The palladium(II) complex of *N,N*-diethyl-1-ferrocenyl-3-thiabutanamine: synthesis, solution and solid state structure and catalytic activity in Suzuki-Miyaura reaction

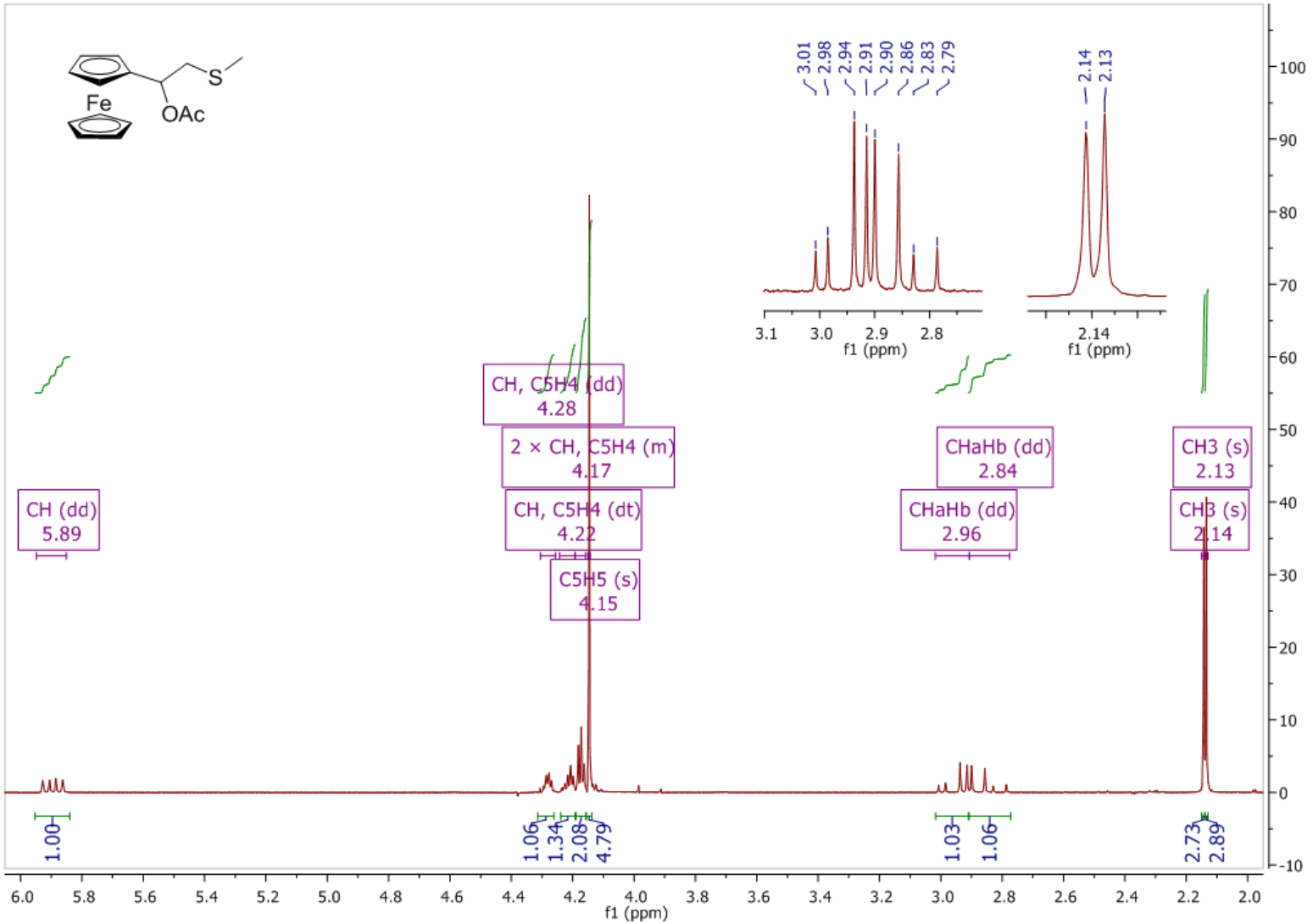
Ivan Damljanović,[a] Dragana Stevanović,[a] Anka Pejović,[a] Danijela Ilić,[b] Marija Živković,[a] Jovana Jovanović,[a] Mirjana Vukićević,[c] Goran A. Bogdanović,[d] Niko S. Radulović*[e] and Rastko D. Vukićević*[a]

[a]*Department of Chemistry, Faculty of Science, University of Kragujevac, R. Domanovića 12, 34000 Kragujevac, Serbia.*
[b]*Faculty of Technical Sciences Kosovska Mitrovica, University of Priština, Kneza Miloša 7, 38220 Kosovska Mitrovica, Serbia.*
[c]*Department of Pharmacy, Faculty of Medical Sciences, University of Kragujevac, S. Markovića 69, 34000 Kragujevac, Serbia.*
[d]*Vinča Institute of Nuclear Sciences, University of Belgrade, PO Box 522, 11001 Belgrade, Serbia.*
[e]*Department of Chemistry, Faculty of Science and Mathematics, University of Niš, Višegradska 33, 18000 Niš, Serbia.*

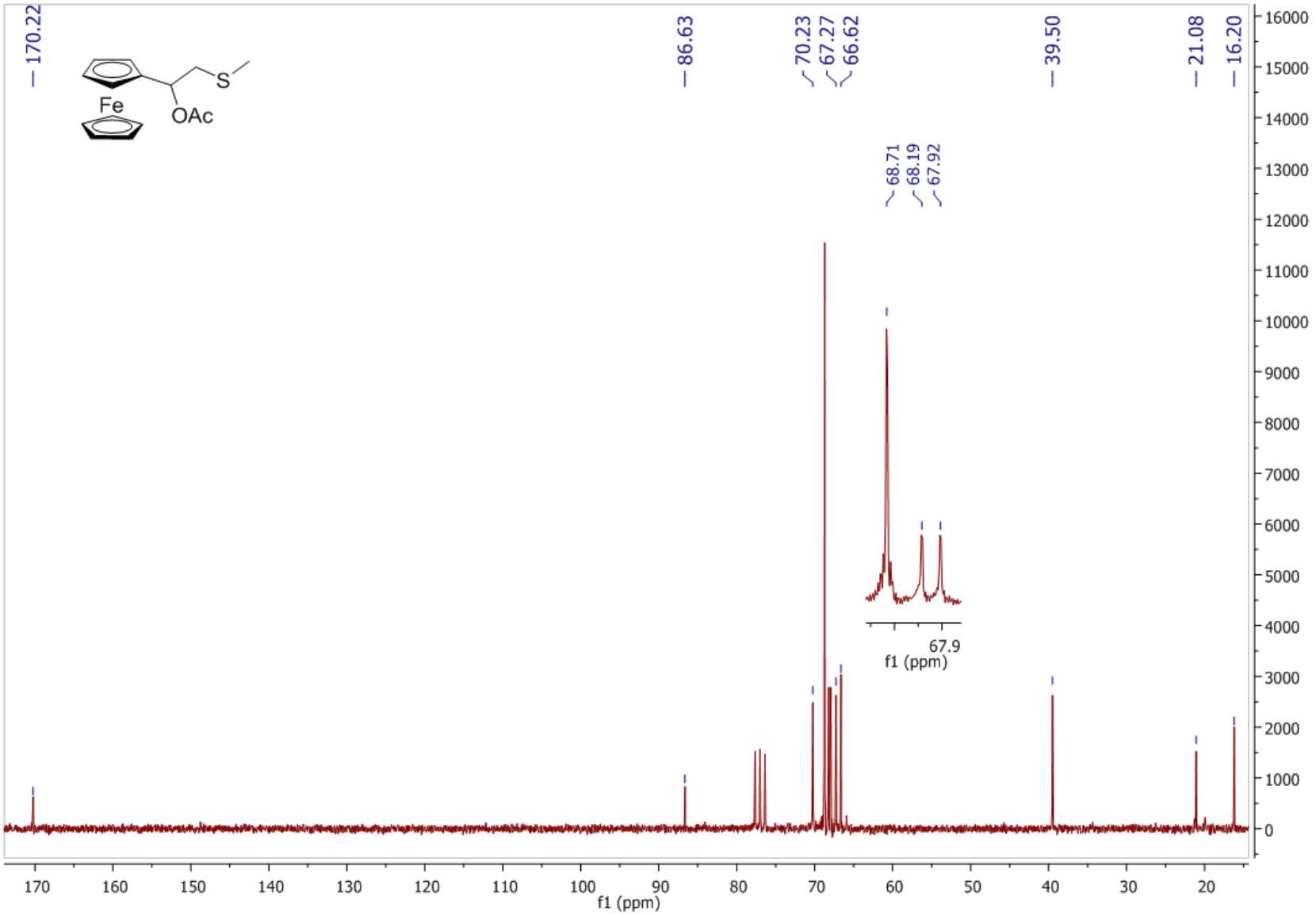
* Corresponding authors: R.D.V.: e-mail, vuk@kg.ac.rs; tel. (+381) 34-30-02-68; fax, (+381) 34-34-50-40. N.S.R.: e-mail, nikoradulovic@yahoo.com; tel. (+381) 62-80-49-210; fax, (+381) 18-533-014.

Table of Contents

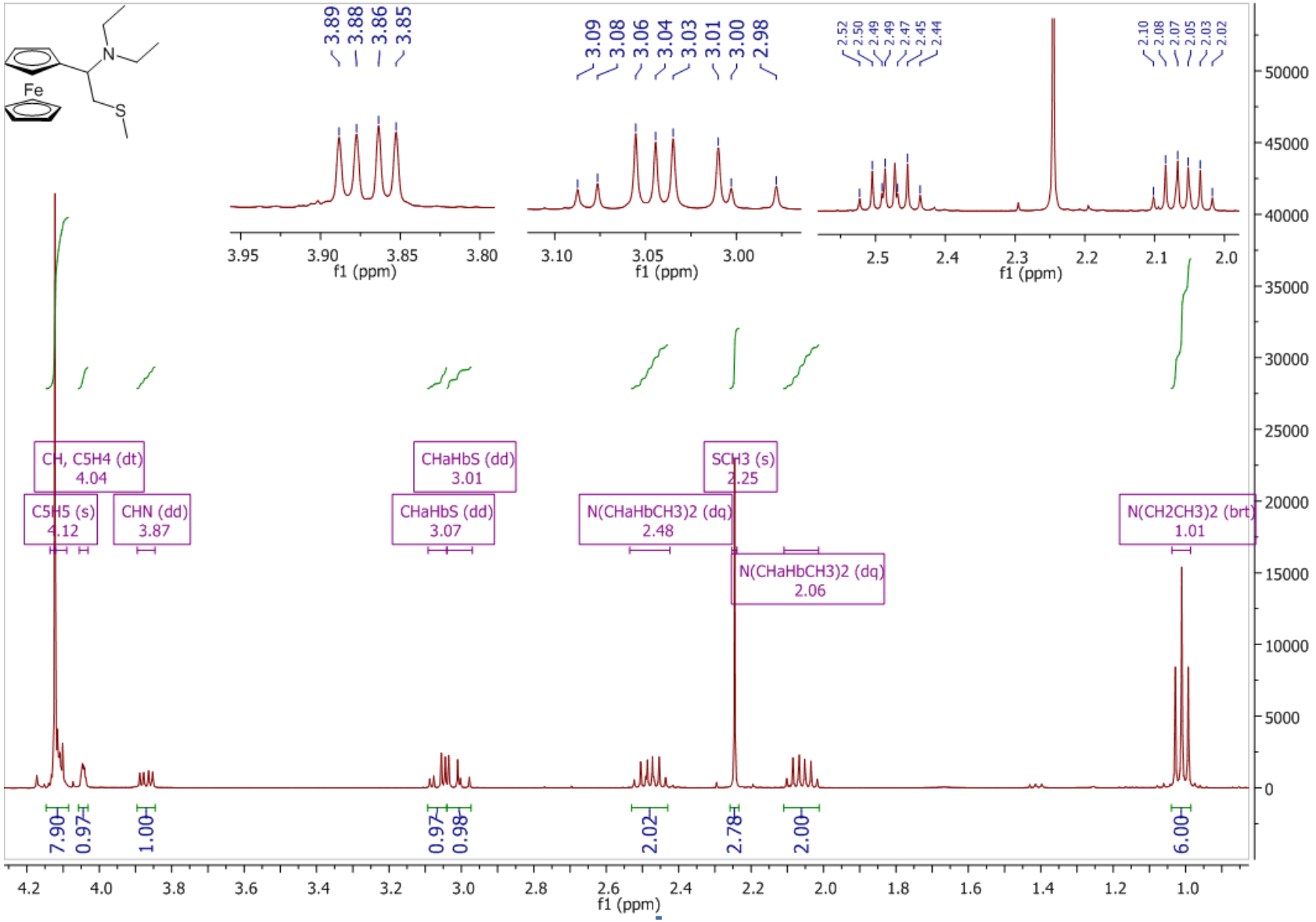
1 ^{1}H and ^{13}C NMR spectra of compounds 4, 5 and 6



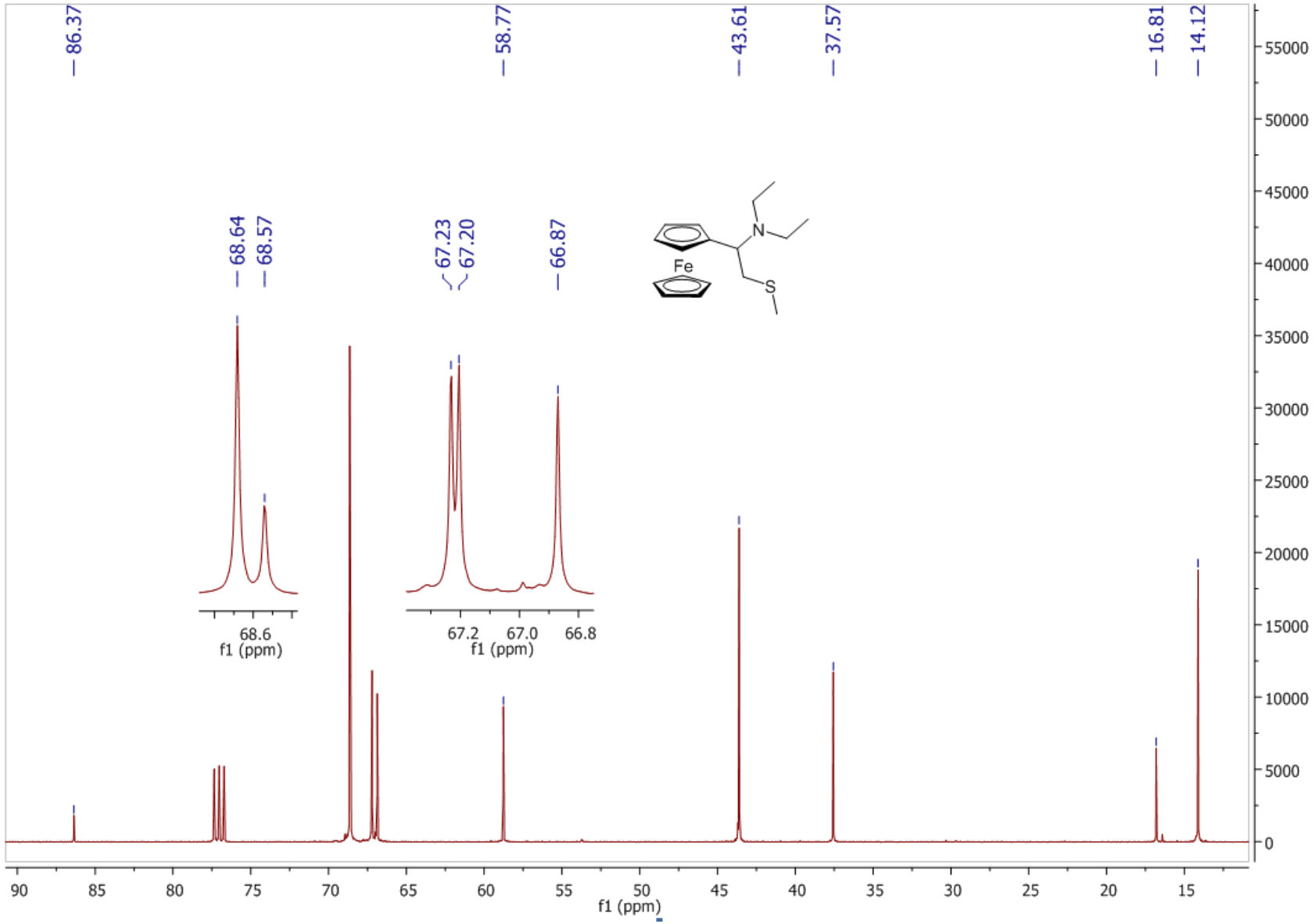
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of 2-(methylthio)-1-ferrocenylethyl acetate (**4**)



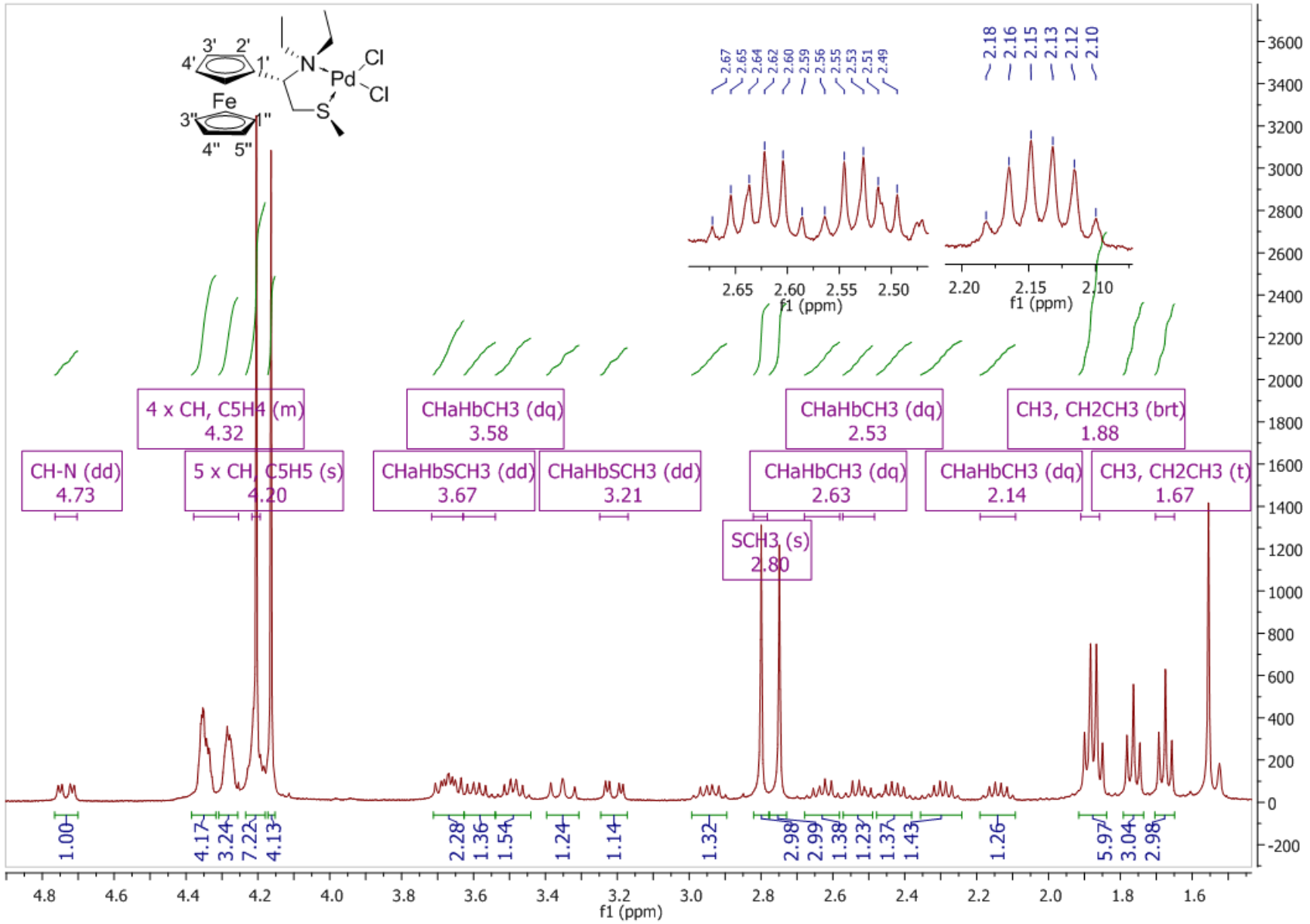
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of 2-(methylthio)-1-ferrocenylethyl acetate (**4**)



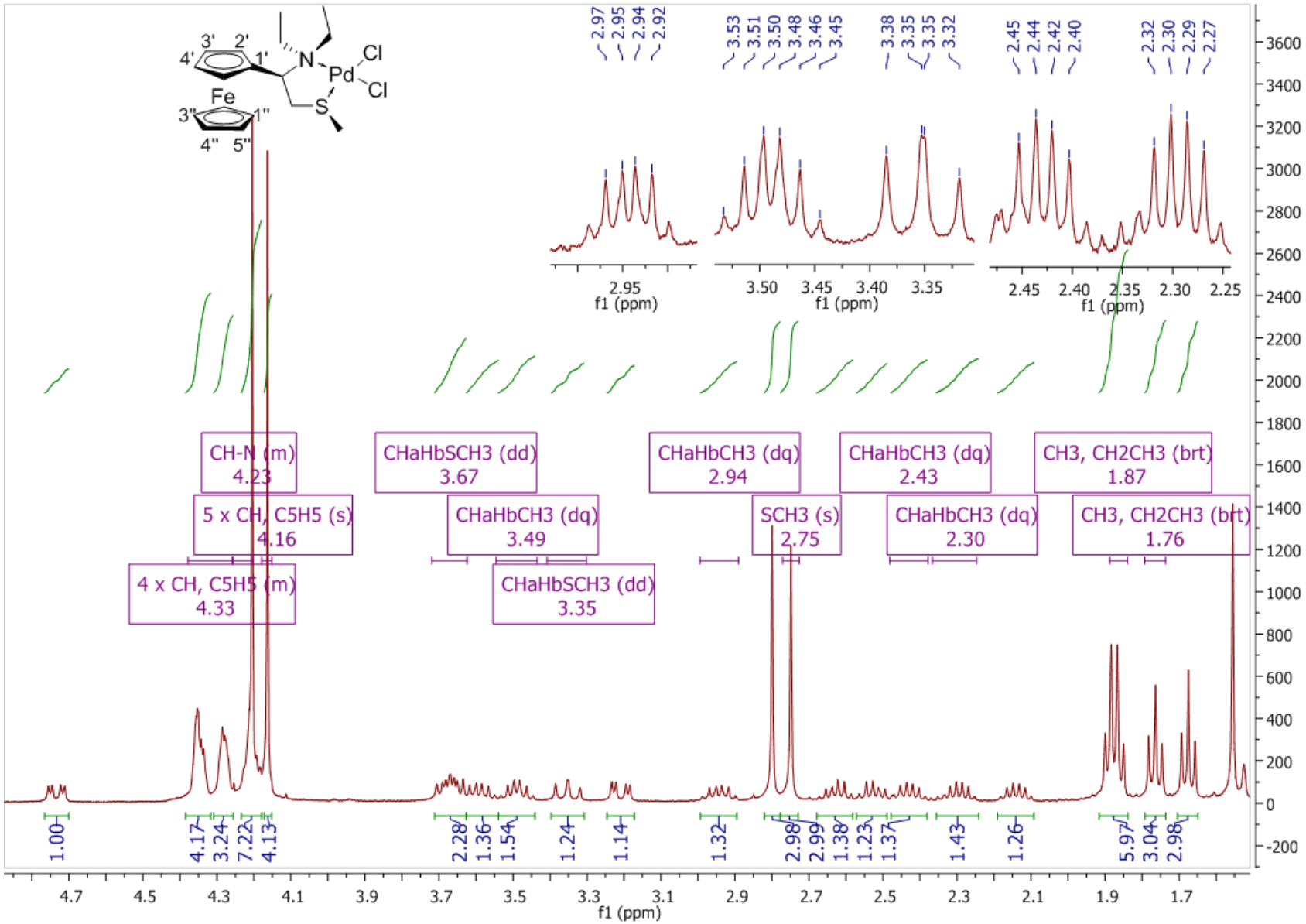
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *N,N*-diethyl-1-ferrocenyl-3-thiabutanamine (**5**)



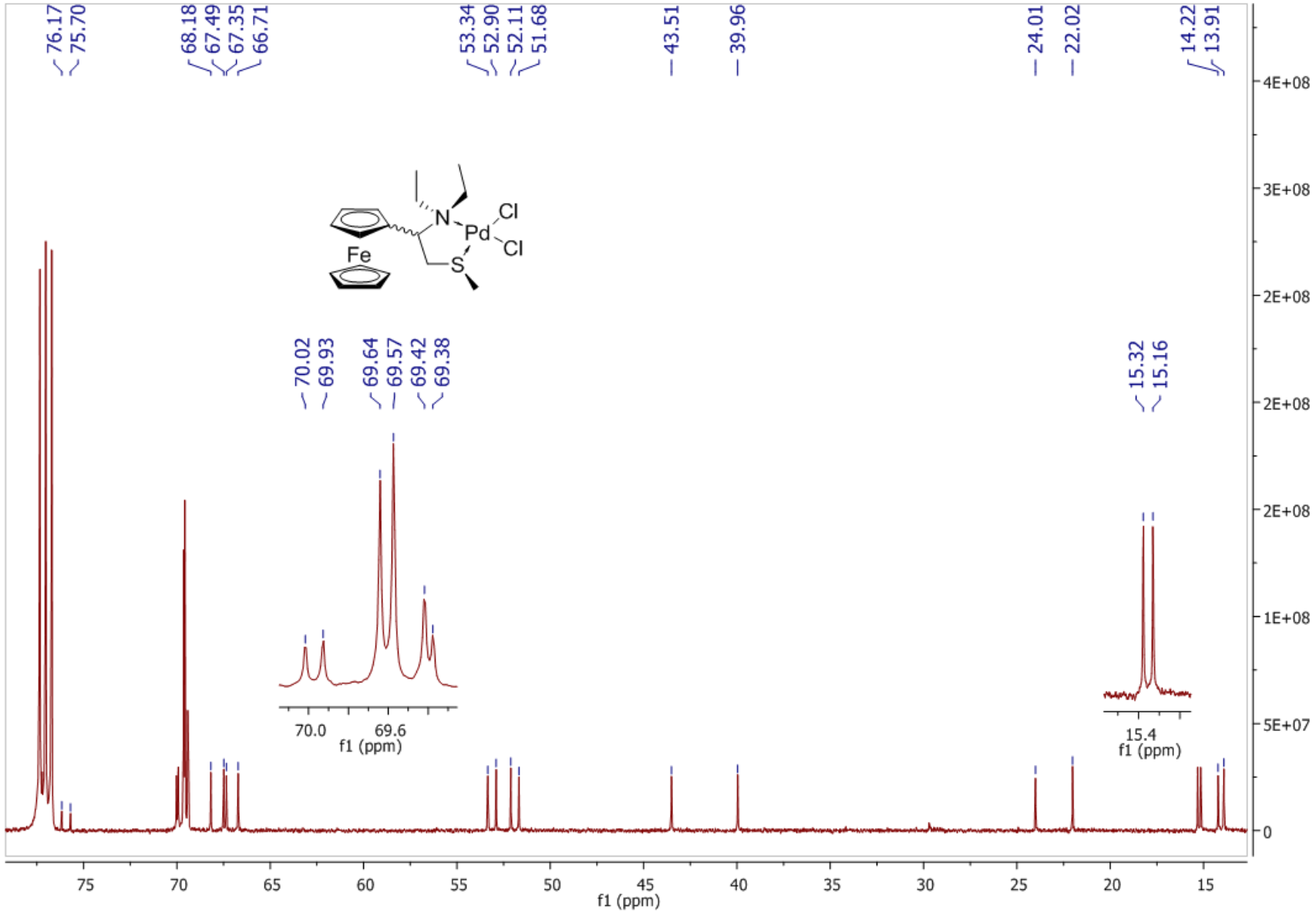
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *N,N*-diethyl-1-ferrocenyl-3-thiabutanamine (**5**)



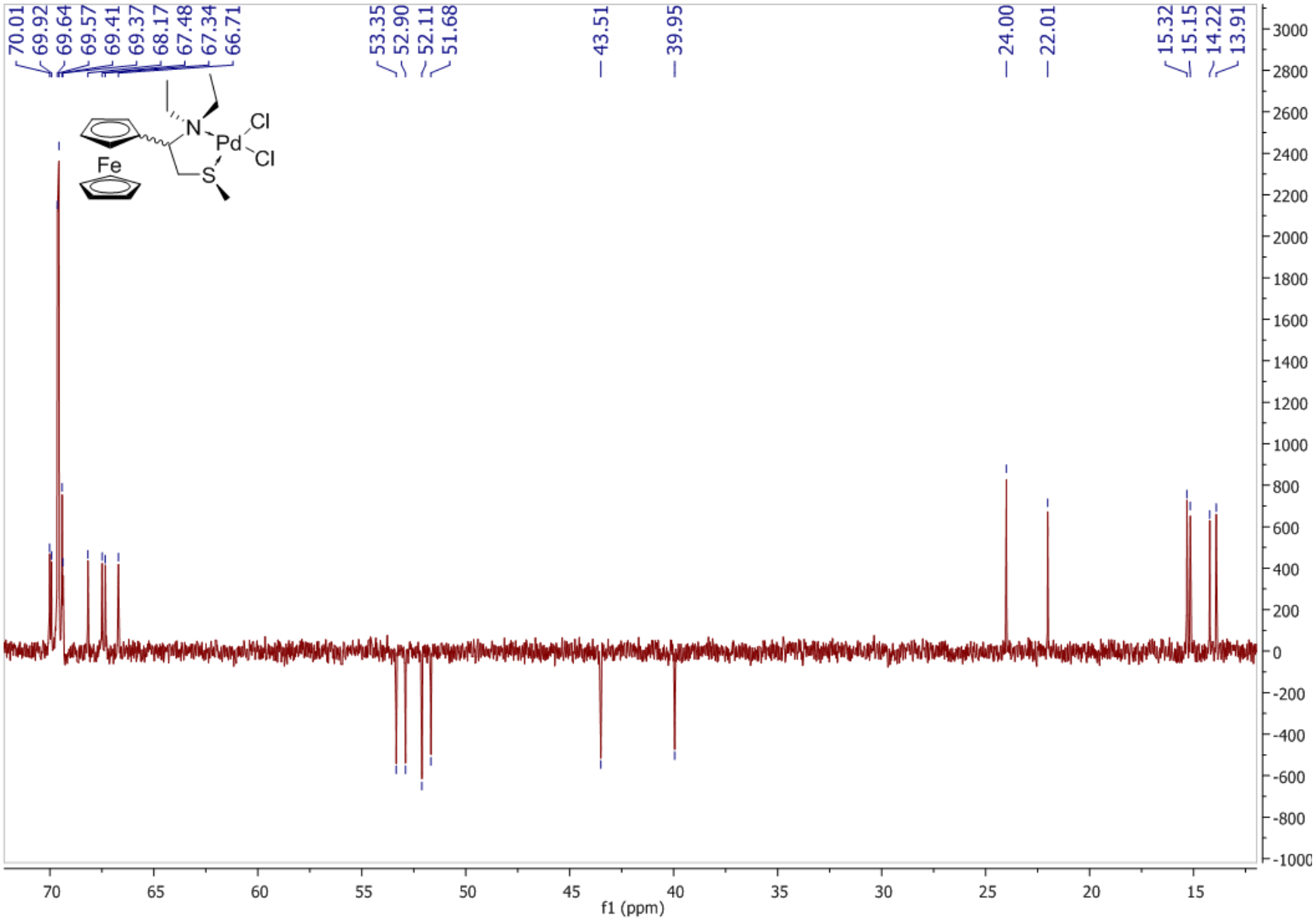
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *trans*-dichlorido-(*N*,*N*-diethyl-1-ferrocenyl-3-thiabutanamine)palladium(II) (*trans*-**6**)



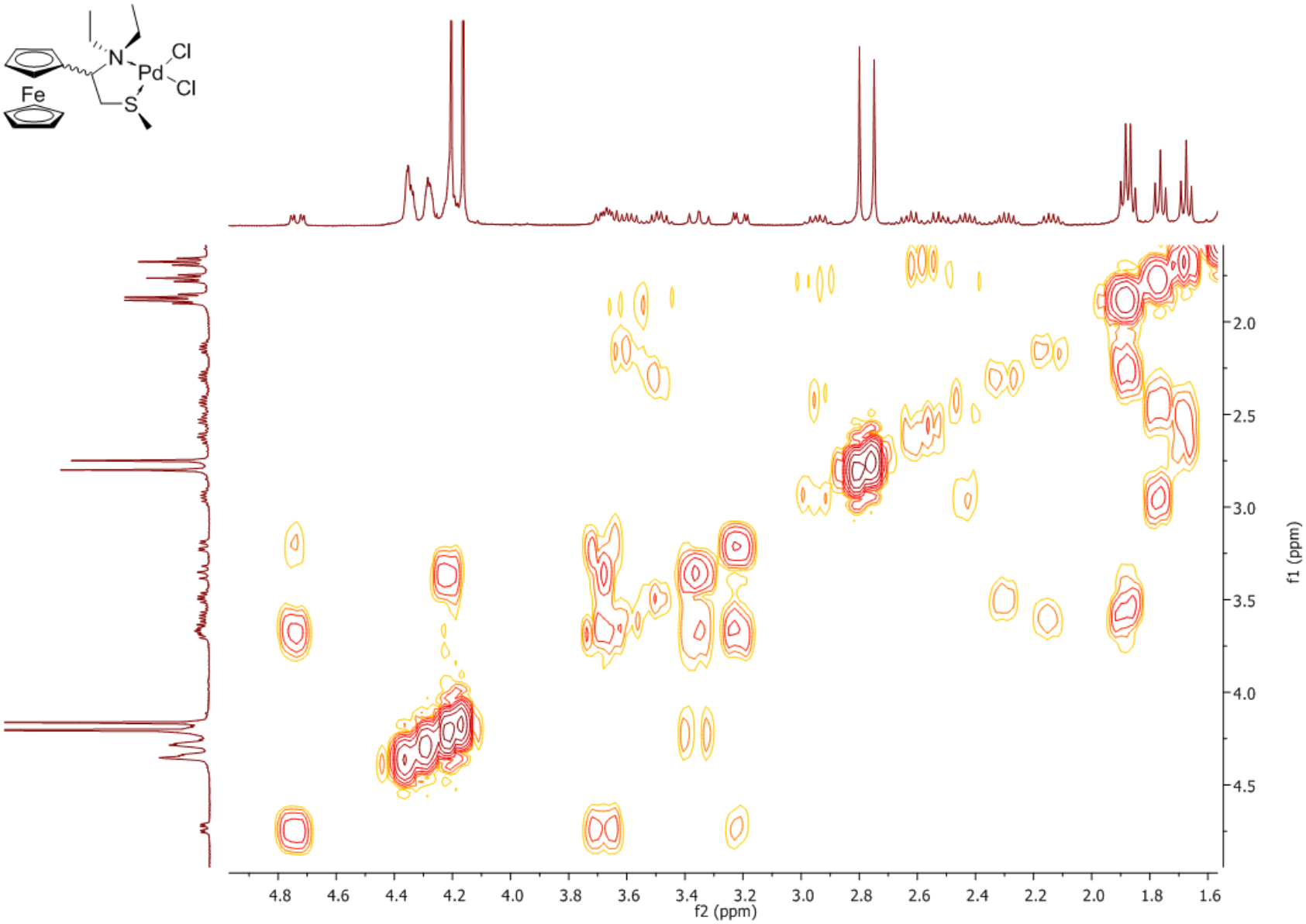
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *cis*-dichlorido-(*N*,*N*-diethyl-1-ferrocenyl-3-thiabutanamine)palladium(II) (*cis*-**6**)



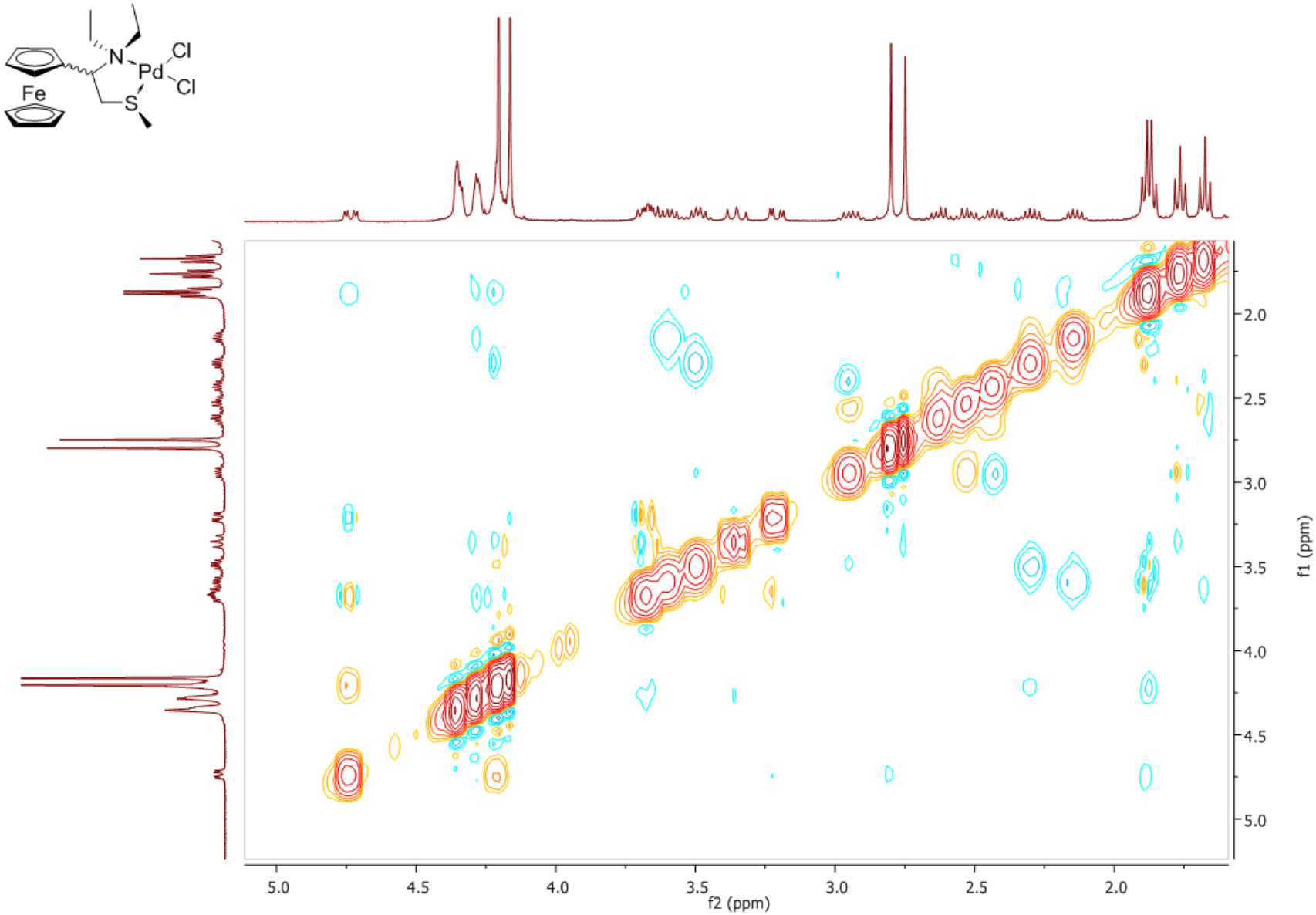
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of dichlorido-(*N*,*N*-diethyl-1-ferrocenyl-3-thiabutanamine)palladium(II) (**6**)



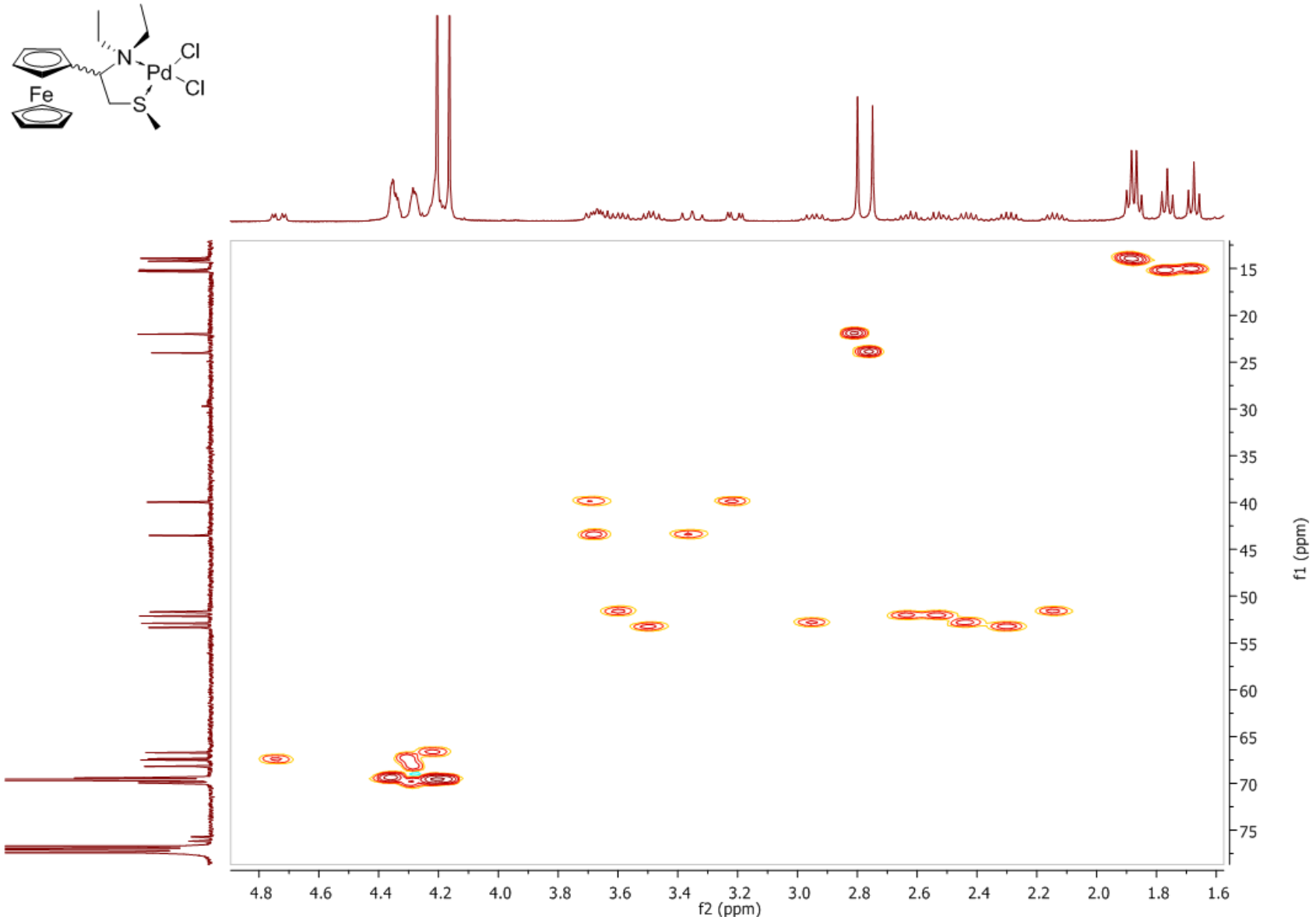
DEPT135 spectrum of dichlorido-(*N*,*N*-diethyl-1-ferrocenyl-3-thiabutanamine)palladium(II) (**6**)



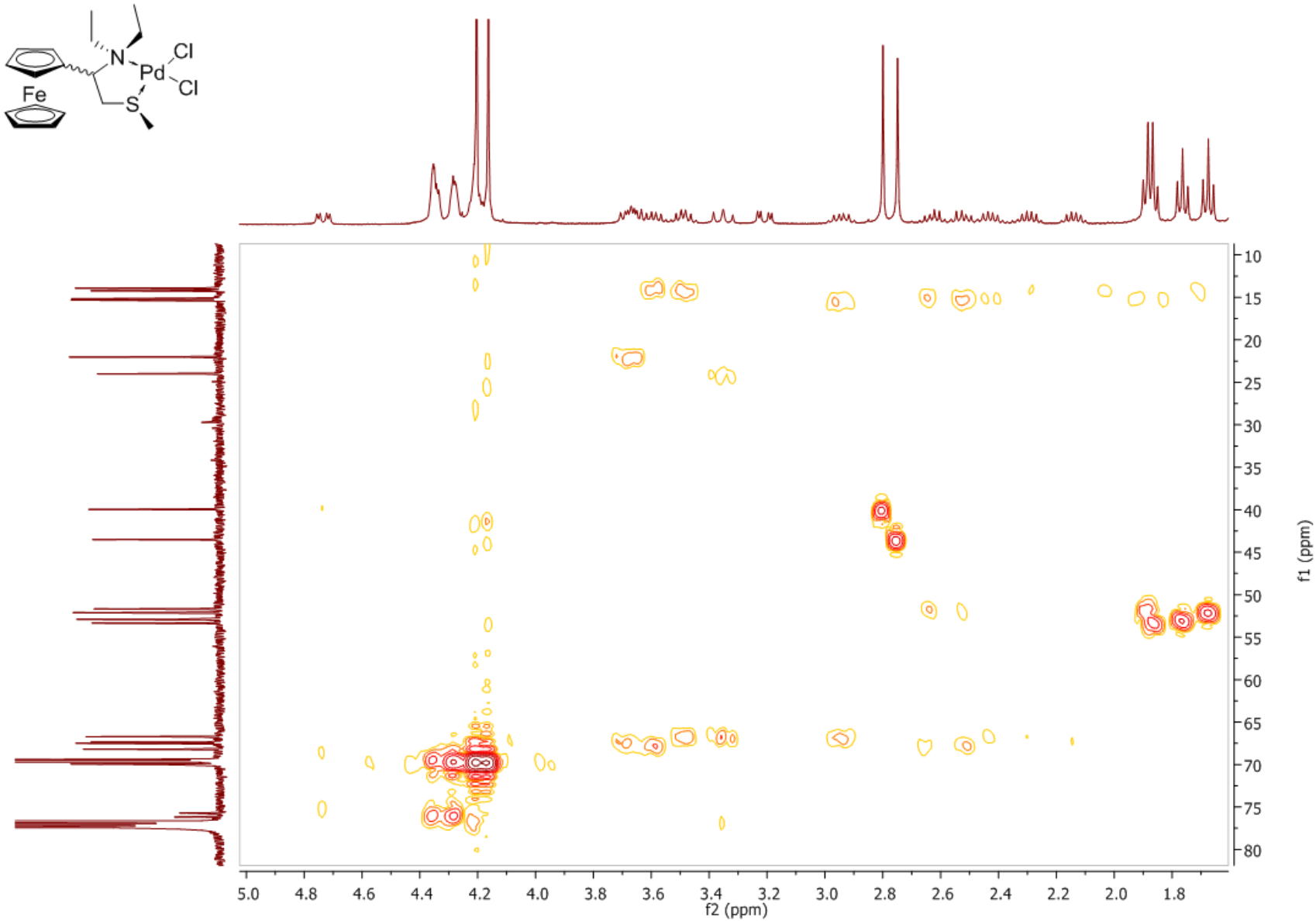
^{1}H-^{1}H COSY spectrum of dichlorido-(*N*,*N*-diethyl-1-ferrocenyl-3-thiabutanamine)palladium(II) (**6**)



NOESY spectrum of dichlorido-(*N*,*N*-diethyl-1-ferrocenyl-3-thiabutanamine)palladium(II) (**6**)



HSQC spectrum of dichlorido-(*N*,*N*-diethyl-1-ferrocenyl-3-thiabutanamine)palladium(II) (**6**)



HMBC spectrum of dichlorido-(*N*,*N*-diethyl-1-ferrocenyl-3-thiabutanamine)palladium(II) (**6**)

2 X-ray crystal structure analyses of 6

2.1 Dichlorido-(*N*,*N*-diethyl-1-ferrocenyl-3-thiabutanamine)palladium(II) monosolvate (6·EtOH), polymorph I

Table S3 Crystallographic data for the crystal structure of **6**·EtOH

Empirical formula	C_{19} H_{31} Cl_2 Fe N O Pd S
Formula weight	554.66
Color, crystal shape	Dark red, prismatic
Crystal size (mm^3)	0.50 x 0.21 x 0.12
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	11.8670(4)
b (Å)	14.7863(4)
c (Å)	13.4527(6)
β (°)	105.836(5)
Volume ($Å^3$)	2270.94(14)
Z	4
D_{calc} (Mg/m^3)	1.622
μ (mm^{-1})	1.766
F(000)	1128
θ range for data collection (°)	3.17 − 29.68
Index ranges	−16<=h<=16, −20<=k<=20, −18<=l<=18
Reflections collected	33237
Independent reflections, R_{int}	5858, 0.0413
Completeness to θ = 27.00°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5858 / 0 / 238
Goodness-of-fit on F^2	1.151
Final R_1/wR_2 indices ($I>2\sigma_I$)	0.0506, 0.0969
Final R_1/wR_2 indices (all data)	0.0667, 0.1037
Largest diff. peak and hole (e $Å^{-3}$)	0.759 and −0.402

Table S4 Selected bond lengths (Å) and bond angles (°) in the crystal structure of **6**·EtOH.

bon	bon
Pd1−N1	N1−Pd1−S1
Pd1−S1	N1−Pd1−Cl1
Pd1−Cl1	S1−Pd1−Cl1
Pd1−Cl2	N1−Pd1−Cl2
Fe1−C9	S1−Pd1−Cl2
Fe1−C8	Cl1−Pd1−Cl2
Fe1−C7	C12−S1−C13
Fe1−C2	C12−S1−Pd1
Fe1−C10	C13−S1−Pd1
Fe1−C4	C16−N1−C14
Fe1−C5	C16−N1−C11
Fe1−C6	C14−N1−C11
Fe1−C3	C16−N1−Pd1
Fe1−C1	C14−N1−Pd1
S1−C12	C11−N1−Pd1
S1−C13	C5−C1−C2
N1−C16	C5−C1−C11
N1−C14	C2−C1−C11
N1−C11	C1−C2−C3
C1−C5	C4−C3−C2
C1−C2	C3−C4−C5
C1−C11	C4−C5−C1
C2−C3	C10−C6−C7
C3−C4	C8−C7−C6
C4−C5	C9−C8−C7
C6−C10	C8−C9−C10
C6−C7	C6−C10−C9
C7−C8	C12−C11−C1
C8−C9	C12−C11−N1
C9−C10	C1−C11−N1
C11−C12	C11−C12−S1
C14−C15	C15−C14−N1
C16−C17	C17−C16−N1
O1−C18	C19−C18−O1
C18−C19	

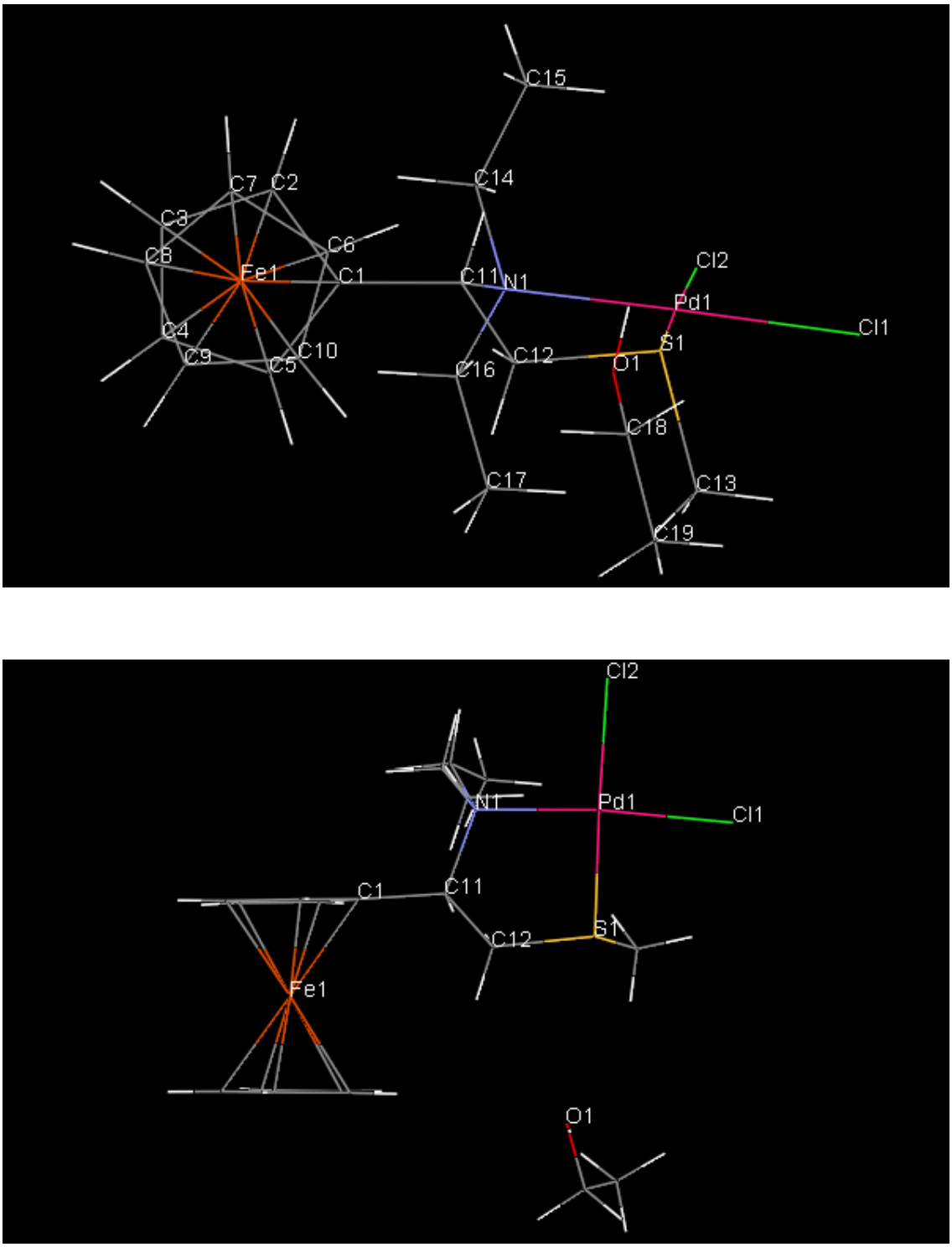


Fig. S1 Crystal structure of **6**·EtOH shown in two orthogonal projections.

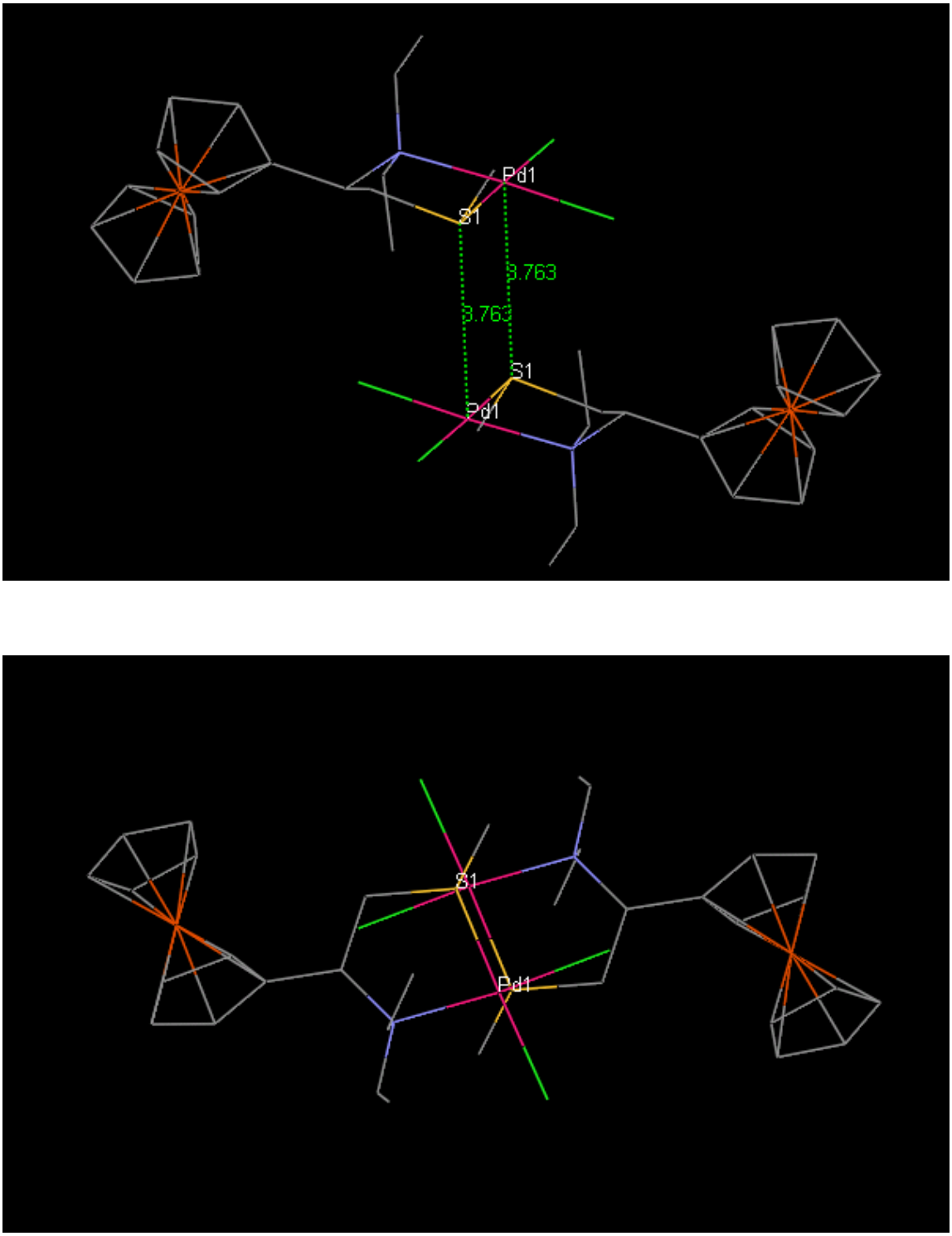


Fig. S2 Molecules of **6** form a dimer (illustrated in two orthogonal projections) with two Pd1…S1^{i} intermolecular contacts [symmetry code: (i) −x+1,−y+1,−z+2]. The Pd1…S1^{i} distance is 3.7633(10) Å.

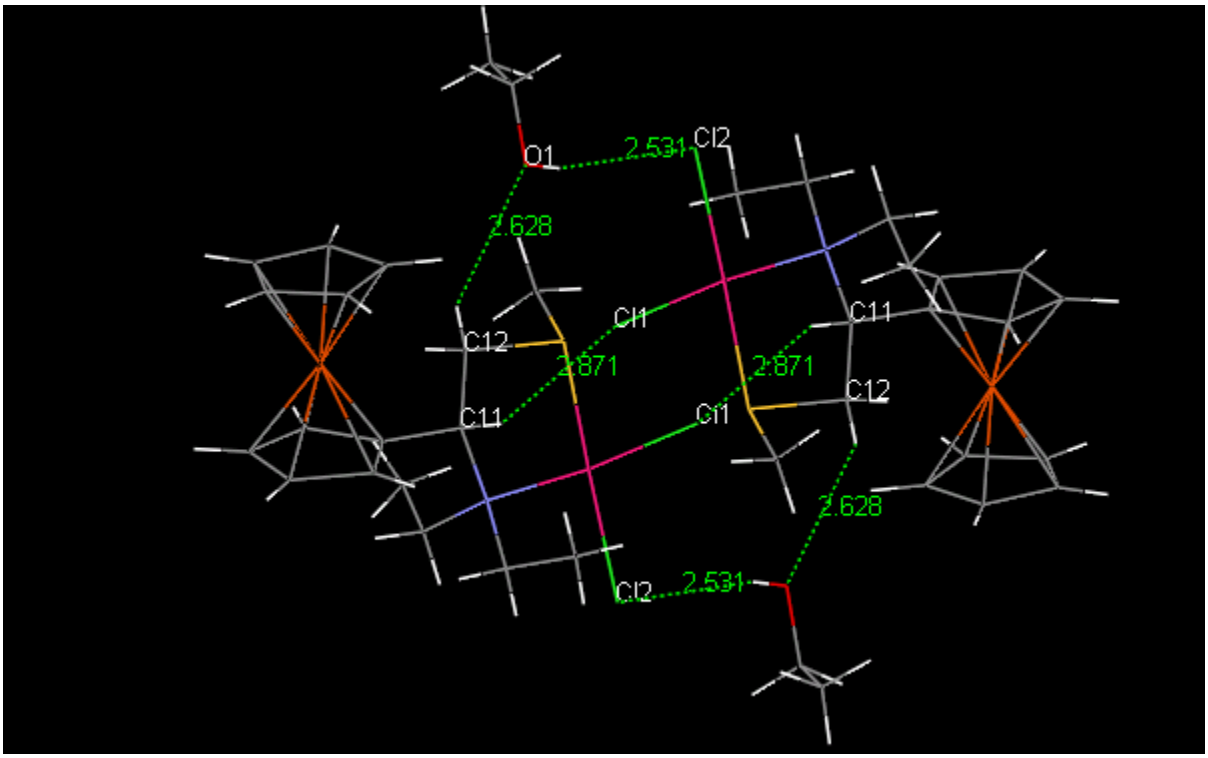


Fig. S3 Two molecules of **6** within the dimer shown in Figure S2 are additionally interconnected by following weak intermolecular interactions: a) C12−H12b…O1 [C12…O1 = 3.302(6) Å, H12b…O1 =2.63 Å, C12−H12b…O1 = 126.8 °], b) C11−H11…Cl1 [C11…Cl1 = 3.741(4) Å, H11…Cl1 = 2.87 Å, C11−H11…Cl1 = 148.3 °] and c) O1−H1…Cl2 [O1…Cl2 =3.321(5) Å, H1…Cl2 = 2.53 Å, O1−H1…Cl2 – 154.8 °].

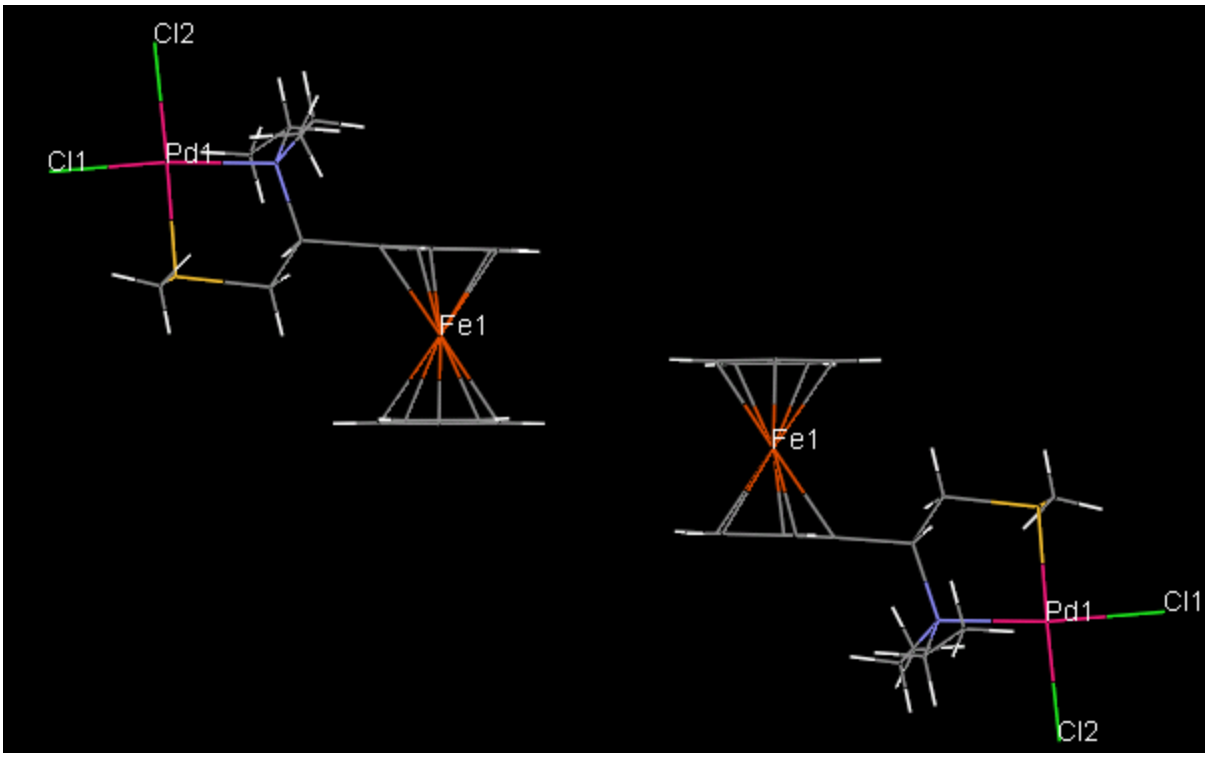


Fig. S4 Molecules of **6** form the dimer with two ferrocene units placed in parallel orientation and direct contact. The formation of the dimer is based on a large stabilizing electrostatic complementarity between two ferrocene units[9].

2.2 Dichlorido-(*N*,*N*-diethyl-1-ferrocenyl-3-thiabutanamine)palladium(II) (6), polymorph II

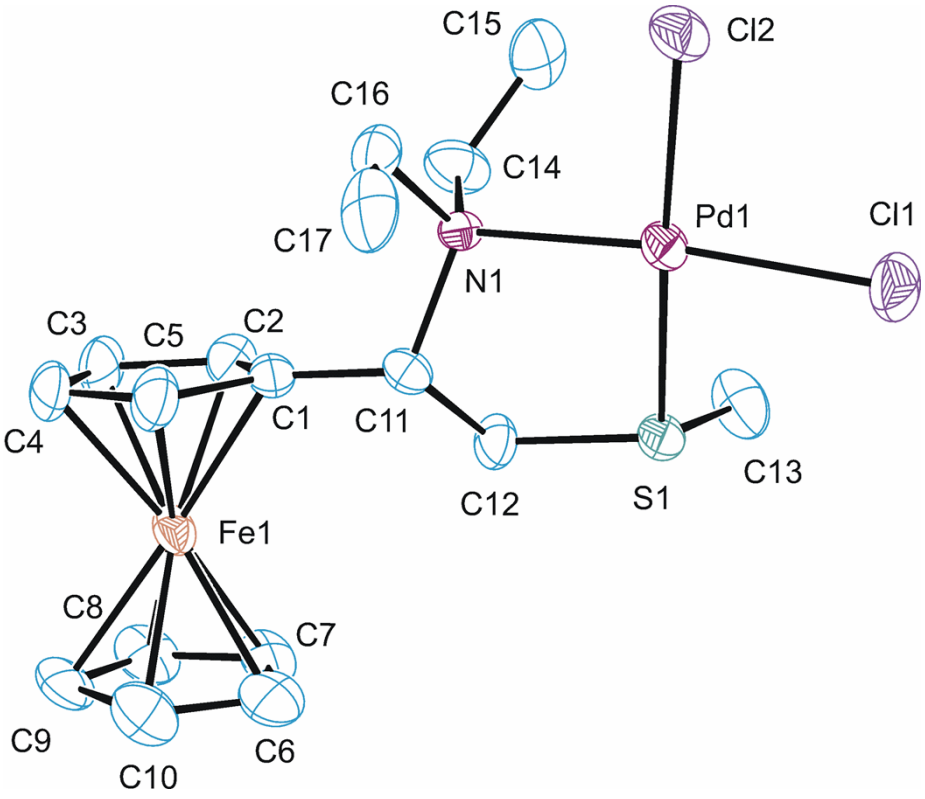


Fig. S5 The molecular structure of **6** in polymorph II with the atom numbering scheme (hydrogen atoms are omitted for clarity). Displacement ellipsoids are drawn at 30% probability level. Other projections of the molecule are given in Figure S6.

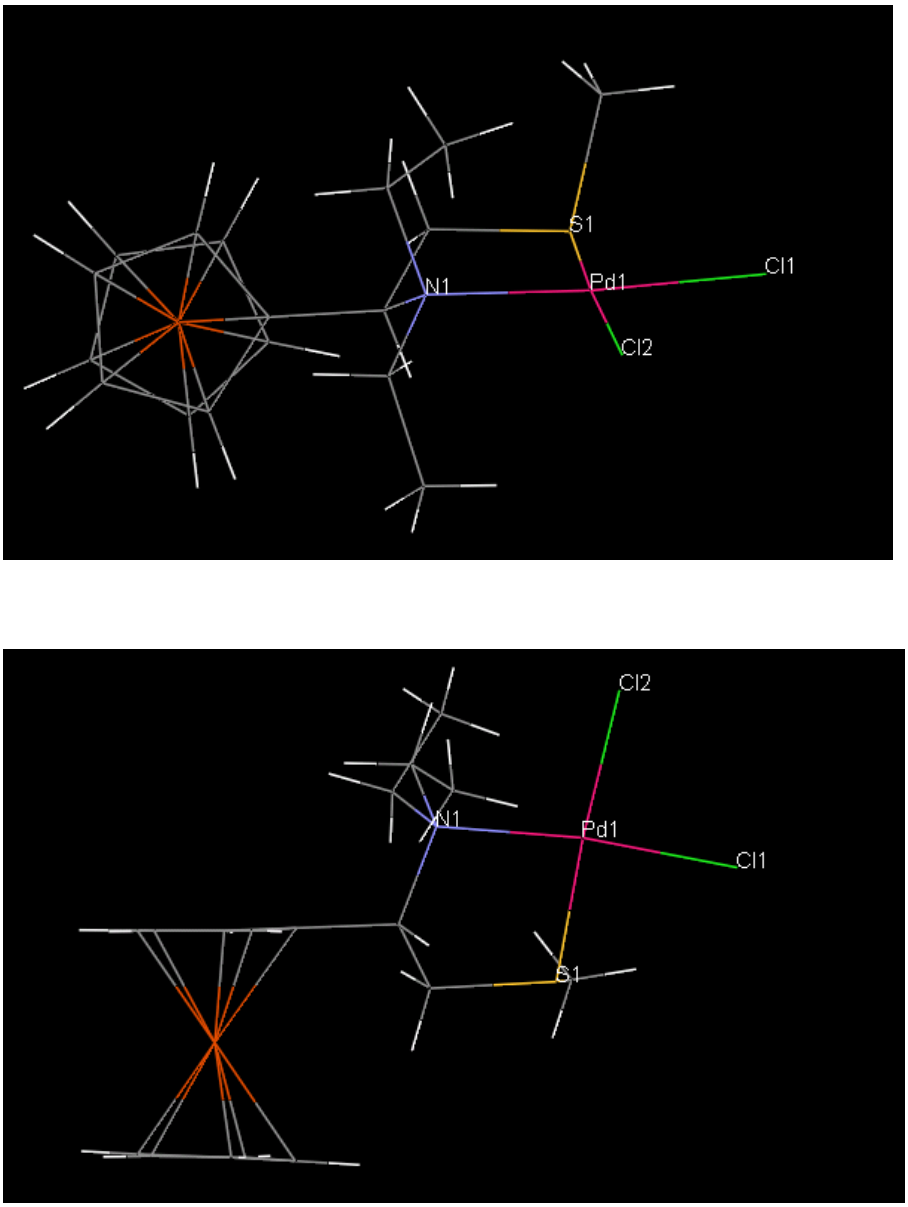
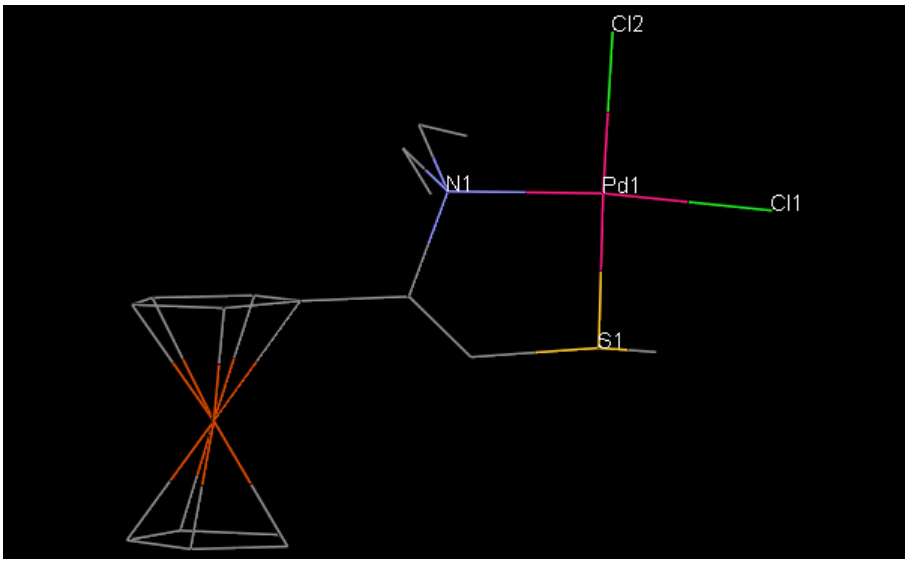
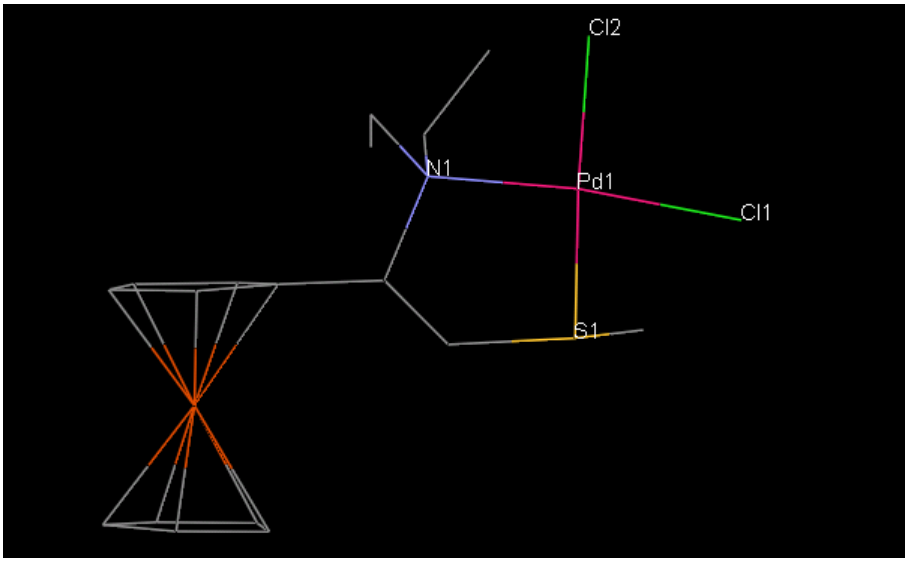


Fig. S6 Crystal structure of **6** (polymorph II) shown in two orthogonal projections.



(a)



(b)

Fig. S7 Polymorphs I (a) and II (b) have different orientation of the two ethyl groups bonded to the N1 atom.

Table S5 Crystallographic data for the crystal structure of **6**.

Empirical formula	C_{17} H_{25} Cl_2 Fe N Pd S
Formula weight	508.59
Color, crystal shape	Dark red, prismatic
Crystal size (mm^3)	0.24 x 0.15 x 0.13
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pna2₁*
Unit cell dimensions	
a (Å)	13.6982(5)
b (Å)	18.1868(7)
c (Å)	7.6277(3)
Volume ($Å^3$)	1900.26(13)
Z	4
D_{calc} (Mg/m^3)	1.778
μ (mm^{-1})	2.098
F(000)	1024
θ range for data collection (°)	3.17 − 29.16
Index ranges	−17<=h<=17, −24<=k<=24, −10<=l<=9
Reflections collected	10081
Independent reflections, R_{int}	4175, 0.0267
Completeness to θ = 27.00°	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4175 / 0 / 212
Goodness-of-fit on F^2	1.139
Final R_1/wR_2 indices ($I > 2\sigma_I$)	0.0571, 0.1423
Final R_1/wR_2 indices (all data)	0.0634, 0.1465
Largest diff. peak and hole (e $Å^{-3}$)	1.268 and −1.169

Table S6 Selected bond lengths (Å) and bond angles (°) in the crystal structure of **6**.

bon	bon
Pd1-N1	N1-Pd1-S1
Pd1-S1	N1-Pd1-Cl1
Pd1-Cl1	S1-Pd1-Cl1
Pd1-Cl2	N1-Pd1-Cl2
Fe1-C2	S1-Pd1-Cl2
Fe1-C7	Cl1-Pd1-Cl2
Fe1-C8	C13-S1-C12
Fe1-C5	C13-S1-Pd1
Fe1-C4	C12-S1-Pd1
Fe1-C3	C16-N1-C14
Fe1-C9	C16-N1-C11
Fe1-C1	C14-N1-C11
Fe1-C10	C16-N1-Pd1
Fe1-C6	C14-N1-Pd1
S1-C13	C11-N1-Pd1
S1-C12	C2-C1-C5
N1-C16	C2-C1-C11
N1-C14	C5-C1-C11
N1-C11	C3-C2-C1
C1-C2	C4-C3-C2
C1-C5	C3-C4-C5
C1-C11	C4-C5-C1
C2-C3	C10-C6-C7
C3-C4	C8-C7-C6
C4-C5	C9-C8-C7
C6-C10	C8-C9-C10
C6-C7	C6-C10-C9
C7-C8	C1-C11-C12
C8-C9	C1-C11-N1
C9-C10	C12-C11-N1
C11-C12	C11-C12-S1
C14-C15	C15-C14-N1
C16-C17	N1-C16-C17

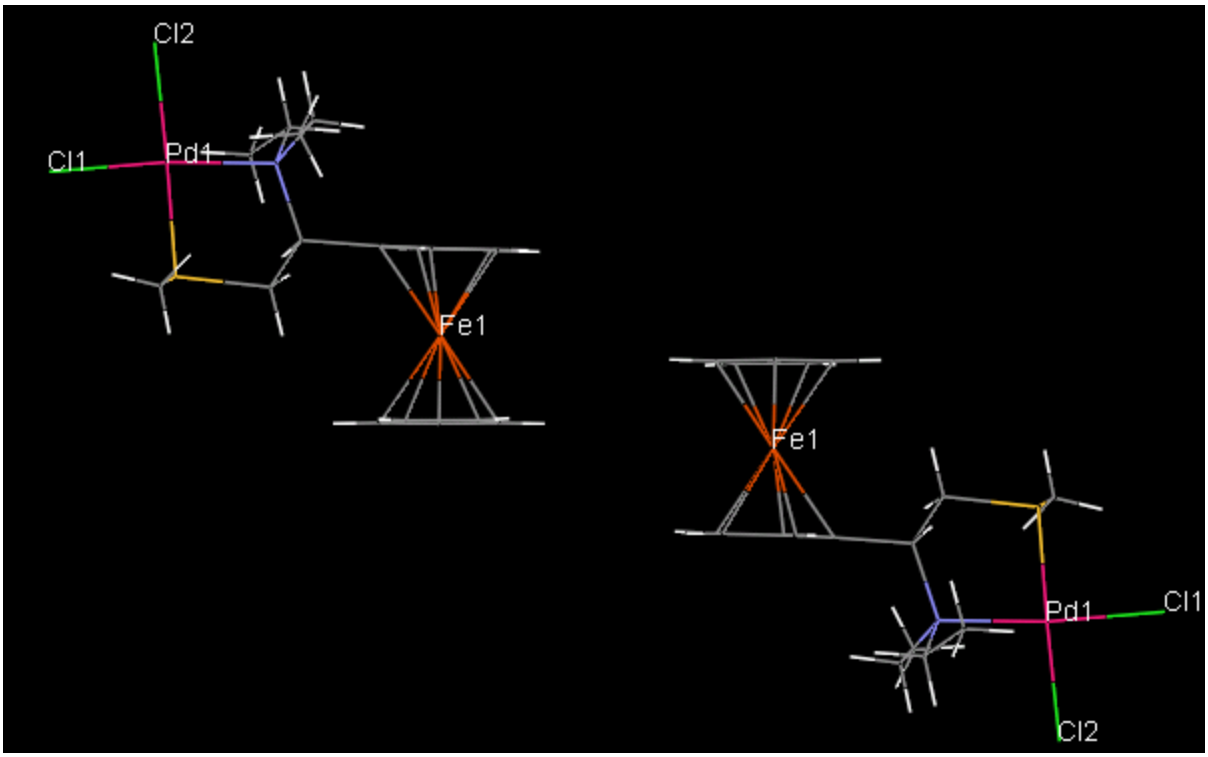


Fig. S4 Molecules of **6** form a dimer with two ferrocene units placed in parallel orientation and direct contact. The formation of the dimer is based on a large stabilizing electrostatic complementarity between two ferrocene units (G. A. Bogdanovic and S. B. Novakovic, *CrystEngComm*, 2011, **13**, 6930–6932).