Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Nitrogen-rich hypergolic ionic salts based on (2-methyltetrazol-5-yl)diazotates

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General Methods: ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz (Buruker Avance 500) nuclear magnetic resonance spectrometers operating at 500 and 100 MHz, respectively, by using [D6]DMSO as solvent and locking solvent. ^{1}H and ^{13}C NMR spectra were internally referenced to [D6]DMSO signal (δ = 2.50 ppm and δ = 39.4 ppm, respectively). IR spectra were recorded using KBr pellets for solids on a Bruker ALPHA FT-IR-Spektrometer. The melting and decomposition points were obtained on a differential scanning calorimeter (METTLER TOLEDO) at a scan rate of 10 °C min^{-1}. Elemental analyses were carried out using an Elementar Vario EL element alanalyzer. High resolution mass spectrometry was recorded on Bruker Apex IV FTMS. Details of the X-ray diffraction analysis of **8** and **9** are presented. Data were collected on a Rigaku Saturn 724 CCD diffractometer employing graphite-monochromated MoKa radiation (λ=0.71073 Å) using omega scans.

X-ray diffraction: For compounds **8** and **9**, data were collected on a Rigaku Saturn 724 CCD diffractometer employing graphite-monochromated MoKa radiation (λ=0.71073 Å) using omega scans. Data collection and reduction were performed and the unit cell was initially refined using CrystalClear SM Expert 2.0 r2.[1] The reflection data were corrected for Lorentz-polarization factors. The structures were solved by direct methods and refined by the least-squares method on F^2 using the SHELXTL-97 suite of programs.[2] All non-hydrogen atoms were refined anisotropically. The structures were solved in the space group P-1 for **8** and P2/c for **9** by analysis of systematic absences.

Ammonium (2-methyltetrazol-5-yl)diazotate (5). *i*-Pentylnitrite (0.36 mL , 2.4 mmol) was added dropwise to a solution of 2-methyl-5-aminotetrazole (198 mg, 2 mmol) in 16 mL acetonitrile at -15 °C. After stirring for 1 h, aqueous ammonia (0.4 mL, 2.6 mmol) was added. The precipitate was filtered, washed with acetonitrile, and dried to yield 268 mg (92%) of product **5**.

White solid (**5**): DSC (10 °C·min^{-1}): 98 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3151, 3056, 2911, 2835, 1697, 1482, 1404, 1308, 1290, 1214, 927, 766, 716 cm^{-1}. ^{1}H NMR (500 MHz, [D6]DMSO): δ = 7.28 (s, 4H), 4.23 (s, 3H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 172.3, 39.2 ppm. Elemental analysis: (C2H7N7O, 145.12) calc.: C 16.55, H 4.86, N 67.56; found: C 16.82, H 4.74, N 67.07.

Hydrazinium (2-methyltetrazol-5-yl)diazotate (6). *i*-Pentylnitrite (0.36 mL , 2.4 mmol) was added dropwise to a solution of 2-methyl-5-aminotetrazole (198 mg, 2 mmol) in 10 mL acetonitrile at -15 °C. After stirring for 1 h, hydrazine hydrate (0.2 mL, 3.3 mmol) was added. The precipitate was filtered, washed with acetonitrile, and dried to yield 268 mg (85%) of product **6**.

Colorless solid (**6**): DSC (10 °C·min^{-1}): 99 °C (m.p.); 120 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3287, 3129, 2954, 2834, 1601, 1468, 1405, 1328, 1230, 1199, 1088, 962, 917, 768, 716 cm^{-1}. ^{1}H NMR (500 MHz, [D6]DMSO): δ = 7.17 (s, 5H), 4.24 (s, 3H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 172.0, 39.2 ppm. Elemental analysis: (C2H8N8O,

160.14) calc.: C 15.00, H 5.04, N 69.97; found: C 14.85, H 5.00, N 69.99.

General procedure to synthesize (2-methyltetrazol-5-yl)diazotates 7-10. *i*-Pentylnitrite (0.36 mL , 2.4 mmol) was added dropwise to a solution of 2-methyl-5-aminotetrazole (198 mg, 2 mmol) in 16 mL acetonitrile at -15 °C. After stirring for 1 h, an aqueous suspension of barium hydroxide (315 mg, 1 mmol) in 7.5 mL water was added. The precipitated white barium salt was filtered, washed with acetonitrile, and dried. Afterwards, the white powder was dissolved in water to mix it with the guanidine based sulfate (1 mmol). The precipitated barium sulfate was filtered off and the filtrate was evaporated completely and dried to give (2-methyltetrazol-5-yl)diazotates **7-10**.

Guanidinium (2-methyltetrazol-5-yl)diazotate (7). Yield 155 mg (83%) of product **7**.
White solid (**7**): DSC (10 °C·min^{-1}): 194 °C (m.p.); 209 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3414, 3315, 3152, 3070, 1675, 1484, 1318, 1265, 919, 766, 680 cm^{-1}. ^{1}H NMR (500 MHz, [D6]DMSO): δ = 7.34 (s, 6H), 4.23 (s, 3H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 172.2, 158.3, 39.2 ppm. Elemental analysis: (C3H9N9O, 187.16) calc.: C 19.25, H 4.85, N 67.35; found: C 18.43, H 4.83, N 63.33. HRMS: calc. for C2H3N6O [*M*]$^{-}$: 127.0374; found: 127.0372; CH6N3 [*M*]$^{+}$: 60.0558; found: 60.0556.

Aminoguanidinium (2-methyltetrazol-5-yl)diazotate (8). Yield 132 mg (65%) of product **8**.
Colorless solid (**8**): DSC (10 °C·min^{-1}): 148 °C (m.p.); 158 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3388, 3322, 3172, 2954, 2840, 1687, 1671, 1493, 1338, 1263, 1021, 904, 766 cm^{-1}. ^{1}H NMR (500 MHz, [D6]DMSO): δ = 7.40 (s, 5H), 4.67 (s, 2H), 4.23 (s, 3H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 172.4, 159.2, 39.1 ppm. Elemental analysis: (C3H10N10O, 202.18) calc.: C 17.82, H 4.99, N 69.28; found: C 17.52, H 4.76, N 67.86. HRMS: calc. for C2H3N6O [*M*]$^{-}$: 127.0374; found: 127.0373; CH7N4 [*M*]$^{+}$: 75.0666; found: 75.0665.

Diaminoguanidinium (2-methyltetrazol-5-yl)diazotate (9). Yield 143 mg (66%) of product **9**.
White solid (**9**): DSC (10 °C·min^{-1}): 120 °C (m.p.); 151 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3343, 3298, 3171, 2980, 2815, 1692, 1665, 1491, 1390, 1329, 1260, 1166, 1032, 914, 668 cm^{-1}. ^{1}H NMR (500 MHz, [D6]DMSO): δ = 8.25 (s, 4H), 4.60 (s, 4H), 4.22 (s, 3H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 172.7, 160.0. 39.1 ppm. Elemental analysis: (C3H11N11O, 217.19) calc.: C 16.59, H 5.10, N 70.94; found: C 16.65, H 4.80, N 70.27.

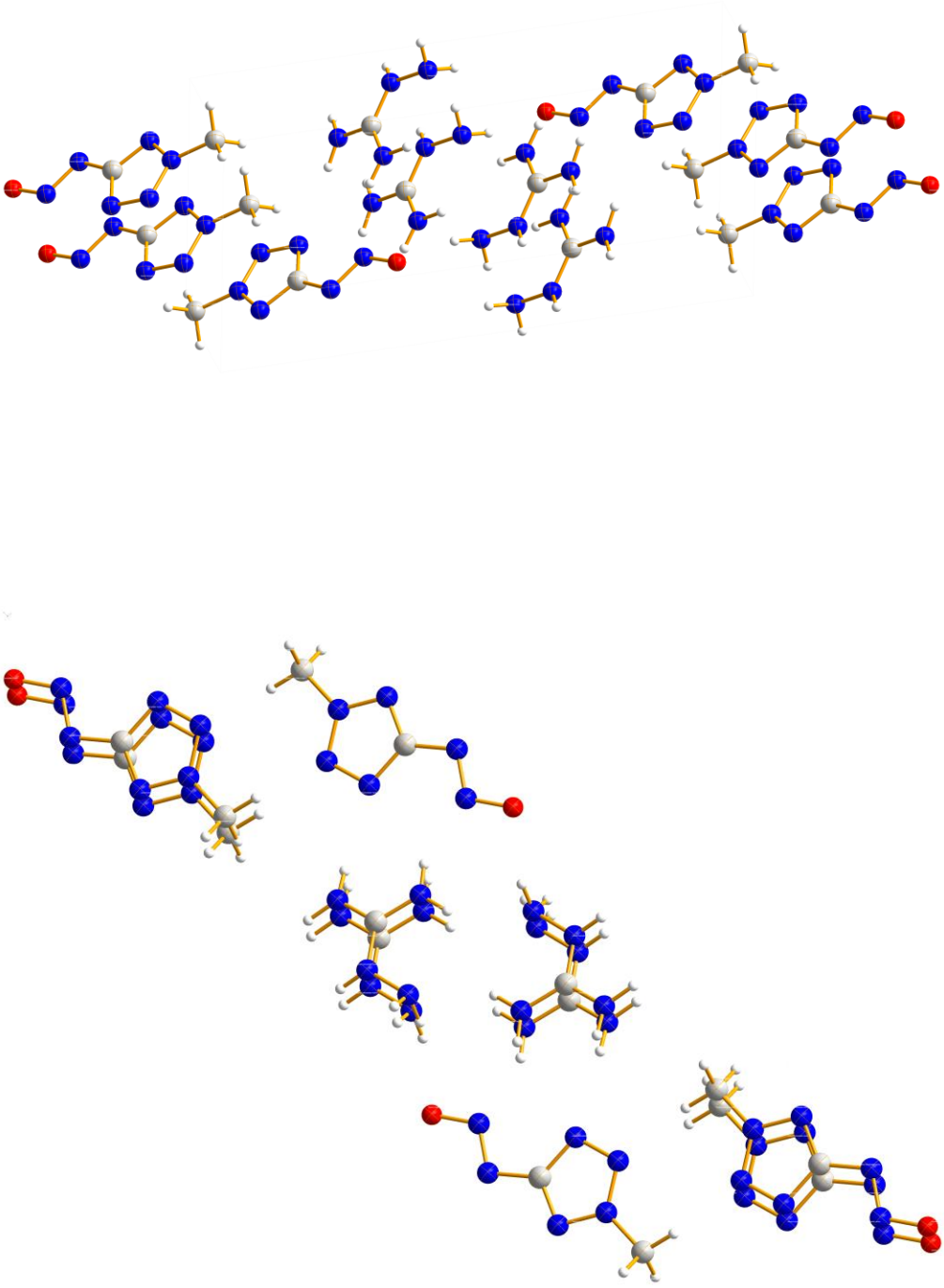
Triaminoguanidinium (2-methyltetrazol-5-yl)diazotate (10). Yield 207 mg (90%) of product **10**.
Colorless solid (**10**): DSC (10 °C·min^{-1}): 152 °C (m.p.); 156 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3320, 3213, 1685, 1481, 1335, 1291, 1256, 1128, 952, 609 cm^{-1}. ^{1}H NMR (500 MHz, [D6]DMSO): δ = 8.62 (s, 3H), 4.52 (s, 6H), 4.19 (s, 3H) ppm. ^{13}C NMR (100 MHz, [D6]DMSO): δ = 173.7, 159.0, 38.9 ppm. Elemental analysis: (C3H12N12O, 232.21) calc.: C 15.52, H 5.21, N 72.38; found: C 14.31, H 5.27, N 68.81. HRMS: calc. for C2H3N6O [*M*]$^{+}$: 127.0374; found: 127.0371; CH6N3 [*M*]$^{-}$: 105.0883; found: 105.0882.

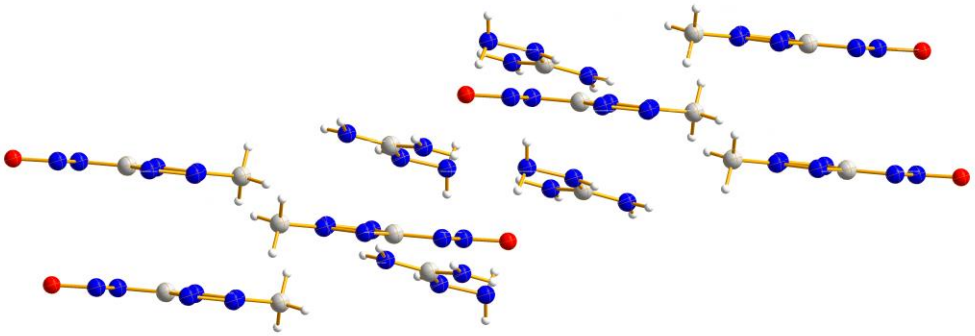
References

1 *CrystalClear: SM Expert 2.0 r2, An Integrated Program for the Collection and Processing of Area Detector Data*, Rigaku Corporation, England, 2009.

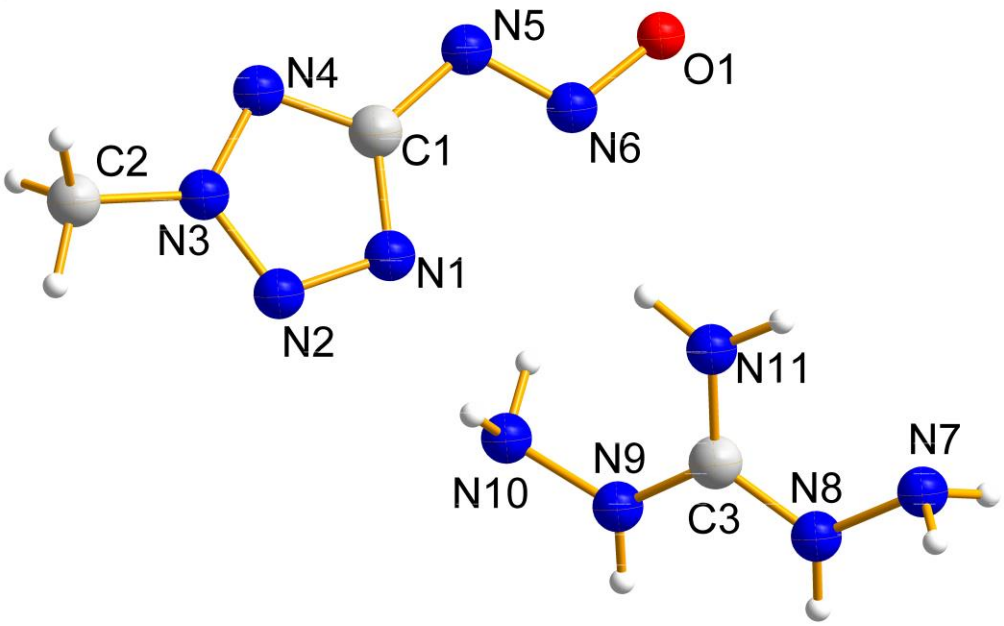
2 G. M. Sheldrick, *SHELXTL-97, Structure Determination Software Suite*, Bruker AXS, Madison, 2008.

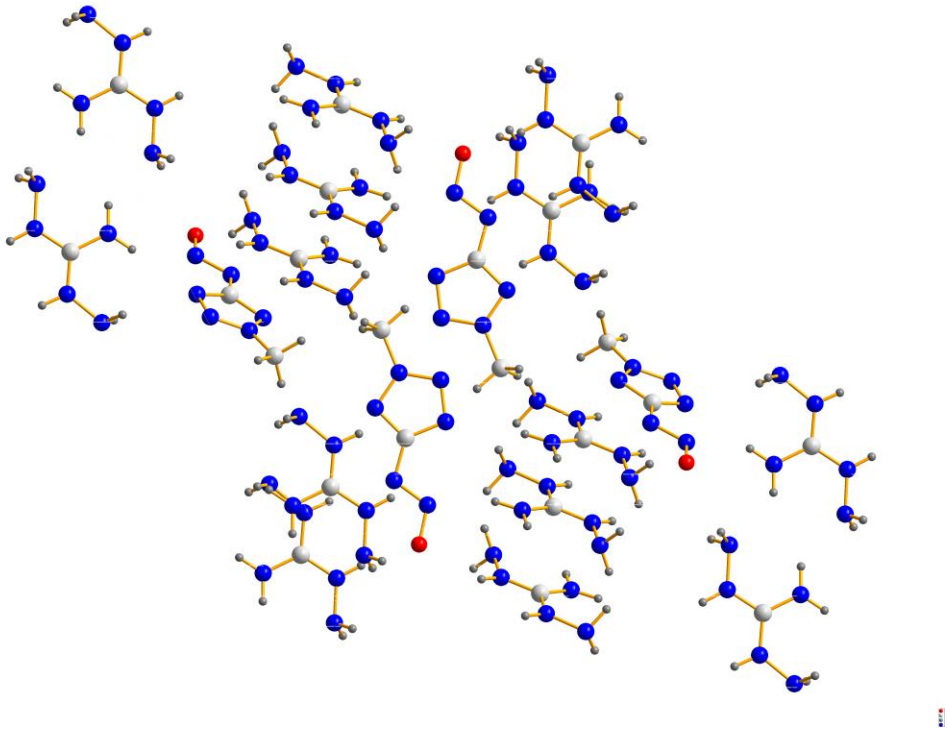
X-ray crystallography of 8

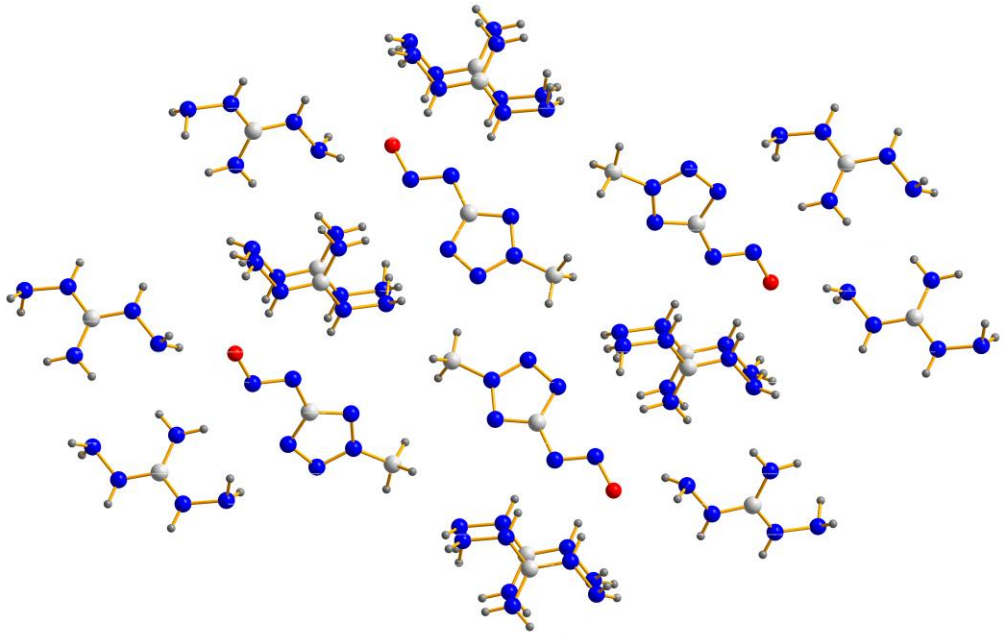


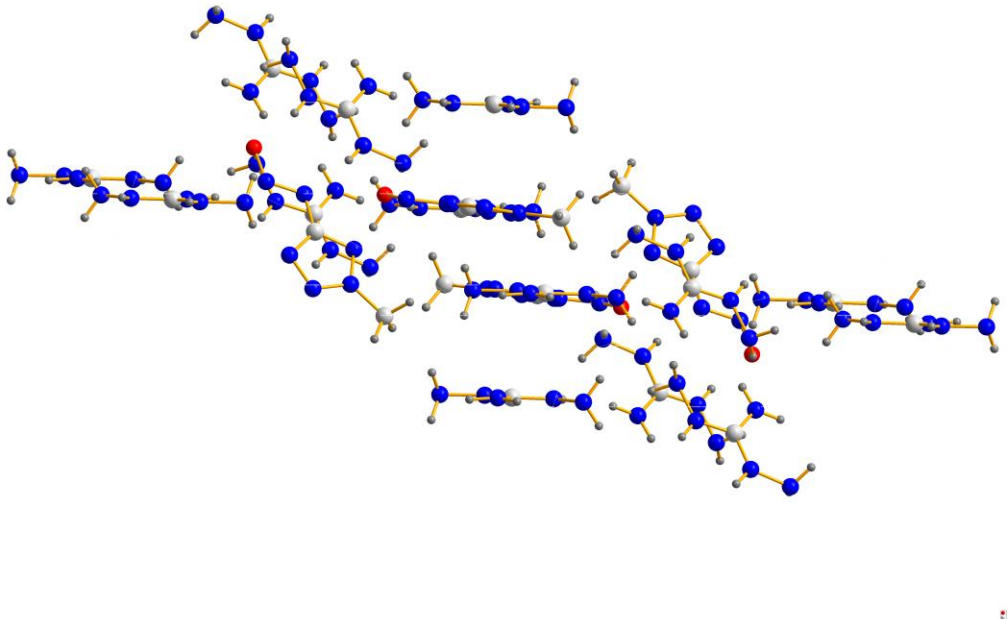


X-ray crystallography of 9

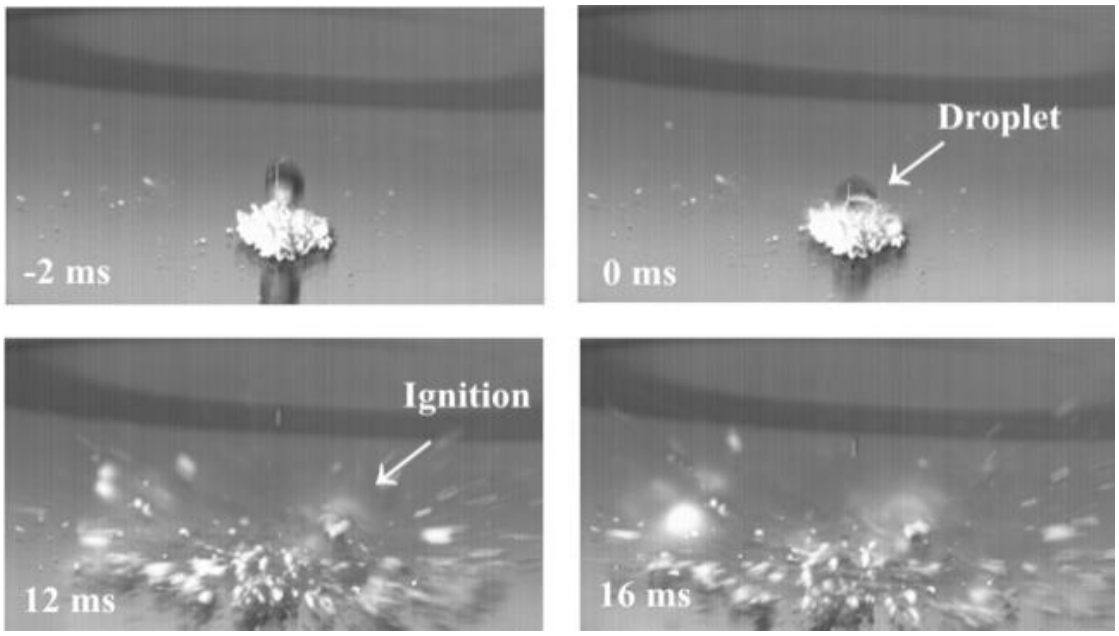








Droplet test of 5



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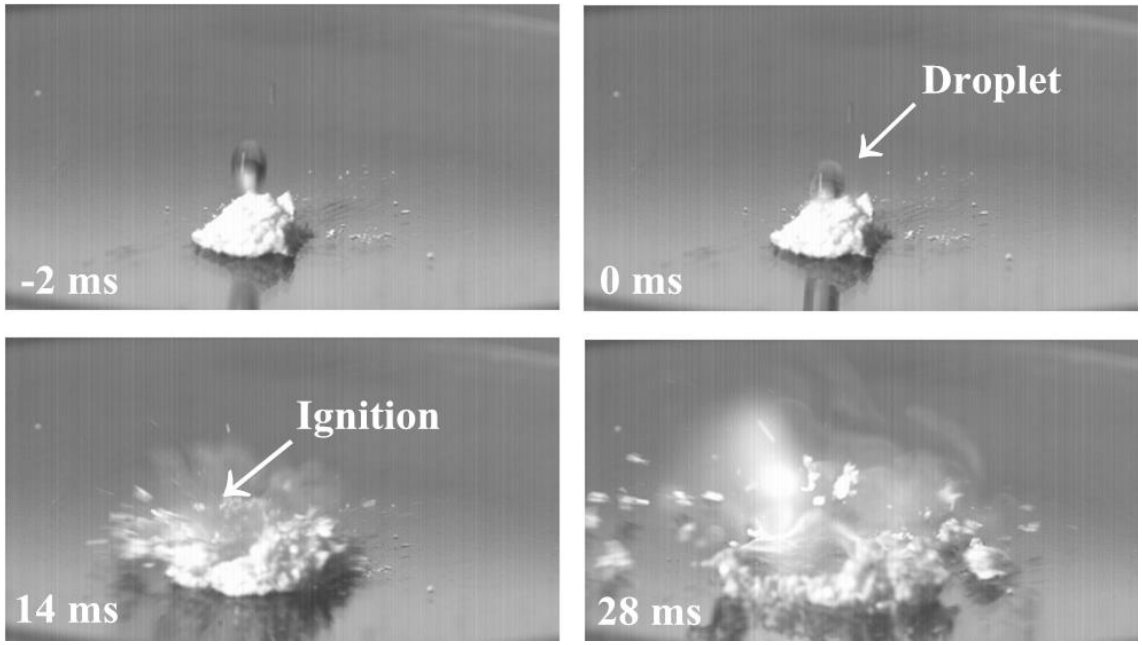

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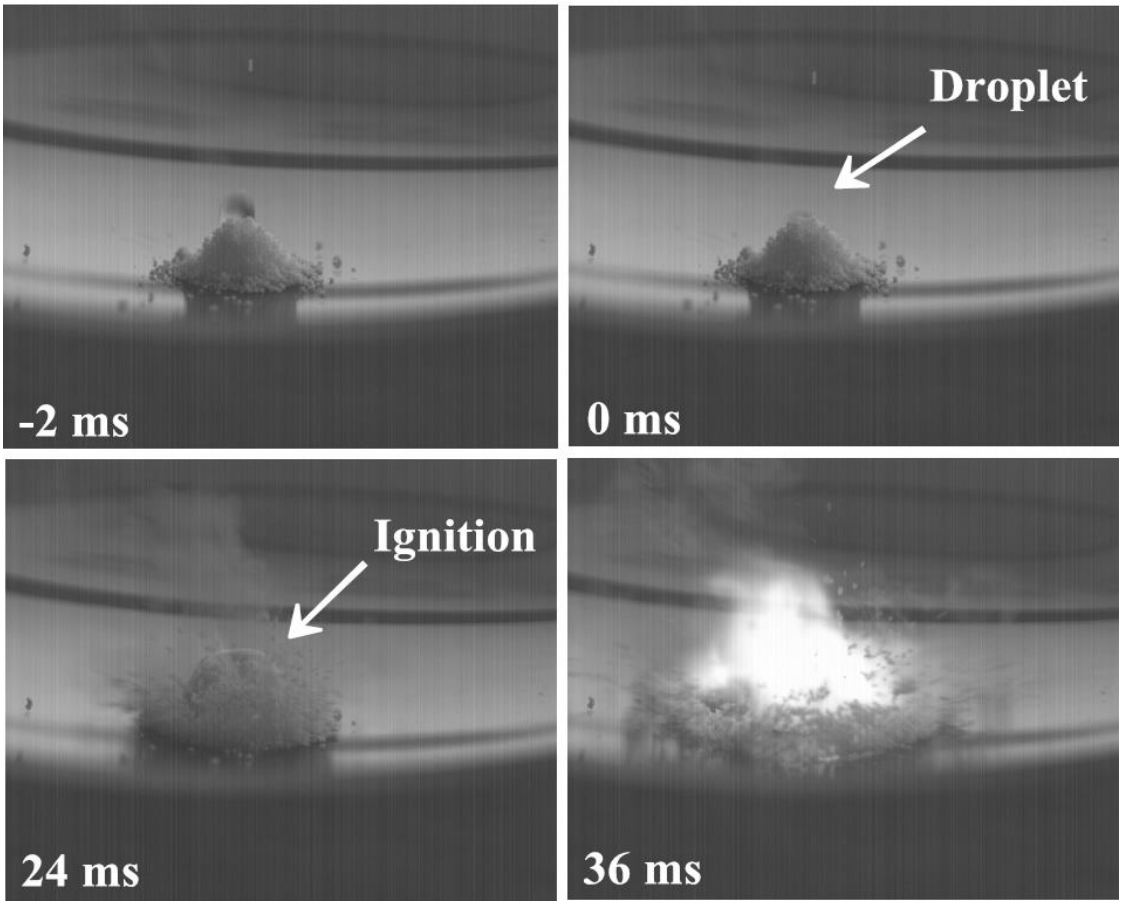

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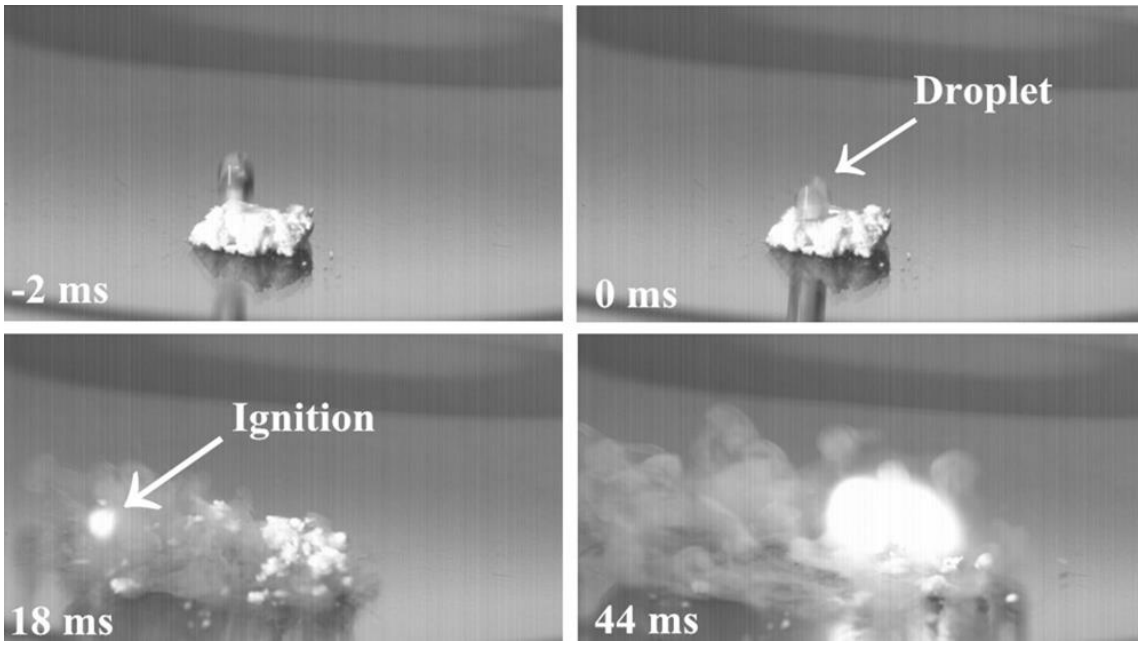
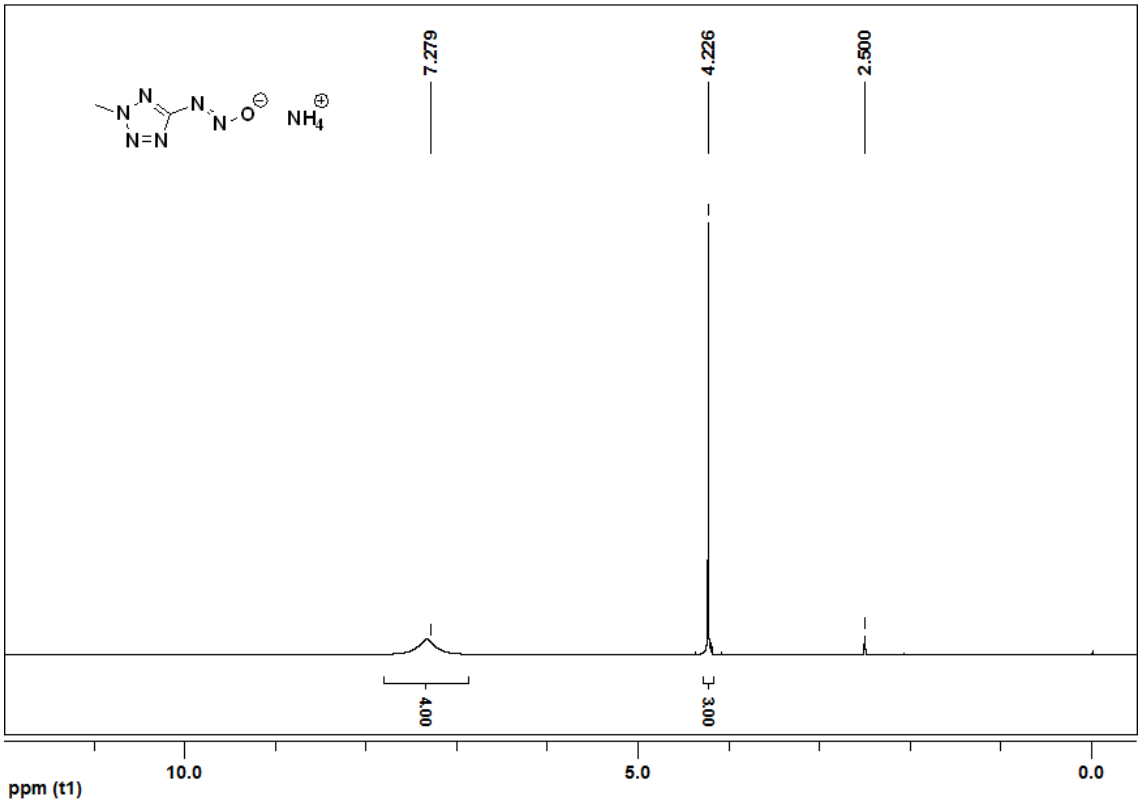
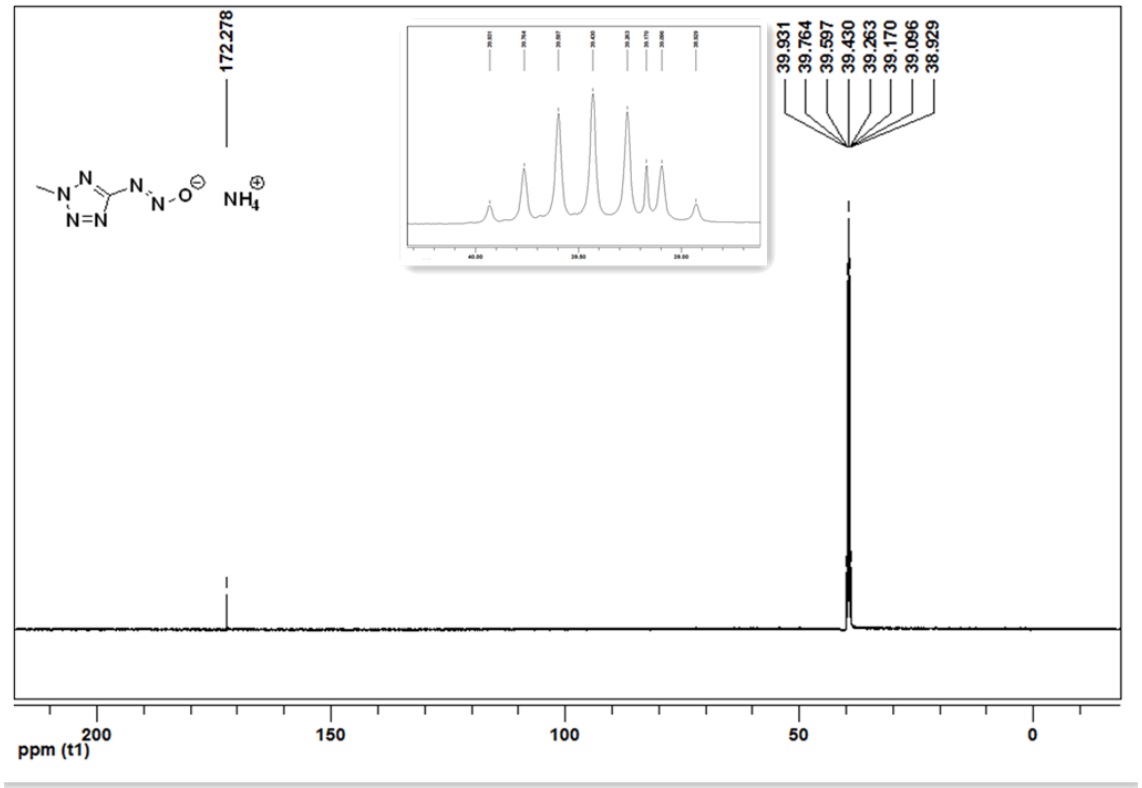


Spectral data of 5





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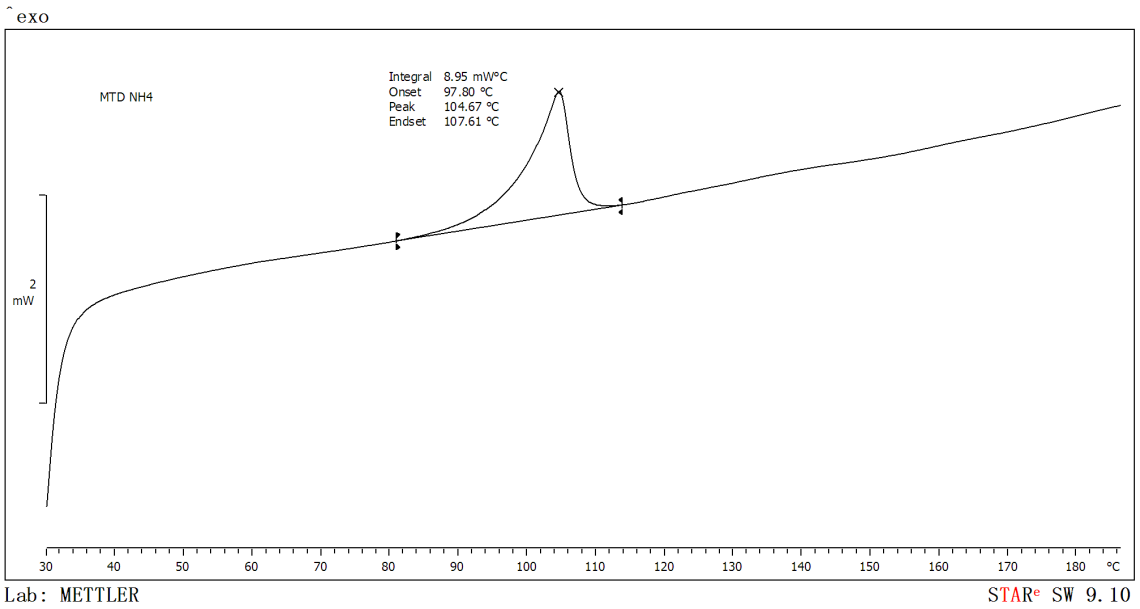

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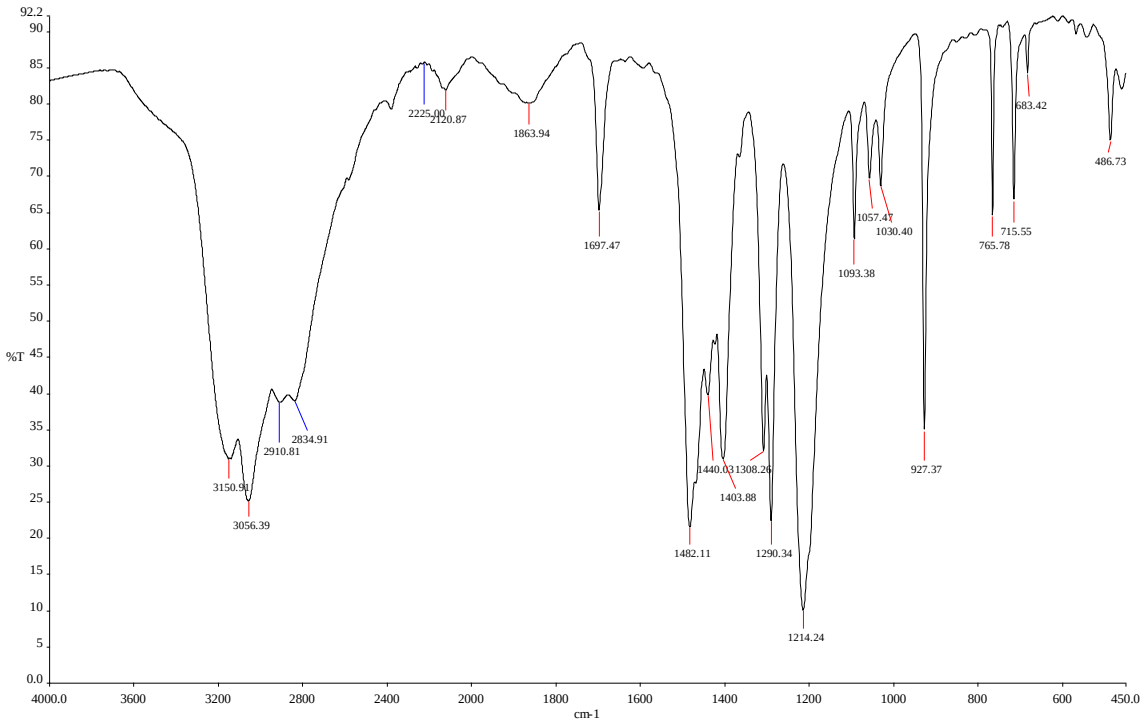

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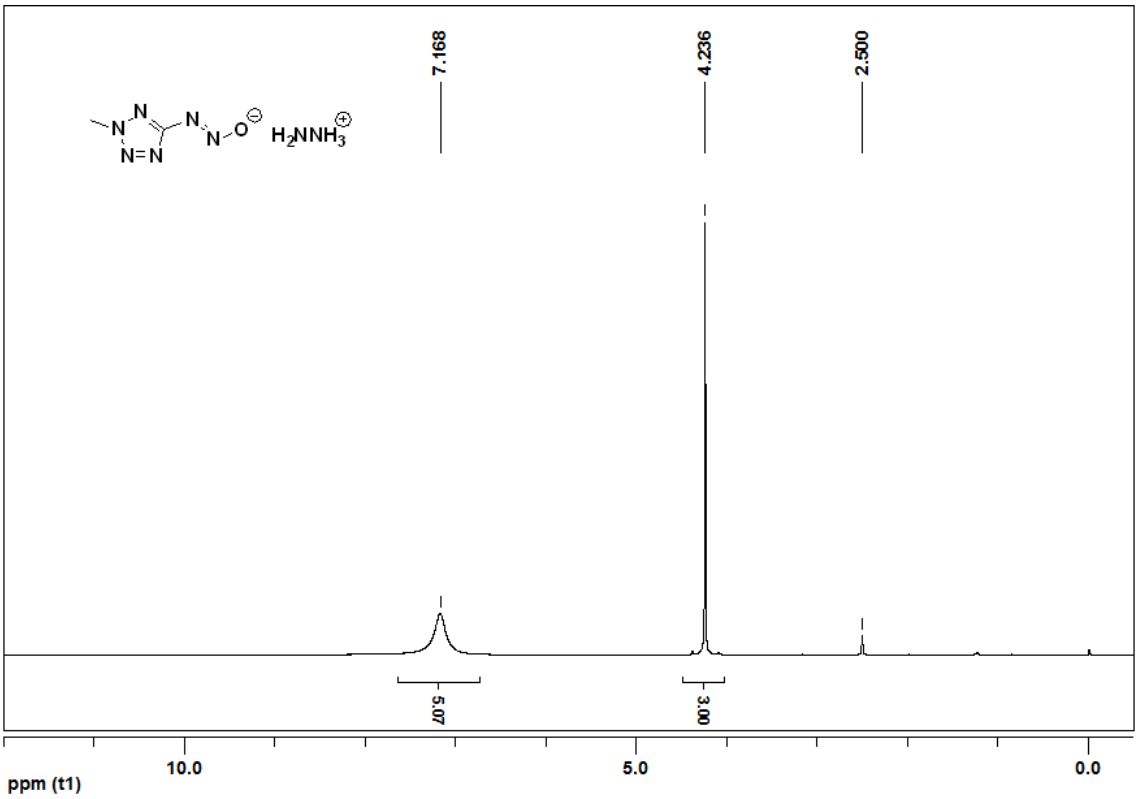

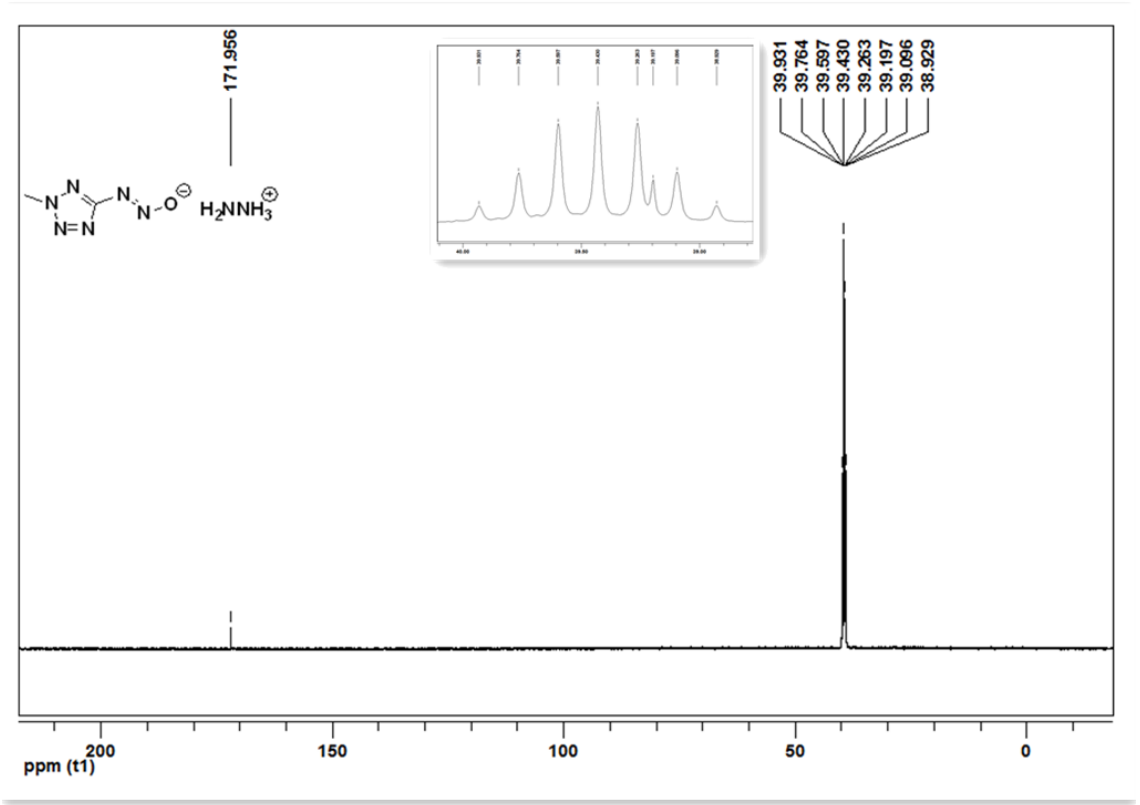

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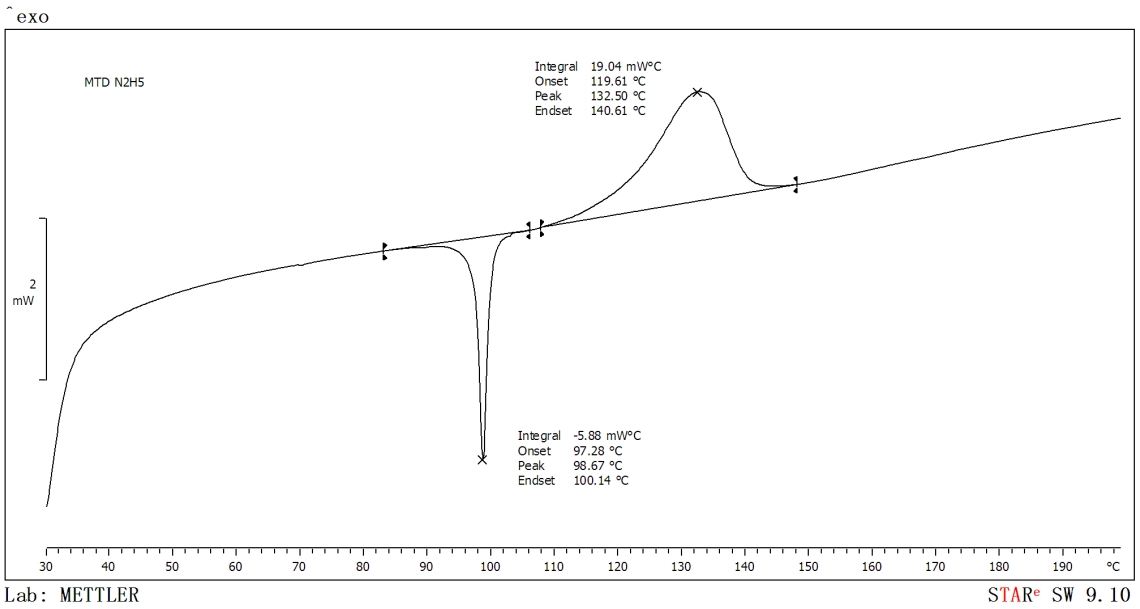

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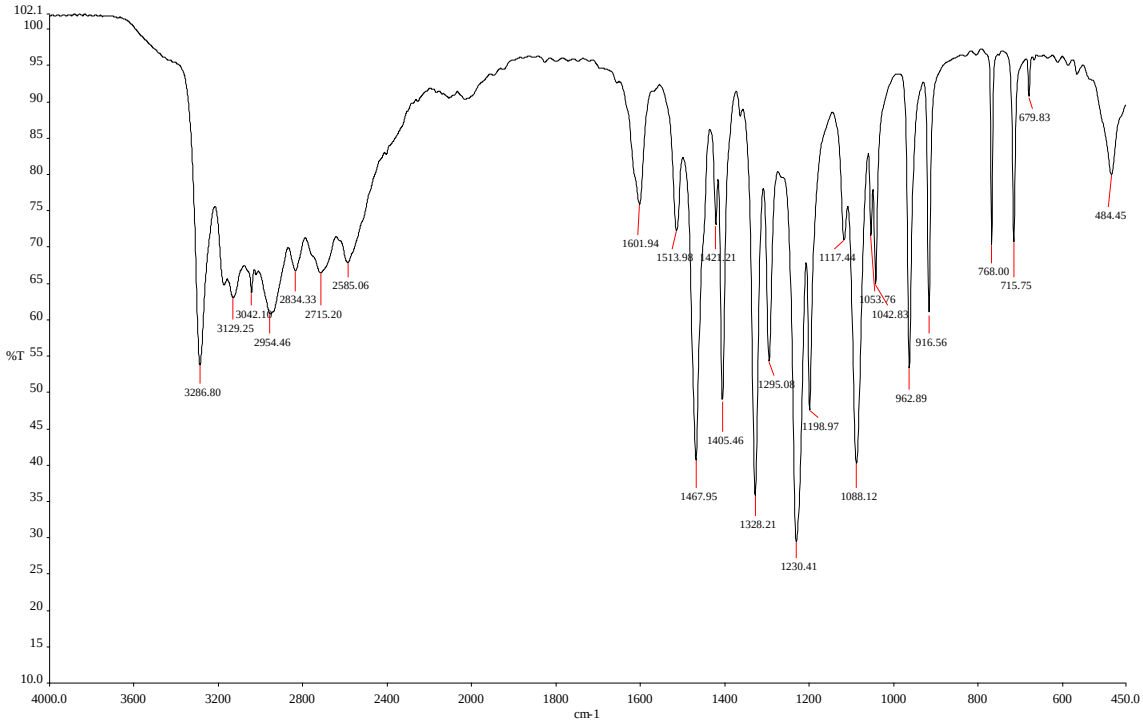

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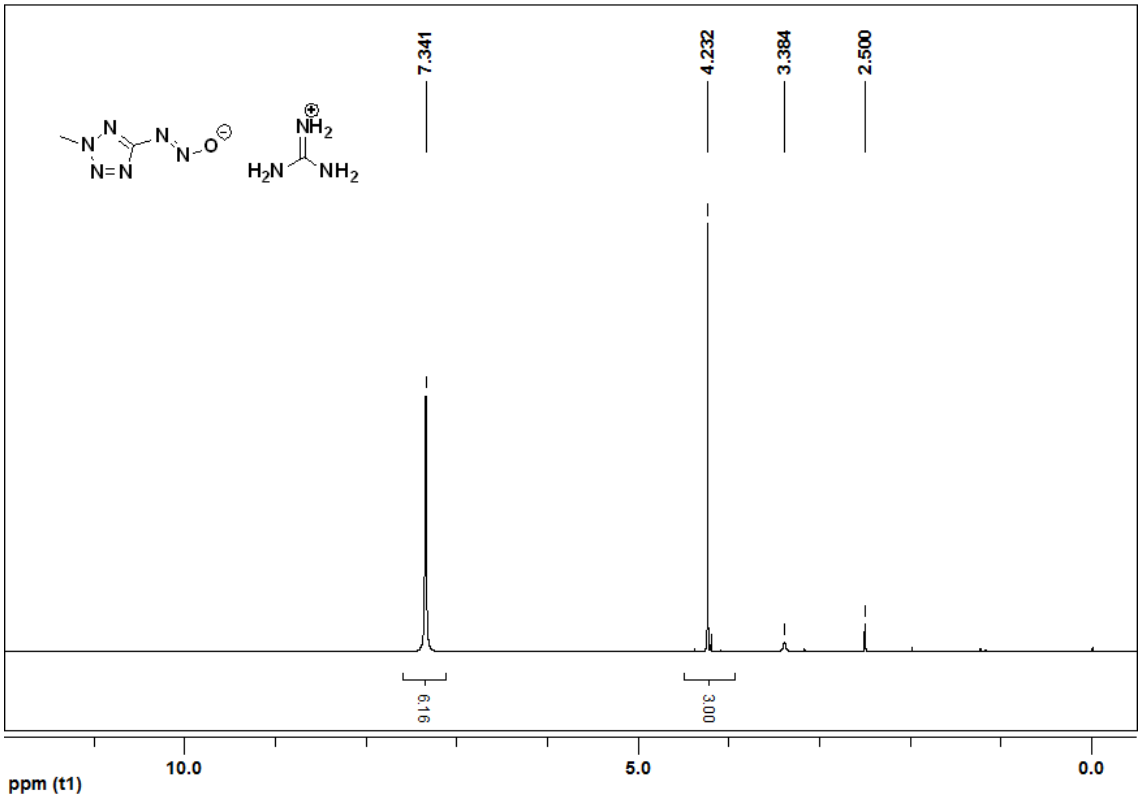

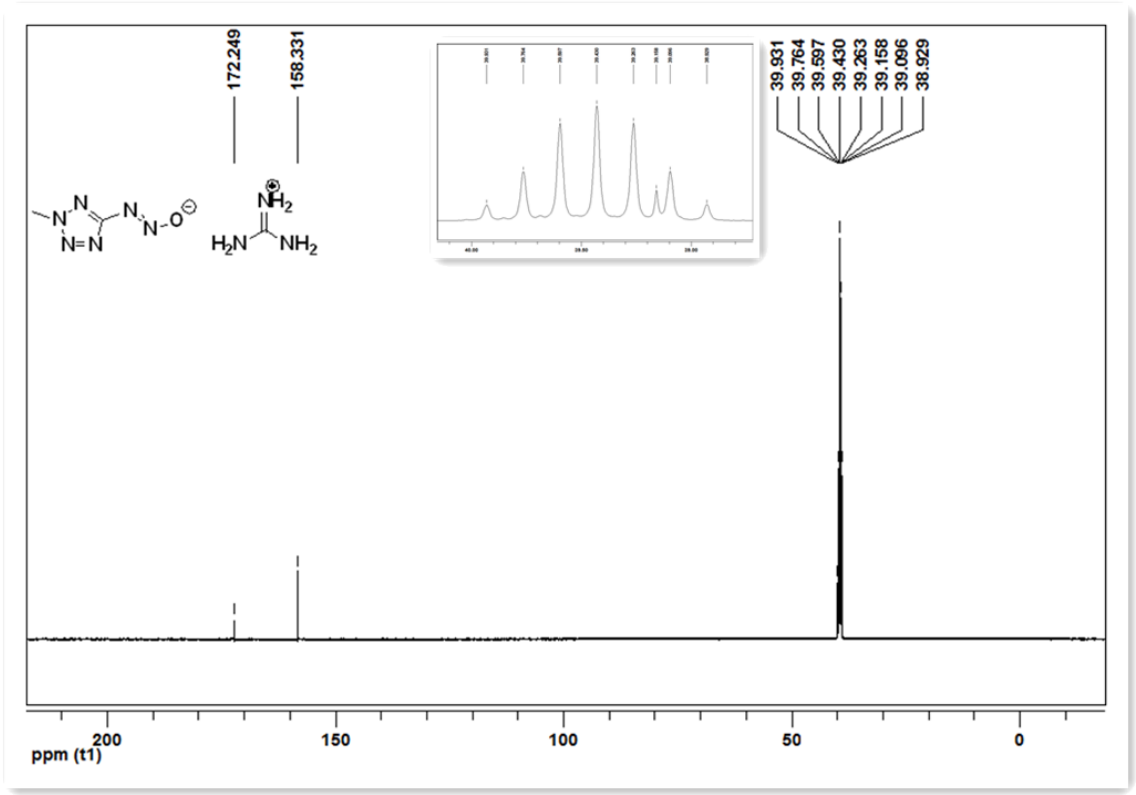

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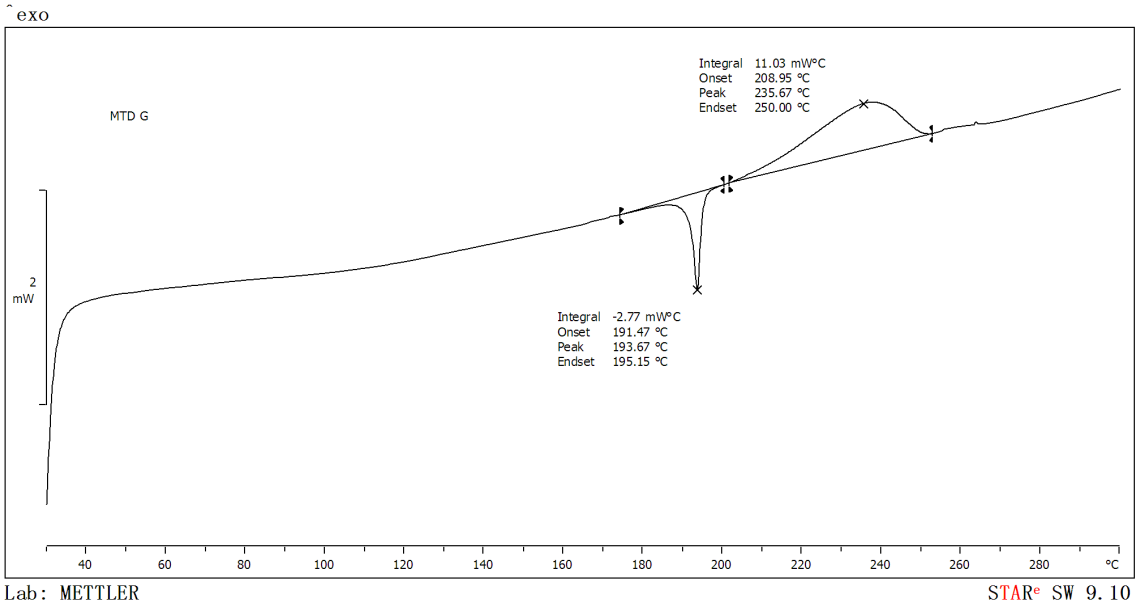

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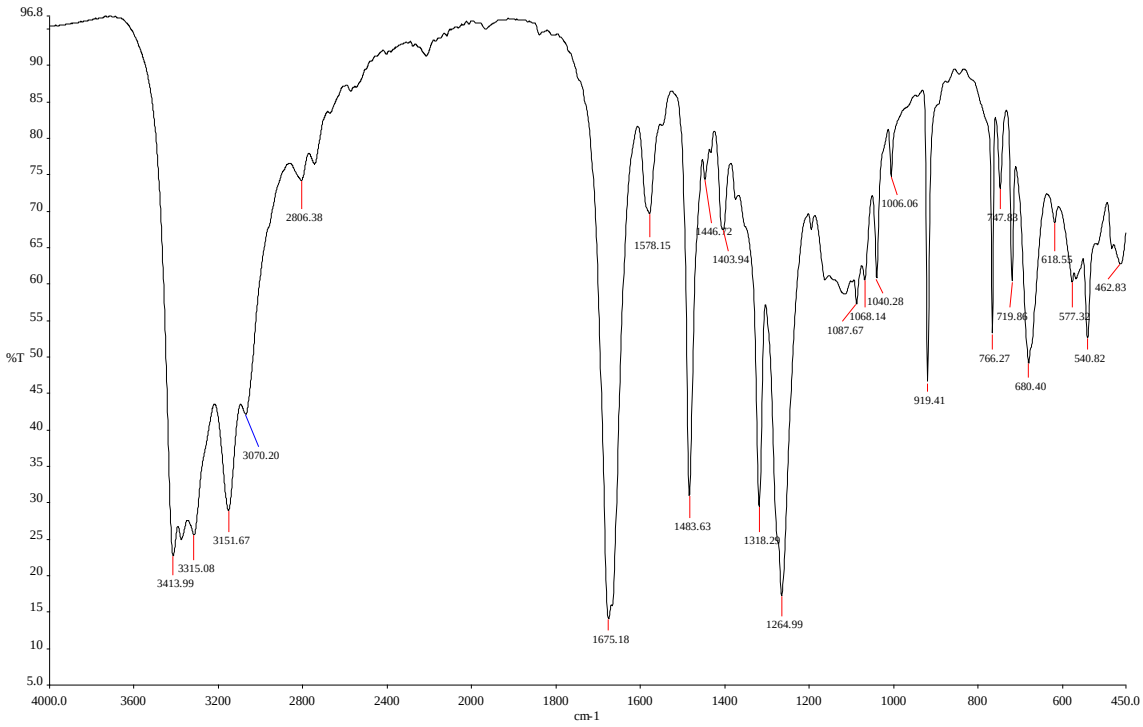
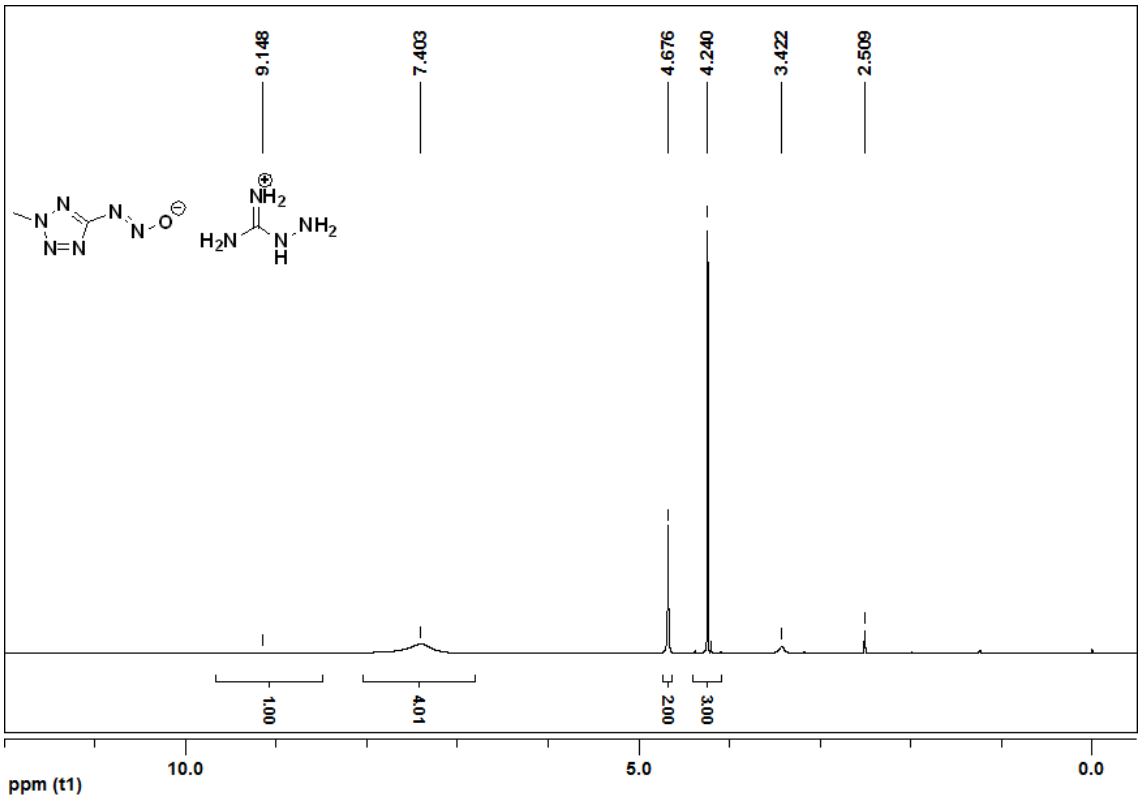
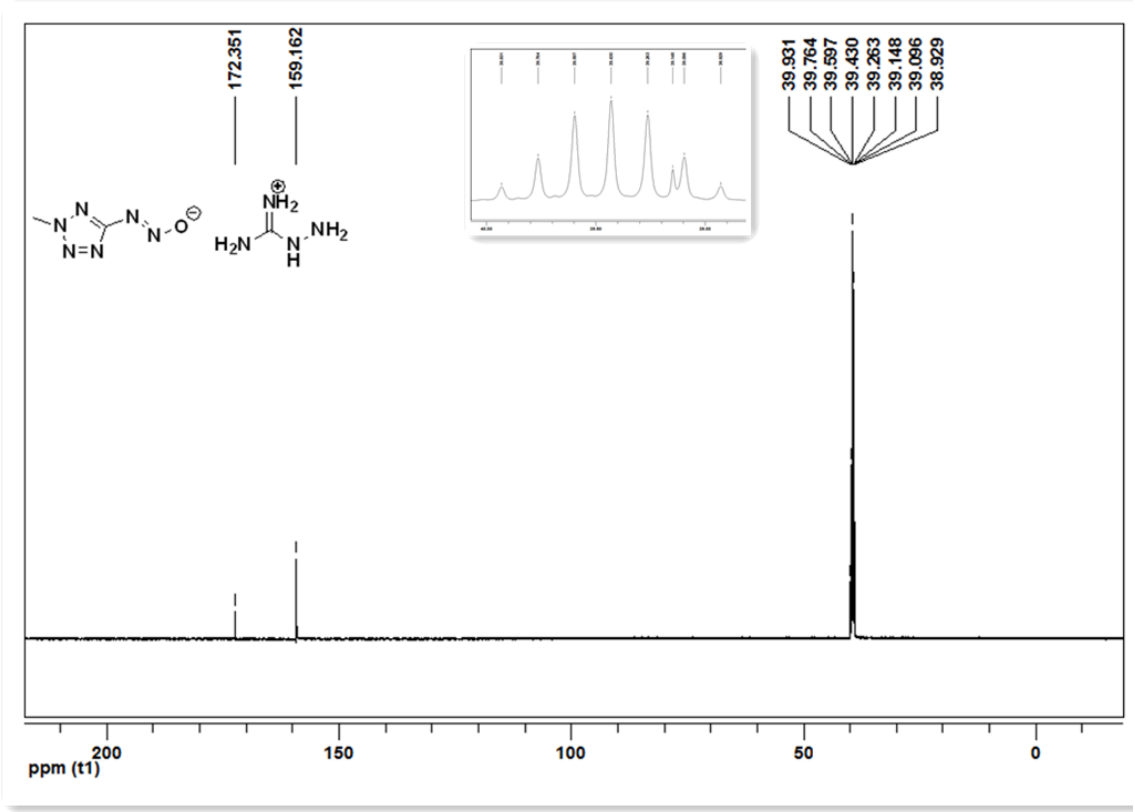


Spectral data of 8.





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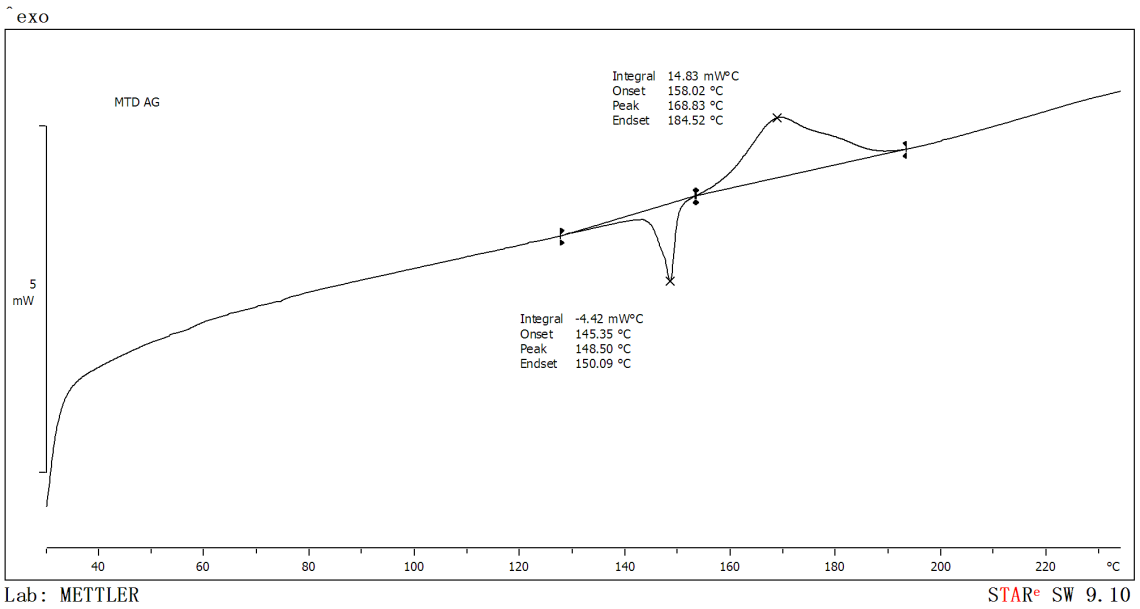

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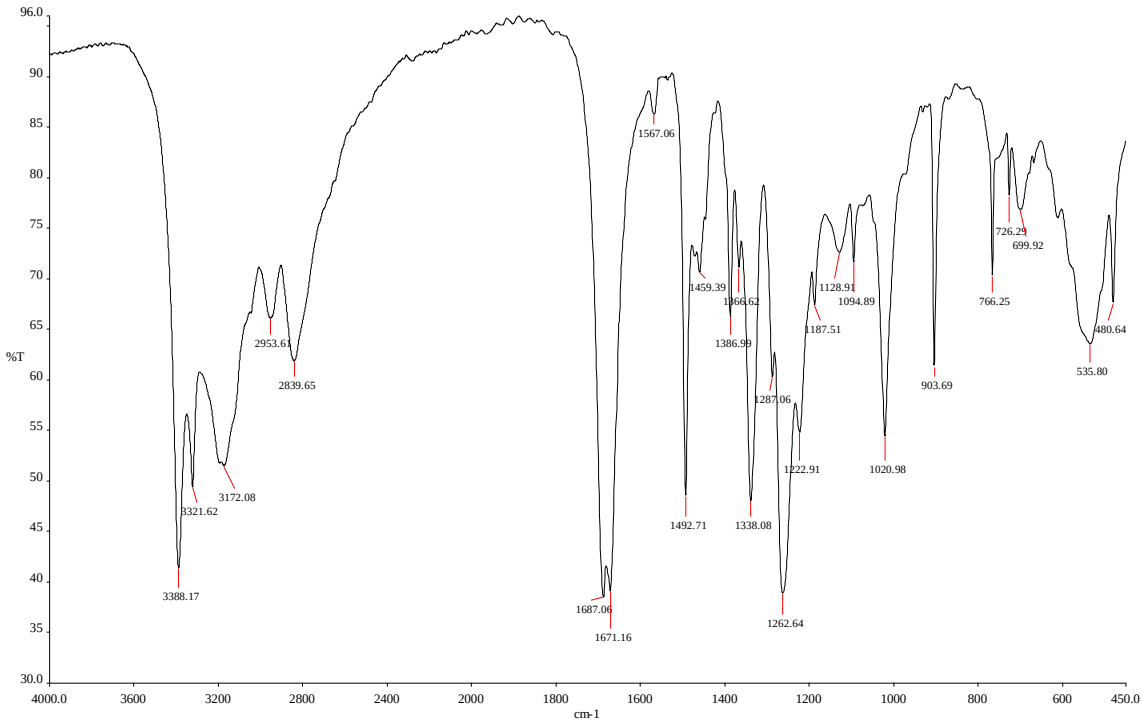
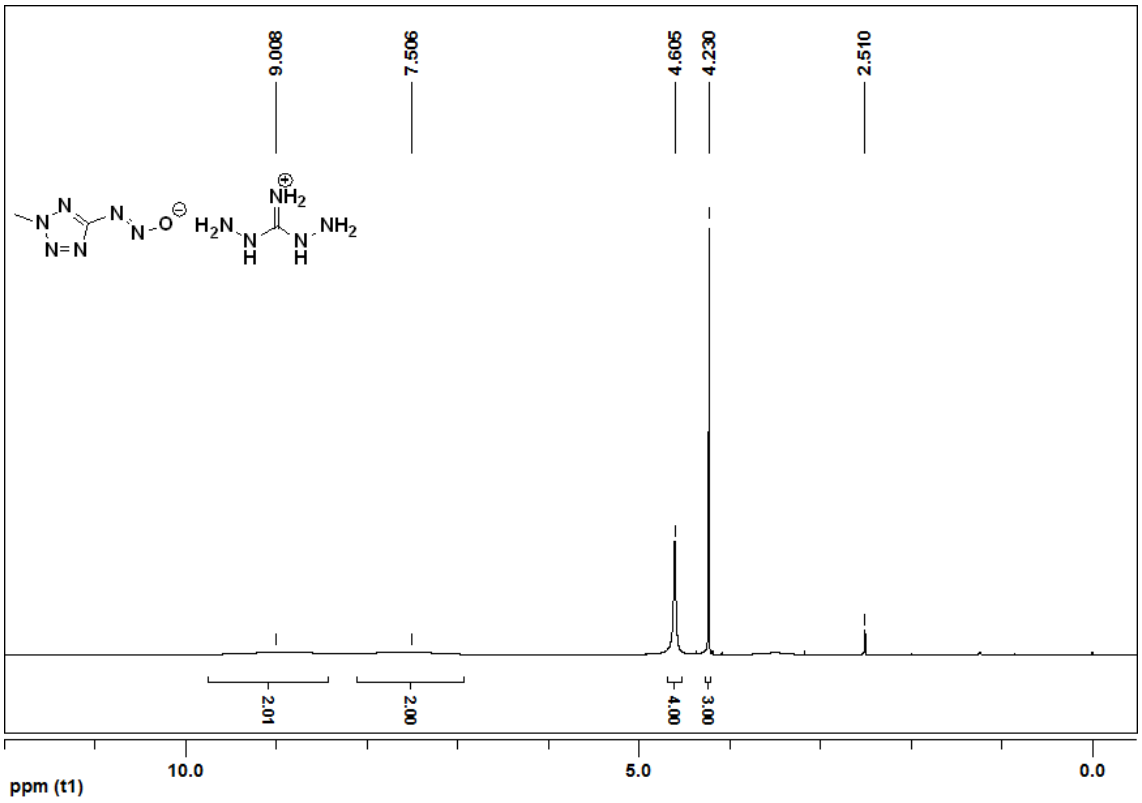
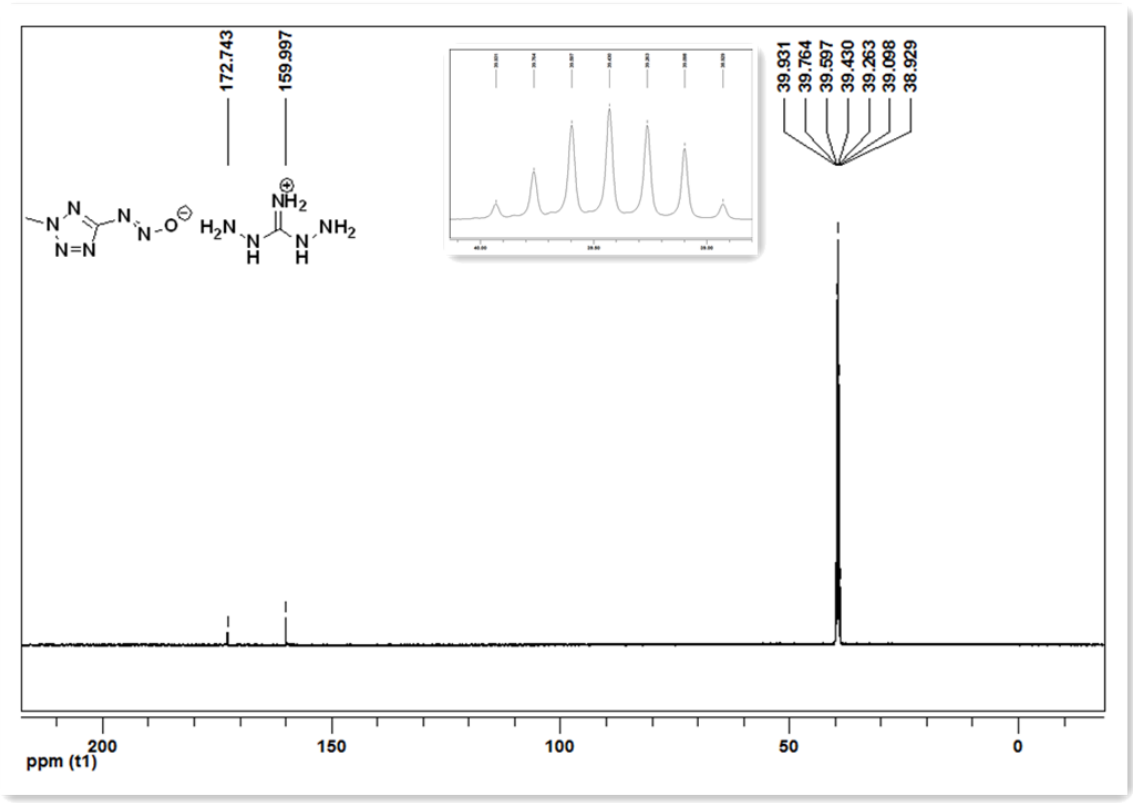


Spectral data of 9.





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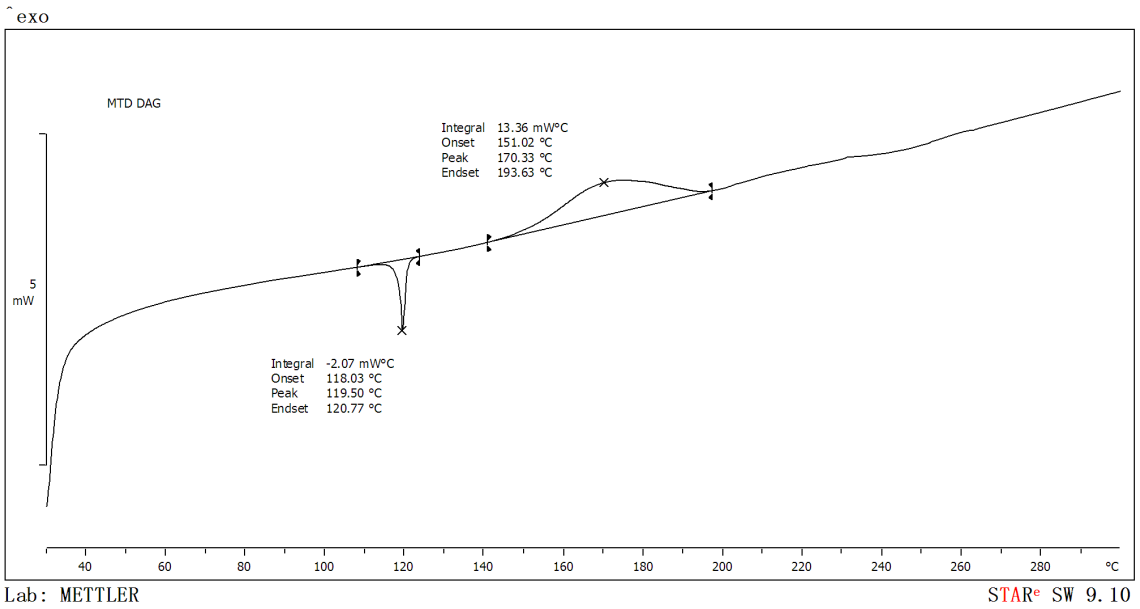

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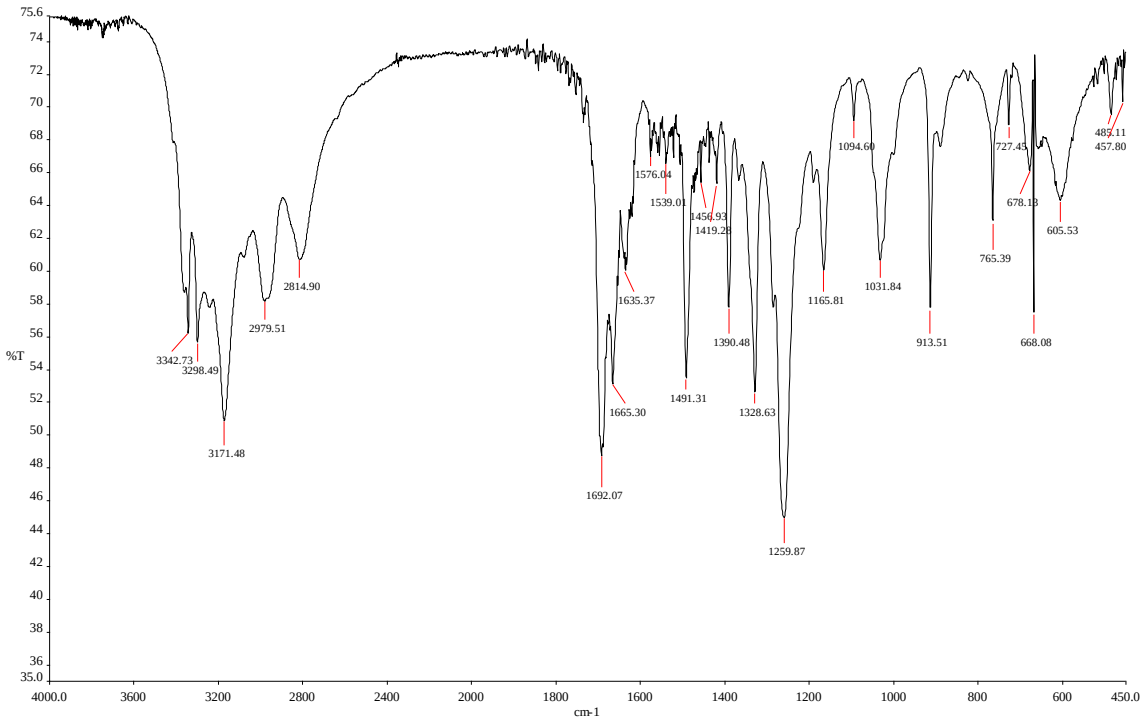
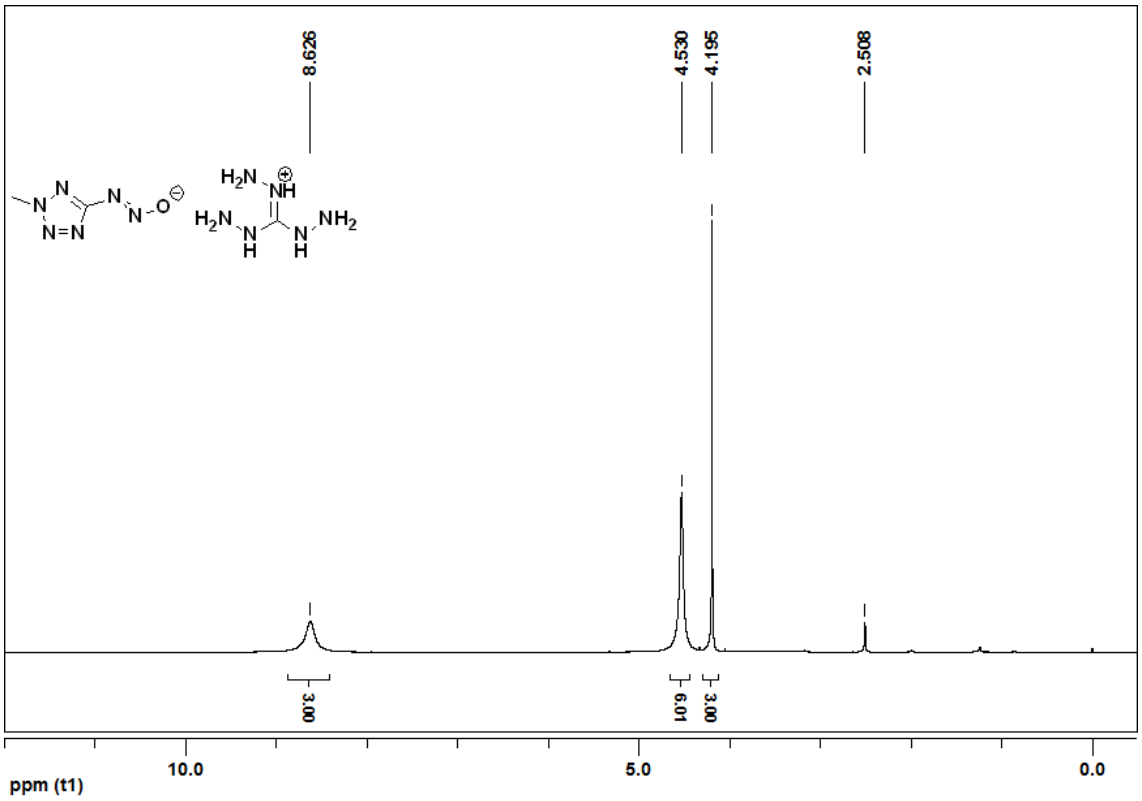
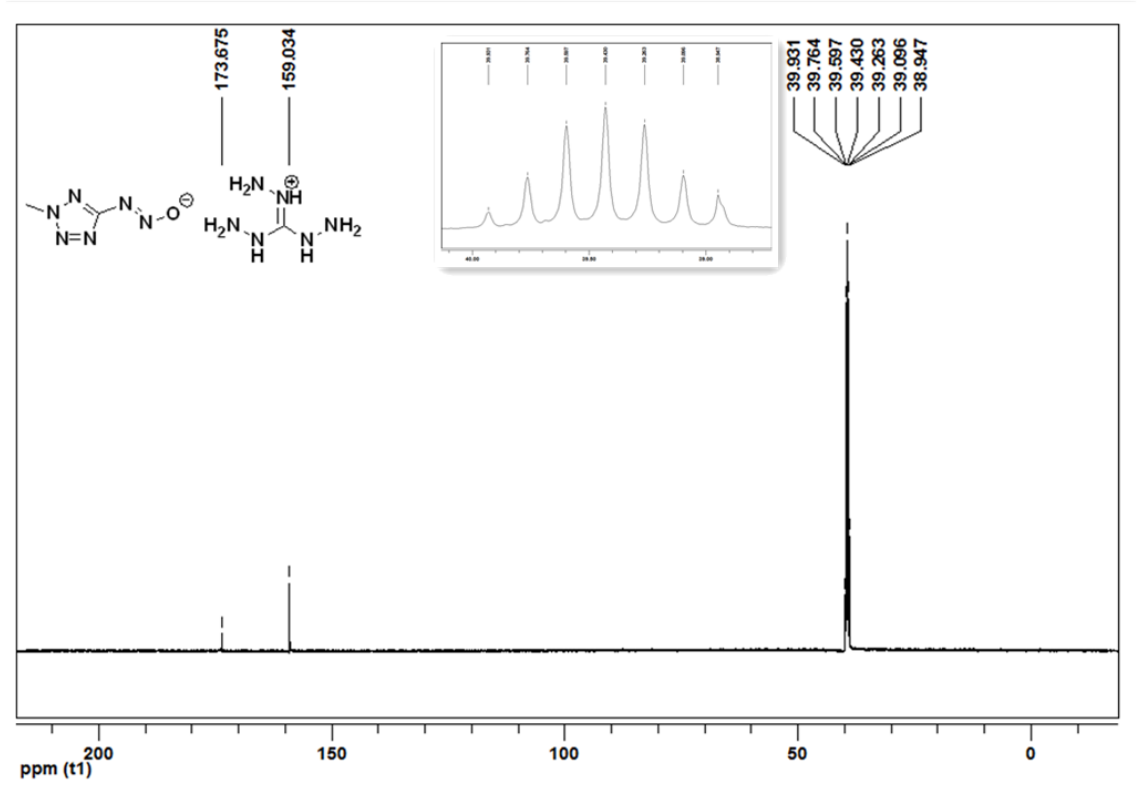


Spectral data of 10.





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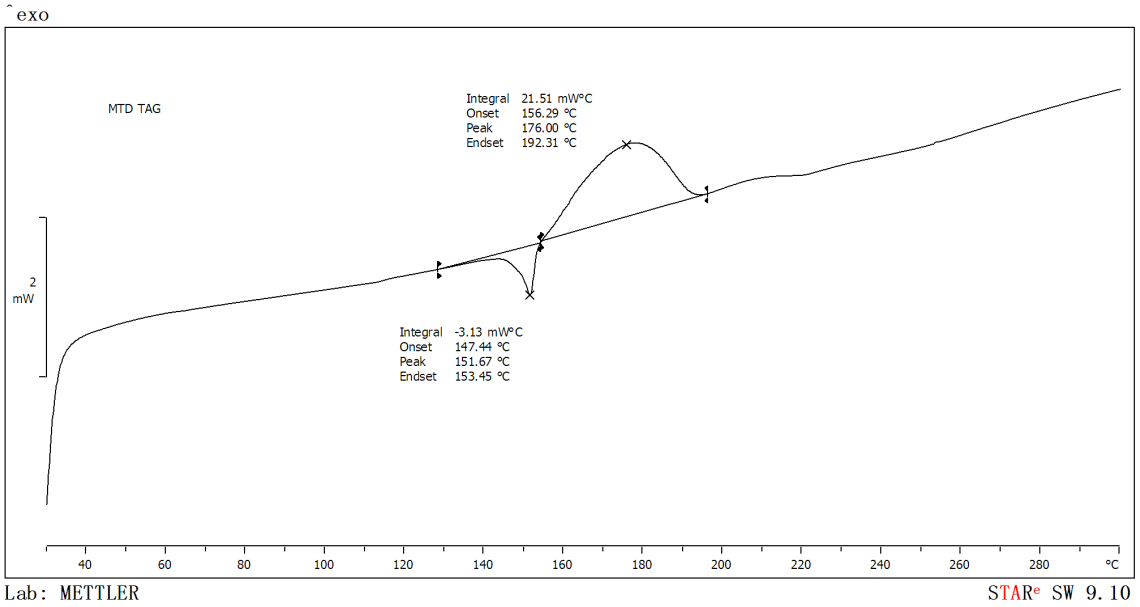

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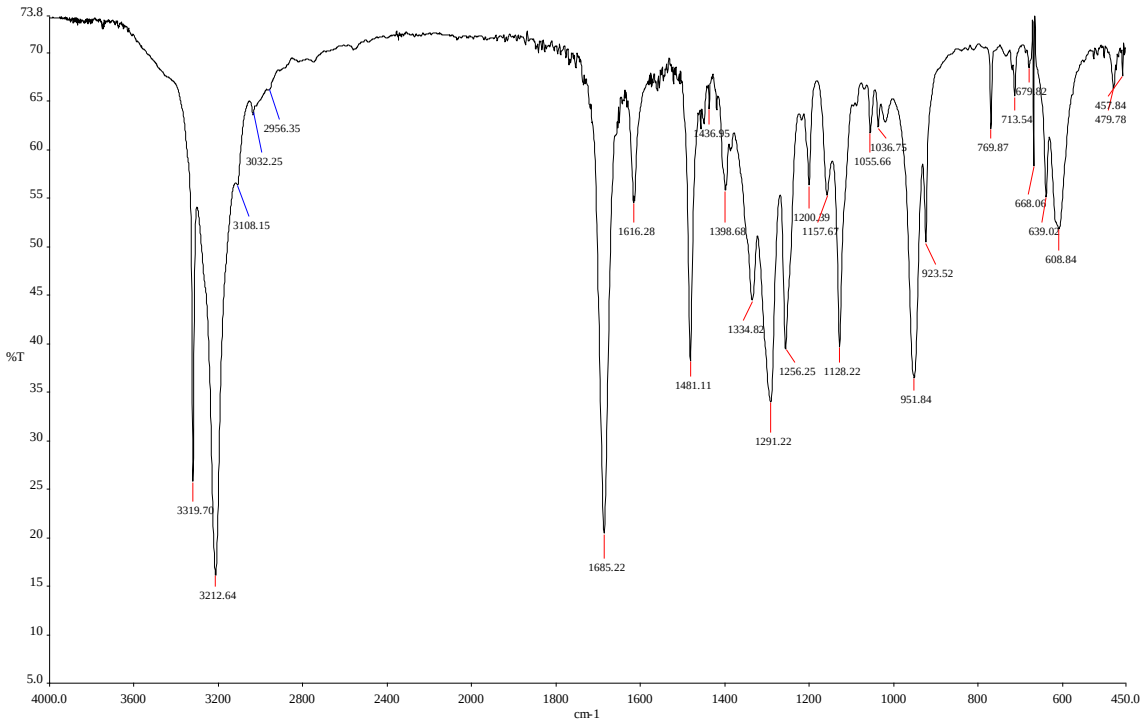


Table S1. Crystal data and structure refinement for **8**.

Identification code	**8**
Empirical formula	$C_3H_{10}N_{10}O$
Formula weight	202.21
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 3.805(3) Å α = 84.83(2) °.
	b = 7.898(6) Å β = 82.81(2) °.
	c = 15.015(11) Å γ = 83.49(2) °.
Volume	443.5(6) $Å^3$
Z	2
Calculated density	1.514 Mg/m^3
Absorption coefficient	0.121 mm^{-1}
F(000)	212
Crystal size	0.27 x 0.13 x 0.04 mm
Theta range for data collection	2.60 to 29.12 °
Limiting indices	-5<=h<=5, -10<=k<=10, -20<=l<=20
Reflections collected / unique	5864 / 2350 [R(int) = 0.0455]
Completeness to theta = 29.12 °	98.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2350 / 0 / 156
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R_1 = 0.0503, wR_2 = 0.0981
R indices (all data)	R_1 = 0.0863, wR_2 = 0.1078
Largest diff. peak and hole	0.310 and -0.289 $e.Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	561(4)	828(2)	3915(1)	36(1)
N(1)	4855(5)	3501(2)	1779(1)	35(1)
N(2)	6476(5)	3907(2)	954(1)	36(1)
N(3)	6865(5)	2497(2)	527(1)	31(1)
N(4)	5626(4)	1149(2)	1020(1)	31(1)
N(5)	2889(5)	772(2)	2526(1)	32(1)
N(6)	1894(5)	1672(2)	3201(1)	34(1)
N(7)	4536(6)	2526(2)	5225(1)	32(1)
N(8)	2420(5)	2191(2)	6055(1)	30(1)
N(9)	-1263(5)	3153(3)	7275(1)	37(1)
N(10)	1508(6)	5074(2)	6234(1)	36(1)
C(1)	4395(5)	1816(2)	1797(1)	29(1)
C(2)	8571(6)	2415(3)	-399(1)	37(1)
C(3)	855(6)	3487(3)	6512(1)	28(1)

Table S3. Bond lengths [Å] and angles [°] for **8**.

O(1)-N(6)	1.289(2)	N(1)-N(2)	1.341(2)
N(1)-C(1)	1.359(3)	N(2)-N(3)	1.320(2)
N(3)-N(4)	1.337(2)	N(3)-C(2)	1.463(3)
N(4)-C(1)	1.333(2)	N(5)-N(6)	1.285(2)
N(5)-C(1)	1.412(3)	N(7)-N(8)	1.417(3)
N(7)-H(7A)	0.85(2)	N(7)-H(7B)	0.89(2)
N(8)-C(3)	1.326(2)	N(8)-H(8)	0.89(2)
N(9)-C(3)	1.340(3)	N(9)-H(9A)	0.86(2)
N(9)-H(9B)	0.93(3)	N(10)-C(3)	1.325(3)
N(10)-H(10A)	0.94(2)	N(10)-H(10B)	0.86(3)
C(2)-H(2A)	0.9800	C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800		
N(2)-N(1)-C(1)	105.59(16)	N(3)-N(2)-N(1)	106.05(16)
N(2)-N(3)-N(4)	114.11(17)	N(2)-N(3)-C(2)	122.72(17)
N(4)-N(3)-C(2)	123.16(17)	C(1)-N(4)-N(3)	101.76(17)
N(6)-N(5)-C(1)	109.34(17)	N(5)-N(6)-O(1)	114.45(17)
N(8)-N(7)-H(7A)	108.4(15)	N(8)-N(7)-H(7B)	105.3(15)
H(7A)-N(7)-H(7B)	110(2)	C(3)-N(8)-N(7)	119.48(18)
C(3)-N(8)-H(8)	115.2(14)	N(7)-N(8)-H(8)	122.4(14)
C(3)-N(9)-H(9A)	119.1(15)	C(3)-N(9)-H(9B)	120.8(15)
H(9A)-N(9)-H(9B)	117(2)	C(3)-N(10)-H(10A)	120.5(15)
C(3)-N(10)-H(10B)	117.0(17)	H(10A)-N(10)-H(10B)	122(2)
N(4)-C(1)-N(1)	112.49(19)	N(4)-C(1)-N(5)	119.91(18)
N(1)-C(1)-N(5)	127.58(19)	N(3)-C(2)-H(2A)	109.5
N(3)-C(2)-H(2B)	109.5	H(2A)-C(2)-H(2B)	109.5
N(3)-C(2)-H(2C)	109.5	H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5	N(10)-C(3)-N(8)	120.2(2)
N(10)-C(3)-N(9)	121.0(2)	N(8)-C(3)-N(9)	118.8(2)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U11	U22	U33	U23	U13	U12
O(1)	28(1)	20(1)	19(1)	-1(1)	4(1)	-6(1)
N(2)	29(1)	24(1)	18(1)	-1(1)	4(1)	-4(1)
C(3)	18(1)	19(1)	18(1)	0(1)	3(1)	1(1)
N(4)	21(1)	18(1)	17(1)	0(1)	3(1)	-1(1)
C(5)	18(1)	17(1)	21(1)	1(1)	2(1)	0(1)
N(6)	20(1)	20(1)	19(1)	0(1)	3(1)	0(1)
N(7)	20(1)	20(1)	17(1)	0(1)	2(1)	0(1)
C(8)	18(1)	19(1)	18(1)	1(1)	3(1)	1(1)
N(9)	25(1)	23(1)	15(1)	0(1)	2(1)	-2(1)
O(10)	26(1)	20(1)	17(1)	0(1)	2(1)	-5(1)
C(11)	19(1)	17(1)	19(1)	2(1)	3(1)	0(1)
N(12)	22(1)	19(1)	16(1)	0(1)	3(1)	-2(1)
N(13)	31(1)	20(1)	18(1)	-2(1)	3(1)	-7(1)
N(14)	30(1)	22(1)	17(1)	-2(1)	4(1)	-8(1)
S(1S)	20(1)	18(1)	24(1)	-1(1)	2(1)	2(1)
O(2S)	23(1)	26(1)	27(1)	-1(1)	-2(1)	-4(1)
C(3S)	28(1)	41(1)	46(1)	12(1)	12(1)	-2(1)
C(4S)	31(1)	31(1)	31(1)	-10(1)	0(1)	-4(1)
O(5S)	24(1)	33(1)	22(1)	1(1)	2(1)	-3(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **8**.

	x	y	z	U(eq)
H(2A)	9548	3498	-604	44
H(2B)	6809	2212	-791	44
H(2C)	10499	1480	-424	44
H(7A)	6510(60)	1900(30)	5230(14)	46(8)
H(7B)	3320(60)	2230(30)	4808(16)	61(8)
H(8)	1510(60)	1200(30)	6202(14)	45(7)
H(9A)	-2530(60)	3990(30)	7533(15)	50(7)
H(9B)	-1960(60)	2060(40)	7431(16)	71(9)
H(10A)	3000(60)	5300(30)	5694(16)	65(8)
H(10B)	440(60)	5870(30)	6549(17)	63(8)

Table S6. Torsion angles [°] for **8**.

C(1)-N(1)-N(2)-N(3)	0.6(2)
N(1)-N(2)-N(3)-N(4)	-0.6(2)
N(1)-N(2)-N(3)-C(2)	-179.42(17)
N(2)-N(3)-N(4)-C(1)	0.3(2)
C(2)-N(3)-N(4)-C(1)	179.10(17)
C(1)-N(5)-N(6)-O(1)	-178.22(15)
N(3)-N(4)-C(1)-N(1)	0.1(2)
N(3)-N(4)-C(1)-N(5)	-178.68(17)
N(2)-N(1)-C(1)-N(4)	-0.5(2)
N(2)-N(1)-C(1)-N(5)	178.21(18)
N(6)-N(5)-C(1)-N(4)	179.87(17)
N(6)-N(5)-C(1)-N(1)	1.2(3)
N(7)-N(8)-C(3)-N(10)	-5.7(3)
N(7)-N(8)-C(3)-N(9)	177.10(19)

Table S7. Crystal data and structure refinement for **9**.

Identification code	**9**
Empirical formula	$C_3H_{11}N_{11}O$
Formula weight	217.23
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2/c
Unit cell dimensions	a = 15.703(5) Å α = 90 °.
	b = 3.7767(11) Å β = 100.331(5) °.
	c = 16.028(5) Å γ = 90 °.
Volume	935.1(5) $Å^3$
Z	4
Calculated density	1.543 Mg/m^3
Absorption coefficient	0.124 mm^{-1}
F(000)	456
Crystal size	0.68 x 0.08 x 0.05 mm
Theta range for data collection	2.68 to 29.11 °
Limiting indices	-20<=h<=21, -5<=k<=5, -19<=l<=21
Reflections collected / unique	7676 / 2503 [R(int) = 0.0283]
Completeness to theta = 29.11 °	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9938 and 0.9205
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2503 / 0 / 169
Goodness-of-fit on F^2	1.001
Final R indices [I>2sigma(I)]	R_1 = 0.0414, wR_2 = 0.1033
R indices (all data)	R_1 = 0.0597, wR_2 = 0.1157
Largest diff. peak and hole	0.254 and -0.209 $e.Å^{-3}$

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1097(1)	9535(3)	3108(1)	27(1)
C(1)	3120(1)	6087(4)	3501(1)	20(1)
C(2)	5201(1)	2570(4)	3699(1)	29(1)
C(3)	1477(1)	7971(4)	5971(1)	19(1)
N(1)	3230(1)	4813(3)	4307(1)	23(1)
N(2)	4016(1)	3390(3)	4462(1)	25(1)
N(3)	4344(1)	3866(3)	3768(1)	23(1)
N(4)	3815(1)	5530(3)	3144(1)	24(1)
N(5)	2389(1)	7735(3)	3045(1)	22(1)
N(6)	1799(1)	8117(3)	3503(1)	23(1)
N(7)	128(1)	5788(4)	6211(1)	23(1)
N(8)	932(1)	7431(4)	6507(1)	23(1)
N(9)	2223(1)	9584(4)	6270(1)	24(1)
N(10)	2849(1)	10378(4)	5773(1)	27(1)
N(11)	1287(1)	6869(4)	5172(1)	24(1)

Table S9. Bond lengths [Å] and angles [°] for **9**.

O(1)-N(6)	1.2849(16)	C(1)-N(4)	1.3362(18)
C(1)-N(1)	1.3604(18)	C(1)-N(5)	1.3929(18)
C(2)-N(3)	1.4552(19)	C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800	C(2)-H(2C)	0.9800
C(3)-N(11)	1.3289(18)	C(3)-N(9)	1.3305(18)
C(3)-N(8)	1.3317(17)	N(1)-N(2)	1.3283(18)
N(2)-N(3)	1.3188(17)	N(3)-N(4)	1.3369(17)
N(5)-N(6)	1.2893(16)	N(7)-N(8)	1.4112(18)
N(7)-H(7A)	0.87(2)	N(7)-H(7B)	0.90(2)
N(8)-H(8)	0.87(2)	N(9)-N(10)	1.4048(16)
N(9)-H(9)	0.87(2)	N(10)-H(10A)	0.89(2)
N(10)-H(10B)	0.95(2)	N(11)-H(11A)	0.90(2)
N(11)-H(11B)	0.89(2)		
N(4)-C(1)-N(1)	112.16(12)	N(4)-C(1)-N(5)	120.38(12)
N(1)-C(1)-N(5)	127.45(12)	N(3)-C(2)-H(2A)	109.5
N(3)-C(2)-H(2B)	109.5	H(2A)-C(2)-H(2B)	109.5
N(3)-C(2)-H(2C)	109.5	H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5	N(11)-C(3)-N(9)	121.34(12)
N(11)-C(3)-N(8)	121.00(13)	N(9)-C(3)-N(8)	117.64(12)
N(2)-N(1)-C(1)	105.98(11)	N(3)-N(2)-N(1)	106.13(11)
N(2)-N(3)-N(4)	114.24(12)	N(2)-N(3)-C(2)	121.66(12)
N(4)-N(3)-C(2)	124.08(12)	C(1)-N(4)-N(3)	101.48(11)
N(6)-N(5)-C(1)	111.11(11)	O(1)-N(6)-N(5)	113.95(11)
N(8)-N(7)-H(7A)	108.0(12)	N(8)-N(7)-H(7B)	106.7(12)
H(7A)-N(7)-H(7B)	110.8(17)	C(3)-N(8)-N(7)	119.35(12)
C(3)-N(8)-H(8)	119.7(14)	N(7)-N(8)-H(8)	120.8(14)
C(3)-N(9)-N(10)	123.75(12)	C(3)-N(9)-H(9)	119.7(13)
N(10)-N(9)-H(9)	116.6(13)	N(9)-N(10)-H(10A)	109.9(14)
N(9)-N(10)-H(10B)	108.2(13)	H(10A)-N(10)-H(10B)	106.1(19)
C(3)-N(11)-H(11A)	121.4(13)	C(3)-N(11)-H(11B)	118.0(13)
H(11A)-N(11)-H(11B)	119.6(18)		

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U11	U22	U33	U23	U13	U12
O(1)	22(1)	36(1)	24(1)	8(1)	8(1)	8(1)
C(1)	20(1)	22(1)	17(1)	0(1)	4(1)	-3(1)
C(2)	24(1)	37(1)	28(1)	3(1)	6(1)	7(1)
C(3)	19(1)	21(1)	16(1)	2(1)	5(1)	3(1)
N(1)	24(1)	29(1)	18(1)	3(1)	5(1)	1(1)
N(2)	25(1)	31(1)	20(1)	3(1)	5(1)	1(1)
N(3)	22(1)	29(1)	19(1)	1(1)	4(1)	2(1)
N(4)	22(1)	33(1)	19(1)	4(1)	5(1)	3(1)
N(5)	21(1)	28(1)	18(1)	3(1)	7(1)	3(1)
N(6)	22(1)	28(1)	21(1)	3(1)	7(1)	2(1)
N(7)	21(1)	26(1)	24(1)	-3(1)	9(1)	-3(1)
N(8)	19(1)	36(1)	16(1)	-4(1)	6(1)	-5(1)
N(9)	21(1)	37(1)	15(1)	-3(1)	6(1)	-6(1)
N(10)	24(1)	36(1)	23(1)	-3(1)	11(1)	-6(1)
N(11)	22(1)	35(1)	16(1)	-4(1)	7(1)	-5(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **9**.

	x	y	z	U(eq)
H(2A)	5459	1375	4227	35
H(2B)	5568	4566	3598	35
H(2C)	5154	895	3226	35
H(7A)	109(11)	3830(50)	6497(12)	32(5)
H(8)	1059(13)	8230(60)	7022(14)	45(6)
H(9)	2335(13)	10260(50)	6797(13)	38(5)
H(10A)	3009(13)	8400(60)	5536(14)	47(6)
H(10B)	2590(13)	11850(60)	5319(14)	47(6)
H(11A)	1629(13)	7400(50)	4794(12)	42(6)
H(11B)	761(14)	5950(50)	4990(13)	38(5)
H(7B)	-282(12)	7300(50)	6311(12)	34(5)

Table S12. Torsion angles [°] for **9**.

N(4)-C(1)-N(1)-N(2)	-0.38(16)
N(5)-C(1)-N(1)-N(2)	178.22(13)
C(1)-N(1)-N(2)-N(3)	0.47(15)
N(1)-N(2)-N(3)-N(4)	-0.42(17)
N(1)-N(2)-N(3)-C(2)	-178.77(12)
N(1)-C(1)-N(4)-N(3)	0.13(15)
N(5)-C(1)-N(4)-N(3)	-178.58(12)
N(2)-N(3)-N(4)-C(1)	0.18(16)
C(2)-N(3)-N(4)-C(1)	178.48(13)
N(4)-C(1)-N(5)-N(6)	-178.24(12)
N(1)-C(1)-N(5)-N(6)	3.3(2)
C(1)-N(5)-N(6)-O(1)	-178.12(12)
N(11)-C(3)-N(8)-N(7)	-2.5(2)
N(9)-C(3)-N(8)-N(7)	178.83(13)
N(11)-C(3)-N(9)-N(10)	2.5(2)
N(8)-C(3)-N(9)-N(10)	-178.85(14)

Heat of formation

As mentioned in the manuscript, the heat of formation for (2-methyltetrazol-5-yl)diazotate anion was determined using an isodesmic reaction (**Scheme S1**).

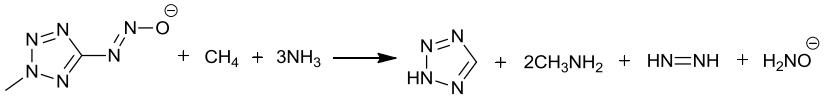
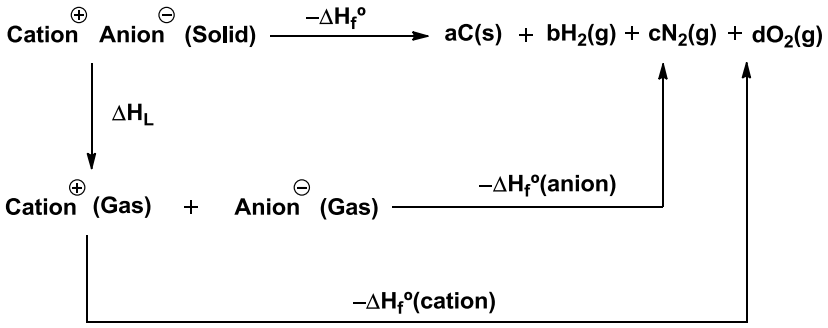


Table S13. Calculated (B3LYP/6-31+G**//MP2/6-311++G**) total energy (E_0), Zero-Point Energy (ZPE), values of thermal correction (H_T), and heats of formation (HOF) of (2-methyltetrazol-5-yl)diazotate anion.

Name	E_0	ZPE	H_T	HOF
(2-methyltetrazol-5-yl)diazotate anion	-480.4925993	0.075329	0.008764	606.6
2*H*-tetrazole	-257.7068416	0.047597	0.004364	318.2
CH_4	-40.3969989	0.044793	0.003812	-74.6
NH_3	-56.4270341	0.034372	0.003818	-45.9
N_2H_2	-110.3916517	0.028442	0.003802	211.9
CH_3NH_2	-95.6223961	0.064026	0.004375	-23.0
H_2NO^-	-130.7801492	0.025259	0.003887	41.9



Scheme S1. Born-Haber cycle for the formation of energetic pyrazolates where a, b, c, and d are the number of moles of the respective products

Based on a Born-Haber energy cycle (**Scheme S1**), the heat of formation of a salt can be simplified by eq 1.

$$\Delta H_f\,^\circ(\text{ionic salt, 298K}) = \Delta H_f\,^\circ(\text{cation, 298K}) + \Delta H_f\,^\circ(\text{anion, 298 K}) - \Delta H_L \quad (1)$$

where ΔH_L is the lattice energy of the salt which could be predicted by the formula suggested by Jenkins et al[3] (eq 2):

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (2)$$

where n_M and n_X depend on the nature of the ions M^{p+} and X^{q-}, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} (eq 3) has the form

$$U_{POT}[\text{kJ mol}^{-1}] = \gamma(\rho/M)^{1/3} + \delta \quad (3)$$

where ρ (g/cm^3) is density, M is the chemical formula mass of the ionic material, e. g, and the coefficients γ

(kJ/mol cm) and δ (kJ/mol) are assigned literature values.[3] For all salts **5**-**10**, the γ is 1981.2 kJ/mol cm and the δ is 103.8 kJ/mol.

Table S14. Calculated (Born-Haber cycle) heats of formation (HOF) of salts **5**-**10**.

Name	ΔH_f °(cation, 298K)	ΔH_f °(anion, 298 K)	ΔH_L	ΔH_f °(ionic salt, 298K)
5	626.4[a]	606.6	539.0	694.0
6	770.0[a]	606.6	529.6	847.0
7	566.7[a]	606.6	514.5	658.8
8	667.4[a]	606.6	494.6	779.4
9	769.0[a]	606.6	488.7	886.9
10	871.0[a]	606.6	478.1	999.5

a Y. Huang, H. Gao, B. Twamley, and J. M. Shreeve, *Chem. –Eur. J.* 2009, **15**, 917-923.

References

3 H. D. B. Jenkins, D. Tudeal, and L. Glasser, *Inorg. Chem.* 2002, **41**, 2364–2367.