

Anions Containing Tripoid Conjugated N₄⁻ System: Salts of 5-(Substituted Amino)-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazol-5-ium-4-ides, as well as their Synthesis, Structure, and Thermal Stability

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Xray crystallographic data

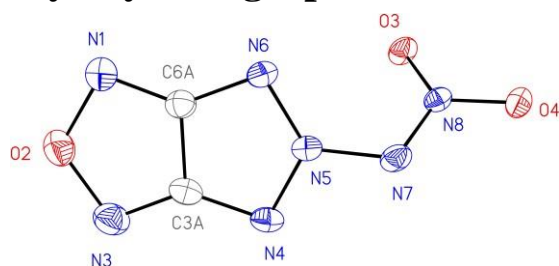


Figure S1. General view of the anion **3a** in crystal. Anisotropic displacement parameters are drawn at 50% probability level.

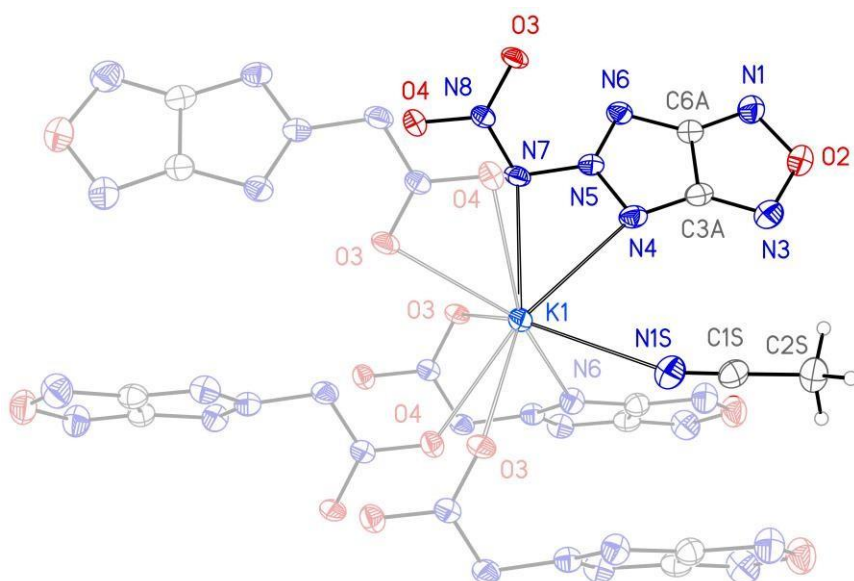


Figure S2. The environment of the potassium cation in crystal **3a** demonstrating its coordination by different heteroatoms of the anion and the acetonitrile molecule. The moieties constituting the asymmetric part of the unit cell are highlighted.

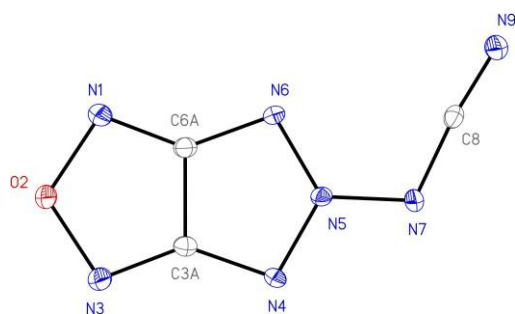


Figure S3. General view of the anion **3b** in crystal. Anisotropic displacement parameters are drawn at 50% probability level.

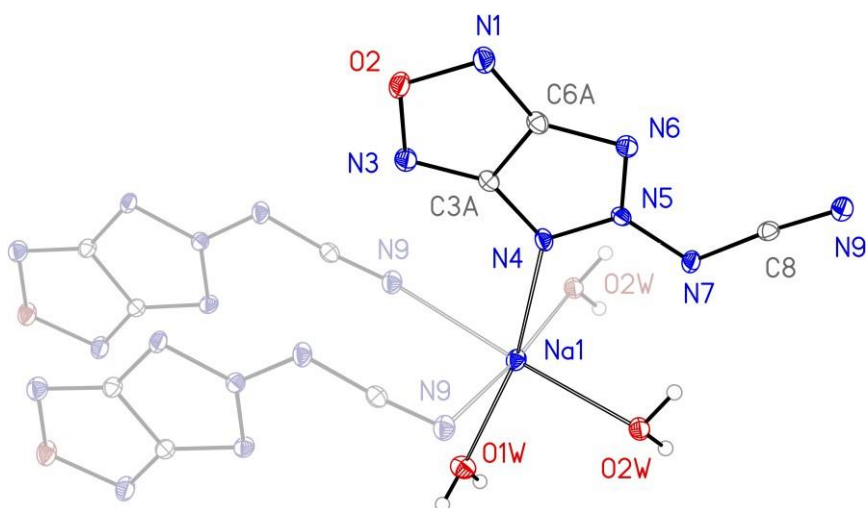


Figure S4. The environment of the sodium cation in crystal **3b** demonstrating its coordination by different heteroatoms of the anion and water molecules. The moieties constituting the asymmetric part of the unit cell are highlighted.

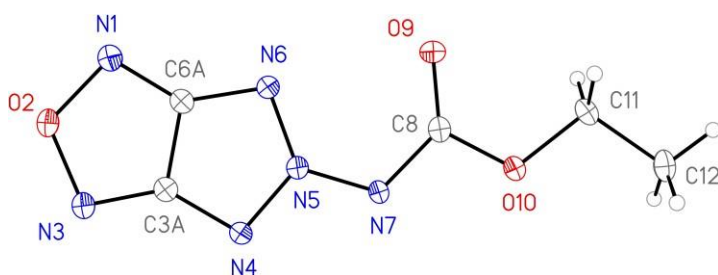


Figure S5. General view of the anion **3c** in crystal. Anisotropic displacement parameters are drawn at 50% probability level.

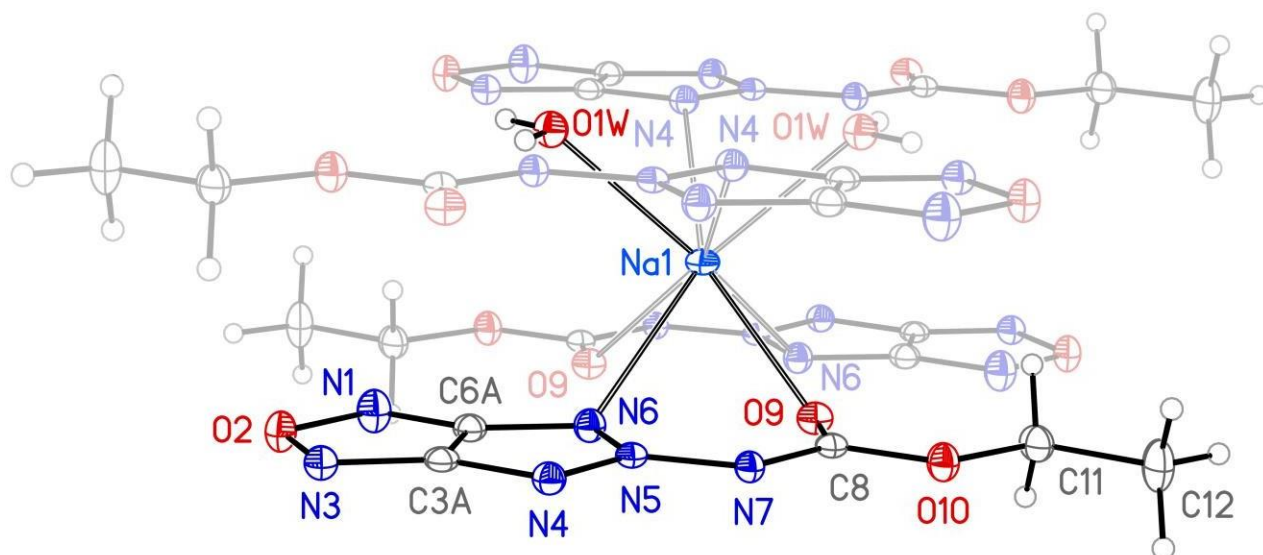


Figure S6. The environment of the sodium cation in crystal **3b** demonstrating its coordination by different heteroatoms of the anion and water molecules. The moieties constituting the asymmetric part of the unit cell are highlighted. The anion and the water molecule lie on a mirror plane and the sodium cation lies on the intersection of a 2-fold axis and a glide plane (sp. gr. $C2/m$).

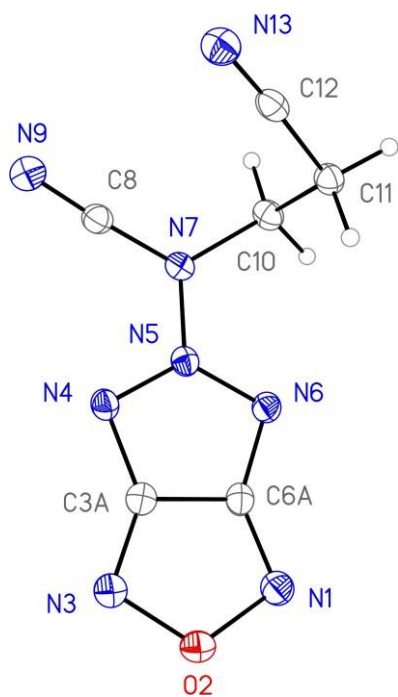


Figure S7. General view of the molecule **4b** in crystal. Anisotropic displacement parameters are drawn at 50% probability level.

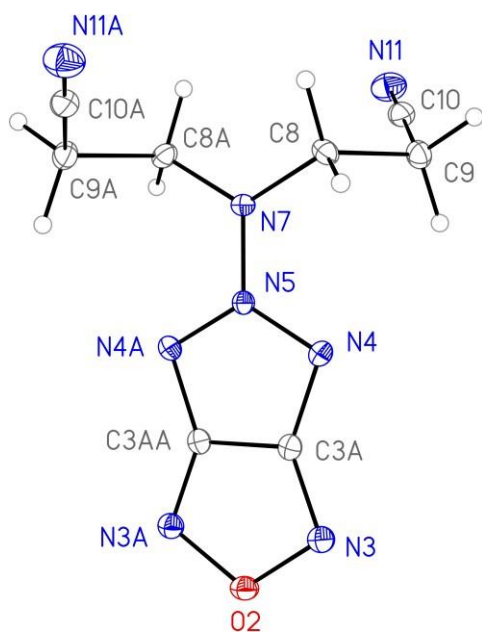


Figure S8. General view of the molecule **6** in crystal. Anisotropic displacement parameters are drawn at 50% probability level.

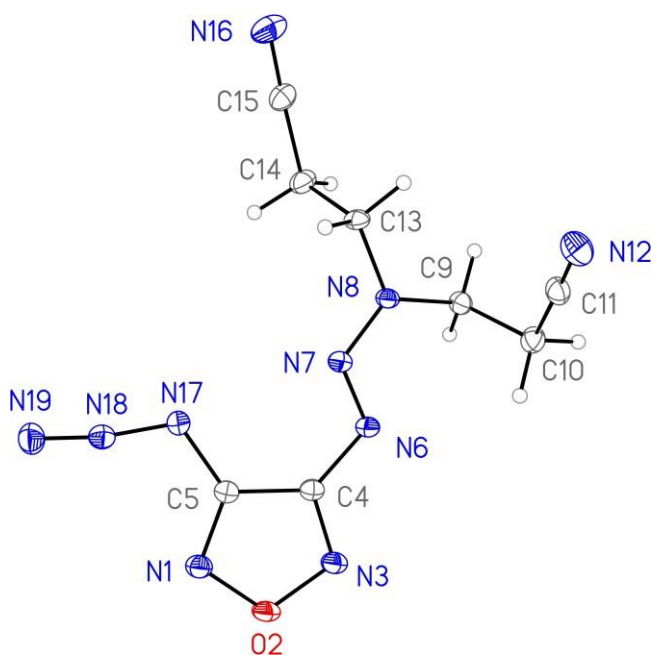


Figure S9. General view of the molecule **7** in crystal. Anisotropic displacement parameters are drawn at 50% probability level.

Table S1. Crystallographic data for crystals of compounds **3a–c**, **4b**, **6–7**.

compound	3a	3b	3c	4b	6	7
CCDC	2183138	2183139	2183140	2183141	2183142	2183143
empirical formula	C ₄ H ₃ KN ₈ O ₃	C ₃ H ₄ N ₇ NaO ₃	C ₅ H ₇ N ₆ NaO ₄	C ₆ H ₄ N ₈ O	C ₈ H ₈ N ₈ O	C ₈ H ₈ N ₁₀ O
T, K	250.24	209.12	238.16	204.17	232.22	260.24
crystal system	140	100	100	120	100	120
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> na2 ₁	<i>C</i> 2/ <i>m</i>	<i>P</i> 2 ₁	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
Z / Z'	4 / 1	4 / 1	4 / 0.5	2 / 1	4 / 0.5	8 / 1
<i>a</i> , Å	16.0696(12)	12.2360(3)	13.1460(11)	6.5170(4)	13.0457(4)	20.5474(19)
<i>b</i> , Å	5.7168(4)	17.6766(3)	6.2603(5)	5.4602(4)	11.8643(4)	6.4371(6)
<i>c</i> , Å	10.2887(7)	3.58020(10)	12.4249(11)	12.1137(8)	6.5869(2)	17.5774(17)
β , °	91.457(3)		117.552(2)	105.382(3)	100.2912(18)	93.468(2)
<i>V</i> , Å ³	944.88(12)	774.36(3)	906.58(13)	415.61(5)	1003.11(6)	2320.6(4)
<i>d</i> _{calc} , g cm ^{−3}	1.759	1.794	1.745	1.631	1.538	1.490
μ (MuK α), mm ^{−1}	5.72	2.00	1.88	1.25	1.14	1.12
2 θ _{max} , °	60.0	60.0	60.0	66.3	60.0	60.0
collected reflns.	11049	19383	7565	6470	5948	9893
unique reflns.	2727	2235	1438	3068	1473	3357
reflns. with <i>I</i> > 2 σ (<i>I</i>)	2347	2128	1266	2561	1336	2787
<i>R</i> ₁	0.0427	0.0274	0.0438	0.0375	0.0330	0.0356
<i>wR</i> ₂	0.1134	0.0713	0.1101	0.0827	0.0910	0.0940
GOF on F ²	1.066	1.049	1.058	1.010	1.038	1.044
ρ _{max} / ρ _{min} , e Å ^{−3}	0.743/-0.363	0.452/-0.211	0.724/-0.527	0.310/-0.197	0.499/-0.295	0.376/-0.227

Table S2. Selected bond lengths and angles of the heterocycles in compounds **3a-c**, **4b**, **6-7**.

compound	3a	3b	3c	4b	6*	7
	bond lengths, Å					
N1–O2	1.407(2)	1.4056(18)	1.405(2)	1.399(2)	1.4118(8)	1.3916(11)
O2–N3	1.400(3)	1.4087(18)	1.408(2)	1.402(2)	1.4118(8)	1.3854(11)
N1–C6A	1.315(3)	1.308(2)	1.311(3)	1.314(3)	1.3114(11)	1.3027(13)
N3–C3A	1.319(3)	1.310(2)	1.310(3)	1.318(3)	1.3114(11)	1.3097(12)
N4–C3A	1.358(3)	1.3695(19)	1.363(3)	1.371(3)	1.3693(10)	
N6–C6A	1.371(3)	1.361(2)	1.368(3)	1.376(2)	1.3693(10)	
N4–N5	1.337(2)	1.3420(18)	1.360(2)	1.328(2)	1.3465(8)	
N5–N6	1.339(2)	1.3535(17)	1.347(2)	1.324(2)	1.3465(8)	
C3A–C6A	1.408(3)	1.414(2)	1.406(3)	1.406(3)	1.4177(15)	1.4381(14)
N5–N7	1.382(2)	1.3368(18)	1.338(2)	1.379(2)	1.3320(14)	
	bond angles, °					
N1–O2–N3	113.97(15)	113.11(11)	113.27(15)	114.05(13)	113.47(8)	111.05(7)
O2–N1–C6A	101.59(17)	102.58(12)	102.47(17)	102.13(16)	102.19(6)	105.12(8)
O2–N3–C3A	102.35(17)	102.49(12)	102.03(16)	101.79(16)	102.19(6)	105.79(8)
N1–C6A–3A	111.71(18)	110.99(14)	110.77(18)	110.96(19)	111.08(5)	108.36(8)
N3–C3A–C6A	110.39(19)	110.82(13)	111.46(19)	111.08(19)	111.08(5)	109.67(9)
C3A–C6A–N6	109.48(17)	109.87(13)	109.70(18)	109.52(18)	109.84(4)	
C6A–C3A–N4	110.11(17)	109.47(14)	110.02(18)	109.73(18)	109.84(4)	
C6A–N6–N5	99.44(15)	100.29(12)	100.73(16)	98.93(16)	99.53(7)	
C3A–N4–N5	99.70(16)	100.44(12)	100.46(16)	98.94(16)	99.53(7)	
N4–N5–N6	121.25(16)	119.92(13)	119.09(16)	122.87(14)	121.27(9)	
N4–N5–N7	114.84(15)	117.27(12)	114.18(16)	118.60(16)	119.37(5)	
N6–N5–N7	123.39(16)	122.81(13)	126.73(17)	118.50(16)	119.37(5)	

*Some bond lengths and angles for **6** are pairwise identical due to C₂ molecular symmetry in the crystal.

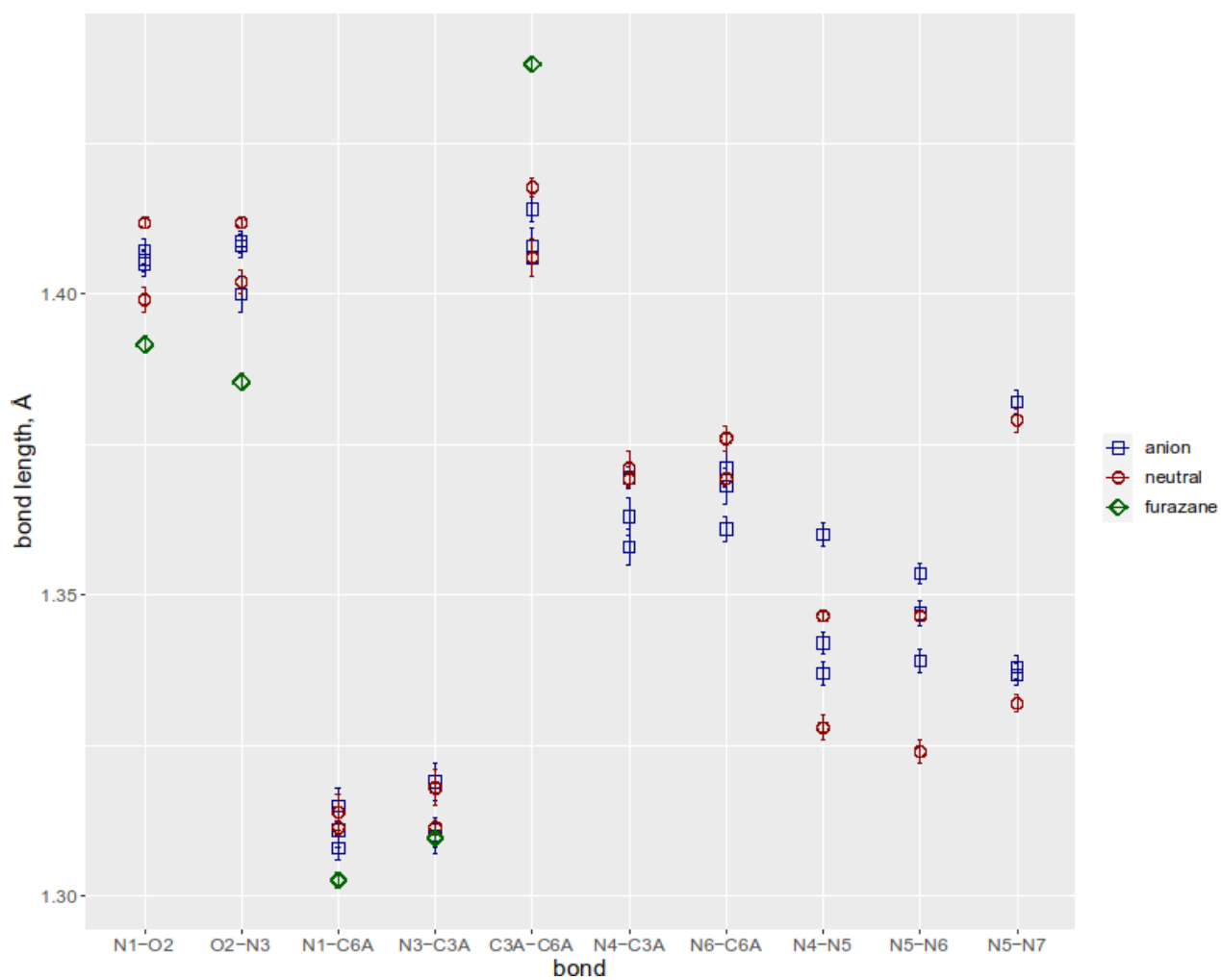


Figure S10. Graphical representation of bond length distribution in anions (**3a-3c**), neutral molecules (**4b** and **6**) and substituted furazane **7**. The s.u. values from the least square refinement are provided with error bars.

Thermal behavior

Table S3. Summary of thermal stability data

Compound	Melting point, °C	Decomposition onset,* °C
3a	152	152
3b	–	190
3c	–	122
4b	76	185
4c	61	233
5	127	127
6	139	234
7	79	79 (221)

*The extrapolated onset temperature of the exothermic peak by DSC at 5 K min⁻¹ rate.

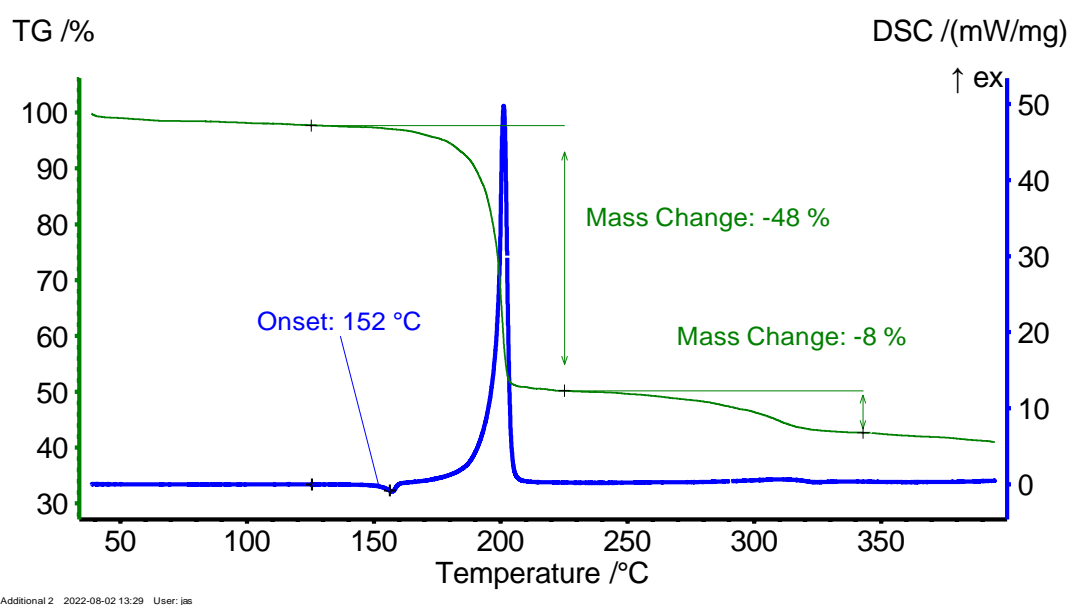


Figure S11. DSC (blue curve) and mass loss (TG, green curve) signals for **3a** heated at 5 K min⁻¹ rate.

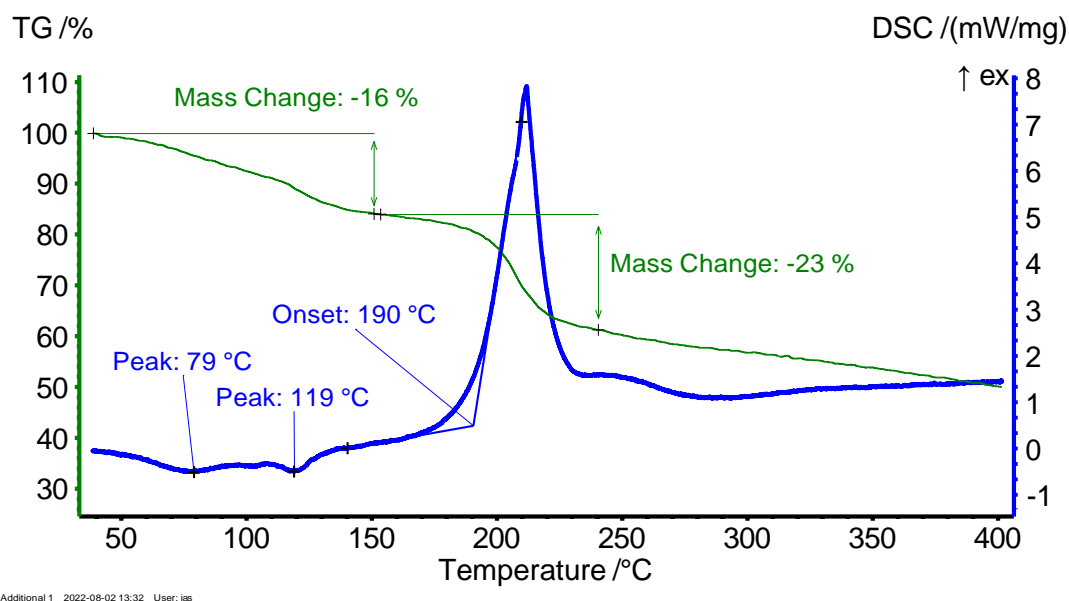


Figure S12. DSC (blue curve) and mass loss (TG, green curve) signals for **3b** heated at 5 K min⁻¹ rate.

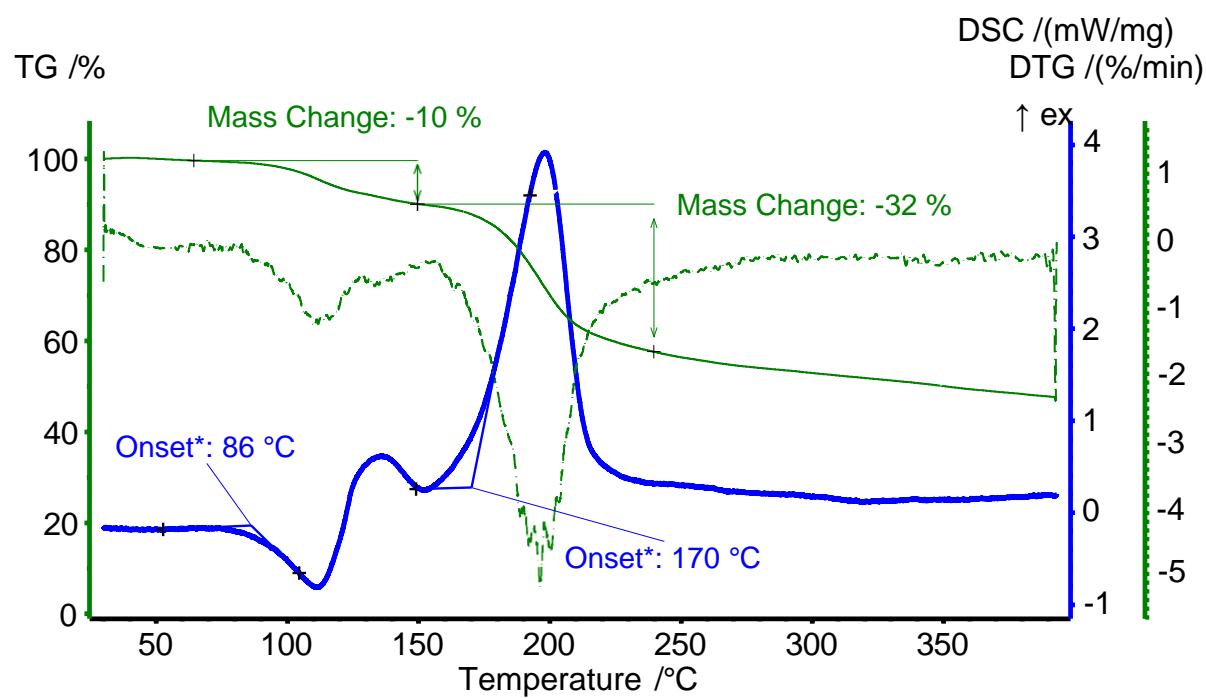


Figure S13. DSC/TG signal for **3c** heated at 5 K min⁻¹ rate.

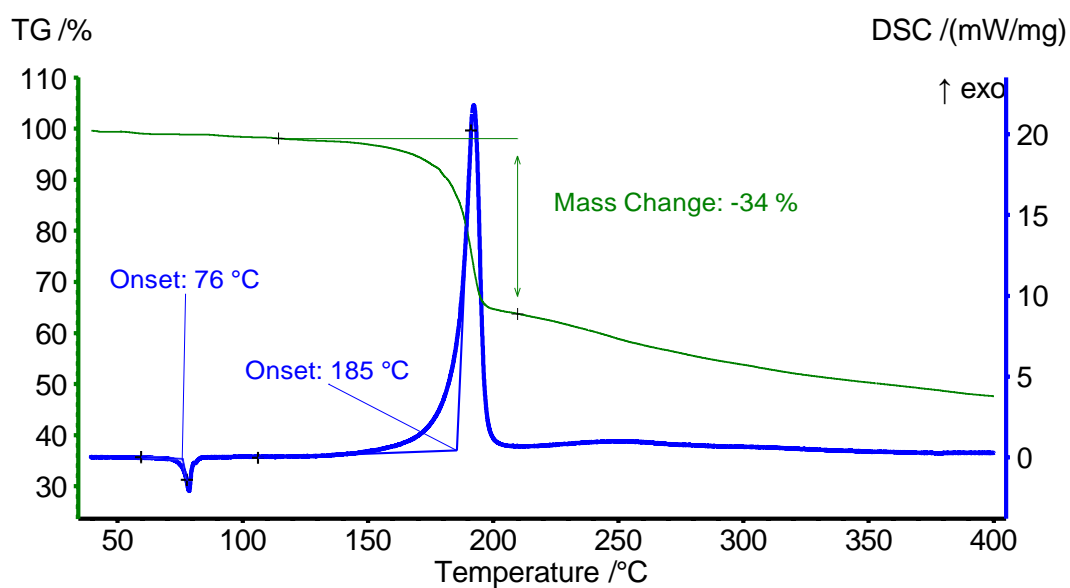


Figure S14. DSC (blue curve) and mass loss (TG, green curve) signals for **4b** heated at 5 K min⁻¹ rate.

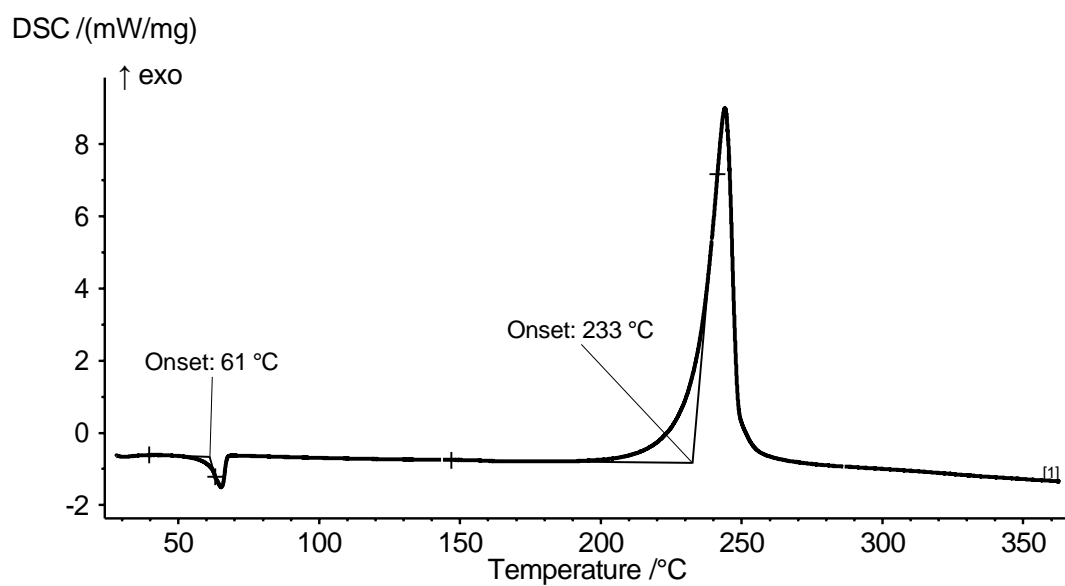


Figure S15. DSC signal for **4c** heated at 5 K min⁻¹ rate.

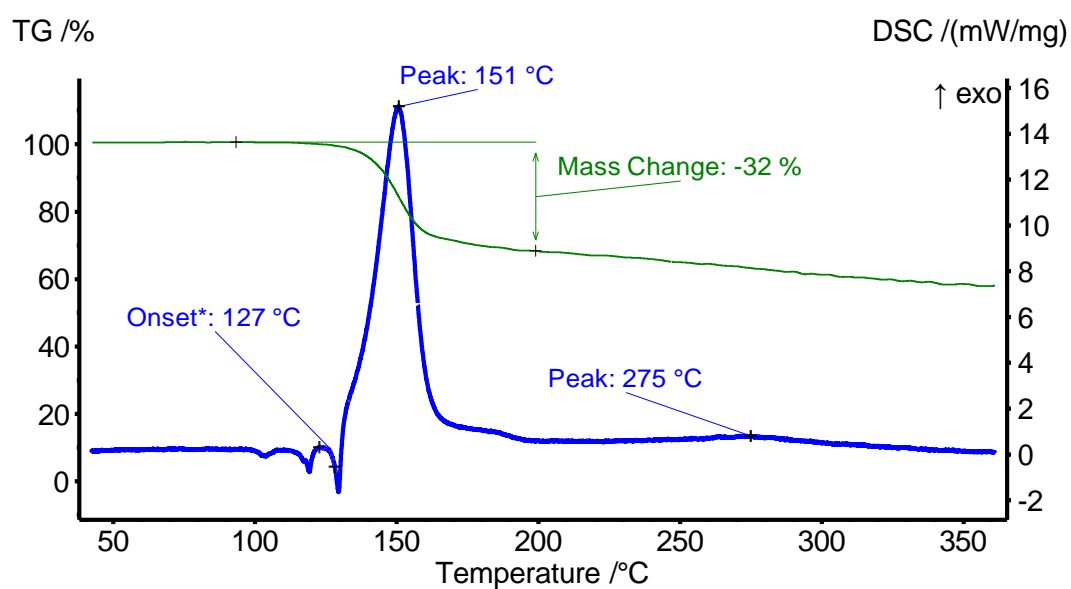
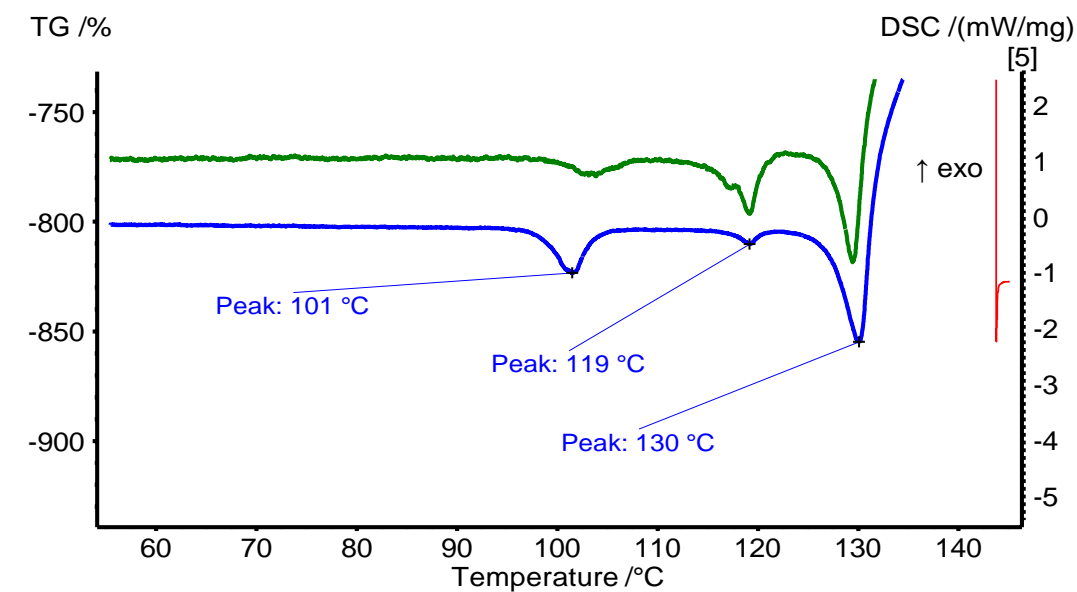
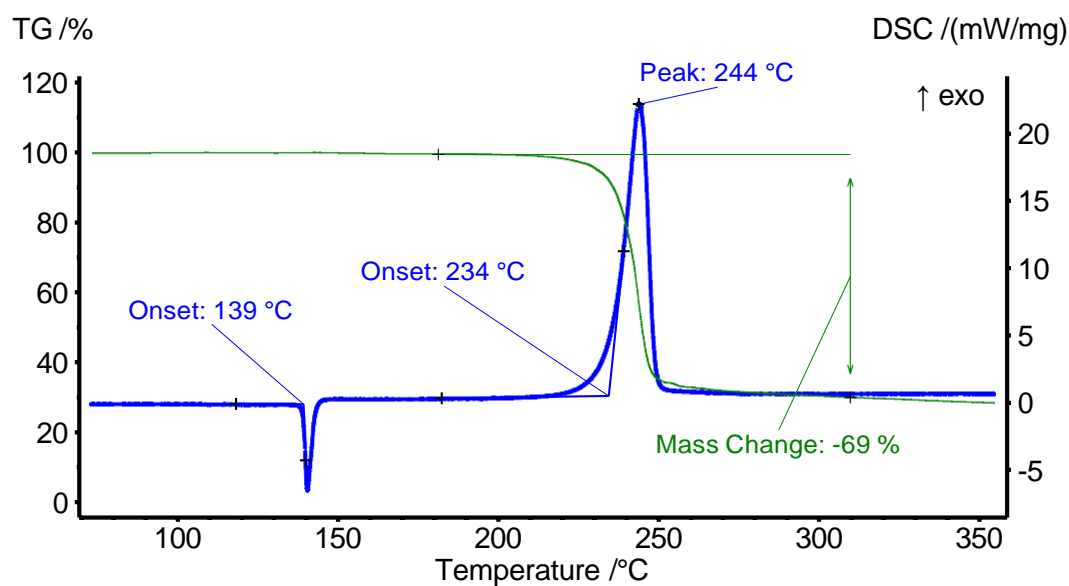


Figure S16. DSC (blue curve) and mass loss (TG, green curve) signals for **5** heated at 5 K min⁻¹ rate.



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Figure S17. The magnified view of DSC (blue curve) signals for **5** heated at 5 K min⁻¹ rate: upper curve corresponds to an experiment with 0.46 mg sample mass, bottom – with 1.56 mg of the sample.



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Figure S18. DSC (blue curve) and mass loss (TG, green curve) signals for **6** heated at 5 K min⁻¹ rate.

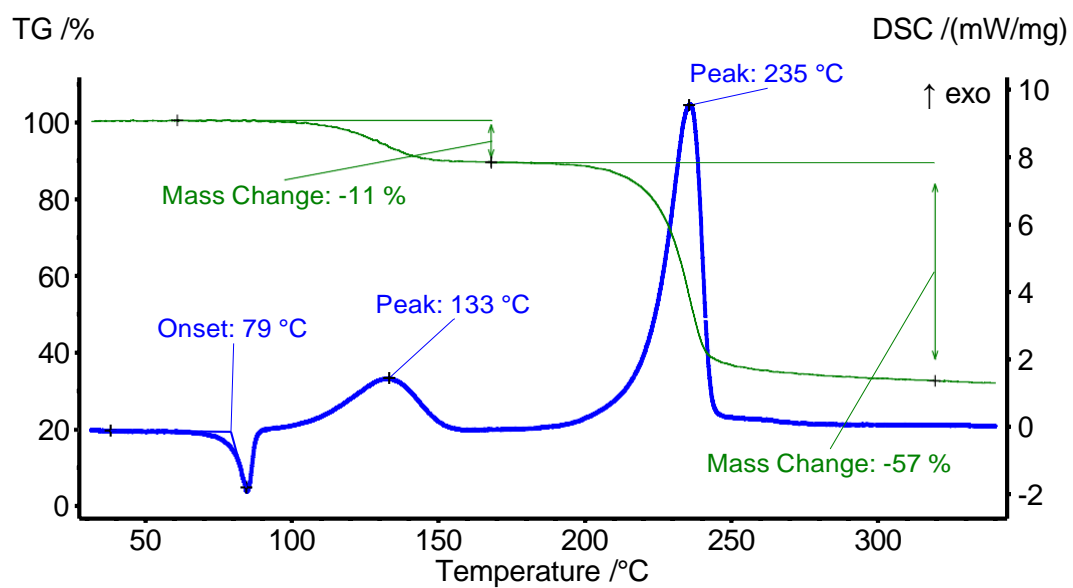
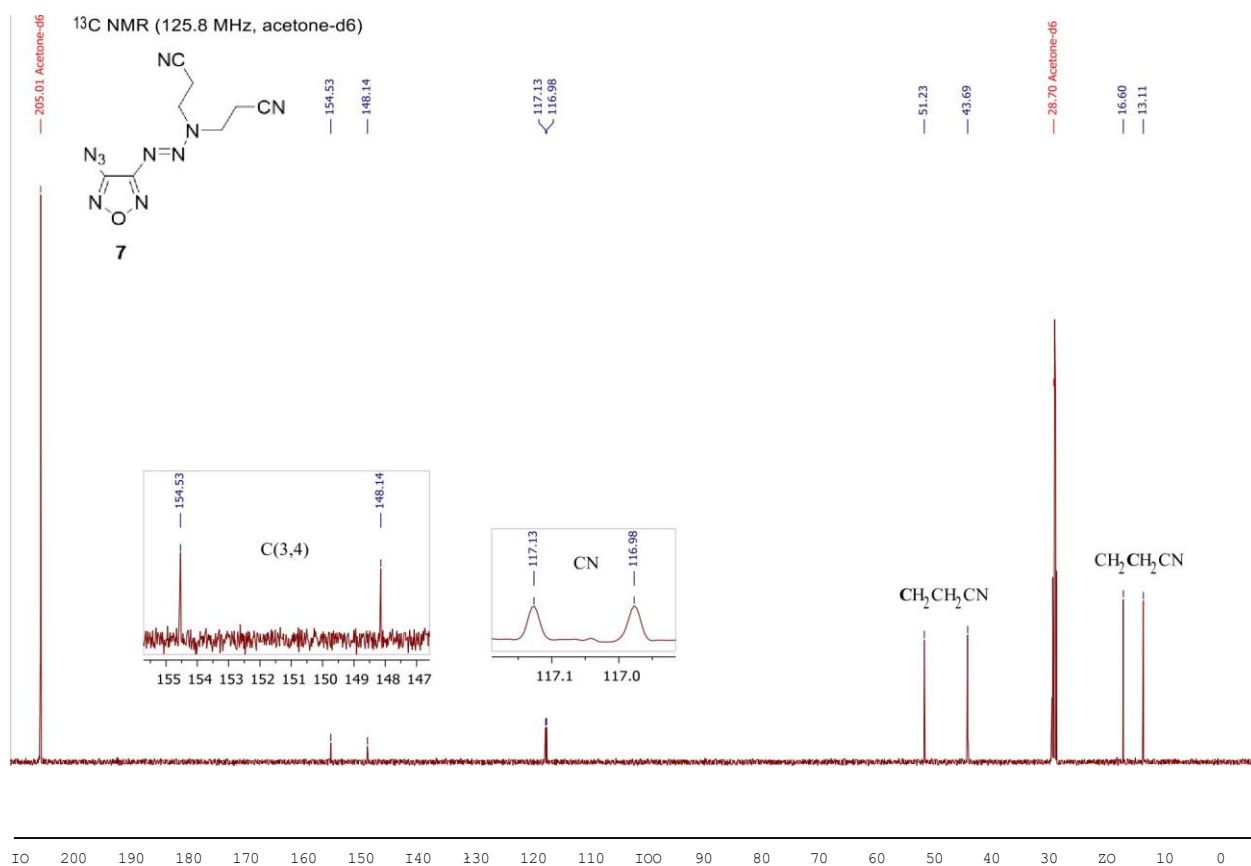
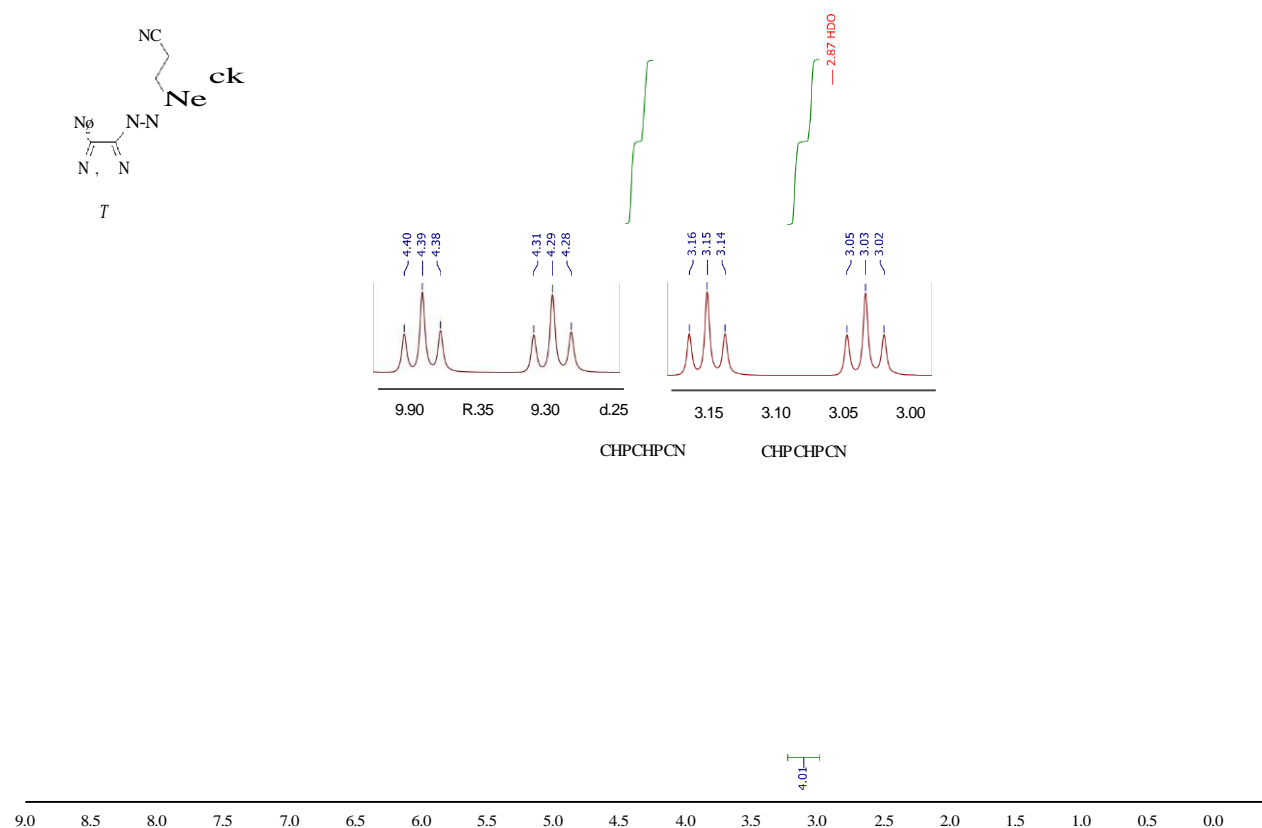


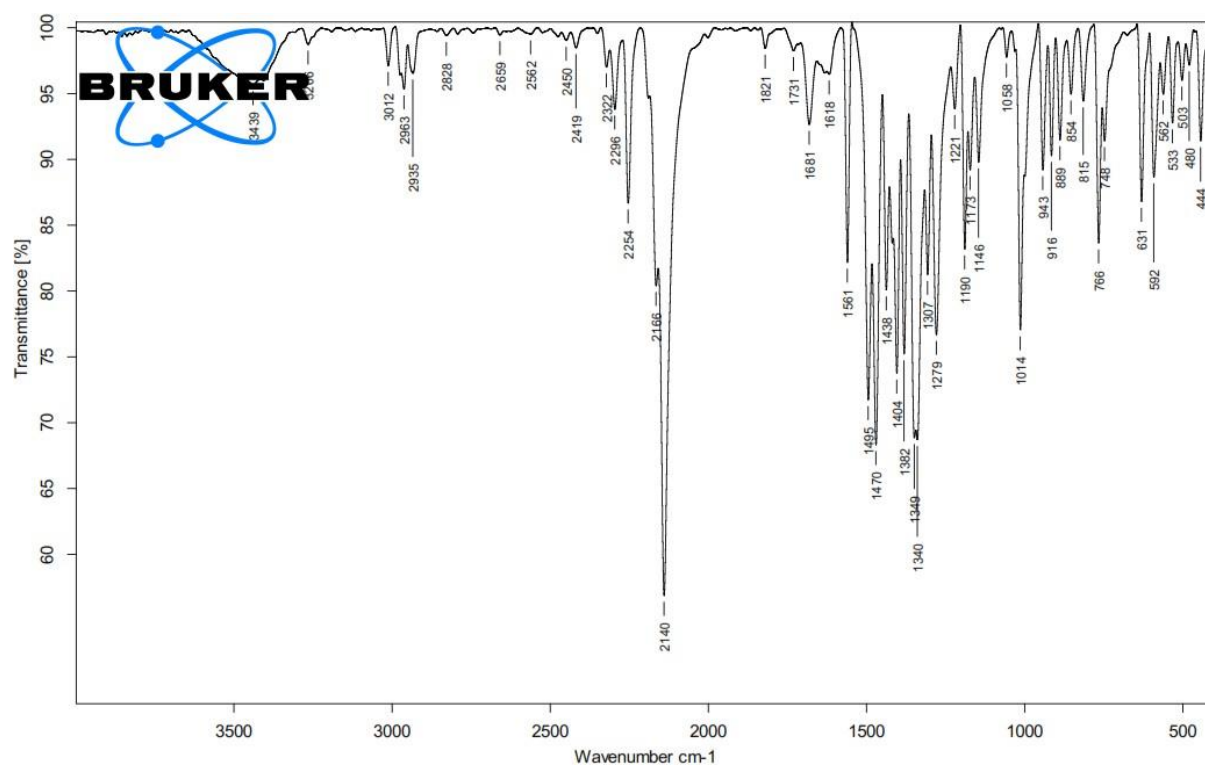
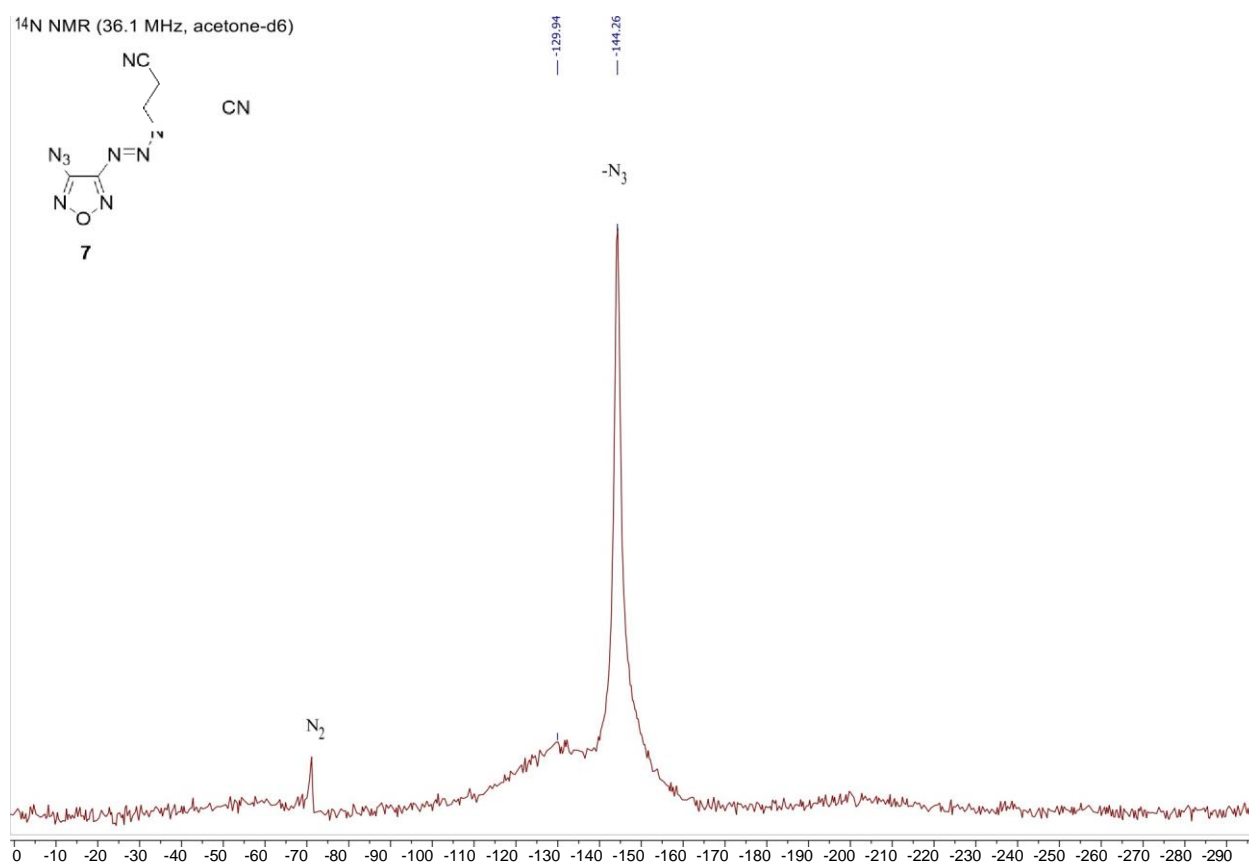
Figure S19. DSC (blue curve) and mass loss (TG, green curve) signals for **7** heated at 5 K min⁻¹ rate.

NMR and IR spectra for compound 7

¹H NMR (500.1 MHz, acetone-d₆)

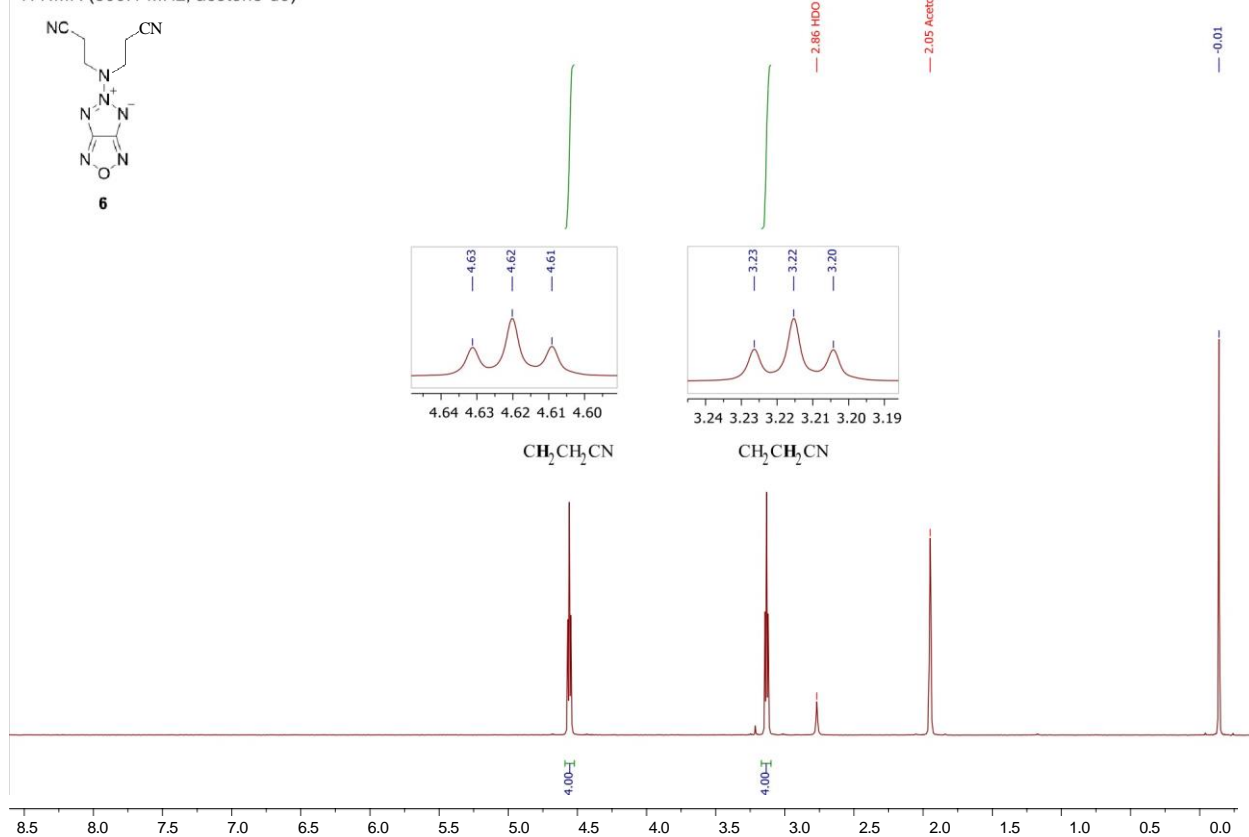


¹⁴N NMR (36.1 MHz, acetone-d₆)

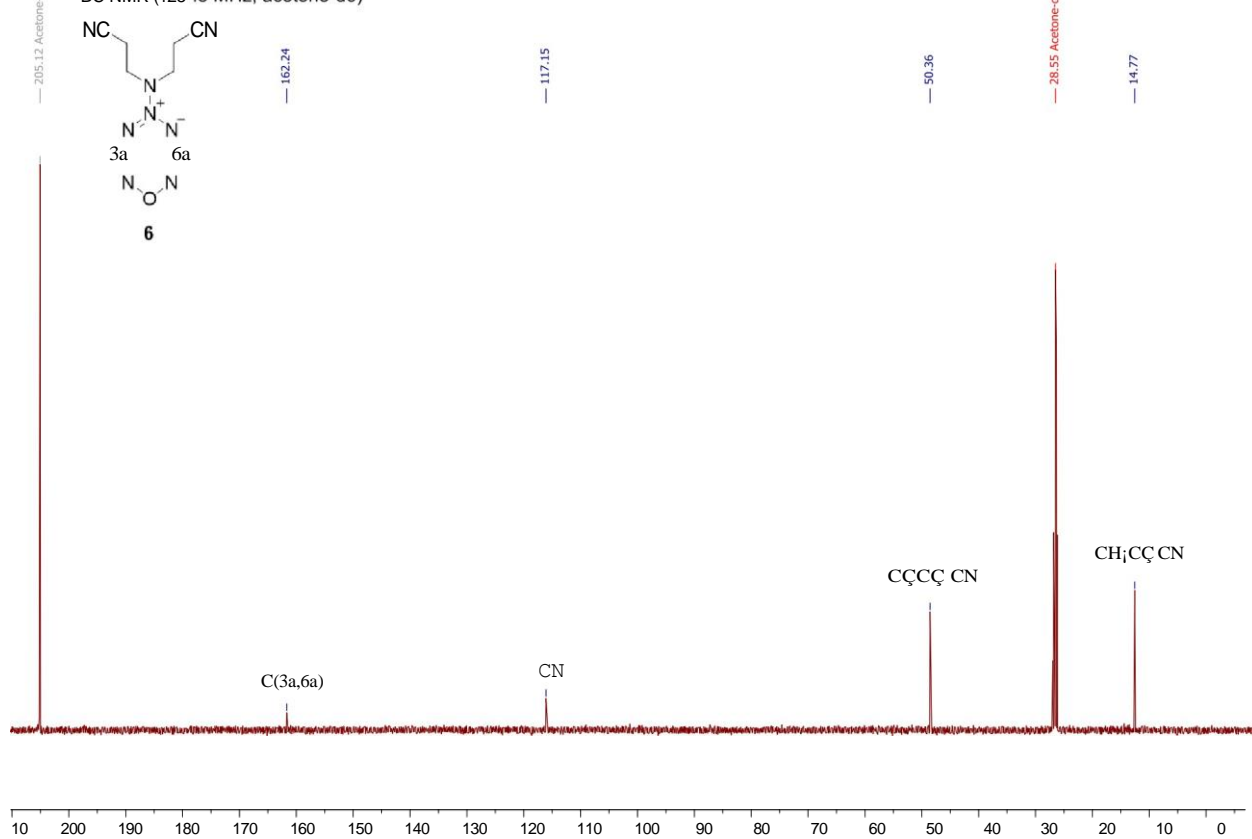


NMR and IR spectra for compound 6

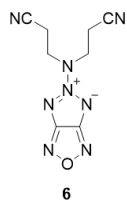
¹H NMR (500.1 MHz, acetone-d₆)



*¹³C NMR (125.8 MHz, acetone-d₆)

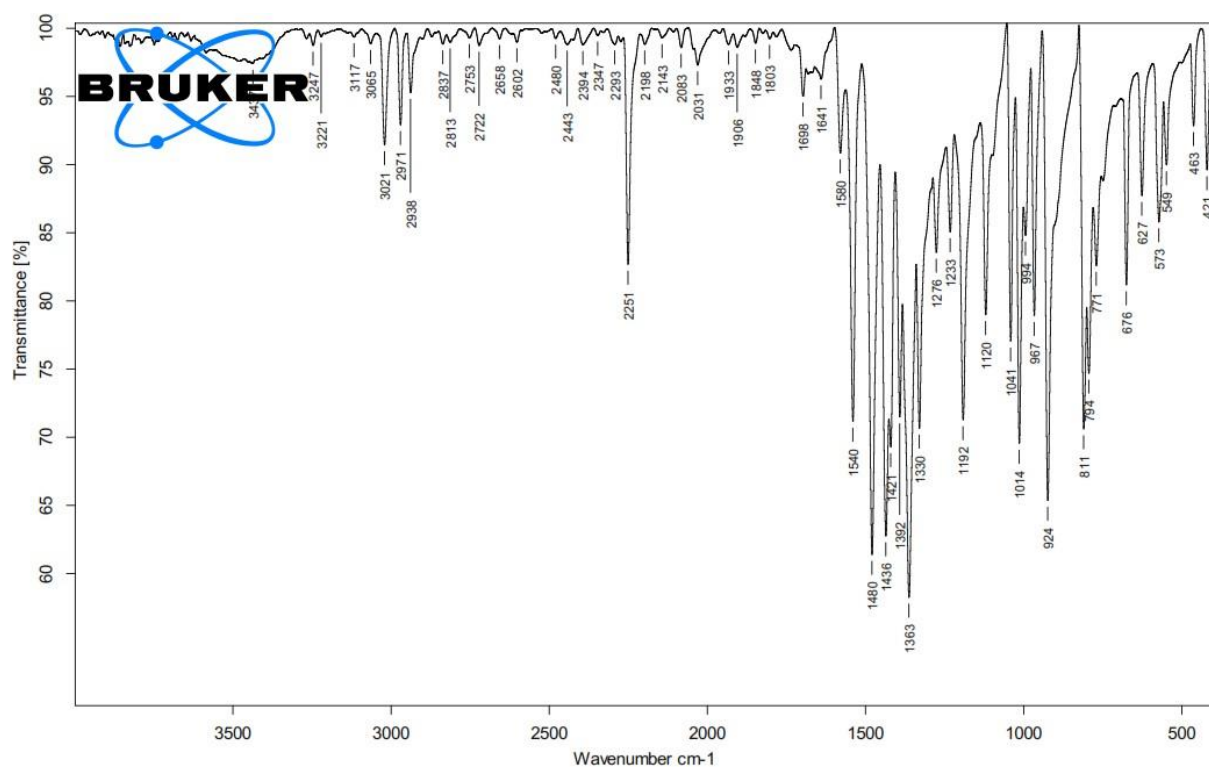
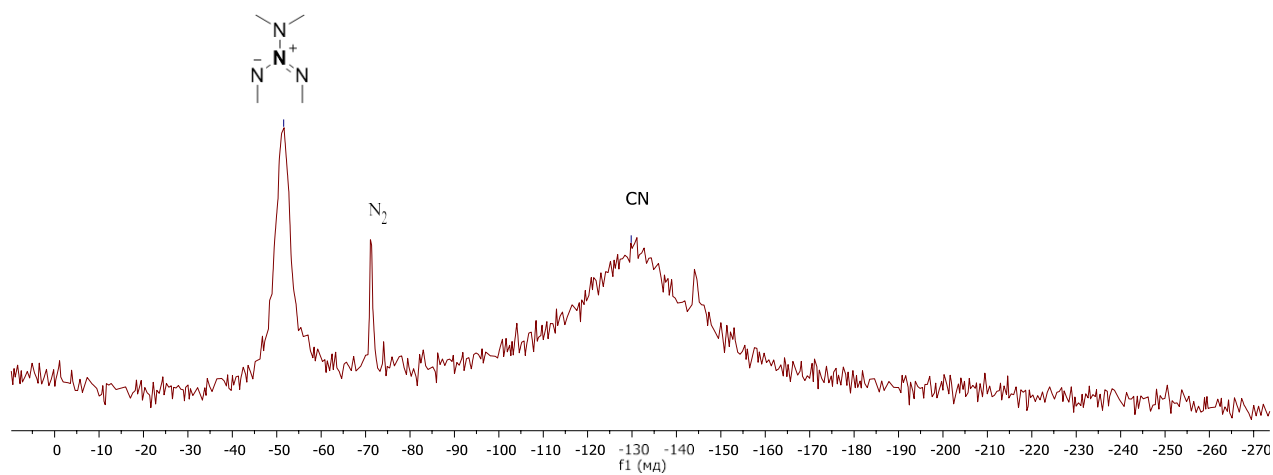


¹⁴N NMR (36.1 MHz, acetone-d₆)



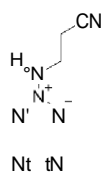
-51.58

-129.84

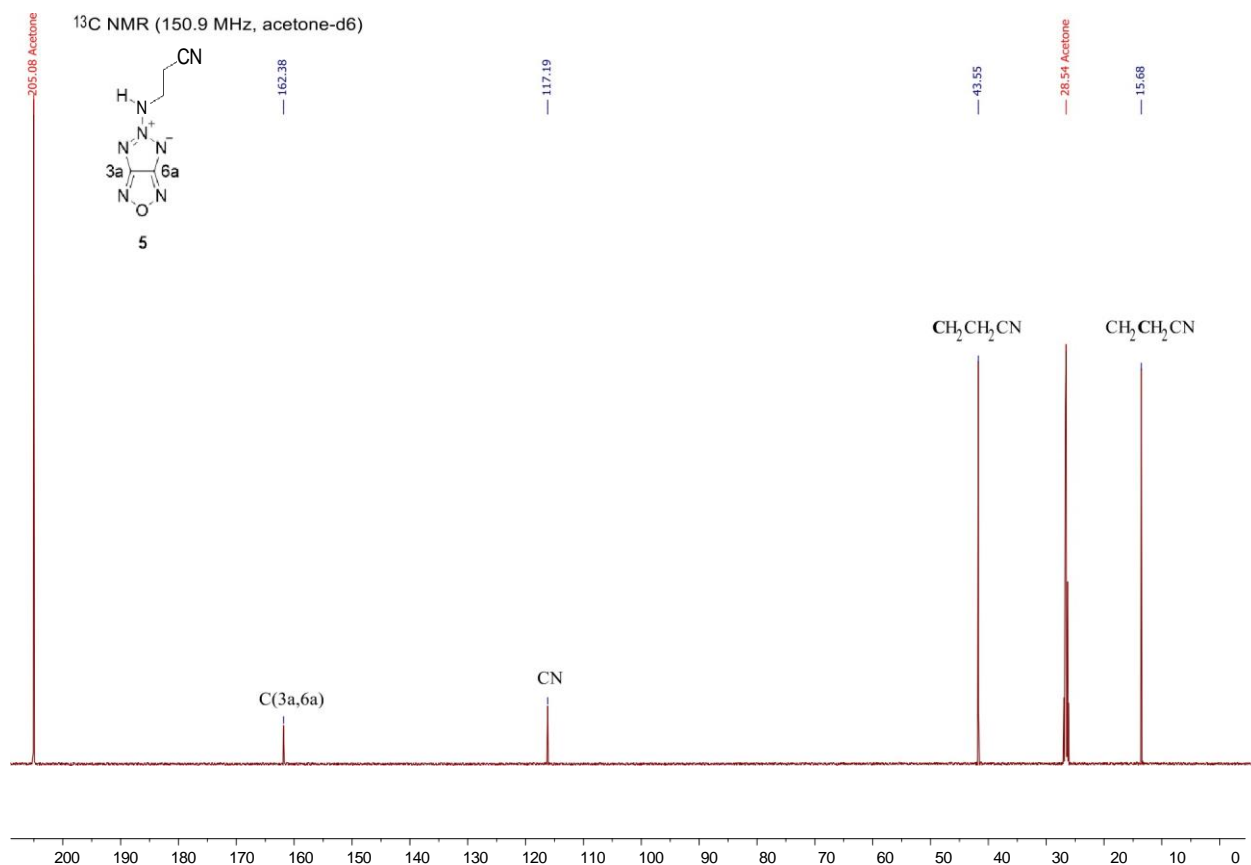
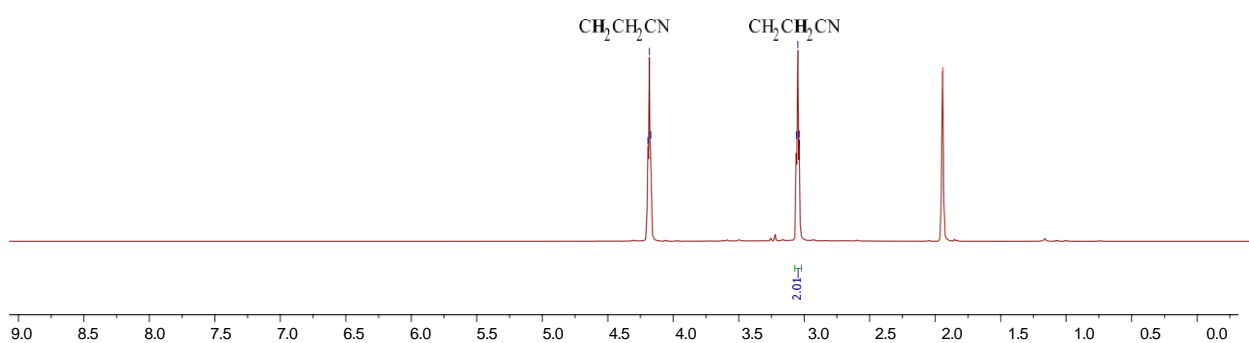
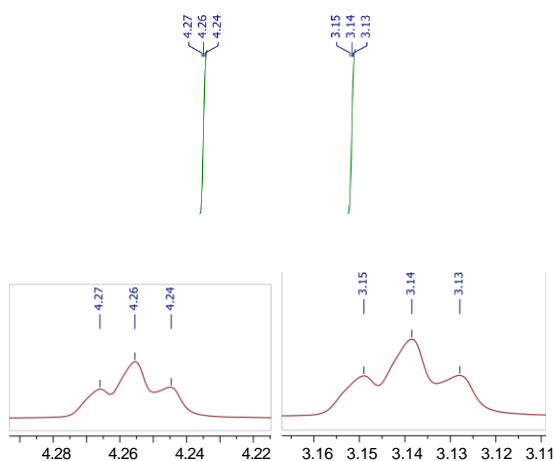


NMR and IR spectra for compound 5

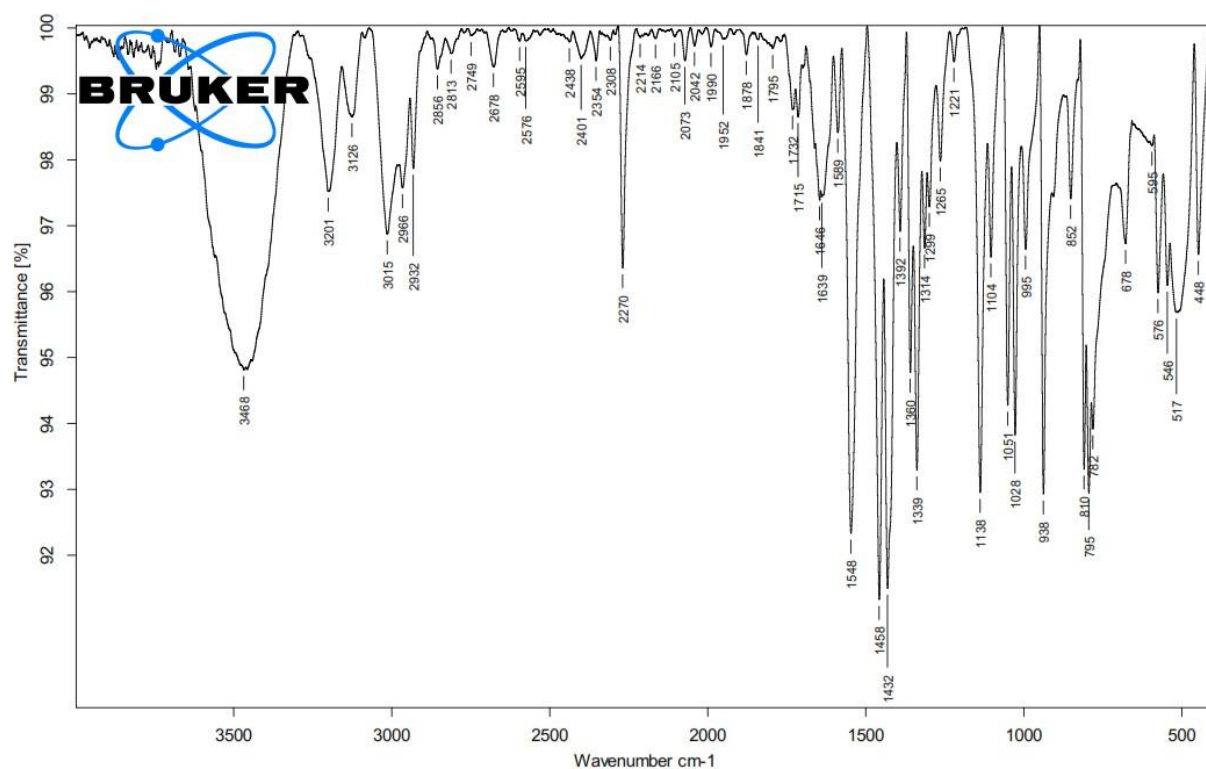
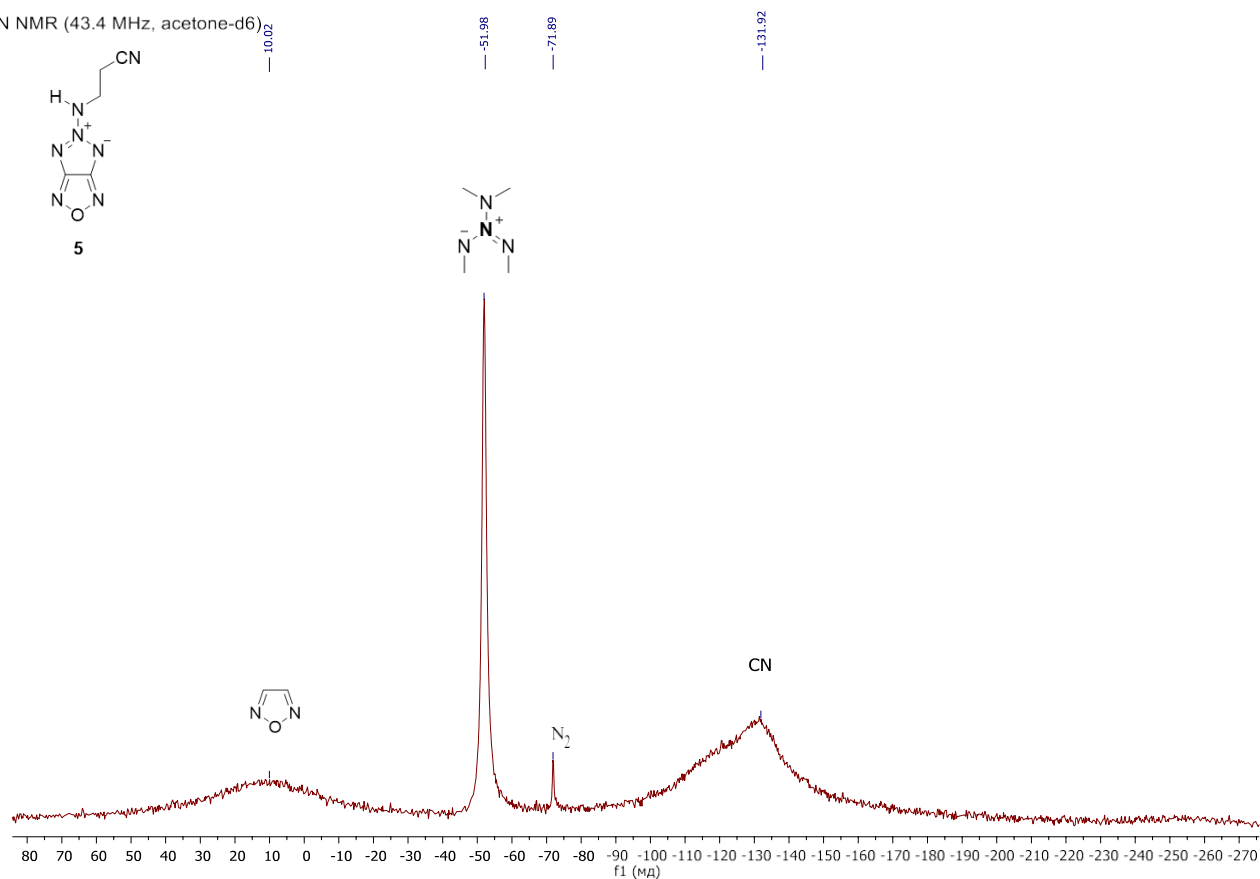
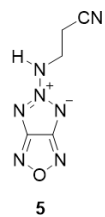
¹H NMR (600.1 MHz, acetone-d₆)



5

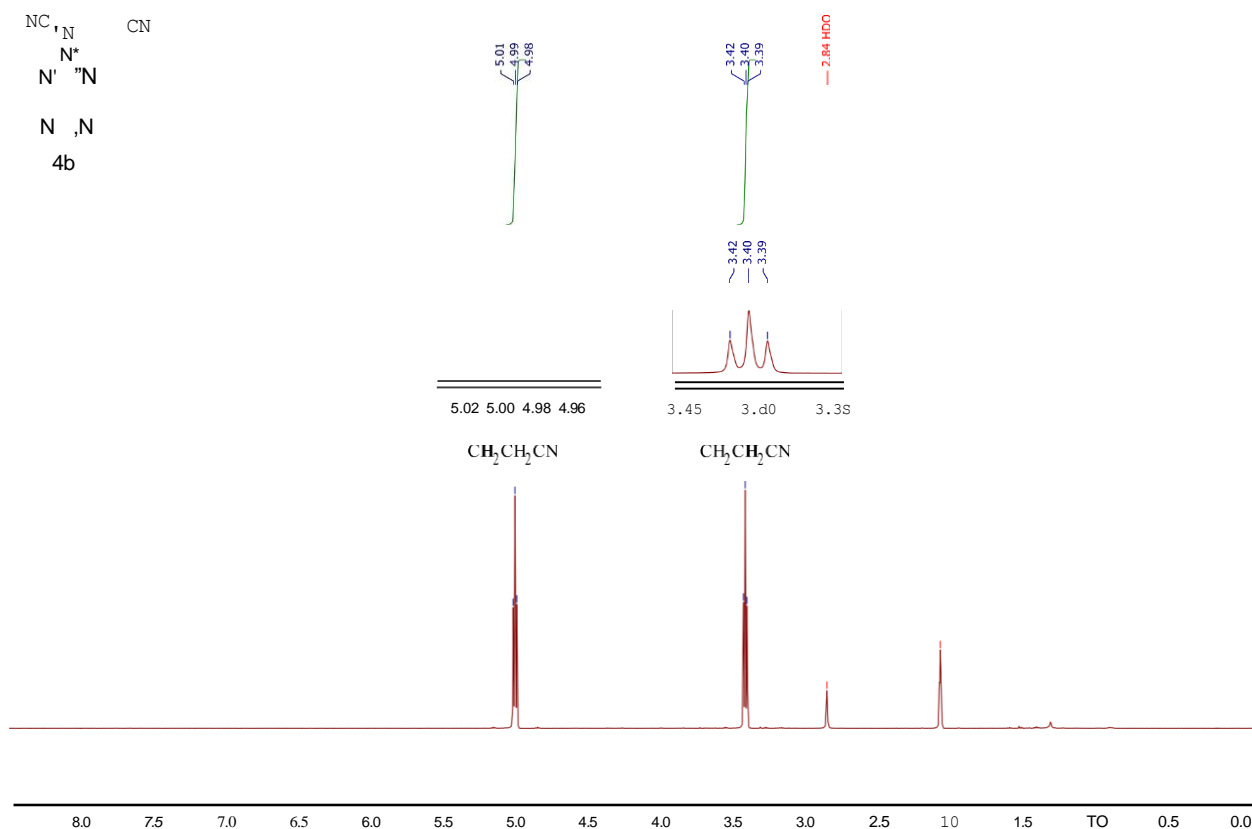
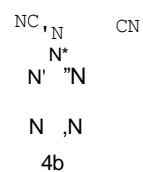


¹⁴N NMR (43.4 MHz, acetone-d₆)

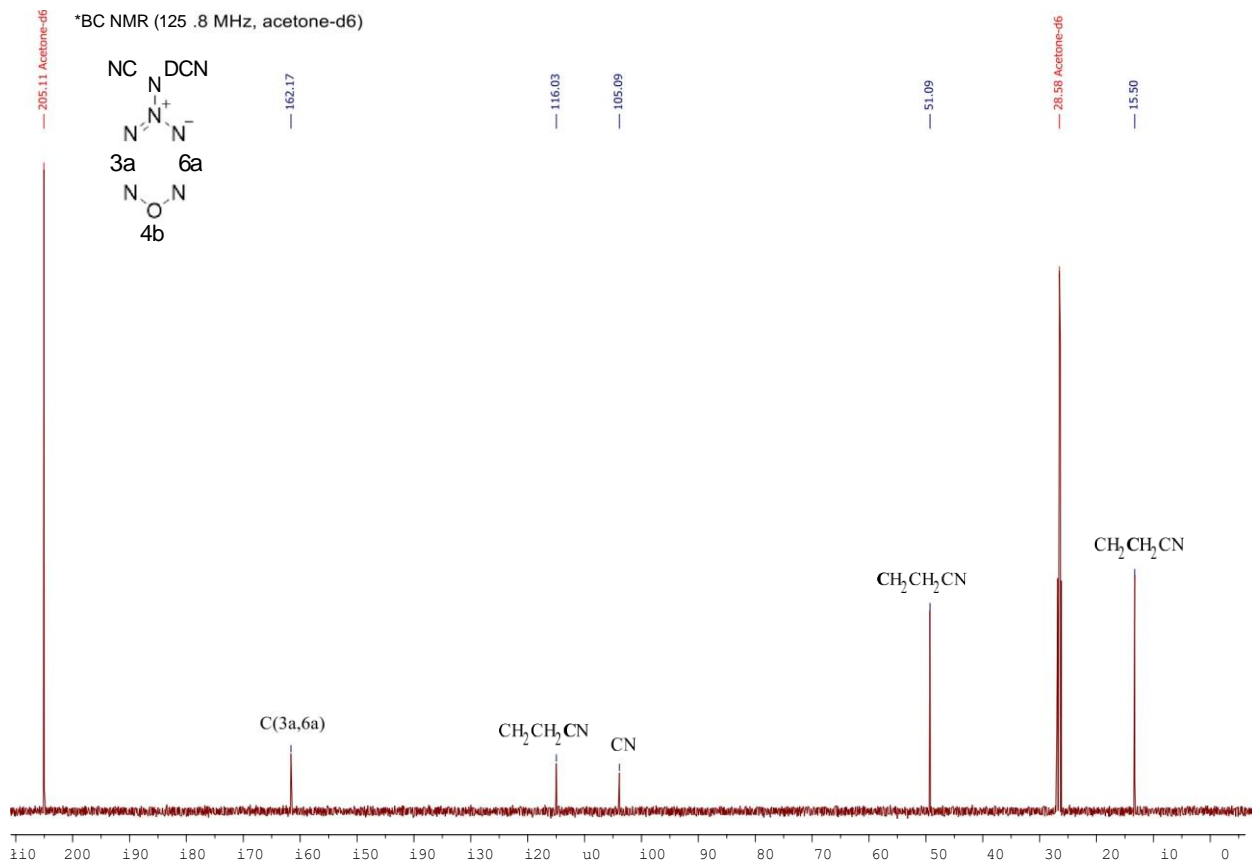
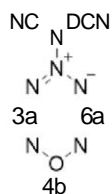


NMR and IR spectra for compound 4b

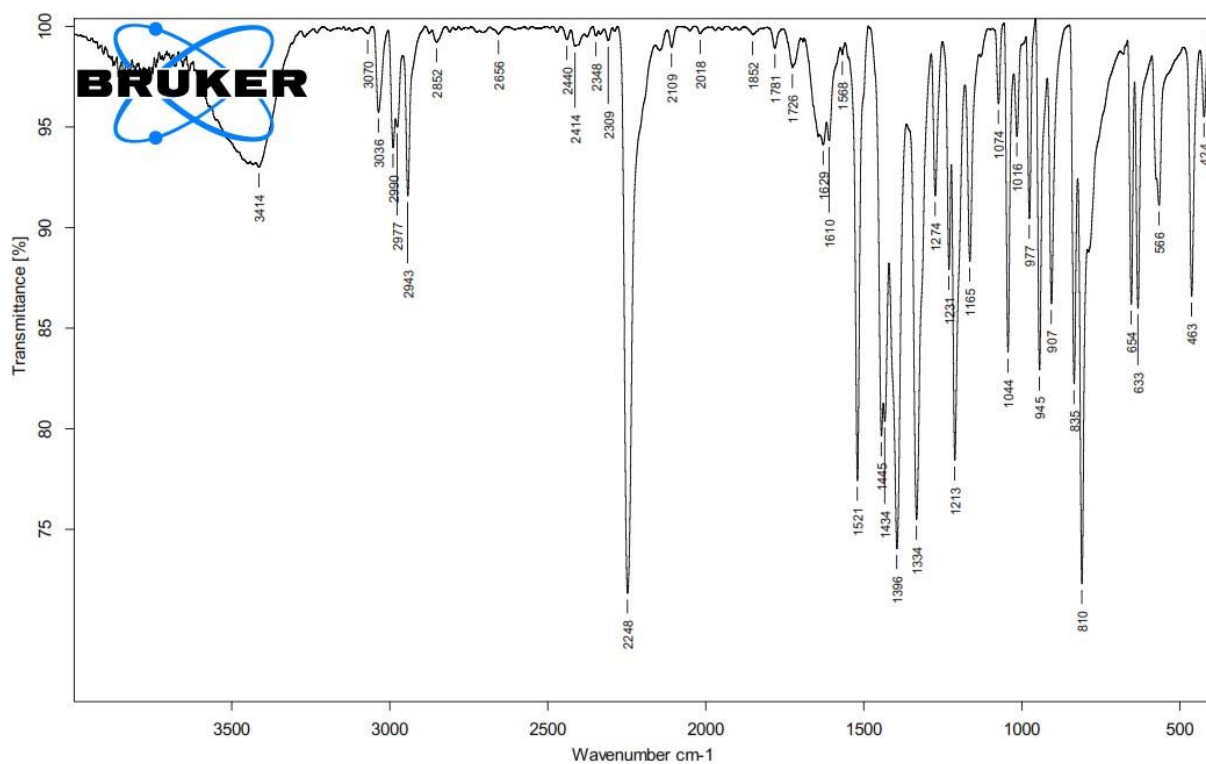
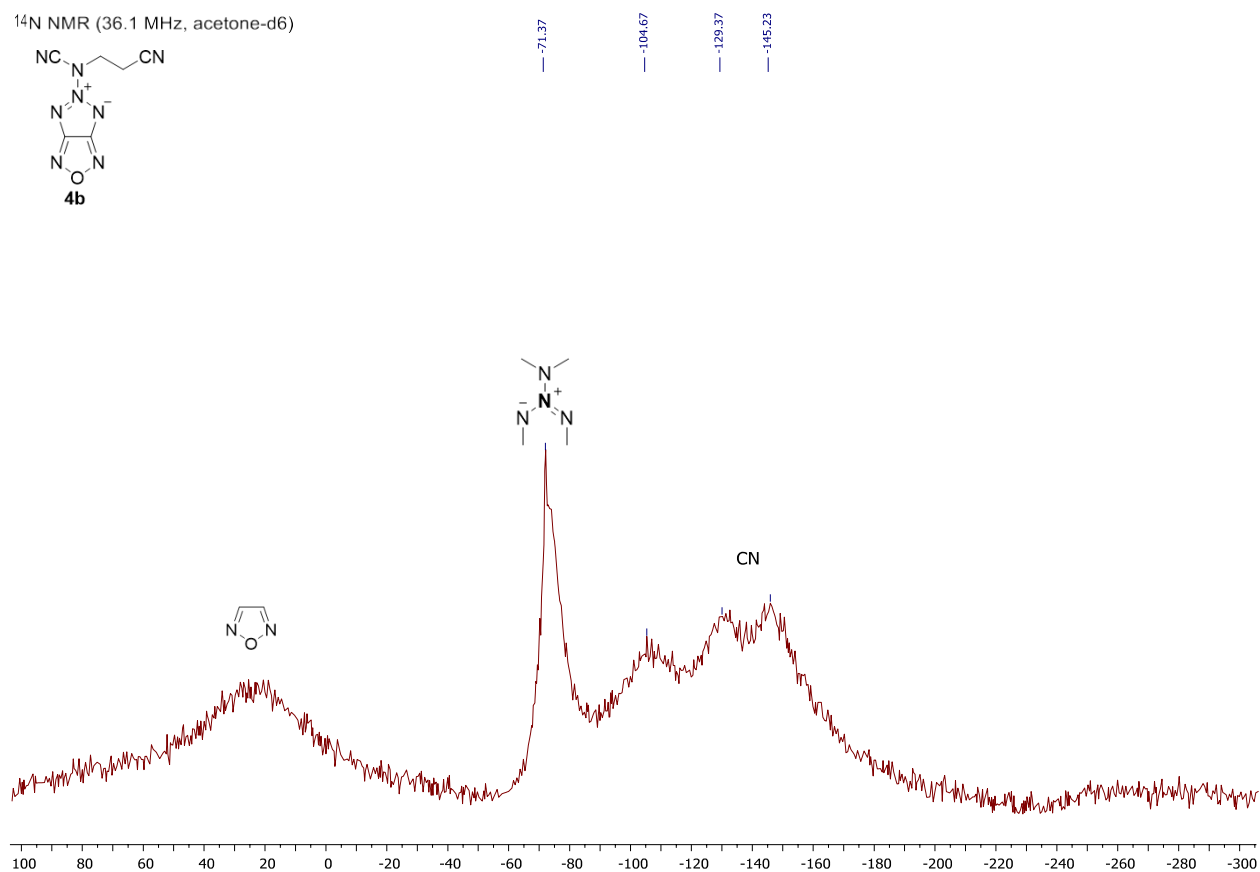
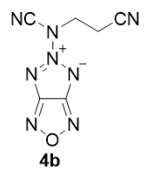
¹H NMR (500.1 MHz, acetone-d₆)



*¹³C NMR (125.8 MHz, acetone-d₆)

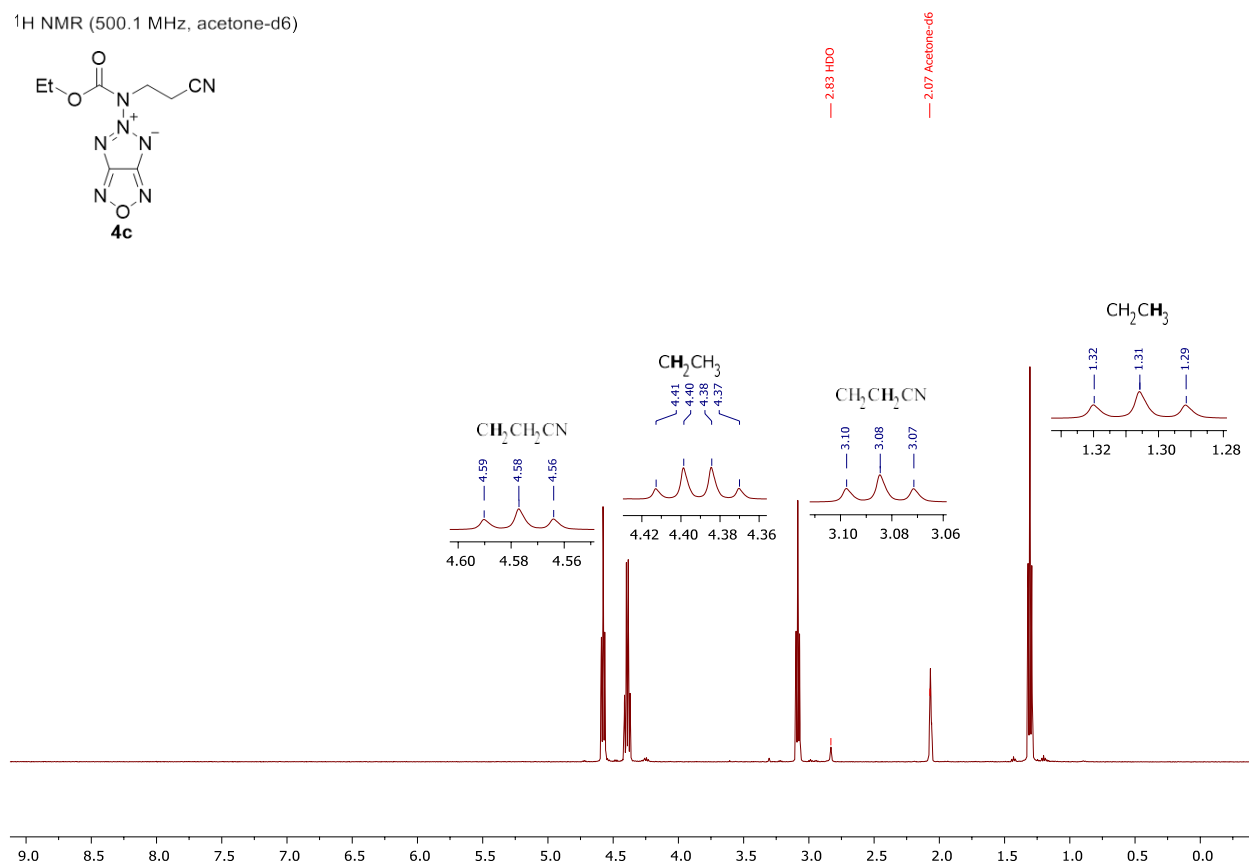
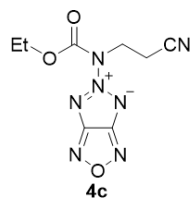


^{14}N NMR (36.1 MHz, acetone- d_6)

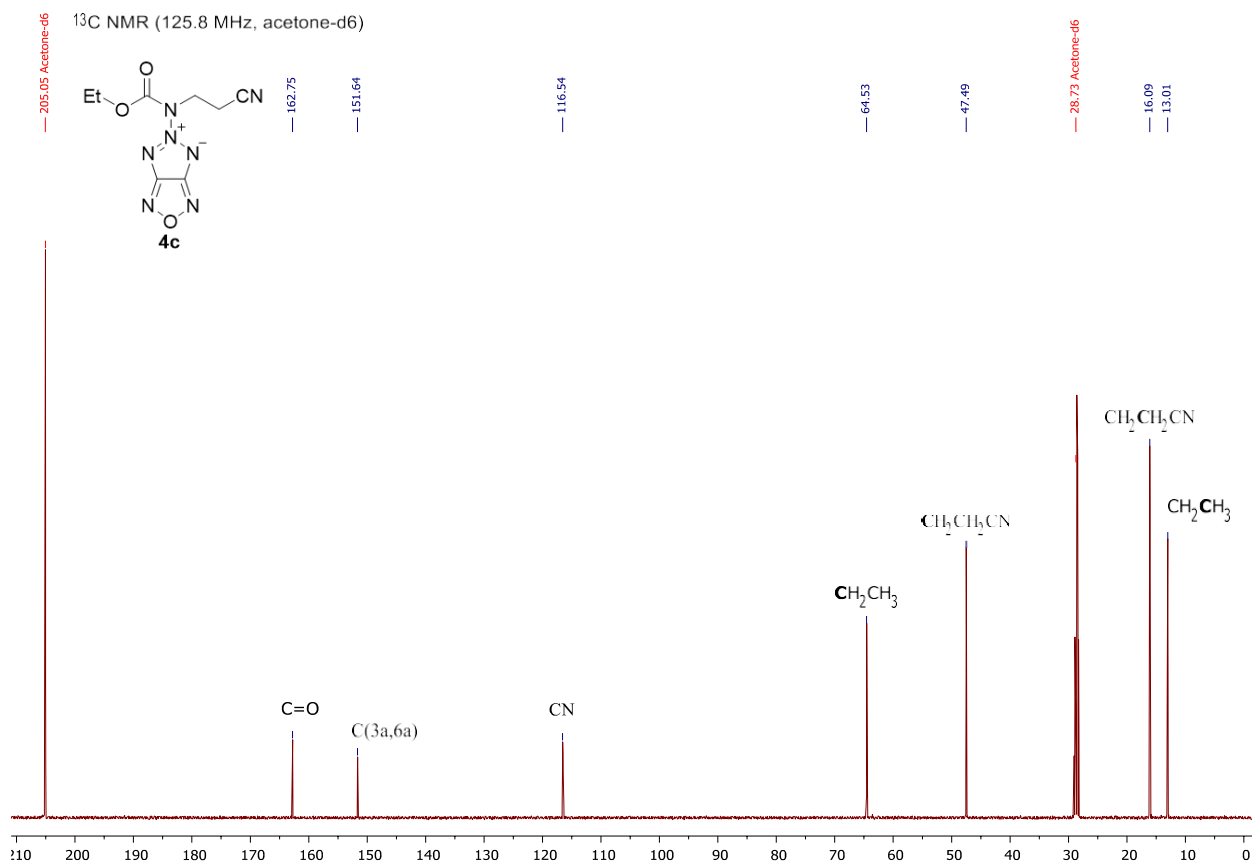
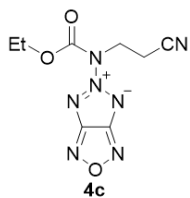


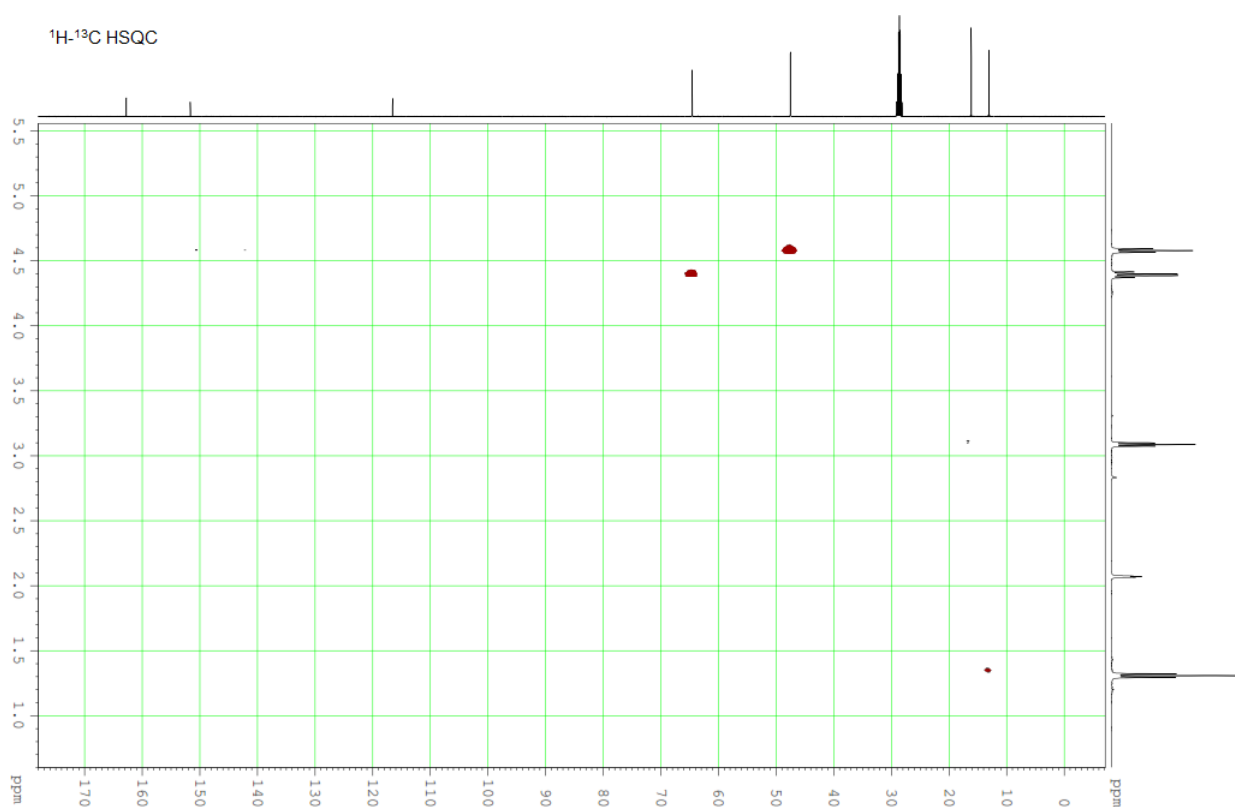
NMR and IR spectra for compound 4c

¹H NMR (500.1 MHz, acetone-d₆)

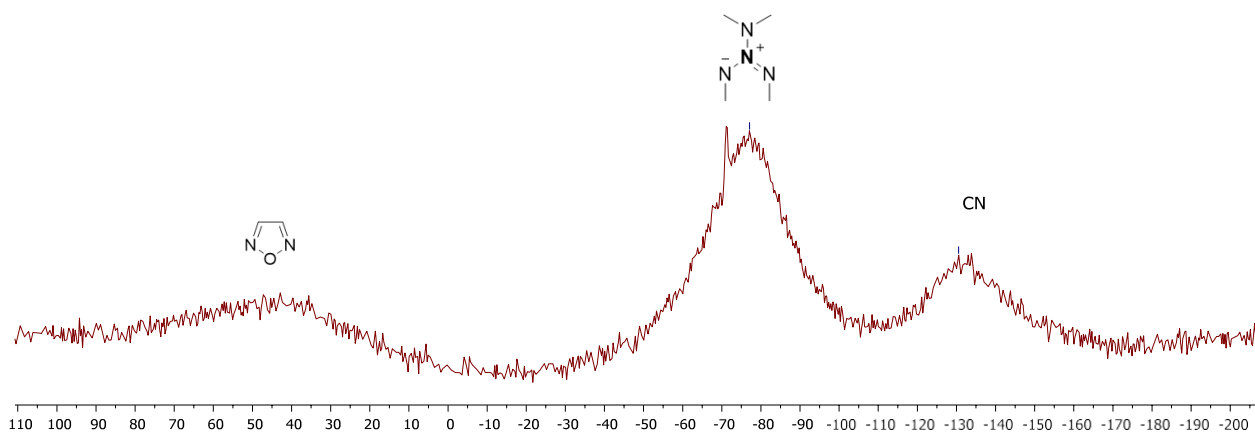
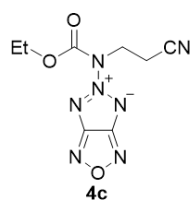


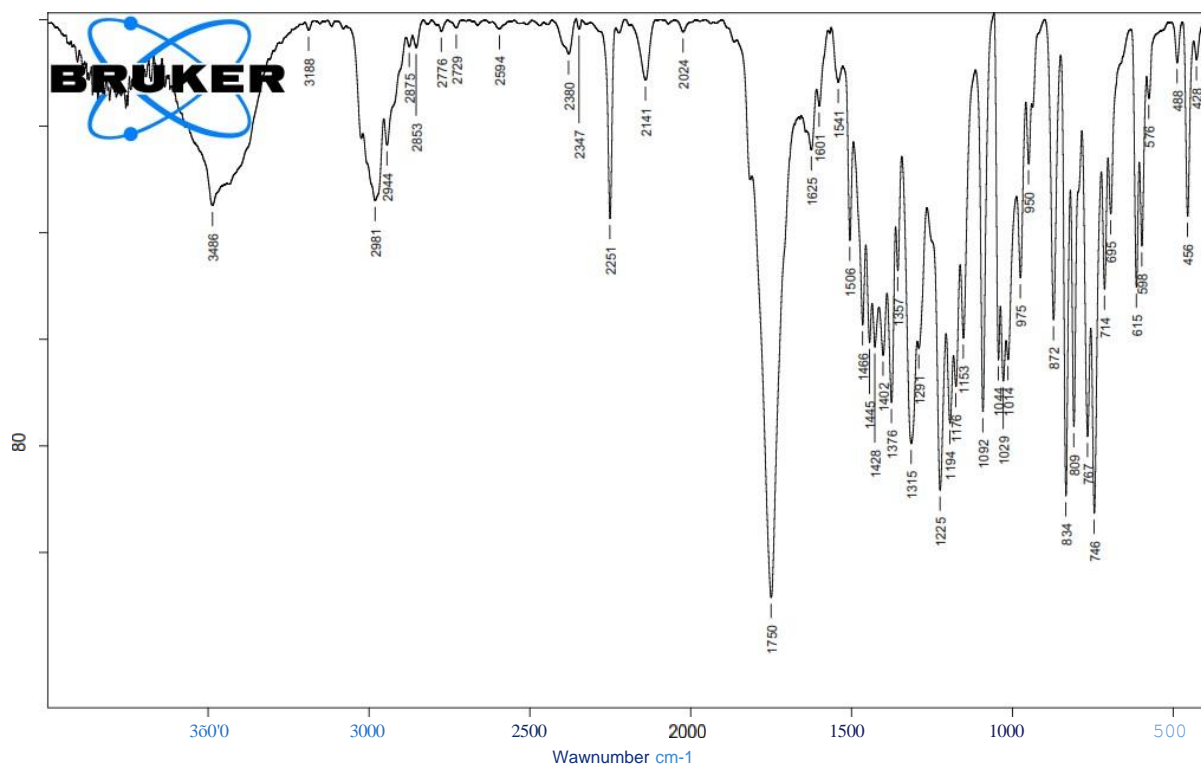
¹³C NMR (125.8 MHz, acetone-d₆)





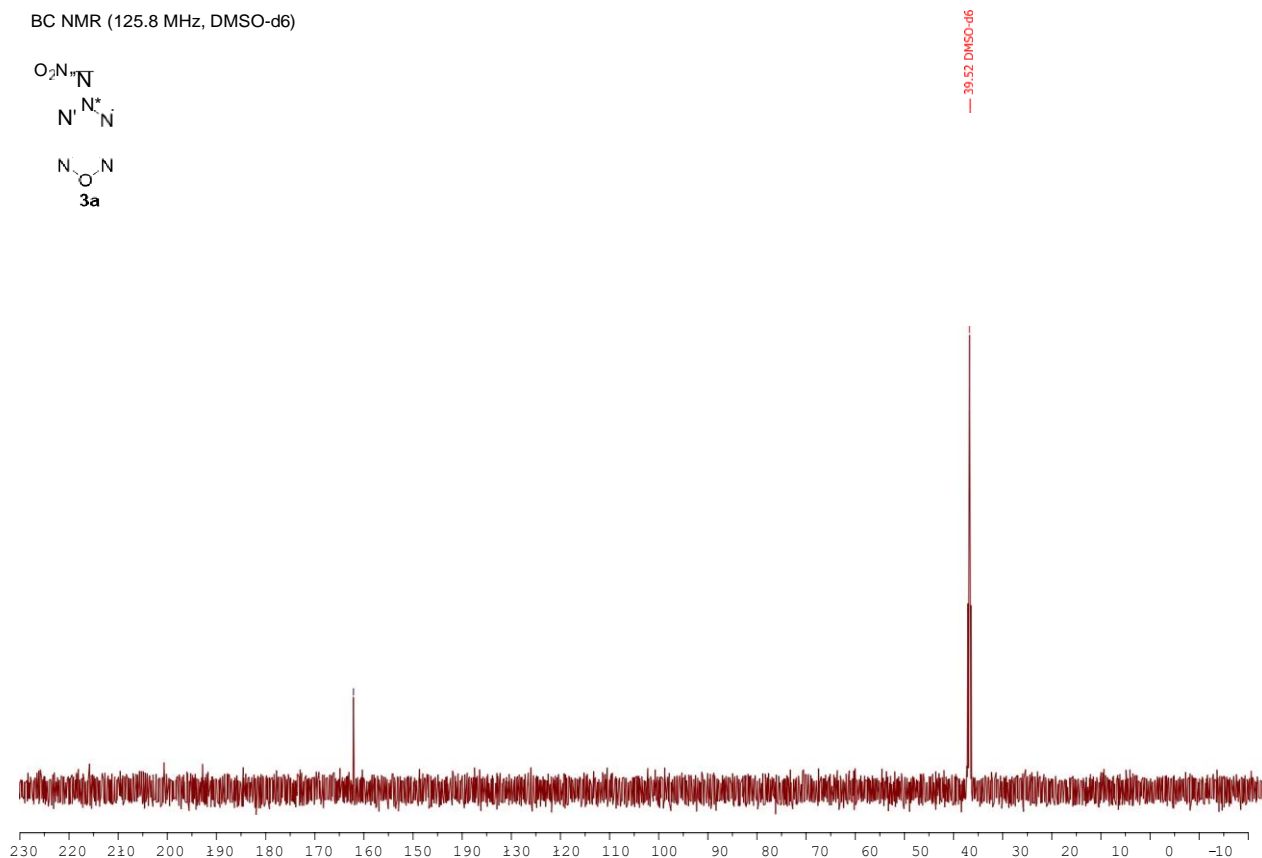
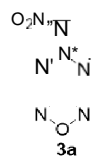
¹⁴N NMR (36.1 MHz, acetone-d₆)



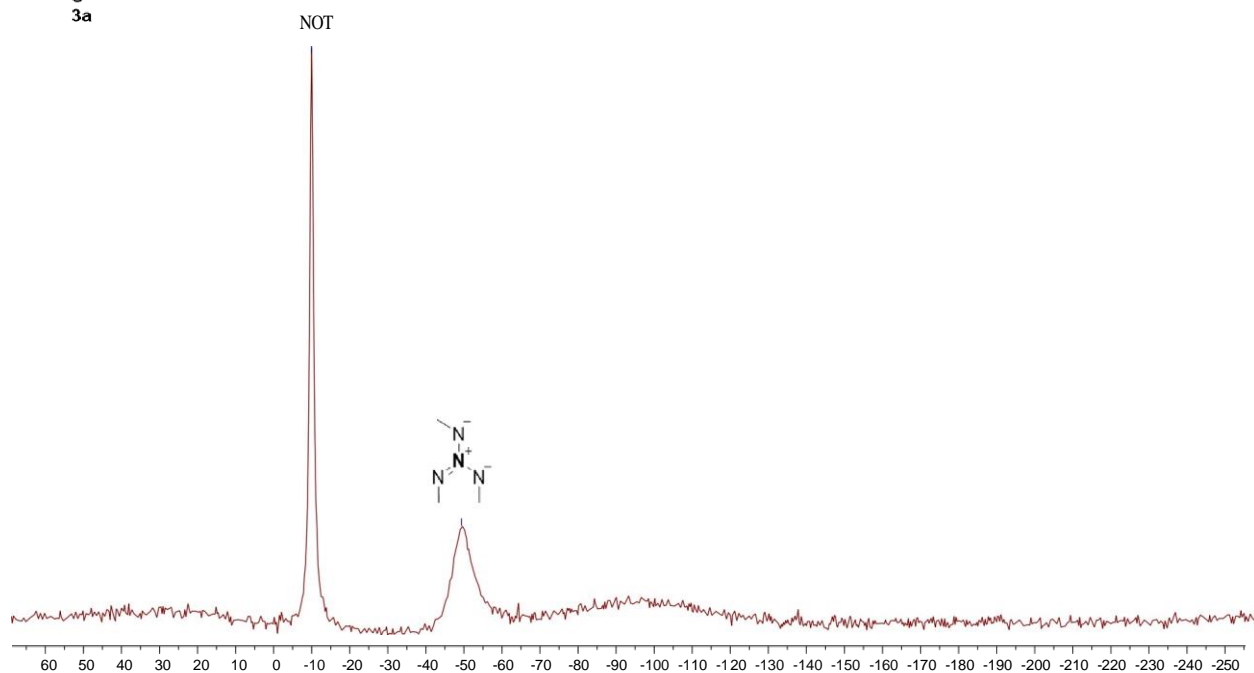
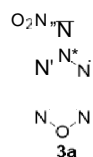


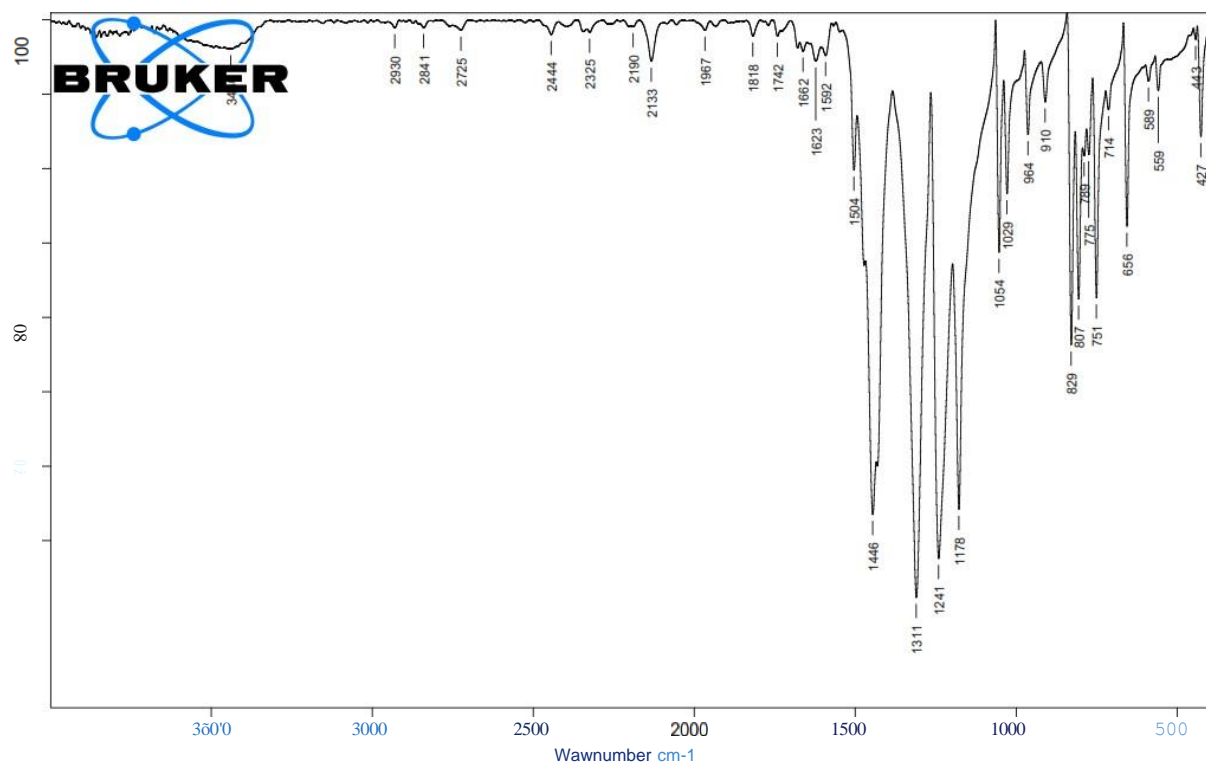
NMR and IR spectra for compound 3a

BC NMR (125.8 MHz, DMSO-d6)

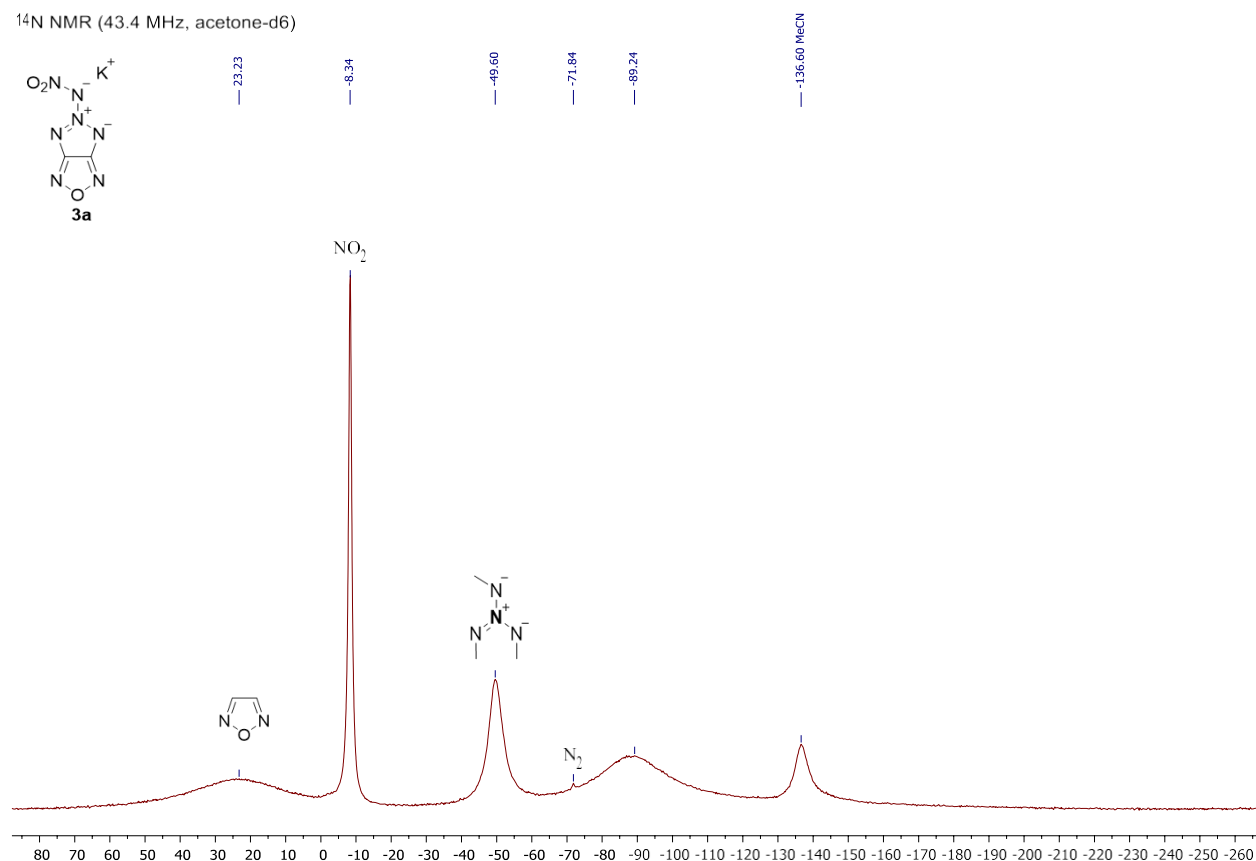
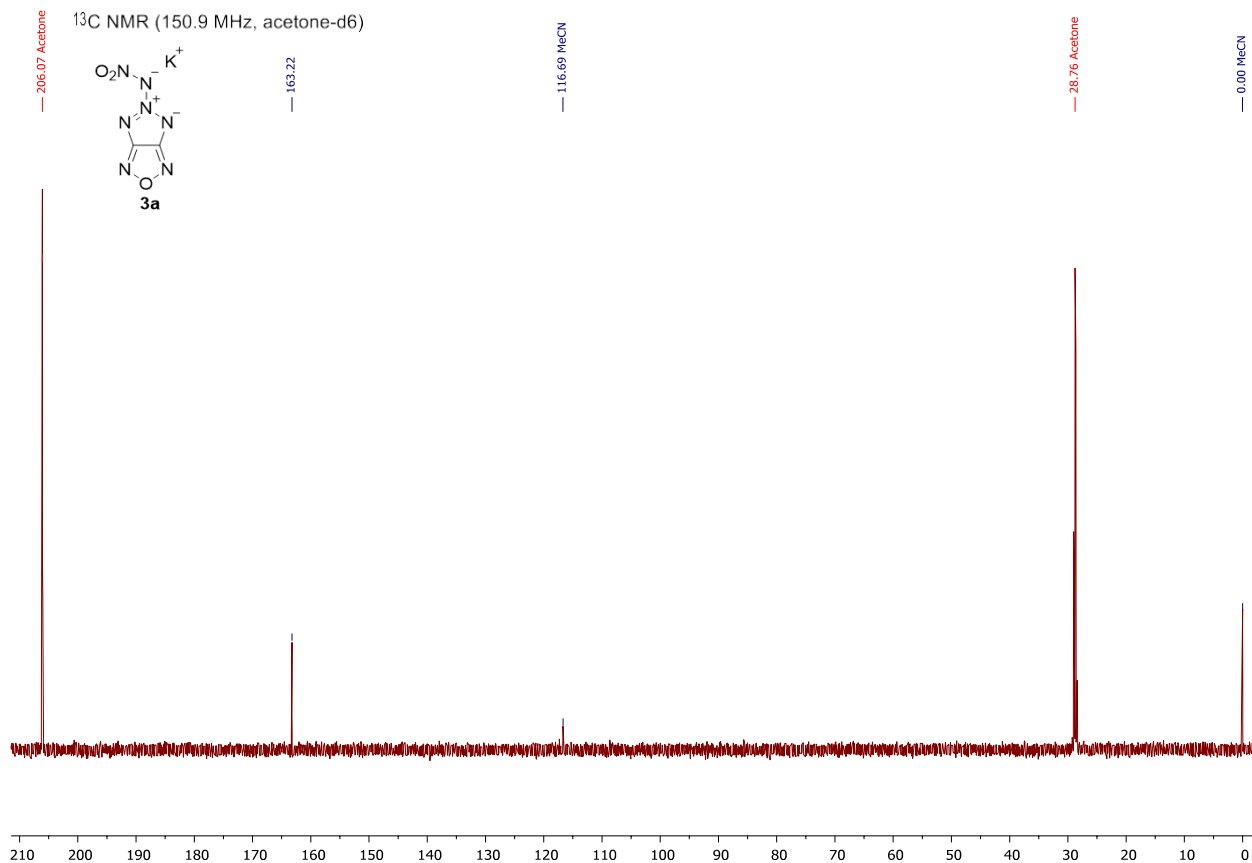


^{14}N NMR (36.1 MHz, DMSO-d6)

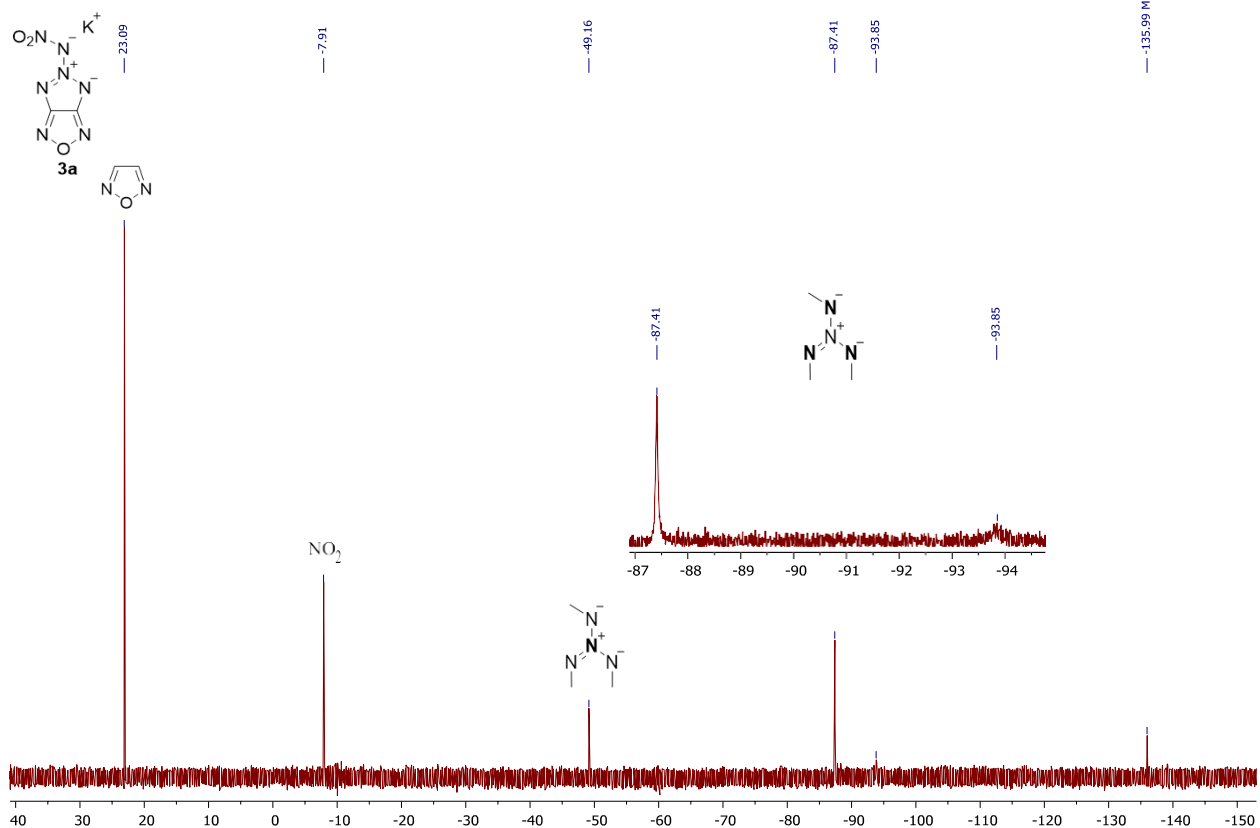




NMR spectra for compound 3a – MeCN complex

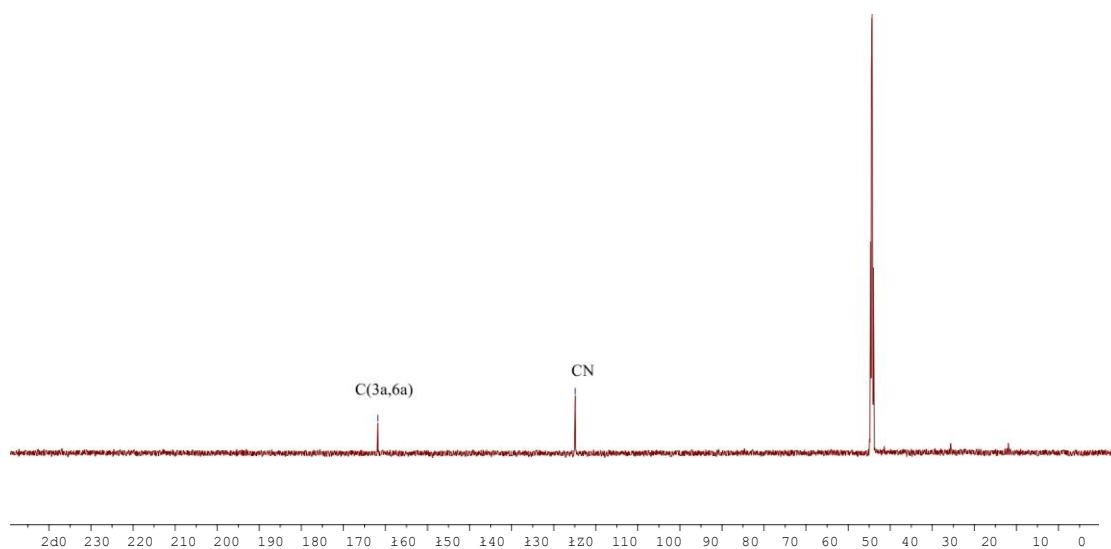


^{15}N NMR (60.8 MHz, acetone- d_6)

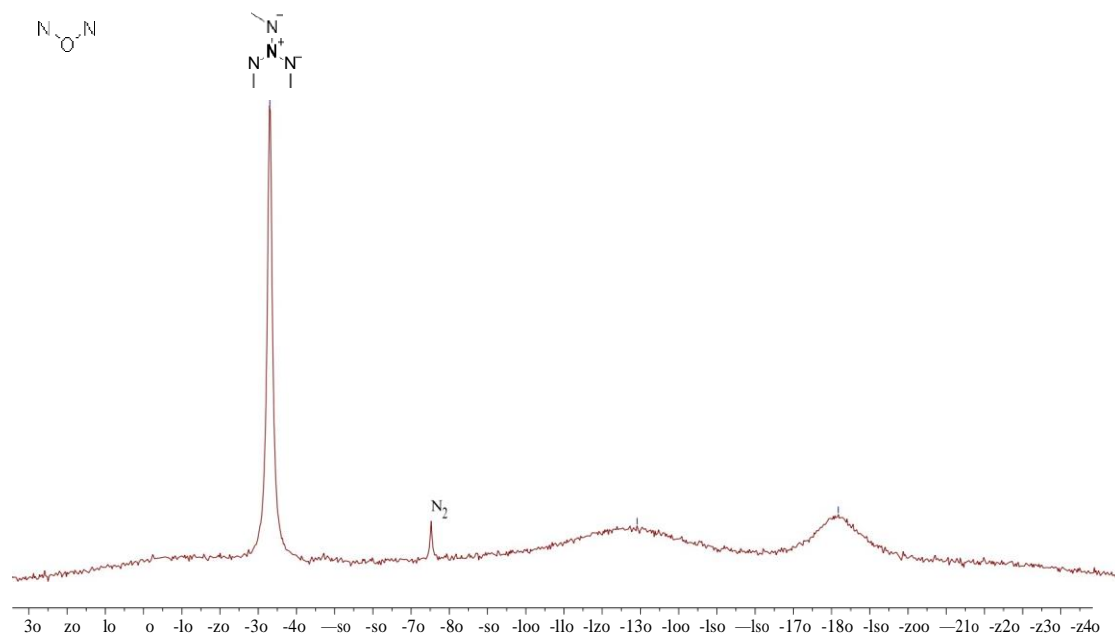


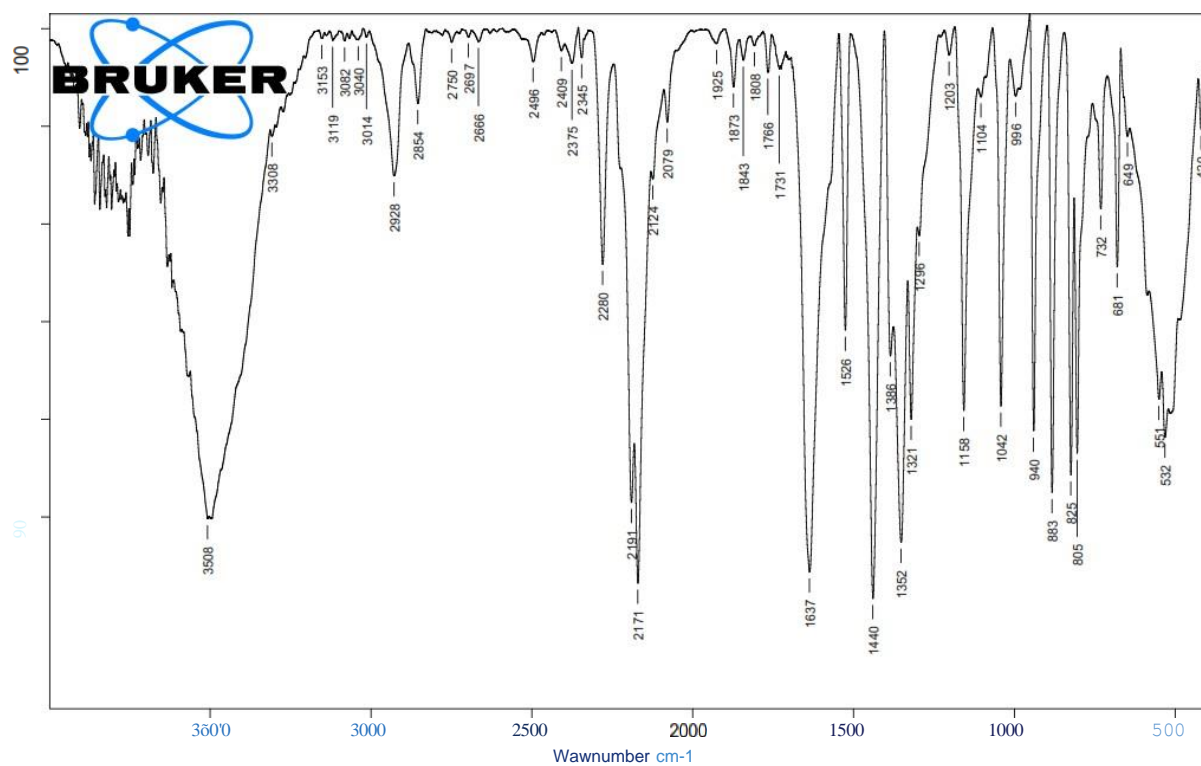
NMR and IR spectra for compound 3b

¹³C NMR (150.9 MHz, methanol-d₄)



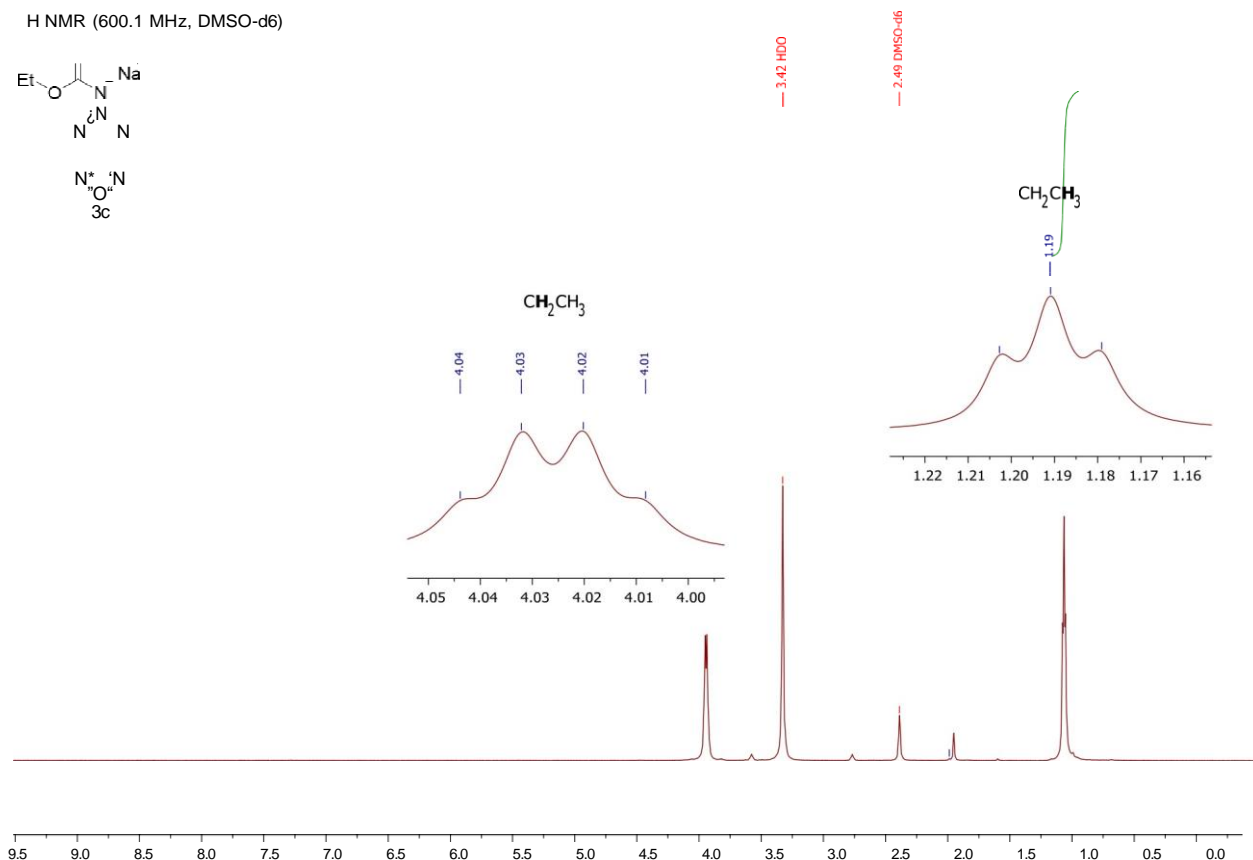
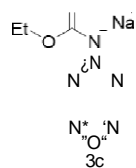
¹⁴N NMR (36.1 MHz, methanol-d₄)



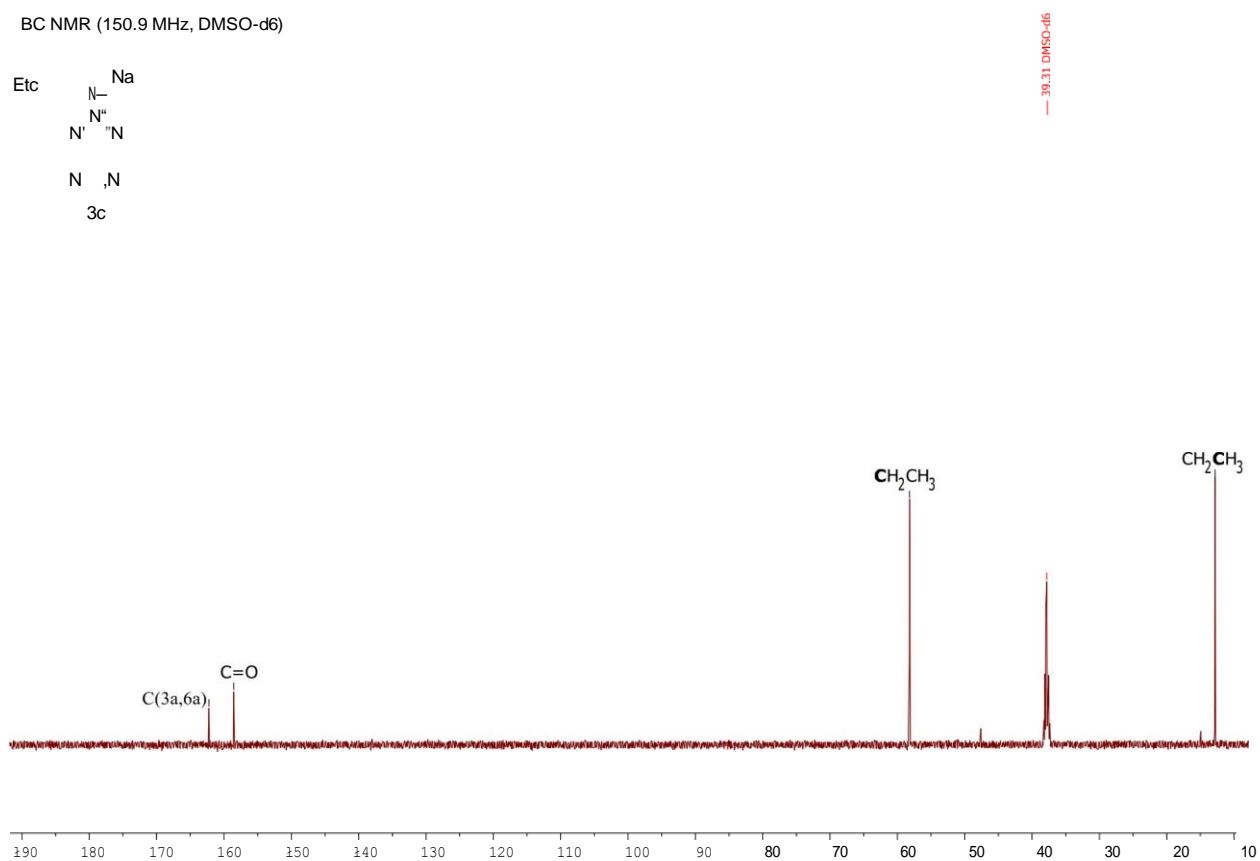
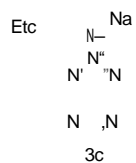


NMR and IR spectra for compound 3c

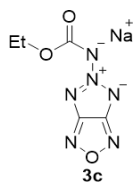
¹H NMR (600.1 MHz, DMSO-d₆)



¹³C NMR (150.9 MHz, DMSO-d₆)



¹⁴N NMR (43.4 MHz, DMSO-d₆)



-29.36

