

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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I General Information

Chemicals

If not otherwise specified, reagents and organic solvents were commercially available and used without further purification. Acetone-*d*₆, CD₃CN and DMSO-*d*₆ were purchased from Cambridge Isotope Laboratories and filtered through Al₂O₃ prior to use. [Me₃NH]⁺[CB₁₁H₁₂-12-CN]⁻ (starting material) was prepared according to the literature [1]. Anhydrous solvents were prepared by passage through activated Al₂O₃ and stored over 3 Å molecular sieves.

Reaction Conditions

Glassware for air-sensitive reactions 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 O₂, H₂O < 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, ¹³C NMR 125.77 MHz, ¹¹B NMR 160.46 MHz) or a Bruker AVANCE III 400 spectrometer (¹H NMR 400.13 MHz, ¹³C NMR 100.62 MHz, ¹¹B 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 CHD₂C(O)CD₃ = 2.05 ppm, residual CHD₂S(O)CD₃ = 2.50 ppm, residual CHD₂CN = 1.94 ppm, ¹³C{¹H}: CD₃C(O)CD₃ = 29.84 ppm, CD₃S(O)CD₃ = 39.52 ppm). ¹¹B and ¹¹B{¹H} NMR spectra were calibrated against external BF₃*Et₂O = 0 ppm (BF₃*Et₂O capillary in C₆D₆).

Solid-state NMR spectra were recorded on a Bruker 400WB AVANCE III spectrometer (^1H 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. ^1H and $^{13}\text{C}\{^1\text{H}\}$ chemical shifts were referenced to adamantane (H = 1.8 ppm, CH_2 = 38.5 ppm). ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were calibrated against external $\text{BF}_3\text{*Et}_2\text{O} = 0$ 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:

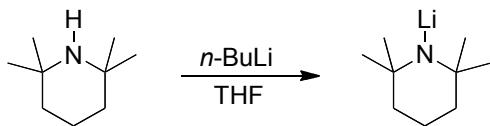
Compound **10a**: C/H/N (%) calculated: 48.00/9.13/11.19; found: 48.34/8.88/11.01.

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

II Experimental Section

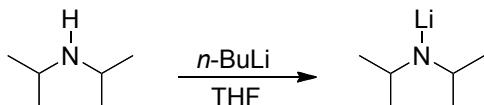
II. a) Amide base formation, lithiation and cupration

Lithium 2,2,6,6-tetramethylpiperidine (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 [NMe₃H][CB₁₁H₁₁-12-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 C₆D₆ 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 p*K*_a value of **6** to be \approx 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 $[\text{NMe}_3\text{H}][\text{CB}_{11}\text{H}_{11}-12-\text{CN}]$ (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 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 $\text{Pd}(\text{OAc})_2$ (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 $[\text{Et}_4\text{N}]^+ \text{Br}^-$ (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 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (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 H₂O, 5 mL) was added, and this aqueous solution was filtered using a pad of celite. To the clear and colorless filtrate, a solution of [Et₄N]⁺ 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{¹¹B} 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, CH₂ of cation), 1.97 (broad signal, 5H, BH), 1.78 (broad signal, 5H, BH), 1.15 (t, *J* = 7.3 Hz, CH₃ of cation).

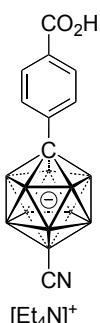
¹¹B NMR (128 MHz, DMSO-*d*₆, 23 °C): δ ca. -11.0 to -15.0 (overlapping signals).

¹¹B{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).

¹³C{¹H} NMR (125 MHz, DMSO-d6, 23 °C): δ 152.70, 145.81, 124.07 (three pyridyl signals), 70.61 (cage C), 51.37 (CH₂ of cation), 7.08 (CH₃ of cation). The B-C signal could not be detected.

High-resolution ESI-MS (negative mode, MeOH): *m/z* calcd for [C₇H₁₄B₁₁N₂]⁻: 245.2253. Found: 245.2266.

Product 10b



A dry 25 mL Schlenk flask equipped with a magnetic stir bar was charged with $[\text{NMe}_3\text{H}][\text{CB}_{11}\text{H}_{11}-12-\text{CN}]$ (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 $\text{Pd}(\text{OAc})_2$ (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 $[\text{Et}_4\text{N}]^+\text{Br}^-$ (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 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (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 $[\text{Et}_4\text{N}]^+\text{Br}^-$ (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).

$^1\text{H}\{^{11}\text{B}\}$ 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).

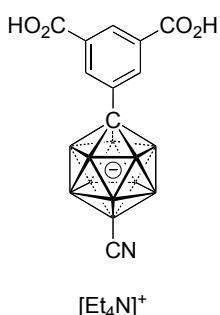
^{11}B NMR (160 MHz, Acetone- d_6 , 23 °C): δ ca.-11.3 to 14.5 (overlapping signals).

$^{11}\text{B}\{^1\text{H}\}$ 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).

$^{13}\text{C}\{^1\text{H}\}$ 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 $[\text{C}_9\text{H}_{15}\text{B}_{11}\text{NO}_2]^-$: 288.2199. Found: 288.2216.

Product 10c



A dry 25 mL Schlenk flask equipped with a magnetic stir bar was charged with [NMe₃H][CB₁₁H₁₁-12-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 [Et₄N]⁺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 CH₂Cl₂/CH₃CN (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 $[\text{Et}_4\text{N}]^+\text{Br}^-$ (400 mg, 1.9 mmol, 1.68 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 **10c** (338.8 mg, 65% yield).

$^1\text{H}\{^{11}\text{B}\}$ 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, CH₂ of cation), 2.01 (broad signal, 5H, BH), 1.80 (broad signal, 5H, BH), 1.16 (t, *J* = 7.3 Hz, 12H, CH₃ of cation).

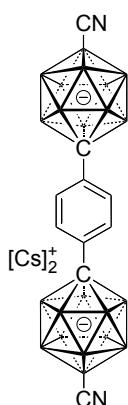
^{11}B NMR (160 MHz, DMSO-*d*₆, 23 °C): δ *ca.* -11.0 to 15.0 (overlapping signals).

$^{11}\text{B}\{^1\text{H}\}$ 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).

$^{13}\text{C}\{^1\text{H}\}$ 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 (CH₂ of cation), 7.08 (CH₃ of cation). The B-C signal could not be detected.

High-resolution ESI-MS (negative mode, MeOH): *m/z* calcd for [C₁₀H₁₅B₁₁NO₄]⁻: 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).

$^1\text{H}\{\text{B}\}$ 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).

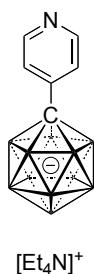
^{11}B NMR (160 MHz, DMSO-*d*₆, 23 °C): δ *ca.* -11.5 to 14.5 (overlapping signals).

$^{11}\text{B}\{\text{H}\}$ 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).

$^{13}\text{C}\{\text{H}\}$ 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 [C₁₀H₂₄B₂₂N₂]²⁻: 205.2066. Found: 205.2074.

Product 10e



A dry 100 mL Schlenk flask equipped with a magnetic stir bar was charged with $[\text{NMe}_3\text{H}][\text{CB}_{11}\text{H}_{12}]$ (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 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 $\text{Pd}(\text{OAc})_2$ (164.7 mg, 0.22 mmol, 0.09 equiv), tris(o-methoxyphenyl)phosphine (83.2 mg, 0.47 mmol, 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 $[\text{Et}_4\text{N}]^+\text{Br}^-$ (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 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (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 $[\text{Et}_4\text{N}]^+\text{Br}^-$ (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).

$^1\text{H}\{^{11}\text{B}\}$ 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).

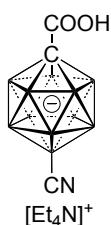
^{11}B NMR (128 MHz, Acetone- d_6 , 23 °C): δ -6.99 (d, J = 137 Hz, 1B, B-12), *ca.* -12.4 (overlapping d, J = *ca.* 130 Hz, 5B), *ca.* -13.4 (overlapping d, J = *ca.* 130 Hz, 5B).

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

$^{13}\text{C}\{^1\text{H}\}$ 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 $[\text{C}_7\text{H}_{14}\text{B}_{11}\text{N}_2]^-$: 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 [NMe₃H][CB₁₁H₁₁-12-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 CO₂ 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 [Et₄N]⁺ Br⁻ (400 mg, 1.9 mmol, 2.68 equiv) in water (4 mL) was added, the resulting white solid 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{¹¹B} NMR (400 MHz, DMSO-*d*₆, 23 °C): δ 12.70 (broad s, 1H, COOH), 3.20 (q, *J* = 7.3 Hz, 8H, CH₂ of cation), 1.87 (broad, 5H, BH), 1.65 (broad signal, 5H, BH), 1.15 (t, *J* = 7.3 Hz, 12H, CH₃ of cation).

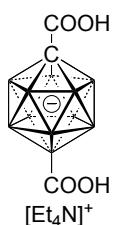
¹¹B NMR (128 MHz, DMSO-*d*₆, 23 °C): δ ca. -11.5 to -16.5 (overlapping signals).

¹¹B{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).

¹³C{¹H} NMR (101 MHz, DMSO-*d*₆, 23 °C): δ 166.63 (C-COOH), 69.40 (cage C), 51.38 (CH₂ of cation), 7.08 (CH₃ of cation). The B-C signal could not be detected.

High-resolution ESI-MS (negative mode, MeOH): m/z calcd for $[\text{C}_3\text{H}_{11}\text{B}_{11}\text{NO}_2]^-$: 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 H₂O, 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 $CHD_2C(O)CD_3$ 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, CH₂ 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, CH₃ 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).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, Acetone- d_6 , 23 °C): δ 168.31 (C-COOH), 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 $[\text{C}_3\text{H}_{12}\text{B}_{11}\text{O}_4]^-$: 231.1832. Found: 231.1846.

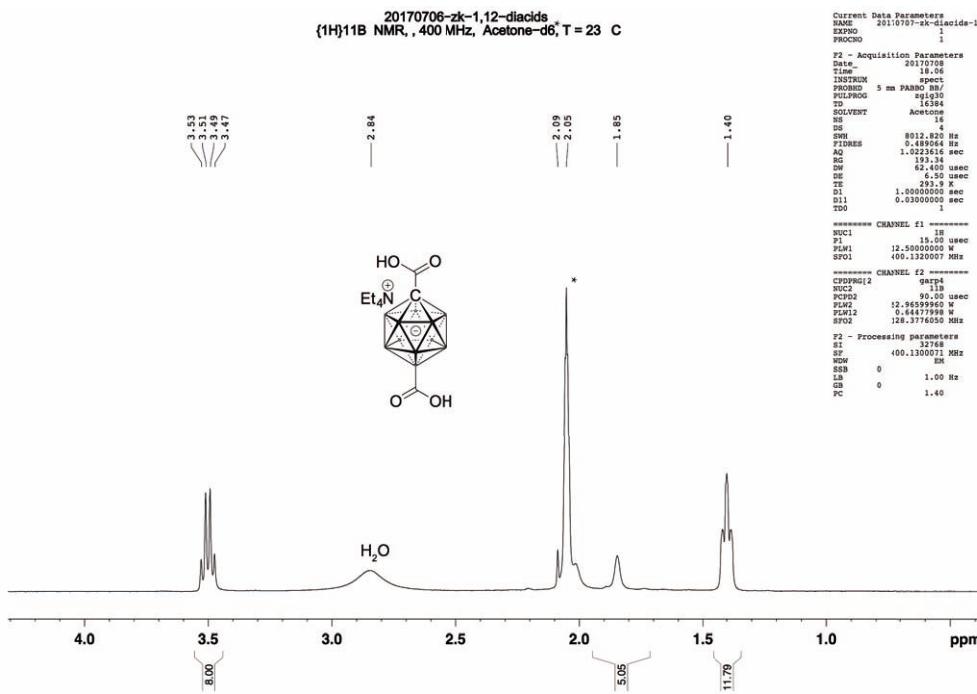


Figure S1. $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **10g** (400 MHz, 25 °C, Acetone-*d*₆). Cation signals appear at 3.50 and 1.40 ppm; B–H signals are seen at 2.02 (overlapping with solvent residual peak) and 1.85 ppm.

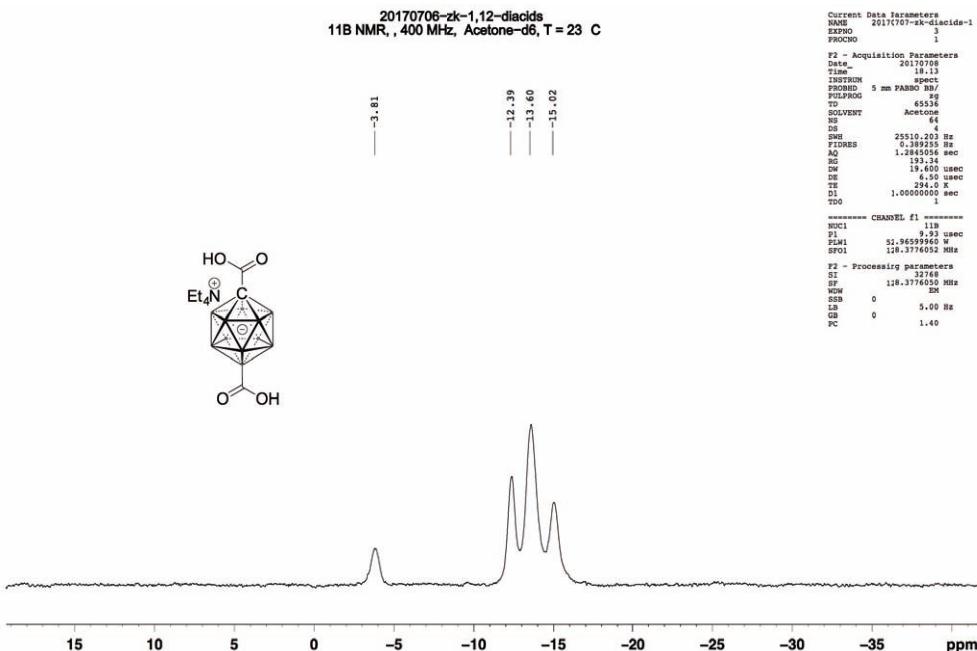


Figure S2. ^{11}B NMR spectrum of **10g** (128 MHz, 25 °C, Acetone-*d*₆).

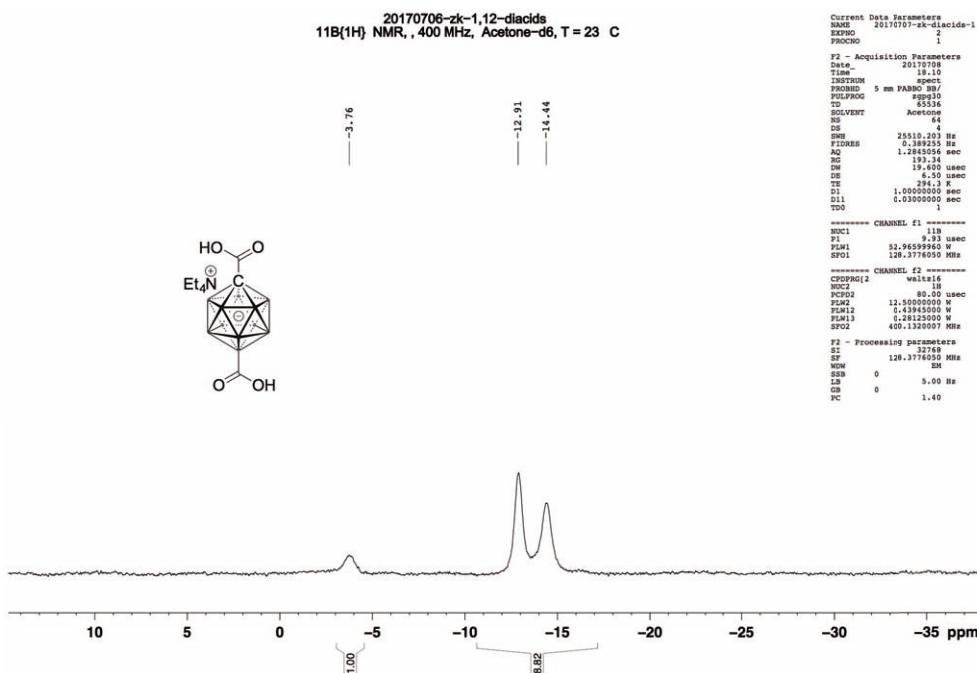


Figure S3. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **10g** (128 MHz, 25 °C, Acetone- d_6).

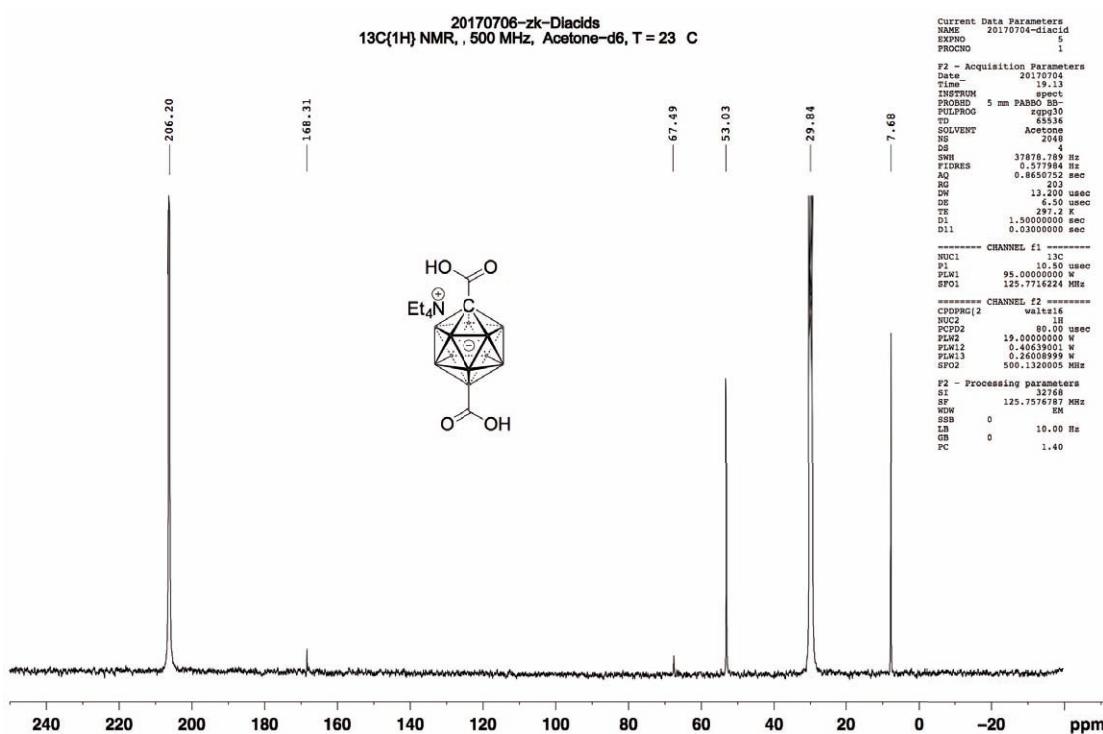
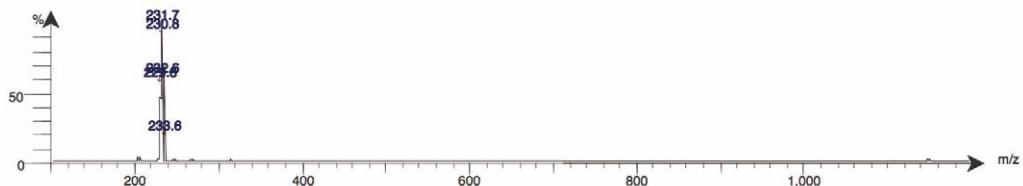
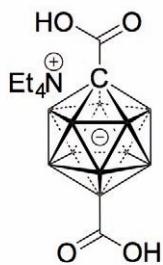
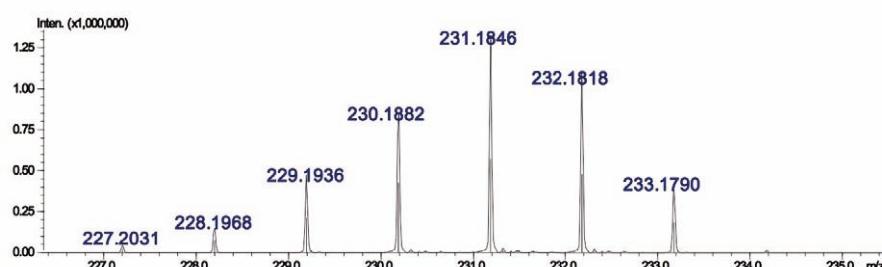


Figure S4. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of **10g** (125 MHz, 25 °C, Acetone- d_6). Cation signals appear at 53.03 ppm and 7.68 ppm; C-CO₂H and the cage carbon atom are seen at 168.31 ppm and 67.49 ppm. The B(12)-CO₂H signal could not be detected.



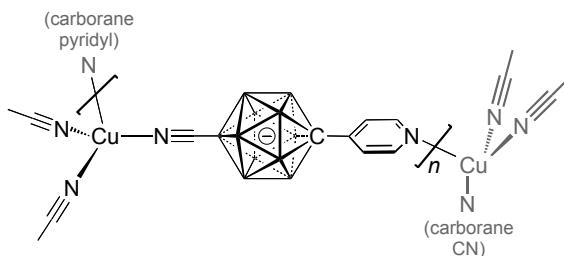
Low-resolution full-range ESI-MS negative mode



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 $[(\text{MeCN})_2\text{Cu}-1\text{-pyridyl-CB}_{11}\text{H}_{10}-12\text{-CN}]_n$, 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 CD₃CN gave a solubility high enough for $^1\text{H}\{^{11}\text{B}\}$, ^{11}B NMR and $^{11}\text{B}\{^1\text{H}\}$ measurements (ca. 1.5 mg/mL). This concentration was not sufficient to obtain $^{13}\text{C}\{^1\text{H}\}$ data. Upon dissolution, **11** probably breaks up into monomers, *i.e.* $[\text{Cu}(\text{solv})_n][\text{10a}]$.

$^1\text{H}\{^{11}\text{B}\}$ NMR (500 MHz, CD₃CN, 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, CH₃CN), 1.82 (broad signal, 5H, BH).

^{11}B NMR (160 MHz, CD₃CN, 23 °C): δ *ca.* -11.3 to -14.8 (overlapping signals).

$^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CD₃CN, 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)-CB₁₁H₁₀-12-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:

^1H 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, CH₃CN 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).

$^{11}\text{B}\{^1\text{H}\}$ 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).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 25 °C): δ 150.77 (two overlapping pyridyl signals), 122.64 (pyridyl signal), 117.22 (CH₃CN), 72.76 (cage C), 3.61 (CH₃CN). The B-C signal could not be detected.

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

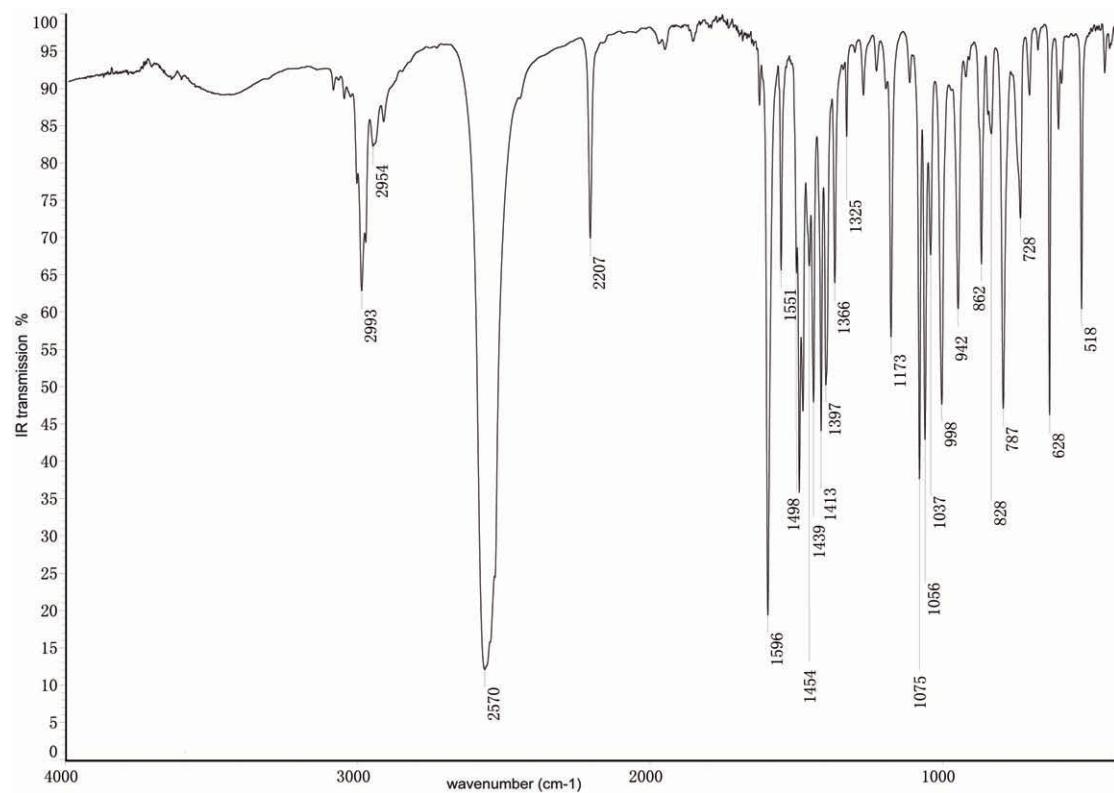


Figure S6. IR spectrum of **10a** (KBr pellet).

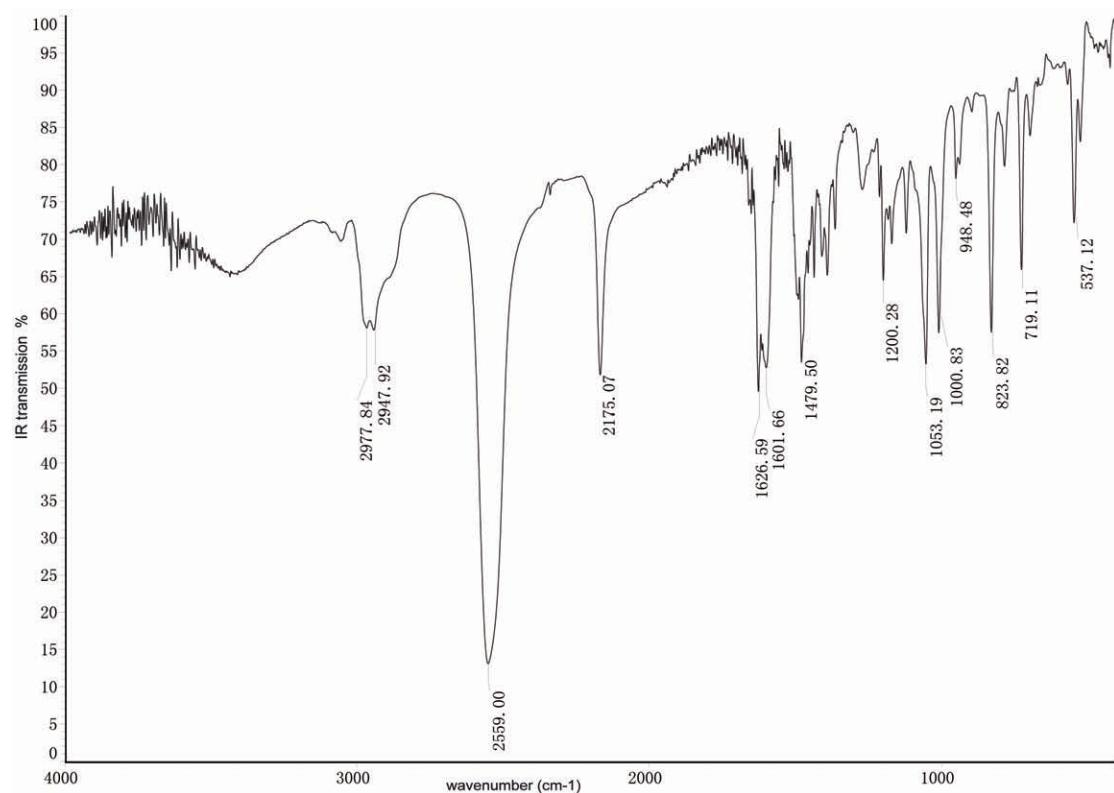


Figure S7. IR spectrum of **11** (KBr pellet).

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 ₂ NO ₆	C ₁₁ H ₂₃ B ₁₁ N ₂ O	C ₁₀ H ₆₄ B ₂₂ N ₄	C ₂₀ H ₃₁ B ₂₂ N ₃	C ₁₁ H ₃₁ B ₁₁ N ₂ O 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
R1	0.0844	266/67	0.0647	0.0845	0.1201	0.0540	0.0460
wR2	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 $[Li(THF)_3]_2[CB_{11}H_{10-12}-CN]$ suitable for X-ray diffraction within 3 d at 25 °C.

Bond precision:	C-C = 0.0079 Å	Wavelength=0.71073	
Cell:	a=10.4350(11)	b=10.8304(13)	c=18.597(2)
	alpha=87.873(9)	beta=74.958(10)	gamma=64.502(12)
Temperature:	170 K		
	Calculated	Reported	
Volume	1825.3(4)	1825.3(4)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C ₂₆ H ₅₈ B ₁₁ Li ₂ N ₀₆	C ₂₆ H ₅₈ B ₁₁ Li ₂ N ₀₆	
Sum formula	C ₂₆ H ₅₈ B ₁₁ Li ₂ N ₀₆	C ₂₆ H ₅₈ B ₁₁ Li ₂ N ₀₆	
Mr	613.52	613.52	
D _x , g cm ⁻³	1.116	1.116	
Z	2	2	
μ (mm ⁻¹)	0.069	0.069	
F ₀₀₀	660.0	660.0	
F _{000'}	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		
Correction method= # Reported T Limits: Tmin=0.906 Tmax=1.000			
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		

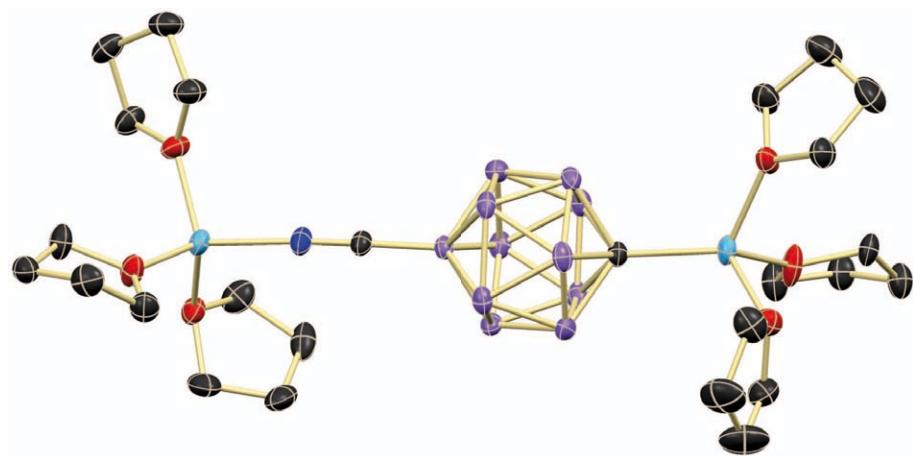


Figure S8. ORTEP representation of **7**. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

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-C₅N(H)H₄-CB₁₁H₁₀-12-CN]•THF suitable for X-ray diffraction within 14 d at 25 °C.

Bond precision: C-C = 0.0040 Å 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	C ₇ H ₁₅ B ₁₁ N ₂ , C ₄ H ₈ O	C ₇ H ₁₅ B ₁₁ N ₂ , C ₄ H ₈ O
Sum formula	C ₁₁ H ₂₃ B ₁₁ N ₂ O	C ₁₁ H ₂₃ B ₁₁ N ₂ 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

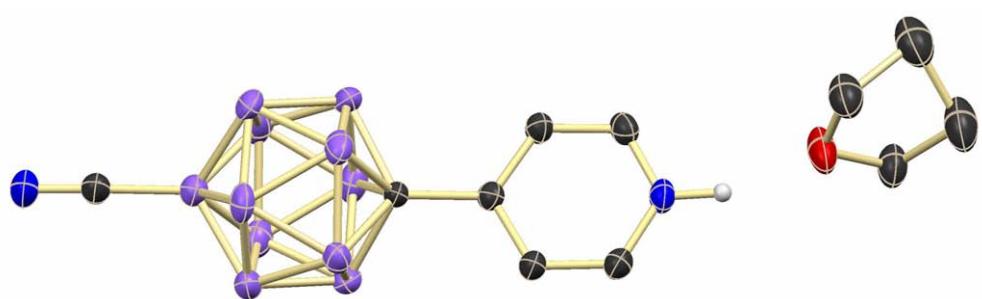


Figure S9. ORTEP representation of internally protonated **10a**·THF. Hydrogen atoms except for N–H are omitted for clarity; 25% displacement ellipsoids.

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 [Et₄N]₂[12-CN-B₁₁H₁₀-C₆H₄-CB₁₁H₁₀-12-CN] suitable for X-ray diffraction within 6 d at 25 °C.

The [12-CN-B₁₁H₁₀-C₆H₄-CB₁₁H₁₀-12-CN]²⁻ anion lies about an inversion center, with the [Et₄N]⁺ cation in a general position.

Bond precision: C-C = 0.0036 Å 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	C ₁₀ H ₂₄ B ₂₂ N ₂ , 2(C ₈ H ₂₀ N)	C ₁₀ H ₂₄ B ₂₂ N ₂ , 2(C ₈ H ₂₀ N)
Sum formula	C ₂₆ H ₆₄ B ₂₂ N ₄	C ₂₆ H ₆₄ B ₂₂ N ₄
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

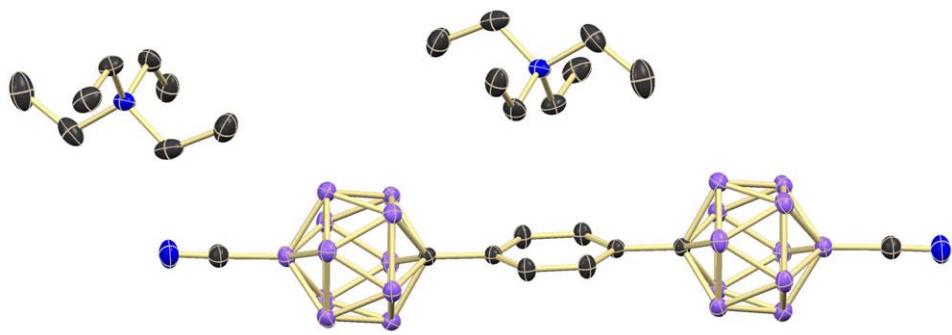


Figure S10. ORTEP representation of **10d**. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

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 $[\text{Et}_4\text{N}][(\text{1-C}_5\text{NH}_4\text{-CB}_{11}\text{H}_{11})_2\text{H}]$ 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 $[\text{Et}_4\text{N}]^+$ cation lies on an inversion center.

Bond precision:	$\text{C-C} = 0.0046 \text{ \AA}$	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		

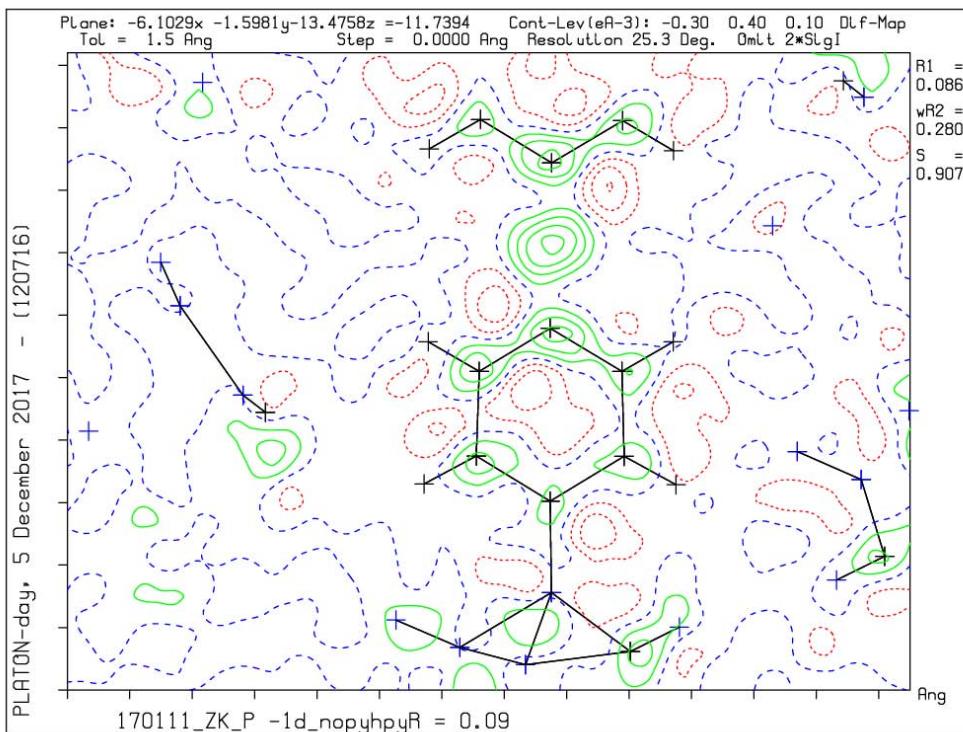


Figure S11. Difference density map of a model without any proton between the two nitrogen atoms of the pyridine rings showing the residual electron density of the proton inbetween the two pyridine rings.



Figure S12. ORTEP representation of **10e** with bridging proton between two pyridylcarborane anions; the disordered $[\text{Et}_4\text{N}]^+$ 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 [Et₄N][1-COOH-CB₁₁H₁₀-12-CN] suitable for X-ray diffraction within 14 d at 25 °C.

Structure **10f** showed an R value of 12.01%. This is primarily attributed to the floppiness of the ethyl substituents of [Et₄N]⁺, and in particular the CH₃ 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 Å	Wavelength=0.71073	
Cell:	a=7.444(4) alpha=91.55(5)	b=7.573(5) beta=106.37(5)	c=9.562(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	C ₃ H ₁₁ B ₁₁ N O ₂ , C ₈ H ₂₀ N	C ₈ H ₂₀ N, C ₃ H ₁₁ B ₁₁ N O ₂	
Sum formula	C ₁₁ H ₃₁ B ₁₁ N ₂ O ₂	C ₁₁ H ₃₁ B ₁₁ N ₂ O ₂	
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		

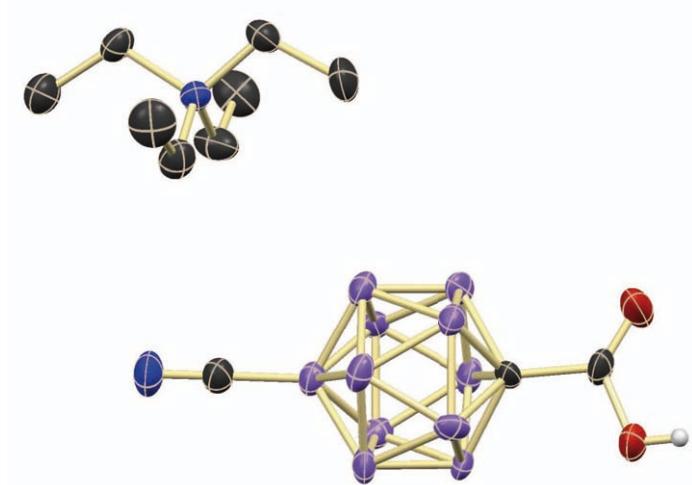


Figure S13. ORTEP representation of **10f**. Hydrogen atoms except for O–H are omitted for clarity; 25% displacement ellipsoids.

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 [Et₄N]⁺ [1-COOH-CB₁₁H₁₀-12-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 [Et₄N]⁺ counterion. Similar indistinguishability of C(cage) and B positions has been observed with other carboranes.[4]

Bond precision:	B-B = 0.0034 Å	Wavelength=0.71073	
Cell:	a=12.3385(9) alpha=90	b=12.3385(9) beta=90	c=13.745(2) 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	C ₃ H ₁₂ B ₁₁ O ₄ , C ₈ H ₂₀ N	C ₃ H ₁₂ B ₁₁ O ₄ , C ₈ H ₂₀ N	
Sum formula	C ₁₁ H ₃₂ B ₁₁ N O ₄	C ₁₁ H ₃₂ B ₁₁ N O ₄	
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	

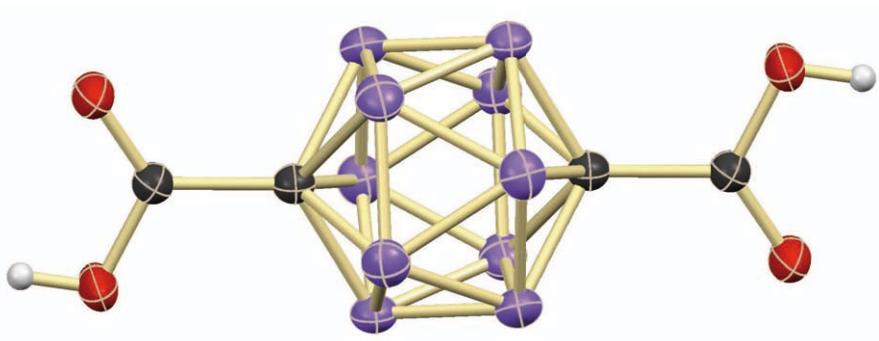


Figure S14. ORTEP representation of **10g**; the disordered $[\text{Et}_4\text{N}]^+$ cation is not shown. Hydrogen atoms except for O–H are omitted for clarity; 25% displacement ellipsoids.

Product 11 (CCDC1559908)

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

Bond precision: C-C = 0.0043 Å 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

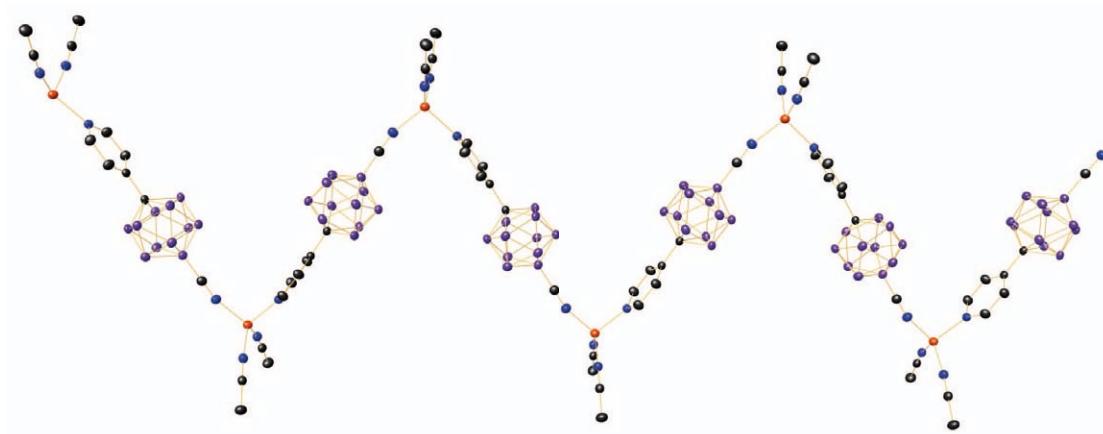


Figure S15. ORTEP representation of **11**, showing one chain from the side. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

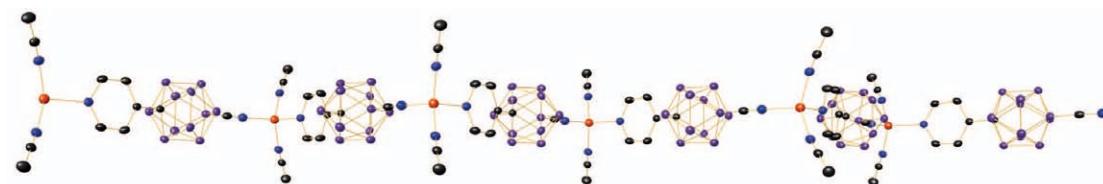


Figure S16. ORTEP representation of **11**, showing one chain from the top. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

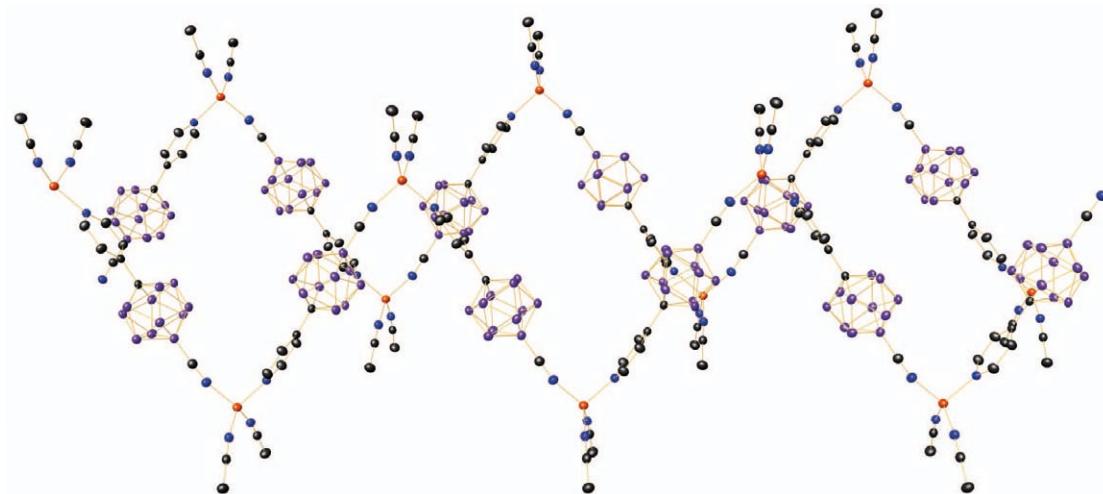


Figure S17. ORTEP representation of **11**, showing two chain from the side. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

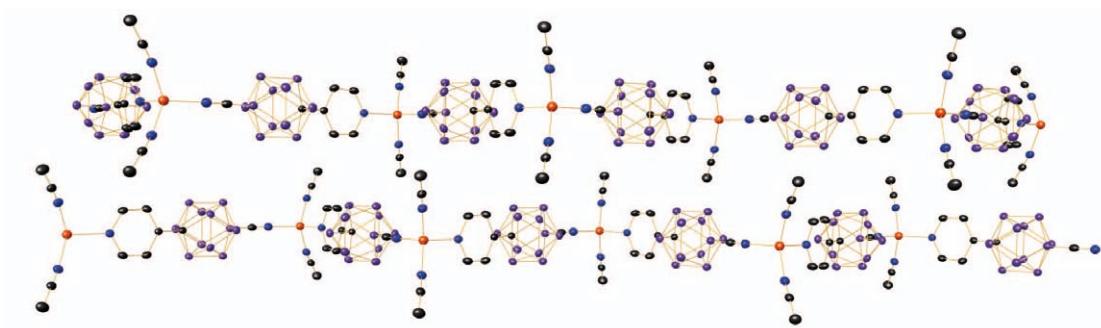


Figure S18. ORTEP representation of **11**, showing two chains from the top. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

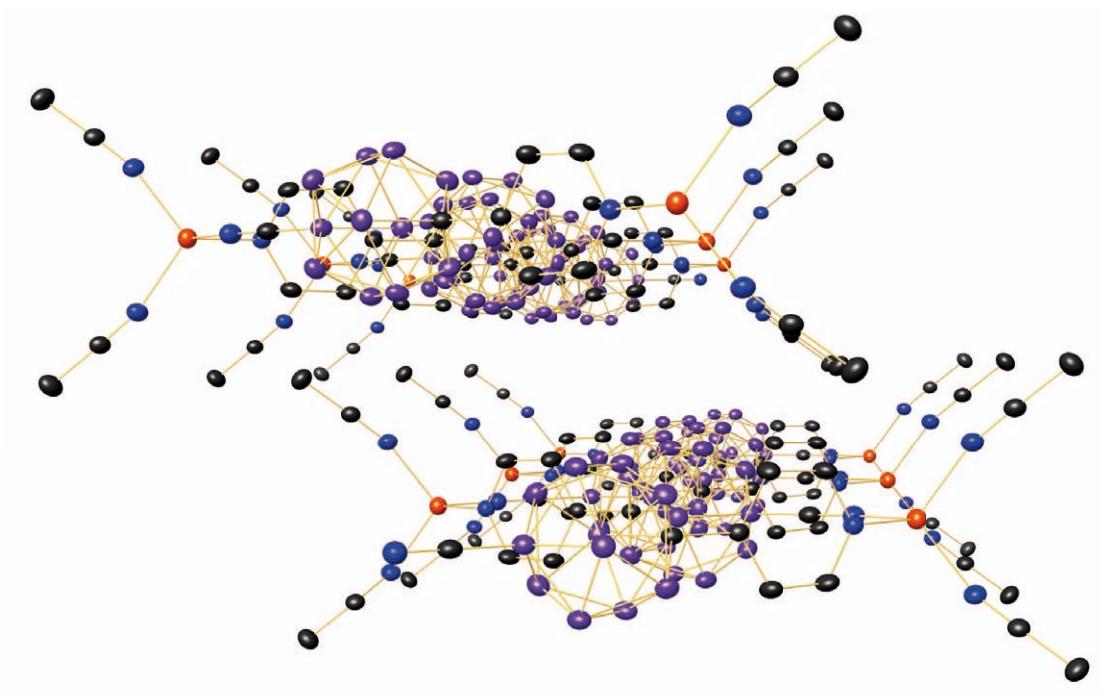


Figure S19. ORTEP representation of **11**, showing the intercalation of two chains forming a channel-like arrangement. Hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

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^{*}

Current Data Parameters
NAME 20170105-zk-12-CN-1-p-DMSC
EXPO 3
PROCNO 1

```

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Date : 20170106
Time : 13:12
INSTRUM: spect
PROBID: 5 mm PABO/Bf
PULPROG: zg3r30
TD: 16384
SOLVENT: DMSO
NS: 16
SWH: 8012.820 Hz
FIDRES: 0.483064 Hz
AQ: 1.022616 sec
RG: 107.6
DW: 62.400 usec
DE: 6.50 usec
TE: 25.1 K
D1: 1.000000 sec
D11: 0.0300000 sec
TDO: 1

```

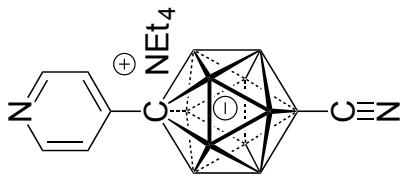
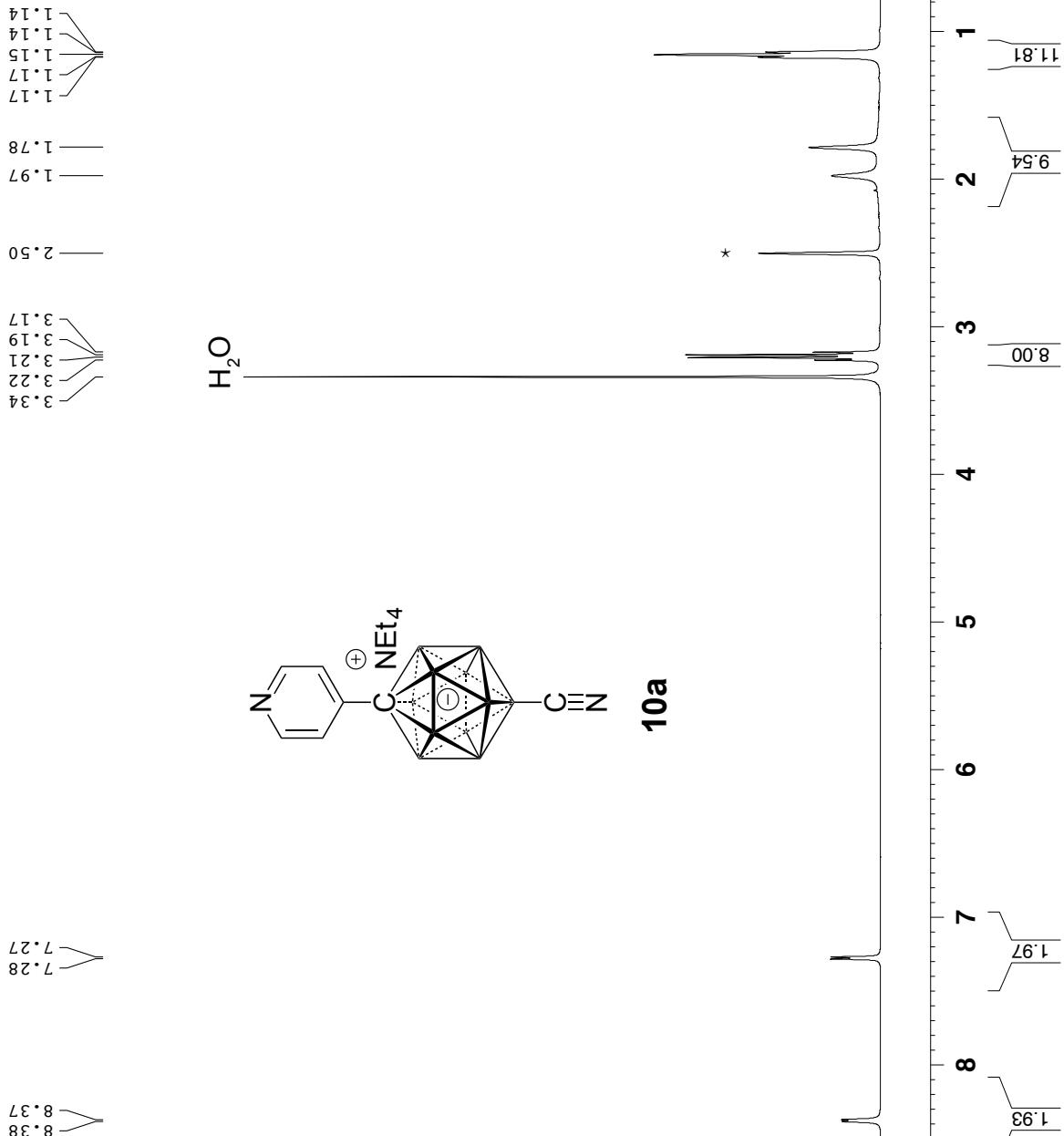
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P1           15.00 usec
PLW1        12.50000000 MHz
SFO1        400.13200000 MHz

===== CHANNEL f2 =====
CPDPRG[2      garp4
NUC2          1.1B
PCPDG[2      90.00 usec
PLW2        52.9599996 W
PLW12       0.64477998 W
SFO2        128.3776050 MHz

F2 - Processing Parameters
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SF           400.1300035 MHZ
WDW          EM
SSB          0
LB           1.00 Hz
GB           0
PC           1.40

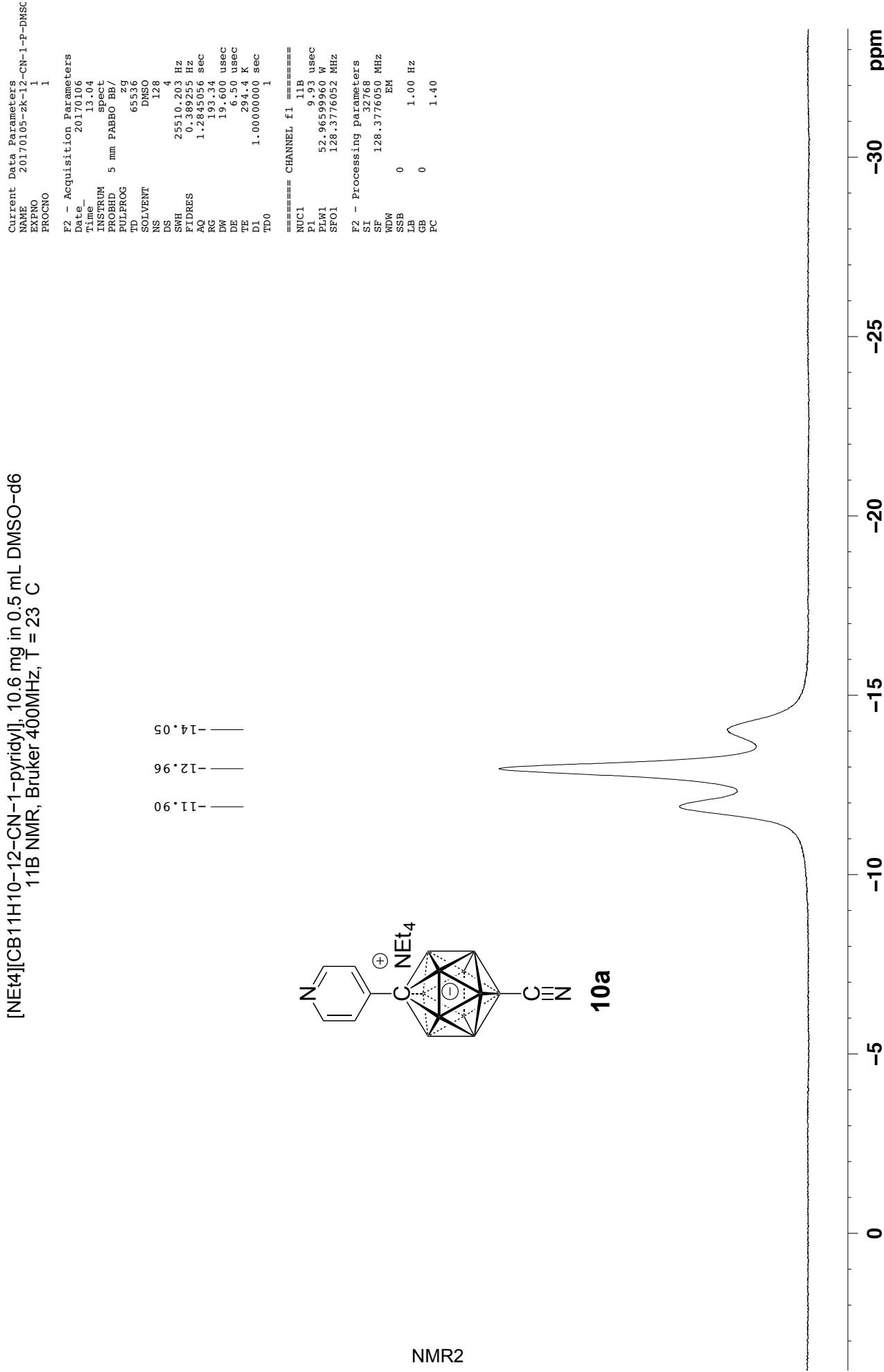
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10a

NMR1

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



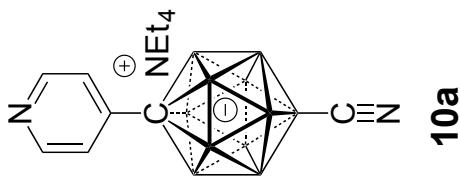
[NEt₄][CB11H₁₀₋₁₂-CN-1-pyridyl], 10.6 mg in 0.5 mL DMSO-d₆
 11B{¹H} NMR, Bruker 400MHz, T = 23 °C

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 PROCN0 1

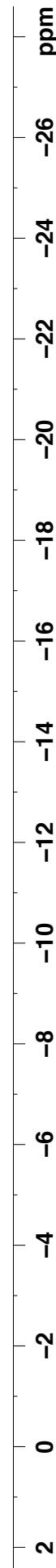
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 TD 65536
 SOLVENT DMSO
 NS 128
 DS 25510.203 Hz
 FIDRES 0.38955 Hz
 AQ 1.2845056 sec
 RG 193.34
 DW 19.600 usec
 DE 6.50 usec
 TE 295.4 K
 D1 1.0000000 sec
 D11 0.0300000 sec
 TDO 1

===== CHANNEL f1 ======
 NUC1 11B
 P1 9.93 usec
 PLW1 52.9659960 W
 SF01 128.3776050 MHz
 ===== CHANNEL f2 ======
 CPDPRG[2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PLW2 12.5000000 W
 PLW1.2 0.43945000 W
 PLW1.3 0.28125000 W
 SF02 400.1120007 MHz
 ===== Processing parameters ======
 SI 32768
 SF 128.3776050 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

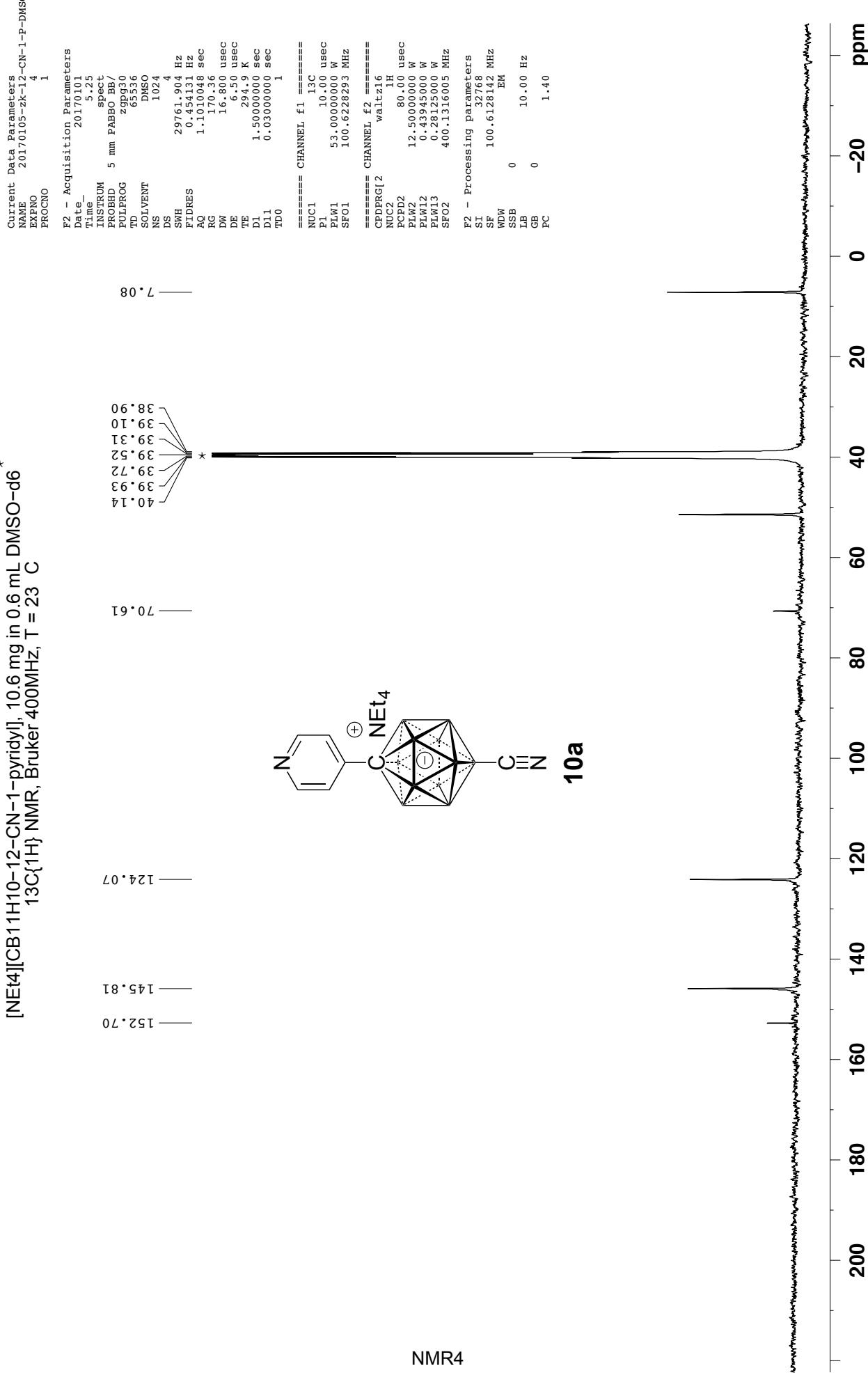
-12.55
 -13.41



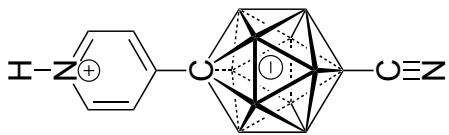
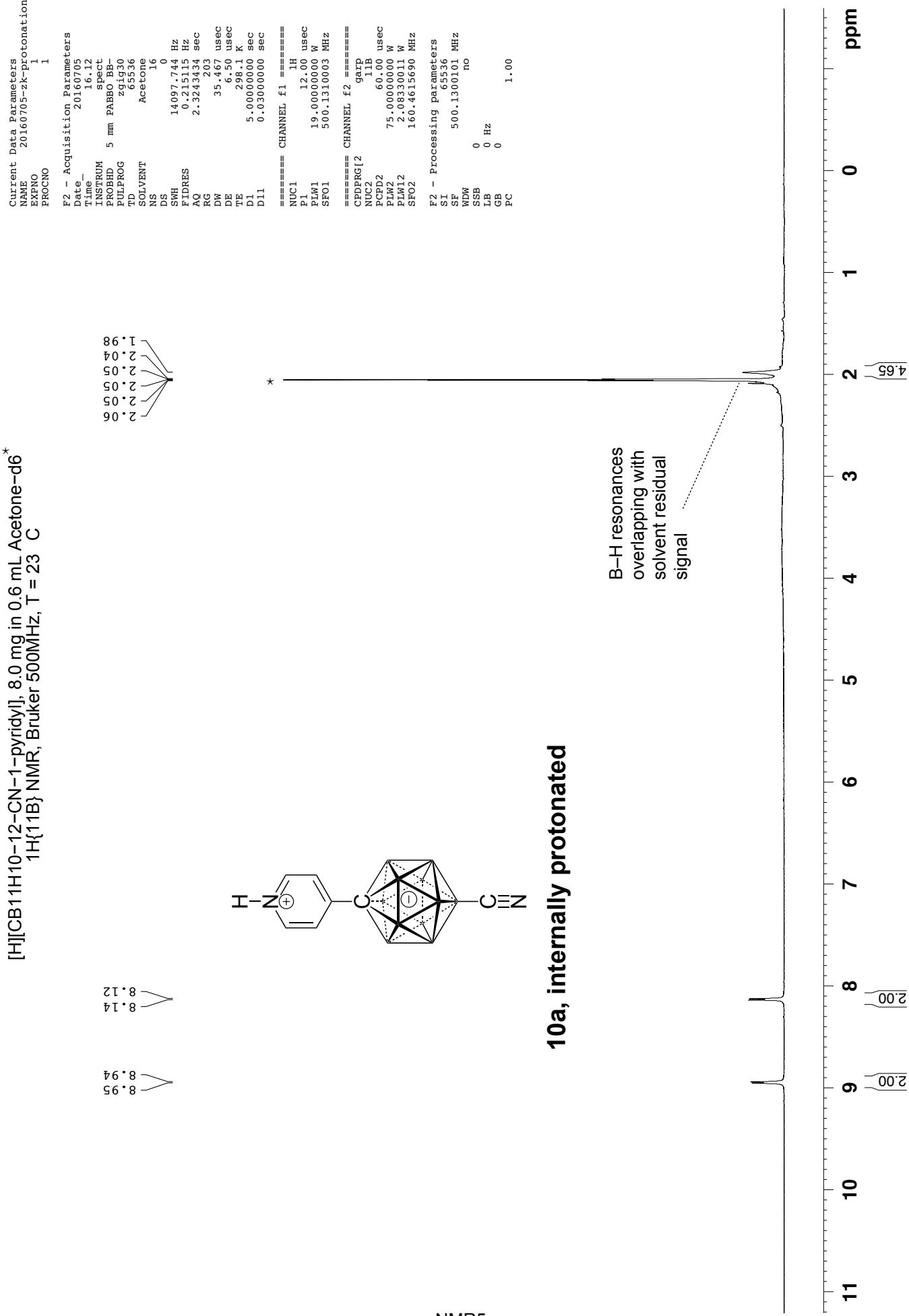
NMR3



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



[H][CB11H10-12-CN-1-pyridyl], 8.0 mg in 0.6 mL Acetone-d₆^{*}



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

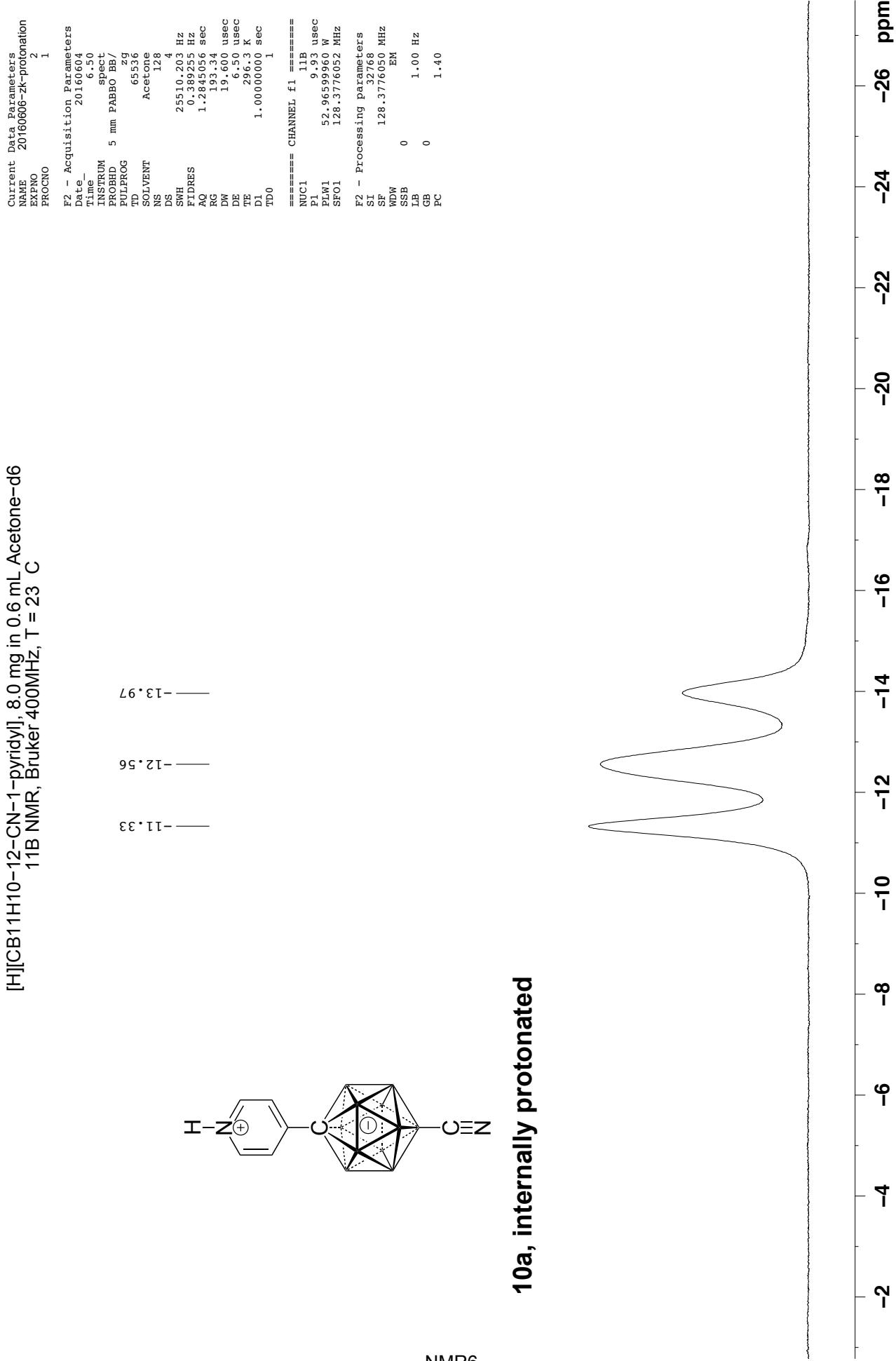
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SOLVENT   Acetone
NS        128
DS        4
SWH      25510.203 Hz
FIDRES  0.389255 Hz
AQ       1.284056 sec
RG       193.34
DW       19.600 usec
DE       6.50 usec
TE       296.3 K
D1      1.0000000 sec
TD0      1

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

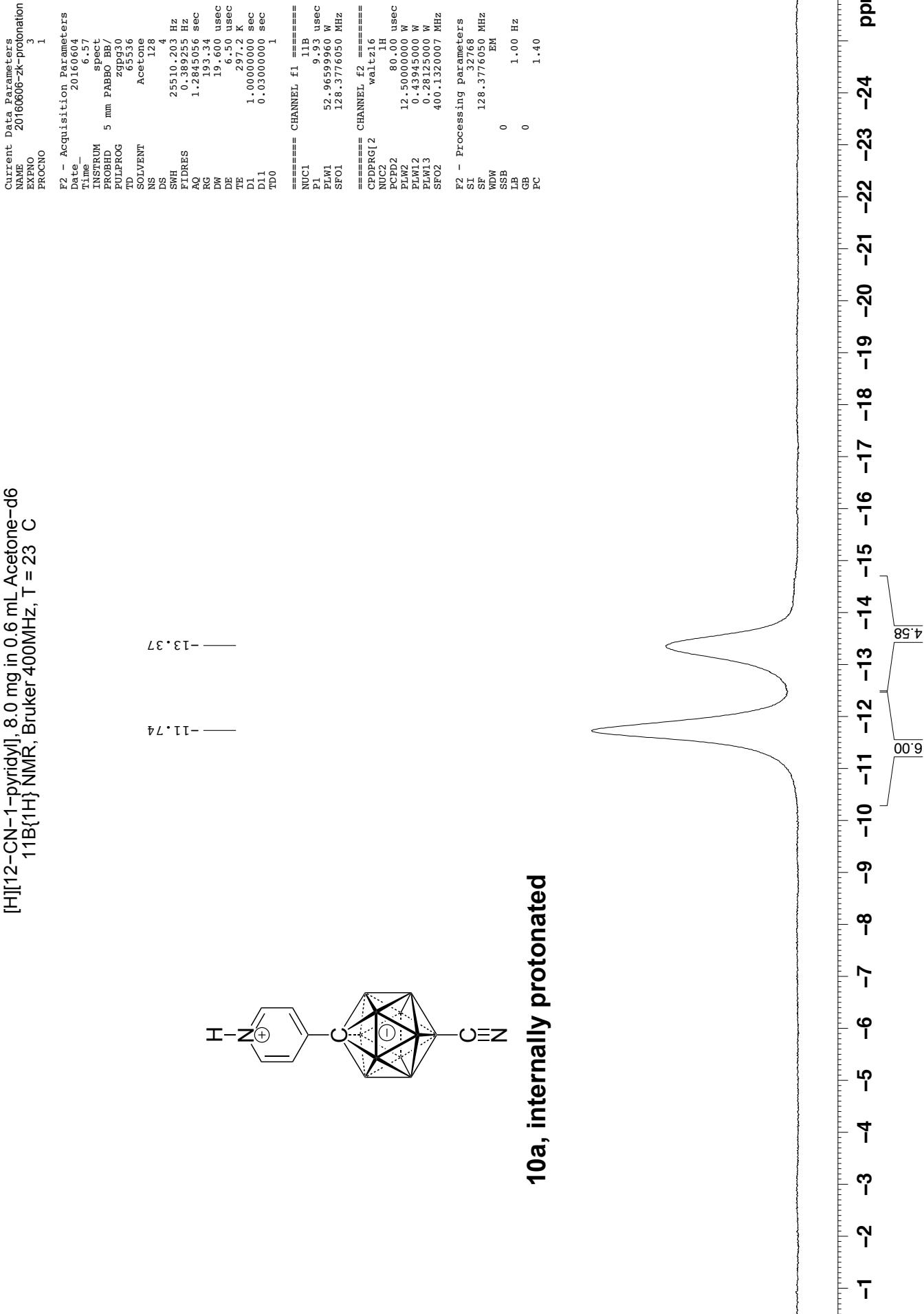
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WDW
SSB      0
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PC      1.40

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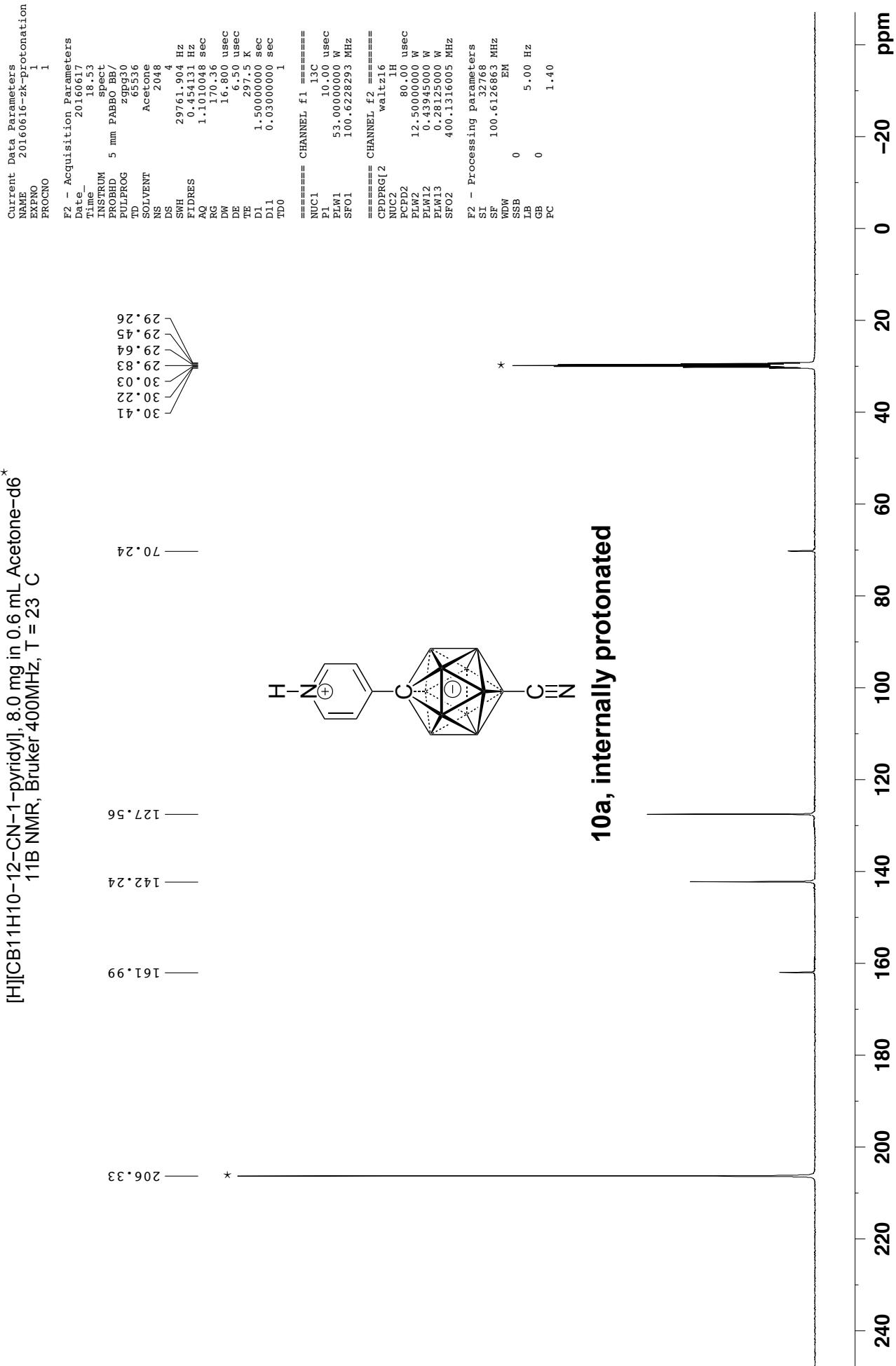


10a, internally protonated

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



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



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

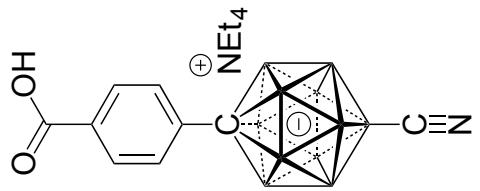
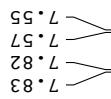
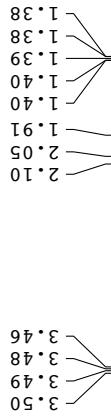
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NS       65536
SWH     12500.000 Hz
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RG      1114
DW      40.000 usec
DE      6.50 usec
TE      296.9 K
D1      5.000000 sec
D11     0.03000000 sec

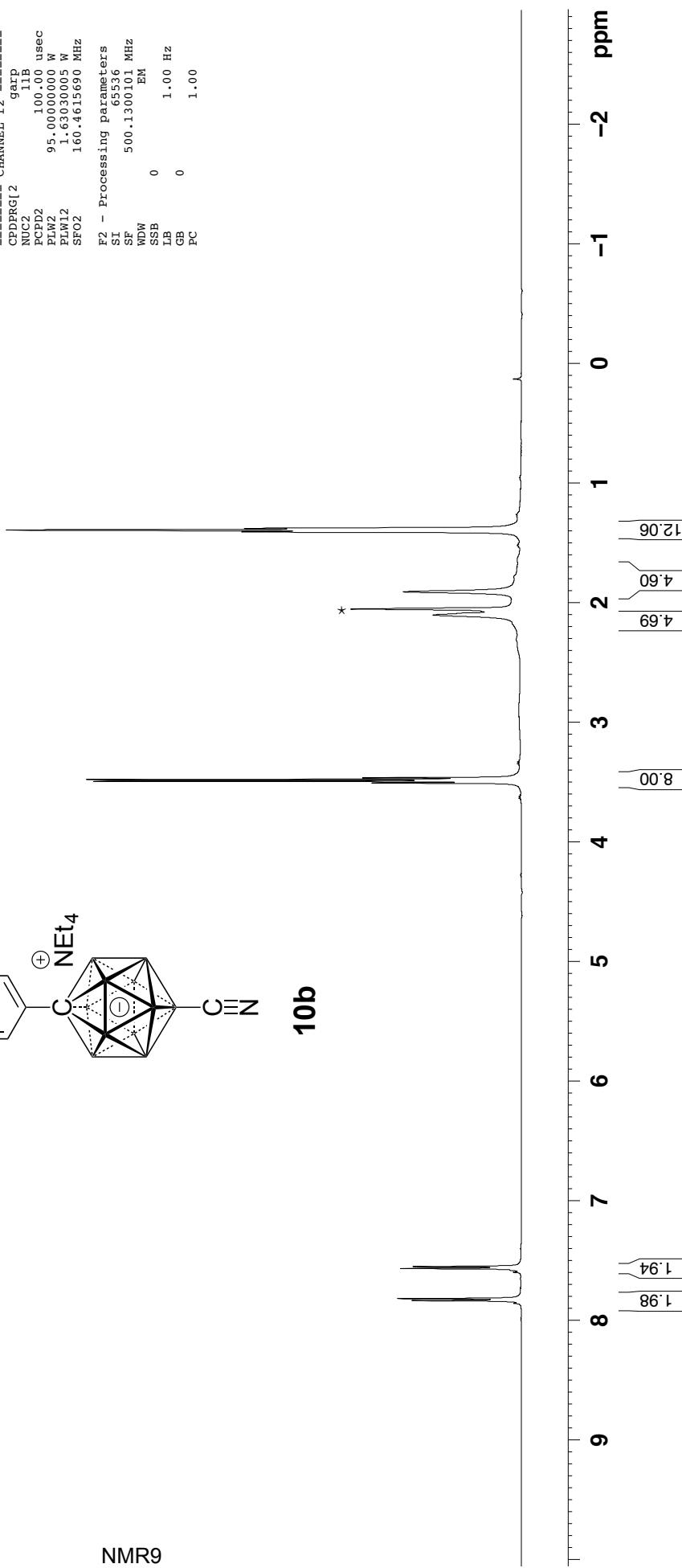
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SFO1

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NUC2    11B
PCP12   100.00 usec
PLW2   95.00000000 W
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SFO2   160.4615690 MHz

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NMR9

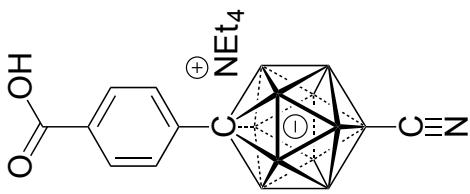
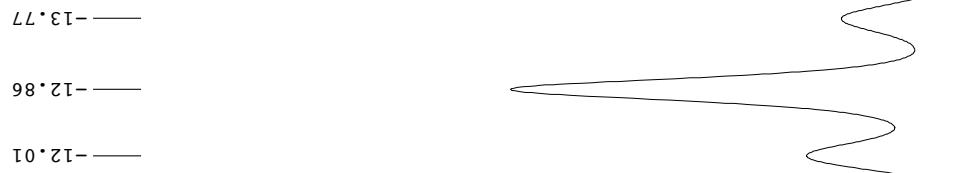


[NEt₄][CB11H10-12-CN-1-benacid], 10 mg in 0.5 mL Acetone-d₆
 11B NMR, Bruker 500MHz, T = 23 °C

```

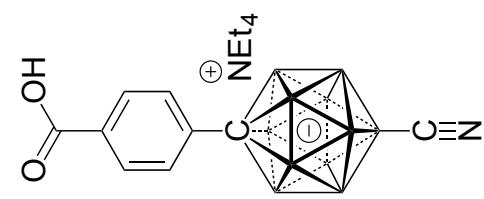
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EXPNO     1
PROCNO    1
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PULPROG  zgpg3d
TD        64098
SOLVENT   Acetone
NS        32
DS        0
SWH      32051.281 Hz
FIDRES  0.500036 Hz
AQ        0.999288 sec
RG        203
DW        15.600 usec
DE        16.00 usec
TE        295.9 K
D1        1.0000000 sec
        0
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NUC1     11B
P1        10.00 usec
PLW1    75.0000000 W
SFO1    160.4615792 MHz
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SSB      0
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```



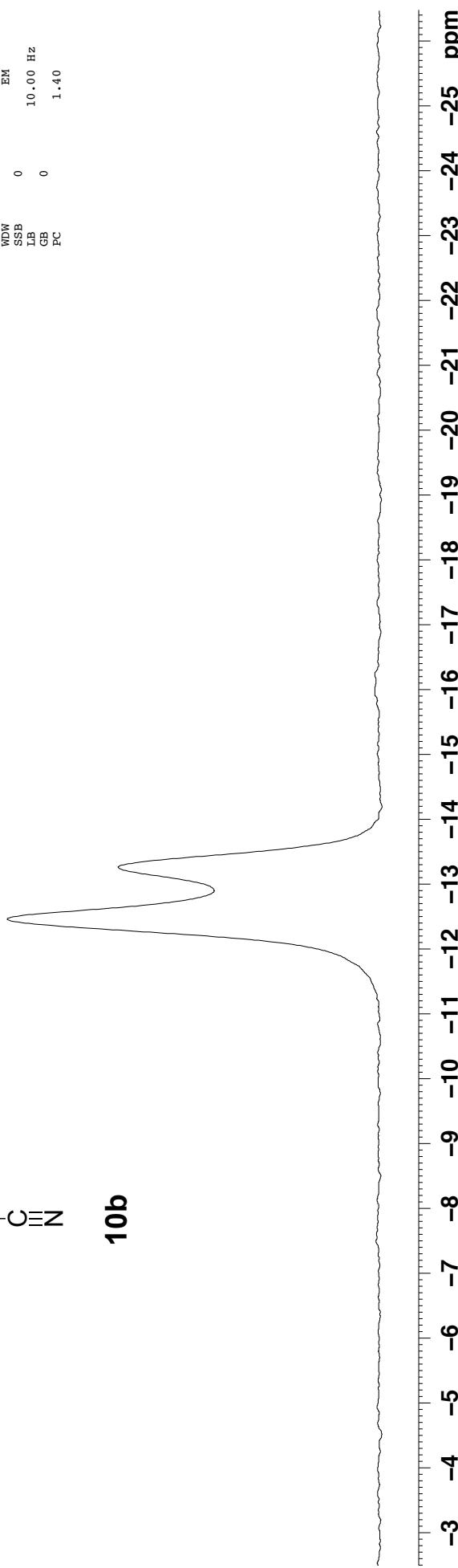
[NEt₄][CB11H₁₀-12-CN-1-benzoic], 10 mg in 0.5 mL Acetone-d₆
¹¹B{¹H} NMR, Bruker 500MHz, T = 23 °C

```
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NAME      2016012zK-12-CN-1-benzoic
EXPNO     2
PROCNO    1
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Time      15:56
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PULPROG  zgpg30
TD        6536
SOLVENT   Acetone
NS        32
DS        0
SWH      32051.281 Hz
FIDRES   1.0223616 sec
AQ        203
RG        15.600 usec
DW        6.500 usec
DE        26.5 K
TE        5.000000 sec
D1        0.0300000 sec
D11
NUC1     11B
P1        10.00 usec
PLW1    75.0000000 W
SFO1    160.4615792 MHz
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CPDPFG[2 CHANNEL f1
NUC2     1H
PDPD2   80.00 usec
PLW2    19.0000000 W
PLW12   0.45750001 W
PLW13   0.27360001 W
SFO2    500.1330885 MHz
===== CHANNEL f2 =====
NUC2     1H
PDPD2   80.00 usec
PLW2    19.0000000 W
PLW12   0.45750001 W
PLW13   0.27360001 W
SFO2    500.1330885 MHz
F2 - Processing parameters
SI        32768
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WDW
SSB      0
LB        10.00 Hz
GB      1.40
PC
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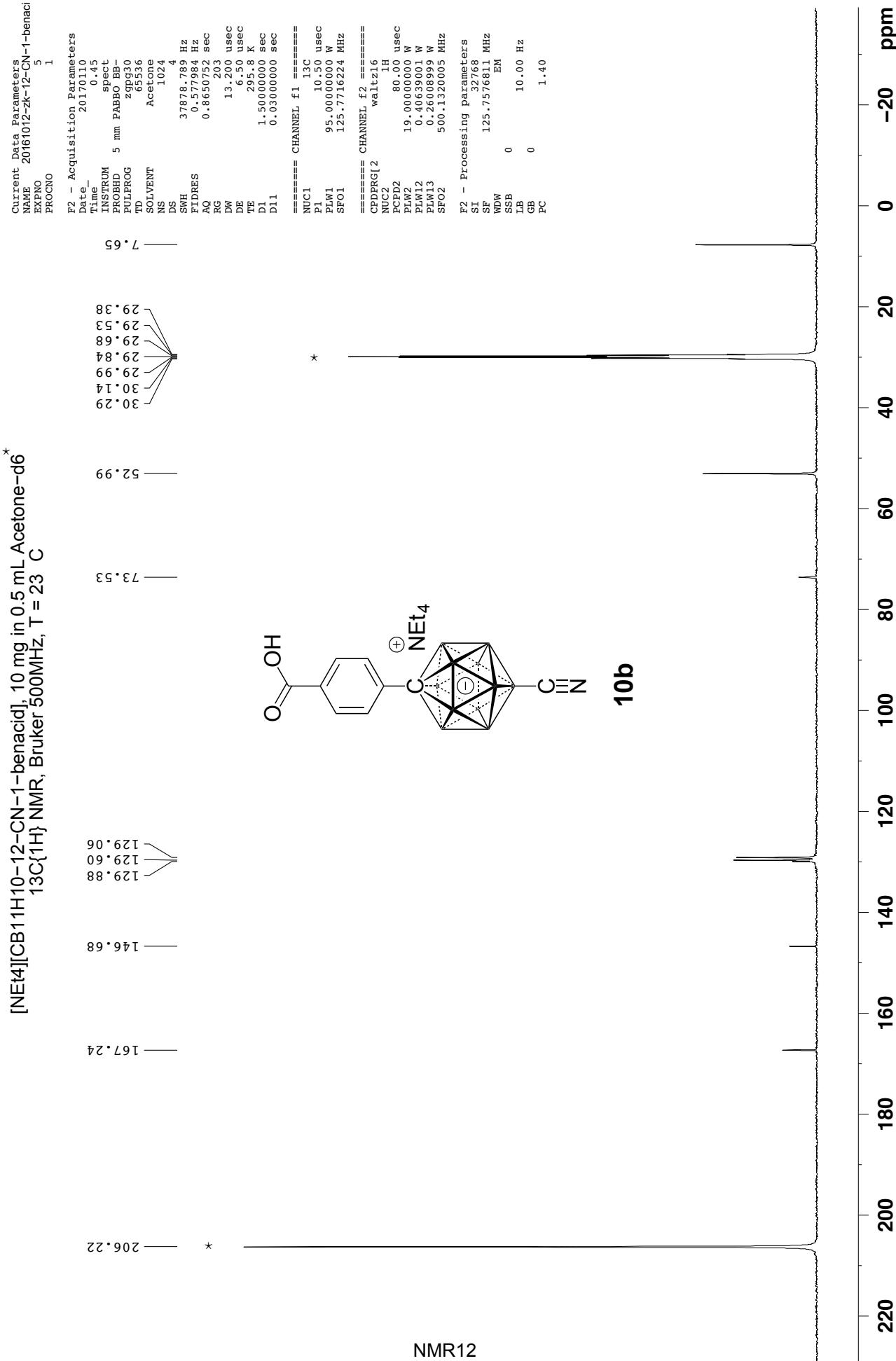


10b

—12.47
—13.27



[NEt₄][CB11H₁₀-12-CN-12-CN-1-benacid], 10 mg in 0.5 mL Acetone-d₆^{*}



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

Current Data Parameters
 NAME 2016026-zk-12-CN-1-bendia
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters

Date 20161026

Time 16.14

INSTRUM spect

PROBHD PABBO BB-

PULPROG zgfg30

TD 65536

SOLVENT DMSO

NS 16

DS 0

SWH 14097.744 Hz

FDRES 0.21115 Hz

AQ 2.324434 sec

RG 181

DW 35.467 usec

DE 6.50 usec

TB 237.7 K

D1 5.0000000 sec

D1L 0.03000000 sec

===== CHANNEL f1 =====

NUC1 1H

P1 12.00 usec

PLW1 19.0000000 W

SFO1 500.1310003 MHz

===== CHANNEL f2 =====

CPDRG1[2

garp

NUC2 11B

PCPD2 60.00 usec

PLW2 75.0000000 W

PLW12 2.08330011 W

SFO2 160.4615690 MHz

F2 - Processing parameters

SI 65536

SF 500.1300055 MHz

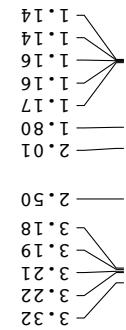
WDW no

SSB 0 Hz

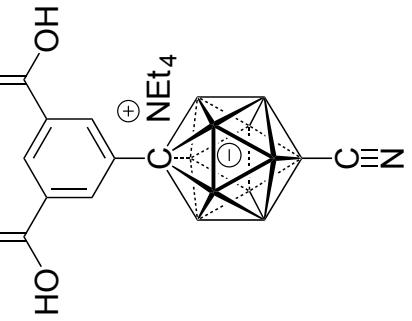
LB 0 Hz

GB 0

PC 1.00



H₂O



10c

13.33

8.28

8.13

8.00

2.01

2.50

3.18

3.21

3.22

3.25

3.19

3.21

3.18

3.16

3.14

3.12

3.10

3.01

2.80

2.78

2.76

2.74

2.72

2.70

2.68

2.66

2.64

2.62

2.60

2.58

2.56

2.54

2.52

2.50

2.48

2.46

2.44

2.42

2.40

2.38

2.36

2.34

2.32

2.30

2.28

2.26

2.24

2.22

2.20

2.18

2.16

2.14

2.12

2.10

2.08

2.06

2.04

2.02

2.00

1.98

1.96

1.94

1.92

1.90

1.88

1.86

1.84

1.82

1.80

1.78

1.76

1.74

1.72

1.70

1.68

1.66

1.64

1.62

1.60

1.58

1.56

1.54

1.52

1.50

1.48

1.46

1.44

1.42

1.40

1.38

1.36

1.34

1.32

1.30

1.28

1.26

1.24

1.22

1.20

1.18

1.16

1.14

1.12

1.10

1.08

1.06

1.04

1.02

1.00

0.98

0.96

0.94

0.92

0.90

0.88

0.86

0.84

0.82

0.80

0.78

0.76

0.74

0.72

0.70

0.68

0.66

0.64

0.62

0.60

0.58

0.56

0.54

0.52

0.50

0.48

0.46

0.44

0.42

0.40

0.38

0.36

0.34

0.32

0.30

0.28

0.26

0.24

0.22

0.20

0.18

0.16

0.14

0.12

0.10

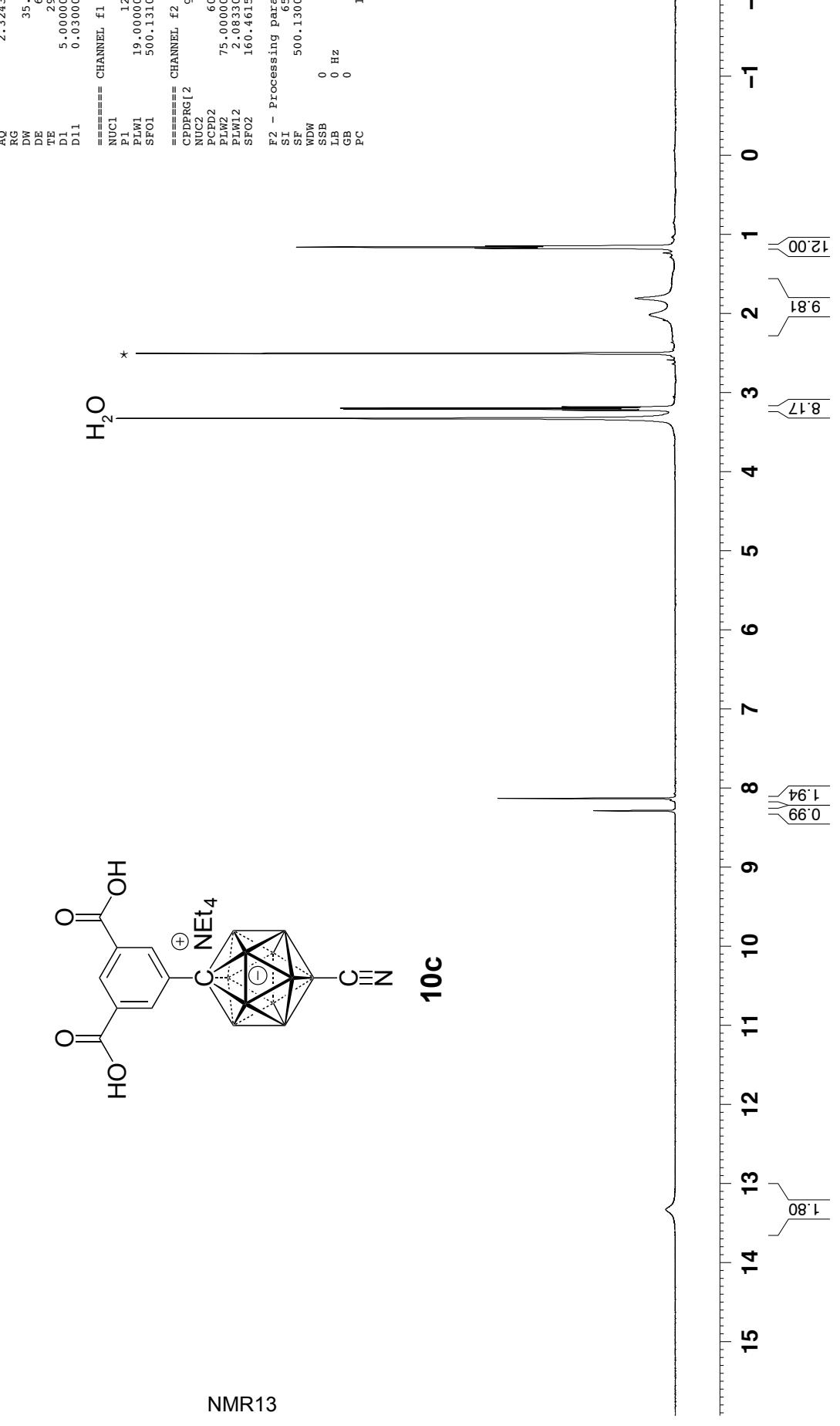
0.08

0.06

0.04

0.02

0.00



NMR13

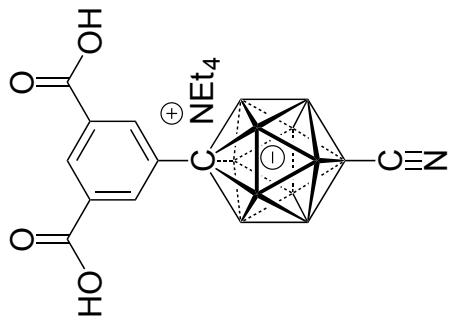
[NEt₄][CB11H10-12-CN-1-Bendi acids], 6.6 mg in 0.6 mL DMSO-d₆
 11B NMR, Bruker 500MHz, T = 23 °C

```

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  zg3d
TD        19226
SOLVENT   DMSO
NS        32
DS        0
SWH      32051.281 Hz
FIDRES   1.667080 Hz
AQ        0.2599256 sec
RG        203
DW        15.600 usec
DE        16.00 usec
TE        297.3 K
D1        0.5000000 sec
D1        0.5000000 sec
===== CHANNEL f1 =====
NUC1      11B
P1        10.00 usec
P1W1     75.0000000 W
SF        160.4615792 MHz
SSB       0
LB        10.00 Hz
GB        0
PC        1.40
F2 - Processing parameters
SI        32768
SF        160.4615993 MHz
WDW      EM
SSB       0
LB        10.00 Hz
GB        0
PC        1.40

```

-12.05
 —
 -12.99
 —



10c

NMR14



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

```

Current Data Parameters
NAME 2016026-2k-12-CN-1-bendia
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20161026
Time_ 16.11
INSTRUM spect
PROBID 5 mm PABBO BB-
PULPROG zgppg90
TD 19226
SWH 32
SOLVENT DMSO
NS 32
DS 0
SFH 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 0.5000000 sec
D11 0.0300000 sec

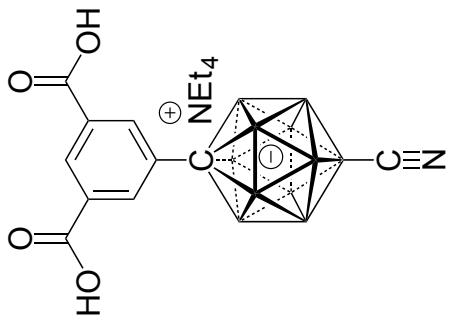
===== CHANNEL f1 =====
NUC1 11B
P1 10.00 usec
PLW1 75.0000000 W
SF01 160.44615792 MHz

===== CHANNEL f2 =====
CPDPKG[2
NUC2 1H
PCPD2 80.00 usec
PLW2 19.0000000 W
PLW12 0.42250001 W
PLW13 0.27360001 W
SF02 500.1330885 MHz

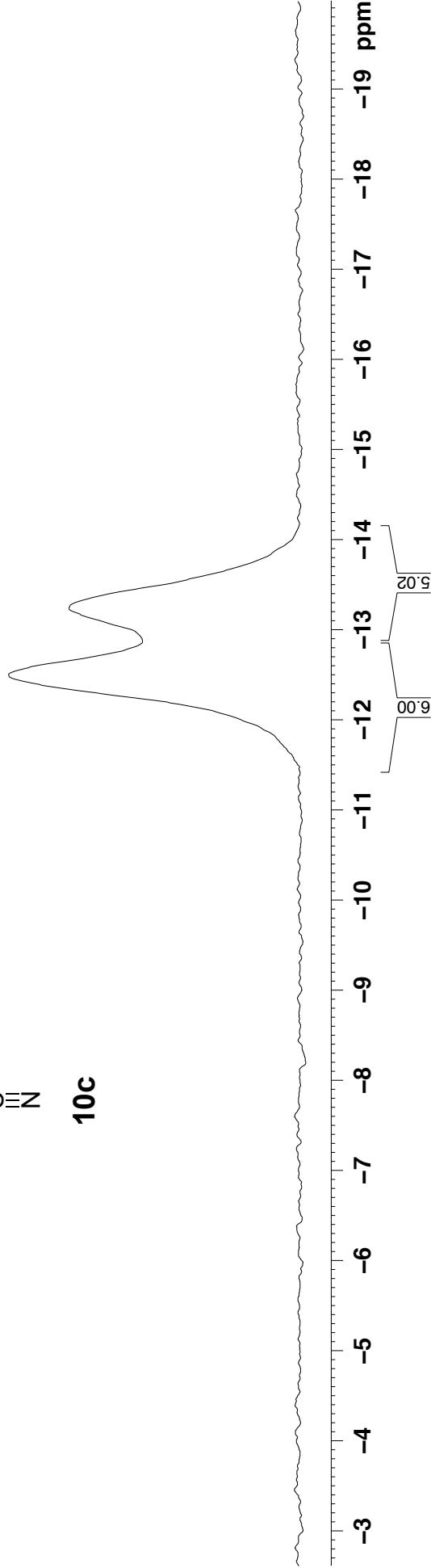
F2 - Processing parameters
SI 32768
SF 160.4415993 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

```

-12.50
 -13.23



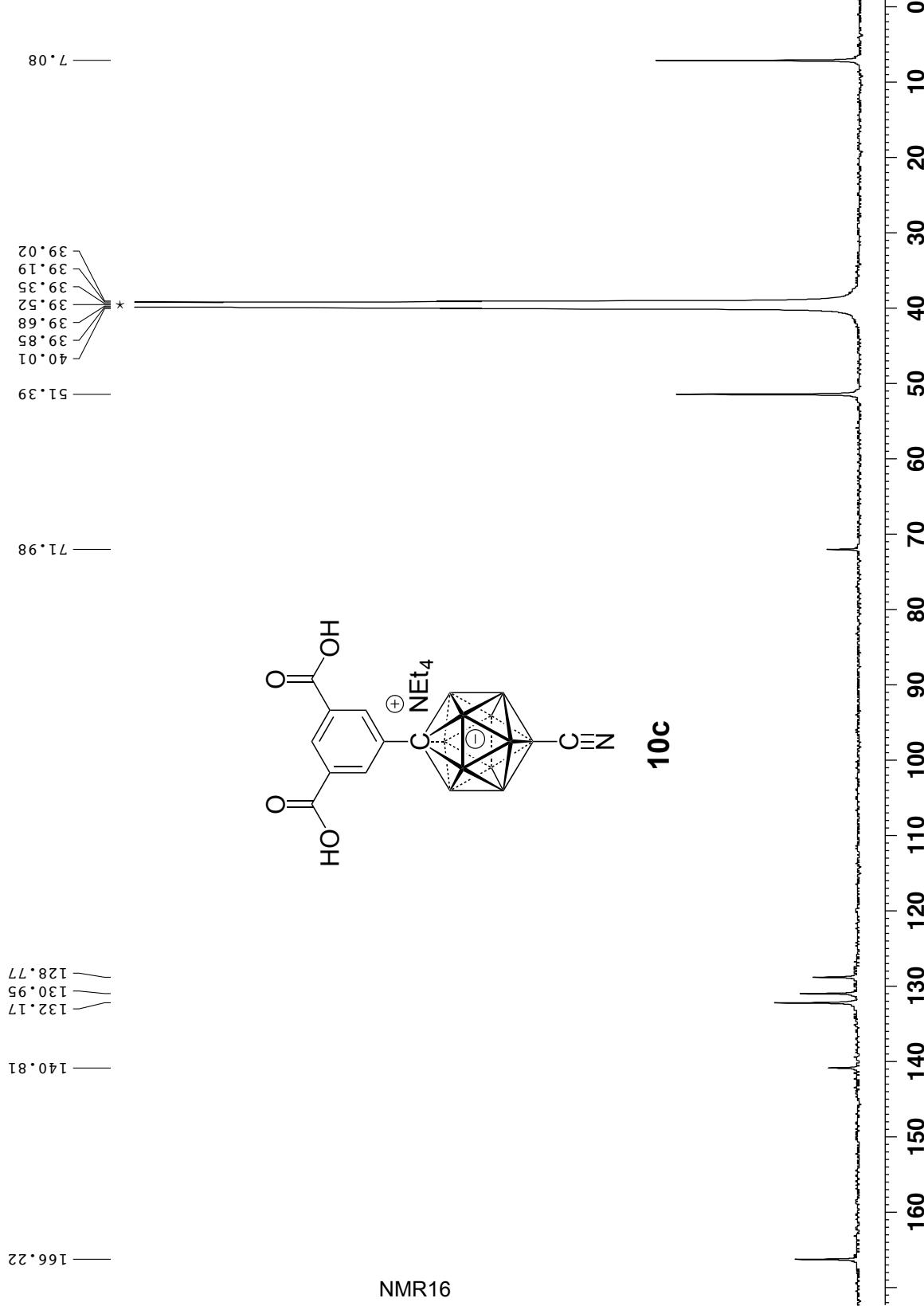
NMR15



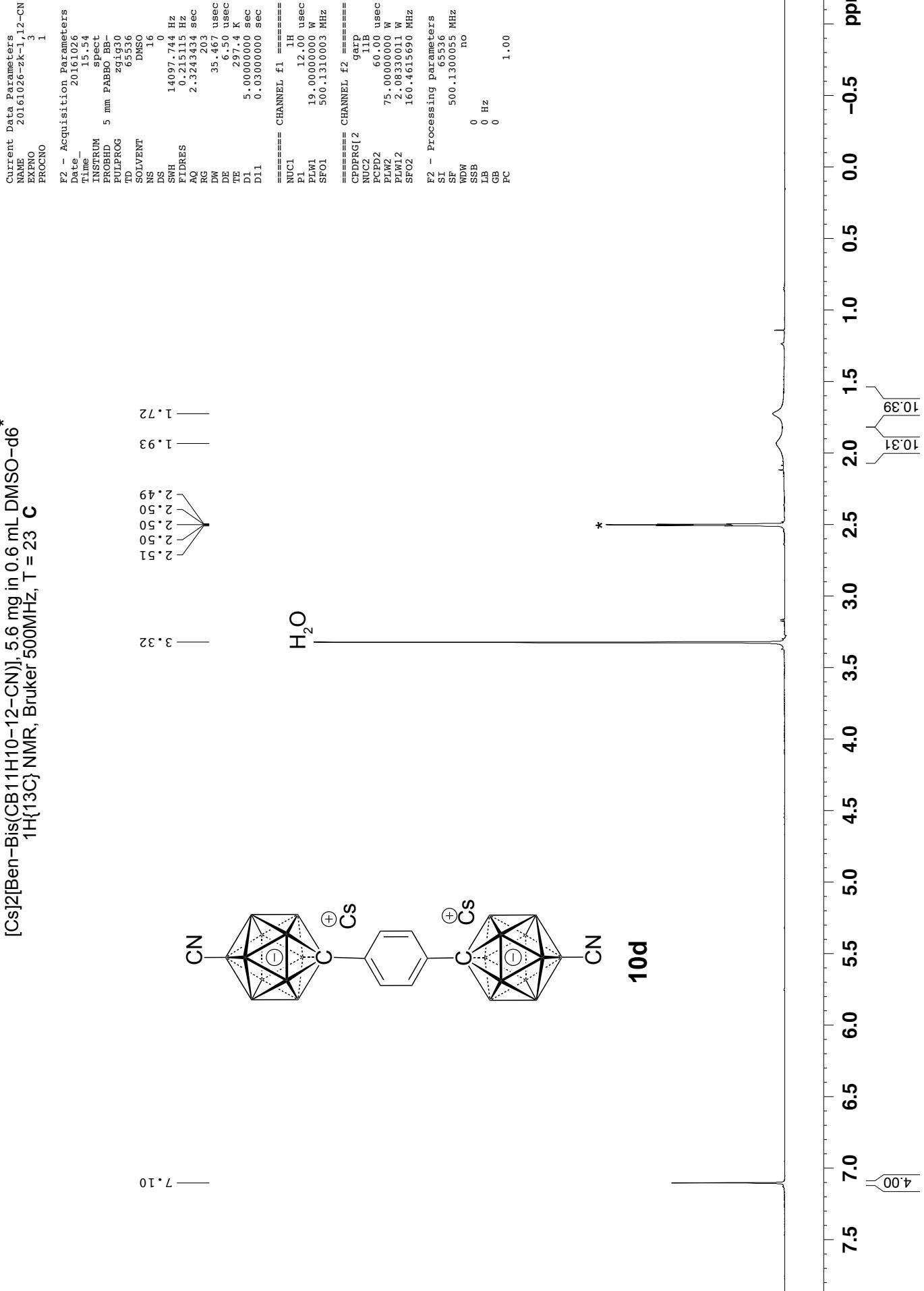
[NEt₄][CB11H_{10-12-CN-11-Bendi acids], 6.6 mg in 0.6 mL DMSO-d₆^{*}}

Current Data Parameters
NAME 20161026-zk-12-CN-1-bendia
Ex+XENO 1
PROCNO 1

F2 - Acquisition Parameters
date 20161123
time_ spect
INSTRUM PABIO
PROBID 5 mm PABIO_BB-
PULPROG zgpp30
TD 65336
SOLVENT DMSO
NS 3072
DS 37878.789 Hz
SWH 0.877984 Hz
AQ 0.8850752 sec
RG 203
DW 13.200 usec
DE 6.50 usec
TE 296.6 K
D1 1.5000000 sec
D11 0.0300000 sec
===== CHANNEL f1 =====
NUC1 13C
P1 10.50 usec
PLW1 95.000000 W
SFO1 125.7716224 MHz
===== CHANNEL f2 =====
CPDPRG[2 walt216
NUC2 1H
PCPD2 80.00 usec
PLW2 0.3994700 W
PLW12 0.2556600 W
SFW13 500.1320005 MHz
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7578464 MHz
WDW 0
SSB LB 10.00 Hz
GB 0 1.40
PC

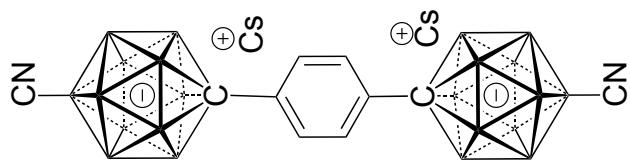


[Cs]2[Bis(CB11H10–12–CN)]^{*}, 5.6 mg in 0.6 mL DMSO-d₆
 1H{¹³C} NMR, Bruker 500MHz, T = 23 °C

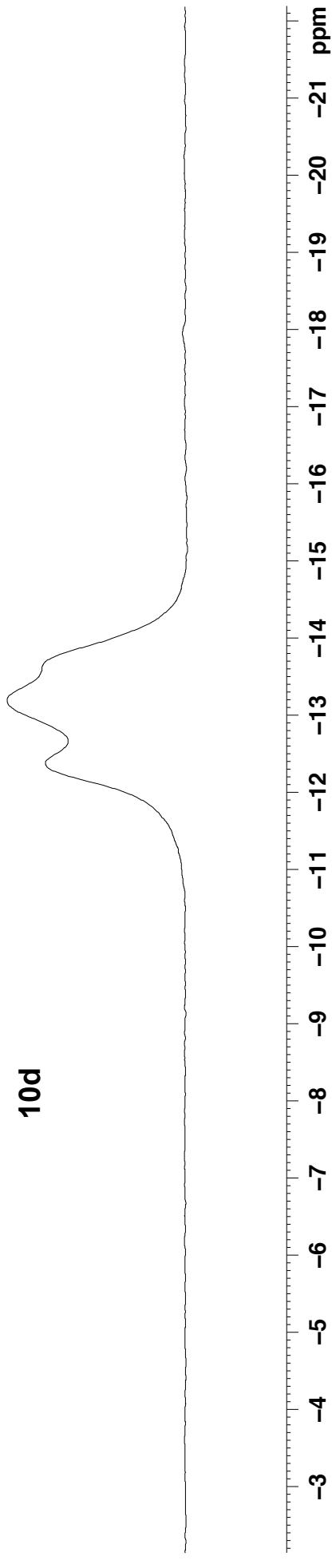


[Cs]2[Ben-Bis(CB11H10-12-CN)], 5.6 mg in 0.6 mL DMSO-d6
 11B NMR, Bruker 500MHz, T = 23 °C

```
Current Data Parameters
NAME      2016026-zk-1,12-CN
EXPNO     1
PROCNO    1
F2 - Acquisition Parameters
Date_     20161026
Time      15.50
INSTRUM  spect
PROBID   5 mm PABBO BB-
PULPROG  zg3d
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      236.8 K
D1      0.5000000 sec
        ===== CHANNEL f1 =====
NUC1     11B
P1      10.00 usec
PLW1    75.0000000 W
SFO1    160.4615792 MHz
F2 - Processing parameters
SI       32768
SF      160.4615993 MHz
WDW
SSB      0
LB      10.00 Hz
GB      0
PC      1.40
```



10d



[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     2
PROCNO    1

F2 - Acquisition parameters
Date_     2016.02.6
Time      15.52
INSTRUM  spect
PROBID   5 mm PABBO BB-
PULPROG zpp930
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      0.5000000 sec
D11     0.0300000 sec

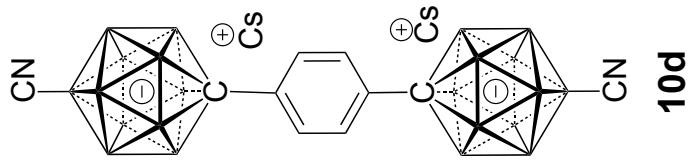
===== CHANNEL f1 =====
NUC1      11B
P1        10.00 usec
PLW1    75.0000000 W
SFO1    160.4615792 MHz

===== CHANNEL f2 =====
CPDPRG[2
NUC2      1H
PCPD2    19.0000000 W
PLW2    0.42150001 W
PLW13   0.23736001 W
SFO2    500.1330885 MHz

F2 - Processing parameters
SI        32768
SF      160.461593 MHz
WDW        EM
SSB        0
LB        10.00 Hz
GB        1.40
PC        1

```

— -12.81



10d

NMR19

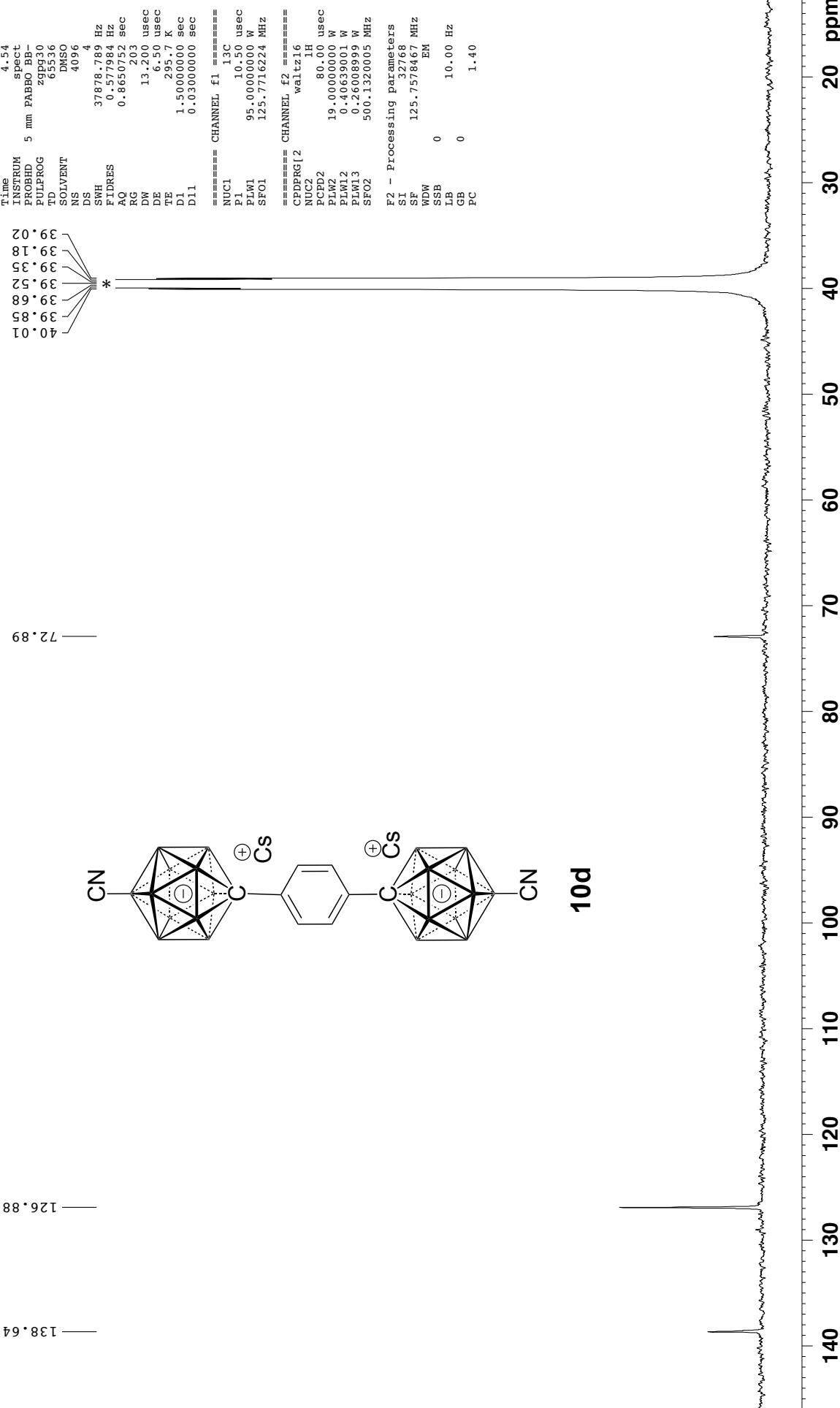
-2 -3 -4 -5 -6 -7 -8 -9 -10 -11 -12 -13 -14 -15 -16 -17 -18 -19 -20 -21 -22 -23 ppm

[Cs]2[Ben-Bis(CB11H10-12-CN)], 5.6 mg in 0.6 mL DMSO-d6*

NAME 20161026-ZK-1,12-C
EXPGO 1
PROCNO 1

F2 - Acquisition Parameters

Date 20161129
Time 4.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG 2DPPG30
TD 6536
SOLVENT DMSO
NS 4096
DS 37878.789 Hz
FIDRES 0.577984 Hz
AQ 0.8630752 sec
RG 203
DW 13.200 usec
DE 6.50 usec
TE 295.7 K
D1 1.5000000 sec
D11 0.03000000 sec
===== CHANNEL f1 ======
NUC1 13C
P1 10.50 usec
PLW1 95.0000000 W
SF01 125.7716224 MHz
===== CHANNEL f2 ======
CPDRG[2] waltz16
NUC2 1H
PCP2 80.00 usec
PLW2 19.0000000 W
PLW12 0.40659001 W
PLW13 0.26008999 W
SF02 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



[NEt₄][CB11H11-1-Pyridine], 15.6 mg in 0.6 mL Acetone-d₆^{*}

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

Current Data Parameters
NAME 20170409-2K-1-P
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20170411
Time 6.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg3g30
TD 16384
SOLVENT Acetone
NS 16
DS 4
SWH 8012.820 Hz
FIDRES 0.483064 Hz
AO 1.0223616 sec
RG 86.58
DW 62.400 usec
DE 6.50 usec
TE 296.0 K
D1 1.0000000 sec
D11 0.0300000 sec
TD0 1

===== CHANNEL f1 =====

NUC1 1H
P1 15.00 usec
PLW1 12.5000000 W
SFO1 400.1320007 MHz

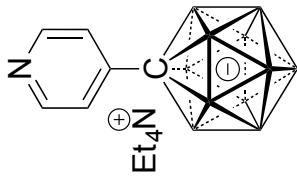
===== CHANNEL f2 =====

CPDRG[2 gtp4
NUC2 1H
PCPD2 90.00 usec
PLW2 52.9659960 W
PLW12 0.64477998 W
SFO2 128.3776050 MHz

F2 - Processing parameters

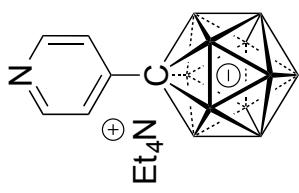
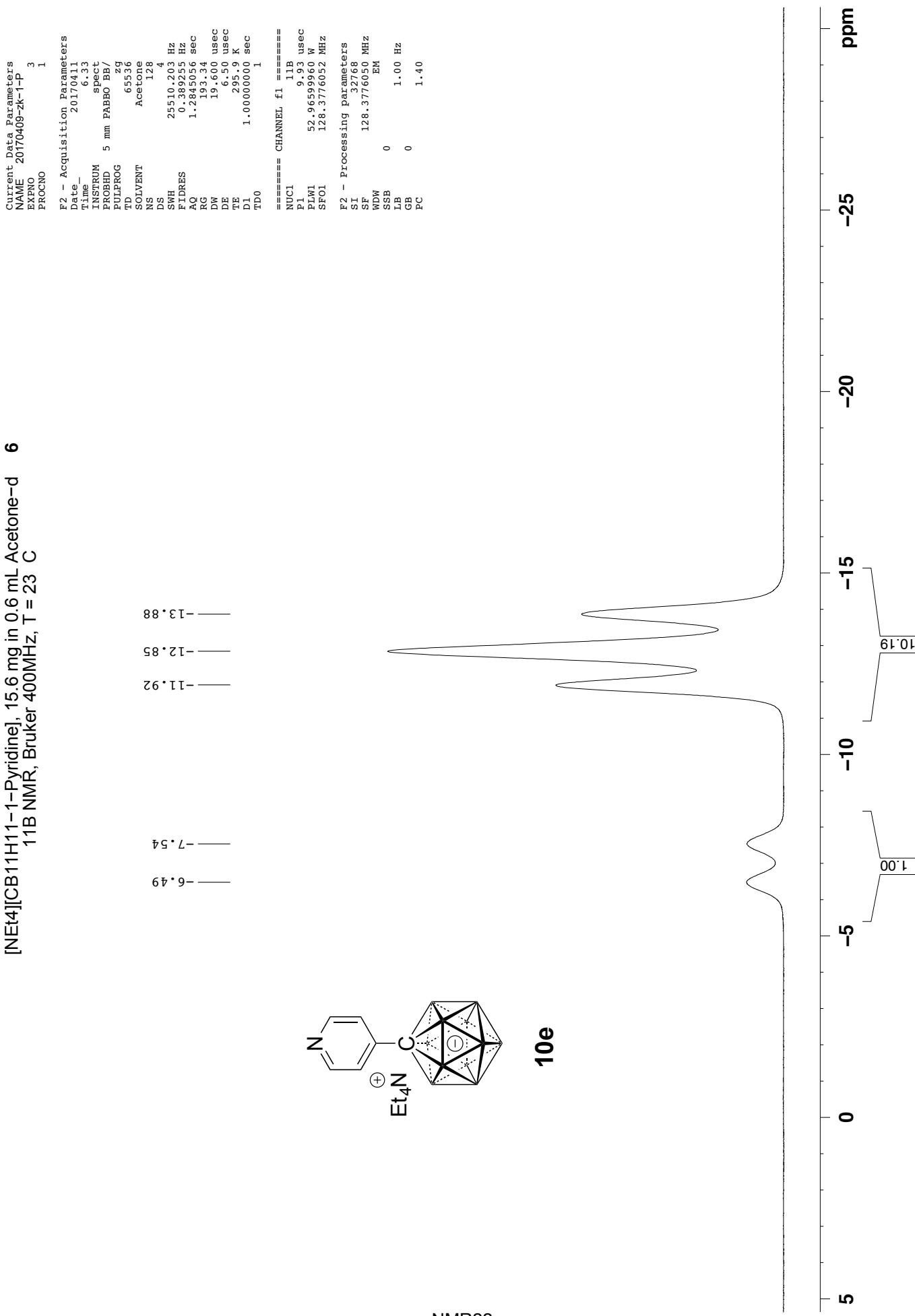
S1 32/68
SF 400.1300073 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

10e

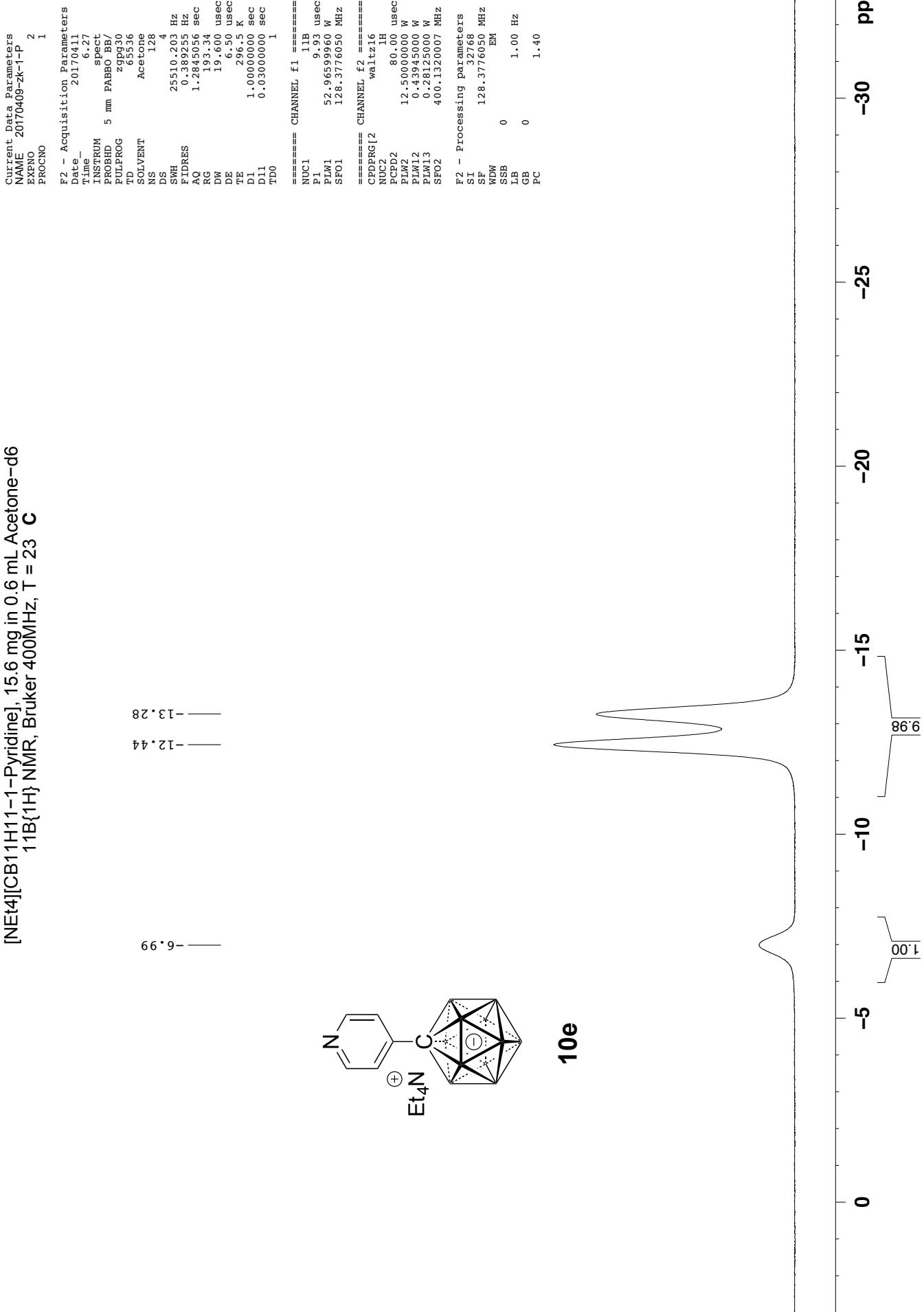


NMR21

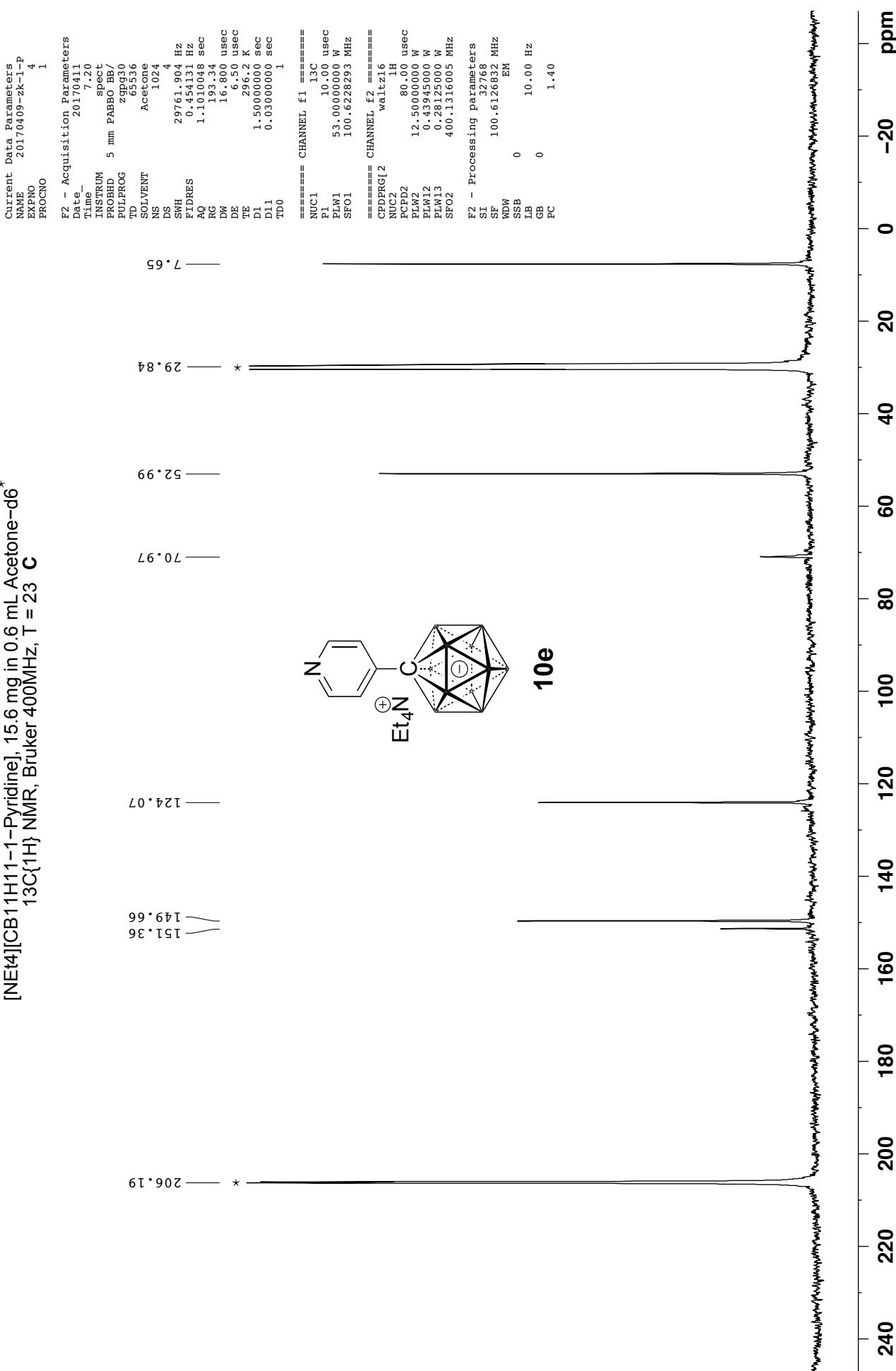
[NEt₄][CB11H₁₁-1-Pyridine], 15.6 mg in 0.6 mL Acetone-d₆ 11B NMR, Bruker 400MHz, T = 23 °C



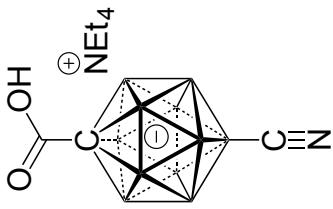
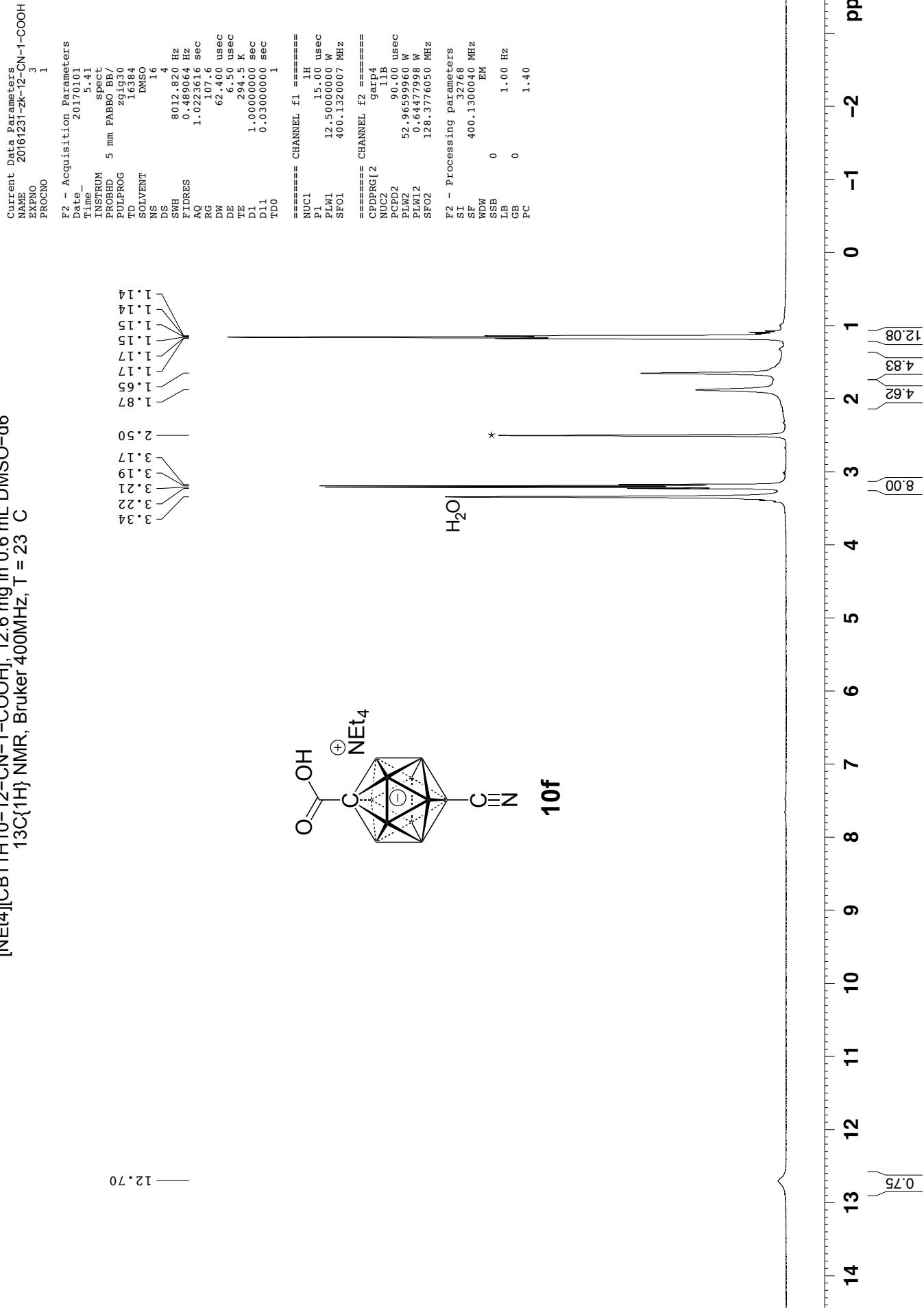
[NEt₄][CB11H₁₁-1-Pyridine], 15.6 mg in 0.6 mL Acetone-d₆
 11B{¹H} NMR, Bruker 400MHz, T = 23 °C



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



[NEt₄][CB11H₁₀-12-CN-1-COOH], 12.6 mg in 0.6 mL DMSO-d₆^{*}



[NEt₄][CB11H<sub>10-12-CN-1-COOH]], 12.6 mg in 0.6 mL DMSO-d₆
 11B NMR, Bruker 400MHz, T = 23 C</sub>

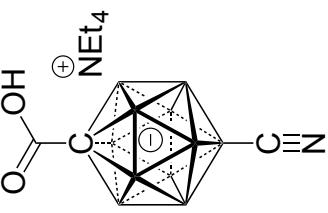
Current Data Parameters
 NAME 20161231-2k-12-CN-1-COOH
 EXPNO 1
 PROCN0 1

F2 - Acquisition Parameters
 Date 2017/01/01
 Time 5.34

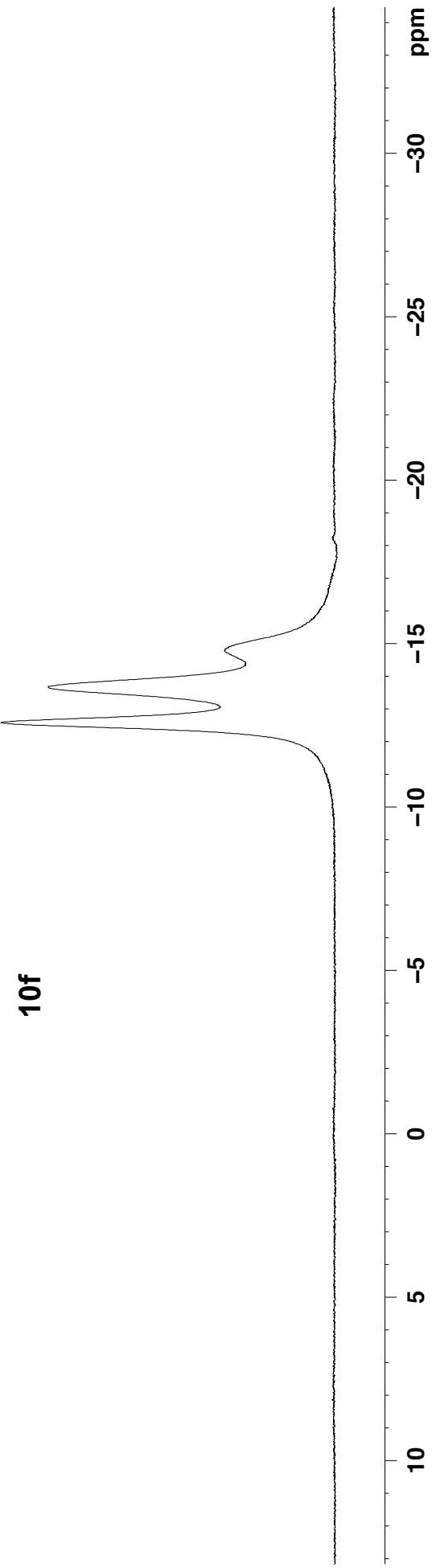
INSTRUM 5 mm PABBO BB/
 PULPROG 29
 TD 65536
 SOLVENT DMSO
 NS 128
 DS 4

SWH 25510.203 Hz
 FIDRES 0.389255 Hz
 AQ 1.2815036 sec
 RG 193.34

DW 19.600 usec
 DE 6.50 usec
 TE 294.0 K
 D1 1.0000000 sec
 TDO 1



-14.79
 -13.68
 -12.60



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

```

Current Data Parameters
NAME      20161231-1K-12-O-N-1-COOH
EXPNO     1
PROCNO    1

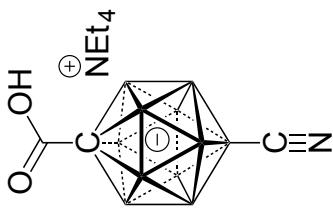
F2 - Acquisition Parameters
Date_      20170101
Time_      5.40
INSTRUM   spect
PROBID    5 mm PABBO BB/
PULPROG  zgpp30
TD        6536
SOLVENT   DMSO
NS        128
DS        4
SWH      25510.203 Hz
FIDRES   0.389255 Hz
AQ        1.284056 sec
RG        193.34
DW        19.600 usec
DE        6.50 usec
TE        294.8 K
TPE       1.0000000 sec
D1        0.0300000 sec
D11       1
TD0       1

===== CHANNEL f1 =====
NUC1      P1
PLW1     52.9659960 W
SF01     128.3778050 MHz

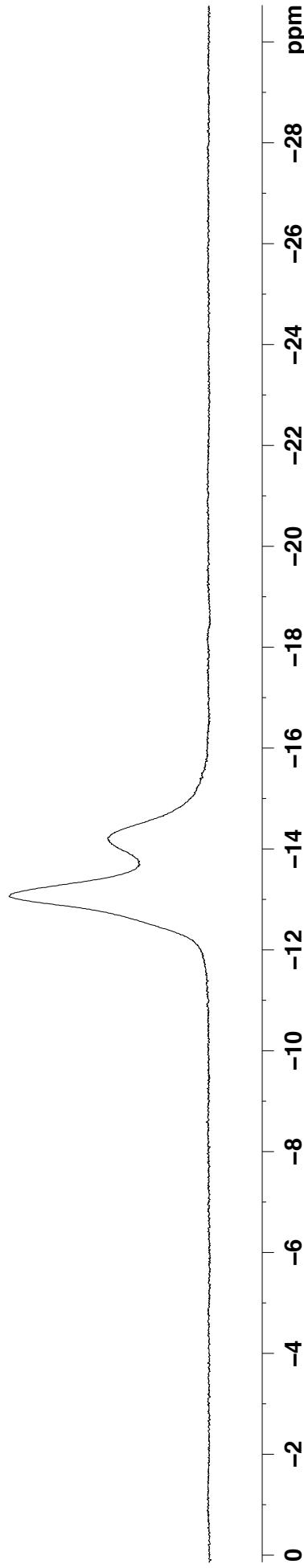
===== CHANNEL f2 =====
CPDPRG[2
NUC2      1H
PLW2     12.5000000 W
SF02     32768
PLW12    0.4394500 W
PLW13    0.2812500 W
SF012    400.1320007 MHz

F2 - Processing parameters
SI        32768
SP        128.3778050 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40

```



10f



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

```

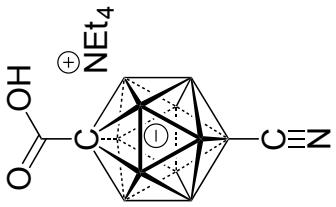
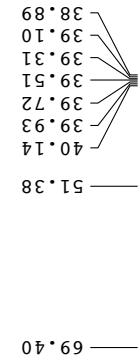
Current Data Parameters
NAME          20161231-ZK-12-CN-1-COOH
EXPNO         4
PROCNO        1
F2 - Acquisition Parameters
Date_        20170103
Time_        6.57
INSTRUM      spect
PROBHD      5 mm PABBO BB/
PULPROG     zgpg36
TD          65536
SOLVENT      DMSO
NS           1024
DS            4
SWH         29761.904 Hz
FIDRES     0.45131 Hz
AQ          1.1010048 sec
RG           193.34
DW           16.800 usec
DE           6.50 usec
TE           295.9 K
D1          1.5000000 sec
D11          0.03000000 sec
TD0             1
TDC           1

===== CHANNEL f1 =====
NUC1        13C
P1          10.00 usec
PLW1      53.000000 W
SFO1    100.6228293 MHz

===== CHANNEL f2 =====
NUC2        1H
PCPD2      80.00 usec
PLW2      12.500000 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

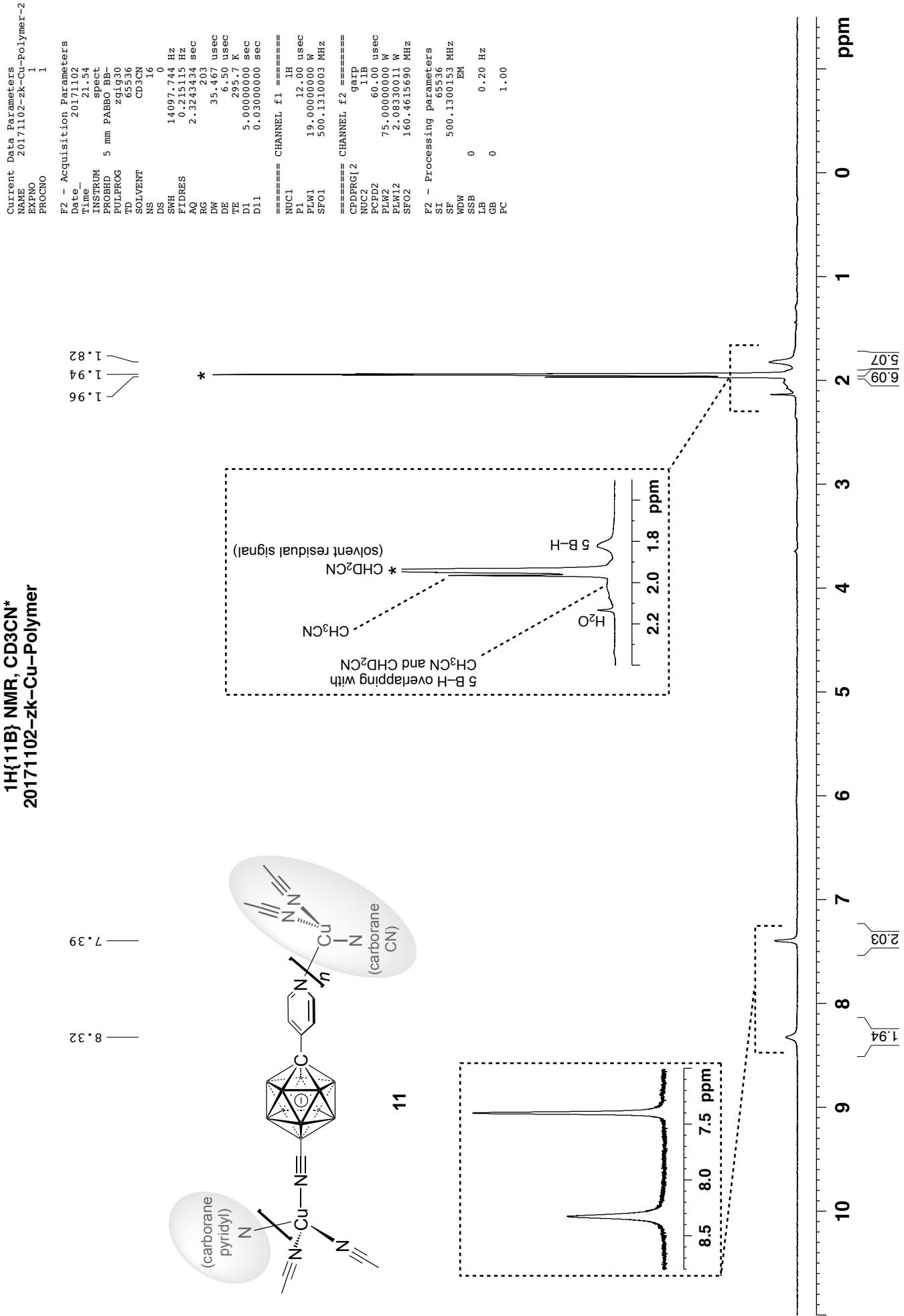
```



10f



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



**11B NMR, CD3CN
20171102-zk-Cu-Polymer**

```

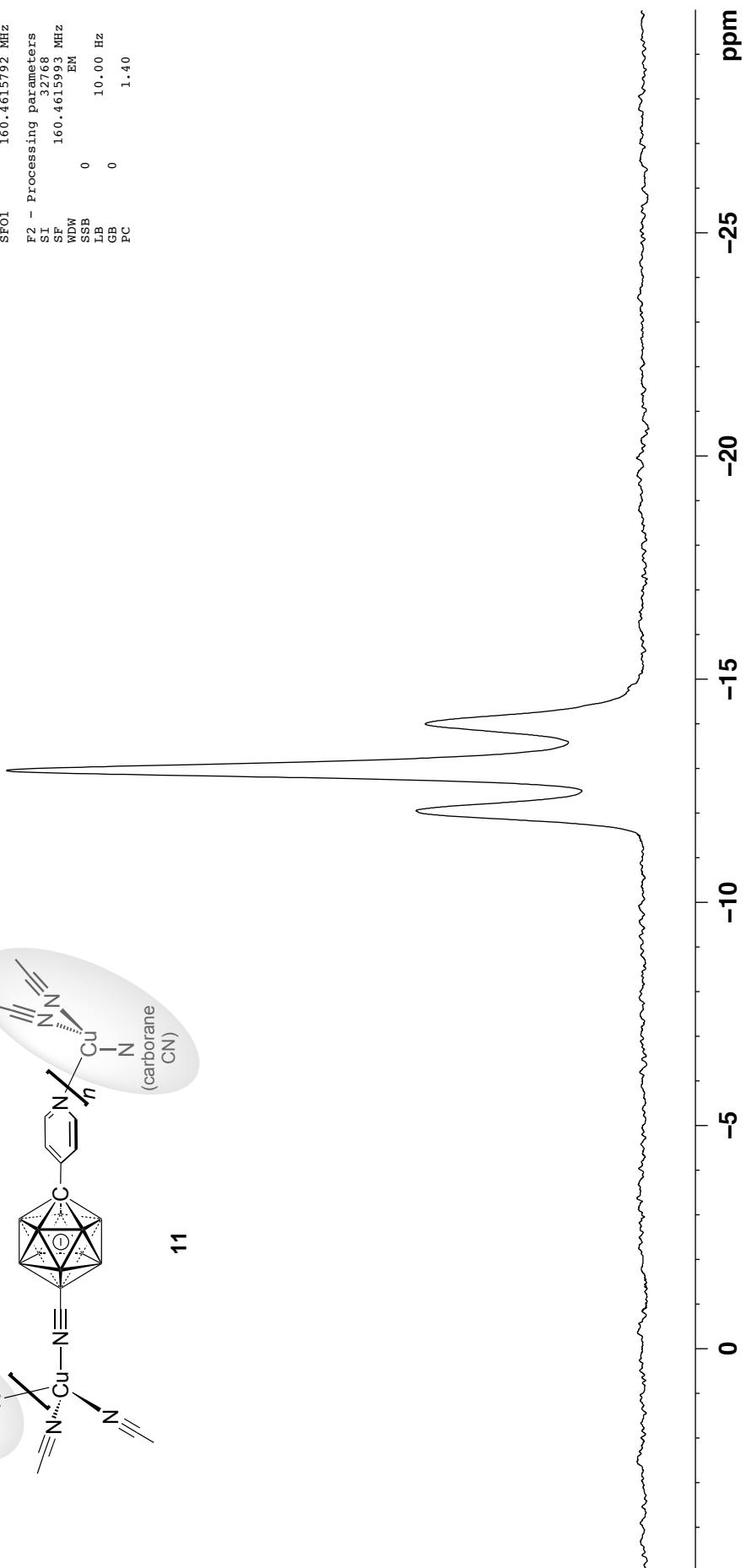
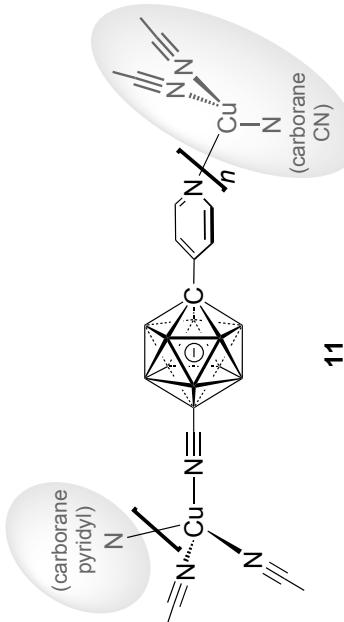
Current Data Parameters
NAME      20171102-zk-Cu-Polymer-2
EXPO      2
PROCNO   1

F2 - Acquisition Parameters
Date_    20171102
Time_    21:57
INSTRUM  5 mm PABBO spect
PROBID   PABBO BB-
PULPROG  zg3248
TD       32768
SWH     0.000102 Hz
FIDRES  0.499988 sec
AQ      64
RG      203
DW      15.000 usec
DE      16.000 usec
TE      295.9 K
D1      0.5000000 sec

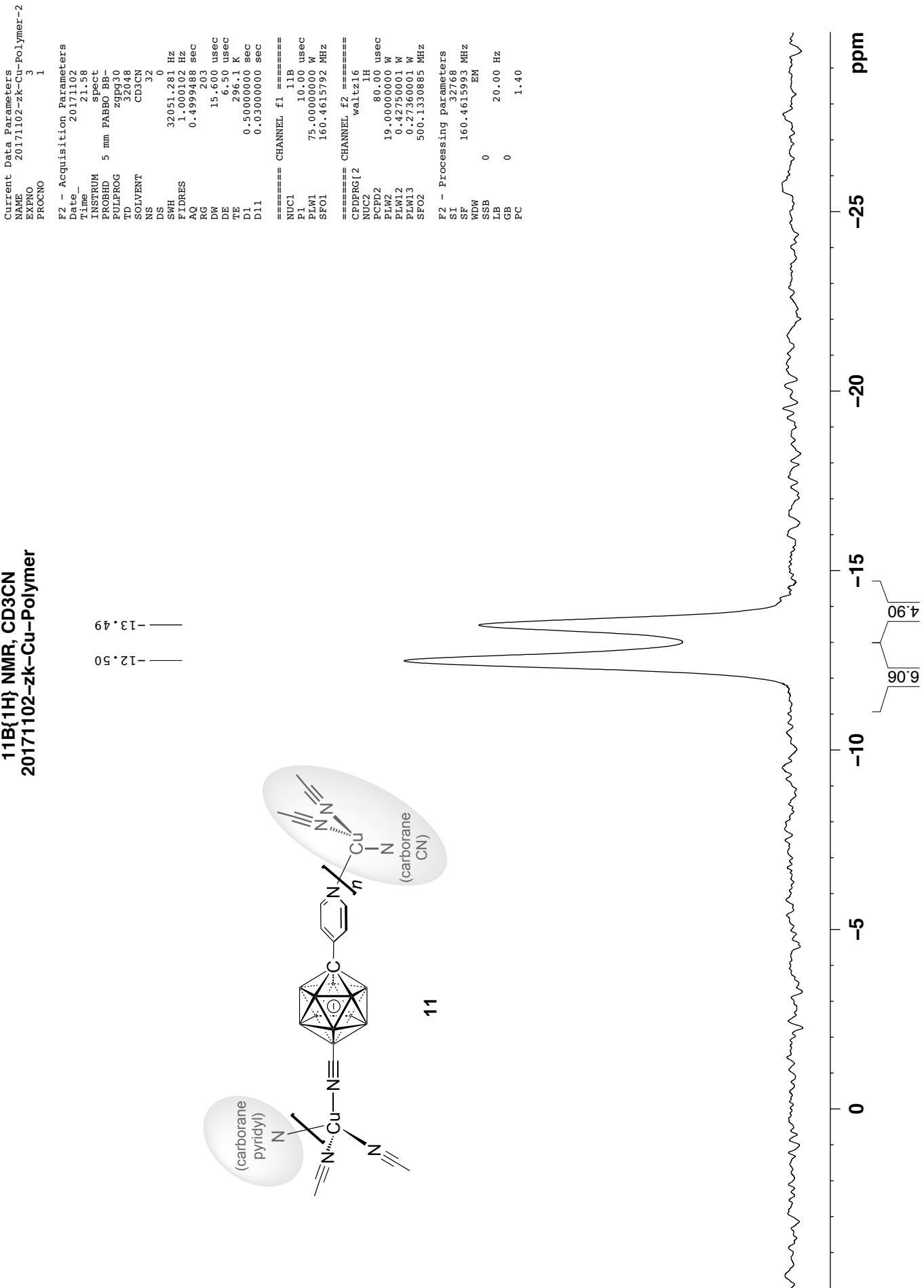
===== CHANNEL f1 =====
NUC1    11B
P1      10.00 usec
PLW1   75.0000000 W
SF01   16.4615792 MHz
SFO1   32.768

F2 - Processing parameters
SI      32768
SF      16.0-46.1593 MHz
WDW
SSB    0
LB     10.00 Hz
GB    0
PC     1.40

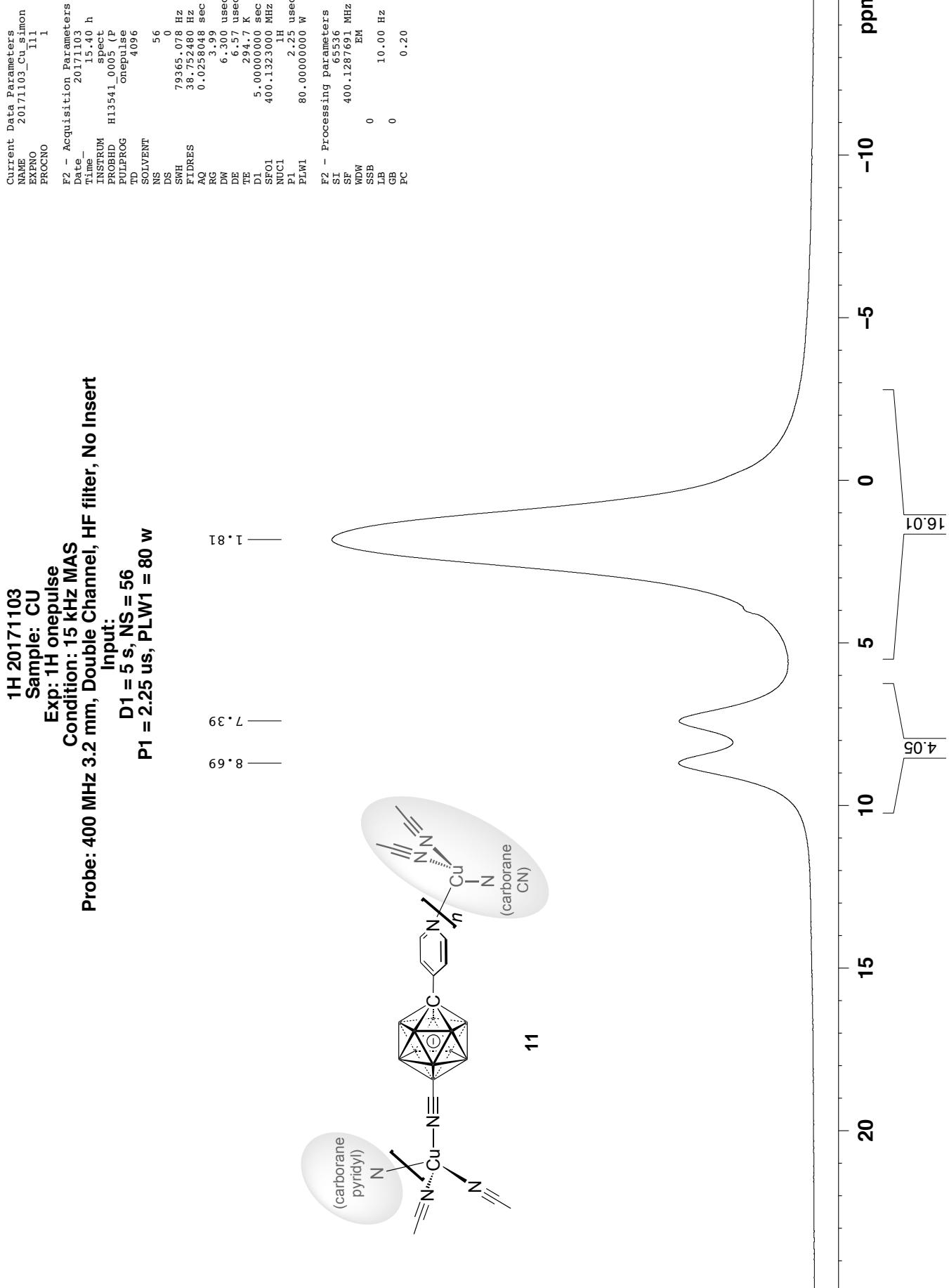
```



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



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



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

EXPTNO 1172

F2 - Acquisition Parameters

Date 20171103

Time 15:52 h

INSTRUM spect

PROBHD H13541_0005 (P

PULPROG solidecho

TD 5120

NS 512

SOLVENT

DS 0

SWH 64102.562 Hz

FLDRES 25.040094 Hz

AQ 0.039360 sec

RG 32.49

DW 7.800 usec

DE 6.50 usec

TE 294.5 K

D1 0.5000000 sec

D6 0.0000556 sec

D7 0.0004500 sec

SFO1 128.3776050 MHz

NUC1 11B

P1 180.0000000 w

PLW1 1.80 usec

P2 - Processing parameters

S1 1.28.3771266 MHz

SF 1.28.3771266 MHz

WDW 0

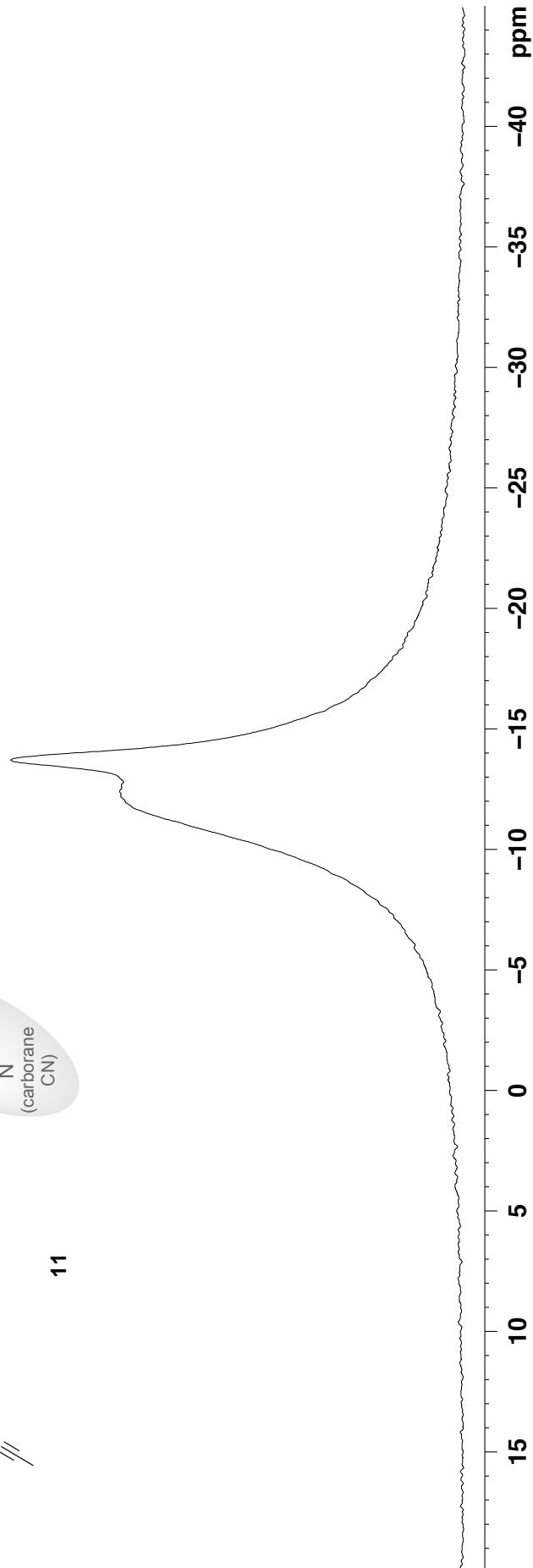
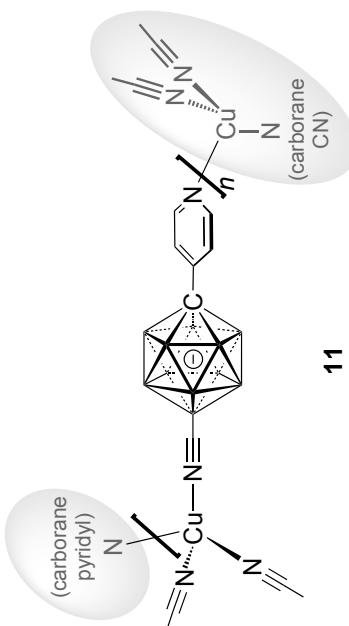
SSB 0

LB 10.00 Hz

GB 0

PC 1.40

-13.72
-12.31



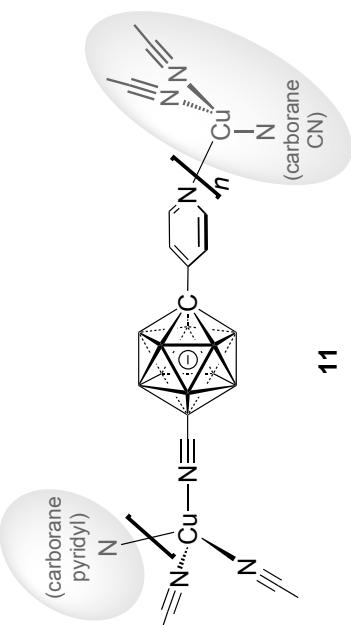
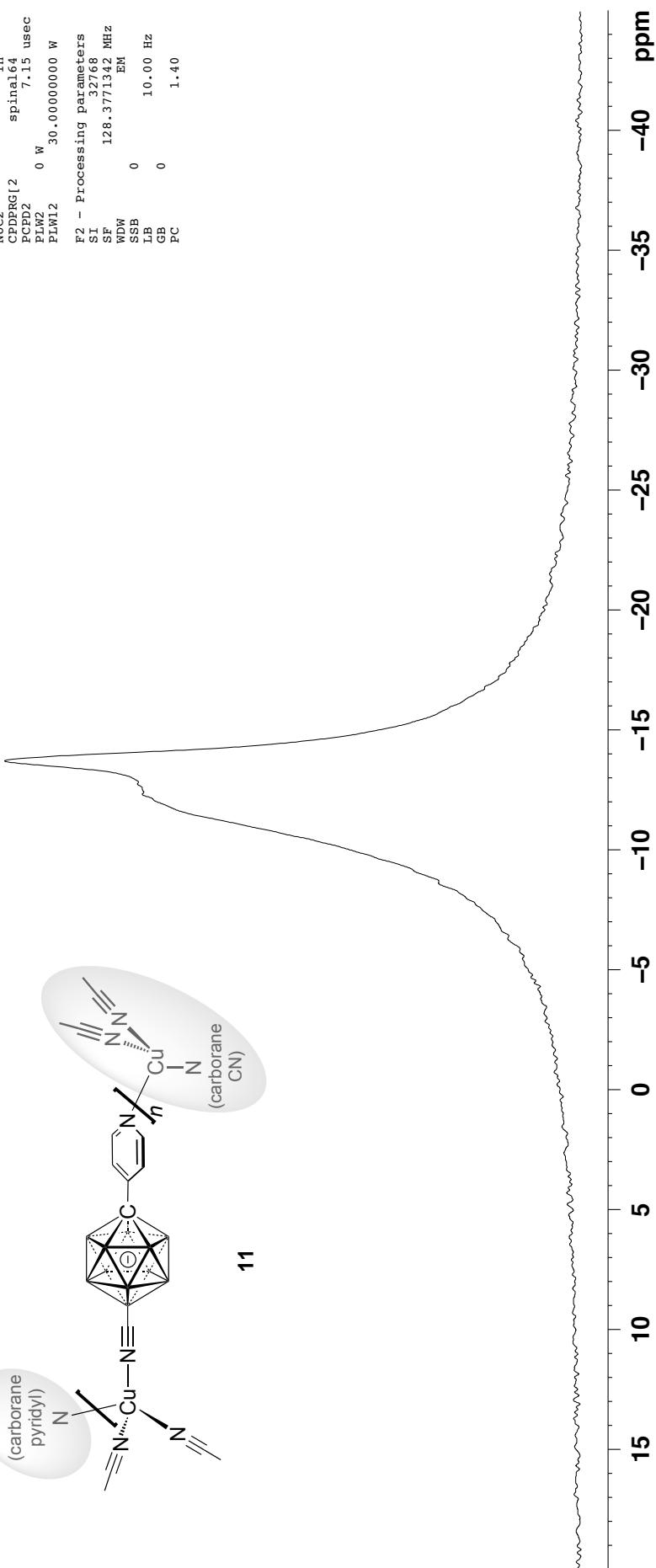
11B{¹H} 20171103
Sample: CU
Exp: 11B Hpdec_se
Condition: 18 kHz MAS
Probe: 400 MHz 3.2 mm, Double Channel, HF filter, No Insert
Input:
D1 = 0.5 s, NS = 32
P15 = 2000 us, p1 = 1.8 us, PLW1 = 180 w, PLW12 = 30, pcpd2 = 7.15

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 64102.562 Hz
 SWH 25.040064 Hz
 FIDRES 0.0399360 sec
 AQ 3.99
 RG 7.800 usec
 DW 6.50 usec
 DE 294.5 K
 CNST31 15000.0000000
 D1 3.0000000 sec
 D2 0.00006397 sec
 D3 0.00005837 sec
 P15 2000.00 usec
 ZGOPTNS SF01 128.3776050 MHz
 NUC1 11B
 P1 0.00000000 W
 P2 1.80 usec
 P3 3.60 usec
 PLW1 180.0000000 W
 SF02 400.1308003 MHz
 NUC2 1H
 CPDPRG12 CPD2 7.15 usec
 PLW2 0 W
 PLW12 30.0000000 W

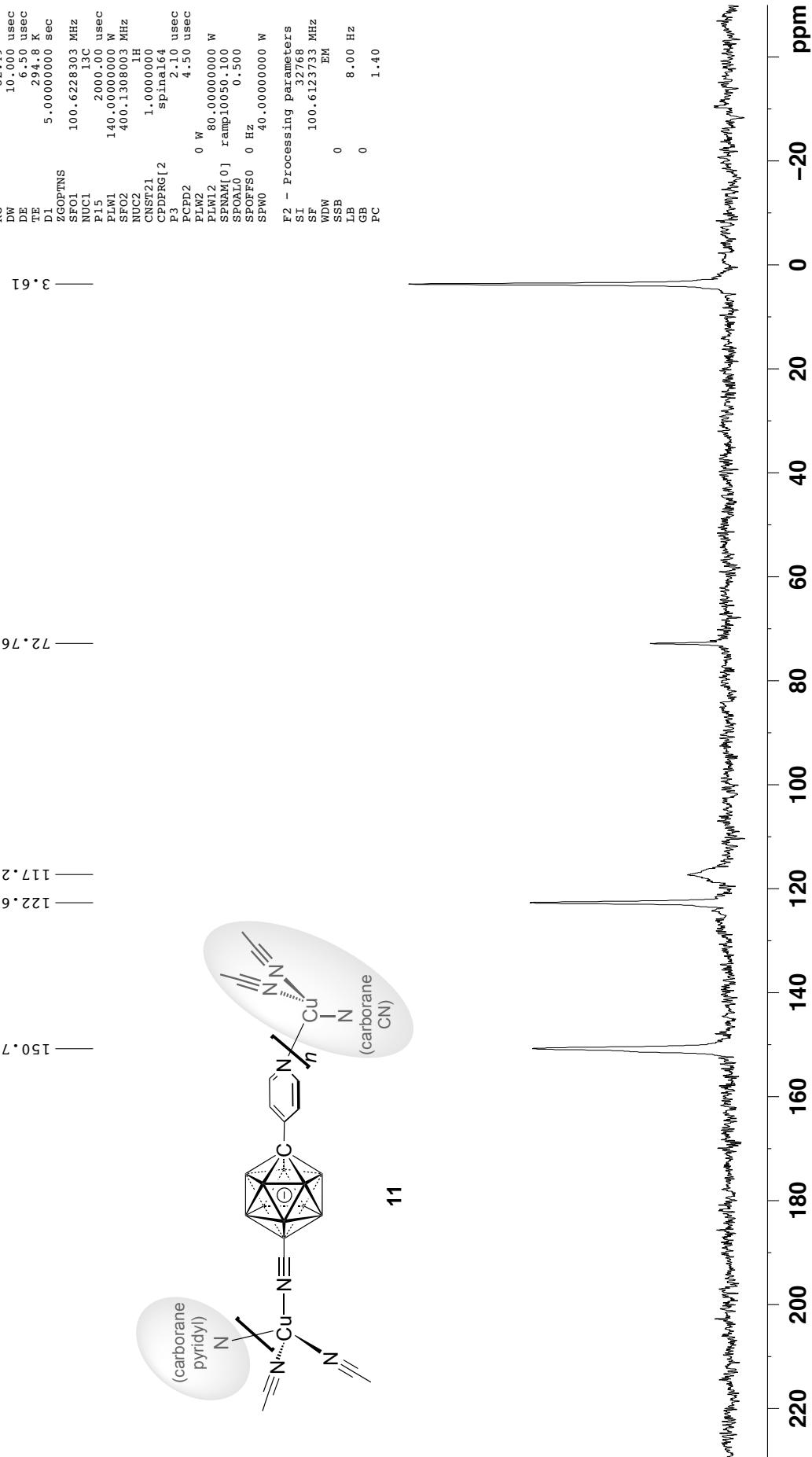
F2 - Processing parameters
 SI 32768
 SF 128.3771342 MHz
 WDW EM
 SSB 0
 LB 10.00 Hz
 GB 0
 PC 1.40

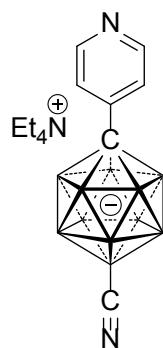
-12.42
 -13.71



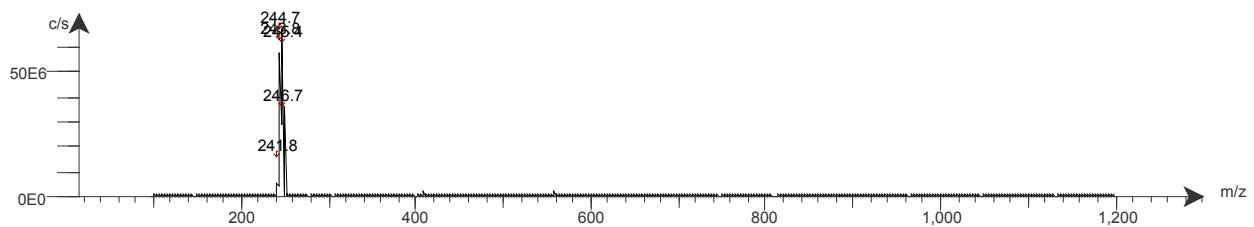
11

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

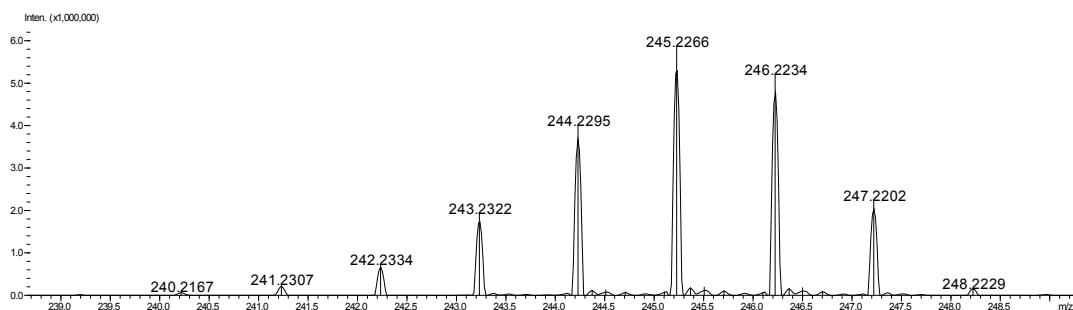




10a

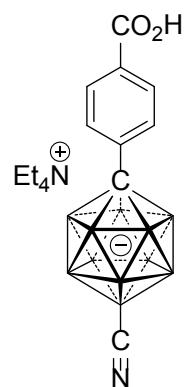


Low-resolution full-range ESI-MS negative mode

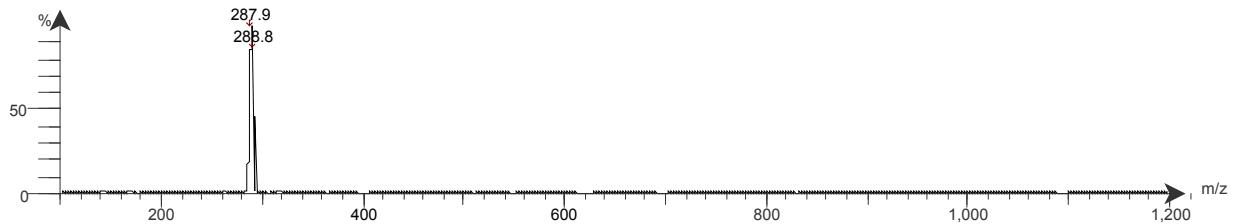


High-resolution ESI-MS negative mode

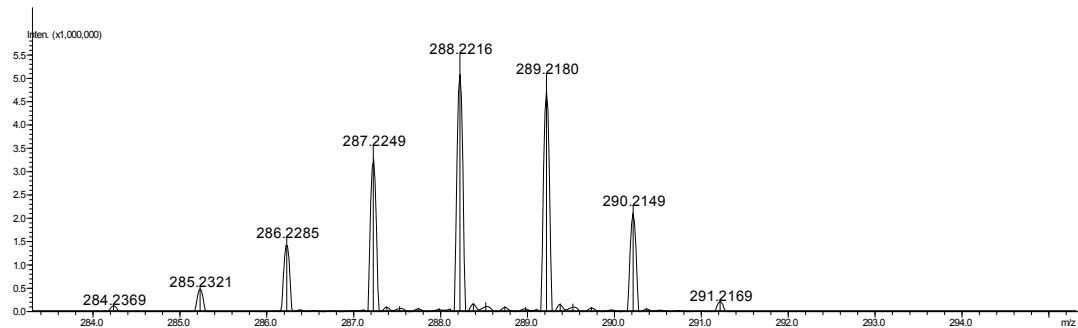
MS1



10b

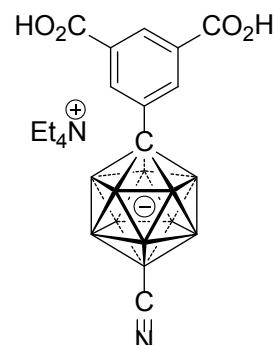


Low-resolution full-range ESI-MS negative mode

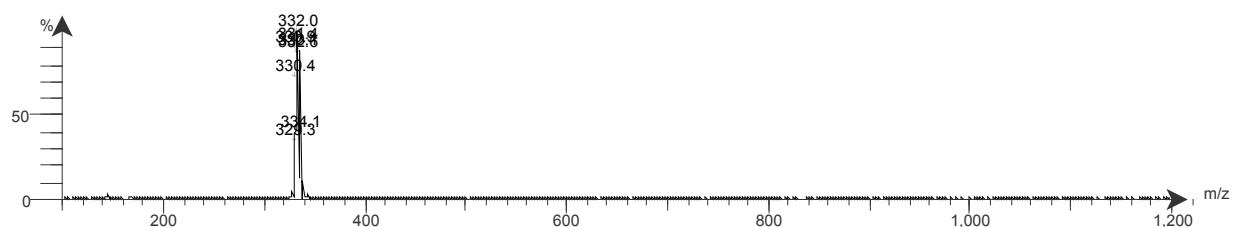


High-resolution ESI-MS negative mode

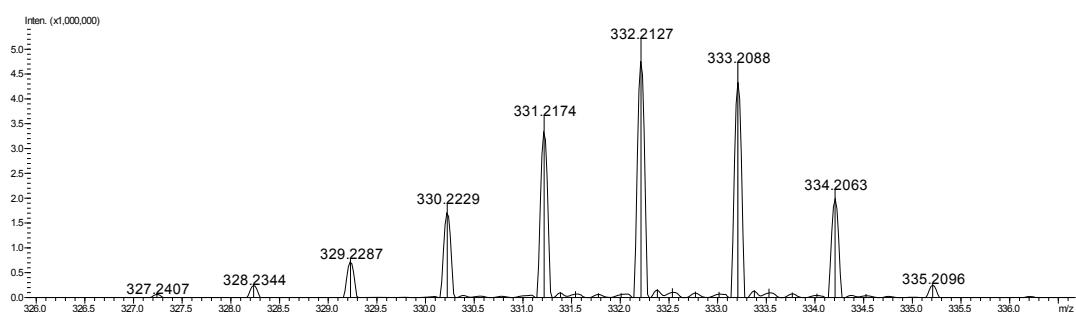
MS2



10c

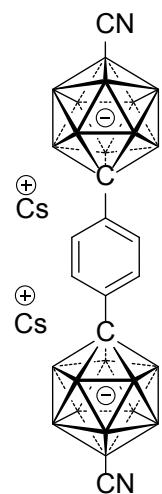


Low-resolution full-range ESI-MS negative mode

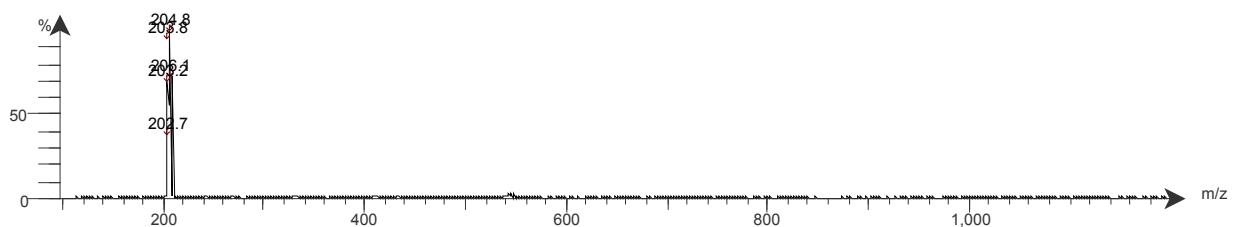


High-resolution ESI-MS negative mode

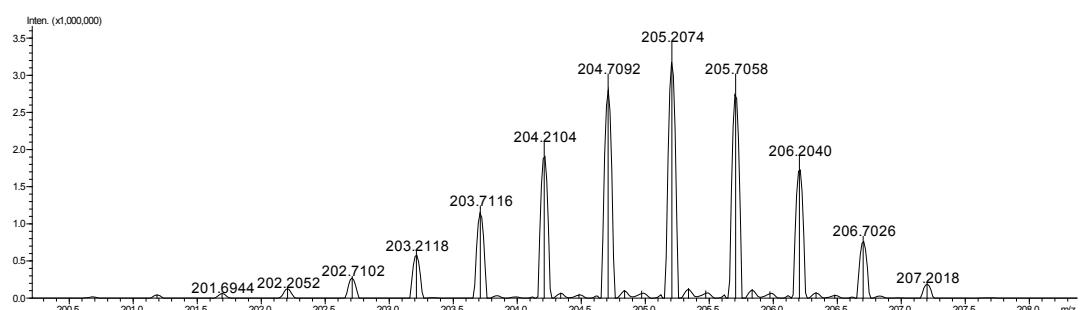
MS3



10d

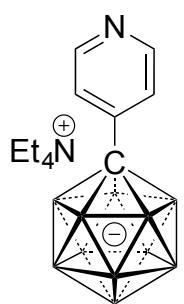


Low-resolution full-range ESI-MS negative mode

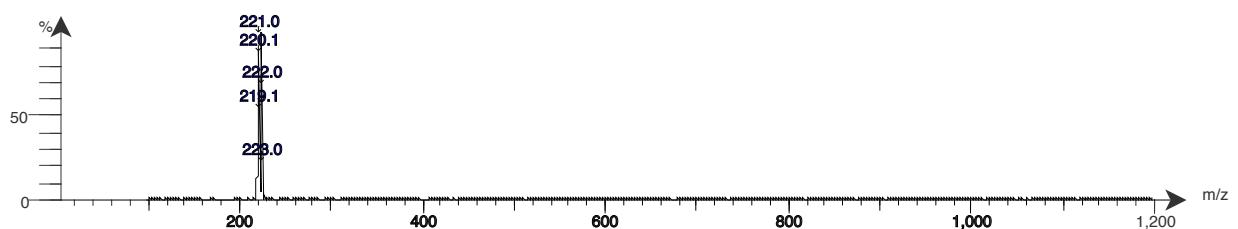


High-resolution ESI-MS negative mode

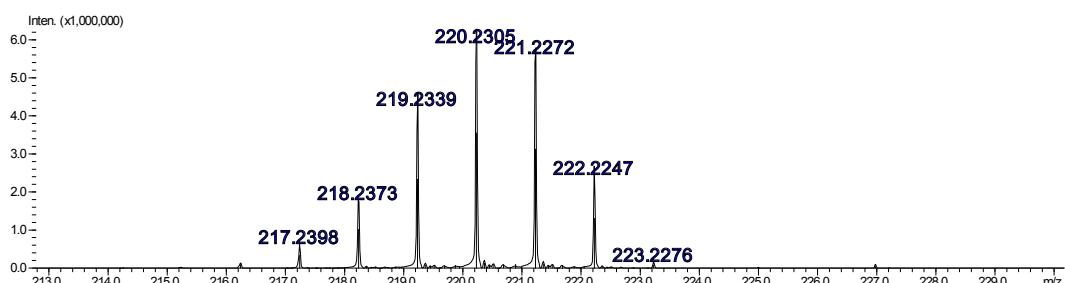
MS4



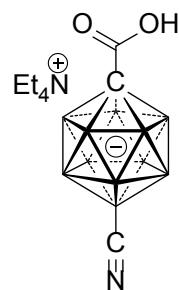
10e



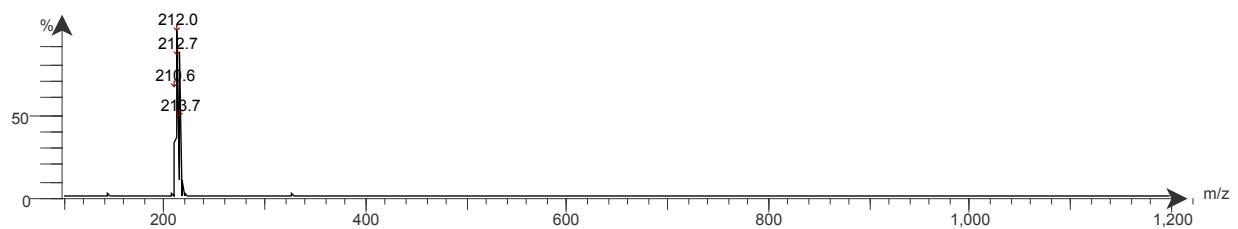
Low-resolution full-range ESI-MS negative mode



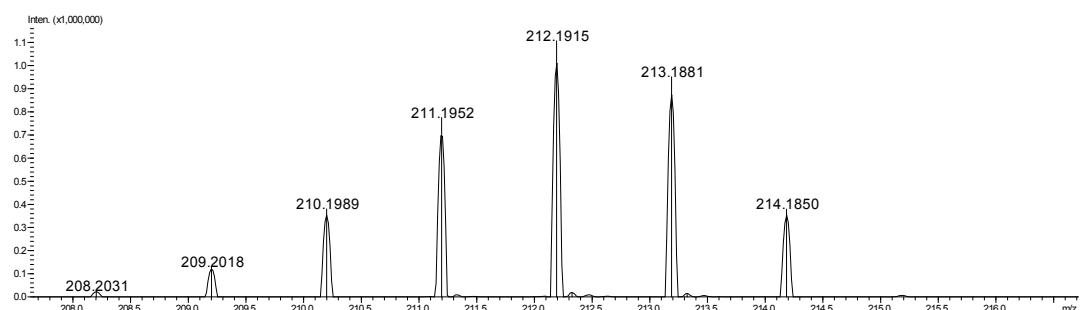
High-resolution ESI-MS negative mode



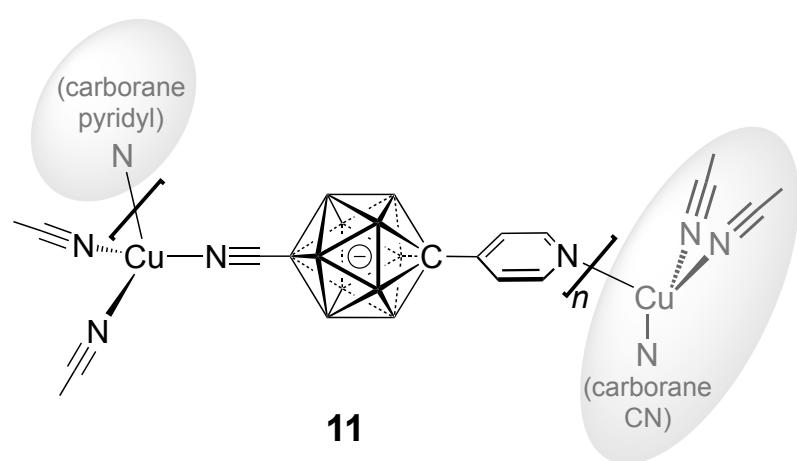
10f



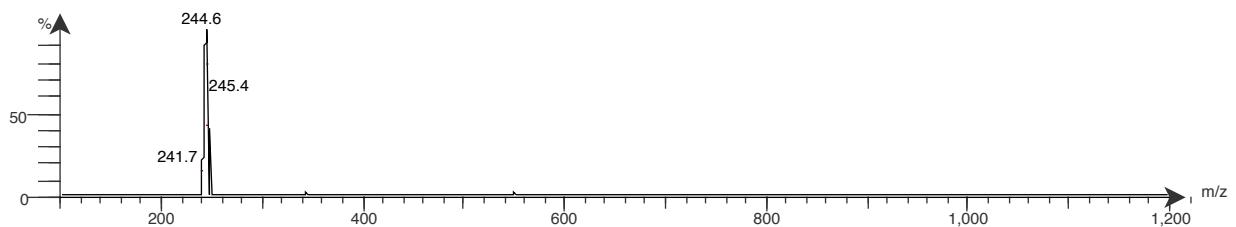
Low-resolution full-range ESI-MS negative mode



High-resolution ESI-MS negative mode



dissolved in MeCN, MS eluent = MeOH



Low-resolution full-range ESI-MS negative mode

MS7