Electronic Supplementary Information

B-N Bond Formation through Palladium-Catalyzed, Microwave-Assisted Cross-Coupling of Nitrogen Compounds with Iodo-dodecaborate

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Contents

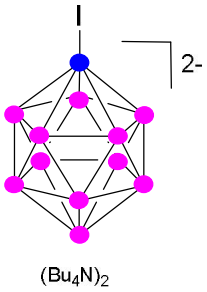
General Considerations

Unless otherwise stated, commercially available reagents were used without further purification. $B_{12}H_{11}I$ was prepared according to the literature procedure with some modification.[1] 4-Nitroaniline (>99%), 2,4-dinitroaniline, 2-nitroaniline, 3-nitroaniline, 4-cyanoaniline, N-methyl 4-aminobenzoate (98%), imidazole, pyrazole, pyrrol, indole, carbazole (98%), iodine (>99%), Davephos, Ru-Phos, Brettphos, Johnphos, Sphos, and tertbutyl Davephos (99%), $Pd_2(dba)_3$ (99%), anhydrous K_3PO_4 (>98%), KtBuO (>98%), K_2CO_3 (>99.0%), toluene (99.8%) and 1,4-dioxane (99.8%) were from Sigma-Aldrich and were used as received. Dichloromethane, acetonitrile and silica gel (Grade 60, 230-400 Mesh) were from Carl Roth. Celite (545 filter aid, not acid washed, powder) was from Fisher. Deuterated solvents were from SigmaAldrich and Deutero.

All cross-coupling reactions were performed in an oven dried 10 mL reaction round bottom flask. Thin-layer chromatography (TLC) AluSil plates were from Macherey-Nagel. TLC samples for borane-containing compounds were stained with 1 wt. % $PdCl_2$ in 6 M HCl and were developed using a heat gun. ^{1}H NMR, ^{11}B NMR, and ^{13}C NMR spectra were recorded on a JOEL 400 MHz spectrometer at 25 °C. Chemical shifts were referenced relative to residual solvent. The following abbreviations are used to describe peak patterns where appropriate: br = broad, s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet. MestReNova V10.0.2-15465 S_3 software was used to visualize the spectra. Coupling constants (J) are reported in Hertz (Hz). Mass spectra in the negative-ion mode were recorded with a Bruker Ultraflex TOF spectrometer. The reactions were performed in an open vessel microwave oven (CEM Discover, Model 908860, or HNZXIB, Model MCR-3).

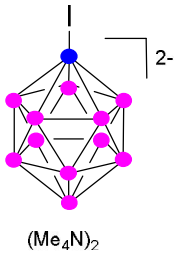
Experimental Procedures

General procedure for the synthesis of $(Bu_4N)_2B_{12}H_{11}I$ (1)



($Cs_2B_{12}H_{12}$ (1.0 g, 2.5 mmol, 1.0 equiv) was added to an 250 round bottom flask. The flask was charged with 30 ml of phosphate buffer solution (0.1 M, pH=7.2), the resulting mixture was heated up to 40 ºC for 3-5 mins until all $Cs_2B_{12}H_{12}$ was completely dissolved and the solution became clear. Subsequently, I_2 (592 mg, 2.4 mmol, 1.0 equiv) dissolved in 100 ml MeOH was added dropwise to the reaction vessel over 30-40 mins. After completion of the addition of I_2, the reaction mixture was stirred for 3-5 mins until the reaction solution became colorless. Completion of the reaction was determined by ^{11}B-NMR. The contents of the flask were subsequently concentrated under reduced pressure yielding a white powder. The powder was washed several time with MeOH and then filtered through a filter paper on a fritted funnel to yield a white solid, which was dissolved in water and treated with 2.4 equivalent of tetrabutylammonium bromide resulting in a white precipitate. The precipitate was dried *in vacuo* to produce the title compound, (1.77 g, 96 % yield). ^{11}B-NMR (129 MHz, acetone-d_6) δ = -21.47 (S, IB, B-I), -17.12 (d, *J*= 135,1B, B-H) -15.26 (d, *J*= 137 , 5B, B-H) , -13.73 (d, *J*= 171 , 5B, B-H). HRMS (ESI/TOF) m/z calcd for $B_{12}H_{11}I$ $(M\text{-}I)^{-1}$: 141.2056; Found: 141.2065, HRMS (ESI/TOF) m/z calcd for $B_{12}H_{11}I$ $(M+C_{16}H_{36}N)^{-1}$: 510.3958; Found: 510.4064.

General procedure for the synthesis of $(Me_4N)_2B_{12}H_{11}I$ (1)



The above procedure was used. The water solution was treated with 2.4 equivalent of tetramethylammonium bromide resulting in a white precipitate, the precipitate was dried *in vacuo* to produce the title compound, (1.9 g, 90 % yield).

General procedure for Pd-catalyzed cross-coupling amination

An oven-dried 10 mL round bottom flask was charged with 1.0 equiv of $(Me_4N)_2$ or $(Bu_4N)_2B_{12}H_{11}I$, $Pd_2(dba)_3$ (10-15 mol%), Davephos ligand (20 mol%), amine (2.0 equiv), and K*t*BuO (2.5 equiv), subsequently 2.0 ml of anhydrous DMSO or DMF was added. The reaction flask was filled with N_2 and connected to a condenser. The round bottom flask was submitted to microwave irradiation at 150 ºC, power 300 W, for 15 mins with stirring (high) until the starting $(Bu_4N)_2$/$(Me_4N)_2B_{12}H_{11}I$ had been completely consumed as judged by ^{11}B-NMR and TLC. The mixture was cooled to room temperature and then filtrated through a funnel filled with cotton, celite and filter paper. The resulting solution was

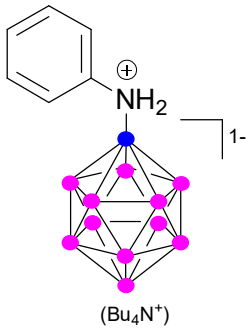
concentrated under reduced pressure. The crude material was checked by TLC (usually by using acetonitrile: DCM (1:4 or 1:2) after that the mixture was purified by column chromatography on silica gel (eluting with acetonitrile-DCM mixtures).

Experimental details and characterization data

Remarks:

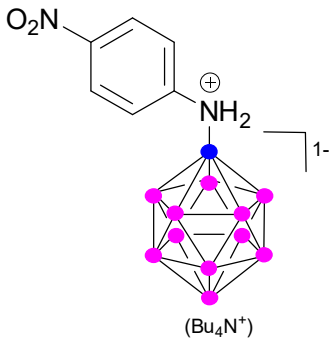
1- We did not notice an effect of using Bu_4N or Me_4N as counter cation.
2- All compounds can be obtained as solids by precipitating with acetonitrile: Et_2O (1:10) or acetone-Et_2O (1:10).
3- In case of using $(Me_4N)_2[B_{12}H_{11}I]^{2-}$, we noticed in some compounds that methyl peak in ^{1}H-NMR and ^{13}C -NMR disappeared, most probably due to exchange of the cation with potassium from Bu_tOK.

$(Bu_4N)[B_{12}H_{11}NH_2C_6H_5]$ (3a)



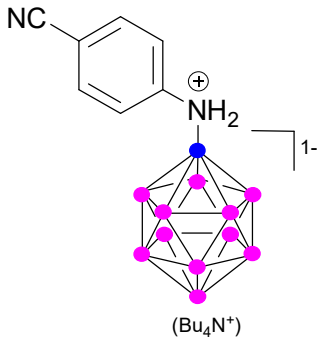
Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (18.0 mg, 0.02 mmol, 0.15 equiv), Davephos ligand (16.0 mg, 0.04 mmol, 0.30 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv) aniline (25 μL, 0.266 mmol, 2.0 equiv), DMSO 2ml. The crude product was purified by flash column chromatography on silica gel (Acetonitrile/DCM = 1:5) to afford the product as a yellow oil (41 mg, 65 % yield). ^{1}H NMR (400 MHz, acetone-d_6) δ = 0.94 – 1.06 (t, *J*=7.4, 12H), 1.37 – 1.51 (dt, *J*=14.9, 7.4, 8H), 1.76 – 1.89 (m, 8H), 3.38 – 3.50 (m, 8H), 7.22 – 7.29 (t, *J*=7.2, 1H), 7.31 – 7.44 (m, 4H), 7.81 – 7.93 (s, 1H). ^{13}C NMR (400 MHz, Acetonitrile-d_3) δ = 13.78, 20.29, 24.26, 59.24, 124.13, 127.97, 129.62, 139.14.^{11}B NMR (129 MHz, acetone-d_6) δ = -18.79(1B, *J*=130, d), -17.06 (5B, *J*=103, d), -16.54 (5B, *J*=103, d), -4.63(1B, s). HRMS (ESI/TOF) m/z calcd for $C_6H_{18}NB_{12}$ $(M+H)^{-1}$: 234.2638; Found: 234.2689.

$(Bu_4N)[B_{12}H_{11}NH_2C_6H_5$-4-$NO_2]$(3b)



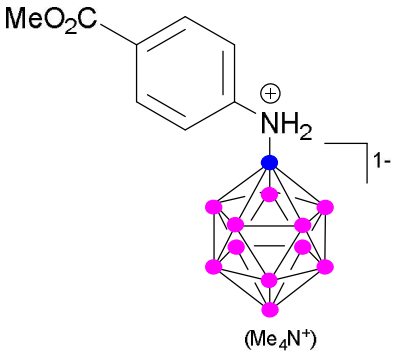
Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K^{t}BuO (37.0 mg, 0.333 mmol, 2.5 equiv), 4-nitroaniline (36.7mg, 0.266 mmol, 2.0 equiv), DMSO 2ml. The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as a orange oil in (60 mg, 84 % yield). ^{1}H NMR (401 MHz, Acetonitrile-d_3) δ = 0.89 – 0.98 (t, *J*=7.3, 24H), 1.26 – 1.41 (h, *J*=7.3, 16H), 1.51 – 1.65 (p, *J*=8.6, 8.2, 16H), 3.01 – 3.13 (m, 16H), 5.97 – 6.08 (s, 1H), 6.96 – 7.06 (d, *J*=8.4, 2H), 7.83 – 7.92 (d, *J*=9.5, 2H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ = 1.32, 13.79, 20.26, 24.28, 59.24, 113.70, 120.80, 125.89, 127.09. ^{11}B NMR (129 MHz, Acetonitrile-d_3) δ = -18.82(1B, d, *J*=130), -16.81(10B, d, *J*=103), -4.66 (1B, s). HRMS (TOF) m/z calcd for $C_6H_{17}N_2O_2B_{12}$ $(M+H)^{-1}$: 279.2489; Found: 279.2554. $C_{22}H_{52}N_3O_2B_{12}$ $(M+Bu_4N)^{-1}$: 520.5268; Found: 520.5412. $C_6H_{16}N_2O_2B_{12}$ $(M)^{-2}$: 139.1208; Found: 139.1227.

$(Bu_4N)[B_{12}H_{11}NH_2C_6H_5$-4-CN] (3c)



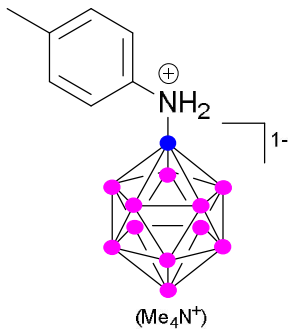
Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv) 2-nitroaniline (32mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as yellow oil in (55 mg, 84 % yield). ^{1}H NMR (401 MHz, Acetonitrile-d_3) δ = 0.93 – 0.99 (t, *J*=12.0, 12H), 1.29 – 1.40 (h, *J*=14.5, 8H), 1.54 – 1.64 (p, *J*=10.0, 11H), 3.04 – 3.10 (m, *J*=5.3, 9H), 7.16 – 7.29 (s, 1H), 7.34 – 7.38 (d, *J*=9, 2H), 7.70 – 7.75 (d, *J*=9, 2H). ^{13}C NMR (101 MHz, Acetonitrile-D_3) δ = 13.78, 20.28, 24.26, 41.29, 59.23, 119.23, 124.94, 133.92, 143.55. ^{11}B NMR (129 MHz, Acetonitrile-d_3) δ = -18.89 (1B, d, *J*=130), -17.21(5B, d, *J*=100), -16.73(5B, d, *J*=100), -4.82(1B, s). HRMS (TOF) m/z calcd for $C_7H_{16}N_2B_{12}$ $(M)^{-2}$: 129.1259; Found: 129.1276. HRMS (TOF) m/z calcd for $C_6H_{18}N_2O_2B_{12}$ $(M+H)^{-1}$ 259.2591; Found: 259.2652.

$(Me_4N)[B_{12}H_{11}NH_2C_6H_5$-4-$CO_2$Me] (3d)



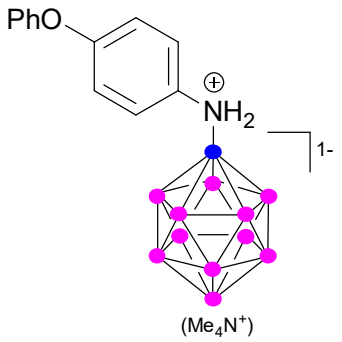
Following the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (150 mg, 0.361 mmol, 1.0 equiv), $Pd_2(dba)_3$ (33 mg, 0.0361 mmol, 0.10 equiv), Davephos ligand (28.5 mg, 0.0722 mmol, 0.20 equiv.), K*t*BuO (101 mg, 0.903 mmol, 2.5 equiv), 4-aminobenzoate (109 mg, 0.722 mmol, 2.0 equiv), (DMF 3.6ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as yellow oil in (102 mg, 81 % yield).^{1}H NMR (401 MHz, Acetonitrile-d_3) δ = 0.11 – 1.79 (11H), 3.86 (s, 12H), 7.27 – 7.36 (m, 2H), 7.41 – 7.57 (d, *J*=5.6, 2H), 7.94 – 8.04 (s, 1H).^{11}B NMR (129 MHz, Acetonitrile-d_3) δ = -18.98(1B, d, *J*=113), -16.94 (10B,d, *J*=121) -4.71(1B, s).HRMS (TOF) m/z calcd for $C_8H_{20}NO_2B_{12}$ $(M)^{-2}$: 145.6311; Found: 145.6315. HRMS (TOF) m/z calcd for $C_8H_{21}NO_2B_{12}$ $(M+H)^{-1}$ 292.2694; Found: 292.2735.

$(Me_4N)[B_{12}H_{11}NH_2C_6H_5$-4-Me] (3e)



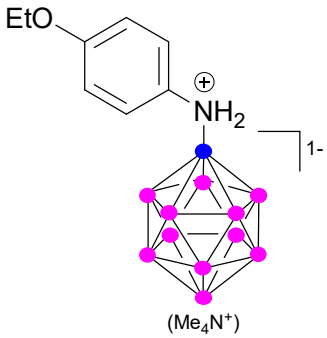
Following the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (150 mg, 0.361 mmol, 1.0 equiv), $Pd_2(dba)_3$ (33 mg, 0.0361 mmol, 0.10 equiv), Davephos ligand (28.5 mg, 0.0722 mmol, 0.20 equiv.), K^{t}BuO (101 mg, 0.903 mmol, 2.5 equiv), 4-aminobenzoate (109 mg, 0.722 mmol, 2.0 equiv), (DMSO 3.6ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as yellow oil in (55 mg, 70 % yield). ^{1}H NMR (401 MHz, Acetonitrile-d_3) δ = 2.32 (s, 3H), 2.36 (s, 12H), 7.01(s, 1H), 7.08-7.10(d, 2H, *J*= 8), 7.17-7.19 (d, *J*=8, 2H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ = 1.32, 20.72, 123.67, 129.82, 136.46, 137.62. ^{11}B NMR (129 MHz, Acetonitrile-d_3) δ = -19.20 (1B, d, *J*=132), -17.05(10B,d, *J*=126), -4.58 (1B, s). HRMS (TOF) m/z calcd for $C_7H_{20}NB_{12}$ $(M+H)^{-1}$: 248.2784; Found: 248.2852.

$(Me_4N)[B_{12}H_{11}NH_2C_6H_5$-4-phenoxy] (3f)



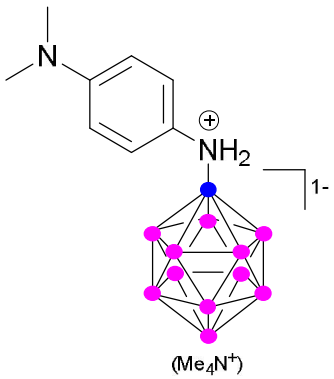
Following the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.204 mmol, 1.0 equiv), $Pd_2(dba)_3$ (18.5 mg, 0.0204 mmol, 0.10 equiv), Davephos ligand (16 mg, 0.041 mmol, 0.20 equiv.), K*t*BuO (57 mg, 0.51 mmol, 2.5 equiv), 4-phenoxyaniline (186 mg, 0.408 mmol, 2.0 equiv), (DMSO 2.4ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as yellow oil in (35 mg, 52 % yield). ^{1}H NMR (401 MHz, Acetonitrile-d_3) δ = 0.46-1.49 (11H, BH), 2.27(s, 12H), 6.96-6.99(m, 2H), 7.01-7.03(m, 2H), 7.14-7.16(1H), 7.18-7.42 (4H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ = 1.32, 56.23, 119.50, 119.88, 124.69, 125.61, 131.02, 134.61, 157.04, 157.91. ^{11}B NMR (129 MHz, Acetonitile-D_3) δ = -19.08(d, 1B, J=137), -17.00 (d, 10B, J=121), -4.56 (s,1B). HRMS (TOF) m/z calcd for $C_{12}H_{21}NOB_{12}$ $(M)^{-2}$: 162.6415; Found: 162.6427, m/z calcd for $C_{12}H_{22}NOB_{12}$ $(M+H)^{-1}$: 326.2904, Found: 326.2961.

$(Me_4N)[B_{12}H_{11}NH_2C_6H_5$-4-ethoxy] (3g)



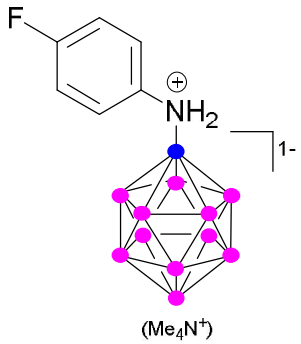
Following the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.204 mmol, 1.0 equiv), $Pd_2(dba)_3$ (18.5 mg, 0.0204 mmol, 0.10 equiv), Davephos ligand (16 mg, 0.041 mmol, 0.20 equiv.), K*t*BuO (57 mg, 0.51 mmol, 2.5 equiv), 4-ethoxyaniline (137.2 mg, 0.408 mmol, 2.0 equiv), (DMSO 2.4ml). The crude was tested by ^{11}B-NMR and the spectrum showed that conversion of $(Me4N)_2$ $B_{12}H_{11}I$ was >90%, the reaction provided $B_{12}H_{12}$ as major product and less than 10% of B-N product.

$(Me_4N)[B_{12}H_{11}NH_2C_6H_5$-4-N(Me)$_2$] (3h)



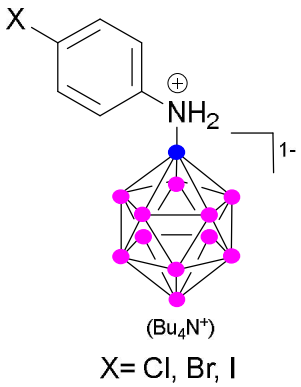
Following the general procedure using $(Bu4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv), N,N-dimethy-p-phenylenediamine (40mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml).The crude was tested by ^{11}B-NMR and the spectrum showed that conversion of $(Me_4N)_2$ $B_{12}H_{11}I$ was >90%, the reaction provided $B_{12}H_{12}$ as major product and less than 10% of B-N product.

$(Me_4N)[B_{12}H_{11}NH_2C_6H_5$-4-F] (3i)



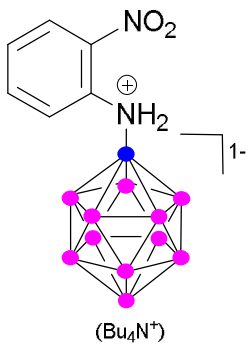
Following the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.204 mmol, 1.0 equiv), $Pd_2(dba)_3$ (18.5 mg, 0.0204 mmol, 0.10 equiv), Davephos ligand (16 mg, 0.041 mmol, 0.20 equiv.), K*t*BuO (57 mg, 0.51 mmol, 2.5 equiv), 4-phenoxyaniline (186 mg, 0.408 mmol, 2.0 equiv), (DMSO 2.4ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as yellow oil in (41 mg, 52 % yield). ^{1}H NMR (401 MHz, Acetonitrile-d_3) δ = 0.4-1.4(11H, BH, 2.25 (s, 12H), 7.09-7.12(d,2H), 7.23- 7.24 (d,2H). ^{11}B NMR (129 MHz, Acetonitrile-d_3) δ = -19.03 (1B, d, J=141), -16.87 (10B, d, J=117), -4.63 (s, 1B). ^{19}F NMR (377 MHz, Acetonitrile-d_3) δ = -117.04. ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ = 115.95, 116.18, 125.73, 125.81, 135.25. HRMS (TOF) m/z calcd for $C_6H_{17}NFB_{12}$ $(M+H)^{-1}$: 252.2533, Found: 252.2599.

(Bu_4N) $[B_{12}H_{11}NH_2C_6H_5$-4-Cl (3j) , $(Bu_4N)[B_{12}H_{11}NH_2C_6H_5$-4-Br (3k) $(Bu_4N)[B_{12}H_{11}NH_2C_6H_5$-4-I (3l)



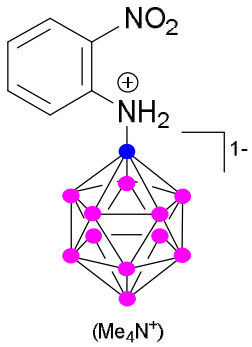
Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv), 4-haloaniline (....mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml). The crude was tested by ^{11}B-NMR and the spectrum showed that conversion of $(Bu_4N)_2$ $B_{12}H_{11}I$ was <5%, We expected that the reaction provided C-N product of haloaniline as major product and less than 2-5 % of B-N product.

$(Bu_4N)[B_{12}H_{11}NH_2C_6H_5$-2-$NO_2$] (3m)



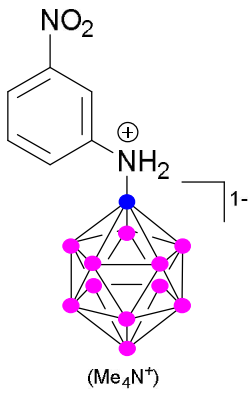
Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv) 2-nitroaniline (37mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as orange oil in (60 mg, 83 % yield). ^{1}H NMR (401 MHz, Acetonitrile-d_3) δ = 0.29 – 1.59 (BH,12H), 6.20 – 6.32 (d, J=12.4, 1H), 7.04 – 7.17 (d, J=13.8, 1H), 7.78 – 7.92 (s, 1H), 8.12 – 8.25 (s, 1H), 8.54 – 8.74 (s, 1H).. ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ = 100.00, 112.37, 120.78, 125.62, 133.27, 133.91. ^{11}B NMR (129 MHz, Acetonitrile-d_3) δ = -18.82, -16.81(10B, ^{11}B NMR (129 MHz, acetone-D_6) δ = -19.12(1B, d, J=130), -16.99 (5B, d, J=103), -16.12(5B,d, J=103), -5.19(s, 1B) HRMS (TOF) m/z calcd for $C_6H_{17}N_2O_2B_{12}$ $(M+H)^{-1}$: 279.2489; Found: 279.2553. $C_6H_{16}N_2O_2B_{12}$ $(M)^{-2}$: 139.6247; Found: 139.1230.

$(Me_4N)[B_{12}H_{11}NH_2C_6H_5\text{-}2\text{-}NO_2]$ (3m)



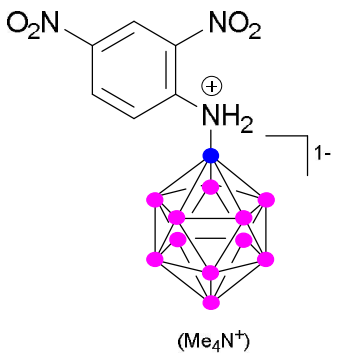
Following the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (150 mg, 0.361 mmol, 1.0 equiv), $Pd_2(dba)_3$ (33 mg, 0.0361 mmol, 0.10 equiv), Davephos ligand (28.5 mg, 0.0722 mmol, 0.20 equiv.), K*t*BuO (101 mg, 0.903 mmol, 2.5 equiv) 3-nitroaniline (100mg, 0.722 mmol, 2.0 equiv), (DMF 3.6ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as orange oil in (60 mg, 83 % yield).^{1}H NMR (401 MHz, acetone-d_6) δ = 0.48 – 1.81 (m, 12H), 3.23 – 3.39 (s, 12H), 6.25 – 6.54 (m, 1H), 7.02 – 7.27 (d, 1H), 7.78 – 7.90 (d, *J*=8.7, 1H), 8.13 – 8.29 (d, *J*=9.0, 1H), 8.57 – 9.20 (s, 1H). ^{13}C NMR (101 MHz, acetone-D_6) δ = 29.84, 55.96, 117.38, 123.40, 125.97, 134.19, 163.24, 167.20. HRMS (TOF) m/z calcd for $C_6H_{16}N_2O_2B_{12}$ $(M)^{-2}$: 139.6247; Found: 139.1232.

$(Me_4N)[B_{12}H_{11}NH_2C_6H_5\text{-}3\text{-}NO_2]$ (3n)



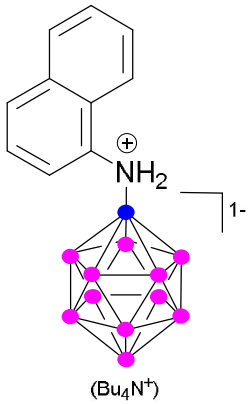
Following the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (150 mg, 0.361 mmol, 1.0 equiv), $Pd_2(dba)_3$ (33 mg, 0.0361 mmol, 0.10 equiv), Davephos ligand (28.5 mg, 0.0722 mmol, 0.20 equiv.), K*t*BuO (101 mg, 0.903 mmol, 2.5 equiv) 3-nitroaniline (100mg, 0.722 mmol, 2.0 equiv), (DMF 3.6ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as orange oil (60 mg, 83 % yield). ^{1}H NMR (401 MHz, Acetonitrile-d_3) δ 0.28 – 1.78 (s, 12H), 2.81 – 3.24 (s, 12H), 7.50 – 7.62 (m, 1H), 7.65 – 7.67 (m, 1H),8.07 – 8.12 (m, 1H), 8.37 – 8.42 (m, 1H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ = 1.32, 49.92, 119.31, 122.96, 130.59, 131.00, 140.26, 148.93. ^{11}B NMR (129 MHz, Acetonitrile-d_3) δ = -18.70 (1B, d, *J*=130), -17.32 (5B, d, *J*= 103), -16.48 (5B, d, *J*=103), -4.83(1B, s). HRMS (TOF) m/z calcd for $C_6H_{16}N_2O_2B_{12}$ $(M)^{-2}$: 139.6247; Found: 139.1211.

$(Me_4N)[B_{12}H_{11}NH_2C_6H_5\text{-}2,4\text{-dinitro}]$ (3o)



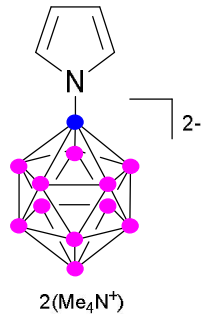
zsFollowing the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (150 mg, 0.361 mmol, 1.0 equiv), $Pd_2(dba)_3$ (33 mg, 0.0361 mmol, 0.10 equiv), Davephos ligand (28.5 mg, 0.0722 mmol, 0.20 equiv.), K*t*BuO (101 mg, 0.903 mmol, 2.5 equiv), 2,4-dinitroaniline (132.2 mg, 0.722 mmol, 2.0 equiv), (DMF 3.6ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as yellow oil in (130 mg, 78 % yield). ^{1}H NMR (401 MHz, acetone-d_6) δ = 0.8-1.6 (BH, 11H)3.38 (s, 12H), 7.82-7.88(d, J=10, 1H), 7.86, 8.42- 8.46(d, J=10, 1H), 8.84- 8.88(d, *J*=3, 1H), 9.14(s, 1H).^{13}C NMR (101 MHz, acetone-d_6) δ = 29.84, 55.93, 117.66, 121.93, 124.82, 127.38, 133.29, 153.15.^{11}B NMR (129 MHz, acetone-d_6) δ = -18.43(d, 1B, *J*=128), -16.76(d, 5B, *J*=114), -16.00(d, 5B, *J*=114), -5.90 (s, 1B).). HRMS (TOF) m/z calcd for $C_6H_{15}N_3O_4B_{12}$ $(M)^{-2}$: 161.6134; Found: 161.6146.

$(Bu_4N)[B_{12}H_{11}NH_2$-naphthyl] (4)



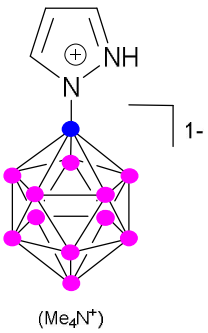
Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv), 1-naphthyl amine (36 mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as yellow oil in (16 mg, 23 % yield). ^{1}H NMR (401 MHz, Acetonitrile-d_3) δ = 0.96- 0.99(s, 12H), 1.31-1.40(m, 8H), 1.56-1.64 (m, 8H),3.06-3.10 (m, 8H), 7.38-7.40(d, 1H), 7.49-7.53(t, 1H), 7.57-7.64(m, 2H), 7.86-7.88(d, 1H), 7.94-7.96(d, 1H), 8.13- 8.15(d, 1H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ = 12.86, 19.37, 23.35, 58.39, 121.36, 123.02, 124.99, 126.08, 126.54, 127.58, 128.15, 134.05. ^{11}B NMR (129 MHz, acetone-d_6) δ = -18.85(d, 1B, *J*=135), -16.77(d, 10B, *J*=126), -4.37(s, 1B). HRMS (TOF) m/z calcd for $C_{10}H_{20}NB_{12}$ $(M+H)^{-1}$: 284.2786, Found: 284.2866.

$(Me_4N)[B_{12}H_{11}$-pyrrole] (5a)



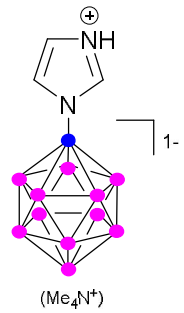
Following the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.204 mmol, 1.0 equiv), $Pd_2(dba)_3$ (18.5 mg, 0.0204 mmol, 0.10 equiv), Davephos ligand (16 mg, 0.041 mmol, 0.20 equiv.), K*t*BuO (57 mg, 0.51 mmol, 2.5 equiv), pyrrol (33 mg, 0.408 mmol, 2.0 equiv), (DMSO 2.4ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as yellow oil in (74mg, 87 % yield). ^{1}H NMR (401 MHz, acetone-d_6) δ = 5.12-5.13(t, J= 2.0, 2H), 6.27 (b, 2H). ^{13}C NMR (101 MHz, acetone-d_6) δ = 29.84, 105.39, 125.23. ^{11}B NMR (129 MHz, acetone-d_6) δ = -20.46 (d, *J*= 127, 1B), -17.50 (d, *J*= 146, 5B), -16.23 (d, *J*= 146, 5B), -2.96 (s,1B). HRMS (TOF) m/z calcd for $C_4H_{15}NB_{12}$ $(M)^{-2}$: 103.6204, Found: 103.6217.

$(Me_4N)[B_{12}H_{11}$-pyrazole] (5b)



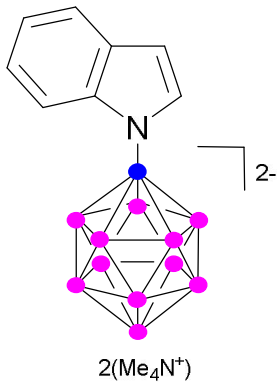
Following the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.204 mmol, 1.0 equiv), $Pd_2(dba)_3$ (18.5 mg, 0.0204 mmol, 0.10 equiv), Davephos ligand (16 mg, 0.041 mmol, 0.20 equiv.), K*t*BuO (57 mg, 0.51 mmol, 2.5 equiv), pyrazole (33 mg, 0.408 mmol, 2.0 equiv), (DMSO 2.4ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as yellow oil in (60 mg, 87% yield). ^{1}H NMR (401 MHz, Acetonitrile-d_3) δ = 6.50- 6.51(t, *J*=3, 1H), 7.80- 7.81(d, *J*=2, 1H), 7.90- 7.91(d, *J*=2, 1H),. ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ = 108.41, 133.35, 138.35. ^{11}B NMR (129 MHz, Acetonitrile-d_3) δ = -18.40 (d, *J*=126, 1B), -16.61(d, *J*=130, 10B), -5.86 (s, 1B). HRMS (TOF) m/z calcd for $C_3H_{15}N_2B_{12}$ $(M+H)^{-1}$: 209.2432, Found: 209.2474.

$(Me_4N)[B_{12}H_{11}$-imidazole] (5c)



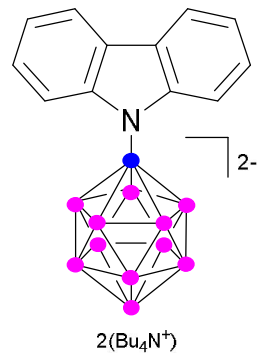
Following the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.204 mmol, 1.0 equiv), $Pd_2(dba)_3$ (18.5 mg, 0.0204 mmol, 0.10 equiv), Davephos ligand (16 mg, 0.041 mmol, 0.20 equiv.), K*t*BuO (57 mg, 0.51 mmol, 2.5 equiv), imidazole(56 mg, 0.408 mmol, 2.0 equiv), (DMSO 2.4ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as yellow oil in (36mg, 85 % yield). ^{1}H NMR (401 MHz, acetone-d_6) δ = 7.32-7.33(d, J=4.0, 2H), 8.32(s, 1H). ^{13}C NMR (101 MHz, acetone-d_6) δ =118.32, 125.93, 135.91. ^{11}B NMR (129 MHz, acetone-d6) δ = -18.23(d, *J*= 131, 1B), -15.79(d, J= 127, 10B), -4.93(s, 1B). HRMS (TOF) m/z calcd for $C_3H_{15}N_2B_{12}$ $(M+H)^{-1}$: 209.2421, Found: 209.2476.

$(Me_4N)[B_{12}H_{11}$-indole] (5d)



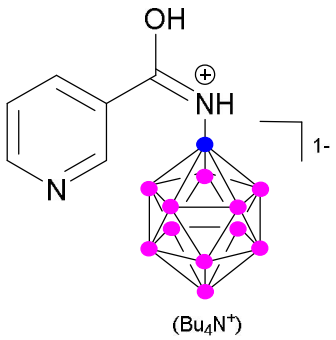
Following the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.204 mmol, 1.0 equiv), $Pd_2(dba)_3$ (18.5 mg, 0.0204 mmol, 0.10 equiv), Davephos ligand (16 mg, 0.041 mmol, 0.20 equiv.), K*t*BuO (57 mg, 0.51 mmol, 2.5 equiv), indole (92 mg, 0.408 mmol, 2.0 equiv), (DMSO 2.4ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as a yellow oil in (55mg, 82 % yield).^{1}H NMR (401 MHz, acetone-D_6) δ = 3.00 (s, 12H), 6.27-6.31(dt, 1H), 6.49-6.66(dt,1H) , 7.13- 7.73(d, 1H), 7.73(s, 1H), 8.21- 8.24(d, 1H). ^{13}C NMR (101 MHz, acetoneE-D_6) δ = 41.04, 115.22, 116.29, 117.48, 120.55, 122.16, 129.89, 131.92, 143.15.^{11}B NMR (129 MHz, acetone-D_6) δ = -19.57 (1B, d, *J*=--), -17.58 (5B, d, *J*=153), -16.38 (5B, d, *J*=129), -3.32(1B, s). HRMS (TOF) m/z calcd for $C_8H_{17}NB_{12}$ $(M)^{-2}$: 128.6283, Found: 128.6305.

$(Bu_4N)[B_{12}H_{11}$-carbazole] (5e)



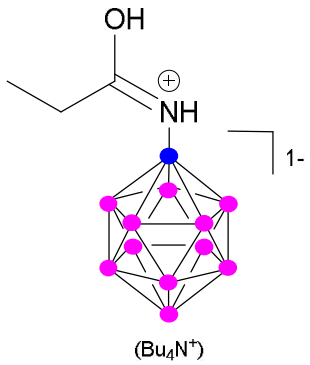
Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv), Carbazole (88 mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as a yellow oil in (61 mg, 83 % yield). ^{1}H NMR (401 MHz, acetone-d_6) δ = 0.84 – 0.99 (t, *J*=6.0, 24H), 1.22 – 1.41 (m, 16H), 1.58 – 1.77 (m, 16H), 3.16 – 3.30 (m, 16H), 6.82 – 6.93 (m, 2H), 7.04 – 7.18 (m, 2H), 7.79 – 7.90 (d, *J*=6.7, 2H), 9.07 – 9.16 (d, *J*=8.9, 2H). ^{11}B NMR (129 MHz, acetone-d_6) δ = -17.84 (d,1B), -17.15 (d, *J*= 129, 5B), -16.05 (d, *J*= 129, 5B), -4.09 (s, 1B). ^{13}C NMR (101 MHz, acetone-d_6) δ = 13.91, 20.29, 24.38, 59.16, 116.51, 118.18, 118.70, 123.43, 124.93, 148.20. HRMS (TOF) m/z calcd for $C_{12}H_{20}NB_{12}(M)^{-2}$: 153.6363, Found: 153.6396.

$(Bu_4N)[B_{12}H_{11}$-3-nicotinamide] (6a)



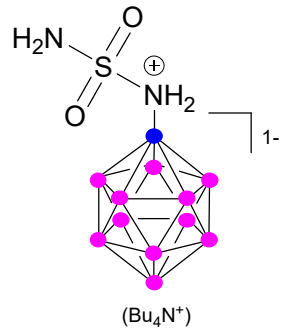
Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv), 3-nicotinamide (33mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5) to afford the product as yellow oil in (58mg, 86% yield). ^{1}H NMR (401 MHz, acetone-D_6) δ = 0.94-0.98 (t, 12H), 1.38- 1.47 (m, 8H), 1.75-1.83 (m, 8H), 3.38-3.42 (m,8H), 6.28 (s, 1H), 7.38-7.41(m, 1H), 8.06- 8.09 (1H), 8.60-8.62 (1H), 8.97 (1H). ^{13}C NMR (101 MHz, acetone-d_6) δ = 13.87, 20.26, 24.40, 29.84, 59.26, 123.81, 134.00, 134.87, 149.29, 151.55, 167.38. ^{11}B NMR (129 MHz, acetone-d_6) δ = -18.96 (d, *J*=137, 1B), -16.80 (d, *J*= 121,10B), -6.57 (s, 1B). HRMS (TOF) m/z calcd for $C_6H_{15}N_2OB_{12}$ $(M)^{-2}$: 130.1155, Found: 130.1255.

$(Bu_4N)[B_{12}H_{11}$-propanamide] (6b)



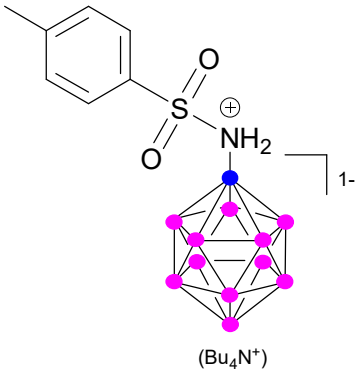
Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv), propanamide (26mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5) to afford the product as yellow oil in (49mg, 80 % yield). ^{1}H NMR (401 MHz, Acetonitrile-d_3) δ = 0.94-0.99 (Me, 15H), 1.32-1.37 (3, 7H), 1.57-1.65 (m, 8H), 2.5 (m, 2H), 3.06- 3.12 (m, 8H).^{13}C NMR (101 MHz, Acetonitrile-d_3) δ = 10.82, 13.78, 20.30, 24.31, 30.88, 59.29, 176.07, 207.56. ^{11}B NMR (129 MHz, Acetonitrile-d_3) δ = -20.3 (d, *J*=123, 1B), -17.3 (d, *J*=148, 5B), -16.0 (d, *J*=150 , 5B),, -5.2 (s, 1B). HRMS (TOF) m/z calcd for $C_3H_{17}NOB_{12}$ $(M)^{2-}$: 106.6256, Found:106.6189, HRMS (TOF) m/z calcd for $C_3H_{17}NOB_{12}$ $(M+H)^{1-}$: 214.2585, Found: 214.2448.

$(Bu_4N)[B_{12}H_{11}$-sulfamide] (6c)



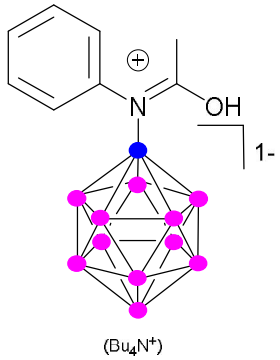
Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv), sulfamide (26mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5) to afford the product as yellow oil in (18 mg, 28 % yield). ^{1}H NMR (401 MHz, acetone-d_6) δ = 0.84 – 0.99 (t, *J*=6.0, 12H), 1.22 – 1.41 (m, 8H), 1.58 – 1.77 (m, 8H), 3.16 – 3.30 (m, 8H), 5.8(broad s).^{11}B NMR (129 MHz, acetone-D_6) δ = -20.14 (d, *J*=132 , 1B), -17.16(d, *J*= 184, 5B), -16.45(d, *J*= 184, 5B), -6.04(s, 1B). HRMS (TOF) m/z calcd for $N_2H_{14}O_2SB_{12}$ $(M)^{-2}$: 118.0989, Found:118.1006.

$(Bu_4N)[B_{12}H_{11}$-p-toluenesulfonamide] (6d)



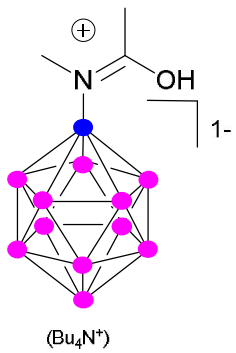
Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv), p-toluenesulfonamide (46mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5) to afford the product as yellow oil in (16mg, 35 % yield). ^{1}H NMR (401 MHz, acetone-d_6) δ = 0.84 – 0.99 (t, *J*=6.0, 12H), 1.22 – 1.41 (m, 8H), 1.58 – 1.77 (m, 8H), 2.15 (s, 3H), 3.16 – 3.30 (m, 8H), 7.37-7.39(d, *J*=8,2H), 7. 72-7.74(d, *J*=8,2H). ^{13}C NMR (101 MHz, acetone-d_6) δ = 13.9, 20.3, 21.3, 24.5, 59.3, 126.9, 122, 128.7, 130.1.^{11}B NMR (129 MHz, acetone-D_6) δ = -20.21 (d, *J*=132 , 1B), -17.37 (d, *J*= 184, 5B), -16.46(d, *J*= 184, 5B), -5.84(s, 1B). HRMS (TOF) m/z calcd for $C_7H_{19}NO_2SB_{12}$ $(M)^{-2}$: 155.6171, Found:155.6033, HRMS (TOF) m/z calcd for $C_7H_{19}NO_2SB_{12}$ $(M+C_{16}H_{36}N)^{-1:}$ 553.5193, Found: 553.4841. HRMS (TOF) m/z calcd for $C_7H_{19}NO_2SB_{12}$ $(M+H)^{-1:}$ 312.2415, Found: 312.2200.

$(Bu_4N)[B_{12}H_{11}$-acetanilide] (6e)



Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv), acetanilide (35 mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:3) to afford the product as yellow oil in (55mg, 80% yield). ^{1}H NMR (401 MHz, acetone-d_6) δ = 0.96-0.99(t, 12H), 1.38, 1.40- 1.47 (m, 8H), 1.76, - 1.84 (m, 8H), 2.09 (s, 3H), 7.18-7.20 d, 2H), 7.34-7.40 (m, 3H), 11.75 (b, 1H). ^{13}C NMR (101 MHz, acetone-d_6) δ = 13.88, 18.03, 20.34, 24.40, 59.29, 125.60, 127.15, 128.40, 129.53, 130.13, 175.63. ^{11}B NMR (129 MHz, acetone-d_6) δ = -19.0 (d, *J*=115, 1B), -17.4 (d, *J*=130, 5B), -15.8 (d, *J*=130, 5B), -2.8 (s, 1B). HRMS (TOF) m/z calcd for $C_8H_{19}NOB_{12}$ $(M)^{2-}$: 137.6336, Found:137.6318, HRMS (TOF) m/z calcd for $C_8H_{19}NOB_{12}$ $(M+C_{16}H_{36}N)^{1-:}$ 517.5523, Found: 517.5437. HRMS (TOF) m/z calcd for $C_8H_{19}NOB_{12}$ $(M+H)^{1-:}$ 276.2745, Found: 276.2683.

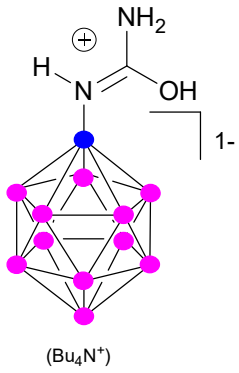
$(Bu_4N)[B_{12}H_{11}$-N-methylacetamide] (6f)



Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv), N-methylacetamide (20 mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:3) to afford the product as yellow oil in (51mg, 83% yield). ^{1}H NMR (401 MHz, acetone-d_6) δ = 0.94- 0.97 (t, 12H), 1.40-1.42 (m,8H), 1.80-1.82(m,8H), , 2.37(s, 3H), 2.60(s,3H), 3.31- 3.43(m,8H), 7.91(s), 11.54(s).^{13}C NMR (101 MHz, acetone-d_6) δ = 13.13, 18.31, 19.55, 23.66, 25.46, 53.19, 58.56, 173.67. ^{11}B NMR (129 MHz, acetone-d_6) δ = -19.89 (d, *J*=117, 1B), -18.02 (d, *J*=156, 5B), -16.76 (d, *J*=156, 5B), -3.05(s, 1B). HRMS (TOF) m/z calcd for $C_3H_{18}NOB_{12}$ $(M)^{2-}$: 106.6256, Found:106.6236, HRMS (TOF) m/z calcd for $C_3H_{18}NOB_{12}$ $(M+C_{16}H_{36}N)^{1-:}$

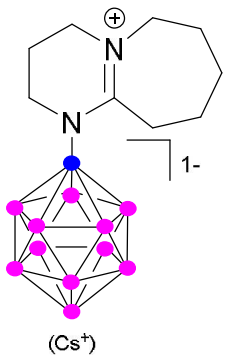
455.5364, Found: 455.5306. HRMS (TOF) m/z calcd for $C_3H_{19}NOB_{12}$ $(M+H)^{1-:}$ 214.2585, Found: 214.2543.

(Bu_4N)[N-$B_{12}H_{11}$-urea] (6g)



Following the general procedure using $(Bu_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.133 mmol, 1.0 equiv), $Pd_2(dba)_3$ (12.2 mg, 0.0133 mmol, 0.10 equiv), Davephos ligand (10.5 mg, 0.0266 mmol, 0.20 equiv.), K*t*BuO (37.0 mg, 0.333 mmol, 2.5 equiv), N-methylacetamide (20 mg, 0.266 mmol, 2.0 equiv), (DMSO 2ml). The crude product was purified by flash column chromatography on silica gel (Acetonitrile/DCM = 1:5 to 1:3) to afford the product as yellow oil in (51mg, 83% yield). ^{1}H NMR (401 MHz, acetonitrile-d_3) = 0.99- 1.02 (t, 12H), 1.31-1.42 (m,8H), 1.60-1.68 (m, 6H), 3.10- 3.15 (m,8H).^{13}C NMR (101 MHz, Acetonitrile-d_3) δ = 13.80, 18.31, 20.33, 24.31, 41.35, 59.30. ^{11}B NMR (129 MHz, Acetonitrile-d_3) δ = -20.49 (d, *J*=127, 1B), -17.43 (d, *J*=119, 5B), -16.57 (d, *J*=119, 5B), -5.71 (s, 1B). HRMS (TOF) m/z calcd for $C_1H_{16}N_2OB_{12}$ $(M-H)^{2-}$: 106.6256, Found:106.6236, HRMS (TOF) m/z found $C_1H_{16}N_2OB_{12}$ $(M-H+C_{16}H_{36}N)^{1-:}$ 442.5. HRMS (TOF) m/z found for $C_1H_{16}N_2OB_{12}$ $(M-H+Na)^{1-}$: 223.2. HRMS (TOF) m/z found for $C_1H_{16}N_2OB_{12}$ $(M-H)^{1-}$: 201.2, HRMS (TOF) m/z found for $C_1H_{16}N_2OB_{12}$ $(M-H)^{2-}$: 100.1.

Cs [$B_{12}H_{11}$-DBU] (7)



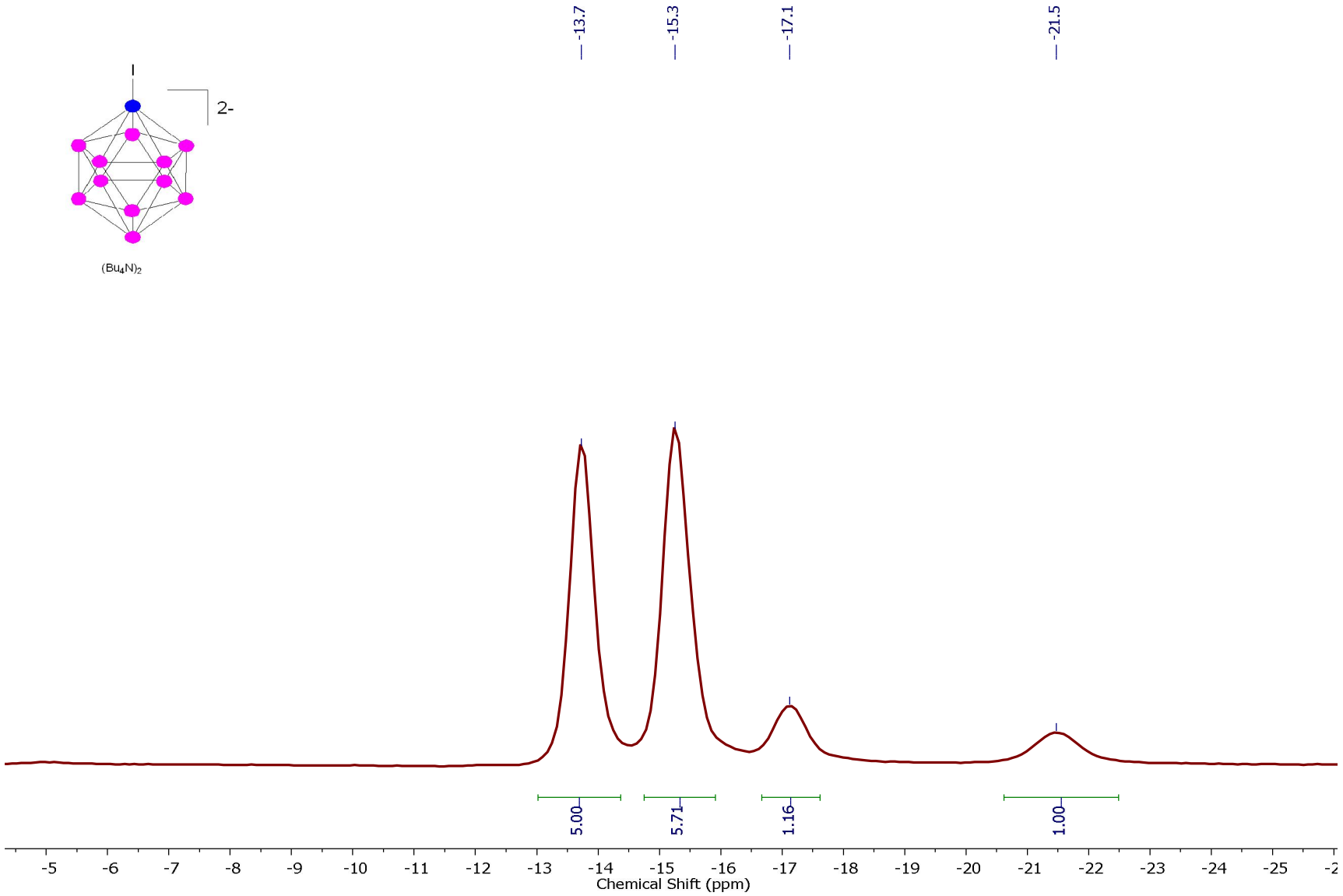
Following the general procedure using $(Me_4N)_2$ $B_{12}H_{11}I$ (100 mg, 0.204 mmol, 1.0 equiv), $Pd_2(dba)_3$ (18.5 mg, 0.0204 mmol, 0.10 equiv), Davephos ligand (16 mg, 0.041 mmol, 0.20 equiv.), DBU (62 mg, 0.408 mmol, 2.0 equiv), (DMSO 2.4ml). The crude product was purified by flash column chromatography on silica gel (acetonitrile/DCM = 1:5 to 1:2) to afford the product as Me_3N-salt as a light-yellow oil. The purified compound was dissolved in MeOH and precipitated as Cs-salt (white solide in (70 mg, 80 % yield) by adding 1.5 equiv. Of CsF in MeOH.^{1}H NMR (401 MHz, Acetonitrile-d_3) δ = 1.57(m, 4H), 1.66- 1.68(m, 2H), 1.80-1.84(m, 2H), 1.94-2.21(m, 2H), 3.28- 3.46(m, 4H), 3.69-3.70(m, 2H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ = 22.51, 25.86, 27.23, 29.41, 30.74, 50.09, 50.55, 54.78. ^{11}B NMR (129 MHz, Acetonitrile-d_3) δ = -18.28(d,1B), -17.07(d, *J*= 121, 5B), -16.29(d, *J*= 113, 5B), -2.70(s, 1B). HRMS (TOF) m/z calcd for $C_9H_{27}N_2B_{12}$ $(M+H)^{-1:}$ 293.3375, Found: 293.3425.

References

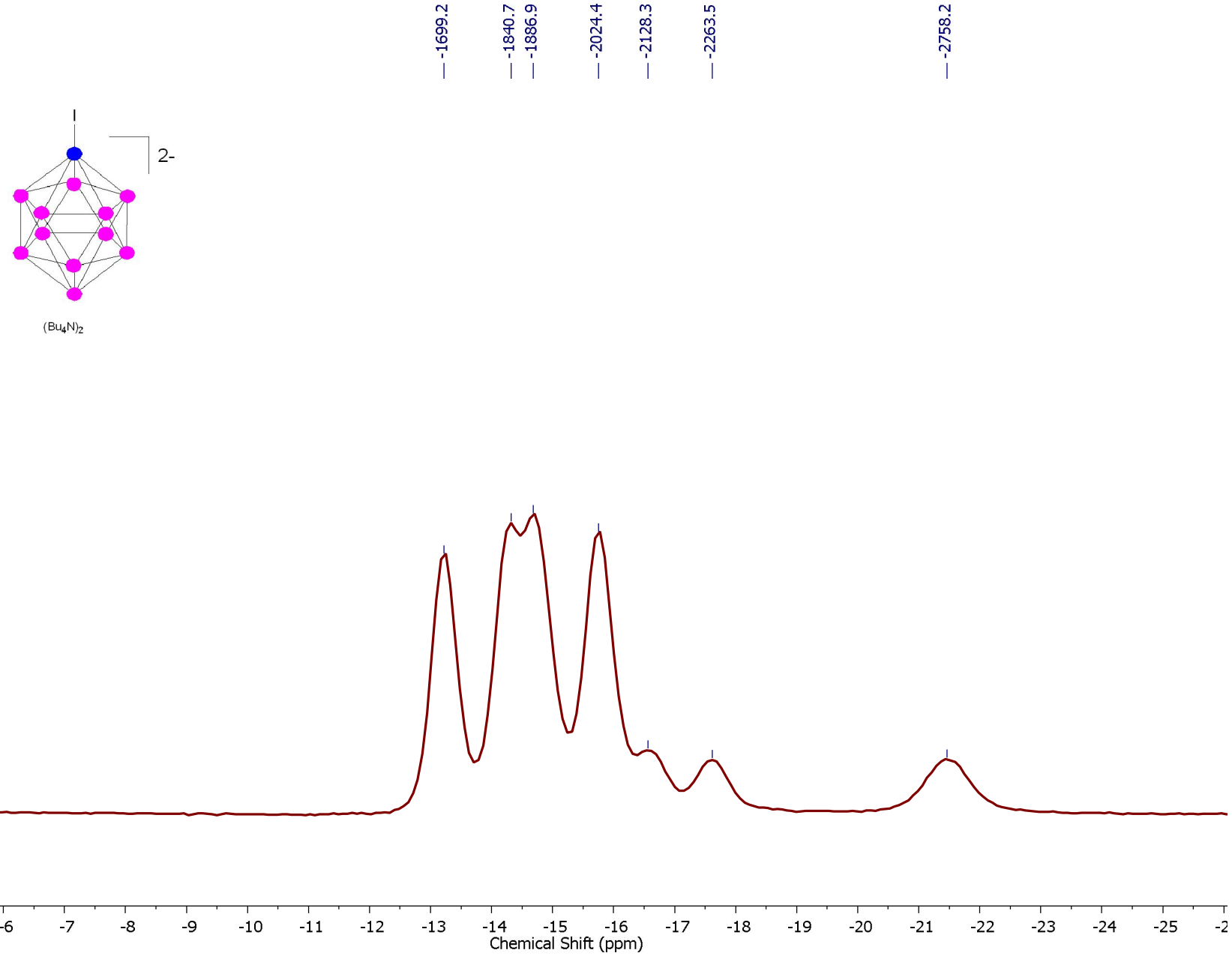
[1] W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, E. L. Muetterties, *Inorg. Chem.* **1964**, *3*, 159-167.

NMR Spectra

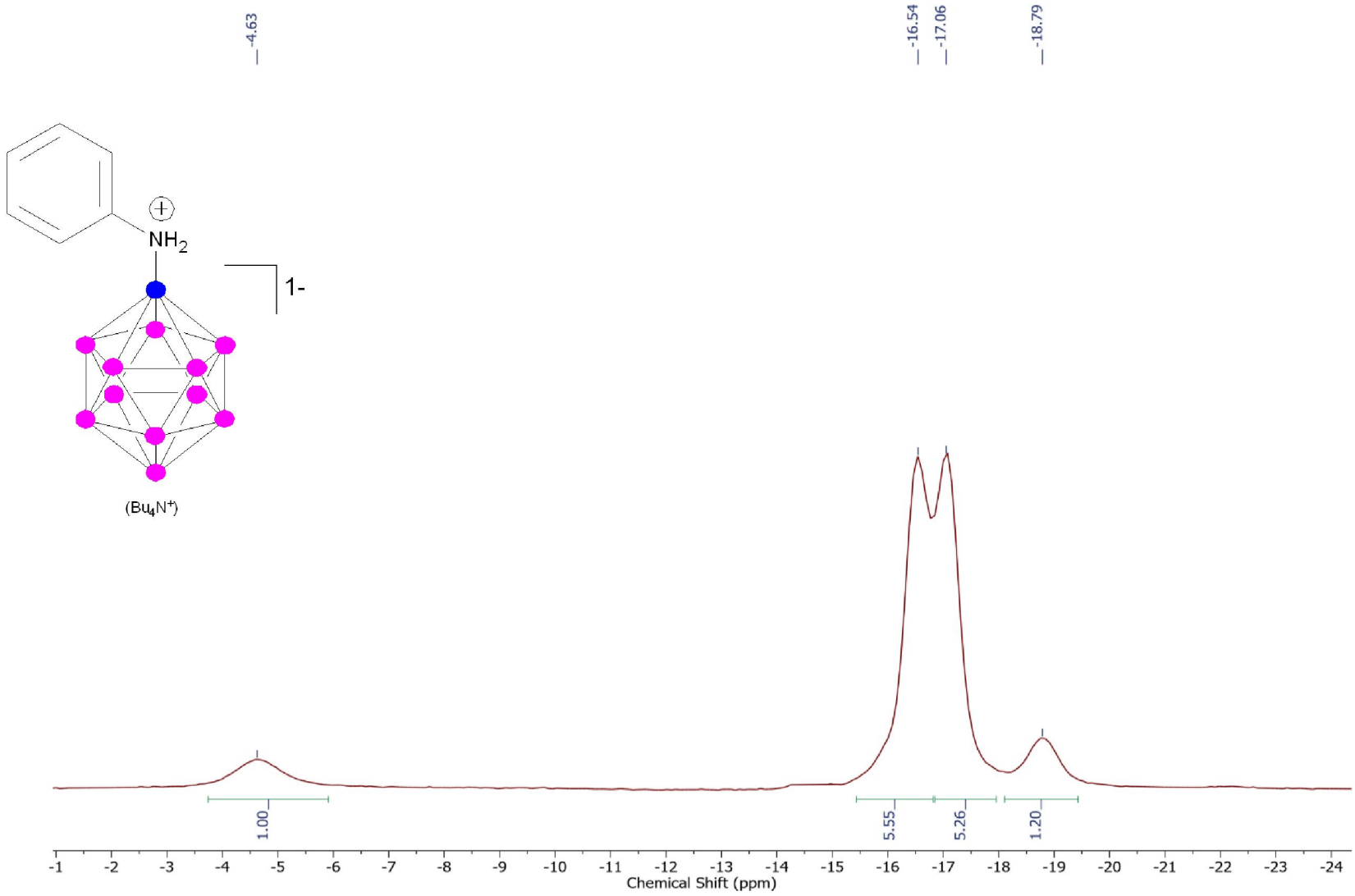
$^{11}B\{^{1}H\}$ NMR spectrum of 1 in Acetone-d_6 at 298K



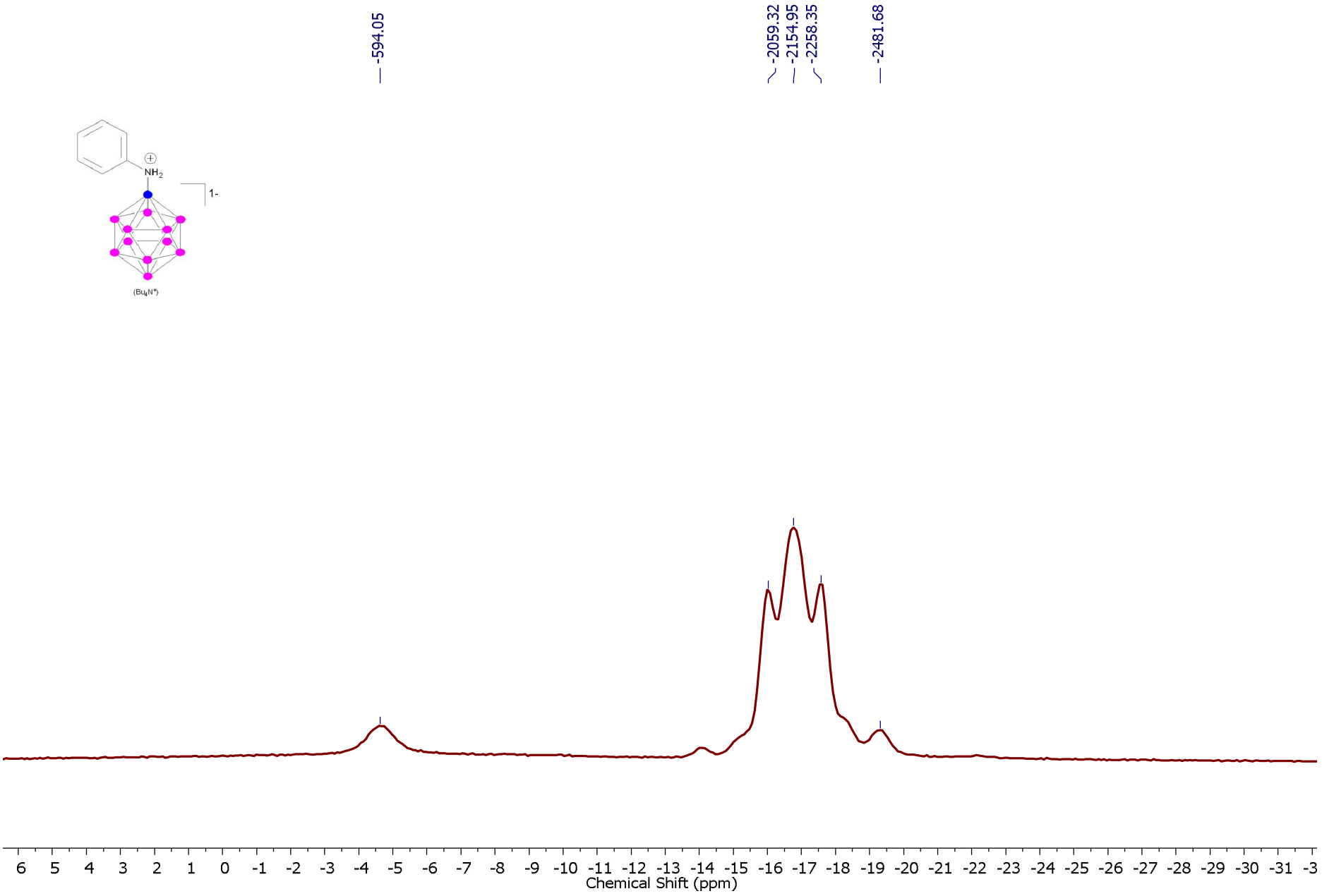
^{11}B NMR spectrum of 1 in Acetone-d_6 at 298K



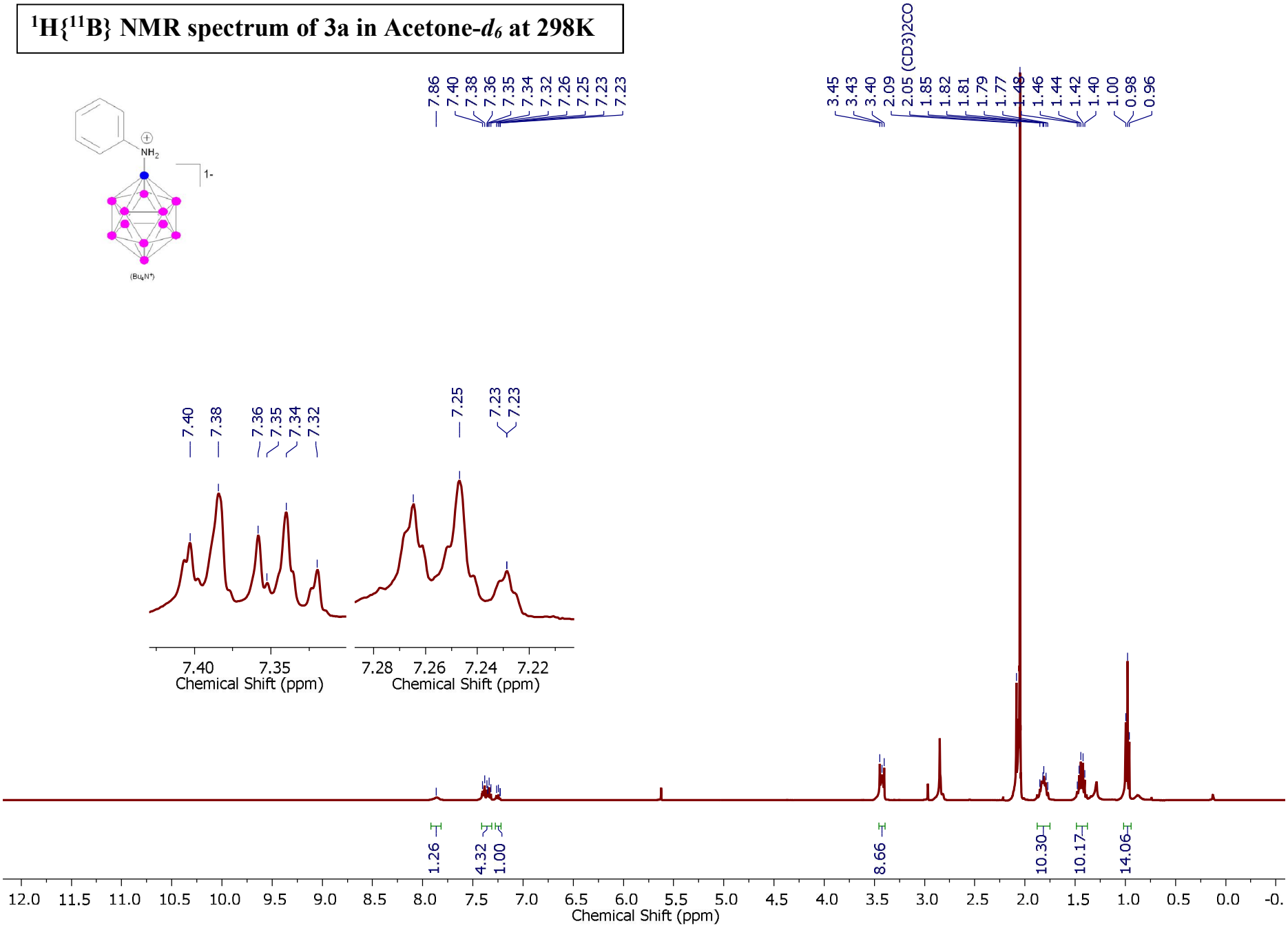
^{11}B {^{1}H} NMR spectrum of 3a in Acetone-d_6 at 298K



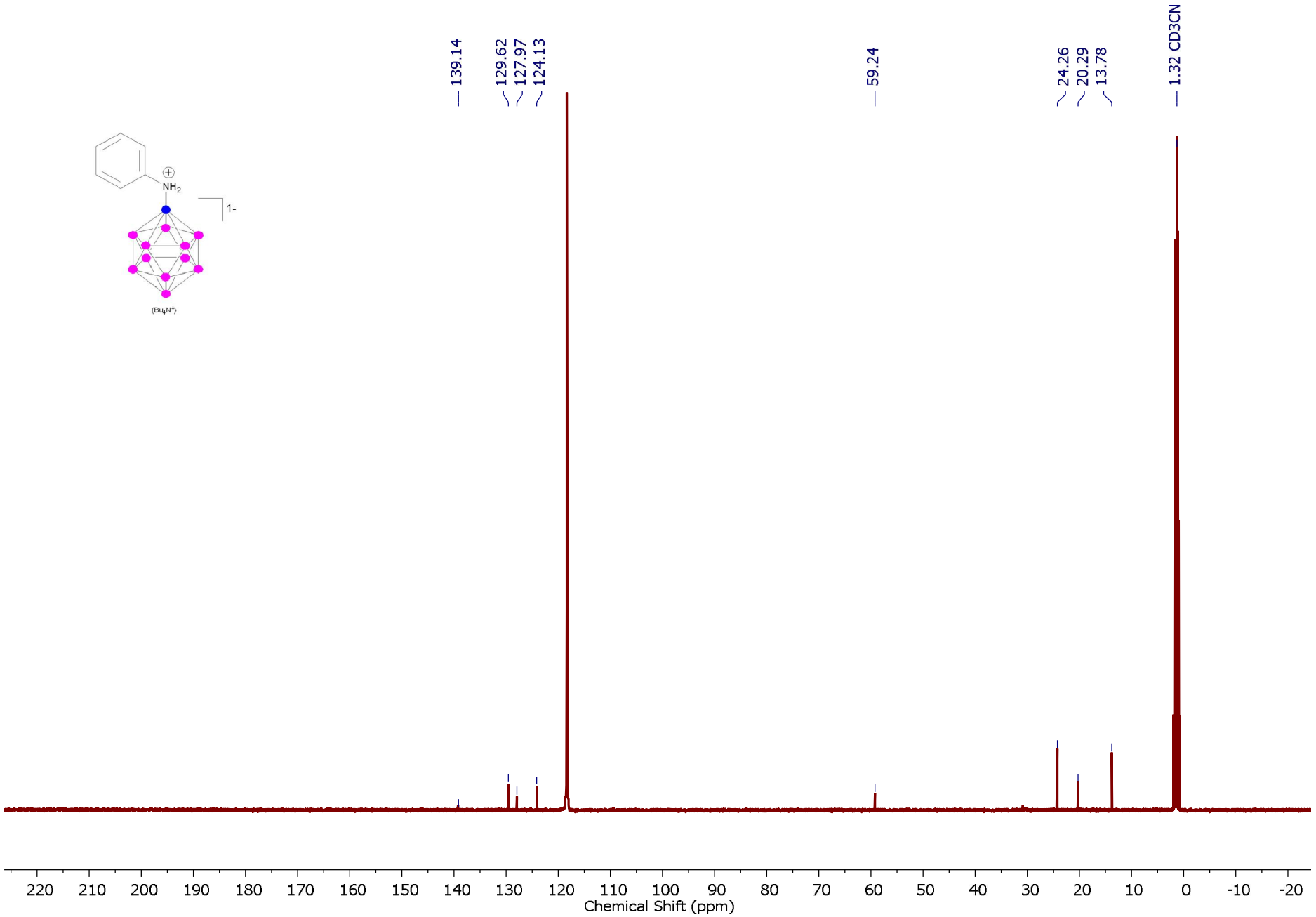
^{11}B NMR spectrum of 3a in Acetone-d_6 at 298K



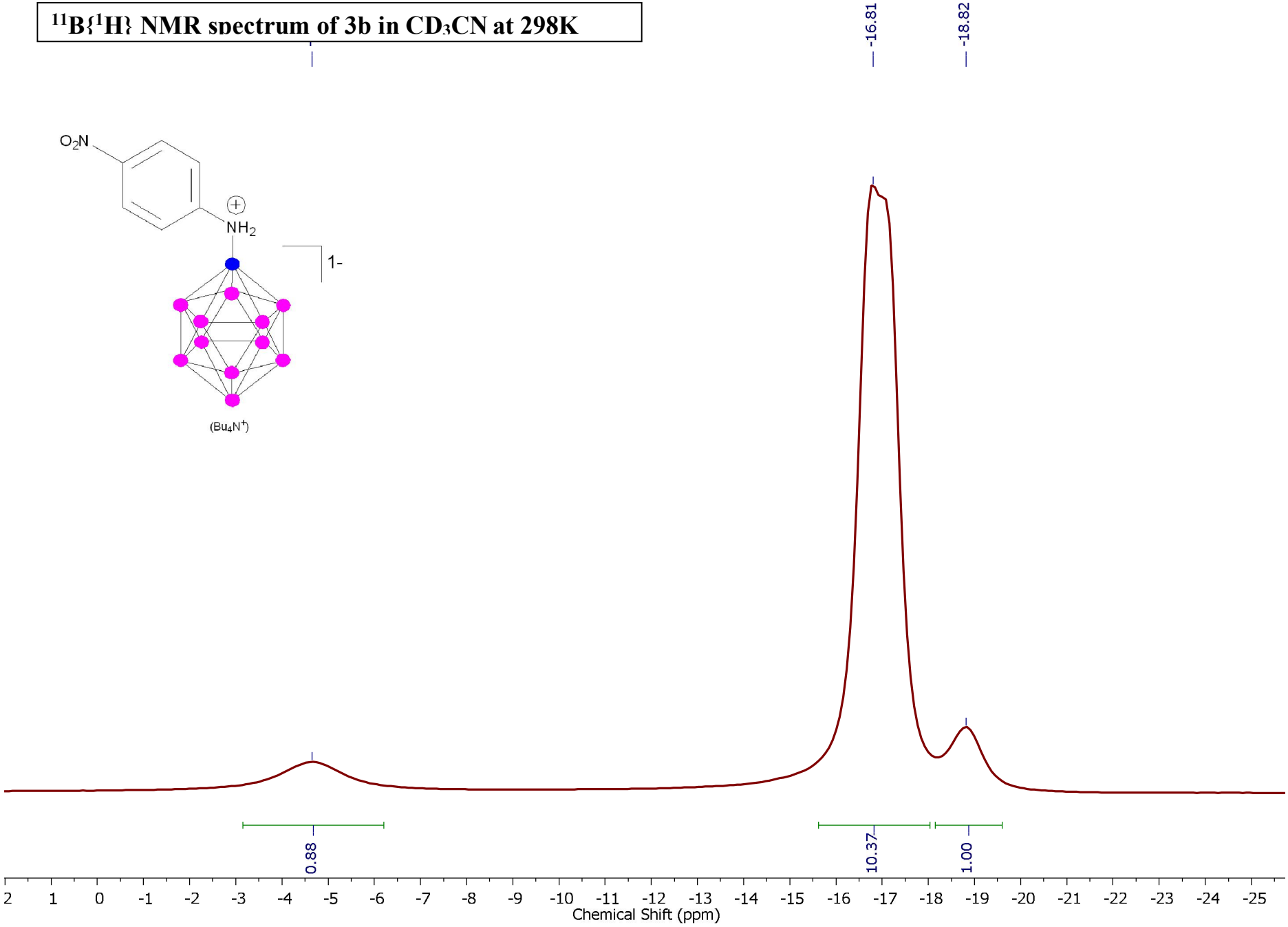
$^{1}H\{^{11}B\}$ NMR spectrum of 3a in Acetone-d_6 at 298K



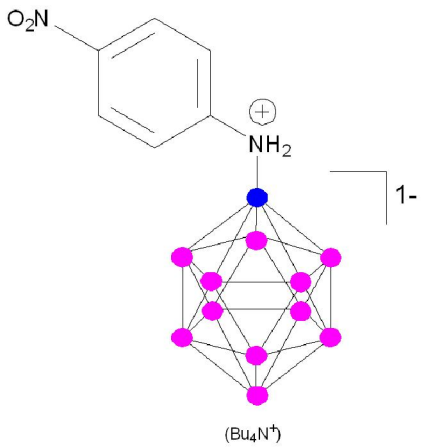
^{13}C NMR spectrum of 3a in CD_3CN at 298K



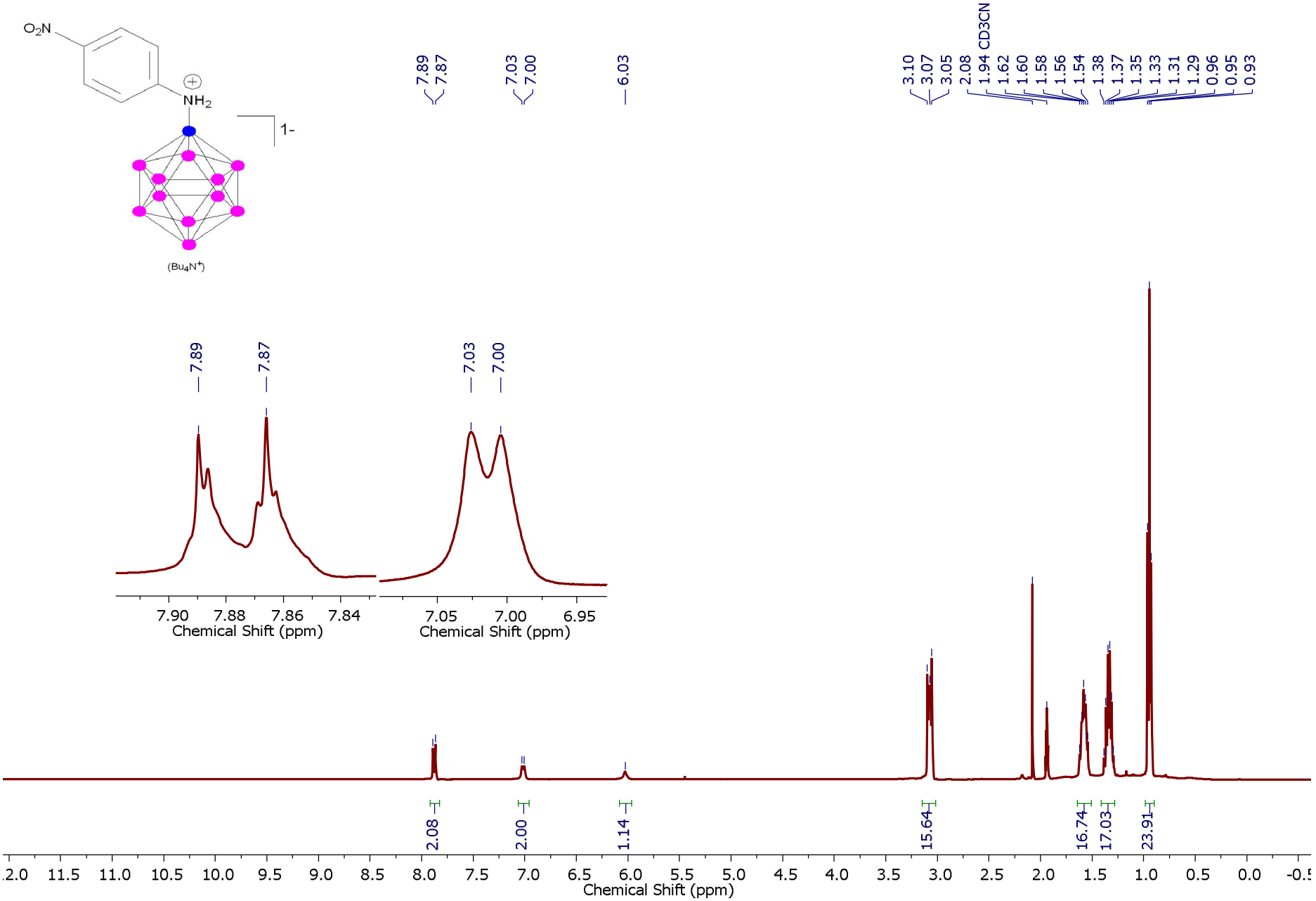
$^{11}B\{^1H\}$ NMR spectrum of 3b in CD_3CN at 298K



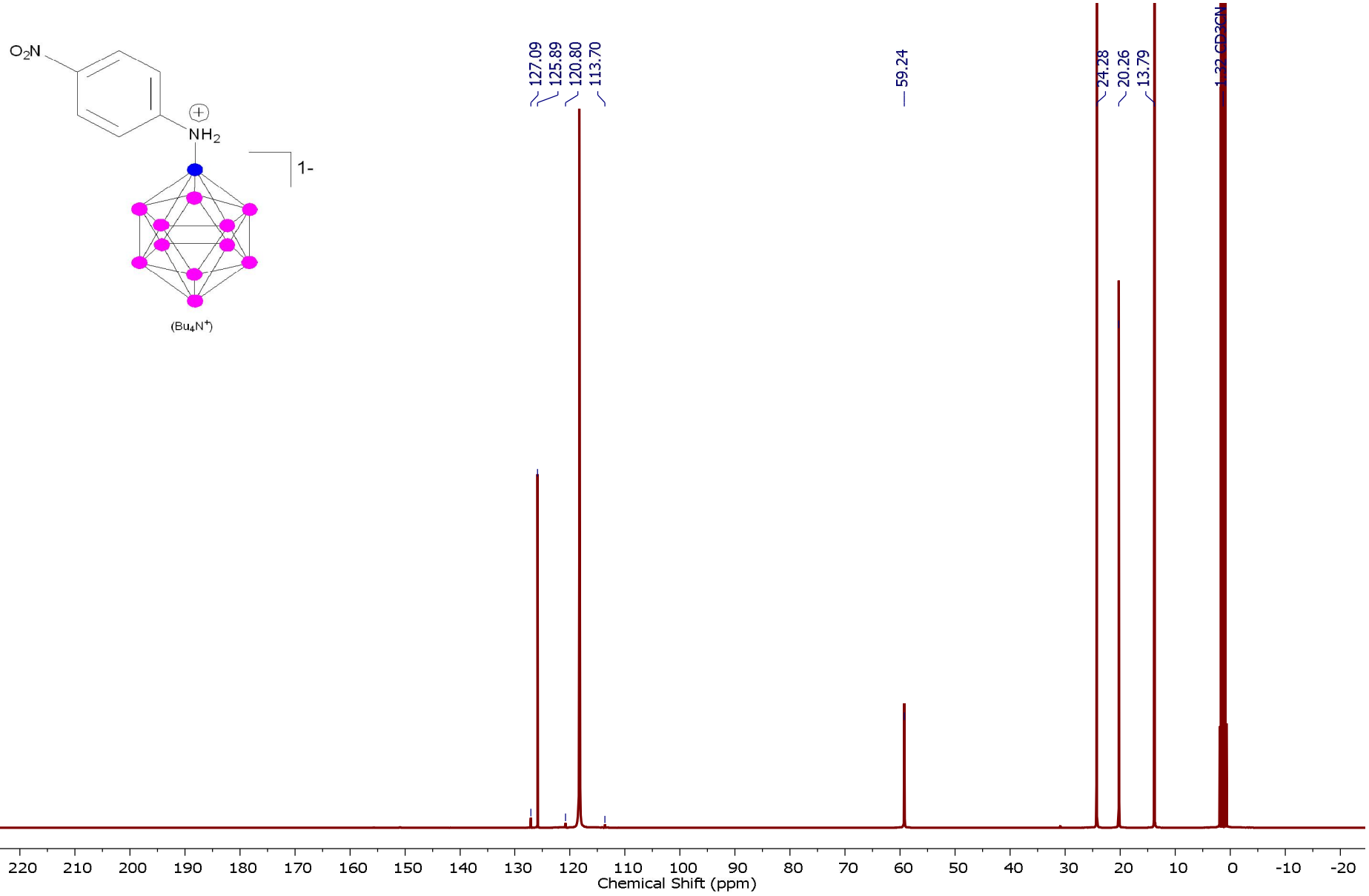
^{11}B NMR spectrum of 3b in CD_3CN at 298K



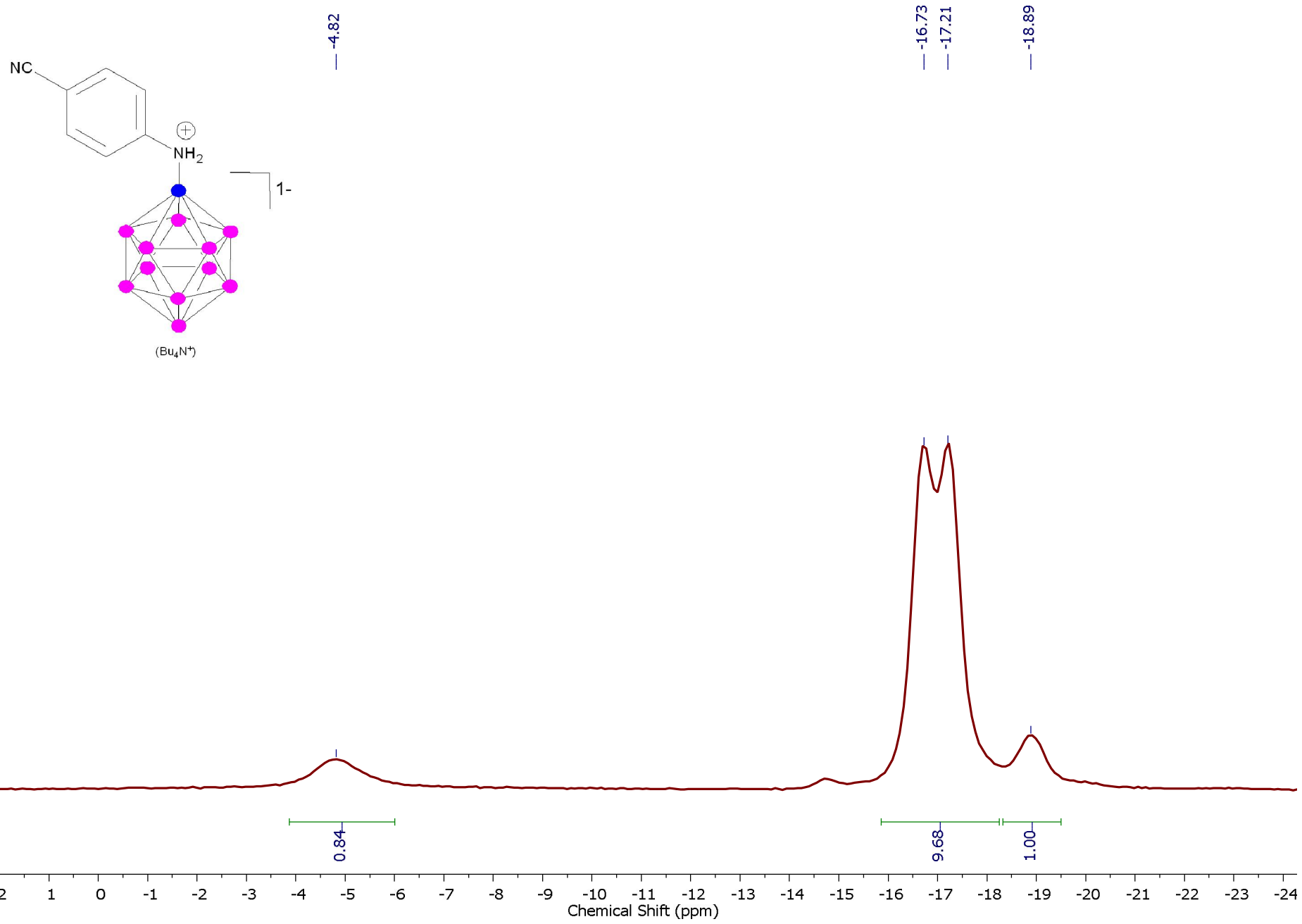
$^{1}H\{^{11}B\}$ NMR spectrum of 3b in CD_3CN at 298K



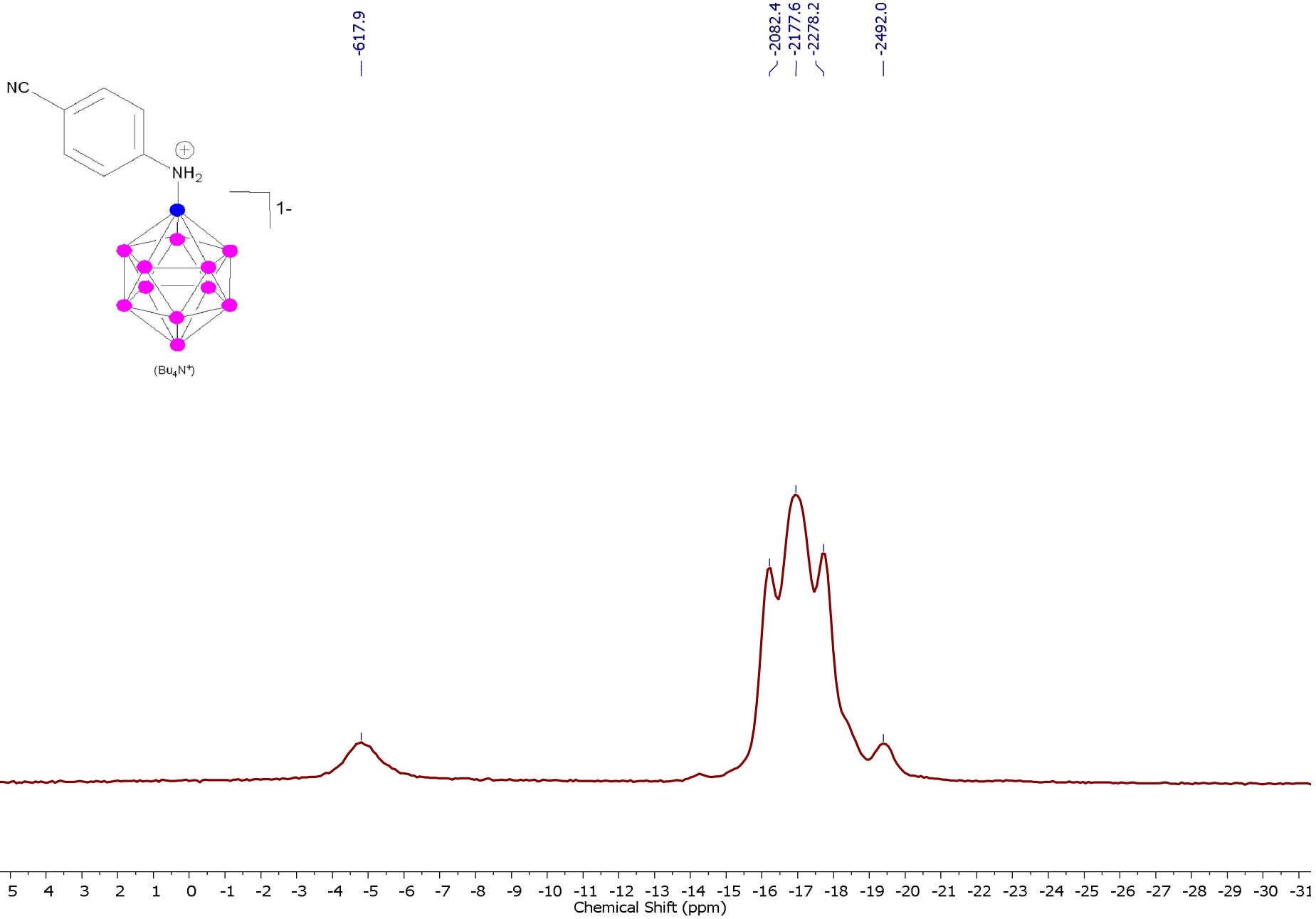
^{13}C NMR spectrum of 3b in CD_3CN at 298K



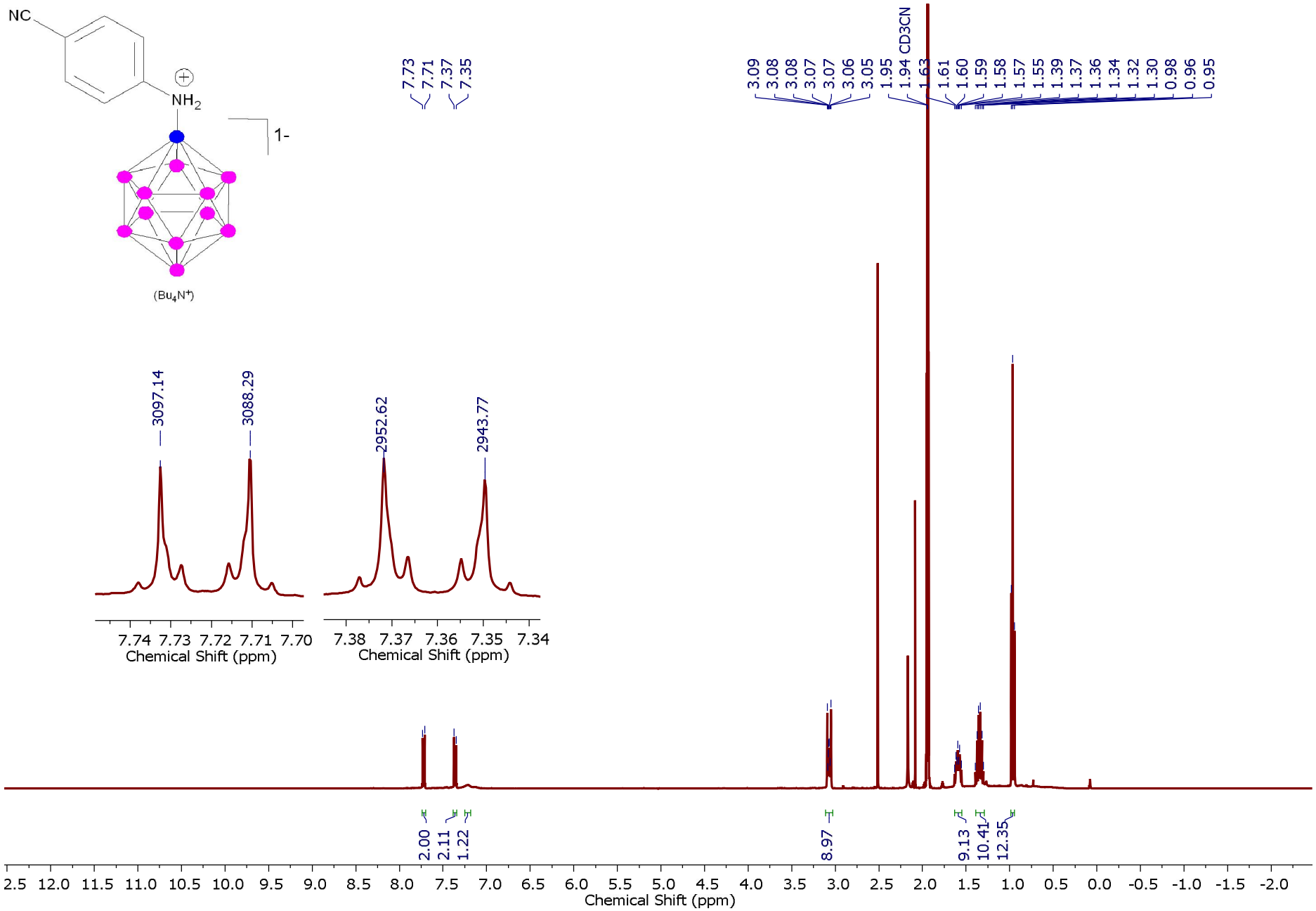
$^{11}B\{^{1}H\}$ NMR spectrum of 3c in CD_3CN at 298K



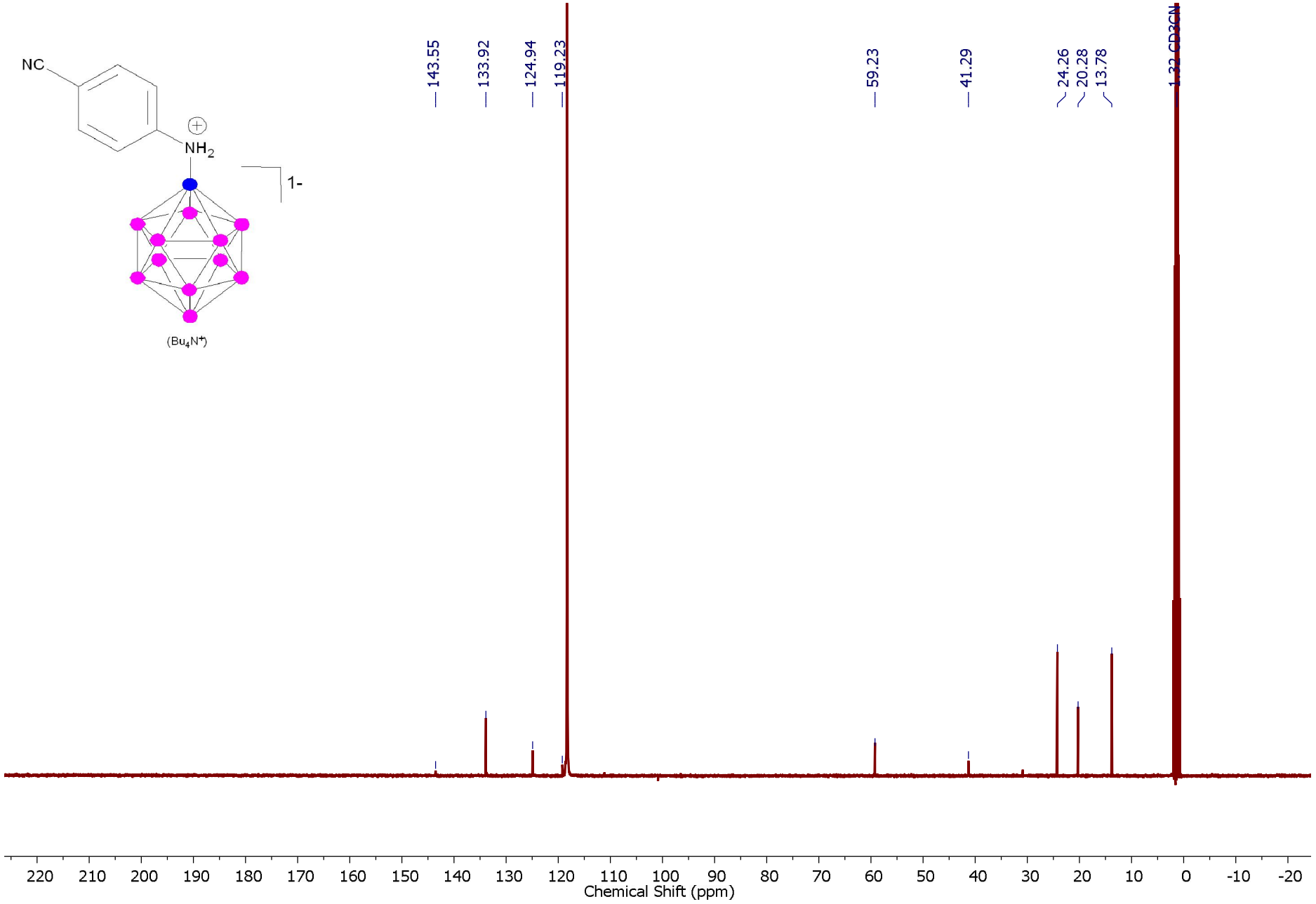
^{11}B NMR spectrum of 3c in CD_3CN at 298K



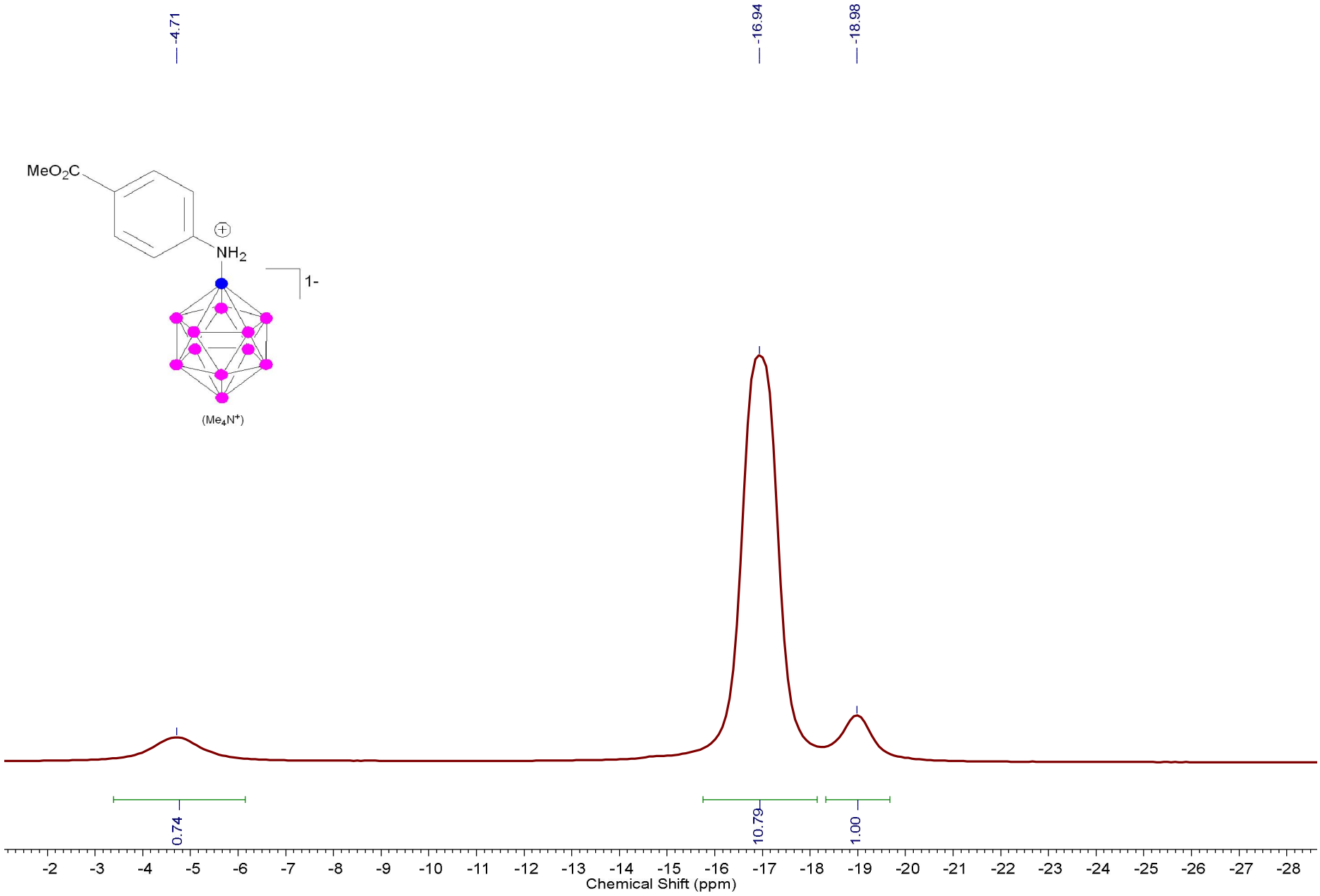
$^{1}H\{^{11}B\}$ NMR spectrum of 3c in CD_3CN at 298K



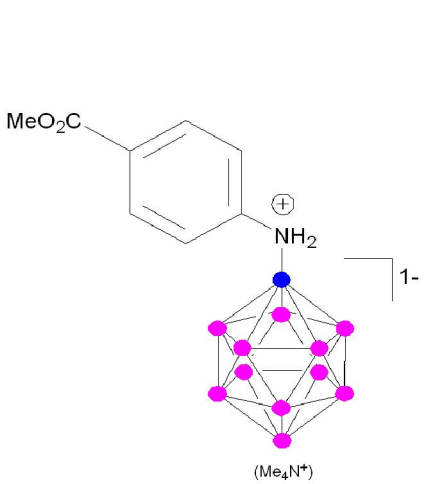
^{13}C NMR spectrum of 3c in CD_3CN at 298K



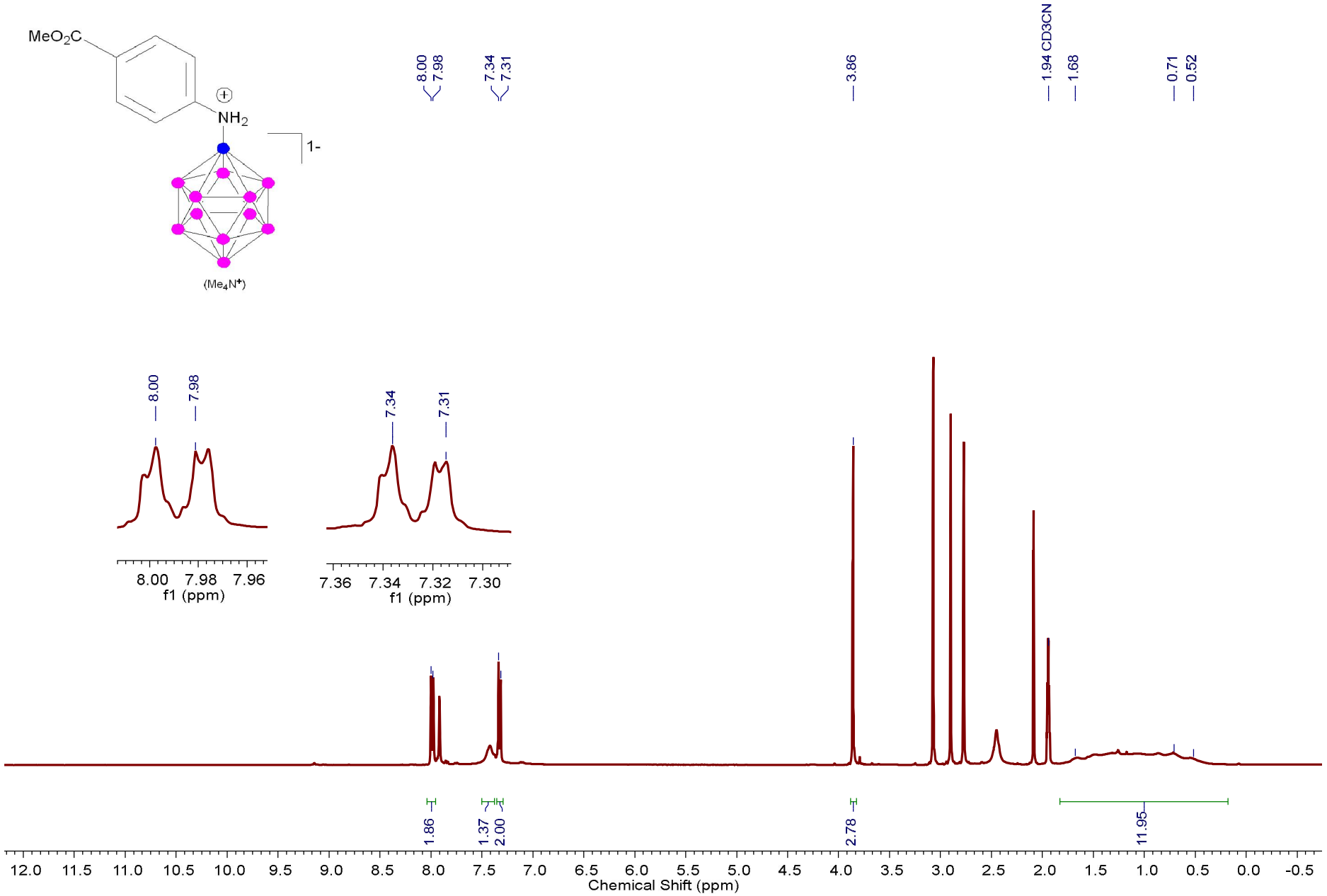
$^{11}B\{1H\}$ NMR spectrum of 3d in CD_3CN at 298K



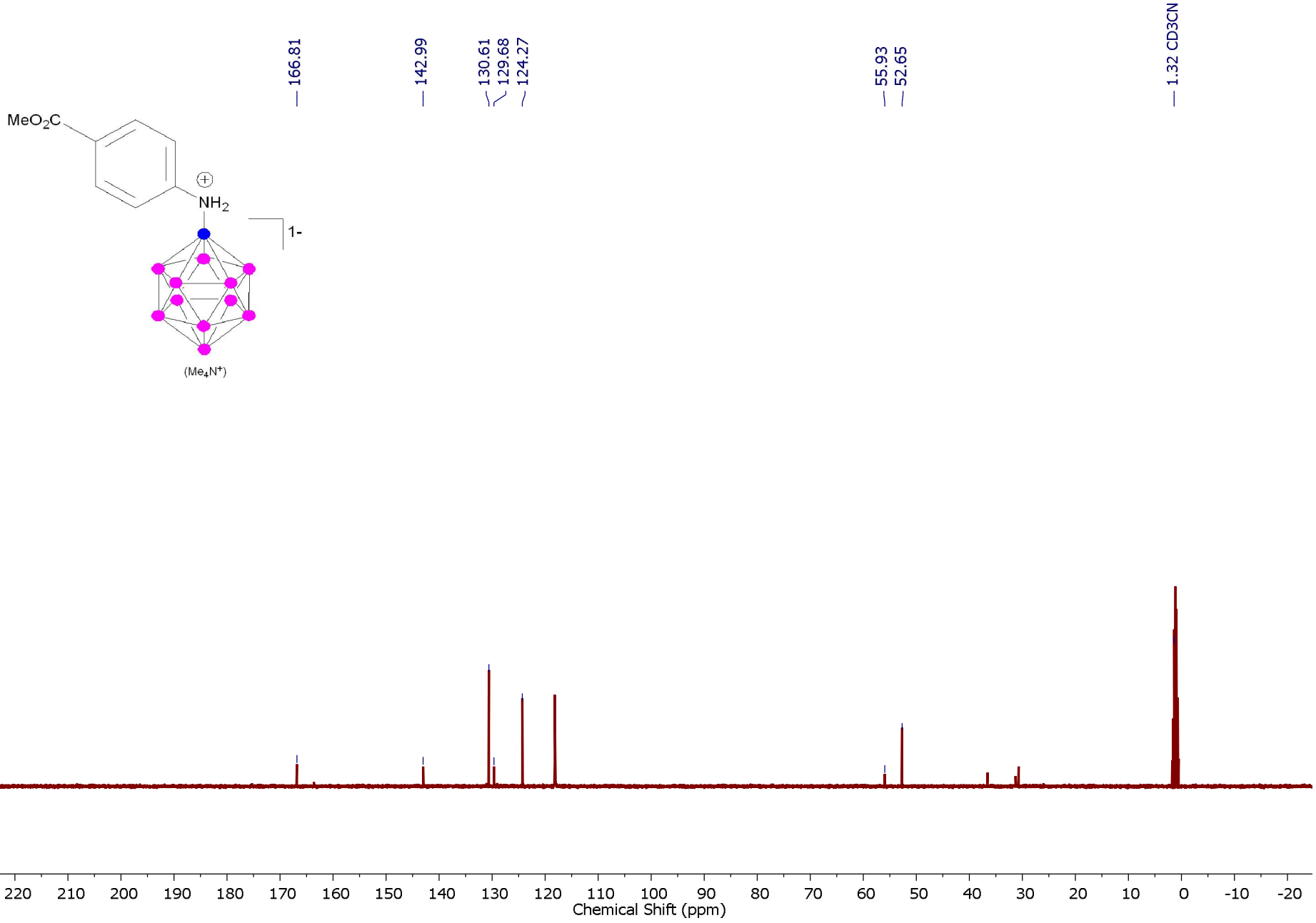
^{11}B NMR spectrum of 3d in CD_3CN at 298K



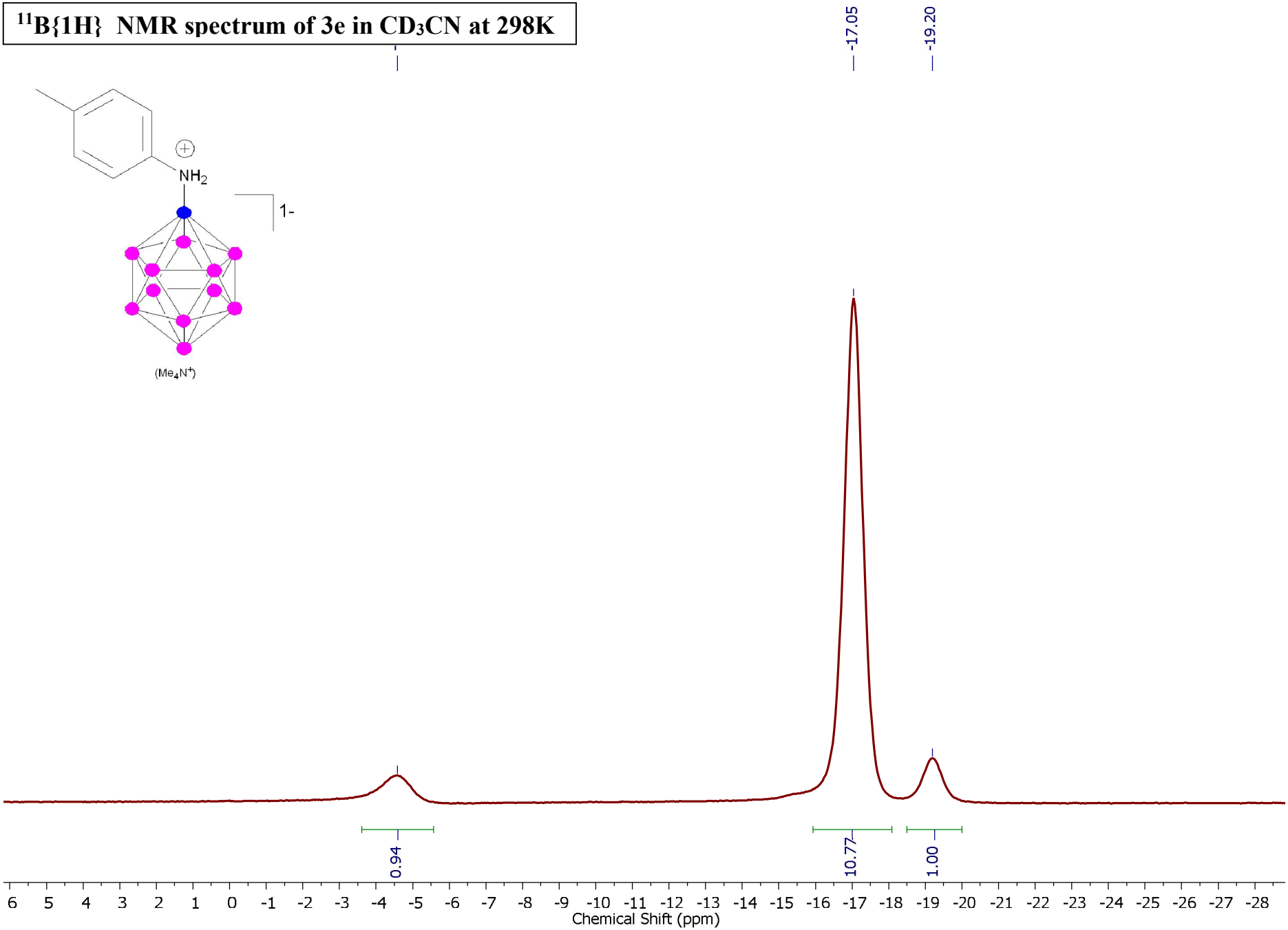
$^{1}H\{^{11}B\}$ NMR spectrum of 3d in CD_3CN at 298K



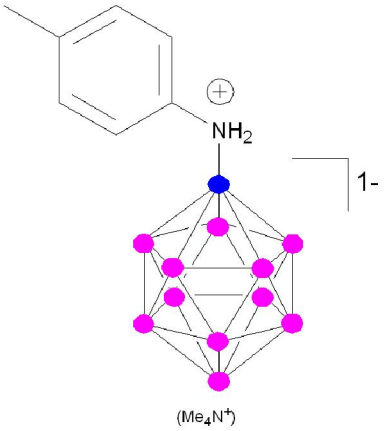
^{13}C NMR spectrum of 3d in CD_3CN at 298K



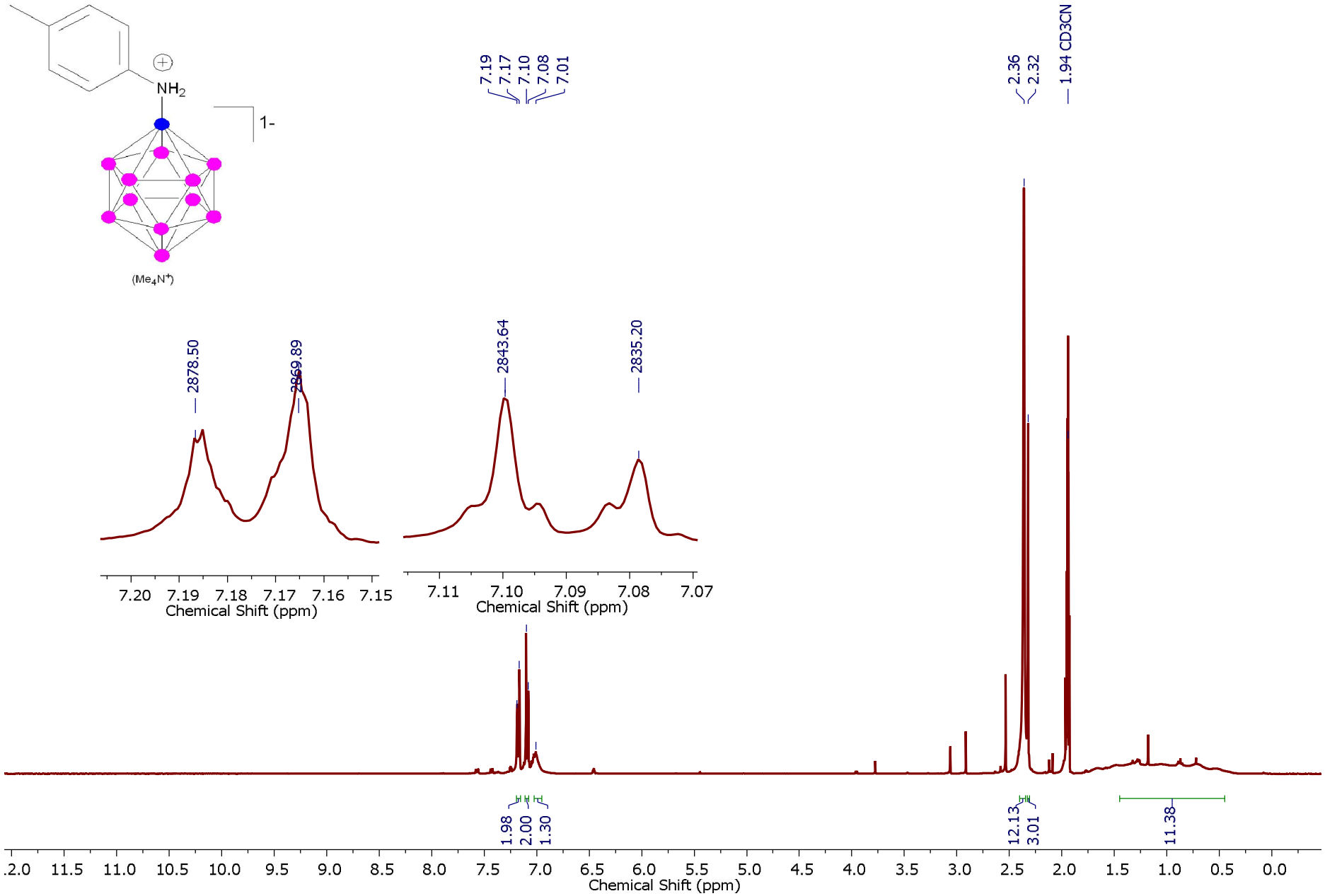
$^{11}B\{1H\}$ NMR spectrum of 3e in CD_3CN at 298K



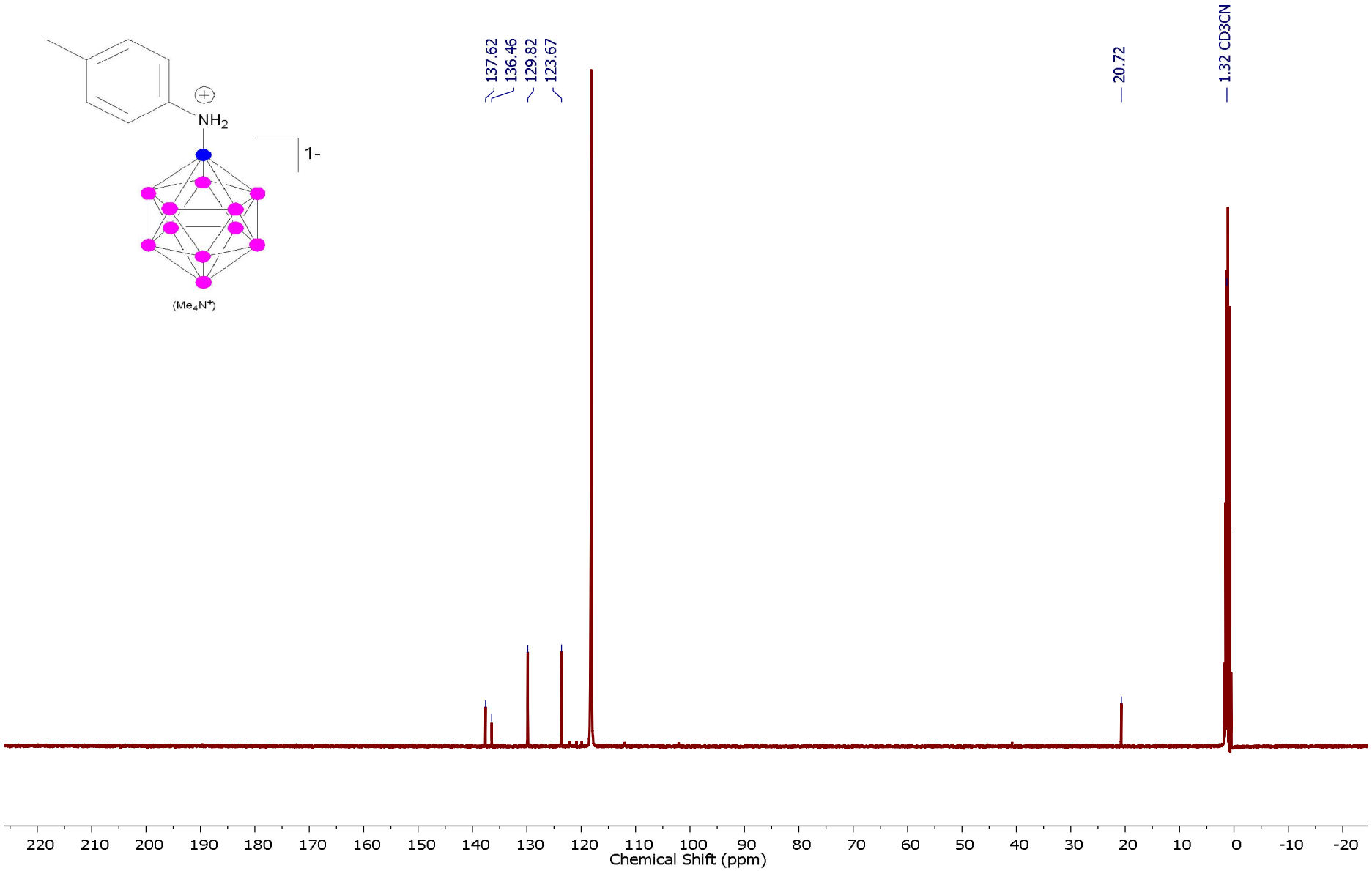
^{11}B NMR spectrum of 3e in CD_3CN at 298K



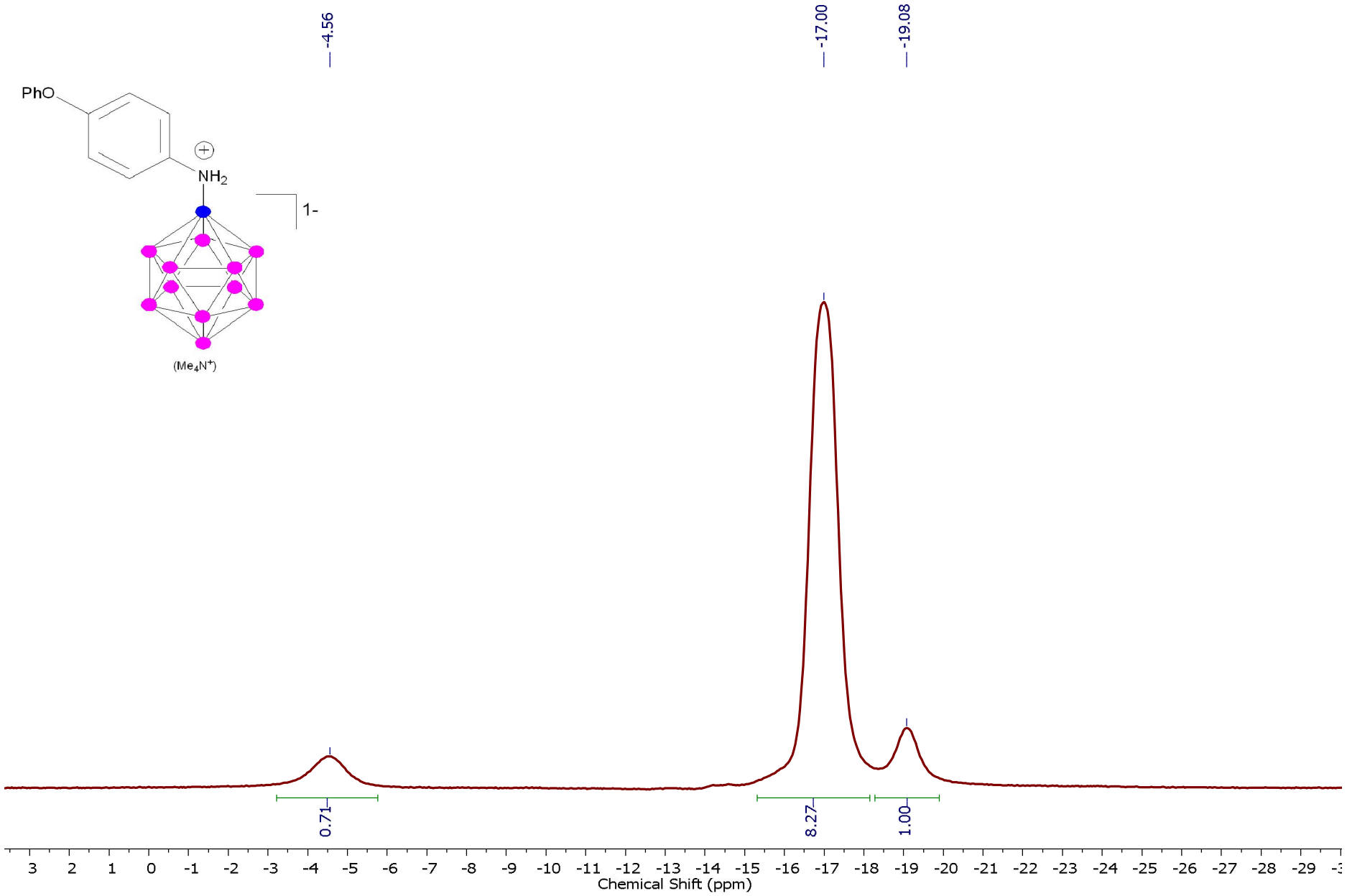
$^{1}H\{^{11}B\}$ NMR spectrum of 3e in CD_3CN at 298K



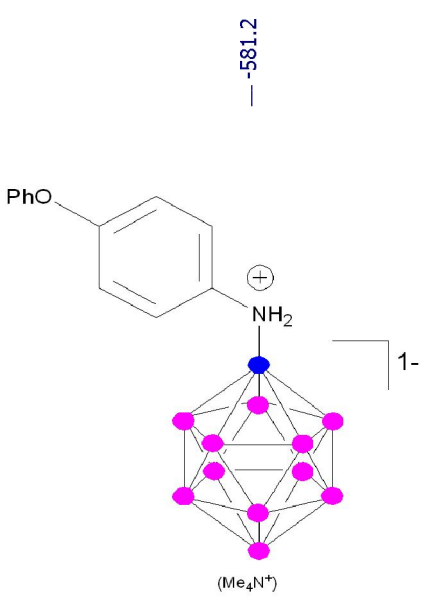
^{13}C NMR spectrum of 3e in CD_3CN at 298K



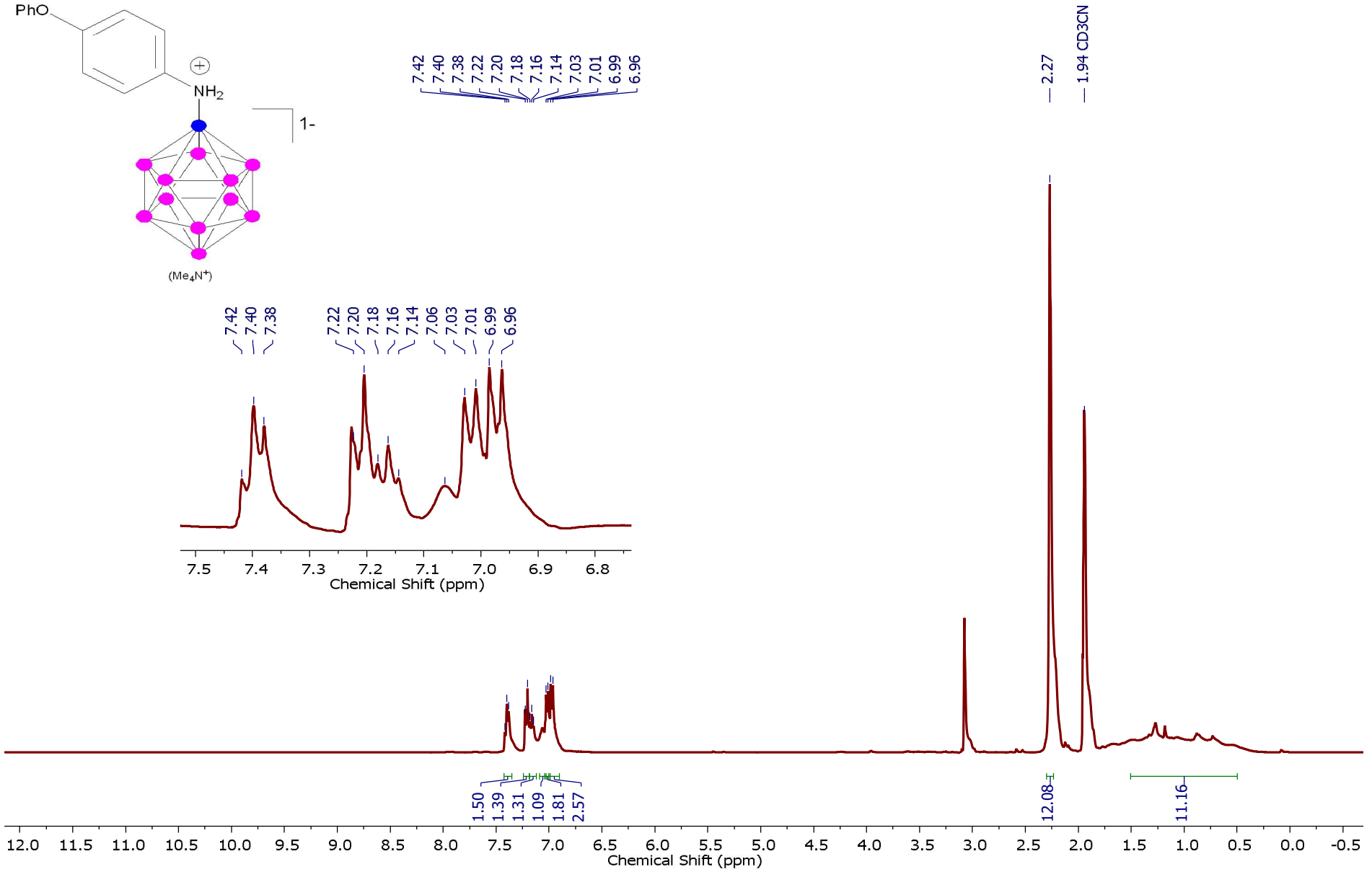
$^{11}B\{1H\}$ NMR spectrum of 3f in CD_3CN at 298K



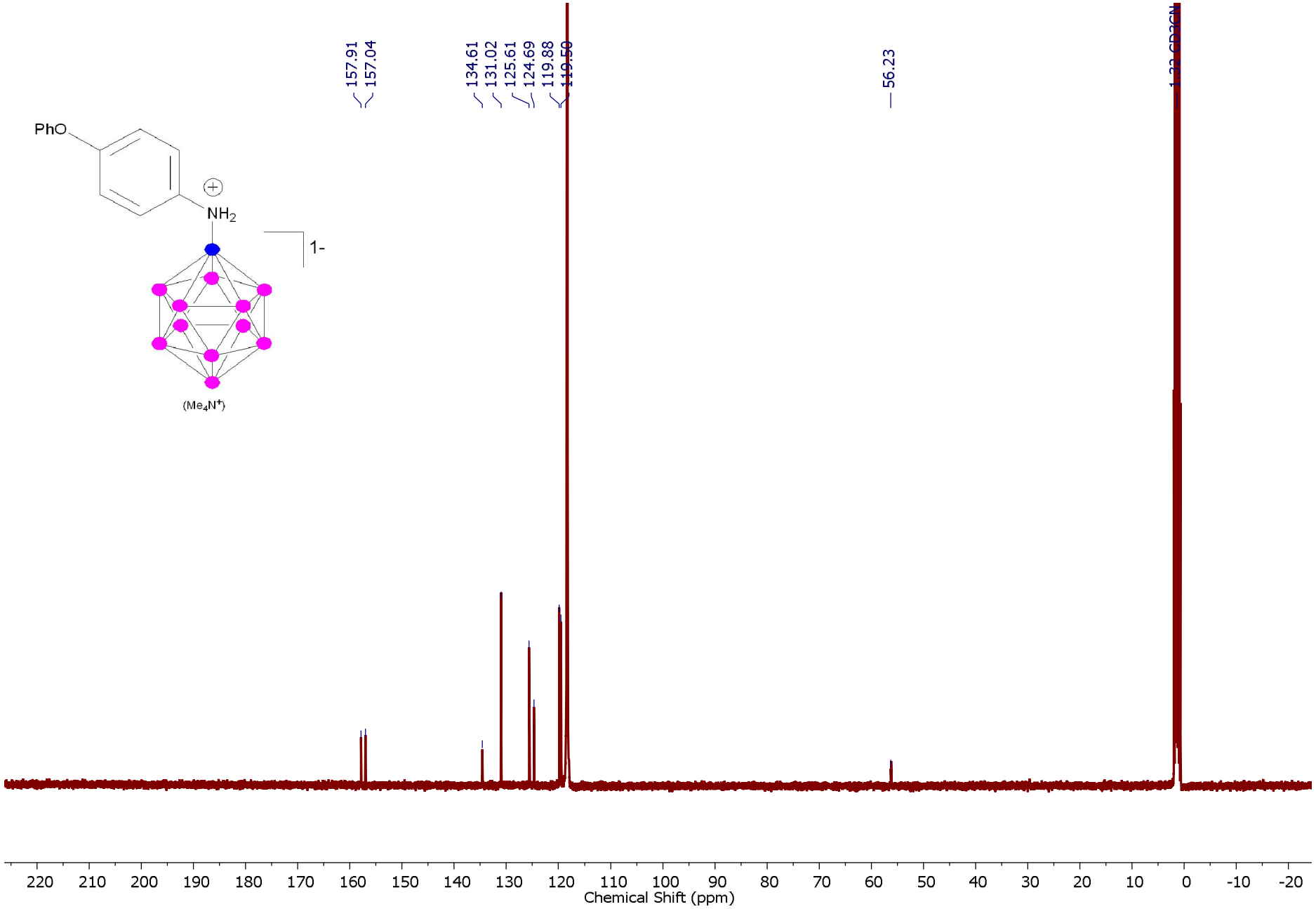
^{11}B NMR spectrum of 3f in CD_3CN at 298K



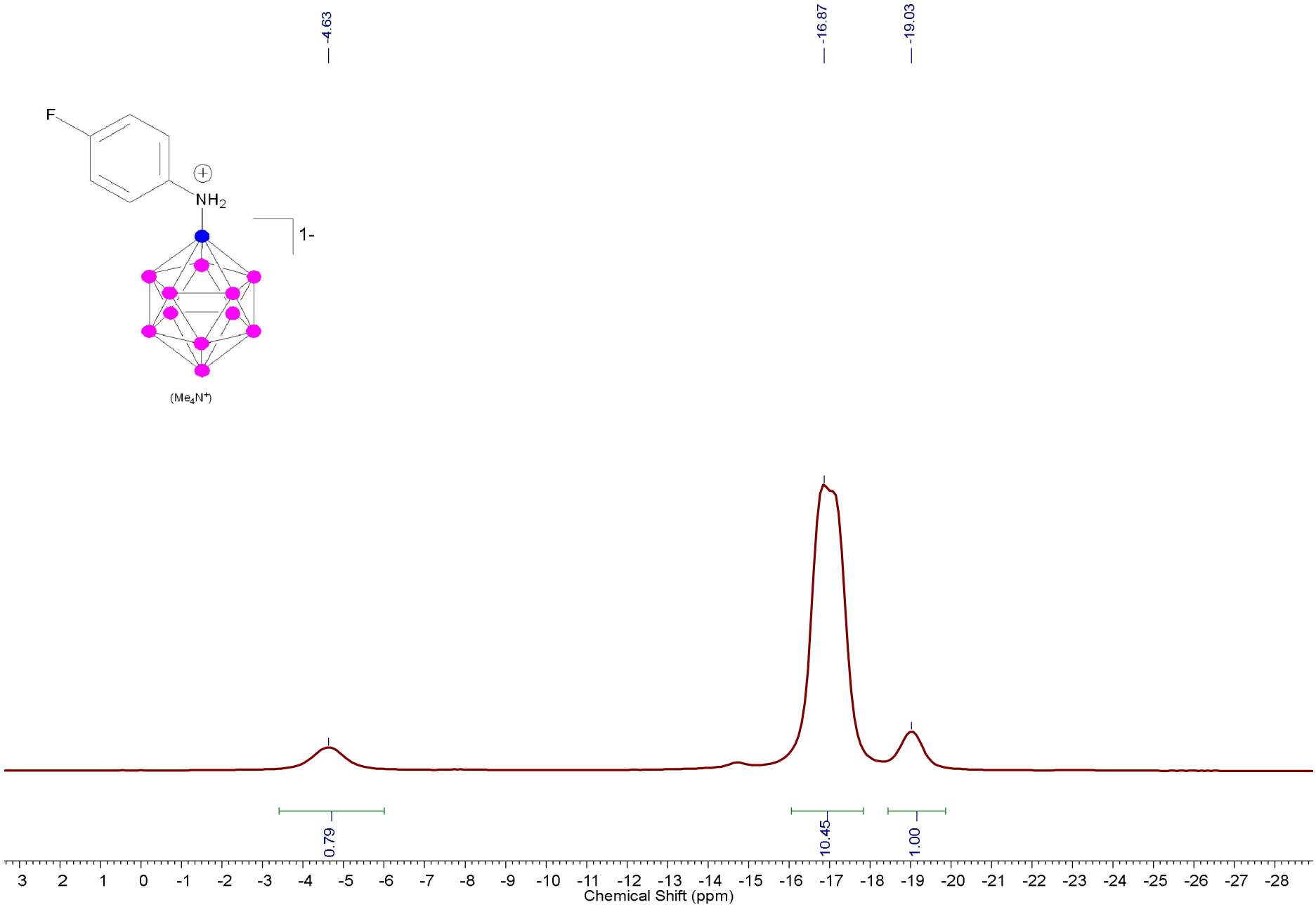
$^{1}H\{^{11}B\}$ NMR spectrum of 3f in CD_3CN at 298K



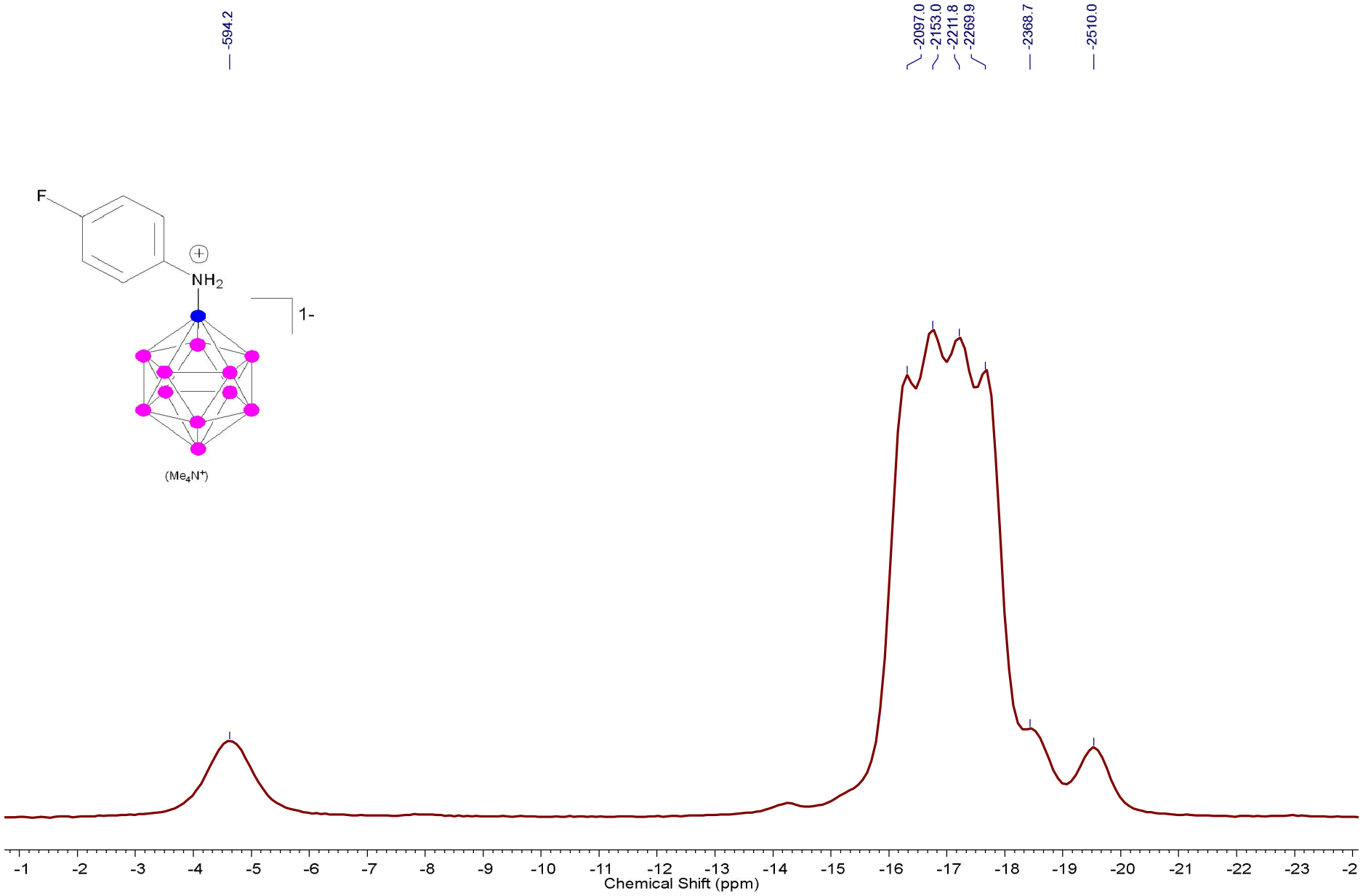
^{13}C NMR spectrum of 3f in CD_3CN at 298K



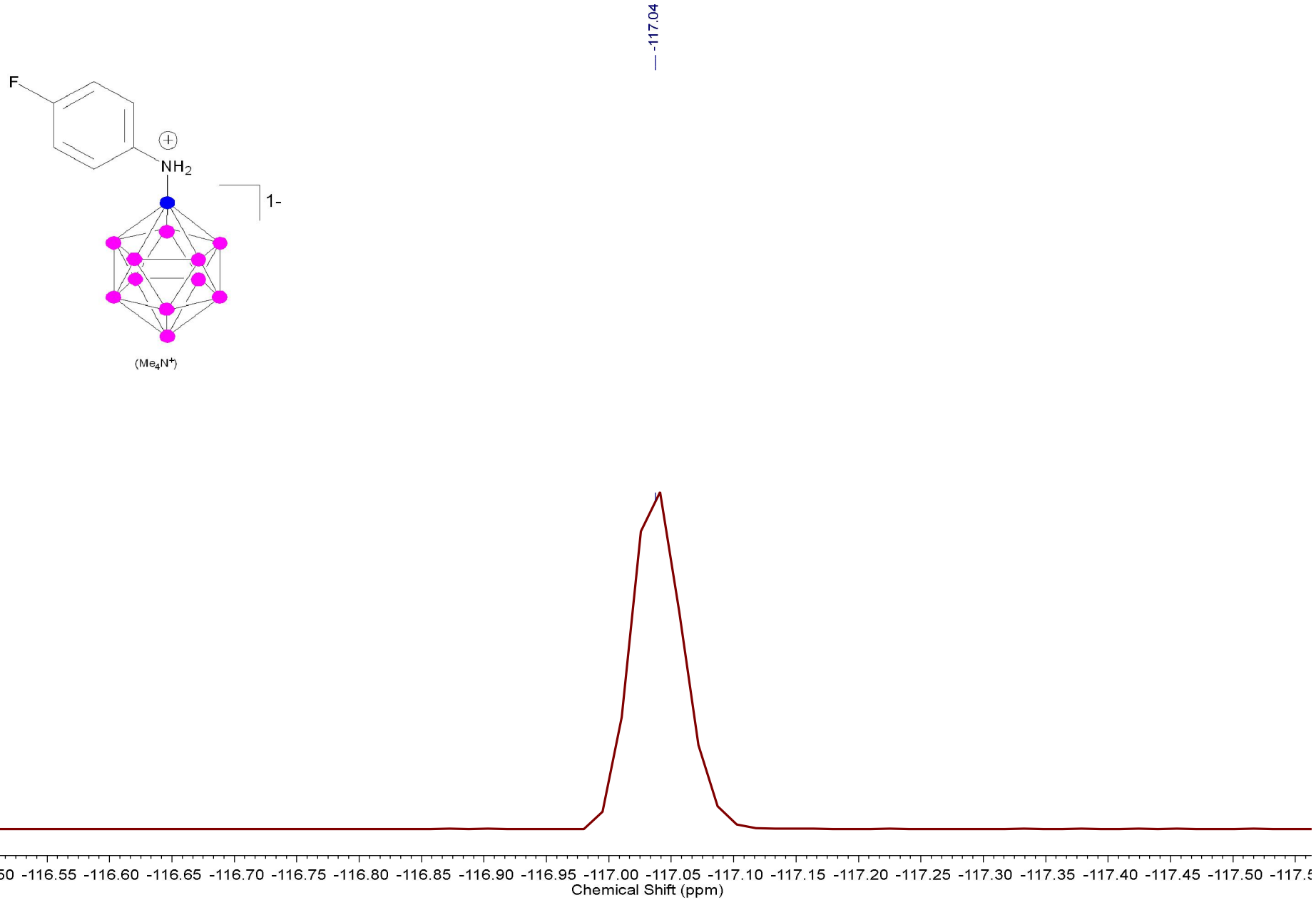
$^{11}B\{^{1}H\}$ NMR spectrum of 3i in CD_3CN at 298K



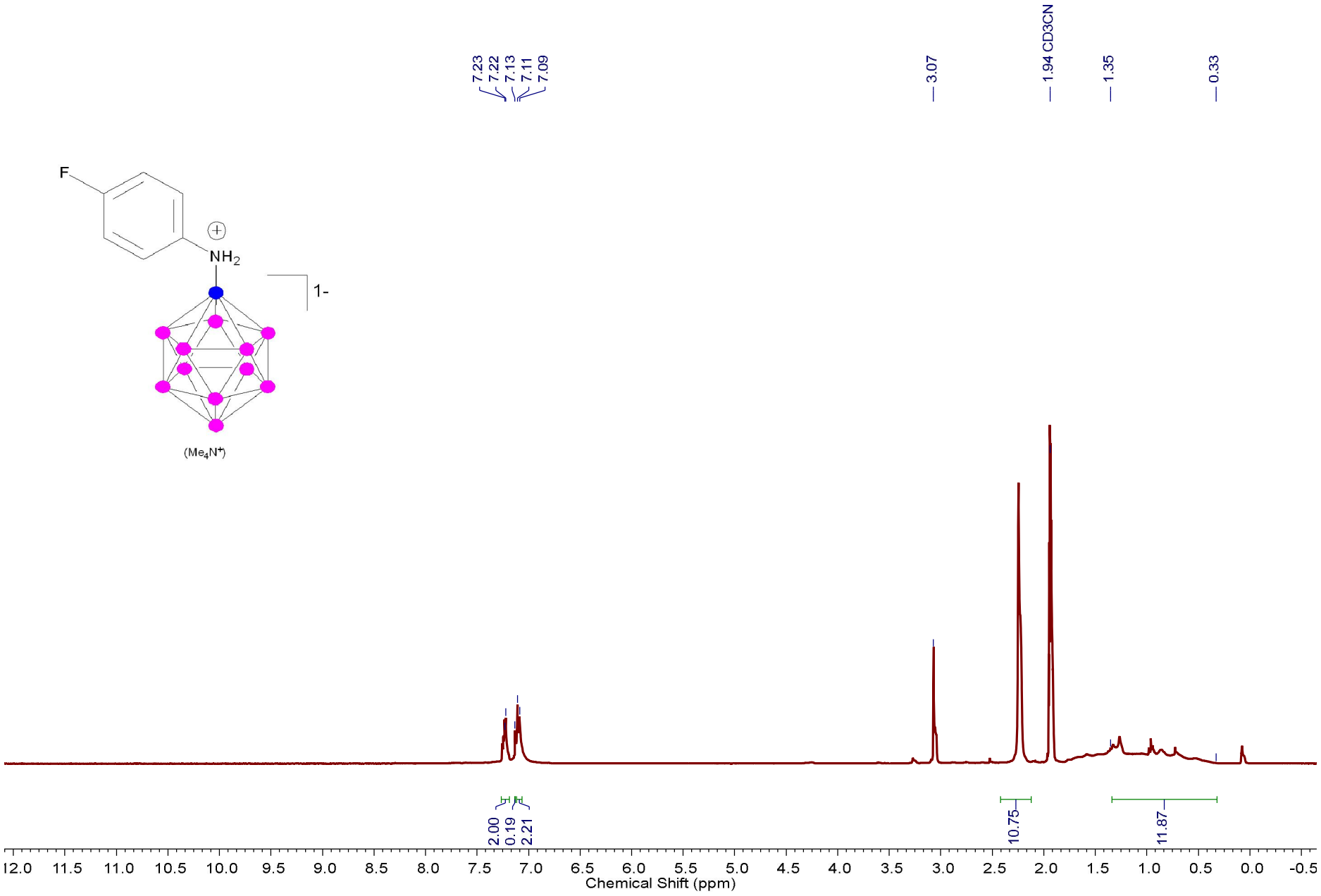
^{11}B NMR spectrum of 3i in CD_3CN at 298K



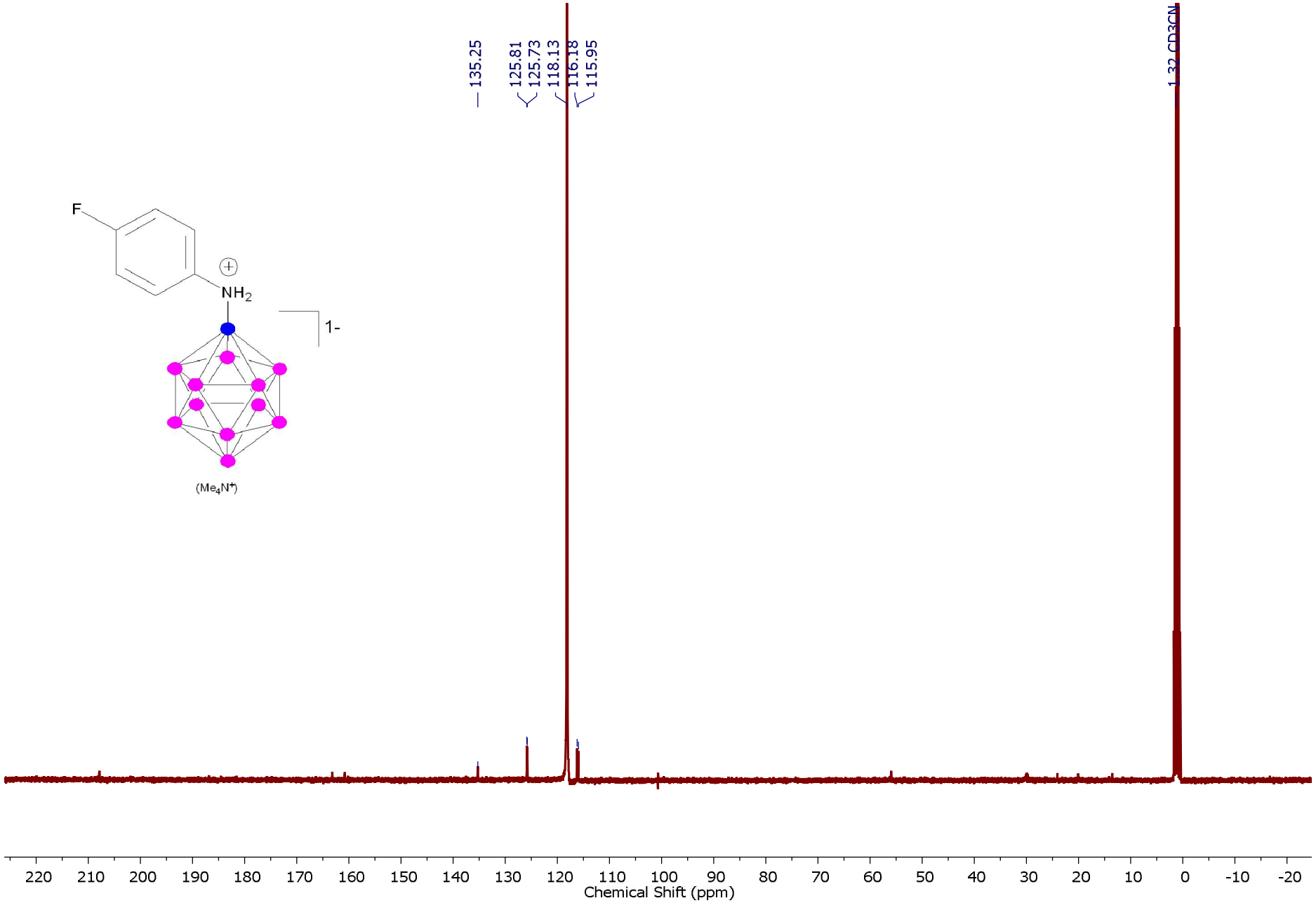
^{9}F NMR spectrum of 3i in CD_3CN at 298K



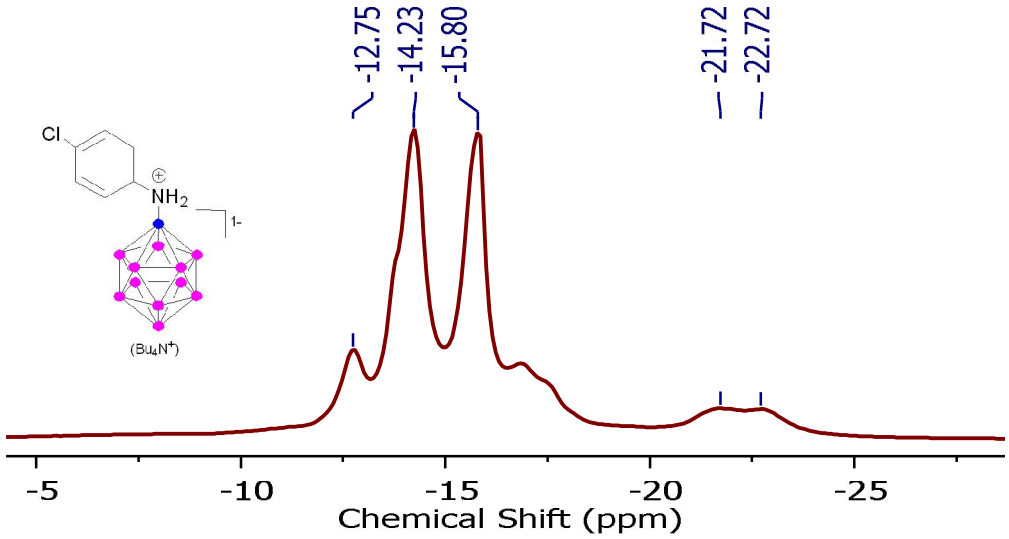
$^{1}H\{^{11}B\}$ NMR spectrum of 3i in CD_3CN at 298K

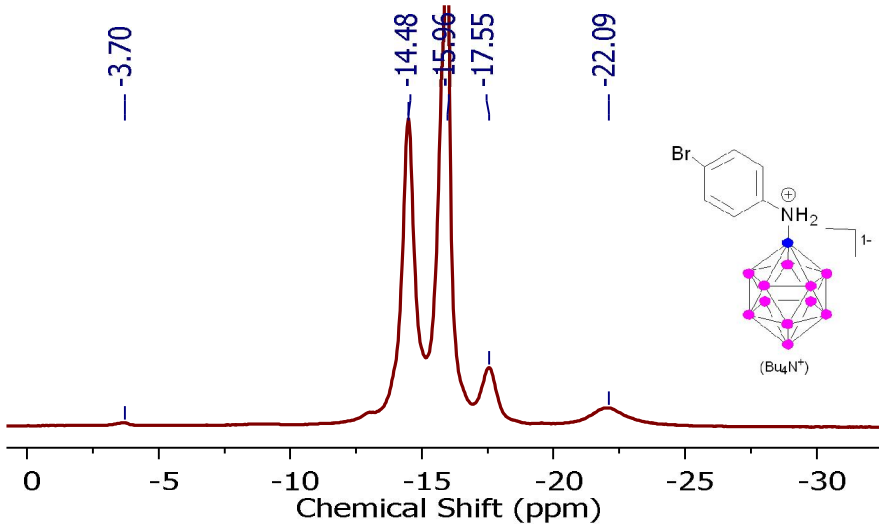


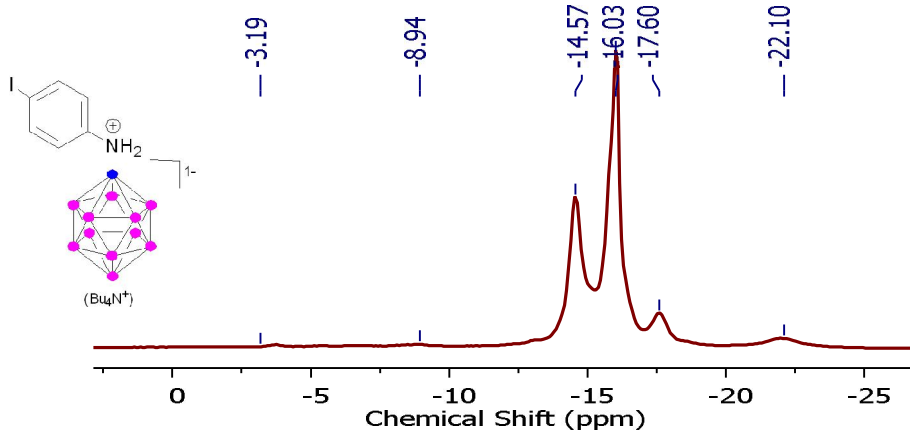
^{13}C NMR spectrum of 3i in CD_3CN at 298K



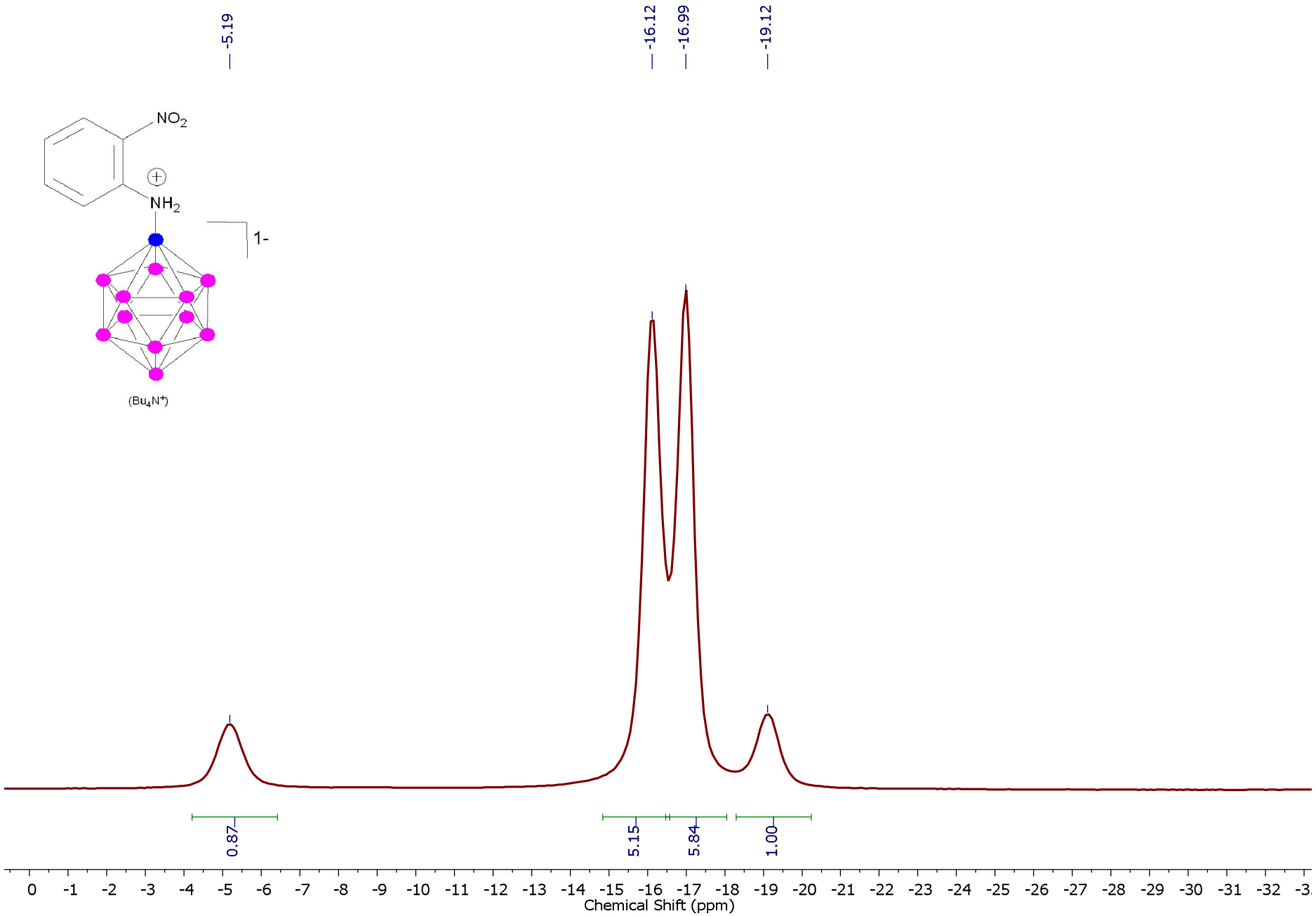
$^{11}B\{^{1}H\}$ crude NMR spectrum of 3J, 3K, and 3I at 298K



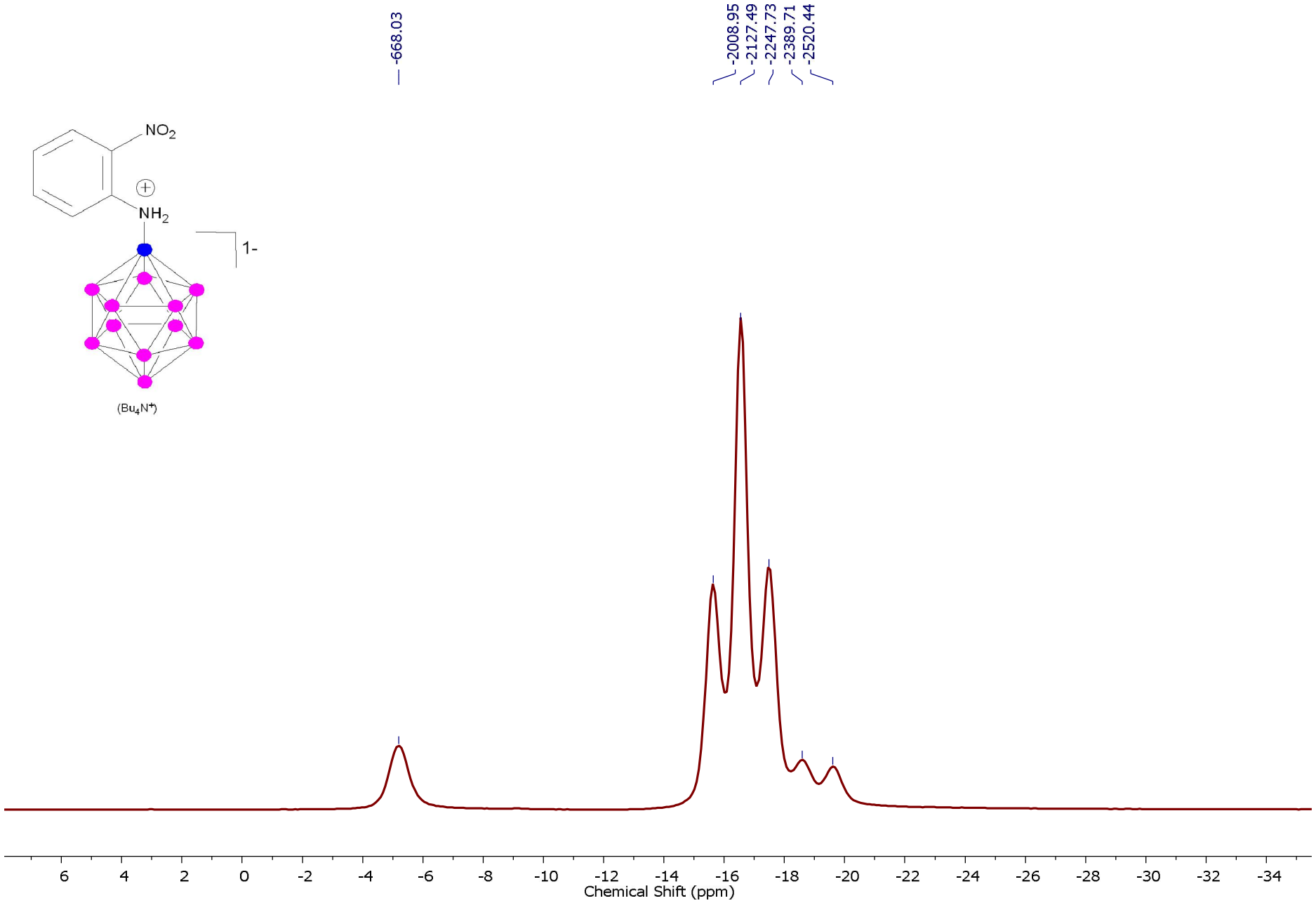




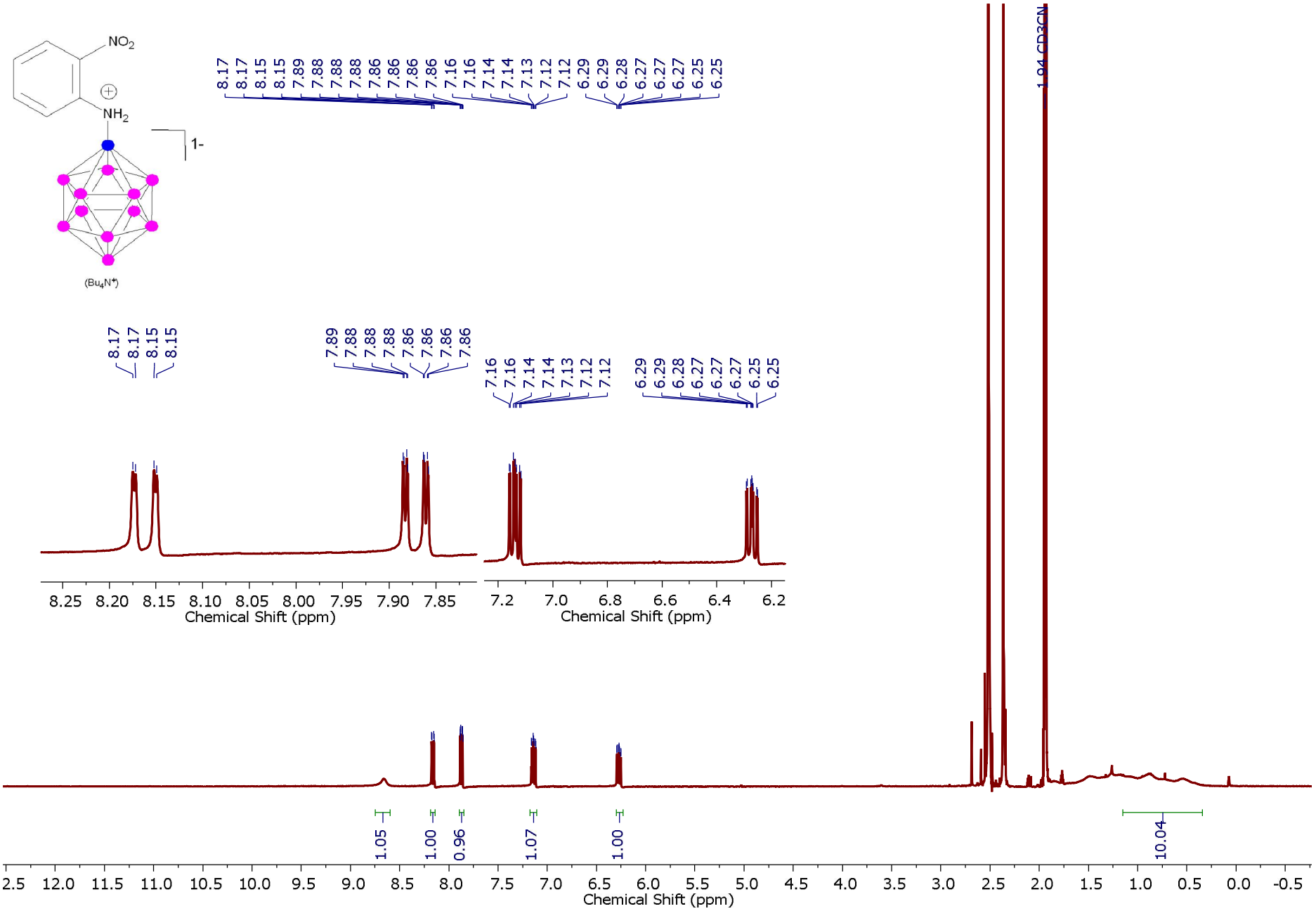
$^{11}B\{^{1}H\}$ NMR spectrum of 3m in CD_3CN at 298K



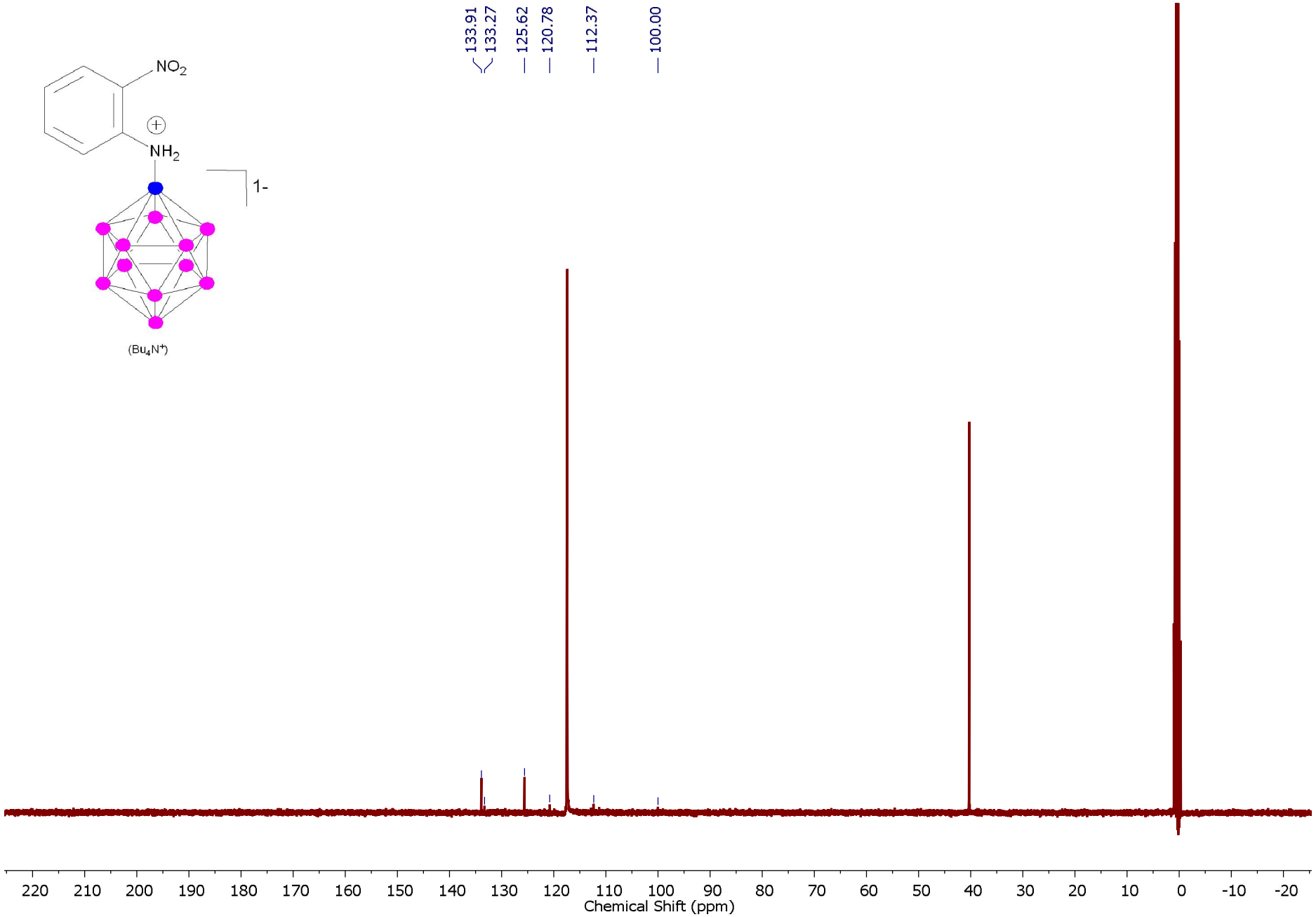
^{11}B NMR spectrum of 3m in CD_3CN at 298K



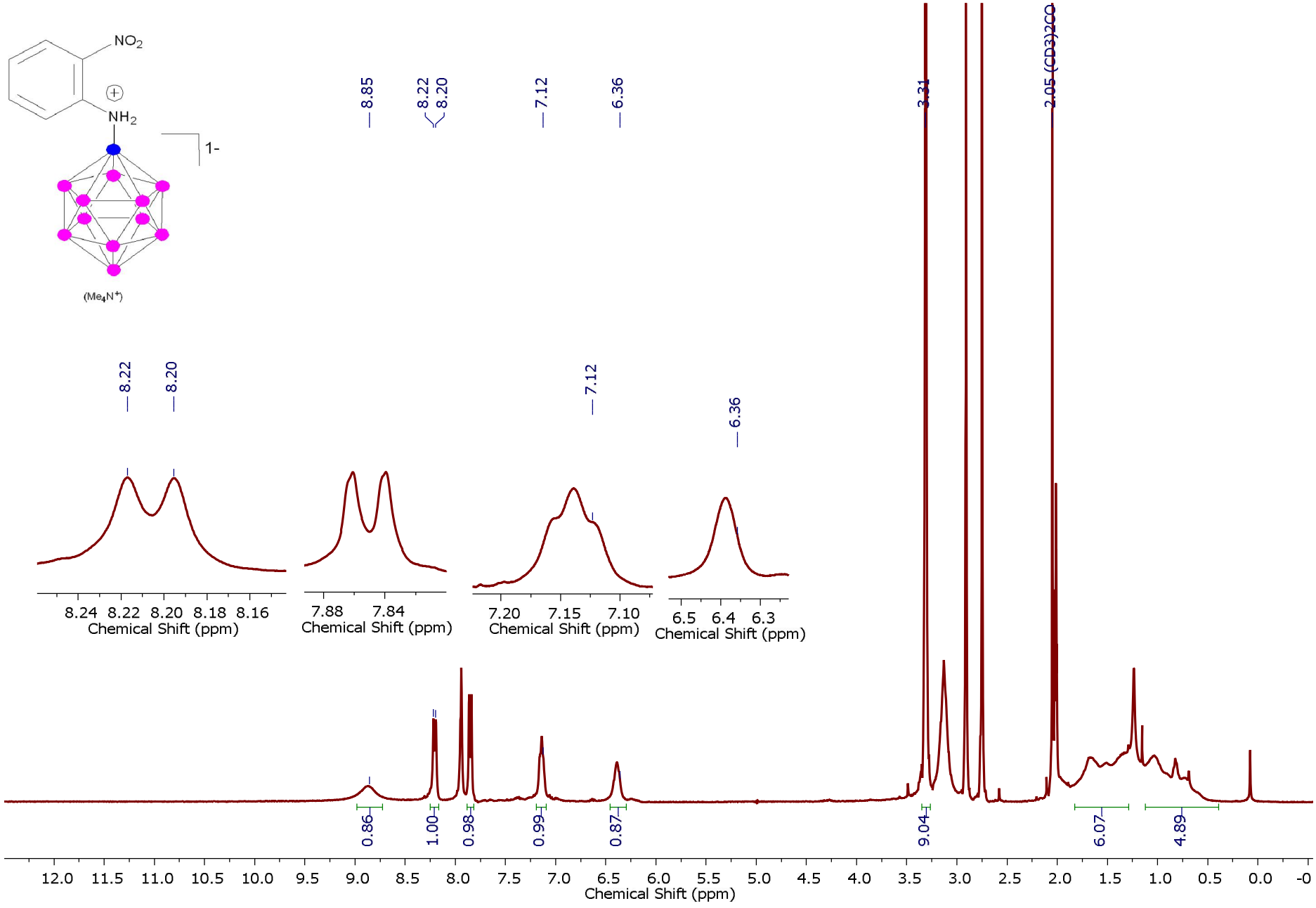
$^{1}H\{^{11}B\}$ NMR spectrum of 3m (Bu4N) in CD_3CN at 298K



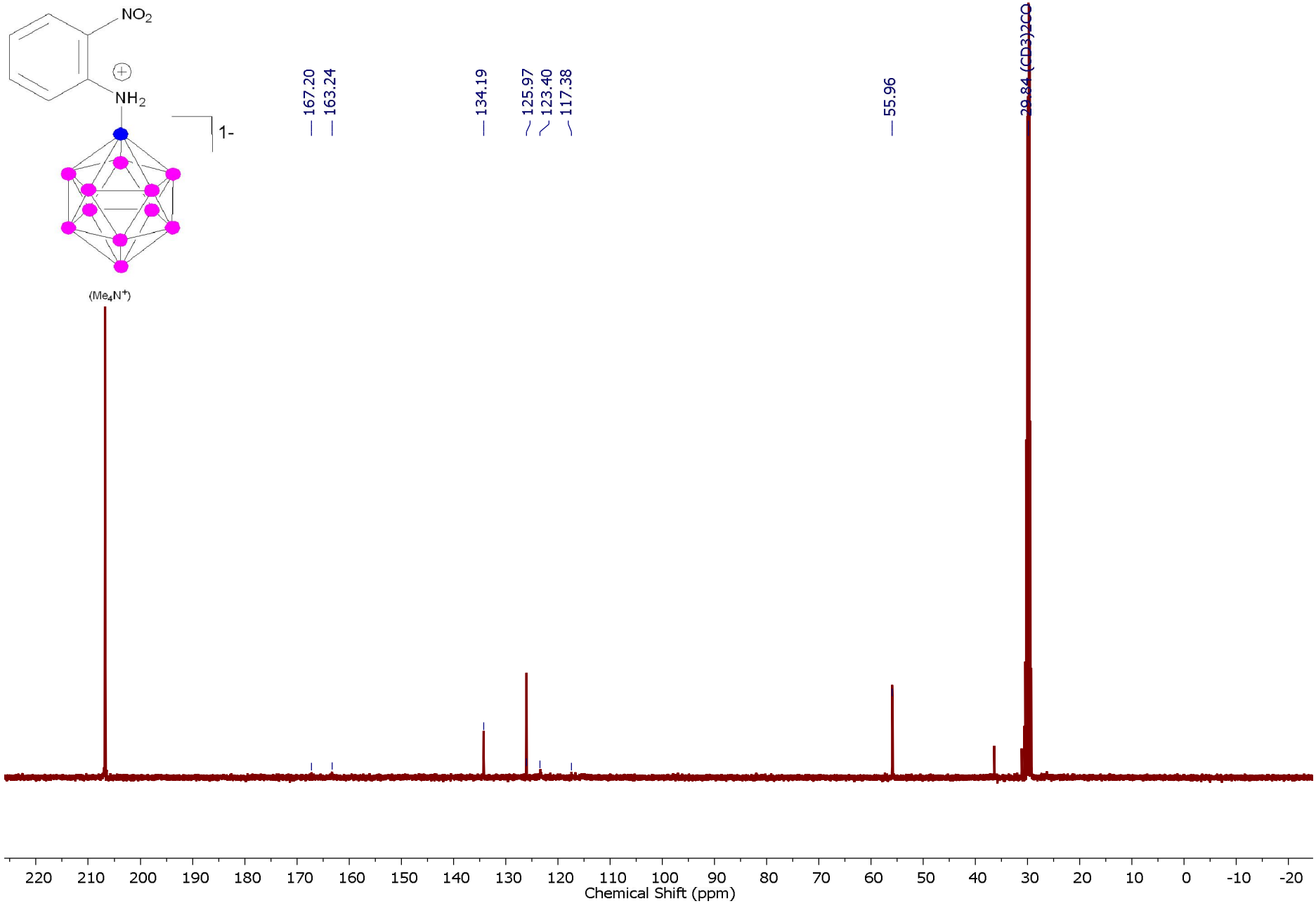
^{13}C NMR spectrum of 3m (Bu_4N) in CD_3CN at 298K



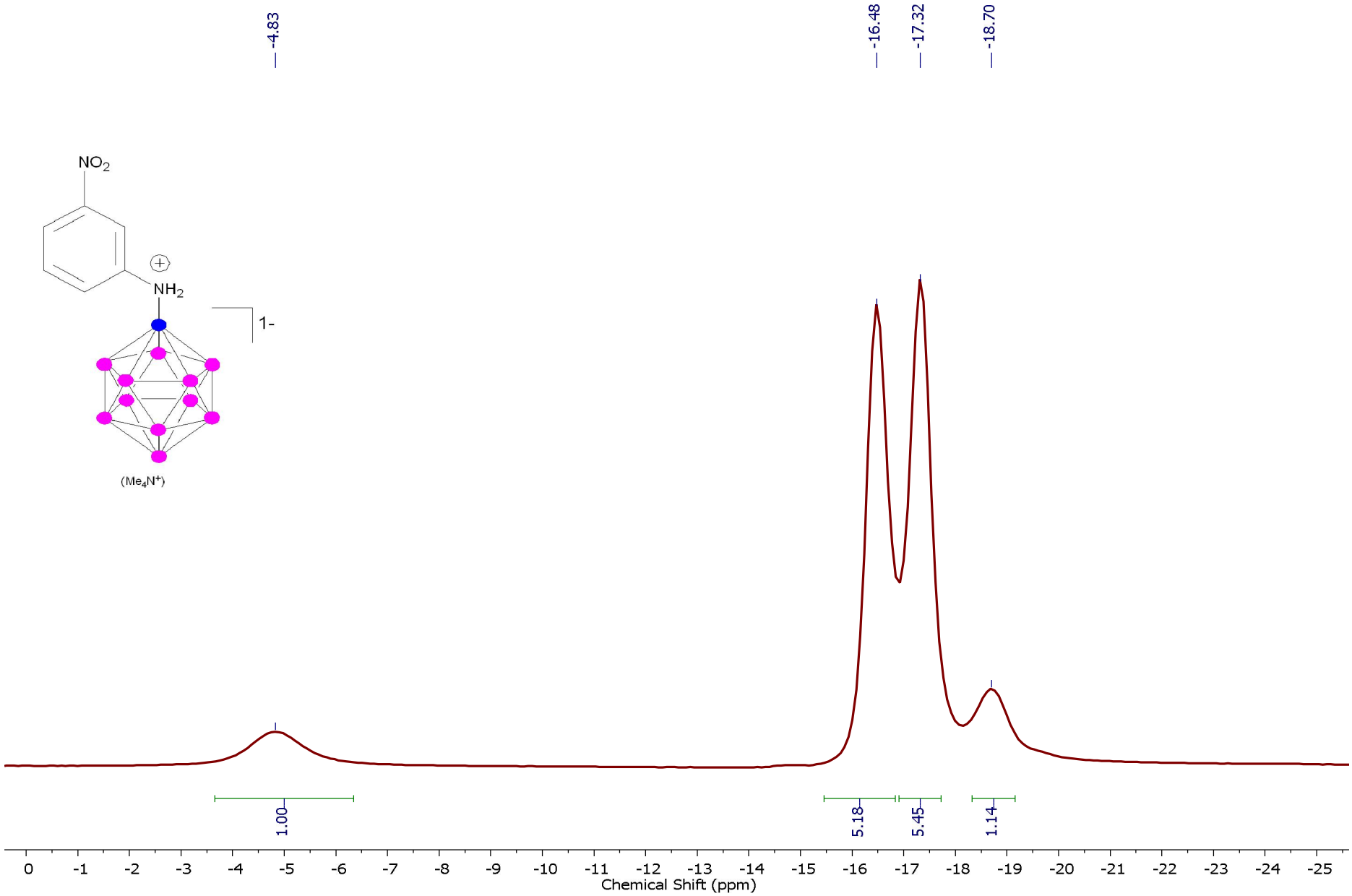
$^{1}H\{^{11}B\}$ NMR spectrum of 3m (Me_4N) in CD_3CN at 298K



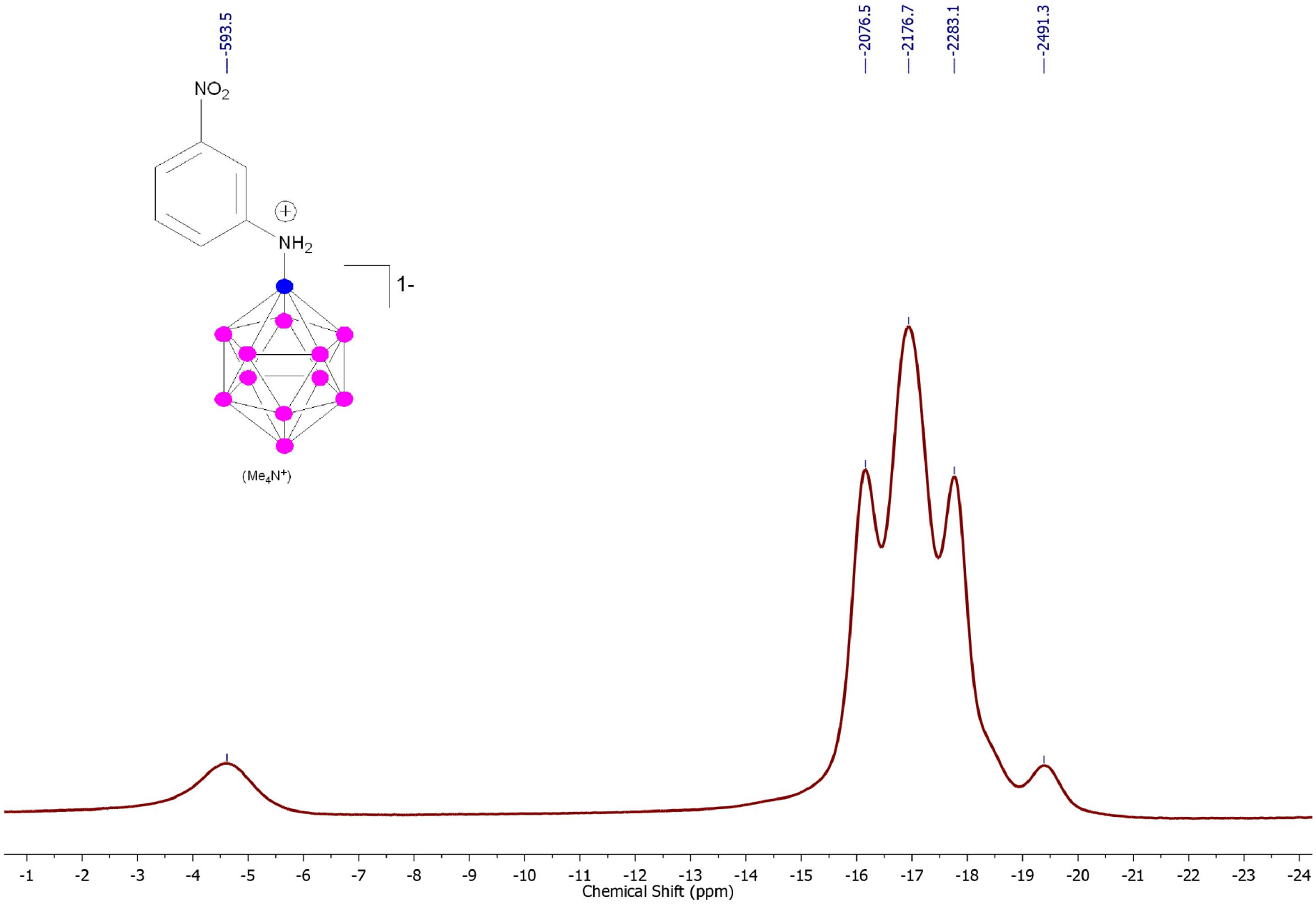
^{13}C NMR spectrum of 3m (Me_4N) in CD_3CN at 298K



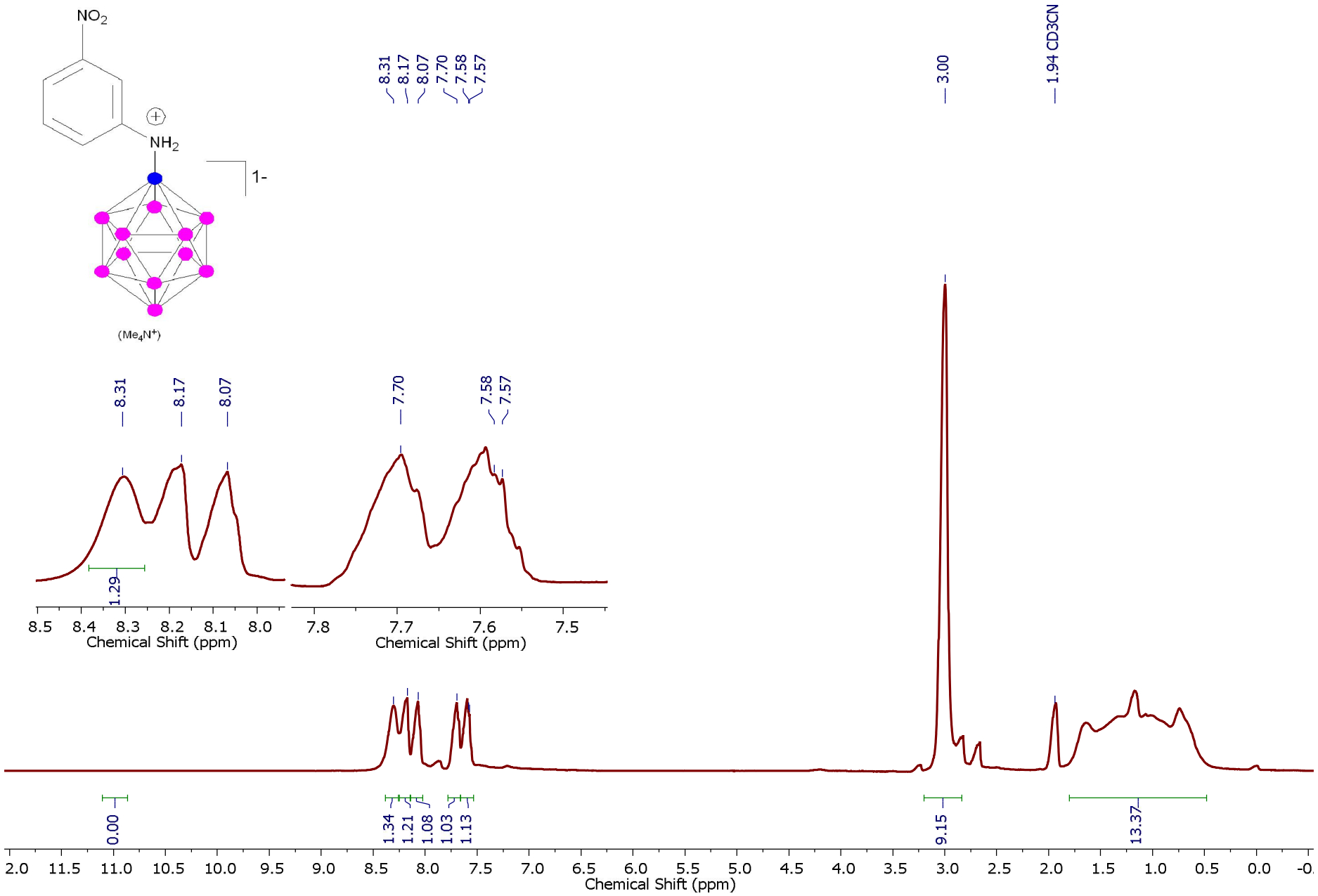
$^{11}B\{^1H\}$ NMR spectrum of 3n in CD_3CN at 298K



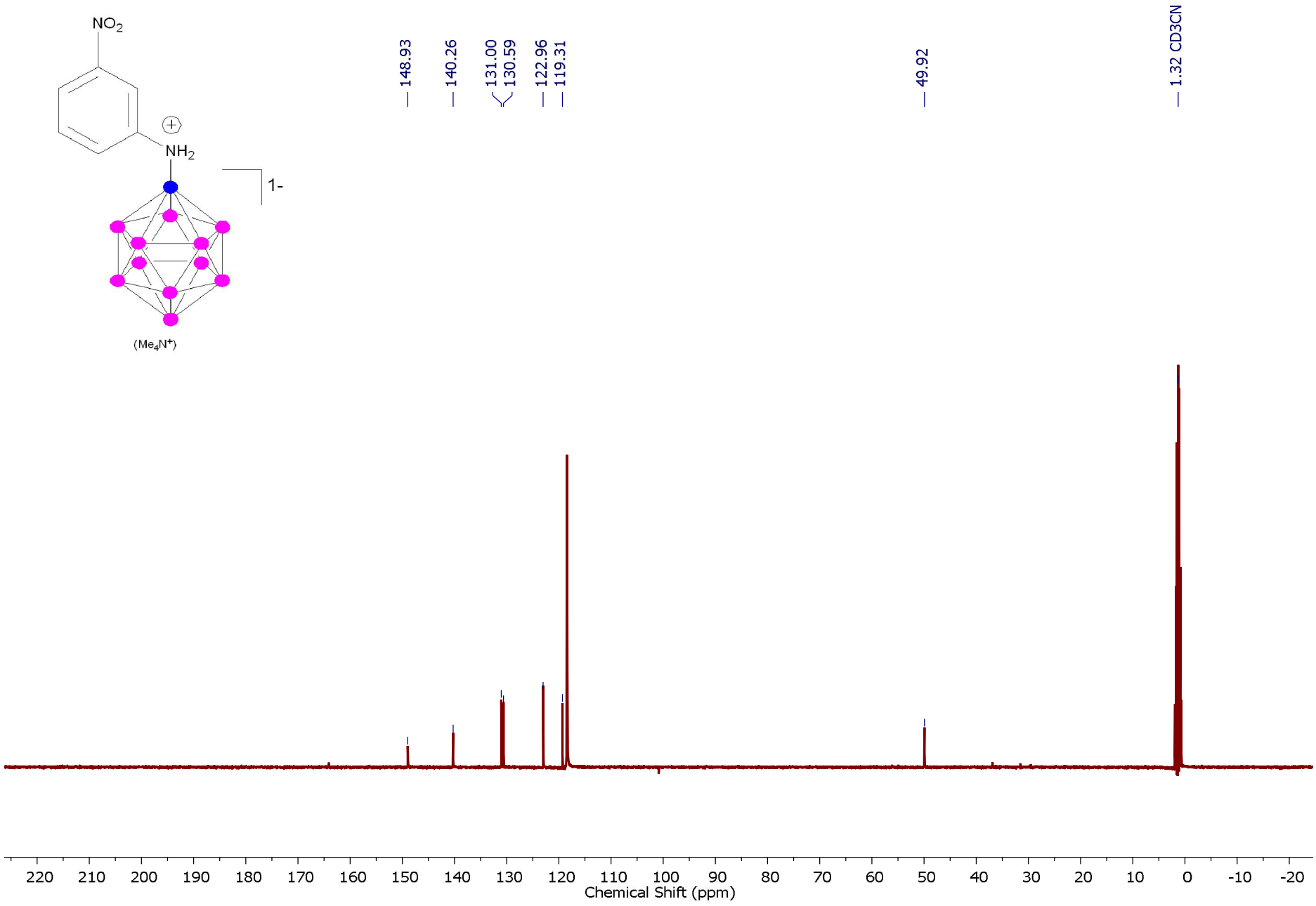
^{11}B NMR spectrum of 3n in CD_3CN at 298K



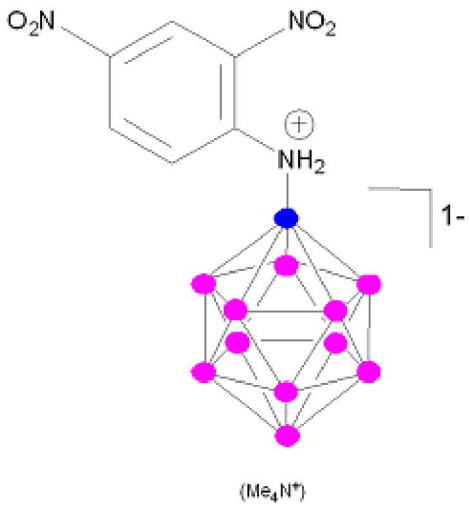
$^{1}H\{^{11}B\}$ NMR spectrum of 3n in CD_3CN at 298K



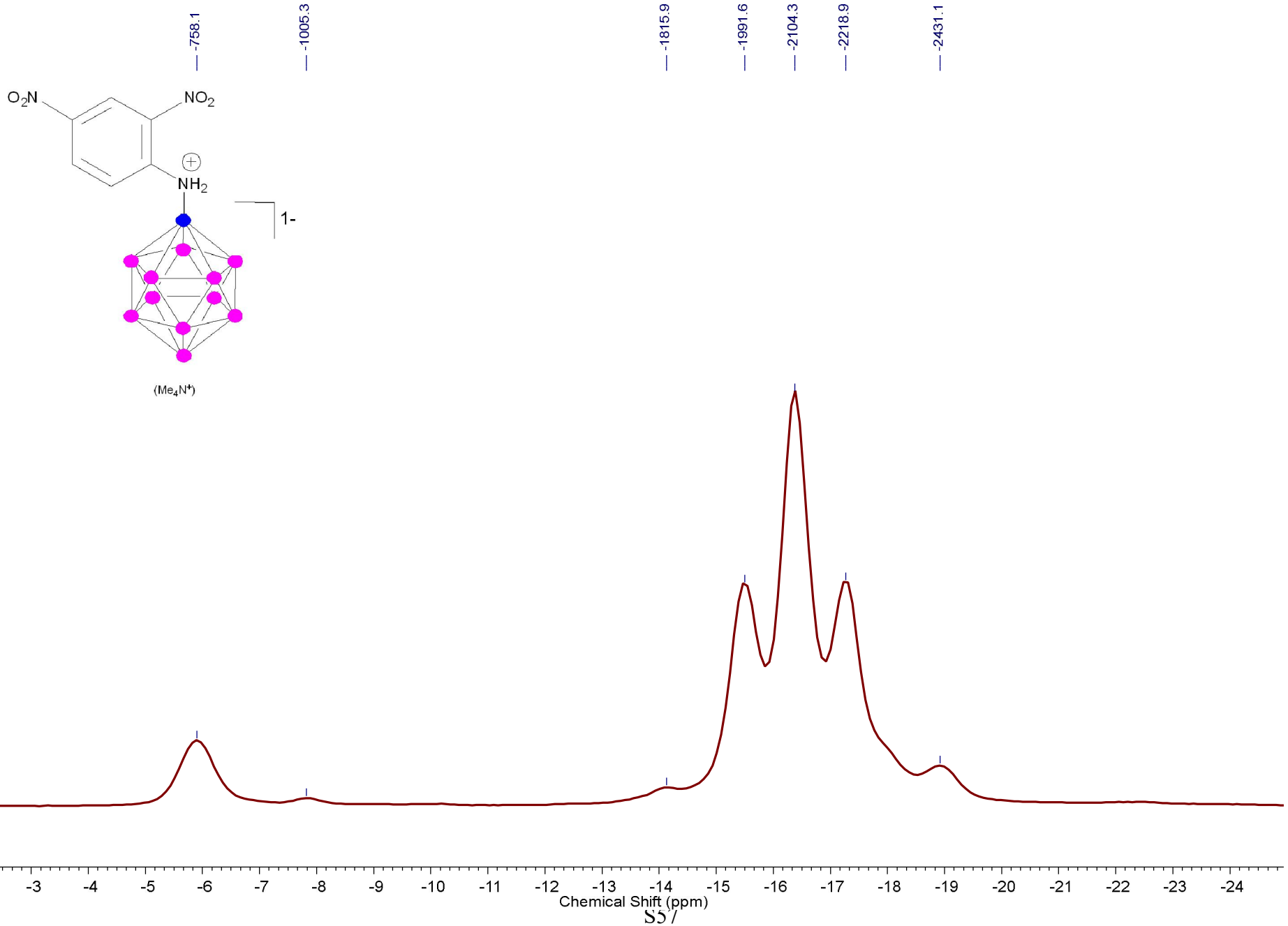
^{13}C NMR spectrum of 3n in CD_3CN at 298K



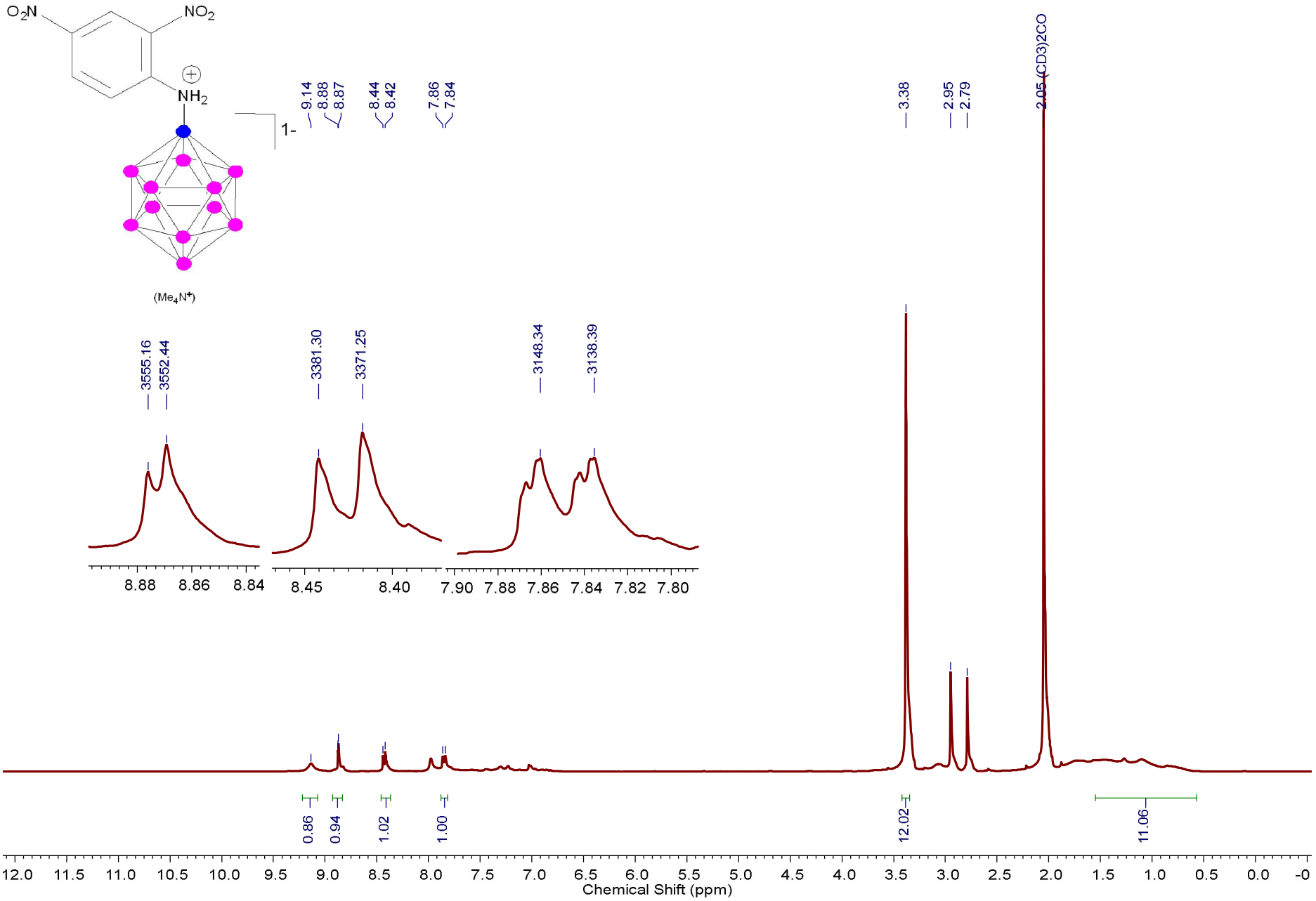
$^{11}B\{^{1}H\}$ NMR spectrum of 3o in CD_3CN at 298K



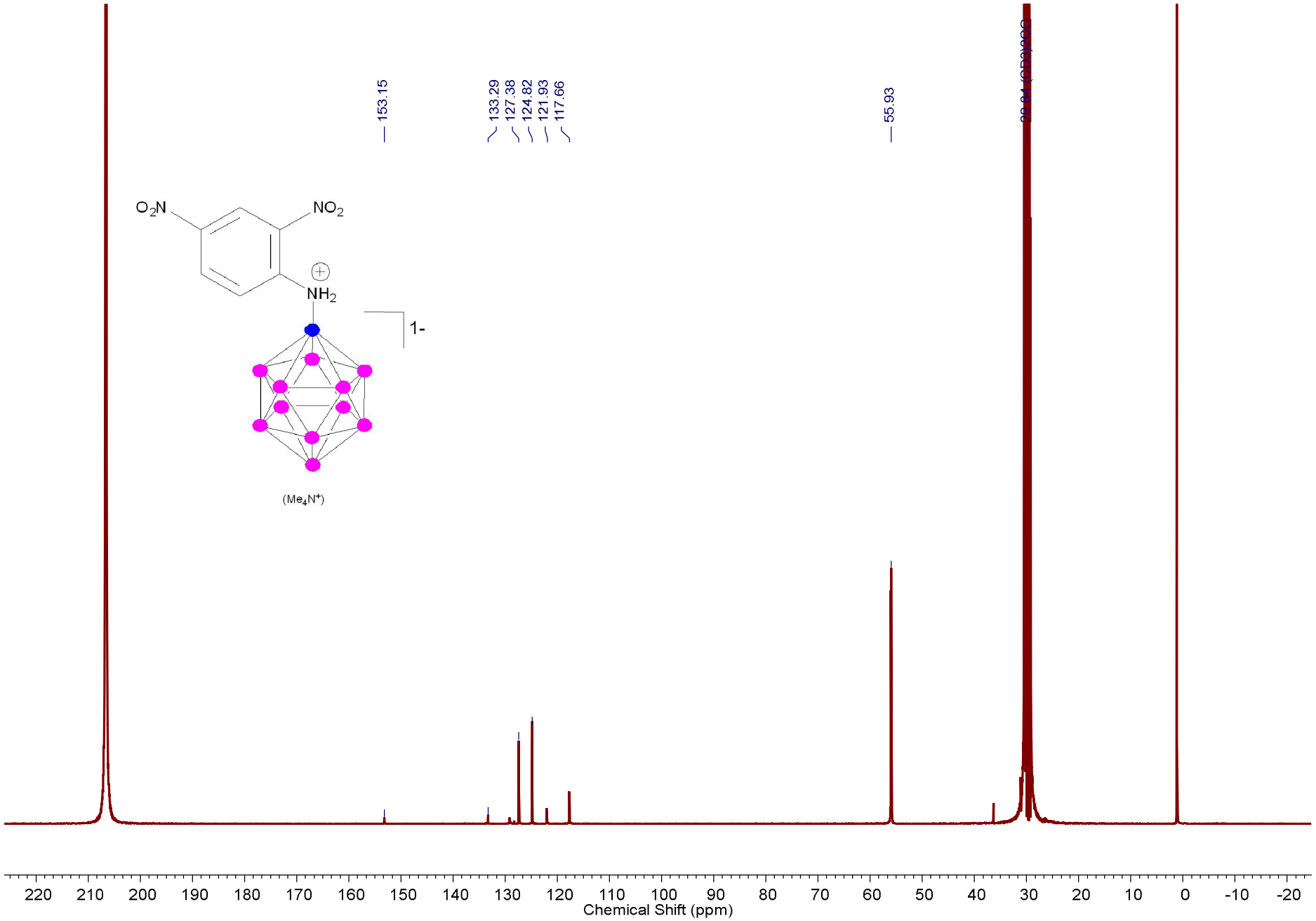
^{11}B NMR spectrum of 3o in CD_3CN at 298K



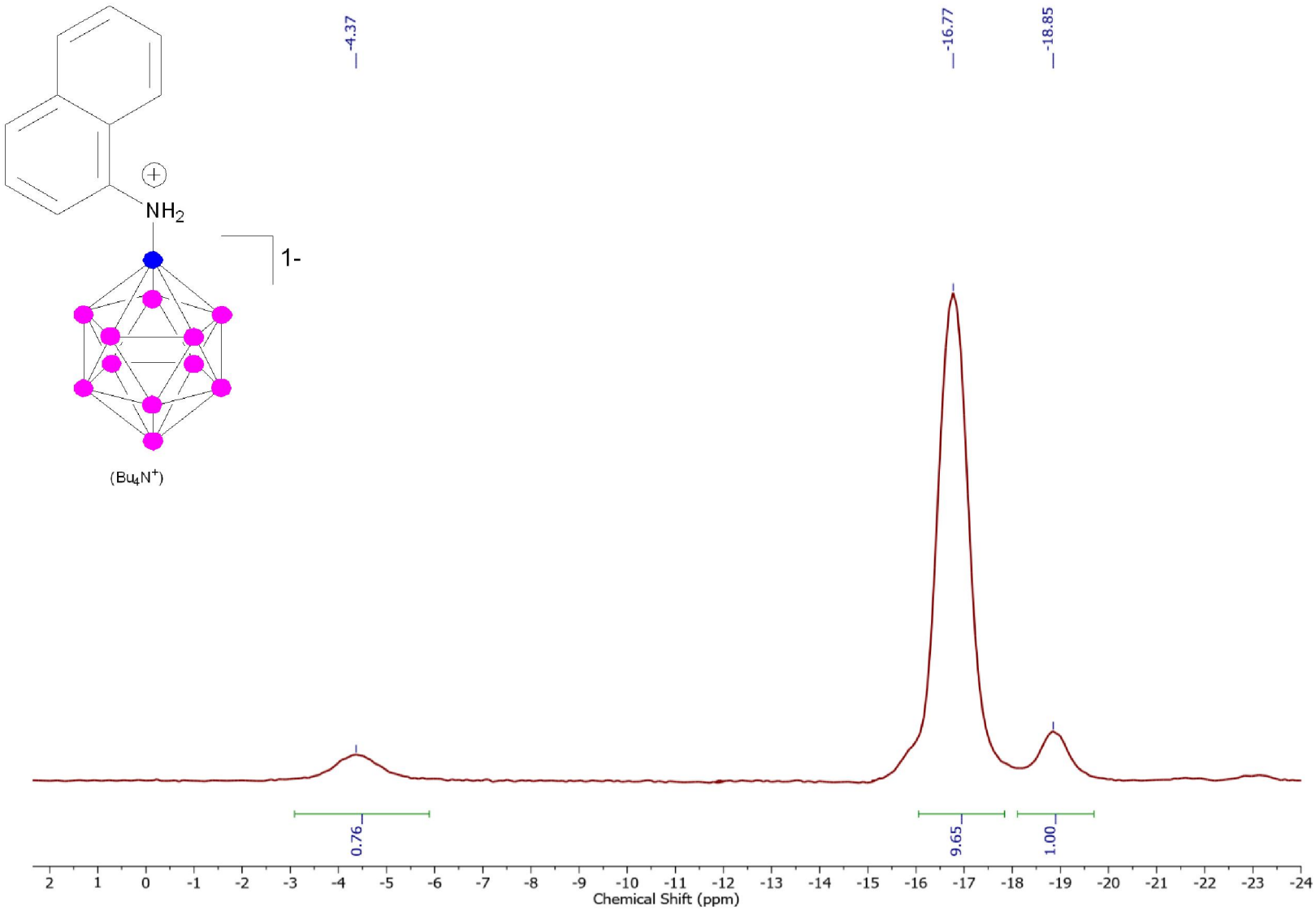
$^{1}H\{^{11}B\}$ NMR spectrum of 3o in CD_3CN at 298K



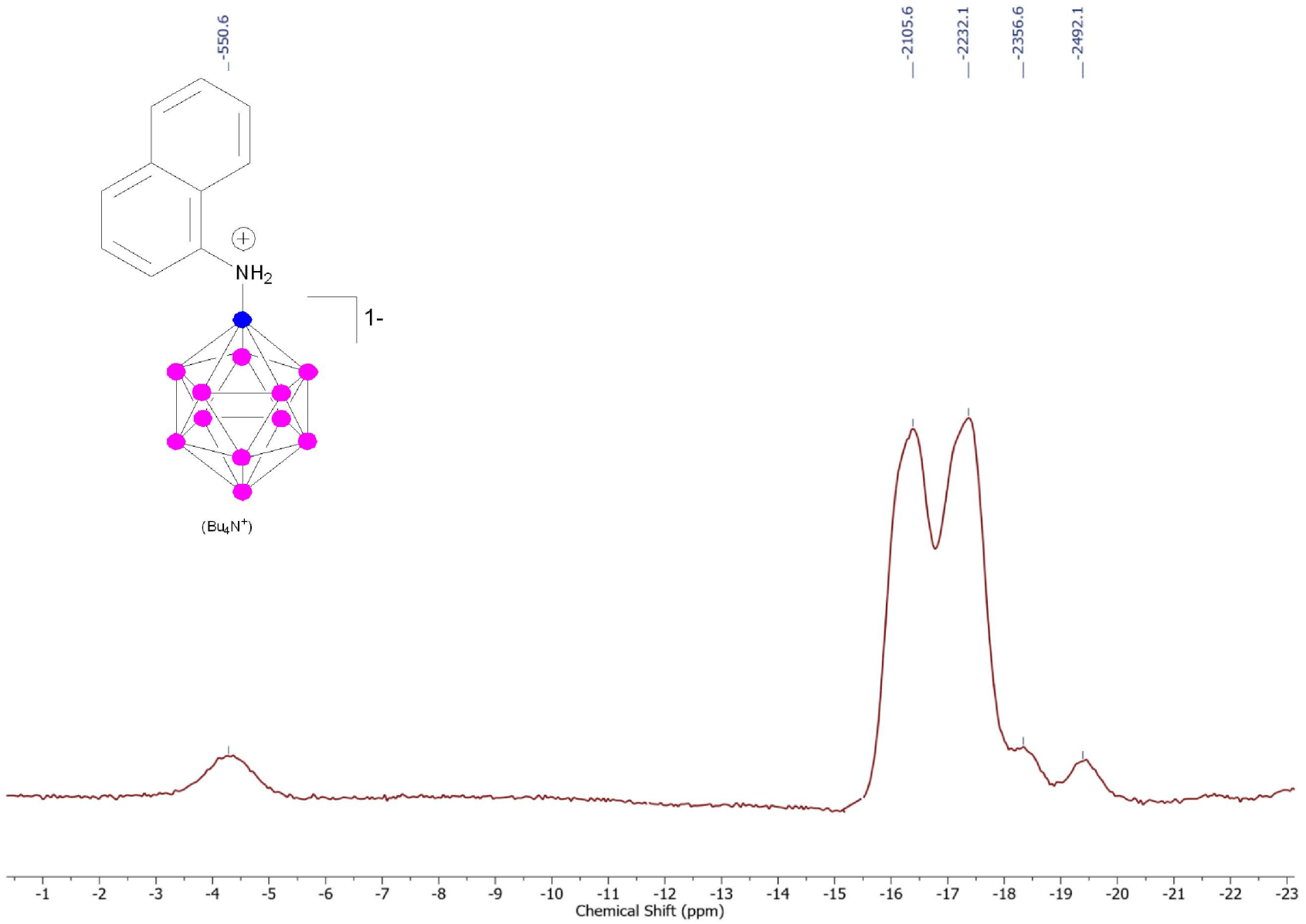
^{13}C NMR spectrum of 3o in CD_3CN at 298K



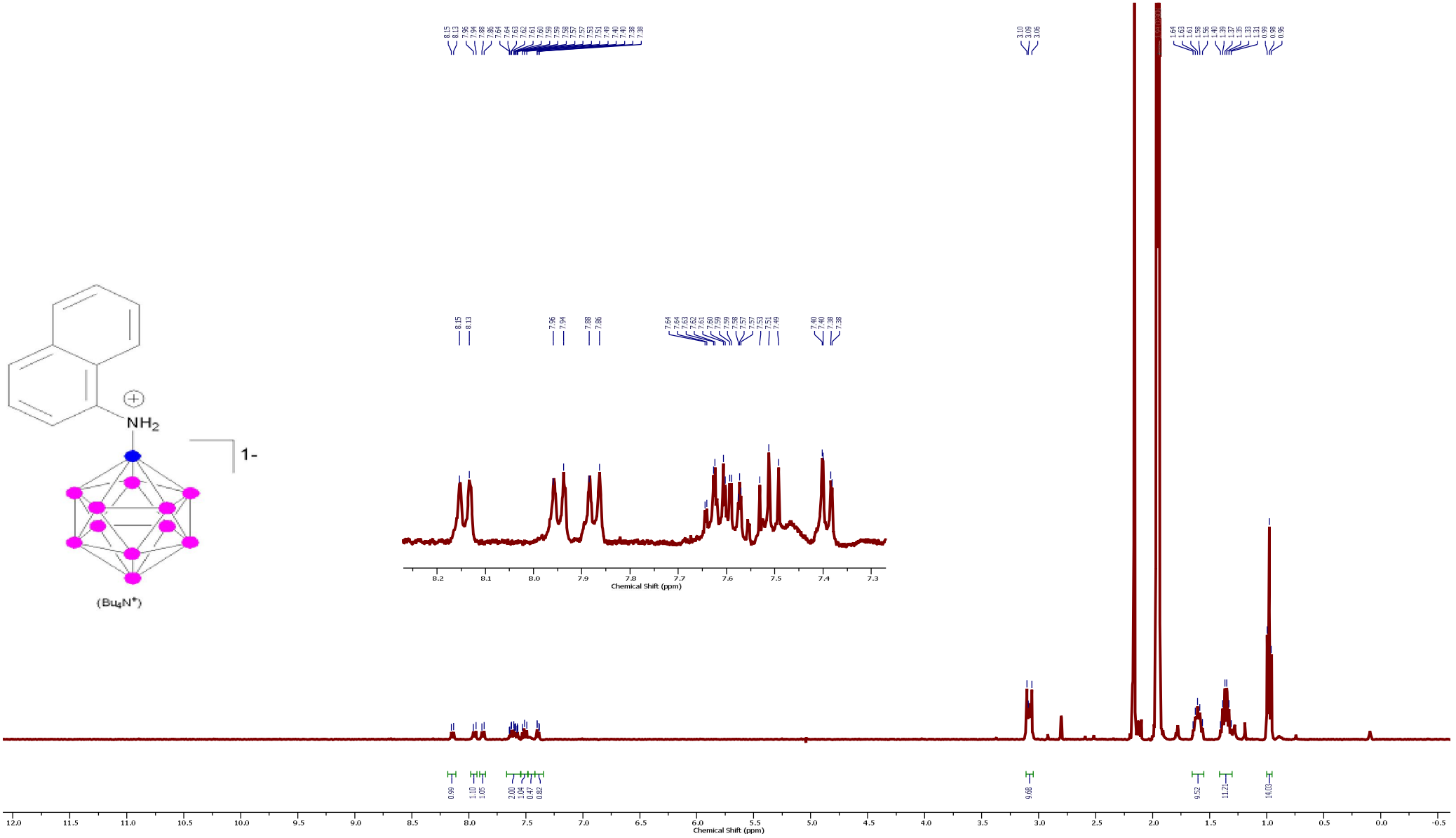
$^{11}B\{^{1}H\}$ NMR spectrum of 4 in CD_3CN at 298K



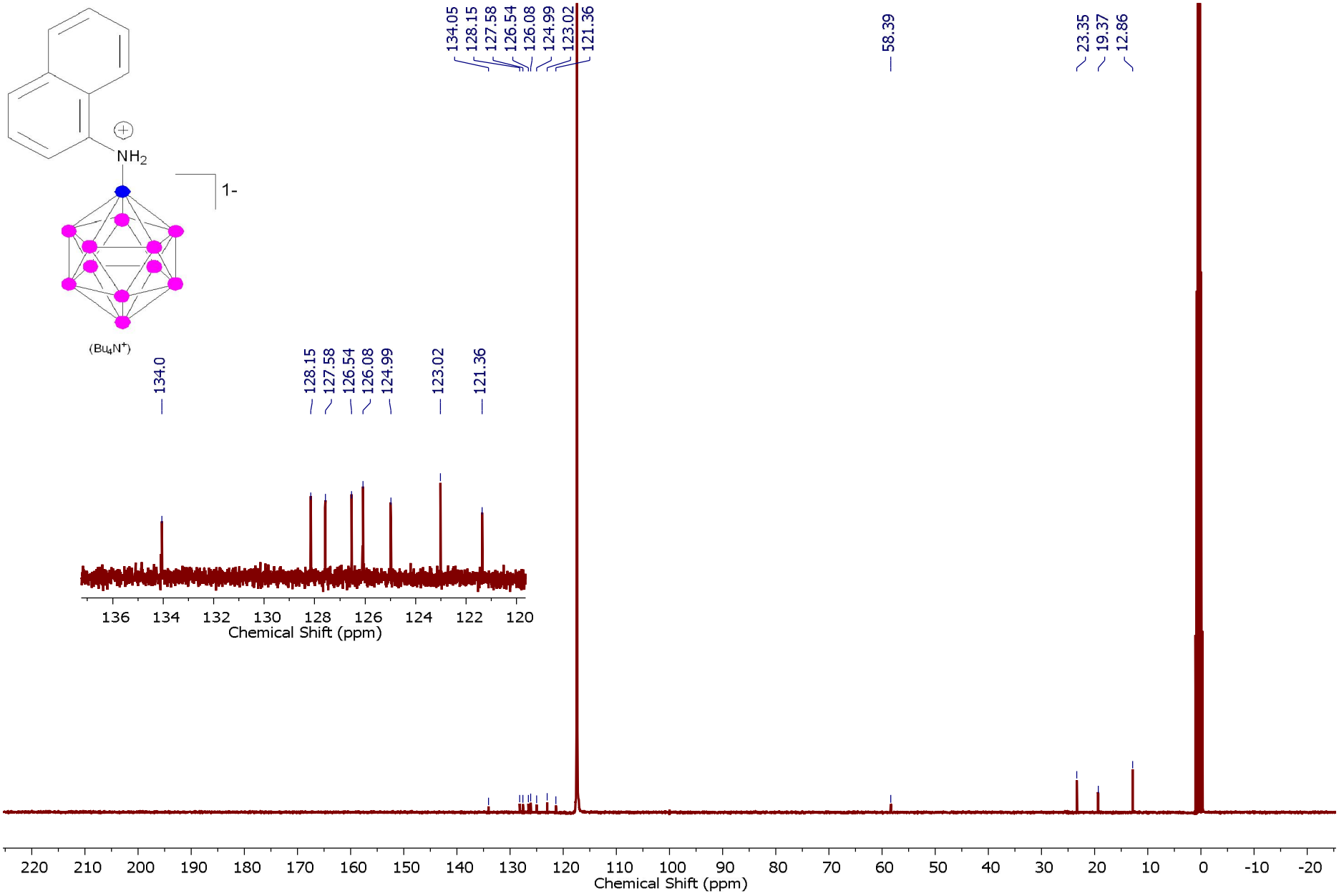
^{11}B NMR spectrum of 4 in CD_3CN at 298K



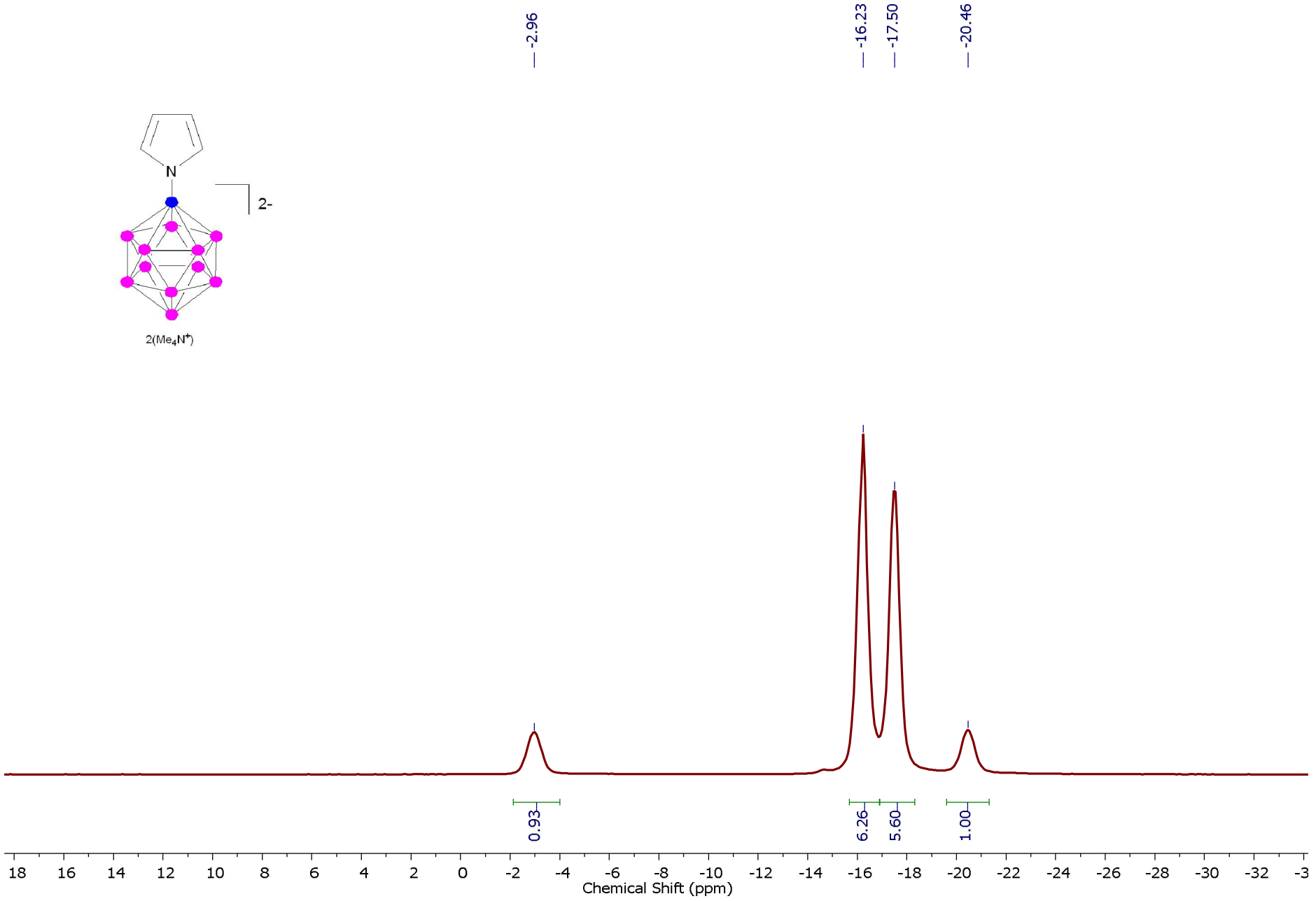
$^{1}H\{^{11}B\}$ NMR spectrum of 4 in CD_3CN at 298K



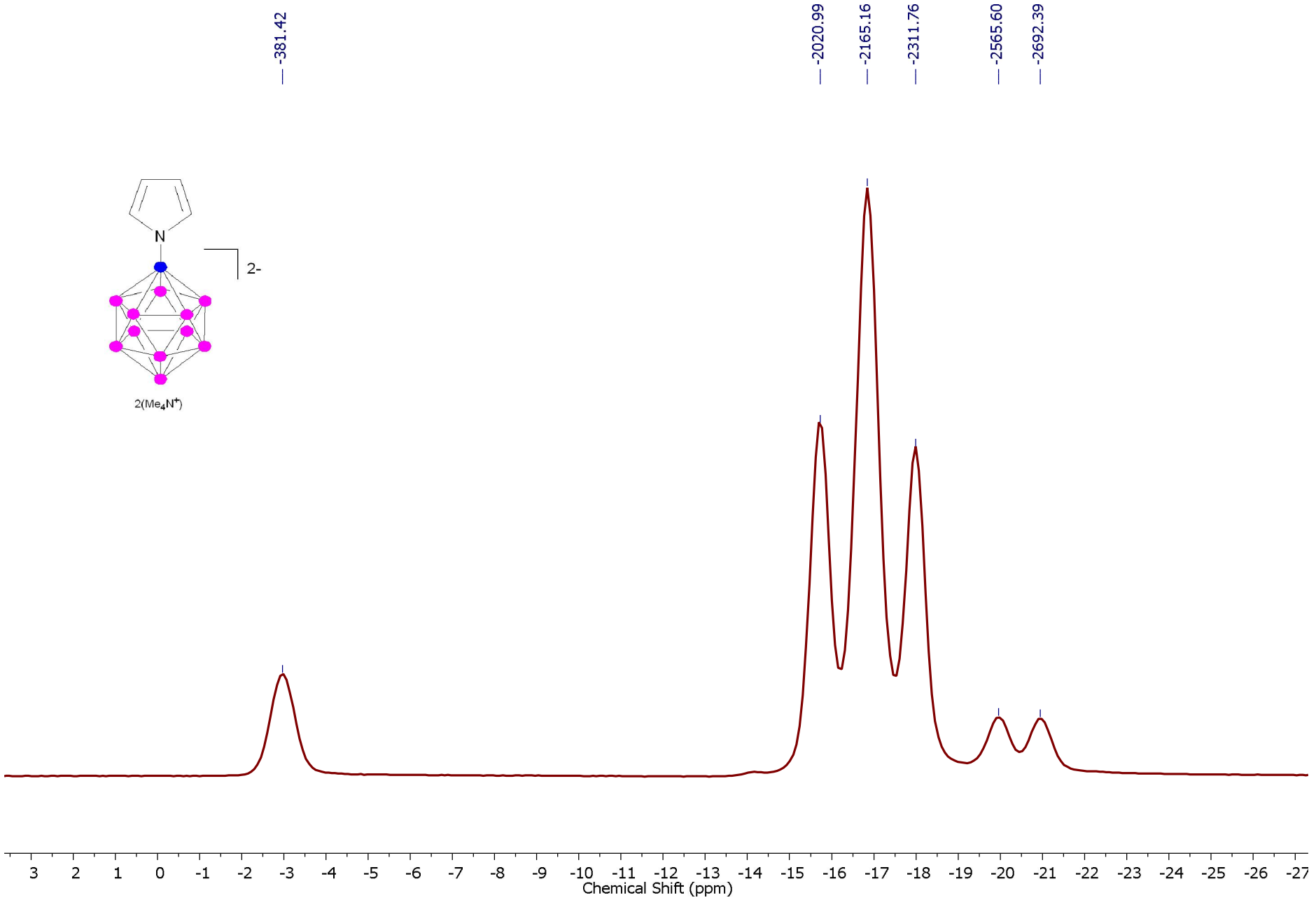
^{13}C NMR spectrum of 4 in CD_3CN at 298K



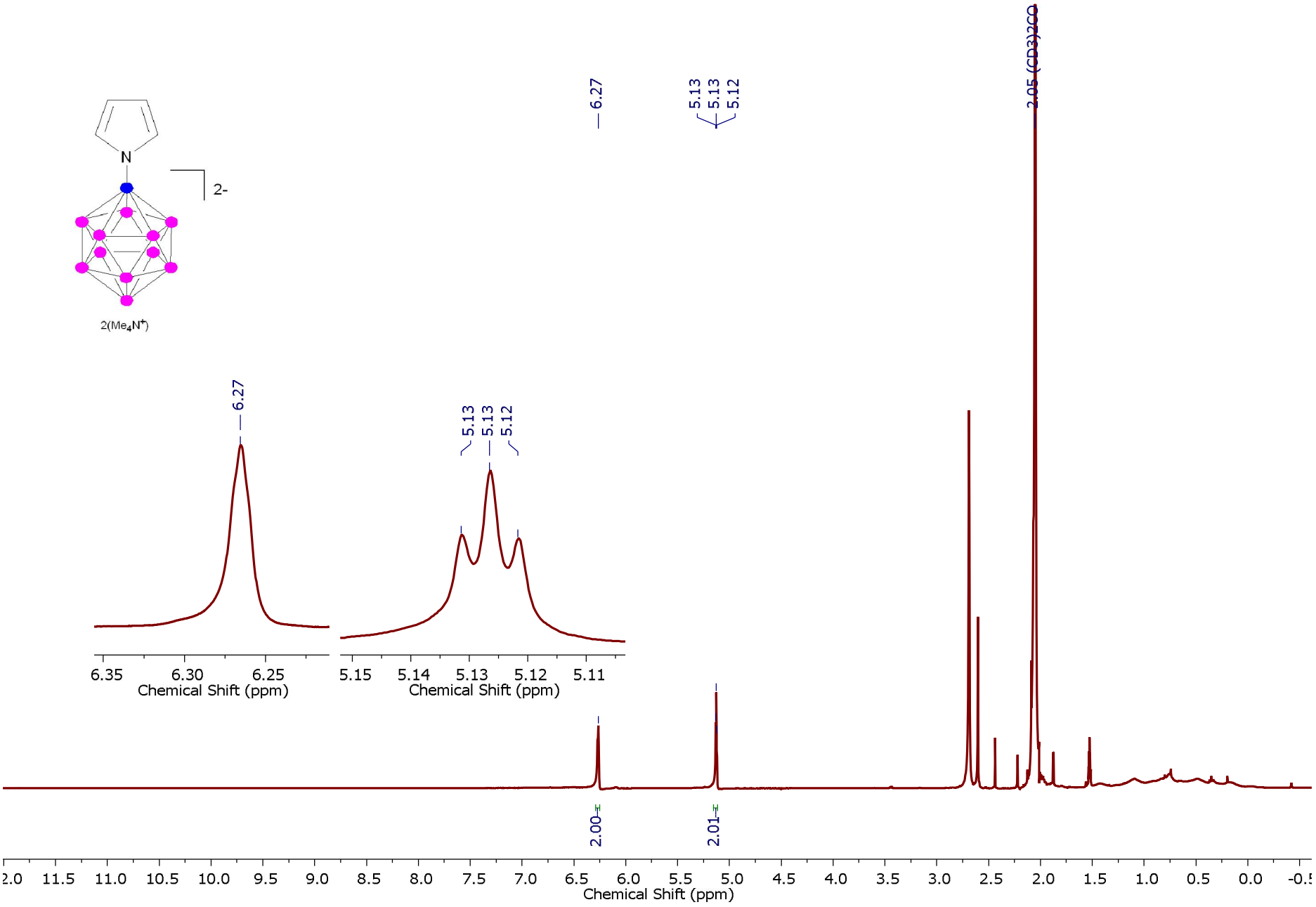
$^{11}B\{^1H\}$ NMR spectrum of 5a in Acetone-d_6 at 298K



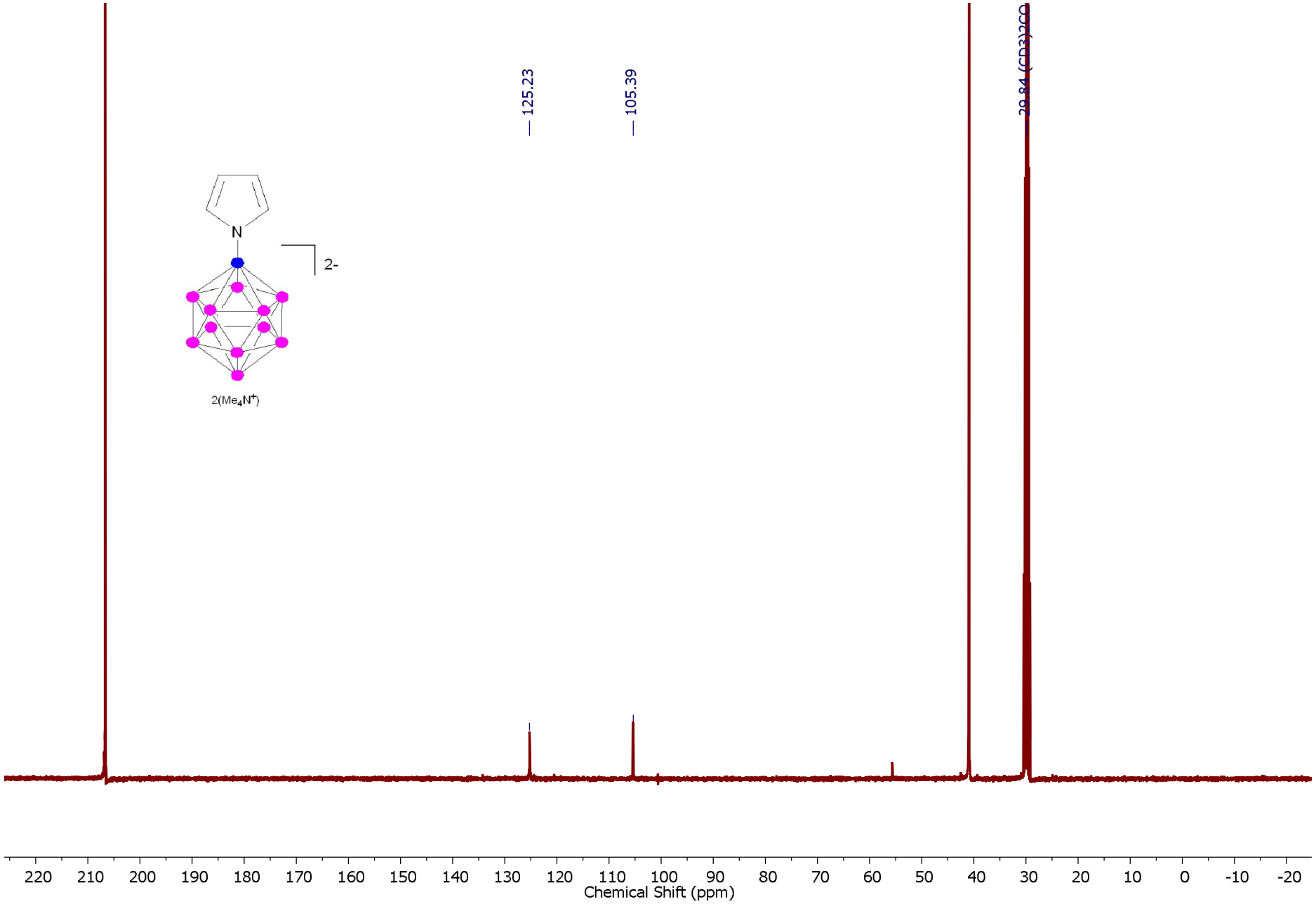
^{11}B NMR spectrum of 5a in Acetone-d_6 at 298K



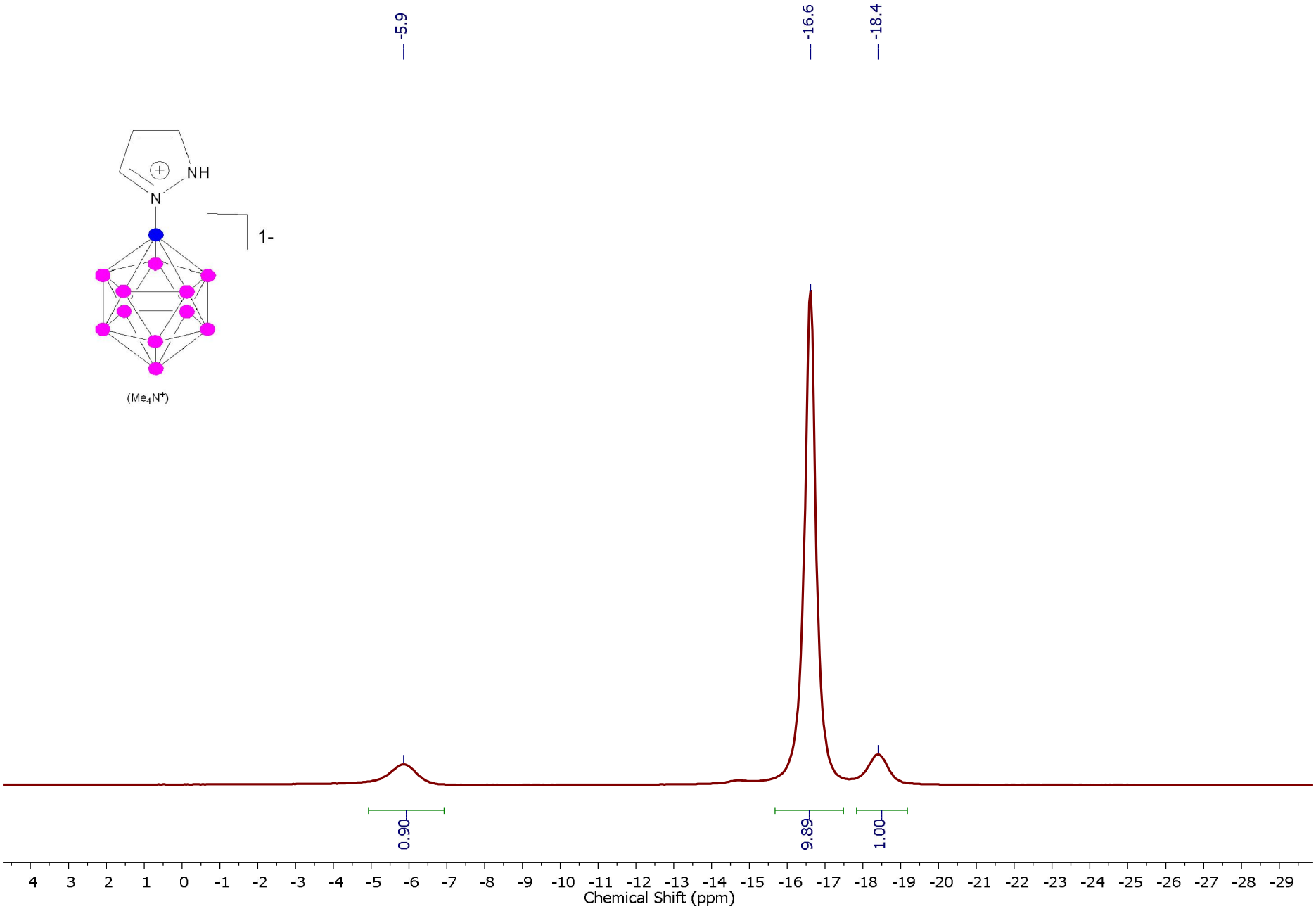
$^{1}H\{^{11}B\}$ NMR spectrum of 5a in Acetone-d_6 at 298K



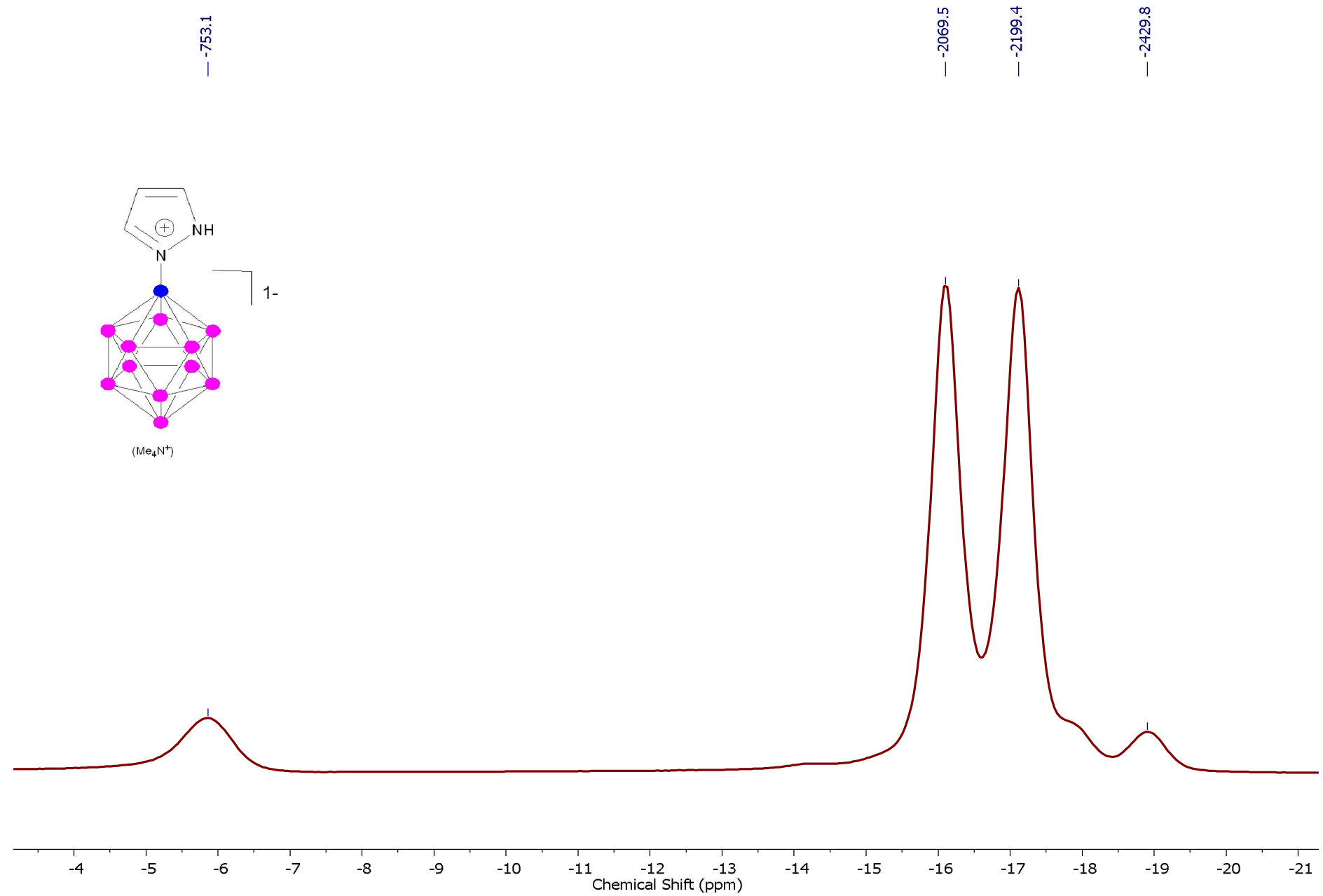
^{13}C NMR spectrum of 5a in Acetone-d_6 at 298K



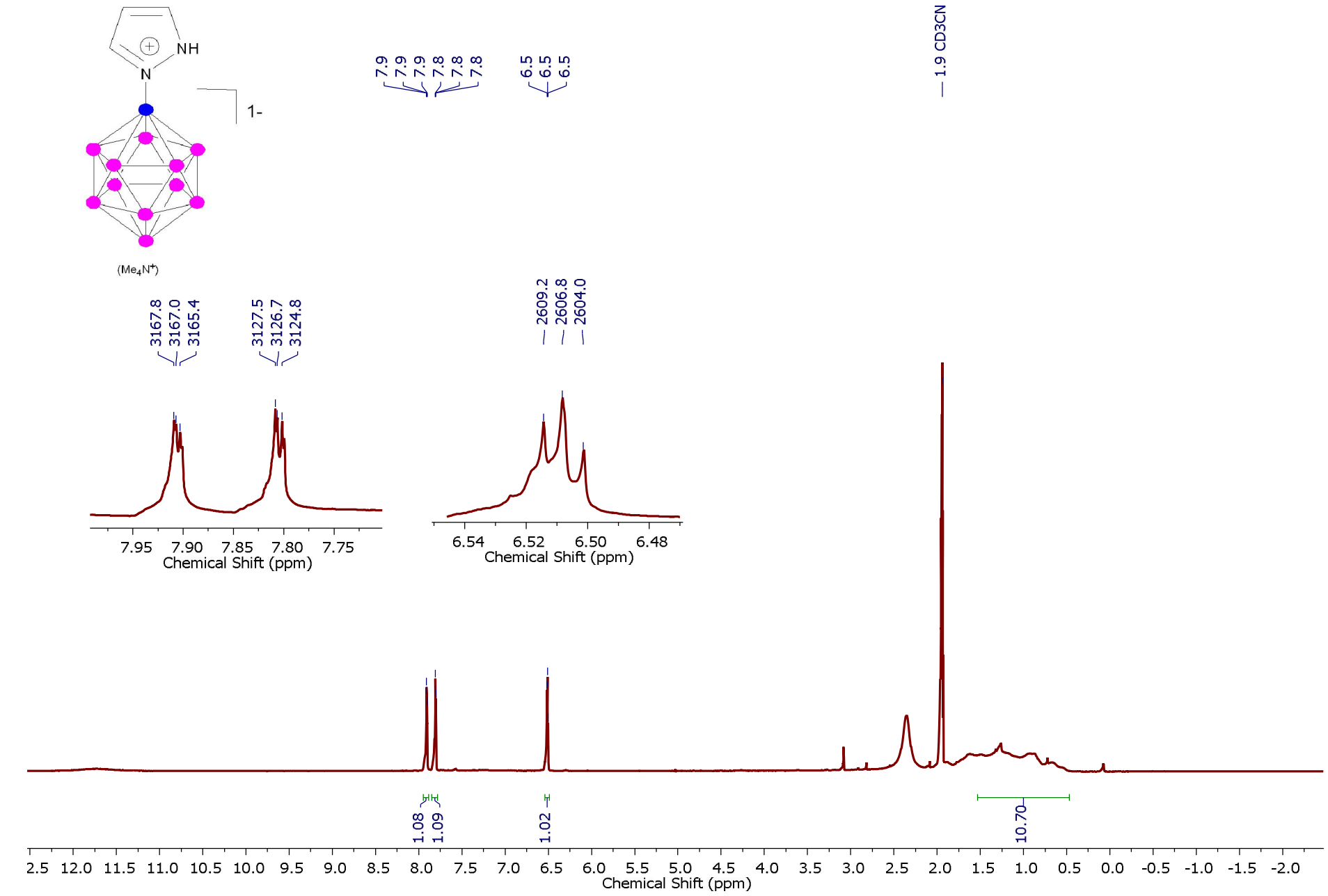
$^{11}B\{^{1}H\}$ NMR spectrum of 5b in CD_3CN at 298K



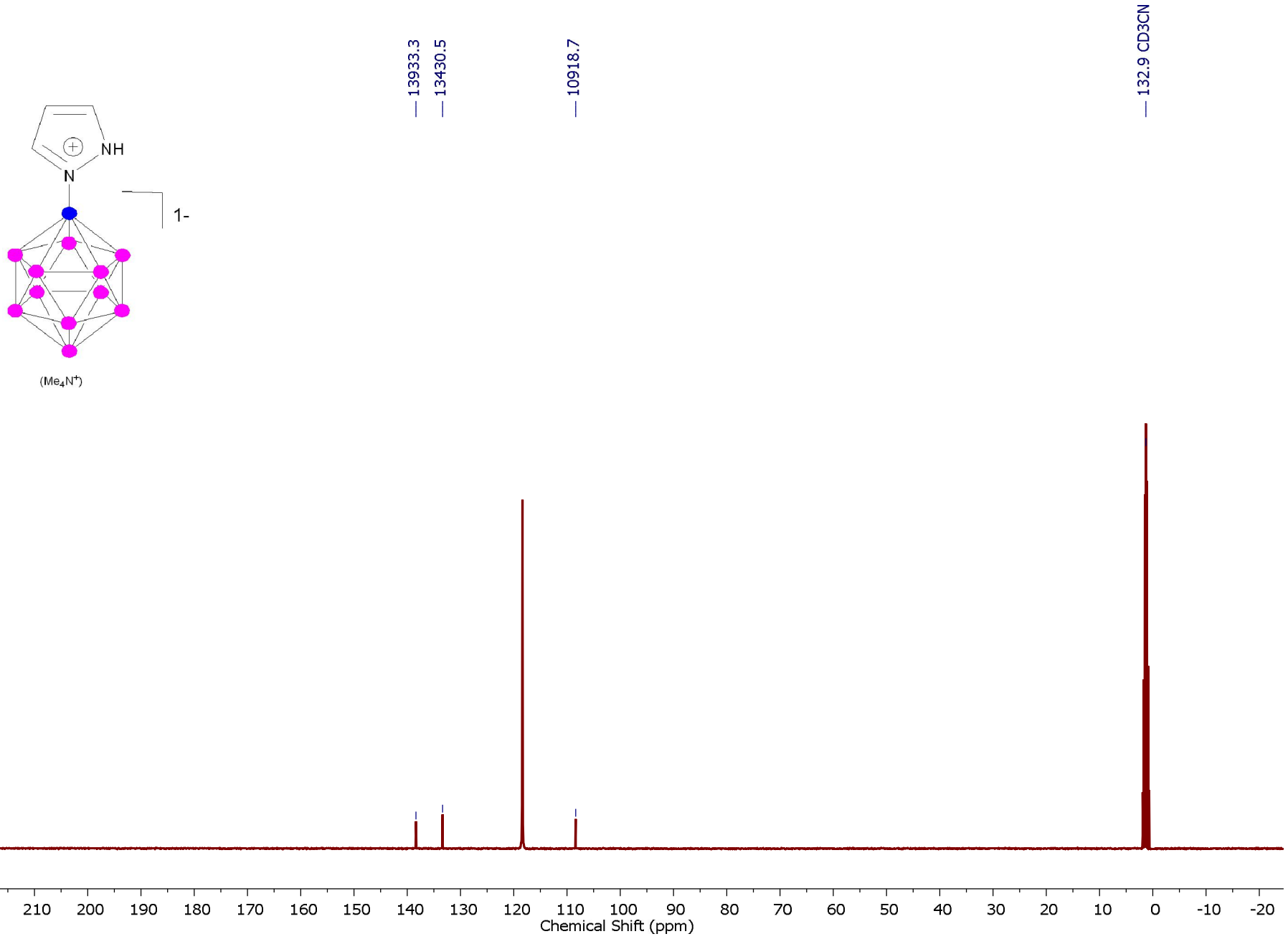
^{11}B NMR spectrum of 5b in CD_3CN at 298K



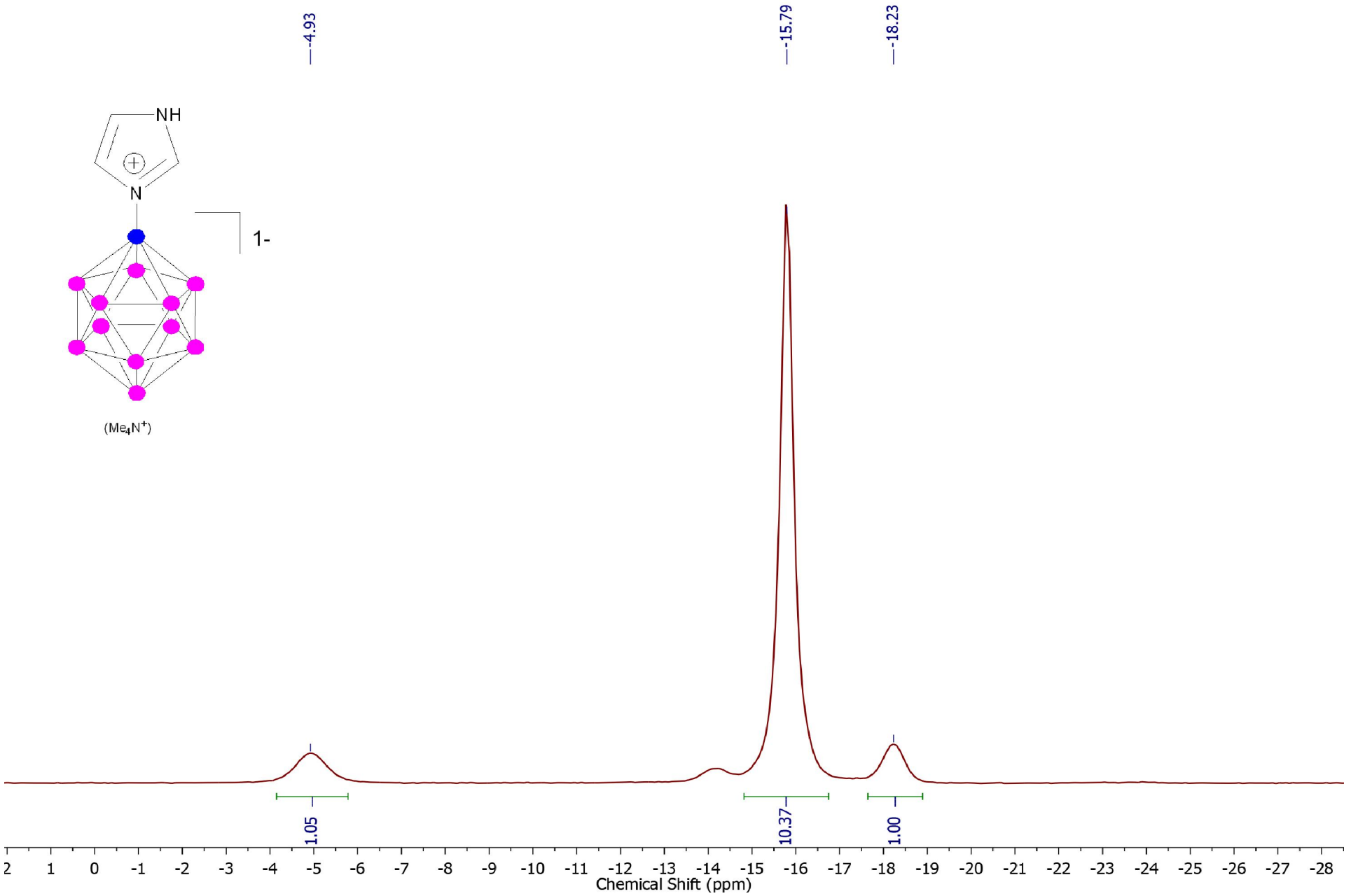
$^{1}H\{^{11}B\}$ NMR spectrum of 5b in CD_3CN at 298K



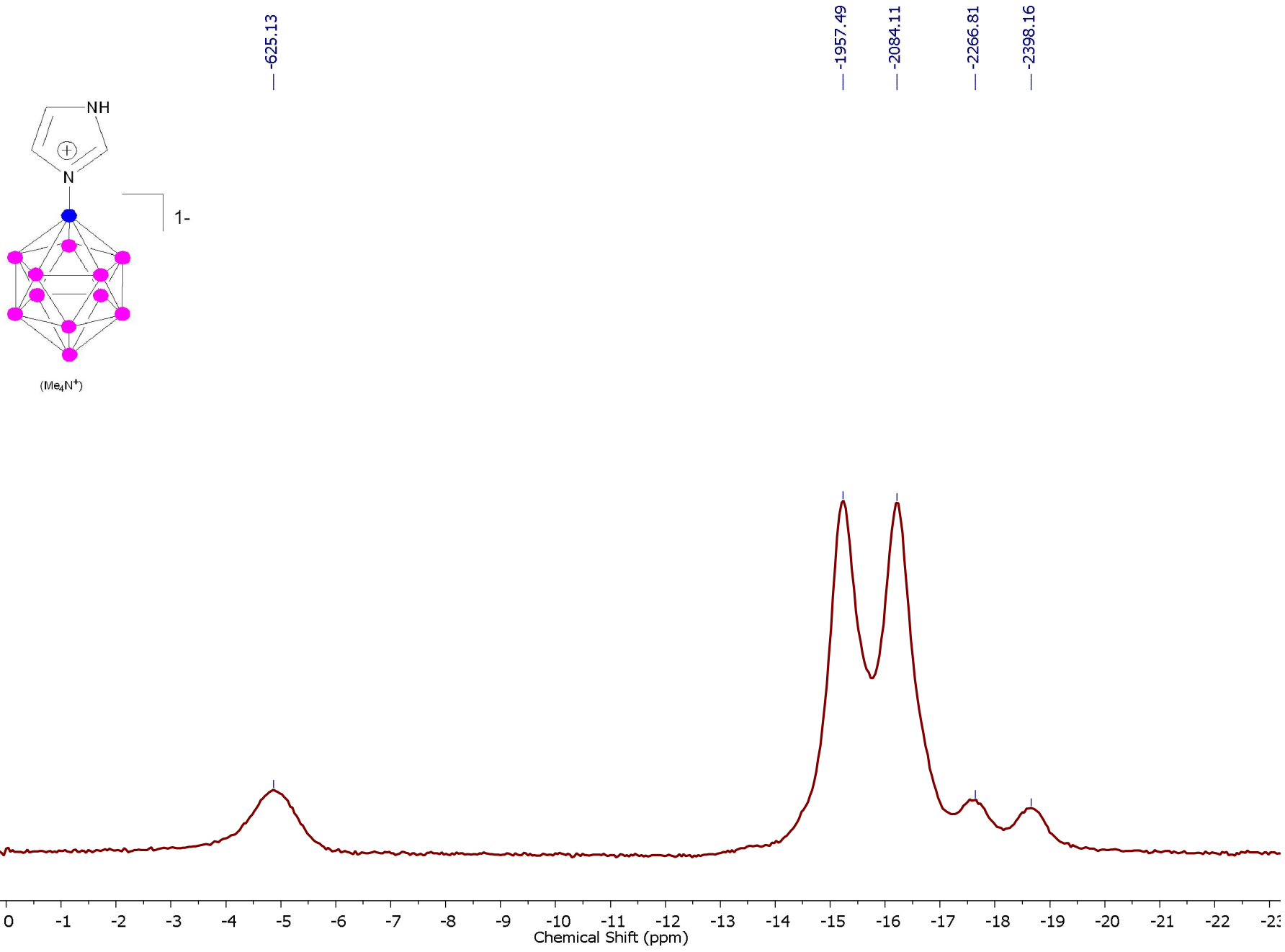
^{13}C NMR spectrum of 5b in CD_3CN at 298K



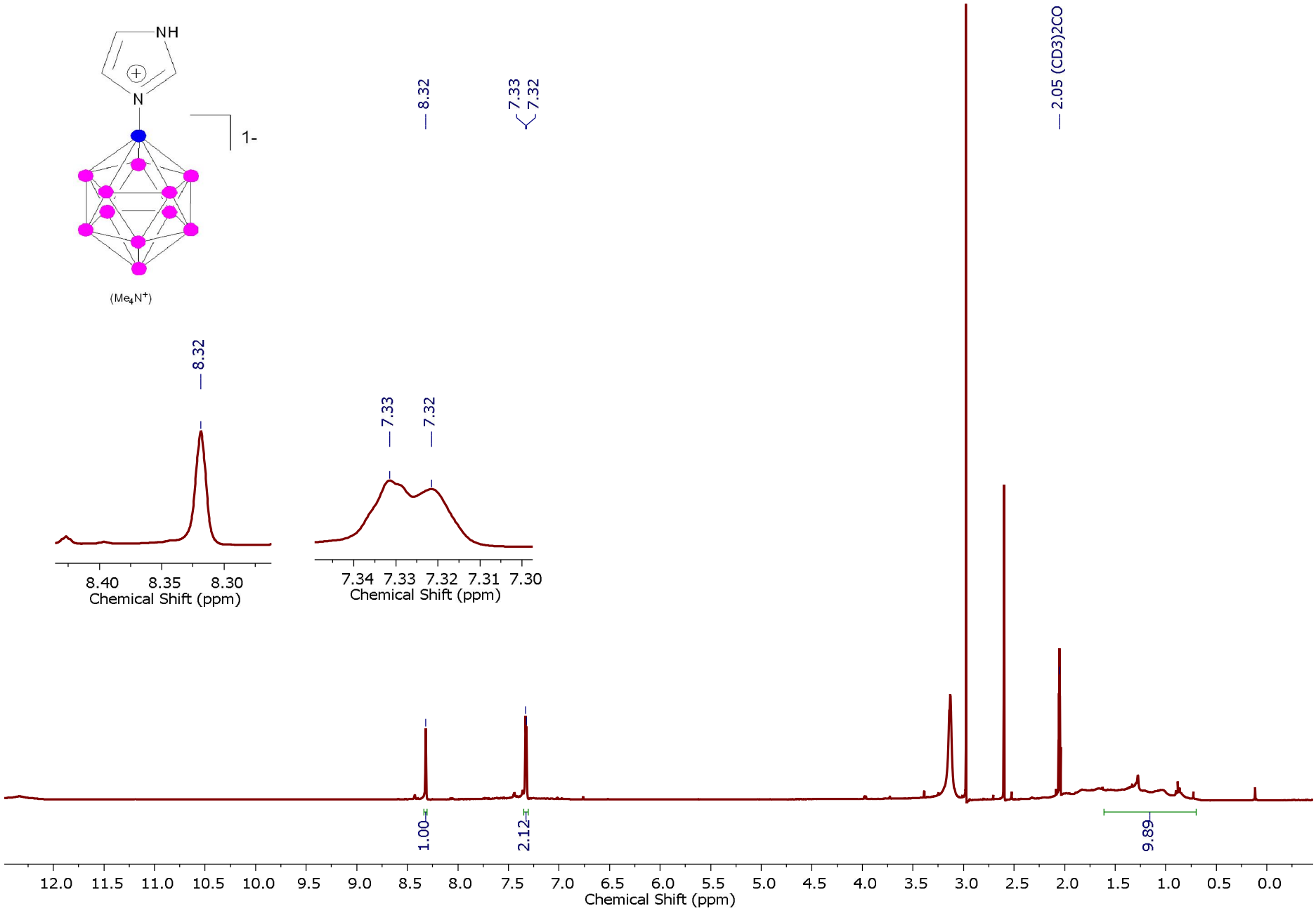
$^{11}B\{^{1}H\}$ NMR spectrum of 5c in Acetone-d_6 at 298K



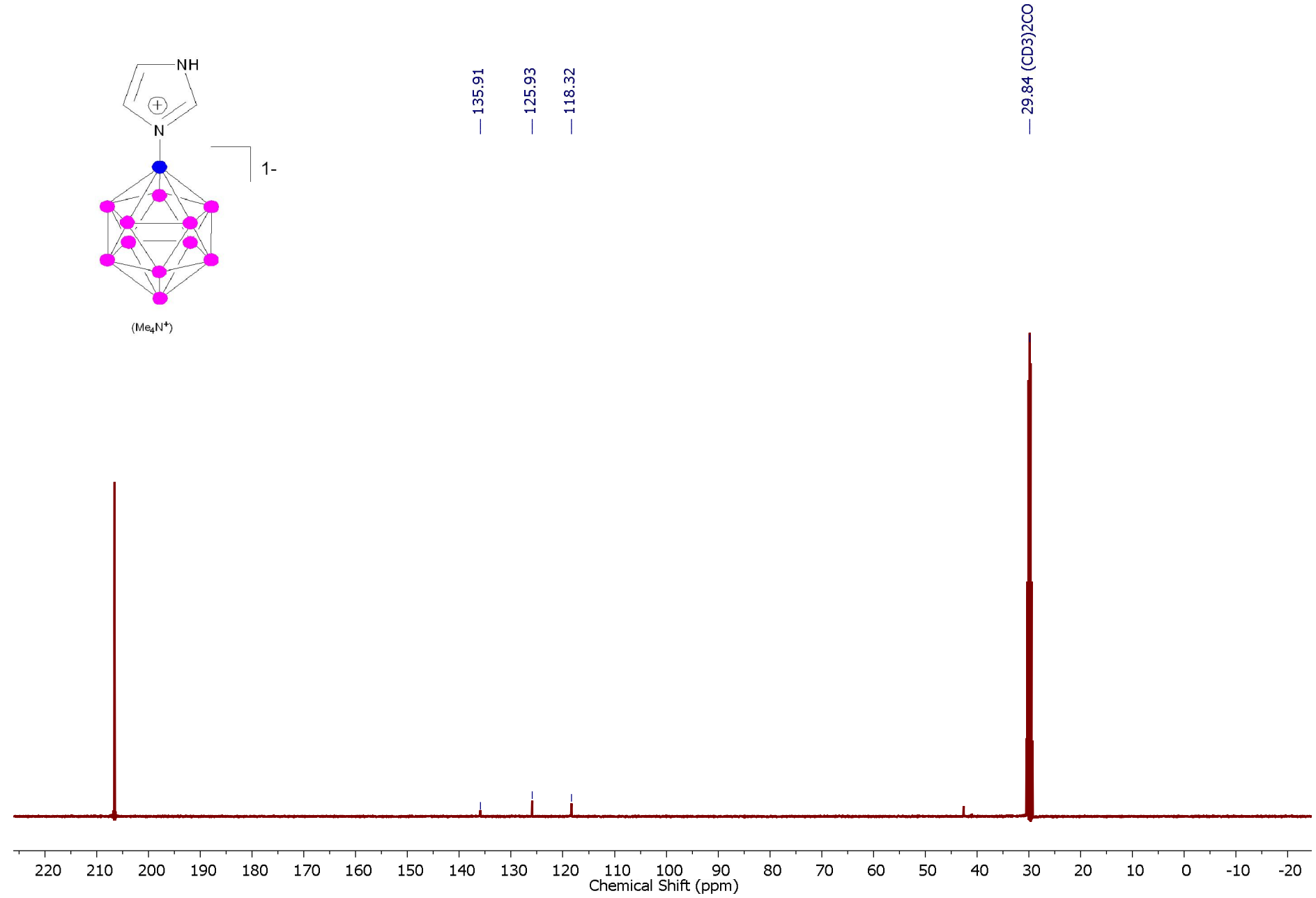
^{11}B NMR spectrum of 5c in Acetone-d_6 at 298K



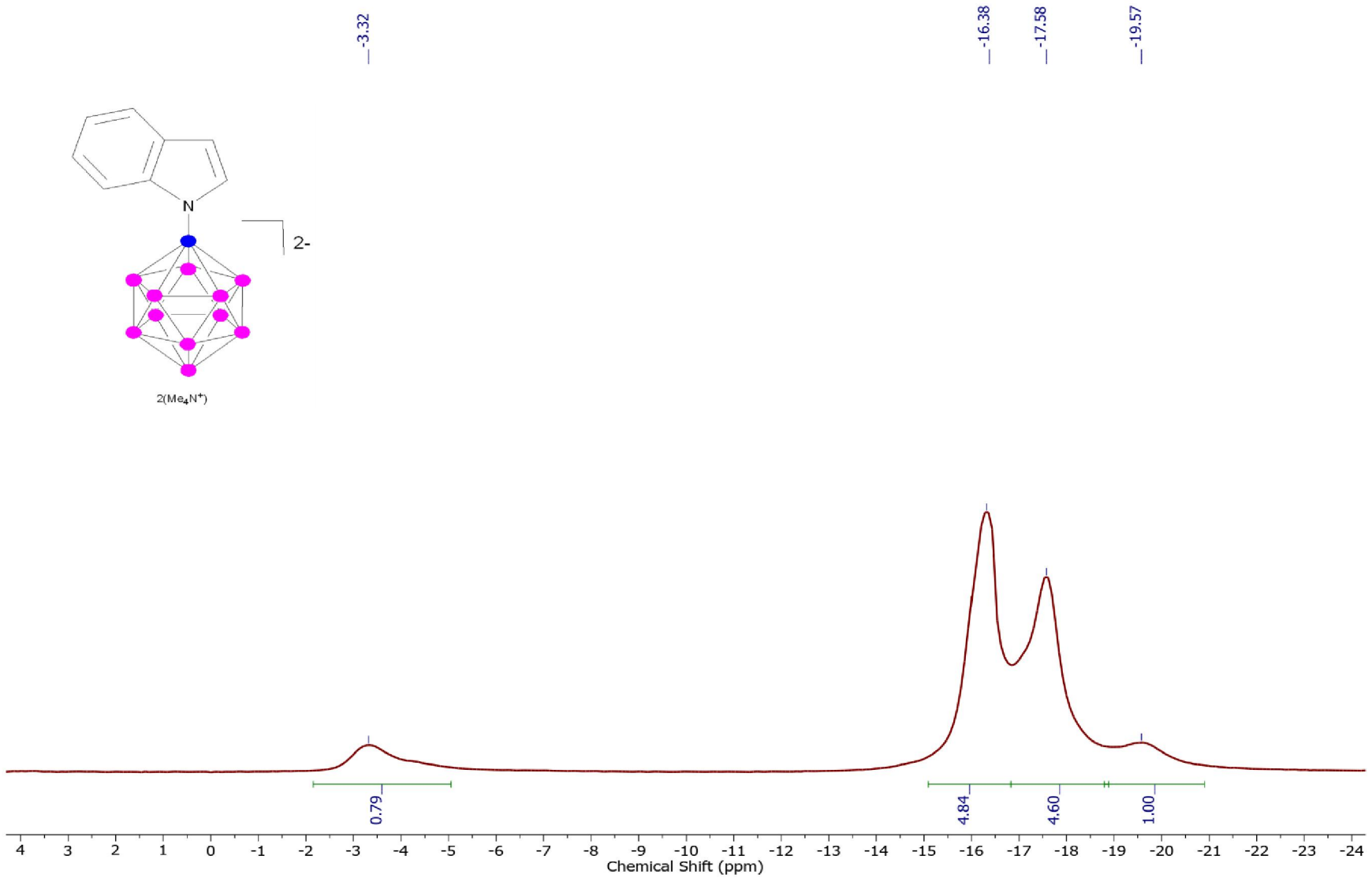
$^{1}H\{^{11}B\}$ NMR spectrum of 5c in Acetone-d_6 at 298K



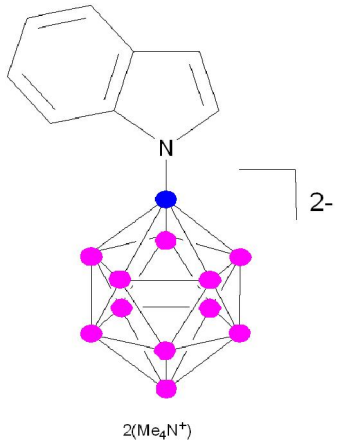
^{13}C NMR spectrum of 5c in Acetone-d_6 at 298K



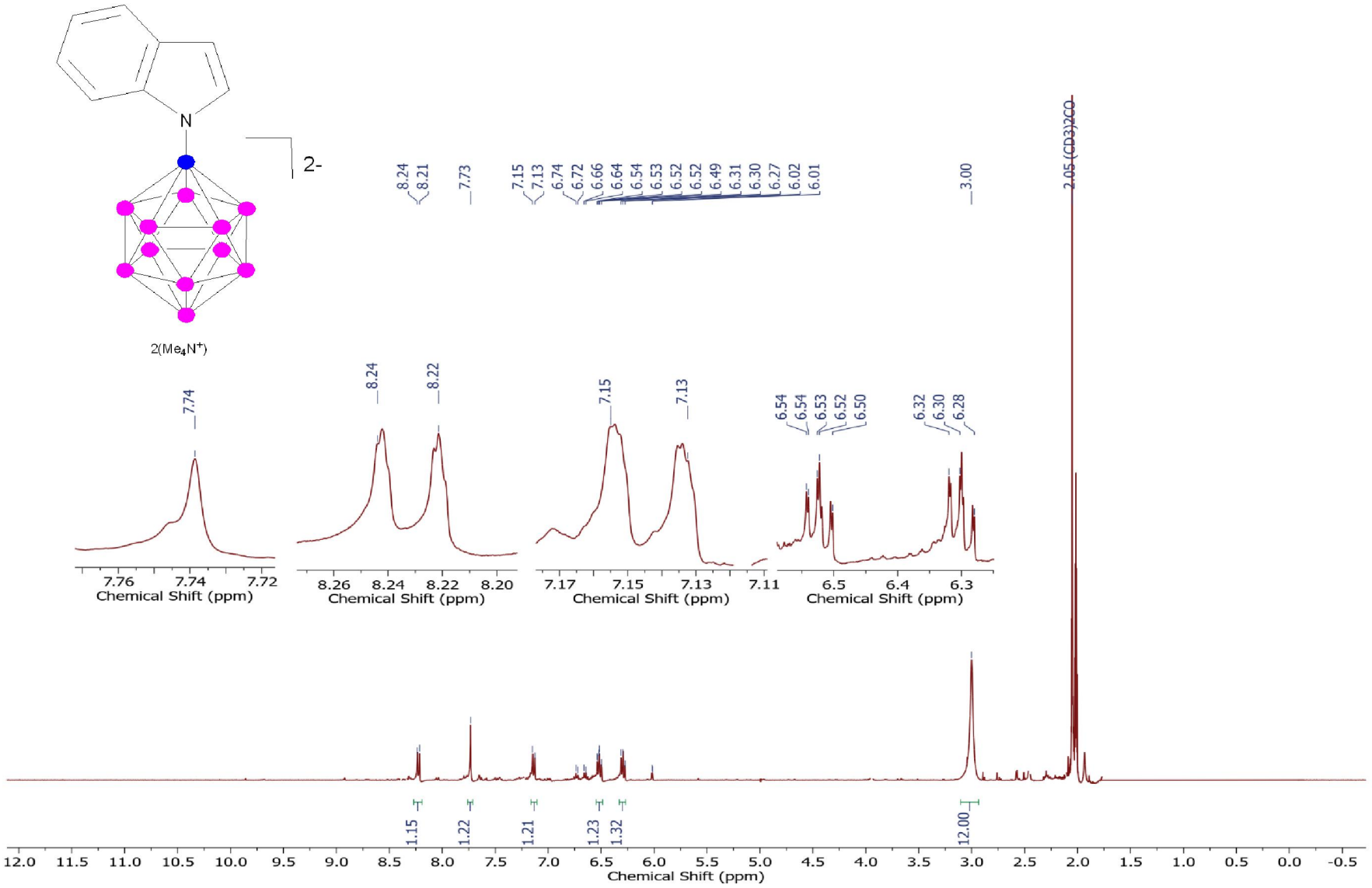
$^{11}B\{^{1}H\}$ NMR spectrum of 5d in Acetone-d_6 at 298K



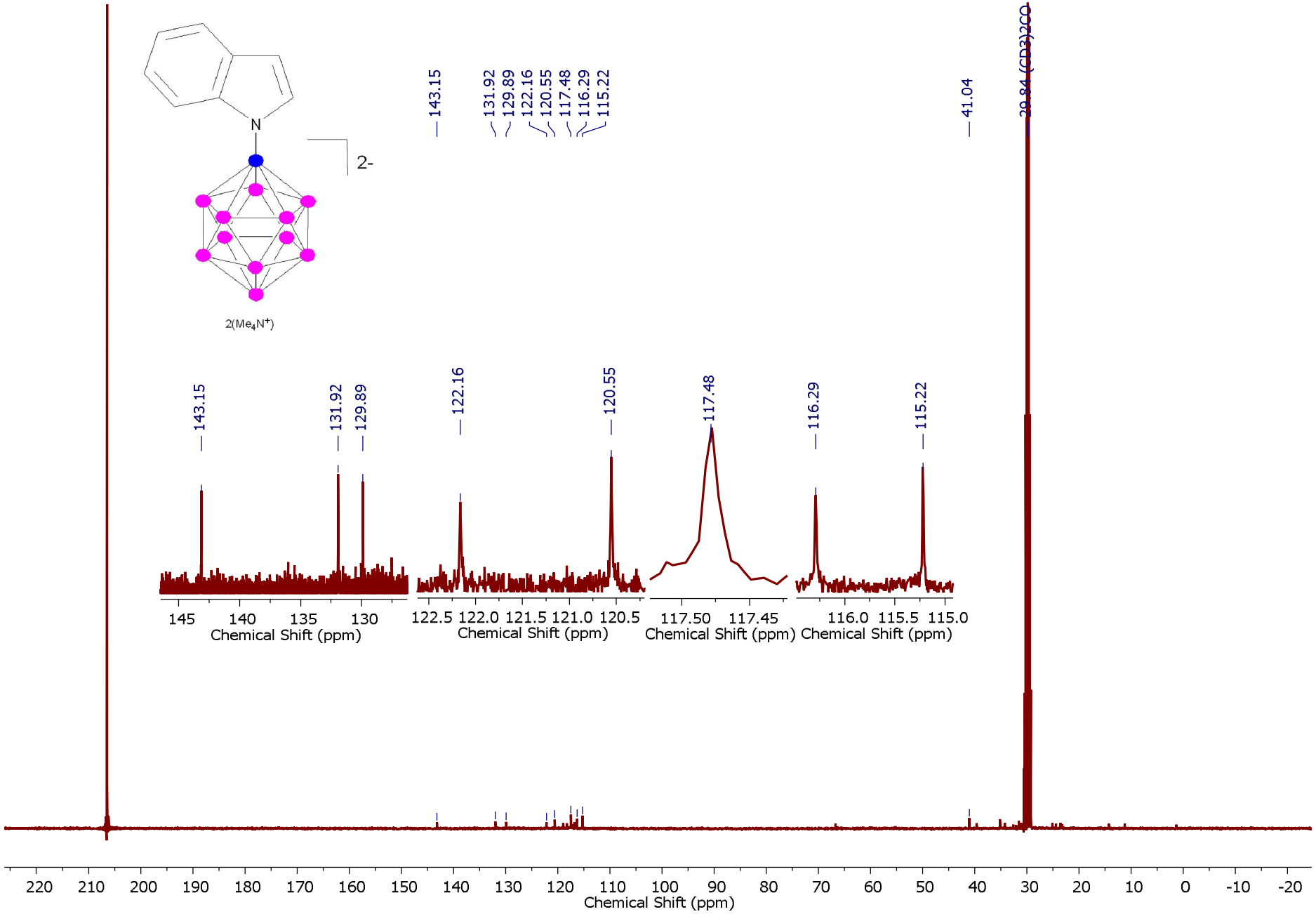
^{11}B NMR spectrum of 5d in Acetone-d_6 at 298K



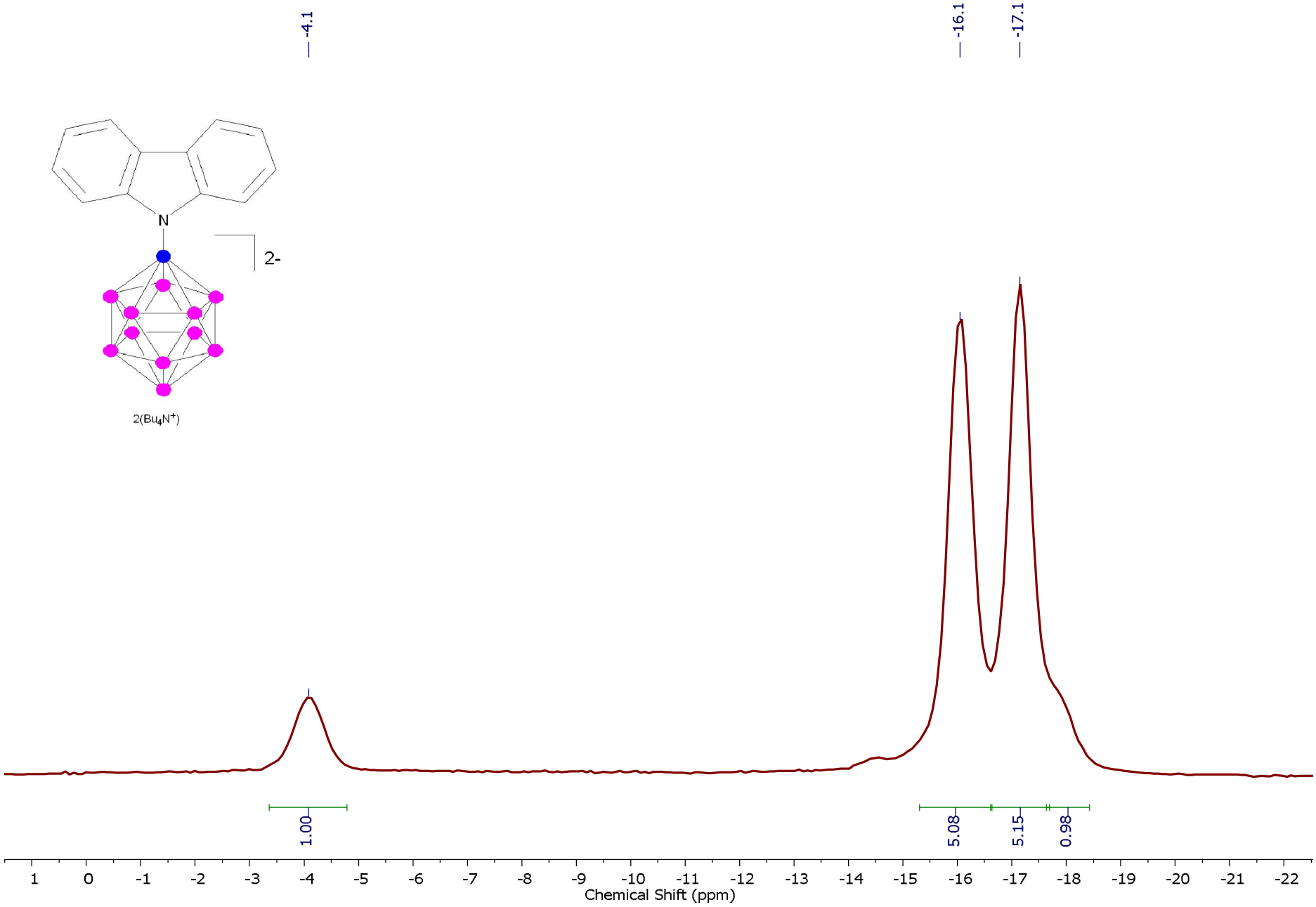
$^{1}H\{^{11}B\}$ NMR spectrum of 5d in Acetone-d_6 at 298K



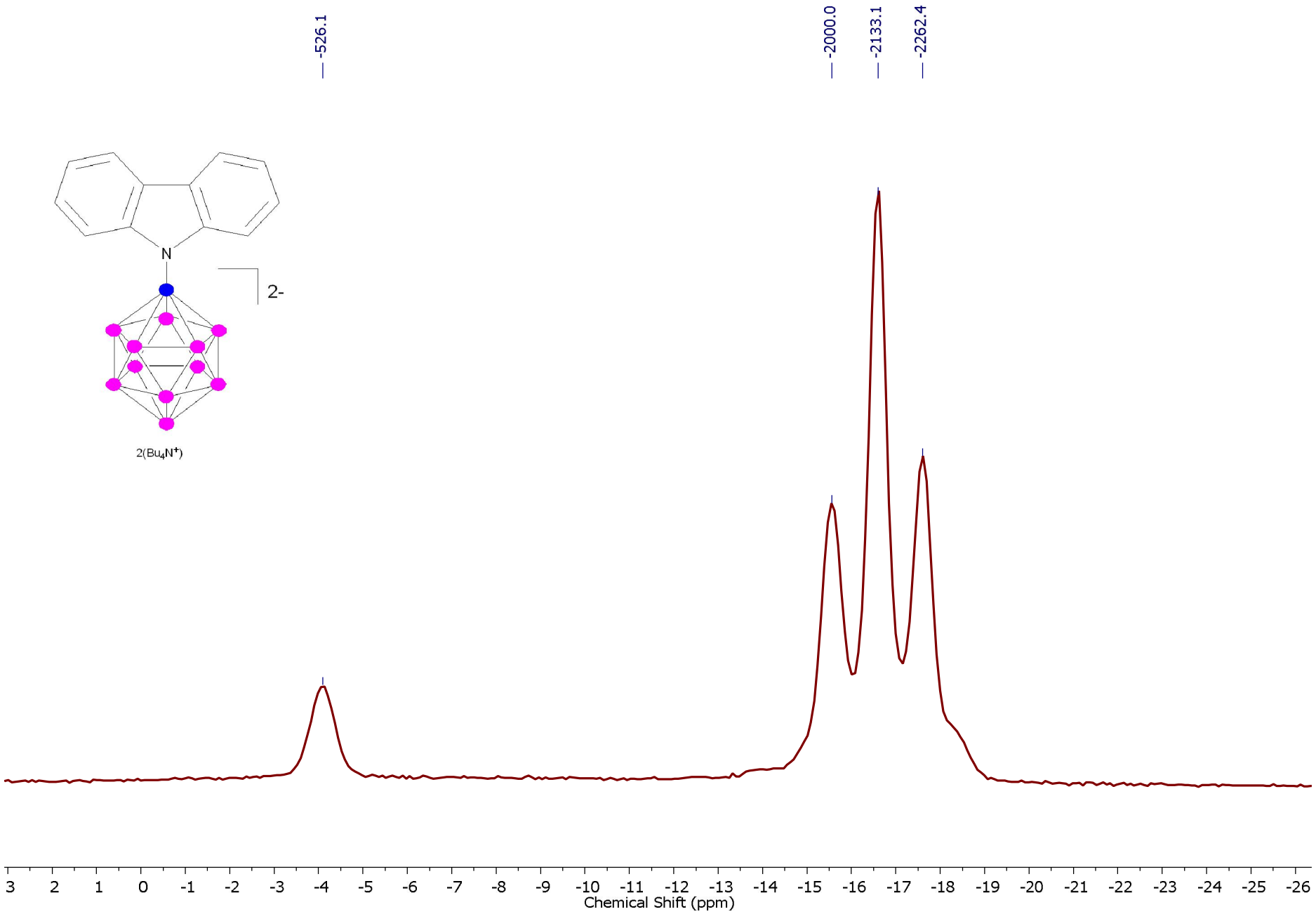
^{13}C NMR spectrum of 5d in Acetone-d_6 at 298K



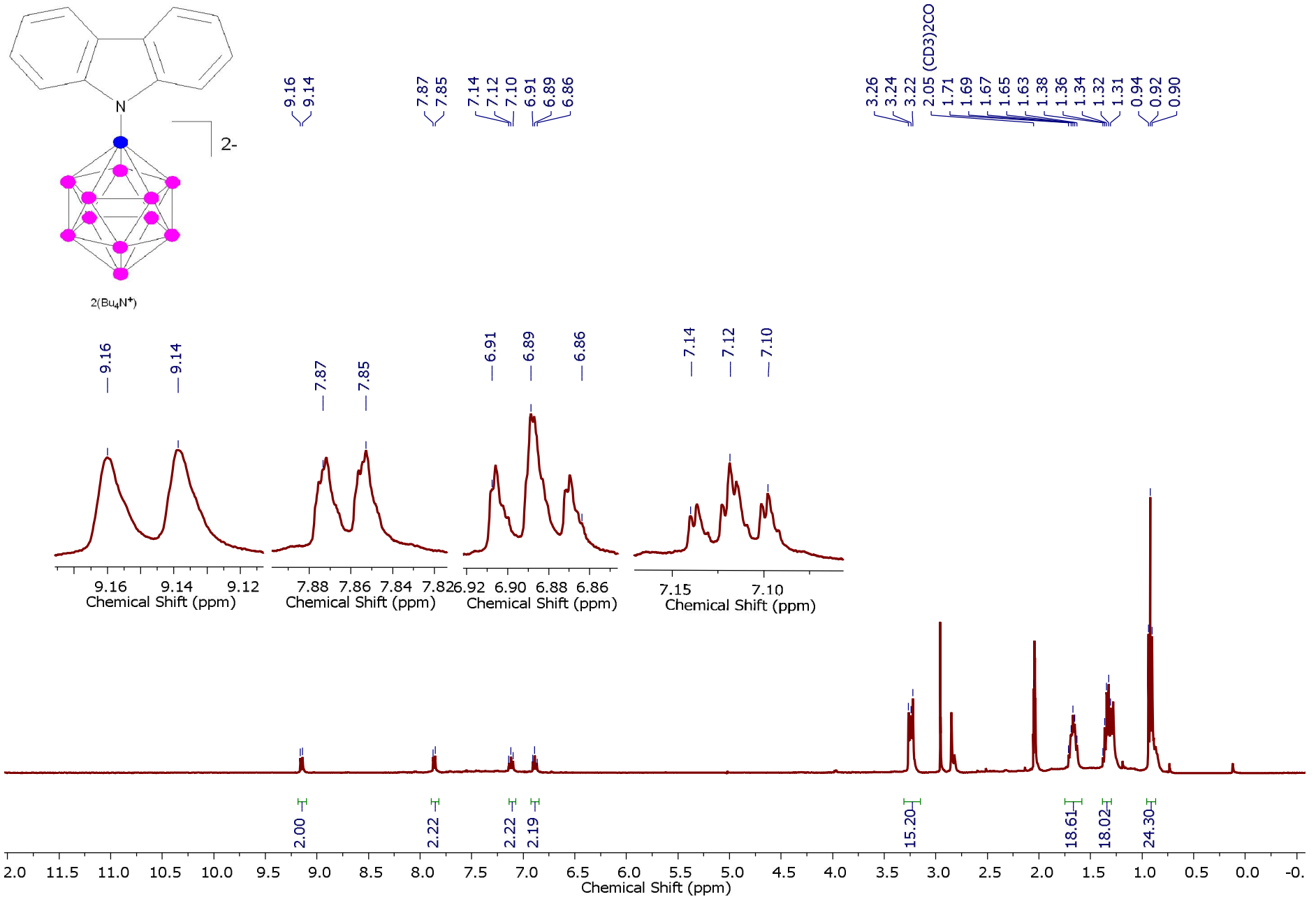
$^{11}B\{^{1}H\}$ NMR spectrum of 5e in Acetone-d_6 at 298K



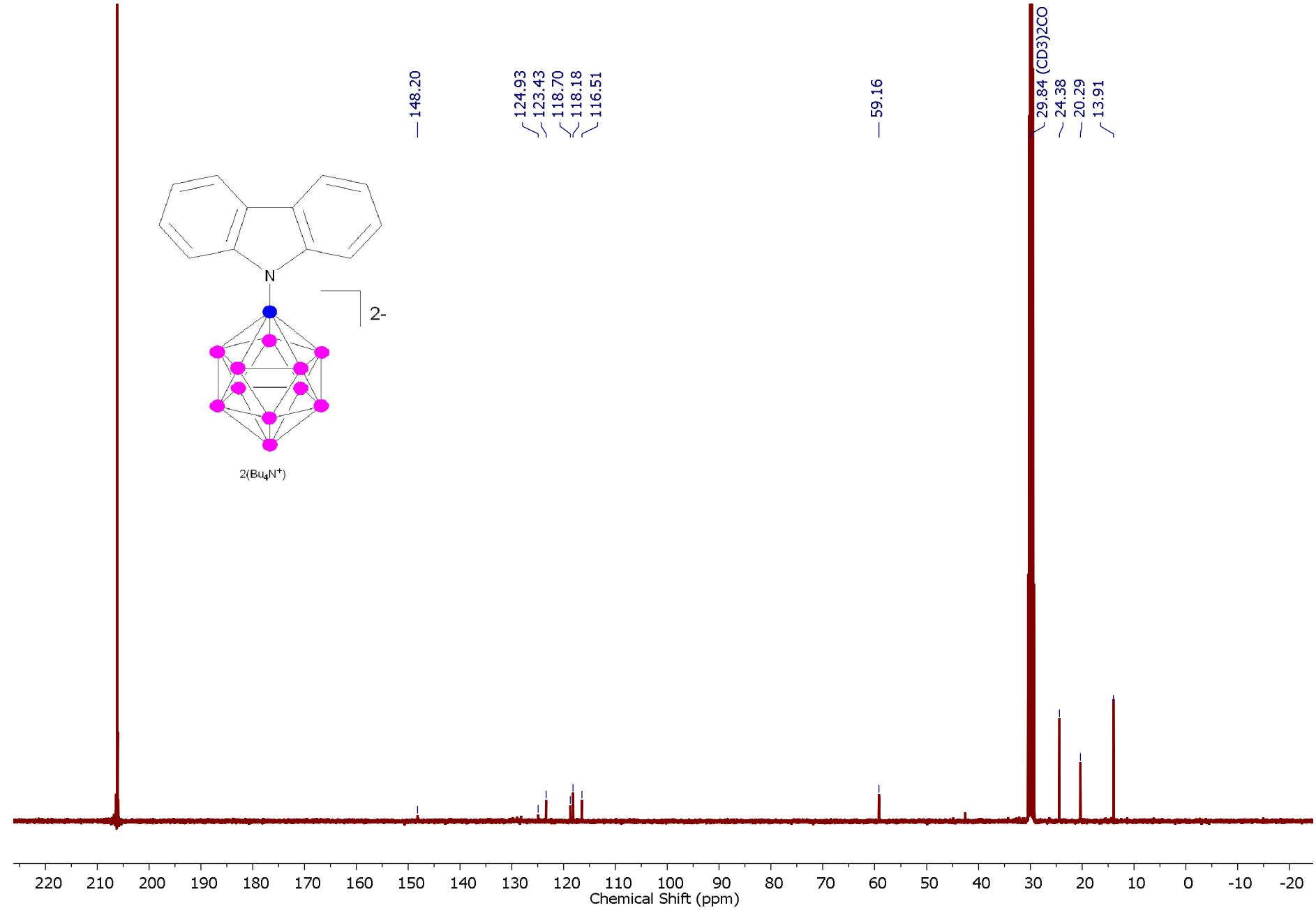
^{11}B NMR spectrum of 5e in Acetone-d_6 at 298K



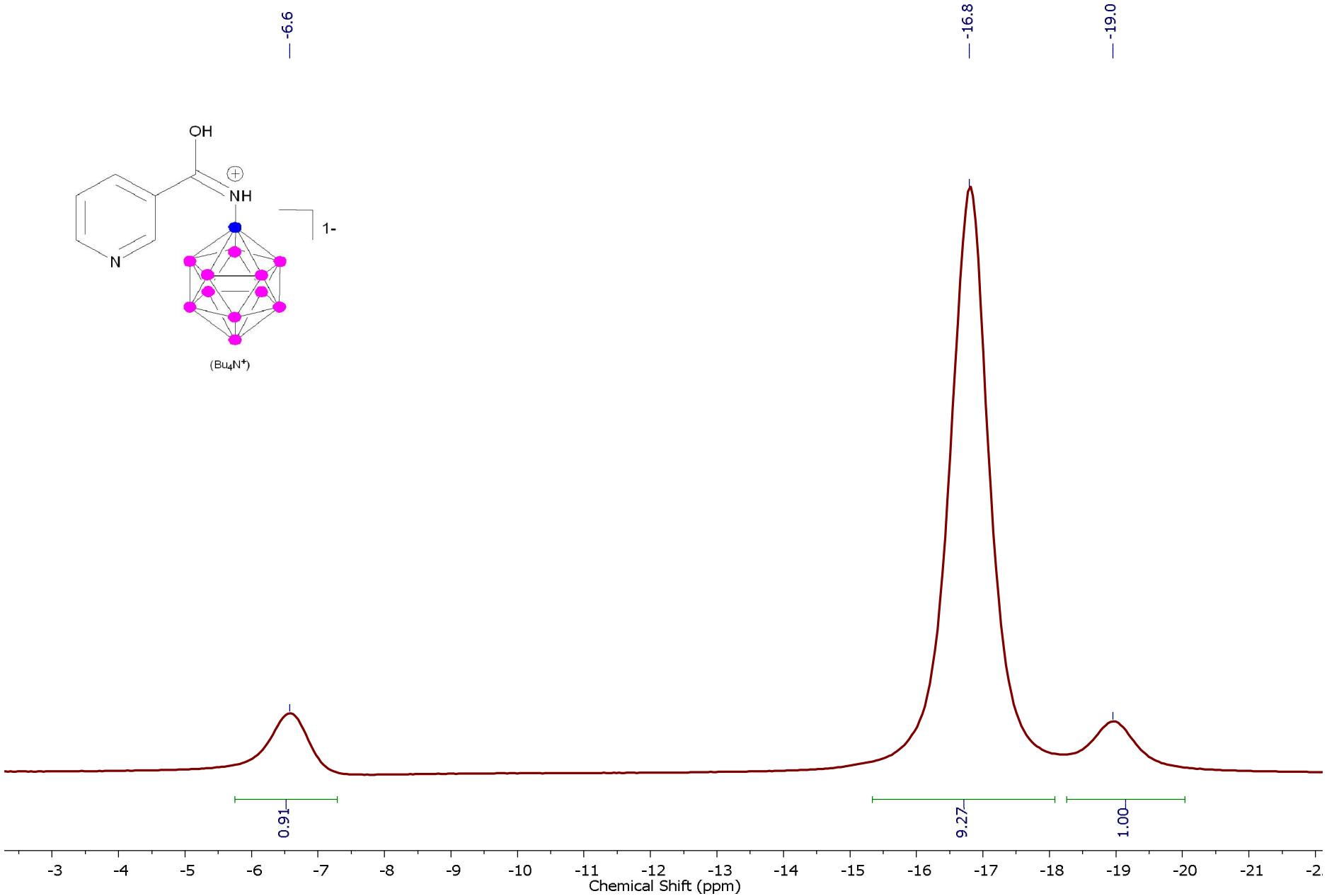
$^{1}H\{^{11}B\}$ NMR spectrum of 5e in Acetone-d_6 at 298K



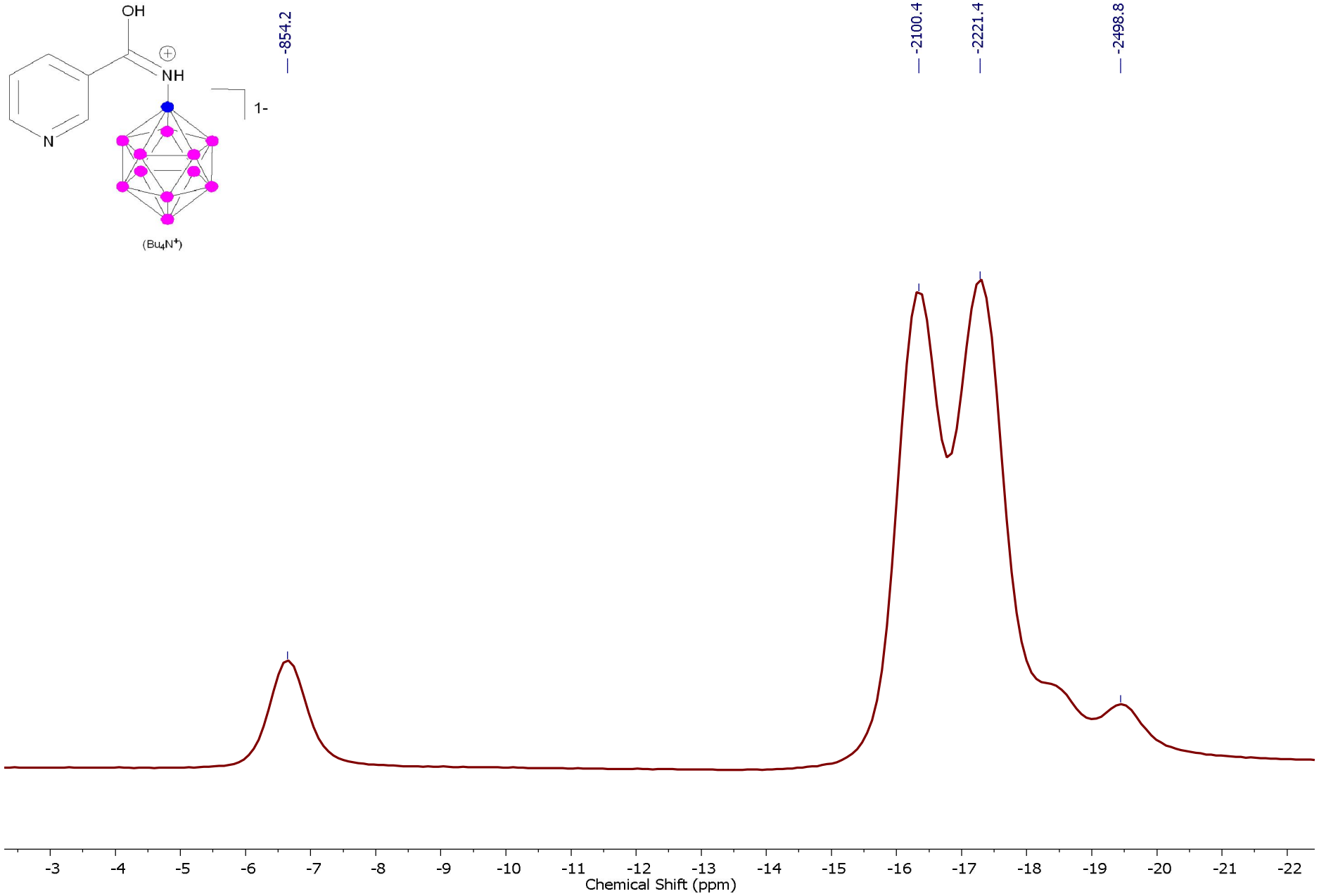
^{13}C NMR spectrum of 5e in Acetone-d_6 at 298K



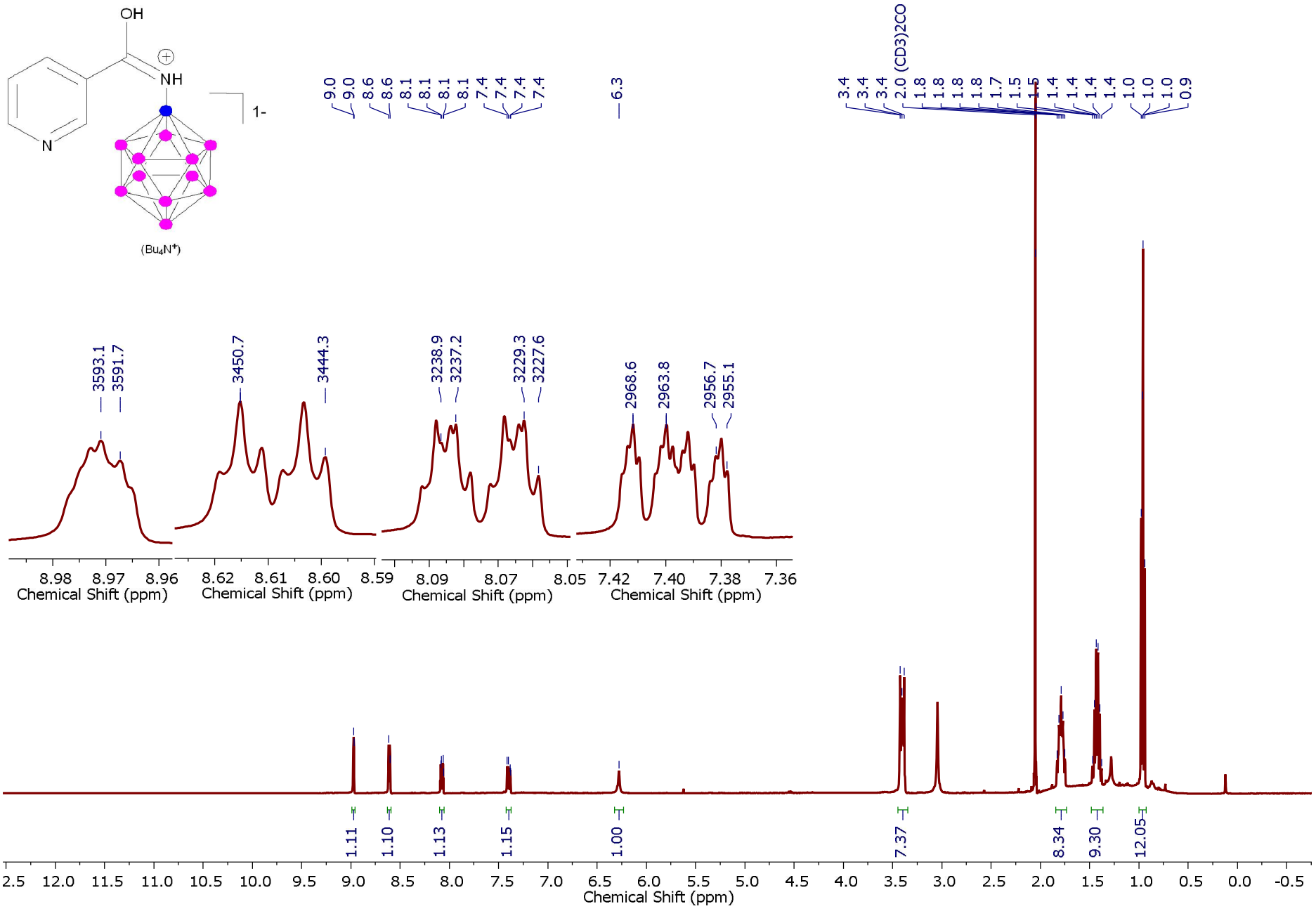
$^{11}B\{^{1}H\}$ NMR spectrum of 6a in Acetone-d_6 at 298K



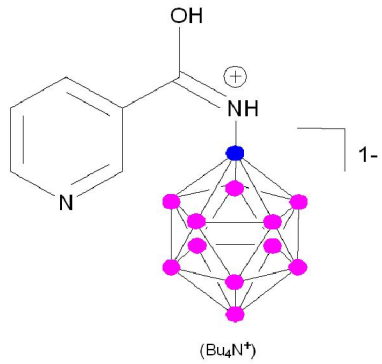
^{11}B NMR spectrum of 6a in Acetone-d_6 at 298K



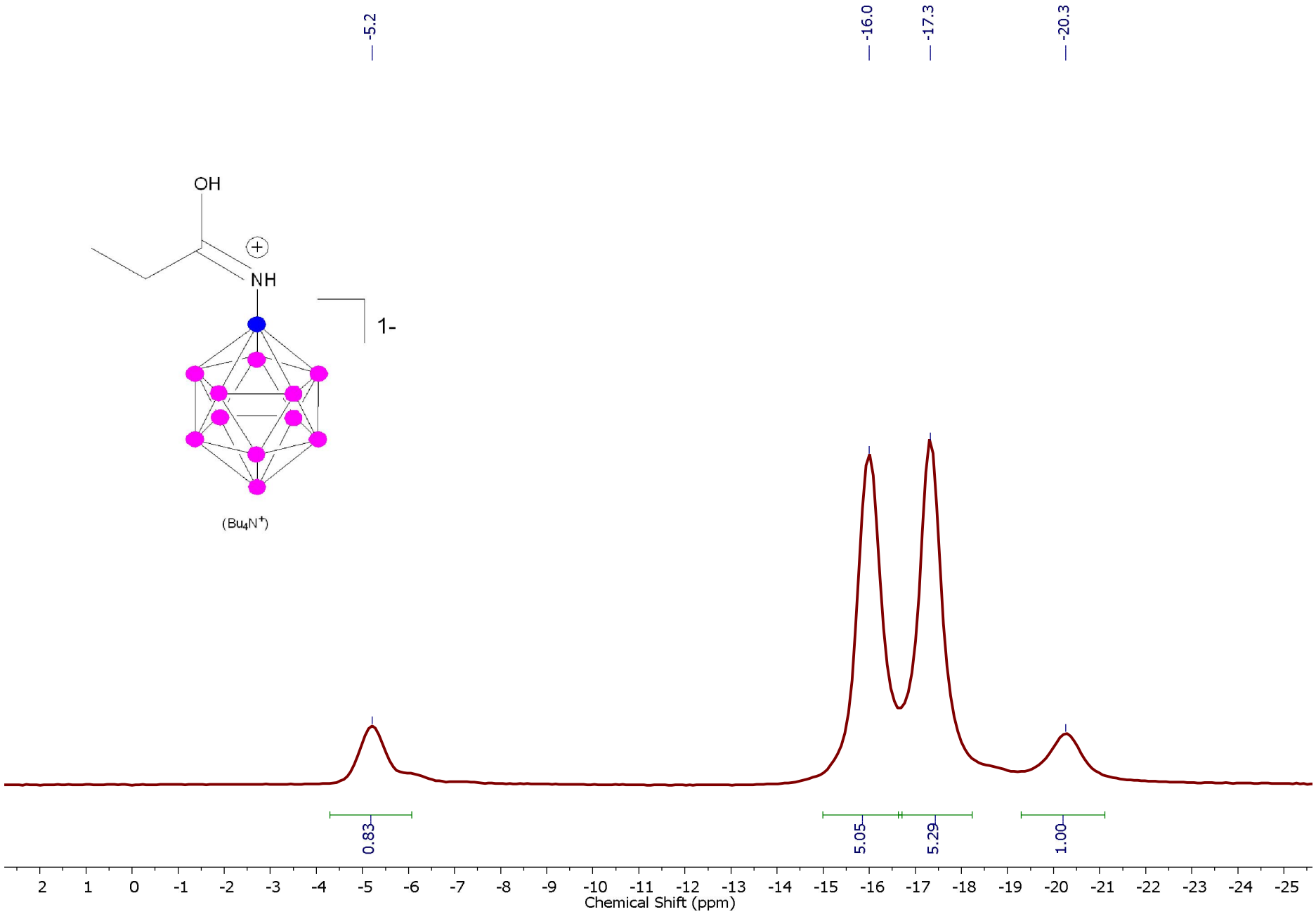
$^{1}H\{^{11}B\}$ NMR spectrum of 6ain Acetone-d_6 at 298K



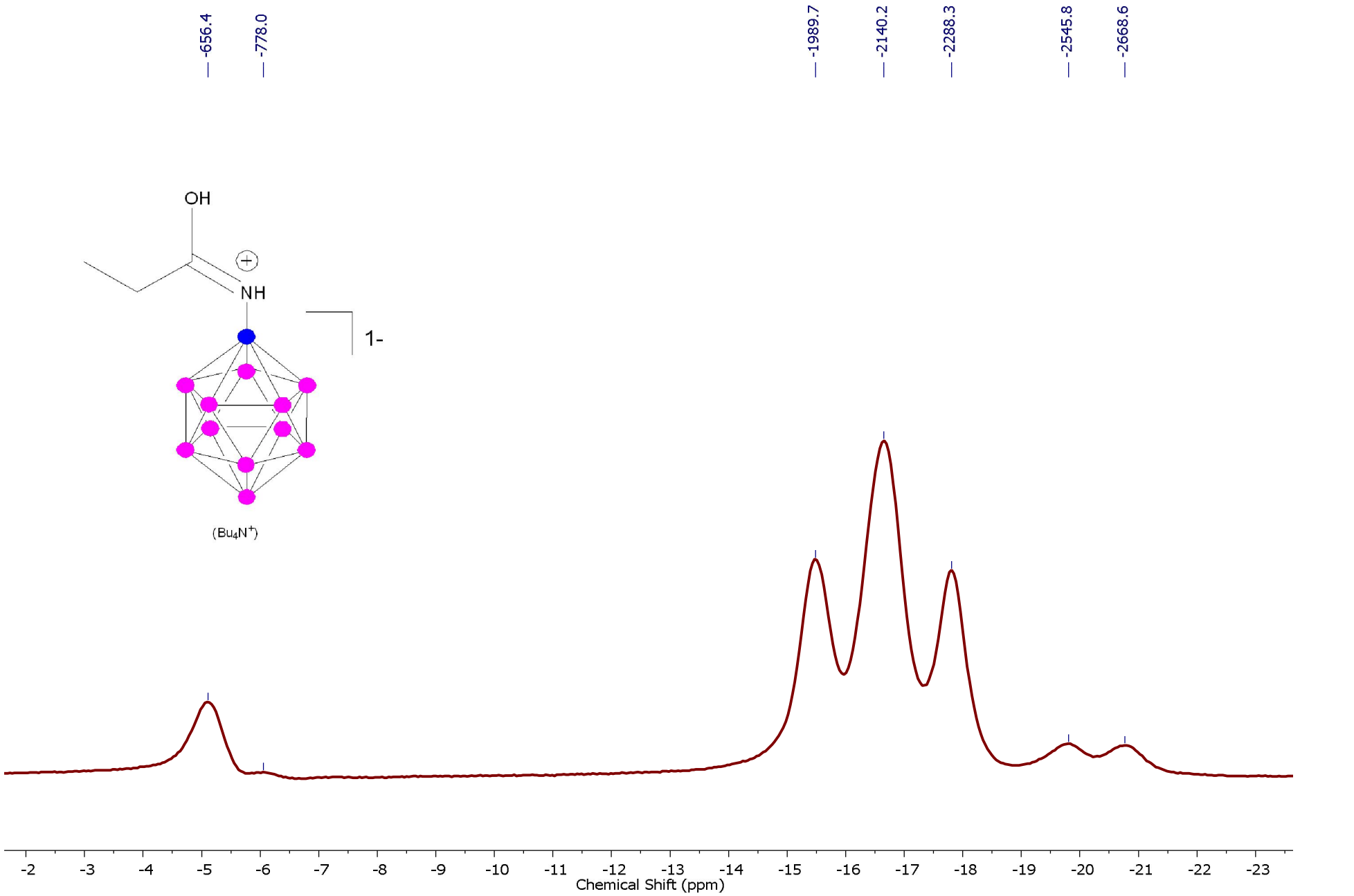
^{13}C NMR spectrum of 6a in Acetone-d_6 at 298K



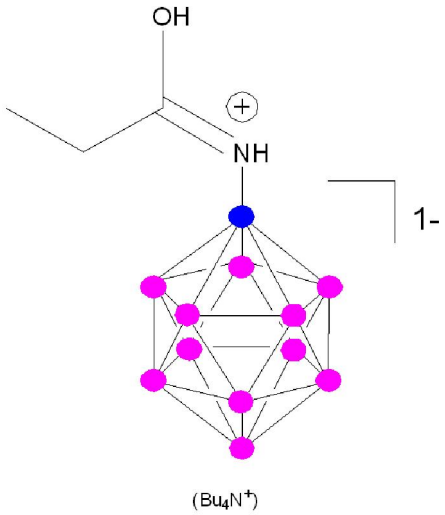
$^{11}B\{^{1}H\}$ NMR spectrum of 6b in CD_3CN at 298K



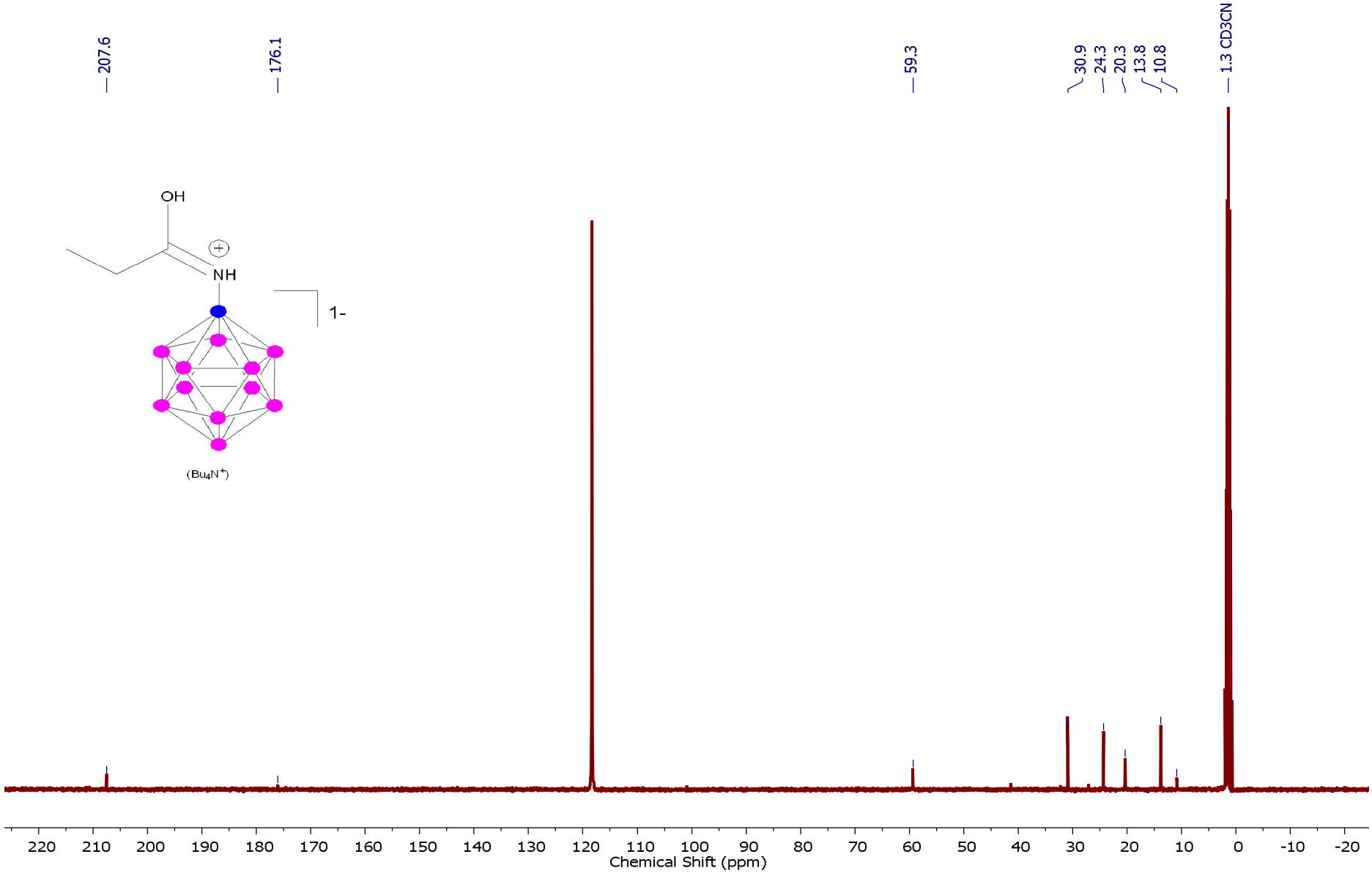
^{11}B NMR spectrum of 6b in CD_3CN at 298K



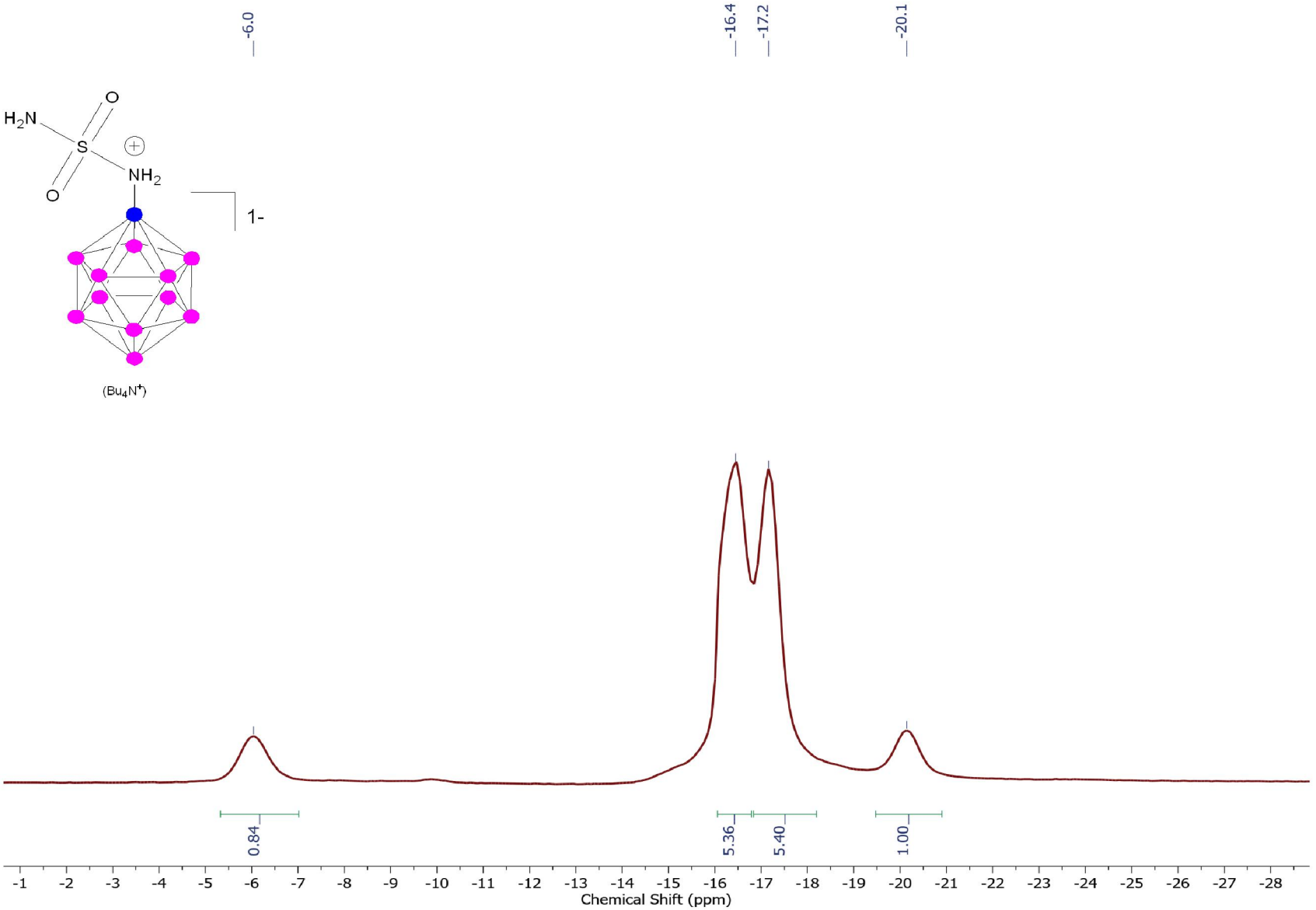
$^{1}H\{^{11}B\}$ NMR spectrum of 6b in CD_3CN at 298K



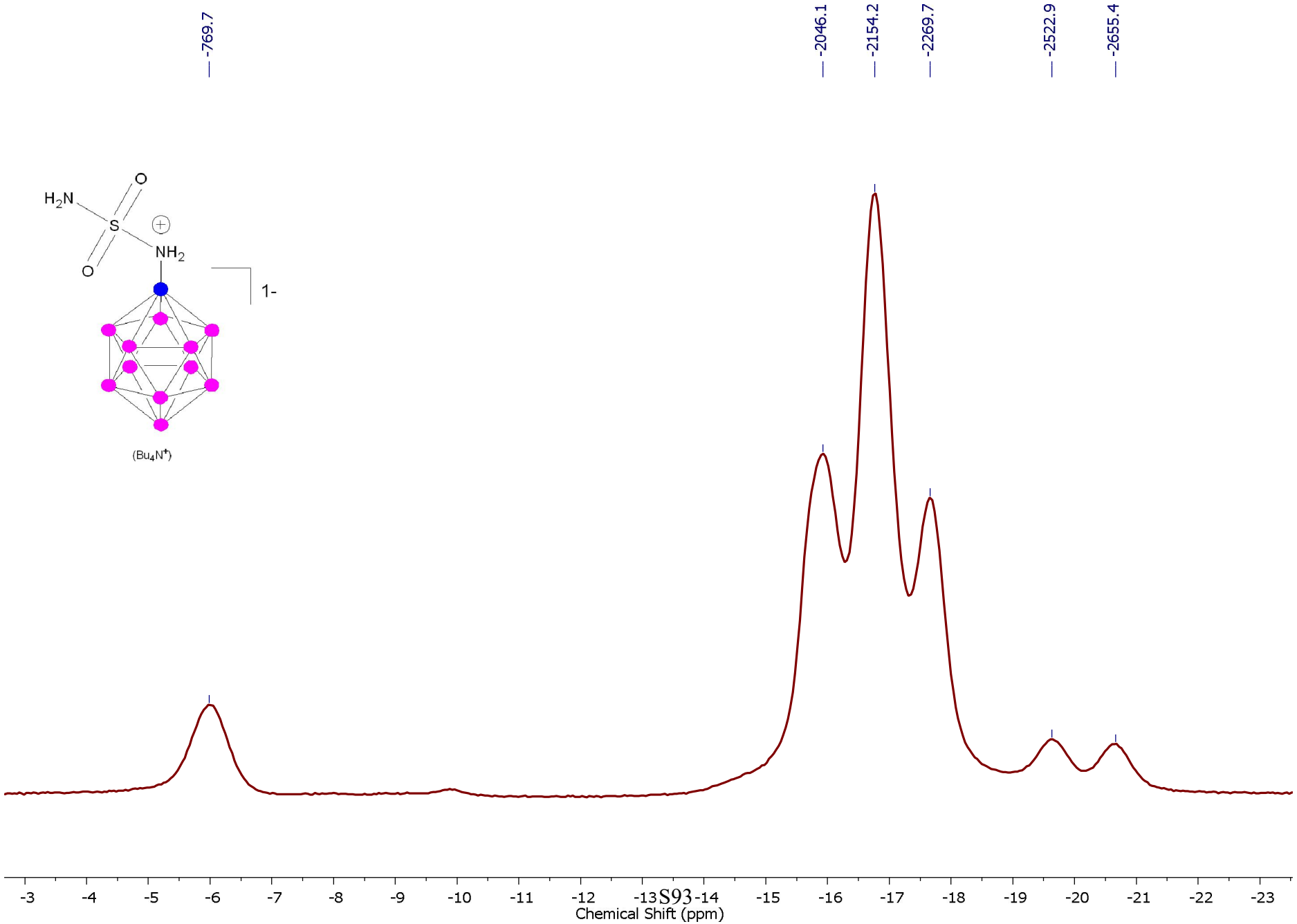
^{13}C NMR spectrum of 6b in CD_3CN at 298K



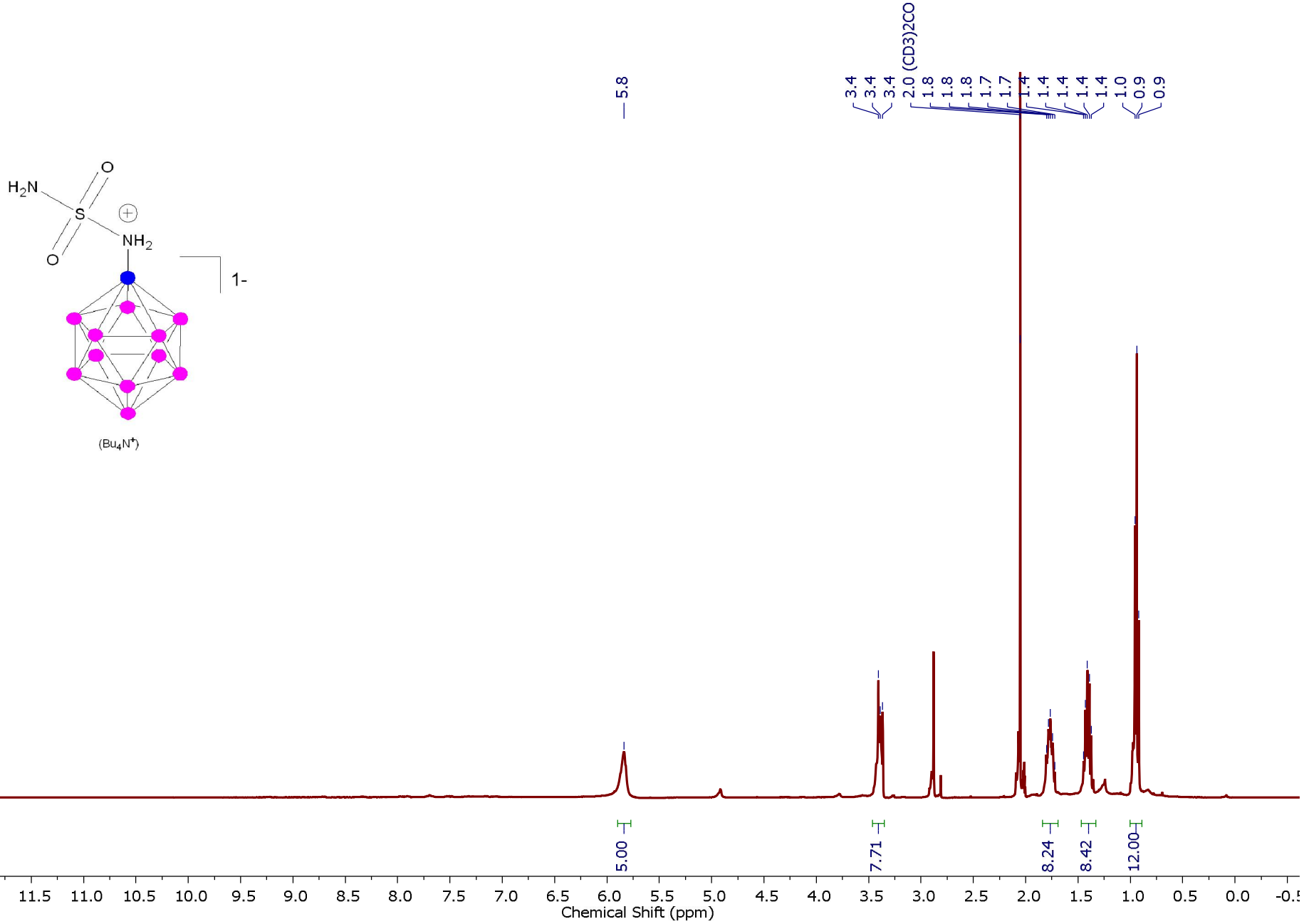
$^{11}B\{^1H\}$ NMR spectrum of 6c in Acetone-d_6 at 298K



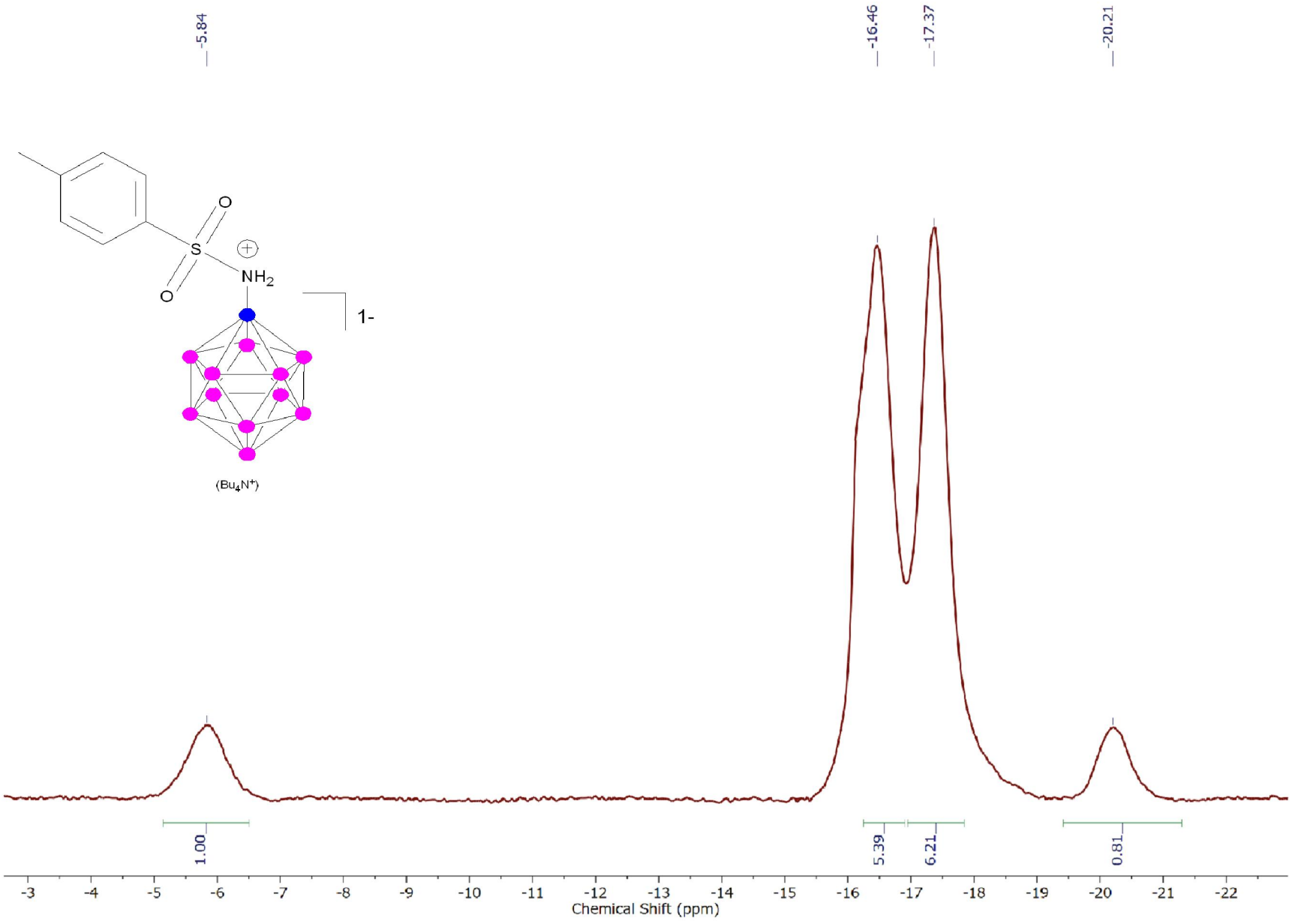
^{11}B NMR spectrum of 6c in Acetone-*d*$_6$ at 298K



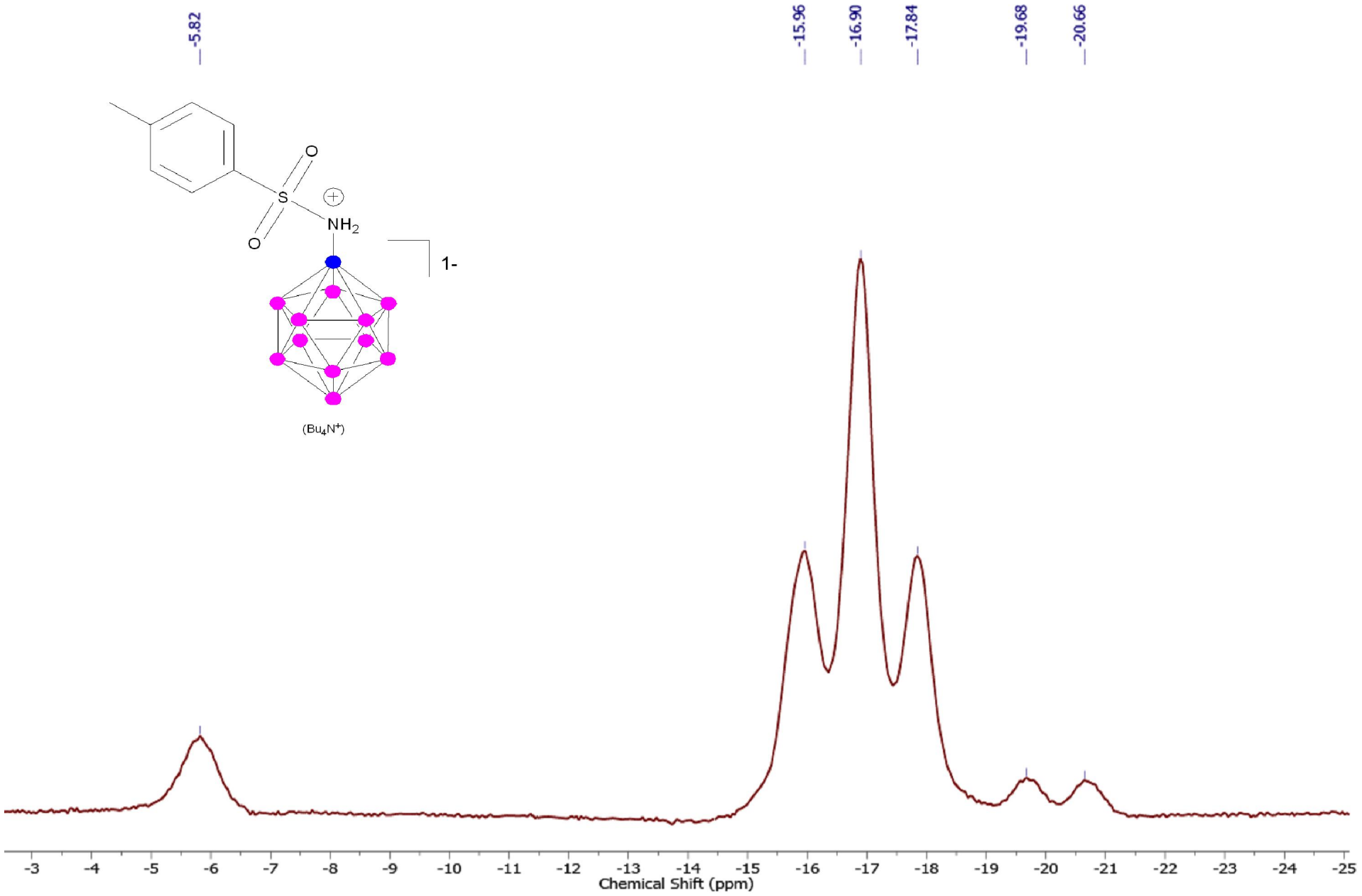
$^{1}H\{^{11}B\}$ NMR spectrum of 6c in Acetone-d_6 at 298K



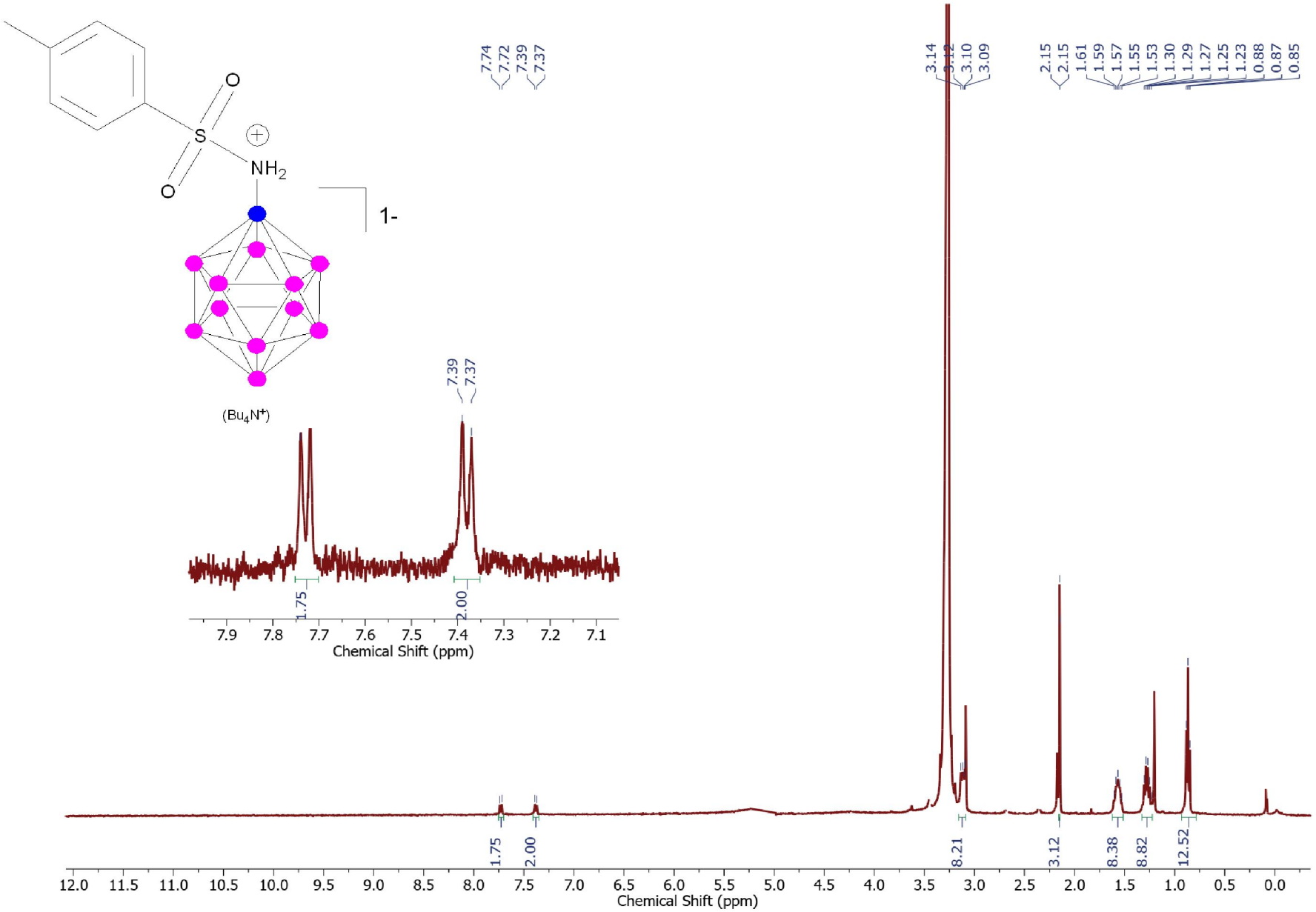
$^{11}B\{^{1}H\}$ NMR spectrum of 6d in Acetone-d_6 at 298K



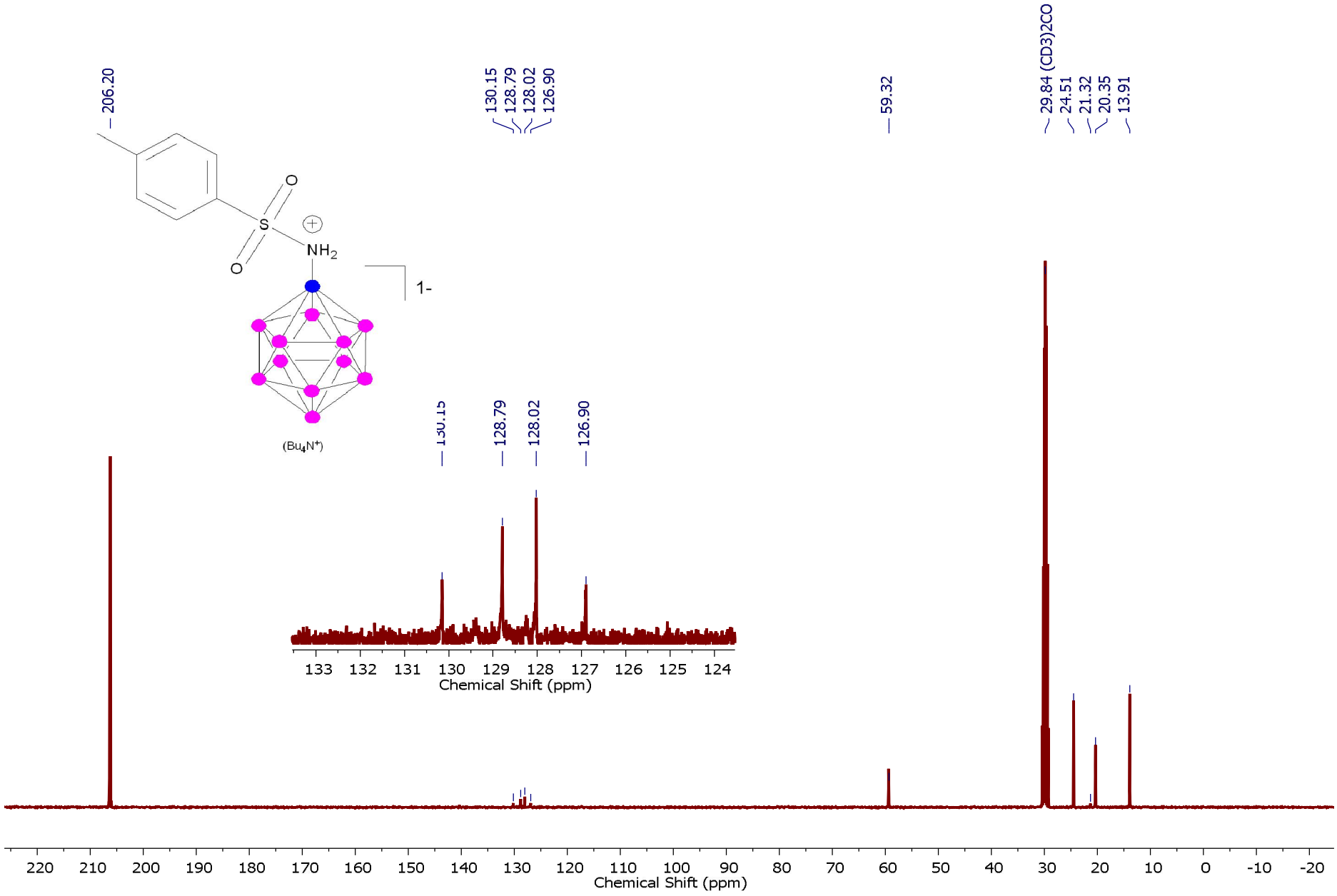
^{11}B NMR spectrum of 6d in CD_3CN at 298K



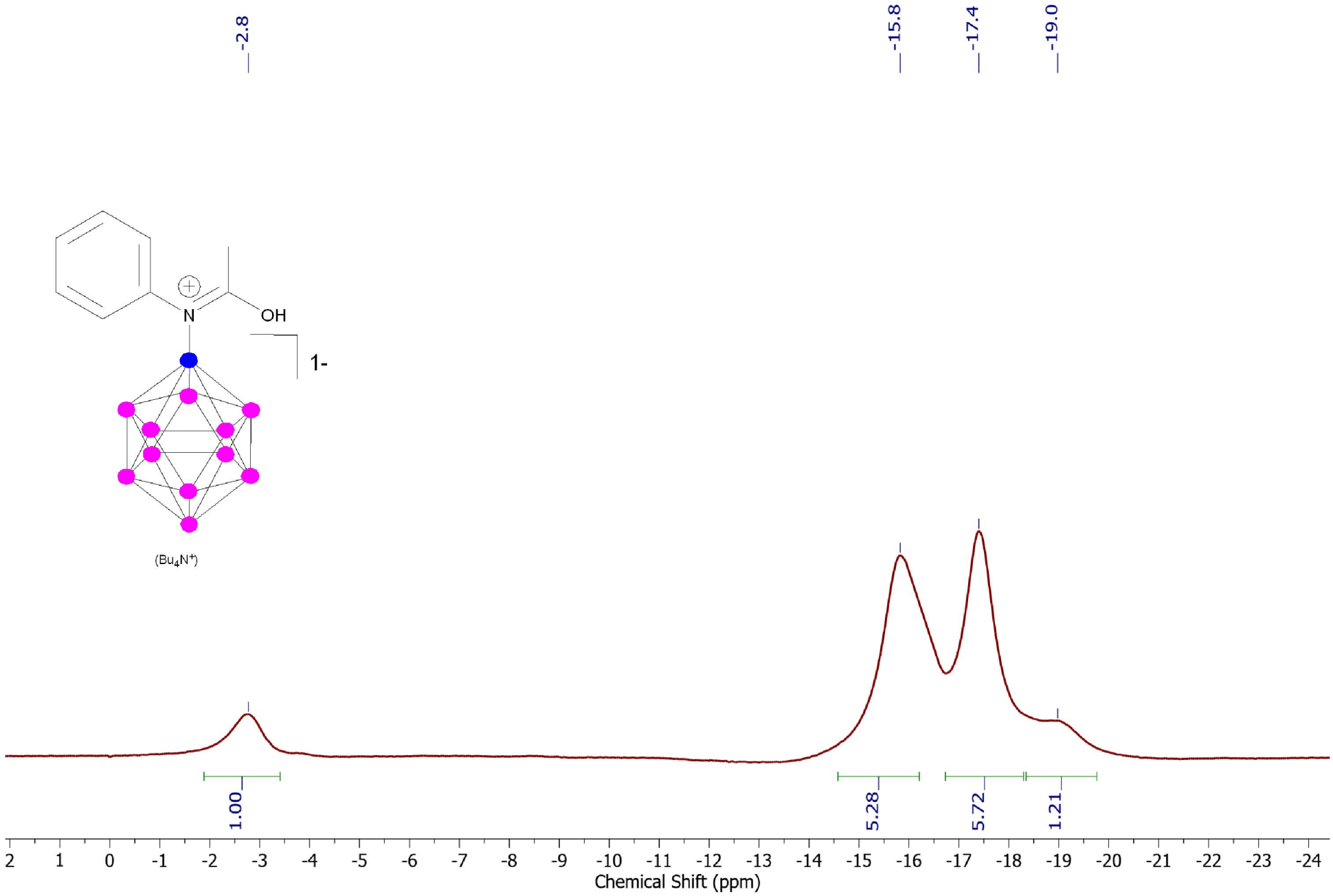
$^{1}H\{^{11}B\}$ NMR spectrum of 6d in Acetone-d_6 at 298K



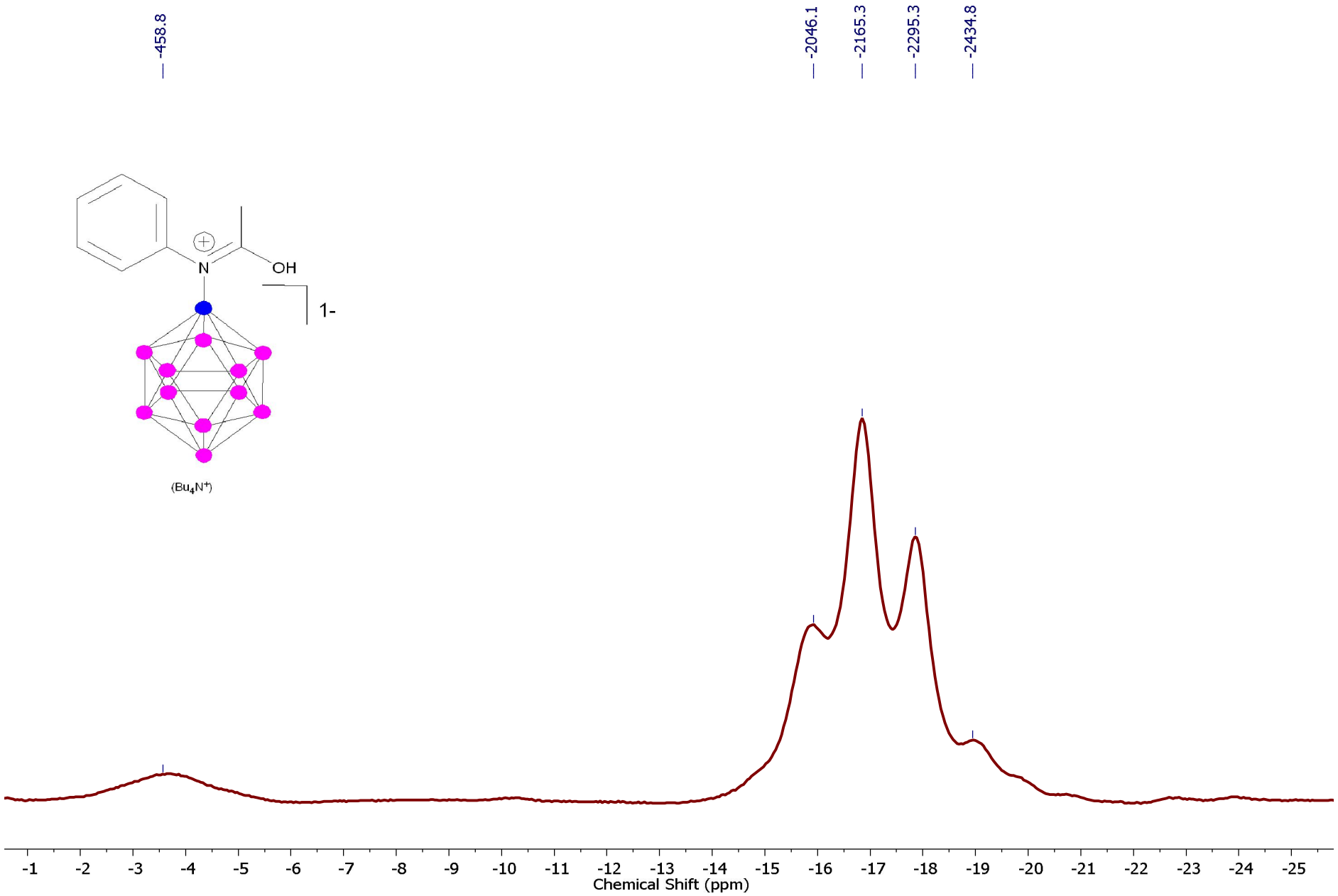
^{13}C NMR spectrum of 6d in Acetone-d_6 at 298K



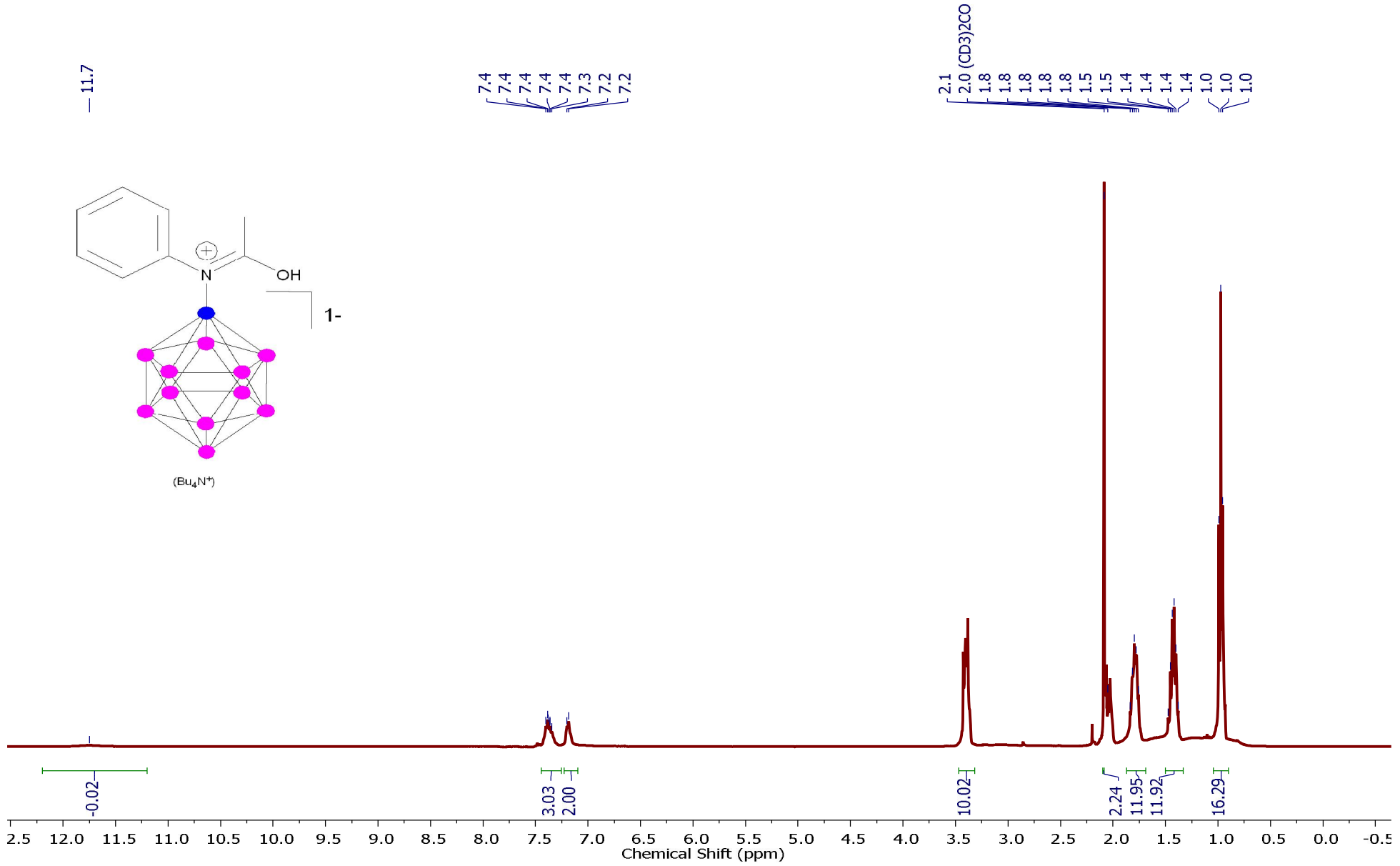
$^{11}B\{^{1}H\}$ NMR spectrum of 6e in Acetone-d_6 at 298K



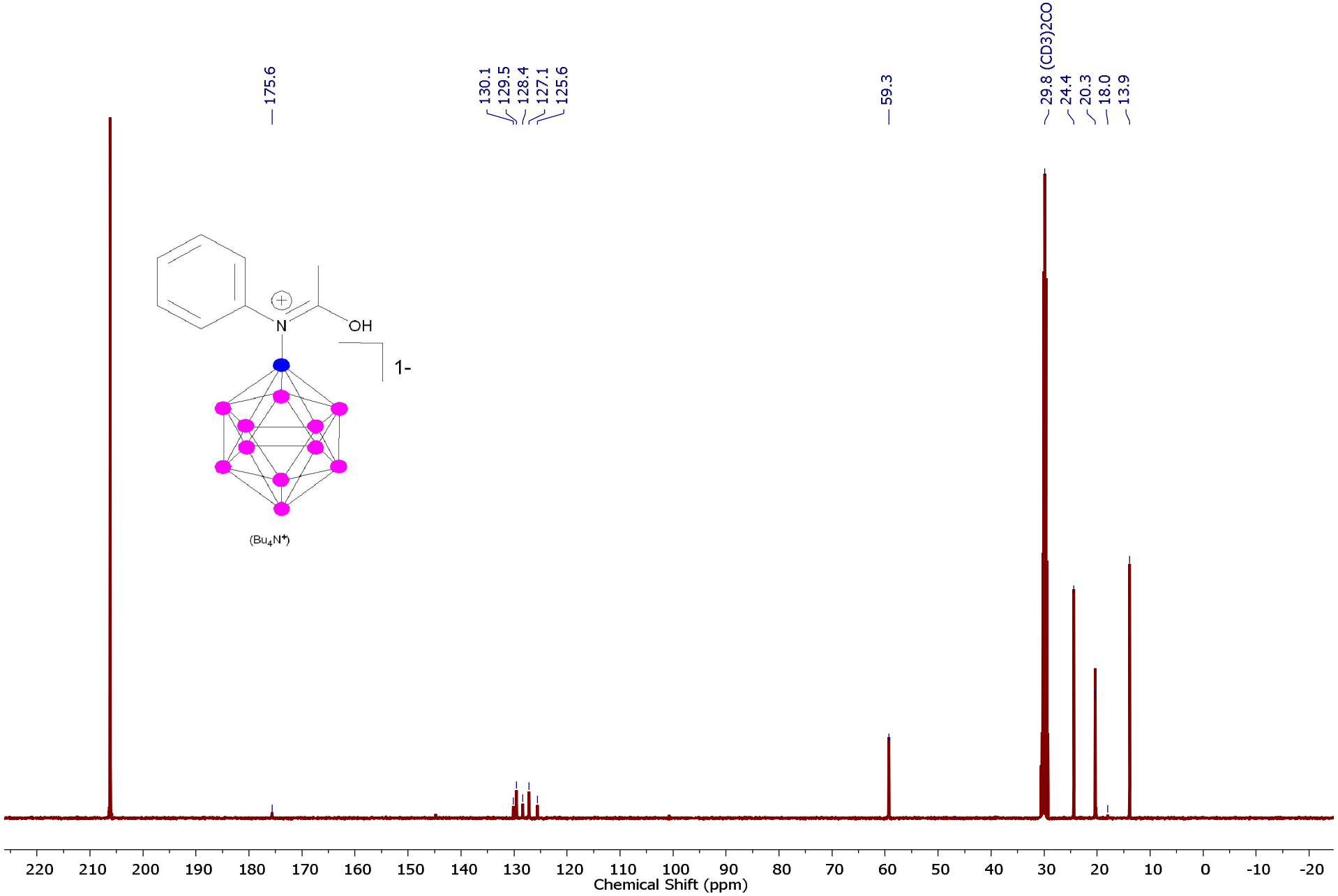
^{11}B NMR spectrum of 6e in Acetone-d_6 at 298K



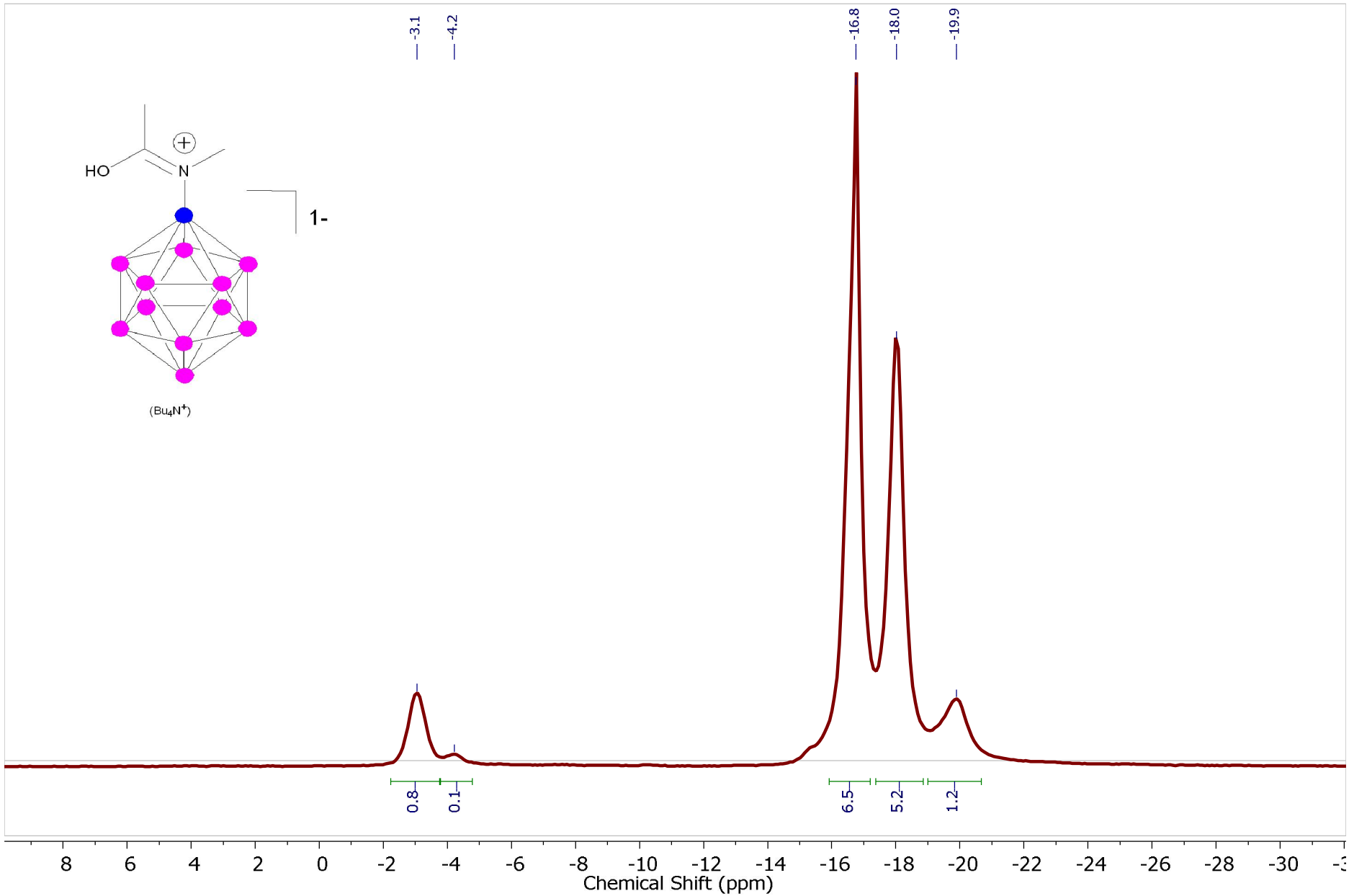
$^{1}H\{^{11}B\}$ NMR spectrum of 6e in Acetone-d_6 at 298K



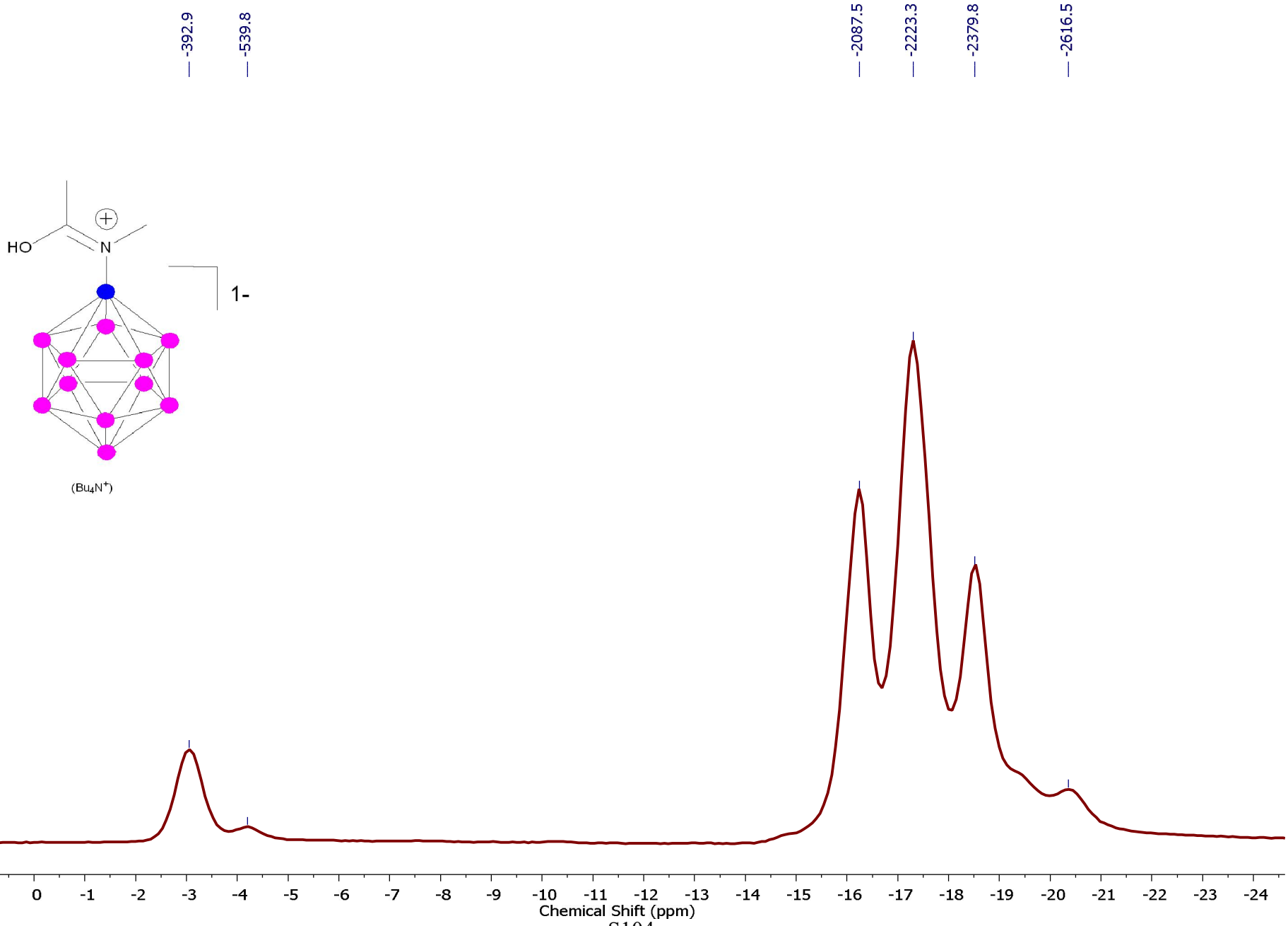
^{13}C NMR spectrum of 6e in Acetone-d_6 at 298K



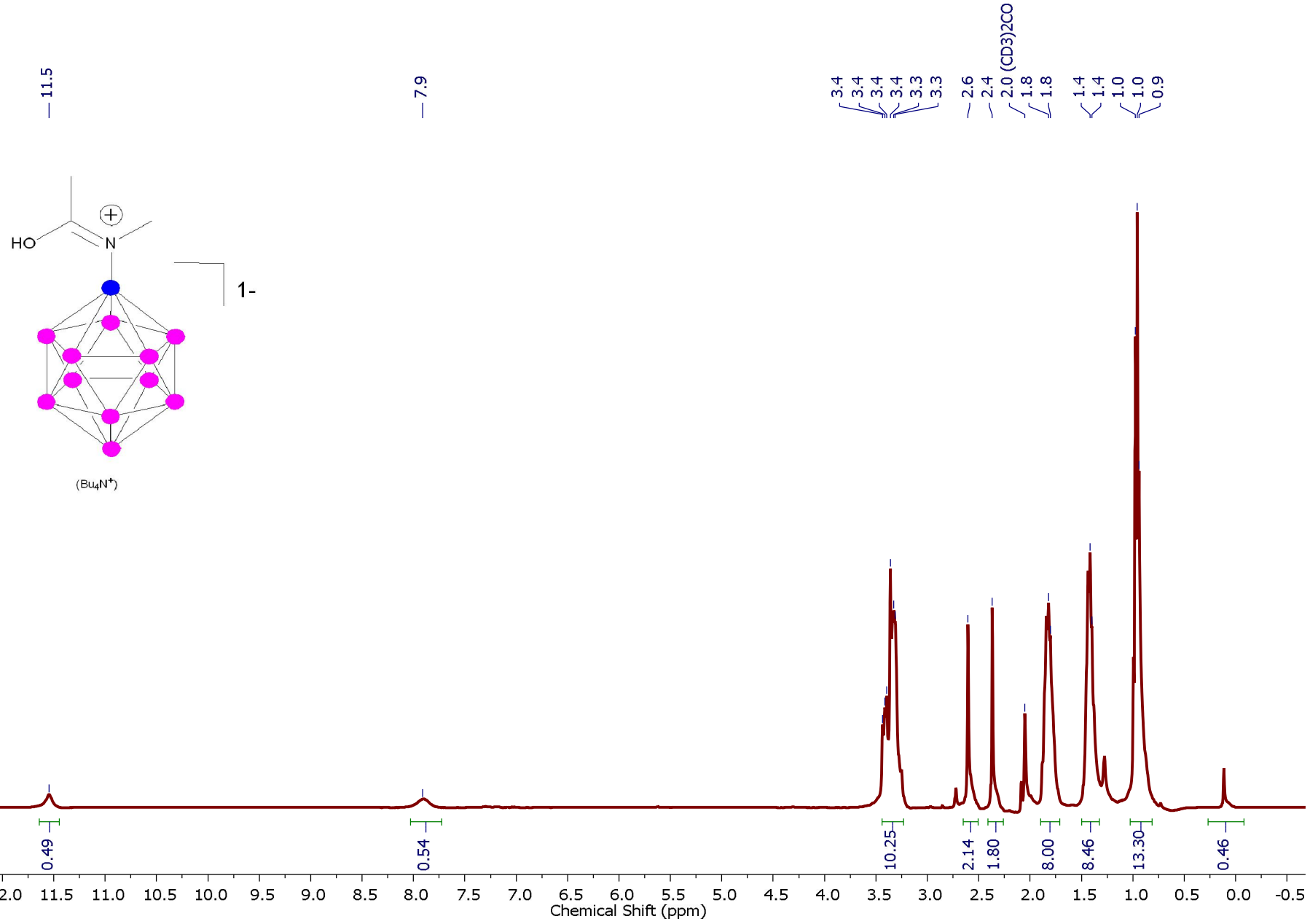
$^{11}B\{^1H\}$ NMR spectrum of 6f in Acetone-d_6 at



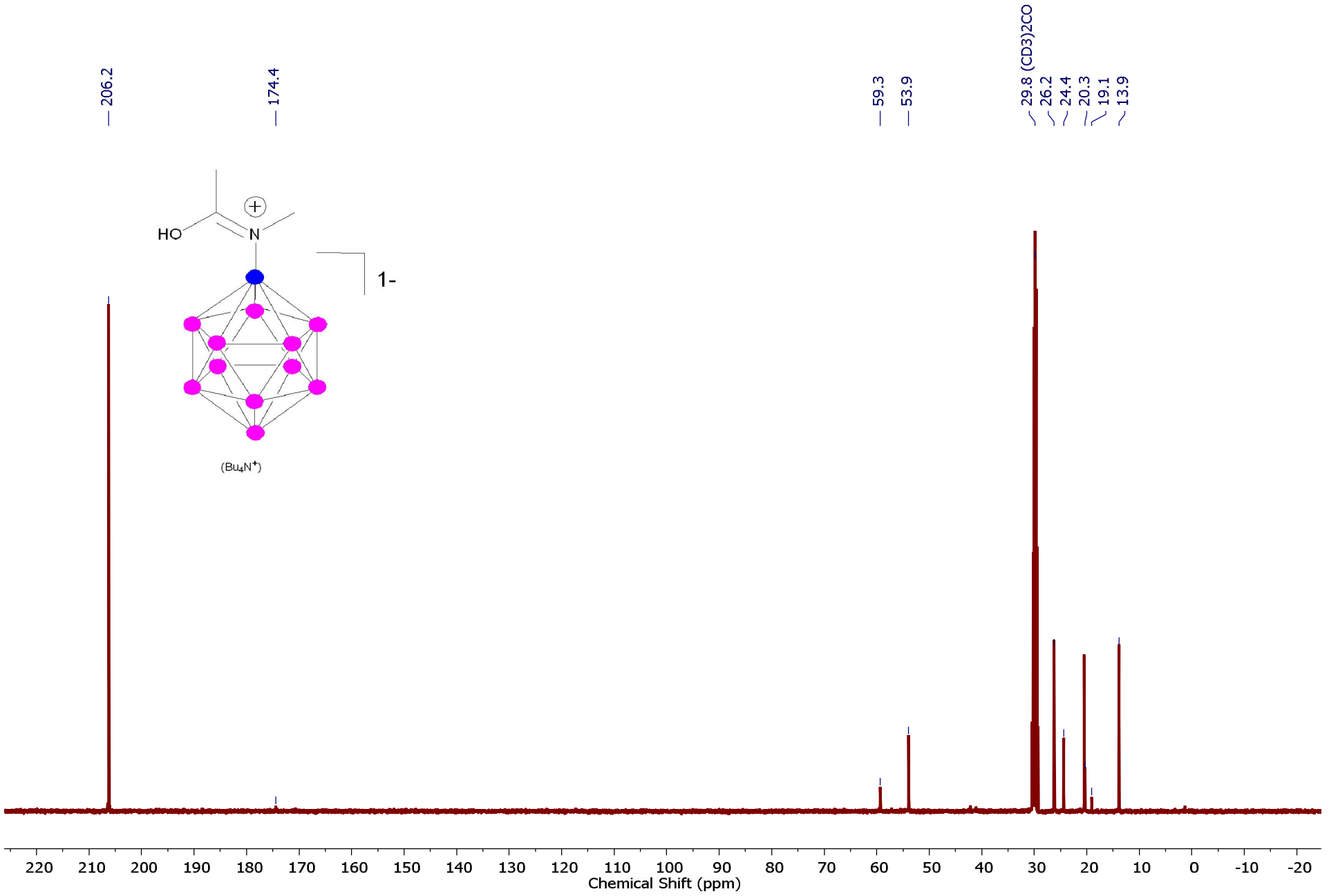
^{11}B NMR spectrum of 6f in Acetone-d_6 at 298K



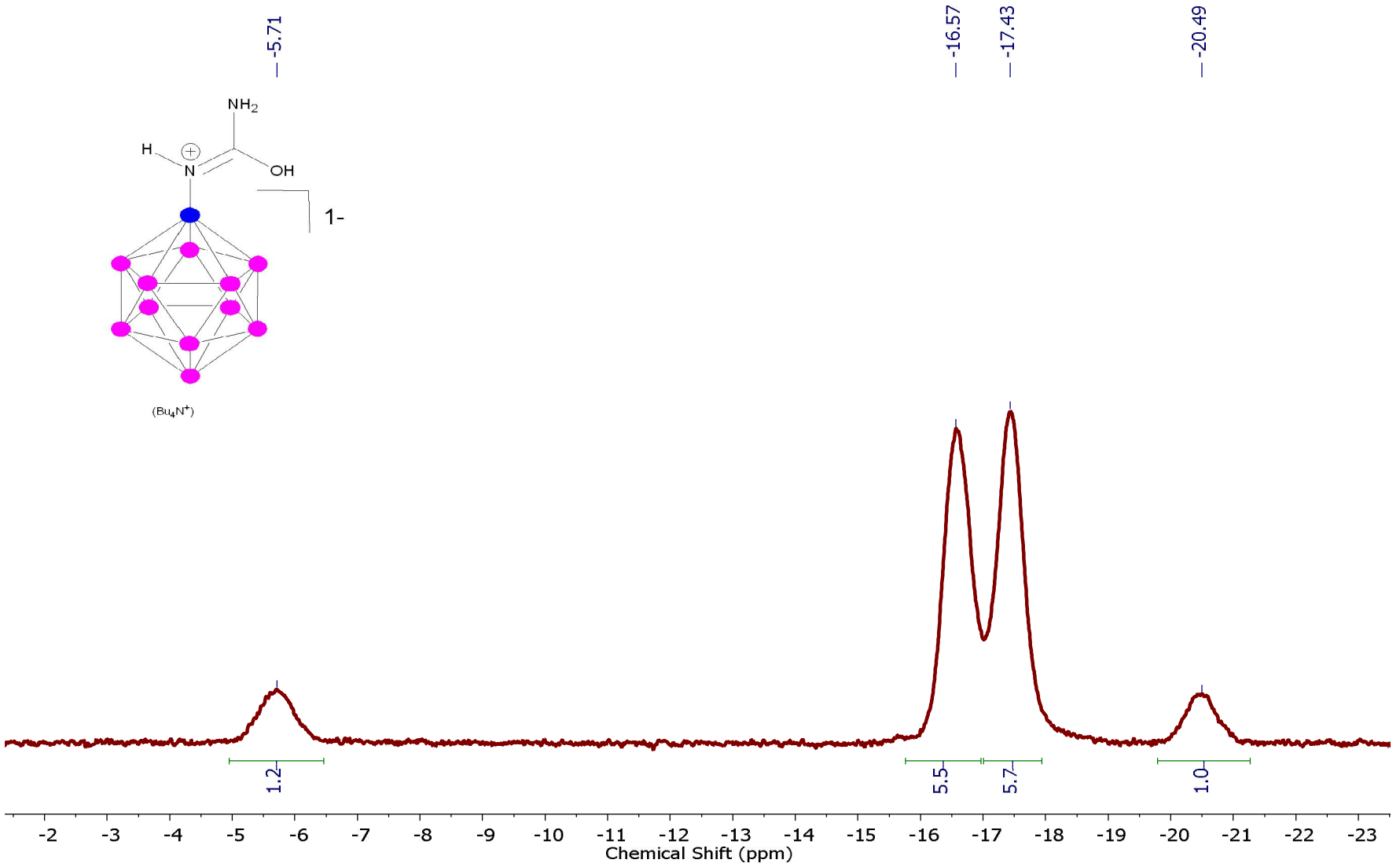
$^{1}H\{^{11}B\}$ NMR spectrum of 6f in Acetone-d_6 at 298K



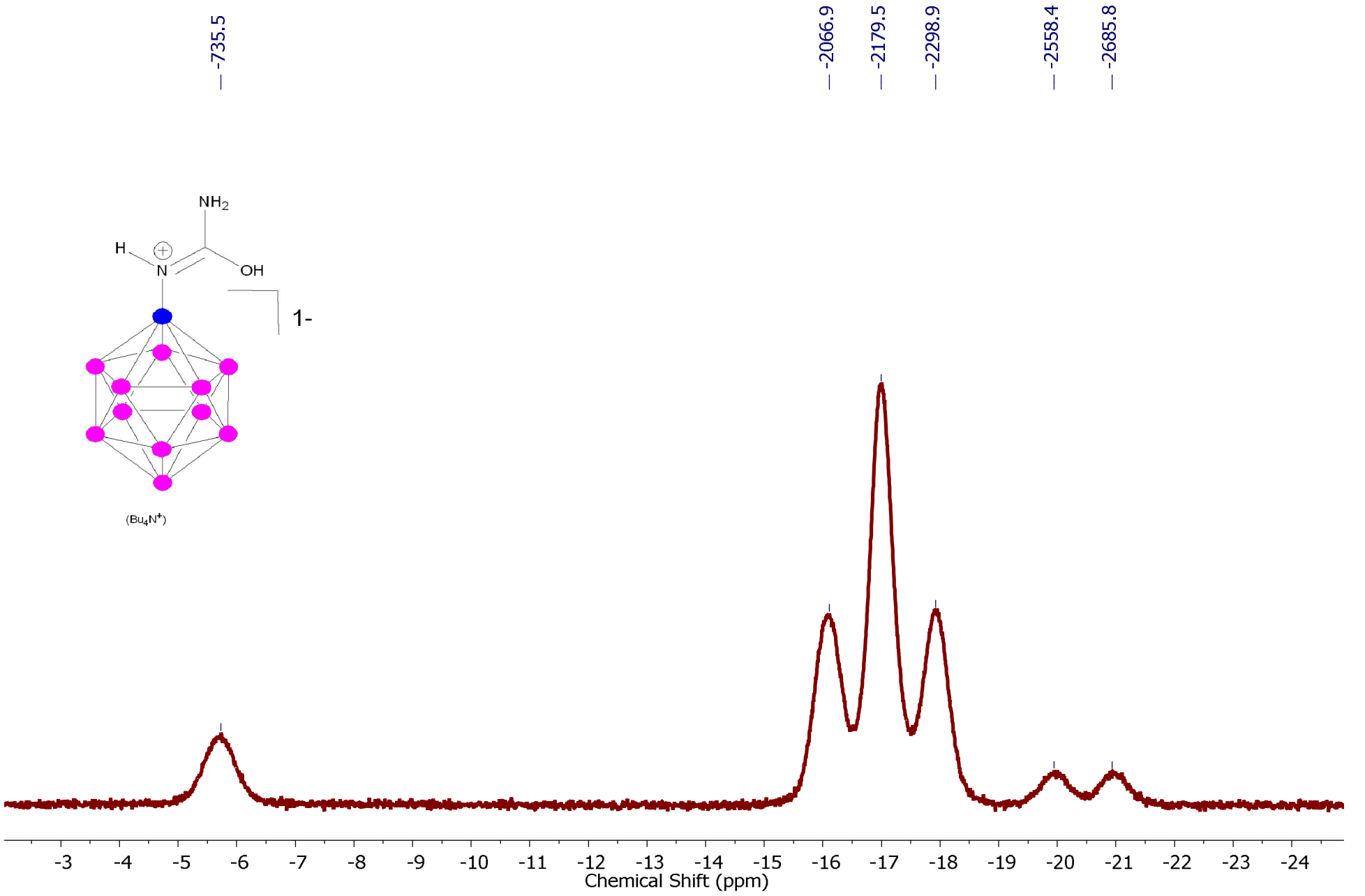
^{13}C NMR spectrum of 6f in Acetone-d_6 at 298K



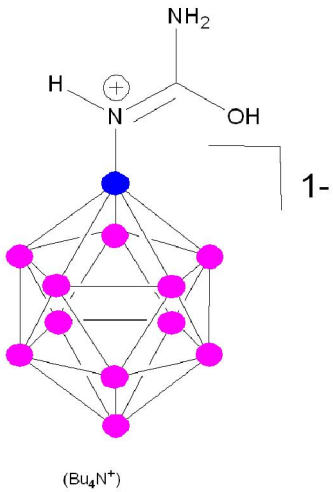
^{11}B {^{1}H} NMR spectrum of 6g in Acetonitrile-d_6 at 298K



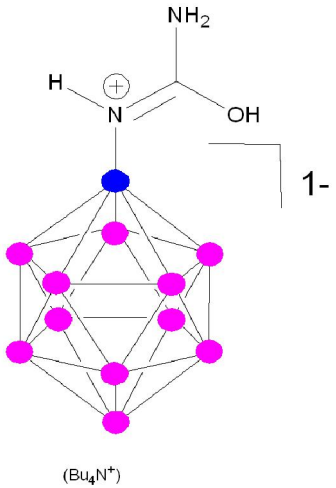
^{11}B NMR spectrum of 6g in Acetonitrile-d_6 at 298K



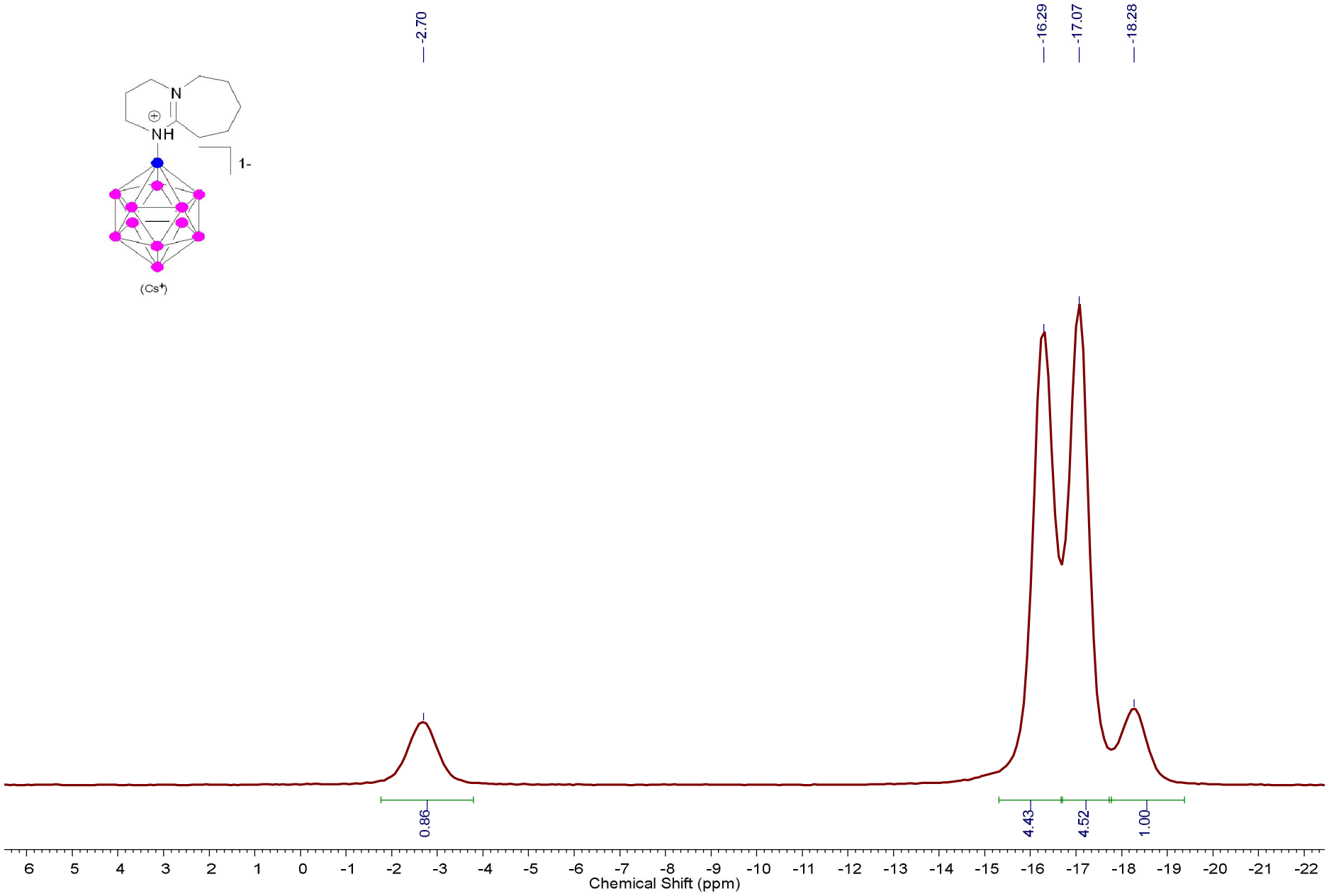
$^{1}H\{^{11}B\}$ NMR spectrum of 6g in Acetonitrile-d_6 at 298K



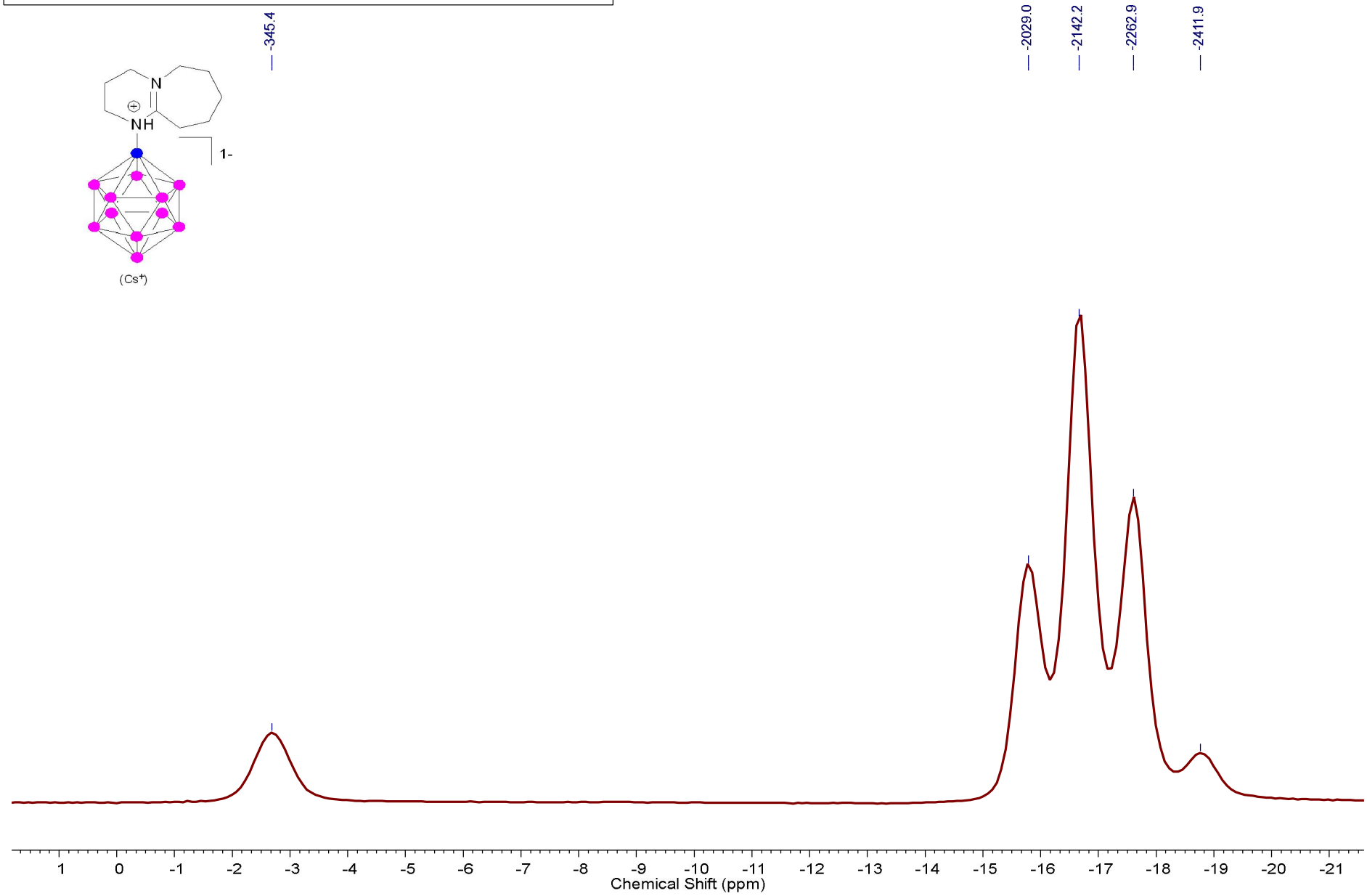
^{13}C NMR spectrum of 6g in Acetonitrile-d_6 at 298K



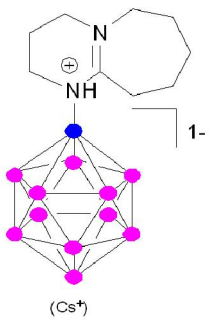
$^{11}B\{^{1}H\}$ NMR spectrum of 7 in CD_3CN at 298K



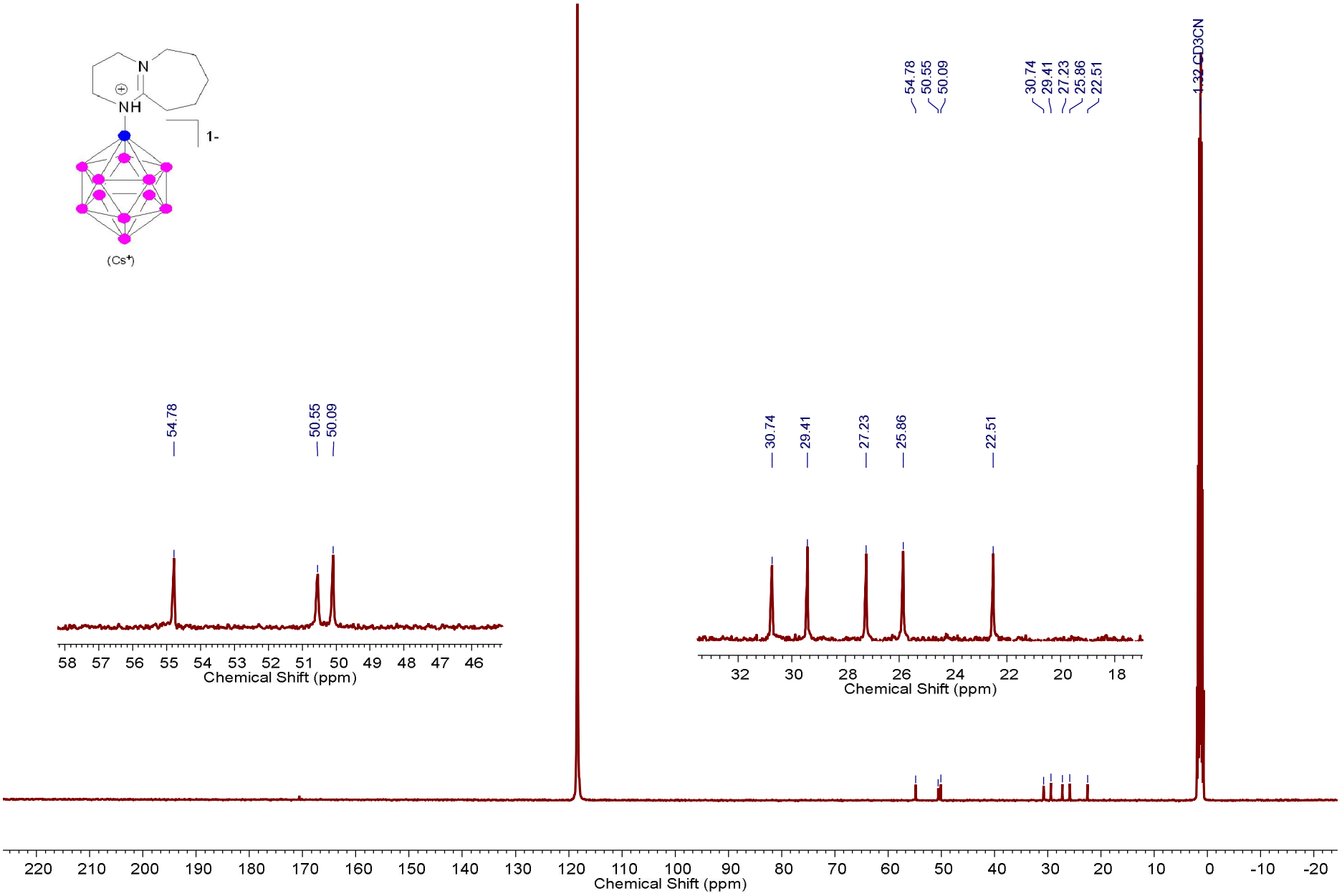
^{11}B NMR spectrum of 7 in CD_3CN at 298K



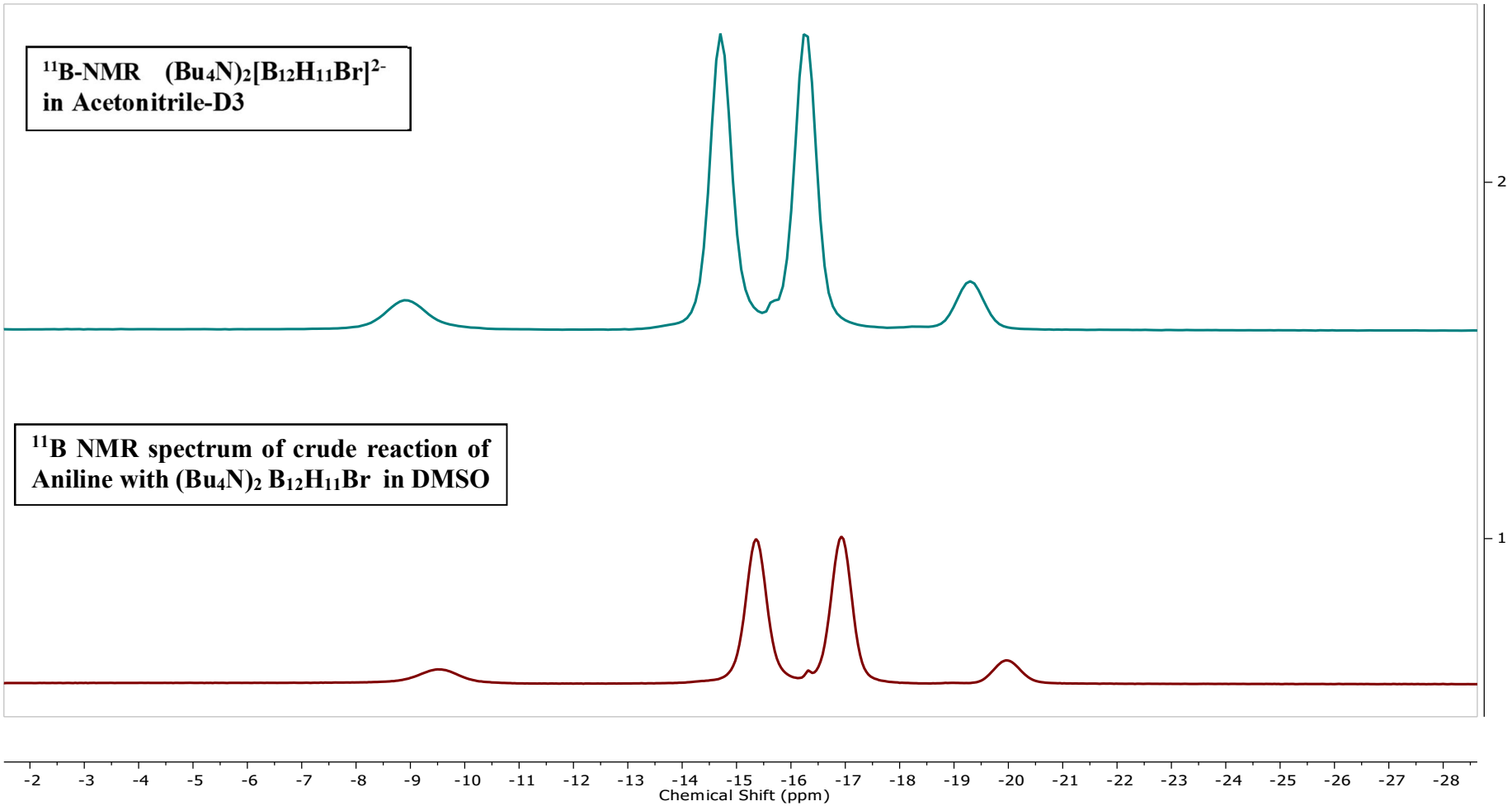
$^{1}H\{^{11}B\}$ NMR spectrum of 7 in CD_3CN at 298K



^{13}C NMR spectrum of 7 in CD_3CN at 298K

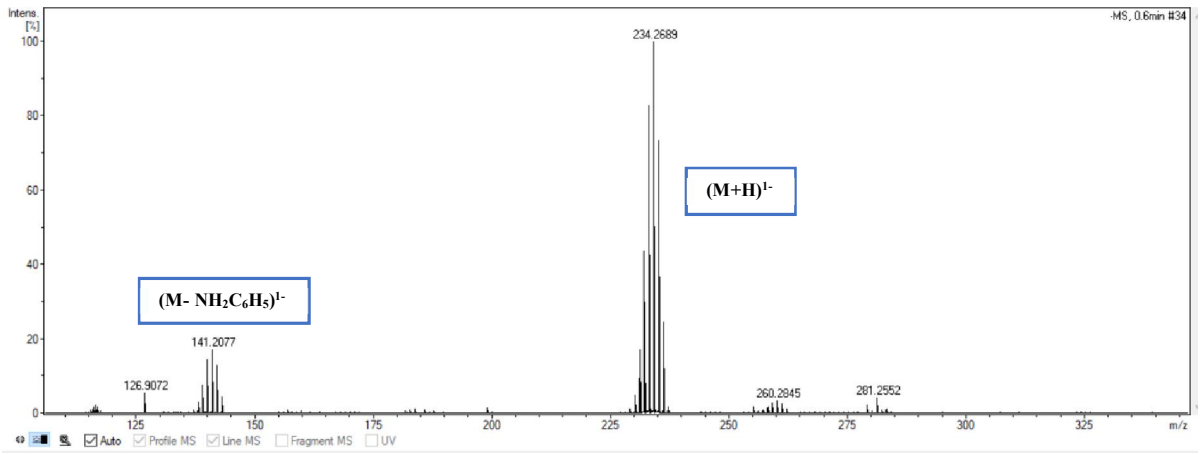


Reaction of $(Bu_4N)_2$ $B_{12}H_{11}Br$ with aniline

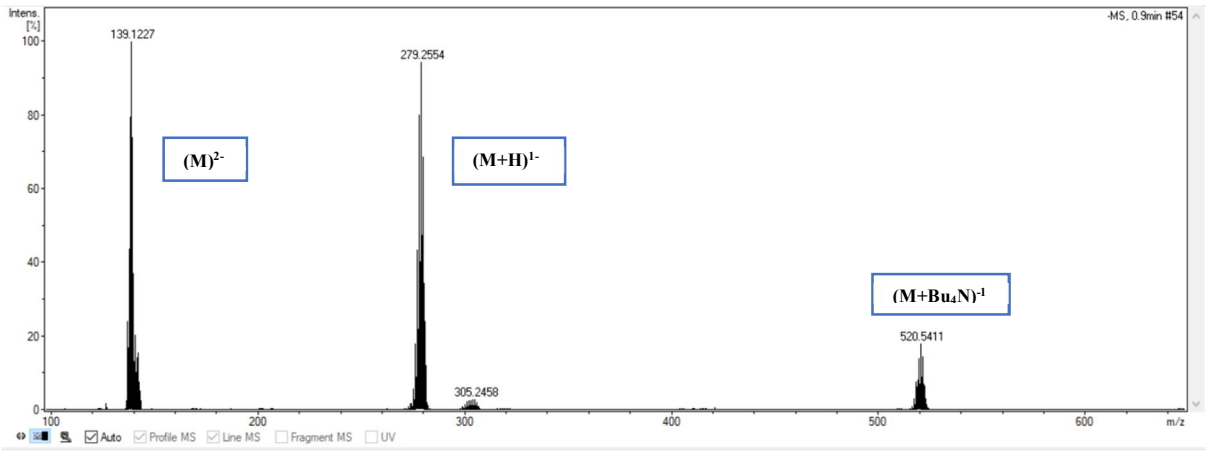


Mass Spectra

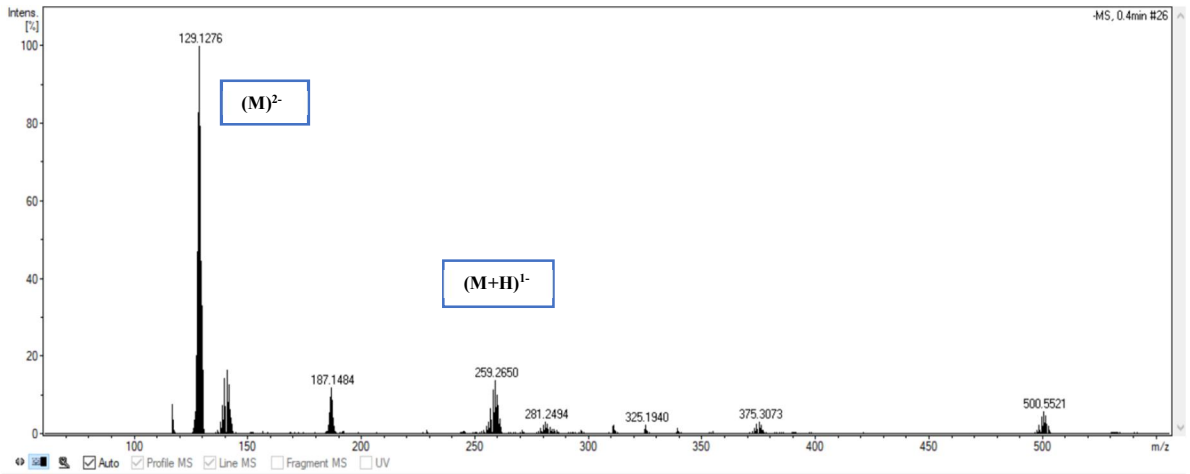
HRMS (TOF) (Negative Mode) for $(Bu_4N)[B_{12}H_{11}NH_2C_6H_5]$ (3a)



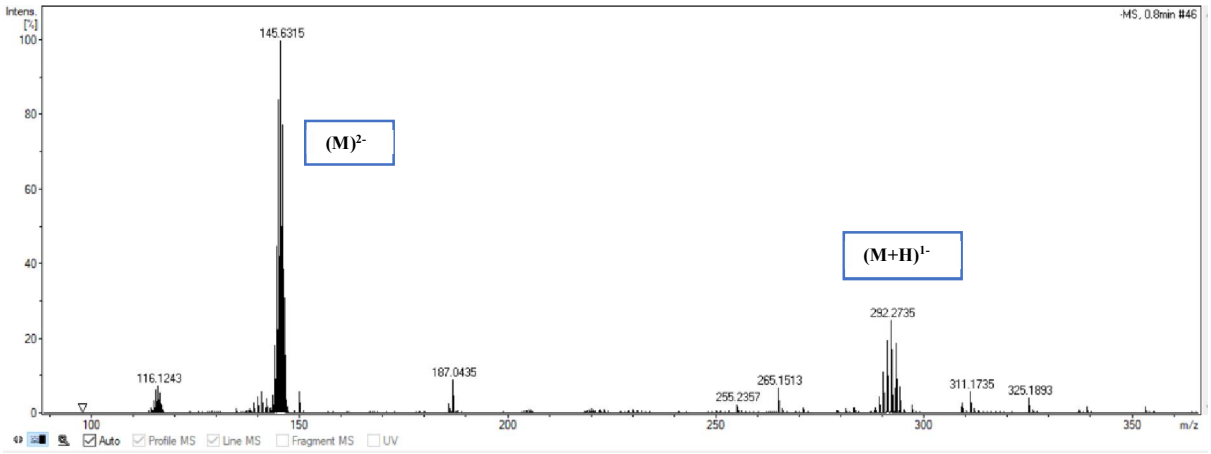
HRMS (TOF) (Negative Mode) for $(Bu_4N)[B_{12}H_{11}NH_2C_6H_5\text{-}4\text{-}NO_2]$(3b)



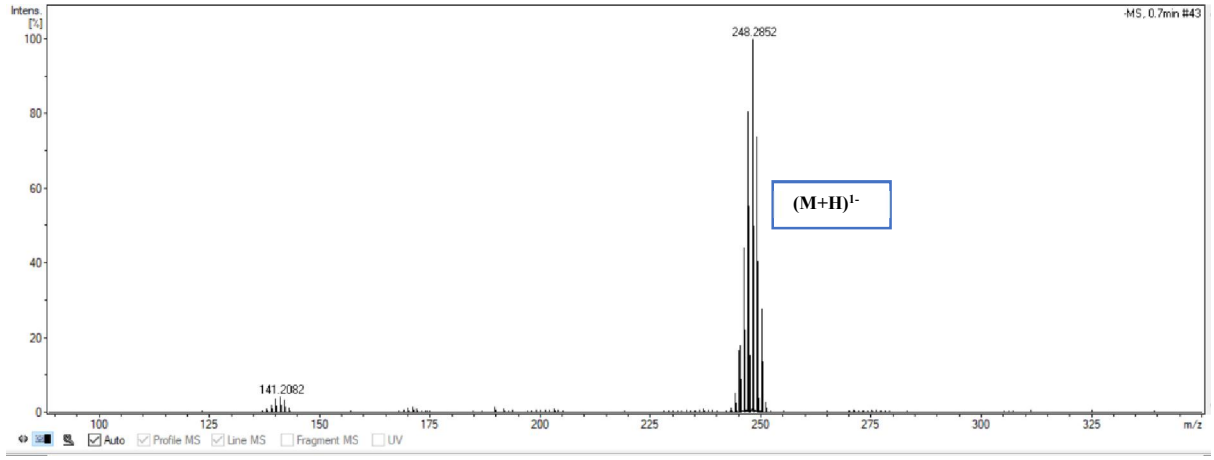
HRMS (TOF) (Negative Mode) for $(Bu_4N)[B_{12}H_{11}NH_2C_6H_5\text{-}4\text{-}CN]$ (3c)



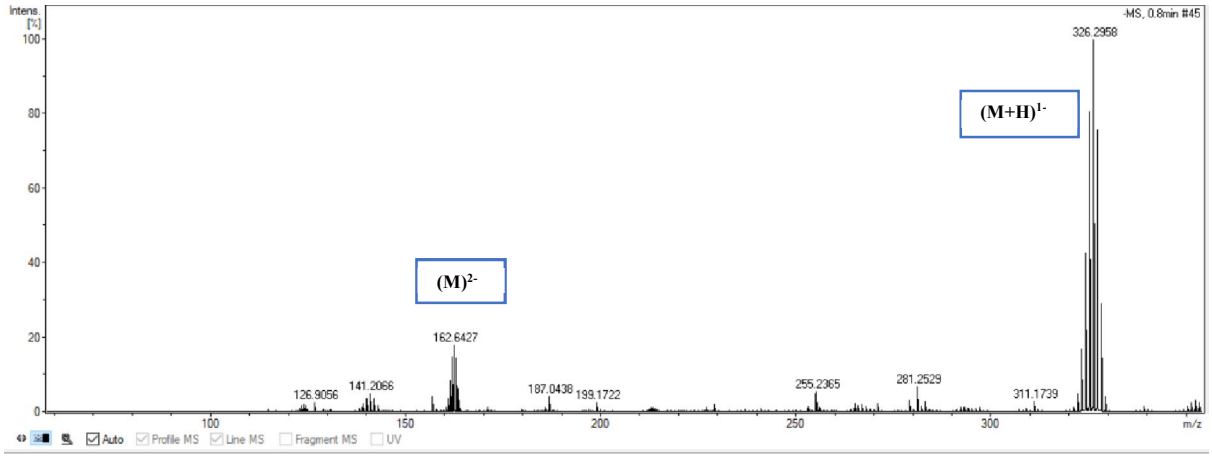
HRMS (TOF) (Negative Mode) for $(Me_4N)[B_{12}H_{11}NH_2C_6H_5\text{-}4\text{-}CO_2Me]$ (3d)



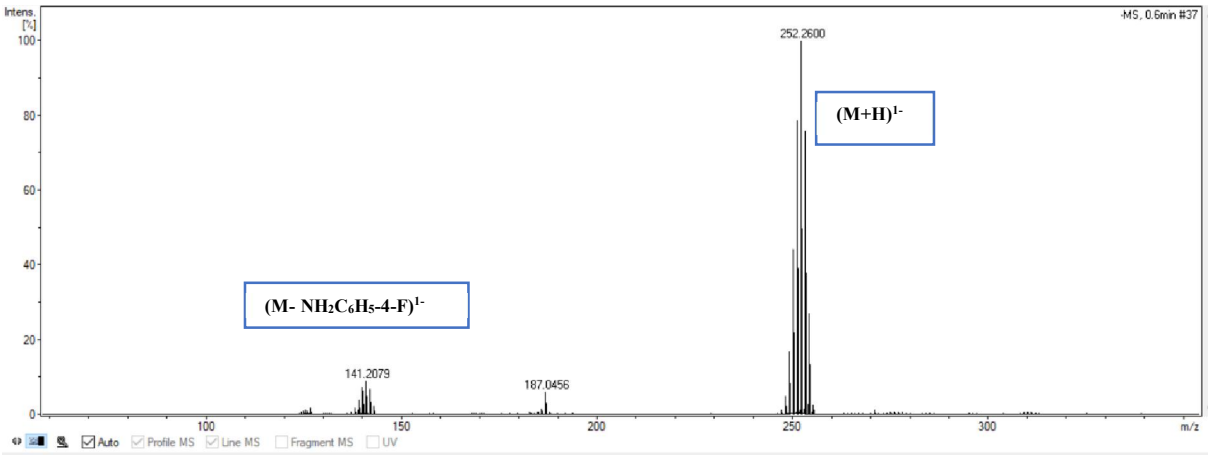
HRMS (TOF) (Negative Mode) for $(Me_4N)[B_{12}H_{11}NH_2C_6H_5\text{-}4\text{-}Me]$ (3e)



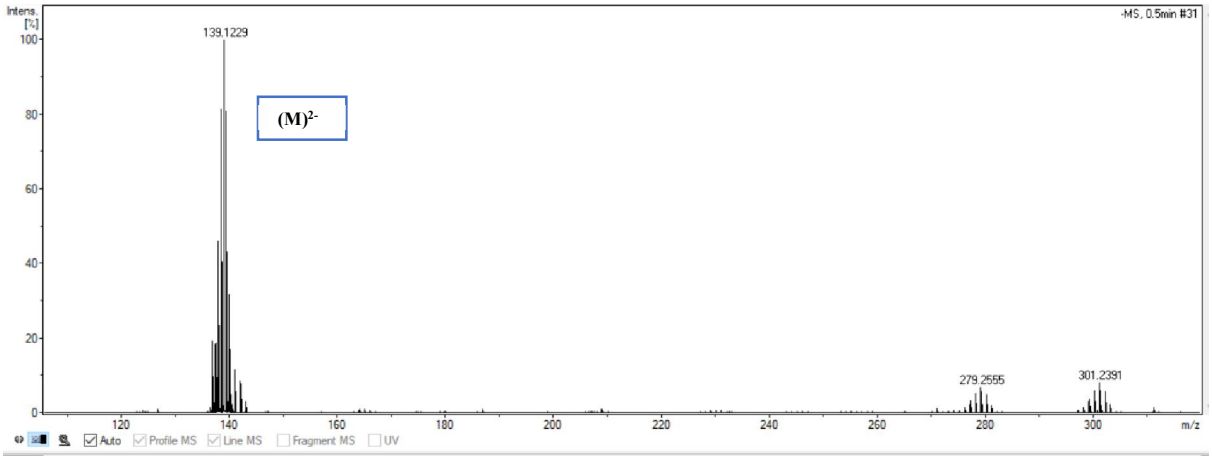
HRMS (TOF) (Negative Mode) for $(Me_4N)[B_{12}H_{11}NH_2C_6H_5\text{-}4\text{-}phenoxy]$ (3f)



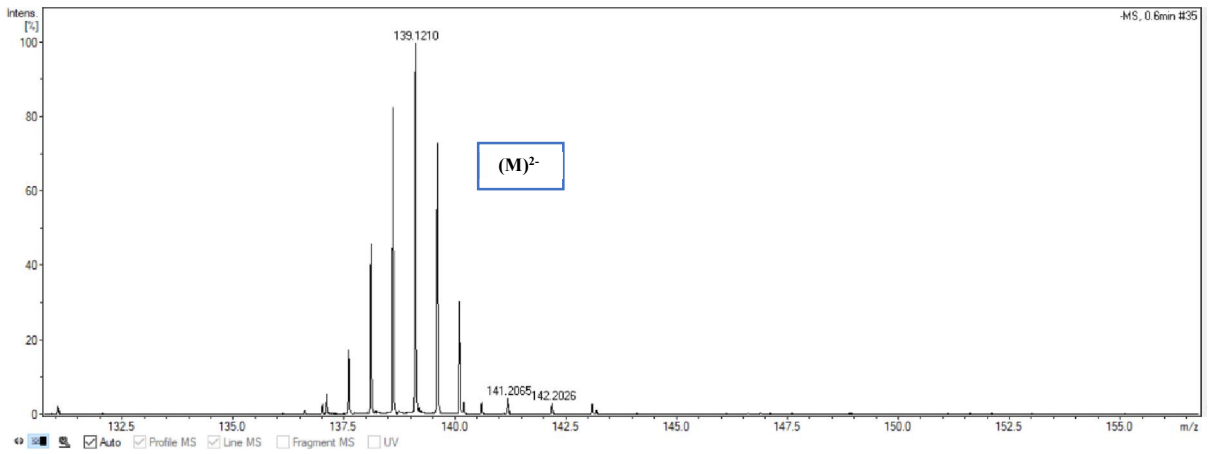
HRMS (TOF) (Negative Mode) for $(Me_4N)[B_{12}H_{11}NH_2C_6H_5\text{-}4\text{-}F]$ (3i)



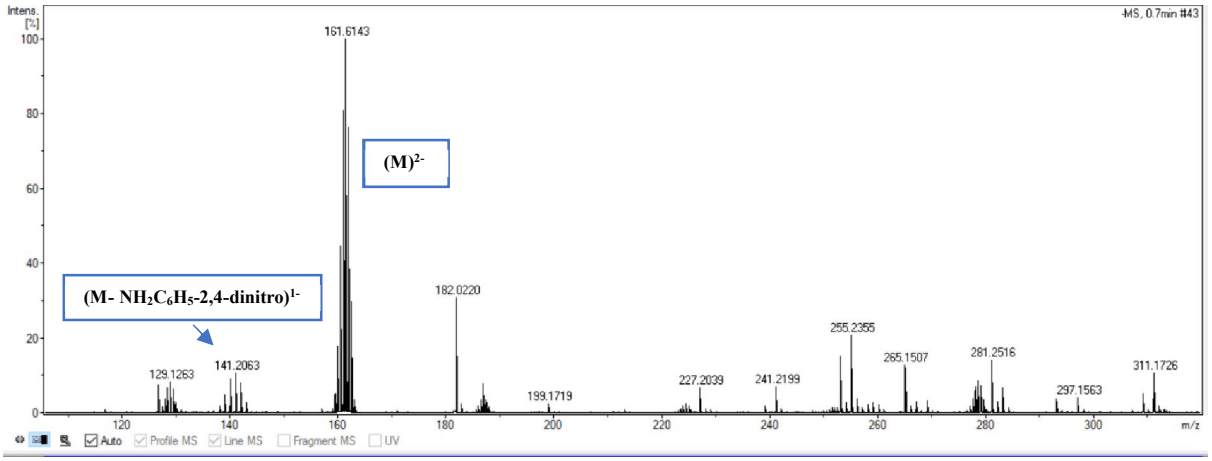
HRMS (TOF) (Negative Mode) for $(Bu_4N)[B_{12}H_{11}NH_2C_6H_5\text{-}2\text{-}NO_2]$ (3m)



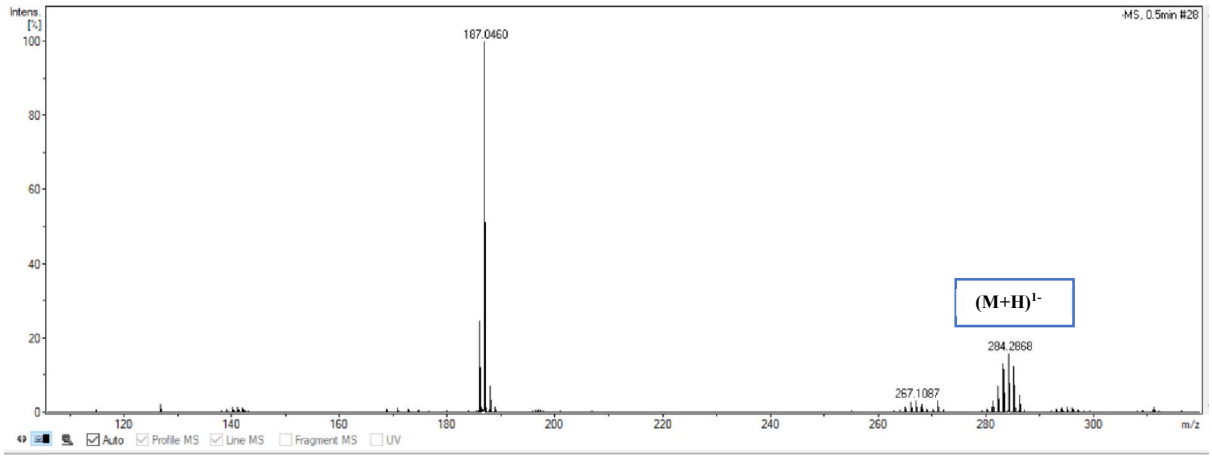
HRMS (TOF) (Negative Mood) for $(Me_4N)[B_{12}H_{11}NH_2C_6H_5\text{-}3\text{-}NO_2]$ (3n)



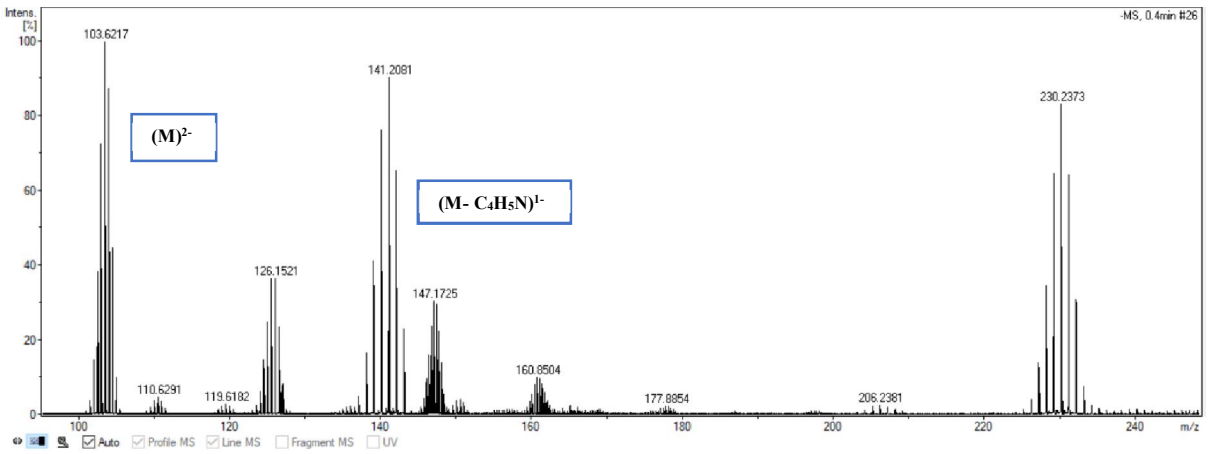
HRMS (TOF) (Negative Mode) for $(Me_4N)[B_{12}H_{11}NH_2C_6H_5$-2,4-dinitro] (3o)



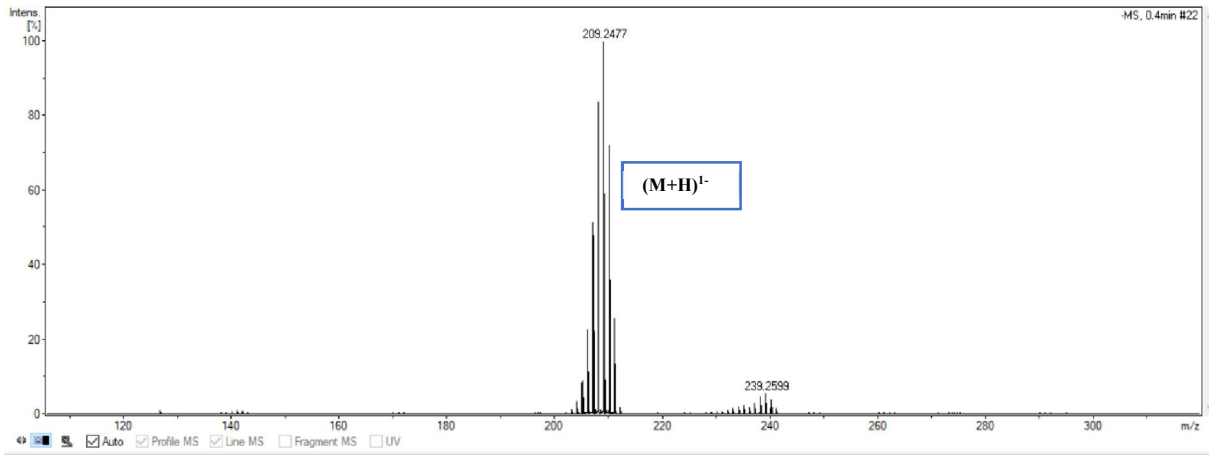
HRMS (TOF) (Negative Mode) for $(Bu_4N)[B_{12}H_{11}NH_2$-naphthyl] (4)



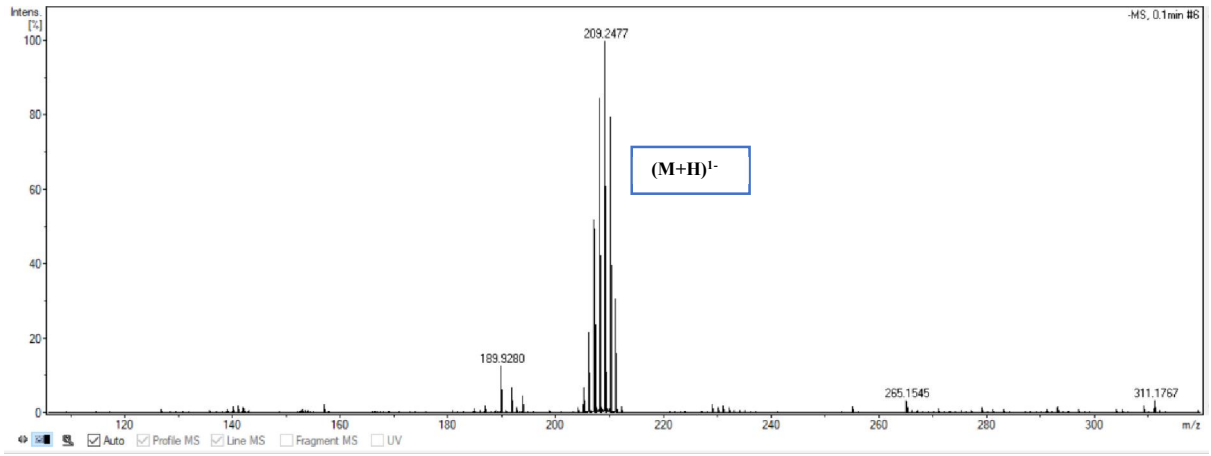
HRMS (TOF) (Negative Mode) for $(Me_4N)[B_{12}H_{11}$-pyrrole] (5a)



HRMS (TOF) (Negative Mode) for $(Me_4N)[B_{12}H_{11}$-pyrazole] (5b)

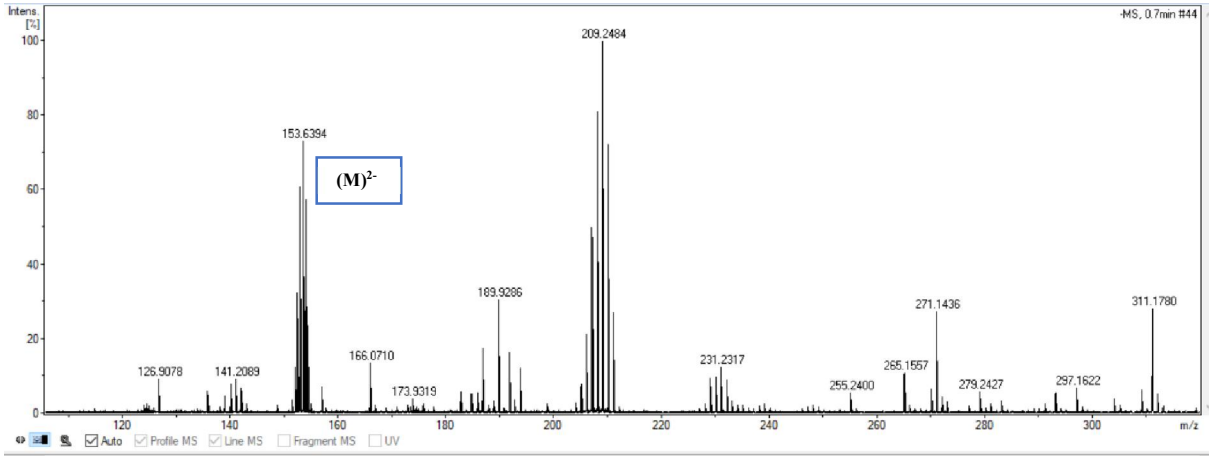


HRMS (TOF) (Negative Mode) for $(Me_4N)[B_{12}H_{11}$-imidazole] (5c)

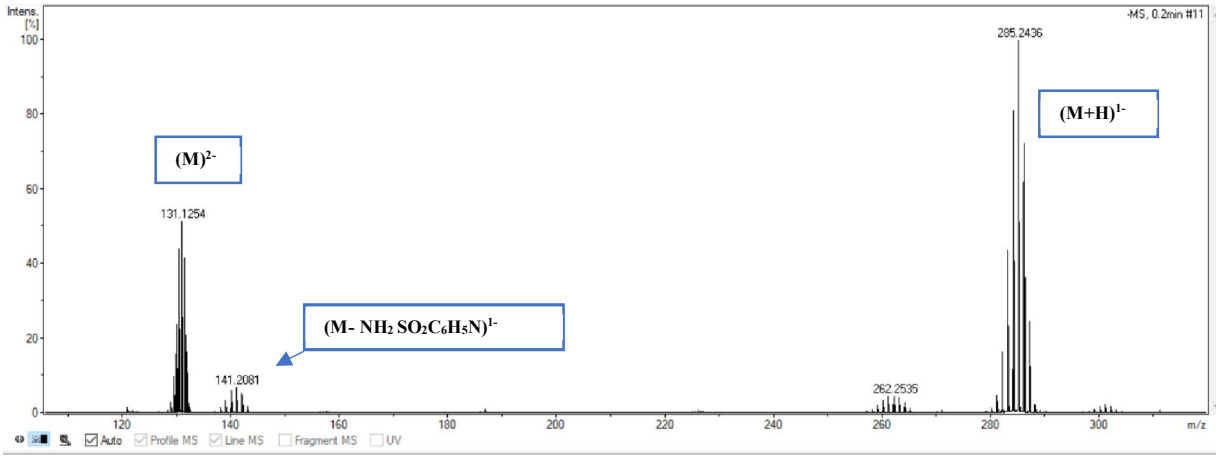


HRMS (TOF) (Negative Mode) for $(Me_4N)[B_{12}H_{11}$-indole] (5d)

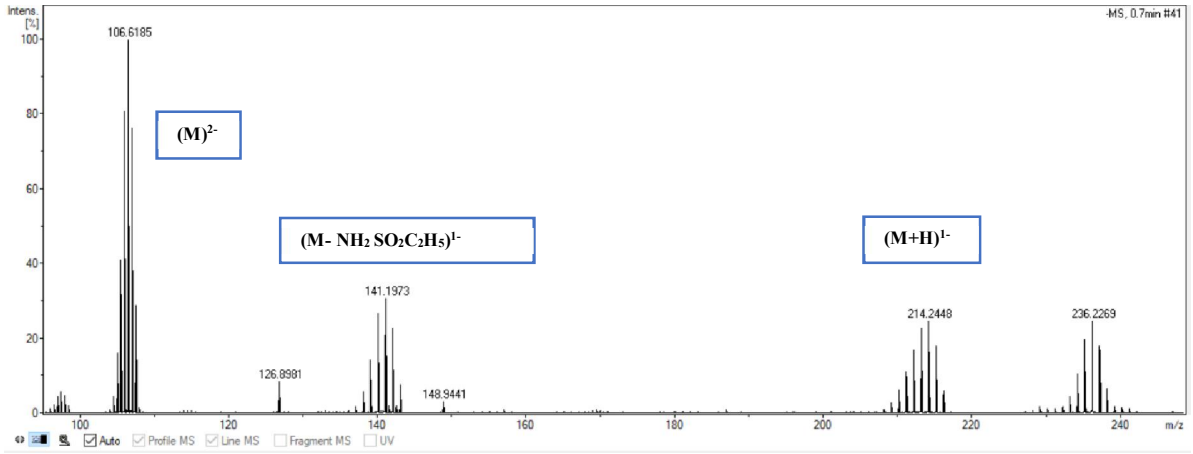
HRMS (TOF) (Negative Mode) for $(Bu_4N)[B_{12}H_{11}$-carbazole] (5e)



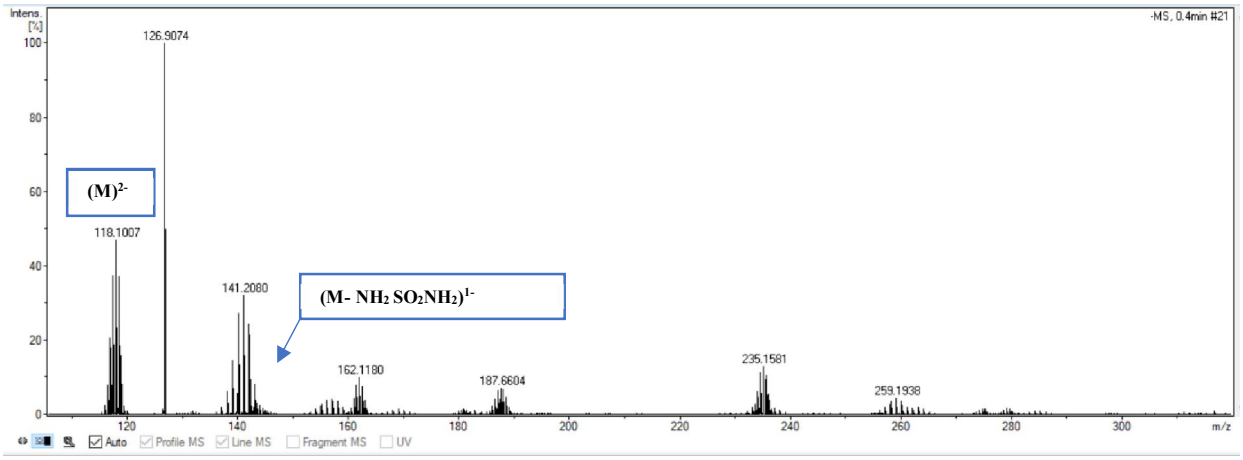
HRMS (TOF) (Negative Mode) for $(Bu_4N)[B_{12}H_{11}$-3-nicotinamide] (6a)



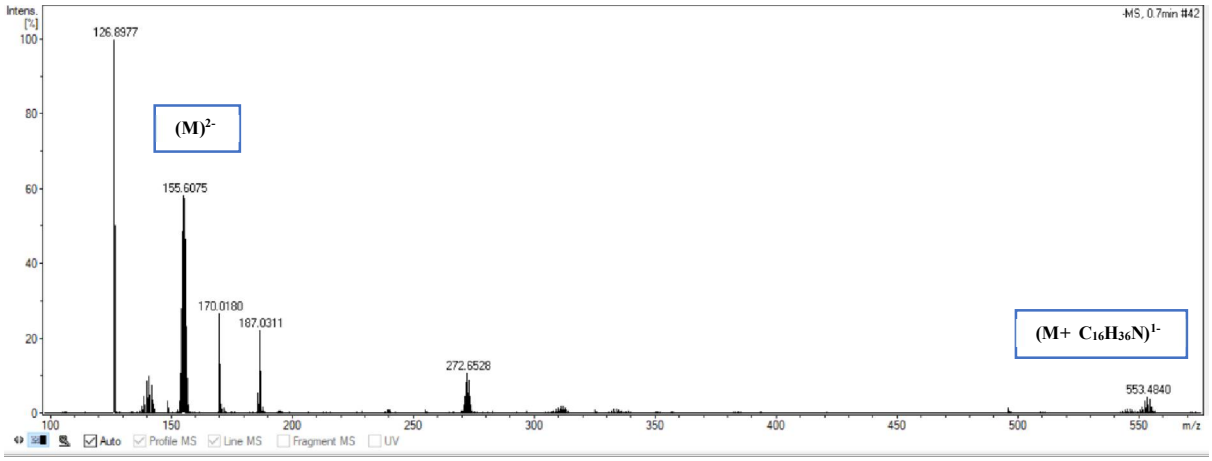
HRMS (TOF) (Negative Mode) for $(Bu_4N)[B_{12}H_{11}$-propanamide] (6b)



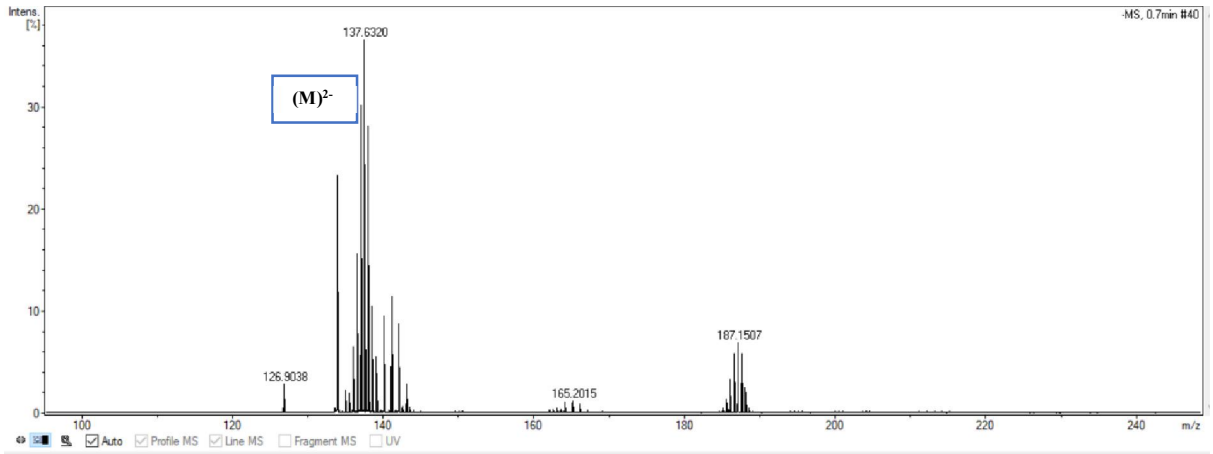
HRMS (TOF) (Negative Mode) for $(Bu_4N)[B_{12}H_{11}$-sulfamide] (6c)



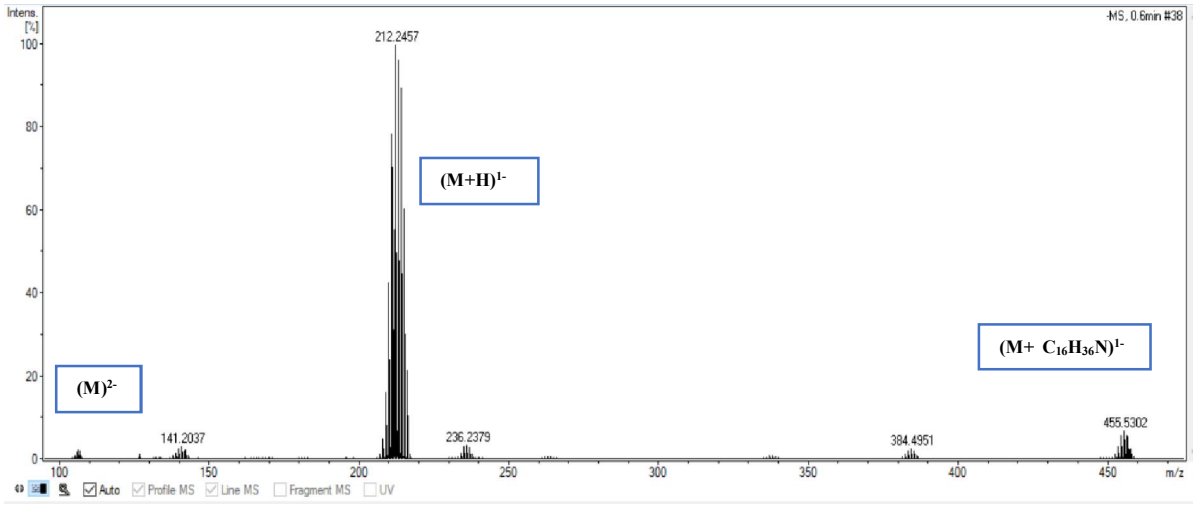
HRMS (TOF) (Negative Mode) for $(Bu_4N)[B_{12}H_{11}$-p-toluenesulfonamide] (6d)



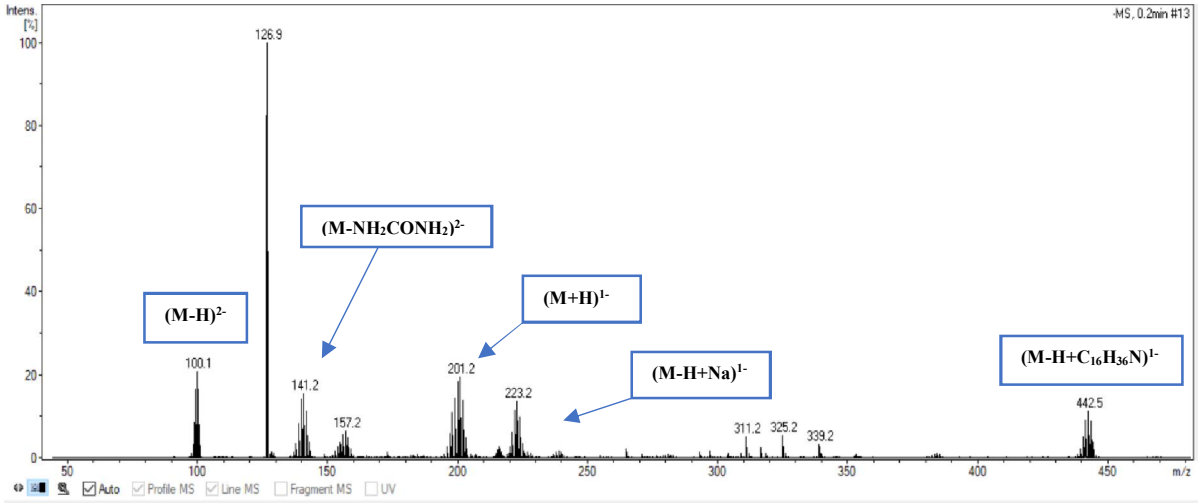
HRMS (TOF) (Negative Mode) for $(Bu_4N)[B_{12}H_{11}$-acetanilide] (6e)



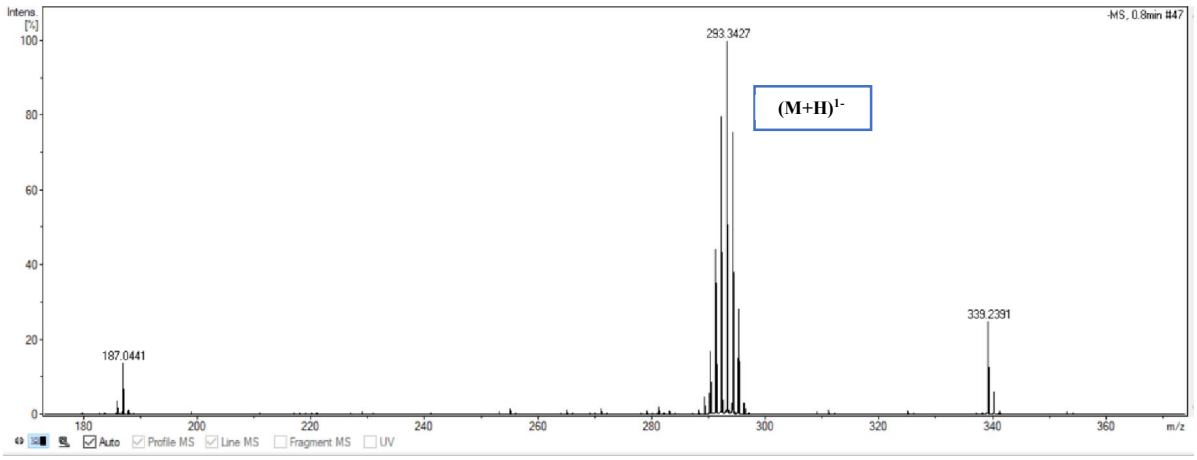
HRMS (TOF) (Negative Mode) for $(Bu_4N)[B_{12}H_{11}$-N-methylacetamide] (6f)



HRMS (TOF) (Negative Mode) for $(Bu_4N)[N\text{-}B_{12}H_{11}$-urea] (6g)

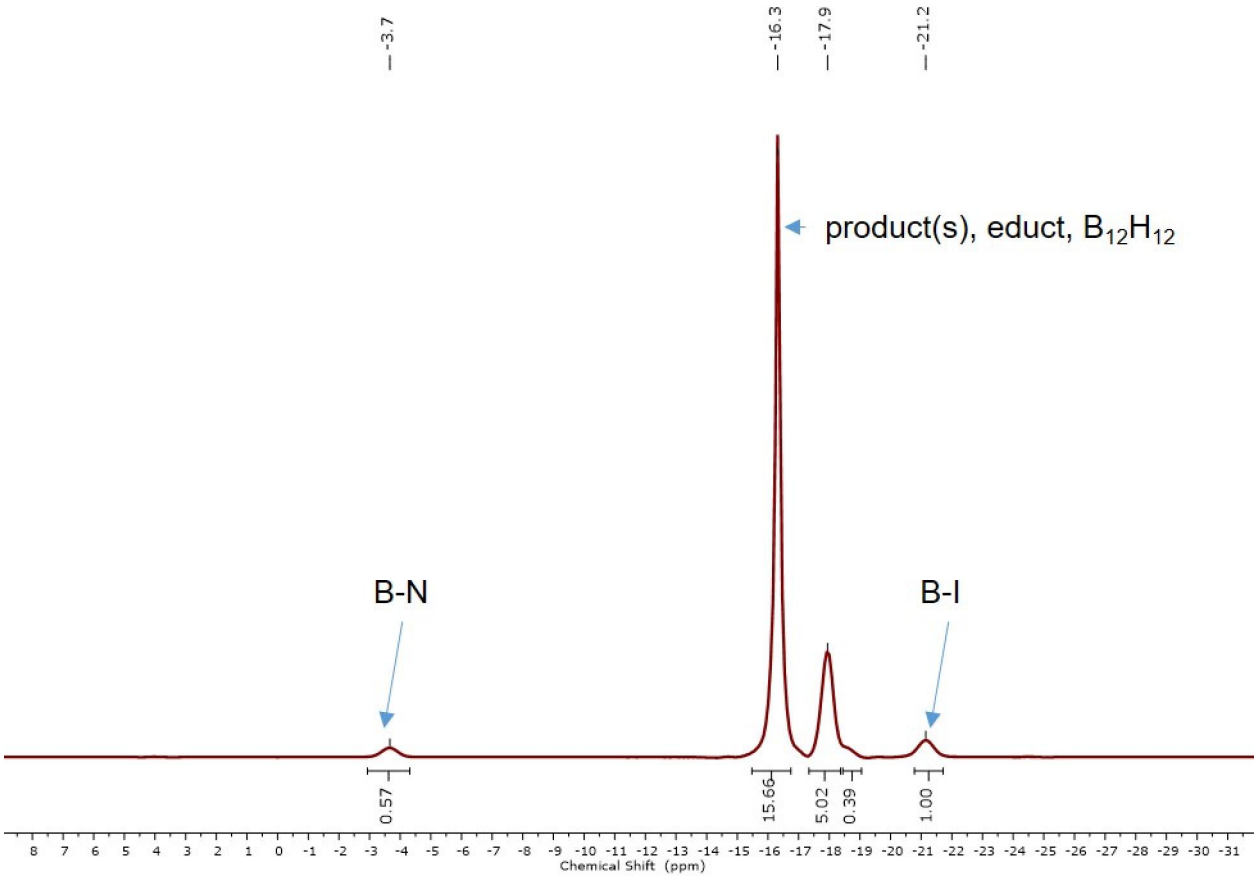


HRMS (TOF) (Negative Mode) for Cs $[B_{12}H_{11}$-DBU] (7)



Clarifying our approach to calculate the yield and conversion percent from ^{11}B-crude NMR

Example for Entry 2, Table 1



Total sum of integrals: 22
For the product B-N signal, and for the educt B-I signal, 11 additional B atoms are hidden in the remaining peaks (summing up to 12 B atoms each). Then the conversion can be determined by dividing the integral of the B-I resonance by the total sum of the integrals, multiplying the value by 12, and by 100, to get the conversion in %:
Conversion [%]: ([Integral_of_B-I_atom]/[total_sum_of_integrals])*12*100 = (1/22)*12*100 = 54.5%
The same applies to the yield (in %) of the desired product:
Yield [%]: ([Integral_of_B-N_atom]/[total_sum_of_integrals])*12*100 = (0.57/22)*12*100 = 31.1%
The values obtained were rounded to the nearest 5%.