SUPPORTING INFORMATION

"Reported, but still unknown."
A closer look into 3,4-*bis*- and 3,4,5-*tris*(trifluoromethyl)pyrazoles.

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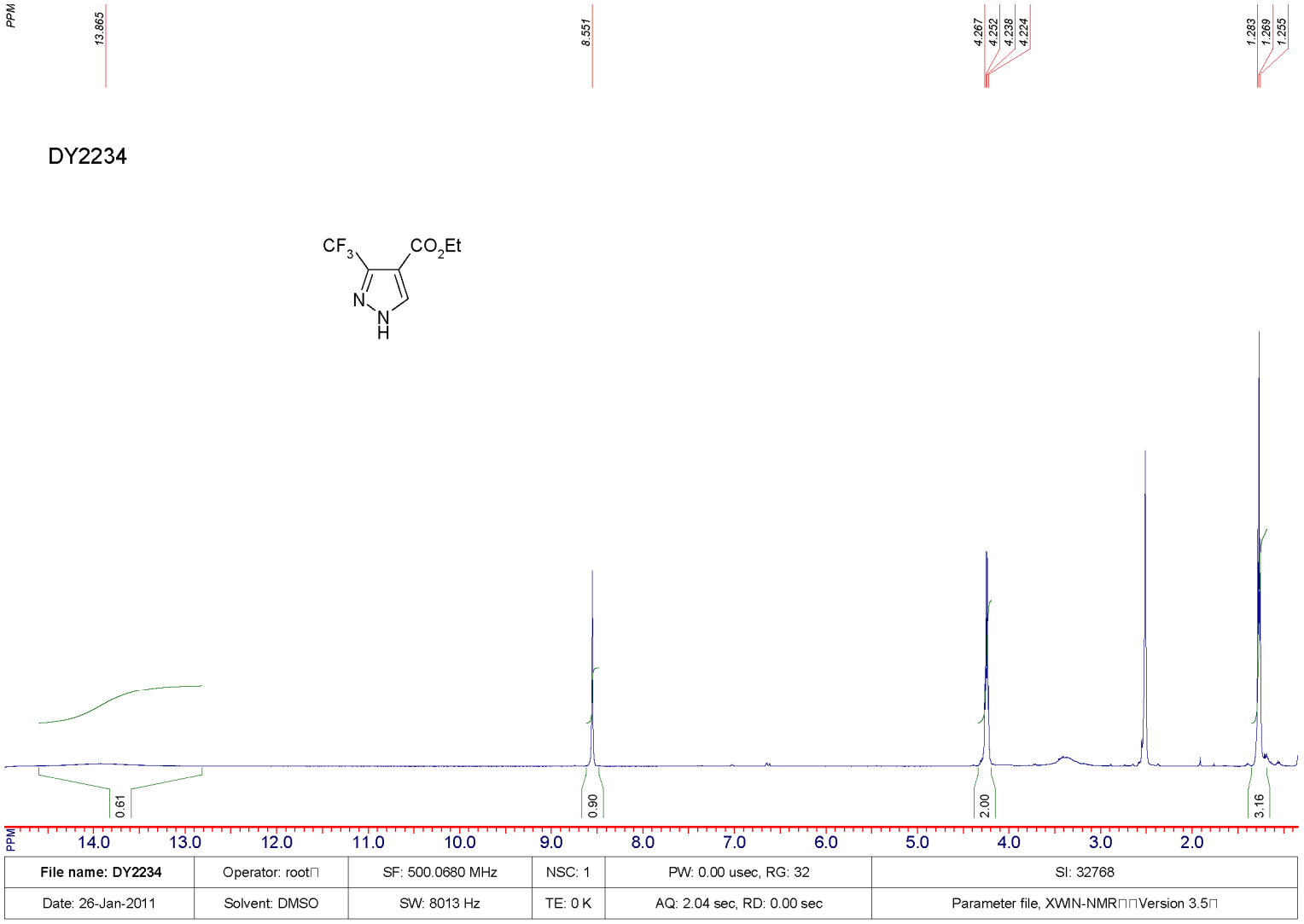
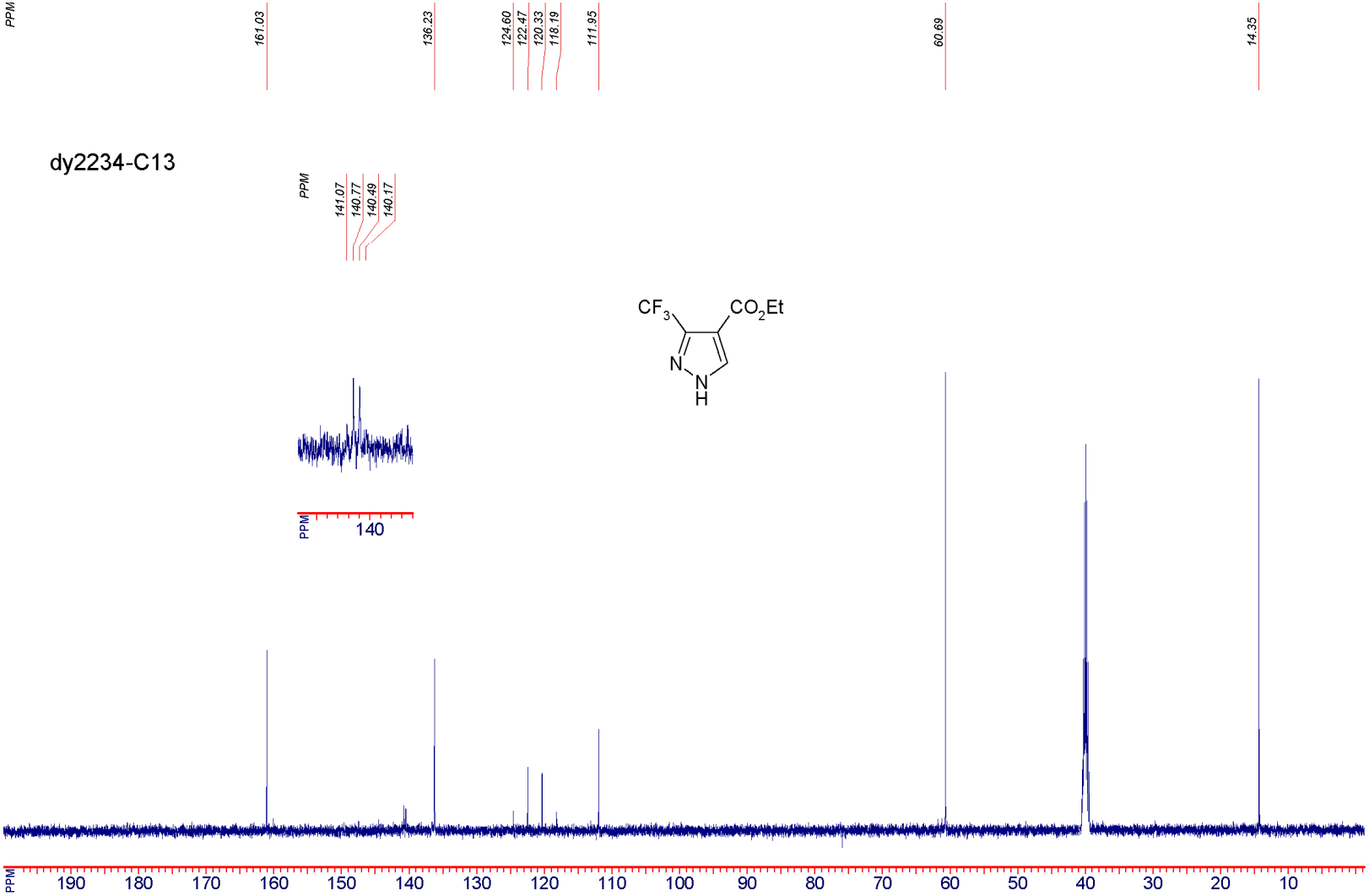
1. Copies of NMR spectra

Compound 15



File name: DY2234	Operator: root⊓	SF: 500.0680 MHz	NSC: 1	PW: 0.00 usec, RG: 32	SI: 32768
Date: 26-Jan-2011	Solvent: DMSO	SW: 8013 Hz	TE: 0 K	AQ: 2.04 sec, RD: 0.00 sec	Parameter file, XWIN-NMR⊓⊓Version 3.5⊓

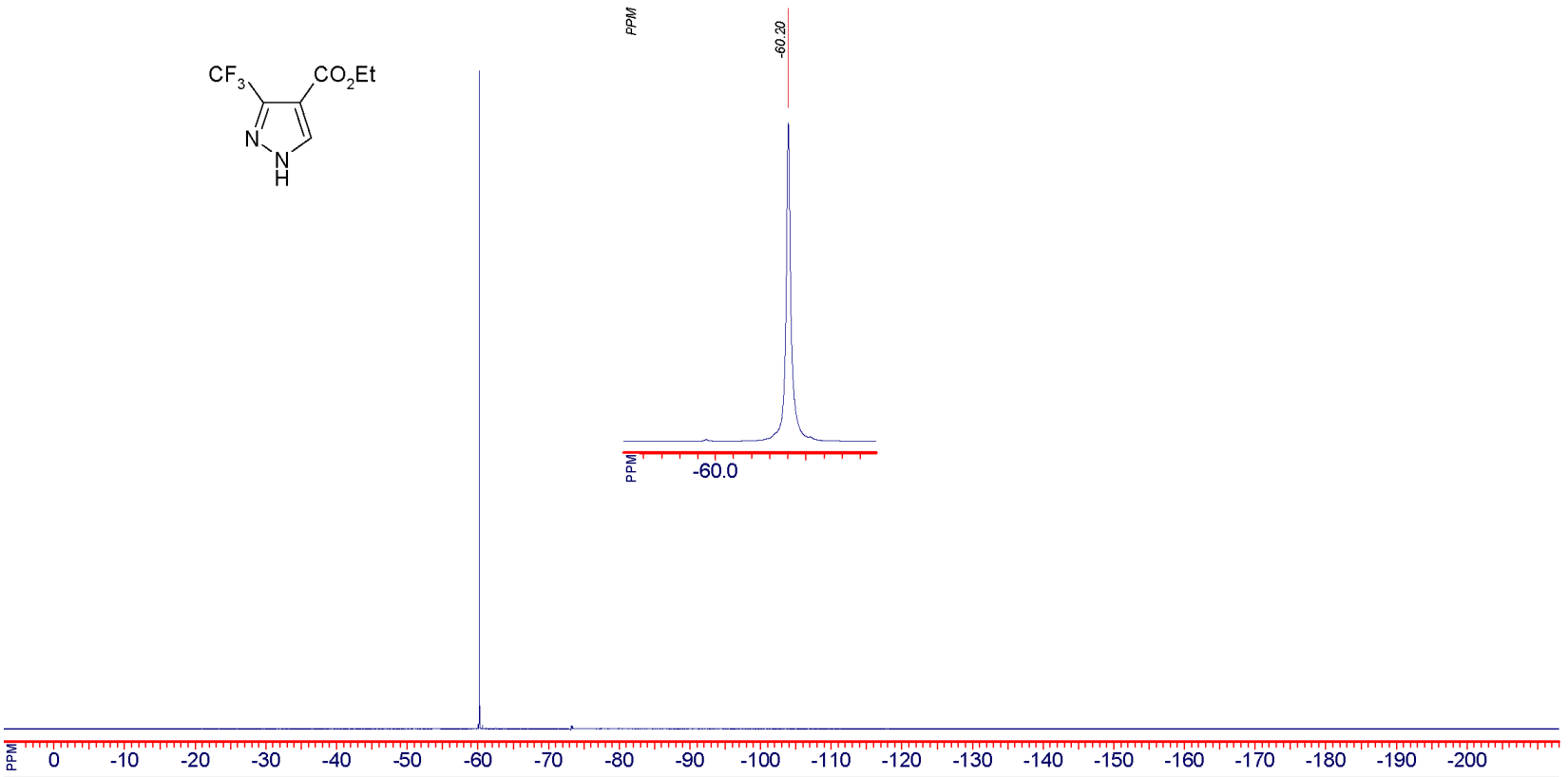
Compound 15



File name: dy2234-C13	Operator: root⊓	SF: 125.7422 MHz	NSC: 80	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 26-Jan-2011	Solvent: dmso	SW: 32680 Hz	TE: 681 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR⊓⊓Version 3.5⊓

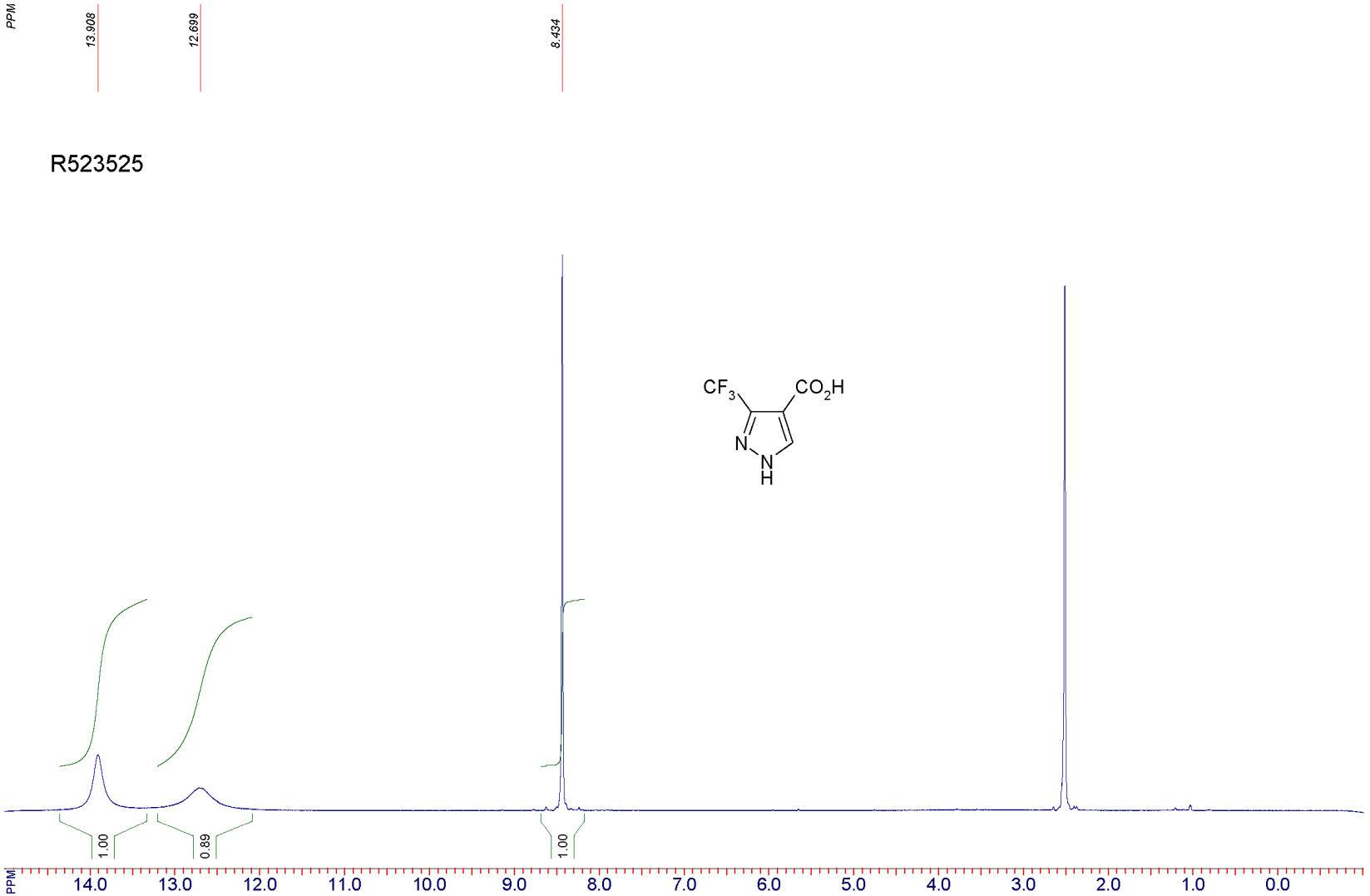
Compound 15

DY2234-F19.fid



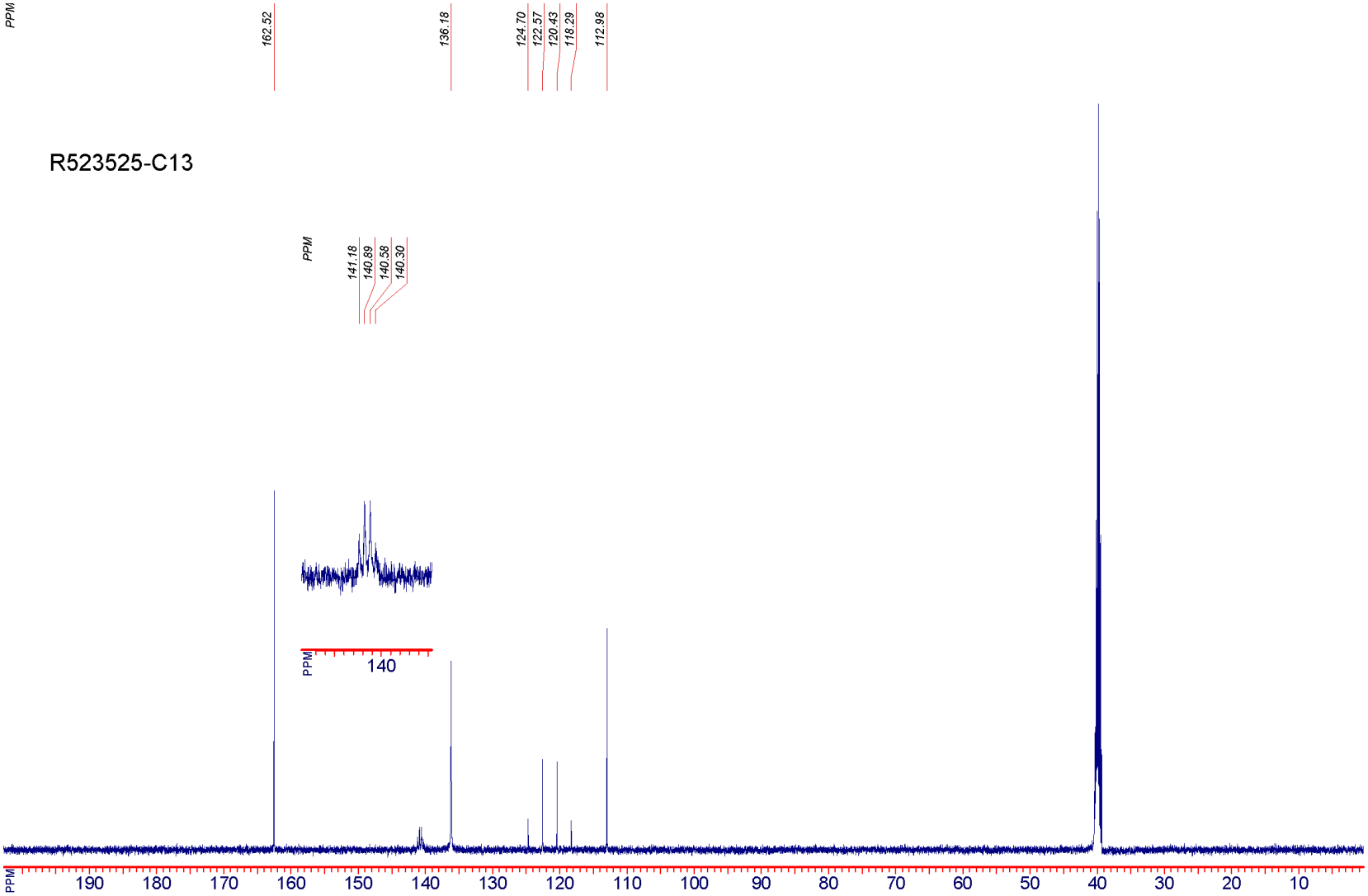
File name: DY2234-F19.fid	Operator:	SF: 376.2981 MHz	NSC: 0	PW: 3.00 usec, RG: 22	SI: 131072
Date: 27-Jan-2011	Solvent: dmso-d6	SW: 82816 Hz	TE: 293 K	AQ: 0.77 sec, RD: 0.00 sec	□

Compound 6



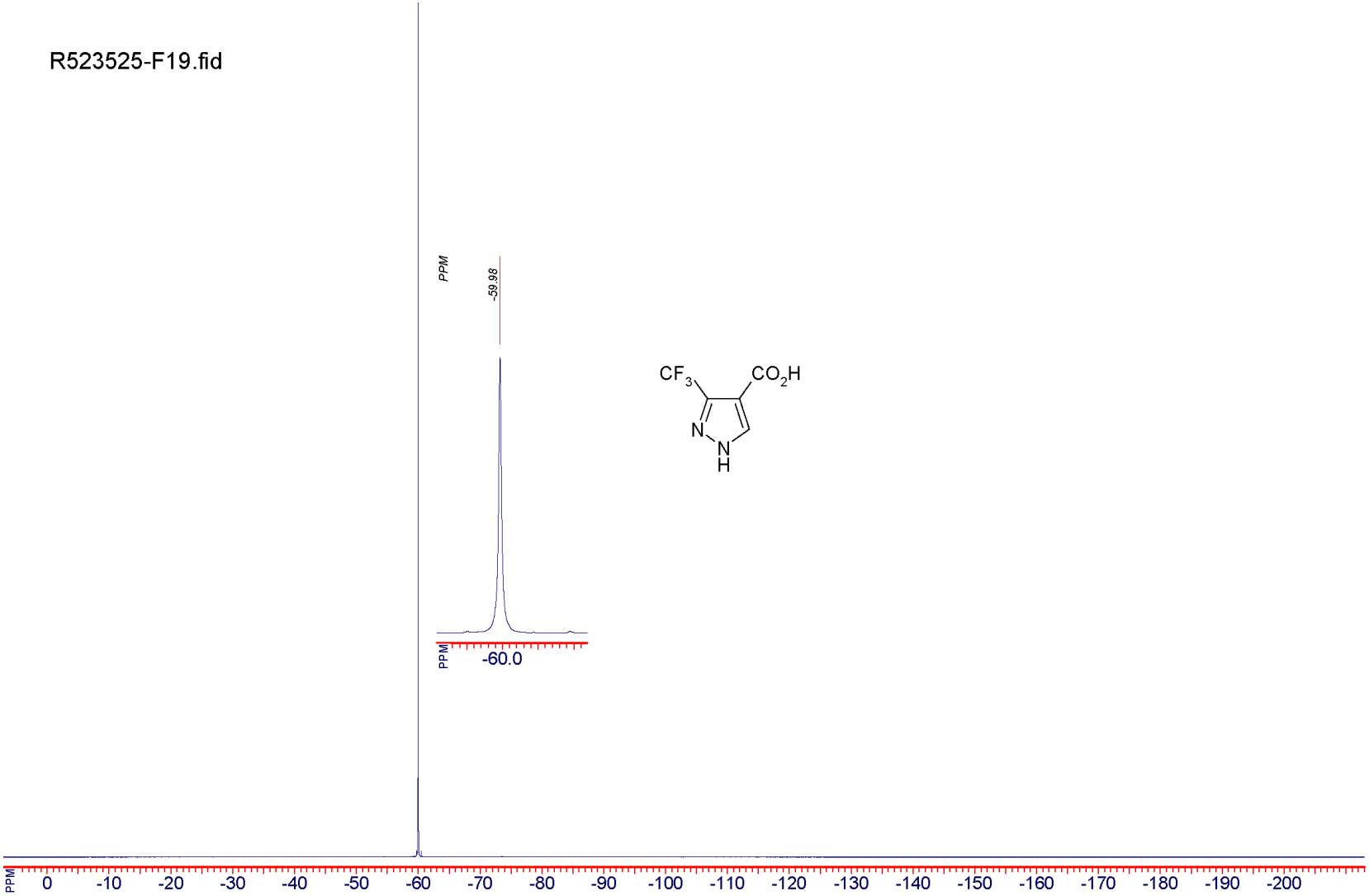
File name: R523525	Operator: root□	SF: 500.0680 MHz	NSC: 1	PW: 0.00 usec, RG: 32	SI: 32768
Date: 21-Jan-2011	Solvent: DMSO	SW: 8013 Hz	TE: 0 K	AQ: 2.04 sec, RD: 0.00 sec	Parameter file, XWIN-NMR□□Version 3.5□

Compound 6



File name: R523525-C13	Operator: root⊓	SF: 125.7422 MHz	NSC: 284	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 21-Jan-2011	Solvent: dmso	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR⊓⊓Version 3.5⊓

Compound 6



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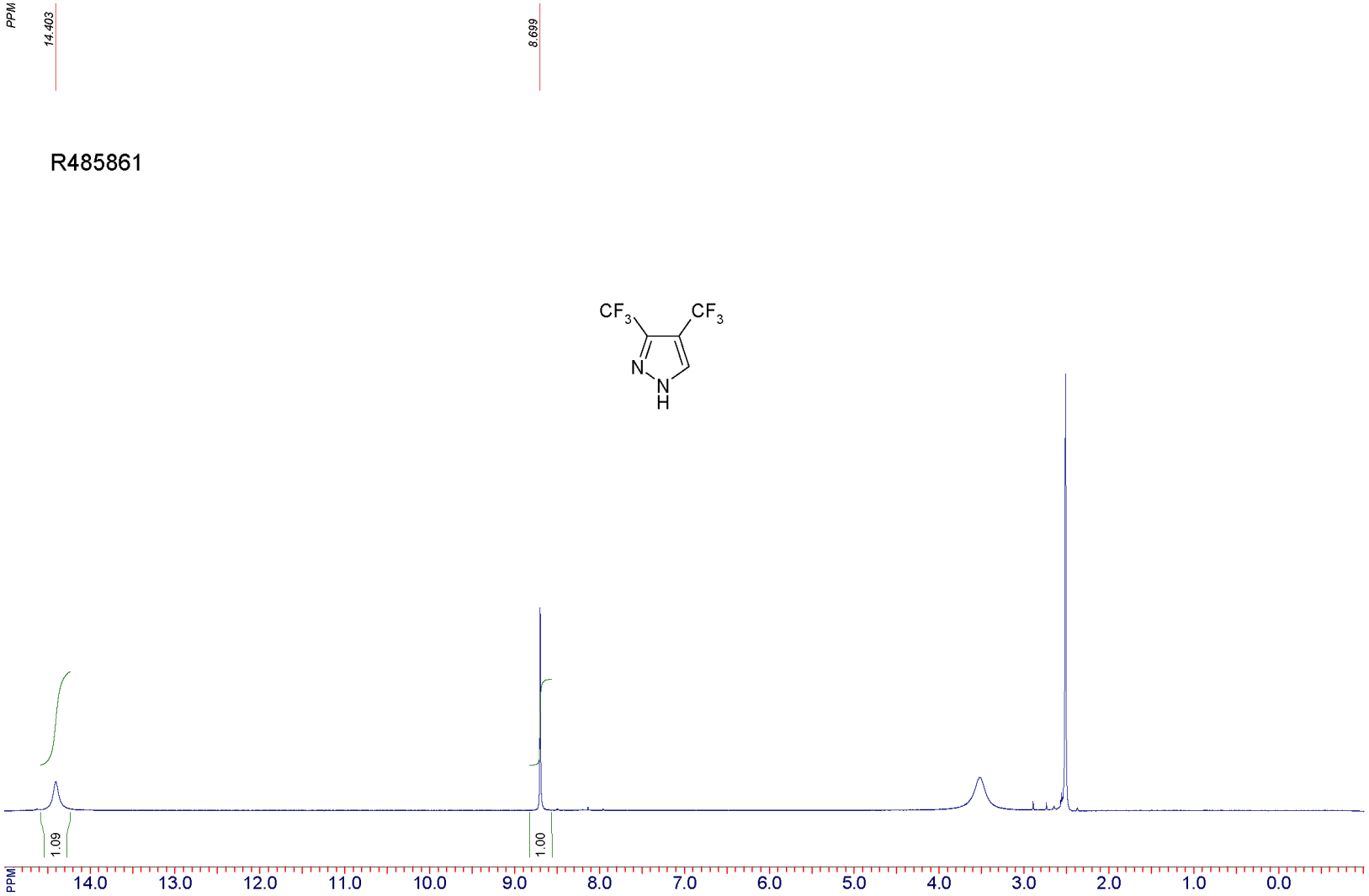
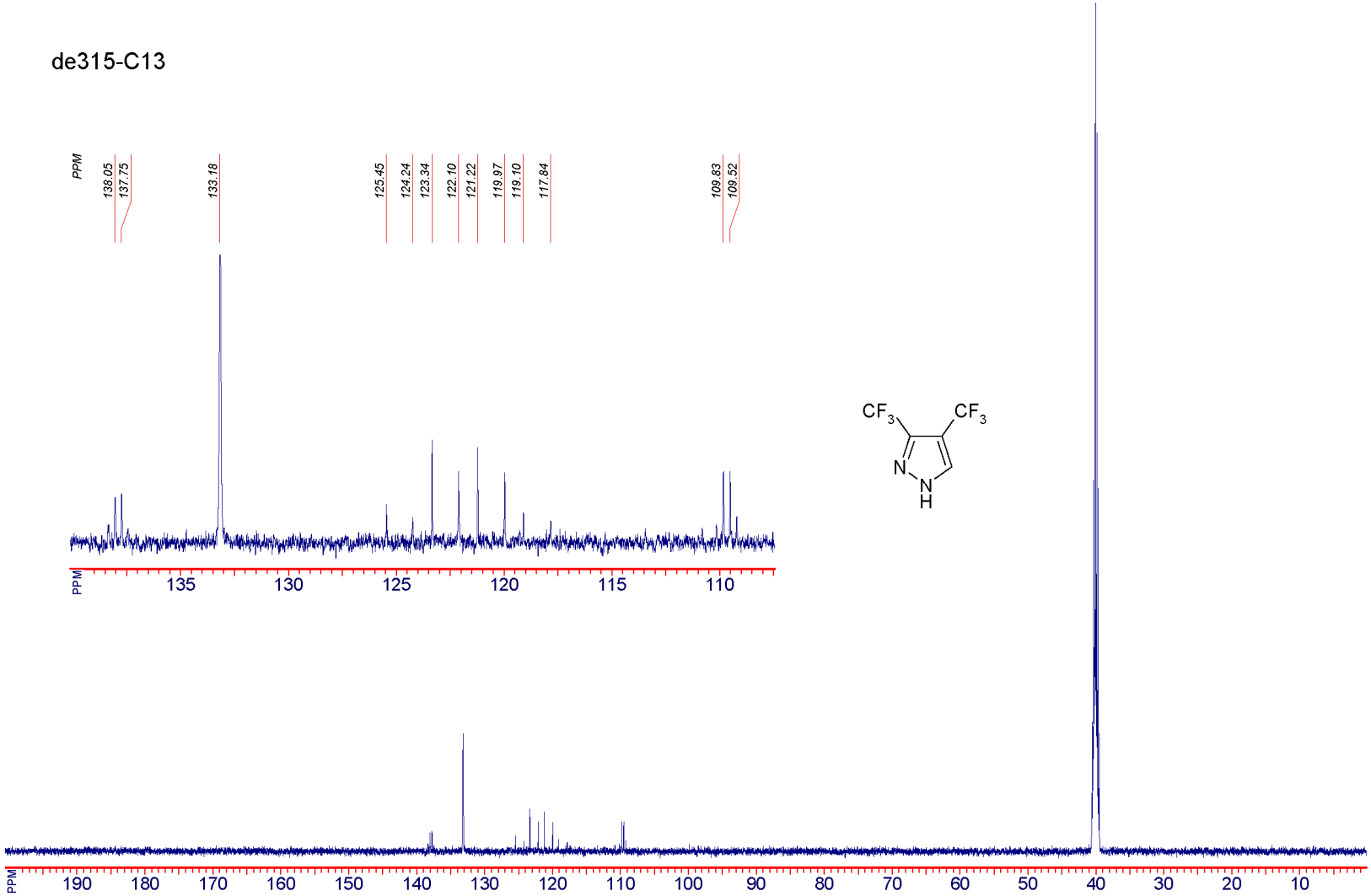
Date: 21-Jan-2011	Solvent: dmso-d6	SW: 82816 Hz	TE: 293 K	AQ: 0.77 sec, RD: 0.00 sec	⊓

Compound 4



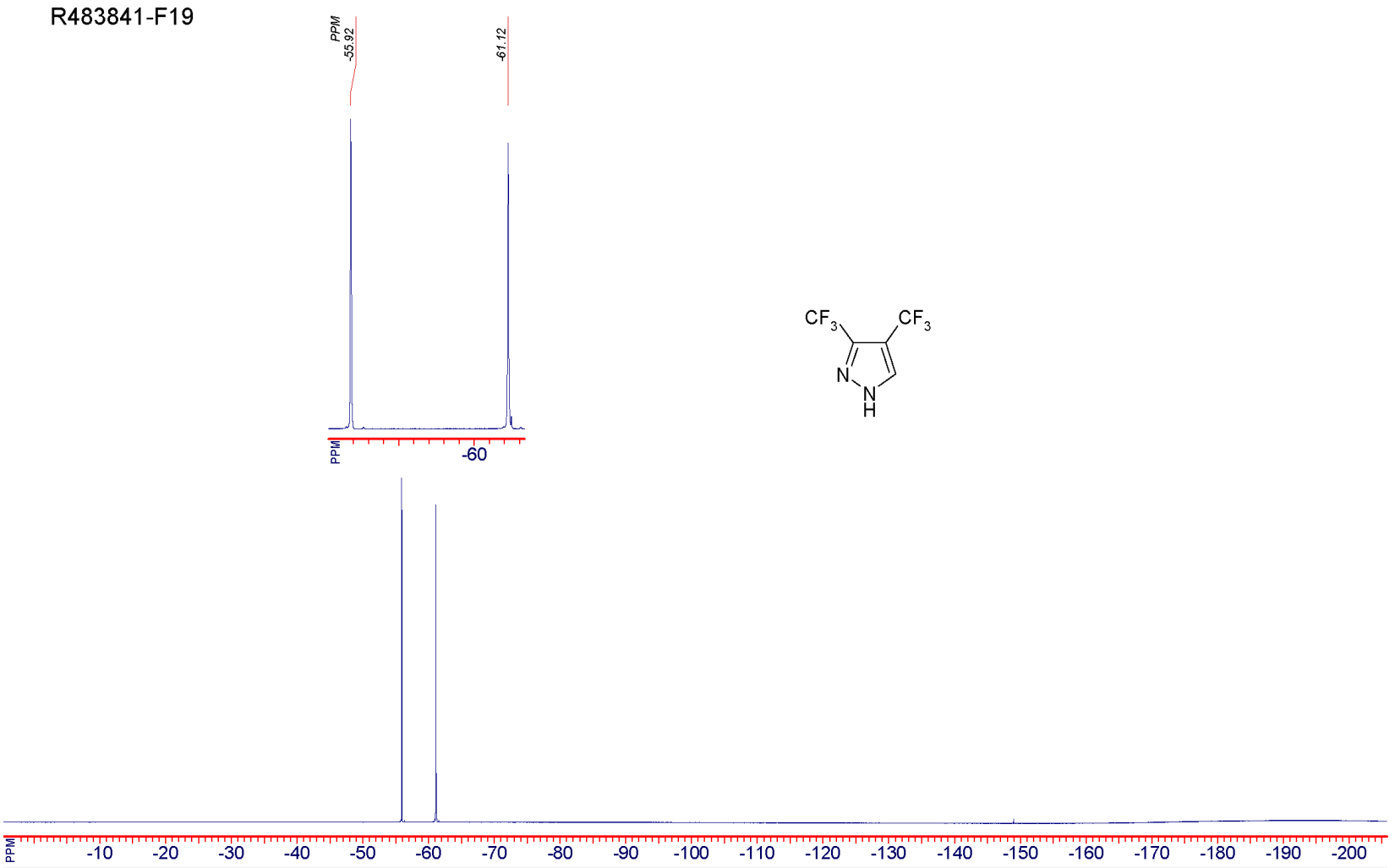
File name: R485861	Operator: root⊓	SF: 500.1300 MHz	NSC: 1	PW: 0.00 usec, RG: 40	SI: 32768
Date: 10-Feb-2009	Solvent: CDCl3	SW: 8013 Hz	TE: 680 K	AQ: 2.04 sec, RD: 0.00 sec	Parameter file, XWIN-NMR⊓⊓Version 3.5⊓

Compound 4



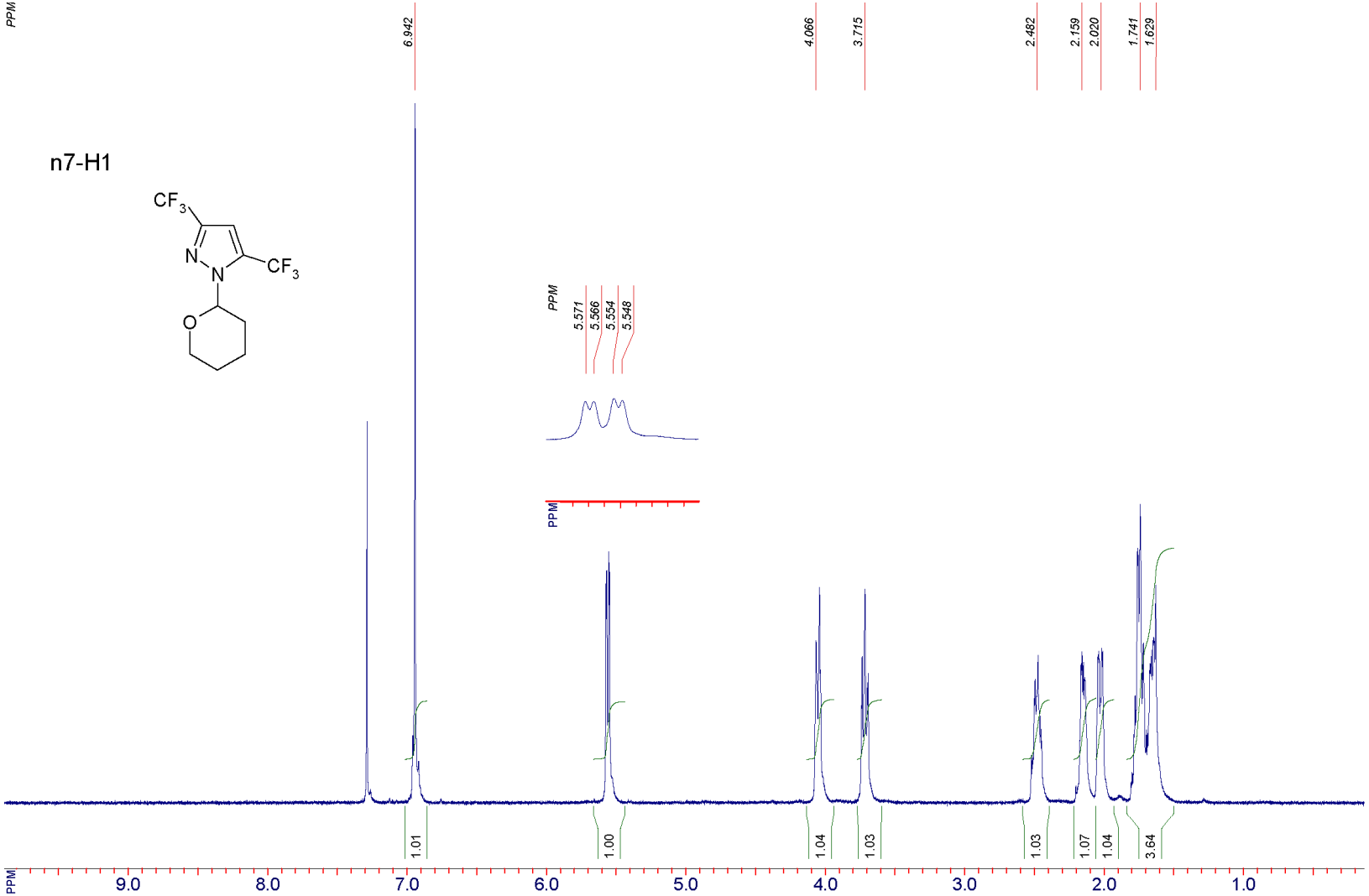
File name: de315-C13	Operator: root⊓	SF: 125.7422 MHz	NSC: 618	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 07-Feb-2011	Solvent: dmso-d6	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR⊓⊓Version 3.5⊓

Compound 4



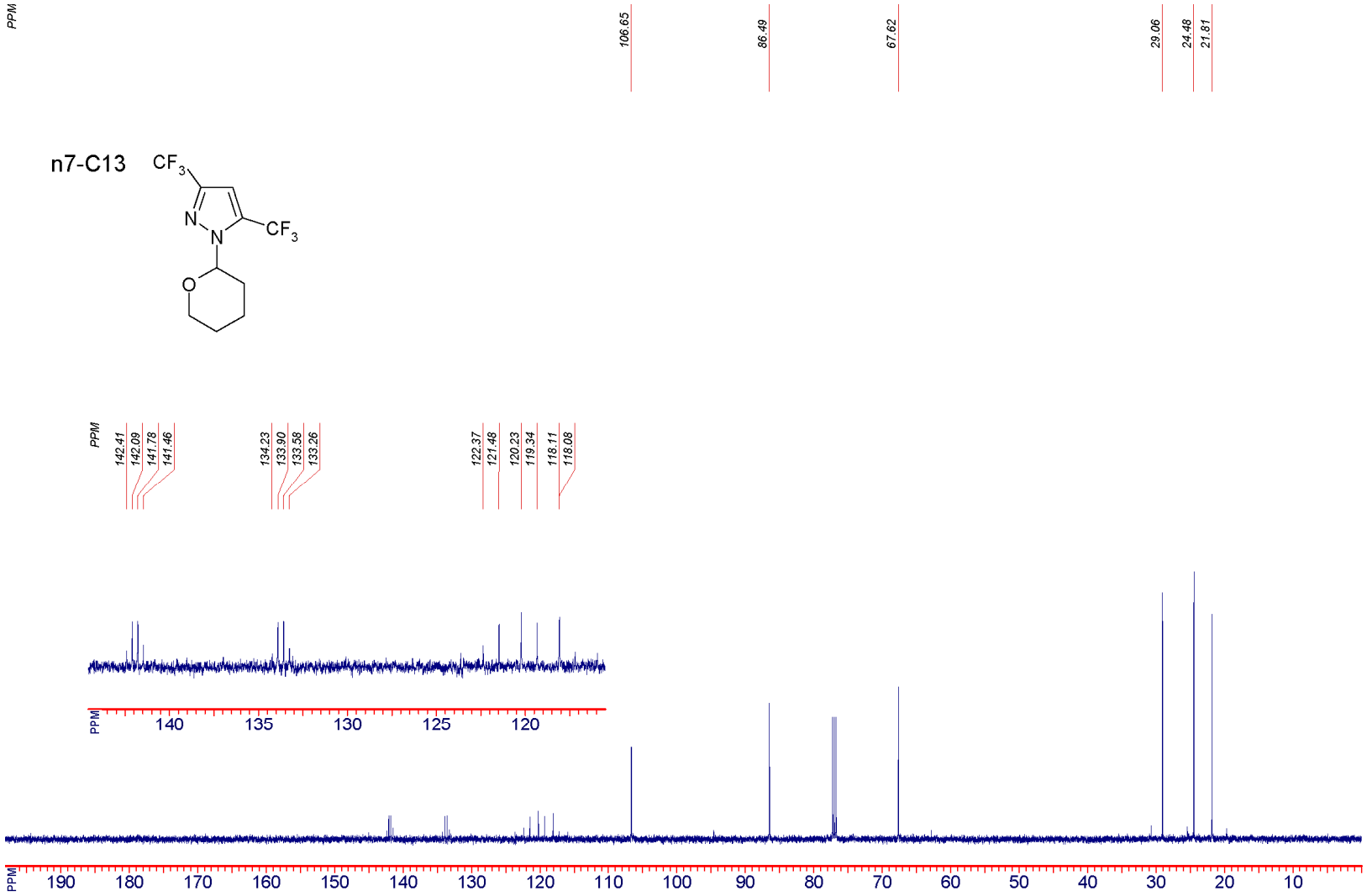
File name: R483841-F19	Operator: psmП	SF: 470.5926 MHz	NSC: 4	PW: 0.00 usec, RG: 128	SI: 65536
Date: 31-Jan-2009	Solvent: DMSO	SW: 99010 Hz	TE: 677 K	AQ: 0.66 sec, RD: 0.00 sec	Parameter file, XWIN-NMRПППVersion 3.5П

Compound 12



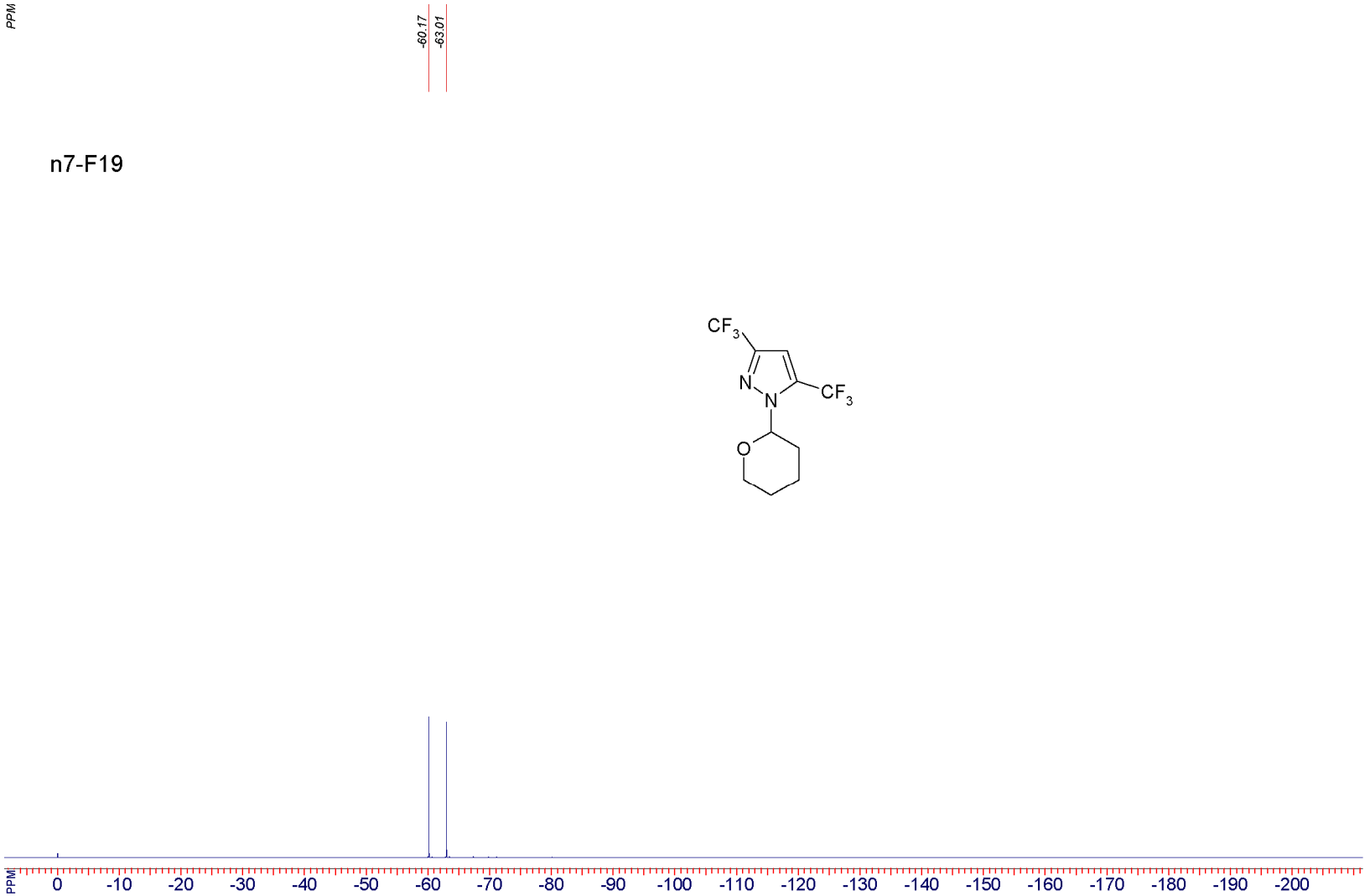
File name: n7-H1	Operator: root⊓	SF: 500.1300 MHz	NSC: 1	PW: 0.00 usec, RG: 40	SI: 32768
Date: 29-Sep-2009	Solvent: DMSO	SW: 8013 Hz	TE: 682 K	AQ: 2.04 sec, RD: 0.00 sec	Parameter file, XWIN-NMR⊓⊓Version 3.5⊓

Compound 12



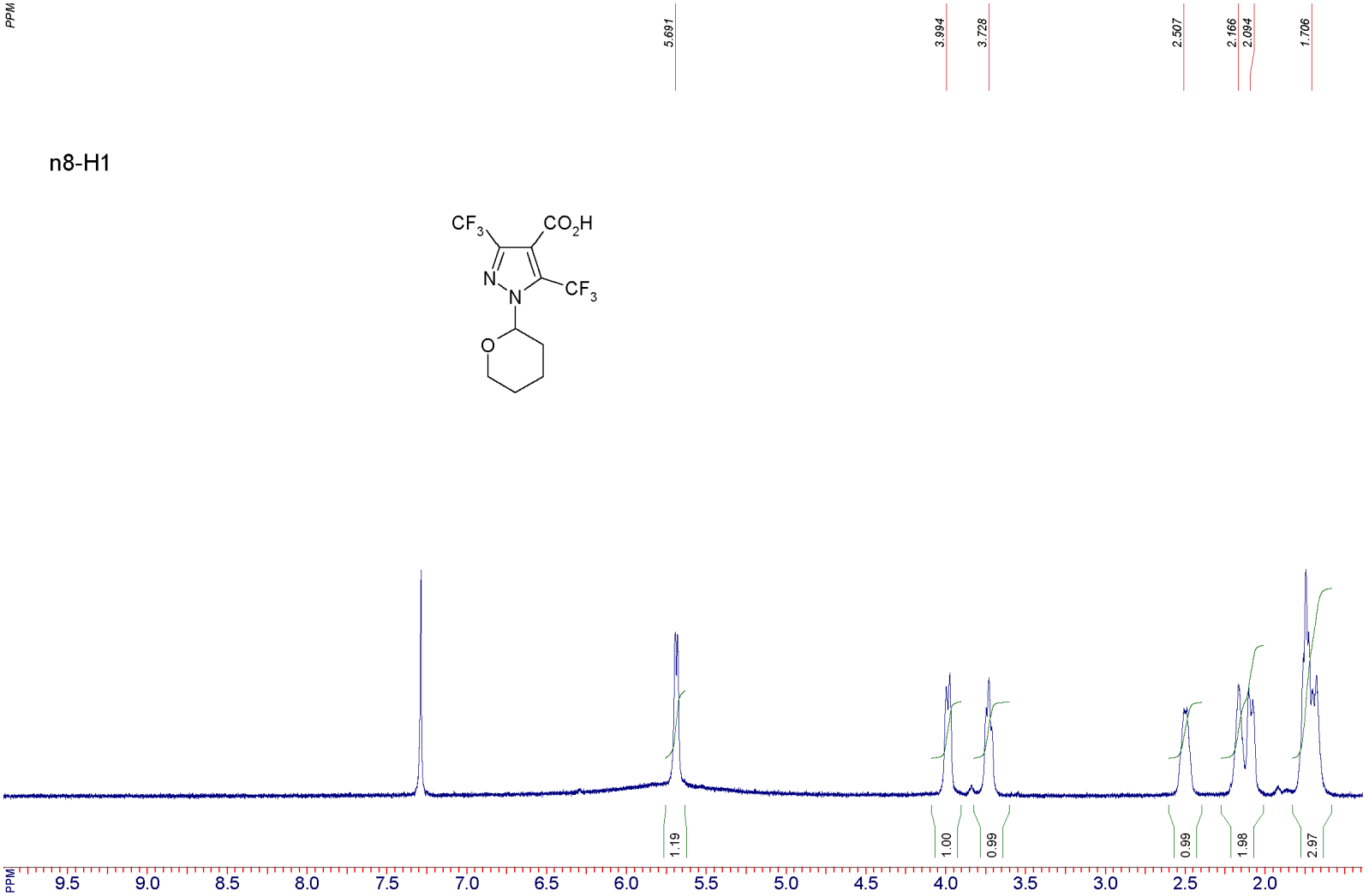
File name: n7-C13	Operator: root⊓	SF: 125.7422 MHz	NSC: 41	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 06-Jun-2011	Solvent: cdcl3	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR⊓⊓Version 3.5⊓

Compound 12



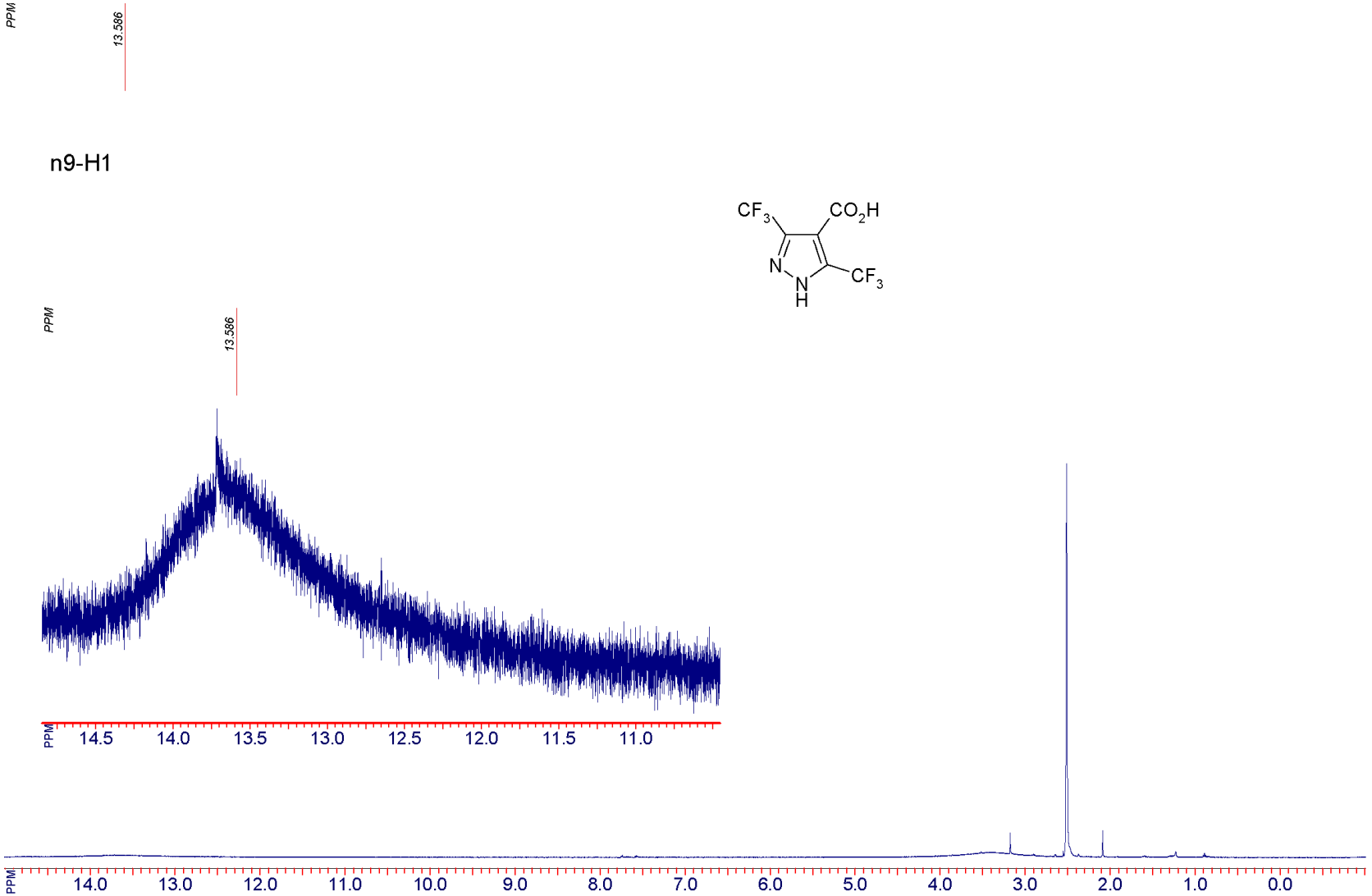
File name: n7-F19	Operator:	SF: 376.2973 MHz	NSC: 0	PW: 3.00 usec, RG: 24	SI: 131072
Date: 06-Jun-2011	Solvent: cdcl3	SW: 82816 Hz	TE: 293 K	AQ: 0.77 sec, RD: 0.00 sec	□

Compound 17



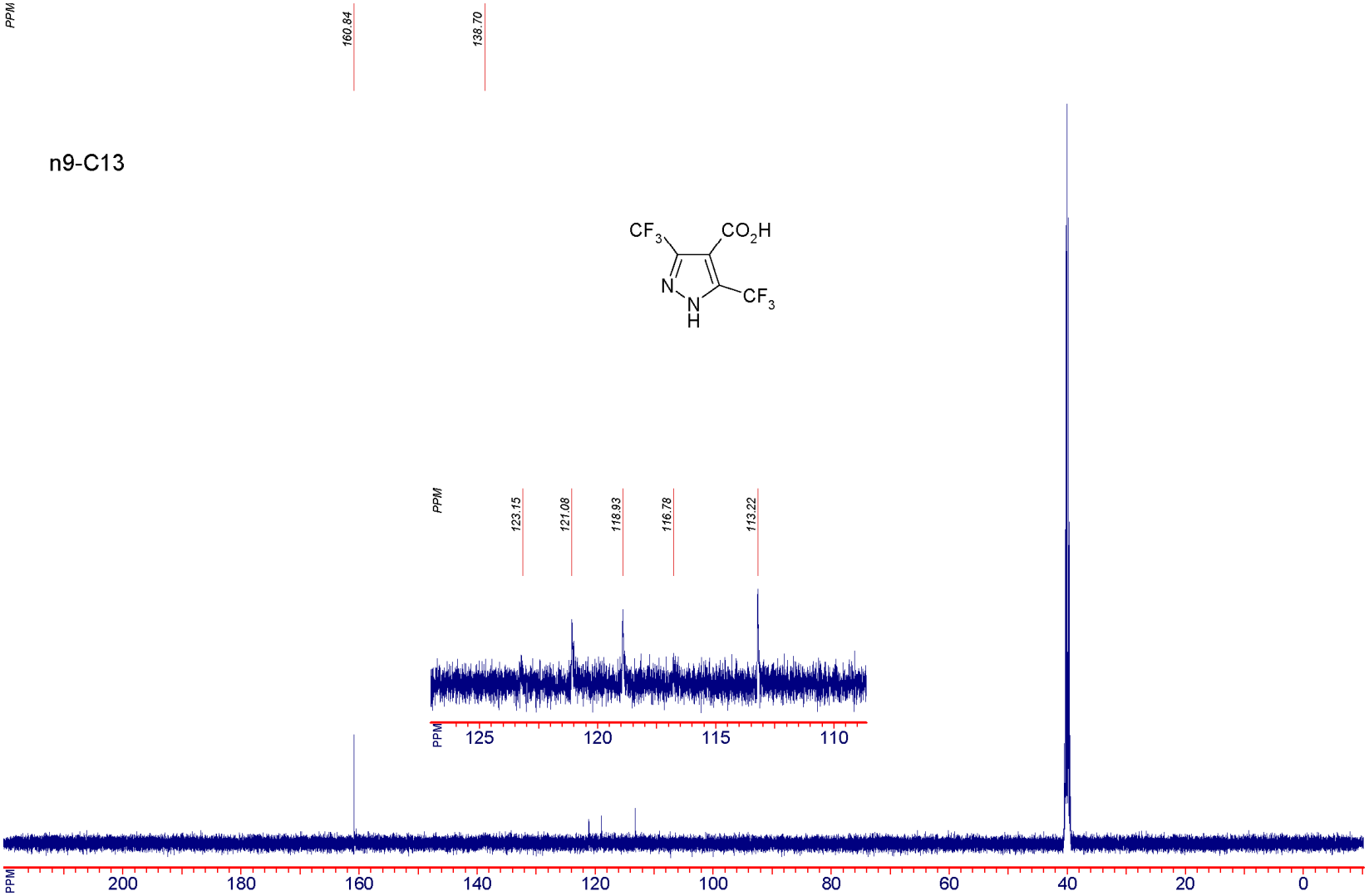
File name: n8-H1	Operator: root⊓	SF: 500.1300 MHz	NSC: 1	PW: 0.00 usec, RG: 40	SI: 32768
Date: 08-Sep-2009	Solvent: CDCl3	SW: 8013 Hz	TE: 0 K	AQ: 2.04 sec, RD: 0.00 sec	Parameter file, XWIN-NMR⊓⊓Version 3.5⊓

Compound 11



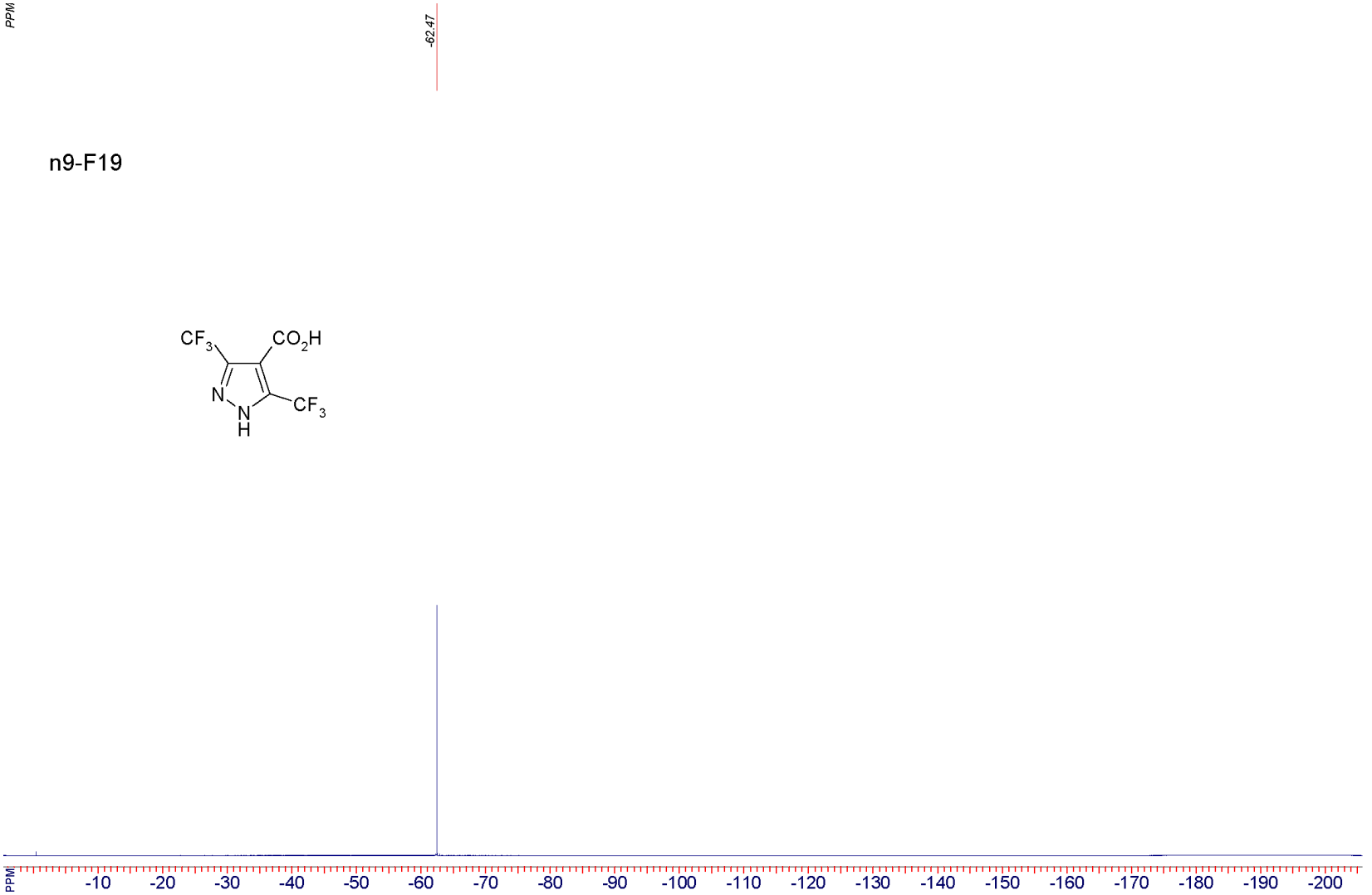
File name: n9-H1	Operator: root⊓	SF: 500.1300 MHz	NSC: 1	PW: 0.00 usec, RG: 40	SI: 32768
Date: 17-Oct-2009	Solvent: CDCl3	SW: 8013 Hz	TE: 0 K	AQ: 2.04 sec, RD: 0.00 sec	Parameter file, XWIN-NMR⊓⊓Version 3.5⊓

Compound 11



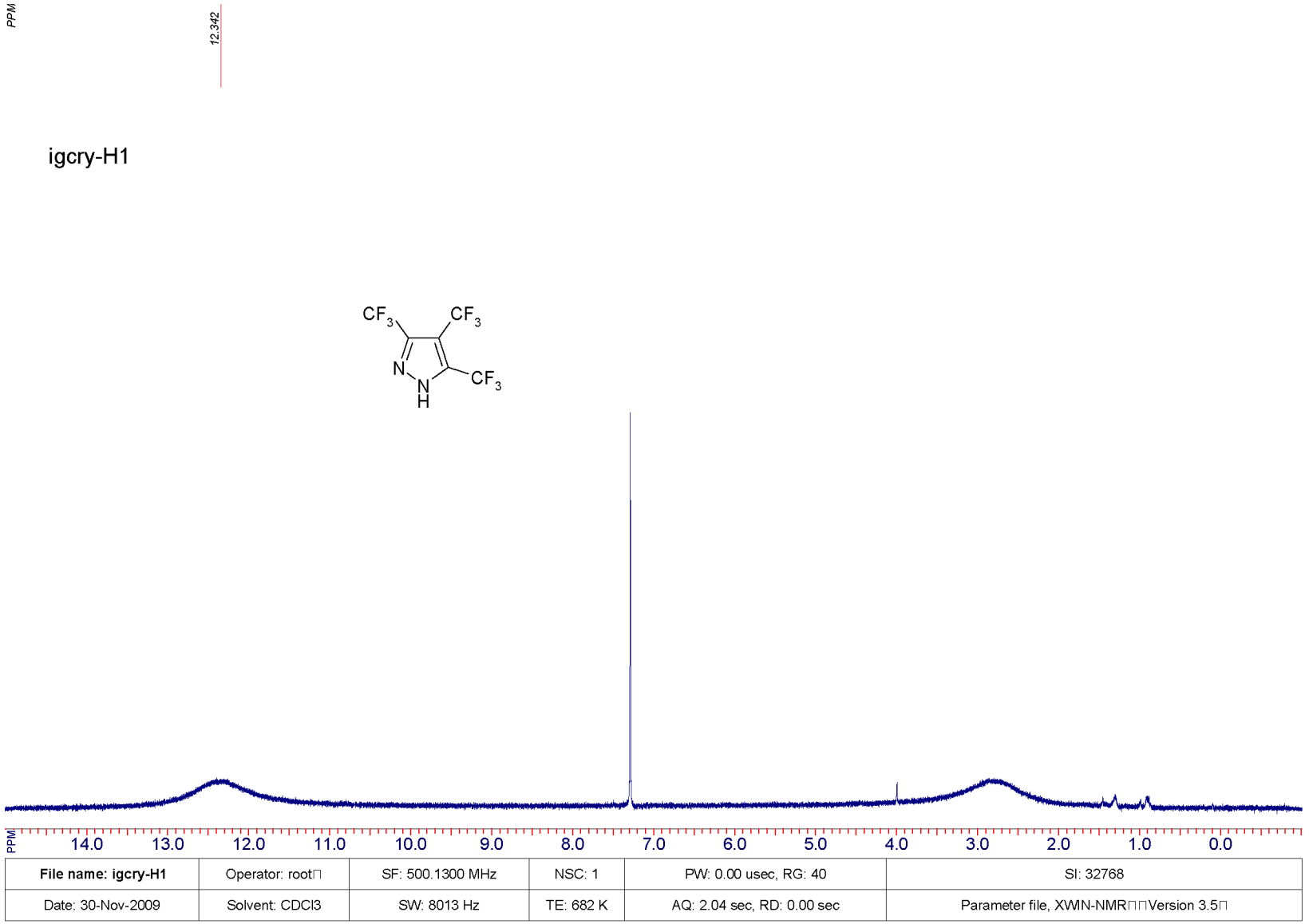
File name: n9-C13	Operator: root⊓	SF: 125.7578 MHz	NSC: 627	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 10-Sep-2009	Solvent: CDCl3	SW: 28986 Hz	TE: 682 K	AQ: 1.77 sec, RD: 0.00 sec	Parameter file, XWIN-NMR⊓⊓Version 3.5⊓

Compound 11



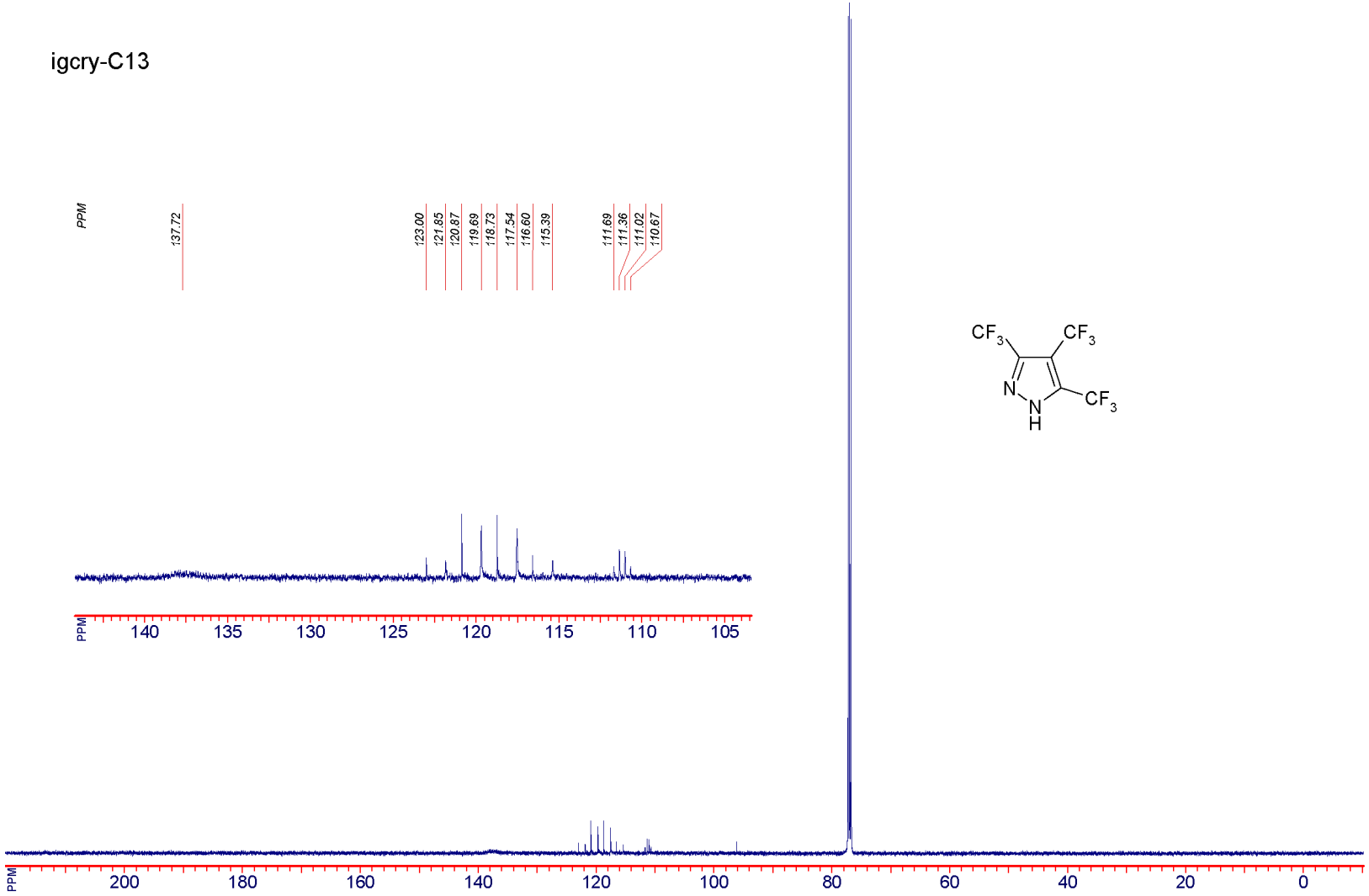
File name: n9-F19	Operator: psm⊓	SF: 470.5926 MHz	NSC: 8	PW: 0.00 usec, RG: 512	SI: 65536
Date: 14-Aug-2009	Solvent: C6D6	SW: 99010 Hz	TE: 679 K	AQ: 0.66 sec, RD: 0.00 sec	Parameter file, XWIN-NMR⊓⊓Version 3.5⊓

Compound 3



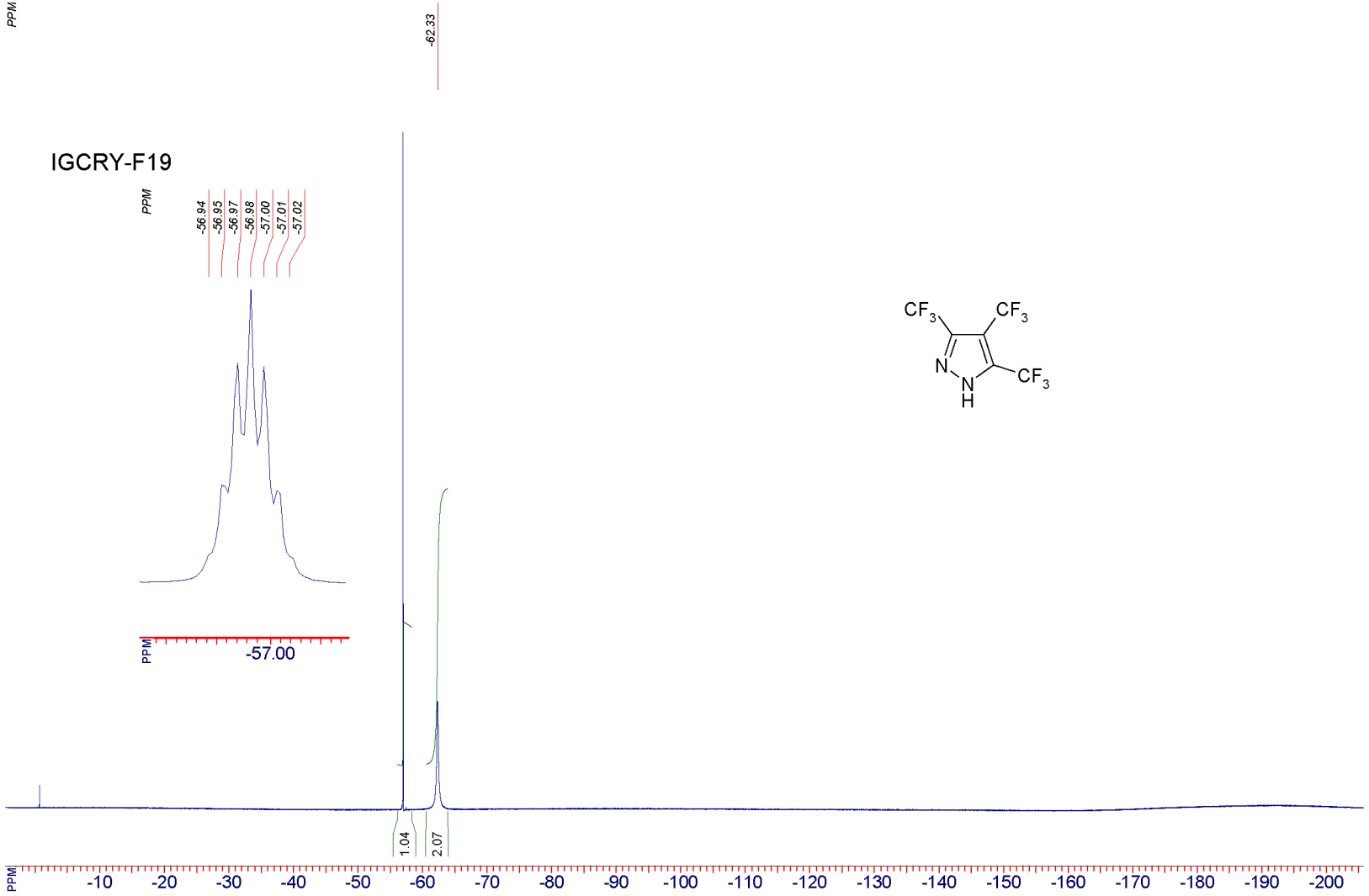
File name: igcry-H1	Operator: rootП	SF: 500.1300 MHz	NSC: 1	PW: 0.00 usec, RG: 40	SI: 32768
Date: 30-Nov-2009	Solvent: CDCl3	SW: 8013 Hz	TE: 682 K	AQ: 2.04 sec, RD: 0.00 sec	Parameter file, XWIN-NMRПППVersion 3.5П

Compound 3



File name: igcry-C13	Operator: root⊓	SF: 125.7578 MHz	NSC: 5120	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 01-Dec-2009	Solvent: CDCl3	SW: 28986 Hz	TE: 681 K	AQ: 1.77 sec, RD: 0.00 sec	Parameter file, XWIN-NMR⊓⊓Version 3.5⊓

Compound 3



File name: IGCRY-F19	Operator: psmΠ	SF: 470.5926 MHz	NSC: 4	PW: 0.00 usec, RG: 512	SI: 65536
Date: 05-Dec-2009	Solvent: C6D6	SW: 99010 Hz	TE: 0 K	AQ: 0.66 sec, RD: 0.00 sec	Parameter file, XWIN-NMRΠΠVersion 3.5Π

2. Determinations of pK_a values of pyrazoles 4 and 5.

pK_a values of pyrazoles **4** and **5** were determined by potentiometric titration using an automatic pH-meter with glass electrode. To measure ionization constants a certain amount of the sample was dissolved in a water-acetonitrile solution containing 0.15 M KCl to adjust the ionic strength. Titrations of the compounds were performed in aqueous-acetonitrile mixture with the percentage ratio of the solvents ranging from 80:20 to 35:65, respectively. The solutions were titrated with 0.07 M KOH at a constant temperature of 23 ºC. On the basis of the obtained potentiometric curves (Figure 1) the ionization constants in the aqueous-acetonitrile solutions (psK_a values) were calculated. Aqueous pK_a values were obtained by extrapolation to 100% water using a linear relationship between psK_a value and acetonitrile concentration (Figure 2).[1,2]

The obtained pK_a values are summarized in Table 1.

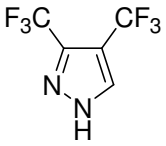
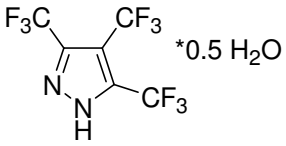
Compound		pK_a
4		8.2±0.1
5		4.5±0.1

Table 1. Ionization constants of pyrazoles **4** and **5** in aqueous solution.

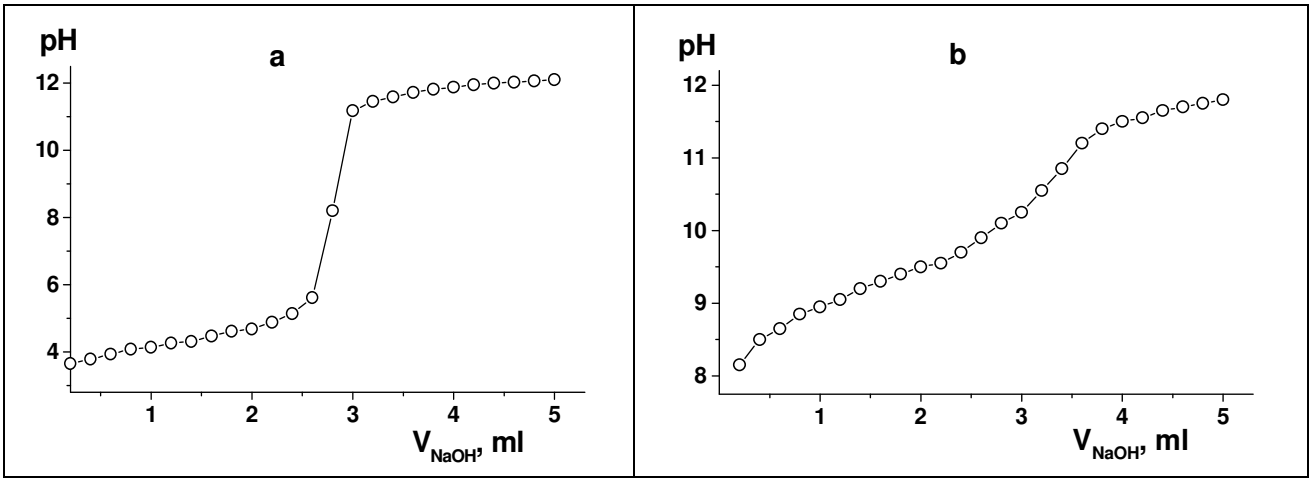


Figure 1. Potentiometric titration curves for pyrazole **5** (a) and pyrazole **4** (b). C_{BH} = 0.01 M, C_{NaOH} = 0.07 M, C_{H_2O}:C_{CH_3CN} (%) = 80:20 (2). V_0 = 20 mL.

Figure 2. Determination of ionization constants of pyrazole **5** (1) and pyrazole **4** (2) in aqueous solution.

1. Albert, A.; Sergeant, E. P. Ionization constants of acids and bases, Wiley, Inc., New York, **1962**.

2. Denesh, I. Titration in non-aqueous media [Russian translation], Mir, Moscow, **1971**.

3. Fluorescence measurements.

Fluorescent properties of compounds **4** and **5** were investigated in DMSO solution. The organic solvent was of spectroscopic grade. Fluorescence emission spectra were measured at LS55 spectrofluorometer The spectra were recorded within the range 300-600 nm. The data collection frequency was 0.5 nm. The excitation and emission slits were 15 and 20 nm, respectively. The excitation wavelength was 277 nm. The spectra were obtained after subtracting the background of the solvent. The fluorescence maxima agreed within 0.5-1.0 nm in independent parallel measurements (Figure 1).

Figure 1. Fluorescence emission spectra of pyrazole **5** (1) and pyrazole **4** (2) in DMSO solution. $C_{sub}= 5\cdot10^{-4}$ M. $\lambda^{exi}= 277$ nm. L = 1cm, slits 15; 20.