Electronic Supplementary Material (ESI) for Analyst.

Aluminum Foil as Single-Use Substrate for MALDI-MS Fingerprinting of Different Melanoma Cell Lines

SUPPORTING INFORMATION

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SI-I. Cells culturing and sample preparation

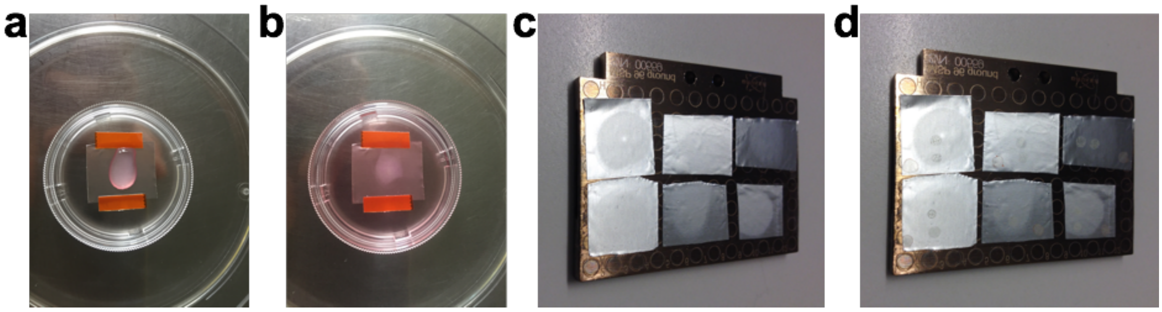

Figure S1. Optical image of a) cells suspension deposited on aluminium foil, b) over-night incubated sample, c) aluminium foil with fixed cells position on target MALDI plate before and d) after matrix deposition.

SI-II. The intact cell MALDI MS of cell pellets

Premixing approach.
1 μL of cells suspension in PBS was mixed with 1 μL of SA matrix. Thereafter, 1 μL of the obtained solution was deposited on a MALDI plate and dried at RT.
Layer-by-layer approach.
0.5 μL of SA matrix was deposited at MALDI target plate and dried at RT. Thereafter, 0.5 μL of cells suspension (10^4 cells/μL in PBS) was placed above it and dried at RT. Finally, 0.5 μL of the SA matrix were deposited at the same spot and dried at RT.

An average cell spectrum was collected from 500 random laser shots at 20 Hz laser frequency. The instrumental parameters were fixed as following: laser attenuator – 90% within the range of 30% to 70% laser intensity; delayed ion extraction time – 400 ns; detector gain – 19.4×; electronic gain – enhanced (100 mV). The ion source voltages were at the optimized values: ion source 1 – 20.0 kV; ion source 2 – 18.5 kV; lens – 8.5 kV.

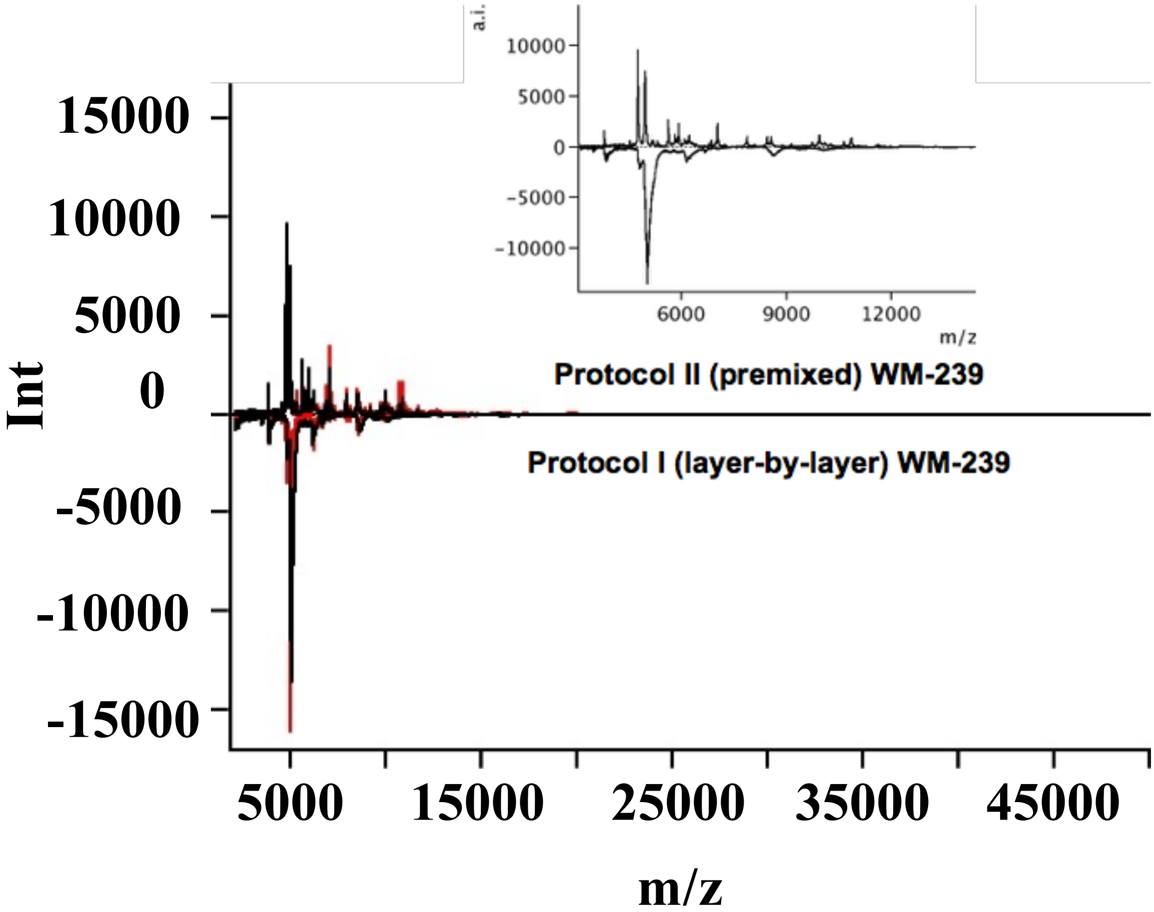

Figure S2. The characteristic MALDI-MS fingerprint spectra obtained for WM-239 melanoma cell line by using premixed approach (upper spectra) and layer-by-layer approach (lower spectra). Experimental conditions: SA matrix.

SI-III. The full list of the resolved peaks (S/N ≥ 3) obtained for melanoma cells by the intact cell MALDI

	5.36	5.65	5.83	5.94	6.12	6.17	6.33	6.54	6.66	6.89	7	7.65	7.87	8.55	8.72	8.85	9.15	9.37	10	10.28	10.84	11.07	11.3	11.6	11.8	12.35	13.78	14	14.97	15.32	17.9	26.1	36
s1 (Sbcl2)	20	28	6	3	4	3	11	16	12	14.5	12	25	7	5	4	3	10	7	43	8	5	21	100	32	5	3	55	45	7	25	9	1	4
s2 (Sbcl2)	19	31	7	3	3	1	11.5	18	13	14	12	26	7	5	4.5	5	8	8	45	9	4.5	25	100	34.5	5	4	58	48	7	27	9	1	4
s3 (Sbcl2)	19	29	6	2	3	3	10.5	17	11	13	9	24.5	6	5	5	4.5	9	7	38	8	6	21	100	30	5	4	55	38	7	23.5	10	1	4
s4 (Sbcl2)	24	32	7	4	3.5	4	15	16	15	13	10	30	8	6	5	5	9	8	44	9	5	25.5	100	34	5	6	53	43	11	33	11	1	6
s5 (Sbcl2)	20	31	7	0	4	3	13	18	12	15	11	31	8	5	5	5	10	7.5	40	8	6	24.5	100	32.5	5	6	59	47	11.5	29	13	1	6
s6 (Sbcl2)	24.5	29	7	3	4	4	14.5	16	15	13	11	29	7.5	5	5	5	10	7	43	9	6	2	100	30	5.5	8	50	39	11	30	12	1	6
s7 (Sbcl2)	14	39	10	4	2	3.5	16	24	14	17	19	27	14	18	4	5	10	12	90	14	5	28	100	57	8	6	62	57	9	28	5	1	3
s8 (Sbcl2)	15	38	9	3	3	3	15	21	14	16	15	30	9	7	5	3	10.5	10	60	10	5	24	100	40	5	4	57	48	8	27.5	4.5	1	3
s9 (Sbcl2)	20	43	12	4	6	4.5	18	24.5	18	20	16	33.5	10	9	5	5.5	11	12	67	12	4	26	100	48	5	5.5	59	50	9.5	31	6	4	4
s10 (WM-115)	100	26	13	7	24	17	21	32	26	4	3	11	19	10	27	44	24	8	28	10	26	5	28	6	15	63	13	14	7	6	8	4	2
s11 (WM-115)	100	26	12	9	23	16	23	31	28	3	4	8	20	12	27	42	18	9	34	12	24	6	23	8	14	57	11	16	6	6	8	4	2
s12 (WM-115)	100	20	12	7.5	21	16	19	25	27	2.5	3	8	18	10	26	41	16	9	26.5	10	20	4	18	6	13.5	62	6	12	7	6	8	4	2
s13 (WM-115)	100	20	12	7.5	21	16	19	26	27	2.5	3	8	18	10	26	41	16.5	9	26.5	10	20	4	18	6	13.5	62	6	12	7	6	8	4	2
s14 (WM-115)	100	23	9	11	33	22	22	25	27	3	2	8	21	7	26	37	19	11	27.5	14	15	5	38	7	14	75	6	10	7	8	6	5	2
s15 (WM-115)	100	21	8	11	35	20.5	24	25	31	3	3	9.5	23	9	29	40	19	13	37	16	18	7	51	9.5	18	89	6.5	12	4	11	8	3	2
s16 (WM-115)	100	25	17.5	8	19	14	21	34	26	3	3.5	7	22	10	22	39	21	8.5	32	12	21	5	18	16	13	34	13	16	4	5	7	3	2
s17 (WM-115)	100	28	17	6	18	15	21	37	22	3	3.5	10	25	11	24	39	18	10	36	12	22	7	23	7	15	38	16	21.5	4	6	9	4	2
s18 (WM-115)	100	25	16	10	22	21	27	55	32	5	4	11	43	18	30	53	34.5	14	72	21	38	12	24	7	26	70	14	23	9	7	12	3	4
s19 (WM-239)	10	3	0	2	16	20	3	4	5	4	3.5	3	13	2	6	3	2.5	3	1	7	3	2	6	3	3.5	100	1	3	5	4	10	3	2
s20 (WM-239)	10	3	0	2	18	18.5	3	5	6.5	3	4	4	11	2	6.5	3	2	3	1	11	4.5	3	7	6	5	100	1	3	8	6	9.5	3	2
s21 (WM-239)	20	3	0	4.5	23	21	6	5	14	4	3	5	15	3	12	6.5	6	4.5	2	13	3	2	14	5	7	100	2	3	11	5	9	4	2
s22 (WM-239)	26	4	2	4	15	19	5	5	12	4	4	6	18	3	12	6.5	6	5.5	1	13	4	3	13	5	6	100	3	4	13	8	18	3	5
s23 (WM-239)	21	4	3	5	19	19	6.5	5	12	3	3	6	16	3	11	6	7	6	1	16	4	4	17	10	6	100	2	4	12	8	11	3	3
s24 (WM-239)	26.5	4	3	4	18	15	7	6	15.5	3	3	8	21	3	12	7.5	7	5	1	15	4	3	22	4.5	7	100	3	3.5	12.5	9	15.5	3	4
s25 (WM-239)	85	32	8	9	18	29	21	36	28	3	4	11	35	11	21	23	21	4	1	10	16	5	20	5	15	100	13	11	10	4	20	5	5
s26 (WM-239)	69	30	9	9.5	13.5	23.5	22	40	27.5	4	3	10	29	12	21	20	17	6	1	11	15	5	22.5	7	14	100	10	12.5	10	6	15	3	3
s27 (WM-239)	83	26	8	10.5	18	28	21.5	35	30	3	3.5	9	25	6	21	20	14	6	1	9	10	3.5	22	5	11	100	3	6	9	5	13	4	2

Intensity of the characteristic peaks in fingerprints, derived from different samples. Spectra1 – 3 are obtained from sample 1, spectra 4 – 6 are obtained from sample 2 and spectra 7 – 9 are obtained from sample 3.

Table S1. Average intensity (%) of the characteristic peaks with the respect to the same sample

m/z	Sbcl2-1	Sbcl2-2	Sbcl2-3	WM-115-1	WM-115-2	WM-115-3	WM-239-1	WM-239-2	WM-239-3
5.36	19.33	22.83	16.33	100.00	100.00	100.00	13.33	24.50	79.00
5.65	29.33	30.67	40.00	24.00	21.33	26.00	3.00	3.83	29.33
5.83	6.33	7.00	10.33	12.33	9.67	16.83	0.00	2.67	8.33
5.94	2.67	2.33	3.67	7.83	9.83	8.00	2.83	4.33	9.67
6.12	3.33	3.83	3.67	22.67	29.67	19.67	19.00	17.33	16.50
6.17	2.33	3.67	3.67	16.33	19.50	16.67	19.83	17.67	26.83
6.33	11.00	14.17	16.33	21.00	21.67	23.00	4.00	6.17	21.50
6.54	17.00	16.67	23.17	29.33	25.33	42.00	4.67	5.33	37.00
6.66	12.00	14.00	15.33	27.00	28.33	26.67	8.50	13.17	28.50
6.89	13.83	13.67	17.67	3.17	2.83	3.67	3.67	3.33	3.33
7	11.00	10.67	16.67	3.33	2.67	3.67	3.50	3.33	3.50
7.65	25.17	30.00	30.17	9.00	8.50	9.33	4.00	6.67	10.00
7.87	6.67	7.83	11.00	19.00	20.67	30.00	13.00	18.33	29.67
8.55	4.83	5.33	11.33	10.67	8.67	13.00	2.33	3.00	9.67
8.72	4.50	5.00	4.67	26.67	27.00	25.33	8.17	11.67	21.00
8.85	4.17	5.00	4.50	42.33	39.33	43.67	4.17	6.67	21.00
9.15	9.00	9.67	10.50	19.33	18.17	24.50	3.50	6.67	17.33
9.37	7.33	7.50	11.33	8.67	11.00	10.83	3.50	5.50	5.33
10	42.00	42.33	72.33	29.50	30.33	46.67	1.33	1.00	1.00
10.28	8.33	8.67	12.00	10.67	13.17	15.00	10.33	14.67	10.00
10.84	5.17	5.67	4.67	23.33	17.67	27.00	3.50	4.00	13.67
11.07	22.33	17.33	26.00	5.00	5.33	8.00	2.33	3.33	4.50
11.3	100.00	100.00	100.00	23.00	35.67	21.67	9.00	17.33	21.50
11.6	32.17	32.17	48.33	6.67	7.50	10.00	4.67	6.50	5.67
11.8	5.00	5.17	6.00	14.17	15.17	18.00	5.17	6.33	13.33
12.35	3.67	6.67	5.17	60.67	75.33	47.33	100.00	100.00	100.00
13.78	56.00	54.00	59.33	10.00	6.17	14.33	1.33	2.67	8.67
14	43.67	43.00	51.67	14.00	11.33	20.17	3.00	3.83	9.83
14.97	7.00	11.17	8.83	6.67	6.00	5.67	8.00	12.50	9.67
15.32	25.17	30.67	28.83	6.00	8.33	6.00	5.00	8.33	5.00
17.9	9.33	12.00	5.17	8.00	7.33	9.33	9.50	14.83	16.00
26.1	1.00	1.00	2.00	4.00	4.00	3.33	3.33	3.00	4.00
36	4.00	6.00	3.33	2.00	2.00	2.67	2.00	4.00	3.33

Table S2. Standard deviation of the characteristic peaks intensity with the respect to the same sample

m/z	Sbcl2-1	Sbcl2-2	Sbcl2-3	WM-115-1	WM-115-2	WM-115-3	WM-239-1	WM-239-2	WM-239-3
5.36	0.47	2.01	2.62	0.00	0.00	0.00	4.71	2.48	7.12
5.65	1.25	1.25	2.16	2.83	1.25	1.41	0.00	0.24	2.49
5.83	0.47	0.00	1.25	0.47	1.70	0.62	0.00	0.47	0.47
5.94	0.47	1.70	0.47	0.85	1.65	1.63	1.18	0.47	0.62
6.12	0.47	0.24	1.70	1.25	6.18	1.70	2.94	1.70	2.12
6.17	0.94	0.47	0.62	0.47	2.55	3.09	1.03	1.89	2.39
6.33	0.41	0.85	1.25	1.63	2.05	2.83	1.41	0.85	0.41
6.54	0.82	0.94	1.55	3.09	0.47	9.27	0.47	0.47	2.16
6.66	0.82	1.41	1.89	0.82	1.89	4.11	3.94	1.65	1.08
6.89	0.62	0.94	1.70	0.62	0.24	0.94	0.47	0.47	0.47
7	1.41	0.47	1.70	0.47	0.47	0.24	0.41	0.47	0.41
7.65	0.62	0.82	2.66	1.41	0.71	1.70	0.82	0.94	0.82
7.87	0.47	0.24	2.16	0.82	2.05	9.27	1.63	2.05	4.11
8.55	0.24	0.47	4.78	0.94	1.25	3.56	0.47	0.00	2.62
8.72	0.41	0.00	0.47	0.47	1.41	3.40	2.72	0.47	0.00
8.85	0.85	0.00	1.08	1.25	1.70	6.60	1.65	0.62	1.41
9.15	0.82	0.47	0.41	3.40	1.18	7.18	1.78	0.47	2.87
9.37	0.47	0.41	0.94	0.47	1.63	2.32	0.71	0.41	0.94
10	2.94	1.70	12.81	3.24	4.73	17.99	0.47	0.00	0.00
10.28	0.47	0.47	1.63	0.94	2.46	4.24	2.49	1.25	0.82
10.84	0.62	0.47	0.47	2.49	2.05	7.79	0.71	0.00	2.62
11.07	1.89	10.85	1.63	0.82	1.25	2.94	0.47	0.47	0.71
11.3	0.00	0.00	0.00	4.08	13.57	2.62	3.56	3.68	1.08
11.6	1.84	1.65	6.94	0.94	1.47	4.24	1.25	2.48	0.94
11.8	0.00	0.24	1.41	0.62	2.01	5.72	1.43	0.47	1.70
12.35	0.47	0.94	0.85	2.62	11.03	16.11	0.00	0.00	0.00
13.78	1.41	3.74	2.05	2.94	0.24	1.25	0.47	0.47	4.19
14	4.19	3.27	3.86	1.63	0.94	3.01	0.00	0.24	2.78
14.97	0.00	0.24	0.62	0.47	1.41	2.36	2.45	0.41	0.47
15.32	1.43	1.70	1.55	0.00	2.05	0.82	0.82	0.47	0.82
17.9	0.47	0.82	0.62	0.00	0.94	2.05	0.41	2.90	2.94
26.1	0.00	0.00	1.41	0.00	0.82	0.47	0.47	0.00	0.82
36	0.00	0.00	0.47	0.00	0.00	0.94	0.00	0.82	1.25

Table S3. Average intensity of the characteristic peaks collected from different sample

m/z	Sbcl2, %	WM-115, %	WM-239, %
5.36	19.50	100.00	38.94
5.65	33.33	23.78	12.06
5.83	7.89	12.94	3.67
5.94	2.89	8.56	5.61
6.12	3.61	24.00	17.61
6.17	3.22	17.50	21.44
6.33	13.83	21.89	10.56
6.54	18.94	32.22	15.67
6.66	13.78	27.33	16.72
6.89	15.06	3.22	3.44
7	12.78	3.22	3.44
7.65	28.44	8.94	6.89
7.87	8.50	23.22	20.33
8.55	7.17	10.78	5.00
8.72	4.72	26.33	13.61
8.85	4.56	41.78	10.61
9.15	9.72	20.67	9.17
9.37	8.72	10.17	4.78
10	52.22	35.50	1.11
10.28	9.67	12.94	11.67
10.84	5.17	22.67	7.06
11.07	21.89	6.11	3.39
11.3	100.00	26.78	15.94
11.6	37.56	8.06	5.61
11.8	5.39	15.78	8.28
12.35	5.17	61.11	100.00
13.78	56.44	10.17	4.22
14	46.11	15.17	5.56
14.97	9.00	6.11	10.06
15.32	28.22	6.78	6.11
17.9	8.83	8.22	13.44
26.1	1.33	3.78	3.44
36	4.44	2.22	3.11

Table S4. Standard deviation of the characteristic peaks intensity collected from different samples

m/z	Sbcl2	WM-115	WM-239
5.36	2.66	0.00	28.69
5.65	4.75	1.91	12.22
5.83	1.75	2.96	3.47
5.94	0.57	0.91	2.93
6.12	0.21	4.19	1.04
6.17	0.63	1.42	3.91
6.33	2.19	0.83	7.79
6.54	2.99	7.10	15.09
6.66	1.37	0.72	8.54
6.89	1.85	0.34	0.16
7	2.75	0.42	0.08
7.65	2.32	0.34	2.45
7.87	1.83	4.84	6.95
8.55	2.95	1.77	3.31
8.72	0.21	0.72	5.42
8.85	0.34	1.81	7.42
9.15	0.61	2.75	5.92
9.37	1.85	1.06	0.91
10	14.22	7.90	0.16
10.28	1.66	1.78	2.13
10.84	0.41	3.84	4.68
11.07	3.55	1.34	0.89
11.3	0.00	6.31	5.20
11.6	7.62	1.42	0.75
11.8	0.44	1.62	3.61
12.35	1.22	11.44	0.00
13.78	2.20	3.34	3.19
14	3.94	3.70	3.04
14.97	1.71	0.42	1.86
15.32	2.29	1.10	1.57
17.9	2.81	0.83	2.83
26.1	0.47	0.31	0.42
36	1.13	0.31	0.83

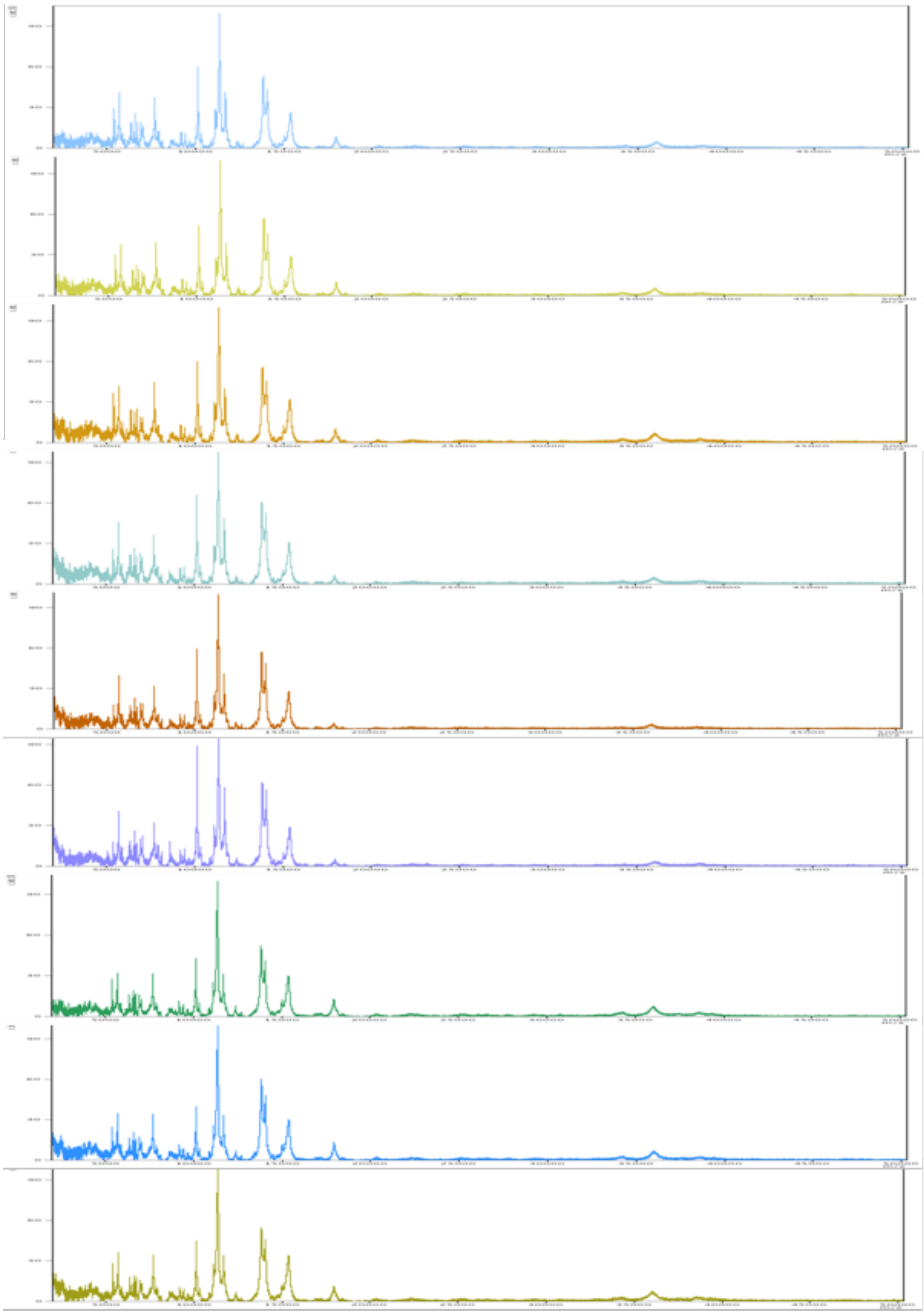

Figure S3. Reproducibility of Sbcl2 fingerprints (sample 1, spectra 1 – 3; sample 2 spectra 4 – 6, sample 3 spectra 7 – 9).

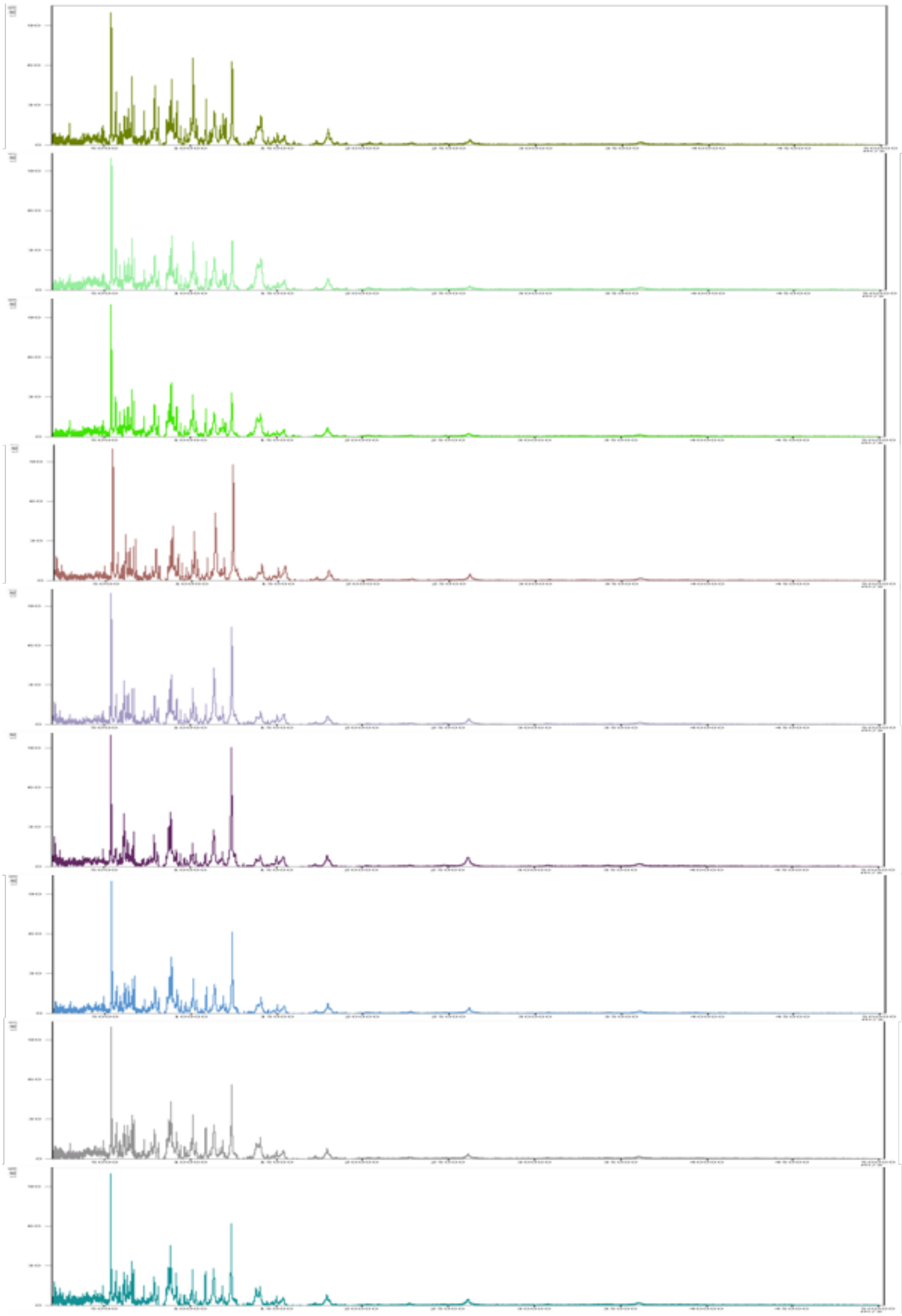

Figure S4. Reproducibility of WM-115 fingerprints (sample 1, spectra 1 – 3; sample 2 spectra 4 – 6, sample 3 spectra 7 – 9).

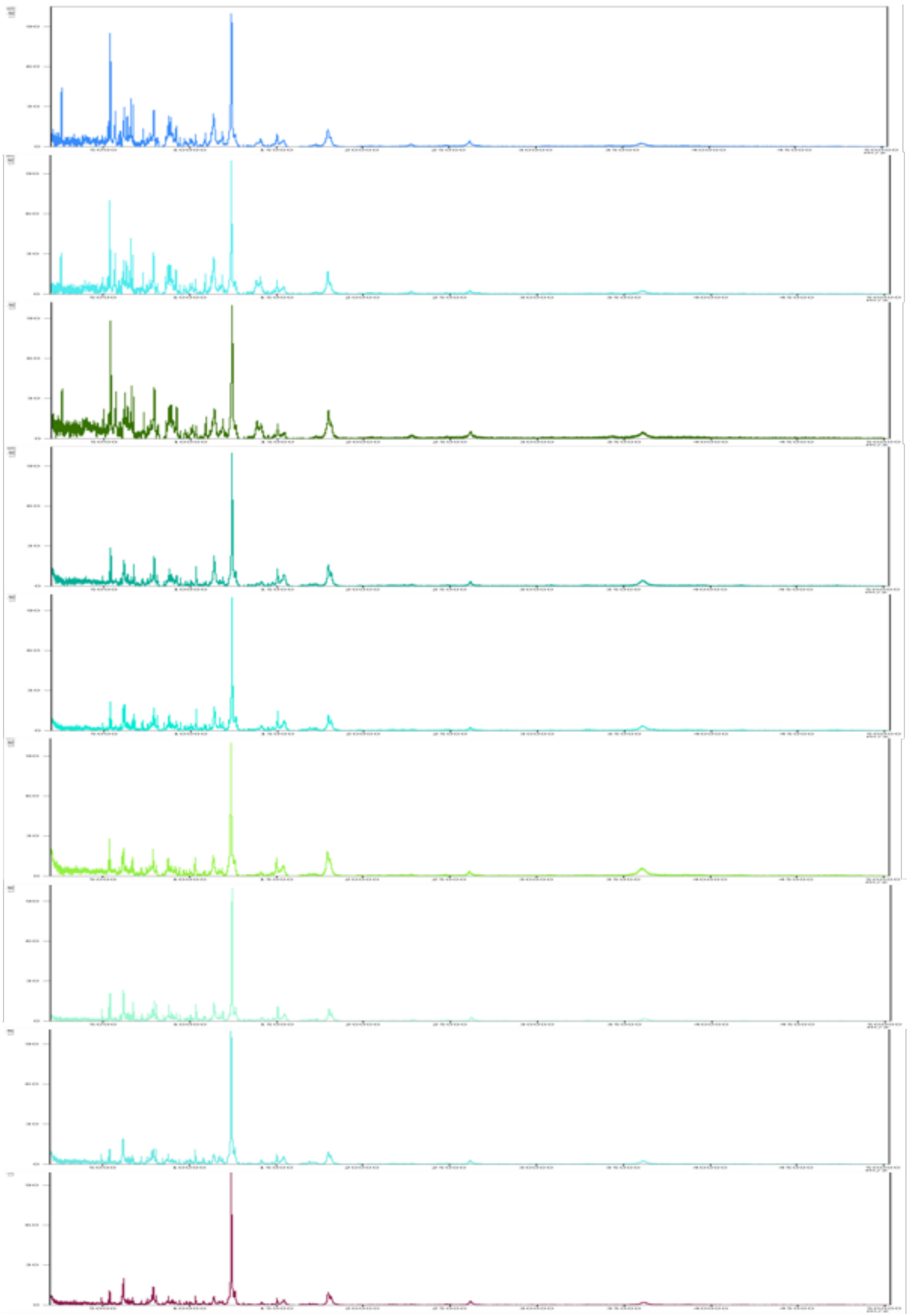

Figure S5. Reproducibility of WM-115 fingerprints (sample 1, spectra 1 – 3; sample 2 spectra 4 – 6, sample 3 spectra 7 – 9).

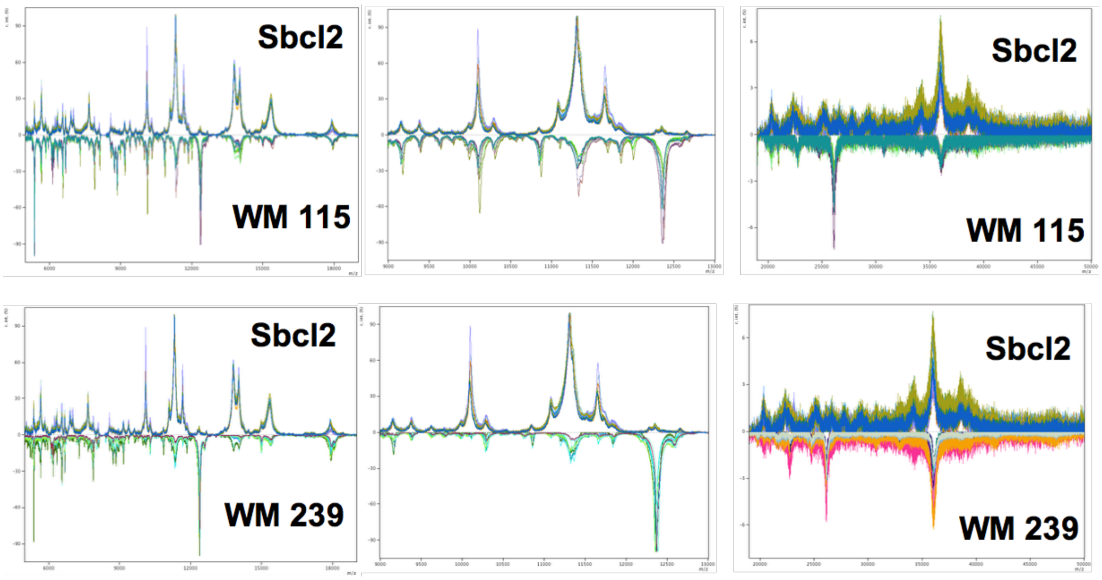

Figure S6. Nine overlapped characteristic MALDI-MS fingerprint spectra obtained for Sbcl2, WM-115 and WM-239 melanoma cell lines representing cancer progression (RGP, VGP and metastatic, respectively). For better visualisation of the obtained MS spectra, the obtained full spectra are separated in 3 *m/z* ranges (i.e. *m/z* intervals from 5000 to 19000, from 9000 to 13000 and from 19000 to 50000). Experimental conditions: methanol/acetone fixation protocol, SA matrix.

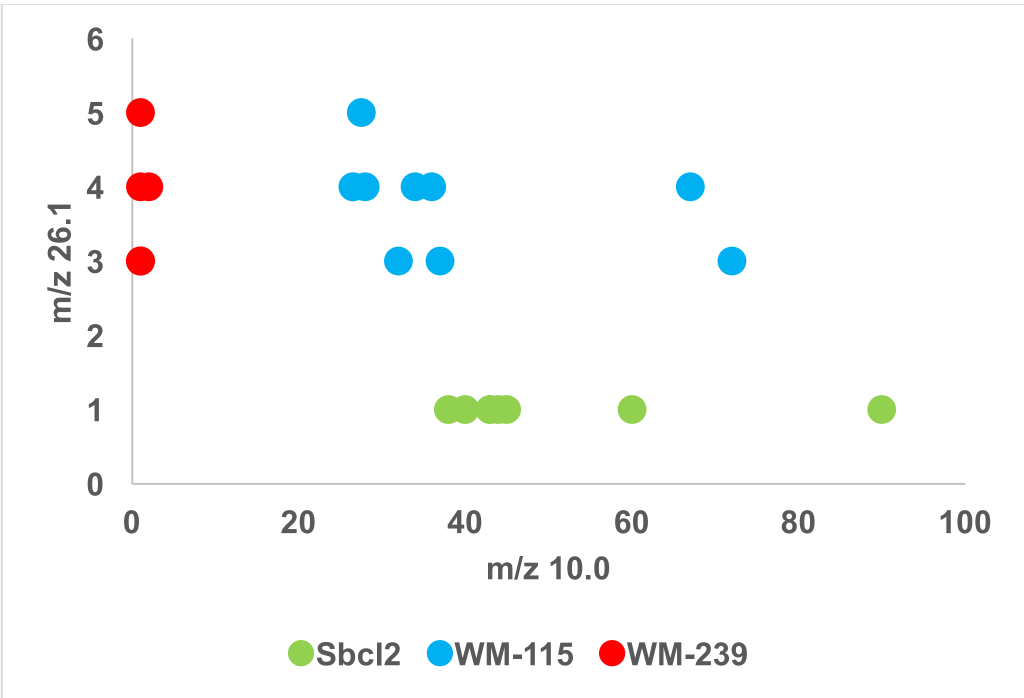

Figure S7. A plot of m/z equal to 26,100 versus m/z equal to 10,000 for Sbcl2, WM-115 and WM-239 melanoma cell lines representing cancer progression (RGP, VGP and metastatic, respectively).

SI-IV. The MS fingerprints of melanoma cells obtained by the intact cell MALDI-MS of cell pellets

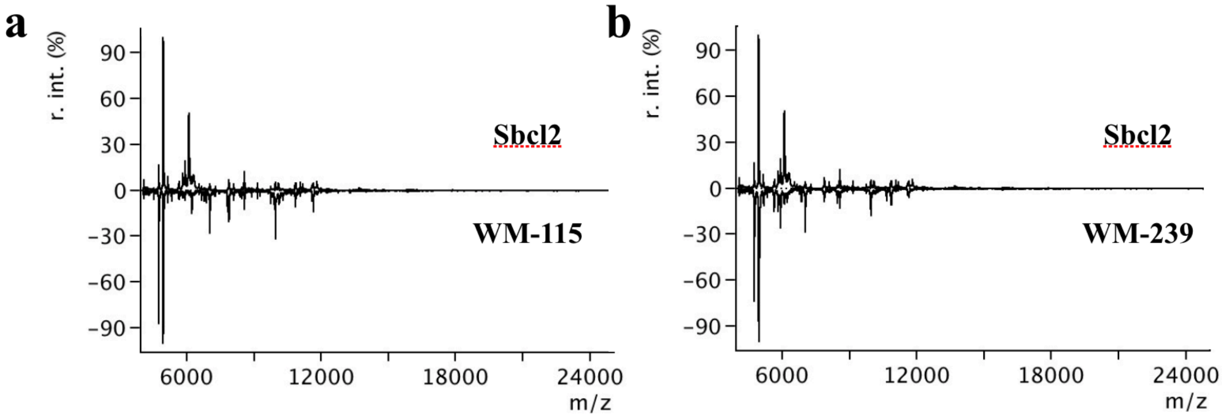

Figure S8. The characteristic MALDI-MS fingerprint spectra obtained for cell pellets of Sbcl2, WM-115 and WM-239 melanoma cell lines representing cancer progression (RGP, VGP and metastatic, respectively). For better visualisation the data are presented as the following pairs: Sbcl2 *vs* WM-115 (a) and Sbcl2 *vs* WM-239 (b). Experimental conditions: 10^4 cells/µL, SA matrix, premixing approach.

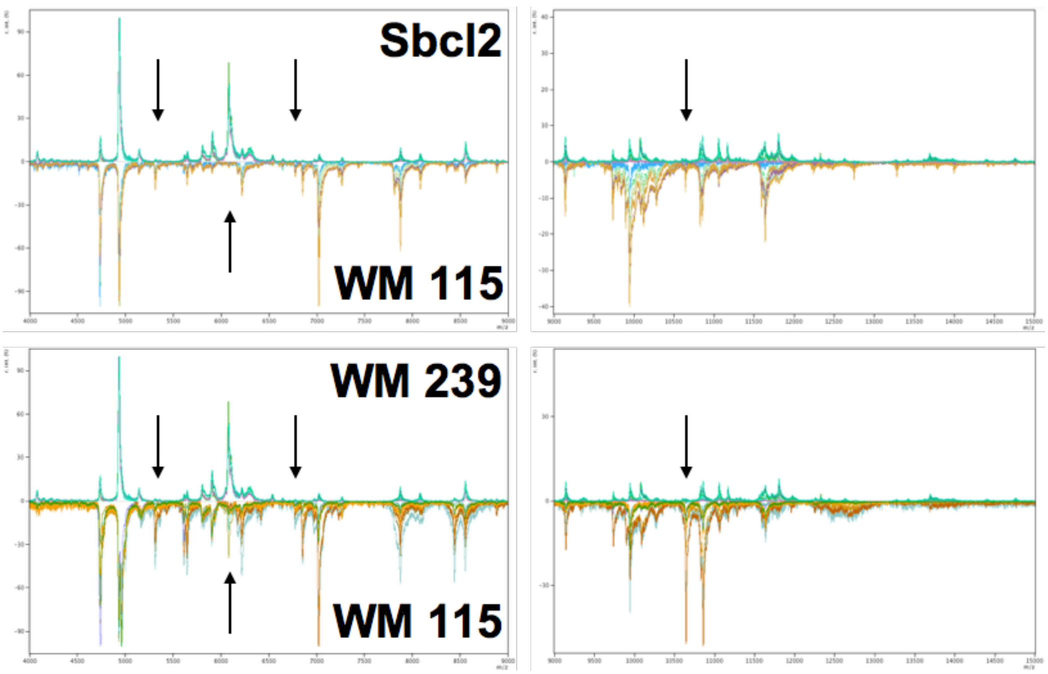

Figure S9. Nine overlapped characteristic MALDI-MS fingerprint spectra obtained for cell pellets of Sbcl2, WM-115 and WM-239 melanoma cell lines representing cancer progression (RGP, VGP and metastatic, respectively). For better visualisation of the obtained MS spectra, the obtained full spectra are separated in 2 *m*/*z* ranges (i.e. *m*/*z* intervals from 4000 to 9000, from and from 9000 to 15000). Experimental conditions: 10^4 cells/µL, SA matrix, premixing approach.