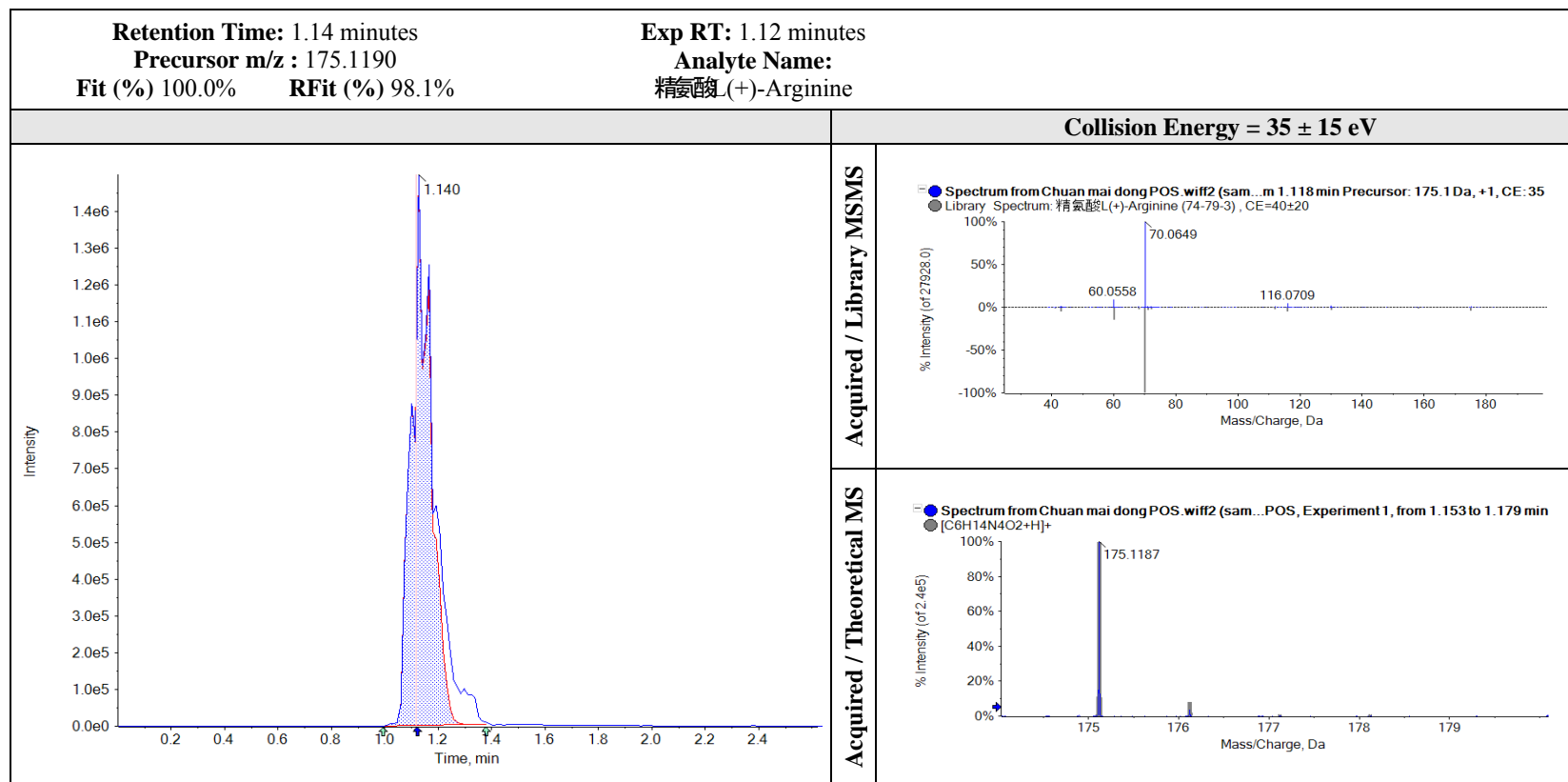


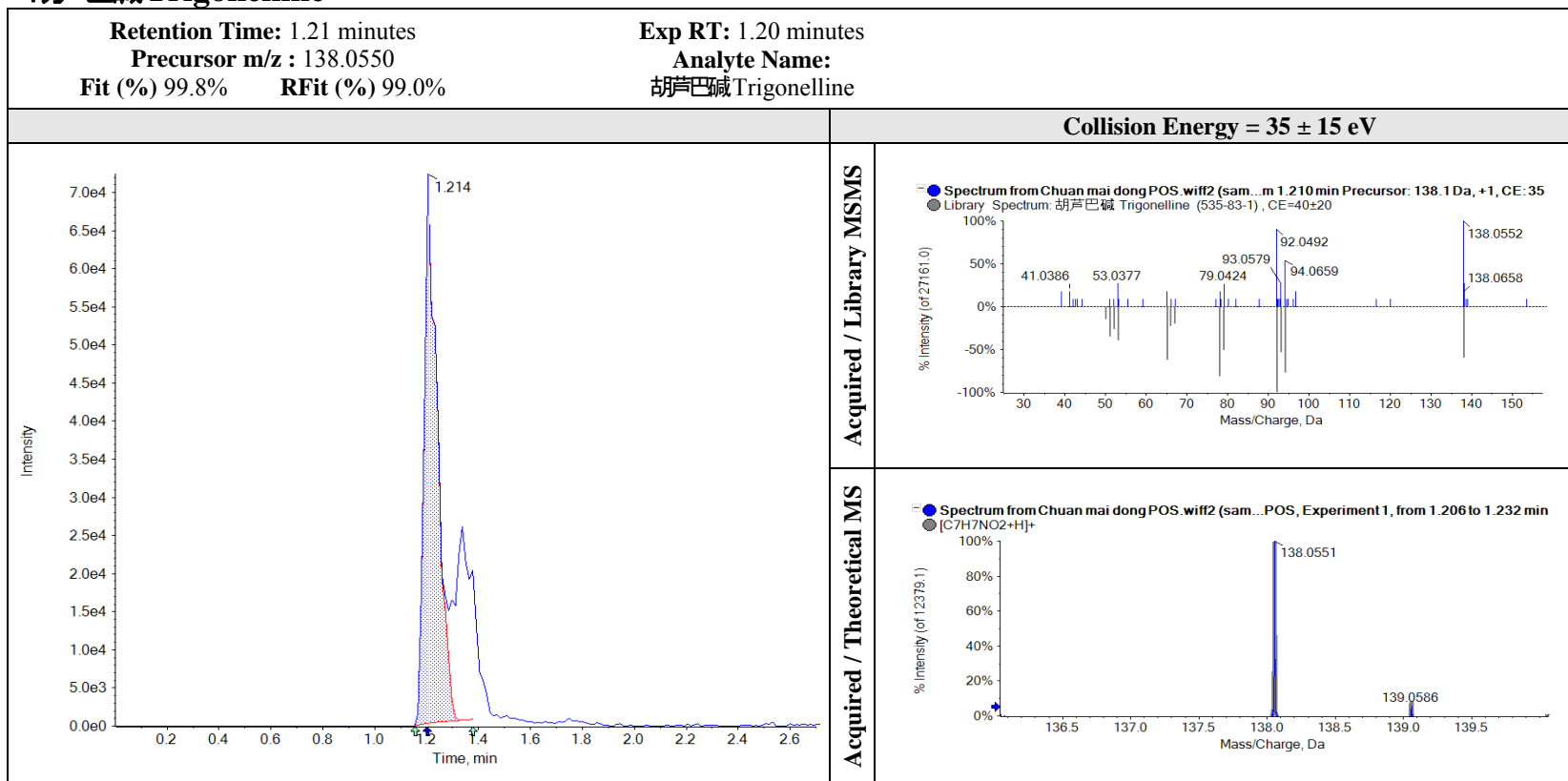
Table S1 MS fragmentation pathways for representative compounds of CMD in UPLC-Q/TOF-MS analysis

MS fragmentation pathways for different chemical constituents of CMD in positive ion mode

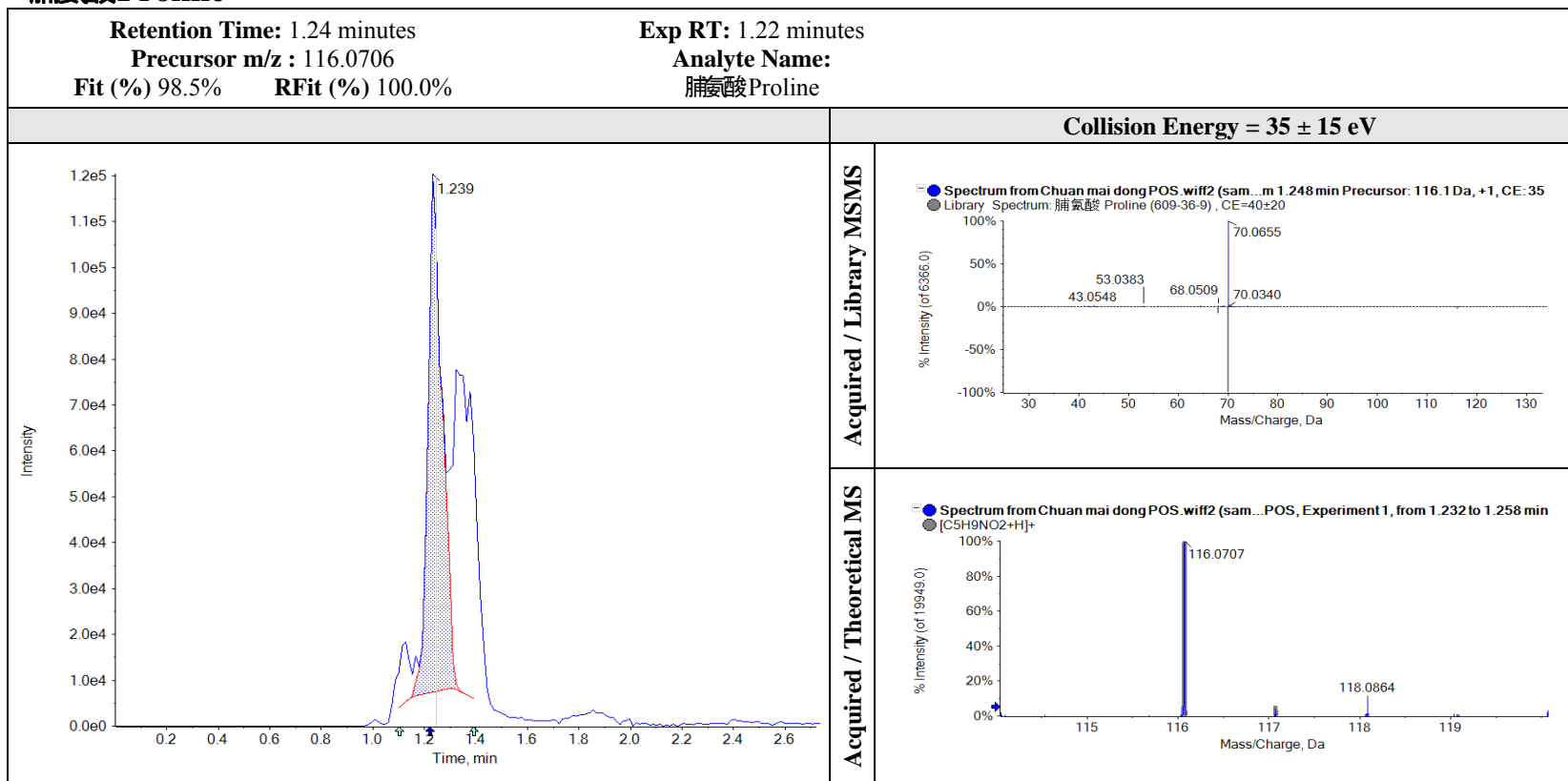
精氨酸L(+)-Arginine



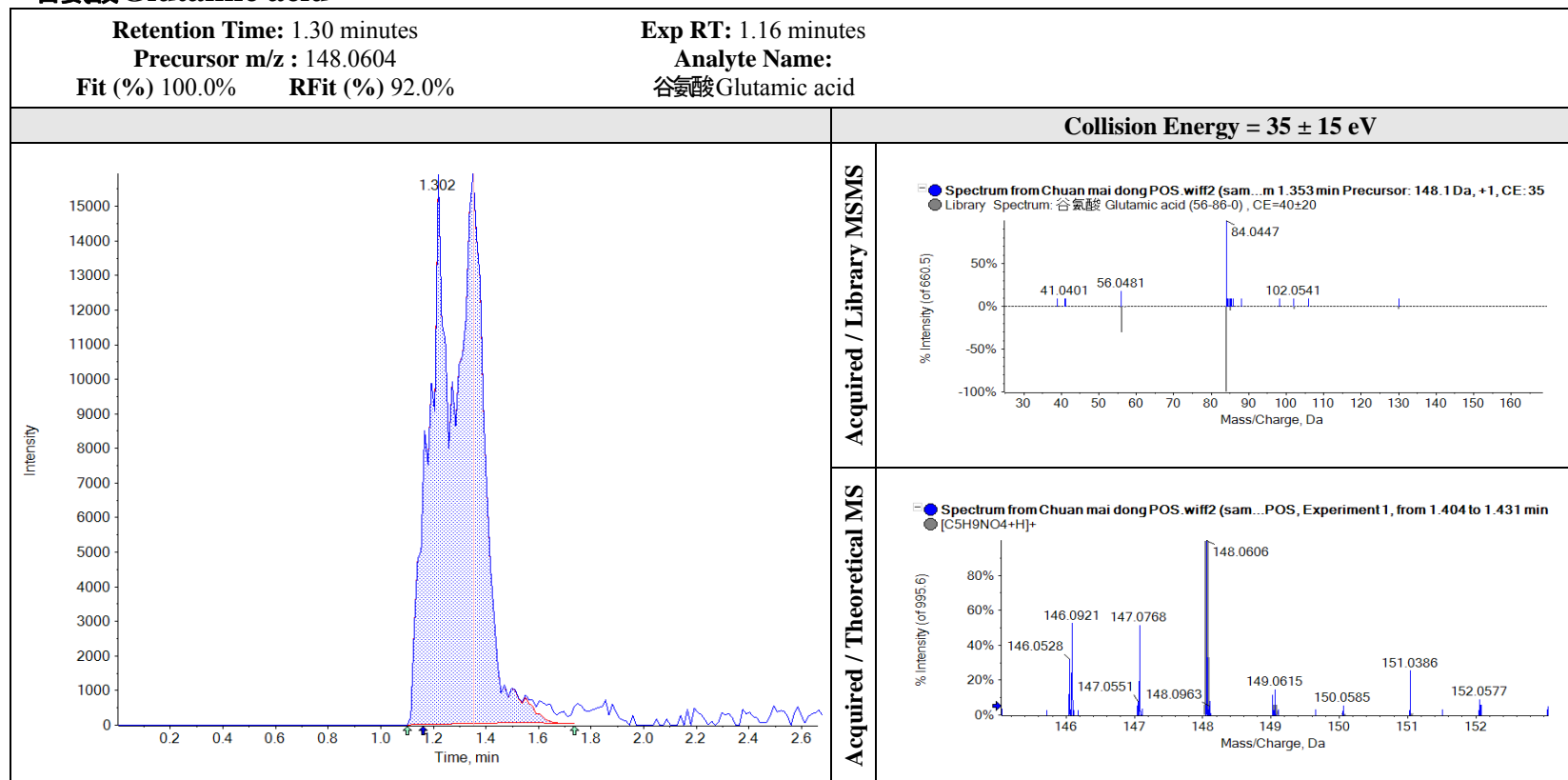
胡芦巴碱 Trigonelline



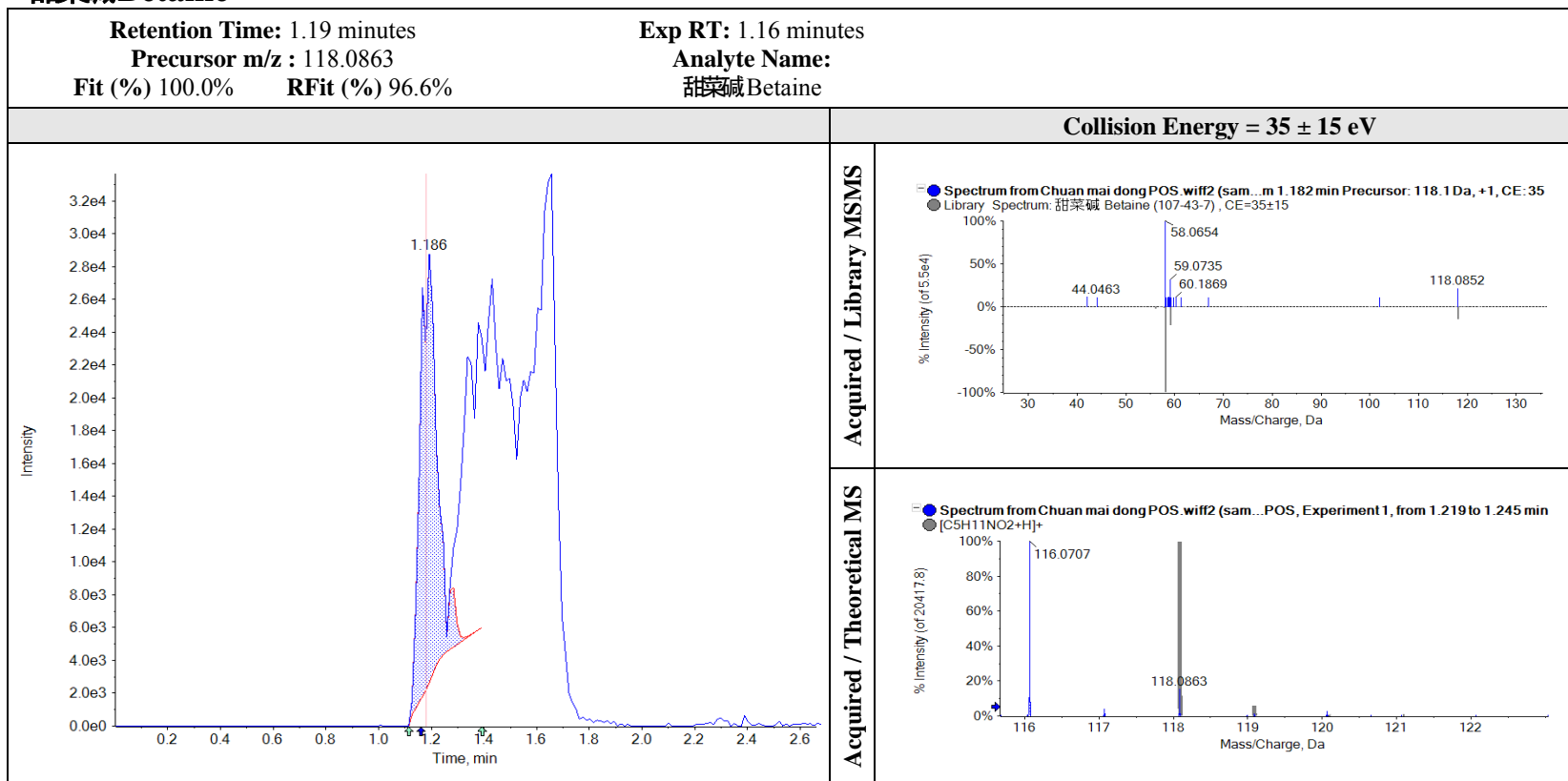
脯氨酸 Proline



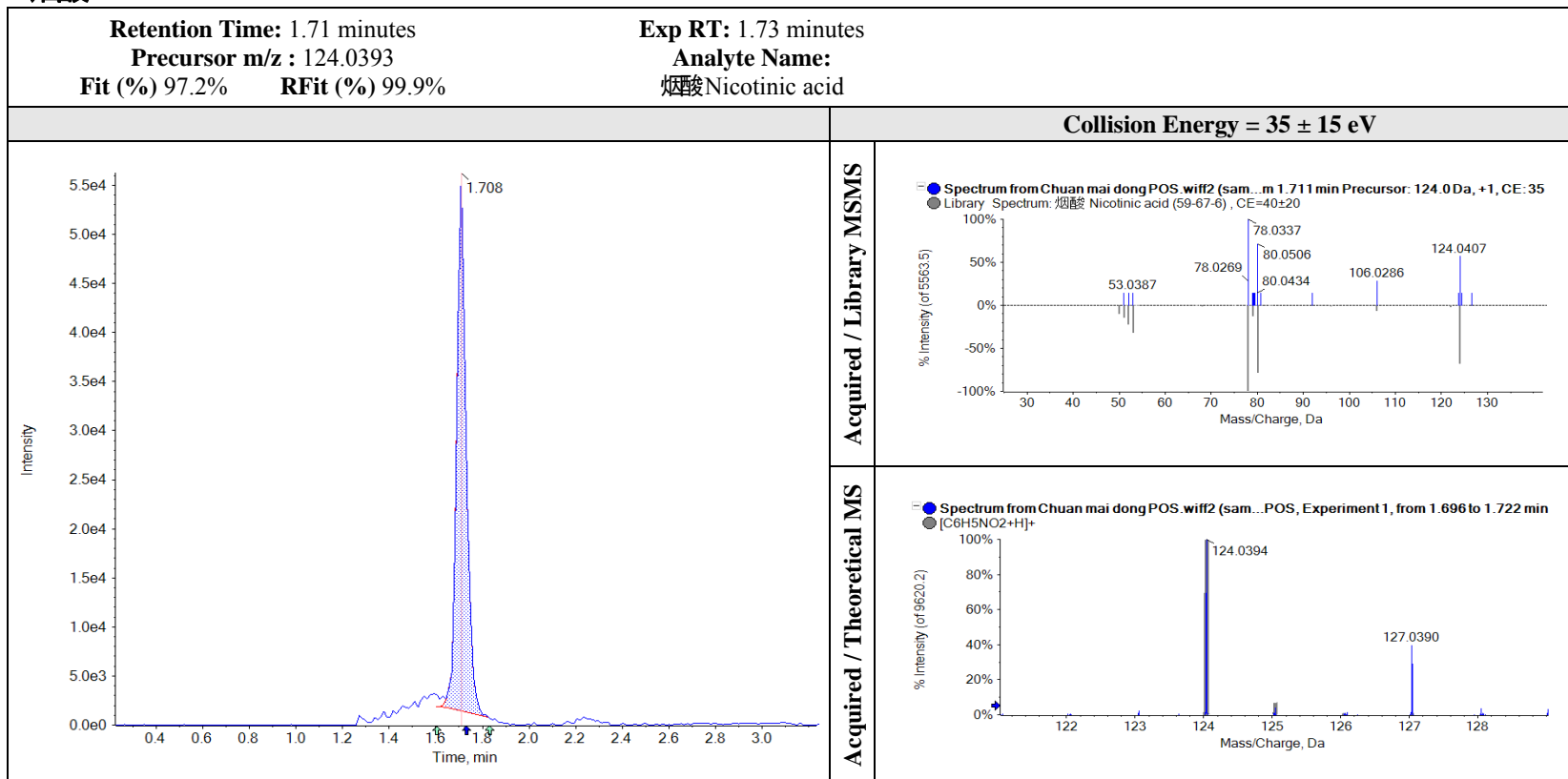
谷氨酸 Glutamic acid



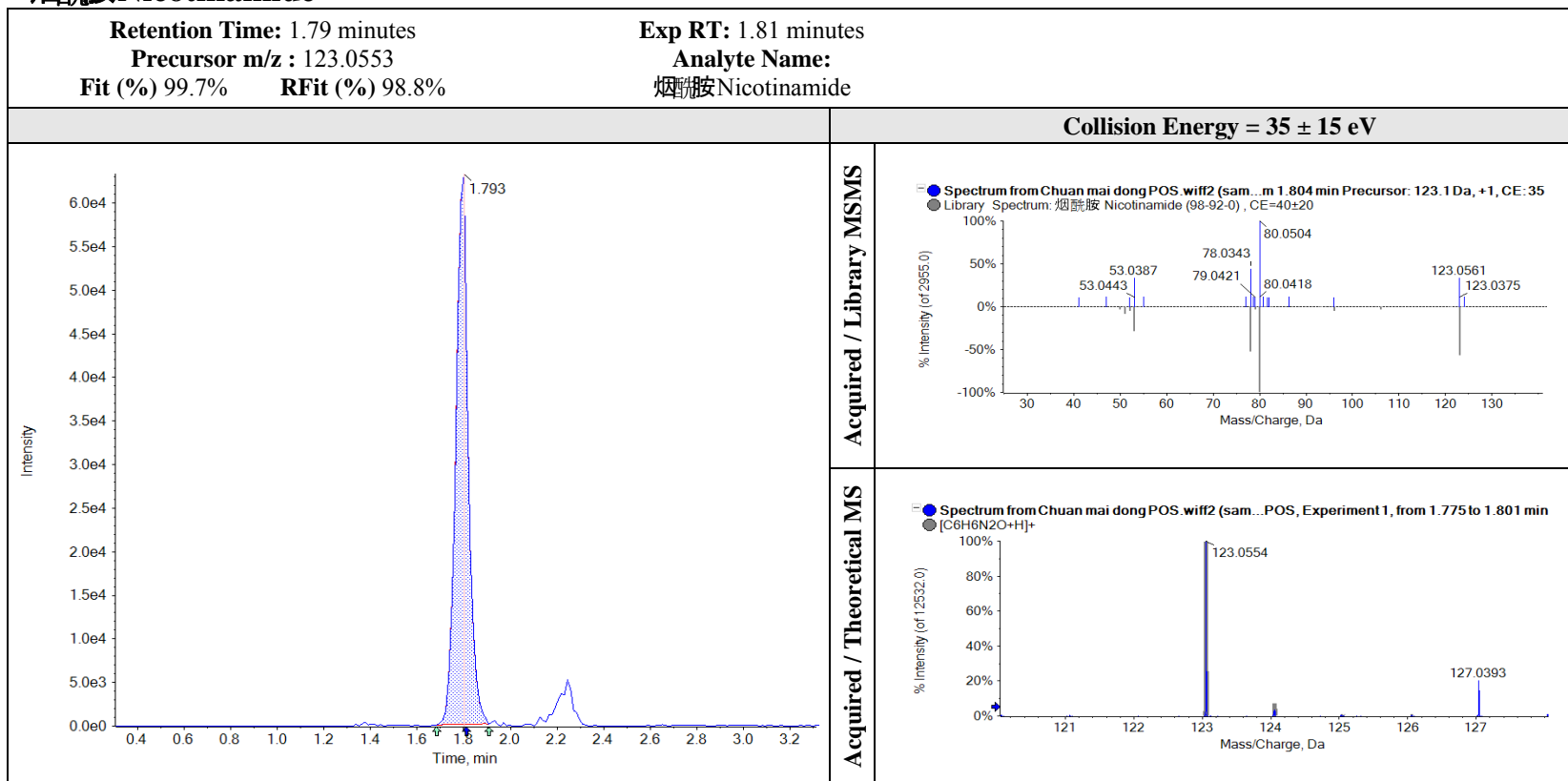
甜菜碱 Betaine



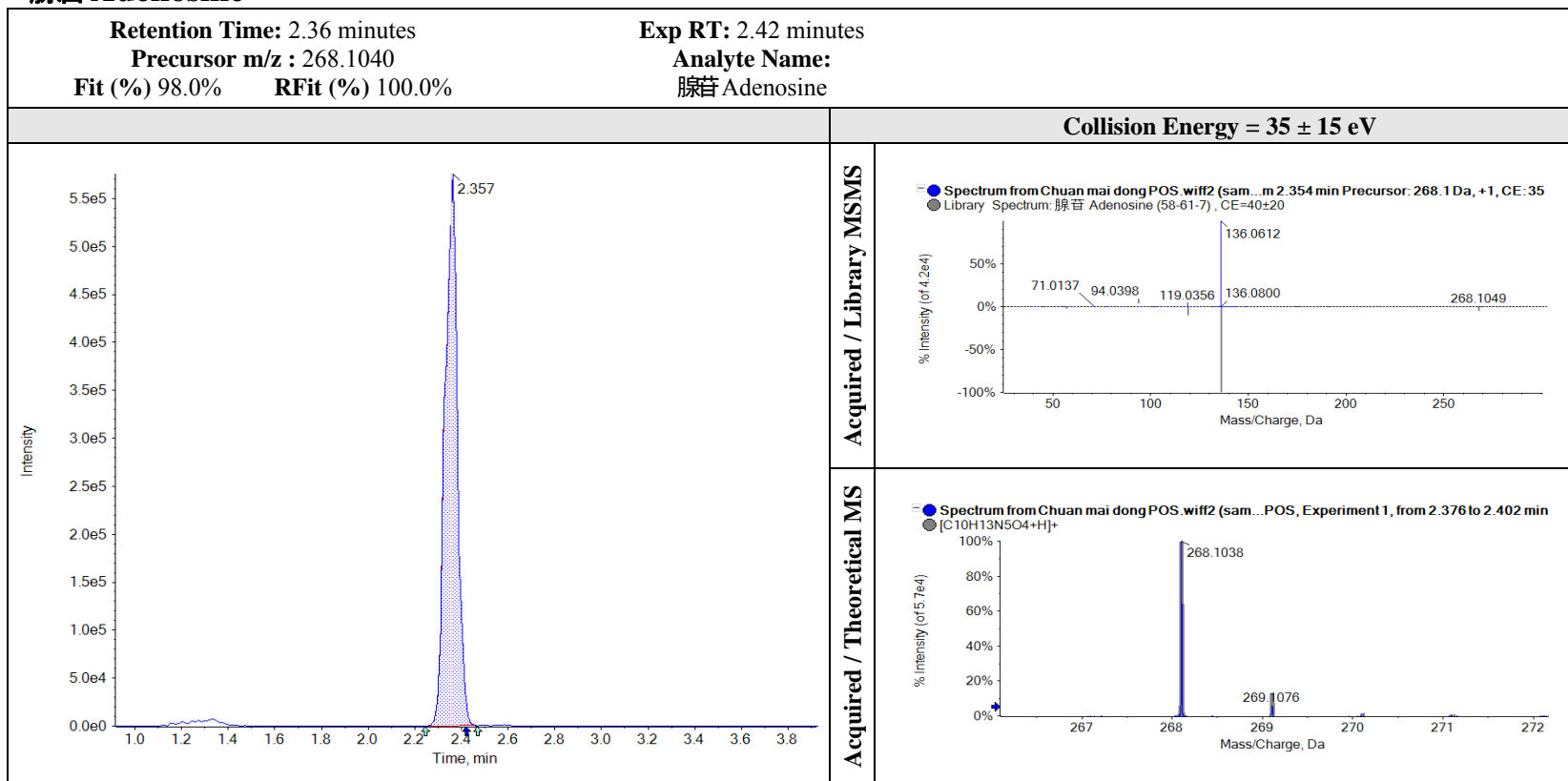
烟酸 Nicotinic acid



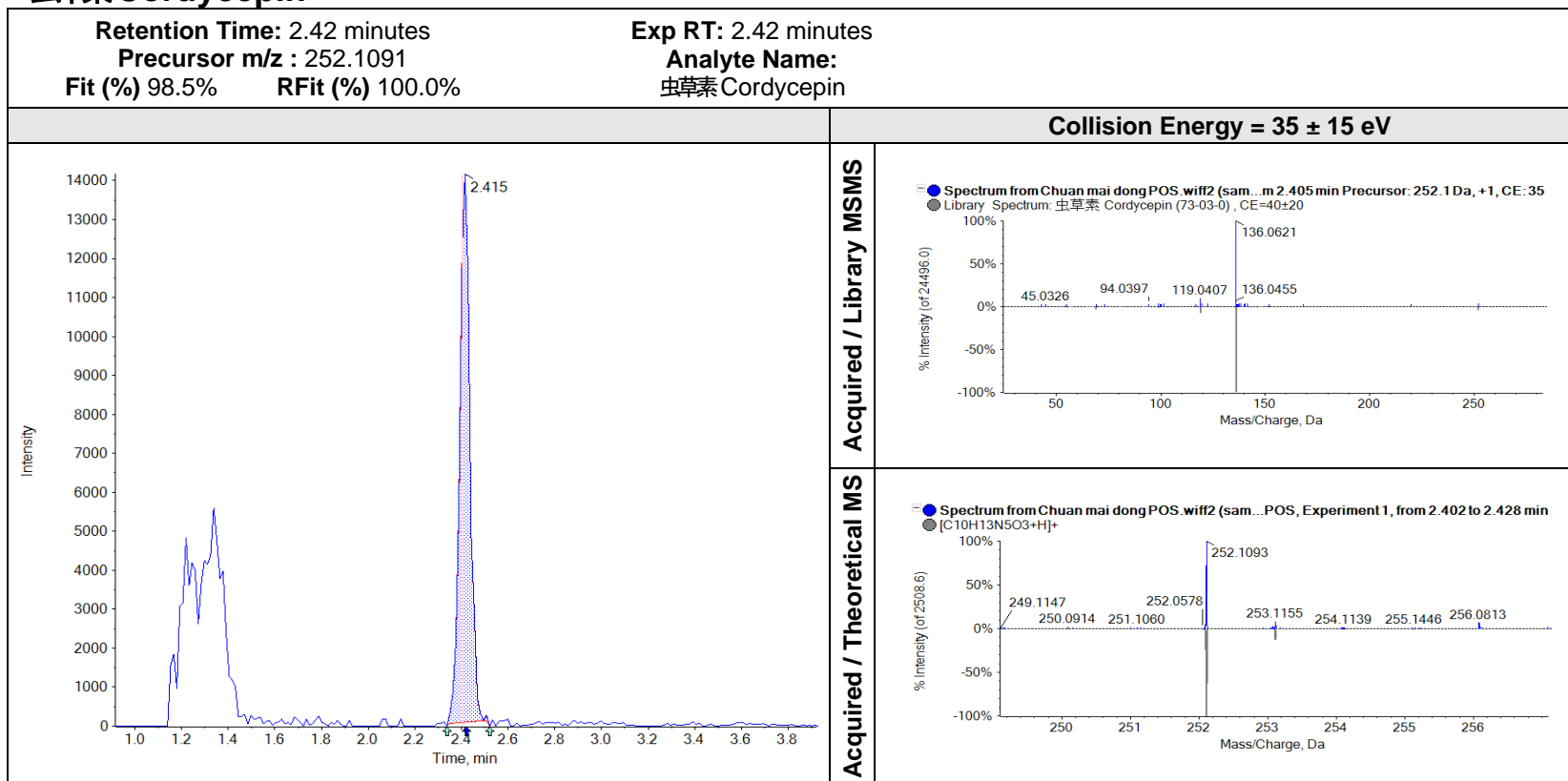
烟酰胺 Nicotinamide



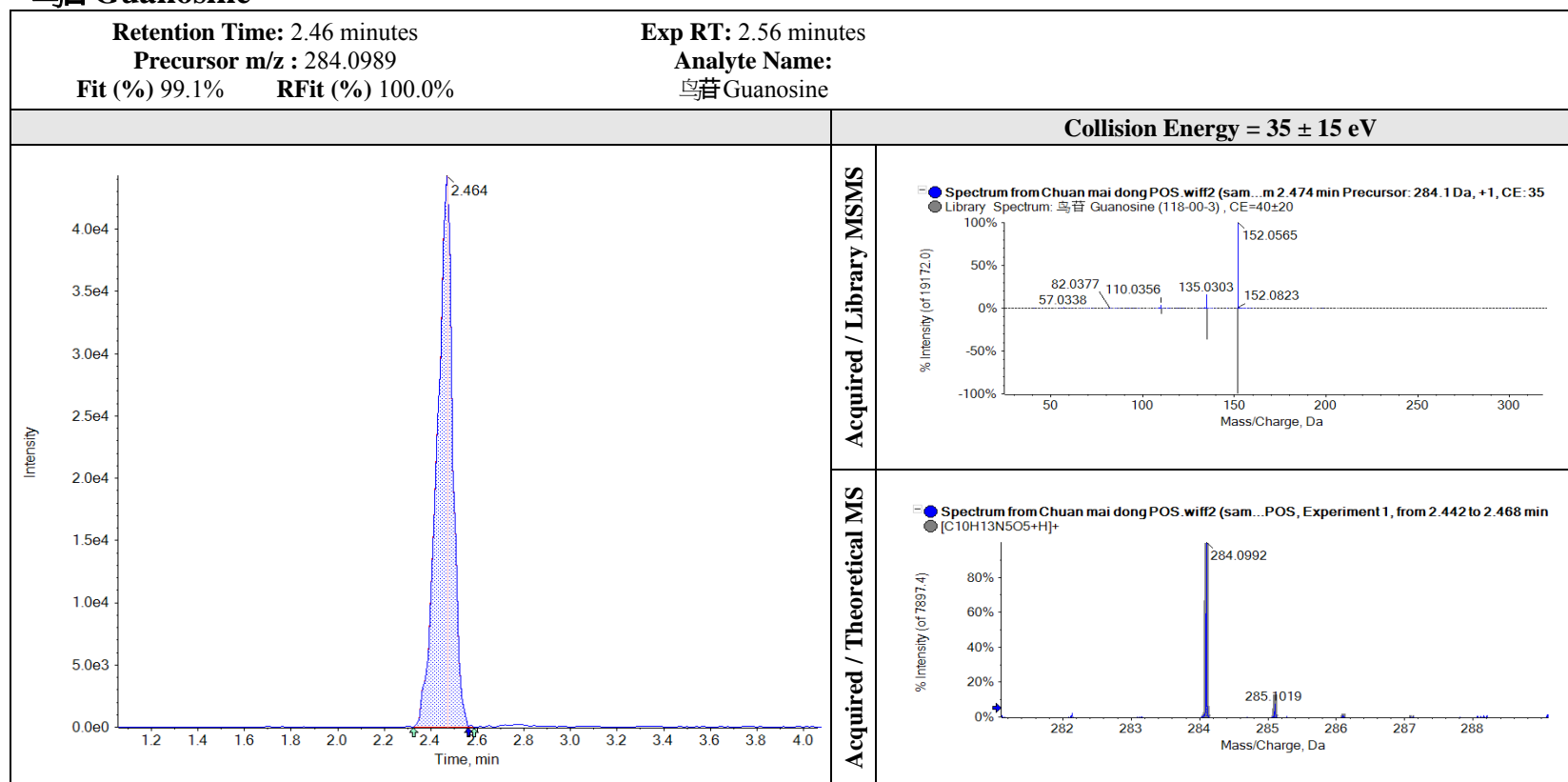
腺苷 Adenosine



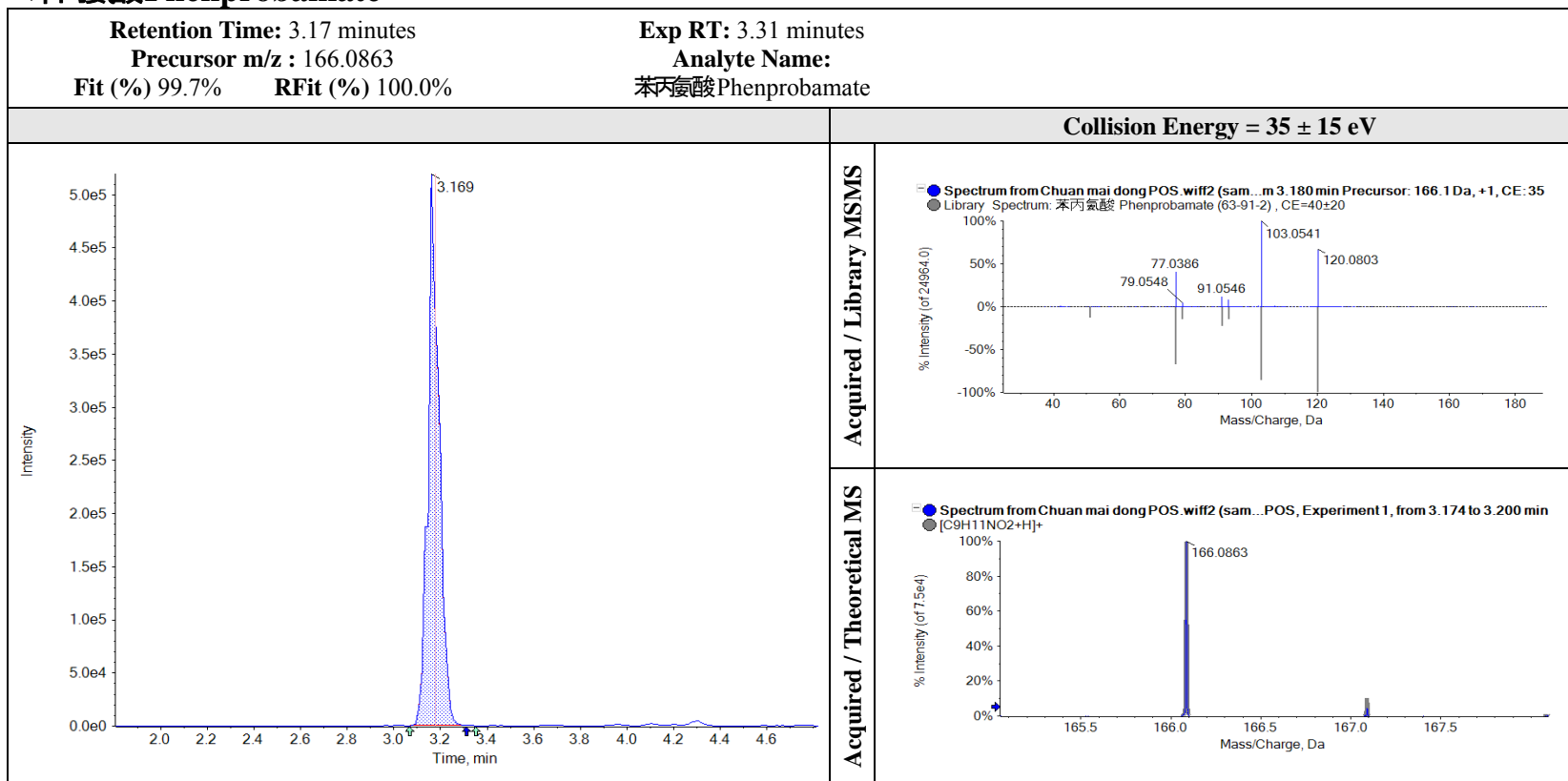
虫草素 Cordycepin



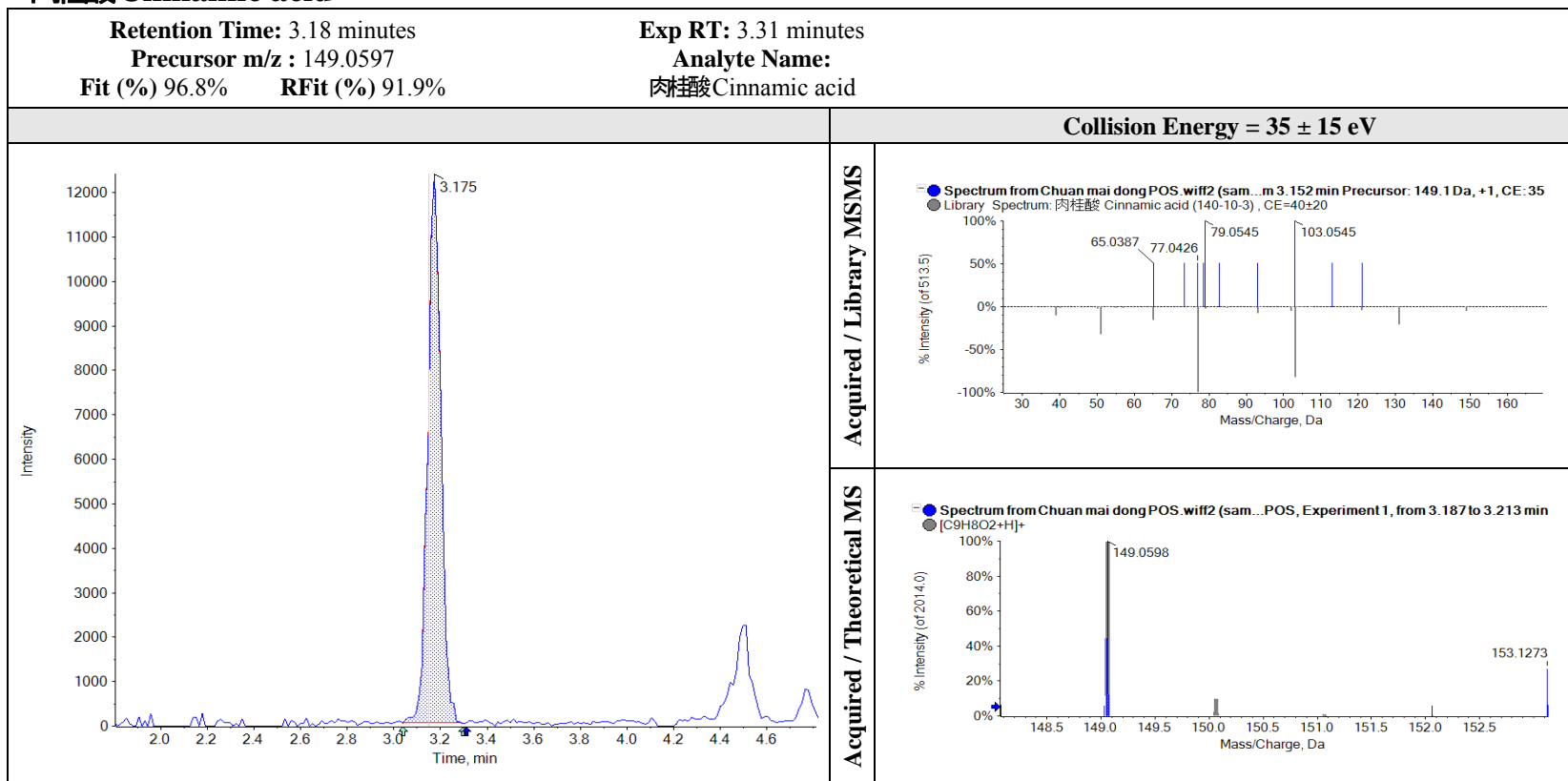
鸟苷 Guanosine



苯丙氨酸 Phenprobamate



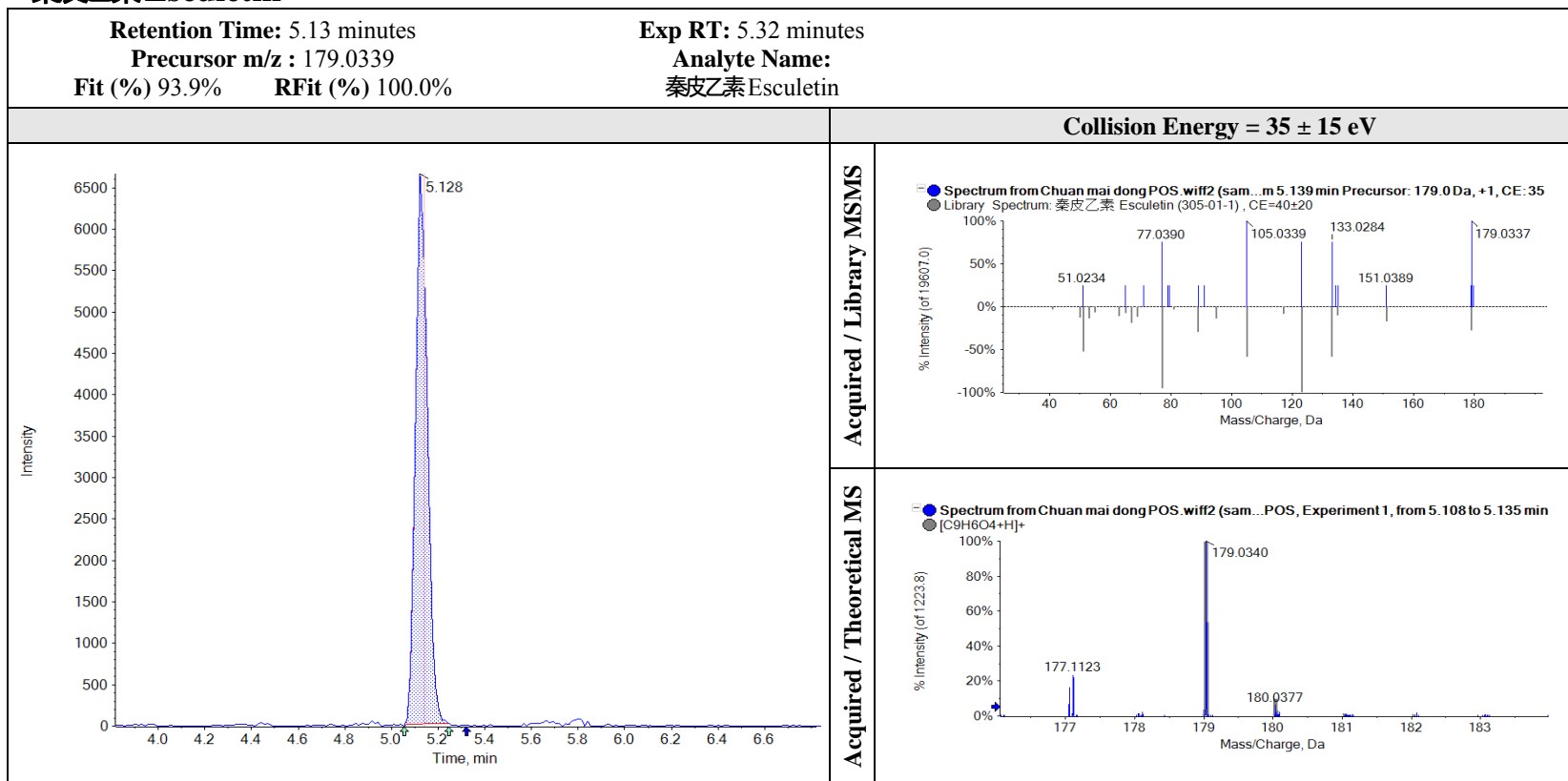
肉桂酸 Cinnamic acid



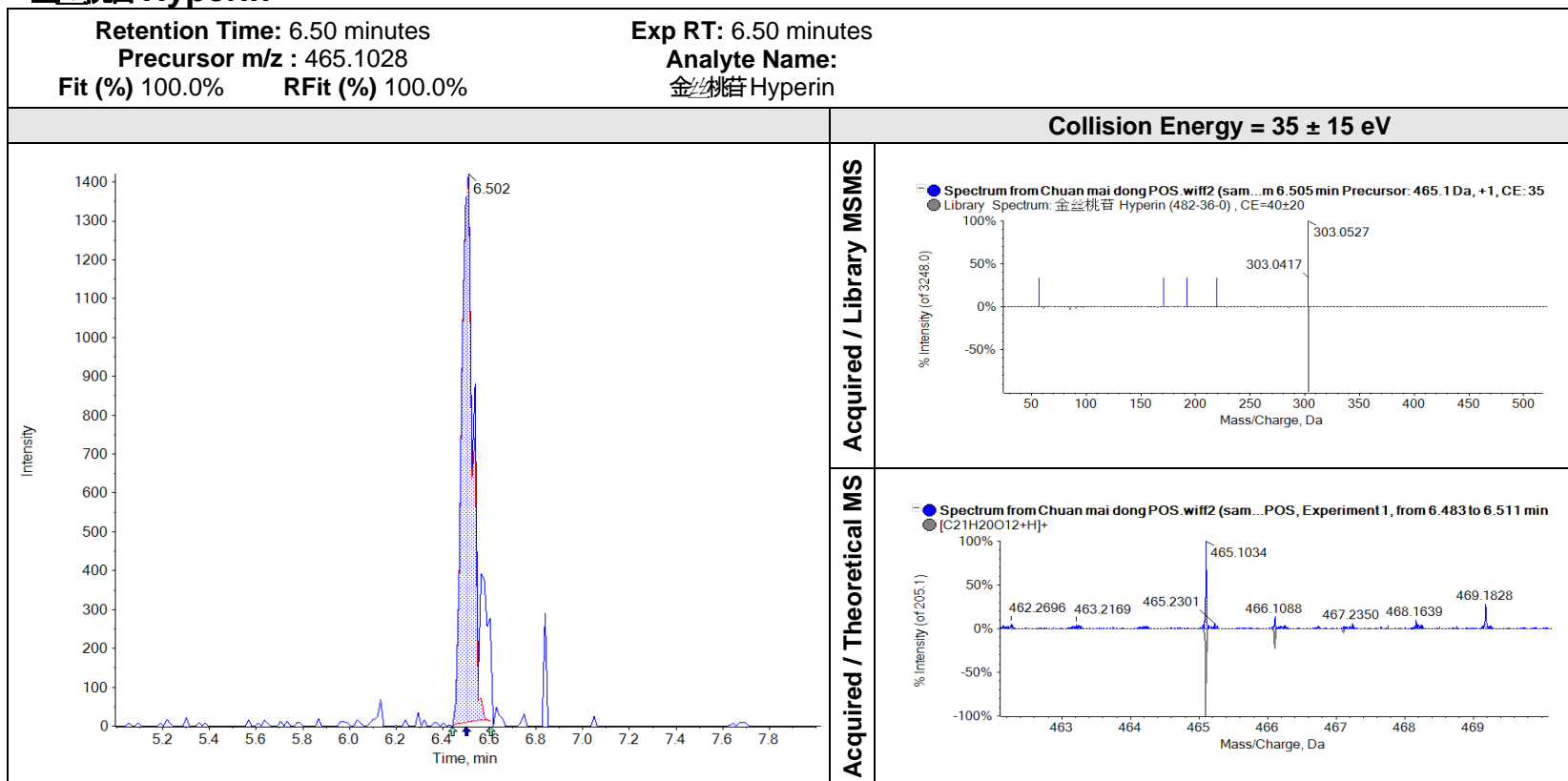
对羟基苯甲酸 4-Hydroxybenzoic acid

<p>Retention Time: 4.73 minutes Exp RT: 4.81 minutes</p> <p>Precursor m/z : 139.0390 Analyte Name:</p> <p>Fit (%) 76.9% RFit (%) 98.6% 对羟基苯甲酸 4-Hydroxybenzoic acid</p>	
<p>Collision Energy = 35 ± 15 eV</p>	
	<p>Acquired / Library MSMS</p>
	<p>Acquired / Theoretical MS</p>

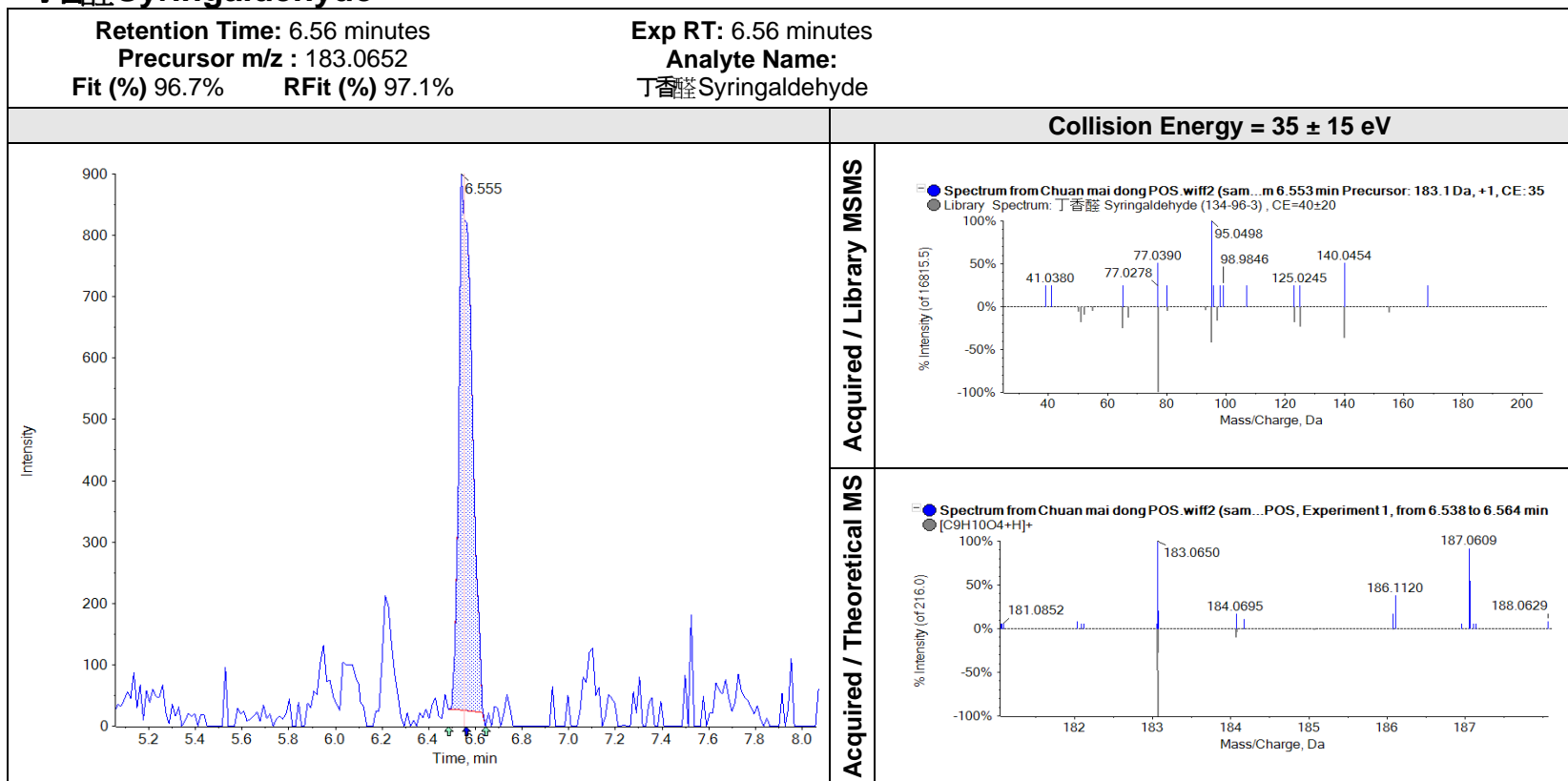
秦皮乙素 Esculetin



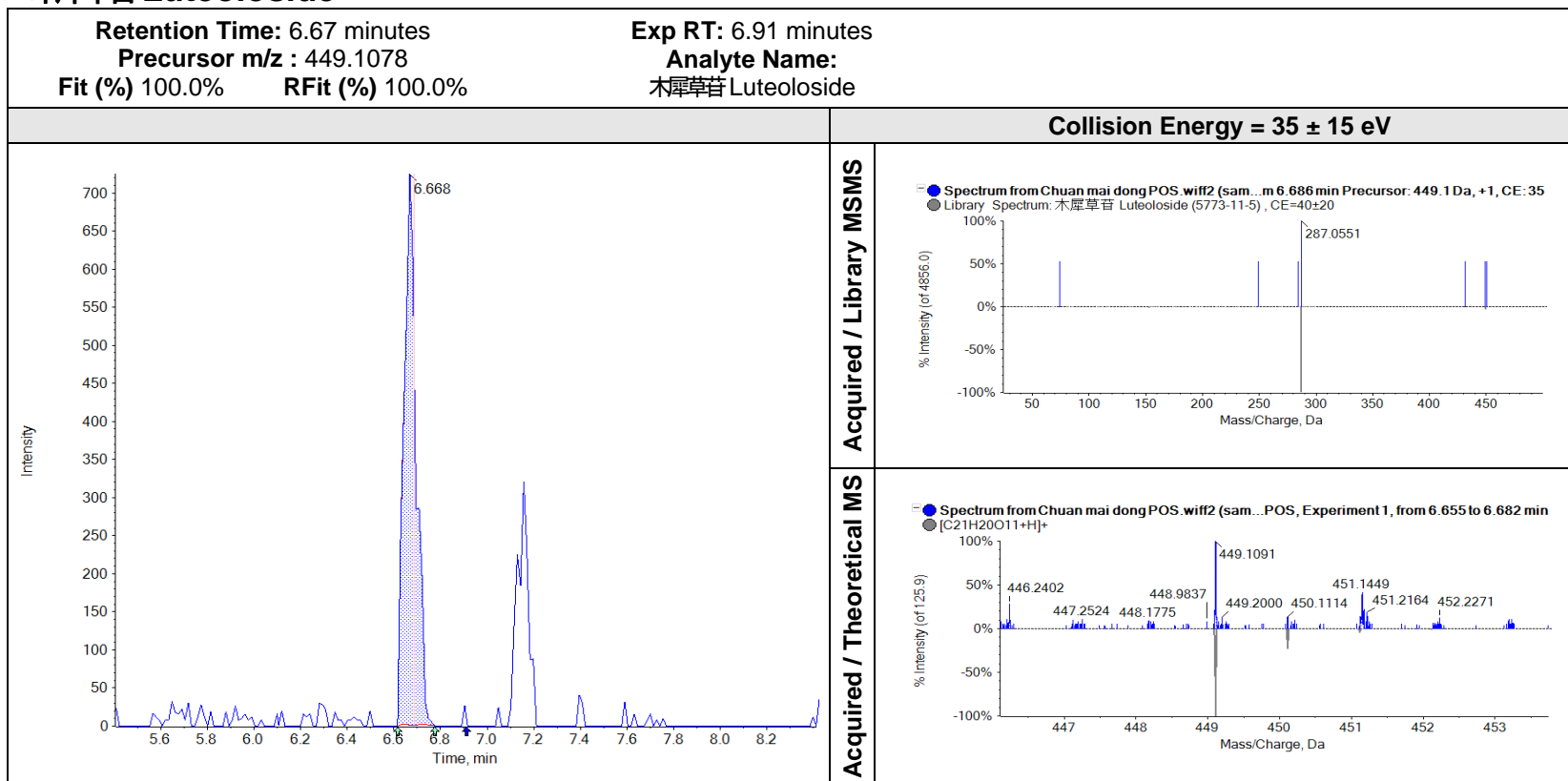
金丝桃苷 Hyperin



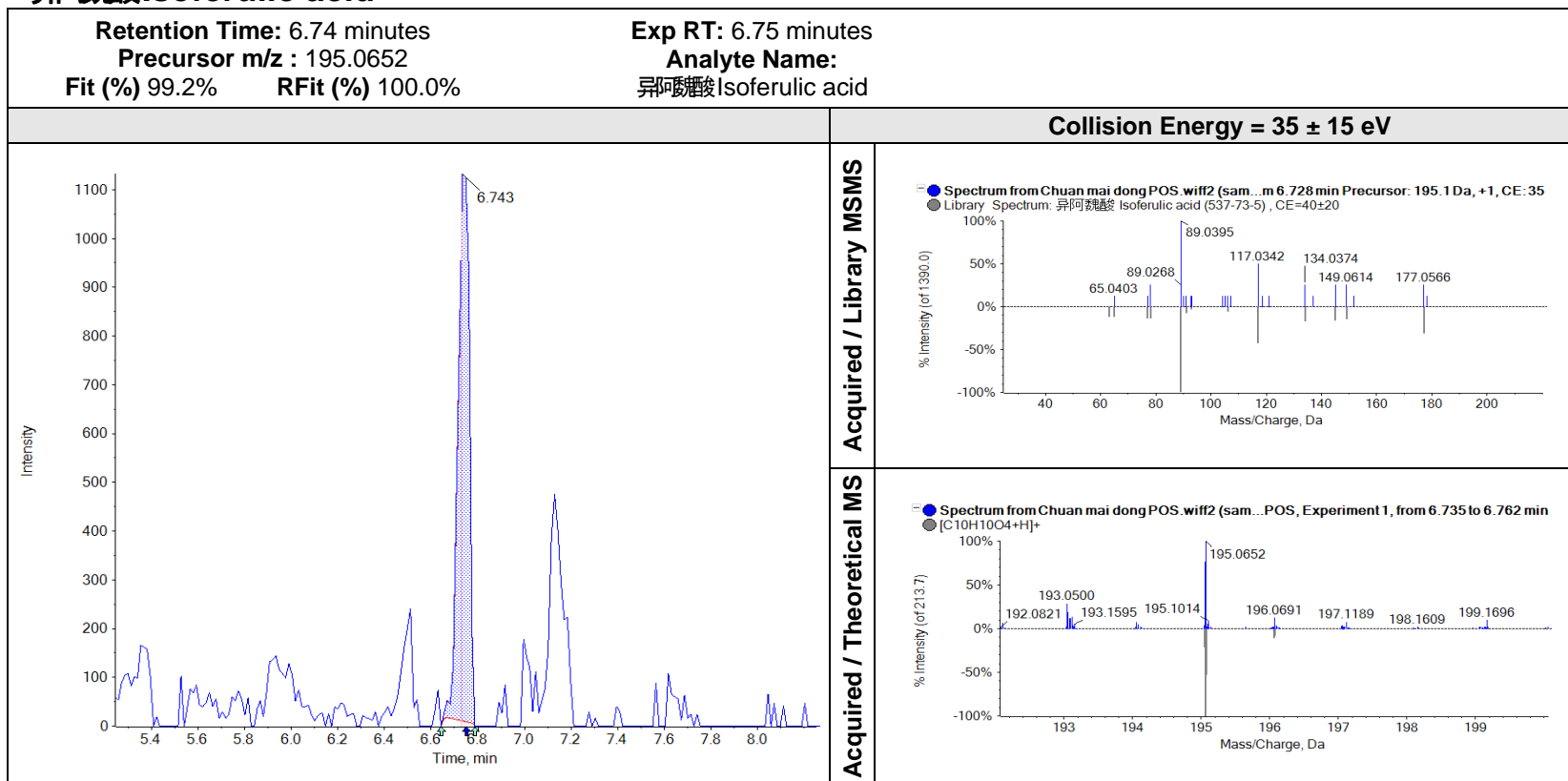
丁香醛 Syringaldehyde



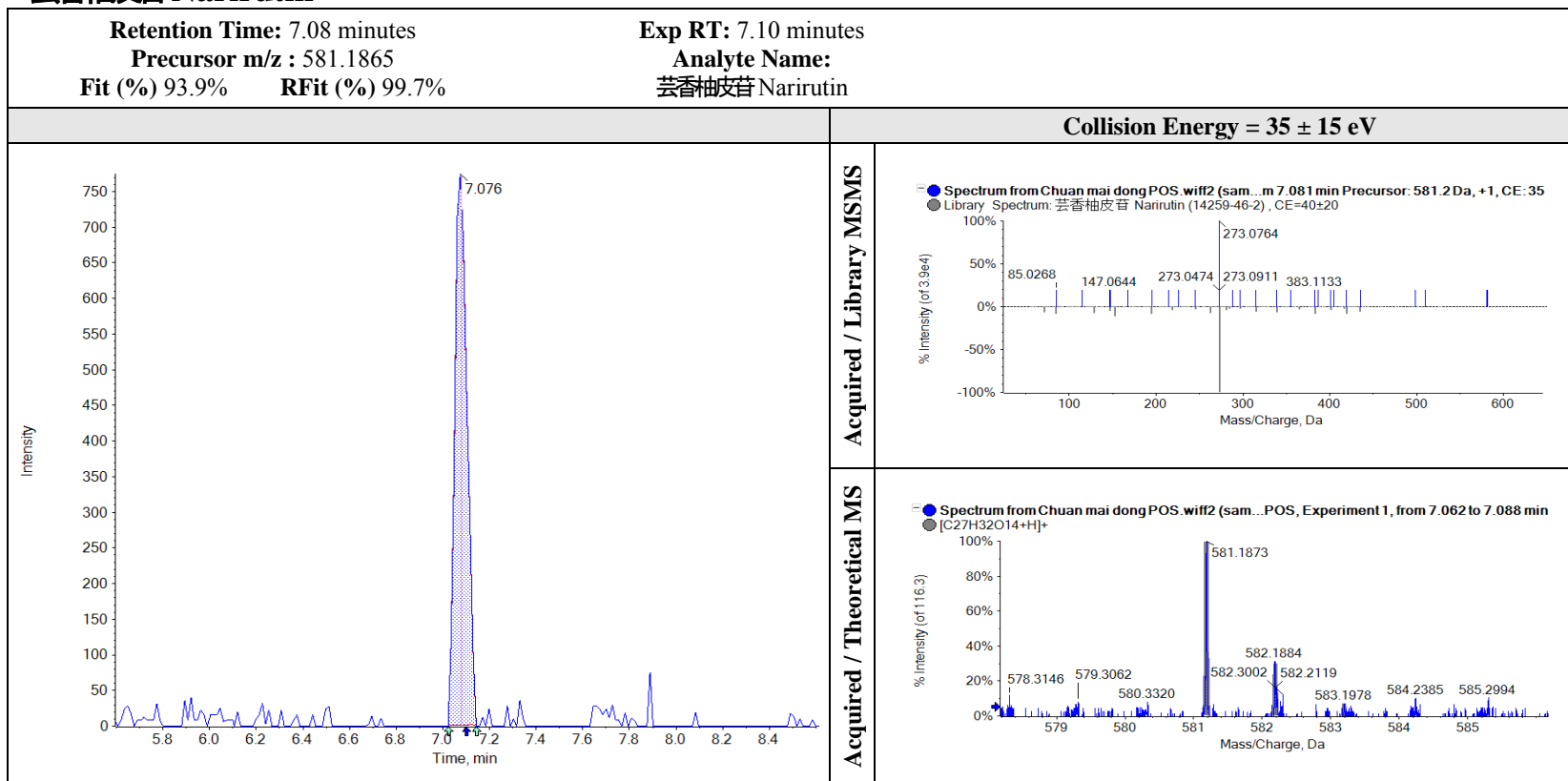
木犀草苷 Luteoloside



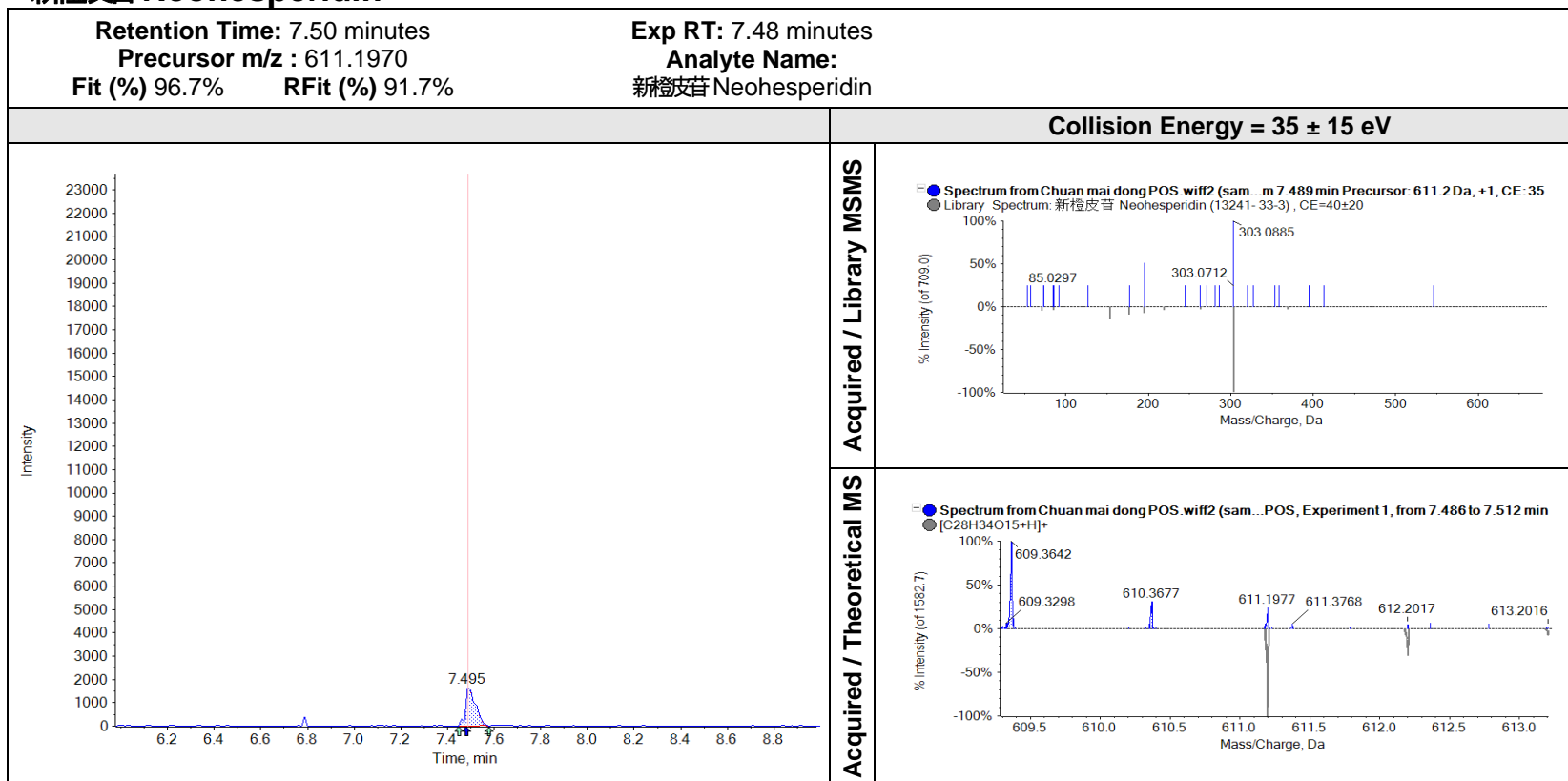
异阿魏酸 Isoferulic acid



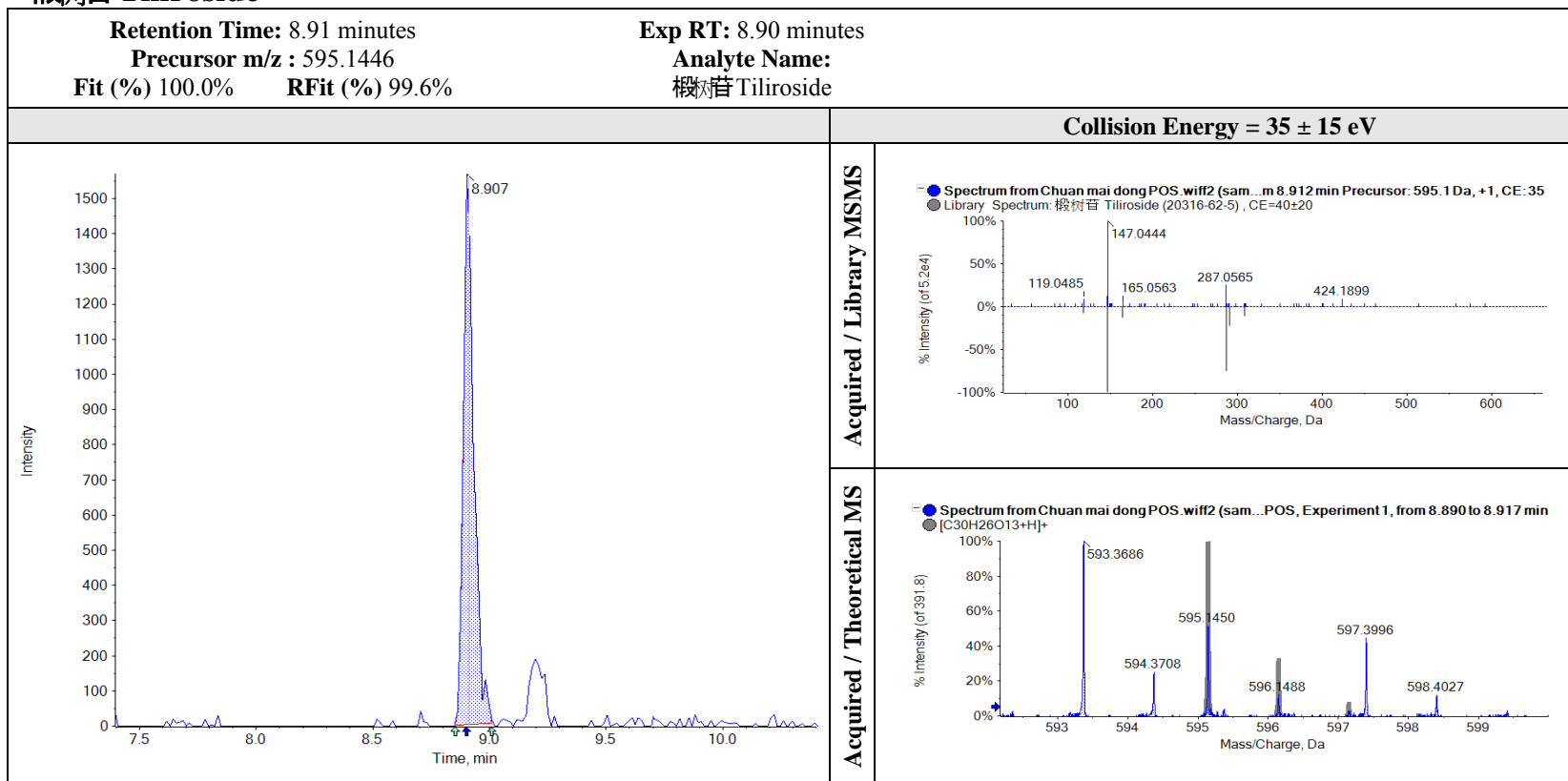
芸香柚皮苷 Narirutin



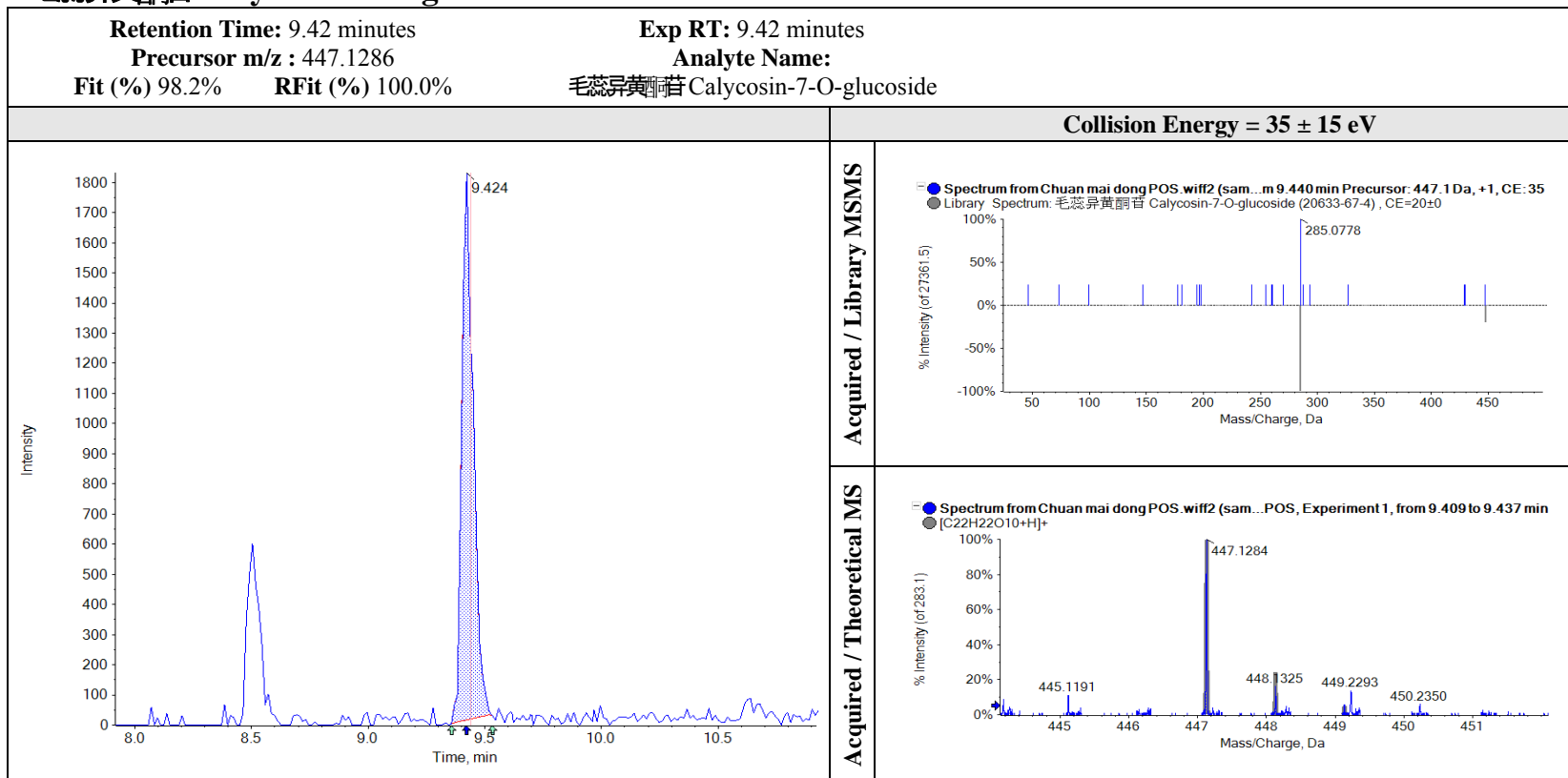
新橙皮苷 Neohesperidin



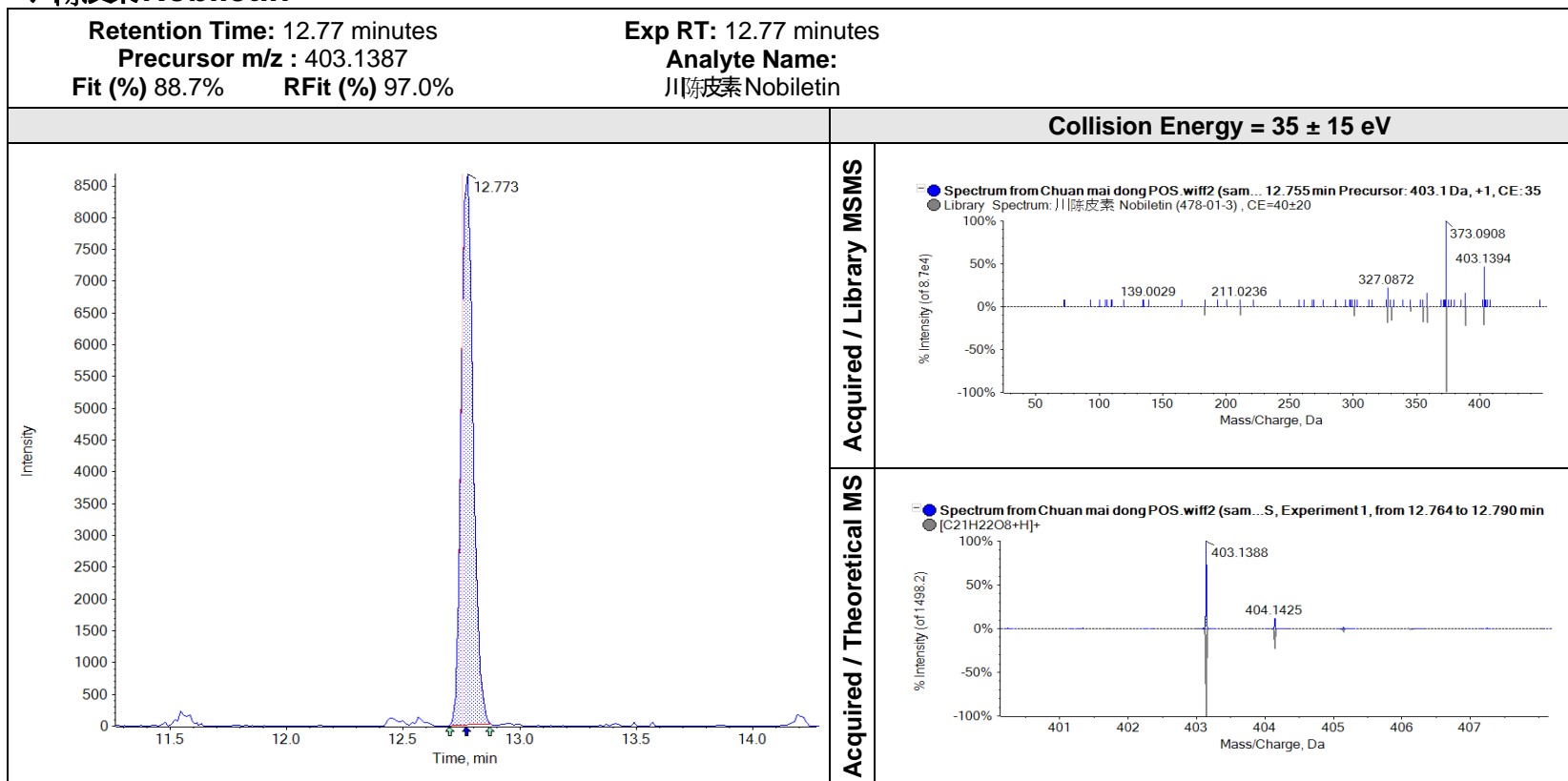
槲寄生 Tiliroside



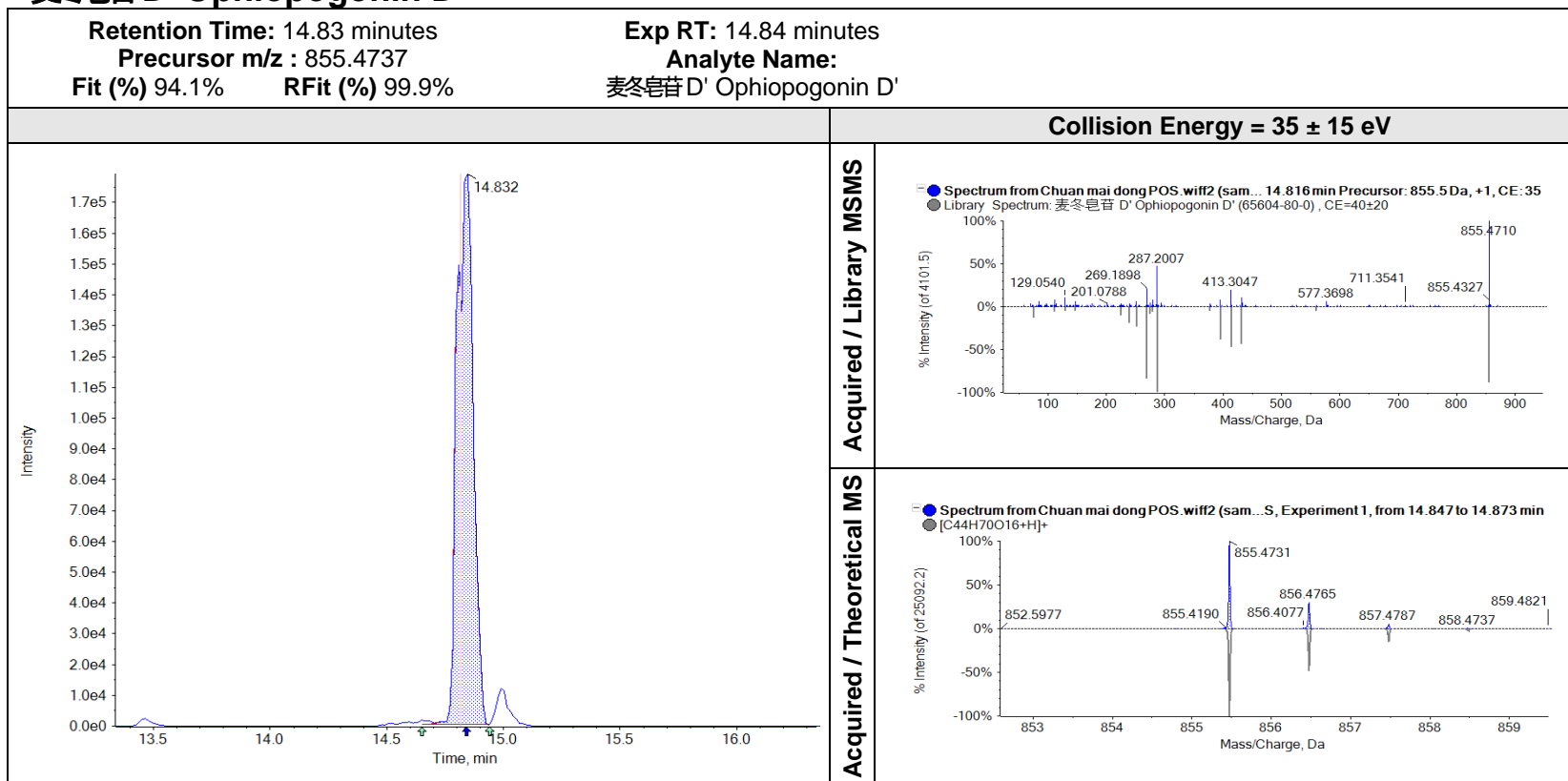
毛蕊异黄酮苷 Calycosin-7-O-glucoside



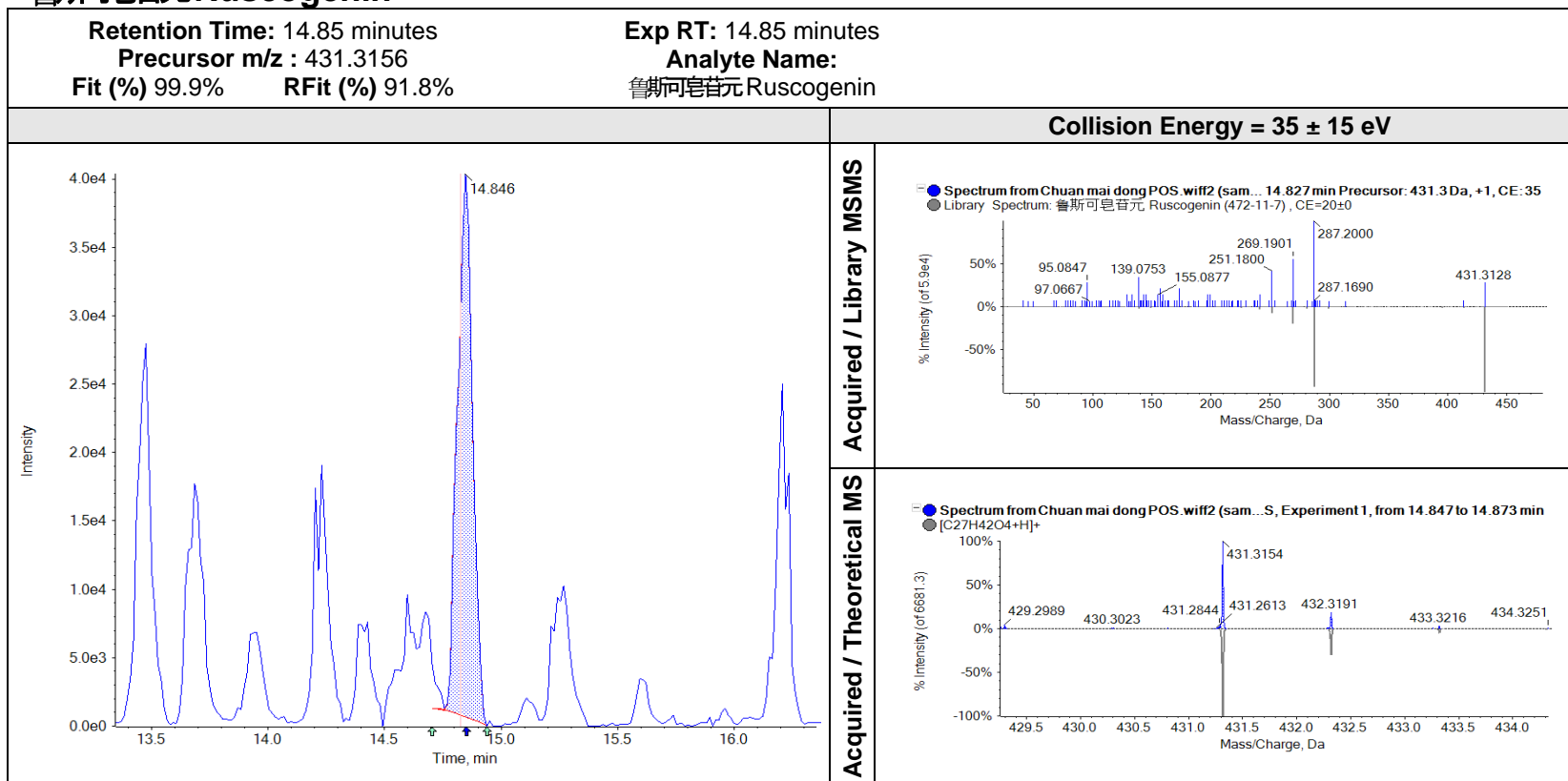
川陈皮素 Nobiletin



麦冬皂苷 D' Ophiopogonin D'

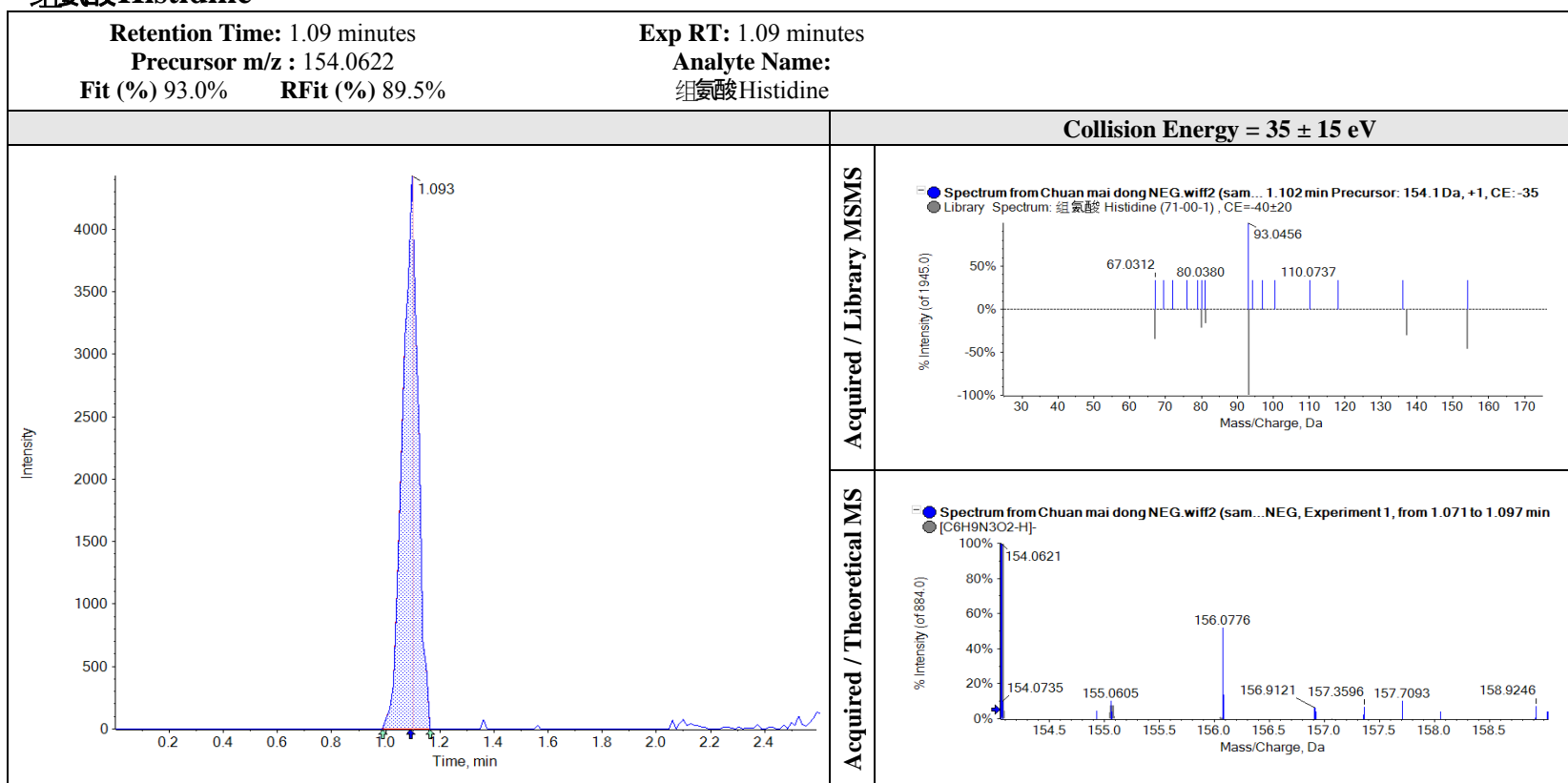


鲁斯可皂苷元 Ruscogenin

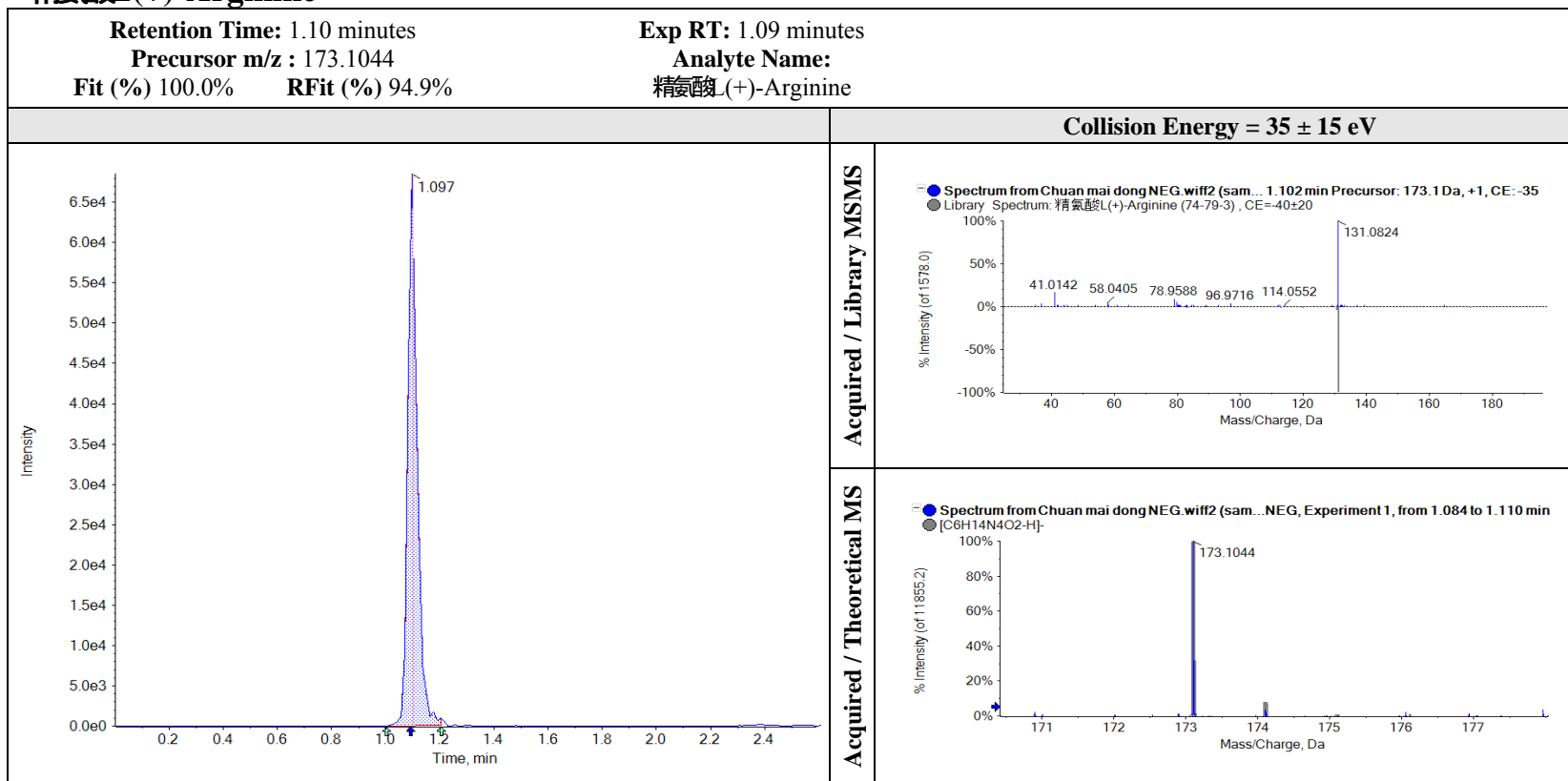


MS fragmentation pathways for different chemical constituents of CMD in negative ion mode

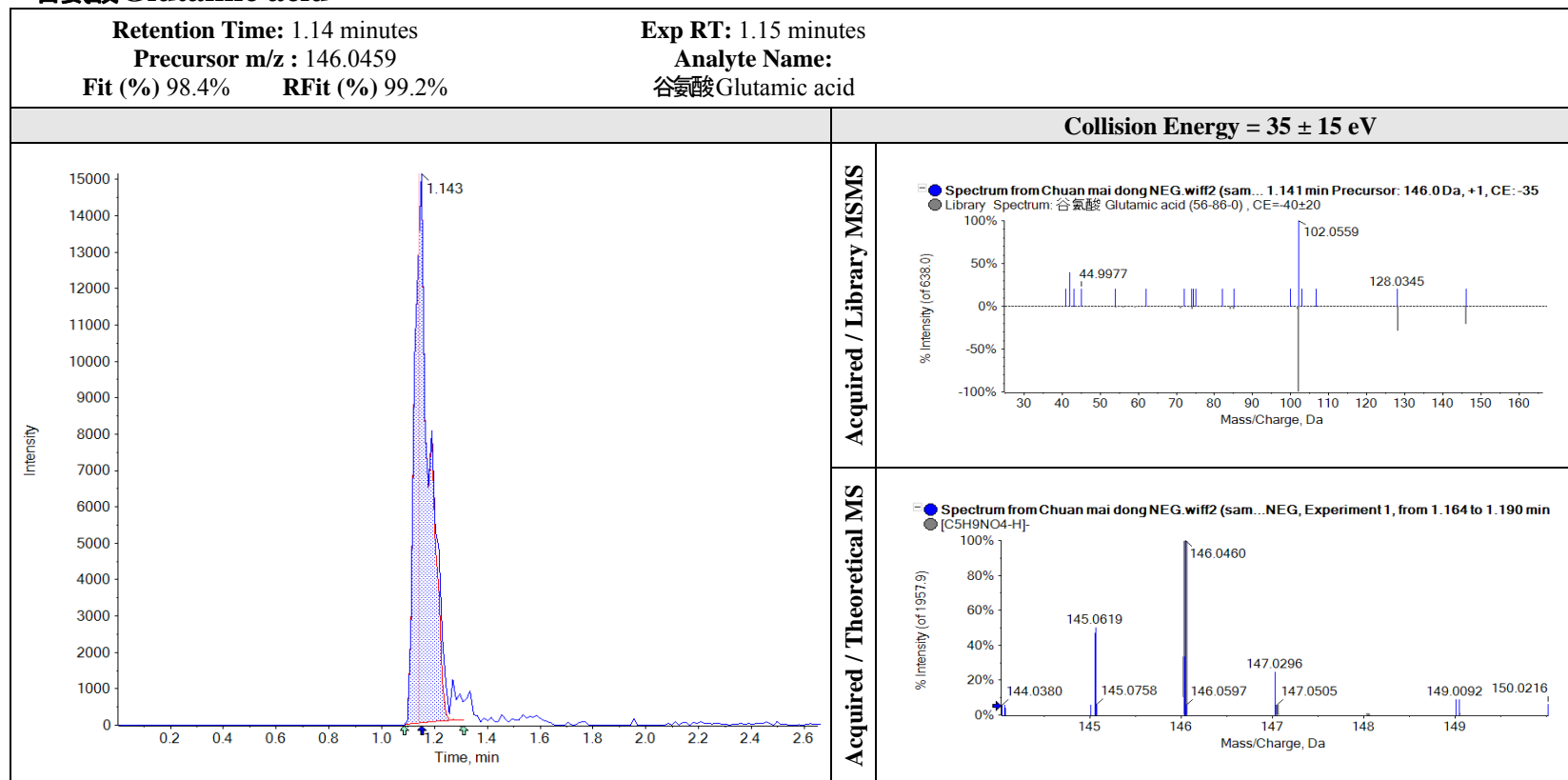
组氨酸 Histidine



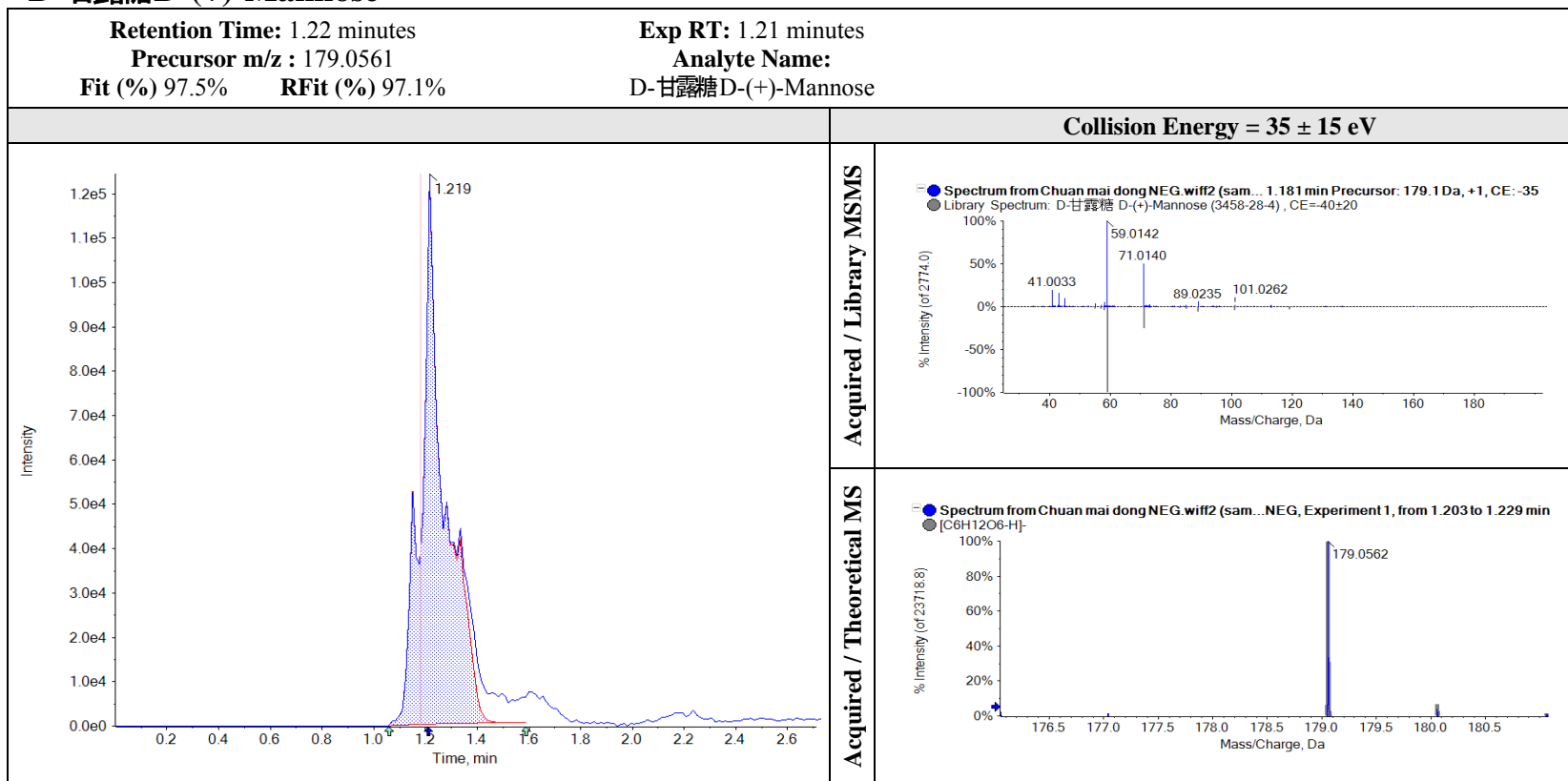
精氨酸L(+)-Arginine



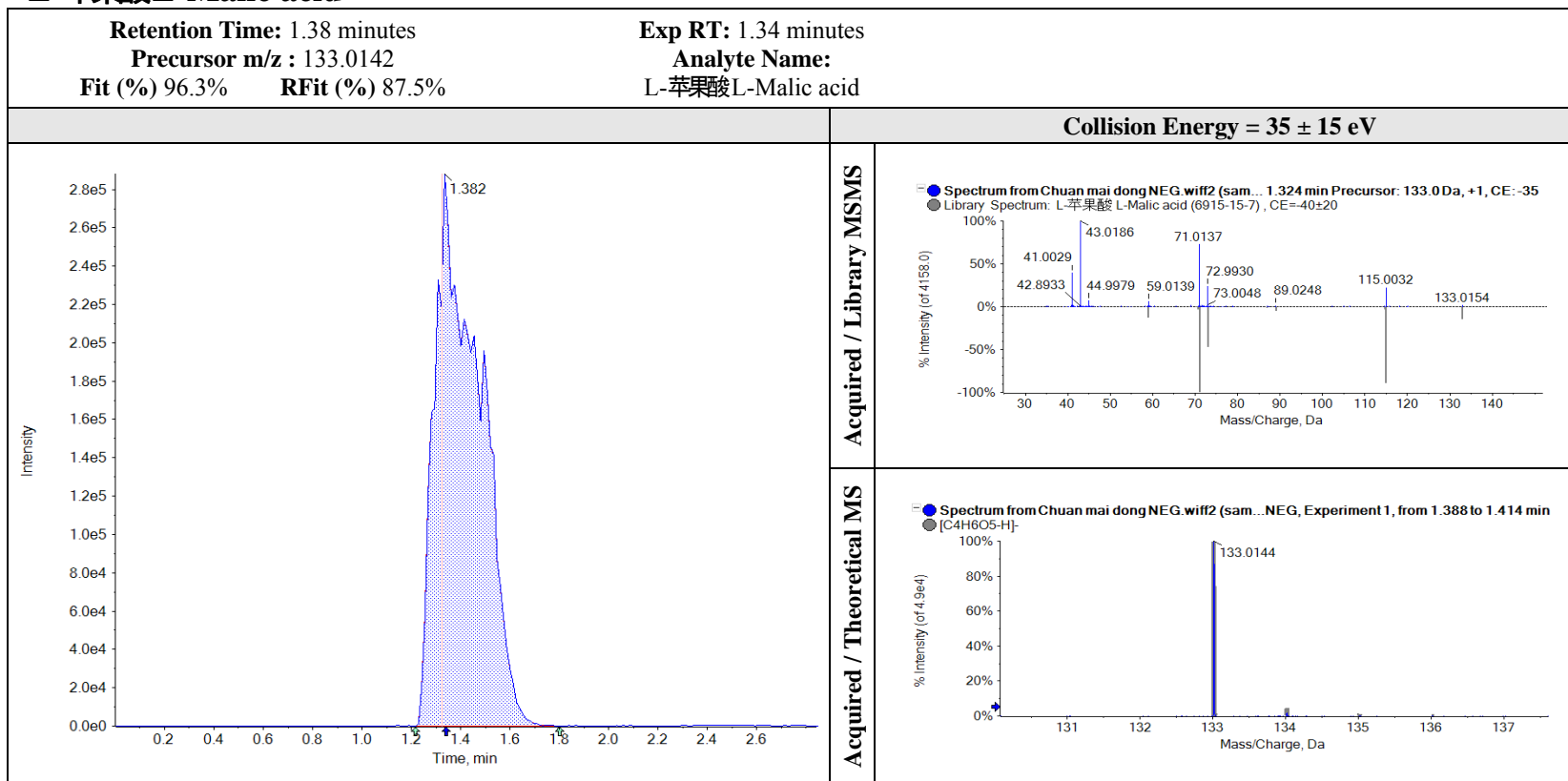
谷氨酸 Glutamic acid



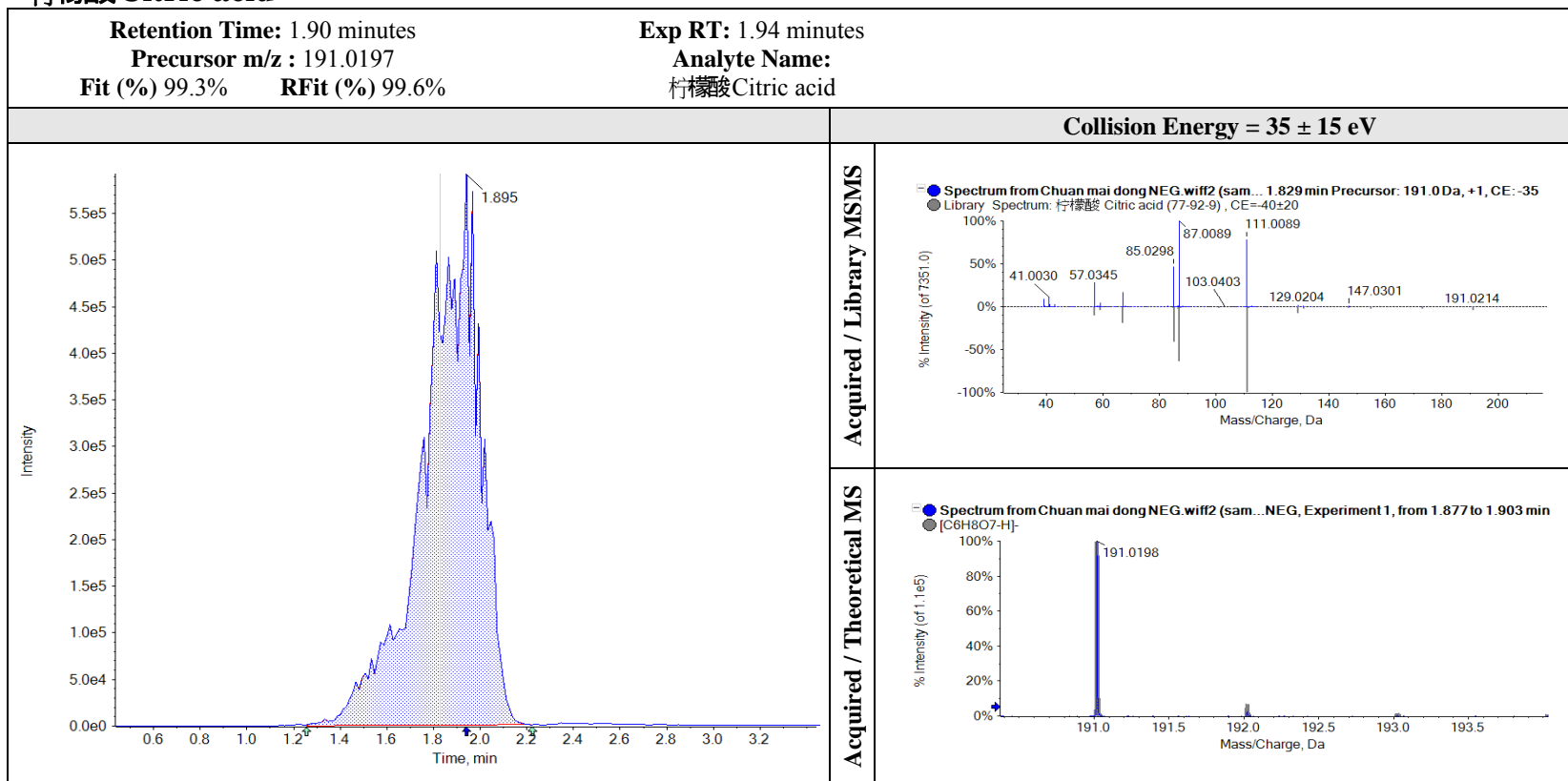
D-甘露糖D-(+)-Mannose



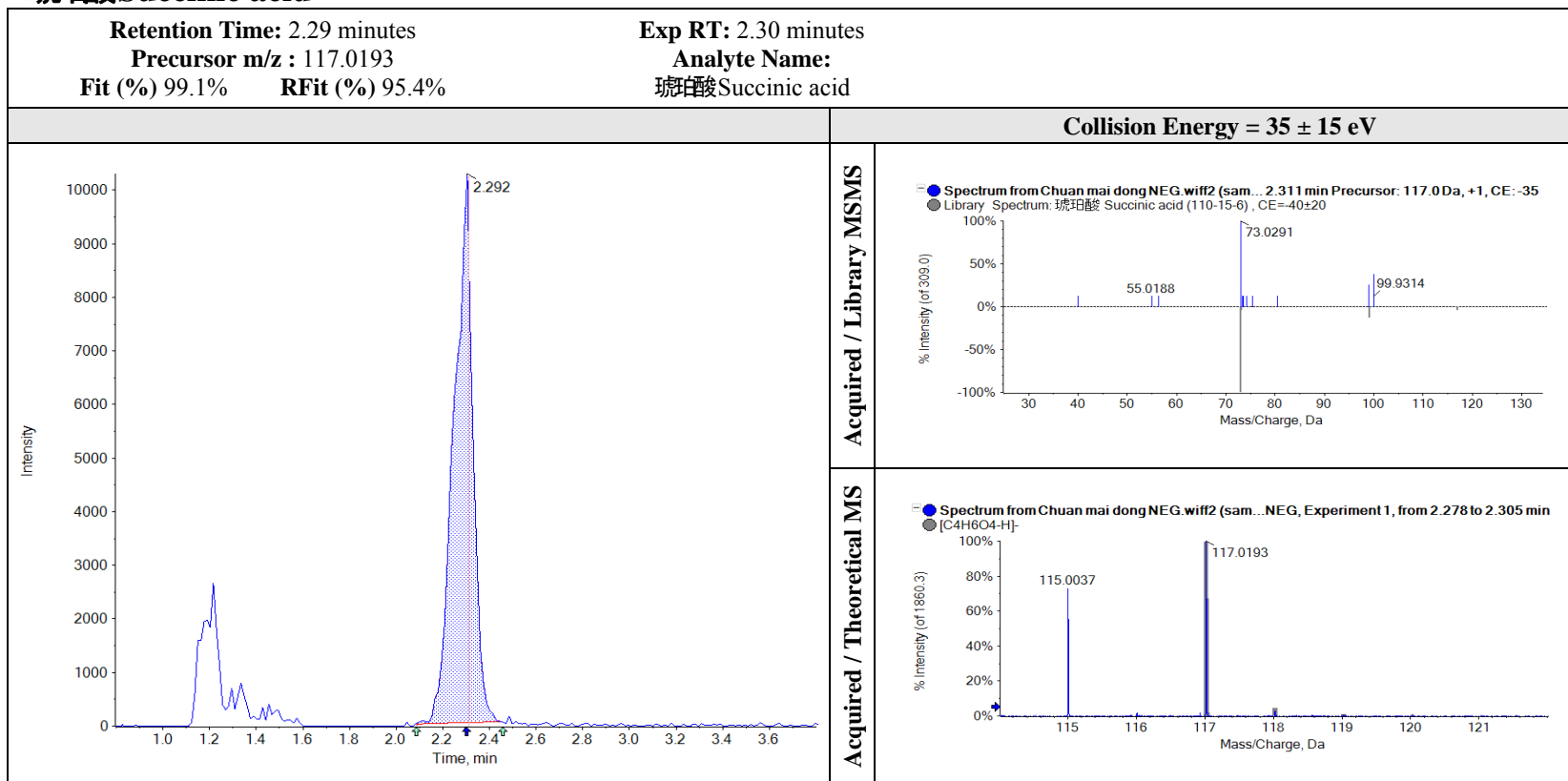
L-苹果酸 L-Malic acid



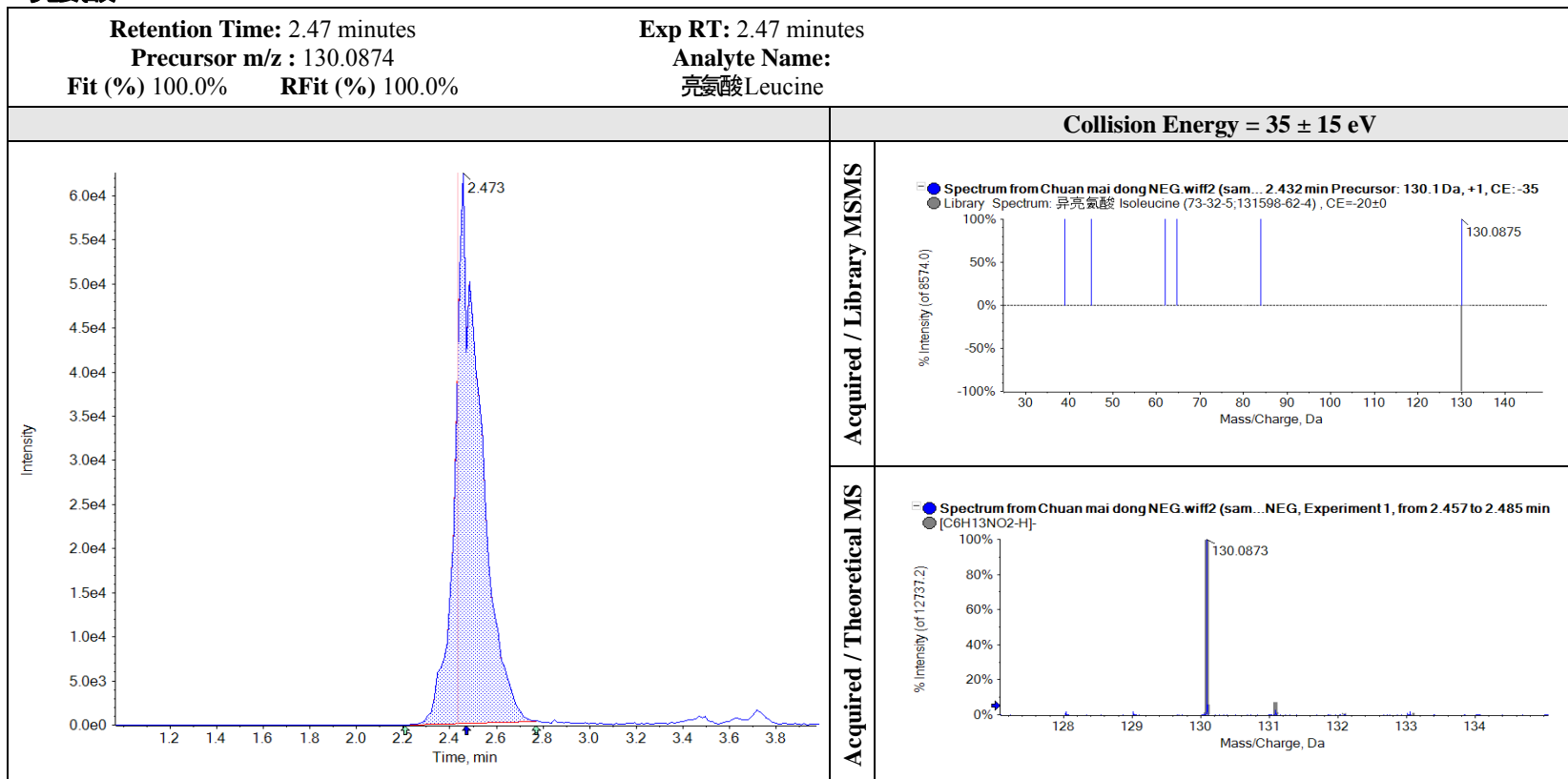
柠檬酸 Citric acid



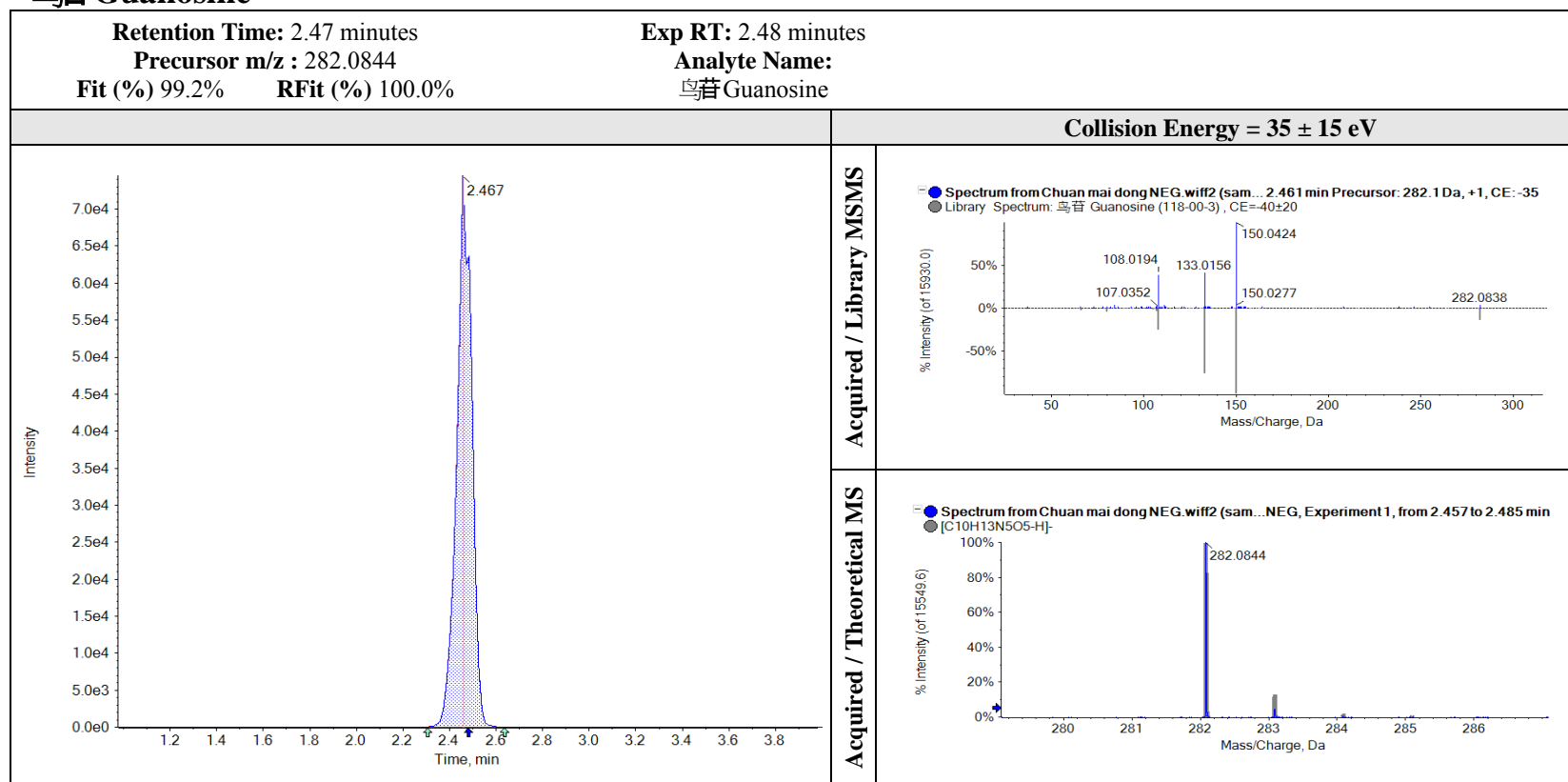
琥珀酸 Succinic acid



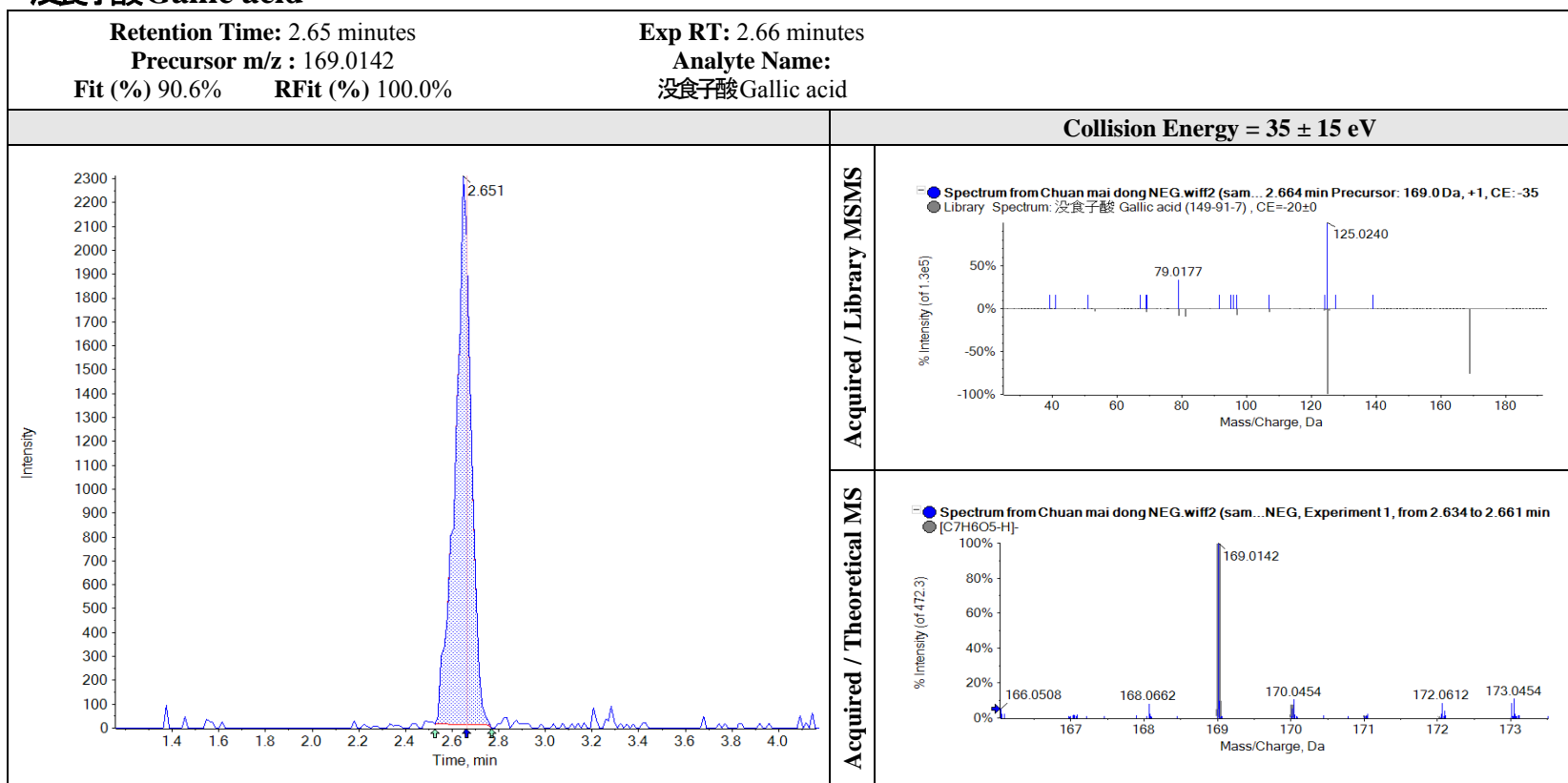
亮氨酸 Leucine



鸟苷 Guanosine



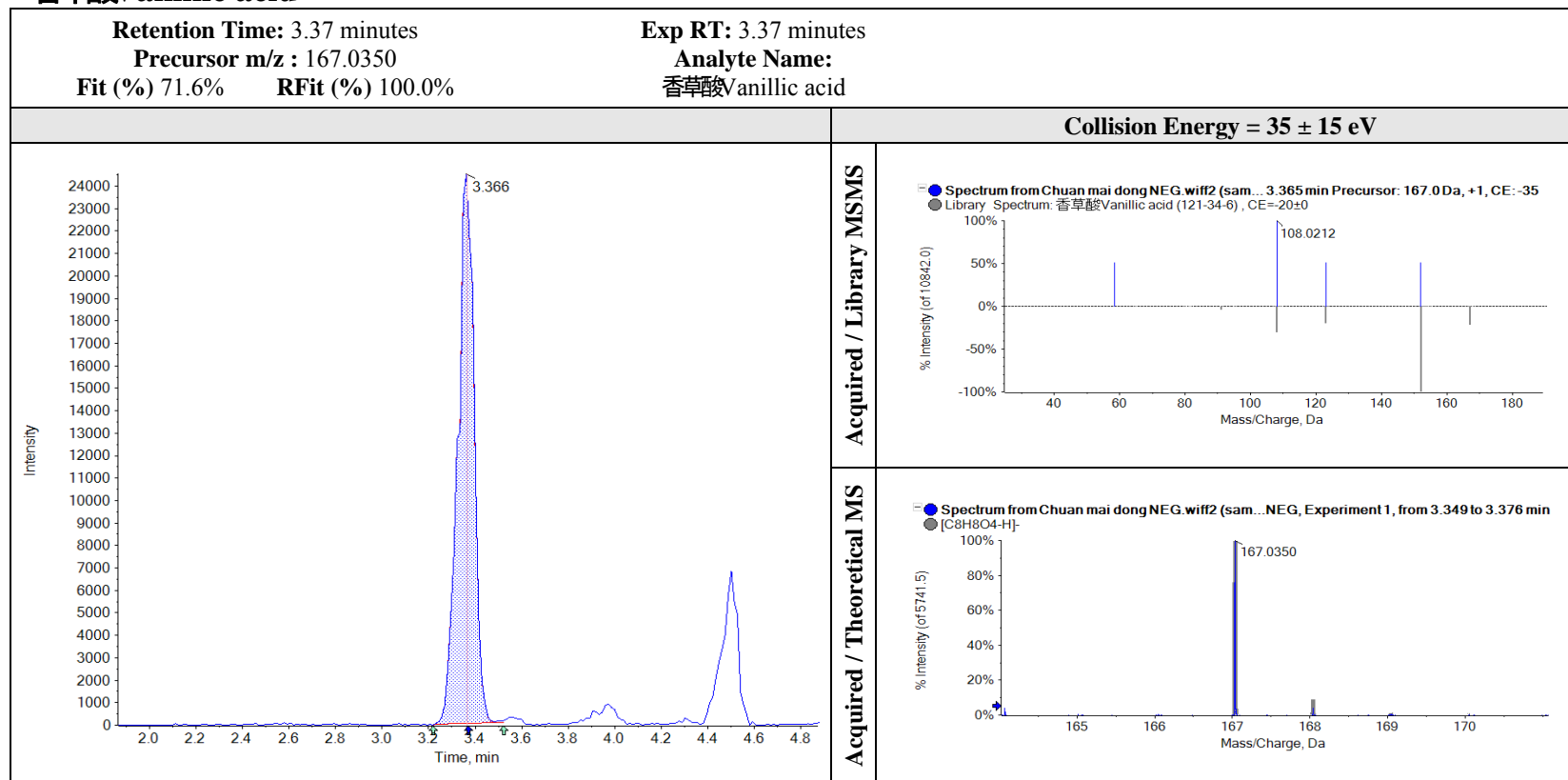
没食子酸 Gallic acid



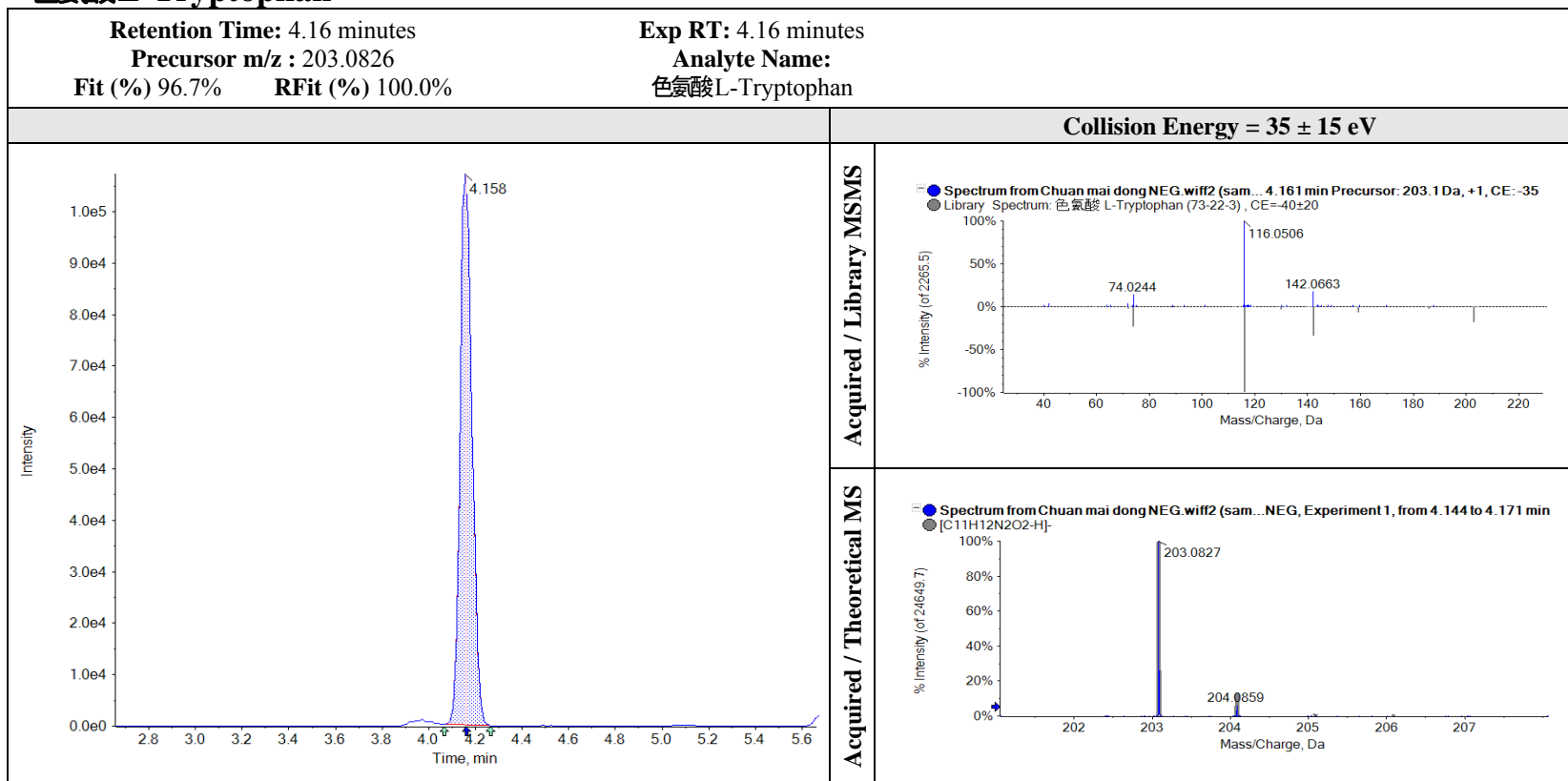
苯丙氨酸 Phenprobamate

<p>Retention Time: 3.18 minutes Exp RT: 3.18 minutes Precursor m/z : 164.0717 Analyte Name: Fit (%) 97.9% RFit (%) 98.0% 苯丙氨酸 Phenprobamate</p>	
<p>Collision Energy = 35 ± 15 eV</p>	
	<p>Acquired / Library MSMS</p>
	<p>Acquired / Theoretical MS</p>

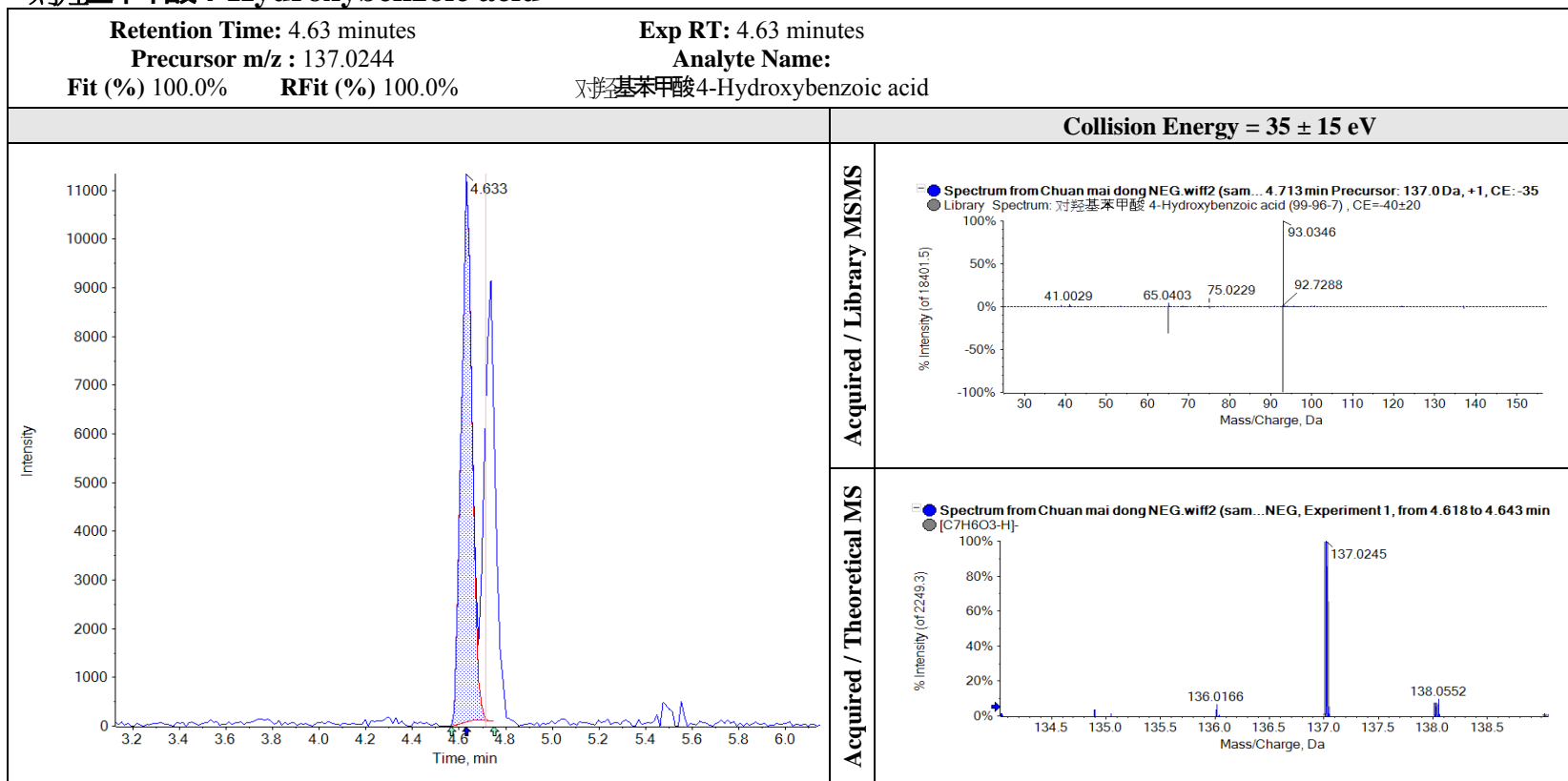
香草酸 Vanillic acid



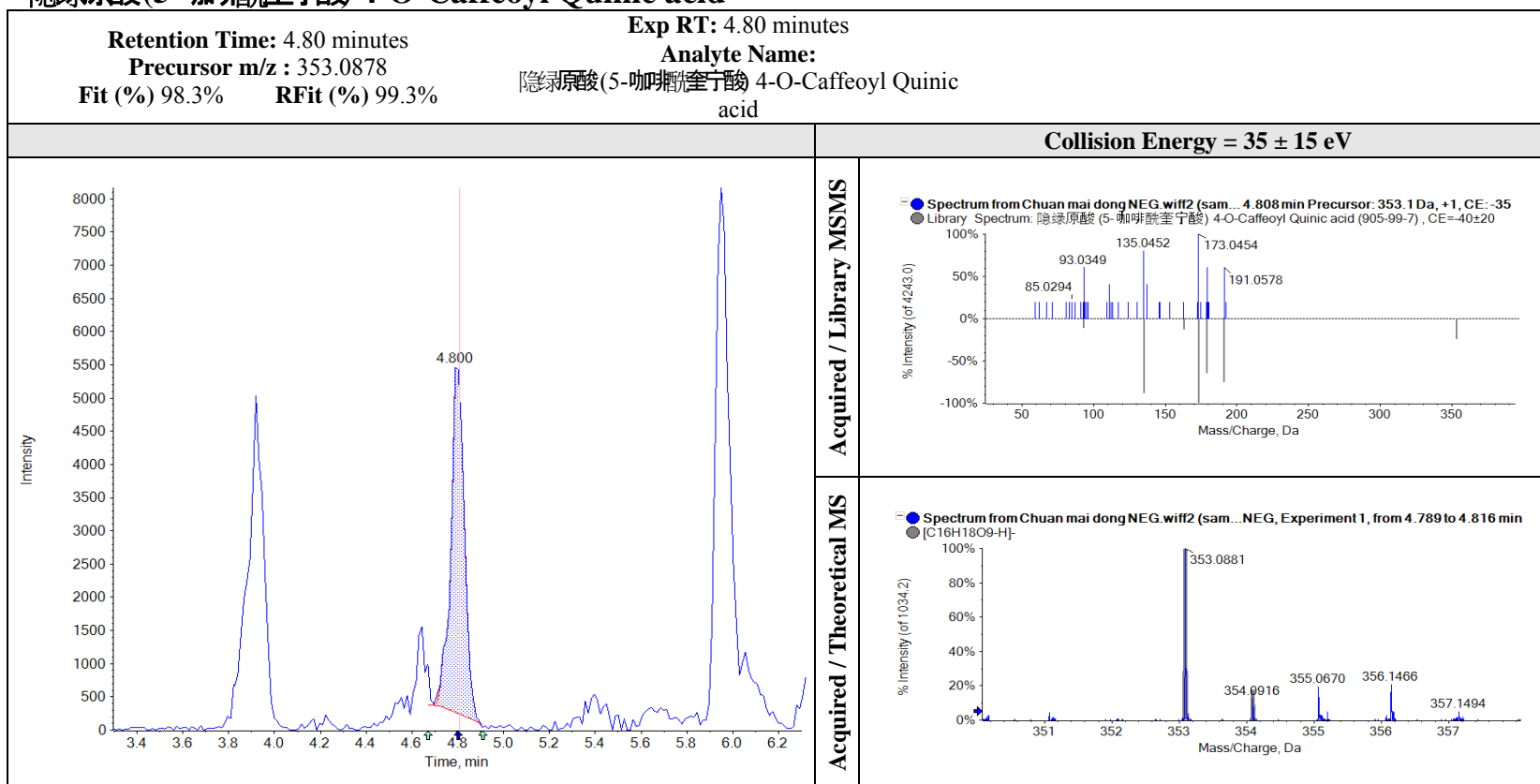
色氨酸 L-Tryptophan



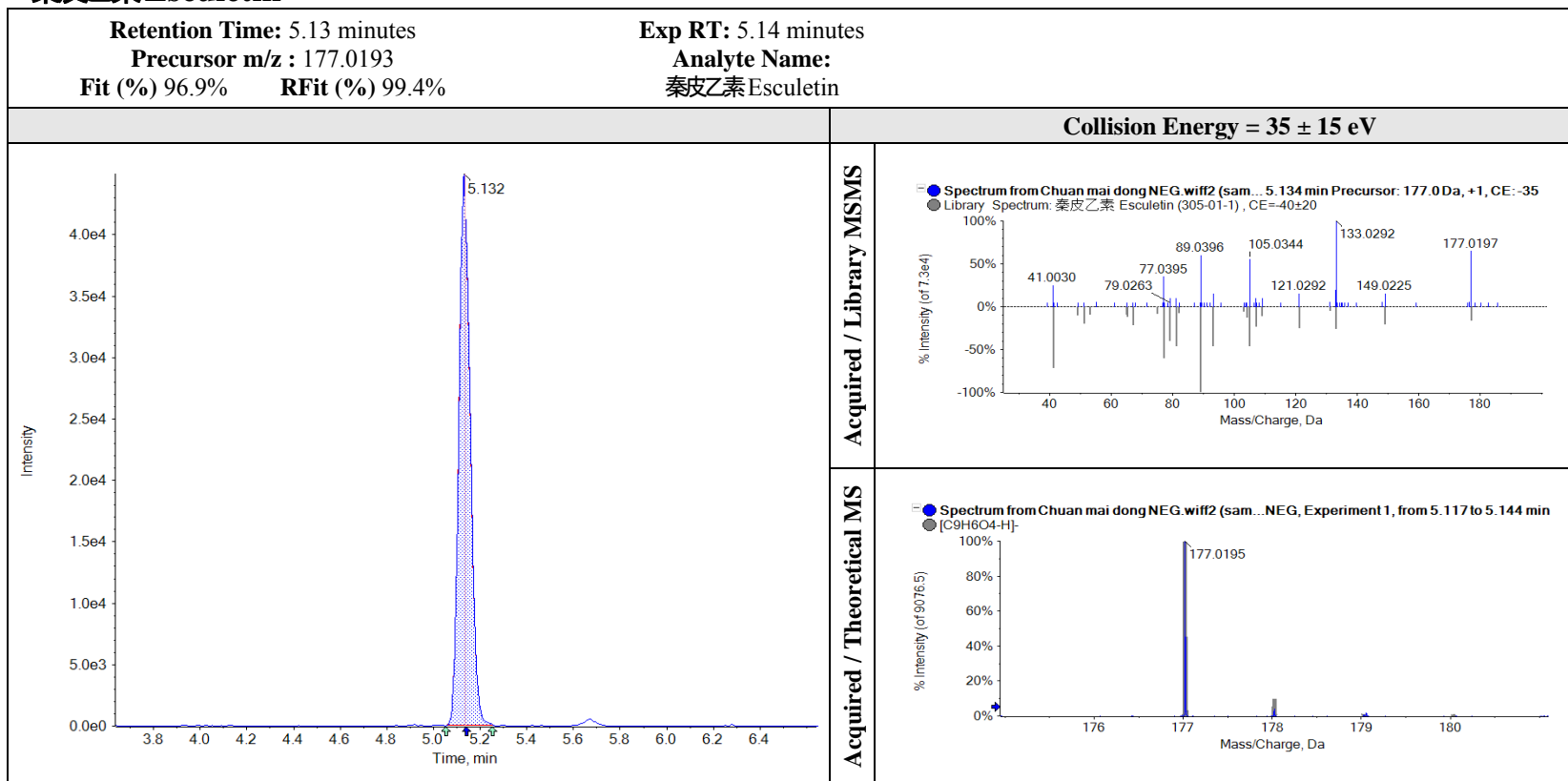
对羟基苯甲酸 4-Hydroxybenzoic acid



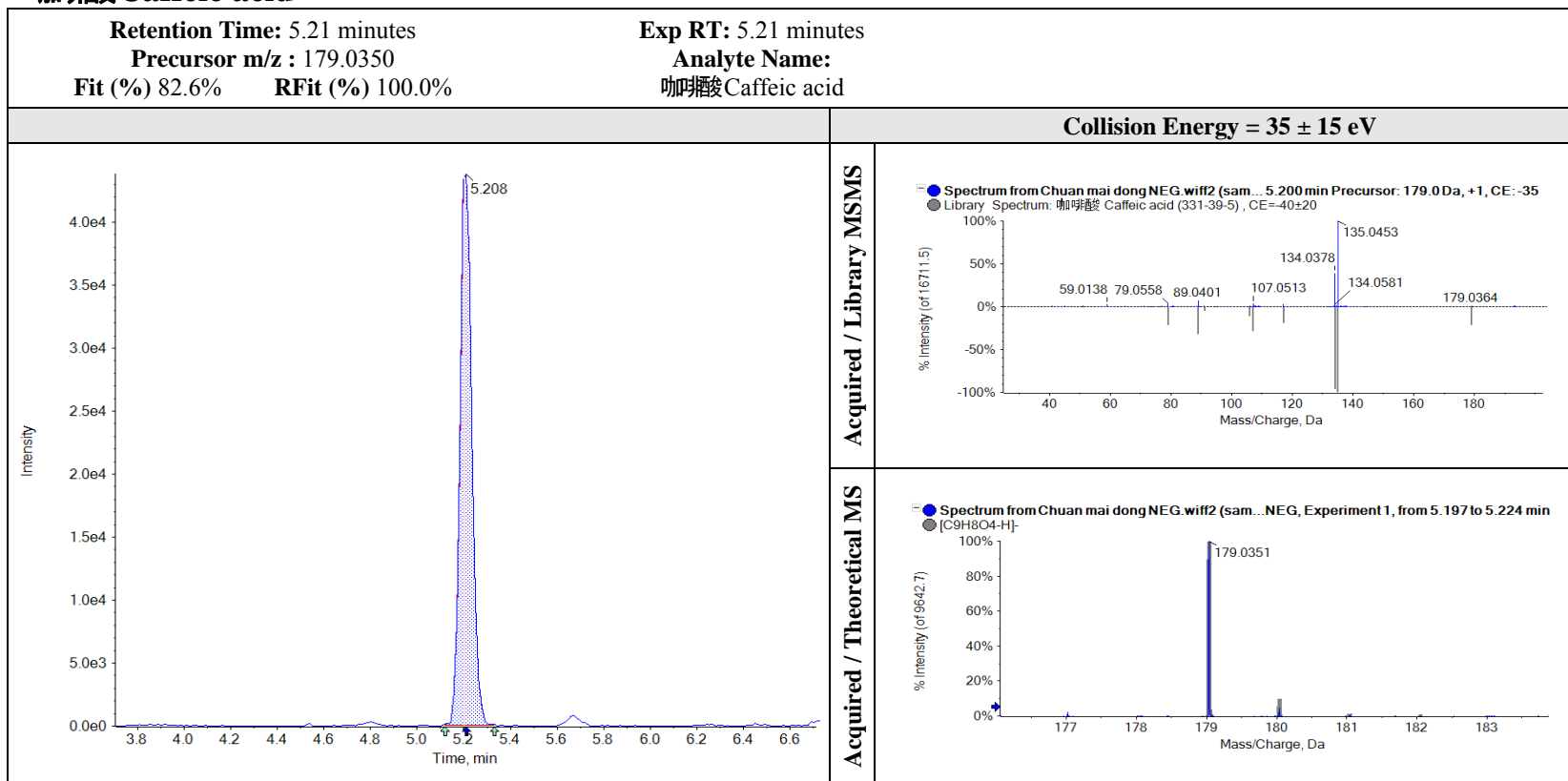
隐绿原酸(5-咖啡酰奎宁酸) 4-O-Caffeoyl Quinic acid



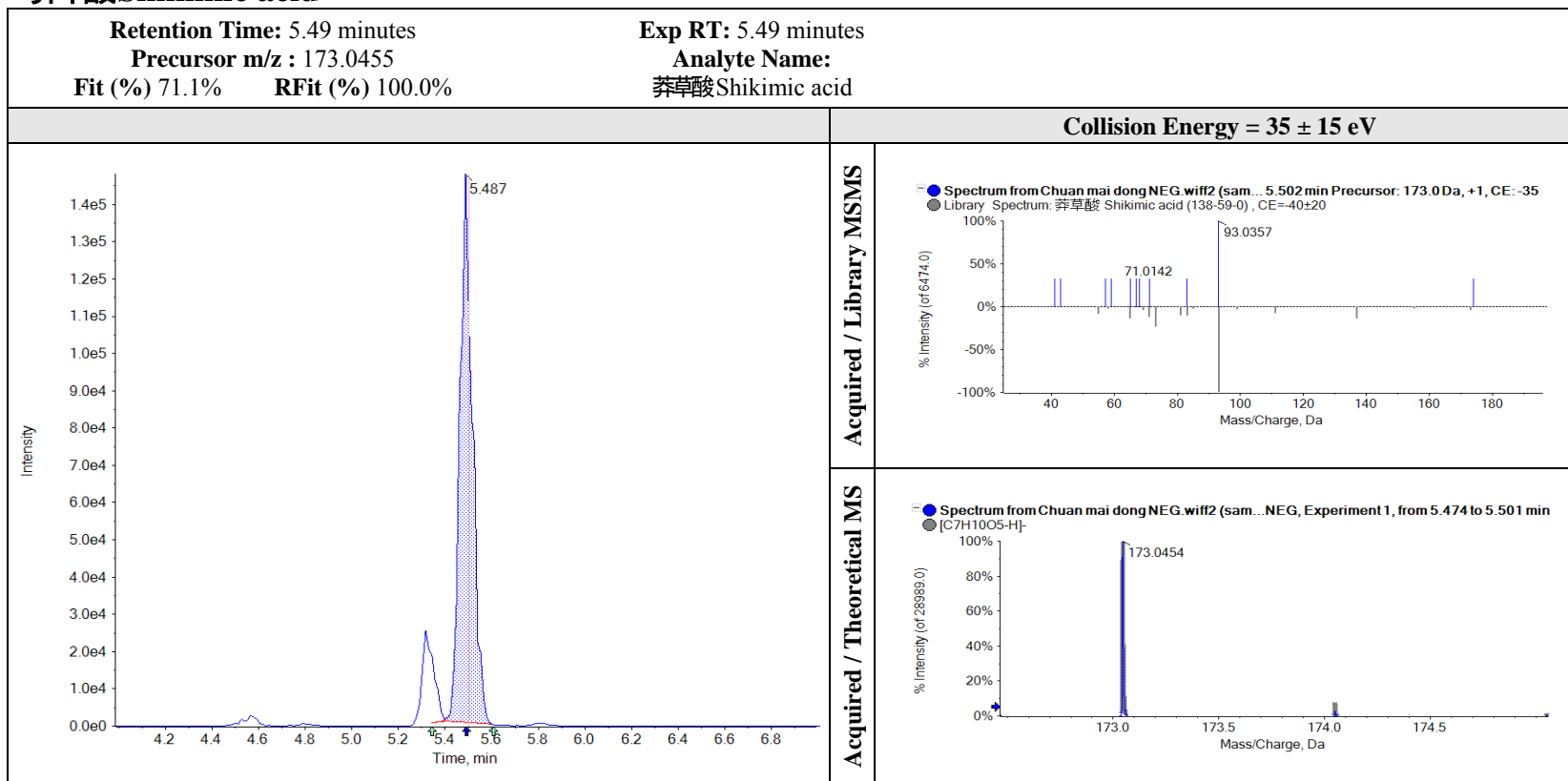
秦皮乙素 Esculetin



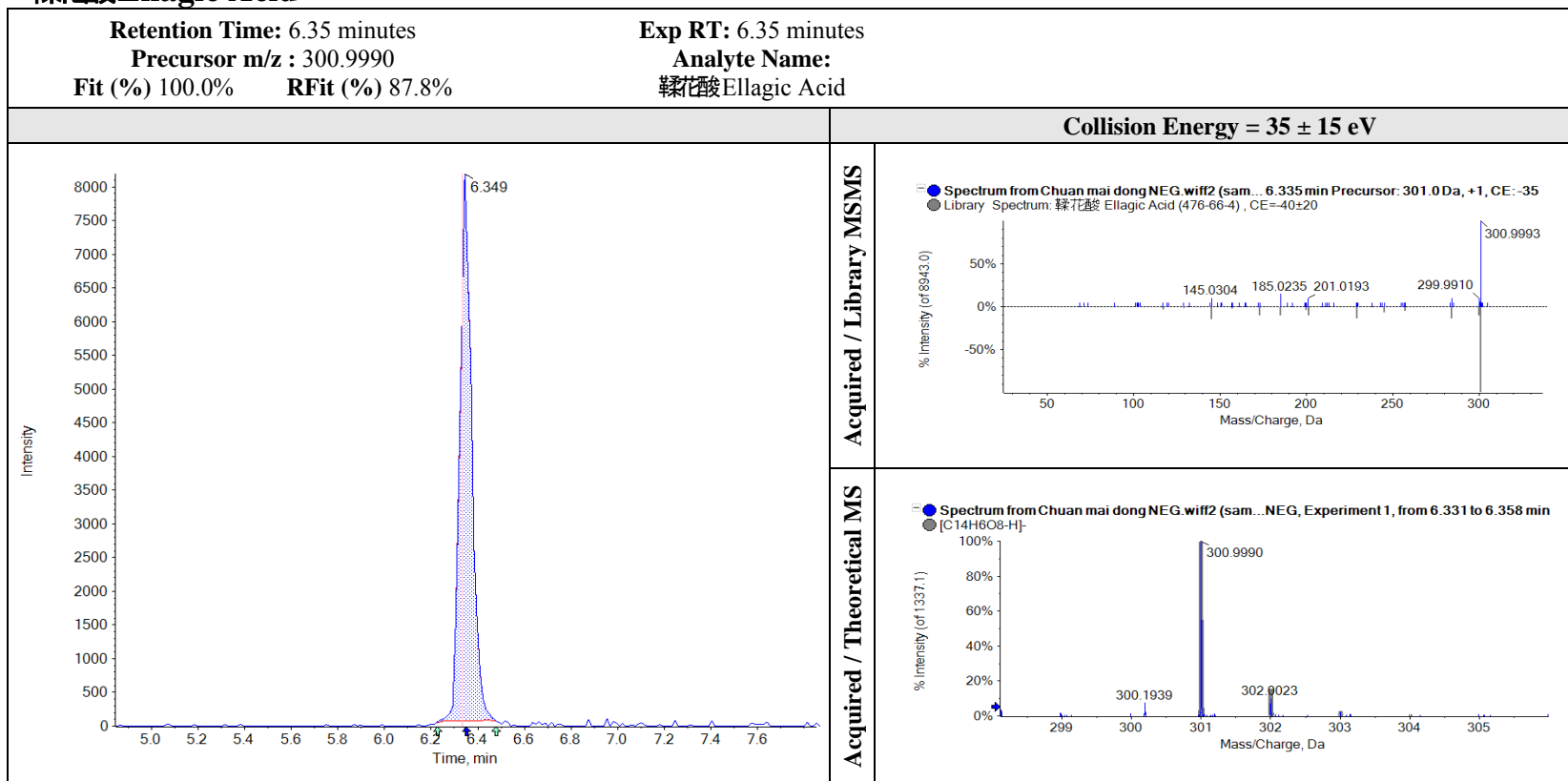
咖啡酸 Caffeic acid



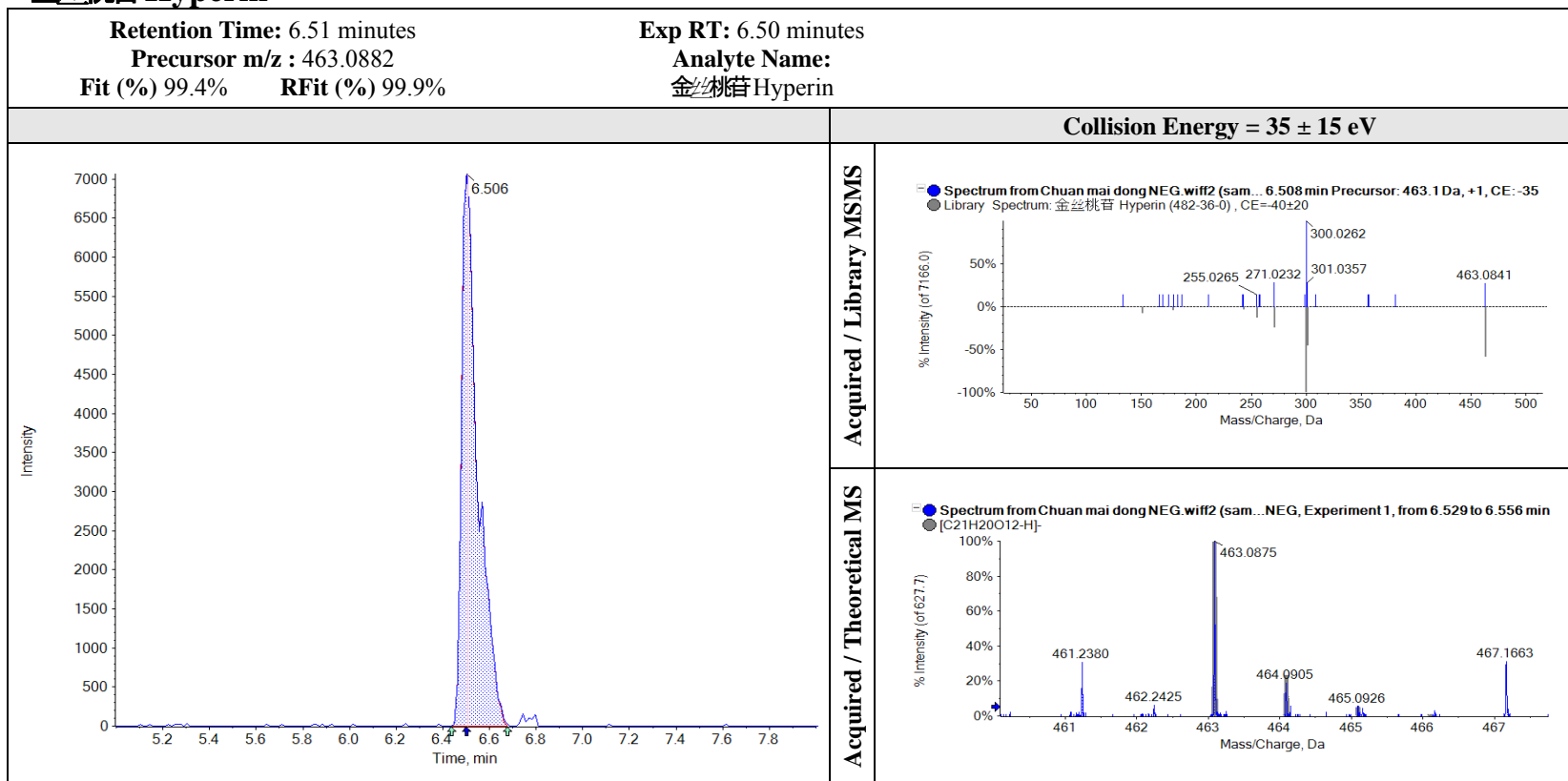
莽草酸 Shikimic acid



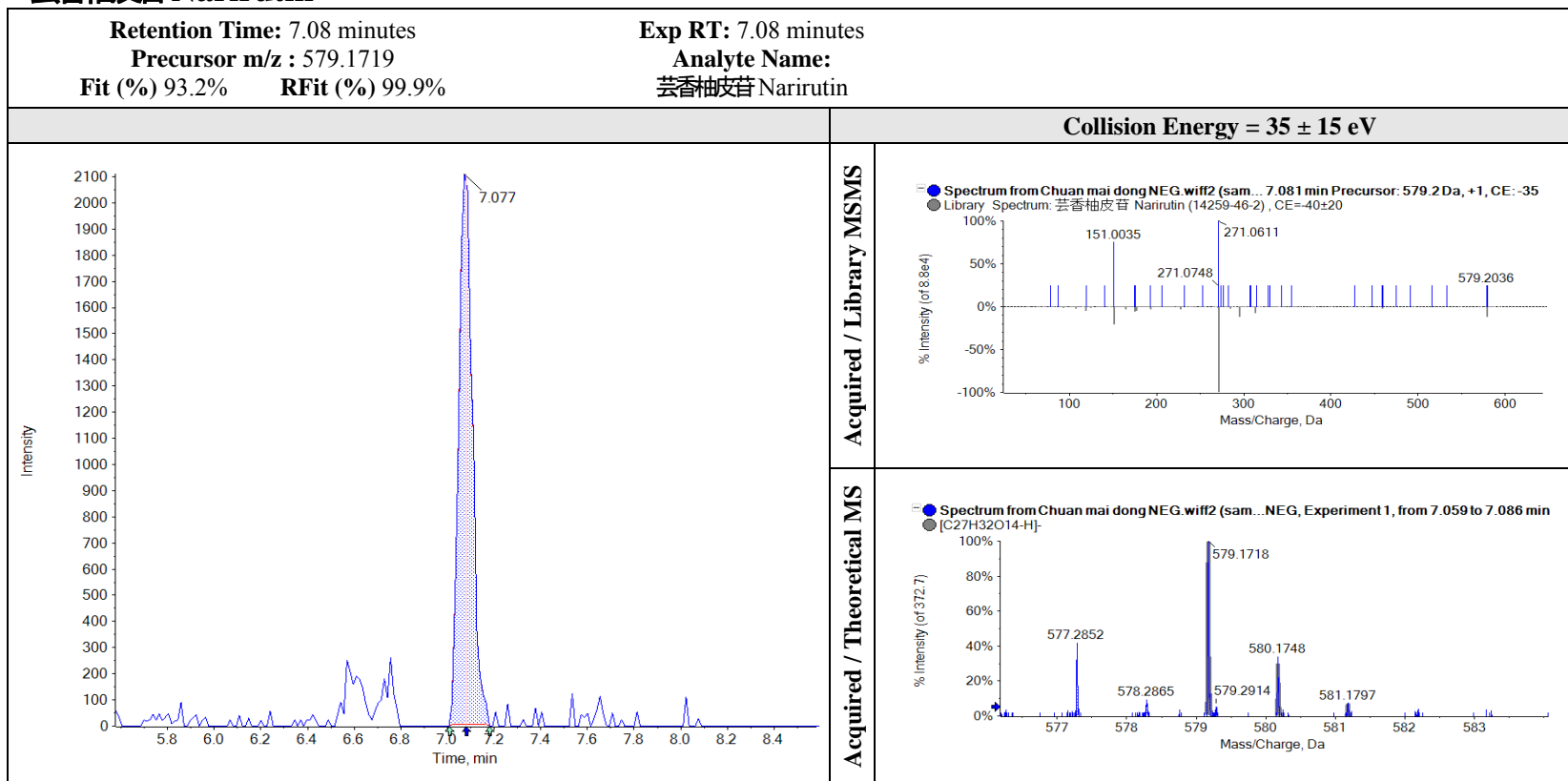
鞣花酸 Ellagic Acid



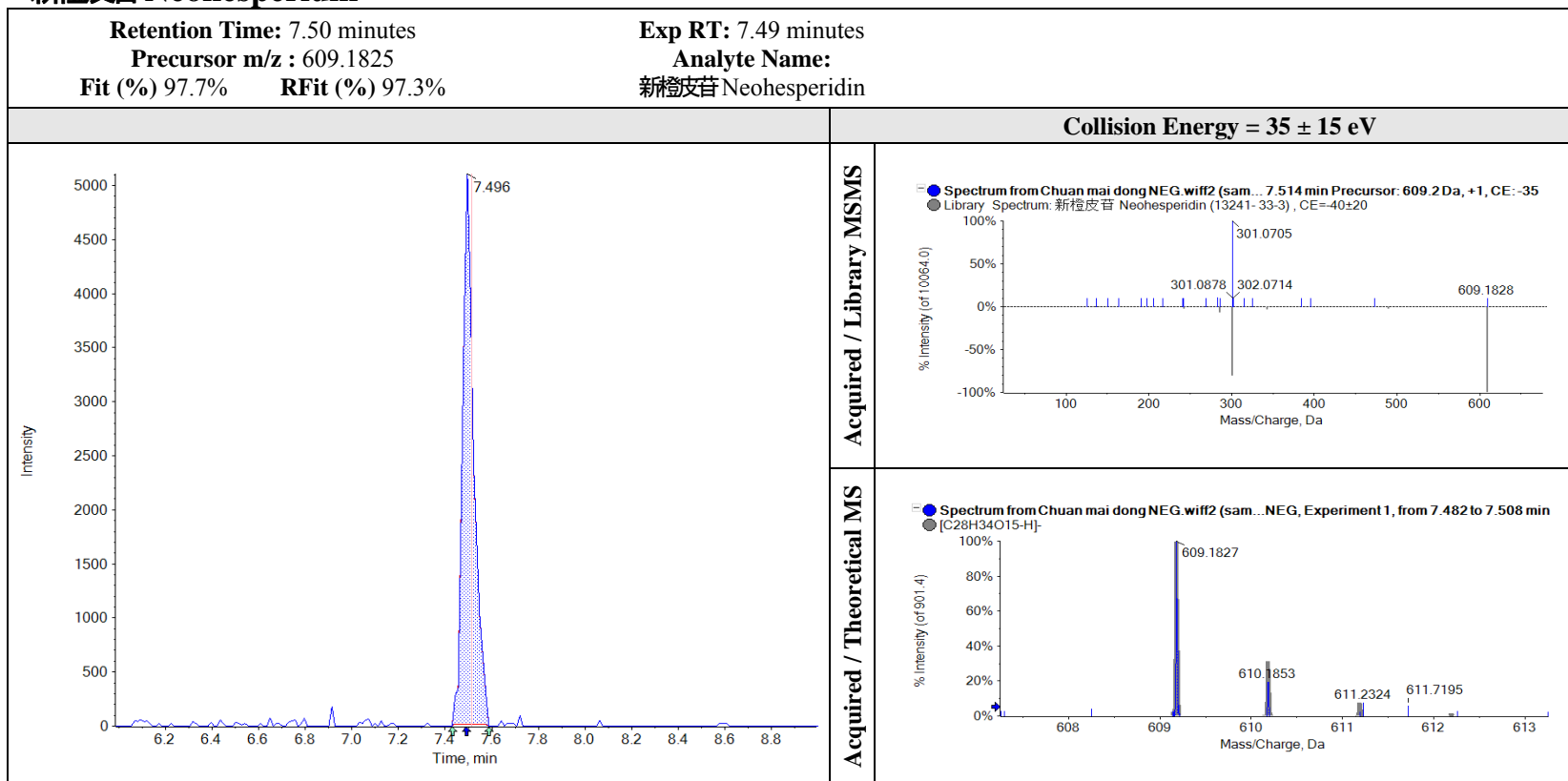
金丝桃苷 Hyperin



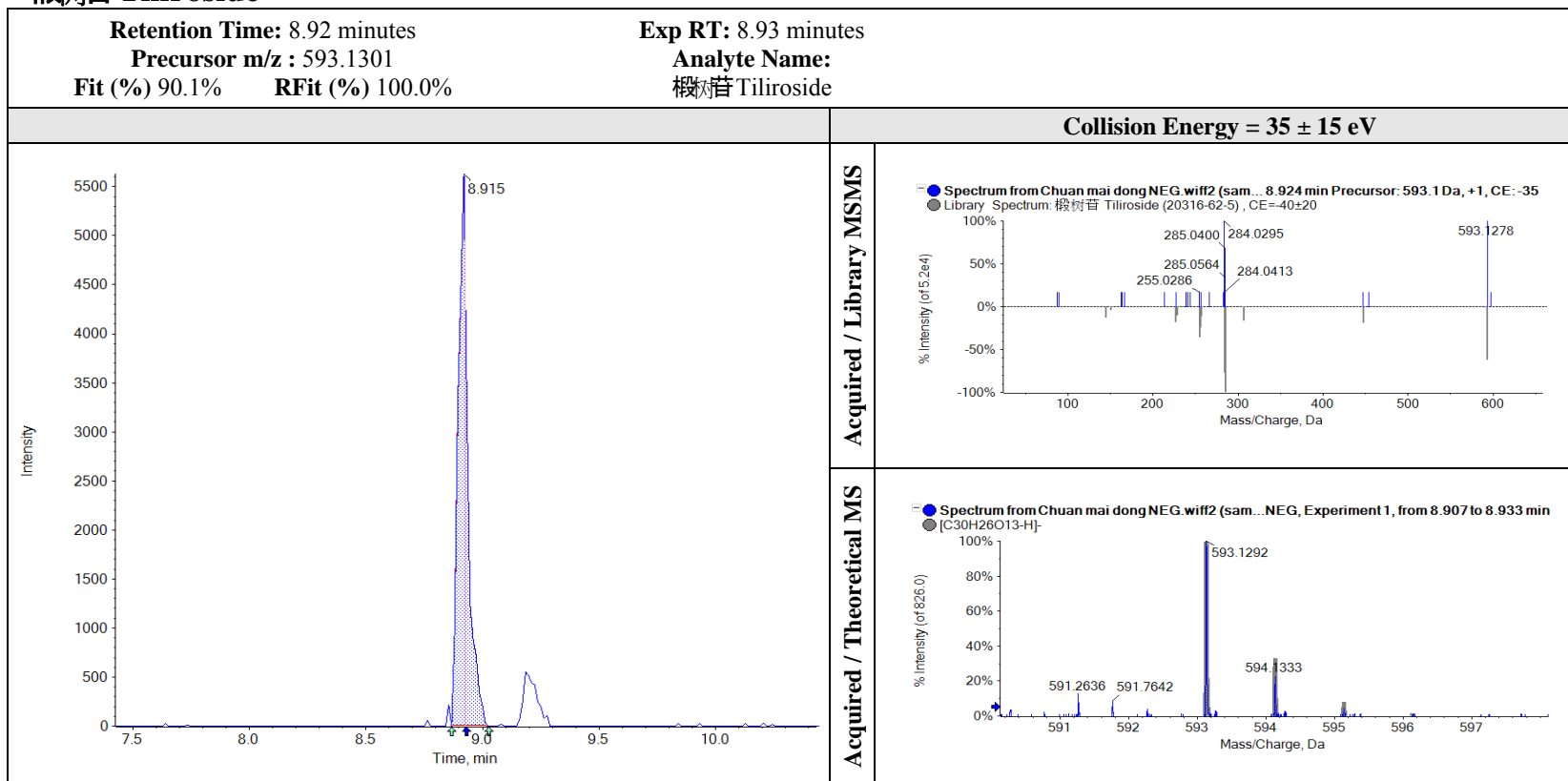
芸香柚皮苷 Narirutin



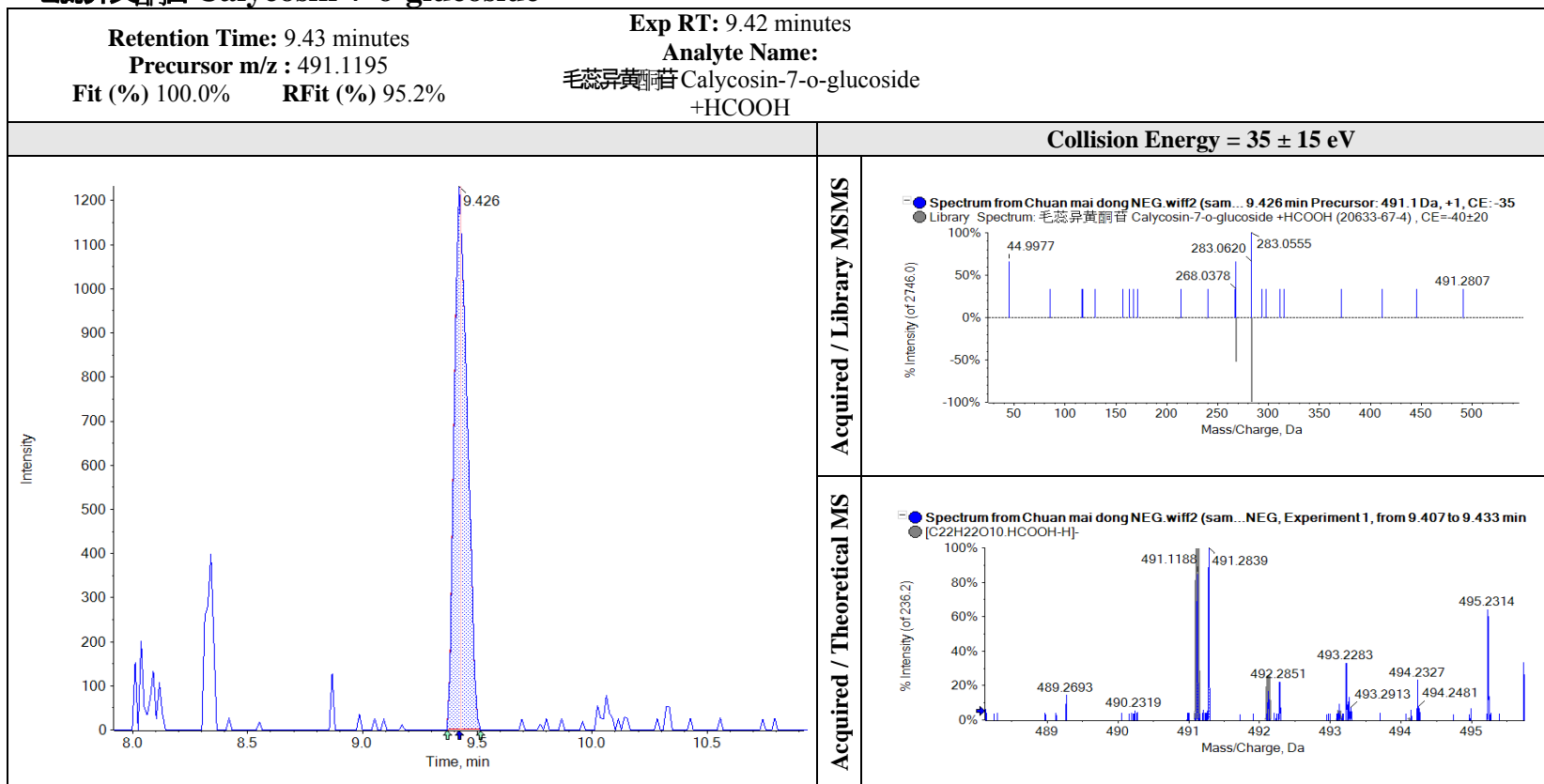
新橙皮苷 Neohesperidin



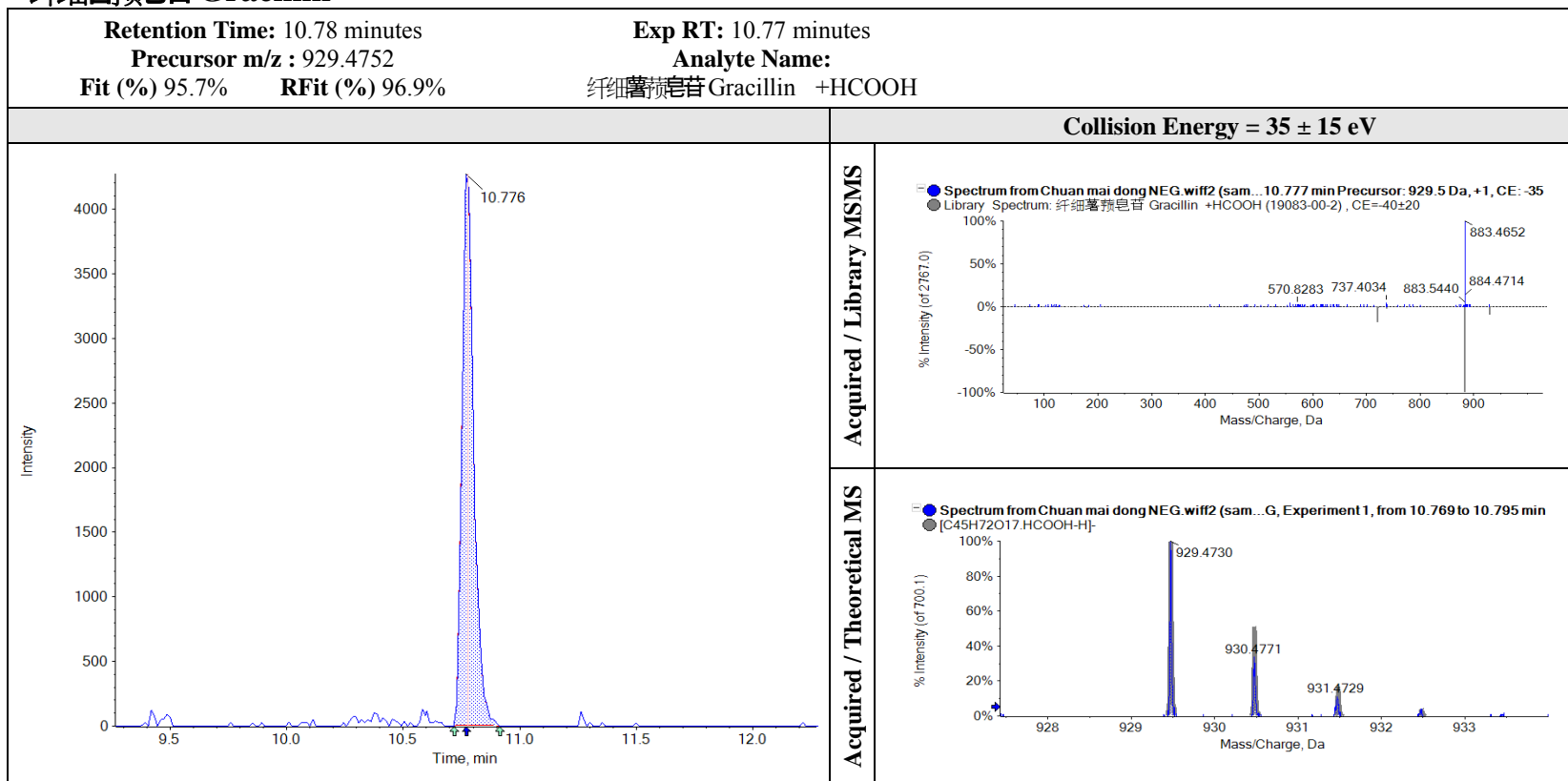
槲寄生 Tiliroside



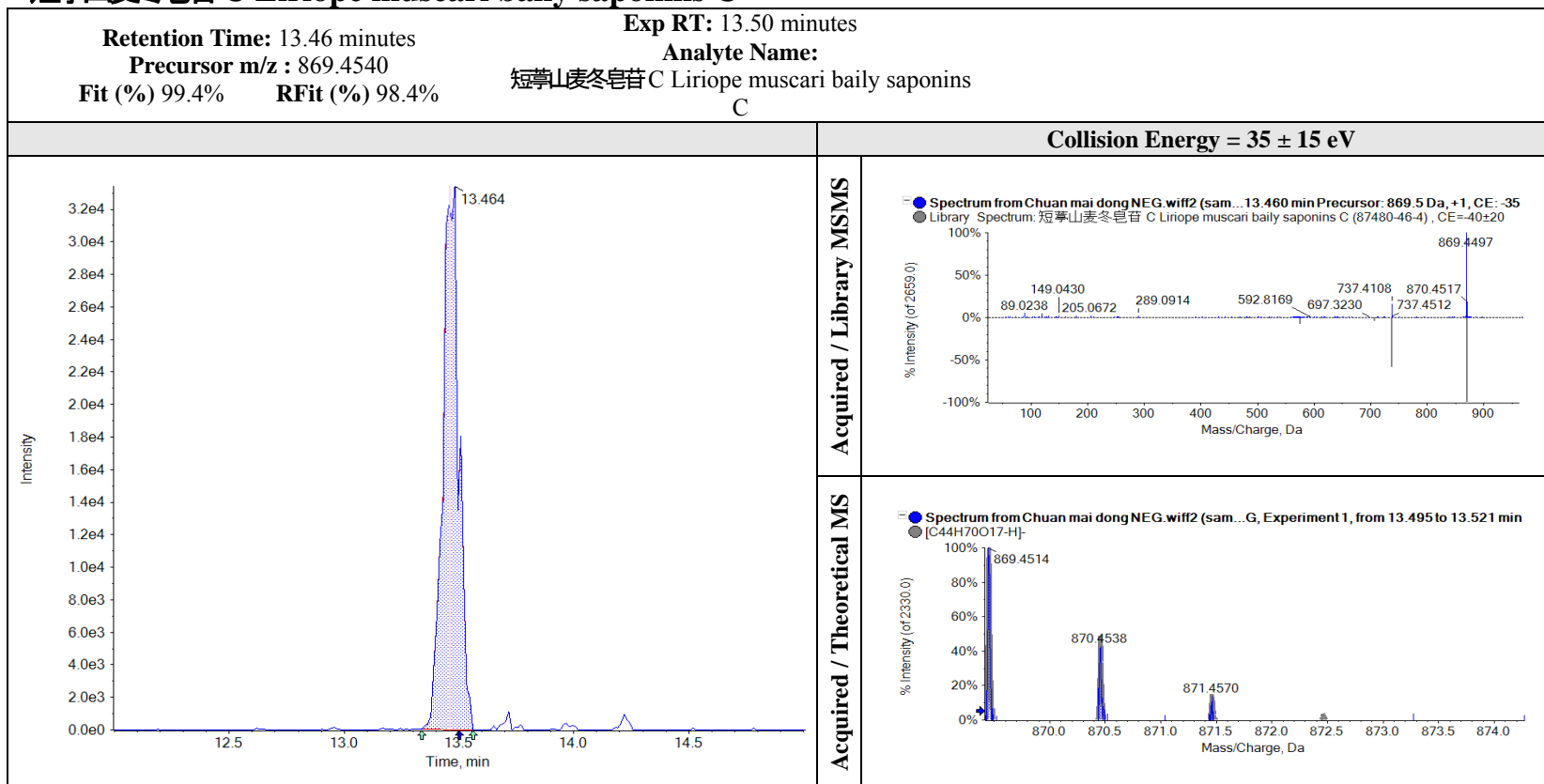
毛蕊异黄酮苷 Calycosin-7-o-glucoside



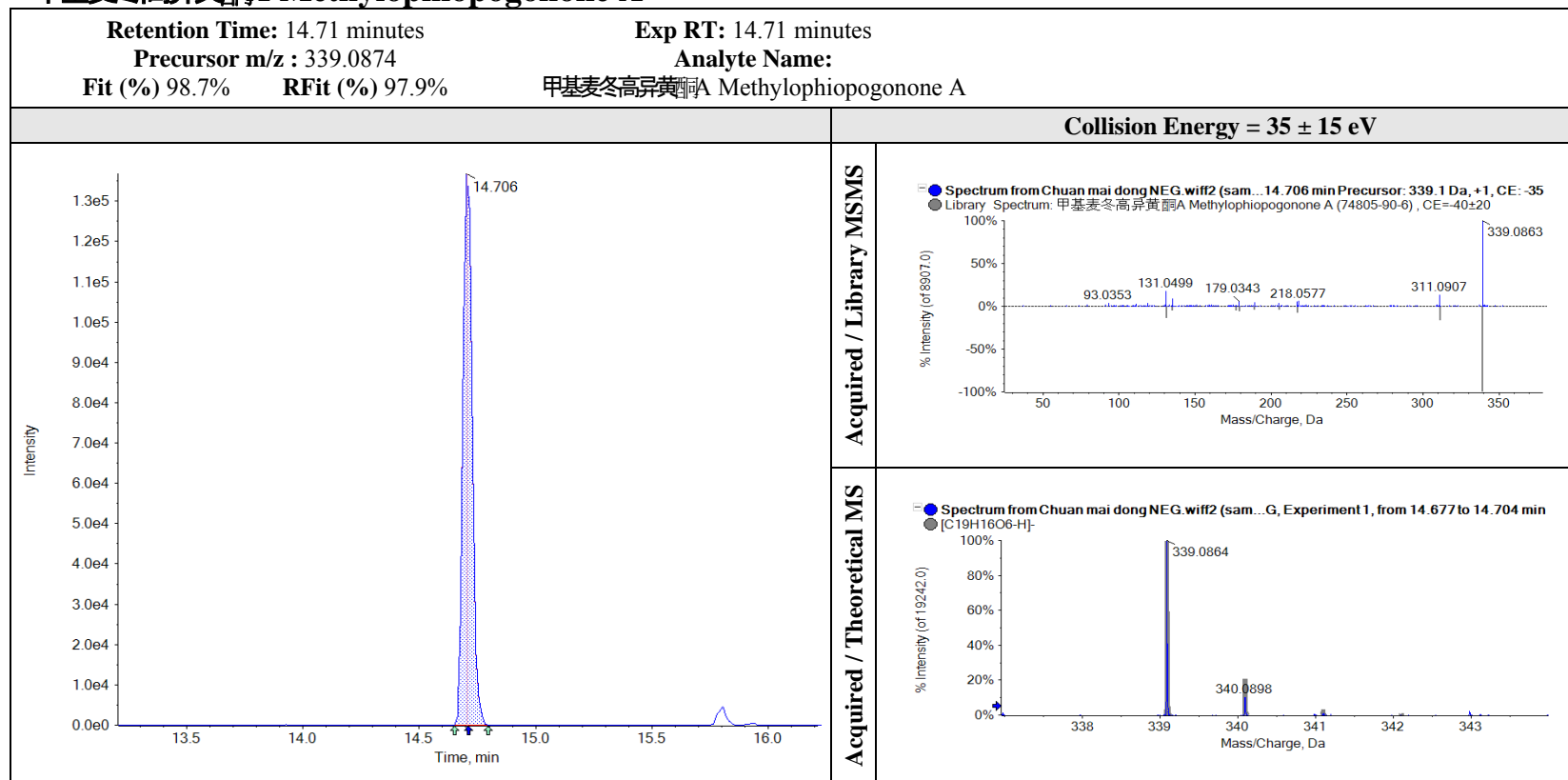
纤细薯蓣皂苷 Gracillin



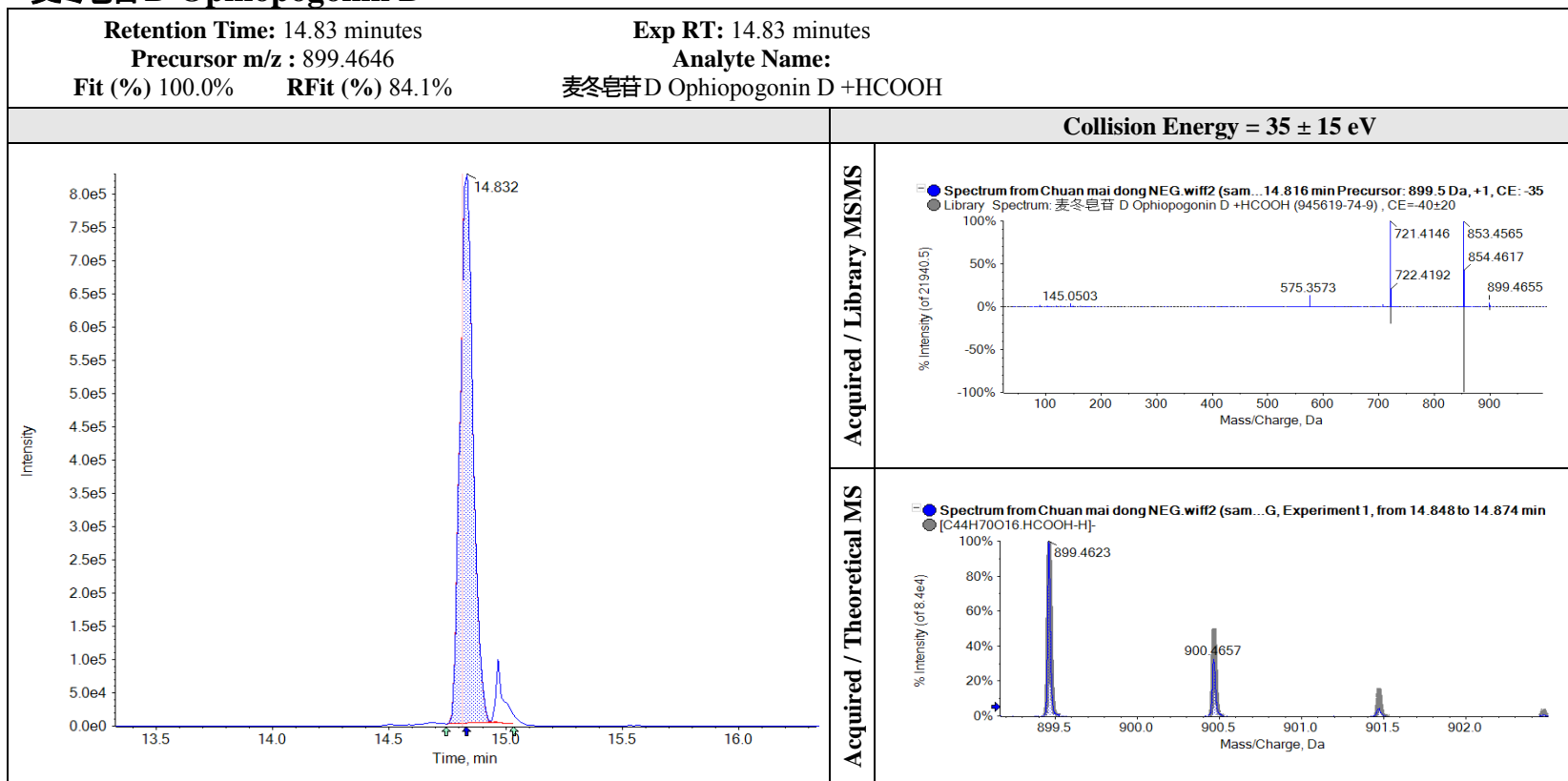
短葶山麦冬皂苷 C Liriope muscari baily saponins C



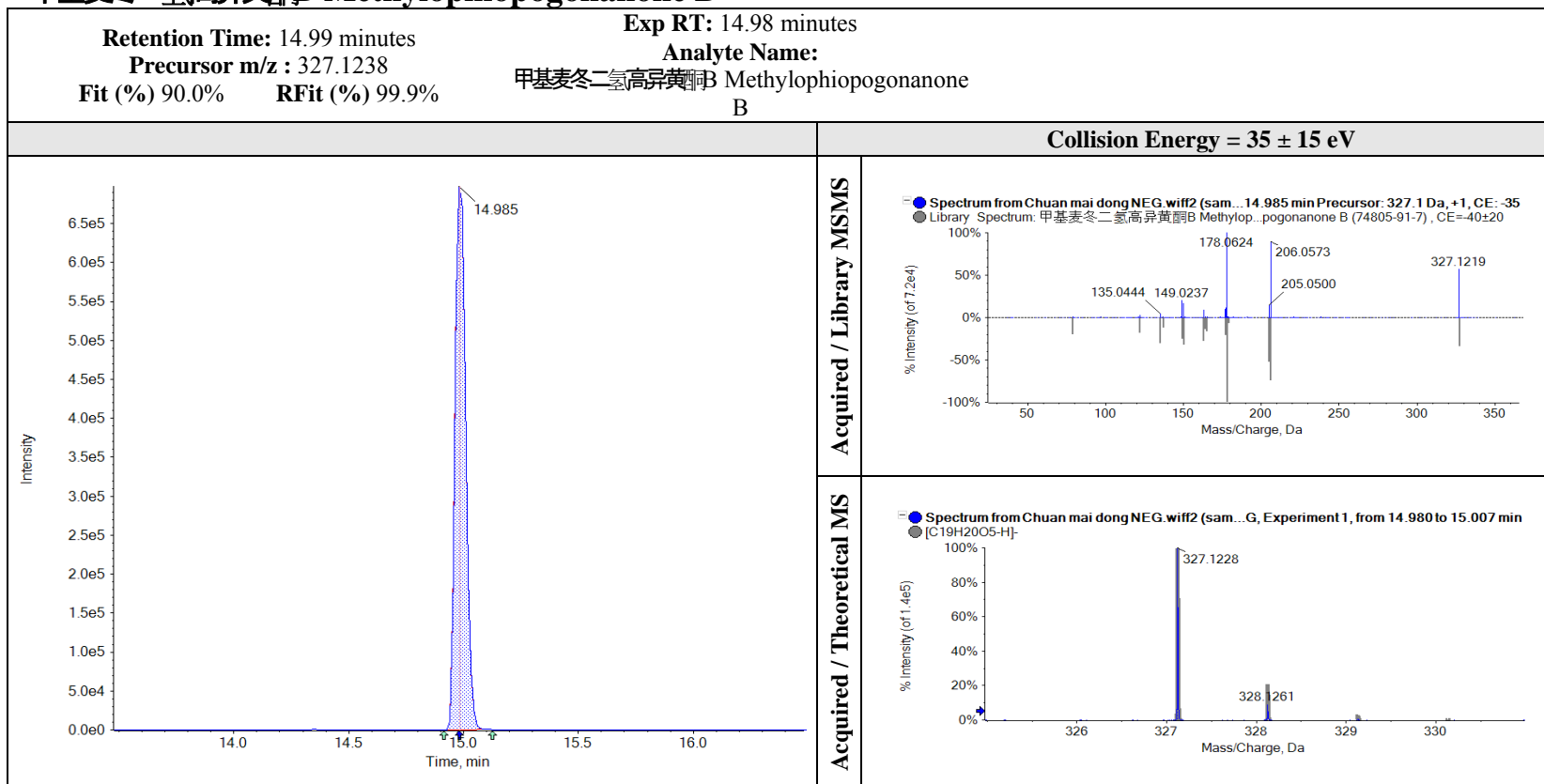
甲基麦冬高异黄酮A Methylophiopogonone A



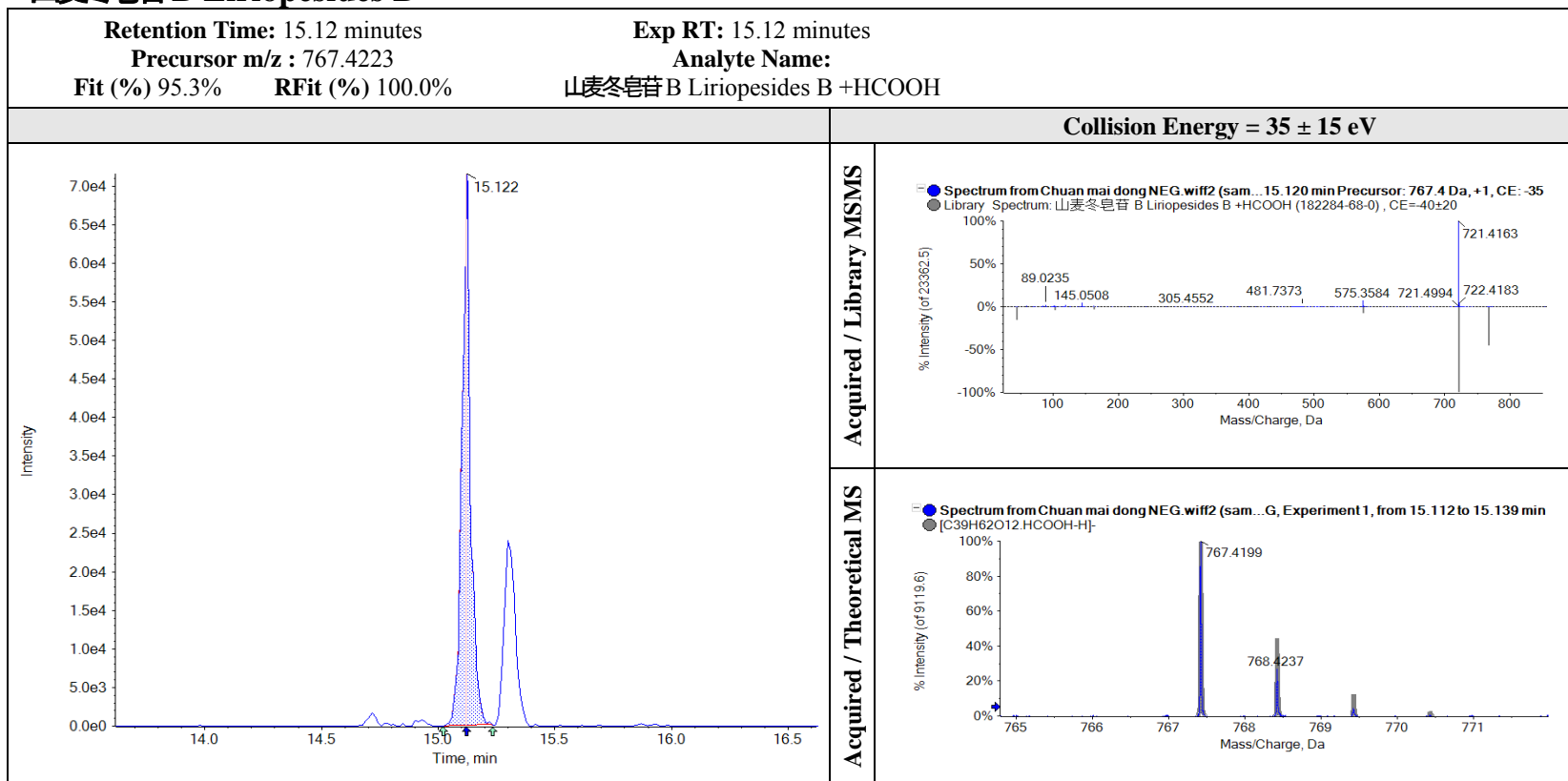
麦冬皂苷D Ophiopogonin D



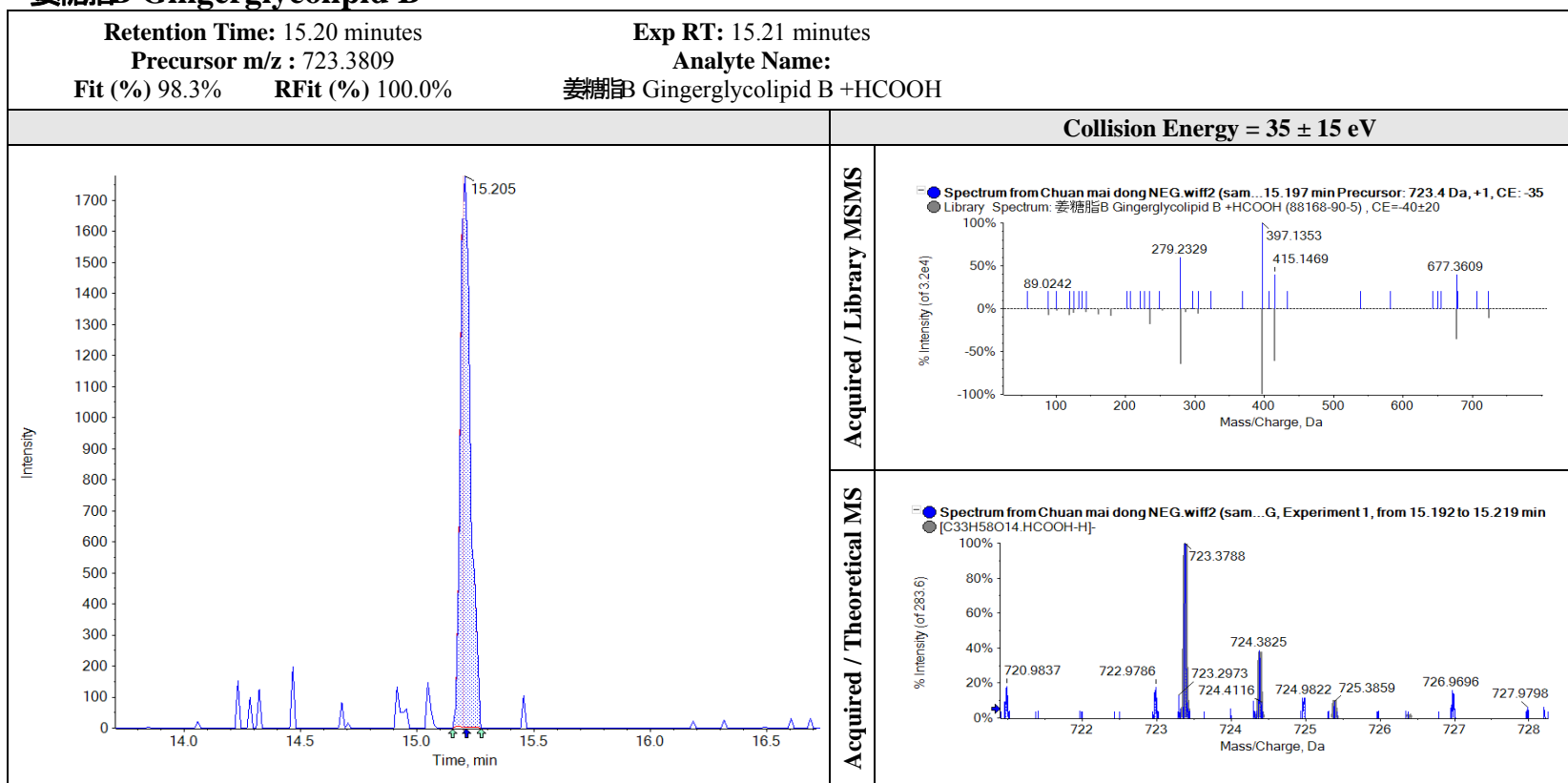
甲基麦冬二氢高异黄酮B Methylophiopogonanone B



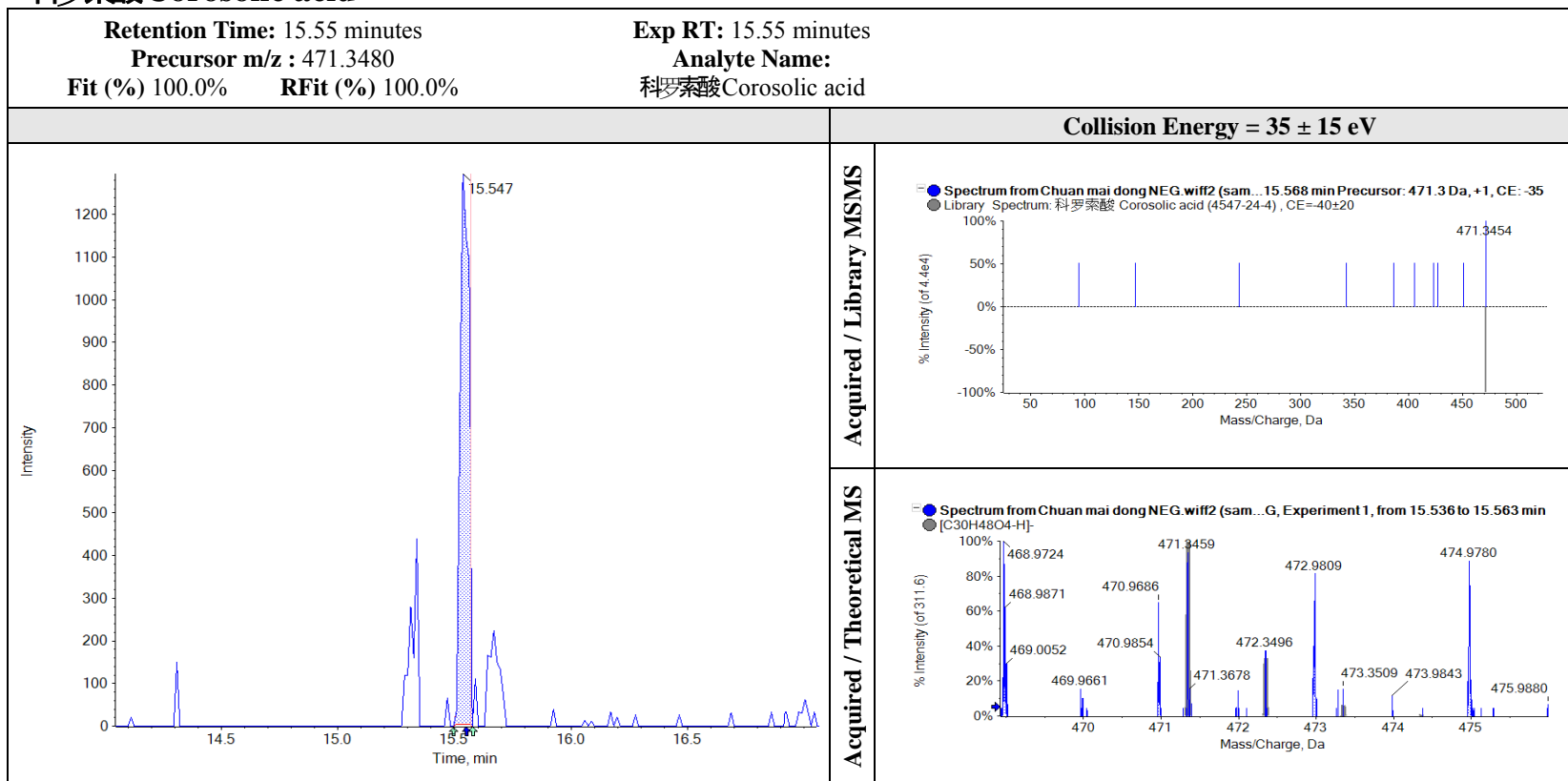
山麦冬皂苷 B Liriopesides B



姜糖苷B Gingerglycolipid B



科罗素酸 Corosolic acid



麦冬黄烷酮C Ophiopogonanone C

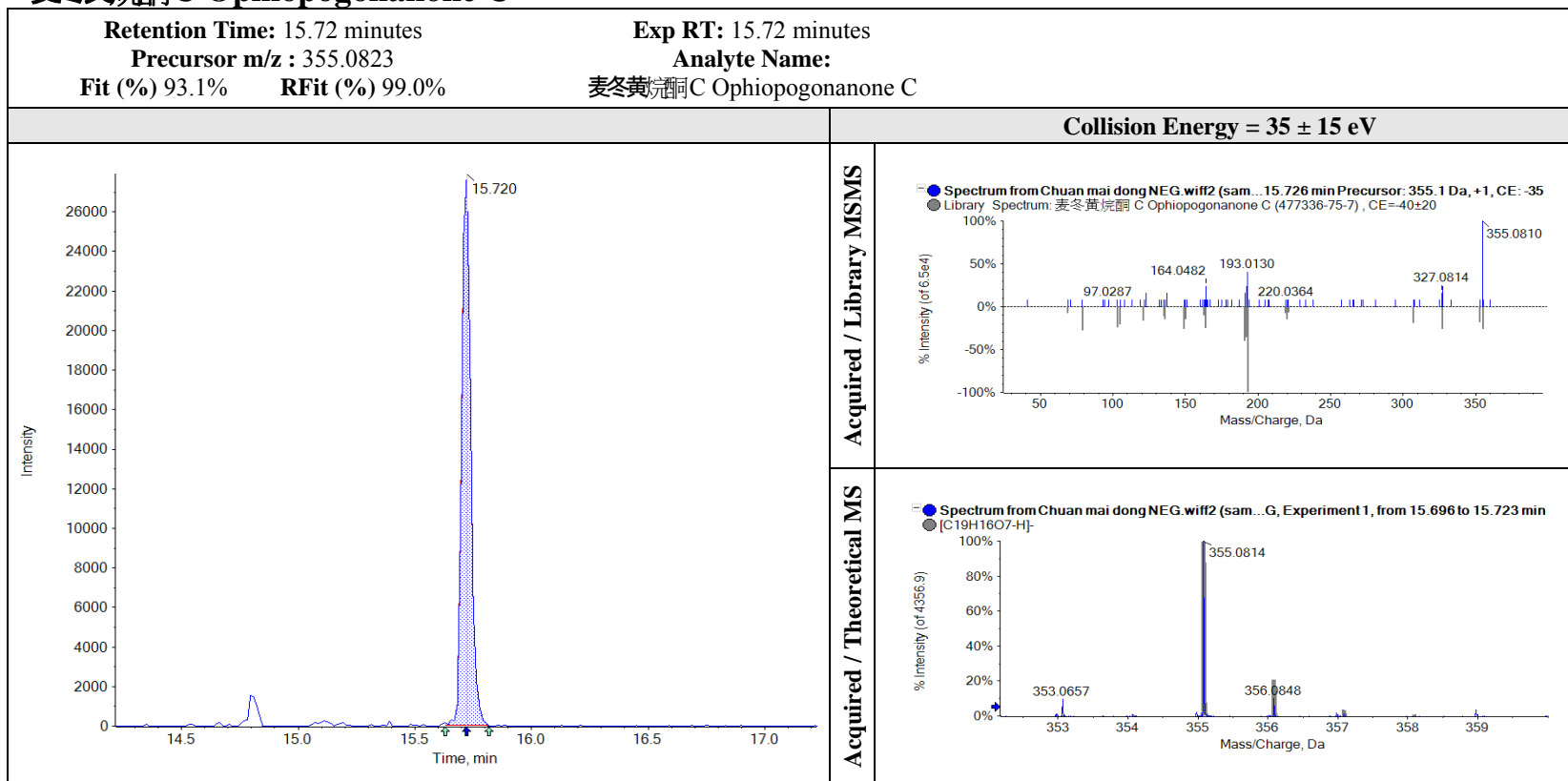
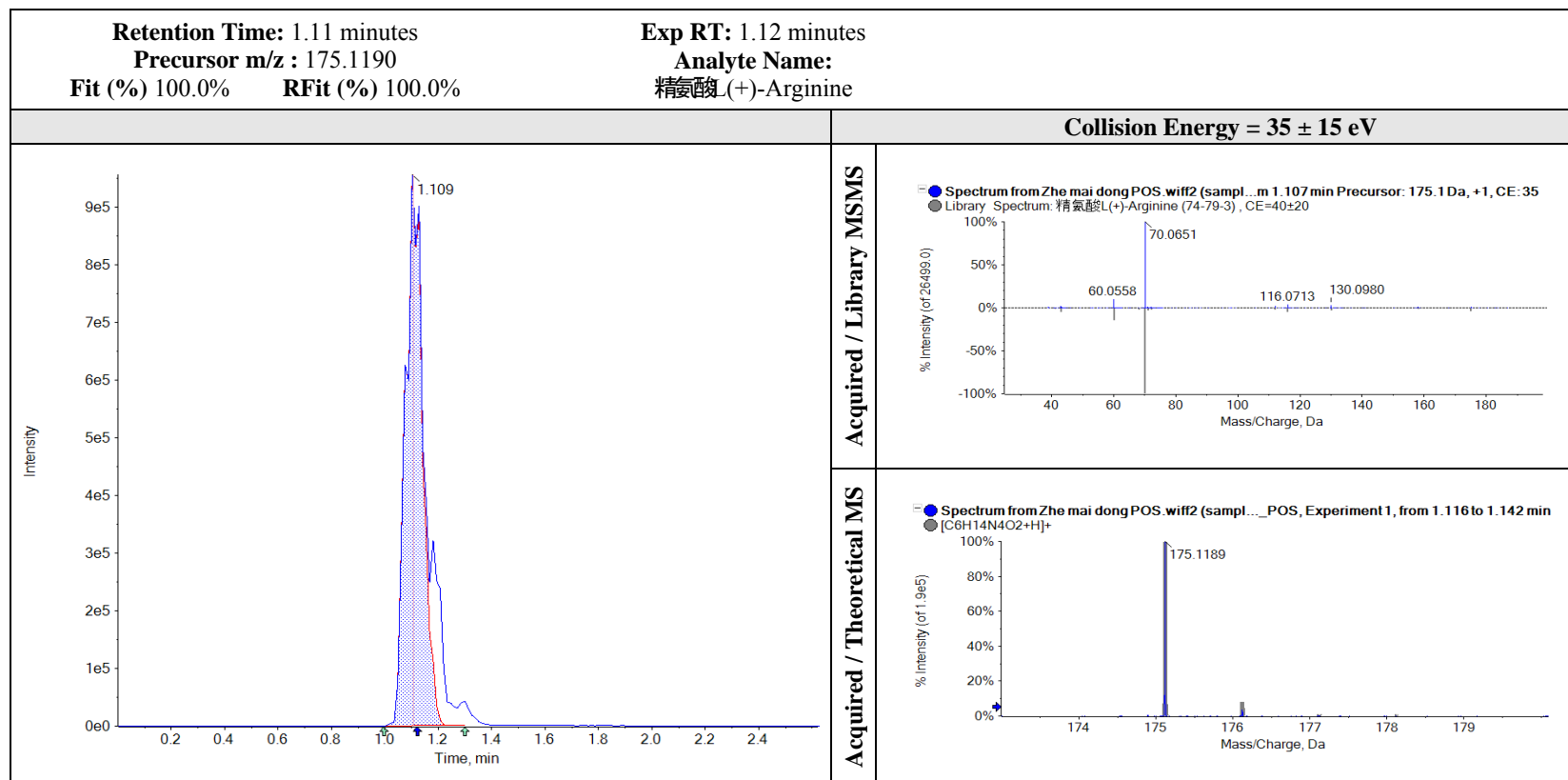


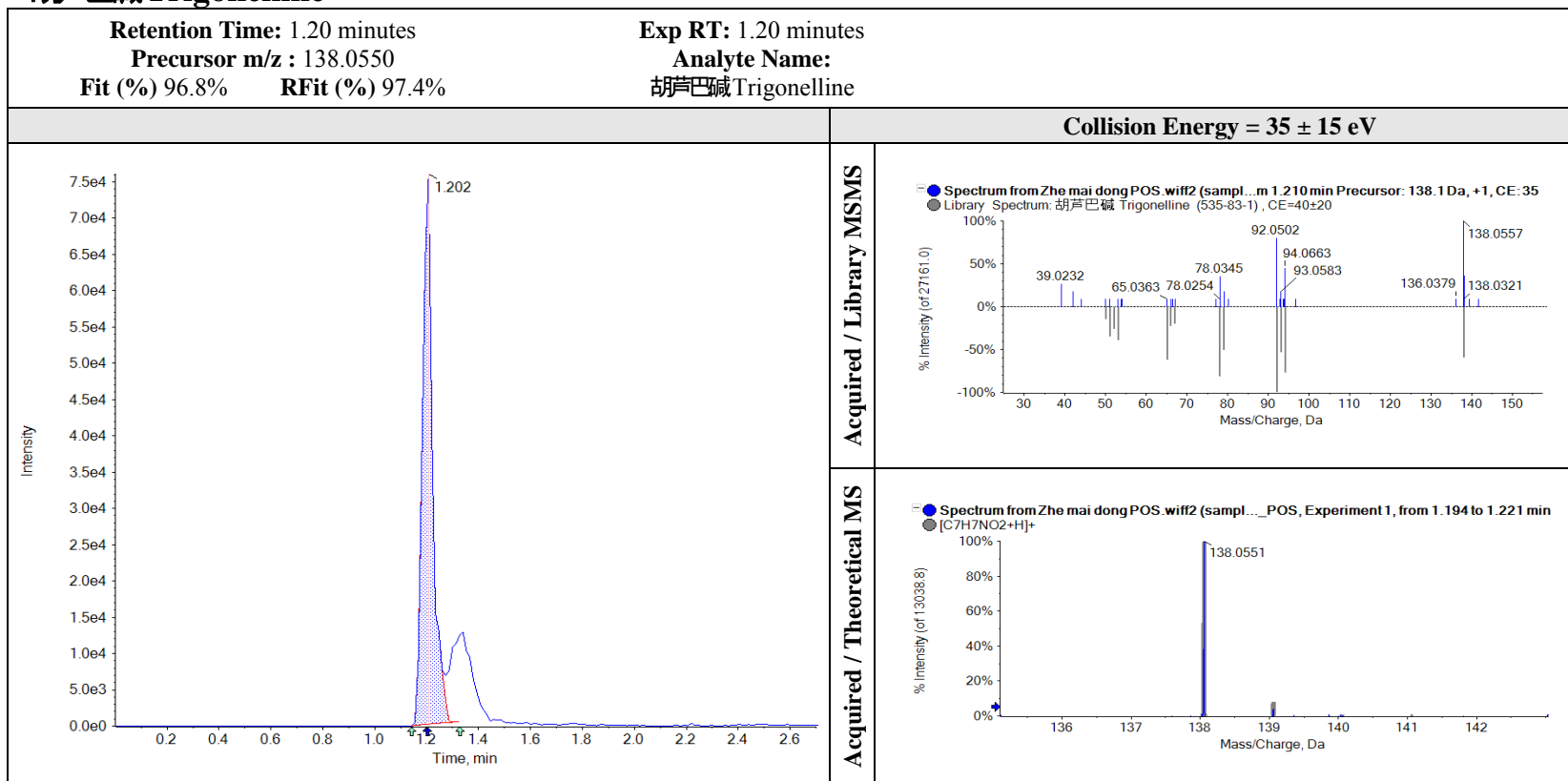
Table S2 MS fragmentation pathways for representative compounds of ZMD in UPLC-Q/TOF-MS analysis

MS fragmentation pathways for different chemical constituents of ZMD in positive ion mode

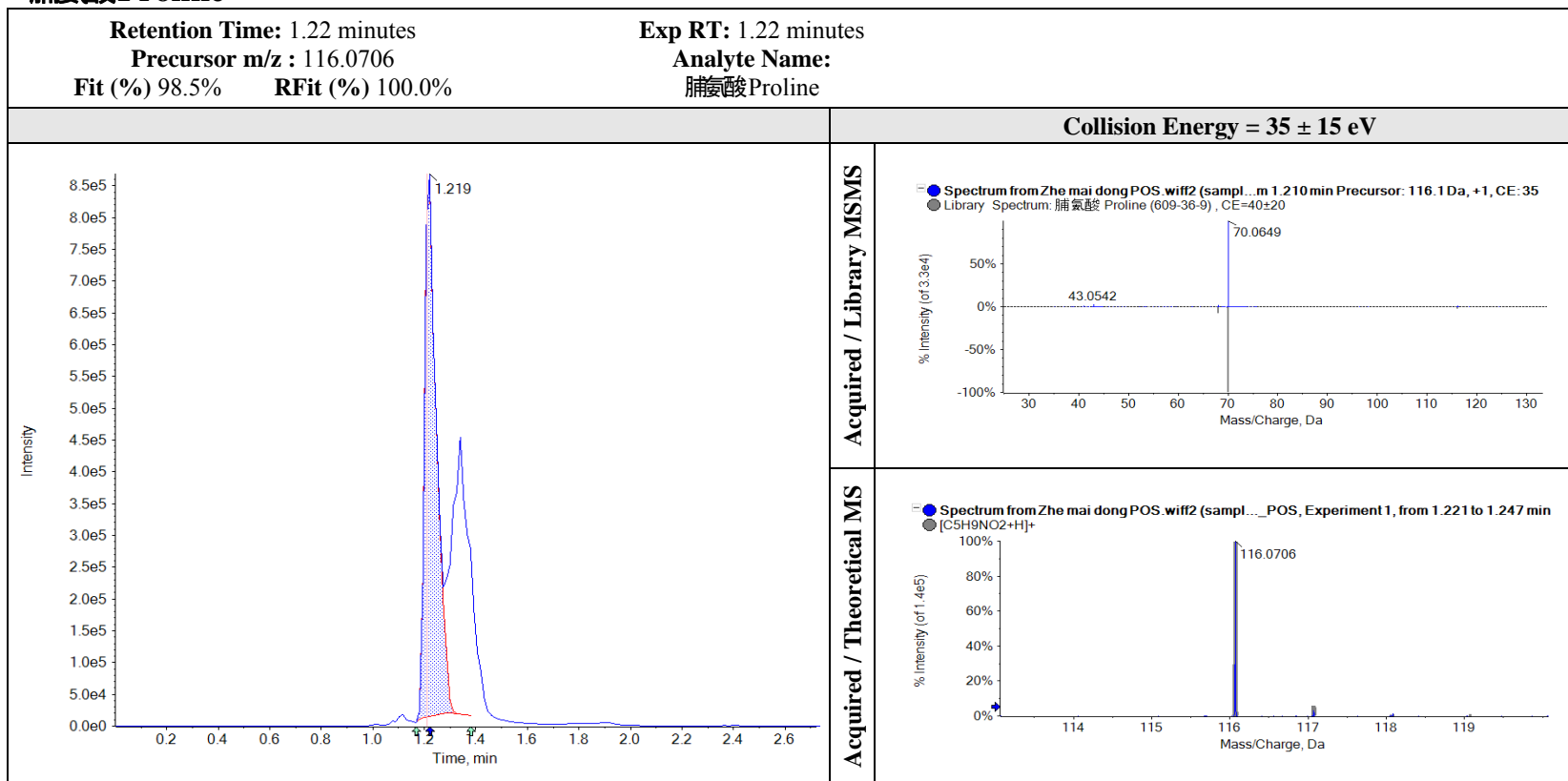
精氨酸 L(+)-Arginine



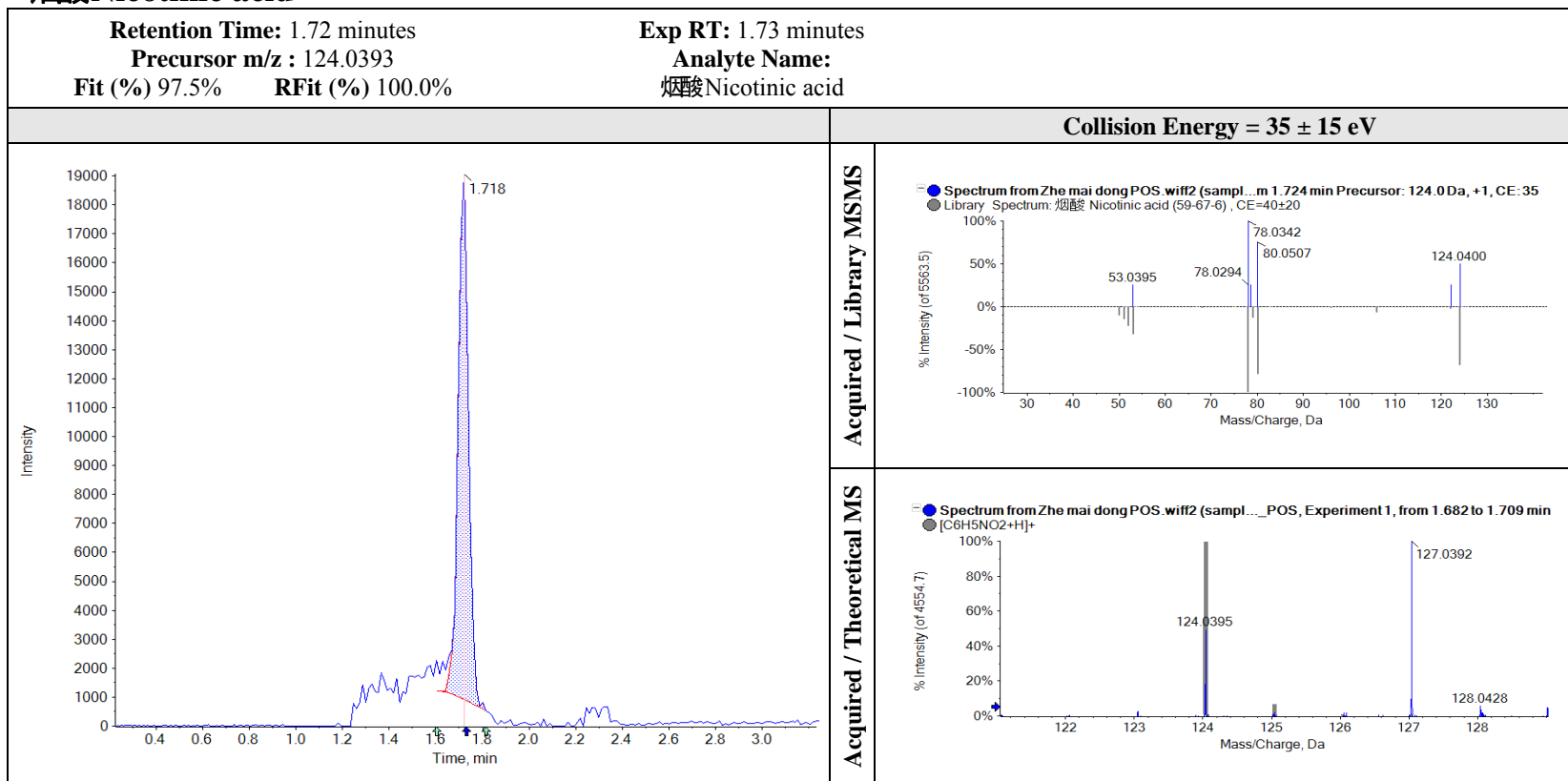
胡芦巴碱 Trigonelline



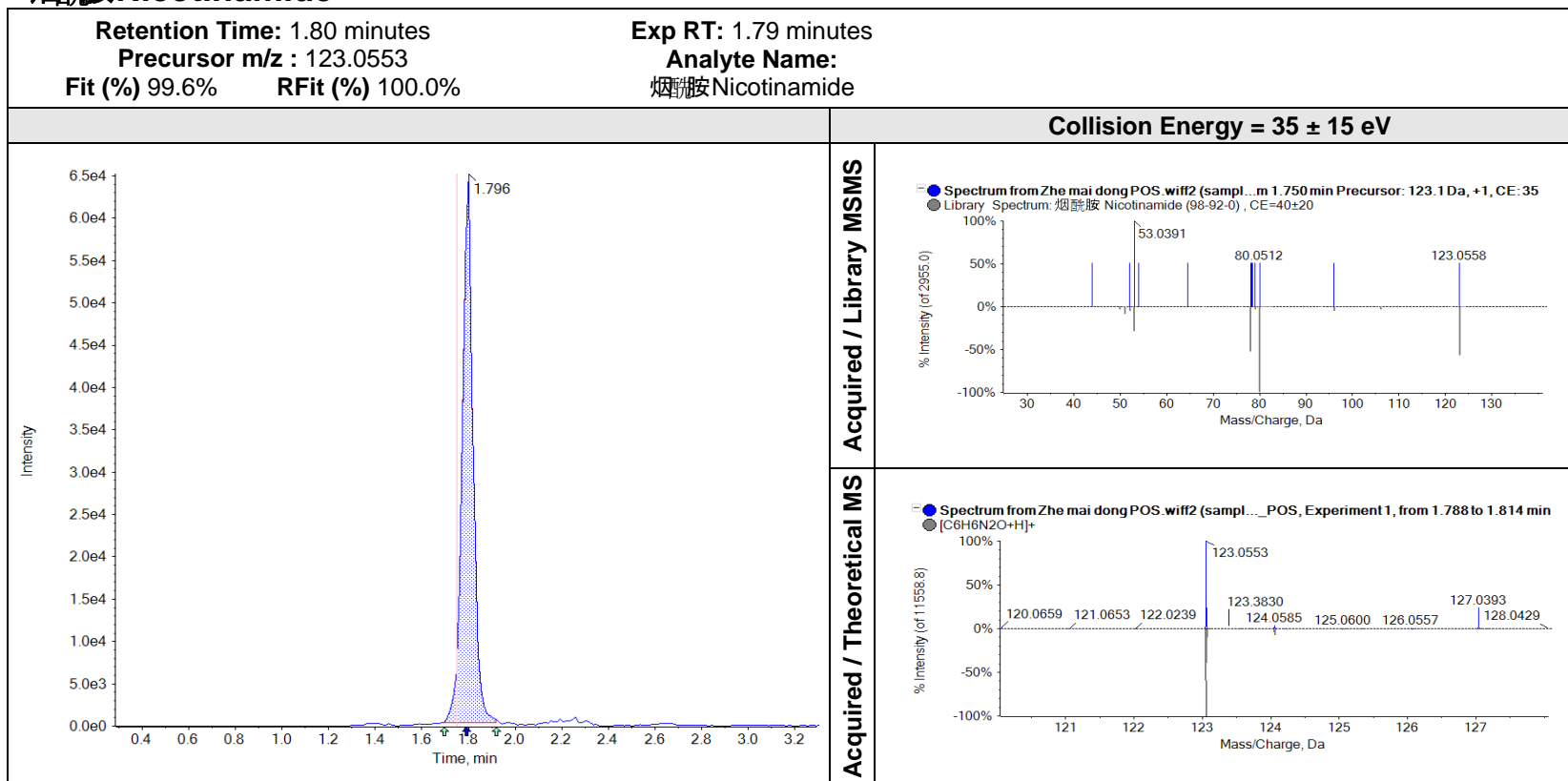
脯氨酸 Proline



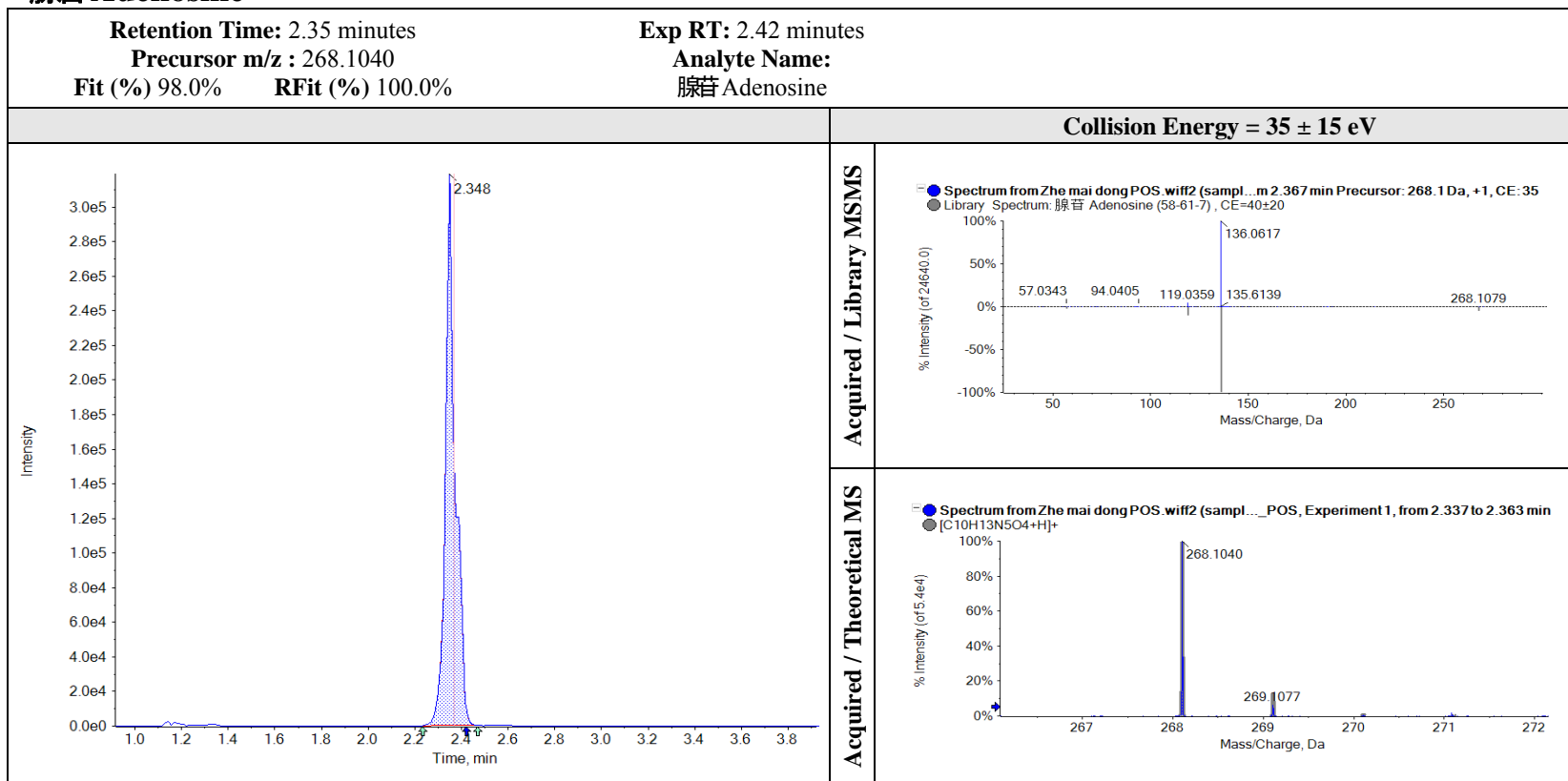
烟酸 Nicotinic acid



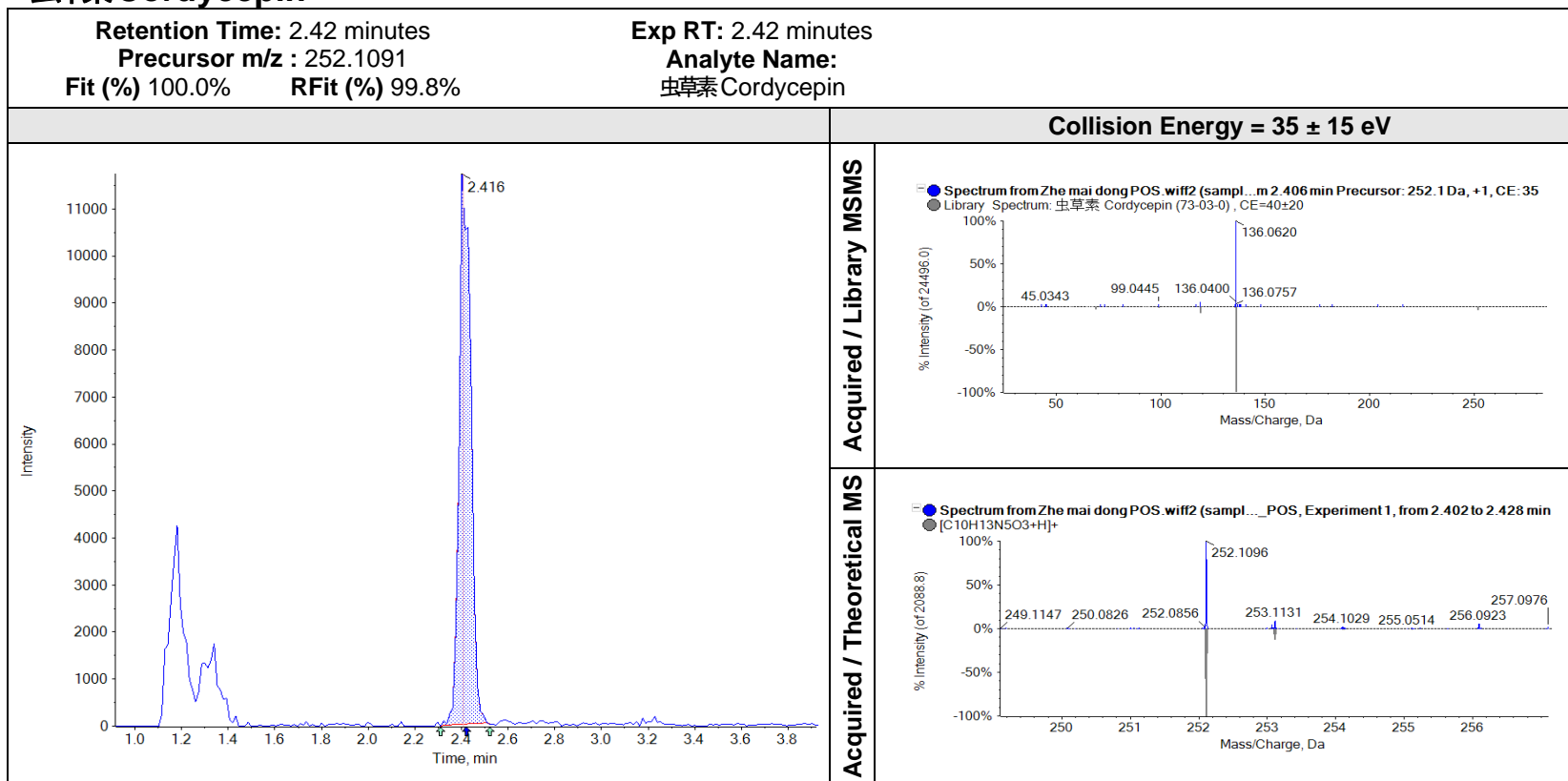
烟酰胺 Nicotinamide



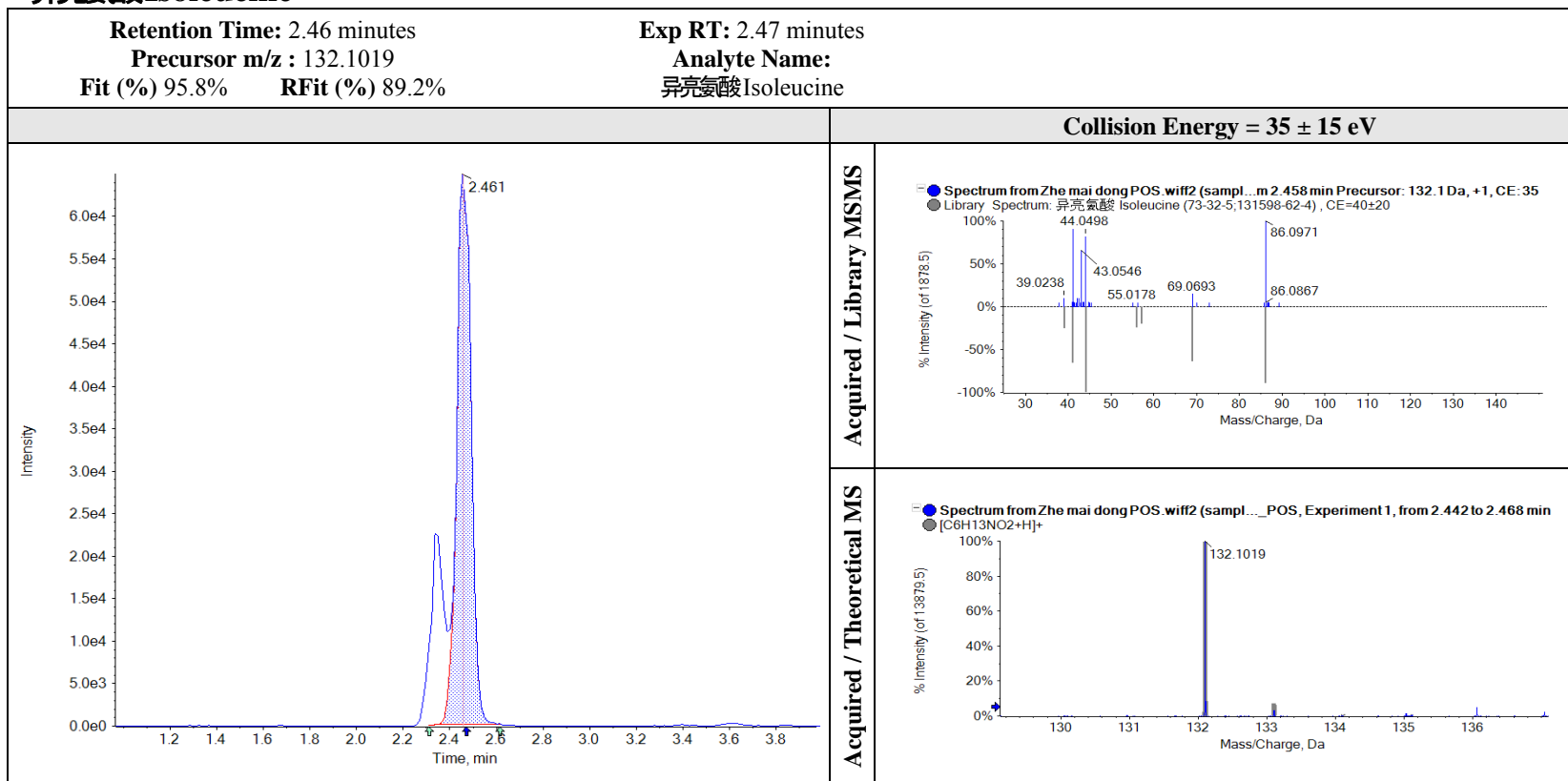
腺苷 Adenosine



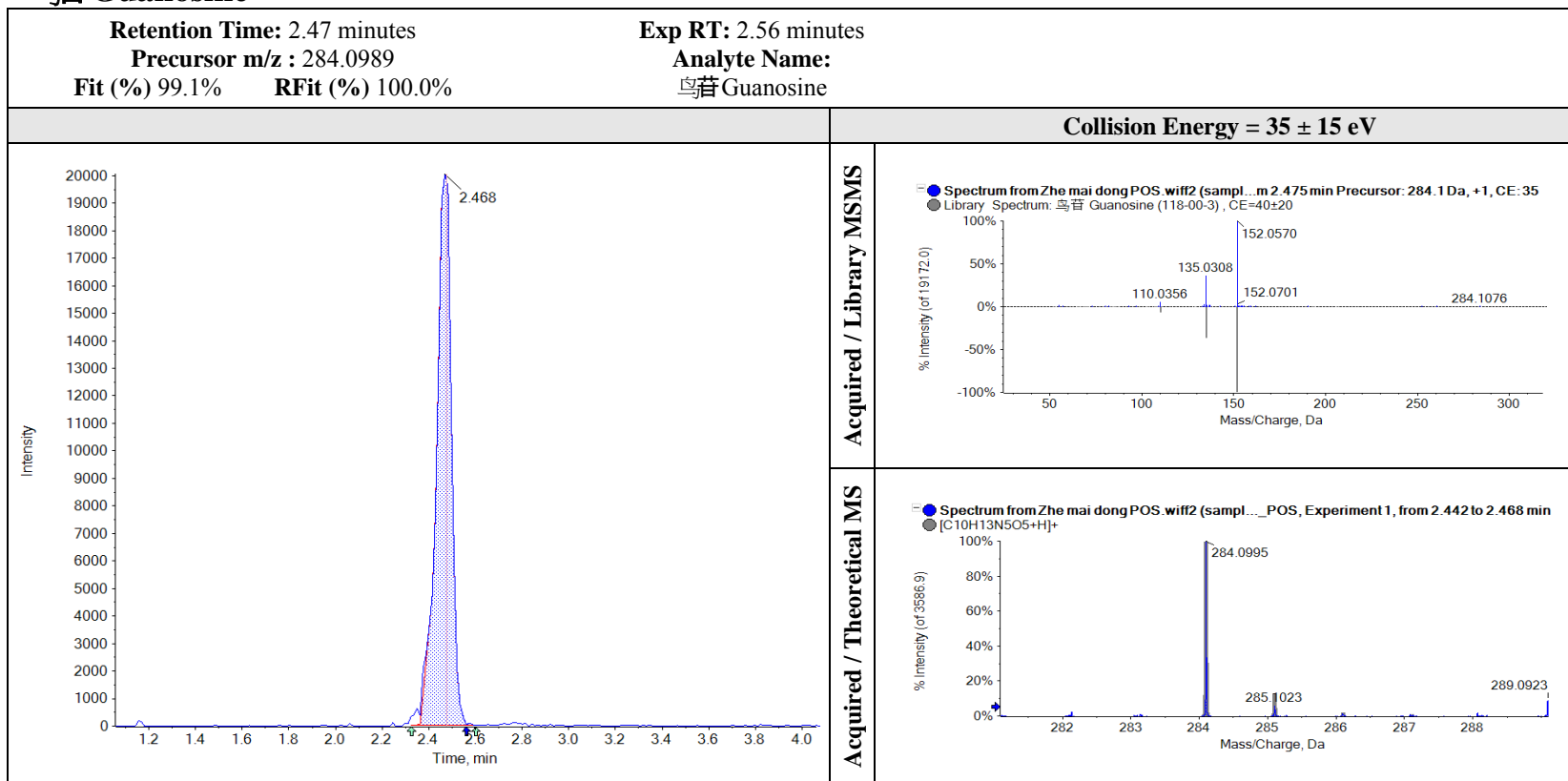
虫草素 Cordycepin



异亮氨酸 Isoleucine



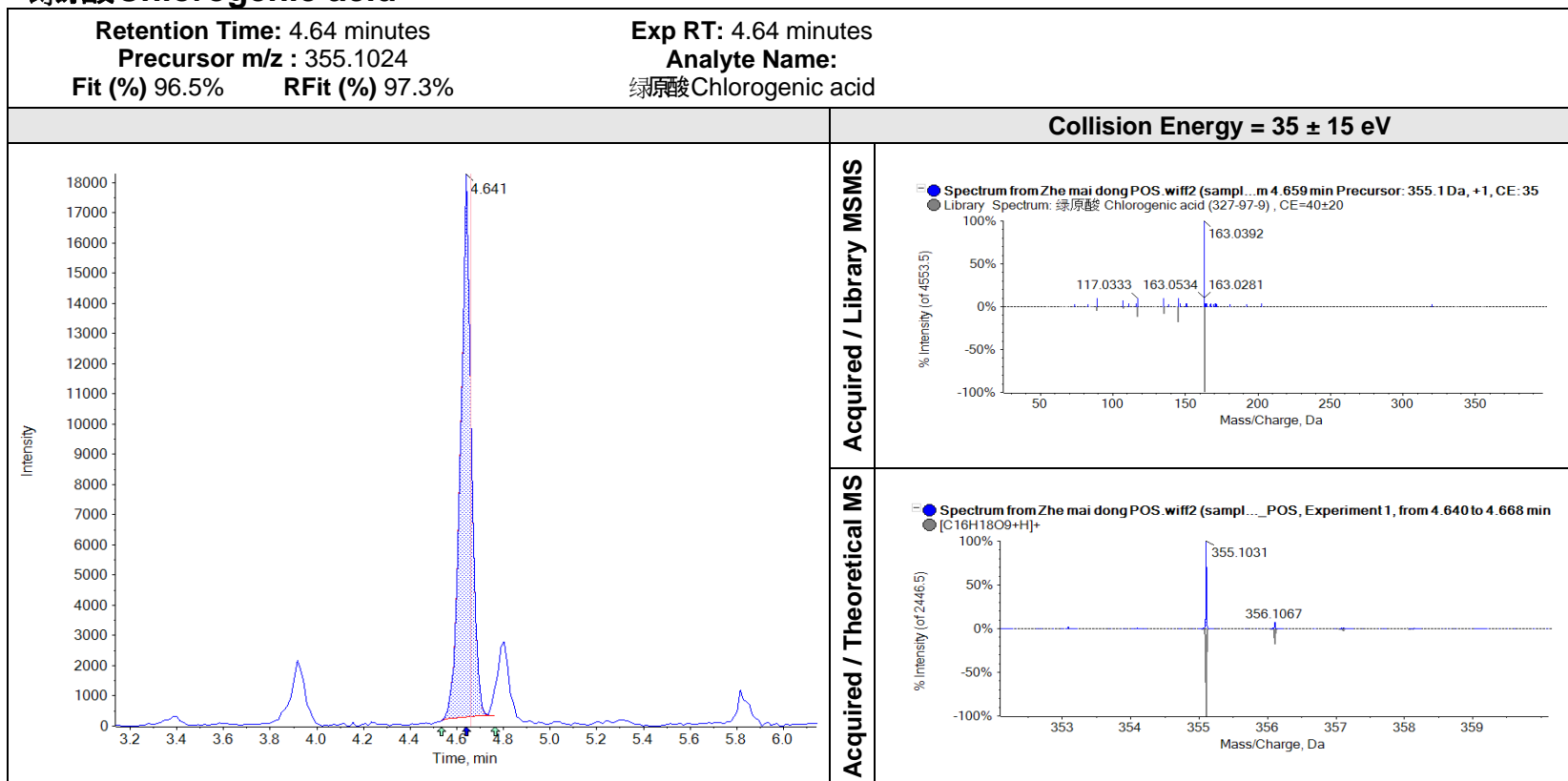
鸟苷 Guanosine



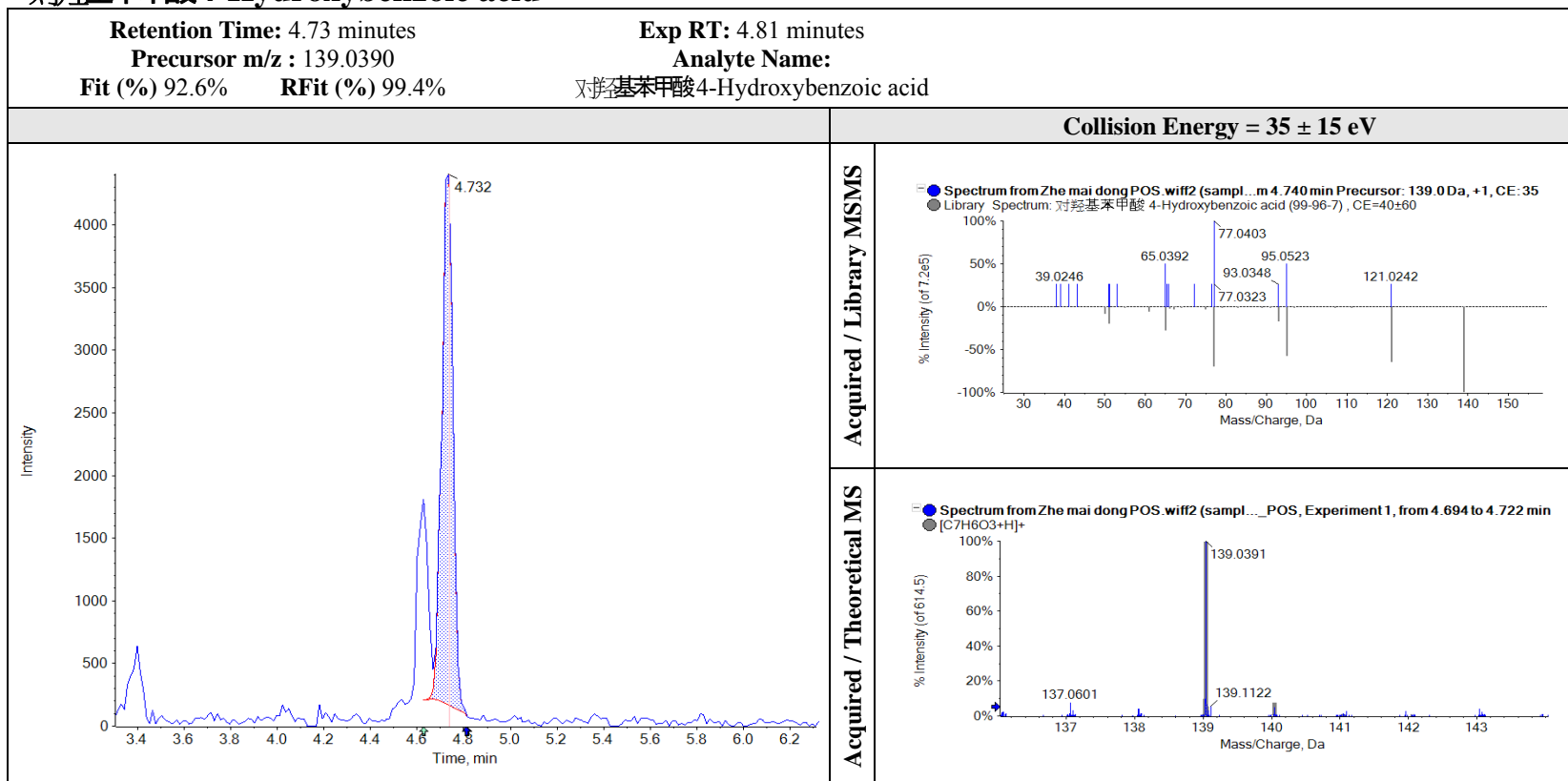
苯丙氨酸 Phenprobamate

<p>Retention Time: 3.17 minutes Exp RT: 3.31 minutes</p> <p>Precursor m/z : 166.0863 Analyte Name:</p> <p>Fit (%) 96.9% RFit (%) 100.0% 苯丙氨酸 Phenprobamate</p>	
<p>Collision Energy = 35 ± 15 eV</p>	
	<p>Acquired / Library MSMS</p>
<p>Acquired / Theoretical MS</p>	

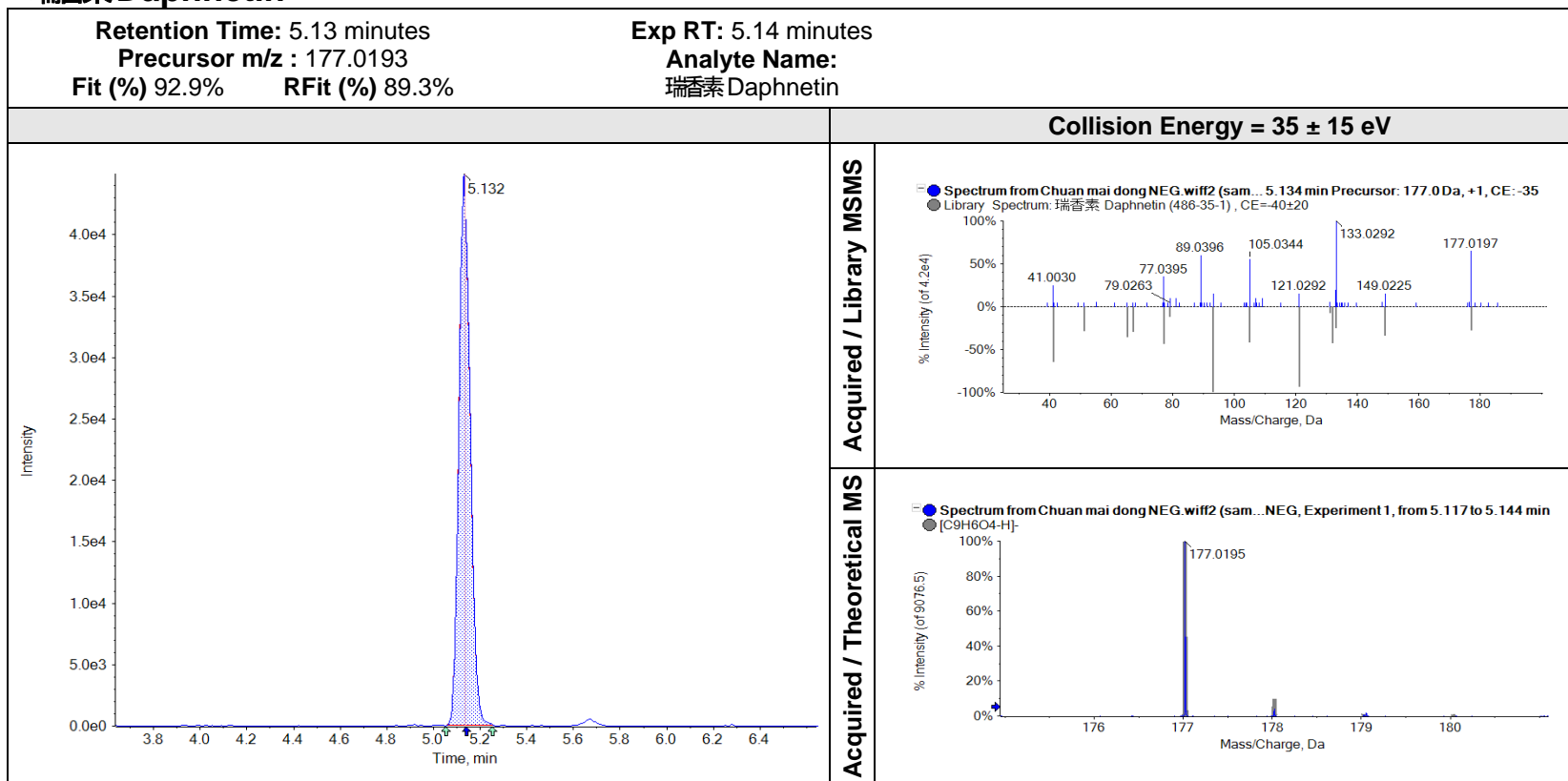
绿原酸 Chlorogenic acid



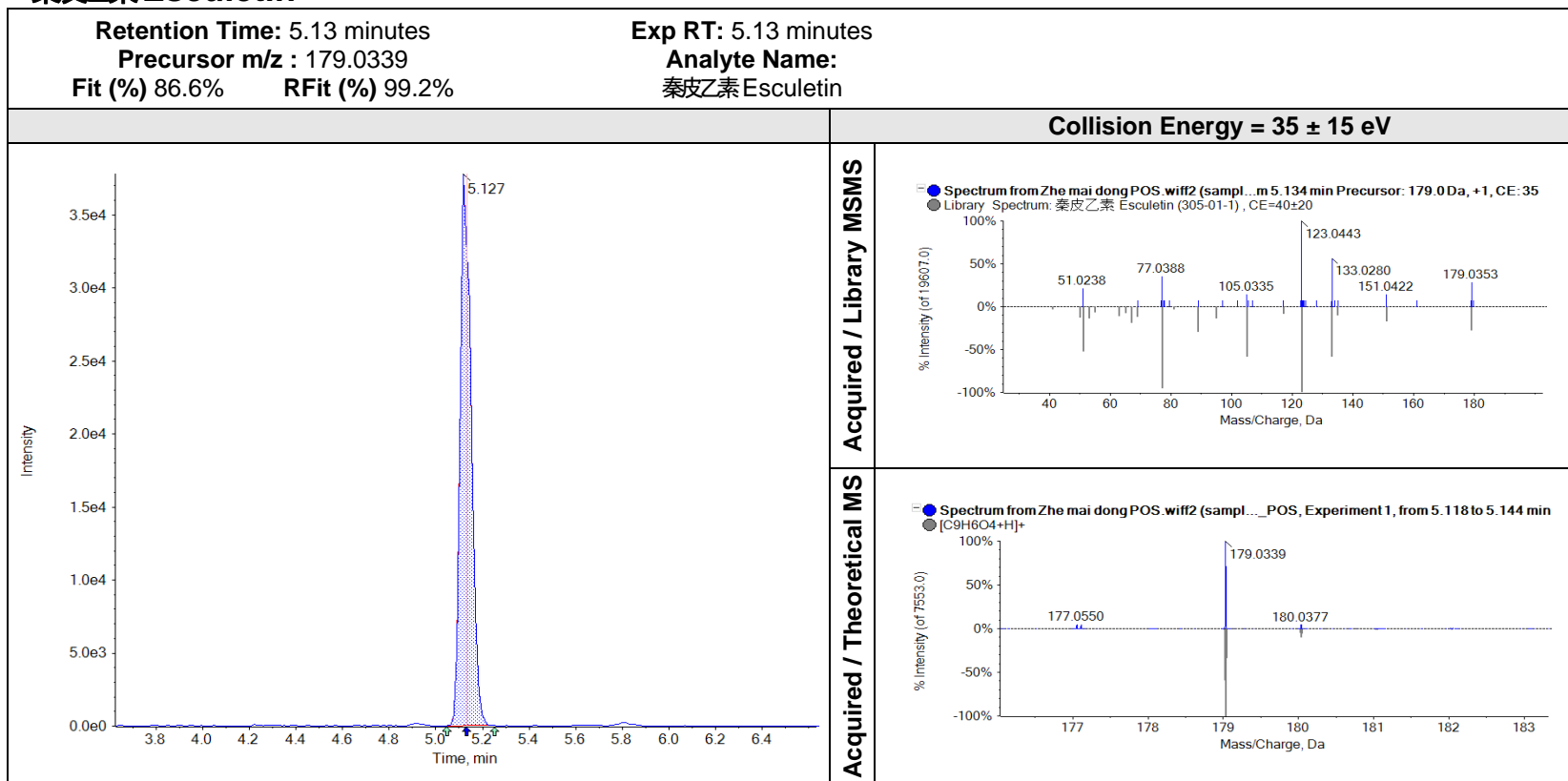
对羟基苯甲酸 4-Hydroxybenzoic acid



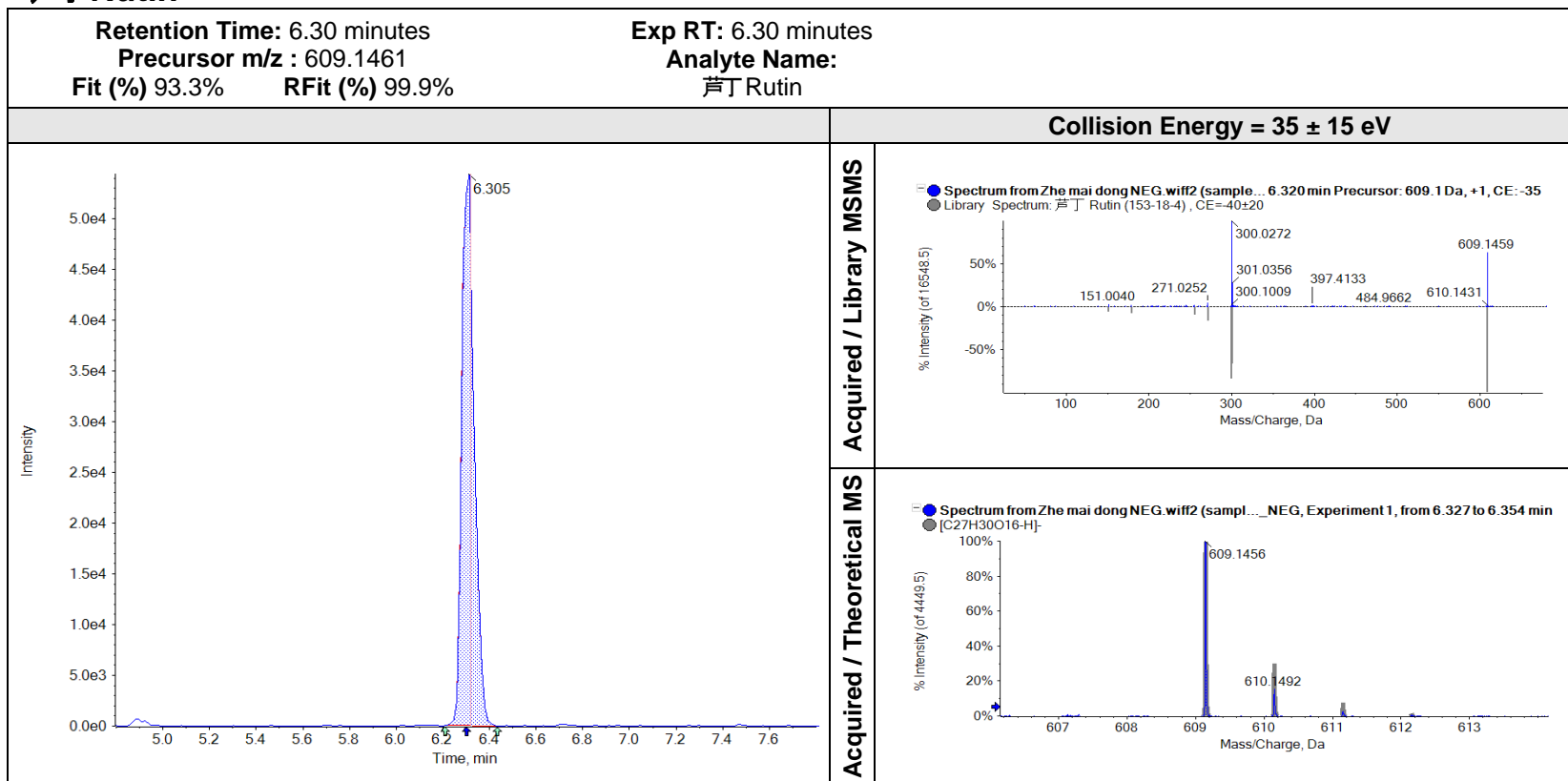
瑞香素 Daphnetin



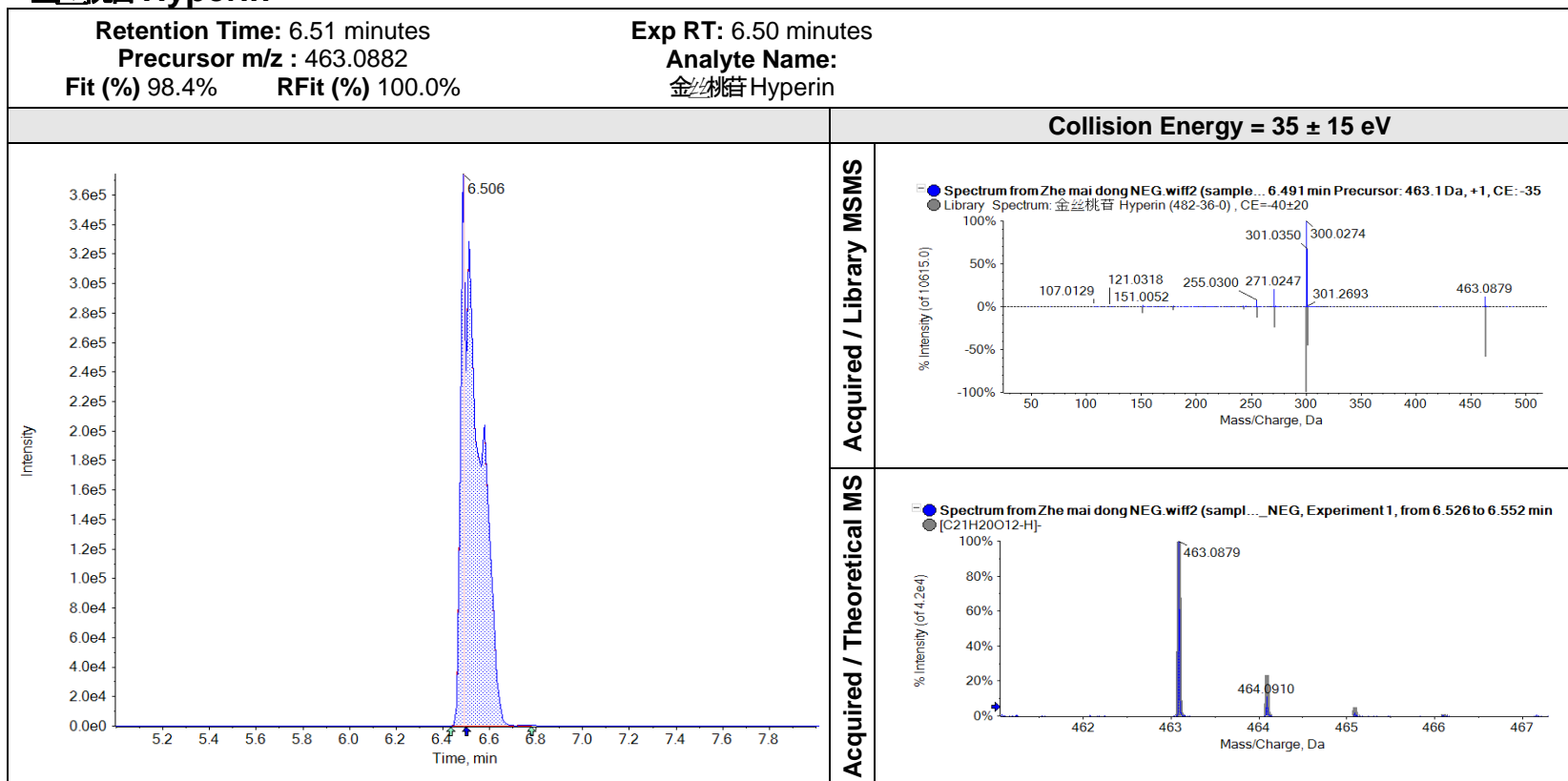
秦皮乙素 Esculetin



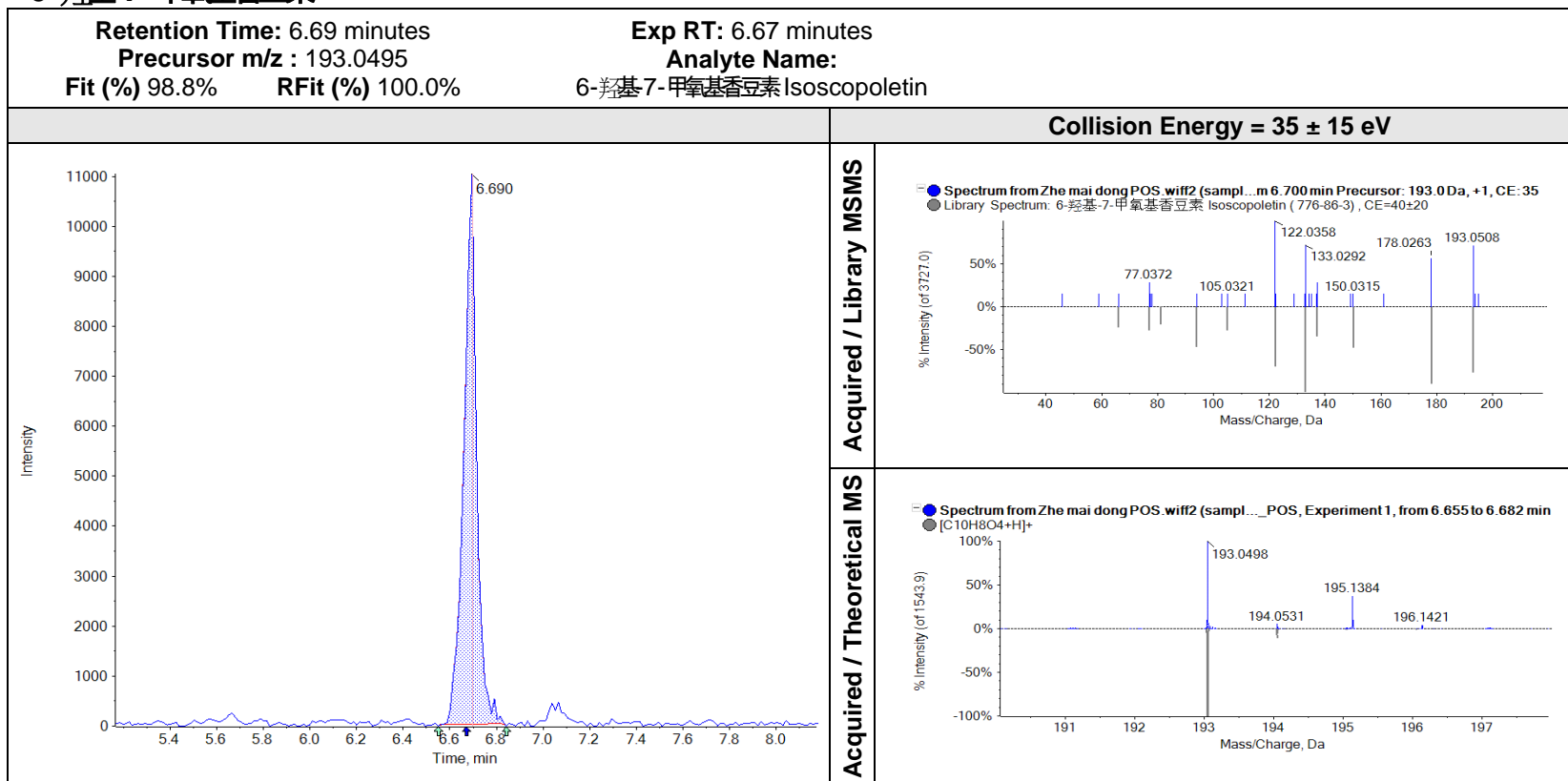
芦丁Rutin



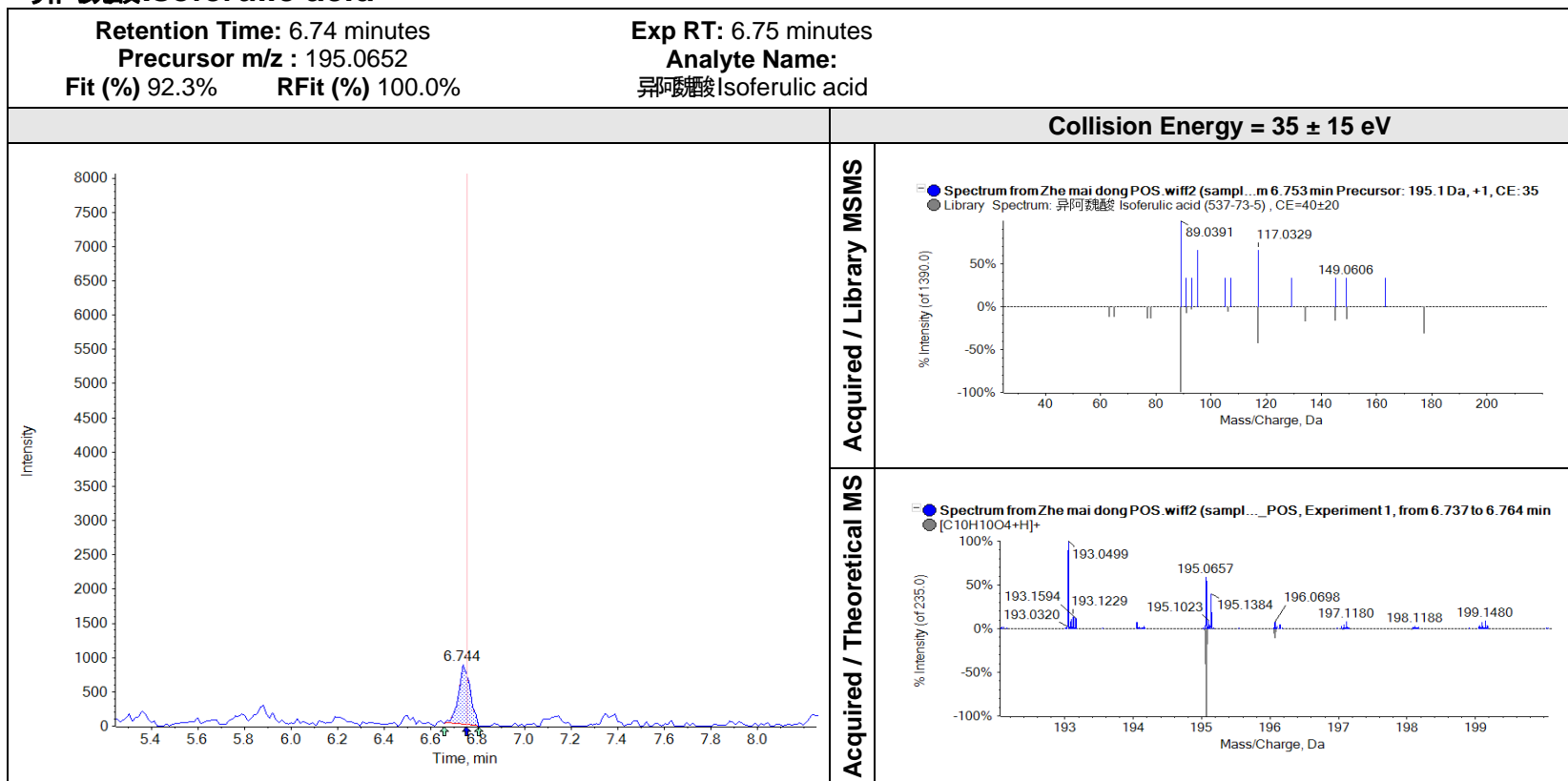
金丝桃苷 Hyperin



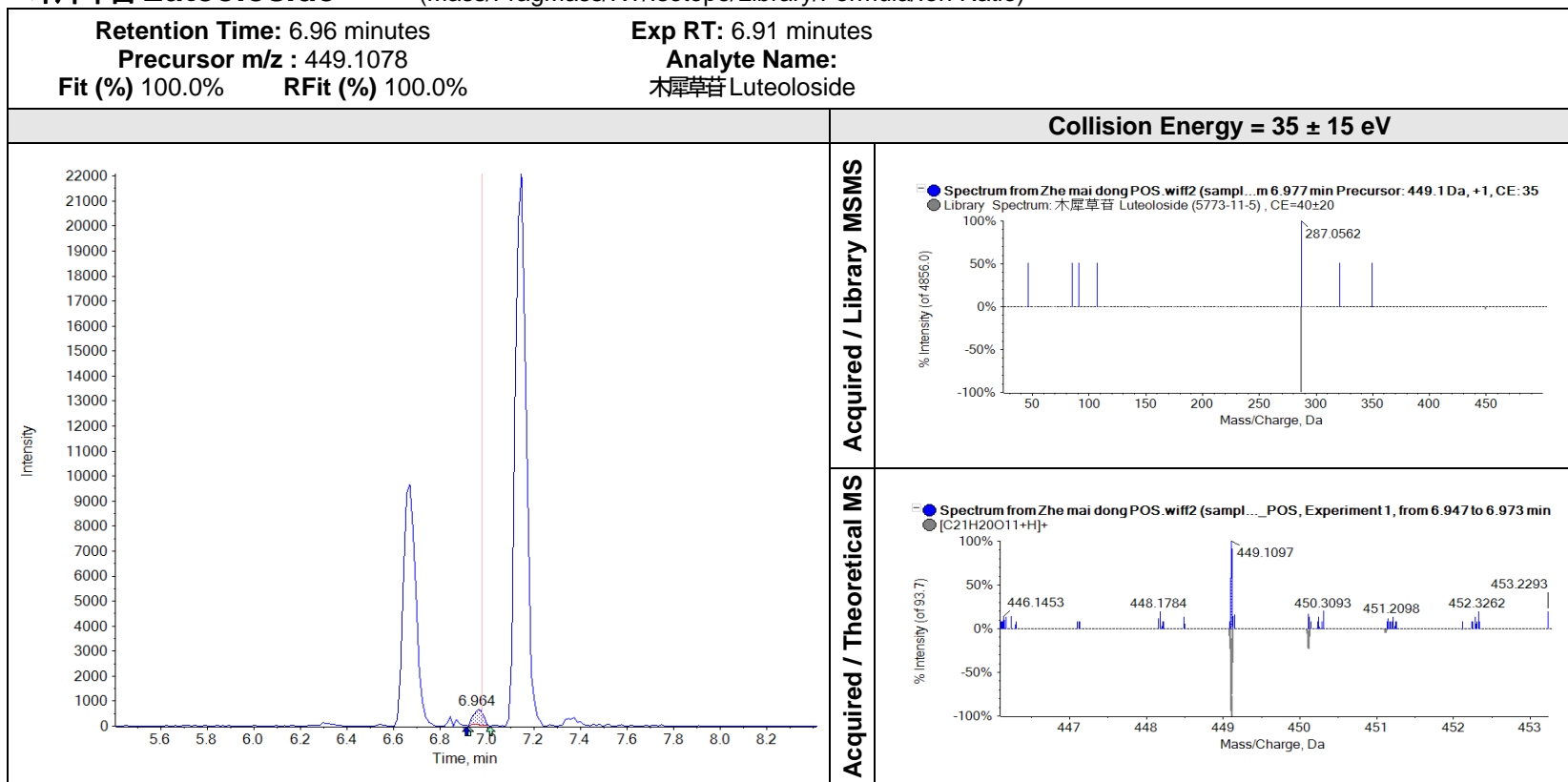
6-羟基-7-甲氧基香豆素



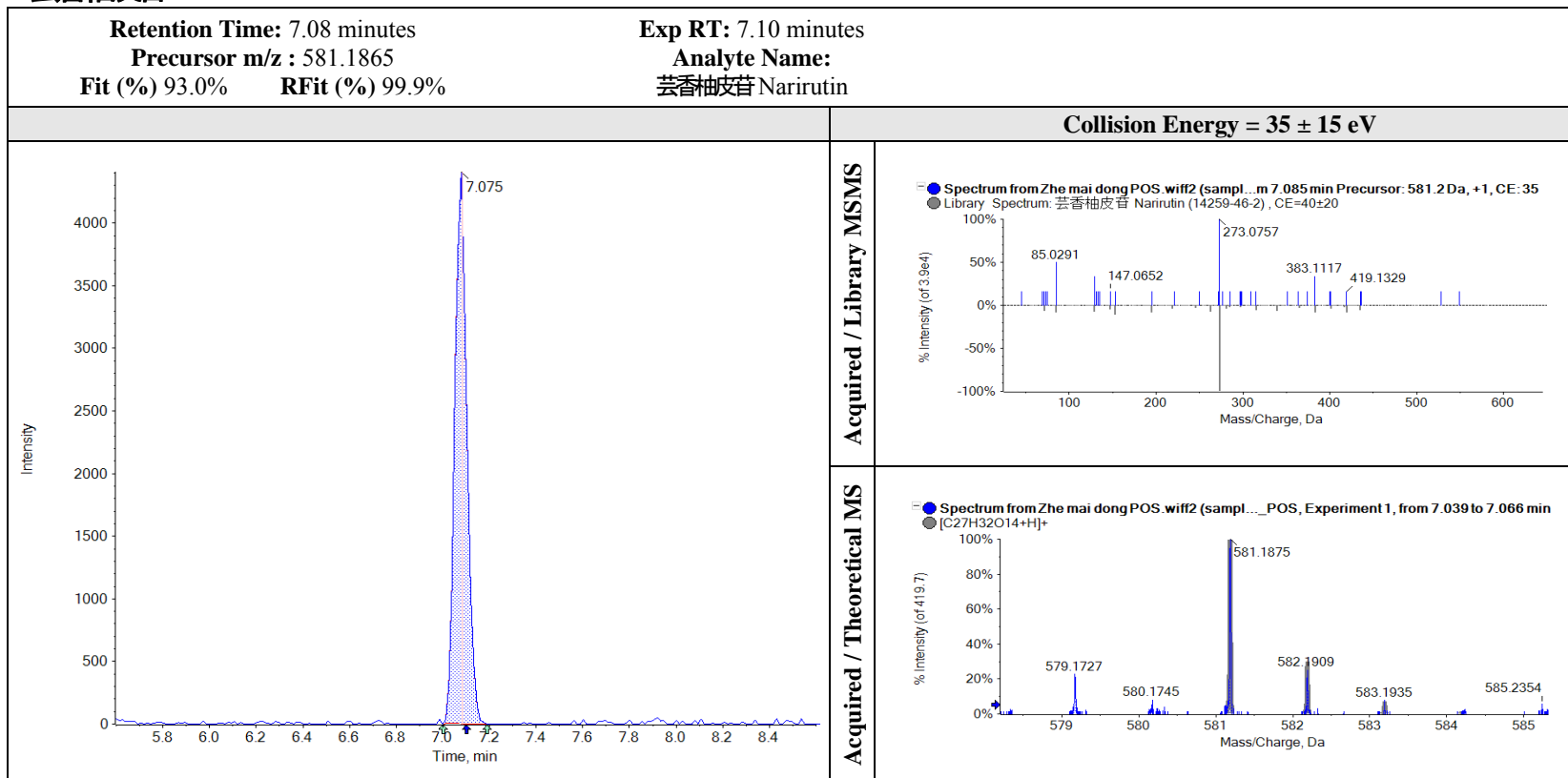
异阿魏酸 Isoferulic acid



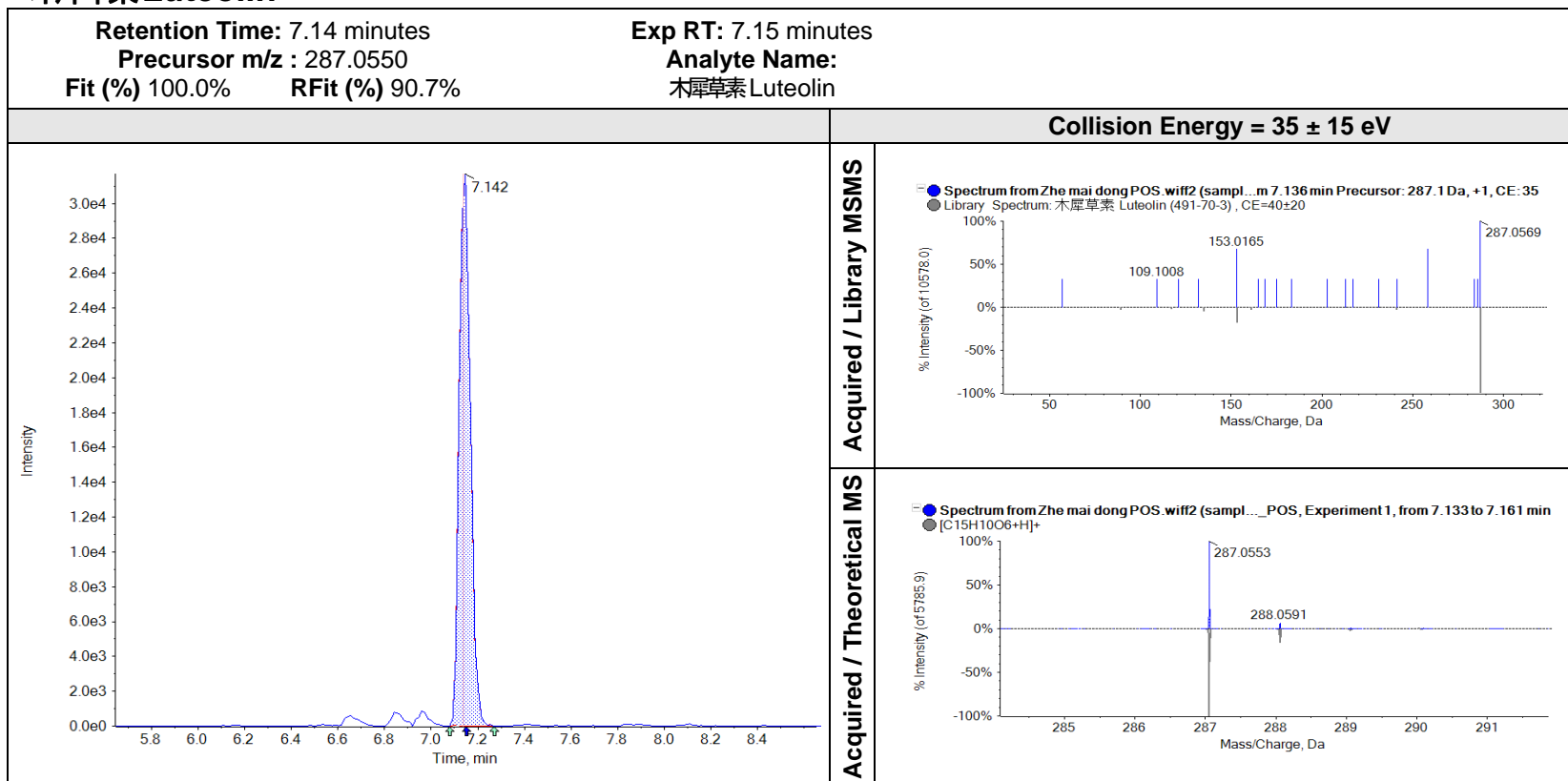
木犀草苷 Luteoloside (Mass/FragMass/RT/Isotope/Library/Formula/Ion Ratio) ✓ ● ● ▲ ✓ ● ●



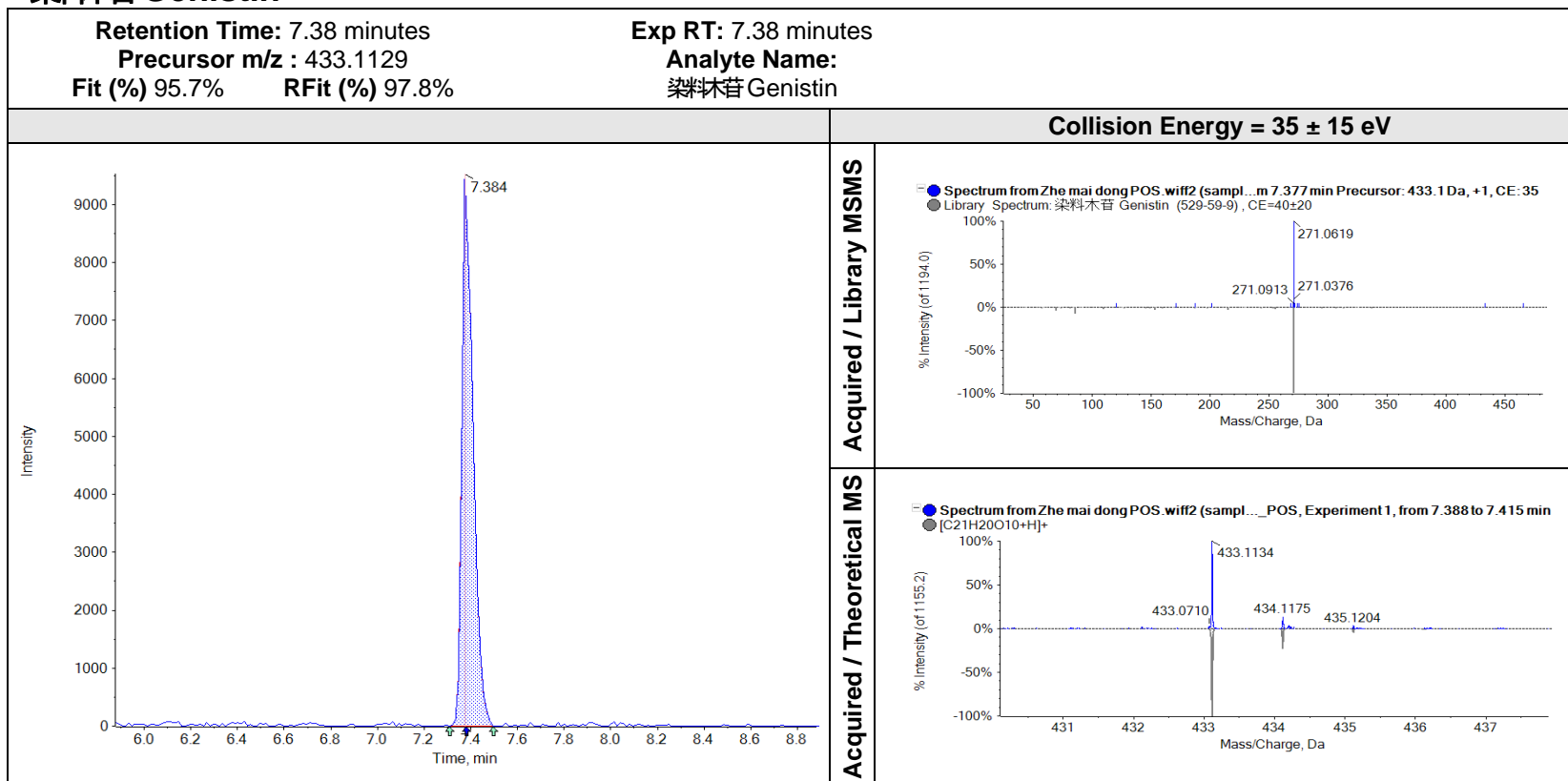
芸香柚皮苷 Narirutin



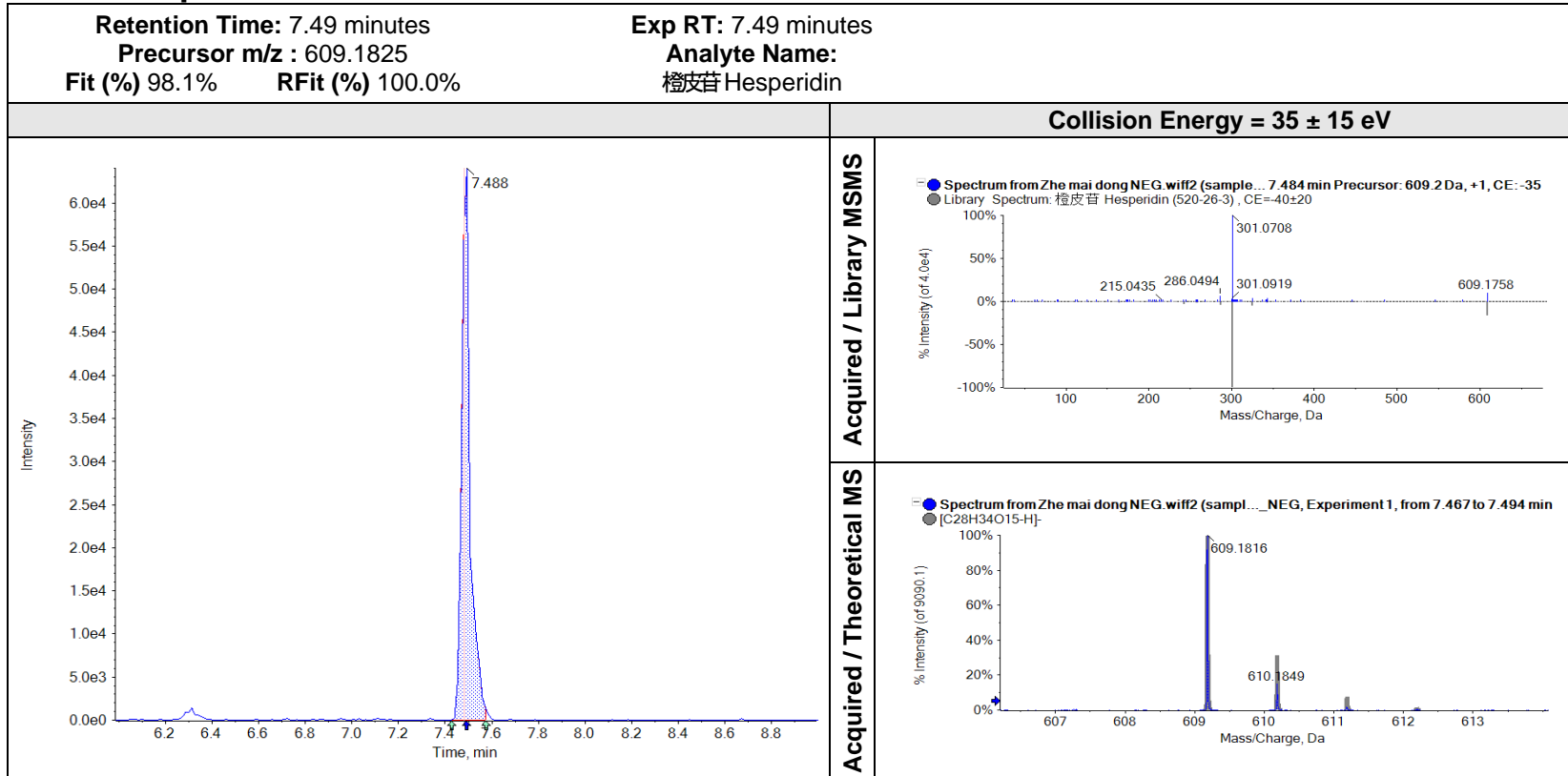
木犀草素 Luteolin



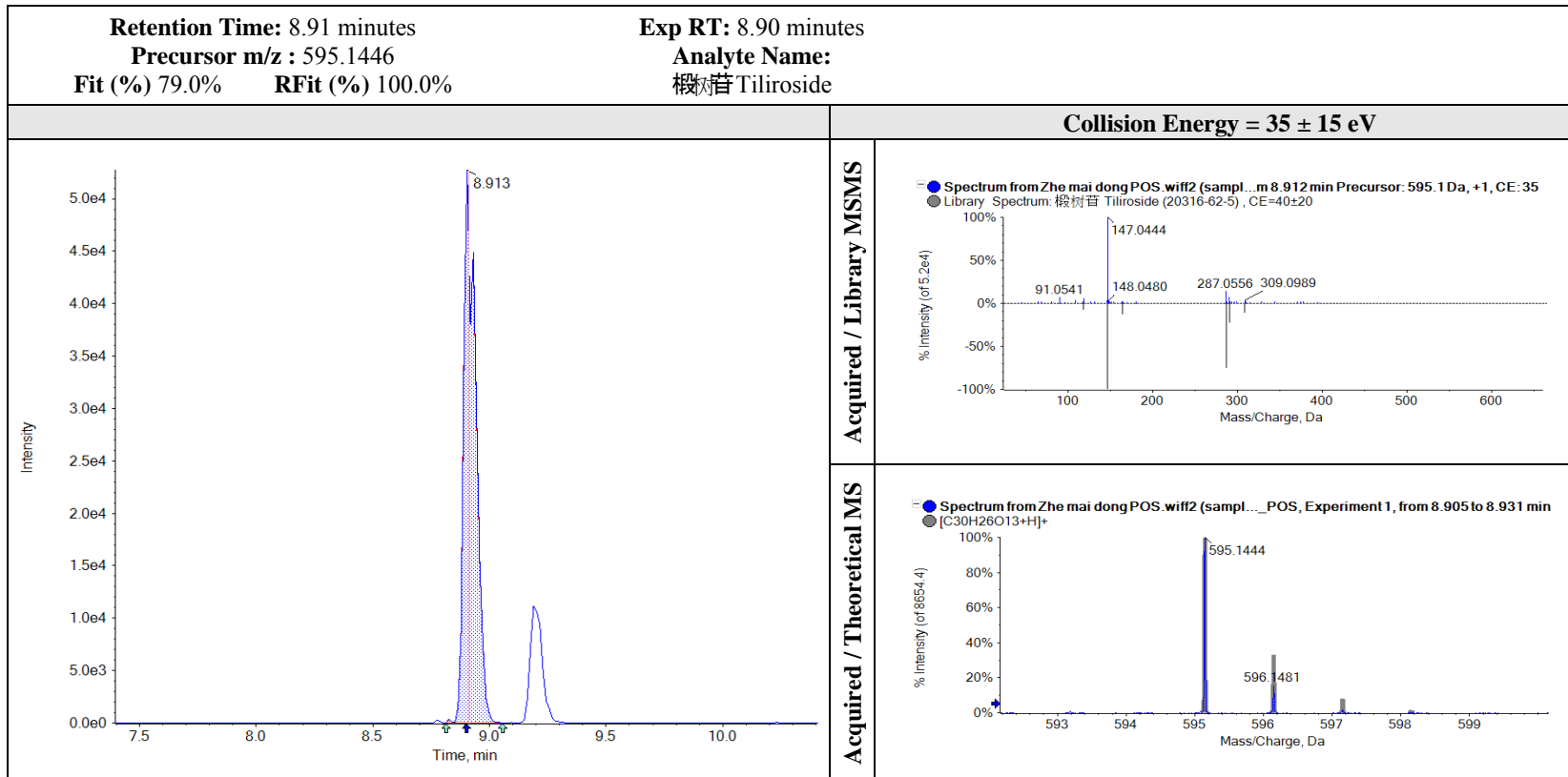
染料木苷 Genistin



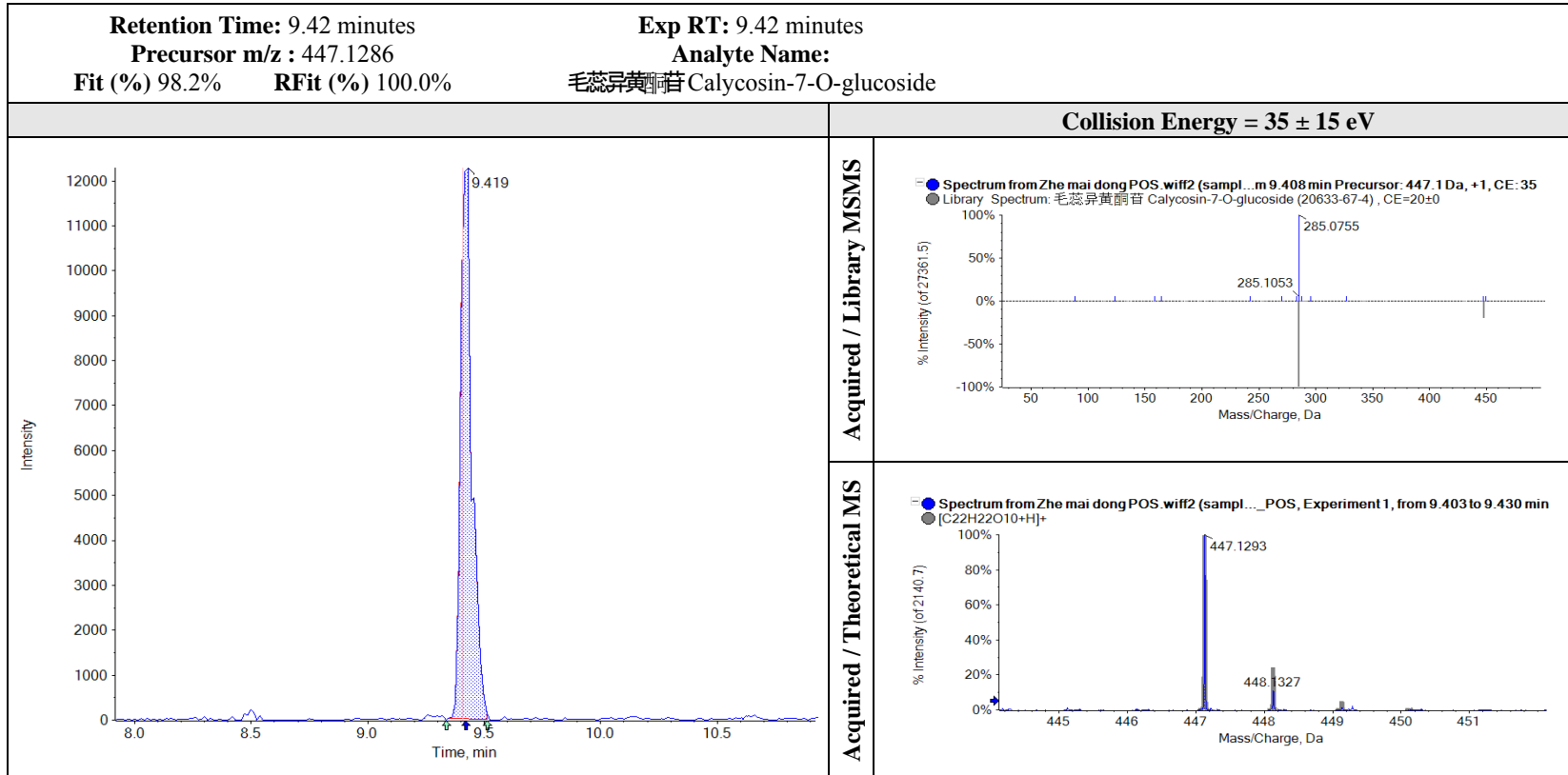
橙皮苷 Hesperidin

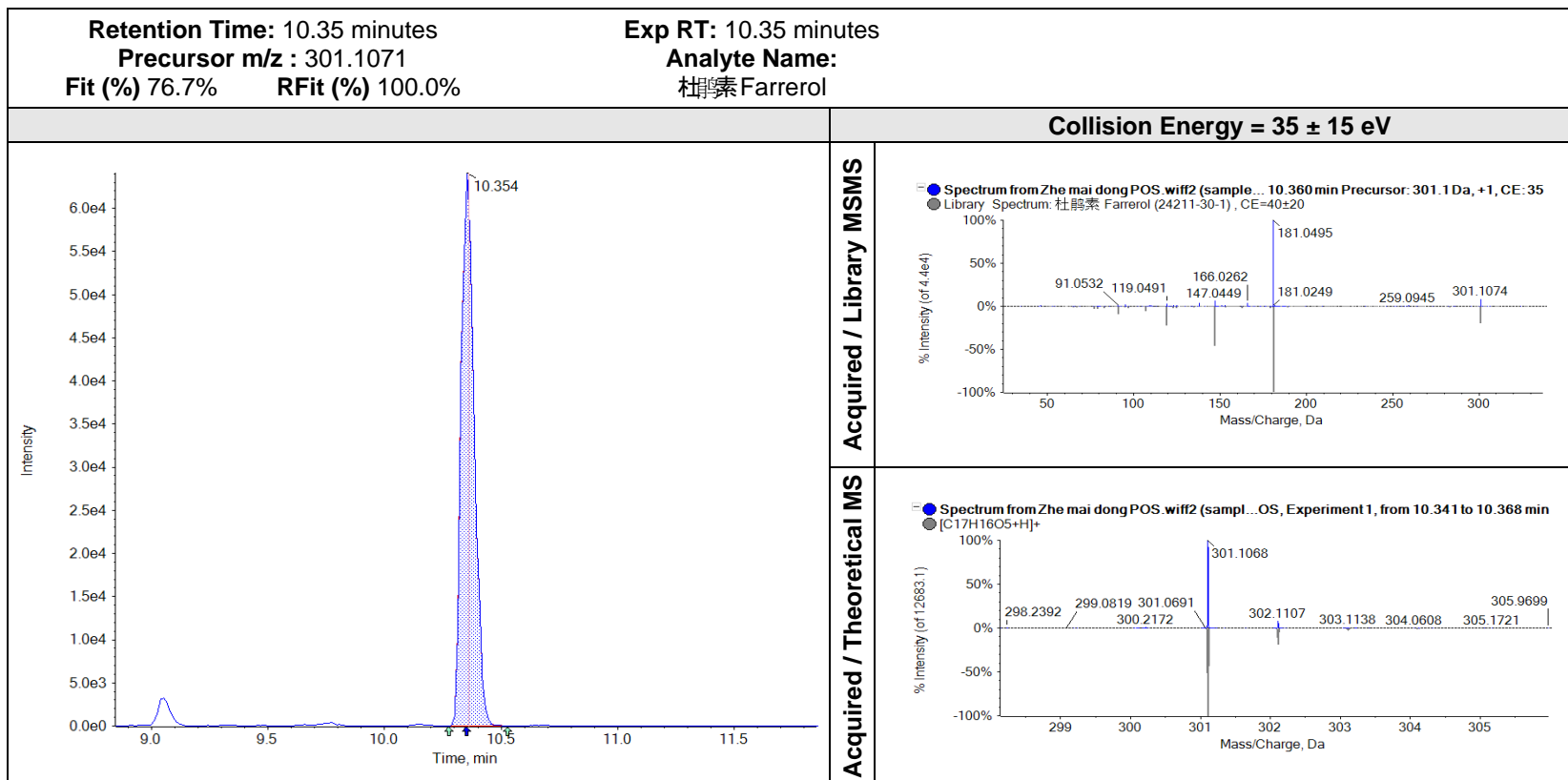


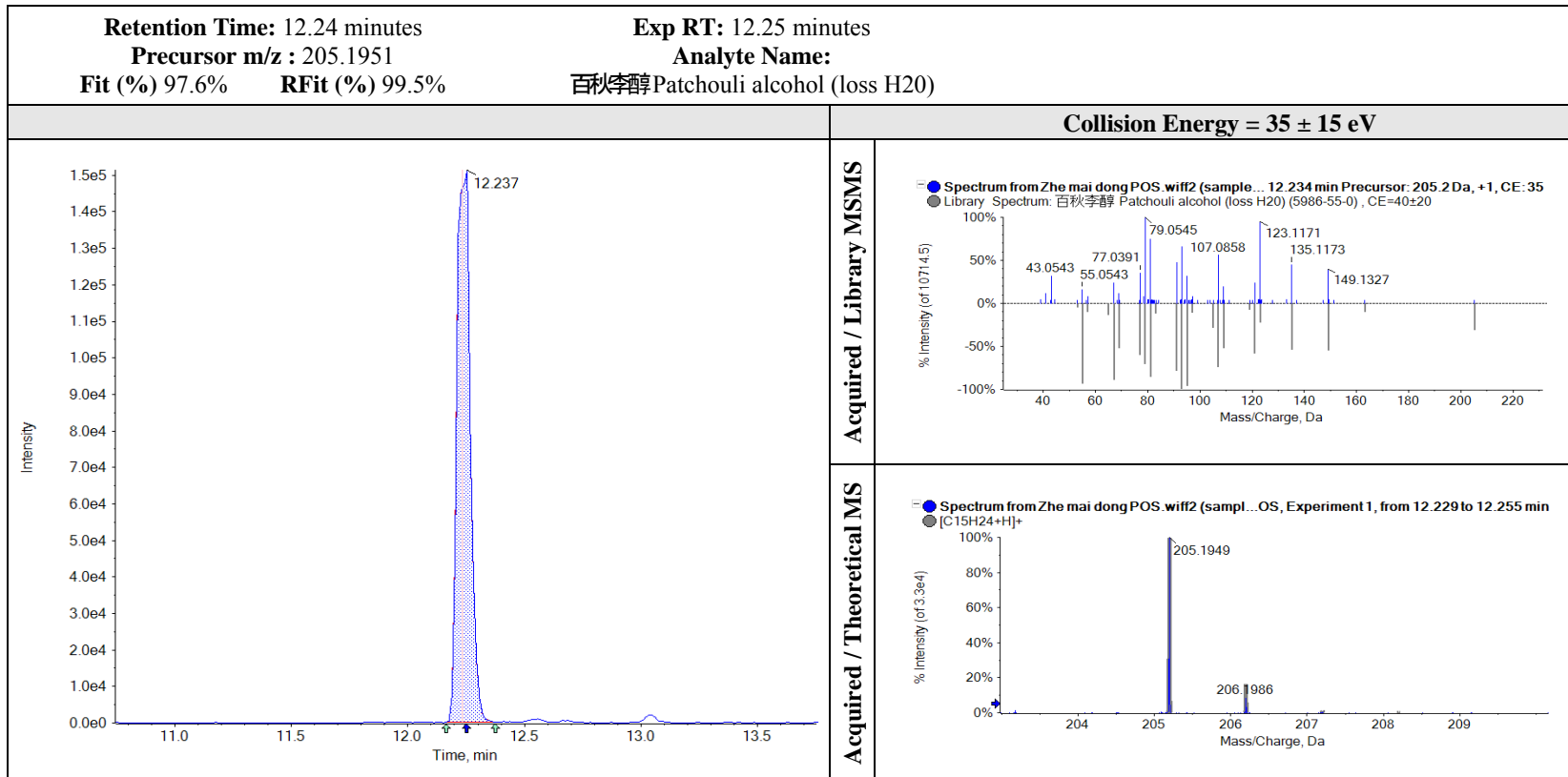
红车轴草素 7-O-D-葡萄糖苷 Pratensein-7-O-glucoside

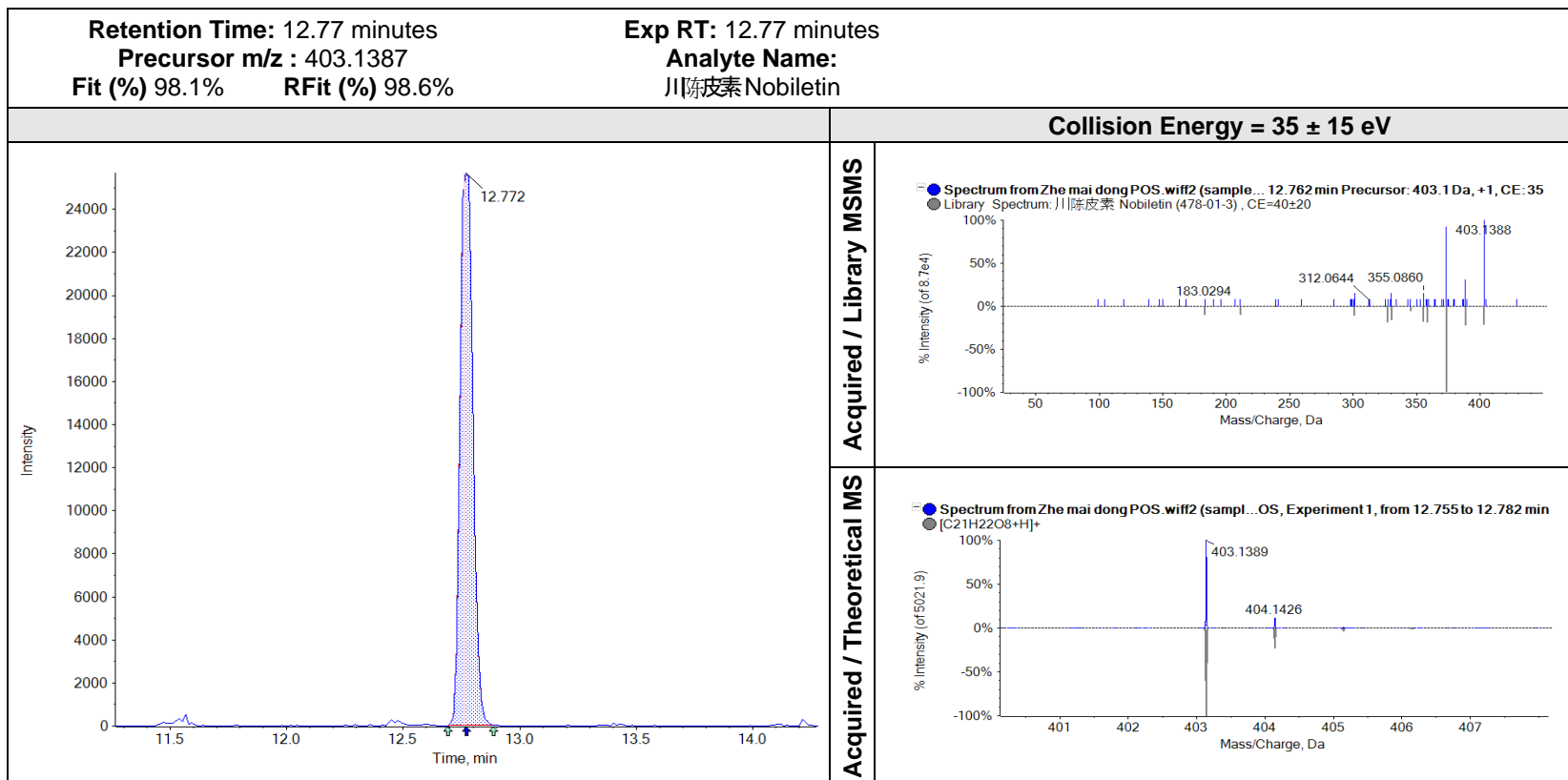


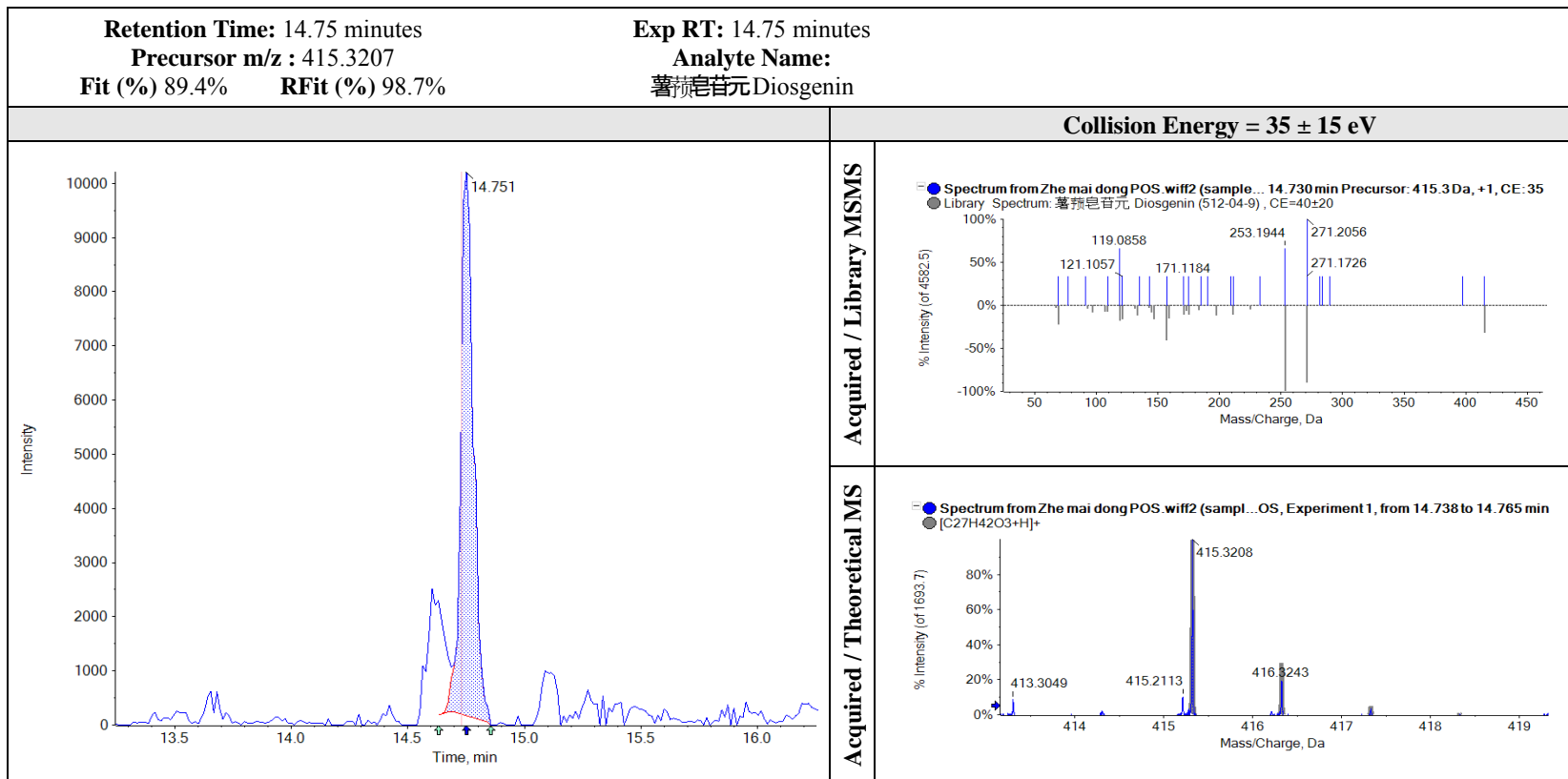
毛蕊异黄酮苷 Calycosin-7-O-glucoside



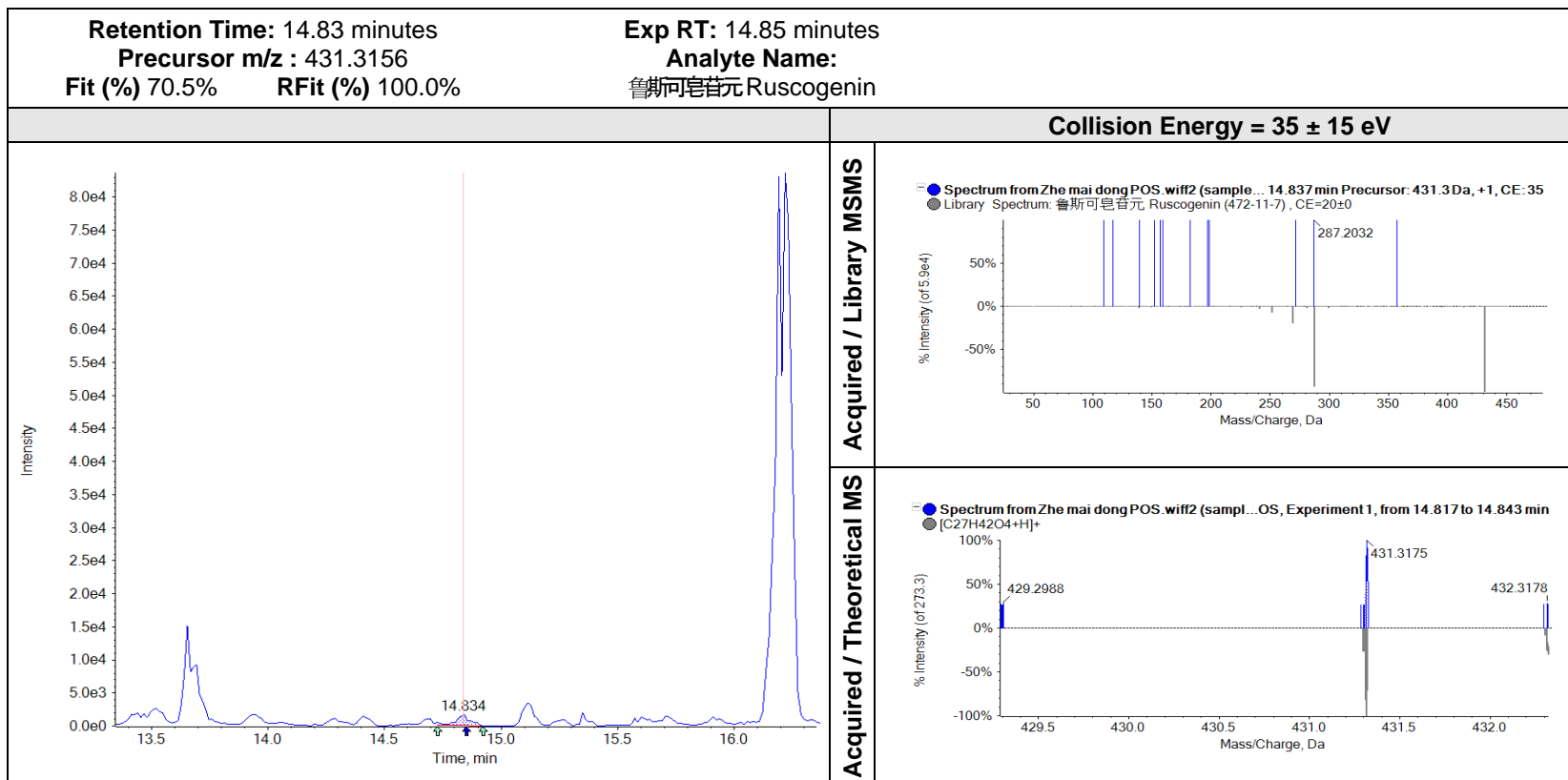


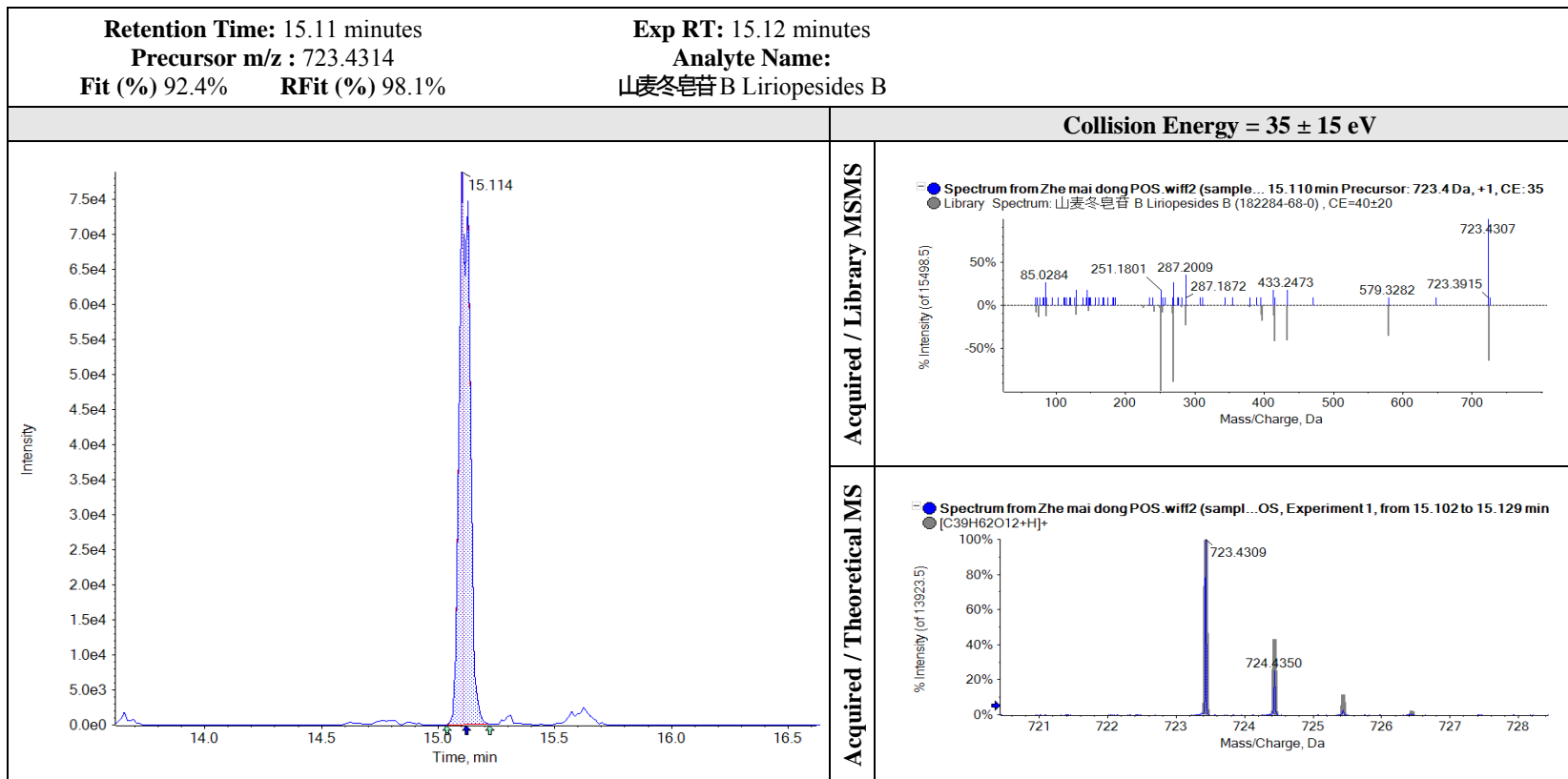






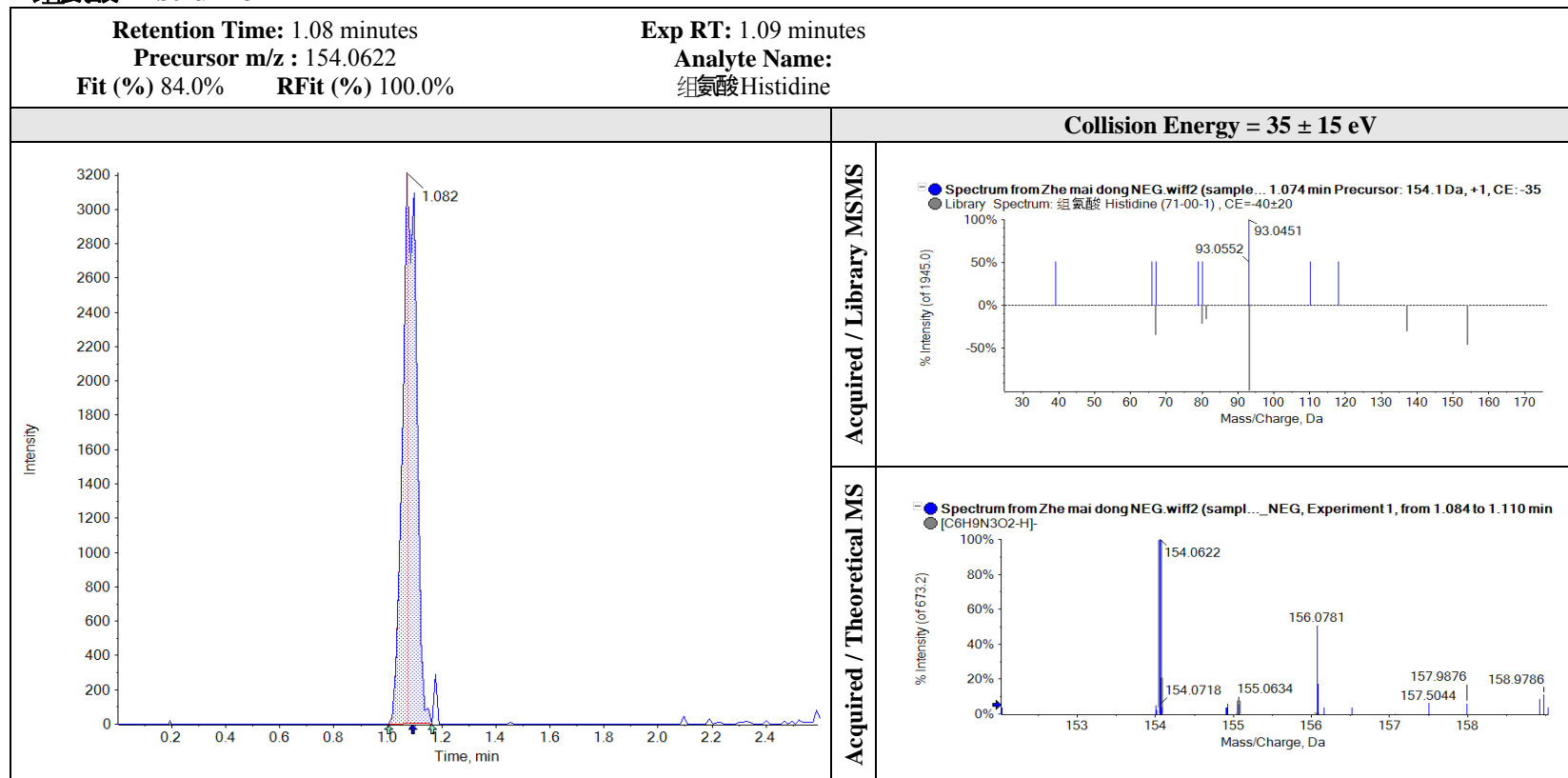
薯蓣皂苷元 Ruscogenin





MS fragmentation pathways for different chemical constituents of ZMD in negative ion mode

组氨酸 Histidine



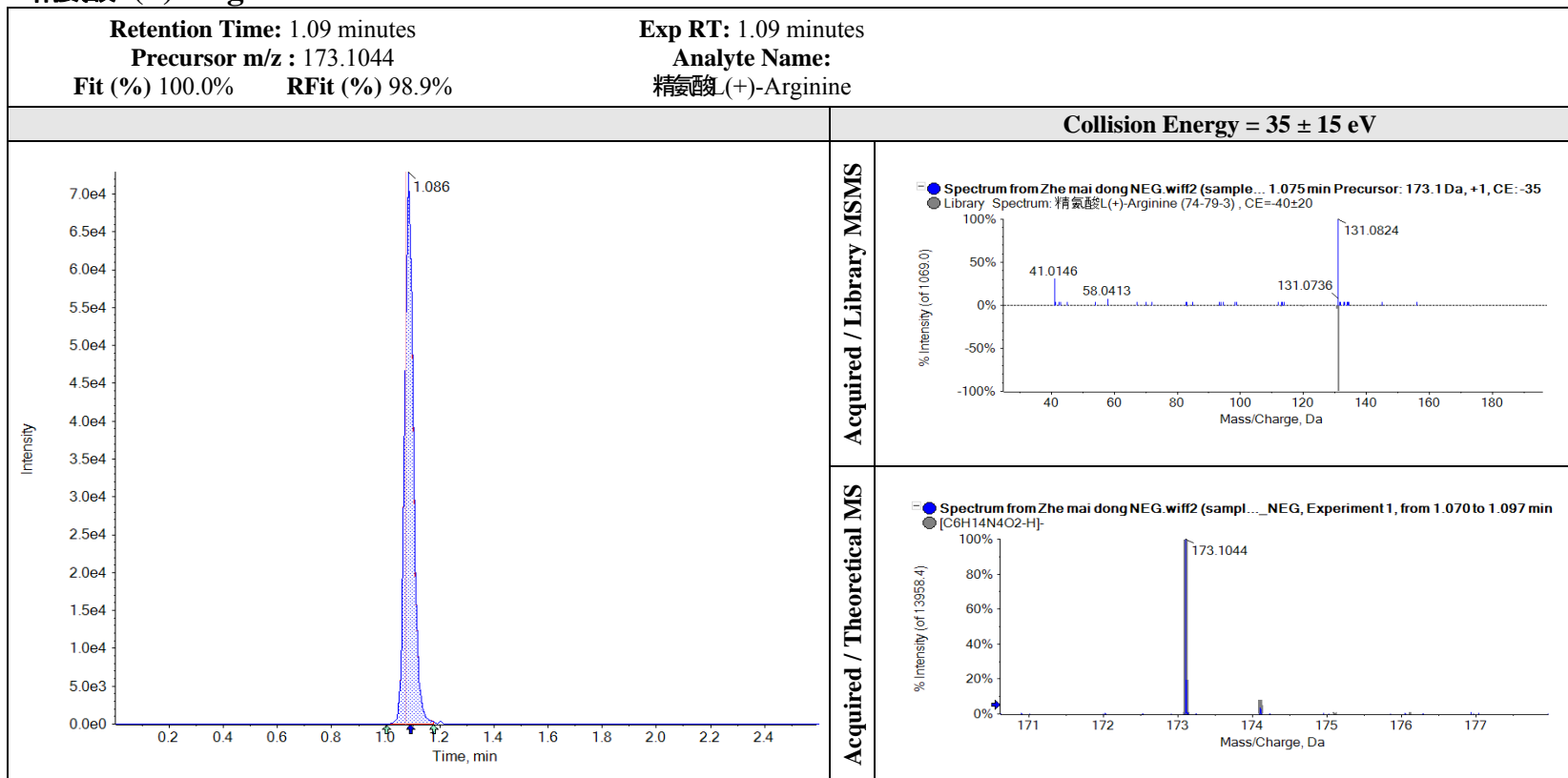


with SCIEX OS 1.3.1

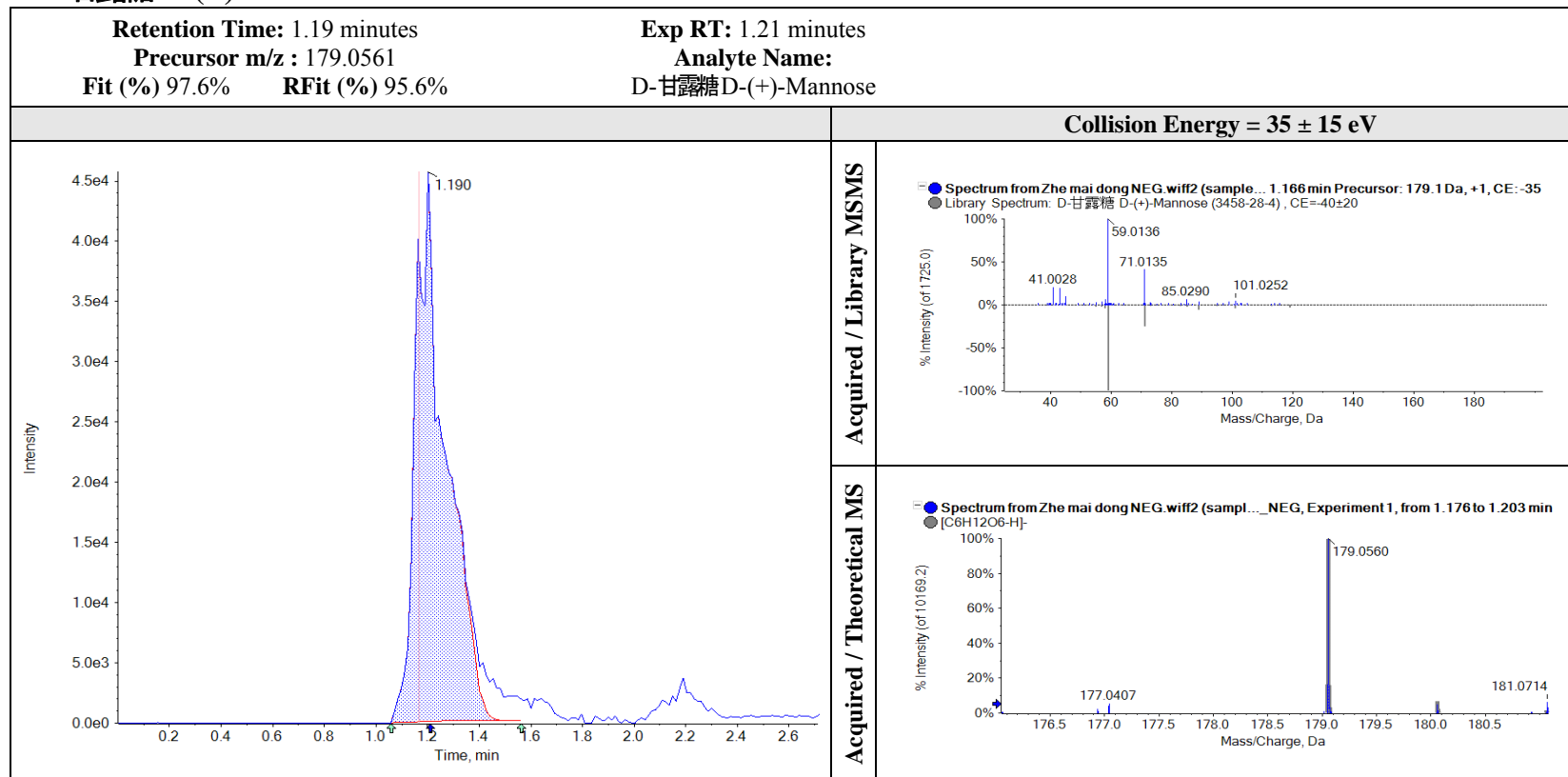
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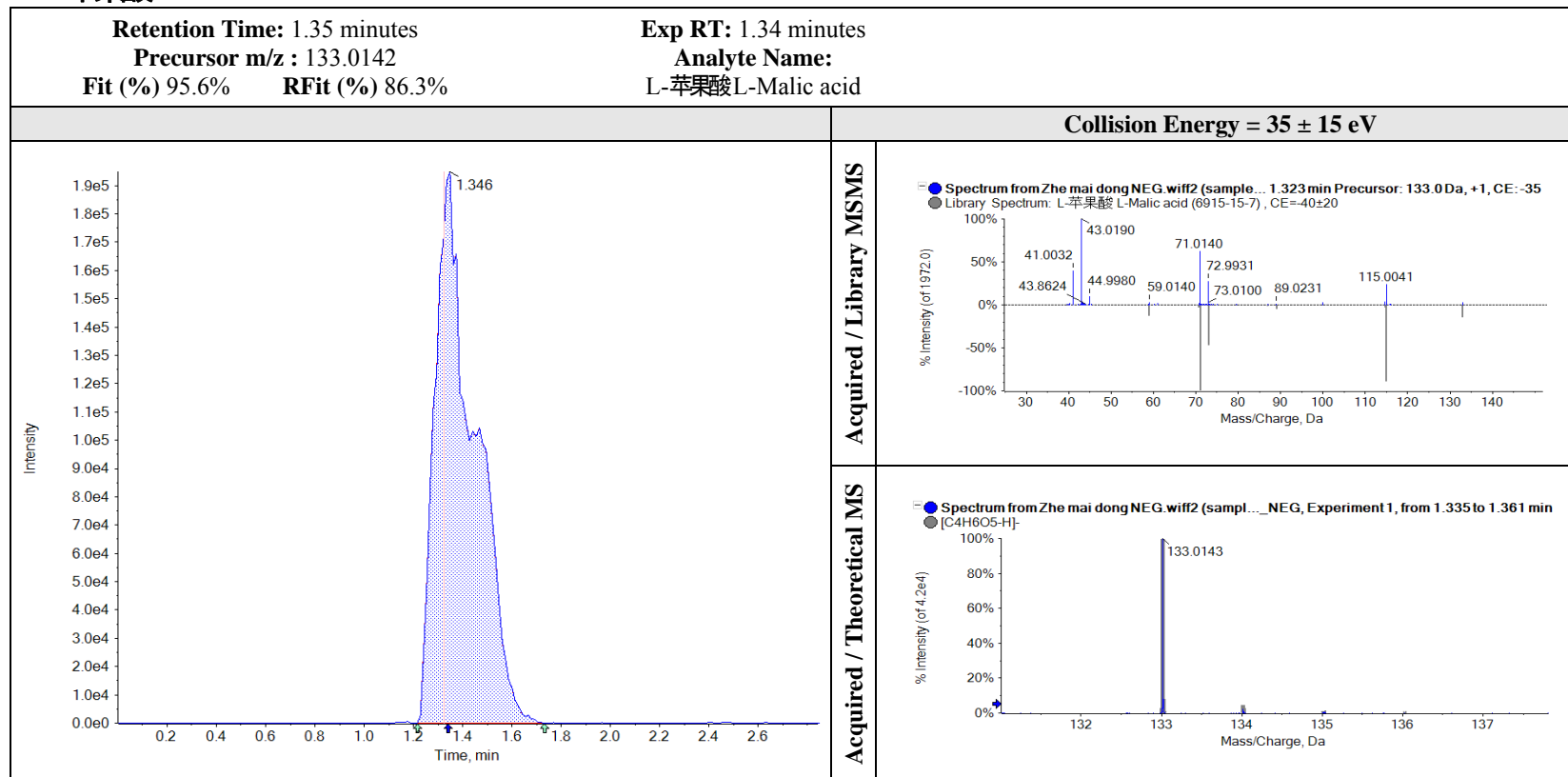
精氨酸L(+)-Arginine



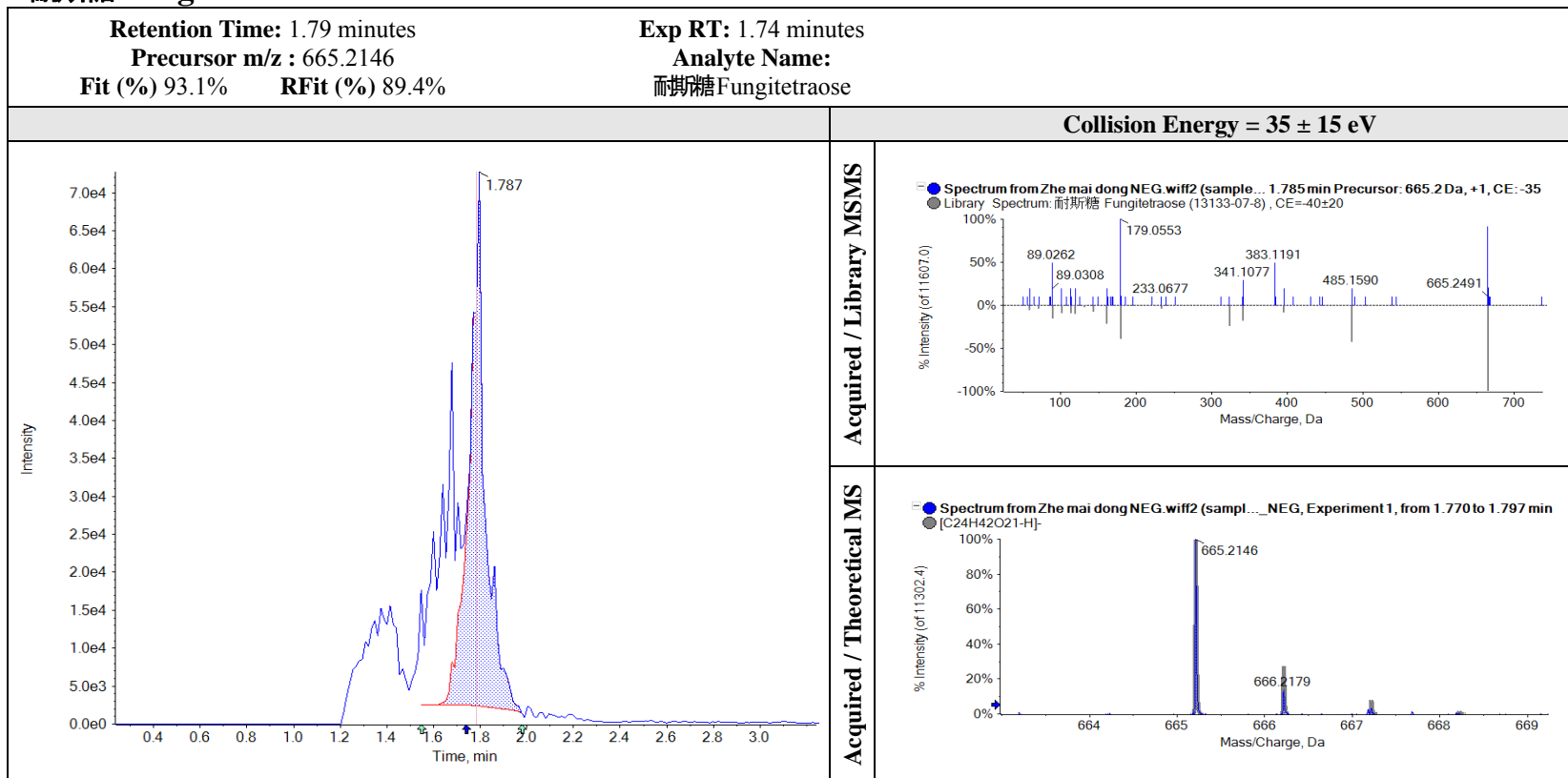
D-甘露糖D-(+)-Mannose



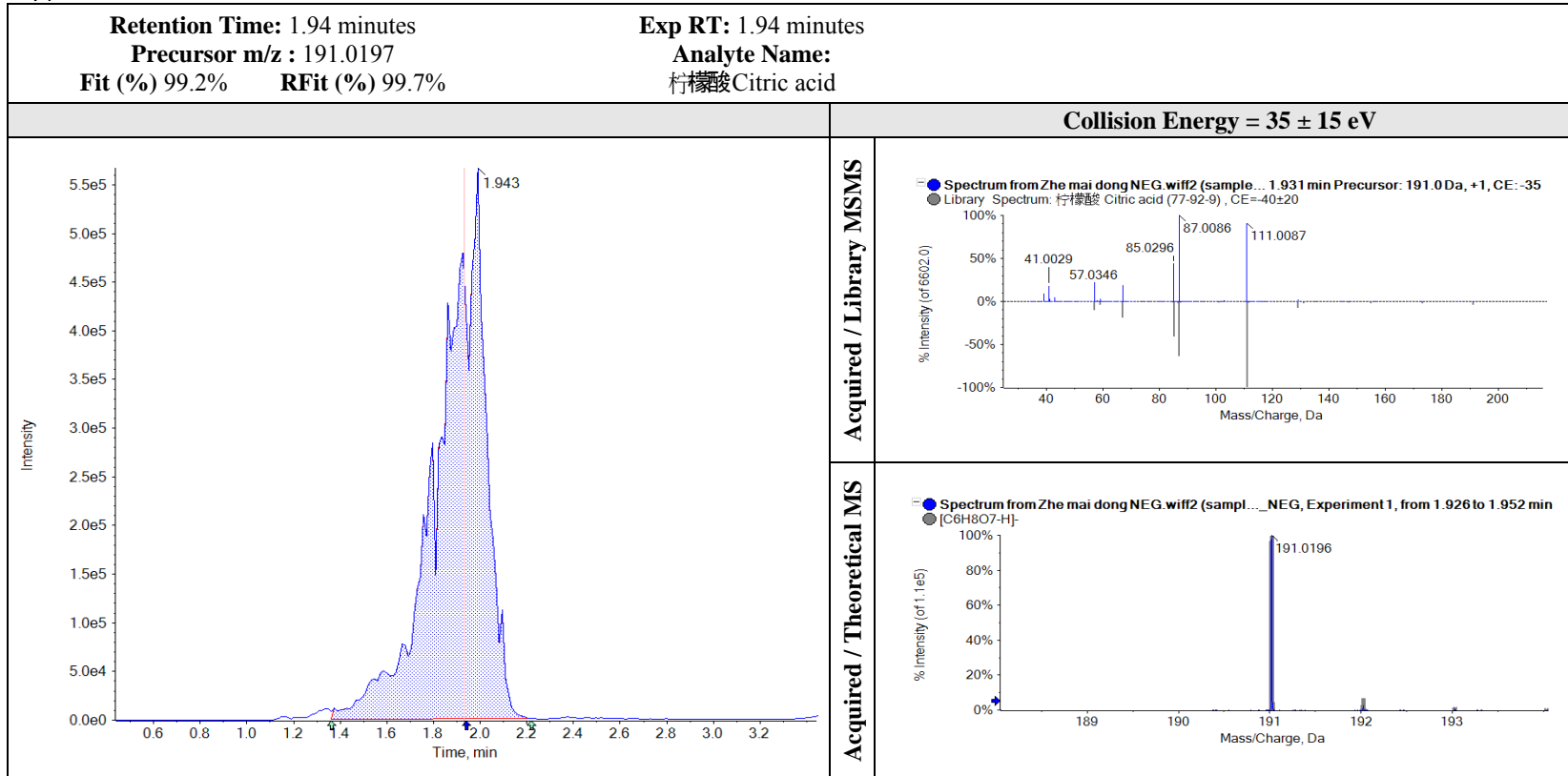
L-苹果酸 L-Malic acid



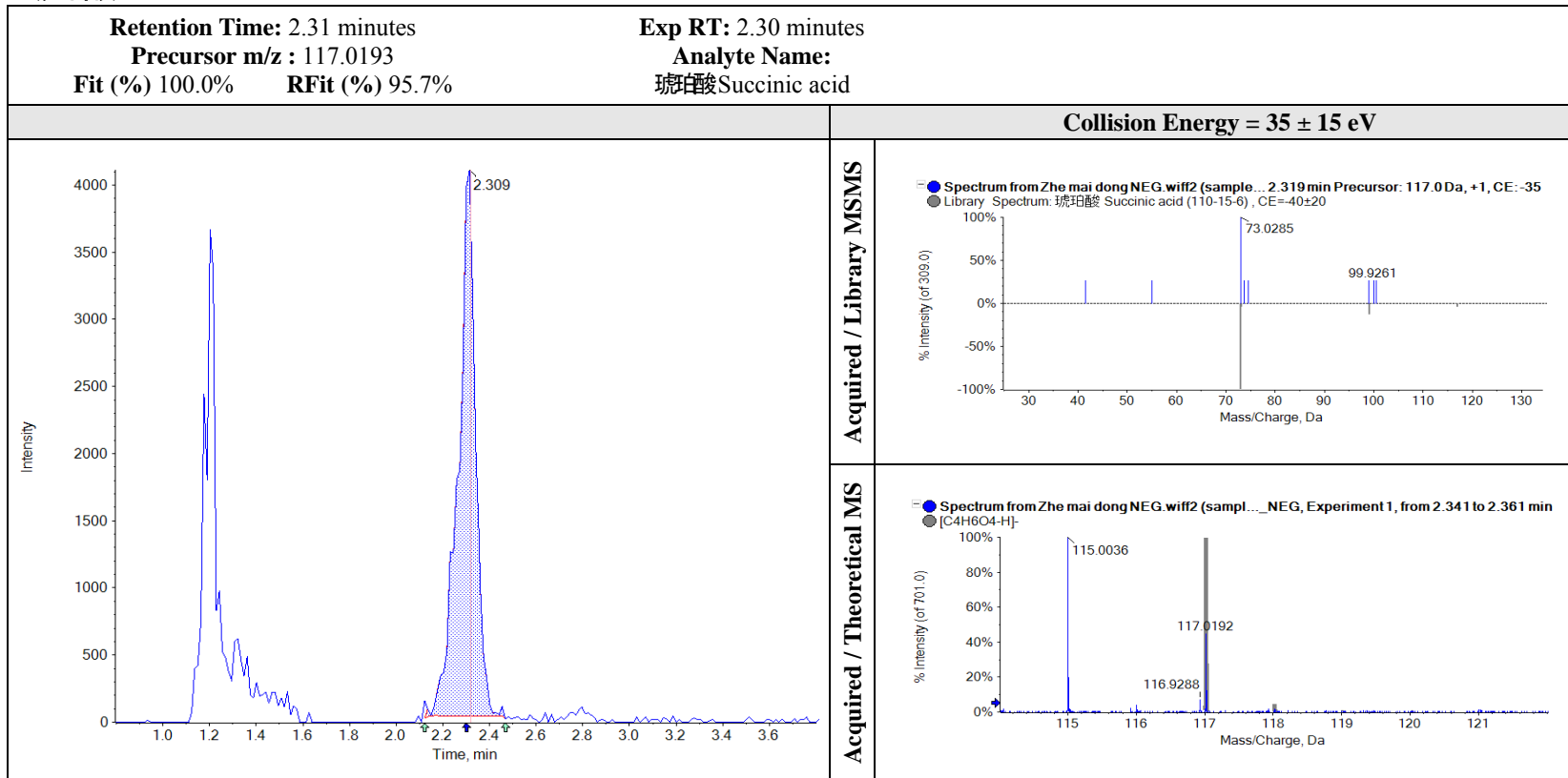
而琪糖 Fungitetraose



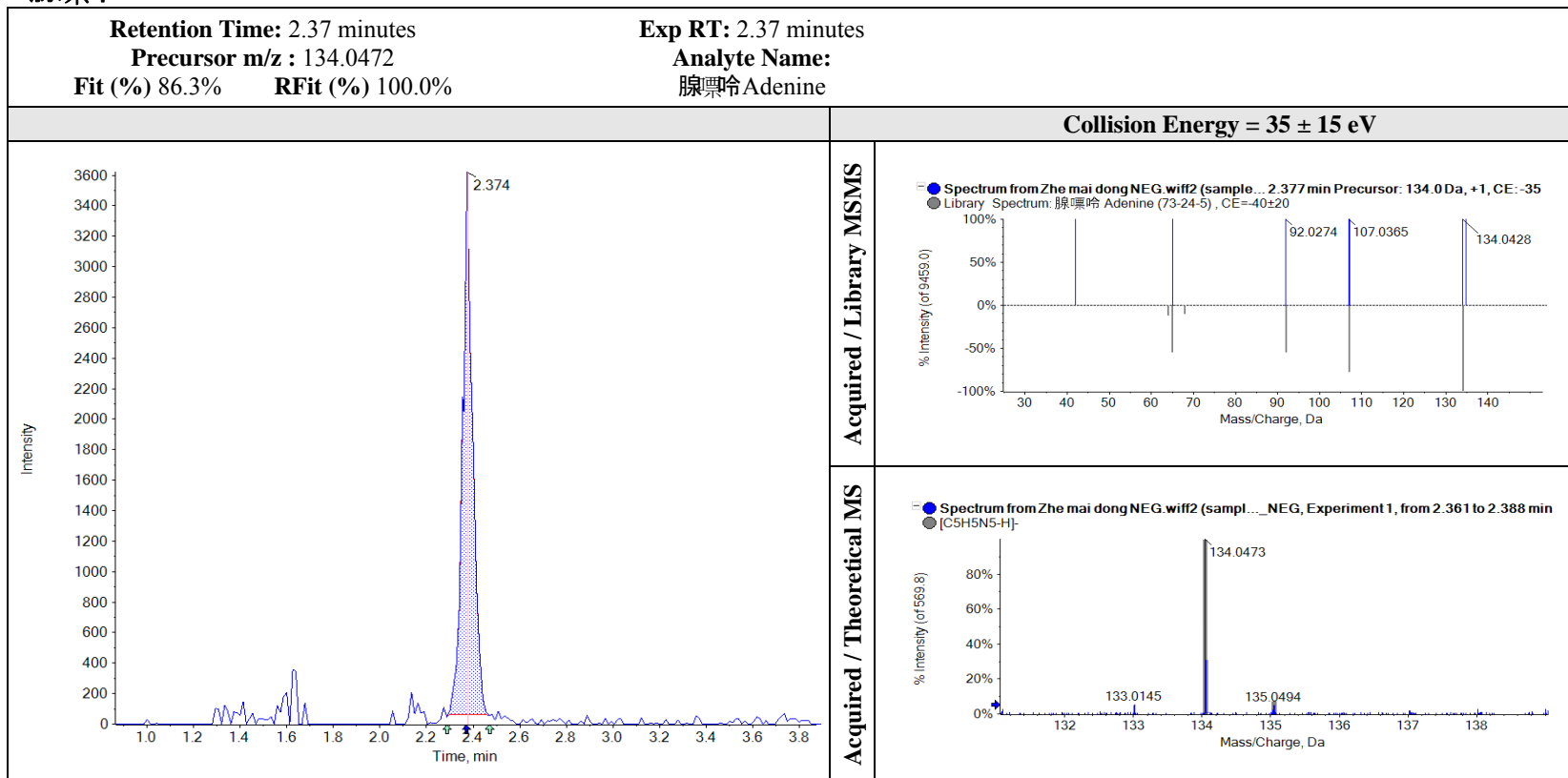
柠檬酸 Citric acid



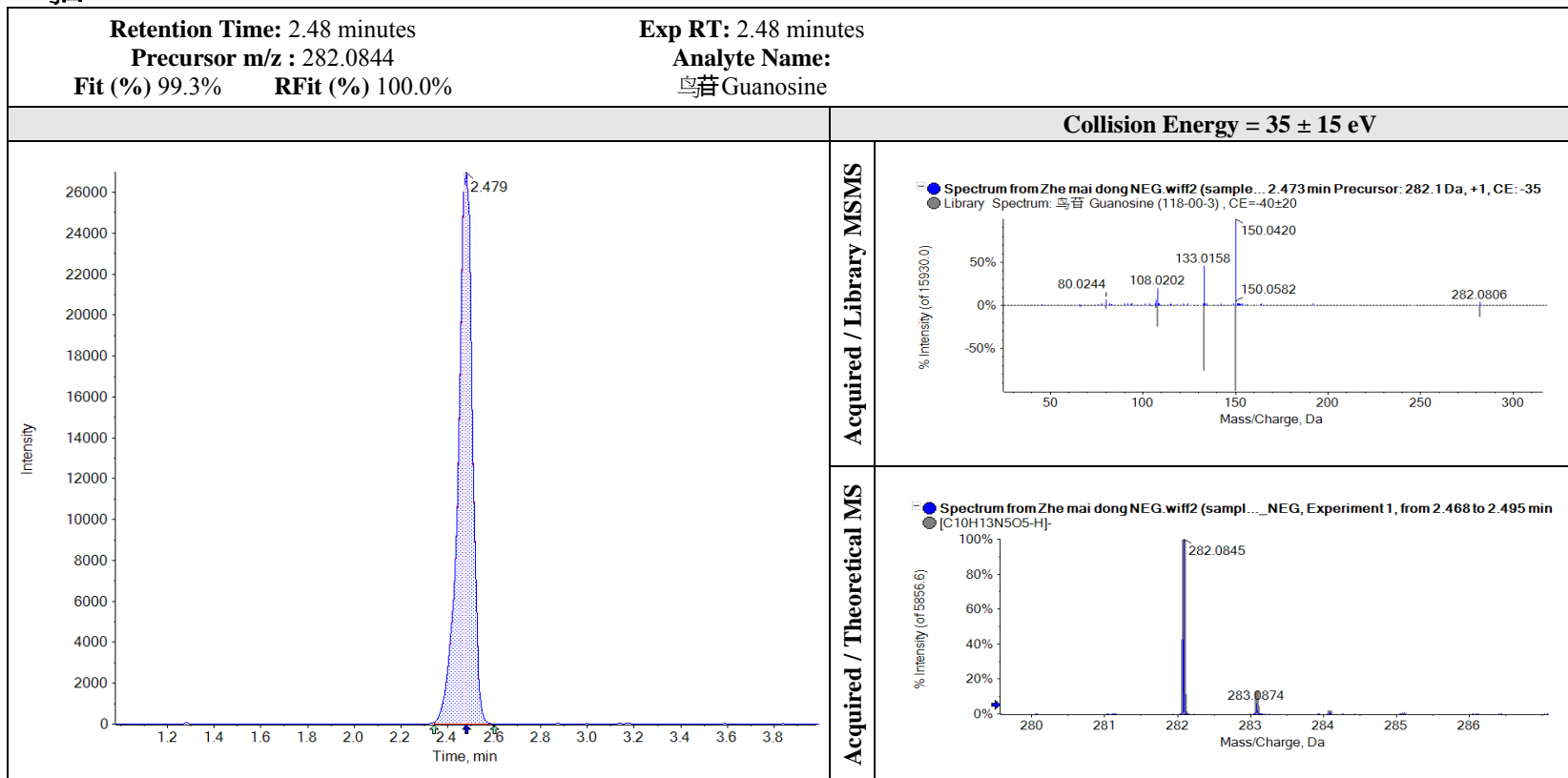
琥珀酸 Succinic acid



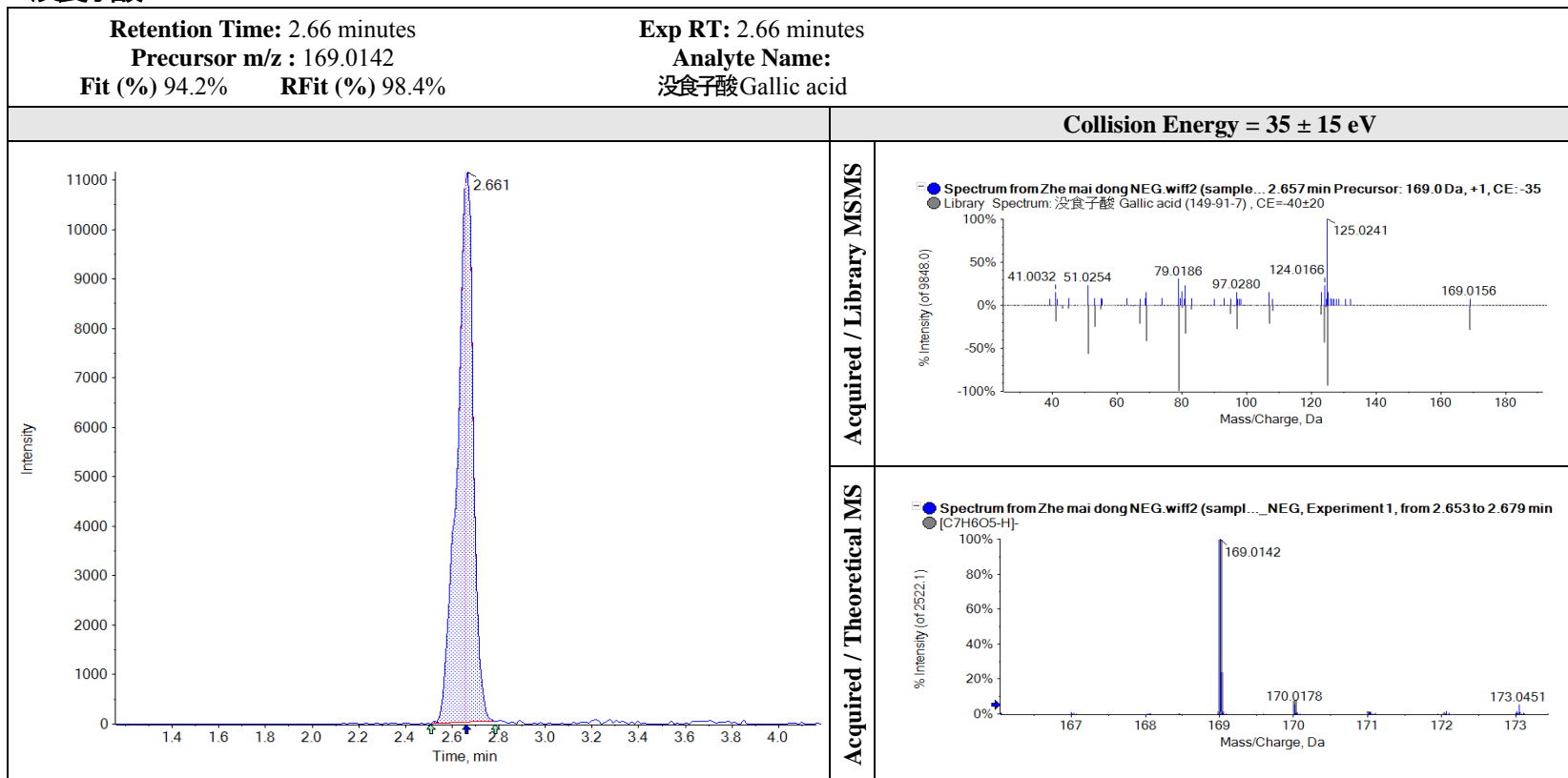
腺嘌呤 Adenine



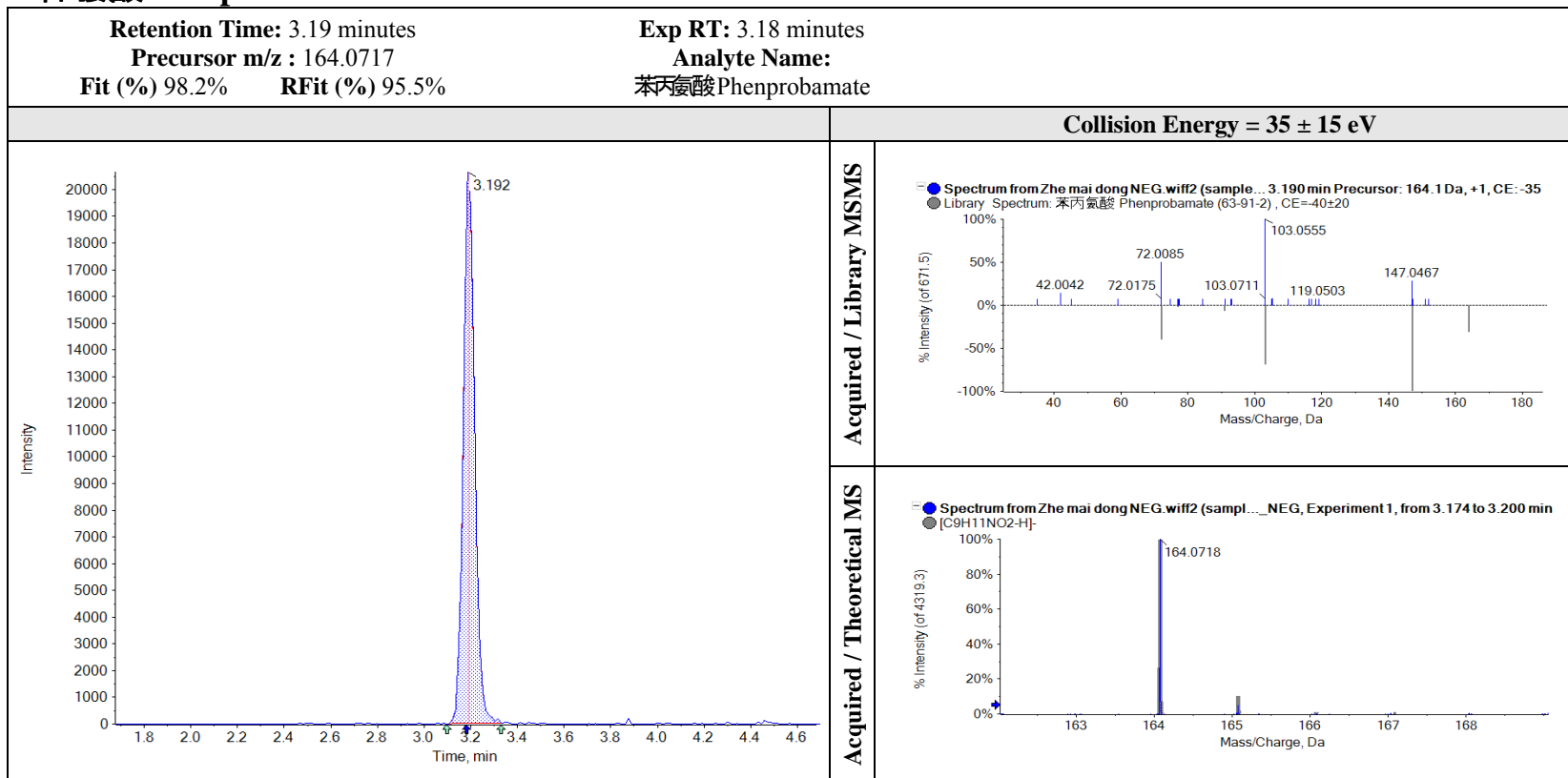
鸟苷 Guanosine



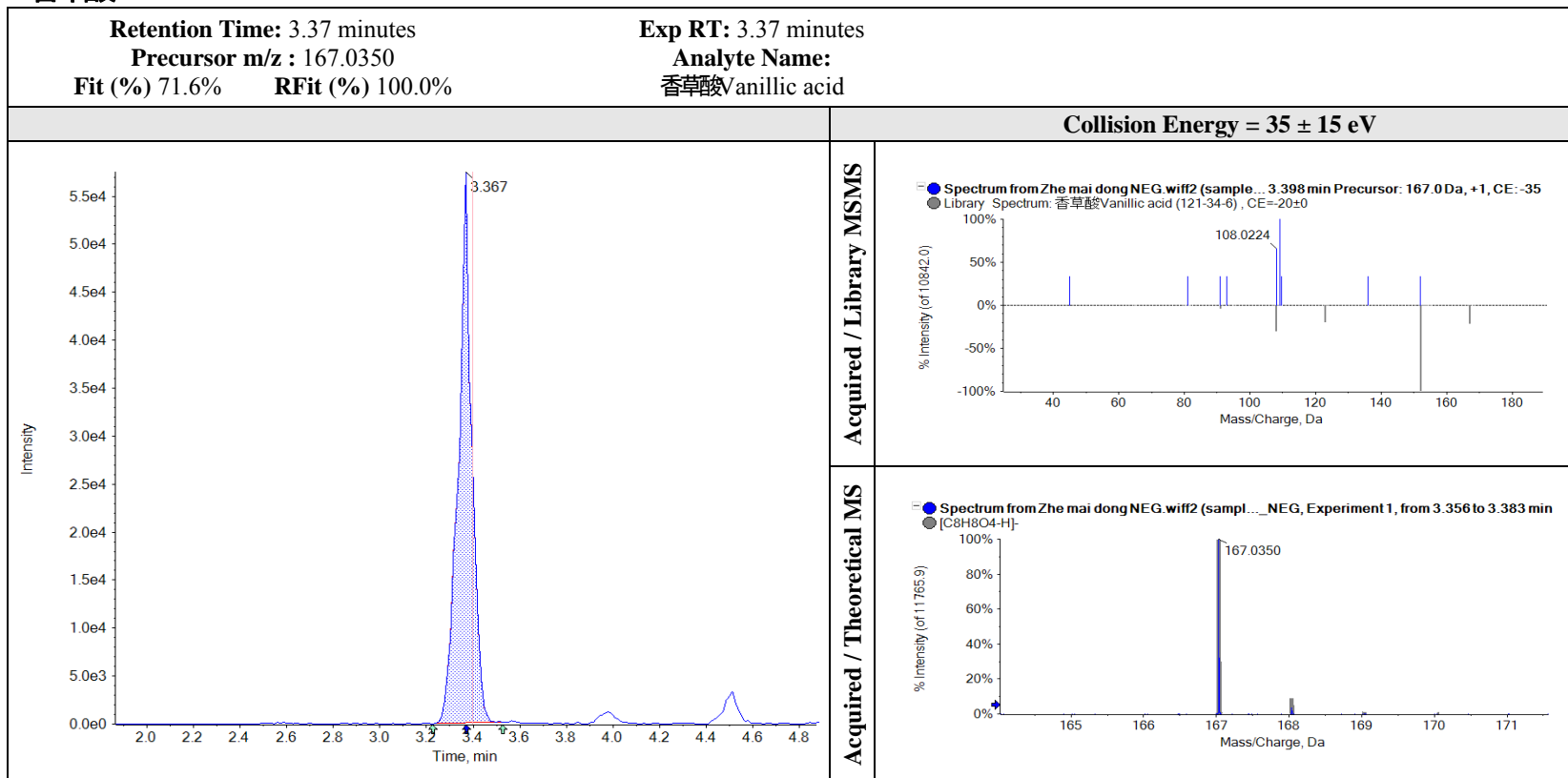
没食子酸 Gallic acid



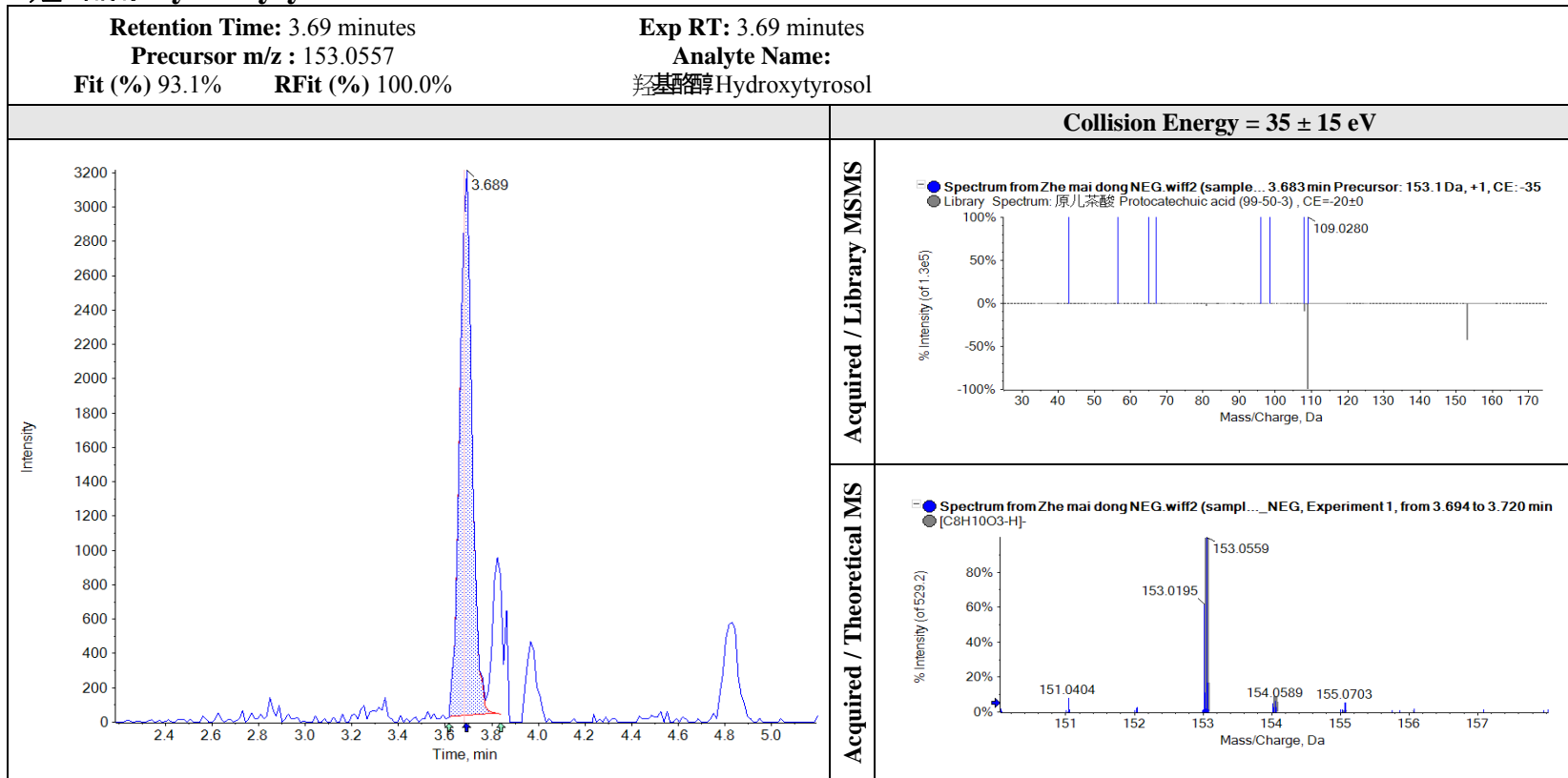
苯丙氨酸 Phenprobamate



香草酸 Vanillic acid



羟基酪醇 Hydroxytyrosol



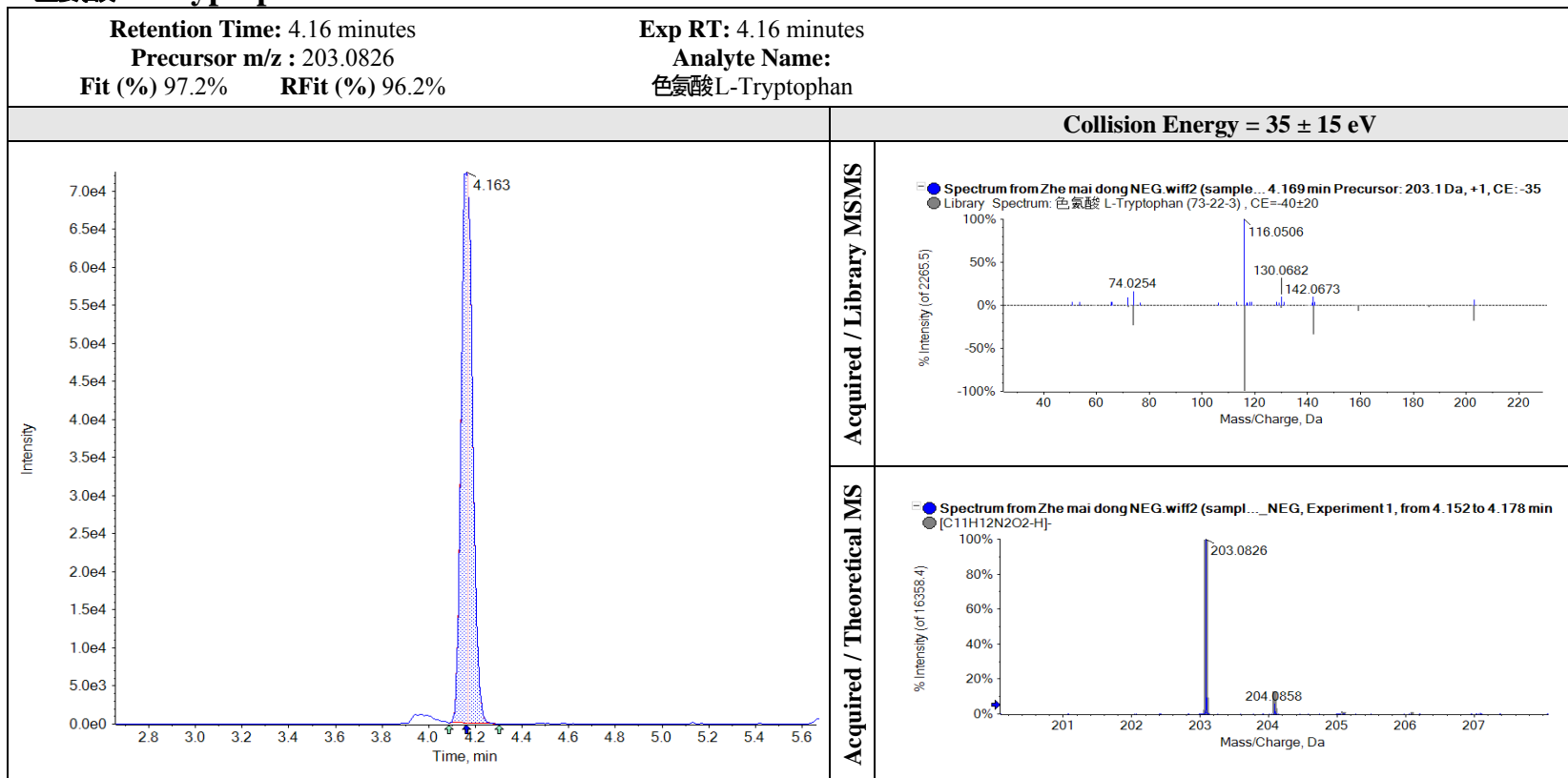


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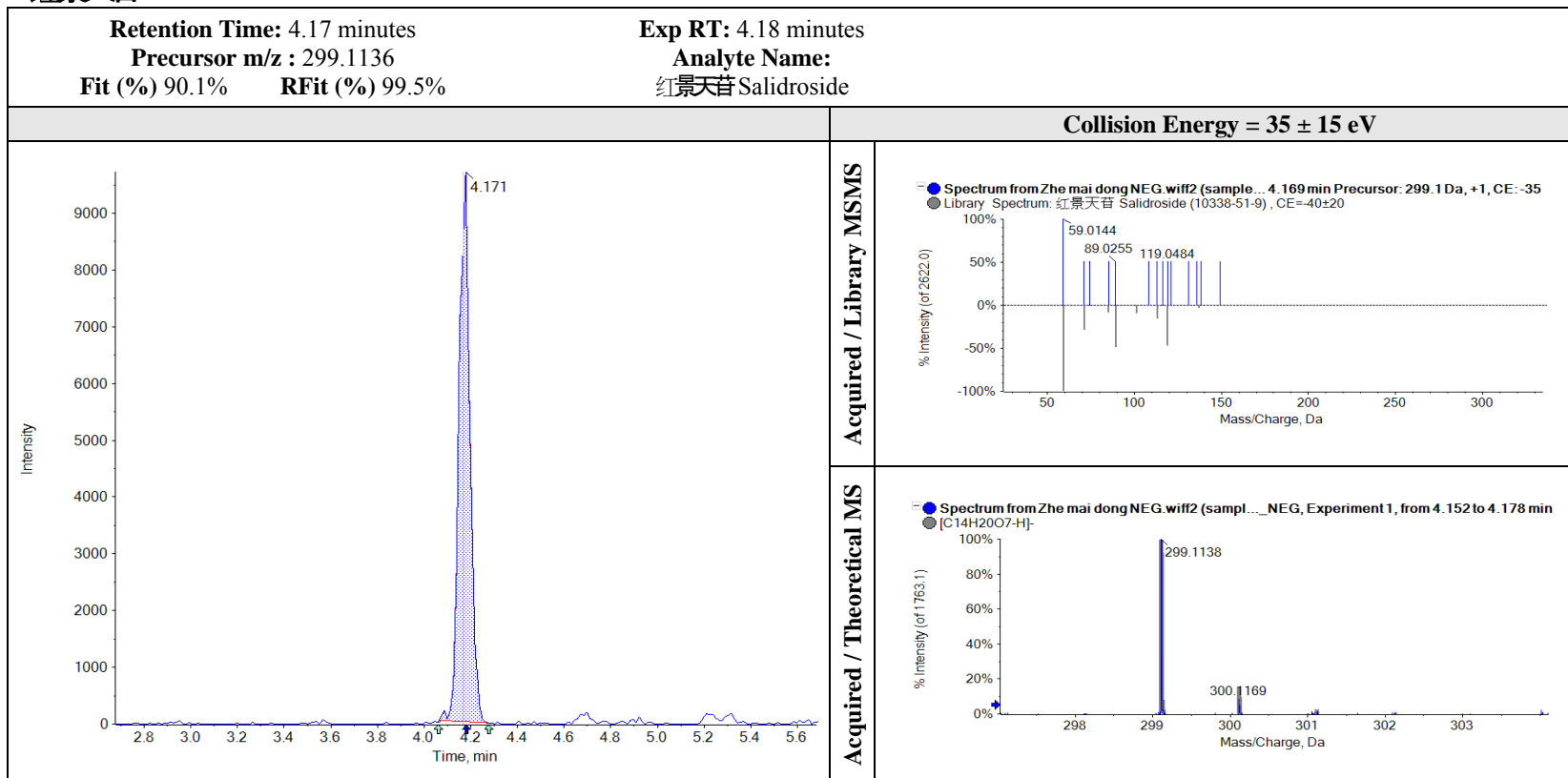
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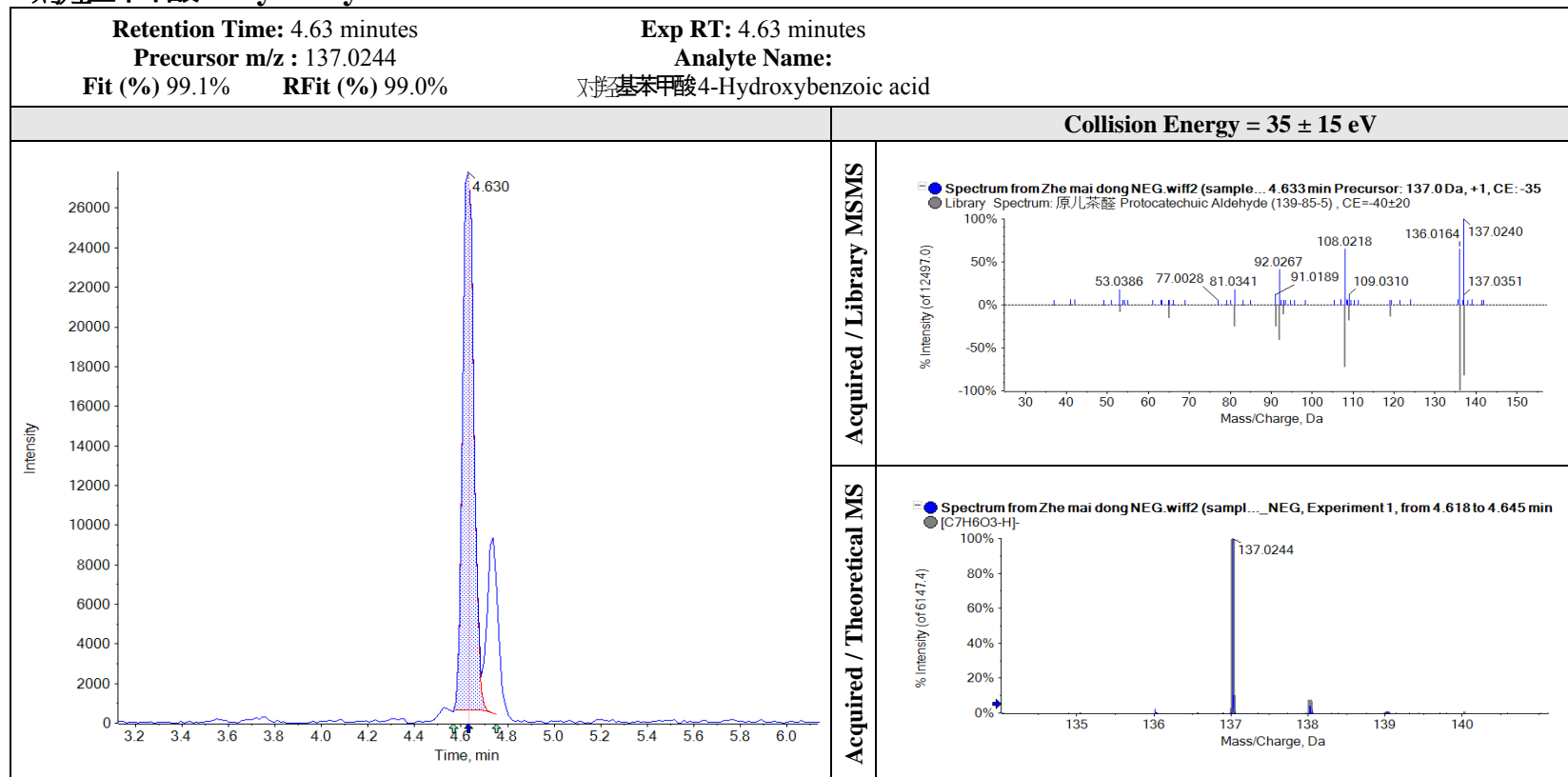
色氨酸 L-Tryptophan



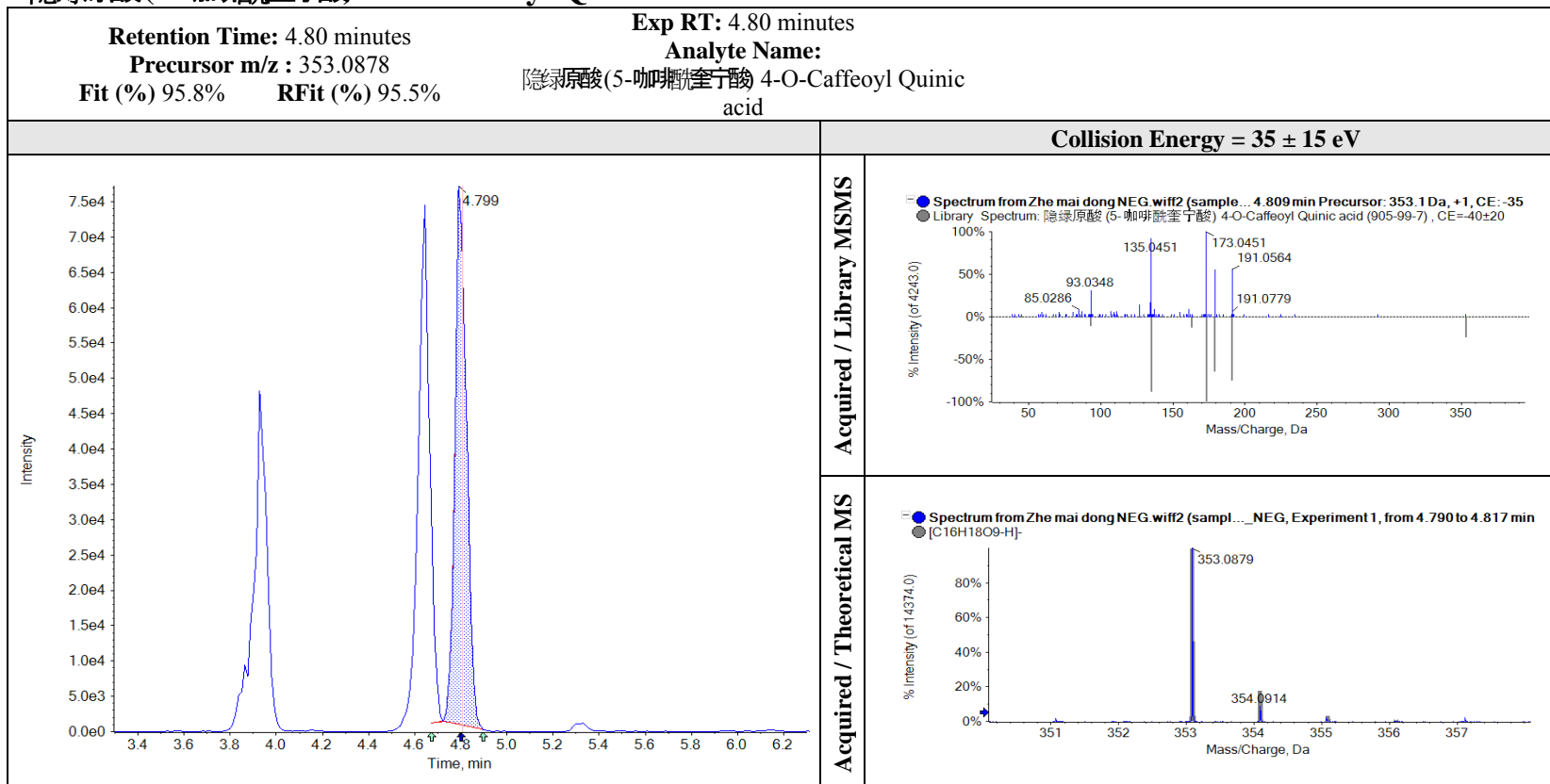
红景天苷 Salidroside



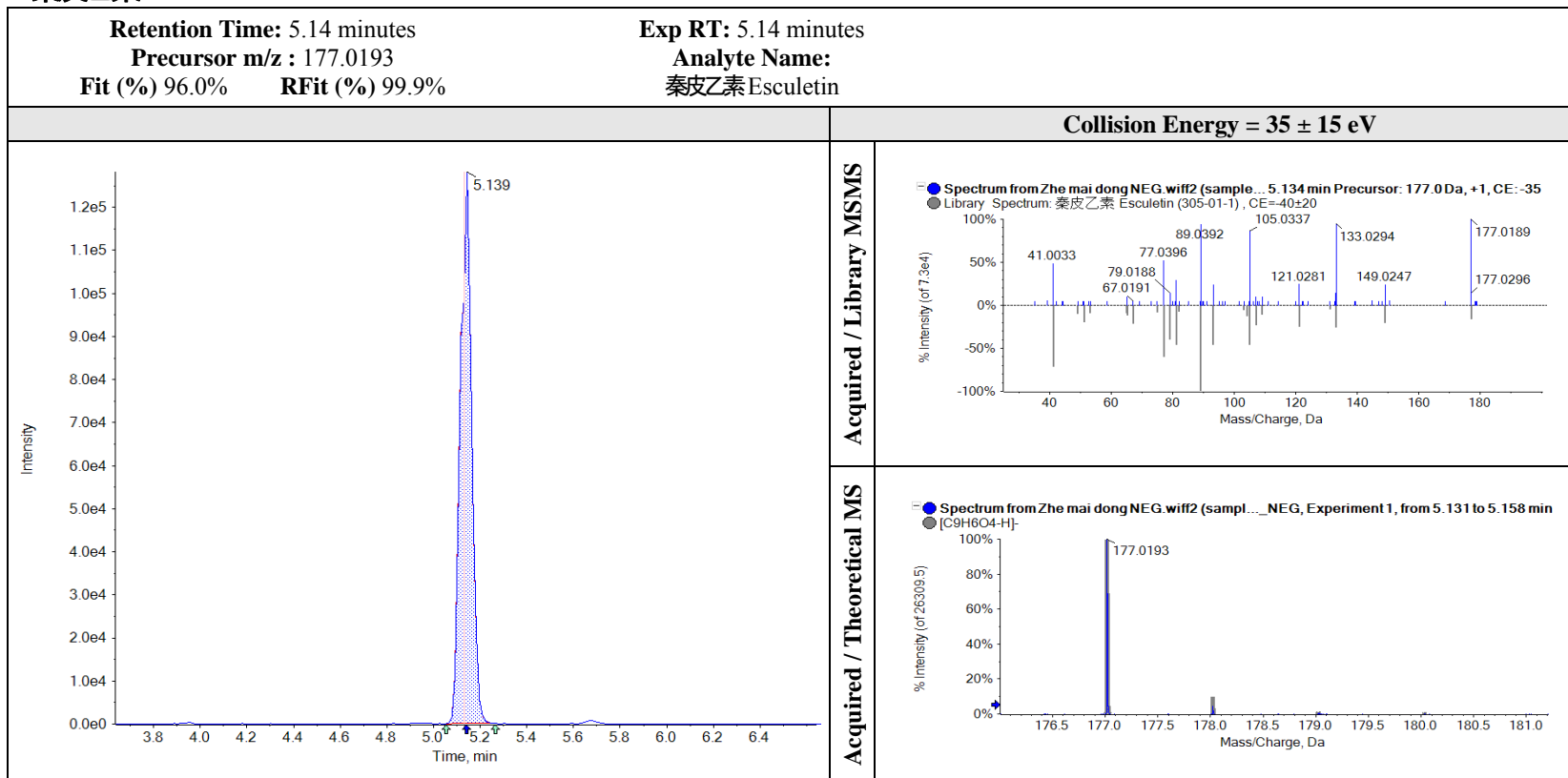
对羟基苯甲酸 4-Hydroxybenzoic acid



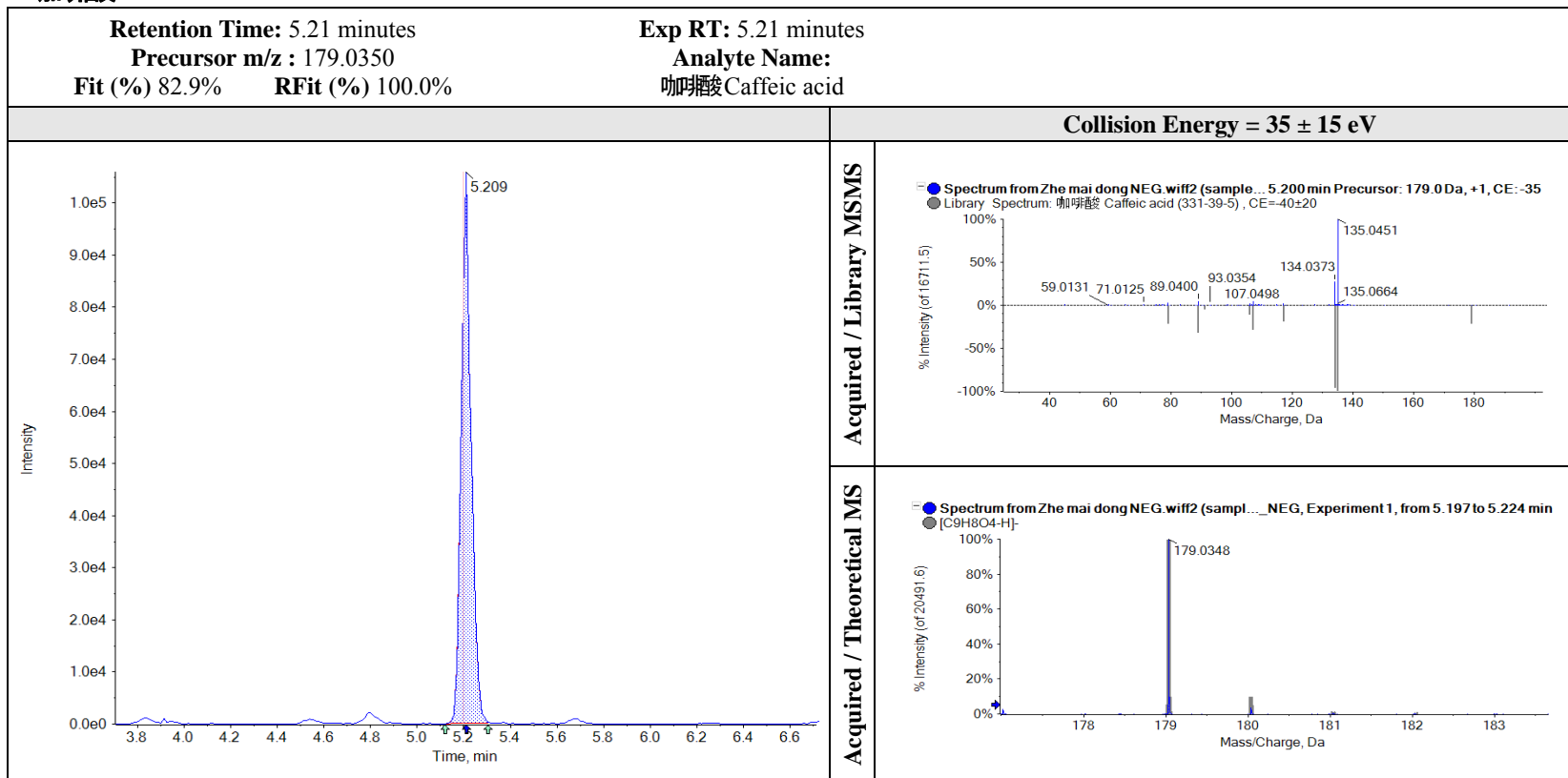
隐绿原酸(5-咖啡酰奎宁酸) 4-O-Caffeoyl Quinic acid



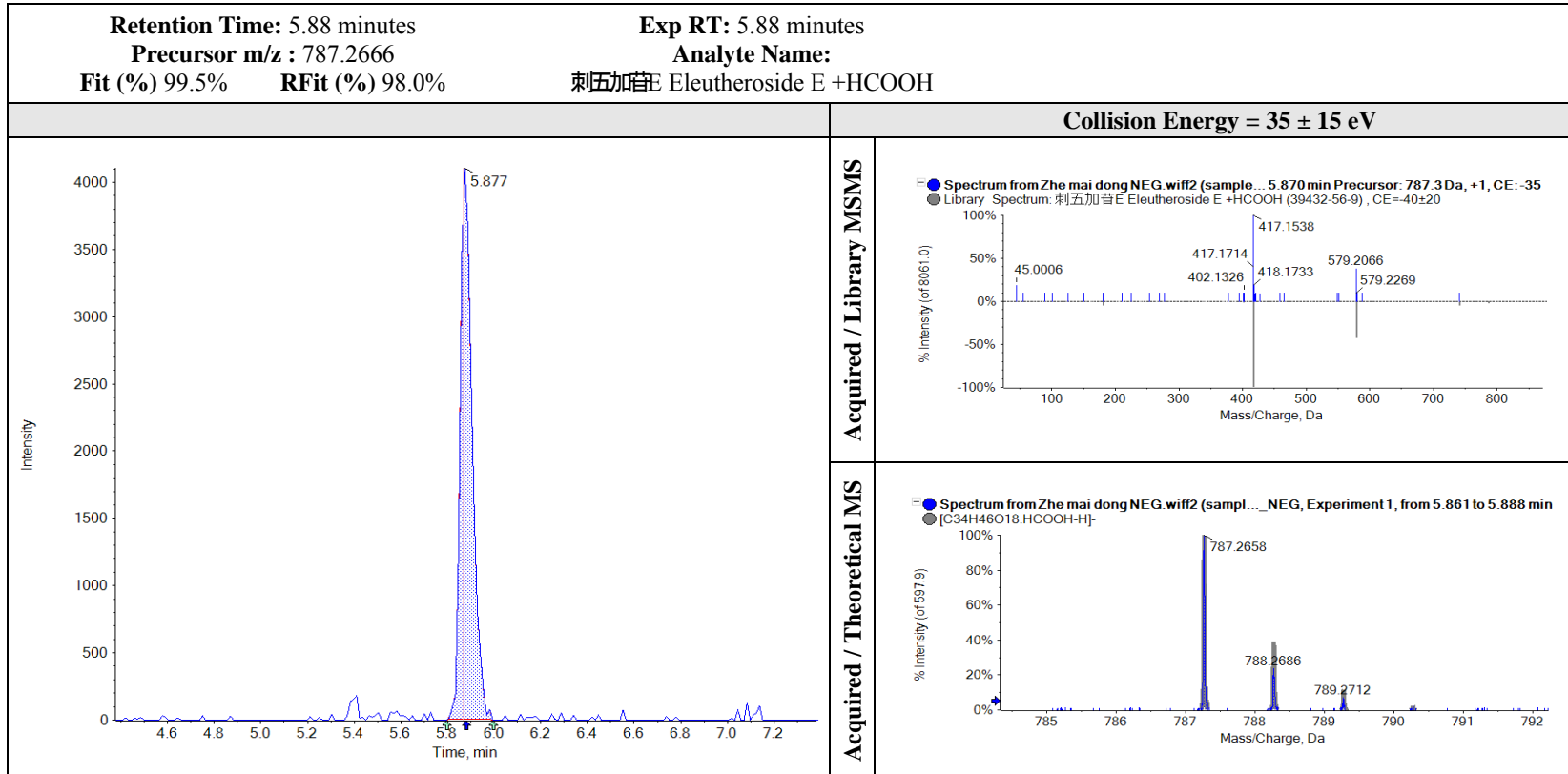
秦皮乙素 Esculetin



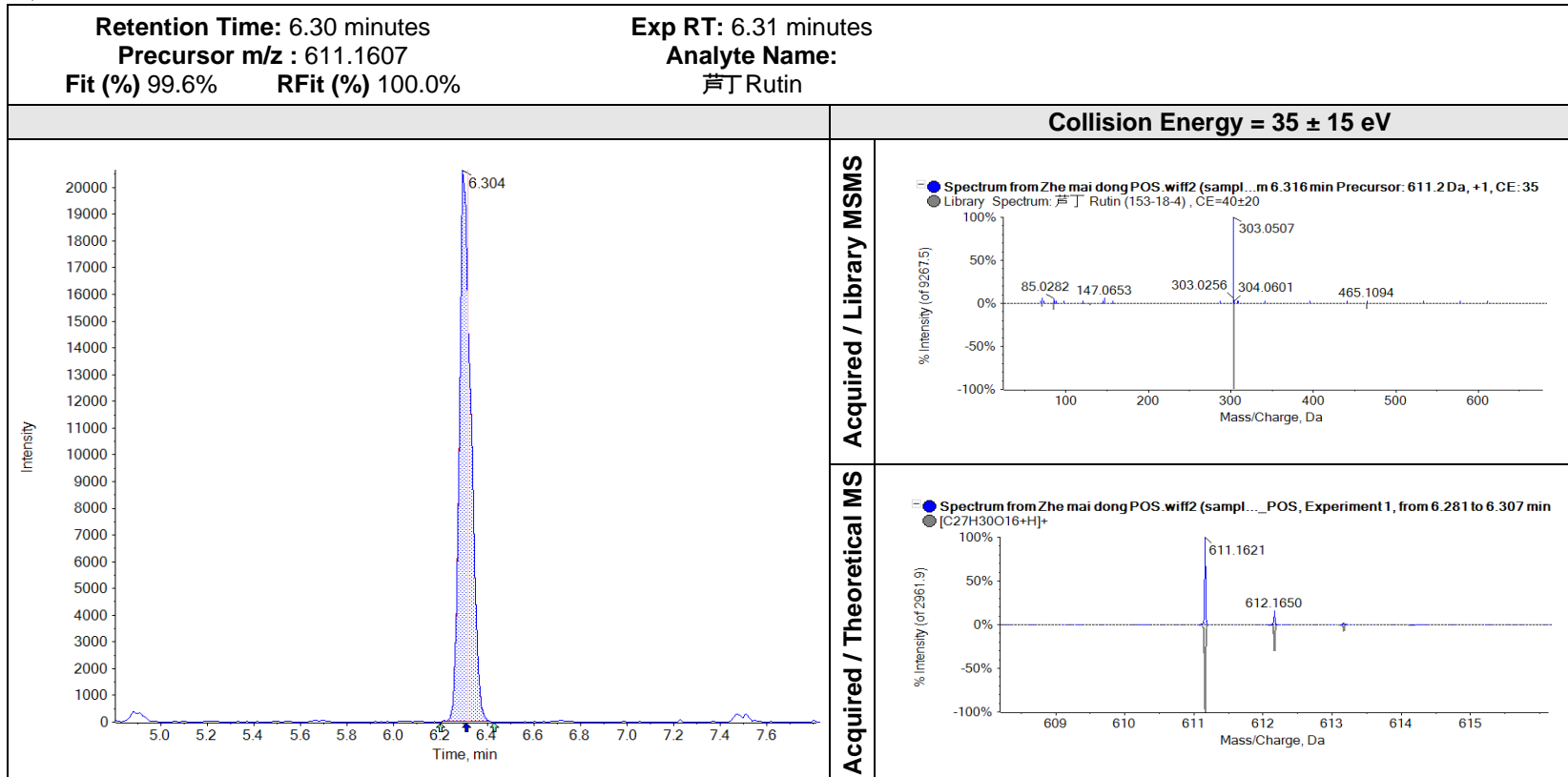
咖啡酸 Caffeic acid



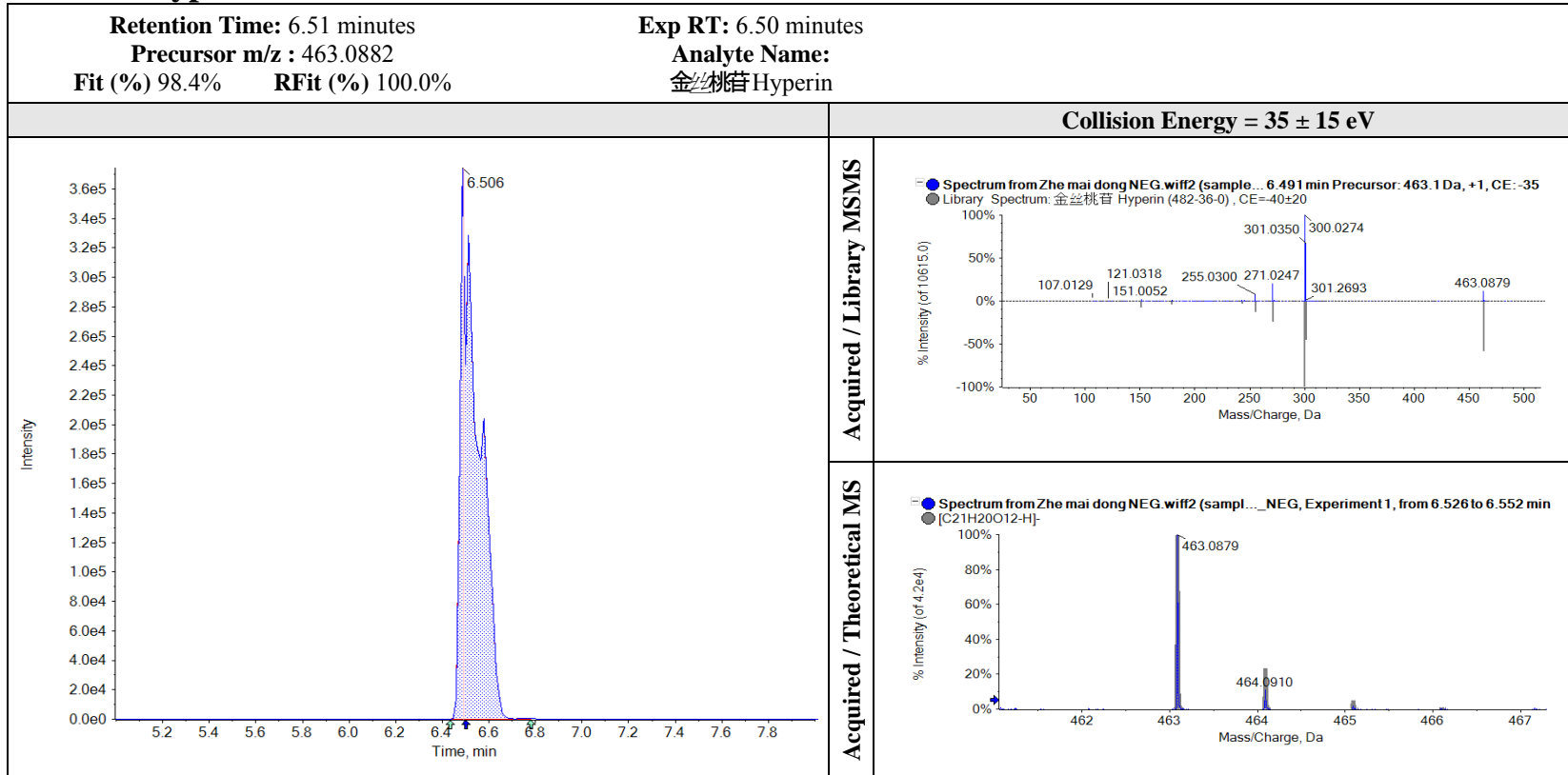
刺五加苷E Eleutheroside E



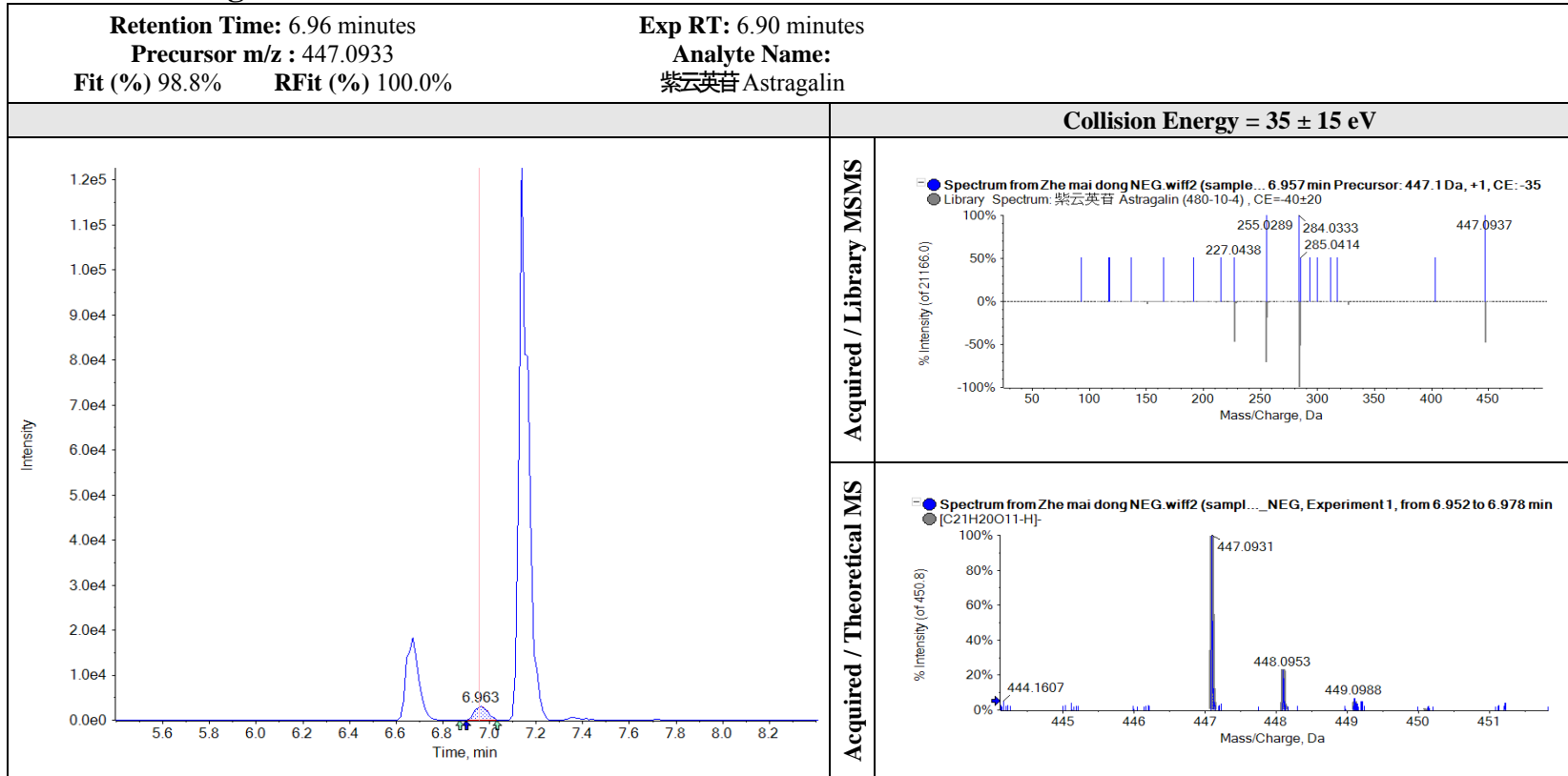
芦丁Rutin



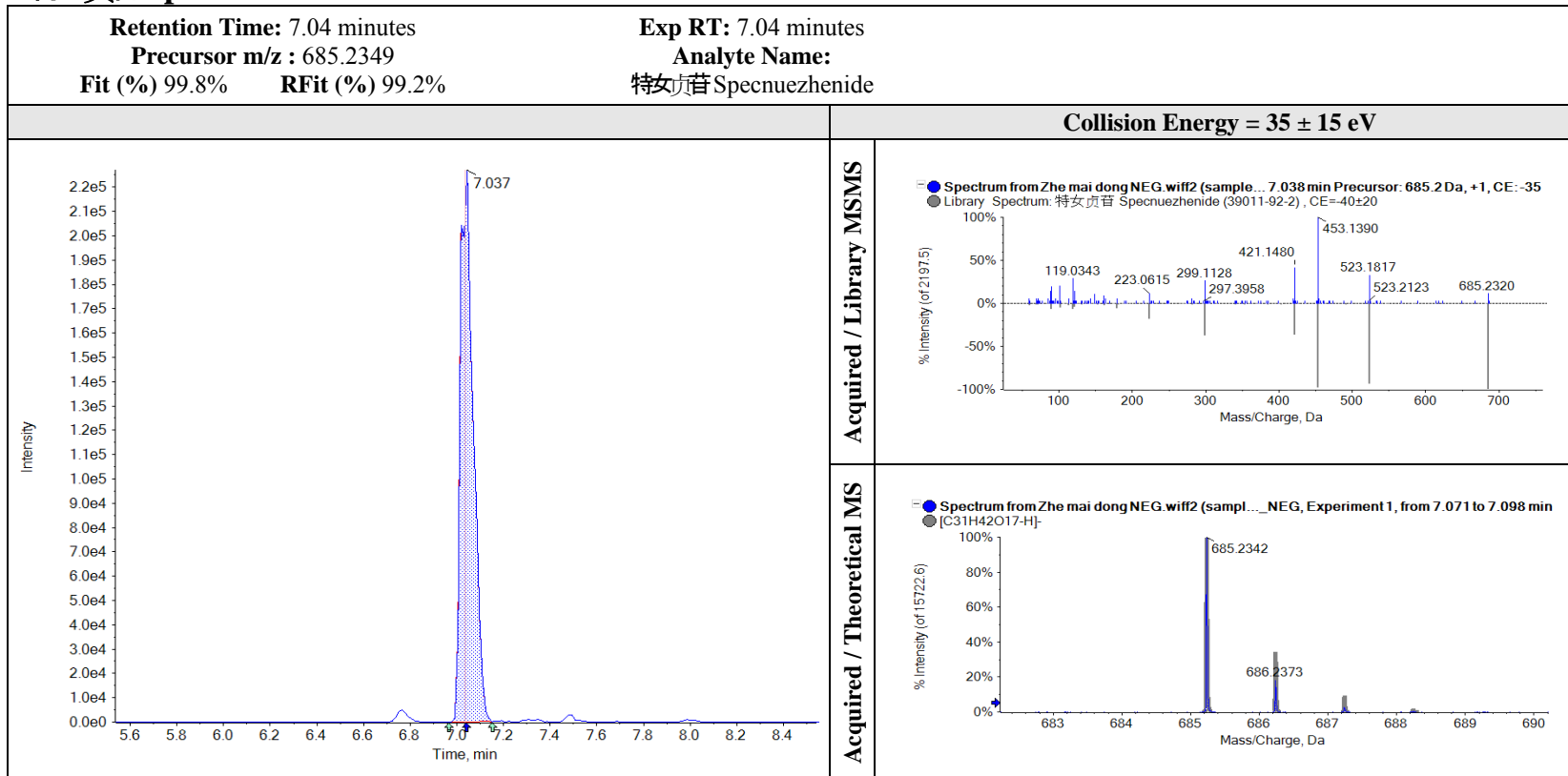
金丝桃苷 Hyperin



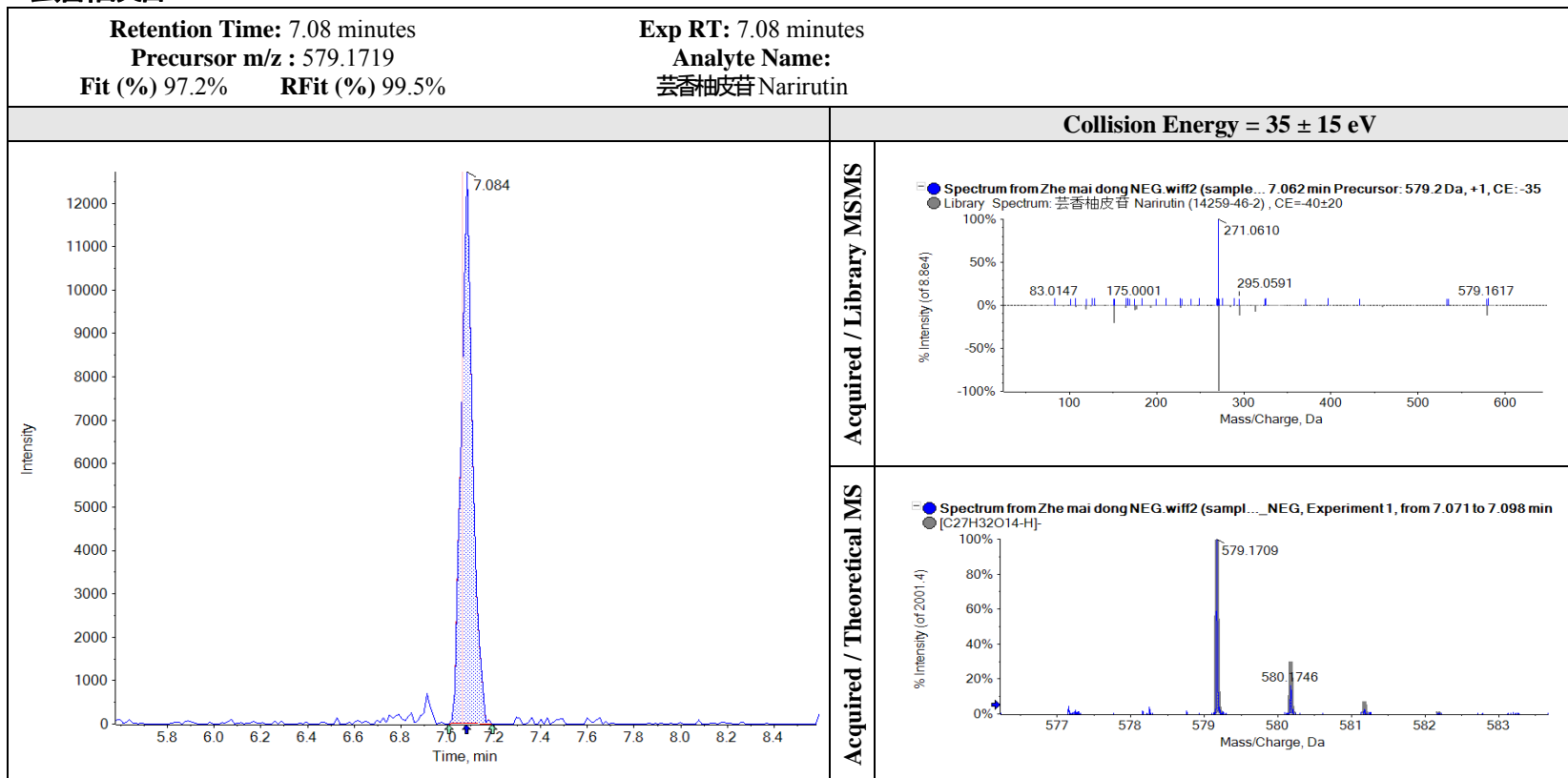
紫云英苷 Astragalin



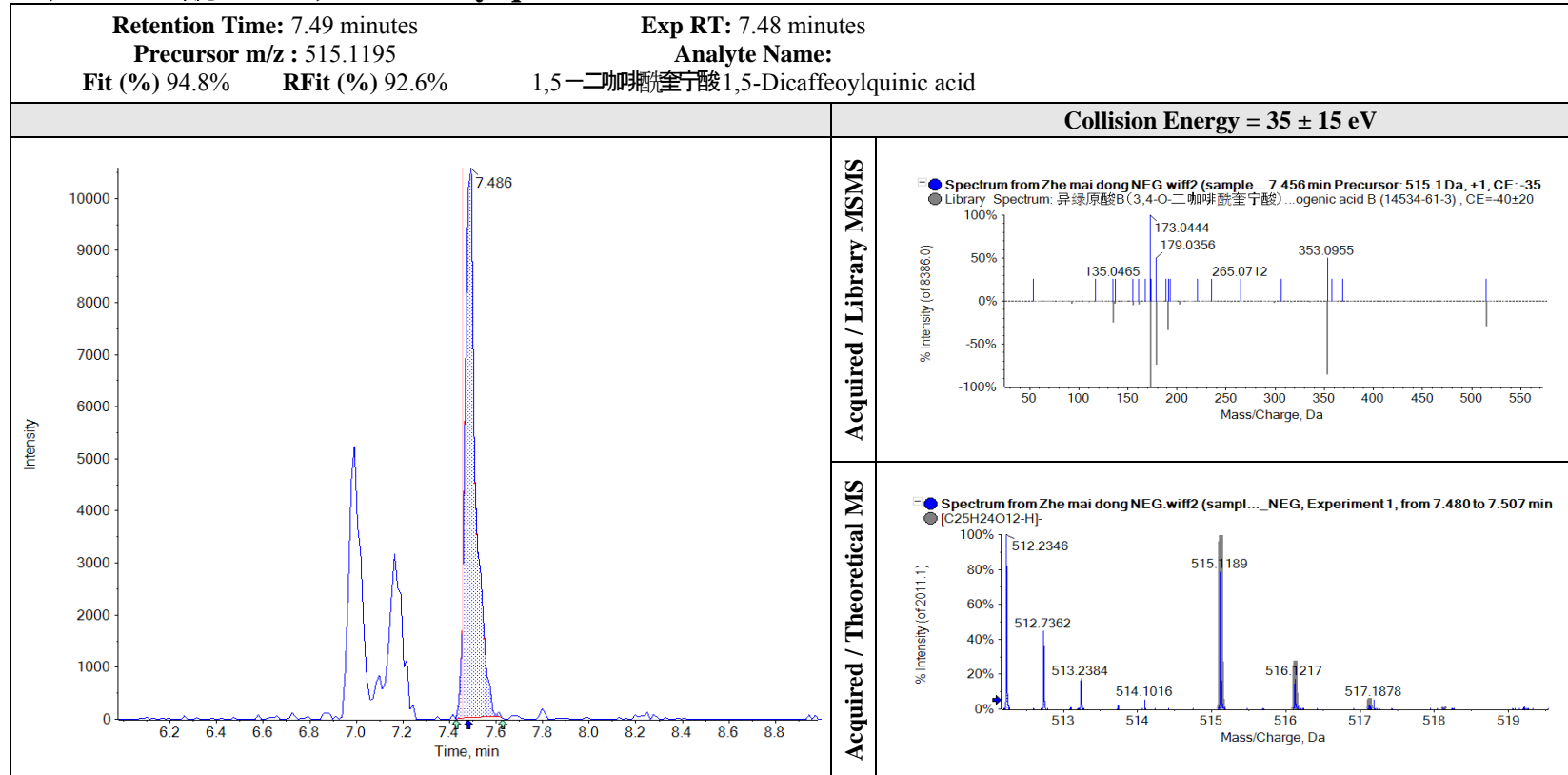
特女贞苷 Specnuezhenide



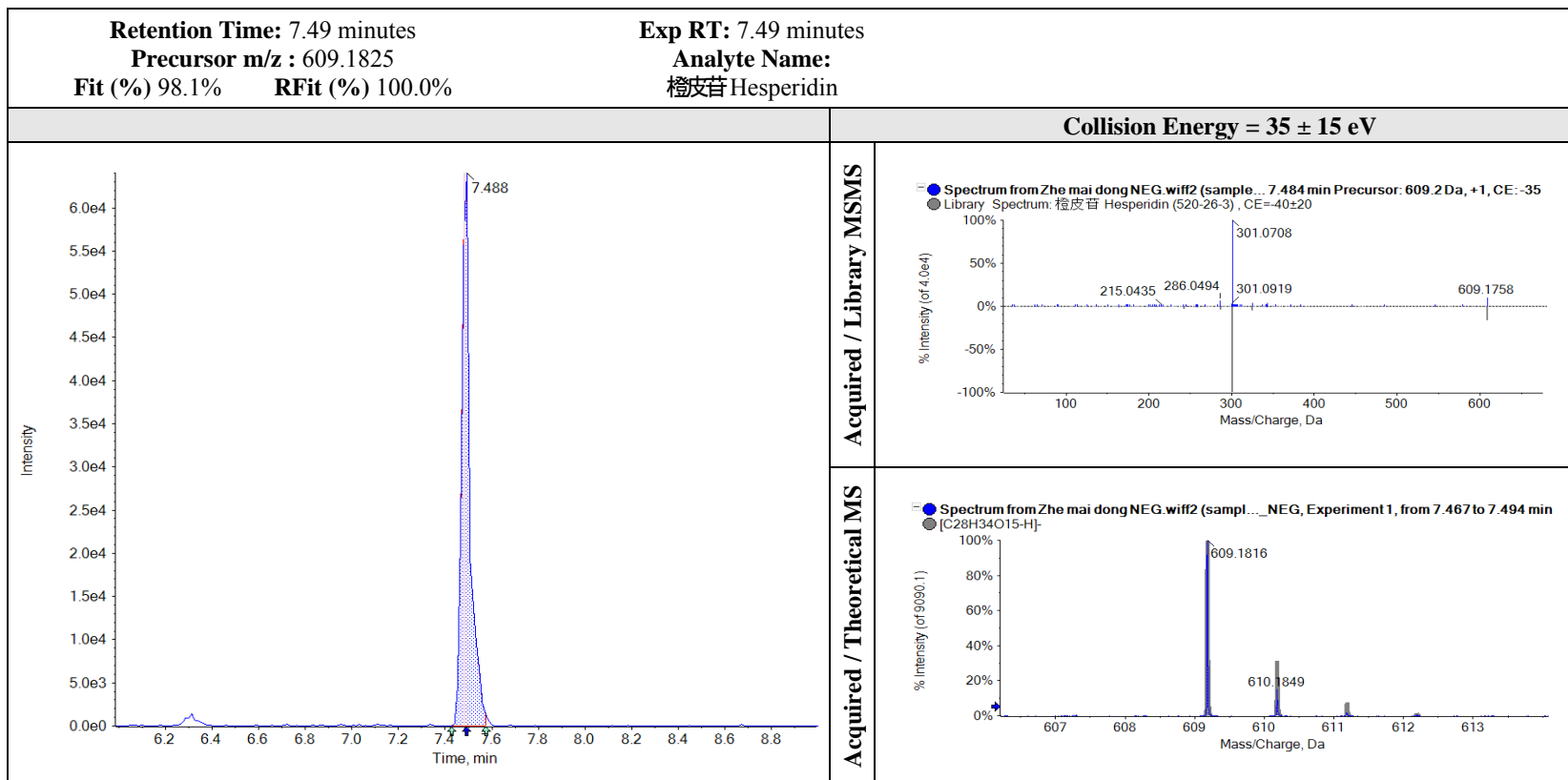
芸香柚皮苷 Narirutin



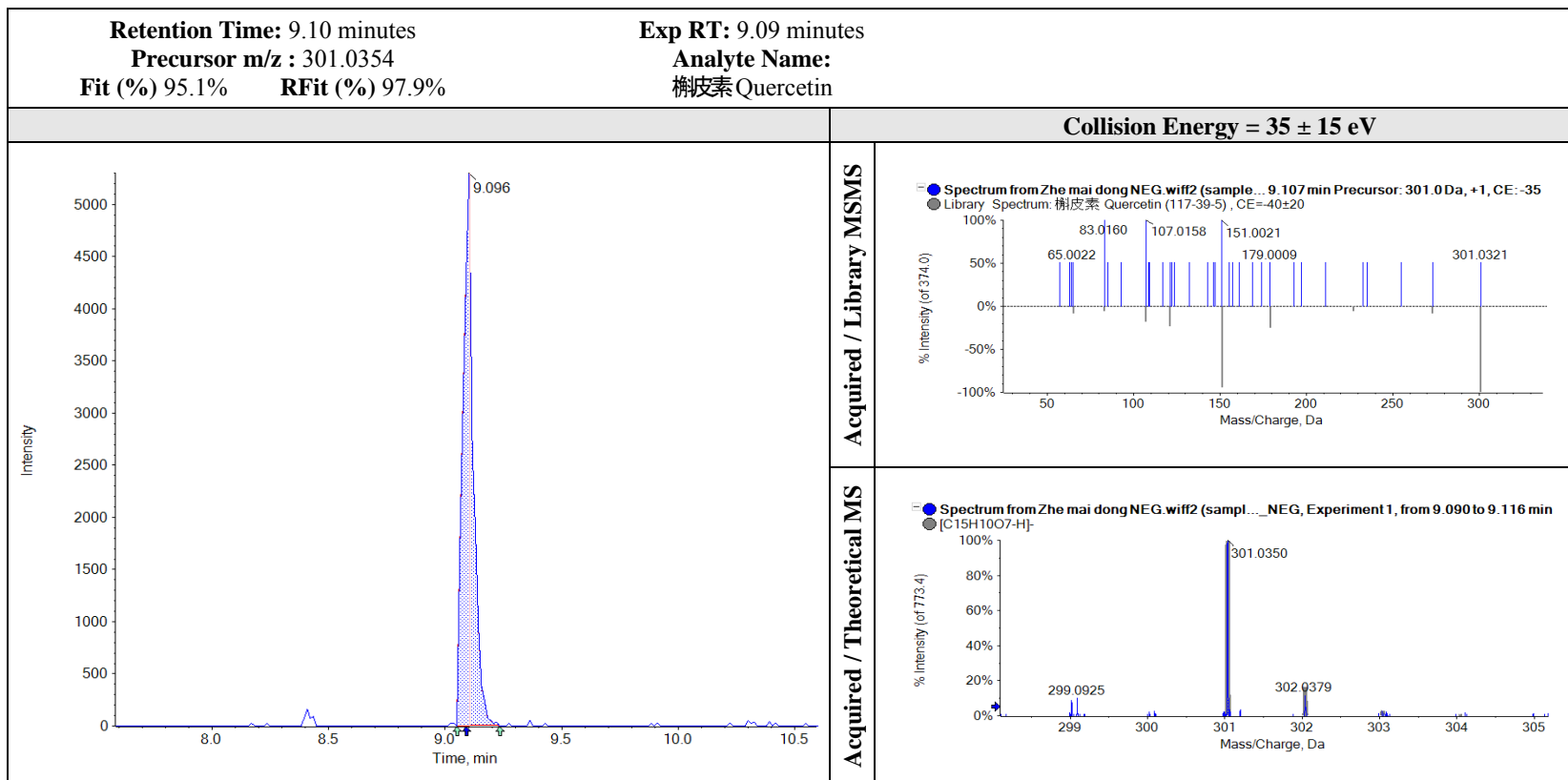
1,5-二咖啡酰奎宁酸 1,5-Dicaffeoylquinic acid



橙皮苷 Hesperidin



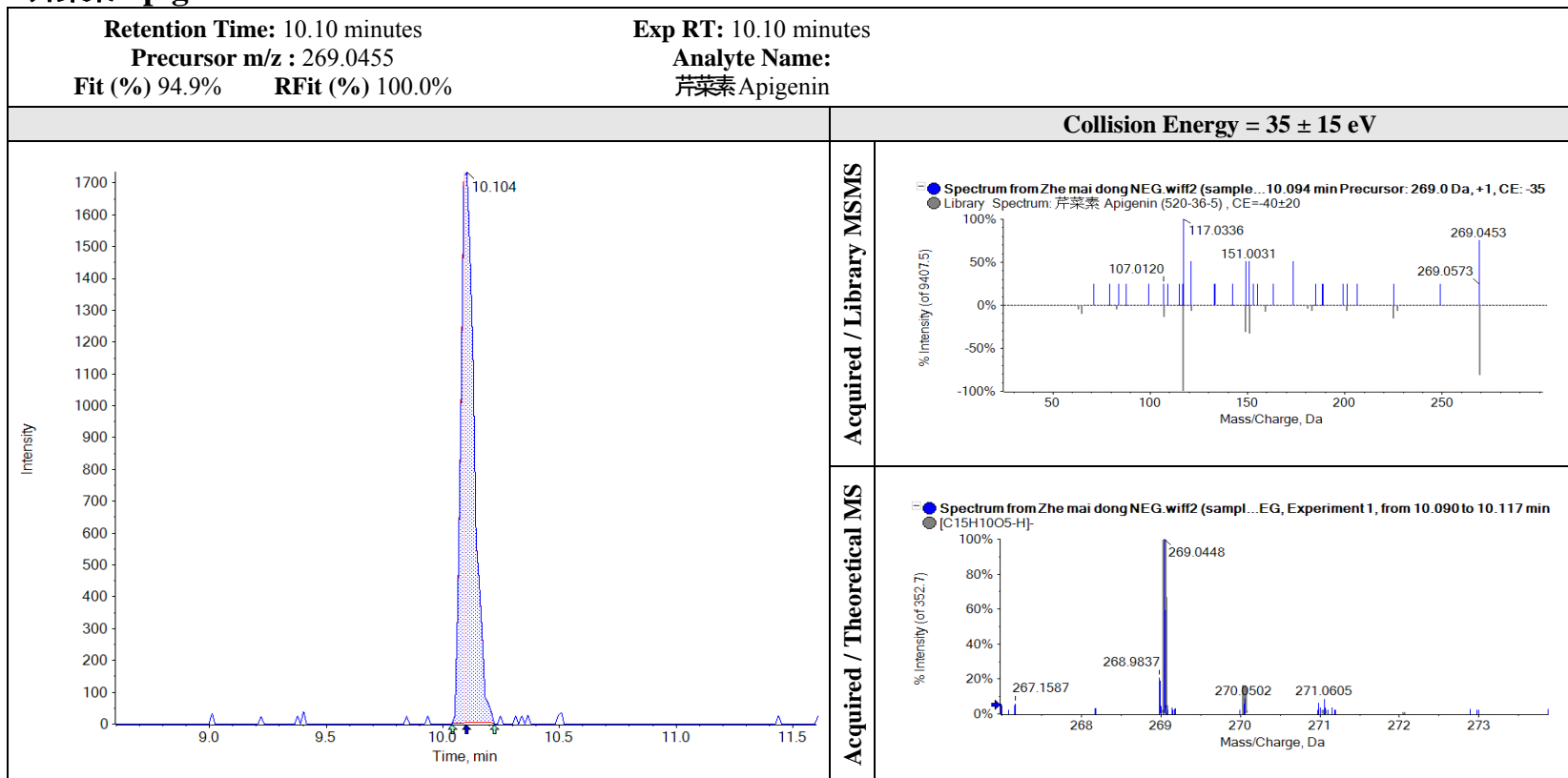
槲皮素 Quercetin



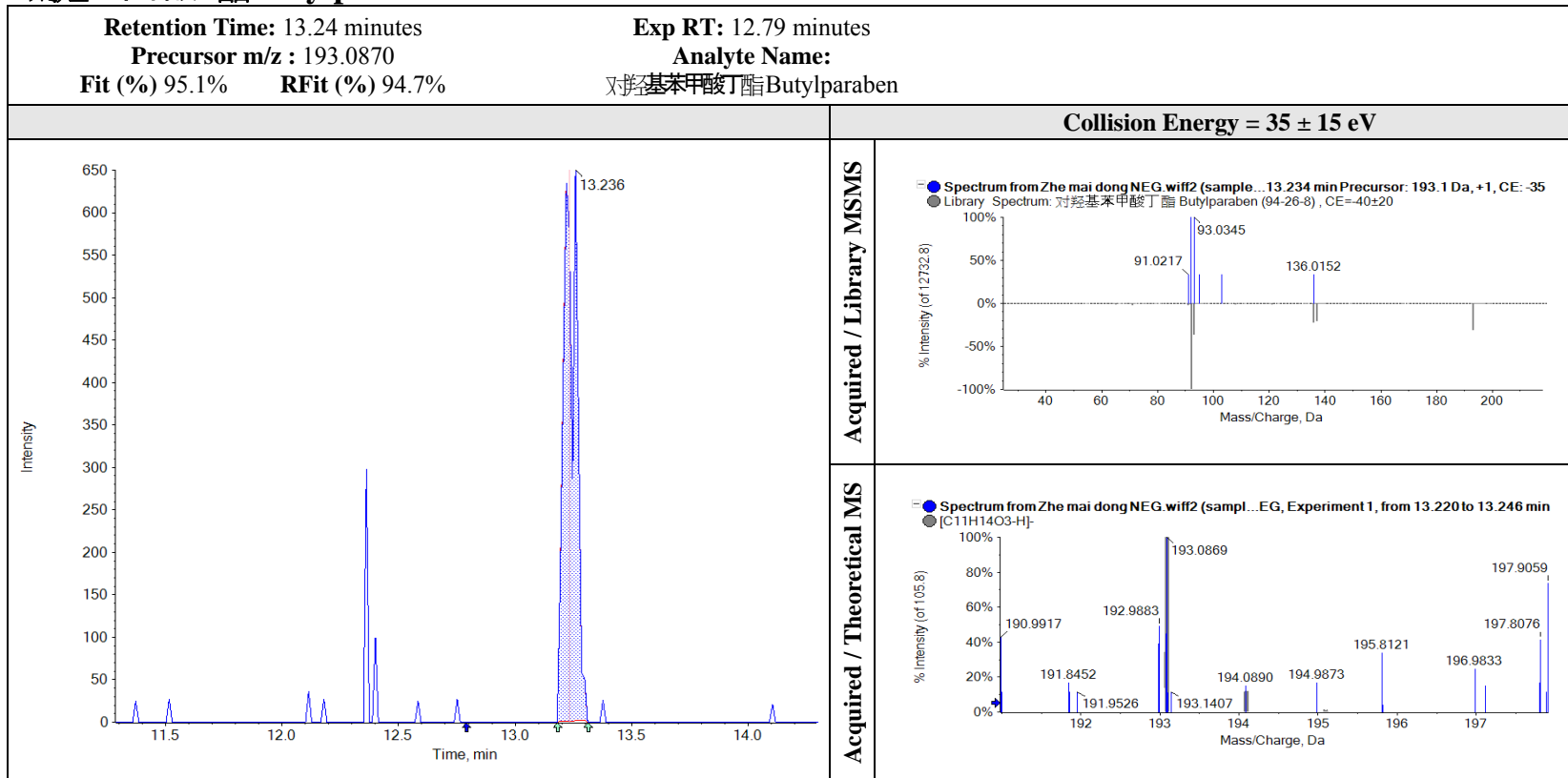
毛蕊异黄酮苷 Calycosin-7-o-glucoside

<p>Retention Time: 9.43 minutes Precursor m/z : 491.1195 Fit (%) 99.7% RFit (%) 98.1%</p>		<p>Exp RT: 9.42 minutes Analyte Name: 毛蕊异黄酮苷 Calycosin-7-o-glucoside +HCOOH</p>	
		Collision Energy = 35 ± 15 eV	
	Acquired / Library MSMS	<p>● Spectrum from Zhe mai dong NEG.wiff2 (sample... 9.434 min Precursor: 491.1 Da, +1, CE: -35) ● Library Spectrum: 毛蕊异黄酮苷 Calycosin-7-o-glucoside +HCOOH (20633-67-4) , CE=-40±20</p>	
	Acquired / Theoretical MS	<p>● Spectrum from Zhe mai dong NEG.wiff2 (sampl..._NEG, Experiment 1, from 9.403 to 9.429 min) ● [C22H22O10.HCOOH-H]-</p>	

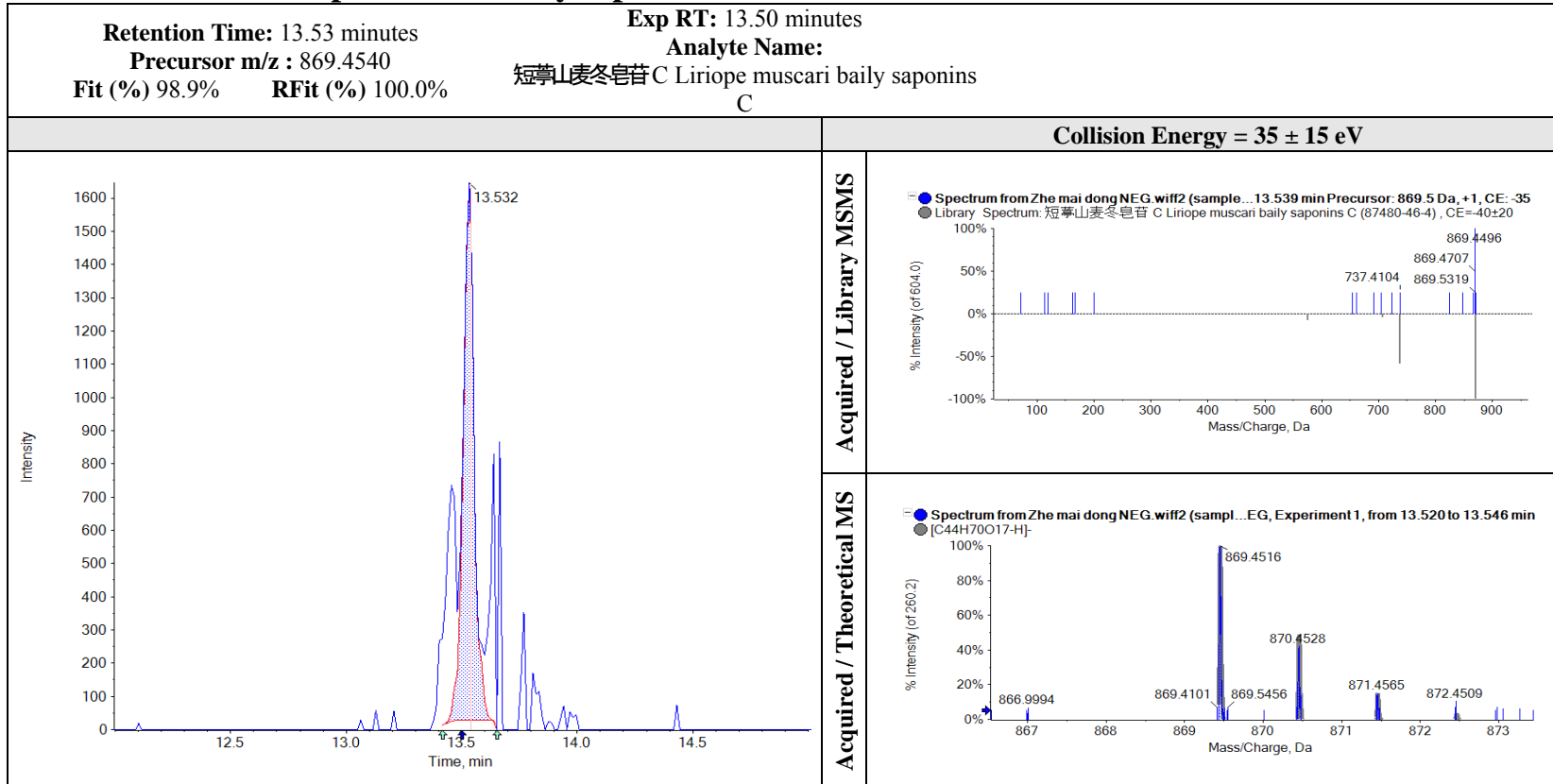
芹菜素 Apigenin



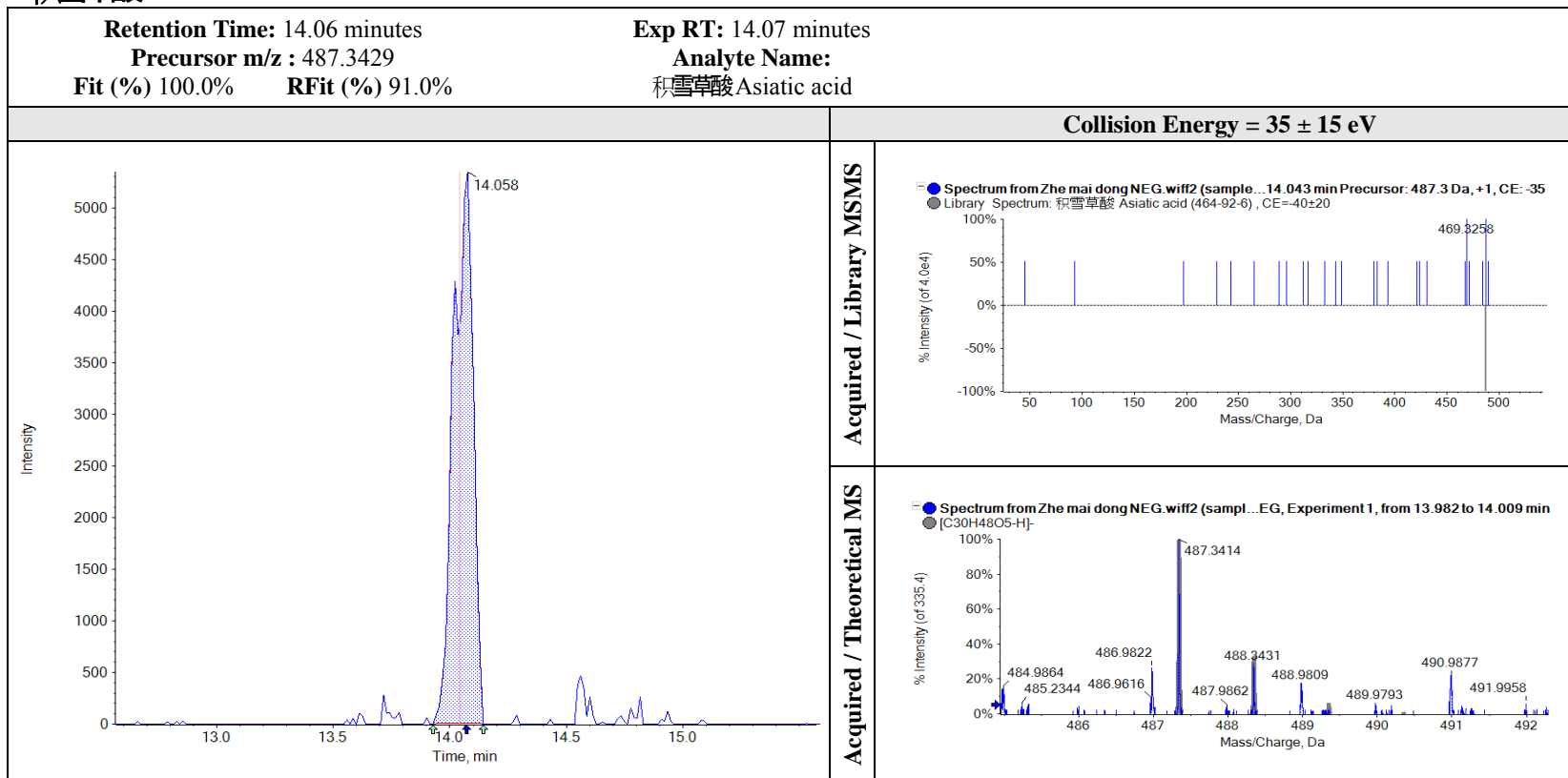
对羟基苯甲酸丁酯 Butylparaben



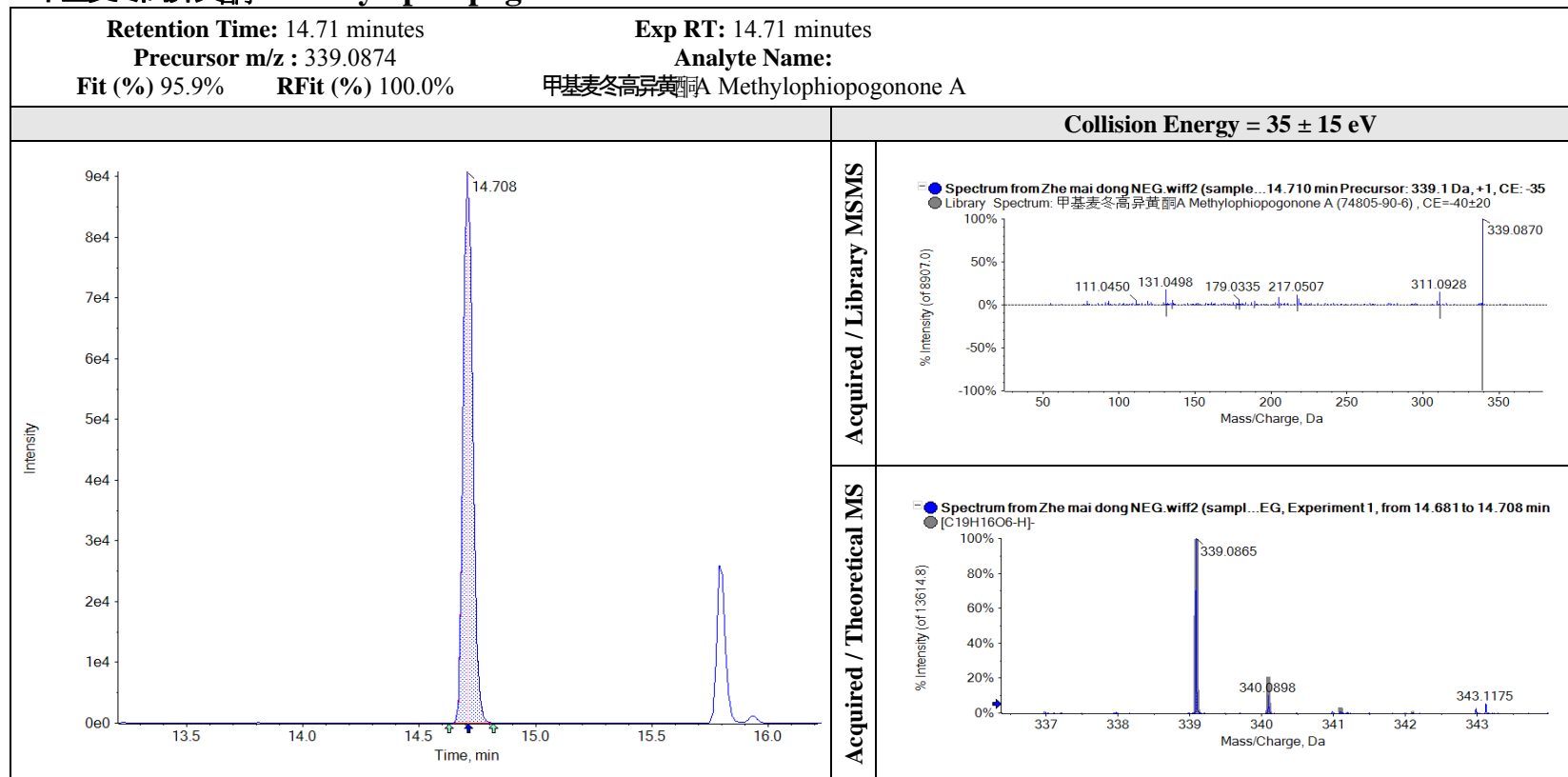
短葶山麦冬皂苷 C Liriope muscari baily saponins C



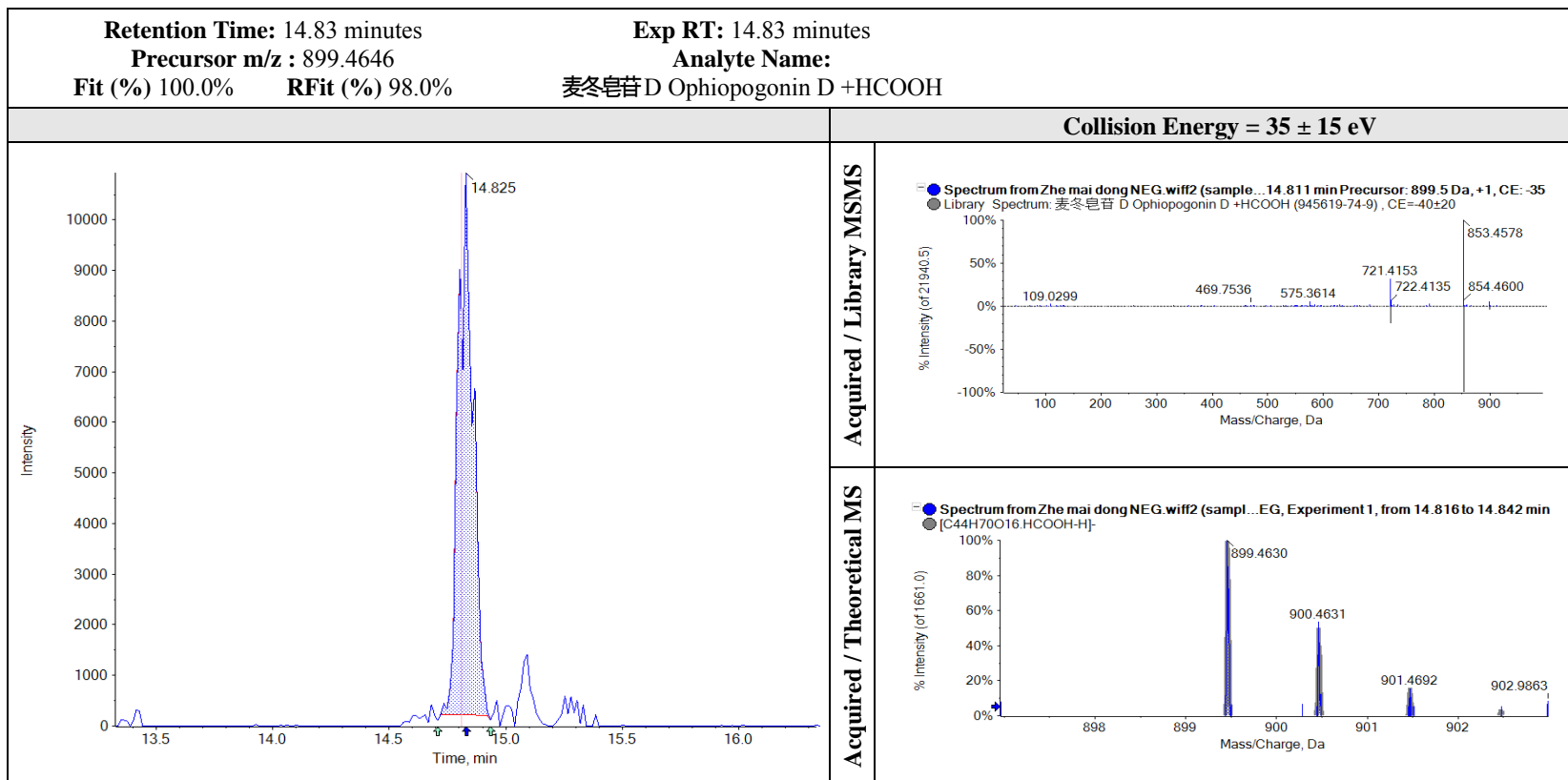
积雪草酸 Asiatic acid

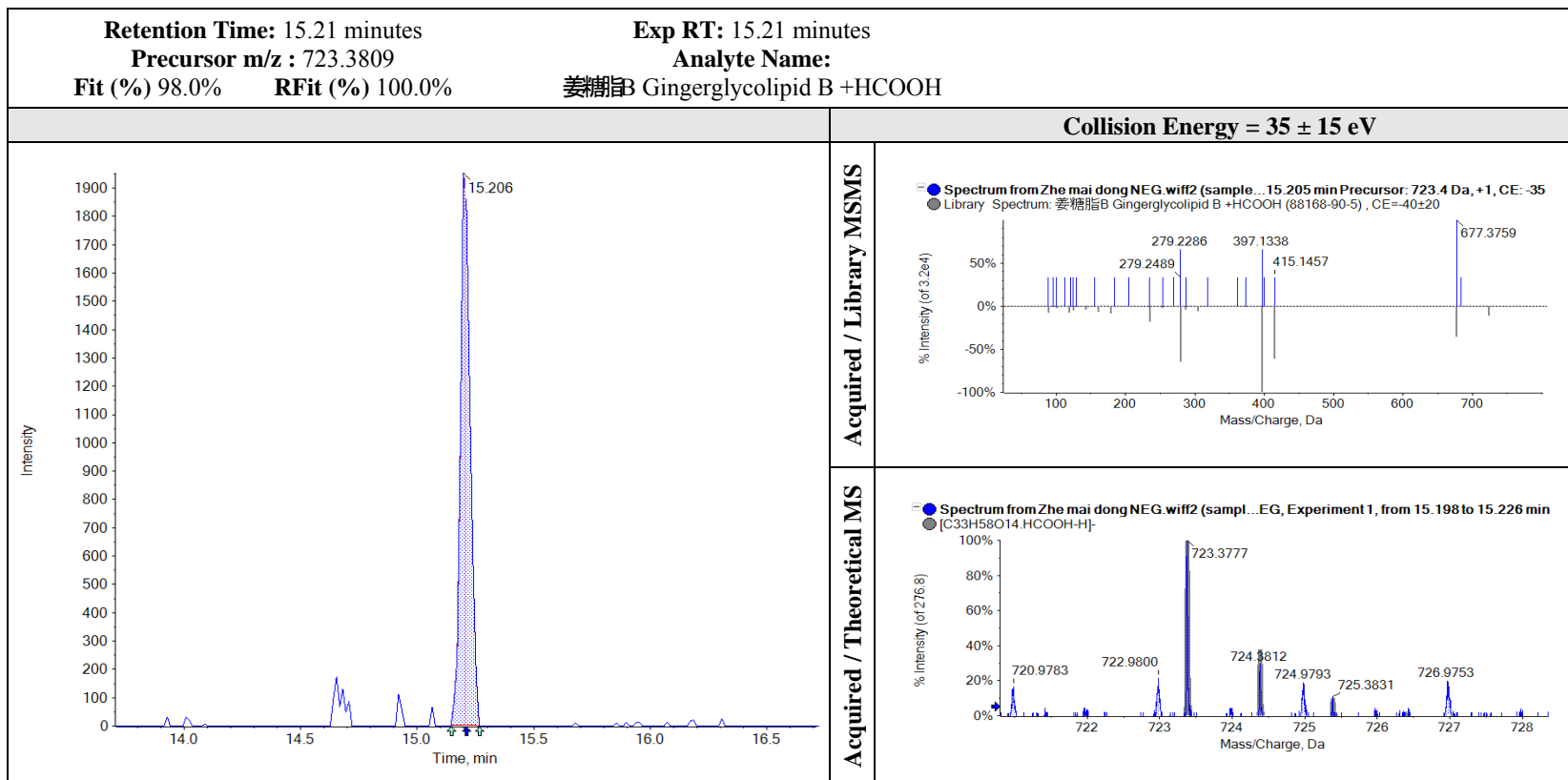


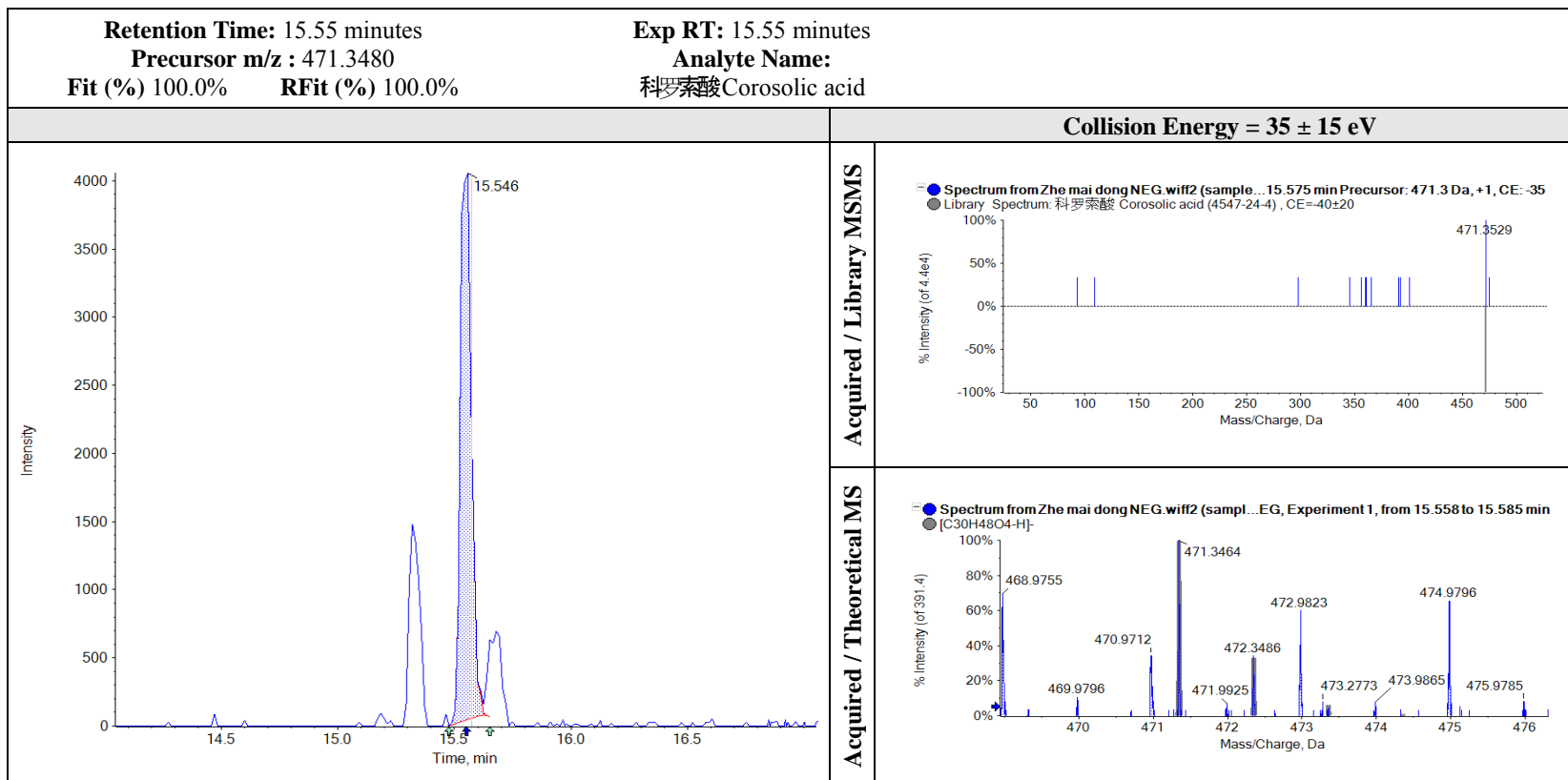
甲基麦冬高异黄酮A Methylophiopogonone A

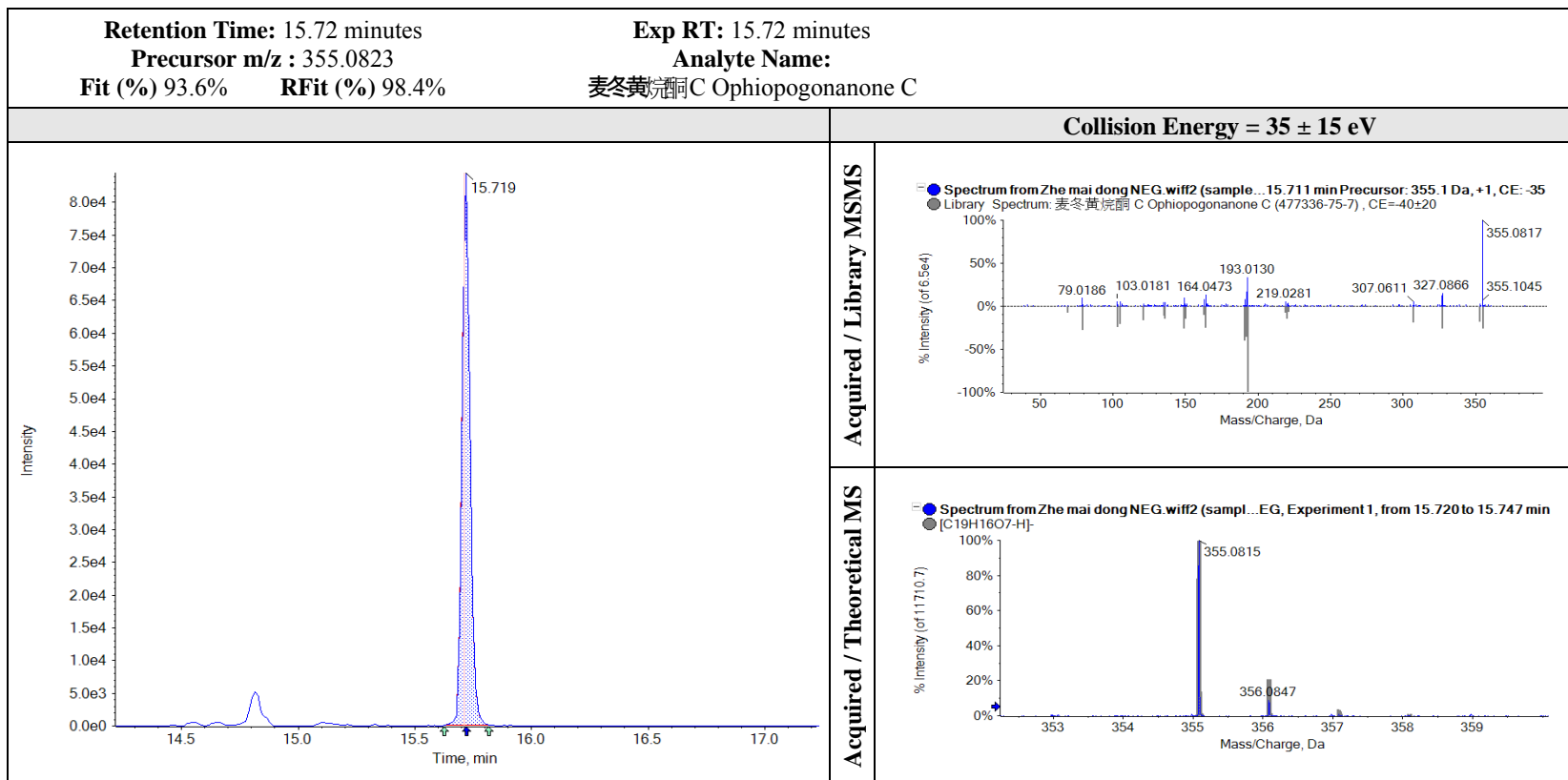


麦冬皂苷D Ophiopogonin D









齐墩果酸 Oleanolic acid

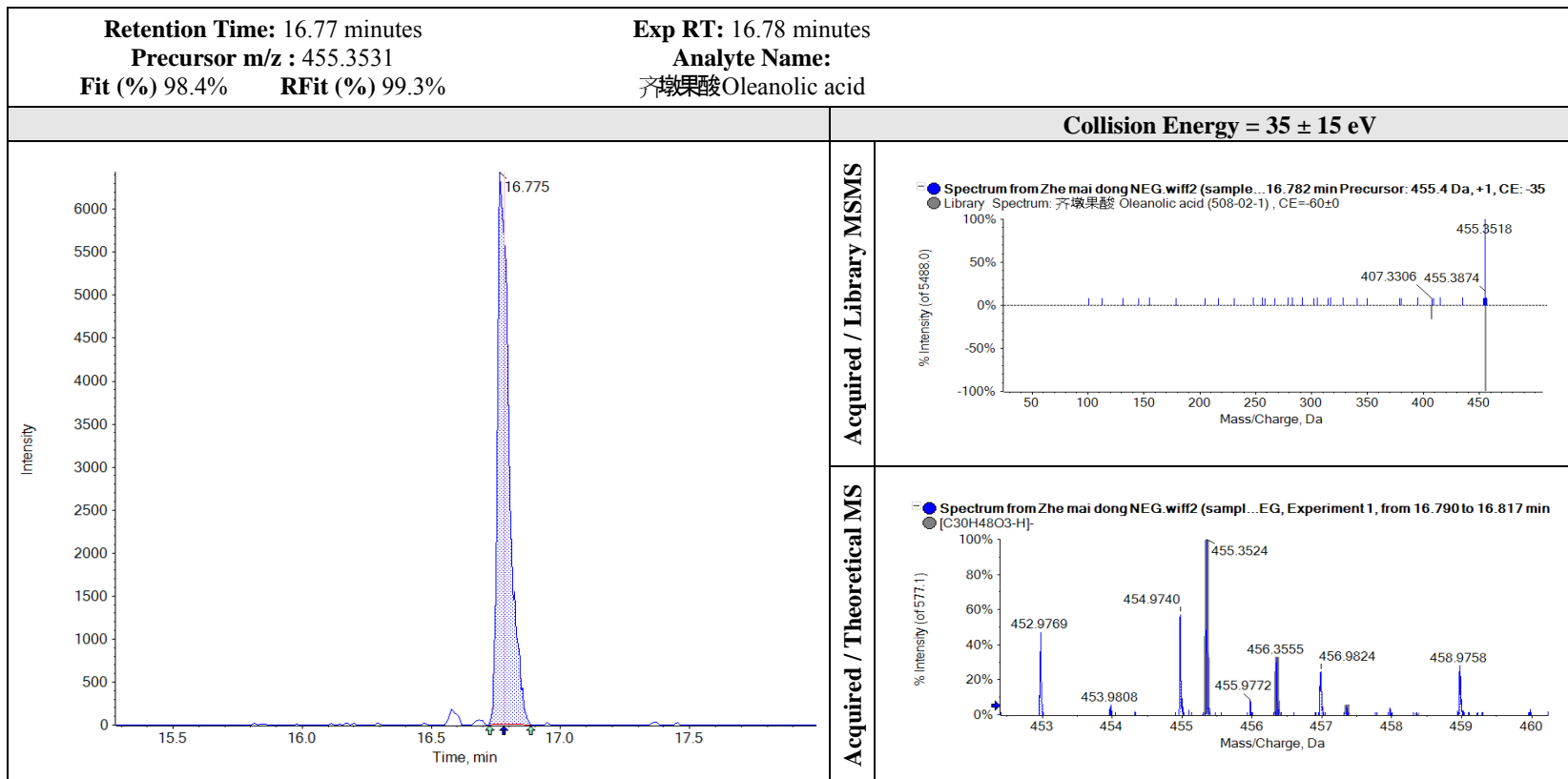


Table S3 The different chemical constituents between CMD and ZMD in GC-MS analysis

NO.	RT(min)	Name	Match	VIP	T-test	Fold change (ZMD/CMD)
1	16.19	D-Fructose	928	1.34	0.031	0.87
2	8.80	glycerol	922	1.92	0.000	1.22
3	11.69	Malic acid	910	1.32	0.034	-1.20
4	26.80	Sucrose	907	1.63	0.004	-1.06
5	9.25	Glycine	894	1.94	0.000	-9.42
6	9.13	L-Proline	888	1.76	0.001	-8.10
7	8.67	Monoethanolamine	882	1.82	0.001	-7.41
8	8.82	Phosphoric acid	873	1.43	0.019	0.51
9	18.86	Inositol	864	1.80	0.001	-2.41
10	16.40	d-Glucose	857	1.46	0.016	0.86
11	16.34	d-Galactose	852	1.31	0.037	0.54
12	10.01	Serine	827	1.35	0.029	-7.38
13	12.35	Threonate	814	1.50	0.012	-2.79
14	12.21	4-Aminobutanoic acid	798	1.68	0.003	-10.95
15	16.28	D-Mannoheptulose	755	1.57	0.007	-0.57
16	20.03	2-(beta-D-Glucosyl)-sn-glycerol	736	1.57	0.007	-2.88
17	26.78	Trehalose	714	1.34	0.031	-0.69

Table S4 The significantly different chemical constituents between CMD and ZMD (ESI+)

NO.	RT (min)	Name	molecular weight	VIP	T-test	Fold change (ZMD/CMD)
1	12.90	Thymidine	242.0903	1.44	0.002	-1.32
2	11.13	Chlorogenic Acid	354.0951	1.20	0.019	5.38
3	8.35	Indole-3-carboxylic acid	161.0477	1.45	0.002	2.39
4	6.79	Pyridoxal Phosphate	247.0246	1.24	0.014	1.18
5	9.74	LysoPC(18:2(9Z,12Z))	519.3325	1.21	0.018	6.69
6	8.90	Traumatic Acid	228.1362	1.26	0.012	2.75
7	8.90	LPA(0:0/18:0)	438.2746	1.22	0.017	1.07
8	13.75	LysoPC(22:2(13Z,16Z))	575.3951	1.54	0.001	2.60
9	1.91	L-Cysteine	121.0197	1.59	0.000	-3.09
10	0.96	alpha-Tocopherol	430.3811	1.69	0.000	-2.96
11	9.85	LysoPE (0:0/18:3(6Z,9Z,12Z))	475.2699	1.05	0.048	-0.88
12	1.23	5-Hydroxyisourate	184.0233	1.47	0.001	-1.82
13	15.00	MG(0:0/22:1(13Z)/0:0)	412.3553	1.31	0.008	-0.73
14	12.69	Dihydroquercetin	304.0583	1.18	0.022	-0.71
15	8.34	Cytidine	243.0855	1.41	0.003	2.80
16	12.16	Glutinosone	220.1463	1.20	0.019	-0.93
17	12.68	Glutathione	307.0838	1.54	0.000	-1.52
18	9.53	L-Cystathionine	222.0674	1.29	0.009	-1.78
19	18.14	L-Arginine	174.1117	1.14	0.028	-0.36
20	8.35	Cadaverine	102.1157	1.30	0.009	3.72
21	11.13	Pyridoxine 5-phosphate	249.0402	1.42	0.003	3.27
22	5.19	Stearoylethanolamide	327.3137	1.34	0.006	-1.60
23	1.19	6-Gingerol	294.1831	1.08	0.041	-1.56
24	15.09	Gibberellin A53	348.1937	1.18	0.022	-1.57
25	7.58	Calystegin A3	159.0895	1.25	0.014	-2.21

**Table S5 The significantly different chemical constituents between CMD and ZMD
(ESI-)**

NO.	RT (min)	Name	molecular weight	VIP	T-test	Fold change (ZMD/CMD)
1	1.17	Geranyl diphosphate	314.0684	1.09	0.049	-1.34
2	1.00	Gibberellin A53	348.1937	1.23	0.021	-1.28
3	8.68	Gibberellin A86	380.1471	1.63	0.000	-5.04
4	4.28	Glutinosone	220.1463	1.23	0.023	2.26
5	18.20	Isovaleric acid	102.0681	1.21	0.024	-0.58
6	7.11	Kynurenic acid	189.0426	1.78	0.000	-2.90
7	6.05	LysoPC(18:4(6Z,9Z,12Z,15Z))	515.3012	1.42	0.005	-3.41
8	6.04	LysoPE(0:0/16:1(9Z))	451.2699	1.32	0.011	-3.56
9	11.60	LysoPE(0:0/22:0)	537.3794	1.09	0.049	1.80
10	12.61	LysoPE(0:0/22:1(13Z))	535.3638	1.37	0.008	1.80
11	14.05	PC(14:0/20:0)	761.5935	1.37	0.008	-0.75
12	10.04	PC(18:0/P-18:0)	773.6298	1.17	0.032	1.90
13	9.43	PC(20:0/24:0)	901.7500	1.51	0.002	3.41
14	14.15	Pelargonidin 3-O-(6-O-malonyl-β-D-glucoside)	518.1060	1.32	0.012	1.21
15	4.77	Pyruvate	88.0160	1.72	0.000	-1.46
16	10.81	Quercetin	302.0427	1.13	0.040	-0.99
17	4.77	Taurine	125.0147	1.78	0.000	-1.51