Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Crystal Structure of a Carborane *endo*/*exo*-Dianion and its Use in the Synthesis of Ditopic Ligands for Supramolecular Frameworks

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Table of Contents

I	**General Information**	**p. S2–S3**
II	**Experimental Section**	**p. S4–S25**
III	**X-ray Crystallography**	**p. S26–S42**
IV	**References**	**p. S43**
V	**NMR Spectra**	**p. NMR1–NMR35**
VI	**Mass Spectra**	**p. MS1–MS7**

I General Information

Chemicals

If not otherwise specified, reagents and organic solvents were commercially available and used without further purification. Acetone-*d₆*, CD_3CN and DMSO-*d₆* were purchased from Cambridge Isotope Laboratories and filtered through Al_2O_3 prior to use. $[Me_3NH]^+[CB_{11}H_{12}\text{-}12\text{-}CN]^-$ (starting material) was prepared according to the literature [1]. Anhydrous solvents were prepared by passage through activated Al_2O_3 and stored over 3 Å molecular sieves.

Reaction Conditions

Glassware for air-sensitive reations was dried at 200 °C for at least 6 h and allowed to cool in a vacuum.

Lithium diisopropylamide (LDA) and lithium 2,2,4,4-tetramethylpiperidin-1-ide (LiTMP) were prepared from the free amine and *n*-butyllithium in a glovebox under a nitrogen atmosphere with O_2, $H_2O < 1$ ppm.

Characterization

Thin-layer chromatography (TLC) was carried out using silica gel 60, F254 with a thickness of 0.25 mm. Column chromatography was performed on silica gel 60 (200-30 mesh).

Solution-phase NMR spectra were recorded on a Bruker AVANCE III 500 spectrometer (^1H NMR 500.13 MHz, ^{13}C NMR 125.77 MHz, ^{11}B NMR 160.46 MHz) or a Bruker AVANCE III 400 spectrometer (^1H NMR 400.13 MHz, ^{13}C NMR 100.62 MHz, ^{11}B NMR 128.38 MHz) at 23 °C. Data are reported as follows: Chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc.), coupling constant *J* in Hz, integration, and (where applicable) interpretation. Signals were referenced against solvent peaks (residual $C\mathit{H}D_2C(O)CD_3 = 2.05$ ppm, residual $C\mathit{H}D_2S(O)CD_3 = 2.50$ ppm, residual $C\mathit{H}D_2CN = 1.94$ ppm, $^{13}C\{^1H\}$: $\mathit{C}D_3C(O)\mathit{C}D_3 = 29.84$ ppm, $\mathit{C}D_3S(O)\mathit{C}D_3 = 39.52$ ppm). ^{11}B and $^{11}B\{^1H\}$ NMR spectra were calibrated against external $BF_3{*}Et_2O = 0$ ppm ($BF_3{*}Et_2O$ capillary in C_6D_6).

Solid-state NMR spectra were recorded on a Bruker 400WB AVANCE III spectrometer (^{1}H NMR 400.13 MHz, ^{13}C NMR 100.61 MHz, ^{11}B NMR 128.37 MHz) with a 3.2 mm probe at 25 °C. The magic-angle-spin (MAS) frequency was set to 15 kHz. ^{1}H and ^{13}C{1H} chemical shifts were referenced to adamantane (H = 1.8 ppm, CH_2 = 38.5 ppm). ^{11}B and ^{11}B{^{1}H} NMR spectra were calibrated against external BF_3*Et_2O = 0 ppm.

Low-resolution ESI-MS data were recorded on Advion Expression CMS instrument. High-resolution MS data were recorded using IT-TOF detection (Shimadzu, Japan) equipped with an electrospray ionization source (ESI). Accurate mass determination was corrected by calibration using sodium trifluoroacetate clusters as a reference.

IR spectra were recorded on a Nicolet iS10 FT-IR spectrometer as KBr pellets and are reported as wavenumbers (ν, cm^{-1}).

Single-crystal X-ray diffraction studies were performed on an Oxford Diffraction Gemini A Ultra diffractometer equipped with an 135mm Atlas CCD detector and using Mo K-α radiation.

Remark about elemental analysis:

Elemental analysis of boron-containing compounds performed by our department has resulted in inconsistent C/H/N values for identical crystalline batches. The reason seems to be irreproducible formation of boron nitride species as a result of incomplete combustion, at least on our instrument. This finding is in agreement with publications reporting the same phenomenon (Dalton Trans. 2015, 44, 9766–9781; Chem. Eur. J. 2008, 14, 1918–1923 and references cited therein).

We therefore refrained from "submitting until the numbers are right" and shipped two random samples to an external laboratory in Shanghai in order to test whether purity as indicated by NMR and mass spectra corresponds to purity as indicated by elemental analysis. The results were as follows:

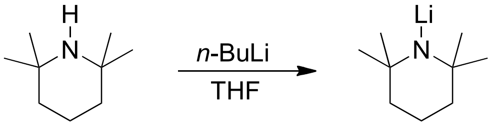
Compound **10a**: C/H/N (%) calculated: 48.00/9.13/11.19; found: 48.34/8.88/11.01.

Compound **10c**: C/H/N (%) calculated: 46.75/7.63/6.06; found: 46.89/7.42/6.12.

II Experimental Section

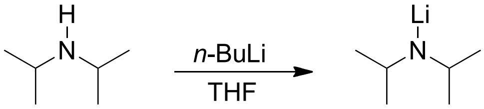
II. a) Amide base formation, lithiation and cupration

Lithium 2,2,6,6-tetramethylpiperidide (LiTMP)



A dry 25 mL vial, equipped with a magnetic stir bar, was charged with 2,2,6,6-tetramethylpiperidine (420.5 mg, 2.98 mmol, 1 equiv) and capped with a rubber septum. Anhydrous THF (4 mL) was then added to the vial via a syringe, and the resulting solution was stirred at 25 °C. A solution of n-BuLi (1.61 M in hexane, 1.8 mL, 2.90 mmol, 0.97 equiv) was slowly dropped into the reaction flask via a syringe over 5 min, and the resulting solution was stirred at 25 °C for 1 h. This solution was used within hours for deprotonation experiments.

Lithium diisopropylamide (LDA)



A dry 25 mL vial, equipped with a magnetic stir bar, was charged with diisopropylamine (301.4 mg, 2.98 mmol, 1 equiv) and capped with a rubber septum. Anhydrous THF (4 mL) was then added to the vial via a syringe, and the resulting solution was stirred at 25 °C. A solution of n-BuLi (1.61 M in hexane, 1.7 mL, 2.74 mmol, 0.97 equiv) was slowly dropped into the reaction flask via a syringe over 5 min, and the resulting solution was stirred at 25 °C for 1 h. This solution was used within hours for deprotonation experiments.

Lithiation and cupration of 6

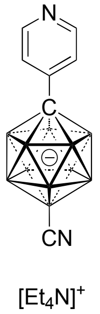
Lithiation: A dry 20 mL glass vial, equipped with a magnetic stir bar, was charged with $[NMe_3H][CB_{11}H_{11}\text{-}12\text{-}CN]$ (40 mg, 0.175 mmol, 1 equiv). Anhydrous THF (2 mL) was then added to the flask, and the resulting solution was stirred at 25 °C for 5 min. A solution of LiTMP (0.45 M in THF, 1.36 mL, 0.61 mmol, 3.5 equiv) was slowly added to the reaction vial via a syringe over 5 min. After 1 h of stirring at 25 °C, a dark red solution was obtained. From such solutions, clean deprotonation could be confirmed by NMR spectroscopy. Spectra were obtained by transferring 0.5 mL of solution to an NMR tube containing a sealed capillary with C_6D_6 for locking and shimming.

Remark: When LDA was used in place of LiTMP under the same conditions, *ca.* 50% deprotonation of **6** was observed. Based on this finding, we estimate the pK_a value of **6** to be ≈36.[2]

Cupration: The reaction mixture was cooled to 0 °C in an ice bath, and CuI (36.7 mg, 0.193 mmol, 1.10 equiv) was added the reaction flask. Then the ice-bath was removed. After 1 h of stirring at 25 °C, a green solution was obtained. Transmetalation to the cuprate was confirmed by NMR spectroscopy. These solutions were used for Pd-catalyzed cross coupling reactions.

II. b) Preparation of ligands 10a–g

Product 10a



A dry 50 mL Schlenk flask equipped with a magnetic stir bar was charged with $[NMe_3H][CB_{11}H_{11}\text{-}12\text{-}CN]$ (282 mg, 1.236 mmol, 1 equiv) and capped with a rubber septum. Anhydrous THF (5 mL) was then added to the flask and the resulting solution was stirred at 25 °C for 5 min. A solution of LiTMP (0.8 M in THF, 5.0 mL, 4.0 mmol, 3.23 equiv) was slowly added to the reaction flask via a syringe over 5 min. After 1 h of stirring at 25 °C, a dark red solution was obtained. The reaction mixture was cooled to 0 °C in an ice bath and CuI (266.2 mg, 1.368 mmol, 1.10 equiv) was added the reaction flask. Then the ice-bath was removed. After 1 h of stirring at 25 °C, a green solution was obtained. A solution of $Pd(OAc)_2$ (26.2 mg, 0.1167 mmol, 0.09 equiv), tris(o-methoxyphenyl)phosphine (83.2 mg, 0.236 mmol, 0.19 equiv), and 4-iodopyridine (342.1 mg, 1.669 mmol, 1.35 equiv) in anhydrous THF (4 mL) was added to the reaction mixture at 0 °C. The mixture was stirred at 25 °C for 16 h. Water (4 mL) was slowly added, and THF was removed using a rotary evaporator. A solution of $[Et_4N]^+ Br^-$ (1.04 g, 5.0 mmol, 4.0 equiv) in water (15 mL) and ethyl acetate (20 mL) were added, the reaction mixture was stirred for 5 h for cation exchange. The aqueous layer was extracted with ethyl acetate (2 x 30 mL). The combined organic layers were dried over magnesium sulfate, filtered into a 250 mL one-necked round-bottom flask and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica gel with CH_2Cl_2/CH_3CN (4:1 v/v) as the eluent. The combined eluates were concentrated with a rotary evaporator and then dried in a vacuum at 60 °C overnight to afford compound 1 as a slightly yellow solid. The solid was added to a 100 mL one-necked round-bottom flask, then the HCl solution (0.5 M in H_2O, 10 mL, 5 mmol) was added and extracted with diethyl ether (3 x 30 mL). The combined organic extracts were dried over magnesium sulfate, filtered into a 200 mL one-necked round-bottom flask and concentrated using a rotary evaporator. NaOH solution (1 M in H_2O, 5 mL) was added, and this aqueous solution was filtered using a pad of celite. To the clear and colorless filtrate, a solution of $[Et_4N]^+ Br^-$ (519.1 mg, 2.47 mmol, 2.0 equiv) in water (10 mL) was added to, and the resulting white solid was collected by filtration and dried in a vacuum at 60 °C to give **10a** (324.5 mg, 70% yield).

$^1H\{^{11}B\}$ NMR (400 MHz, DMSO-d_6, 23 °C): δ 8.37 (d, J = 5.4 Hz, 2H, ArH), δ 8.27 (d, J = 5.4 Hz, 2H, ArH), 3.20 (q, J = 7.3 Hz, 8H, CH_2 of cation), 1.97 (broad signal, 5H, BH), 1.78 (broad signal, 5H, BH), 1.15 (t, J = 7.3 Hz, CH_3 of cation).

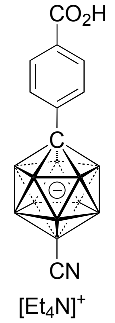
^{11}B NMR (128 MHz, DMSO-d_6, 23 °C): δ c*a.* -11.0 to -15.0 (overlapping signals).

$^{11}B\{^1H\}$ NMR (128 MHz, DMSO-d_6, 23 °C): δ *ca.* -11.5 to -14.5 (overlapping signals with peaks at -12.54 and -13.41).

$^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d6, 23 °C): δ 152.70, 145.81, 124.07 (three pyridyl signals), 70.61 (cage C), 51.37 (CH_2 of cation), 7.08 (CH_3 of cation). The B-C signal could not be detected.

High-resolution ESI-MS (negative mode, MeOH): *m/z* calcd for $[C_7H_{14}B_{11}N_2]^-$: 245.2253. Found: 245.2266.

Product 10b



A dry 25 mL Schlenk flask equipped with a magnetic stir bar was charged with $[NMe_3H][CB_{11}H_{11}\text{-}12\text{-}CN]$ (201.2 mg, 0.882 mmol, 1 equiv) and capped with a rubber septum. Anhydrous THF (5 mL) was then added to the flask, and the resulting solution was stirred at 25 °C for 5 min. A solution of LiTMP (0.8 M in THF, 3.75 mL, 3.0 mmol, 3.40 equiv) was slowly added to the reaction flask via a syringe over 5 min. After 1 h of stirring at 25 °C, a dark red solution was obtained. The reaction mixture was cooled to 0 °C in an ice bath, and CuI (201.1 mg, 1.055 mmol, 1.12 equiv) was added to the reaction flask. Then the ice bath was removed. After 1 h of stirring at 25 °C, a green solution was obtained. A solution of $Pd(OAc)_2$ (17.8 mg, 0.080 mmol, 0.09 equiv), tris(o-methoxyphenyl)phosphine (77.7 mg, 0.221 mmol, 0.25 equiv) and ethyl 4-iodobenzoate (419.1 mg, 1.599 mmol, 1.81 equiv) in anhydrous THF (4.0 mL) was added to the reaction mixture at 0 °C. The reaction mixture was stirred at 25 °C and checked by MS and TLC analysis until no starting material remained. Water (4.0 mL) was slowly added, and THF was removed using a rotary evaporator. A solution of $[Et_4N]^+Br^-$ (740 mg, 3.53 mmol, 4.0 equiv) in water (15 mL) and ethyl acetate (20 mL) were added, and the resulting mixture was stirred for 5 h for cation exchange. The aqueous layer was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over magnesium sulfate, filtered into a 250 mL one-necked round-bottom flask and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica gel with CH_2Cl_2/CH_3CN (8:1 v/v) as the eluent. The combined eluates were concentrated with a rotary evaporator and dried in a vacuum at 60 °C overnight to afford the crude product as a yellow solid. Then the solid and sodium hydroxide (100 mg, 2.5 mmol, 2.8 equiv) were added to a 25 mL one-necked round-bottom flask equipped with a magnetic stir bar. Water (10.0 mL), methanol (5.0 ml) and NaOH (1 M, *ca.* 3 equiv, for hydrolysis of the ester) were added to the flask, and the resulting mixture was stirred at 60 °C for 3 h. Methanol was removed using rotary evaporator, and the aqueous phase was acidified with 1 M

HCl (pH = 2) and extracted with diethyl ether (3 x 40 mL). The combined organic extracts were dried over magnesium sulfate, filtered and concentrated using a rotary evaporator. A solution of $[Et_4N]^+Br^-$ (400 mg, 1.9 mmol, 2.15 equiv) in water (5 mL) was added, and the resulting white solid was collected by filtration through a glass frit and dried in a vacuum at 60 °C to give **10b** (221.2mg, 60% yield).

$^1H\{^{11}B\}$ NMR (500 MHz, Acetone-d_6, 23 °C): δ 7.82 (d, J = 8.5, 2H, ArH), 7.56 (d, 2H, J = 8.5, ArH), 3.48 (q, J = 7.3 Hz, 8H, CH_2 of cation), 2.10 (broad signal overlapping with solvent residual signal, 5H, BH), 1.91 (broad signal, 5H, BH), 1.39 (t, J = 7.3 Hz, 12H, CH_3 of cation).

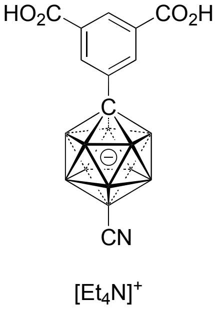
^{11}B NMR (160 MHz, Acetone-d_6, 23 °C): δ *ca.*-11.3 to 14.5 (overlapping signals).

$^{11}B\{^1H\}$ NMR (160 MHz, Acetone-d_6, 23 °C): δ *ca.* -11.3 to -14.5 (overlapping signals with peaks at -12.5 and -13.3).

$^{13}C\{^1H\}$ NMR (125 MHz, Acetone-d_6, 23 °C): δ 167.24 (C=O), 146.68, 129.88, 129.60, 129.05 (4 aromatic signals), 73.53 (cage C), 52.99 (CH_2 of cation), 7.65 (CH_3 of cation). The B-C signal could not be detected.

High-resolution ESI-MS (negative mode, MeOH): *m/z* calcd for $[C_9H_{15}B_{11}NO_2]^-$: 288.2199. Found: 288.2216.

Product 10c



A dry 25 mL Schlenk flask equipped with a magnetic stir bar was charged with $[NMe_3H][CB_{11}H_{11}\text{-}12\text{-}CN]$ (257.4 mg, 1.128 mmol, 1 equiv) and capped with a rubber septum. Anhydrous THF (5 mL) was then added to the flask, and the resulting solution was stirred at 25 °C for 5 min. A solution of LiTMP (0.8 M in THF, 6.0 mL, 4.8 mmol, 3.75 equiv) was slowly added to the reaction flask via a syringe over 5 min. After 1 h of stirring at 25 °C, a dark red solution was obtained. The reaction mixture was cooled to 0 °C in an ice bath, and CuI (243.7 mg, 1.280 mmol, 1.13 equiv) was added to the reaction flask. Then the ice bath was removed. After 1 h of stirring at 25 °C, a green solution was obtained. A solution of $Pd(OAc)_2$ (25.5 mg, 0.1136 mmol, 0.09 equiv), tris(o-methoxyphenyl)phosphine (99.5 mg, 0.282 mmol, 0.25 equiv) and dimethyl 5-iodoisophthalate (467.5 mg, 1.461 mmol, 1.30 equiv) in anhydrous THF (4.0 mL) was added to the reaction mixture at 0 °C. The reaction mixture was stirred at 25 °C for 18 h. Water (4.0 mL) was slowly added, and THF was removed using a rotary evaporator. A solution of $[Et_4N]^+Br^-$ (947 mg, 4.5 mmol, 4.0 equiv) in water (15 mL) and ethyl acetate (20 mL) were added, and the resulting mixture was stirred for 5 h for cation exchange. The aqueous layer was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over magnesium sulfate, filtered into a 200 mL one-necked round-bottom flask and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica gel with CH_2Cl_2/CH_3CN (8:1 v/v) as the eluent. The combined eluates were concentrated with a rotary evaporator and dried in a vacuum at 60 °C overnight to afford the crude product as a yellow solid. Then the crude product and sodium hydroxide (200 mg, 5 mmol, 4.4 equiv) were added to a 25 mL one-necked round-bottom flask equipped with a magnetic stir bar. Water (10.0 mL) and methanol (5.0 ml) were added to the flask and the resulting mixture was stirred at 60 °C for 3 h for ester hydrolysis. Methanol was removed using a rotary evaporator, and the aqueous phase was acidified with 1 M HCl (pH = 2) and extracted with diethyl ether (3 x 40 mL). The combined organic extracts were dried over magnesium sulfate, filtered and concentrated using a rotary evaporator. A solution of $[Et_4N]^+Br^-$ (400 mg, 1.9 mmol, 1.68 equiv) in water (5 mL) was added, and the resulting white solide was collected by filtration through a glass frit and dried in a vacuum at 60 °C to give **10c** (338.8mg, 65% yield).

$^1H\{^{11}B\}$ NMR (500 MHz, DMSO-d_6, 23 °C): δ 13.33 (broad signal, 2H, OH), 8.28 (s, 1H, ArH), 8.13 (s, 2H, ArH), 3.20 (q, J = 7.3 Hz, 8H, CH_2 of cation), 2.01 (broad signal, 5H, BH), 1.80 (broad signal, 5H, BH), 1.16 (t, J = 7.3 Hz, 12H, CH_3 of cation).

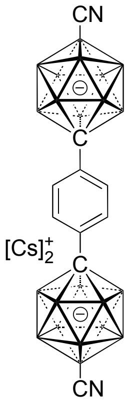
^{11}B NMR (160 MHz, DMSO-d_6, 23 °C): δ *ca.*-11.0 to 15.0 (overlapping signals).

$^{11}B\{^1H\}$ NMR (160 MHz, DMSO-d_6, 23 °C): δ *ca.* -11.0 to -14.0 (overlapping signals with peaks at -12.5 and -13.2).

$^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d6, 23 °C): δ 166.22 (C=O), 140.81, 132.17, 130.95, 128.77 (4 phenyl signals), 71.98 (cage C), 51.39 (CH_2 of cation), 7.08 (CH_3 of cation). The B-C signal could not be detected.

High-resolution ESI-MS (negative mode, MeOH): *m/z* calcd for $[C_{10}H_{15}B_{11}NO_4]^-$: 332.2097. Found: 332.2127.

Product 10d



A dry 25 mL Schlenk flask equipped with a magnetic stir bar was charged with [NMe_3H][$CB_{11}H_{11}$-12-CN] (112.2 mg, 0.5 mmol, 1 equiv) and capped with a rubber septum. Anhydrous THF (5 mL) was then added to the flask, and the resulting solution was stirred at 25 °C for 5 min. A solution of LiTMP (0.8 M in THF, 2.0 mL, 1.6 mmol, 3.20 equiv) was slowly added to the reaction flask via a syringe over 5 min. After 1 h of stirring at 25 °C, a dark red solution was obtained. The reaction mixture was cooled to 0 °C in an ice bath, and CuI (106.0 mg, 0.55 mmol, 1.10 equiv) was added to the reaction flask. Then the ice bath was removed. After 1 h of stirring at 25 °C, a green solution was obtained. A solution of $Pd(OAc)_2$ (10.10 mg, 0.04 mmol, 0.09 equiv), tris(o-methoxyphenyl)phosphine (44.05 mg, 0.13 mmol, 0.25 equiv) and dimethyl 1,4-diiodobenzene (73.4 mg, 0.22 mmol, 0.44 equiv) in anhydrous THF (4.0 mL) was added to the reaction mixture at 0 °C. The reaction mixture was stirred at 25 °C for 2 days. Water (4.0mL) was slowly added, and THF was removed using a rotary evaporator. A solution of $[Et_4N]^+Br^-$ (420 mg, 2.0 mmol, 4.0 equiv) in water (15 mL) and ethyl acetate (20 mL) were added, and the resulting mixture was stirred for 5 h for cation exchange. The aqueous layer was extracted with ethyl acetate (2 x 30 mL). The combined organic layers were dried over magnesium sulfate, filtered into a 250 mL one-necked round-bottom flask and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica gel with CH_2Cl_2/CH_3CN (3:1 v/v) as the eluent. The combined eluates were concentrated with a rotary evaporator and dried in a vacuum at 60 °C overnight to afford the crude product as a slightly yellow solid. The solid was added to a 100 mL one-necked round-bottom flask, then the HCl solution (1 M in H_2O, 10 mL, 5 mmol) was added and extracted with diethyl ether (3 x 30 mL). The combined organic layers were dried over Cs_2CO_3 and filtered into a 200 mL one-necked round flask. To the flask a solution of Cs_2CO_3 (488.73 mg, 1.5 mmol, 3 equiv) in water (5 mL) was added. Most of the solvent was removed using a rotary evaporator, and acetone (50 mL) was added to the remaining solid. The solution was filtered into a 200 mL one-necked round-bottom flask, and to this solution water (50 mL) was added. Acetone was removed using a rotary evaporator, and the aqueous layer was filtered into a 150 mL one-necked round-bottom flask using a pad of celite. Most of the solvent was removed using a rotary evaporator. The white solide was collected by filtration through a glass frit and dried in a vacuum at 60 °C to give **10d** (84 mg, 50% yield).

^{1}H{^{11}B} NMR (500 MHz, DMSO-*d*$_6$, 23 °C): δ 7.10 (s, 4H, ArH), 1.93 (broad signal 10H, BH), 1.72 (broad signal 10H, BH).

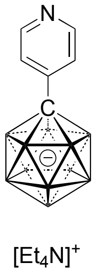
^{11}B NMR (160 MHz, DMSO-*d*$_6$, 23 °C): δ *ca.*-11.5 to 14.5 (overlapping signals).

^{11}B{^{1}H} NMR (160 MHz, DMSO-*d*$_6$, 23 °C): δ *ca.* -11.5 to -14.5 (overlapping signals with a peak at -12.8 and -13.2).

^{13}C{^{1}H} NMR (125 MHz, DMSO-*d*$_6$, 23 °C): δ 138.64, 126.88 (two aromatic signals), 72.89 (cage C). The B-C signal could not be detected.

High-resolution ESI-MS (negative mode, MeOH): *m/z* calcd for $[C_{10}H_{24}B_{22}N_2]^{2-}$: 205.2066. Found: 205.2074.

Product 10e



A dry 100 mL Schlenk flask equipped with a magnetic stir bar was charged with $[NMe_3H][CB_{11}H_{12}]$ (500 mg, 2.46 mmol, 1 equiv) and capped with a rubber septum. Anhydrous THF (25 mL) was then added to the flask and the resulting solution was stirred at 25 °C for 5 min. A solution of n-BuLi (1.60 M in Hexane, 5.0 mL, 8.0 mmol, 3.25 equiv) was slowly added to the reaction flask via a syringe over 5 min. After 1 h of stirring at 25 °C, a yellow solution was obtained. The reaction mixture was cooled to 0 °C in an ice bath, and CuI (515.3 mg, 2.71 mmol, 1.10 equiv) was added the reaction flask. Then the ice-bath was removed. After 1 h of stirring at 25 °C, a green solution was obtained. A solution of Pd(OAc)2 (164.7 mg, 0.22 mmol, 0.09 equiv), tris(o-methoxyphenyl)phosphine (83.2 mg, 0.47mmol, 0.19 equiv) and 4-iodopyridine (680.8 mg, 3.32 mmol, 1.35 equiv) in anhydrous THF (10 mL) was added to the reaction mixture at 0 °C. The mixture was stirred at 25 °C for 16 h. Water (20 mL) was slowly added, and THF was removed using a rotary evaporator. A solution of $[Et_4N]^+Br^-$ (1.54 g, 7.38 mmol, 3.0 equiv) in water (15 mL) and ethyl acetate (20 mL) were added, and the resulting mixture was stirred for 5 h for cation exchange. The aqueous layer was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over magnesium sulfate, filtered into a 200 mL one-necked round-bottom flask and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica gel with CH_2Cl_2/CH_3CN (4:1 v/v) as the eluent. The combined eluates were concentrated with a rotary evaporator and then dried in a vacuum at 60 °C overnight to afford compound **x** as a slightly yellow solid. The crude product was added to a 100 mL one-necked round-bottom flask, then the HCl solution (0.5 M in H_2O, 20 mL, 10 mmol) was added and extracted with diethyl ether (3 x 40 mL). The combined organic extracts were dried over magnesium sulfate, filtered into a 200 mL one-necked round-bottom flask and concentrated using a rotary evaporator. NaOH solution (1 M in H_2O, 10 mL) was added, and this aqueous solution was filtrated using a pad of celite. To the clear and colorless filtrate, a solution of $[Et_4N]^+Br^-$ (1.03 g, 4.92 mmol, 2.0 equiv) in water (10 mL) was added to the filtrate, and the resulting white solide was collected by filtration through a glass frit and dried in a vacuum at 60 °C to give **10e** (688.7 mg, 80% yield).

^{1}H{^{11}B} NMR (400 MHz, Acetone-d_6, 23 °C): δ 8.32 (d, *J* = 5.8 Hz, 2H, ArH), 7.38 (d, *J* = 5.8 Hz, 2H, ArH), 3.48 (q, *J* = 7.3 Hz, 8H, CH_2 of cation), 2.00 (broad signal overlapping with solvent residual signal, 5H, BH), 1.81 (broad signal, 1H, BH), 1.72 (broad signal, 5H, BH), 1.39 (t, *J* = 7.3 Hz, 12H, CH_3 of cation).

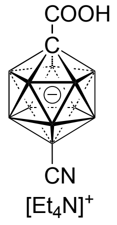
^{11}B NMR (128 MHz, Acetone-d_6, 23 °C): δ -6.99 (d, *J* = 137 Hz, 1B, B-12), *ca.* -12.4 (overlapping d, *J* = *ca.* 130 Hz, 5B), *ca.* -13.4 (overlapping d, *J* = *ca.* 130 Hz, 5B).

^{11}B{^{1}H} NMR (128 MHz, Acetone-d_6, 23 °C): δ -6.99 (1B), -12.44 (5B), -13.27 (5B).

^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6, 23 °C): δ 151.36, 149.66, 124.07 (three pyridyl signals), 70.97 (cage C), 52.99 (CH_2 of cation), 7.65 (CH_3 of cation). The B-C signal could not be detected.

High-resolution ESI-MS (negative mode, MeOH): *m/z* calcd for $[C_7H_{14}B_{11}N_2]^-$: 220.2301. Found: 220.2305.

Product 10f (prepared according to the literature [3])



A dry 25 mL Schlenk tube equipped with a magnetic stir bar was charged with $[NMe_3H][CB_{11}H_{11}\text{-}12\text{-}CN]$ (211.2 mg, 0.708 mmol, 1 equiv) and capped with a rubber septum. Anhydrous THF (5 mL) was then added to the flask and the resulting solution was stirred at 25 °C for 5 min. A solution of LiTMP (0.8 M in THF, 3.8 mL, 3.0 mmol, 4.23 equiv) was slowly added to the reaction flask via a syringe over 5 min. After 1 h of stirring at 25 °C, a dark red solution was obtained. Dry CO_2 gas was then bubbled through the mixture at 0 °C (2-3 bubbles/s) for 10 min. Then the mixture was warmed to 25 °C and stirred for 10 h. Water (3 mL) was slowly added and the solution was concentrated on a rotary evaporator, the residue was dissolved in water (20 mL), washed with diethyl ether (under these basic conditions the dianionic product was in the water layer), and the aqueous phase was acidified with 1 M HCl (pH = 2) and extracted with diethyl ether (3 x 20 mL). The combined organic extracts were dried over magnesium sulfate, filtered and concentrated using a rotary evaporator. A solution of $[Et_4N]^+ Br^-$ (400 mg, 1.9 mmol, 2.68 equiv) in water (4 mL) was added, the resulting white solide was collected by filtration through a glass frit and dried in a vacuum at 60 °C to give **10f** (268.0 mg, 85% yield).

$^1H\{^{11}B\}$ NMR (400 MHz, DMSO-d_6, 23 °C): δ 12.70 (broad s, 1H, COOH), 3.20 (q, J = 7.3 Hz, 8H, CH_2 of cation), 1.87 (broad, 5H, BH), 1.65 (broad signal, 5H, BH), 1.15 (t, J = 7.3 Hz, 12H, CH_3 of cation).

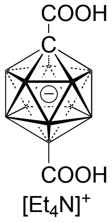
^{11}B NMR (128 MHz, DMSO-d_6, 23 °C): δ ca. -11.5 to -16.5 (overlapping signals).

$^{11}B\{^1H\}$ NMR (128 MHz, DMSO-d_6, 23 °C): δ ca. -11.7 to -15.5 (overlapping signals with peaks at -13.07 and -14.21).

$^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6, 23 °C): δ 166.63 (C-*C*OOH), 69.40 (cage C), 51.38 (CH_2 of cation), 7.08 (CH_3 of cation). The B-C signal could not be detected.

High-resolution ESI-MS (negative mode, MeOH): *m/z* calcd for $[C_3H_{11}B_{11}NO_2]^-$: 212.1886. Found: 212.1915.

Product 10g



A PTFE-lined cylinder-shaped steel autoclave (25 mL) was charged with **10f** (10.0 mg, 0.028 mmol), 0.75 mL of conc. aq. HCl and 0.25 mL of glacial acetic acid. The autoclave was sealed and heated to 180 °C for 3h. The resulting cloudy solution was concentrated using a rotary evaporator. NaOH solution (0.1 M in H_2O, 3 mL) was added, and this aqueous solution was filtrated using a pad of celite. To the clear and colorless filtrate, $[Et_4N]^+ Br^-$ (15 mg, 0.065 mmol) was added, followed by conc. aq. HCl until the solution was acidic. The resulting white precipitate was collected by filtration and dried in a vacuum at 60 °C to give a colorless solid (10.1 mg). According to NMR spectra, the purity at this stage was ca. 90% This was solid was suspended in hexane (2 mL), and acetone (ca. 1.5 mL) was added until the compound was dissolved completely. Concentration on a rotary evaporator afforded colorless crystals that were collected by filtration and dried overnight in a vacuum at 60 °C to give **10g** (5.6 mg).

Spectra of this compound are shown in Figures S1–5. NMR spectra revealed that the isolated material still contained a small amount of acetone (2.09 ppm *vs* $C\mathit{H}D_2C(O)CD_3$ at 2.05 ppm), which could not be removed even upon prolonged drying in a vacuum. The procedure was repeated multiple times and worked as described above on a small scale, but attempts to synthesize larger amounts of **10g** were not successful.

$^1H\{^{11}B\}$ NMR (400 MHz, Acetone-*d*$_6$, 23 °C): δ 3.50 (q, *J* = 7.3 Hz, 8H, CH_2 of cation), 2.02 (broad signal overlapping with solvent residual signal, 5H, BH), 1.85 (broad signal, 5H, BH), 1.40 (t, *J* = 7.3 Hz, 12H, CH_3 of cation).

^{11}B NMR (128 MHz, Acetone-*d*$_6$, 23 °C): δ -3.81 (s, 1B, B-12), *ca.* -13.0 (overlapping d, *J* = *ca.* 130 Hz, 5B), *ca.* -14.3 (overlapping d, *J* = *ca.* 130 Hz, 5B).

$^{11}B\{^1H\}$ NMR (128 MHz, Acetone-*d*$_6$, 23 °C): δ -3.76 (1B), -12.91 (5B), -14.44 (5B).

$^{13}C\{^1H\}$ NMR (101 MHz, Acetone-d_6, 23 °C): δ 168.31 (C-*C*OOH), 67.49 (cage C), 53.03 (CH_2 of cation), 7.68 (CH_3 of cation). The B-C signal could not be detected.

High-resolution ESI-MS (negative mode, MeOH): *m/z* calcd for $[C_3H_{12}B_{11}O_4]^-$: 231.1832. Found: 231.1846.

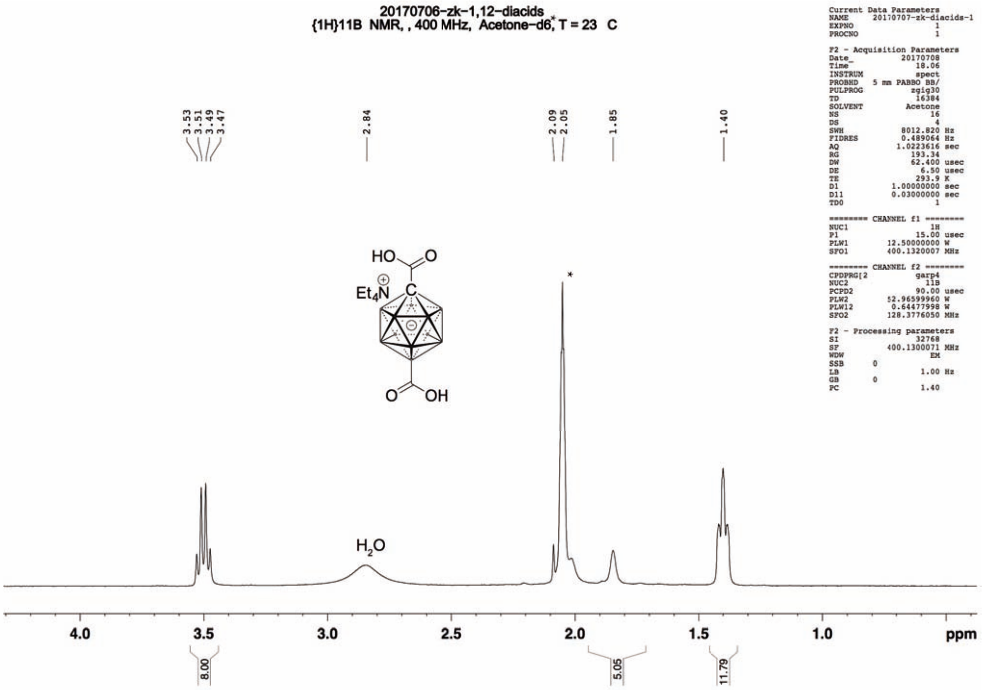


Figure S1. ^{1}H{^{11}B} NMR spectrum of **10g** (400 MHz, 25 °C, Acetone-d_6). Cation signals appear at 3.50 and 1.40 ppm; B–H signals are seen at 2.02 (overlapping with solvent residual peak) and 1.85 ppm.

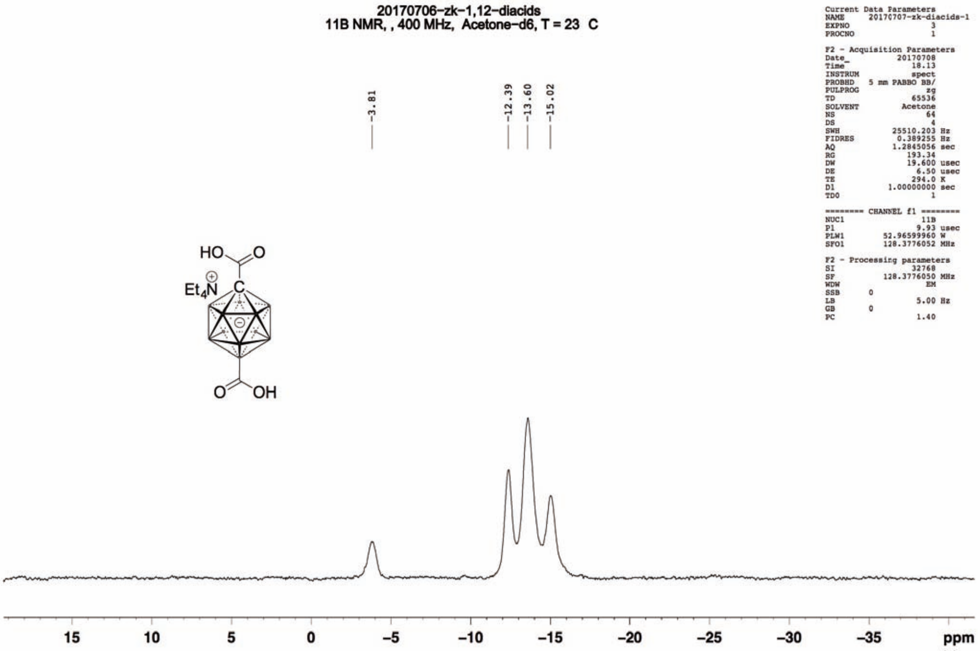
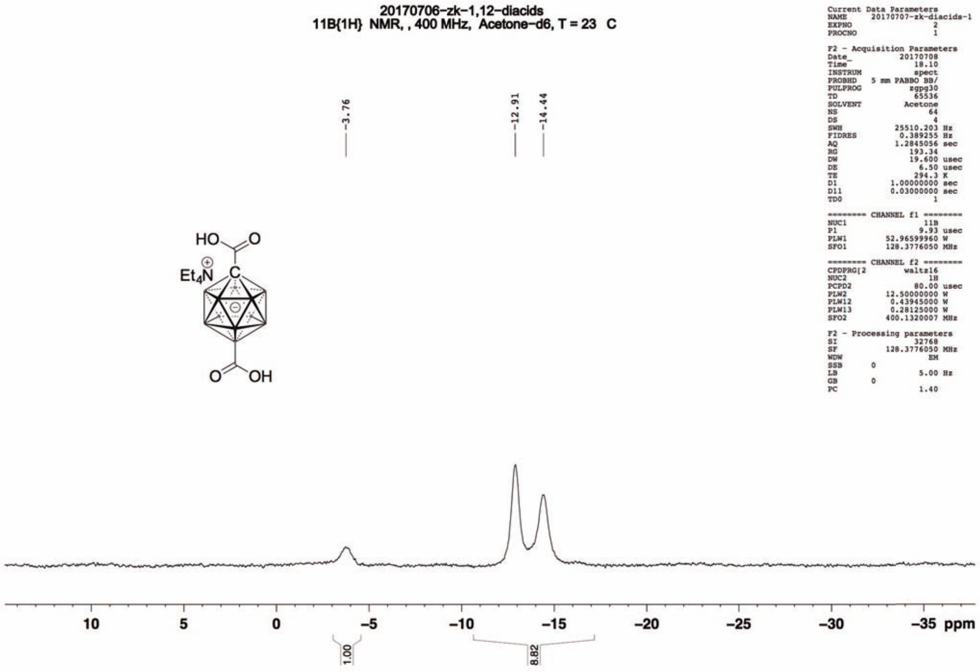


Figure S2. ^{11}B NMR spectrum of **10g** (128 MHz, 25 °C, Acetone-d_6).



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PROCNO                   1

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NS                     64
DS                      4
SWH             25510.203 Hz
FIDRES           0.389255 Hz
AQ              1.2845056 sec
RG                 193.34
DW                 19.600 usec
DE                   6.50 usec
TE                  294.3 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1

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SFO1          128.3776050 MHz

======== CHANNEL f2 ========
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SFO2          400.1320007 MHz

F2 - Processing parameters
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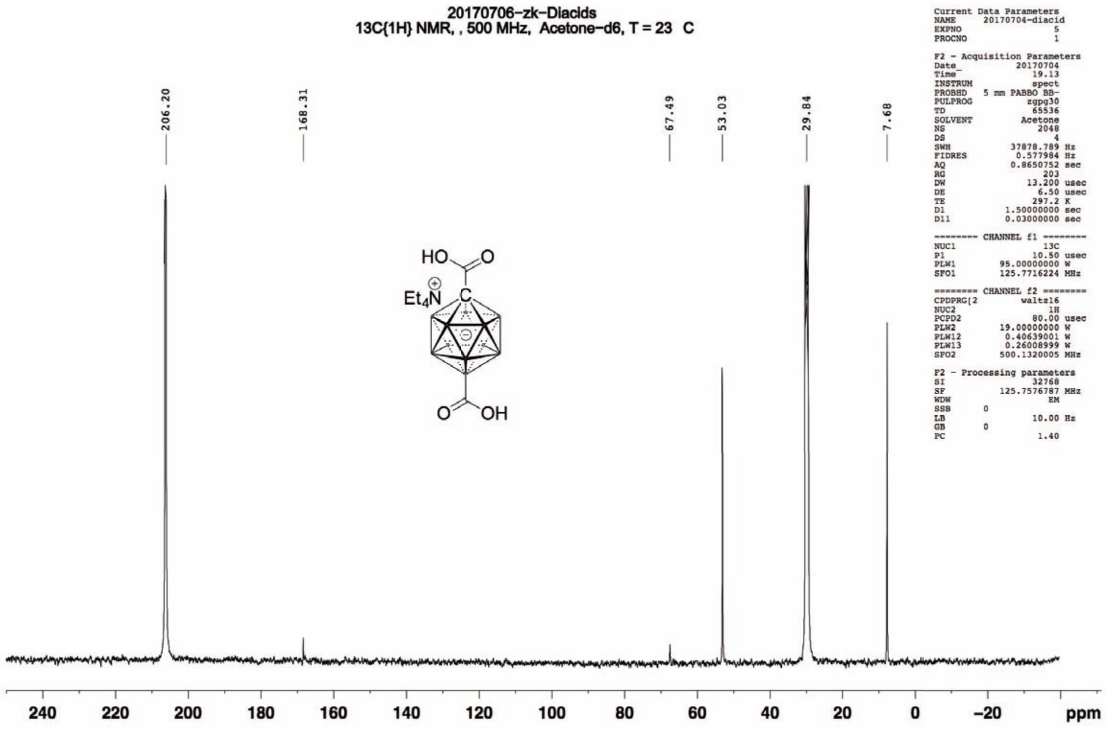
Figure S3. ^{11}B{^{1}H} NMR spectrum of **10g** (128 MHz, 25 °C, Acetone-d_6).



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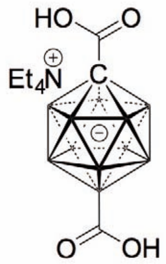
NS                   2048
DS                      4
SWH             37878.789 Hz
FIDRES           0.577984 Hz
AQ              0.8650752 sec
RG                    203
DW                 13.200 usec
DE                   6.50 usec
TE                  297.2 K
D1             1.50000000 sec
D11            0.03000000 sec

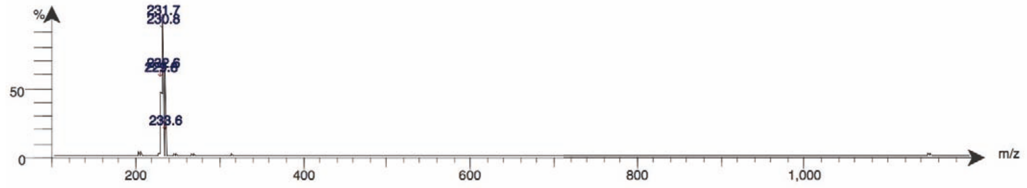
======== CHANNEL f1 ========
NUC1                  13C
P1                  10.50 usec
PLW1          95.00000000 W
SFO1          125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.40639001 W
PLW13          0.26008999 W
SFO2          500.1320005 MHz

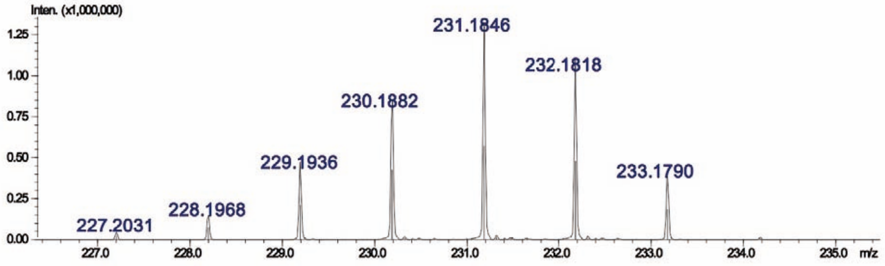
F2 - Processing parameters
SI                  32768
SF            125.7576787 MHz
WDW                    EM
SSB       0
LB                  10.00 Hz
GB        0
PC                   1.40
```

Figure S4. ^{13}C{^{1}H} NMR spectrum of **10g** (125 MHz, 25 °C, Acetone-d_6). Cation signals appear at 53.03 ppm and 7.68 ppm; C-*C*O$_2$H and the cage carbon atom are seen at 168.31 ppm and 67.49 ppm. The B(12)-*C*O$_2$H signal could not be detected.





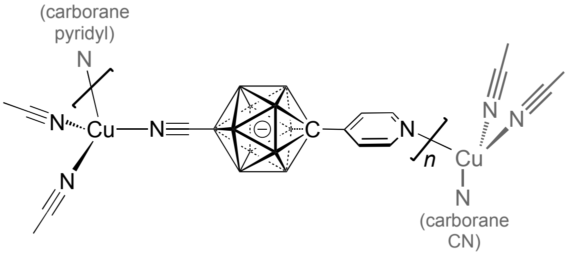
Low-resolution full-range ESI-MS negative mode



High-resolution ESI-MS negative mode

Figure S5. Mass spectra of **10g**.

II. c) Preparation of polymer 11 based on ligand 10a and Cu(I)



In a 4 mL glass vial **10a** (10 mg, 0.027 mmol) and CuI (5.2 mg, 0.027 mmol) were dissolved in MeCN (0.7 mL) at 25 °C, and the mixture was stirred for 4 h. Slow evaporation of ca. 70% of the solvent afforded colorless crystals of the composition $[((MeCN)_2Cu)$-1-pyridyl-$CB_{11}H_{10}$-12-$CN]_n$, which were initially characterized by X-ray crystallography (50% yield). Solution-phase and solid-state NMR measurements of crystalline product were in agreement with the structure determined by X-ray diffraction (see below).

Solution-phase NMR: Several deuterated solvents were tested, but only CD_3CN gave a solubility high enough for $^1H\{^{11}B\}$, ^{11}B NMR and $^{11}B\{^1H\}$ measurements (ca. 1.5 mg/mL). This concentration was not sufficient to obtain $^{13}C\{^1H\}$ data. Upon dissolution, **11** probably breaks up into monomers, *i.e.* $[Cu(solv)_n]$[**10a**].

$^1H\{^{11}B\}$ NMR (500 MHz, CD_3CN, 23 °C): δ 8.32 (broad signal, coupling not resolved, 2H), 7.39 (broad signal, coupling not resolved, 2H), 2.00 (broad signal overlapping with solvent residual signal, 5H, BH), 1.96 (s, 6H, CH_3CN), 1.82 (broad signal, 5H, BH).

^{11}B NMR (160 MHz, CD_3CN, 23 °C): δ c*a.* -11.3 to -14.8 (overlapping signals).

$^{11}B\{^1H\}$ NMR (160 MHz, CD_3CN, 23 °C): δ *ca.* -11.6 to -14.4 (overlapping signals with peaks at -12.50 and -13.49).

ESI-MS (negative mode, dissolved in MeCN, MS eluent = MeOH):
Only the signal of the monomeric [1-(4-pyridyl)-$CB_{11}H_{10}$-12-$CN]^-$ was detected, *m/z* 245.4 (calculated 245.2).
The spectrum matched with that of isolated **10a** and is displayed on p. MS7.

Solid-state NMR:

^{1}H NMR (400 MHz, 25 °C): δ ca. 10.7 to 6.0 (2 overlapping broad signals with peaks at 8.69 and 7.39, 4 H, ArH), ca. 5.2 to -3 (overlapping broad signals, 16 H, CH_3CN and BH) .

^{11}B NMR (128 MHz, 25 °C): δ ca. -4 to -21 (broad overlapping signals with peaks at -12.31 and -13.72).

^{11}B{^{1}H} NMR (128 MHz, 25 °C): δ ca. -4 to -21 (broad overlapping signals with a shoulder at -12.42 and a peak at -13.71).

^{13}C{^{1}H} NMR (101 MHz, 25 °C): δ 150.77 (two overlapping pyridyl signals), 122.64 (pyridyl signal), 117.22 ($CH_3\mathit{C}N$), 72.76 (cage C), 3.61 ($\mathit{C}H_3CN$). The B-C signal could not be detected.

Product **11** was in addition analyzed by IR spectrocopy, and a comparison of the IR spectra of **10a** and **11** is shown in Figures S6/S7.

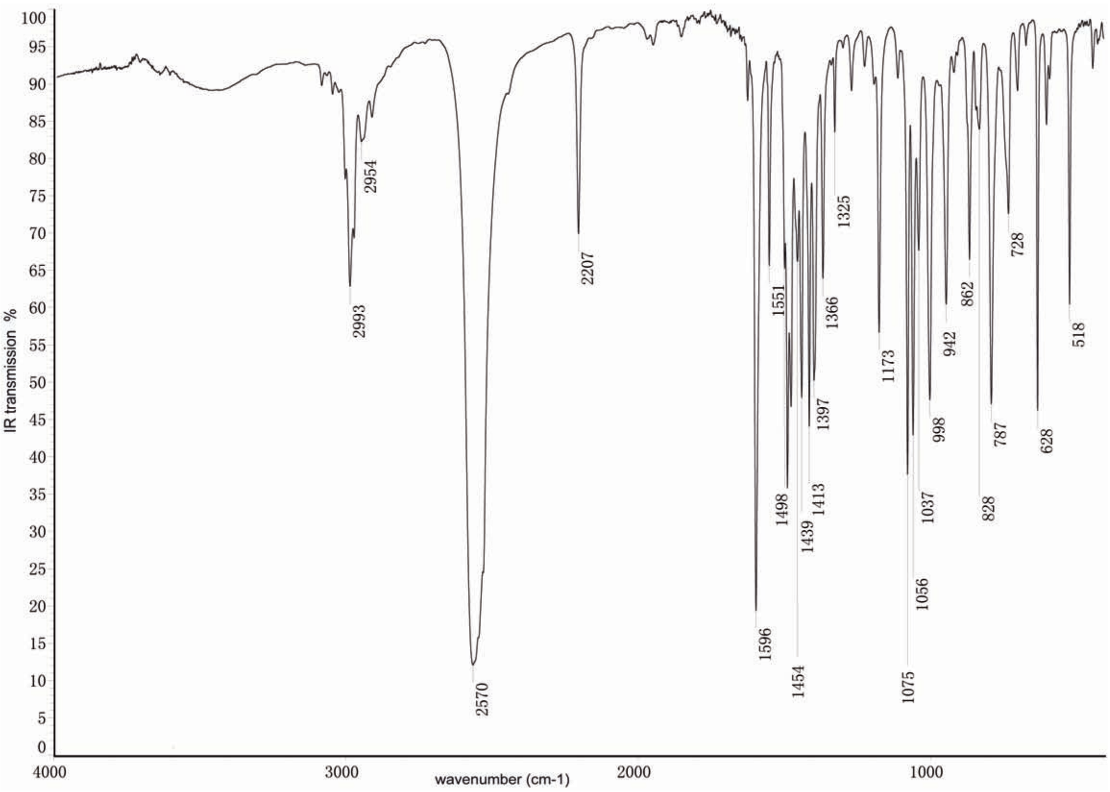


Figure S6. IR spectrum of **10a** (KBr pellet).

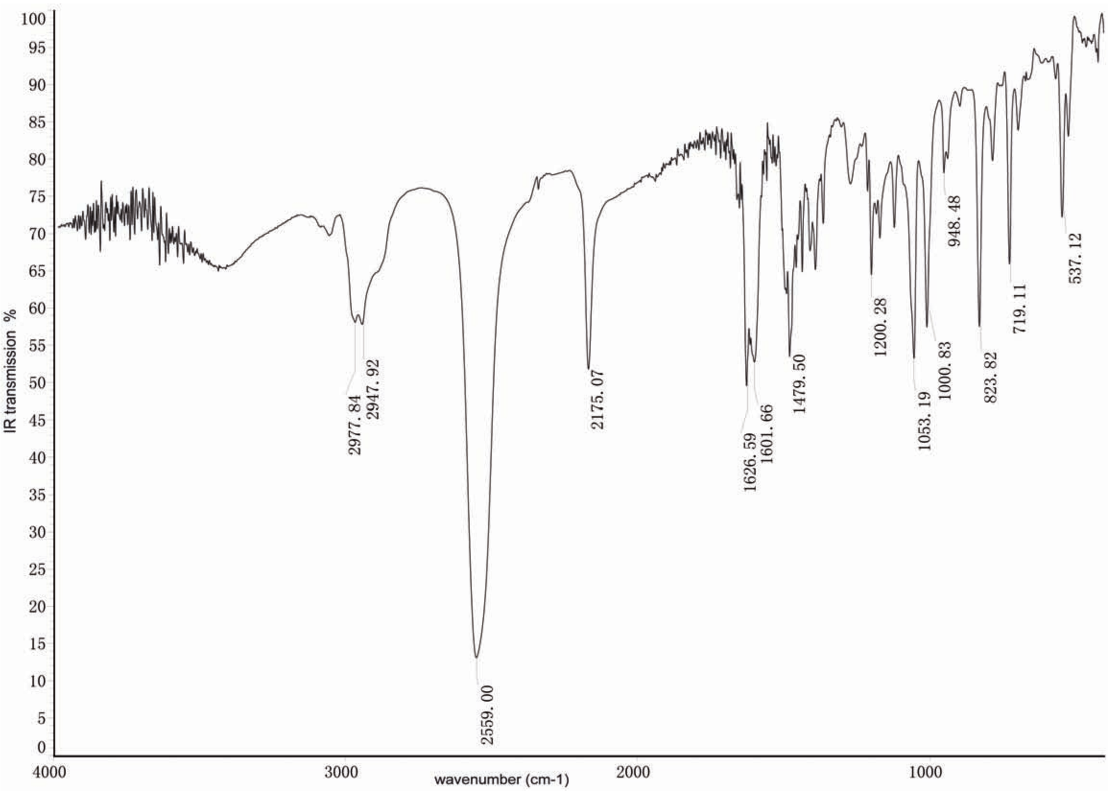


Figure S7. IR spectrum of **11** (KBr pellet).

III X-ray Crystallography

General remarks

CCDC1559903–1559909 contain the supplementary crystallographic data for this publication. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

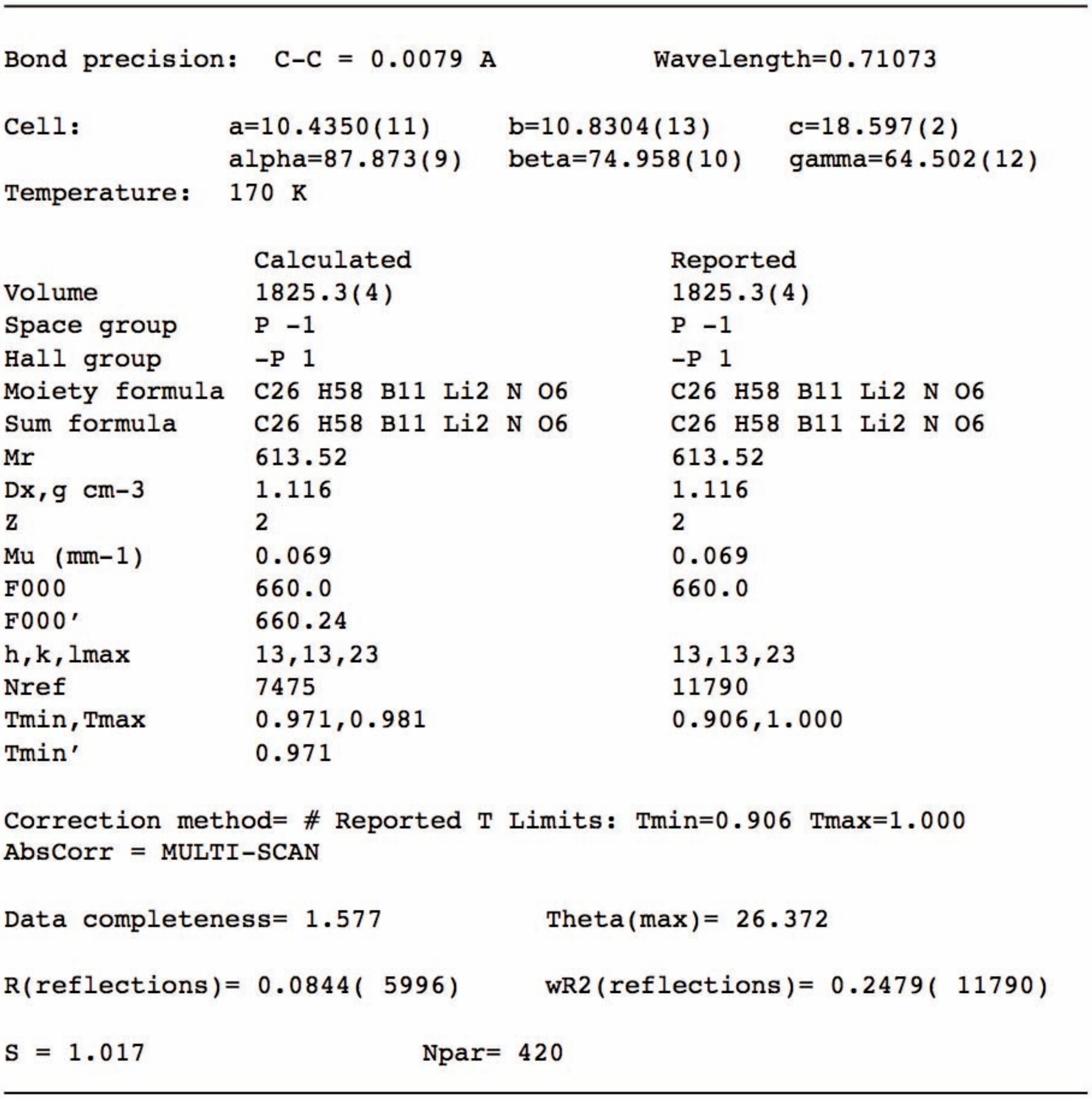
Crystals of **7**, **10e** and **11** were measured at 170 K, while compounds **10a**, **10d**, **10f** and **10g** were measured at room temperature because the X-ray facility of our department does not routinely offer measurements at 170 K with nitrogen cooling.

Summary of data

Product	**7**	**10a**	**10d**	**10e**	**10f**	**10g**	**11**
Empirical formula	$C_{26}H_{58}B_{11}Li_2NO_6$	$C_{11}H_{23}B_{11}N_2O$	$C_{10}H_{64}B_{22}N_4$	$C_{20}H_{31}B_{22}N_3$	$C_{11}H_{31}B_{11}N_2O_2$	$C_{11}H_{12}B_{11}NO_4$	$C_{11}H_{20}B_{11}CuN_4$
M (g/mol)	613.52	318.22	670.63	551.30	342.29	341.13	390.77
T (K)	170	293	293	170	293	293	170
Crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic	tetragonal	orthorhombic
Space group	$P\ \bar{1}$	$P\ 1\ 2_1/c$	$P\ \bar{1}$	$P\ \bar{1}$	P1	I4/m	Pnma
a (Å)	10.4350(11)	7.4039(6)	8.5061(6)	10.2902(11)	7.444(4)	12.3385(9)	17.345(2)
b (Å)	10.8304(13)	14.0616(14)	10.3155(9)	10.7001(12)	7.573(5)	12.3385(9)	12.6451(12)
c (Å)	18.597(2)	18.0481(15)	12.1216(11)	16.1214(14)	9.562(5)	13.745(2)	9.1310(7)
α (°)	87.873(9)	90.00	91.607(7)	73.928(9)	91.55(5)	90.00	90.00
β (°)	74.958(10)	92.372(7)	96.421(7)	86.356(8)	106.37(5)	90.00	90.00
γ (°)	64.502(12)	90.00	92.598(6)	88.275(9)	91.65(5)	90.00	90.00
Volume (Å^3)	1825.3(4)	1877.4(3)	1055.26(15)	1702.1(3)	516.6(5)	2092.5(4)	2002.7(3)
Z	2	4	1	2	1	4	4
D_{calc} (g/cm^3)	1.116	1.126	1.055	1.115	1.100	1.147	1.296
μ (mm^{-1})	0.069	0.061	0.053	0.055	0.062	0.070	1.093
F (000)	660	664	358	604	182	768	792
N (coll. refl.)	11790	3430	3863	6154	2429	994	1913
N (parameters/restraints)	420/0	230/1	239/0	449/0	236/14	93/1	137/0
*R*1	0.0844	266/67	0.0647	0.0845	0.1201	0.0540	0.0460
*wR*2	0.2479	0.0785	0.1885	0.2915	0.3464	0.1529	0.1098
GOF	1.017	0.2265	1.022	0.0985	1.068	1.082	1.055
CCDC	1559909	1559903	1559904	1559905	1559906	1559907	1559908

Product 7 (CCDC1559909)

In a glovebox, a solution of **7** (0.5 mL) in a 4 mL glass vial, obtained by deprotonation with LiTMP in THF as described in the experimental section, was placed in a 20 mL glass vial containing hexane (4 mL). Vapor diffusion afforded colorless crystals of the composition $[Li(THF)_3]_2[CB_{11}H_{10}\text{-}12\text{-}CN]$ suitable for X-ray diffraction within 3 d at 25 ^{o}C.



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                 alpha=87.873(9)   beta=74.958(10)   gamma=64.502(12)
Temperature:     170 K

                 Calculated                  Reported
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Hall group       -P 1                        -P 1
Moiety formula   C26 H58 B11 Li2 N O6        C26 H58 B11 Li2 N O6
Sum formula      C26 H58 B11 Li2 N O6        C26 H58 B11 Li2 N O6
Mr               613.52                      613.52
Dx,g cm-3        1.116                       1.116
Z                2                           2
Mu (mm-1)        0.069                       0.069
F000             660.0                       660.0
F000'            660.24
h,k,lmax         13,13,23                    13,13,23
Nref             7475                        11790
Tmin,Tmax        0.971,0.981                 0.906,1.000
Tmin'            0.971

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AbsCorr = MULTI-SCAN

Data completeness= 1.577          Theta(max)= 26.372

R(reflections)= 0.0844( 5996)     wR2(reflections)= 0.2479( 11790)

S = 1.017                  Npar= 420
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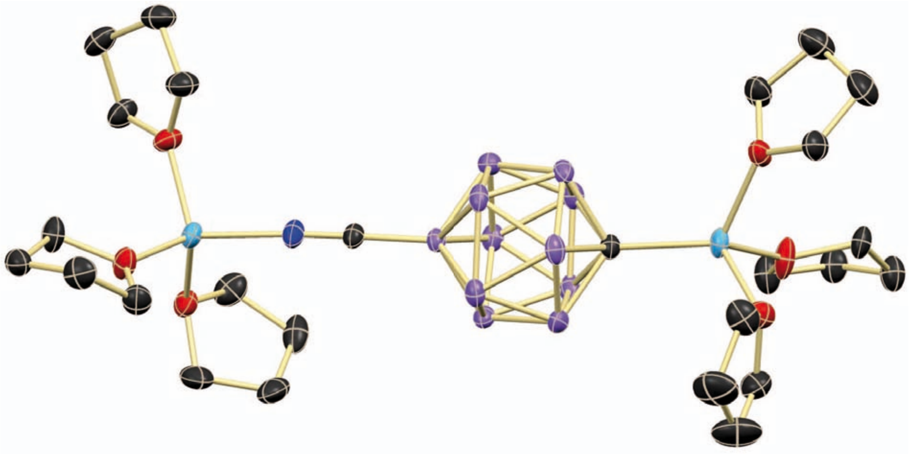
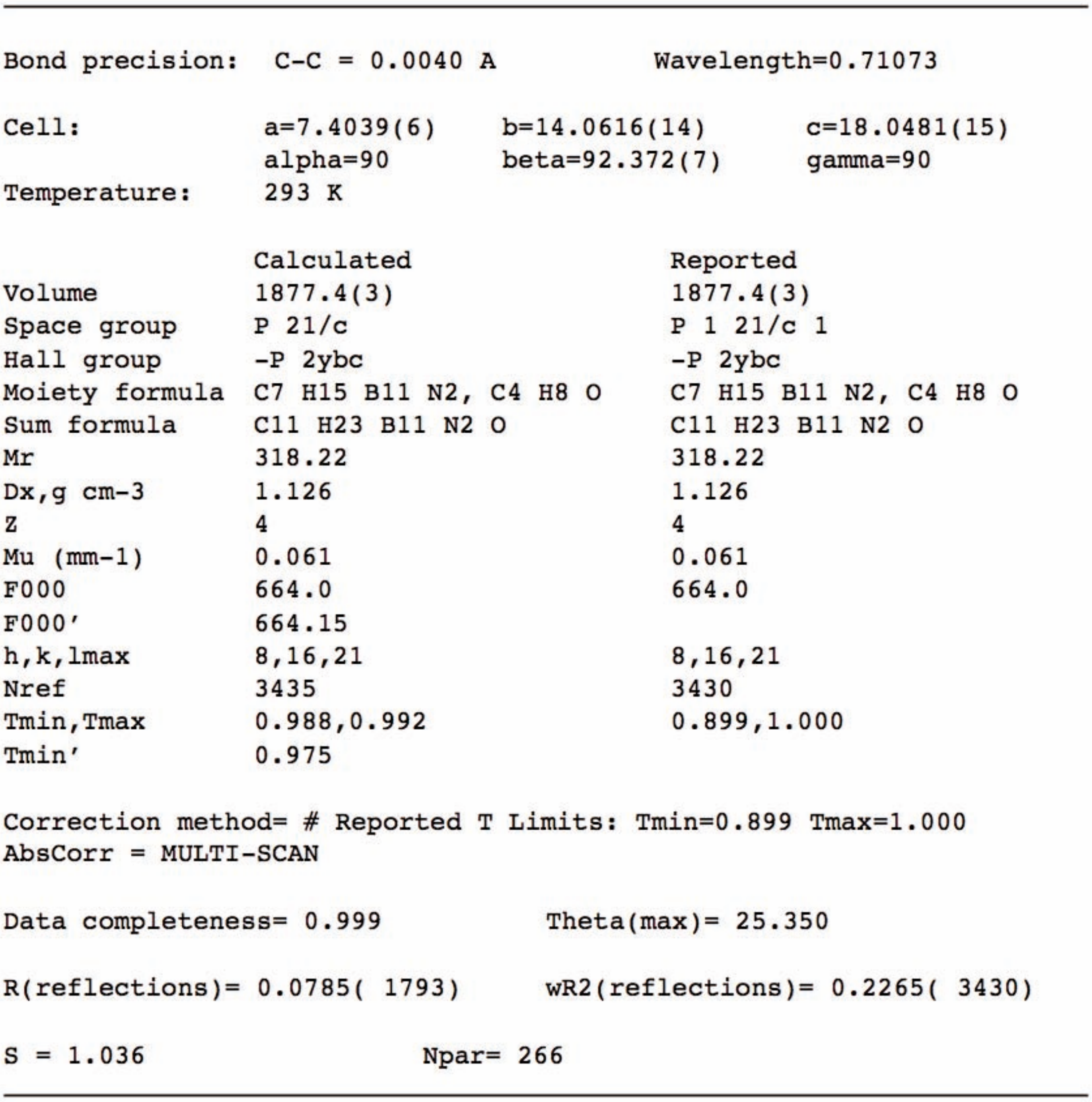


Figure S8. ORTEP representation of **7**. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

Product 10a (CCDC1559903)

The compound (5 mg) was dissolved in THF (0.5 mL) in a 4 mL glass vial, which was placed in a 20 mL glass vial containing hexane (4 mL). Vapor diffusion afforded colorless crystals of the composition [1-$C_5N(H)H_4$-$CB_{11}H_{10}$-12-CN]•THF suitable for X-ray diffraction within 14 d at 25 ^{o}C.



```
Bond precision:   C-C = 0.0040 A          Wavelength=0.71073

Cell:            a=7.4039(6)     b=14.0616(14)       c=18.0481(15)
                 alpha=90        beta=92.372(7)      gamma=90
Temperature:     293 K

                Calculated                   Reported
Volume          1877.4(3)                    1877.4(3)
Space group     P 21/c                       P 1 21/c 1
Hall group      -P 2ybc                      -P 2ybc
Moiety formula  C7 H15 B11 N2, C4 H8 O       C7 H15 B11 N2, C4 H8 O
Sum formula     C11 H23 B11 N2 O             C11 H23 B11 N2 O
Mr              318.22                       318.22
Dx,g cm-3       1.126                        1.126
Z               4                            4
Mu (mm-1)       0.061                        0.061
F000            664.0                        664.0
F000'           664.15
h,k,lmax        8,16,21                      8,16,21
Nref            3435                         3430
Tmin,Tmax       0.988,0.992                  0.899,1.000
Tmin'           0.975

Correction method= # Reported T Limits: Tmin=0.899 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 25.350

R(reflections)= 0.0785( 1793)     wR2(reflections)= 0.2265( 3430)

S = 1.036                   Npar= 266
```

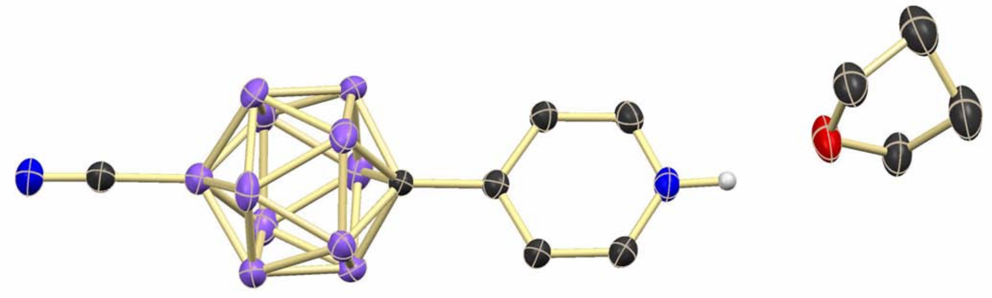
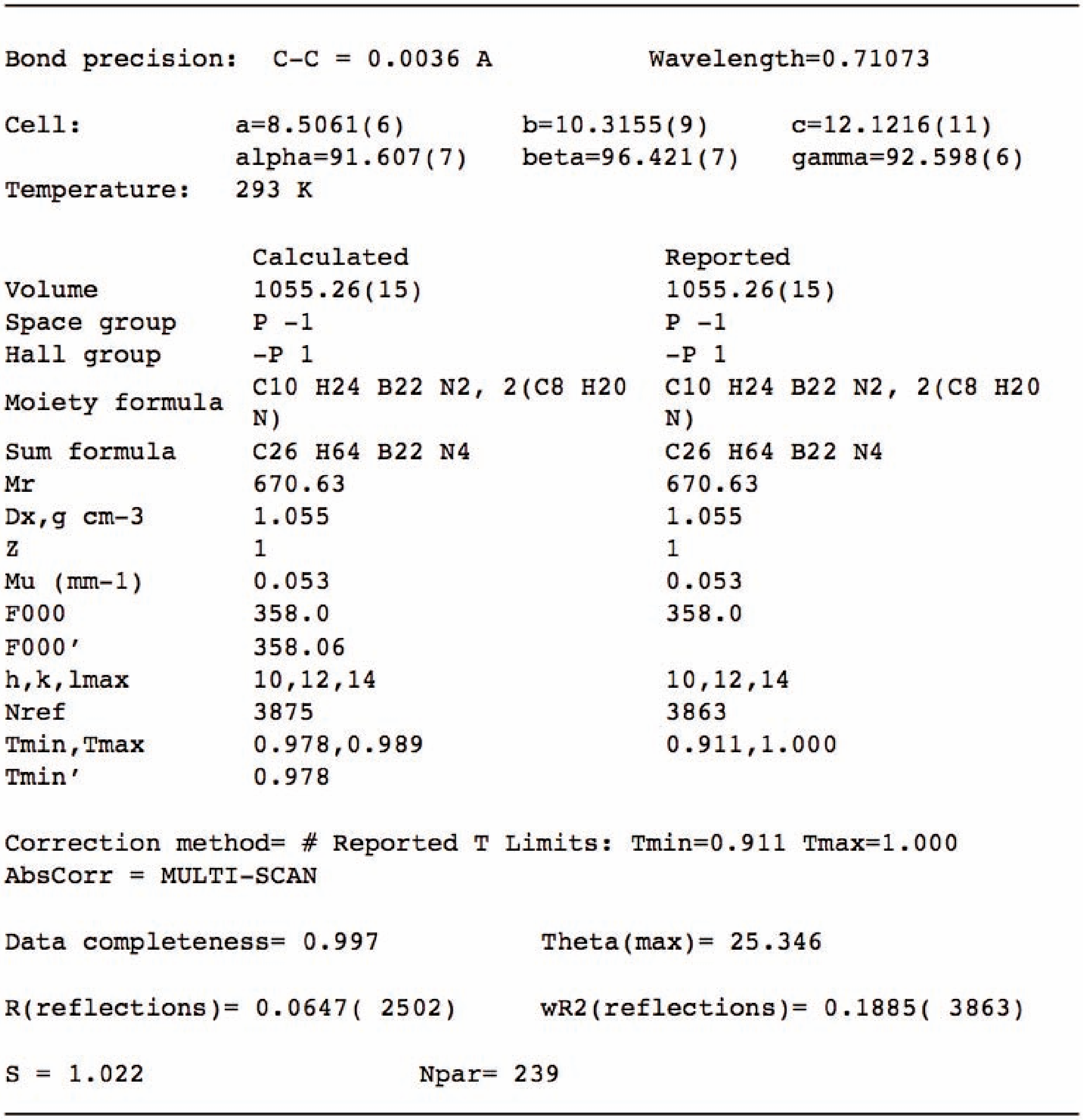


Figure S9. ORTEP representation of internally protonated **10a**•THF. Hydrogen atoms except for N–H are omitted for clarity; 25% displacement ellipsoids.

Product 10d (CCDC1559904)

The compound (15 mg) was dissolved in acetone (0.5 mL) in a 1 mL glass vial. The resulting colorless solution was filtered into an 18 cm long glass NMR tube. Slow evaporation of the solvent afforded colorless crystals of the composition $[Et_4N]_2[12\text{-}CN\text{-}B_{11}H_{10}\text{-}C_6H_4\text{-}CB_{11}H_{10}\text{-}12\text{-}CN]$ suitable for X-ray diffraction within 6 d at 25 °C.

The $[12\text{-}CN\text{-}B_{11}H_{10}\text{-}C_6H_4\text{-}CB_{11}H_{10}\text{-}12\text{-}CN]^{2-}$ anion lies about an inversion center, with the $[Et_4N]^+$ cation in a general position.



```
Bond precision:   C-C = 0.0036 A          Wavelength=0.71073

Cell:            a=8.5061(6)       b=10.3155(9)      c=12.1216(11)
                 alpha=91.607(7)   beta=96.421(7)    gamma=92.598(6)
Temperature:     293 K

                  Calculated                  Reported
Volume            1055.26(15)                 1055.26(15)
Space group       P -1                        P -1
Hall group        -P 1                        -P 1
Moiety formula    C10 H24 B22 N2, 2(C8 H20    C10 H24 B22 N2, 2(C8 H20
                  N)                          N)
Sum formula       C26 H64 B22 N4              C26 H64 B22 N4
Mr                670.63                      670.63
Dx,g cm-3         1.055                       1.055
Z                 1                           1
Mu (mm-1)         0.053                       0.053
F000              358.0                       358.0
F000'             358.06
h,k,lmax          10,12,14                    10,12,14
Nref              3875                        3863
Tmin,Tmax         0.978,0.989                 0.911,1.000
Tmin'             0.978

Correction method= # Reported T Limits: Tmin=0.911 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 25.346

R(reflections)= 0.0647( 2502)     wR2(reflections)= 0.1885( 3863)

S = 1.022                    Npar= 239
```

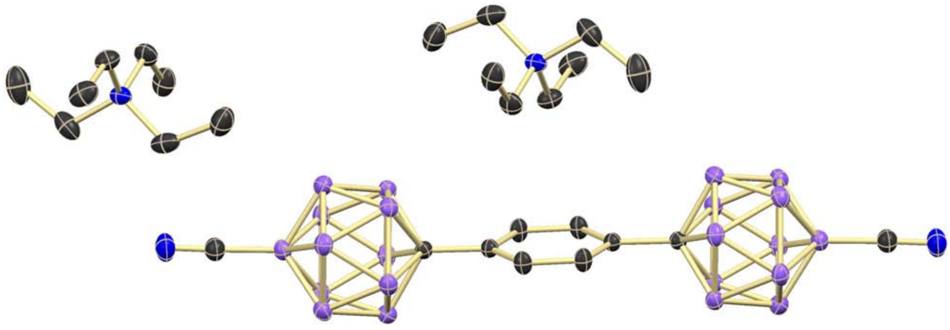
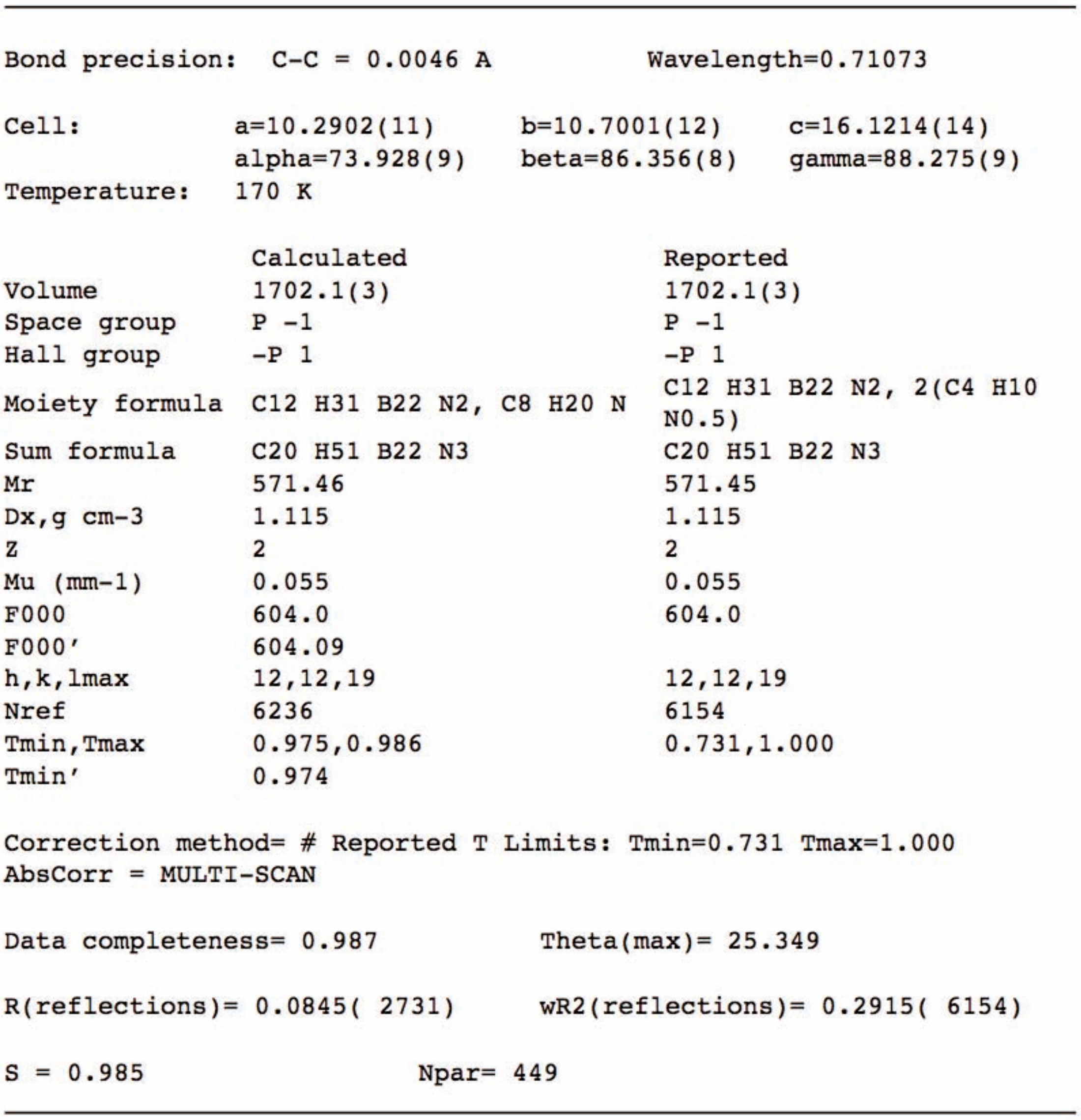


Figure S10. ORTEP representation of **10d**. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

Product 10e (CCDC 1559905)

The compound (5 mg) was dissolved in acetone (0.5 mL) in a 4 mL glass vial, which was placed in a 20 mL glass vial containing hexane (4 mL). Vapor diffusion afforded colorless crystals of the composition $[Et_4N][(1\text{-}C_5NH_4\text{-}CB_{11}H_{11}])_2H]$ suitable for X-ray diffraction within 14 d at 5 °C.

The proton inbetween the two pyridine molecules was refined at the position where it shows up in the difference electron density map (see Figure S11). This leads to unusually long N-H bonds and therefore to 4 Alert level A alerts in the Checkcif report. The N atom of the $[Et_4N]^+$ cation lies on an inversion center.



```
Bond precision:   C-C = 0.0046 A          Wavelength=0.71073

Cell:            a=10.2902(11)     b=10.7001(12)    c=16.1214(14)
                 alpha=73.928(9)   beta=86.356(8)   gamma=88.275(9)
Temperature:     170 K

                  Calculated                    Reported
Volume            1702.1(3)                     1702.1(3)
Space group       P -1                          P -1
Hall group        -P 1                          -P 1
Moiety formula    C12 H31 B22 N2, C8 H20 N      C12 H31 B22 N2, 2(C4 H10
                                                N0.5)
Sum formula       C20 H51 B22 N3                C20 H51 B22 N3
Mr                571.46                        571.45
Dx,g cm-3         1.115                         1.115
Z                 2                             2
Mu (mm-1)         0.055                         0.055
F000              604.0                         604.0
F000'             604.09
h,k,lmax          12,12,19                      12,12,19
Nref              6236                          6154
Tmin,Tmax         0.975,0.986                   0.731,1.000
Tmin'             0.974

Correction method= # Reported T Limits: Tmin=0.731 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.987          Theta(max)= 25.349

R(reflections)= 0.0845( 2731)     wR2(reflections)= 0.2915( 6154)

S = 0.985                   Npar= 449
```

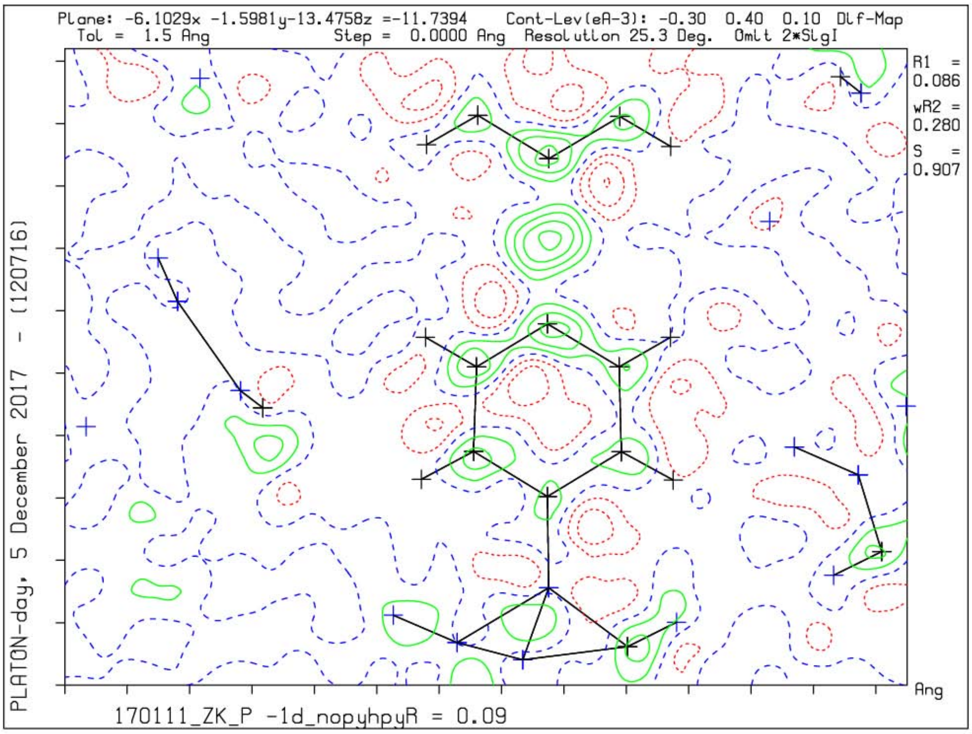


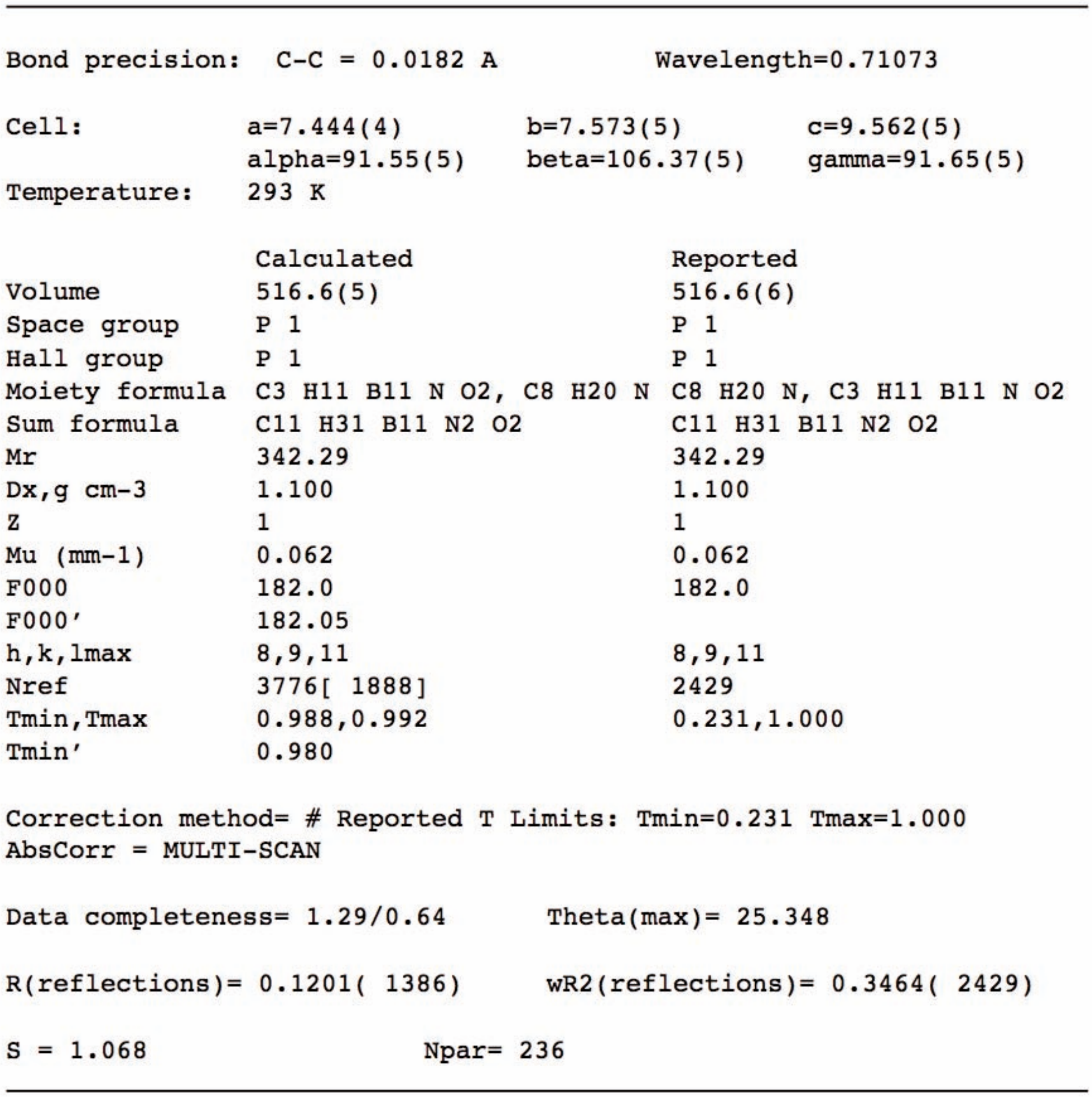
Figure S11. Difference density map of a model without any proton between the two nitrogen atoms of the pyridine rings showing the residual electron density of the proton inbetween the two pyridine rings.

Figure S12. ORTEP representation of **10e** with bridging proton between two pyridylcarborane anions; the disordered $[Et_4N]^+$ cation is not shown. Hydrogen atoms except for N–H are omitted for clarity; 25% displacement ellipsoids.

Product 10f (CCDC1559906)

The compound (5 mg) was dissolved in THF (0.5 mL) in a 4 mL glass vial, which was placed in a 20 mL glass vial containing hexane (4 mL). Vapor diffusion afforded colorless crystals of the composition [Et_4N][1-COOH-$CB_{11}H_{10}$-12-CN] suitable for X-ray diffraction within 14 d at 25 ^{o}C.

Structure **10f** showed an R value of 12.01%. This is primarily attributed to the floppiness of the ethyl substituents of [Et_4N]$^+$, and in particular the CH_3 groups. The respective anisotropic displacement parameters are rather large, and the thermal ellipsoids deviate from spherical shape because of movement along the elongated displacement directions with low activation energy in the solid state.



```
Bond precision:   C-C = 0.0182 A          Wavelength=0.71073

Cell:           a=7.444(4)        b=7.573(5)         c=9.562(5)
                alpha=91.55(5)    beta=106.37(5)     gamma=91.65(5)
Temperature:    293 K

                Calculated                  Reported
Volume          516.6(5)                    516.6(6)
Space group     P 1                         P 1
Hall group      P 1                         P 1
Moiety formula  C3 H11 B11 N O2, C8 H20 N  C8 H20 N, C3 H11 B11 N O2
Sum formula     C11 H31 B11 N2 O2           C11 H31 B11 N2 O2
Mr              342.29                      342.29
Dx,g cm-3       1.100                       1.100
Z               1                           1
Mu (mm-1)       0.062                       0.062
F000            182.0                       182.0
F000'           182.05
h,k,lmax        8,9,11                      8,9,11
Nref            3776[ 1888]                 2429
Tmin,Tmax       0.988,0.992                 0.231,1.000
Tmin'           0.980

Correction method= # Reported T Limits: Tmin=0.231 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.29/0.64       Theta(max)= 25.348

R(reflections)= 0.1201( 1386)      wR2(reflections)= 0.3464( 2429)

S = 1.068                   Npar= 236
```

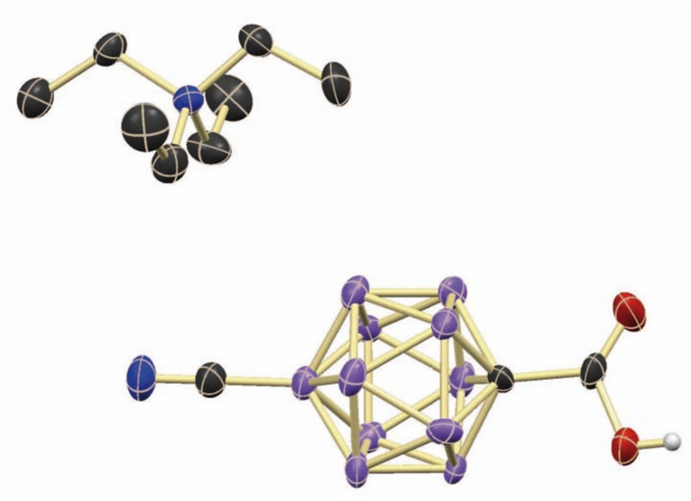
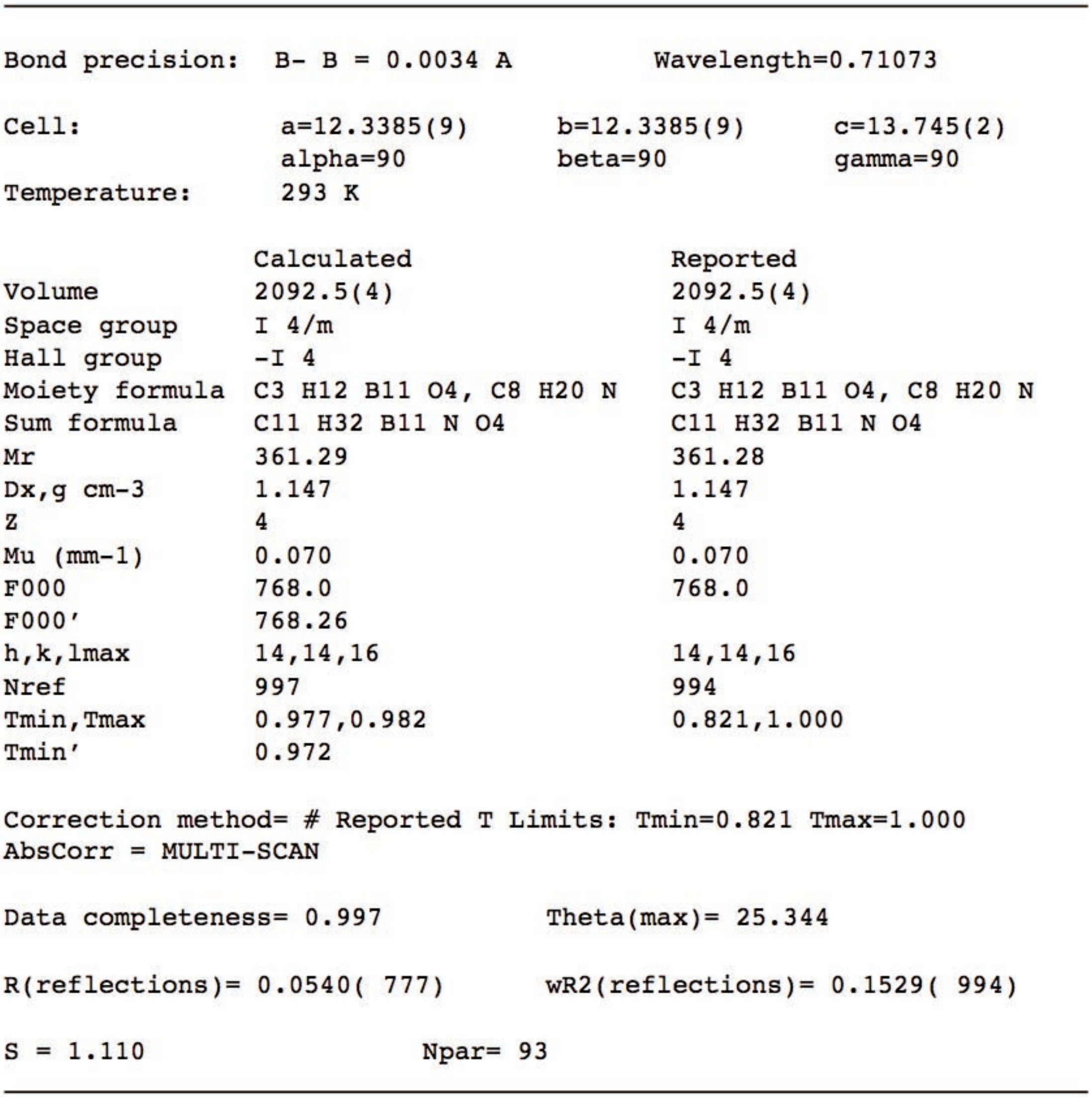


Figure S13. ORTEP representation of **10f.** Hydrogen atoms except for O–H are omitted for clarity; 25% displacement ellipsoids.

Product 10g (CCDC1559907)

The compound (10 mg) was dissolved in MeCN (0.5 mL) in a 1 mL glass vial. The resulting colorless solution was filtered into an 18 cm long glass NMR tube and layered with diethyl ether (1 mL). Colorless crystals of the composition [Et_4N] [1-COOH-$CB_{11}H_{10}$-12-COOH] suitable for X-ray diffraction grew within 7 d at 25 °C.

The 2/m and 4-fold crystallographically-imposed symmetry in this structure results in disorder of the cage anion and the [Et_4N]$^+$ counterion. Similar indistinguishability of C(cage) and B positions has been observed with other carboranes.[4]



```
Bond precision:   B- B = 0.0034 A          Wavelength=0.71073

Cell:              a=12.3385(9)      b=12.3385(9)      c=13.745(2)
                   alpha=90          beta=90           gamma=90
Temperature:       293 K

                 Calculated                  Reported
Volume           2092.5(4)                   2092.5(4)
Space group      I 4/m                       I 4/m
Hall group       -I 4                        -I 4
Moiety formula   C3 H12 B11 O4, C8 H20 N     C3 H12 B11 O4, C8 H20 N
Sum formula      C11 H32 B11 N O4            C11 H32 B11 N O4
Mr               361.29                      361.28
Dx,g cm-3        1.147                       1.147
Z                4                           4
Mu (mm-1)        0.070                       0.070
F000             768.0                       768.0
F000'            768.26
h,k,lmax         14,14,16                    14,14,16
Nref             997                         994
Tmin,Tmax        0.977,0.982                 0.821,1.000
Tmin'            0.972

Correction method= # Reported T Limits: Tmin=0.821 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 25.344

R(reflections)= 0.0540( 777)      wR2(reflections)= 0.1529( 994)

S = 1.110                    Npar= 93
```

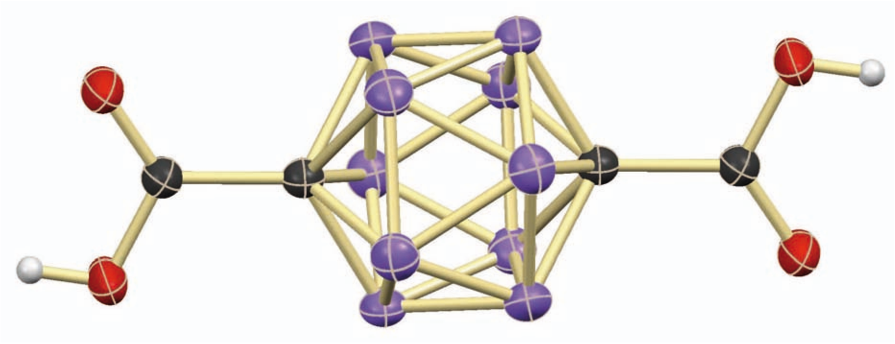
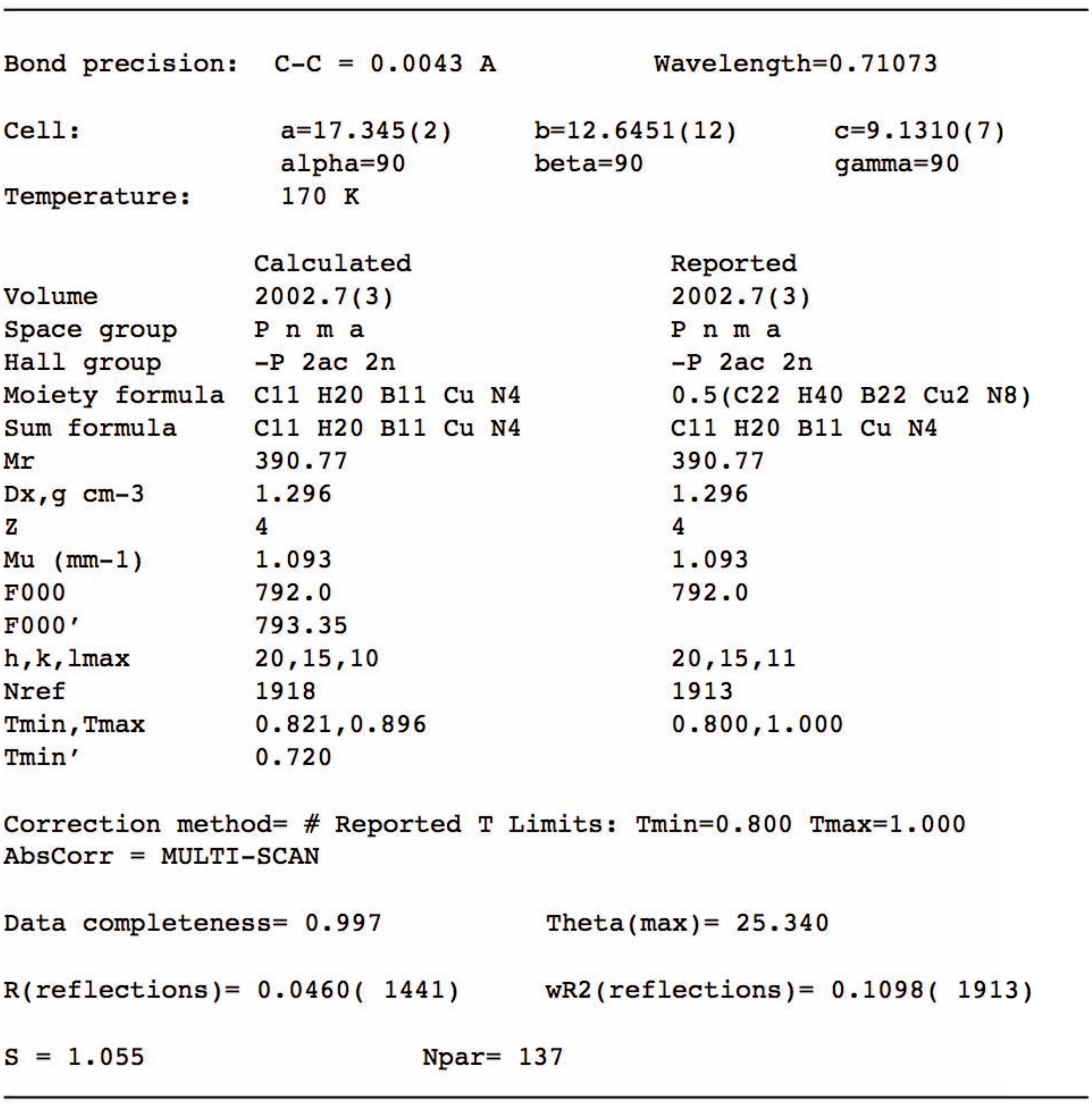


Figure S14. ORTEP representation of **10g**; the disordered $[Et_4N]^+$ cation is not shown. Hydrogen atoms except for O–H are omitted for clarity; 25% displacement ellipsoids.

Product 11 (CCDC1559908)

Colorless crystals suitable for X-ray diffraction were obtained as described in the experimental section.



```
Bond precision:   C-C = 0.0043 A          Wavelength=0.71073

Cell:              a=17.345(2)     b=12.6451(12)      c=9.1310(7)
                   alpha=90        beta=90            gamma=90
Temperature:       170 K

                Calculated                 Reported
Volume          2002.7(3)                  2002.7(3)
Space group     P n m a                    P n m a
Hall group      -P 2ac 2n                  -P 2ac 2n
Moiety formula  C11 H20 B11 Cu N4          0.5(C22 H40 B22 Cu2 N8)
Sum formula     C11 H20 B11 Cu N4          C11 H20 B11 Cu N4
Mr              390.77                     390.77
Dx,g cm-3       1.296                      1.296
Z               4                          4
Mu (mm-1)       1.093                      1.093
F000            792.0                      792.0
F000'           793.35
h,k,lmax        20,15,10                   20,15,11
Nref            1918                       1913
Tmin,Tmax       0.821,0.896                0.800,1.000
Tmin'           0.720

Correction method= # Reported T Limits: Tmin=0.800 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 25.340

R(reflections)= 0.0460( 1441)     wR2(reflections)= 0.1098( 1913)

S = 1.055                 Npar= 137
```

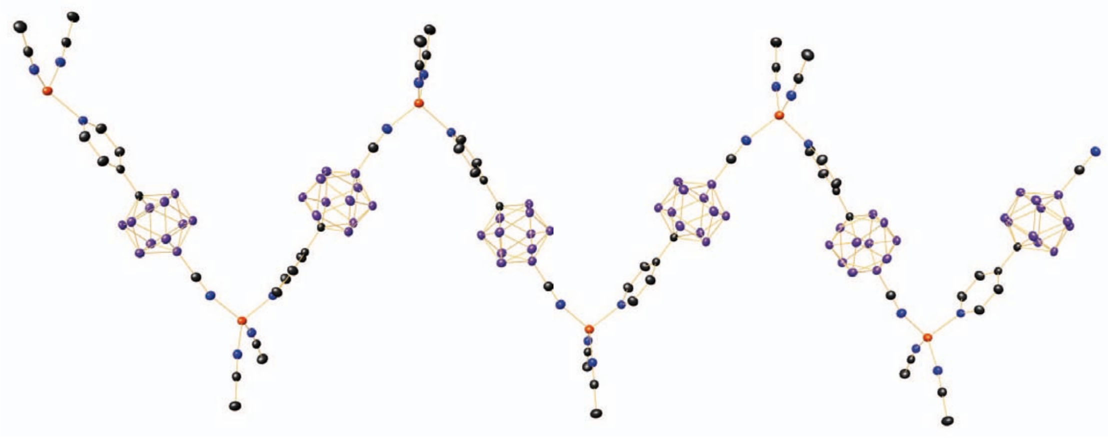


Figure S15. ORTEP representation of **11**, showing one chain from the side. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

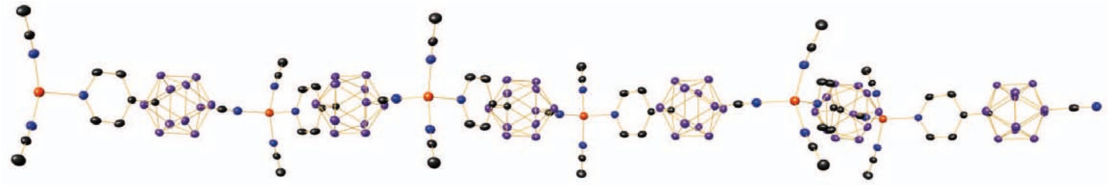


Figure S16. ORTEP representation of **11**, showing one chain from the top. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

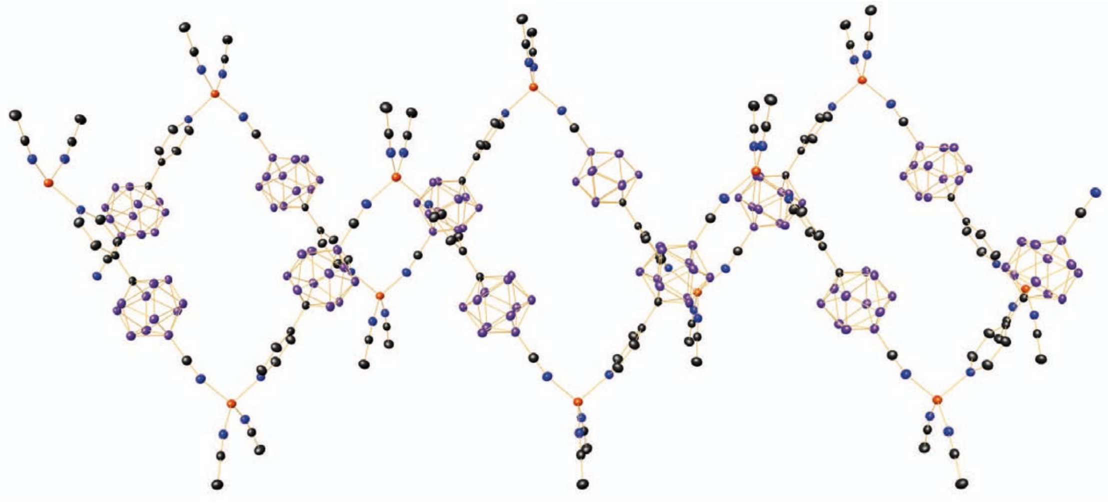


Figure S17. ORTEP representation of **11**, showing two chain from the side. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

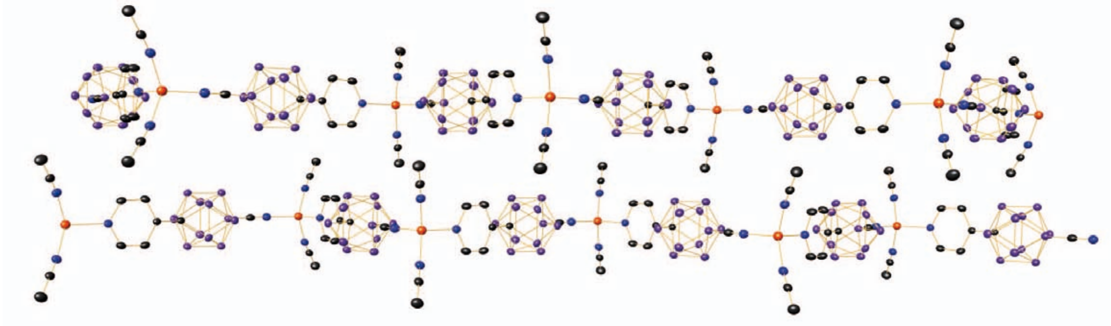


Figure S18. ORTEP representation of **11**, showing two chains from the top. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

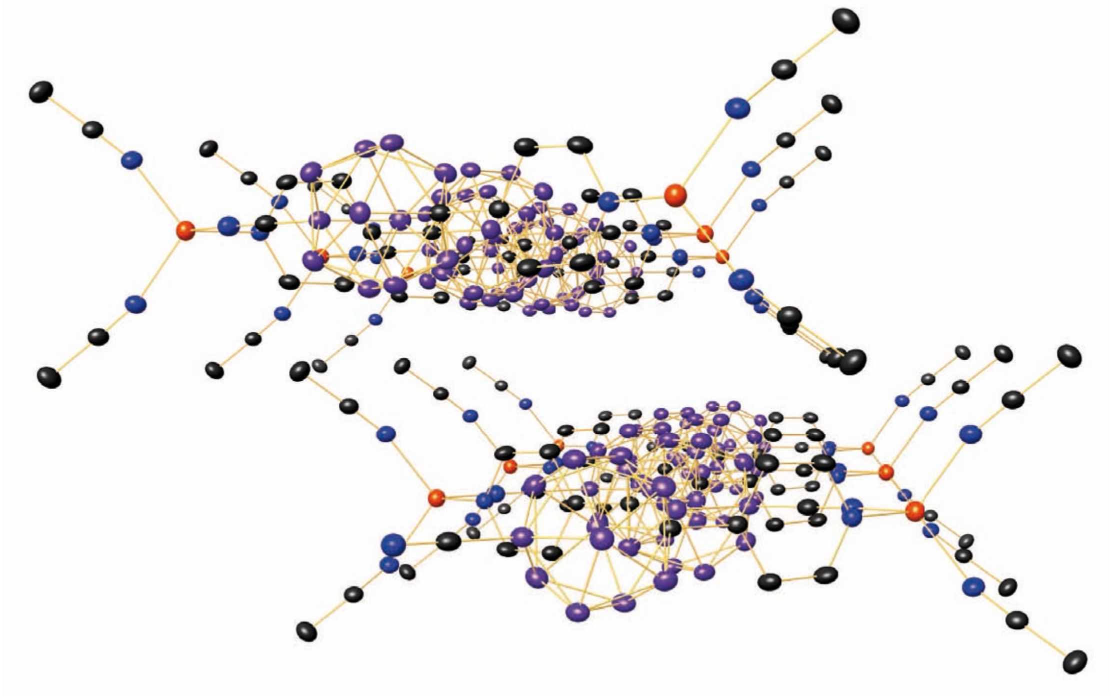


Figure S19. ORTEP representation of **11**, showing the intercalation of two chains forming a channel-like arrangement. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

IV References

[1] A. J. Rosenbaum, D. H. Juers, M. A. Juhasz, *Inorg. Chem.* **2013**, *52*, 10717.

[2] a) M. W. Rathke, R. Kow, *J. Am. Chem. Soc.* **1972**, *94*, 6854; b) R. A. Olofson, C. M. Dougherty, *J. Am. Chem. Soc.* **1973**, *95*, 582; c) F. E. Romesberg, J. H. Gilchrist, A. T. Harrison, D. J. Fuller, D. B. Collum, *J. Am. Chem. Soc.* **1991**, *113*, 5751; d) D. B. Collum, *Acc. Chem. Res.* **1993**, *26*, 227; e) P. G. Williard, Q.-Y. Liu, *J. Am. Chem. Soc.* **1993**, *115*, 3380.

[3] F. Šembera, J. Plutnar, A. Higelin, Z. Janoušek, I. Císařová, J. Michl, *Inorg. Chem.* **2016**, *55*, 3797.

[4] Z. Xie, C.-W. Tsang, E. T.-P. Sze, Q. Yang, D. T. W. Chan, T. C. W. Wak, *Inorg. Chem.* **1998**, *37*, 6444.

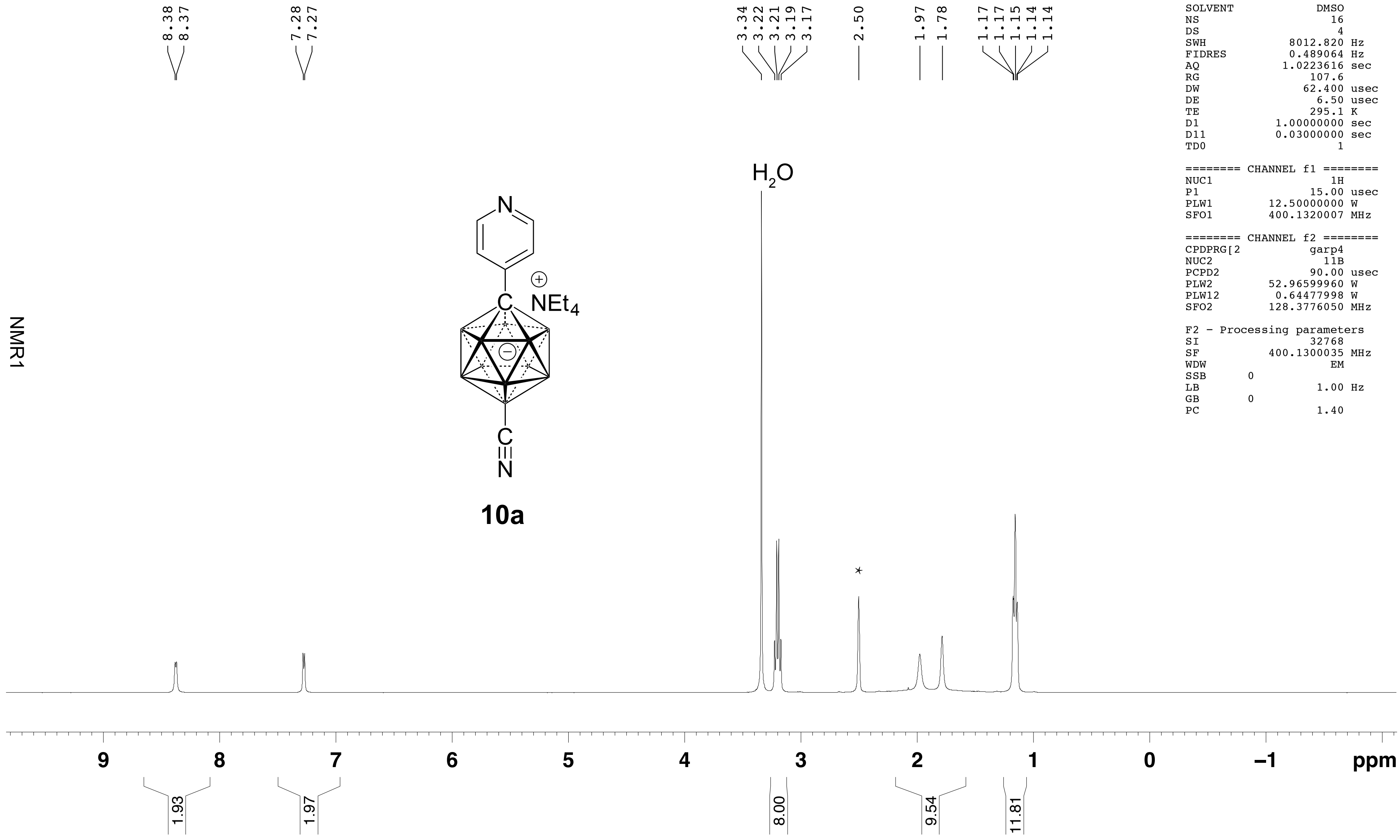
V NMR Spectra

NMR data are shown on pages NMR1–NMR35.

V Mass Spectra

MS data are shown on pages MS1–MS7.

[NEt4][CB11H10−12−CN−1−pyridyl], 10.6 mg in 0.5 mL DMSO−d6*
1H{11B} NMR, Bruker 400MHz, T = 23 C



10a

```
Current Data Parameters
NAME     20170105-zk-12-CN-1-P-DMSC
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170106
Time                 13.12
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgig30
TD                   16384
SOLVENT               DMSO
NS                      16
DS                       4
SWH               8012.820 Hz
FIDRES            0.489064 Hz
AQ               1.0223616 sec
RG                   107.6
DW                  62.400 usec
DE                    6.50 usec
TE                   295.1 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1

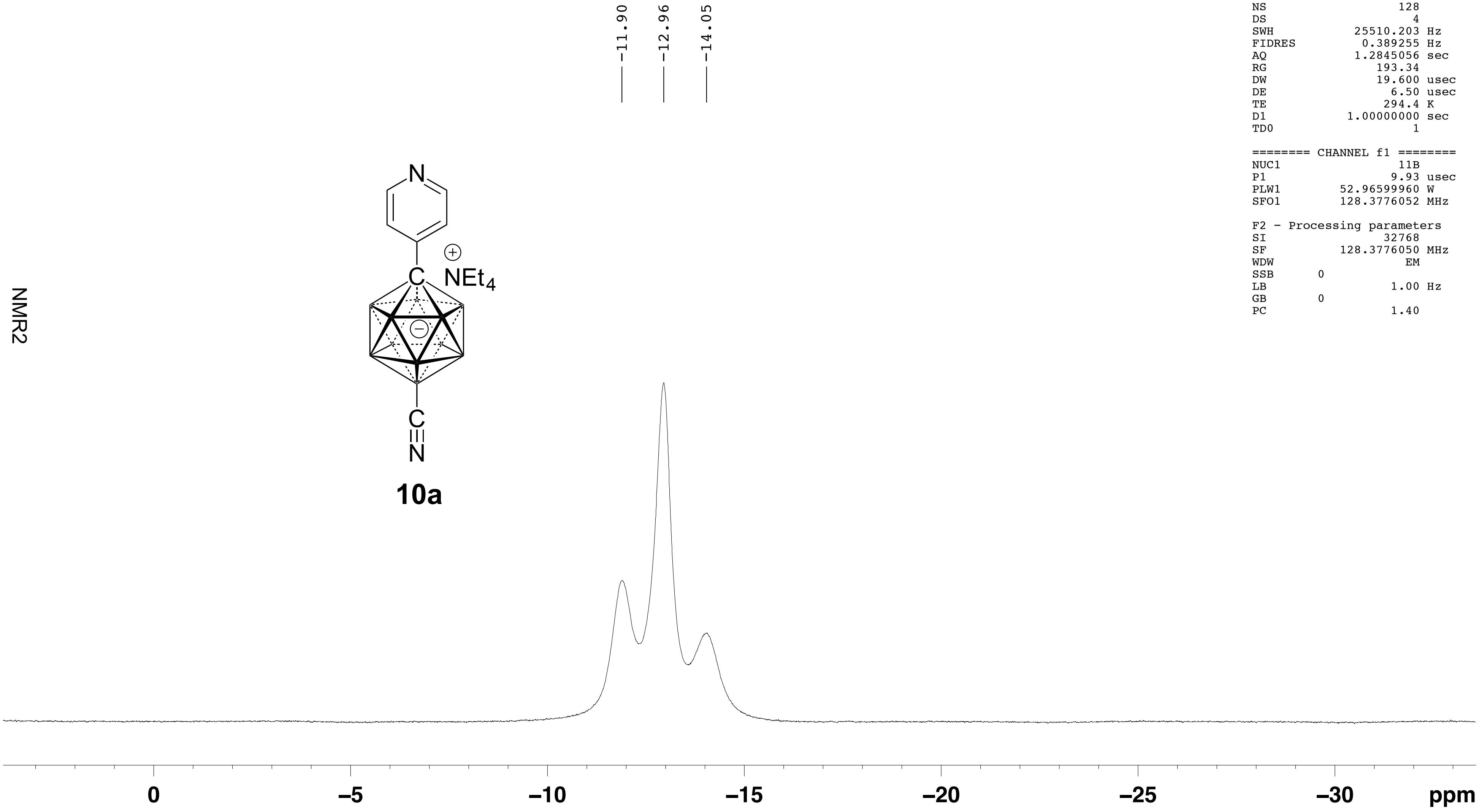
======== CHANNEL f1 ========
NUC1                    1H
P1                   15.00 usec
PLW1           12.50000000 W
SFO1           400.1320007 MHz

======== CHANNEL f2 ========
CPDPRG[2             garp4
NUC2                   11B
PCPD2                90.00 usec
PLW2           52.96599960 W
PLW12           0.64477998 W
SFO2           128.3776050 MHz

F2 - Processing parameters
SI                   32768
SF             400.1300035 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```

[NEt4][CB11H10−12−CN−1−pyridyl], 10.6 mg in 0.5 mL DMSO−d6
11B NMR, Bruker 400MHz, T = 23 C

NMR2



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Current Data Parameters
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EXPNO                     1
PROCNO                    1

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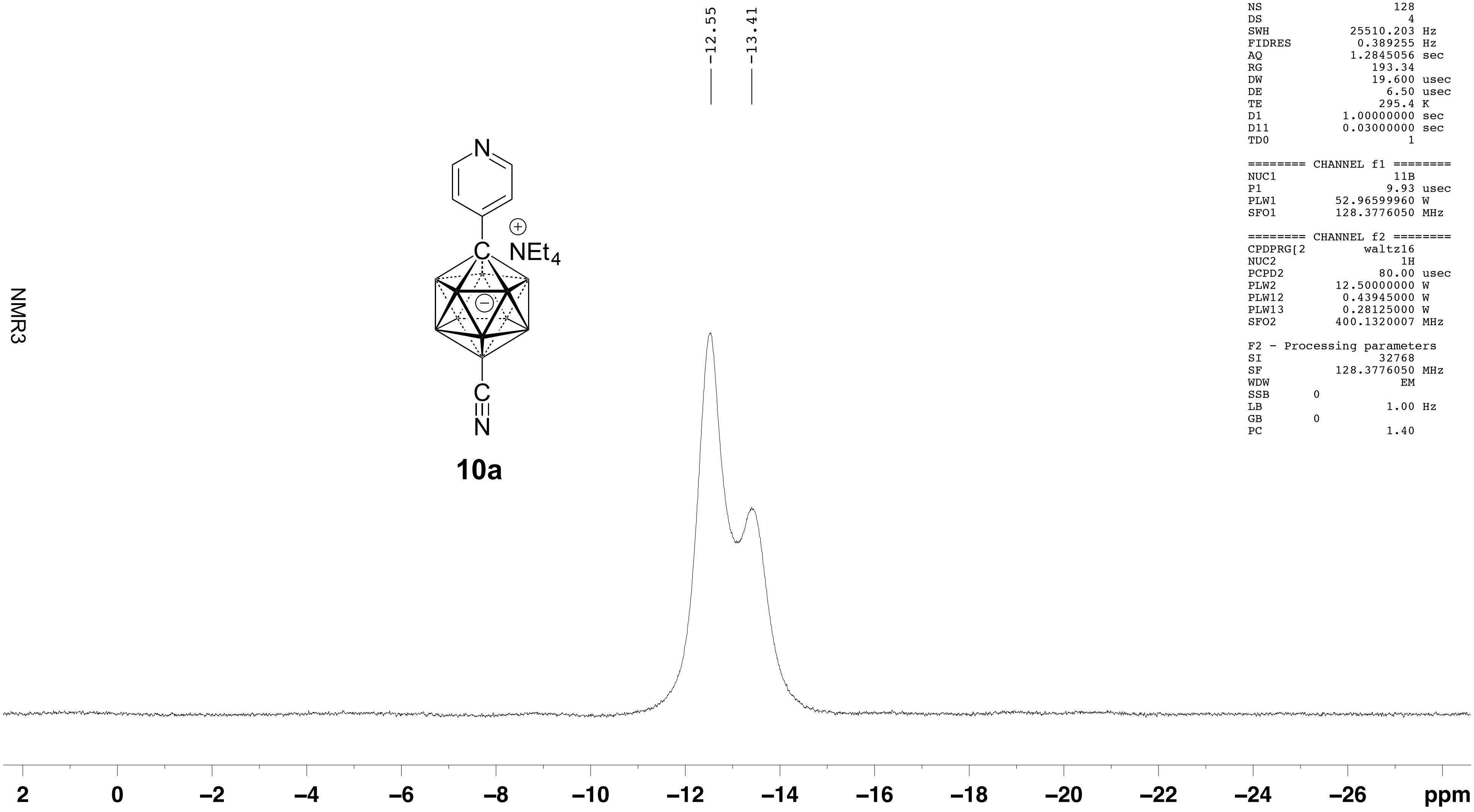
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG              zg
TD                65536
SOLVENT            DMSO
NS                  128
DS                    4
SWH           25510.203 Hz
FIDRES         0.389255 Hz
AQ            1.2845056 sec
RG               193.34
DW               19.600 usec
DE                 6.50 usec
TE                294.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                11B
P1                 9.93 usec
PLW1        52.96599960 W
SFO1        128.3776052 MHz

F2 - Processing parameters
SI                32768
SF          128.3776050 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

[NEt4][CB11H10−12−CN−1−pyridyl], 10.6 mg in 0.5 mL DMSO−d6
11B{1H} NMR, Bruker 400MHz, T = 23 C



10a

```
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
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Time              13.10
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT           DMSO
NS                 128
DS                   4
SWH          25510.203 Hz
FIDRES        0.389255 Hz
AQ           1.2845056 sec
RG              193.34
DW              19.600 usec
DE                6.50 usec
TE               295.4 K
D1          1.00000000 sec
D11         0.03000000 sec
TD0                  1

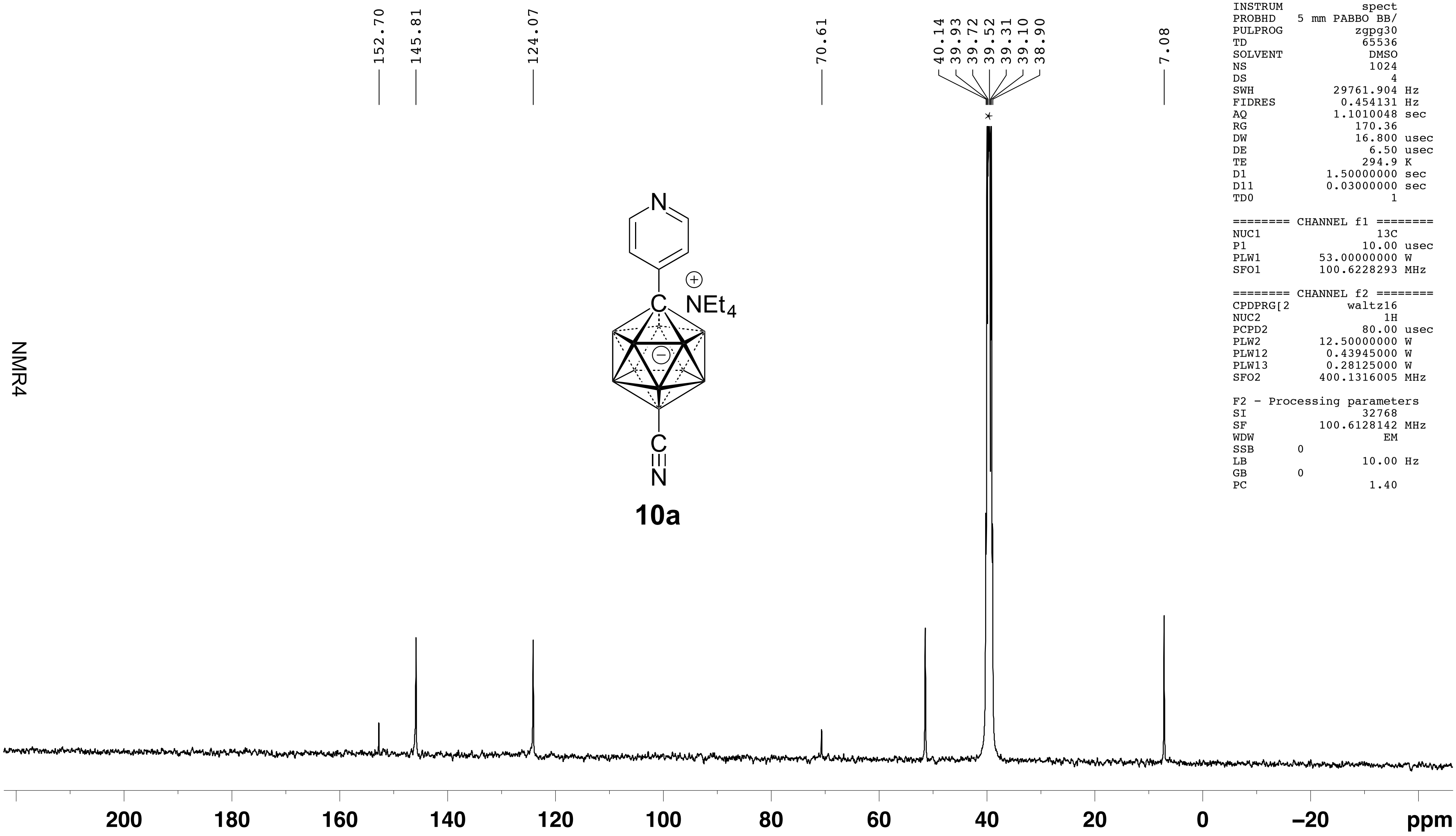
======== CHANNEL f1 ========
NUC1               11B
P1                9.93 usec
PLW1       52.96599960 W
SFO1      128.3776050 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            80.00 usec
PLW2       12.50000000 W
PLW12       0.43945000 W
PLW13       0.28125000 W
SFO2      400.1320007 MHz

F2 - Processing parameters
SI               32768
SF         128.3776050 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```

NMR4

[NEt4][CB11H10−12−CN−1−pyridyl], 10.6 mg in 0.6 mL DMSO−d6*
13C{1H} NMR, Bruker 400MHz, T = 23 C



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Current Data Parameters
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EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
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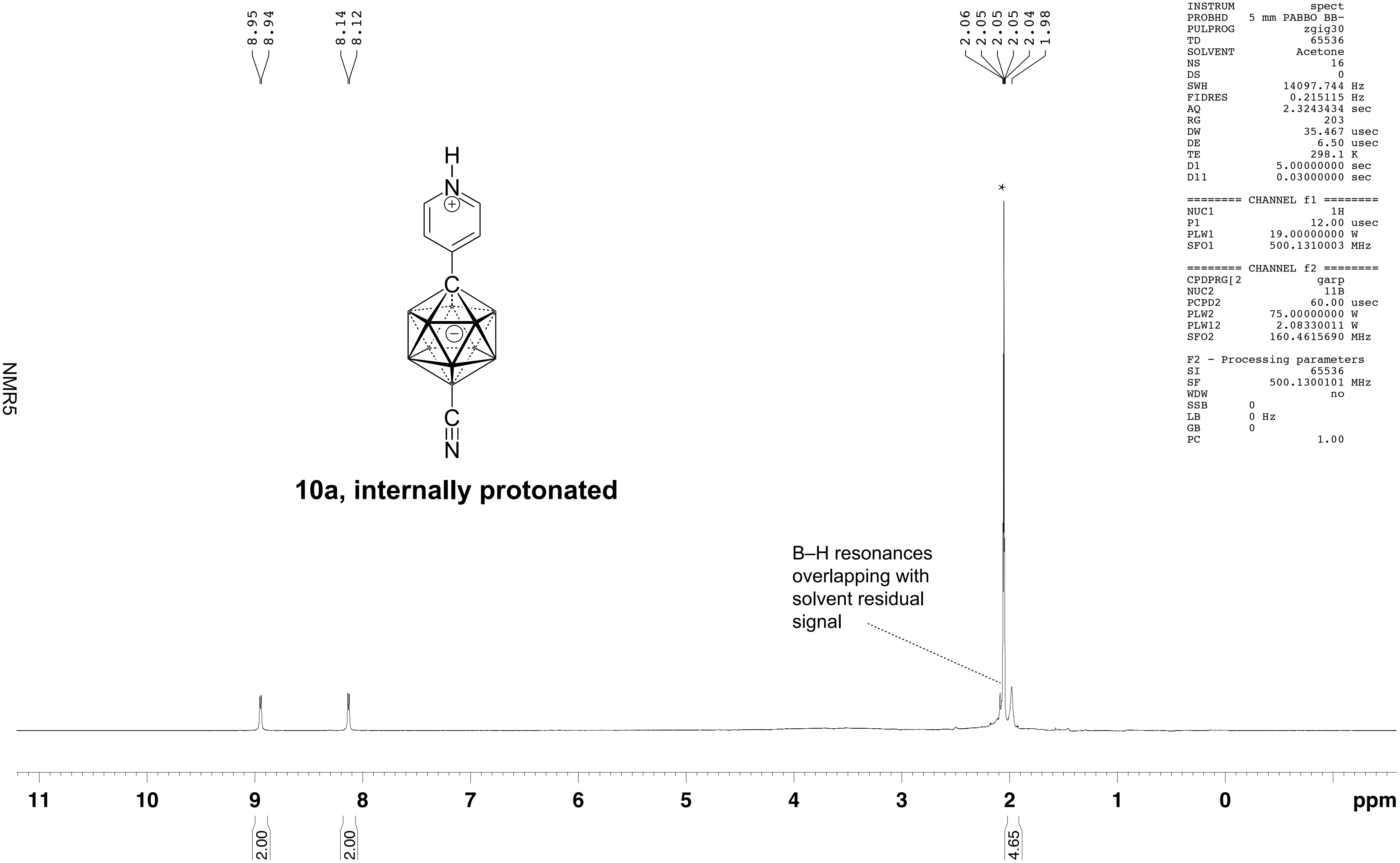
Time               5.25
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               170.36
DW               16.800 usec
DE                 6.50 usec
TE                294.9 K
D1           1.50000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PLW1        53.00000000 W
SFO1        100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PLW2        12.50000000 W
PLW12        0.43945000 W
PLW13        0.28125000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6128142 MHz
WDW                  EM
SSB      0
LB                10.00 Hz
GB       0
PC                 1.40
```

[H][CB11H10−12−CN−1−pyridyl], 8.0 mg in 0.6 mL Acetone−d6*
1H{11B} NMR, Bruker 500MHz, T = 23 C



10a, internally protonated

```
Current Data Parameters
NAME     20160705-zk-protonation
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20160705
Time              16.12
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgig30
TD                65536
SOLVENT         Acetone
NS                   16
DS                    0
SWH           14097.744 Hz
FIDRES         0.215115 Hz
AQ            2.3243434 sec
RG                  203
DW               35.467 usec
DE                 6.50 usec
TE                298.1 K
D1           5.00000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PLW1        19.00000000 W
SFO1        500.1310003 MHz

======== CHANNEL f2 ========
CPDPRG[2           garp
NUC2                11B
PCPD2             60.00 usec
PLW2        75.00000000 W
PLW12        2.08330011 W
SFO2        160.4615690 MHz

F2 - Processing parameters
SI                65536
SF          500.1300101 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 1.00
```

NMR5

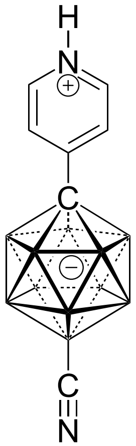
[H][CB11H10−12−CN−1−pyridyl], 8.0 mg in 0.6 mL Acetone−d6
11B NMR, Bruker 400MHz, T = 23 C

```
Current Data Parameters
NAME     20160606-zk-protonation
EXPNO                    2
PROCNO                   1

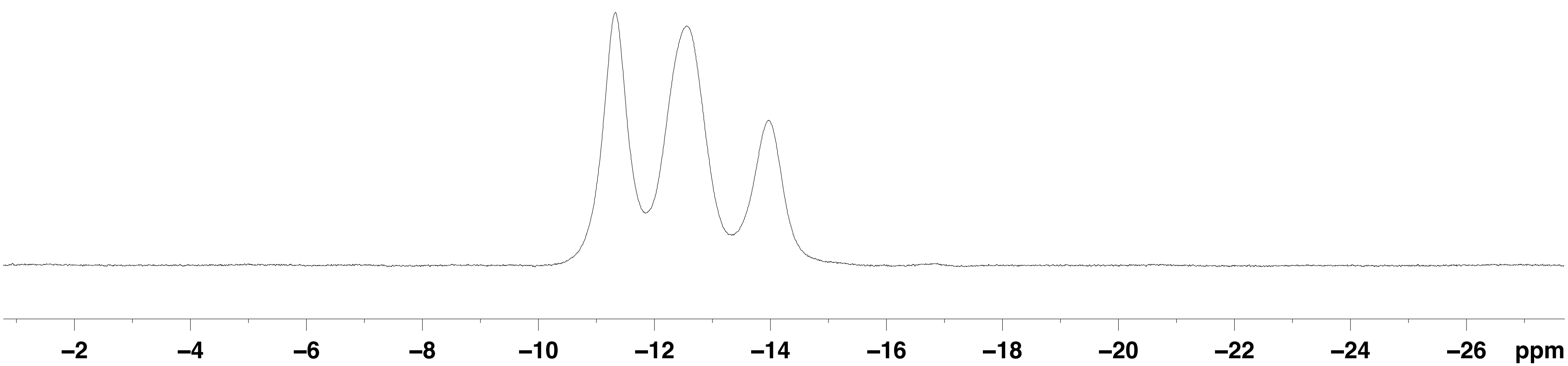
F2 - Acquisition Parameters
Date_           20160604
Time                6.50
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 65536
SOLVENT          Acetone
NS                   128
DS                     4
SWH            25510.203 Hz
FIDRES          0.389255 Hz
AQ             1.2845056 sec
RG                193.34
DW                19.600 usec
DE                  6.50 usec
TE                 296.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 11B
P1                  9.93 usec
PLW1         52.96599960 W
SFO1        128.3776052 MHz

F2 - Processing parameters
SI                 32768
SF          128.3776050 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



10a, internally protonated



NMR6

[H][12−CN−1−pyridyl], 8.0 mg in 0.6 mL Acetone−d6
11B{1H} NMR, Bruker 400MHz, T = 23 C

```
Current Data Parameters
NAME      20160606-zk-protonation
EXPNO                       3
PROCNO                      1

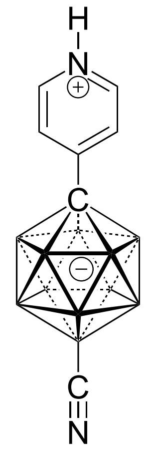
F2 - Acquisition Parameters
Date_               20160604
Time                    6.57
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT              Acetone
NS                      128
DS                        4
SWH               25510.203 Hz
FIDRES             0.389255 Hz
AQ                1.2845056 sec
RG                   193.34
DW                   19.600 usec
DE                     6.50 usec
TE                    297.2 K
D1               1.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    11B
P1                     9.93 usec
PLW1            52.96599960 W
SFO1            128.3776050 MHz

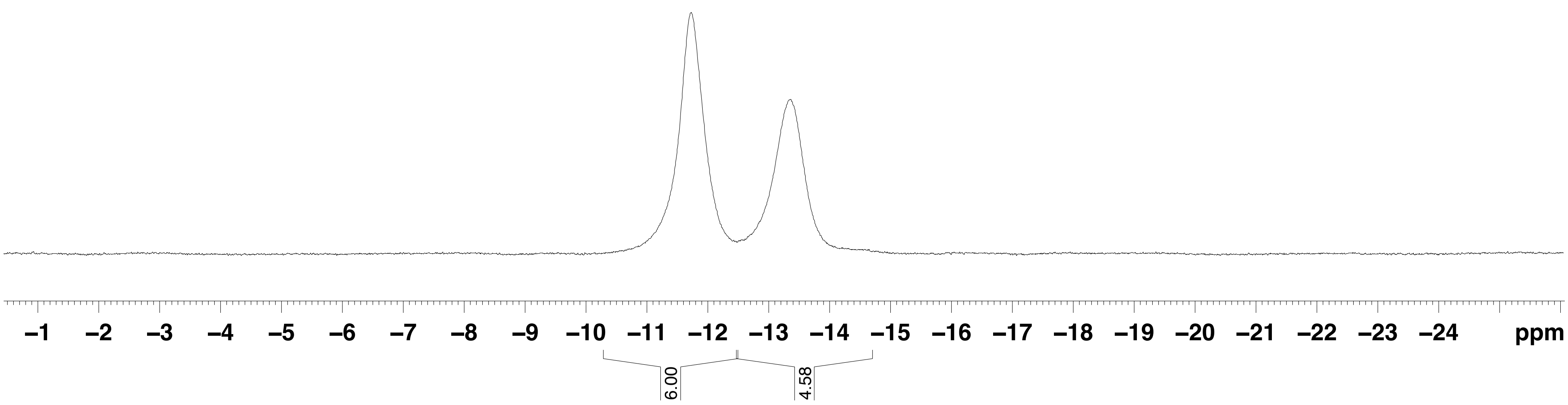
======== CHANNEL f2 ========
CPDPRG[2            waltz16
NUC2                     1H
PCPD2                 80.00 usec
PLW2            12.50000000 W
PLW12            0.43945000 W
PLW13            0.28125000 W
SFO2            400.1320007 MHz

F2 - Processing parameters
SI                    32768
SF              128.3776050 MHz
WDW                      EM
SSB      0
LB                     1.00 Hz
GB       0
PC                     1.40
```

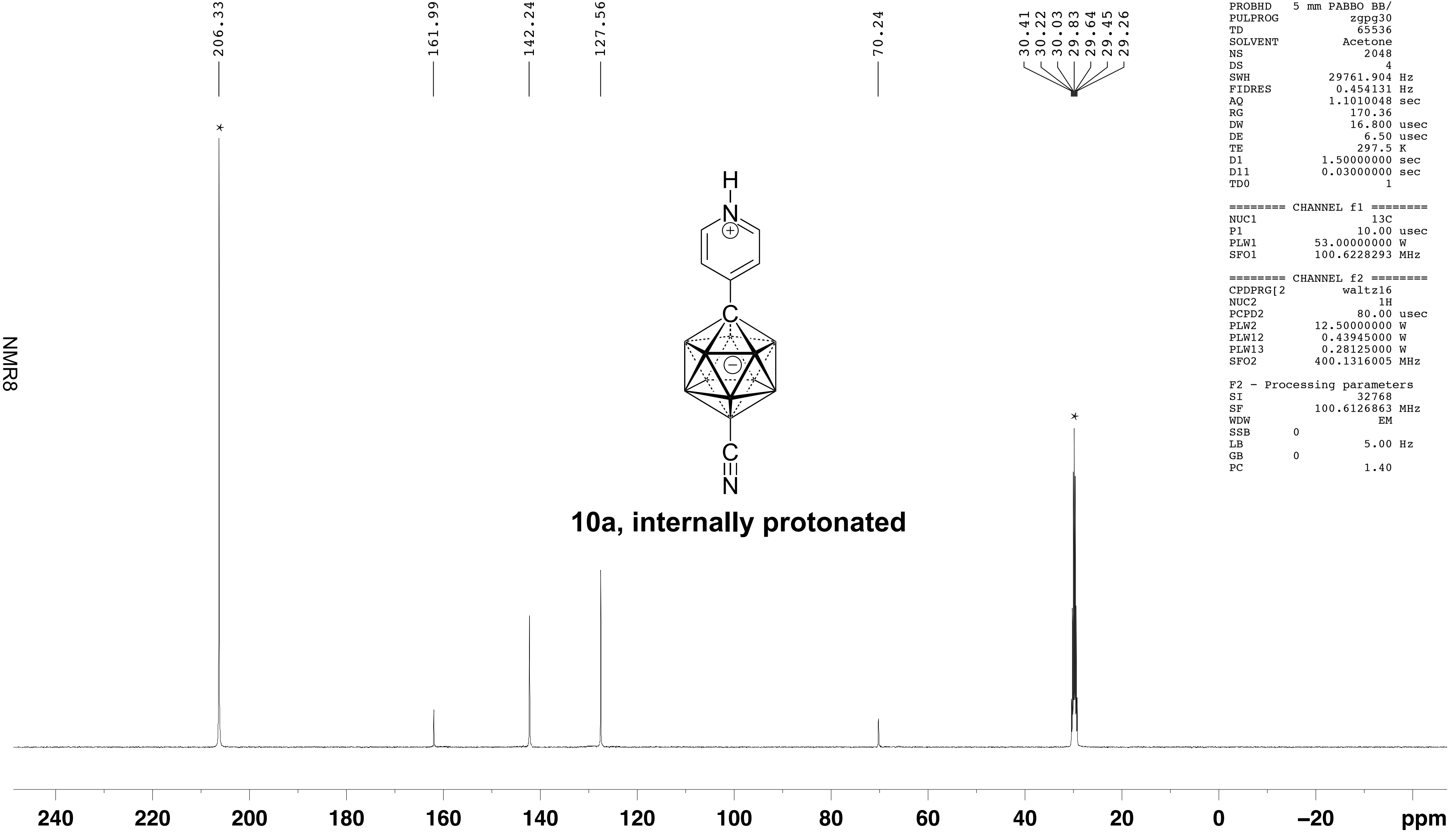
NMR7



10a, internally protonated



[H][CB11H10−12−CN−1−pyridyl], 8.0 mg in 0.6 mL Acetone−d6*
11B NMR, Bruker 400MHz, T = 23 C



10a, internally protonated

```
Current Data Parameters
NAME     20160616-zk-protonation
EXPNO                  1
PROCNO                 1

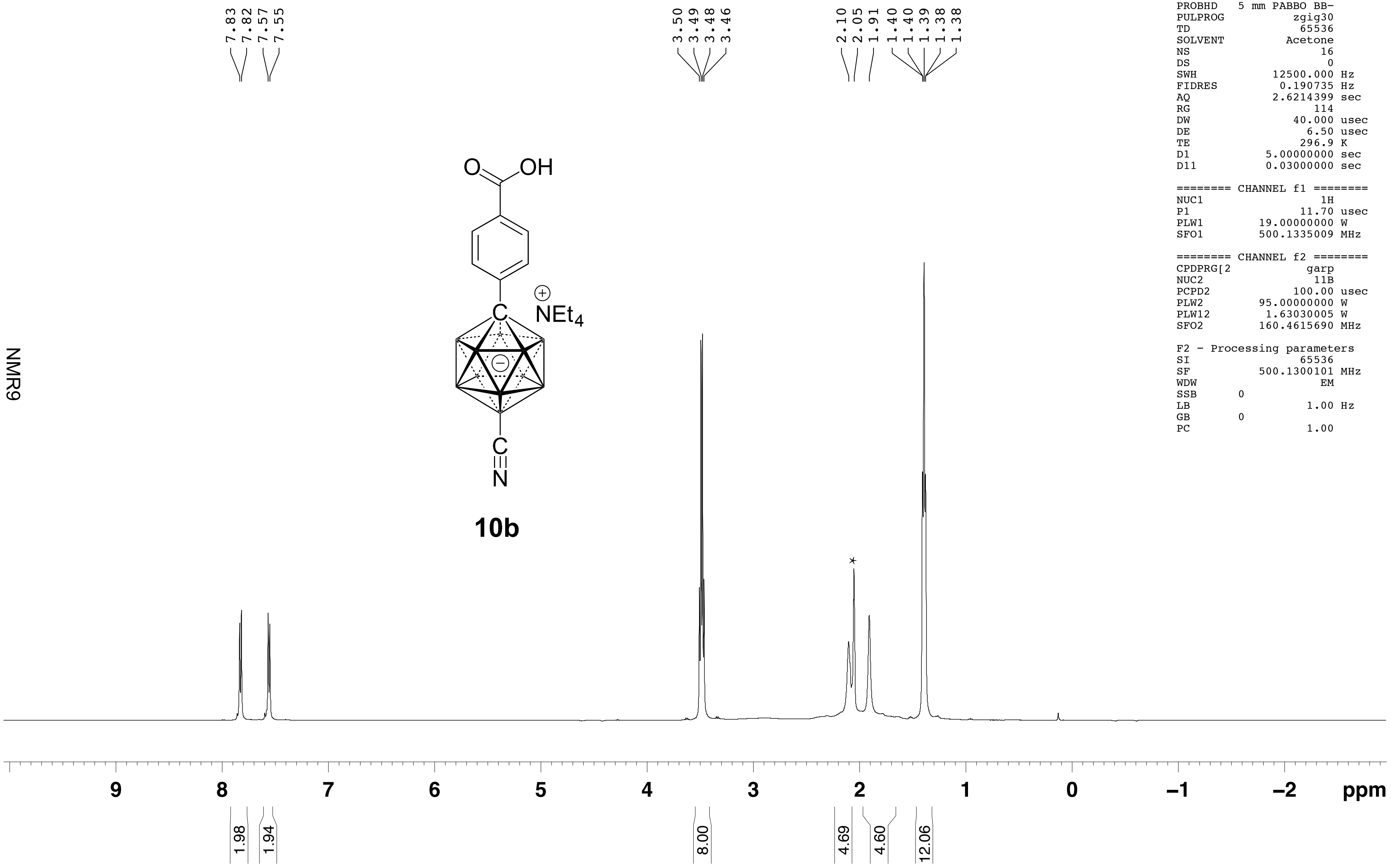
F2 - Acquisition Parameters
Date_           20160617
Time               18.53
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT          Acetone
NS                  2048
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                170.36
DW                16.800 usec
DE                  6.50 usec
TE                 297.5 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PLW1         53.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         12.50000000 W
PLW12         0.43945000 W
PLW13         0.28125000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6126863 MHz
WDW                   EM
SSB      0
LB                  5.00 Hz
GB       0
PC                  1.40
```

[NEt4][CB11H10−12−CN−1−benacid], 10 mg in 0.5 mL Acetone−d6*
1H{11B} NMR, Bruker 500MHz, T = 23 C



10b

```
Current Data Parameters
NAME     20161012-zk-12-CN-1-benaci
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_            20170110
Time                 0.02
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgig30
TD                 65536
SOLVENT          Acetone
NS                    16
DS                     0
SWH            12500.000 Hz
FIDRES          0.190735 Hz
AQ             2.6214399 sec
RG                   114
DW                40.000 usec
DE                  6.50 usec
TE                 296.9 K
D1            5.00000000 sec
D11           0.03000000 sec

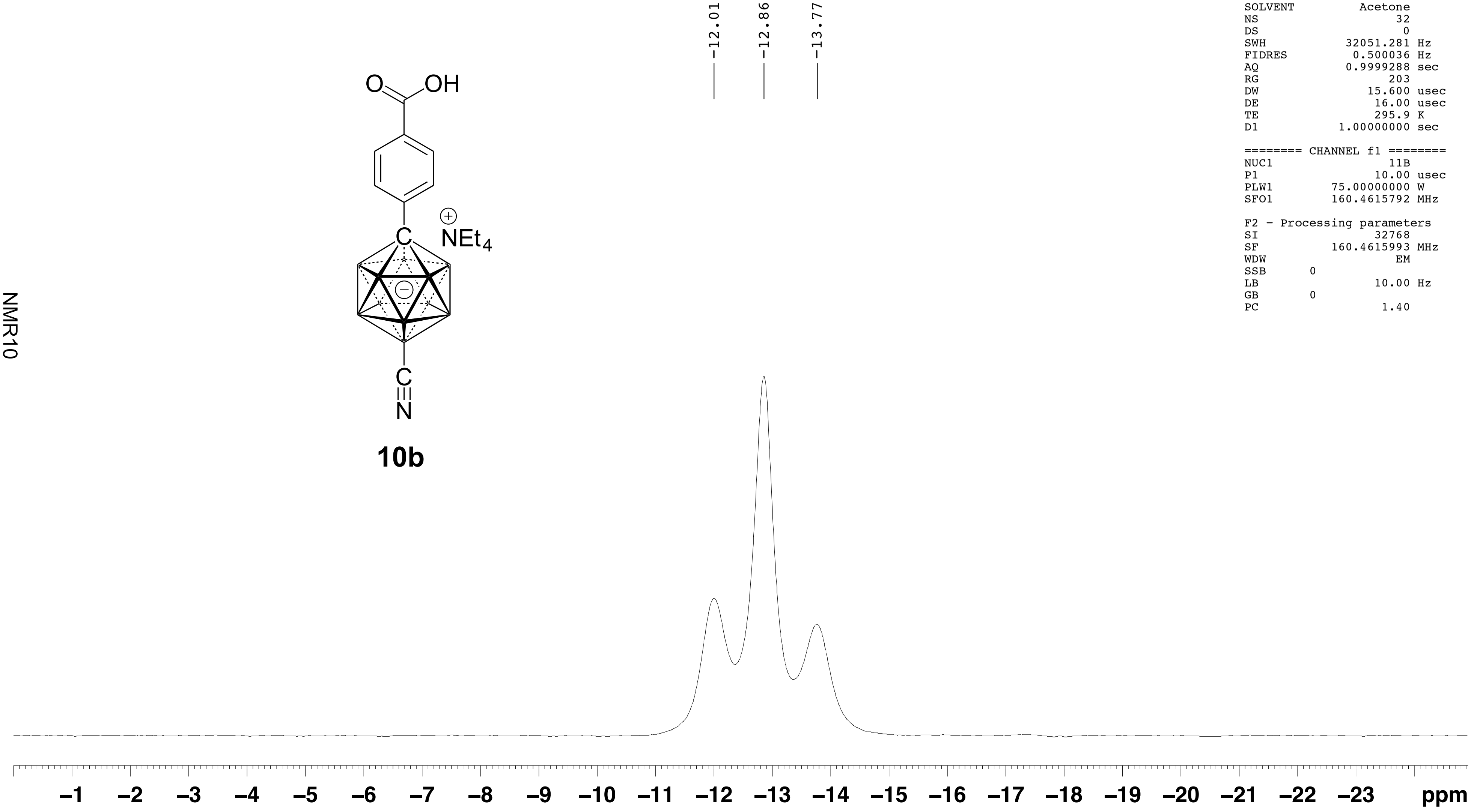
======== CHANNEL f1 ========
NUC1                  1H
P1                 11.70 usec
PLW1         19.00000000 W
SFO1        500.1335009 MHz

======== CHANNEL f2 ========
CPDPRG[2            garp
NUC2                 11B
PCPD2             100.00 usec
PLW2         95.00000000 W
PLW12         1.63030005 W
SFO2        160.4615690 MHz

F2 - Processing parameters
SI                 65536
SF           500.1300101 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.00
```

NMR10

[NEt4][CB11H10−12−CN−1−benacid], 10 mg in 0.5 mL Acetone−d6
11B NMR, Bruker 500MHz, T = 23 C



10b

```
Current Data Parameters
NAME     20161012-zk-12-CN-1-benacid
EXPNO                     1
PROCNO                    1

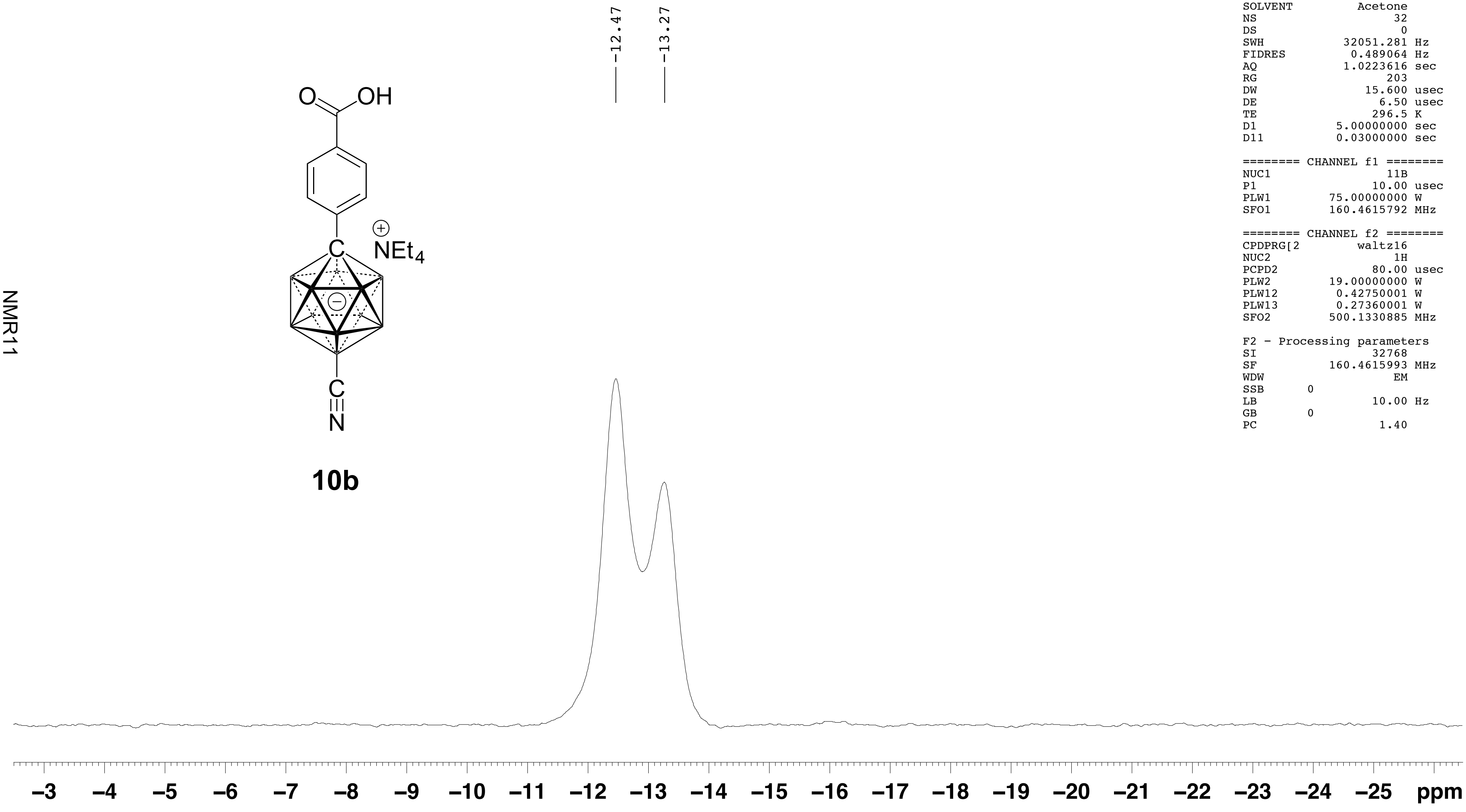
F2 - Acquisition Parameters
Date_          20151012
Time              15.52
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG              zg
TD                64098
SOLVENT         Acetone
NS                   32
DS                    0
SWH           32051.281 Hz
FIDRES         0.500036 Hz
AQ            0.9999288 sec
RG                  203
DW               15.600 usec
DE                16.00 usec
TE                295.9 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                11B
P1                10.00 usec
PLW1        75.00000000 W
SFO1        160.4615792 MHz

F2 - Processing parameters
SI                32768
SF          160.4615993 MHz
WDW                  EM
SSB      0
LB                10.00 Hz
GB       0
PC                 1.40
```

NMR11

[NEt4][CB11H10−12−CN−1−benacid], 10 mg in 0.5 mL Acetone−d6
11B{1H} NMR, Bruker 500MHz, T = 23 C



10b

```
Current Data Parameters
NAME     20161012-zk-12-CN-1-benacid
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_             20151012
Time                 15.56
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT           Acetone
NS                     32
DS                      0
SWH             32051.281 Hz
FIDRES           0.489064 Hz
AQ              1.0223616 sec
RG                    203
DW                 15.600 usec
DE                   6.50 usec
TE                  296.5 K
D1             5.00000000 sec
D11            0.03000000 sec

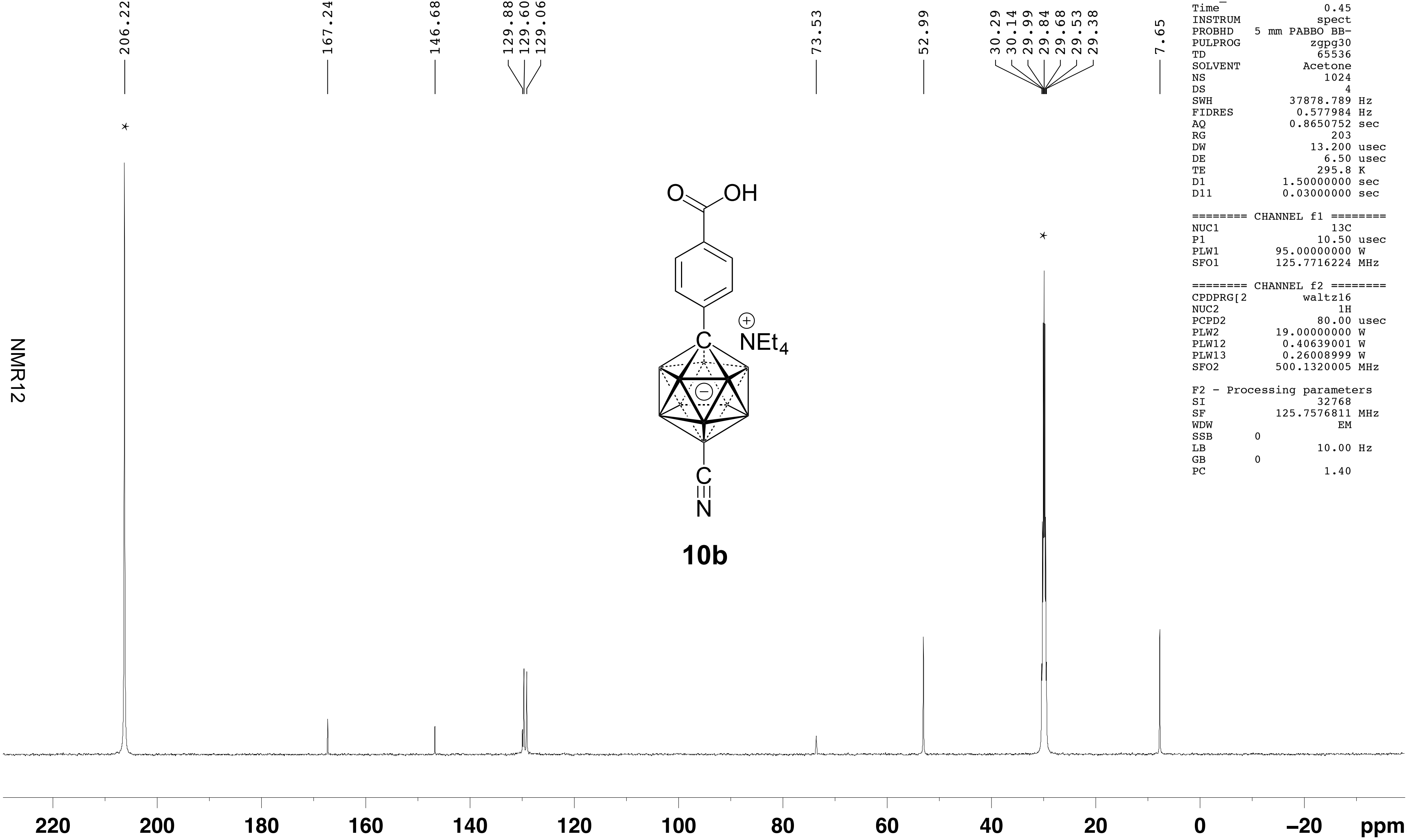
======== CHANNEL f1 ========
NUC1                  11B
P1                  10.00 usec
PLW1          75.00000000 W
SFO1          160.4615792 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.42750001 W
PLW13          0.27360001 W
SFO2          500.1330885 MHz

F2 - Processing parameters
SI                  32768
SF            160.4615993 MHz
WDW                    EM
SSB      0
LB                  10.00 Hz
GB       0
PC                   1.40
```

[NEt4][CB11H10−12−CN−1−benacid], 10 mg in 0.5 mL Acetone−d6*
13C{1H} NMR, Bruker 500MHz, T = 23 C

NMR12



```
Current Data Parameters
NAME     20161012-zk-12-CN-1-benaci
EXPNO                     5
PROCNO                    1

F2 - Acquisition Parameters
Date_            20170110
Time                 0.45
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT          Acetone
NS                  1024
DS                     4
SWH            37878.789 Hz
FIDRES          0.577984 Hz
AQ             0.8650752 sec
RG                   203
DW                13.200 usec
DE                  6.50 usec
TE                 295.8 K
D1            1.50000000 sec
D11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.50 usec
PLW1         95.00000000 W
SFO1         125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.40639001 W
PLW13         0.26008999 W
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7576811 MHz
WDW                   EM
SSB       0
LB                 10.00 Hz
GB        0
PC                  1.40
```

NMR13

[NEt4][CB11H10−12−CN−1−Bendiacids], 6.6 mg in 0.6 mL DMSO−d6*
1H{11B} NMR, Bruker 500MHz, T = 23 C

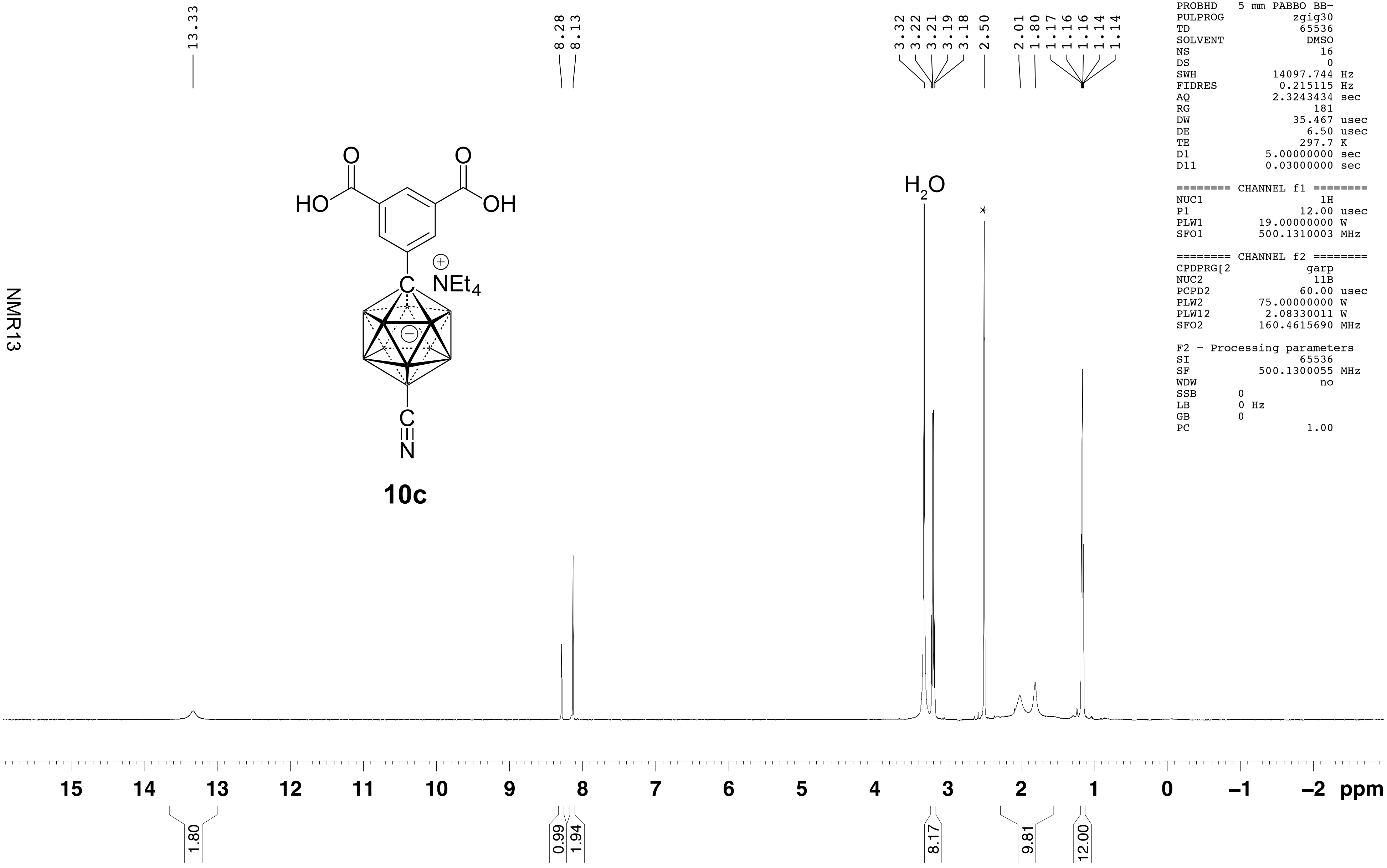
```
Current Data Parameters
NAME     20161026-zk-12-CN-1-bendia
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_            20161026
Time                16.14
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgig30
TD                  65536
SOLVENT              DMSO
NS                     16
DS                      0
SWH             14097.744 Hz
FIDRES           0.215115 Hz
AQ              2.3243434 sec
RG                    181
DW                 35.467 usec
DE                   6.50 usec
TE                  297.7 K
D1             5.00000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PLW1          19.00000000 W
SFO1        500.1310003 MHz

======== CHANNEL f2 ========
CPDPRG[2             garp
NUC2                  11B
PCPD2               60.00 usec
PLW2          75.00000000 W
PLW12          2.08330011 W
SFO2        160.4615690 MHz

F2 - Processing parameters
SI                  65536
SF          500.1300055 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```



10c

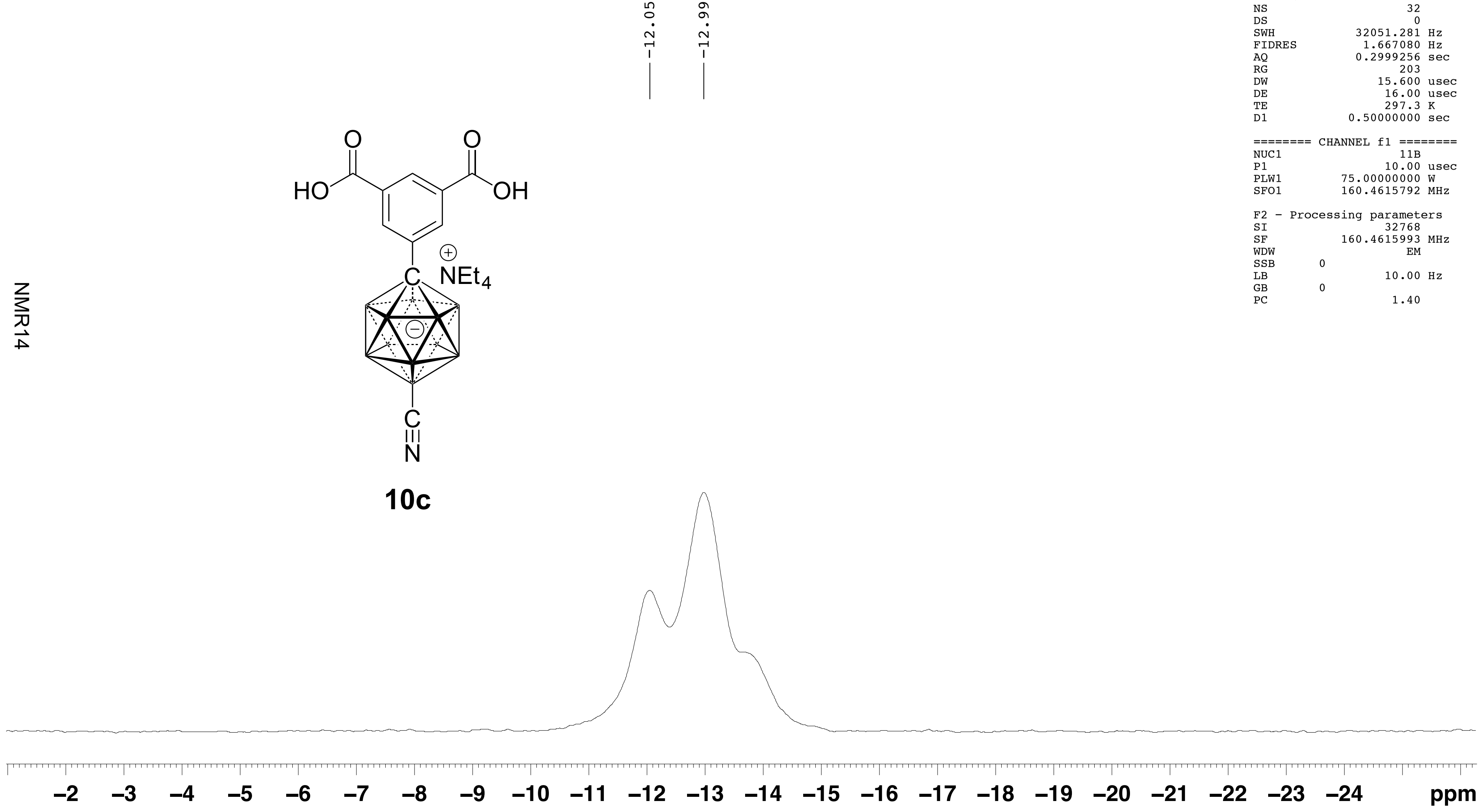
[NEt4][CB11H10−12−CN−1−Bendiacids], 6.6 mg in 0.6 mL DMSO−d6
11B NMR, Bruker 500MHz, T = 23 C

```
Current Data Parameters
NAME     20161026-zk-12-CN-1-bendia
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_          20161026
Time              16.10
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG              zg
TD                19226
SOLVENT            DMSO
NS                   32
DS                    0
SWH           32051.281 Hz
FIDRES         1.667080 Hz
AQ            0.2999256 sec
RG                  203
DW               15.600 usec
DE                16.00 usec
TE                297.3 K
D1           0.50000000 sec

======== CHANNEL f1 ========
NUC1                 11B
P1                 10.00 usec
PLW1        75.00000000 W
SFO1        160.4615792 MHz

F2 - Processing parameters
SI                32768
SF          160.4615993 MHz
WDW                  EM
SSB      0
LB                10.00 Hz
GB       0
PC                 1.40
```



10c

NMR14

[NEt4][CB11H10−12−CN−1−Bendiacids], 6.6 mg in 0.6 mL DMSO−d6
11B{1H} NMR, Bruker 500MHz, T = 23 C

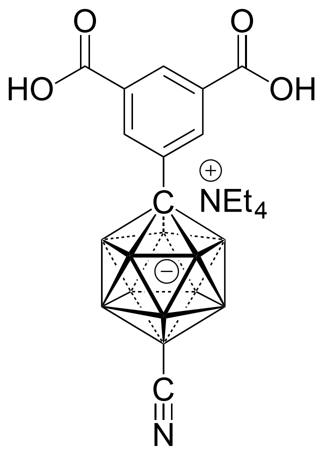
```
Current Data Parameters
NAME    20161026-zk-12-CN-1-bendia
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20161026
Time                 16.11
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   19226
SOLVENT               DMSO
NS                      32
DS                       0
SWH              32051.281 Hz
FIDRES            1.667080 Hz
AQ               0.2999256 sec
RG                     203
DW                  15.600 usec
DE                    6.50 usec
TE                   297.5 K
D1              0.50000000 sec
D11             0.03000000 sec

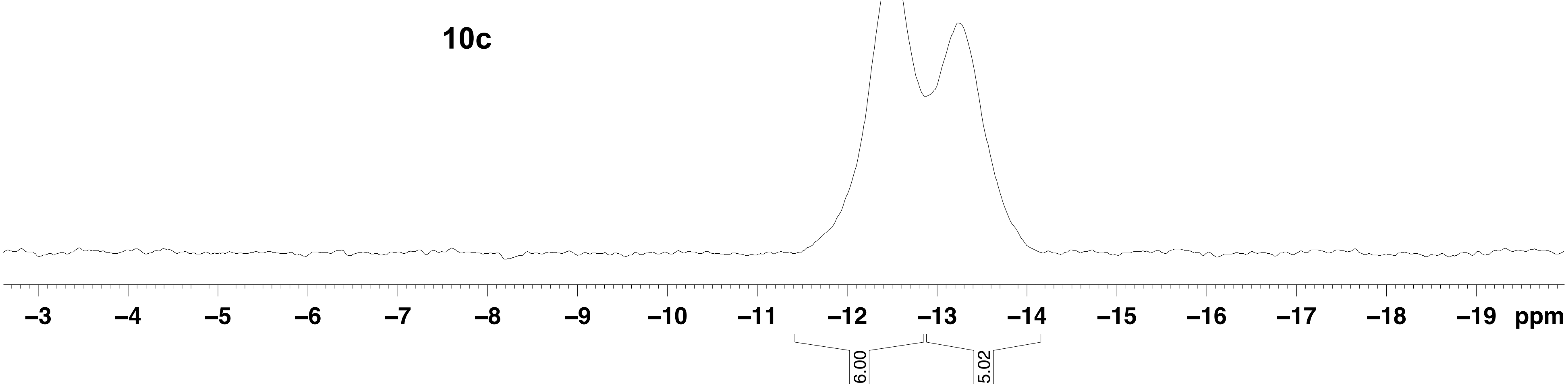
======== CHANNEL f1 ========
NUC1                   11B
P1                   10.00 usec
PLW1           75.00000000 W
SFO1           160.4615792 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.42750001 W
PLW13           0.27360001 W
SFO2           500.1330885 MHz

F2 - Processing parameters
SI                   32768
SF             160.4615993 MHz
WDW                     EM
SSB      0
LB                   10.00 Hz
GB       0
PC                    1.40
```



10c



NMR15

[NEt4][CB11H10−12−CN−1−Bendiacids], 6.6 mg in 0.6 mL DMSO−d6*
13C{1H} NMR, Bruker 500MHz, T = 23 C

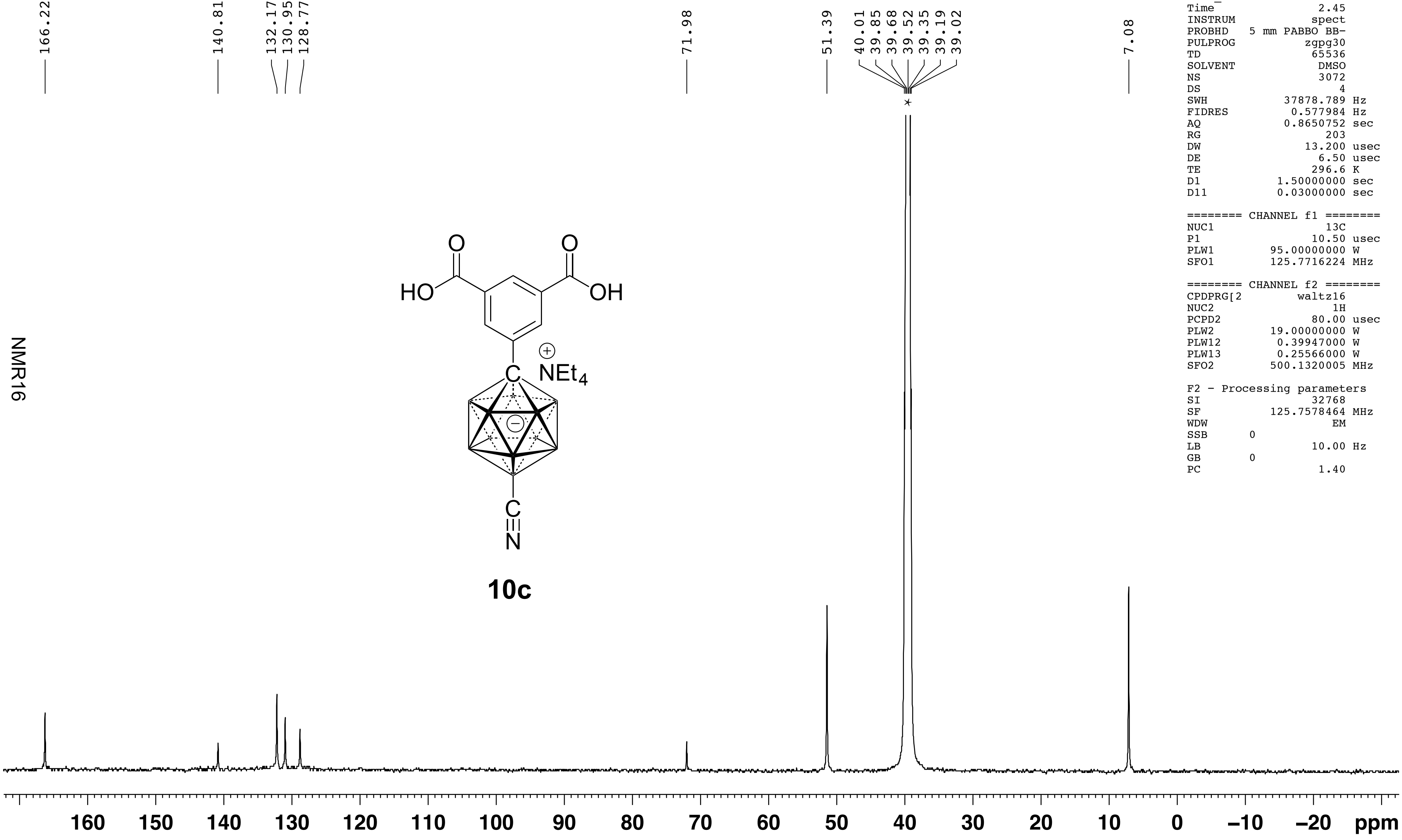
```
Current Data Parameters
NAME     20161026-zk-12-CN-1-bendia
E++XPNO                   1
PROCNO                    1

F2 - Acquisition Parameters
Date_            20161123
Time                 2.45
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT             DMSO
NS                  3072
DS                     4
SWH            37878.789 Hz
FIDRES          0.577984 Hz
AQ             0.8650752 sec
RG                   203
DW                13.200 usec
DE                  6.50 usec
TE                 296.6 K
D1            1.50000000 sec
D11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.50 usec
PLW1         95.00000000 W
SFO1         125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.39947000 W
PLW13         0.25566000 W
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7578464 MHz
WDW                   EM
SSB      0
LB                 10.00 Hz
GB       0
PC                  1.40
```



10c

NMR16

NMR17

[Cs]2[Ben−Bis(CB11H10−12−CN)], 5.6 mg in 0.6 mL DMSO−d6*
1H{13C} NMR, Bruker 500MHz, T = 23 **C**

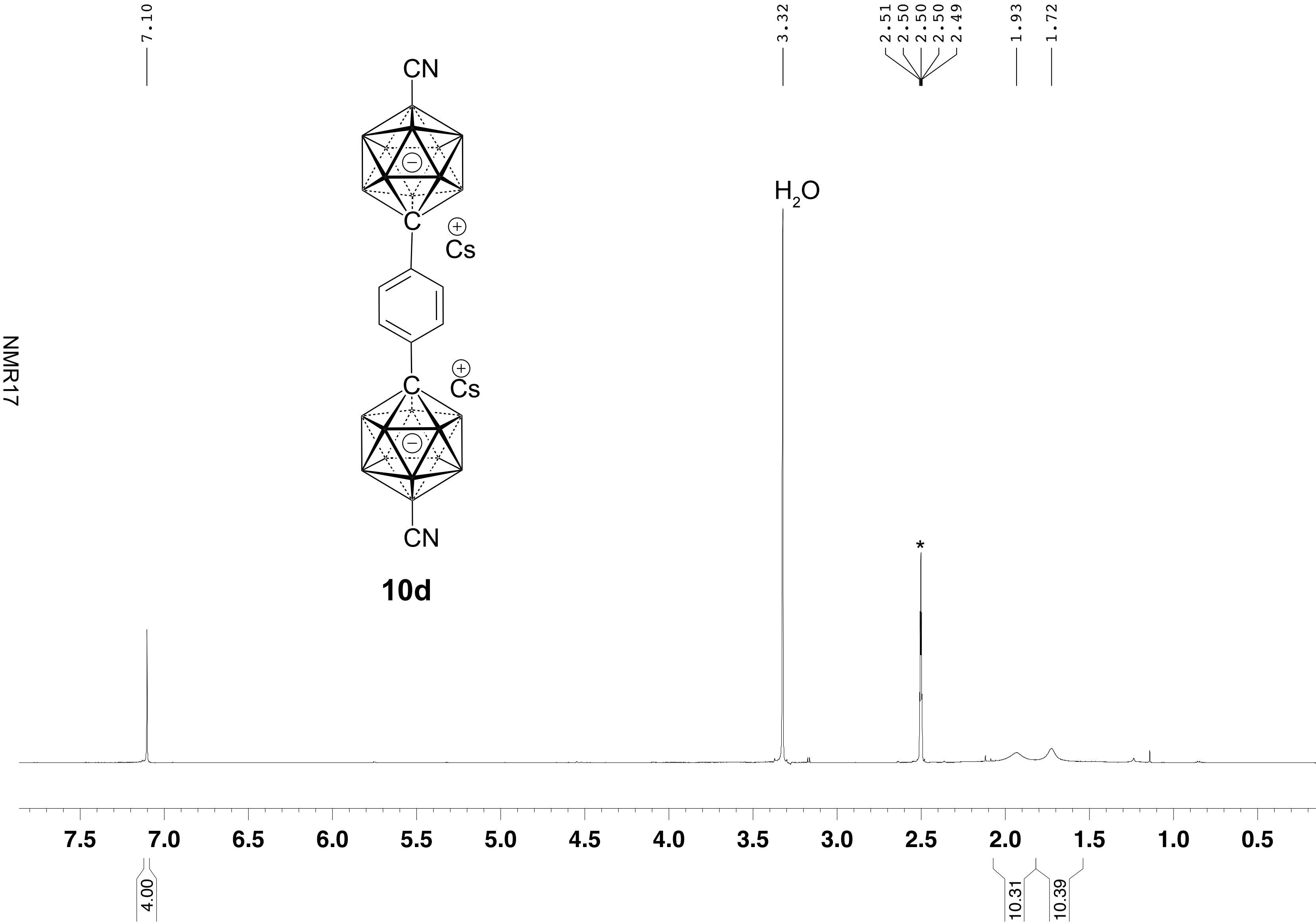
```
Current Data Parameters
NAME     20161026-zk-1,12-CN
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161026
Time               15.54
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgig30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     0
SWH           14097.744 Hz
FIDRES         0.215115 Hz
AQ            2.3243434 sec
RG                   203
DW                35.467 usec
DE                  6.50 usec
TE                 297.4 K
D1            5.00000000 sec
D11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PLW1         19.00000000 W
SFO1         500.1310003 MHz

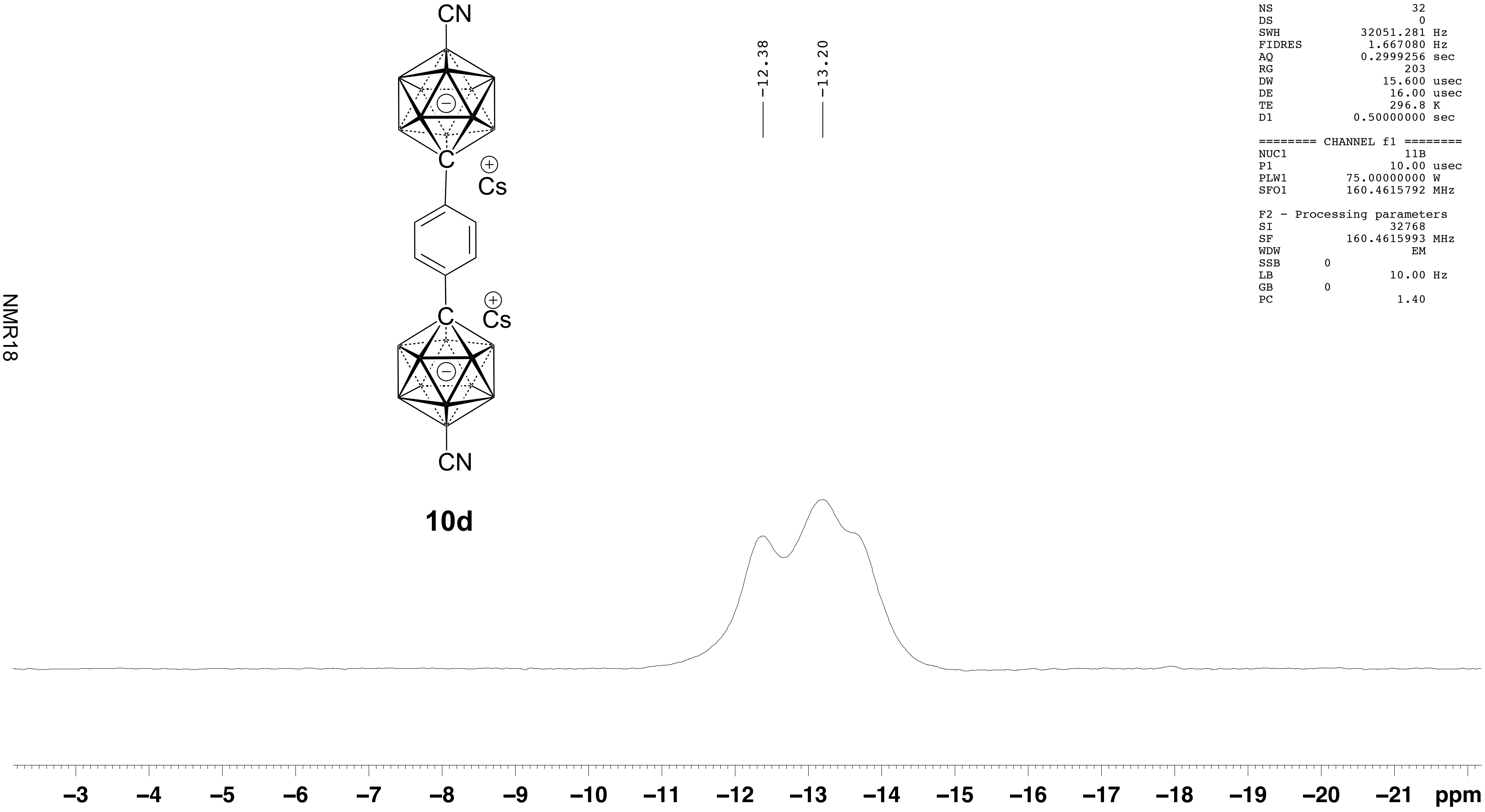
======== CHANNEL f2 ========
CPDPRG[2            garp
NUC2                 11B
PCPD2              60.00 usec
PLW2         75.00000000 W
PLW12         2.08330011 W
SFO2         160.4615690 MHz

F2 - Processing parameters
SI                 65536
SF           500.1300055 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```



10d

[Cs]2[Ben−Bis(CB11H10−12−CN)], 5.6 mg in 0.6 mL DMSO−d6
11B NMR, Bruker 500MHz, T = 23 C



10d

```
Current Data Parameters
NAME     20161026-zk-1,12-CN
EXPNO                  1
PROCNO                 1

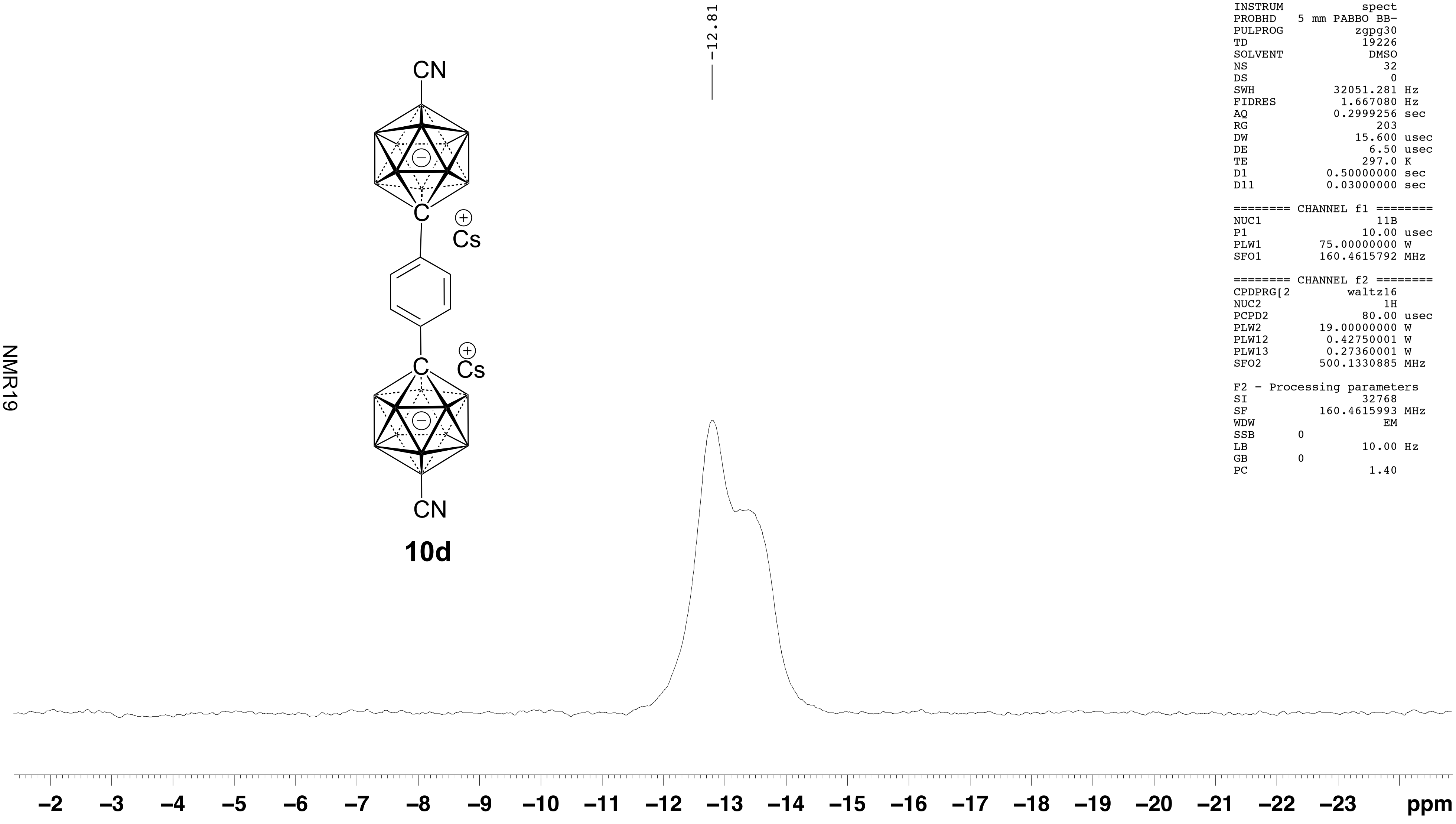
F2 - Acquisition Parameters
Date_          20161026
Time              15.50
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG              zg
TD                19226
SOLVENT            DMSO
NS                   32
DS                    0
SWH           32051.281 Hz
FIDRES         1.667080 Hz
AQ            0.2999256 sec
RG                  203
DW               15.600 usec
DE                16.00 usec
TE                296.8 K
D1           0.50000000 sec

======== CHANNEL f1 ========
NUC1                11B
P1                10.00 usec
PLW1        75.00000000 W
SFO1        160.4615792 MHz

F2 - Processing parameters
SI                32768
SF          160.4615993 MHz
WDW                  EM
SSB      0
LB                10.00 Hz
GB       0
PC                 1.40
```

NMR18

[Cs]2[Ben−Bis(CB11H10−12−CN)], 5.6 mg in 0.6 mL DMSO−d6
1H{11B} NMR, Bruker 500MHz, T = 23 C



10d

```
Current Data Parameters
NAME     20161026-zk-1,12-CN
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_            20161026
Time                15.52
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  19226
SOLVENT              DMSO
NS                     32
DS                      0
SWH           32051.281 Hz
FIDRES         1.667080 Hz
AQ            0.2999256 sec
RG                    203
DW                 15.600 usec
DE                   6.50 usec
TE                  297.0 K
D1             0.50000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  11B
P1                  10.00 usec
PLW1          75.00000000 W
SFO1         160.4615792 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.42750001 W
PLW13          0.27360001 W
SFO2         500.1330885 MHz

F2 - Processing parameters
SI                  32768
SF           160.4615993 MHz
WDW                    EM
SSB      0
LB                  10.00 Hz
GB       0
PC                   1.40
```

NMR19

[Cs]2[Ben−Bis(CB11H10−12−CN)], 5.6 mg in 0.6 mL DMSO−d6*
13C{1H} NMR, Bruker 500MHz, T = 23 C

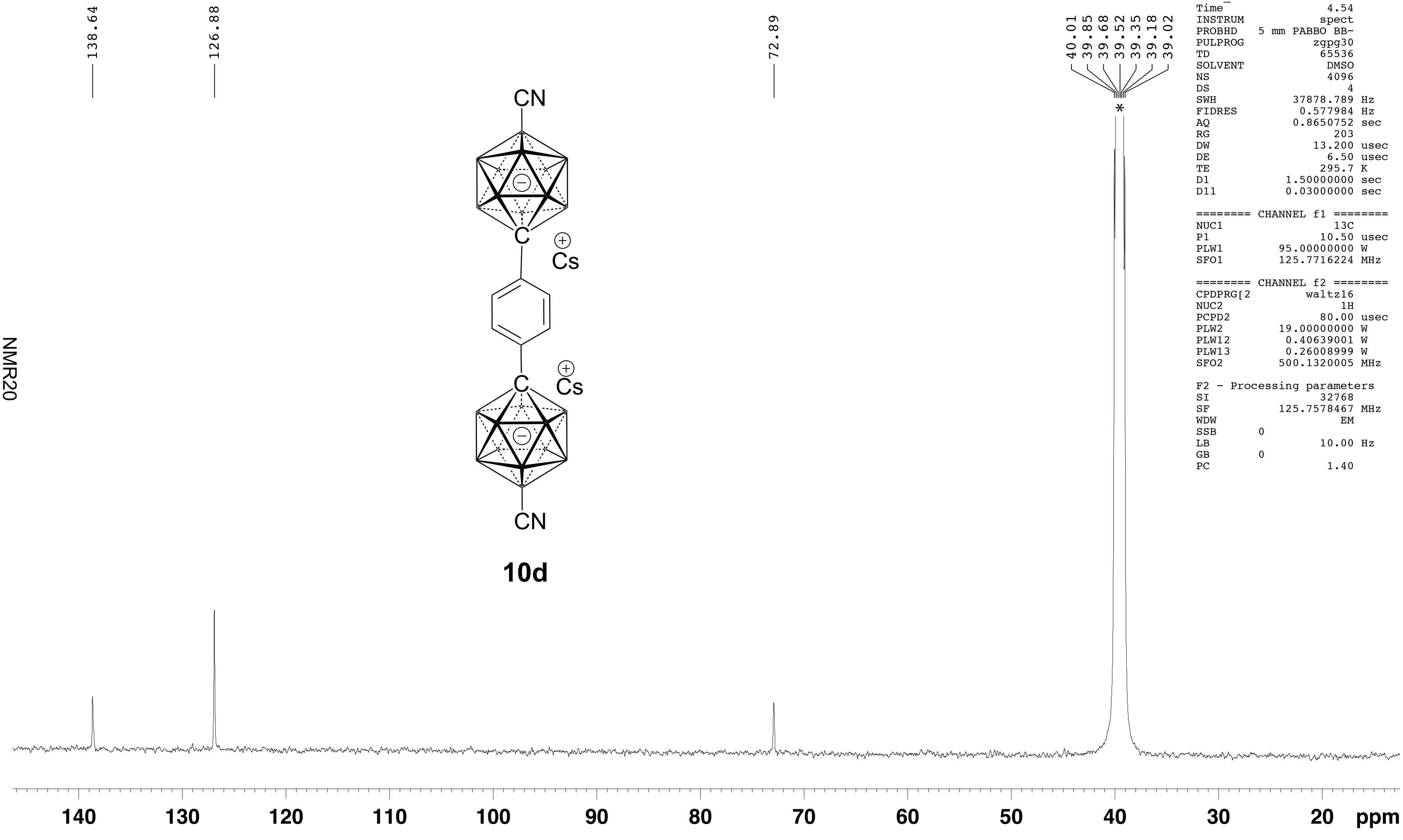
```
Current Data Parameters
NAME     20161026-zk-1,12-CN
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_             20161129
Time                  4.54
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT              DMSO
NS                   4096
DS                      4
SWH             37878.789 Hz
FIDRES           0.577984 Hz
AQ              0.8650752 sec
RG                    203
DW                 13.200 usec
DE                   6.50 usec
TE                  295.7 K
D1             1.50000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.50 usec
PLW1          95.00000000 W
SFO1          125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.40639001 W
PLW13          0.26008999 W
SFO2          500.1320005 MHz

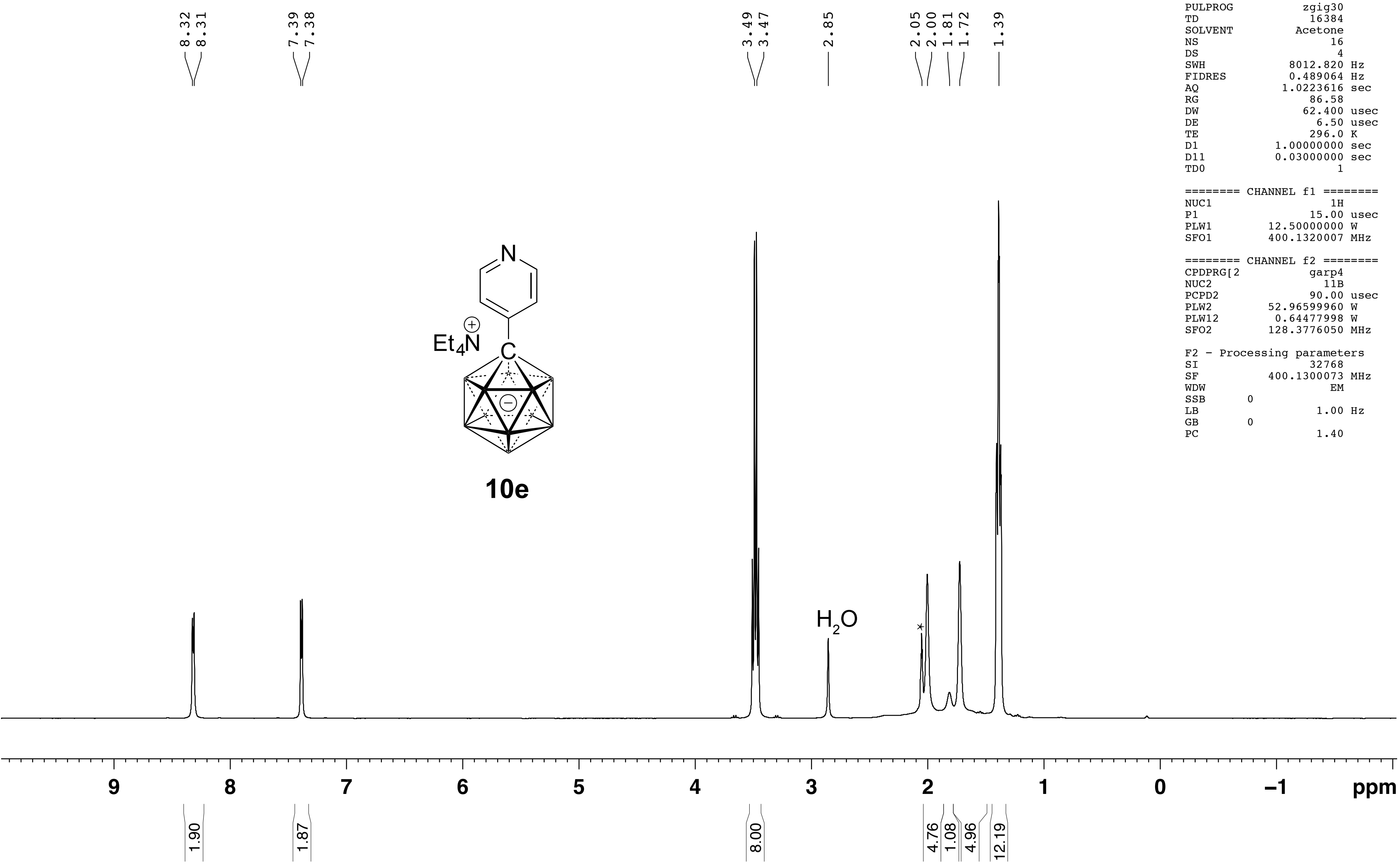
F2 - Processing parameters
SI                  32768
SF            125.7578467 MHz
WDW                    EM
SSB      0
LB                  10.00 Hz
GB       0
PC                   1.40
```



10d

NMR20

[NEt4][CB11H11−1−Pyridine], 15.6 mg in 0.6 mL Acetone−d6*
1H{11B} NMR, Bruker 400MHz, T = 23 **C**



10e

```
Current Data Parameters
NAME   20170409-zk-1-P
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20170411
Time                 6.21
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgig30
TD                  16384
SOLVENT           Acetone
NS                     16
DS                      4
SWH              8012.820 Hz
FIDRES           0.489064 Hz
AQ              1.0223616 sec
RG                  86.58
DW                 62.400 usec
DE                   6.50 usec
TE                  296.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1

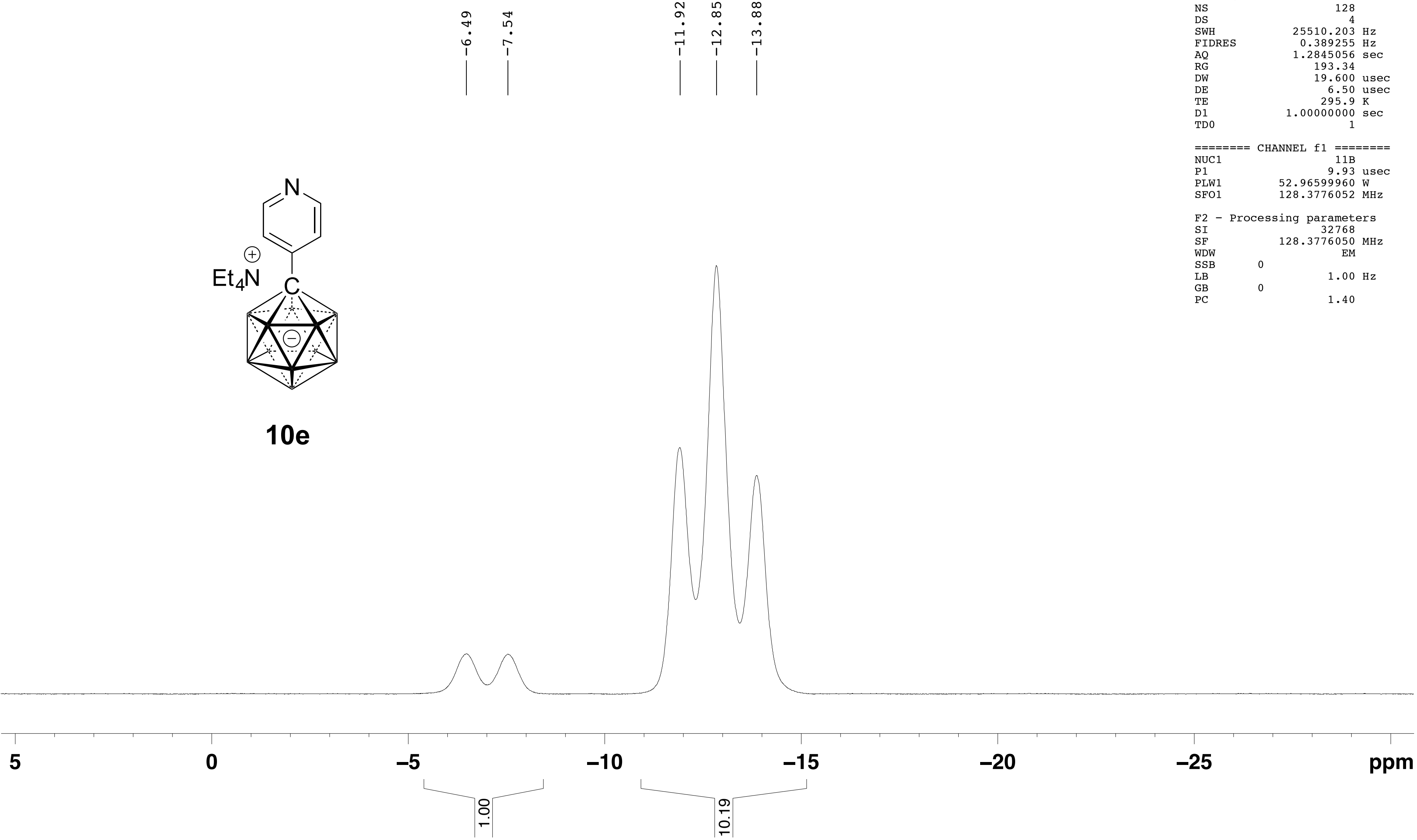
======== CHANNEL f1 ========
NUC1                   1H
P1                  15.00 usec
PLW1          12.50000000 W
SFO1          400.1320007 MHz

======== CHANNEL f2 ========
CPDPRG[2            garp4
NUC2                  11B
PCPD2               90.00 usec
PLW2          52.96599960 W
PLW12          0.64477998 W
SFO2          128.3776050 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300073 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

NMR21

[NEt4][CB11H11-1-Pyridine], 15.6 mg in 0.6 mL Acetone-d 6
11B NMR, Bruker 400MHz, T = 23 C



```
Current Data Parameters
NAME   20170409-zk-1-P
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20170411
Time                   6.33
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                  zg
TD                    65536
SOLVENT             Acetone
NS                      128
DS                        4
SWH               25510.203 Hz
FIDRES             0.389255 Hz
AQ                1.2845056 sec
RG                   193.34
DW                   19.600 usec
DE                     6.50 usec
TE                    295.9 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    11B
P1                     9.93 usec
PLW1            52.96599960 W
SFO1            128.3776052 MHz

F2 - Processing parameters
SI                    32768
SF              128.3776050 MHz
WDW                      EM
SSB      0
LB                     1.00 Hz
GB       0
PC                     1.40
```

[NEt4][CB11H11−1−Pyridine], 15.6 mg in 0.6 mL Acetone−d6
11B{1H} NMR, Bruker 400MHz, T = 23 **C**

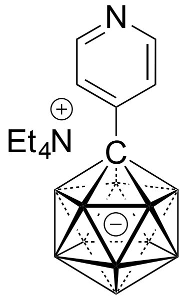
```
Current Data Parameters
NAME    20170409-zk-1-P
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170411
Time                6.27
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT         Acetone
NS                  128
DS                    4
SWH           25510.203 Hz
FIDRES         0.389255 Hz
AQ            1.2845056 sec
RG               193.34
DW               19.600 usec
DE                 6.50 usec
TE                296.5 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

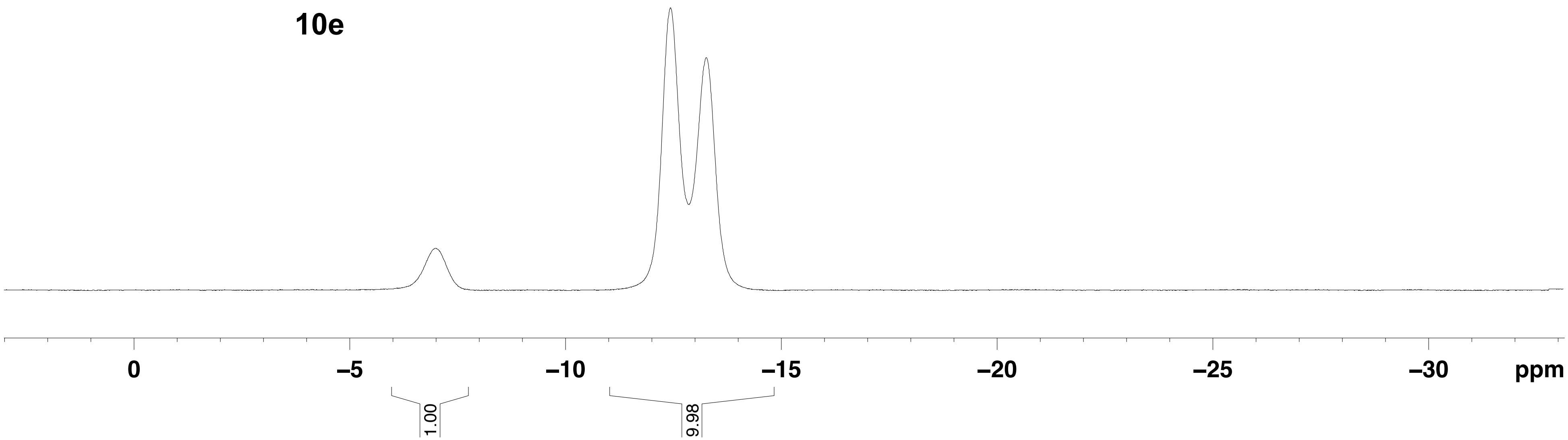
======== CHANNEL f1 ========
NUC1                 11B
P1                  9.93 usec
PLW1         52.96599960 W
SFO1         128.3776050 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         12.50000000 W
PLW12         0.43945000 W
PLW13         0.28125000 W
SFO2         400.1320007 MHz

F2 - Processing parameters
SI                 32768
SF           128.3776050 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

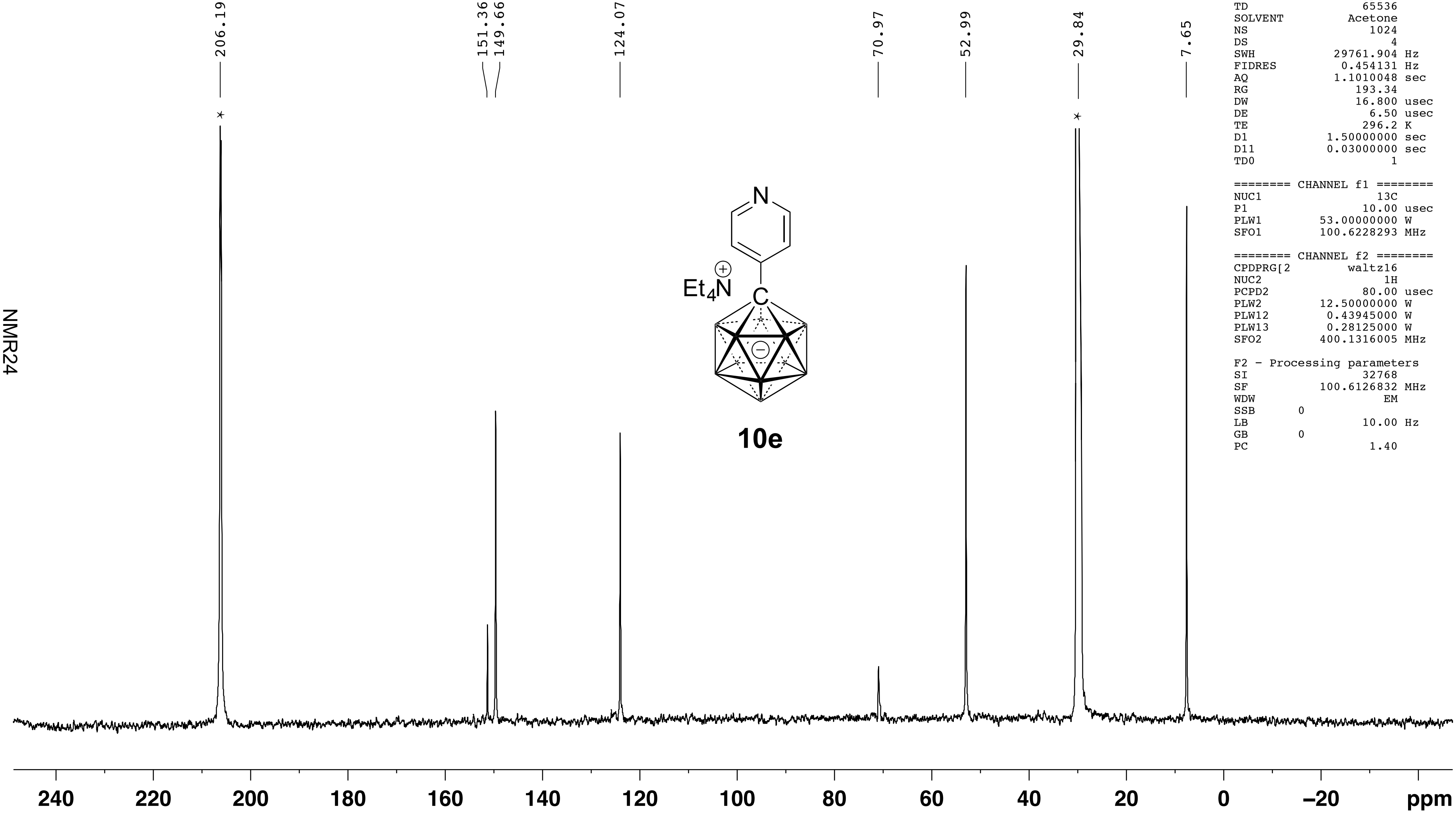


10e



NMR23

[NEt4][CB11H11-1-Pyridine], 15.6 mg in 0.6 mL Acetone-d6*
13C{1H} NMR, Bruker 400MHz, T = 23 **C**



10e

```
Current Data Parameters
NAME     20170409-zk-1-P
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170411
Time                7.20
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT          Acetone
NS                  1024
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                193.34
DW                16.800 usec
DE                  6.50 usec
TE                 296.2 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PLW1         53.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         12.50000000 W
PLW12         0.43945000 W
PLW13         0.28125000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6126832 MHz
WDW                   EM
SSB       0
LB                 10.00 Hz
GB        0
PC                  1.40
```

[NEt4][CB11H10−12−CN−1−COOH], 12.6 mg in 0.6 mL DMSO−d6*
13C{1H} NMR, Bruker 400MHz, T = 23 C

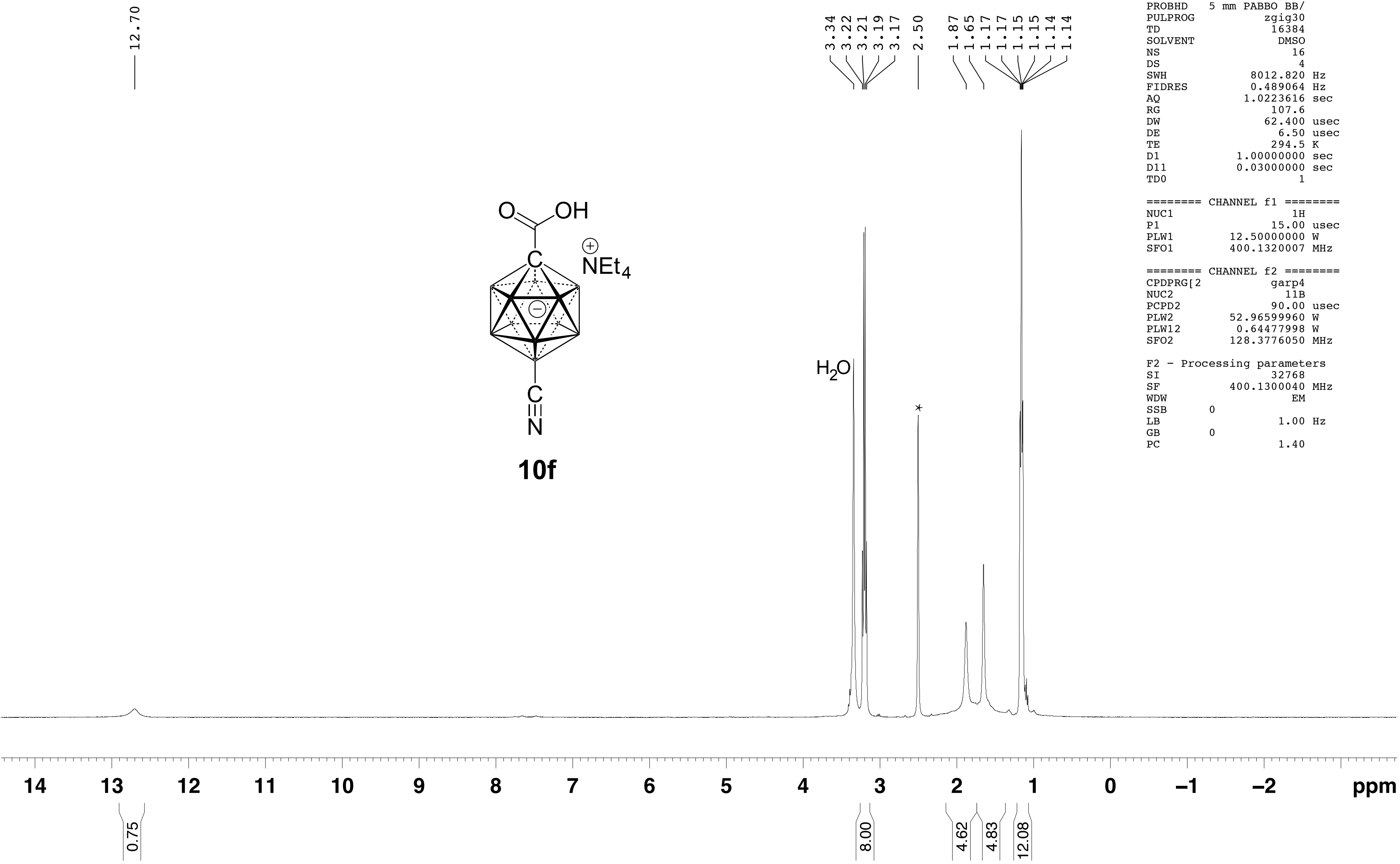
```
Current Data Parameters
NAME     20161231-zk-12-CN-1-COOH
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_              20170101
Time                   5.41
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG              zgig30
TD                    16384
SOLVENT                DMSO
NS                       16
DS                        4
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                1.0223616 sec
RG                    107.6
DW                   62.400 usec
DE                     6.50 usec
TE                    294.5 K
D1               1.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    15.00 usec
PLW1            12.50000000 W
SFO1            400.1320007 MHz

======== CHANNEL f2 ========
CPDPRG[2              garp4
NUC2                    11B
PCPD2                 90.00 usec
PLW2            52.96599960 W
PLW12            0.64477998 W
SFO2            128.3776050 MHz

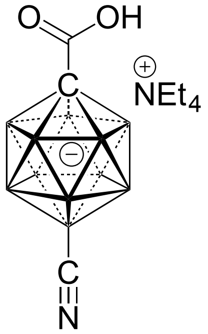
F2 - Processing parameters
SI                    32768
SF              400.1300040 MHz
WDW                      EM
SSB      0
LB                     1.00 Hz
GB       0
PC                     1.40
```



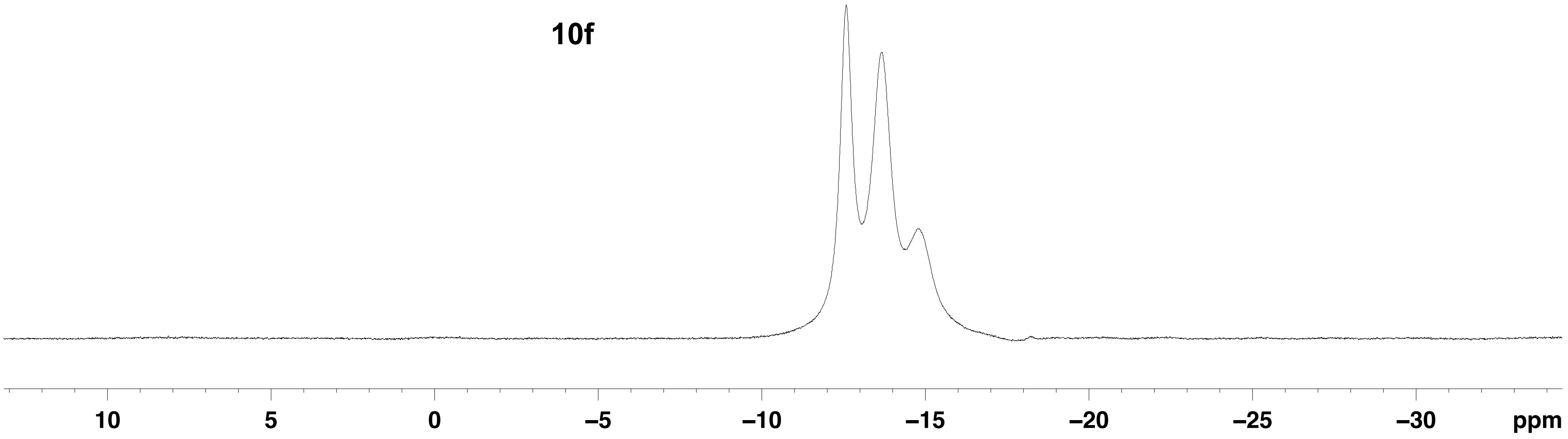
10f

NMR26

[NEt4][CB11H10−12−CN−1−COOH], 12.6 mg in 0.6 mL DMSO−d6
11B NMR, Bruker 400MHz, T = 23 C



10f



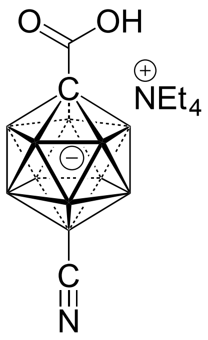
```
Current Data Parameters
NAME     20161231-zk-12-CN-1-COOH
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20170101
Time               5.34
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG              zg
TD                65536
SOLVENT            DMSO
NS                  128
DS                    4
SWH           25510.203 Hz
FIDRES         0.389255 Hz
AQ            1.2845056 sec
RG               193.34
DW               19.600 usec
DE                 6.50 usec
TE                294.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                11B
P1                 9.93 usec
PLW1        52.96599960 W
SFO1        128.3776052 MHz

F2 - Processing parameters
SI                32768
SF          128.3776050 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

[NEt4][CB11H10−12−CN−1−COOH], 12.6 mg in 0.6 mL DMSO−d6
11B{1H} NMR, Bruker 400MHz, T = 23 C



10f

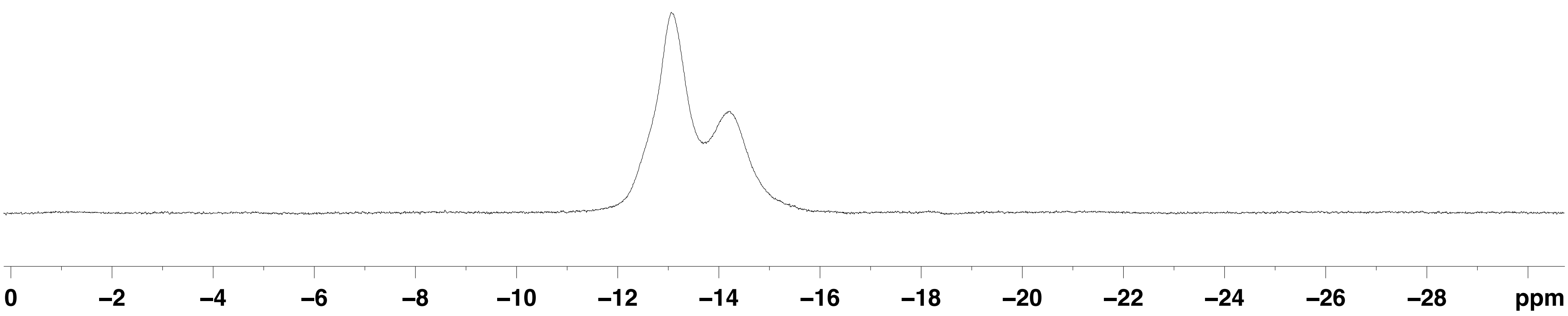
```
Current Data Parameters
NAME     20161231-zk-12-CN-1-COOH
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170101
Time                 5.40
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT              DMSO
NS                    128
DS                      4
SWH             25510.203 Hz
FIDRES           0.389255 Hz
AQ              1.2845056 sec
RG                 193.34
DW                 19.600 usec
DE                   6.50 usec
TE                  294.8 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  11B
P1                   9.93 usec
PLW1          52.96599960 W
SFO1         128.3776050 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PLW2          12.50000000 W
PLW12          0.43945000 W
PLW13          0.28125000 W
SFO2         400.1320007 MHz

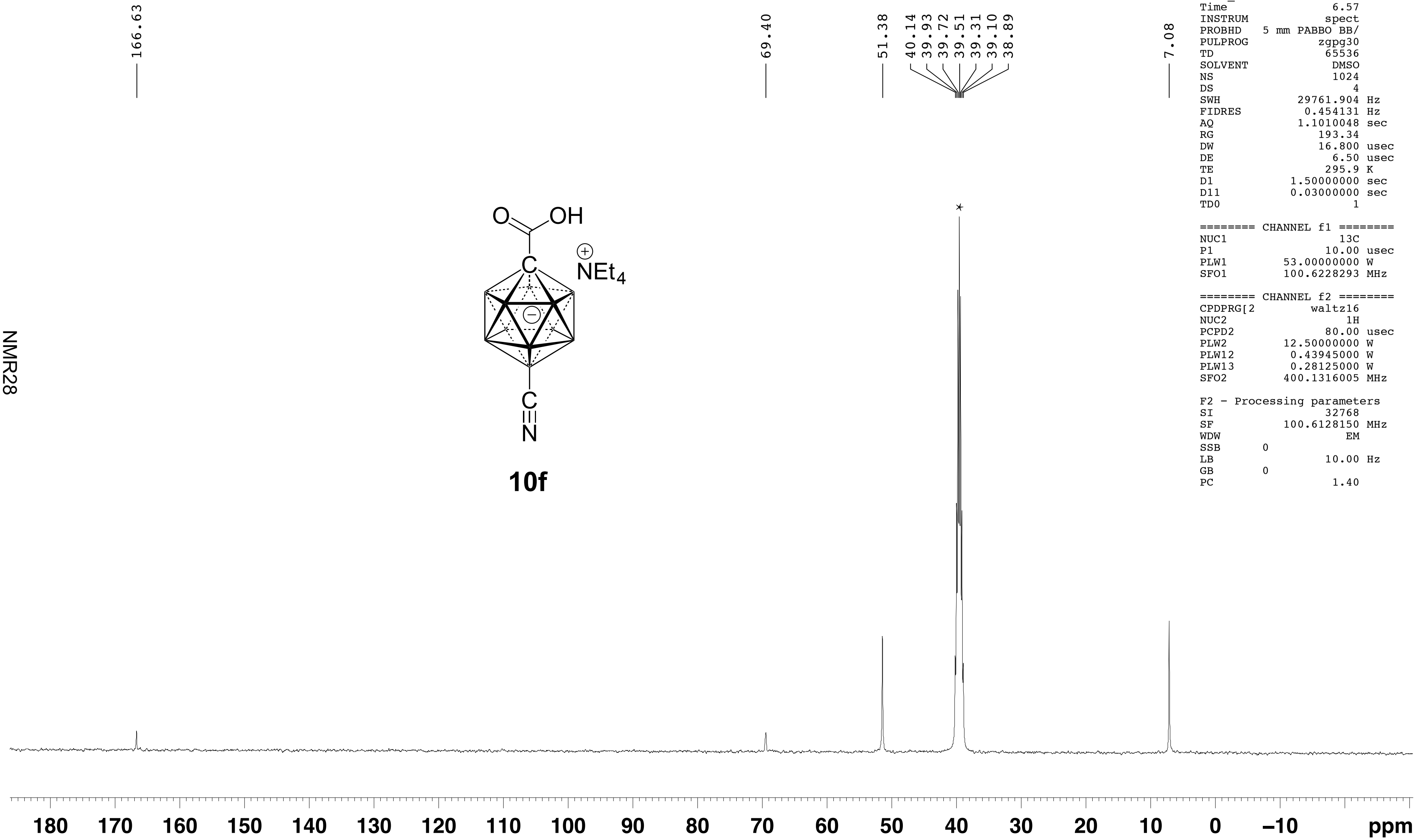
F2 - Processing parameters
SI                  32768
SF           128.3776050 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```



NMR27

[NEt4][CB11H10−12−CN−1−COOH], 12.6 mg in 0.6 mL DMSO−d6*
13C{1H} NMR, Bruker 400MHz, T = 23 C

NMR28



10f

```
Current Data Parameters
NAME     20161231-zk-12-CN-1-COOH
EXPNO                     4
PROCNO                    1

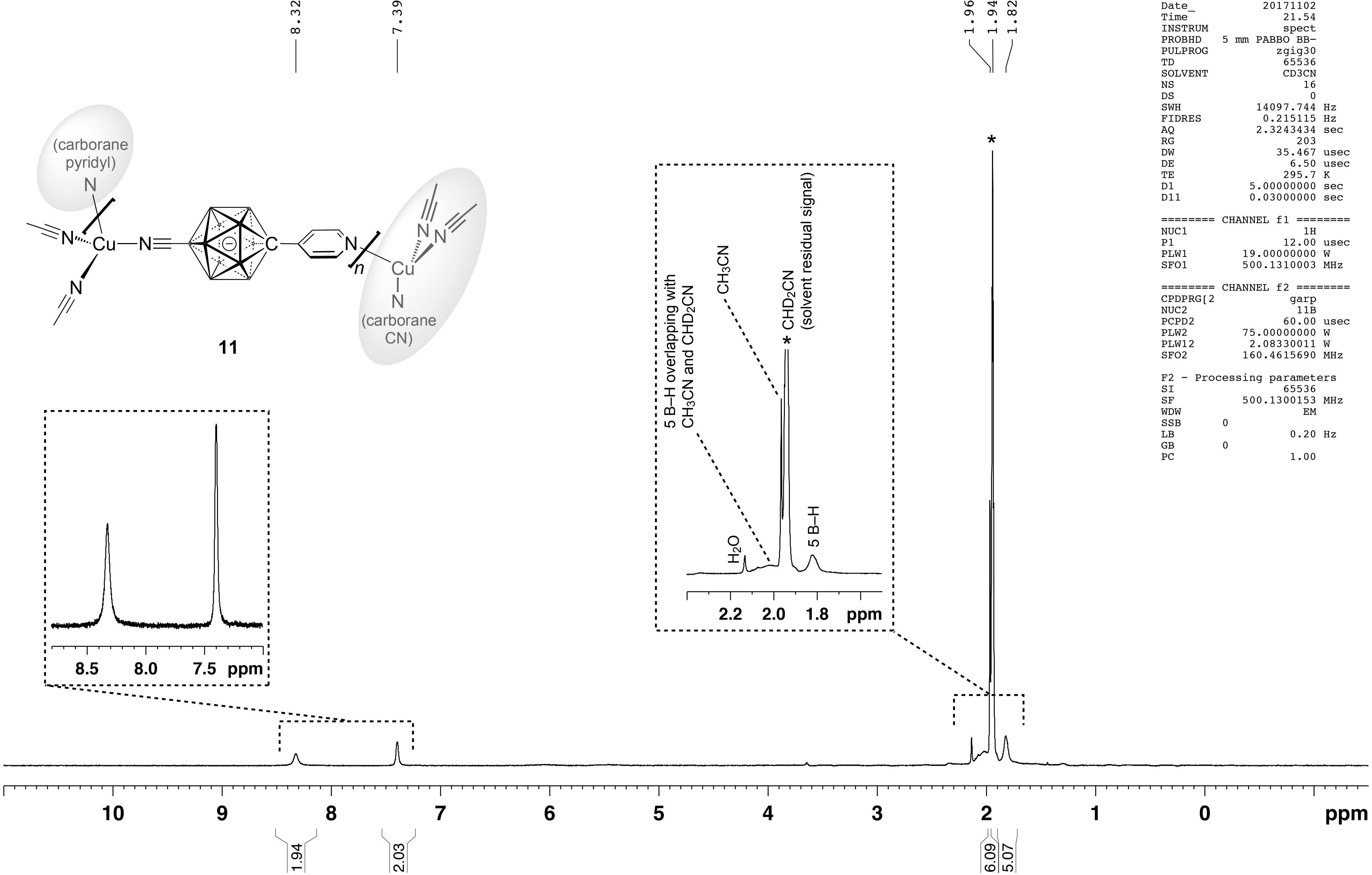
F2 - Acquisition Parameters
Date_            20170103
Time                 6.57
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT             DMSO
NS                  1024
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                193.34
DW                16.800 usec
DE                  6.50 usec
TE                 295.9 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PLW1         53.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         12.50000000 W
PLW12         0.43945000 W
PLW13         0.28125000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6128150 MHz
WDW                   EM
SSB      0
LB                 10.00 Hz
GB       0
PC                  1.40
```

1H{11B} NMR, CD3CN*
20171102–zk–Cu–Polymer



11

```
Current Data Parameters
NAME     20171102-zk-Cu-Polymer-2
EXPNO                       1
PROCNO                      1

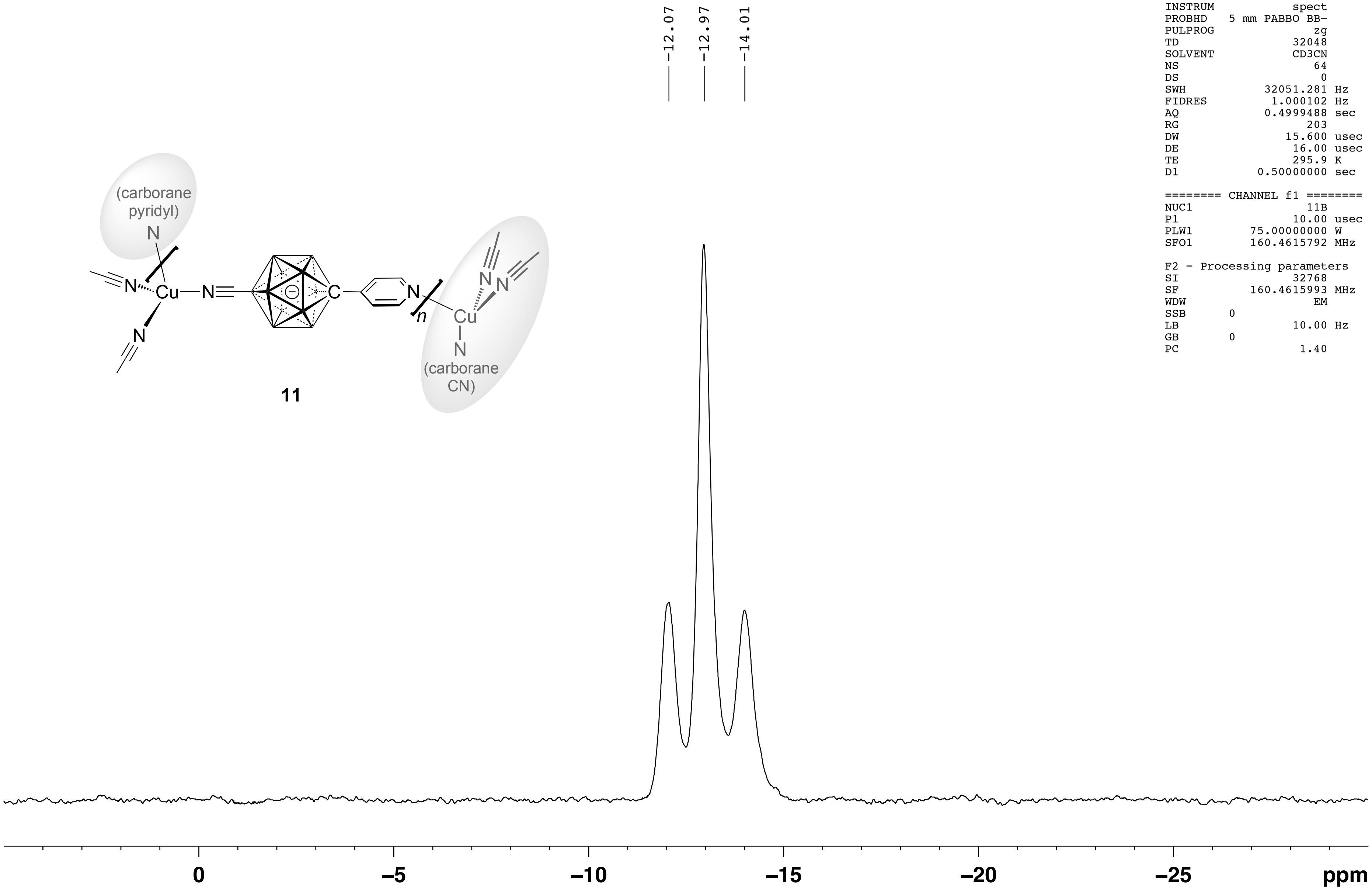
F2 - Acquisition Parameters
Date_            20171102
Time                21.54
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgig30
TD                  65536
SOLVENT             CD3CN
NS                     16
DS                      0
SWH             14097.744 Hz
FIDRES           0.215115 Hz
AQ              2.3243434 sec
RG                    203
DW                 35.467 usec
DE                   6.50 usec
TE                  295.7 K
D1             5.00000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PLW1          19.00000000 W
SFO1          500.1310003 MHz

======== CHANNEL f2 ========
CPDPRG[2             garp
NUC2                  11B
PCPD2               60.00 usec
PLW2          75.00000000 W
PLW12          2.08330011 W
SFO2          160.4615690 MHz

F2 - Processing parameters
SI                  65536
SF            500.1300153 MHz
WDW                    EM
SSB      0
LB                   0.20 Hz
GB       0
PC                   1.00
```

11B NMR, CD3CN
20171102–zk–Cu–Polymer



11

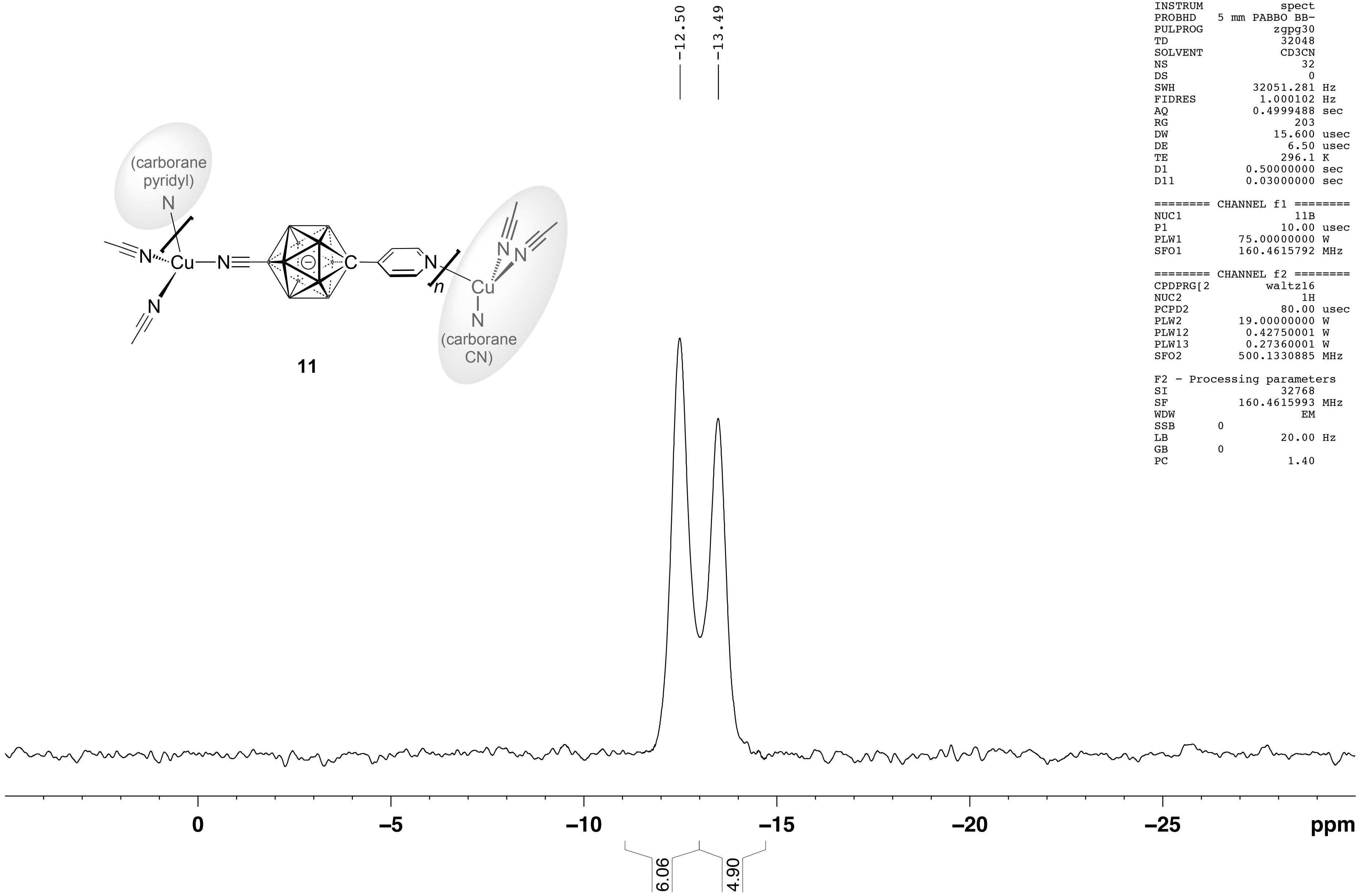
```
Current Data Parameters
NAME     20171102-zk-Cu-Polymer-2
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20171102
Time                21.57
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG                zg
TD                  32048
SOLVENT             CD3CN
NS                     64
DS                      0
SWH             32051.281 Hz
FIDRES           1.000102 Hz
AQ              0.4999488 sec
RG                    203
DW                 15.600 usec
DE                  16.00 usec
TE                  295.9 K
D1             0.50000000 sec

======== CHANNEL f1 ========
NUC1                  11B
P1                  10.00 usec
PLW1          75.00000000 W
SFO1         160.4615792 MHz

F2 - Processing parameters
SI                  32768
SF           160.4615993 MHz
WDW                    EM
SSB      0
LB                  10.00 Hz
GB       0
PC                   1.40
```

11B{1H} NMR, CD3CN
20171102–zk–Cu–Polymer



11

```
Current Data Parameters
NAME     20171102-zk-Cu-Polymer-2
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_          20171102
Time              21.58
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                32048
SOLVENT           CD3CN
NS                   32
DS                    0
SWH           32051.281 Hz
FIDRES         1.000102 Hz
AQ            0.4999488 sec
RG                  203
DW               15.600 usec
DE                 6.50 usec
TE                296.1 K
D1           0.50000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                11B
P1                10.00 usec
PLW1        75.00000000 W
SFO1        160.4615792 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2             80.00 usec
PLW2        19.00000000 W
PLW12        0.42750001 W
PLW13        0.27360001 W
SFO2        500.1330885 MHz

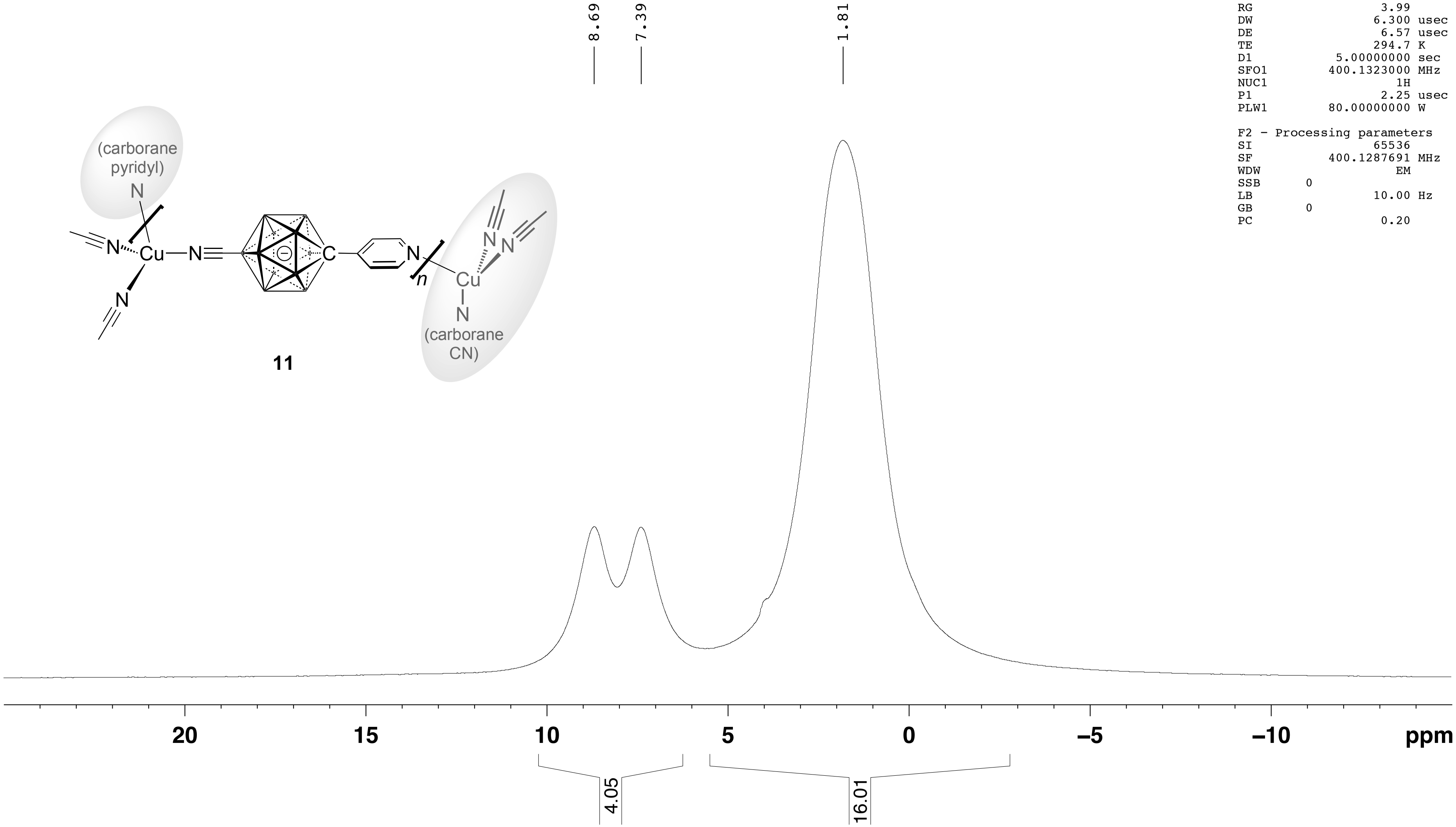
F2 - Processing parameters
SI                32768
SF          160.4615993 MHz
WDW                  EM
SSB      0
LB                20.00 Hz
GB       0
PC                 1.40
```

1H 20171103
Sample: CU
Exp: 1H onepulse
Condition: 15 kHz MAS
Probe: 400 MHz 3.2 mm, Double Channel, HF filter, No Insert
Input:
D1 = 5 s, NS = 56
P1 = 2.25 us, PLW1 = 80 w

```
Current Data Parameters
NAME      20171103_Cu_simon
EXPNO                   111
PROCNO                    1

F2 - Acquisition Parameters
Date_              20171103
Time                15.40 h
INSTRUM               spect
PROBHD   H13541_0005 (P
PULPROG            onepulse
TD                     4096
SOLVENT
NS                       56
DS                        0
SWH           79365.078 Hz
FIDRES        38.752480 Hz
AQ           0.0258048 sec
RG                     3.99
DW                6.300 usec
DE                 6.57 usec
TE                  294.7 K
D1           5.00000000 sec
SFO1        400.1323000 MHz
NUC1                     1H
P1                 2.25 usec
PLW1        80.00000000 W

F2 - Processing parameters
SI                    65536
SF          400.1287691 MHz
WDW                      EM
SSB      0
LB                10.00 Hz
GB       0
PC                     0.20
```



11

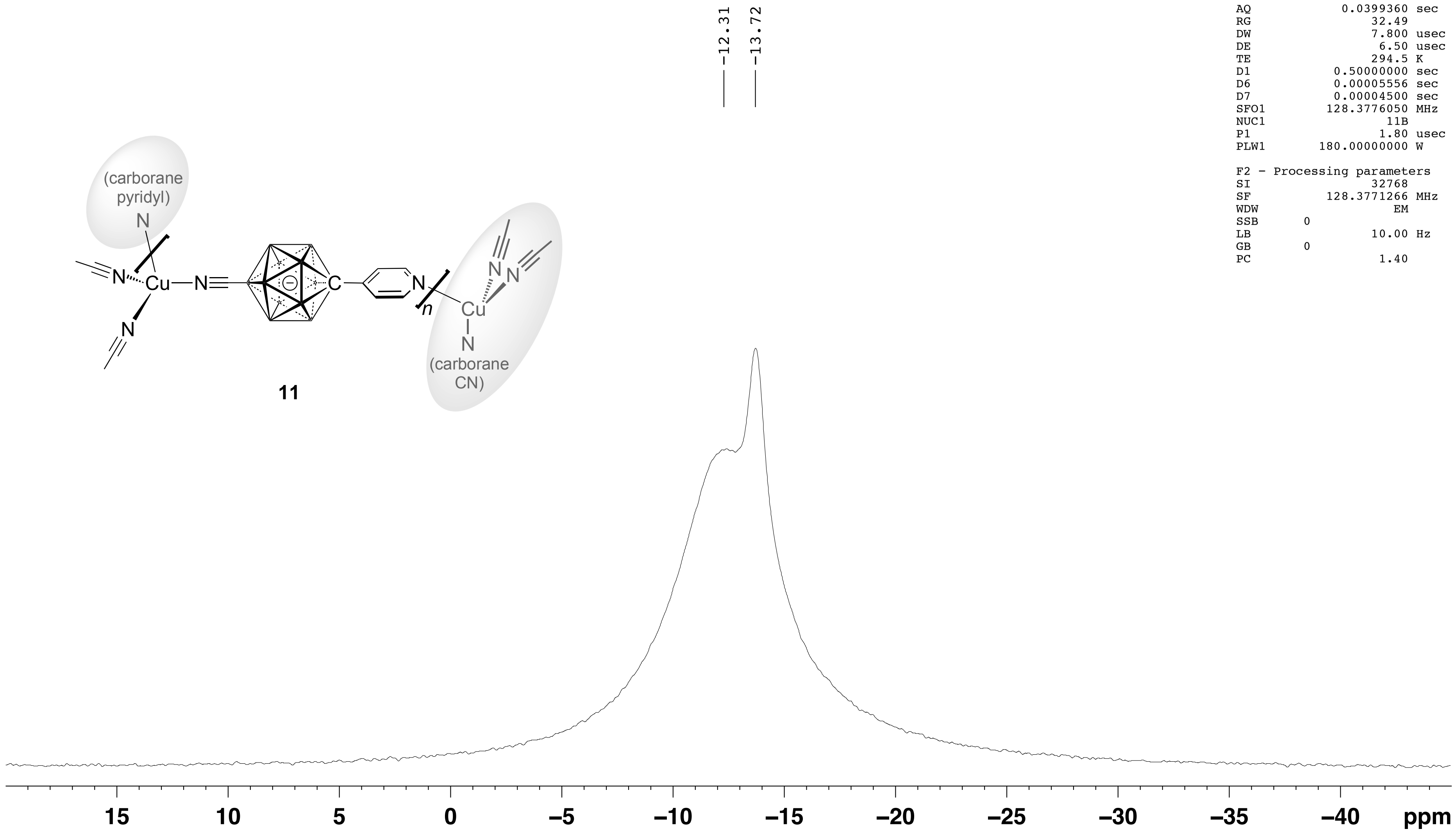
NMR32

11B 20171103
Sample: CU
Exp: 11B solidecho
Condition: 15 kHz MAS
Probe: 400 MHz 3.2 mm, Double Channel, HF filter, No Insert
Input:
D1 = 0.5 s, NS = 512
P1 = 1.8 us, P2 = 3.6 us, PLW1 = 180 w

```
Current Data Parameters
NAME     20171103_Cu_simon
EXPNO                 1122
PROCNO                   1

F2 - Acquisition Parameters
Date_             20171103
Time                 15.52 h
INSTRUM              spect
PROBHD   H13541_0005 (P
PULPROG          solidecho
TD                    5120
SOLVENT
NS                     512
DS                       0
SWH             64102.562 Hz
FIDRES          25.040064 Hz
AQ              0.0399360 sec
RG                   32.49
DW                   7.800 usec
DE                    6.50 usec
TE                   294.5 K
D1             0.50000000 sec
D6             0.00005556 sec
D7             0.00004500 sec
SFO1          128.3776050 MHz
NUC1                   11B
P1                    1.80 usec
PLW1         180.00000000 W

F2 - Processing parameters
SI                   32768
SF            128.3771266 MHz
WDW                     EM
SSB      0
LB                   10.00 Hz
GB       0
PC                    1.40
```



11

NMR33

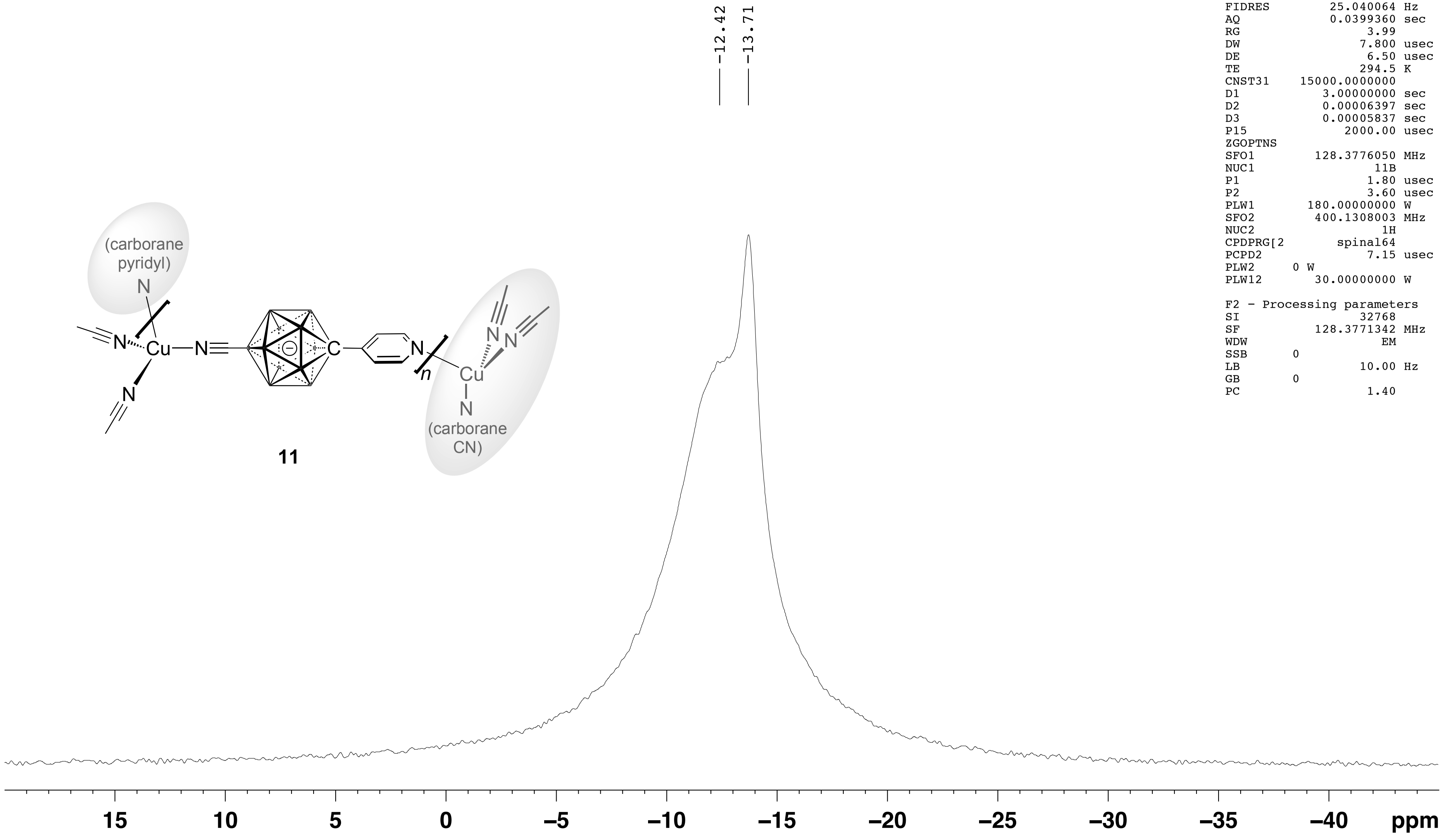
NMR34

11B{1H} 20171103
Sample: CU
Exp: 11B Hpdec_se
Condition: 18 kHz MAS
Probe: 400 MHz 3.2 mm, Double Channel, HF filter, No Insert
Input:
D1 = 0.5 s, NS = 32
P15 = 2000 us, p1 = 1.8 us, PLW1 = 180 w, PLW12 = 30, pcpd2 = 7.15

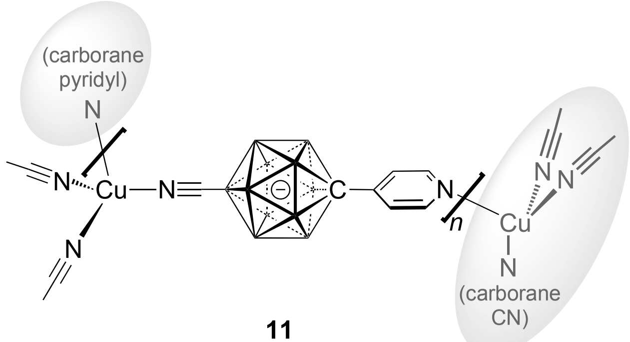
```
Current Data Parameters
NAME     20171103_Cu_simon
EXPNO                 1131
PROCNO                   1

F2 - Acquisition Parameters
Date_            20171103
Time                15.58 h
INSTRUM             spect
PROBHD    H13541_0005 (P
PULPROG         hpdec_se
TD                   5120
SOLVENT
NS                     32
DS                      0
SWH            64102.562 Hz
FIDRES         25.040064 Hz
AQ             0.0399360 sec
RG                   3.99
DW                  7.800 usec
DE                   6.50 usec
TE                  294.5 K
CNST31    15000.0000000
D1             3.00000000 sec
D2             0.00006397 sec
D3             0.00005837 sec
P15               2000.00 usec
ZGOPTNS
SFO1         128.3776050 MHz
NUC1                  11B
P1                   1.80 usec
P2                   3.60 usec
PLW1         180.00000000 W
SFO2         400.1308003 MHz
NUC2                   1H
CPDPRG[2         spinal64
PCPD2                7.15 usec
PLW2      0 W
PLW12         30.00000000 W

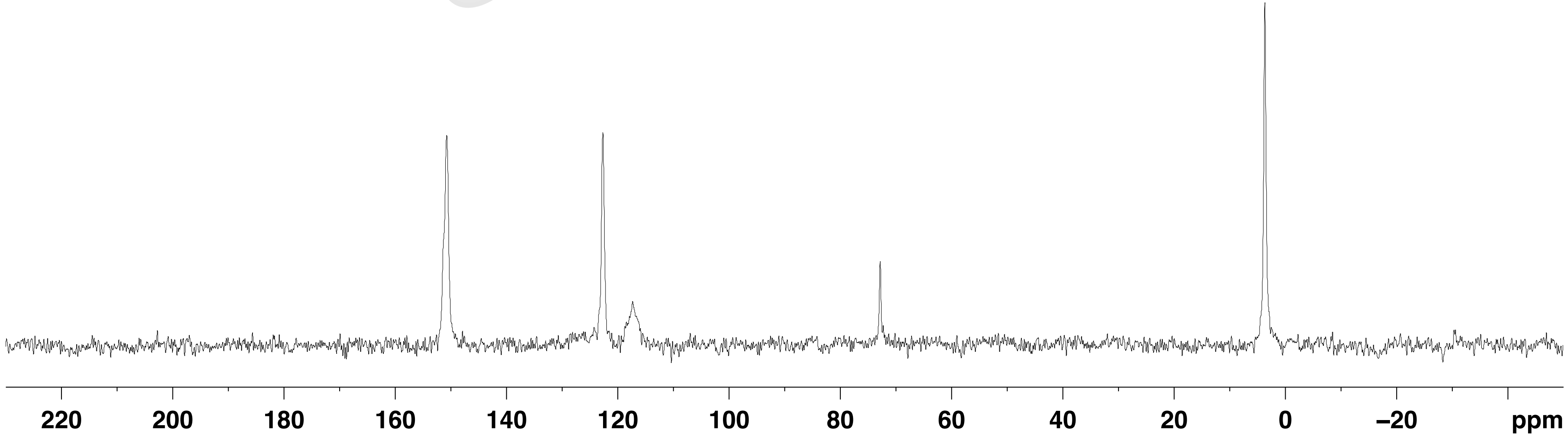
F2 - Processing parameters
SI                  32768
SF           128.3771342 MHz
WDW                    EM
SSB      0
LB                  10.00 Hz
GB       0
PC                   1.40
```



13C–1H 20171103
Sample: CU
Exp: 13C–1H CP
Condition: 15 kHz MAS
Probe: 400 MHz 3.2 mm, Double Channel, HF filter, No Insert
Input:
D1 = 5s, NS = 1024
P15 = 2000, P3 = 2.1 us, PCPD2 = 4.2, SPW0 = 40, PLW1 = 140 w, PLW12 = 80



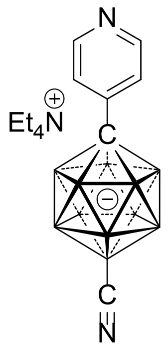
11



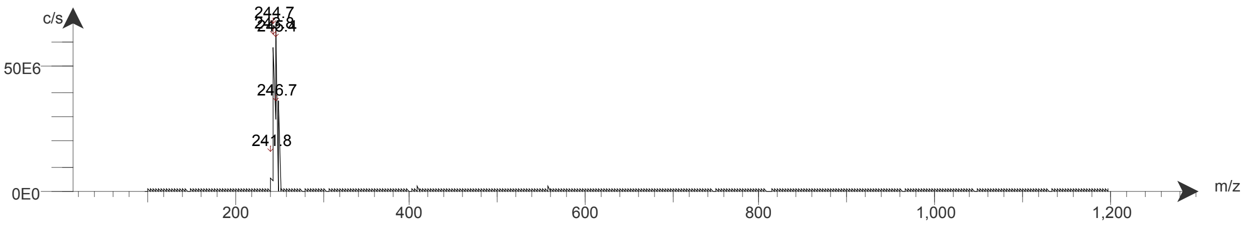
```
Current Data Parameters
NAME     20171103_Cu_simon
EXPNO                 1312
PROCNO                   1

F2 - Acquisition Parameters
Date_           20171103
Time               17.42 h
INSTRUM            spect
PROBHD   H13541_0005 (P
PULPROG               cp
TD                  4096
SOLVENT
NS                  1024
DS                     0
SWH            50000.000 Hz
FIDRES         24.414062 Hz
AQ             0.0409600 sec
RG                 32.49
DW                10.000 usec
DE                  6.50 usec
TE                 294.8 K
D1            5.00000000 sec
ZGOPTNS
SFO1         100.6228303 MHz
NUC1                 13C
P15              2000.00 usec
PLW1        140.00000000 W
SFO2         400.1308003 MHz
NUC2                  1H
CNST21         1.0000000
CPDPRG[2       spinal64
P3                  2.10 usec
PCPD2               4.50 usec
PLW2      0 W
PLW12        80.00000000 W
SPNAM[0]  ramp10050.100
SPOAL0             0.500
SPOFFS0   0 Hz
SPW0         40.00000000 W

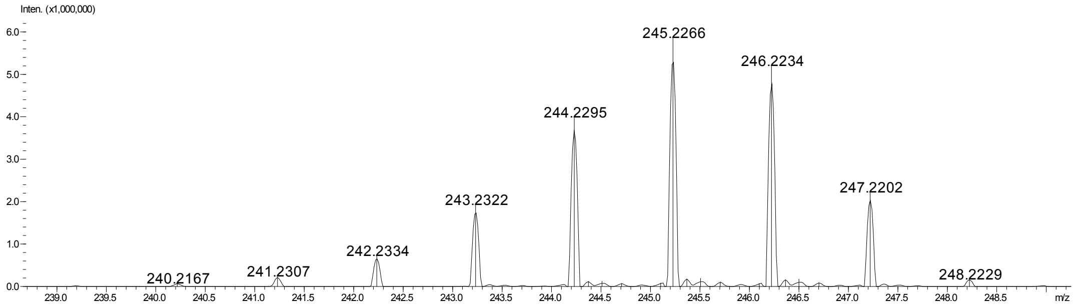
F2 - Processing parameters
SI                 32768
SF           100.6123733 MHz
WDW                   EM
SSB       0
LB                  8.00 Hz
GB        0
PC                  1.40
```



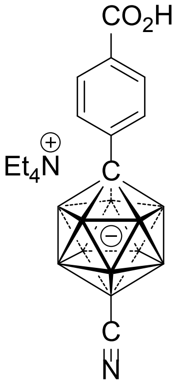
10a



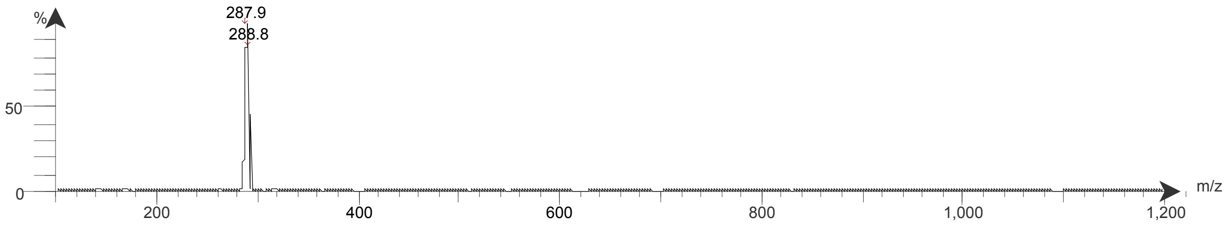
Low-resolution full-range ESI-MS negative mode



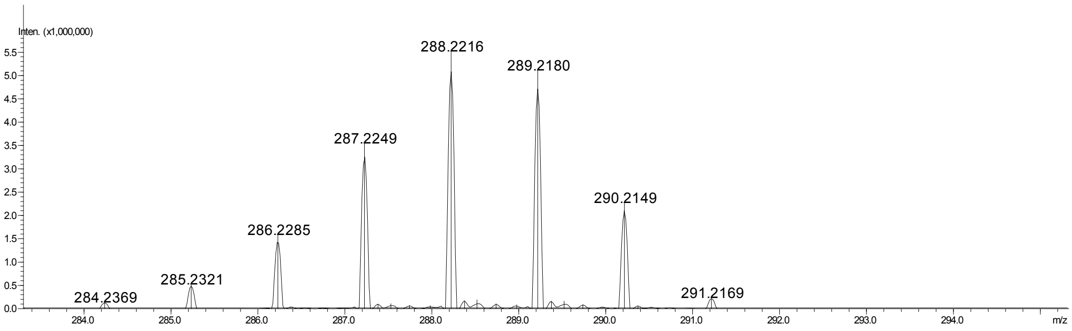
High-resolution ESI-MS negative mode



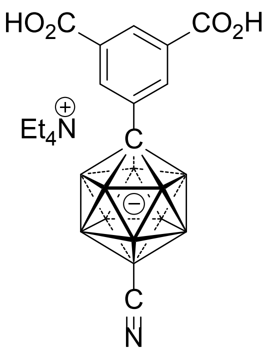
10b



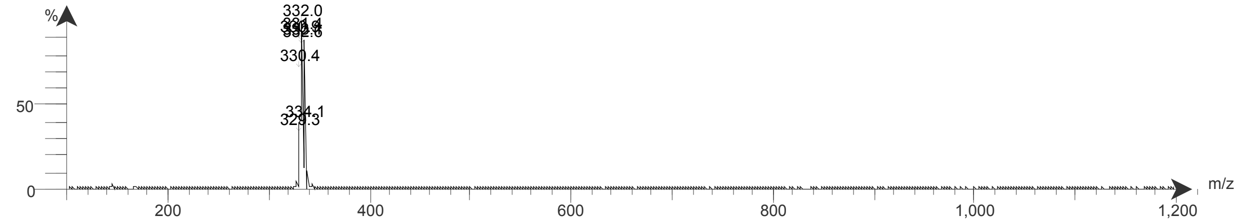
Low-resolution full-range ESI-MS negative mode



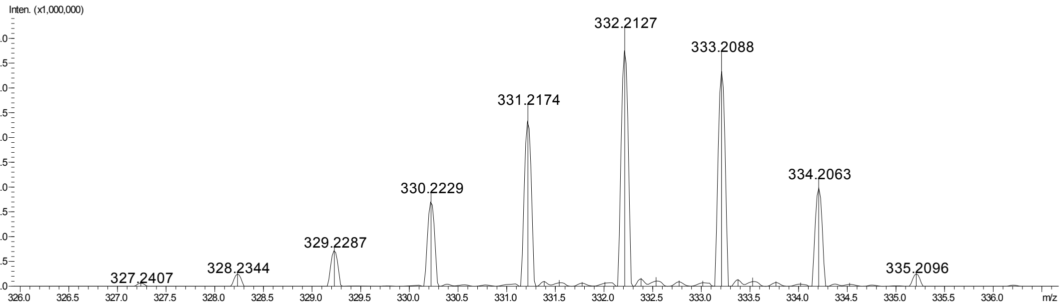
High-resolution ESI-MS negative mode



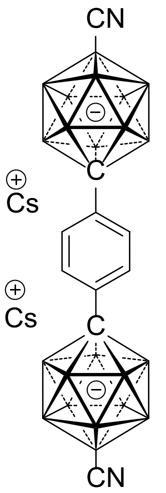
10c



Low-resolution full-range ESI-MS negative mode



High-resolution ESI-MS negative mode



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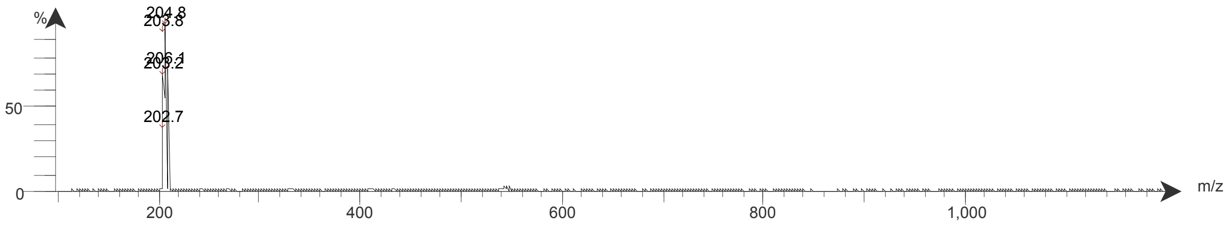
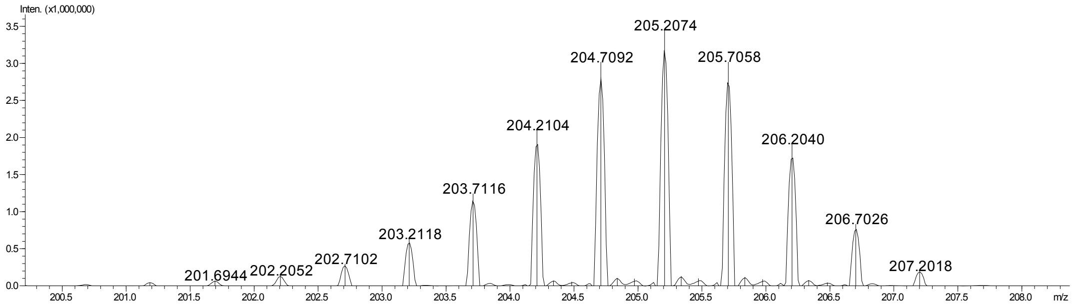
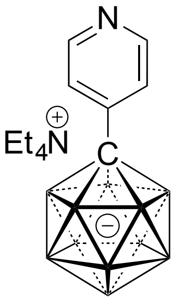


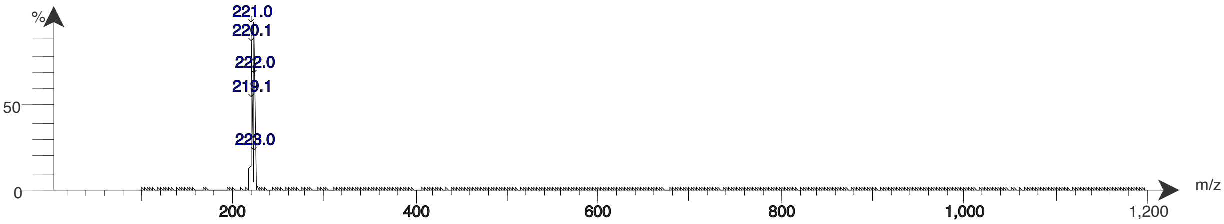
Low-resolution full-range ESI-MS negative mode



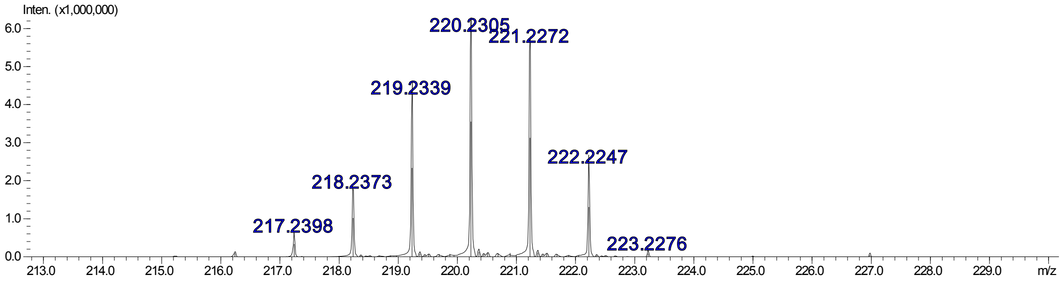
High-resolution ESI-MS negative mode



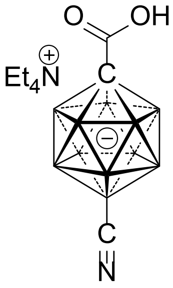
10e



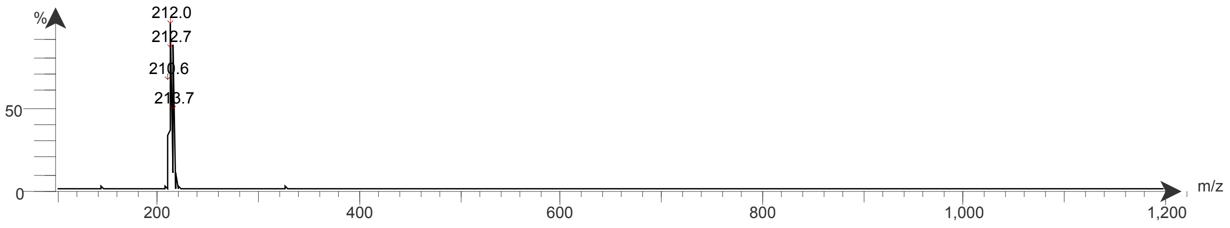
Low-resolution full-range ESI-MS negative mode



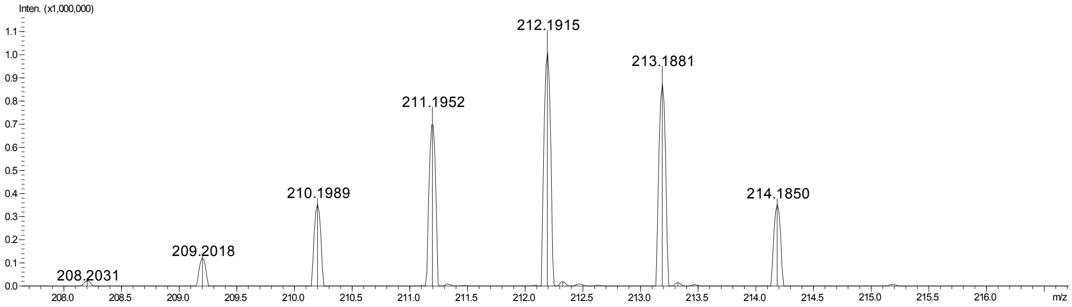
High-resolution ESI-MS negative mode



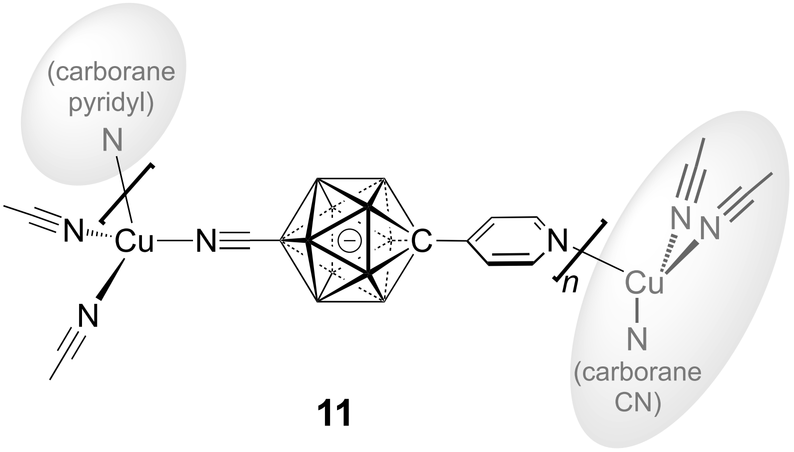
10f



Low-resolution full-range ESI-MS negative mode

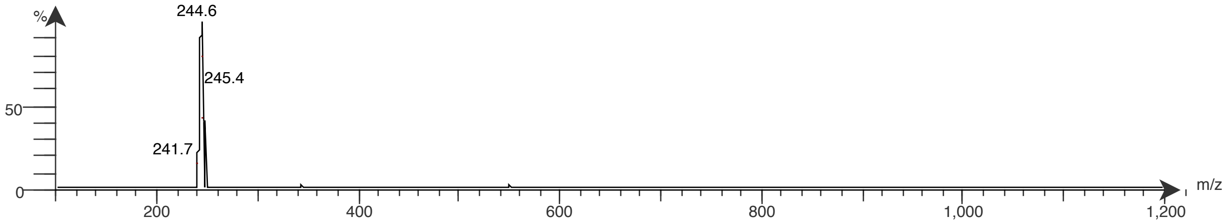


High-resolution ESI-MS negative mode



11

dissolved in MeCN, MS eluent = MeOH



Low-resolution full-range ESI-MS negative mode