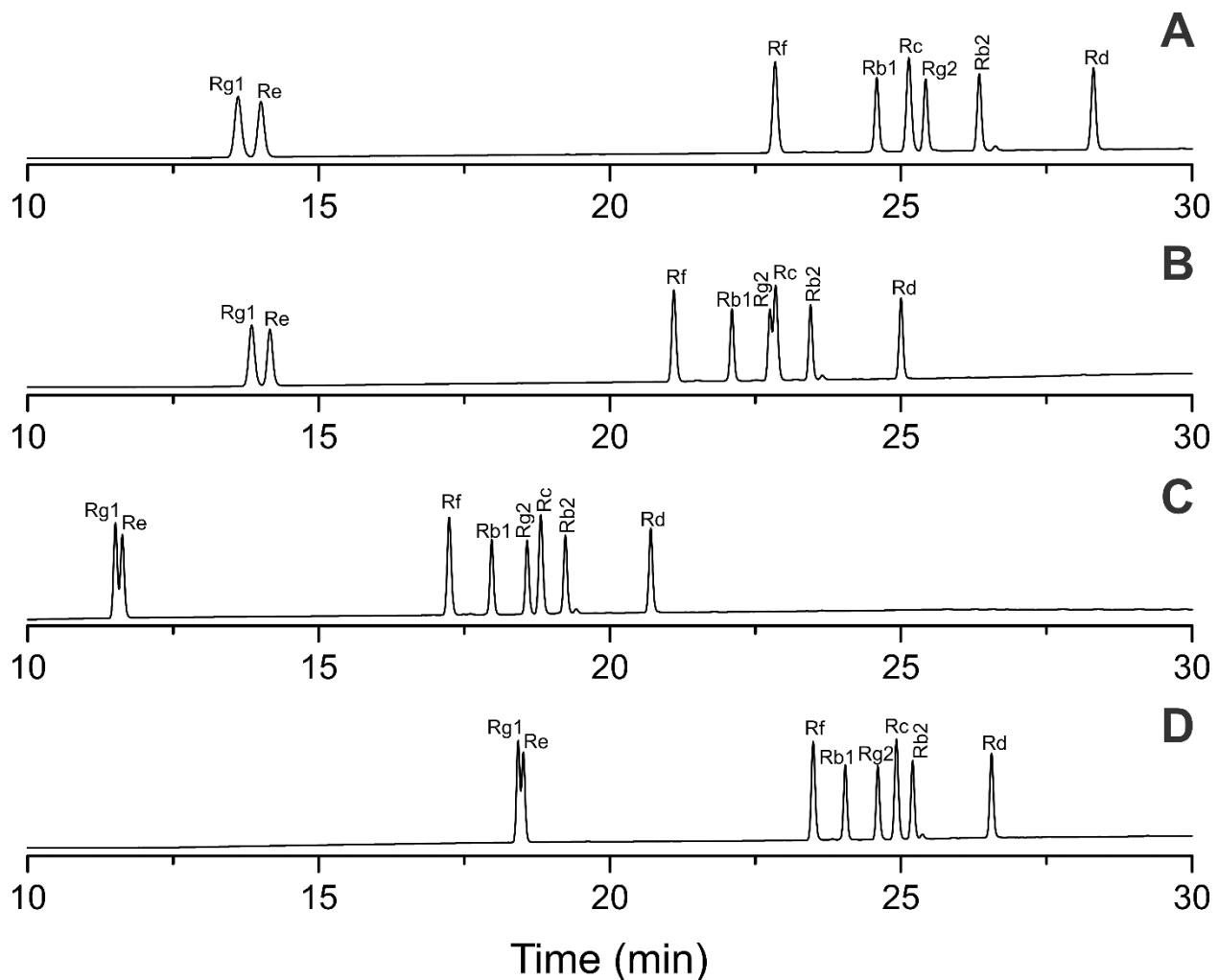
Gradient C			Gradient D		
Time	H <sub>2</sub> O (%)	ACN (%)	Time	H <sub>2</sub> O (%)	ACN (%)
-3.0	79	21	-3.0	82	18
0.0	79	21	0.0	82	18
5.0	79	21	10.0	82	18
25.0	50	50	30.0	50	50
30.0	0	100			



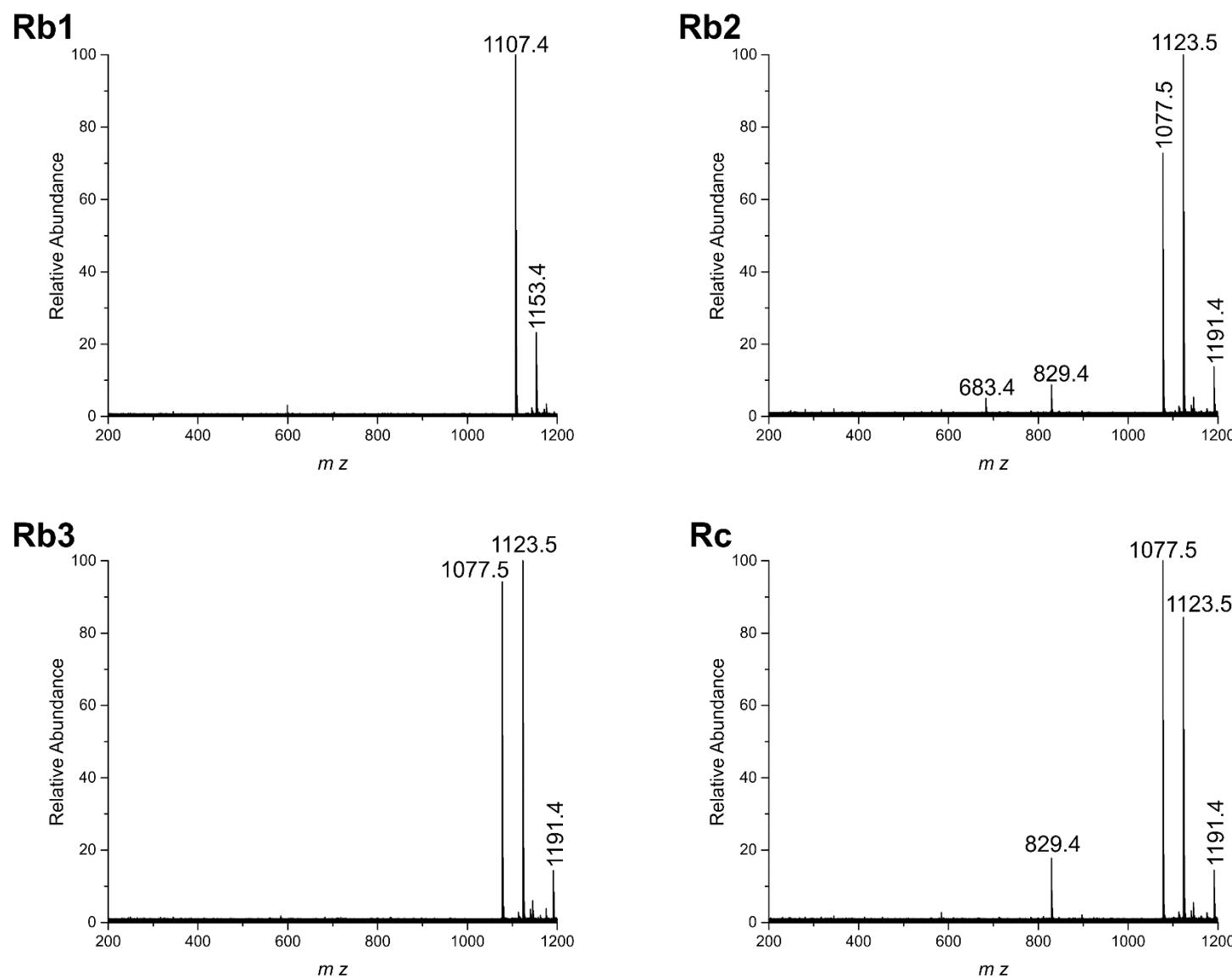
**Fig. S1.** Molecular structures for the seven ginsenosides in SRM 3389.



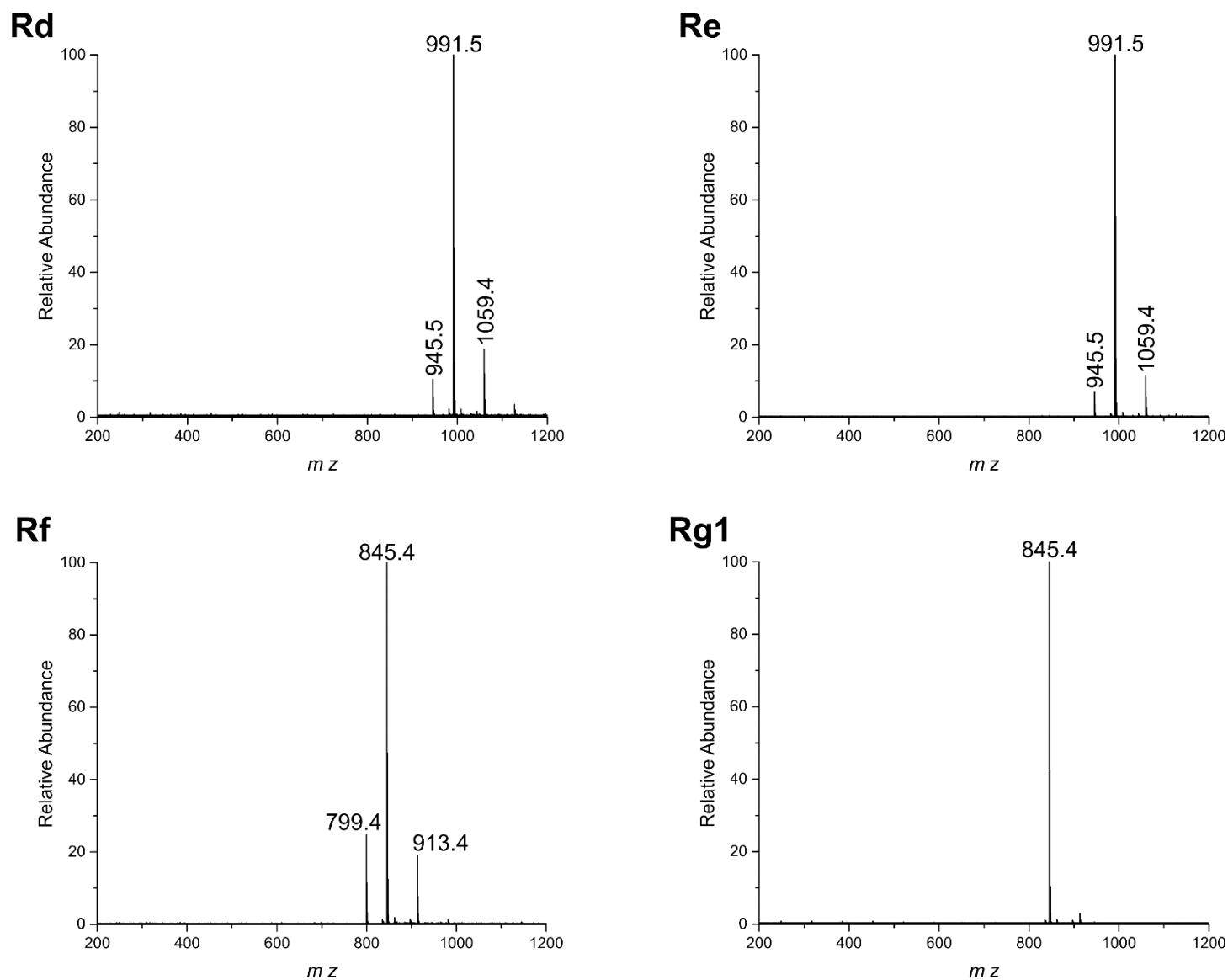
**Fig. S2.** Molecular structures for the five ginsenosides included in the present study not in SRM 3389.



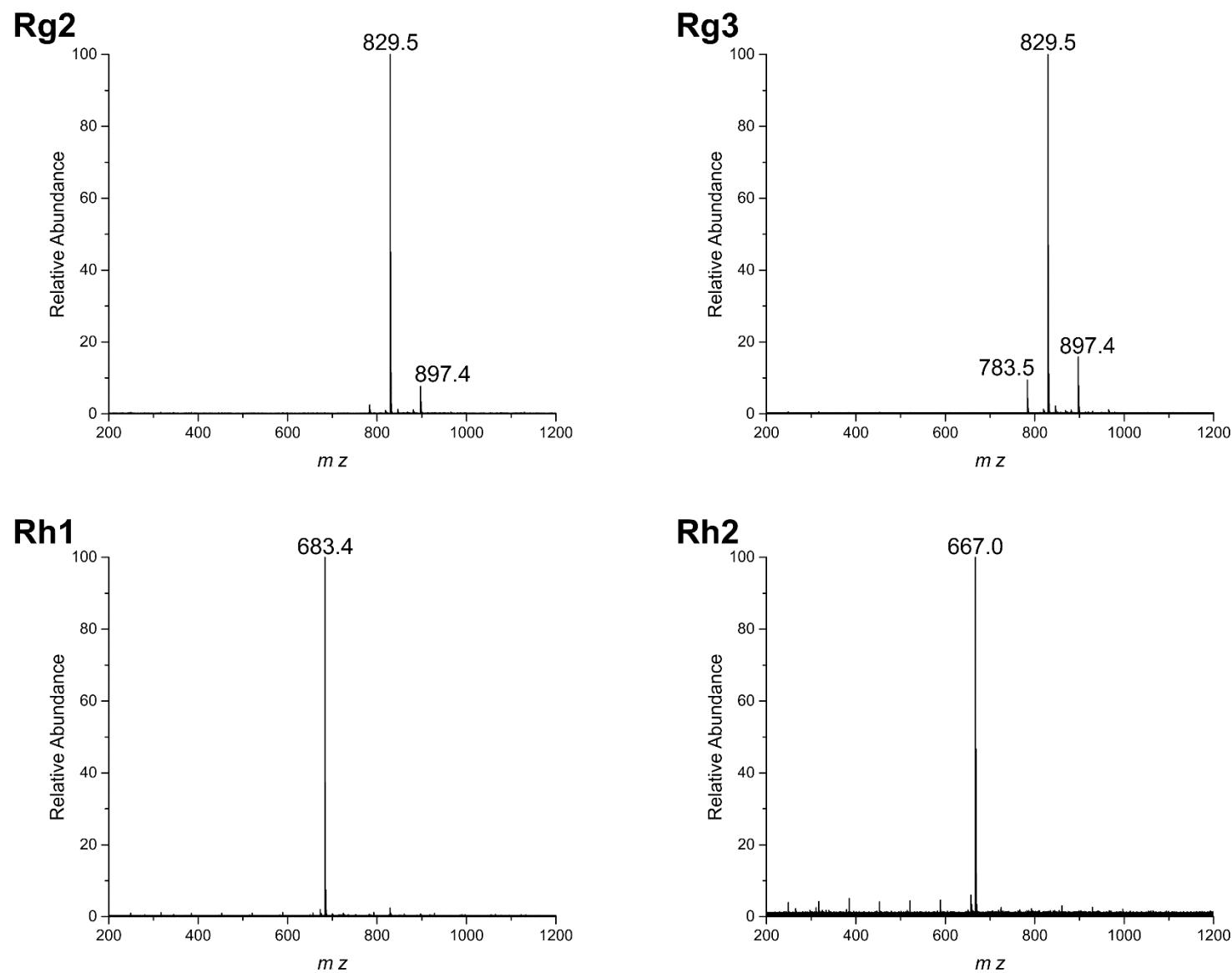
**Fig. S3.** LC separations of an eight ginsenoside mixture under the following mobile phase programs using H<sub>2</sub>O and ACN: (A) linear gradient from 20 % ACN to 23 % ACN over 10 min and linear gradient to 42 % ACN over 19 min; (B) linear gradient from 20 % ACN to 23 % ACN over 10 min and linear gradient to 50 % ACN over 20 min; (C) isocratic at 21 % ACN for 5 min, linear gradient to 50 % ACN over 20 min, and linear gradient to 100 % ACN over 5 min; (D) isocratic at 18 % ACN for 10 min and linear gradient to 50 % ACN over 20 min.



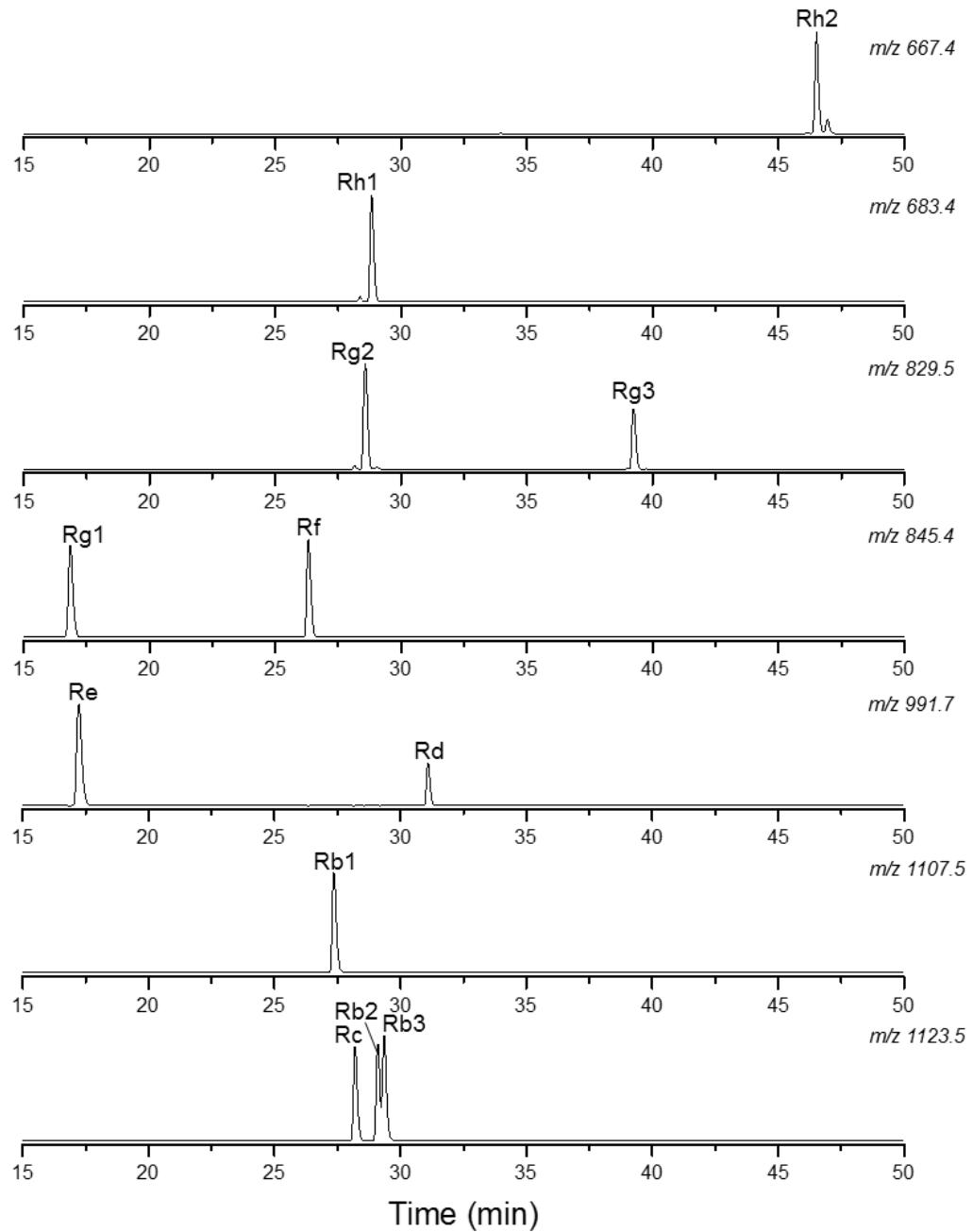
**Fig. S4.** Mass spectra of ginsenoside Rb1 (1101.31 g/mol), Rb2 (1079.29 g/mol), Rb3 (1079.29 g/mol), and Rc (1079.29 g/mol).



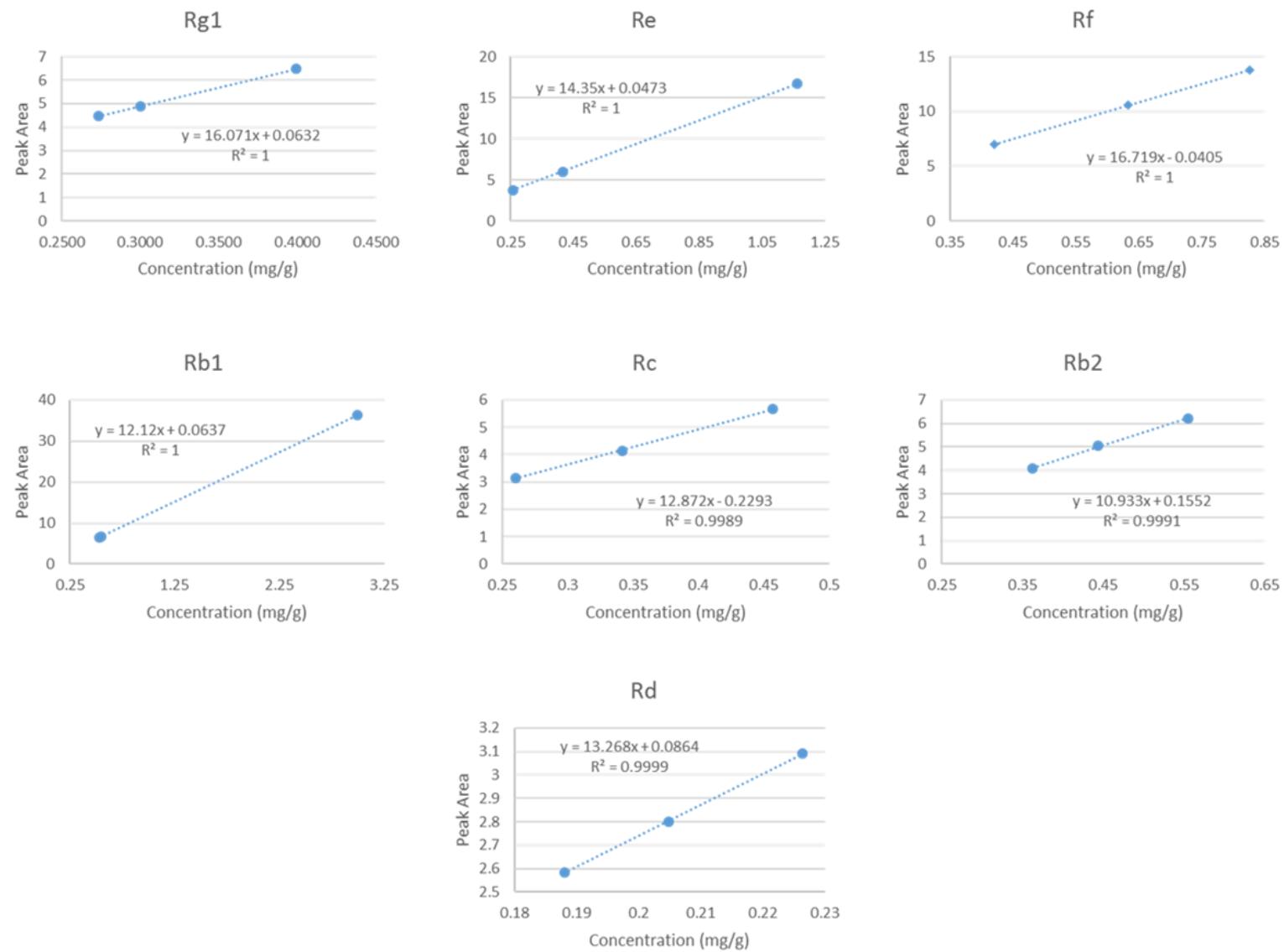
**Fig. S5.** Mass spectra of ginsenoside Rd (1079.29 g/mol), Re (947.17 g/mol), Rf (801.03 g/mol), and Rg1 (801.03 g/mol).



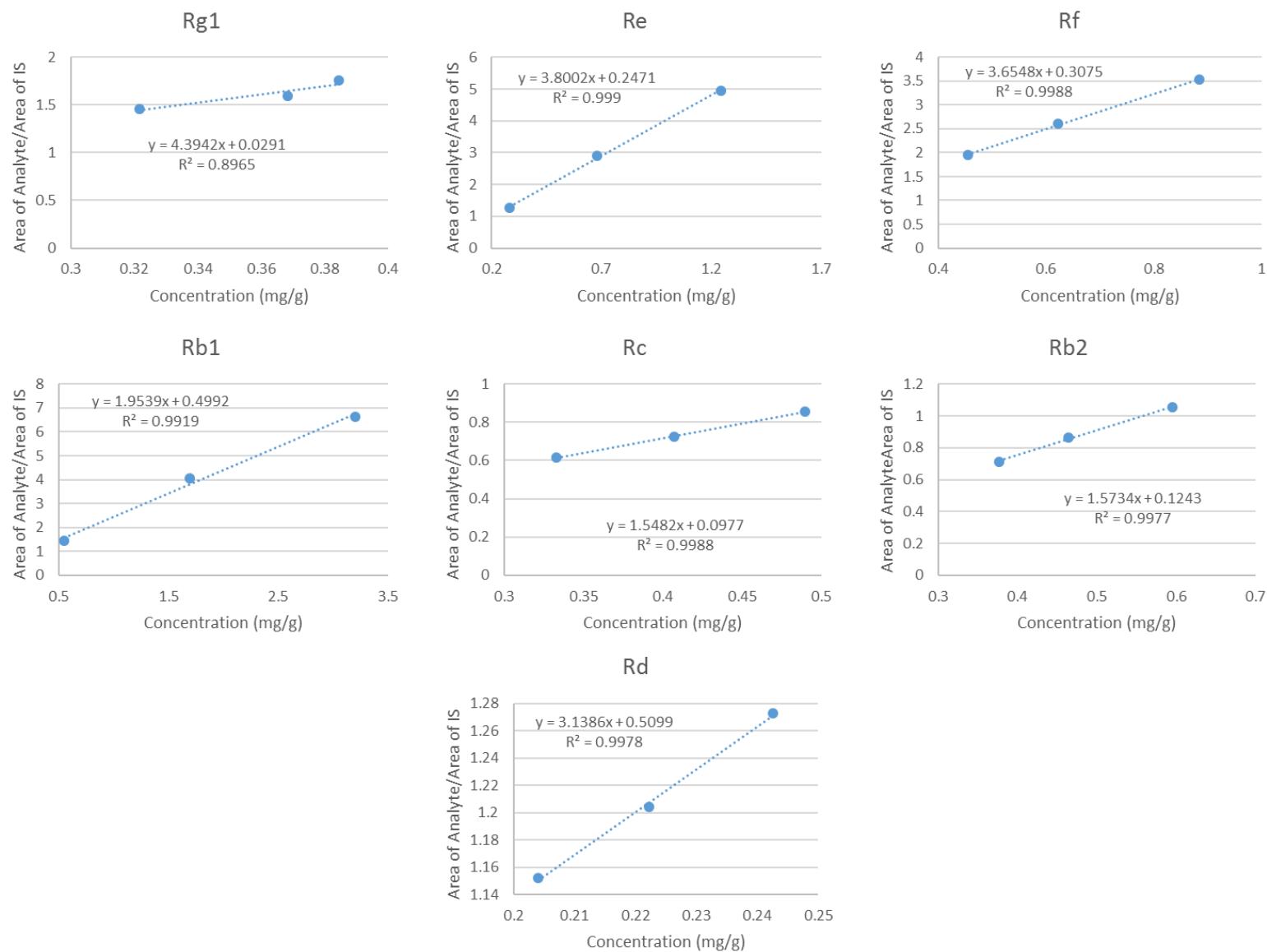
**Fig. S6.** Mass spectra of ginsenoside Rg2 (785.03 g/mol), Rg3 (785.03 g/mol), Rh1 (638.89 g/mol), and Rh2 (622.89 g/mol).



**Figure S7.** LC/MS chromatograms in SIM mode for the 12 ginsenoside mixture under the initial separation conditions. The separation conditions included a 0.7 mL/min flow rate, 25 °C column temperature, and the mobile phase gradient summarized in Table 1.



**Figure S8.** Calibration curves for the three calibrants used for the LC/UV measurements of SRM 3389.



**Figure S9.** Calibration curves for the three calibrants used for the LC/MS measurements of SRM 3389.