Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for:

Three and Four Coordinate Fe Carbodiphosphorane Complexes

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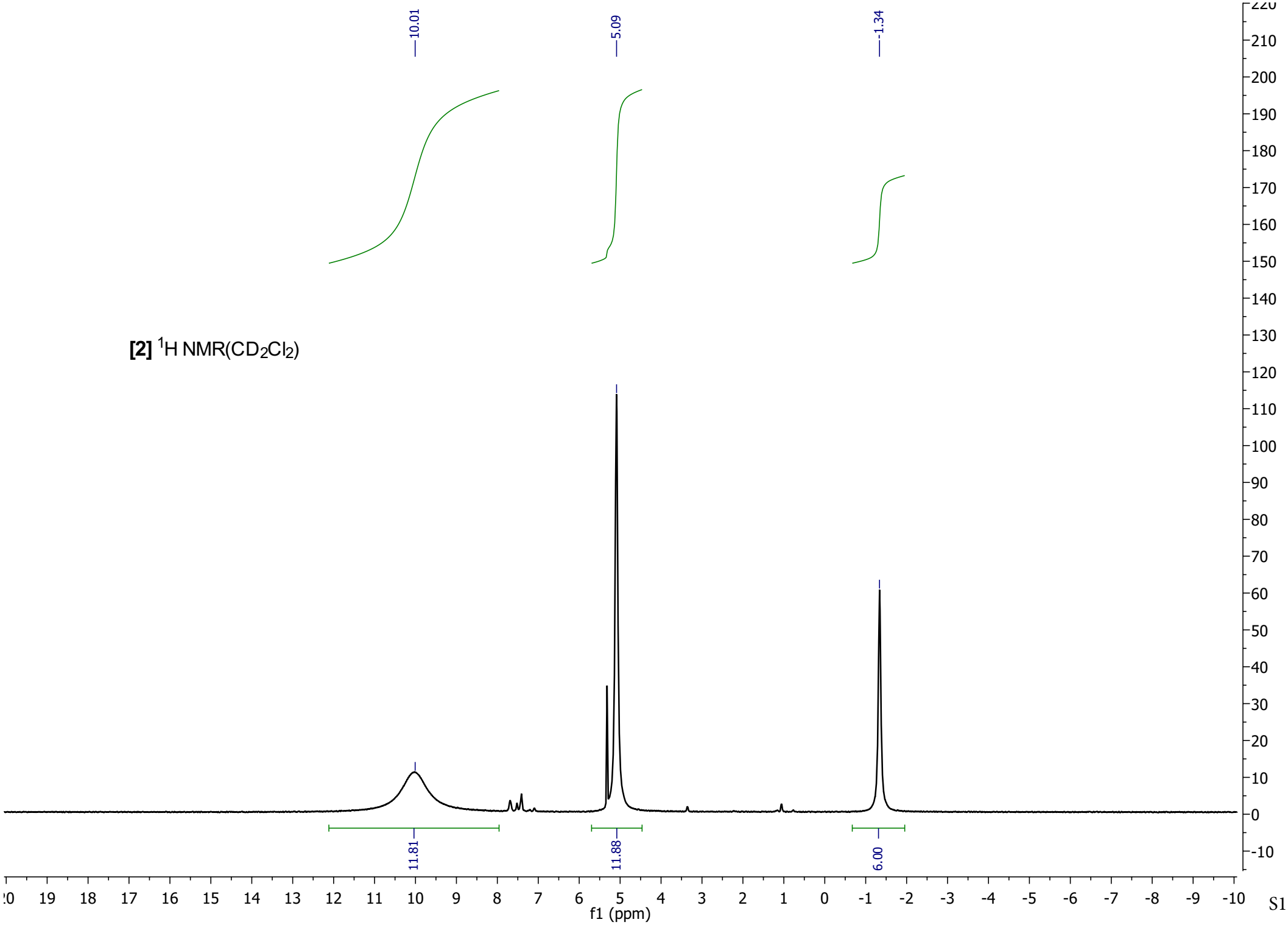
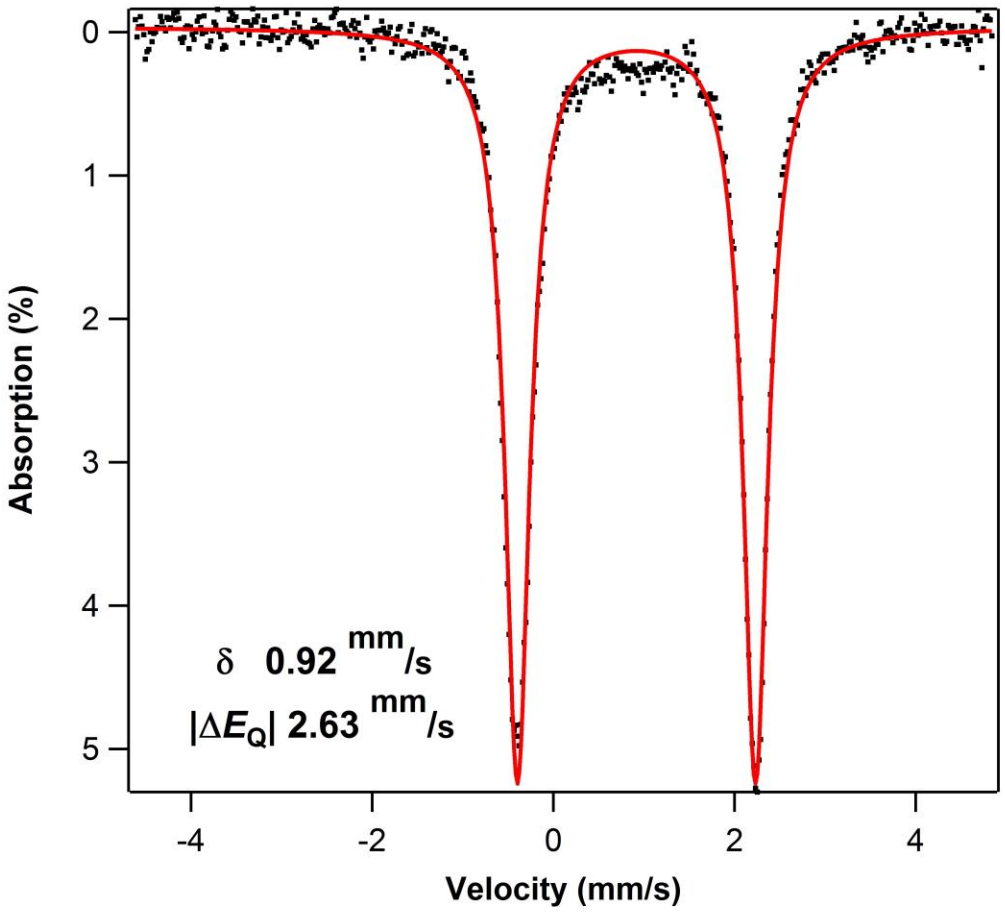
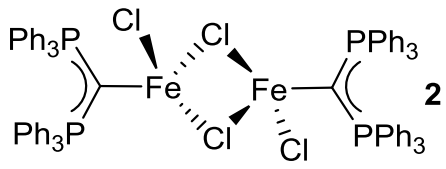
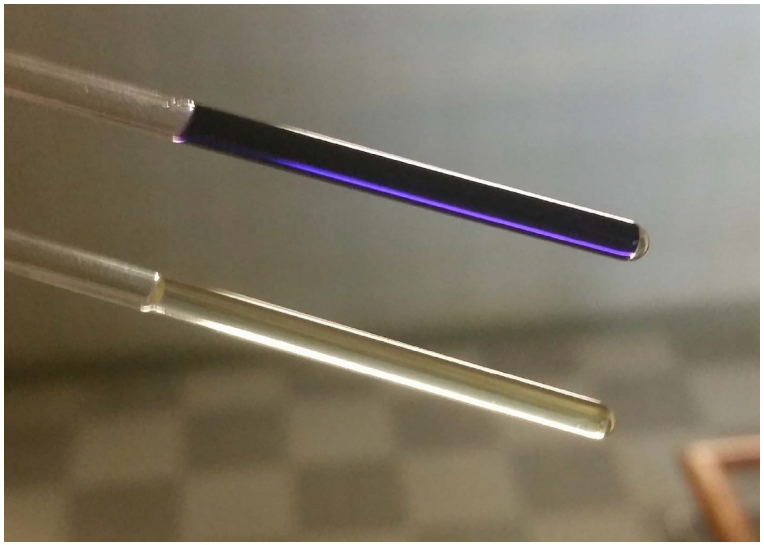

10.01
5.09
1.34
[2] 1H NMR(CD2Cl2)
11.81
11.88
6.00
f1 (ppm)





2

^{57}Fe Mössbauer spectrum was collected at 90K on a constant acceleration spectrometer (SEE Co, Minneapolis, MN). Isomer shifts are reported relative to Fe foil at room temperature. Data was analyzed and simulated using the Igor Pro 6 software (WaveMetrics, Portland, OR) with Lorentzian fitting functions. The sample (30 mg) was suspended in Paratone oil and immobilized by rapid freezing in liquid nitrogen



[2] in $CDCl_3$

[2] in CD_2Cl_2

[2] + $CDCl_3$
^1H NMR ($CDCl_3$):

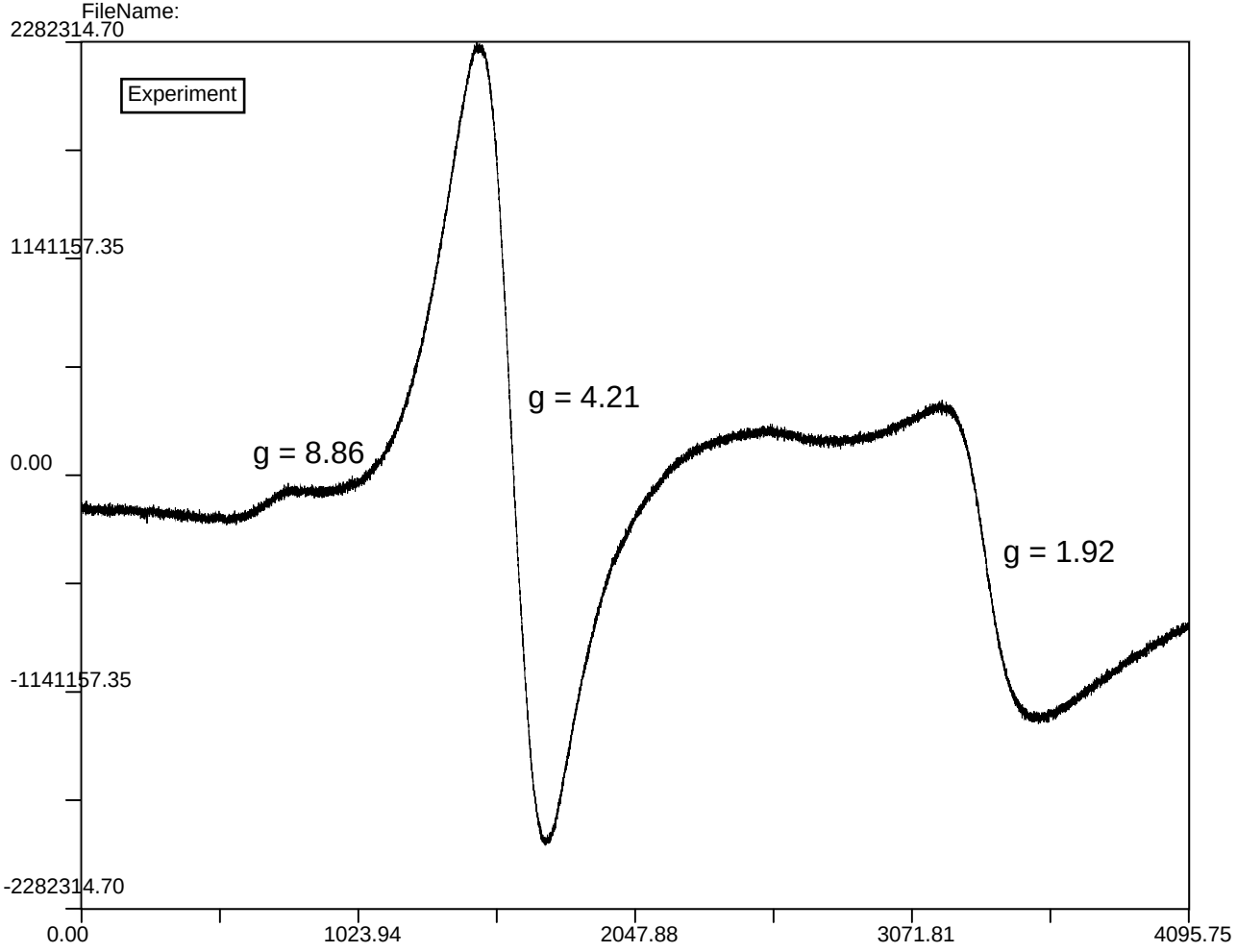
Public EPR Software Tools
National Institute of Environmental Health Sciences
National Institutes of Health, USA
http://epr.niehs.nih.gov/

Spectral Parameters:

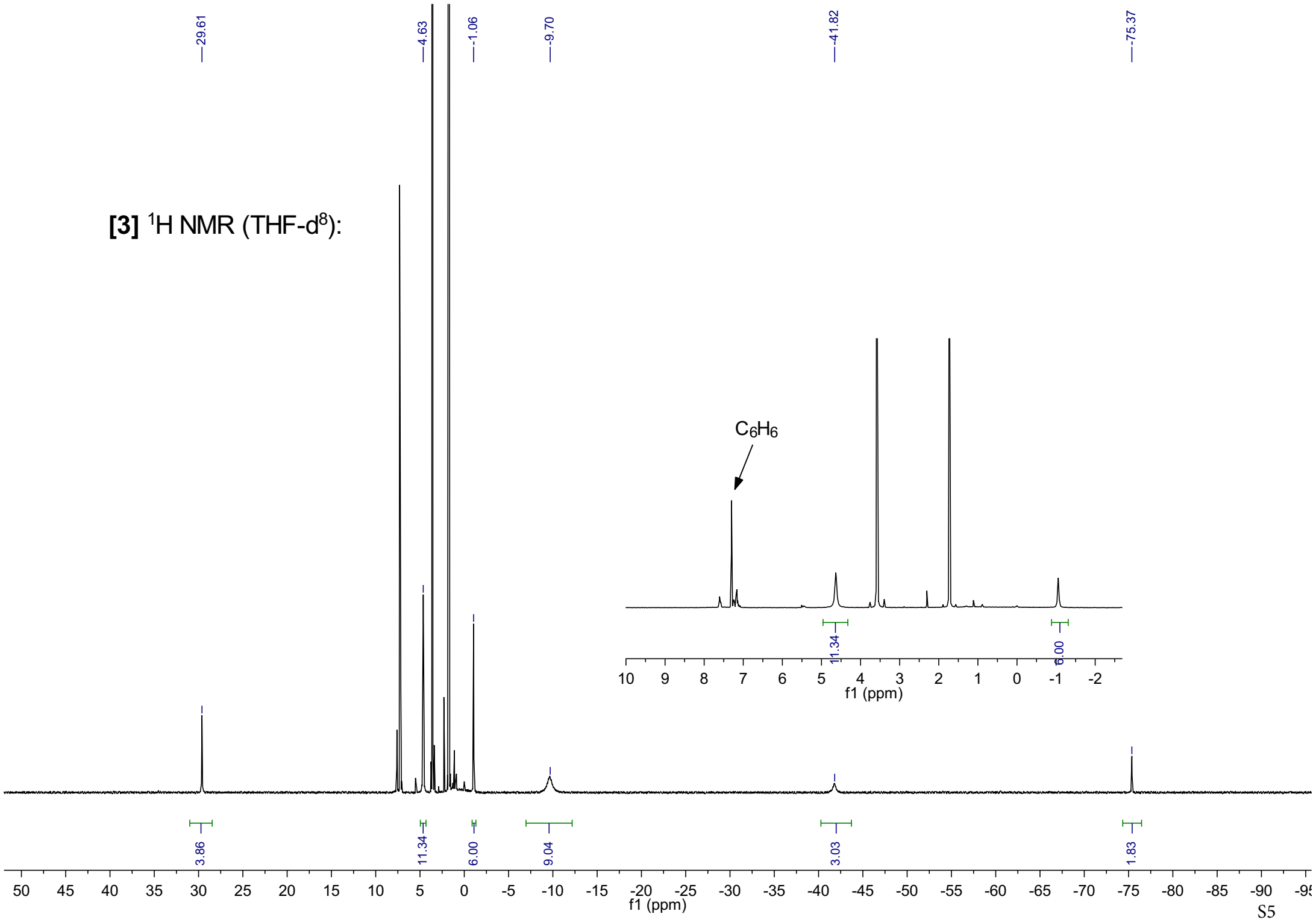
Field Center:	2047.875 G	Time Constant:	0.010000
Scan Range:	4095.750 G	Rec. Gain:	632.455505
Data Points:	16384	MW Freq.:	9.387916 GHz
Mod. Amp.:	4.000000 G	MW Power:	0.542300 mw
Mod. Freq:	100.000000 KHz		

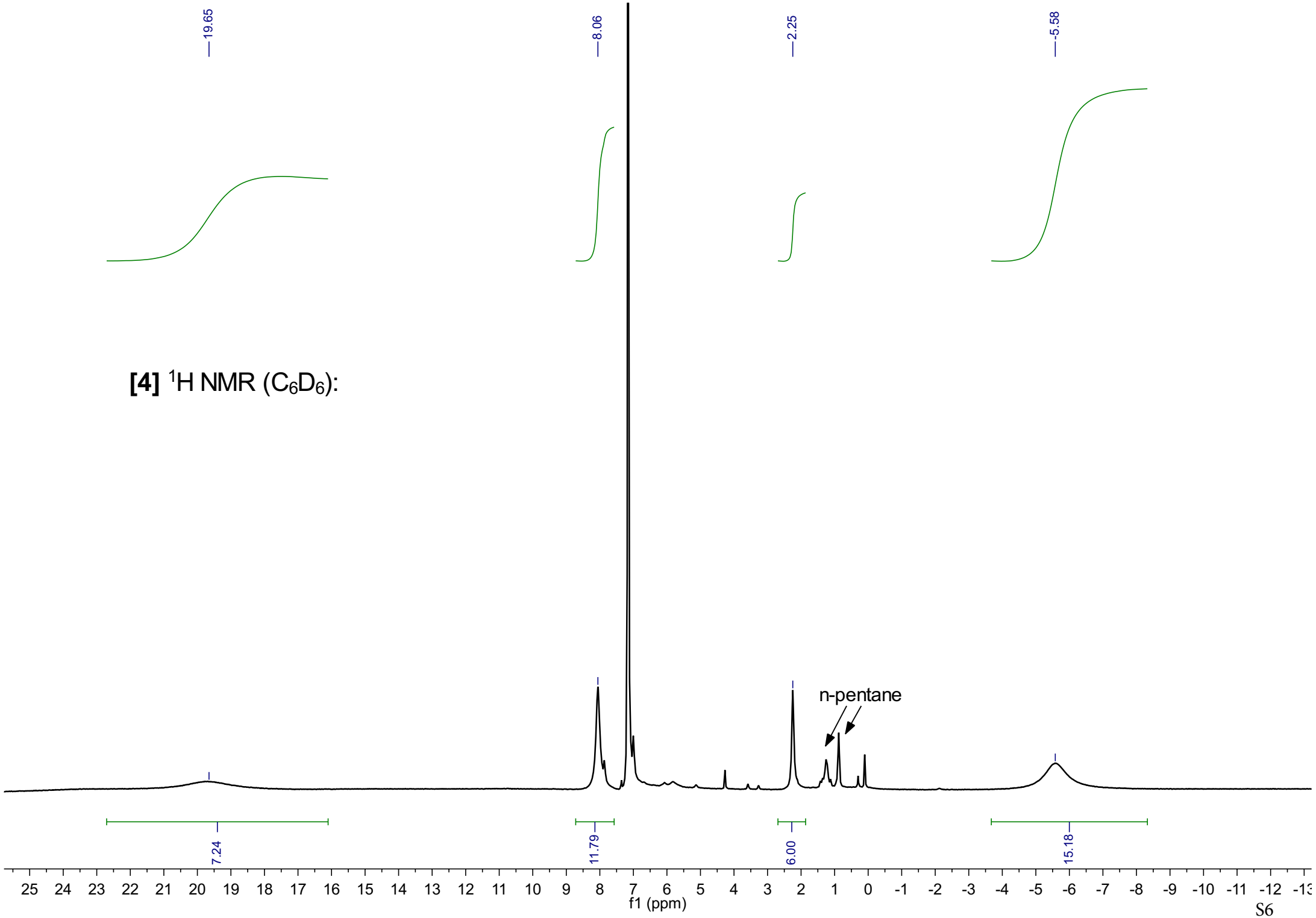
Comment: [**2**] in frozen CDCl3 at 50K

FileName:



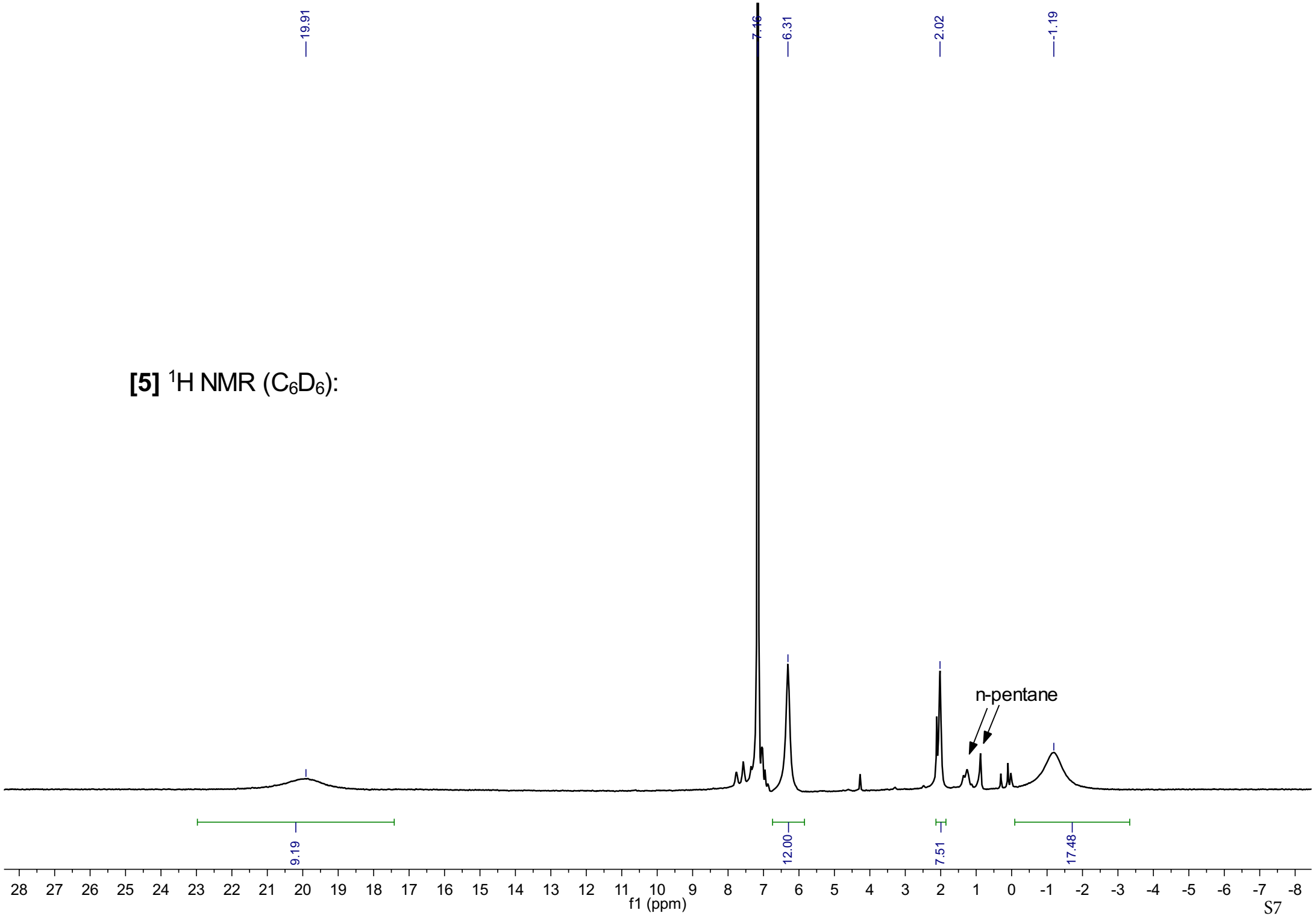
[3] ^{1}H NMR (THF-d^{8}):





[4] ^{1}H NMR (C_6D_6):

[5] ^{1}H NMR (C_6D_6):


19.91
7.16
6.31
2.02
1.19
n-pentane
9.19
12.00
7.51
17.48
28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8
f1 (ppm)

X-ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount, and placed under a N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Kappa Apex II diffractometer using a graphite monochromator with Mo Kα (λ = 0.71073 Å) radiation. The data were collected at 150(2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method SADABS. In cases where non-merohedral twinning was detected, the data was indexed with CELLNOW to determine the contributions of the respective crystal domains, and the data were corrected for absorption effects using TWINABS. The heavy atom positions were determined employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F, minimizing the function $\omega (F_o-F_c)^2$ where the weight ω is defined as $4F_o^2/2\sigma (F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of positional disordering. The final models of twinned structures were obtained by refinement against the twinned data. C-H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

	[2] (monomer + dimer)	**[2] (dimer only)**	**[3]**
Formula	$C_{76.5}H_{66}Cl_5Fe_2O_{0.5}P_4$	$C_{74}H_{60}Cl_4Fe_2P_4$	$C_{55}H_{52}FeOP_2$
wt	1406.12	1326.60	846.76
Cryst. syst.	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	P21/c
a(Å)	14.084(2)	11.3479(10)	11.1700(11)
b(Å)	15.641(2)	16.1979(15)	23.928(2)
c(Å)	17.663(3)	17.6503(17)	17.1484(16)
α(deg)	116.156(7)	79.585(4)	90
β(deg)	90.164(8)	88.787(4)	106.051(5)
γ(deg)	90.169(8)	86.895(4)	90
V(Å^3)	3492.3(9)	3196.0(5)	4404.6(7)
Z	2	2	4
d(calc) gcm^{-3}	1.337	1.383	1.277
Radiation	Mo Kα	Mo Kα	Mo Kα
R(int)	0.0559	0.0269	0.1865
μ, mm^{-1}	0.741	0.767	0.455
Total data	54410	67951	53935
$>2\sigma(F_O^2)$	12042	14591	7850
Variables	806	757	532
R ($>2\sigma$)	0.0716	0.0270	0.0795
R_w	0.2074	0.0715	0.1829
GOOF	1.050	1.023	1.022

	[5]
Formula	$C_{44}H_{48}F_3FeNO_3P_2SSi$
wt	901.86
Cryst. syst.	Monoclinic
Space group	$P2_1/n$
a(Å)	11.2805(11)
b(Å)	19.2156(16)
c(Å)	21.726(2)
α(deg)	90
β(deg)	103.818(4)
γ(deg)	90
V(Å^3)	4573.1(7)
Z	4
d(calc) gcm^{-3}	1.310
Radiation	Mo Kα
R(int)	0.0716
μ, mm^{-1}	0.548
Total data	52032
>2σ(F_O^2)	10473
Variables	514
R (>2σ)	0.0604
R_w	0.1753
GOOF	1.029