Improved synthesis of icosahedral carboranes containing exopolyhedral B–C and C–C bonds

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Supporting Information (SI)

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1. General Considerations

Meta-$C_2B_{10}H_{12}$ (Katchem), *ortho*-$C_2B_{10}H_{12}$ (Boron Specialties), were sublimed prior to use. XPhos (Sigma-Aldrich) and SPhos (Ark Pharm) were used as received. XPhos-Pd-G3 and SPhos-Pd-G3 were prepared according to literature procedures[1]. Iodomethane (Sigma-Aldrich), Bromoethane (Sigma-Aldrich), Iodobenzene (Sigma-Aldrich), 2-Bromothiophene (Oakwood), and 4-Bromobenzotrifluoride (Oakwood) were stored over molecular sieves in ambient conditions and used as is. Iodotoluene (Sigma-Aldrich) was used as received. Grignard reagents were prepared by the dropwise addition of alkyl or aryl halides to an excess of Magnesium chips (Sigma-Aldrich) in anhydrous ether and left to stir overnight at room temperature (MeMgI and EtMgBr were instead stirred at reflux overnight) and filtered before use. The concentration of the Grignard reagents was determined by titration of iodine (~63.5 mg in 5 mL of anhydrous THF) with a 0.20 mL aliquot until the equivalence point was observed. Fluoronaphthalene (Oakwood Chemical) was stirred over CaH_2 then distilled under vacuum and stored in an N_2-filled glovebox. Isopropoxytrimethylsilane (Sigma-Aldrich) and solid KHMDS (Sigma-Aldrich) were stored in an N_2-filled glovebox and used as received. KHMDS solution (Sigma-Aldrich, anhydrous, 1M in THF) was used as received. 6-fluoroquinoline (Oakwood Chemical), 2-chloropyridine (Oakwood Chemical), 2-fluoropyridine (Oakwood Chemical) and 2,6-difluoropyridine (Oakwood Chemical) were stored over 3 Å molecular sieves in ambient conditions. Perfluorobenzene (Oakwood Chemical) and 2,2'-bipyridine (Oakwood Chemical) were stored in ambient conditions and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. Glass-backed Silica Gel 60 GLA TLC plates were purchased from Fisher Scientific. Silica used for flash column chromatography was SiliaFlash® G60 60-200 μm (70-230 mesh) purchased from Silicycle.

All experiments were performed air and moisture free under an atmosphere of nitrogen using standard Schlenk techniques. Anhydrous dioxane (Sigma-Aldrich) was used as received. THF, diethyl ether, and methyl *tert*-butyl ether (MTBE) used for reactions were purified and dried using a Grubbs column. All post-Schlenk work-up and characterization was performed under ambient conditions. The "ambient conditions" for this manuscript refer to room temperature (20 - 25˚C) and uncontrolled laboratory air. Thin layer chromatography (TLC) samples for carborane-containing compounds were stained with 1 wt. % $PdCl_2$ in 6M HCl and developed with heat.

2. Instrumentation

^{1}H, $^{13}C\{^{1}H\}$, ^{11}B, $^{11}B\{^{1}H\}$, ^{19}F, NMR spectra were recorded on either a Bruker DRX500, Bruker AV500 or Bruker AVIII 400 spectrometer in ambient conditions unless stated otherwise. MestreNova v6.0.2-5475 software was used to process the FID data and visualize the spectra. ^{1}H and ^{13}C NMR spectra were referenced to residual solvent resonances in deuterated solvents ($CDCl_3$: ^{1}H, 7.26 ppm; ^{13}C, 77.16 ppm. Acetone-d_6: ^{1}H, 2.05 ppm; ^{13}C, 29.84 ppm. Note: due to high humidity H_2O resonances are often present). ^{11}B and $^{11}B\{^{1}H\}$ NMR spectra were referenced externally to $Et_2O{\cdot}BF_3$ (δ = 0 ppm). ^{19}F NMR spectra were referenced externally to fluorobenzene (δ = -113.15 ppm).

Gas Chromatography Mass Spectrometry (GC-MS) measurements were carried out using an Agilent Model 7693 Autosampler, 7890B Gas Chromatograph, and 7250 Q-TOF Mass Selective Detector in the Electron Ionization mode. Sample injection was carried out on an Agilent HP5-MS column with dimensions 30 m x 250 µm x 0.25 µm. Ultra High Purity Grade He (Airgas) was used as carrier gas. Data collection and analysis were performed using Mass Hunter Acquisition and Qualitative Analysis software (Agilent).

3. Experimental

1. Precursor Synthesis

9-I-1,2-dicarba-*closo*-dodecaborane (9-I-oCB)[2], 9-I-1,7-dicarba-*closo*-dodecaborane (9-I-mCB)[2], 9,12-I_2-1,2-dicarba-*closo*-doedecaborane (9,12-I_2-oCB)[3], 9,12-Br_2-1,2-dicarba-*closo*-doedecaborane (9,12-Br_2-oCB)[2], and 9-Br, 10-I-1,7-dicarba-*closo*-dodecaborane (9-Br-10-I-mCB)[2] were synthesized according to or adapted from previously reported procedures. All characterization data are consistent with those previous reports.

2. Kumada-type Cross-Coupling with Iodo-carboranes

Optimization of Kumada Cross-Coupling Protocol

9,12-I_2-oCB (40 mg, 0.1 mmol) or 9,12-Br_2-oCB (30 mg, 0.1 mmol), catalyst (0.002 mmol, 2 mol%), phosphine ligand (0.002 mmol, 2 mol%), and additive (if applicable, 0.002 mmol, 2 mol%) were added to an oven-dried reaction tube with a PTFE septum cap. The reaction tube was evacuated and backfilled with N_2 three times before transferring into an N_2-filled glovebox. Under an inert atmosphere, anhydrous solvent (0.6 mL) was added before the dropwise addition of ethylmagnesium bromide in diethyl ether (~2 M, 4.2-5.0 eq.). The reaction mixture was heated and the reaction progress was monitored by GC-MS after 2.5 hours.

Table S1. Kumada coupling optimizations

Entry #	Substrate	Ligand	Grig. Eq.	Additive	Solvent	Temp.	% Conversion by GC-MS
1	I_2-oCB	XPhos	5.0 eq.	CuI	THF	75 °C	2

2	I_2-oCB	XPhos	4.2 eq	-----	Dioxane	65 ^oC	30
3	I_2-oCB	XPhos	4.2 eq	-----	Dioxane	75 ^oC	89
4	I_2-oCB	SPhos	4.2 eq	-----	Dioxane	75 ^oC	90
5	Br_2-oCB	XPhos	4.2 eq	-----	Dioxane	75 ^oC	0

Note: Although most entries and products utilize XPhos-Pd-G3 and XPhos ligand catalytic system, Entry 4 as well as products **1A^{I}** and **1D^{I}** provide evidence to suggest that SPhos-Pd-G3 and SPhos ligand would be competent in these transformations. When using EtMgBr, only slight variations in isolated yields were observed and reaction times remained consistent between using XPhos or SPhos.

Procedure for Kumada Cross-Coupling with 9,12-I_2-oCB

9,12-I_2-oCB (0.5-1 mmol), L-Pd-G3 (2 mol%), and L (2 mol%) were added to an oven-dried Schlenk flask and evacuated/backfilled with N_2 three times before leaving under an inert atmosphere. Using a syringe, anhydrous dioxane (6 mL) was added to dissolve all solids. Next the Grignard reagent (~2 M, 2.1-4.2 mmol, 4.2 eq.) was added dropwise to this stirring solution at room temperature. The reaction mixture was then stirred at 75 ^oC until the reaction was determined to be complete by GC-MS. The reaction mixture was then diluted with Et_2O (~20 mL) and the excess Grignard was quenched by the addition of H_2O. The solution was transferred to a separatory funnel and the aqueous layer was extracted with Et_2O (3 x 20 mL). During the extraction, brine (~5 mL) was added to improve separation between organic and aqueous layers. The organic fractions were combined and dried with $MgSO_4$, then filtered into a round-bottomed flask. The solvent was removed under reduced pressure to yield the crude product as a colored oil or solid. The crude product was dry loaded onto silica and purified using silica gel column chromatography to yield the desired product (see product details for exact purification conditions).

Procedure for Kumada Cross-Coupling with 9-I-oCB, 9-I-mCB, or 9-Br-10-I-mCB

Mono-iodinated carborane (9-I-oCB, 9-I-mCB, or 9-Br-10-I-mCB; 0.5-1 mmol), L-Pd-G3 (1-1.5 mol%), and L (1-1.5 mol%) were added to an oven-dried Schlenk flask and evacuated/backfilled with N_2 three times before leaving under an inert atmosphere. Using a syringe, anhydrous dioxane (6 mL) was added to dissolve all solids before the dropwise addition of the chosen Grignard reagent (~2 M, 3.2 mmol, 3.2 eq.) to the stirring solution at room temperature. The reaction mixture was then left to stir at 75 ^oC until the reaction was confirmed complete by GC-MS. Once the reaction was complete, the solution was diluted with Et_2O (~20 mL) and the excess Grignard was quenched by the addition of H_2O. The solution was transferred to a separatory funnel and the aqueous layer was extracted with Et_2O (3 x 20 mL). During the extraction, brine (~5 mL) was added to improve separation between organic and aqueous layers. The organic fractions were combined and dried with $MgSO_4$, the filtered into a round-bottomed flask. The solvent was removed under reduced pressure to yield the crude product as a colored oil or solid. The crude product was dry loaded onto silica and purified using silica gel flash column chromatography to yield the desired product (see product details for exact purification conditions).

Table S2. Masses and reaction times for the synthesis of products **1A-1J**.

Product	Iodocarborane	L-Pd-G3	L	Time
1A	9,12-I_2-oCB (394 mg, 1.0 mmol)	XPhos-Pd-G3 (16.8 mg, 0.02 mmol)	XPhos (9.4 mg, 0.02 mmol)	2.5 h
1A^{I}	9,12-I_2-oCB (197 mg, 0.5 mmol)	SPhos-Pd-G3 (7.8 mg, 0.01 mmol)	SPhos (4.1 mg, 0.01 mmol)	2.5 h

1B	9,12-I_2-oCB (394 mg, 1.0 mmol)	XPhos-Pd-G3 (16.8 mg, 0.02 mmol)	XPhos (9.4 mg, 0.02 mmol)	1.5 h
1C	9,12-I_2-oCB (394 mg, 1.0 mmol)	XPhos-Pd-G3 (16.8 mg, 0.02 mmol)	XPhos (9.4 mg, 0.02 mmol)	3.0 h
1D	9-I-oCB (270 mg, 1.0 mmol)	XPhos-Pd-G3 (12.6 mg, 0.01 mmol)	XPhos (7.1 mg, 0.01 mmol)	2.0 h
1D[I]	9-I-oCB (135 mg, 0.5 mmol)	SPhos-Pd-G3 (5.9 mg, 0.005 mmol)	SPhos (3.2 mg, 0.005 mmol)	2.0 h
1E	9-I-oCB (270 mg, 1.0 mmol)	XPhos-Pd-G3 (8.4 mg, 0.01 mmol)	XPhos (4.7 mg, 0.01 mmol)	0.75 h
1F	9-I-oCB (270 mg, 1.0 mmol)	XPhos-Pd-G3 (8.4 mg, 0.01 mmol)	XPhos (4.7 mg, 0.01 mmol)	2.0 h
1G	9-I-oCB (270 mg, 1.0 mmol)	XPhos-Pd-G3 (8.4 mg, 0.01 mmol)	XPhos (4.7 mg, 0.01 mmol)	4.0 h
1H	9-I-mCB (270 mg, 1.0 mmol)	XPhos-Pd-G3 (8.4 mg, 0.01 mmol)	XPhos (4.7 mg, 0.01 mmol)	1.0 h
1I	9-Br-10-I-mCB (350 mg, 1.0 mmol)	XPhos-Pd-G3 (8.4 mg, 0.01 mmol)	XPhos (4.7 mg, 0.01 mmol)	1.0 h
1J	9-Br-10-I-mCB (350 mg, 1.0 mmol)	XPhos-Pd-G3 (8.4 mg, 0.01 mmol)	XPhos (4.7 mg, 0.01 mmol)	3.0 h

3. S_NAr Conditions with Carborane and (Hetero)arenes

Optimization of S_NAr Protocol

O-carborane (oCB) (29 mg, 0.2 mmol, 1 eq.) was added to an oven-dried reaction tube and sealed with a PTFE septum cap. The reaction tube was evacuated and backfilled with N_2 three times and transferred into an N_2-filled glovebox. Under an inert atmosphere, base (0.2-0.6 mmol) and solvent (0.6 mL) were added, and the reaction tube was stirred at room temperature for 30 minutes. 2-chloropyridine (19 µL, 0.2 mmol, 1 eq.) was added dropwise to this solution, and the reaction mixture was stirred at room temperature for 14 hours. Reaction progress was monitored by GC-MS.

Table S3. Optimization table for S_NAr reactions with 2-chloropyridine.

Entry	Base	Base eq.	Solvent	Conc. (M)	% Conversion by GC-MS
1	^{n}BuLi	2	THF	0.33	0
2	KHMDS	2	THF	0.33	92
3	KHMDS	1	THF	0.33	80
4	KHMDS	3	THF	0.33	99
5	LiHMDS	3	THF	0.33	45
6	NaHMDS	3	THF	0.33	90
7	KHMDS	3	MTBE	0.33	86
8	KHMDS	3	Ether	0.33	90
9	KHMDS	3	DME	0.33	98
10	KHMDS	3	THF	0.2	100

11	KHMDS	3	THF	0.4	100

General procedure for C-functionalized carboranes

To an oven-dried reaction vessel equipped with a stir bar and septum, carborane (oCB, mCB, **1E**, or **2A = CB**, 0.50-1.50 mmol, 1.0-2.0 eq.), solvent (~2 mL), and KHMDS (0.23-4.50 mmol, 1.0-6.0 eq.) were added. After stirring at room temperature for 30-60 minutes, the aryl halide (0.46-1.50 mmol, 1.0-2.0 eq.) was added to the K_2[**CB**] solution. The vessel was sealed, and the reaction was stirred for 14 hours at 25-80°C. Reaction progress was monitored *via* GC-MS, and upon completion the reaction was quenched by the addition of sat. $Et_3N{\cdot}HCl$ or sat. $NaHCO_3$. The resulting biphasic mixture was transferred to a separatory funnel, and the organic and aqueous layers were separated. The aqueous phase was extracted with ethyl acetate (3 x 10 mL), and the organic phases were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to yield the crude product, which was then purified using silica gel flash column chromatography to yield the desired product. Specific reaction conditions are listed in Table S4.

Table S4. Reaction conditions for S_NAr products 2A-2I.

Product	Aryl Halide	CB	KHMDS	Solvent	Temp. (°C)
2A	2-chloropyridine (70.9 µL, 0.75 mmol)	oCB (108 mg, 0.75 mmol)	449 mg, 2.25 mmol	THF	25
2B	6-chloro-2,2'-bipyridine (142 mg, 0.75 mmol)	oCB (108 mg, 0.75 mmol)	449 mg, 2.25 mmol	THF	25
2C*	6,6'-dichloro-2,2'-bipyridine (169 mg, 0.75 mmol)	oCB (216 mg, 1.5 mmol)	898 mg, 4.50 mmol	MTBE	25
2D	fluoronaphthalene (96.8 mg, 0.75 mmol)	oCB (108 mg, 0.75 mmol)	449 mg, 2.25 mmol	THF	80
2E*	6-fluoroquinoline (91.3 µL, 0.75 mmol)	oCB (108 mg, 0.75 mmol)	449 mg, 2.25 mmol	THF	80
2F	2,6-difluoropyridine (68.1 µL, 0.75 mmol)	oCB (216 mg, 1.5 mmol)	898 mg, 4.50 mmol	Et_2O	25
2G	2-fluoropyridine (130 µL, 1.5 mmol)	mCB (108 mg, 0.75 mmol)	449 mg, 2.25 mmol	Et_2O	25
2H*	hexafluorobenzene (53.1 µL, 0.46 mmol)	**2A** (50.8 mg, 0.23 mmol)	45.9 mg, 0.23 mmol	DME	25
2I	2-fluoropyridine (129 µL, 1.5 mmol)	**1E** (79.1 mg, 0.50 mmol)	209 mg, 1.05 mmol	Et_2O	25

* = See product details for changes that were made to the General Procedure.

4. Product Details

9,12-(CH_2CH_3)$_2$-1,2-dicarba-*closo*-dodecaborane (1A and 1A^I)

Purification: Hexanes (**R_f** : 0.31) , 144 mg (72%, average of isolated yields obtained for **1A** and **1A^I**), clear liquid

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.38 (s, 2H, $C_{carborane}$-H), 2.97 – 1.28 (m, 8H, $B_{carborane}$-*H*), 0.87 (m, br, 6H, Et-CH_3), 0.69 (s, br, 4H, Et-CH_2-B). **^{11}B NMR (128 MHz, $CDCl_3$):** δ 9.14 (s, 2B), -8.97 (d, 2B, $^1J_{BH}$ = 148 Hz), -14.86 (d, 4B, $^1J_{BH}$ = 166 Hz), -16.84 (d, 2B, $^1J_{BH}$ = 200 Hz). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 47.52, 13.38, 8.94 (br). **GC-MS** *m/z*: 200.2560 (calc. 200.2568)

9,12-(CH_3)$_2$-1,2-dicarba-*closo*-dodecaborane (1B)

Purification: Hexanes (**R_f** : 0.45), 114 mg (66%), white solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.34 (s, 2H, $C_{carborane}$-H), 2.96 – 1.24 (m, 8H, $B_{carborane}$-*H*), 0.20 (s, br, 6H, B-CH_3). **^{11}B NMR (128 MHz, $CDCl_3$):** δ 7.13 (s, 2B), -7.66 (d, 2B, $^1J_{BH}$ = 148 Hz), -14.14 (d, 4B, $^1J_{BH}$ = 148 Hz), -16.64 (d, 2B, $^1J_{BH}$ = 181 Hz). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 47.38 B-CH_3 not observed due to B-C coupling. **GC-MS** *m/z*: 172.2252 (calc. 172.2255)

9,12-(C_6H_5)-1,2-dicarba-*closo*-dodecaborane (1C)

Purification: 3:7 CH_2Cl_2:Hexanes + 1% TFA (**R_f** : 0.35), 170 mg (57%), white solid

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.17 (m, 4H), 7.04 (m, 6H), 4.64 (s, 2H, $C_{carborane}$-H), 3.32 – 1.42 (m, 8H, $B_{carborane}$-*H*). **^{11}B NMR (128 MHz, $(CD_3)_2CO$):** δ 7.02 (s, 2B), -9.93 (d, 2B, $^1J_{BH}$ = 152 Hz), -14.16 (d, 4B, $^1J_{BH}$ = 166 Hz), -16.42 (d, 2B, $^1J_{BH}$ = 180 Hz). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 132.75, 127.01, 126.76, 50.88. **GC-MS** *m/z*: 296.2563 (calc. 296.2568)

9-CH_2CH_3-1,2-dicarba-*closo*-dodecaborane (1D and 1D^I)

Purification: 2:8 CH_2Cl_2:Hexanes (**R_f** : 0.57), 126 mg (78%, average of isolated yields obtained for **1D** and **1D^I**), clear liquid

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.48 (s, 1H, $C_{carborane}$-H), 3.41 (s, 1H, $C_{carborane}$-H), 3.02 – 1.34 (m, 9H, $B_{carborane}$-*H*), 0.86 (s, br, 3H, Et-CH_3), 0.72 (s, br, 2H, Et-CH_2-B). **^{11}B NMR (128 MHz, $CDCl_3$):** δ 9.39 (s, 1B), -2.42 (d, 1B, $^1J_{BH}$ = 163 Hz), -9.24 (d, 2B, $^1J_{BH}$ = 148 Hz), -14.10 – -15.82 (m, 6B). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 53.11, 47.80, 13.45, 10.00 (q, br, $^1J_{CB}$ = 60.00 Hz). **GC-MS** *m/z*: 172.2241 (calc. 172.2252)

9-CH_3-1,2-dicarba-*closo*-dodecaborane (1E)

Purification: 2:8 CH_2Cl_2:Hexanes (**R_f**: 0.50), 134 mg (86%), white solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.49 (s, 1H, $C_{carborane}$-H), 3.37 (s, 1H, $C_{carborane}$-H), 3.00 – 1.34 (m, 9H, $B_{carborane}$-*H*), 0.24 (s, br, 3H, B-CH_3). **^{11}B NMR (128 MHz, $CDCl_3$):** δ 7.25 (s, 1B), -1.78 (d, 1B, $^1J_{BH}$ = 148 Hz), -8.57 (d, 2B, $^1J_{BH}$ = 148 Hz), -13.59 (d, 2B, $^1J_{BH}$ = 148 Hz), -14.59 (d, 2B, $^1J_{BH}$ = 132 Hz), -15.72 (d, 2B, $^1J_{BH}$ = 181 Hz). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 53.45, 47.21, B-CH_3 not observed due to B-C coupling. **GC-MS** *m/z*: 158.2094 (calc. 158.2099)

9-(4-CH_3-C_6H_4)-1,2-dicarba-*closo*-dodecaborane (1F)

Purification: 1:9 CH_2Cl_2:Hexanes (**R_f**: 0.25), 157 mg (67%), white solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, 2H, $^1J_{HH}$ = 7.72 Hz), 7.06 (d, 2H, $^1J_{HH}$ = 7.35 Hz), 3.58 (s, 1H, $C_{carborane}$-H), 3.48 (s, 1H, $C_{carborane}$-H), 3.25 – 1.60 (m, 9H, $B_{carborane}$-*H*), 2.30 (s, 3H). **^{11}B NMR (128 MHz, $CDCl_3$):** δ 7.50 (s, 1B), -2.41 (d, 1B, $^1J_{BH}$ = 163 Hz), -8.95 (d, 2B, $^1J_{BH}$ = 150 Hz), -14.08 – -15.68 (m, 6B). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 136.91, 132.37, 128.27, 53.09, 48.64, 21.20. **GC-MS** *m/z*: 234.2406 (calc. 234.2412)

9-(2-C_4H_3S)-1,2-dicarba-*closo*-dodecaborane (1G)

Purification: 2:8 CH_2Cl_2:Hexanes (**R_f**: 0.34), 183 mg (77%, average of two independent runs), white solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (dd, 1H, $^1J_{HH}$ = 4.61 Hz, $^2J_{HH}$ = 0.80 Hz), 7.01 (m, 2H), 3.60 (s, 1H, $C_{carborane}$-H), 3.49 (s, 1H, $C_{carborane}$-H), 3.20 – 1.50 (m, 9H, $B_{carborane}$-*H*). **^{11}B NMR (128 MHz, $CDCl_3$):** δ 4.49 (s, 1B), -2.22 (d, 1B, $^1J_{BH}$ = 149 Hz), -8.82 (d, 2B, $^1J_{BH}$ = 155 Hz), -13.97 – -15.75 (m, 6B). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 130.75, 127.91, 127.80, 53.00, 48.87. **GC-MS** *m/z*: 226.1815 (calc. 226.1819)

9-CH_3-1,7-dicarba-*closo*-dodecaborane (1H)

Purification: Hexanes (**R_f**: 0.71), 54 mg (34%), white solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.33 – 1.57 (m, 9H, $B_{carborane}$-*H*), 2.86 (s, 2H, $C_{carborane}$-H), 0.36 (s, 3H). **^{11}B NMR (128 MHz, $CDCl_3$):** δ -0.69 (s, 1B), -6.35 (d, 2B, $^1J_{BH}$ = 160 Hz), -9.72 (d, 1B, $^1J_{BH}$ = 148 Hz), -13.10 (d, 2B, $^1J_{BH}$ = 160 Hz), -14.32 (d, 2B, $^1J_{BH}$ = 160 Hz), -17.98 (d, 1B, $^1J_{BH}$ = 184 Hz), -21.23 (d, 1B, $^1J_{BH}$ = 180 Hz). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 54.34, B-CH_3 not observed due to B-C coupling. **GC-MS** *m/z*: 158.2092 (calc. 158.2099)

9-Br-10-(CH_3)-1,7-dicarba-*closo*-dodecaborane (1I)

Purification: 1:9 CH_2Cl_2:Hexanes (**R_f**: 0.52), 192 mg (81%), white solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.49 – 1.70 (m, 8H, $B_{carborane}$-*H*), 2.91 (s, 2H, $C_{carborane}$-H), 0.46 (s, 3H). **^{11}B NMR (128 MHz, $CDCl_3$):** δ -1.05 (s, 1B), -5.89 (d, 2B), -5.89 (s, 1B), -13.84 (d, 4B, $^1J_{BH}$ = 158 Hz),

-21.80 (d, 2B, $^1J_{BH}$ = 182 Hz). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 52.61, B-CH_3 not observed due to B-C coupling. **GC-MS** *m/z*: 237.1175 (calc. 237.1167)

9-Br-10-(4-CF_3-C_6H_4)-1,7-dicarba-*closo*-dodecaborane (1J)

Purification: 1:9 CH_2Cl_2:Hexanes (**R_f**: 0.38), 272 mg (75%), light yellow solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, br, 2H, $^1J_{HH}$ = 7.77 Hz), 7.57 (d, br, 2H, $^1J_{HH}$ = 7.94 Hz), 3.71 – 1.64 (m, 8H, $B_{carborane}$-*H*), 3.07 (s, 2H, $C_{carborane}$-H). **^{11}B NMR (128 MHz, $CDCl_3$):** δ -1.18 (s, 1B), -6.03 (s, 1B), -6.44 (d, 2B), -13.15 (d, 2B), -13.90 (d, 2B), -20.31 (d, 1B), -21.27 (d, 1B). **^{13}C NMR (100 MHz, $(CD_3)_2CO$):** δ 133.81, 129.35 (q), 126.02, 124.16 (d, br), 123.33, 53.42. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.59 (s, 3F). **GC-MS** *m/z*: 367.1208 (calc. 367.1198)

1-(2)-pyridine-1,2-dicarba-*closo*-dodecaborane (2A)

Purification: Acetone/hexanes gradient (10%-50% acetone; **R_f** : 0.40 in 25% acetone in hexanes), 129 mg (78%), white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (m, 1H), 7.70 (m, 1H), 7.53 (d, 1H, $^1J_{HH}$ = 7.89 Hz), 7.31 (m, 1H), 4.99 (s, 1H, $C_{carborane}$-*H*), 3.00-1.68 (m, 10H, $B_{carborane}$-*H*). **^{11}B NMR (160 MHz, $CDCl_3$):** δ -1.97- -4.81(m, 2B), -8.21 (d, 2B, $^1J_{BH}$ = 150 Hz), -9.23- -14.19 (m, 6B). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 56.95, δ 75.37, δ 121.65, δ 124.42, δ 137.47, δ 148.86, δ 151.14. **GC-MS** *m/z*: 221.2165 (calc. 221.2208)

1-(6)-2,2'-bipyridine-1,2-dicarba-*closo*-dodecaborane (2B)

The 6-chloro-2,2'-bipyridine substrate was synthesized through the adaptation of a previously reported procedure.[4]

Purification: Hexanes (**R_f** : 0.30), 96 mg (43%), white solid. Single crystals for X-ray diffraction analysis were grown by dissolving product hot hexanes and acetone and cooling to room temperature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (dq, 1H, $^1J_{HH}$ = 4.8, $^2J_{HH}$ = 0.8 Hz), 8.45 (dd, 1H, $^1J_{HH}$ = 7.9, $^2J_{HH}$ = 0.8 Hz), 8.25 (td, 1H, $^1J_{HH}$ = 7.9, $^2J_{HH}$ = 1.0 Hz), 7.84 (t, 2H, $^1J_{HH}$ = 7.9 Hz), 7.56 (dd, 1H, $^1J_{HH}$ = 7.9, $^2J_{HH}$ = 0.8 Hz), 7.35 (m, 1H), 5.03 (s, 1H, $C_{carborane}$-*H*), 3.08-1.70 (m, 10H, $B_{carborane}$-*H*). **^{11}B NMR (160 MHz, $CDCl_3$):** δ -0.61- -5.17 (m, 2B), -8.22 (d, 2B, $^1J_{BH}$ = 150 Hz), -9.38- -15.58 (m, 6B). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 56.94, 75.49, 121.23, 121.60, 121.77, 124.54, 137.15, 138.58, 149.54, 150.34, 154.83, 155.46. **GC-MS** *m/z*: 298.2426 (calc. 298.2473)

1-(6,6')-2,2'-bipyridine-di-1,2-dicarba-*closo*-dodecaborane (2C)

The 6-chloro-2,2'-bipyridine substrate was synthesized through the adaptation of a previously reported procedure.[4]

*This reaction was done in 8 mL solvent and dried with Na_2SO_4.

*Purification: silica gel column chromatography with boiling 1,2-dichloroethane (**R_f** : 0.95), then dissolved in CH_2Cl_2 and stirred with activated carbon at room temperature for 6 hours. Product was filtered through a pad of Celite, then concentrated *in vacuo.* 240 mg (73%), white solid. Single crystals suitable for X-ray diffraction studies were obtained *via* slow evaporation of a hot, concentrated solution of 1,2-dichloroethane.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.67 (2H, dd, $^1J_{HH}$ = 7.9 Hz, $^2J_{HH}$ = 0.8 Hz), 8.07 (2H, t, $^1J_{HH}$ = 7.9 Hz), 7.80 (2H, dd, $^1J_{HH}$ = 7.9 Hz, $^2J_{HH}$ = 0.8 Hz), 5.74 (2H, br s, $C_{carborane}$-*H*), 3.31 – 1.59 (20H, br m, $B_{carborane}$-*H*). **^{11}B NMR (160 MHz):** δ -2.65 – -5.60 (4B, m), -8.00 – -16.40 (6B, m). **^{13}C NMR (126 MHz, $(CD_3)_2CO$):** δ 59.32, 123.18, 123.28, 140.34, 151.08, 154.84

1-(1)-napththalene-1,2-dicarba-*closo*-dodecaborane (2D)

Purification: Hexanes (**R_f** : 0.33), 132 mg (65%), white powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, 1H, $^1J_{HH}$ = 8.96 Hz), 7.90 (d, 1H, $^1J_{HH}$ = 7.98 Hz), 7.80 (d, 1H, $^1J_{HH}$ = 8.20 Hz), 7.60 (m, 1H), 7.53 (m, 1H), 7.41 (t, 1H, $^1J_{HH}$ = 7.98 Hz), 4.64 (s, 1H, $C_{carborane}$-*H*), 3.76-1.58 (m, 10H, $B_{carborane}$-*H*). **^{11}B NMR (160 MHz, $CDCl_3$):** δ -2.79 (d, 2B, $^1J_{BH}$ = 148 Hz), -7.94- -11.43 (m, 6B), -13.40 (d, 2B, $^1J_{BH}$ = 164 Hz).**^{13}C NMR (126 MHz, $CDCl_3$)**: δ 61.28, 124.52, 124.65, 126.25, 127.34, 128.34, 128.82, 129.93, 130.02, 131.88, 134.91. **GC-MS** *m/z*: 270.2393 (calc. 270.2412)

1-(6)-quinoline-1,2-dicarba-*closo*-dodecaborane (2E)

*Isopropoxytrimethylsilane (1 eq.) was added to 6-fluoroquinoline. This mixture was then added to the solution of K_2[oCB].

*Purification: Acetone/hexanes gradient (10%-90% acetone; **R_f** : 0.40 in 25% acetone in hexanes). The crude product was stirred with activated charcoal in 1,2-dichlorethane at 40˚C, then filtered through a pad of Celite and concentrated *in vacuo.* 96 mg (47%), white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (m, 1H), 8.18 (m, 1H), 8.09 (d, 1H), 7.99 (d, 1H), 7.67 (m, 2H), 4.10 (s, 1H, $C_{carborane}$-*H*), 3.38-1.68 (m, 10H, $B_{carborane}$-*H*). **^{11}B NMR (160 MHz, $CDCl_3$):** δ -1.53 (d, 1B, $^1J_{BH}$ = 150 Hz), -3.72 (s, 1B, $^1J_{BH}$ = 142 Hz), -8.44 (d, 2B, $^1J_{BH}$ = 74 Hz), -9.38- -13.35 (m, 6B). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 60.44, 76.05, 122.25, 127.60, 127.80, 128.01, 130.48, 131.62, 136.63, 148.20, 152.30. **GC-MS** *m/z*: 271.2364 (calc. 271.2364)

1-(2,6)-pyridine-di-1,2-dicarba-*closo*-dodecaborane (2F)

Purification: Hexanes (**R_f** : 0.27), 204 mg (75%), white solid. Single crystals suitable for X-ray diffraction studies were obtained by dissolving product in hot hexanes and cooling to room temperature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (m, 1H), 7.61 (d, 2H, $^1J_{HH}$ = 7.91 Hz), 4.48 (s, 2H, $C_{carborane}$-*H*), 3.19-1.61 (m, 10H, $B_{carborane}$-*H*), **^{11}B NMR (160 MHz, $CDCl_3$):** δ -1.37- -4.26 (m, 2B), -8.07 (d, 2B, $^1J_{BH}$

= 151 Hz), 9.23- -15.79 (m, 6B). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 56.73, 74.13, 122.91, 139.36, 150.62. **GC-MS** *m/z*: 363.3980 (calc. 363.3993)

1,7-(2,2)-dipyridine-di-1,7-dicarba-*closo*-dodecaborane (2G)

Purification: Hexanes (**R_f** : 0.80), 156 mg (70%), white solid. Single crystals suitable for X-ray diffraction studies were obtained *via* slow evaporation dichloromethane.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (dq, 2H, $^1J_{HH}$ = 4.81 Hz, $^2J_{HH}$ = 1.93 Hz, $^3J_{HH}$ = 0.93 Hz), 7.78 (td, 2H, $^1J_{HH}$ = 7.79 Hz, $^2J_{HH}$ = 1.88 Hz), 7.47 (dt, 2H, $^1J_{HH}$ = 8.05 Hz, $^2J_{HH}$ = 1.00 Hz), 7.24-7.25 (m, 2H), 4.32-1.67 (m, 10H, $B_{carborane}$-*H*). **^{11}B NMR (160 MHz, $CDCl_3$):** δ -5.38 (d, 2B, $^1J_{BH}$ = 159 Hz), -10.33 (d, 6B, $^1J_{BH}$ = 158 Hz), -12.78 (d, 2B, $^1J_{BH}$ = 183 Hz). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 78.86, 122.13, 123.67, 136.94, 149.02, 152.89. **GC-MS** *m/z*: 298.2460 (calc. 298.2473)

1,4-((1)-[(2)-pyridine]-1,2-dicarba-*closo*-dodecaborane)-2,3,5,6-tetrafluorobenzene (2H)

Purification: 9:1 hexanes acetone (**R_f** : 0.25) Yield 74%. Single crystals suitable for X-ray diffraction studies were obtained by dissolving product in hot hexanes and cooling to room temperature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, 1H), 7.49 (m, 1H), 7.21 (m, 1H), 3.52-2.22 (m, 20H, $B_{carborane}$-*H*). **^{11}B NMR (160 MHz, $CDCl_3$):** δ -0.40 (d, 1B, $^1J_{BH}$ = 126 Hz), -2.80 (d, 1B, $^1J_{BH}$ = 144Hz), -8.77 (m, 6B). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 31.09, 71.95, 83.77, 124.05, 124.51, 137.44, 148.39, 150.08. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -130.13 (s, 4F). This product was not detected by GC-MS.

1,2-(2,2)-dipyridine-9-methyl-1,2-dicarba-*closo*-dodecaborane (2I)

Purification: 10% acetone in hexanes gradient (**R_f** : 0.35) 60 mg (38%), white solid. Single crystals for X-ray diffraction analysis were grown by dissolving product in hot hexanes and cooling to room temperature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dq, 2H, $^1J_{HH}$ = 4.8, $^2J_{HH}$ = 0.9 Hz), 7.65 (m, 2H), 7.54 (tt, 2H, $^1J_{HH}$ = 7.8, $^2J_{HH}$ = 1.7 Hz), 7.11 (m, 2H, $^1J_{HH}$ = 4.8, $^2J_{HH}$ = 0.8 Hz), 4.50-1.69 (m, 9H, $B_{carborane}$-*H*), 0.35 (s, 3H). **^{11}B NMR (160 MHz, $CDCl_3$):** δ 7.60 (s, 1B), -1.50 (d, 1B, $^1J_{BH}$ = 144 Hz), -7.06- -11.85 (m, 8B). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 76.22, 82.45, 124.12, 124.15, 125.30, 125.58, 136.58, 148.55, 148.58, 149.14, 149.38. **GC-MS** *m/z*: 312.2616 (calc. 312.2630).

4. References

1. Bruno, N. C.; Tudge, M. T.; Buchwald, S. L. *Chem. Sci.* **2013**, 4, 916-920.
2. Dziedzic, R. M.; Saleh, L. M. A.; Axtell, J. C.; Martin, J. L.; Stevens, S. L.; Royappa, A. T.; Rheingold, A. L.; Spokoyny, A. M. *J. Am. Chem. Soc.* **2016**, *138*, 9081-9084.
3. Kirlikovali, K. O.; Axtell, J. C., Gonzalez, A.; Phung, A. C.; Khan, S. I.; Spokoyny, A. M. *Chem. Sci.* **2016**, *7*, 5132-5138.
4. Jung, J.-C.; Jung, Y.-J.; Park, O.-S., PREPARATION OF 2-CHLOROPYRIDINE. Synthetic Communications 2001, 31 (16), 2507-2511.

5. Crystal Structure Data

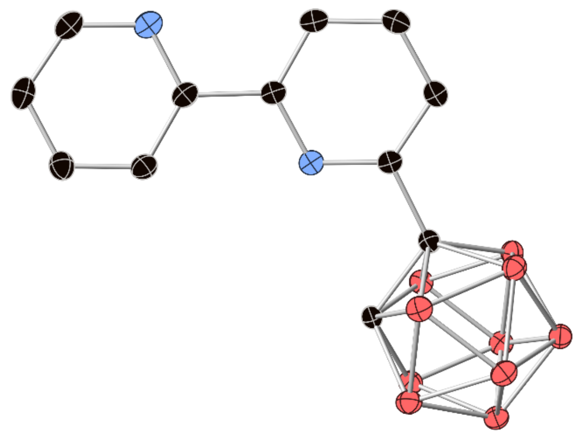


Figure S1. Single crystal X-ray structure of **2B**. H-atoms are omitted for clarity.

Table S4. Crystal data and structure refinement for **2B**.

Compound	**2B**	
Empirical formula	C12 H18 B10 N2	
Formula weight	298.38	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 25.1102(12) Å	α= 90°.
	b = 7.1488(4) Å	β= 122.287(2)°.
	c = 20.7681(9) Å	γ = 90°.
Volume	3151.6(3) $Å^3$	
Z	8	
Density (calculated)	1.258 Mg/m^3	
Absorption coefficient	0.470 mm^{-1}	
F(000)	1232	
Crystal size	0.29 x 0.28 x 0.26 mm^3	
Theta range for data collection	4.165 to 68.312°.	
Index ranges	-29<=h<=30, -8<=k<=8, -23<=l<=25	
Reflections collected	10354	
Independent reflections	2846 [R(int) = 0.0300]	
Completeness to theta = 67.679°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.7008	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2846 / 0 / 261	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.1165	
R indices (all data)	R1 = 0.0464, wR2 = 0.1200	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.266 and -0.263 e.$Å^{-3}$	

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for spok106_0m_a (**2B**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(2)	8440(1)	5658(2)	5967(1)	20(1)
N(1)	7252(1)	4803(2)	3995(1)	16(1)
C(10)	6634(1)	4524(2)	3558(1)	16(1)
C(6)	7507(1)	4986(2)	4750(1)	16(1)
C(11)	6369(1)	4351(2)	2716(1)	16(1)
C(9)	6237(1)	4383(2)	3832(1)	19(1)
C(2)	9474(1)	5697(2)	6160(1)	22(1)
C(5)	8203(1)	5255(2)	5232(1)	17(1)
C(1)	9066(1)	5878(2)	6411(1)	21(1)
C(12)	6864(1)	4553(2)	2439(1)	16(1)
C(4)	8578(1)	5056(2)	4926(1)	19(1)
C(8)	6505(1)	4572(2)	4609(1)	21(1)
C(3)	9224(1)	5275(2)	5400(1)	22(1)
C(7)	7145(1)	4898(2)	5075(1)	20(1)
B(5)	5390(1)	3798(2)	1231(1)	17(1)
B(7)	6538(1)	5610(2)	1576(1)	18(1)
B(3)	5789(1)	2785(2)	2154(1)	17(1)
B(8)	6678(1)	3149(2)	1689(1)	19(1)
B(6)	5742(1)	6025(2)	1290(1)	18(1)
B(10)	5938(1)	4020(2)	942(1)	17(1)
B(9)	5970(1)	2015(2)	1477(1)	18(1)
B(4)	6584(1)	2355(2)	2436(1)	18(1)
B(2)	5651(1)	5240(2)	2041(1)	17(1)
B(1)	6355(1)	6386(2)	2249(1)	17(1)

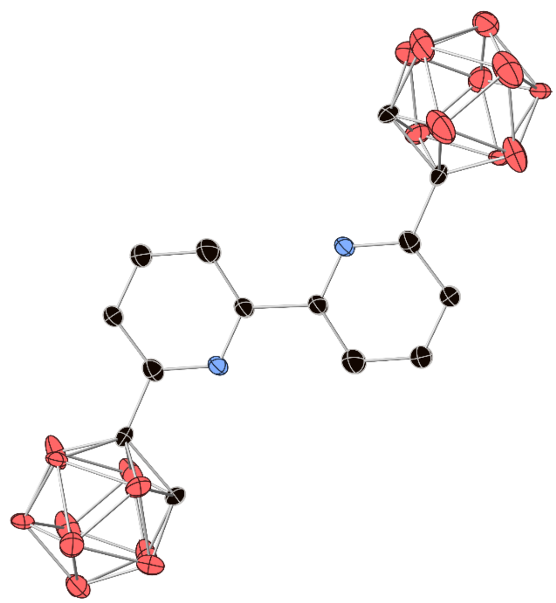


Figure S2. Single crystal X-ray structure of **2C**. H-atoms are omitted for clarity.

Table S6. Crystal data and structure refinement for **2C**.

Compound	**2C**	
Empirical formula	C14 H28 B20 N2	
Formula weight	440.58	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.5443(8) Å	α= 98.131(8)°.
	b = 7.6742(10) Å	β= 99.051(7)°.
	c = 21.996(3) Å	γ = 90.522(7)°.
Volume	1244.3(3) $Å^3$	
Z	2	
Density (calculated)	1.176 Mg/m^3	
Absorption coefficient	0.394 mm^{-1}	
F(000)	452	
Crystal size	0.28 x 0.25 x 0.05 mm^3	
Theta range for data collection	2.055 to 65.982°.	
Index ranges	-8<=h<=8, -7<=k<=8, -26<=l<=26	
Reflections collected	14151	
Independent reflections	4012 [R(int) = 0.0663]	
Completeness to theta = 65.982°	97.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6341	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4012 / 0 / 326	
Goodness-of-fit on F^2	1.549	
Final R indices [I>2sigma(I)]	R1 = 0.1231, wR2 = 0.3291	
R indices (all data)	R1 = 0.1309, wR2 = 0.3435	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.349 and -0.405 e.$Å^{-3}$	
Twinned	pseudomerohedral	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for spok119_0m (**2C**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(2)	8502(6)	6109(6)	478(2)	18(1)
N(1)	10621(6)	1531(6)	4521(2)	19(1)
C(9)	6704(7)	7438(7)	1217(2)	17(1)
C(13)	10447(8)	3732(7)	688(3)	23(1)
C(12)	9894(8)	3733(8)	1259(3)	26(1)
C(3)	10066(7)	2080(8)	3971(3)	22(1)
C(14)	9703(7)	4954(7)	306(3)	21(1)
C(2)	11215(8)	3452(7)	3782(2)	21(1)
C(7)	9657(7)	298(8)	4687(3)	24(1)
C(5)	7495(10)	157(11)	3766(4)	46(2)
C(10)	7994(7)	6096(7)	1036(3)	21(1)
B(14)	7478(8)	9592(8)	1277(3)	21(1)
B(7)	10381(12)	4974(10)	3331(3)	35(2)
C(6)	8070(9)	-413(10)	4336(4)	38(2)
C(1)	12920(10)	4269(9)	4298(3)	32(2)
B(18)	6268(9)	10798(9)	1814(3)	25(1)
C(11)	8654(8)	4933(8)	1447(3)	22(1)
B(6)	11727(8)	3264(8)	3041(3)	20(1)
B(12)	5175(9)	7108(9)	1694(3)	24(1)
B(9)	14041(14)	6314(13)	3497(4)	49(2)
B(10)	12166(10)	5441(9)	2943(3)	27(2)
C(4)	8486(8)	1451(8)	3586(3)	29(1)
B(19)	5549(9)	10726(9)	1000(3)	25(1)
B(4)	13351(9)	2777(11)	3683(3)	31(2)
B(17)	4801(9)	9262(10)	2076(3)	28(2)
B(11)	4468(8)	7067(10)	877(3)	26(1)
B(15)	3681(9)	9181(10)	747(3)	26(1)
B(1)	11134(14)	5586(11)	4151(4)	42(2)
B(3)	14725(12)	4659(12)	3965(4)	44(2)
C(8)	5854(7)	8626(8)	691(3)	23(1)
B(13)	7012(8)	8665(8)	1946(3)	22(1)

B(16)	3238(9)	8294(10)	1419(3)	27(2)
B(20)	3926(9)	10555(10)	1493(3)	29(2)
B(8)	11787(15)	6880(9)	3613(3)	45(2)
B(5)	14019(10)	4067(12)	3148(3)	36(2)
B(2)	13430(16)	6367(11)	4252(3)	48(3)

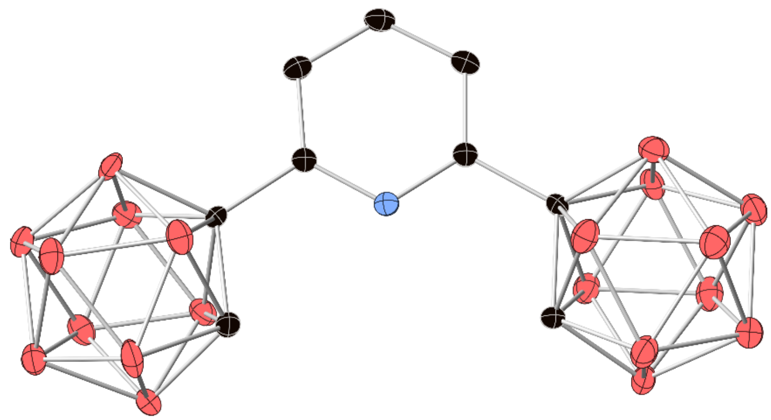


Figure S3. Single crystal X-ray structure of **2F**. H-atoms omitted for clarity.

Table S8. Crystal data and structure refinement for **2F**.

Compound	**2F**	
Empirical formula	C9 H25 B20 N	
Formula weight	363.50	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I-42d	
Unit cell dimensions	a = 14.9695(6) Å	α= 90°.
	b = 14.9695(6) Å	β= 90°.
	c = 19.0130(10) Å	γ = 90°.
Volume	4260.5(4) $Å^3$	
Z	8	
Density (calculated)	1.133 Mg/m^3	
Absorption coefficient	0.051 mm^{-1}	
F(000)	1488	
Crystal size	0.33 x 0.3 x 0.28 mm^3	
Theta range for data collection	1.731 to 27.458°.	
Index ranges	-14<=h<=18, -19<=k<=14, -24<=l<=19	
Reflections collected	11221	
Independent reflections	2441 [R(int) = 0.0667]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4915 and 0.4383	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2441 / 0 / 137	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0474, wR2 = 0.1236	
R indices (all data)	R1 = 0.0525, wR2 = 0.1292	
Absolute structure parameter	-0.3(10)	

Extinction coefficient	n/a
Largest diff. peak and hole	0.250 and -0.261 e.Å^{-3}

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for spok75_0m_a (**2F**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	1870(2)	7500	6250	12(1)
C(1)	1940(1)	5894(1)	6173(1)	12(1)
C(2)	3025(1)	5981(2)	6233(1)	16(1)
C(3)	1405(1)	6738(1)	6218(1)	12(1)
C(4)	475(1)	6700(2)	6216(1)	14(1)
C(5)	11(2)	7500	6250	16(1)
B(1)	2575(2)	5764(2)	5418(1)	18(1)
B(2)	3569(2)	5230(2)	5718(2)	20(1)
B(3)	3493(2)	5093(2)	6648(2)	21(1)
B(4)	2460(2)	5543(2)	6942(1)	18(1)
B(5)	1659(2)	5051(2)	5611(1)	18(1)
B(6)	2694(2)	4595(2)	5321(1)	19(1)
B(7)	3267(2)	4176(2)	6080(1)	18(1)
B(8)	2579(2)	4374(2)	6836(1)	19(1)
B(9)	1588(2)	4914(2)	6540(1)	17(1)
B(10)	2088(2)	4066(2)	6016(2)	19(1)

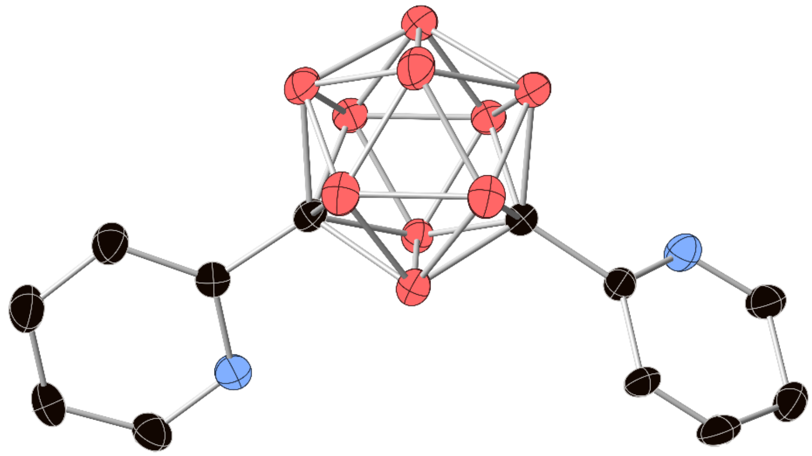


Figure S4. Single crystal X-ray structure of **2G**. H-atoms omitted for clarity.

Table S10. Crystal data and structure refinement for **2G**.

Compound	**2G**	
Empirical formula	C12 H18 B10 N2	
Formula weight	298.38	
Temperature	100.15 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.6774(4) Å	α= 90°.
	b = 7.4665(3) Å	β= 104.1230(10)°.
	c = 20.6215(8) Å	γ = 90°.
Volume	1594.31(11) $Å^3$	
Z	4	
Density (calculated)	1.243 Mg/m^3	
Absorption coefficient	0.465 mm^{-1}	
F(000)	616	
Crystal size	0.28 x 0.26 x 0.23 mm^3	
Theta range for data collection	4.302 to 68.354°.	
Index ranges	-12<=h<=12, -8<=k<=7, -24<=l<=24	
Reflections collected	11345	
Independent reflections	2906 [R(int) = 0.0376]	
Completeness to theta = 67.679°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5210 and 0.4338	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2906 / 343 / 254	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1180	
R indices (all data)	R1 = 0.0472, wR2 = 0.1217	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.248 and -0.324 e.$Å^{-3}$	

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for spok71_0m_a (**2G**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	6616(1)	9187(2)	4954(1)	26(1)
N(2')	3332(13)	5530(20)	2560(6)	24(2)
C(3)	7608(1)	8219(2)	4859(1)	20(1)
C(9)	3049(10)	4610(20)	3624(6)	23(1)
C(8)	3853(1)	5133(2)	3187(1)	20(1)
C(1)	7255(1)	6836(2)	4308(1)	19(1)
C(2)	5305(1)	5252(2)	3450(1)	19(1)
C(6)	8078(1)	10709(2)	5852(1)	29(1)
C(12)	2108(10)	5440(30)	2301(6)	28(2)
C(4)	8862(1)	8426(2)	5241(1)	29(1)
C(11)	1243(1)	5036(2)	2724(1)	28(1)
C(7)	6860(1)	10408(2)	5444(1)	28(1)
C(12')	1724(9)	4650(30)	3364(7)	27(1)
C(5)	9091(1)	9697(2)	5748(1)	34(1)
B(10)	5862(1)	5690(2)	4283(1)	20(1)
B(8)	7531(1)	7252(2)	3529(1)	23(1)
B(2)	6232(1)	6187(2)	2956(1)	23(1)
B(1)	5954(1)	7325(2)	3661(1)	19(1)
B(7)	6069(1)	3543(2)	3961(1)	24(1)
B(4)	7375(1)	4600(2)	4533(1)	24(1)
B(9)	8406(1)	5560(2)	4065(1)	26(1)
B(6)	7749(1)	5089(2)	3204(1)	28(1)
B(5)	6303(1)	3851(2)	3139(1)	25(1)
B(3)	7652(1)	3453(2)	3824(1)	29(1)
N(2)	3222(11)	4740(30)	3615(7)	27(2)
C(10)	1929(13)	4560(40)	3402(9)	29(2)
C(10')	1936(11)	5520(30)	2327(8)	26(2)
C(9')	3360(20)	5520(30)	2501(9)	24(2)

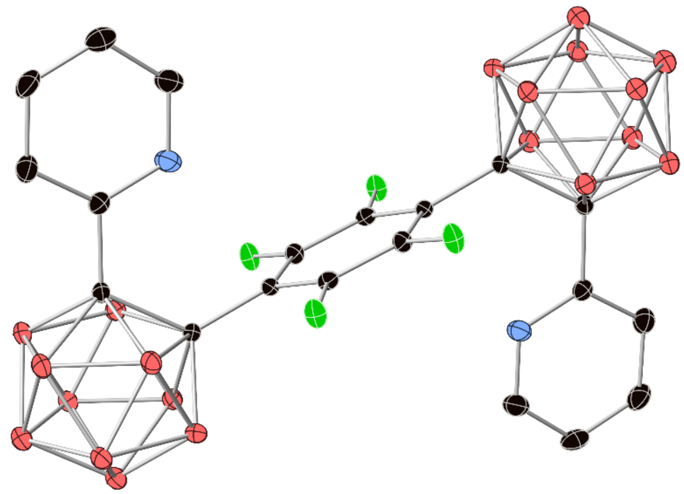


Figure S5. Single crystal X-ray structure of **2H**. H-atoms omitted for clarity.

Table S12. Crystal data and structure refinement for **2H**.

Compound	**2H**	
Empirical formula	C20 H28 B20 F4 N2	
Formula weight	588.64	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 7.2661(12) Å	α= 90°.
	b = 15.0779(18) Å	β= 90.604(5)°.
	c = 13.2917(16) Å	γ = 90°.
Volume	1456.1(3) $Å^3$	
Z	2	
Density (calculated)	1.343 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	596	
Crystal size	0.32 x 0.29 x 0.25 mm^3	
Crystal color, habit	Colorless block	
Theta range for data collection	2.702 to 28.296°.	
Index ranges	-9<=h<=8, -19<=k<=19, -17<=l<=17	
Reflections collected	13668	
Independent reflections	3596 [R(int) = 0.0356]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3343 and 0.2814	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3596 / 0 / 208	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0489, wR2 = 0.1211	
R indices (all data)	R1 = 0.0605, wR2 = 0.1274	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.368 and -0.261 e.$Å^{-3}$	

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for spok41_a (**2H**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(2)	3265(1)	3442(1)	5279(1)	16(1)
F(1)	1817(1)	4550(1)	4076(1)	16(1)
N(1)	4107(2)	4811(1)	7532(1)	18(1)
C(9)	4179(2)	4208(1)	5177(1)	11(1)
C(8)	5795(2)	4375(1)	5716(1)	11(1)
C(10)	3402(2)	4807(1)	4508(1)	12(1)
C(1)	6704(2)	3706(1)	6403(1)	11(1)
C(2)	6212(2)	3575(1)	7656(1)	12(1)
C(6)	2146(2)	5245(1)	8885(1)	19(1)
C(7)	2804(2)	5337(1)	7915(1)	21(1)
C(3)	4768(2)	4167(1)	8116(1)	13(1)
C(4)	4205(2)	4022(1)	9097(1)	19(1)
C(5)	2863(2)	4580(1)	9483(1)	22(1)
B(9)	9938(2)	3234(1)	7420(1)	15(1)
B(4)	5494(2)	2768(1)	6821(1)	14(1)
B(6)	7176(3)	1923(1)	6913(1)	16(1)
B(10)	8837(3)	2243(1)	7843(1)	17(1)
B(5)	9338(3)	2377(1)	6546(1)	17(1)
B(8)	8158(2)	3294(1)	8322(1)	15(1)
B(1)	8247(2)	4078(1)	7327(1)	13(1)
B(3)	7275(2)	2700(1)	5908(1)	14(1)
B(2)	8990(2)	3506(1)	6220(1)	14(1)
B(7)	6462(3)	2490(1)	8013(1)	16(1)

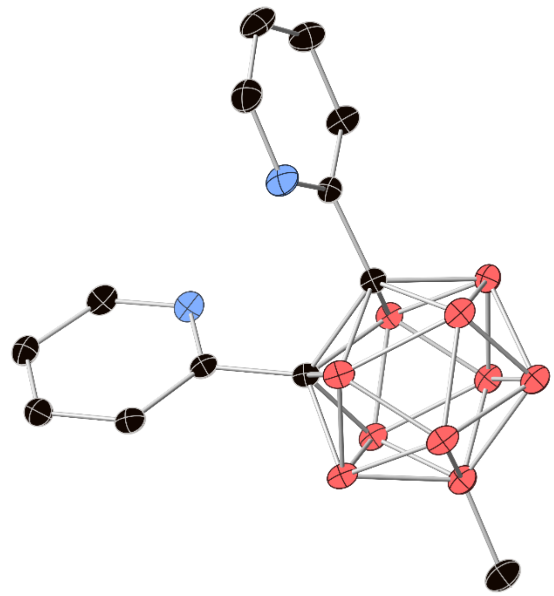


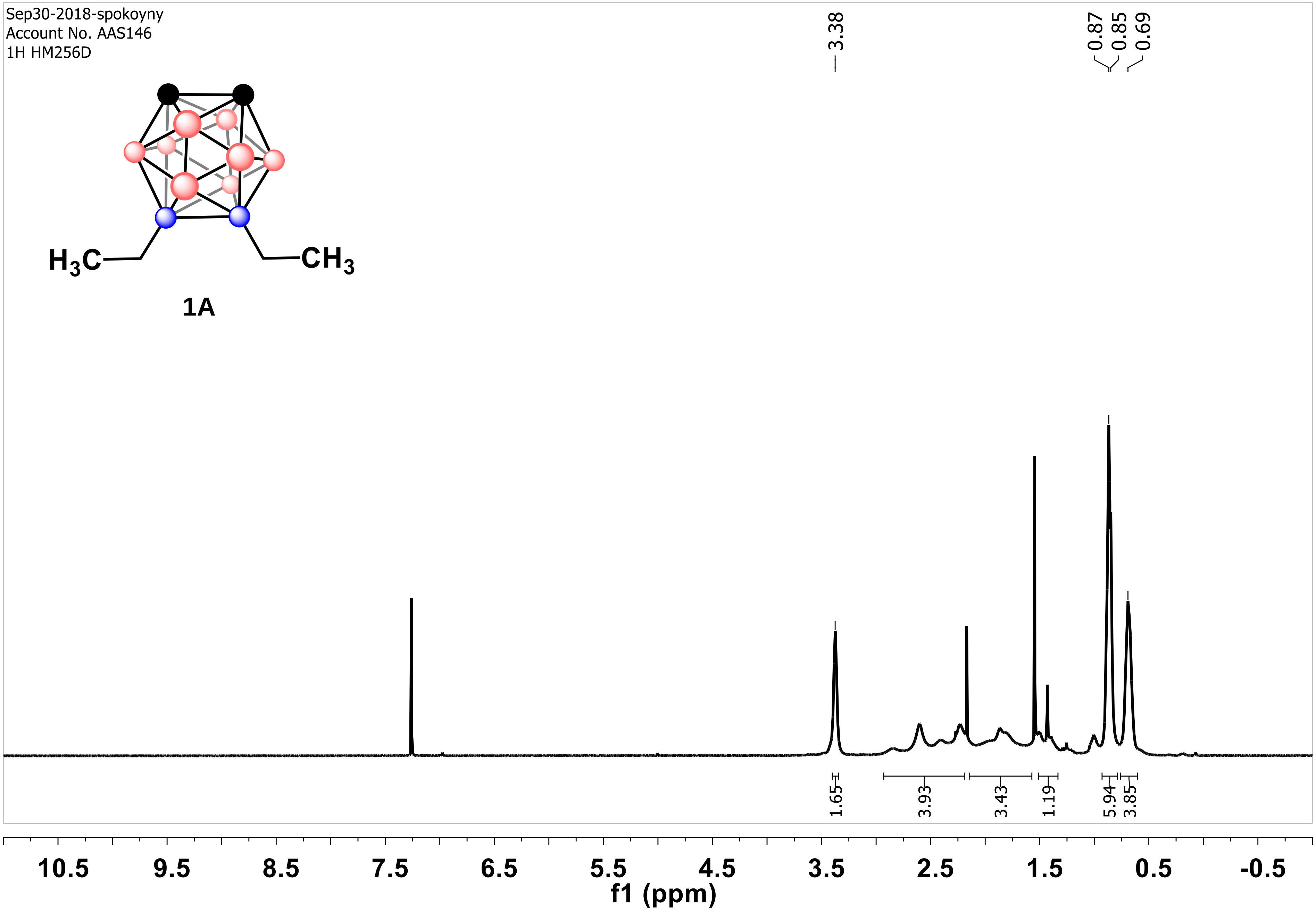
Figure S6. Single crystal X-ray structure of **2I**. H-atoms omitted for clarity.

Table S14. Crystal data and structure refinement for **2I**.

Compound	**2I**	
Empirical formula	C13 H20 B10 N2	
Formula weight	312.41	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 12.747(3) Å	α= 90°.
	b = 14.141(4) Å	β= 90°.
	c = 18.749(5) Å	γ = 90°.
Volume	3379.4(15) $Å^3$	
Z	8	
Density (calculated)	1.228 Mg/m^3	
Absorption coefficient	0.063 mm^{-1}	
F(000)	1296	
Crystal size	0.27 x 0.25 x 0.22 mm^3	
Theta range for data collection	2.410 to 30.311°.	
Index ranges	-16<=h<=18, -15<=k<=16, -17<=l<=24	
Reflections collected	16565	
Independent reflections	3733 [R(int) = 0.0416]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.6984	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3733 / 0 / 227	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0523, wR2 = 0.1442	
R indices (all data)	R1 = 0.0648, wR2 = 0.1559	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.783 and -0.390 e.$Å^{-3}$	

Table S15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for spok121_a (**2I**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	5344(1)	8076(1)	4433(1)	20(1)
N(2)	3205(1)	6177(1)	4603(1)	19(1)
C(13)	3681(1)	6055(1)	3990(1)	14(1)
C(4)	4423(1)	8317(1)	4385(1)	14(1)
C(12)	4230(1)	5177(1)	3841(1)	17(1)
C(2)	3575(1)	6922(1)	3446(1)	14(1)
C(1)	3977(1)	8125(1)	3666(1)	13(1)
C(11)	4272(1)	4383(1)	4346(1)	19(1)
C(10)	3783(1)	4496(1)	4978(1)	19(1)
C(5)	3917(1)	8774(1)	4935(1)	21(1)
C(9)	3268(1)	5409(1)	5084(1)	21(1)
C(8)	5779(1)	8300(1)	5051(1)	23(1)
C(7)	5330(1)	8750(1)	5629(1)	24(1)
C(6)	4382(1)	8995(1)	5569(1)	24(1)
C(3)	2499(1)	7382(1)	1367(1)	25(1)
B(4)	2770(1)	7907(1)	3633(1)	14(1)
B(3)	4602(1)	7379(1)	3053(1)	16(1)
B(5)	3722(1)	6702(1)	2555(1)	16(1)
B(8)	2412(1)	8387(1)	2790(1)	17(1)
B(9)	2596(1)	7024(1)	2912(1)	16(1)
B(2)	4414(1)	8748(1)	2932(1)	17(1)
B(6)	4242(1)	7865(1)	2213(1)	17(1)
B(7)	3428(1)	8913(1)	2350(1)	18(1)
B(10)	2993(1)	7639(1)	2108(1)	17(1)
B(1)	3283(1)	9066(1)	3287(1)	16(1)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0.69
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CH_3
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3.93
3.43
1.19
5.94
3.85
10.5
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6.5
5.5
4.5
3.5
2.5
1.5
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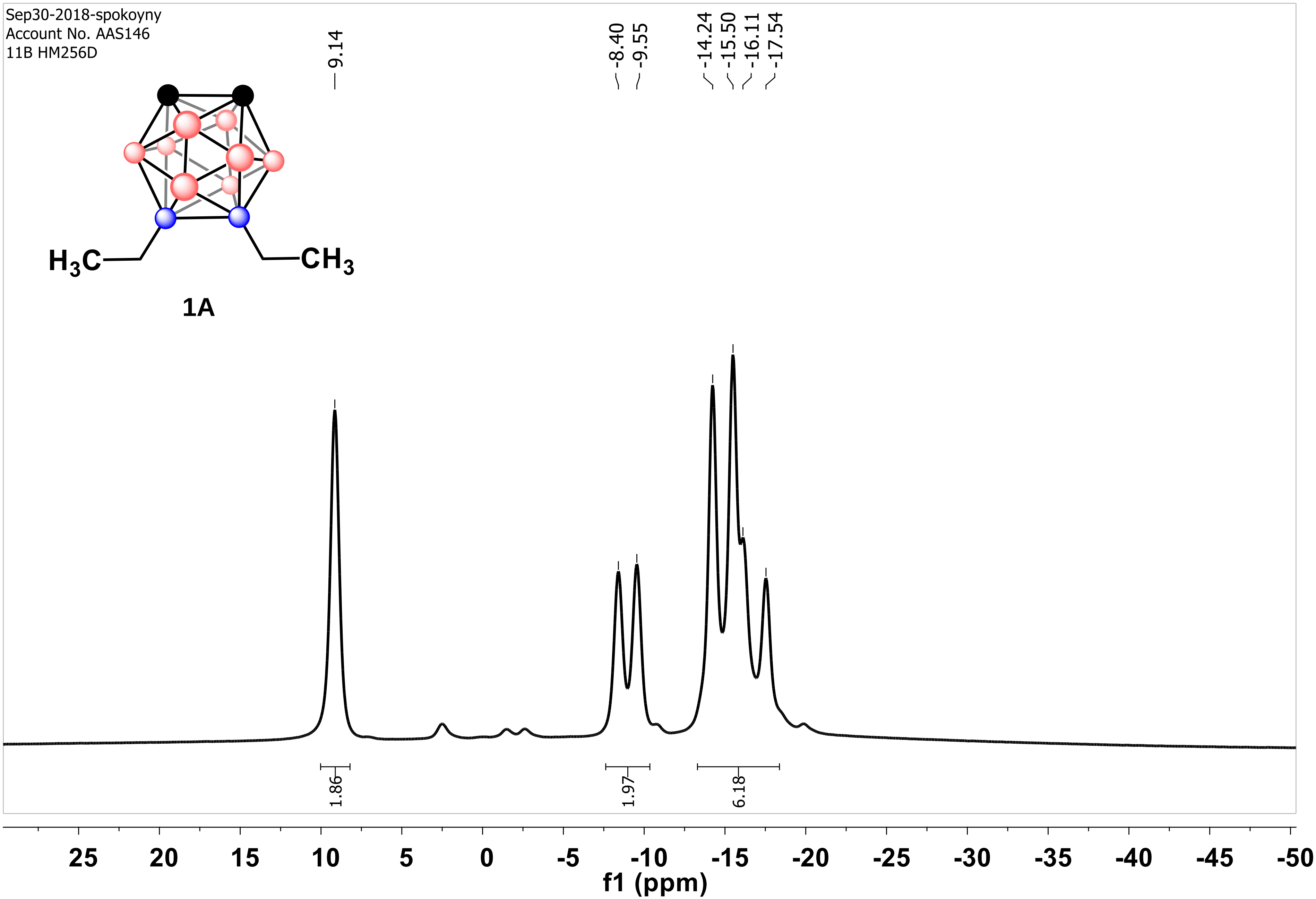
Sep30-2018-spokoyny
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-16.11
-17.54
1.86
1.97
6.18
25
20
15
10
5
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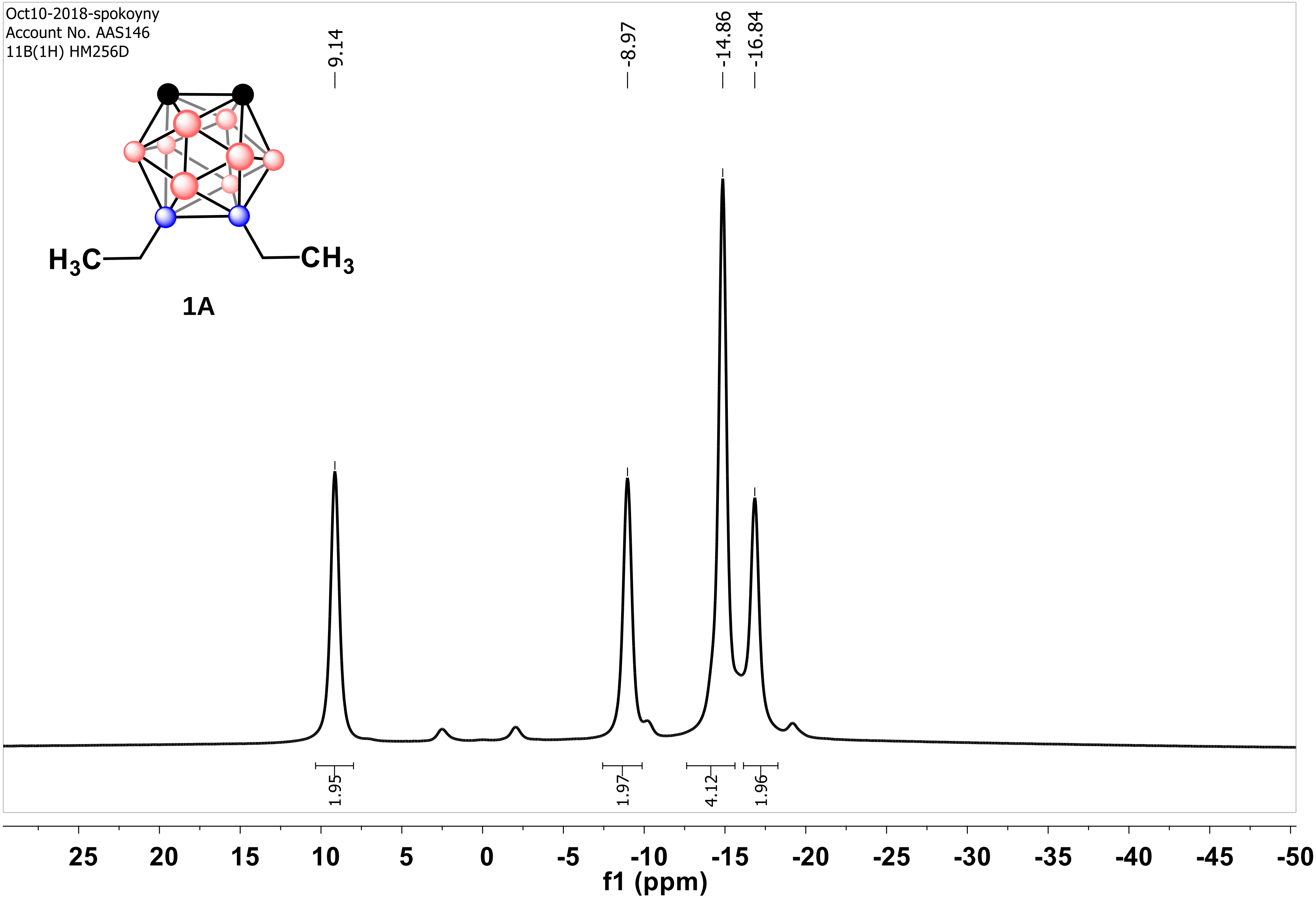
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)



Oct10-2018-spokoyny
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-14.86
-16.84
H3C
CH3
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1.97
4.12
1.96
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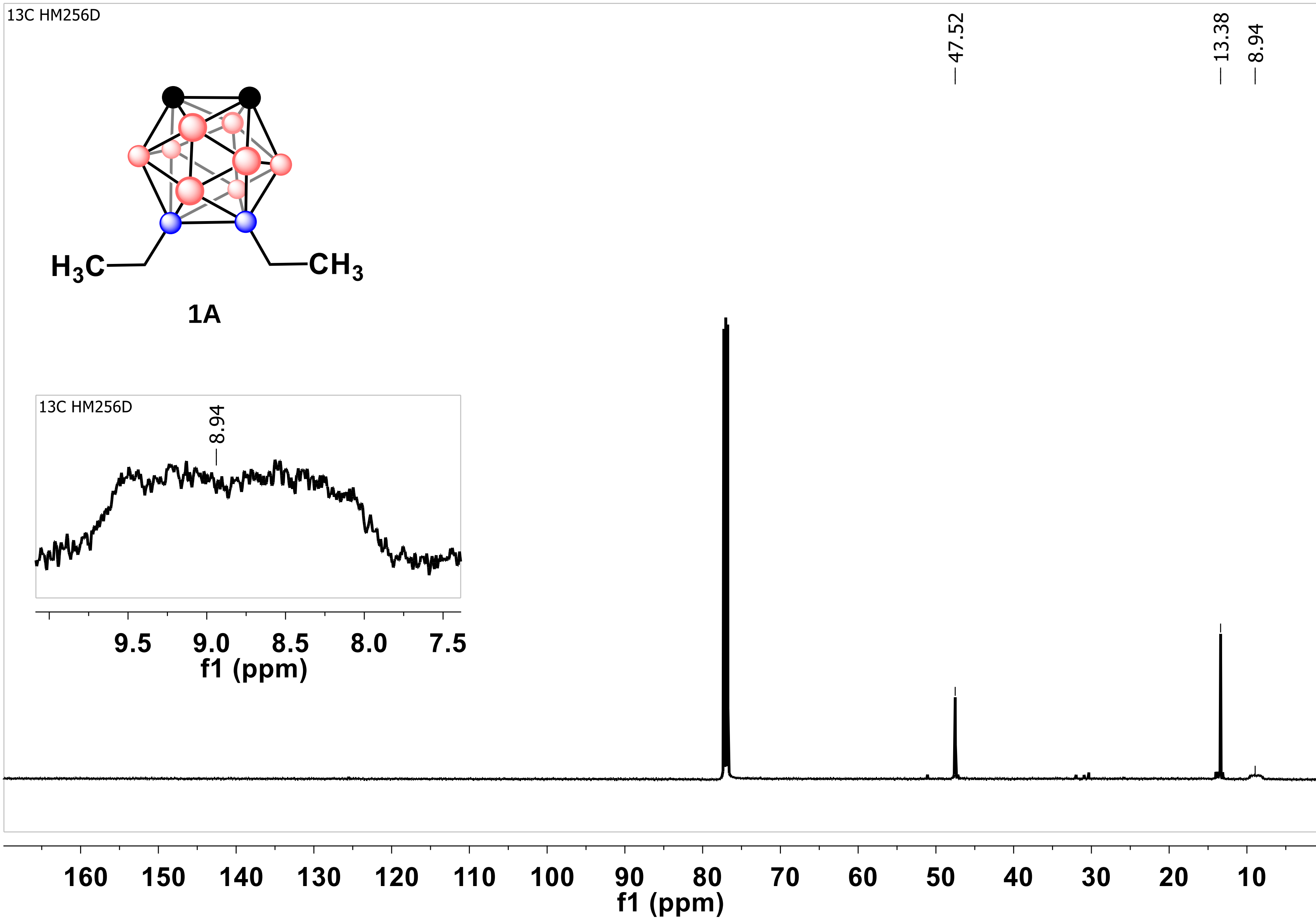
f1 (ppm)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8.94
H3C
CH3
1A
13C HM256D
8.94
9.5
9.0
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7.5
f1 (ppm)
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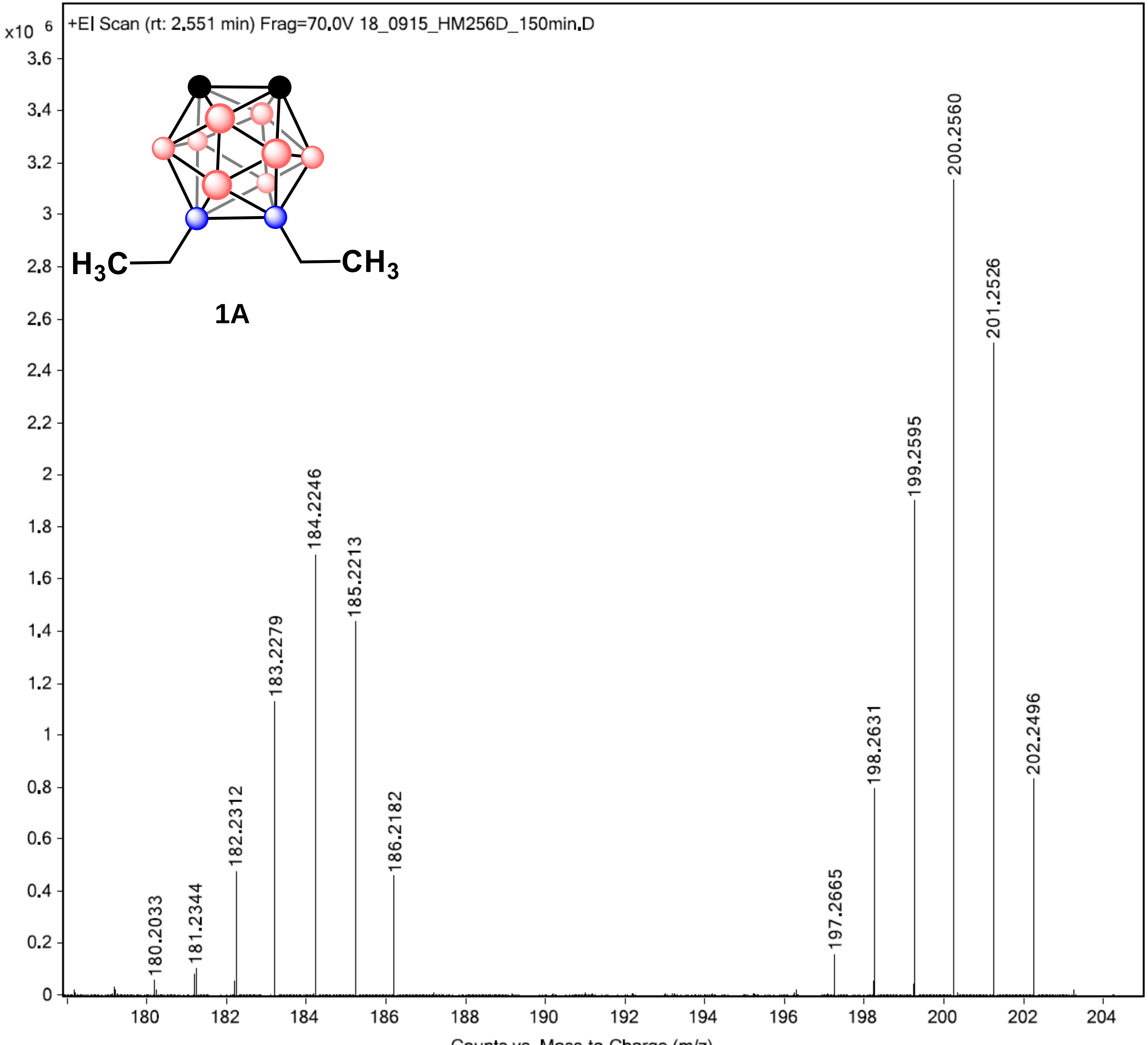
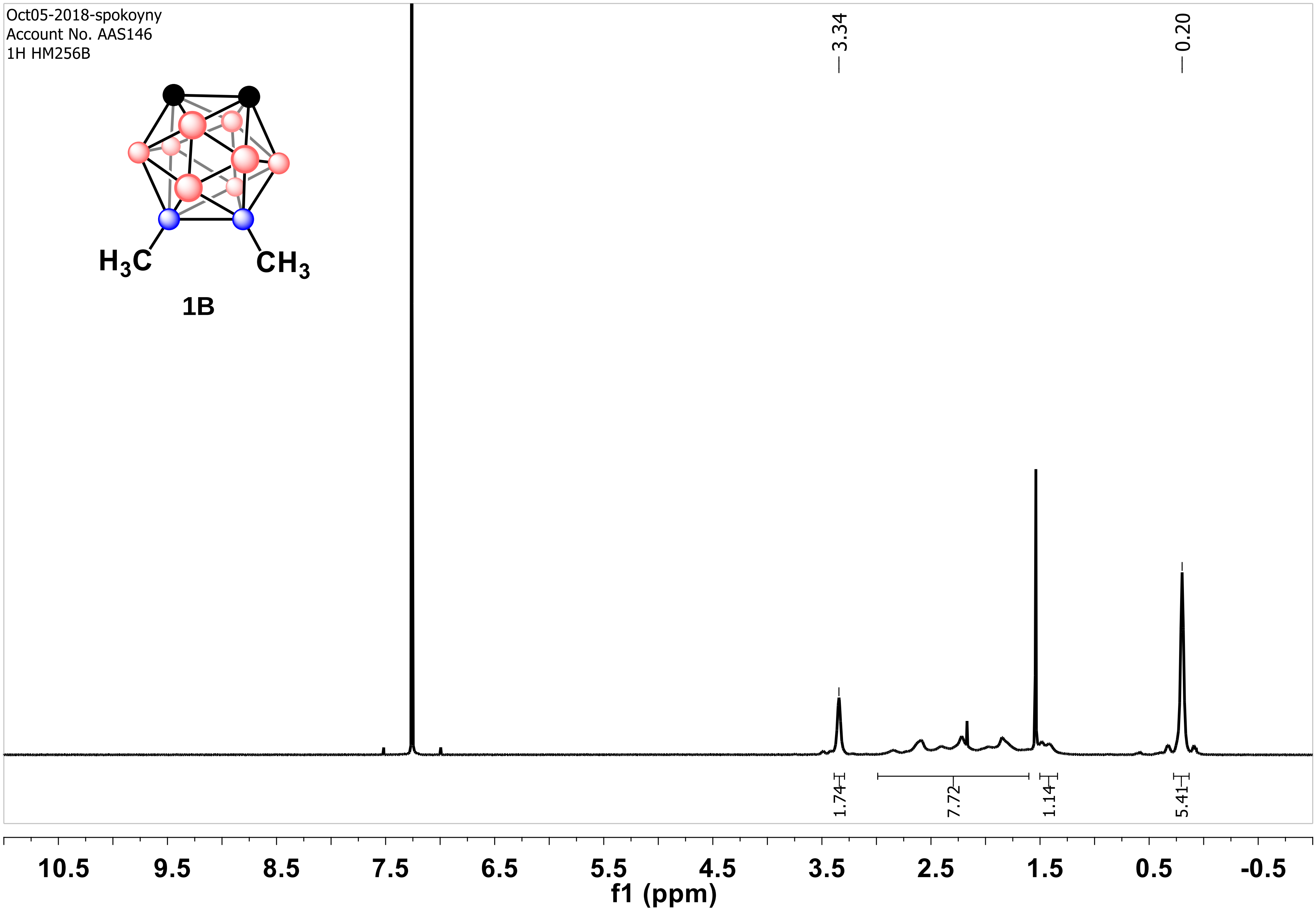
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Mills_Generic_Carboranes_7min_highEV.M Comment Acquired Time 9/15/2018 4:59:32 PM (UTC-07:00)





Oct05-2018-spokoyny
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10.5
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5.5
4.5
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1.5
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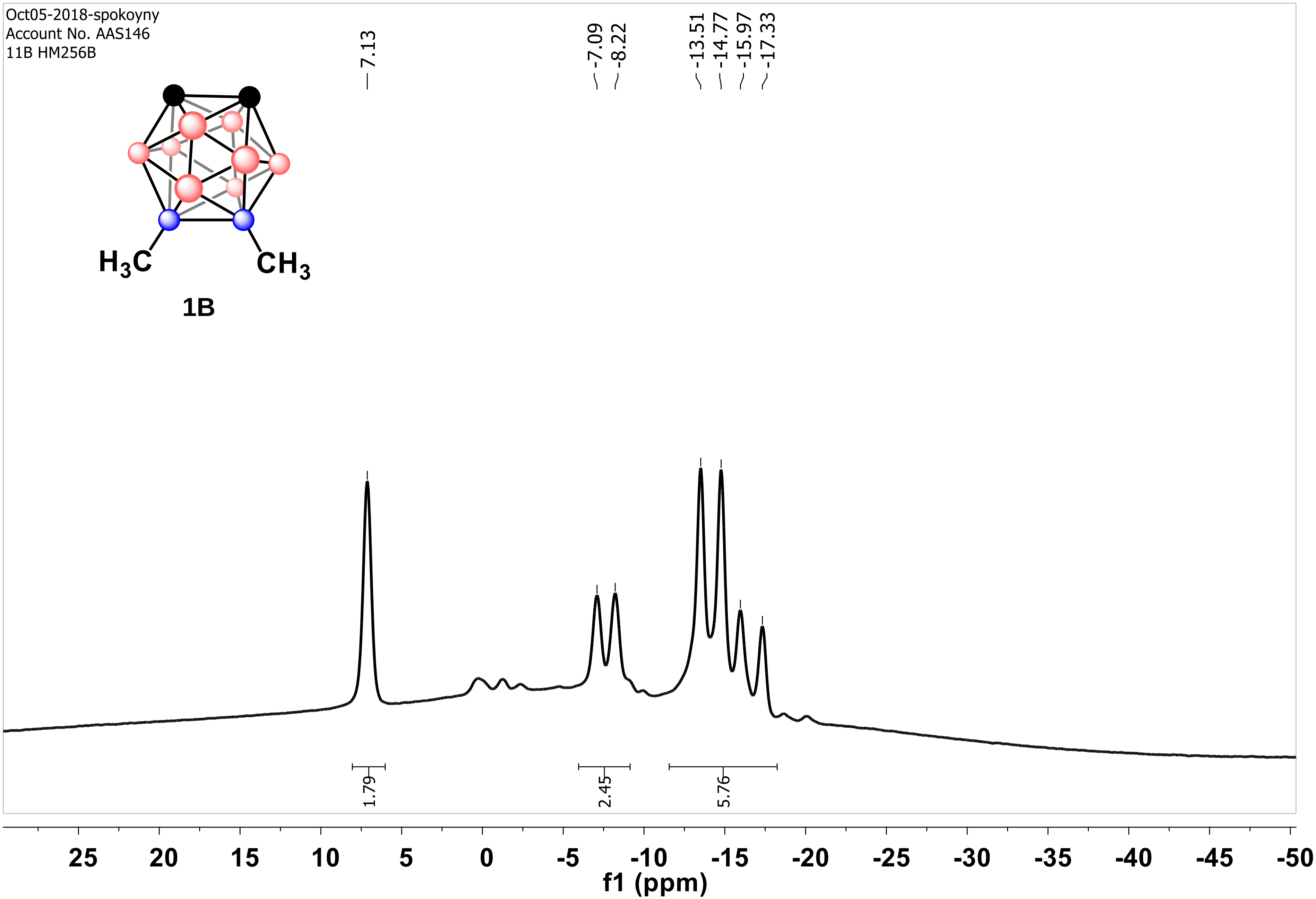
f1 (ppm)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-15.97
-17.33
1.79
2.45
5.76
25
20
15
10
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-25
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-35
-40
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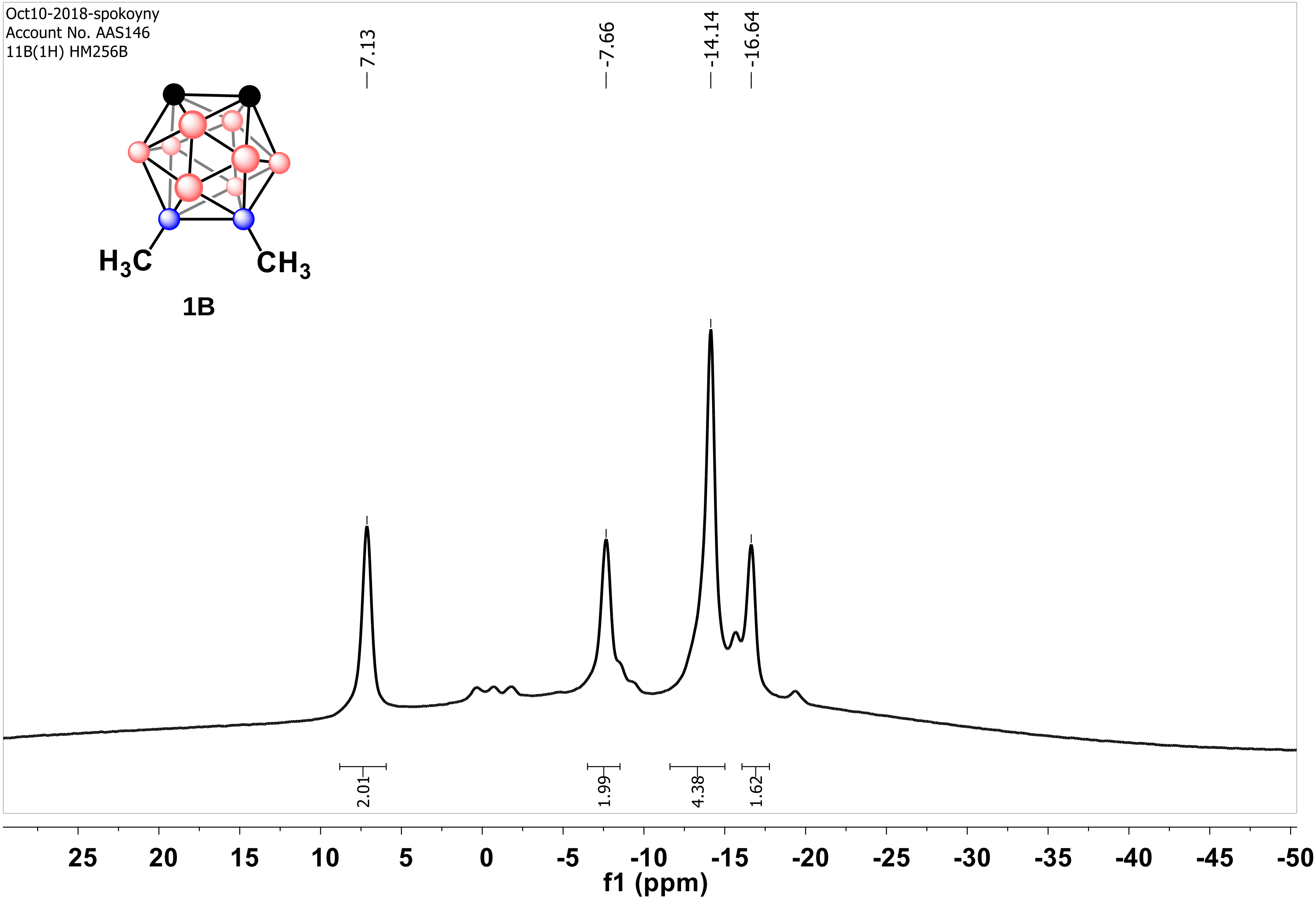
-50
f1 (ppm)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-16.64
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2.01
1.99
4.38
1.62
25
20
15
10
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-10
-15
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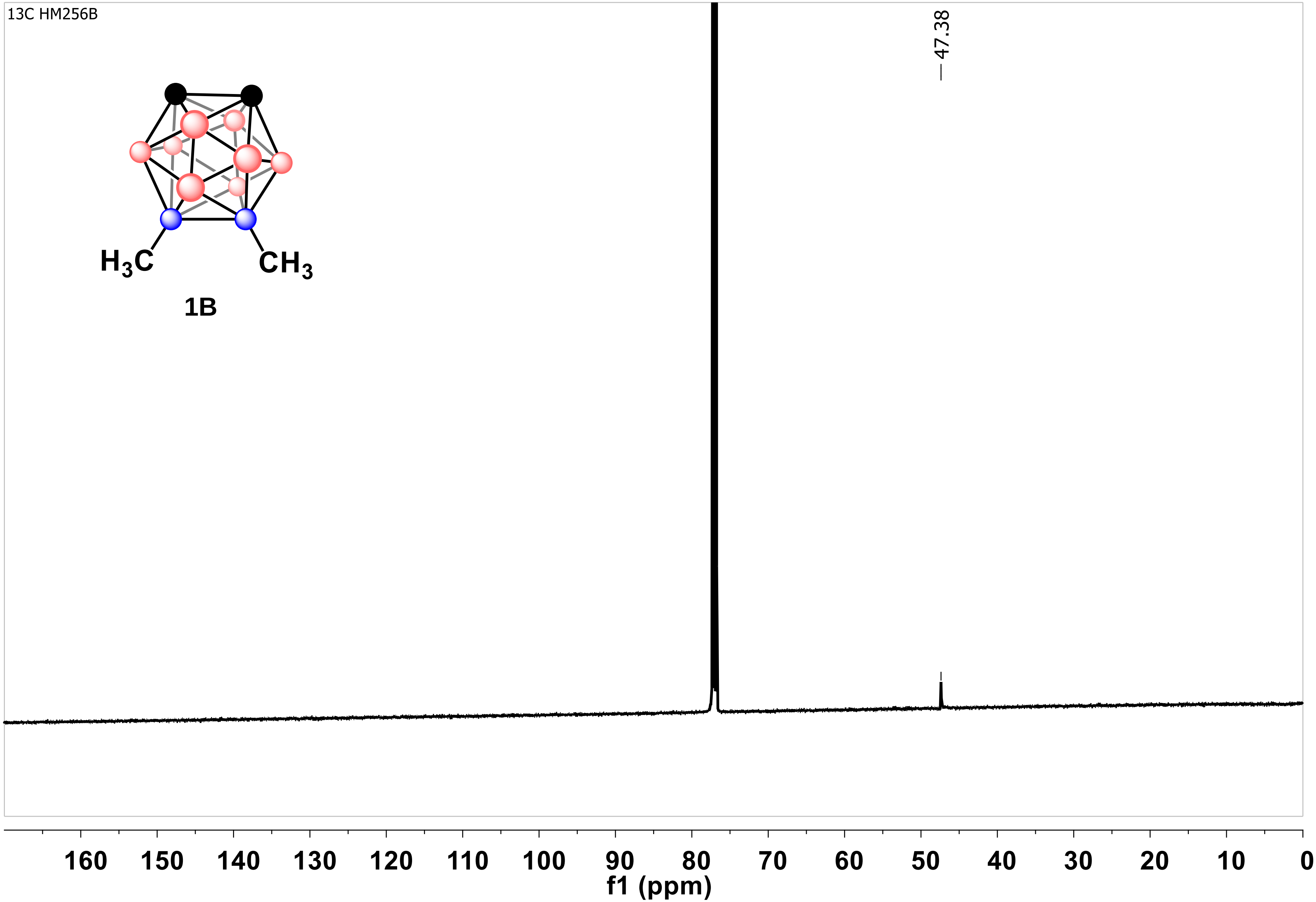
-25
-30
-35
-40
-45
-50
f1 (ppm)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H3C
CH3
1B
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130
120
110
100
90
80
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50
40
30
20
10
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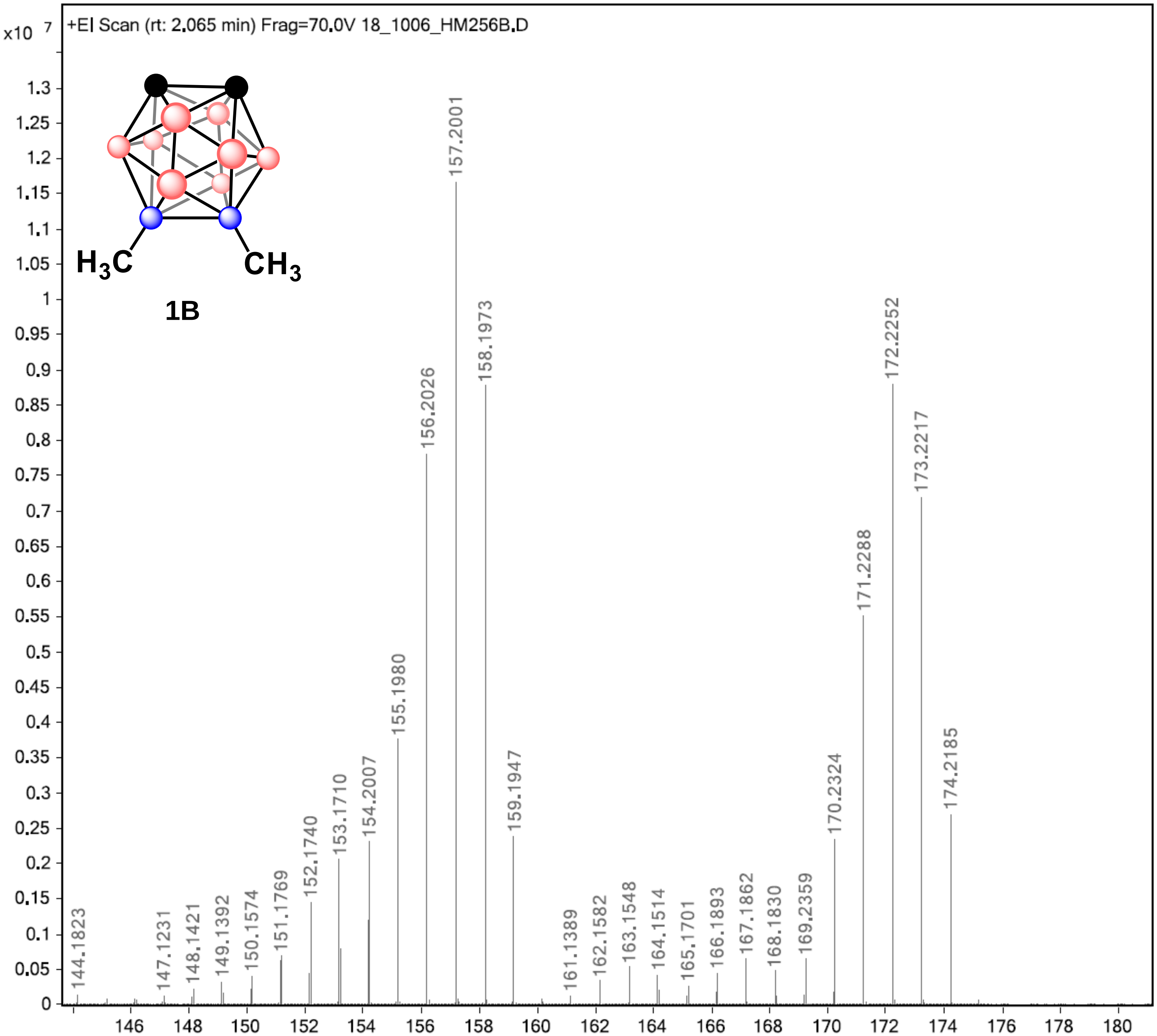
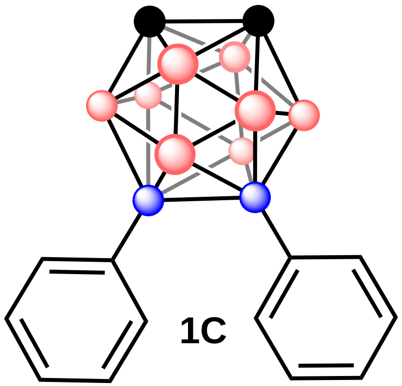
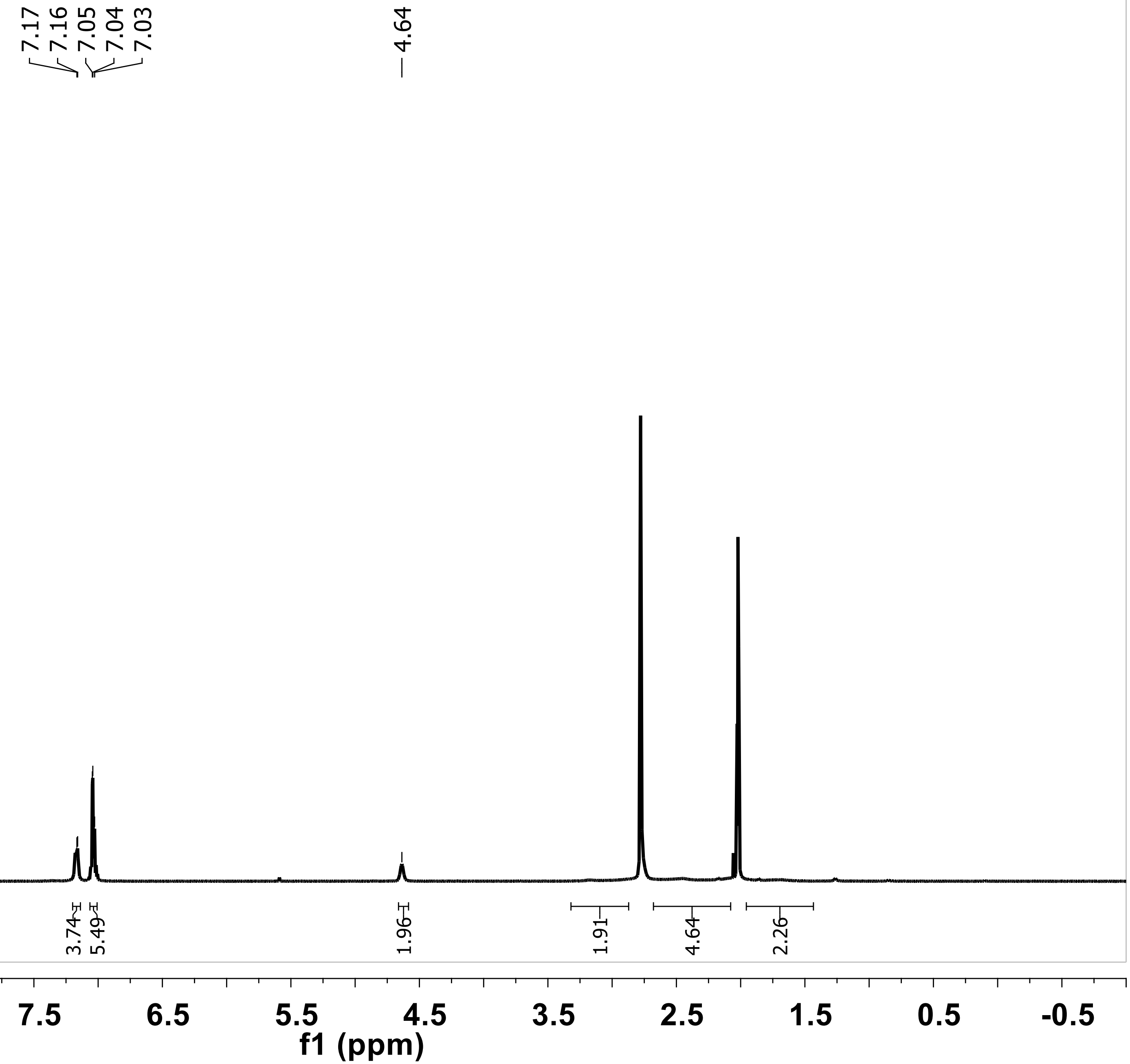
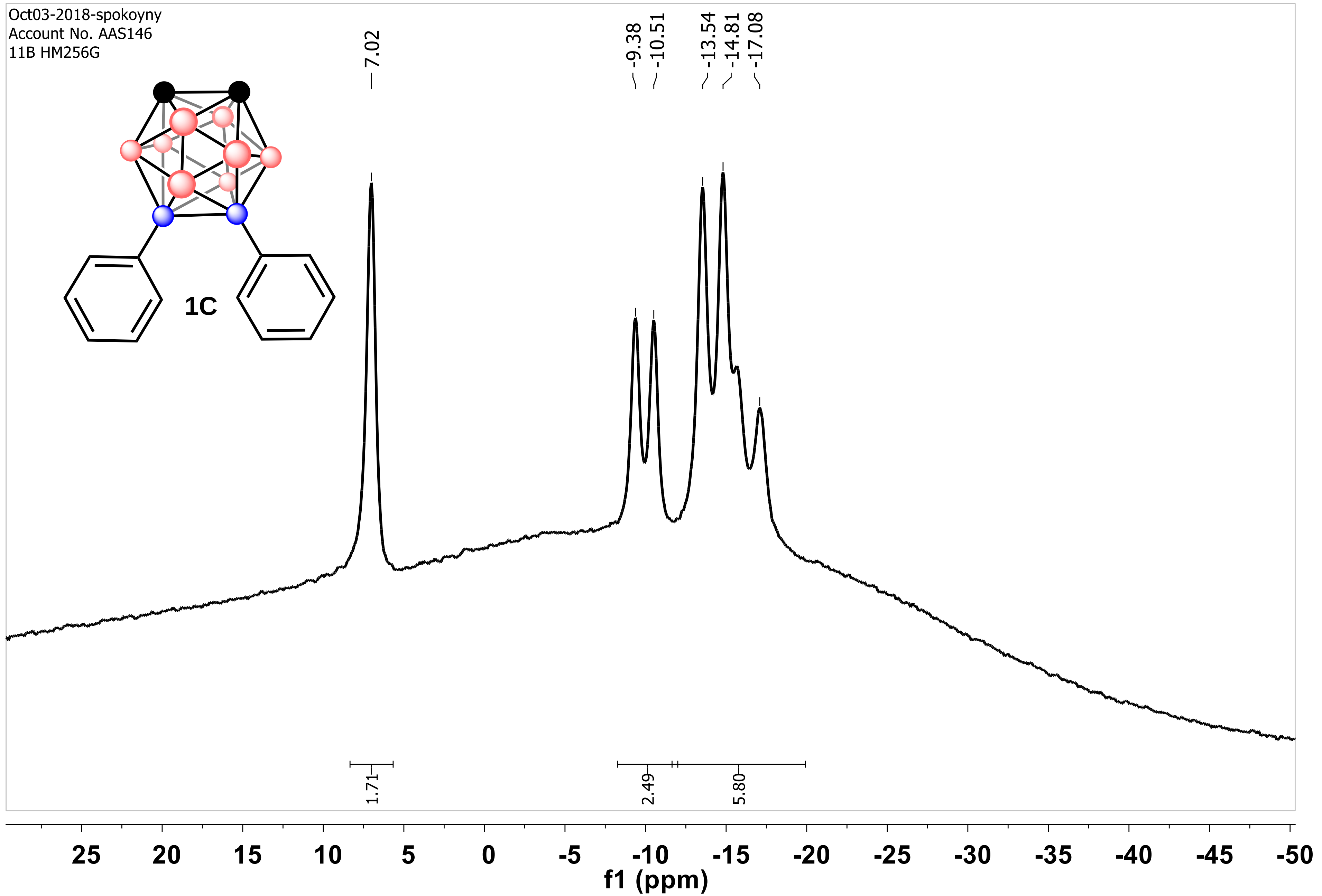


Oct03-2018-spokoyny
Account No. AAS146
1H HM256G



1C




Oct03-2018-spokoyny
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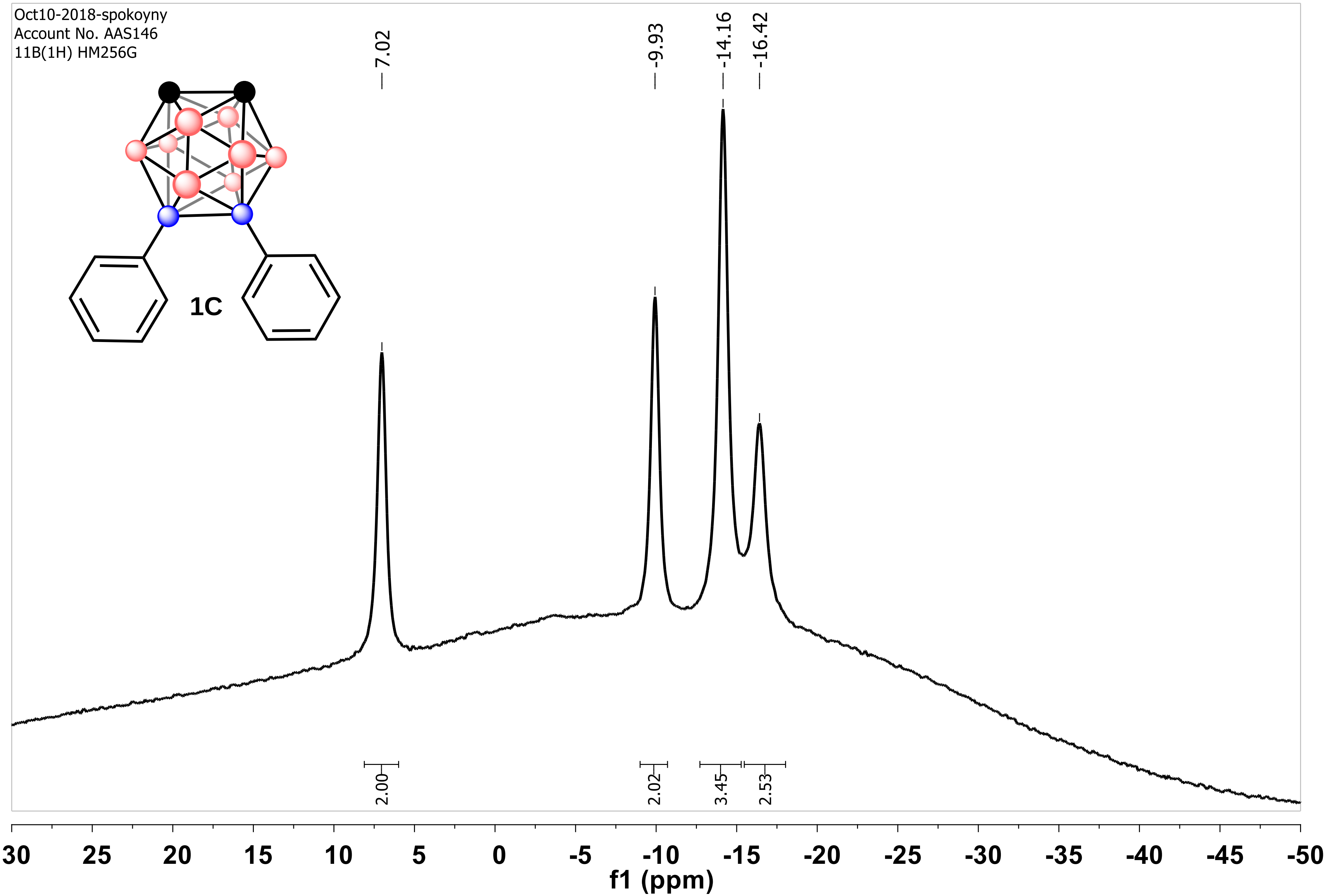
-17.08
1.71
2.49
5.80
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)



Oct10-2018-spokoyny
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3.45
2.53
30
25
20
15
10
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0
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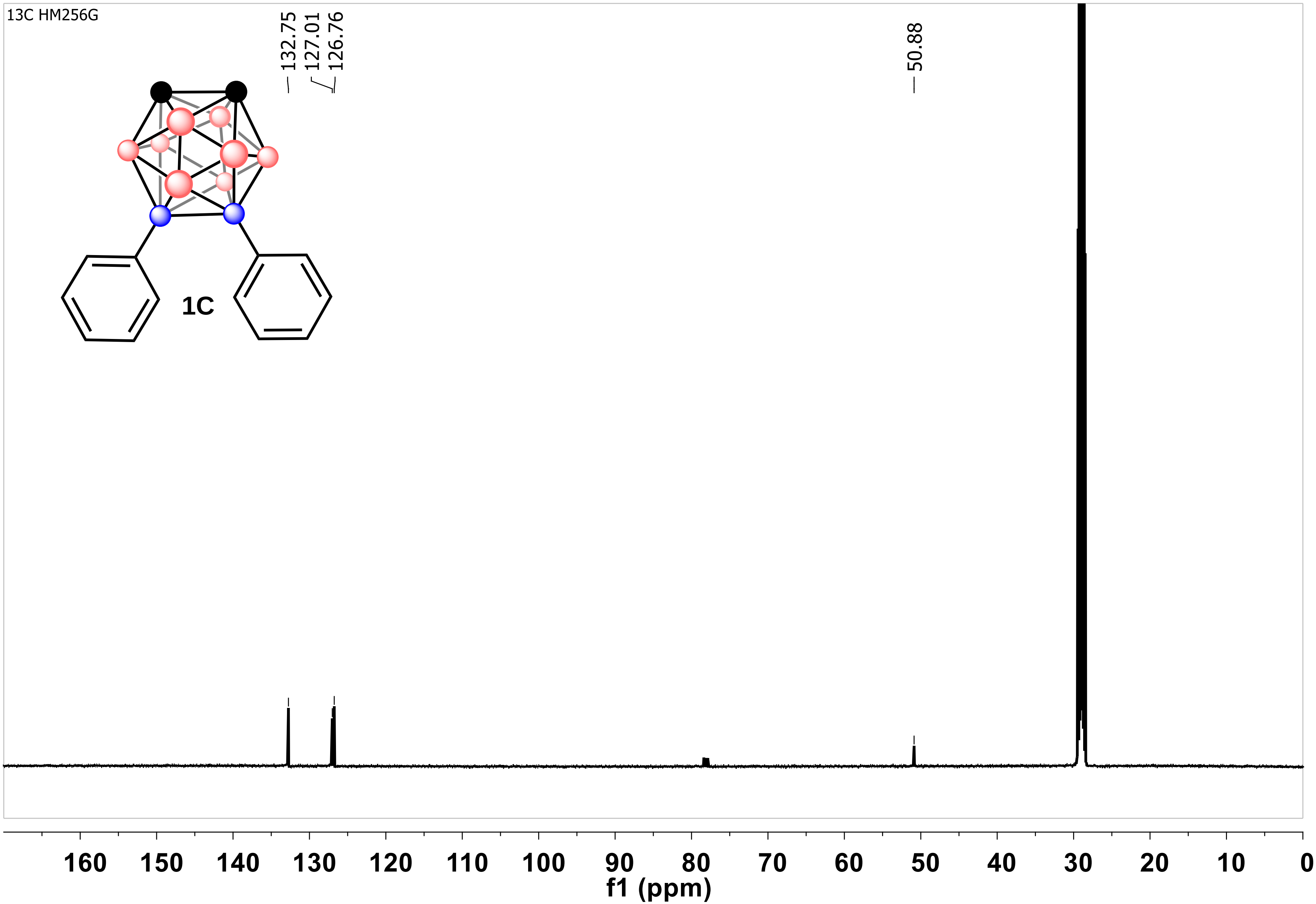
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)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126.76
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100
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60
50
40
30
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10
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f1 (ppm)

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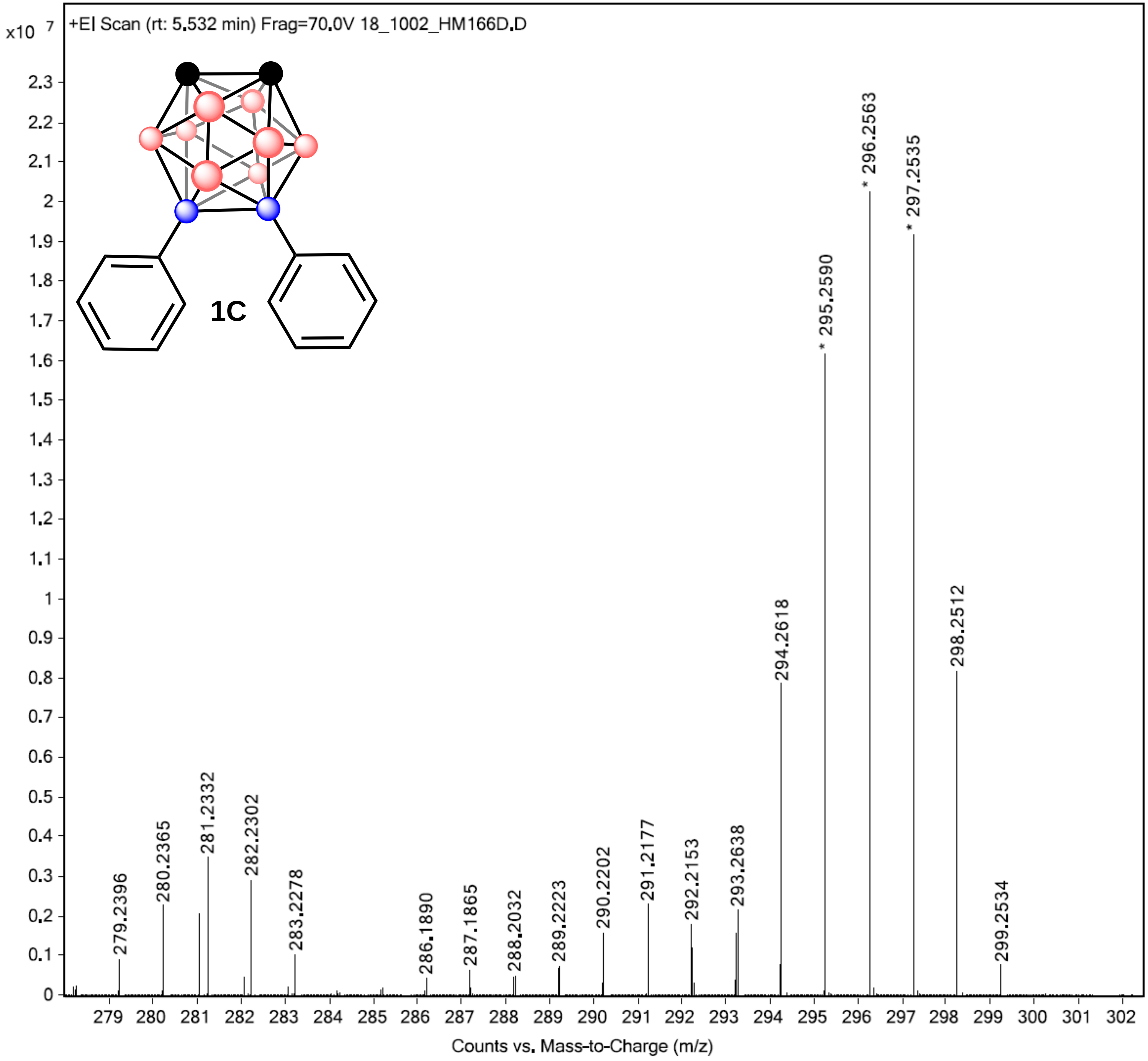

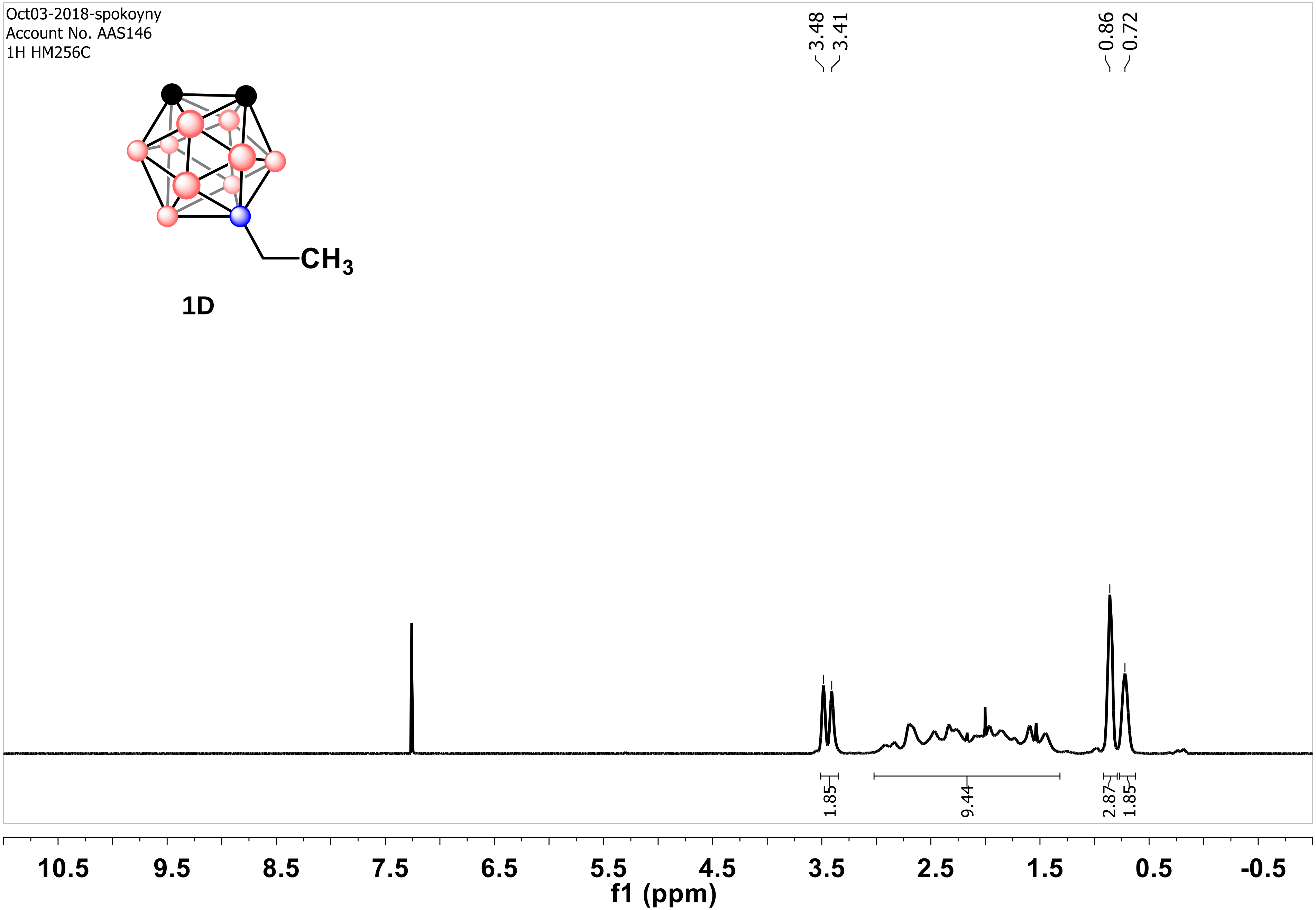
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1.85
10.5
9.5
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5.5
4.5
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1.5
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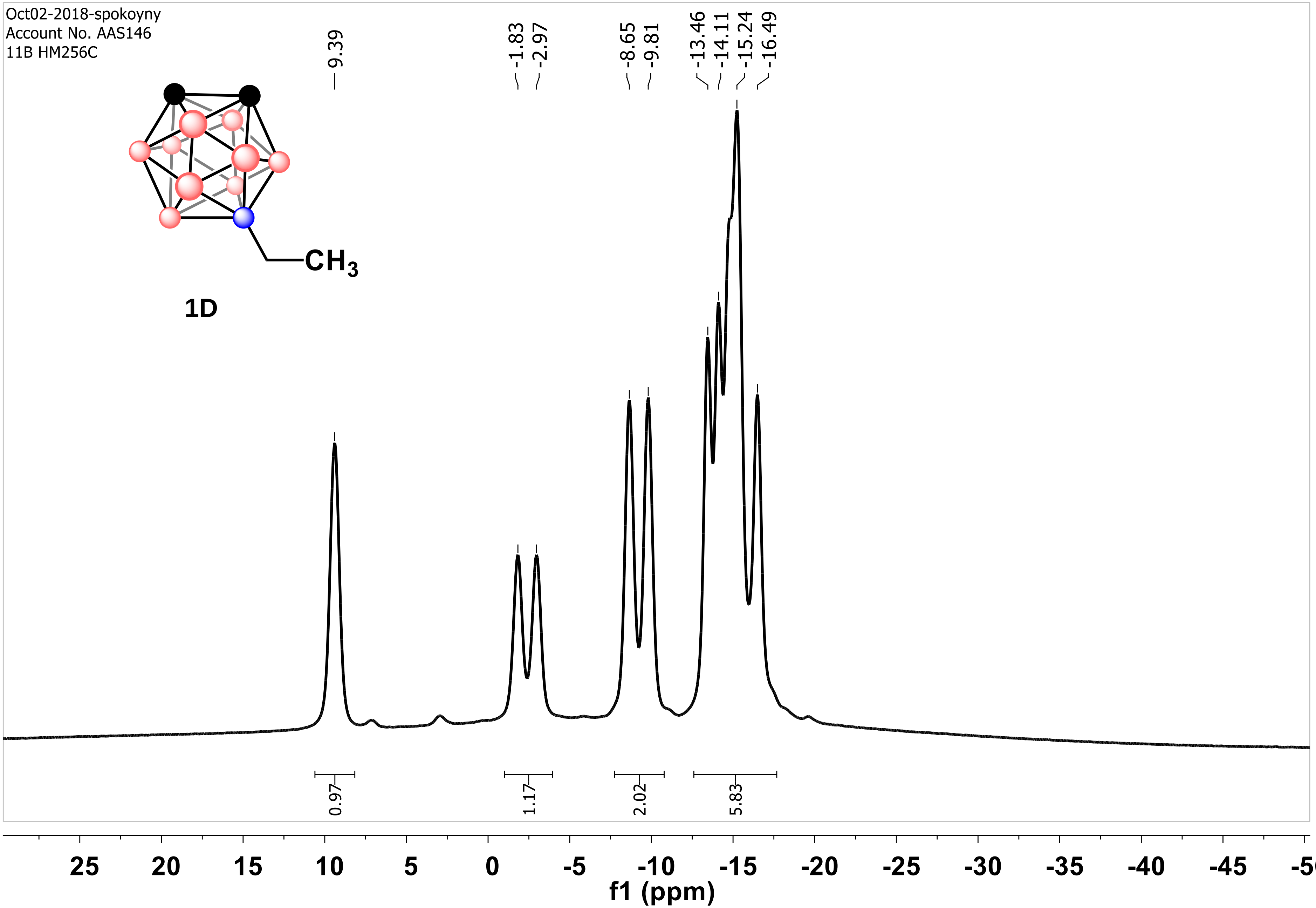
f1 (ppm)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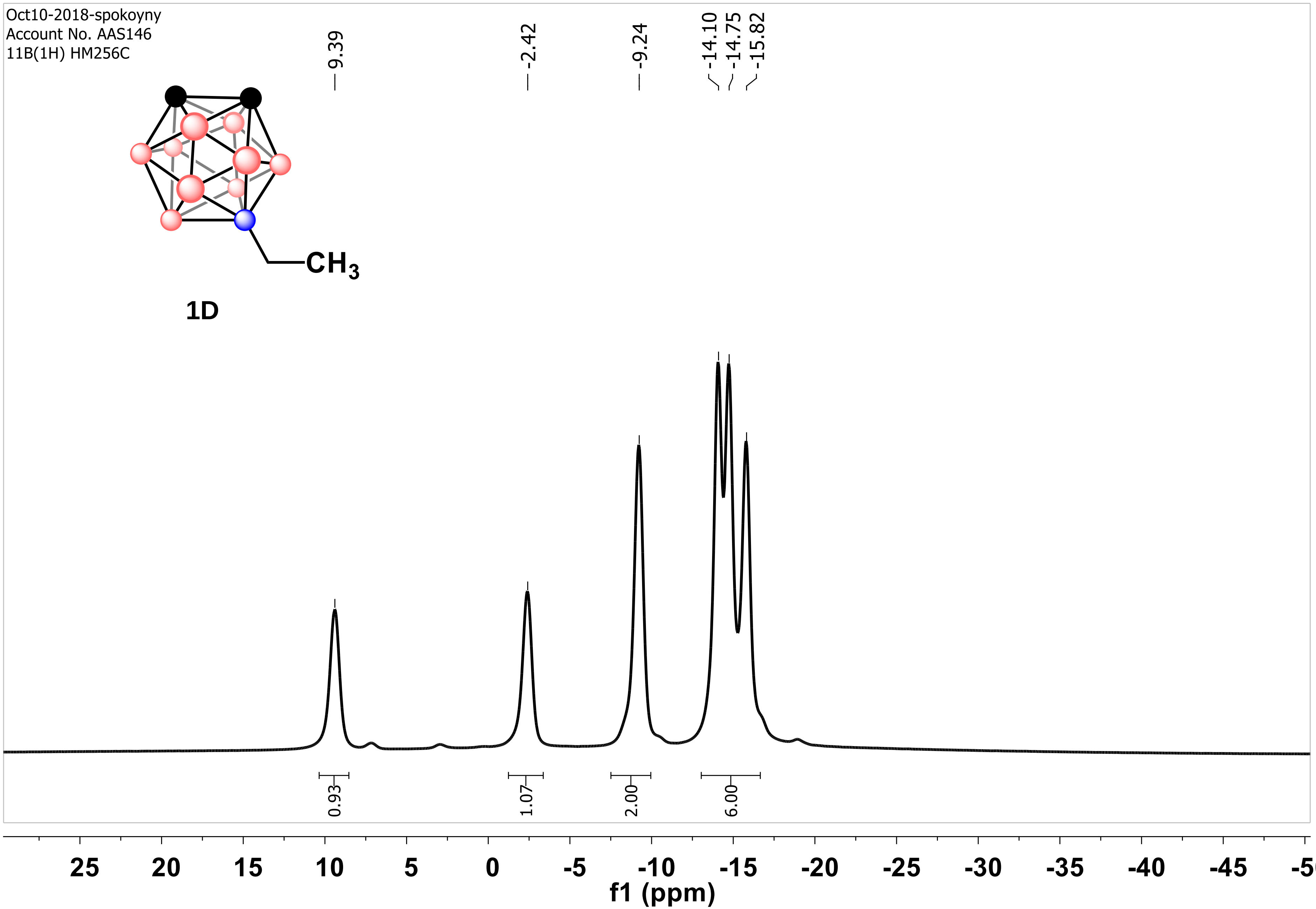
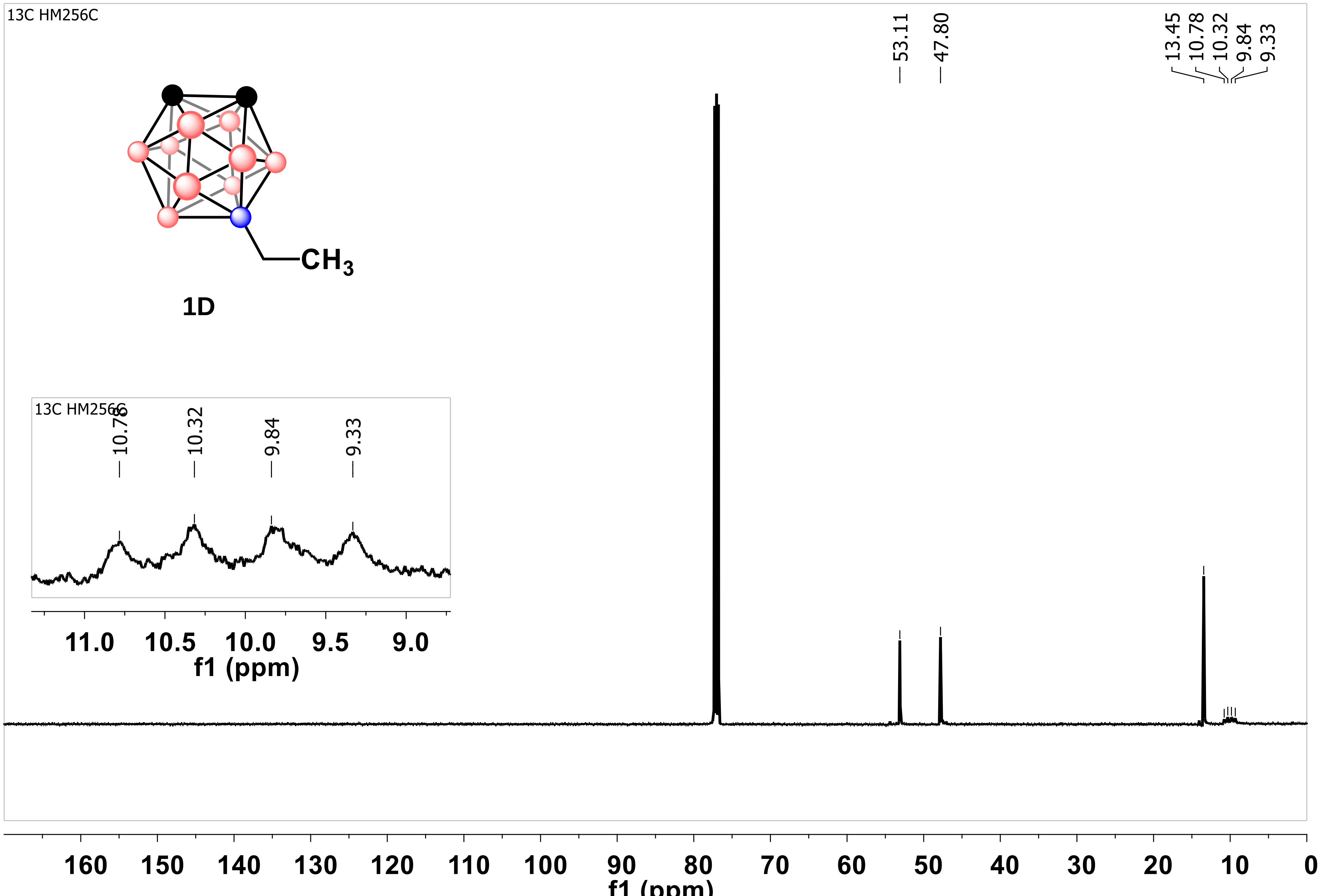
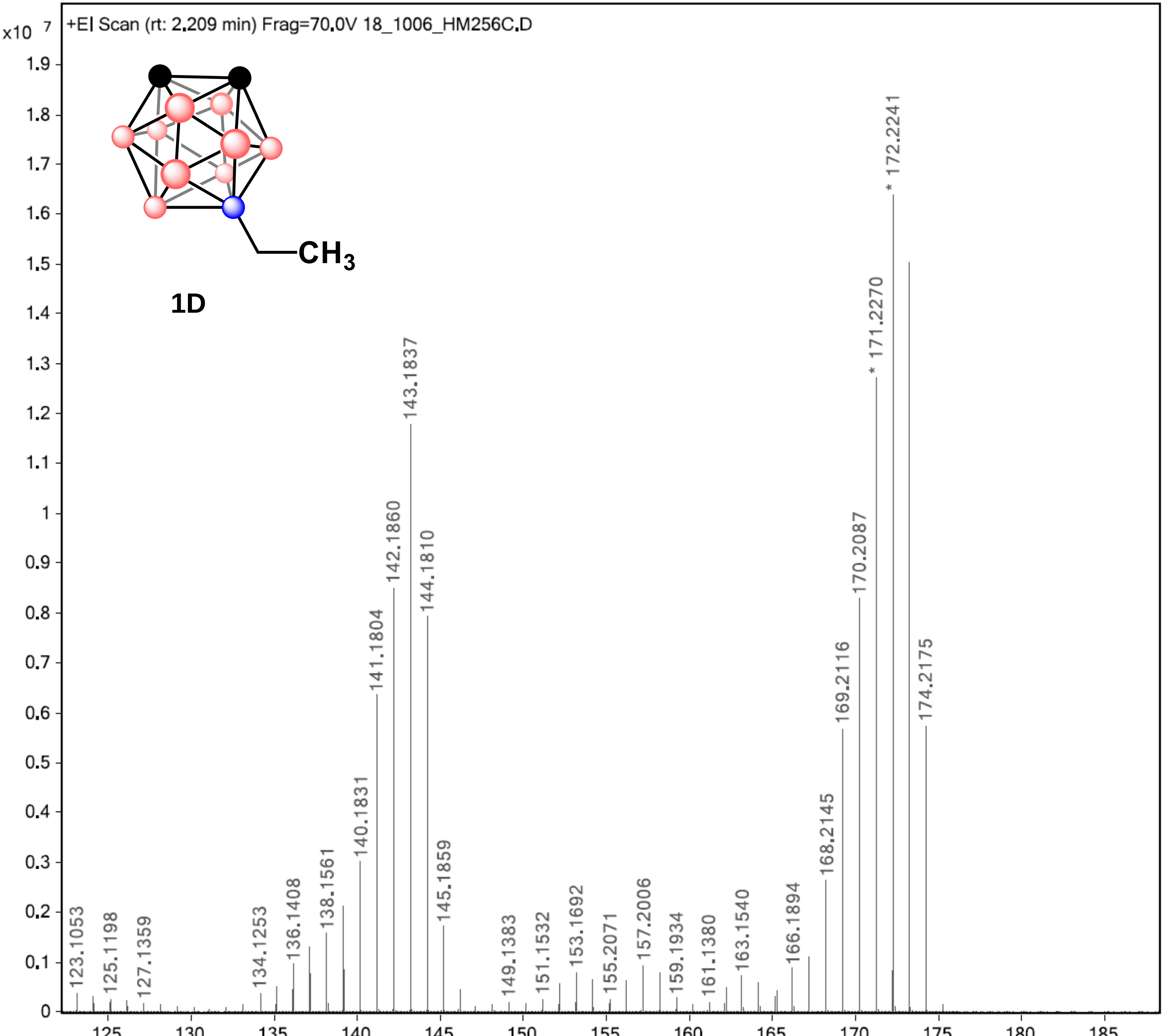
-2.97
-8.65
-9.81
-13.46
-14.11
-15.24
-16.49
CH3
1D
0.97
1.17
2.02
5.83
25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

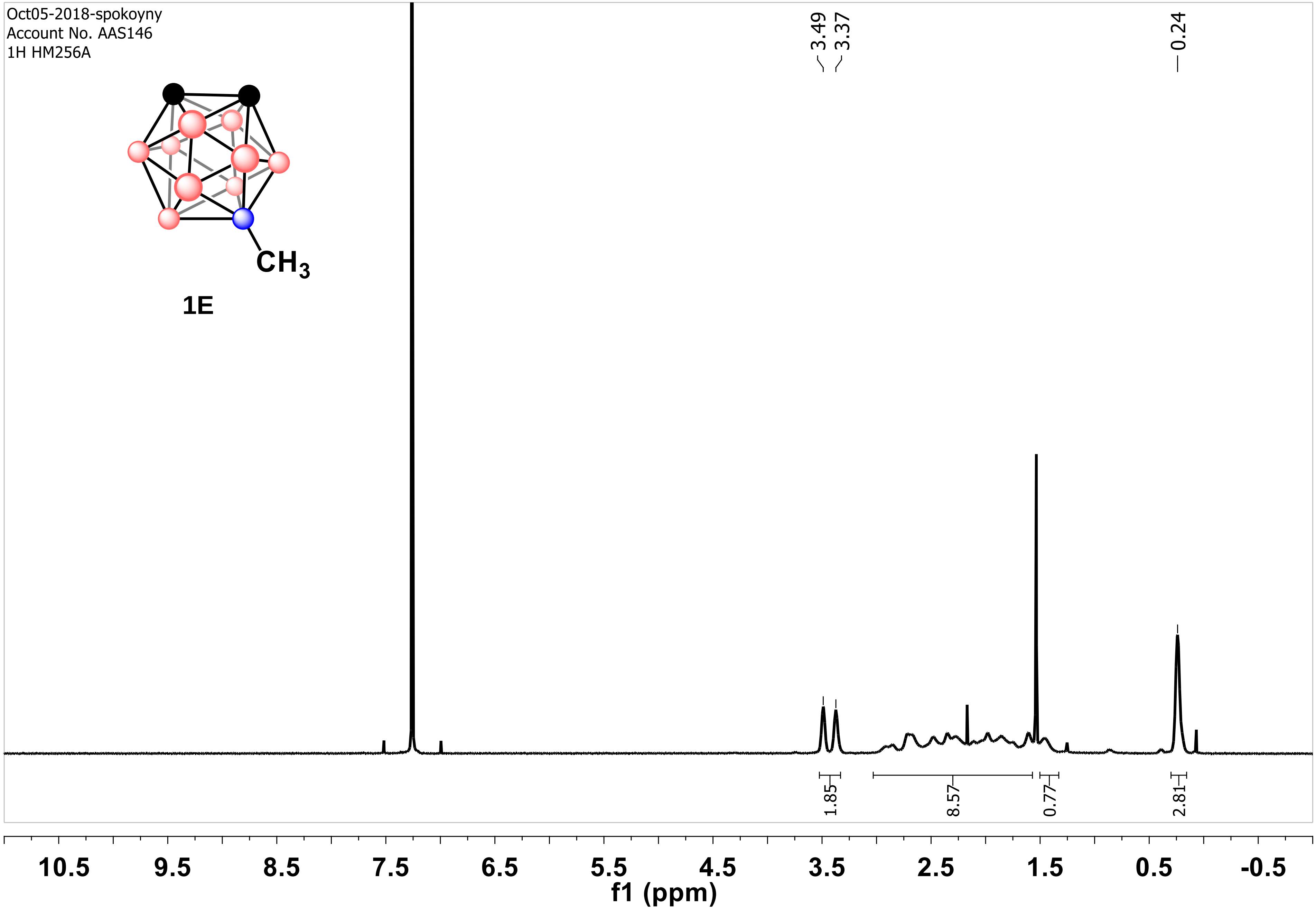

Oct10-2018-spokoyny
Account No. AAS146
11B(1H) HM256C
9.39
-2.42
-9.24
-14.10
-14.75
-15.82
CH3
1D
0.93
1.07
2.00
6.00
25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

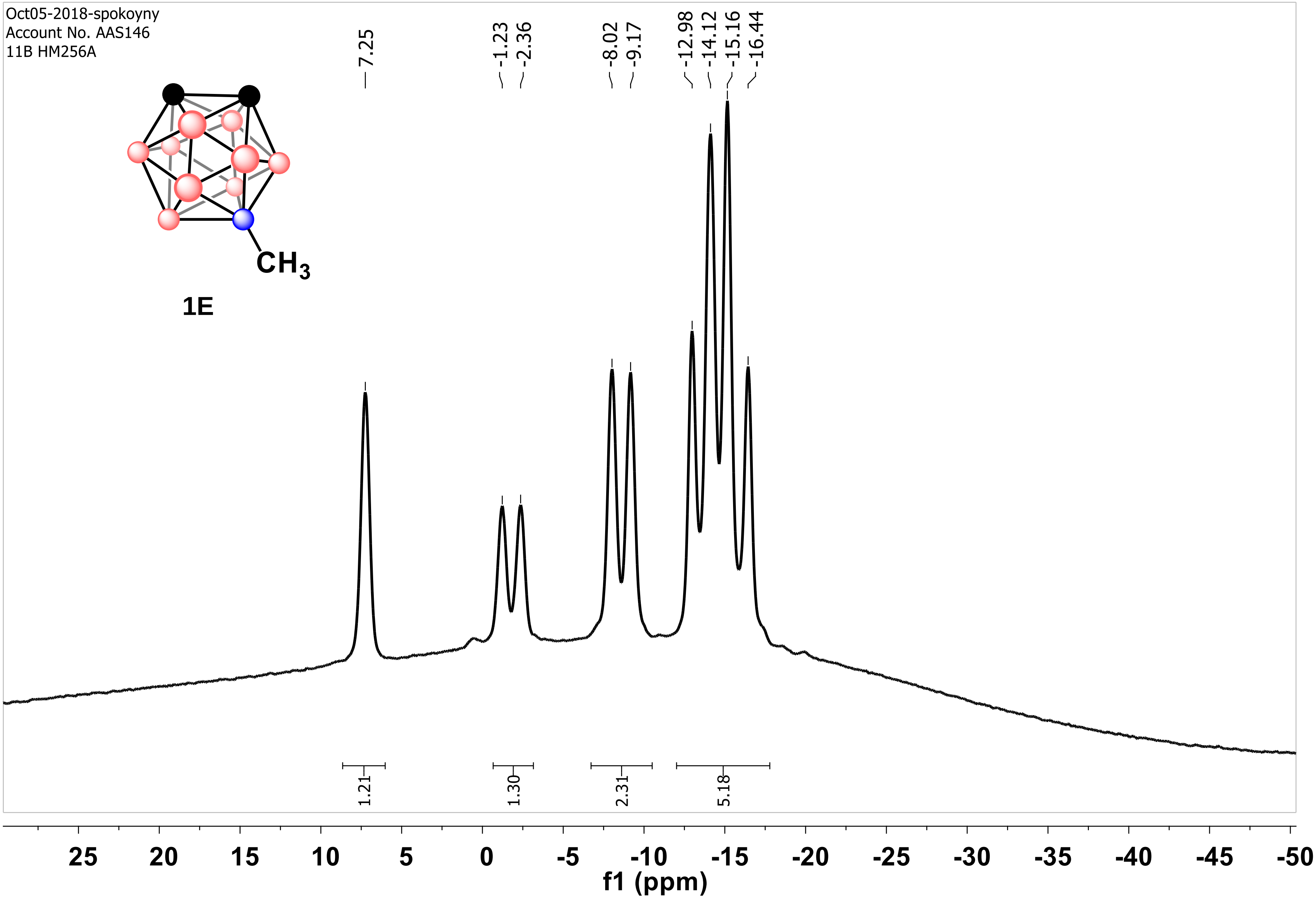

13C HM256C
53.11
47.80
13.45
10.78
10.32
9.84
9.33
CH3
1D
13C HM256C
10.78
10.32
9.84
9.33
11.0
10.5
10.0
9.5
9.0
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Mills_Generic_Carboranes_7min_highEV.M **Comment** **Acquired Time** 10/6/2018 11:45:51 AM (UTC-07:00)

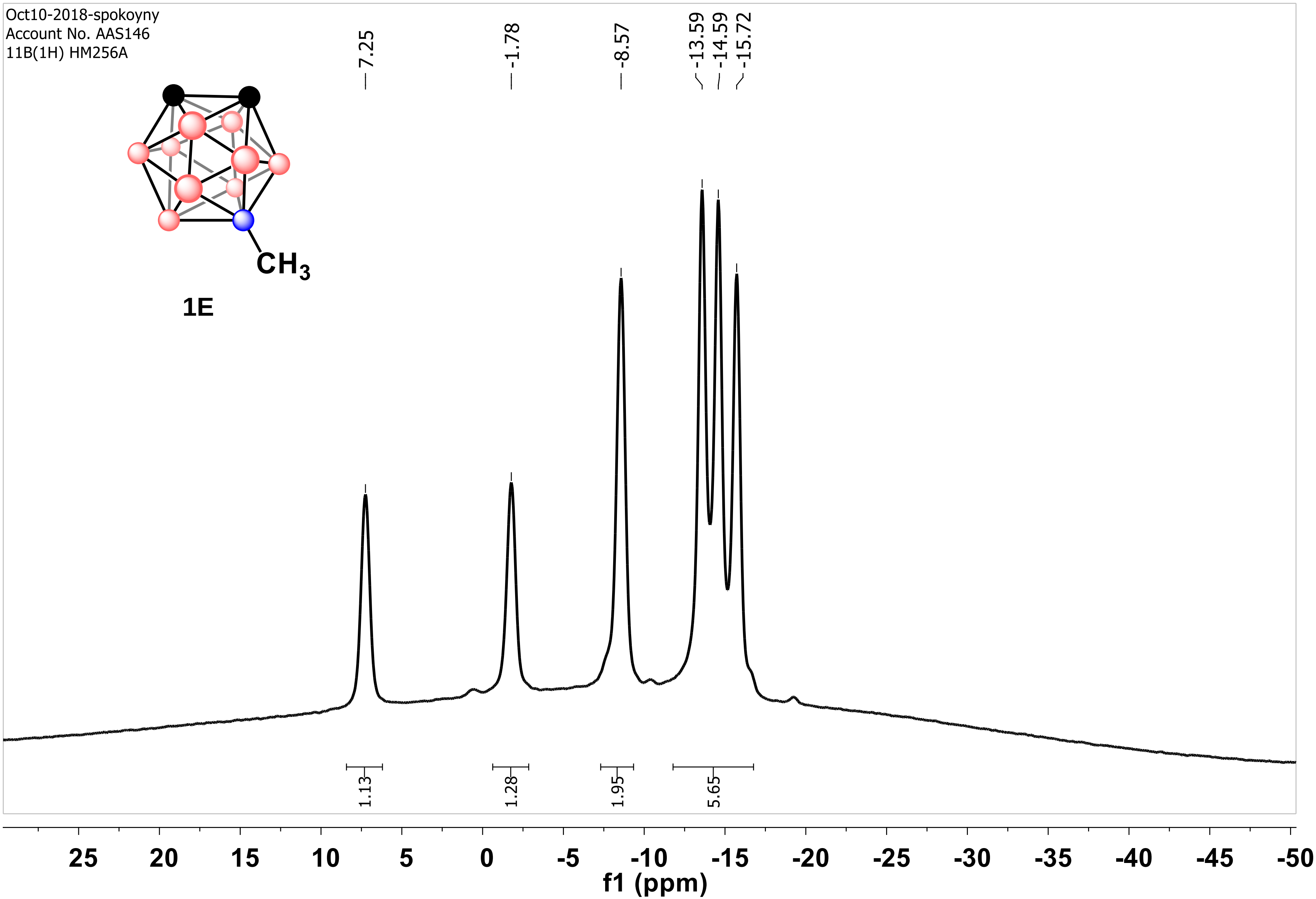


Oct05-2018-spokoyny
Account No. AAS146
1H HM256A

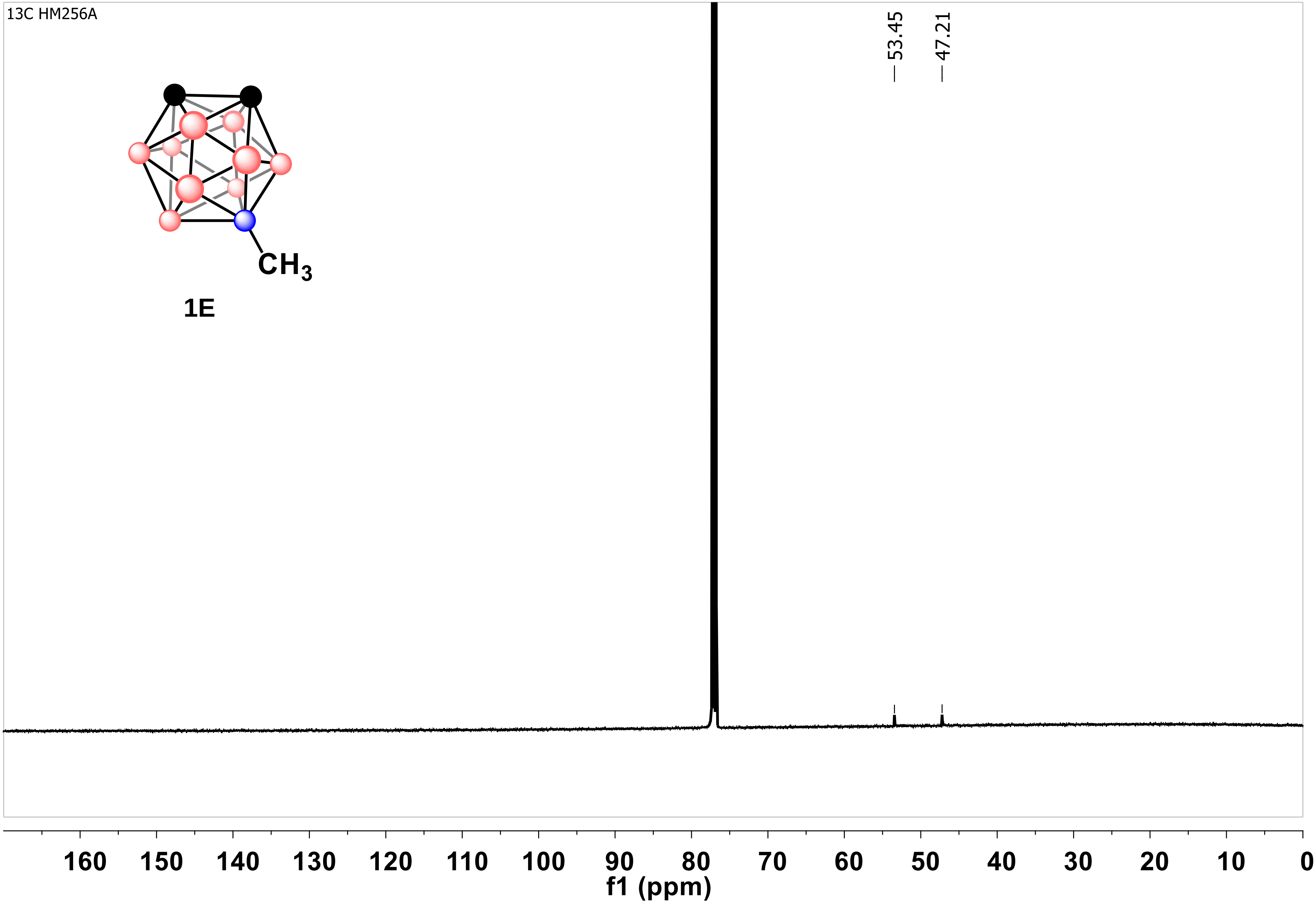




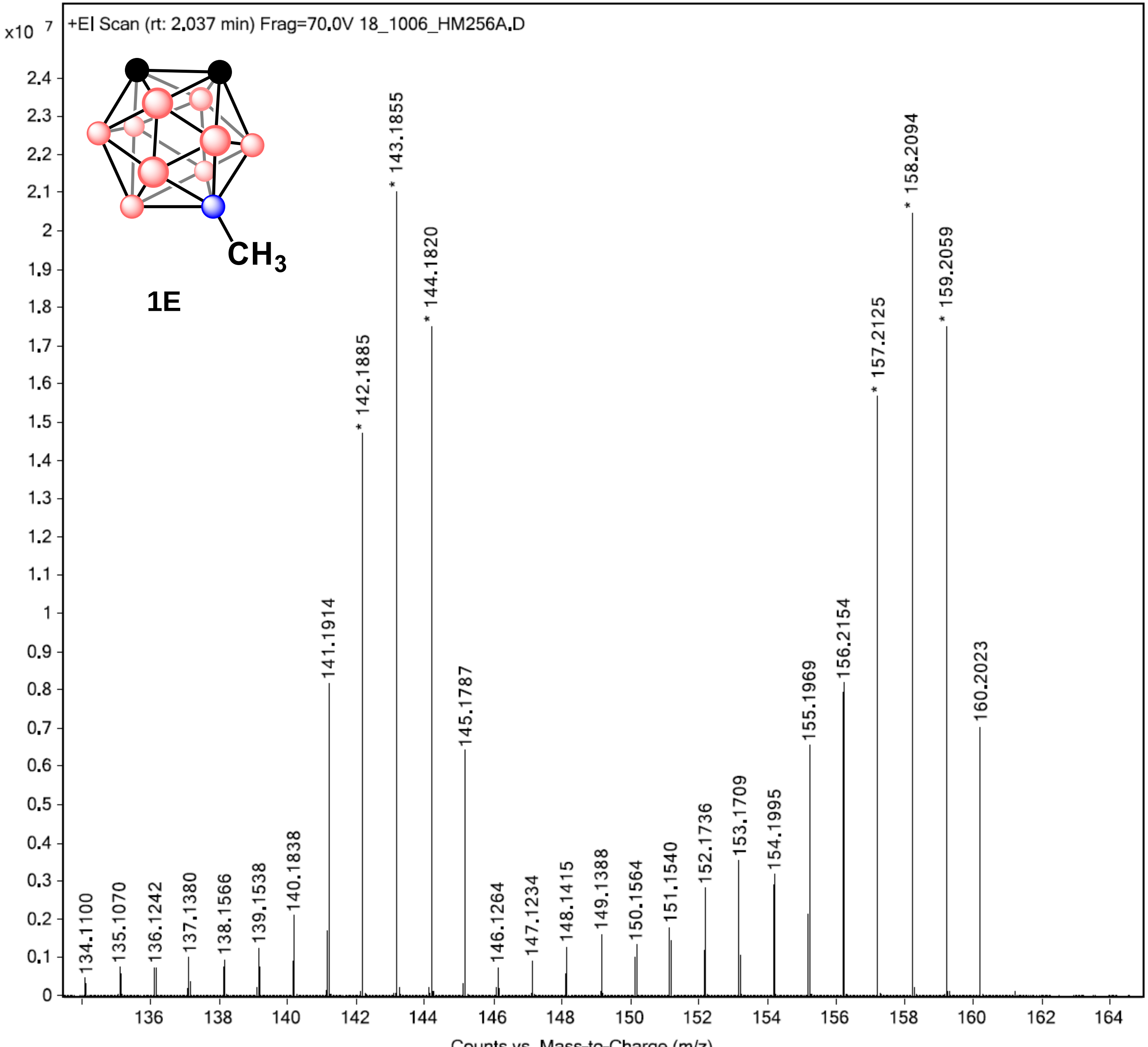
Oct05-2018-spokoyny
Account No. AAS146
11B HM256A
7.25
-1.23
-2.36
-8.02
-9.17
-12.98
-14.12
-15.16
-16.44
CH3
1E
1.21
1.30
2.31
5.18
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

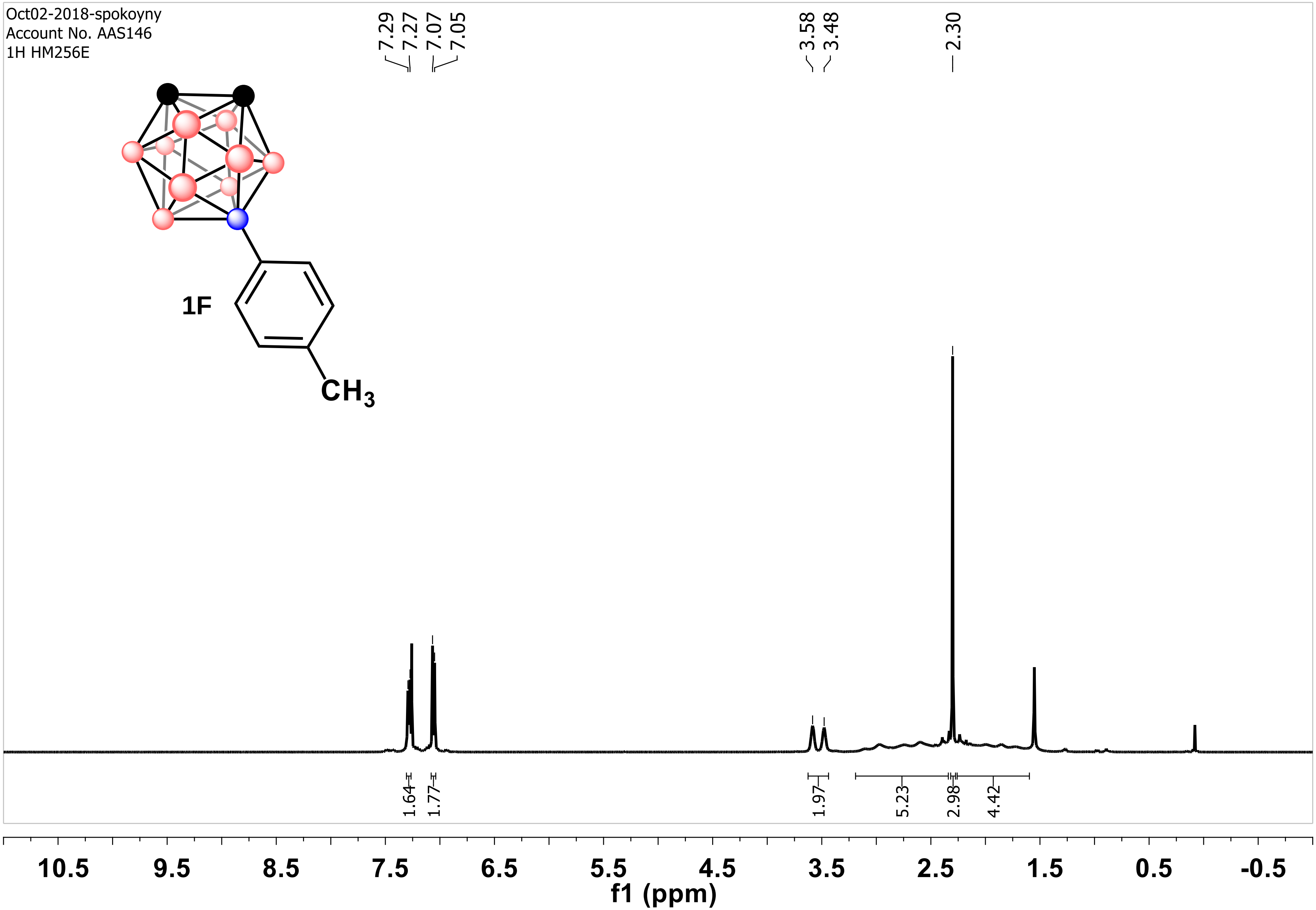


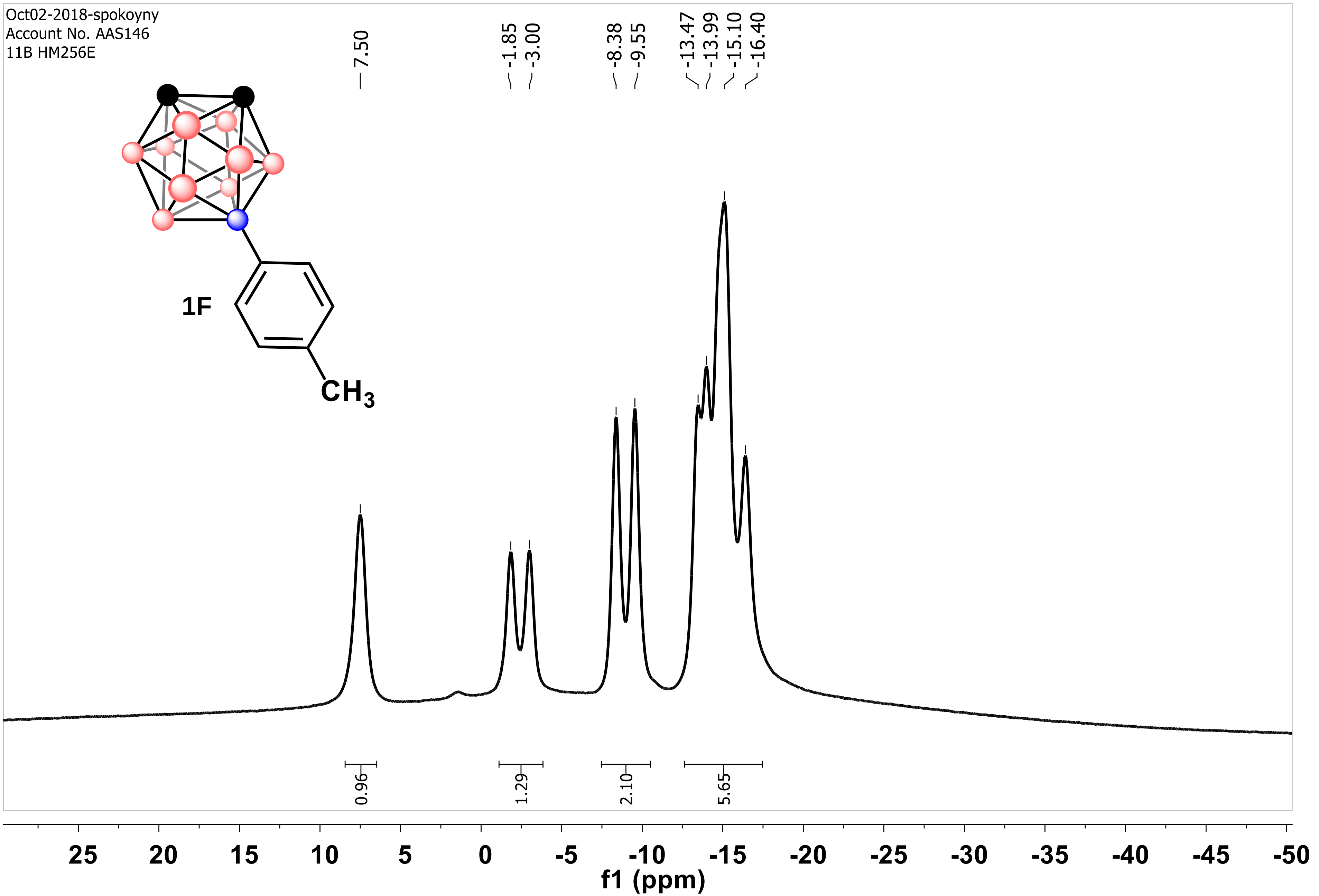
Oct10-2018-spokoyny
Account No. AAS146
11B(1H) HM256A
CH3
1E
7.25
-1.78
-8.57
-13.59
-14.59
-15.72
1.13
1.28
1.95
5.65
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)


13C HM256A
53.45
47.21
CH_3
1E
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

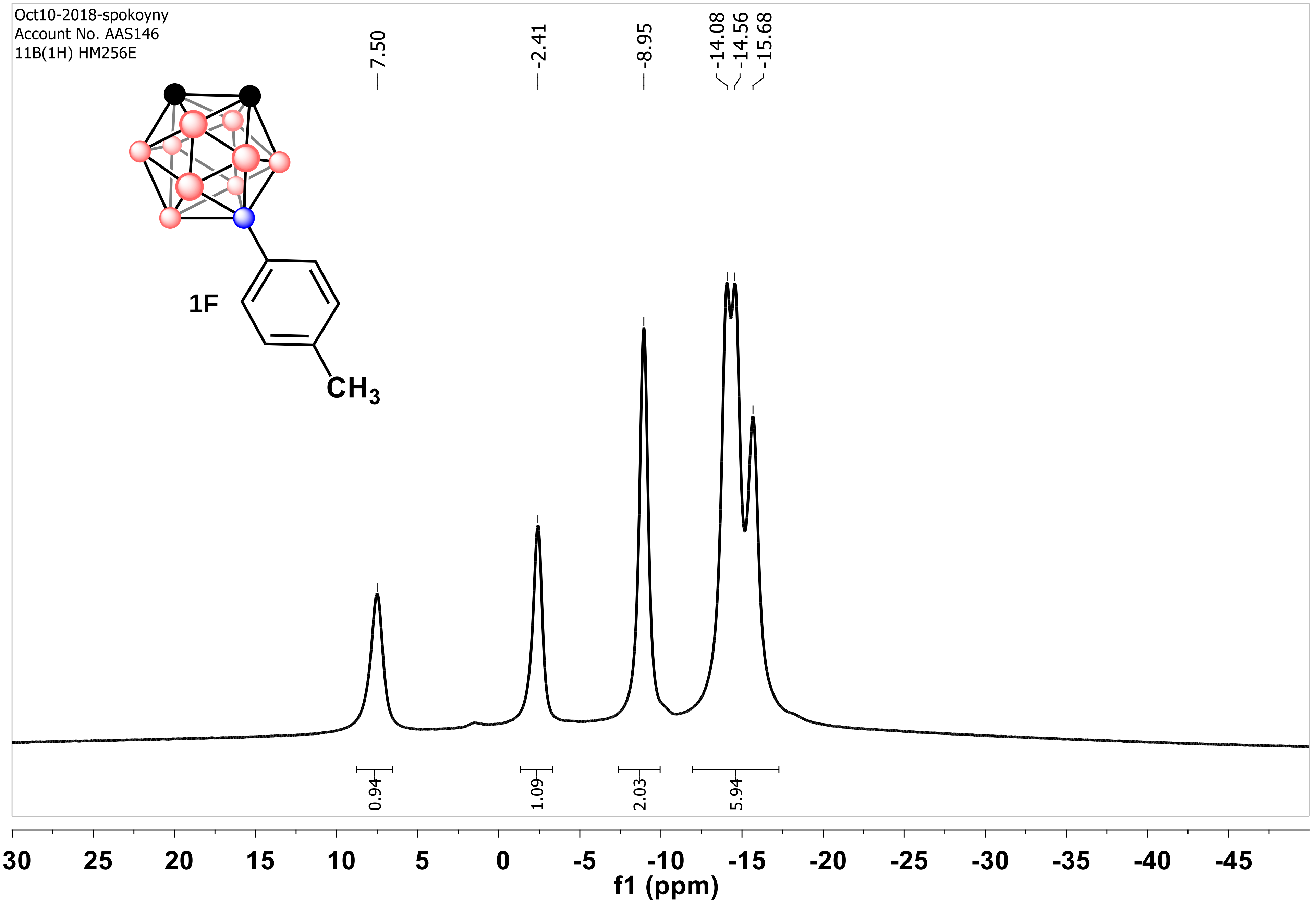
Mills_Generic_Carboranes_7min_highEV.M **Comment** **Acquired Time** 10/6/2018 11:24:54 AM (UTC-07:00)



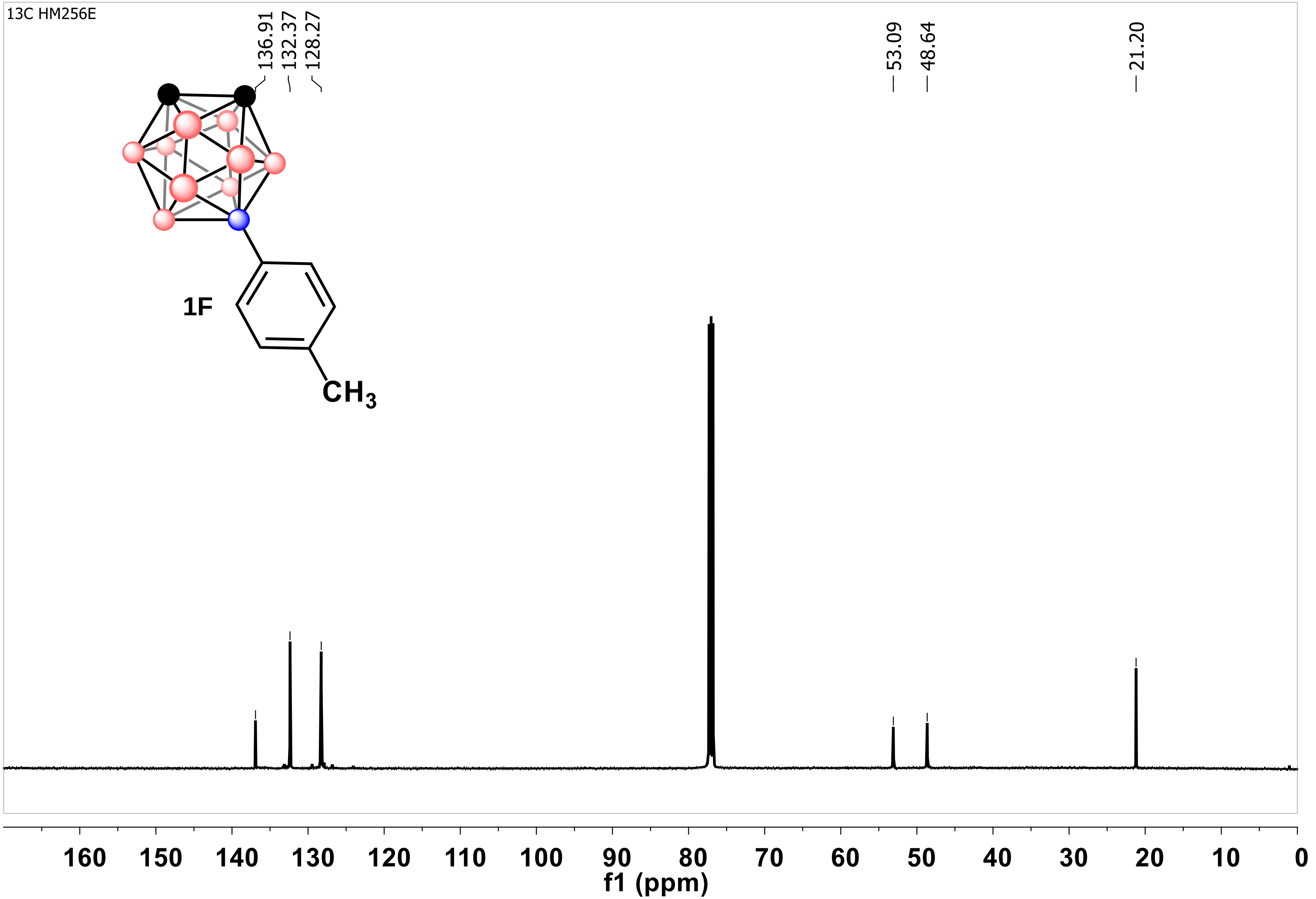

Oct02-2018-spokoyny
Account No. AAS146
1H HM256E
7.29
7.27
7.07
7.05
3.58
3.48
2.30
1F
CH3
1.64
1.77
1.97
5.23
2.98
4.42
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)



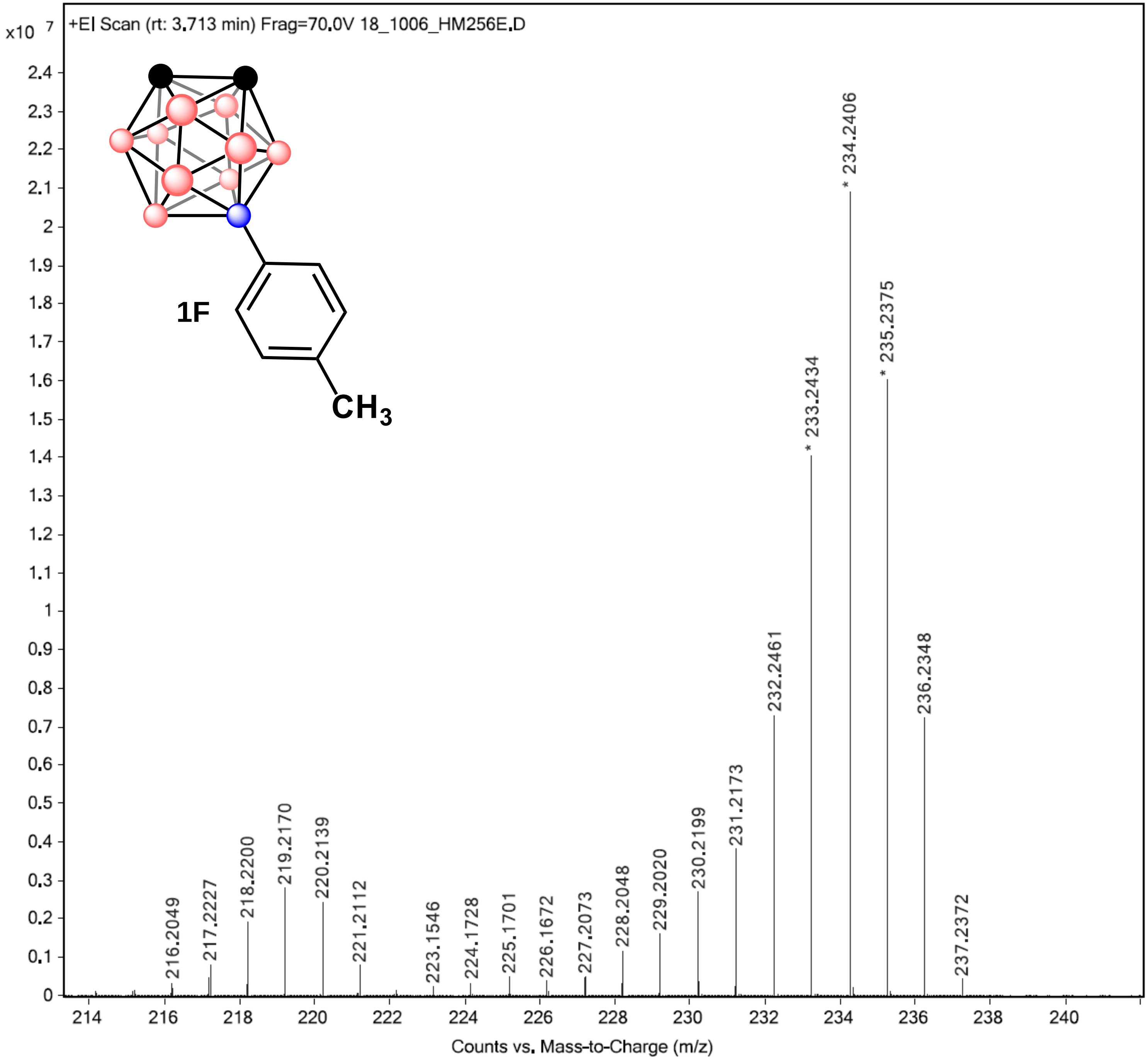
Oct02-2018-spokoyny
Account No. AAS146
11B HM256E
7.50
-1.85
-3.00
-8.38
-9.55
-13.47
-13.99
-15.10
-16.40
1F
CH3
0.96
1.29
2.10
5.65
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

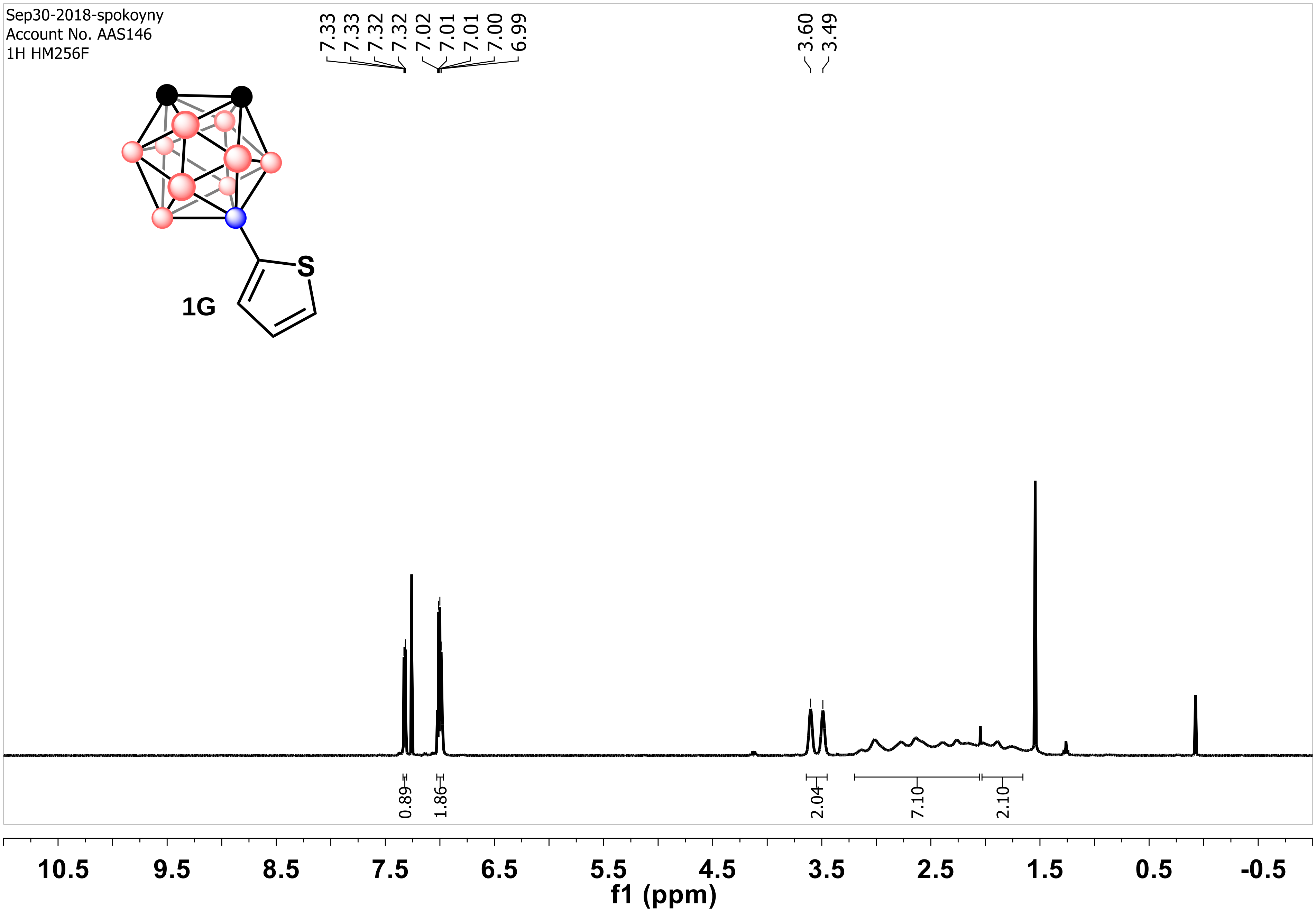


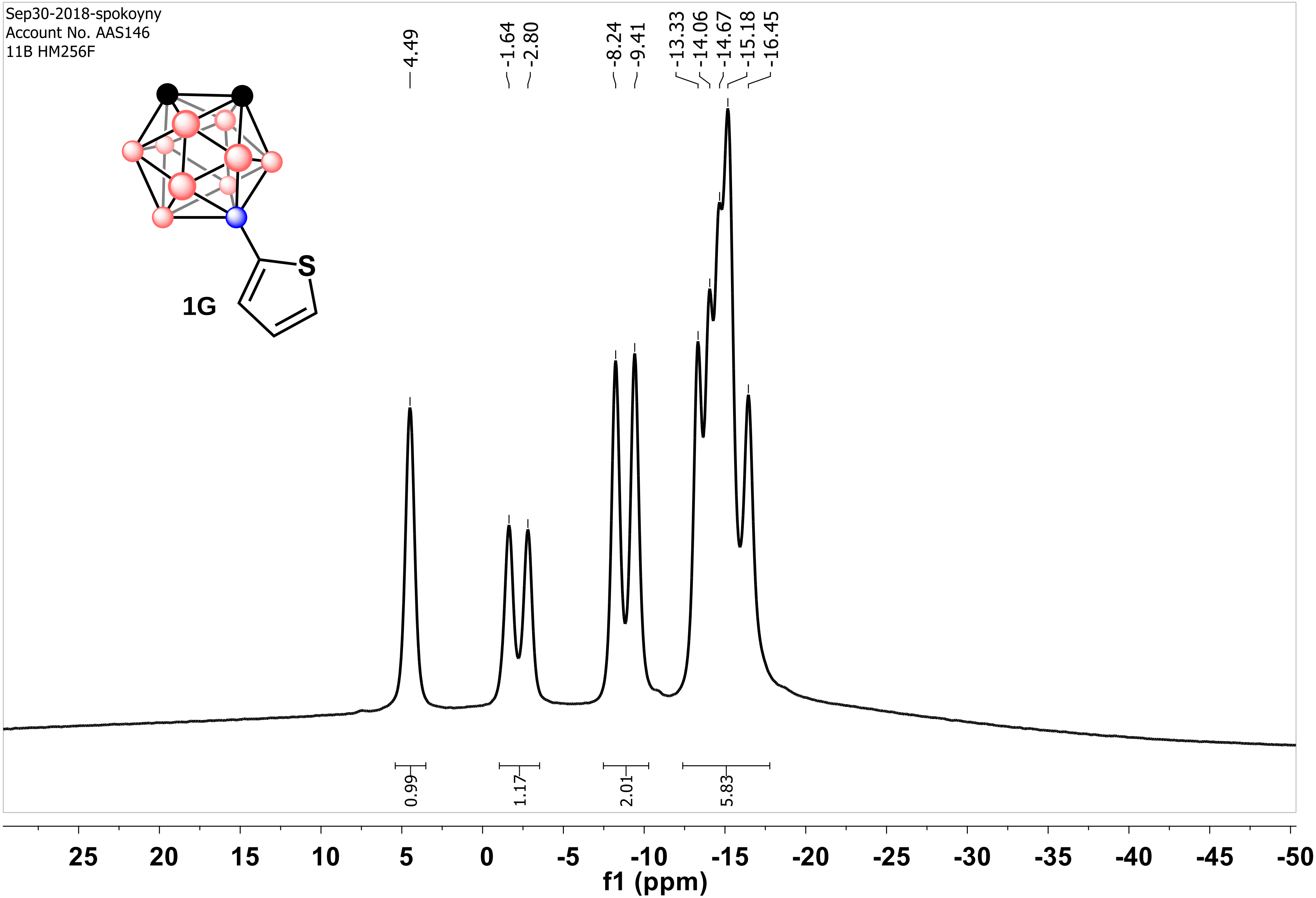
Oct10-2018-spokoyny
Account No. AAS146
11B(1H) HM256E
7.50
-2.41
-8.95
-14.08
-14.56
-15.68
1F
CH3
0.94
1.09
2.03
5.94
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

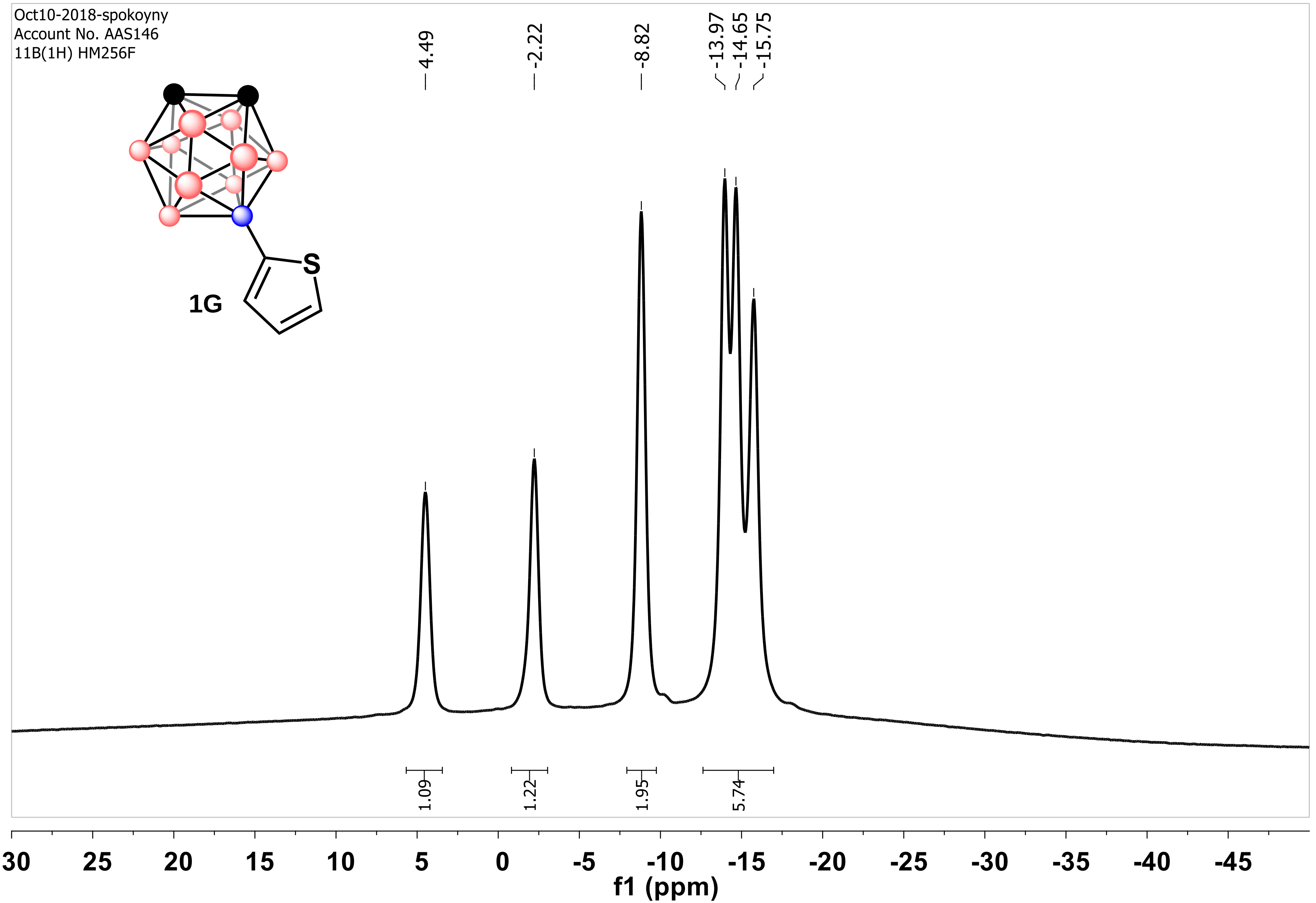

13C HM256E
136.91
132.37
128.27
53.09
48.64
21.20
1F
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

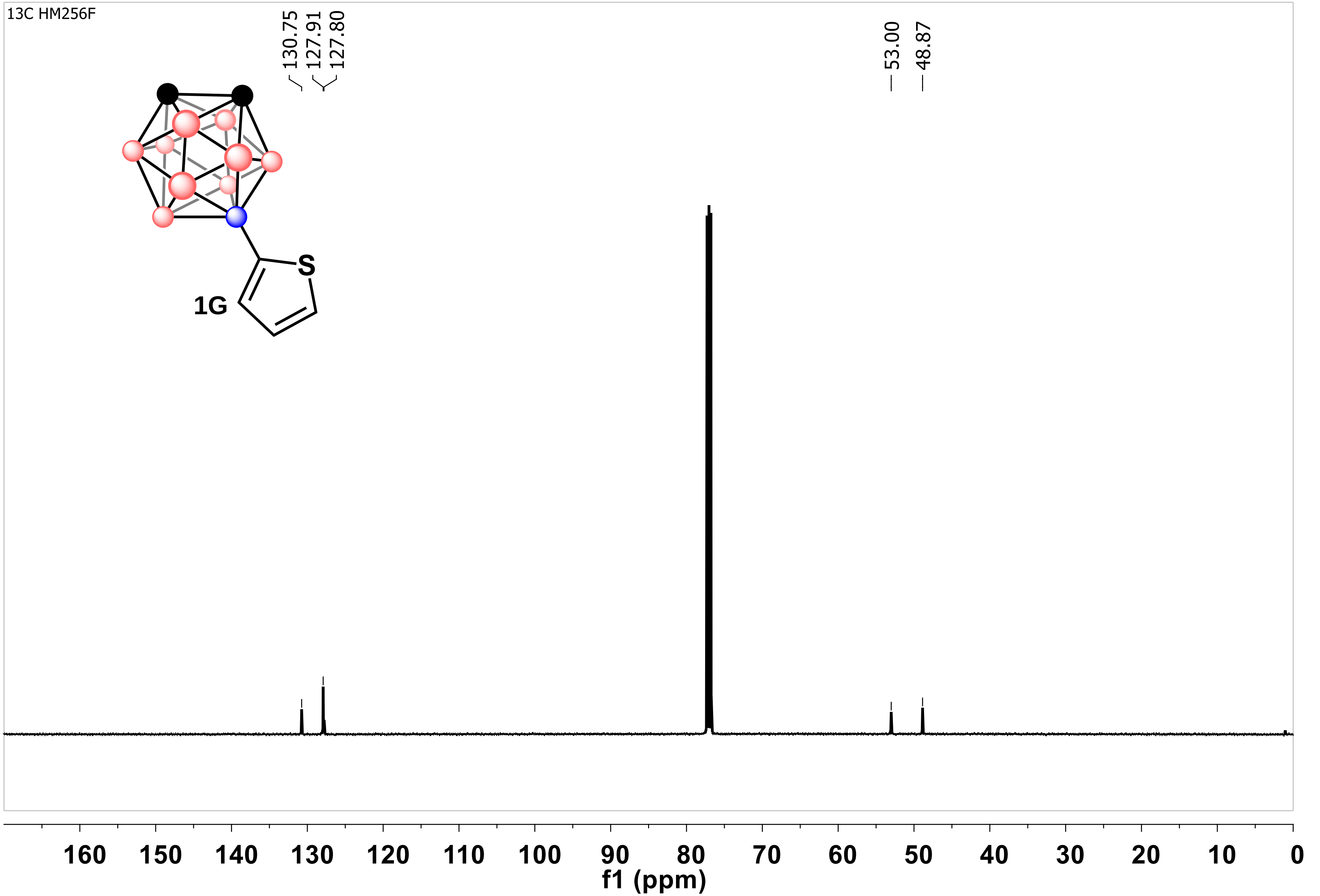
Mills_Generic_Carboranes_7min_highEV.M **Comment** **Acquired Time** 10/6/2018 11:56:20 AM (UTC-07:00)



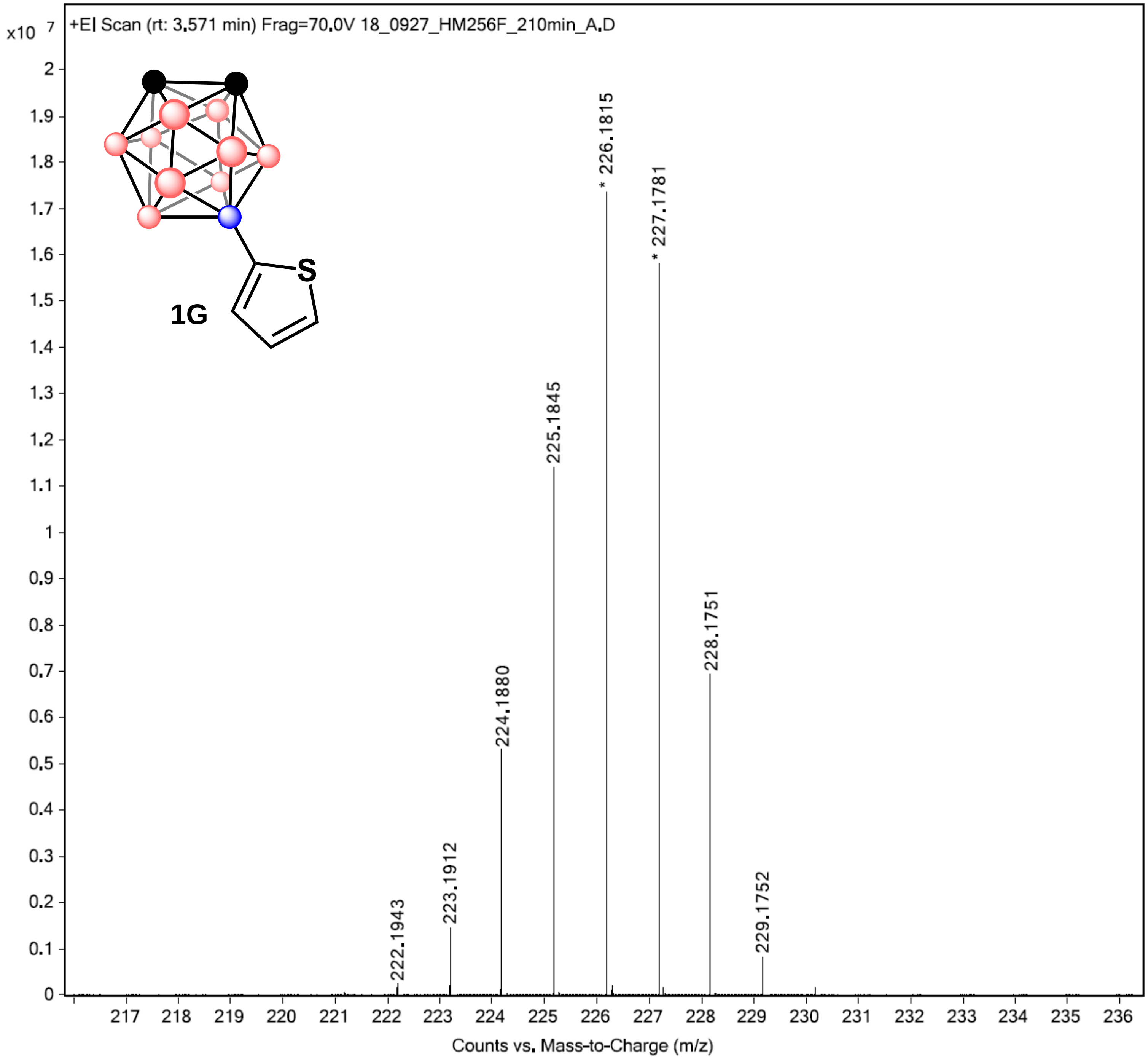

Sep30-2018-spokoyny
Account No. AAS146
1H HM256F
7.33
7.33
7.32
7.32
7.02
7.01
7.01
7.00
6.99
3.60
3.49
S
1G
0.89
1.86
2.04
7.10
2.10
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

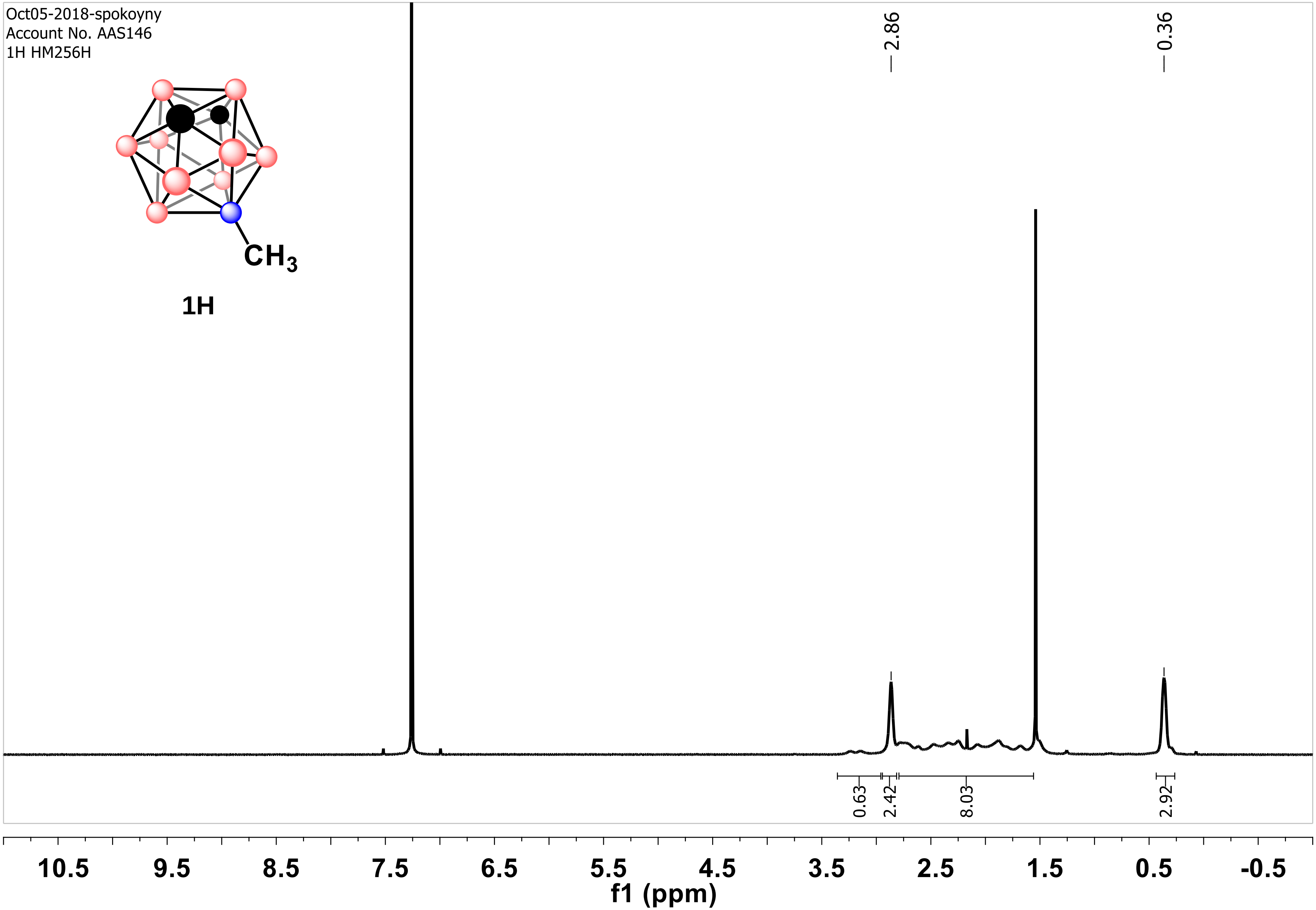

Sep30-2018-spokoyny
Account No. AAS146
11B HM256F
1G
S
4.49
-1.64
-2.80
-8.24
-9.41
-13.33
-14.06
-14.67
-15.18
-16.45
0.99
1.17
2.01
5.83
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)


Oct10-2018-spokoyny
Account No. AAS146
11B(1H) HM256F
4.49
-2.22
-8.82
-13.97
-14.65
-15.75
S
1G
1.09
1.22
1.95
5.74
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

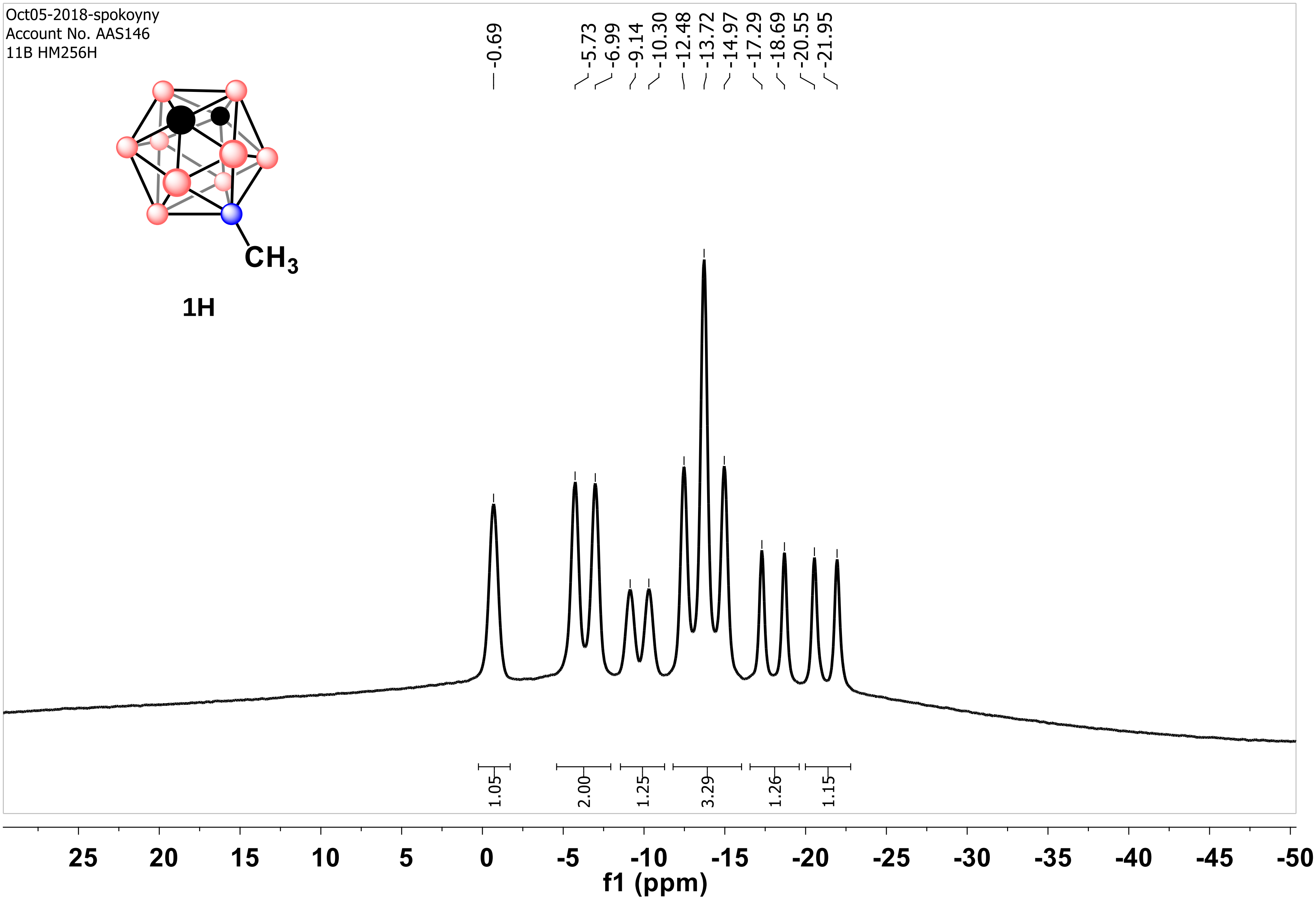

13C HM256F
130.75
127.91
127.80
53.00
48.87
1G
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Mills_Generic_Carboranes_7min_highEV.M **Comment** **Acquired Time** 9/27/2018 8:35:46 PM (UTC-07:00)

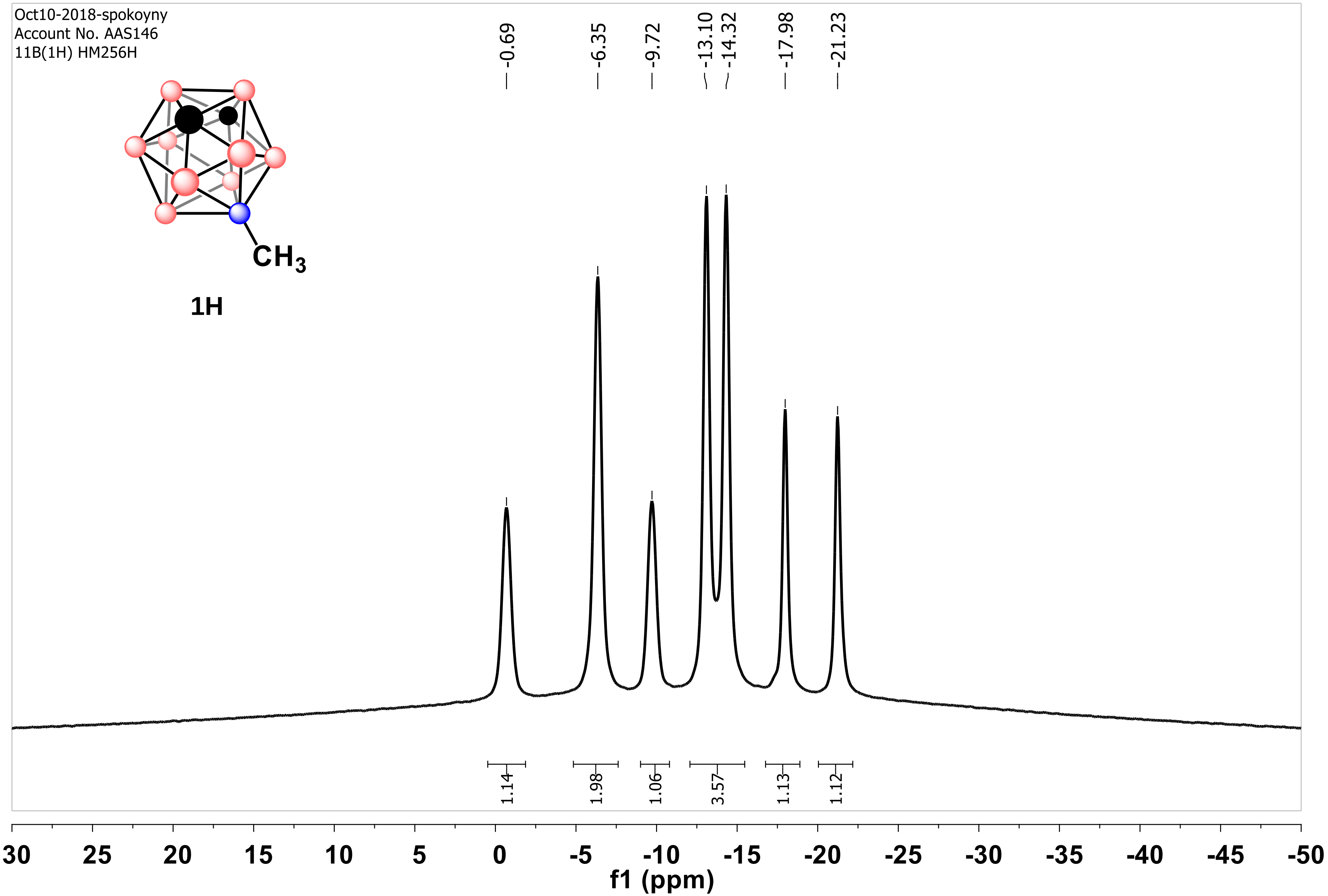




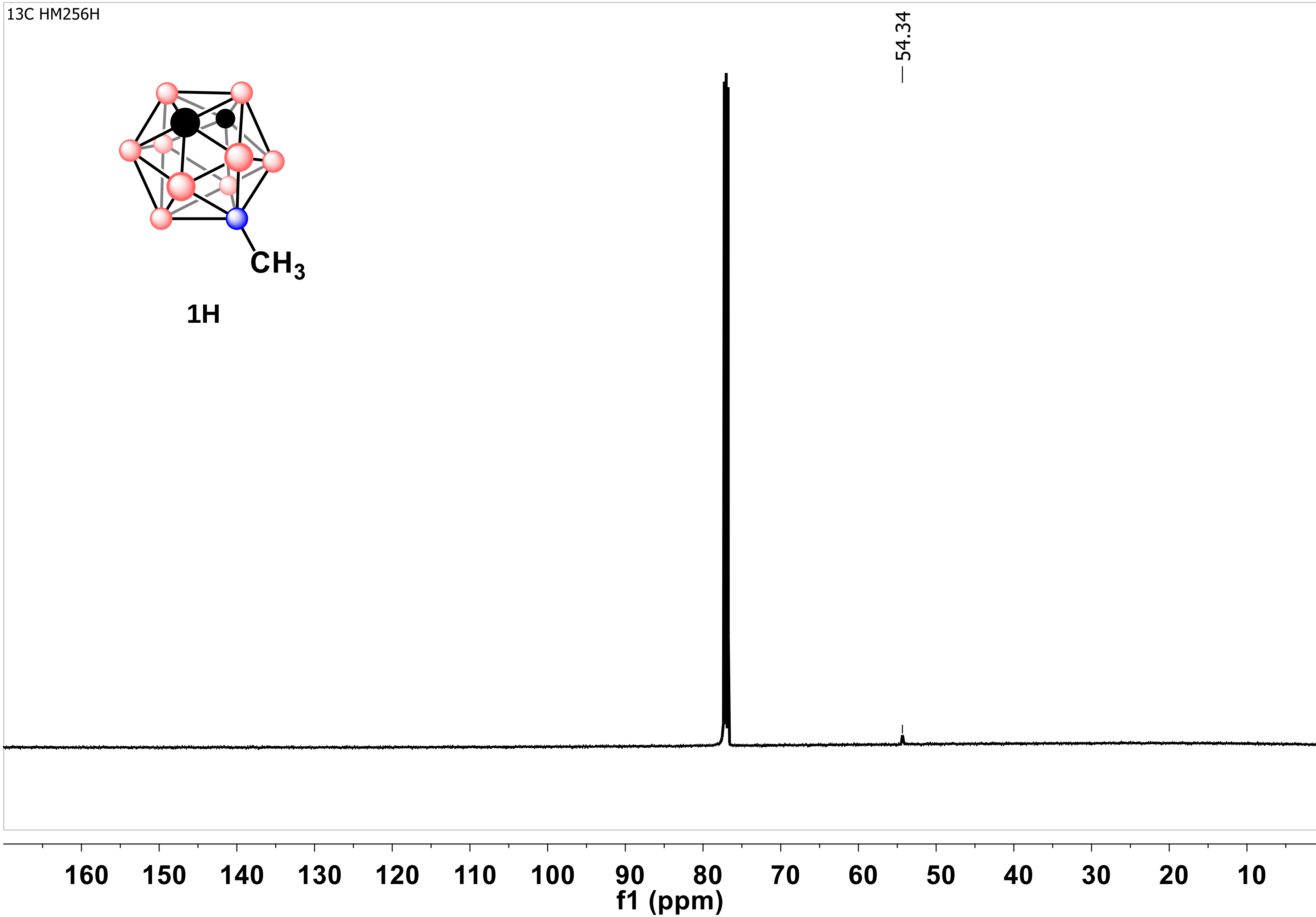
Oct05-2018-spokoyny
Account No. AAS146
1H HM256H
CH3
1H
2.86
0.36
0.63
2.42
8.03
2.92
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)



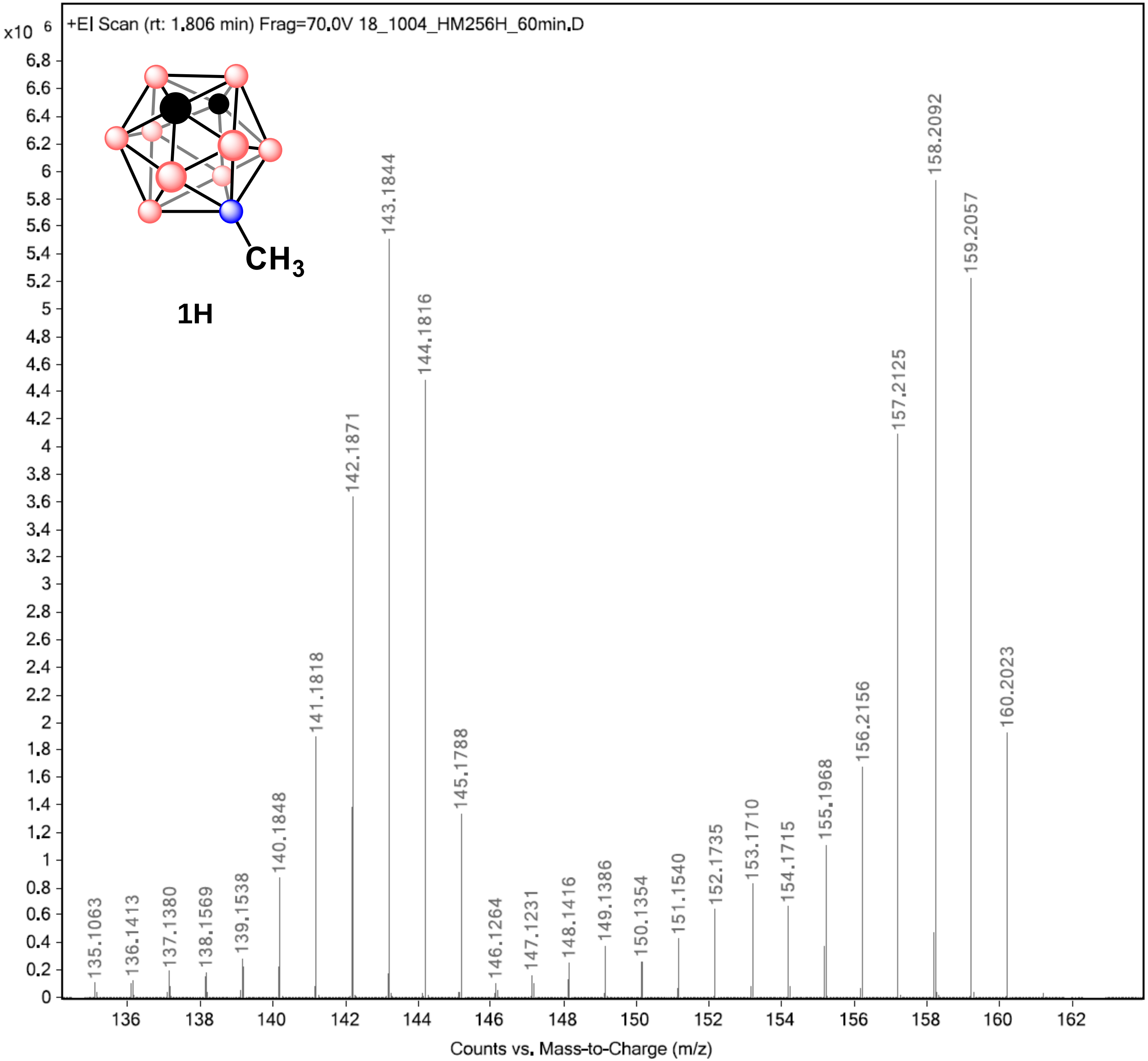
Oct05-2018-spokoyny
Account No. AAS146
11B HM256H
CH3
1H
-0.69
-5.73
-6.99
-9.14
-10.30
-12.48
-13.72
-14.97
-17.29
-18.69
-20.55
-21.95
1.05
2.00
1.25
3.29
1.26
1.15
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)



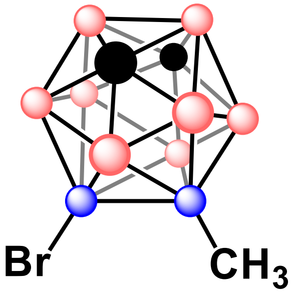
Oct10-2018-spokoyny
Account No. AAS146
11B(1H) HM256H
CH3
1H
-0.69
-6.35
-9.72
-13.10
-14.32
-17.98
-21.23
1.14
1.98
1.06
3.57
1.13
1.12
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)


13C HM256H
54.34
CH3
1H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

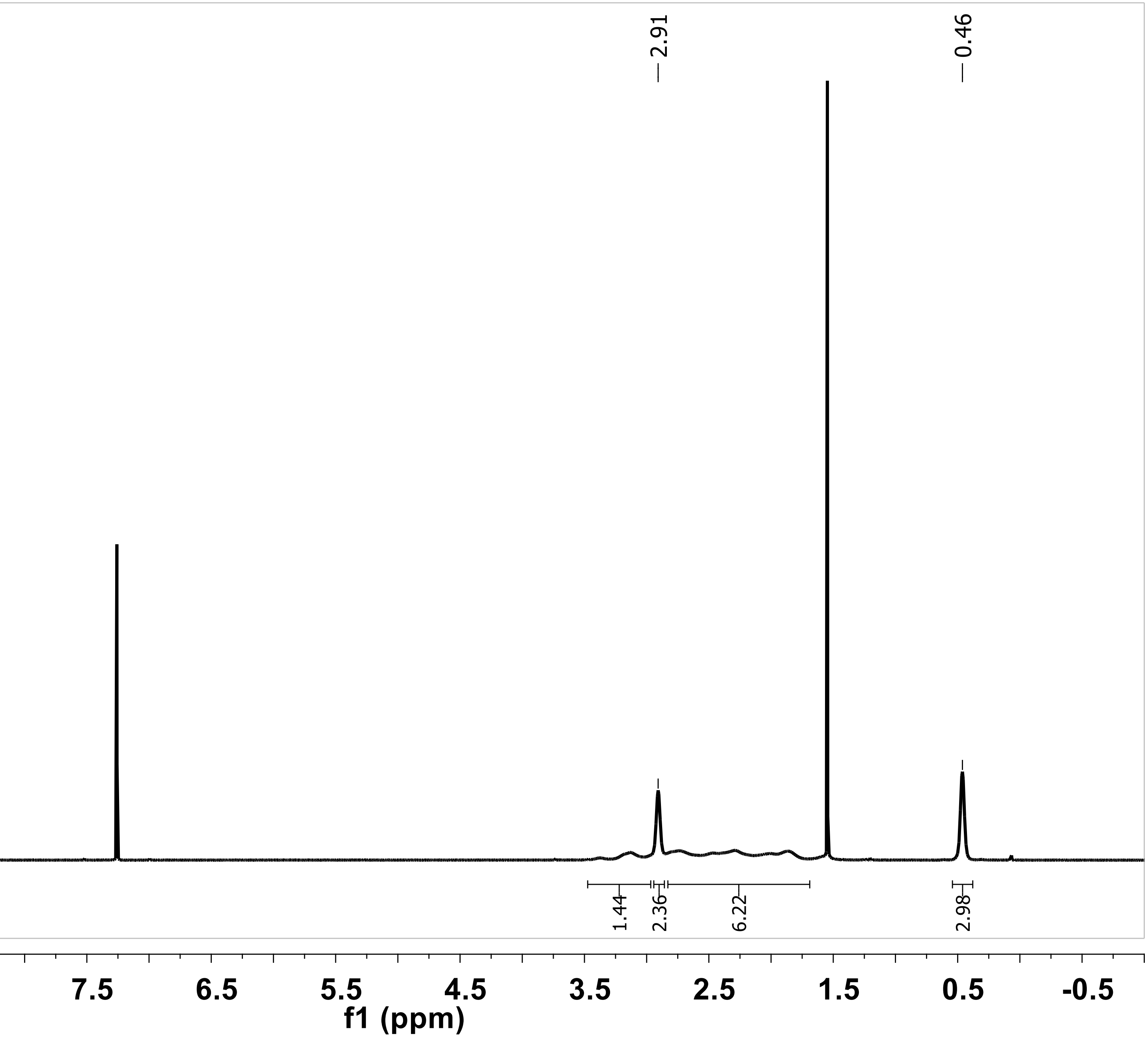
Mills_Generic_Carboranes_7min_highEV.M Comment Acquired Time 10/4/2018 12:45:45 PM (UTC-07:00)

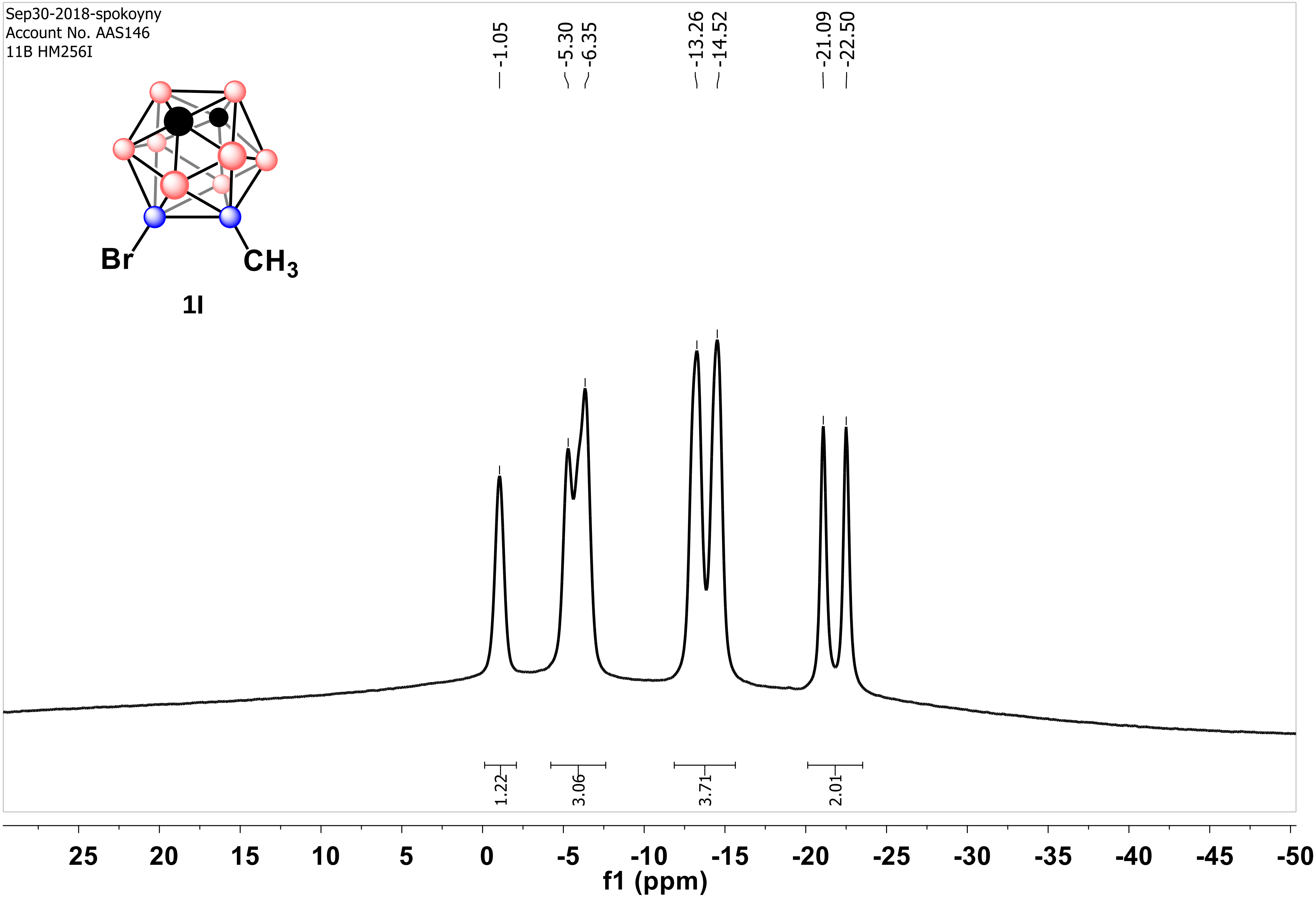


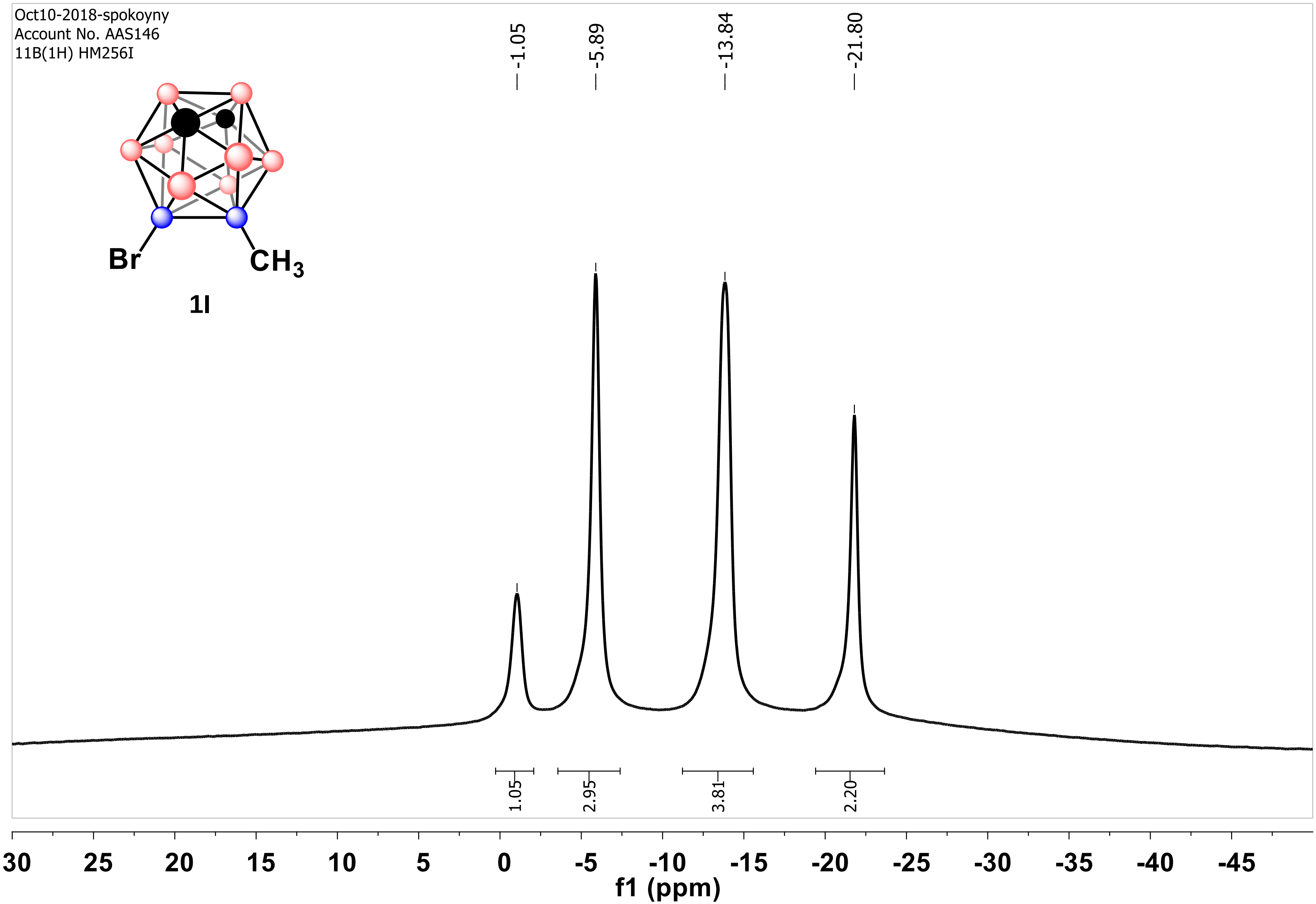
Sep30-2018-spokoyny
Account No. AAS146
1H HM256I

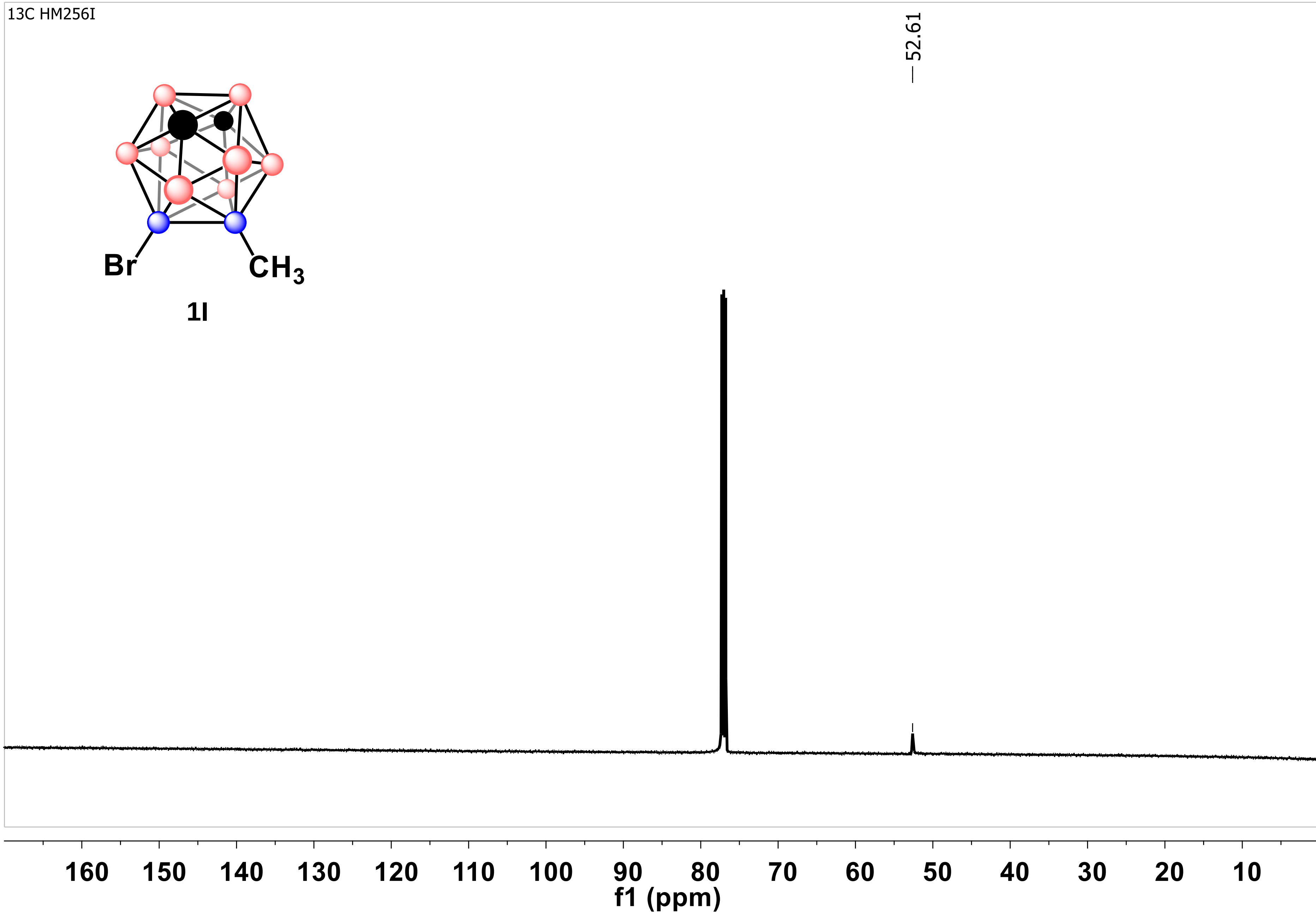


1l

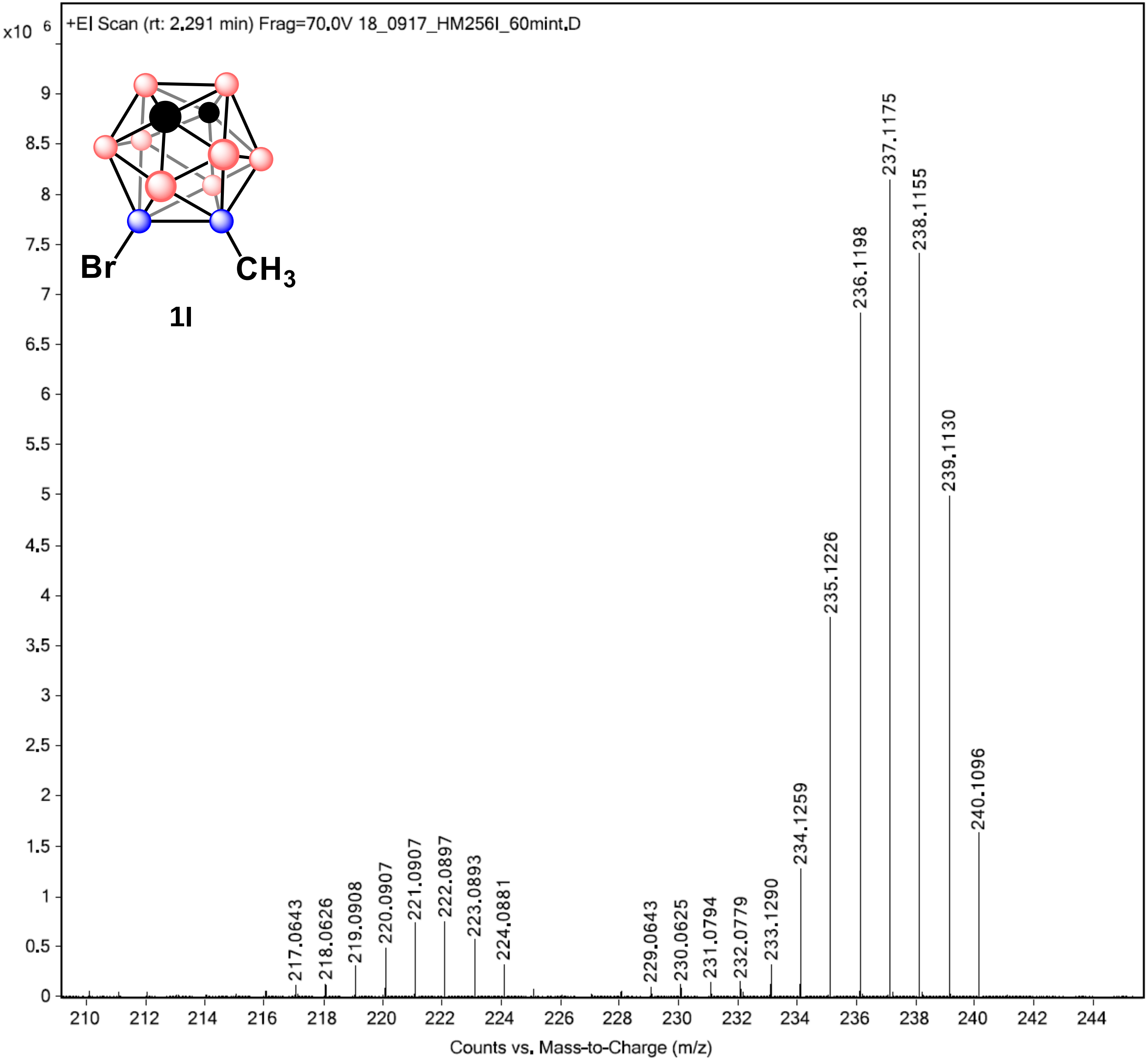


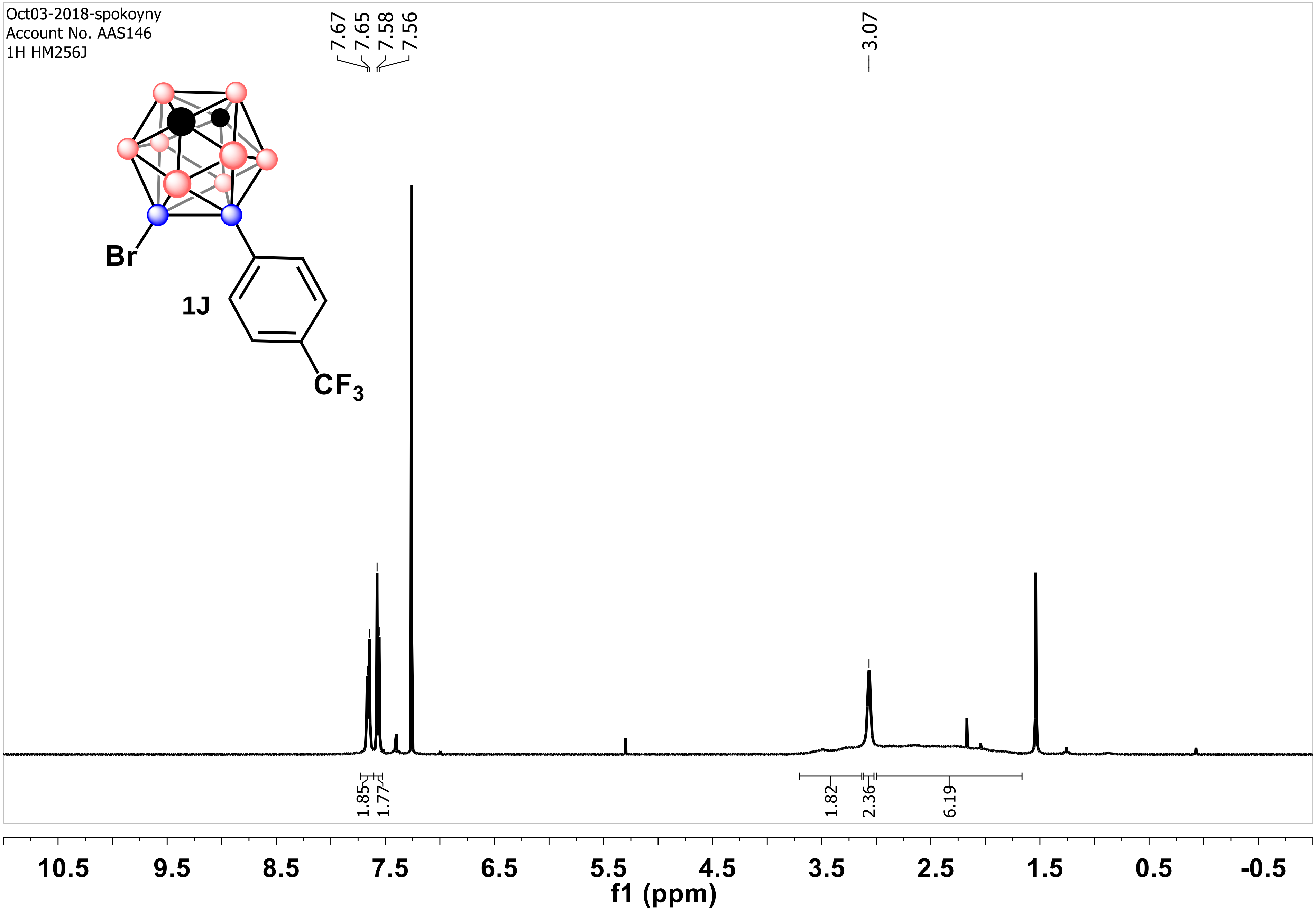

Sep30-2018-spokoyny
Account No. AAS146
11B HM256I
Br
CH3
1l
-1.05
-5.30
-6.35
-13.26
-14.52
-21.09
-22.50
1.22
3.06
3.71
2.01
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)


Oct10-2018-spokoyny
Account No. AAS146
11B(1H) HM256I
Br
CH3
1l
-1.05
-5.89
-13.84
-21.80
1.05
2.95
3.81
2.20
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

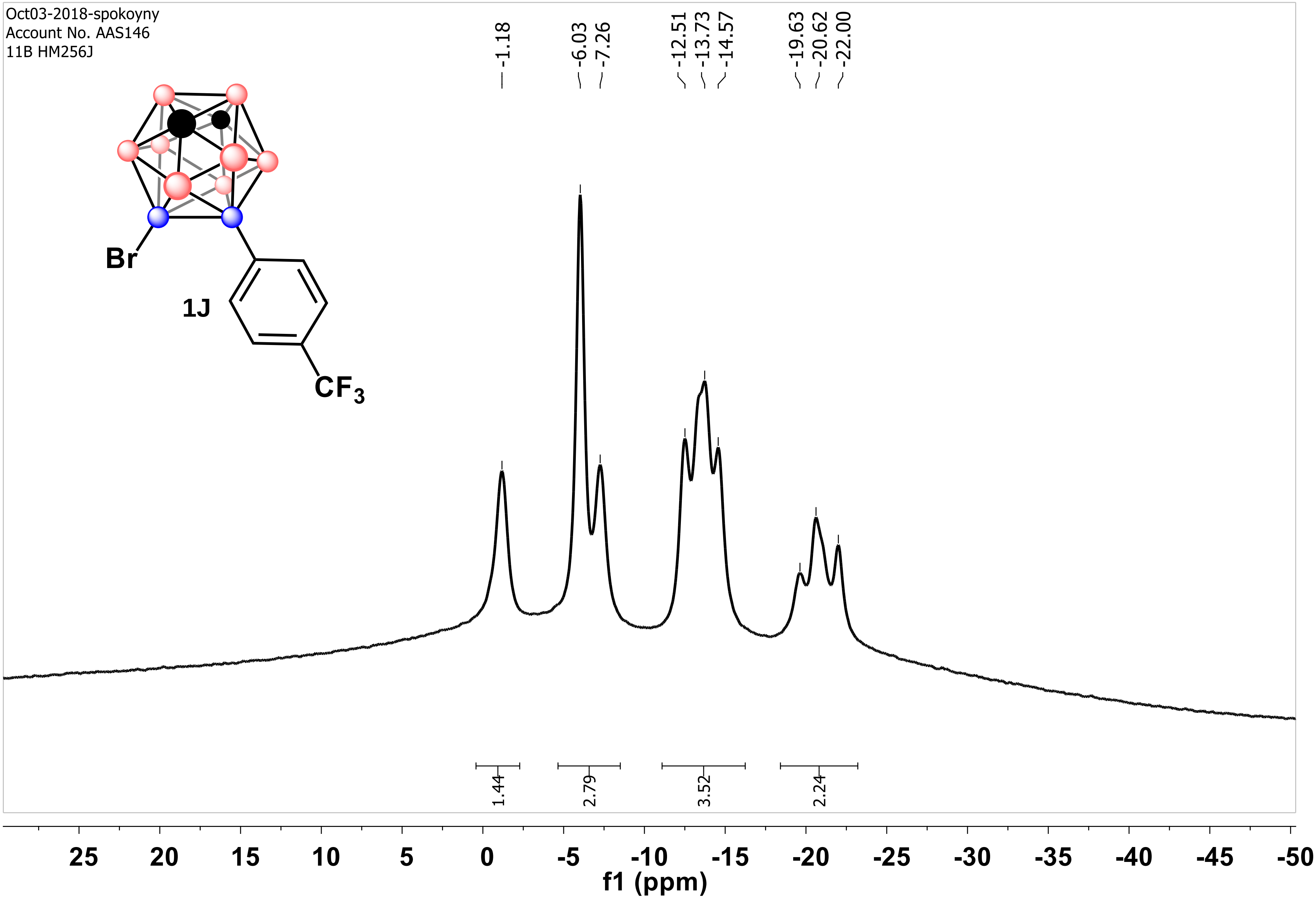

13C HM256I
52.61
Br
CH3
1l
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

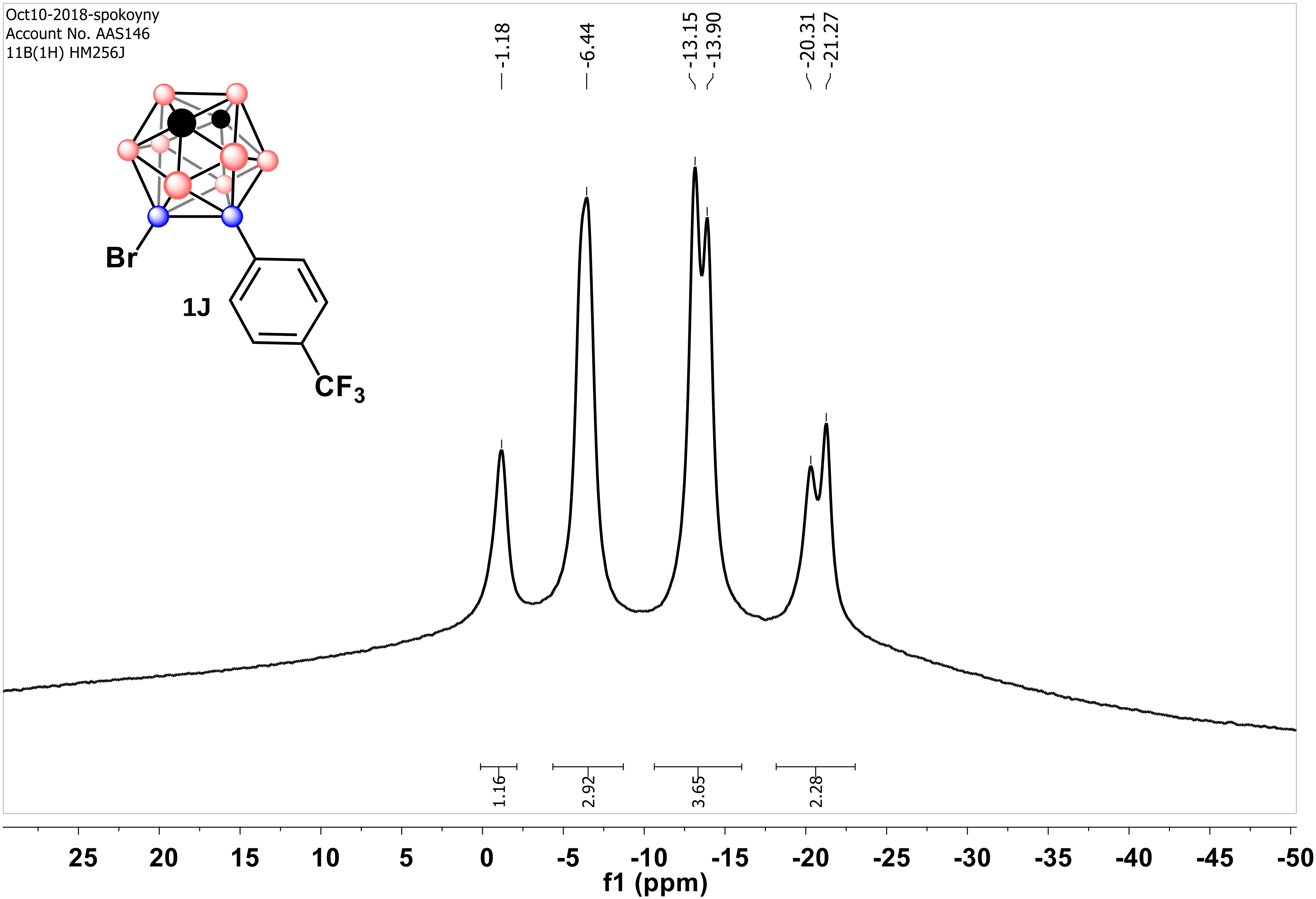
Mills_Generic_Carboranes_7min_highEV.M **Comment** **Acquired Time** 9/17/2018 12:30:38 PM (UTC-07:00)

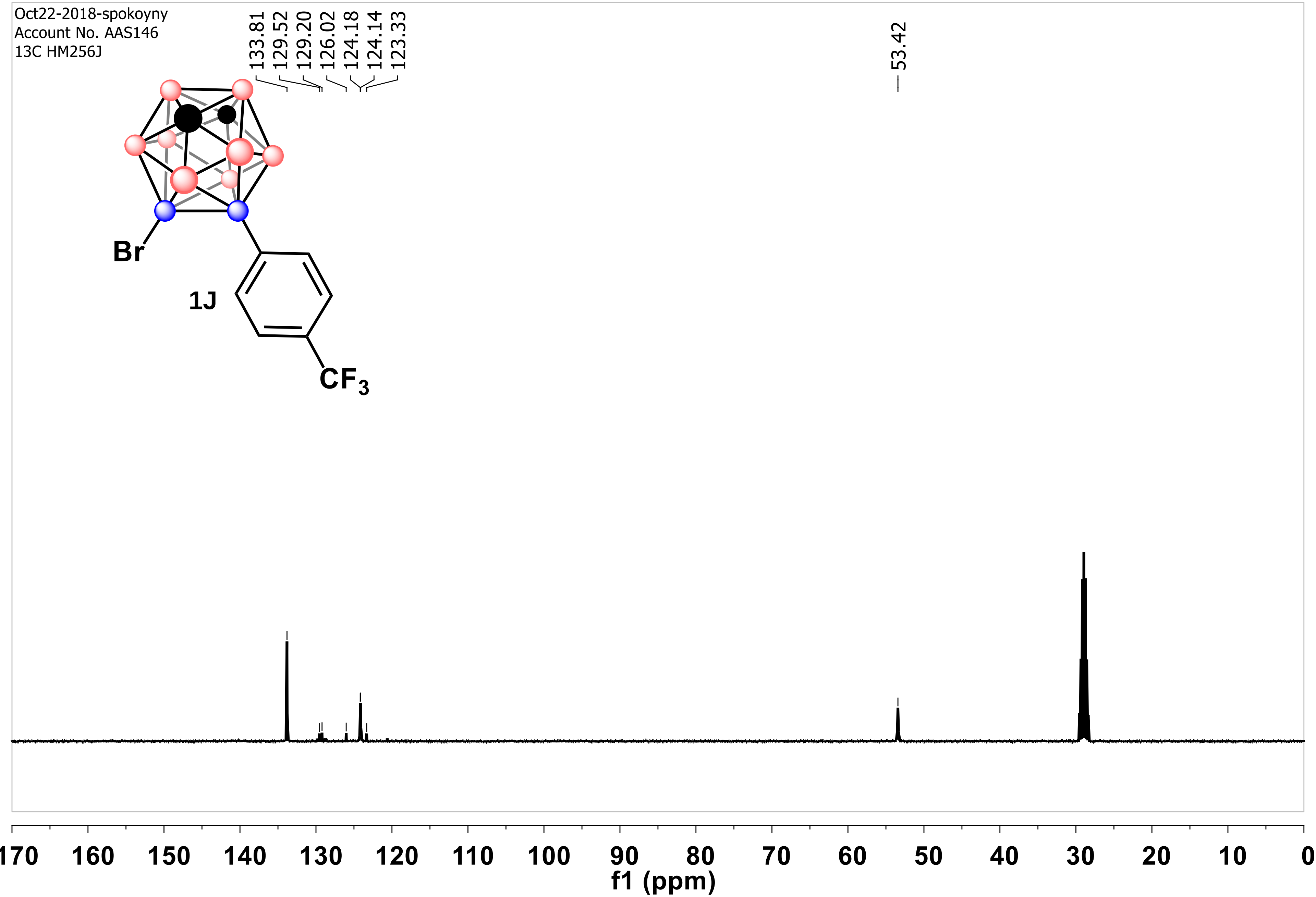




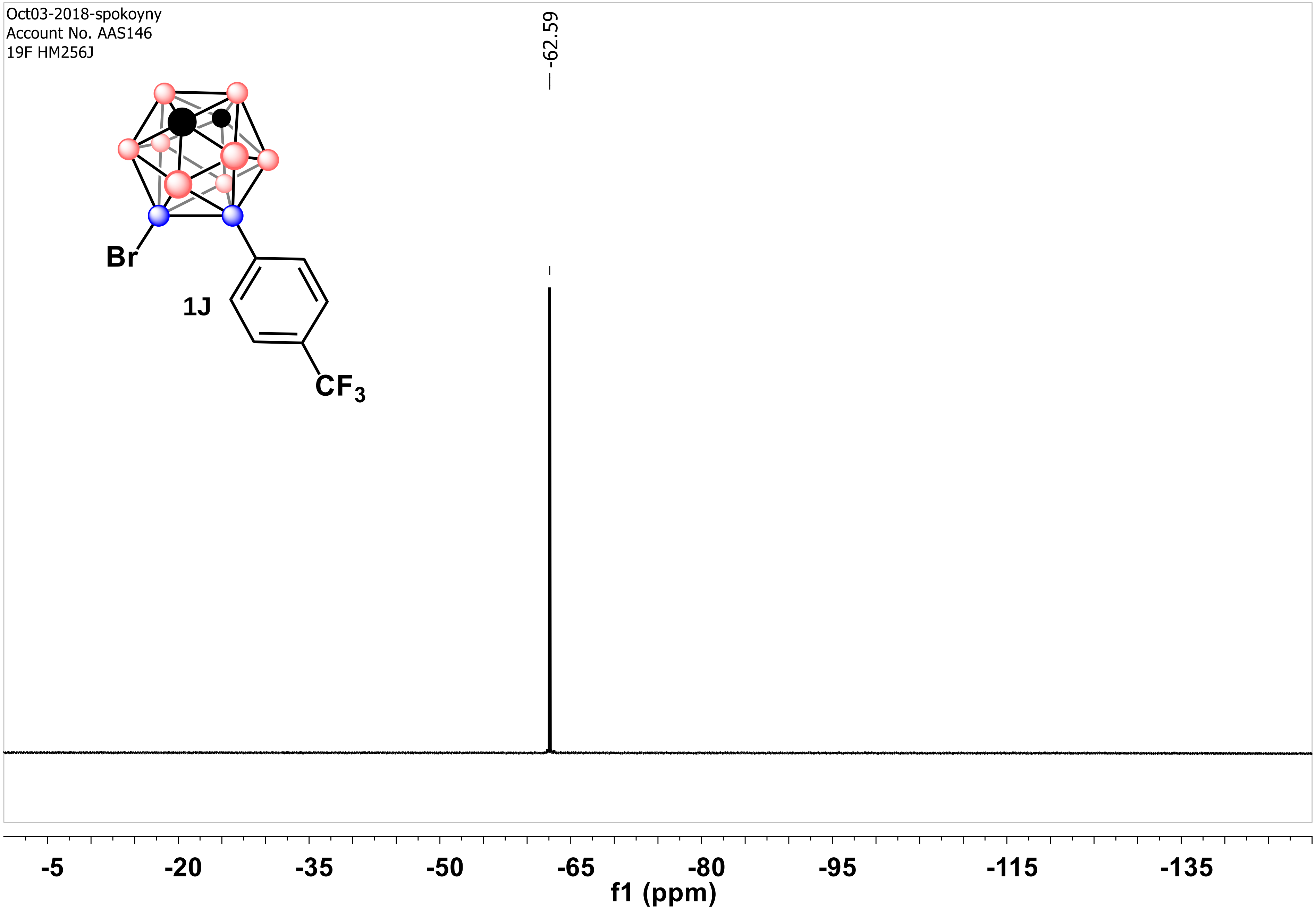
Oct03-2018-spokoyny
Account No. AAS146
1H HM256J
7.67
7.65
7.58
7.56
3.07
Br
1J
CF_3
1.85
1.77
1.82
2.36
6.19
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


Oct03-2018-spokoyny
Account No. AAS146
11B HM256J
-1.18
-6.03
-7.26
-12.51
-13.73
-14.57
-19.63
-20.62
-22.00
Br
1J
CF3
1.44
2.79
3.52
2.24
25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

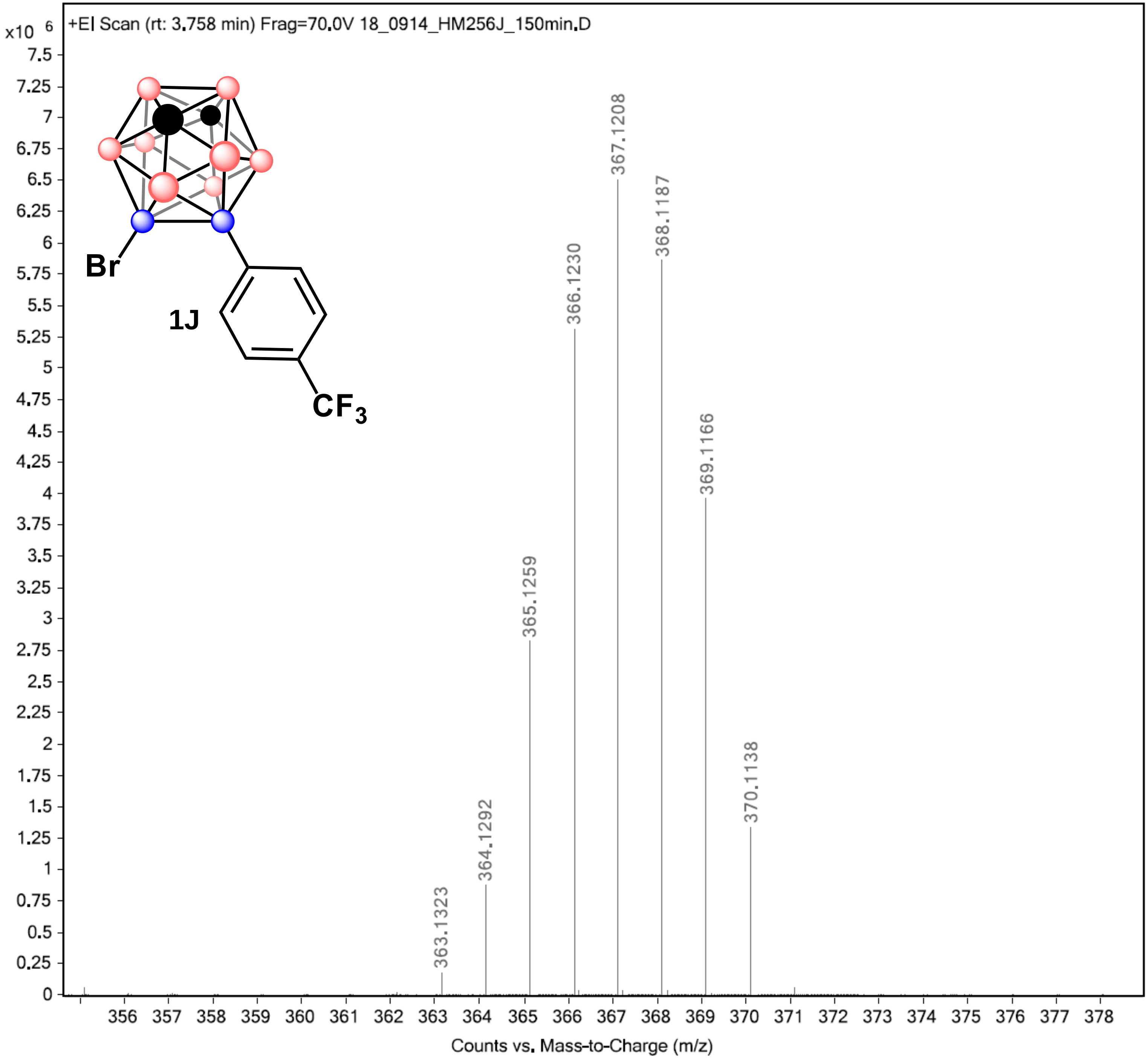

Oct10-2018-spokoyny
Account No. AAS146
11B(1H) HM256J
Br
1J
CF3
-1.18
-6.44
-13.15
-13.90
-20.31
-21.27
1.16
2.92
3.65
2.28
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

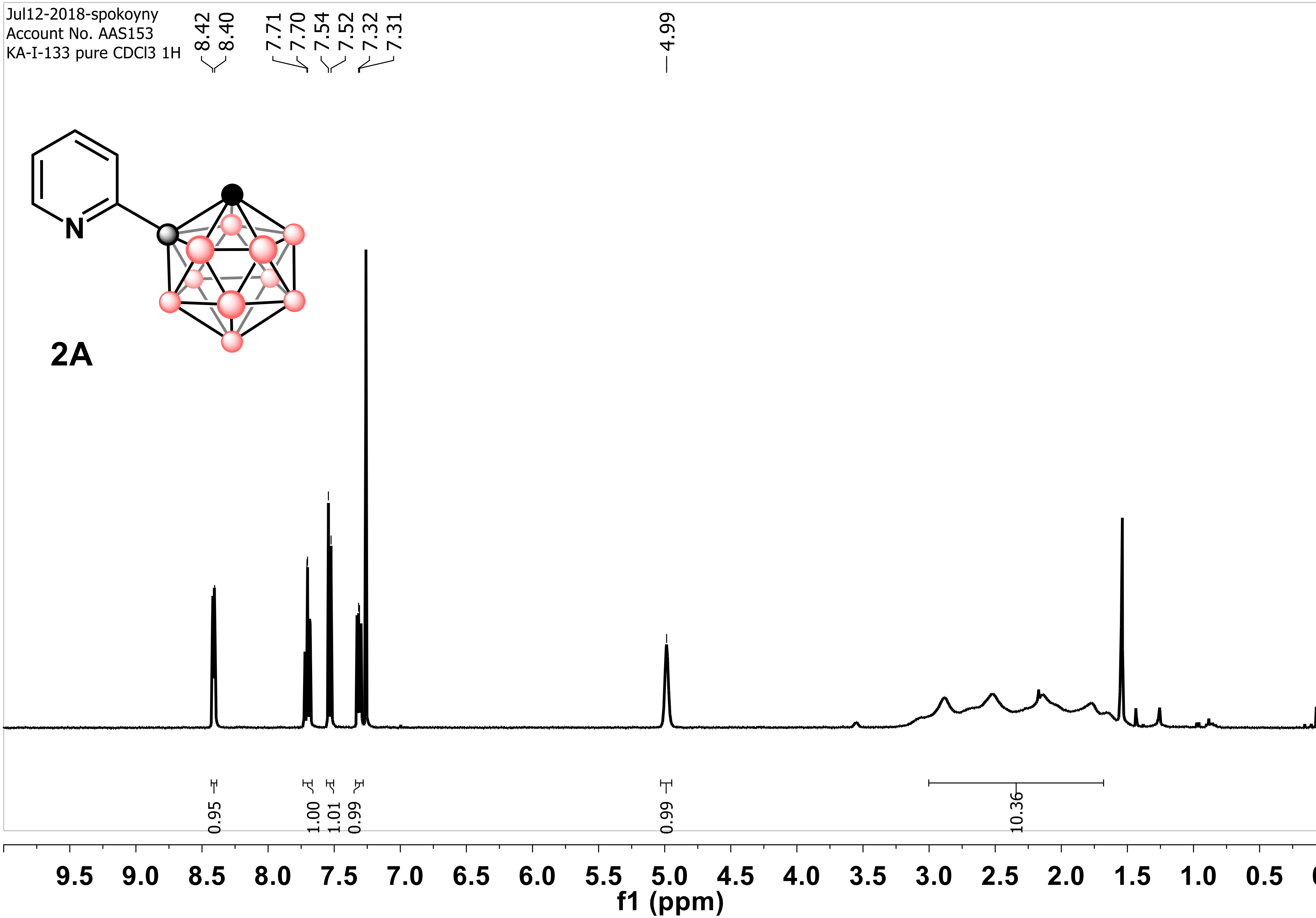


Oct22-2018-spokoyny
Account No. AAS146
13C HM256J
133.81
129.52
129.20
126.02
124.18
124.14
123.33
53.42
Br
1J
CF3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

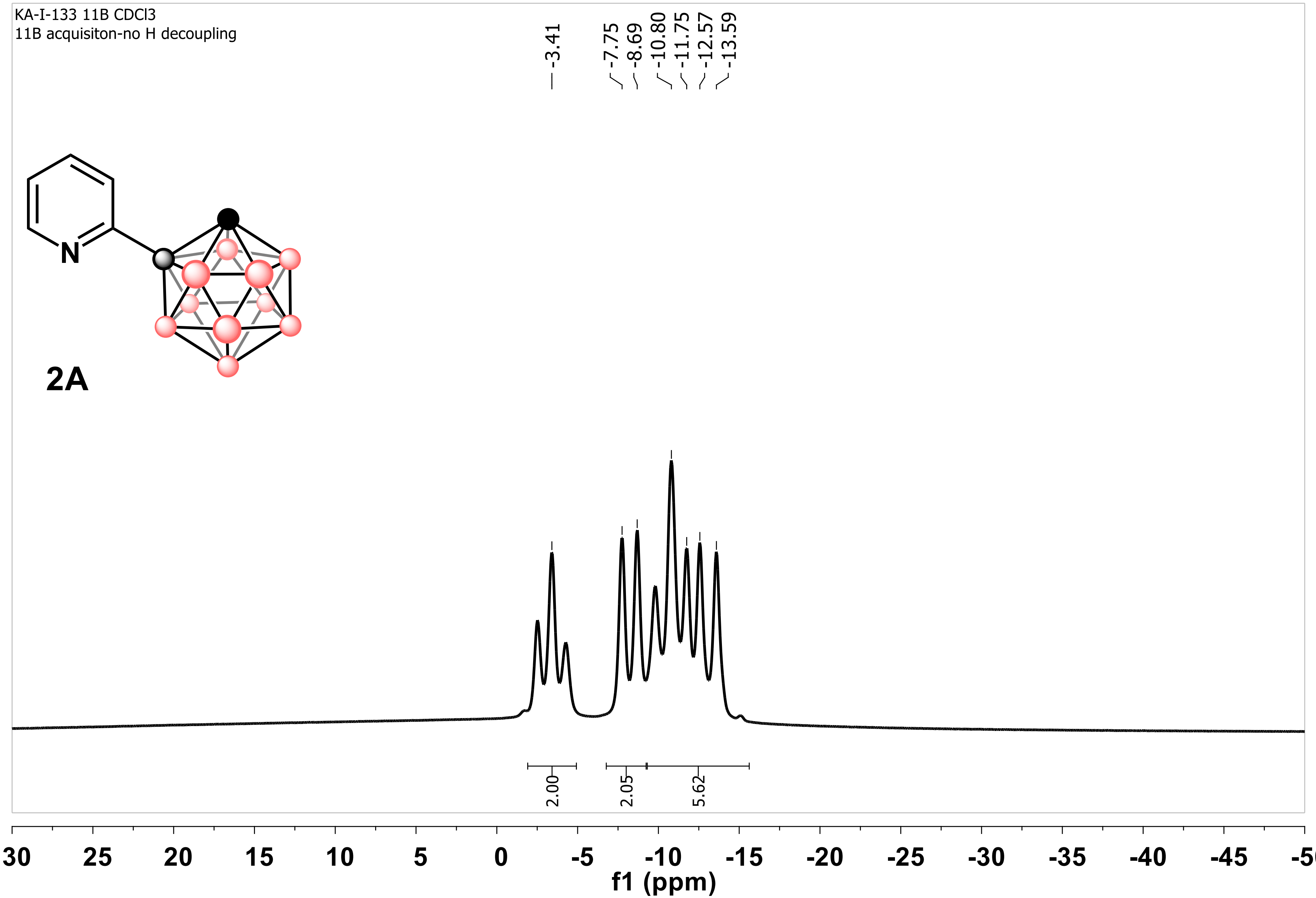

Oct03-2018-spokoyny
Account No. AAS146
19F HM256J
-62.59
Br
1J
CF3
-5
-20
-35
-50
-65
-80
-95
-115
-135
f1 (ppm)

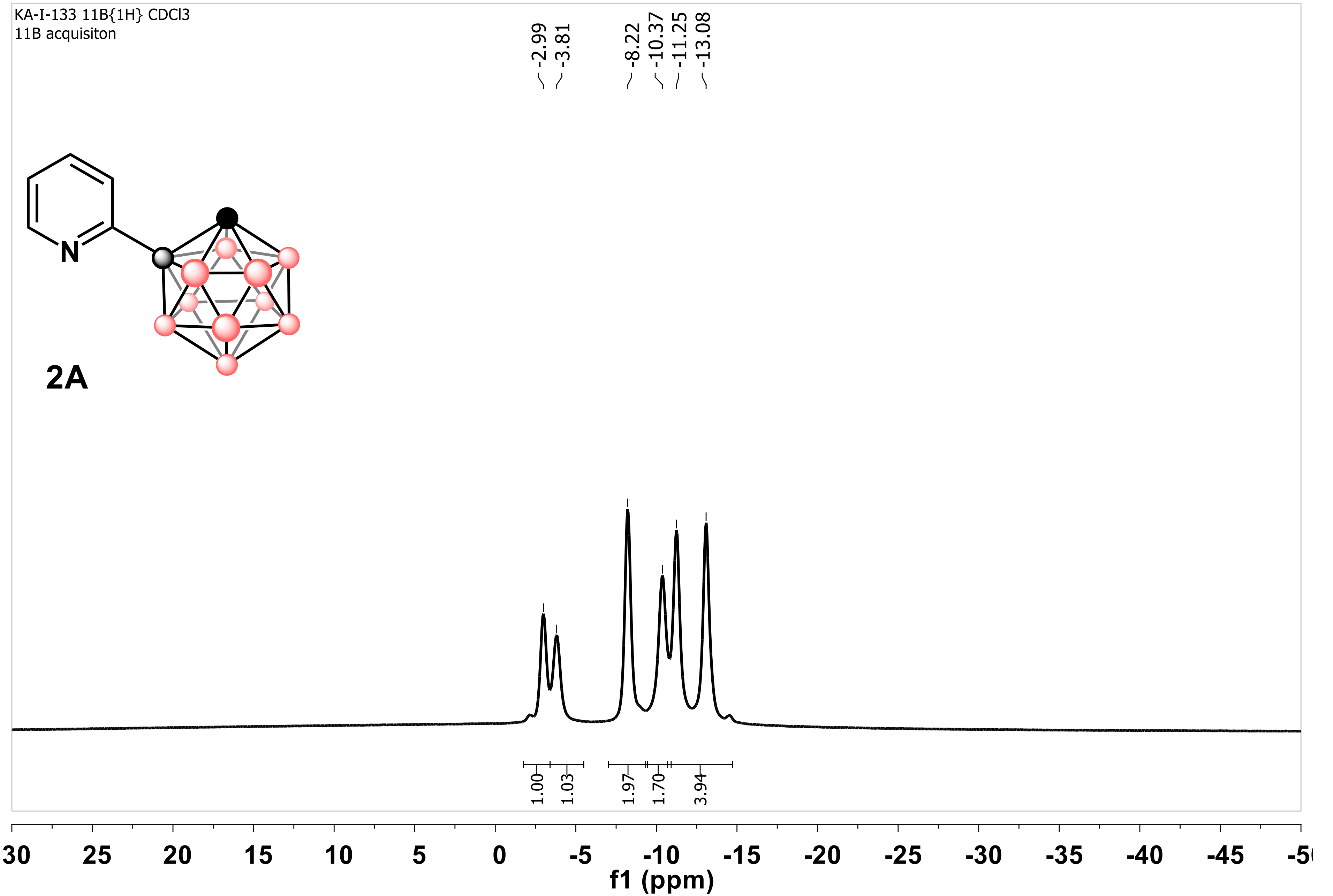
Mills_Generic_Carboranes_7min_highEV.M Comment Acquired Time 9/14/2018 7:02:35 PM (UTC-07:00)

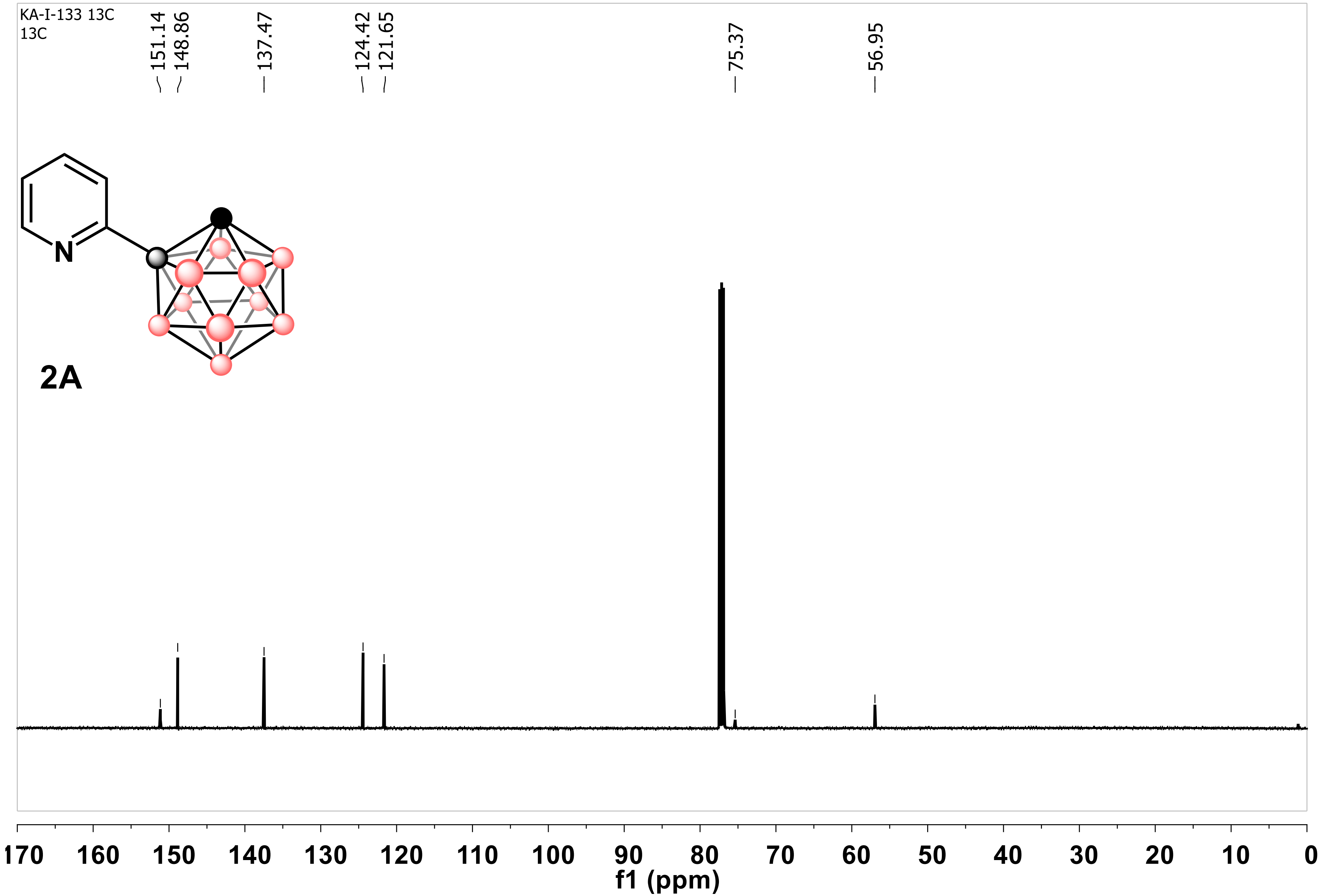


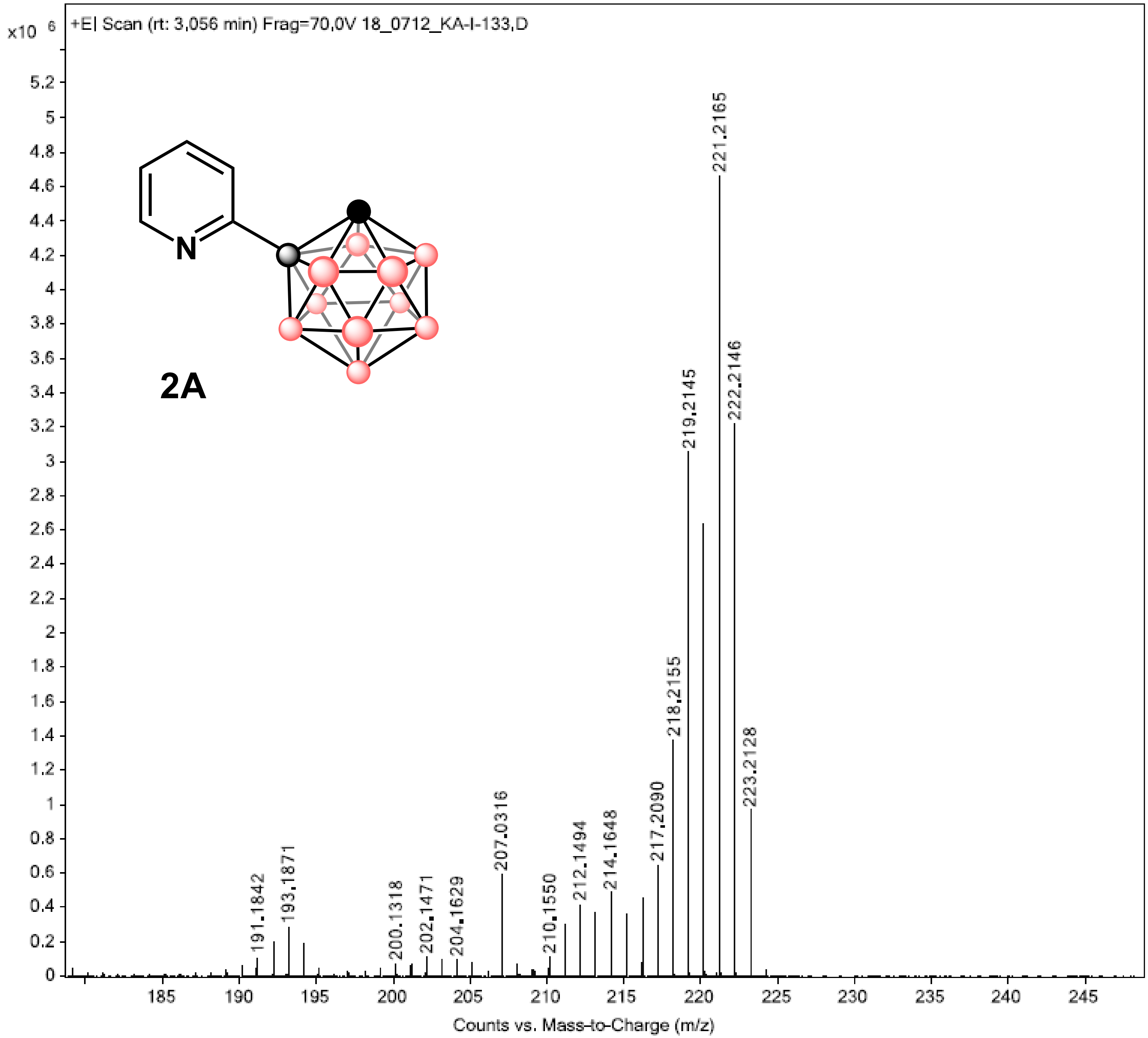


Jul12-2018-spokoyny
Account No. AAS153
KA-I-133 pure CDCl3 1H
8.42
8.40
7.71
7.70
7.54
7.52
7.32
7.31
4.99
N
2A
0.95
1.00
1.01
0.99
0.99
10.36
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

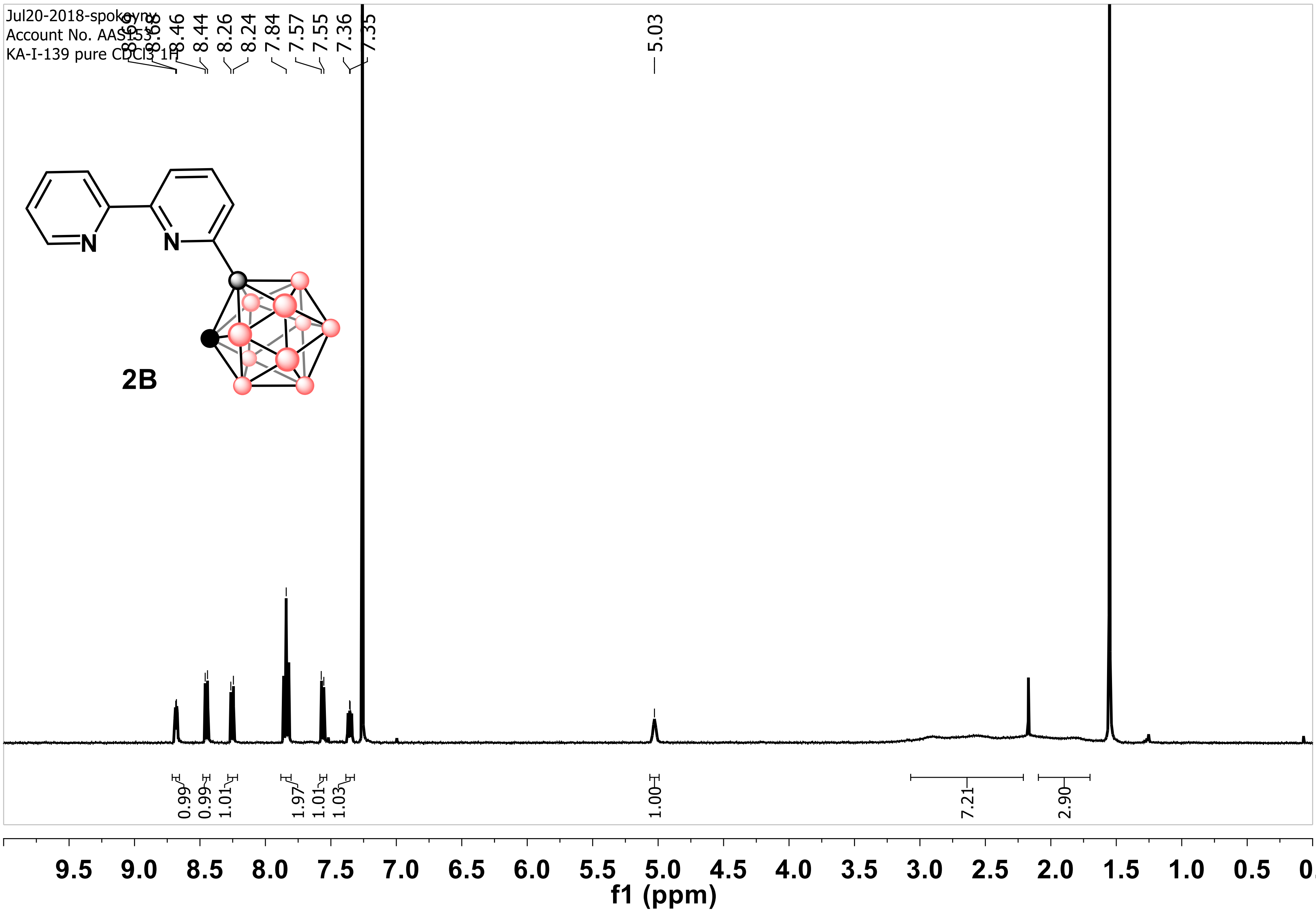

KA-I-133 11B CDCl3
11B acquisiton-no H decoupling
-3.41
-7.75
-8.69
-10.80
-11.75
-12.57
-13.59
N
2A
2.00
2.05
5.62
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

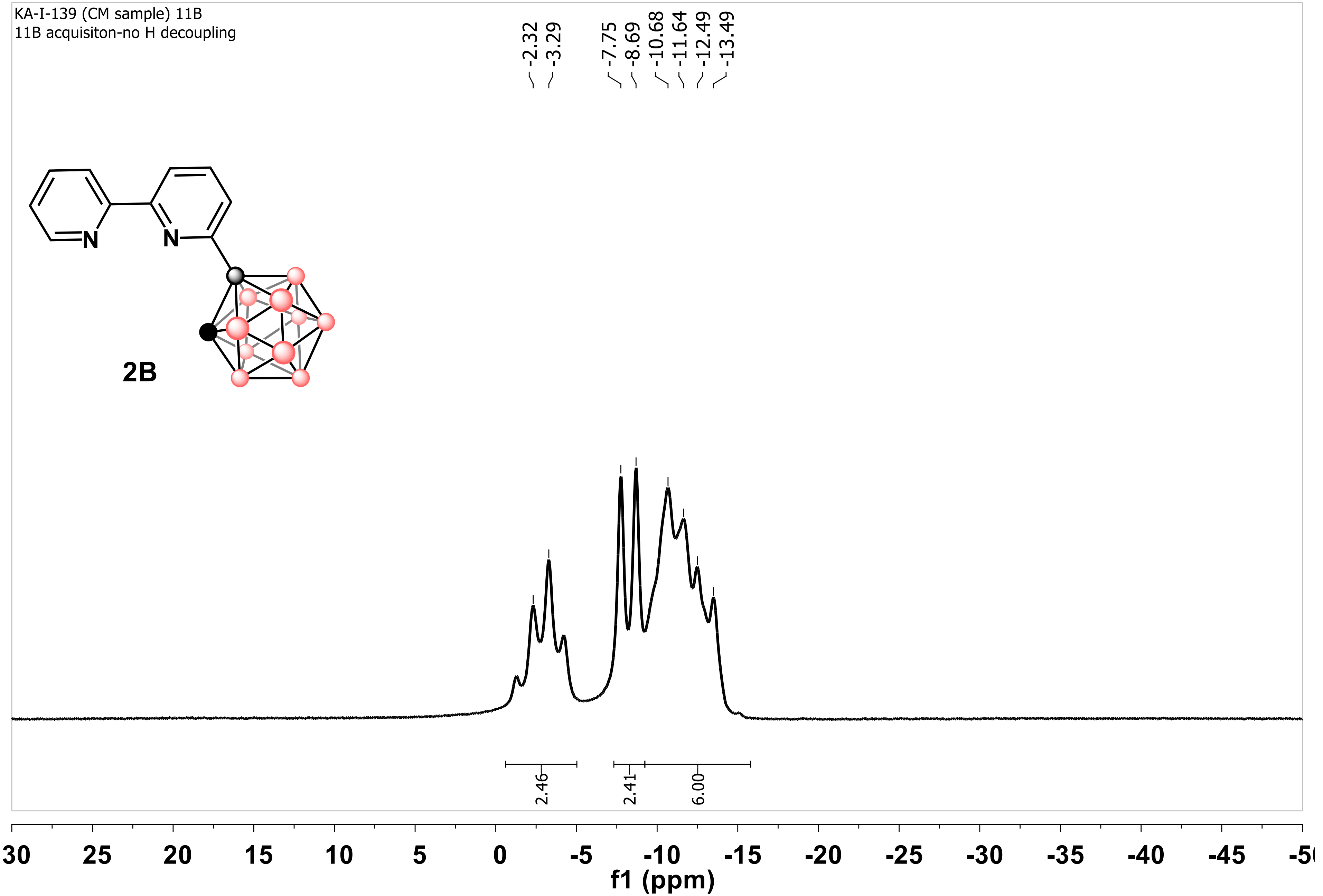

KA-I-133 11B{1H} CDCl3
11B acquisiton
-2.99
-3.81
-8.22
-10.37
-11.25
-13.08
N
2A
1.00
1.03
1.97
1.70
3.94
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

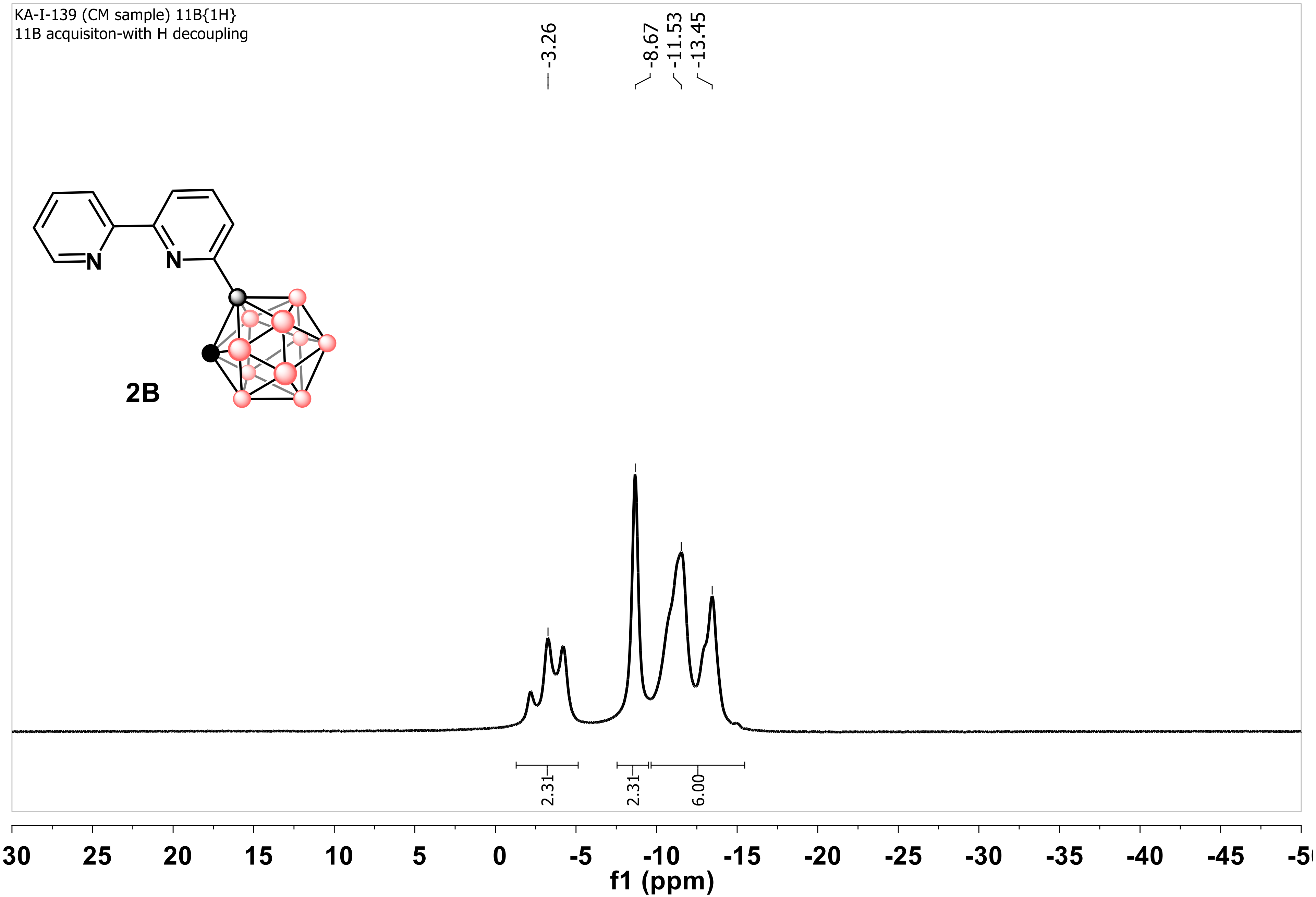

KA-I-133 13C
13C
151.14
148.86
137.47
124.42
121.65
75.37
56.95
N
2A
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

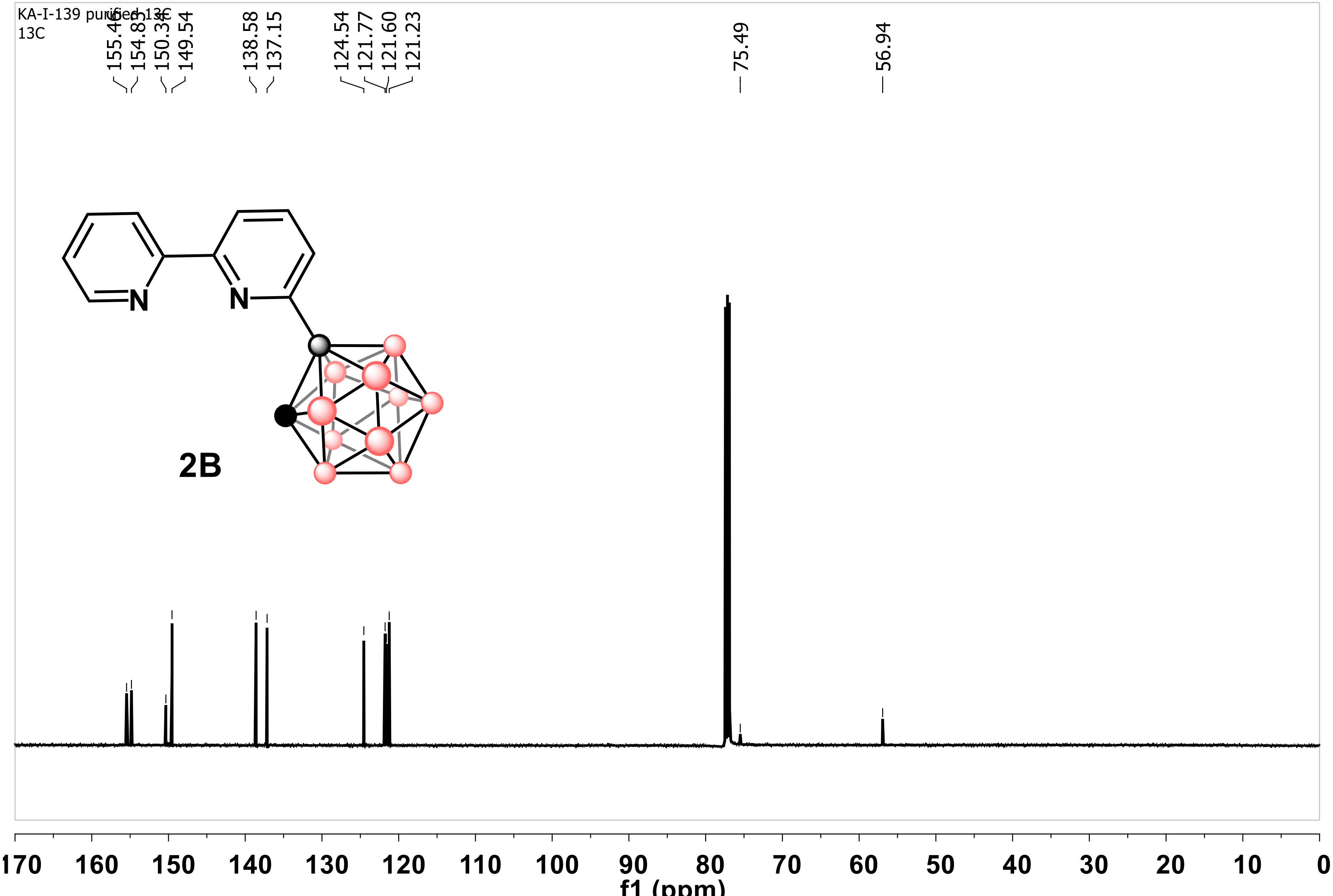


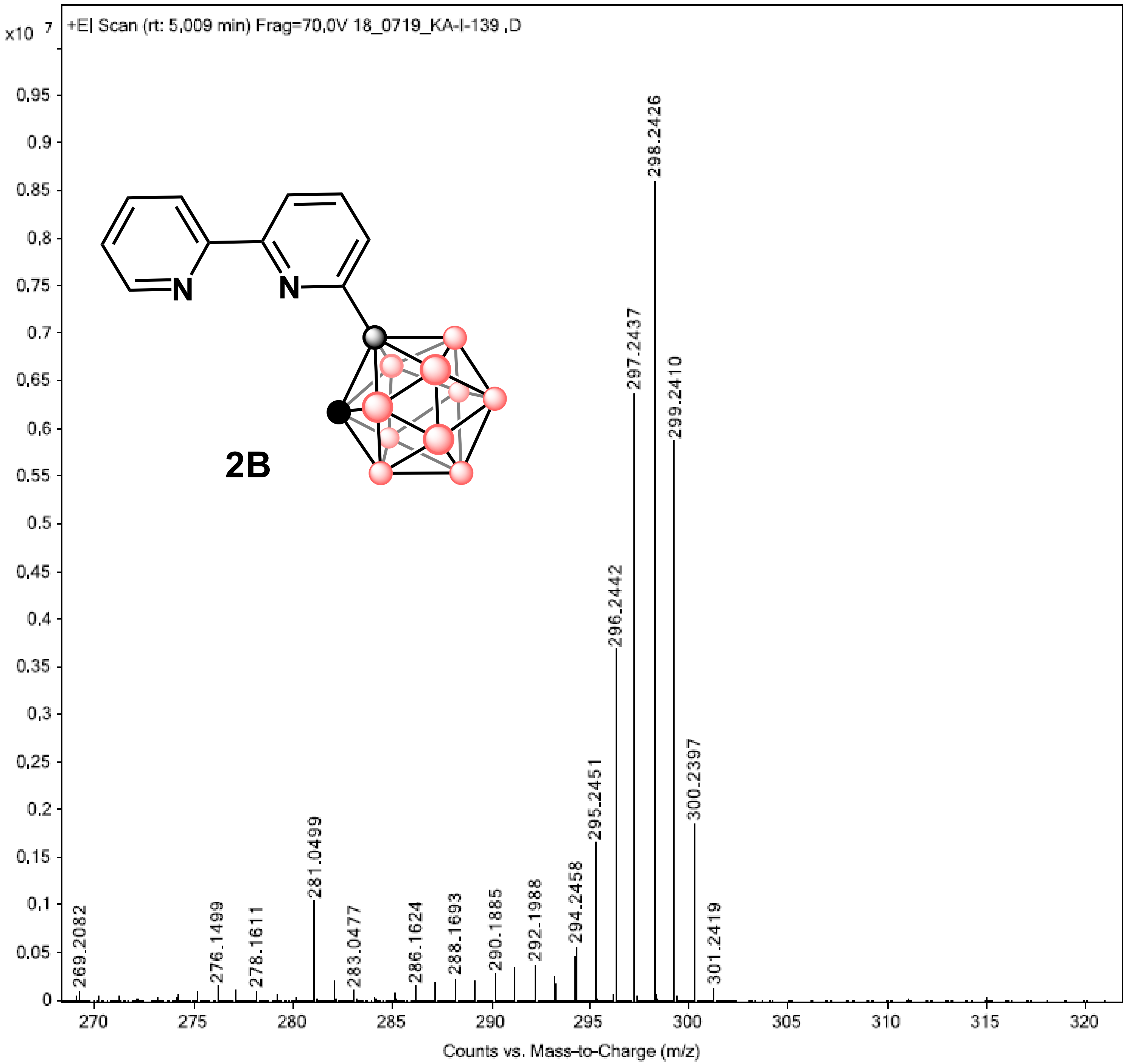
+EI Scan (rt: 3,056 min) Frag=70,0V 18_0712_KA-I-133,D
x10 6
N
2A
221.2165
222.2146
219.2145
218.2155
223.2128
217.2090
214.1648
212.1494
210.1550
207.0316
204.1629
202.1471
200.1318
193.1871
191.1842
Counts vs. Mass-to-Charge (m/z)

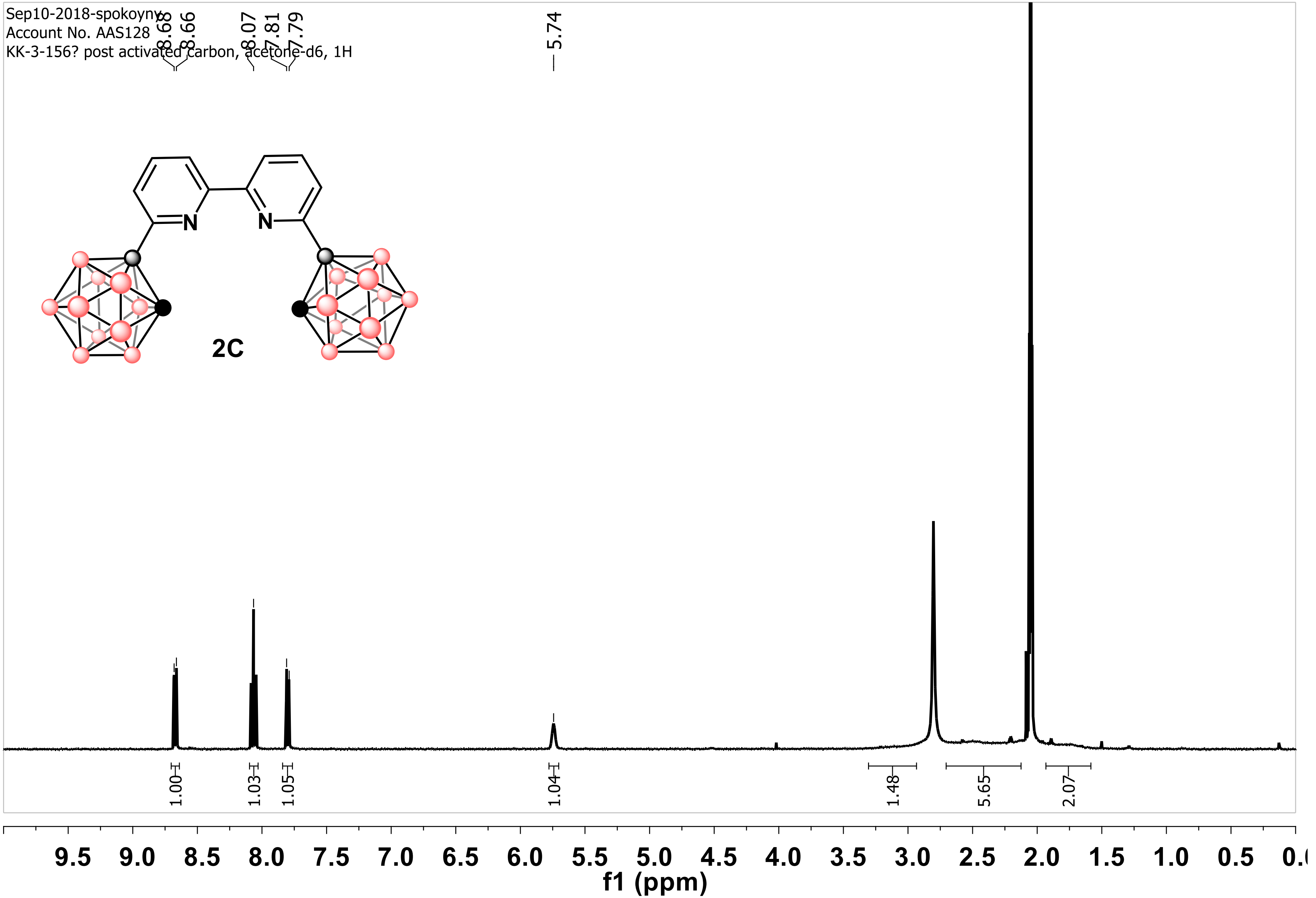

Jul20-2018-spokoyny
Account No. AAS153
KA-I-139 pure CDCl3 1H
8.46
8.44
8.26
8.24
7.84
7.57
7.55
7.36
7.35
5.03
N
N
2B
0.99
0.99
1.01
1.97
1.01
1.03
1.00
7.21
2.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


KA-I-139 (CM sample) 11B
11B acquisiton-no H decoupling
-2.32
-3.29
-7.75
-8.69
-10.68
-11.64
-12.49
-13.49
N
N
2B
2.46
2.41
6.00
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

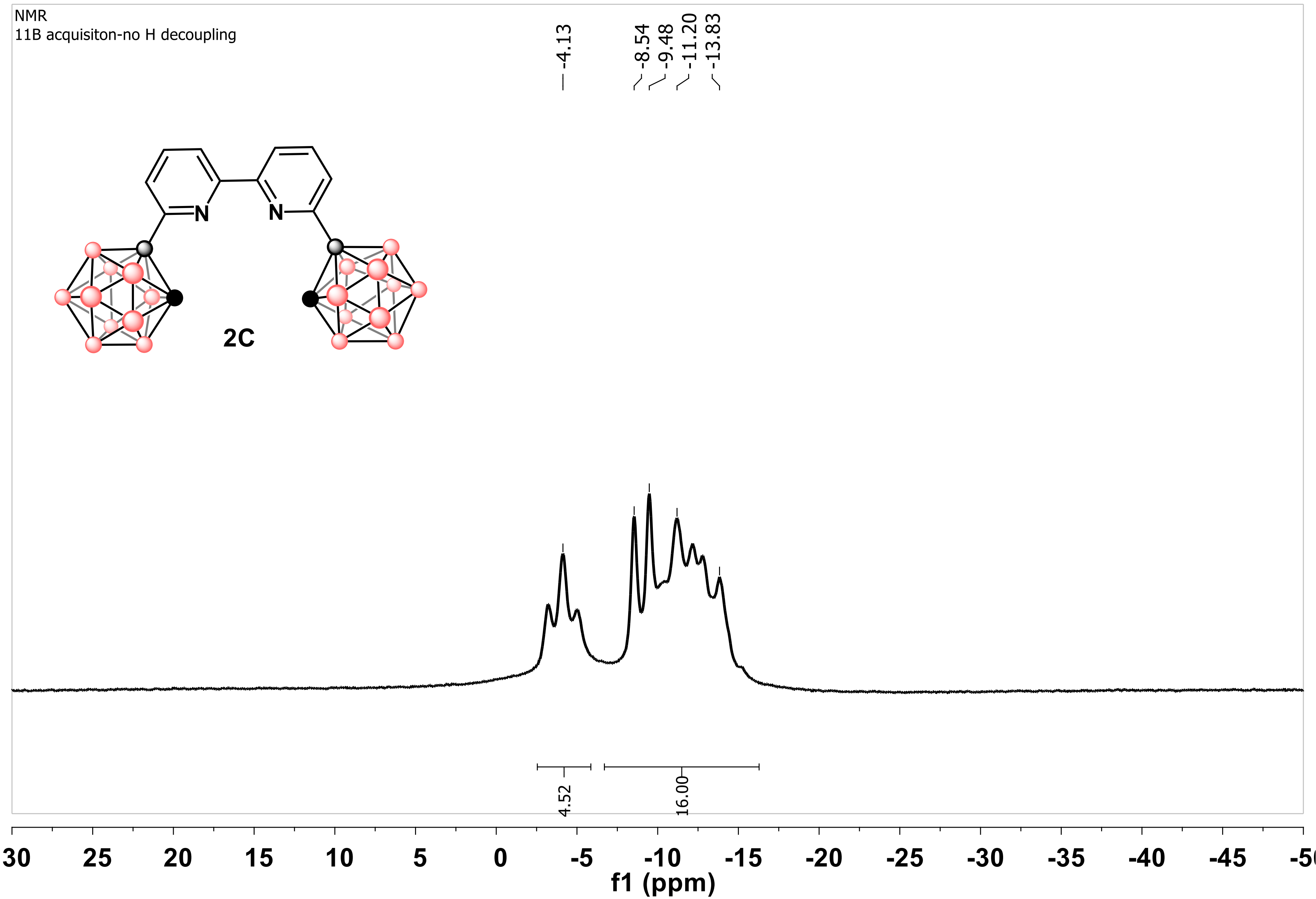

KA-I-139 (CM sample) 11B{1H}
11B acquisiton-with H decoupling
-3.26
-8.67
-11.53
-13.45
N
N
2B
2.31
2.31
6.00
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

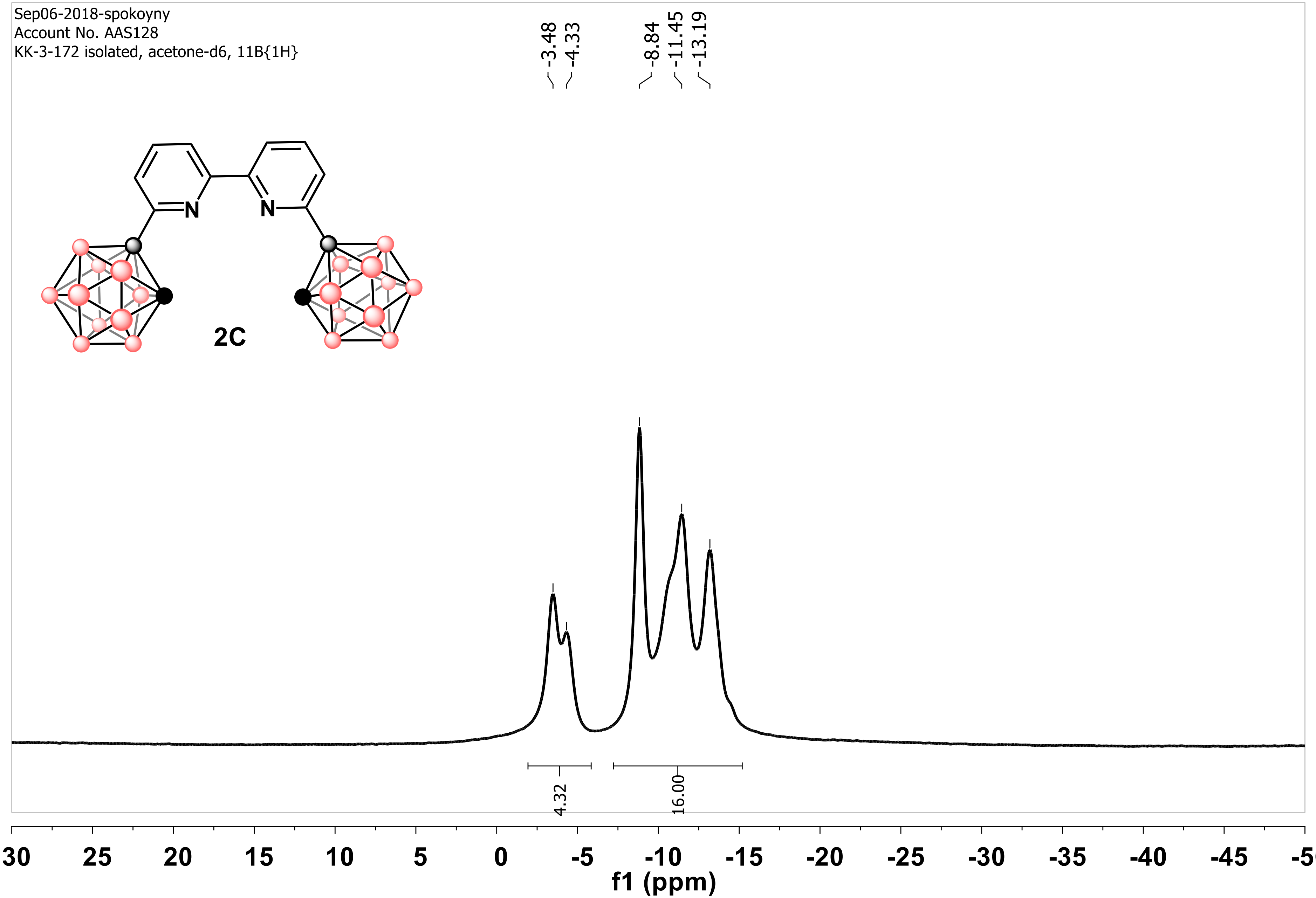

KA-I-139 purified 13C
13C
155.46
154.83
150.34
149.54
138.58
137.15
124.54
121.77
121.60
121.23
75.49
56.94
N
N
2B
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


+EI Scan (rt: 5,009 min) Frag=70,0V 18_0719_KA-I-139 ,D
x10 7
0,95
0,9
0,85
0,8
0,75
0,7
0,65
0,6
0,55
0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
N
N
2B
298.2426
297.2437
299.2410
296.2442
295.2451
300.2397
281.0499
294.2458
292.1988
290.1885
288.1693
286.1624
283.0477
278.1611
276.1499
269.2082
301.2419
270
275
280
285
290
295
300
305
310
315
320
Counts vs. Mass-to-Charge (m/z)

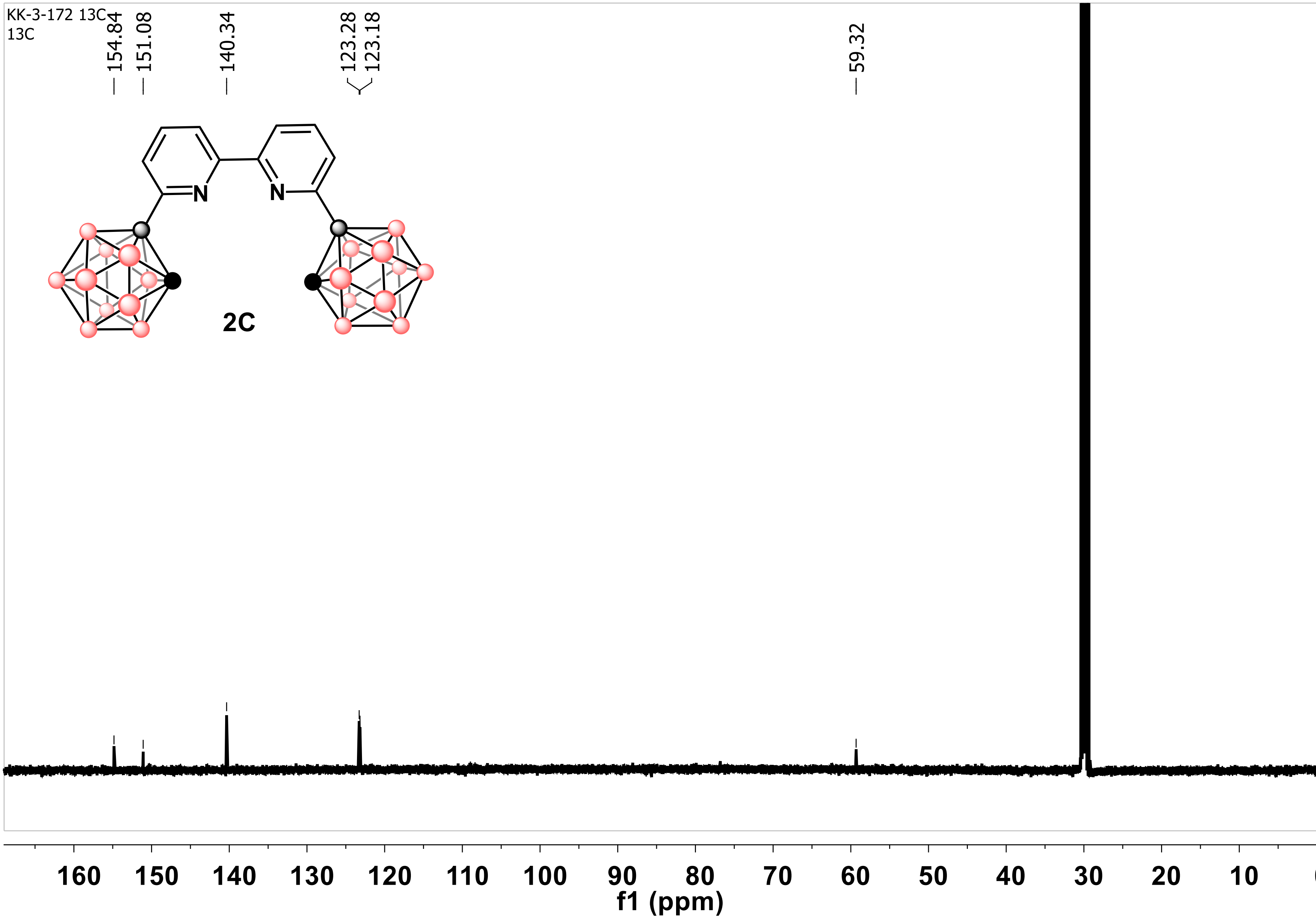


Sep10-2018-spokoyny
Account No. AAS128
KK-3-156? post activated carbon, acetone-d6, 1H
8.68
8.66
8.07
7.81
7.79
5.74
N
N
2C
1.00
1.03
1.05
1.04
1.48
5.65
2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

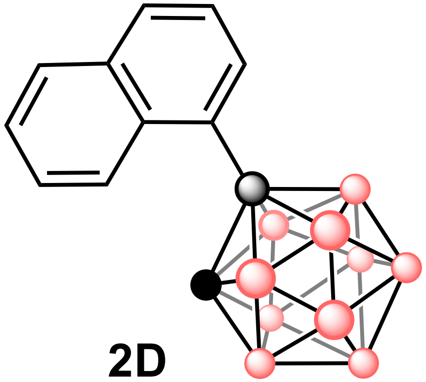

NMR
11B acquisiton-no H decoupling
-4.13
-8.54
-9.48
-11.20
-13.83
N
N
2C
4.52
16.00
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)



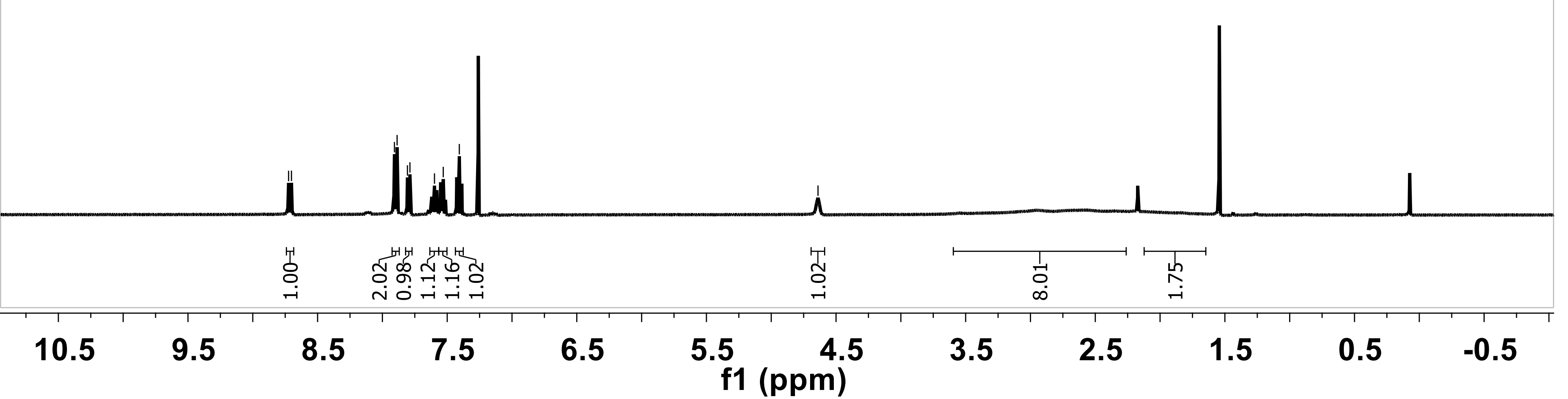
Sep06-2018-spokoyny
Account No. AAS128
KK-3-172 isolated, acetone-d6, 11B{1H}
-3.48
-4.33
-8.84
-11.45
-13.19
N
N
2C
4.32
16.00
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

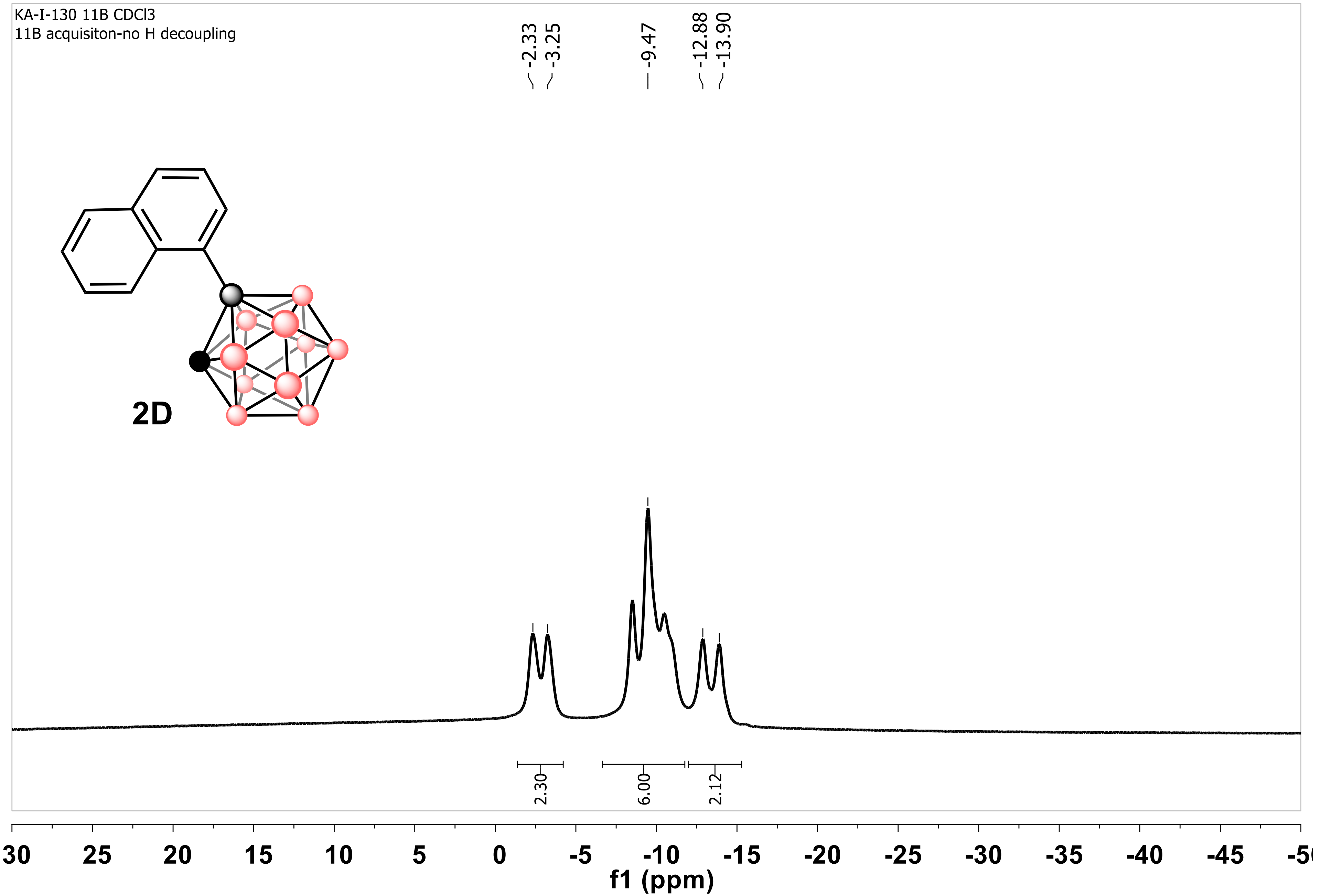

KK-3-172 13C
13C
154.84
151.08
140.34
123.28
123.18
59.32
N
N
2C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

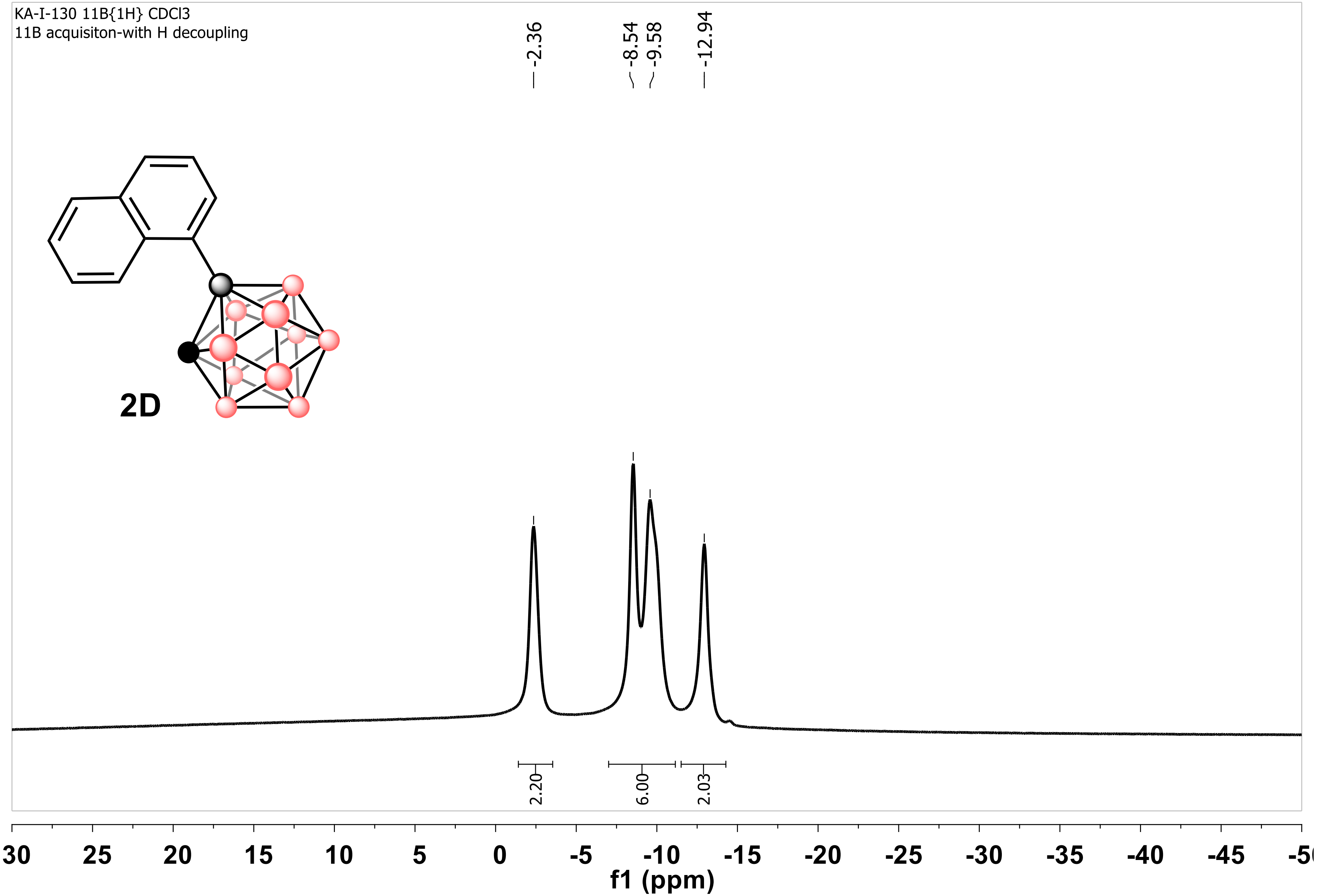
Jul10-2018-spokoyny
Account No. AAS153
KA-I-130 purified CDCl3 1H



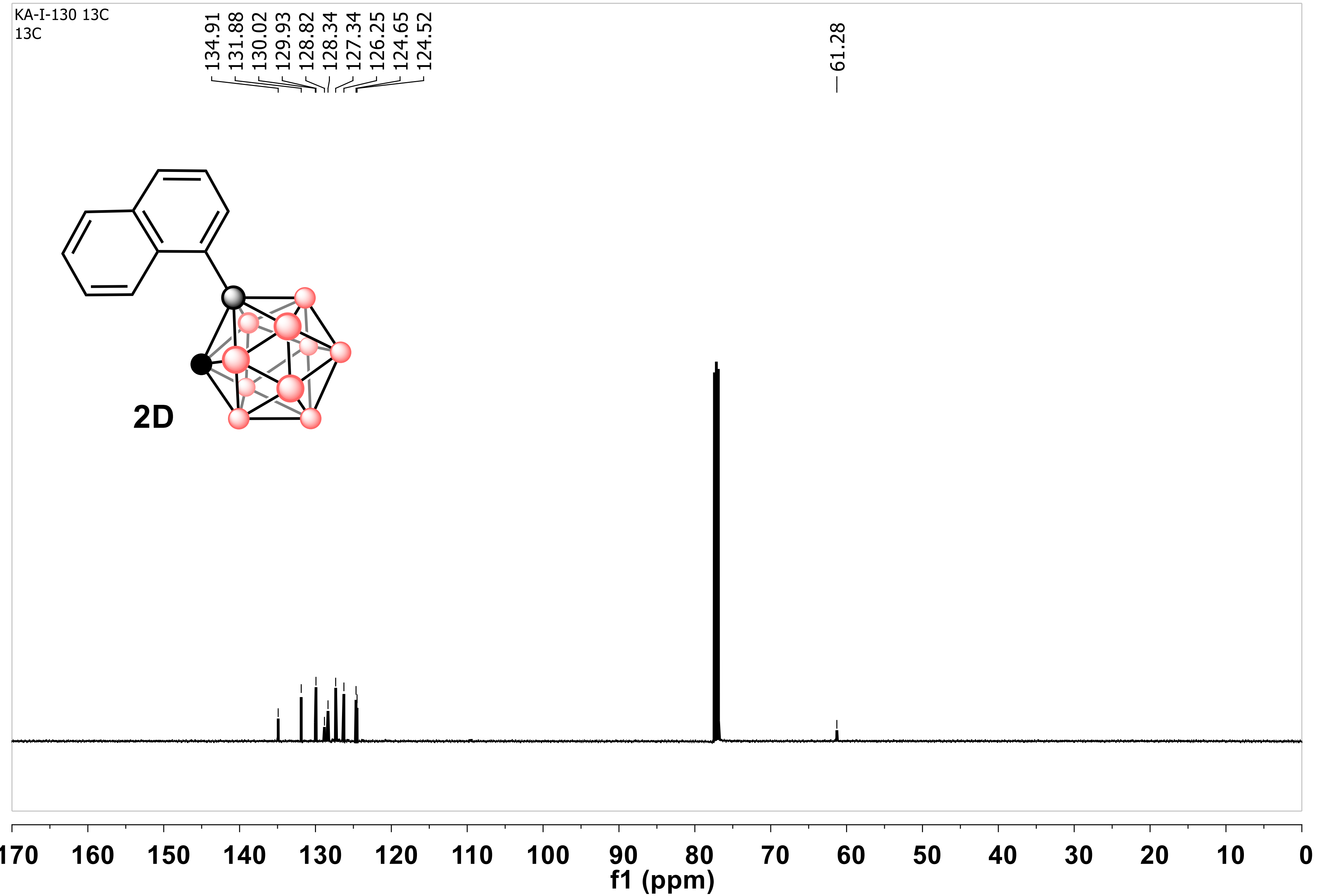
2D

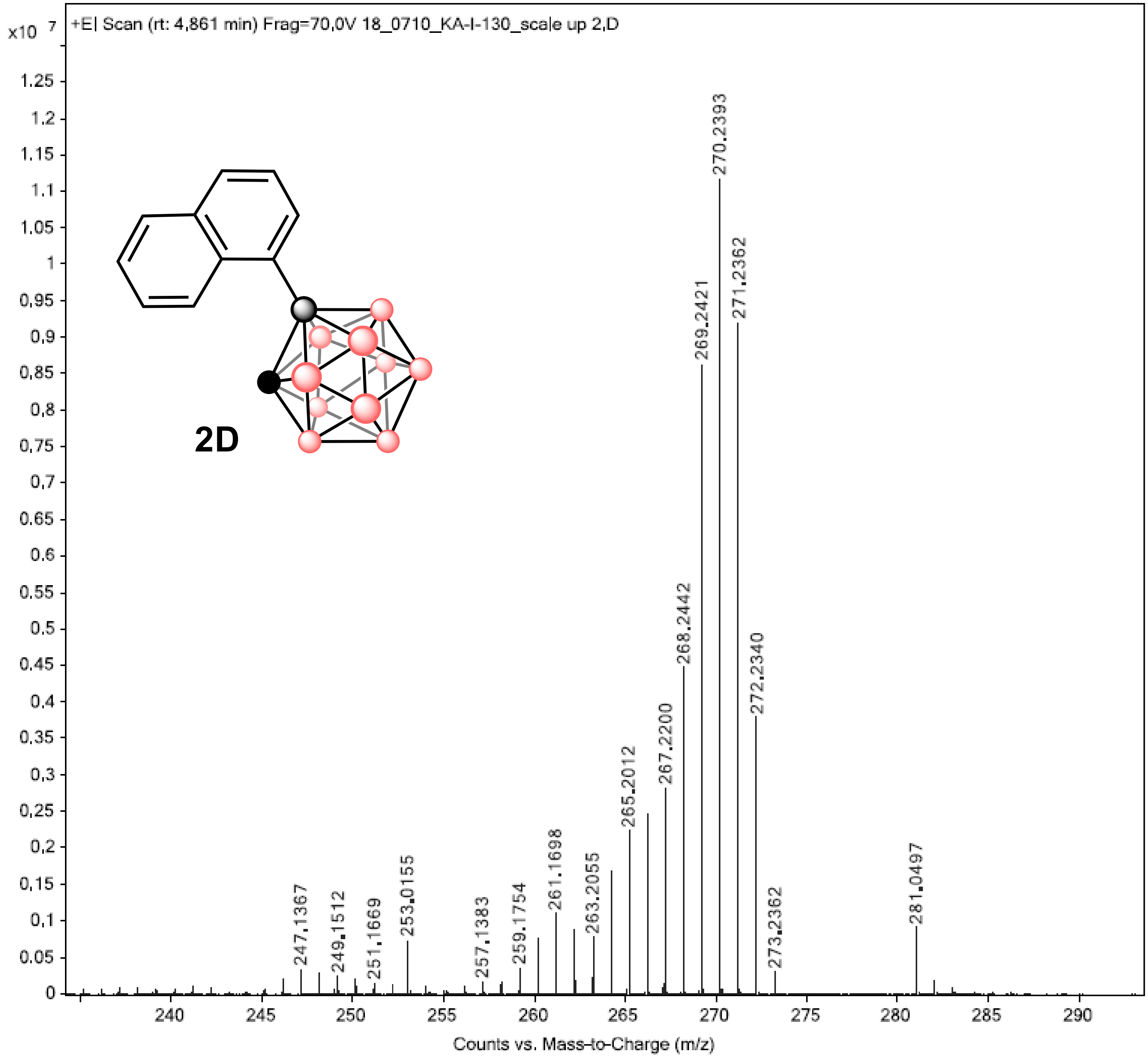



KA-I-130 11B CDCl3
11B acquisiton-no H decoupling
-2.33
-3.25
-9.47
-12.88
-13.90
2D
2.30
6.00
2.12
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

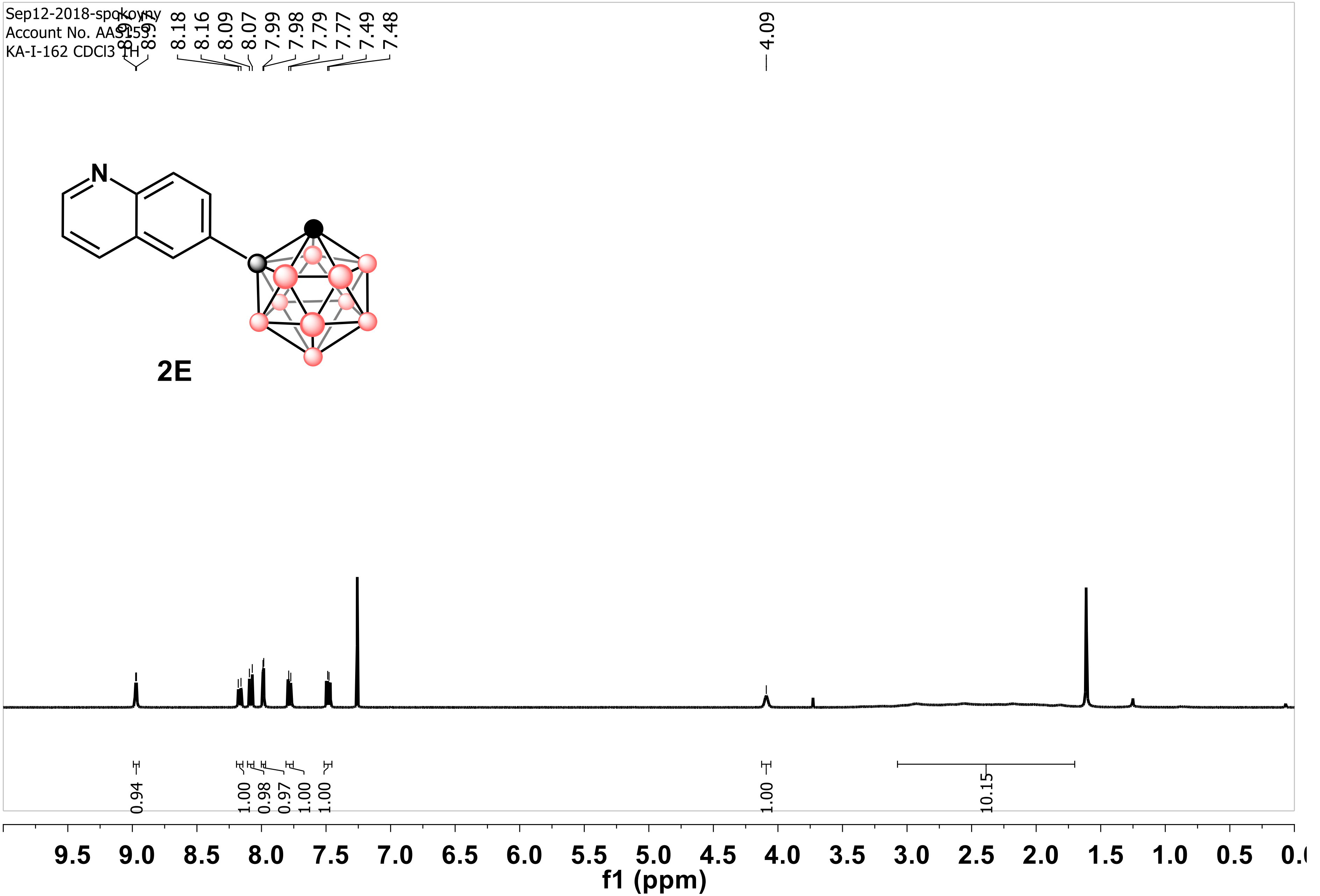


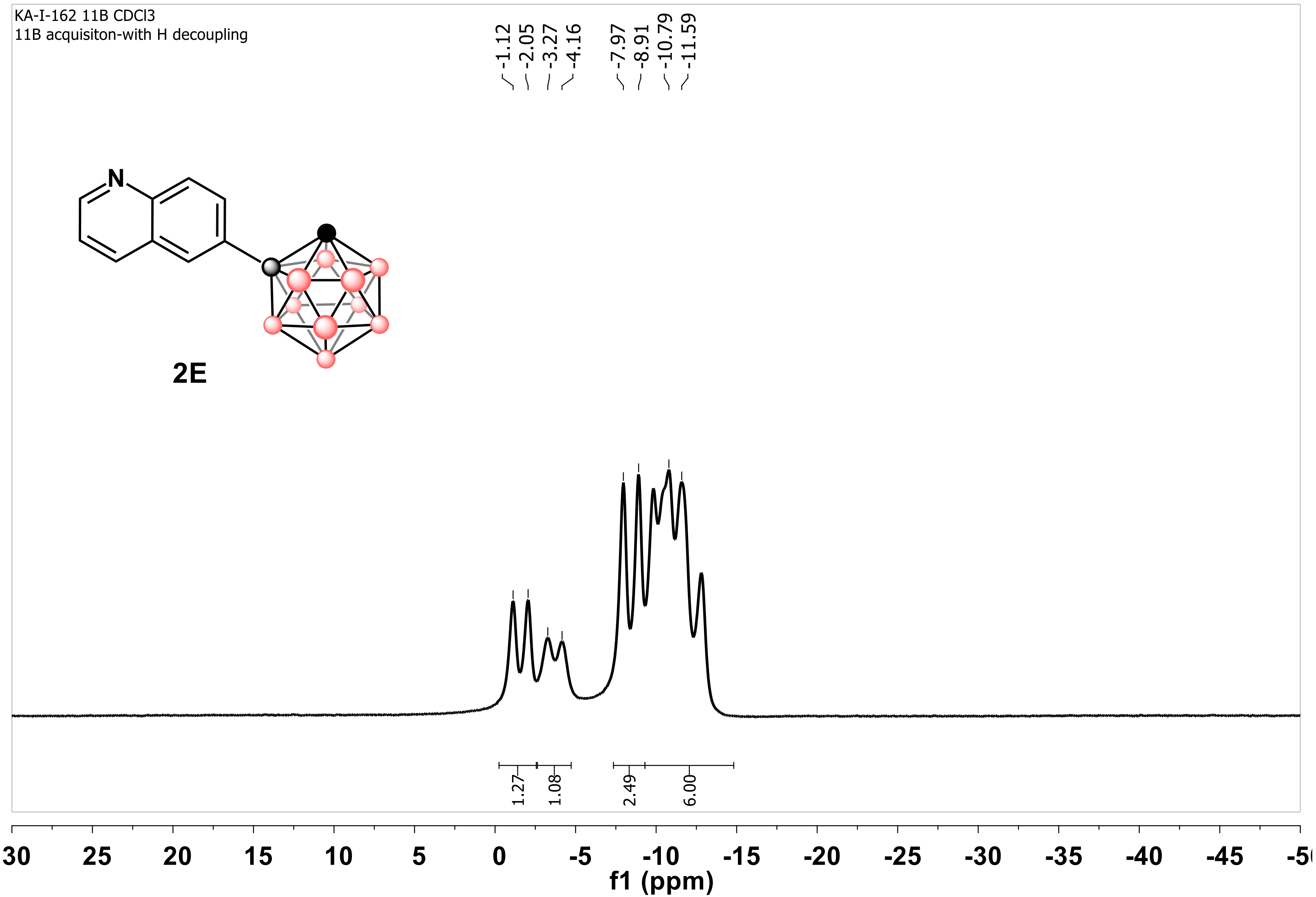
KA-I-130 11B{1H} CDCl3
11B acquisiton-with H decoupling
-2.36
-8.54
-9.58
-12.94
2D
2.20
6.00
2.03
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

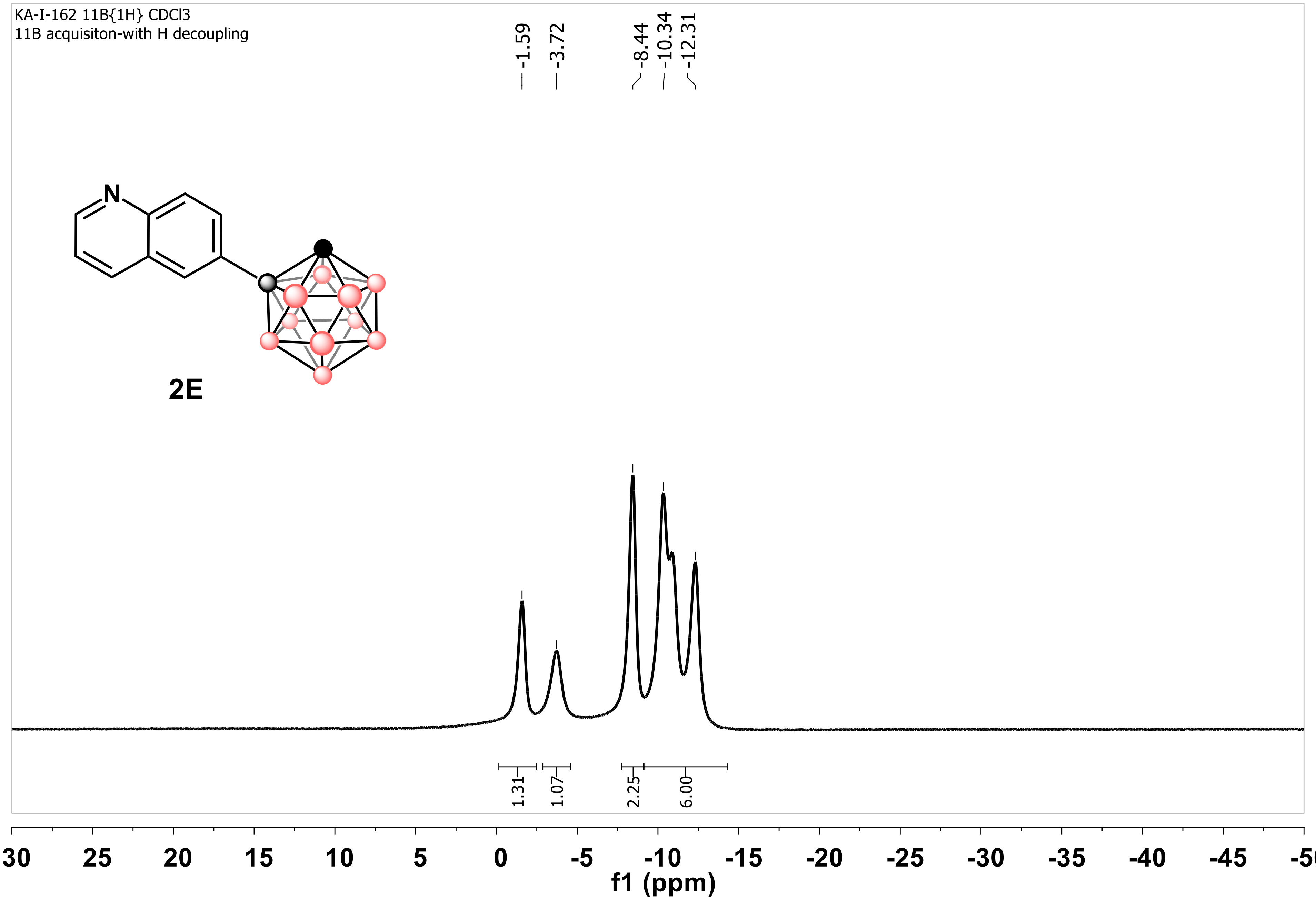

KA-I-130 13C
13C
134.91
131.88
130.02
129.93
128.82
128.34
127.34
126.25
124.65
124.52
61.28
2D
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



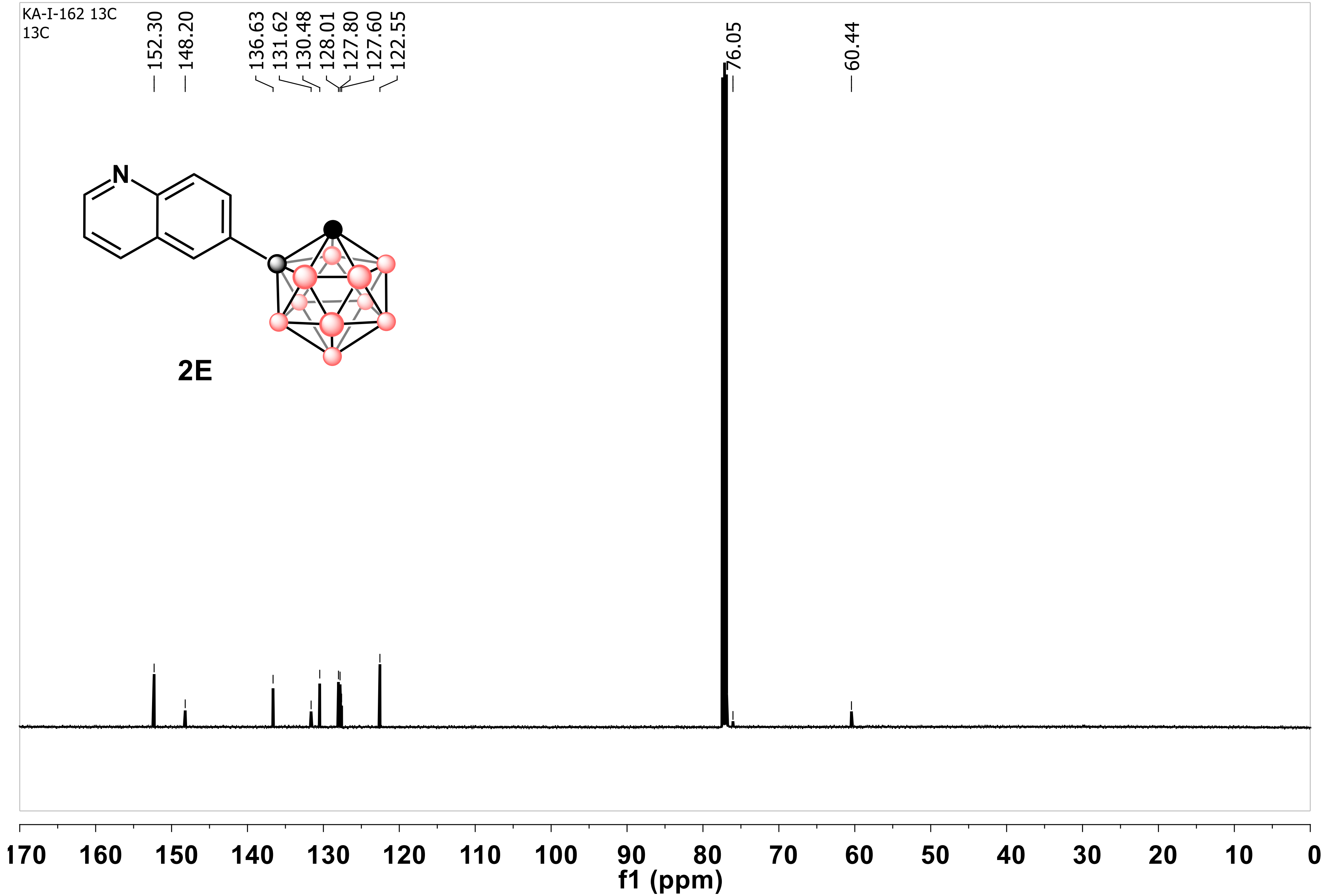
+EI Scan (rt: 4,861 min) Frag=70,0V 18_0710_KA-I-130_scale up 2,D
x10 7
2D
270.2393
271.2362
269.2421
268.2442
272.2340
267.2200
265.2012
261.1698
263.2055
281.0497
253.0155
247.1367
249.1512
251.1669
257.1383
259.1754
273.2362
Counts vs. Mass-to-Charge (m/z)

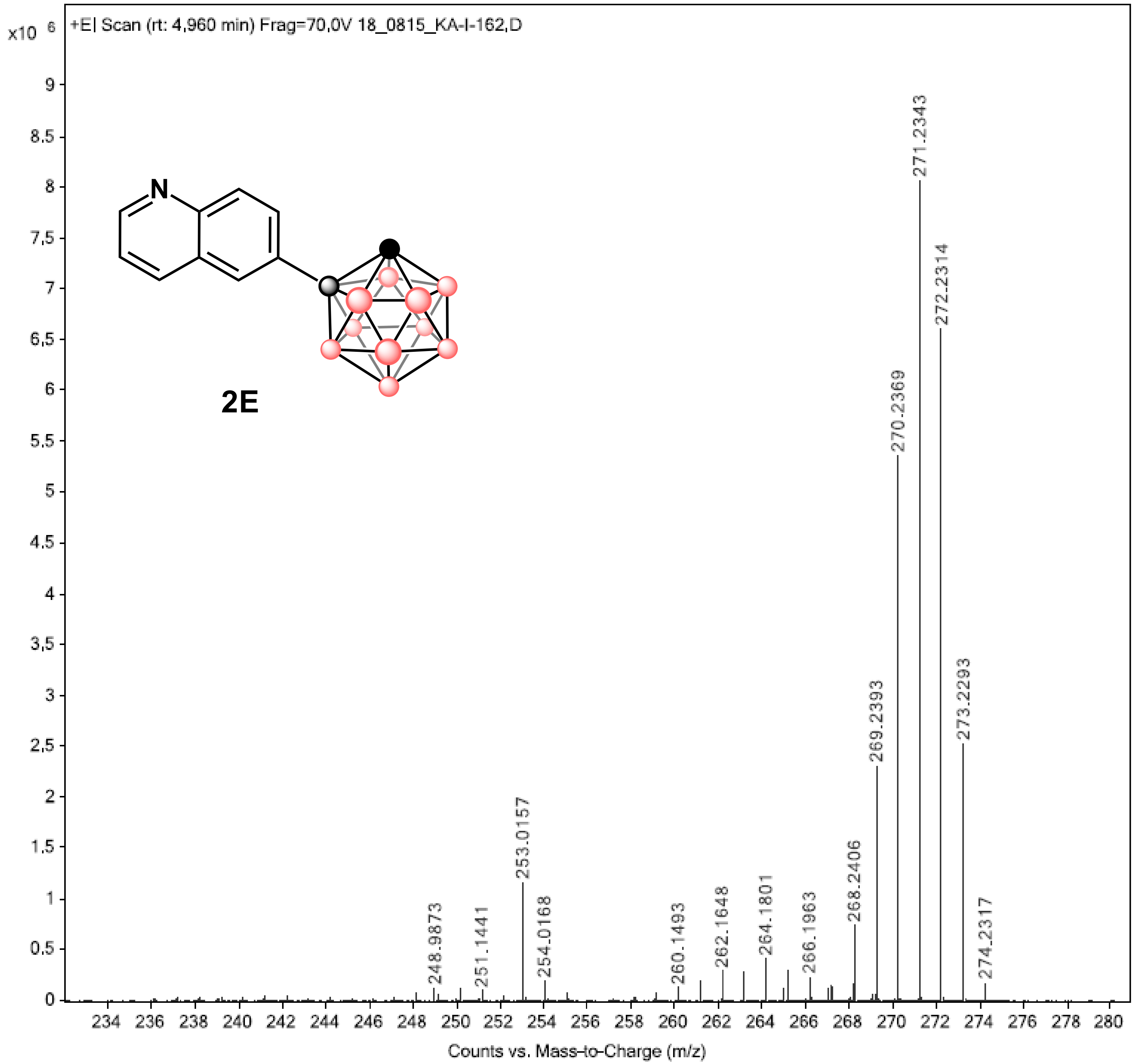

Sep12-2018-spokoyny
Account No. AAS153
KA-I-162 CDCl3 1H
8.18
8.16
8.09
8.07
7.99
7.98
7.79
7.77
7.49
7.48
4.09
N
2E
0.94
1.00
0.98
0.97
1.00
1.00
1.00
10.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


KA-I-162 11B CDCl3
11B acquisiton-with H decoupling
-1.12
-2.05
-3.27
-4.16
-7.97
-8.91
-10.79
-11.59
N
2E
1.27
1.08
2.49
6.00
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

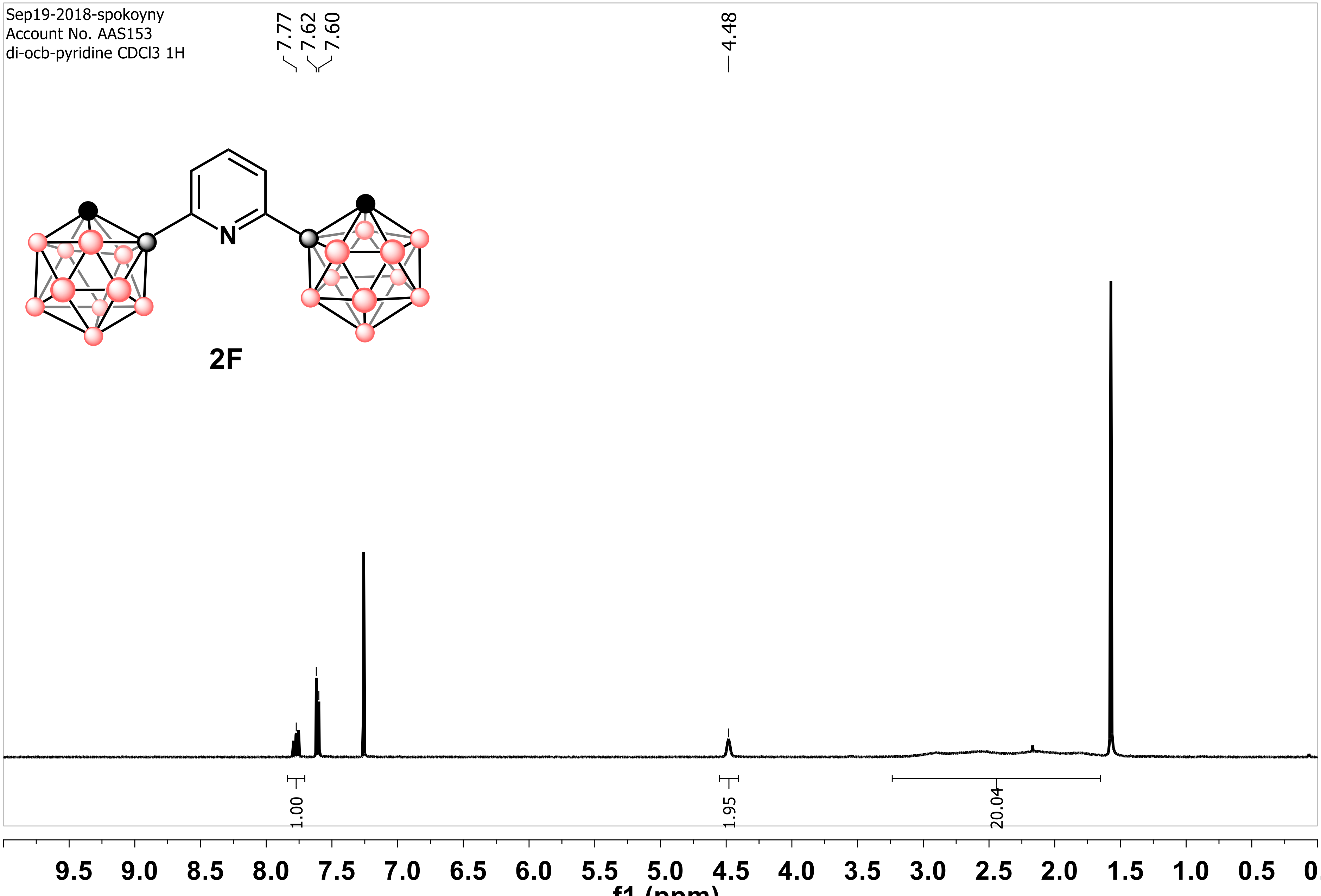


KA-I-162 11B{1H} CDCl3
11B acquisiton-with H decoupling
-1.59
-3.72
-8.44
-10.34
-12.31
N
2E
1.31
1.07
2.25
6.00
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

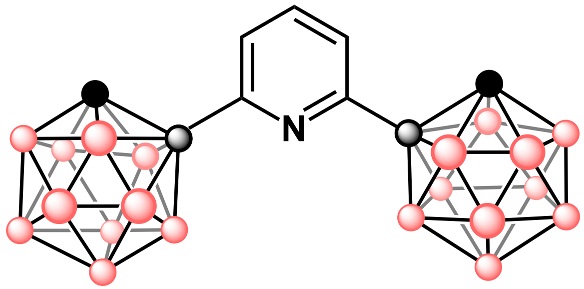

KA-I-162 13C
13C
152.30
148.20
136.63
131.62
130.48
128.01
127.80
127.60
122.55
76.05
60.44
N
2E
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



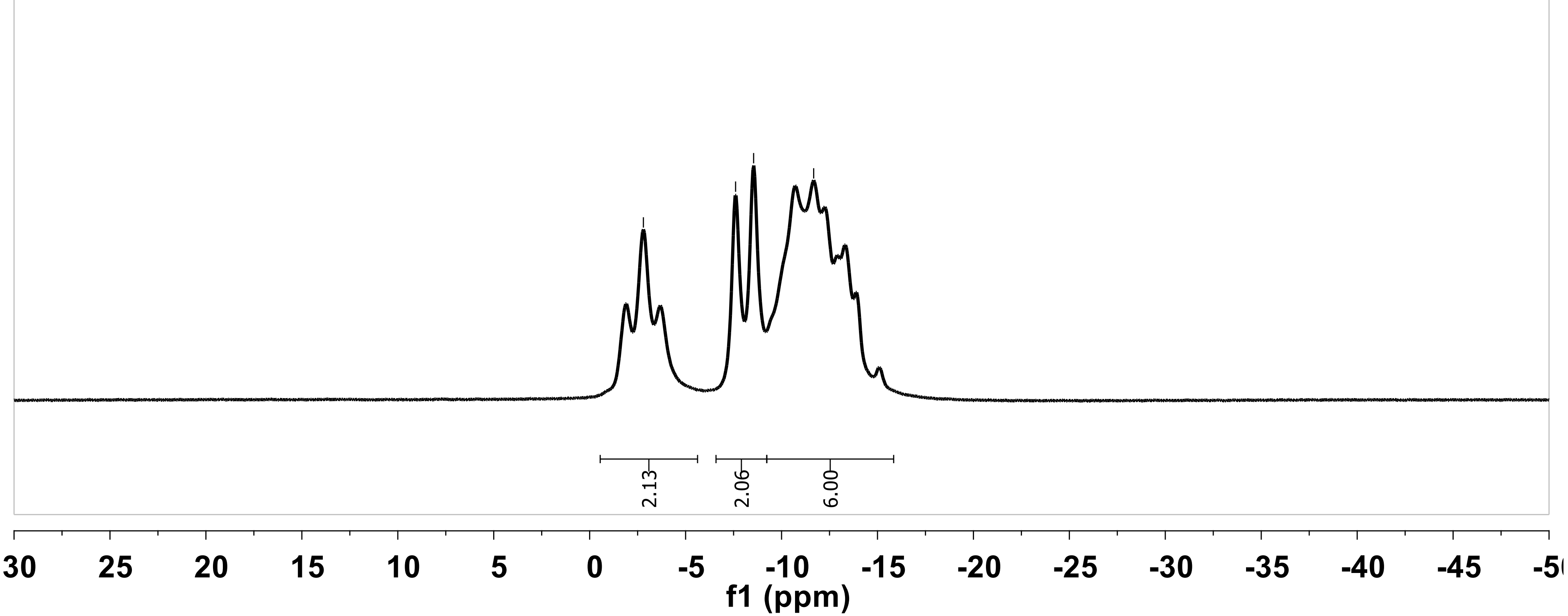
x10 6
+EI Scan (rt: 4,960 min) Frag=70,0V 18_0815_KA-I-162,D
N
2E
271.2343
272.2314
270.2369
269.2393
273.2293
253.0157
268.2406
264.1801
262.1648
266.1963
254.0168
260.1493
251.1441
248.9873
274.2317
Counts vs. Mass-to-Charge (m/z)

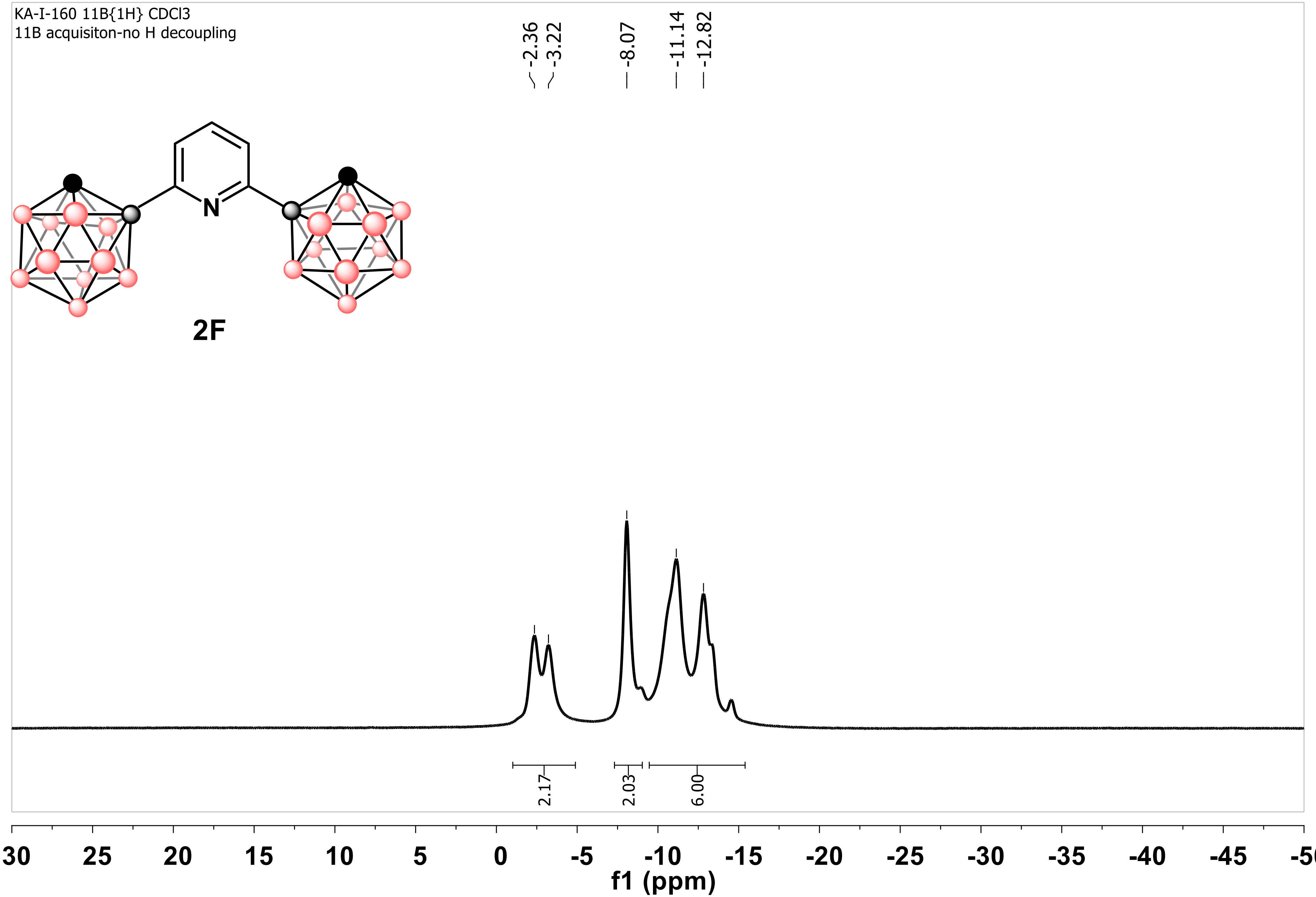

Sep19-2018-spokoyny
Account No. AAS153
di-ocb-pyridine CDCl3 1H
7.77
7.62
7.60
4.48
N
2F
1.00
1.95
20.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

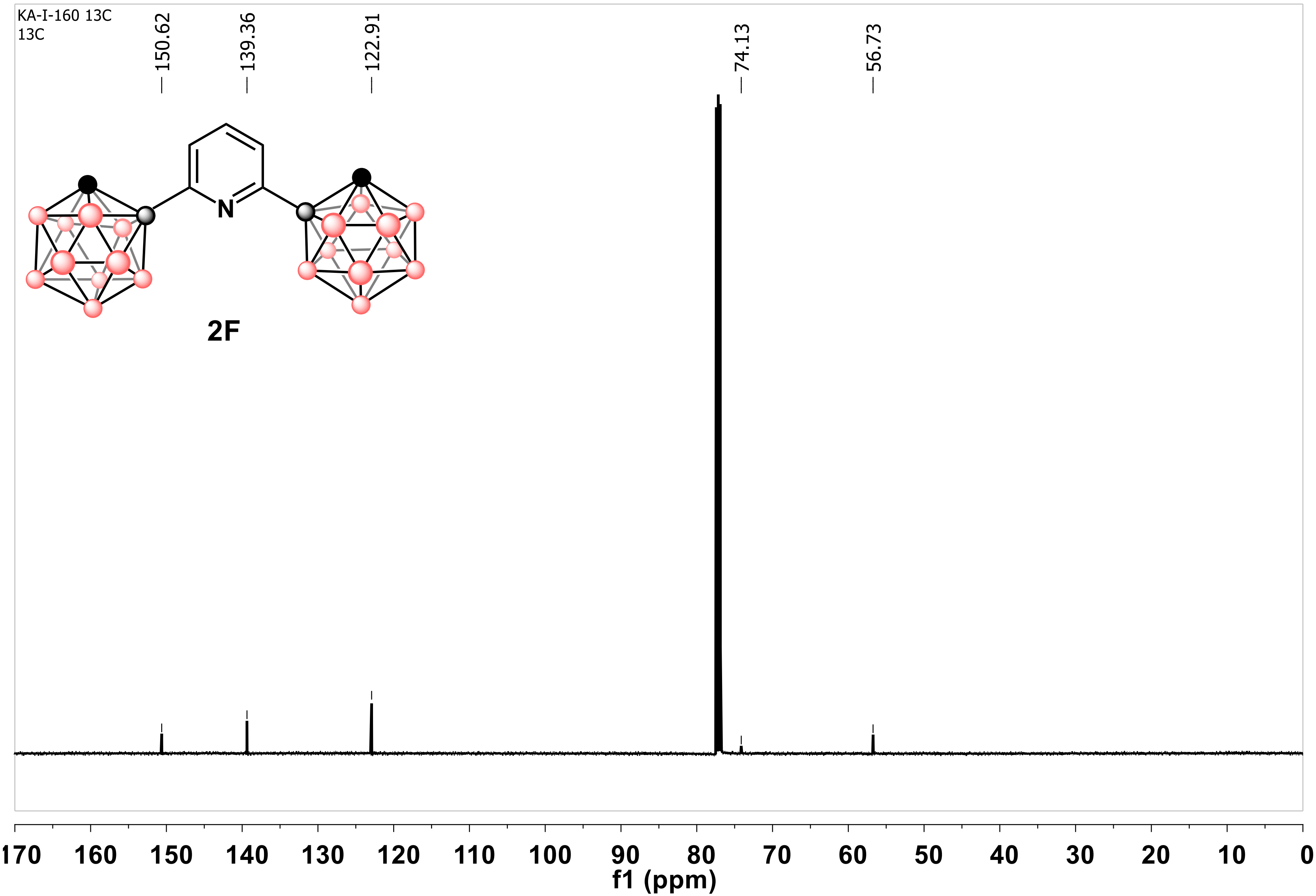
KA-I-160 11B CDCl3
11B acquisiton-no H decoupling

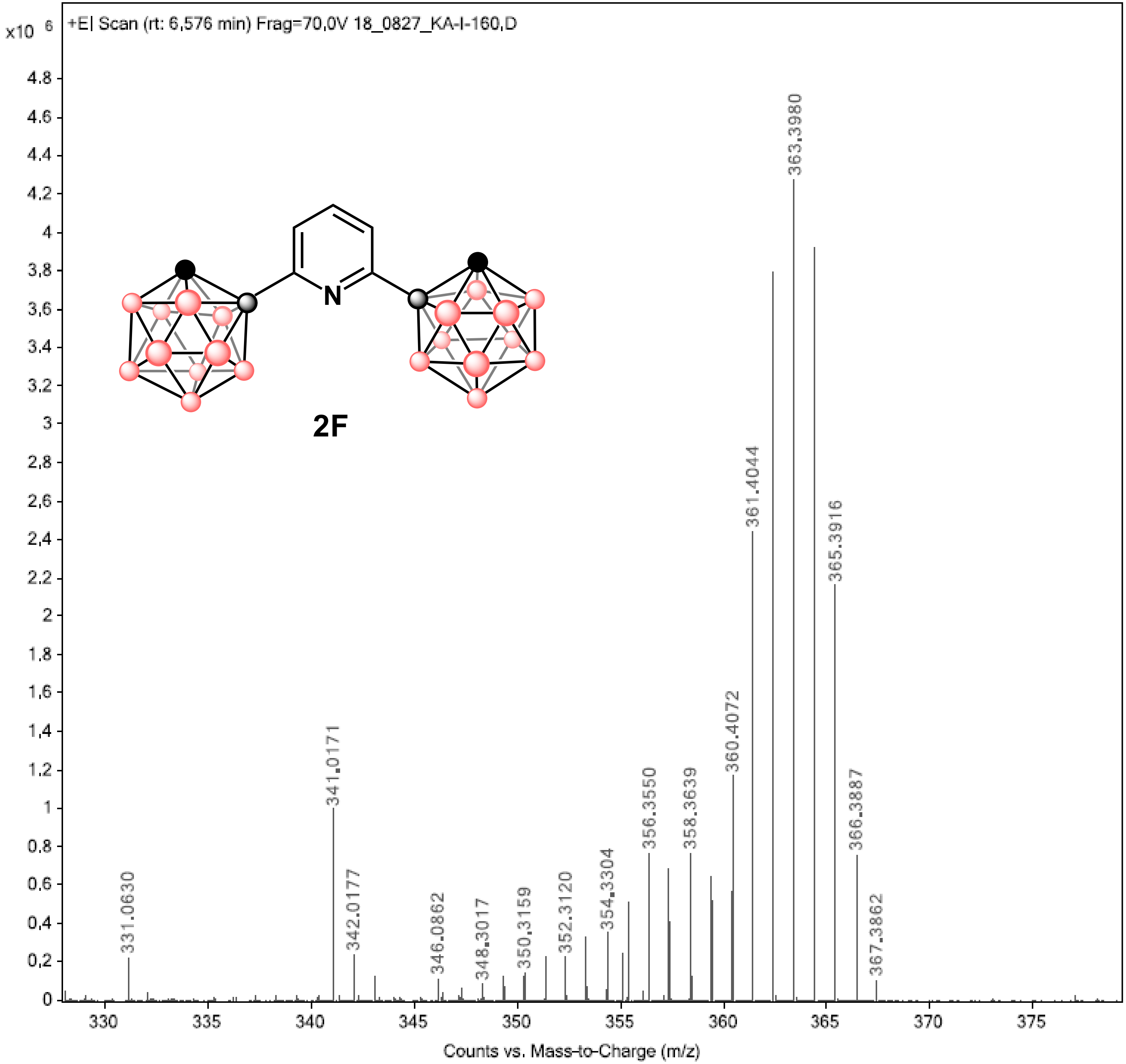


2F

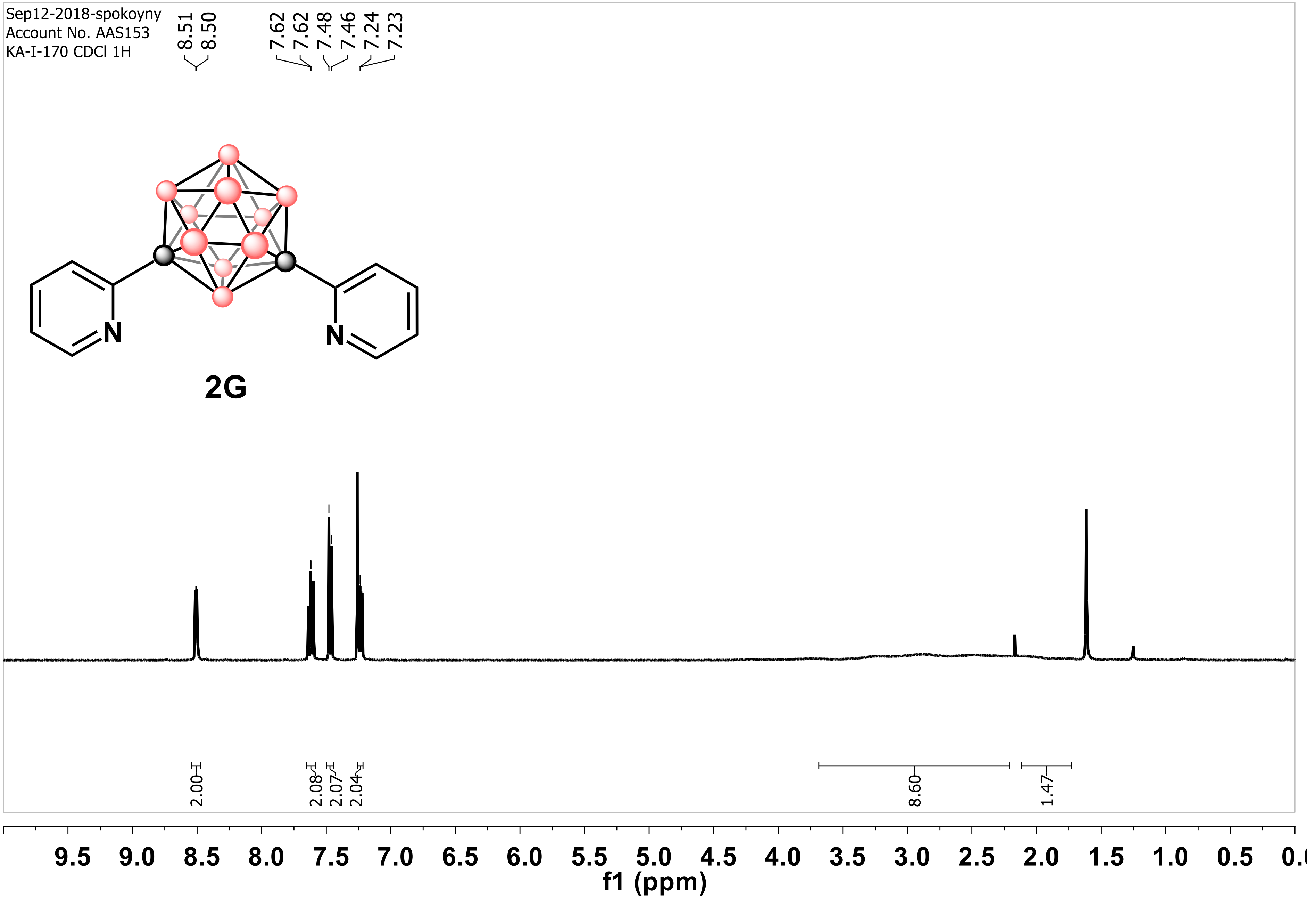



KA-I-160 11B{1H} CDCl3
11B acquisiton-no H decoupling
-2.36
-3.22
-8.07
-11.14
-12.82
N
2F
2.17
2.03
6.00
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)


KA-I-160 13C
13C
150.62
139.36
122.91
74.13
56.73
N
2F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

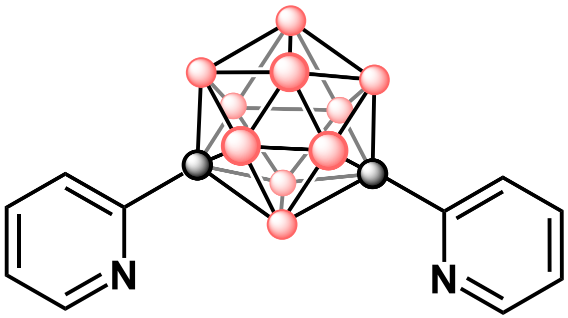


x10 6
+EI Scan (rt: 6,576 min) Frag=70,0V 18_0827_KA-I-160,D
2F
N
331.0630
341.0171
342.0177
346.0862
348.3017
350.3159
352.3120
354.3304
356.3550
358.3639
360.4072
361.4044
363.3980
365.3916
366.3887
367.3862
Counts vs. Mass-to-Charge (m/z)

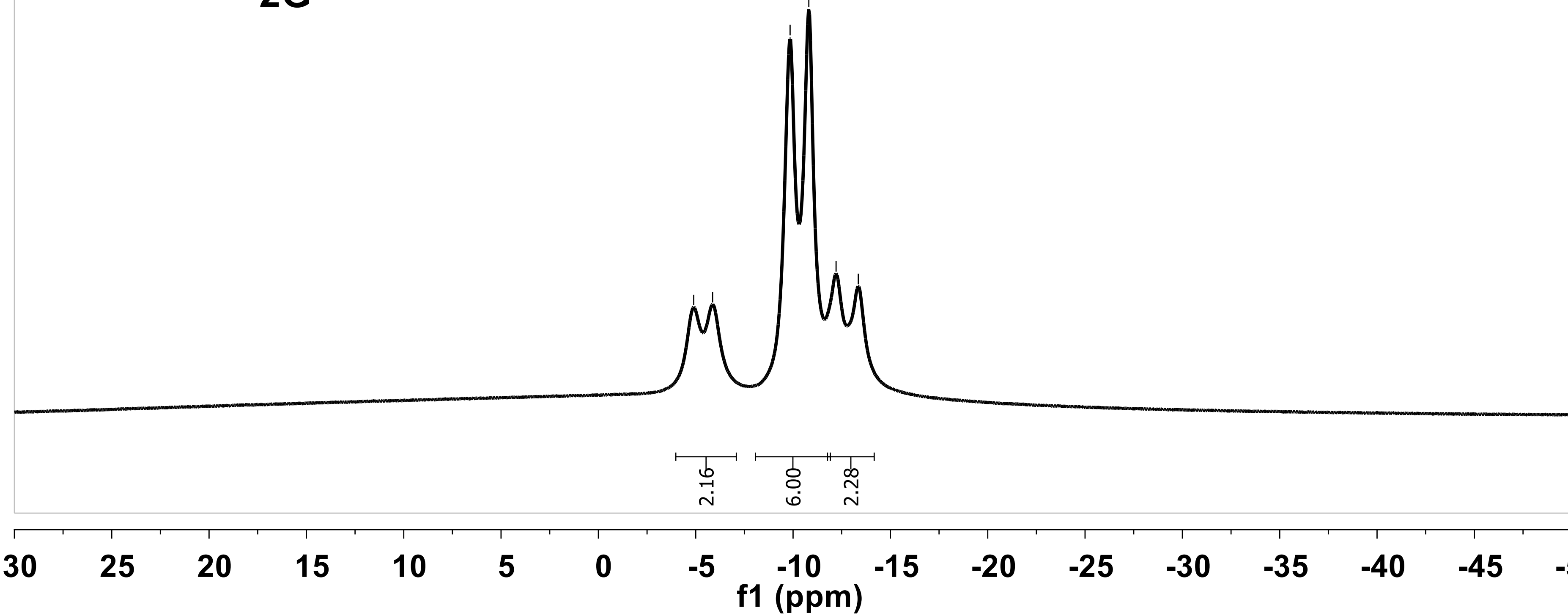


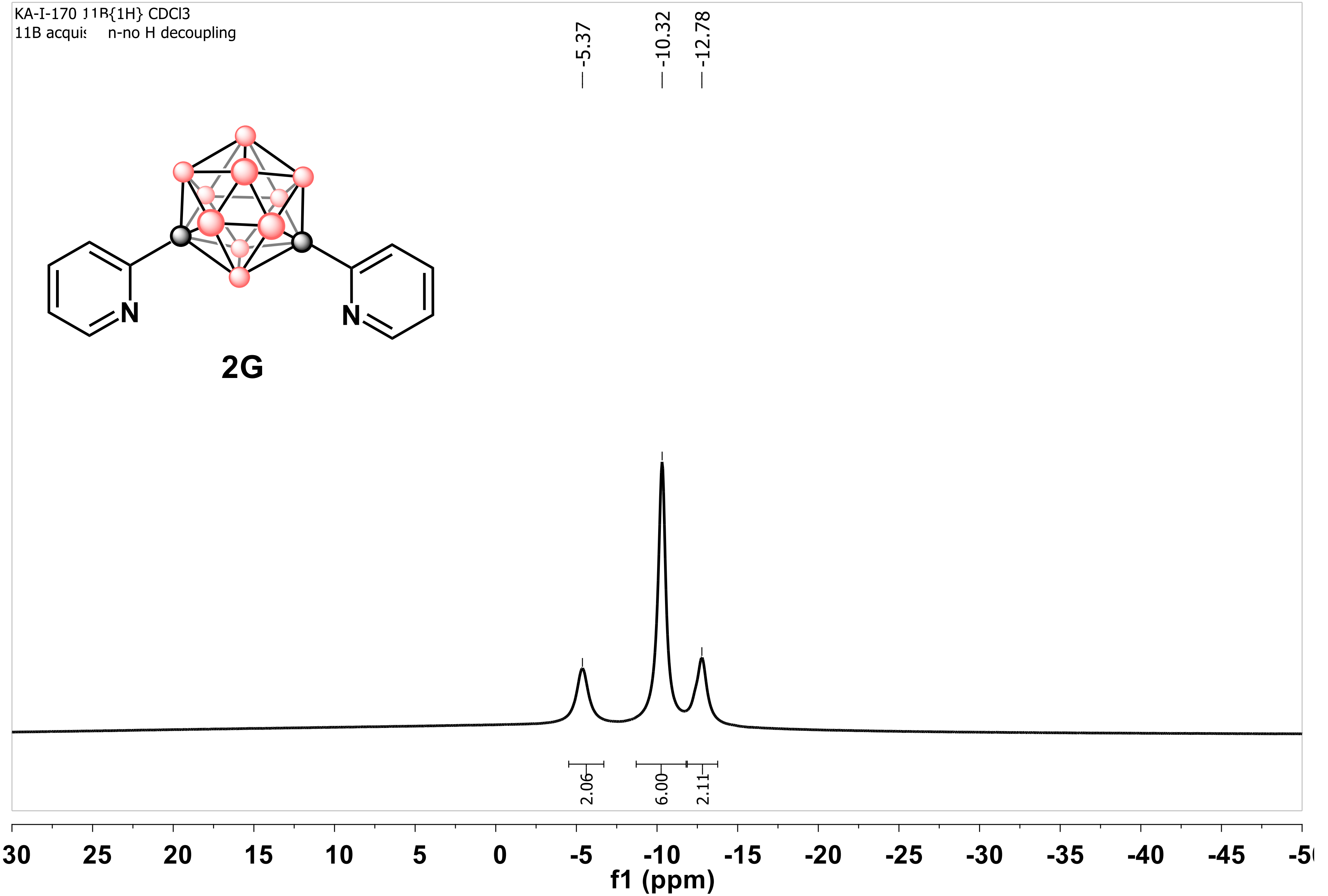
Sep12-2018-spokoyny
Account No. AAS153
KA-I-170 CDCl 1H
8.51
8.50
7.62
7.62
7.48
7.46
7.24
7.23
N
N
2G
2.00
2.08
2.07
2.04
8.60
1.47
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

KA-I-170 11B CDCl3
11B acquisiton-no H decoupling

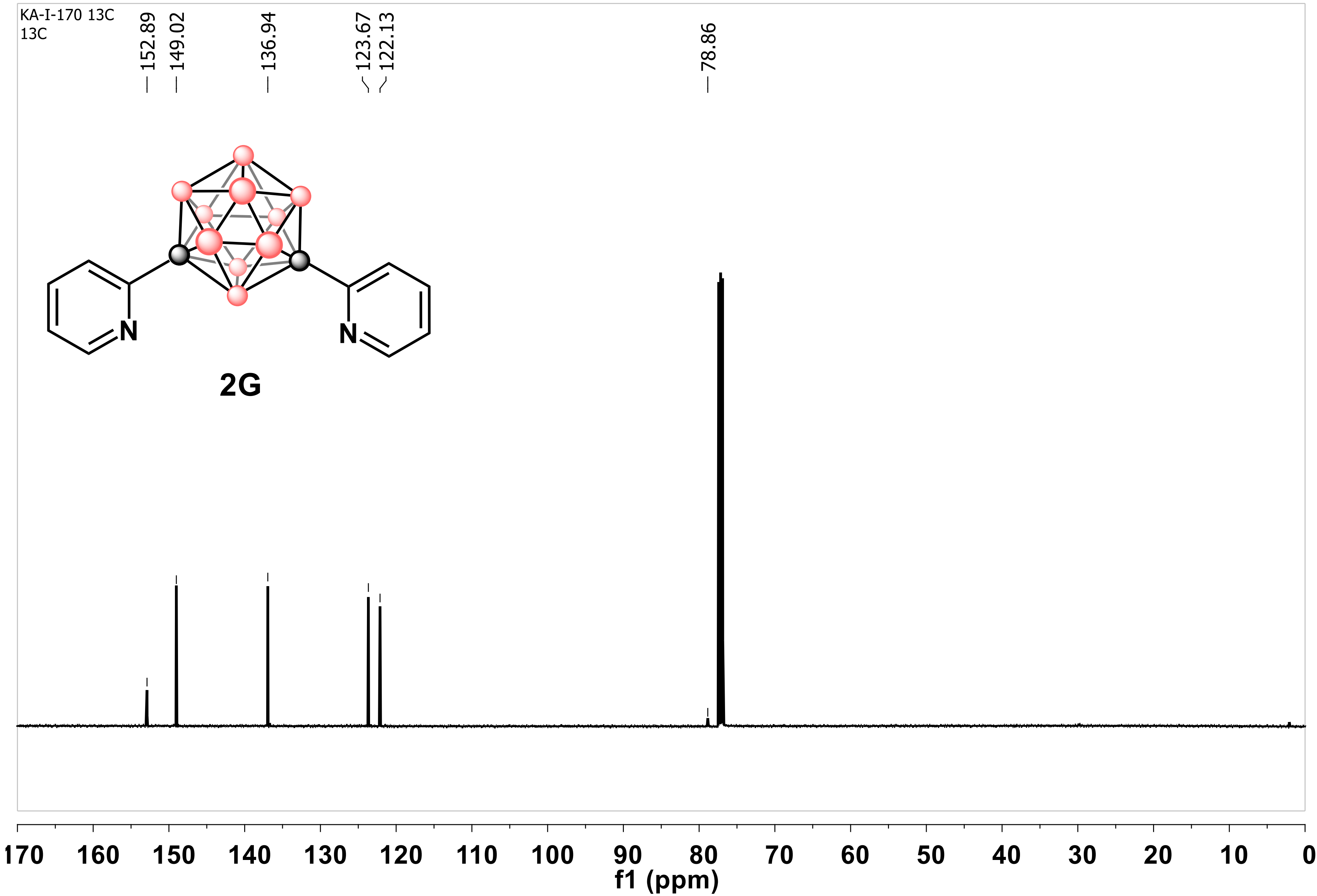


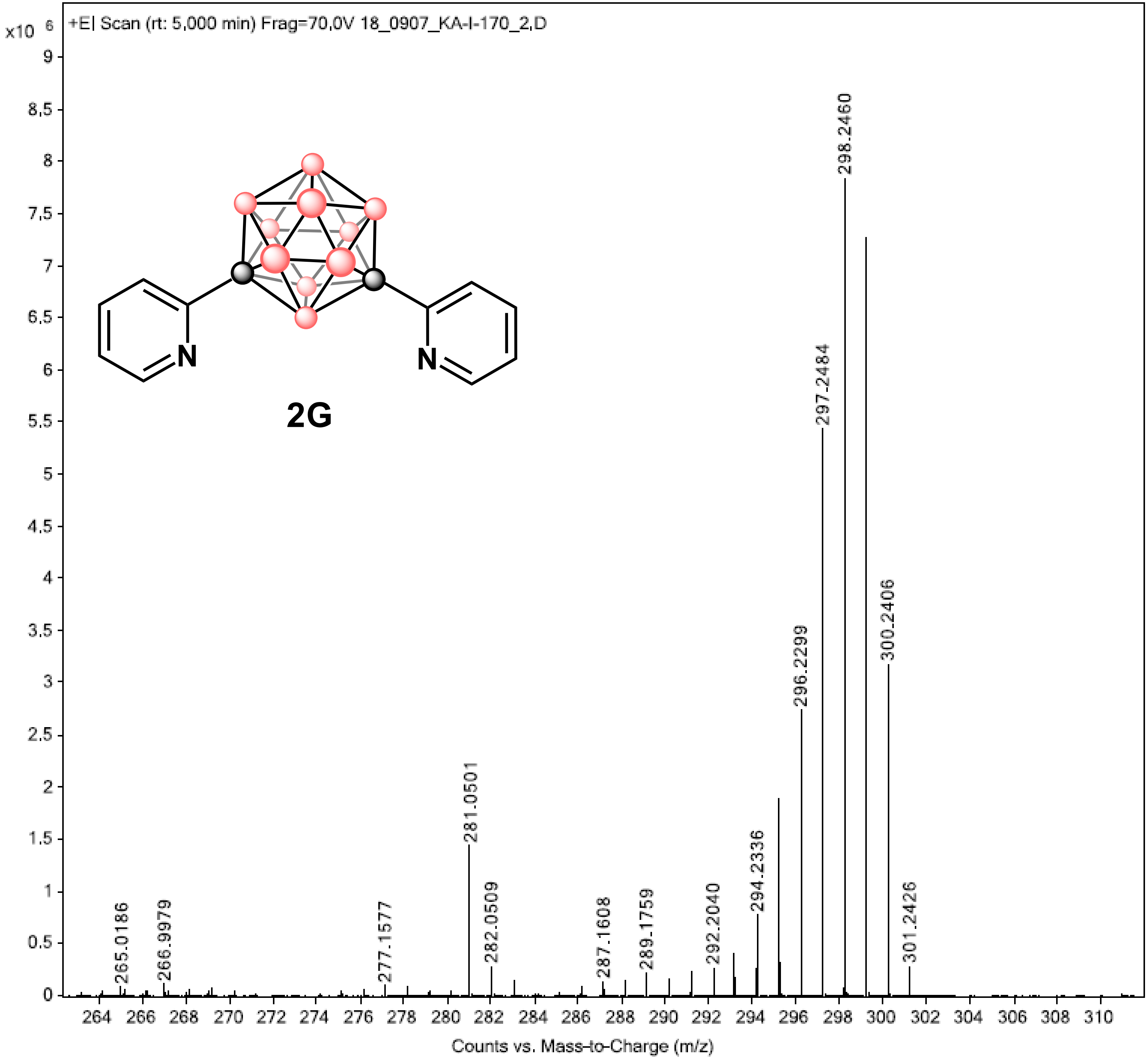
2G

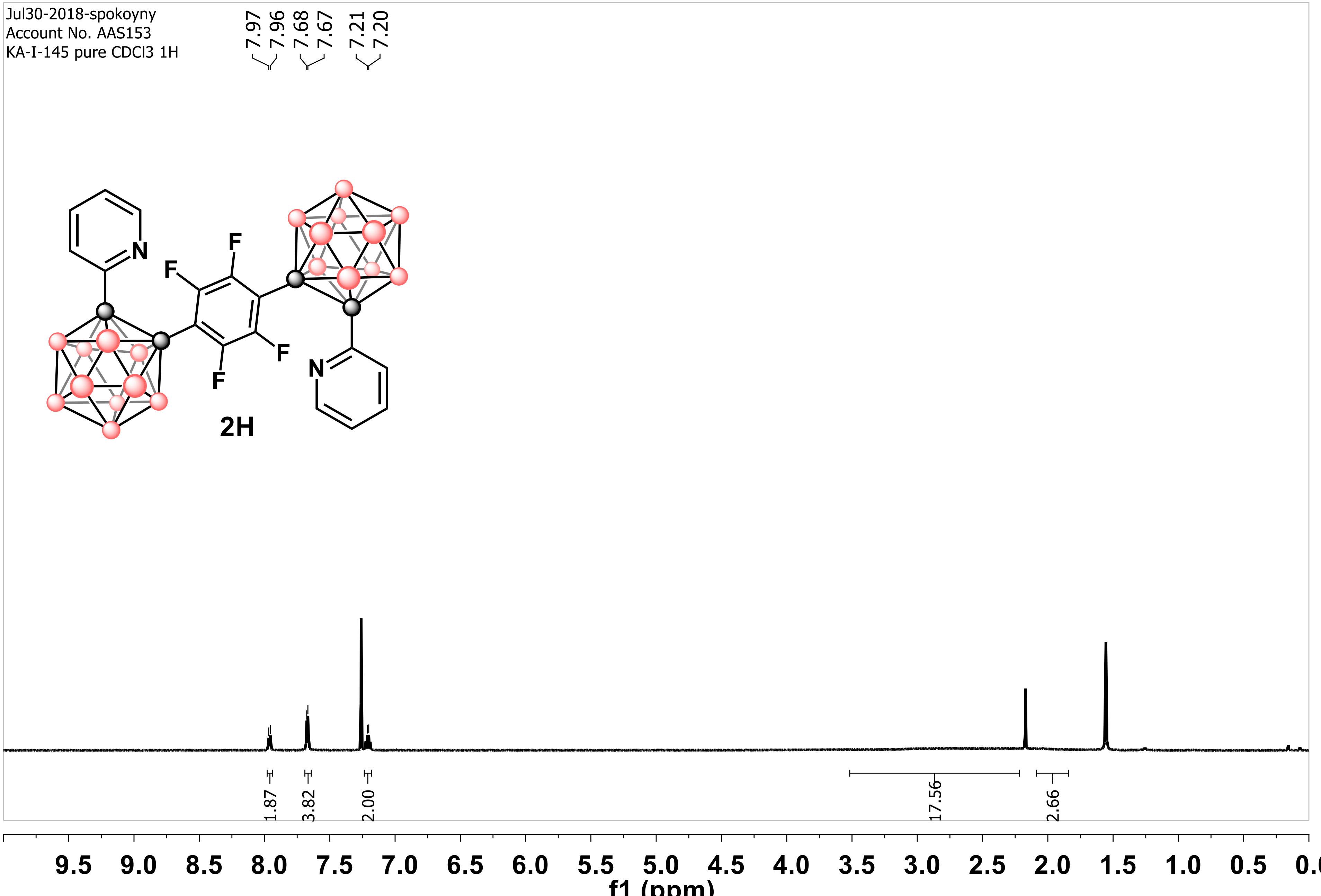


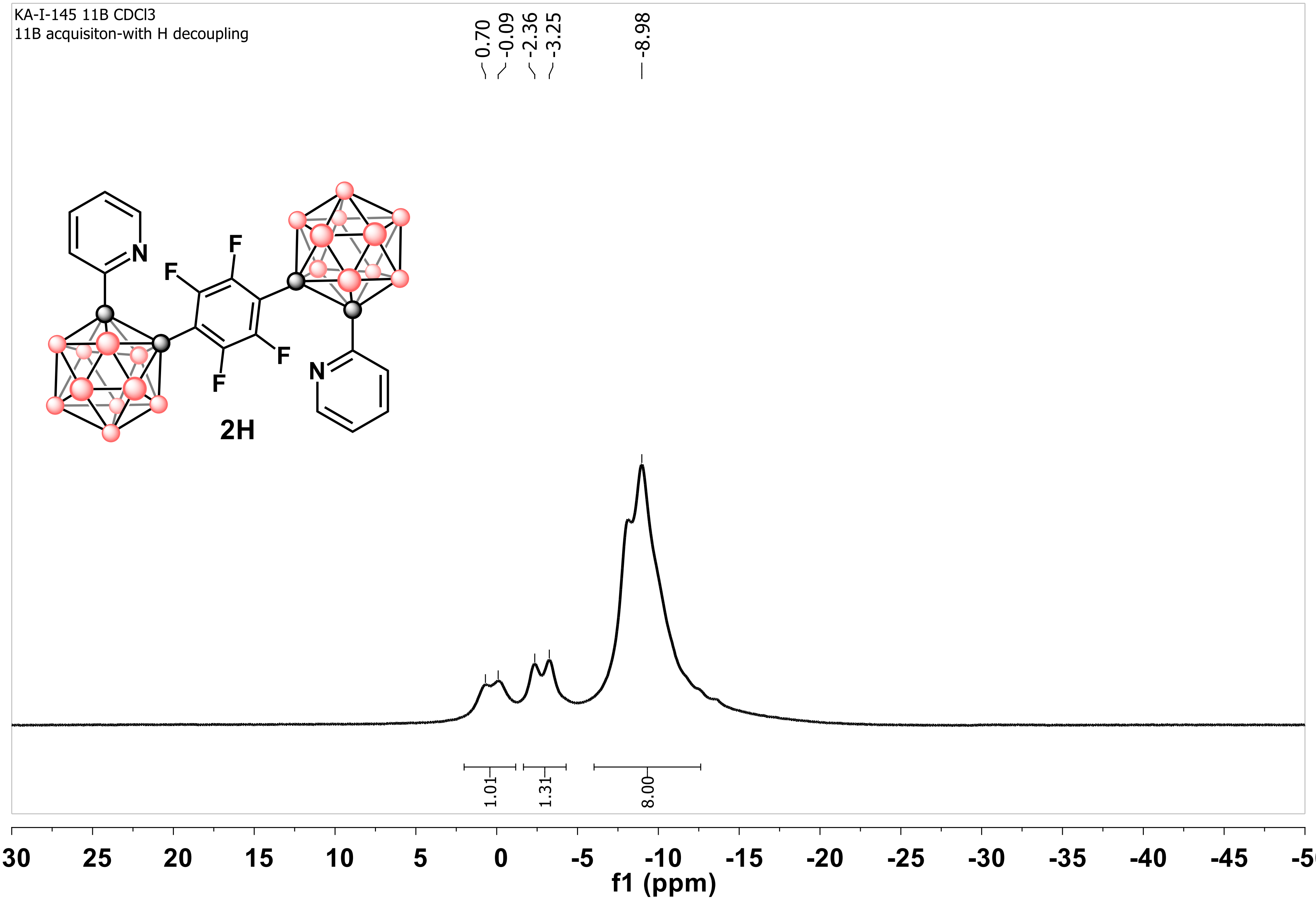


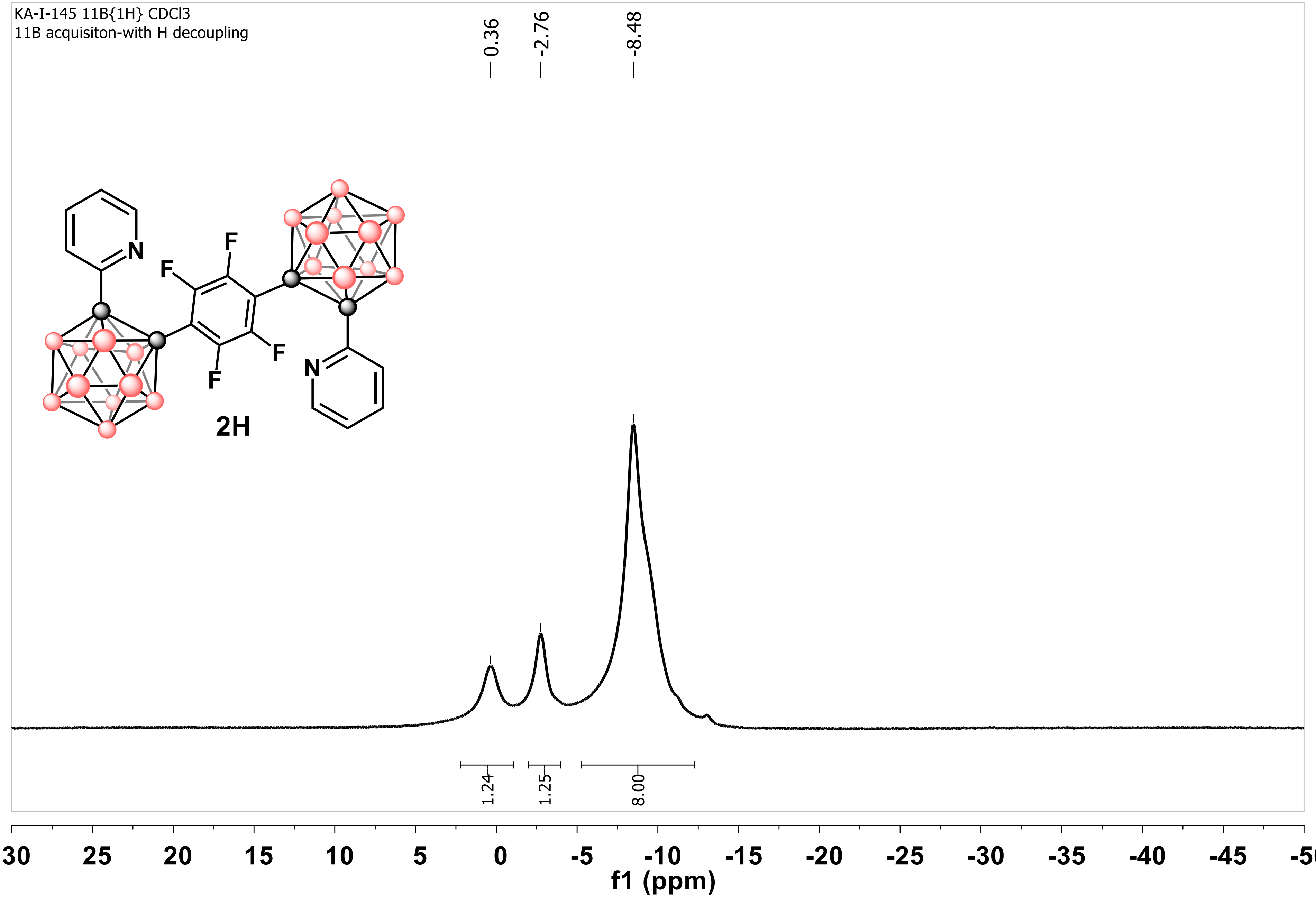
KA-I-170 1 1B{1H} CDCl3
11B acqui n-no H decoupling
-5.37
-10.32
-12.78
N
N
2G
2.06
6.00
2.11
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)


KA-I-170 13C
13C
152.89
149.02
136.94
123.67
122.13
78.86
N
N
2G
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

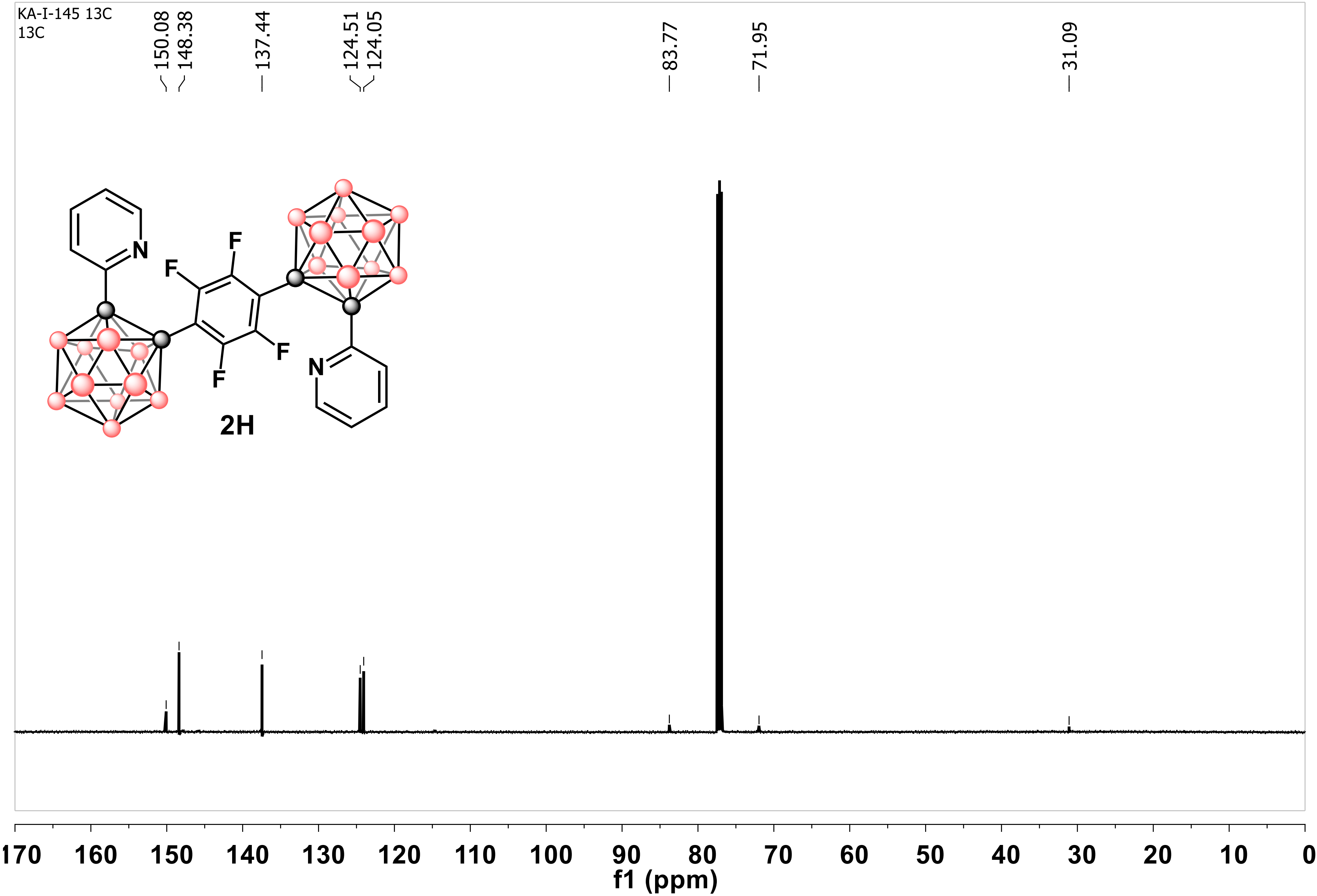

+EI Scan (rt: 5,000 min) Frag=70,0V 18_0907_KA-I-170_2,D
x10 6
2G
N
N
298.2460
297.2484
300.2406
296.2299
281.0501
294.2336
282.0509
301.2426
292.2040
289.1759
287.1608
277.1577
266.9979
265.0186
Counts vs. Mass-to-Charge (m/z)

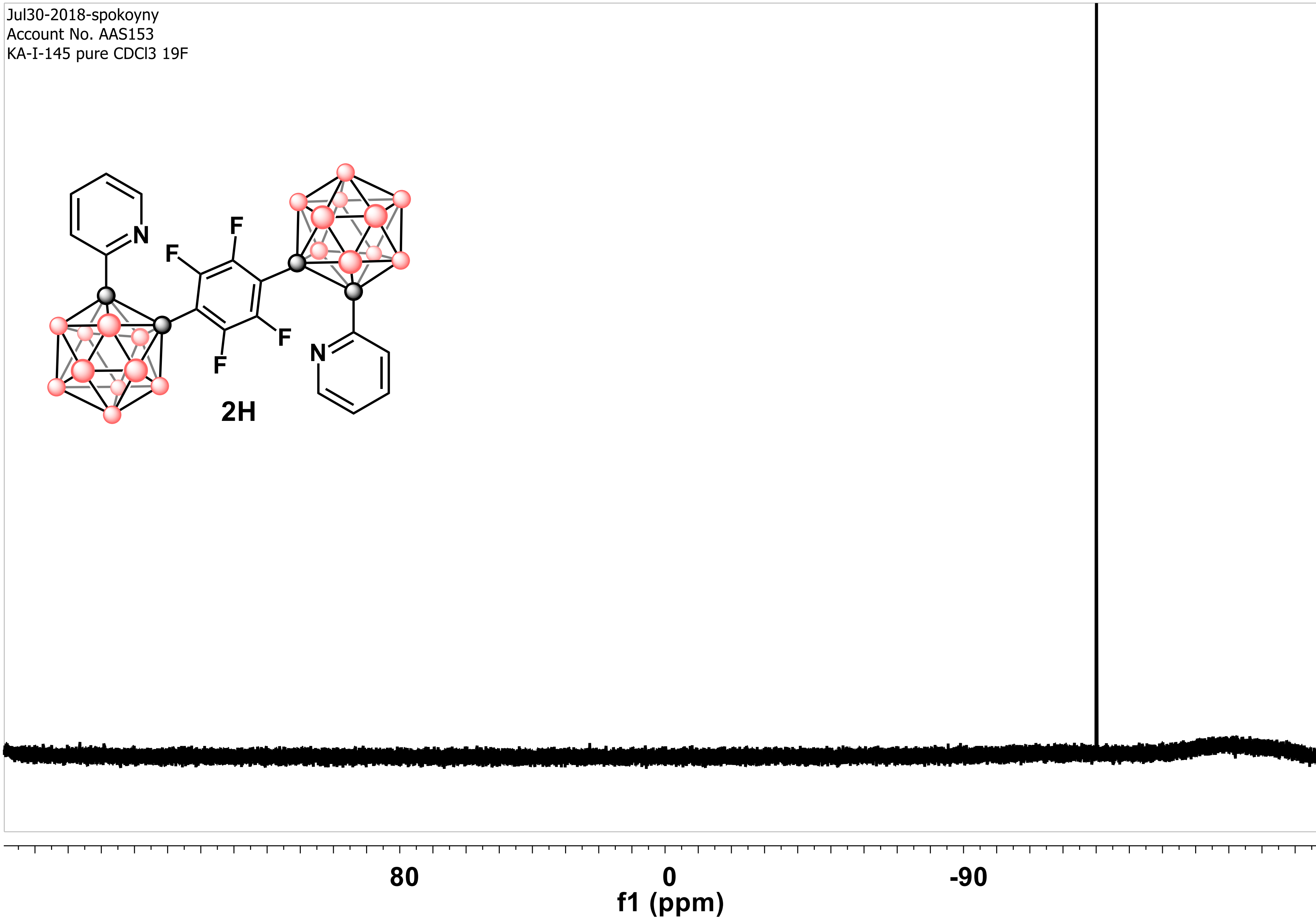

Jul30-2018-spokoyny
Account No. AAS153
KA-I-145 pure CDCl3 1H
7.97
7.96
7.68
7.67
7.21
7.20
F
F
F
F
N
N
2H
1.87
3.82
2.00
17.56
2.66
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

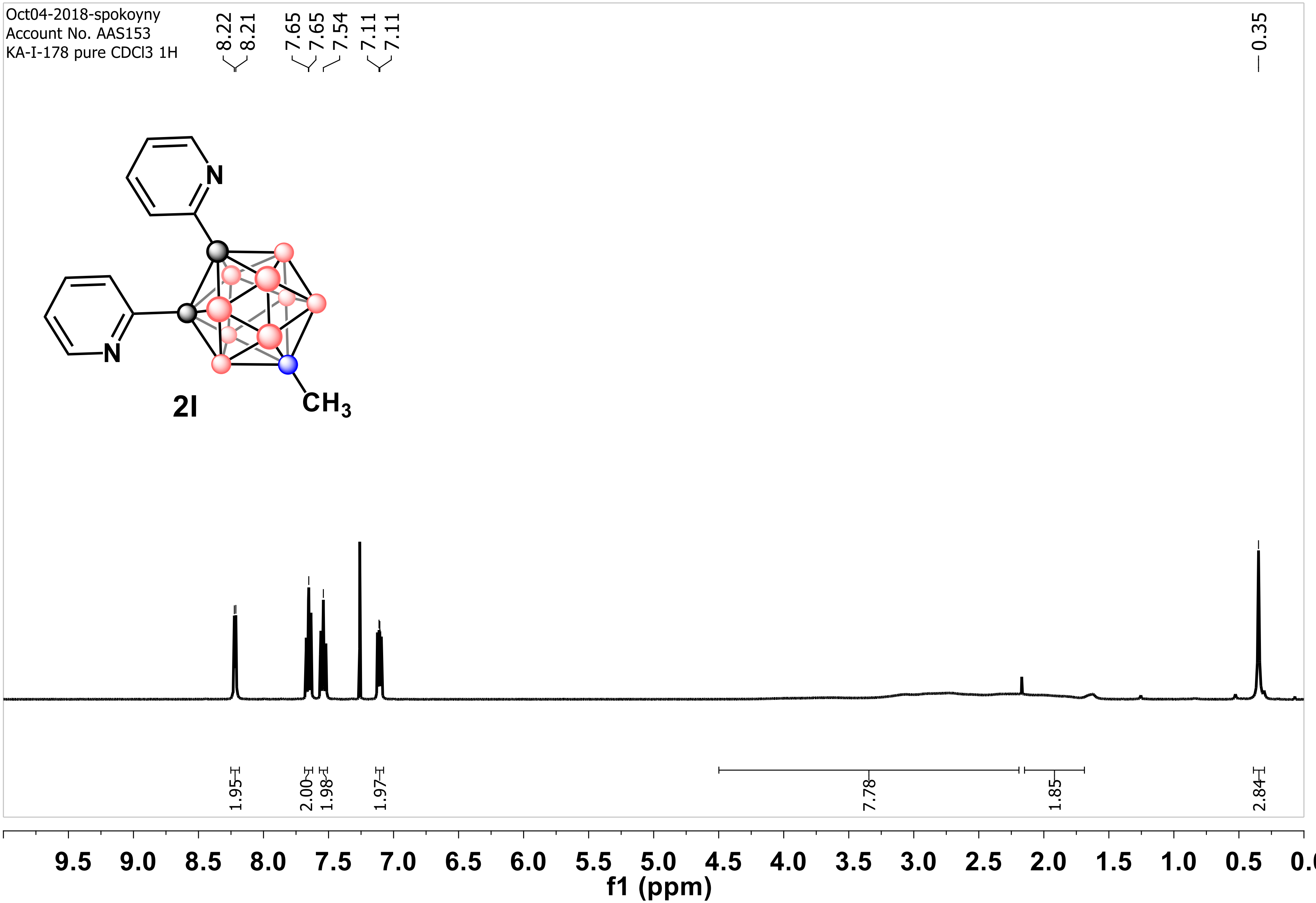

KA-I-145 11B CDCl3
11B acquisiton-with H decoupling
0.70
-0.09
-2.36
-3.25
-8.98
2H
1.01
1.31
8.00
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

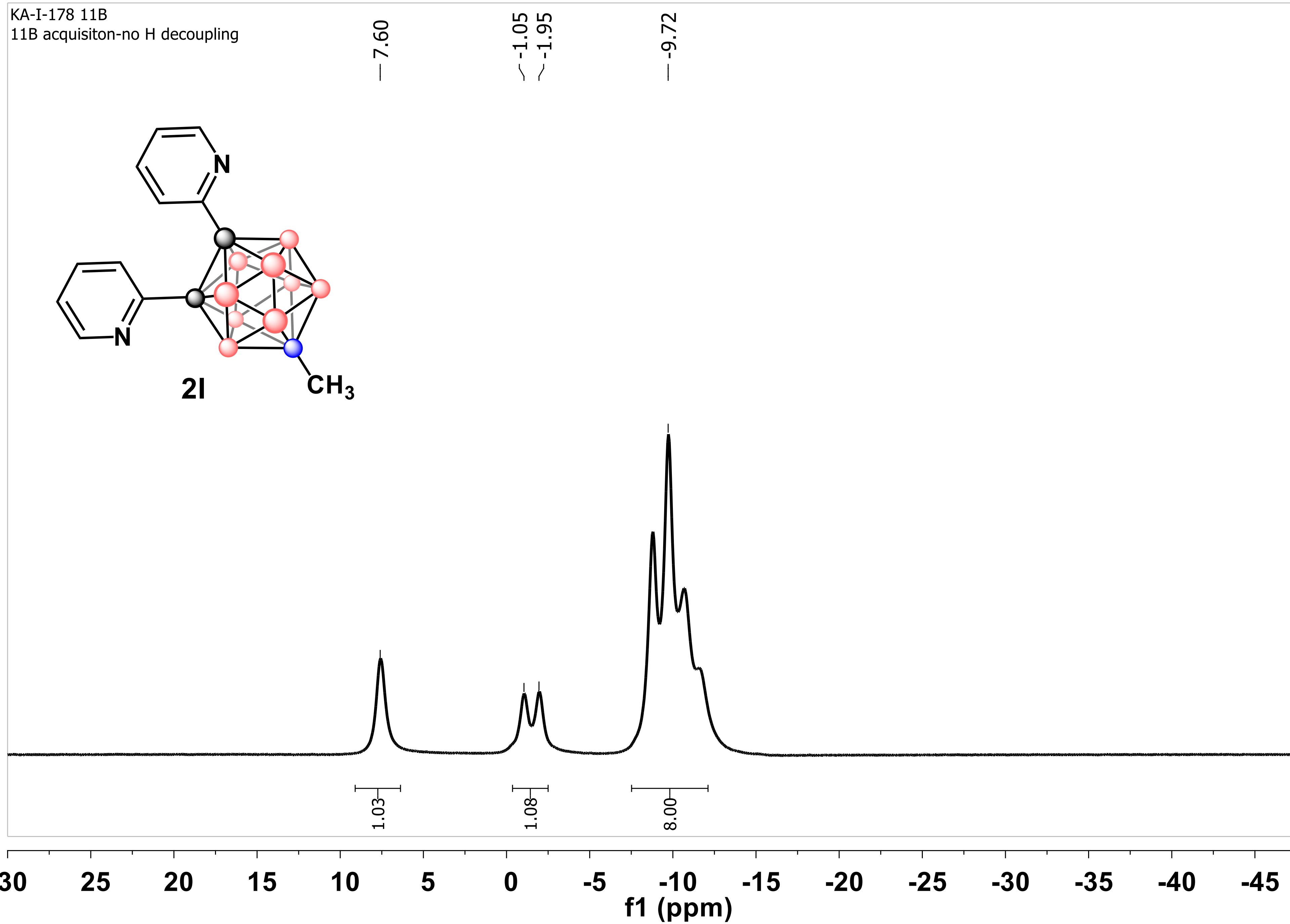


KA-I-145 11B{1H} CDCl3
11B acquisiton-with H decoupling
0.36
-2.76
-8.48
F
F
F
F
N
N
2H
1.24
1.25
8.00
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

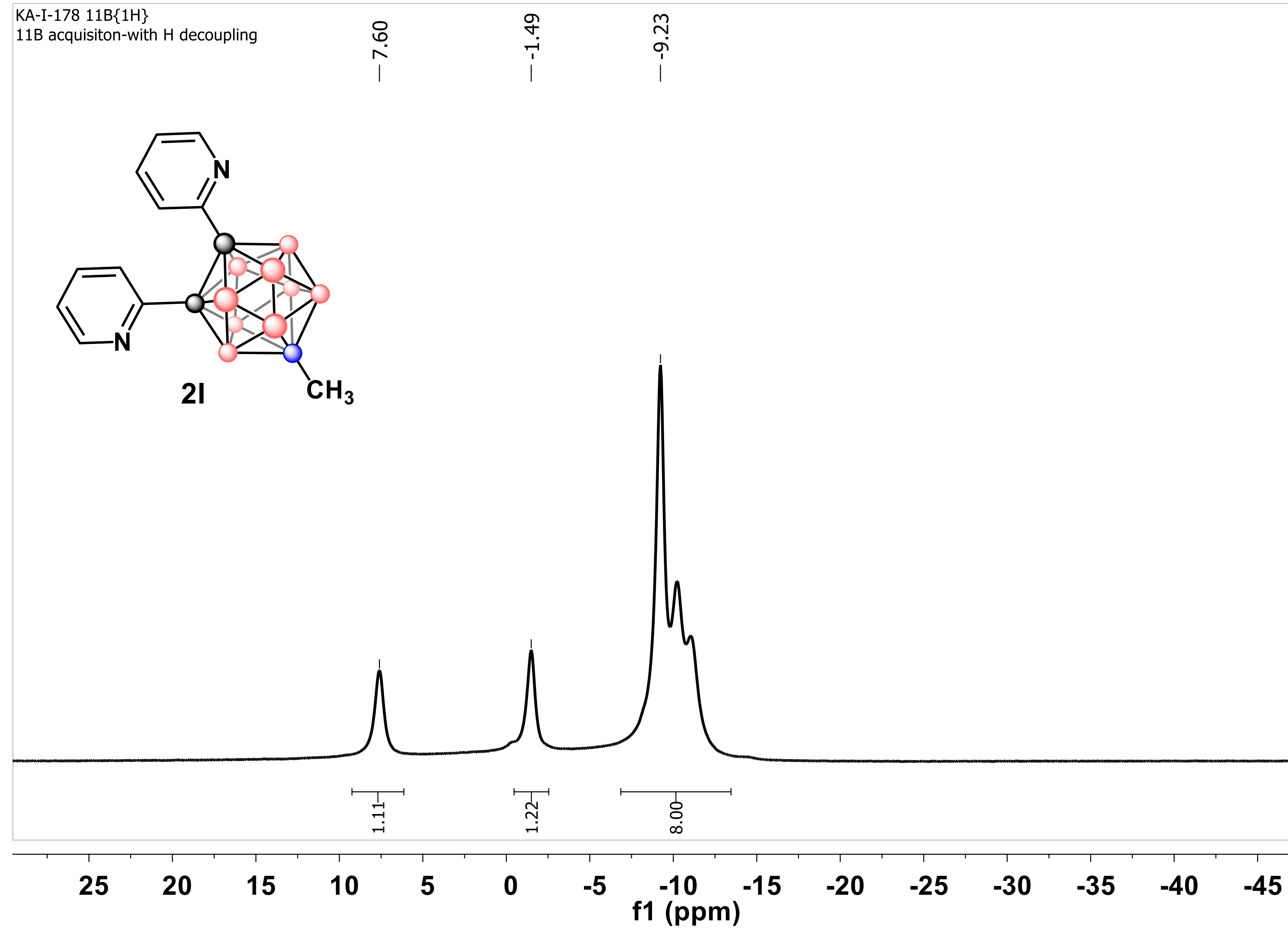

KA-I-145 13C
13C
150.08
148.38
137.44
124.51
124.05
83.77
71.95
31.09
F
F
F
F
N
N
2H
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

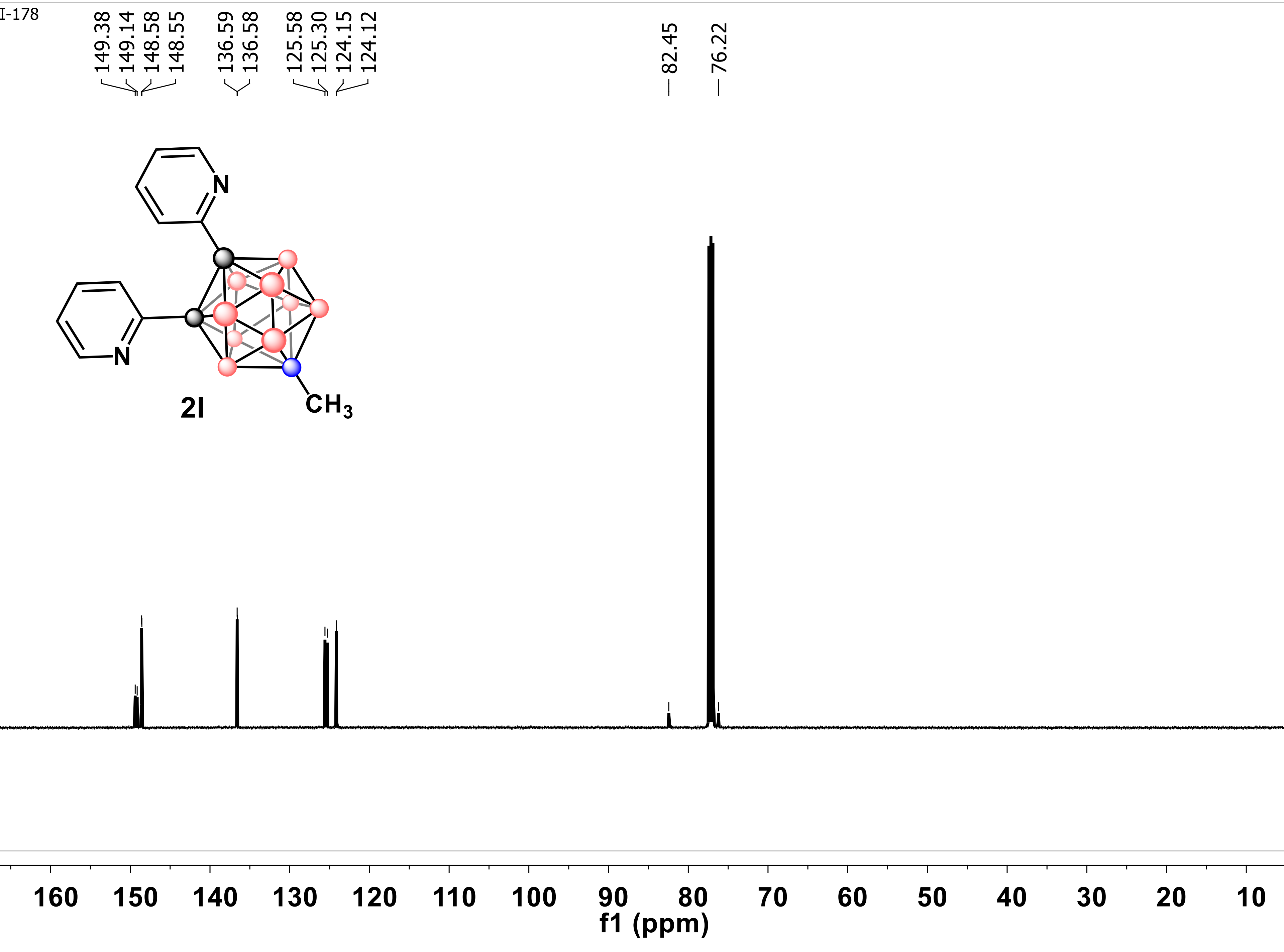

Jul30-2018-spokoyny
Account No. AAS153
KA-I-145 pure CDCl3 19F
F
F
F
F
N
N
2H
80
0
-90
f1 (ppm)

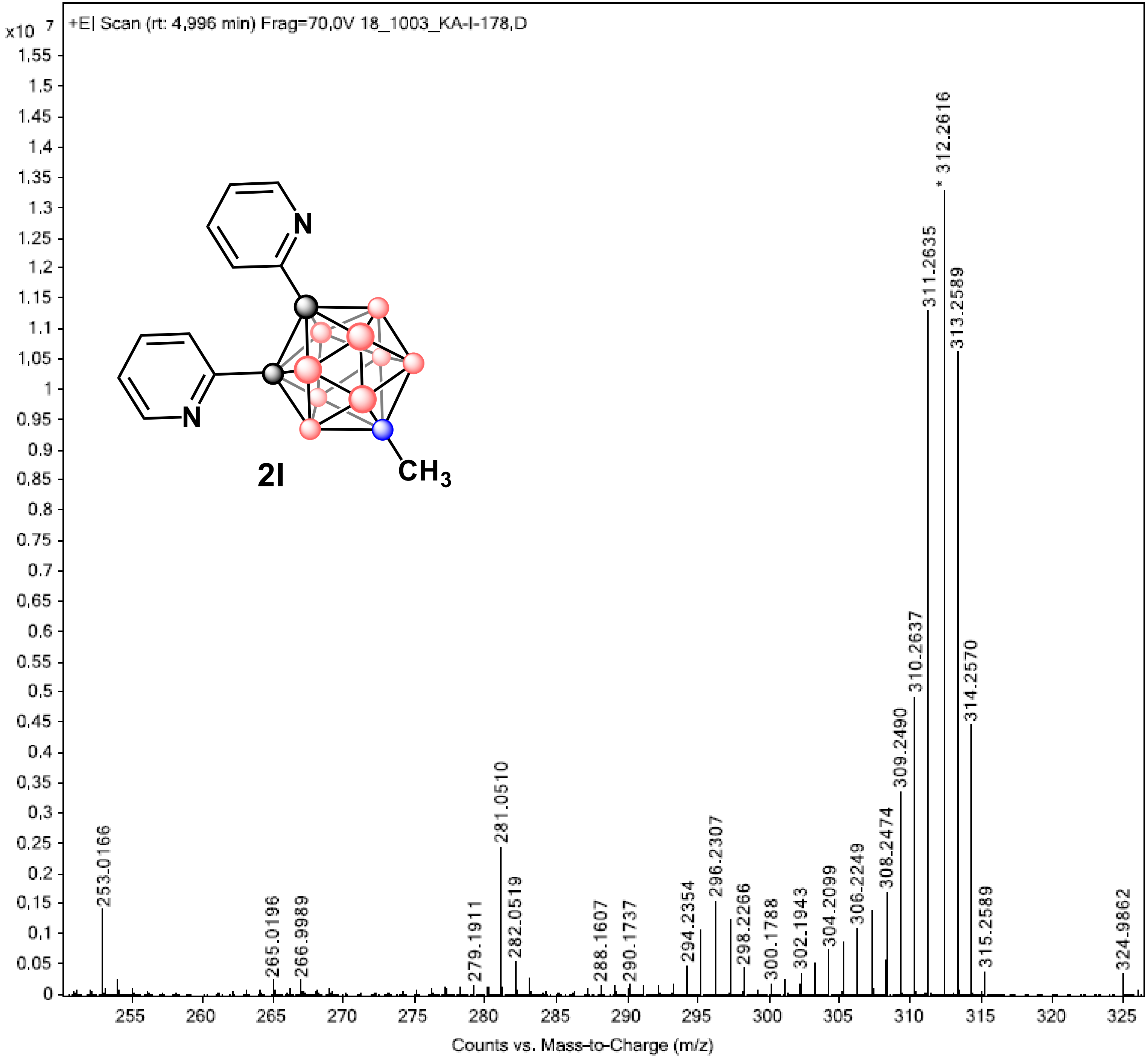

Oct04-2018-spokoyny
Account No. AAS153
KA-I-178 pure CDCl3 1H
8.22
8.21
7.65
7.65
7.54
7.11
7.11
0.35
N
N
2l
CH3
1.95
2.00
1.98
1.97
7.78
1.85
2.84
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



KA-I-178 11B
11B acquisiton-no H decoupling
7.60
-1.05
-1.95
-9.72
N
N
2l
CH3
1.03
1.08
8.00
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)


KA-I-178 11B{1H}
11B acquisiton-with H decoupling
7.60
-1.49
-9.23
N
N
2l
CH3
1.11
1.22
8.00
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)


I-178
149.38
149.14
148.58
148.55
136.59
136.58
125.58
125.30
124.15
124.12
82.45
76.22
N
N
2l
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



+EI Scan (rt: 4,996 min) Frag=70,0V 18_1003_KA-I-178,D
x10 7
1,55
1,5
1,45
1,4
1,35
1,3
1,25
1,2
1,15
1,1
1,05
1
0,95
0,9
0,85
0,8
0,75
0,7
0,65
0,6
0,55
0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
N
N
CH3
2l
* 312.2616
311.2635
313.2589
310.2637
314.2570
309.2490
308.2474
306.2249
304.2099
302.1943
300.1788
298.2266
296.2307
294.2354
290.1737
288.1607
282.0519
281.0510
279.1911
266.9989
265.0196
253.0166
315.2589
324.9862
255
260
265
270
275
280
285
290
295
300
305
310
315
320
325
Counts vs. Mass-to-Charge (m/z)