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5-Amino-1*H*-Tetrazole-based Multi-Coloured Smoke Signals Applying the Concept of Fuel Mixes

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Supporting Information

1. Explanation of Triangle Diagrams

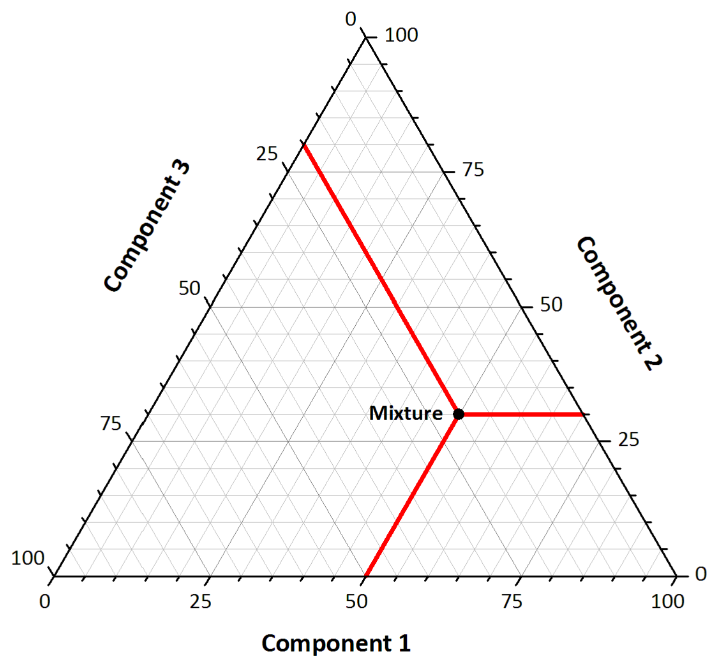

Figure 1: Triangle diagram and how to read it.

The illustration within a triangle diagram (Fig. 1) is a powerful tool to summarize the results of all kind of pyrotechnical formulations. In detail, this diagram includes three axes representing three different components from 0 to 100 %. Every point defines an unique ratio of the components applied. Since the reading direction is unintuitive for diagrams with three axes, it is marked with red lines in Fig. 1 for a mixture containing 50 % of component 1, 30 % of component 2 and 20 % of component 3. Therefore, it is mandatory that the percentages of all three components results in 100 %. The artificial lines at the scale of every axe additionally support the given reading direction. Triangle diagrams offer promising advantages for pyrotechnics. They can discover hidden trends and relationships between different ratios of components, and for this reason, lead quickly to an optimum pyrotechnical formulation. A more detailed explanation and study exercises is given by Kosanke (K. L. Kosanke, B. J. Kosanke, *Selected pyrotechnic publications of K. L. and B. J. Kosanke*, Journal of Pyrotechnics, Whitewater, CO, USA, **1995**).

Testing Protocol

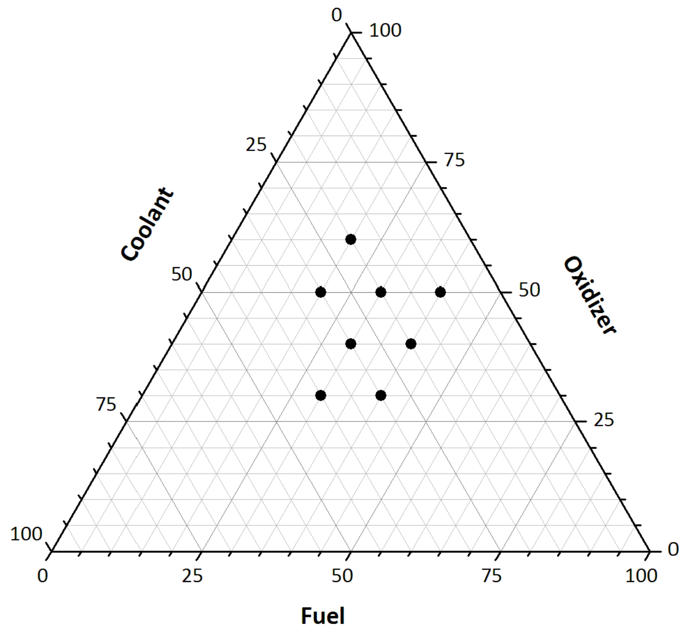

Figure 2: Triangle diagram of initial burning tests.

The testing protocol includes eight preliminary fuel mixes for initial burning tests. Therefore, the resulting smoke formulations have a fixed amount of 30 % dye, while the remaining 70 % is one of the specific fuel mixes consisting of various ratios of oxidizer, fuel and coolant (Figure 2). A more detailed explanation and study exercises is given by Domanico (J. A. Domanico, *Using a Standard Testing Protocol to Qualify Candidate Low Toxicity Colored Smoke Dyes*, 35th International Pyrotechnics Seminar, Fort Collins, CO, USA, **2008**).

2. Aerosol Determination

The arising aerosol of four pellets (2.0 g) per formulation was collected and averaged.

Table 1: Aerosol of yellow-, green, red- and violet-colored smoke formulations based on fuel mixes **FM1**, **FM2**, **FM3** and **Ref-FM**.

	Y1	**Y2**	**Y3**	**G1**	**G2**	**G3**	**Ref-Y**	**Ref-G**
Aerosol /g	0.584	0.418	0.593	0.720	0.486	0.636	0.670	0.642

	R1	**R2**	**R3**	**V1**	**V2**	**V3**	**Ref-R**	**Ref-V**
Aerosol /g	0.499	0.590	0.574	0.575	0.522	0.578	0.729	0.652

3. Smoke Characterization

Table 2: Properties of yellow-, green, red- and violet-colored smoke formulations based on fuel mixes **FM1**, **FM2**, **FM3** and **Ref-FM**.

	BT /s	**BR** /g s^{-1}	**Y** /%	**RH** /%	**T%** /%	m_{HPLC} /mg	**IS** /J	**FS** /N	**ESD** /J	T_{onset} /°C
Y1	15	0.34	29	26	59	354	40	360	1.0	184
Y2	26	0.10	21	23	56	233	40	360	0.4	189
Y3	29	0.10	30	33	49	292	40	360	0.5	187
Ref-Y	13	0.43	33	29	73	435	40	360	0.3	178
G1	20	0.32	36	33	–	–	40	360	0.4	192
G2	45	0.08	24	34	–	–	40	360	0.2	198
G3	31	0.12	31	33	–	–	40	360	0.5	194
Ref-G	19	0.41	32	28	–	–	30	360	0.2	172
R1	20	0.29	29	29	76	457	40	360	0.5	184
R2	75	0.07	25	28	58	351	40	360	0.7	182
R3	41	0.07	28	29	72	432	40	360	0.5	189
Ref-R	21	0.29	36	28	86	514	40	360	0.6	172
V1	23	0.28	29	28	–	–	40	360	0.2	182
V2	27	0.07	26	26	–	–	40	360	0.3	186
V3	27	0.08	29	29	–	–	40	360	0.3	180
Ref-V	15	0.43	32	28	–	–	30	360	0.7	178

Annotation: measured for 2.0 g pellet; BT = burn time; BR = burn rate (10.0 g pellet); Y = yield; RH = relative humidity; T% = transfer rate; m_{HPLC} *= dye content present in aerosol; IS = impact sensitivity; FS = friction sensitivity; ESD = electric discharge sensitivity;* T_{onset} *= onset temperature of decomposition.*

The solution of violet smoke dye mix in acetonitrile already degraded during measurement. A change of the coloured solution was observed within a few hours. The green formulations applying two dyes will be addressed in the future.

4. HPLC strategy

A Thermo Scientific™ DIONEX™ UltiMate™ 3000 HPLC System (accucore RP-MS column (3.0 x 150.0 mm, particle size 2.6 µm) with a DAD-3000 photometer and Chromeleon® 7.2 Chromatography Management Software was used to quantify the amount of dye. The single component devices were: SRD-3400 4-channel Degaser Eluenten-Rack, HPG-3400SD Gradient Pump, WPS-3000TSL (Analytical) Autosampler, TCC-3000SD Column oven.

Mobile Phase: Eluent A = water/acetonitrile (95/5), eluent B = water/acetonitrile (5/95).
Gradient: 0 min (50 % A), 5 min (0 % A), 8 min (0 % A), 14 min (50 % A).
Flow rate: 0.3 mL min^{-1}
Injection volume: 5 µL
DAD: 220 nm, 250 nm, 3D-area: 190–800 nm
Column temperature: 30 °C
Sample temperature: 20 °C

5. Burn rate

Compositions were pressed into cardboard tube for burn rate studies. The cardboard rolls, cylindrical and open on both ends, had a 2.5 cm inner diameter, 3.0 cm height, and a 1.6 mm wall thickness. The compositions (10.0 g) were pressed with a consolidation dead load of 3.0 t for 10.0 s. The pellets were ignited at the top using a resistance heating Kanthal® A1 wire (FeCrAl, 0.8 mm diameter, 2.9 Ω m^{-1}). Upon testing of formulations with 3 g pyrotechnical payload and cylindrical pellet sizes of 1 cm diameter and 2.8 cm height, some of those formulations burned with an open flame and produced no smoke anymore. The so obtained values should be treated with care, since a lot of factors such as the surface, pressure, humidity and the pellet size influence the observed burn rate. Large deviations are obtained for different pellet sizes/payloads (Table 3).

Table 3: Burn rate of yellow-, green, red- and violet-colored smoke formulations based on fuel mixes **FM1**, **FM2**, **FM3** and **Ref-FM**.

	BT /s 10 g pellets	**BR** /g s^{-1} 10 g pellets	**BR** /g s^{-1} 3 g pellets	**BT** /s 3 g pellets
Y1	15	0.34	0.10	25
Y2	26	0.10	flame	n.d.
Y3	29	0.10	flame	n.d.
Ref-Y	13	0.43	0.08	37
G1	20	0.32	0.09	38
G2	45	0.08	n.d.	n.d.
G3	31	0.12	n.d.	n.d.
Ref-G	19	0.41	n.d.	n.d.
R1	20	0.29	n.d.	n.d.
R2	75	0.07	n.d.	n.d.
R3	41	0.07	n.d.	n.d.
Ref-R	21	0.29	n.d.	n.d.
V1	23	0.28	n.d.	n.d.
V2	27	0.07	n.d.	n.d.
V3	27	0.08	n.d.	n.d.
Ref-V	15	0.43	n.d.	n.d.

Annotation: BT = burn time; BR = burn rate, n.d. = not determined, flame = no smoke formation was observed, instead the pellet burned with an open flame.

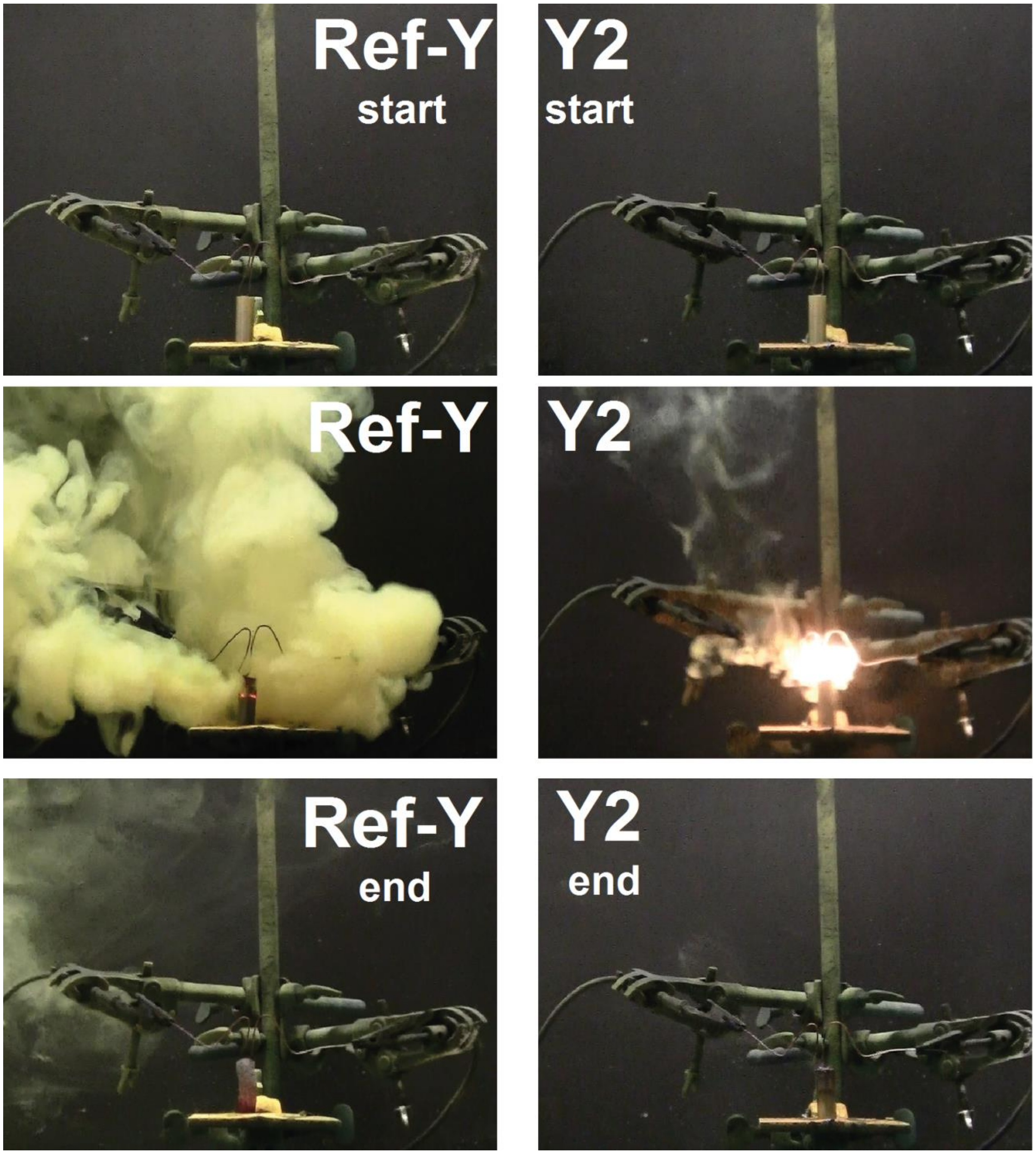

Figure 3: Burning of Ref-Y and Y2 with a pellet size of 3 g.

6. DTA of tested formulations

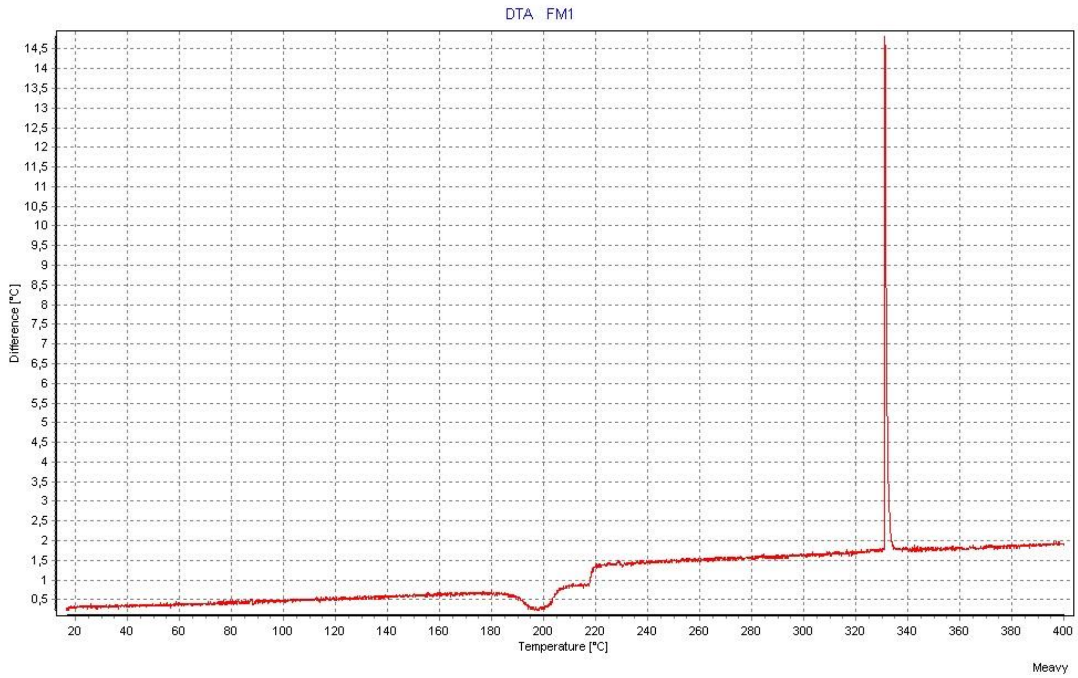

Figure 4: DTA of FM1.

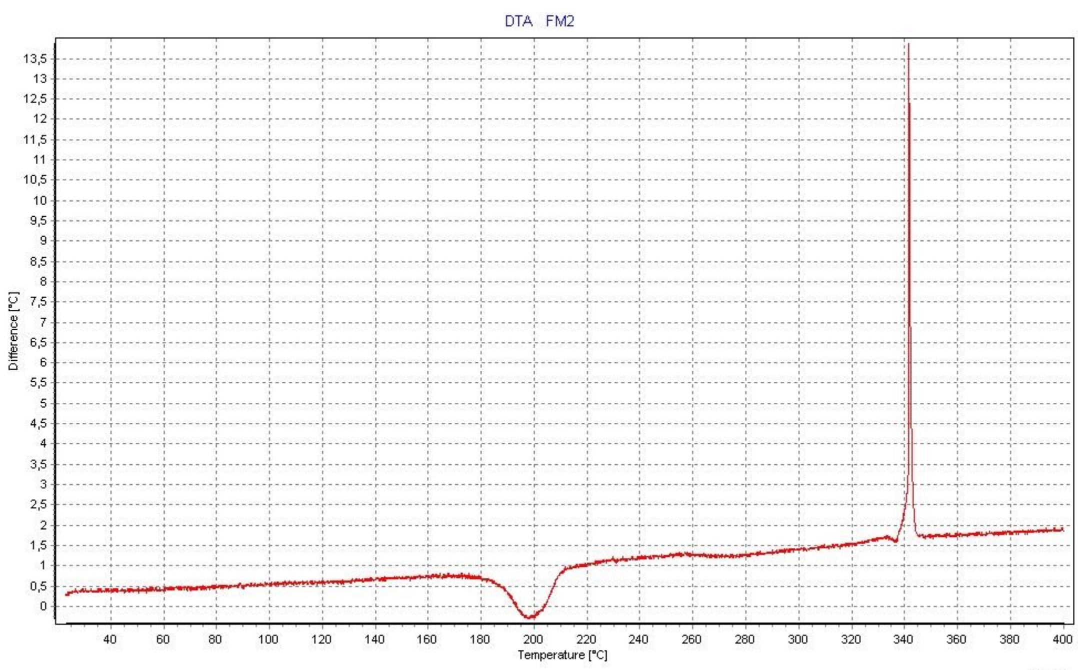

Figure 5: DTA of FM2.

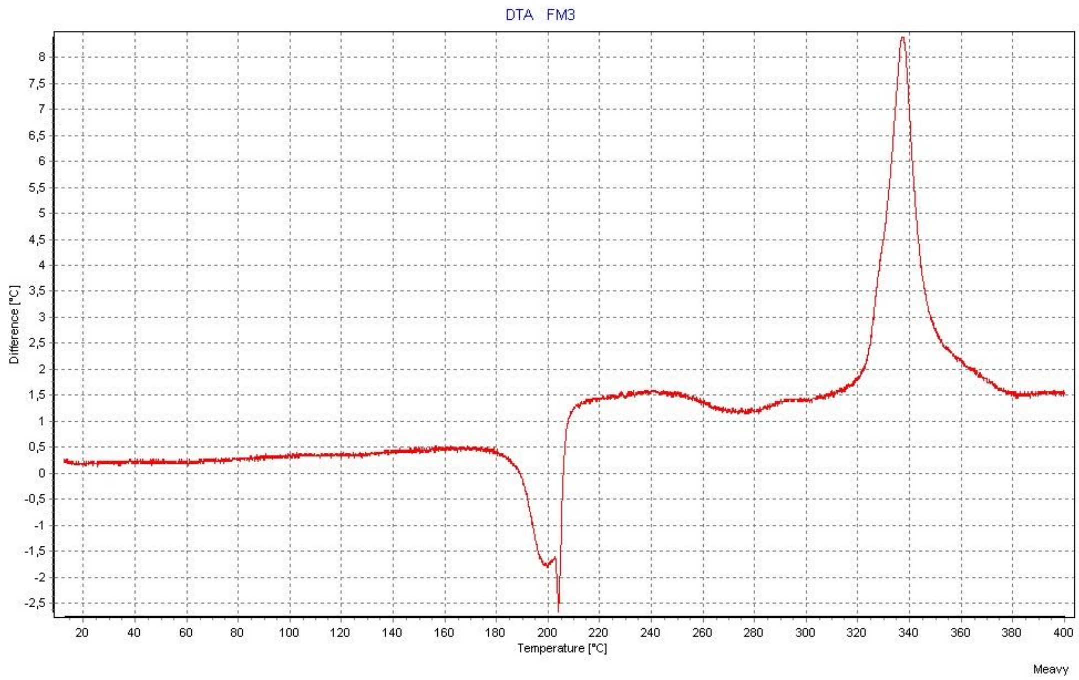

Figure 6: DTA of FM3.

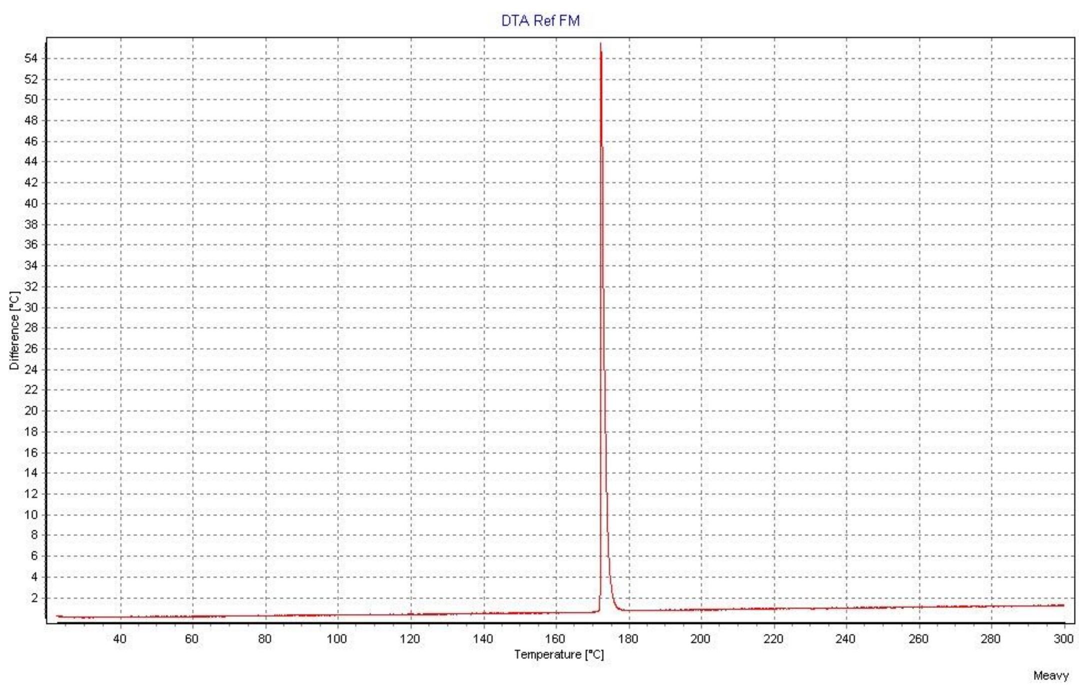

Figure 7: DTA of Ref-FM.

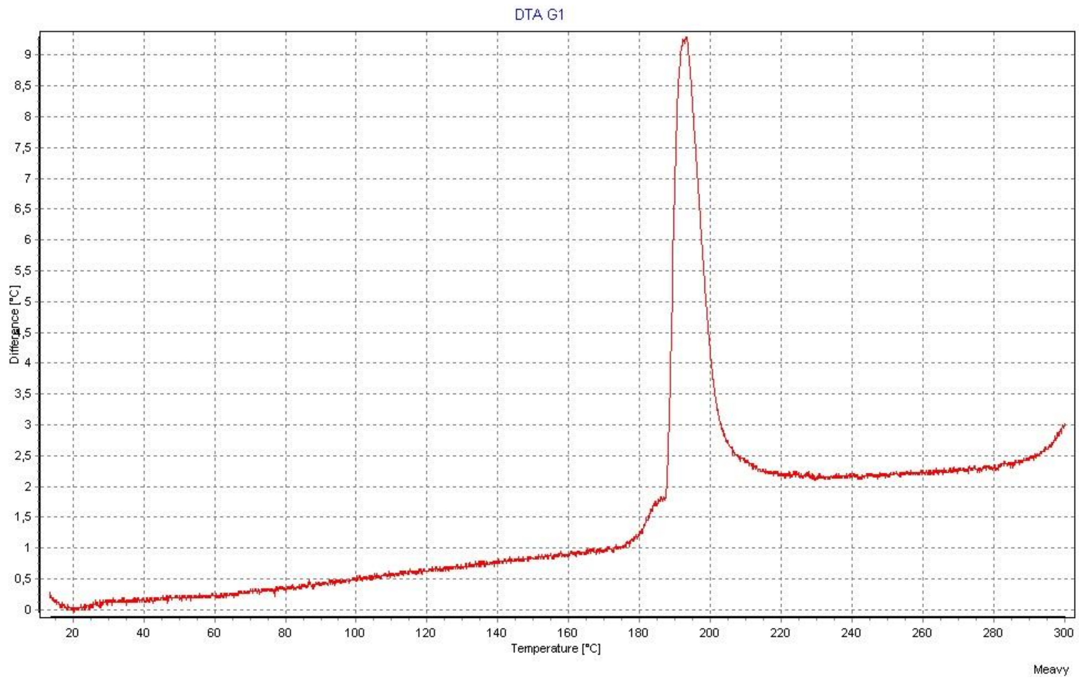

Figure 8: DTA of G1.

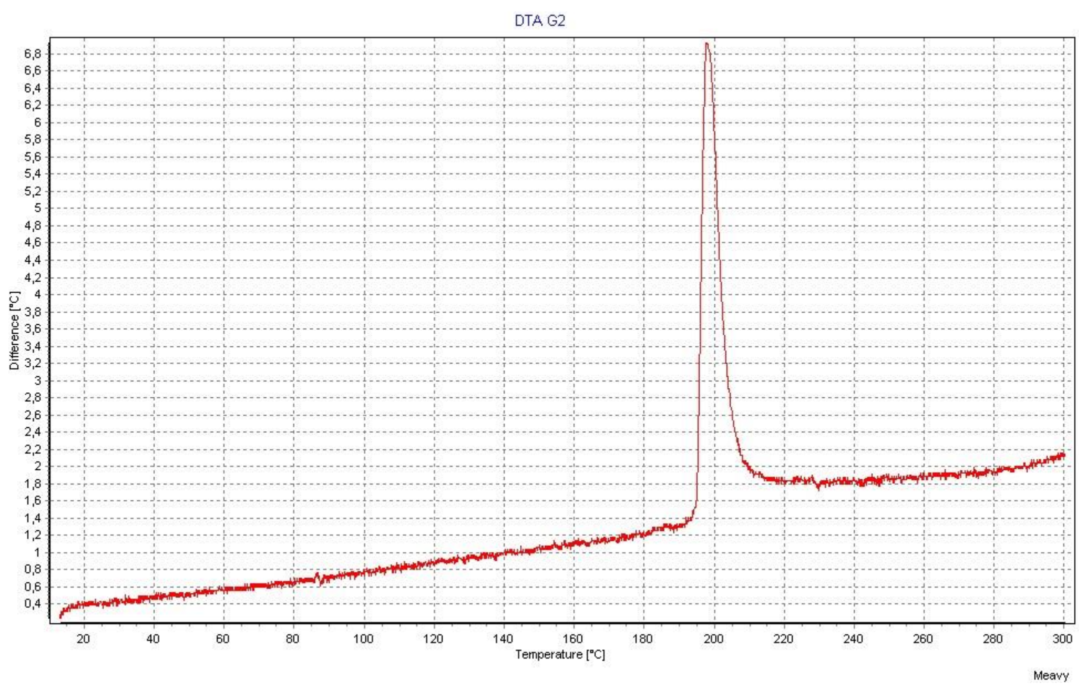

Figure 9: DTA of G2.

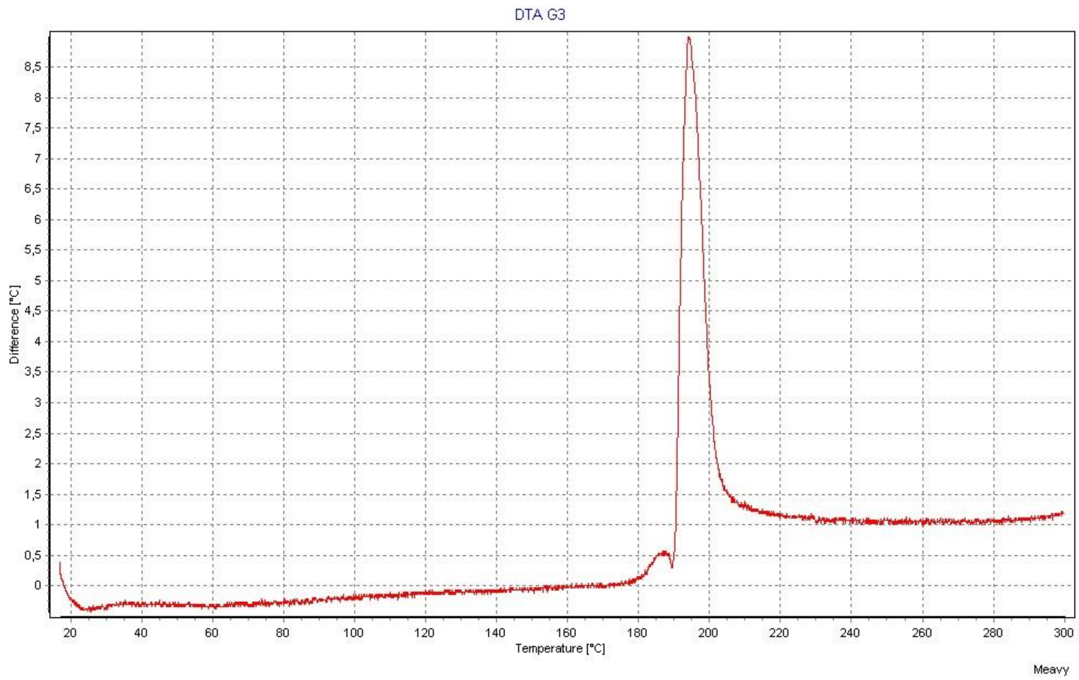

Figure 10: DTA of G3.

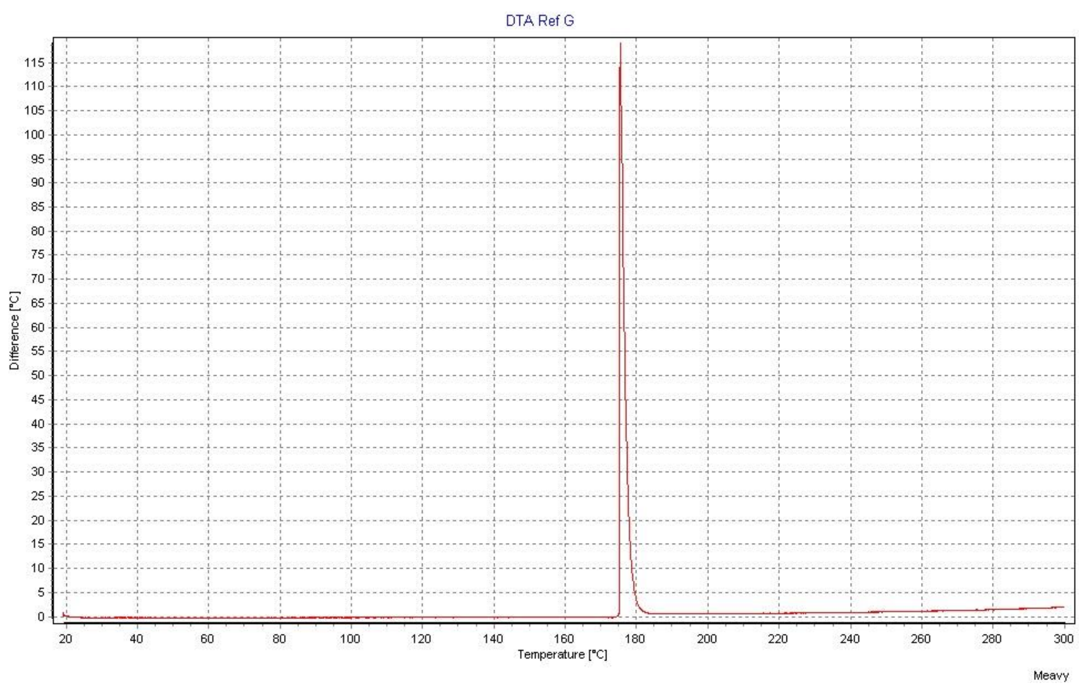

Figure 11: DTA of Ref-G.

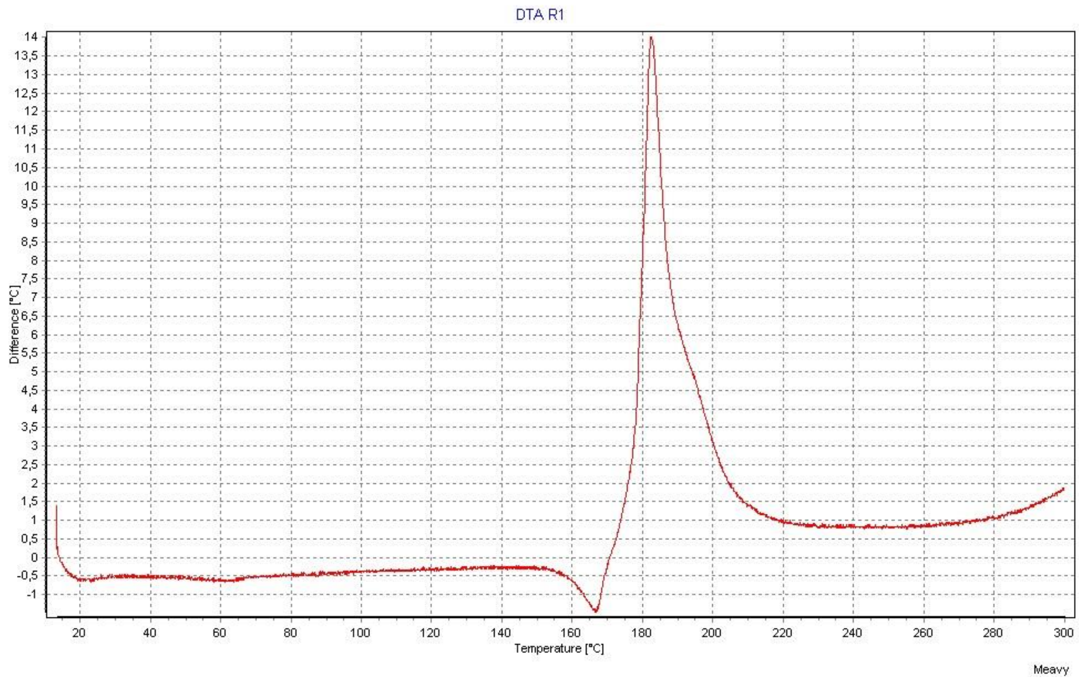

Figure 12: DTA of R1.

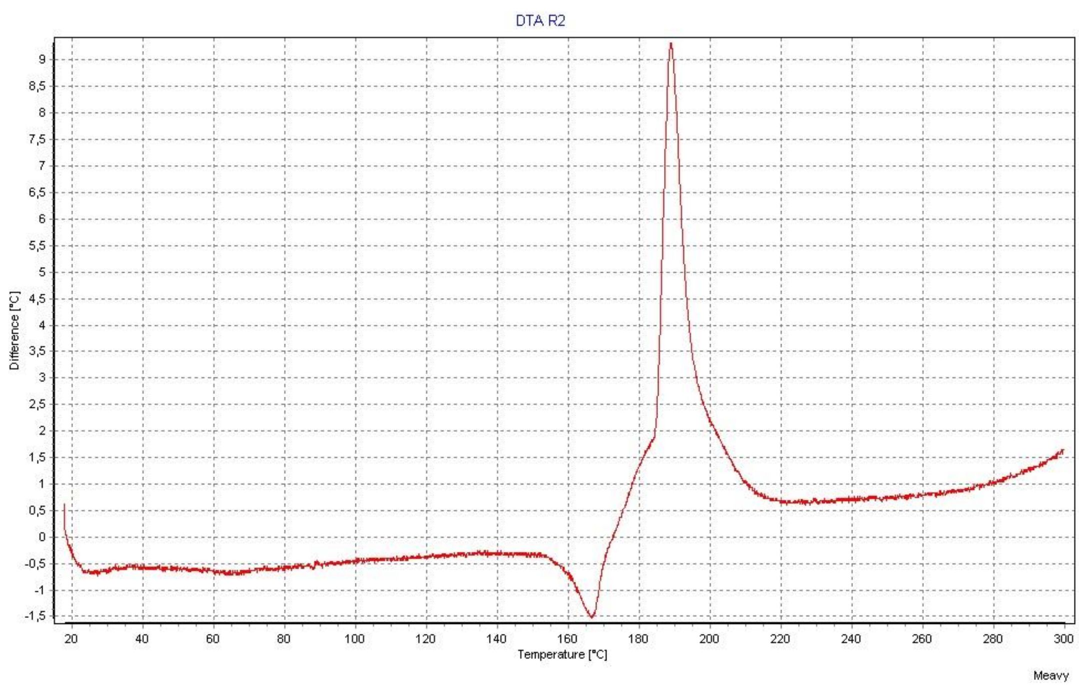

Figure 13: DTA of R2.

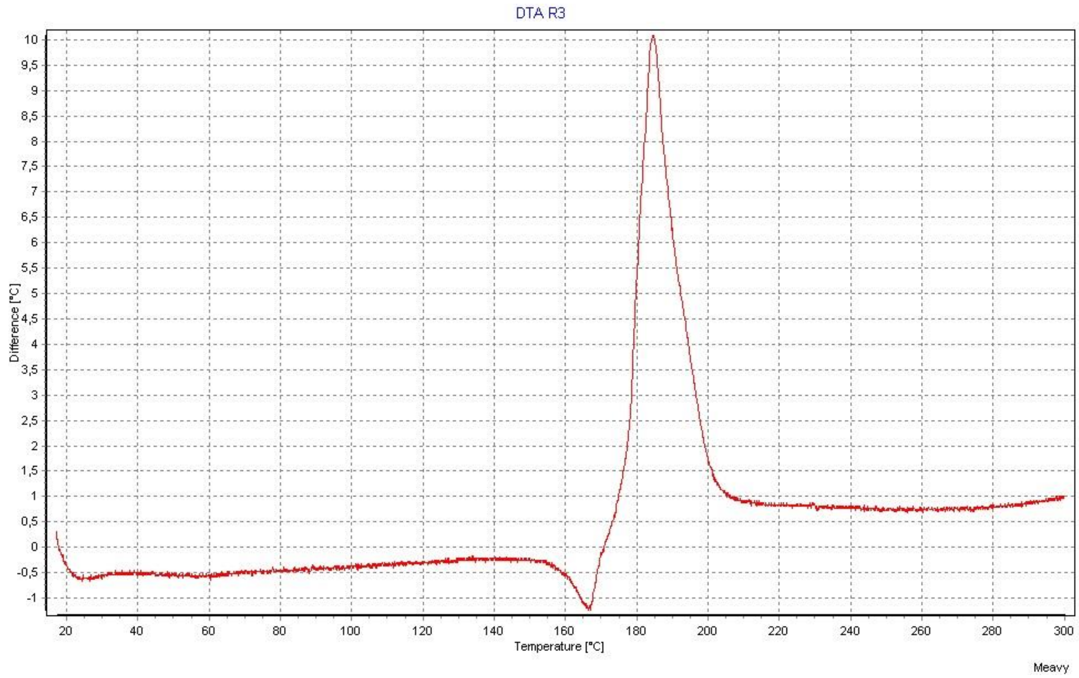

Figure 14: DTA of R3.

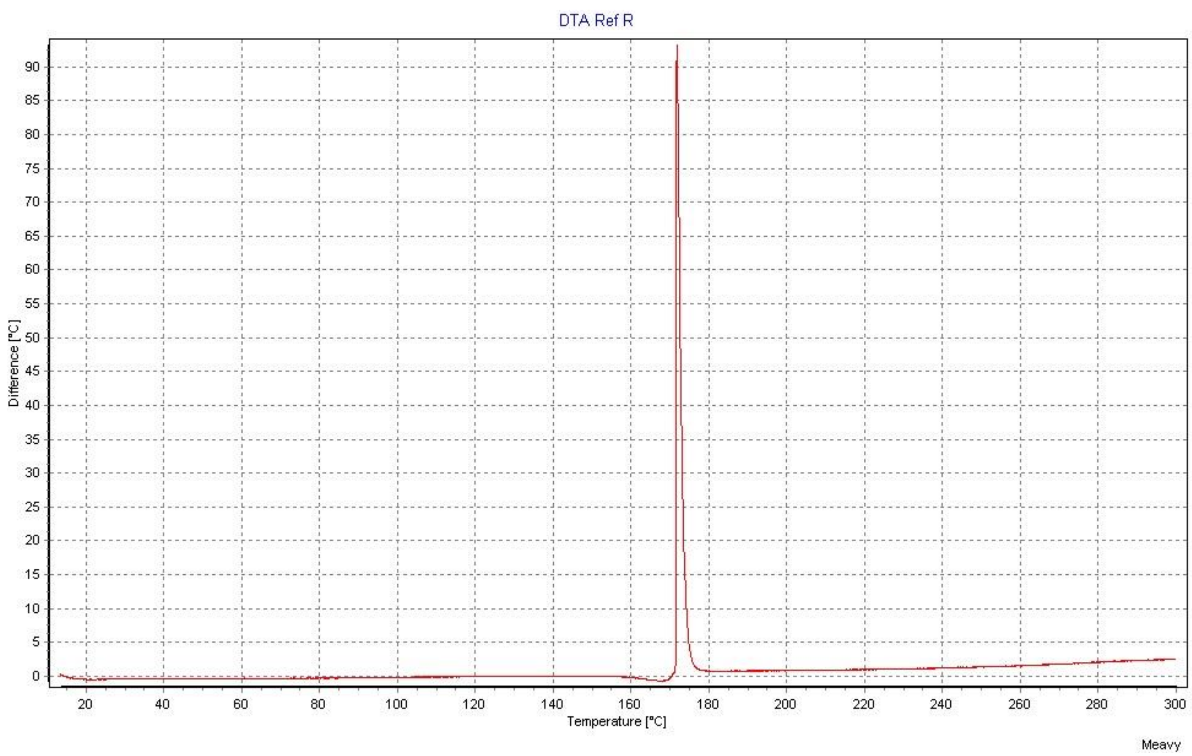

Figure 15: DTA of Ref-R.

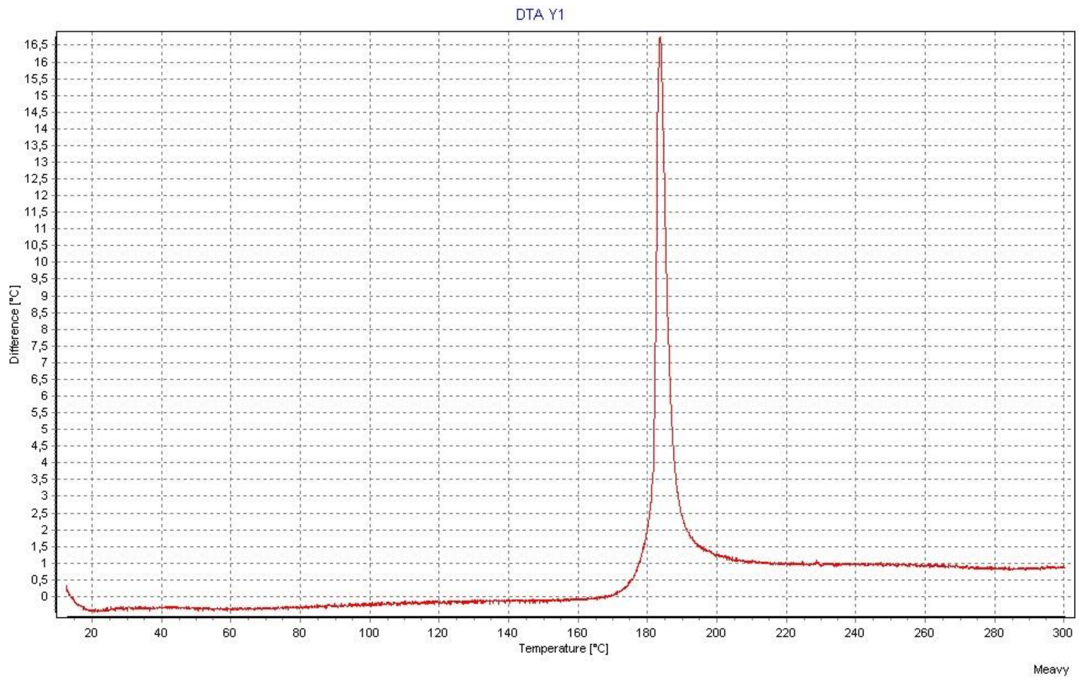

Figure 16: DTA of Y1.

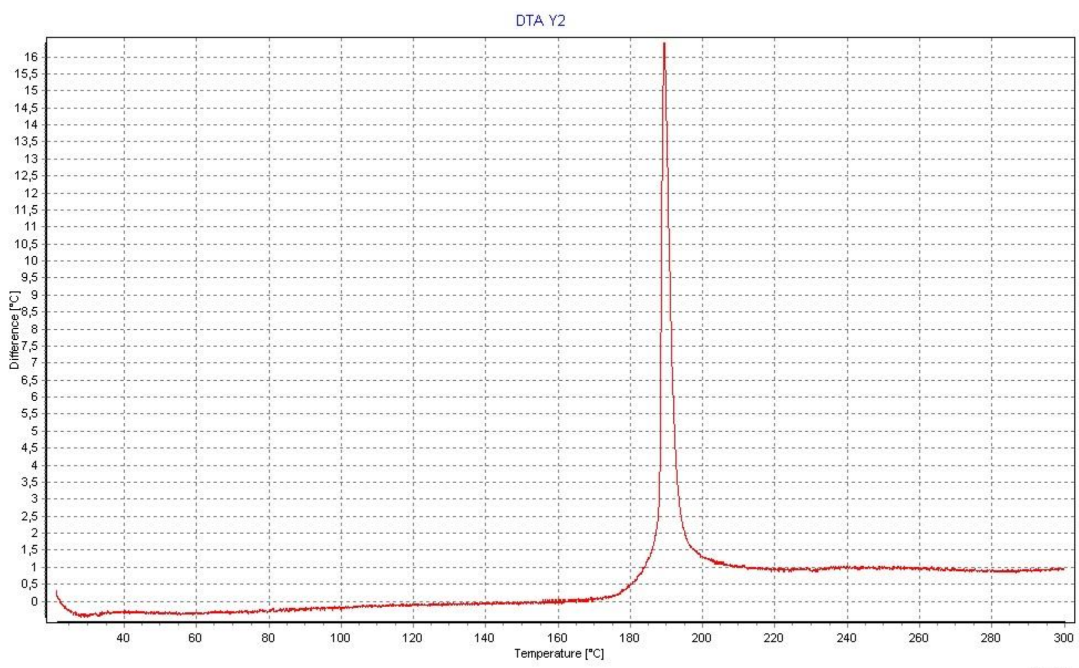

Figure 17: DTA of Y2.

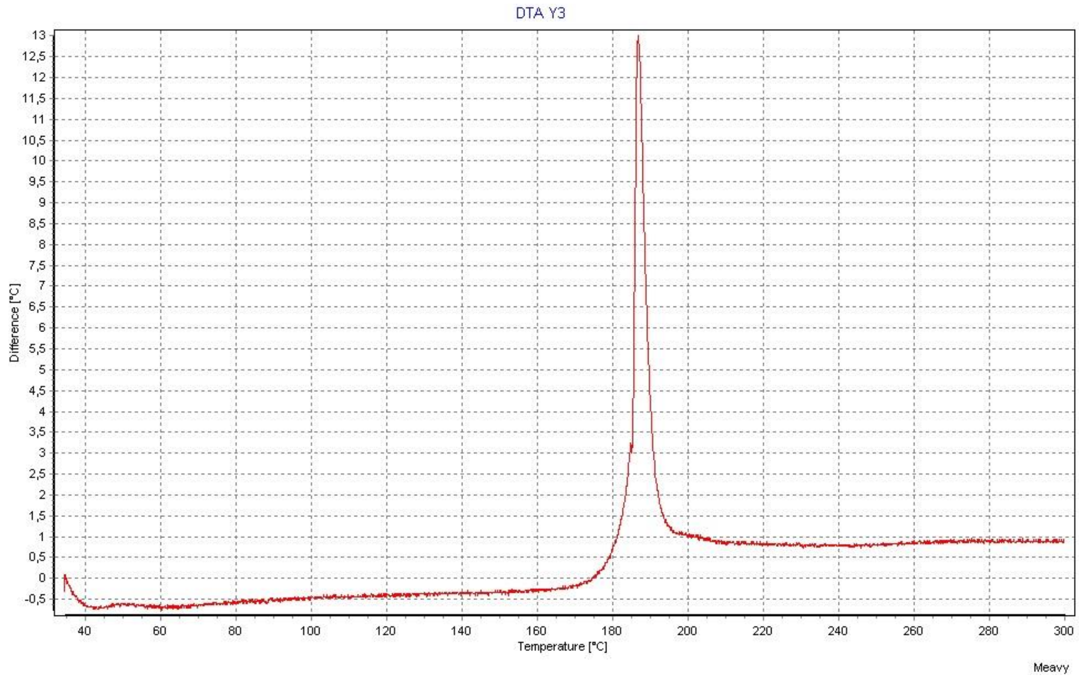

Figure 18: DTA of Y3.

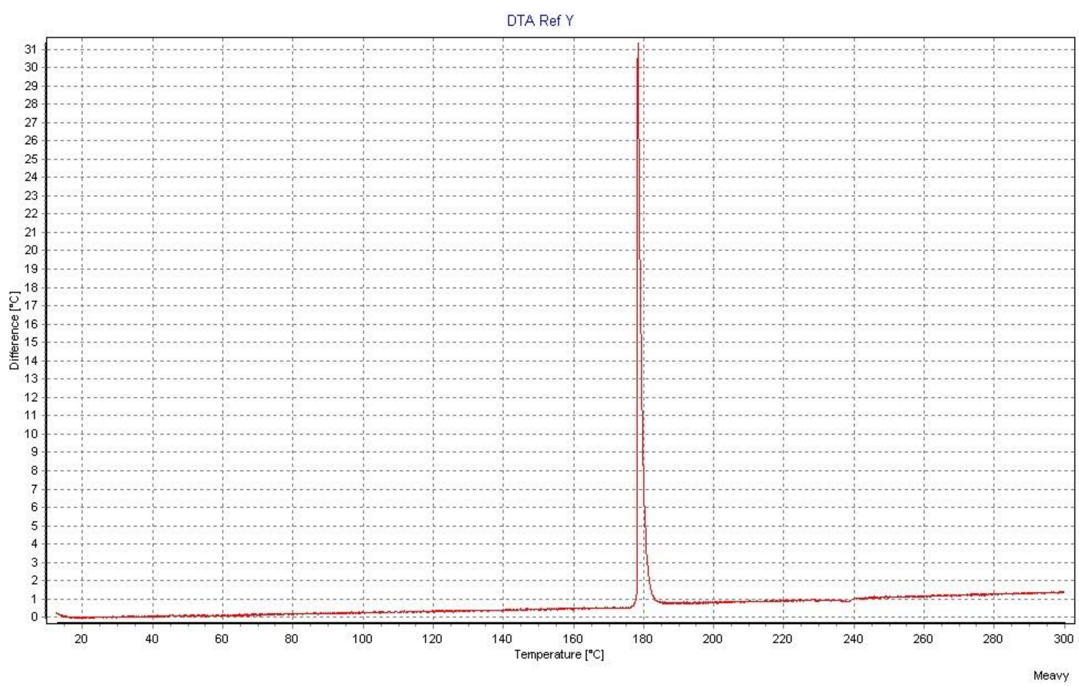

Figure 19: DTA of Ref-Y.

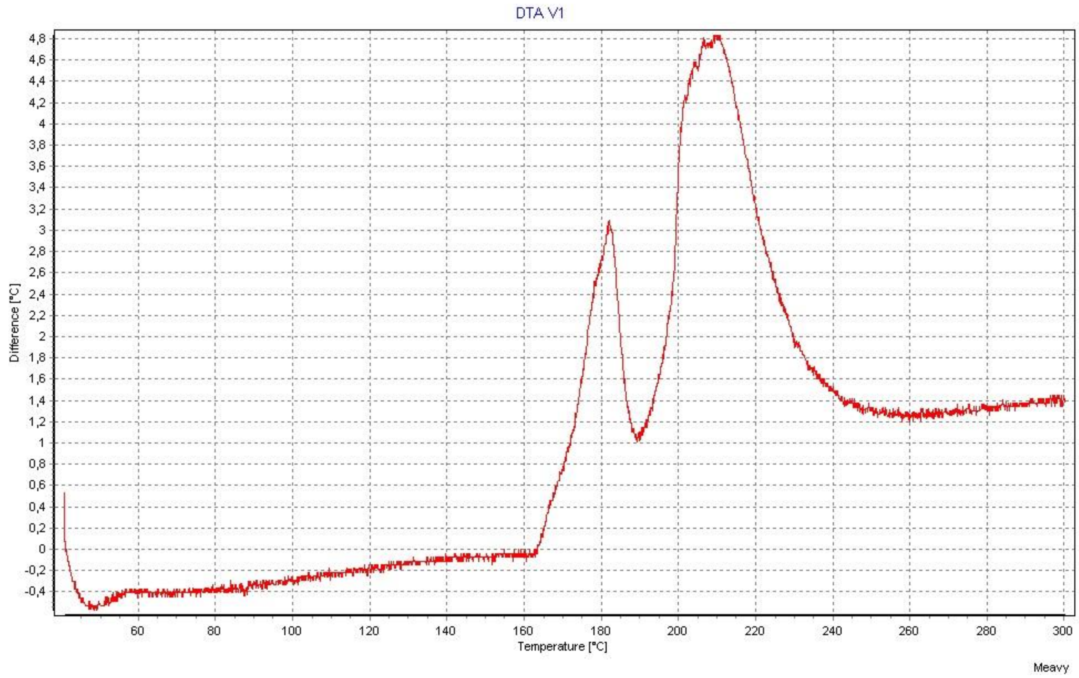

Figure 20: DTA of V1.

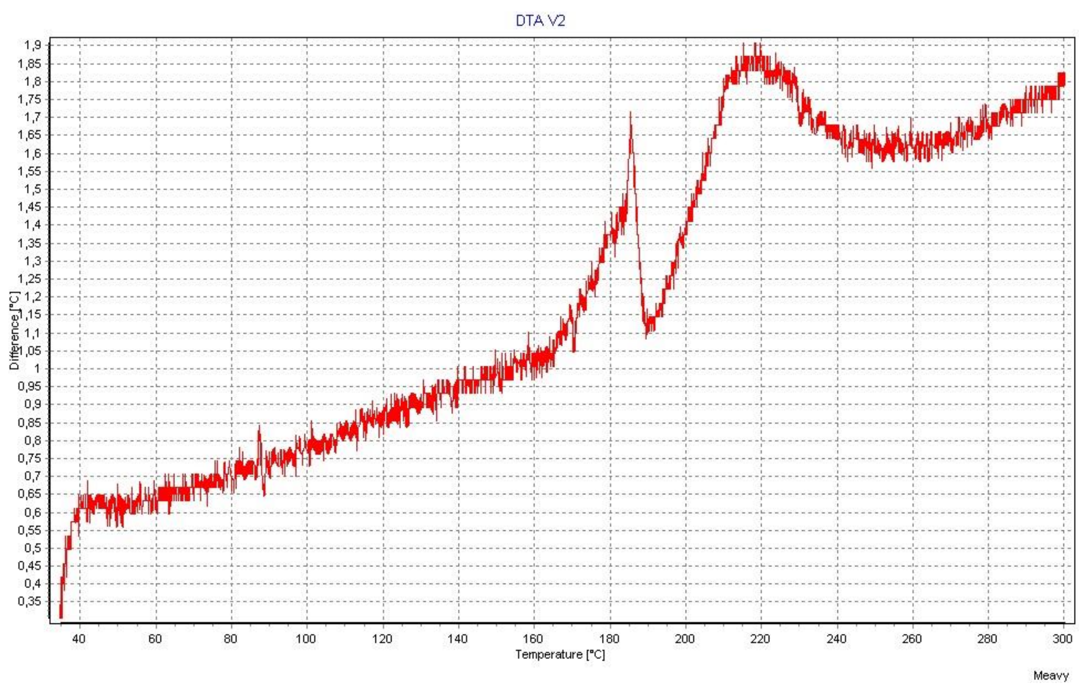

Figure 21: DTA of V2.

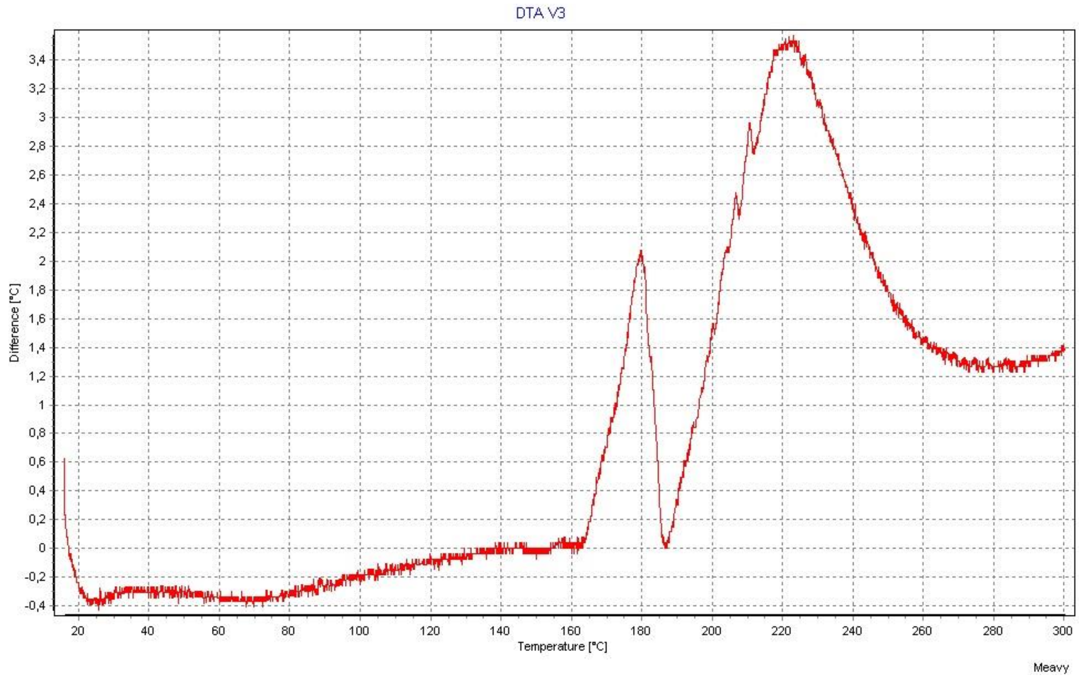

Figure 22: DTA of V3.

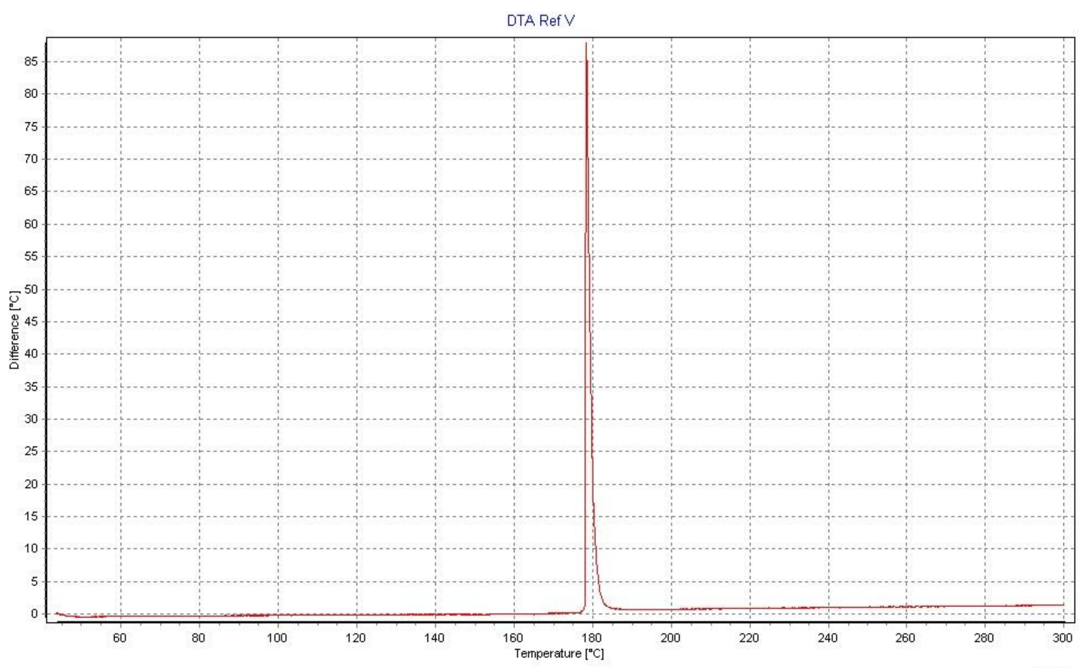

Figure 23: DTA of Ref-V.

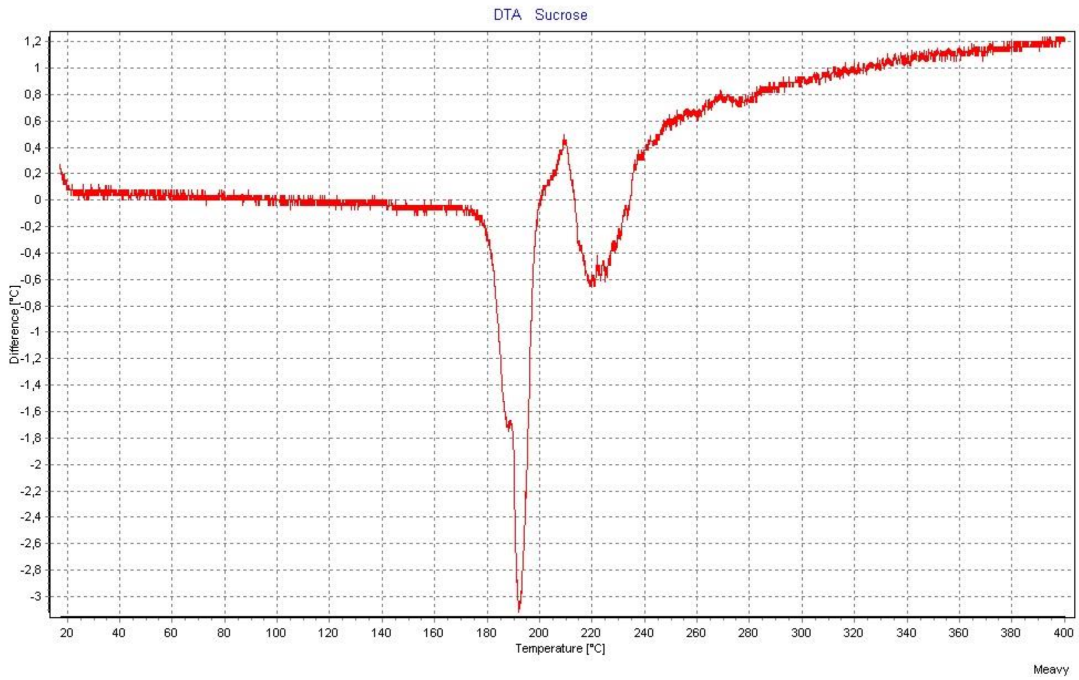

Figure 24: DTA of sucrose.

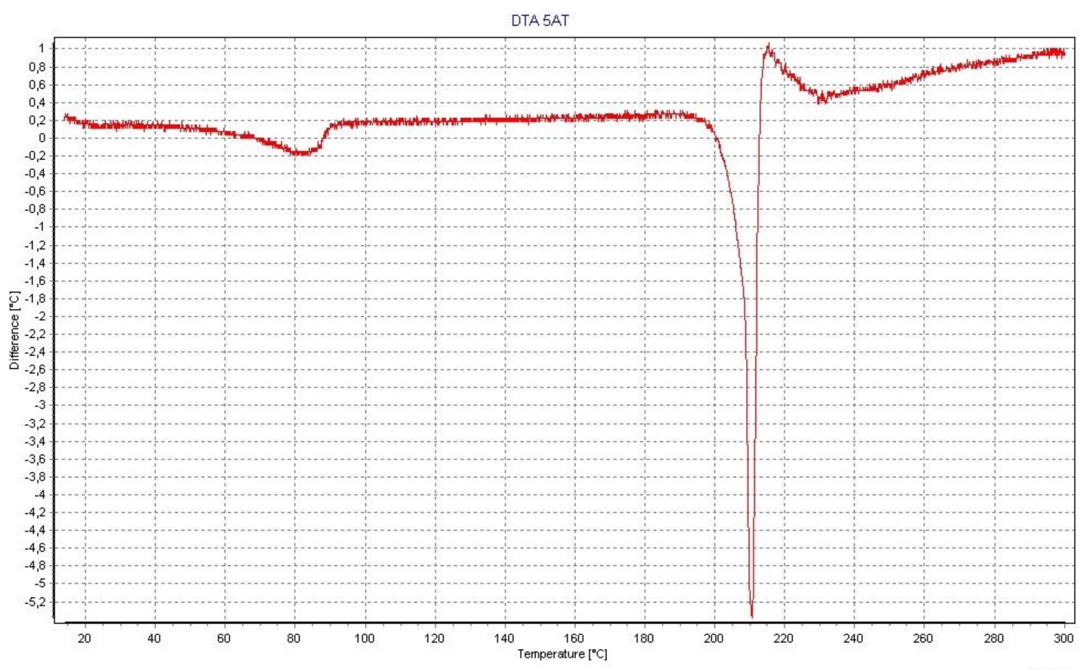

Figure 25: DTA of 5-AT.