Comparison of the thermal stability of diazonium salts and their corresponding triazenes

SUPPORTING INFORMATION

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Contents

1 General Methods

All reagents and solvents were commercially available and were used without further purification unless stated otherwise. Petroleum ether refers to the 40-60 °C fraction.

For the measurement of ^{1}H, ^{13}C and ^{19}F NMR spectra a Bruker Fourier^{300} (300 MHz), 400 UltraShield^{TM} (400 MHz) or Ascend^{TM}500 (500 MHz) were used. The obtained chemical shifts δ are reported in ppm and are referenced to the residual solvent signal or to the standard trifluorotoluene (-63.72 ppm) in ^{19}F NMR. Spin-spin coupling constants *J* are given in Hz. ^{13}C spectra are reported as obtained at default temperature (room temperature about 18 °C).

The flow setup consisted of PFA tubing of 0.8 mm ID and two pumps. The residence coils were made from the tubing by taking the appropriate length for the desired volume.

Column chromatography was performed using 60 A (40-64 micron) silica and solvent mixtures of petroleum ether and ethyl acetate or dichloromethane.

High resolution mass spectral (HRMS) data were obtained on a Waters MALDI-TOF mx at Cardiff University or on a Thermo Scientific LTQ Orbitrap XL by the EPSRC UK National Mass Spectrometry Facility at Swansea University.

IR spectra were obtained from a Shimadzu IR-Affinity-1S FTIR and melting points using a Gallenkamp apparatus and are reported uncorrected.

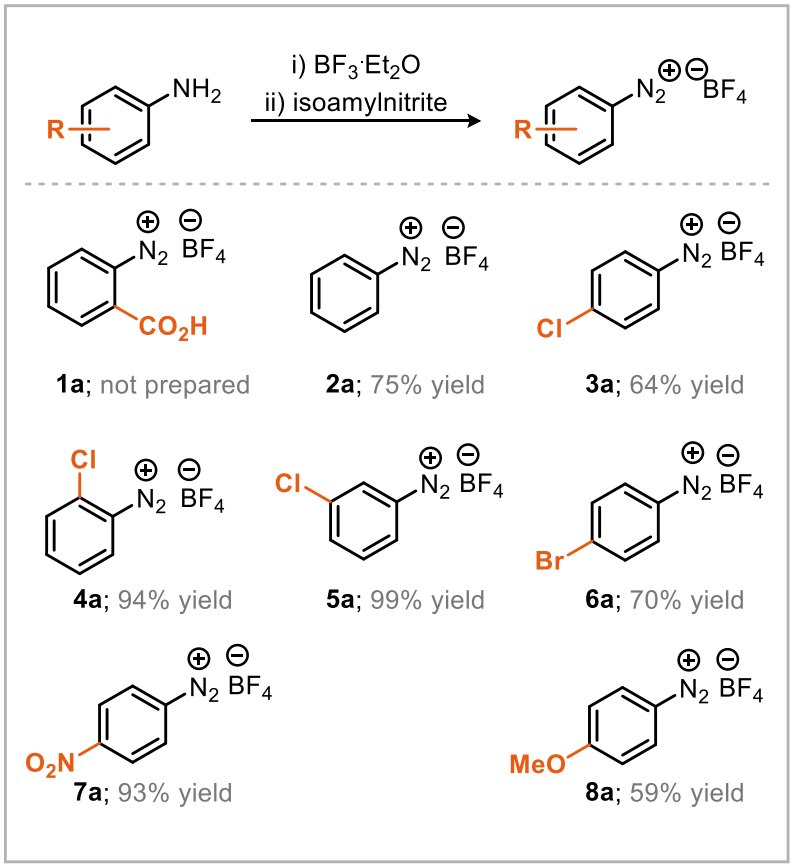
DSC measurements were performed using a TA instruments Q100 in aluminium pans and were hermetically sealed. The sample (and reference) were heated from 20 °C to a temperature in the range of 160 - 250 °C at a rate of 20 °C min^{-1}. Onset temperatures were calculated by the instrument software and initial decomposition temperatures were estimated by eye (at the point where the data starts to rise away from the previous baseline).

References to spectroscopic data are given for known compounds.

2 General procedures

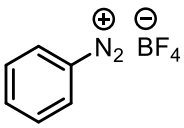
2.1 General Procedure for the Preparation of Diazonium Salts 2a – 8a

The aniline (5.0 mmol) was dissolved in MeCN (10 mL). After cooling with ice-water $BF_3{\cdot}Et_2O$ (0.95 mL, 7.5 mmol, 1.5 equiv) was added. Isoamylnitrite (0.709 g, 6.0 mmol, 1.2 equiv) in MeCN (5 mL) was then added slowly at 0 °C and the reaction mixture stirred for 30 min. After precipitation with Et_2O (30 mL) the product was suction filtered, washed with Et_2O and air dried to yield the corresponding diazonium salt (Scheme 1).



Scheme SI1. Preparation of Diazonium Salts

benzenediazonium tetrafluoroborate (2a)[1]



Following the general procedure, the title compound **2a** was obtained from aniline as an off-white solid in 75% yield (0.351 g).

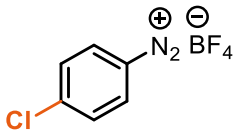
^{1}H NMR (400 MHz, DMSO) δ 8.73 – 8.59 (m, 2H, ArH), 8.26 (t, J = 7.7 Hz, 1H, ArH^2), 7.98 (t, J = 8.2 Hz, 2H, ArH^{1,4}) ppm.

^{13}C NMR (101 MHz, DMSO) δ 141.5 (ArC), 133.0 (ArC), 131.5 (ArC), 116.5 ppm.

IR: 3107, 2295, 1570, 1462, 1312, 1020, 754, 665 cm^{-1}.

HRMS (EI+): [$C_6H_5N_2$] Calcd. 105.0453, Found 105.0452.

4-chlorobenzenediazonium tetrafluoroborate (3a)[1]



Following the general procedure, the title compound **3a** was obtained from *p*-chloroaniline as a colourless solid in 63% yield (0.712 g).

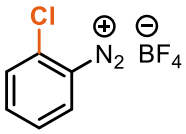
^{1}H NMR (400 MHz, DMSO) δ 8.71 – 8.65 (m, 2H, ArH), 8.14 – 8.08 (m, 2H, ArH) ppm.

^{13}C NMR (101 MHz, DMSO) δ 146.5 (ArC), 134.5 (ArC), 131.5 (ArC), 115.0 (ArC) ppm.

IR: 3107, 2295, 1570, 1462, 1312, 1020, 754, 665 cm^{-1}.

HRMS (EI+): [$C_6H_4N_2Cl$]$^{+}$ Calcd. 139.0063, Found 139.0059.

2-chlorobenzenediazonium tetrafluoroborate (4a)[2]



Following the general procedure, the title compound **4a** was obtained from *o*-chloroaniline as a colourless solid in 94% yield (1.063 g).

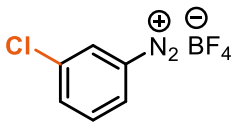
^{1}H NMR (400 MHz, DMSO) δ 8.85 (dd, *J* = 8.3, 1.5 Hz, 1H, ArH), 8.32 – 8.24 (m, 1H, ArH), 8.20 (dd, *J* = 8.3, 1.1 Hz, 1H, ArH), 7.99 – 7.91 (m, 1H, ArH) ppm.

^{13}C NMR (101 MHz, DMSO) δ 142.5 (ArC), 135.5 (ArC), 134.5 (ArC), 132.5 (ArC), 130.0 (ArC), 116.5 (ArC) ppm.

IR: 3100, 2361, 2291, 1566, 1474, 1464, 1034, 773, 677 cm^{-1}.

HRMS (EI+): [$C_6H_4N_2Cl$]$^{+}$ Calcd. 139.0063, Found 139.0057.

3-chlorobenzenediazonium tetrafluoroborate (5a)[2]



Following the general procedure, the title compound 5a was obtained from *m*-chloroaniline as a slightly pink solid in 99% yield (1.118 g).

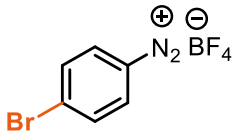
^{1}H NMR (400 MHz, DMSO) δ 8.86 (t, *J* = 2.0 Hz, 1H, ArH), 8.69 – 8.63 (m, 1H, ArH), 8.40 – 8.34 (m, 1H, ArH), 8.01 (t, *J* = 8.3 Hz, 1H, ArH) ppm.

^{13}C NMR (101 MHz, DMSO) δ 141.0 (ArC), 134.5 (ArC), 133.0 (ArC), 131.5 (ArC), 131.5 (ArC), 118.0 (ArC) ppm.

IR: 3103, 2359, 2305, 1558, 1466, 1020, 885, 793, 652, 519 cm^{-1}.

HRMS (EI+): $[C_6H_4N_2Cl_1]^+$ Calcd. 139.0058, Found 139.0054.

4-bromobenzenediazonium tetrafluoroborate (6a)[1]



Following the general procedure, the title compound **6a** was obtained from *p*-bromoaniline as a colourless solid in 70% yield (0.949 g).

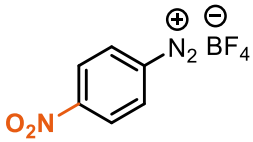
^{1}H NMR (400 MHz, DMSO) δ 8.62 – 8.52 (m, 1H, ArH), 8.29 – 8.21 (m, 1H, ArH) ppm.

^{13}C NMR (101 MHz, DMSO) δ 136.5 (ArC), 134.5 (ArC), 134.0 (ArC), 115.0 (ArC) ppm.

IR: 3105, 2290, 1555, 1022, 1011, 829, 521 cm^{-1}.

HRMS (ES+): $[C_6H_4N_2Br]^+$ Calcd. 182.9558, Found 182.9555.

4-nitrobenzenediazonium tetrafluoroborate (7a)[1]



Following the general procedure, the title compound **7a** was obtained from *p*-nitroaniline as a grey solid in 93% yield (1.102 g).

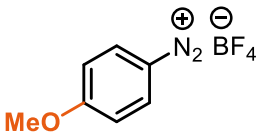
^{1}H NMR (400 MHz, DMSO) δ 8.97 – 8.89 (m, 2H, ArH), 8.77 – 8.67 (m, 2H, ArH) ppm.

^{13}C NMR (101 MHz, DMSO) δ 153.5 (ArC), 134.5 (ArC), 126.0 (ArC), 122.0 (ArC) ppm.

IR: 3119, 2359, 2307, 1539, 1336, 1317, 1030, 866, 743, 662, 525 cm^{-1}.

HRMS (EI+): $[C_6H_4N_3O_2]^+$ Calcd. 150.0304, Found 150.0302.

4-methoxybenzenediazonium tetrafluoroborate (8a)[1]



Following the general procedure, the title compound **8a** was obtained from *p*-methoxyaniline as a brown solid in 59% yield (0.659 g).

^{1}H NMR (400 MHz, DMSO) δ 8.64 – 8.56 (m, 2H, ArH), 7.52 – 7.44 (m, 2H, ArH), 4.04 (s, 3H, OCH_3) ppm.

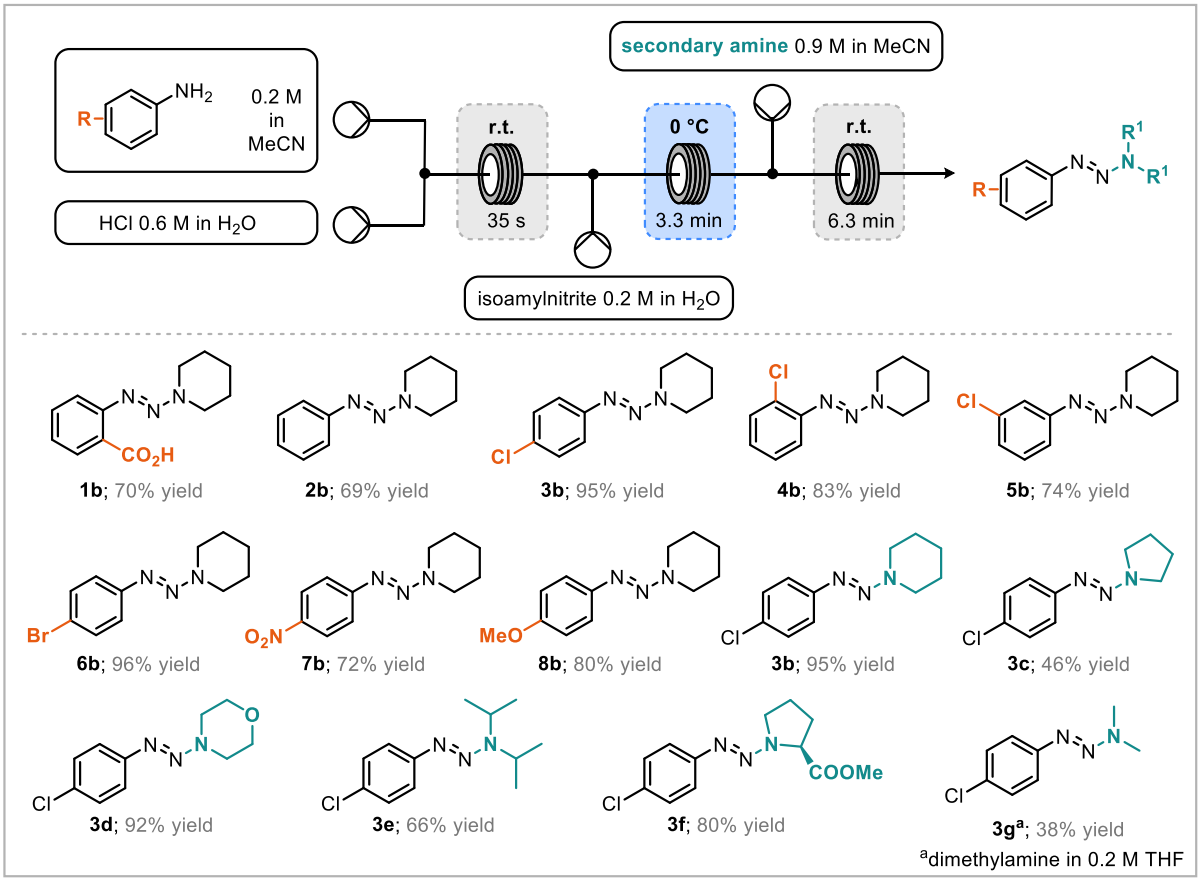
^{13}C NMR (101 MHz, DMSO) δ 169.0 (ArC), 136.0 (ArC), 117.5 (ArC), 103.5 (ArC), 57.5 OCH_3) ppm.

IR: 3121, 2251, 1582, 1568, 1493, 1441, 1344 ; 1287, 1030, 997, 841, 685 cm^{-1}.

HRMS (EI+): $[C_7H_7O_1N_2]^+$ calc. 135.0553, found 135.0549.

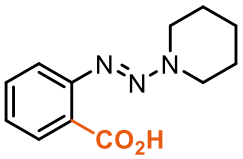
1.2 General Method for the Preparation of Triazenes 1a – 8b and 3c – 3g in Flow

Solutions of the aniline (0.2 M in acetonitrile), HCl (0.6 M in water), isoamylnitrite (0.2 M in acetonitrile) and the secondary amine (0.9 M in acetonitrile) were prepared. These were then pumped through the flow system (see Scheme 6.2) at a flow rate of 0.2 $mLmin^{-1}$. After 20 min steady state was reached and an aliquot of 20 mL (1 mmol, 25 min) was collected. The reaction solution was neutralized with aqueous $NaHCO_3$, extracted with EtOAc (3 x 20 mL), washed with brine and dried over $MgSO_4$. After removing the solvent under reduced pressure, the crude product was further purified by column chromatography (0 to 10% EtOAc in petroleum ether).



Scheme SI2. Preparation of Triazenes Using Continuous Flow Conditions

2-(piperidin-1-yldiazenyl)benzoic acid (1b)



Following the general procedure, the title compound **1b** was obtained from anthranillic acid and piperidine as a pale yellow solid in 70% yield (0.235 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 14.04 (s, 1H, COOH), 8.29 – 8.22 (m, 1H, ArH), 7.73 – 7.67 (m, 1H, ArH), 7.55 – 7.45 (m, 1H, ArH), 7.32 – 7.23 (m, 1H, ArH), 4.03 – 3.75 (m, 4H, CH_2), 1.95 – 1.70 (m, 6H, CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 168.0 (COOH), 148.5 (ArC), 134.0 (ArC), 132.0 (ArC), 126.0 (ArC), 121.0 (ArC), 115.5 (ArC), 54.0 (CH_2), 45.0 (CH_2), 26.0 (CH_2), 24.0 (CH_2), 23.5 (CH_2) ppm.

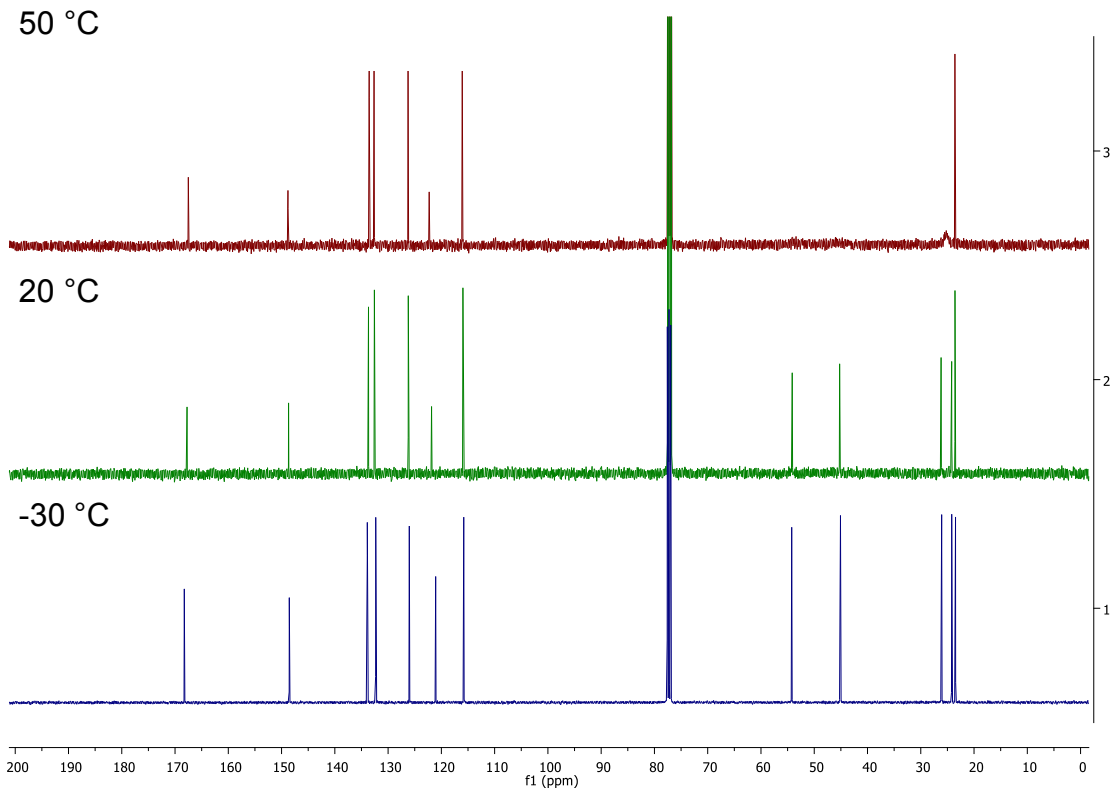
^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 167.5 (COOH), 148.5 (ArC), 133.5 (ArCH), 132.5 (ArCH), 126.0 (ArCH), 122.0 (ArC), 116.0 (ArCH), 54.0 (CH_2), 45.0 (CH_2), 26.0 (CH_2), 24.0 (CH_2), 23.5 (CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 167.5 (COOH), 149.0 (ArC), 133.5 (ArCH), 132.5 (ArCH), 126.5 (ArC)H, 122.5 (ArC), 116.0 (ArCH), 25.0 (CH_2), 23.5 (CH_2) ppm.

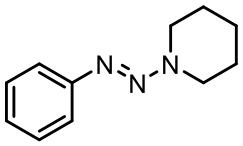
mp (acetone): 88 - 90 °C.

IR: 2945, 1703, 1704, 1593, 1410, 1109, 766, 692, 608 cm^{-1}.

HRMS (EI+): [$C_{12}H_{15}O_2N_3$] Calcd. 233.1164, Found 233.1162.



1-(phenyldiazenyl)piperidine (2b)[3]



Following the general procedure, the title compound **2b** was obtained from aniline and piperidine as an orange oil (which slowly solidified) in 69% yield (0.130 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.46 – 7.40 (m, 2H, ArH), 7.37 – 7.30 (m, 2H, ArH), 7.19 – 7.12 (m, *J* = 7.3 Hz, 1H, ArH), 3.84 – 3.71 (m, 4H, CH_2), 1.77 – 1.64 (m, 6H, CH_2) ppm.

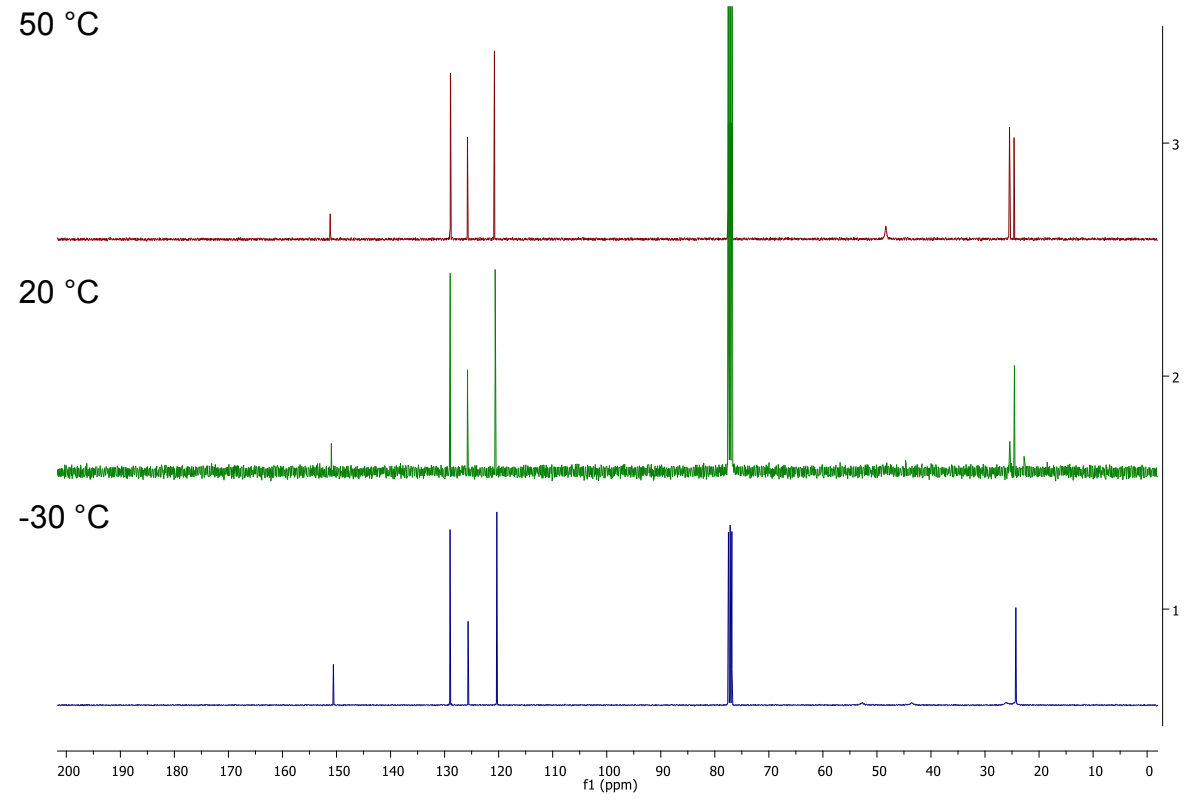
^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 150.5 (ArC), 129.0 (ArCH), 125.5 (ArC), 120.5 (ArCH), 52.5 (CH_2), 43.5 (CH_2), 26.0 (CH_2), 24.5 (CH_2), 24.0 (CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 151.0 (ArC), 129.0 (ArCH), 126.0 (ArC), 120.5 (ArCH), 25.5 (CH_2), 24.5 (CH_2) ppm.

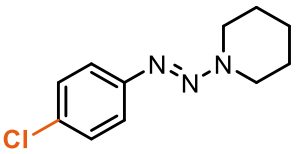
^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 151.0 (ArC), 129.0 (ArCH), 126.0 (ArC), 121.0 (ArCH), 48.5 (CH_2), 25.5 (CH_2), 24.5 (CH_2) ppm.

IR: 2940, 2922, 2855, 1591, 1580, 1483, 1408, 1186, 764, 694 cm^{-1}.

HRMS (EI+): [$C_{11}H_{15}N_3$] Calcd. 189.1266, Found 189.1263.



1-((4-chlorophenyl)diazenyl)piperidine (3b)[3]



Following the general procedure, the title compound **3b** was obtained from 4-chloroaniline and piperidine as a pale yellow solid in 95% yield (0.213 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.38 – 7.34 (m, 2H, ArH), 7.31 – 7.25 (m, 2H, ArH), 3.83 – 3.71 (m, 4H, CH_2), 1.77 – 1.63 (m, 6H, CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 149.0 (ArC^5), 130.5 (ArC^2), 129.0 (ArCH), 121.5 (ArCH), 53.0 (CH_2), 43.5 (CH_2), 26.0 (CH_2), 24.0 (CH_2) ppm.

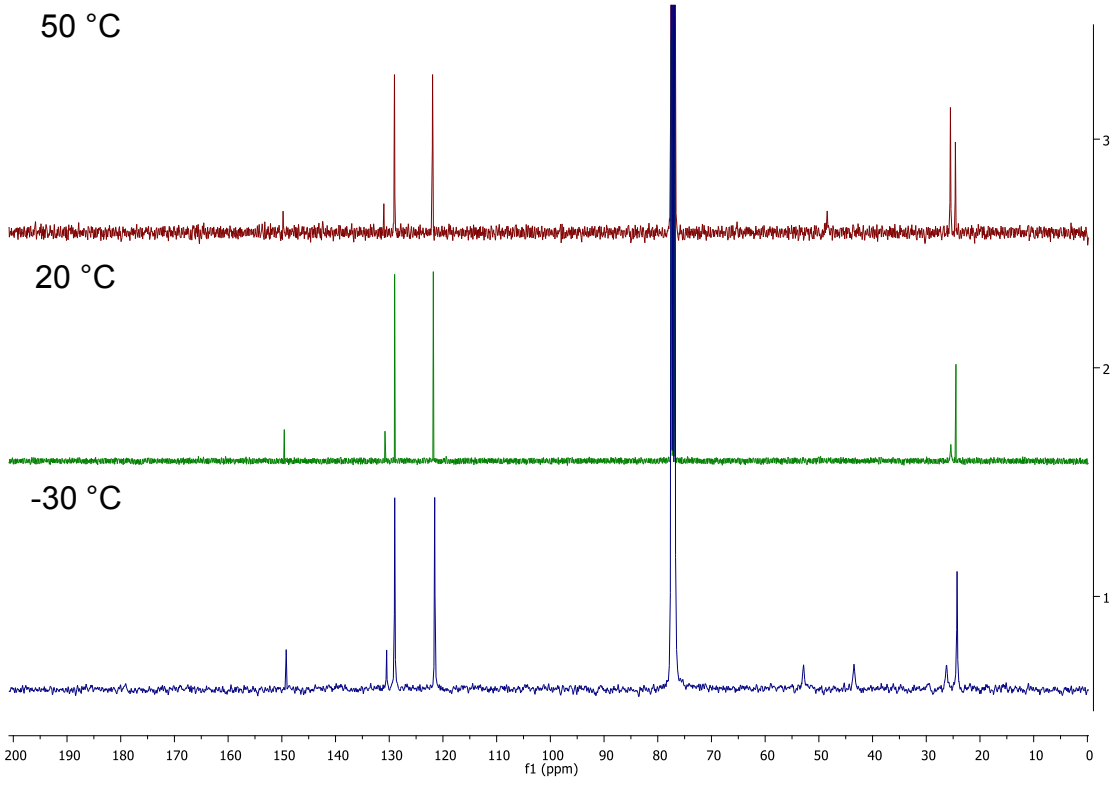
^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 149.5 (ArC), 131.0 (ArC), 129.0 (ArCH), 122.0 (ArCH), 25.5 (CH_2), 24.5 (CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 150.0 (ArC), 131.0 (ArC), 129.0 (ArCH), 122.0 (ArCH), 48.5 (CH_2), 25.5 (CH_2), 24.5 (CH_2) ppm.

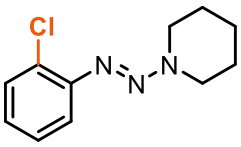
mp (DCM): 53 - 54 °C.

IR: 2936, 2853, 1329, 831, 521 cm^{-1}.

HRMS (EI+): [$C_{11}H_{14}N_3Cl$] Calcd. 223.0876, Found 223.0883.



1-((2-chlorophenyl)diazenyl)piperidine (4b)



Following the general procedure, the title compound **4b** was obtained from *o*-chloroaniline and piperidine as an orange oil (which slowly solidified) in 83% yield (0.185 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.44 (dd, *J* = 8.1, 1.6 Hz, 1H, ArH), 7.38 (dd, *J* = 8.0, 1.4 Hz, 1H, ArH), 7.23 – 7.17 (m, 1H, ArH), 7.09 – 7.03 (m, 1H, ArH), 3.93 – 3.74 (m, 4H, CH_2), 1.81 – 1.64 (m, 6H, CH_2) ppm.

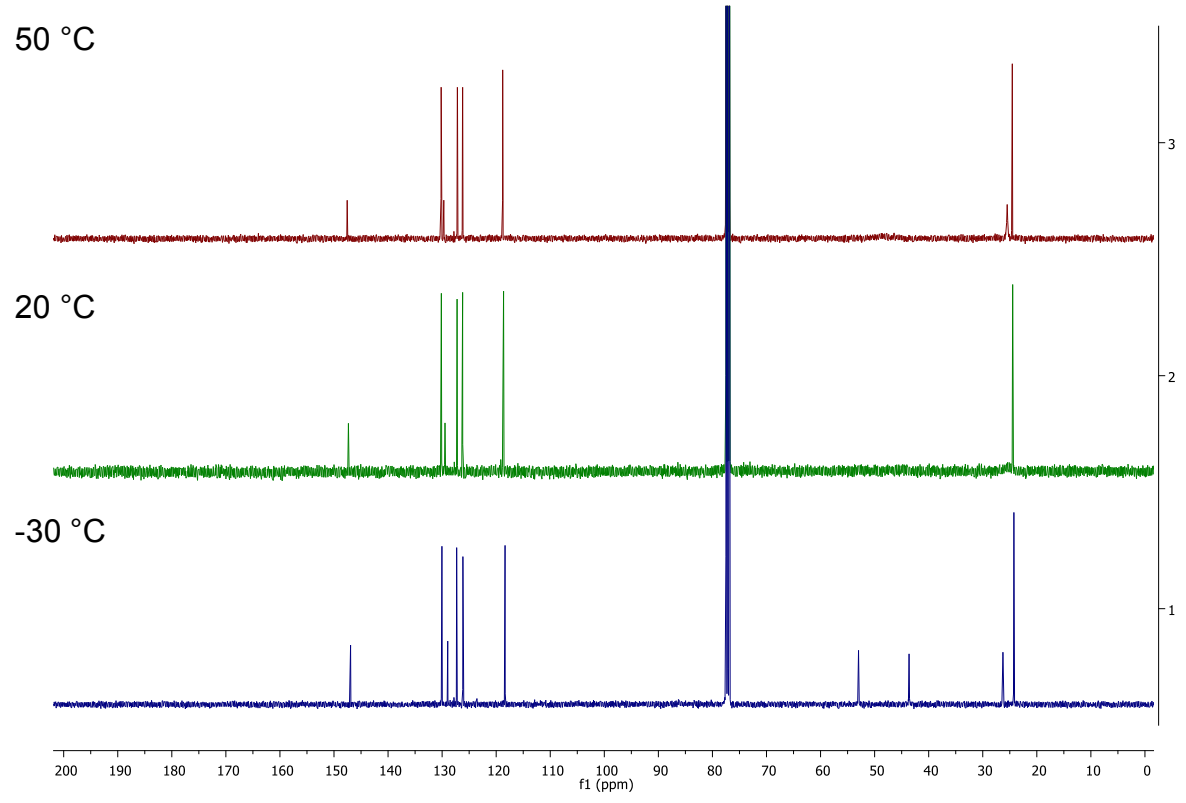
^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 147.0 (ArC), 130.0 (ArCH), 129.0 (ArC), 127.5 (ArCH), 126.0 (ArHC), 118.5 (ArCH), 53.0 (CH_2), 43.5 (CH_2), 26.5 (CH_2), 24.0 (CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 147.5 (ArC), 130.0 (ArCH), 129.5 (ArC), 127.0 (ArCH), 126.0 (ArCH), 118.5 (ArCH), 24.5 (CH_2) ppm.

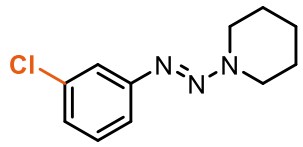
^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 147.5 (ArC), 130.0 (ArCH), 129.5 (ArC), 127.0 (ArCH), 126.0 (ArCH), 119.0 (ArCH), 25.5 (CH_2), 24.5 (CH_2) ppm.

IR: 2945, 2855, 1468, 1402, 1184, 760, 698, 556 cm^{-1}.

HRMS (FTMS+ p NSI): [$C_{11}H_{14}N_3Cl$] Calcd. 224.0949, Found 224.0950.



1-((3-chlorophenyl)diazenyl)piperidine (5b)



Following the general procedure, the title compound **5b** was obtained from *m*-chloroaniline and piperidine as a red oil in 74% yield (0.165 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.44 (t, J = 1.9 Hz, 1H, ArH), 7.31 – 7.27 (m, 1H, ArH), 7.24 (t, J = 7.8 Hz, 1H, ArH), 7.12 – 7.08 (m, 1H, ArH), 3.86 – 3.74 (m, 4H, CH_2[10,11]), 1.77 – 1.65 (m, 6H, CH_2[12,13,14]) ppm.

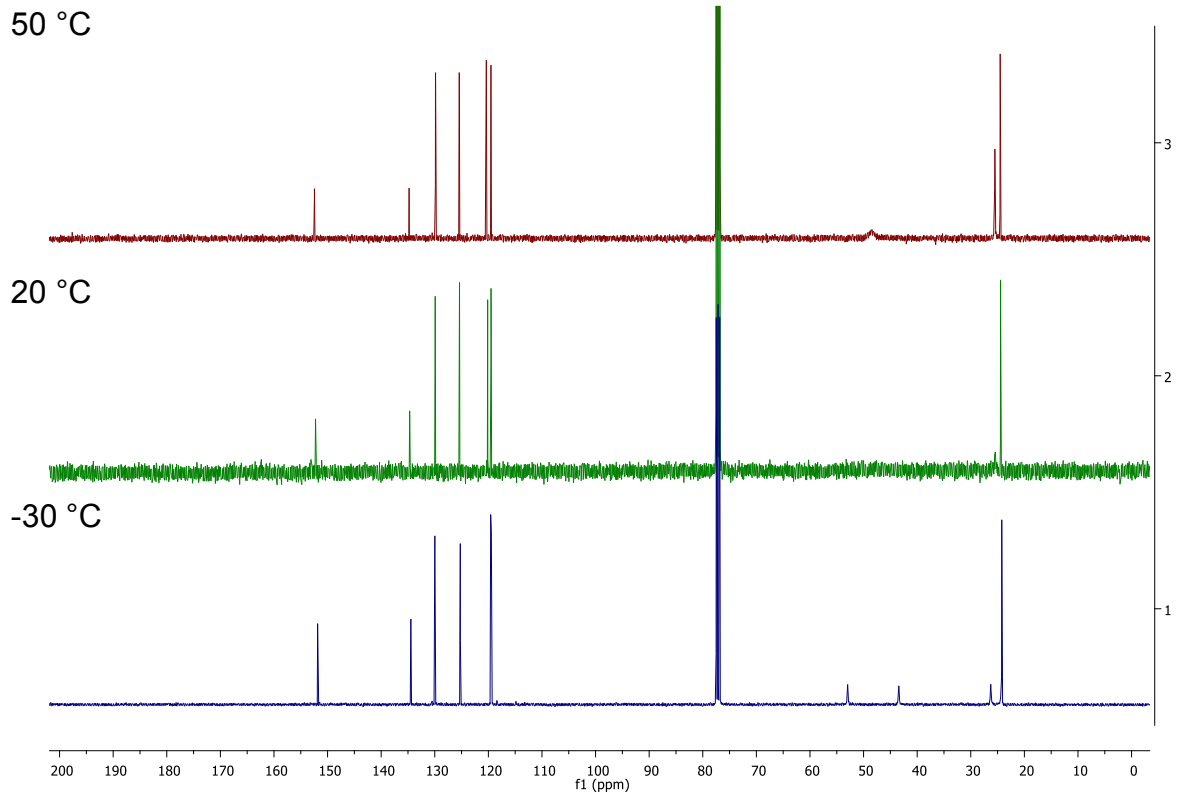
^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 152.0 (ArC), 134.5 (ArC), 130.0 (ArCH), 125.0 (ArCH), 119.5 (2 ArCH), 53.0 (CH_2), 43.5 (CH_2), 26.5 (CH_2), 24.0 (CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 152.5 (ArC), 134.5 (ArC), 130.0 (ArCH), 125.5 (ArCH), 120.0 (ArCH), 119.5 (ArCH), 24.5 (CH_2) ppm.

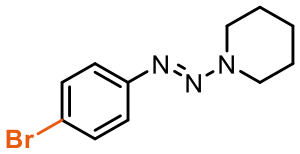
^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 152.5 (ArC), 135.0 (ArC), 130.0 (ArCH), 125.5 (ArCH), 120.5 (ArCH), 119.5 (ArCH), 48.5 (CH_2), 25.5 (CH_2), 24.5 (CH_2) ppm.

IR: 2938, 2855, 2361, 1418, 1362, 1107, 997, 854, 781, 687 cm^{-1}.

HRMS (FTMS+ p NSI): [$C_{11}H_{15}N_3Cl$] Calcd. 224.0949, Found 224.0950.



1-((4-bromophenyl)diazenyl)piperidine (6b)[4]



Following the general procedure, the title compound **6b** was obtained from 4-bromoaniline and piperidine as a pale orange solid in 96% yield (0.257 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.46 – 7.39 (m, 2H, ArH), 7.34 – 7.27 (m, 2H, ArH), 3.85 – 3.69 (m, 4H, CH_2), 1.78 – 1.63 (m, 6H, CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 149.5 (ArC), 132.0 (ArCH), 122.0 (ArCH), 118.5 (ArC), 53.0 (CH_2), 43.5 (CH_2), 26.0 (CH_2), 24.5 (CH_2) ppm.

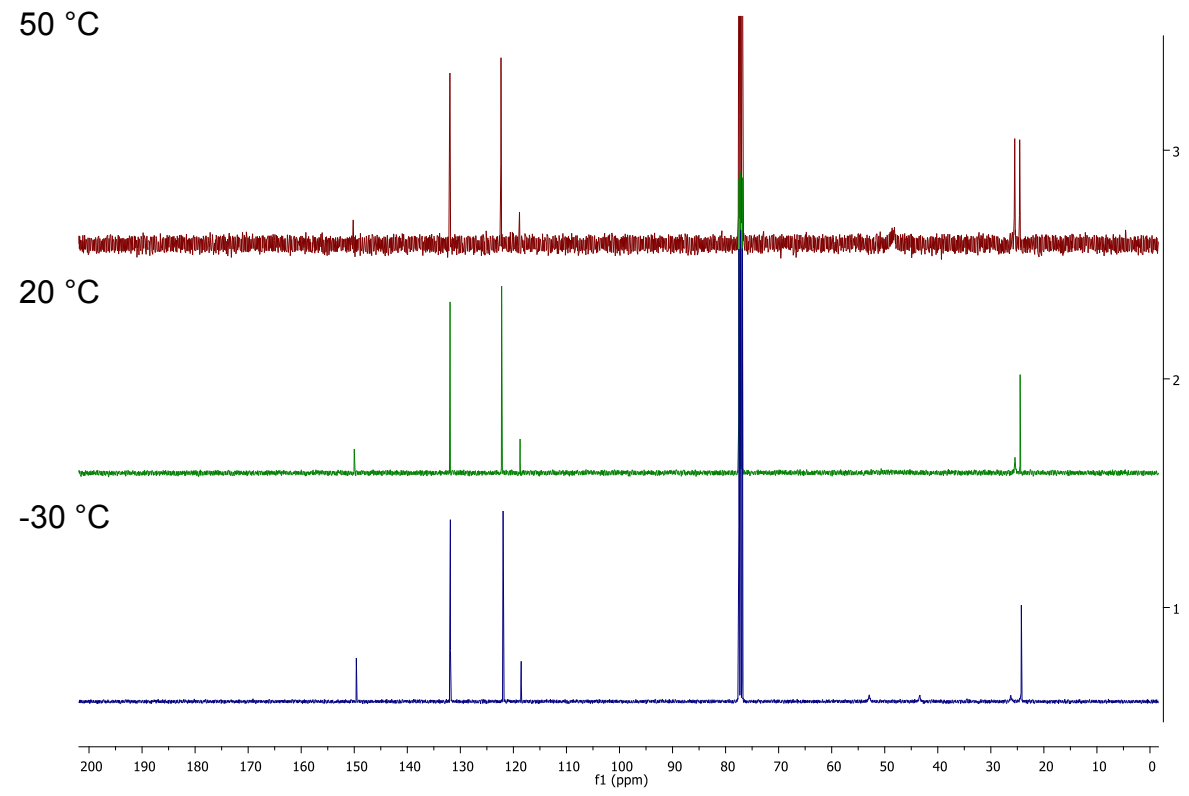
^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 150.0 (ArC), 132.0 (ArCH), 122.0 (ArCH), 118.5 (ArC), 25.5 (CH_2), 24.5 (CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 150.0 (ArC), 132.0 (ArCH), 122.5 (ArCH), 119.0 (ArC), 25.5 (CH_2), 24.5 (CH_2) ppm.

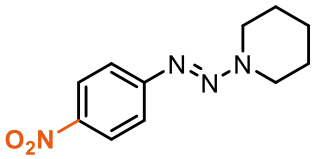
mp (DCM): 58 - 60 °C.

IR: 2934, 2851, 2361, 1427, 1109, 1186, 827, 704, 629, 517 cm^{-1}.

HRMS (FTMS+ p NSI): [$C_{11}H_{14}N_3Br$] Calcd. 267.0371, Found 267.0372



1-((4-nitrophenyl)diazenyl)piperidine (7b)[3]



Following the general procedure, the title compound **7b** was obtained from 4-nitroaniline and piperidine as an orange solid in 72% yield (0.168 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.25 – 8.08 (m, 2H, ArH), 7.57 – 7.42 (m, 2H, ArH), 4.01 – 3.72 (s, 4H, CH_2), 1.90 – 1.57 (s, 6H, CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 156.0 (ArC), 144.0 (ArC), 125.0 (ArCH), 120.5 (ArCH), 53.5 (CH_2), 43.5 (CH_2), 26.5 (CH_2), 24.5 (CH_2), 24.0 (CH_2) ppm.

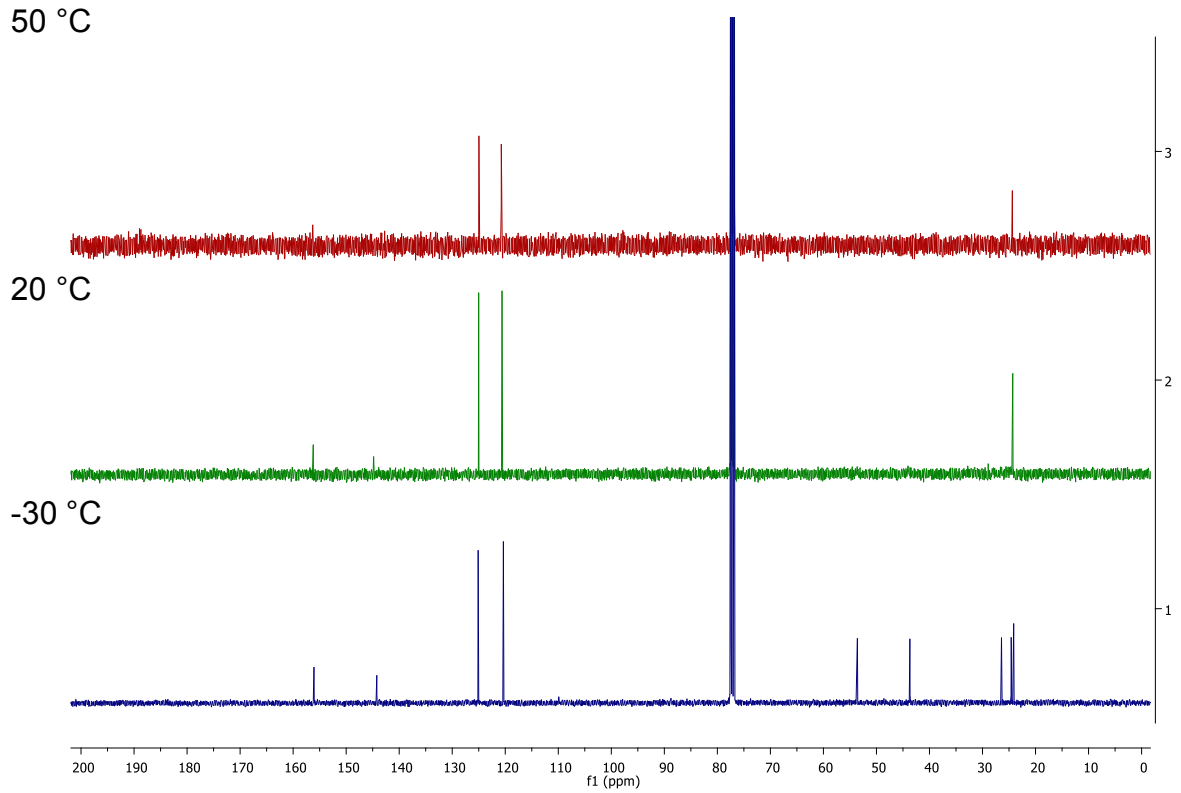
^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 156.0 (ArC), 145.0(ArC), 125.0 (ArCH), 120.5 (ArCH), 24.5 (CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 156.0 (ArC), 125.0 (ArCH), 121.0 (ArCH), 24.5 (CH_2) ppm.

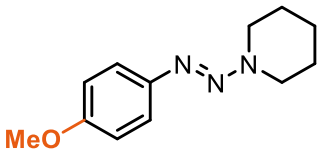
mp (DCM): 96 - 98 °C.

IR: 2945, 2855, 2361, 1506, 1285, 1098, 851, 694 cm^{-1}.

HRMS (FTMS+ p NSI): [$C_{11}H_{14}N_4O_2$] Calcd. 234.1117, Found 234.1118.



1-((4-methoxyphenyl)diazenyl)piperidine (8b)



Following the general procedure, the title compound **8b** was obtained from *p*-anisidine and piperidine as an orange oil in 80% yield (0.176 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.44 – 7.37 (m, 2H, ArH), 6.92 – 6.85 (m, 2H, ArH), 3.81 (s, 3H, CH_3), 3.77 – 3.68 (m, 4H, CH_2), 1.87 – 1.52 (m, 6H, CH_2) ppm.

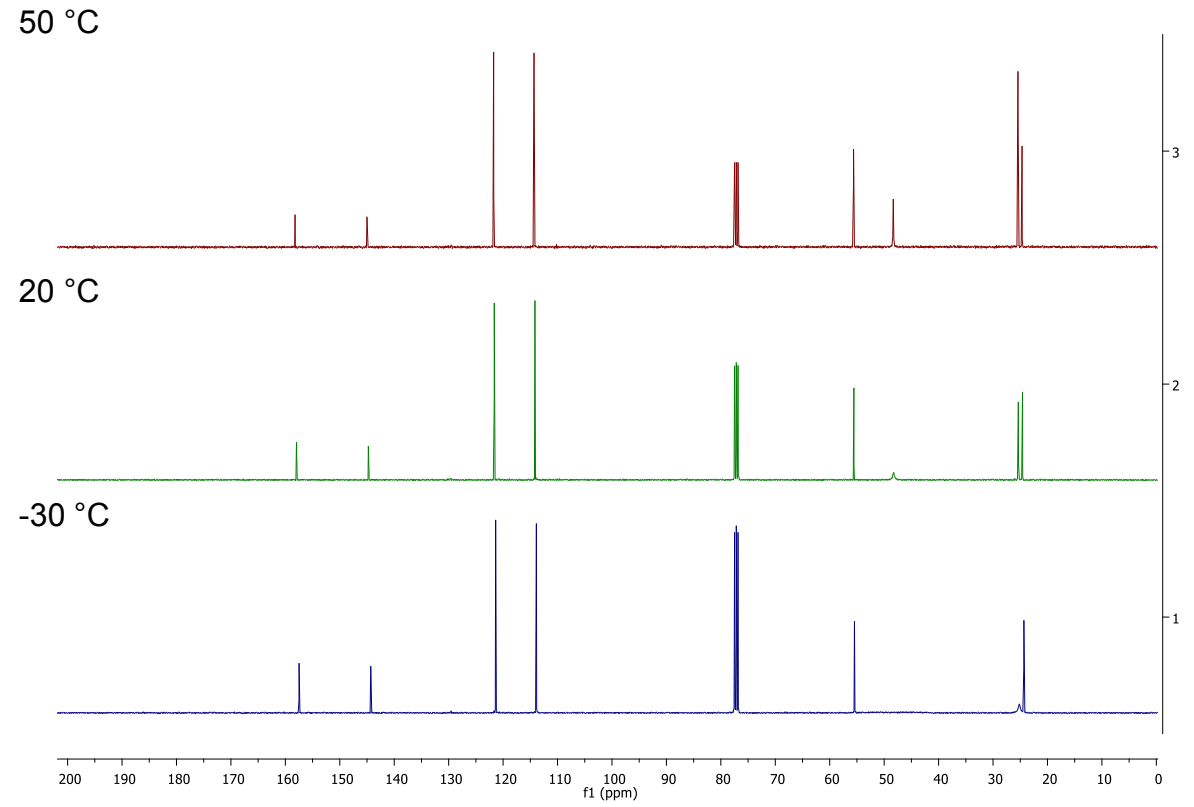
^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 157.5 (ArC), 144.5 (ArC), 121.5 (ArCH), 114.0 (ArCH), 55.5 (CH_3), 25.0 (CH_2), 24.5 (CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 158.0 (ArC), 145.0 (ArCH), 121.5 (ArCH), 114.0 (ArC), 55.5 (CH_3), 48.5 (CH_2), 25.5 (CH_2), 24.5 (CH_2) ppm.

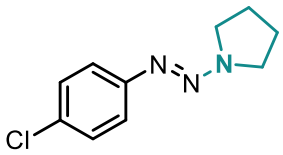
^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 158.0 (ArC), 145.0 (ArCH), 121.5 (ArCH), 114.0 (ArC), 55.5 (CH_3), 48.5 (CH_2), 25.5 (CH_2), 24.5 (CH_2) ppm.

IR: 2936, 2833, 2359, 1506, 1456, 1246, 1101, 835 cm^{-1}.

HRMS (FTMS+ p NSI): [$C_{12}H_{18}ON_3$] Calcd. 220.1444, Found 220.1444.



1-((4-chlorophenyl)diazenyl)pyrrolidine (3c)



Following the general procedure, the title compound **3c** was obtained from *p*-chloroaniline and pyrrolidine as a pale yellow solid in 46% yield (0.096 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.35 – 7.29 (m, 2H, ArH), 7.25 (d, J = 7.5 Hz, 2H, ArH), 4.05 – 3.50 (m, 4H, CH_2), 2.08 – 1.93 (m, 4H, CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 150.0 (ArC), 130.0 (ArC), 129.0 (ArCH), 121.5 (ArCH), 51.5 (CH_2), 46.5 (CH_2), 24.0 (CH_2), 23.5 (CH_2) ppm.

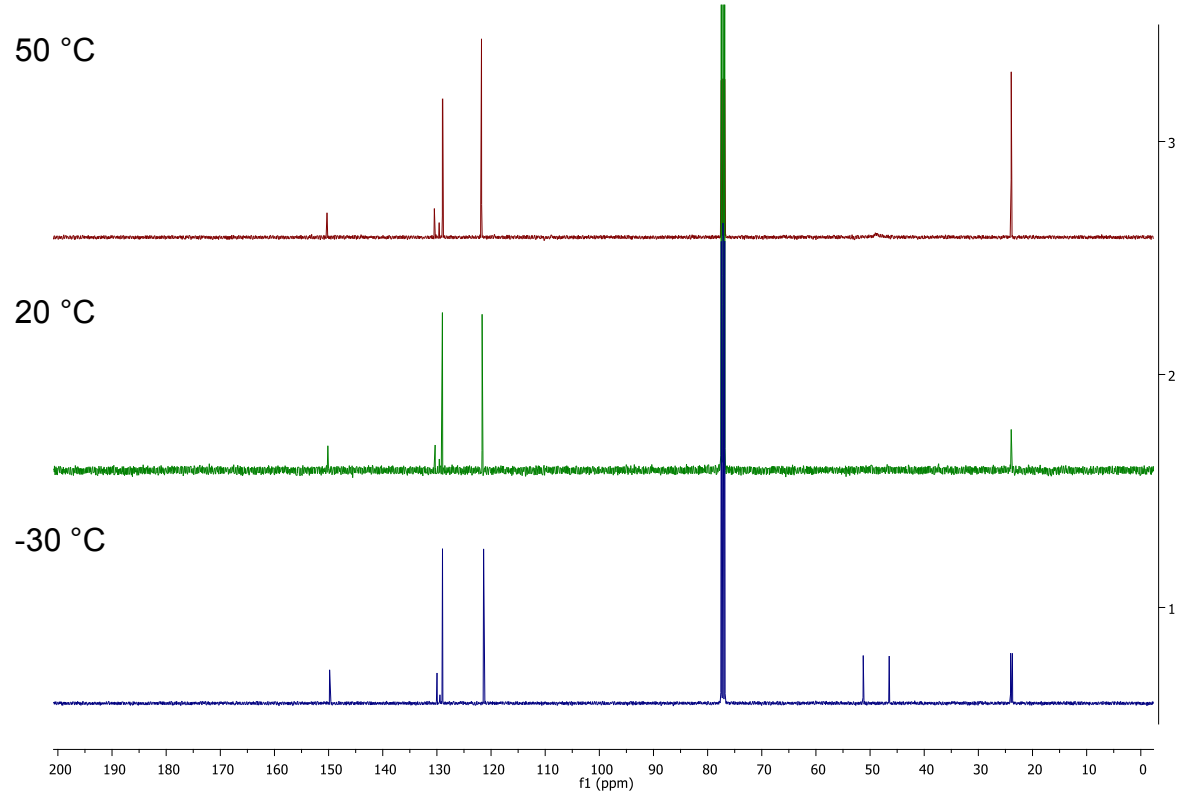
^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 150.0 (ArC), 130.5 (ArC), 129.0 (ArCH),122.0 (ArCH), 24.0 (CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 150.0 (ArC), 130.5 (ArC), 129.0 (ArCH), 121.5 (ArCH), 24.0 (CH_2) ppm.

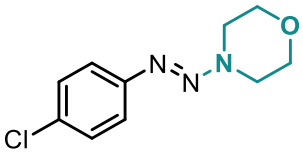
mp (DCM): 48 - 50 °C.

IR: 3952, 2963, 2837, 2785, 2172, 1659, 1639, 1248, 1090, 1040, 883 cm^{-1}.

HRMS(FTMS+ p NSI): [$C_{10}H_{13}N_3Cl$] Calcd. 210.0798, Found 210.0797.



4-((4-chlorophenyl)diazenyl)morpholine (3d)



Following the general procedure, the title compound **3d** was obtained from *p*-chloroaniline and morpholine as an orange solid in 92% yield (0.208 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.39 (d, J = 8.7 Hz, 2H, ArH), 7.31 (d, J = 8.7 Hz, 2H, ArH), 3.88 – 3.82 (m, 4H, CH_2), 3.82 – 3.76 (m, 4H, CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 148.5 (ArC), 131.5 (ArC), 129.0 (ArCH), 122.0 (ArCH), 66.5 (CH_2), 51.5 (CH_2), 44.0 (CH_2) ppm.

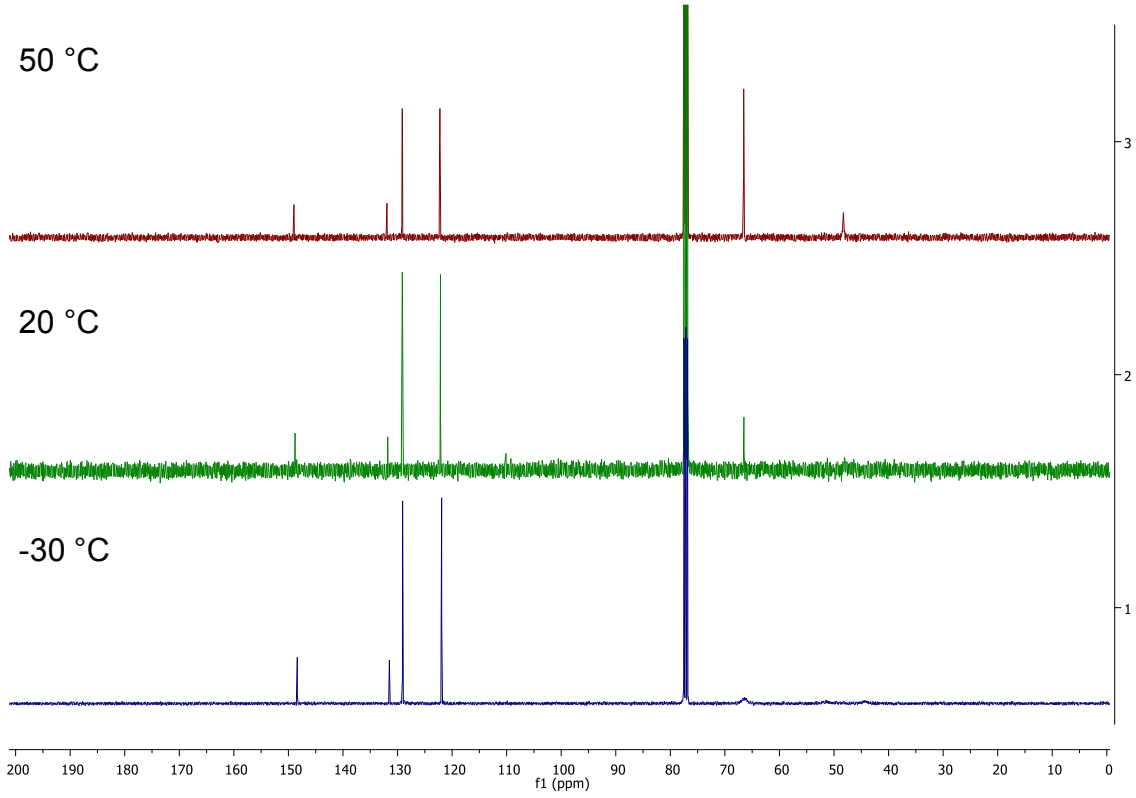
^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 149.0 (ArC), 132.0 (ArC), 129.0 (ArCH), 122.0 (ArCH), 66.5 (CH_2) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 149.0 (ArC), 132.0 (ArC), 129.0 (ArCH), 122.0 (ArCH), 66.5 (CH_2), 48.0 (CH_2) ppm.

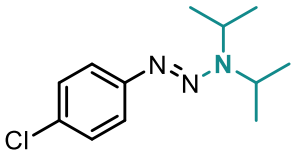
mp (DCM): 40 - 42 °C.

IR: 2858, 1437, 1400, 1342, 1153, 1099, 1004, 937, 626, 549 cm^{-1}.

HRMS (EI^+): [$C_{10}H_{12}ClN_3O$] Calcd. 225.0669, Found 225.0677.



1-(4-chlorophenyl)-3,3-diisopropyltriaz-1-ene (3e)



Following the general procedure, the title compound **3e** was obtained from *p*-chloroaniline and diisopropylamine as an orange oil in 66% yield (0.157 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.34 (d, J = 8.7 Hz, 2H, ArH), 7.27 (d, J = 8.7 Hz, 2H, ArH), 4.49 – 4.88 (m, 1H, CH), 4.21 – 3.69 (m, 1H, CH), 1.49 – 1.08 (m, 12H, CH_3) ppm.

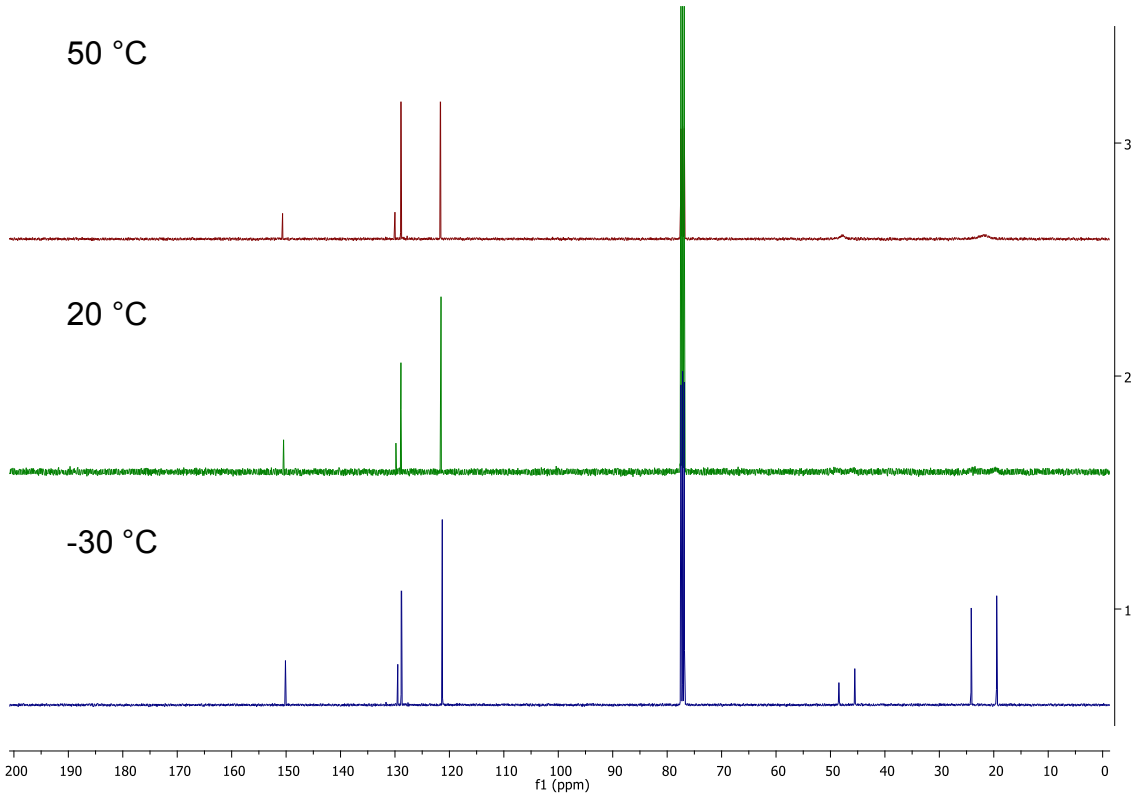
^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 150.0 (ArC), 129.5 (ArC), 129.0 (ArC), 121.5 (ArC), 48.5 (CH), 46.5 (CH), 24.0 (CH_3), 19.5 (CH_3) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 150.5 (ArC), 130.0 (ArC), 129.0 (ArCH), 121.5 (ArCH) ppm.

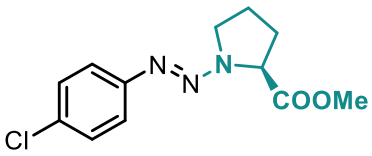
^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 155.5 (ArC), 130.0 (ArC), 129.0 (ArCH), 121.5 (ArCH), 48.0 (CH), 21.5 (CH_2) ppm.

IR: 2972, 1481, 1296, 1159, 1087, 831, 536, 486 cm^{-1}.

HRMS: [$C_{12}H_{19}N_3Cl$] Calcd. 240.1267, Found 240.1268.



methyl-((4-chlorophenyl)diazenyl)-L-prolinate (3f)



Following the general procedure, the title compound **3f** was obtained from *p*-chloroaniline and L-proline methyl ester hydrochloride as an orange oil in 80% yield (0.215 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.38 – 7.32 (m, 2H, ArH), 7.30 – 7.25 (m, 2H, ArH), 4.87 – 4.47 (m, 1H, CH), 4.24 – 3.48 (m, 2H, CH_2), 3.75 (s, 3H, CH_3), 2.43 – 2.27 (m, 1H, CH_2), 2.28 – 1.95 (m, 3H, CH_2) ppm.

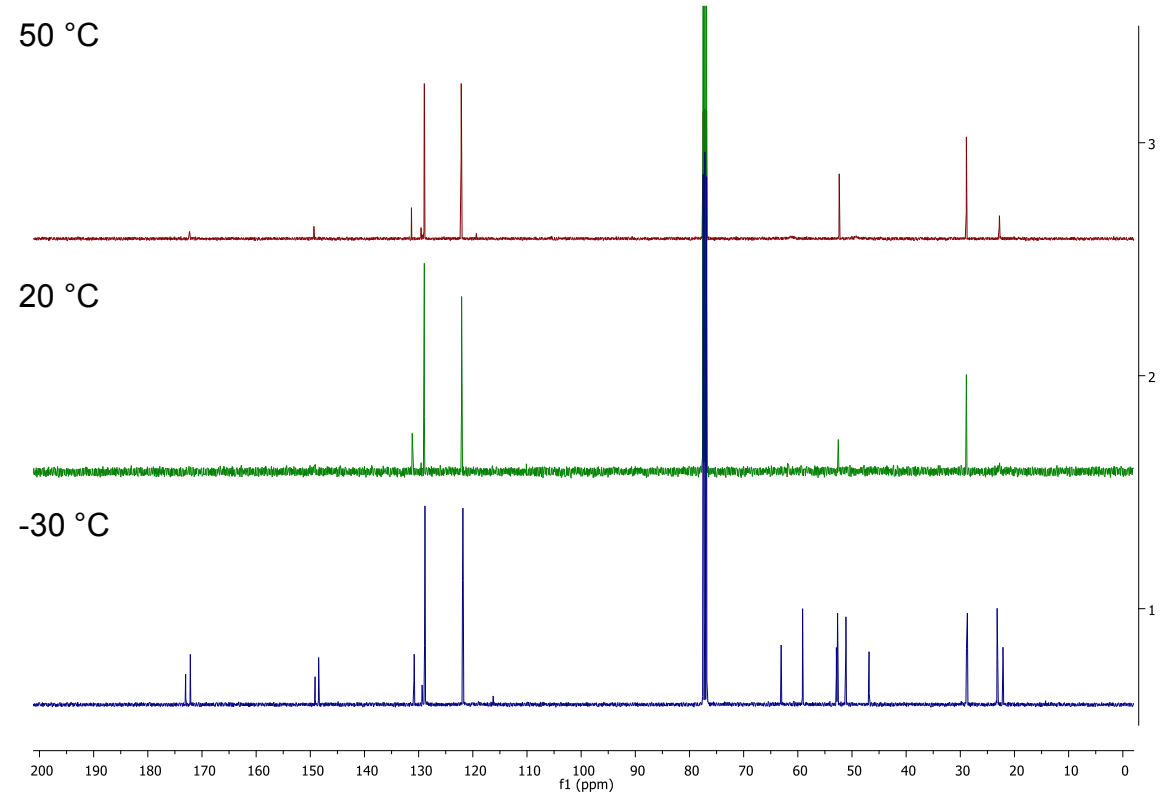
^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 173.0 (COOH), 172.0 (COOH), 149.0 (ArC), 148.5 (ArC), 131.0 (2 ArC), 129.0 (2 ArC), 122.0 (2 ArC), 63.0 (CH), 59.0 (CH), 53.0 (CH), 52.5 (CH), 51.0 (CH), 47.0 (CH), 29.0 (CH), 28.5 (CH), 23.0 (CH), 22.0 (CH) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 131.0 (ArC), 129.0 (ArC), 122.0 (ArC), 52.5 (CH), 29.0 (CH) ppm.

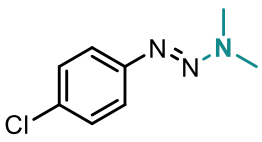
^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 171.5 (COOH), 148.5 (ArC), 130.5 (ArC), 128.0 (ArC), 121.0 (ArC), 51.5 (CH), 28.0 (CH), 22.0 (CH) ppm.

IR: 2951, 1740, 1429, 1325, 1200, 1088, 831, 521 cm^{-1}.

HRMS (EI^+): [$C_{12}H_{15}N_3O_2CL$] Calcd. 268.0853, Found 268.0849.



1-(4-chlorophenyl)-3,3-dimethyltriaz-1-ene (3g)



The general procedure was slightly modified for the preparation of title compound **3g**. The dimethylamine solution was prepared in THF and the general procedure followed with *p*-chloroaniline for all other steps to yield the product as a pale orange solid in 38% yield (0.097 g).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.36 (d, J = 8.6 Hz, 2H, ArH), 7.28 (d, J = 8.7 Hz, 2H, ArH), 3.34 (bs, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, -30 °C) δ 149.5 (ArC), 130.0 (ArC), 129.0 (ArCH), 121.5 (ArCH), 43.5 (CH_2), 36.0 (CH_2) ppm.

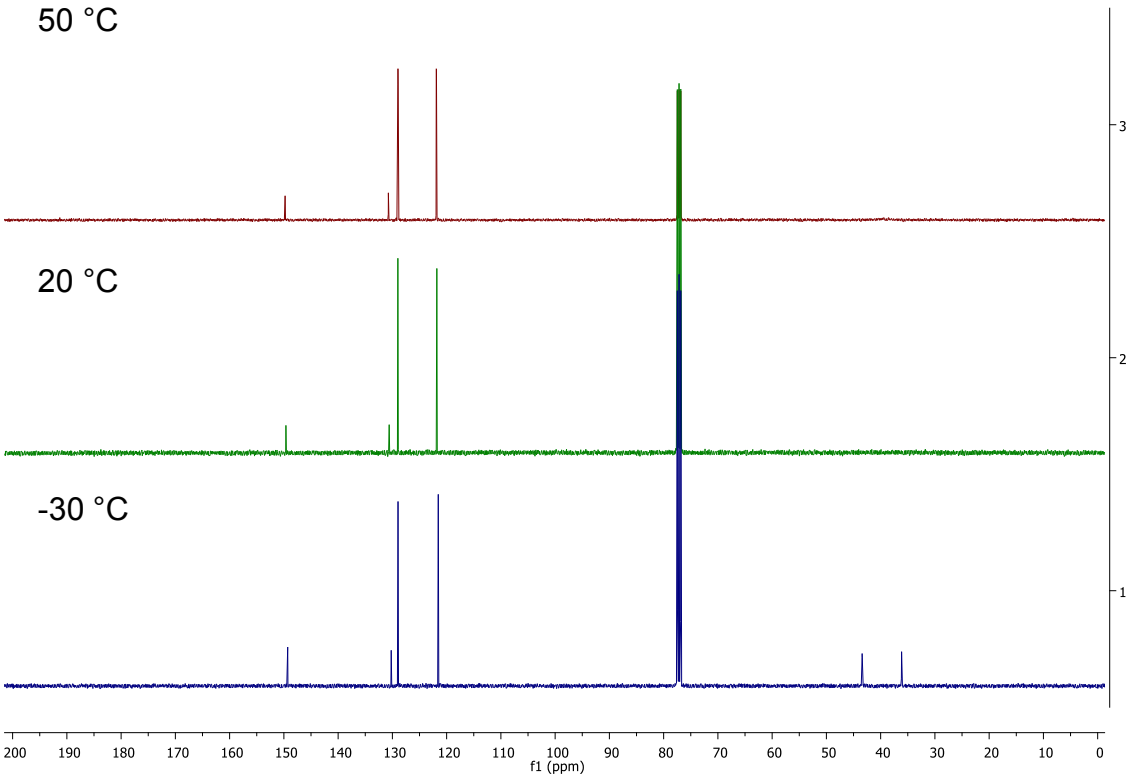
^{13}C NMR (101 MHz, $CDCl_3$, rt) δ 149.5 (ArC), 130.5 (ArC), 129.0 (ArCH), 122.0 (ArCH) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 150.0 (ArC), 130.5 (ArC), 129.0 (ArCH), 122.0 (ArCH) ppm.

mp (DCM) 47 - 49 °C.

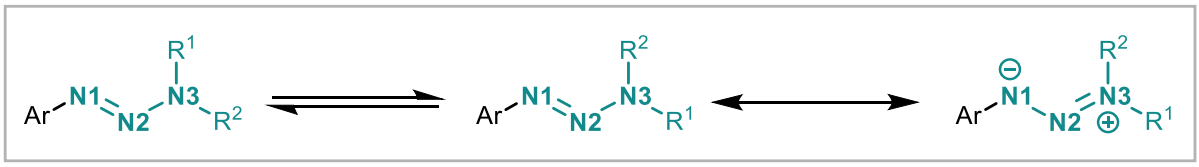
IR: 2924, 2905, 1441, 1381, 1333, 1314, 1080, 833, 816, 515 cm^{-1}.

HRMS (FTMS+ p NSI): [$C_8H_{11}N_3Cl$] Calcd. 184.0636, Found 184.0635.



3 Restricted Rotation in Triazenes

When we investigated the formation of triazenes, we noticed discrepancies between the expected and observed NMR spectra, most prominent in the secondary amine peaks in ^{13}C NMR spectra. We attributed those to a restricted rotation around the N-N bond of the triazene bridge and started to investigate this using VT NMR (Scheme SI3).[5] When the rotation of the N2-N3 bond is slow compared to the NMR time scale, the substituents on N3 are inequivalent and therefore show two distinct sets of peaks in the NMR spectrum. This can be achieved by cooling the sample down and is called the low limit. In the other extreme, when the rotation is fast compared to the NMR time scale, the substituents become equivalent and only one set of peaks in the NMR can be observed. The high limit can be achieved by heating the sample up. In between these two states, the peaks are broad and can sometimes disappear, which is called coalescence. Indeed, in our systems (400 MHz, rt), we mostly did not observe the signals of the substituents at all, meaning we were in coalescence, which lead us to investigate the restricted rotation.



Scheme SI3. Restricted Rotation in Triazenes

The restricted rotation of triazenes has first been mentioned and discussed in 1968 by Akhtar *et al*.[6] The authors demonstrated that electron withdrawing groups give rise to a higher double bond character meaning that triazenes with electron withdrawing groups on the aromatic ring rotate more slowly compared to triazenes with electron neutral or electron donating groups. A few more groups have since reported restricted rotation in triazenes.[7-14] The partial double bond character in triazenes can also be displayed in crystal structures of

triazenes, where the N2-N3 bond is, dependent on the substitution on the triazene, shorter than expected for an isolated N-N bond.[13] Even though restricted rotation in triazenes has been discussed in early literature, it is hardly acknowledged in recent literature. Reports show the broadened peaks in NMR spectra, but do not elaborate on this phenomenon and instead report them as normal peaks.We have investigated the restricted rotation for 13 triazenes and have calculated the rotational barrier for 1-((4-methoxyphenyl)diazenyl) piperidine.

We observed restricted rotation in all triazenes prepared. Our first triazene made within the group **3b** was in coalescence at room temperature, with only one full peak (C3) instead of the expected three for the amine substituents in the ^{13}C NMR (Figure SI1). Upon heating the same sample up to 50 °C the second peak (C2, C4) became sharper and a third one appeared (C1, C5). When cooling down to -30 °C, the peaks unmerge to form four new peaks (C1, C5, C2, C4) with the last one under the first sharp original one (C3). However, none of these are very sharp, showing that neither high nor low limit were reached.

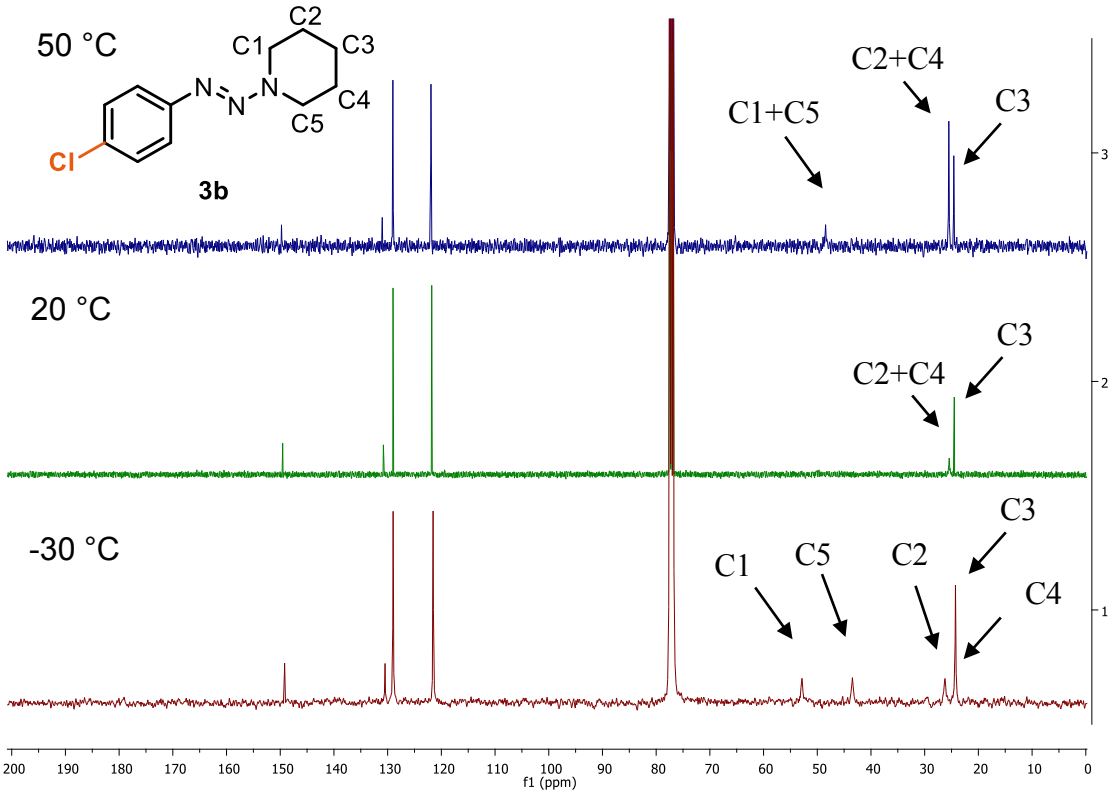
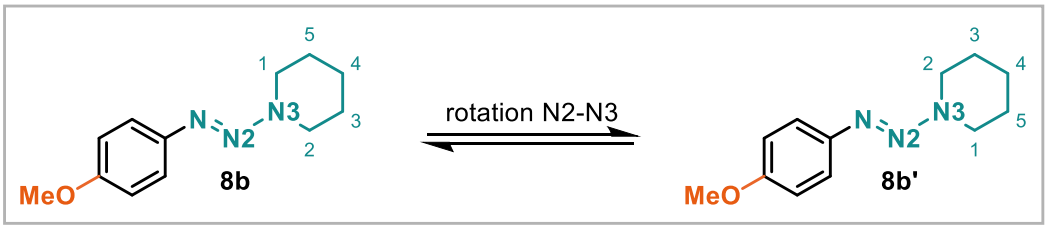


Figure SI1. VT NMR of *p*-chlorotriazene **3b**

When we investigated this further, we found high rotational barriers for triazenes containing electron withdrawing groups on the aromatic system, which resulted in a high coalescence temperature and lower barriers and coalescence temperature for triazenes with electron donating groups, in congruence with Akhtar and *et al*.[6]

We decided to investigate the example of triazene **8b** 1-((4-methoxyphenyl)diazenyl) piperidine further, as it seemed most likely to be able to reach the low and high limit upon cooling and heating further. The maximum range for the solvent $CDCl_3$ of -60 to +50 °C was investigated in 10 °C steps. Even though the high and low limit were not completely reached, we decided to calculate the activation energy *via* the line widths method which needs the peak position in high and low limit and calculate the coalescence temperature. This can then be compared to the observed coalescence temperature. For that the signals of C1 and C5 were used (Scheme SI4, Figure SI2 and Figure SI3).



Scheme SI4. Rotation around N2-N3 Bond for 1-((4-methoxyphenyl)diazenyl)piperidine **8b**

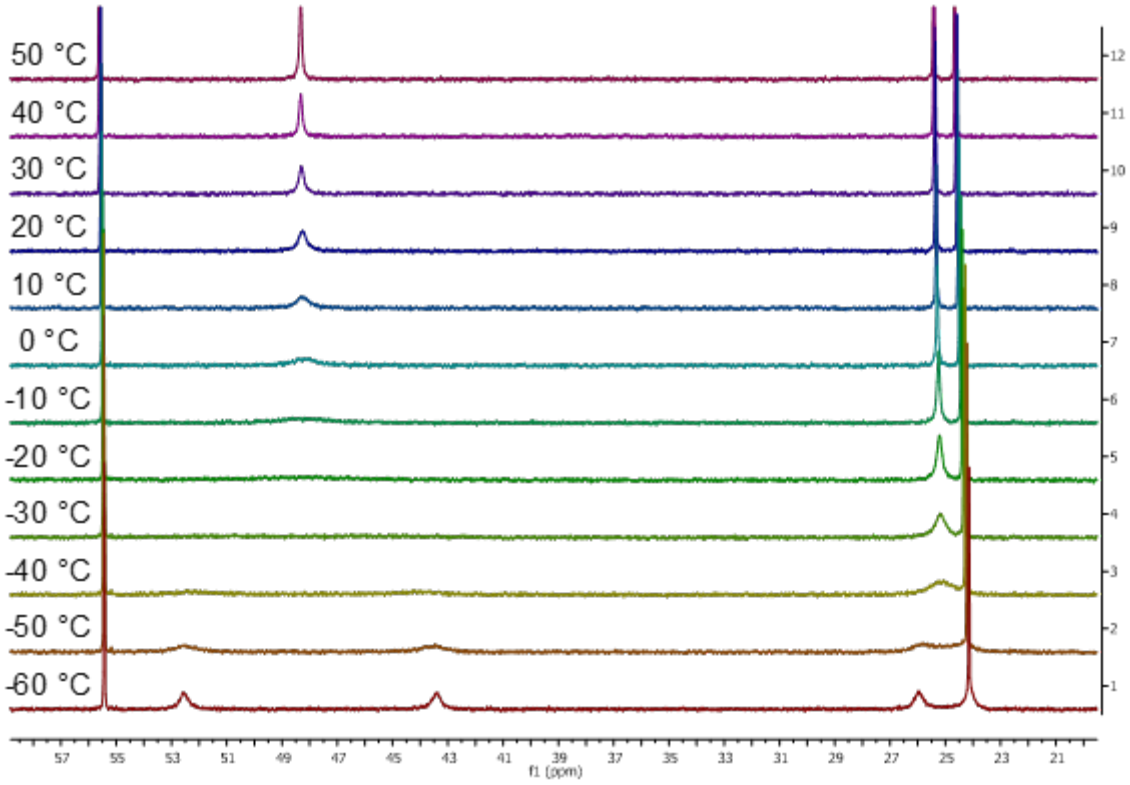


Figure SI2. VT NMR for 1-((4-methoxyphenyl)diazenyl)piperidine **8b**, Zoom on Aliphatic Signals C1-C[5]

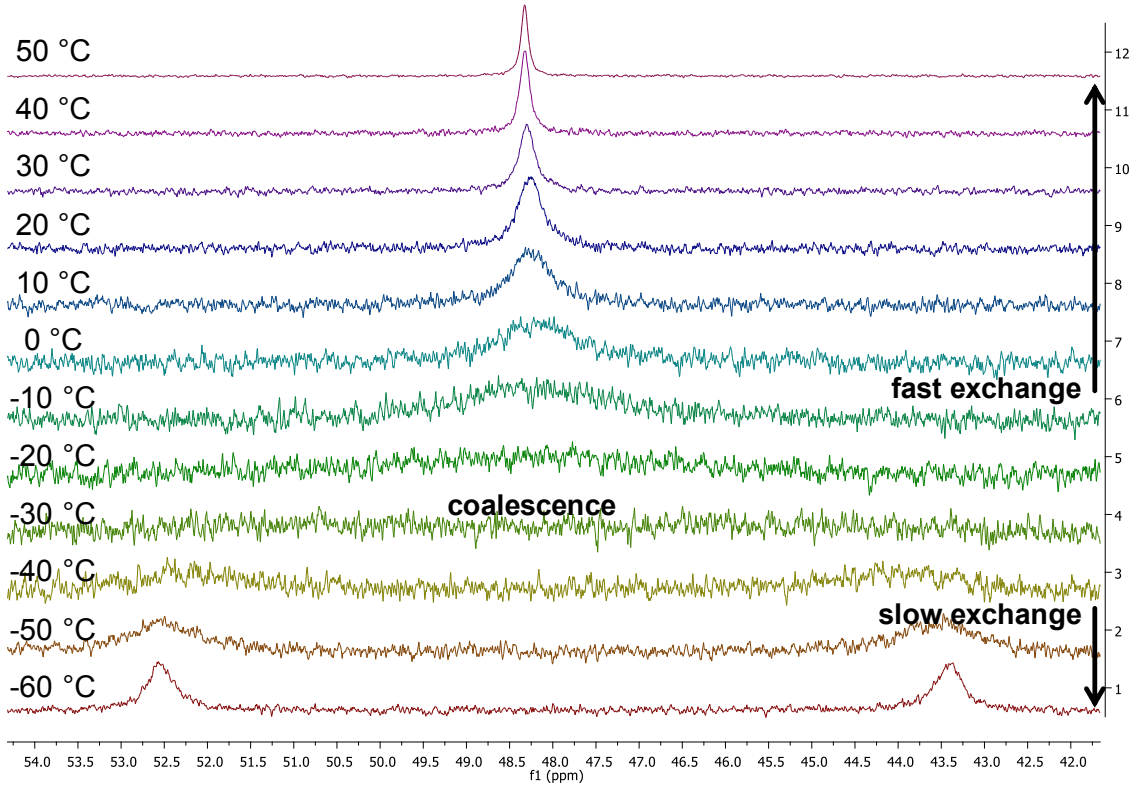


Figure SI3. VT NMR for 1-((4-methoxyphenyl)diazenyl)piperidine **8b**, Zoom on Signals C2 and C2 with Exchange Rate Regimes

3.1 Activation Energy Calculations

For a symmetrical exchange, when both signals have the same intensity, the following equations can be used to calculate the exchange rates. It is described as the line shape analysis as the additional line width $\Delta\upsilon$ of signals is taken into account (Figure SI4).

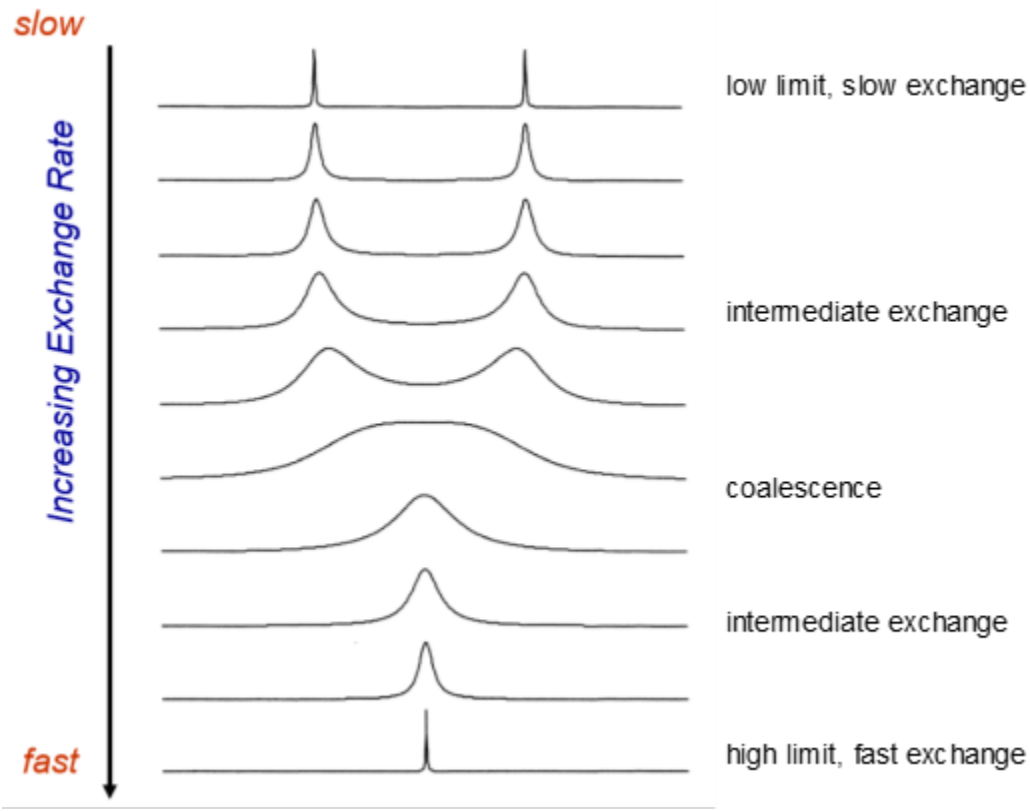


Figure SI4. NMR Signal Dependency on Exchange Rate[5]

fast exchange:

$$k = \frac{\pi \cdot (\delta_{A,0} - \delta_{B,0})^2}{2\Delta\upsilon}$$

at coalescence:

$$k = \frac{\pi \cdot (\delta_{A,0} - \delta_{B,0})^2}{\sqrt{2}}$$

intermediate exchange:

$$k = \frac{\pi \cdot \sqrt{(\delta_{A,0} - \delta_{B,0})^2 - (\delta_{A,c} - \delta_{B,C})^2}}{\sqrt{2}}$$

slow exchange:

$$k = \Delta\Delta\upsilon \cdot \pi$$

$\Delta\Delta\upsilon$: additional line width in Hz

$$\Delta\Delta\upsilon = \Delta\upsilon_{A,T} - \Delta\upsilon_{A,n}$$

$\delta_{A,0}$: position peak A in Hz at low limit

$\delta_{B,0}$: position peak B in Hz at low limit

$\delta_{A,c}$: position peak A in Hz at coalescence

$\delta_{B,C}$: position peak B in Hz at coalescence

$\Delta\upsilon_{A,T}$: line width of peak A at temperature T

$\Delta\upsilon_{A,n}$: natural line width of peak A (e.g. high or low limit)

From rate constants at different temperatures, the Arrhenius equation can be used to plot the Arrhenius plot (ln(k) vs 1/T). From the slope the activation energy can be calculated.

$$k = Ae^{-\frac{E_A}{RT}}$$

$$\ln(k) = \ln(A) - \frac{E_A}{R}\frac{1}{T}$$

A: pre-exponential factor

E_A: activation energy

R: gas constant

As an alternative to the line shape analysis, the activation energy can be estimated from the peak positions at the low limit and the coalescence temperature only. To increase accuracy, the coalescence temperature can be determined on more than one field strength.

$$E_A = RT_C \left[22.96 + ln \frac{T_C}{\delta_{A,0} - \delta_{B,0}} \right]$$

The exchange rate regimes were estimated to be: -60 °C - -40 °C slow exchange, -30 °C coalescence, -20 °C – 50 °C fast exchange. The line widths were calculated using the Bruker software topspin 3.5 (Table 2.2). Due to some peaks being poorly resolved, not all line widths could be determined.

The positions of peak A and B in Hz at low limit were obtained from the spectrum at -60 °C:

$\delta_{A,0} = 5310\ Hz$

$\delta_{B,0} = 4379\ Hz$

The natural line width was determined from the highly resolved methoxy peak:

$\Delta\upsilon_{A,n} = 2.02\ Hz$

From the line width in each spectrum the rate constants could be calculated (Table SI1). These were then used in an Arrhenius plot (Figure SI5). The exchange rate at the point of coalescence is an outlier so that it was not taken into account for the trendline. From the slope (m) of the trendline the activation energy was calculated.

$$E_A = -m \cdot R$$

$$E_A = 46.8 \pm 2.4\ kJmol^{-1}$$

Table SI1. Exchange Rate Calculations

temperature [°C]	exchange rate regime -	$\Delta\upsilon_{A,T}$ [Hz]	$\Delta\Delta\upsilon$ [Hz]	exchange rate [s^{-1}]
-20	fast	825.815	823.80	1650
-10	fast	461.293	459.27	2959
0	fast	133.723	131.70	10320
10	fast	54.401	52.38	25948
20	fast	34.721	32.70	41564
30	fast	21.232	19.21	70747
40	fast	13.89	11.87	114507
50	fast	9.75	7.73	175834

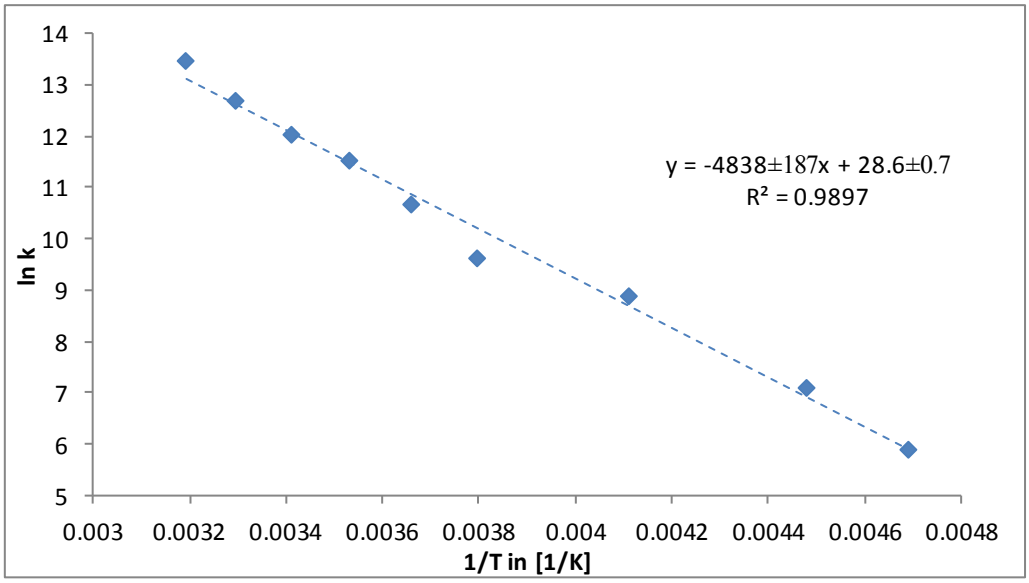


Figure SI5. Arrhenius Plot

The coalescence temperature was estimated by plotting the activation energy vs coalescence temperature in the estimate (Figure SI6).

$$E_A = RT_C\left[22.96 + ln\frac{T_C}{\upsilon_{A,0} - \upsilon_{B,0}}\right]$$

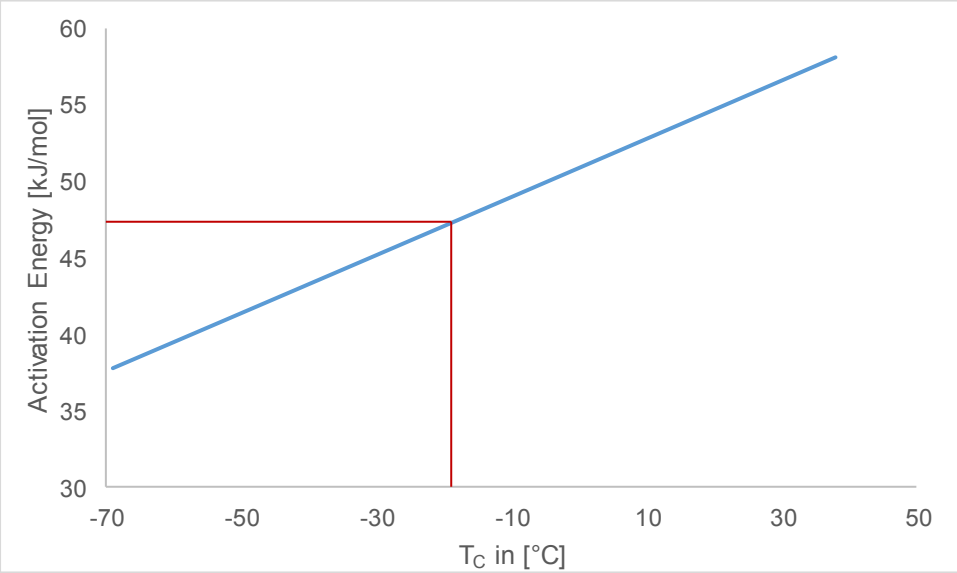
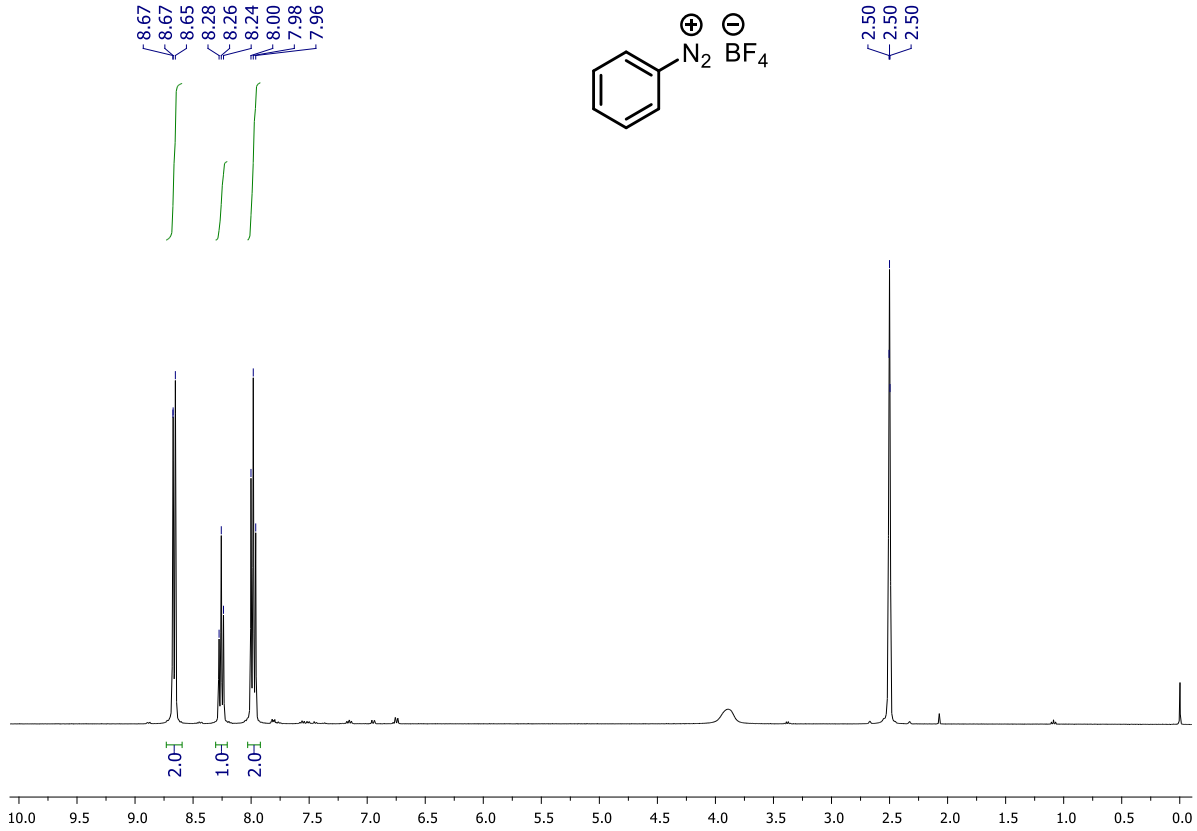


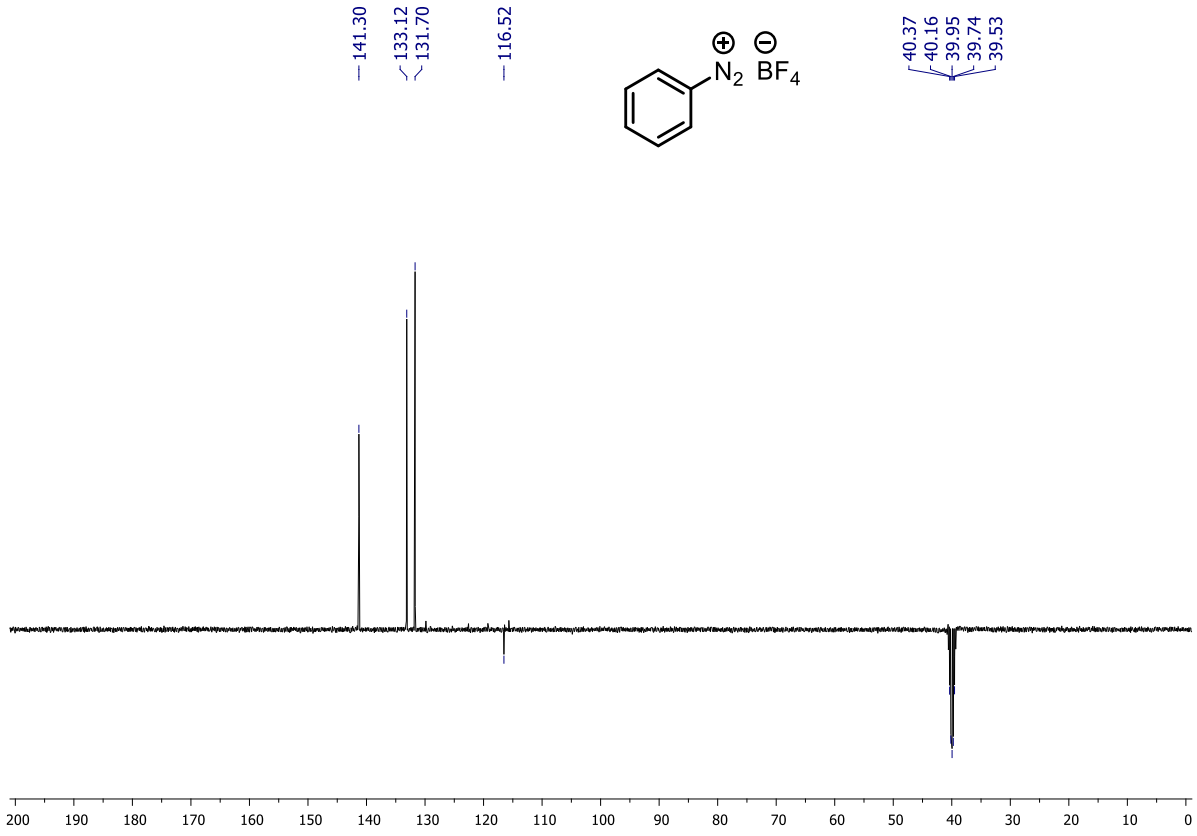
Figure SI6. Determination of the Coalescence Temperature

The activation energy was calculated to be 46.8 ±2.4 kJmol^{-1} which leads to a coalescence temperature of -22 °C. This is in congruence with the observations made in the spectra. The coalescence temperature and the calculated activation energy are comparable to the values reported by Akhtar and co-workers for the corresponding dimethylamine triazene (T_C = -44 °C, 31.0 kJmol^{-1})[6] and by Foster and co-workers for the pyrrolidine triazene (T_C = -19 °C, 50.2 kJmol^{-1})[11].

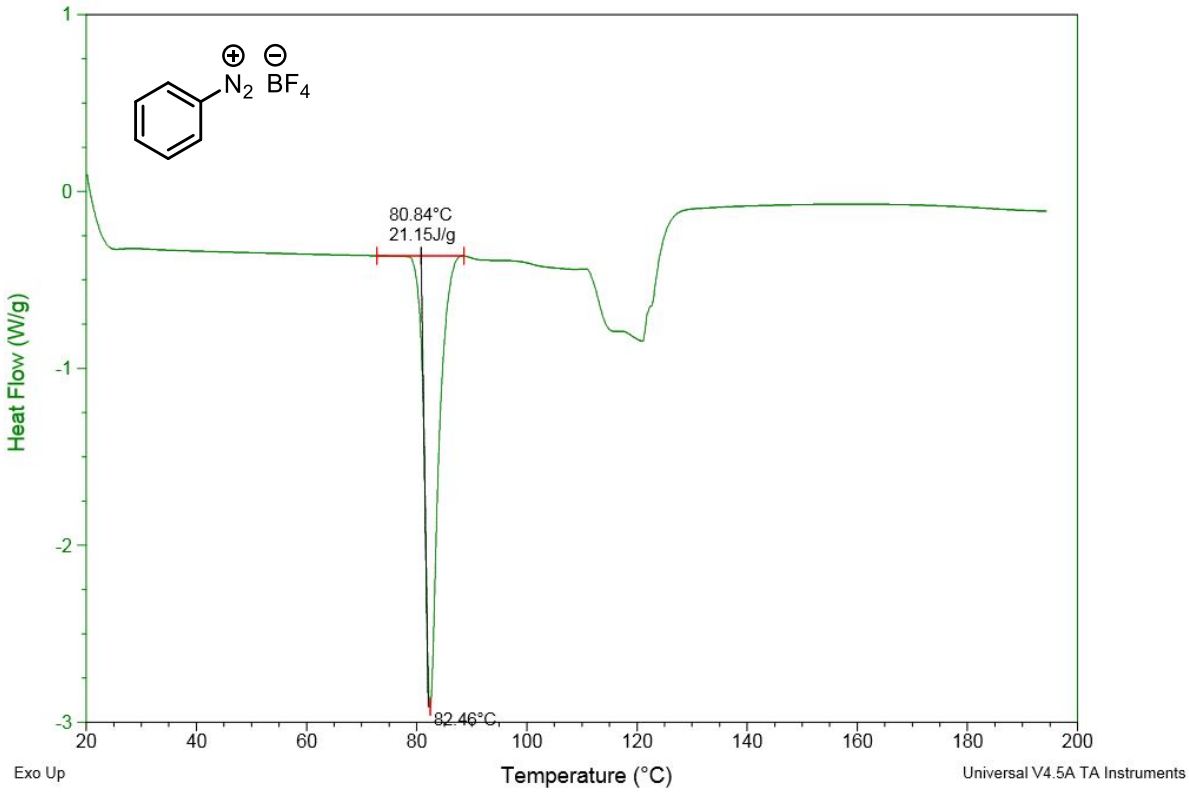
4 NMR and DSC data

benzenediazonium tetrafluoroborate (2a)

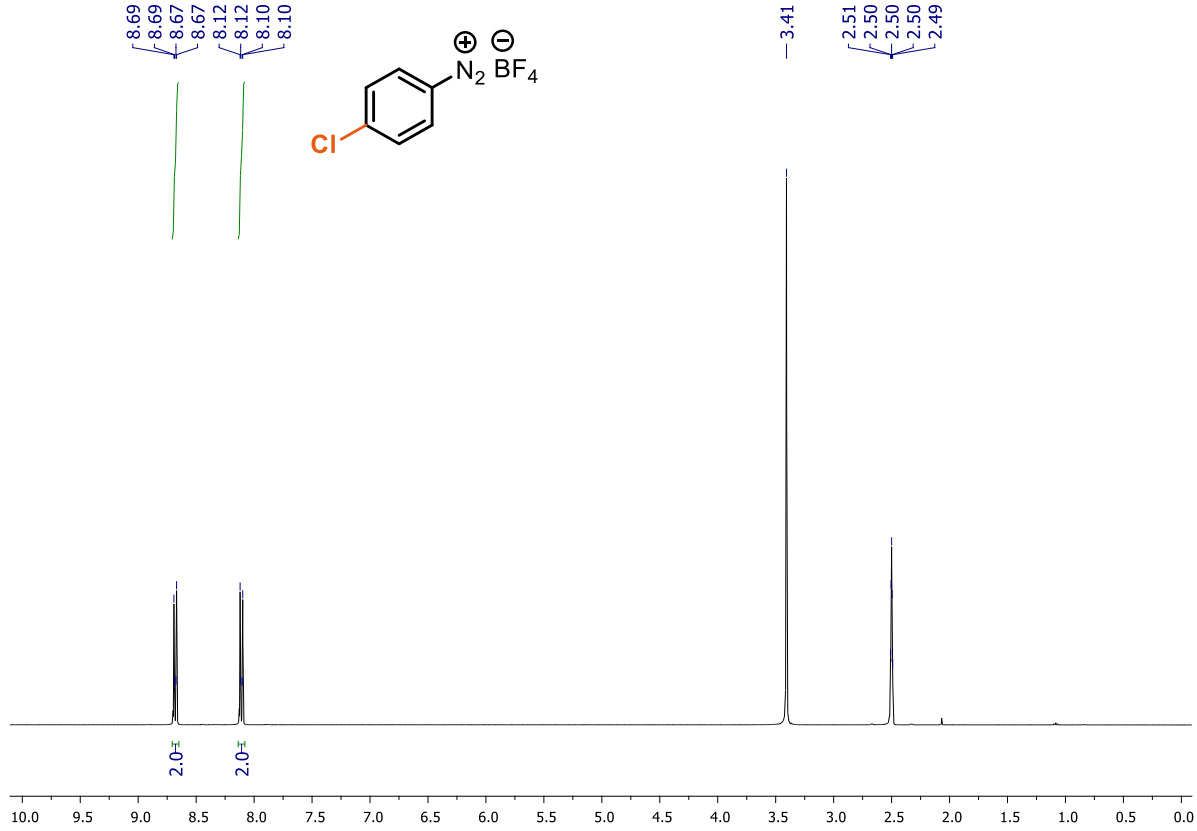


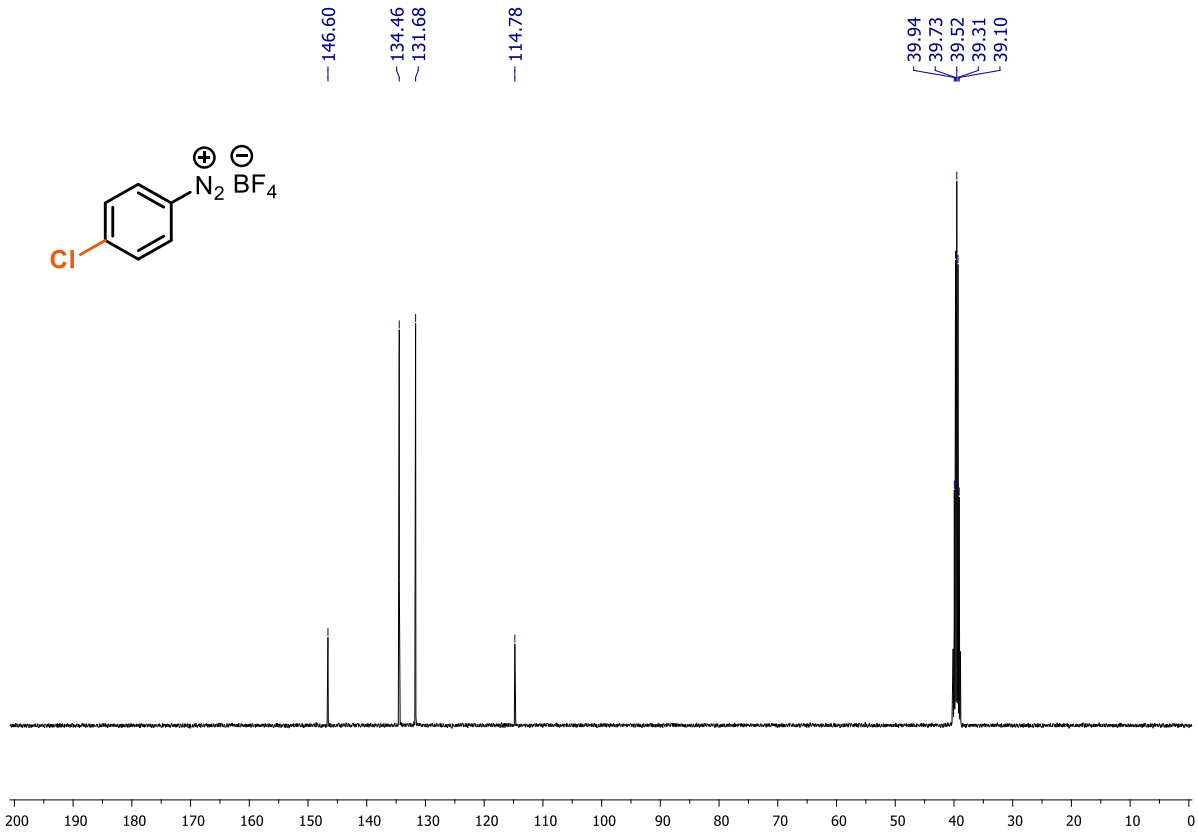


DSC

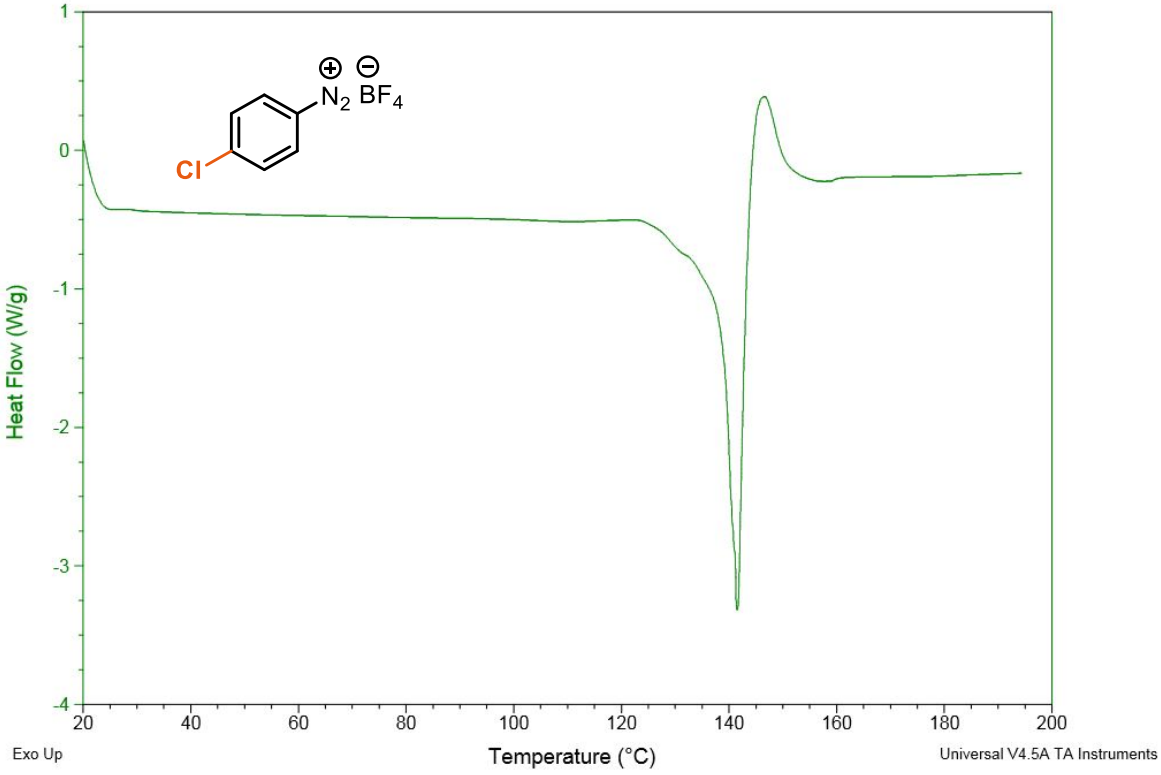

1
0
-1
-2
-3
Heat Flow (W/g)
80.84°C
21.15J/g
82.46°C
20
40
60
80
100
120
140
160
180
200
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

4-chlorobenzenediazonium tetrafluoroborate (3a)

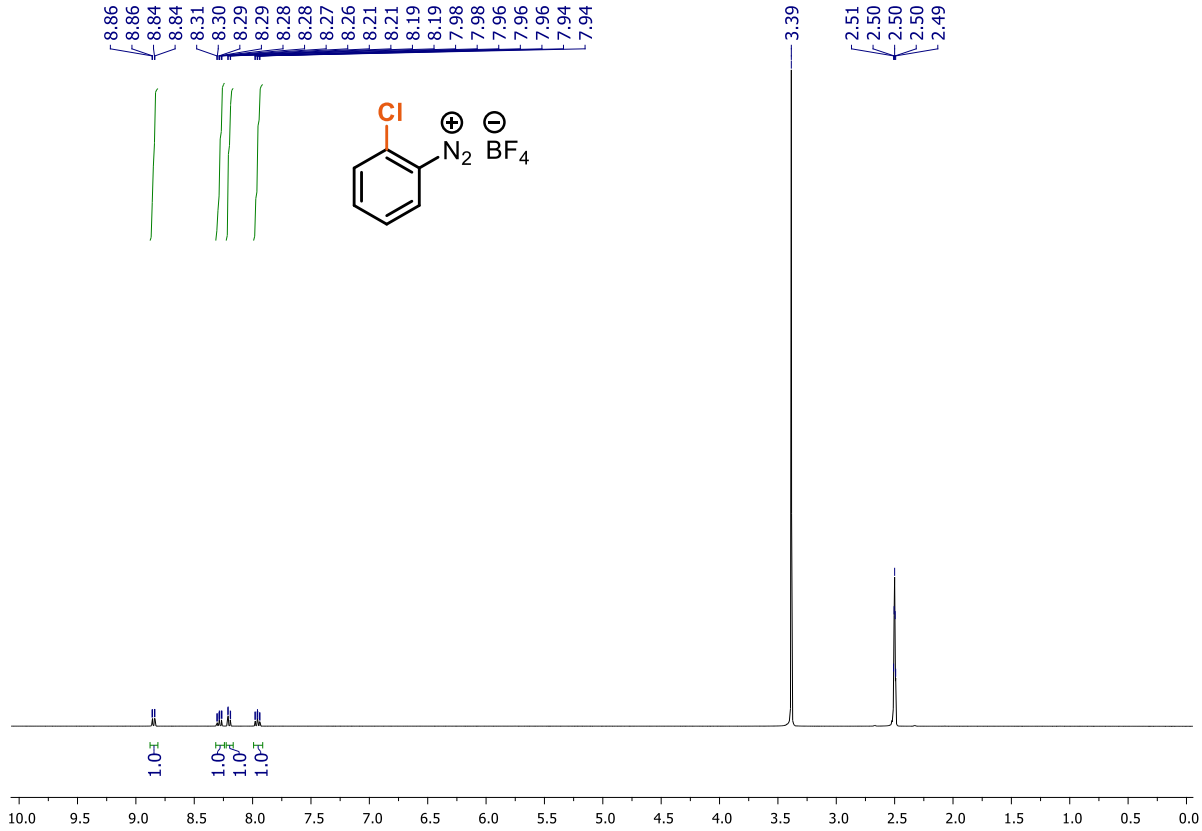


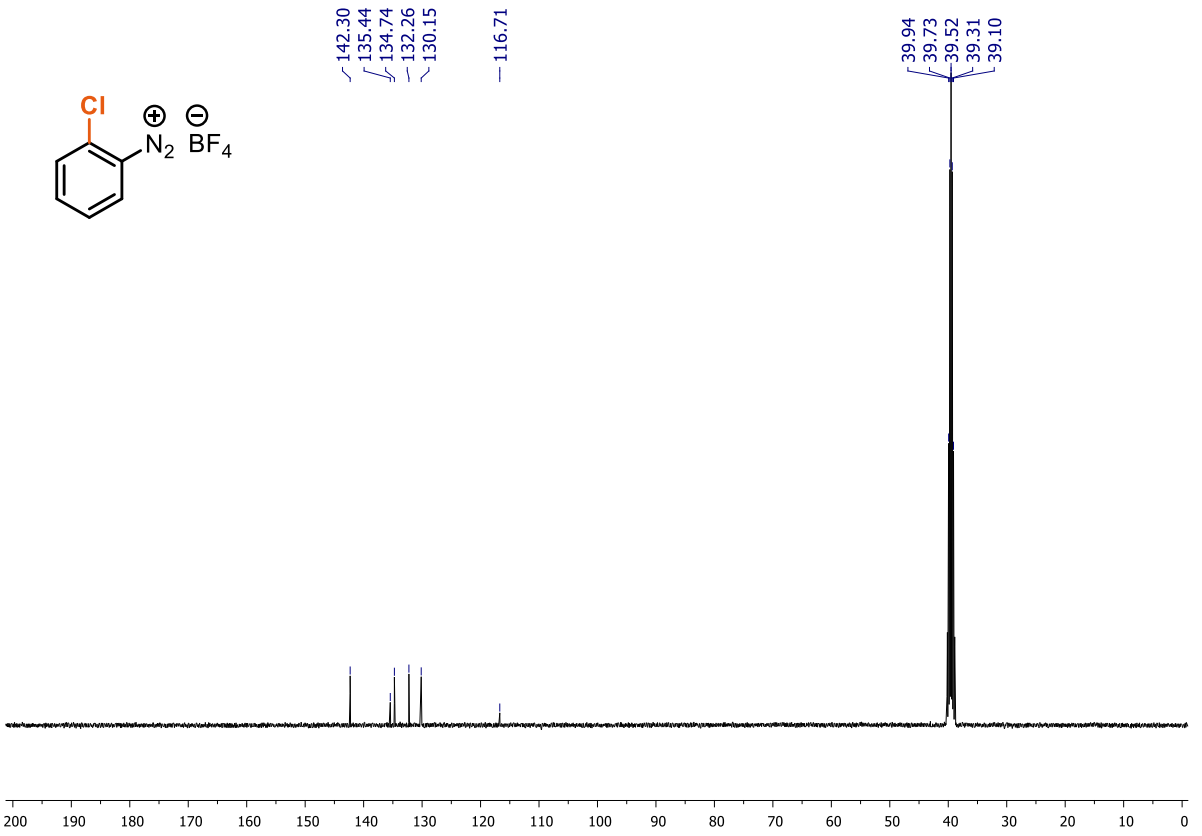


DSC

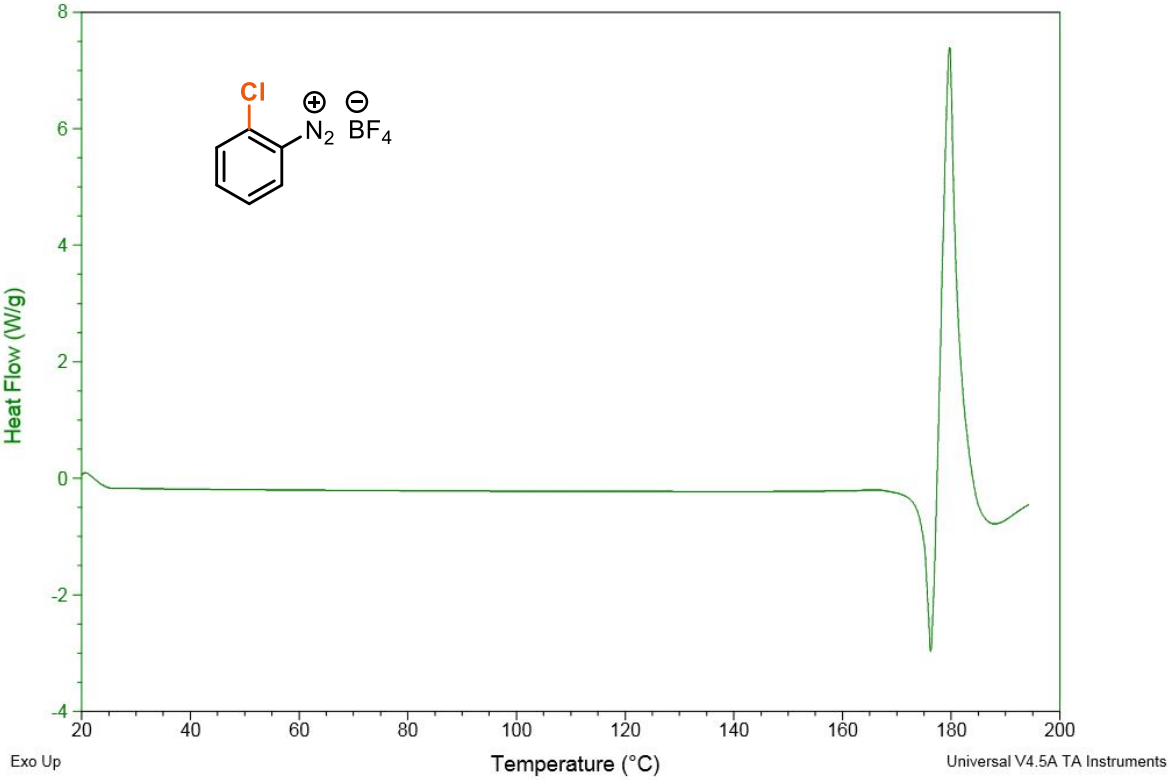

1
0
-1
-2
-3
-4
Heat Flow (W/g)
20
40
60
80
100
120
140
160
180
200
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
Cl
N2 BF4

2-chlorobenzenediazonium tetrafluoroborate (4a)

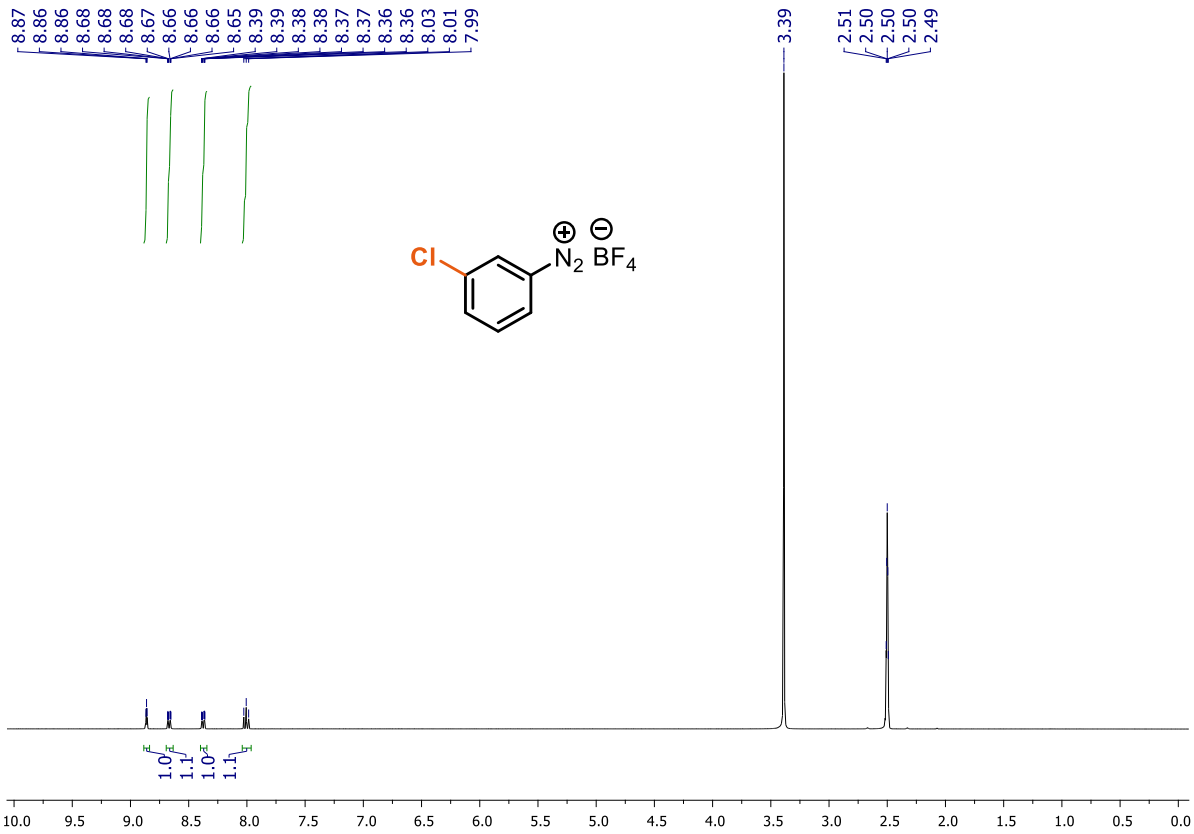


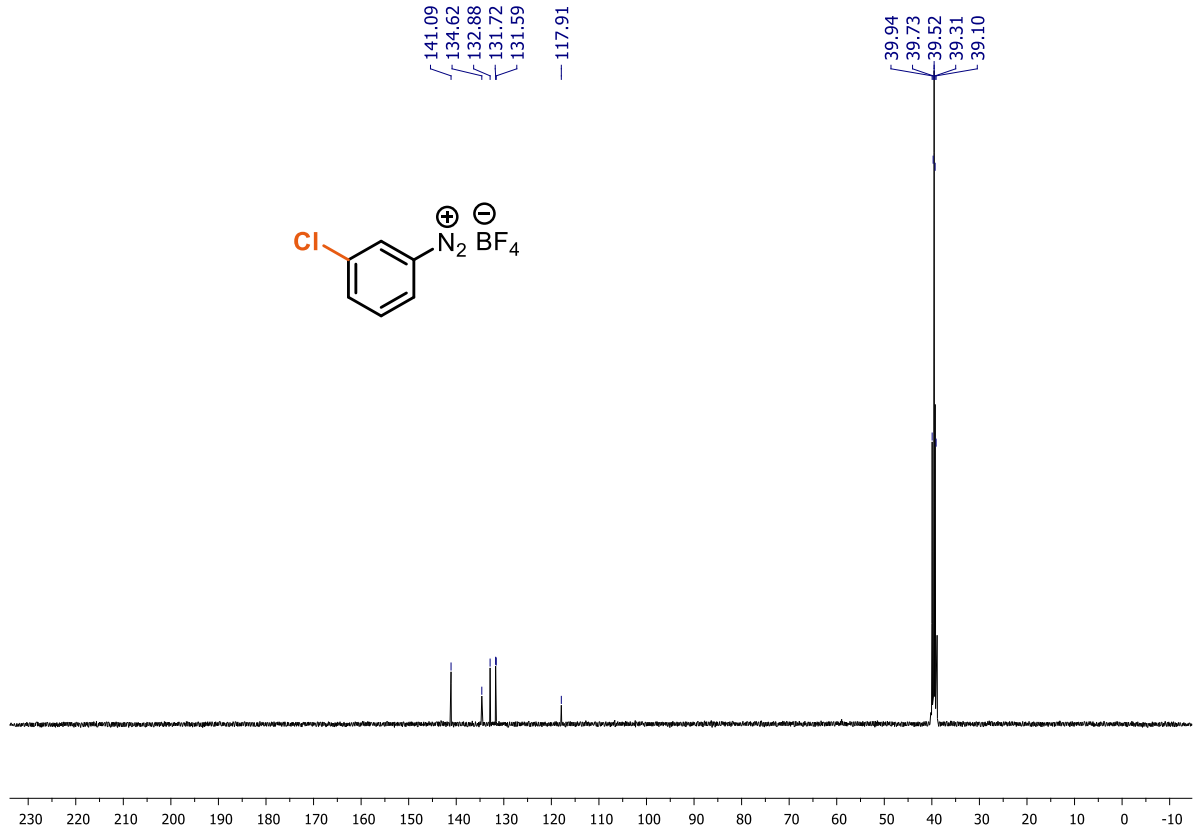


DSC

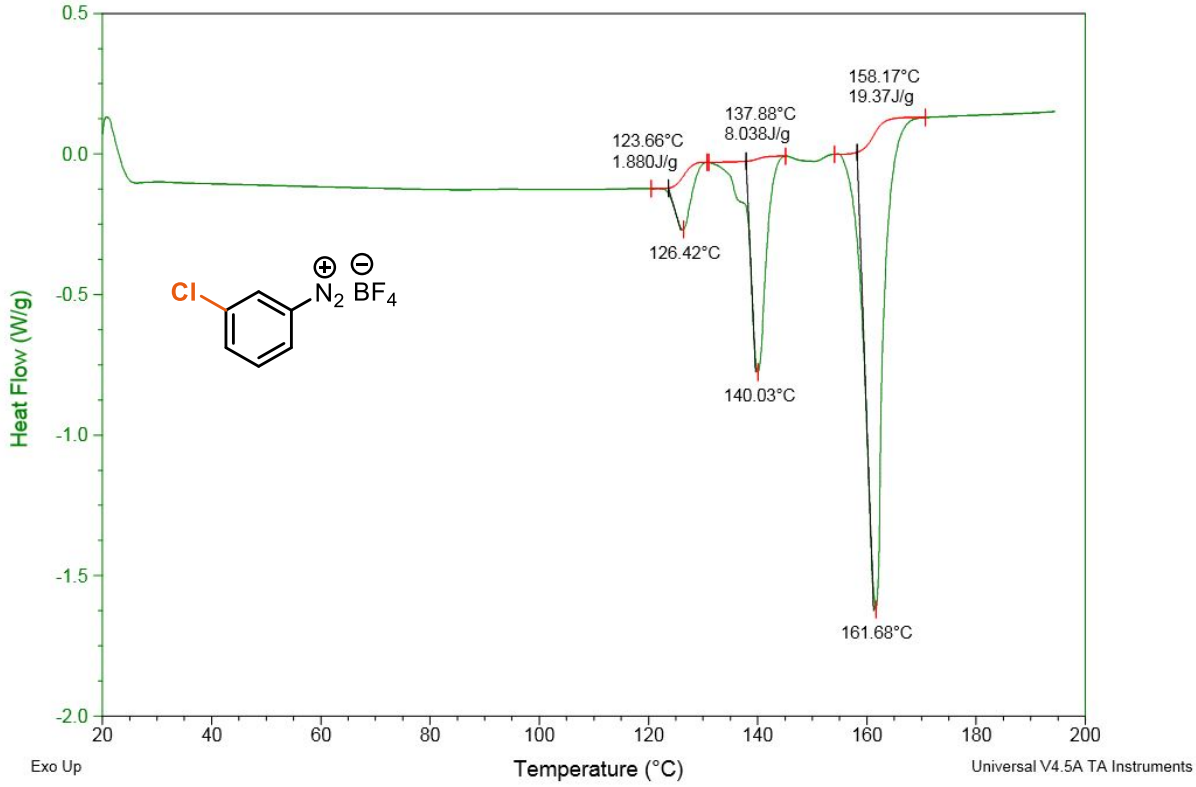

Cl
N2 BF4
Heat Flow (W/g)
8
6
4
2
0
-2
-4
20
40
60
80
100
120
140
160
180
200
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments

3-chlorobenzenediazonium tetrafluoroborate (5a)

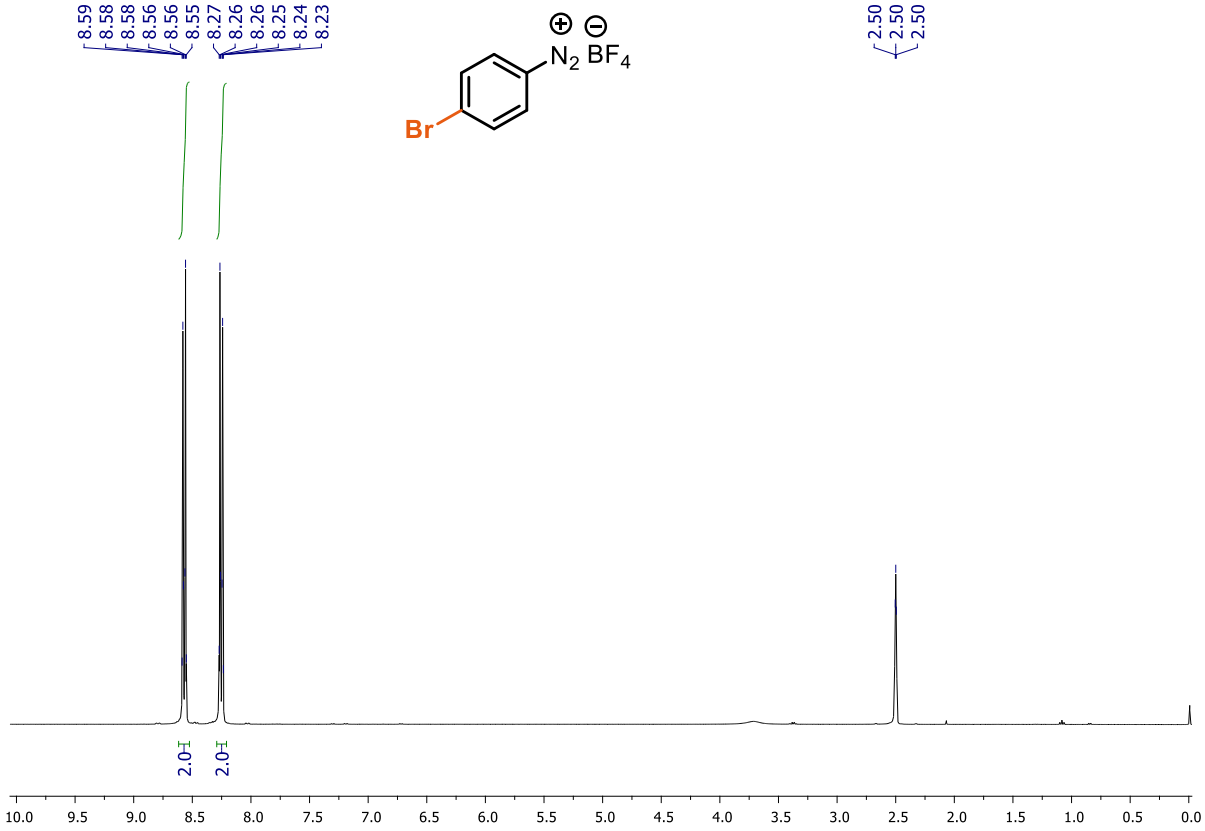


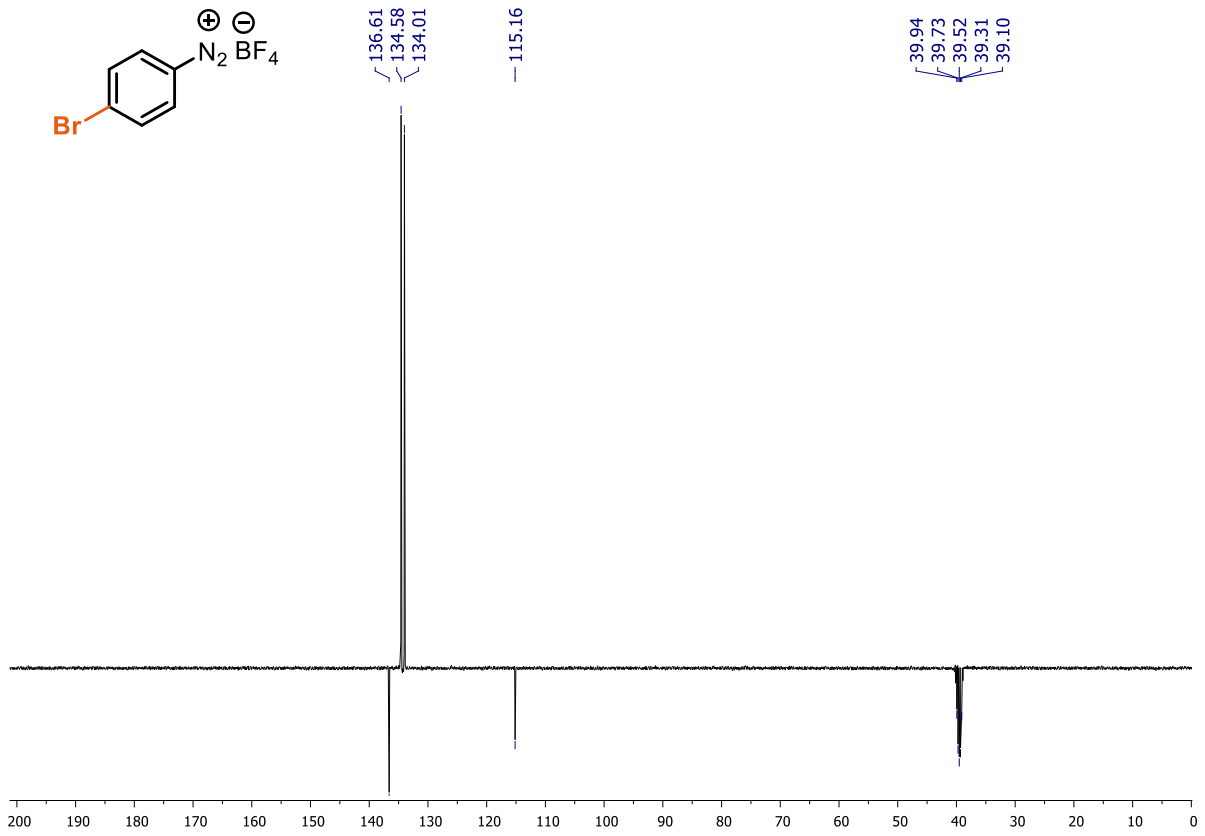


DSC

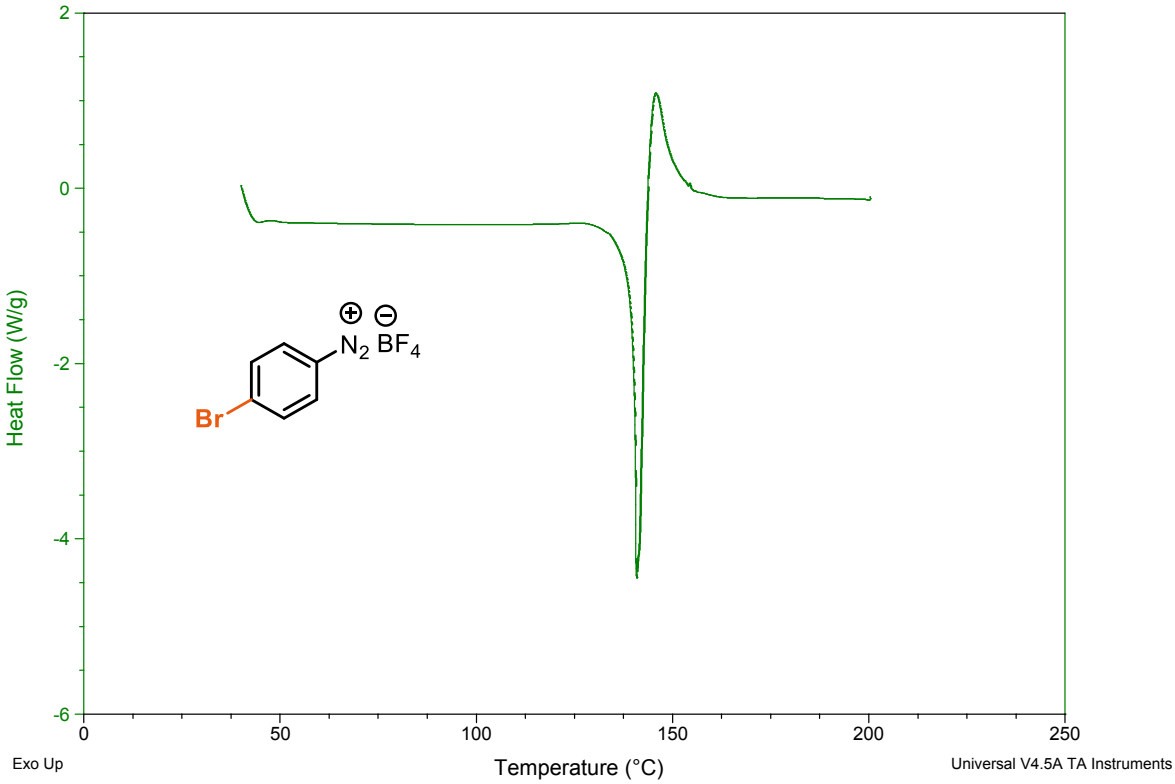

0.5
0.0
-0.5
-1.0
-1.5
-2.0
Heat Flow (W/g)
20
40
60
80
100
120
140
160
180
200
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
123.66°C
1.880J/g
126.42°C
137.88°C
8.038J/g
140.03°C
158.17°C
19.37J/g
161.68°C
Cl
N2 BF4

4-bromobenzenediazonium tetrafluoroborate (6a)

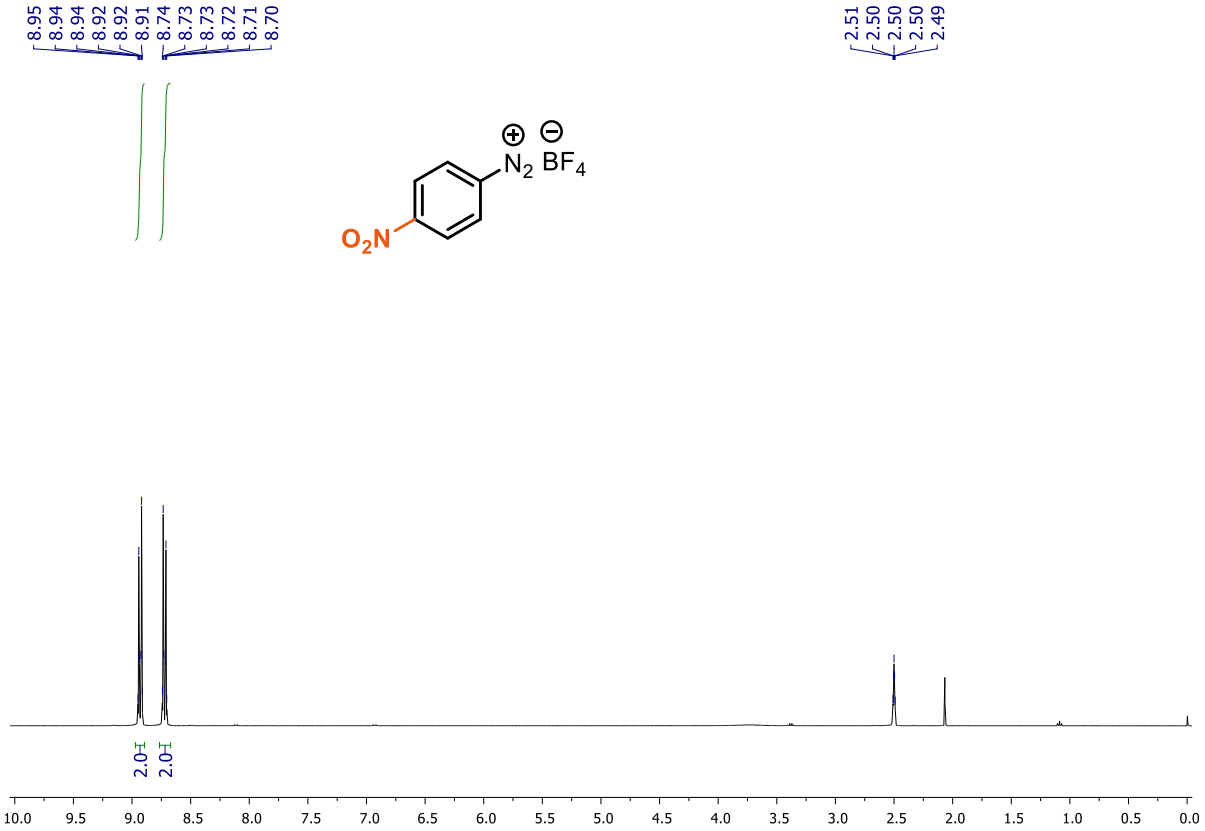


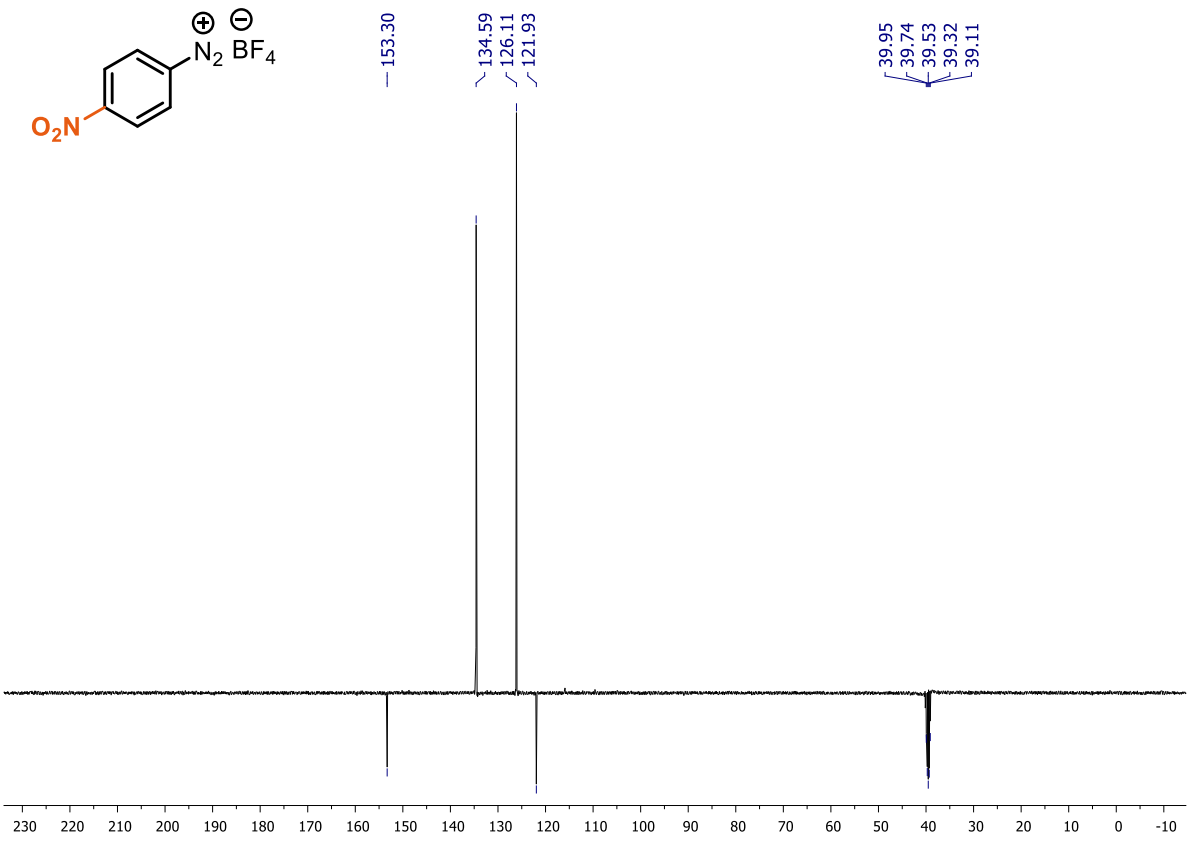


DSC

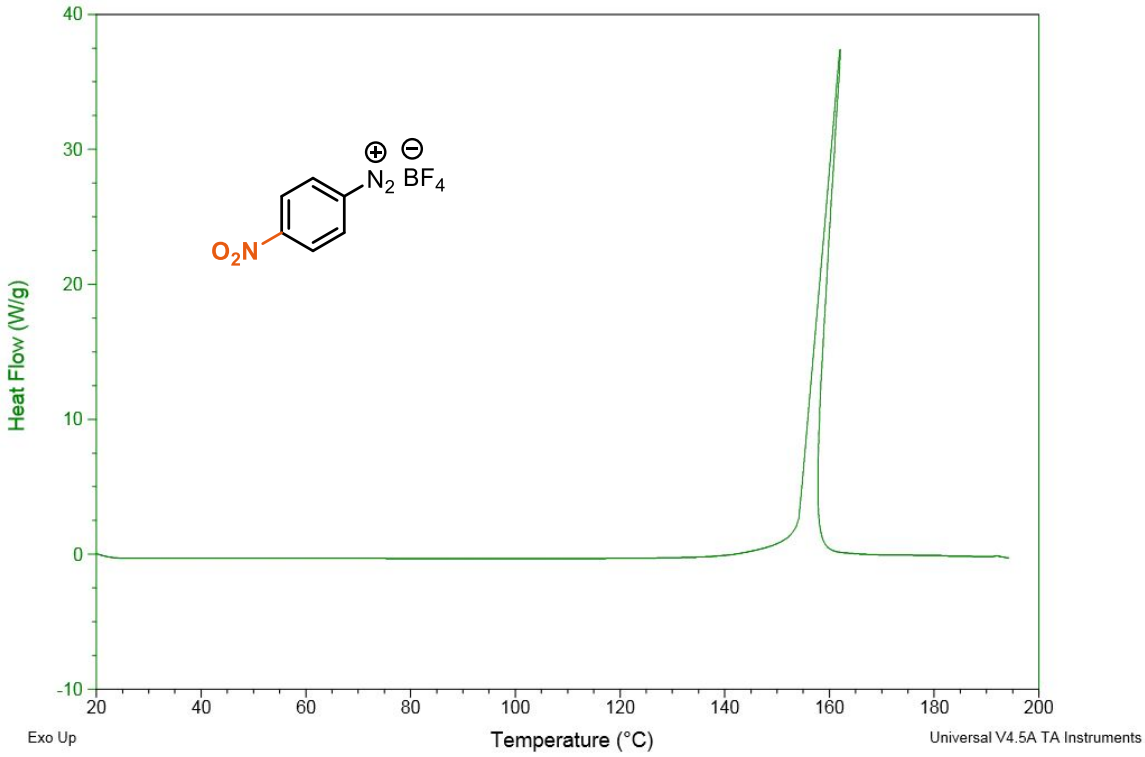

2
0
-2
-4
-6
Heat Flow (W/g)
0
50
100
150
200
250
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
Br
N2 BF4

4-nitrobenzenediazonium tetrafluoroborate (7a)

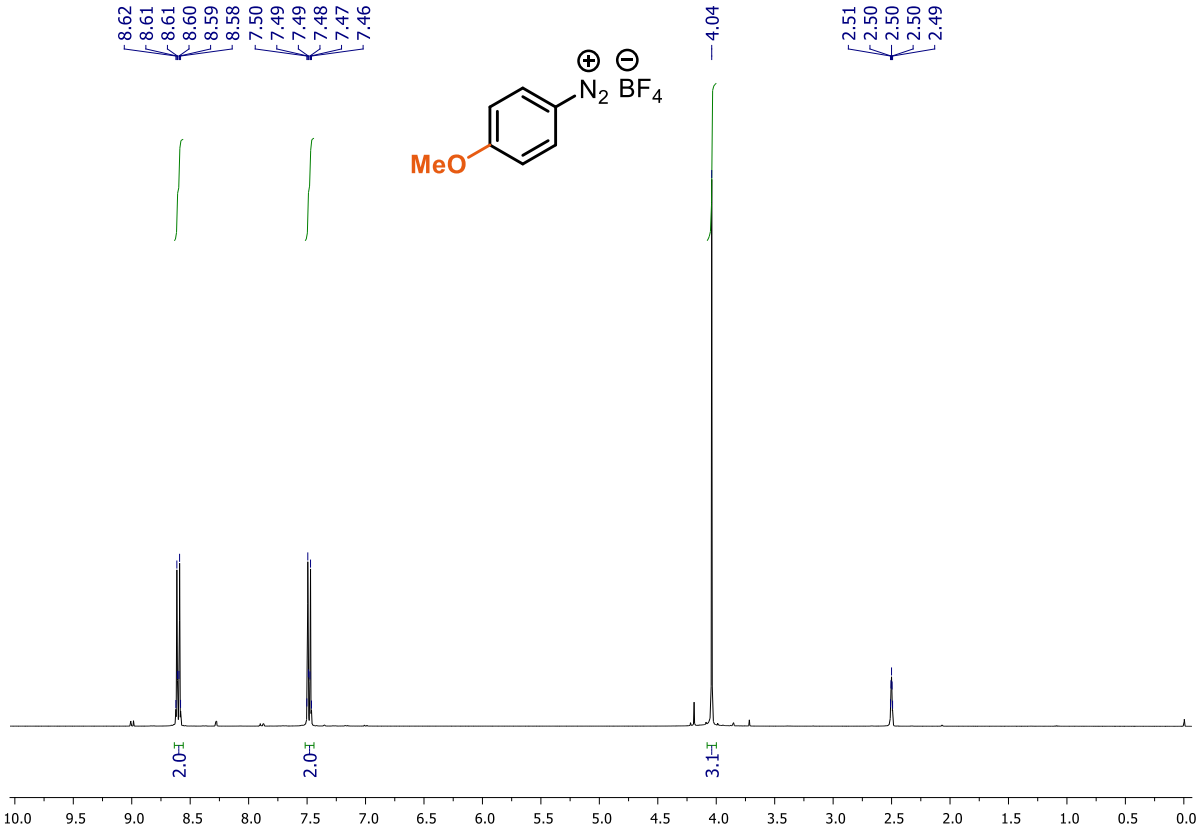


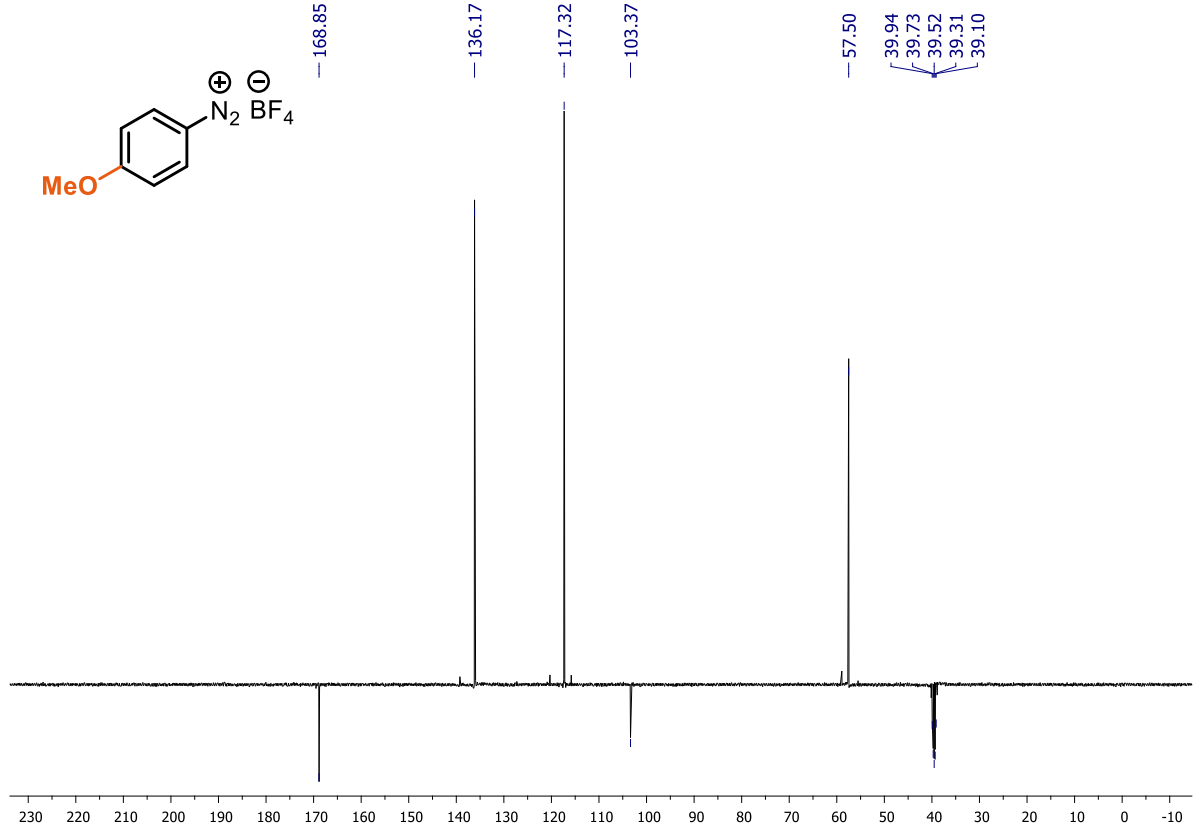


DSC

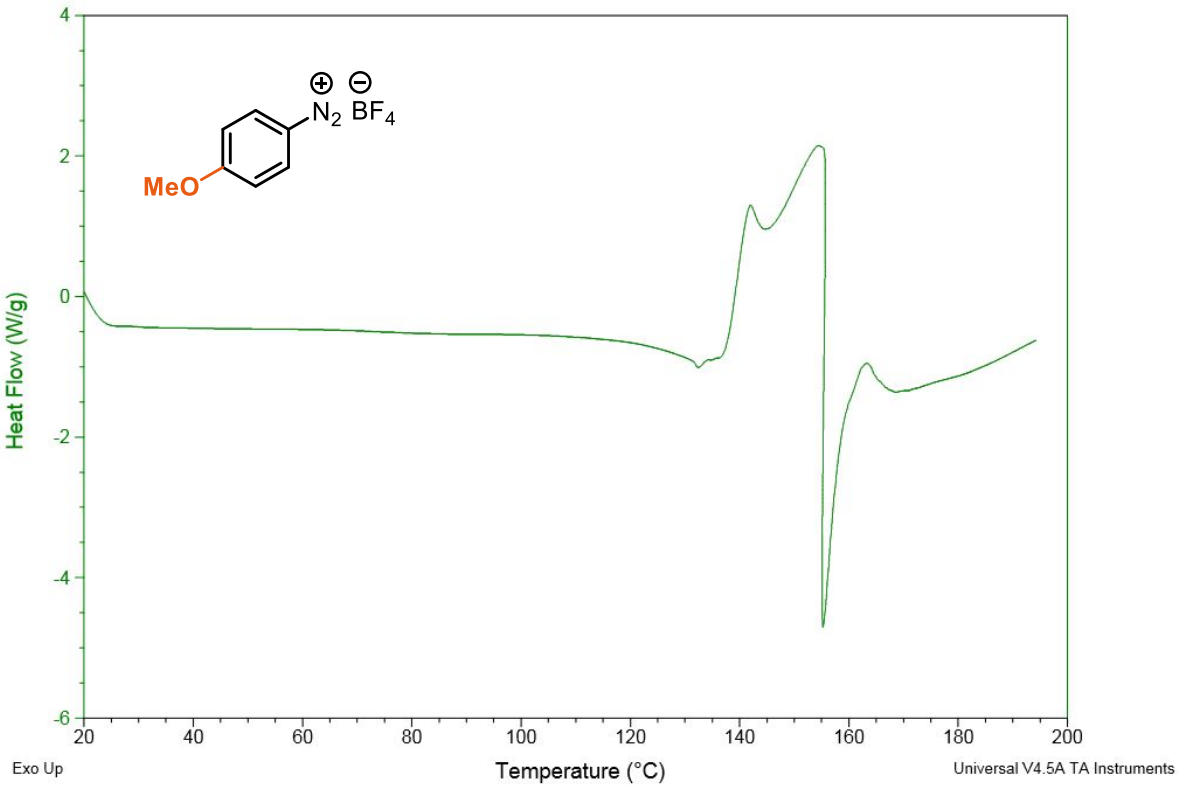

40
30
20
10
0
-10
Heat Flow (W/g)
20
40
60
80
100
120
140
160
180
200
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
O_2N
N_2 BF_4

4-methoxybenzenediazonium tetrafluoroborate (8a)

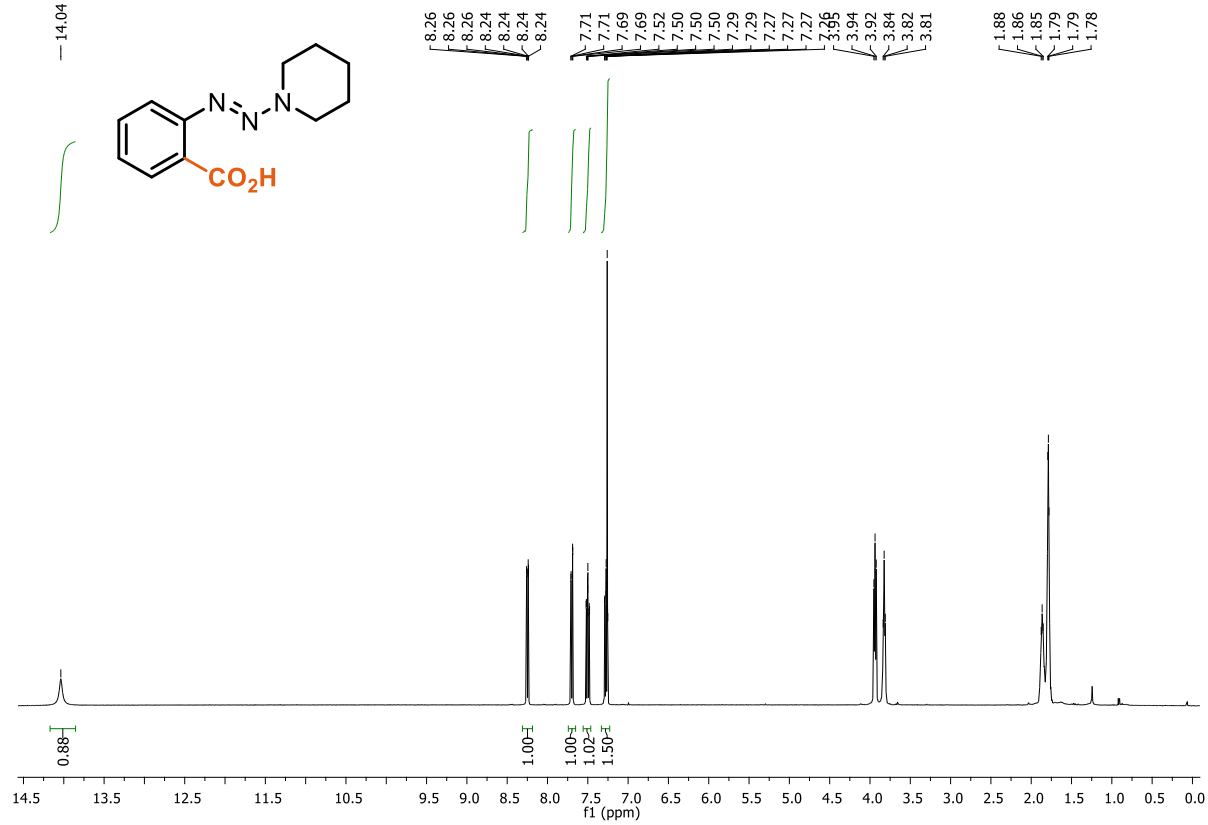


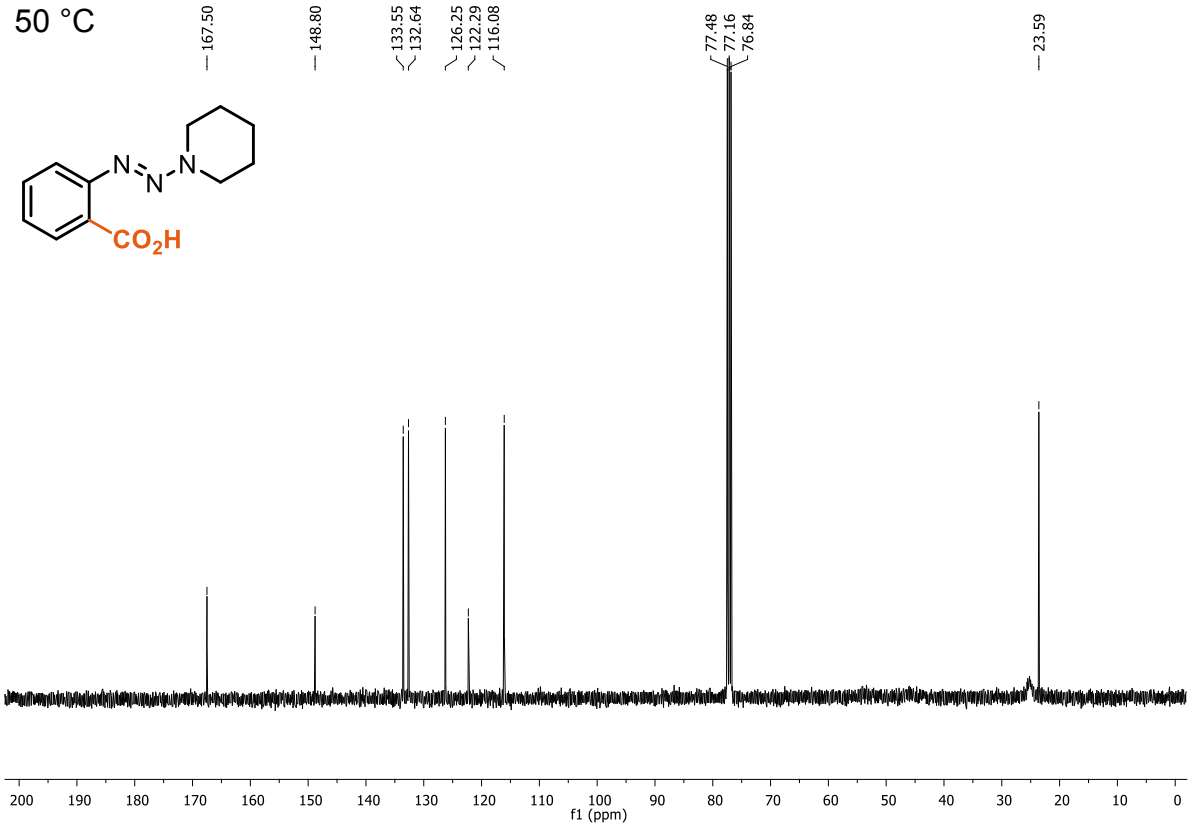


DSC

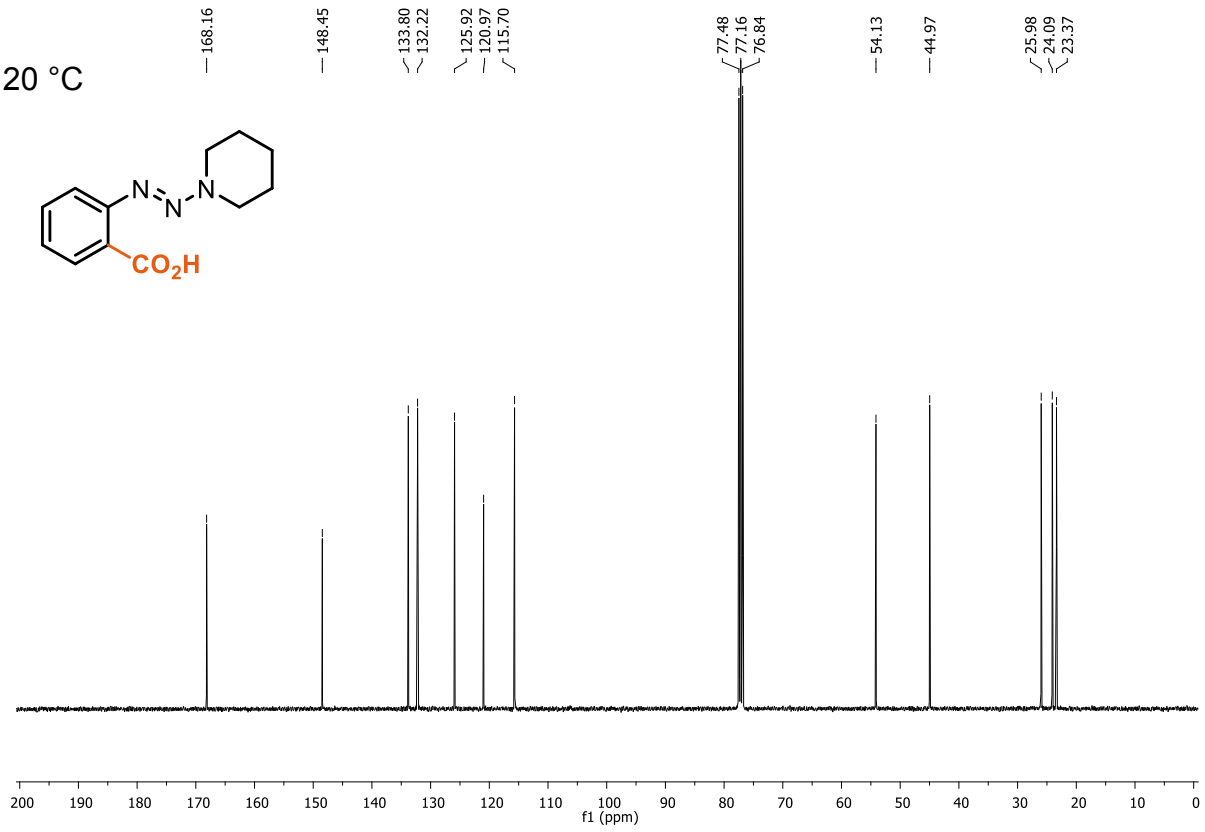

4
2
0
-2
-4
-6
Heat Flow (W/g)
20
40
60
80
100
120
140
160
180
200
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
MeO
N2 BF4

2-(piperidin-1-yldiazenyl)benzoic acid (1b)

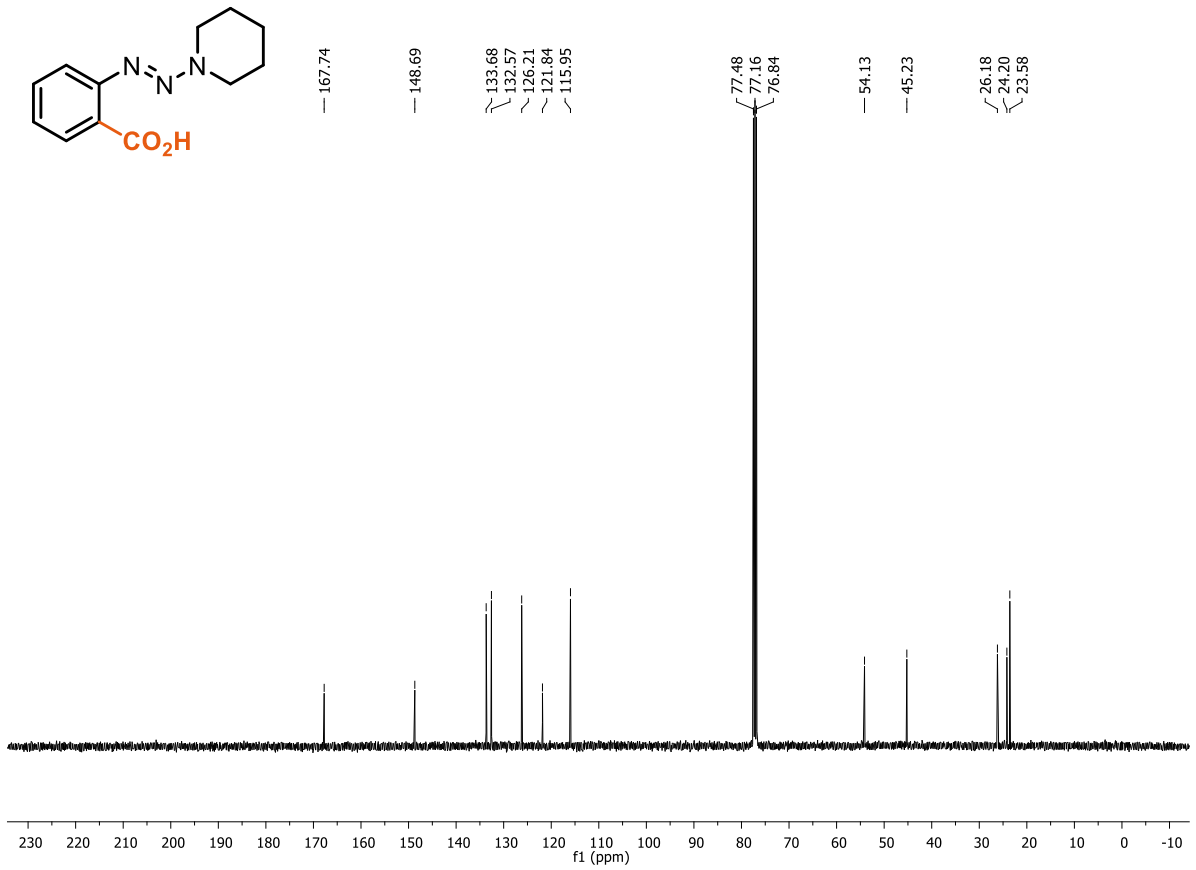




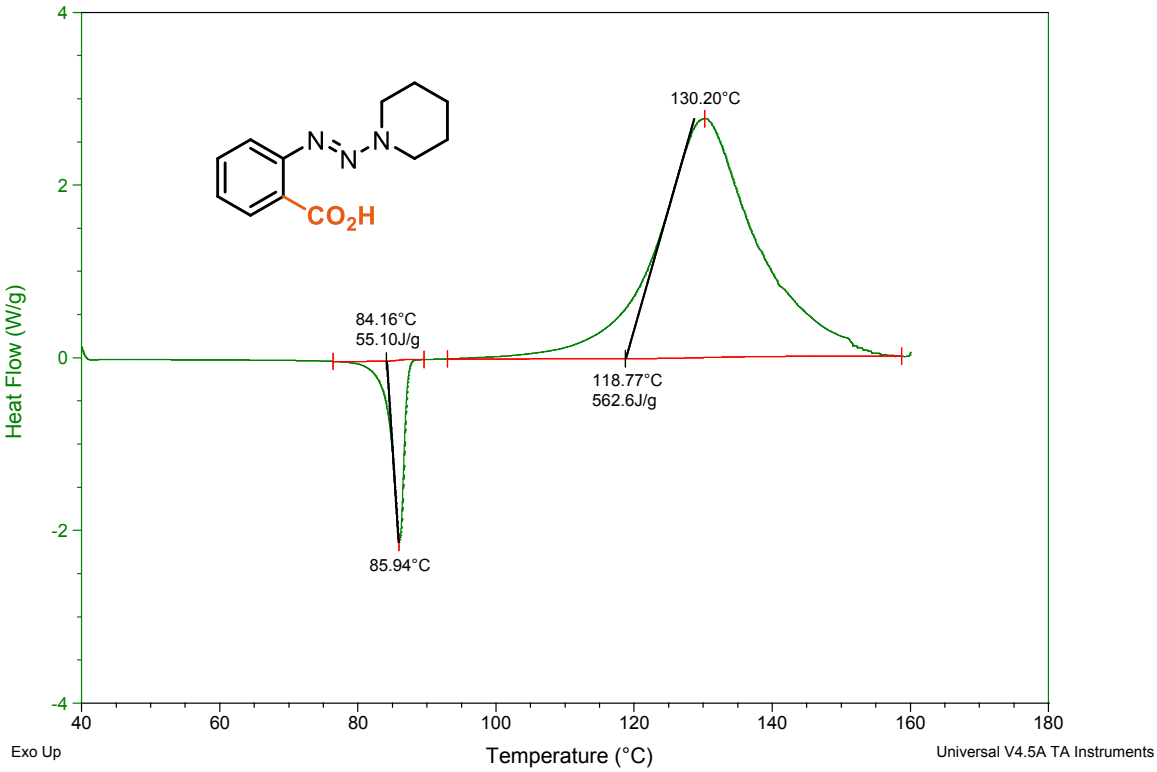
20 °C


168.16
148.45
133.80
132.22
125.92
120.97
115.70
77.48
77.16
76.84
54.13
44.97
25.98
24.09
23.37
CO2H
f1 (ppm)

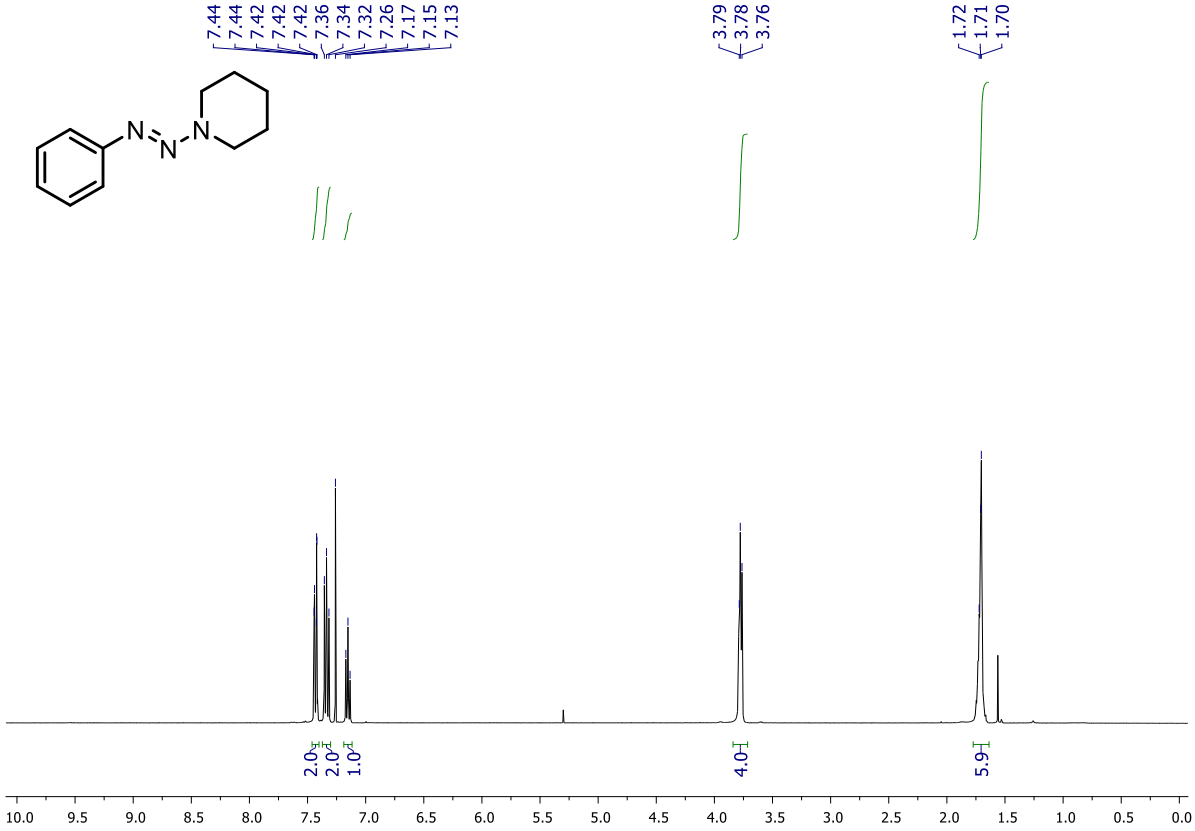
-30 °C

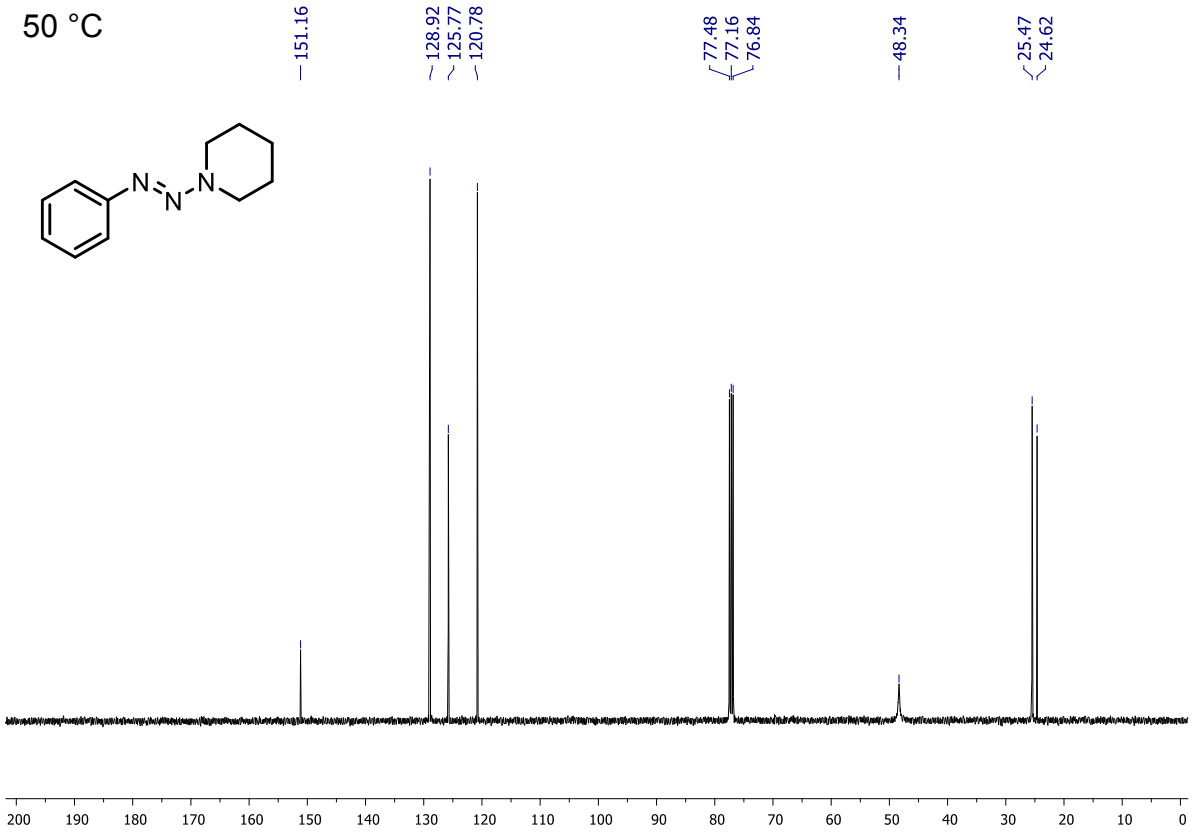

167.74
148.69
133.68
132.57
126.21
121.84
115.95
77.48
77.16
76.84
54.13
45.23
26.18
24.20
23.58
CO2H
f1 (ppm)

DSC

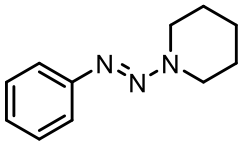

130.20°C
84.16°C
55.10J/g
118.77°C
562.6J/g
85.94°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

1-(phenyldiazenyl)piperidine (2b)



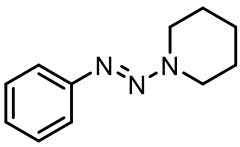


20 °C



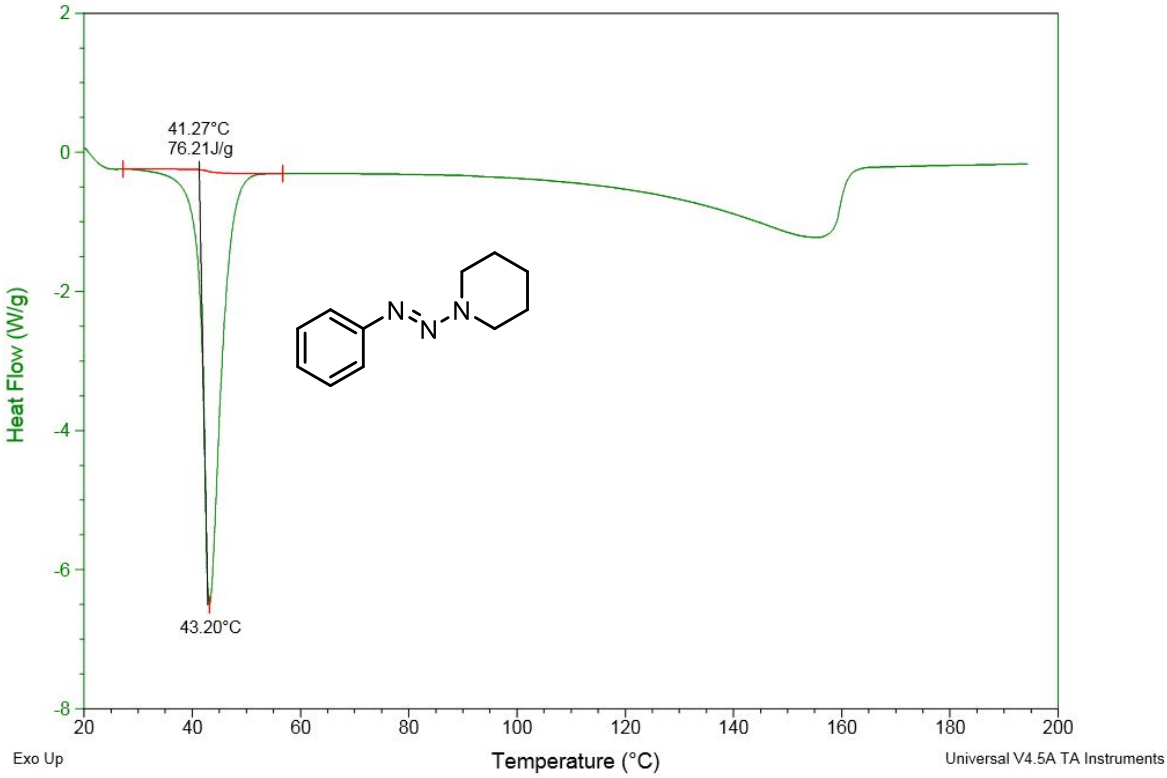
150.96
128.97
125.76
120.64
77.48
77.16
76.84
25.41
24.55
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

-30 °C

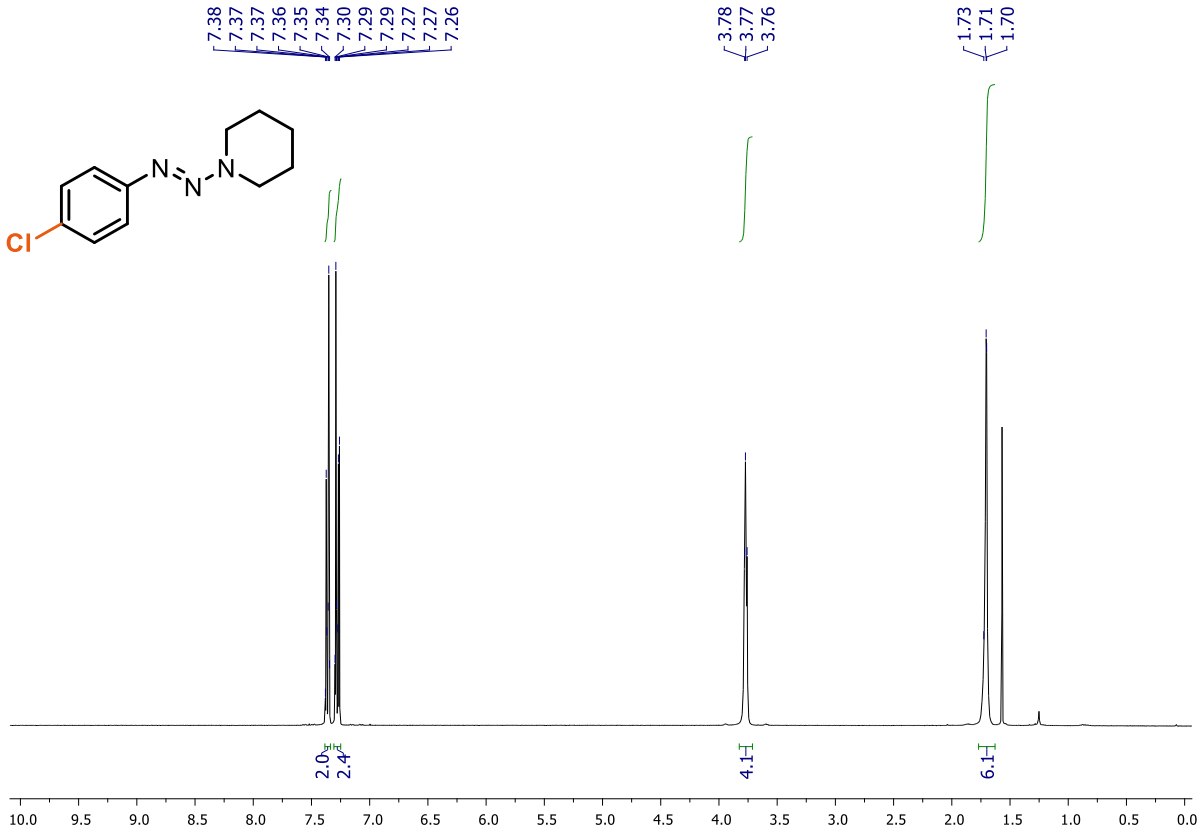


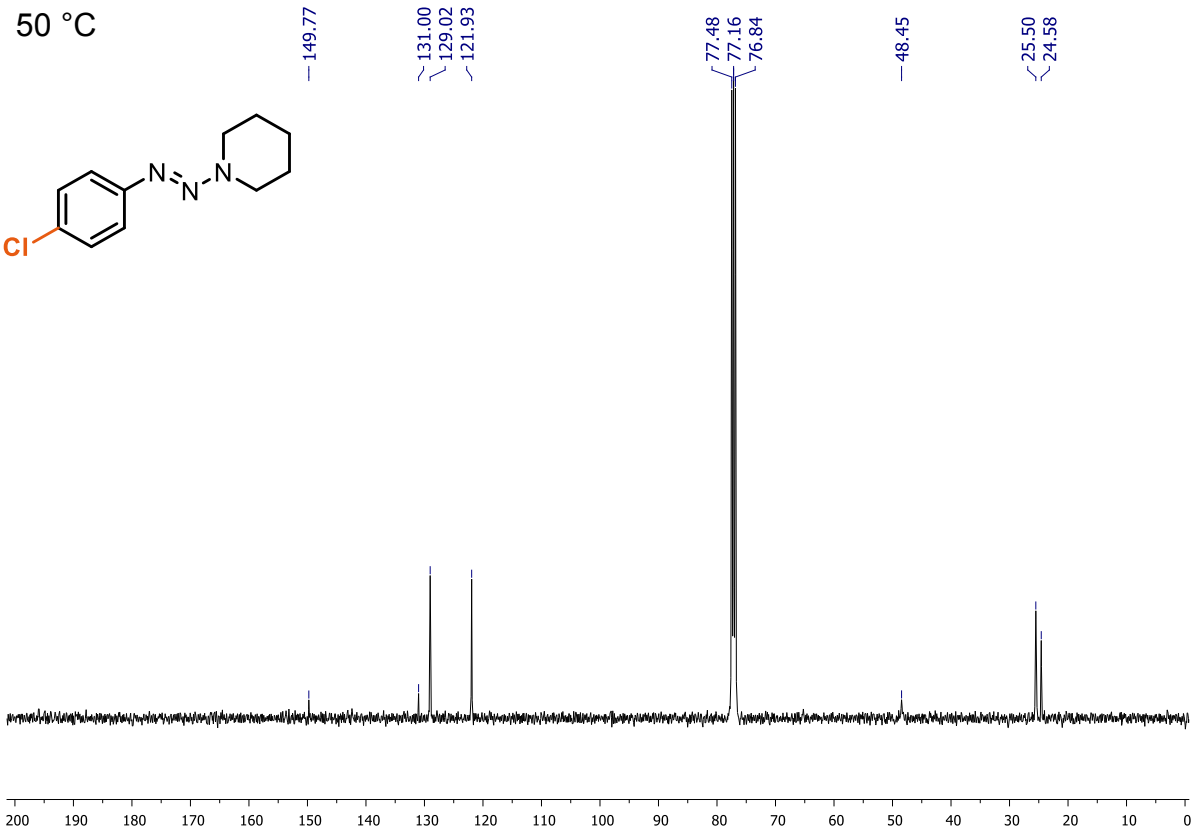
150.58
128.99
125.66
120.34
77.48
77.16
76.84
52.72
43.56
26.11
24.37
24.29
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

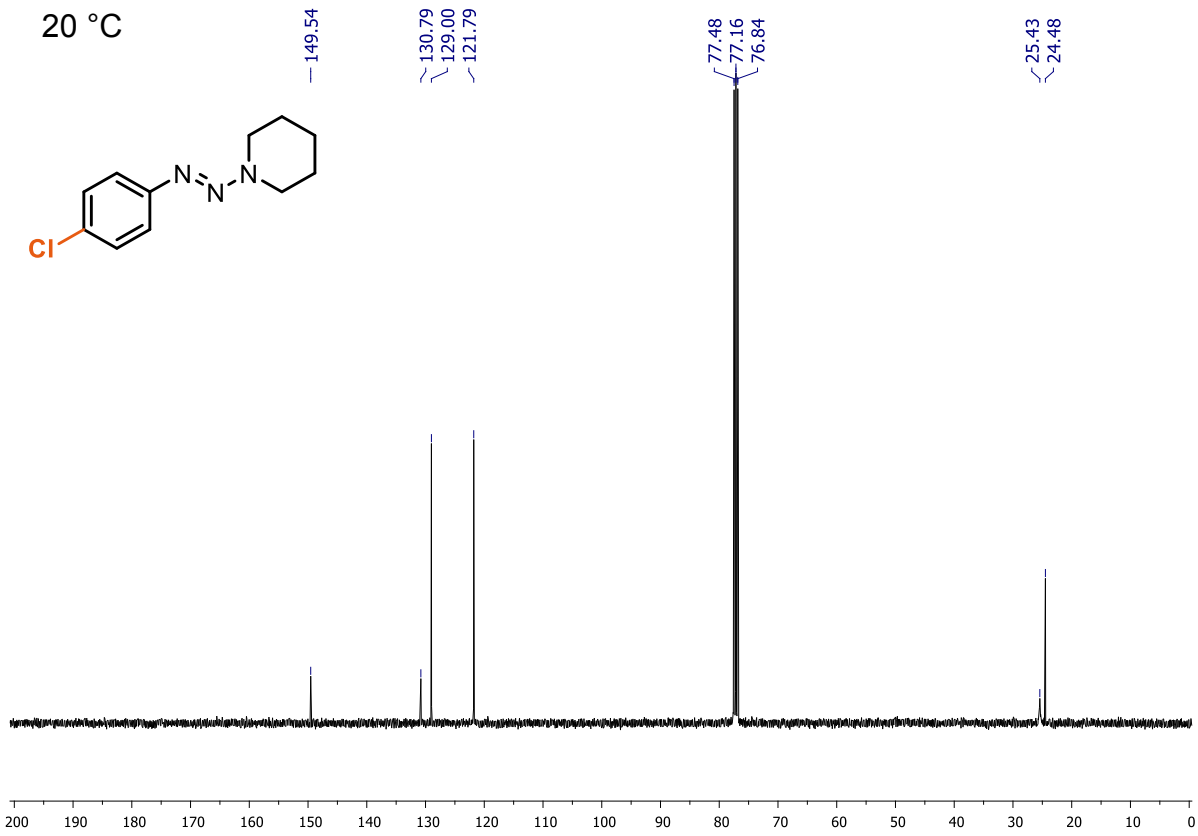
DSC

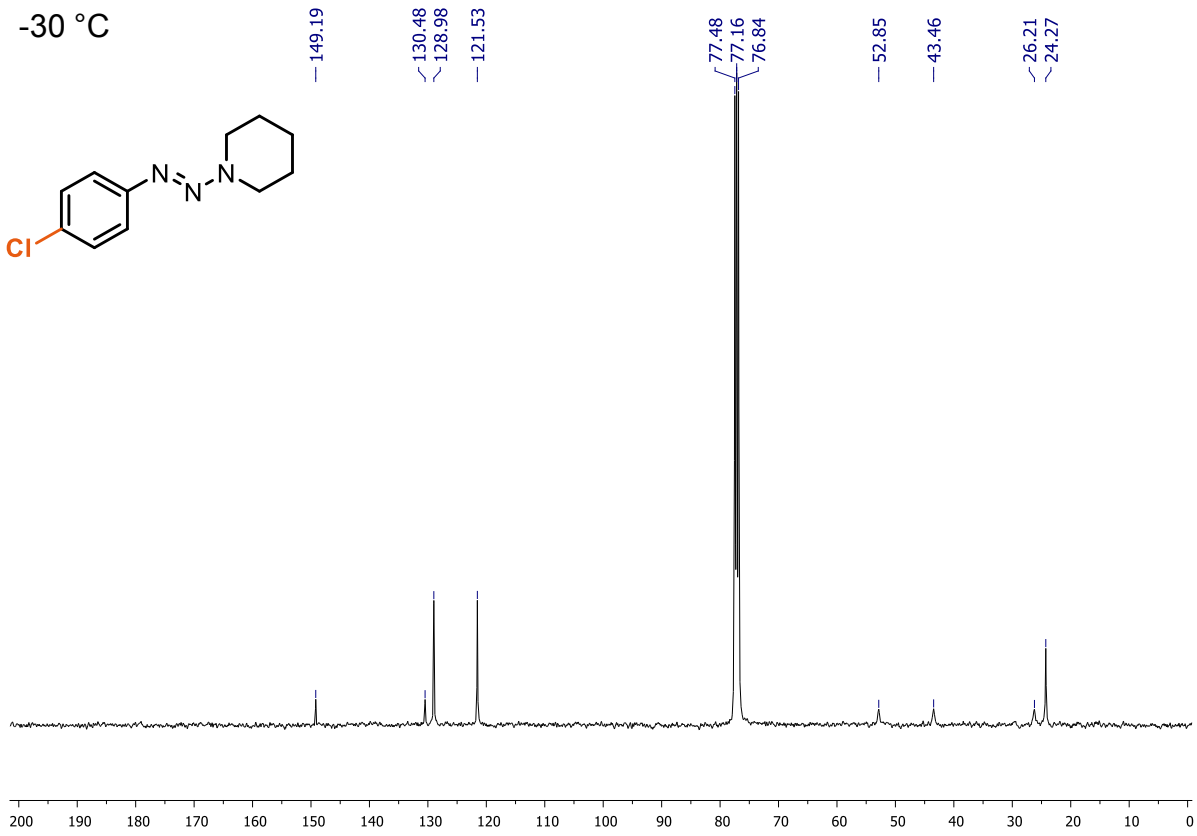

41.27°C
76.21J/g
43.20°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

1-((4-chlorophenyl)diazenyl)piperidine (3b)

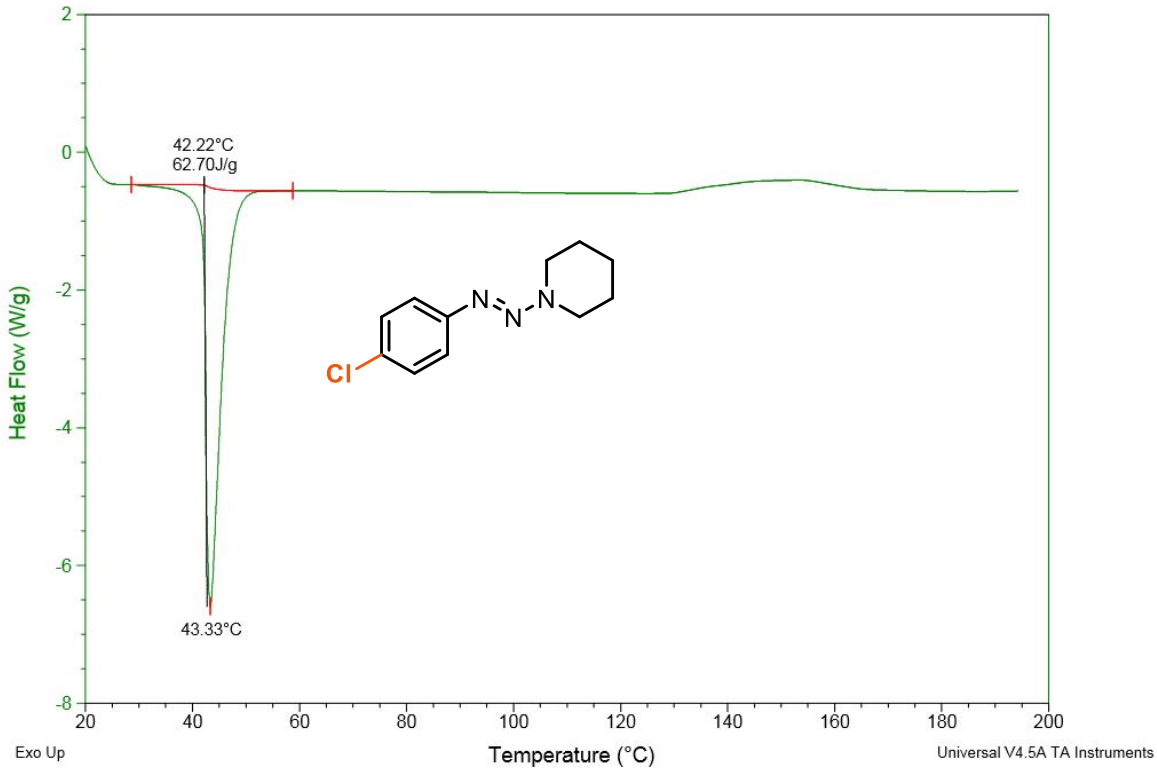




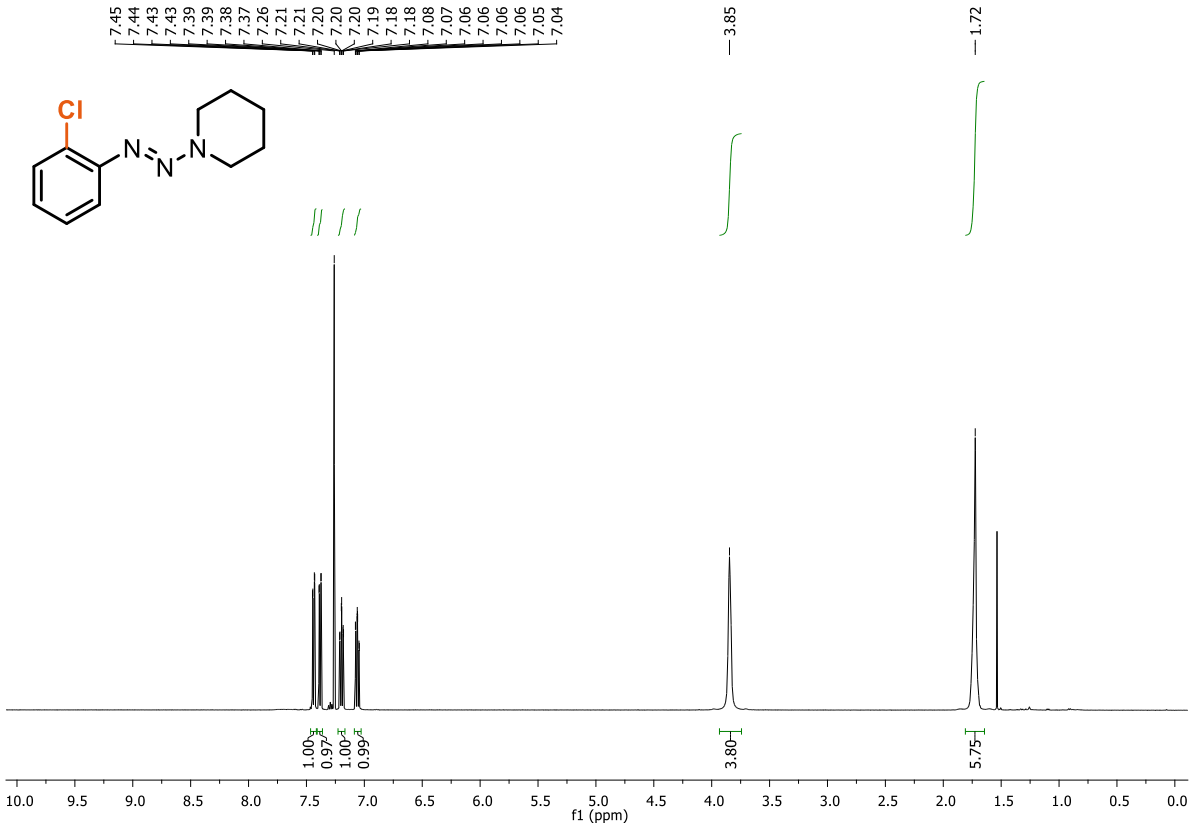

20 °C
149.54
130.79
129.00
121.79
77.48
77.16
76.84
25.43
24.48
Cl
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

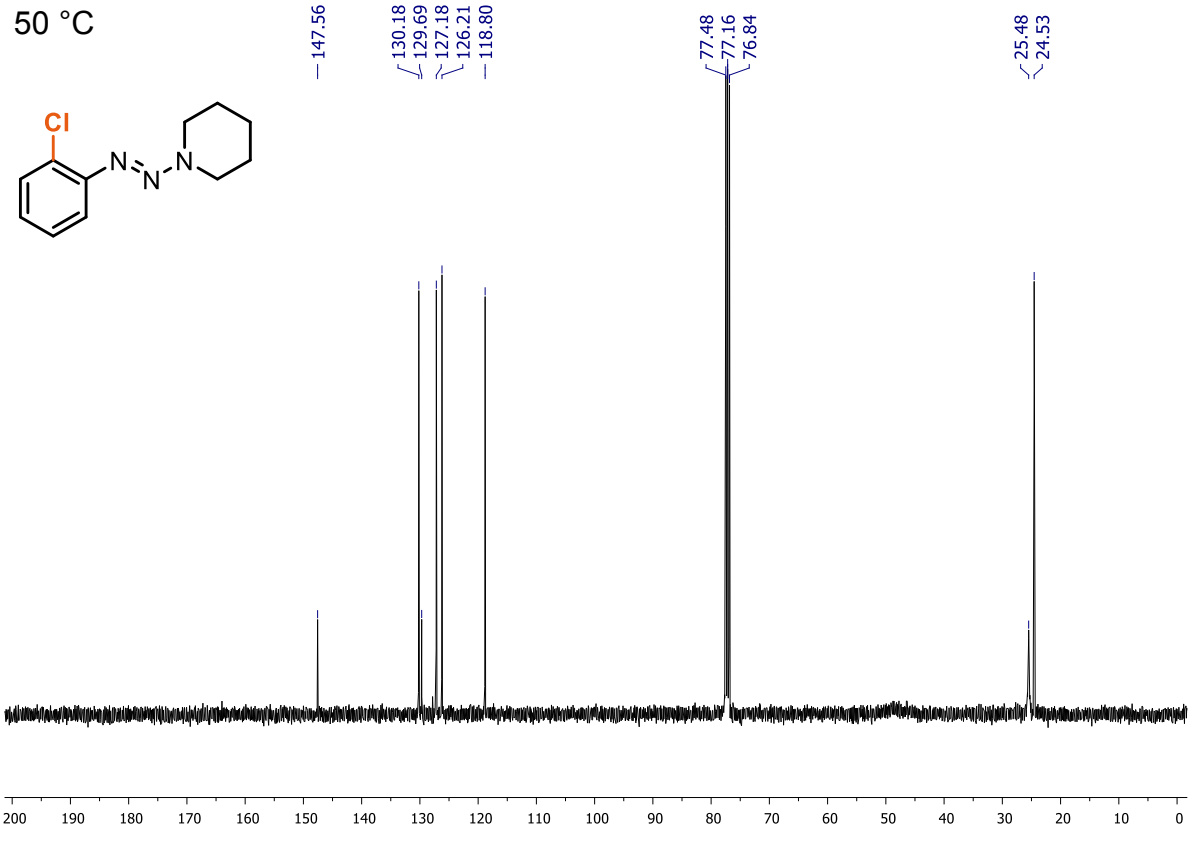

-30 °C
149.19
130.48
128.98
121.53
77.48
77.16
76.84
52.85
43.46
26.21
24.27
Cl
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

DSC

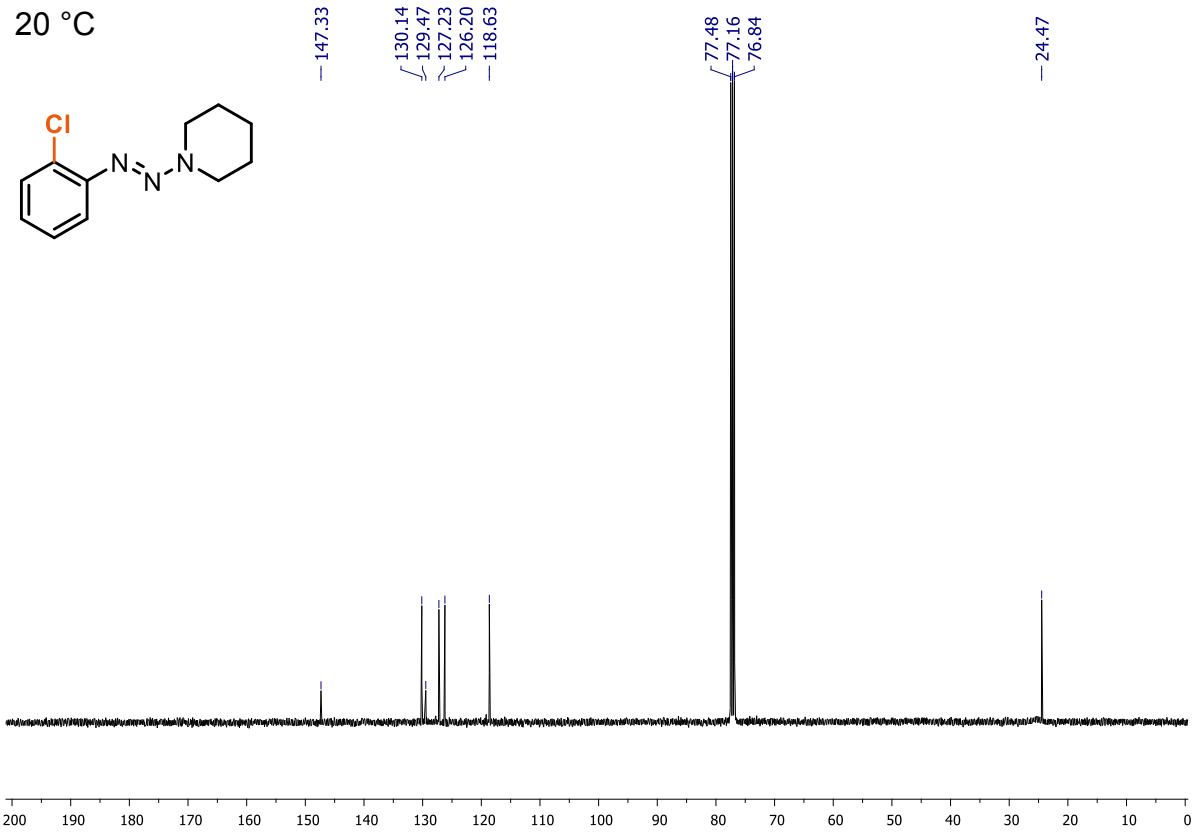

42.22°C
62.70J/g
43.33°C
Cl
N
N
N
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
2
0
-2
-4
-6
-8
20
40
60
80
100
120
140
160
180
200

1-((2-chlorophenyl)diazenyl)piperidine (4b)

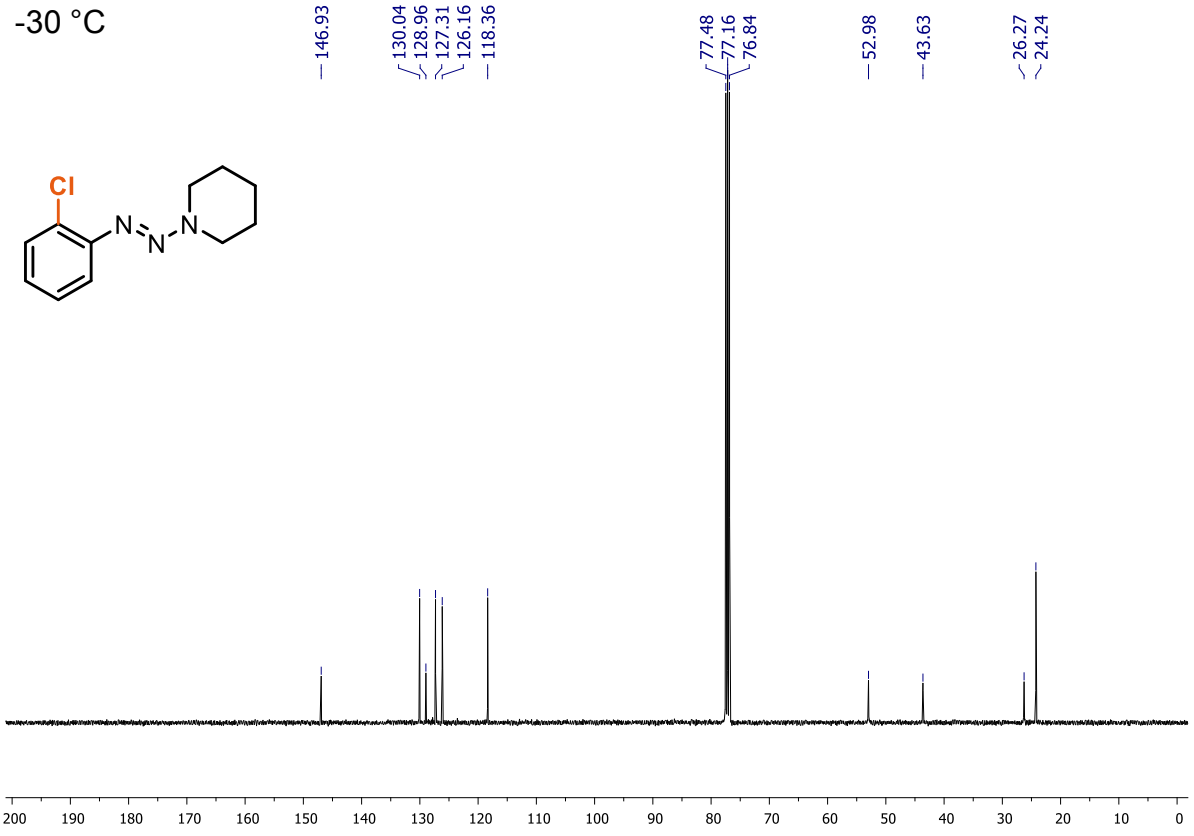




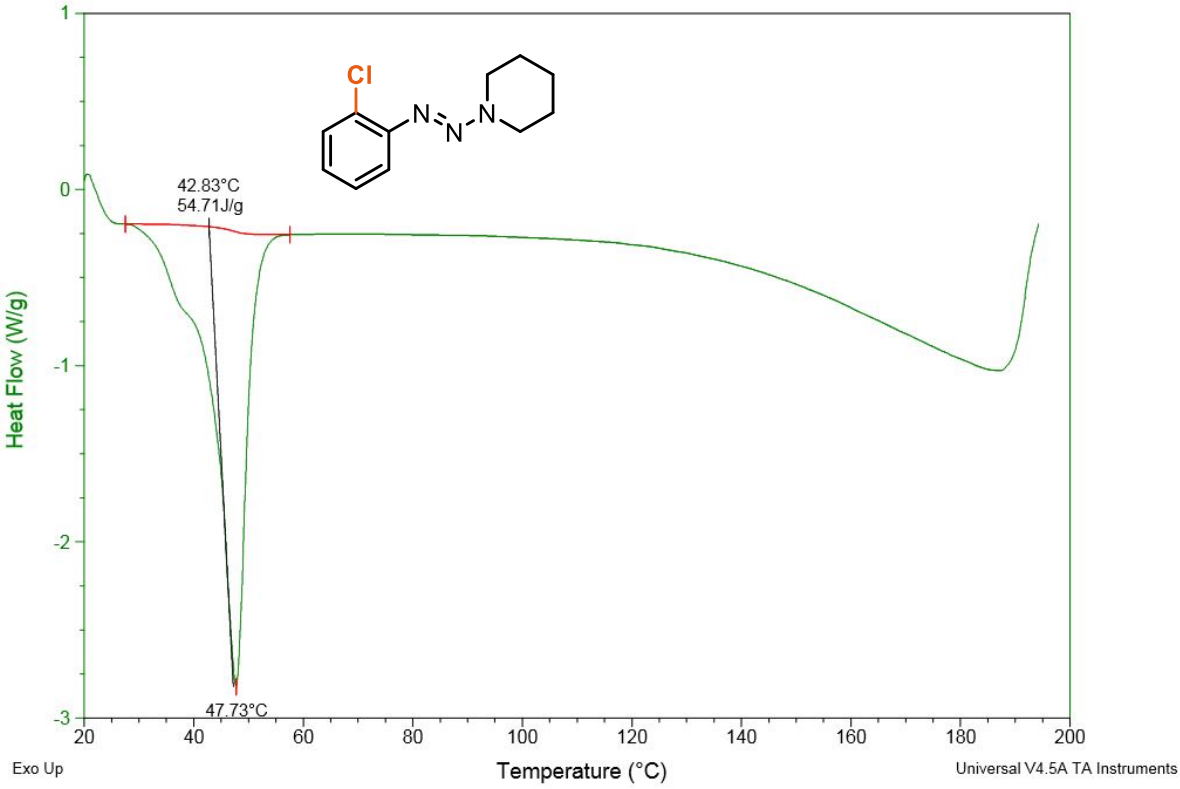
20 °C


147.33
130.14
129.47
127.23
126.20
118.63
77.48
77.16
76.84
24.47
Cl
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

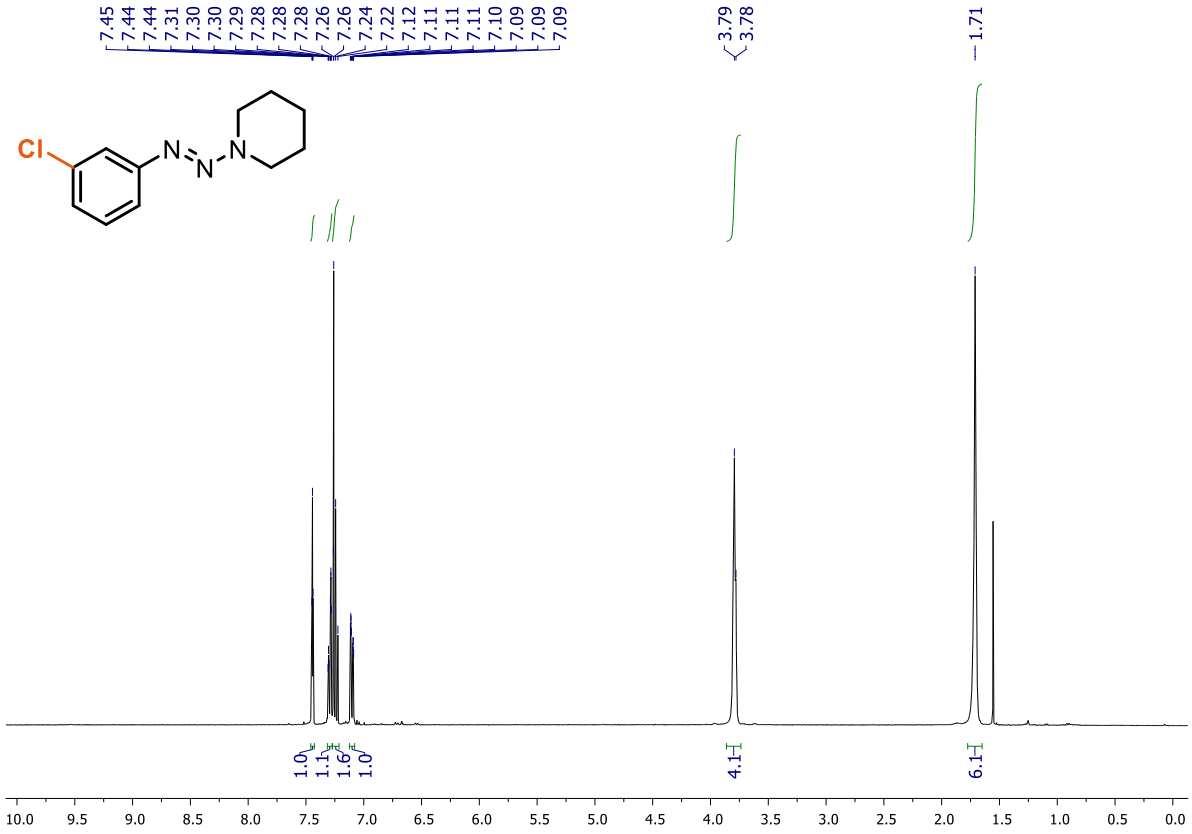
-30 °C

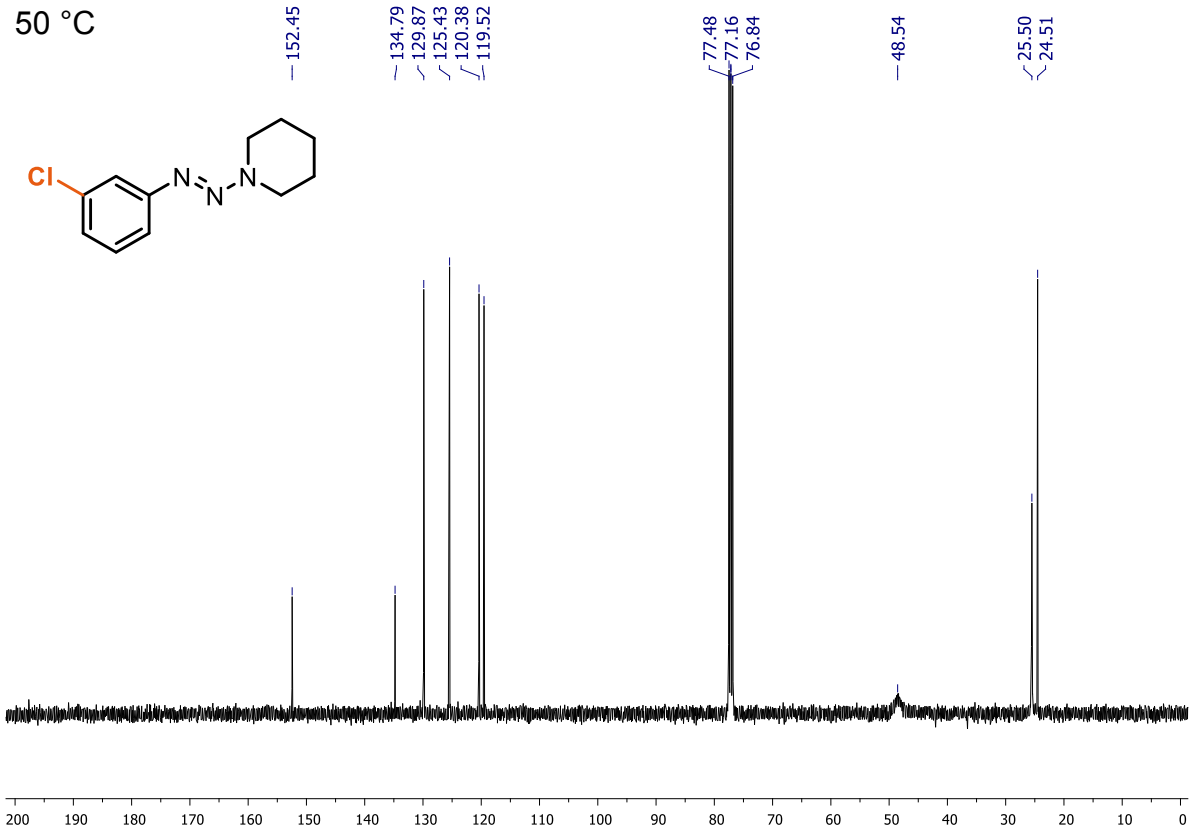

146.93
130.04
128.96
127.31
126.16
118.36
77.48
77.16
76.84
52.98
43.63
26.27
24.24
Cl
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

DSC

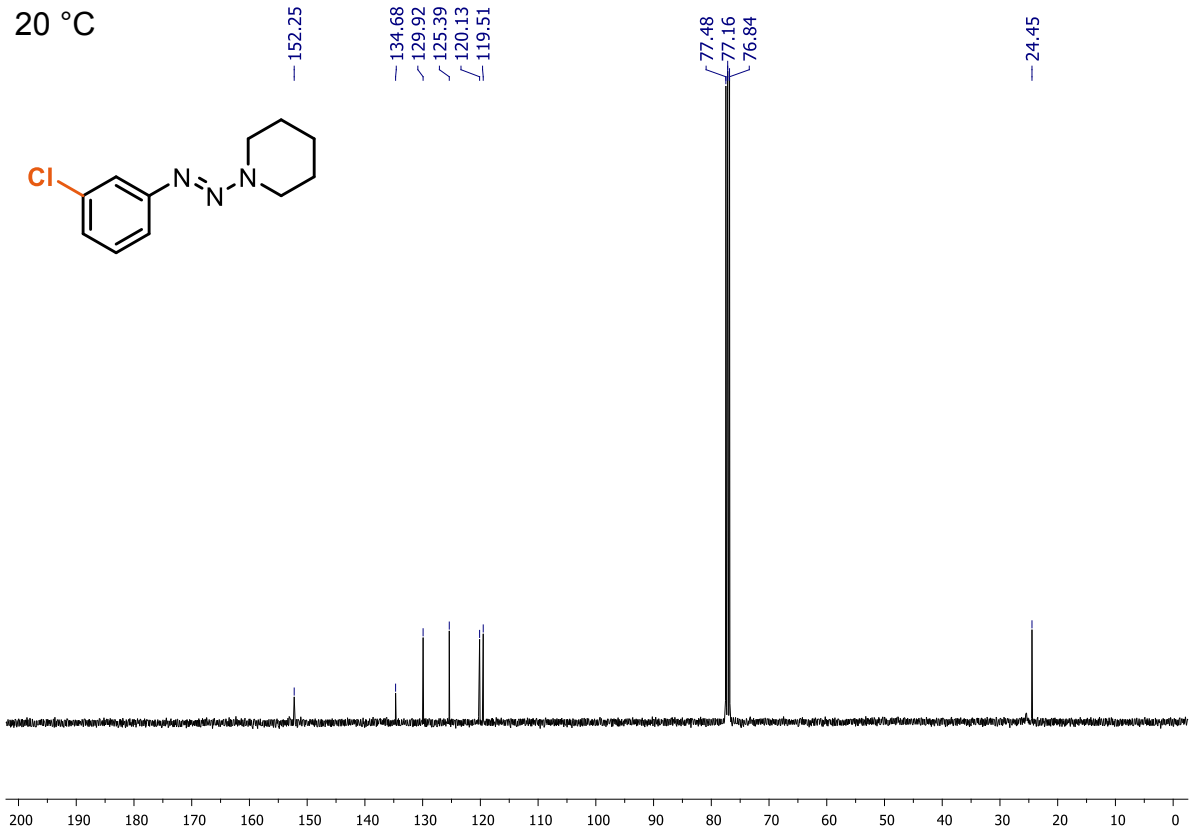

Cl
N
N
N
42.83°C
54.71J/g
47.73°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
1
0
-1
-2
-3
20
40
60
80
100
120
140
160
180
200

1-((3-chlorophenyl)diazenyl)piperidine (5b)

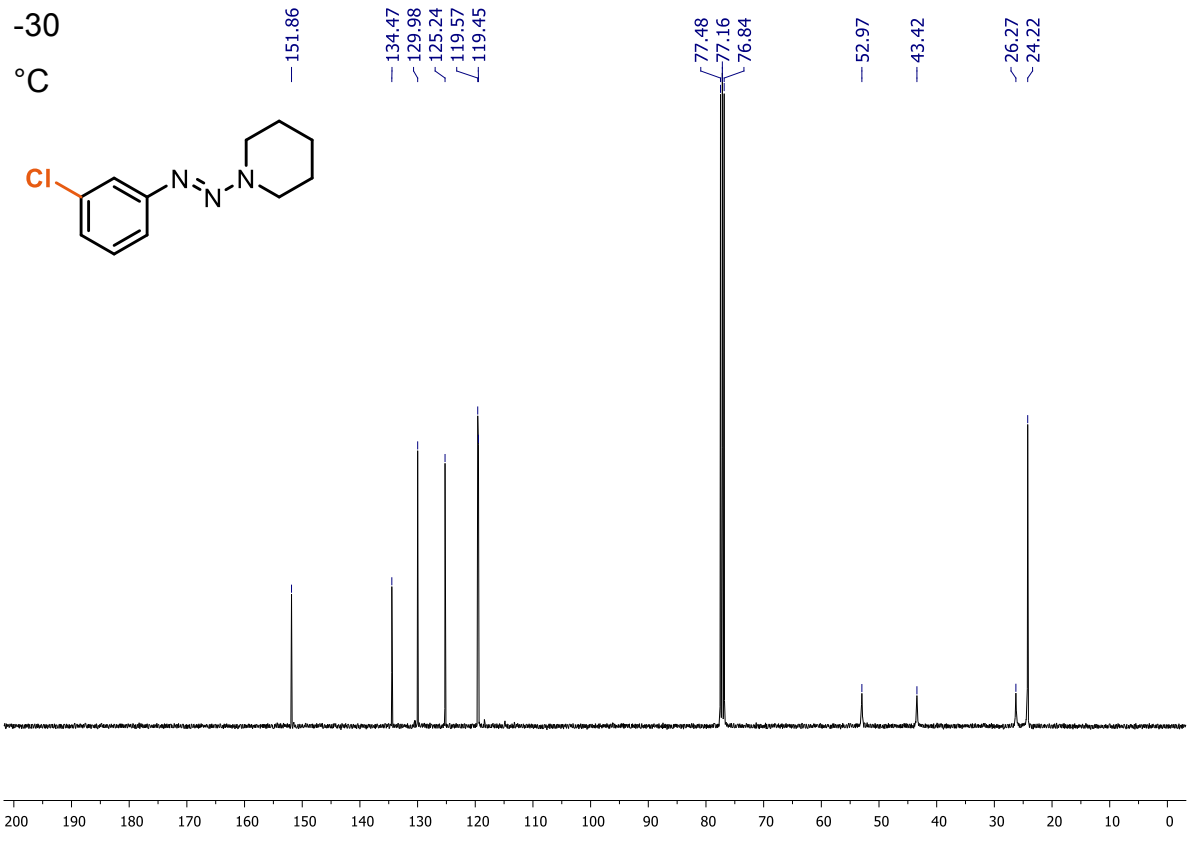




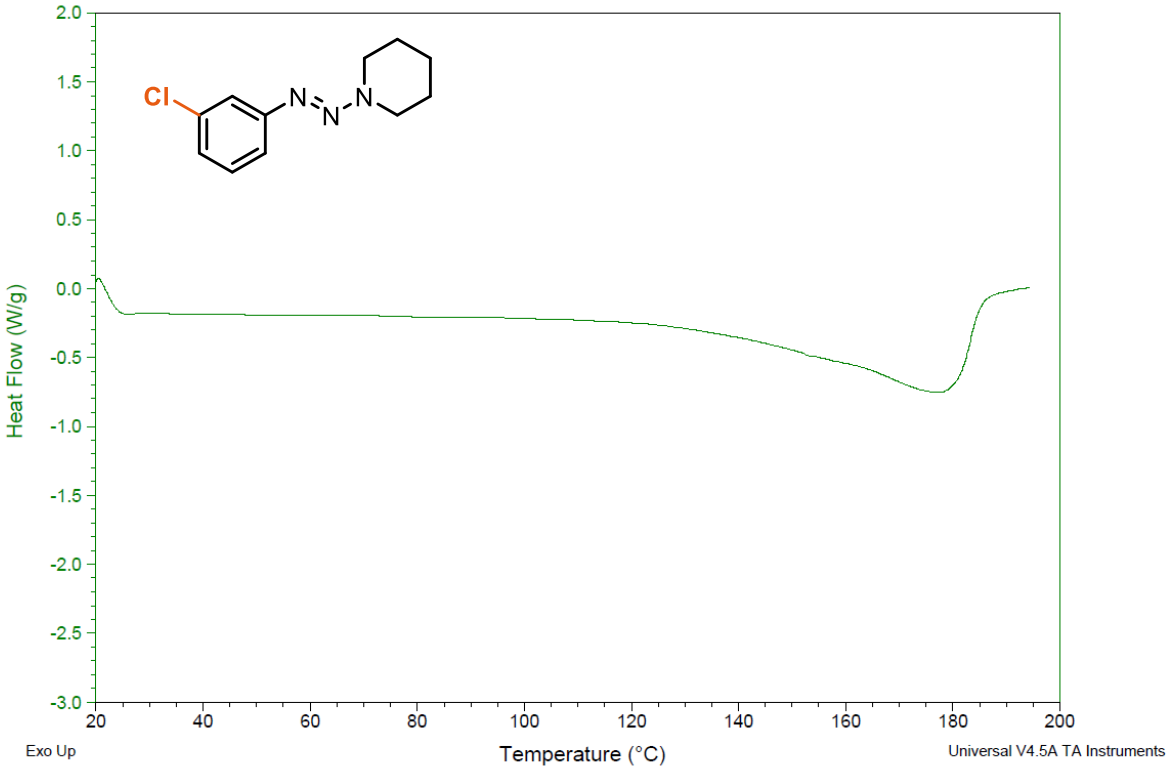
20 °C


152.25
134.68
129.92
125.39
120.13
119.51
77.48
77.16
76.84
24.45
Cl
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

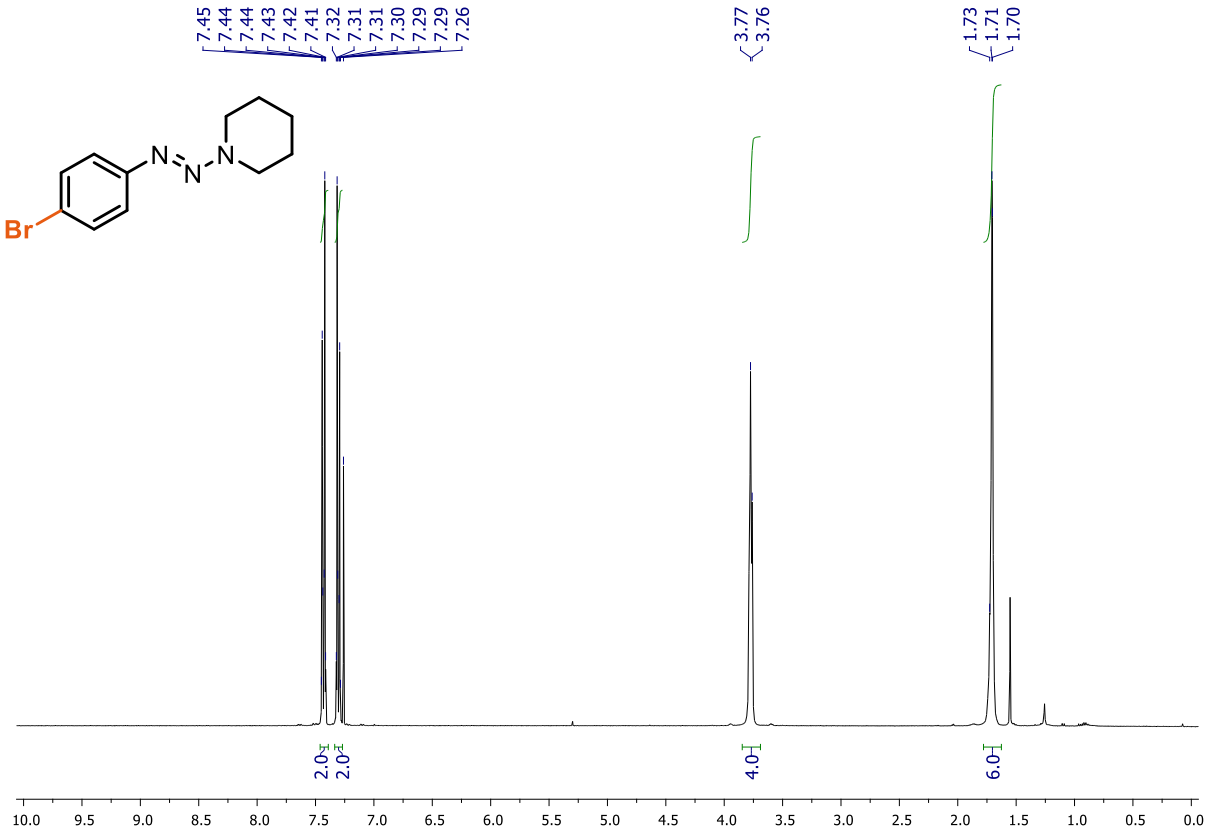
-30 °C

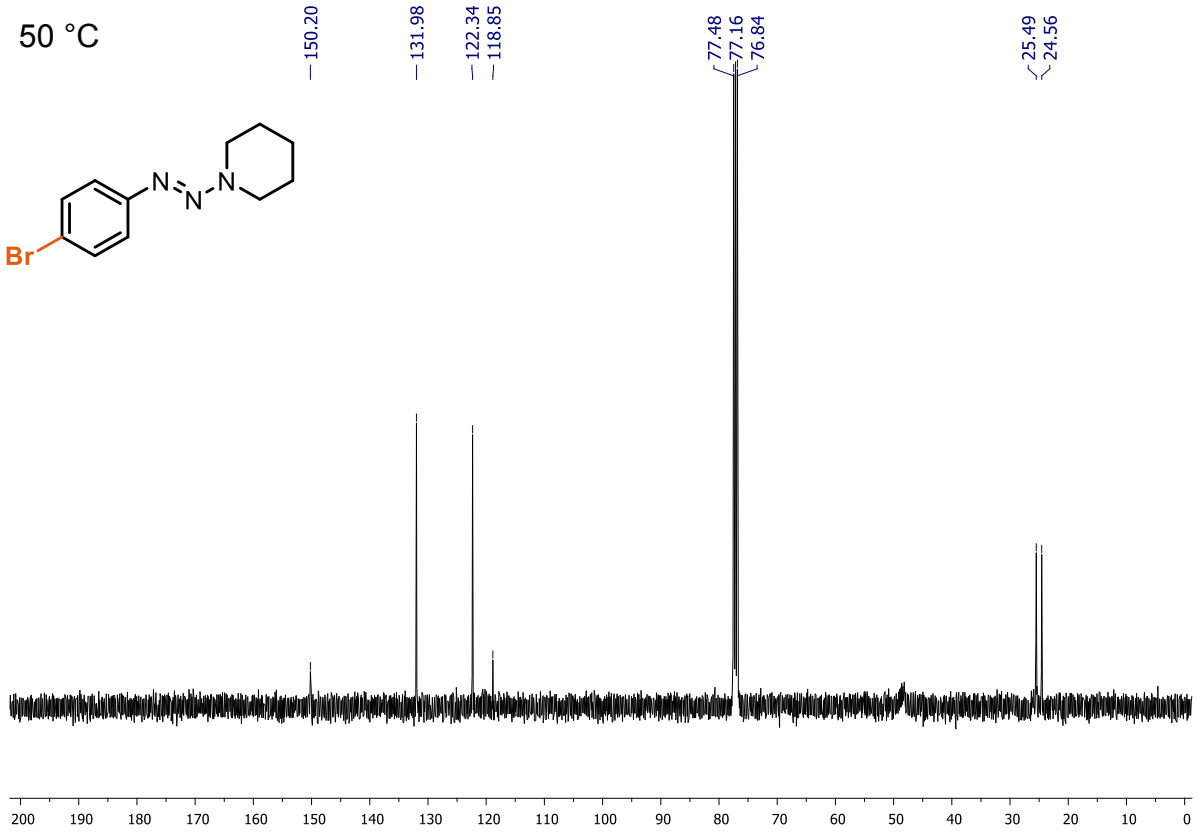

151.86
134.47
129.98
125.24
119.57
119.45
77.48
77.16
76.84
52.97
43.42
26.27
24.22
Cl
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

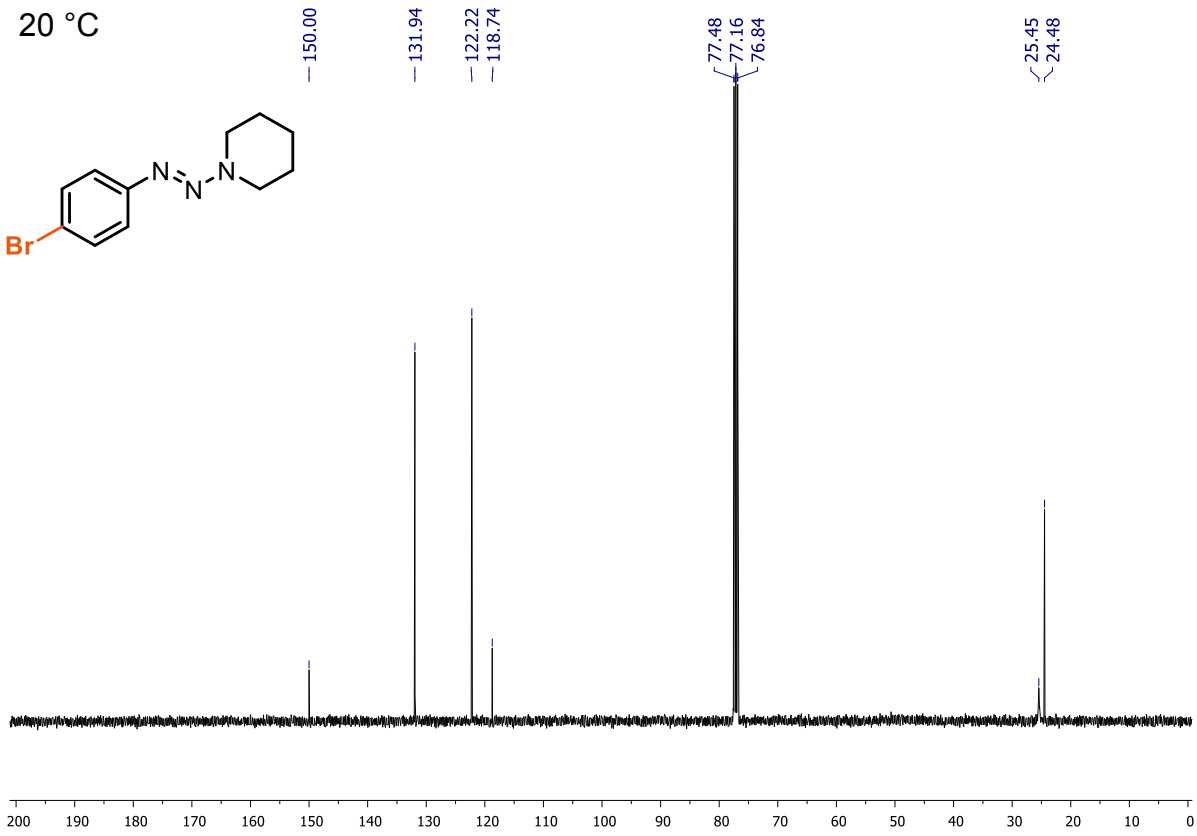
DSC

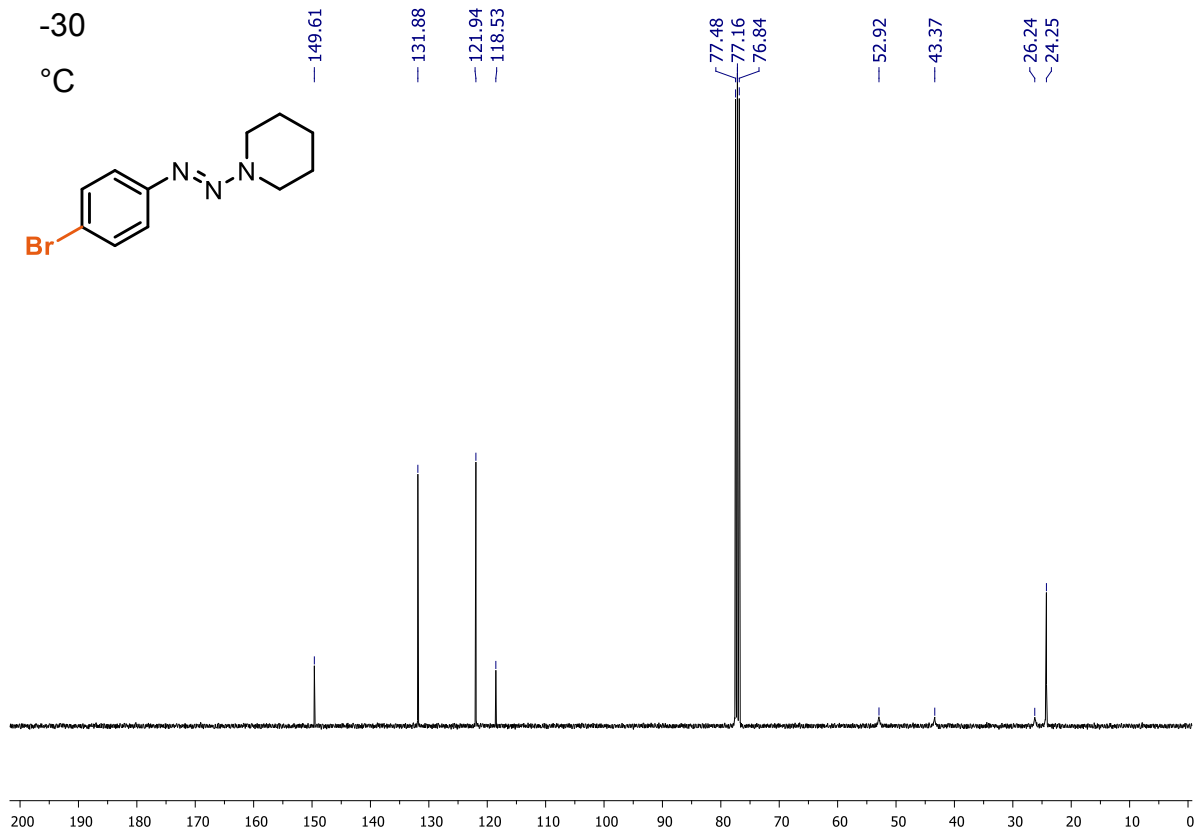

Cl
N
N
N
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
Heat Flow (W/g)
20
40
60
80
100
120
140
160
180
200
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments

1-((4-bromophenyl)diazenyl)piperidine (6b)

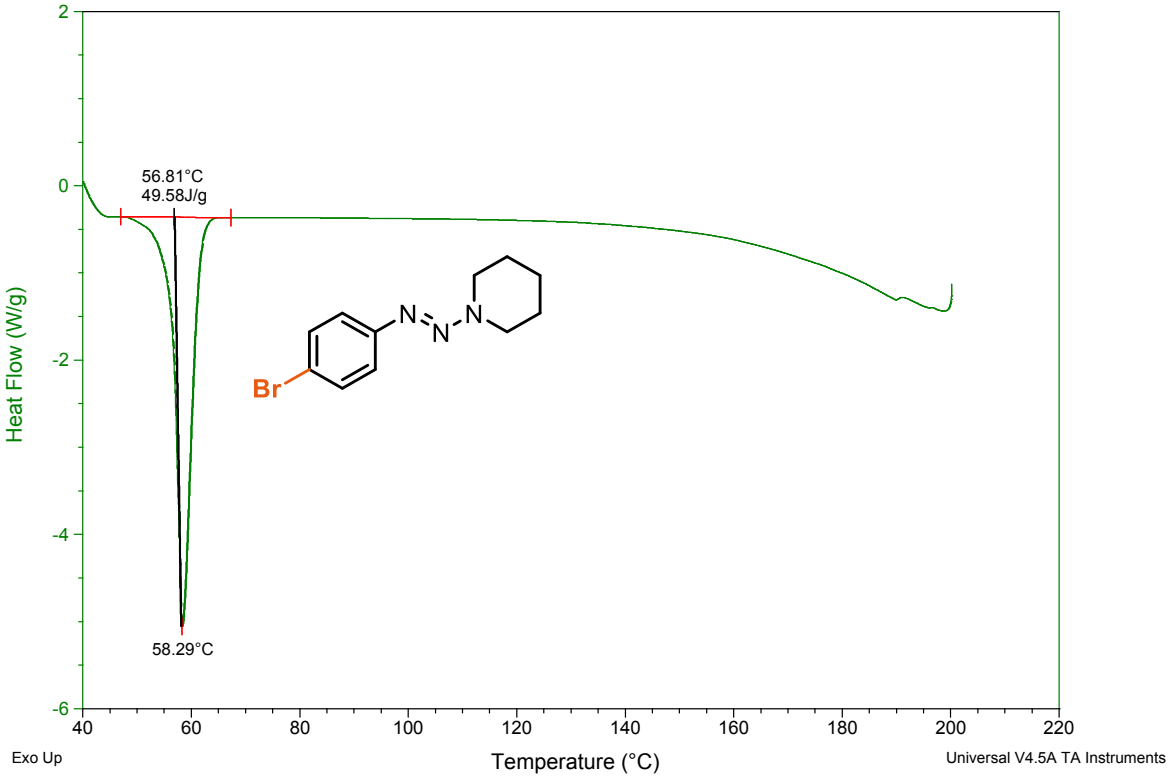




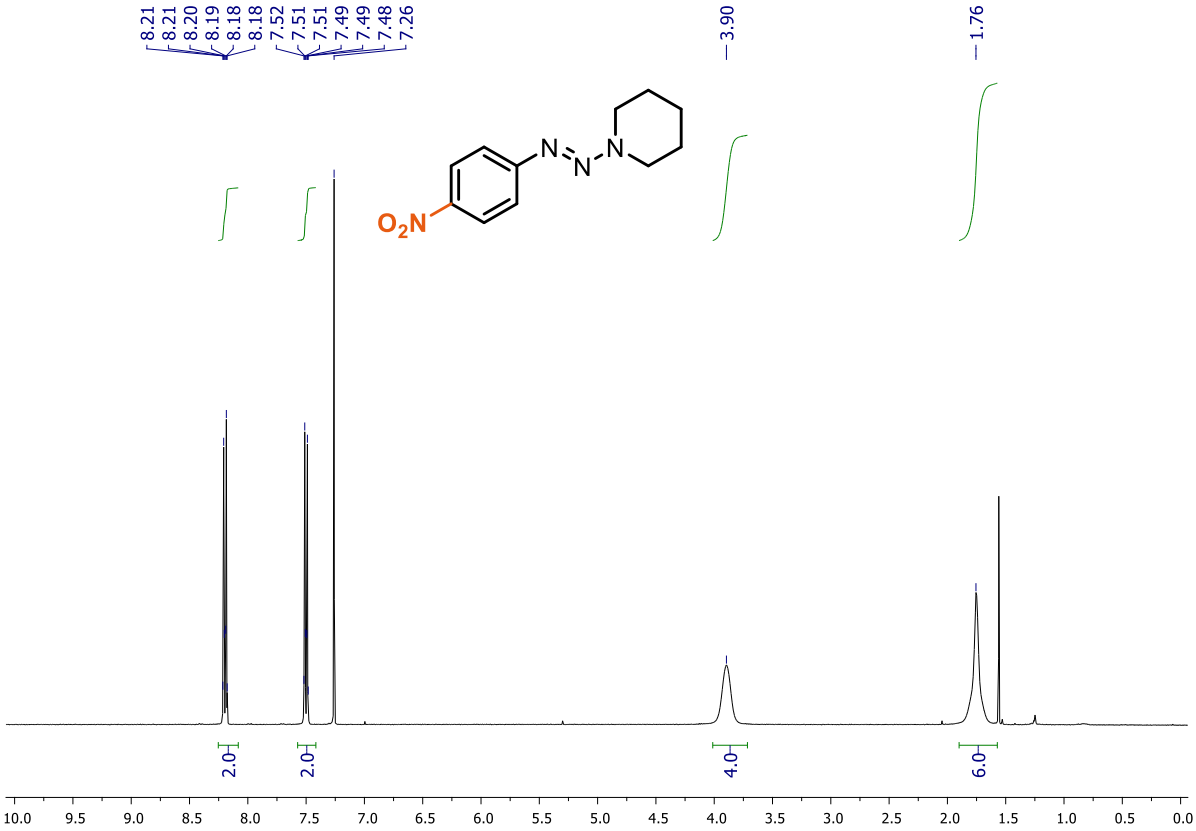

20 °C
150.00
131.94
122.22
118.74
77.48
77.16
76.84
25.45
24.48
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

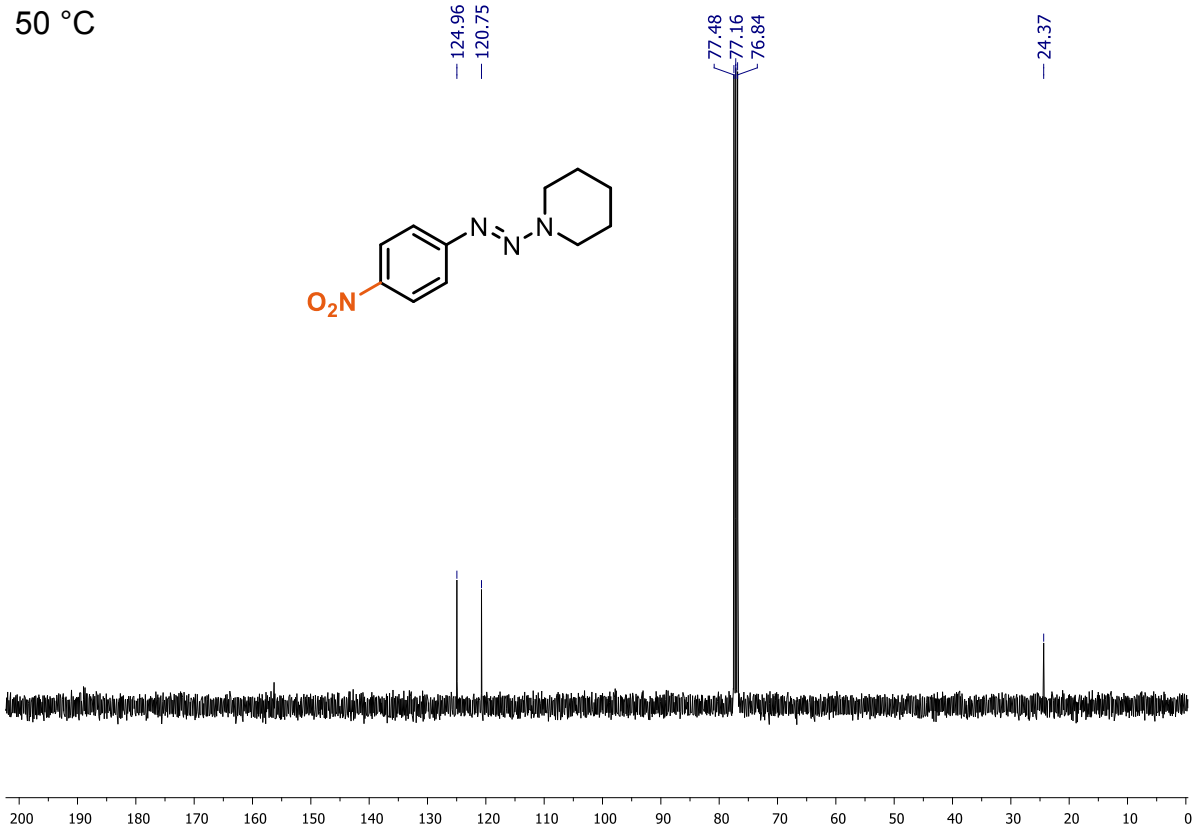

-30
°C
149.61
131.88
121.94
118.53
77.48
77.16
76.84
52.92
43.37
26.24
24.25
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

DSC

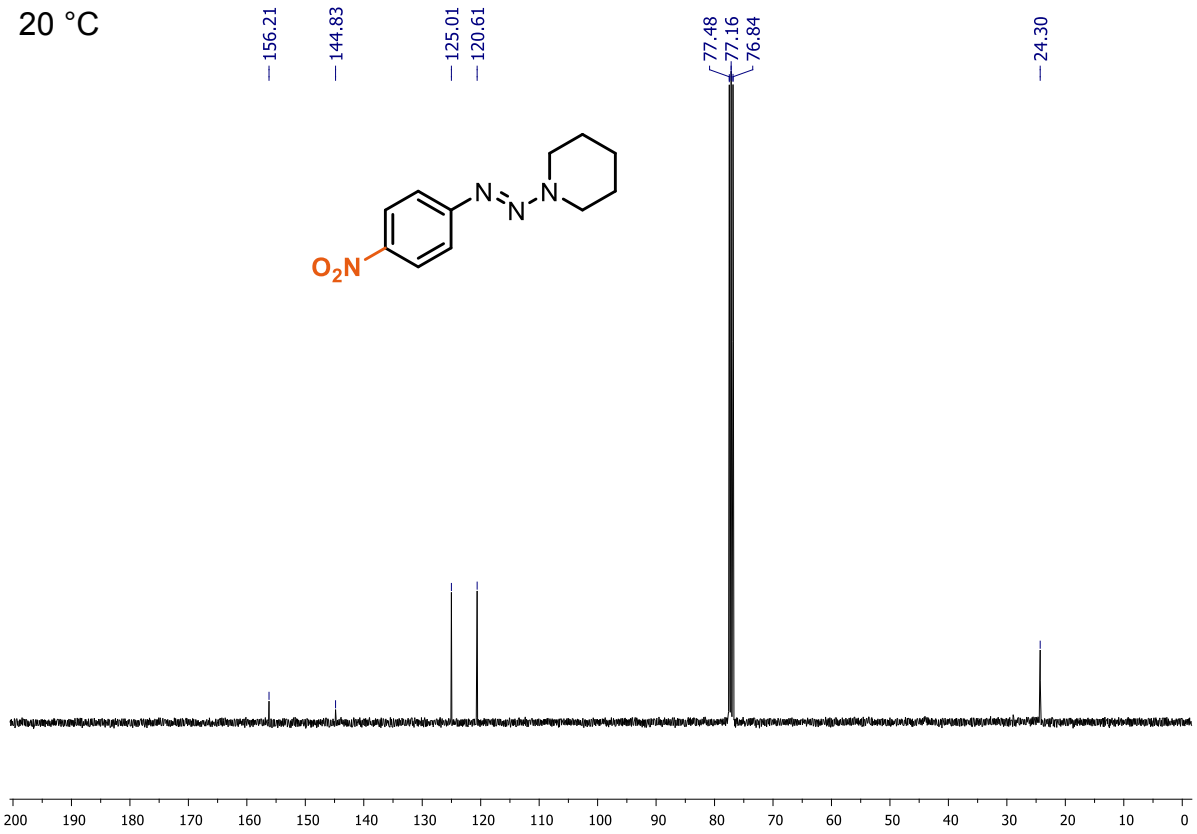

56.81°C
49.58J/g
58.29°C
Br
N
N
N
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
2
0
-2
-4
-6
40
60
80
100
120
140
160
180
200
220

1-((4-nitrophenyl)diazenyl)piperidine (7b)

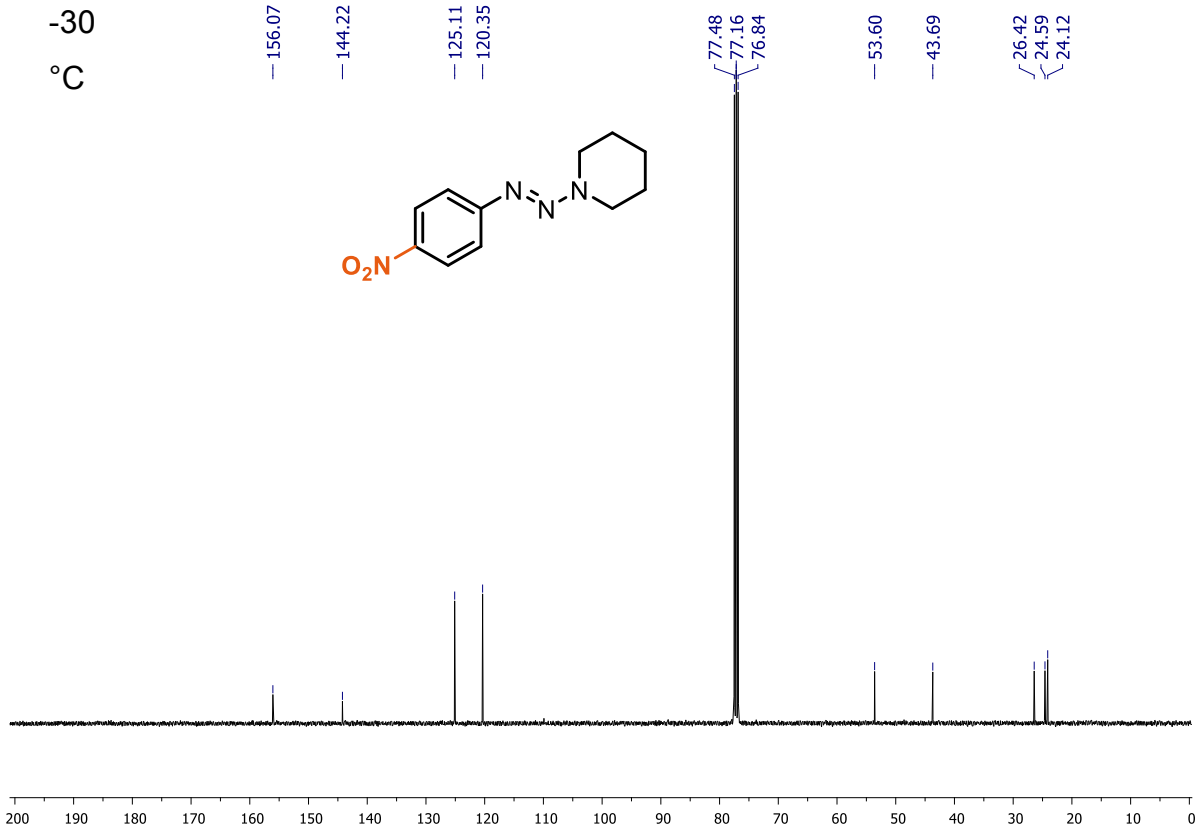




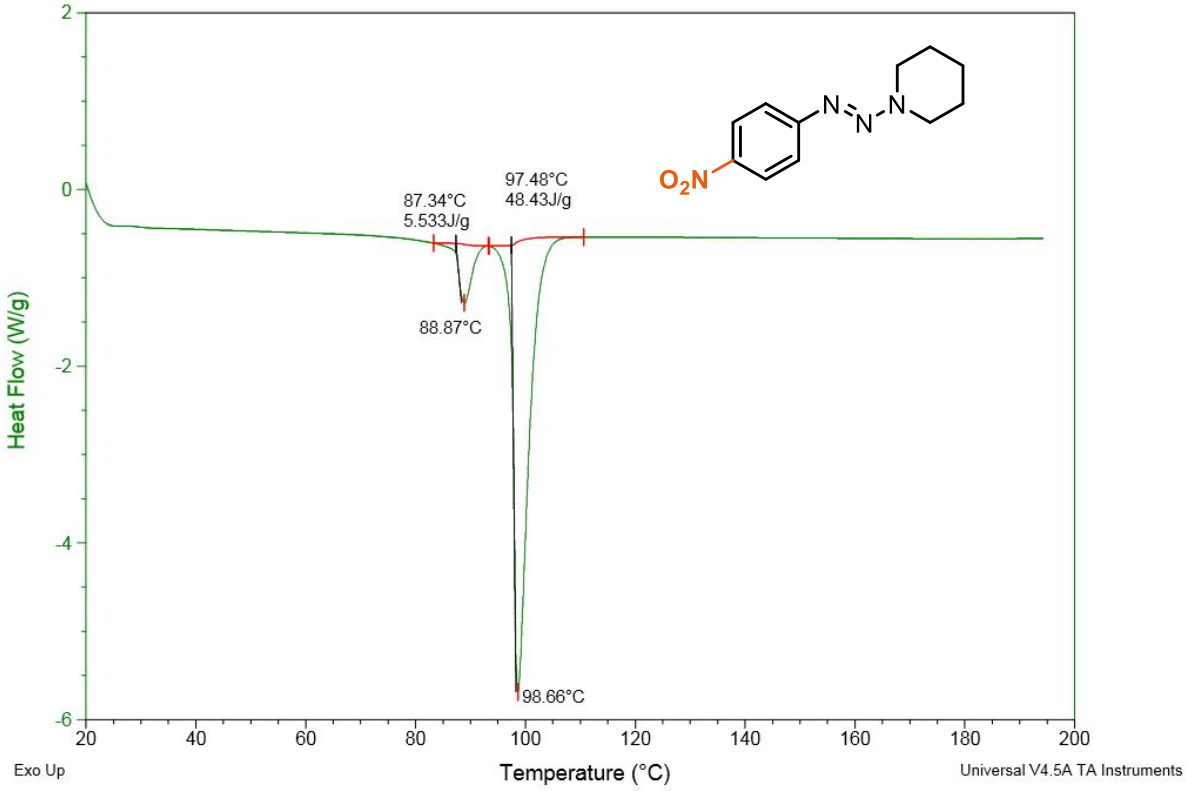
20 °C


156.21
144.83
125.01
120.61
77.48
77.16
76.84
24.30
O2N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

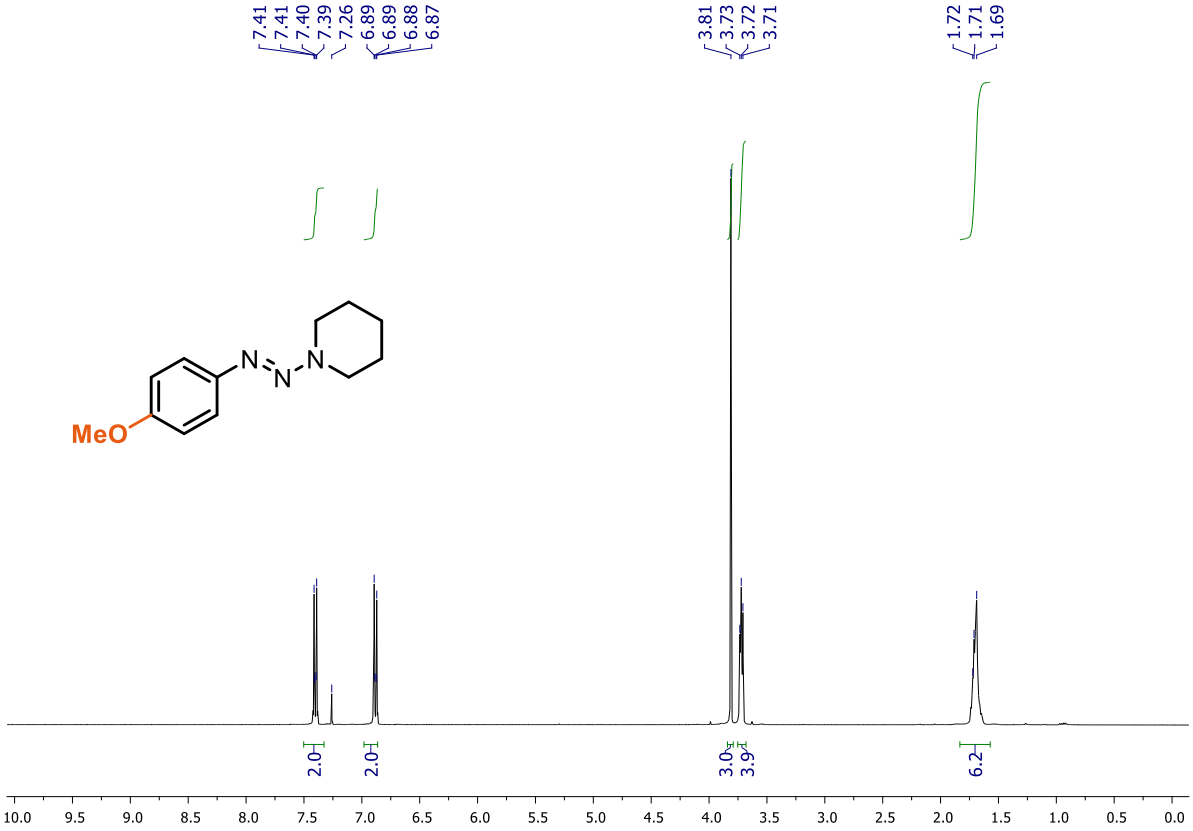
-30 °C

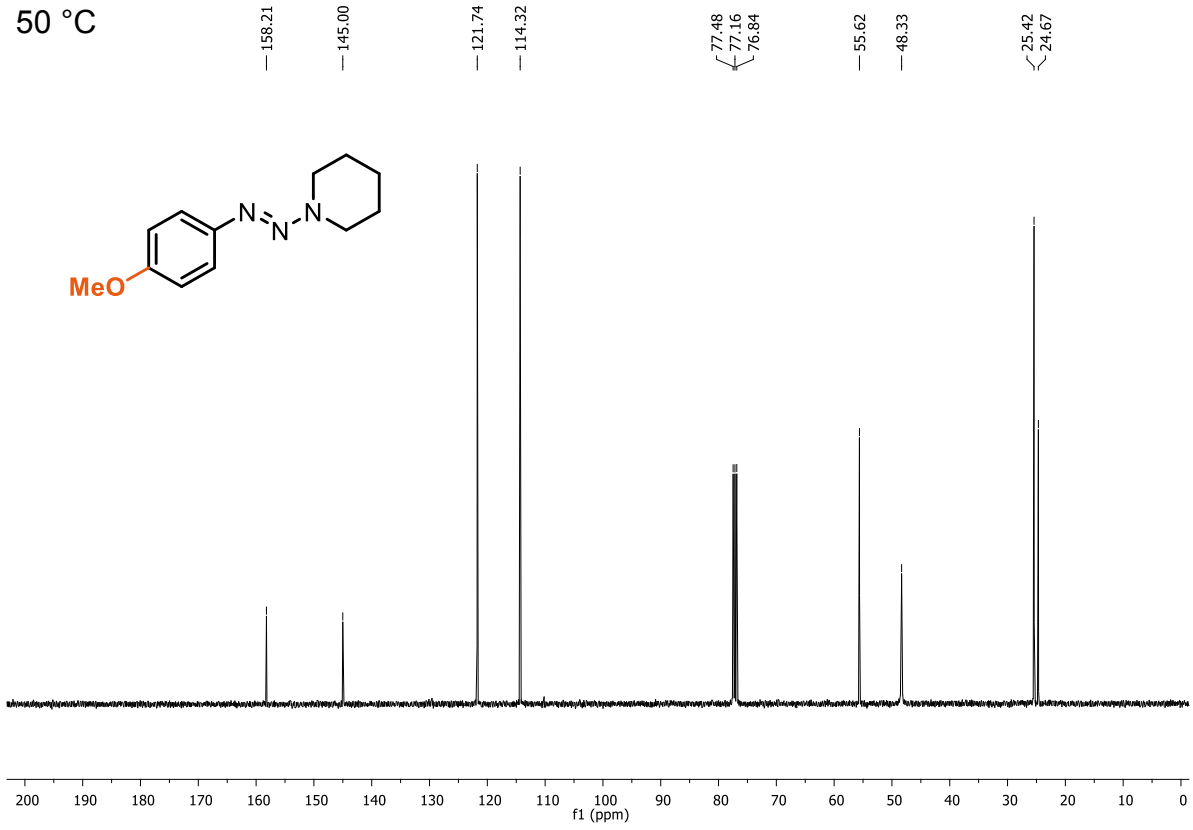

156.07
144.22
125.11
120.35
77.48
77.16
76.84
53.60
43.69
26.42
24.59
24.12
O2N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

DSC

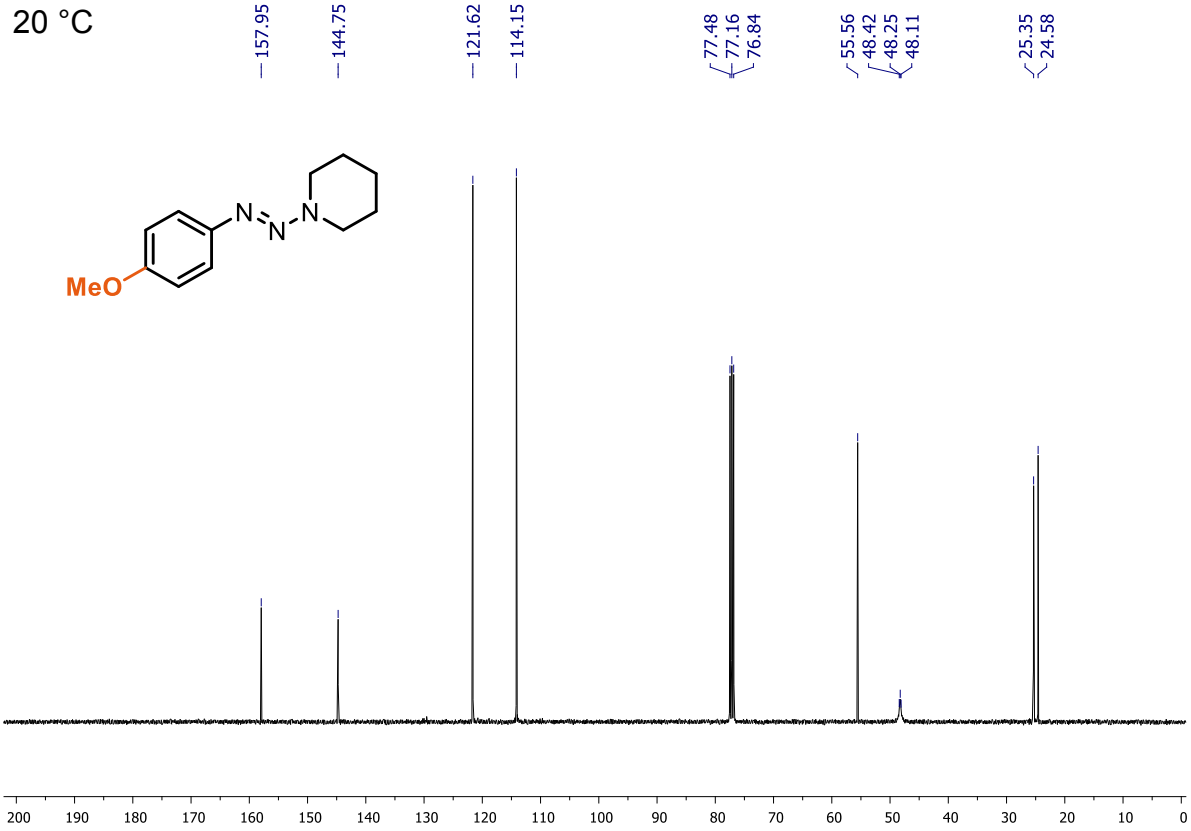

2
0
-2
-4
-6
Heat Flow (W/g)
87.34°C
5.533J/g
88.87°C
97.48°C
48.43J/g
98.66°C
O2N
N
N
N
20
40
60
80
100
120
140
160
180
200
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments

1-((4-methoxyphenyl)diazenyl)piperidine (8b)

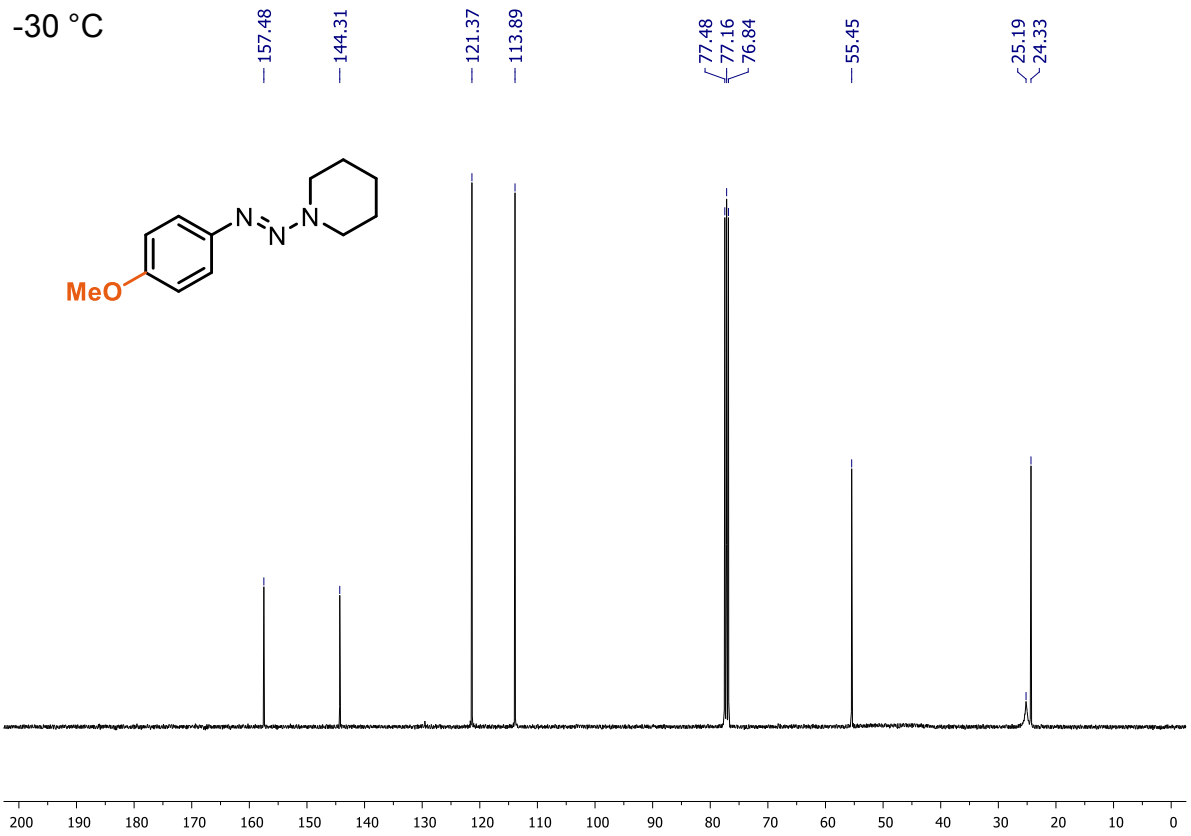




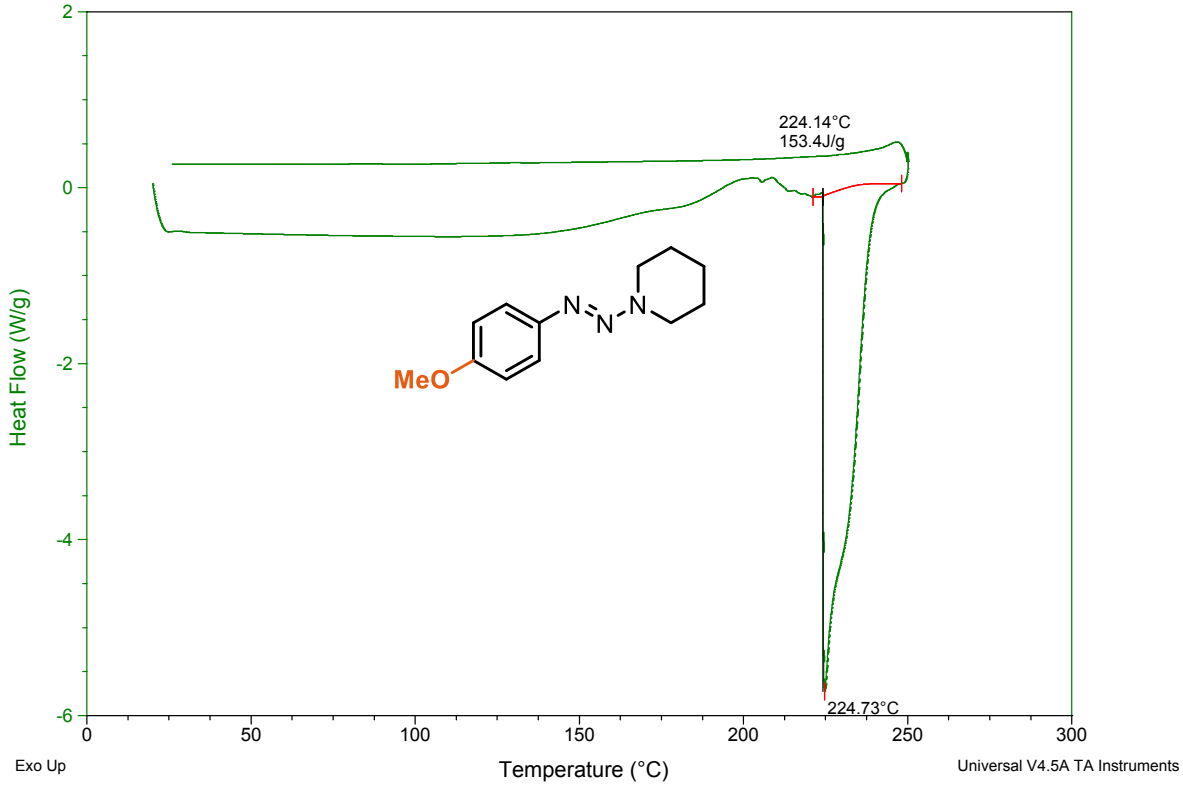
20 °C


157.95
144.75
121.62
114.15
77.48
77.16
76.84
55.56
48.42
48.25
48.11
25.35
24.58
MeO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

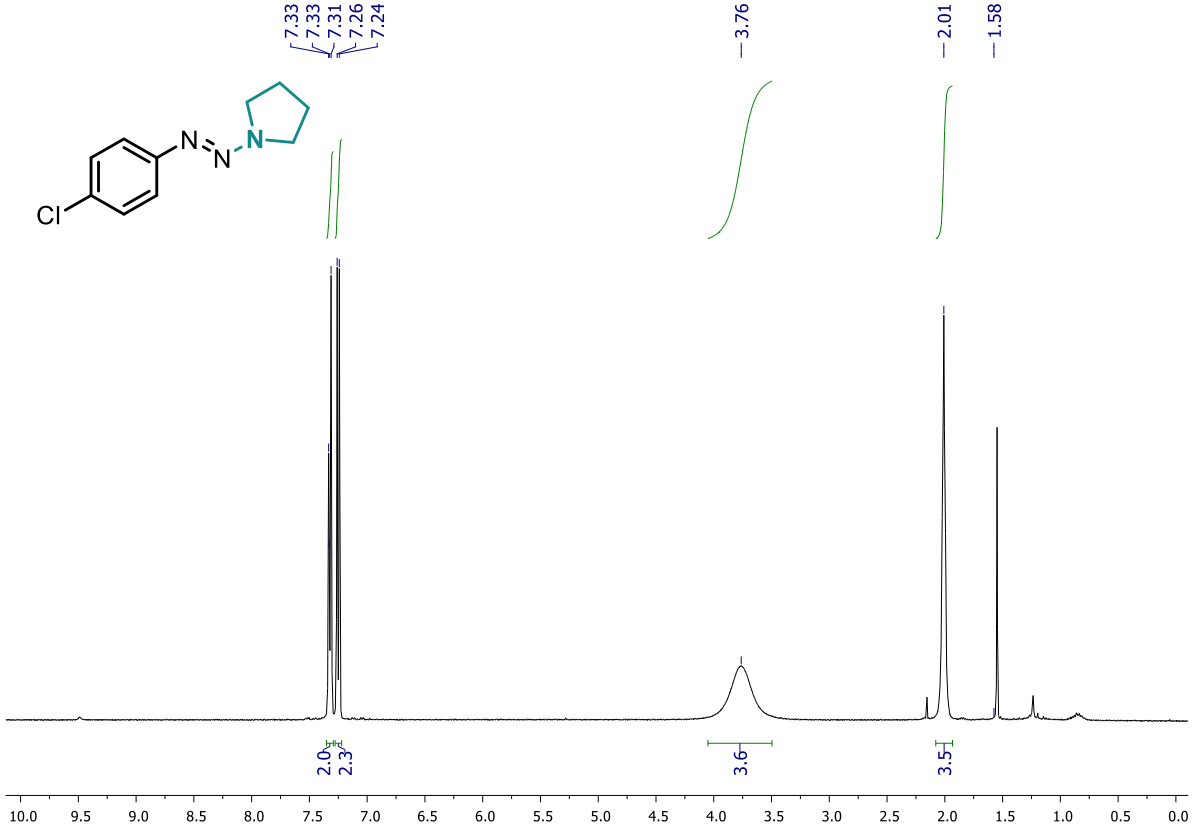
-30 °C

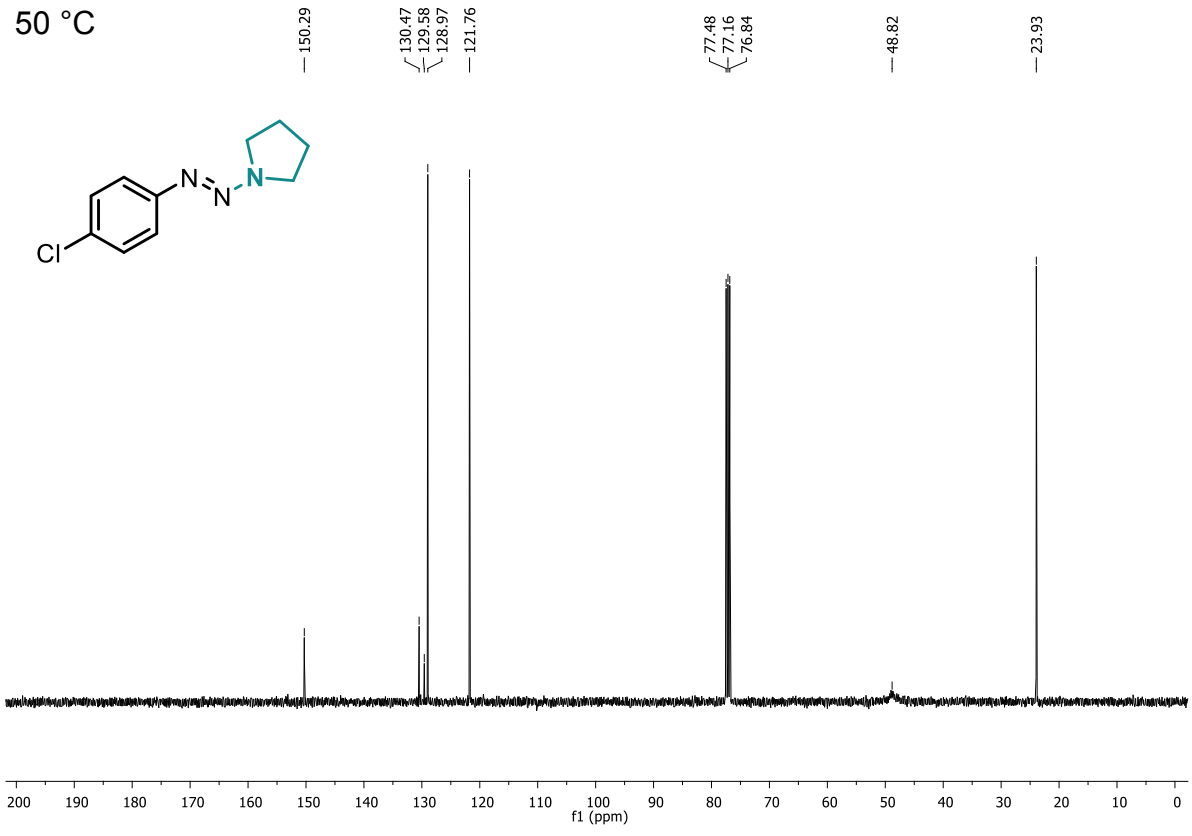

157.48
144.31
121.37
113.89
77.48
77.16
76.84
55.45
25.19
24.33
MeO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

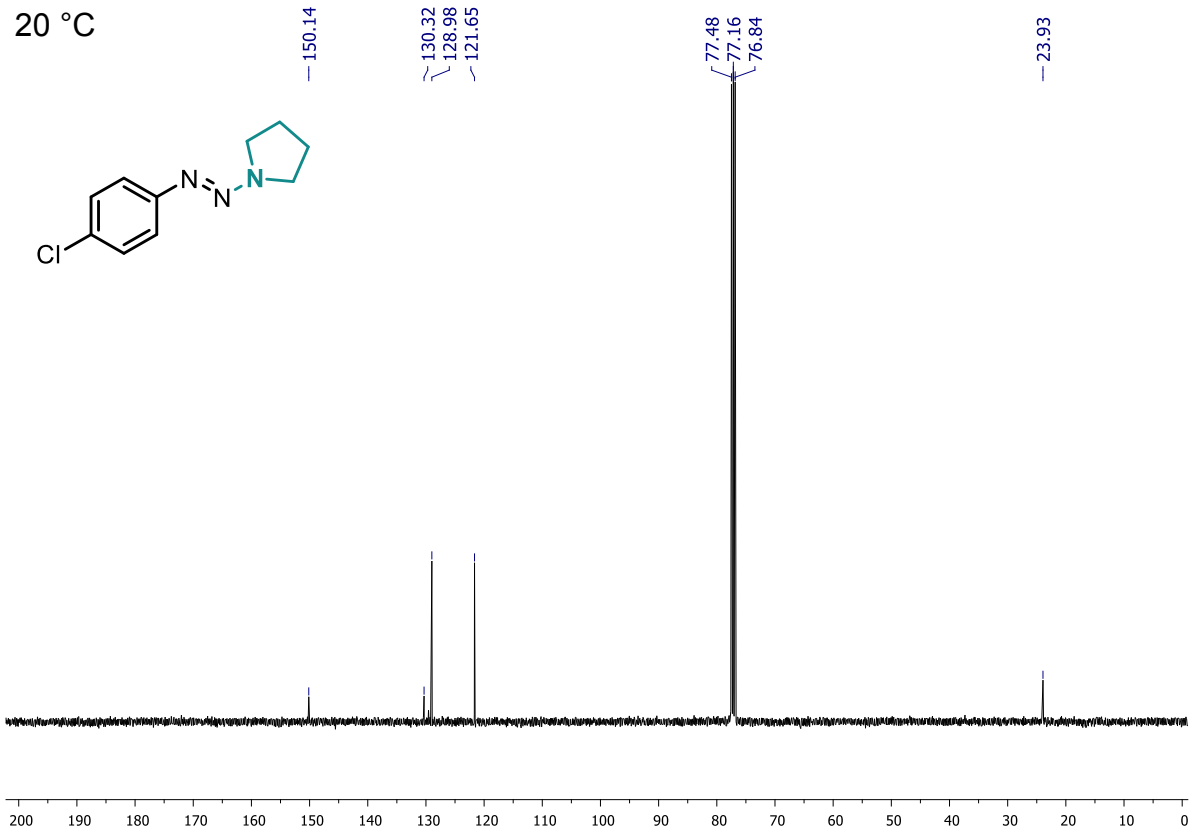
DSC

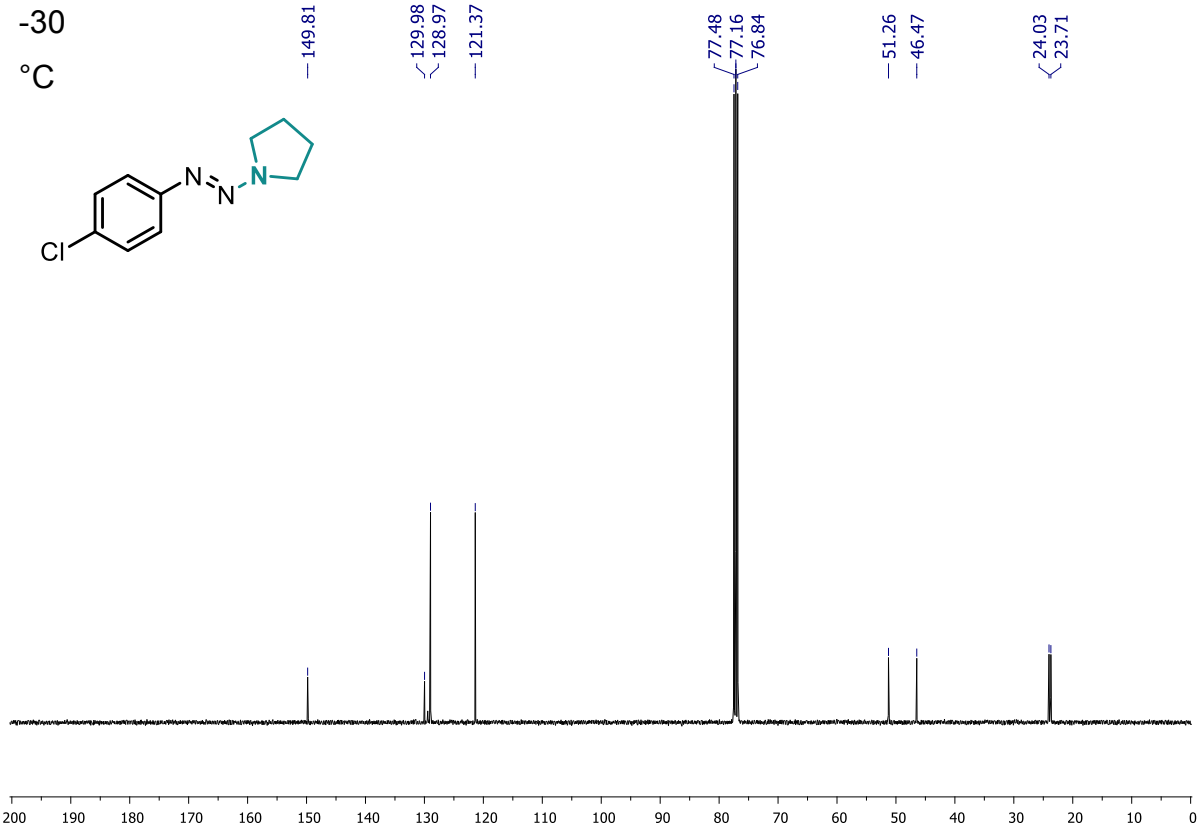

224.14°C
153.4J/g
224.73°C
MeO
N
N
N
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
2
0
-2
-4
-6
0
50
100
150
200
250
300

1-((4-chlorophenyl)diazenyl)pyrrolidine (3c)

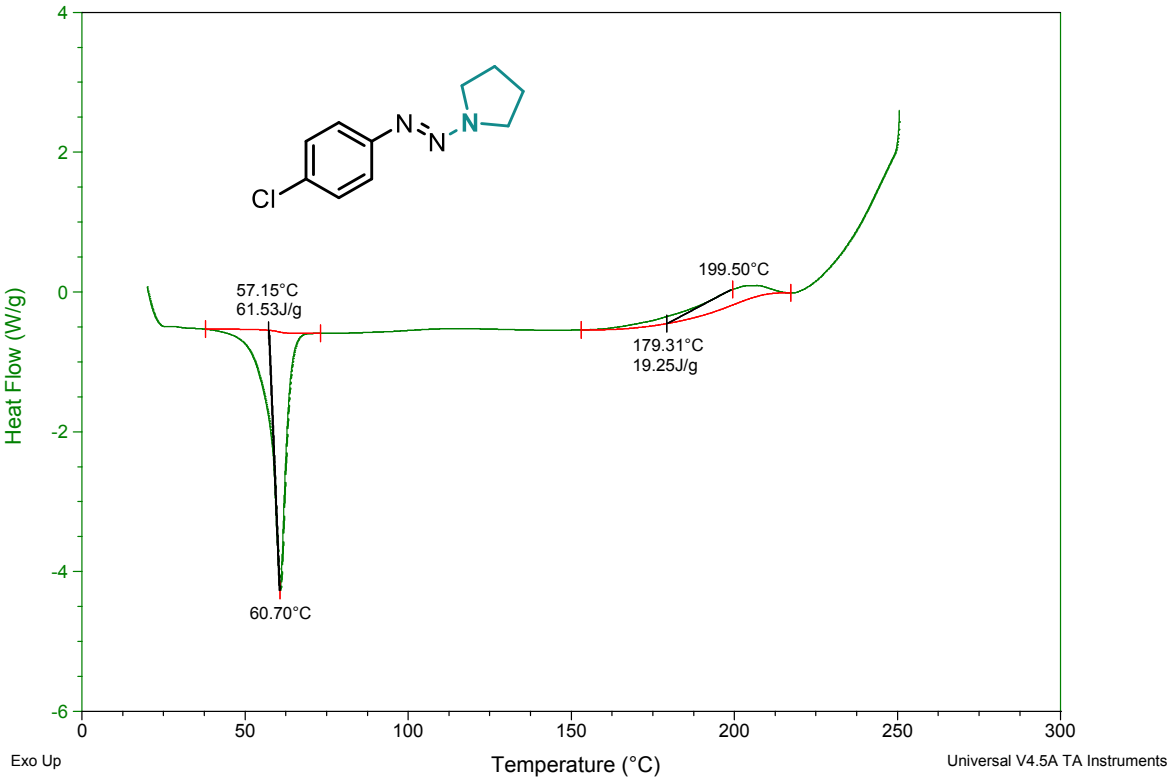




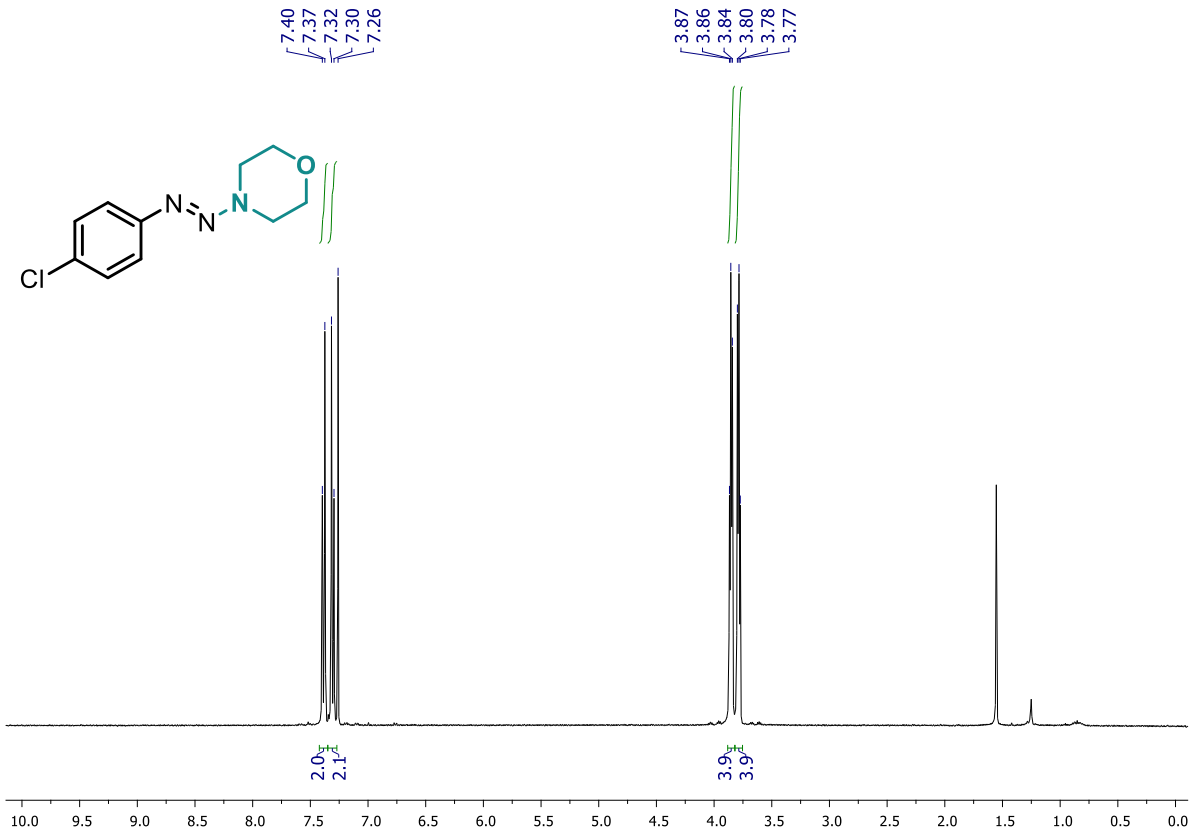

20 °C
150.14
130.32
128.98
121.65
77.48
77.16
76.84
23.93
Cl
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

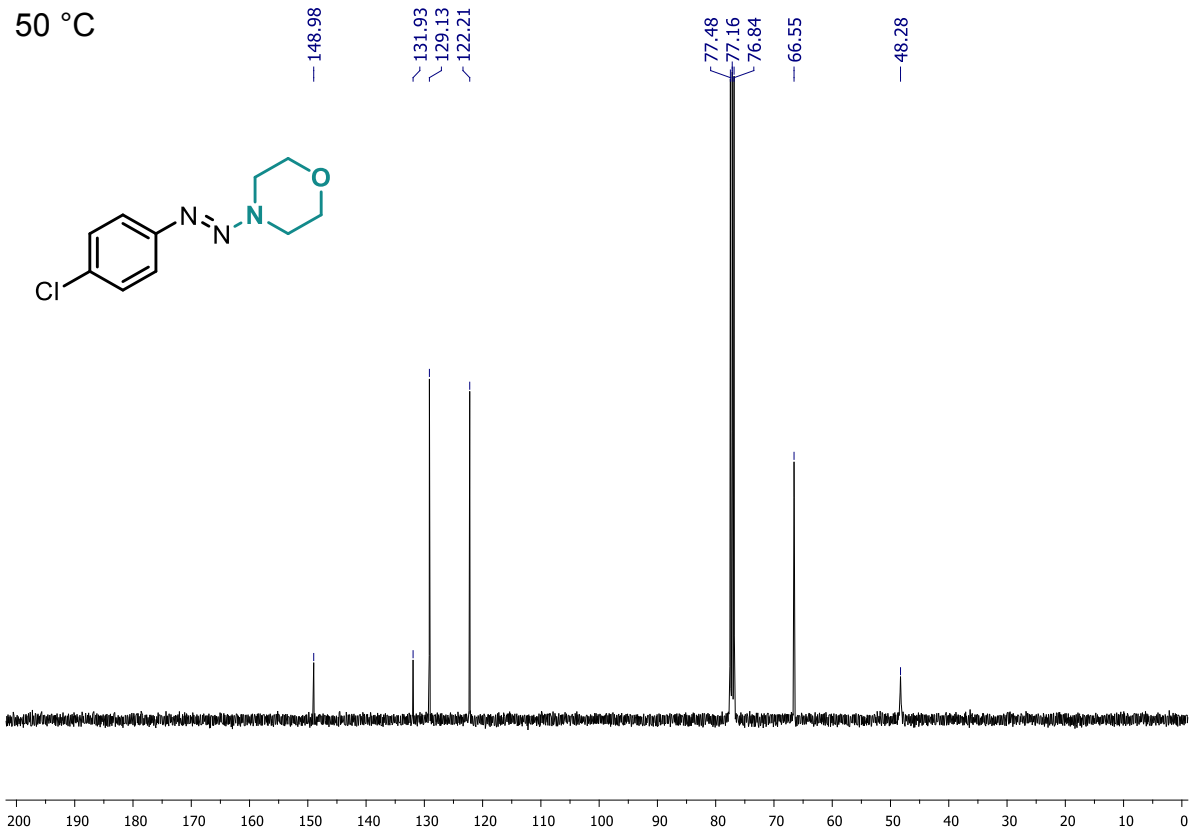

-30
°C
149.81
129.98
128.97
121.37
77.48
77.16
76.84
51.26
46.47
24.03
23.71
Cl
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

DSC

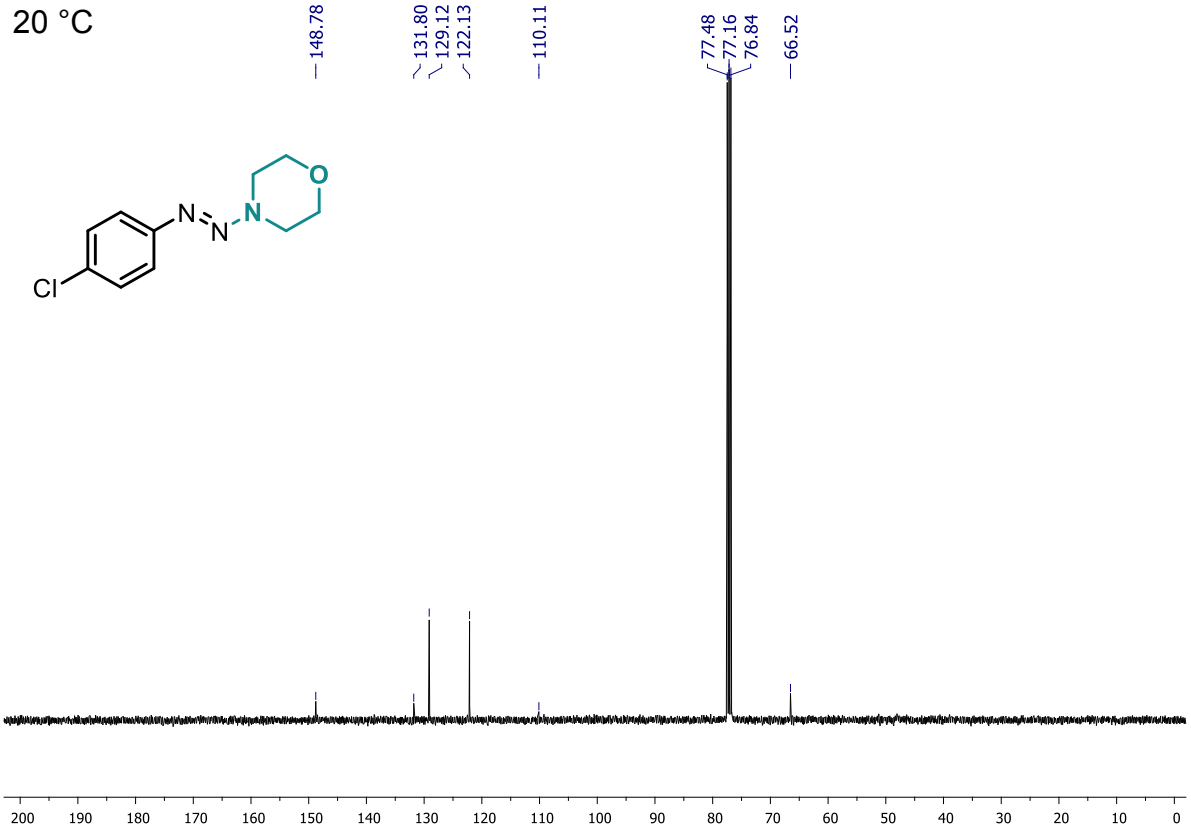

Cl
N
N
N
57.15°C
61.53J/g
60.70°C
199.50°C
179.31°C
19.25J/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

4-((4-chlorophenyl)diazenyl)morpholine (3d)

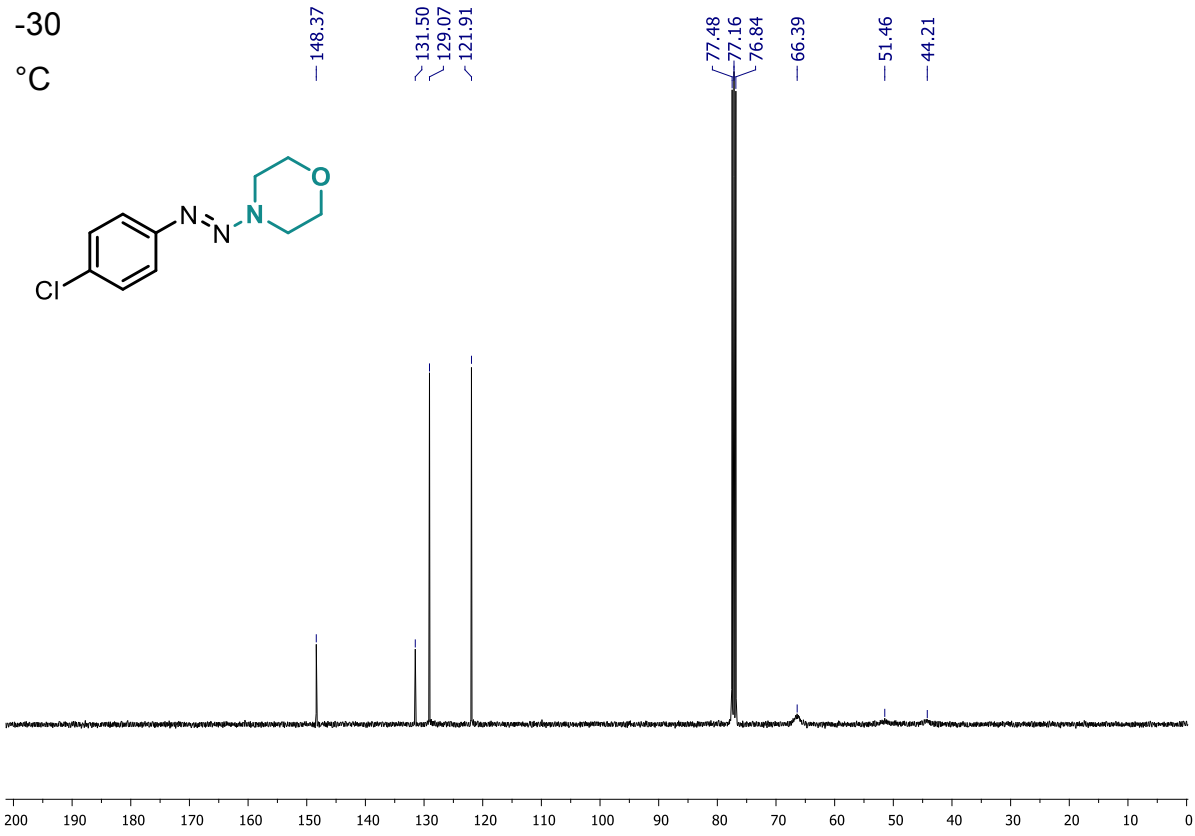




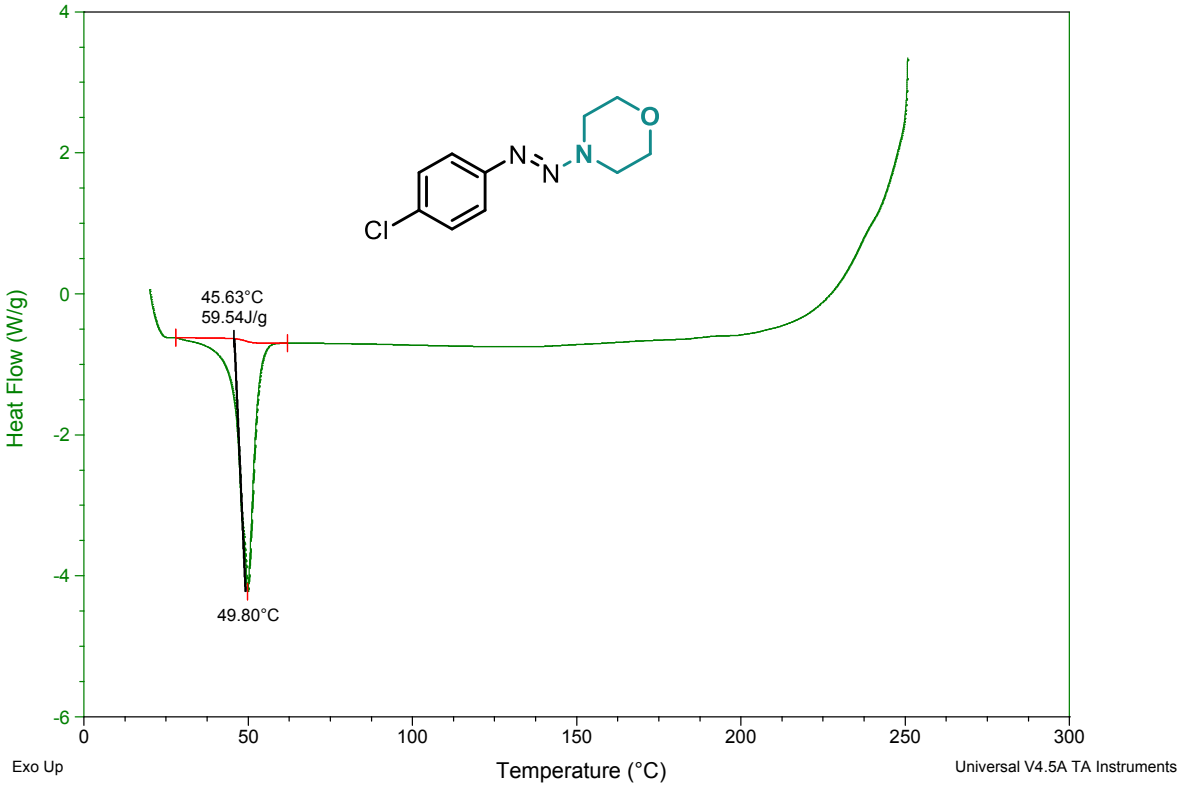
20 °C


148.78
131.80
129.12
122.13
110.11
77.48
77.16
76.84
66.52
O
N
N
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

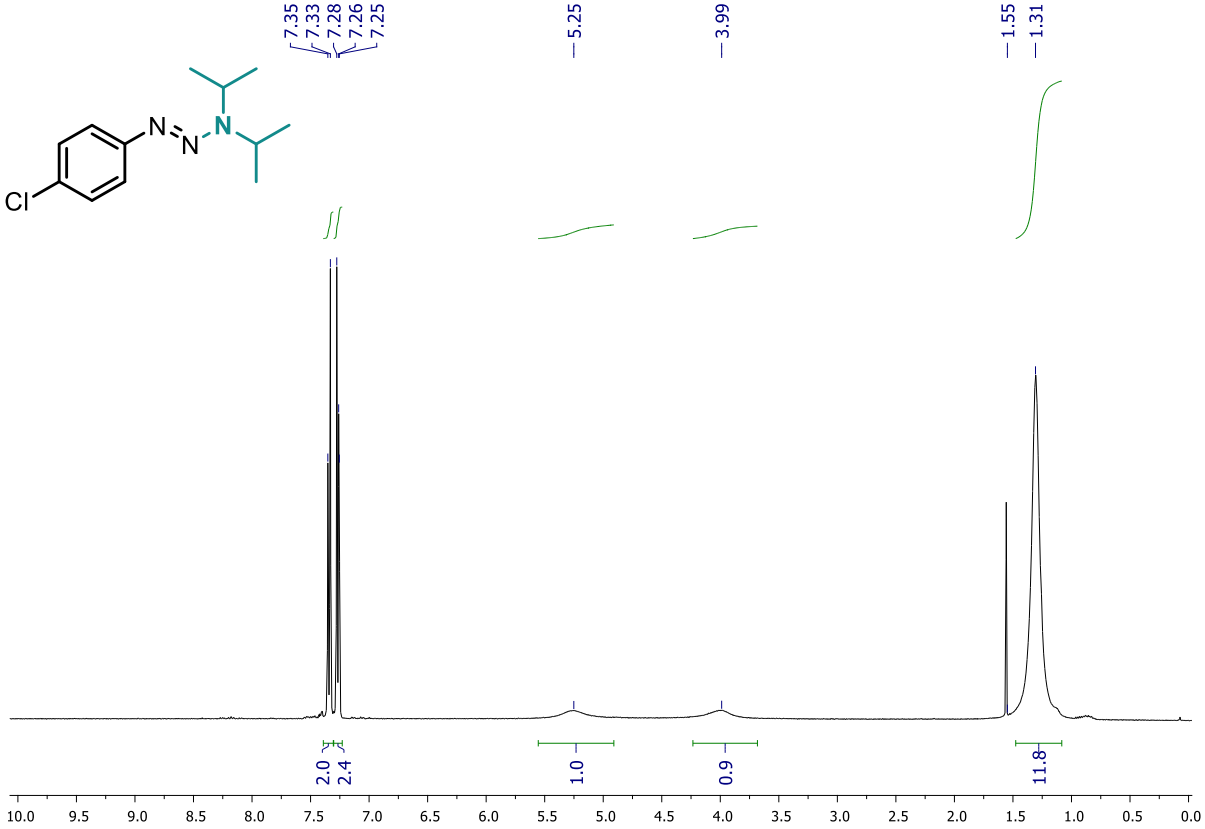
-30 °C

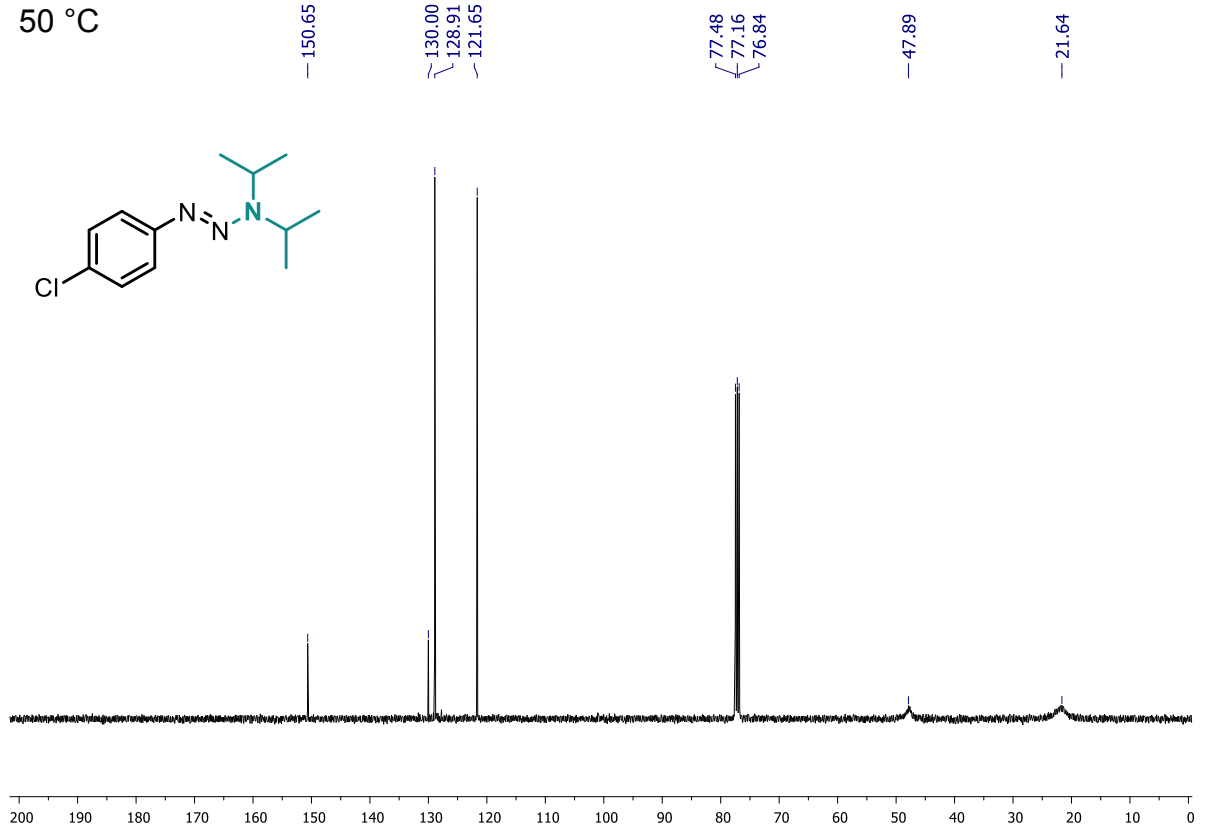

148.37
131.50
129.07
121.91
77.48
77.16
76.84
66.39
51.46
44.21
O
N
N
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

DSC

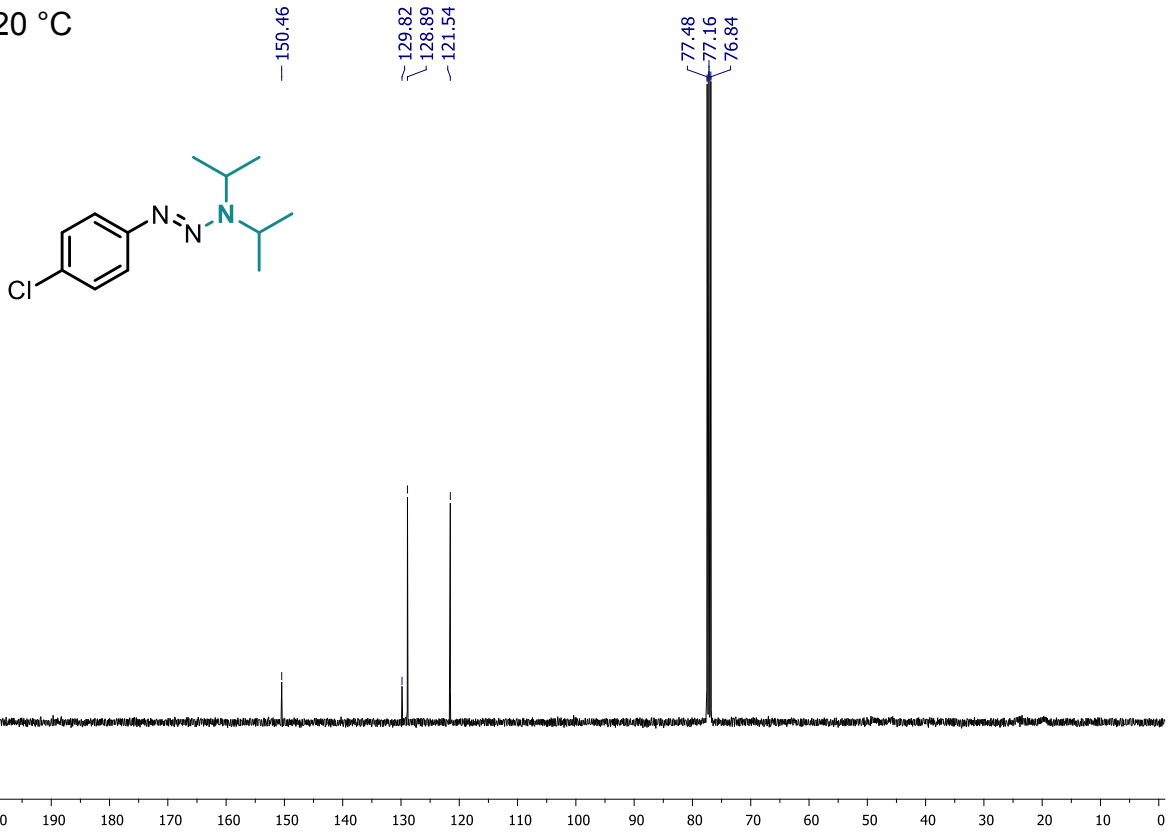

4
2
0
-2
-4
-6
Heat Flow (W/g)
45.63°C
59.54J/g
49.80°C
Cl
N
N
O
0
50
100
150
200
250
300
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

1-(4-chlorophenyl)-3,3-diisopropyltriaz-1-ene (3e)

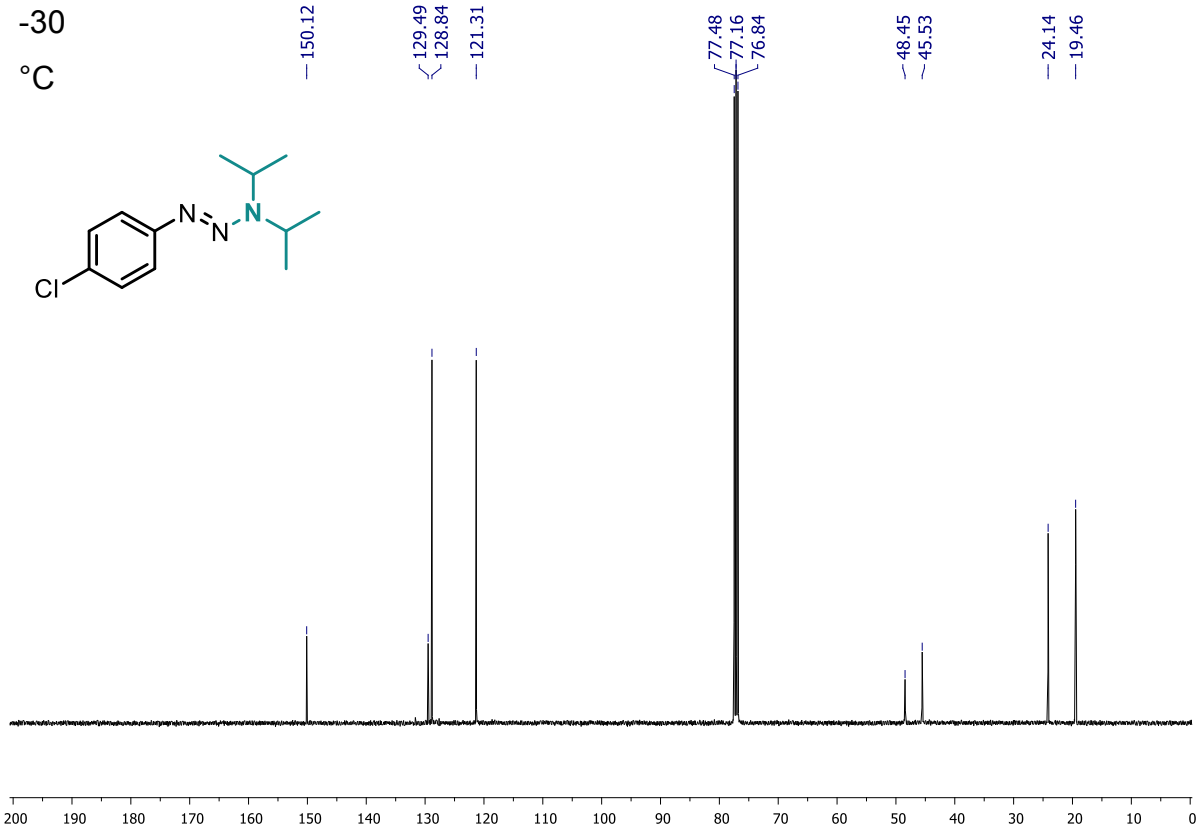




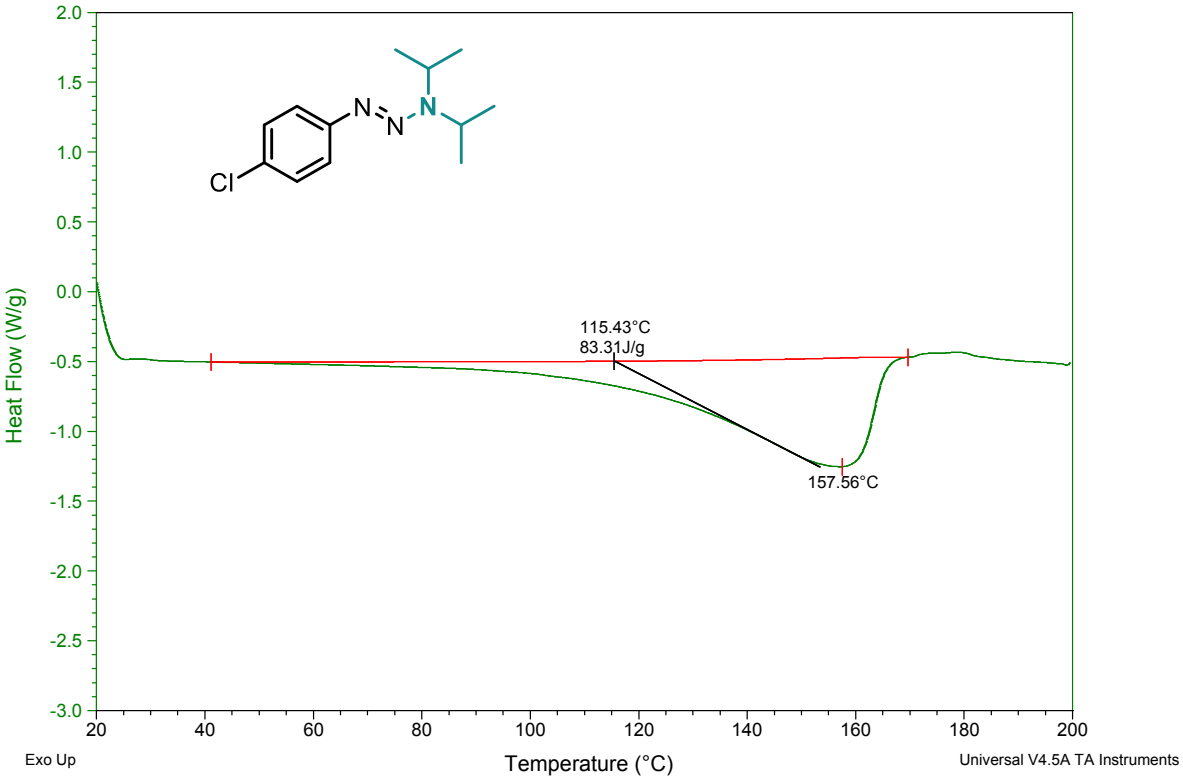
20 °C


150.46
129.82
128.89
121.54
77.48
77.16
76.84
N
N
N
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

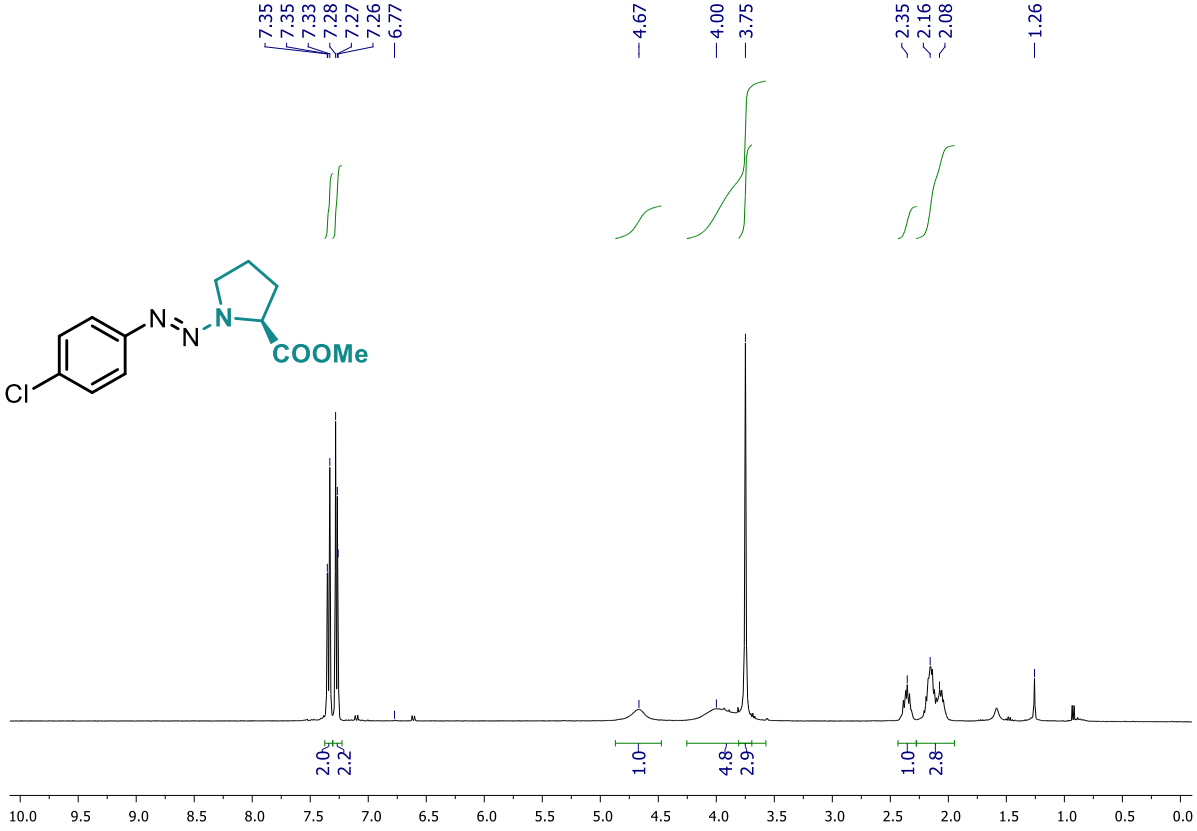
-30 °C

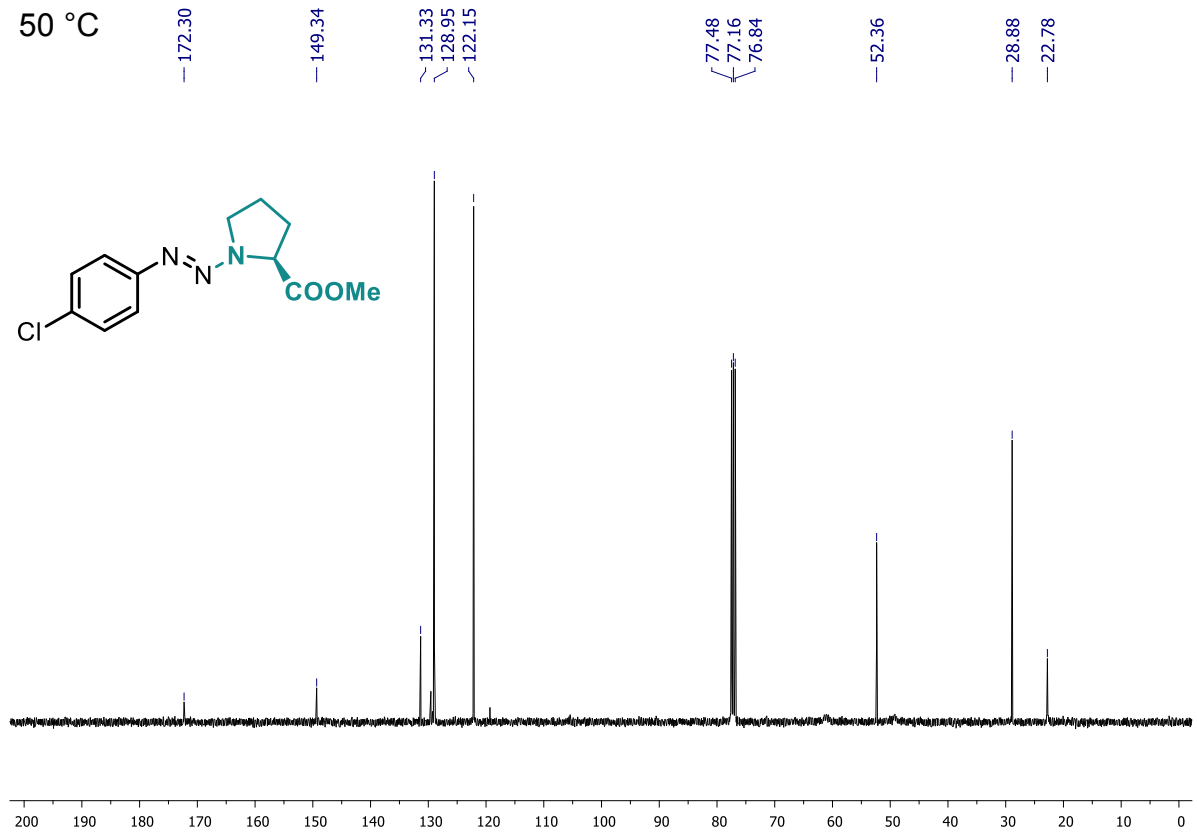

150.12
129.49
128.84
121.31
77.48
77.16
76.84
48.45
45.53
24.14
19.46
N
N
N
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

DSC

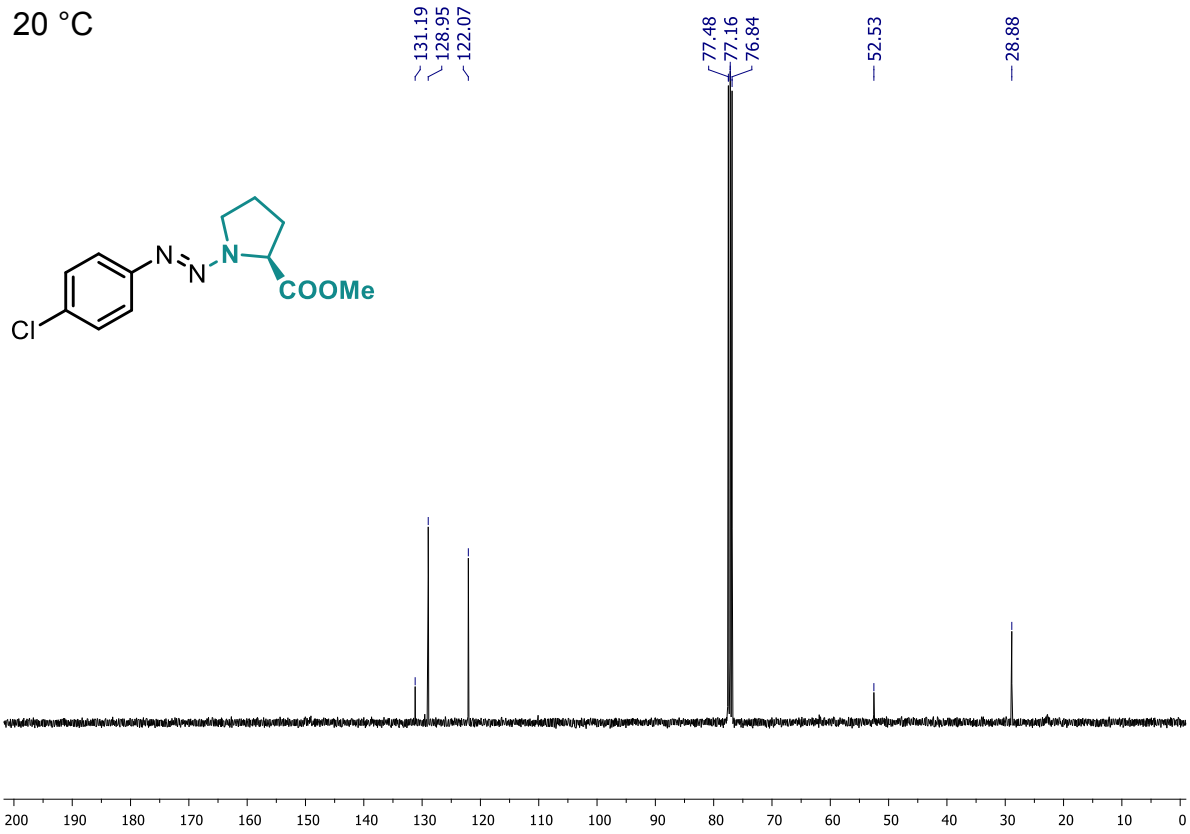

2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
Heat Flow (W/g)
Cl
N
N
115.43°C
83.31J/g
157.56°C
20
40
60
80
100
120
140
160
180
200
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments

methyl-((4-chlorophenyl)diazenyl)-L-prolinate (3f)

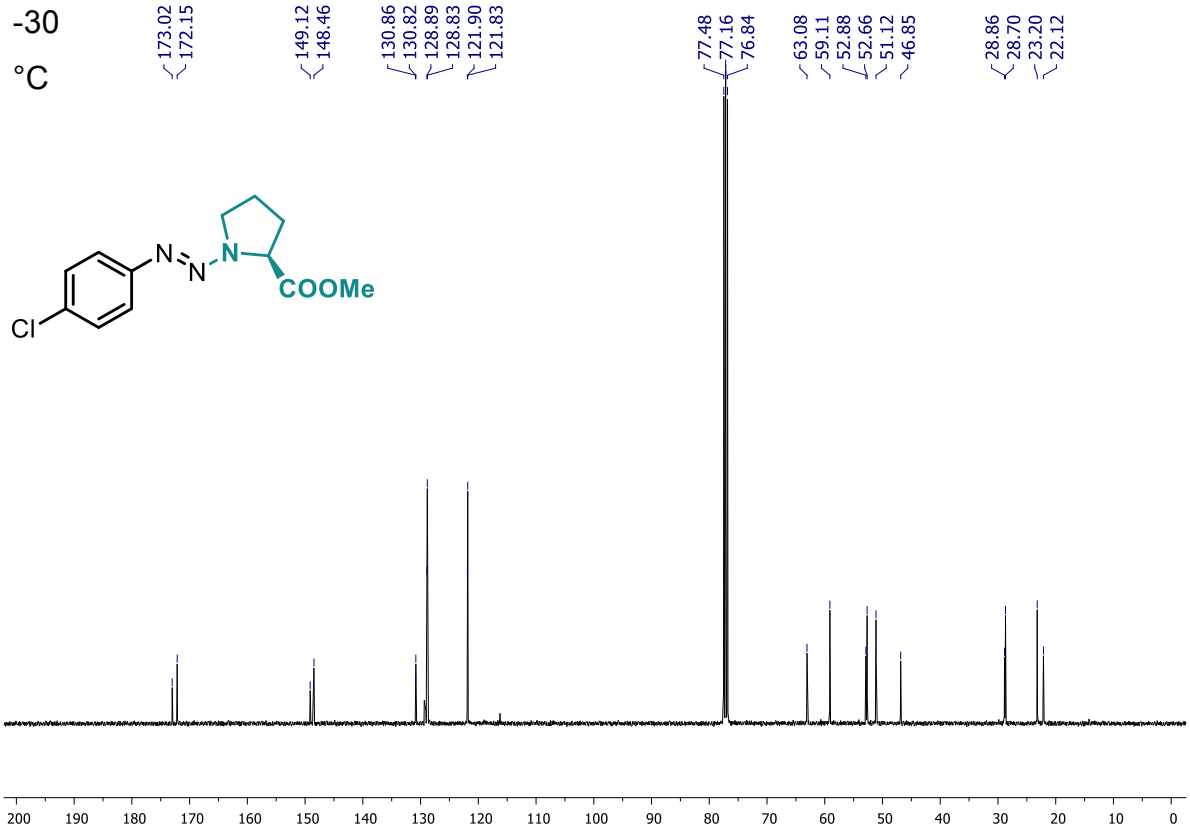




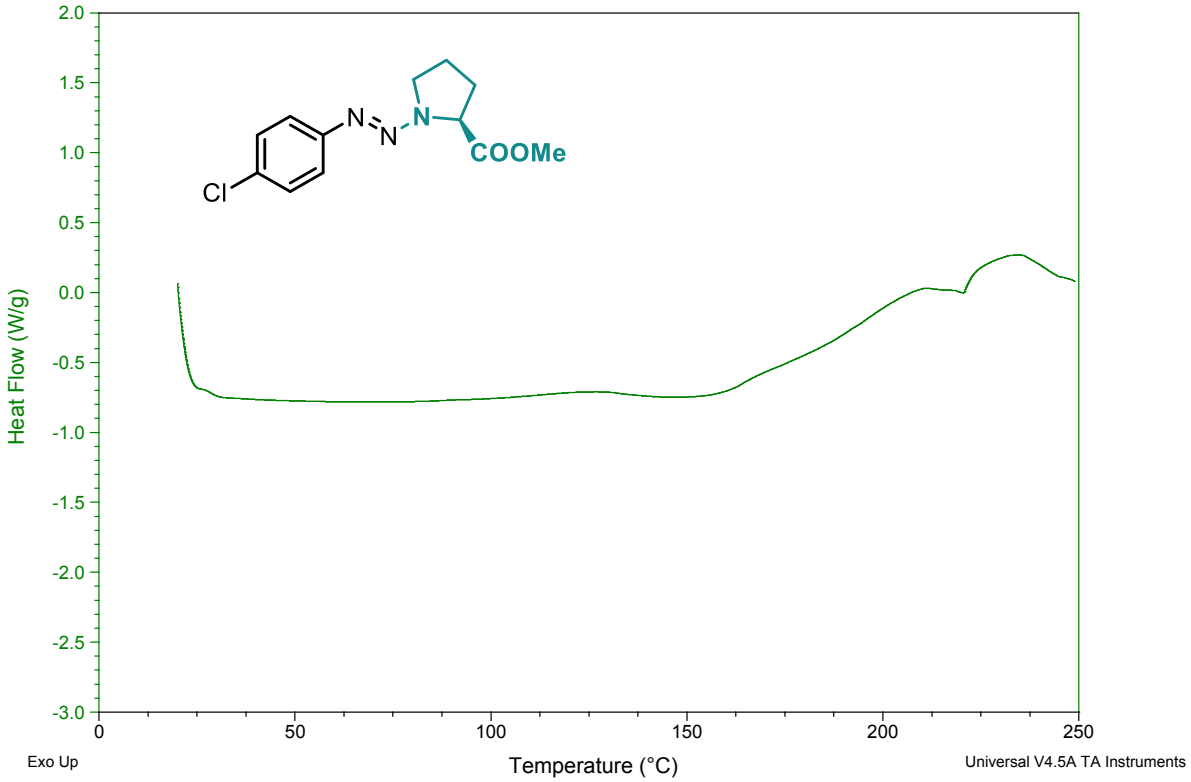
20 °C


131.19
128.95
122.07
77.48
77.16
76.84
52.53
28.88
N
N
N
COOMe
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

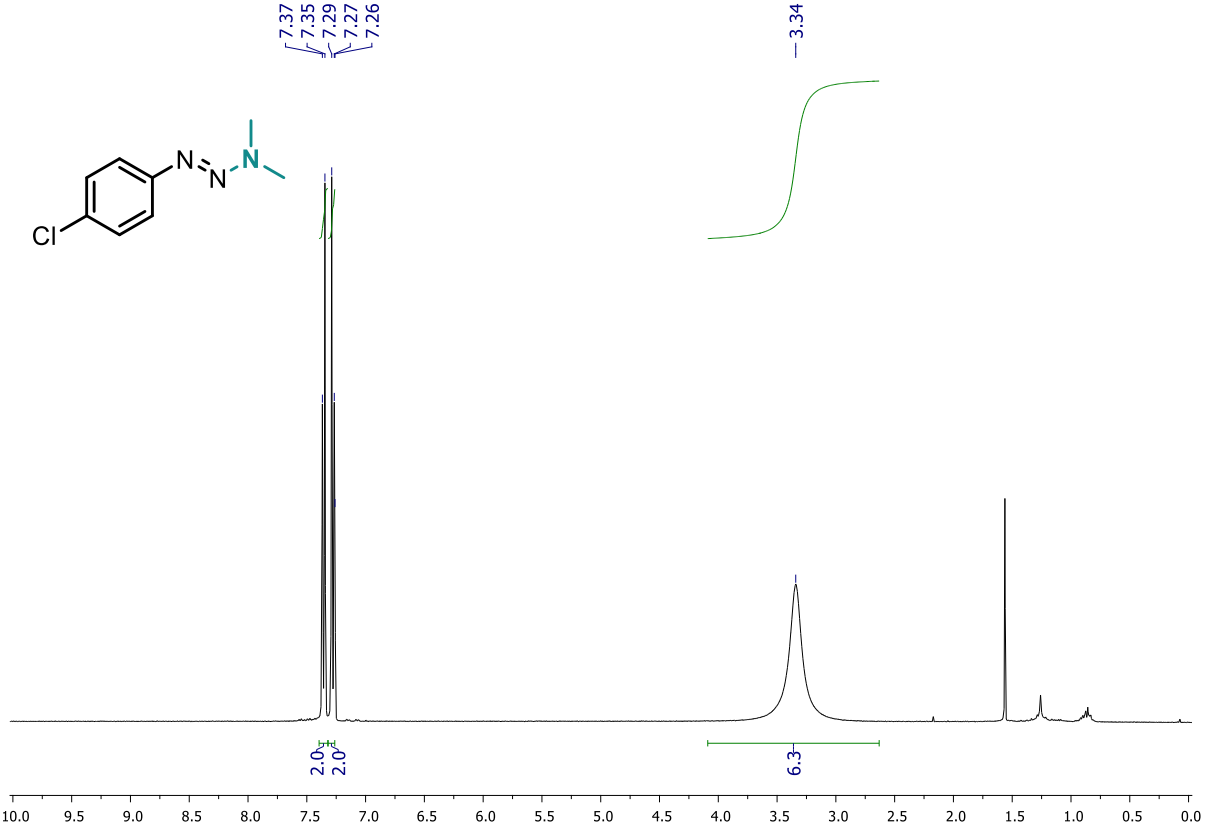
-30 °C

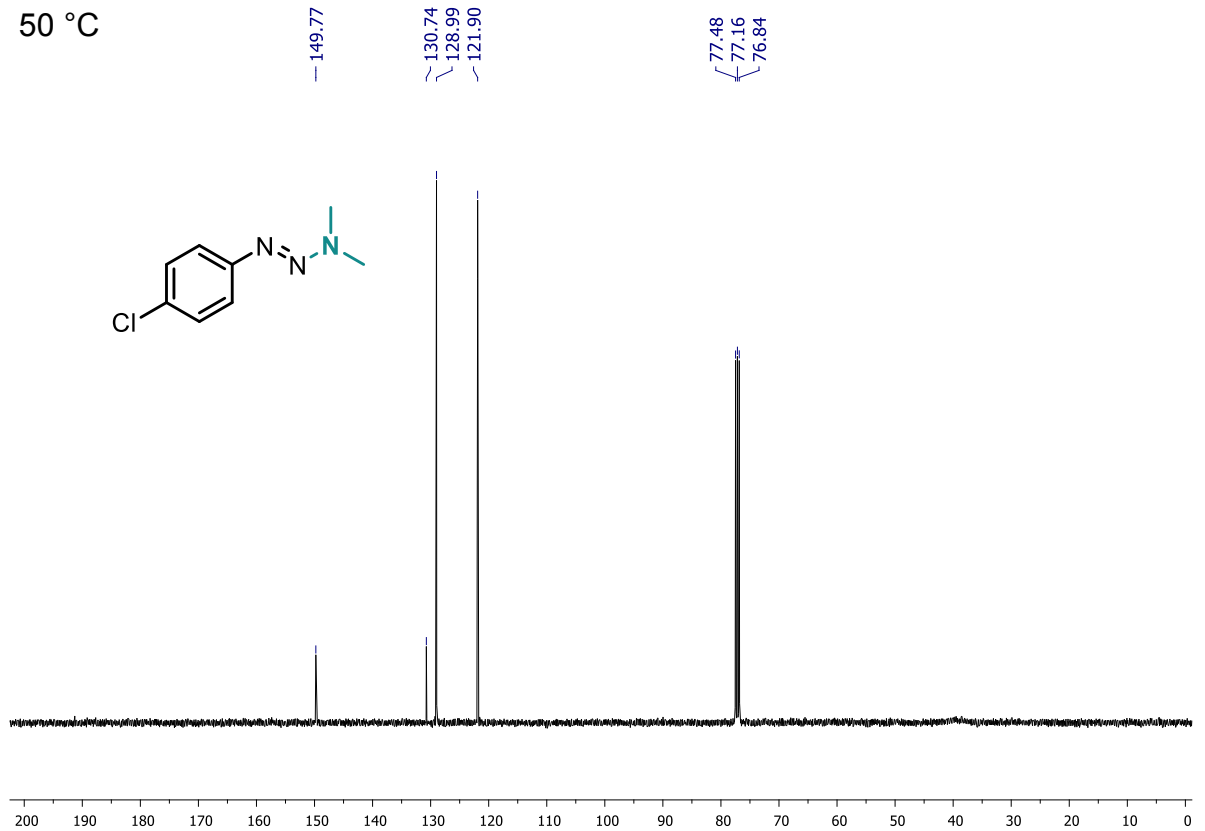

173.02
172.15
149.12
148.46
130.86
130.82
128.89
128.83
121.90
121.83
77.48
77.16
76.84
63.08
59.11
52.88
52.66
51.12
46.85
28.86
28.70
23.20
22.12
N
N
N
COOMe
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

DSC

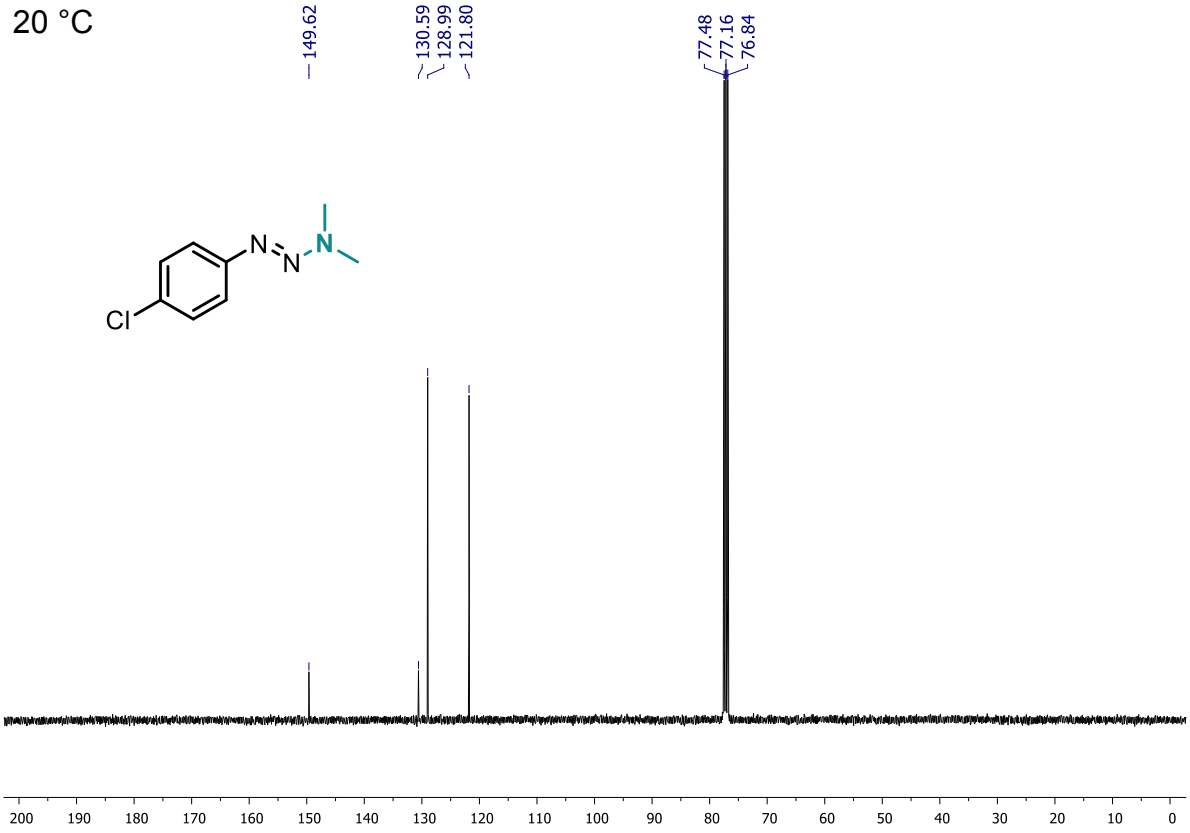

2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
Heat Flow (W/g)
Cl
N
N
N
COOMe
0
50
100
150
200
250
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments

1-(4-chlorophenyl)-3,3-dimethyltriaz-1-ene (3g)

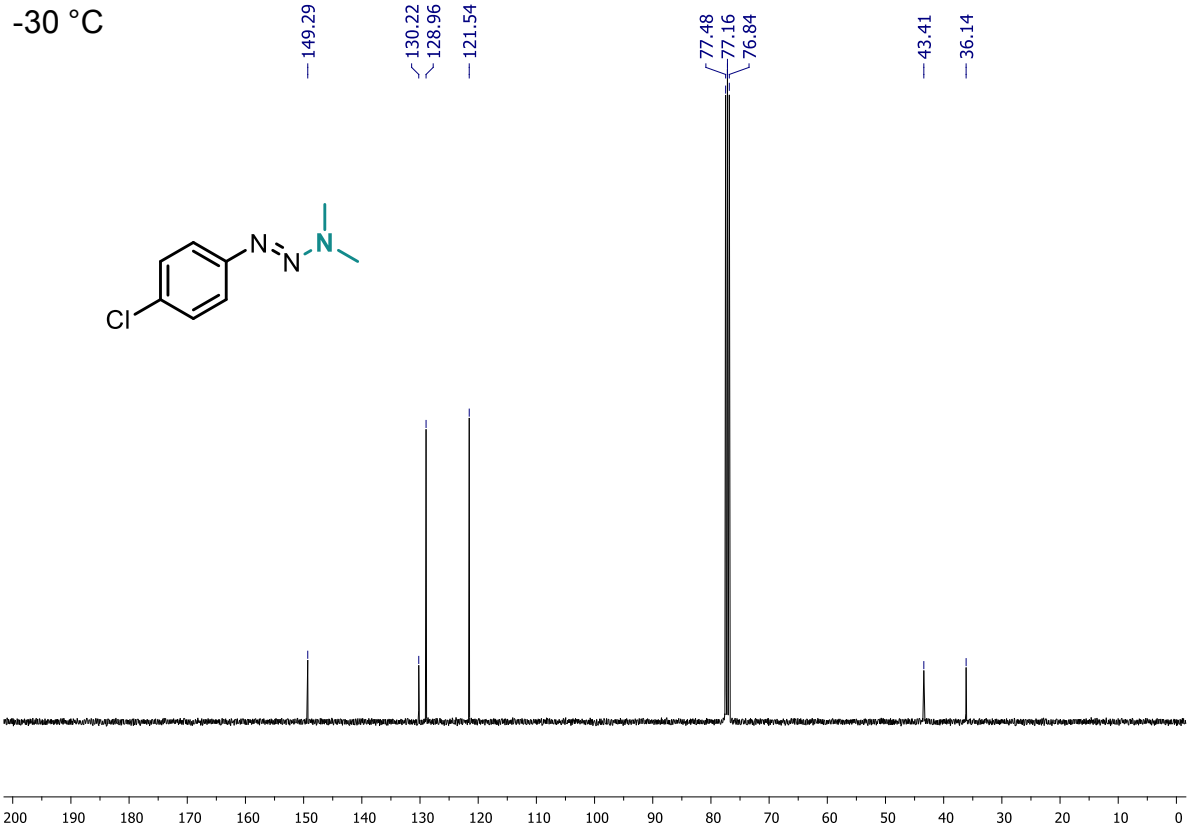




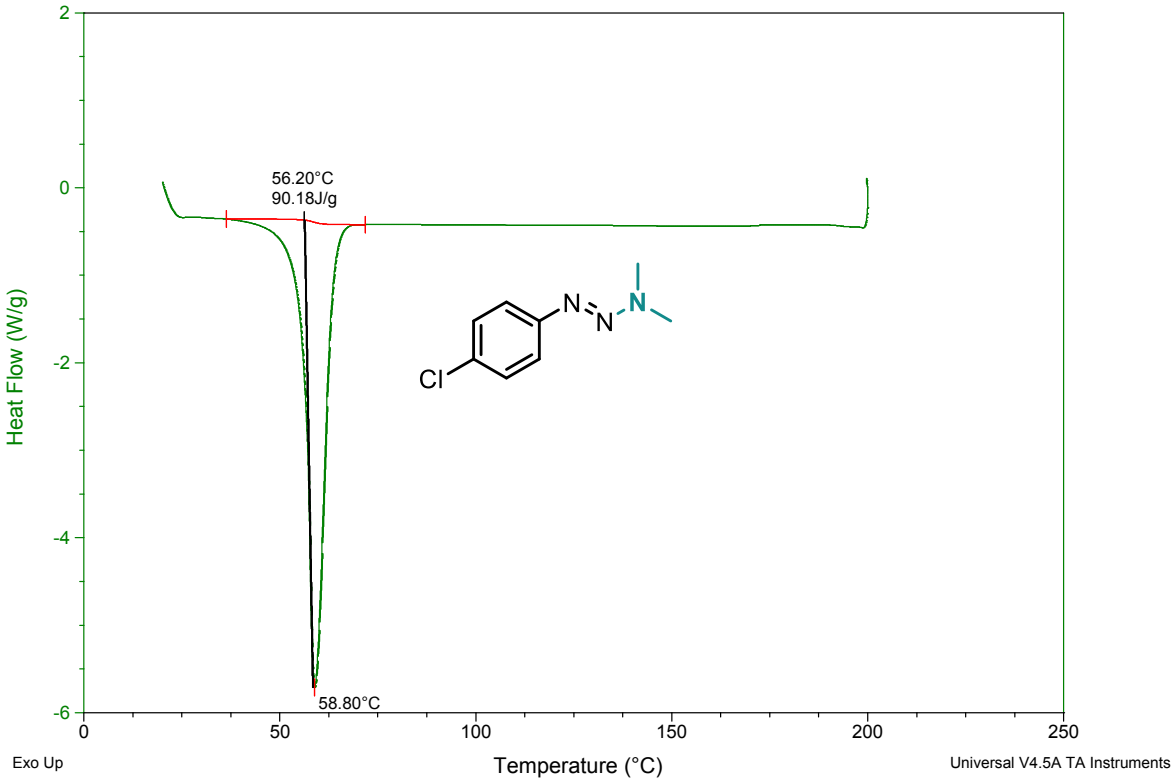
20 °C


149.62
130.59
128.99
121.80
77.48
77.16
76.84
N
N
N
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

-30 °C


149.29
130.22
128.96
121.54
77.48
77.16
76.84
43.41
36.14
N
N
N
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

DSC


2
0
-2
-4
-6
Heat Flow (W/g)
56.20°C
90.18J/g
58.80°C
Cl
N
N
N
0
50
100
150
200
250
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments

5 DSC Interpretation Summary Table

	Intital Decomp. Temp.	Comments	Physical form (at rt)
2a	110 °C	Melting endotherm – followed by a broader endotherm at *ca*. 110 °C, could signify an endothermic Balz-Schiemann process followed by an endothermic phase transition (boiling) of the resulting fluorobenzene	Solid
3a	140 °C	Melting endotherm followed by (overlapped with) an exotherm – may indicate decomposition immediately on formation of liquid phase.	Solid
4a	170 °C	Melting endotherm followed by (overlapped with) an exotherm – may indicate decomposition immediately on formation of liquid phase.	Solid
5a	>200 °C	Three endotherms but no exotherm – no evidence of significant exotherm due to decomposition	Solid
6a	140 °C	Melting endotherm followed by (overlapped with) an exotherm – may indicate decomposition immediately on formation of liquid phase.	Solid
7a	150 °C	No sharp endotherm due to melting – decomposition with "thermal runaway" (as discussed in text).	Solid
8a	140 °C	No sharp endotherm due to melting – exotherm followed by (overlapped with) endotherm – the exotherm is consistent with decomposition.	Solid
1b	100 °C	Melting endotherm – followed by significant exotherm due to decomposition.	Solid
2b	>200 °C	Melting endotherm – followed by a second endotherm starting at *ca*. 160 °C and extending over a wide temperature range; behaviour	Solid

		consistent with evaporation – no exotherm indicative of decomposition.	
3b	>200 °C	Melting endotherm – followed by slight baseline fluctuation between *ca*. 120 °C and 160 °C (or possibly a weak exotherm over this temperature range) – no significant exotherm due to decomposition.	Solid
4b	>200 °C	Melting endotherm – followed by a second endotherm from *ca*. 120 °C to 190 °C; behaviour consistent with evaporation – no exotherm indicative of decomposition	Solid
5b	>200 °C	Broad endotherm from *ca*. 120 °C and extending over a wide temperature range; behaviour consistent with evaporation – no exotherm indicative of decomposition	Liquid
6b	>200 °C	Melting endotherm – followed by a second endotherm starting at *ca*. 140 °C and extending over a wide temperature range; behaviour consistent with evaporation – no exotherm indicative of decomposition.	Solid
7b	>200 °C	Melting endotherm (preceded by a small endotherm) – no significant exotherm indicative of decomposition.	Solid
8b	150 °C	No sharp endotherm due to melting – broad exotherm starting at *ca*. 150 °C consistent with decomposition (followed by significant endotherm at *ca*. 220 °C)	Liquid
3c	150 °C	Melting endotherm – followed by significant exotherm due to decomposition.	Solid
3d	>200 °C	Melting endotherm – no significant exotherm indicative of decomposition below 200 °C – data recorded above 200 °C shows a significant exotherm indicative of decomposition.	Solid
3e	>200 °C	No sharp endotherm due to melting	Liquid

		– Broad endotherm from *ca*. 40 °C and extending over a wide temperature range; behaviour consistent with evaporation – no significant exotherm indicative of decomposition.	
3f	150 °C	No sharp endotherm due to melting – broad exotherm starting at *ca*. 150 °C due to decomposition.	Liquid
3g	>200 °C	Melting endotherm – no significant exotherm indicative of decomposition below 200 °C.	Solid

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