Cyanotetrazolylborohydride (CTB) Anion-Based Ionic Liquids with low viscosity and high density as ultra-short-ignition Hypergolic Fuels

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1. General information

Reagents.

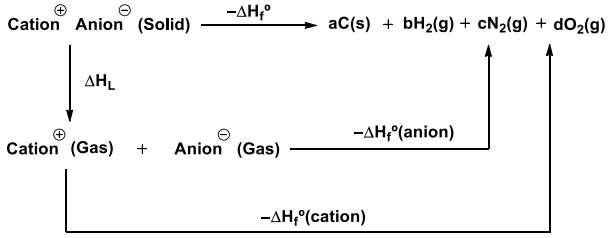
$NaBH_3CN$ 95% (Energy Chemical), 1*H*-Tetrazole 98% (Adamas), Allyl Bromide 99% (Adamas), 1-Ethyl-3-methylimidazolium chloride 98% (Adamas), 1-Butyl-3-methylimidazolium chloride 99% (Adamas), 1-Allyl-3-Methylimidazolium Chloride 96% (Adamas), 1-Butyl-1-Methylpyrrolidinium Bromide 97% (Adamas), 1-Ethyl-1-Methylpyrrolidinium Bromide 97% (Adamas), 7, 1-Ethylpyridinium Bromide 99% (Adamas), 1-Butylpyridinium Bromide 99% (Adamas), 1-allylpyridinium bromide was synthesized according to the reported methods.[1]

Characterization.

^1H, ^{13}C, ^{11}B NMR spectra were recorded on Bruker 400 AVANCE spectrometer (400, 101, 128 MHz, respectively). IR spectra were performed on IRAffinity-1s. High resolution mass spectra were performed on Bruker Apex IV FTMS. Elemental analysis was performed on EA3000. Thermal property measurements were performed on DSC-60. The densities of ionic liquids were measured on analytical balance and 2 mL volumetric flask at 25 °C. The viscosity measurements were performed on AR2000ex at 25 °C. The heat of formation were calculated by Explo5 (version 6.02) software. Ignition of HILs with WFNA and N_2O_4 were recorded with Fastcam SA4 high speed camera.

2. Computational methods for heats of formation.

Heat of formation of cations were calculated using the Gaussian 09 and isodesmic reaction (Table S1).[2] The geometric optimization of the structures and frequency analyses were accomplished by using the B3LYP with the 6—31+G** basis set,[3] and single-point energies were calculated at the MP2/6—311++G** level and G2 method. Heat of formation (HOF) of all the ILs were calculated based on the Born–Haber energy cycle (Scheme S1). Lattice energies were predicted by using the approach of Jenkins et al (see Eqs. (1)(2)(3)).[4] Where ΔH_L is the lattice energy of the salt; ΔH_f^θ is the heats of formation; U_{POT} is the lattice potential energy; ρ is the density; Mw is the formula weight; n_M and n_X depend on the ions Mp^{q+} and Xq^{p-} of salt MpXq; R is the constant, 8.314 mol K^{-1}; T is the thermodynamic temperature at 298 K.



Scheme S1. Born-Harber cycle for the formation of ionic liquids

$$\Delta H_f^\theta\,(ionic\ salt, 298\,K) = \sum \Delta H_f^\theta\,(cation, 298\,K) + \sum \Delta H_f^\theta\,(anion, 298\,K) - \Delta H_L \quad (1)$$

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

$$U_{POT}\,(kJ\ mol^{-1}) = 1981.2\,(\rho_m / M_m)^{1/3} + 103.8 \quad (3)$$

Table S1. Isodesmic reactions for the HOFs calculation of cations and anions.

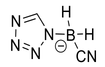
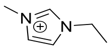
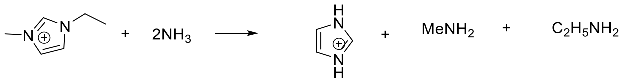
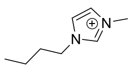
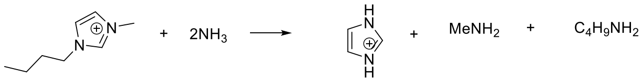
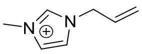
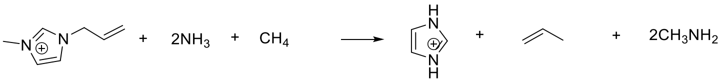
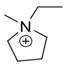
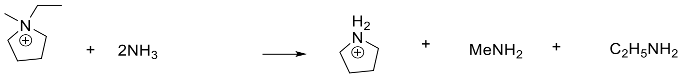
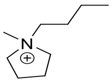
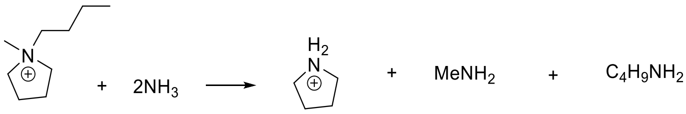
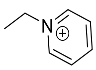
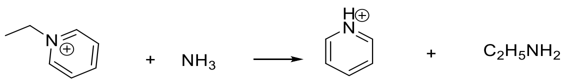
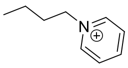
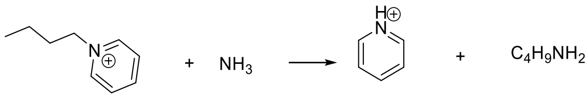
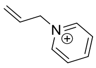
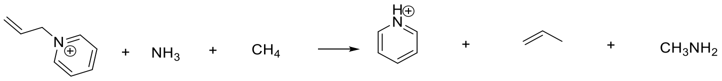
ions	Isodesmic reaction
	
	
	
	
	
	
	
	
	

Table S2. Enthalpies of gas-phase species of cations and anions (based on G2 method).

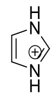
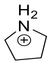
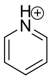
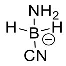
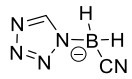
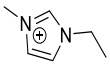
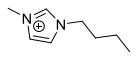
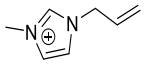
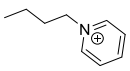
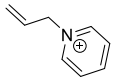
ions	ΔH_f (kJ·mol^{-1})
	722.6
	577.2
	750.3
	115.3
BH_4^-	-58.6
BH_3CN^-	-80.7
$BH_2(CN)_2^-$	-67.5

Table S3. Enthalpies of the gas-phase species of anions and cations based on isodesmic reactions.

Ions	E(MP2)[a]	ZPE[b]	TCH[c]	ΔH_{corr}	ΔH_f (kJ·mol^{-1})
	-375.933225	0.067265	0.075056	-375.8608600	88.0
	-343.756386	0.169167	0.178517	-343.5846353	618.9
	-422.188502	0.225904	0.237989	-421.9595496	555.9
	-381.727693	0.173998	0.184102	-381.5505509	786.7
	-330.1034381	0.22918	0.238961	-329.8736443	476.2
	-408.535176	0.285905	0.298521	-408.2480915	414.4
	-326.525480	0.158887	0.167085	-326.3647501	668.0
	-404.957555	0.215666	0.226631	-404.7395502	651.2
	-364.5180790	0.163696	0.172677	-364.351950	780.2

a) Total energy calculated by B3LYP/6-31+G** method (Hartree/Particle); b) Zero-point correction (Hartree/Particle); c) Thermal correction to enthalpy (Hartree/Particle) d) Heat of formation (kJ/mol).

Table S4. The calculated HOFs of ionic liquids.

HILs	ΔH_{cation}(kJ·mol^{-1})	ΔH_{anion}(kJ·mol^{-1})	ΔH_{lat}(kJ·mol^{-1})	ΔH_{salt}(kJ·g^{-1})
1-CTB	618.9	88.0	450.0638	1.172
2-CTB	555.9	88.0	434.6624	0.847
3-CTB	786.7	88.0	447.0118	1.851
4-CTB	476.2	88.0	445.4365	0.535
5-CTB	414.4	88.0	431.3559	0.284
6-CTB	668.0	88.0	456.6667	1.385
7-CTB	651.2	88.0	438.9421	1.230
8-CTB	780.2	88.0	450.4487	1.832

3. Synthesis of hypergolic ionic liquids

Synthesis of $NaBH_2CN(tetz)$.
Sodium cyanoborohydride (6.284 g, 100 mmol) was added with stirring to 70 mL of toluene in 250 mL round-bottom flask. Then 1H-tetrazole (7.075 g, 101 mmol) of was added. Then the flask was fitted with a reflux condenser and the slurry was reflux 4 hours under Ar atmosphere with continuous rapid stirring. The solution was cooled and the solid was collected on filter paper. Then the solid was recrystallized from THF/ dioxane. And dried in vacuum to yield 10.536 g (81% yield). ^{1}H NMR (400 MHz, D_2O) δ .8.80 (s, 2H), 3.50 – 2.00 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6). δ 150.60, 139.51 (m). ^{11}B (128 MHz, D_2O) δ –24.24 (t, *J* = 102.0 Hz). HRMS (ESI) m/z: $[M]^-$ calcd for $C_2H_3BN_5^-$:108.0487, Found: 108.0488.

*General procedure for preparation of ionic liquids (**1-CTB** – **8-CTB**):*
Synthesis of salt 1: 1-Ethyl-3-methylimidazolium chloride (2.932 g, 20 mmol) was dissolved in 30 mL CH_3CN at room temperature, and then Na**CTB** (3.141 g, 24 mmol) was added. The reaction was stirred for 7 days, then the insoluble solid was filtrated and the solvent was evaporated. The residual substance was extracted with 20 mL of dichloromethane and the solution was washed three time with 1 mL distilled water. And then the dichloromethane was evaporated under reduced pressure. The product was vacuum dried at 50 °C for 24 h to reduce any traces of water and then subjected to further characterization.

1-CTB: Colorless liquid, 81% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.77 (s, 1H), 8.65 (s, 1H), 7.42 – 7.30 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.20-2.10 (m, 2H), 1.45 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, D_2O) δ 147.82, 135.40, 123.39, 121.80, 44.75, 35.59, 14.38. ^{11}B (128 MHz, D_2O) δ −24.78 (t, *J* = 101.1 Hz). IR (KBr): *v* = 3480, 3152, 3115, 2988, 2403, 2320, 2195, 1568, 1470, 1356, 1101; HRMS (ESI) m/z: $[M]^+$ calcd for $C_6H_{11}N_2^+$: 111.0917, found: 111.0916. $[M]^-$ calcd for $C_2H_3BN_5^-$: 108.487, found: 108.0483. Anal. calcd for $C_8H_{14}BN_7$: C 43.86, H 6.44, N 44.76; found: C 44.24, H 5.92, N 44.06.

2-CTB: Colorless liquid, 87% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.79 (s, 1H), 8.67 (s, 1H), 7.43– 7.37 (m, 2H), 4.14 (t, *J* = 5.6 Hz, 2H), 3.87 (s, 3H), 3.20-2.10 (m, 2H), 1.82 – 1.75 (m, 2H), 1.29 – 1.23 (m, 2H), 0.88 (t, *J* = 5.2 Hz, 3H). ^{13}C NMR (100 MHz, D_2O) δ 147.84, 135.71, 123.42, 122.15, 49.24, 35.59, 31.21, 18.71, 12.57; ^{11}B (128 MHz, D_2O) δ −24.75 (t, *J* = 101.4 Hz). IR (KBr): *v* = 3468, 3150, 3113, 2965, 2938, 2876, 2403, 2195, 1574, 1470, 1167; HRMS (ESI) m/z: $[M]^+$ calcd for $C_8H_{15}N_2^+$: 139.1230, found: 139.1225. $[M]^-$ calcd for $C_2H_3BN_5^-$: 108.487, found: 108.484. Anal. calcd for $C_{10}H_{18}BN_7$: C 48.61, H 7.34, N 39.68; found: C48.43, H, 7.29, N 38.96.

3-CTB: Colorless liquid, 82% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.78 (s, 1H), 8.68 (s, 1H), 7.41 (s, 2H), 6.05 – 5.96 (m, 1H), 5.43 – 5.32 (m, 2H), 4.77 (d, *J* = 6 Hz, 2H), 3.88 (s, 3H), 3.20-2.10 (m, 2H). ^{13}C NMR (100 MHz, D_2O) δ 147.85, 135.36, 130.26, 123.51, 122.18, 121.06, 51.44, 35.65. ^{11}B (128 MHz, D_2O) δ−24.75 (t, *J* = 102.7 Hz). IR (KBr): *v* = 3476, 3149, 3115, 2990, 2403, 2195, 1570, 1165, 1101; HRMS (ESI) m/z: $[M]^+$ calcd for $C_7H_{11}N_2^+$: 123.0917, found: 123.0915. $[M]^-$ calcd for $C_2H_3BN_5^-$: 108.487, found: 108.483. Anal. calcd for $C_9H_{15}BN_{10}$: C 46.78, H 6.11, N 42.43; found: C 46.42, H, 6.56, N 41.99.

4-CTB: yellow liquid, 85% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.82 (s, 1H), 3.46 – 3.37 (m, 6H), 3.00 (s, 3H), 2.88 – 2.10 (m, 2H), 2.18 (s, 4H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, D_2O) δ 147.93, 63.74, 59.52, 47.41, 21.27, 8.43. ^{11}B (128 MHz, D_2O) δ−24.72 (t, *J* = 102.8 Hz). IR (KBr): *v* = 3483, 3130, 2987, 2897, 2405, 2193, 1471, 1140, 1101; HRMS (ESI) m/z: $[M]^+$ calcd for $C_7H_{16}N^+$: 114.1277, found: 114.1277. $[M]^-$ calcd for $C_2H_3BN_5^-$: 108.487, found: 108.484. Anal. calcd for $C_9H_{19}BN_6$: C 48.67, H 8.62, N 37.84; found: C 48.65, H, 8.395, N 37.14.

5-CTB: Colorless liquid, 86% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.83 (s, 1H), 3.47 (s, 4H), 3.32 – 3.26 (m, 2H), 2.90 – 2.20 (m, 2H), 1.74 – 1.73 (m, 2H), 1.39 – 1.32 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, D_2O) δ 147.92, 64.20, 64.12, 48.01, 25.05, 21.26, 19.21, 12.76. ^{11}B (128 MHz, D_2O) δ −24.71 (t, *J* = 103.3 Hz). IR (KBr): *v* = 3543, 3128, 2967, 2878, 2401, 2193, 1456, 1140, 1100; HRMS (ESI) m/z: $[M]^+$ calcd for $C_9H_{20}N^+$: 142.1590, found: 142.1587. $[M]^-$ calcd for $C_2H_3BN_5^-$: 108.487, found: 108.484. Anal. calcd for $C_9H_{14}BN_9$: C 52.82, H 9.27, N 33.60; found: C 52.42, H, 9.38, N 33.94.

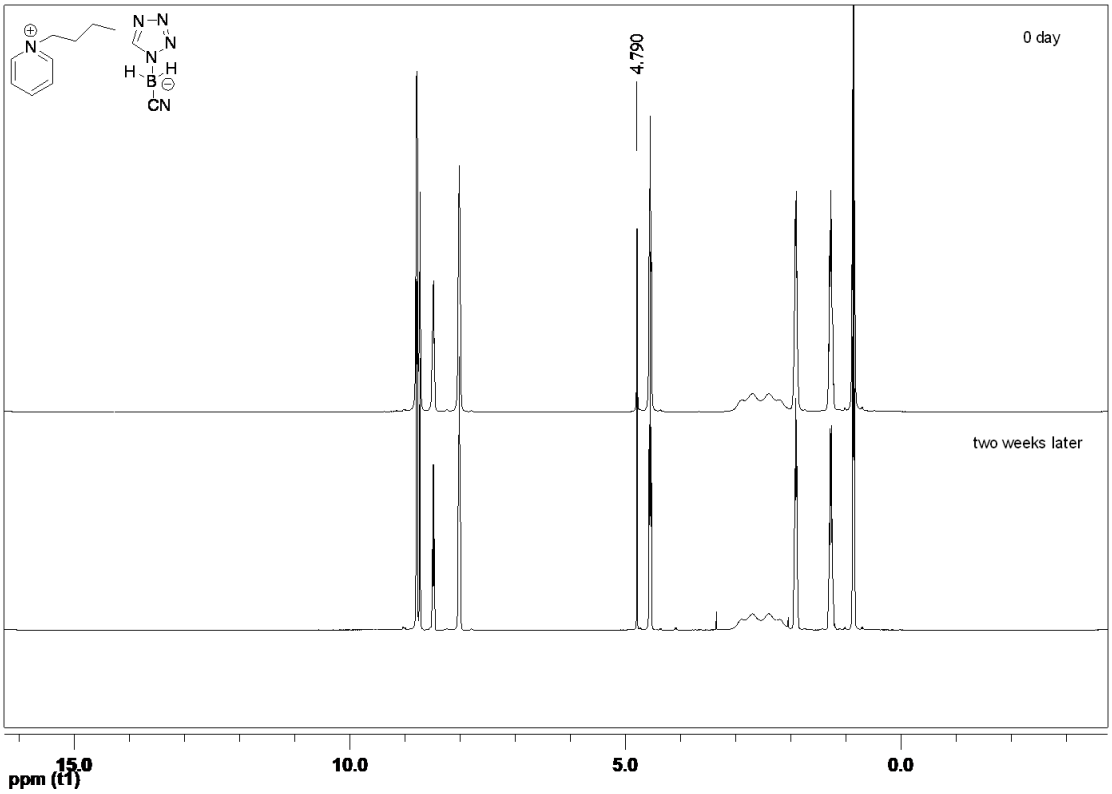
6-CTB: Colorless liquid, 89% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.83 –8.82 (m, 2H), 8.76 (s, 1H), 8.49 (s, 1H), 8.04 – 8.03 (m, 2H), 4.629 (q, *J* = 7.6 Hz, 2H), 3.2 – 2.1 (m, 2H), 1.62 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, D_2O) δ 147.84, 145.38, 143.83, 128.19, 57.32, 15.59. ^{11}B (128 MHz, D_2O) δ −24.76 (t, *J* = 102.0 Hz). IR (KBr): *v* = 3487, 3134, 3066, 2984, 2943, 2403, 21930, 1636, 1489, 1468, 1177, 1140, 1101; HRMS (ESI) m/z: $[M]^+$ calcd for $C_7H_{10}N^+$: 108.0808, found: 108.0804. $[M]^-$ calcd for $C_2H_3BN_5^-$: 108.487, found: 108.484. Anal. calcd for $C_{11}H_{18}BN_9$: C 50.03, H 6.07, N 38.90; found: C 49.61, H, 6.27, N 38.47.

7-CTB: Slight yellow liquid, 80% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.79 − 8.72 (m, 3H), 8.49 − 8.47 (m, 1H), 8.01 (s, 1H), 4.57 − 4.53 (m, 2H), 3.10 − 2.10 (m, 2H),), 1.912 (q, *J* = 7.2 Hz, 2H), 1.314 – 1.240 (m, 2H), 0.855 (t, *J* = 7.2 Hz,

3H). ^{13}C NMR (100 MHz, D_2O) δ 147.76, 145.42, 144.06, 128.17, 128.13, 61.71, 32.55, 18.39, 12.63. ^{11}B (128 MHz, D_2O) δ −24.75 (t, *J* = 101.2 Hz). IR (KBr): *v* = 3474, 3132, 3065, 2965, 2876 2401, 2193, 1637, 1489, 1179, 1099; HRMS (ESI) m/z: $[M]^+$ calcd for $C_9H_{14}N^+$: 136.1121, found: 136.1117. $[M]^-$ calcd for $C_2H_3BN_5^-$: 108.487, found: 108.484. Anal. calcd for $C_{10}H_{14}BN_9$: C 54.12, H 7.02, N 34.43; found: C 53.60, H, 7.25, N 33.97.

8-CTB Slight yellow liquid, 83% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.80 – 8.73 (m, 3H), 8.54 – 8.50 (m, 1H), 6.15 – 6.05 (m, 1H), 5.53 – 5.42 (m, 2H), 5.20 (d, *J* = 6.0 Hz, 2H), 3.00 – 2.00 (m, 2H). ^{13}C NMR (100 MHz, D_2O) δ 147.80, 145.89, 144.14, 129.75, 128.23, 122.07, 63.42. ^{11}B (128 MHz, D_2O) δ−24.76 (t, *J* = 101.4 Hz). IR (KBr): *v* = 3447, 31309, 3065, 2990, 2401, 2322, 2193, 1634, 1487, 1141, 1101; HRMS (ESI) m/z: $[M]^+$ calcd for $C_8H_{10}N_9^+$: 120.0808, found: 120.0809. $[M]^-$ calcd for $C_2H_3BN_5^-$: 108.487, found: 108.484. Anal. calcd for $C_{10}H_{14}BN_9$: C 52.66, H 5.75, N 36.85; found: C 52.32, H, 6.01, N 36.45.

4. Hydrolysis study of hypergolic ionic liquids



5. Reference

[1] a) M. Toure, O. Chuzel, J. Parrain, *J. Am. Chem. Soc.* **2012**, *134*, 17892–17895. b) S. Kulchat, J. Lehn, *Chem. Asian J.* **2015**, *10*, 1861 - 4728.

[2] Gaussian09, RevisionA.02; M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. K. Staroverov, R., J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox Gaussian, Inc., Wallingford CT: **2009**.

[3] R. G. Parrr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.

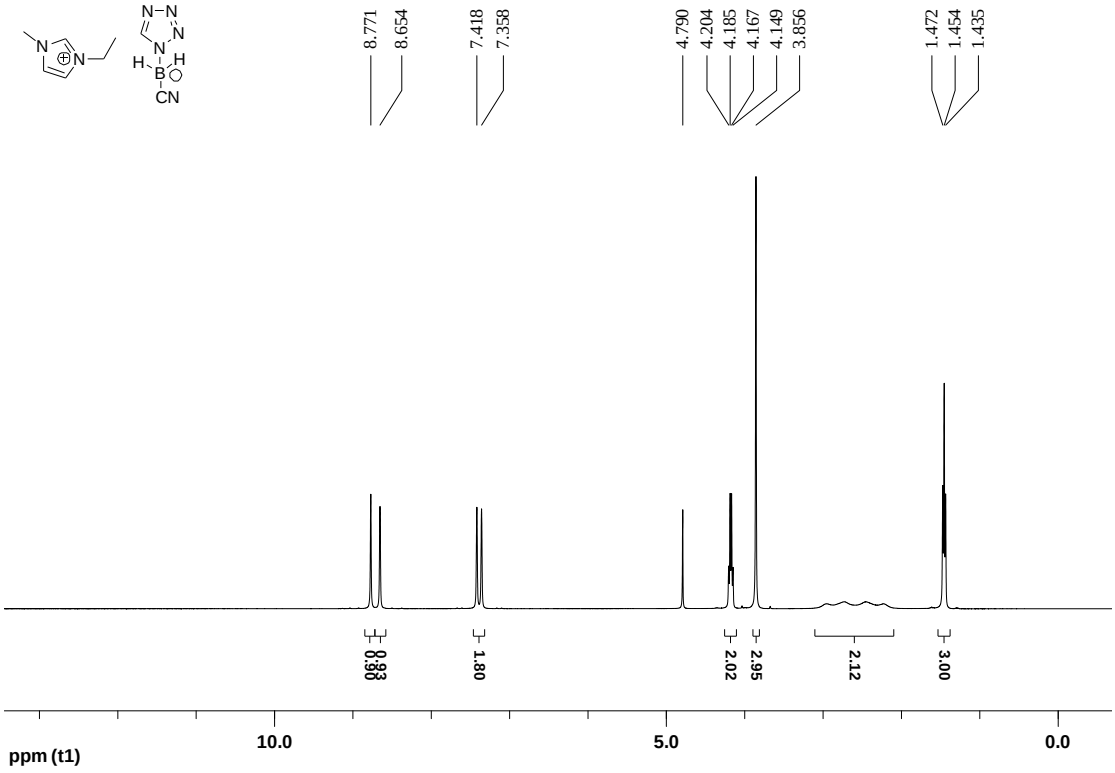
[4] H. D. Jenkins, D. Tudeal, L. Glasser, *Inorg. Chem.* **2002**, *41*, 2364 - 2367.

6. The crystallographic data of NaCTB

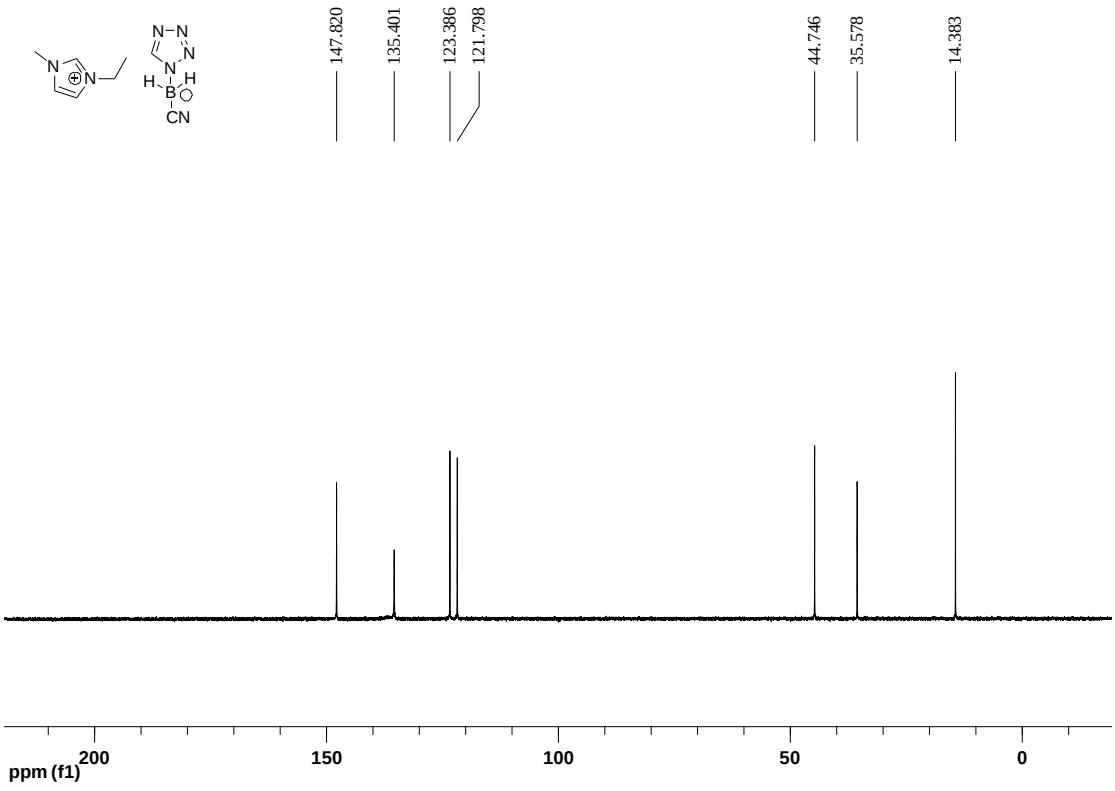
Table S4. Crystallographic data for Na**CTB**

CCDC	1548762
Formula	C32H59B4N20Na4O8
Mr	987.15
crystal system	triclinic
space group	$p2_1/c$
a [Å]	8.9975(8)
b [Å]	15.9489(15)
c [Å]	9.1643(9)
α [Å]	90.00
β [Å]	105.000(2)
γ [Å]	90.00
V [$Å^3$]	1270.3(2)
Z	14
T [K]	296(2)
ρ_{calcd} [$mg \cdot m^{-3}$]	1.406
M [mm^{-1}]	0.206
F(000)	532
θ [°]	2.30 - 31.48
index range	$-13 \leq h \leq 13$
	$-23 \leq K \leq 23$
	$-13 \leq l \leq 12$
reflections collected	13813
independent reflections (Rint)	11907
data/restraints/paraneters	13813/4/641
GOF on F2	1.140
R1 [$I > 2\sigma(I)$]	0.0806
wR2 [$I > 2\sigma(I)$]	0.1994
R1(all data)	0.0806
wR2(all data)	0.2138
largest diff. peak and hole [e $Å^{-3}$]	3.384 and -0.936

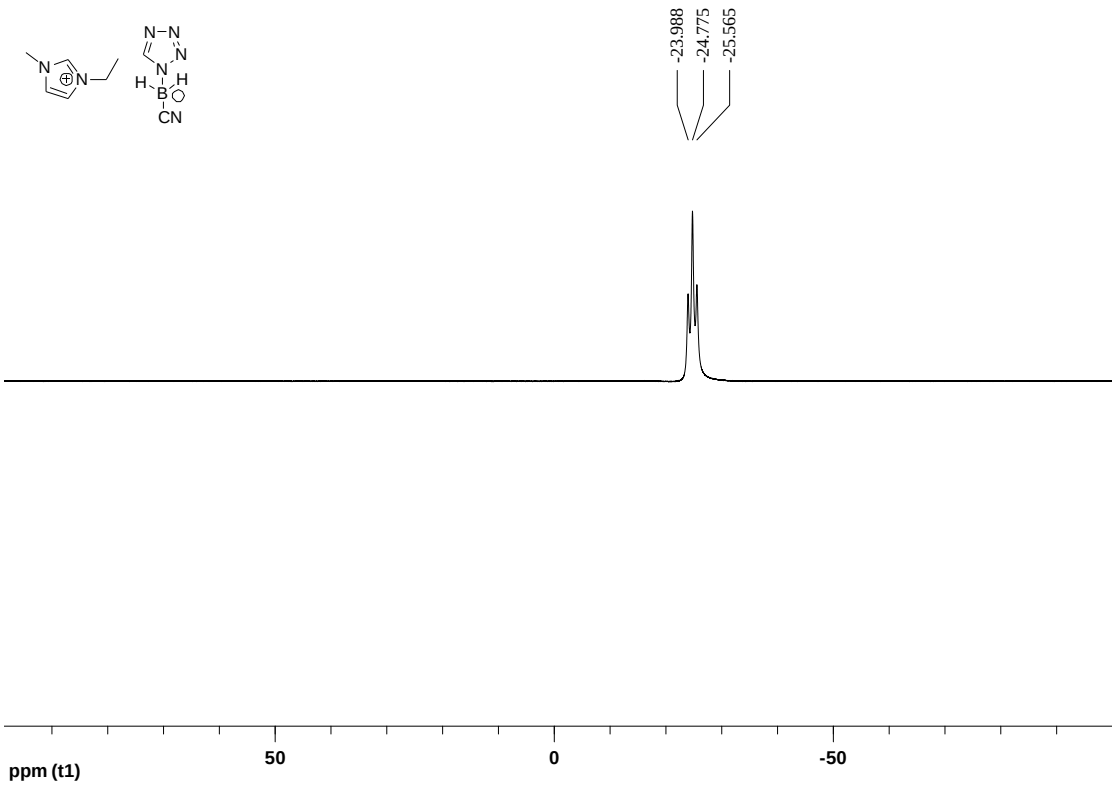
7. Copies of NMR, IR, HRMS Spectra and DSC.



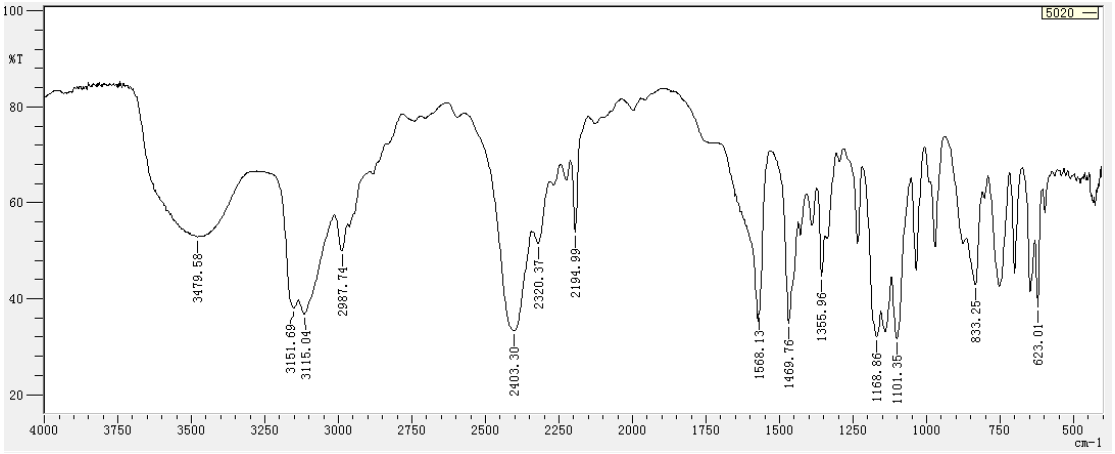
^{1}H NMR spectrum of **1-CTB**



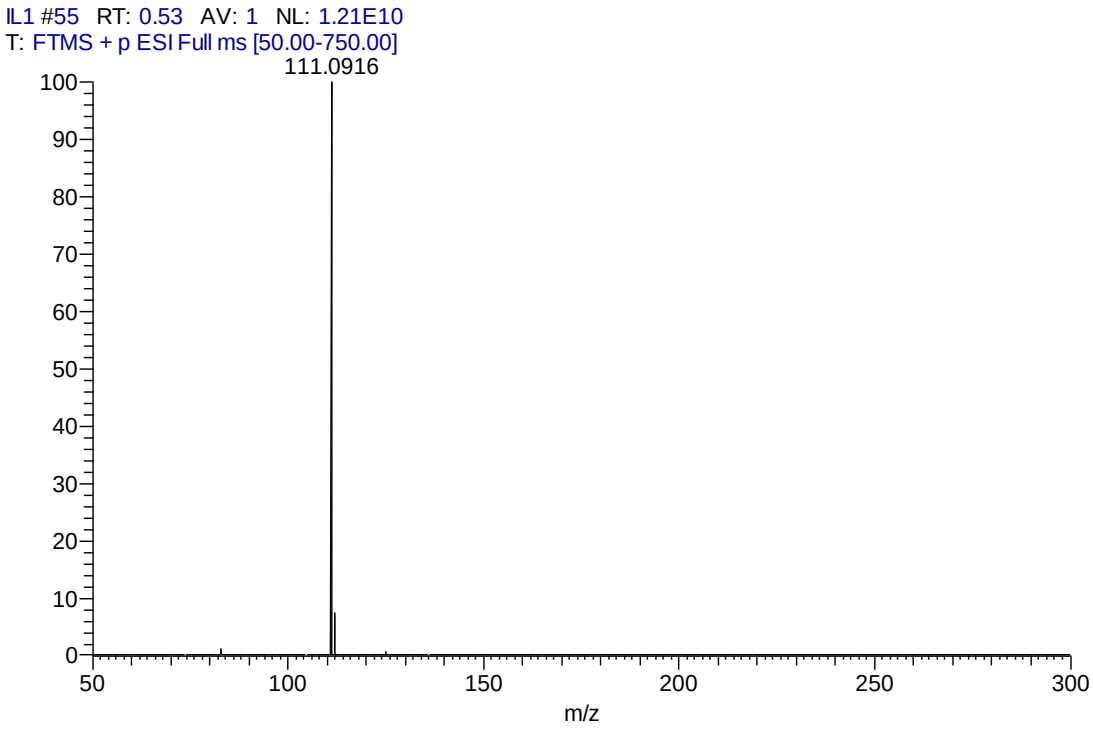
^{13}C NMR spectrum of **1-CTB**



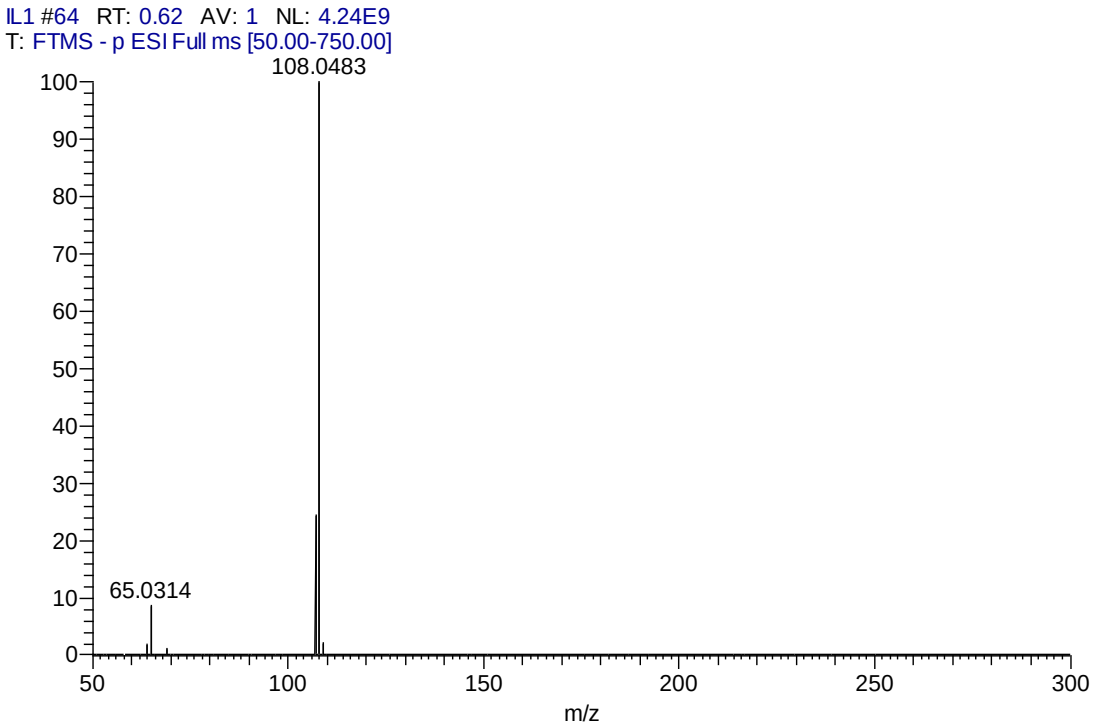
^{11}B NMR spectrum of **1-CTB**



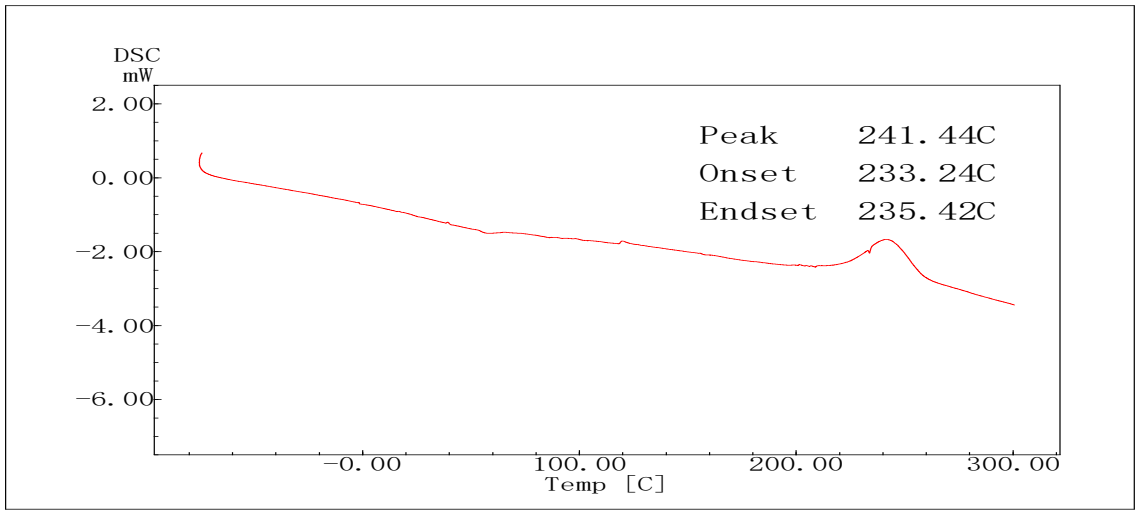
IR spectrum of **1-CTB**



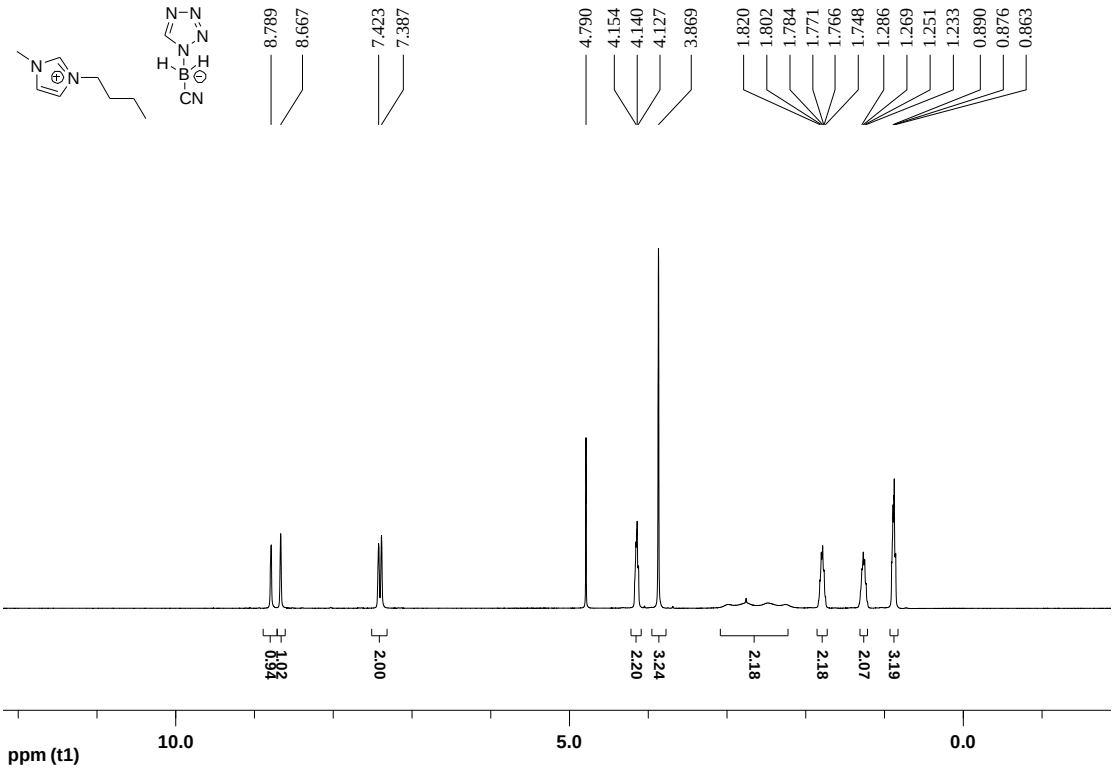
HRMS: cation of compound **1**-**CTB**



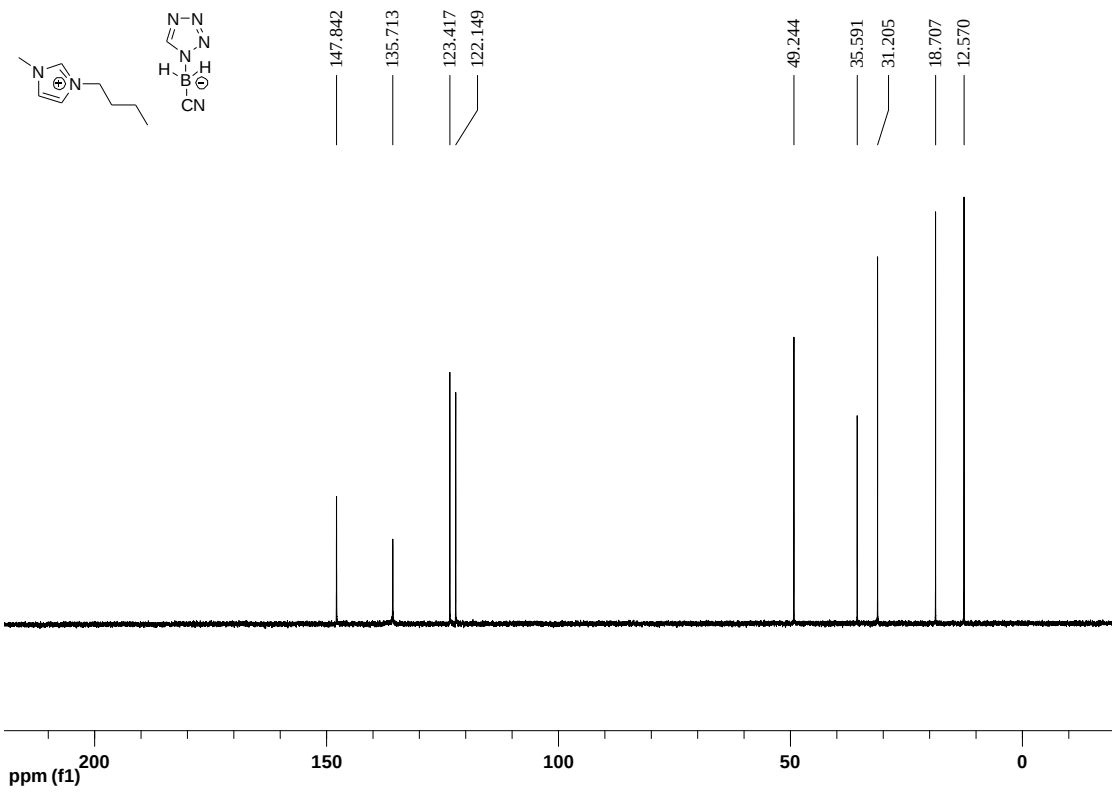
HRMS: anion of compound **1**-**CTB**



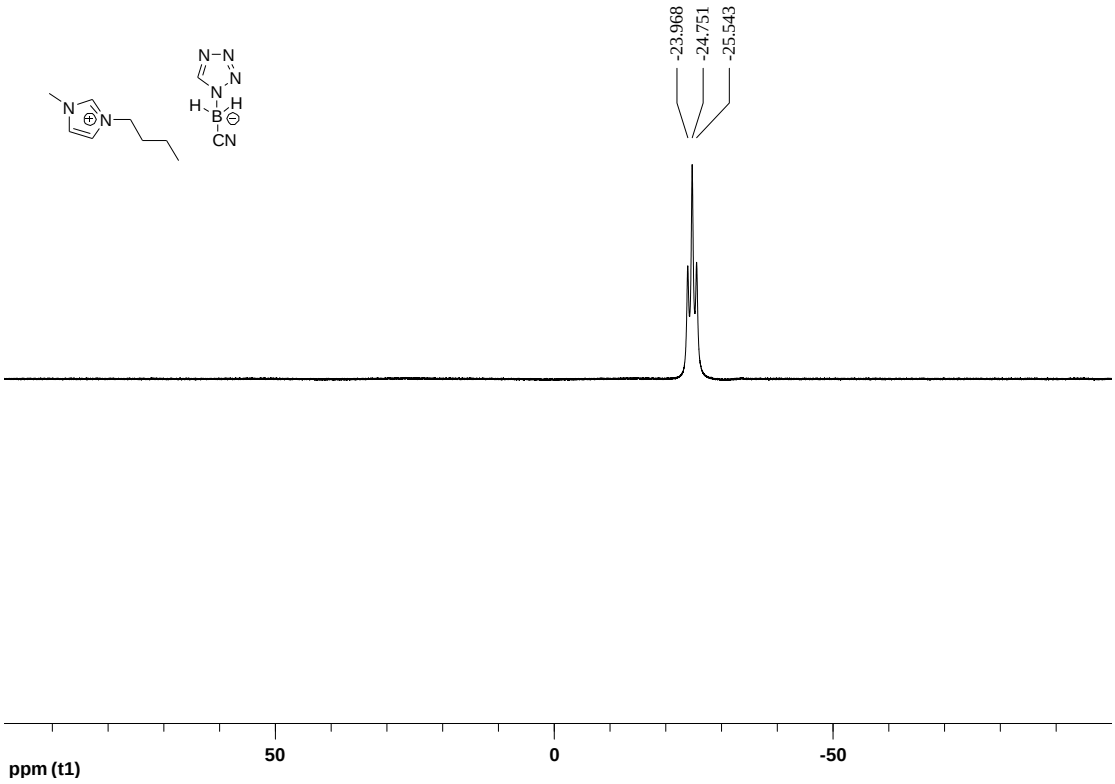
DSC of compound **1-CTB** at a scan of 5 °C min^{-1} under nitrogen atmosphere



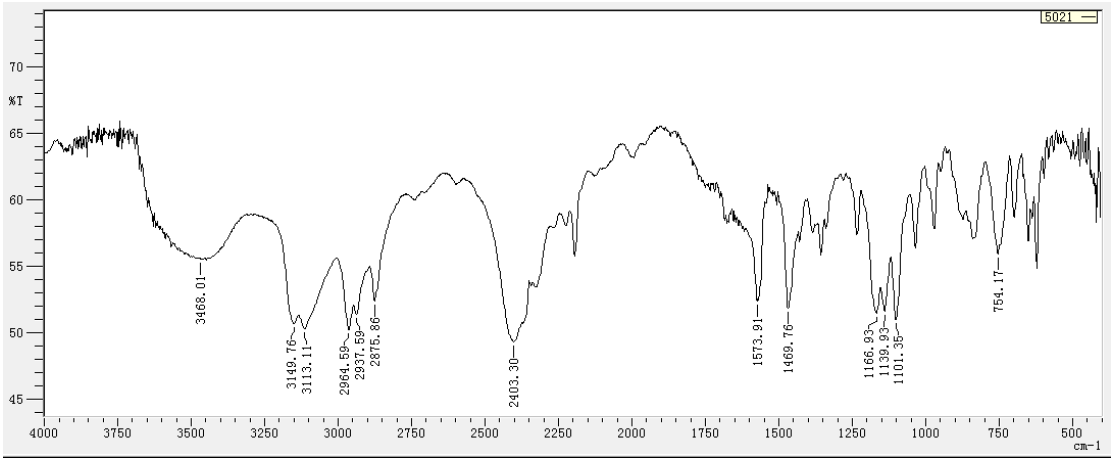
^{1}H NMR spectrum of **2-CTB**



^{13}C NMR spectrum of **2-CTB**

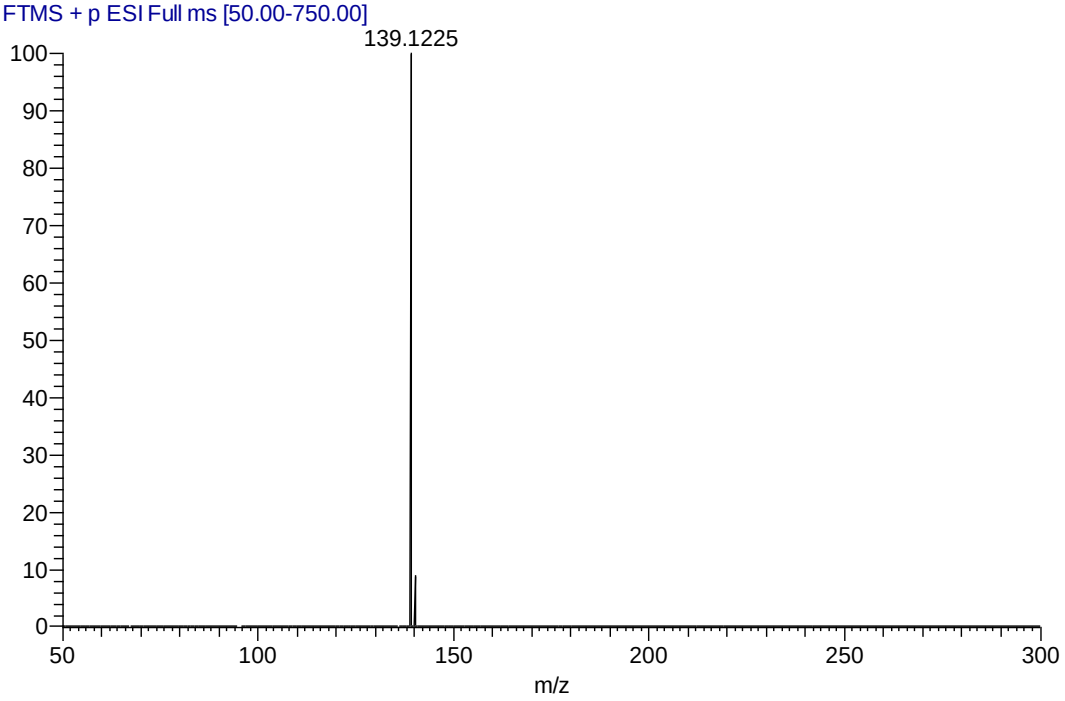


^{11}B NMR spectrum of **2-CTB**

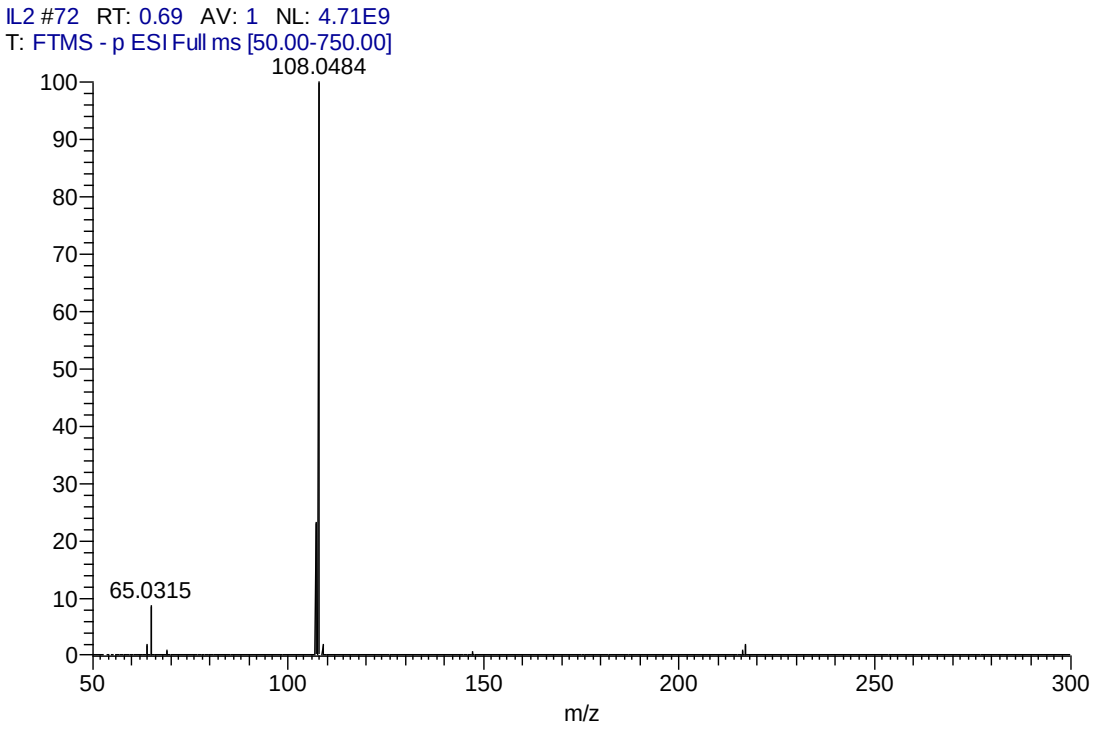


IR spectrum of **2-CTB**

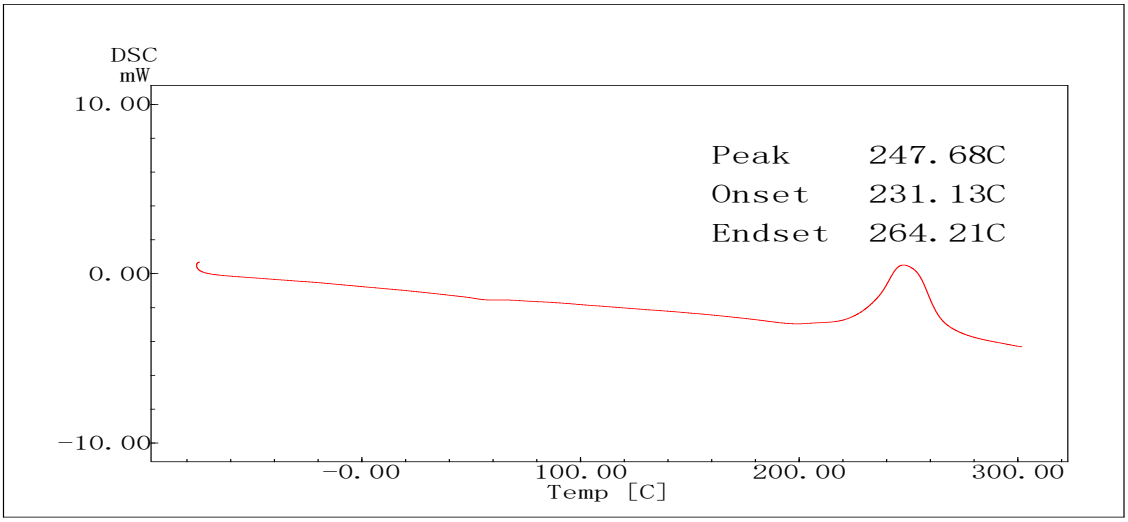
IL2 #73 RT: 0.70 AV: 1 NL: 1.86E10
T: FTMS + p ESI Full ms [50.00-750.00]



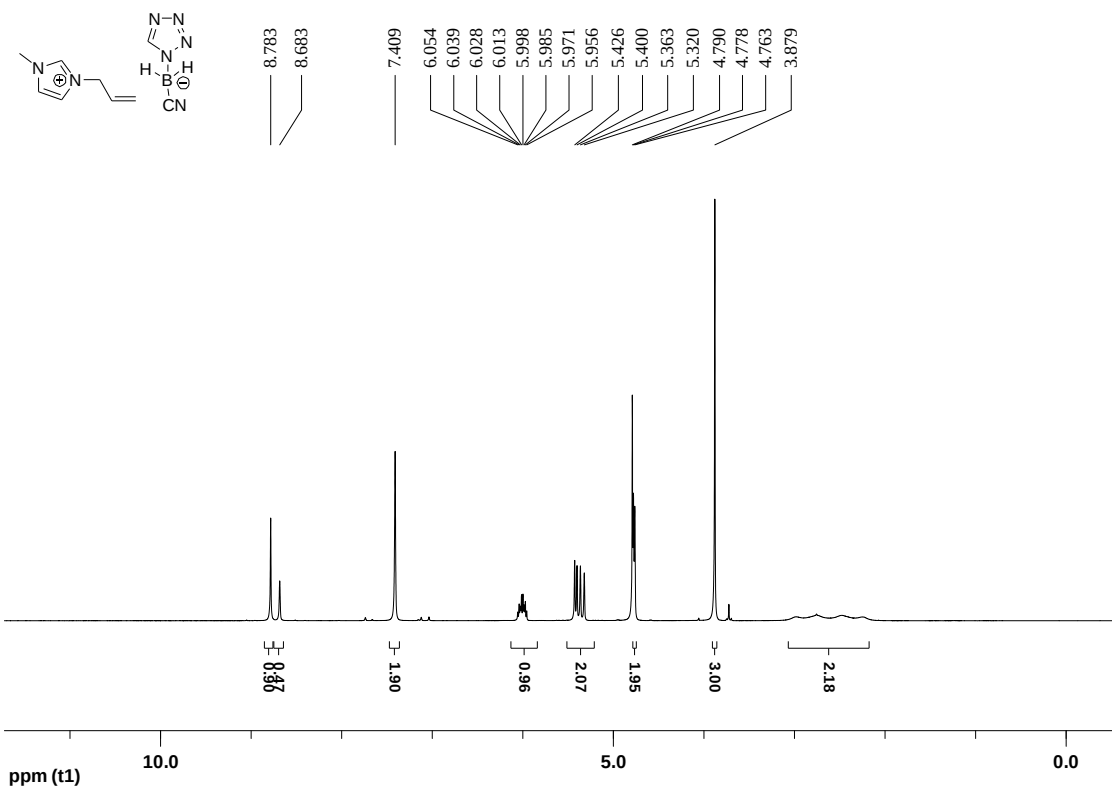
HRMS: cation of compound **2-CTB**



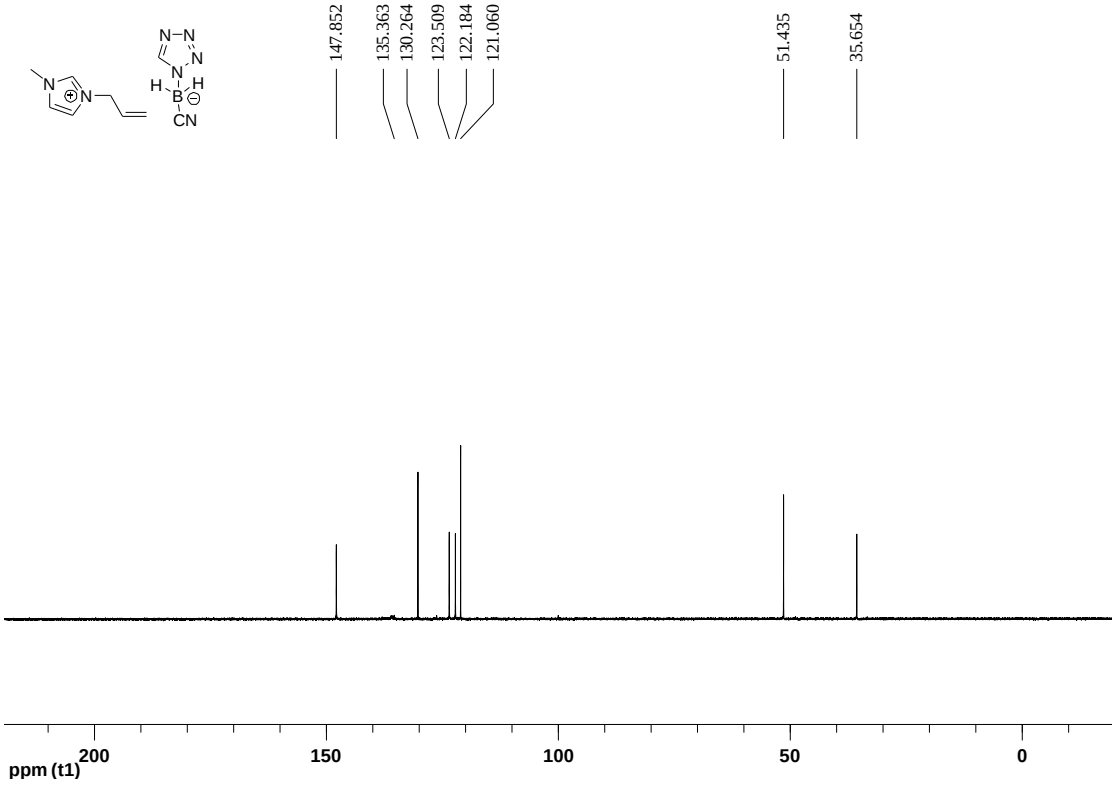
HRMS: anion of compound **2-CTB**



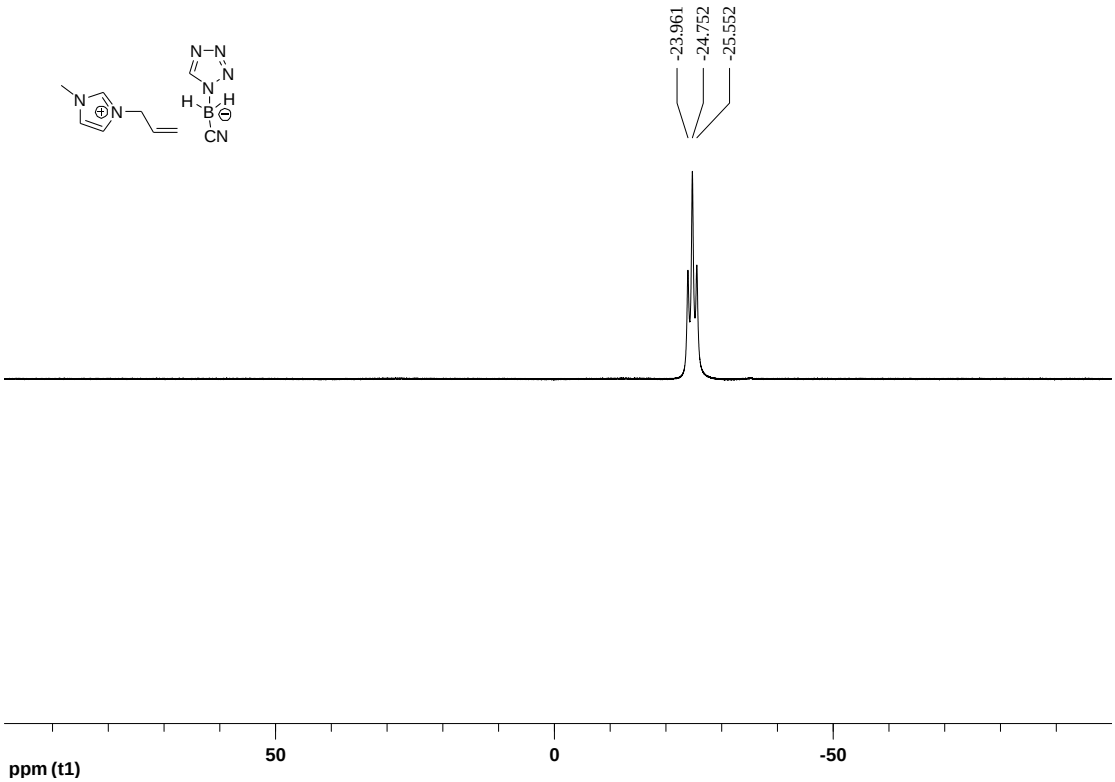
DSC of compound **2-CTB** at a scan of 5 °C min^{-1} under nitrogen atmosphere



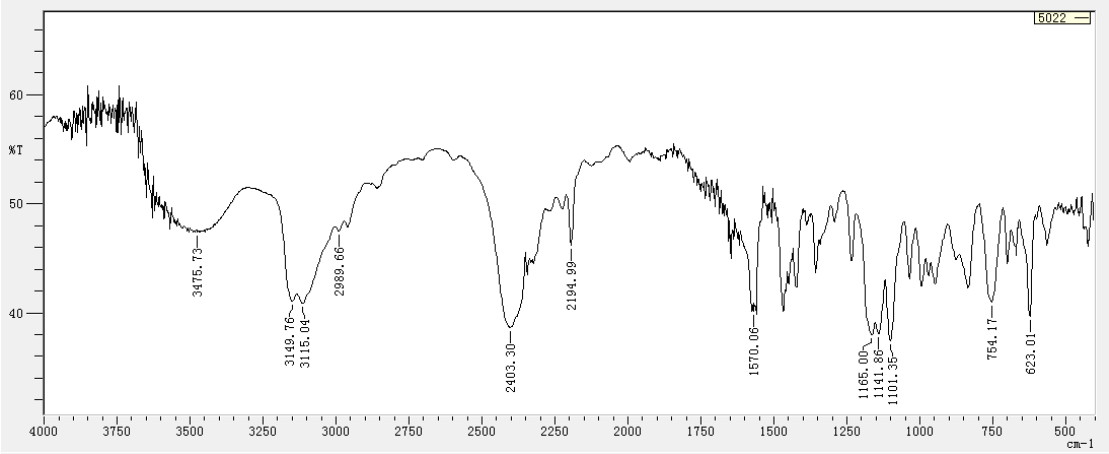
^{1}H NMR spectrum of **3-CTB**



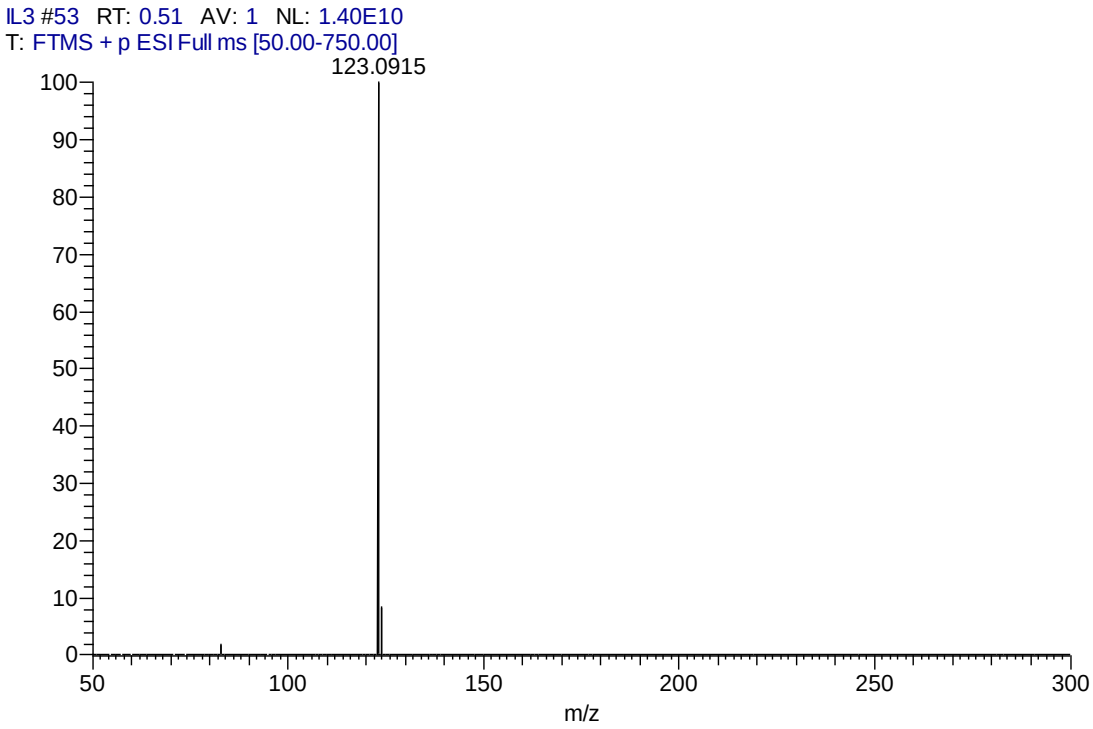
^{13}C NMR spectrum of **3-CTB**



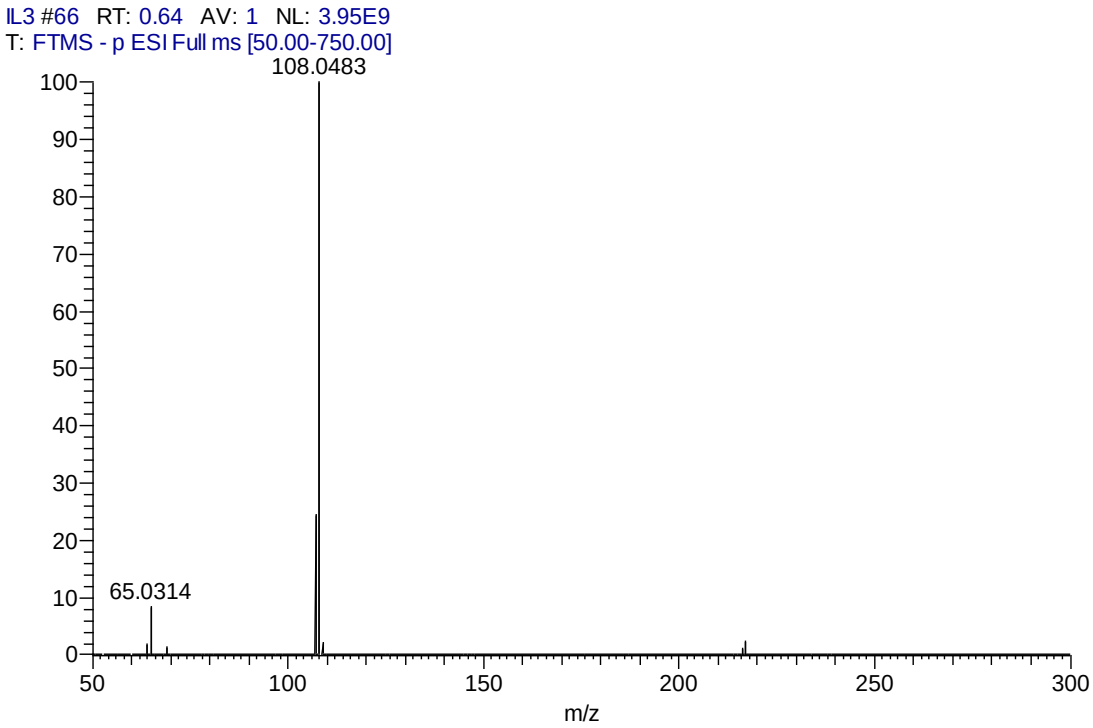
^{11}B NMR spectrum of **3-CTB**



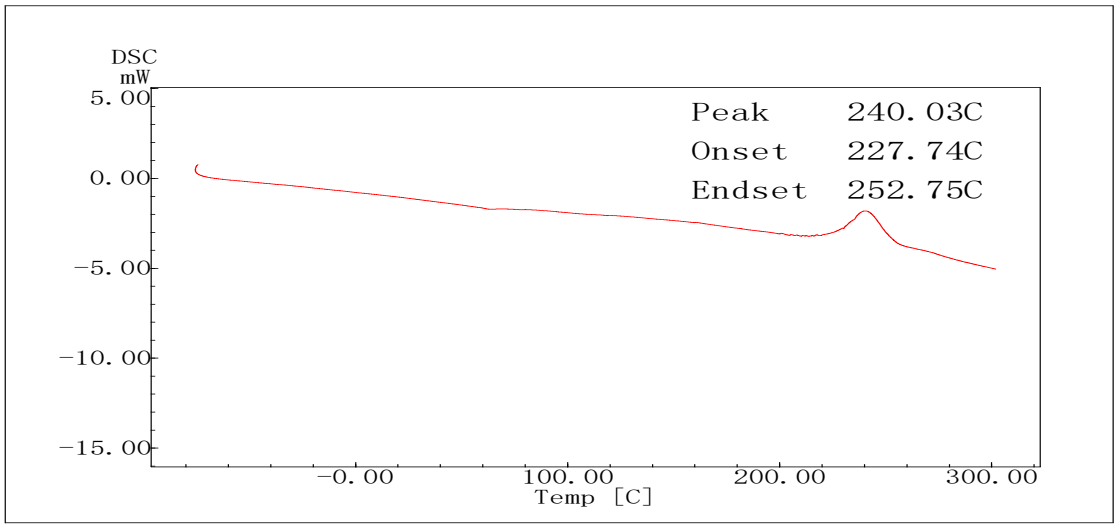
IR spectrum of **3-CTB**

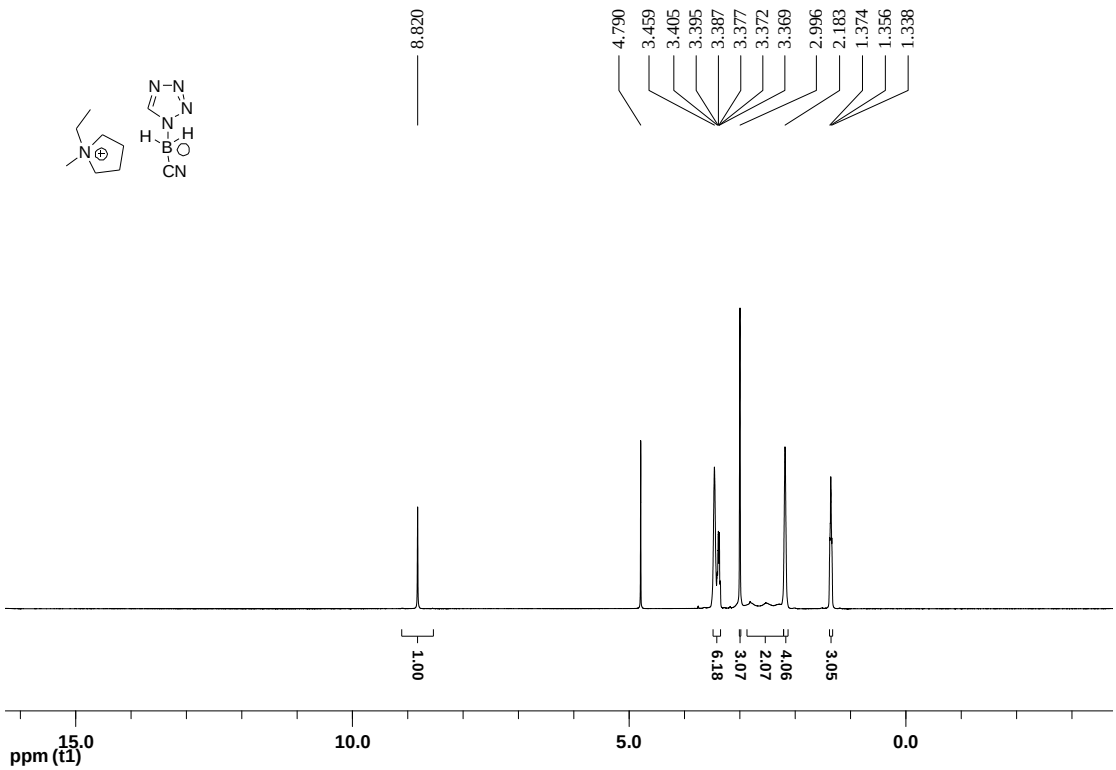


HRMS: cation of compound **3**-**CTB**

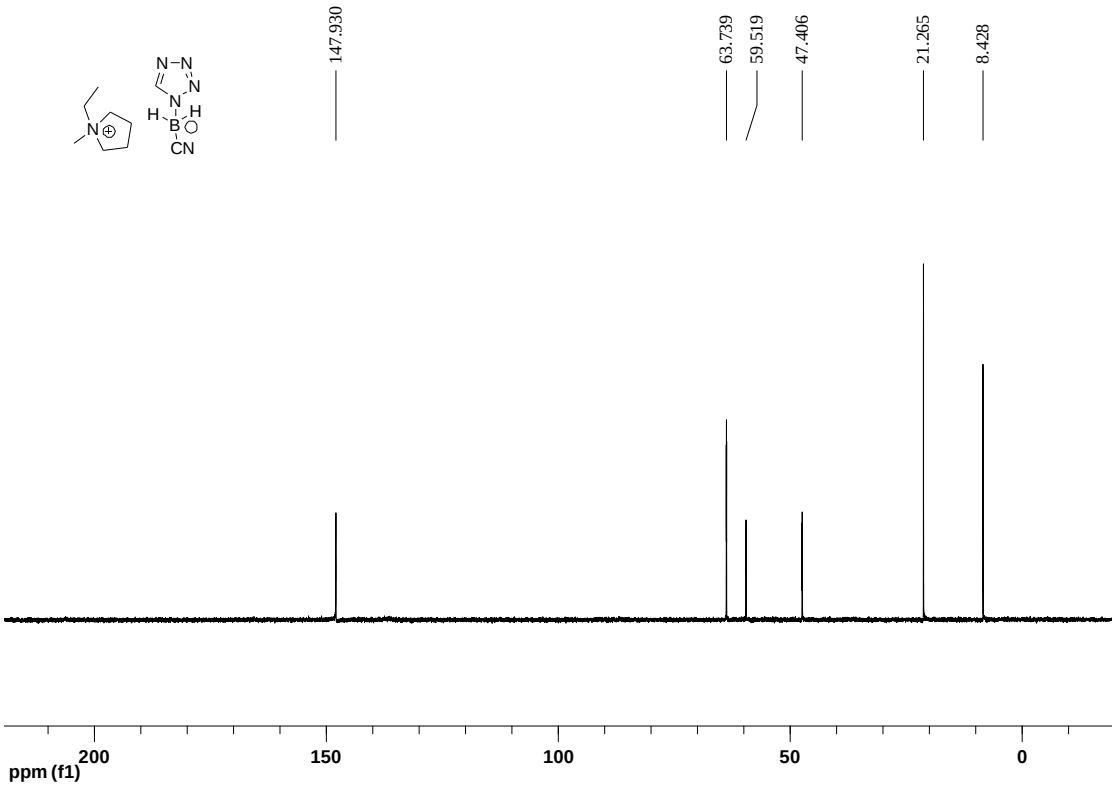


HRMS: anion of compound **3**-**CTB**

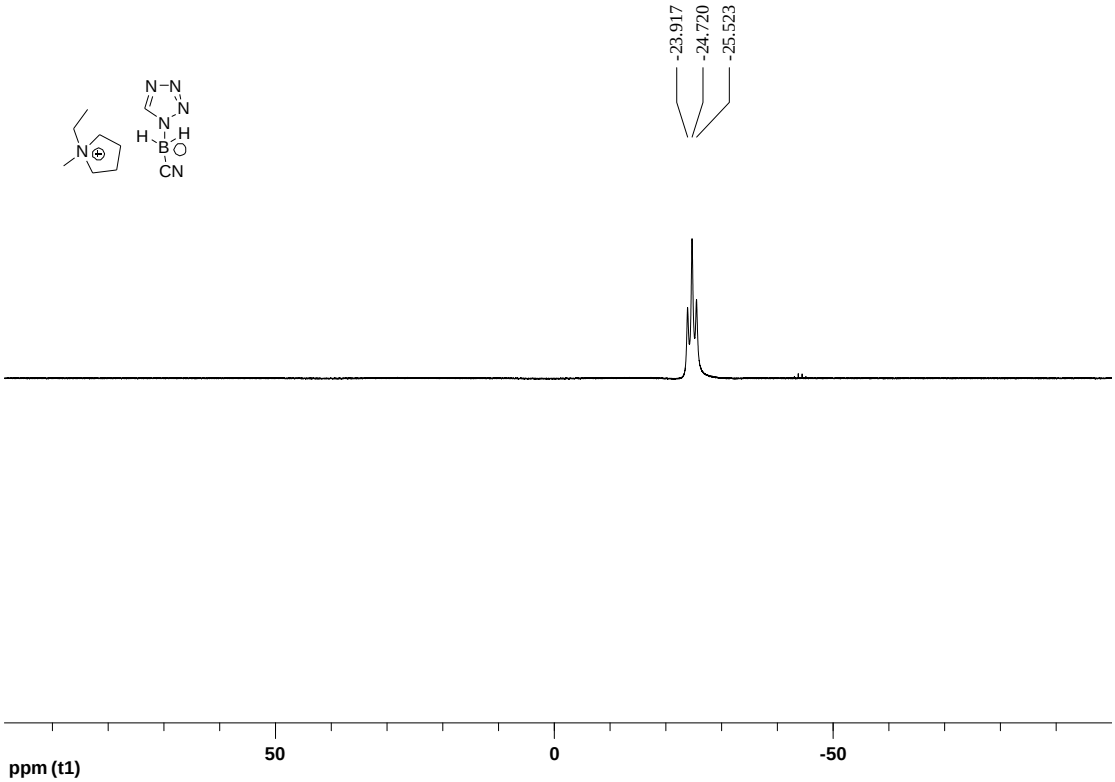




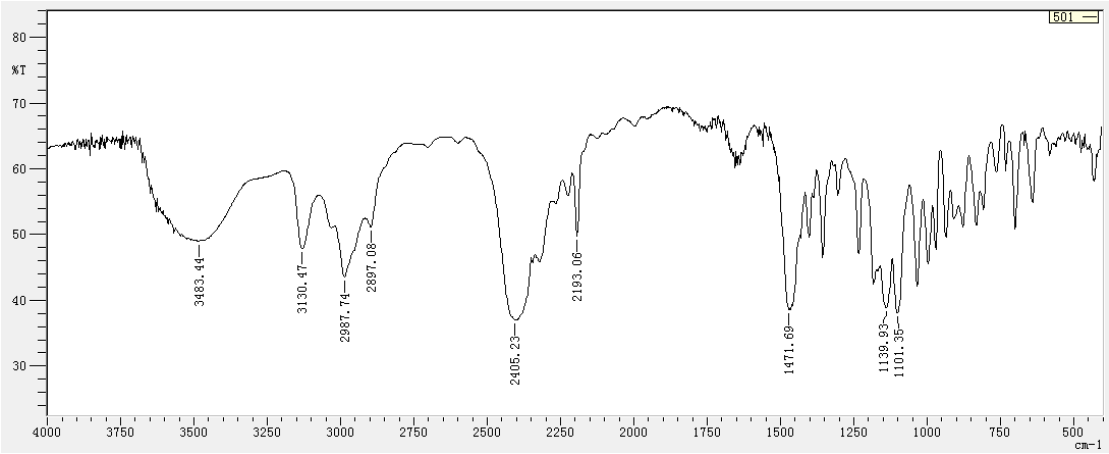
^{1}H NMR spectrum of **4-CTB**



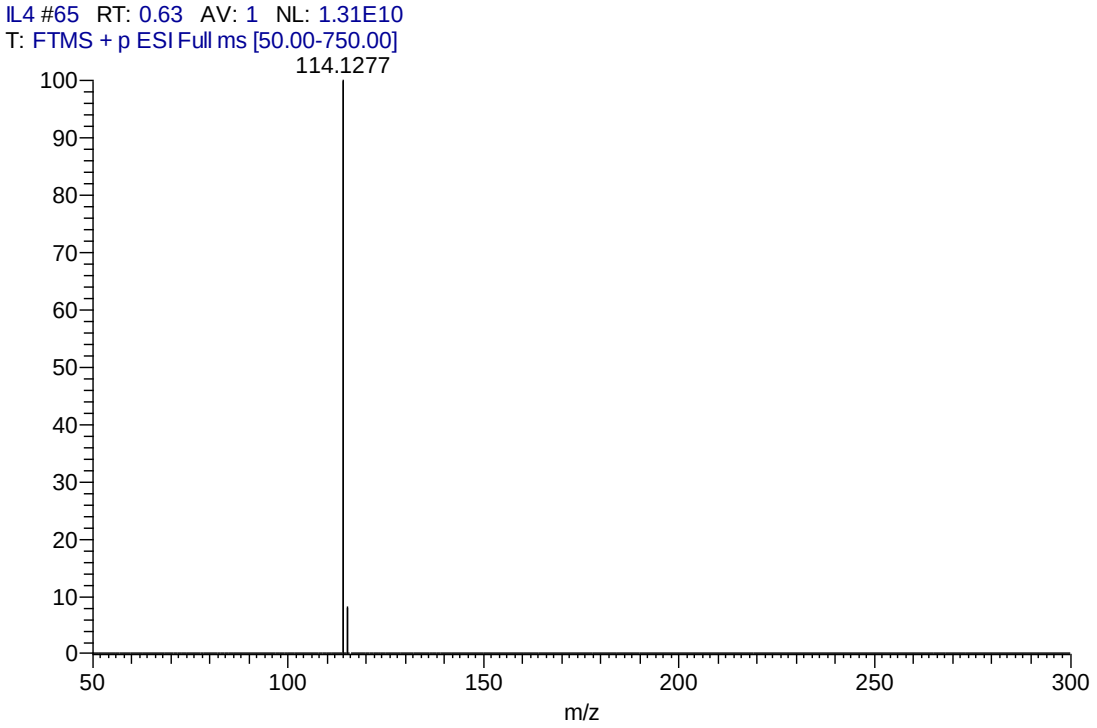
^{13}C NMR spectrum of **4-CTB**



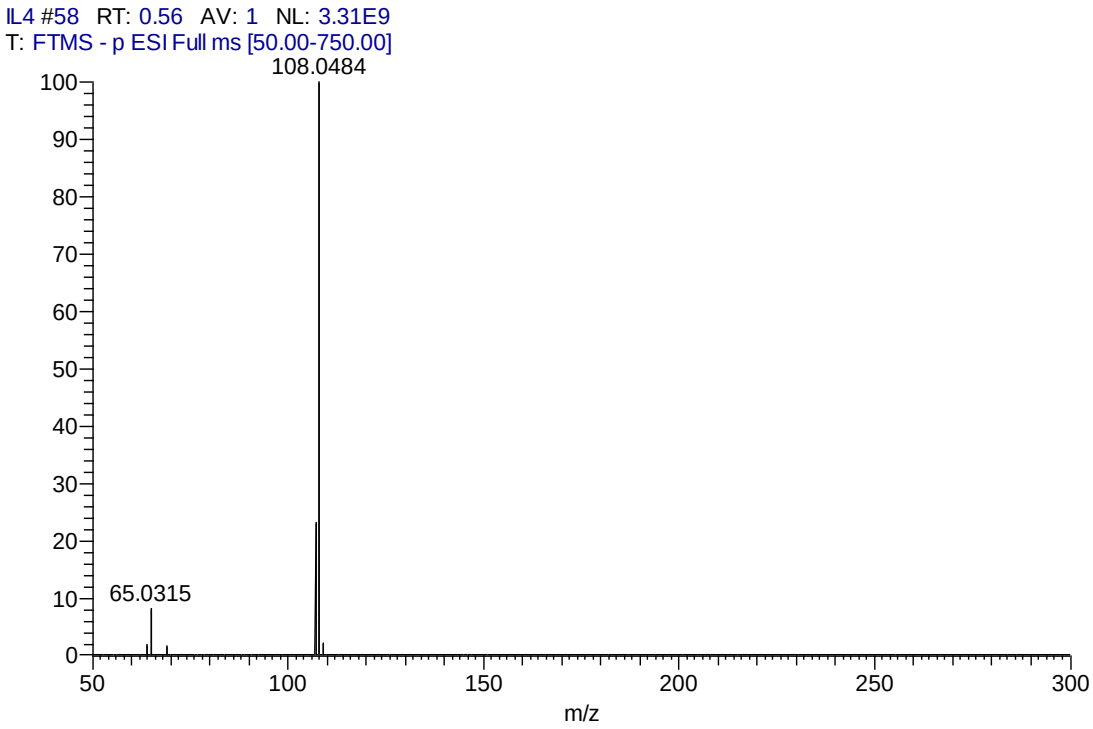
^{11}B NMR spectrum of **4-CTB**



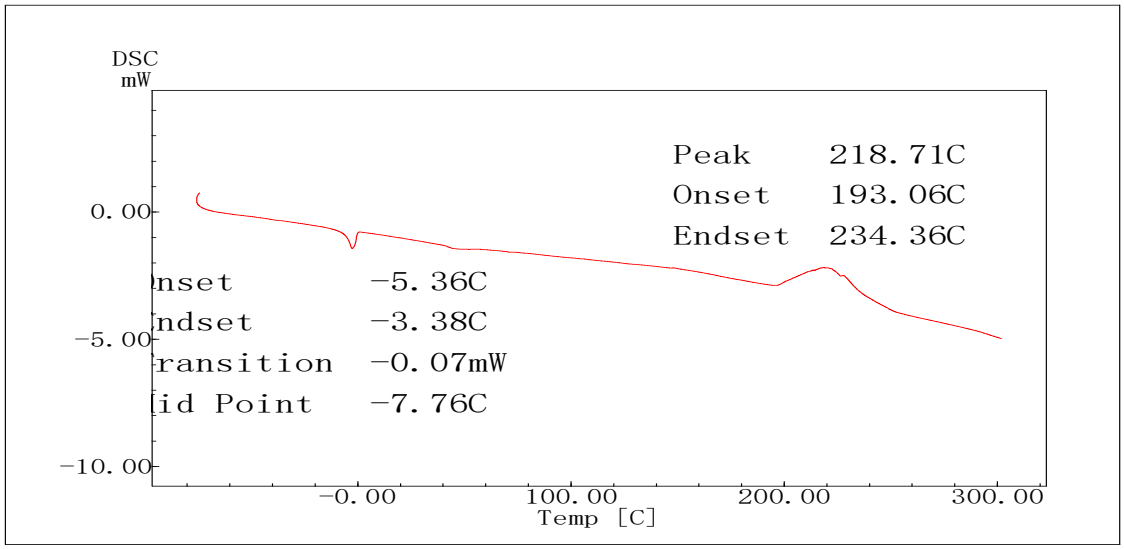
IR spectrum of **4-CTB**



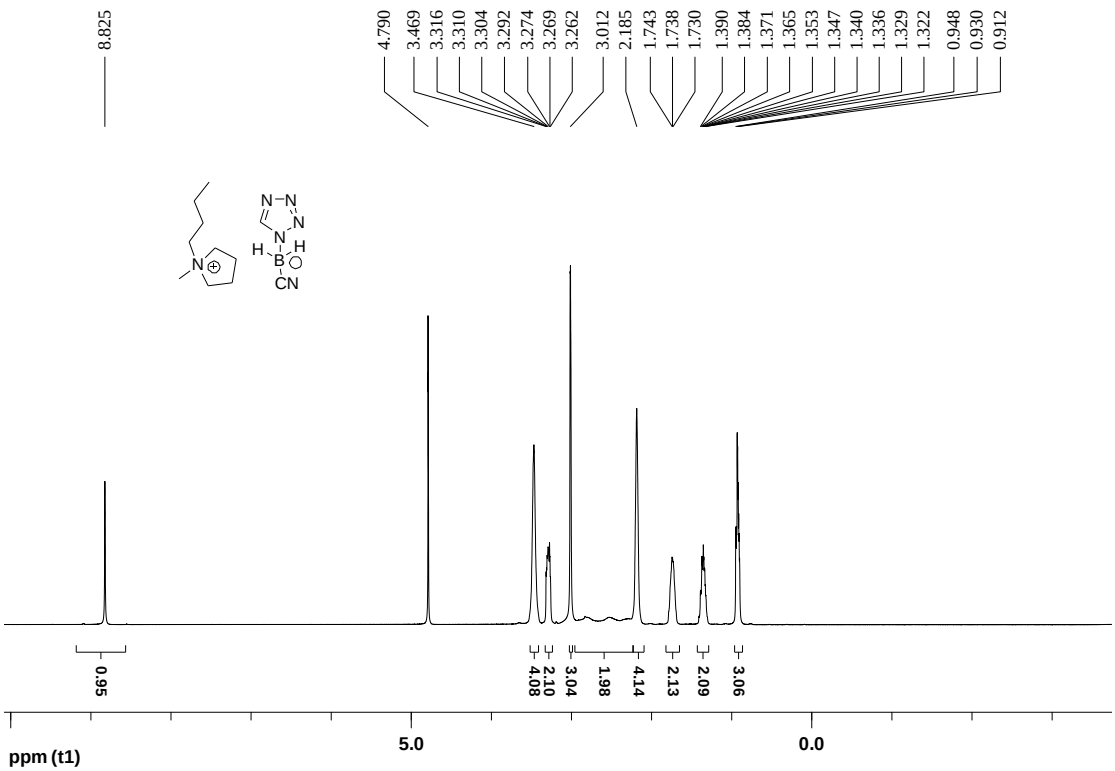
HRMS: cation of compound **4-CTB**



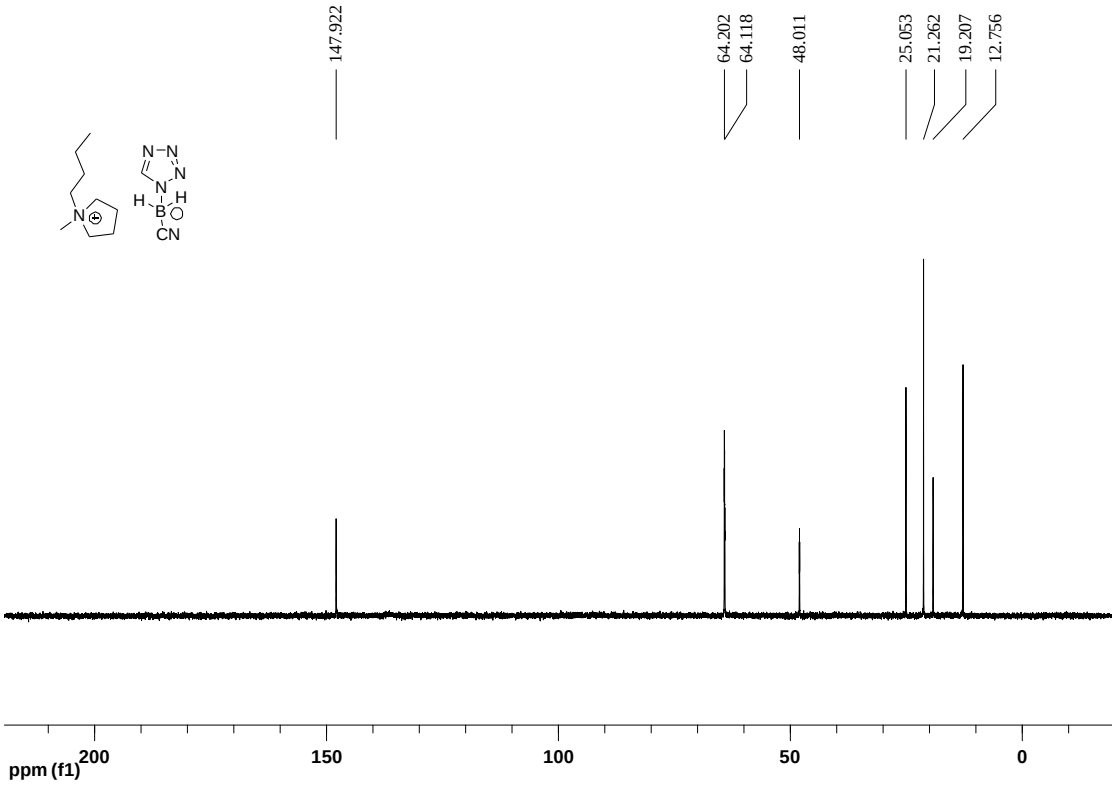
HRMS: anion of compound **4-CTB**



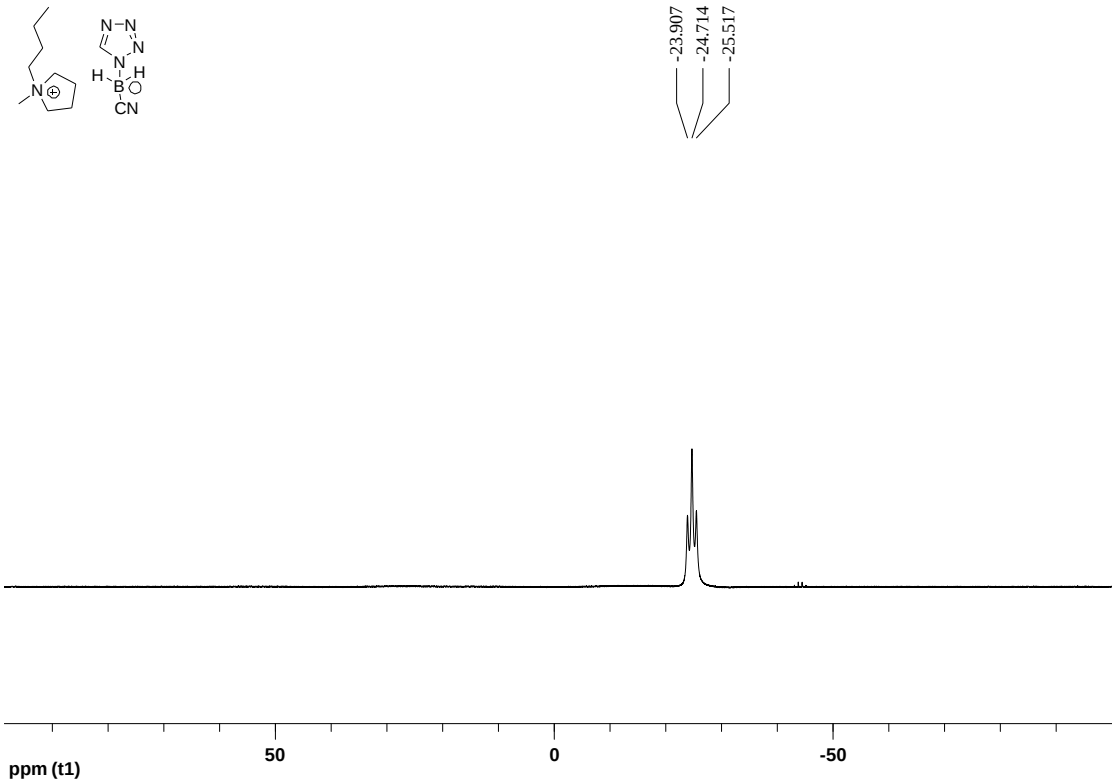
DSC of compound **4-CTB** at a scan of 5 °C min^{-1} under nitrogen atmosphere



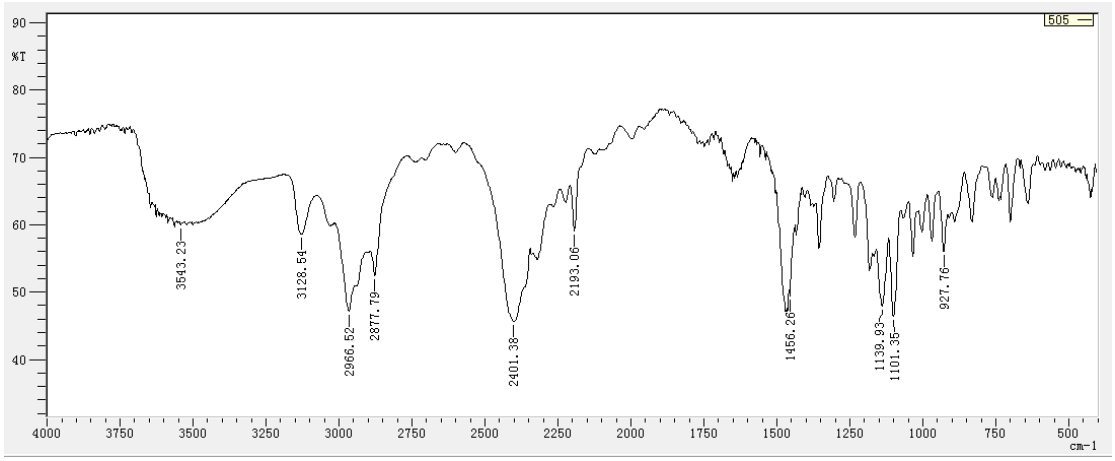
^{1}H NMR spectrum of **5-CTB**



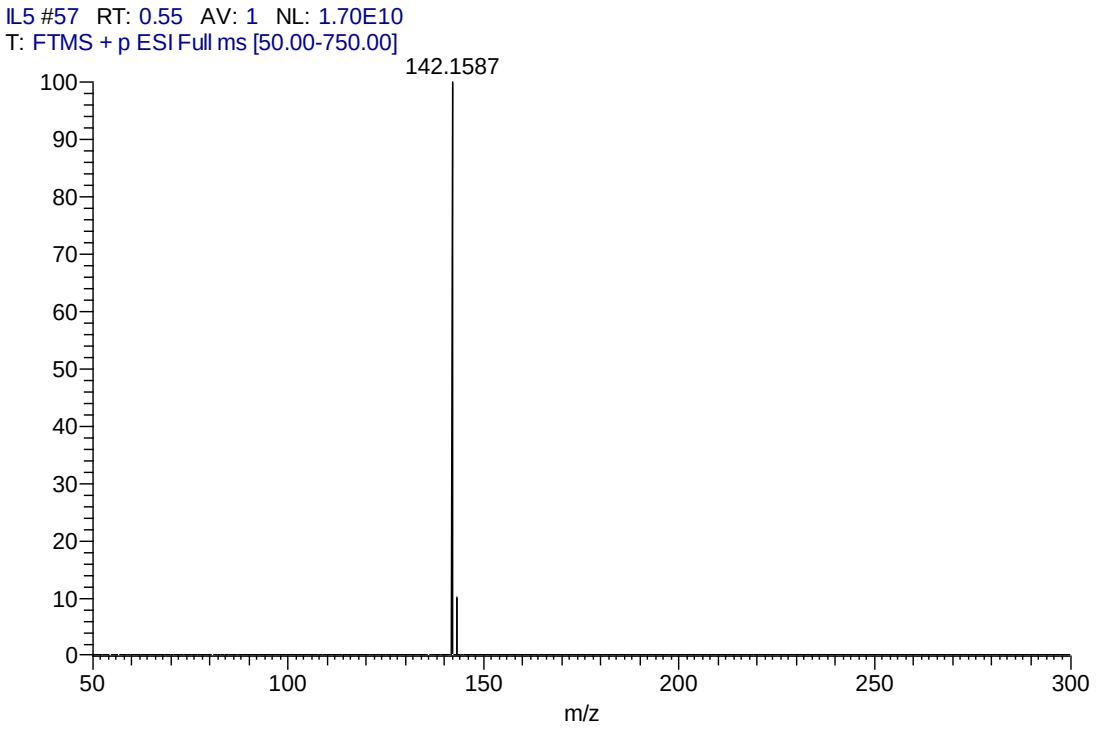
^{13}C NMR spectrum of **5-CTB**



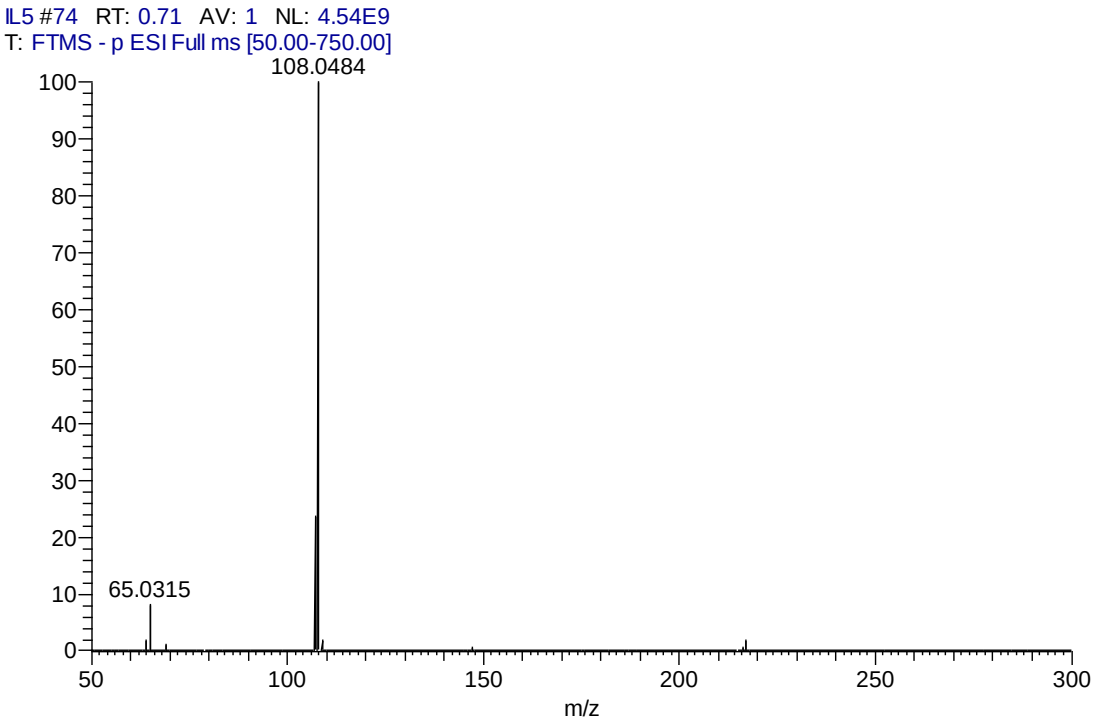
^{11}B NMR spectrum of **5-CTB**



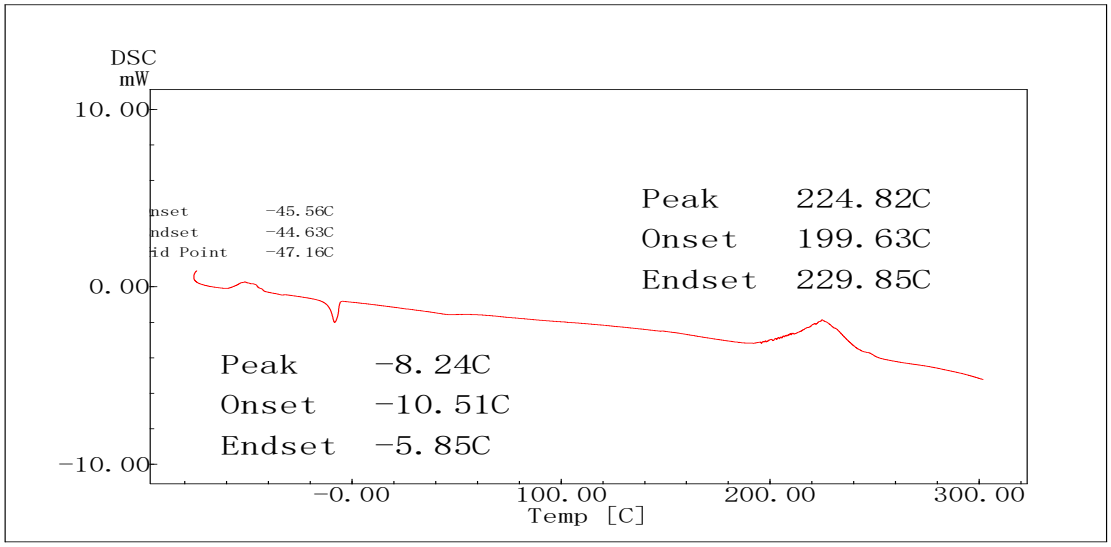
IR spectrum of **5-CTB**



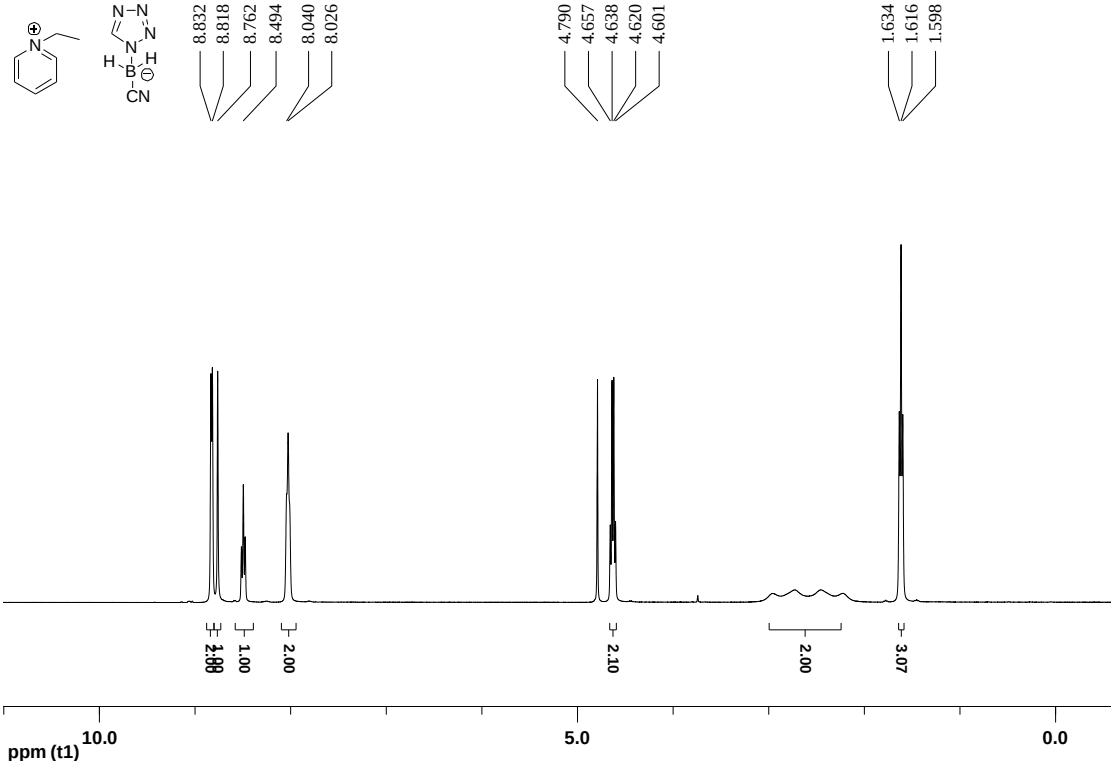
HRMS: cation of compound **5**-**CTB**



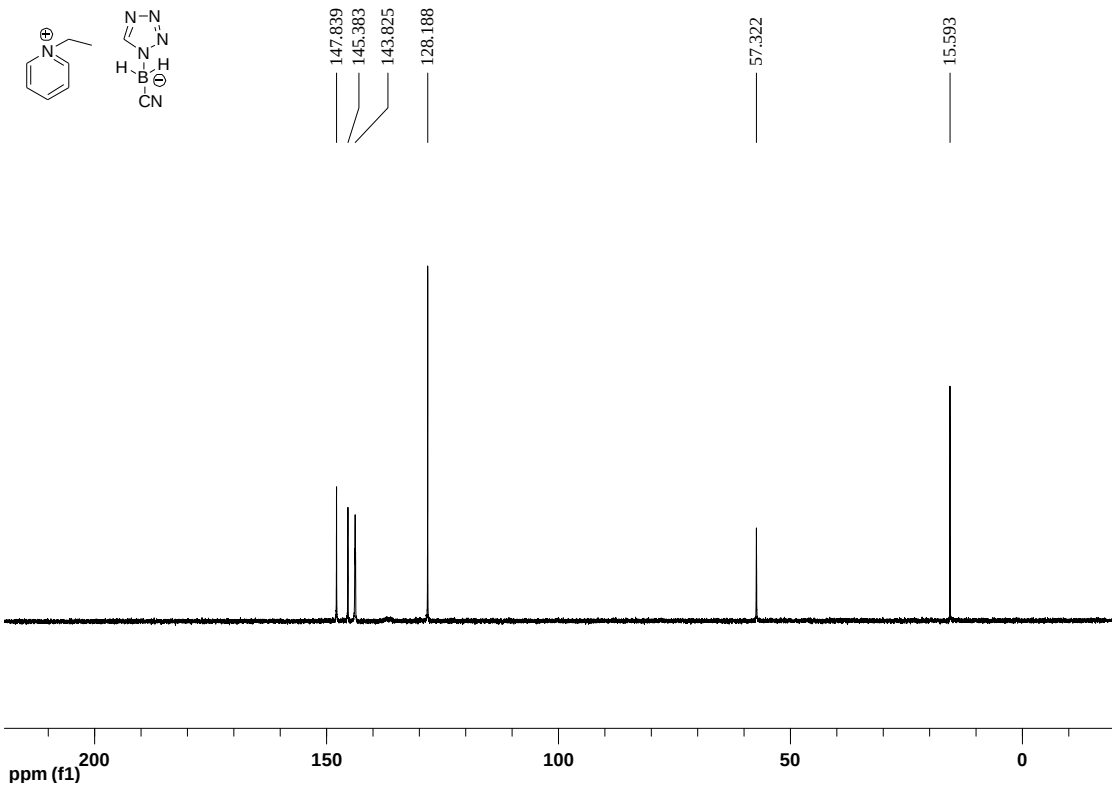
HRMS: anion of compound **5**-**CTB**



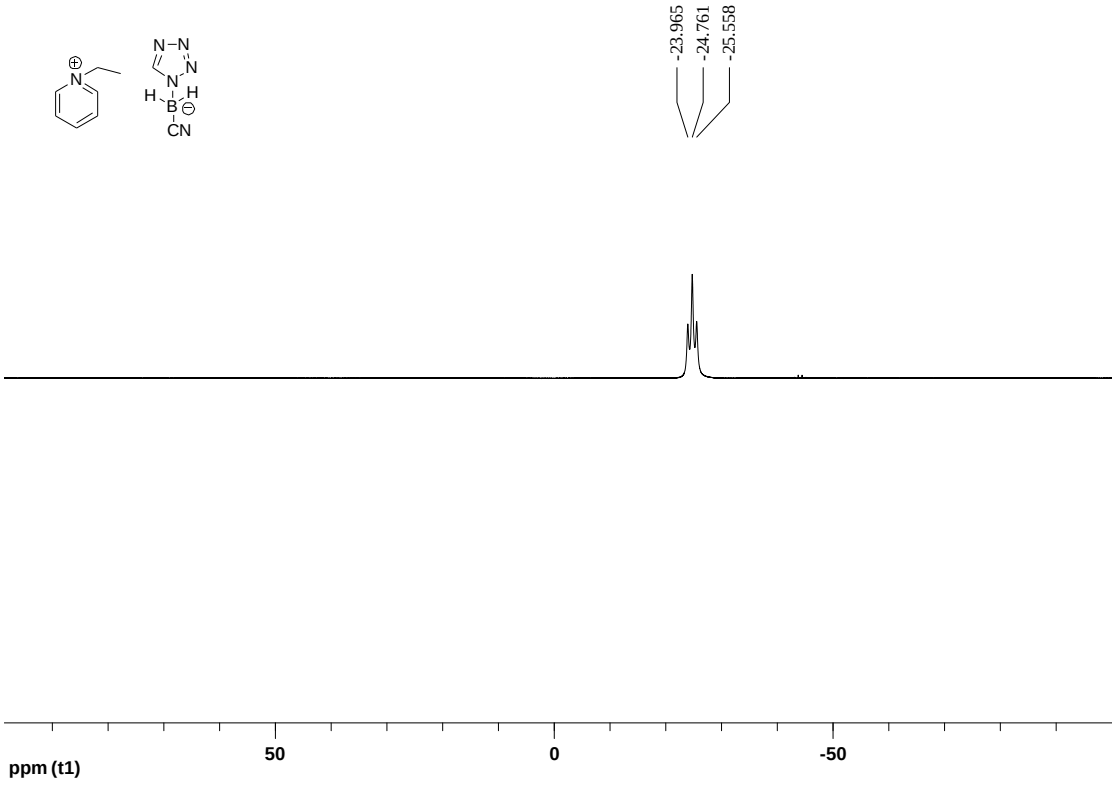
DSC of compound **5-CTB** at a scan of 5 °C min^{-1} under nitrogen atmosphere



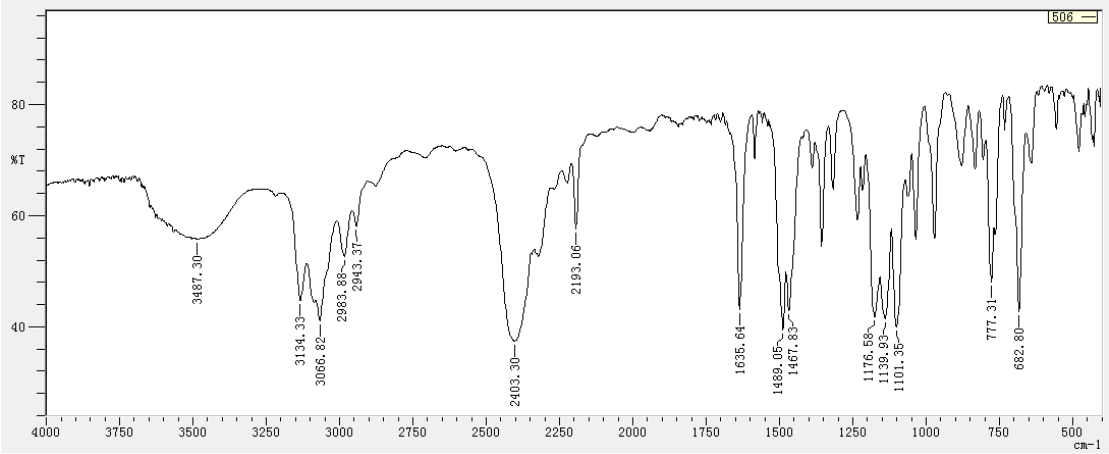
^{1}H NMR spectrum of **6-CTB**



^{13}C NMR spectrum of **6-CTB**

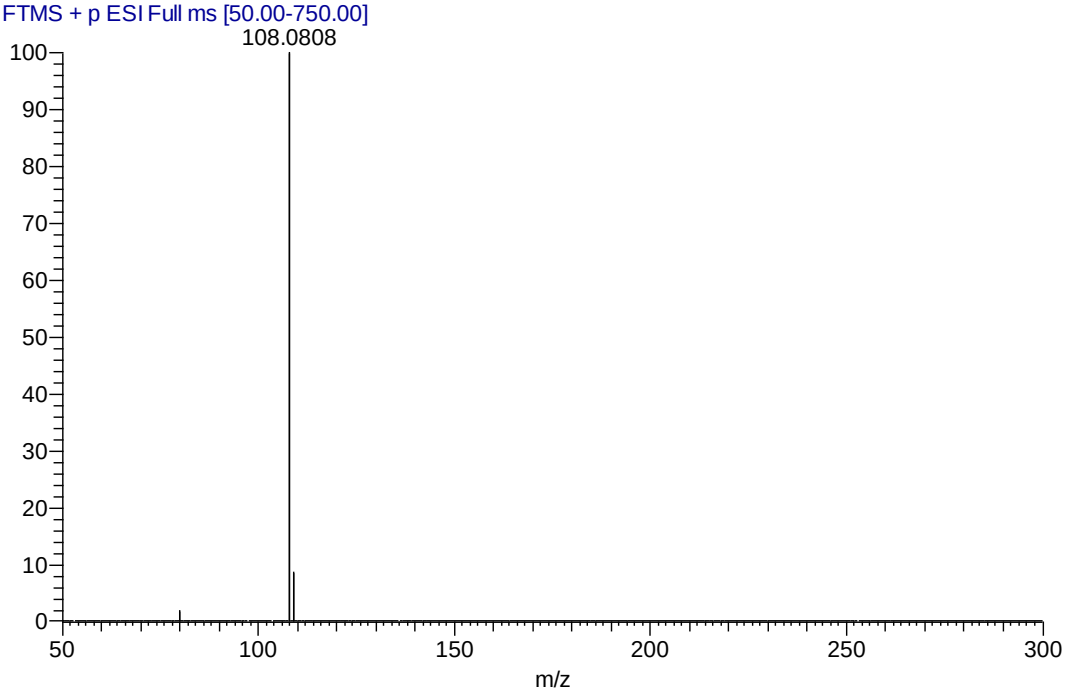


^{11}B NMR spectrum of **6-CTB**

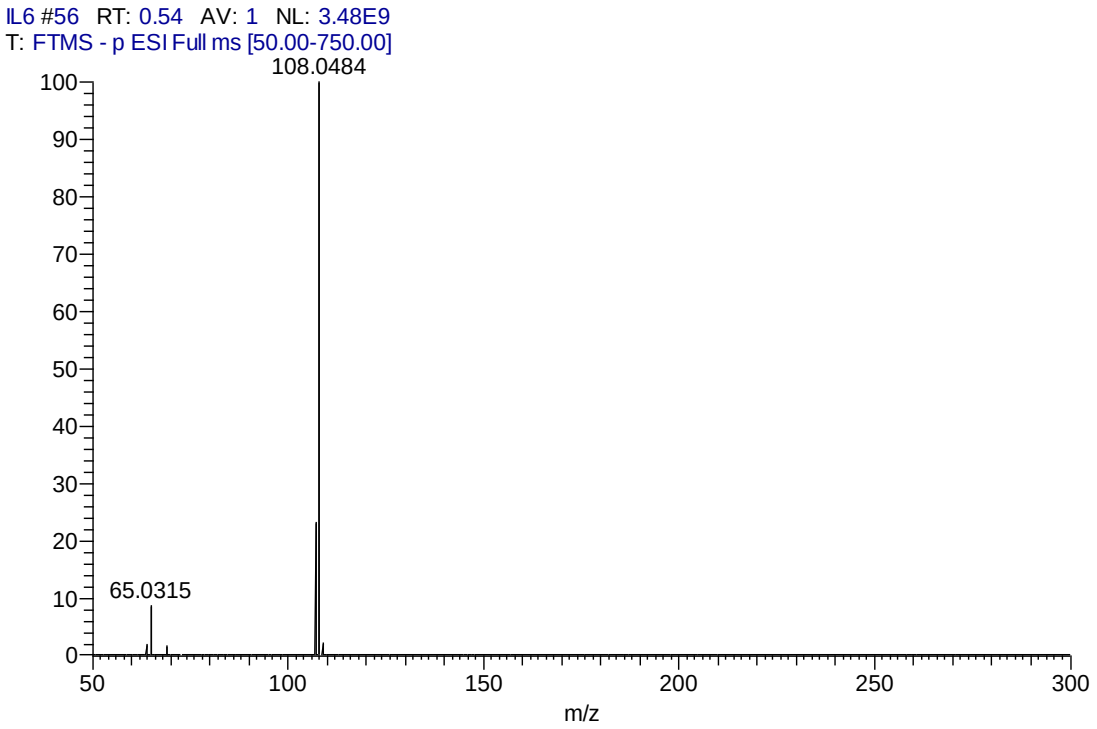


IR spectrum of **6-CTB**

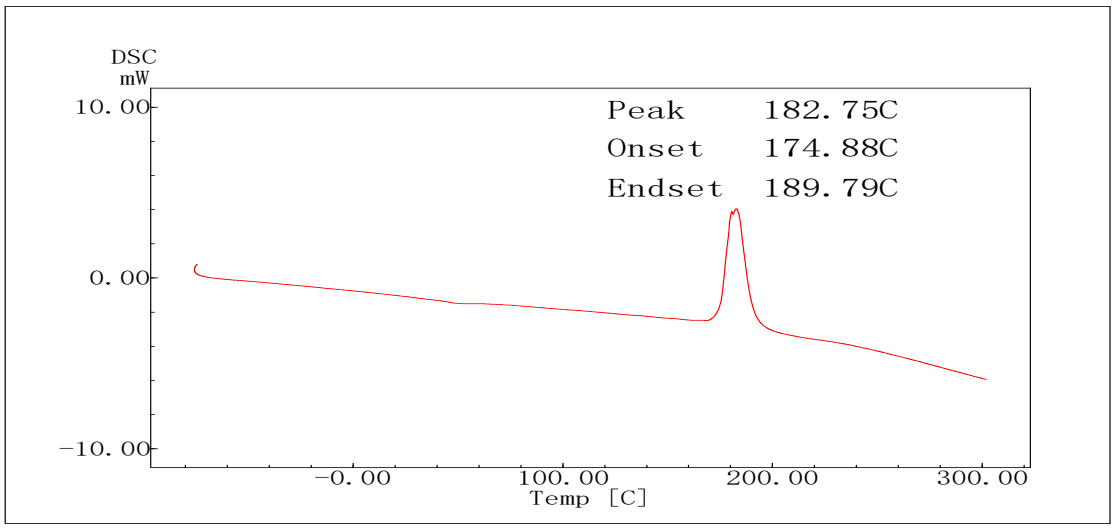
IL6 #61 RT: 0.59 AV: 1 NL: 8.08E9
T: FTMS + p ESI Full ms [50.00-750.00]



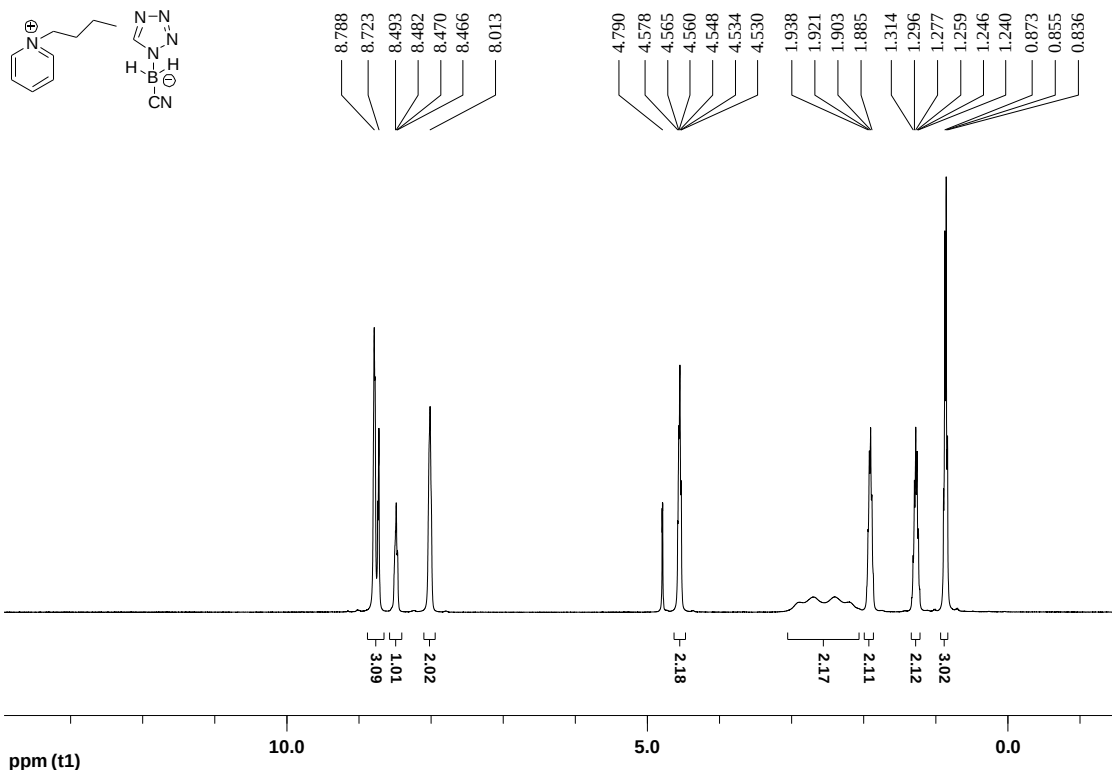
HRMS: cation of compound **6-CTB**



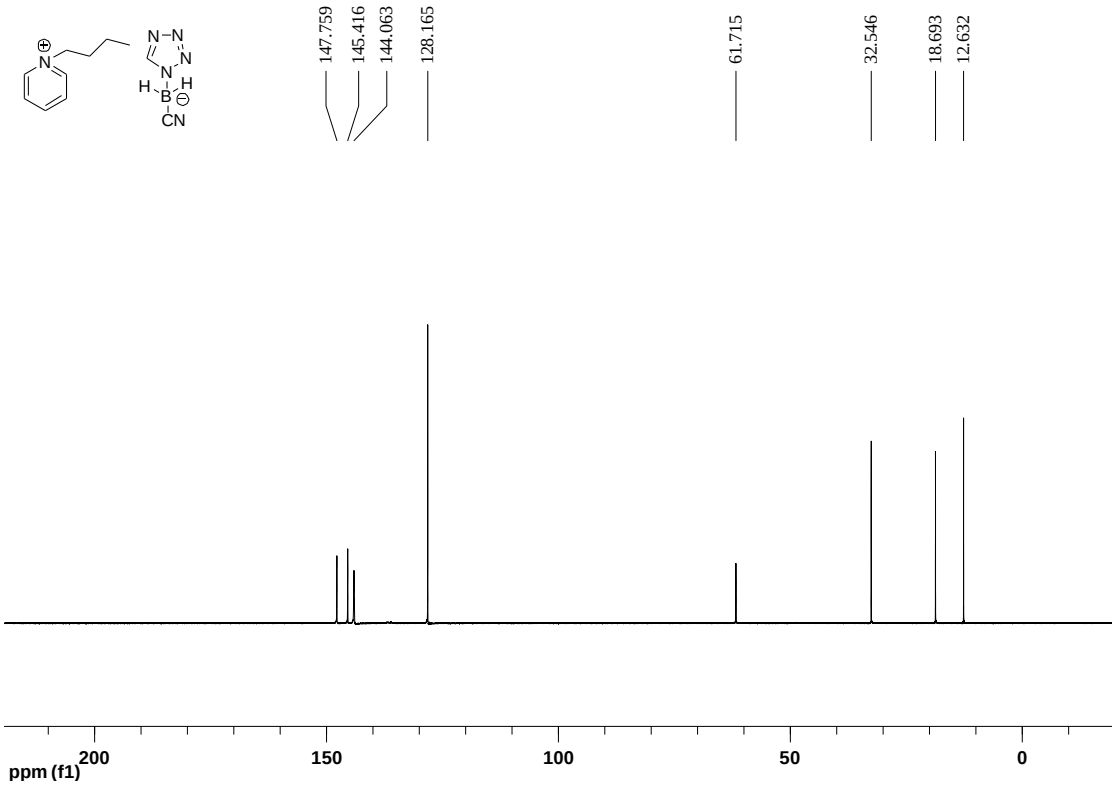
HRMS: anion of compound **6-CTB**



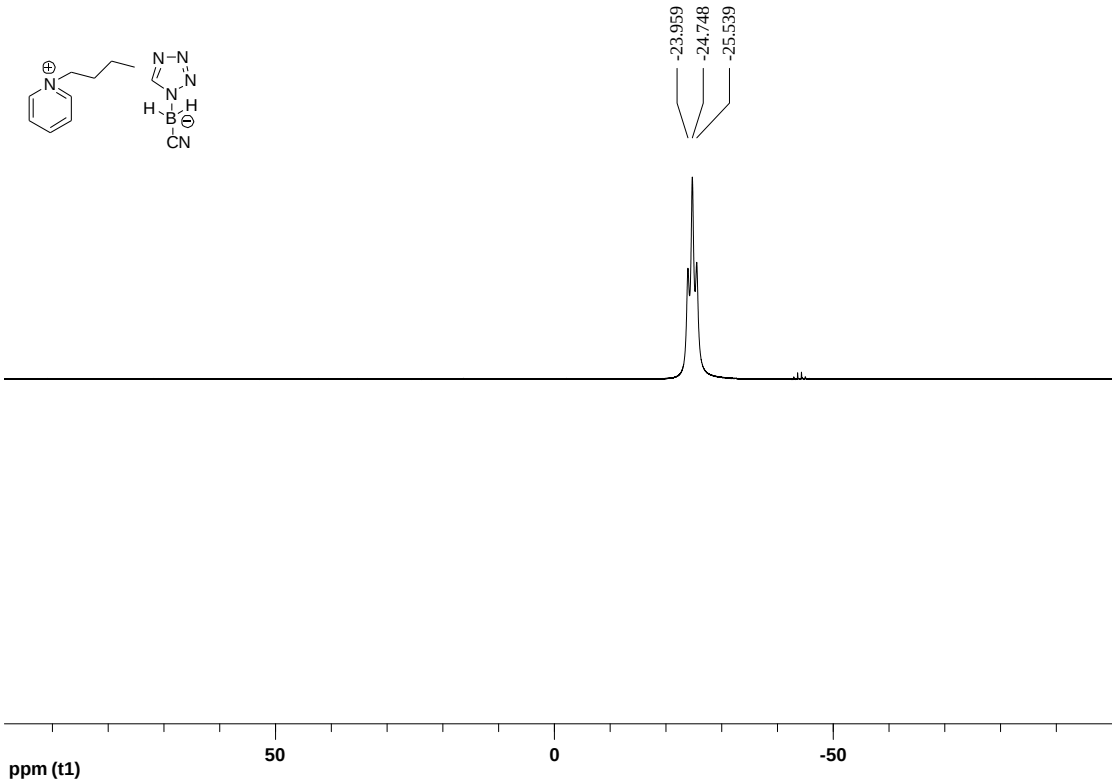
DSC of compound **6-CTB** at a scan of 5 °C min^{-1} under nitrogen atmosphere



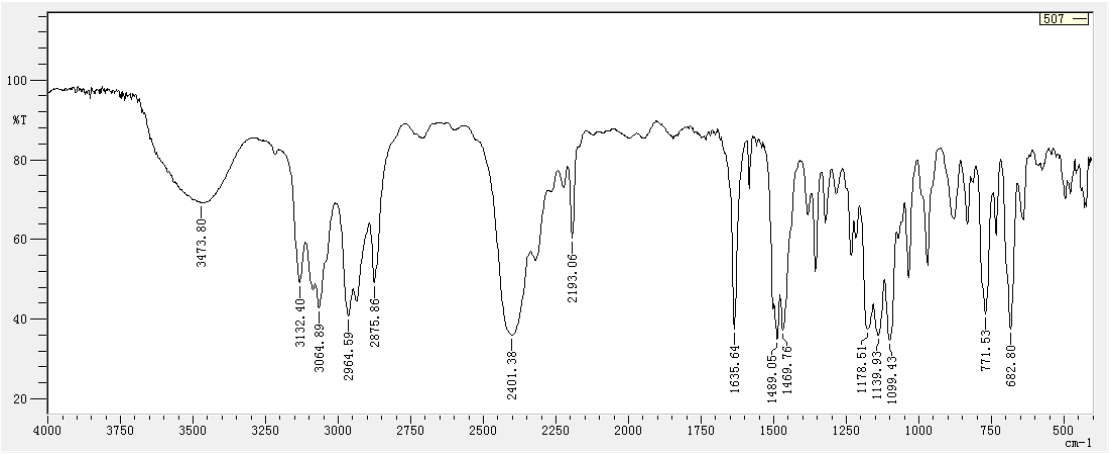
^{1}H NMR spectrum of **7-CTB**



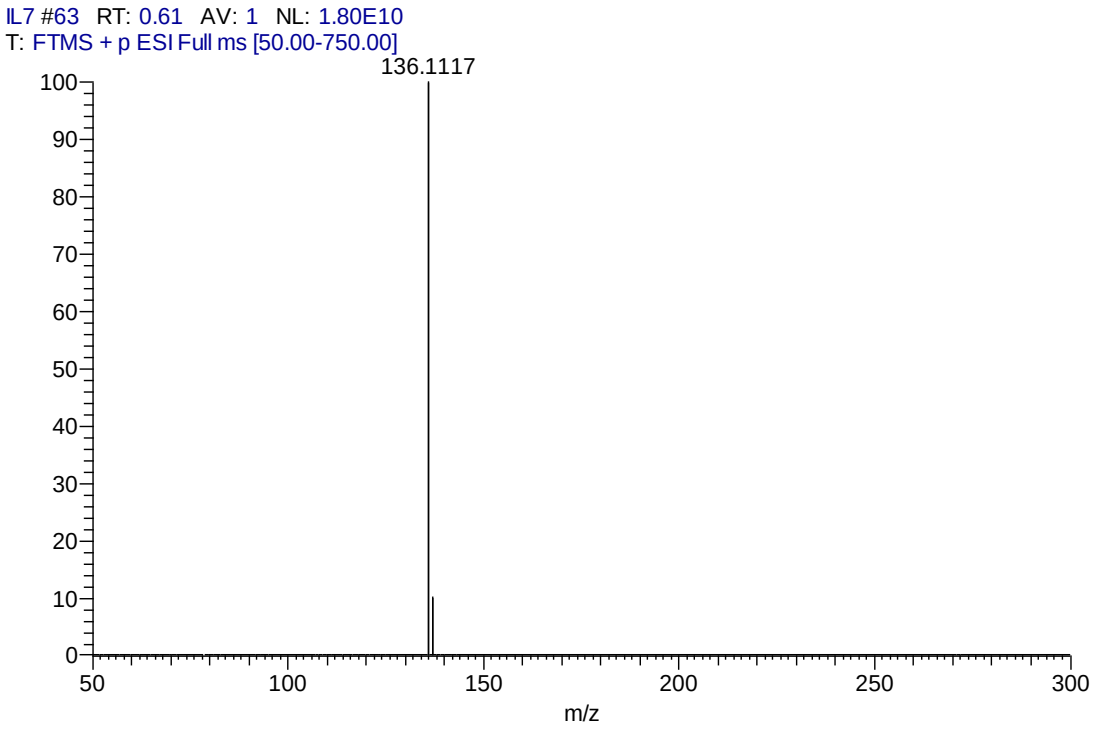
^{13}C NMR spectrum of **7-CTB**



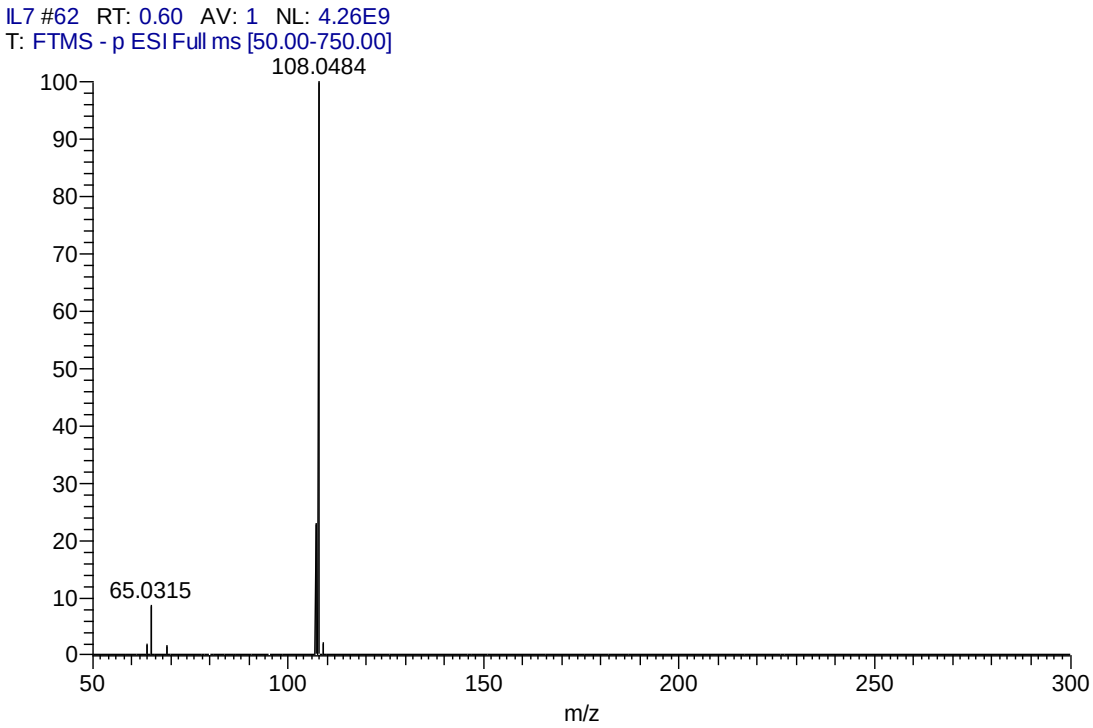
^{11}B NMR spectrum of **7-CTB**



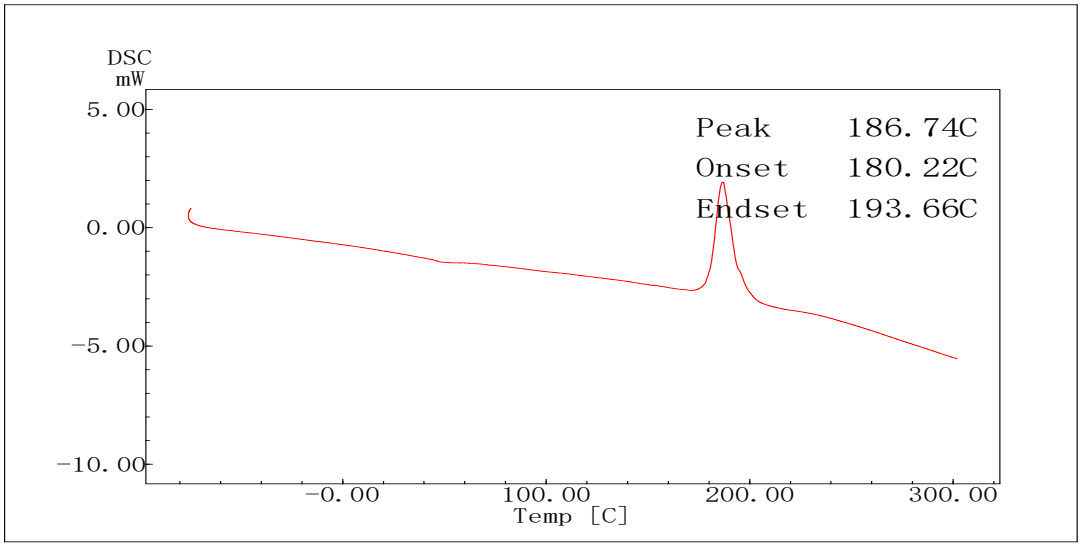
IR spectrum of **7-CTB**



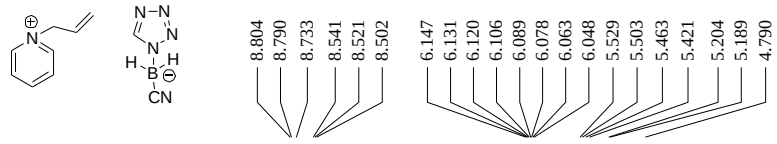
HRMS: cation of compound **7**-**CTB**

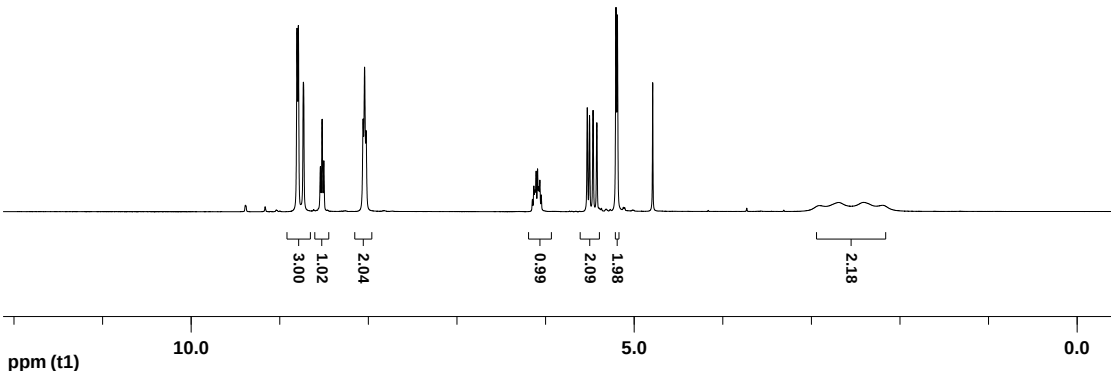


HRMS: anion of compound **7**-**CTB**

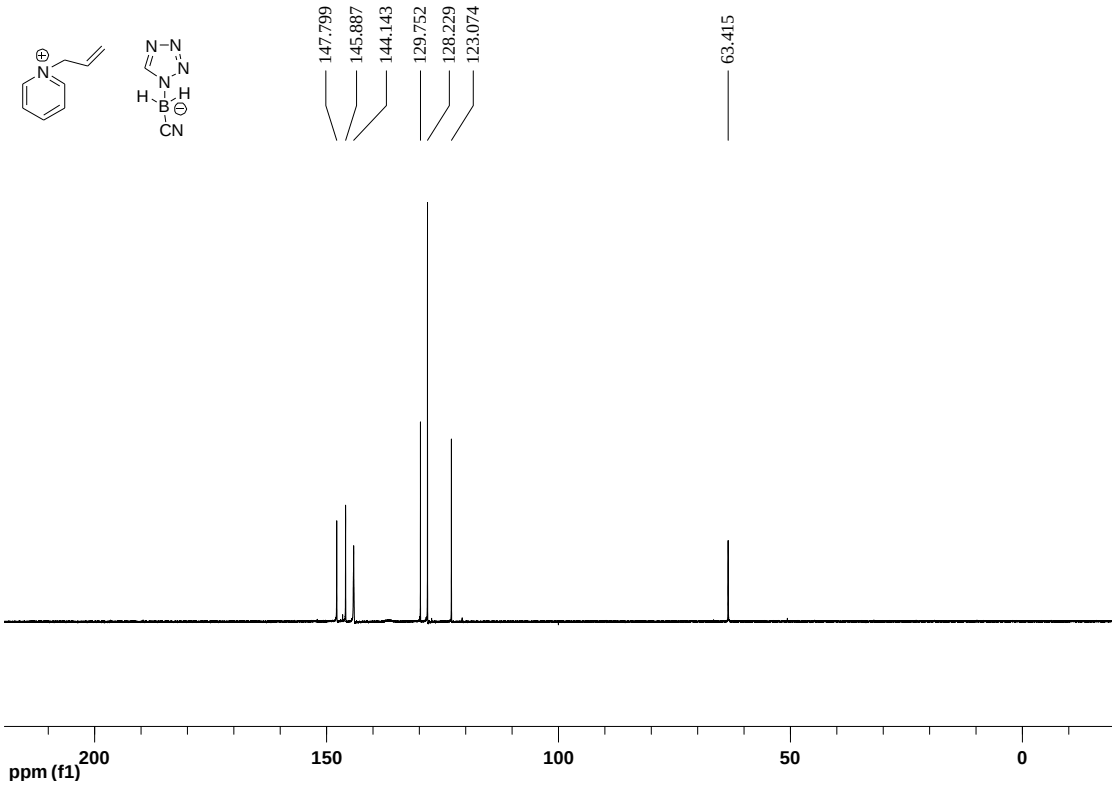


DSC of compound **7-CTB** at a scan of 5 °C min^{-1} under nitrogen atmosphere

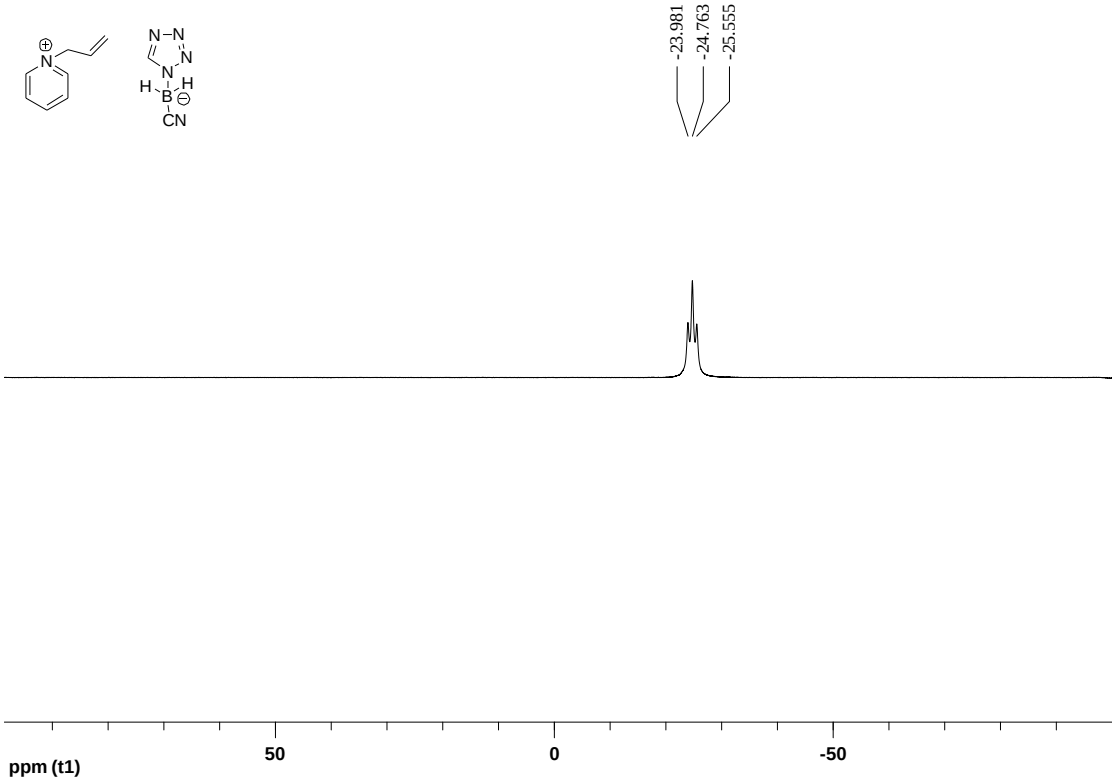




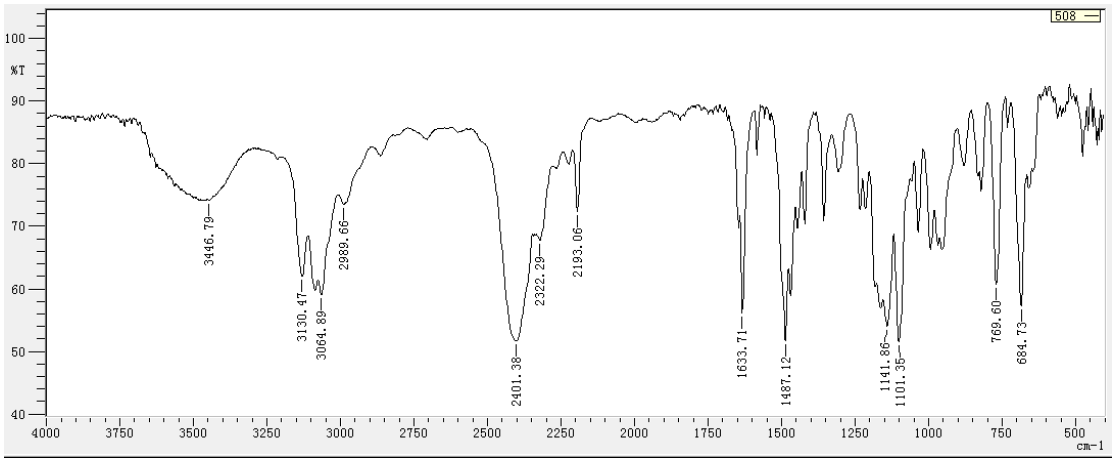
^{1}H NMR spectrum of **8-CTB**



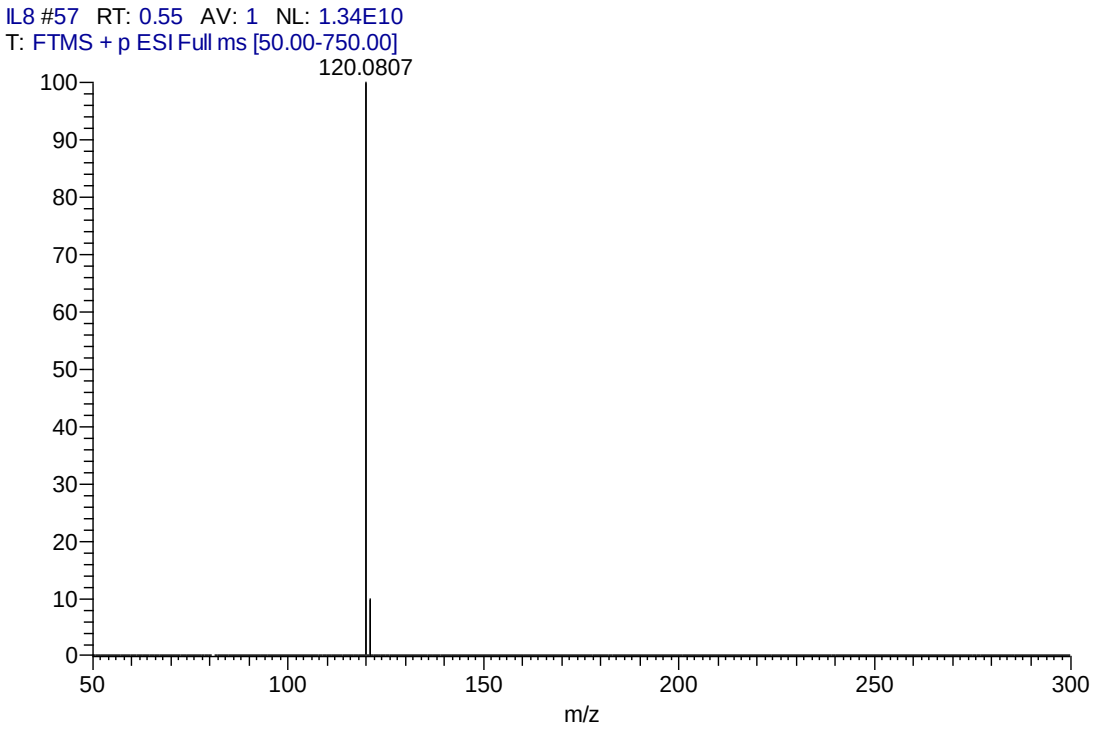
^{13}C NMR spectrum of **8-CTB**



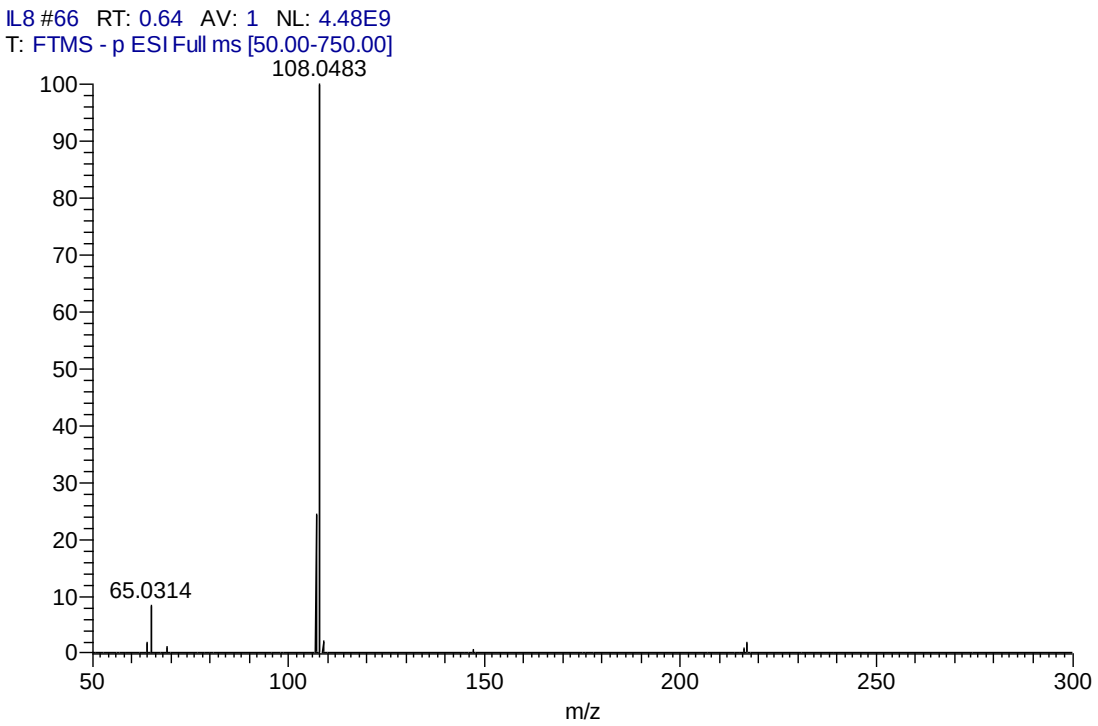
^{11}B NMR spectrum of **8-CTB**



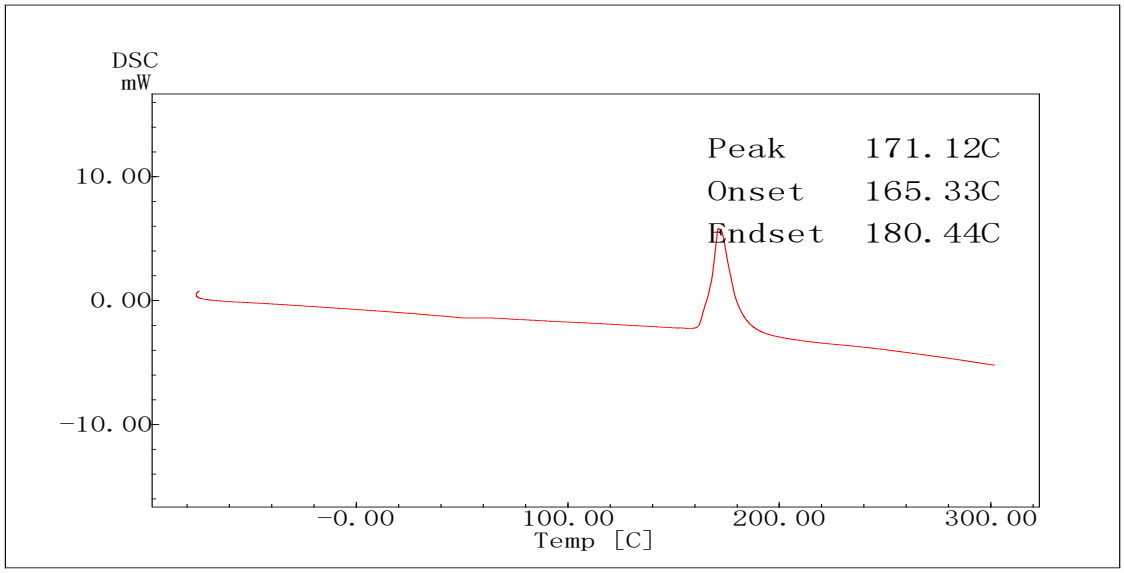
IR spectrum of **8-CTB**



HRMS: cation of compound **8-CTB**



HRMS: anion of compound **8-CTB**



DSC of compound **8-CTB** at a scan of 5 °C min^{-1} under nitrogen atmosphere