Supplementary Information for

The 12-ethynylmonocarba-*closo*-dodecaborate anion as a versatile ligand for Cu(I) alkyne and heterobimetallic Cu(I)/M(II) (M = Pd, Pt) alkynide complexes

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I General Information

I. a) Chemicals, reaction conditions and characterization

If not otherwise specified, reagents and organic solvents were commercially available and used without further purification. Acetone-d_6 and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories and filtered through Al_2O_3 prior to use. [Cs][12-C≡CH-$CB_{11}H_{11}$] was prepared according to the literature.[1a]

Glassware for air-sensitive reations was dried at 200 °C for at least 6 h and allowed to cool in a vacuum.
Air-sensitive reactions were carried out in a glovebox under a nitrogen atmosphere with O_2, H_2O < 1 ppm.

NMR spectra were recorded on a Bruker AVANCE III 500 spectrometer (^{1}H NMR 500.13 MHz, ^{13}C NMR 125.77 MHz, ^{11}B NMR 160.46 MHz) or a Bruker AVANCE III 400 spectrometer (^{1}H 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*H*$D_2C(O)CD_3$ = 2.05 ppm, residual C*H*DCl_2 = 5.32 ppm, residual C*H*$D_2S(O)CD_3$ = 2.50 ppm, ^{13}C{^{1}H}: *C*$D_3C(O)$*C*D_3 = 29.84 ppm, *C*D_2Cl_2 = 53.84 ppm). ^{11}B and ^{11}B{^{1}H} NMR spectra were calibrated against external BF_3*Et_2O = 0 ppm (BF_3*Et_2O capillary in C_6D_6). ^{31}P{^{1}H} NMR spectra were calibrated against external 85% H_3PO_4 = 0 ppm.

IR spectra were recorded on a Nicolet iS10 FT-IR spectrometer as KBr pellets and are reported as wavenumbers (ν, cm^{-1}). Cluster B–H and alkynyl C–H stretchings were assigned according to reference [1b].

Elemental analysis was carried out by the analytical facilities of the Department of Chemistry of Zhejiang University.

Single-crystal X-ray diffraction studies were performed on an Oxford Diffraction Gemini A Ultra diffractometer equipped with 135 mm Atlas CCD detector and using Mo or Cu X-ray sources or on a Bruker D8 Venture instrument with Ga wavelength.

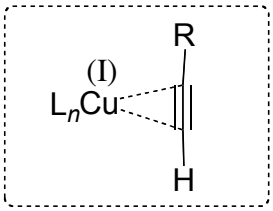
II. b) Literature search on X-ray crystal structures involving terminal alkynes coordinated to Cu(I)

General considerations:

The latest version of The Cambridge Structural Database CSD ConQuest software (CSD System; version 2.0.0) was used for the X-ray structure search in the CCDC database.

URL: https://www.ccdc.cam.ac.uk/solutions/csd-system

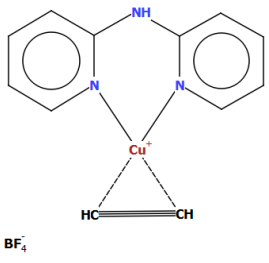
The search was carried out for X-ray crystal structures of complexes including the motif Cu(I)(η^2-RCCH)] (multiple copper centers in one complex allowed, but with no Cu-acetylene-Cu bridging; R = H or R = C)

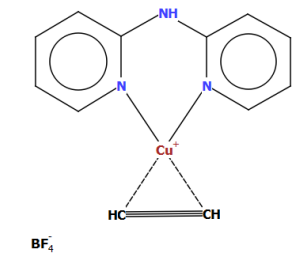
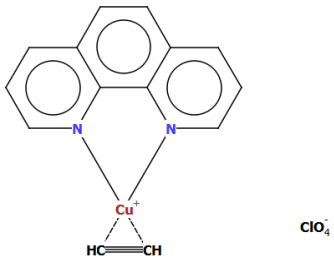


Results:

R = H. For coordination compounds of Cu(I) and unsubstituted acetylene, only three hits were found that correspond to non-bridging complexes (*i.e.*, with one side-on coordination of the acetylene to Cu(I)); molecular drawings corresponding to each X-ray structure along with the corresponding CSD refcodes and the CCDC numbers are provided in **Table S1**.

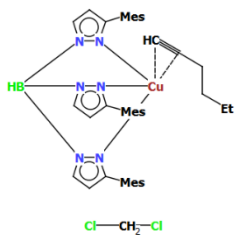
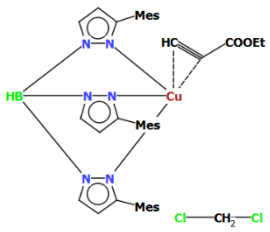
Table S1. Molecular representations of reported X-ray crystal structures of Cu(I)–acetylene complexes.

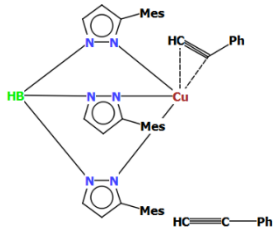
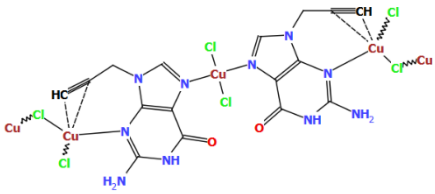
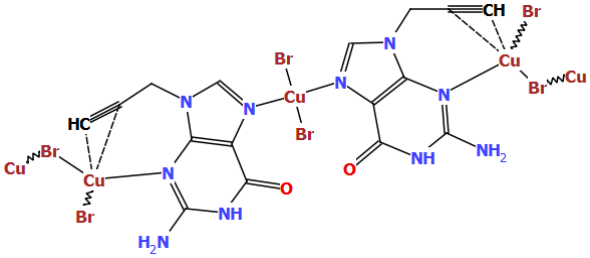
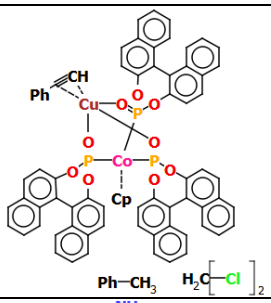
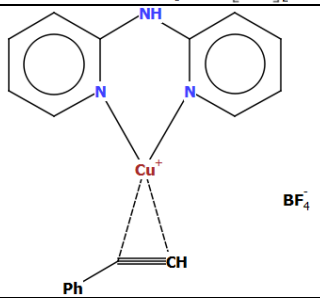
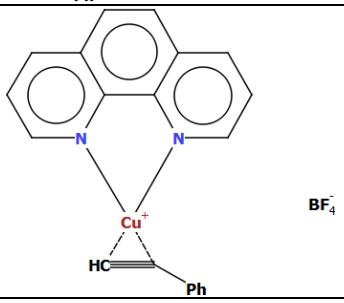
Structure	CSD refcode	CCDC number
	CADZEM	1118977

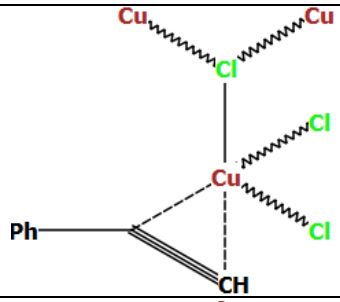
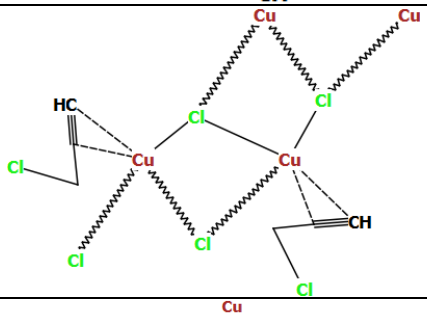
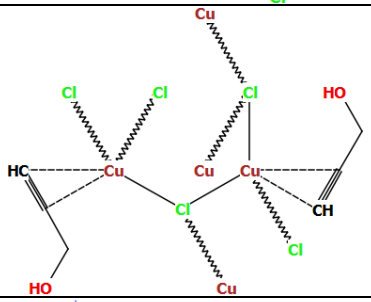
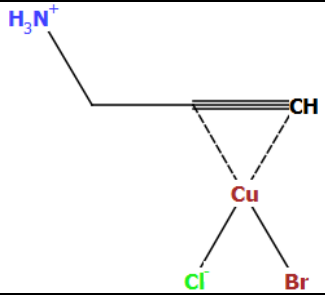
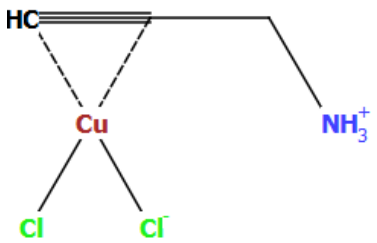
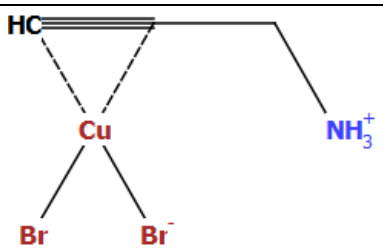
	CADZEM10	1118978
	YAFSON	--

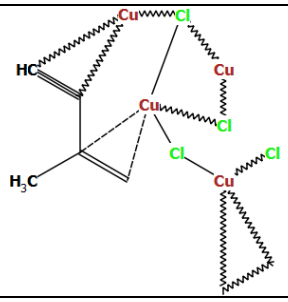
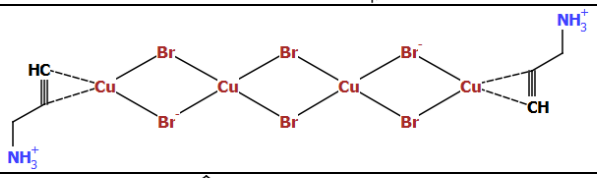
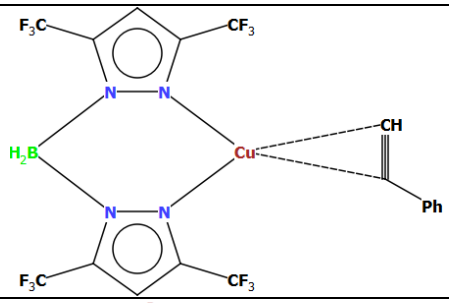
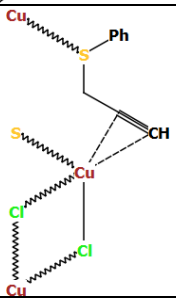
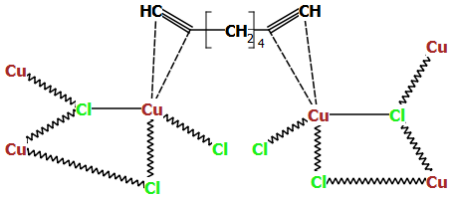
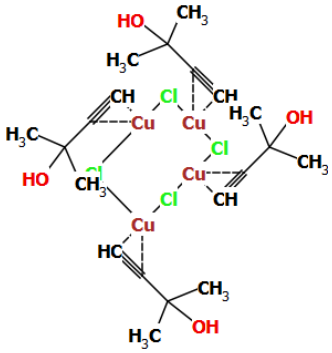
R = C. For coordination compounds of copper and terminal alkyne ligands, 25 hits were found that correspond to complexes with non-bridging terminal alkynes (*i.e.*, with one side-on coordination of the alkyne to Cu(I)). Molecular drawings corresponding to each X-ray structure along with the corresponding CSD refcodes and the CCDC numbers are provided in **Table S2**.

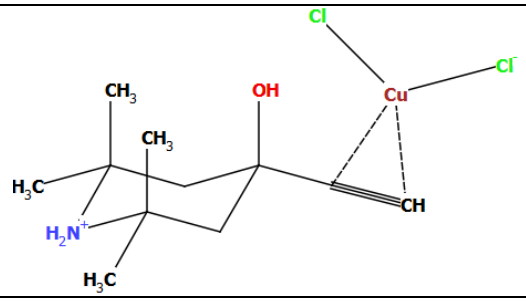
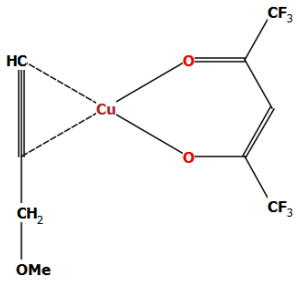
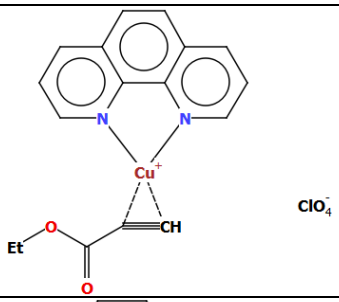
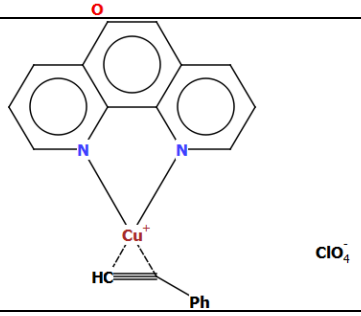
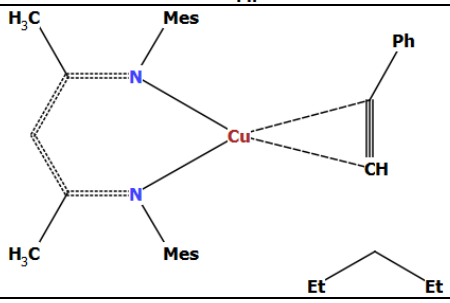
Table S2. Molecular representations of reported X-ray crystal structures of Cu(I)–(terminal alkyne) complexes.

Structure	**CSD refcode**	**CCDC number**
	CAQPAN	849107
	CAQPER	849108

	CAQPIV	867111
	HIPFUJ	808672
	HIPGAQ	808671
	IVUCUX	210585
	JIMSUW	1834245
	JIMTAD	1834246

	LEYGOL	1206364
	LEYGUR	1206365
	LEYHAY	1206366
	MIFMEU	--
	NOSZEA	176124
	NOSZIE	176125

	OFANEO	138842
	PETVOA	610419
	TASNOR	250204
	VEQXIA	818801
	VORTIF	--
	WONMUH	141001

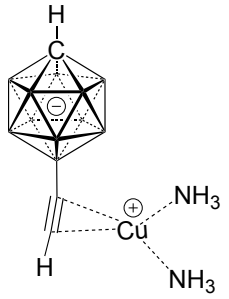
	XEMYAR	753618
	XUMMOH	190274
	YAFSIH	--
	YAFSUT	--
	YECWIN	279255

Four additional hits were found for X-ray structures of multi-metallic and bridging terminal alkyne, CSD refcodes/CCDC numbers: LITVIT/144077; GOXKOT; GOKXEJ/129611; CIKRIX/-- (structures not shown).

II Experimental Section

II. a) Preparation of Compounds 2–4

Compound 2:



A microwave tube (10 mL), equipped a magnetic stir bar, was charged with [Cs][$CB_{11}H_{11}$-12-C≡CH] (200 mg, 0.667 mmol, 1 equiv) and anhydrous EtOH (1 mL). The clear solution was stirred at 0 °C, and an aqueous solution of [$Cu(NH_3)_n$]OH (0.11 M in water, 6 mL, 0.66 mmol, 1.0 equiv, prepared from CuI + aqueous NH_3 solution) was added dropwise over 3 min using a syringe. The resulting mixture was stirred for 1 h at 0 °C. A white precipitate formed, which was separated from the supernatant by centrifugation and washed by three subsequent cycles of suspending it in water (5 mL) followed by centrifugation. Removal of water (containing also CsI) with a syringe and drying in a vacuum at 25 °C for 2 days gave compound **2** (140 mg, 80%).
Compound **2** was kept under nitrogen. Exposure to air over 2-3 days did not lead to significant decomposition; however, prolonged exposure to air (weeks) lead to oxidation as indicated by a color change to green.

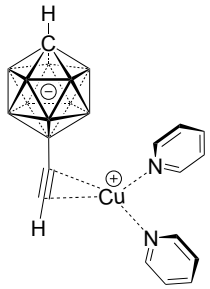
$^{1}H\{^{11}B\}$ NMR (500 MHz, acetone-d_6, 23 °C): δ 3.62 (broad signal, 1H, C≡CH), 3.40-2.61 (very broad signal, 6 H, NH), 2.28 (broad signal, 1H, cage CH), 1.69 (broad overlapping signals, 10H, BH).
^{11}B NMR (160 MHz, acetone-d_6, 23 °C): δ -6.99 (s, B-12), -12.55 (d, J = 137.70 Hz, 5B), -16.66 (d, J = 151.61Hz, 5B).
$^{11}B\{^{1}H\}$ NMR (160 MHz, acetone-d_6, 23 °C): δ -7.00 (1B), -12.55 (5B), -16.66 (5B).
$^{13}C\{^{1}H\}$ NMR (150 MHz, acetone-d_6, 23°C): δ 49.71 (cage C), 84.80 (≡CH). The B-C signal could not be detected unambiguously.
Elemental analysis: Calc. for $C_3H_{18}B_{11}CuN_2$: C 13.62%, H 6.86%, N 10.59; found: C 13.42%, H 7.02%, N 10.47%.

IR (KBr): ν (cm^{-1}) 3374, 3285, 3200 (C–H stretching of C≡C–H), 3055, 2564 (B–H), 1901 (C≡C), 1604, 1214, 1050, 1006, 662.

General procedure for Compounds 3 and 4

In a glovebox, a glass vial (4 mL), equipped a magnetic stir bar, was charged with **2** (15 mg, 0.057 mmol, 1 equiv) pyridine ligand (0.125 mmol, 2.2 equiv) or phosphine ligand (0.228 mmol, 4.0 equiv). Anhydrous EtOH (0.5 mL) was added *via* a syringe, and the resulting mixture was stirred vigorously for 3 h at 25 °C. The resulting white precipitate was collected by filtration through a glass frit and dissolved in acetone (0.5 mL) in a 4 mL glass vial to give a clear solution, followed by addition of anhydrous ethanol (0.5 mL). Slow evaporation at 25 °C afforded colorless crystals within 2 days. The crystals were collected by filtration and dried in a vacuum at 25 °C for 24 h to give compounds **3a–d** and **4a–d**.

Cu($CB_{11}H_{11}$-12-C≡CH)($Py)_2$ (3a)



3a: Prepared following the general procedure, using **2** and pyridine, compound **3a** was obtained as a colorless solid (10 mg, 45%).

$^{1}H\{^{11}B\}$ NMR (500 MHz, acetone-d_6, 23 °C): δ 8.72 (broad signal, 4H, Ar-H), 8.07 (d, 2H, Ar-H), 7.63 (broad signal, 4H, Ar-H), 4.37 (s, 1H, C≡CH), 2.24 (broad signal, 1H, cage CH), 1.59 (overlapping broad signals, 10H, BH).

^{11}B NMR (160 MHz, acetone-d_6, 23 °C): δ -7.30 (s, B-12), -12.55 (d, J = 138.53 Hz, 5B), -16.71 (d, J = 152.64 Hz, 5B).

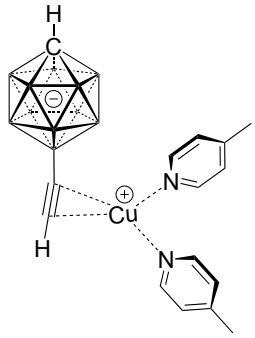
$^{11}B\{^{1}H\}$ NMR (160 MHz, acetone-d_6, 23 °C): δ -7.28(1B), -12.55 (5B), -16.71 (5B).

$^{13}C\{^{1}H\}$ NMR (126 MHz, acetone-d_6, 23 °C): δ 150.90, 139.68, 126.84 (aromatic signals), 85.08 (≡CH), 50.15 (cage C). The B-C signal could not be detected unambiguosly.

High-resolution (+)-EI-MS: *m/z* calcd for $[C_{13}H_{22}B_{11}CuN_2]^+$: 388.2175. Found: 388.2164.

IR (KBr): ν (cm^{-1}) 3176 (C–H stretching of C≡C–H), 3069, 2566 (B–H), 2538 (B–H), 1892 (C≡C), 1605, 1488, 1446, 1046, 754, 693.

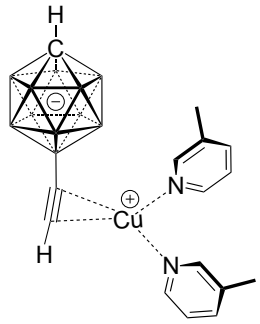
Cu($CB_{11}H_{11}$-12-C≡CH)(4-CH_3Py)$_2$ (3b):



3b: Prepared following the general procedure, using **2** and 4-methylpyridine, compound **3b** was obtained as a colorless solid (12 mg, 50%).

$^{1}H\{^{11}B\}$ NMR (500 MHz, acetone-d_6, 23 °C): δ 8.49 (broad signal, 4H, Ar-H), 7.43 (broad signal, 4H, Ar-H), 4.26 (s, 1H, C≡CH), 2.45 (s, 6H, Ar-CH_3), 2.24 (broad signal, 1H, cage CH), 1.61 (overlapping broad signals, 10H, BH).
^{11}B NMR (160 MHz, acetone-d_6, 23 °C): δ -7.25 (s, B-12), -12.53 (d, J = 138.97 Hz, 5B), -16.72 (d, J = 151.35 Hz, 5B).
$^{11}B\{^{1}H\}$ NMR (160 MHz, acetone-d_6, 23 °C): δ -7.24(1B), -12.53 (5B), -16.72 (5B).
$^{13}C\{^{1}H\}$ NMR (126 MHz, acetone-d_6, 23 °C): δ 151.87, 150.36, 126.89 (aromatic signals), 85.22 (≡CH), 50.03 (cage C), 21.17 (Ar-CH_3), The B-C signal could not be detected unambiguously.
High-resolution (+)-EI-MS: *m/z* calcd for $[C_{15}H_{26}B_{11}CuN_2]^+$: 416.2488. Found: 416.2472.
IR (KBr): ν (cm^{-1}) 3204 (C–H stretching of C≡C–H), 3062, 2559 (B–H), 1901 (C≡C), 1623, 1430, 1047, 804, 722.

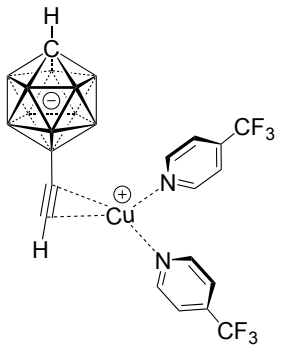
Cu($CB_{11}H_{11}$-12-C≡CH)(3-CH_3Py)$_2$ (3c):



3c: Prepared following the general procedure, using **2** and 3-methylpyridine, compound **3c** was obtained as a colorless solid (12 mg, 50%).

$^{1}H\{^{11}B\}$ NMR (500 MHz, CD_2Cl_2, 23 °C): δ 8.30 (s, 2H, Ar-H), 8.20 (broad signal, coupling not resolved, 2H, Ar-H), 7.75 (m, 2H, Ar-H), 7.39 (m, 2H, Ar-H), 4.17 (s, 1H, C≡CH), 2.38 (s, 6 H, Ar-CH_3), 2.28 (broad signal, 1H, cage CH), 1.60-1.50 (overlapping broad signals, 10H, BH).
^{11}B NMR (160 MHz, acetone-d_6, 23 °C): δ -7.25 (s, B-12), -12.49 (d, J = 138.14 Hz, 5B), -16.69 (d, J = 149.46 Hz, 5B).
$^{11}B\{^{1}H\}$ NMR (160 MHz, acetone-d_6, 23 °C): δ -7.24 (1B), -12.49 (5B), -16.69 (5B).
$^{13}C\{^{1}H\}$ NMR (126 MHz, acetone-d_6, 23 °C): δ 151.25, 148.11, 139.69, 135.90, 125.35 (aromatic signals), 85.30 (≡CH), 49.92 (cage C), 18.34 (Ar-CH_3),. The B-C signal could not be detected unambiguously.
High-resolution (+)-EI-MS: *m/z* calcd for $[C_{15}H_{26}B_{11}CuN_2]^+$: 416.2488. Found: 416.2473.
IR (KBr): ν (cm^{-1}) 3192 (C–H stretching of C≡C–H), 3073, 2918, 2560 (B–H), 2527 (B–H), 1909 (C≡C), 1609, 1484, 1049, 791, 701, 655.

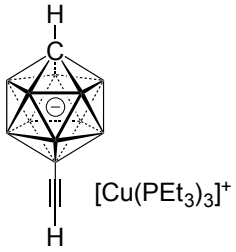
Cu($CB_{11}H_{11}$-12-C≡CH)(4-CF_3Py)$_2$ (3d):



3d: Prepared following the general procedure, using **2** and 4-trifluoromethylpyridine, compound **3d** was obtained as a colorless solid (14 mg, 53%).

$^{1}H\{^{11}B\}$ NMR (500 MHz, acetone-d_6, 23 °C): δ 9.05 (braod signal, coupling not resolved, 4H, Ar-H), 7.94 (d, 4H, J = 4.5 Hz, Ar-H), 4.34 (s, 1H, C≡CH), 2.27 (broad signal, 1H, cage CH), 1.61, 1.59 (overlapping broad signals, 10H, BH).
^{11}B NMR (160 MHz, acetone-d_6, 23 °C): δ -7.62 (s, B-12), -12.57 (d, J = 138.43 Hz, 5B), -16.64 (d, J = 152.47 Hz, 5B).
$^{11}B\{^{1}H\}$ NMR (160 MHz, acetone-d_6, 23 °C): δ -7.60 (1B), -12.57 (5B), -16.64 (5B).
$^{13}C\{^{1}H\}$ NMR (126 MHz, acetone-d_6, 23 °C): δ 152.59, 139.26 (weak, broad), 121.81 (broad) (aromatic signals), 50.34 (cage C). The CF_3, B-C and ≡CH signals could not be detected unambiguously.
High-resolution (+)-EI-MS: *m/z* calcd for $[C_{15}H_{20}B_{11}CuF_6N_2]^+$: 524.1923. Found: 524.1909.
IR (KBr): ν (cm^{-1}) 3184 (C–H stretching of C≡C–H), 3053, 2562 (B–H), 2542 (B–H), 1895 (C≡C), 1617, 1479, 1330, 1134, 1080, 711.

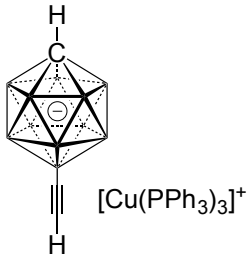
$Cu(CB_{11}H_{11}$-12-C≡CH)$(PEt_3)_3$ (4a):



4a: Prepared following the general procedure, using **2** and 4 equiv of PEt_3, compound **4a** was obtained as a colorless solid (32 mg, 95%).

$^1H\{^{11}B\}$ NMR (400 MHz, acetone-d_6, 23 °C): δ 2.15 (broad signal, 1H, cage CH), 1.87 (m, 18H, CH_2 of PEt_3), 1.85 (s, 1H, C≡CH), 1.73 (broad signal, 5H, BH), 1.64 (broad signal, 5H, BH), 1.16 (broad signal, 27H, CH_3 of PEt_3).
^{11}B NMR (128 MHz, acetone-d_6, 23 °C): δ -7.43 (s, B-12), -12.23 (d, J = 140.12 Hz, 5B), -16.73 (d, J = 151.45 Hz, 5B).
$^{11}B\{^1H\}$ NMR (128 MHz, acetone-d_6, 23 °C): δ -7.41 (1B), -12.23 (5B), -16.73 (5B).
$^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6, 23 °C): δ -9.53.
$^{13}C\{1H\}$ NMR (100 MHz, acetone-d_6, 23°C): δ 81.45 (≡CH), 48.76 (cage C), 16.85, 8.86. The B-C signal could not be detected unambiguously.
High-resolution (+)-ESI-MS: *m/z* calcd for $[C_{18}H_{45}CuP_3]^+$: 417.2030. Found: 417.2019.
IR (KBr): ν (cm^{-1}) 3292 (C–H stretching of C≡C–H), 2965, 2933, 2908, 2873, 2556 (B–H), 1935, 1620, 1450, 1052, 1035, 758, 719.

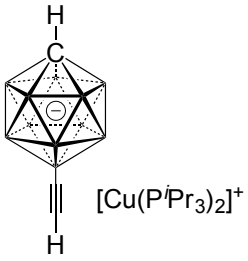
Cu($CB_{11}H_{11}$-12-C≡CH)(PPh_3)$_3$ (4b):



4d: Prepared following the general procedure, using **2** and 4 equiv of PPh_3, compound **4d** was obtained as a colorless solid (50 mg, 86%).

$^{1}H\{^{11}B\}$ NMR (500 MHz, acetone-d_6, 23 °C): δ 7.47 (m, 9H, Ar-H), 7.29 (m, 18H, Ar-H), 7.18 (m, 18H, Ar-H), 2.16 (broad signal, 1H, cage CH), 1.85 (s, 1H, C≡CH), 1.74 (broad signal, 5H, BH), 1.64 (broad signal, 5H, BH).
^{11}B NMR (160 MHz, acetone-d_6, 23 °C): δ -7.58 (s, B-12), -12.36 (d, J = 138.45 Hz, 5B), -16.85 (d, J = 148.64 Hz, 5B).
$^{11}B\{^{1}H\}$ NMR (160 MHz, acetone-d_6, 23 °C): δ -7.64 (1B), -12.36 (5B), -16.85 (5B).
$^{31}P\{^{1}H\}$ NMR (202 MHz, acetone-d_6, 23 °C): δ 0.16.
$^{13}C\{1H\}$ NMR (125 MHz, acetone-d_6, 23°C): δ 134.46 (d, J =13.90 Hz), 132.01 (d, J =30.74 Hz), 131.61, 129.96 (d, J = 7.5 Hz), 81.25 (≡CH), 48.78 (cage C). The B-C signal could not be detected unambiguously.
High-resolution (+)-ESI-MS: *m/z* calcd for $[C_{54}H_{45}CuP_3]^+$: 849.2030. Found: 849.2020.
IR (KBr): ν (cm^{-1}) 3269 (C–H stretching of C≡C–H), 3244, 3055, 2558 (B–H), 1648, 1435, 1095, 1051, 1005, 744, 695, 517.

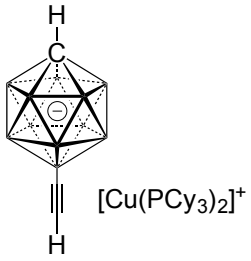
$(CB_{11}H_{11}$-12-C≡CH)$Cu(PiPr_3)_2$ (4c):



4c: Prepared following the general procedure, using **2** and 4 equiv of P*i*Pr_3, compound **4c** was obtained as a colorless solid (30 mg, 95%).

$^1H\{^{11}B\}$ NMR (500 MHz, acetone-d_6, 23 °C): δ 2.32 (m, 6H, CH of $PiPr_3$), 2.16 (broad signal, 1H, cage CH), 1.86 (s, 1H, C≡CH), 1.73 (broad signal, 5H, BH), 1.64 (broad signal, 5H, BH) 1.33 (m, 36H, CH_3 of $PiPr_3$).
^{11}B NMR (160 MHz, acetone-d_6, 23 °C): δ -7.42 (s, B-12), -12.24 (d, J = 139.18 Hz, 5B), -16.73 (d, J = 151.46 Hz, 5B).
$^{11}B\{^1H\}$ NMR (160 MHz, acetone-d_6, 23 °C): δ -7.47 (1B), -12.24 (5B), -16.73 (5B).
$^{31}P\{^1H\}$ NMR (202 MHz, acetone-d_6, 23 °C): δ 27.53 (only one signal was detected).
$^{13}C\{1H\}$ NMR (125 MHz, acetone-d_6, 23°C): δ 81.02 (≡CH), 48.76 (cage C), 23.14, 20.70. The B-C signal could not be detected unambiguously.
High-resolution (+)-ESI-MS: *m/z* calcd for $[C_{18}H_{42}CuP_2]^+$: 383.2058. Found: 383.2041.
IR (KBr): ν (cm^{-1}) 3430, 3283 (C–H stretching of C≡C–H), 2961, 2561 (B–H), 2142, 1463, 1387, 1051, 1006, 883.

$Cu(CB_{11}H_{11}$-12-C≡CH)$(PCy_3)_2$ (4d)

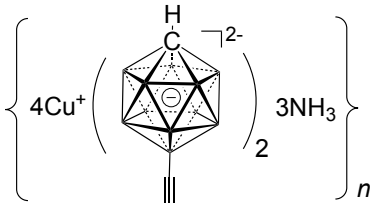


4d: Prepared following the general procedure, using **2** and 4 equiv of PCy_3, compound **4d** was obtained as a colorless solid (40 mg, 83%).

$^{1}H\{^{11}B\}$ NMR (500 MHz, acetone-d_6, 23 °C): 2.15 (broad signal, 1H, cage CH), 2.13-1.93 (overlapping m, 18H, cyclohexyl signals), 1.89-1.78 (m, 13H, cyclohexyl signals overlapping with C≡CH), 1.77-1.68 (m, 11H, cyclohexyl signals overlapping with 5 BH), 1.64 (broad signal, 5H, BH), 1.57-1.44 (m, 12 H, cyclohexyl signals), 1.44-1.21 (m, 18H, cyclohexyl signals).
^{11}B NMR (160 MHz, acetone-d_6, 23 °C): δ -7.54 (s, B-12), -12.35 (d, J = 138.33 Hz, 5B), -16.83 (d, J = 150.02 Hz, 5B).
$^{11}B\{^{1}H\}$ NMR (160 MHz, acetone-d_6, 23 °C): δ -7.58 (1B), -12.35 (5B), -16.85 (5B).
$^{31}P\{^{1}H\}$ NMR (202 MHz, acetone-d_6, 23 °C): δ 13.17.
$^{13}C\{1H\}$ NMR (125 MHz, acetone-d_6, 23°C): δ 81.39 (≡CH), 48.74 (cage C), 33.34 (cyclohexyl CH), 31.39 (cyclohexyl CH_2), 28.02 (cyclohexyl CH_2), 26.82 (cyclohexyl CH_2). The B-C signal could not be detected unambiguously. The four cyclohexyl signals were broad and showed a relative integration of 1:2:2:1; the coupling to ^{31}P was not resolved. In a reference measurement of PCy_3 in acetone-d_6, the $^{13}C\{1H\}$ resonances appeared in a 1:2:2:1 ratio at δ 31.47 (*d*, J = 17.8 Hz), 32.01 (*d*, J = 12.6 Hz), 28.32 (*d*, J = 9.2 Hz), 27.30 (s).
High-resolution (+)-ESI-MS: *m/z* calcd for $[C_{36}H_{66}CuP_2]^+$: 623.3936. Found: 623.3923.
IR (KBr): ν (cm^{-1}) 3305 (C–H stretching of C≡C–H), 2928, 2851, 2554 (B–H), 1447, 1052, 1005.

II. b) Preparation of Compounds 5–7

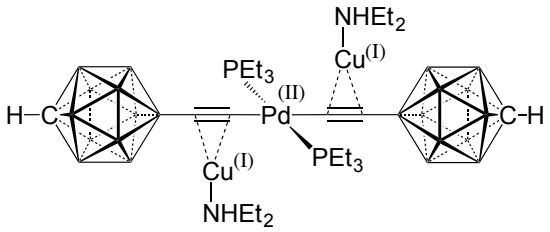
Compound 5:



A microwave tube (25 mL), equipped with a magnetic stir bar, was charged with **2** (150 mg, 0.566 mmol, 1 equiv) and anhydrous EtOH (1 mL). During vigorous stirring at 25 °C, an aqueous solution of $[Cu(NH_3)_2]OH$ (0.18 M in water, 3.8 mL, 0.68 mmol, 1.2 equiv, prepared from CuI (1.2 equiv) in aqueous NH_3) was added. The resulting mixture was stirred for 2 h. The yellow precipitate was separated from the supernatant by centrifugation and three subsequent cycles of suspending in water (5 mL) followed by centrifugation. Removal of water with a syringe and drying in a vacuum at 25 °C for 2 days gave compound **5** as a yellow solid (170 mg, 94%).

The analytical data matched with the ones reported.[1c]

Compound 6a:

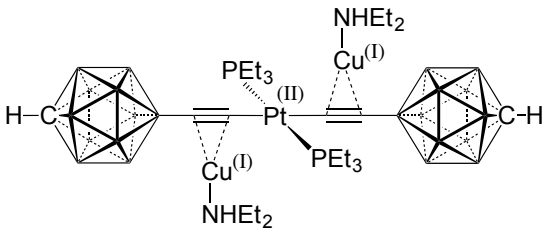


A vial (4 mL), equipped a magnetic stir bar, was charged with **5** (40 mg, 0.078 mmol, 1 equiv), *trans*-dichlorobis(triethylphosphine)palladium(II) (46.4 mg, 0.078 mmol, 1.0 equiv) and anhydrous $HNEt_2$ (2 mL). After stirring for 1 h at 25°C, the white precipitate that formed was collected by filtration through a glass frit and dried in a vacuum at 25 °C to give Compound **6a** (66.8 mg, 90%).

This product exhibits low solubility in acetone, acetonitrile, dichloromethane, dimethyl formamide, dimethyl sulfoxide and tetrahydrofuran. We were not able to obtain satisfactory $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data.

$^1H\{^{11}B\}$ NMR (400 MHz, acetone-d_6, 23 °C): δ 3.00 (m, 8H, CH_2 of $HNEt_2$), 2.27 (broad signal, 2H, cage CH), 2.02 (m, 12H), 1.76 (broad signal, 10H, BH), 1.69 (broad signal, 10H, BH) 1.37 (m, 12H), 1.18 (m, 18H).
^{11}B NMR (128 MHz, acetone-d_6, 23 °C): δ -7.45 (s, B-12), -12.41 (d, J = 148.55 Hz, 5B), -16.36 (d, J = 142.35 Hz, 5B).
$^{11}B\{^1H\}$ NMR (128 MHz, acetone-d_6, 23 °C): δ -7.49 (1B), -12.41 (5B), -16.36 (5B).
Elemental analysis: Calc. for $C_{26}H_{74}B_{22}Cu_2N_2P_2Pd$: C 32.94%, H 7.87%, N 2.95%; found: C 32.86%, H 7.86%, N 2.79%.

Compound 6b:

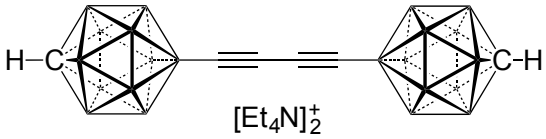


A vial (4 mL), equipped a magnetic stir bar, was charged with **5** (40 mg, 0.078 mmol, 1 equiv), *trans*-diiodobis(triethylphosphine)platinum(II) (53 mg, 0.078 mmol, 1.0 equiv) and anhydrous $HNEt_2$ (2 mL). After stirring for 1 h at 25°C, the white precipitate that formed was collected by filtration through a glass frit and dried in a vacuum at 25 °C to give compound **6b** (74.3 mg, 92%).

This product exhibits low solubility in acetone, acetonitrile, dichloromethane, dimethyl formamide, dimethyl sulfoxide and tetrahydrofuran. We were not able to obtain satisfactory $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data.

$^1H\{^{11}B\}$ NMR (400 MHz, DMSO-d_6, 23 °C): δ 2.72 (m, 8H), 2.36 (broad signal, 2H, cage CH), 1.96 (m, 12H), 1.62 (broad signal, 10H, BH), 1.55 (broad signal, 10H, BH), 1.17 (m, 12H), 1.05 (m, 18H).
^{11}B NMR (128 MHz, DMSO-d_6, 23 °C): δ -6.27 (s, B-12), -12.44 (d, J = 147.75 Hz, 5B), -16.73 (d, J = 144.55 Hz, 5B).
$^{11}B\{^1H\}$ NMR (128 MHz, DMSO-d_6, 23 °C): δ -6.31 (1B), -12.44 (5B), -16.73 (5B).
Elemental analysis: Calc. for $C_{26}H_{74}B_{22}Cu_2N_2P_2Pt$: C 30.12%, H 7.19%, N 2.70%; found: C 29.58%, H 6.96%, N 2.16%.

Compound 7:



A glass vial (4 mL), equipped a magnetic stir bar, was charged with **5** (40 mg, 0.078 mmol, 1 equiv). Anhydrous ethanol (1.0 mL) was added *via* a syringe, and the resulting mixture was stirred vigorously open to air for 2 h at 25 °C. Water (5.0 mL) was slowly added, and ethanol was removed using a rotary evaporator. HCl solution (1 M in H_2O, 5 mL, 5 mmol) was added, and the mixture was extracted with diethyl ether (3 x 15 mL). The combined organic layers were dried over Cs_2CO_3, filtered into a 100 mL one-necked round-bottom flask. To the flask water (8 mL) was added. Diethyl ether was removed using a rotary evaporator, and the turbid water layer was filtered into a 25 mL flask. $[Et_4N]^+Br^-$ (65 mg, 2.21 equiv) was added to the filtrate, and the resulting white solid was collected by filtration through a glass frit and dried in a vacuum at 65 °C for 12 h to give compound **7** (43.9 mg, 95%).

$^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN, 23 °C): δ 3.16 (q, J = 7.26 Hz, 16H, CH_2 of cation), 2.28 (s, 2H, cage CH), 1.57 (overlapping broad signals, 20H, BH), 1.21 (m, 24H, CH_3 of cation).

^{11}B NMR (128 MHz, CD_3CN, 23 °C): δ -7.82 (s, B-12), -12.45 (d, J = 139.34 Hz, 5B), -16.62 (d, J = 150.71 Hz, 5B).

$^{11}B\{^1H\}$ NMR (128 MHz, CD_3CN, 23 °C): δ -7.81 (2B), -12.45 (10B), -16.62 (10B).

$^{13}C\{1H\}$ NMR (101 MHz, CD_3CN, 23 °C): δ 89.92 (broad q, B-C), 80.03 (broad signal, ≡CH), 53.06 (CH_2 of cation), 49.57 (cage C), 7.70 (CH_3 of cation).

High-resolution (–)-ESI-MS: *m/z* calcd for $[C_6H_{22}B_{22}]^{2-}$: 166.1957. Found: 166.1993.

III X-ray Crystallography

General remarks

CCDC1910714–1910719, 1910721 and 1910723–1910725 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.

The structures were solved with the dual-space algorithm using *SHELXT*[2] and were refined by full-matrix least-squares methods on F^2 with *SHELXL-2014*[3] using the GUI *OLEX2*[4]. The graphical output was produced with the help of the program *Mercury*[5].
The terminal hydrogen atoms of the copper-bound alkynes were always found in the difference electron density map and refined at a 20% bigger isotropic value than the corresponding adjacent mother carbon atom. If needed, the C–H distance was restrained to 0.96 Å. Hydrogen atoms of the carboranes bound to a carbon atom were refined with the AFIX 154 command, allowing the C–H distance to vary. If the distances became too short, they were fixed at a minimal distance of 0.96 Å.

Table S3. Summary of X-ray diffraction data.

Compound	**2a**	**3a**	**3b**	**3c**
Empirical formula	$C_9H_{26}B_{11}CuN_2$	$C_{13}H_{22}B_{11}CuN_2$	$C_{15}H_{26}B_{11}CuN_2$	$C_{15}H_{26}B_{11}CuN_2$
M (g/mol)	344.78	388.77	416.83	416.83
Wavelength(Å)	1.34139	0.71073	0.71073	0.71073
T (K)	170	150	296	293
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	C2/c	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	27.1076(7)	8.2894(7)	12.8275(7)	8.3718(8)
b (Å)	7.1263(2)	11.3934(10)	10.7515(5)	11.5149(11)
c (Å)	19.4860(5)	11.7893(10)	17.3597(9)	13.4954(9)
α (°)	90	71.393(7)	90.00	102.473(7)
β (°)	102.529(2)	79.489(7)	108.206(2)	106.926(7)
γ (°)	90	70.380(8)	90.00	107.523(9)
Volume ($Å^3$)	3674.61(17)	990.43(16)	2274.3(2)	1119.18(18)
Z	8	2	4	2
D_{calc} (g/cm^3)	1.246	1.304	1.217	1.237
μ (mm^{-1})	6.329	1.102	0.964	0.979
F (000)	1424	396	856	428
N (coll. refl.)	3494	3596	4462	4083
N (parameters/restraints)	227/0	248/0	268/0	268/0
*R*1	0.0485	0.0435	0.0707	0.0468
*wR*2	0.1006	0.1032	0.1107	0.1155
GOF	1.013	1.050	1.068	1.047
CCDC	1910714	1910715	1910716	1910717

Table S3. (continued).

Compound	**3d**	**4b**	**4c**
Empirical formula	$C_{15}H_{20}B_{11}CuF_6N_2$	$C_{57}H_{57}B_{11}CuP_3$	$C_{21}H_{54}B_{11}CuP_2$
M (g/mol)	524.78	1017.38	551.03
Wavelength(Å)	0.71073	0.71073	0.71073
T (K)	170	150	293
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	10.0994(8)	12.5248(8)	11.9970(7)
b (Å)	11.2360(9)	12.9185(8)	15.5376(7)
c (Å)	11.7320(9)	18.8957(9)	17.7707(8)
α (°)	66.212(7)	106.031(5)	90
β (°)	75.011(7)	97.416(4)	92.697(5)
γ (°)	89.796(7)	104.435(5)	90
Volume ($Å^3$)	1169.09(17)	2780.6(3)	3308.9(3)
Z	2	2	4
D_{calc} (g/cm^3)	1.491	1.215	1.106
μ (mm^{-1})	0.990	0.516	0.767
F (000)	524	1056	1176
N (coll. refl.)	4264	10143	6266
N (parameters/restraints)	320/1	650/90	329/0
*R*1	0.0504	0.0613	0.0424
*wR*2	0.1302	0.1726	0.1107
GOF	1.046	1.034	1.018
CCDC	1910718	1910719	1910721

Table S3. (continued).

Compound	**6a**	**6b**	**7**
Empirical formula	$C_{32}H_{86}B_{22}Cu_2N_2O_2P_2Pd$	$C_{32}H_{86}B_{22}Cu_2N_2O_2P_2Pt$	$C_{22}H_{62}B_{22}N_2$
M (g/mol)	1064.26	1152.97	592.55
Wavelength(Å)	0.71073	0.71073	0.71073
T (K)	293	293	293
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	C2/c
a (Å)	15.7282(9)	15.7322(6)	33.205(4)
b (Å)	10.9616(6)	10.9370(5)	11.124(1)
c (Å)	17.0109(14)	16.9807(11)	22.362(3)
α (°)	90	90	90
β (°)	97.662(6)	97.802(5)	110.903(16)
γ (°)	90	90	90
Volume ($Å^3$)	2906.9(3)	2474.7(2)	7716.4(18)
Z	2	2	8
D_{calc} (g/cm^3)	1.216	1.323	1.020
μ (mm^{-1})	1.115	3.223	0.049
F (000)	1104	1168	2544
N (coll. refl.)	5307	5279	7024
N (parameters/restraints)	294/1	294/0	490/14
*R*1	0.0524	0.0464	0.0904
*wR*2	0.1381	0.1130	0.3023
GOF	1.030	1.059	1.037
CCDC	1910723	1910724	1910725

Crystal structure of 2' (CCDC1910714)

Compound **2** (25 mg) was dissolved in acetone (0.5 mL) in a 4 mL glass vial. The resulting solution was filtered into an 18 cm long glass NMR tube and layered with hexane (1.0 mL). Colorless crystals of the composition $[Cu(CB_{11}H_{11}\text{-}12\text{-}C{\equiv}CH)(H_2N\text{-}C(CH_3)_2CH_2(CH_3)C{=}NH)_2]$ suitable for X-ray diffraction grew within 4 d at 25 °C.

```
Bond precision:  C-C = 0.0050 A          Wavelength=1.34139

Cell:           a=27.1076(7)    b=7.1263(2)         c=19.4860(5)
                alpha=90        beta=102.529(2)     gamma=90
Temperature:    170 K

                Calculated                Reported
Volume          3674.61(17)               3674.60(17)
Space group     C 2/c                     C 1 2/c 1
Hall group      -C 2yc                    -C 2yc
Moiety formula  C9 H26 B11 Cu N2          C9 H26 B11 Cu N2
Sum formula     C9 H26 B11 Cu N2          C9 H26 B11 Cu N2
Mr              344.78                    344.77
Dx,g cm-3       1.246                     1.246
Z               8                         8
Mu (mm-1)       6.335                     6.329
F000            1424.0                    1424.0
F000'           1403.55
h,k,lmax        32,8,23                   32,8,23
Nref            3503                      3494
Tmin,Tmax       0.927,0.969               0.535,0.751
Tmin'           0.531

Correction method= # Reported T Limits: Tmin=0.535 Tmax=0.751
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 54.938

R(reflections)= 0.0485( 2343)     wR2(reflections)= 0.1006( 3494)

S = 1.013                 Npar= 227
```

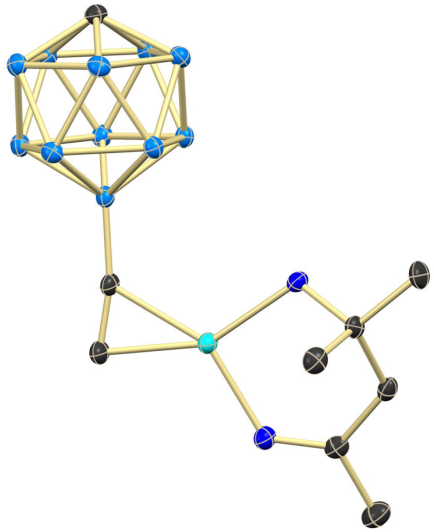


Figure S1. ORTEP representation of **2'**. Hydrogen atoms are omitted for clarity; 30% displacement ellipsoids.

Crystal structure of 3a (CCDC1910715)

Compound **3a** (10 mg) was dissolved in anhydrous ethanol (2.0 mL) in a 4 mL glass vial to give a clear solution, then added 2 drops of acetone. Slow evaporation afforded colorless crystals of the composition [($CB_{11}H_{11}$-12-C≡CH)$Cu(Py)_2$] suitable for X-ray diffraction within 4 d at 25 °C.

```
Bond precision:  C-C = 0.0050 A          Wavelength=0.71073

Cell:          a=8.2894(7)       b=11.3934(10)    c=11.7893(10)
               alpha=71.393(7)   beta=79.489(7)   gamma=70.380(8)
Temperature:   150 K

                Calculated                Reported
Volume          990.43(16)                990.43(16)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C13 H22 B11 Cu N2         C13 H22 B11 Cu N2
Sum formula     C13 H22 B11 Cu N2         C13 H22 B11 Cu N2
Mr              388.79                    388.77
Dx,g cm-3       1.304                     1.304
Z               2                         2
Mu (mm-1)       1.102                     1.102
F000            396.0                     396.0
F000'           396.68
h,k,lmax        9,13,14                   9,13,14
Nref            3612                      3596
Tmin,Tmax       0.627,0.718               0.737,1.000
Tmin'           0.577

Correction method= # Reported T Limits: Tmin=0.737 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.996          Theta(max)= 25.348

R(reflections)= 0.0435( 3067)     wR2(reflections)= 0.1032( 3596)

S = 1.050                 Npar= 248
```

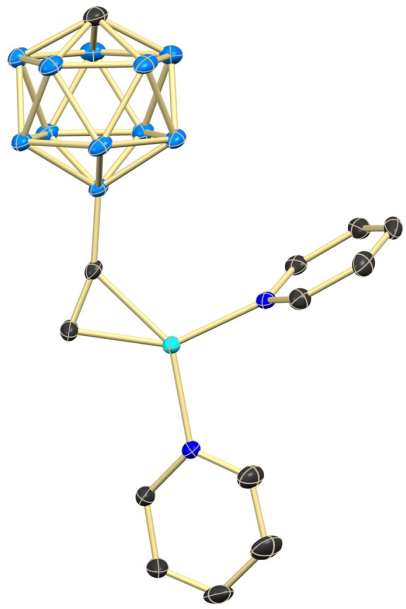


Figure S2. ORTEP representation of **3a**. Hydrogen atoms are omitted for clarity; 30% displacement ellipsoids.

Crystal structure of 3b (CCDC1910716)

Compound **3b** (10 mg) was dissolved in anhydrous ethanol (2.0 mL) in a 4 mL glass vial to give a clear solution. Slow evaporation afforded colorless crystals of the composition [Cu($CB_{11}H_{11}$-12-C≡CH)(4-MePy)$_2$] suitable for X-ray diffraction within 4 d at 25 °C.

```
Bond precision:  C-C = 0.0072 A          Wavelength=0.71073

Cell:           a=12.8275(7)    b=10.7515(5)        c=17.3597(9)
                alpha=90        beta=108.206(2)     gamma=90
Temperature:    296 K

                Calculated                Reported
Volume          2274.3(2)                 2274.3(2)
Space group     P 21/n                    P 1 21/n 1
Hall group      -P 2yn                    -P 2yn
Moiety formula  C15 H26 B11 Cu N2         C15 H26 B11 Cu N2
Sum formula     C15 H26 B11 Cu N2         C15 H26 B11 Cu N2
Mr              416.84                    416.83
Dx,g cm-3       1.217                     1.217
Z               4                         4
Mu (mm-1)       0.964                     0.964
F000            856.0                     856.0
F000'           857.39
h,k,lmax        15,13,21                  15,13,21
Nref            4467                      4462
Tmin,Tmax       0.636,0.714               0.634,0.719
Tmin'           0.611

Correction method= # Reported T Limits: Tmin=0.634 Tmax=0.719
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 25.997

R(reflections)= 0.0707( 2700)     wR2(reflections)= 0.1107( 4462)

S = 1.068                 Npar= 268
```

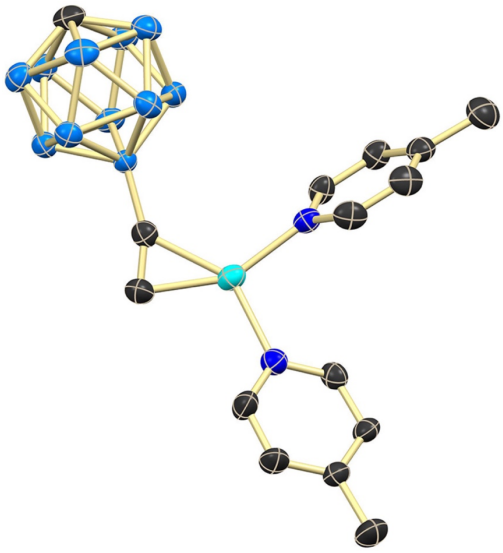


Figure S3. ORTEP representation of **3b**. Hydrogen atoms are omitted for clarity; 30% displacement ellipsoids.

Crystal structure of 3c (CCDC1910717)

Compound **3c** (10 mg) was dissolved in anhydrous ethanol (2.0 mL) in a 4 mL glass vial to give a clear solution. Slow evaporation afforded colorless crystals of the composition [Cu($CB_{11}H_{11}$-12-C≡CH)(3-MePy)$_2$] suitable for X-ray diffraction within 4 d at 25 °C.

```
Bond precision:  C-C = 0.0055 A          Wavelength=0.71073

Cell:          a=8.3718(8)        b=11.5149(11)     c=13.4954(9)
               alpha=102.473(7)   beta=106.926(7)   gamma=107.523(9)
Temperature:   293 K
```

	Calculated	Reported
Volume	1119.2(2)	1119.18(18)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C15 H26 B11 Cu N2	C15 H26 B11 Cu N2
Sum formula	C15 H26 B11 Cu N2	C15 H26 B11 Cu N2
Mr	416.84	416.83
Dx,g cm-3	1.237	1.237
Z	2	2
Mu (mm-1)	0.979	0.979
F000	428.0	428.0
F000'	428.69	
h,k,lmax	10,13,16	10,13,16
Nref	4098	4083
Tmin,Tmax	0.744,0.889	0.712,1.000
Tmin'	0.650	

```
Correction method= # Reported T Limits: Tmin=0.712 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.996          Theta(max)= 25.347

R(reflections)= 0.0468( 3361)     wR2(reflections)= 0.1155( 4083)

S = 1.047                 Npar= 268
```

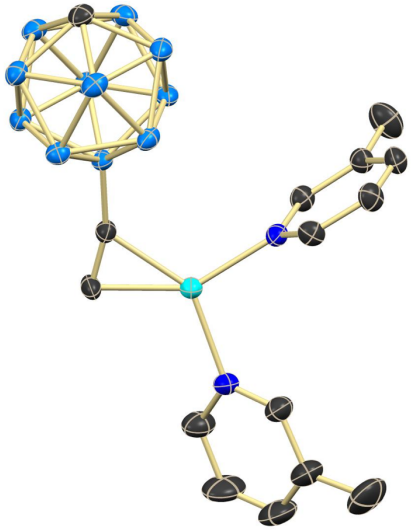


Figure S4. ORTEP representation of **3c**. Hydrogen atoms are omitted for clarity; 30% displacement ellipsoids.

Crystal structure of 3d (CCDC1910718)

Compound **3d** (10 mg) was dissolved in anhydrous ethanol (2.0 mL) in a 4 mL glass vial to give a clear solution. Slow evaporation afforded colorless crystals of the composition [($CB_{11}H_{11}$-12-C≡CH)Cu(4-CF_3Py)$_2$] suitable for X-ray diffraction within 4 d at 25 °C.

```
Bond precision:  C-C = 0.0052 A          Wavelength=0.71073

Cell:          a=10.0994(8)      b=11.2360(9)     c=11.7320(9)
               alpha=66.212(7)   beta=75.011(7)   gamma=89.796(7)
Temperature:   168 K

                Calculated                Reported
Volume          1169.09(18)               1169.09(17)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C15 H20 B11 Cu F6 N2      C15 H20 B11 Cu F6 N2
Sum formula     C15 H20 B11 Cu F6 N2      C15 H20 B11 Cu F6 N2
Mr              524.79                    524.78
Dx,g cm-3       1.491                     1.491
Z               2                         2
Mu (mm-1)       0.990                     0.990
F000            524.0                     524.0
F000'           524.89
h,k,lmax        12,13,14                  12,13,14
Nref            4276                      4264
Tmin,Tmax       0.691,0.888               0.706,1.000
Tmin'           0.616

Correction method= # Reported T Limits: Tmin=0.706 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 25.348

R(reflections)= 0.0504( 3389)     wR2(reflections)= 0.1302( 4264)

S = 1.046                 Npar= 320
```

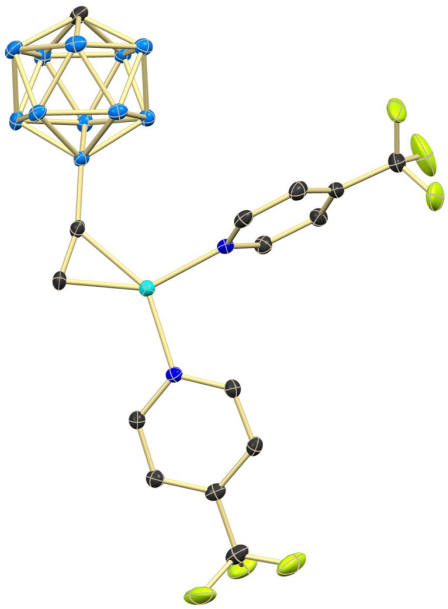


Figure S5. ORTEP representation of **3d**. Hydrogen atoms are omitted for clarity; 30% displacement ellipsoids.

Crystal structure of 4b (CCDC1910719)

Compound **4b** (10 mg) was dissolved in acetone (0.5 mL) in a 4 mL glass vial to give a clear solution, and 1.5 mL anhydrous ethanol was added to the vial. Slow evaporation afforded colorless crystals of the composition $[Cu(PPh_3)_3][12\text{-}C{\equiv}CH\text{-}CB_{11}H_{11}]$ suitable for X-ray diffraction within 4 d at 25 °C.

```
Bond precision:  C-C = 0.0072 A          Wavelength=0.71073

Cell:          a=12.5248(8)       b=12.9185(8)     c=18.8957(9)
               alpha=106.031(5)   beta=97.416(4)   gamma=104.435(5)
Temperature:   150 K

                 Calculated                 Reported
Volume           2780.6(3)                  2780.6(3)
Space group      P -1                       P -1
Hall group       -P 1                       -P 1
Moiety formula   C54 H45 Cu P3, C3 H12 B11  C54 H45 Cu P3, C3 H12 B11
Sum formula      C57 H57 B11 Cu P3          C57 H57 B11 Cu P3
Mr               1017.40                    1017.38
Dx,g cm-3        1.215                      1.215
Z                2                          2
Mu (mm-1)        0.516                      0.516
F000             1056.0                     1056.0
F000'            1057.50
h,k,lmax         15,15,22                   15,15,22
Nref             10181                      10143
Tmin,Tmax        0.805,0.857                0.735,1.000
Tmin'            0.805

Correction method= # Reported T Limits: Tmin=0.735 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.996          Theta(max)= 25.350

R(reflections)= 0.0613( 7231)     wR2(reflections)= 0.1726( 10143)

S = 1.034                 Npar= 650
```

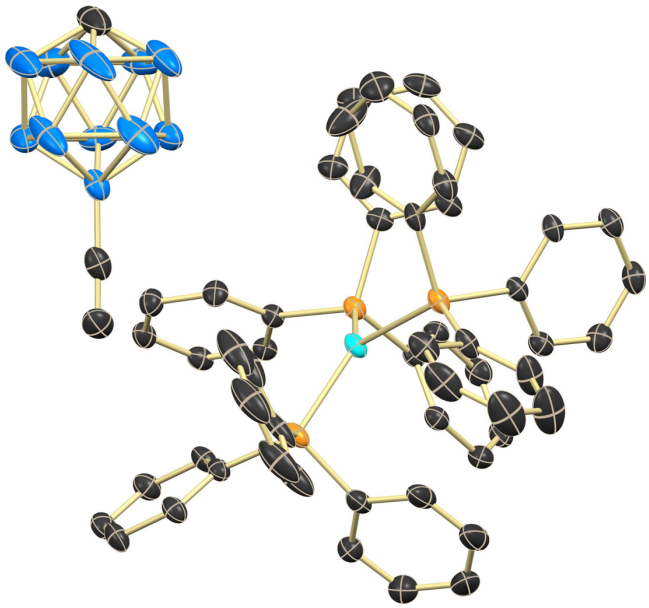


Figure S6. ORTEP representation of **4b**. Hydrogen atoms are omitted for clarity; 30% displacement ellipsoids.

Crystal structures of 4c (CCDC1910721)

Compound **4c** (10 mg) was dissolved in acetone (0.5 mL) in a 4 mL glass vial to give a clear solution, and 1.5 mL anhydrous ethanol was added to the vial. Slow evaporation afforded colorless crystals of the composition $[Cu(P\textit{i}Pr_3)_2][12\text{-}C{\equiv}CH\text{-}CB_{11}H_{11}]$ suitable for X-ray diffraction within 4 d at 25 °C.

Bond precision: C-C = 0.0045 A Wavelength=0.71073

Cell: a=11.9970(7) b=15.5376(7) c=17.7707(8)
alpha=90 beta=92.697(5) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	3308.9(3)	3308.9(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C18 H42 Cu P2, C3 H12 B11	C18 H42 Cu P2, C3 H12 B11
Sum formula	C21 H54 B11 Cu P2	C21 H54 B11 Cu P2
Mr	551.04	551.03
Dx,g cm-3	1.106	1.106
Z	4	4
Mu (mm-1)	0.767	0.767
F000	1176.0	1176.0
F000'	1178.25	
h,k,lmax	14,18,21	14,18,21
Nref	6279	6266
Tmin,Tmax	0.632,0.794	0.884,1.000
Tmin'	0.601	

Correction method= # Reported T Limits: Tmin=0.884 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.679

R(reflections)= 0.0424(4378) wR2(reflections)= 0.1107(6266)

S = 1.018 Npar= 329

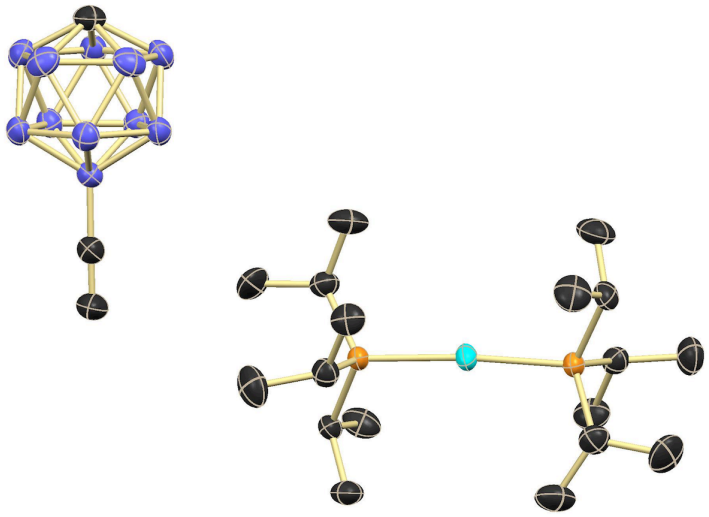


Figure S7. ORTEP representation of **4c**. Hydrogen atoms are omitted for clarity; 30% displacement ellipsoids.

Crystal structure of 6a (CCDC1910723)

Compound **6a** (10 mg) was dissolved in acetone (0.7 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 *trans*-$Pd(PEt_3)_2[(12\text{-}C{\equiv}C\text{-}CB_{11}H_{11})(Cu(HNEt_2))]_2 \cdot 2Me_2CO$ suitable for X-ray diffraction within 10 d at 25 °C.

Bond precision: C-C = 0.0116 A Wavelength=0.71073

Cell: a=15.7282(9) b=10.9616(6) c=17.0109(14)
alpha=90 beta=97.622(6) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	2906.9(3)	2906.9(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C26 H74 B22 Cu2 N2 P2 Pd, 2(C3 H6 O)	C26 H74 B22 Cu2 N2 P2 Pd, 2(C3 H6 O)
Sum formula	C32 H86 B22 Cu2 N2 O2 P2 Pd	C32 H86 B22 Cu2 N2 O2 P2 Pd
Mr	1064.29	1064.26
Dx,g cm-3	1.216	1.216
Z	2	2
Mu (mm-1)	1.115	1.115
F000	1104.0	1104.0
F000'	1103.85	
h,k,lmax	18,13,20	18,13,20
Nref	5319	5307
Tmin,Tmax	0.694,0.846	0.366,1.000
Tmin'	0.634	

Correction method= # Reported T Limits: Tmin=0.366 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.350

R(reflections)= 0.0524(3566) wR2(reflections)= 0.1381(5307)

S = 1.030 Npar= 294

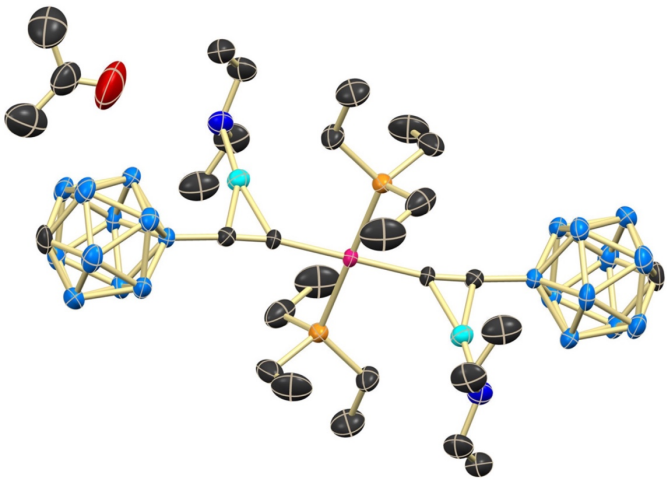


Figure S8. ORTEP representation of **6a**. Hydrogen atoms are omitted for clarity; 30% displacement ellipsoids.

Crystal structure of 6b (CCDC1910724)

Compound **6b** (10 mg) was dissolved in acetone (0.7 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 *trans*-$Pt(PEt_3)_2[(12\text{-}C{\equiv}C\text{-}CB_{11}H_{11})(Cu(HNEt_2))]_2 \cdot 2Me_2CO$ suitable for X-ray diffraction within 10 d at 25 °C.

Bond precision: C-C = 0.0146 A Wavelength=0.71073

Cell: a=15.7322(6) b=10.9370(5) c=16.9807(11)
alpha=90 beta=97.802(5) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	2894.7(3)	2894.7(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C26 H74 B22 Cu2 N2 P2 Pt, 2(C3 H6 O)	C26 H74 B22 Cu2 N2 P2 Pt, 2(C3 H6 O)
Sum formula	C32 H86 B22 Cu2 N2 O2 P2 Pt	C32 H86 B22 Cu2 N2 O2 P2 Pt
Mr	1152.97	1152.95
Dx,g cm-3	1.323	1.323
Z	2	2
Mu (mm-1)	3.223	3.223
F000	1168.0	1168.0
F000'	1166.54	
h,k,lmax	18,13,20	18,13,20
Nref	5296	5279
Tmin,Tmax	0.239,0.476	0.418,1.000
Tmin'	0.198	

Correction method= # Reported T Limits: Tmin=0.418 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 25.350

R(reflections)= 0.0464(4037) wR2(reflections)= 0.1130(5279)

S = 1.059 Npar= 294

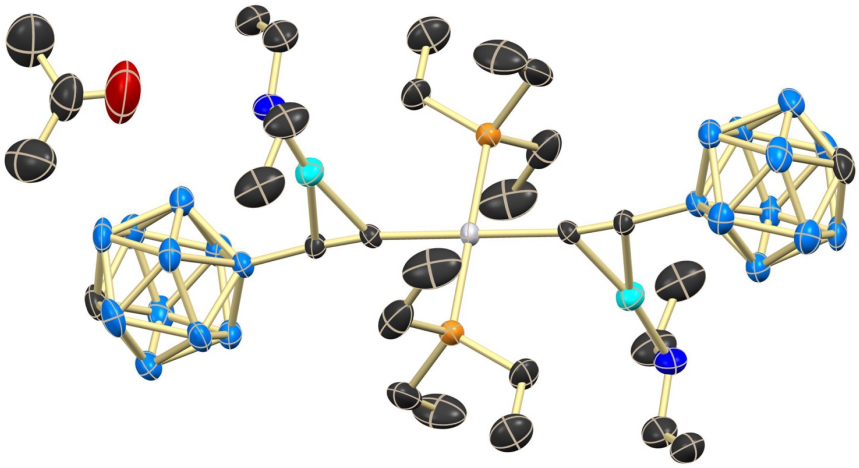


Figure S9. ORTEP representation of **6b**. Hydrogen atoms are omitted for clarity; 30% displacement ellipsoids.

Crystal structure of 7 (CCDC1910725)

Compound **7** (20 mg) was dissolved in acetone (0.7 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 $[CB_{11}H_{11}\text{-}12\text{-}(C{\equiv}C\text{-}C{\equiv}C)\text{-}12\text{-}CB_{11}H_{11}][NEt_4]_2$ suitable for X-ray diffraction within 10 d at 25 °C.

Bond precision: C-C = 0.0054 A Wavelength=0.71073

Cell: a=33.205(4) b=11.124(1) c=22.362(3)
alpha=90 beta=110.903(16) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	7716.3(18)	7716.4(18)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C6 H22 B22, 2(C8 H20 N)	2(C8 H20 N), C6 H22 B22
Sum formula	C22 H62 B22 N2	C22 H62 B22 N2
Mr	592.56	592.55
Dx,g cm-3	1.020	1.020
Z	8	8
Mu (mm-1)	0.049	0.049
F000	2544.0	2544.0
F000'	2544.41	
h,k,lmax	39,13,26	40,13,26
Nref	7057	7024
Tmin,Tmax	0.977,0.986	0.946,1.000
Tmin'	0.977	

Correction method= # Reported T Limits: Tmin=0.946 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.995 Theta(max)= 25.349

R(reflections)= 0.0904(3756) wR2(reflections)= 0.3023(7024)

S = 1.037 Npar= 490

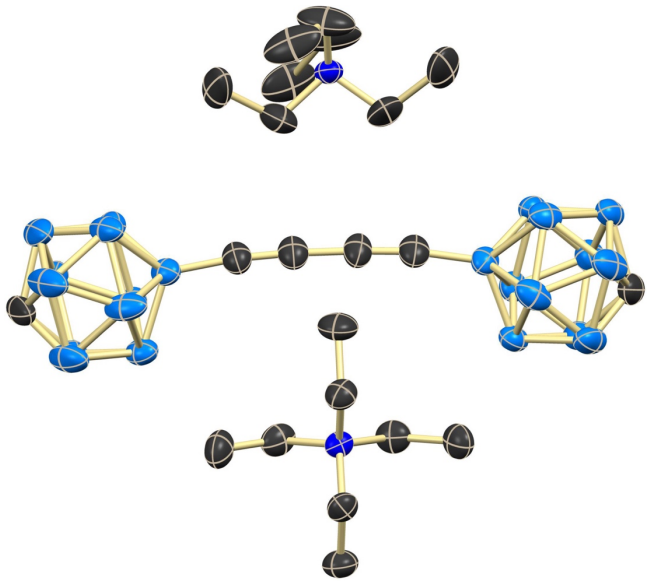


Figure S10. ORTEP representation of **7**. Hydrogen atoms are omitted for clarity; 30% displacement ellipsoids.

IV References

[1] a) Himmelspach, A.; Reiss, G. J.; Finze, M. *Inorg. Chem.* **2012**, *51*, 2679;
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c) Zhang, K.; Shen, Y.; Yang, X.; Liu, J.; Jiang, T.; Finney, N.; Spingler, B.; Duttwyler, S. *Chem. Eur. J.* **2019**, *25*, 8754.

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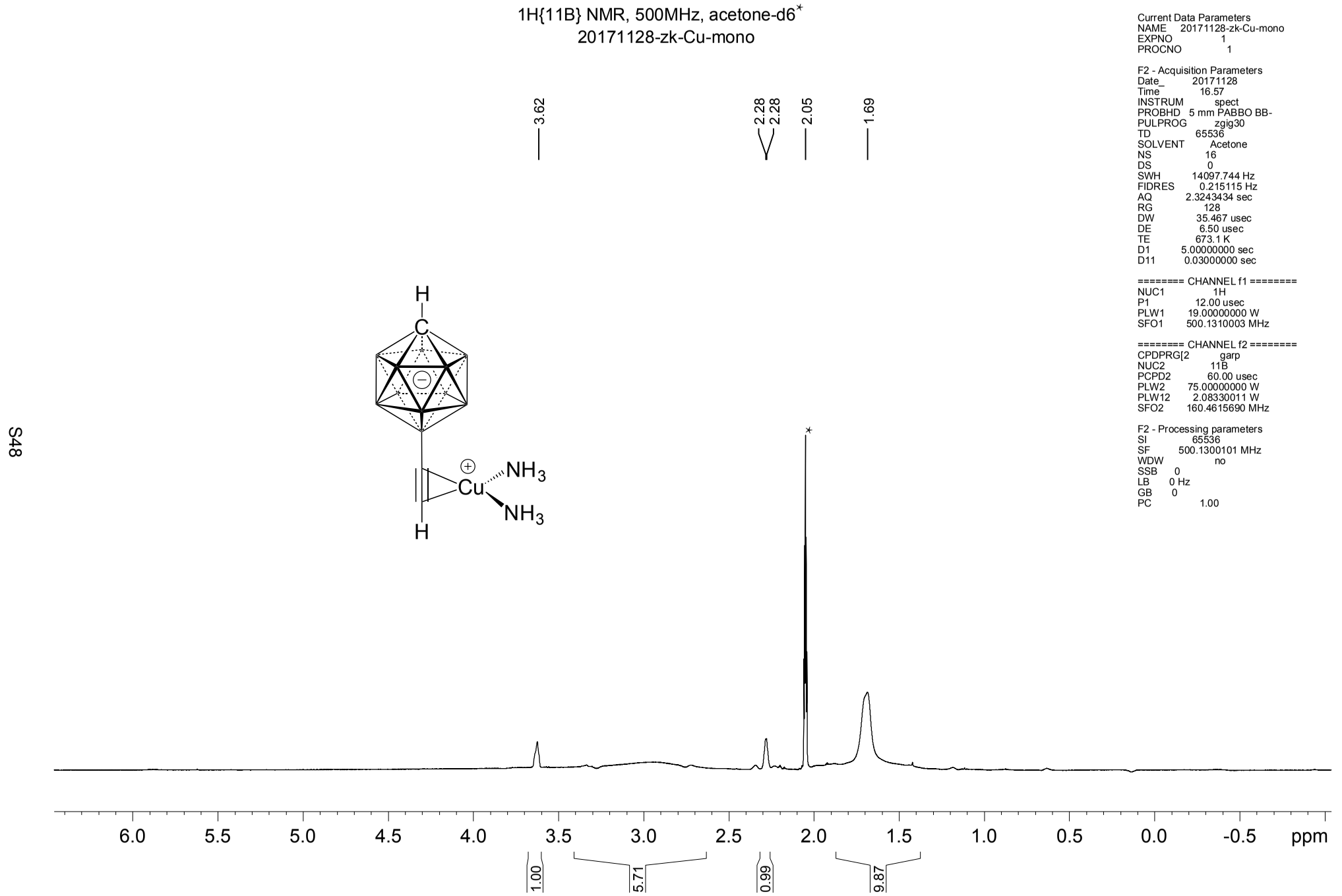
[3] Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3.

[4] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339.

[5] Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Cryst.* **2008**, *41*, 466.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NH3
H
*
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5.5
5.0
4.5
4.0
3.5
3.0
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DE 6.50 usec
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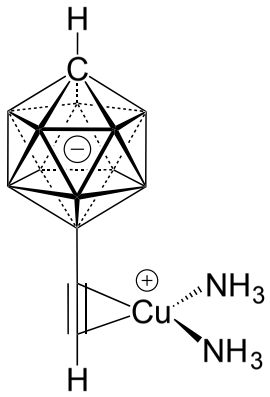
NUC2 11B
PCPD2 60.00 usec
PLW2 75.00000000 W
PLW12 2.08330011 W
SFO2 160.4615690 MHz
F2 - Processing parameters
SI 65536
SF 500.1300101 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00

11B NMR, 160 MHz, acetone-d6
20171128-zk-Cu-mono



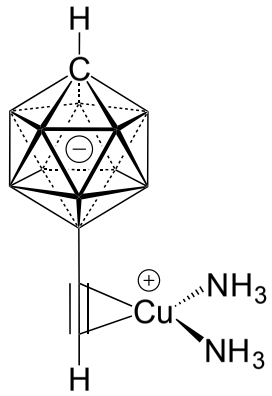
Current Data Parameters
NAME 20171128-zk-Cu-mono
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171128
Time 16.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32048
SOLVENT Acetone
NS 32
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 673.1 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, 160 MHz, acetone-d6
20171128-zk-Cu-mono



Current Data Parameters
NAME 20171128-zk-Cu-mono
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171128
Time 17.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32048
SOLVENT Acetone
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 673.1 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

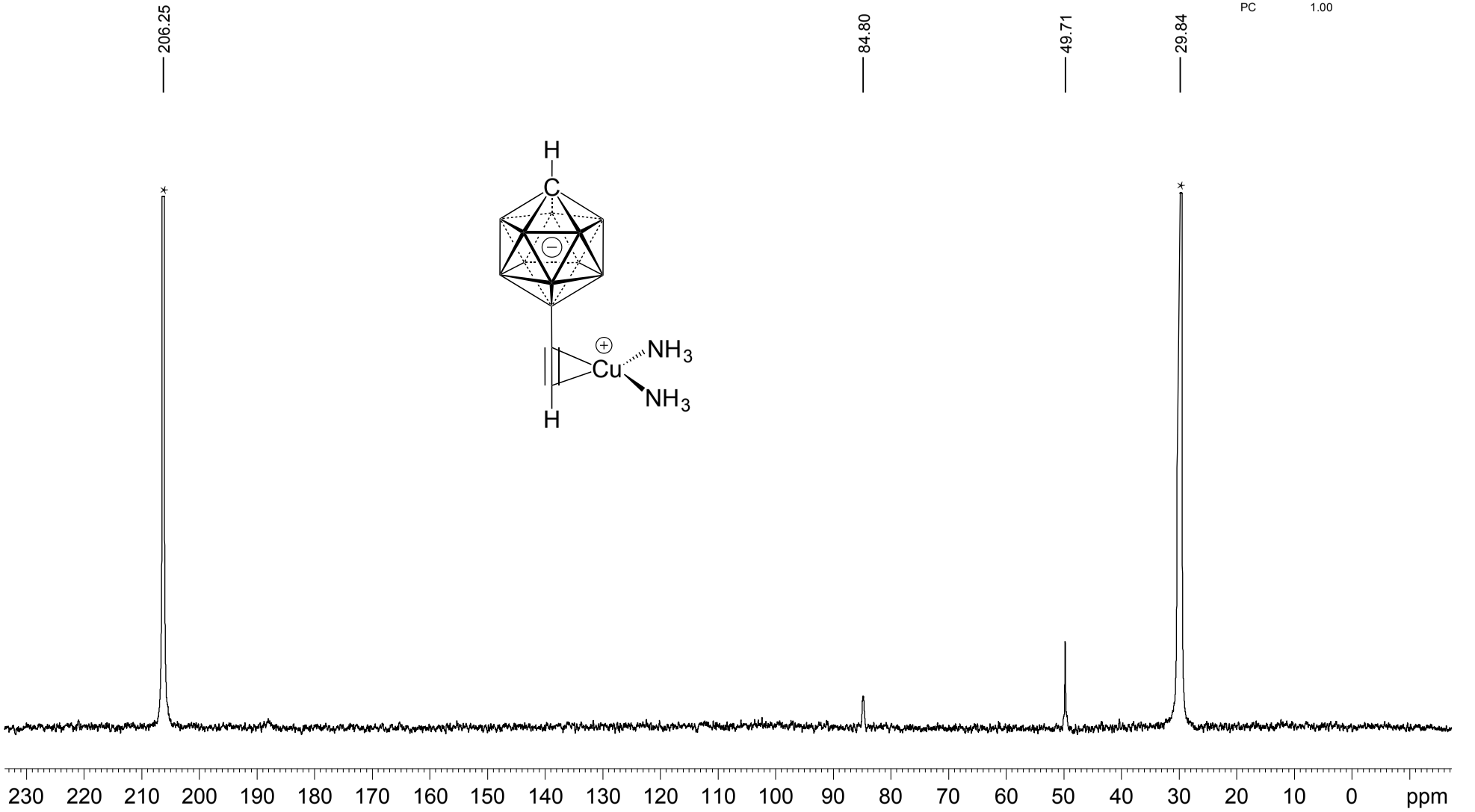
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.42750001 W
PLW13 0.27360001 W
SFO2 500.1330885 MHz

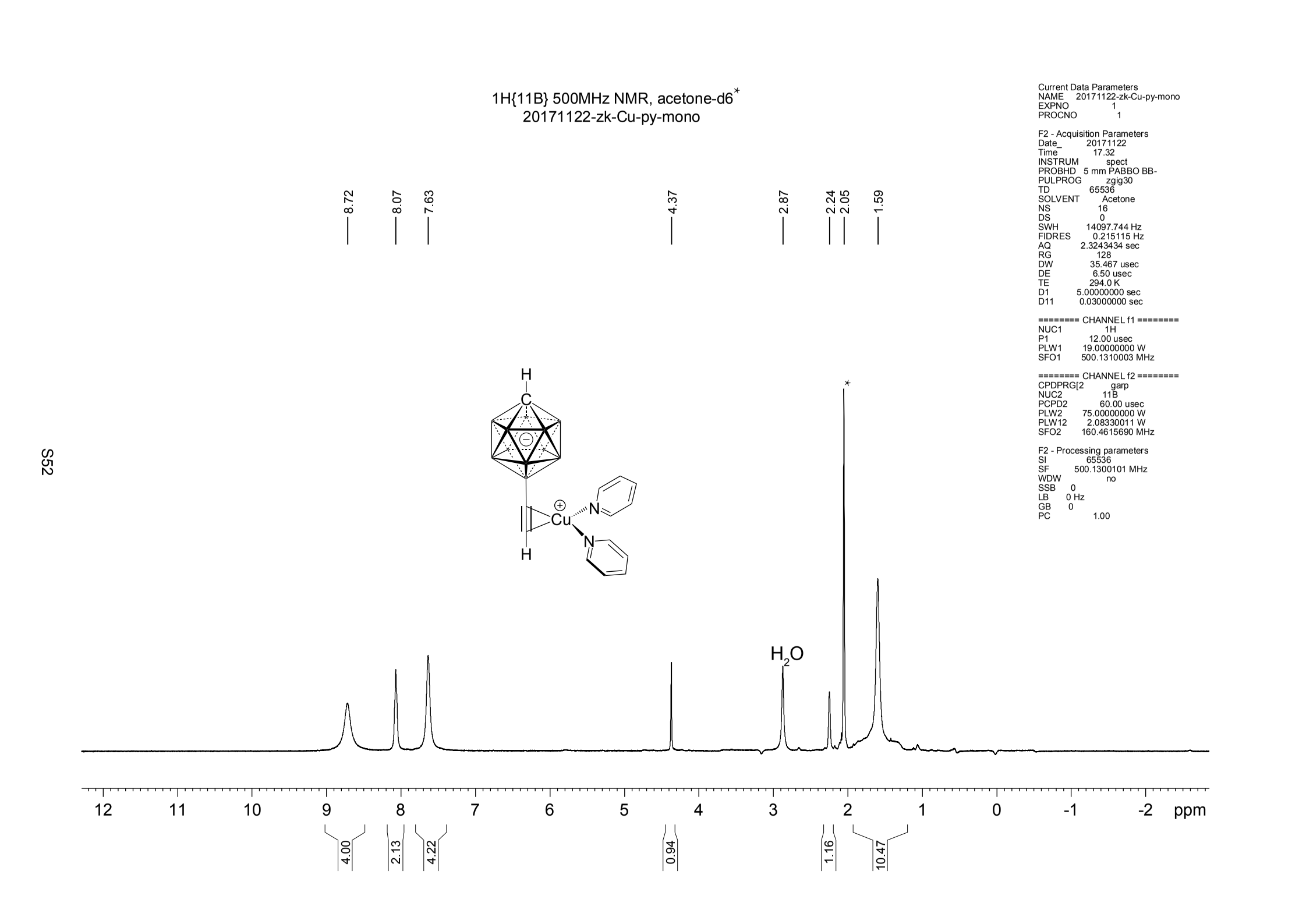
F2 - Processing parameters
SI 32768
SF 160.4615993 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

13C{1H} NMR, 151 MHz, acetone-d6*
20171128-zk-Cu-mono

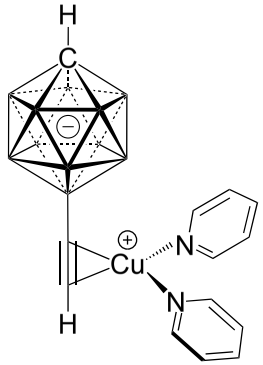
Current Data Parameters
NAME 20171128-zk-Cu-mono-600MH-13C
EXPNO 1
PROCNO 1

F2 - Processing parameters
SI 65536
SF 150.8139882 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.00




1H{11B} 500MHz NMR, acetone-d6*
20171122-zk-Cu-py-mono
Current Data Parameters
NAME 20171122-zk-Cu-py-mono
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171122
Time 17.32
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 128
DW 35.467 usec
DE 6.50 usec
TE 294.0 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
8.72
8.07
7.63
4.37
2.87
2.24
2.05
1.59
H
C
Cu
N
N
H
H2O
*
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
4.00
2.13
4.22
0.94
1.16
10.47

11B 160MHz NMR, acetone-d6
20171122-zk-Cu-py-mono



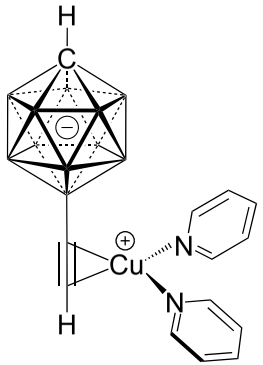
Current Data Parameters
NAME 20171122-zk-Cu-py-mono
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171122
Time 17.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32048
SOLVENT Acetone
NS 32
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 293.9 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} 160MHz NMR, acetone-d6
20171122-zk-Cu-py-mono



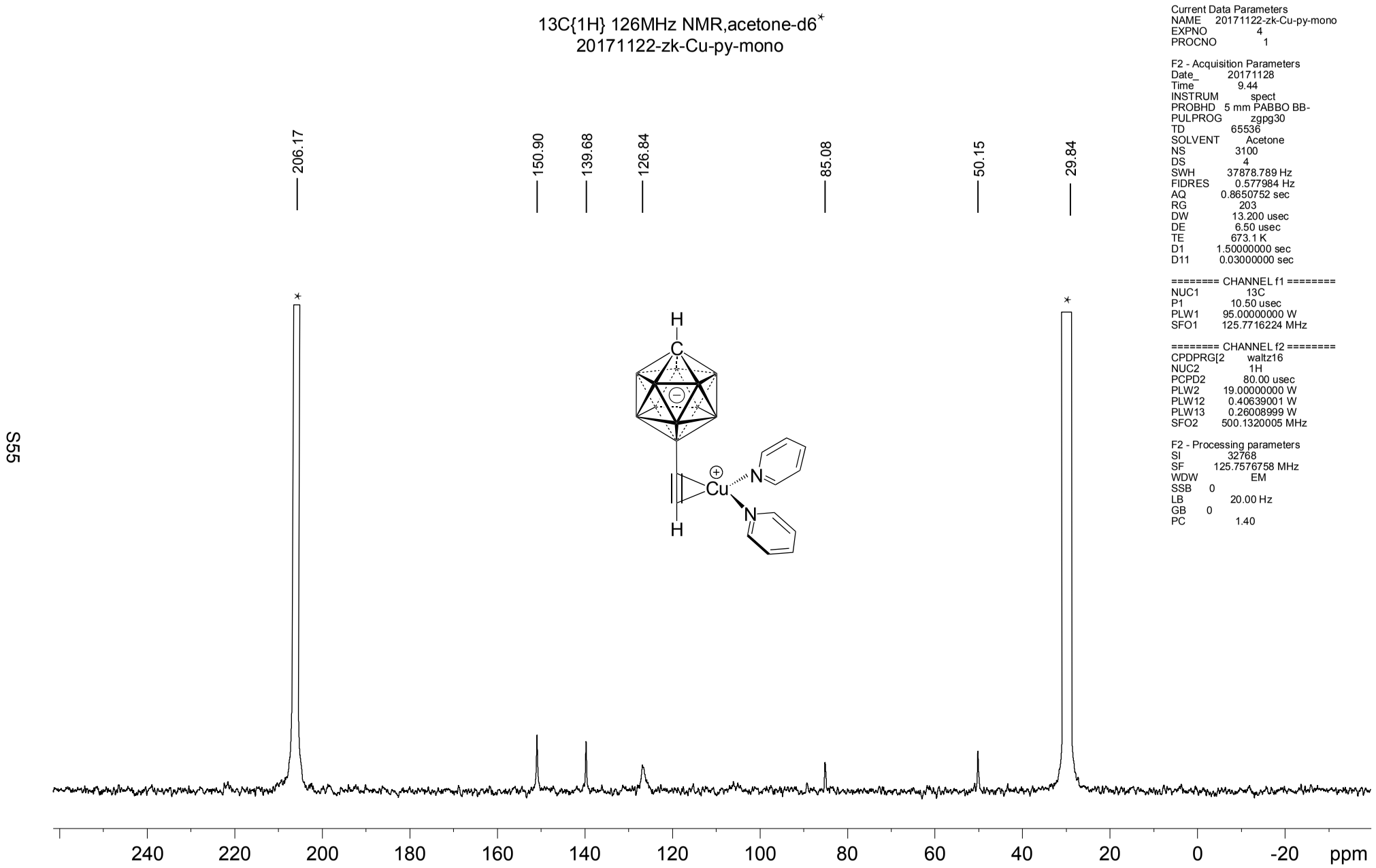
Current Data Parameters
NAME 20171122-zk-Cu-py-mono
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171122
Time 17.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32048
SOLVENT Acetone
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 294.1 K
D1 0.50000000 sec
D11 0.03000000 sec

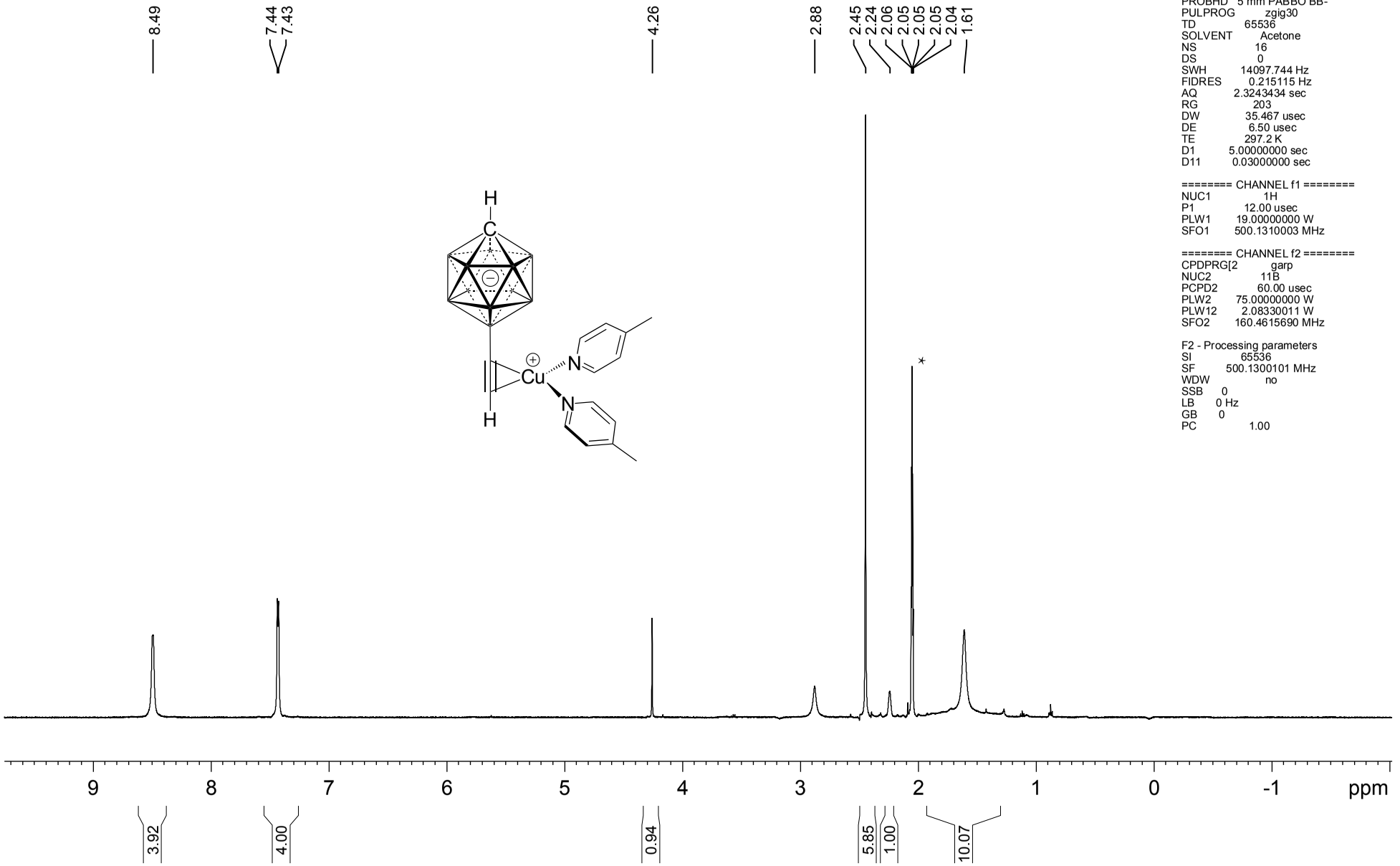
======== CHANNEL f1 ========
NUC1 11B
P1 10.00 usec
PLW1 75.00000000 W
SFO1 160.4615792 MHz

======== 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 10.00 Hz
GB 0
PC 1.40


13C{1H} 126MHz NMR,acetone-d6*
20171122-zk-Cu-py-mono
206.17
150.90
139.68
126.84
85.08
50.15
29.84
*
*
H
C
Cu
N
N
H
Current Data Parameters
NAME 20171122-zk-Cu-py-mono
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171128
Time 9.44
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 3100
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 673.1 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 125.7576758 MHz
WDW EM
SSB 0
LB 20.00 Hz
GB 0
PC 1.40
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

1H{11B} 500MHz NMR, acetone-d6*
20171115-zk-Cu-4CH3py-mono



Current Data Parameters
NAME 20171115-zk-Cu-4CH3py-mono
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171115
Time 16.53
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 297.2 K
D1 5.00000000 sec
D11 0.03000000 sec

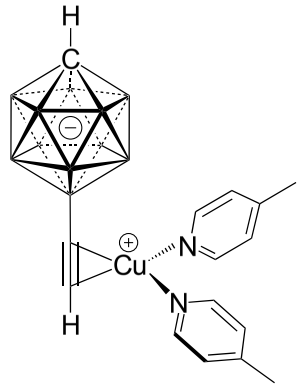
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PLW1 19.00000000 W
SFO1 500.1310003 MHz

======== 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

11B 160MHz NMR, acetone-d6

20171115-zk-Cu-4CH3py-mono



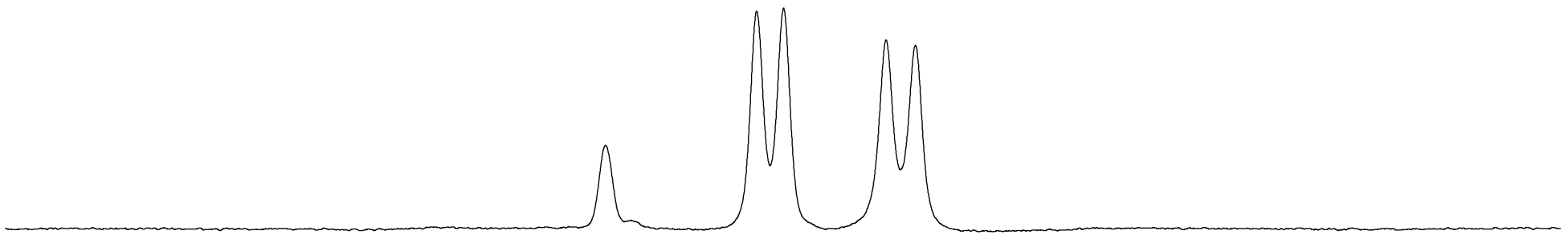
-7.25

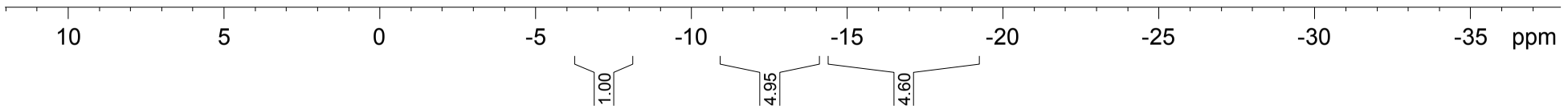
-12.10

-12.97

-16.26

-17.20





1.00

4.95

4.60

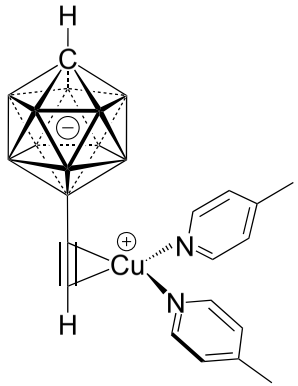
Current Data Parameters
NAME 20171115-zk-Cu-4CH3py-mono
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171115
Time 16.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32048
SOLVENT Acetone
NS 32
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 297.2 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} 160MHz NMR, acetone-d6
20171115-zk-Cu-4CH3py-mono



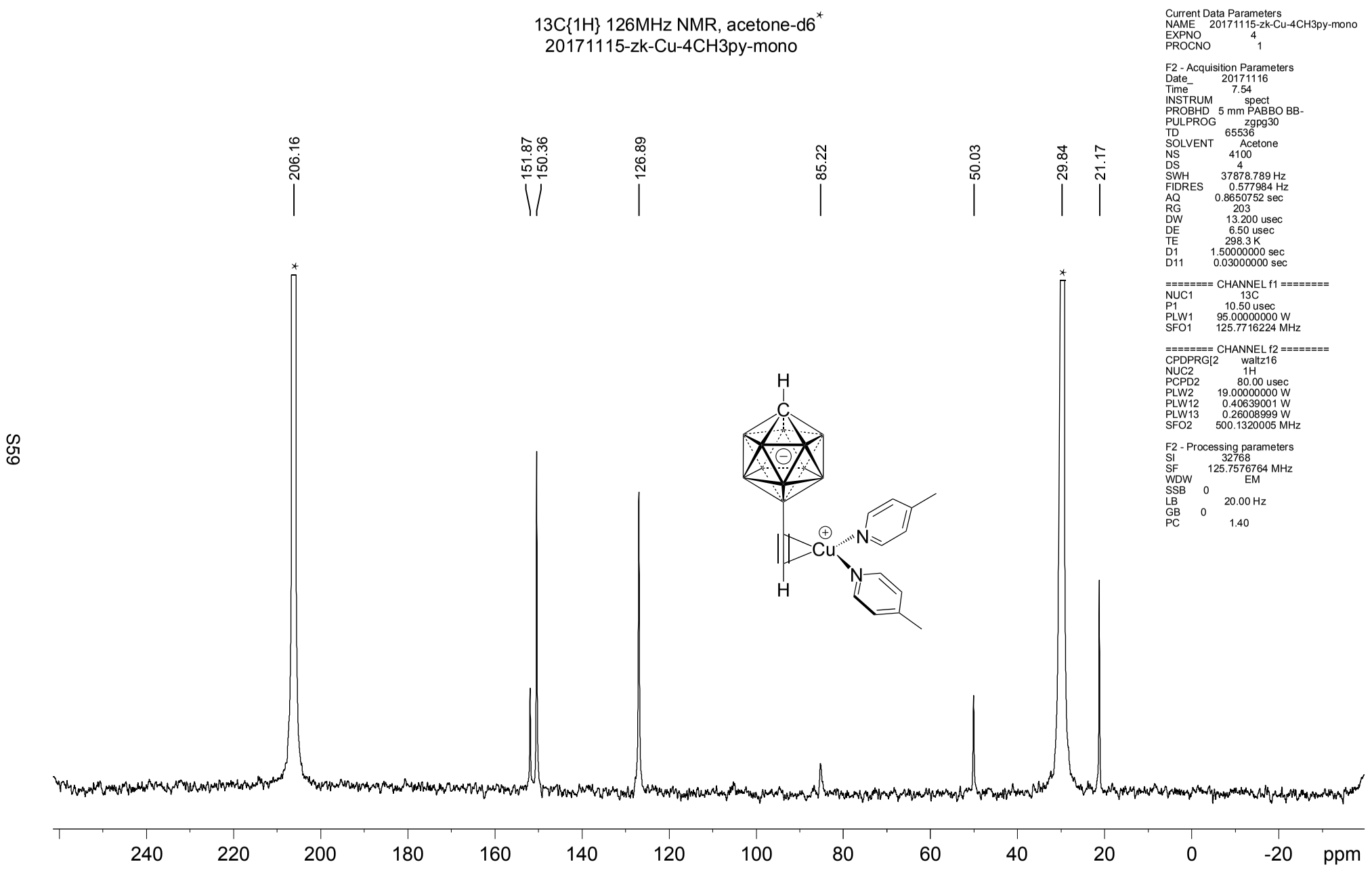
Current Data Parameters
NAME 20171115-zk-Cu-4CH3py-mono
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171115
Time 16.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32048
SOLVENT Acetone
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 297.3 K
D1 0.50000000 sec
D11 0.03000000 sec

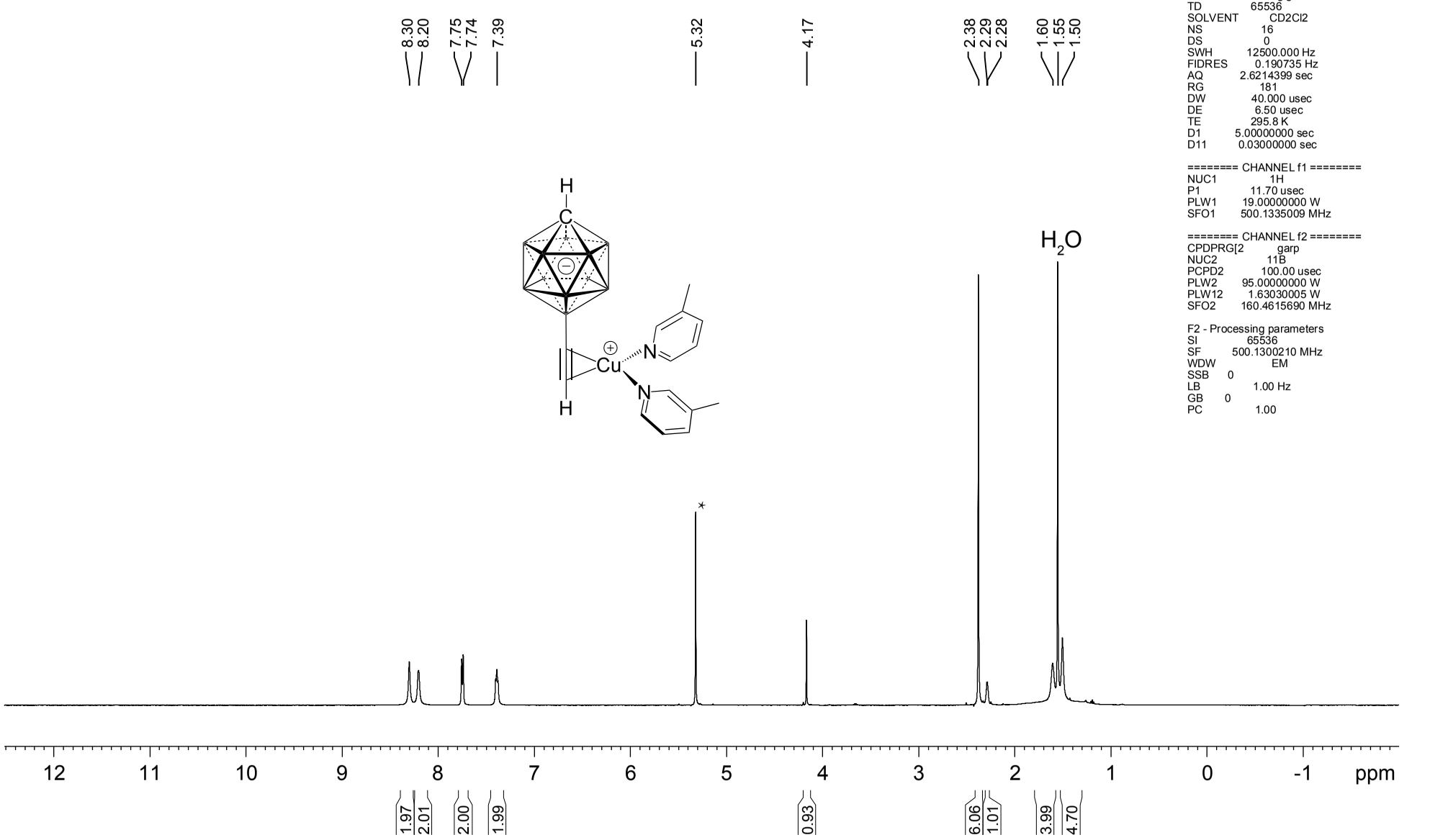
======== CHANNEL f1 ========
NUC1 11B
P1 10.00 usec
PLW1 75.00000000 W
SFO1 160.4615792 MHz

======== 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


13C{1H} 126MHz NMR, acetone-d6*
20171115-zk-Cu-4CH3py-mono
206.16
151.87
150.36
126.89
85.22
50.03
29.84
21.17
Current Data Parameters
NAME 20171115-zk-Cu-4CH3py-mono
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171116
Time 7.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 4100
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 298.3 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 125.7576764 MHz
WDW EM
SSB 0
LB 20.00 Hz
GB 0
PC 1.40
H
C
Cu
N
N
H
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

1H{11B} 500MHz NMR,CD2Cl2*
20171214-zk-Cu-3CH3py-mono



Current Data Parameters
NAME 20171214-zk-Cu-3CH3py-mono-CD2Cl2
EXPNO 1
PROCNO 1

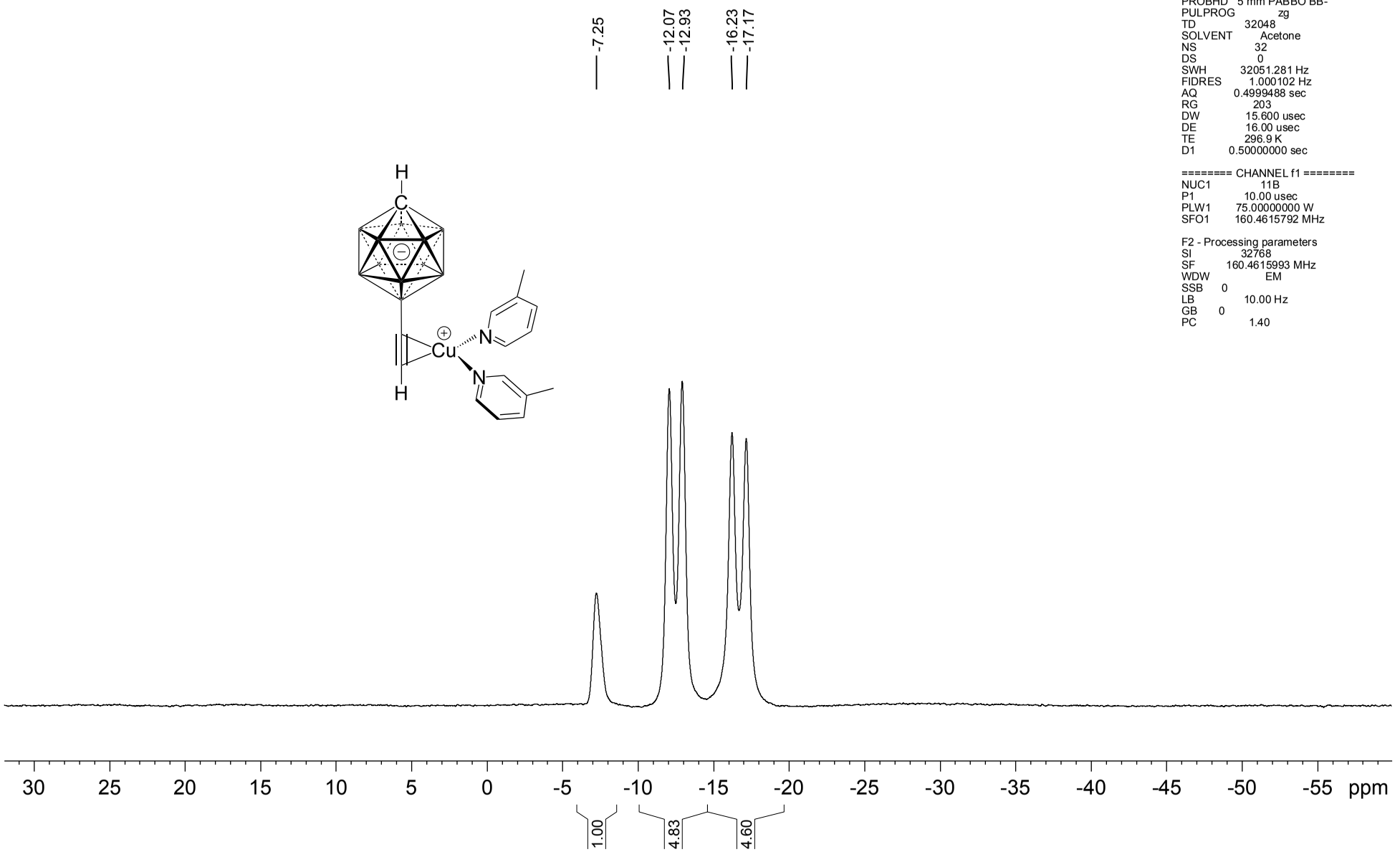
F2 - Acquisition Parameters
Date_ 20171214
Time 21.12
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgig30
TD 65536
SOLVENT CD2Cl2
NS 16
DS 0
SWH 12500.000 Hz
FIDRES 0.190735 Hz
AQ 2.6214399 sec
RG 181
DW 40.000 usec
DE 6.50 usec
TE 295.8 K
D1 5.00000000 sec
D11 0.03000000 sec

======== 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 500.1300210 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

11B 160 MHz NMR, acetone-d6
20171121-zk-Cu-3CH3py-mono



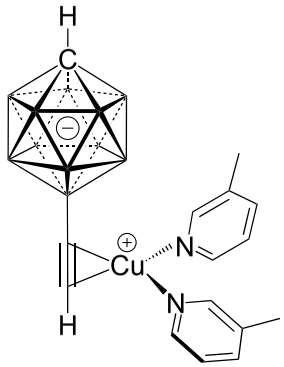
Current Data Parameters
NAME 20171121-zk-Cu-3CH3py-mono-1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171121
Time 17.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32048
SOLVENT Acetone
NS 32
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 296.9 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} 160 MHz NMR, acetone-d6
20171121-zk-Cu-3CH3py-mono



Current Data Parameters
NAME 20171121-zk-Cu-3CH3py-mono-1
EXPNO 3
PROCNO 1

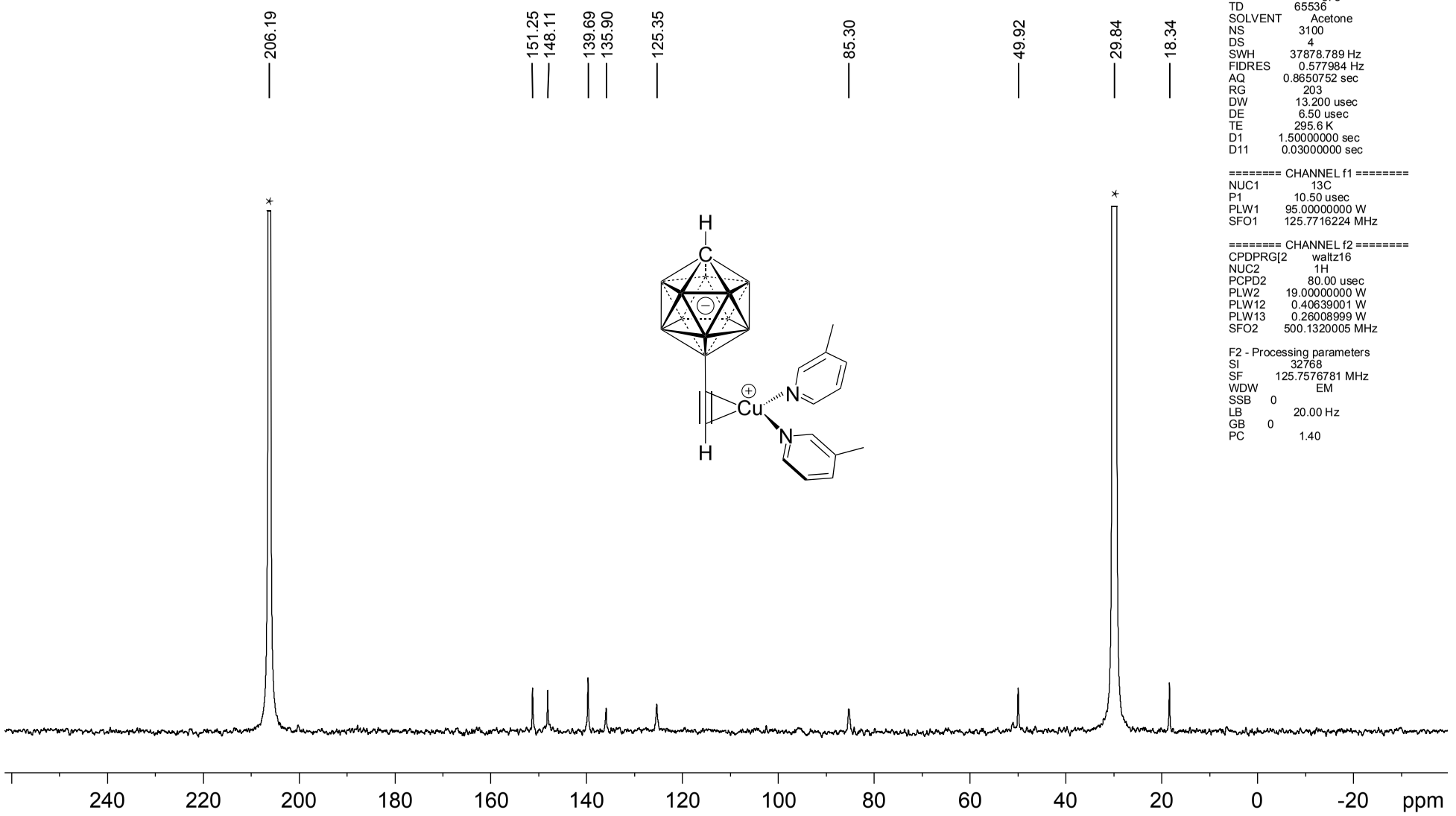
F2 - Acquisition Parameters
Date_ 20171121
Time 17.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32048
SOLVENT Acetone
NS 32
DS 0
SWH 32051.281 Hz
FIDRES 1.000102 Hz
AQ 0.4999488 sec
RG 203
DW 15.600 usec
DE 6.50 usec
TE 297.1 K
D1 0.50000000 sec
D11 0.03000000 sec

======== 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 10.00 Hz
GB 0
PC 1.40

13C{1H} 126 MHz NMR, acetone-d6
20171121-zk-Cu-3CH3py-mono



Current Data Parameters
NAME 20171121-zk-Cu-3CH3py-mono-1
EXPNO 4
PROCNO 1

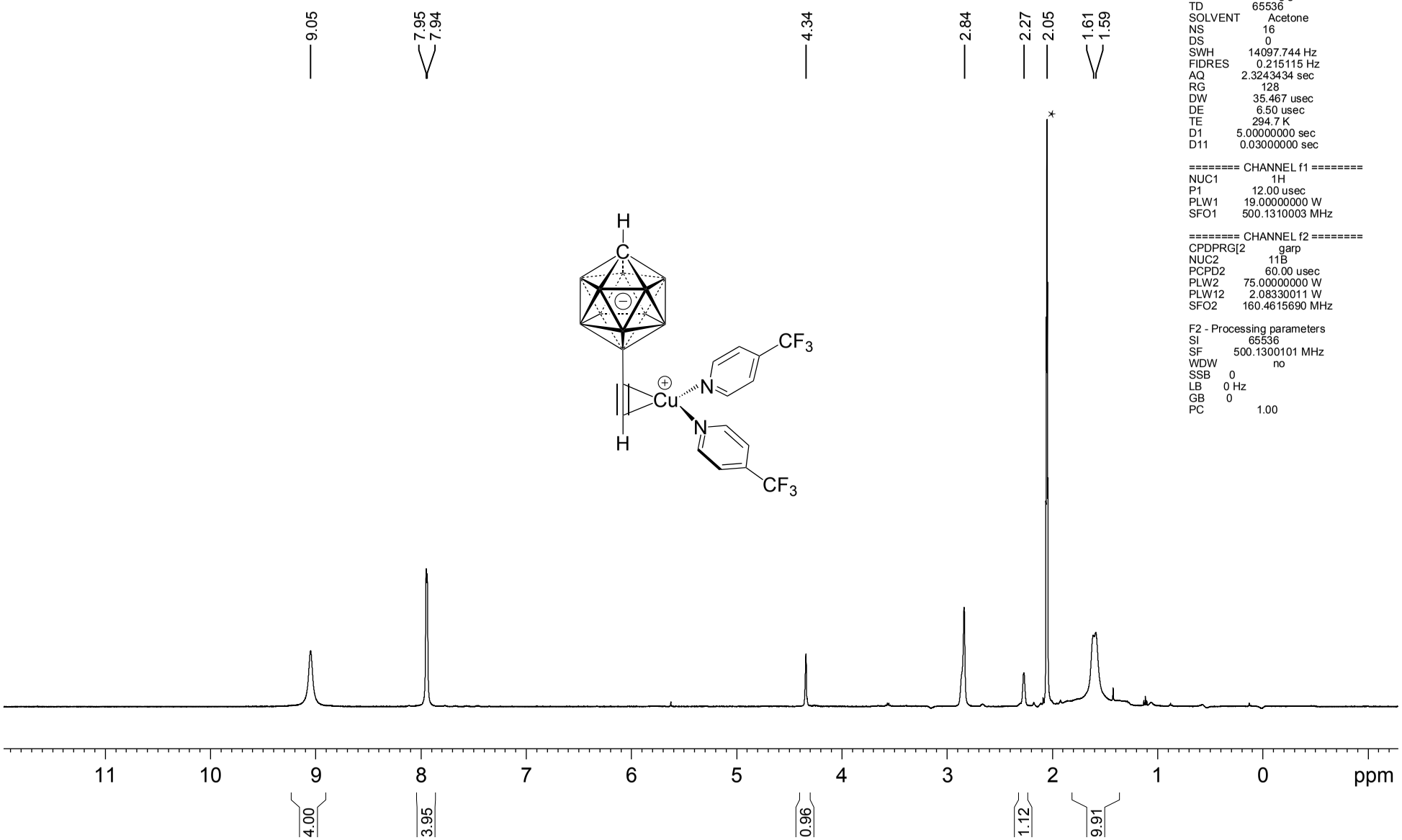
F2 - Acquisition Parameters
Date_ 20171122
Time 12.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 3100
DS 4
SWH 37878.789 Hz
FIDRES 0.577984 Hz
AQ 0.8650752 sec
RG 203
DW 13.200 usec
DE 6.50 usec
TE 295.6 K
D1 1.50000000 sec
D11 0.03000000 sec

======== 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 0.40639001 W
PLW13 0.26008999 W
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7576781 MHz
WDW EM
SSB 0
LB 20.00 Hz
GB 0
PC 1.40

1H{11B} 500MHz NMR,acetone-d6*
20171204-zk-Cu-4CF3Py



Current Data Parameters
NAME 20171204-zk-Cu-4CF3Py
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171204
Time 16.56
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 128
DW 35.467 usec
DE 6.50 usec
TE 294.7 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 500.1300101 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00

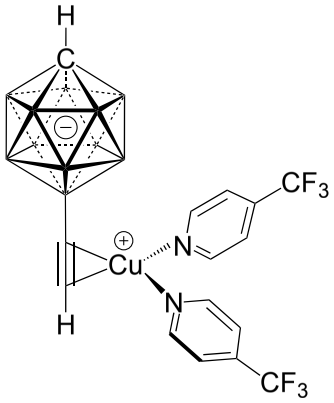
11B 160 MHz NMR, acetone-d6
20171204-zk-Cu-4CF3Py

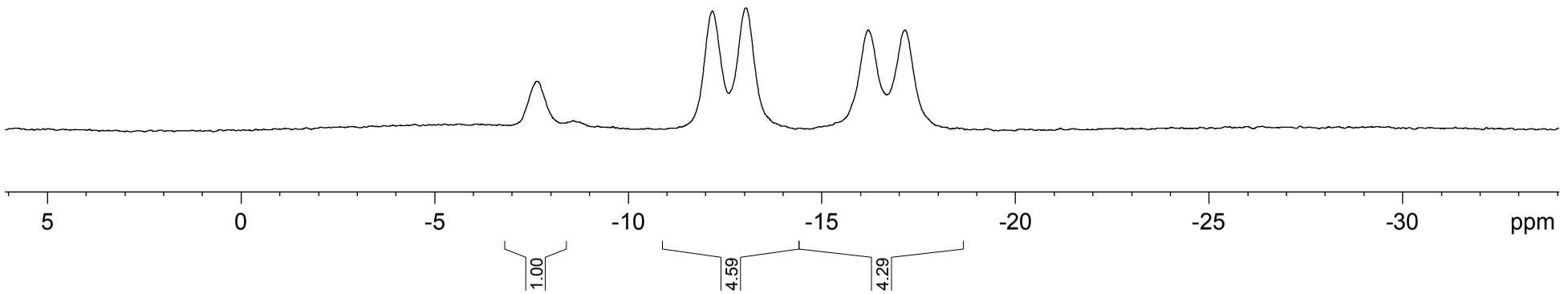
Current Data Parameters
NAME 20171204-zk-Cu-4CF3Py
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171204
Time 17.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32048
SOLVENT Acetone
NS 16
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 294.6 K
D1 0.50000000 sec

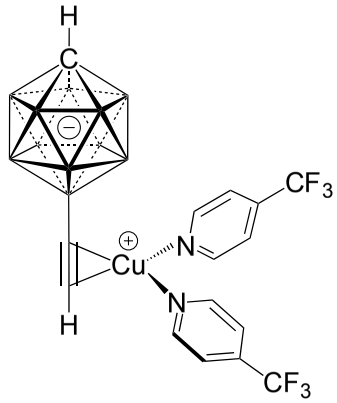
======== CHANNEL f1 ========
NUC1 11B
P1 10.00 usec
PLW1 75.00000000 W
SFO1 160.4615792 MHz

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





11B{1H} 160 MHz NMR, acetone-d6
20171204-zk-Cu-4CF3Py



Current Data Parameters
NAME 20171204-zk-Cu-4CF3Py
EXPNO 3
PROCNO 1

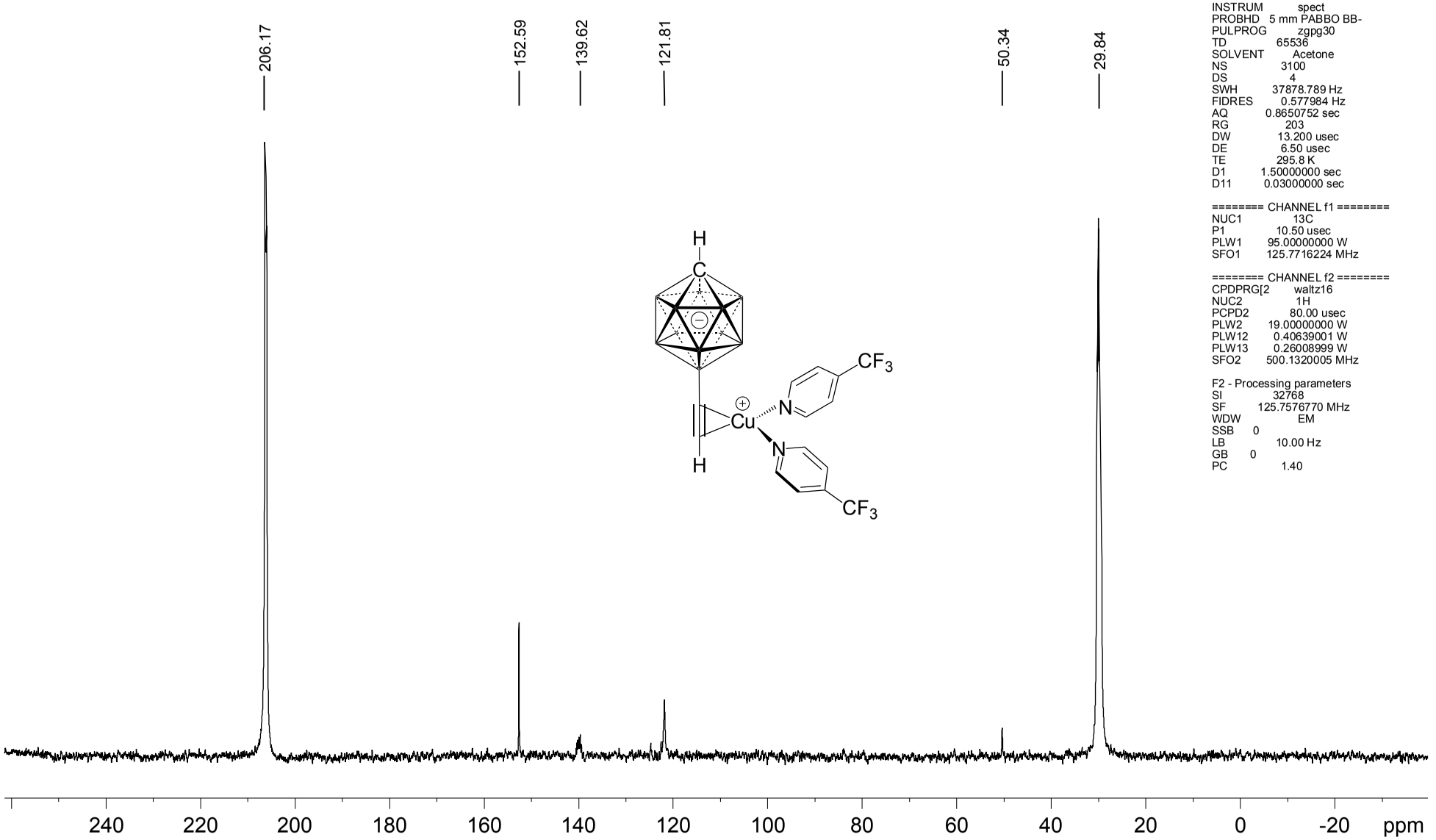
F2 - Acquisition Parameters
Date_ 20171204
Time 17.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32048
SOLVENT Acetone
NS 32
DS 0
SWH 32051.281 Hz
FIDRES 1.000102 Hz
AQ 0.4999488 sec
RG 203
DW 15.600 usec
DE 6.50 usec
TE 295.0 K
D1 0.50000000 sec
D11 0.03000000 sec

======== 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

13C{1H} 500MHz,Acetone-d6
20171204-zk-Cu-4CF3Py-mono



Current Data Parameters
NAME 20171204-zk-Cu-4CF3Py-mono
EXPNO 4
PROCNO 1

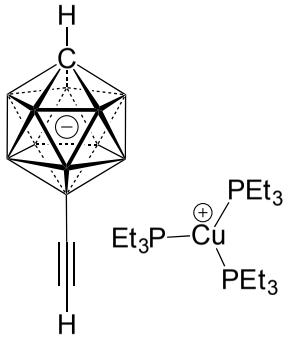
F2 - Acquisition Parameters
Date_ 20171205
Time 12.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 3100
DS 4
SWH 37878.789 Hz
FIDRES 0.577984 Hz
AQ 0.8650752 sec
RG 203
DW 13.200 usec
DE 6.50 usec
TE 295.8 K
D1 1.50000000 sec
D11 0.03000000 sec

======== 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 125.7576770 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

1H{11B} 400MHz NMR,acetone-d6*
20171217-zk-Cu-PEt3-mono



Current Data Parameters
NAME 20171217-zk-Cu-PEt3-mono
EXPNO 1
PROCNO 1

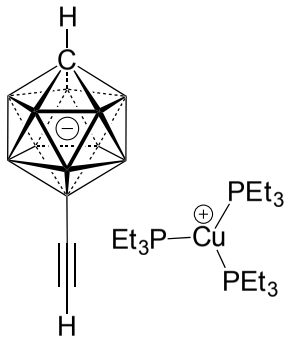
F2 - Acquisition Parameters
Date_ 20171218
Time 4.03
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgig30
TD 16384
SOLVENT Acetone
NS 16
DS 4
SWH 8012.820 Hz
FIDRES 0.489064 Hz
AQ 1.0223616 sec
RG 107.6
DW 62.400 usec
DE 6.50 usec
TE 295.1 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== 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 400.1300072 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

11B 128MHz NMR, acetone-d6
20171217-zk-Cu-PEt3-mono



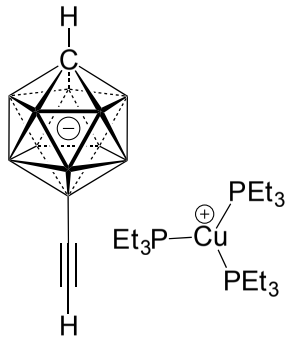
Current Data Parameters
NAME 20171217-zk-Cu-PEt3-mono
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171218
Time 4.15
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 295.2 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

11B{1H} 128MHz NMR, acetone-d6
20171217-zk-Cu-PEt3-mono



-7.41
-12.23
-16.73

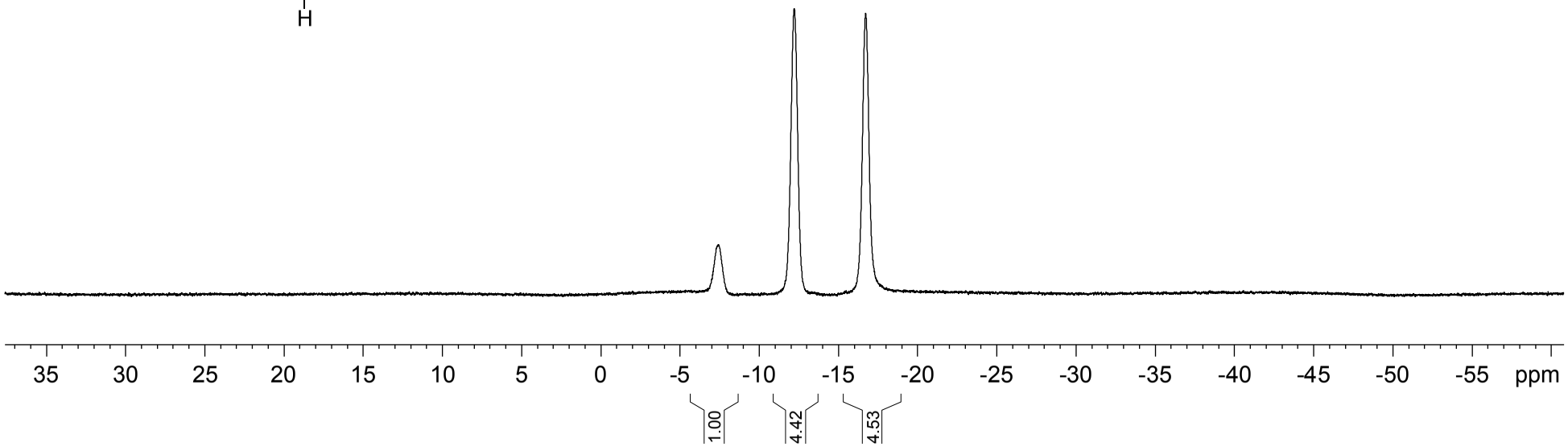
Current Data Parameters
NAME 20171217-zk-Cu-PEt3-mono
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171218
Time 4.09
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 296.1 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

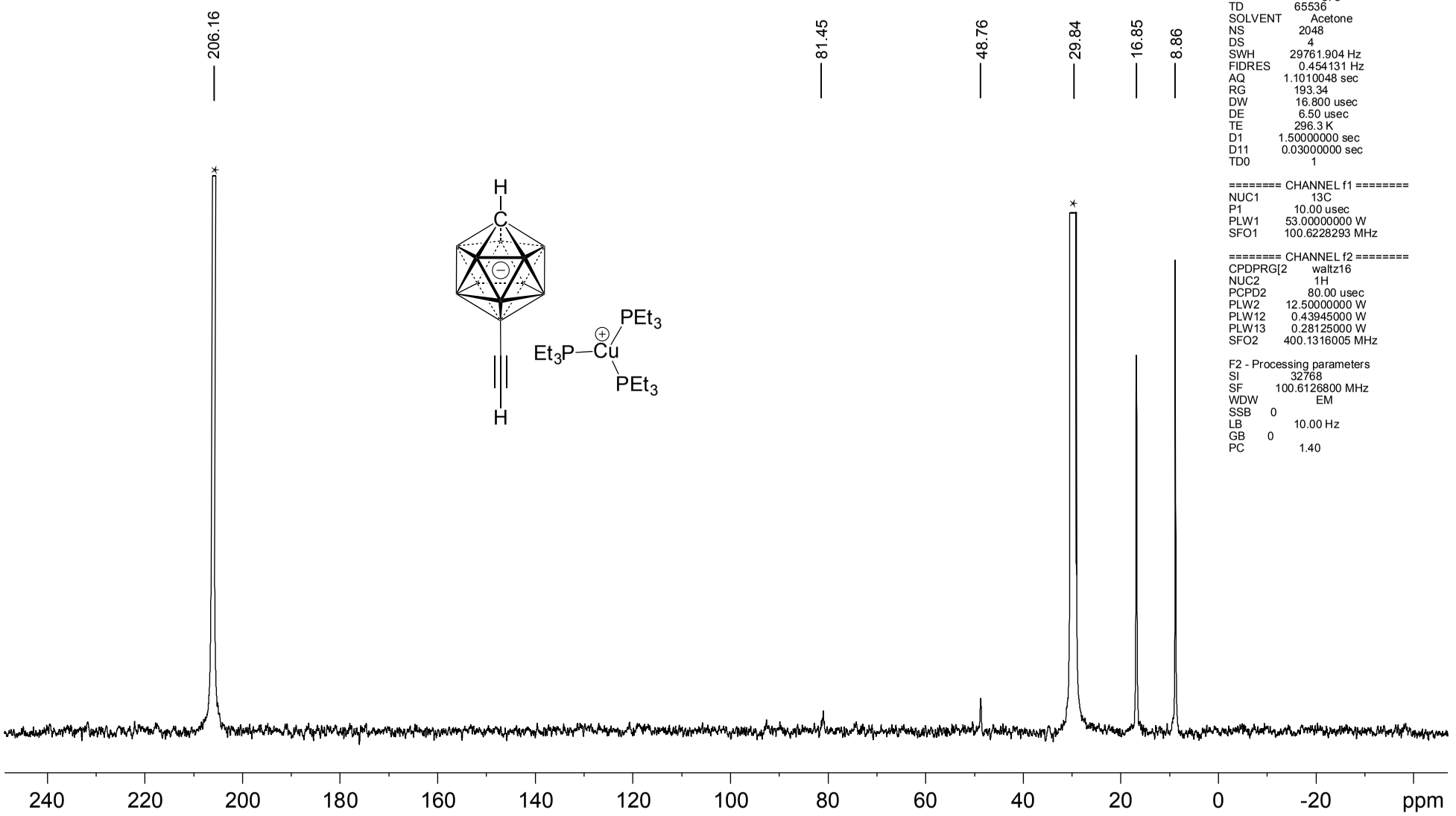
======== CHANNEL f1 ========
NUC1 11B
P1 9.93 usec
PLW1 52.96599960 W
SFO1 128.3776050 MHz

======== 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



13C{1H} 100MHz NMR, acetone-d6*
20171217-zk-Cu-PEt3-mono



Current Data Parameters
NAME 20171217-zk-Cu-PEt3-mono
EXPNO 5
PROCNO 1

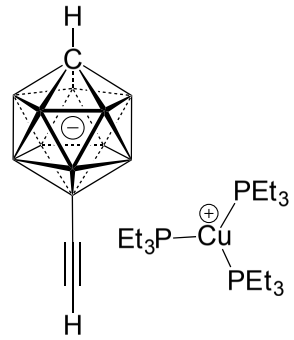
F2 - Acquisition Parameters
Date_ 20171218
Time 5.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 2048
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 193.34
DW 16.800 usec
DE 6.50 usec
TE 296.3 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1

======== 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 100.6126800 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

31P{1H} 162MHz NMR,acetone-d6
20171217-zk-Cu-PEt3-mono



-9.53

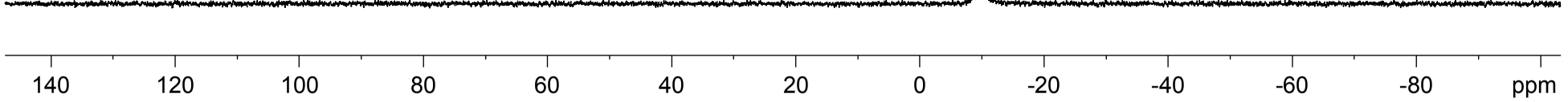
Current Data Parameters
NAME 20171217-zk-Cu-PEt3-mono
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171218
Time 4.22
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 128
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5111808 sec
RG 193.34
DW 7.800 usec
DE 6.50 usec
TE 295.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

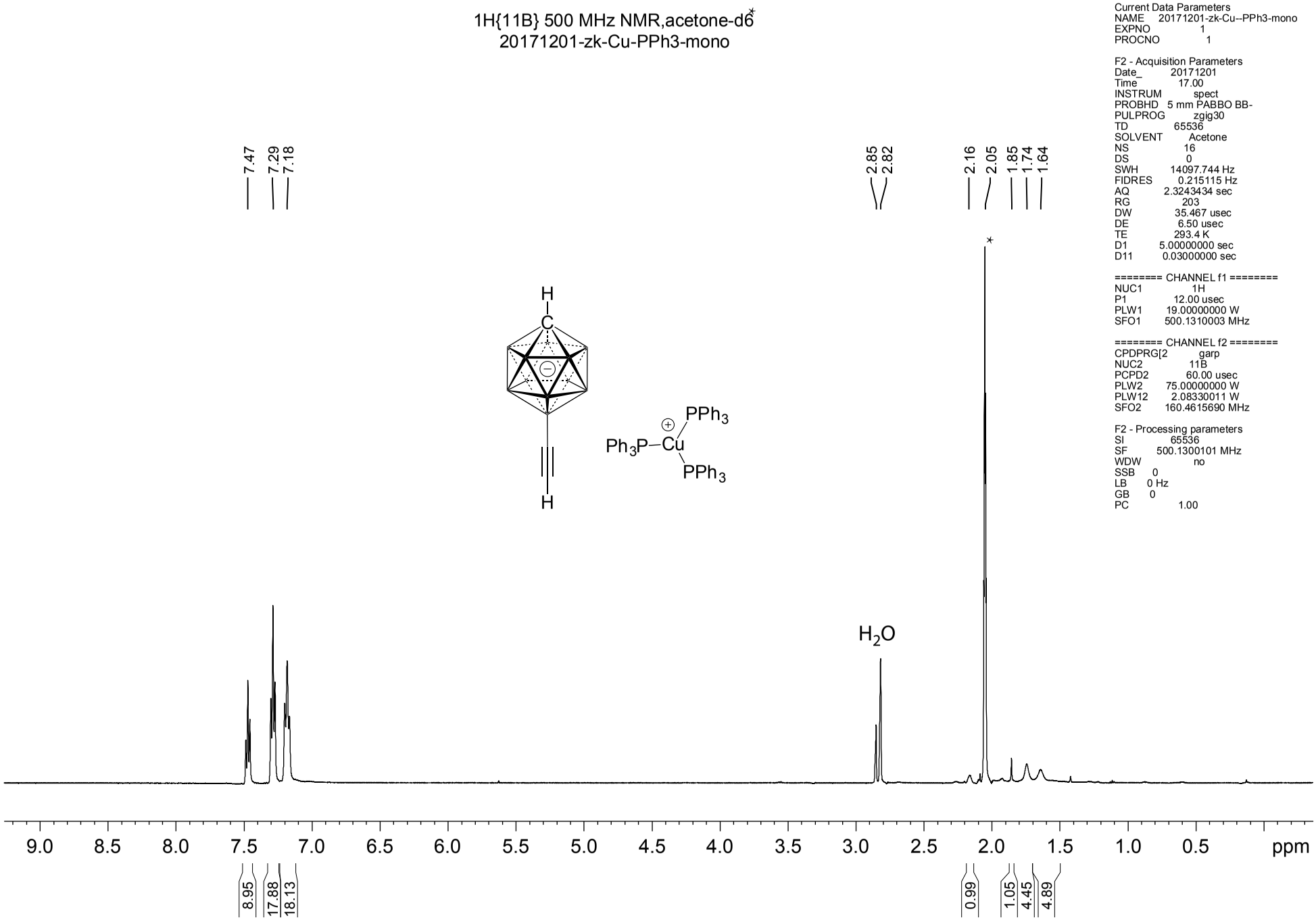
======== CHANNEL f1 ========
NUC1 31P
P1 15.00 usec
PLW1 15.00000000 W
SFO1 161.9674942 MHz

======== 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 161.9755930 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40



1H{11B} 500 MHz NMR,acetone-d6*
20171201-zk-Cu-PPh3-mono



Current Data Parameters
NAME 20171201-zk-Cu--PPh3-mono
EXPNO 1
PROCNO 1

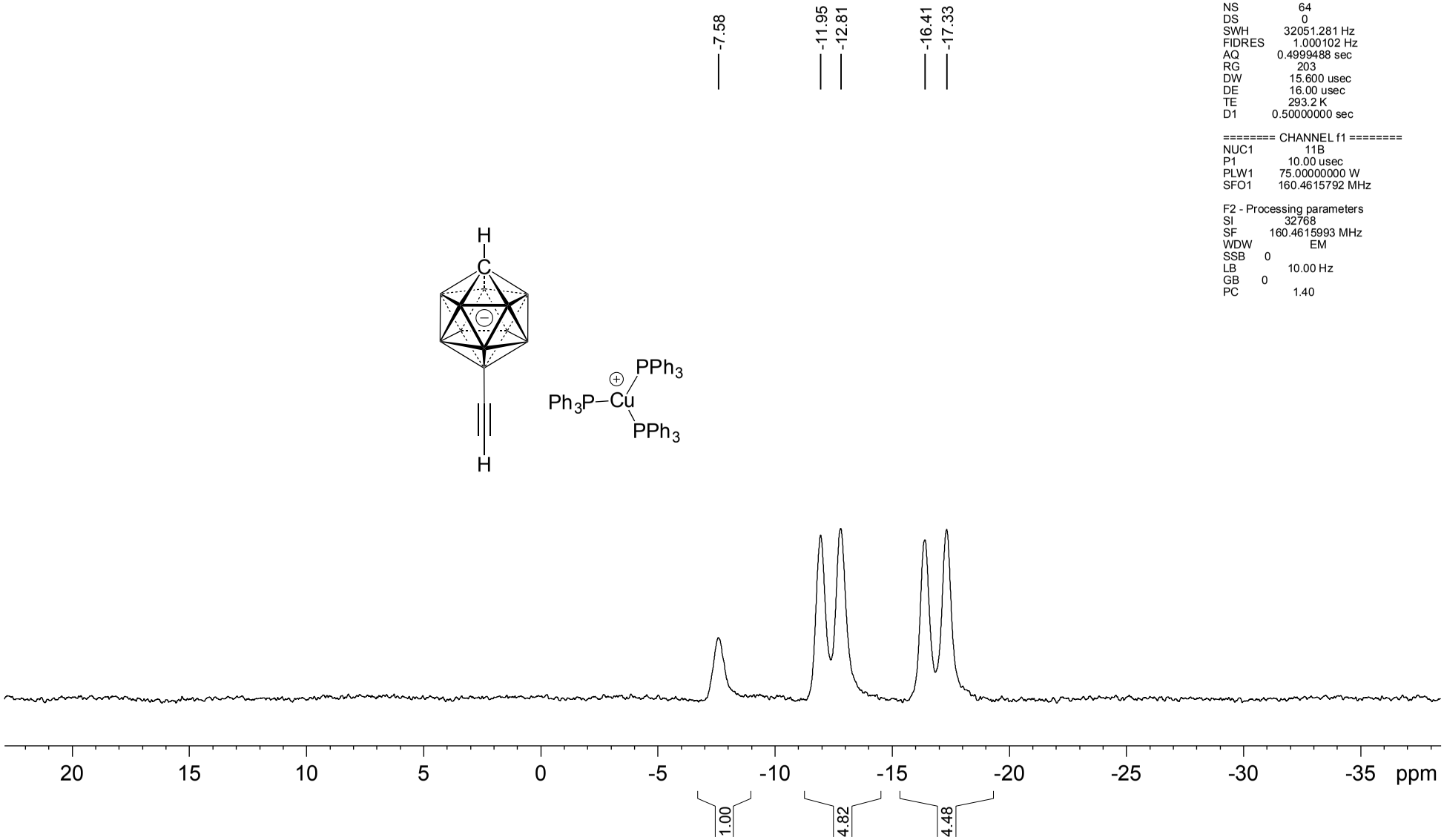
F2 - Acquisition Parameters
Date_ 20171201
Time 17.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgig30
TD 65536
SOLVENT Acetone
NS 16
DS 0
SWH 14097.744 Hz
FIDRES 0.215115 Hz
AQ 2.3243434 sec
RG 203
DW 35.467 usec
DE 6.50 usec
TE 293.4 K
D1 5.00000000 sec
D11 0.03000000 sec

======== 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 500.1300101 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00

11B 160 MHz NMR, acetone-d6
20171201-zk-Cu-PPh3-mono



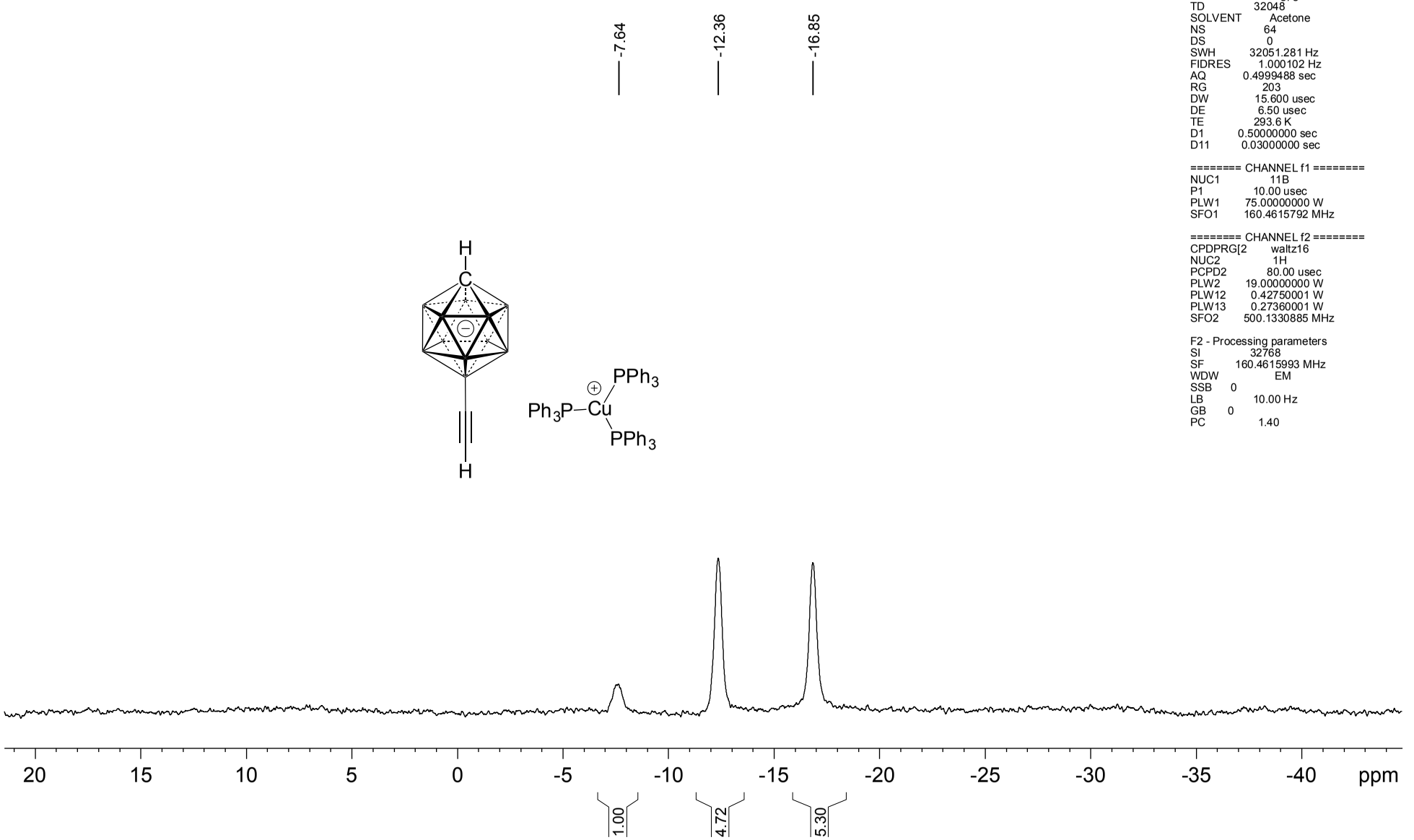
Current Data Parameters
NAME 20171201-zk-Cu--PPh3-mono
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171201
Time 17.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32048
SOLVENT Acetone
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 293.2 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} 160 MHz NMR, acetone-d6
20171201-zk-Cu-PPh3-mono



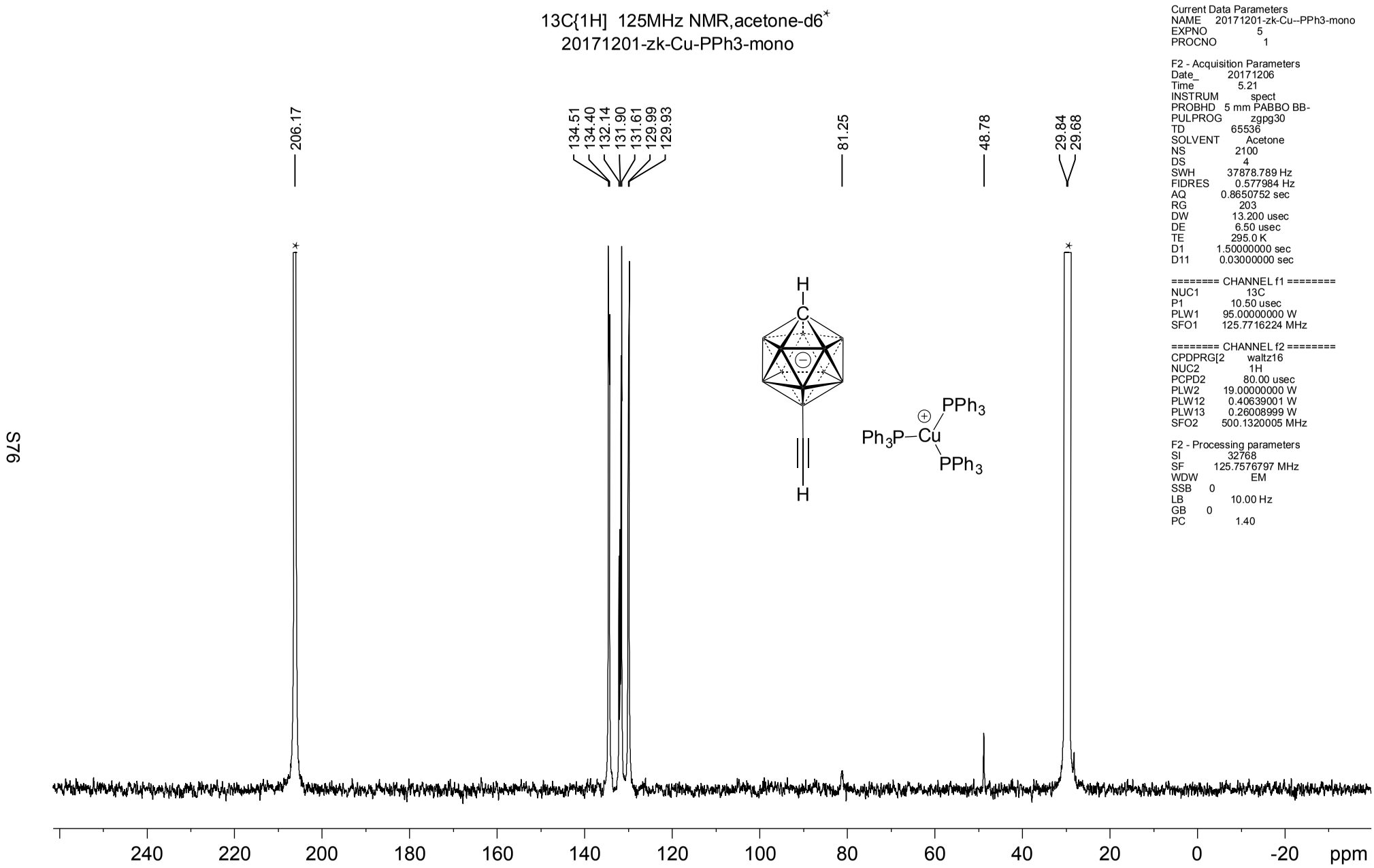
Current Data Parameters
NAME 20171201-zk-Cu--PPh3-mono
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171201
Time 17.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32048
SOLVENT Acetone
NS 64
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 293.6 K
D1 0.50000000 sec
D11 0.03000000 sec

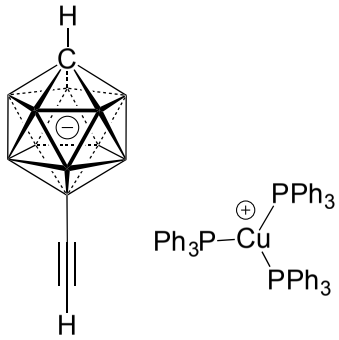
======== CHANNEL f1 ========
NUC1 11B
P1 10.00 usec
PLW1 75.00000000 W
SFO1 160.4615792 MHz

======== 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


13C{1H} 125MHz NMR,acetone-d6*
20171201-zk-Cu-PPh3-mono
206.17
134.51
134.40
132.14
131.90
131.61
129.99
129.93
81.25
48.78
29.84
29.68
H
C
H
PPh3
Ph3P—Cu
PPh3
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm
Current Data Parameters
NAME 20171201-zk-Cu--PPh3-mono
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171206
Time 5.21
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 2100
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 295.0 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 125.7576797 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

31P{1H} 202 MHz NMR, acetone-d6
20171201-zk-Cu-PPh3-mono



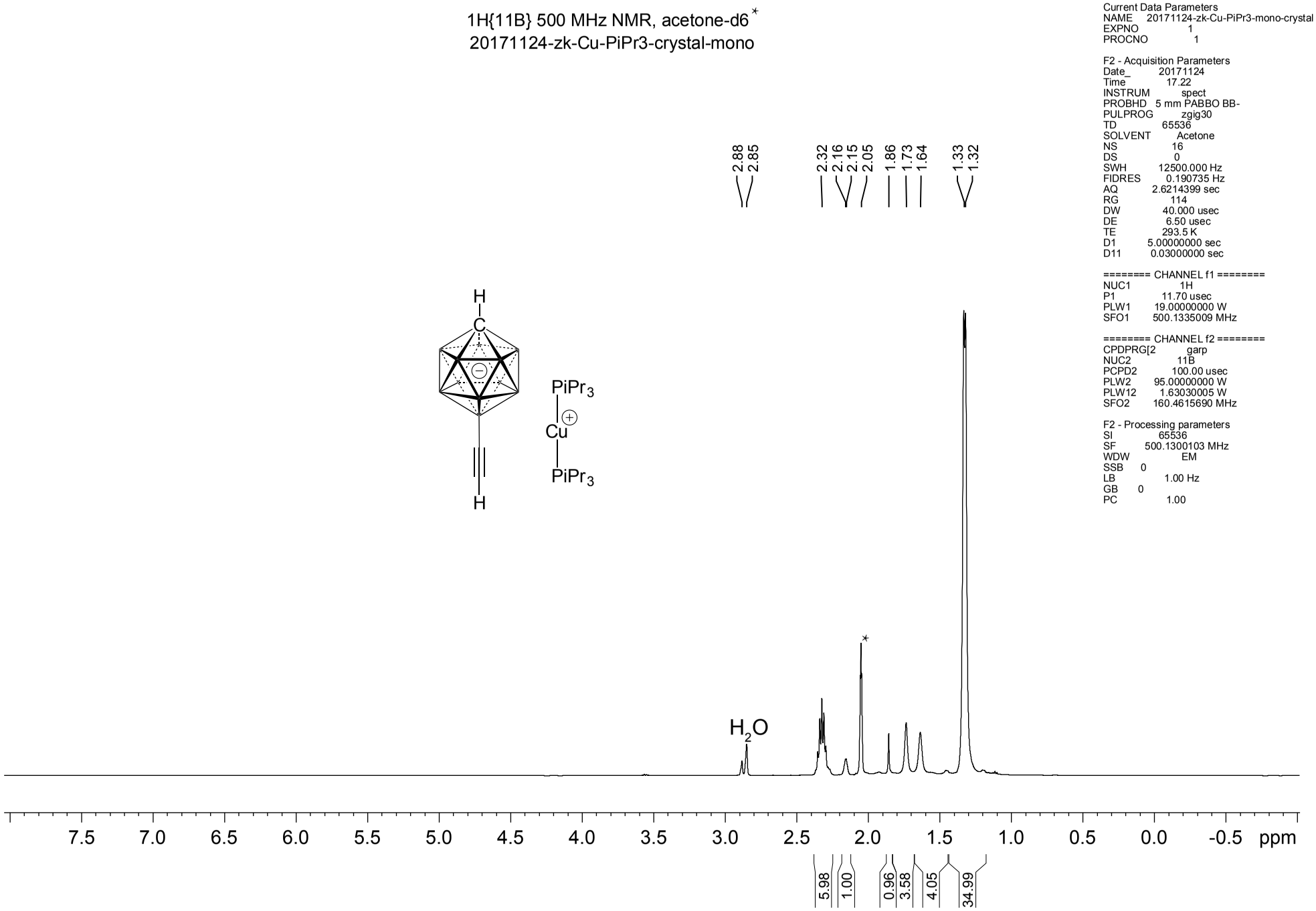
Current Data Parameters
NAME 20171201-zk-Cu--PPh3-mono
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171206
Time 5.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 256
DS 4
SWH 81521.742 Hz
FIDRES 1.243923 Hz
AQ 0.4019541 sec
RG 203
DW 6.133 usec
DE 6.50 usec
TE 294.9 K
D1 2.00000000 sec
D11 0.03000000 sec

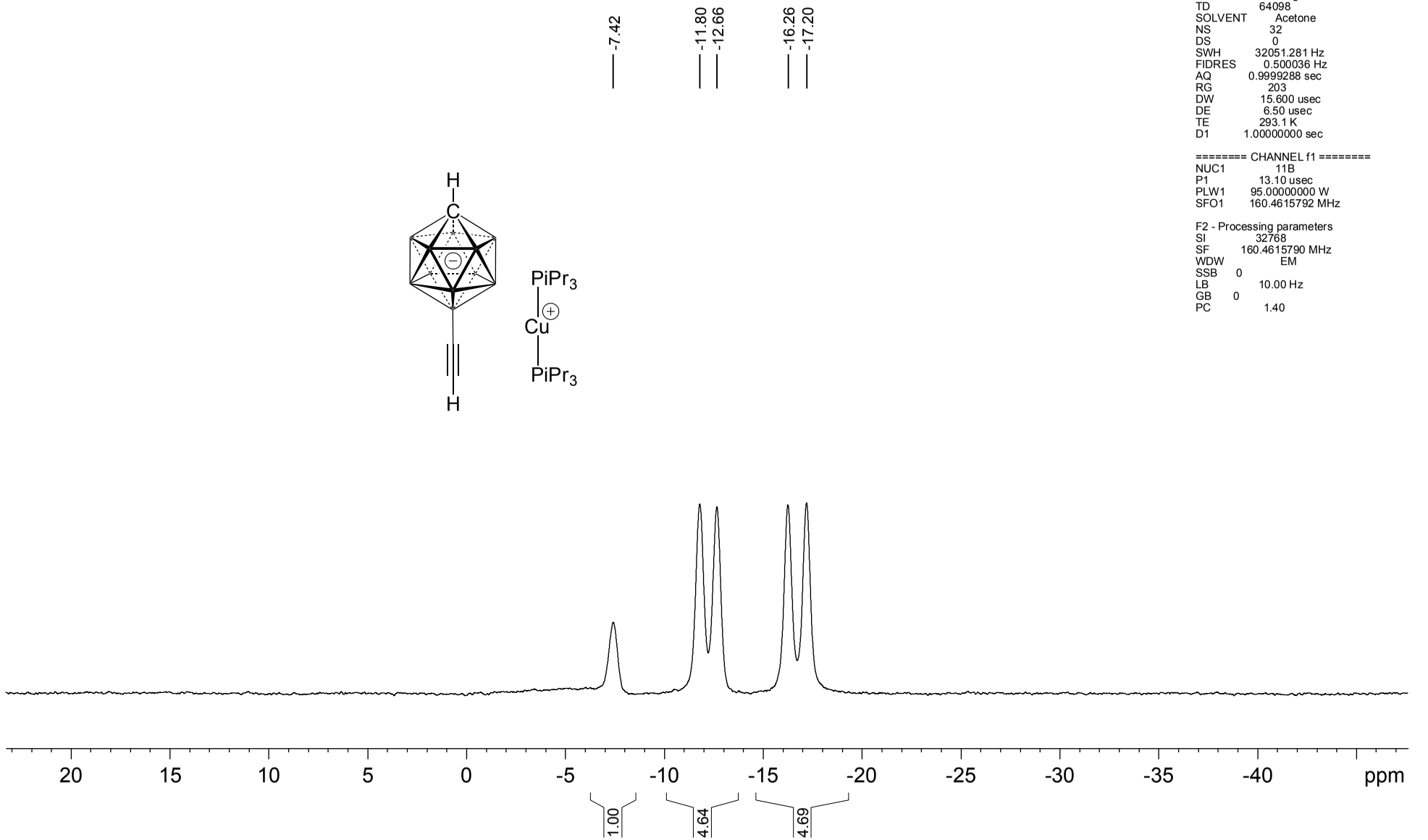
======== CHANNEL f1 ========
NUC1 31P
P1 12.00 usec
PLW1 83.00000000 W
SFO1 202.4563350 MHz

======== 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 202.4563350 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40


1H{11B} 500 MHz NMR, acetone-d6 *
20171124-zk-Cu-PiPr3-crystal-mono
Current Data Parameters
NAME 20171124-zk-Cu-PiPr3-mono-crystal
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171124
Time 17.22
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 293.5 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 500.1300103 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
2.88
2.85
2.32
2.16
2.15
2.05
1.86
1.73
1.64
1.33
1.32
H
C
PiPr3
Cu
PiPr3
H
H2O
*
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
5.98
1.00
0.96
3.58
4.05
34.99

11B 160MHz NMR, acetone-d6
20171124-zk-Cu-PiPr3-crystal-mono



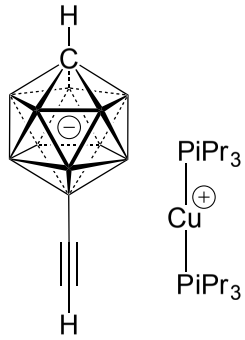
Current Data Parameters
NAME 20171124-zk-Cu-PiPr3-mono-crystal
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171124
Time 17.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
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 6.50 usec
TE 293.1 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 11B
P1 13.10 usec
PLW1 95.00000000 W
SFO1 160.4615792 MHz

F2 - Processing parameters
SI 32768
SF 160.4615790 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40

11B{1H} 160MHz NMR, acetone-d6
20171124-zk-Cu-PiPr3-crystal-mono



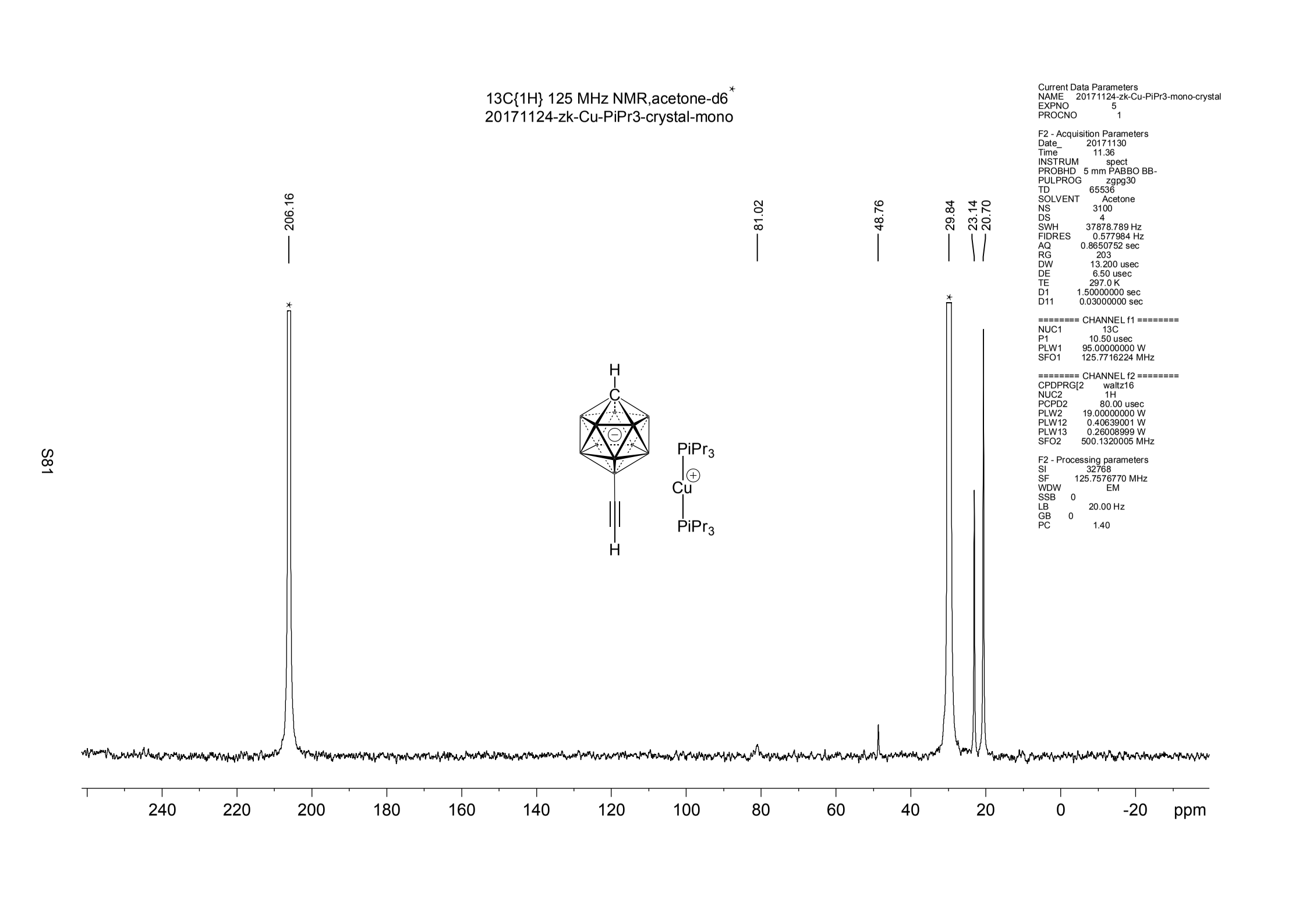
Current Data Parameters
NAME 20171124-zk-Cu-PiPr3-mono-crystal
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171124
Time 17.27
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 293.9 K
D1 1.00000000 sec
D11 0.03000000 sec

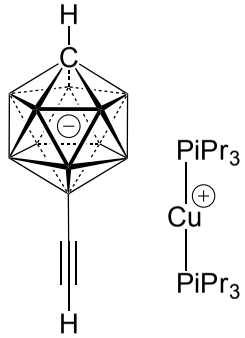
======== CHANNEL f1 ========
NUC1 11B
P1 13.10 usec
PLW1 95.00000000 W
SFO1 160.4615790 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.40639001 W
PLW13 0.26008999 W
SFO2 500.1325007 MHz

F2 - Processing parameters
SI 32768
SF 160.4615790 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


13C{1H} 125 MHz NMR,acetone-d6*
20171124-zk-Cu-PiPr3-crystal-mono
206.16
81.02
48.76
29.84
23.14
20.70
H
C
PiPr3
Cu
PiPr3
H
Current Data Parameters
NAME 20171124-zk-Cu-PiPr3-mono-crystal
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171130
Time 11.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 3100
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 297.0 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 125.7576770 MHz
WDW EM
SSB 0
LB 20.00 Hz
GB 0
PC 1.40
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

31P{1H} 202 MHz NMR, acetone-d6
20171124-zk-Cu-PiPr3-crystal-mono



27.53

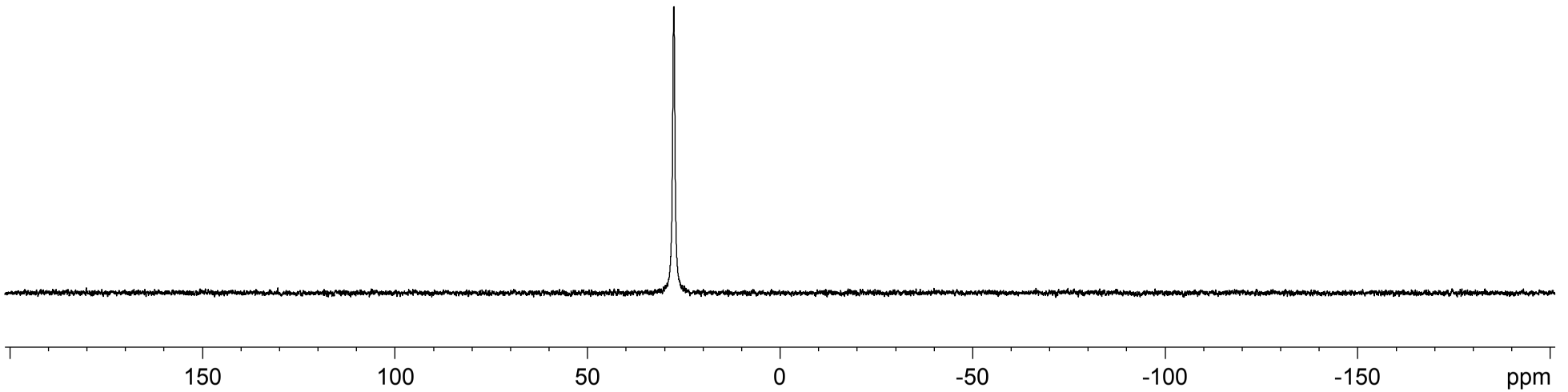
Current Data Parameters
NAME 20171124-zk-Cu-PiPr3-mono-crystal
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171124
Time 17.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 512
DS 4
SWH 81521.742 Hz
FIDRES 1.243923 Hz
AQ 0.4019541 sec
RG 203
DW 6.133 usec
DE 6.50 usec
TE 293.4 K
D1 2.00000000 sec
D11 0.03000000 sec

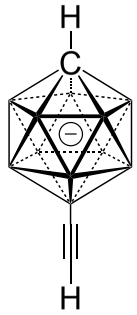
======== CHANNEL f1 ========
NUC1 31P
P1 12.00 usec
PLW1 83.00000000 W
SFO1 202.4563350 MHz

======== 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 202.4563350 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40



1H{11B} 500MHz NMR,acetone-d6*
20171212-zk-Cu-PCy3-mono



$[Cu(PCy_3)_2]^+$

Current Data Parameters
NAME 20171212-zk-Cu-PCy3-mono-pure
EXPNO 1
PROCNO 1

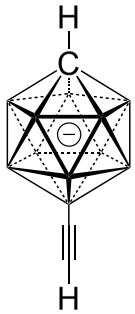
F2 - Acquisition Parameters
Date_ 20171212
Time 19.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgig30
TD 65536
SOLVENT Acetone
NS 16
DS 0
SWH 12500.000 Hz
FIDRES 0.190735 Hz
AQ 2.6214399 sec
RG 114
DW 40.000 usec
DE 6.50 usec
TE 294.9 K
D1 5.00000000 sec
D11 0.03000000 sec

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

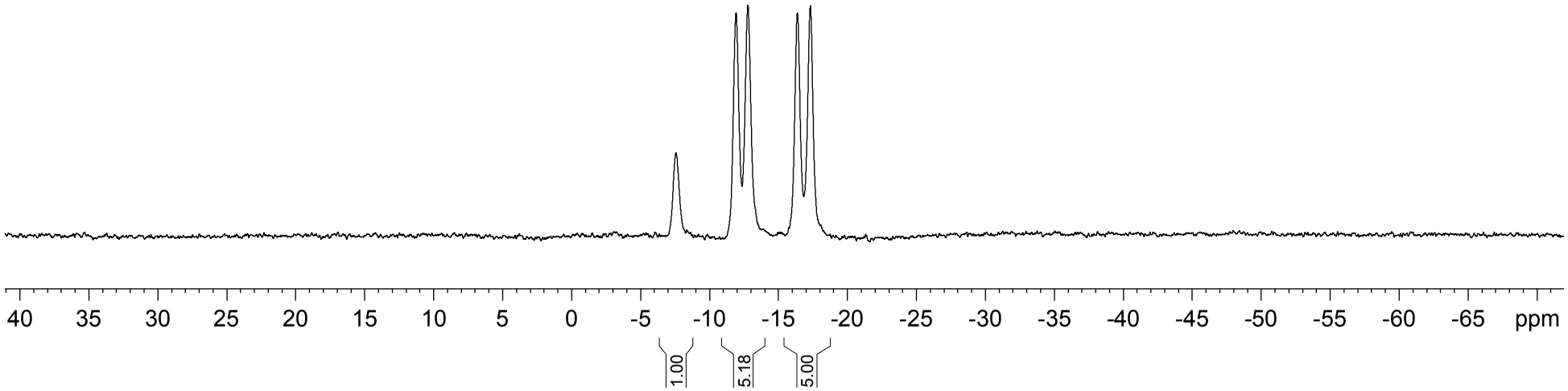
======== CHANNEL f2 ========
CPDPRG[2 garp
NUC2 11B
PCPD2 100.00 usec
PLW2 95.00000000 W
PLW12 1.63030005 W
SFO2 160.4615690 MHz

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

11B 160MHz NMR, acetone-d6
20171130-zk-Cu--PCy3-mono



$[Cu(PCy_3)_2]^+$



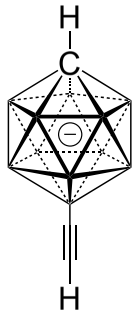
Current Data Parameters
NAME 20171130-zk-Cu--PCy3-mono
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171130
Time 17.44
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32048
SOLVENT Acetone
NS 32
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 294.0 K
D1 0.50000000 sec

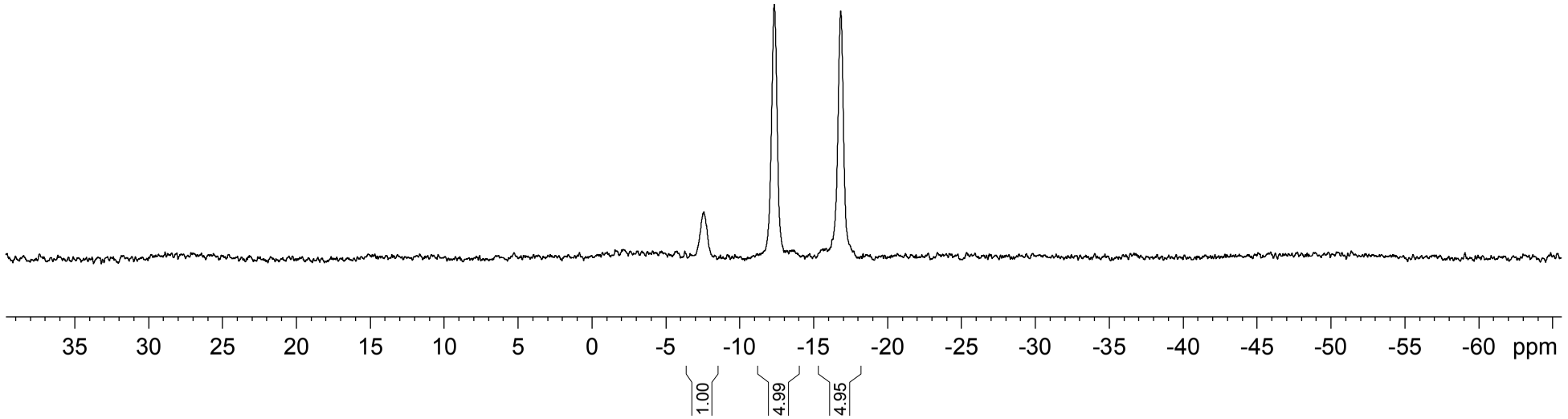
======== CHANNEL f1 ========
NUC1 11B
P1 10.00 usec
PLW1 75.00000000 W
SFO1 160.4615792 MHz

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

11B{1H} 160MHz NMR, acetone-d6
20171130-zk-Cu--PCy3-mono



$[Cu(PCy_3)_2]^+$



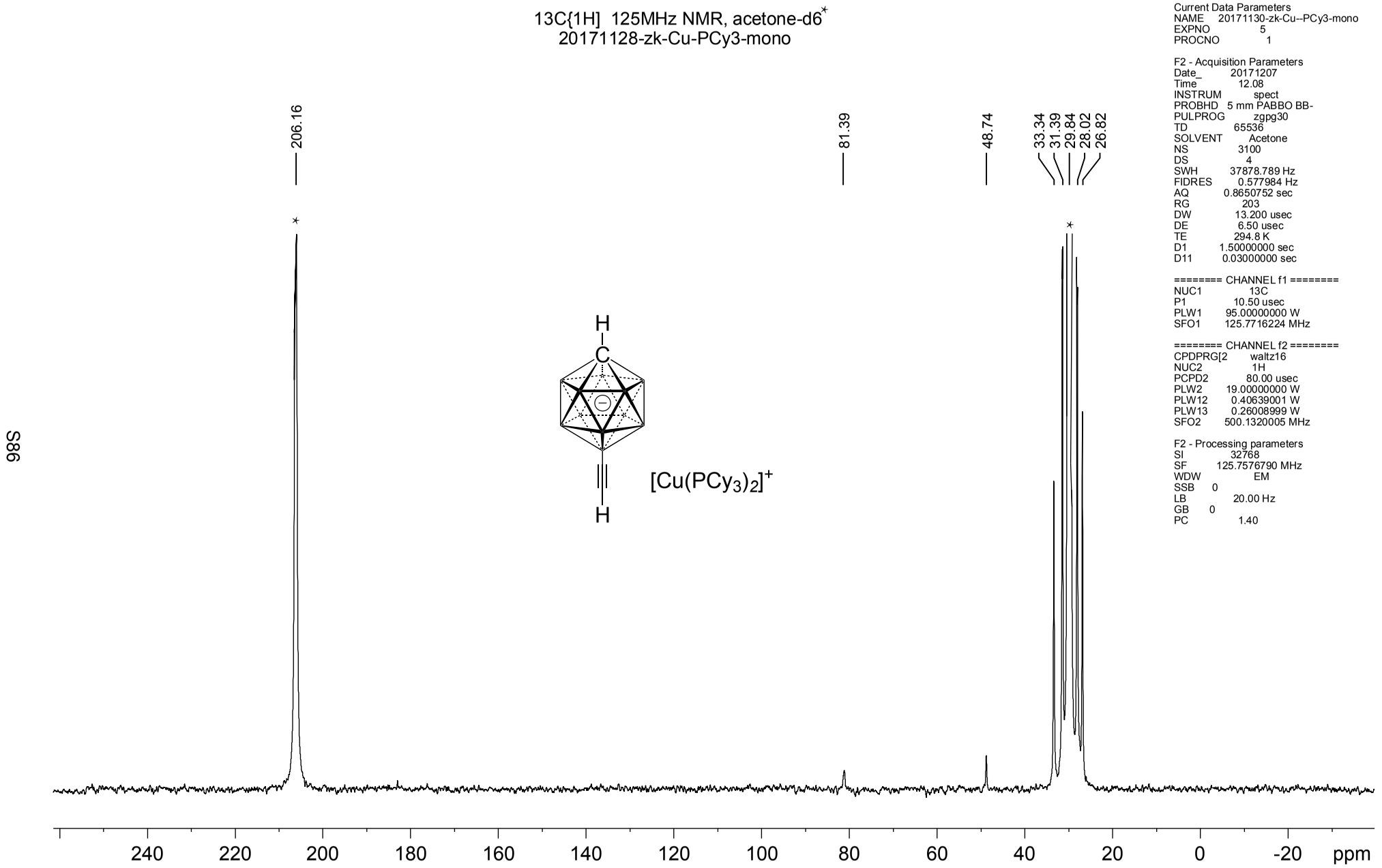
Current Data Parameters
NAME 20171130-zk-Cu--PCy3-mono
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171130
Time 17.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32048
SOLVENT Acetone
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 294.2 K
D1 0.50000000 sec
D11 0.03000000 sec

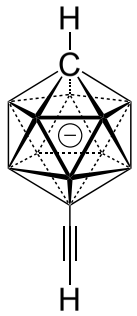
======== CHANNEL f1 ========
NUC1 11B
P1 10.00 usec
PLW1 75.00000000 W
SFO1 160.4615792 MHz

======== 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


13C{1H} 125MHz NMR, acetone-d6*
20171128-zk-Cu-PCy3-mono
206.16
81.39
48.74
33.34
31.39
29.84
28.02
26.82
H
C
H
[Cu(PCy3)2]+
Current Data Parameters
NAME 20171130-zk-Cu--PCy3-mono
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171207
Time 12.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 3100
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 294.8 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 125.7576790 MHz
WDW EM
SSB 0
LB 20.00 Hz
GB 0
PC 1.40
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

31P{1H} 202MHz NMR, acetone-d6
20171128-zk-Cu-PCy3-mono



$[Cu(PCy_3)_2]^+$

13.17

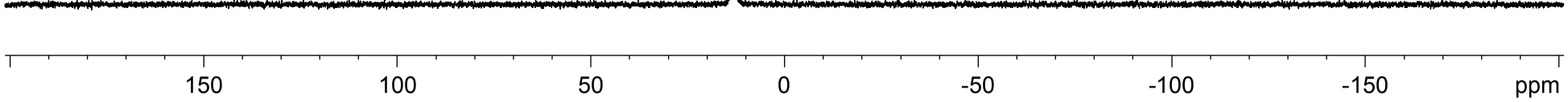
Current Data Parameters
NAME 20171130-zk-Cu--PCy3-mono
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171208
Time 1.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 256
DS 4
SWH 81521.742 Hz
FIDRES 1.243923 Hz
AQ 0.4019541 sec
RG 203
DW 6.133 usec
DE 6.50 usec
TE 296.9 K
D1 2.00000000 sec
D11 0.03000000 sec

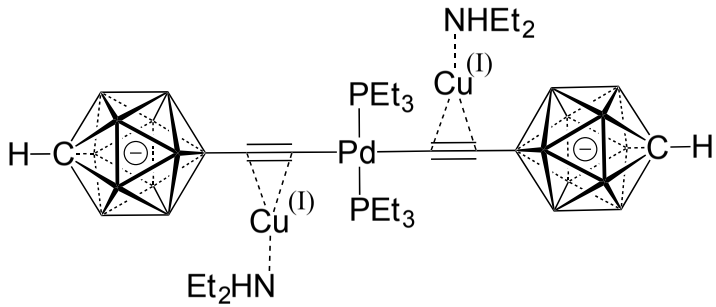
======== CHANNEL f1 ========
NUC1 31P
P1 12.00 usec
PLW1 83.00000000 W
SFO1 202.4563350 MHz

======== 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 202.4563350 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40



1H{11B} 400 MHz NMR, acetone-d6*
20180530-zk-Pd-PEt3-HNEt2



Current Data Parameters
NAME 20180530-zk-Pd-PEt3-HNEt2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180531
Time 1.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgig30
TD 16384
SOLVENT Acetone
NS 32
DS 4
SWH 8012.820 Hz
FIDRES 0.489064 Hz
AQ 1.0223616 sec
RG 193.34
DW 62.400 usec
DE 6.50 usec
TE 293.4 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

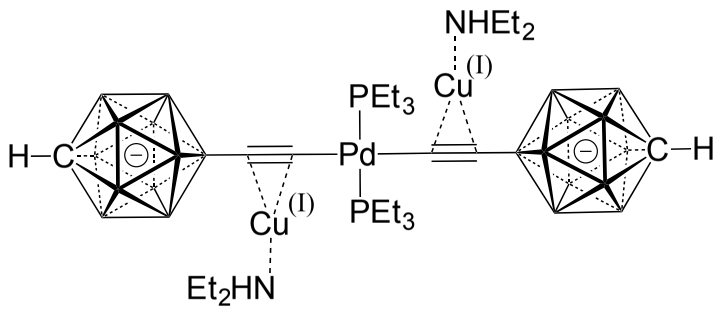
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PLW1 12.50000000 W
SFO1 400.1320007 MHz

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

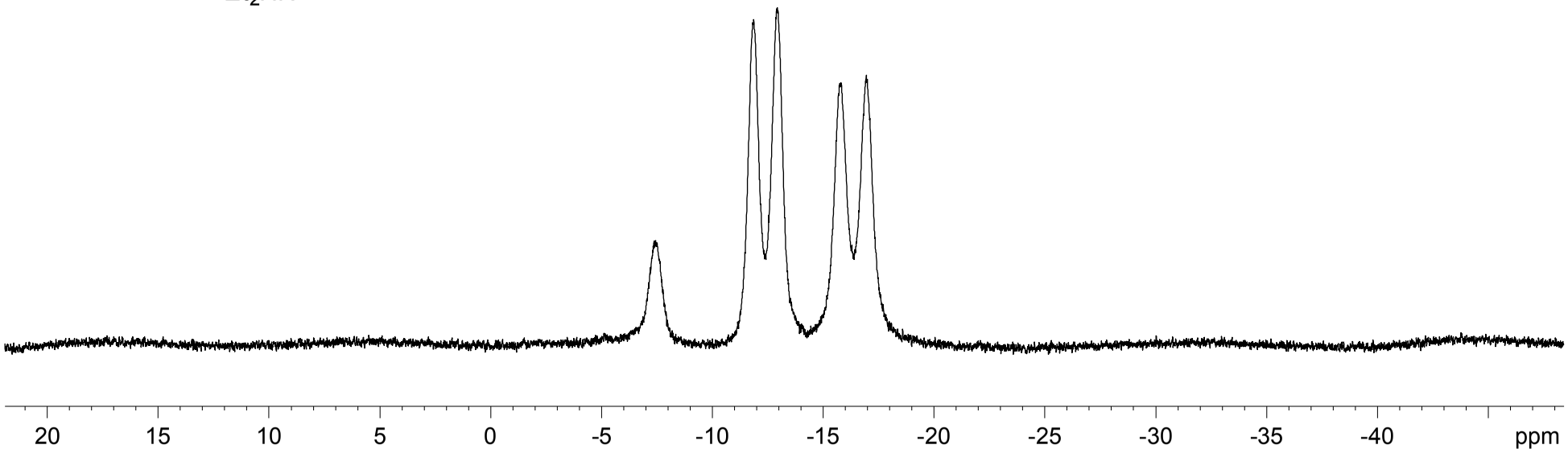
F2 - Processing parameters
SI 32768
SF 400.1300074 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

◊ Because of the overlap with the solvent residual signal, half of the signal was chosen for integration.

11B NMR, 128 MHz NMR, acetone-d6
20180530-zk-Pd-PEt3-HNEt2



-7.45
-11.88
-12.94
-15.83
-16.96



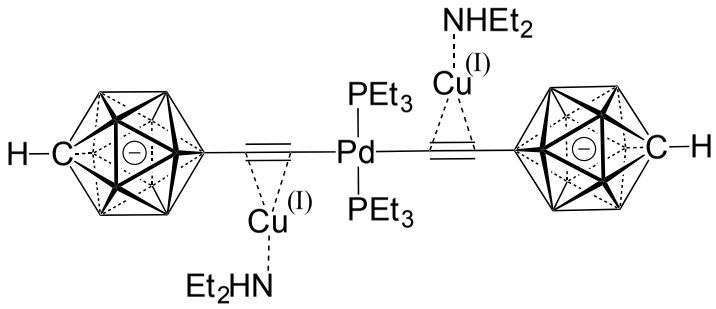
Current Data Parameters
NAME 20180530-zk-Pd-PEt3-HNEt2
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180531
Time 1.30
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 65536
SOLVENT Acetone
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 293.4 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

11B{1H} NMR, 128 MHz NMR, acetone-d6
20180530-zk-Pd-PEt3-HNEt2



Current Data Parameters
NAME 20180530-zk-Pd-PEt3-HNEt2
EXPNO 2
PROCNO 1

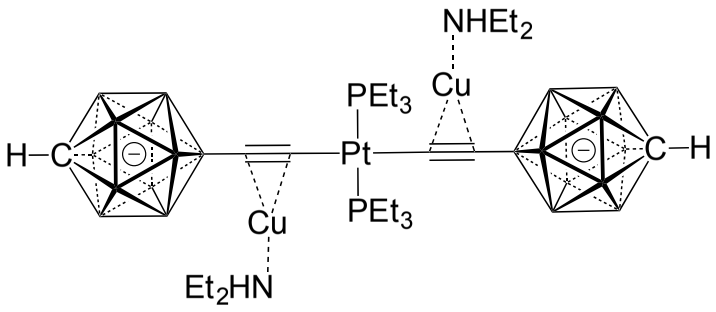
F2 - Acquisition Parameters
Date_ 20180531
Time 1.27
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 64
DS 4
SWH 25510.203 Hz
FIDRES 0.389255 Hz
AQ 1.2845056 sec
RG 193.34
DW 19.600 usec
DE 6.50 usec
TE 294.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== 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

1H{11B} 400 MHz NMR, DMSO-d6 *
20170517-zk-Pt-Cu-HNEt2



Current Data Parameters
NAME 20170519-zk-Pt-Cu-HNEt2
EXPNO 1
PROCNO 1

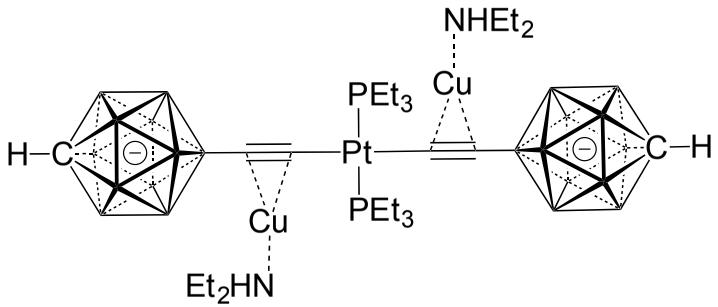
F2 - Acquisition Parameters
Date_ 20170520
Time 11.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgig30
TD 16384
SOLVENT DMSO
NS 16
DS 4
SWH 8012.820 Hz
FIDRES 0.489064 Hz
AQ 1.0223616 sec
RG 193.34
DW 62.400 usec
DE 6.50 usec
TE 294.7 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== 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 400.1300034 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

11B NMR, 128 MHz NMR, DMSO-d6
20170517-zk-Pt-Cu-HNEt2



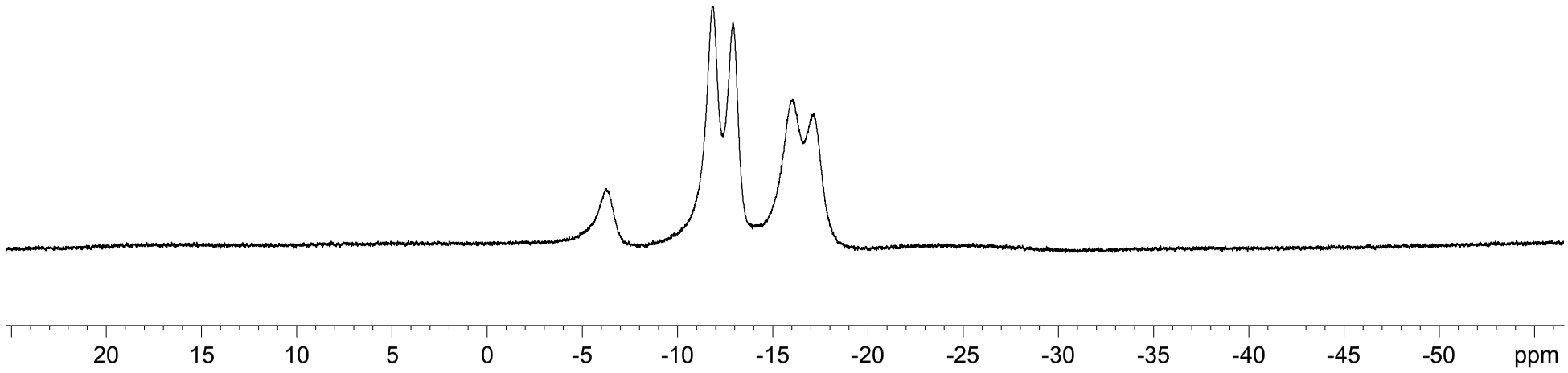
-6.27
-11.88
-12.93
-16.10
-17.19

Current Data Parameters
NAME 20170427-zk-C2-Pt-DMSO
EXPNO 3
PROCNO 1

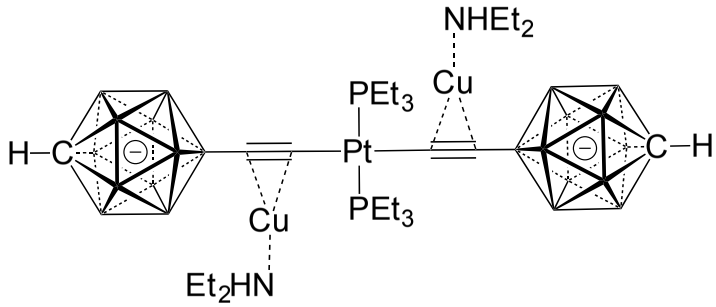
F2 - Acquisition Parameters
Date_ 20170428
Time 23.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 65536
SOLVENT DMSO
NS 128
DS 4
SWH 25510.203 Hz
FIDRES 0.389255 Hz
AQ 1.2845056 sec
RG 193.34
DW 19.600 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1

======== 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



11B{1H} NMR, 128 MHz NMR, DMSO-d6
20170517-zk-Pt-Cu-HNEt2



Current Data Parameters
NAME 20170427-zk-C2-Pt-DMSO
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170428
Time 23.50
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 295.3 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

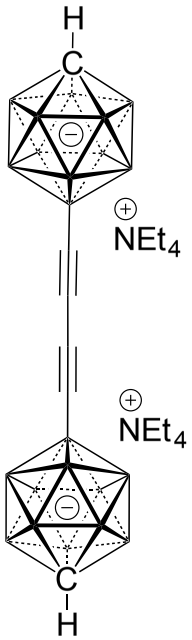
======== CHANNEL f1 ========
NUC1 11B
P1 9.93 usec
PLW1 52.96599960 W
SFO1 128.3776050 MHz

======== 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

1H{11B}, 400 MHz NMR, CD3CN *

[NEt4]2[CB11H11−C2−C2−CB11H11]



3.19 3.17 3.15 3.14 — 2.28 — 2.14 — 1.95 1.95 1.94 1.93 1.93 — 1.57 — 1.23 1.23 1.21 1.20 1.20

H_2O

*

4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

16.00 2.04 19.10 24.52

```
Current Data Parameters
NAME      20170111-zk-DiCC-Crystal
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_           20170112
Time              14.58
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgig30
TD                16384
SOLVENT           CD3CN
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                294.2 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

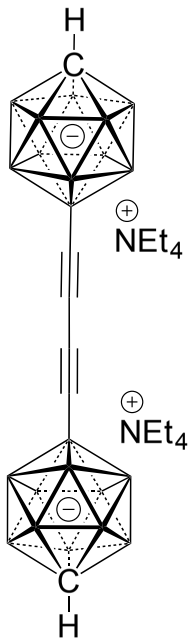
======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PLW1        12.50000000 W
SFO1        400.1320007 MHz

======== 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          400.1300118 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

11B{1H}, 128 MHz NMR, CD3CN

[NEt4]2[CB11H11−C2−C2−CB11H11]




```
Current Data Parameters
NAME      20170111-zk-DiCC-Crystal
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170112
Time              14.50
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG             zg
TD                65536
SOLVENT           CD3CN
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               293.7 K
D1           1.00000000 sec
TD0                   1

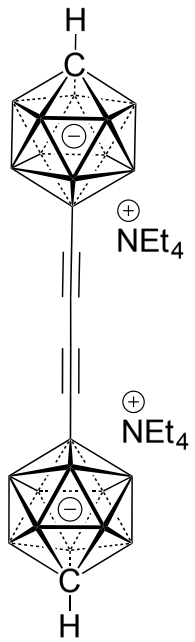
======== CHANNEL f1 ========
NUC1                 11B
P1                  9.93 usec
PLW1        52.96599960 W
SFO1        128.3776052 MHz

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

11B{1H}, 128 MHz NMR, CD3CN

[NEt4]2[CB11H11−C2−C2−CB11H11]

96S

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Current Data Parameters
NAME      20170111-zk-DiCC-Crystal
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170112
Time              14.57
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CD3CN
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               294.5 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                  1

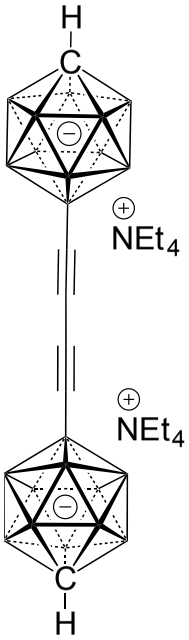
======== CHANNEL f1 ========
NUC1                11B
P1                 9.93 usec
PLW1        52.96599960 W
SFO1       128.3776050 MHz

======== 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
```

13C{1H}, 100 MHz NMR, CD3CN *

[NEt4]2[CB11H11−C2−C2−CB11H11]



Current Data Parameters
NAME 20170111-zk-DiCC-Crystal
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170228
Time 1.26
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 4096
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 294.2 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 100.6126747 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40