Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Bishydrobis(tetrazol-1-yl)borate (BTB) Based Energetic Ionic Liquids with High-Density and Energy Capacity as Hypergolic Fuels

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1. General information

Reagents.

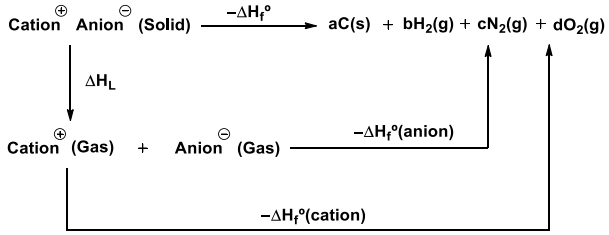
$NaBH_4$ 98% (Energy Chemical), $NaBH_3CN$ 95% (Energy Chemical), KBH_4 98% (Acros), 1H-Tetrazole 98% (Adamas), 5-Amino-1H-Tetrazole 98% (Adamas), Pyrazole 98% (Innochem), Glyoxaline 99% (Innochem), 1-Methylimidazole 99% (Adamas), Allyl Bromide 99% (Adamas), 1,3-Dimethylimdazolium Chloride 98%(TCI), 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), 7, 1-Ethylpyridinium Bromide 99% (Adamas), 1-Butylpyridinium Bromide 99% (Adamas), 1,3-diallyl-1H-imidazolium bromide and 1-allylpyridinium bromide were 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 high speed camera Optronis CR3000*2.

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.

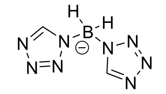
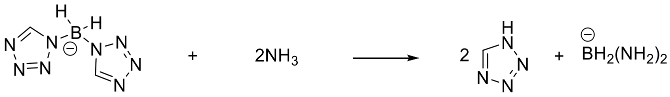
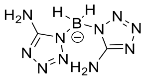
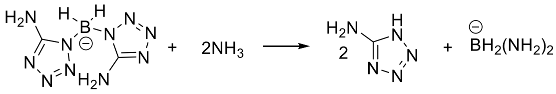
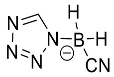
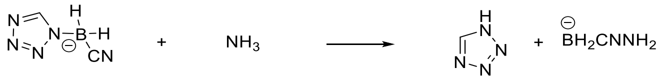
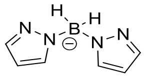
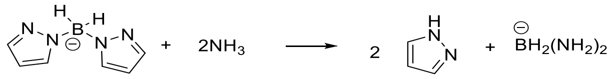
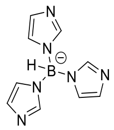
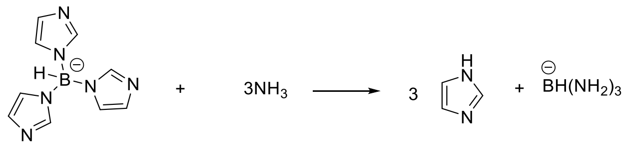
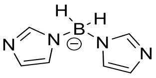
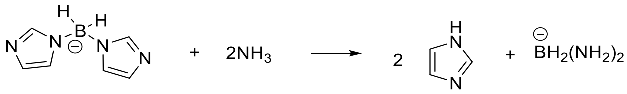
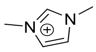
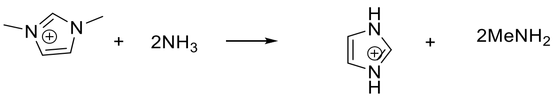
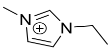
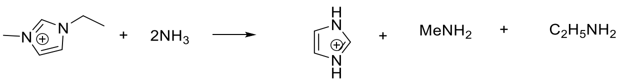
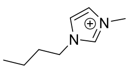
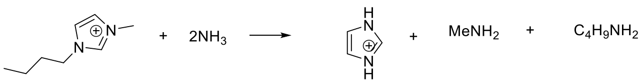
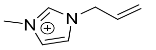
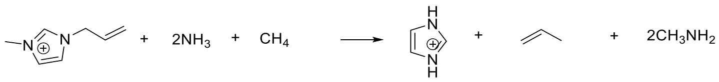
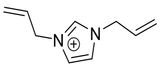
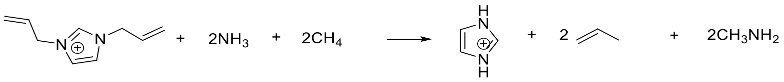
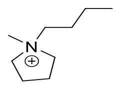
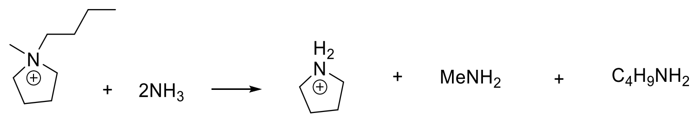
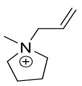
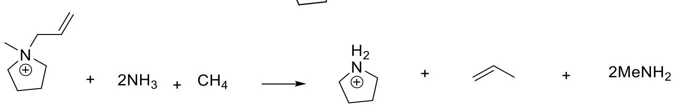
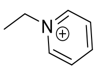
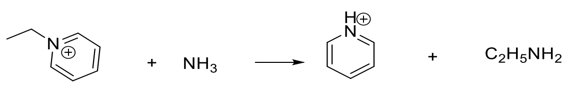
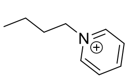
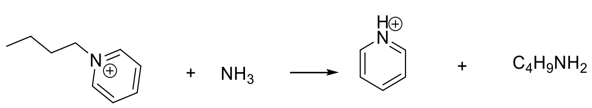
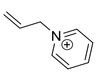
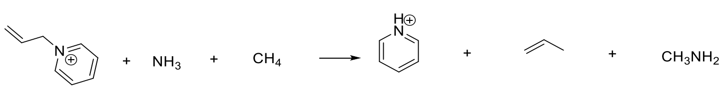
ions	Isodesmic reaction
	
	
	
	
	
	
	
	
	
	
	
	
	
	
	
	

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

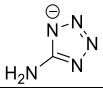
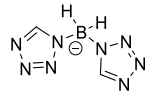
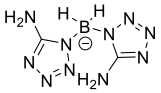
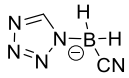
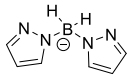
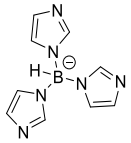
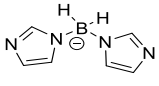
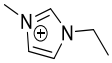
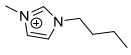
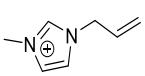
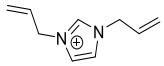
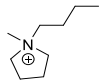
ions	ΔH_f (kJ·mol^{-1})	ΔH_f (kJ·g^{-1})
	722.6	10.459
	577.2	8.002
	750.3	9.366
BH_4^-	-58.6	-3.948
BH_3CN^-	-80.7	-2.025
DCB$^-$	-67.5	-1.041
BCB$^-$	−114.7	-1.457
PB$^-$	−337.9	-5.571
NCA$^-$	−21.7	-0.252
	-163.0	-3.633
	115.3	2.101
	-249.0	4.158
	186.6	2.220

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})
	-540.420651	0.096641	0.106080	-540.3184326	353.5
	-650.970053	0.131355	0.143012	-650.8322949	214.3
	-375.933225	0.067265	0.075056	-375.8608600	88.0
	-476.354694	0.143696	0.153634	-476.2068079	47.4
	-701.018595	0.197654	0.211497	-700.8150037	23.1
	-476.399722	0.144413	0.154389	-476.2511095	-74.7
	-304.537117	0.14057	0.148715	-304.3940250	663.0
	-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

	-458.963760	0.20732	0.21942	-458.7526325	791.5
	-408.535176	0.285905	0.298521	-408.2480915	414.4
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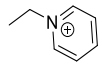
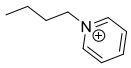
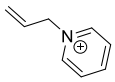
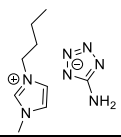
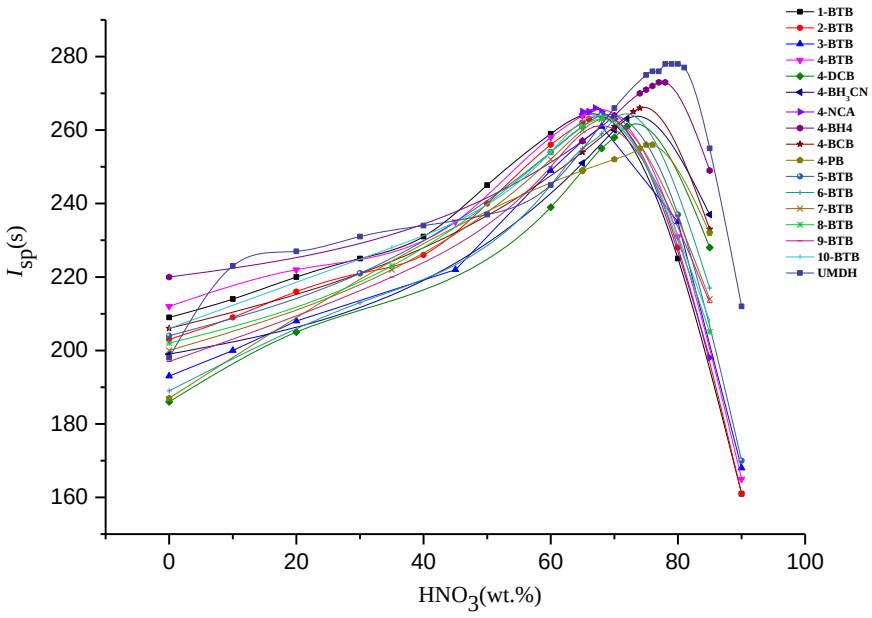
	-326.525480	0.158887	0.167085	-326.3647501	668.0
	-404.957555	0.215666	0.226631	-404.7395502	651.2
	-364.5180790	0.163696	0.172677	-364.351950	780.2

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).

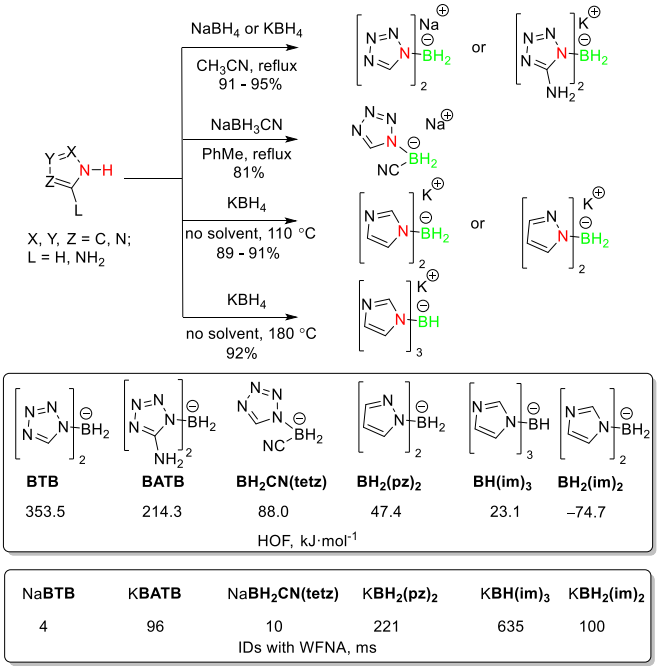
Table S4. The calculated enthalpies of ionic liquids.

HILs	ΔH_{cation}(kJ·mol^{-1})	ΔH_{anion}(kJ·mol^{-1})	ΔH_{lat}(kJ·mol^{-1})	ΔH_{salt}(kJ·mol^{-1})
1-BTB	663.0	353.5	451.1123	2.279
2-BTB	618.9	353.5	441.3525	2.026
3-BTB	555.9	353.5	436.4220	1.726
4-BTB	786.7	353.5	431.1310	2.444
5-BTB	791.5	353.5	424.0732	2.402
6-BTB	414.4	353.5	425.6674	1.167
7-BTB	586.2	353.5	433.4548	1.827
8-BTB	668.0	353.5	444.4210	2.227
9-BTB	651.2	353.5	430.5152	2.000
10-BTB	780.2	353.5	441.1251	2.555
4-DCB	786.7	-67.5	453.4138	1.413
4-BH_3CN	786.7	-80.7	466.5188	1.469
4-NCA	786.7	−21.7	454.3038	1.485
4-BH_4	786.7	-58.6	478.8907	1.806
4-BCB	786.7	−114.7	438.4118	1.157
4-PB	786.7	−337.9	446.4035	0.013
	555.9	186.6	465.1709	1.242

3. Explo5 program for specific impulse



4. Synthesis of hypergolic ionic liquids



Synthesis of NaBTB.
Sodium borohydride, $NaBH_4$ (4g, 106 mmol), was added with stirring to 70 mL of anhydrous acetonitrile in 250 mL round-bottom flask. While rapidly stirring the mixture, 1H-tetrazole (14.814 g, 106 mmol) was added slowly in small portions. Then the flask was fitted with a reflux condenser and the slurry was reflux 4 days under Ar atmosphere with continuous rapid stirring. The solution was cooled and the solid was collected on filter paper and then dried in vacuum to yield 17.512 g (95 % yield). ^{1}H NMR (400 MHz, D_2O) δ 8.93 (s, 2H), 4.2-3.5 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6). δ 147.75. ^{11}B (128 MHz, D_2O) δ -11.66. HRMS (ESI) m/z: $[M]^-$ calcd for $C_2H_4BN_8^-$:151.0657, Found: 151.0658.

Synthesis of KBATB.
According to the literature[5]: 91% yield. ^{1}H NMR (400 MHz, CD_3CN) δ 8.59 (s, 2H), 4.20 – 3.80 (m, 2H).^{13}C NMR (101 MHz, DMSO-d_6) 147.24. ^{11}B (128 MHz, D_2O) δ −14.656. HRMS (ESI) m/z: $[M]^-$ calcd for $C_2H_6BN_{10}^-$:181.0875, Found: 181.0877.

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.

Synthesis of $KBH_2(pz)_2$.
According to the literature[6]: 91% yield. ^{1}H NMR (400 MHz, D_2O) δ 7.70 (s, 2H), 7.58 (s, 2H), 6.30 – 6.25 (m, 2H), 4.00 - 3.30 (m, 2H).^{13}C NMR (101 MHz, DMSO-d_6). δ 140.26, 135.94, 104.40. ^{11}B (128 MHz, D_2O) δ −7.51 (t, J = 95.9 Hz). HRMS (ESI) m/z: $[M]^-$ calcd for $C_6H_8BN_4^-$:147.0848, Found: 147.0849.

Synthesis of $KBH(im)_3$.
According to the literature[7]: 92% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.26 (s, 2H), 6.82 (s, 2H), 5.00 – 4.00 (m, 1H).^{13}C NMR (101 MHz, DMSO-d_6). δ 139.65, 128.06, 120.54. ^{11}B (128 MHz, D_2O) δ −4.74 (d, J = 99.58 Hz). HRMS (ESI) m/z: $[M]^-$ calcd for $C_9H_{10}BN_6^-$:213.1065, Found: 213.1067.

Synthesis of $KBH_2(im)_2$.
According to the literature[8]: 89% yield. ^{1}H NMR (400 MHz, D_2O) δ 7.61 (s, 2H), 7.03 (s, 2H), 6.96 (s, 2H), 3.90 – 3.20 (m, 2H).^{13}C NMR (101 MHz, D_2O) 141.97, 127.10, 123.39. ^{11}B (128 MHz, D_2O) δ -10.09. HRMS (ESI) m/z: $[M]^-$ calcd for $C_6H_8BN_{14}^-$:147.0848, Found: 147.0849.

*General procedure for preparation of ionic liquids (**1-BTB** – **10-BTB**):*
Synthesis of salt 1: 2.652 1, 3-dimethylimdazolium chloride (20 mmol) was dissolved in 30 mL CH_3CN at room temperature, and then 4.174 g NaBTB 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-BTB: Colorless liquid, 85% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.88 (s, 2H), 8.53 (s, 1H), 7.29 – 7.23 (m, 2H), 4.00 – 3.50 (m, 8H). ^{13}C NMR (100 MHz, D_2O) δ 147.88, 136.32, 123.21, 35.50. ^{11}B (128 MHz, D_2O) δ −11.69. IR (KBr): *ν* = 3466, 3157, 3122, 2961, 2435, 1576, 1464, 1102; HRMS (ESI) m/z: $[M]^+$ calcd for $C_5H_9N_2^+$: 97.0760, found: 97.0763. $[M]^-$ calcd for $C_2H_4BN_8^-$: 151.0657, found: 151.0656. Anal. calcd for $C_7H_{13}BN_{10}$: C 33.89, H 5.28, N 56.47; found: C 33.39, H, 5.39, N 55.48.

2-BTB: Colorless liquid, 80% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.84 (s, 2H), 8.55 (s, 1H), 7.24 – 7.20 (m, 2H), 4.04 -3.40 (m, 7H), 1.27 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, D_2O) δ 147.82, 135.22, 123.24, 121.61, 44.63, 35.53, 14.21. ^{11}B (128 MHz, D_2O) δ −11.74. IR (KBr): *ν* = 3467, 3146, 3116, 2988, 2441, 2364, 1576, 1465, 1357, 1101; HRMS (ESI) m/z: $[M]^+$ calcd for $C_6H_{11}N_2^+$: 111.0917, found: 111.0918. $[M]^-$ calcd for $C_2H_4BN_8^-$: 151.0657, found: 151.0659. Anal. calcd for $C_8H_{15}BN_{10}$: C 36.66, H 5.77, N 53.44; found: C 37.01, H, 5.85, N, 53.01.

3-BTB: Colorless liquid, 84% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.90 (s, 2H), 8.61 (s, 1H), 7.32 – 7.31 (m, 2H), 4.05 – 3.40 (m, 7H), 1.68 – 1.61 (m, 2H), 1.15 – 1.09 (m, 2H), 0.75 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, D_2O) δ 147.90, 135.63, 123.34, 122.04, 49.14, 35.55, 31.10, 18.60, 12.45; ^{11}B (128 MHz, D_2O) δ −11.73. IR (KBr): *ν* = 3451, 3147, 3115, 2963, 2937, 2876, 2437, 2364, 2302, 1569, 1467, 1357, 1169; HRMS (ESI) m/z: $[M]^+$ calcd for $C_8H_{15}N_2^+$: 139.1230, found: 139.1229. $[M]^-$ calcd for $C_2H_4BN_8^-$: 151.0657, found: 151.0656. Anal. calcd for $C_{10}H_{19}BN_{10}$: C 41.40, H 6.60, N 48.27; found: C 41.33, H, 6.58, N, 47.76.

4-BTB: Colorless liquid, 83% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.88 (s, 2H), 8.61 (s, 1H), 7.30 – 7.29 (m, 2H), 5.90 – 5.83 (m, 1H), 5.30 – 5.19 (m, 2H), 4.66 (d, *J* = 6 Hz, 2H), 4.0 – 3.5 (m, 5H). ^{13}C NMR (100 MHz, D_2O) δ 147.89, 135.81, 130.01, 123.40, 122.04, 121.00, 51.34, 35.61. ^{11}B (128 MHz, D_2O) δ −11.71. IR (KBr): *ν* = 3438, 3146, 3116, 2439, 2375, 1570, 1460, 1158, 1101; HRMS (ESI) m/z: $[M]^+$ calcd for $C_7H_{11}N_2^+$: 123.0917, found: 123.0917. $[M]^-$ calcd for $C_2H_4BN_8^-$: 151.0657, found: 151.0658. Anal. calcd for $C_9H_{15}BN_{10}$: C 39.44, H 5.52, N 51.10; found: C 39.41, H, 5.28, N, 50.74.

5-BTB: Slight yellow liquid, 86% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.88 (s, 2H), 8.70 (s, 1H), 7.38 – 7.35 (m, 2H), 5.91 – 5.88 (m, 2H), 5.31 – 5.22 (m, 4H), 4.75 – 4.65 (m, 4H), 4.20 – 3.25 (m, 2H). ^{13}C NMR (100 MHz, D_2O) δ 147.91, 135.27, 130.06, 122.35, 121.12, 51.54. ^{11}B (128 MHz, D_2O) δ −11.74. IR (KBr): *ν* = 3442, 3140, 3109, 2990, 2437, 2360, 2300, 1564, 1157; HRMS (ESI) m/z: $[M]^+$ calcd for $C_9H_{13}N_2^+$: 149.1073, found: 149.1072. $[M]^-$ calcd for $C_2H_4BN_8^-$: 151.0657, found: 151.0656. Anal. calcd for $C_{11}H_{17}BN_{10}$: C 44.02, H 5.71, N 46.67; found: C 43.56, H, 5.56, N, 46.20.

6-BTB: Colorless liquid, 82% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.93 (s, 2H), 4.10 – 3.31 (m, 6H), 3.12 – 3.07 (m, 2H), 2.88 (s, 3H), 2.03 – 2.02 (m, 4H), 1.50 – 1.48 (m, 2H), 1.12 - 1.05 (m, 2H), 0.75 – 0.66 (m, 3H). ^{13}C NMR (100 MHz, D_2O) δ 147.93, 64.11, 63.98, 47.94, 24.90, 21.15, 19.03, 12.61. ^{11}B (128 MHz, D_2O) δ −11.67. IR (KBr): *ν* = 3462, 3127, 2966, 2877, 2437, 2362, 1464, 1356, 1100; HRMS (ESI) m/z: $[M]^+$ calcd for $C_9H_{20}N^+$: 142.1590, found: 142.1589. $[M]^-$ calcd for $C_2H_4BN_8^-$: 151.0657, found: 151.0659. Anal. calcd for $C_{11}H_{24}BN_9$: C 45.06, H 8.25, N 43.00; found: C 44.59, H, 8.11, N, 42.47.

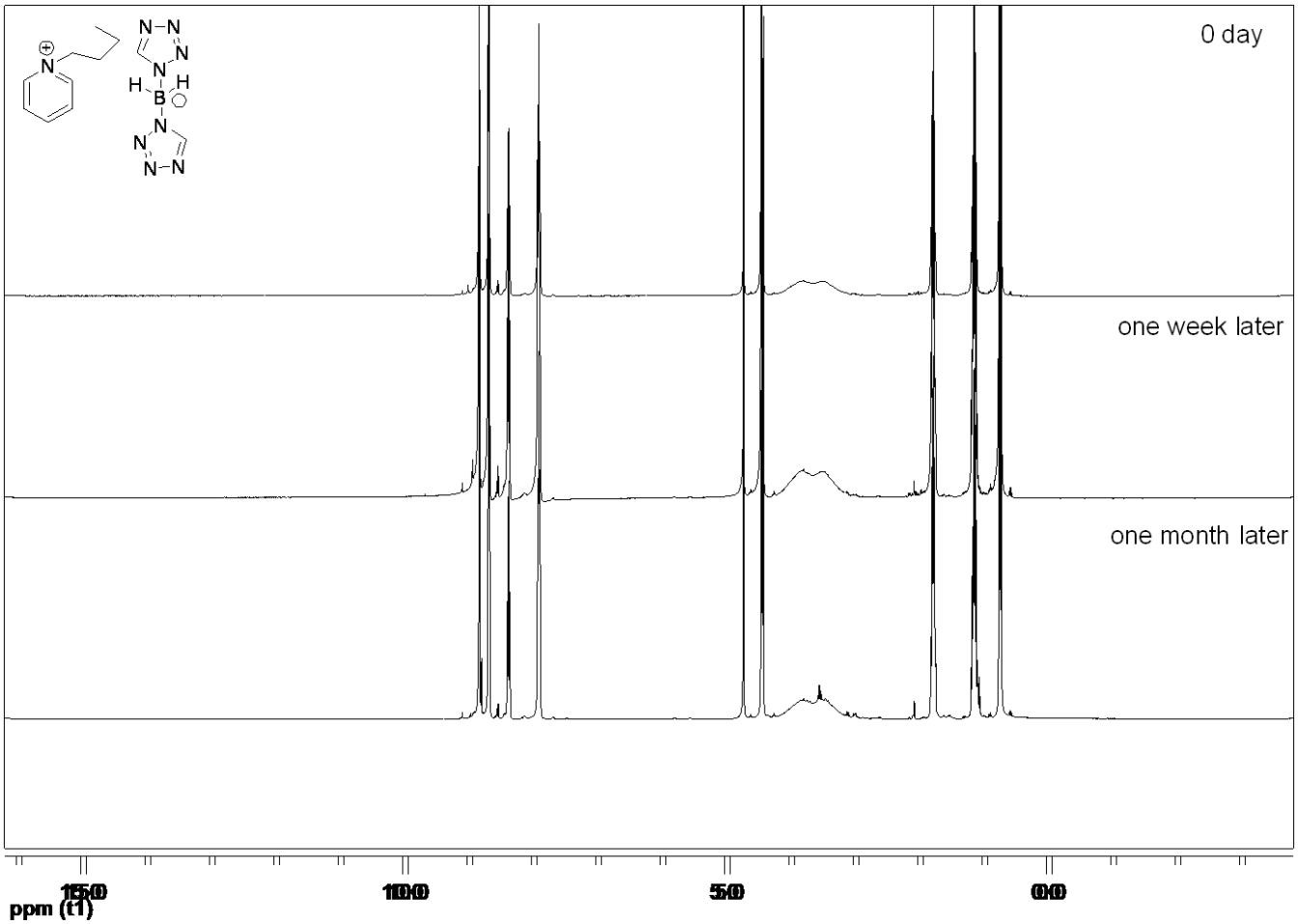
7-BTB: Slight yellow liquid, 80% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.93 (s, 2H), 5.95 – 5.85 (m, 1H), 5.61 – 5.50 (m, 2H), 4.10 – 3.30 (m, 8H), 2.92 (s, 3H), 2.20 – 2.00 (m, 4H). ^{13}C NMR (100 MHz, D_2O) δ 147.98, 128.03, 125.02, 65.64, 63.47, 48.28, 21.21. ^{11}B (128 MHz, D_2O) δ −11.67. IR (KBr): *ν* = 3455, 3128, 2985, 2437, 2364, 1456, 1356, 1102; HRMS (ESI) m/z: $[M]^+$ calcd for $C_8H_{16}N_9^+$: 126.1277, found: 126.1278. $[M]^-$ calcd for $C_2H_4BN_8^-$: 151.0657, found: 151.0656. Anal. calcd for $C_{10}H_{20}BN_9$: C 43.34, H 7.27, N 45.29; found: C 43.14, H, 7.07, N, 44.75.

8-BTB: Colorless liquid, 85% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.87 (s, 2H), 8.74 (d, *J* = 5.6 Hz, 2H), 8.39 (t, *J* = 8 Hz, 1H), 7.94 – 7.92 (m, 2H), 4.55 (q, *J* = 7.2 Hz, 2H), 4.1 – 3.30 (m, 2H), 1.53 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, D_2O) δ 147.88, 145.25, 143.71, 128.07, 57.25, 15.50. ^{11}B (128 MHz, D_2O) δ −11.74. IR (KBr): *ν* = 3447, 3133, 3067, 2982, 2943, 2435, 2358, 1635, 1490, 1357, 1100; HRMS (ESI) m/z: $[M]^+$ calcd for $C_7H_{10}N_9^+$: 108.0808, found: 108.0810. $[M]^-$ calcd for $C_2H_4BN_8^-$: 151.0657, found: 151.0658. Anal. calcd for $C_9H_{14}BN_9$: C 41.72, H 5.45, N 48.66; found: C 41.33, H, 5.36, N, 48.19.

9-BTB: Colorless liquid, 80% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.82 (s, 2H), 8.67 (d, *J* = 5.6, 2H), 8.33 (t, *J* = 7.6 Hz, 1H), 7.88 (t, *J* = 6.4 Hz, 2H), 4.40 (t, *J* = 7.2 Hz, 2H), 4.1 – 3.0 (m, 2H), 1.71 – 1.63 (m, 2H), 1.05 – 0.96 (m, 2H), 0.59 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, D_2O) δ 147.79, 145.24, 143.90, 128.03, 61.54, 32.40, 18.51, 12.45. ^{11}B (128 MHz, D_2O) δ −11.82. IR (KBr): *ν* = 3442, 3132, 3065, 2964, 2937, 2876, 2441, 2360, 1635, 1489, 1356, 1155; HRMS (ESI) m/z: $[M]^+$ calcd for $C_9H_{14}N_9^+$: 136.1121, found: 136.1120. $[M]^-$ calcd for $C_2H_4BN_8^-$: 151.0657, found: 151.0656. Anal. calcd for $C_{11}H_{18}BN_9$: C 46.01, H 6.32, N 43.90; found: C 45.41, H, 6.04, N, 43.30.

10-BTB: Slight yellow liquid, 84% yield. ^{1}H NMR (400 MHz, D_2O) δ 8.89 (s, 2H), 8.75 (d, *J* = 5.2 Hz, 2H), 8.46 (t, *J* = 7.6 Hz, 1H), 7.98 – 7.97 (m, 2H), 6.07 – 5.99 (m, 1H), 5.47 – 5.35 (m, 2H), 5.15 (d, *J* = 5.2 Hz, 2H), 3.86 – 3.50 (m, 2H). ^{13}C NMR (100 MHz, D_2O) δ 147.91, 145.79, 144.08, 129.70, 128.13, 122.93, 63.35. ^{11}B (128 MHz, D_2O) δ −11.72. IR (KBr): *ν* = 3438, 3129, 3064, 2985, 2437, 2364, 1633, 1487, 1156, 1101; HRMS (ESI) m/z: $[M]^+$ calcd for $C_8H_{10}N_9^+$: 120.0808, found: 120.0809. $[M]^-$ calcd for $C_2H_4BN_8^-$: 151.0657, found: 151.0658. Anal. calcd for $C_{10}H_{14}BN_9$: C 44.31, H 5.21, N 46.50; found: C 44.03, H, 5.20, N, 45.97.

5. Hydrolysis study of hypergolic ionic liquids



6. Reference

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7. IDs Test

Table S5. The IDs of *N*-hydroboration salts with WFNA[a].

	NaBTB	KBATB	$NaBH_2CN(tetz)$	$KBH_2(pz)_3$	$KBH(im)_3$	$KBH_2(im)_3$
IDs (ms)	4	96	10	221	635	100

a) The droplet test was performed by directly adding the sample particle (ca. 5 mg) into the oxidizer liquid pool. Although the IDs of solid can be effected by the solid state, the IDs can somewhat reveal the reactivity of the compounds with WFNA.

Table S6. The standard deviation of IDs with WFNA[a].

HILs	Test (ms)			Average value (SD)[b]
	1	2	3	
1-BTB	20	17	18	18 (2)
2-BTB	18	16	18	17 (1)
3-BTB	35	39	40	38 (4)
4-BTB	18	23	20	20 (4)
5-BTB	19	18	21	19 (4)
6-BTB	37	33	38	36 (4)
7-BTB	20	21	17	19 (3)
8-BTB	11	16	15	14 (4)
9-BTB	30	34	29	31 (4)
10-BTB	9	10	9	9 (1)

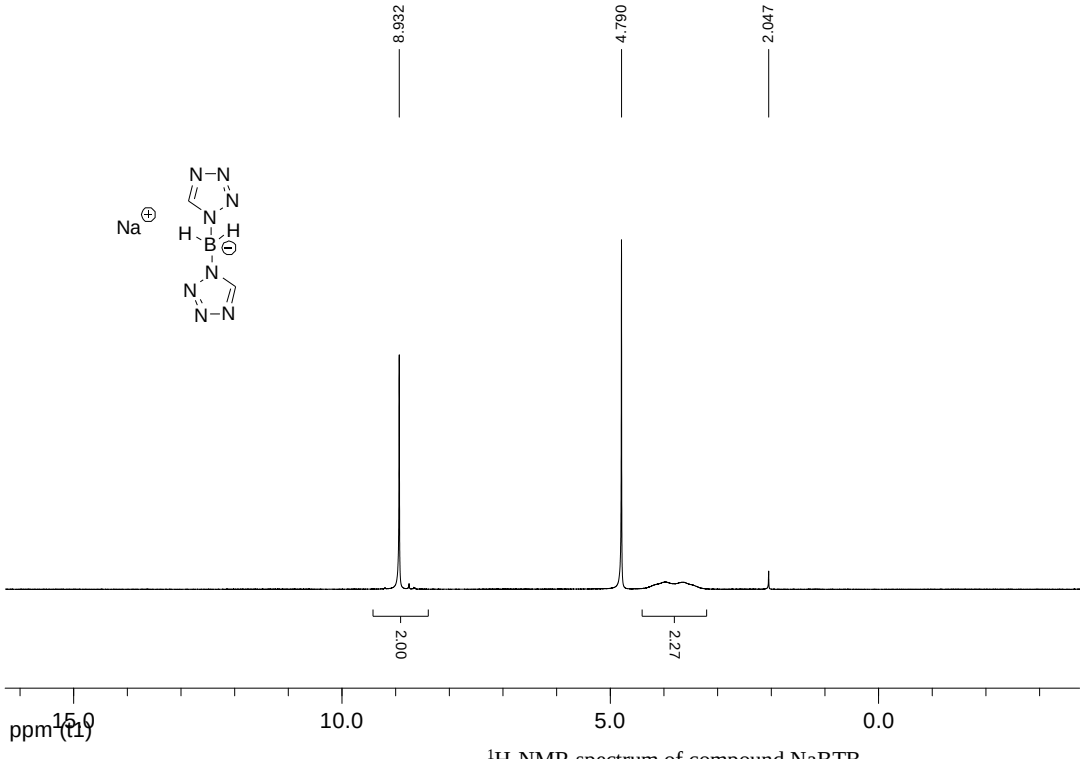
a) Compound **1**-**10**: Each sample was recorded on average of three measurements. b) The values into parenthesis represent standard deviation.

Table S7. The standard deviation of IDs with N_2O_4[a].

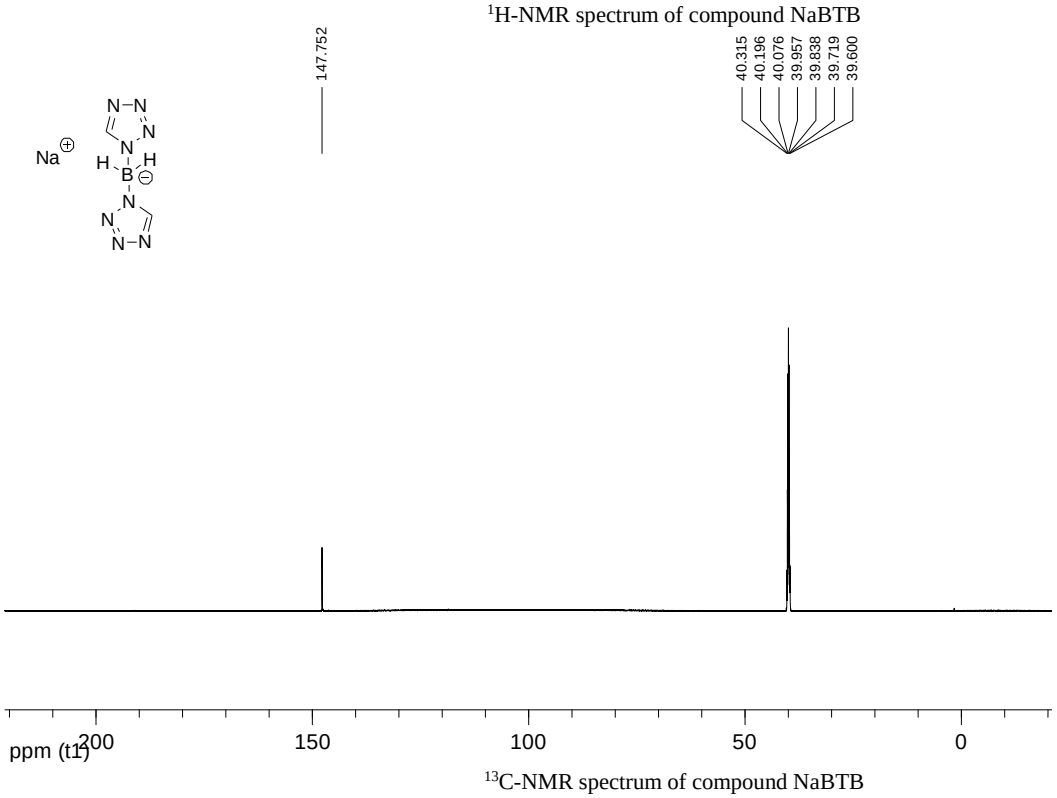
HILs	Test (ms)			Average value (SD)[b]
	1	2	3	
1-BTB	139	97	115	117 (30)
2-BTB	159	175	159	154 (35)
3-BTB	129	101	108	113 (21)
4-BTB	60	47	53	53 (9)
5-BTB	31	26	29	29 (4)
6-BTB	86	69	77	77 (12)
7-BTB	53	46	57	52 (8)
8-BTB	138	156	129	141 (24)
9-BTB	117	105	138	120 (4)
10-BTB	62	51	58	57 (8)

a) Compound **1**-**10**: Each sample was recorded on average of three measurements. b) The values into parenthesis represent standard deviation.

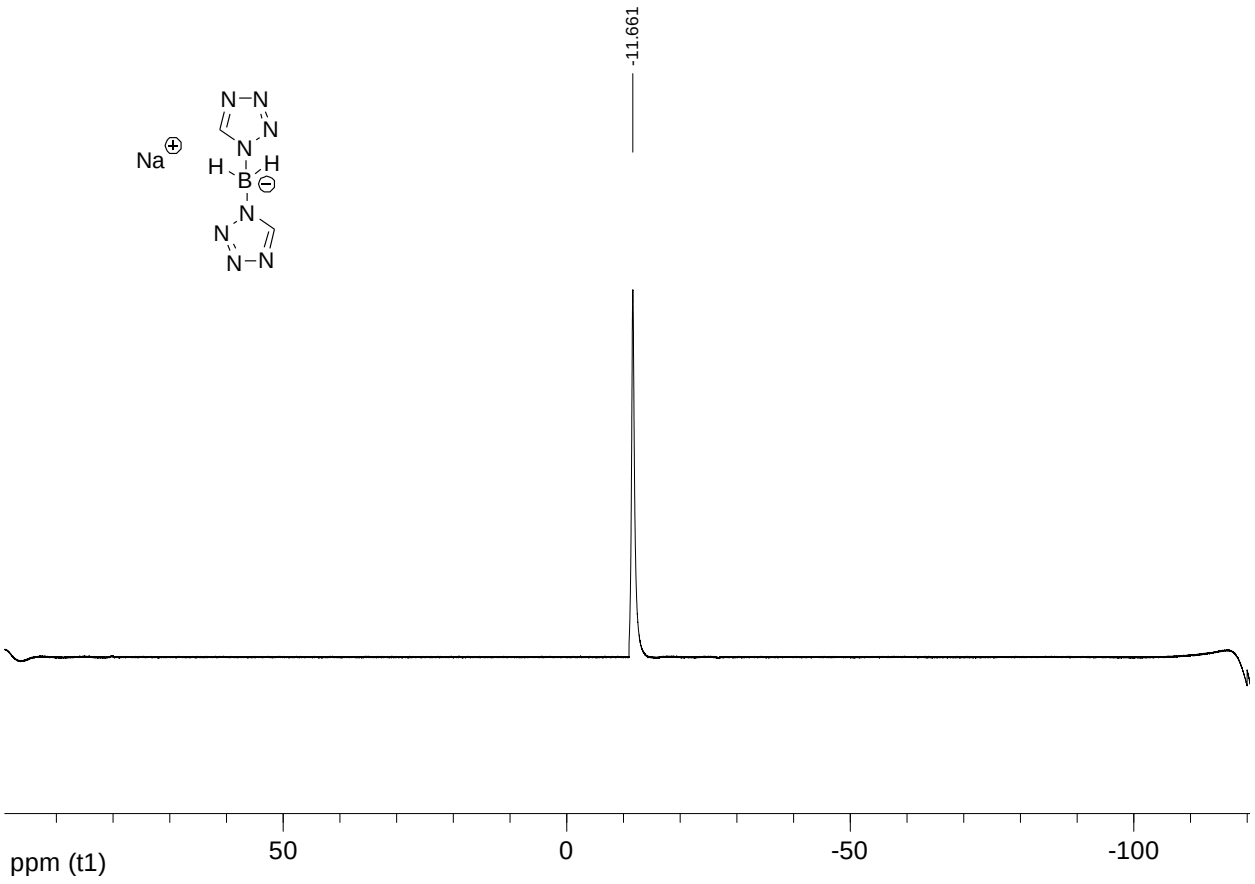
8. Copies of NMR, IR, HRMS Spectra and DSC.



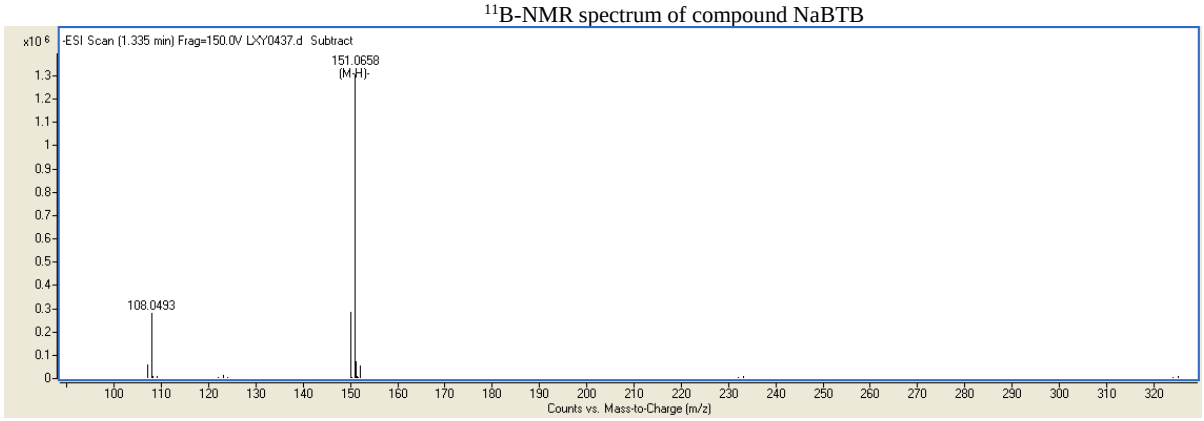
^{1}H-NMR spectrum of compound NaBTB



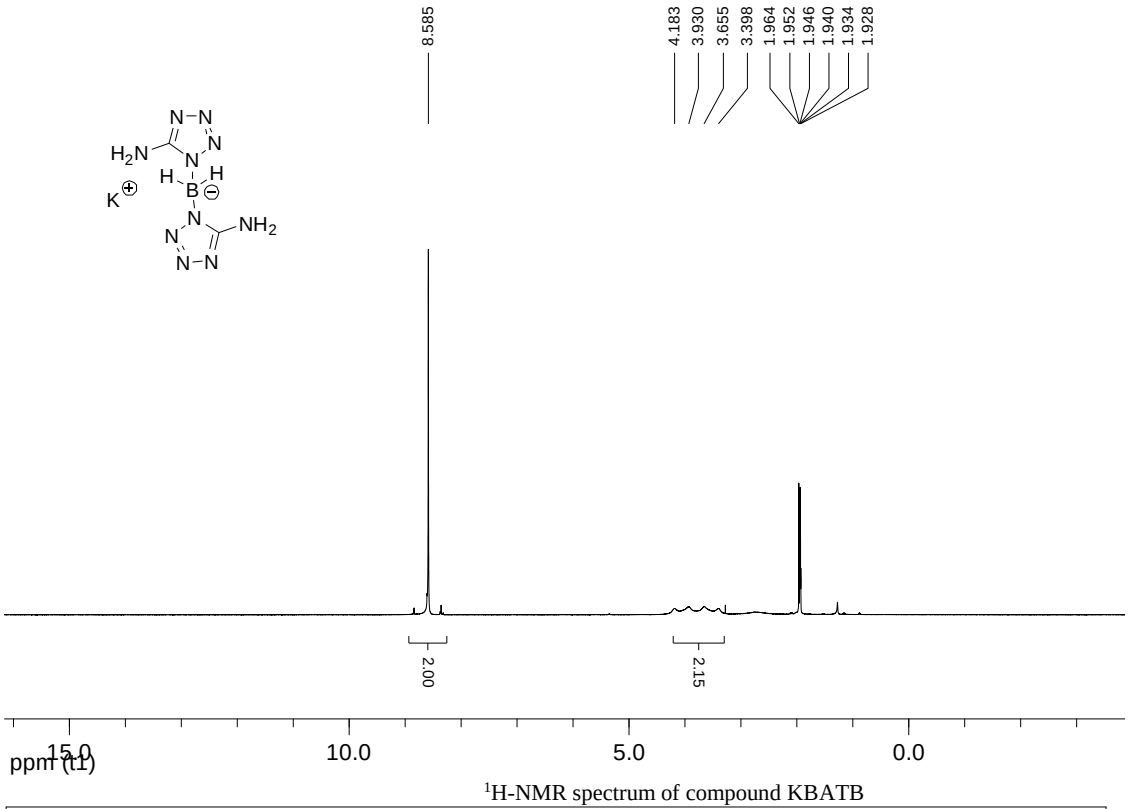
^{13}C-NMR spectrum of compound NaBTB



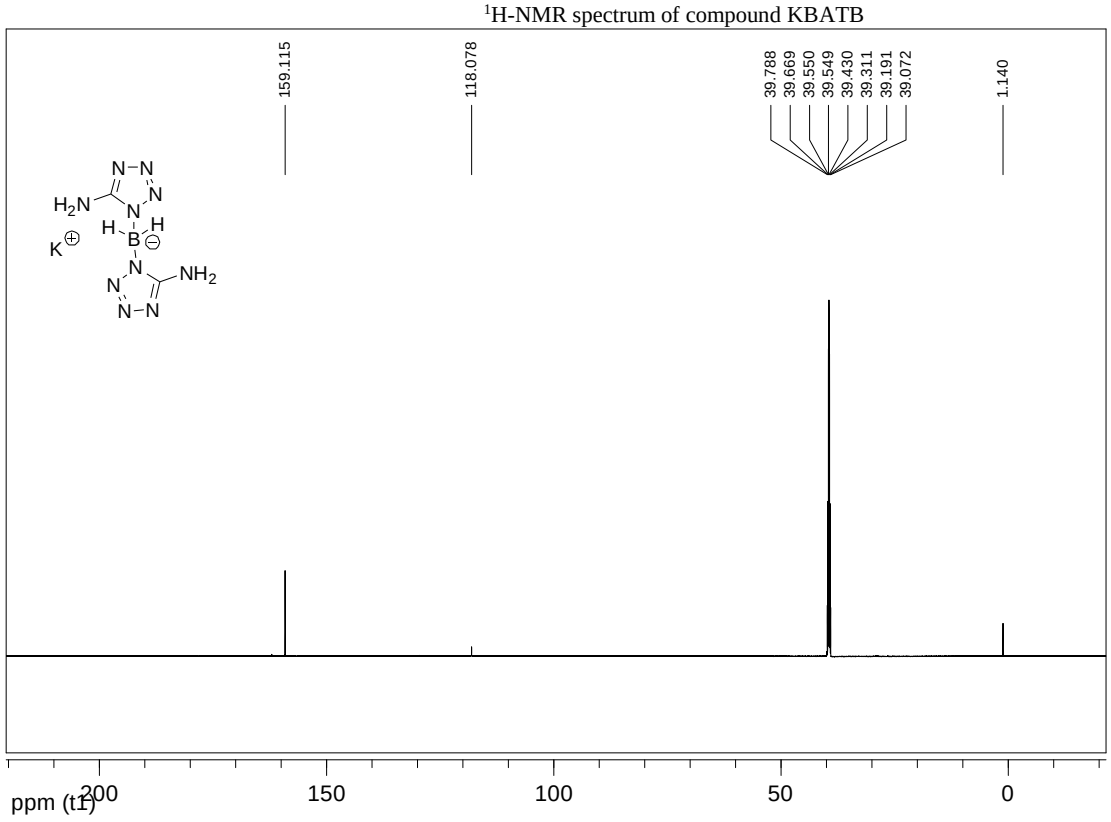
^{11}B-NMR spectrum of compound NaBTB



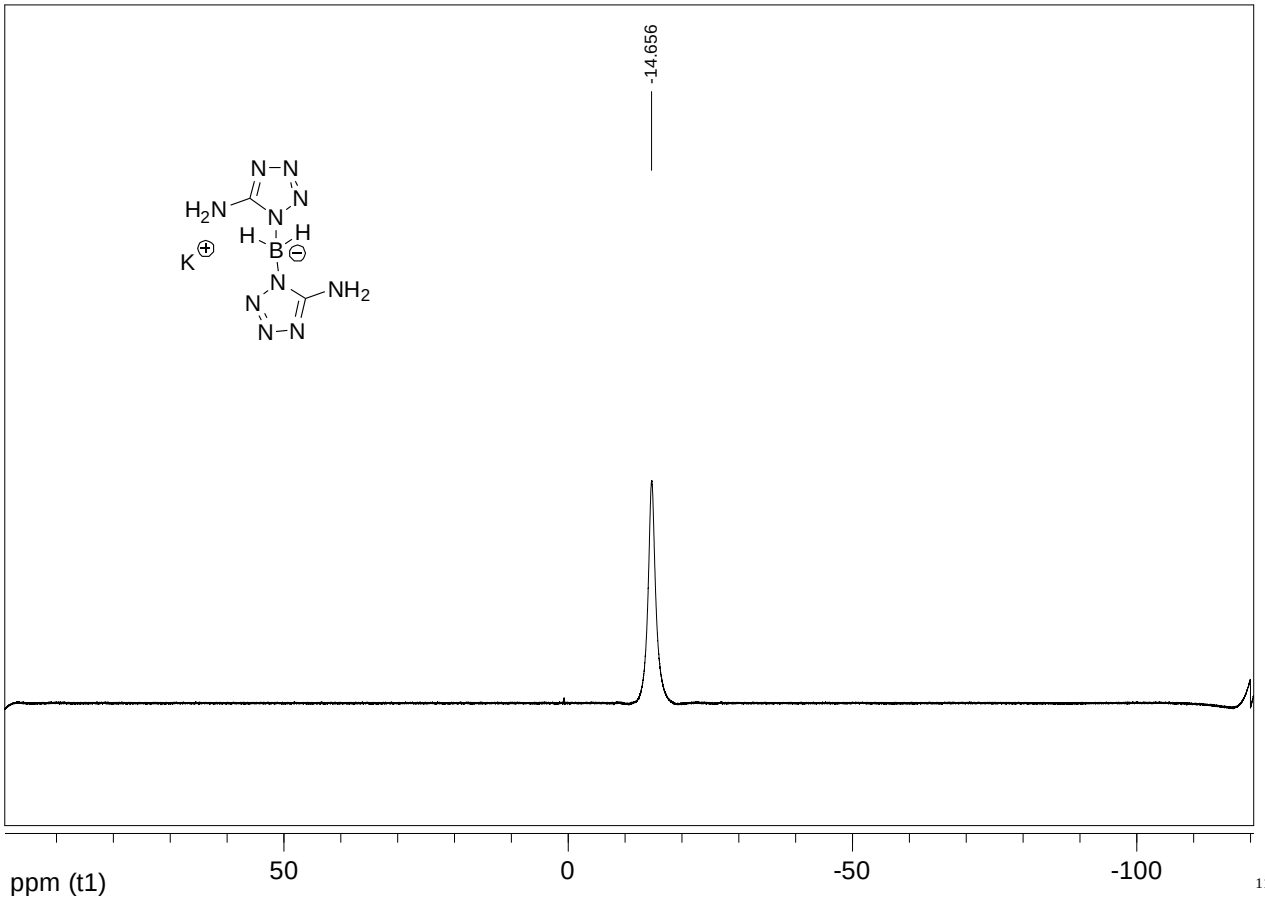
HRMS: BTB^-



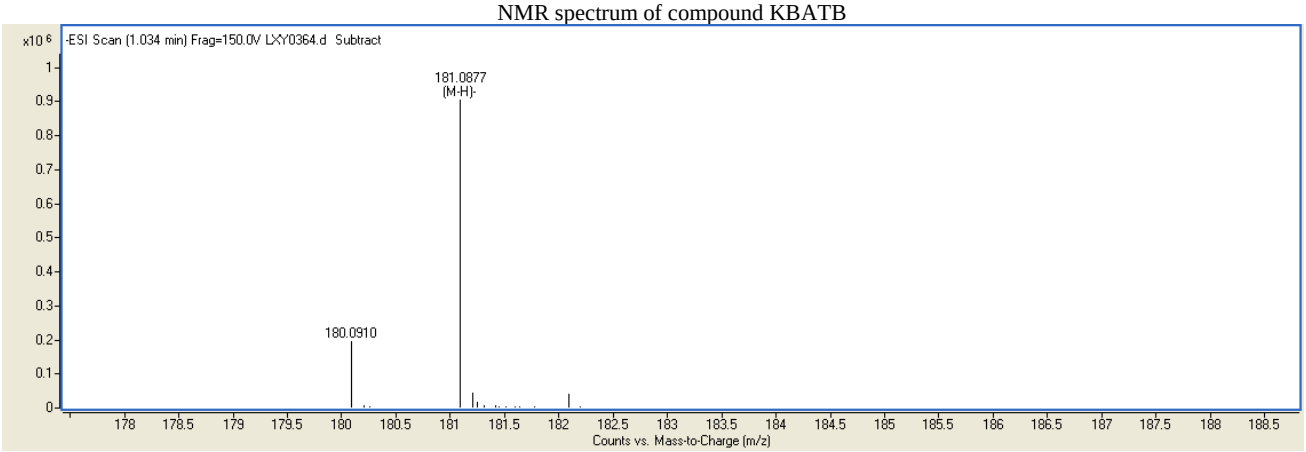
^{1}H-NMR spectrum of compound KBATB



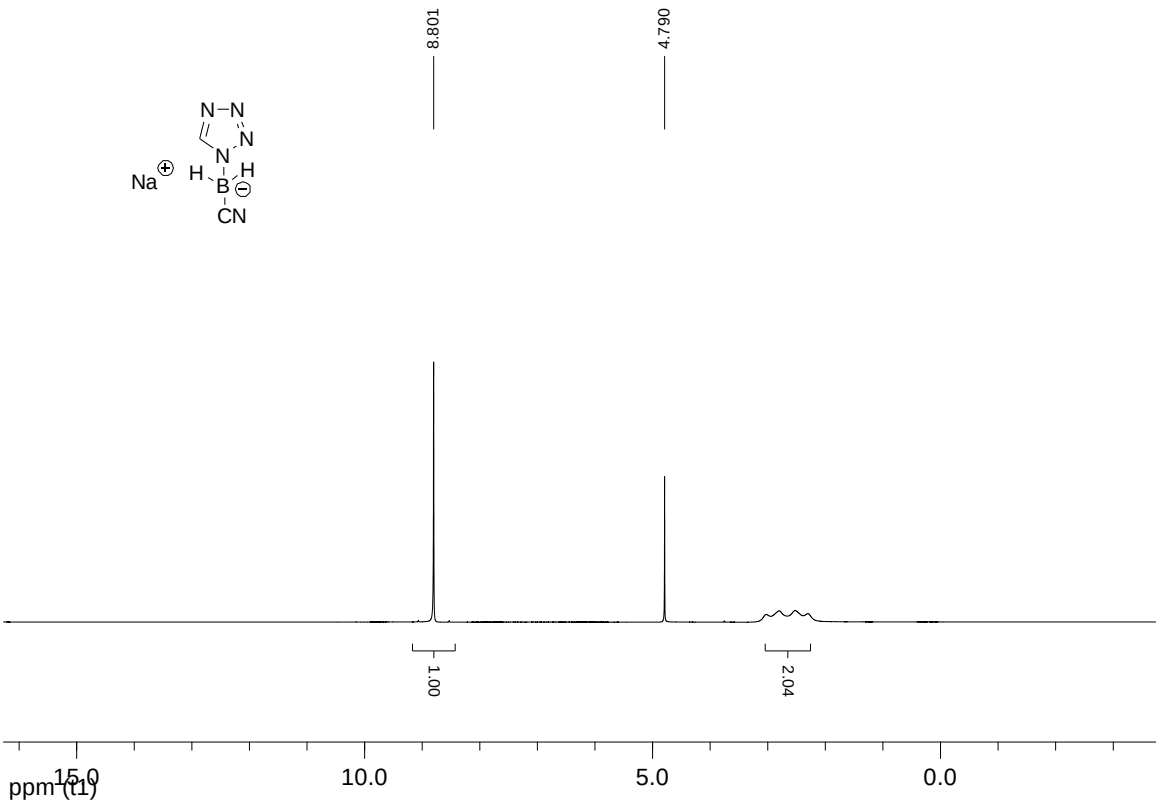
^{13}C-NMR spectrum of compound KBATB



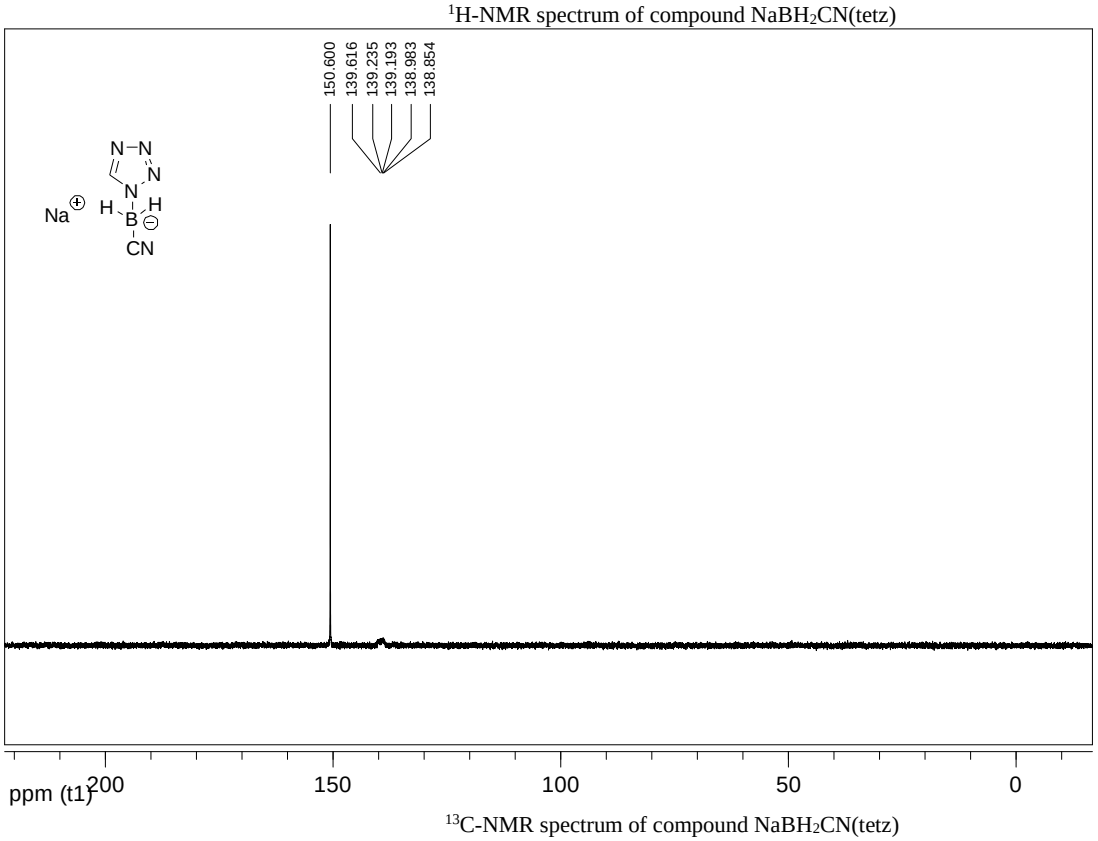
^{11}B-NMR spectrum of compound KBATB



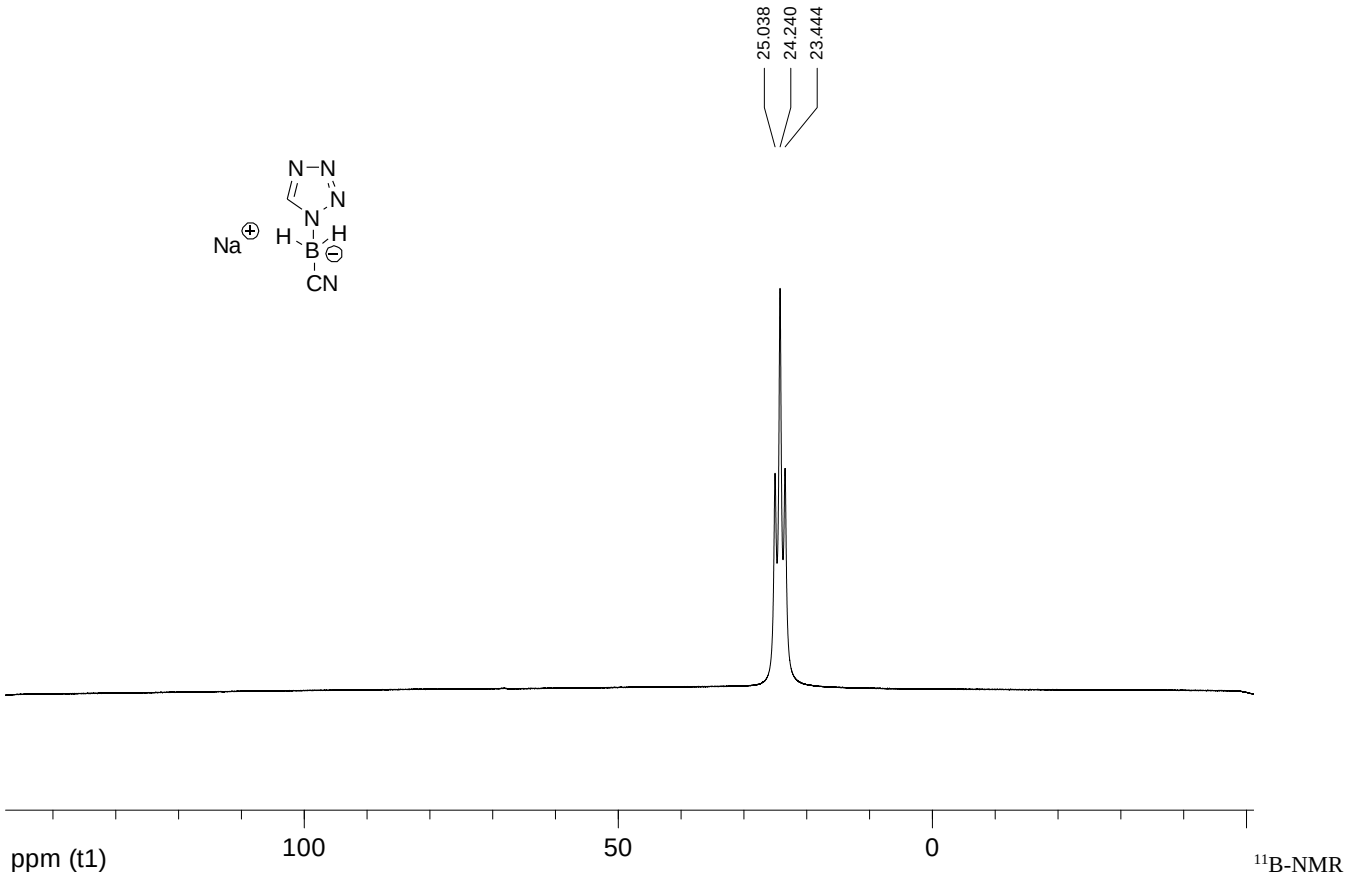
HRMS: $BATB^-$



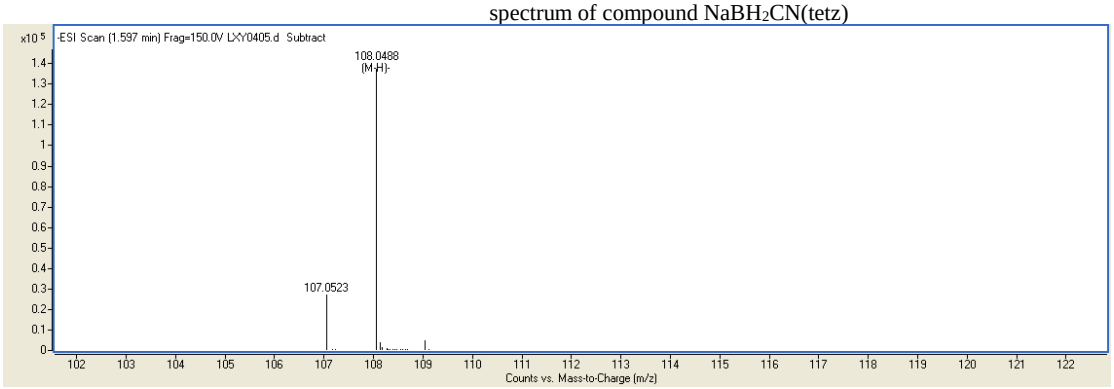
^{1}H-NMR spectrum of compound $NaBH_2CN(tetz)$



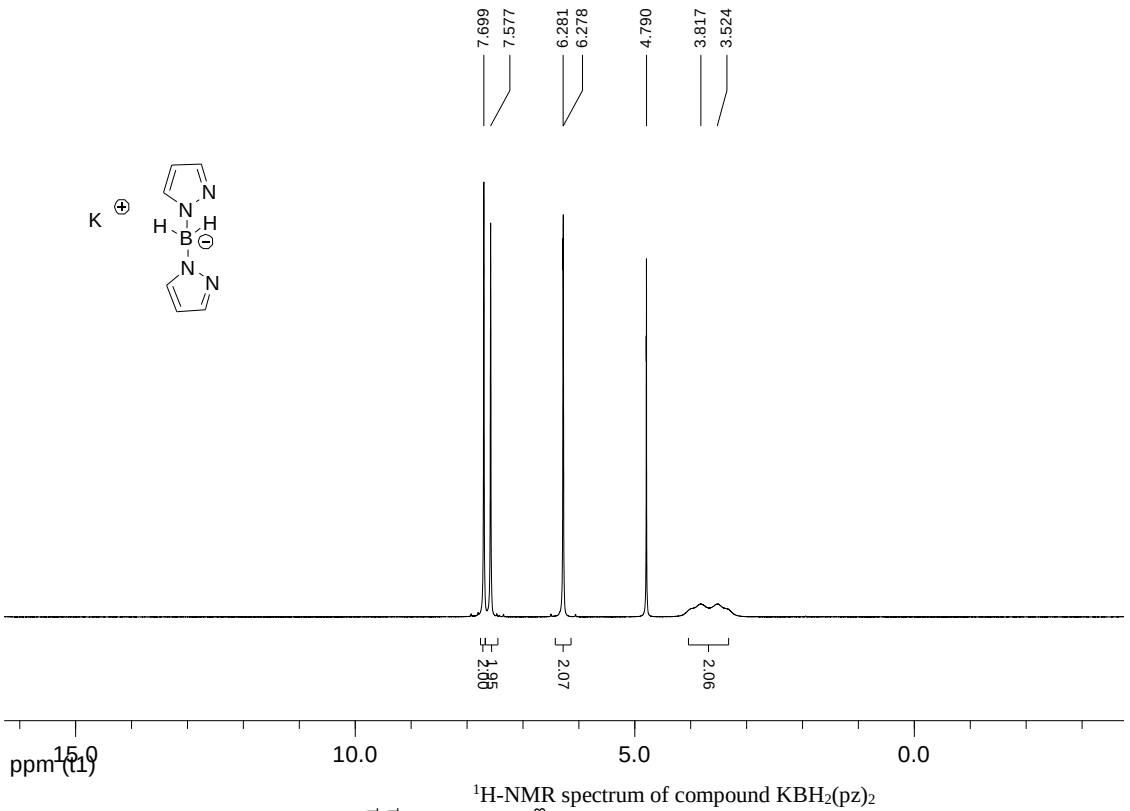
^{13}C-NMR spectrum of compound $NaBH_2CN(tetz)$



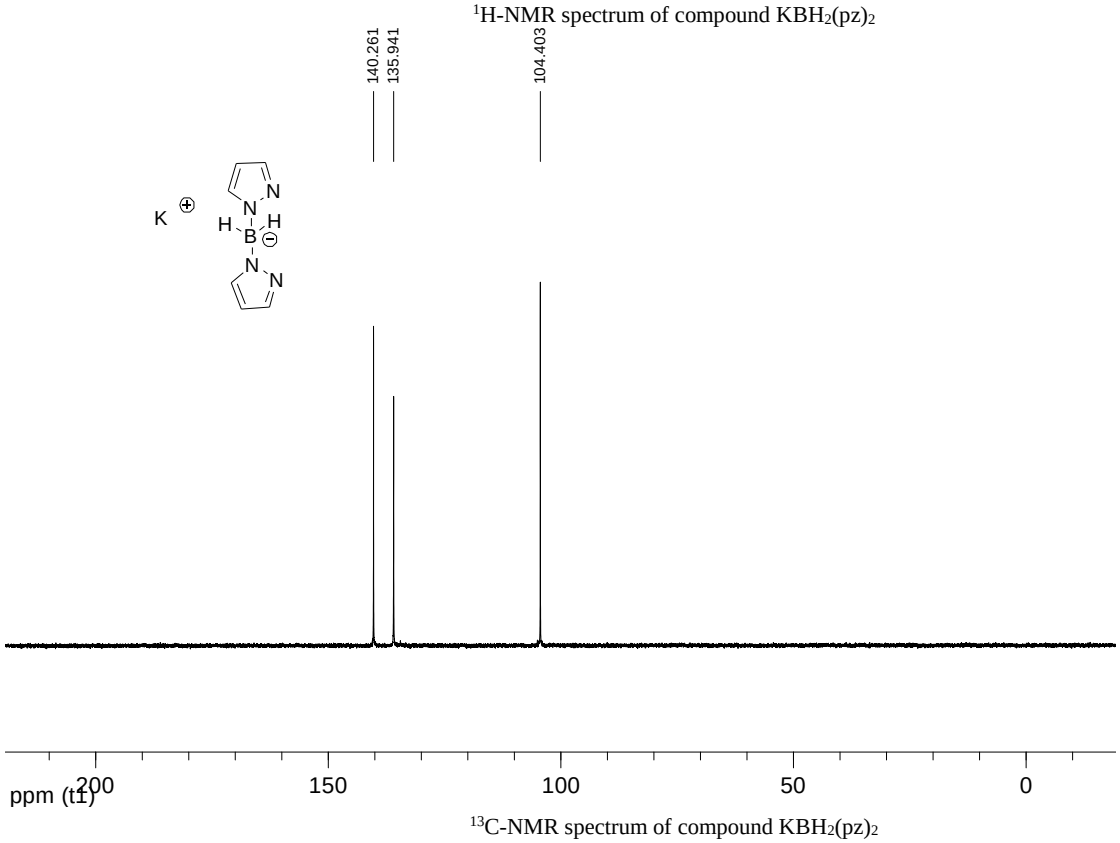
^{11}B-NMR spectrum of compound $NaBH_2CN(tetz)$



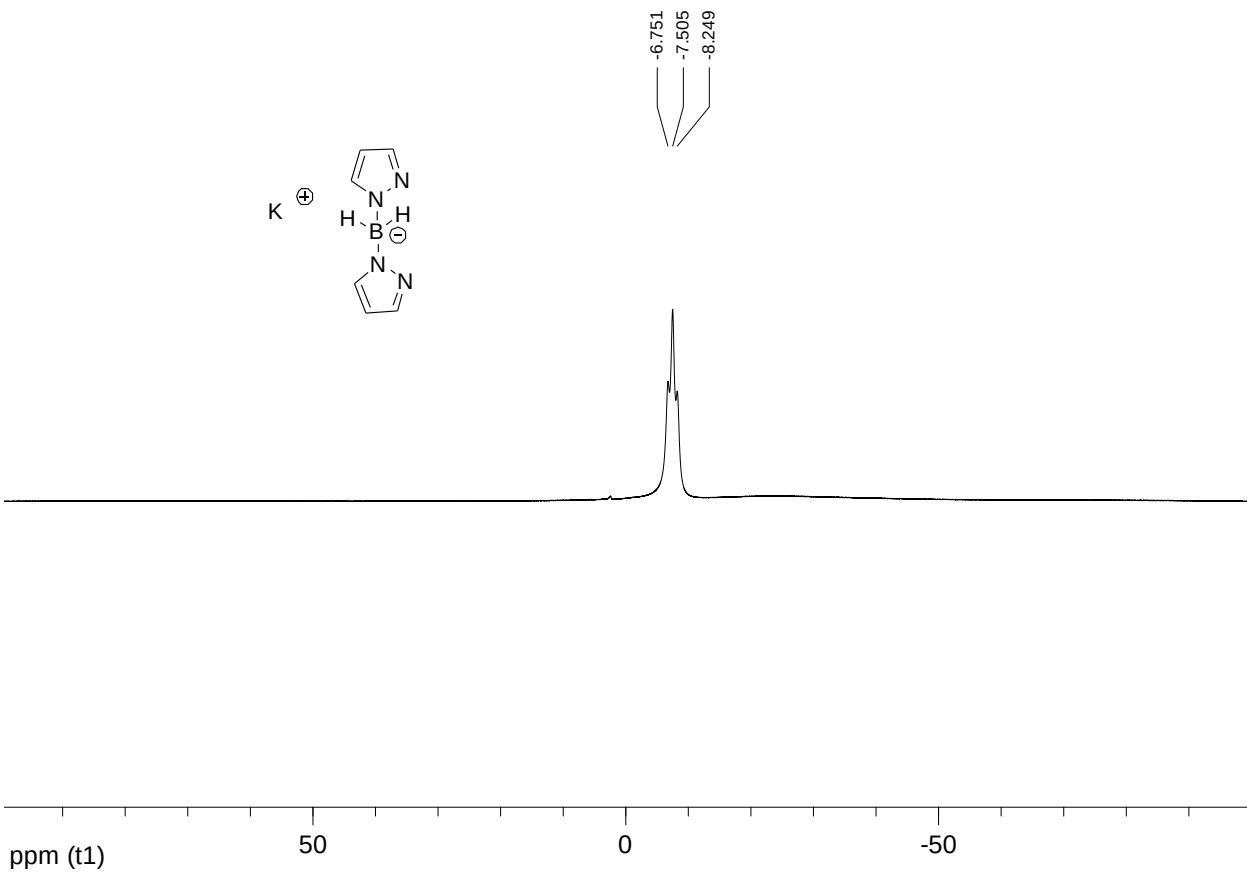
HRMS: $BH_2CN(tetz)^-$



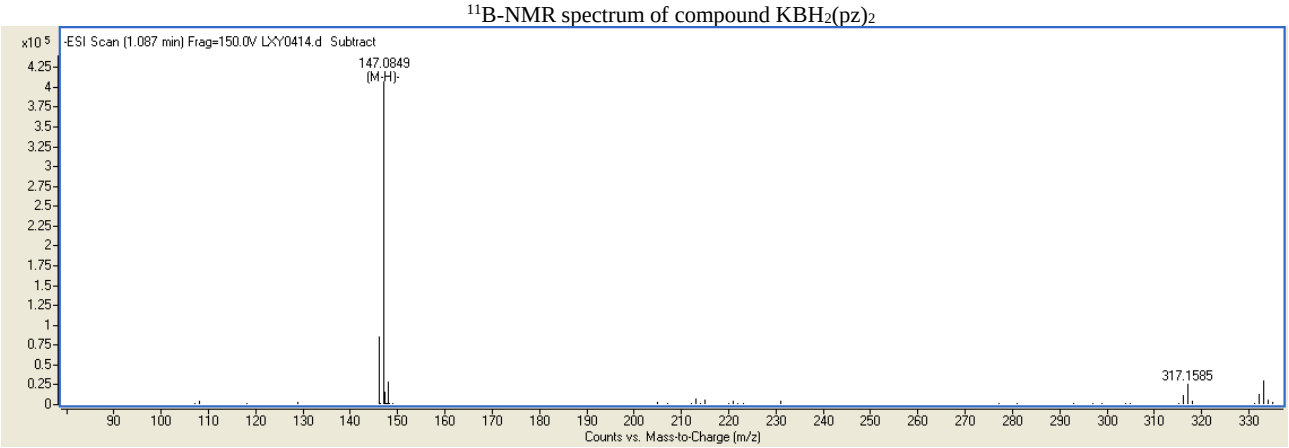
^{1}H-NMR spectrum of compound $KBH_2(pz)_2$



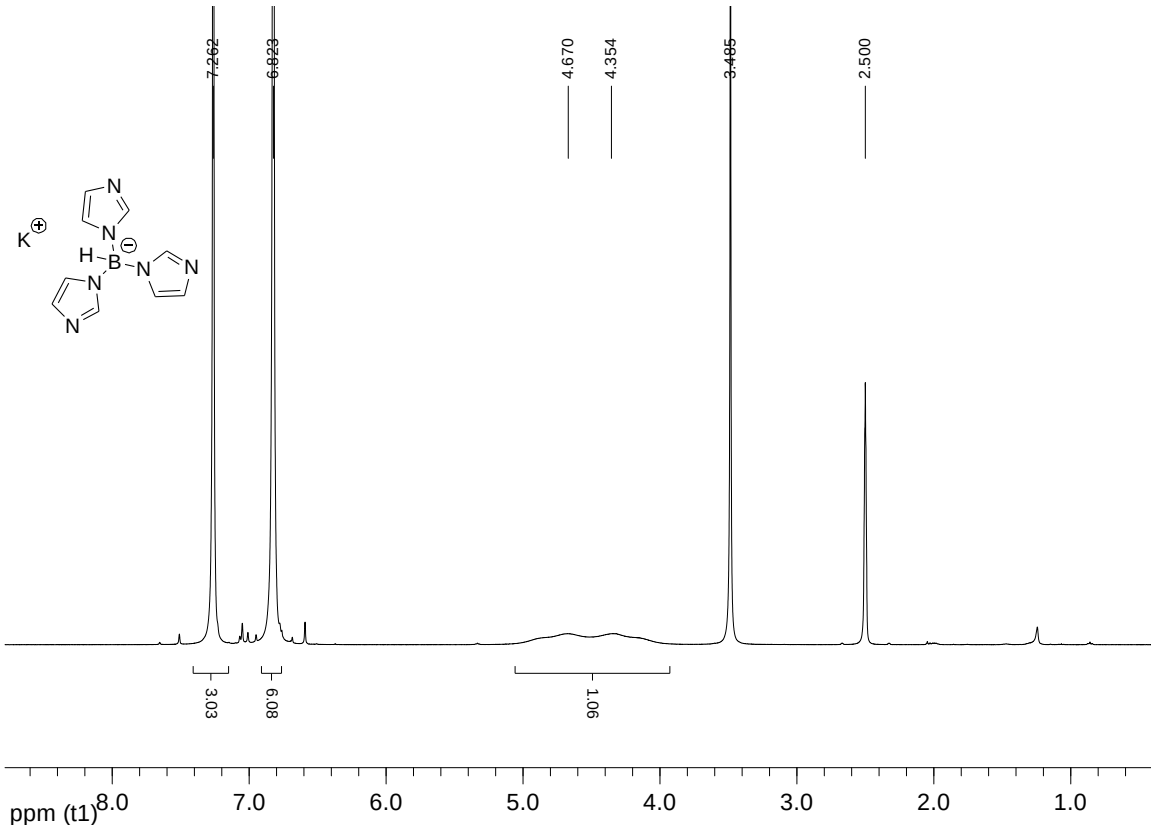
^{13}C-NMR spectrum of compound $KBH_2(pz)_2$



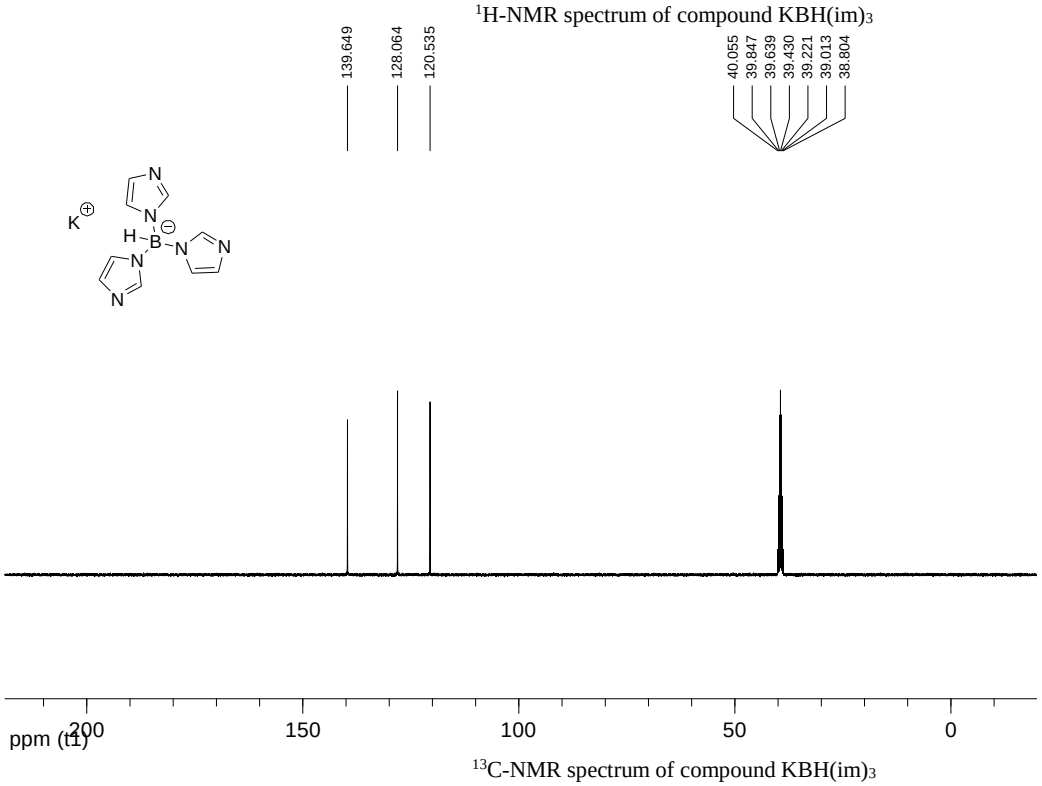
^{11}B-NMR spectrum of compound $KBH_2(pz)_2$



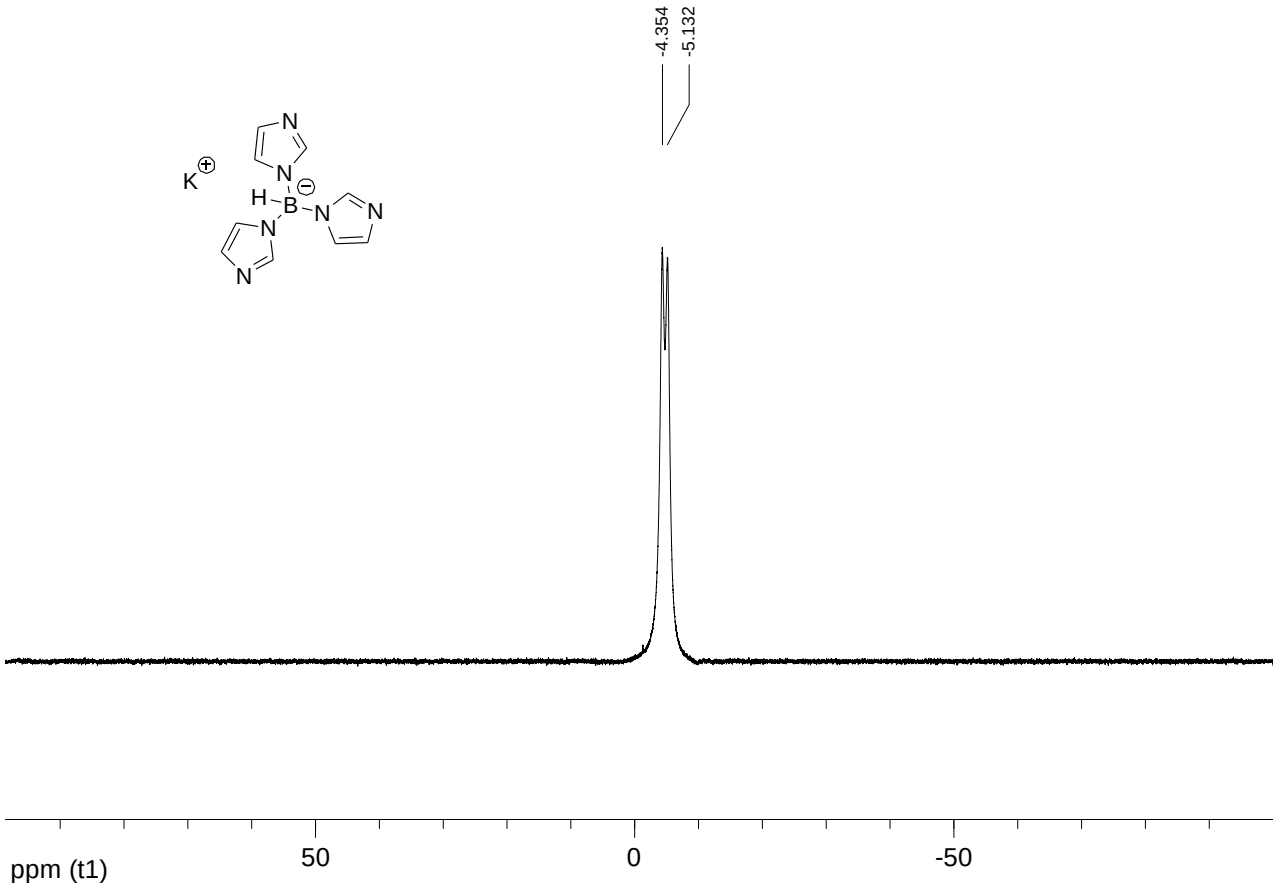
HRMS: $BH_2(pz)_2^-$



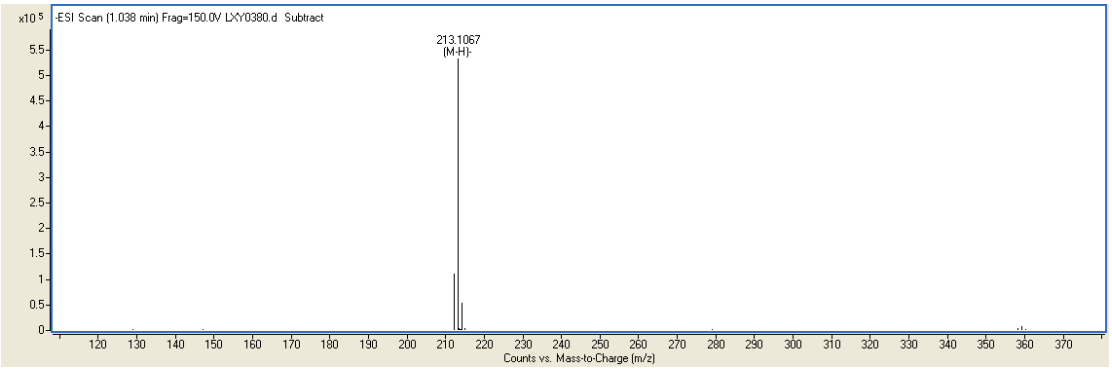
^{1}H-NMR spectrum of compound KBH(im)$_3$



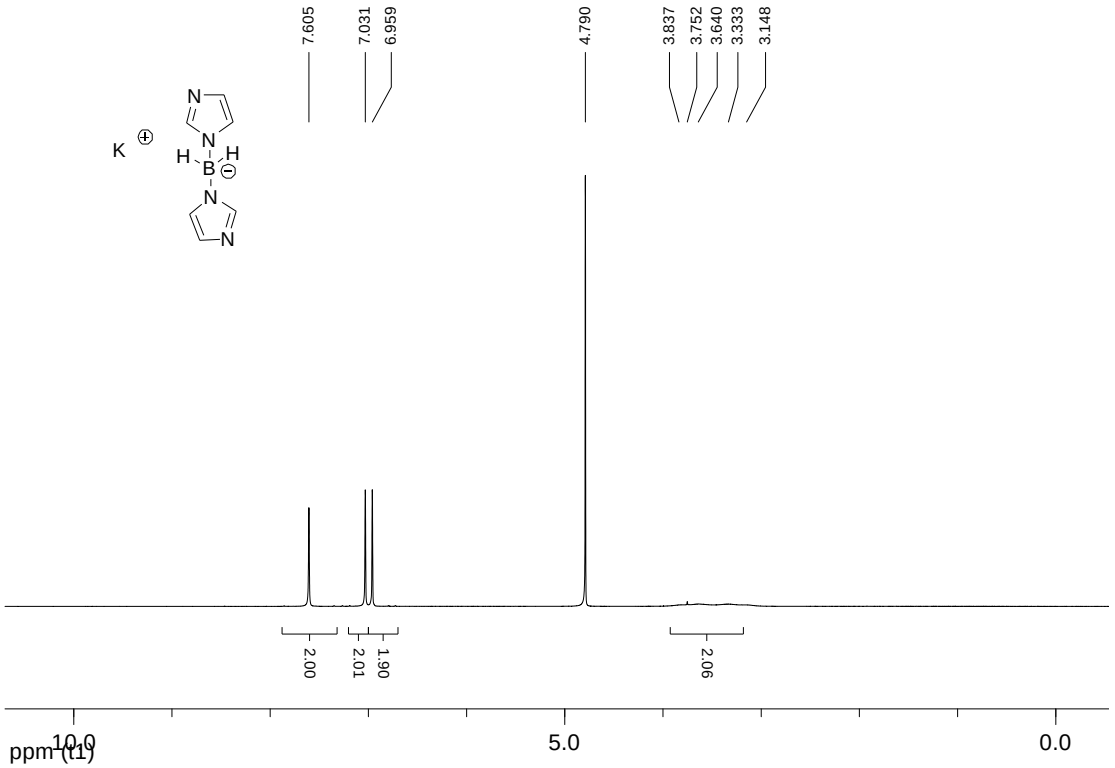
^{13}C-NMR spectrum of compound KBH(im)$_3$



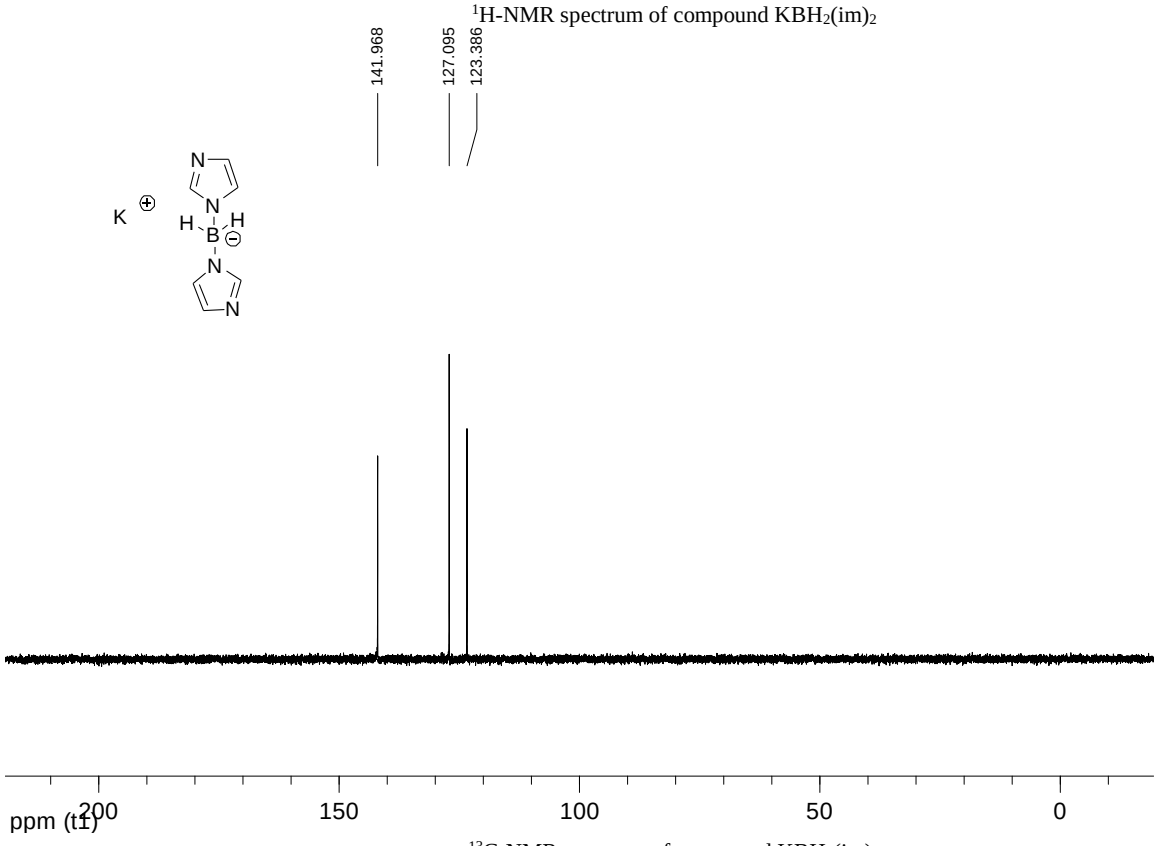
^{11}B-NMR spectrum of compound KBH(im)$_3$



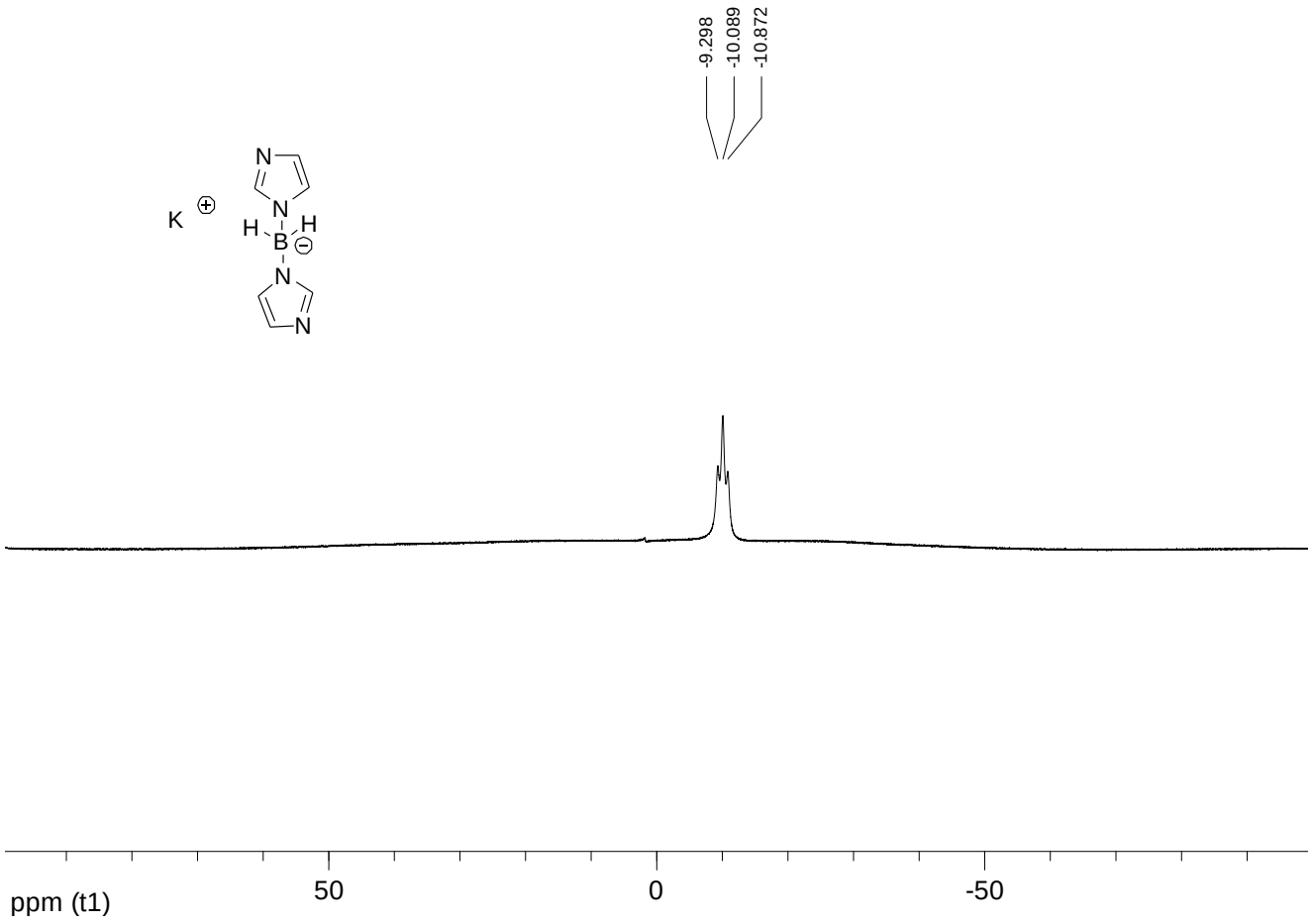
HRMS: BH(im)$_3^-$



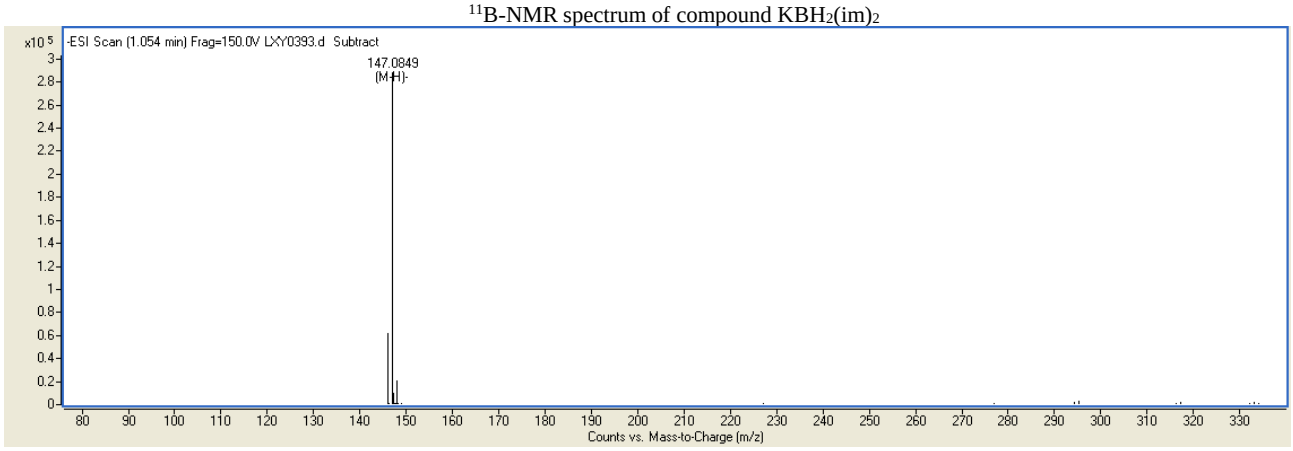
^{1}H-NMR spectrum of compound $KBH_2(im)_2$



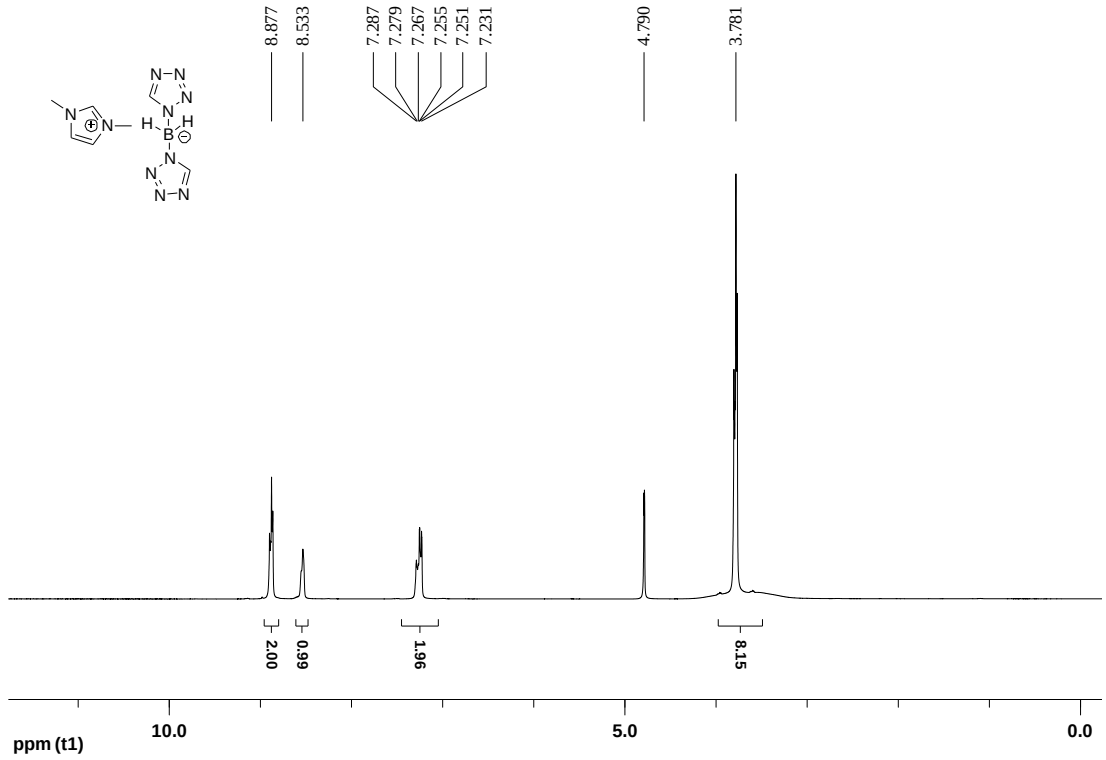
^{13}C-NMR spectrum of compound $KBH_2(im)_2$



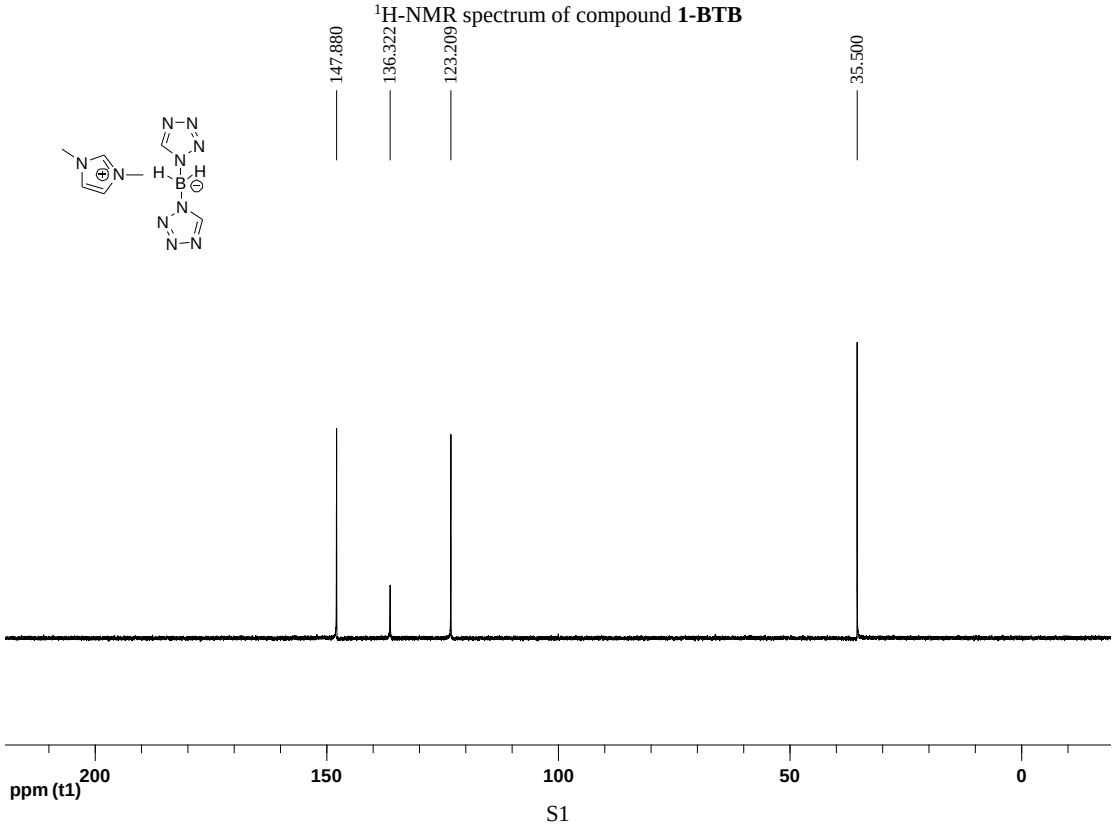
^{11}B-NMR spectrum of compound $KBH_2(im)_2$



HRMS: $BH_2(im)_2^-$

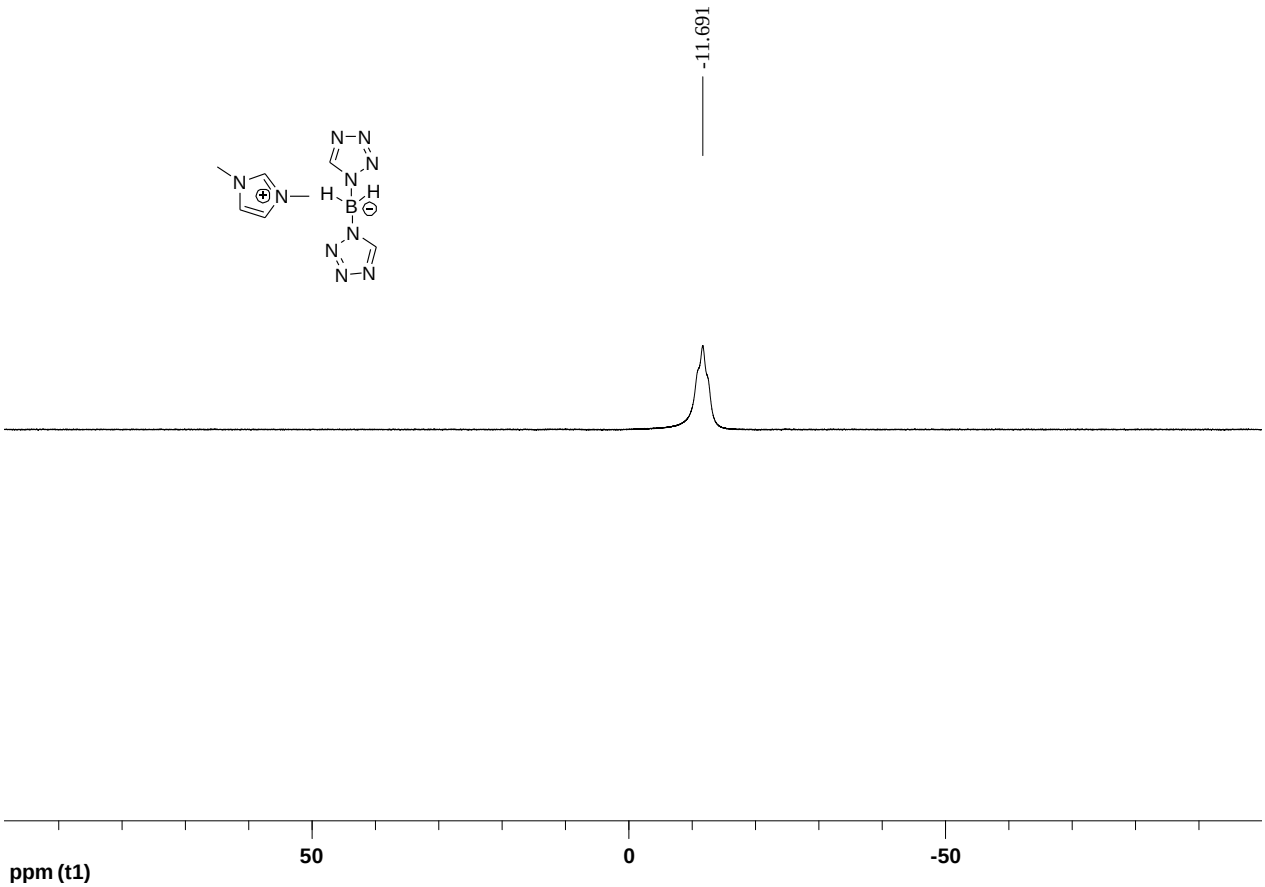


^{1}H-NMR spectrum of compound **1-BTB**

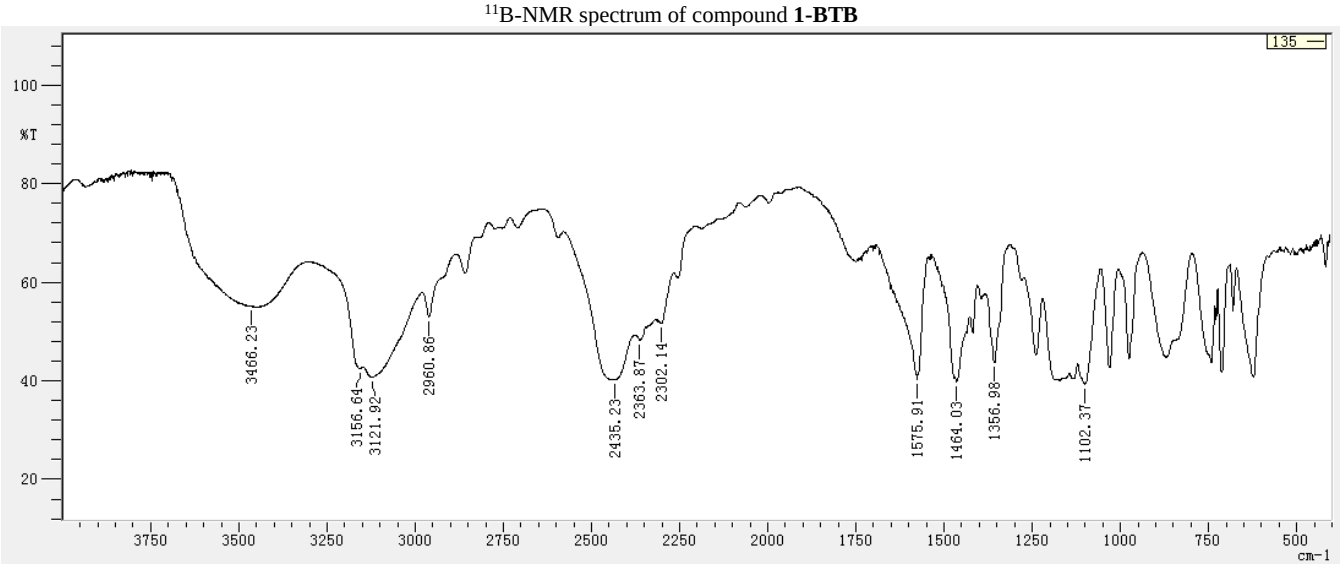


S1

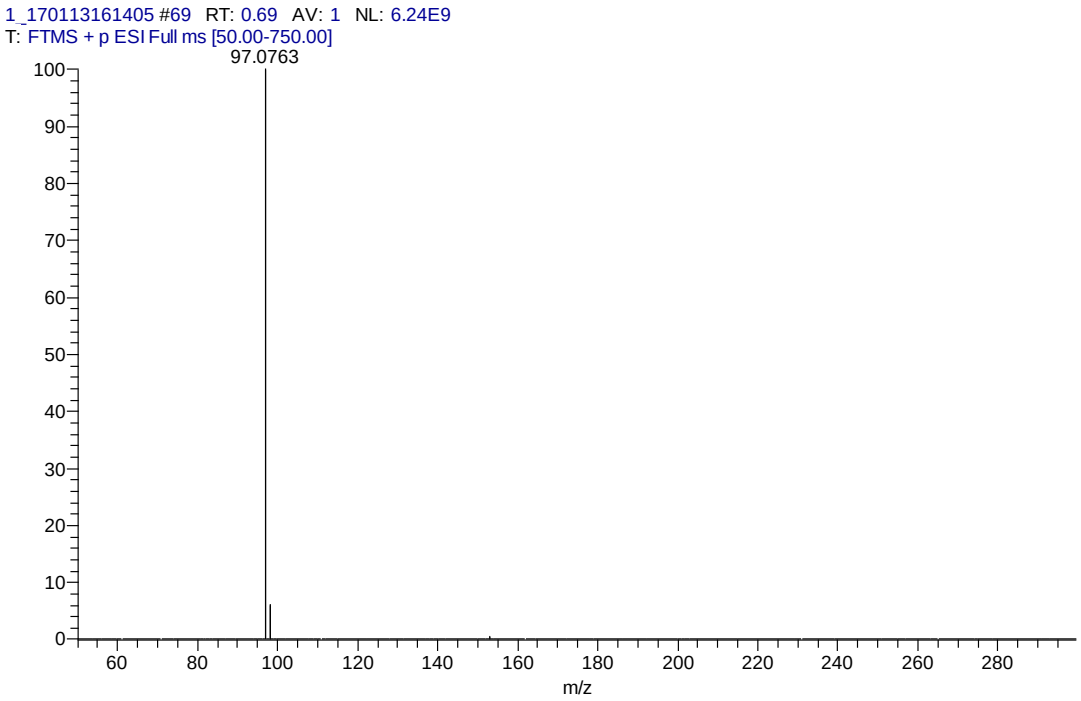
^{13}C-NMR spectrum of compound **1-BTB**



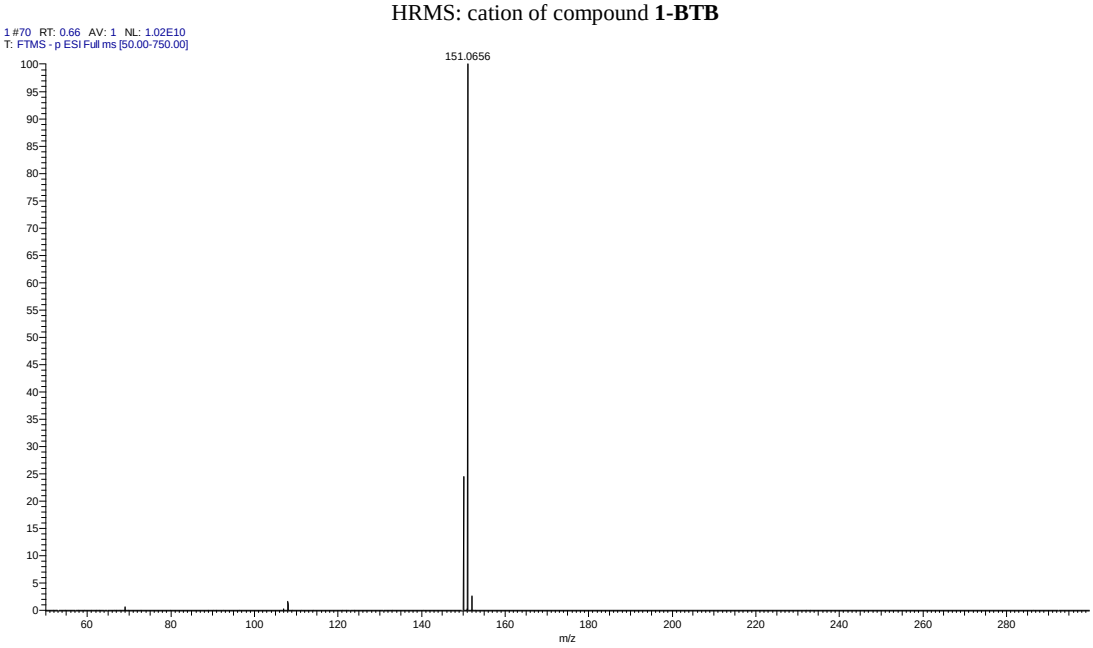
^{11}B-NMR spectrum of compound **1-BTB**



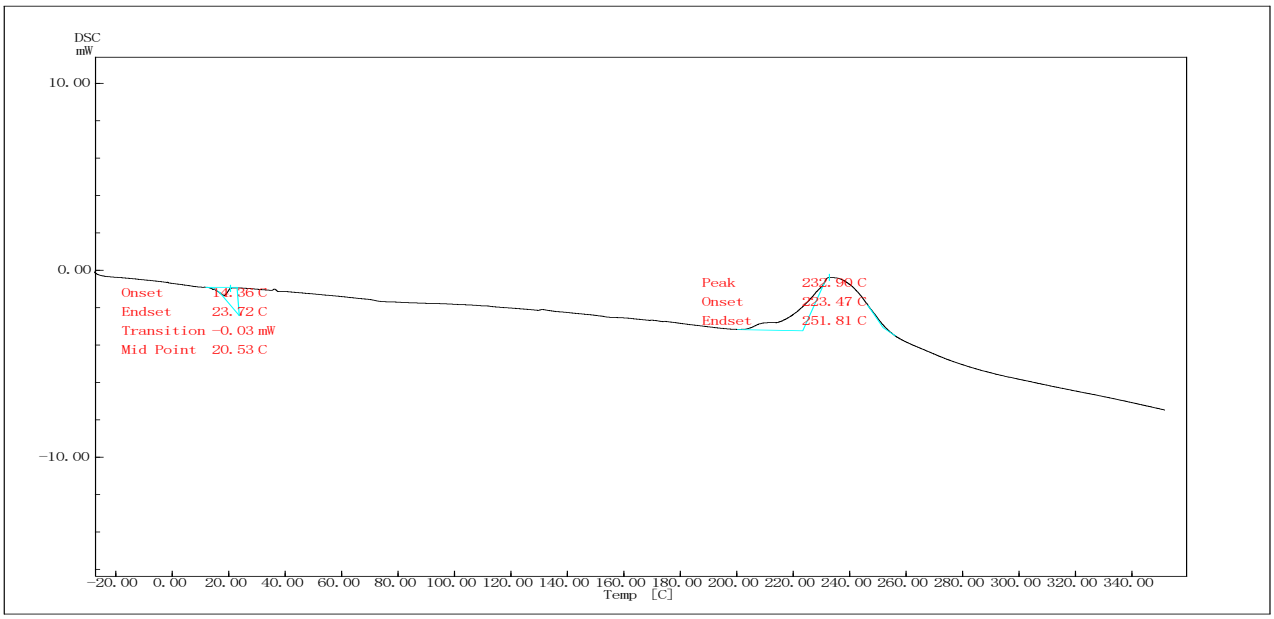
IR spectrum of compound **1-BTB**



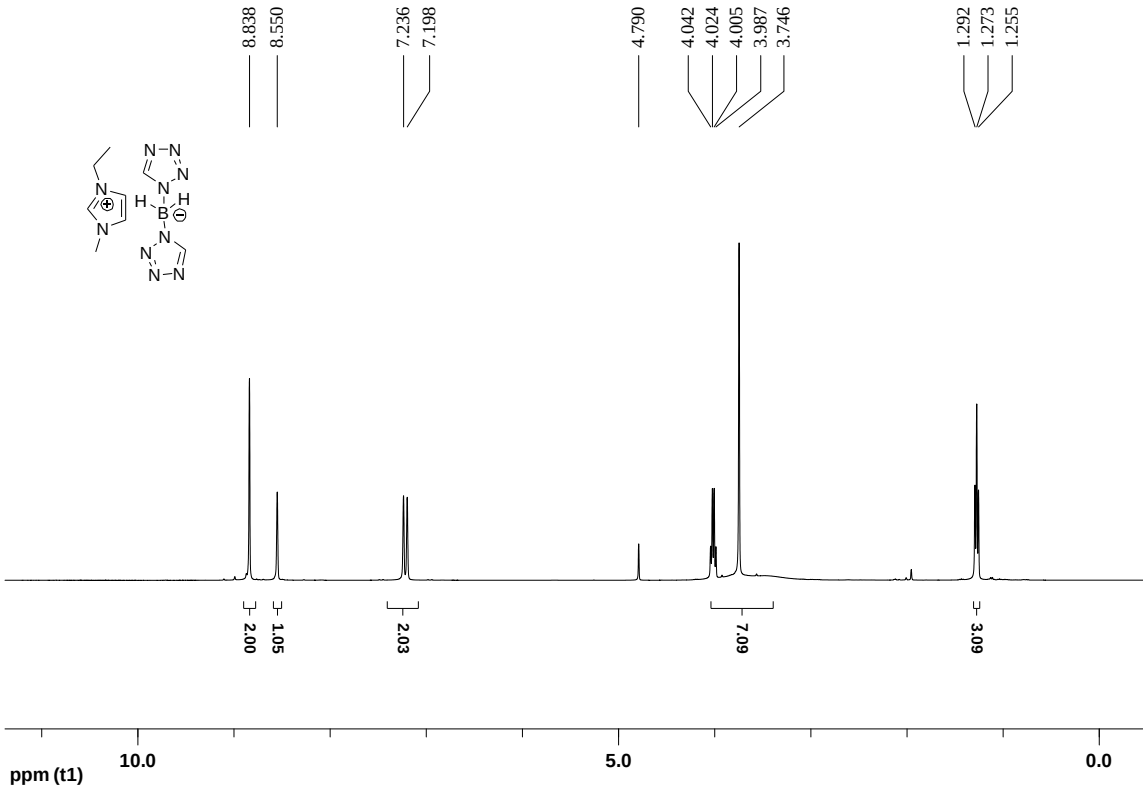
HRMS: cation of compound **1-BTB**



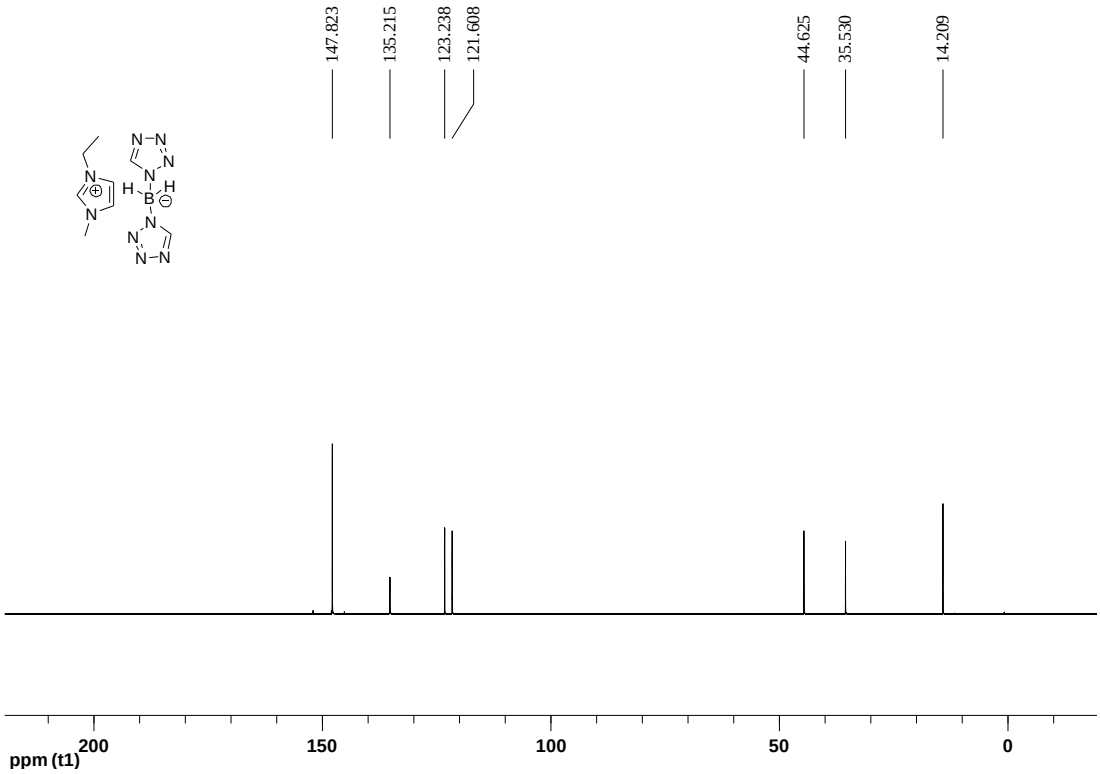
HRMS: cation of compound **1-BTB**



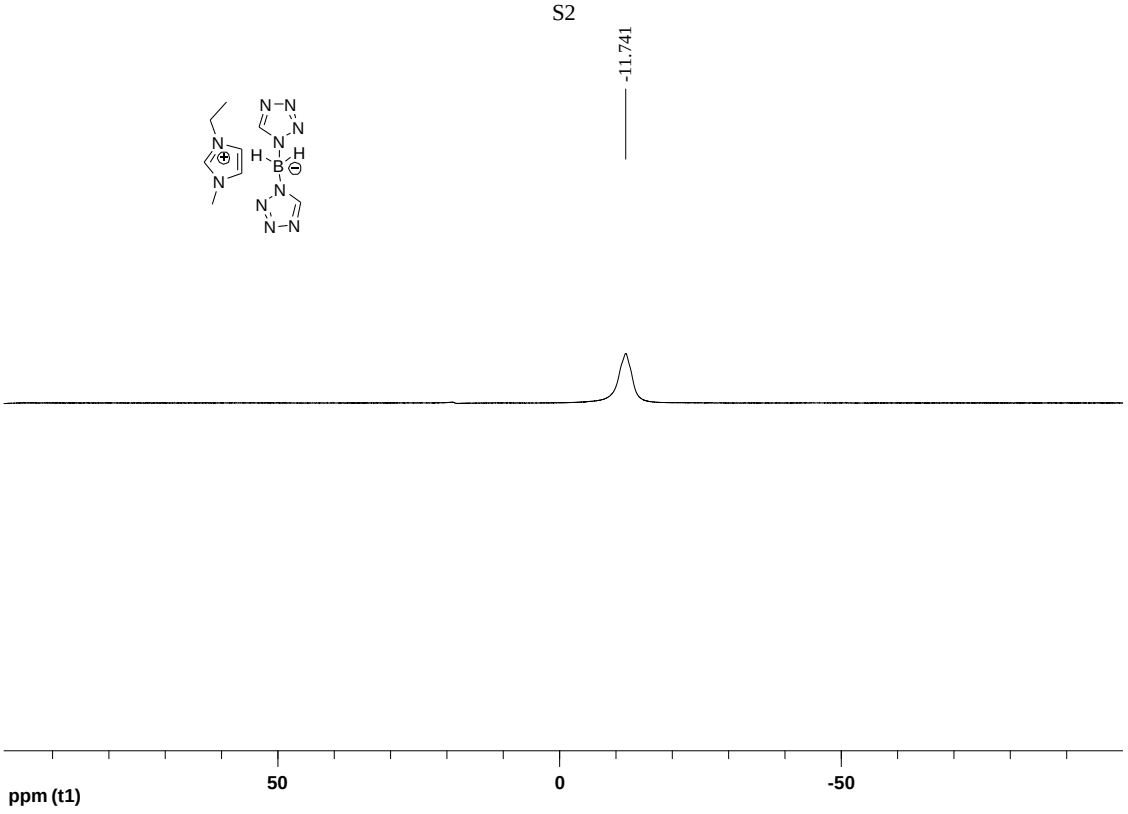
DSC of compound **1-BTB** at a scan rate of 5 ºC min^{-1} under nitrogen atmosphere.



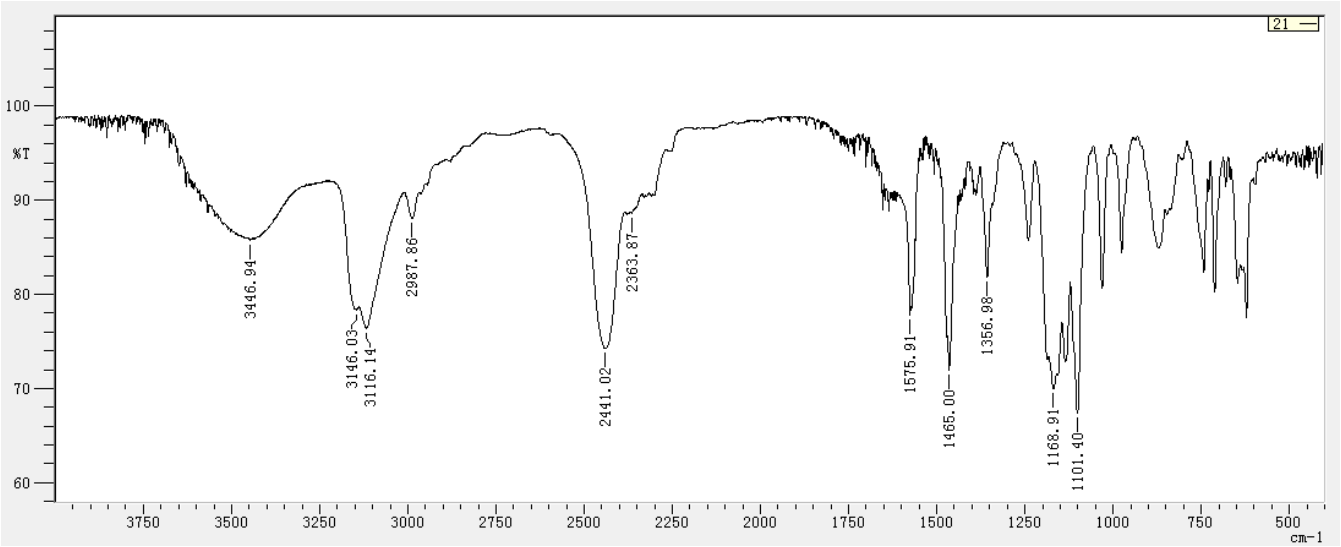
^{1}H-NMR spectrum of compound **2-BTB**



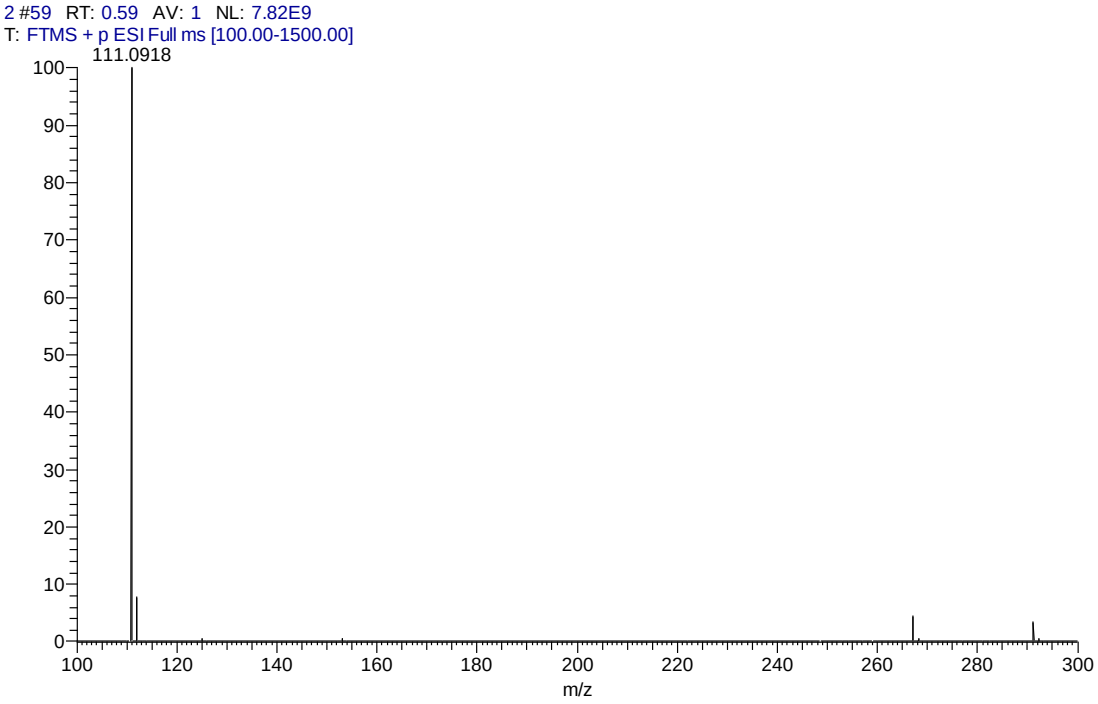
^{13}C-NMR spectrum of compound **2-BTB**



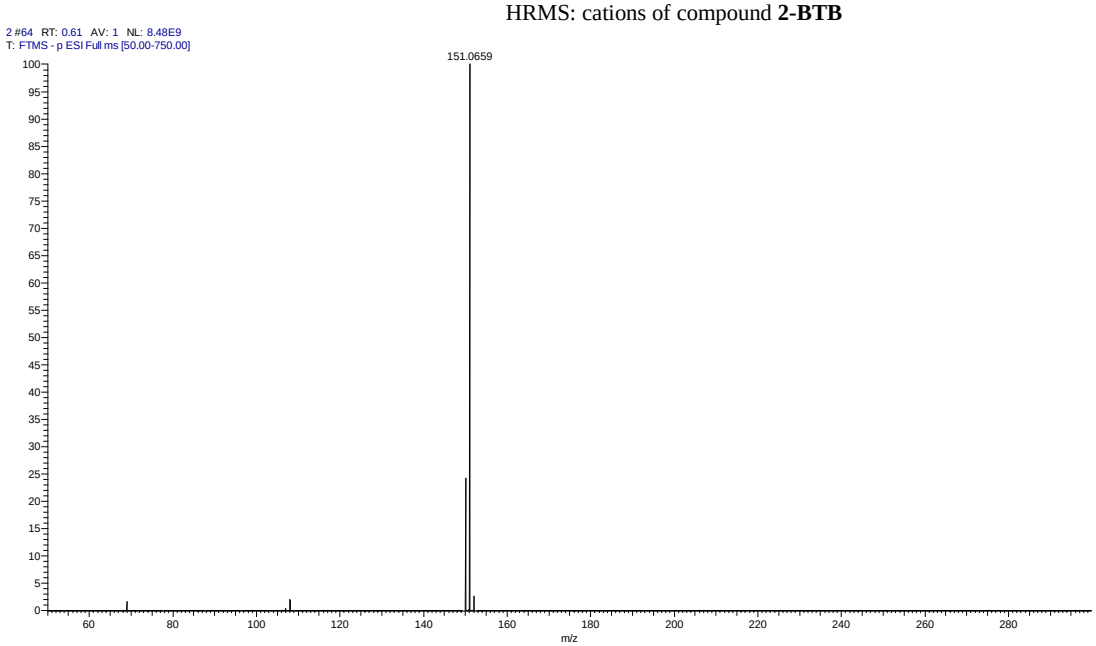
^{11}B-NMR spectrum of compound **2-BTB**



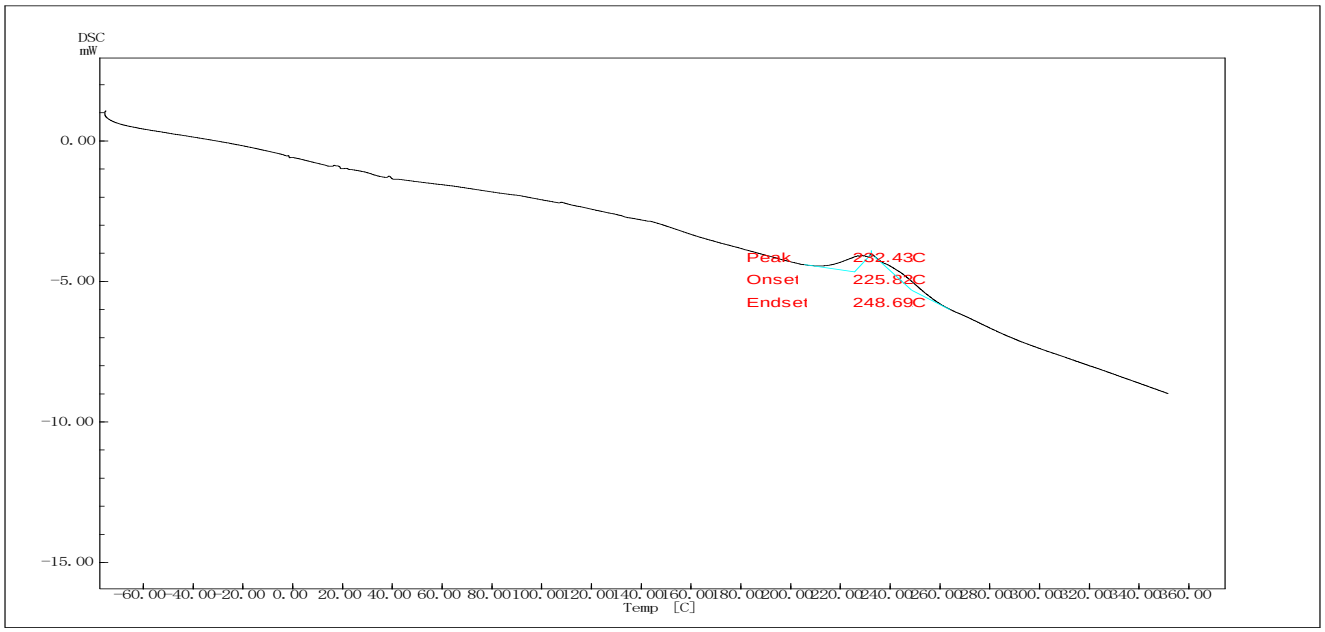
IR spectrum of compound **2-BTB**



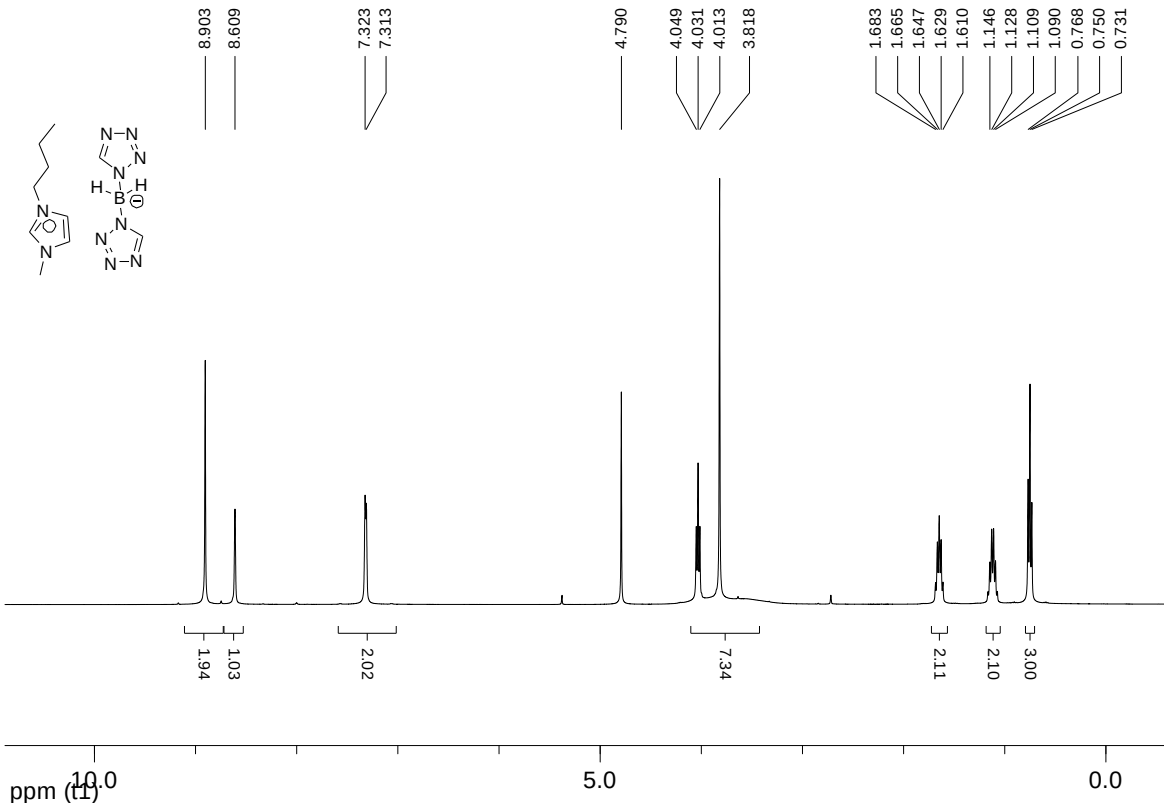
HRMS: cations of compound **2-BTB**



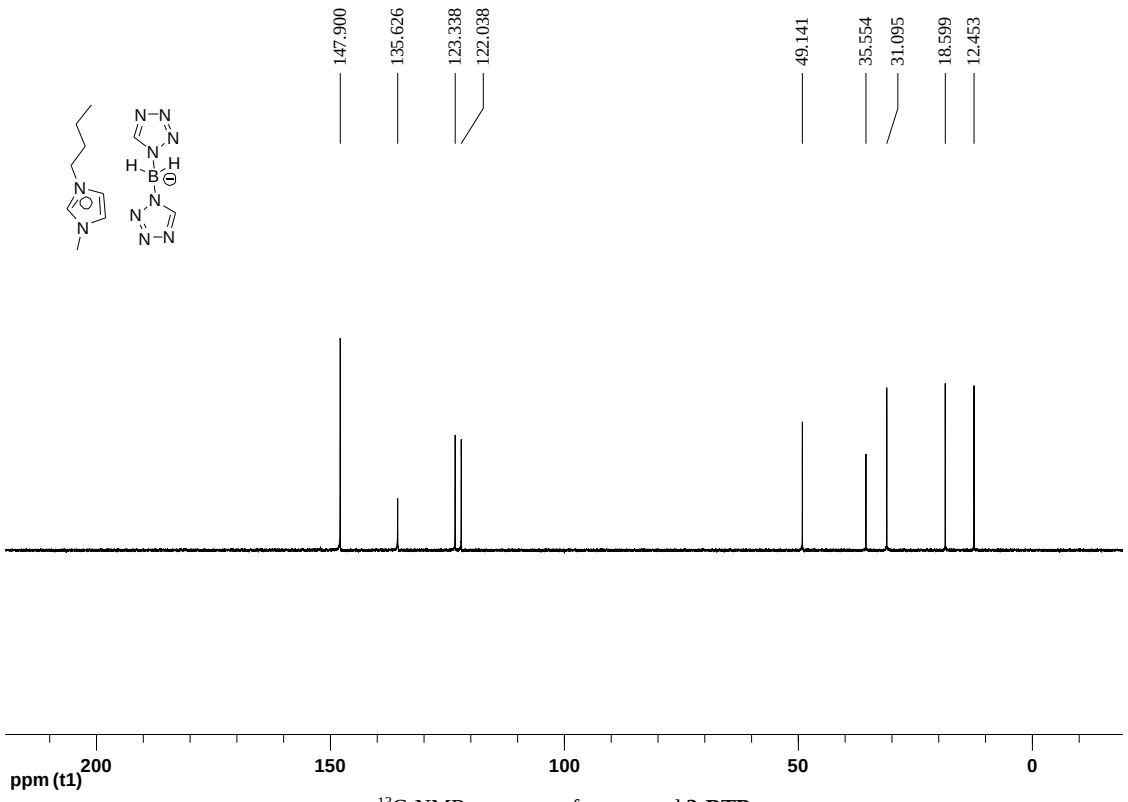
HRMS: anion of compound **2-BTB**



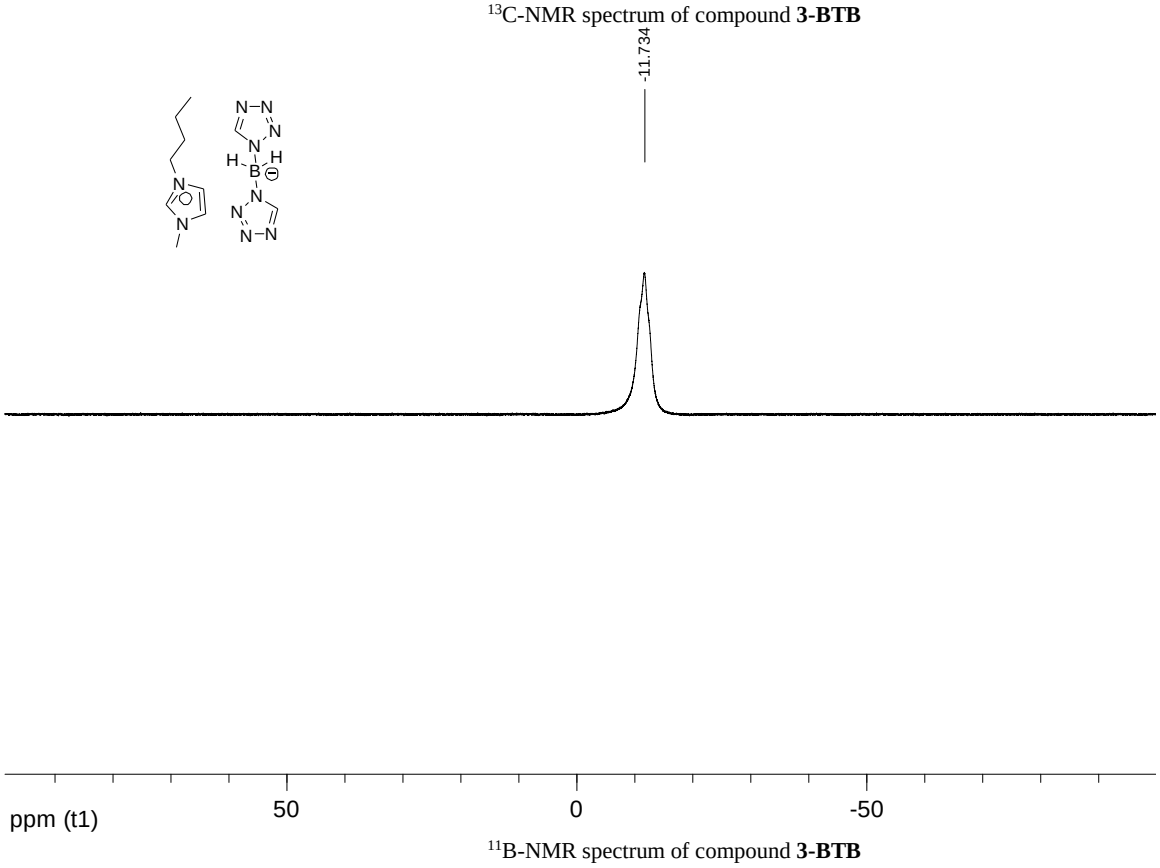
DSC of compound **2-BTB** at a scan rate of 5 ºC min^{-1} under nitrogen atmosphere.



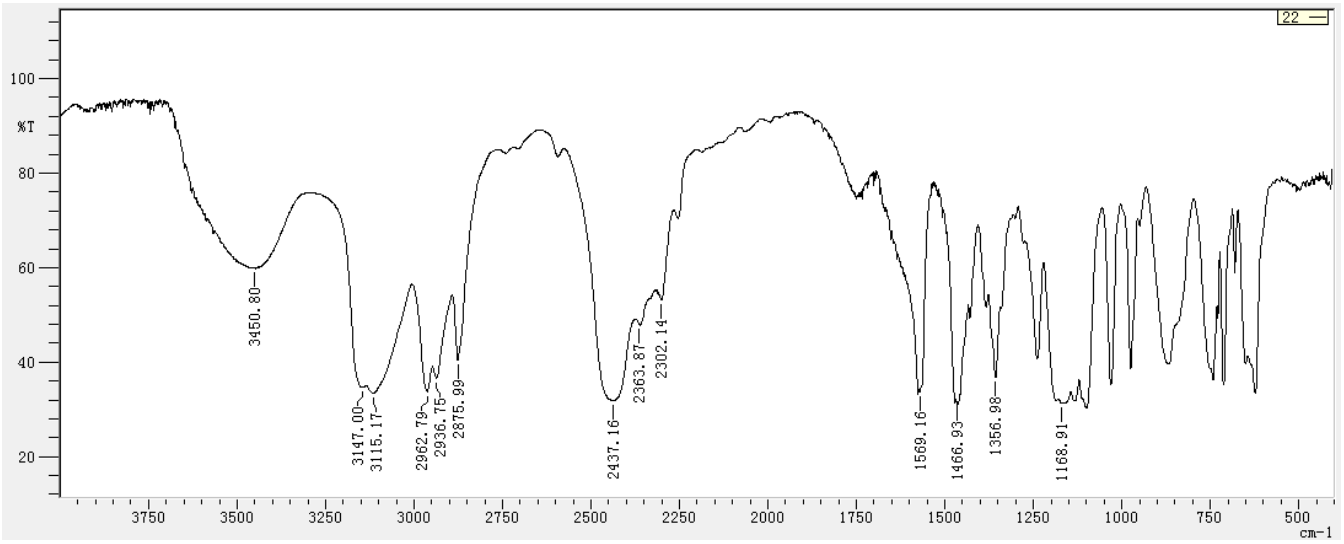
^{1}H-NMR spectrum of compound **3-BTB**



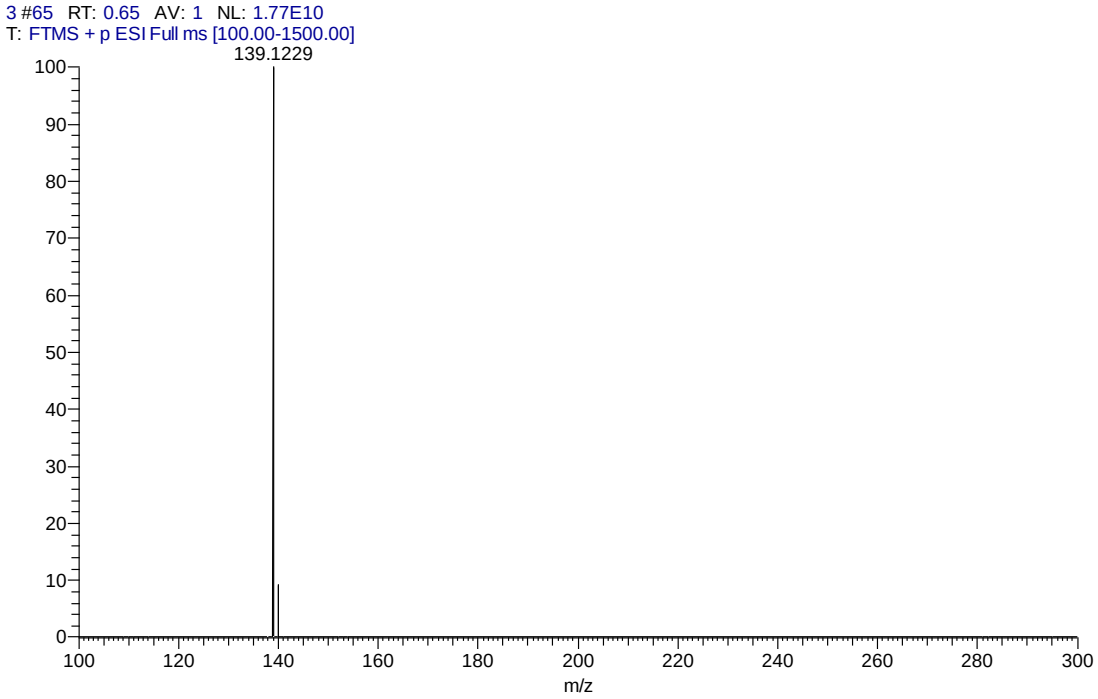
^{13}C-NMR spectrum of compound **3-BTB**



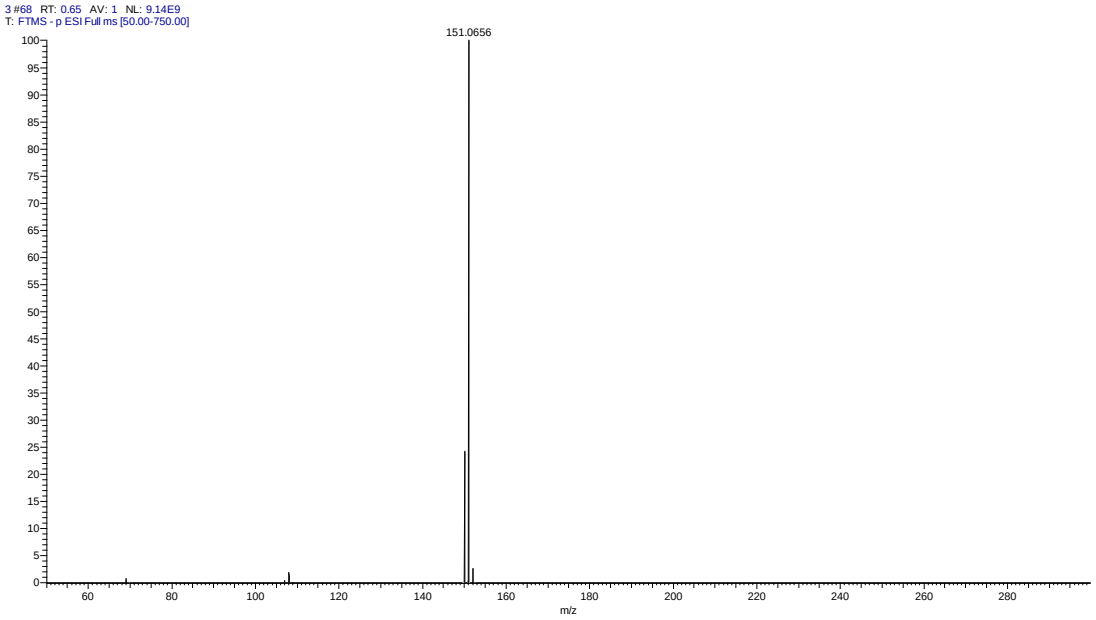
^{11}B-NMR spectrum of compound **3-BTB**



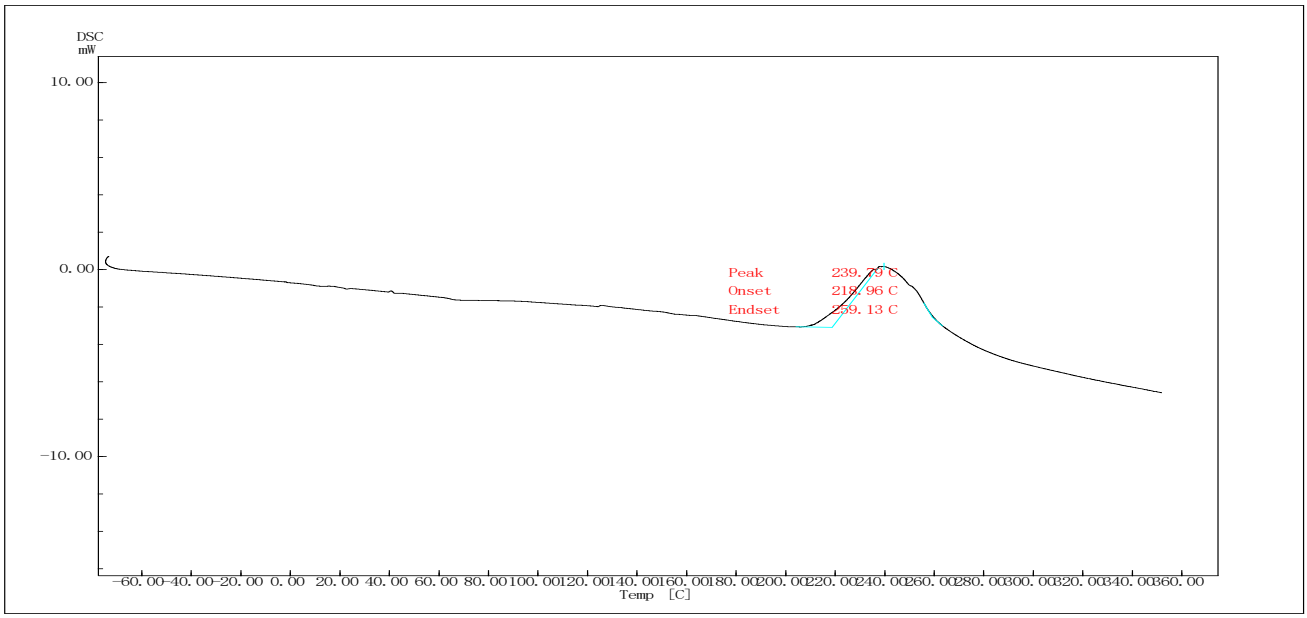
IR spectrum of compound **3-BTB**



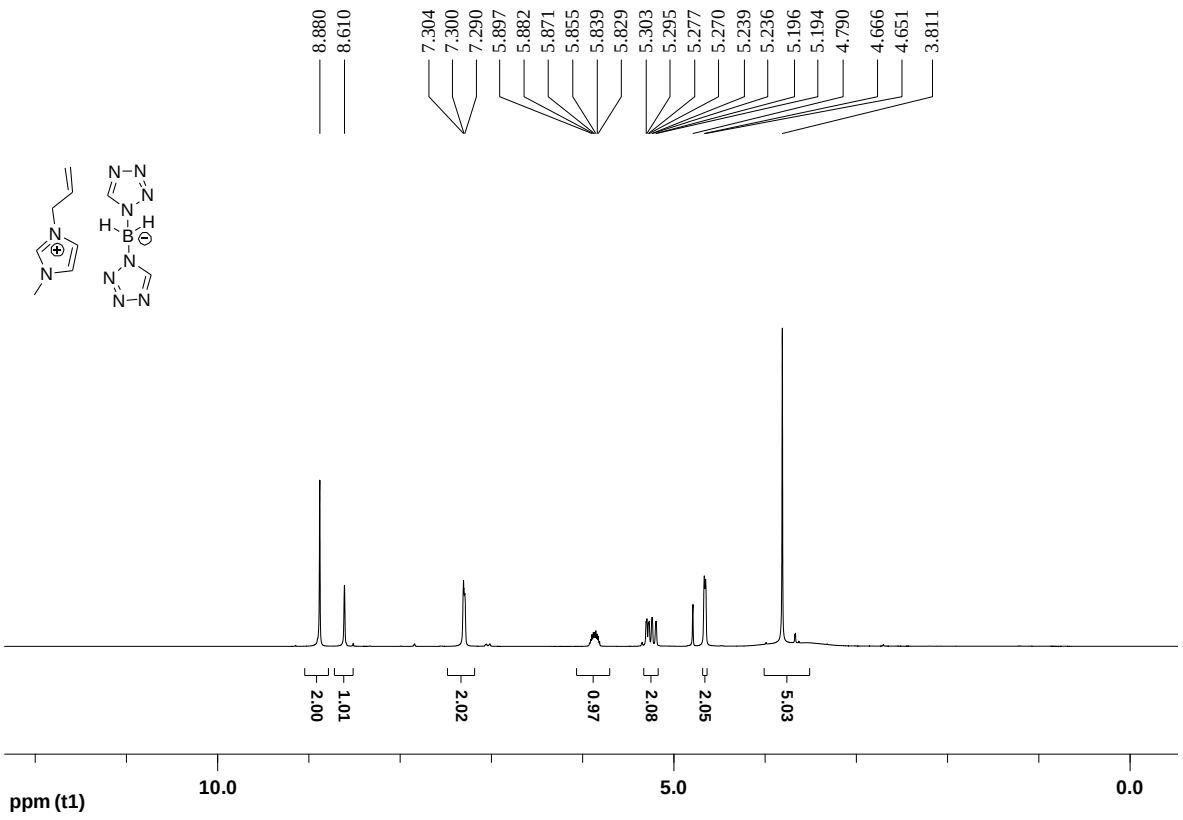
HRMS: cation of compound **3-BTB**



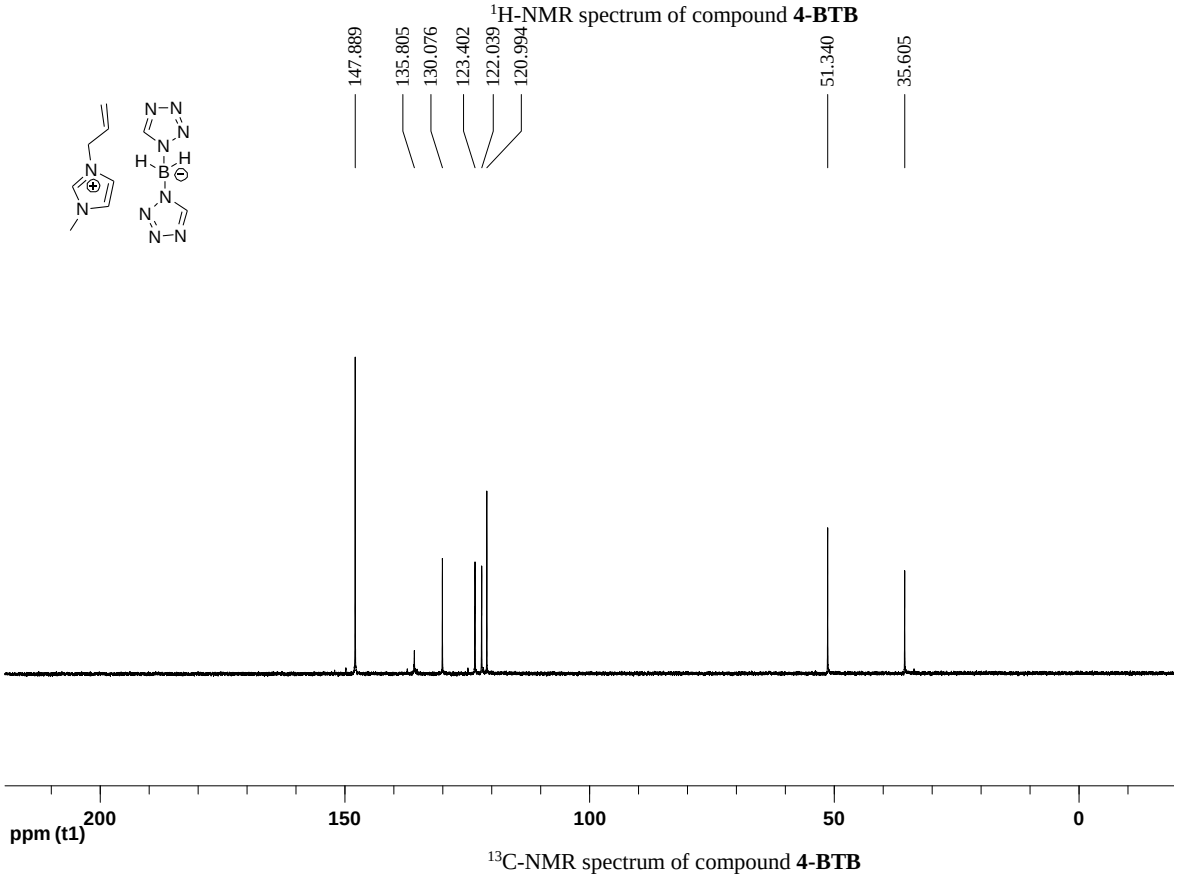
HRMS: anion of compound **3-BTB**



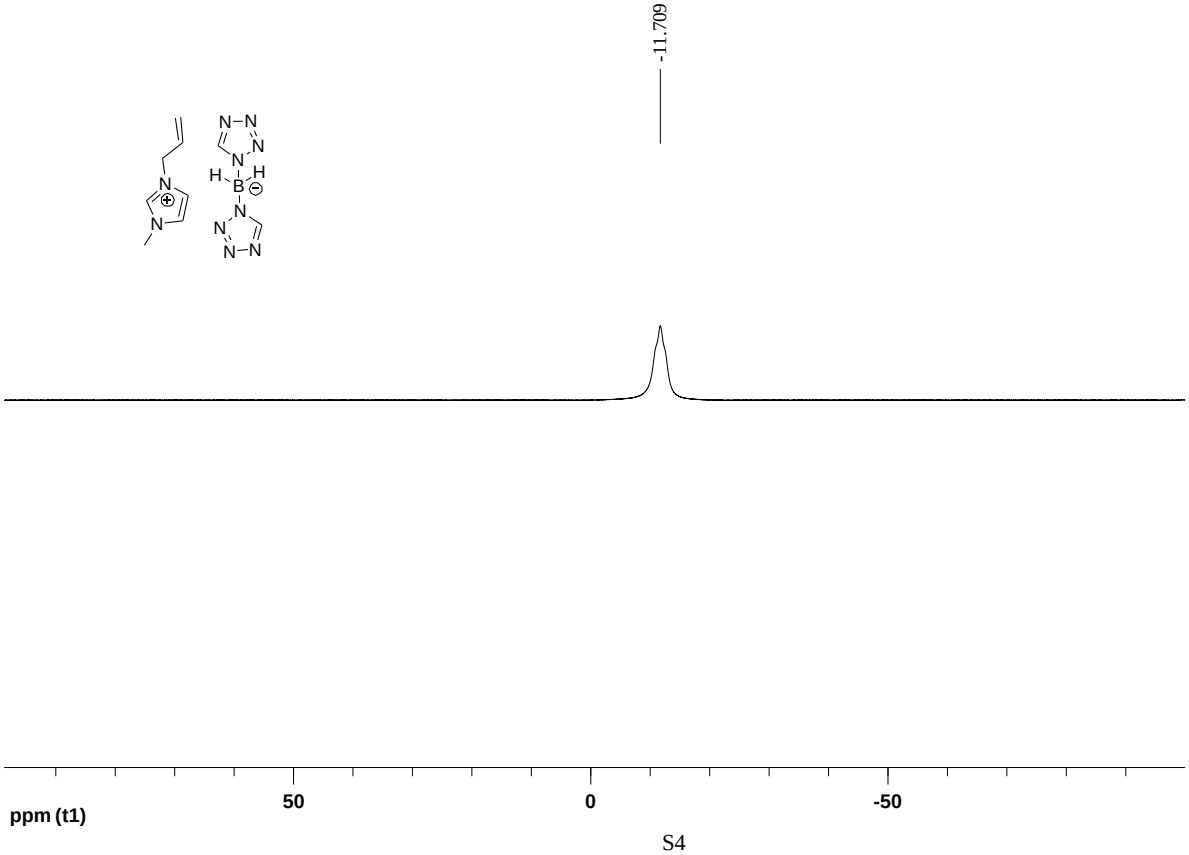
DSC of compound **3-BTB** at a scan rate of 5 ºC min^{-1} under nitrogen atmosphere.



^{1}H-NMR spectrum of compound **4-BTB**

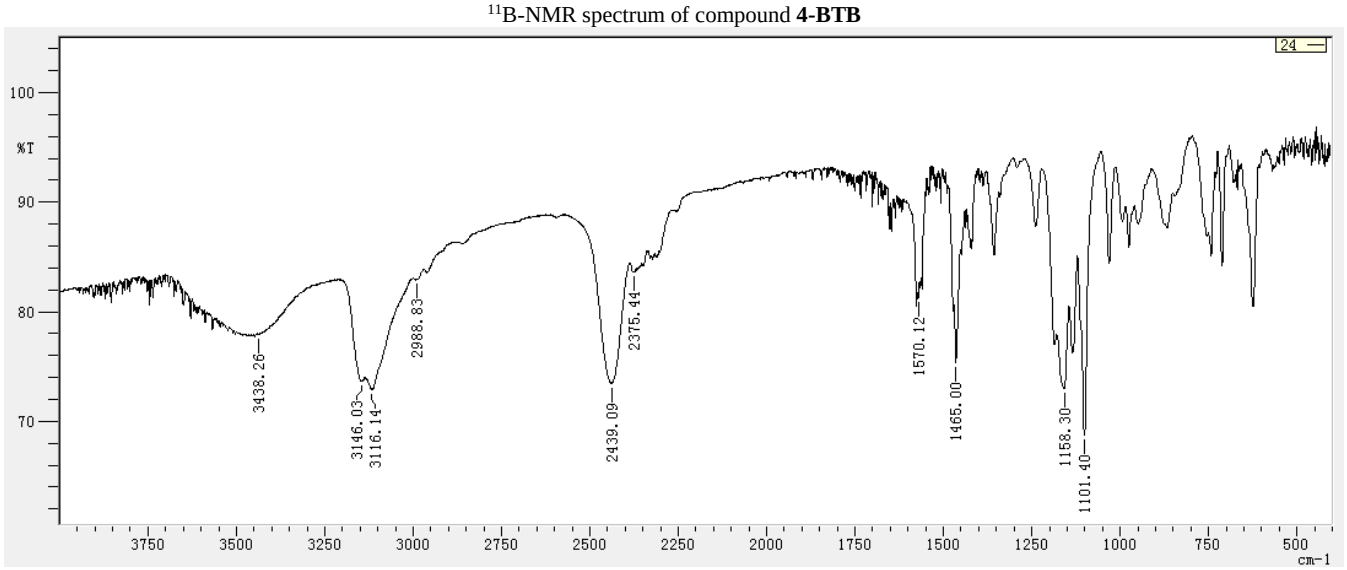


^{13}C-NMR spectrum of compound **4-BTB**

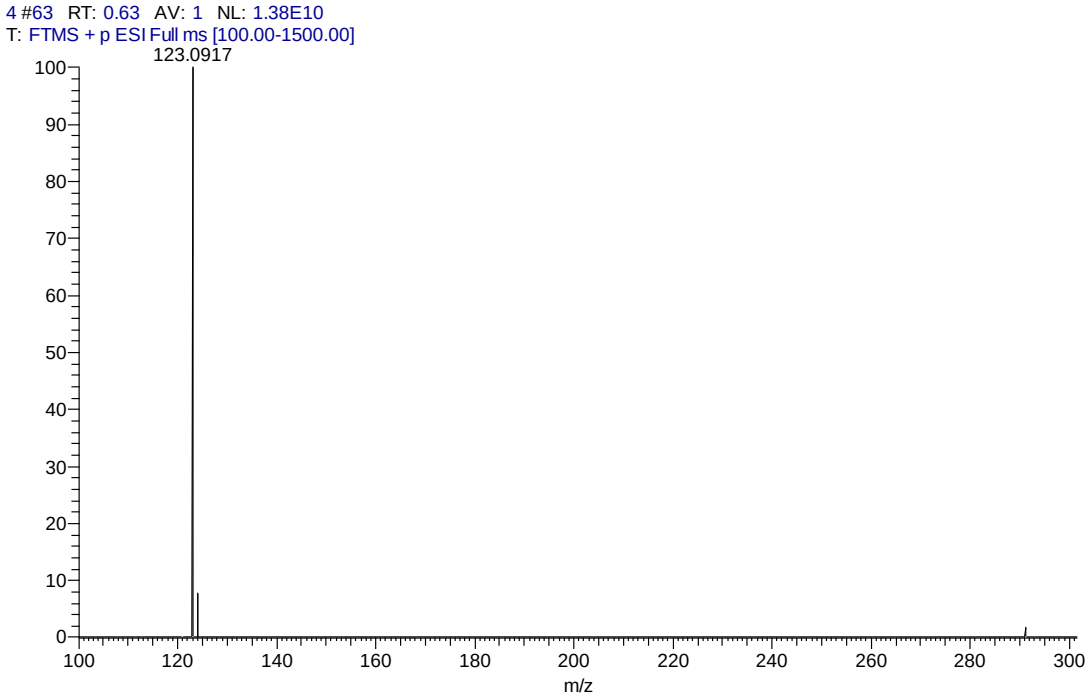


S4

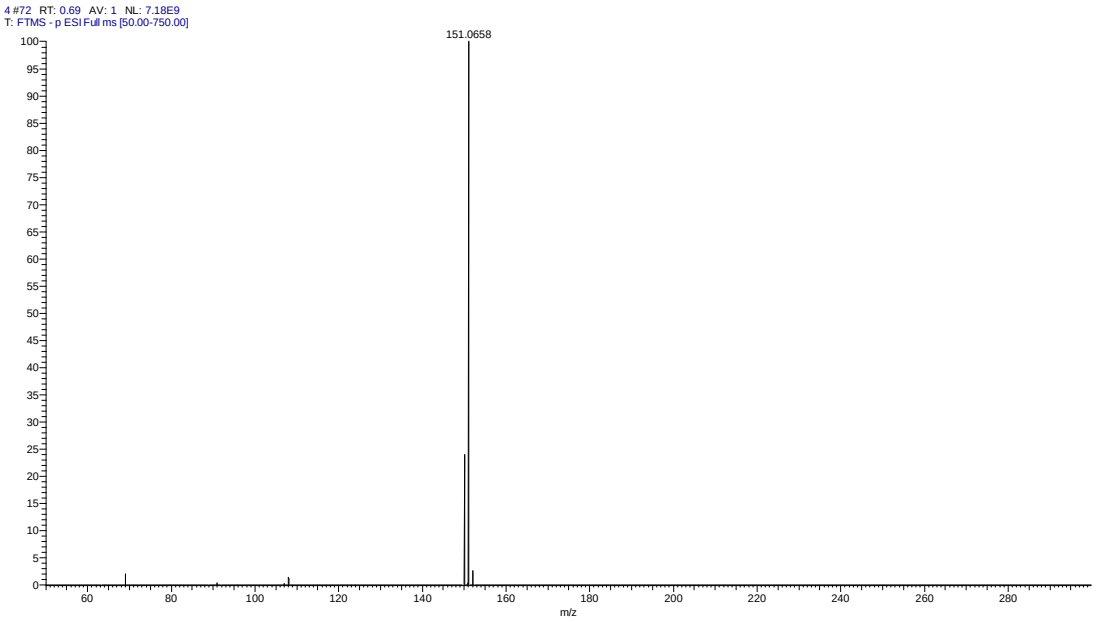
^{11}B-NMR spectrum of compound **4-BTB**



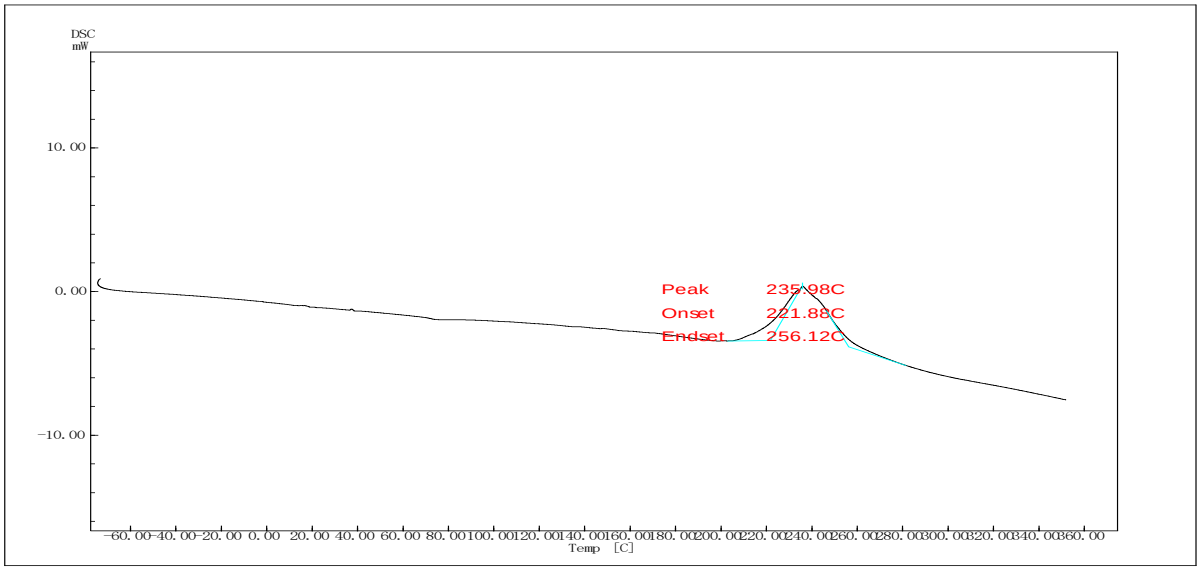
IR spectrum of compound **4-BTB**



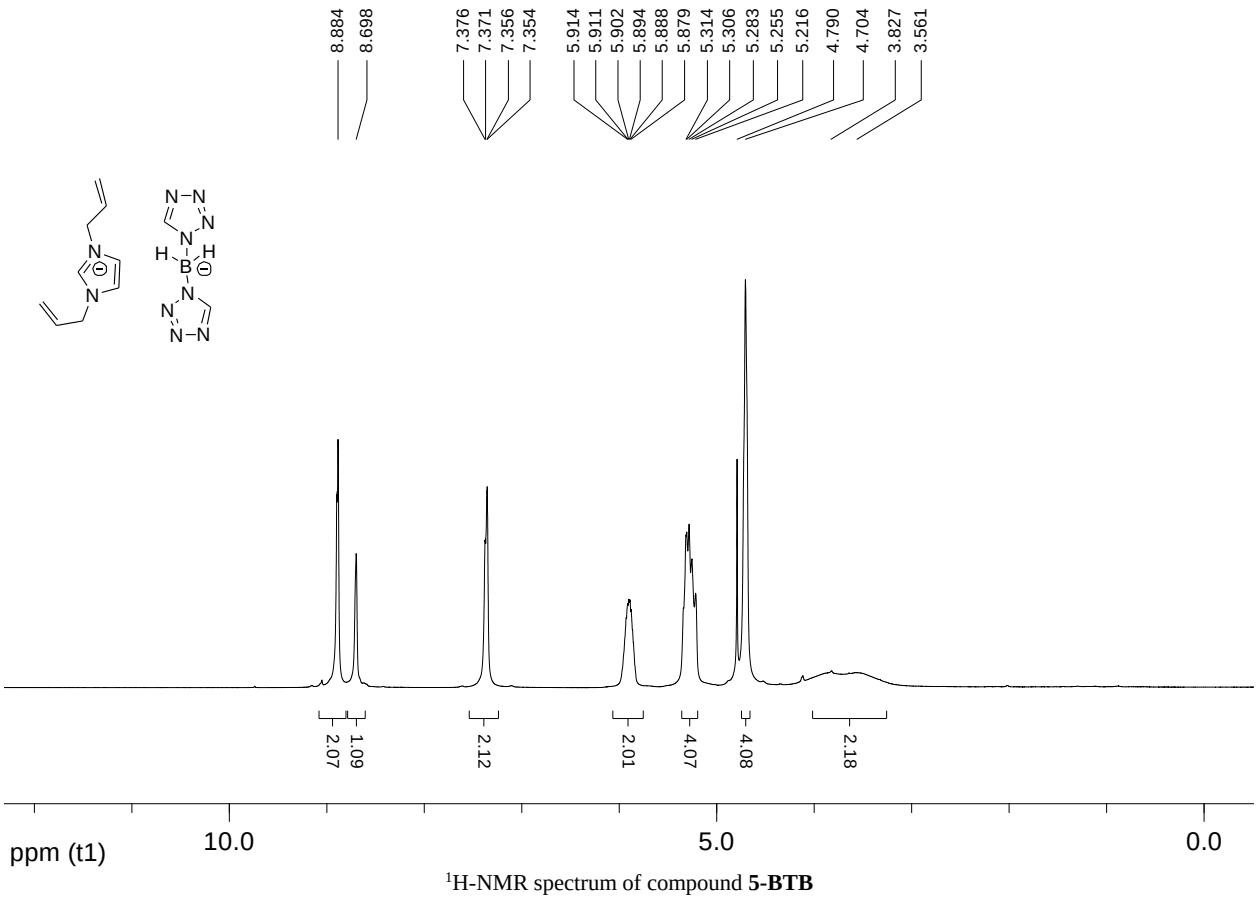
HRMS: cation of compound **4-BTB**



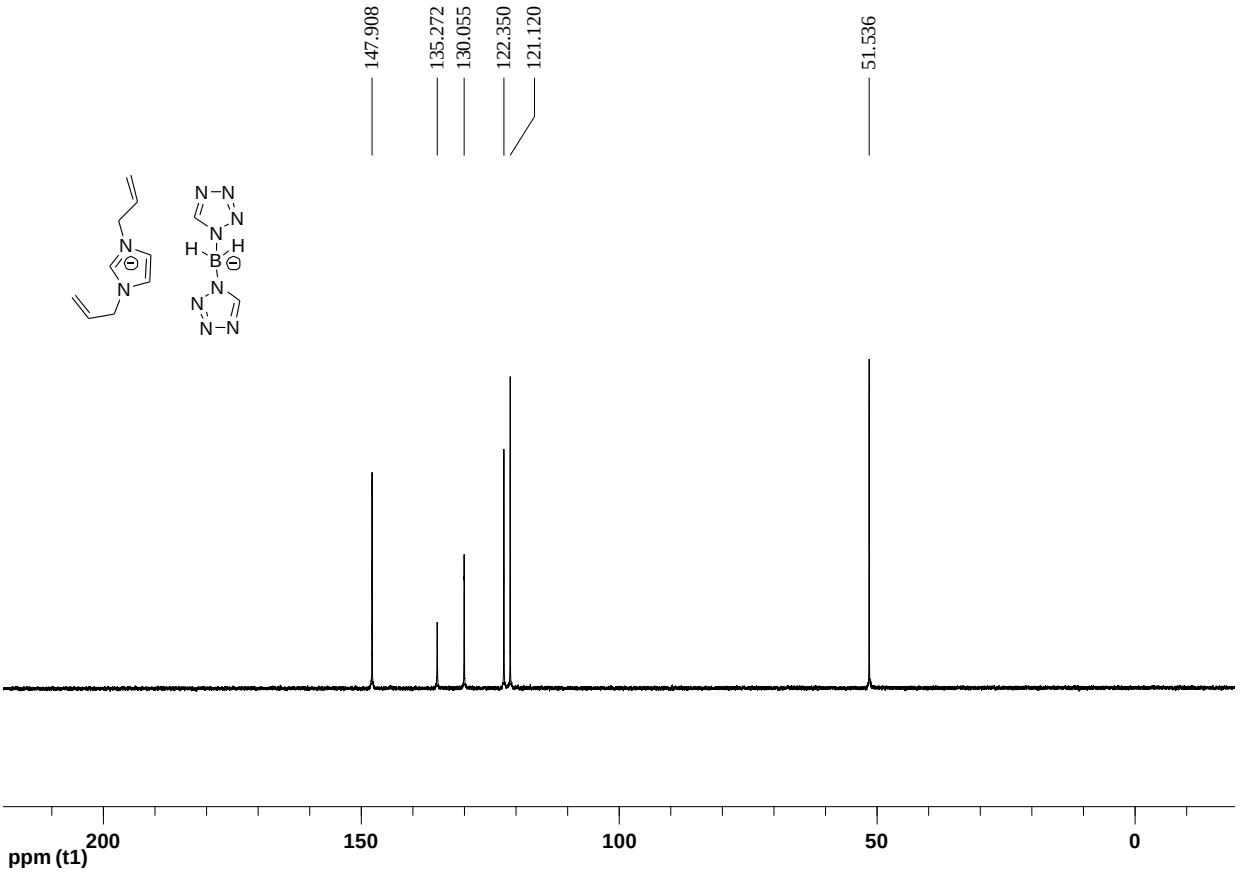
HRMS: anion of compound **4-BTB**



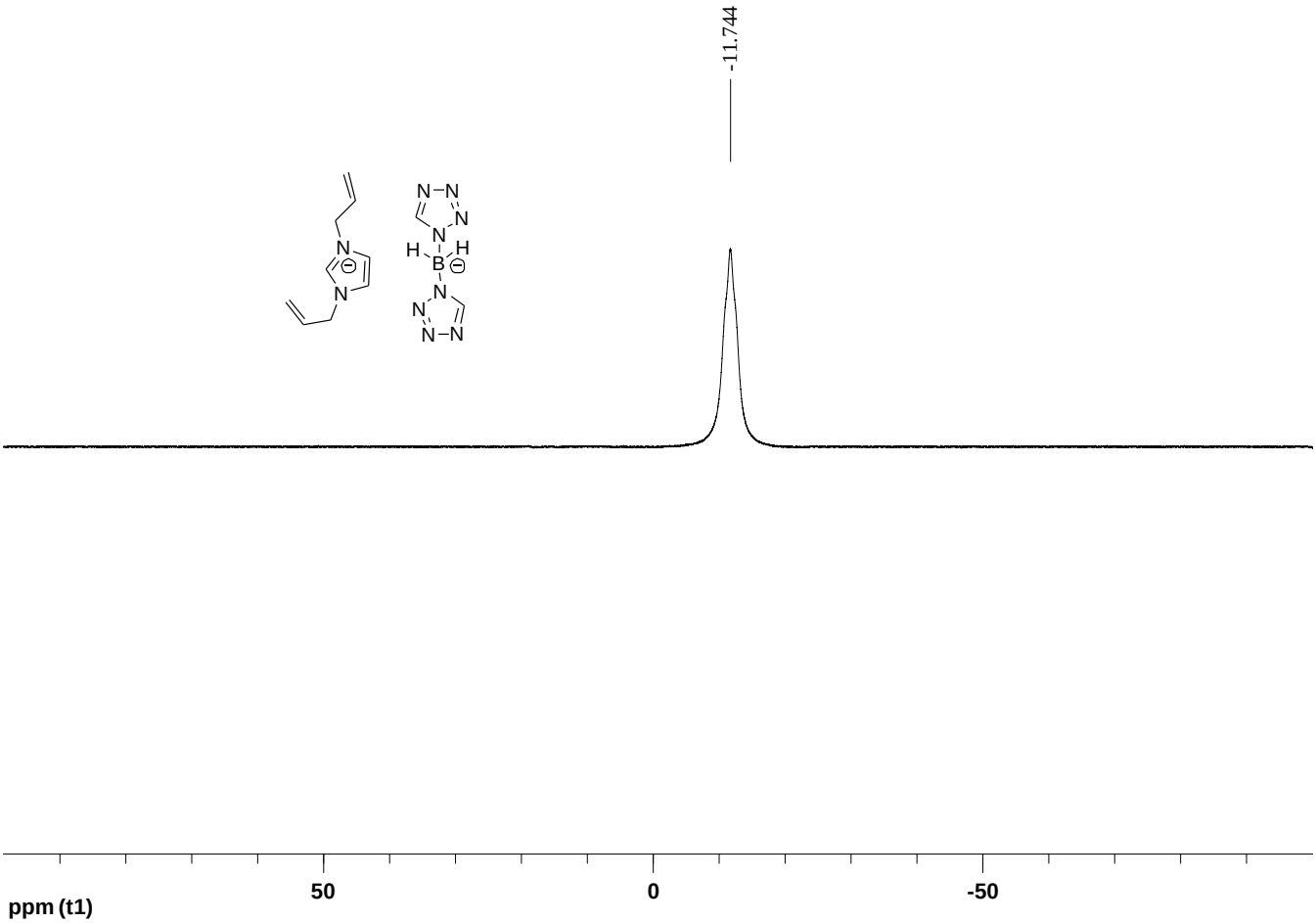
DSC of compound **4-BTB** at a scan rate of 5 ºC min^{-1} under nitrogen atmosphere.



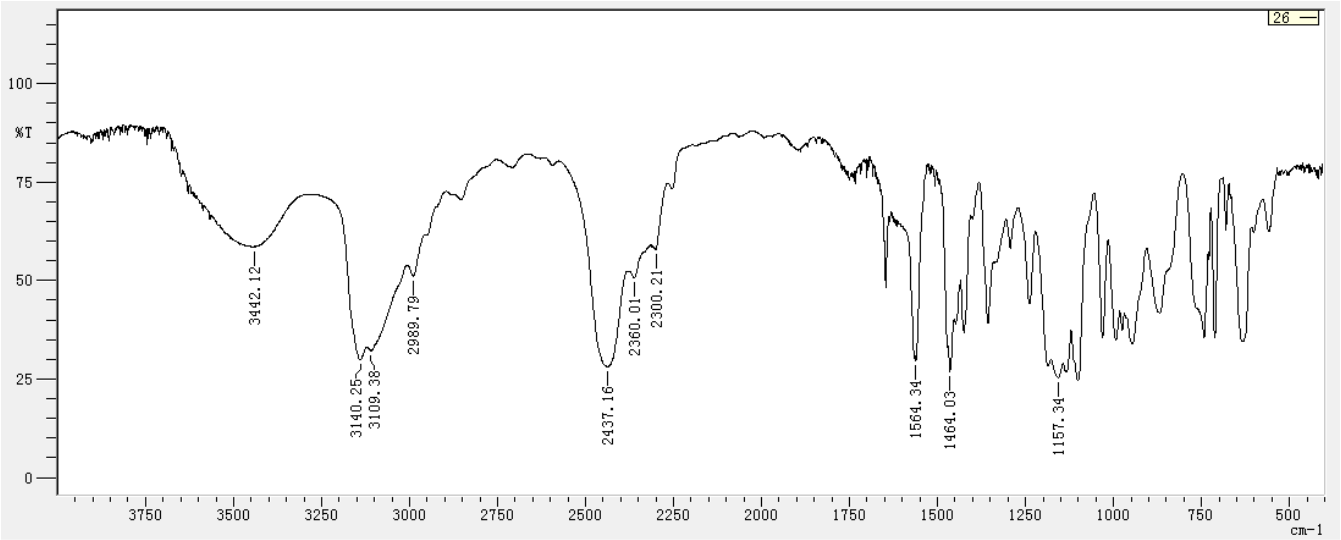
^{1}H-NMR spectrum of compound **5-BTB**



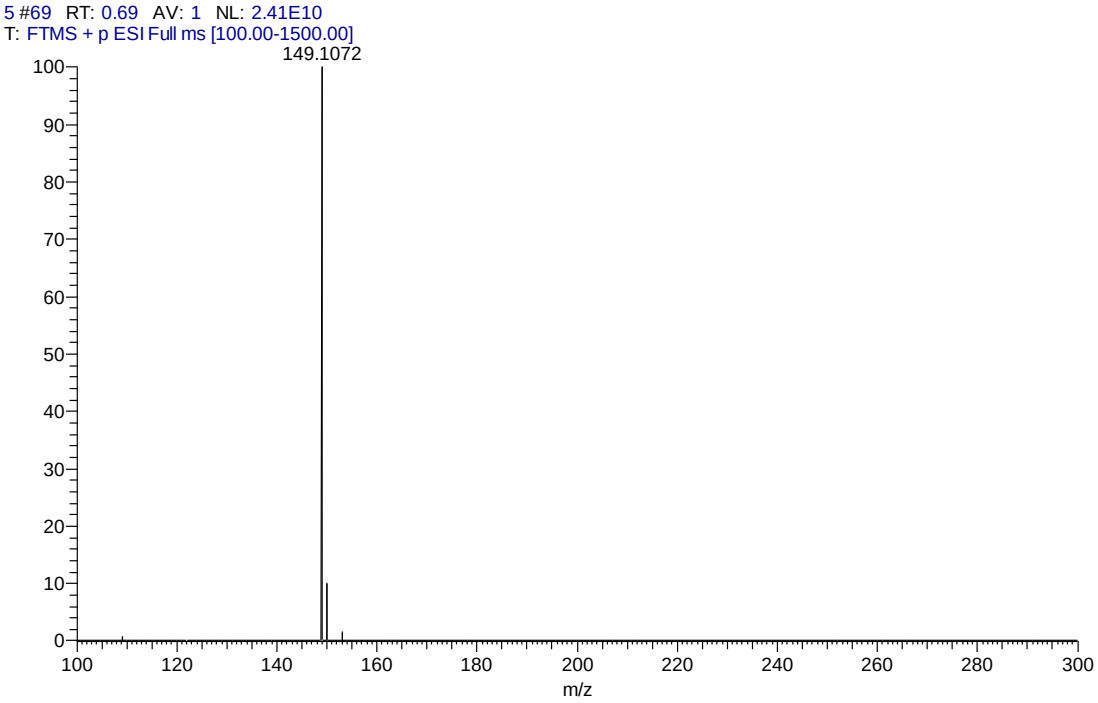
^{13}C-NMR spectrum of compound **5-BTB**



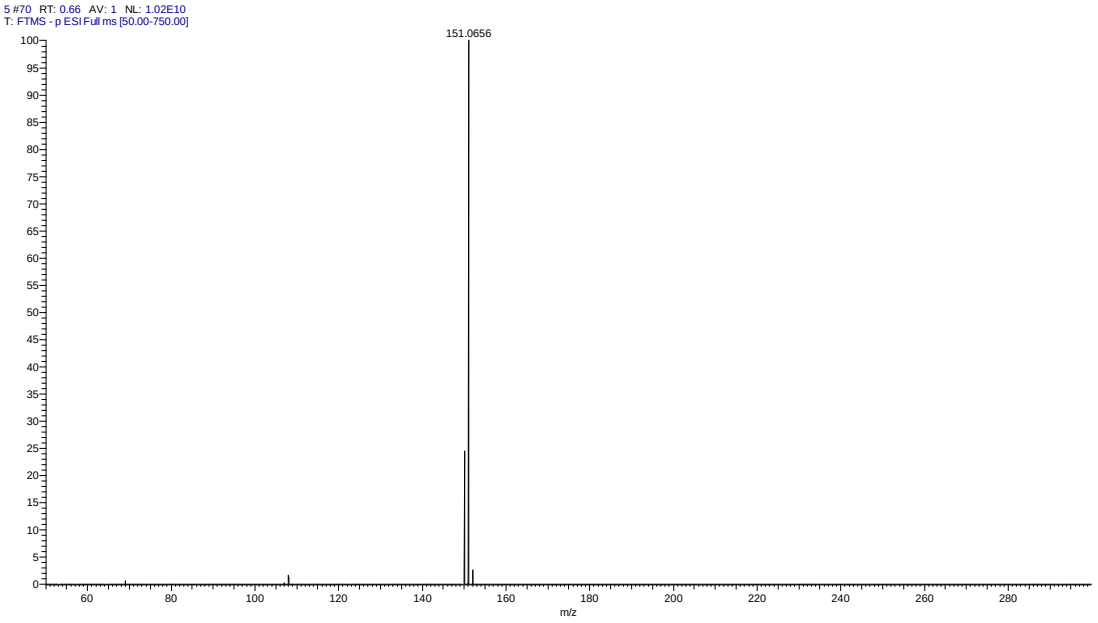
^{11}B-NMR spectrum of compound **5-BTB**



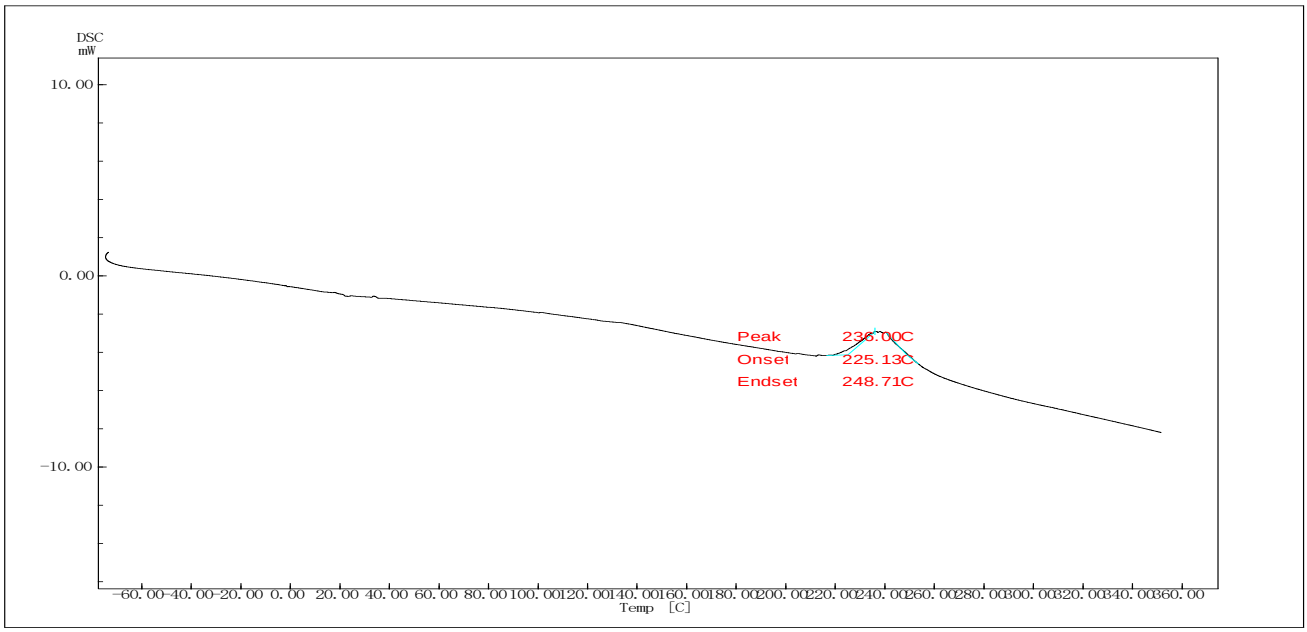
IR spectrum of compound **5-BTB**



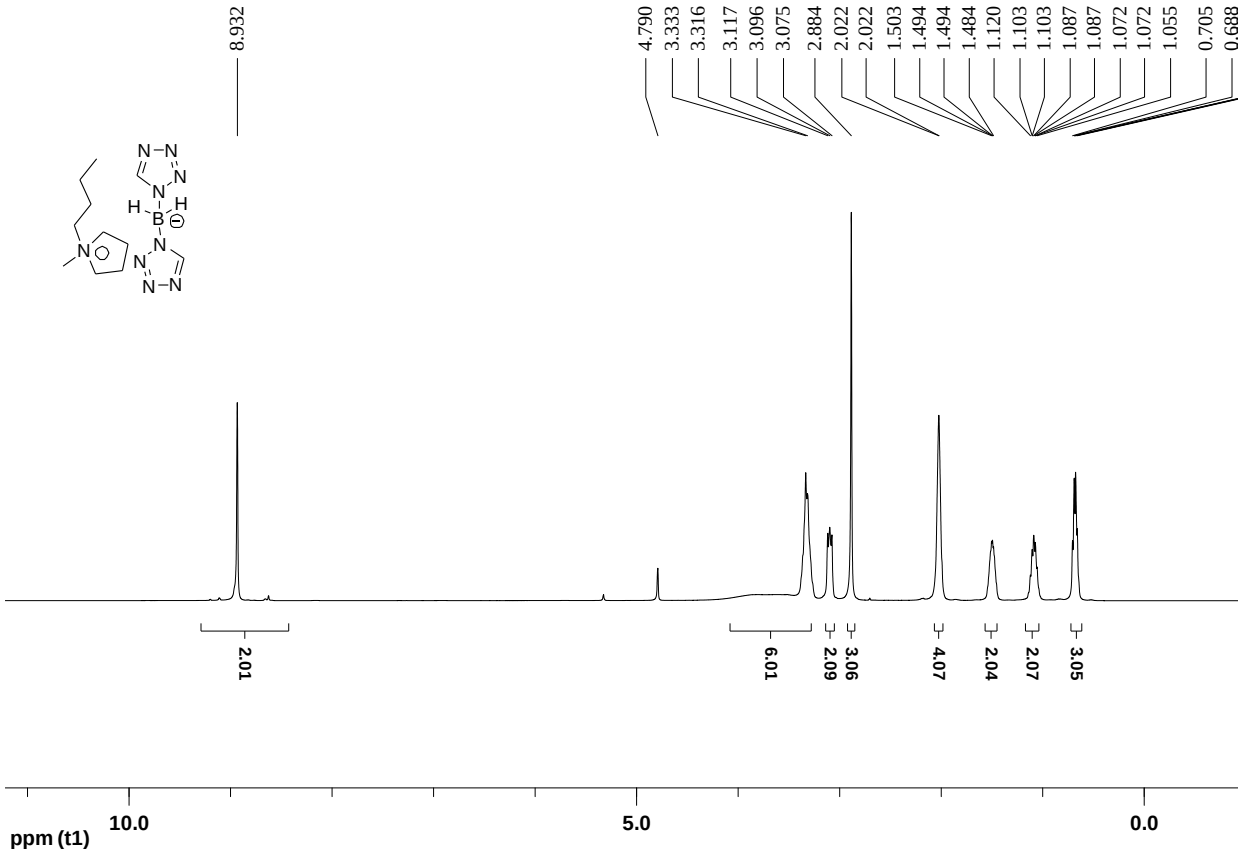
HRMS: cation of compound **5-BTB**



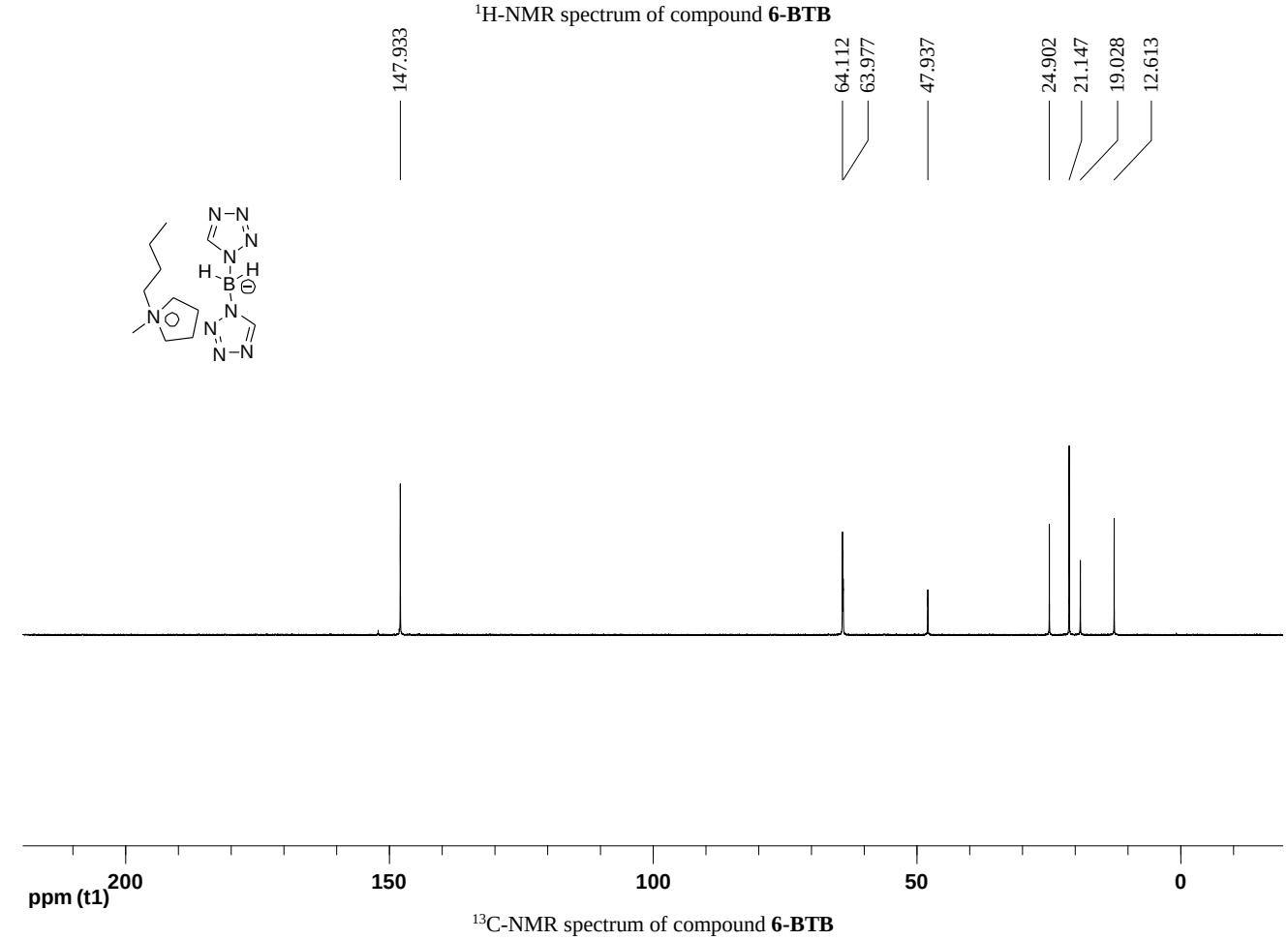
HRMS: anion of compound **5-BTB**



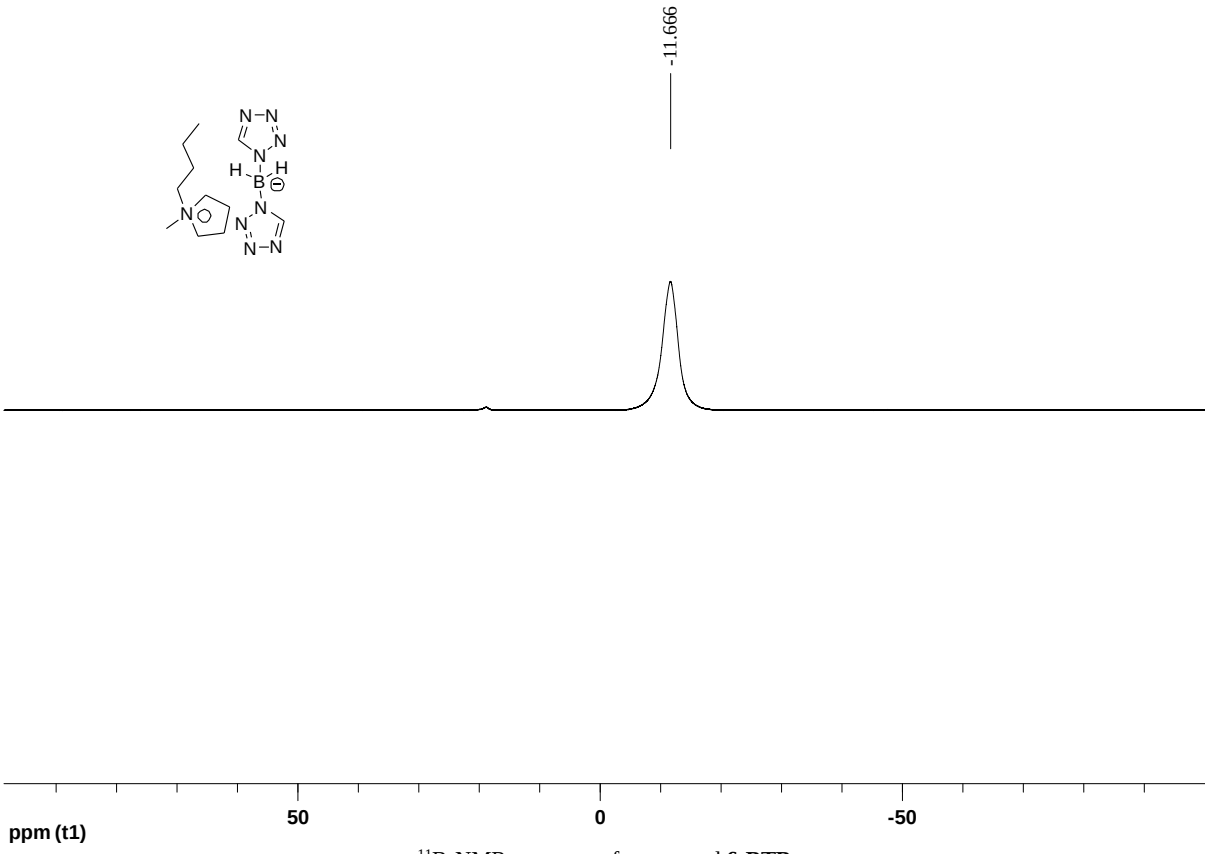
DSC of compound **5-BTB** at a scan rate of 5 ºC min^{-1} under nitrogen atmosphere.



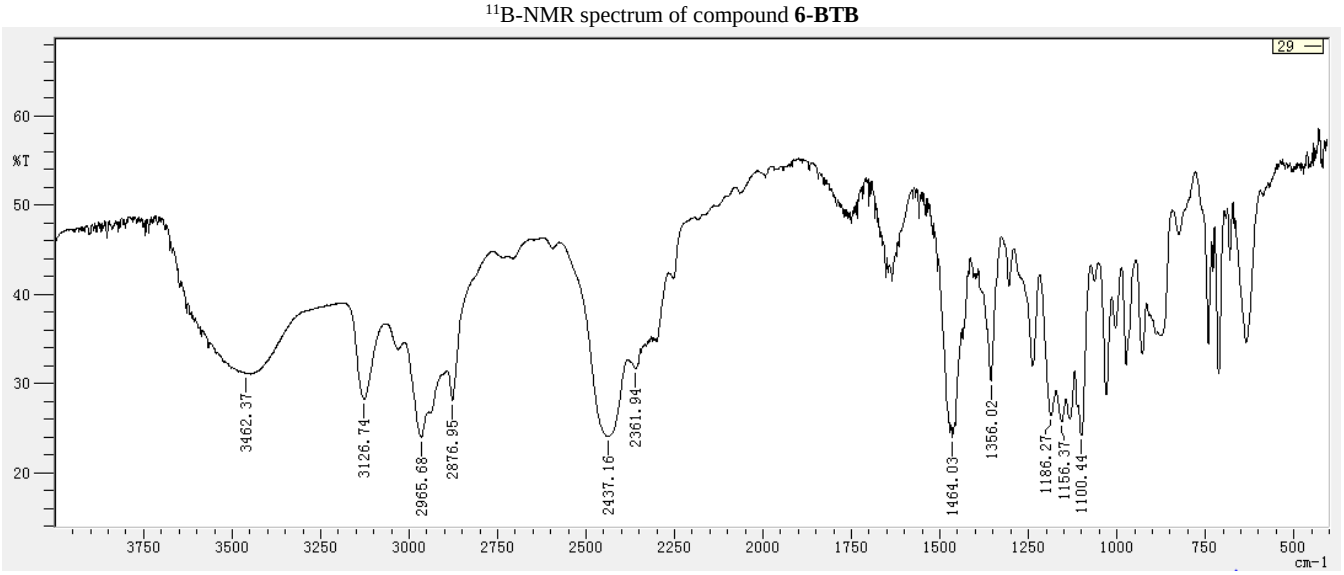
^{1}H-NMR spectrum of compound **6-BTB**



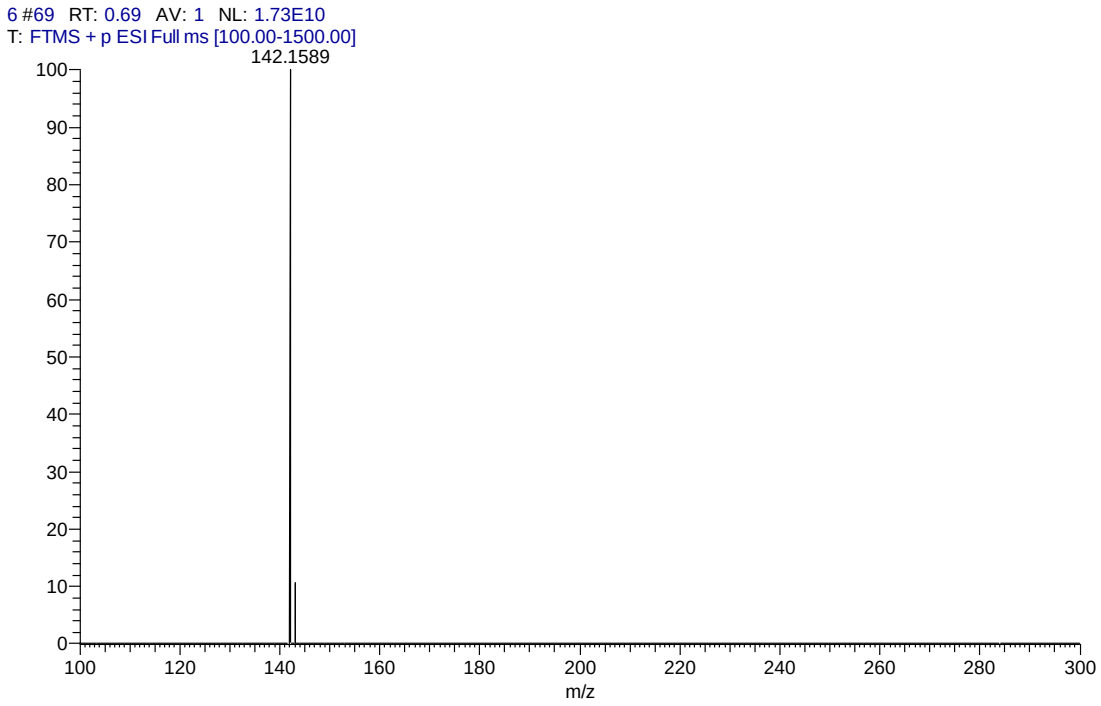
^{13}C-NMR spectrum of compound **6-BTB**



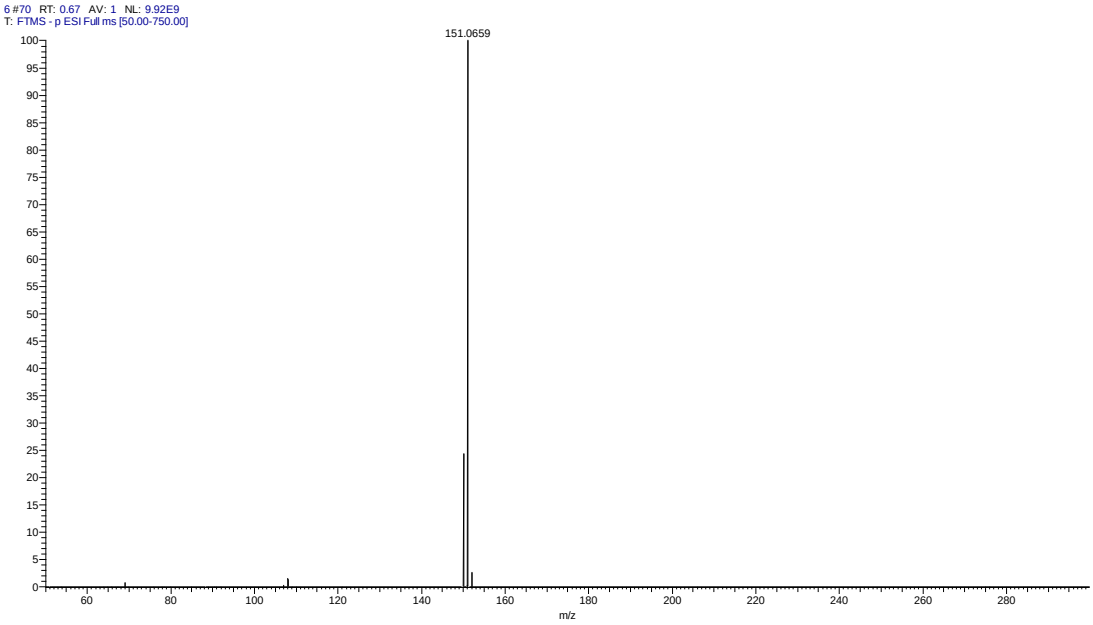
^{11}B-NMR spectrum of compound **6-BTB**



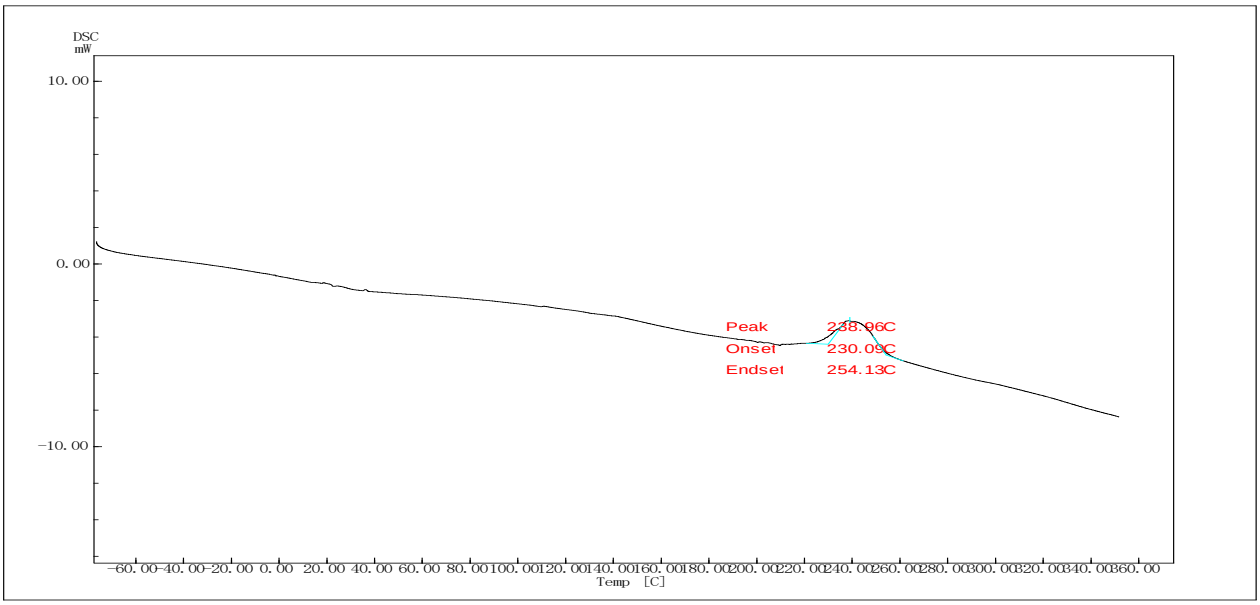
IR spectrum of compound **6-BTB**



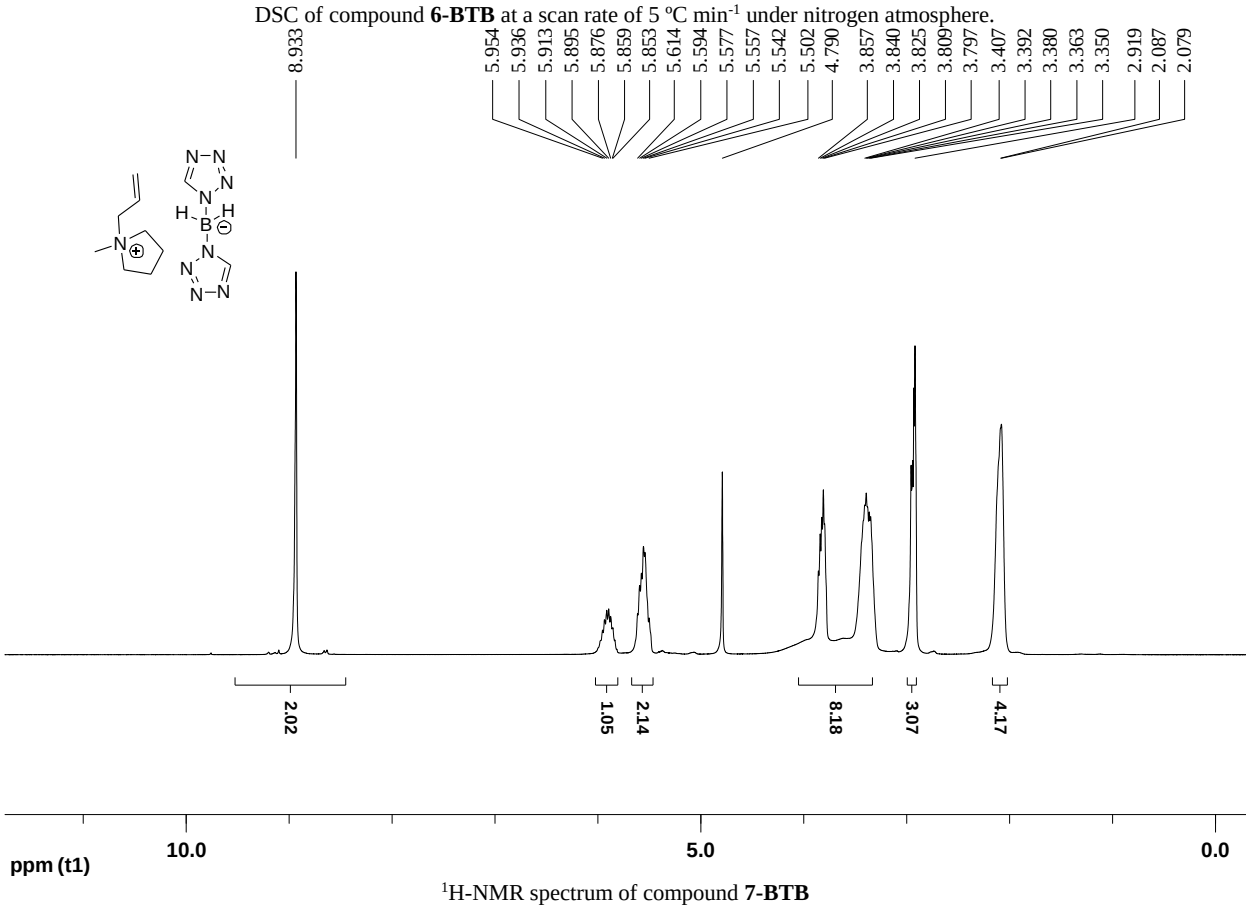
HRMS: cations of compound **6-BTB**



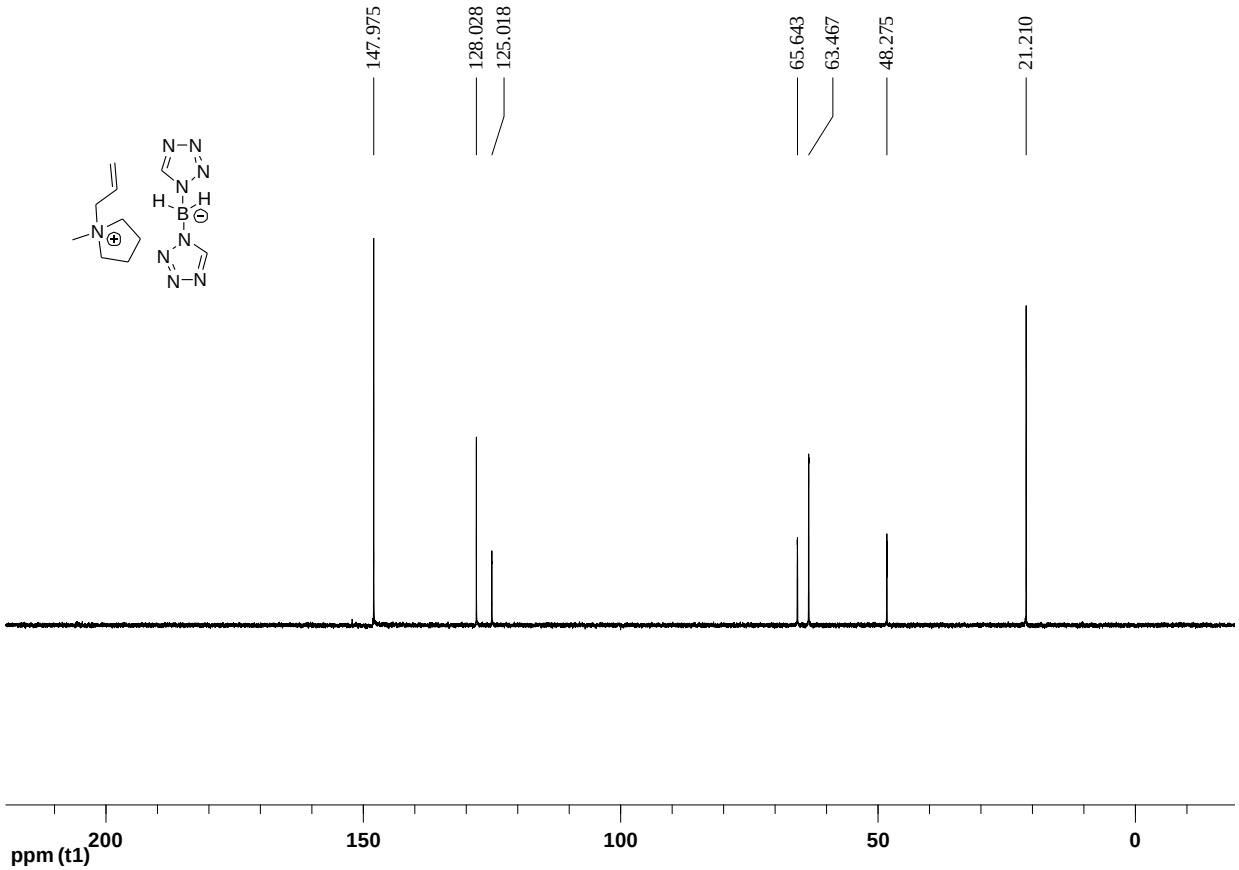
HRMS: anion of compound **6-BTB**



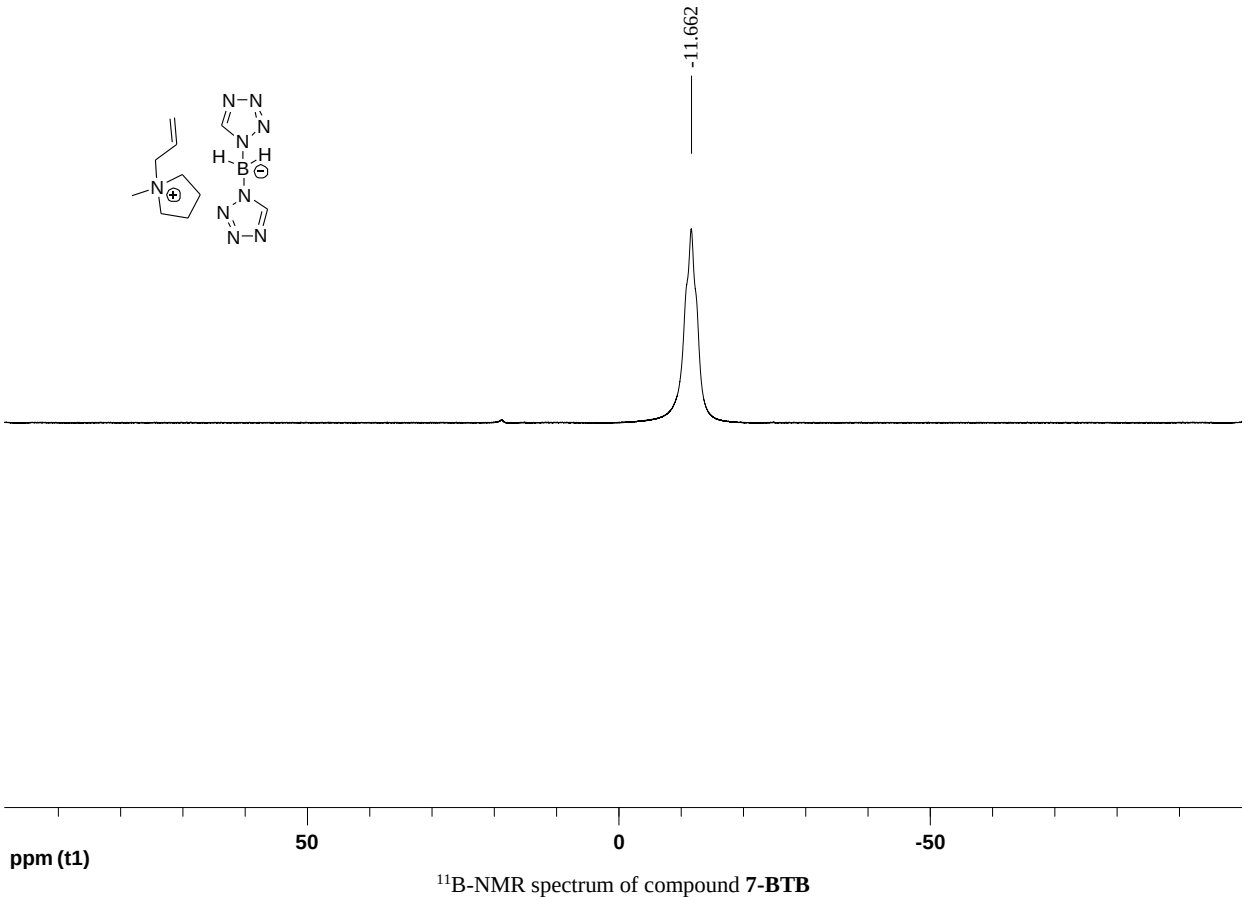
DSC of compound **6-BTB** at a scan rate of 5 ºC min^{-1} under nitrogen atmosphere.



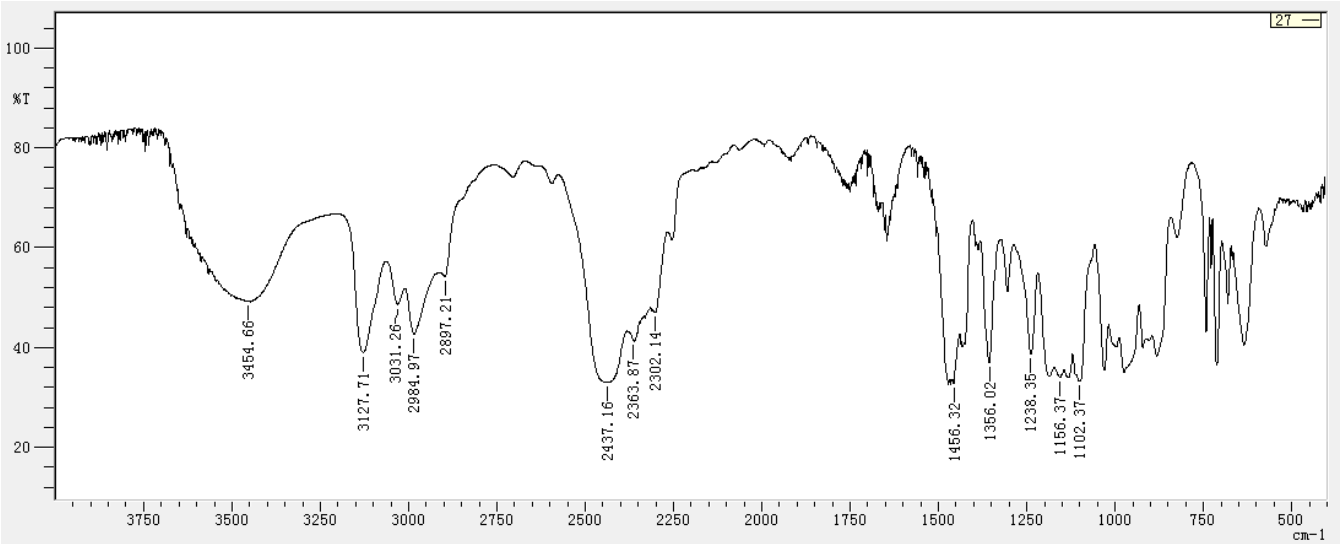
^{1}H-NMR spectrum of compound **7-BTB**



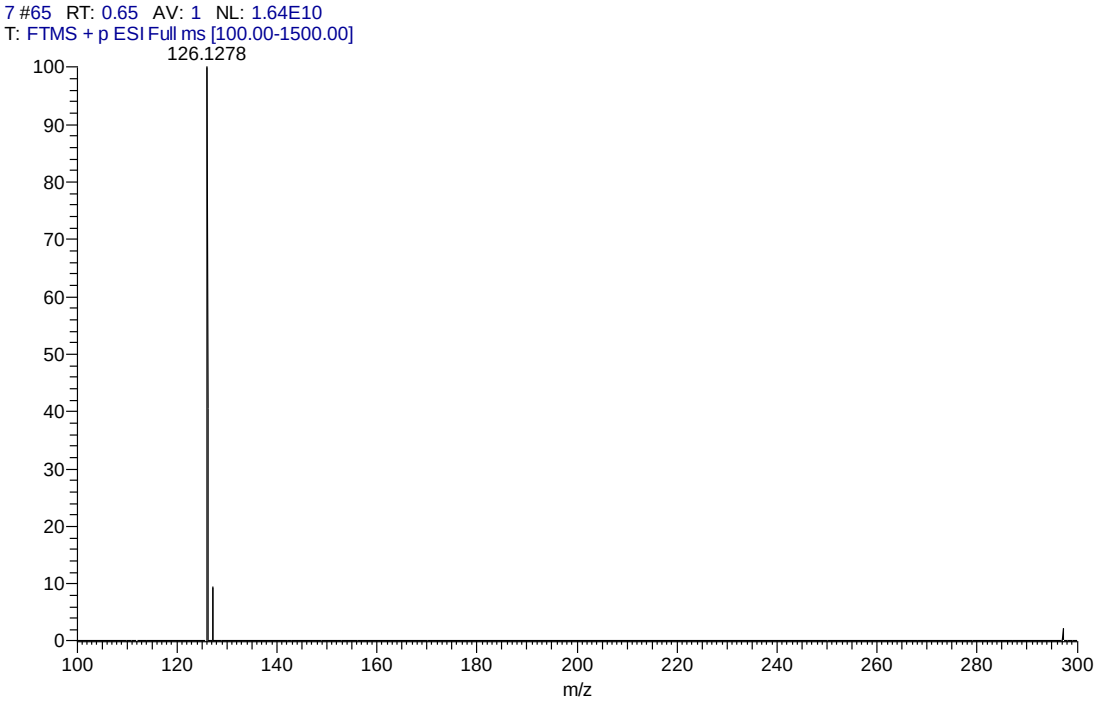
^{13}C-NMR spectrum of compound **7-BTB**



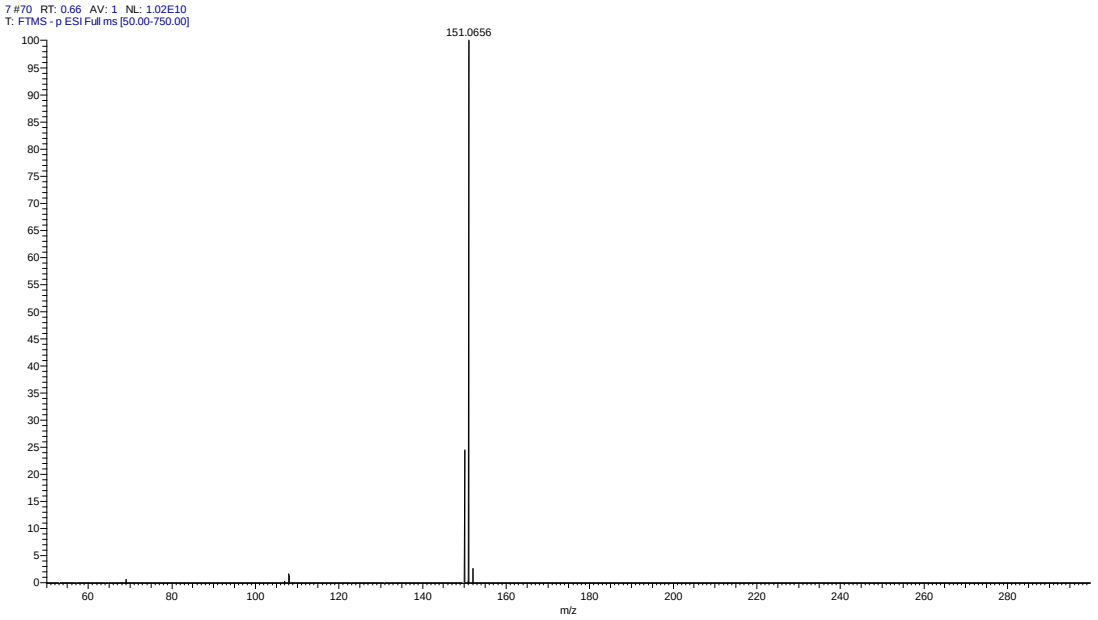
^{11}B-NMR spectrum of compound **7-BTB**



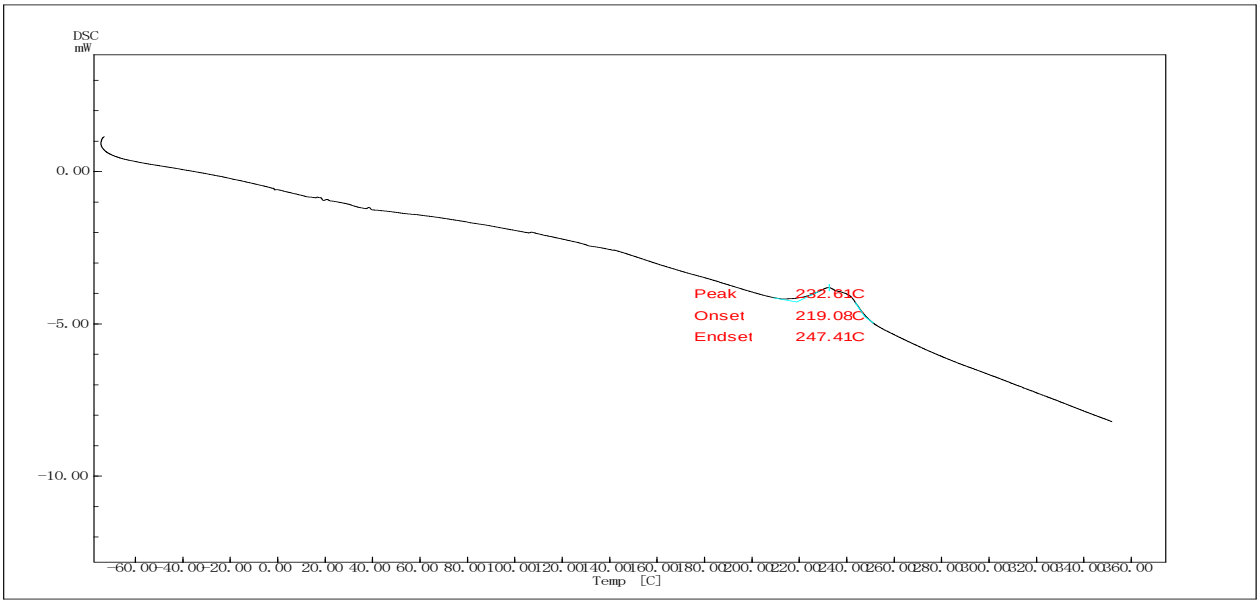
IR spectrum of compound **7-BTB**



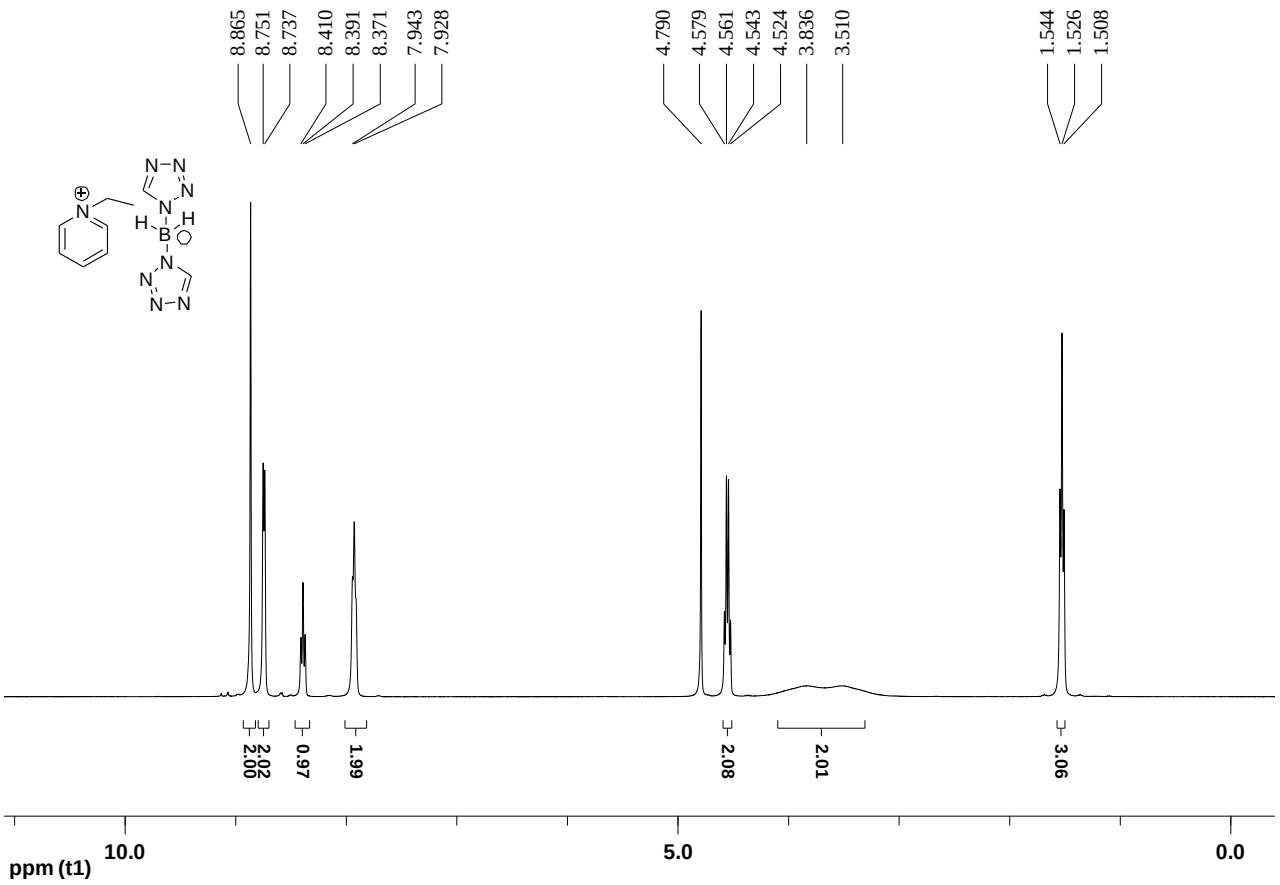
HRMS: anion of compound **7-BTB**



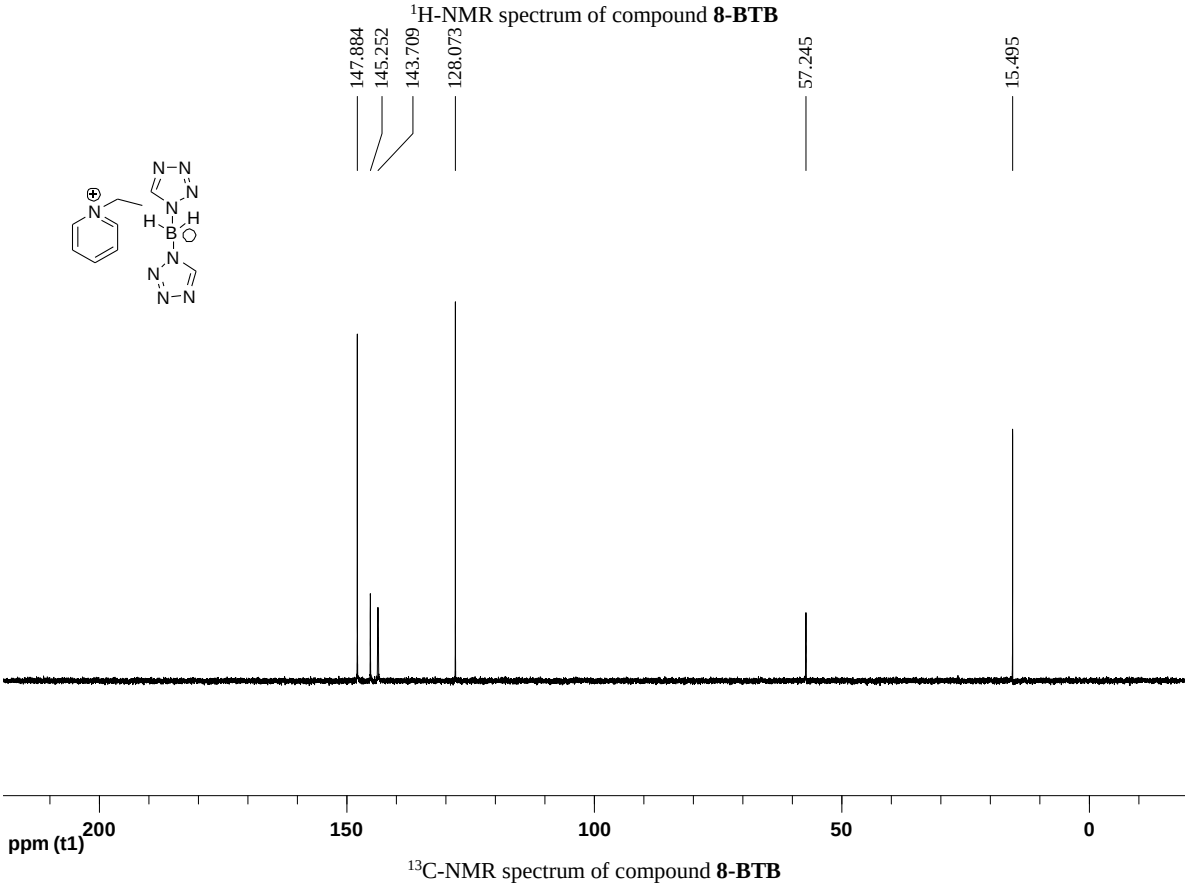
HRMS: anion of compound **7-BTB**



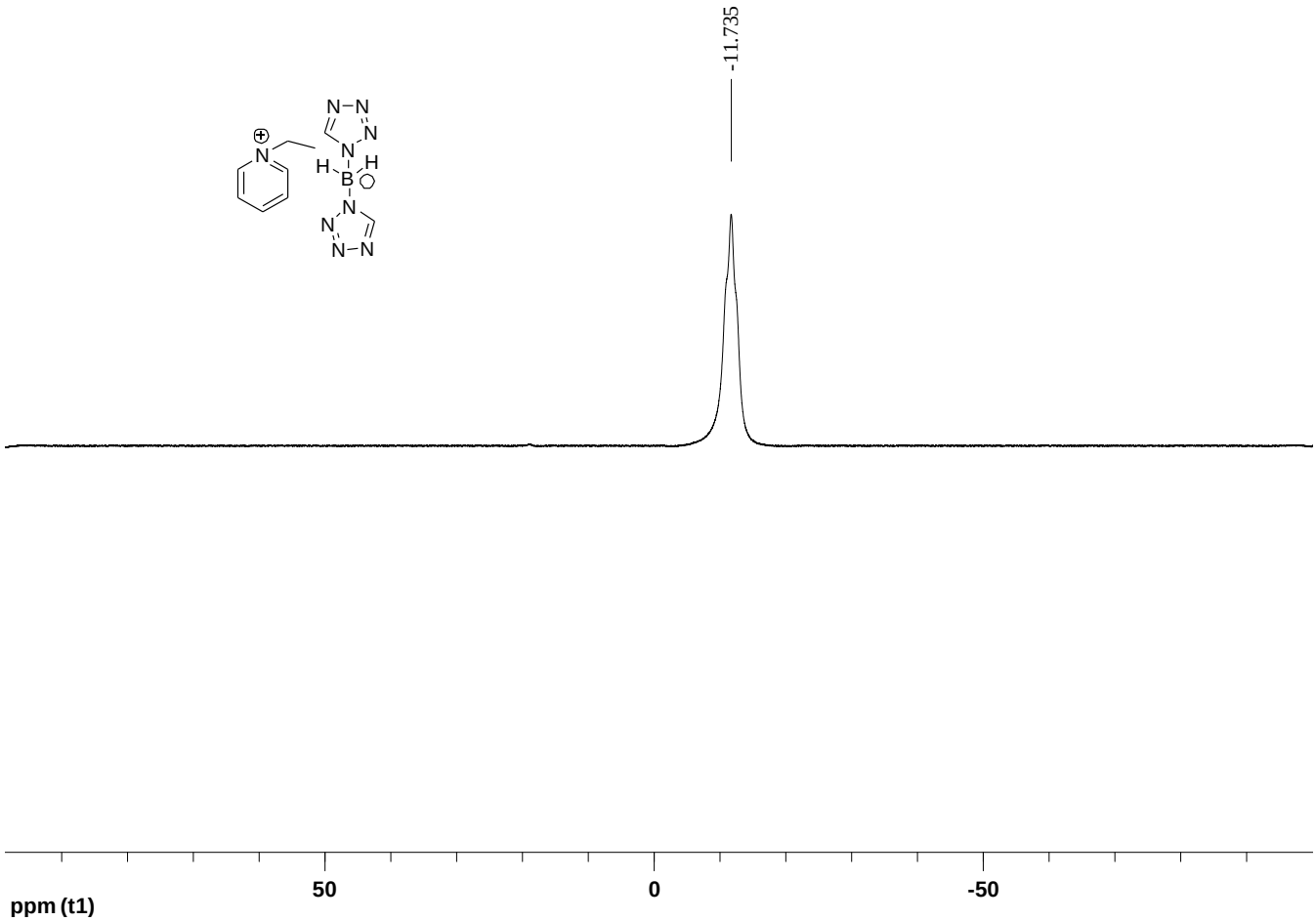
DSC of compound **7-BTB** at a scan rate of 5 ºC min^{-1} under nitrogen atmosphere.



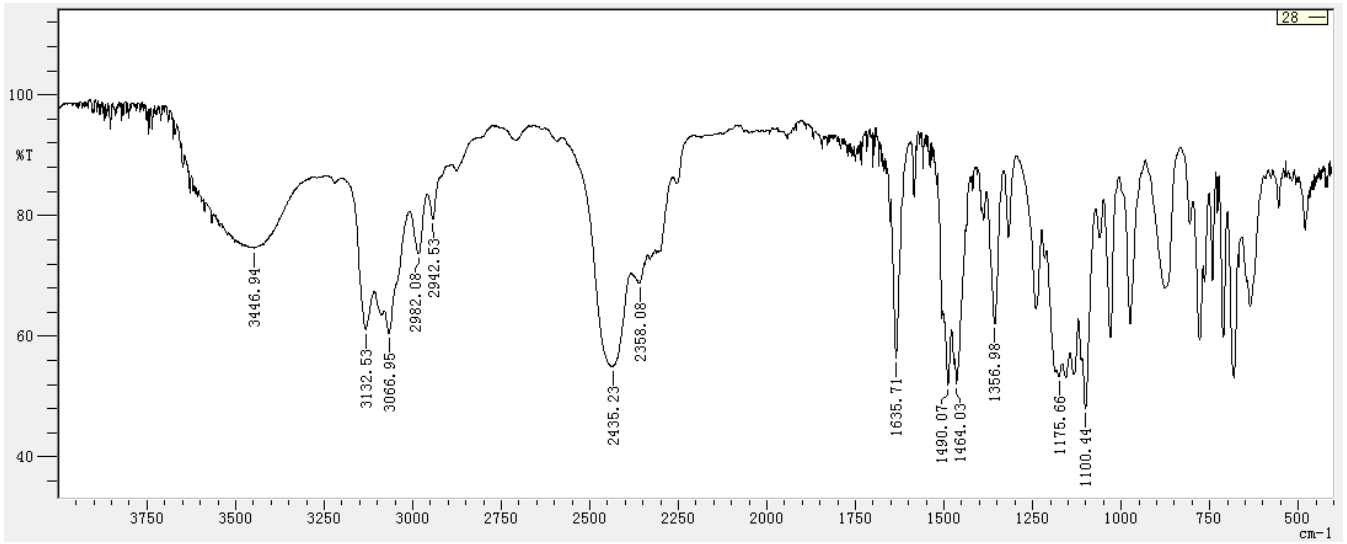
^{1}H-NMR spectrum of compound **8-BTB**



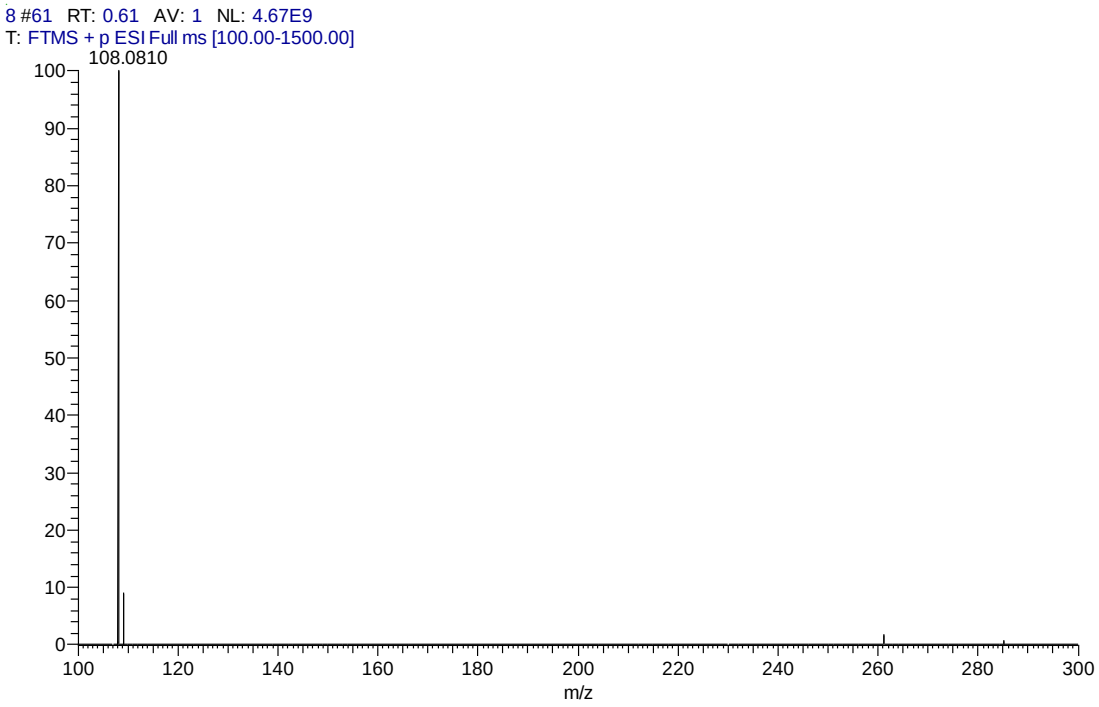
^{13}C-NMR spectrum of compound **8-BTB**



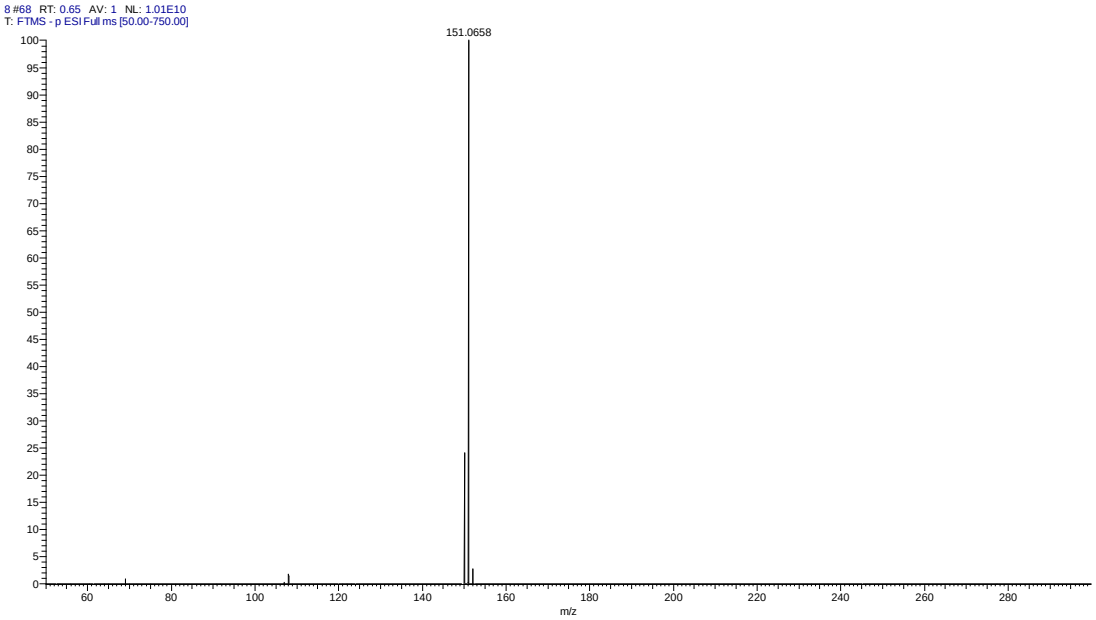
^{11}B-NMR spectrum of compound **8_BTB**



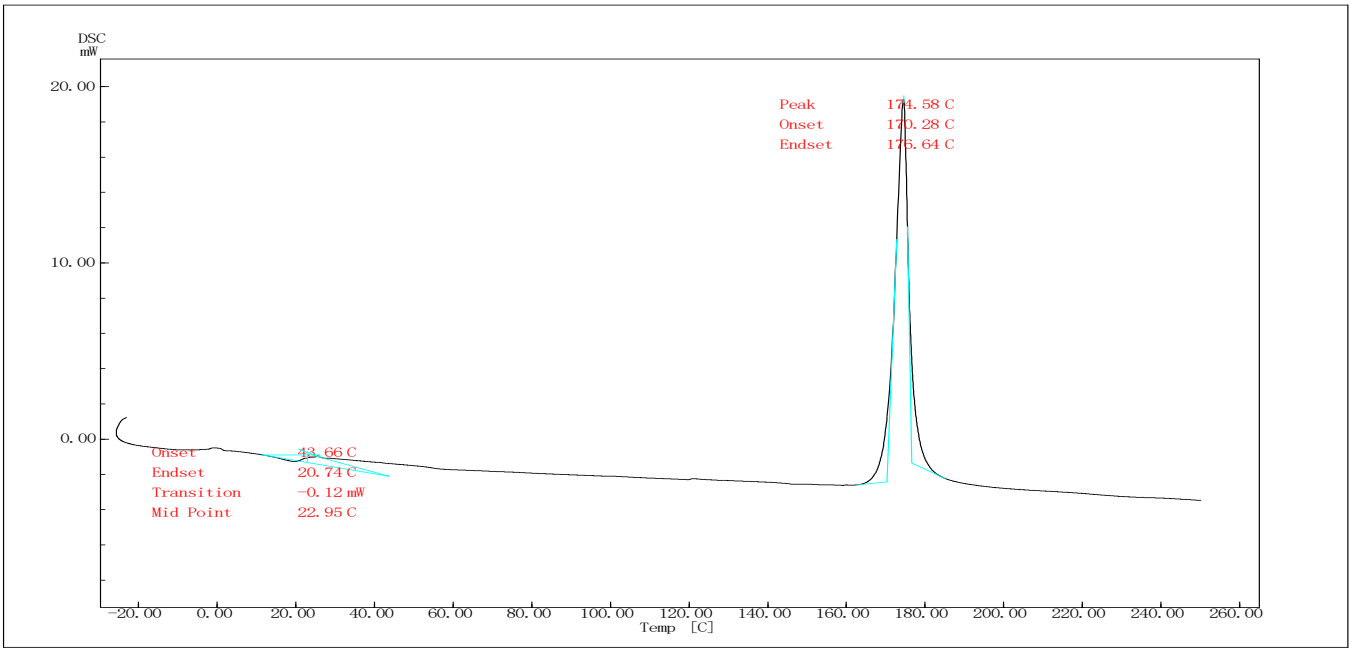
IR spectrum of compound **8-BTB**



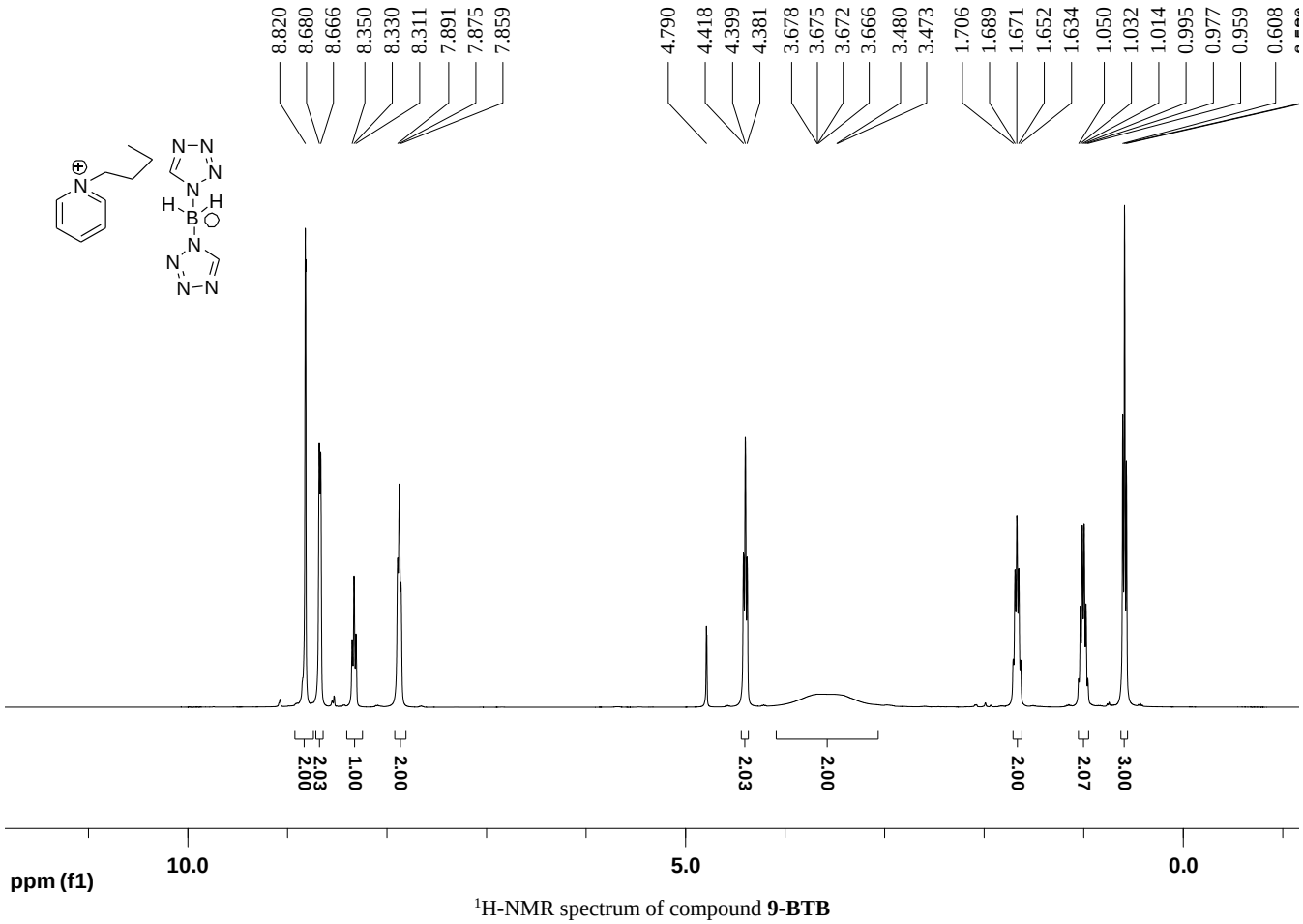
HRMS: cation of compound **8-BTB**



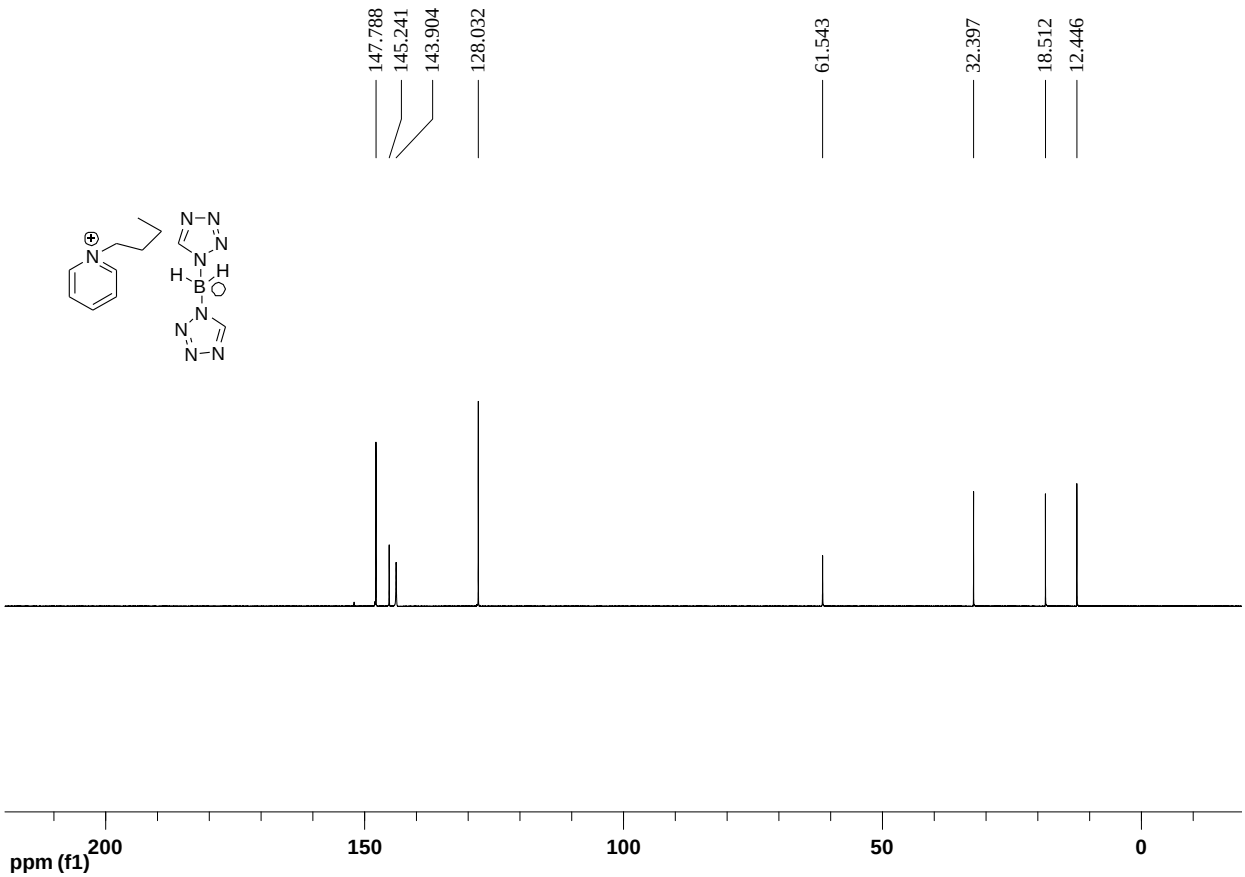
HRMS: anion of compound **8-BTB**



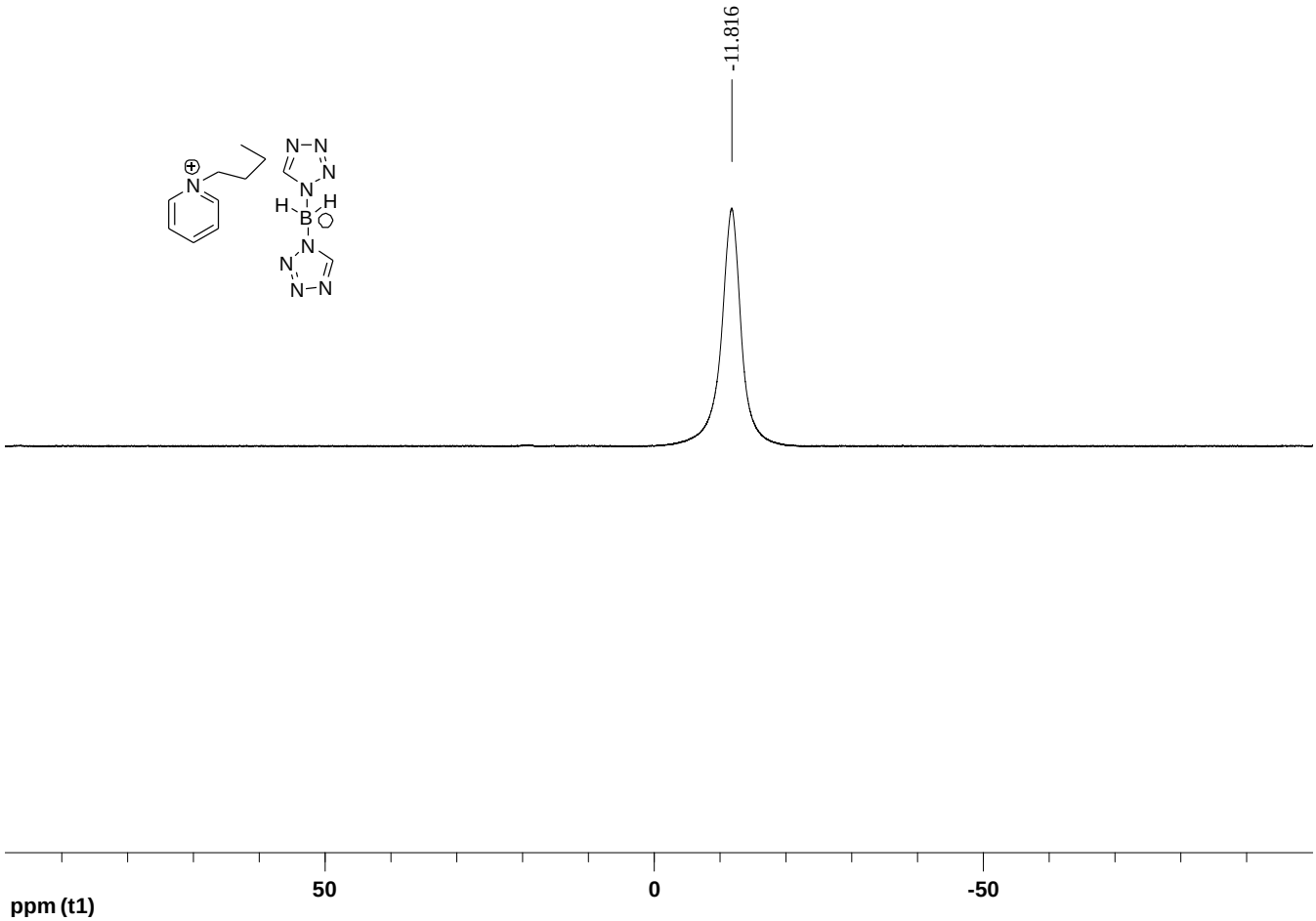
DSC of compound **8-BTB** at a scan rate of 5 ºC min^{-1} under nitrogen atmosphere.



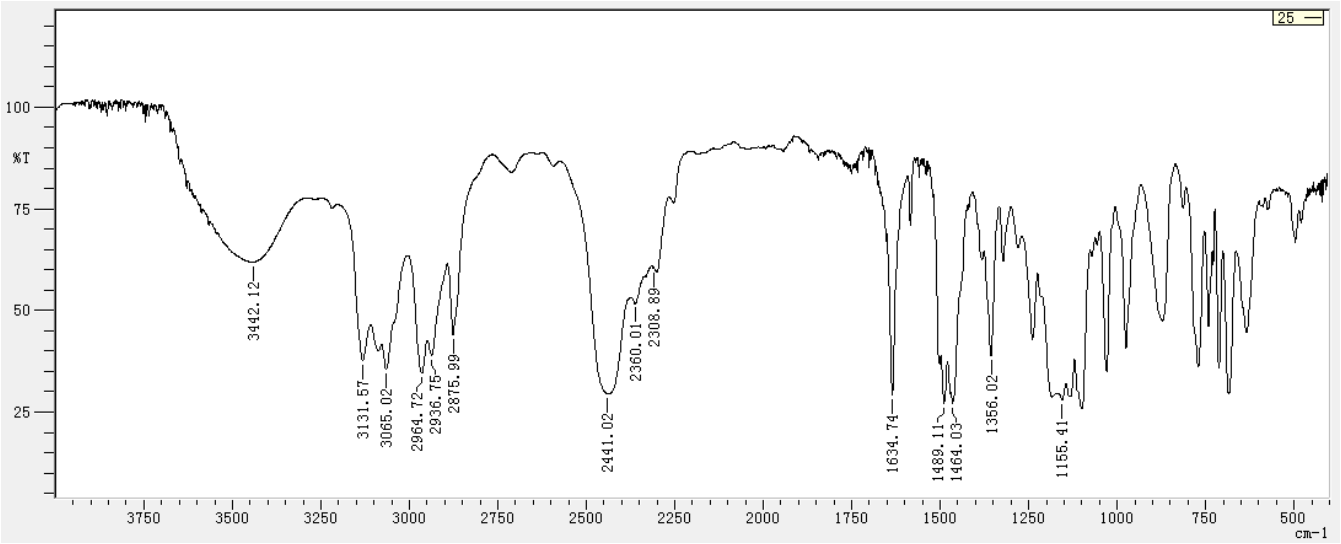
^{1}H-NMR spectrum of compound **9-BTB**



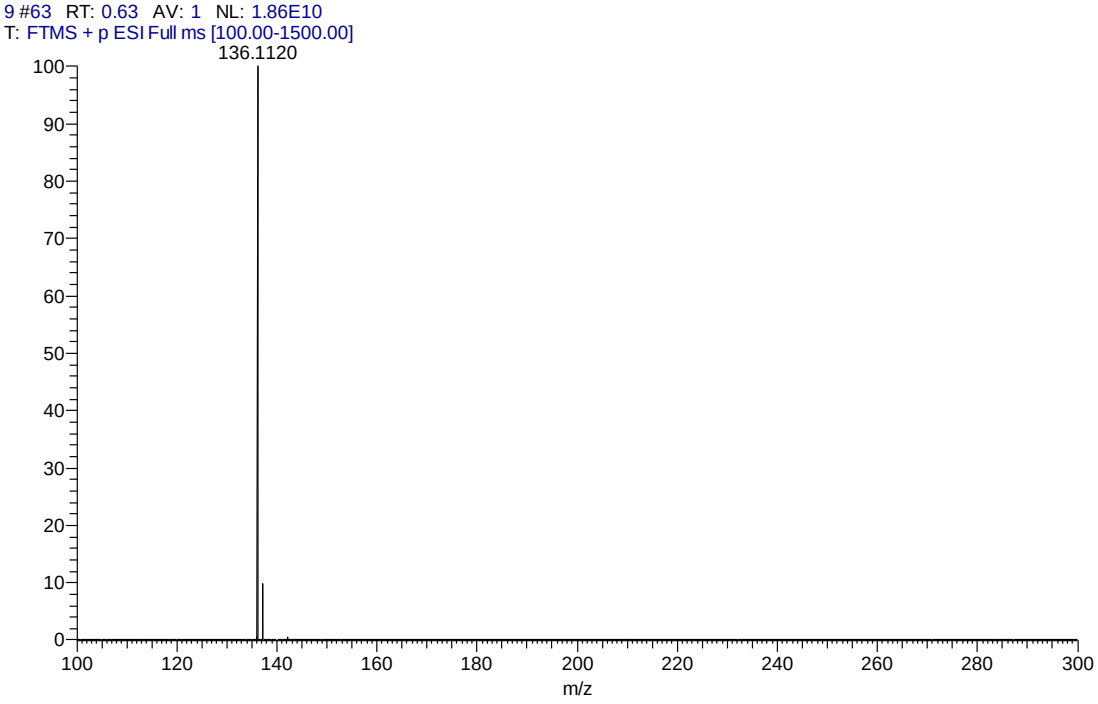
^{13}C-NMR spectrum of compound **9-BTB**



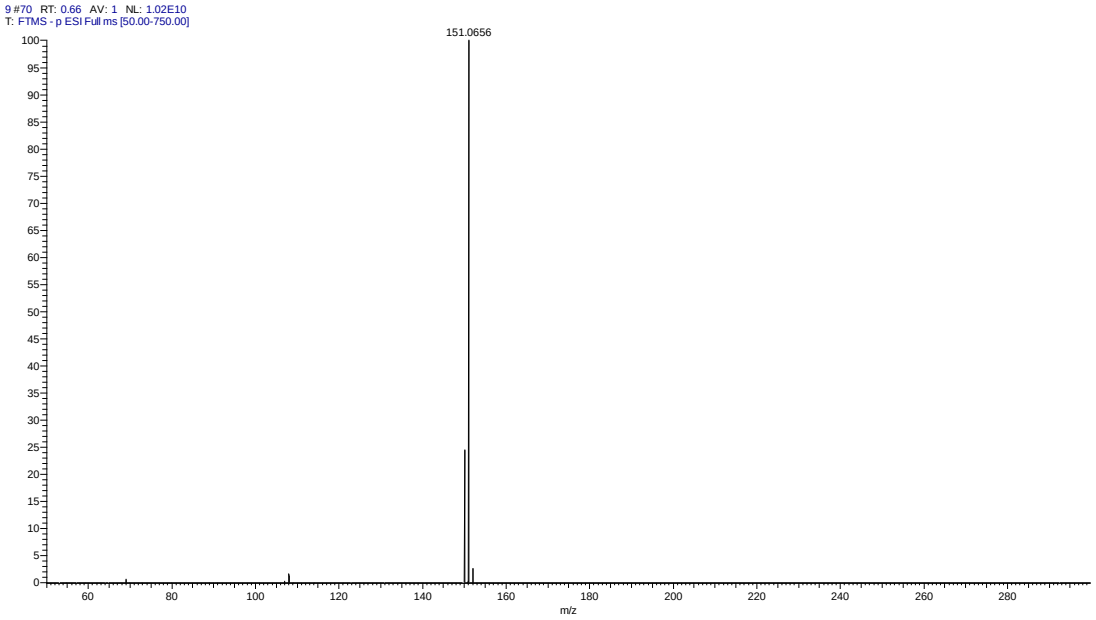
^{11}B-NMR spectrum of compound **9-BTB**



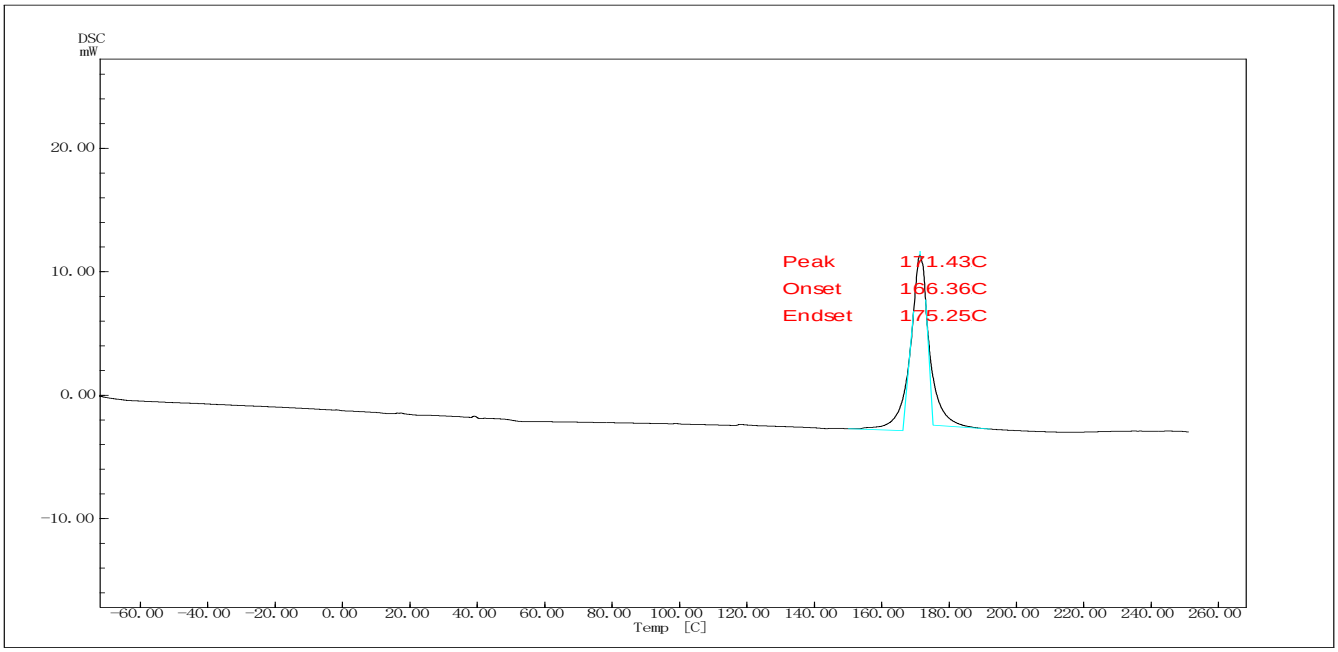
IR spectrum of compound **9-BTB**



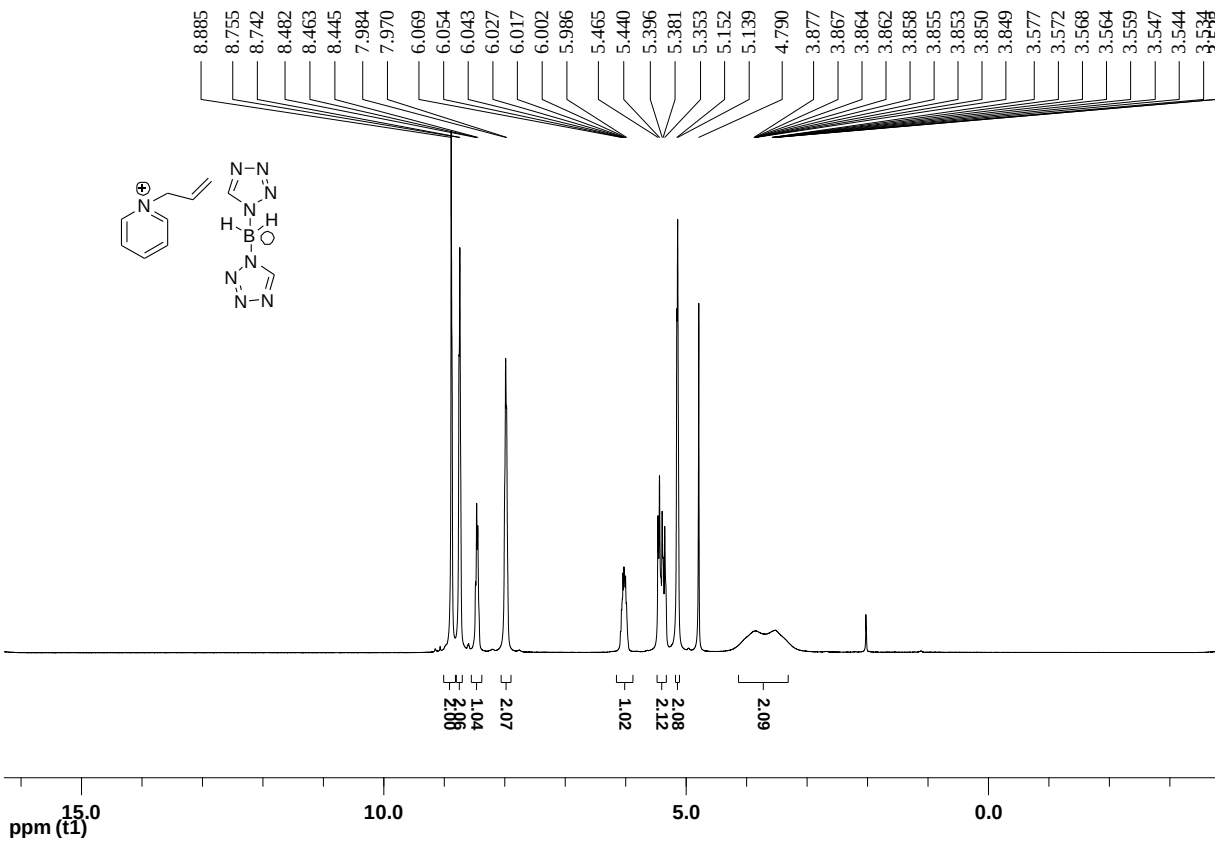
HRMS: cation of compound **9-BTB**



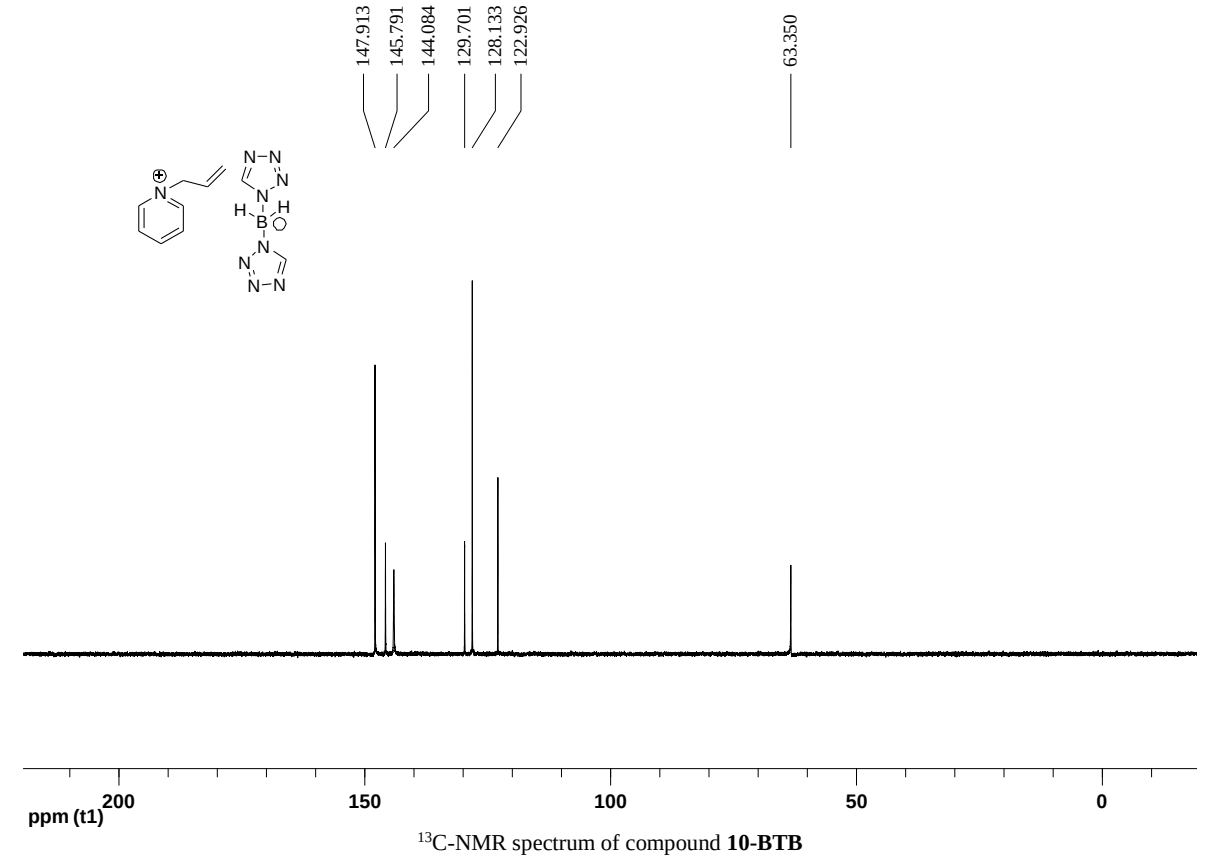
HRMS: anion of compound **9-BTB**



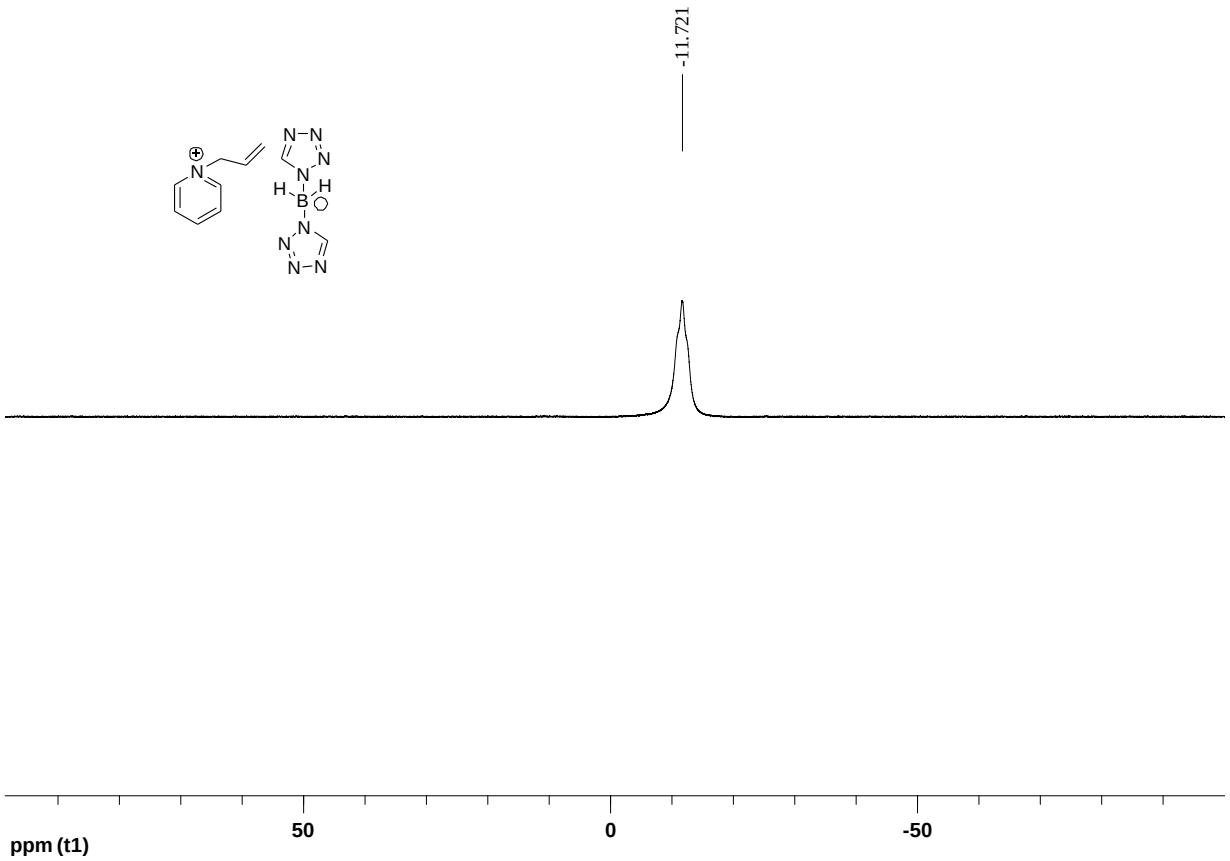
DSC of compound **9-BTB** at a scan rate of 5 ºC min^{-1} under nitrogen atmosphere.



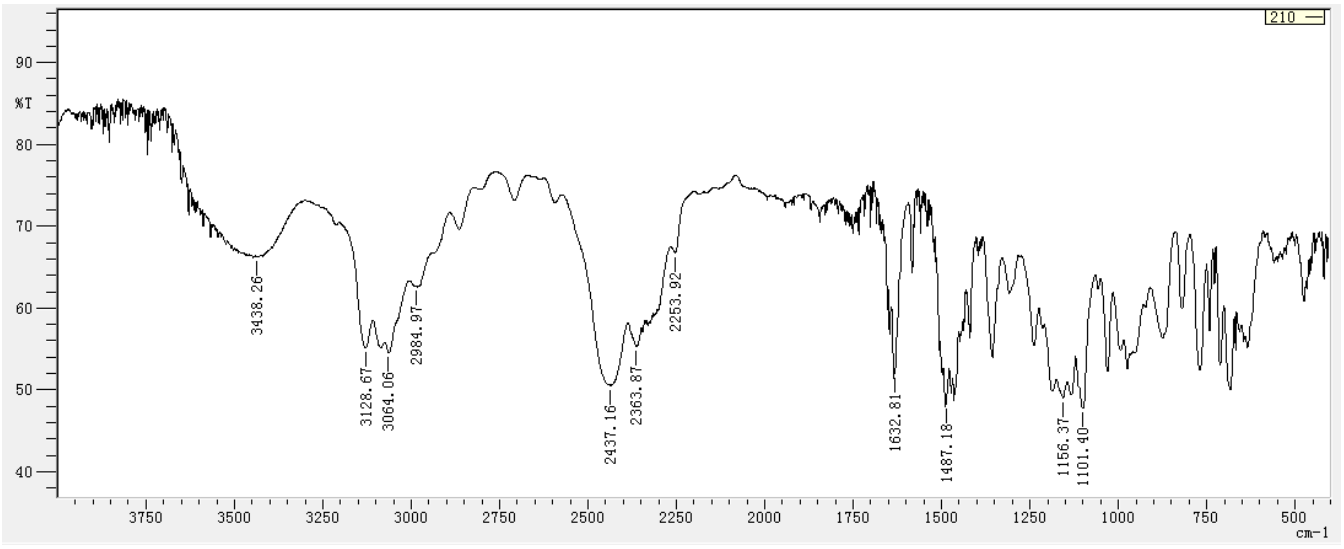
^{1}H-NMR spectrum of compound **10-BTB**



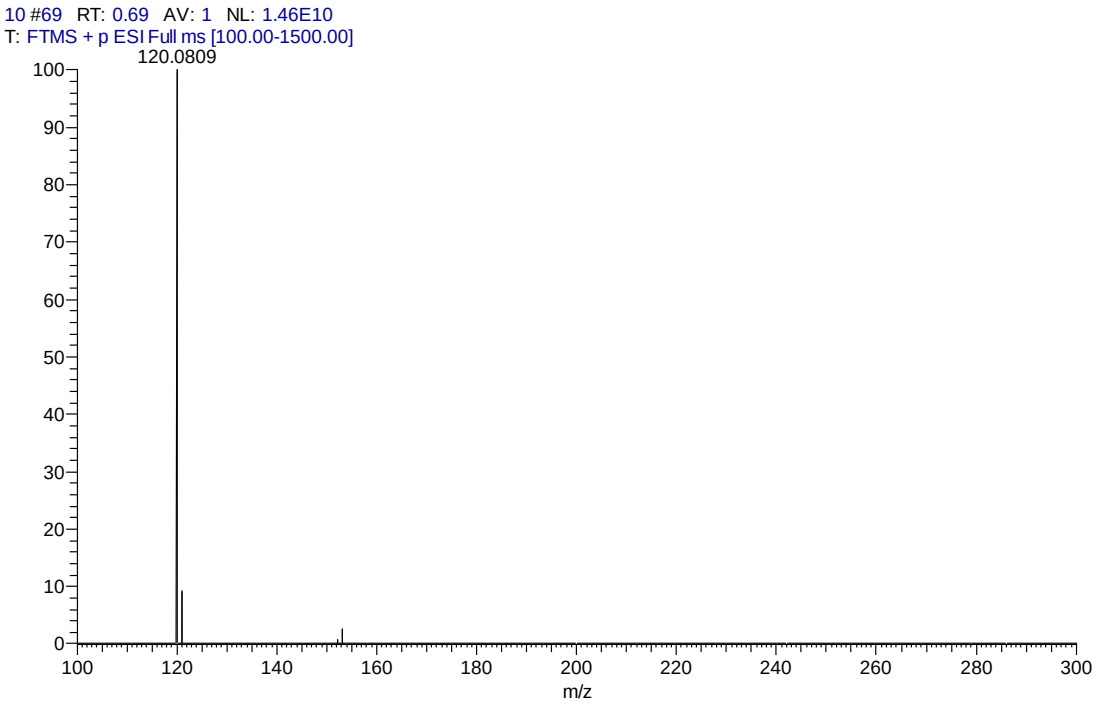
^{13}C-NMR spectrum of compound **10-BTB**



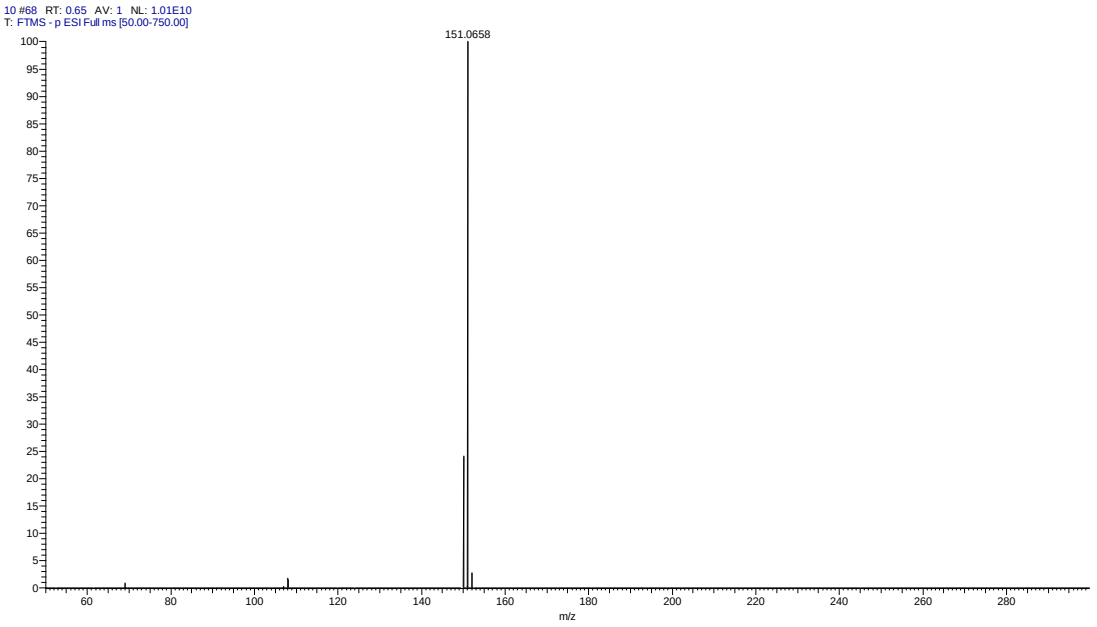
^{11}B-NMR spectrum of compound **10-BTB**



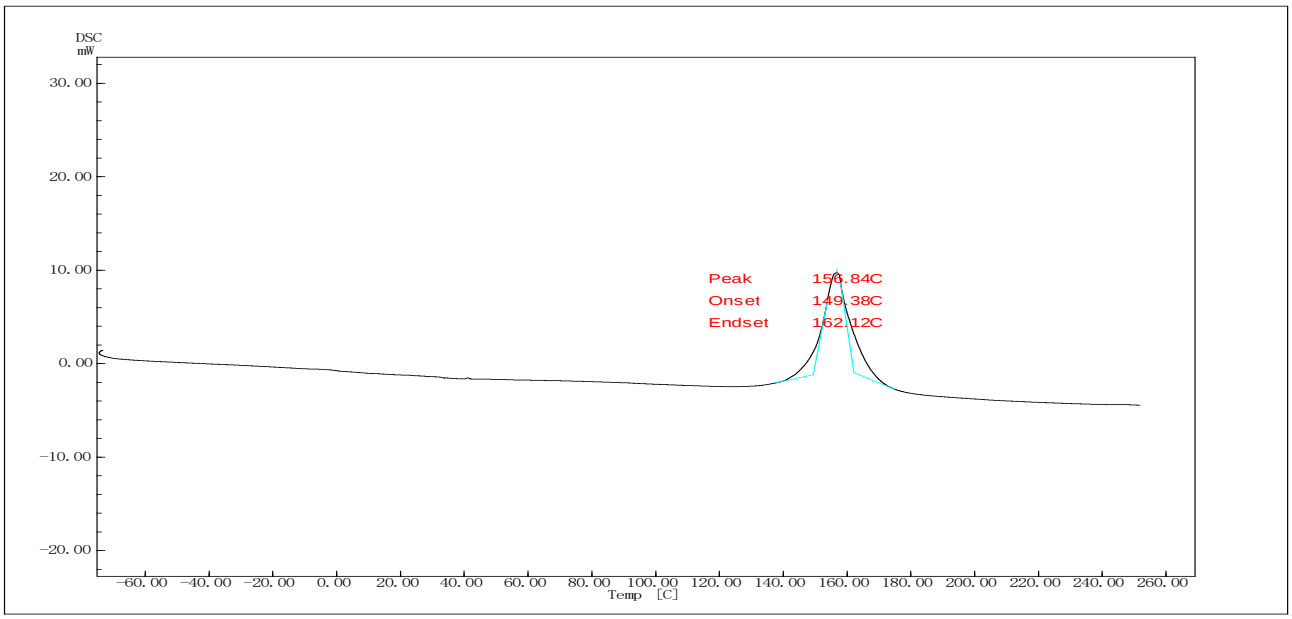
IR spectrum of compound **10-BTB**



HRMS: cation of compound **10-BTB**



HRMS: anion of compound **10-BTB**



DSC of compound **10-BTB** at a scan rate of 5 ºC min^{-1} under nitrogen atmosphere.