

Polycyclic N-Oxides: High Performing, Low Sensitivity Energetic Materials

Supporting Information

Christopher J. Snyder*^a, Lucille A. Wells^a, David E. Chavez^a, Greg H. Imler^b, Damon A. Parrish^b

^(a) *Explosive Science and Shock Physics (M)*
MS C920

Los Alamos National Laboratory
Los Alamos, NM, 87545
csnyder@lanl.gov

^(b) Laboratory for the Structure of Matter
Naval Research Laboratory
4555 Overlook Ave., Washington, D. C. 20375 (USA)

Experimental Procedures and Characterization Data

General. All materials were purchased from commercial suppliers (Fisher, Acros, Aldrich) unless otherwise noted. Analytical thin layer chromatography was performed on precoated Whatman TLC plates with 0.25 mm 60 Å silica gel. Differential Scanning Calorimetry was performed on a TA instruments DSC2926 modulated differential scanning calorimeter. All DSC samples were heated in hermetically sealed aluminum pans at a rate of 10 °C per minute and onset decomposition temperatures were determined when the slope of the trace reached 0.01 W/(g · °C). ¹H and ¹³C NMR spectra were obtained on a Bruker 400 MHz spectrometer and are referenced to an internal standard. Infrared Spectroscopy was performed on a Buck Scientific Model 500 IR Spectrophotometer using KBr. Elemental analyses were performed by Atlantic Microlabs (Norcross, Georgia) or within our own facilities (Elemental analysis was performed using a Perkin Elmer Series II 2400 CHNS/O analyzer).

Caution! *The materials 4, 7 and 8 are explosive materials. Personal protective equipment such as leather or Kevlar gloves, blast shields and safety glasses should be used when working with these materials.*

3-Chloro-6-(3',5'-dimethylpyrazol-1'-yl)-1,2,4,5-tetrazine (1): To a solution 3,6-dichloro-1,2,4,5-tetrazine (3.02 g, 20.0 mmol) in tert-butyl methyl ether (50 mL) is added 2,4,6-collidine (2.422 g, 20.0 mmol). The solution was stirred for 5 minutes. 3,5-Dimethyl pyrazole (1.922 g, 20.0 mmol) was then added portionwise over 5-10 minutes. The reaction mixture was allowed to stir for 30 minutes. The precipitate was filtered, and washed with several portions of hot tert-butyl methyl ether. The filtrate was concentrated to give the product (3.74 g, 89% yield). M. P. 100-102 °C; Decomposition Point 205 °C; ¹H NMR (Acetone-*d*₆) δ (ppm) = 3.22 (s, 3H, CH₃), 2.78 (s, 3H, CH₃), 6.31 (s, 1H, CH); ¹³C NMR (Acetone-*d*₆) δ (ppm) = 12.9 (CH₃), 13.6 (CH₃), 111.8 (dmp-CH), 144.0 (DFP), 153.4, 160.1, 165.6; IR (cm⁻¹) (KBr) = 2928, 1587, 1492 (C=N stretch),

1458 (C=N stretch), 1437, 1396, 1367, 1205, 1148, 1109, 1055, 967, 915, 815, 749 cm^{-1} ; Elemental Analysis calc'd for $\text{C}_7\text{H}_7\text{N}_6\text{Cl}$: C 39.92, H 3.35, N 39.90 %, found: C 39.9, H 3.32, N 39.88%.

(2): To a 100 mL round bottomed flask is added freshly ground potassium carbonate (1.10 g, 8.0 mmol) and anhydrous acetone (15 mL). Difurazanopyrazine (664 mg, 4.00 mmol) was then added and the mixture stirred at ambient temperature. **1** (1.8 g, 8.55 mmol) was then added and the reaction mixture stirred. The reaction was monitored by TLC (1:1 ethyl acetate/hexanes) until the reaction was complete. The reaction was filtered, washed with acetone and concentrated. The residue was triturated with toluene, filtered and air dried to give the product (1.54 g, 75 %). M. P. N/A; Decomposition Point 199 °C. ^1H NMR ($\text{DMSO-}d_6$) δ (ppm) = 2.31(s, 3H, CH_3), 2.67 (s, 3H, CH_3), 6.41 (s, 1H, CH); ^{13}C NMR ($\text{DMSO-}d_6$) δ = 13.53 (CH_3), 14.02 (CH_3), 111.52 (dmp-CH), 143.67, 145.71, 152.25, 157.90, 158.63. IR (KBr) 2926, 2853, 1629, 1583, 1562, 1494 (C=N stretch), 1420, 1387, 1066, 973, 952, 846, 834, 796, 747 cm^{-1} . Elemental Analysis calcd for $\text{C}_{18}\text{H}_{14}\text{N}_{18}\text{O}_2$: C 42.03, H 2.74, N 49.01; found: C 42.05, H 2.71, N 49.03.

(3): To a suspension of **2** (1.5 g, 2.9 mmol) in acetonitrile (30 mL) was bubbled ammonia gas for 10 minutes. The reaction mixture turned dark red and a precipitate begin to form within 5 minutes. The reaction was allowed to stir at ambient temperature for 30 minutes. The slurry was filtered, washed with acetonitrile and air dried to give 825 mg (80%) of the desired product. M.P. N/A; Decomposition Point 261 °C. ^1H NMR ($\text{DMSO-}d_6$) δ (ppm) = 8.6, (s, 1H, NH_2); ^{13}C NMR ($\text{DMSO-}d_6$) δ = 146.31 (DFP), 154.96, 162.93. IR (KBr) 3421(N-H stretch), 3319 (N-H stretch), 3199, 1636, 1578, 1527, 1508 (C=N stretch), 1438, 1385, 1103, 1062, 964, 936, 841 cm^{-1} . Elemental Analysis calcd for $\text{C}_8\text{H}_4\text{N}_{16}\text{O}_2$: C 26.97, H 1.13, N 62.91; found: C 26.99, H 1.10, N 62.93.

(4): To a solution of 90% H_2O_2 (2.26 g, 60.0 mmol) in acetonitrile at 5 °C was added trifluoroacetic anhydride (12.6 g, 60.0 mmol) dropwise over 10 minutes, keeping the reaction temperature below 15 °C. The reaction mixture was stirred 20 minutes at 5 °C, then **3** (1.07 g, 30.0 mmol) was added portionwise as a solid. The reaction mixture was allowed to warm to ambient temperature and stirred 16 hours. The precipitate was filtered and washed with water/acetonitrile to provide 1.0 g (80 %). M.P. N/A; Decomposition Point 228 °C. ^1H NMR ($\text{DMF-}d_6$) δ (ppm) = 9.14 (s, 2H, NH_2); ^{13}C NMR ($\text{DMSO-}d_6$) δ = 145.28, 146.98, 148.19. IR (KBr) 3378 (N-H stretch), 3281, 3244, 3156, 1642, 1627, 1571, 1508 (C=N stretch), 1459, 1396, 1336, 1128, 913, 851 cm^{-1} . Elemental Analysis calcd for $\text{C}_8\text{H}_4\text{N}_{16}\text{O}_6$: C 22.87, H 0.96, N 53.33; found: C 22.88, H 0.99, N 53.30.

(5): To a mixture of 3-Chloro-6-(3',5'-dimethylpyrazol-1'-yl)-1,2,4,5-tetrazine (2.6 g, 12.3 mmol) and difurazano pyrazine (2.04 g, 12.3 mmol) in methylene chloride (30 mL) was added trimethylamine (1.25 g, 12.3 mmol) dropwise over 10 minutes. The reaction mixture turned dark red and a precipitate begin to form within 20 minutes. The reaction was allowed to stir at ambient temperature for 16 hours. The slurry was filtered, washed with methylene chloride and air dried to give 2.72 g (65%) of the desired product. M.P. N/A; Decomposition Point 263 °C. ^1H NMR ($\text{DMSO-}d_6$) δ (ppm) = 2.29, 2.63, 6.38, 12.48, (s, 1H, NH); ^{13}C NMR ($\text{DMSO-}d_6$) δ = 13.5 (CH_3), 13.9 (CH_3), 111.3, 143.4, 144.6, 147.5, 153.0, 157.9, 158.4; IR (KBr) 3588 (N-H stretch), 3118, 2964, 2871, 2782, 1648, 1568, 1494 (C=N stretch), 1428, 1389, 1074, 1054, 977, 950, 836 cm^{-1} . Elemental Analysis calcd for $\text{C}_{11}\text{H}_8\text{N}_{12}\text{O}_2$: C 38.83, H 2.37, N 49.40; found: C 38.80, H 2.40, N 49.38.

(6): Ammonia gas was bubbled into a slurry of DMPTzDFP (3.4 g, 10 mmol) in 50 mL of acetonitrile until the reaction was complete by TLC. The reaction mixture was stirred for an additional 20 minutes, filtered and the filtrate washed with acetonitrile. The red solid was allowed to air dry to give 2.6 g (93%). M.P. N/A; Decomposition Point 241 °C. ¹H NMR (DMSO-*d*₆) δ (ppm) = 7.10 (bs, 4H, NH₂), 8.46 (s, 1H, NH); ¹³C NMR (DMSO-*d*₆) δ = 144.74 (DFP), 155.72, 156.68, 162.81. IR (KBr) 3448 (N-H stretch), 3318 (N-H stretch), 3174, 1535, 1509 (C=N stretch), 1451, 1432, 1399, 1357, 1059, 970, 924, 828 cm⁻¹. Elemental Analysis calcd for C₆H₆N₁₂O₂: C 25.90, H 2.17, N 60.42; found: C 25.91, H 2.19, N 60.39.

(7): To a solution of 90% H₂O₂ (1.51 g, 42.7 mmol) in acetonitrile at 5 °C was added trifluoroacetic anhydride (8.96 g, 42.7 mmol) dropwise over 10 minutes, keeping the reaction temperature below 15 °C. The reaction mixture was stirred 20 minutes at 5 °C, then ATzDFPNH₄ (1.19 g, 4.27 mmol) was added portionwise as a solid. The reaction mixture was allowed to warm to ambient temperature and stirred 16 hours. The precipitate was filtered and washed with water acetonitrile to provide 1.15 g (92 %). M.P. N/A; Decomposition Point 230 °C. ¹H NMR (DMSO-*d*₆) δ (ppm) = 8.85 (s, 2H, NH₂), 12.25 (s, 1H, NH); ¹³C NMR (DMSO-*d*₆) δ = 143.77, 144.83, 146.16, 147.07 IR (KBr) 3552 (N-H stretch), 3482 (N-H stretch), 3422 (N-H stretch), 3300 (N-H stretch), 3140, 3065, 2995, 1653, 1571, 1507 (C=N stretch), 1473, 1452, 1385, 1330, 1277, 1125, 1066, 1015, 928, 839 cm⁻¹. Elemental Analysis calcd for C₆H₃N₁₁O₄: C 24.58, H 1.03, N 52.56; found: C 24.60, H 1.02, N 52.58.

(8): Triethylamine (202 mg, 2.0 mmol), was added to a slurry of **7** (586 mg, 2.0 mmol) in acetonitrile (5 mL) at ambient temperature. The slurry was allowed to react for 15 minutes. 3,6-Dichloro-1,2,4,5-tetrazine (151 mg, 1.0 mmol) was added to the reaction mixture in one portion. The reaction was allowed to stir for 16 hours at ambient temperature. The precipitate was filtered, and washed with acetonitrile to provide 465 mg of product (70%) M.P. N/A; Decomposition Point 226 °C. ¹H NMR (DMF-*d*₆) δ (ppm) = 9.16 (s, 2H, NH₂); ¹³C NMR (DMF-*d*₆) δ = 145.23, 146.48, 147.55, 148.39, 159.46; IR (KBr) 3404 (N-H stretch), 3299, 3236, 3147, 1637, 1560, 1508 (C=N stretch), 1451, 1397, 1330, 1113, 1057 cm⁻¹; Elemental Analysis calcd for C₁₄H₄N₂₆O₈: C 25.31, H 0.61, N 54.82; found: C 25.32, H 0.63, N 54.78.

Single-crystal X-ray Diffraction Analysis

General Considerations

Data collection was performed and the unit cell was initially refined using *APEX3* [v2015.5-2].¹ Data Reduction was performed using *SAINT* [v8.34A]² and *XPREP* [v2014/2]³. Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2014/2].⁴ The structure was solved and refined with the aid of the program *SHELXL-2014/7*.⁵ The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

Single-crystal X-ray Diffraction Analysis of Compound 4.

$C_{14}H_{18}N_{18}O_8$, FW = 566.46, monoclinic, $C2/c$, $a = 11.8361(4) \text{ \AA}$, $b = 11.0288(4) \text{ \AA}$, $c = 17.3634(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 92.3283(10)^\circ$, $\gamma = 90^\circ$, $V = 2264.71(14) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} (150\text{K}) = 1.661 \text{ Mg/m}^3$, $\rho_{\text{calc}} (150\text{K}) = 1.614 \text{ Mg/m}^3$, $\mu = 0.139 \text{ mm}^{-1}$, $F(000) = 1168$, $R_1 = 0.0352$ for 2682 observed ($I > 2\sigma$) reflections and 0.0434 for all 3186 reflections, Goodness-of-fit = 1.045, 183 parameters.

A clear yellow plate crystal of dimensions $0.269 \times 0.251 \times 0.068 \text{ mm}^2$ was mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation ($\lambda = 0.71073$). An Oxford Cobra low temperature device was used to keep the crystals at a constant $150(2)\text{K}$ during data collection.

Single-crystal X-ray Diffraction Analysis of Compound 7.

$C_{10}H_9N_{11}O_6$, FW = 379.28, monoclinic, $P2_1/n$, $a = 5.5158(3) \text{ \AA}$, $b = 9.6613(5) \text{ \AA}$, $c = 27.7811(14) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 93.635(2)^\circ$, $\gamma = 90^\circ$, $V = 1477.47(13) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} (293\text{K}) = 1.705 \text{ Mg/m}^3$, $\mu = 1.254 \text{ mm}^{-1}$, $F(000) = 776$, $R_1 = 0.0621$ for 3101 observed ($I > 2\sigma$) reflections and 0.0700 for all 3431 reflections, Goodness-of-fit = 1.101, 246 parameters.

A clear yellow plate crystal of dimensions $0.238 \times 0.179 \times 0.052 \text{ mm}$ was mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation ($\lambda = 0.71073$). Data was collected at room temperature (20°C).

Single-crystal X-ray Diffraction Analysis of Compound 8.

$C_{26}H_{32}N_{30}O_{12}$, FW = 956.81, triclinic, $P-1$, $a = 9.5919(4) \text{ \AA}$, $b = 12.8830(6) \text{ \AA}$, $c = 17.5266(8) \text{ \AA}$, $\alpha = 100.2430(10)^\circ$, $\beta = 96.5340(10)^\circ$, $\gamma = 101.589(2)^\circ$, $V = 2062.57(16) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} (293\text{K}) =$

1.541 Mg/m³, $\mu = 0.126 \text{ mm}^{-1}$, $F(000) = 988$, $R_1 = 0.0704$ for 3845 observed ($I > 2\sigma$) reflections and 0.1455 for all 7482 reflections, Goodness-of-fit = 1.043, 723 parameters.

A clear orange needle crystal of dimensions 0.227 x 0.077 x 0.062 mm was mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK $_{\alpha}$ radiation ($\lambda = 0.71073$). Data was collected at room temperature (20°C).

References

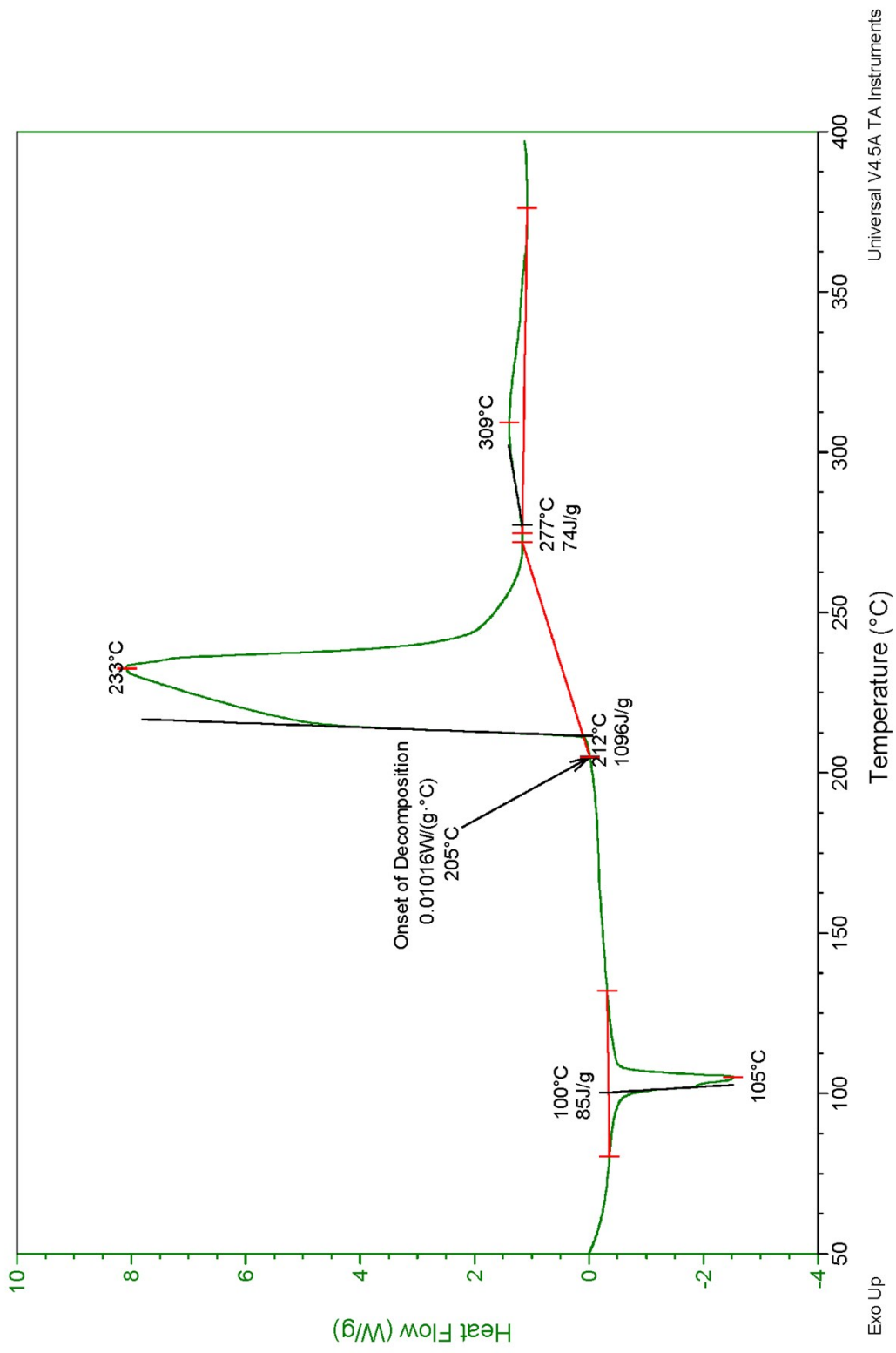
1. Bruker (2015). APEX3 v2015.5-2. Bruker AXS Inc., Madison, Wisconsin, USA.
2. Bruker (2013). SAINT v8.34A. Bruker AXS Inc., Madison, Wisconsin, USA.
3. Bruker (2014). XPREP v2014/2. Bruker AXS Inc., Madison, Wisconsin, USA.
4. Bruker (2014). SADABS v2014/5, Bruker AXS Inc., Madison, Wisconsin, USA.
5. Sheldrick, G. M. (2014). SHELXL-2014/7. University of Göttingen, Germany.

Differential Scanning Calorimetry for Compounds 1-8

File: C:\...52696 Quick Run Chavez\DMPTzCl.001
Operator: H.Tian
Run Date: 04-Jan-2018 17:56
Instrument: DSC Q2000 V24.11 Build 124

DSC

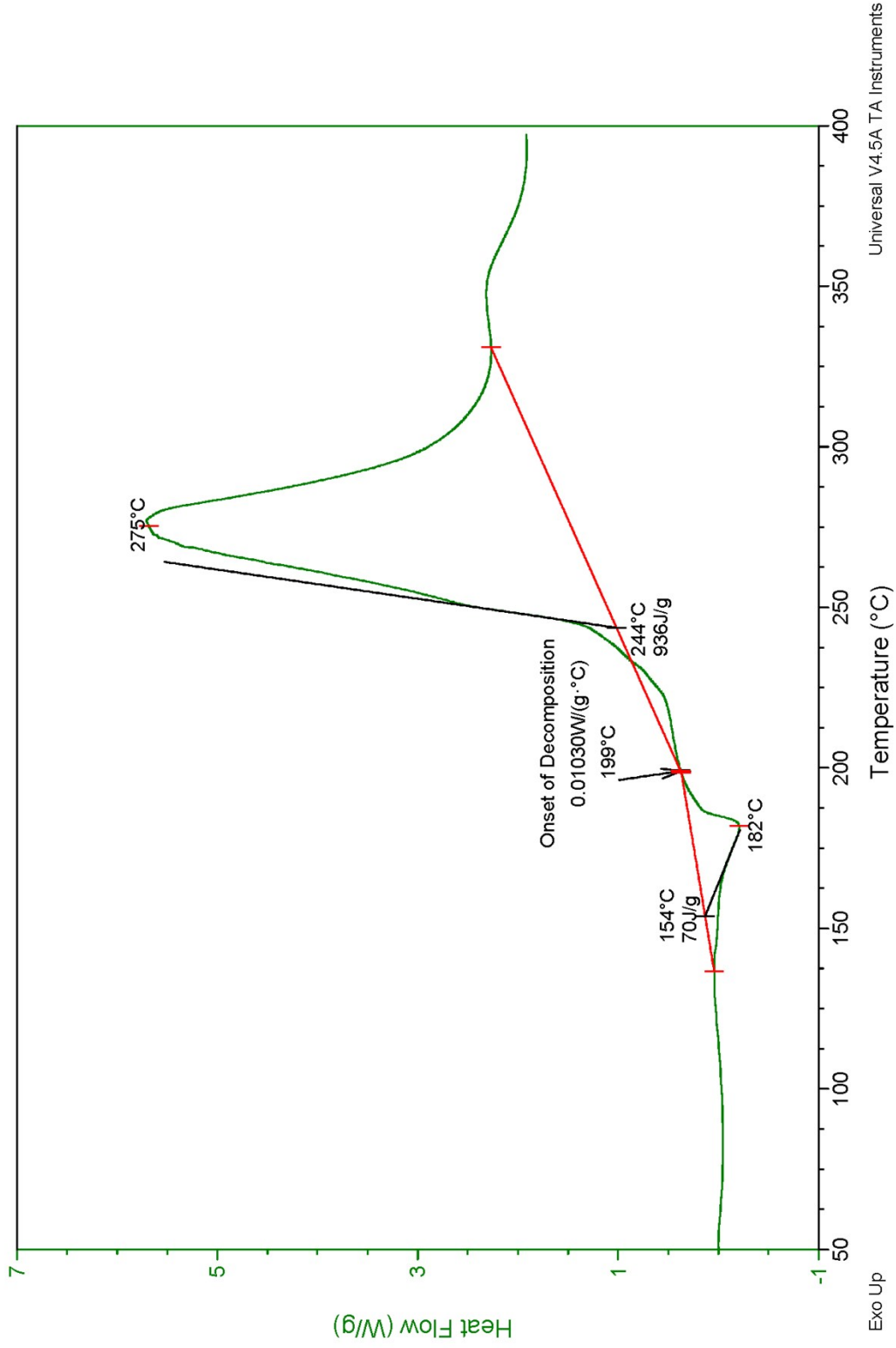
Sample: Compound 1
Size: 0.3210 mg
Method: 10C Ramp



Sample: Compound 2
Size: 0.4130 mg
Method: 10C Ramp

DSC

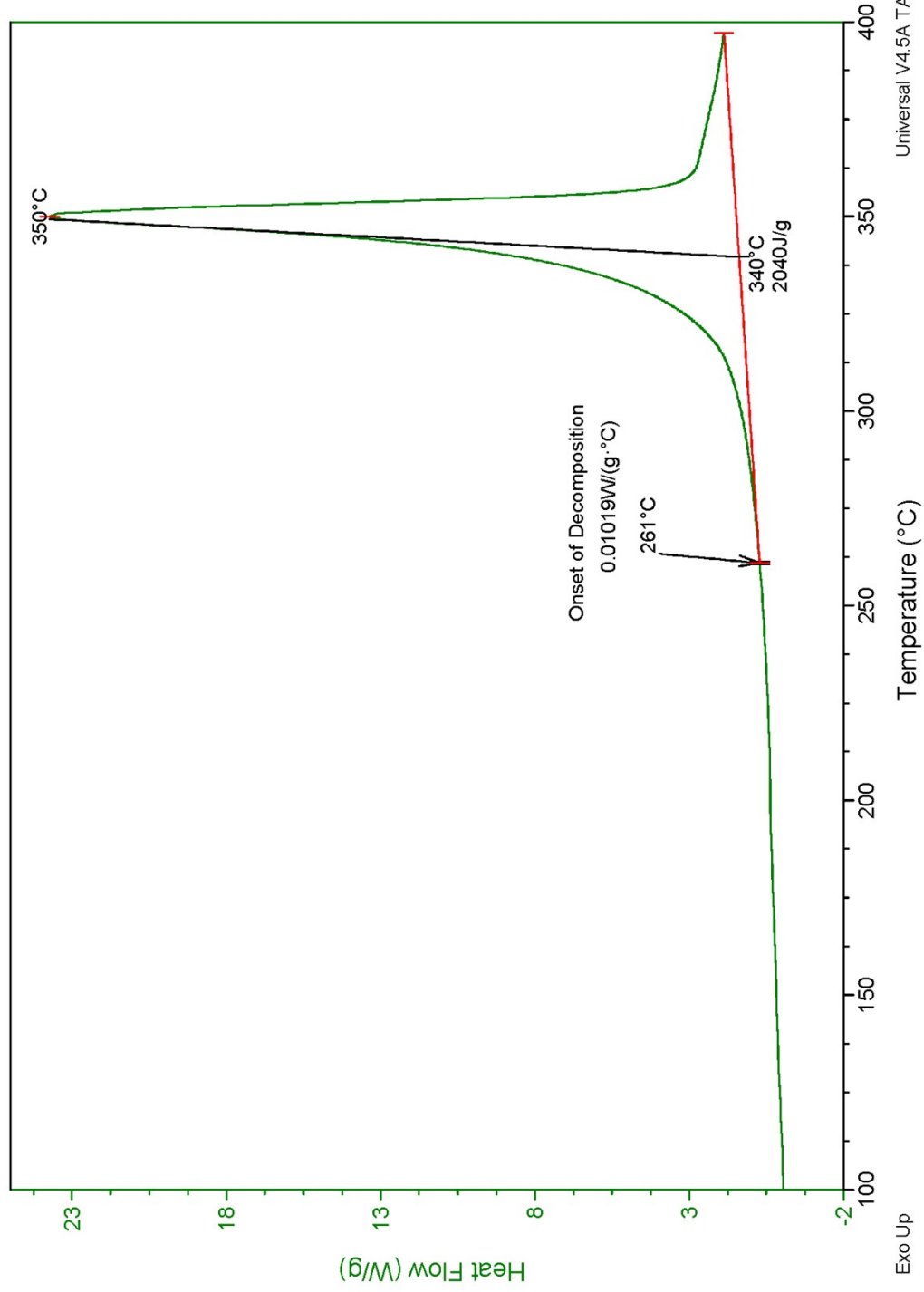
File: C:\...\52582 DEC\DMPTz\2DFP.001
Operator: H.Tian
Run Date: 24-Jul-2017 18:23
Instrument: DSC Q2000 V24.11 Build 124



Sample: Compound 3
Size: 0.4260 mg
Method: 10C Ramp

DSC

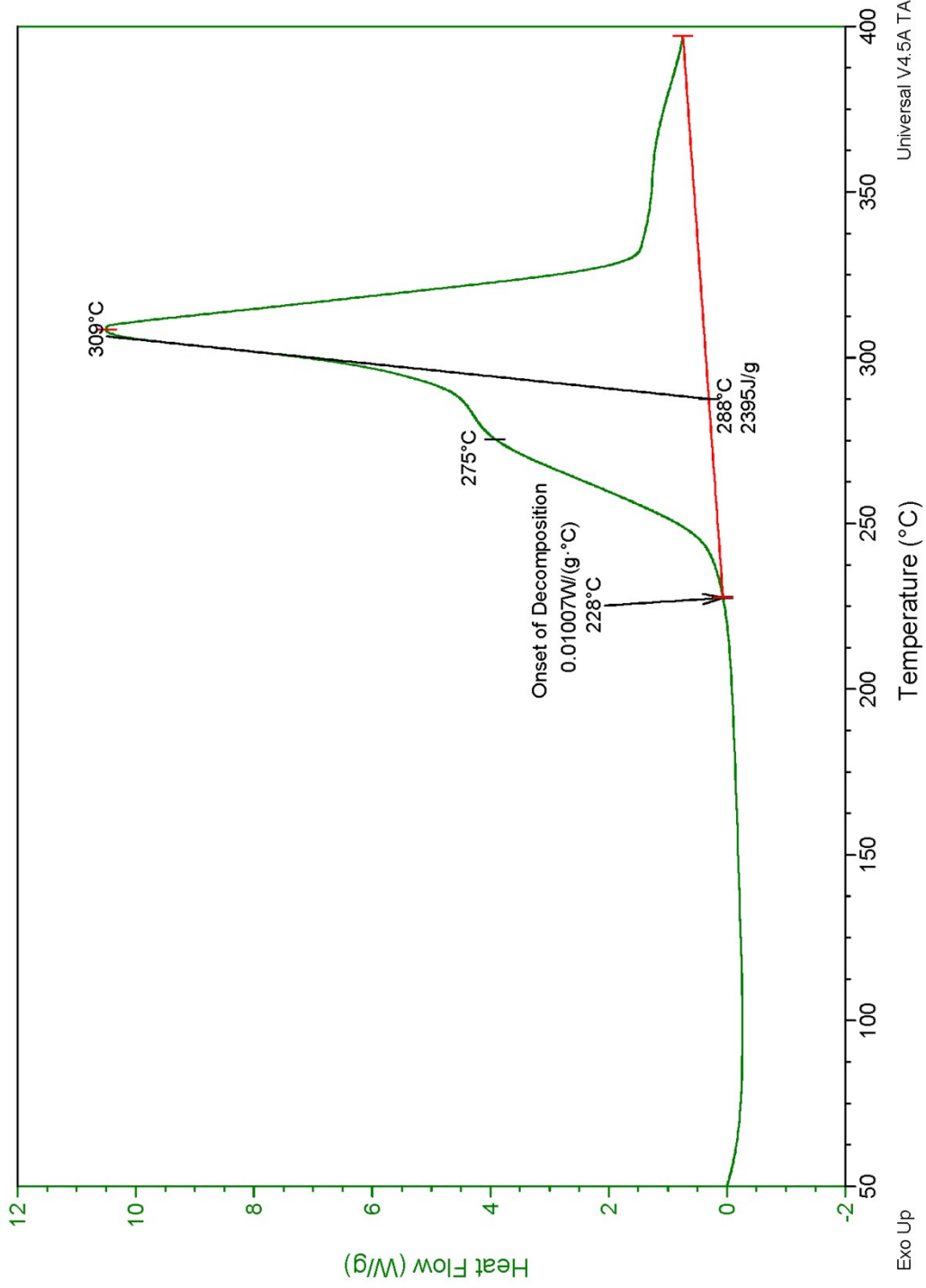
File: C:\...\DSC Q-2000\52582 DEC\DATDFP.001
Operator: H.Tian
Run Date: 24-Jul-2017 19:13
Instrument: DSC Q2000 V24.11 Build 124



Sample: Compound 4
Size: 0.5290 mg
Method: 10C Ramp

DSC

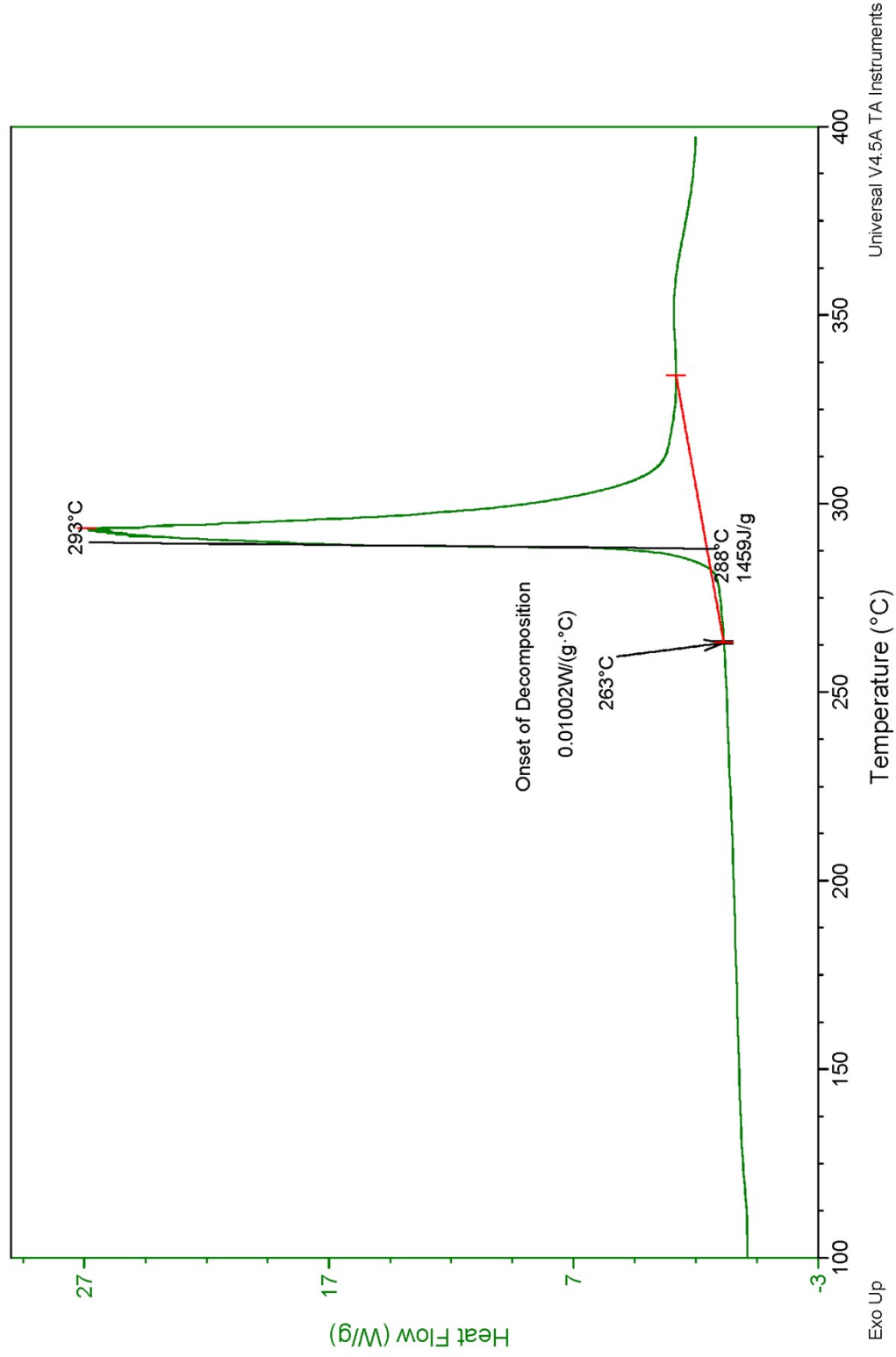
File: C:\...\52677 Chavez\BATDFPTO.001
Operator: H.Tian
Run Date: 28-Nov-2017 14:30
Instrument: DSC Q2000 V24.11 Build 124



Sample: Compound 5
Size: 0.3920 mg
Method: 10C Ramp

DSC

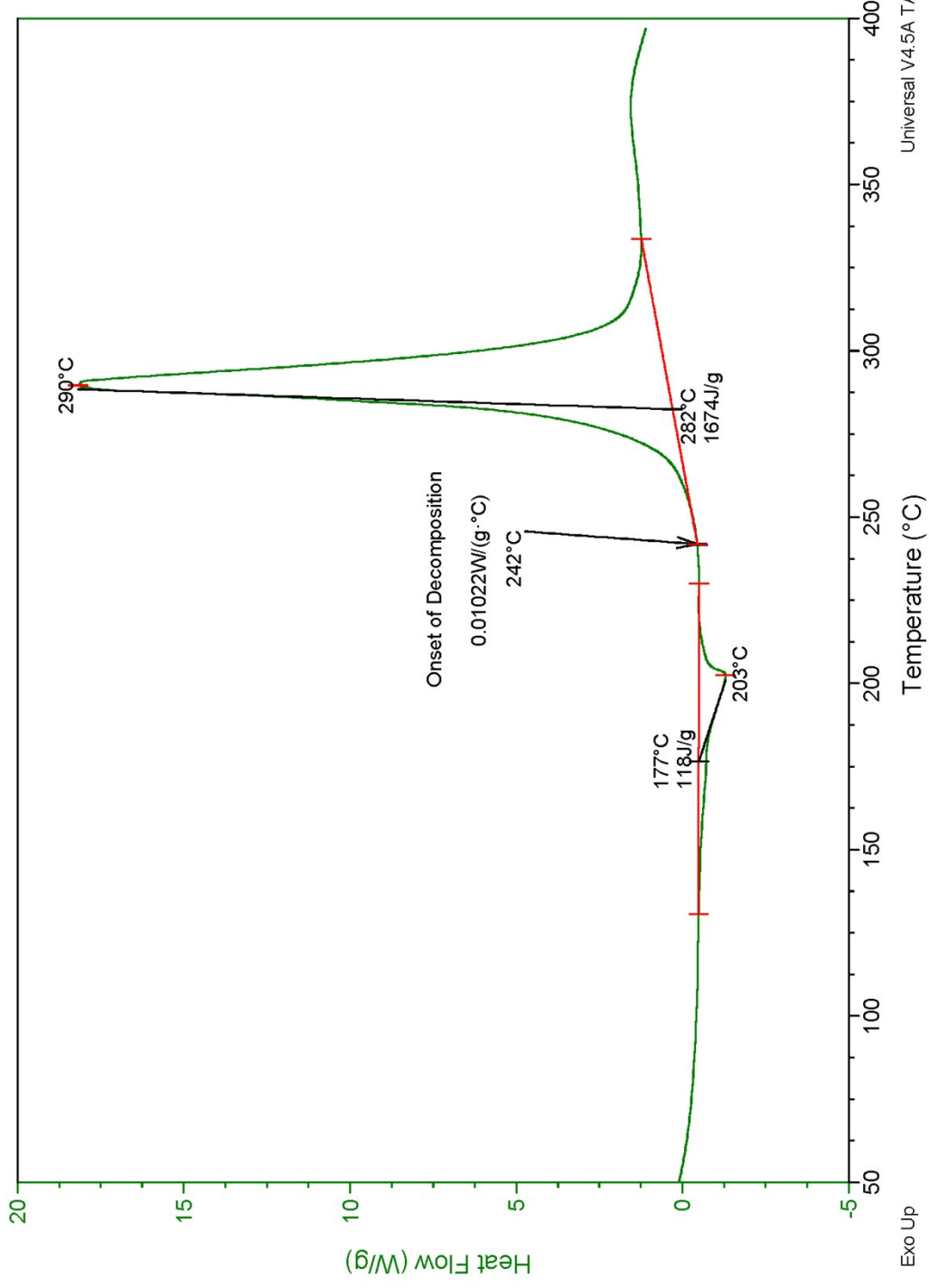
File: C:\...\DSC Q-2000\52582 DEC\DMPTzDFP.001
Operator: H.Tian
Run Date: 24-Jul-2017 17:33
Instrument: DSC Q2000 V24.11 Build 124



Sample: Compound 6
Size: 0.3570 mg
Method: 10C Ramp

DSC

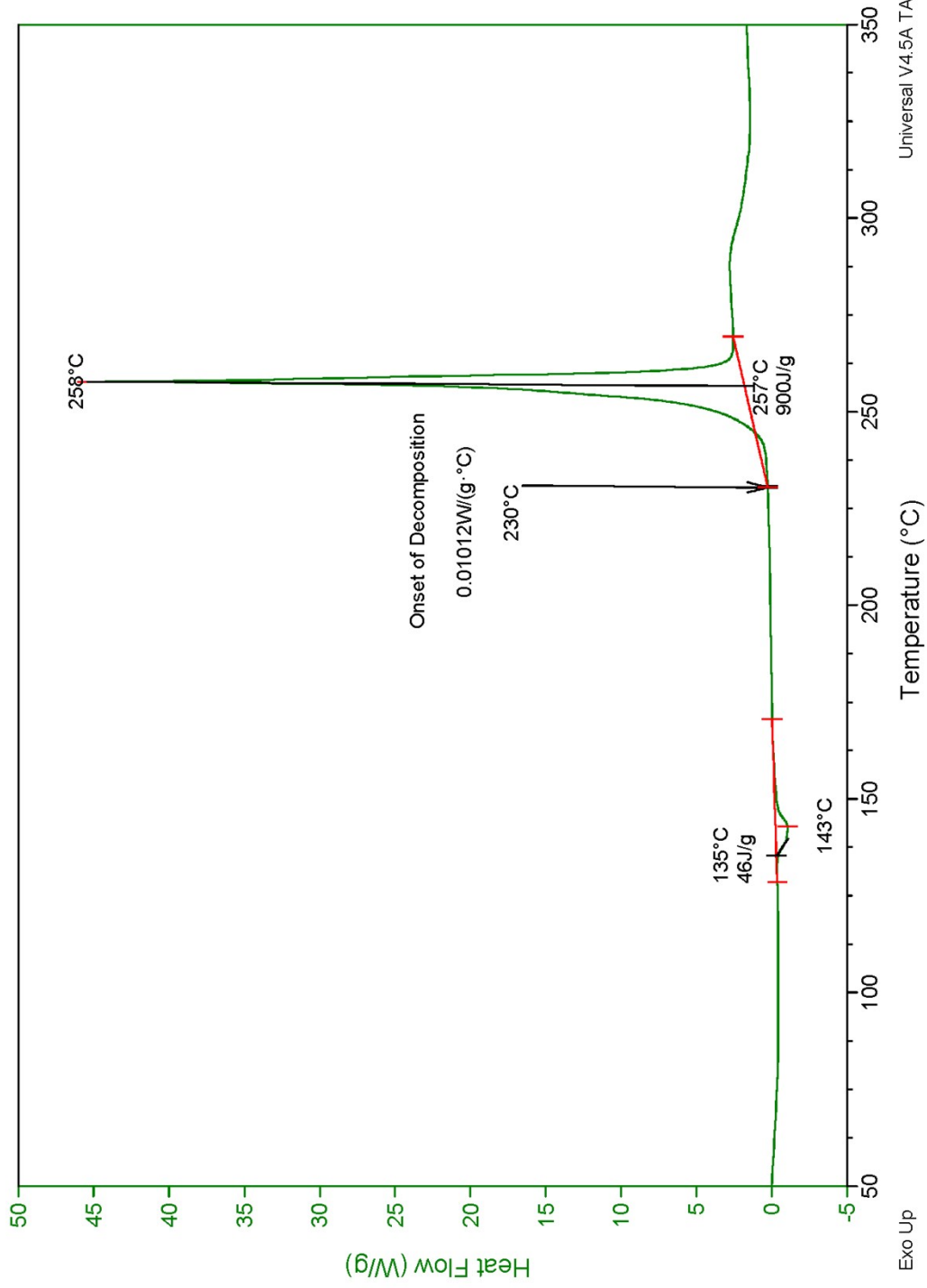
File: C:\... \ATDFPNH4.001
Operator: H.Tian
Run Date: 25-Aug-2017 11:33
Instrument: DSC Q2000 V24.11 Build 124



Sample: Compound 7
Size: 0.4050 mg
Method: 10C Ramp

DSC

File: C:\...\52677 Chavez\ATDFPDO.001
Operator: H.Tian
Run Date: 28-Nov-2017 13:40
Instrument: DSC Q2000 V24.11 Build 124



Sample: Compound 8
Size: 0.2960 mg
Method: 10C Ramp

DSC

File: C:\...\(ATzDFP)2TzTO.001
Operator: H.Tian
Run Date: 25-Aug-2017 14:54
Instrument: DSC Q2000 V24.11 Build 124

