Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

α-C–C Agostic interactions and C–H bond activation in scandium cyclopropyl complexes

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Table S1. Crystallographic data and refinement parameters for complexes **1-3**

	1	**2**	**3**
formula	$C_{32}H_{46}ClN_2Sc$	$C_{35}H_{51}N_2Sc$	$C_{36}H_{53}N_2OSc$
fw	539.12	544.73	574.76
cryst syst.	Monoclinic	monoclinic	Monoclinic
space group	*C*2/*c*	$P2_1/c$	$P\ \bar{1}$
a, Å	21.8616(4)	9.1042(3)	9.7178(2)
b, Å	14.2799(2)	13.1594(4)	21.5807(4)
c, Å	22.0903(4)	27.6815(8)	15.8692(3)
α, deg	90	90	90
β, deg	117.5520(10)	92.220(2)	92.7390(10)
γ, deg	90	90	90
V, Å^3	6114.09(19)	3313.92(18)	3324.24(11)
Z	8	4	4
D_{calcd}, (g/cm^3)	1.171	1.092	1.148
F(000)	2320	1184	1248
T(K)	170(2)	170(2)	170(2)
θ range(deg)	3.382 to 54.941	3.236 to 54.946	3.009 to 54.958
no. of refns collected	31861	27008	35931
no. of unique refns	5721	6246	12198
no. of obsd refns ($I > 2\sigma(I)$)	5457	5535	10803
No. of params	335	353	748
Final R, R_w ($I > 2\sigma(I)$)	0.0460, 0.1169	0.0393,0.1065	0.0420, 0.0941
Goodness-of-fit on F^2	1.029	1.064	1.024
$\Delta\rho_{max,\ min}$, eÅ^{-3}	0.483, -0.355	0.284, -0.393	0.208, -0.322

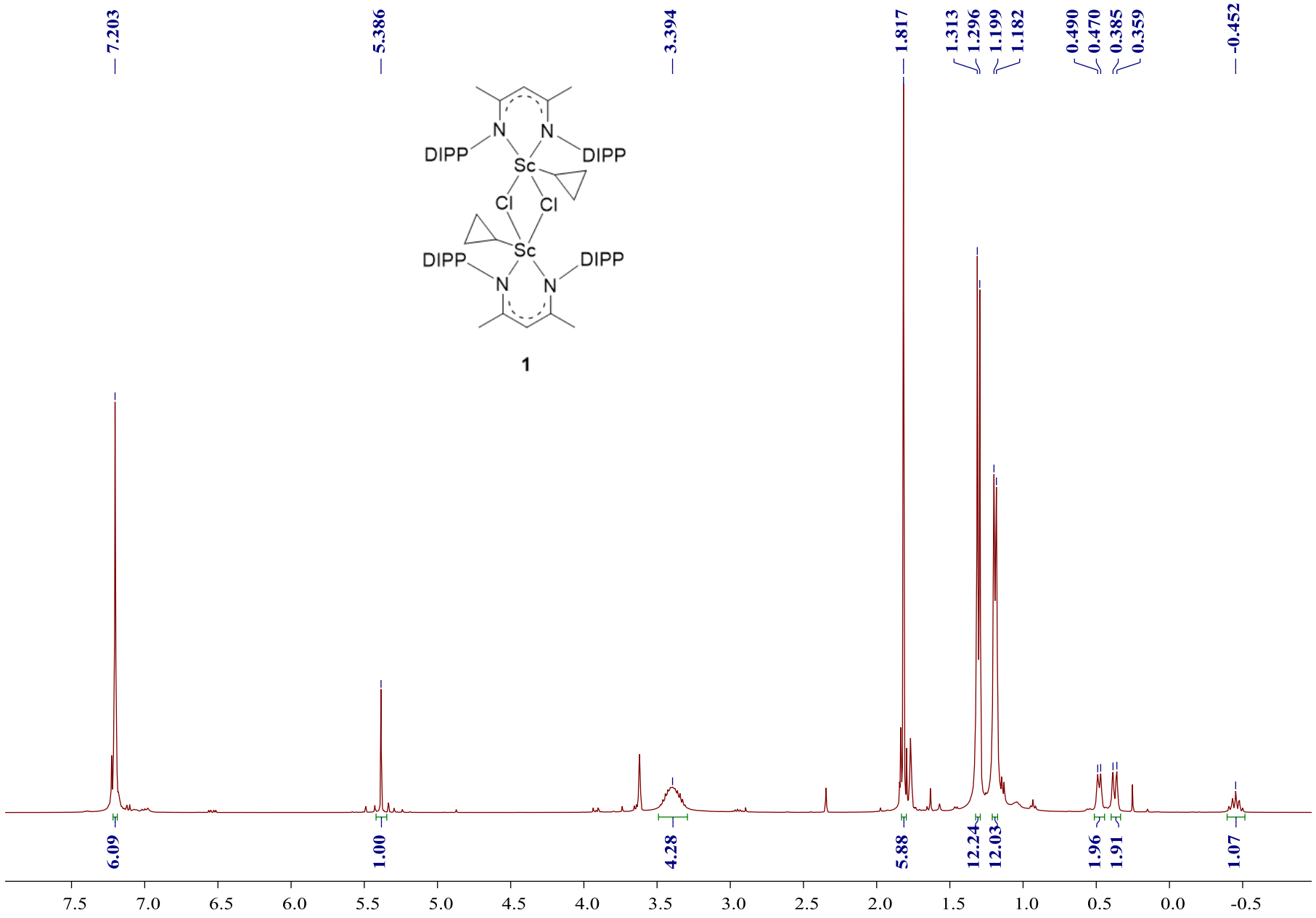


Fig. S1 ^{1}H NMR spectrum of **1** (400 MHz, THF-d_8, 25 ^{o}C).

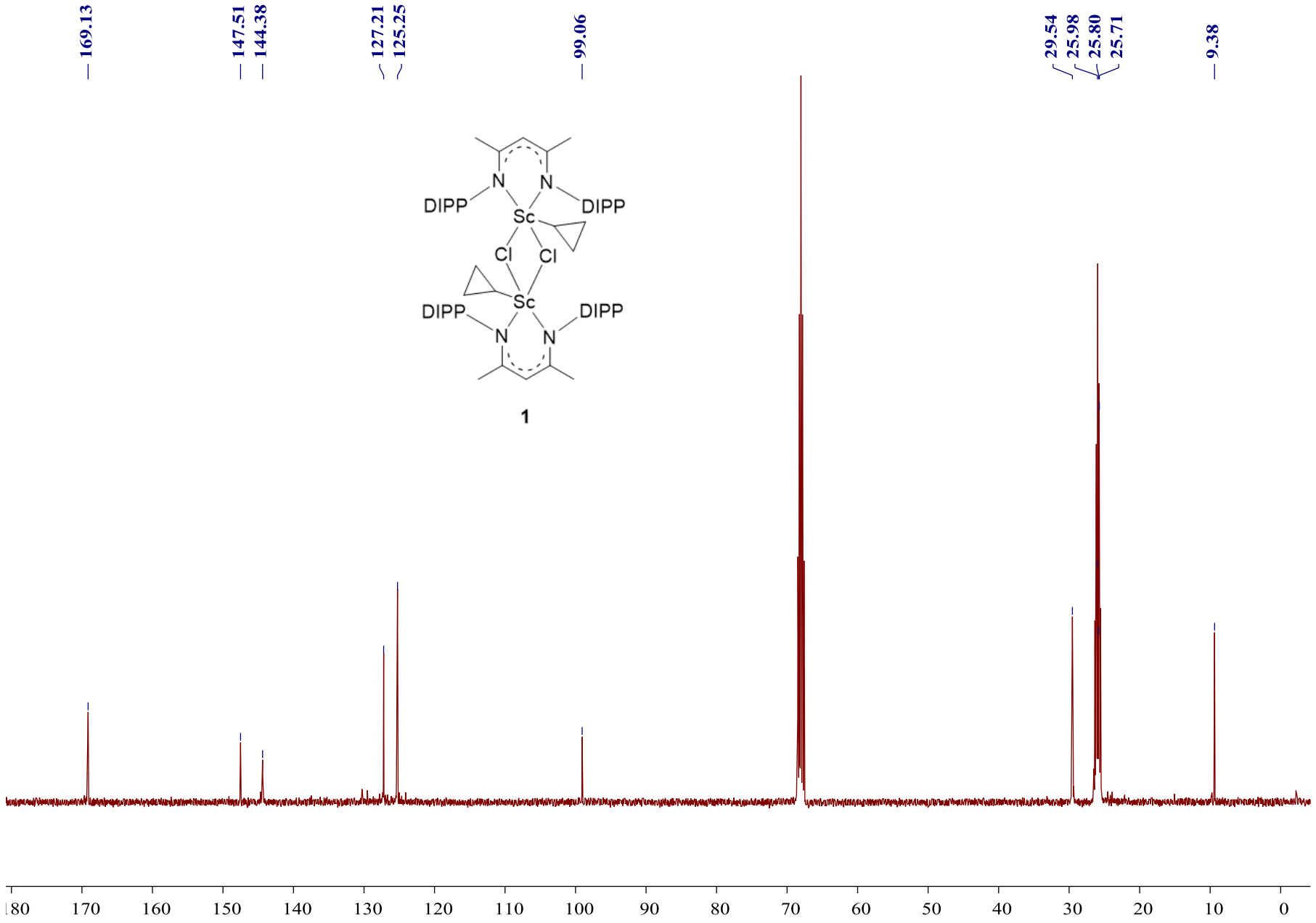


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of **1** (100 MHz, THF-d_8, 25 °C).

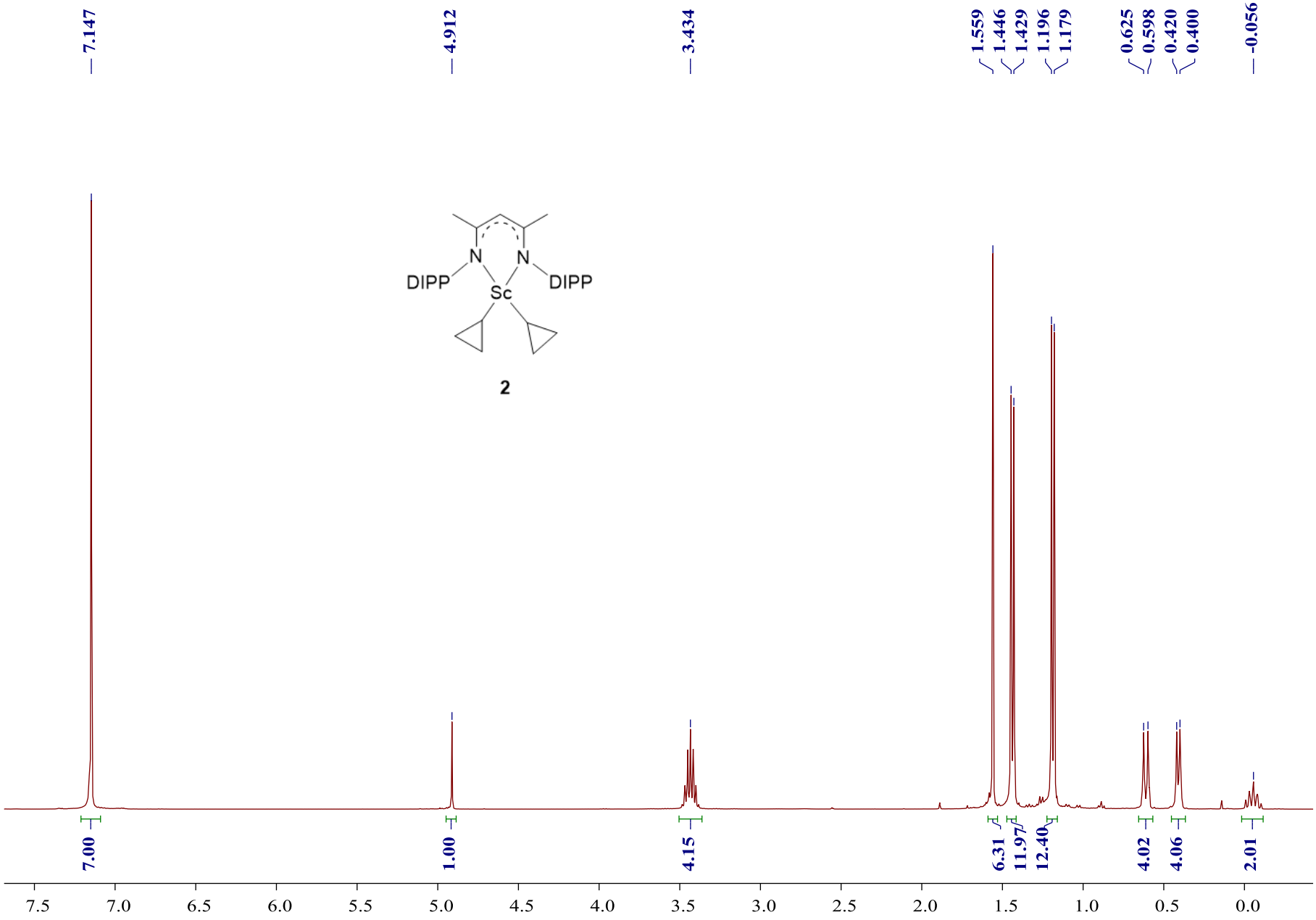


Fig. S3 ^{1}H NMR spectrum of **2** (400 MHz, C_6D_6, 25 ^{o}C).

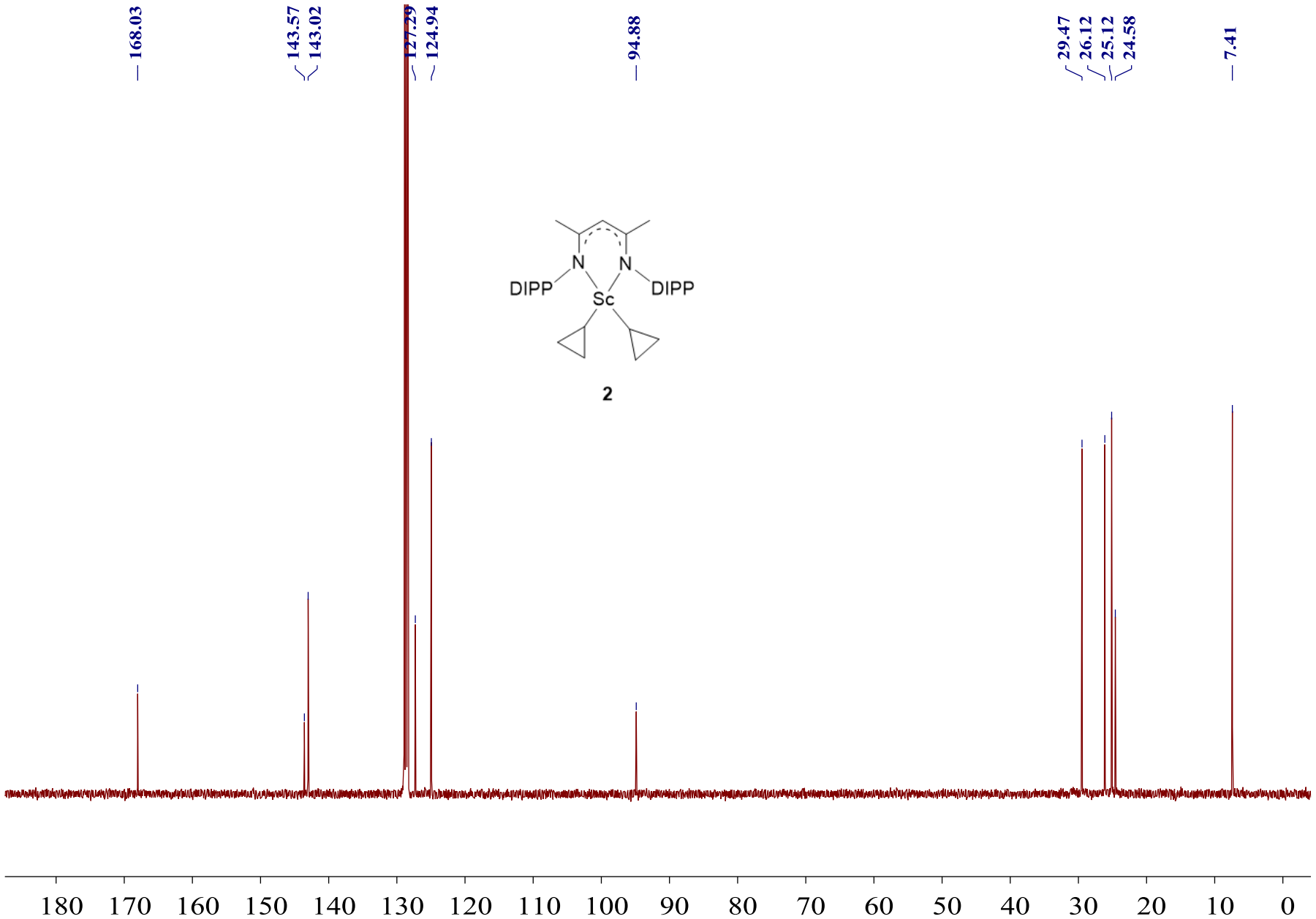


Fig. S4 $^{13}C\{^{1}H\}$ NMR spectrum of **2** (100 MHz, C_6D_6, 25 °C).

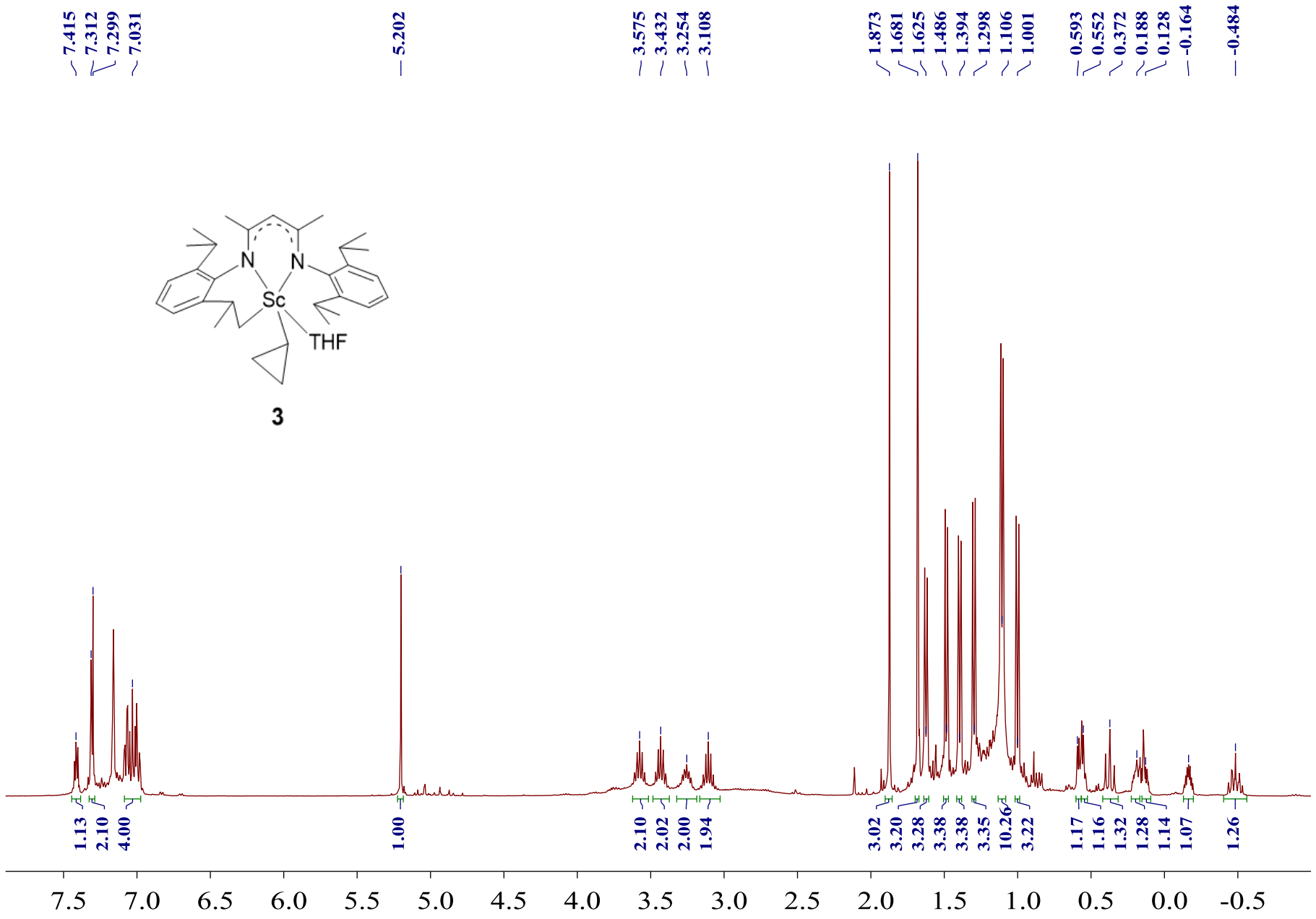


Fig. S5 ^{1}H NMR spectrum of **3** (400 MHz, C_6D_6, 25 ^{o}C).

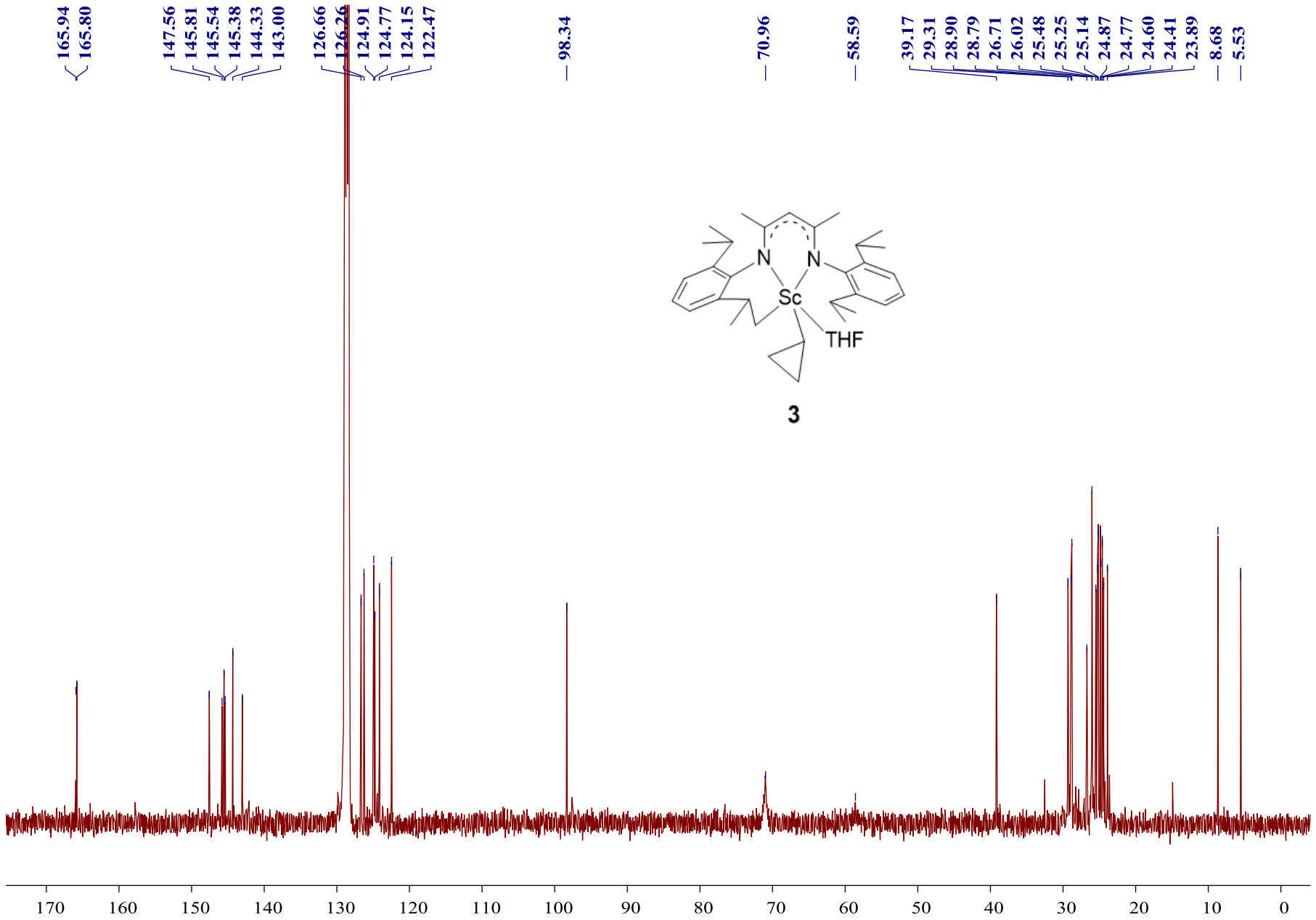


Fig. S6 $^{13}C\{^{1}H\}$ NMR spectrum of **3** (100 MHz, C_6D_6, 25 °C).

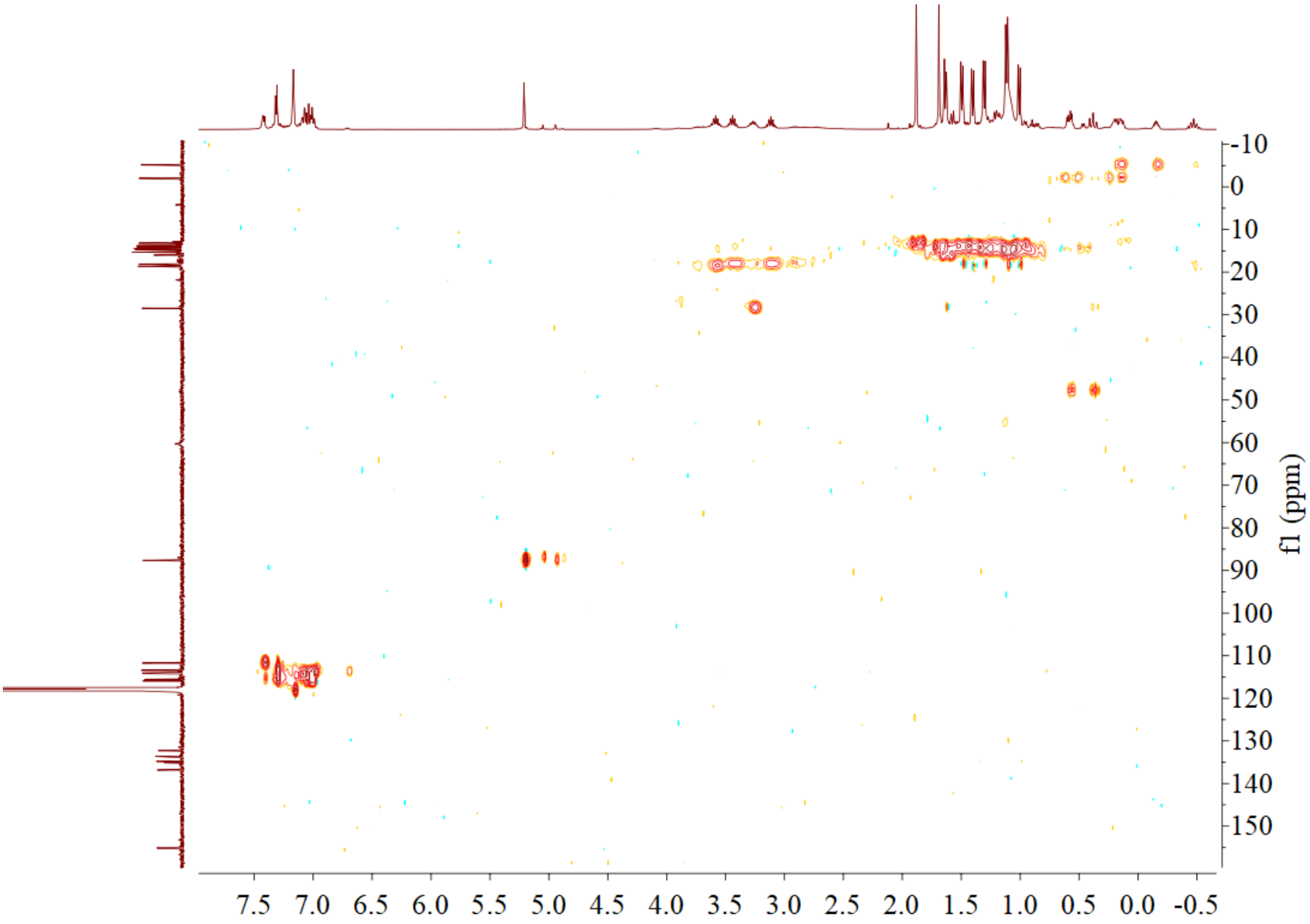


Fig. S7 gHSQC spectrum of **3** (400 MHz, C_6D_6, 25 °C).

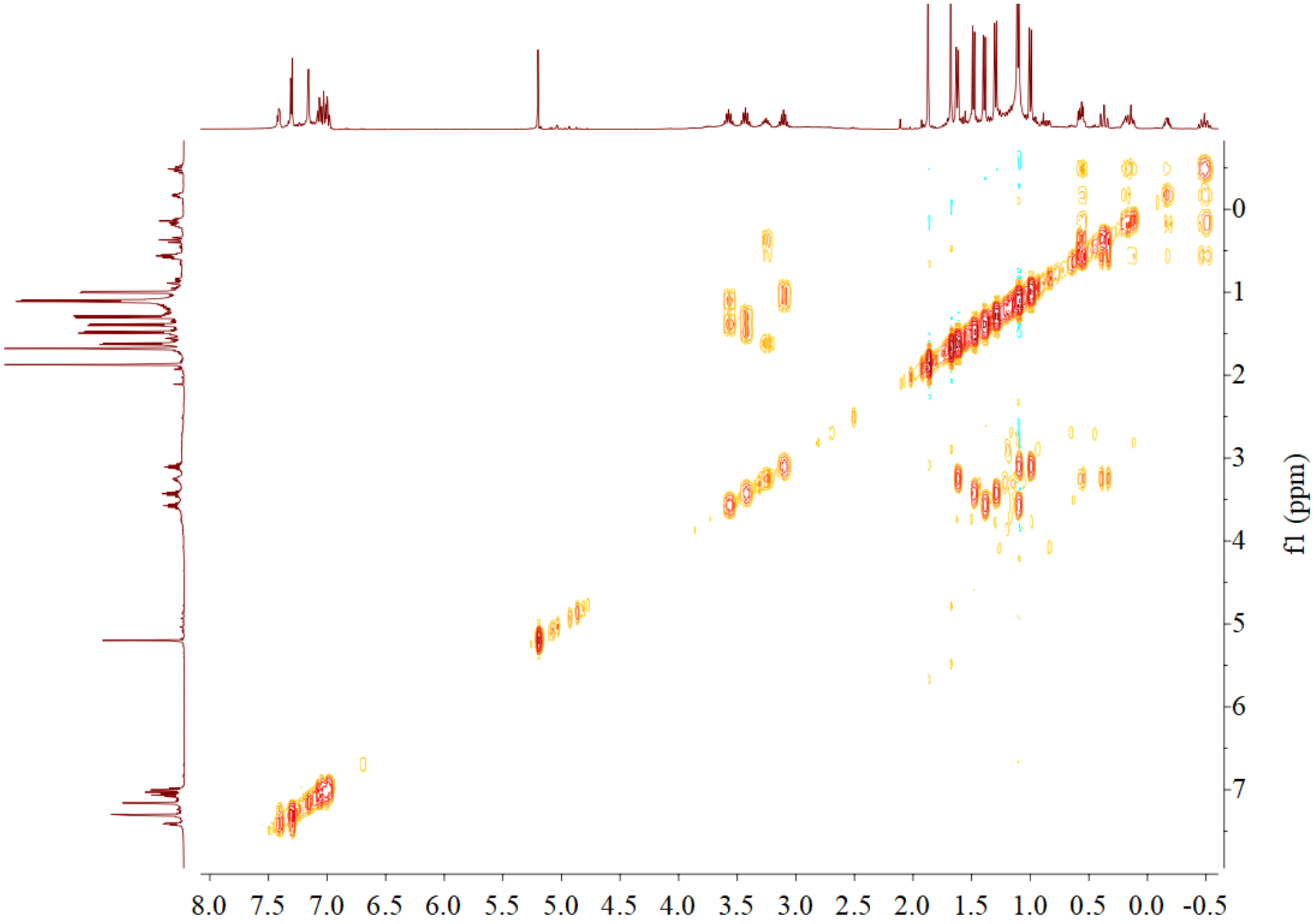


Fig. S8 ^{1}H-^{1}H COSY spectrum of **3** (400 MHz, C_6D_6, 25 ^{o}C).

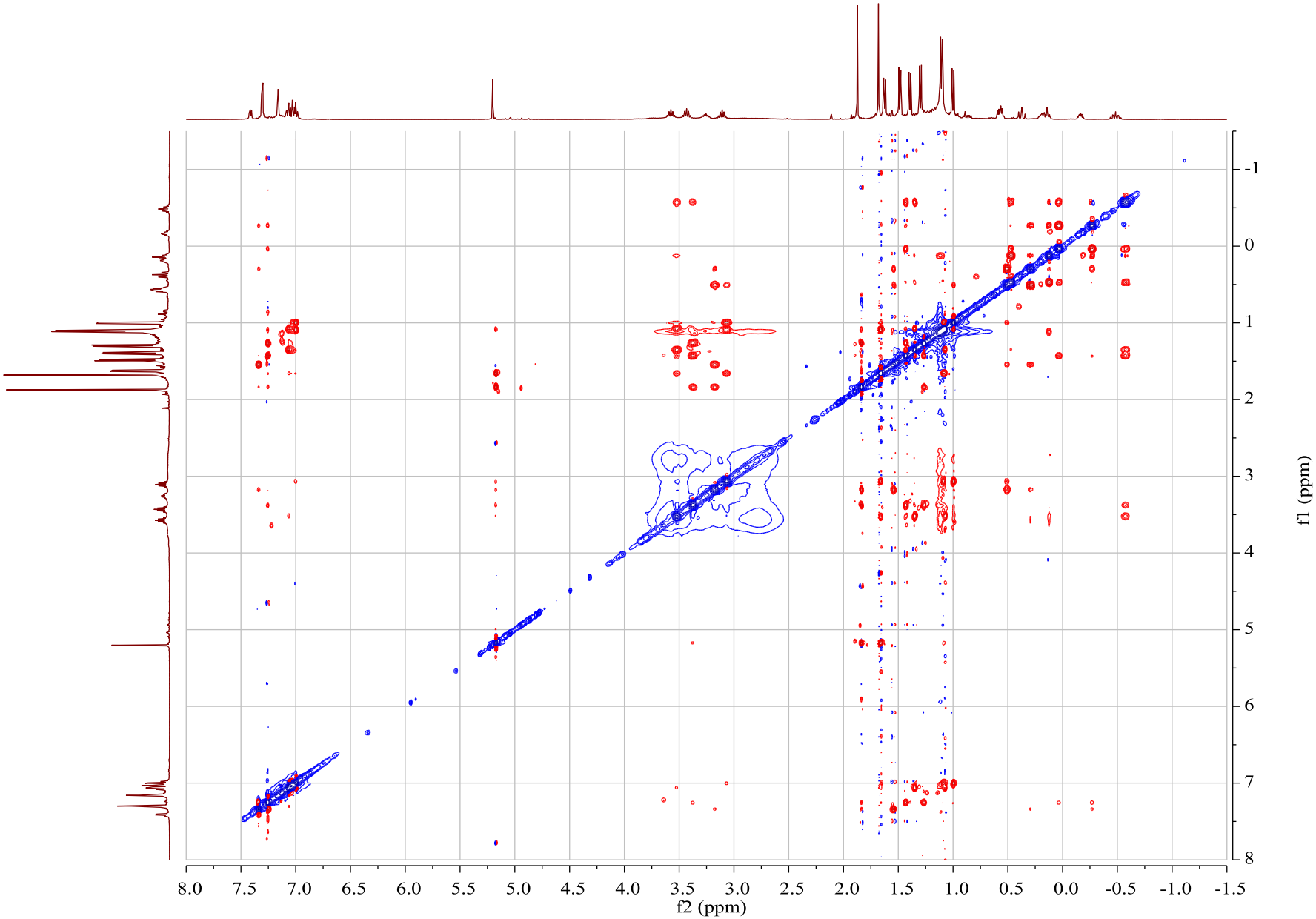


Fig. S9 ^{1}H-^{1}H EXSY & NOESY spectrum of **3** (400 MHz, C_6D_6, 25 ^{o}C).

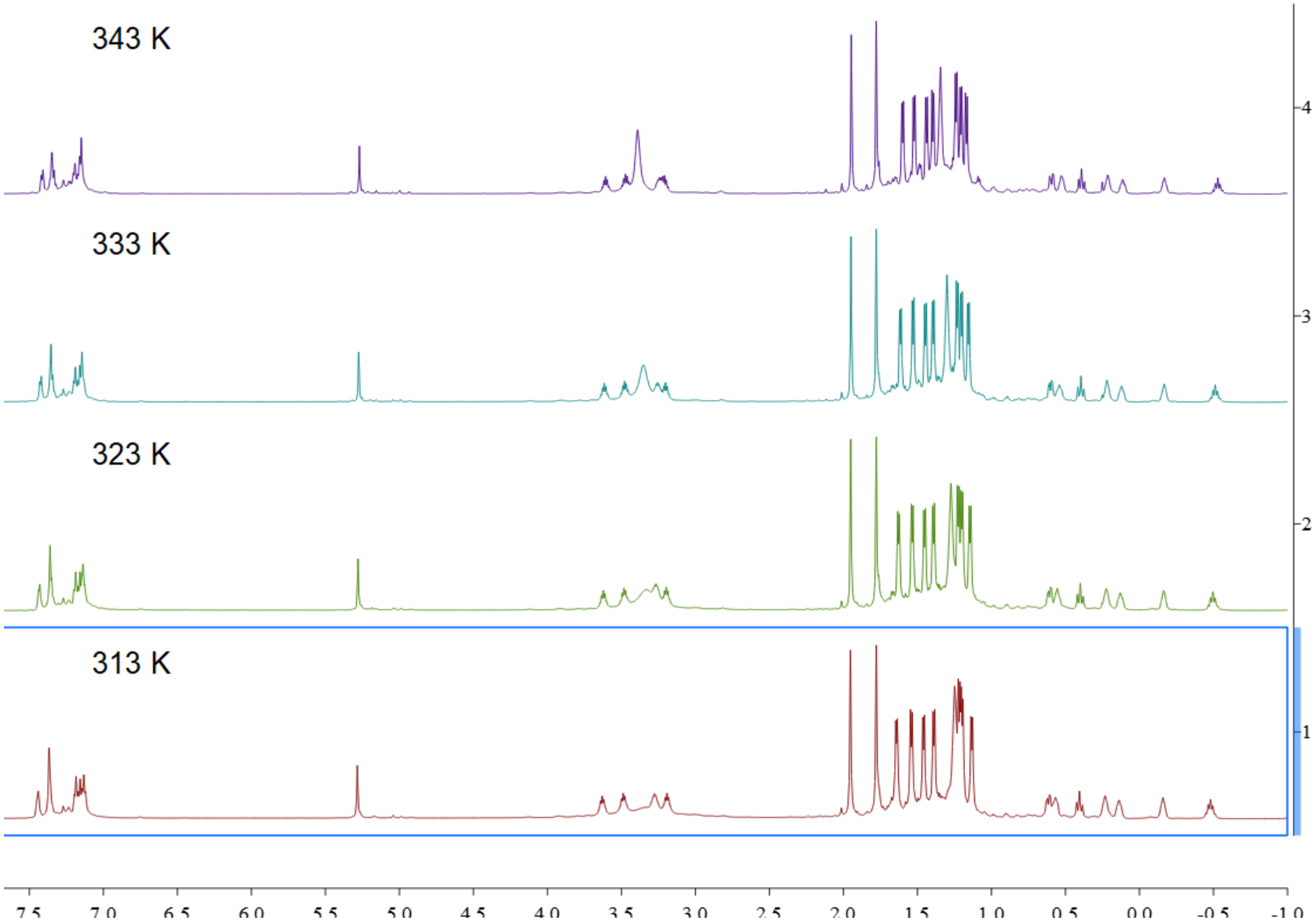


Fig. S10 Variable-Temperature ^{1}H NMR spectra of **3** (400 MHz, C_6D_6) (313 ~ 343 K).

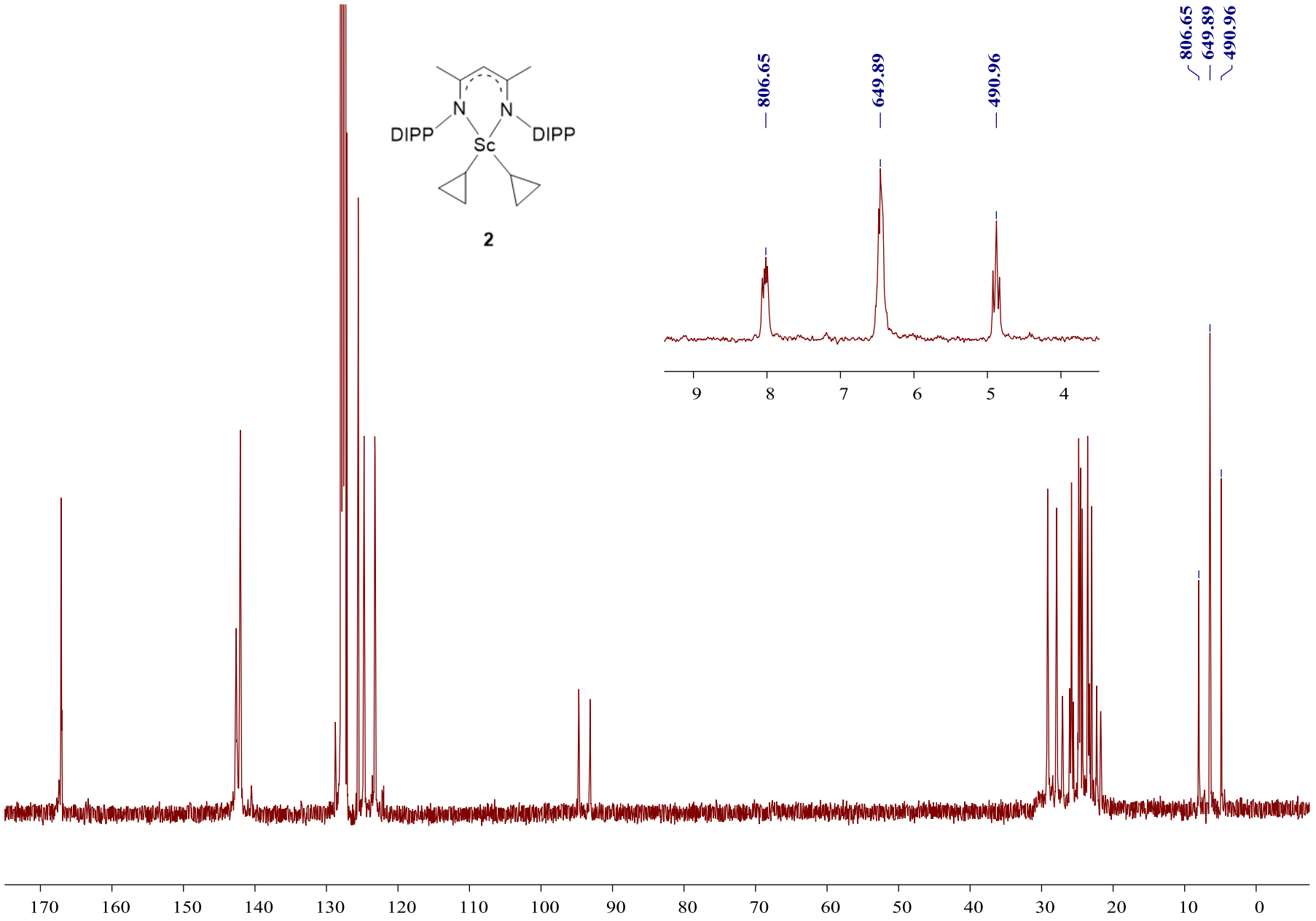


Fig. S11 Non-decoupling ^{13}C NMR spectrum of **2** (100 MHz, C_6D_6, 25 °C).

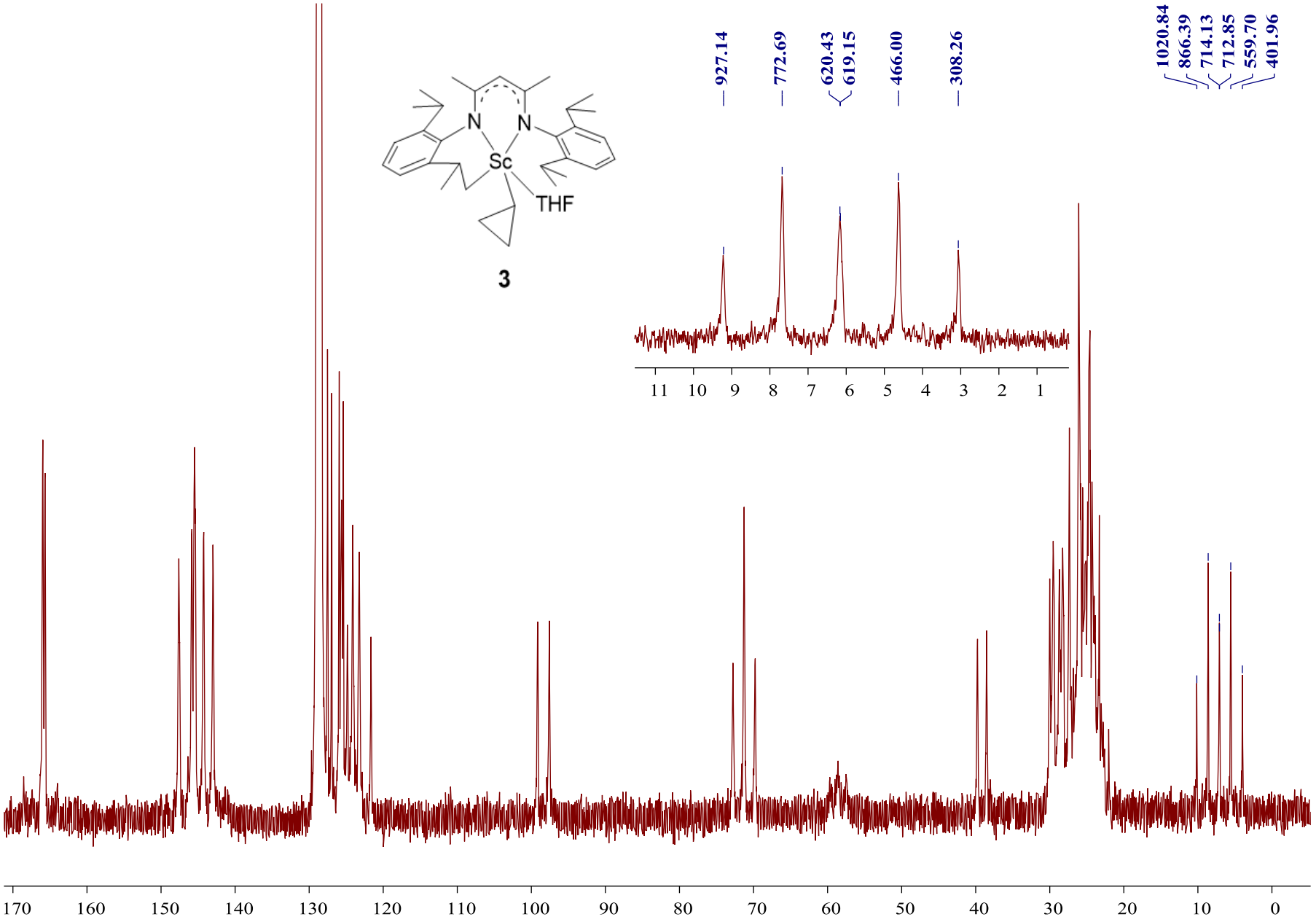


Fig. S12 Non-decoupling ^{13}C NMR spectrum of **3** (100 MHz, C_6D_6, 25 ºC).

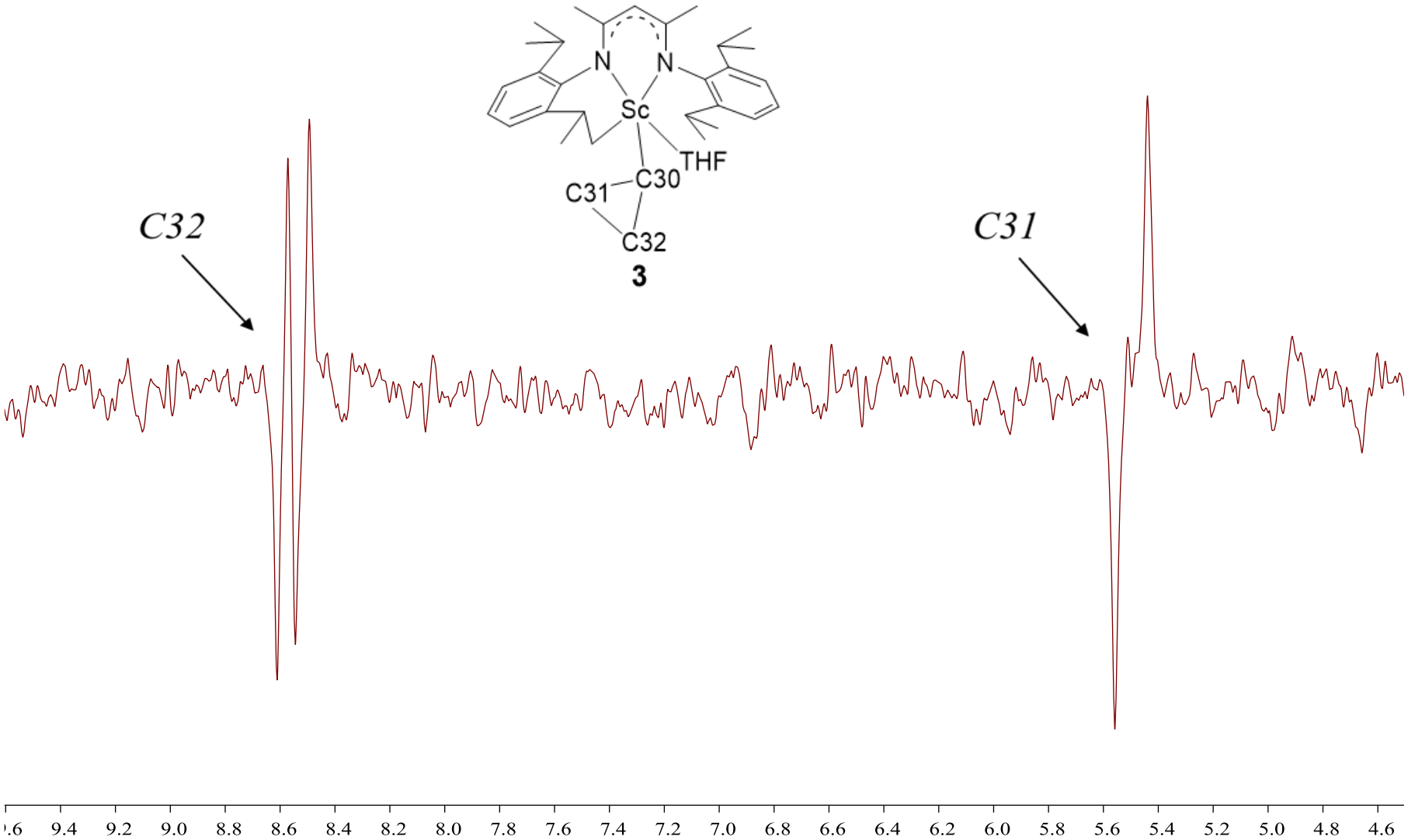


Fig. S13 Expansion plots of the ^{13}C INADEQUATE spectrum (126 MHz, C_6D_6, 25 °C) for **3**, optimized for J = 3 Hz.

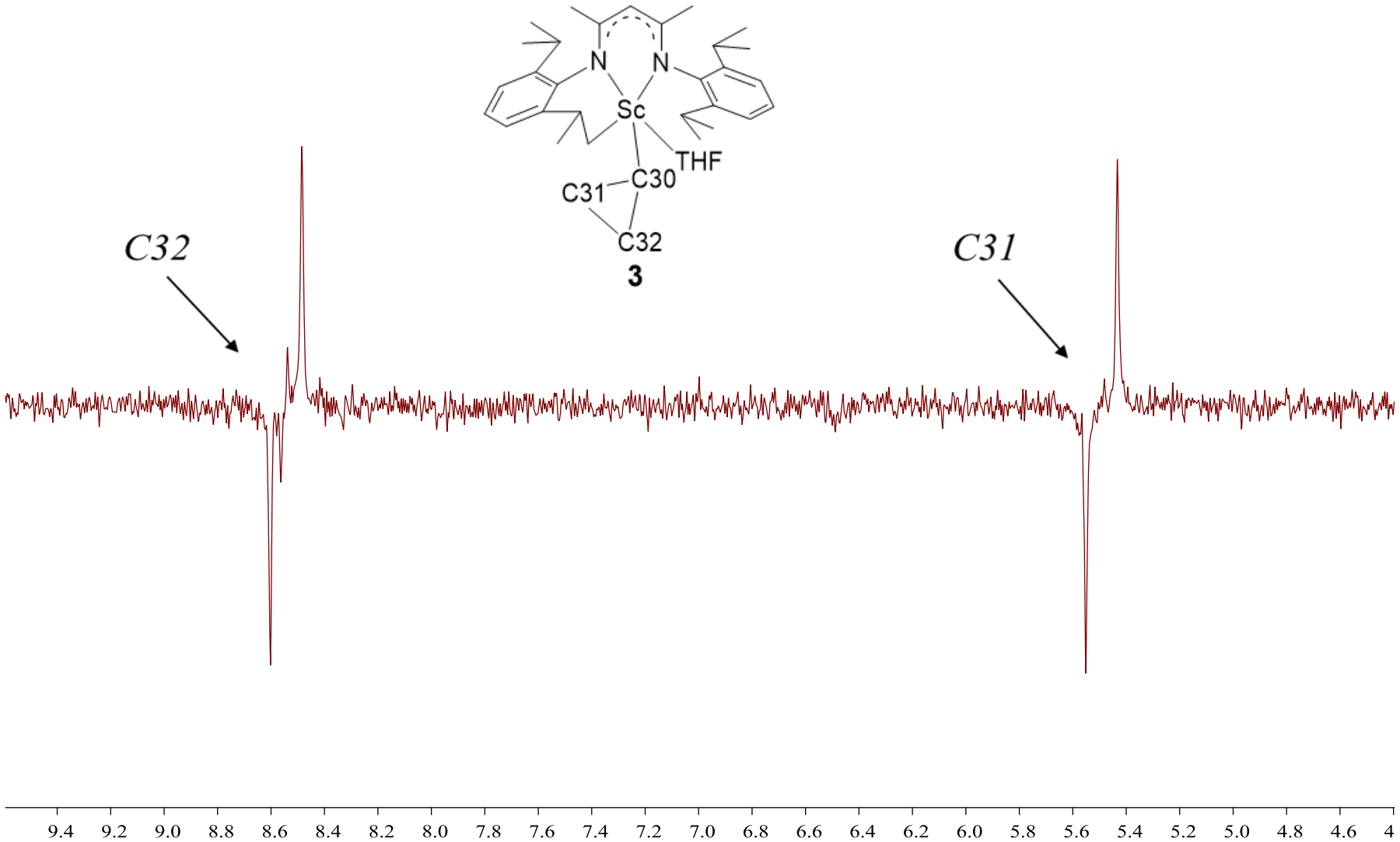


Fig. S14 Expansion plots of the ^{13}C INADEQUATE spectrum (126 MHz, C_6D_6, 25 ^{o}C) for **3**, optimized for J = 15 Hz.

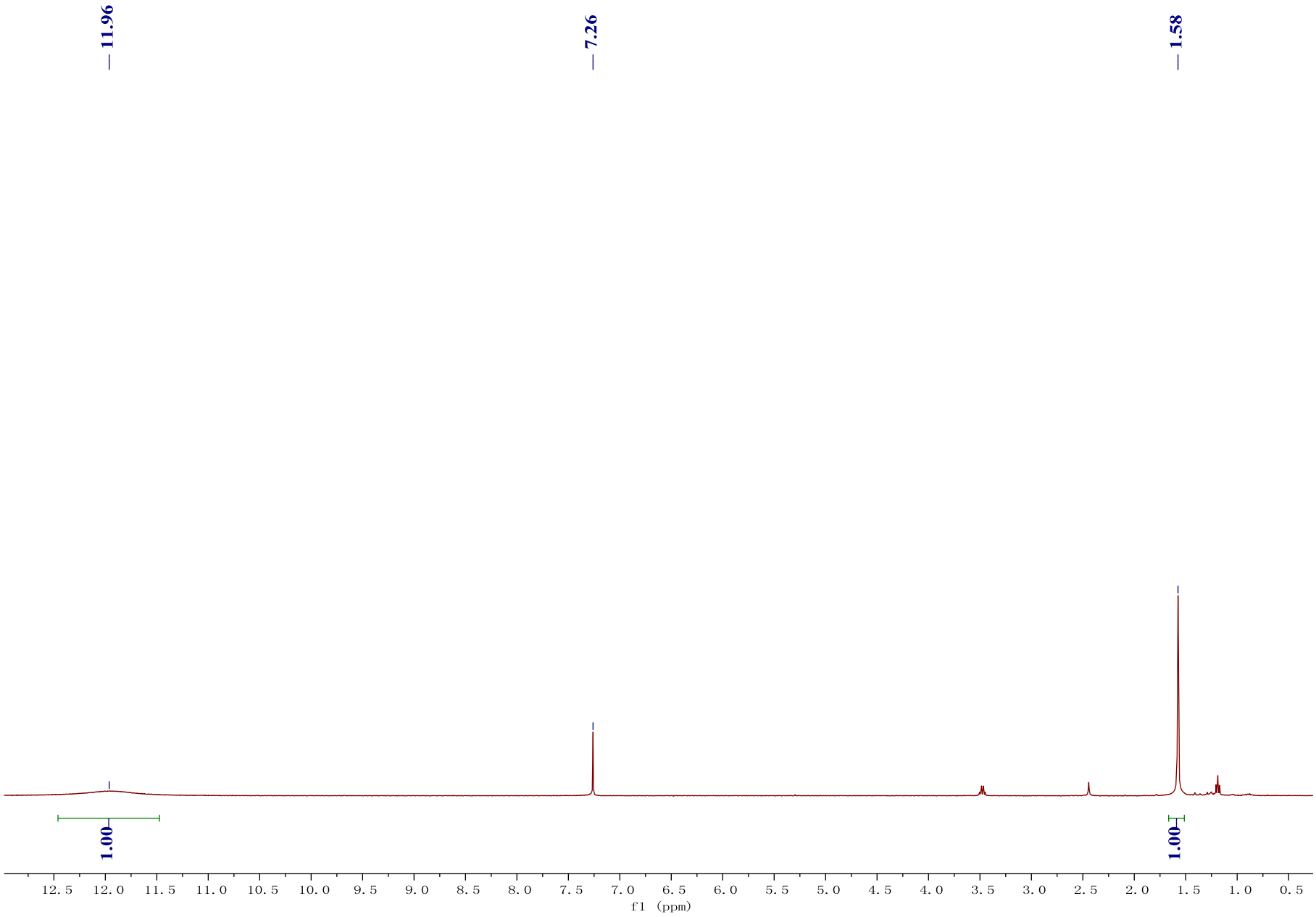


Fig. S15 ^{1}H NMR spectrum of 2,2,3,3-tetradeuteriocyclopropanecarboxylic acid (400 MHz, $CDCl_3$, 25 ^{o}C).

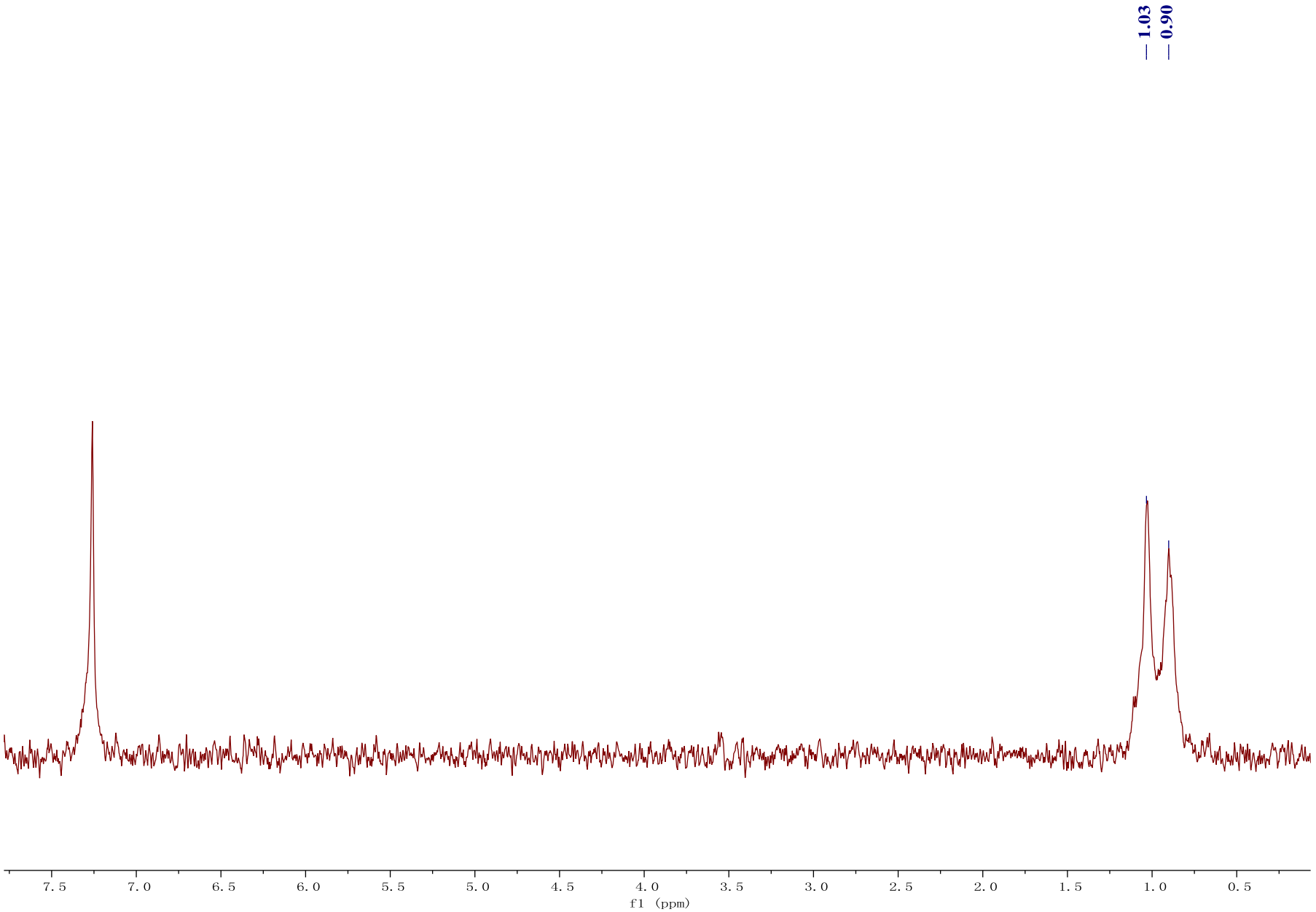


Fig. S16 ^{2}H NMR spectrum of 2,2,3,3-tetradeuteriocyclopropanecarboxylic acid (60 MHz, $CHCl_3$, 25 ^{o}C). $CDCl_3$ as the reference.

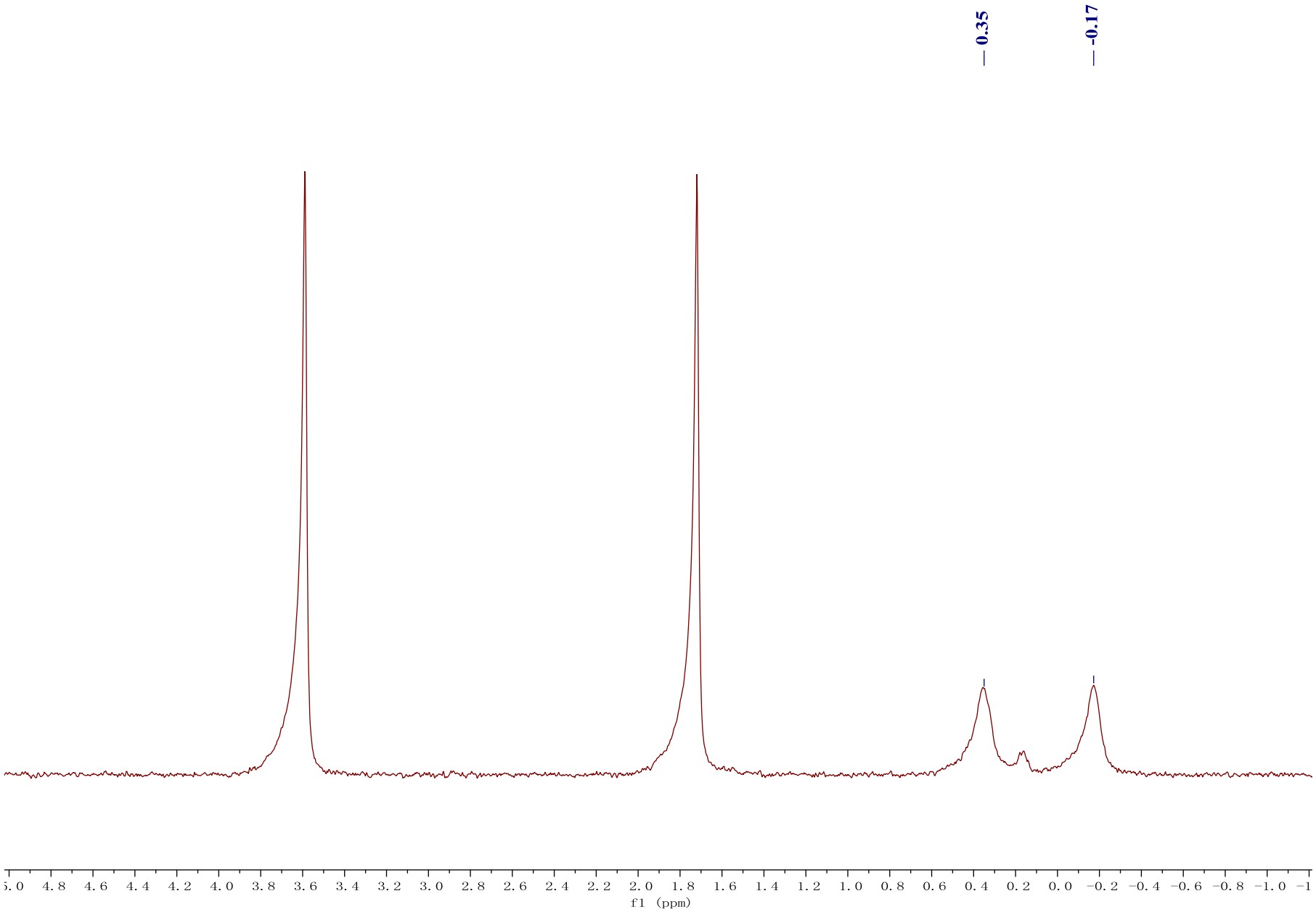


Fig. S17 ^{2}H NMR spectrum of 2,2,3,3-tetradeuteriocyclopropyl lithium (60 MHz, THF, 25 ^{o}C). THF-d_8 as the reference.

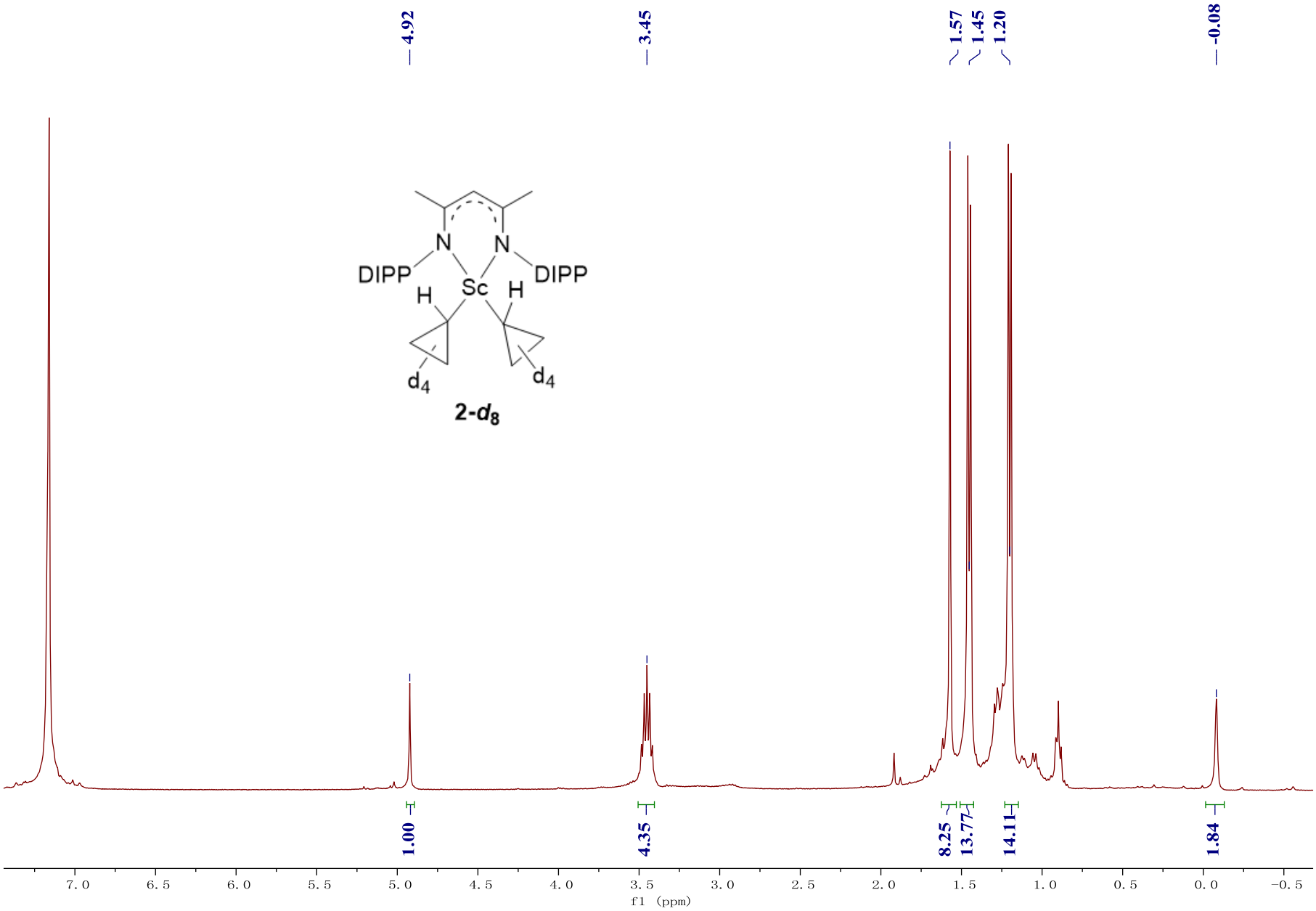


Fig. S18 ^{1}H NMR spectrum of **2-*d*$_8$** (400 MHz, C_6D_6, 25 ^{o}C).

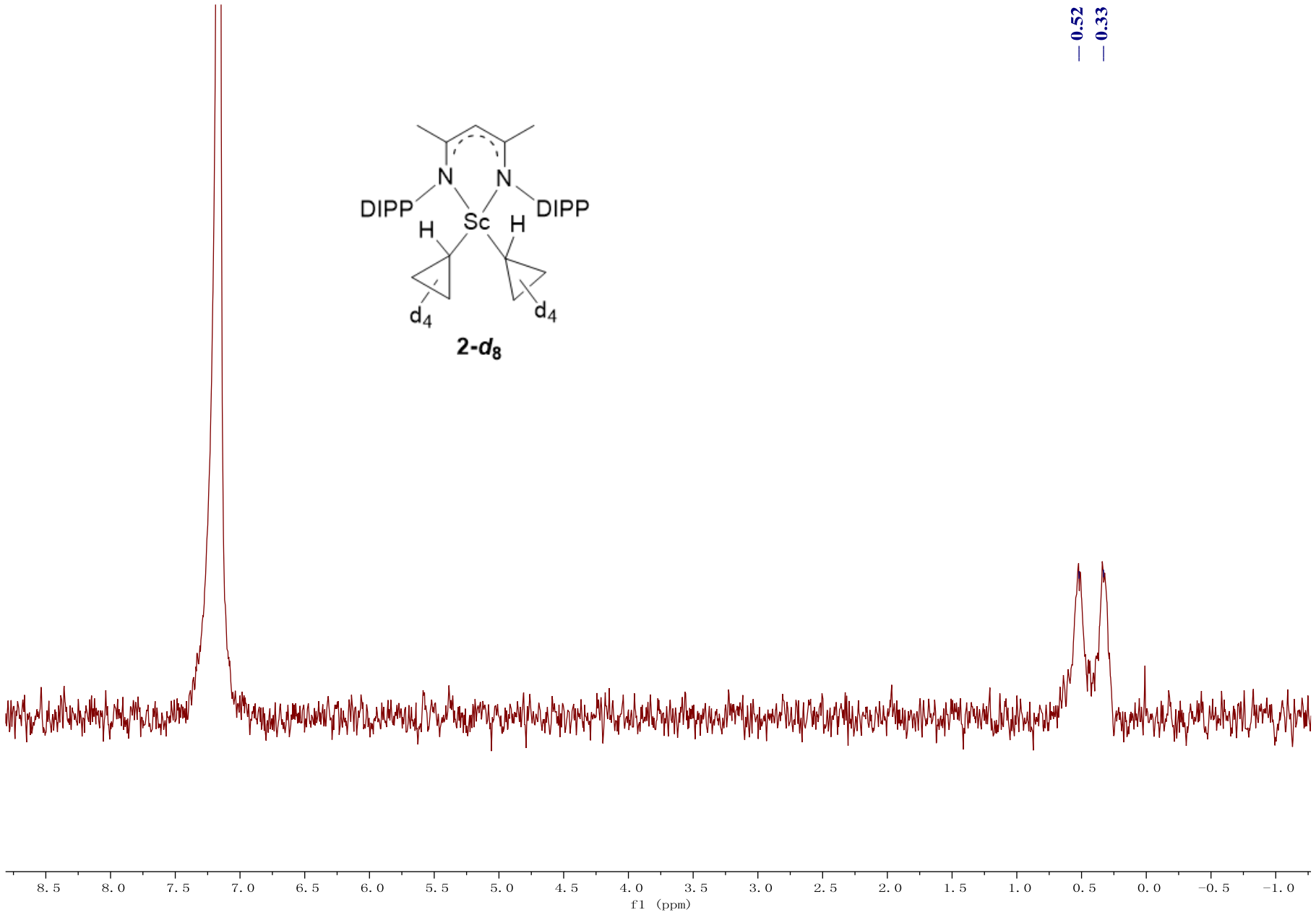


Fig. S19 ^{2}H NMR spectrum of **2-*d*$_8$** (60 MHz, C_6H_6, 25 °C). C_6D_6 as the reference.

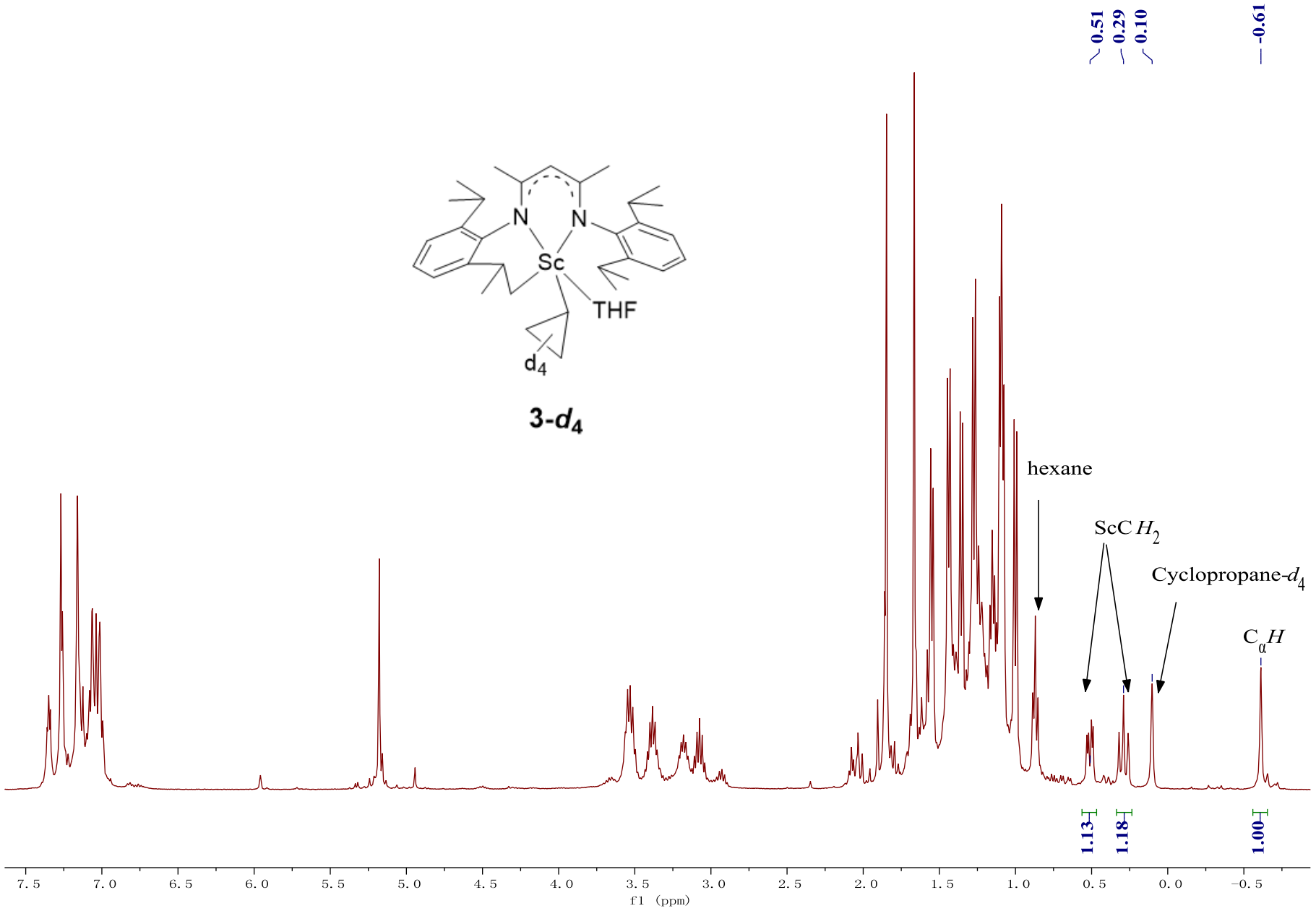


Fig. S20 ^{1}H NMR spectral monitoring of the thermolysis of **2-*d*$_8$** into **3-*d*$_4$** in THF-d_8/C_6D_6 at 65 ºC in 24 h (400 MHz, 25 ºC).

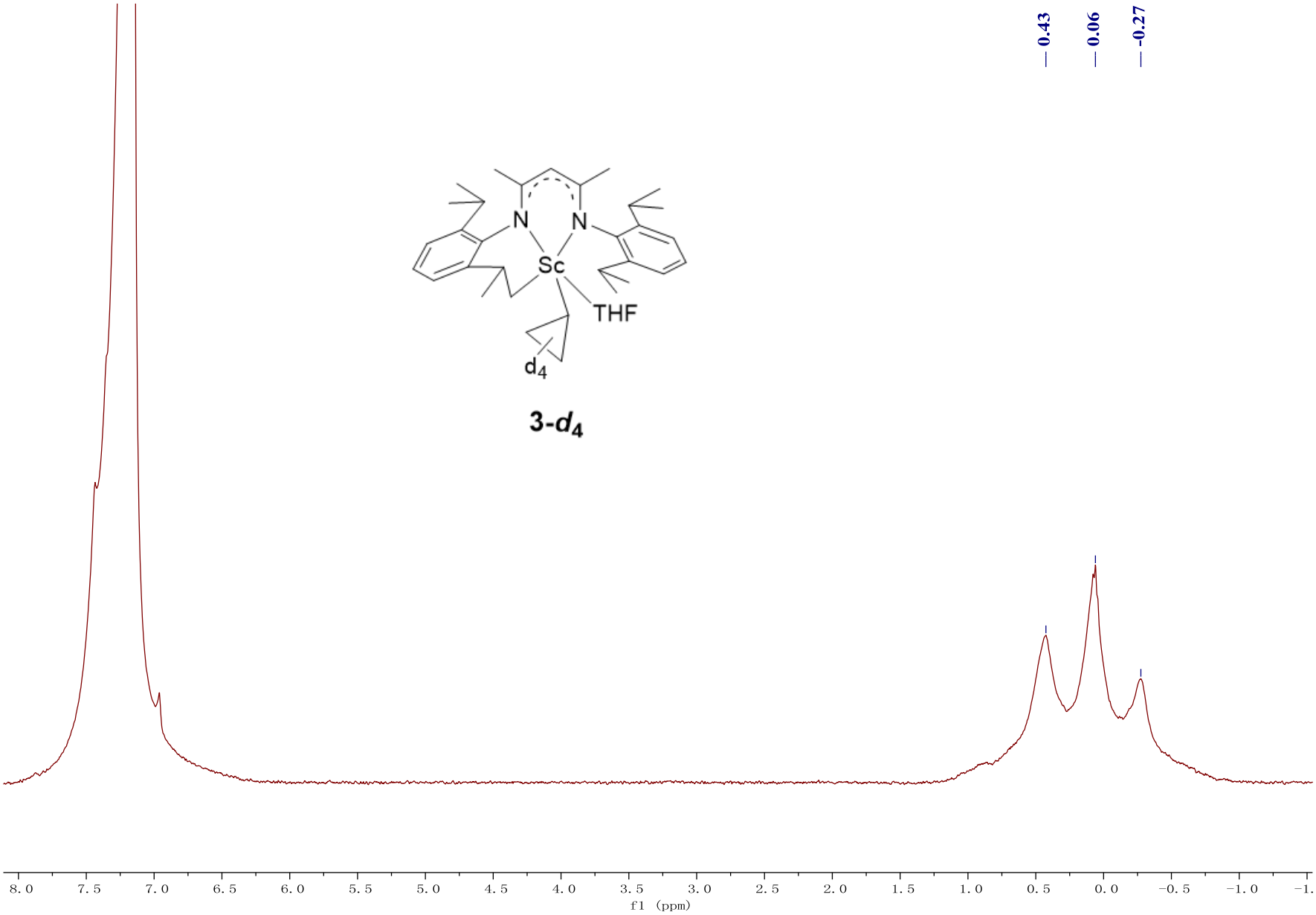


Fig. S21 ^{2}H NMR spectrum of the thermolysis product of **2-*d*$_8$** in THF/C_6H_6 (60 MHz, C_6H_6, 25 ^{o}C). C_6D_6 as the reference.

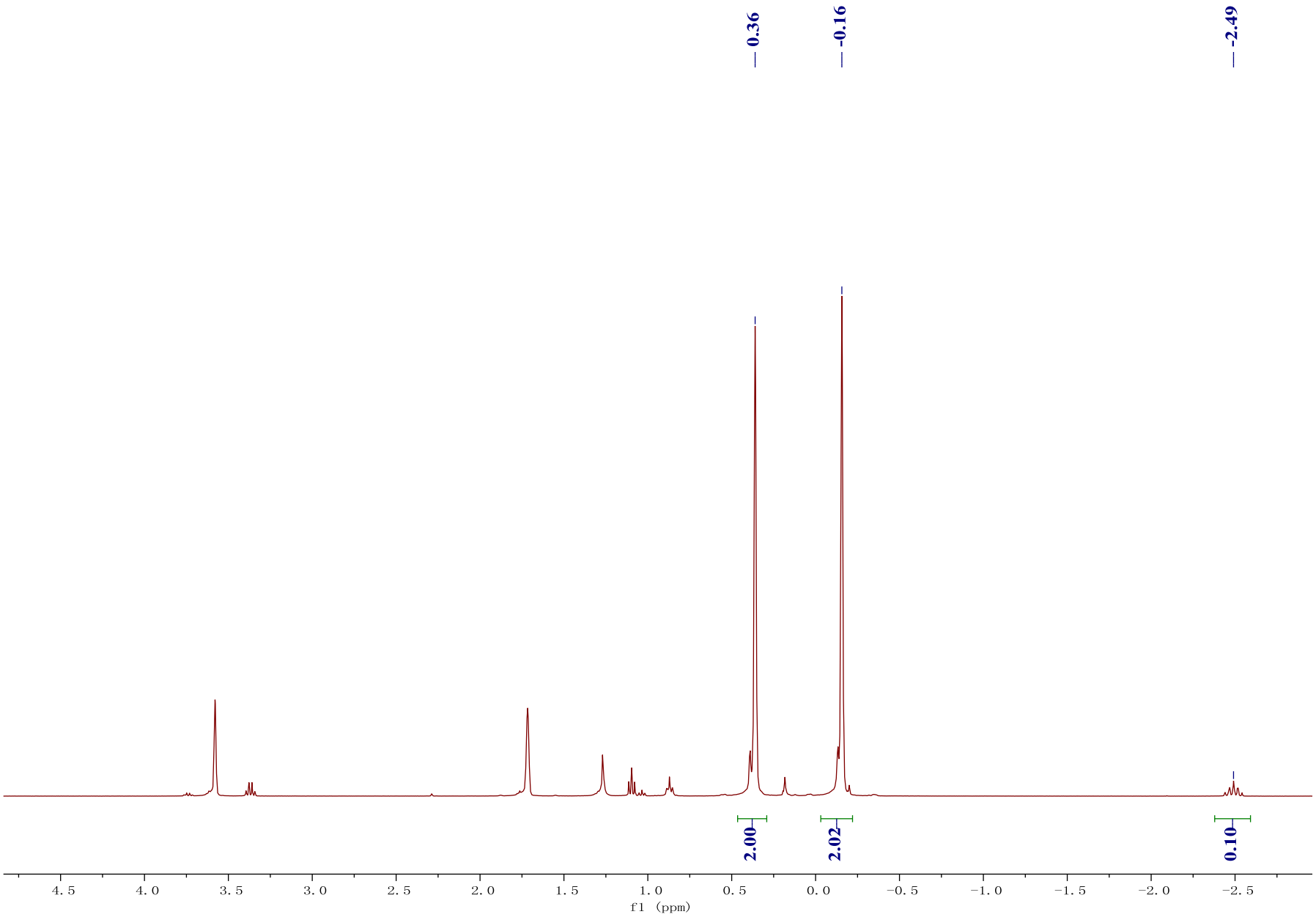


Fig. S22 ^{1}H NMR spectrum of 1-monodeuteriocyclopropyl lithium (400 MHz, THF-d_8, 25 ^{o}C).

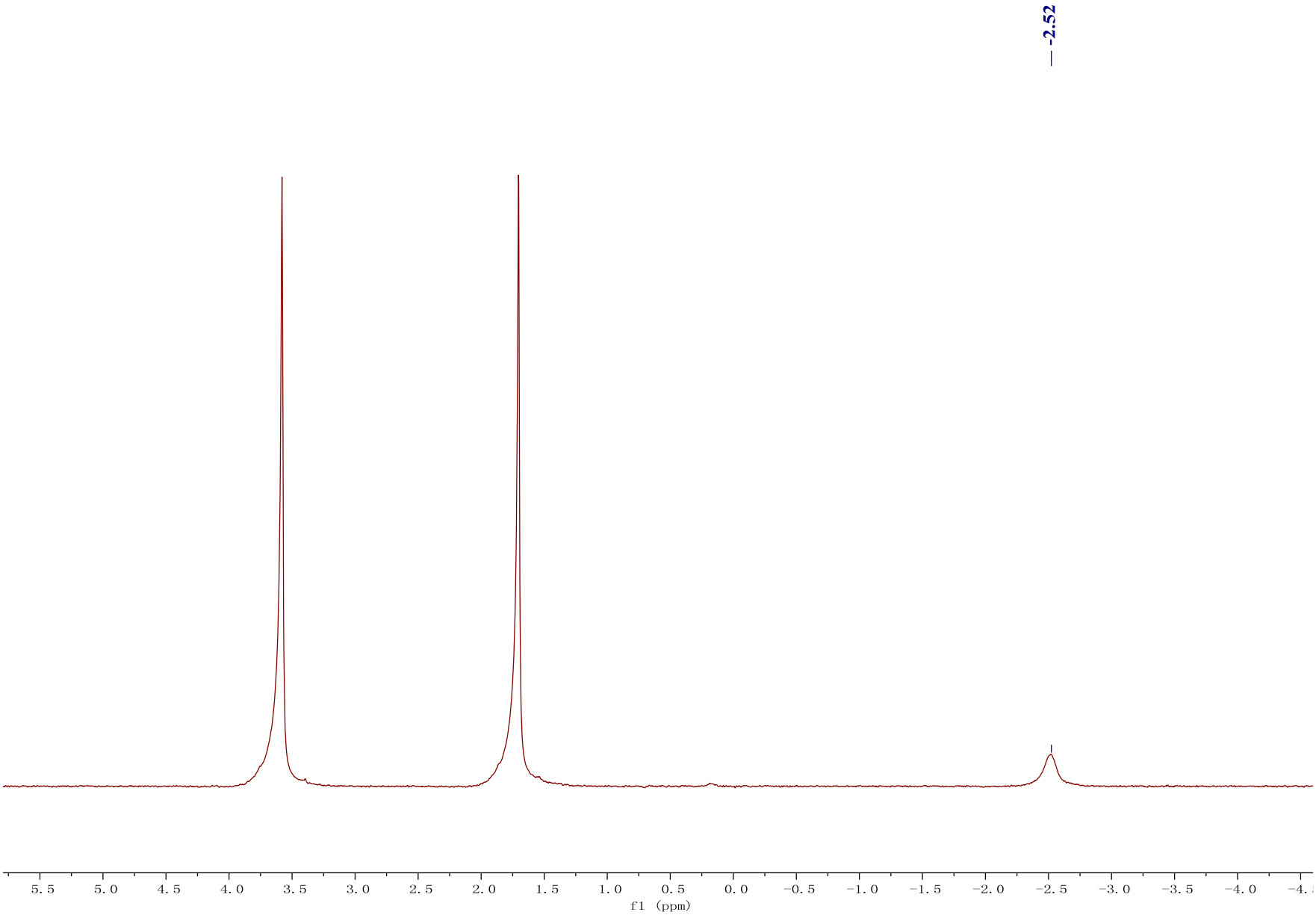


Fig. S23 ^{2}H NMR spectrum of 1-monodeuteriocyclopropyl lithium (60 MHz, THF, 25 ^{o}C). THF-d_8 as the reference.

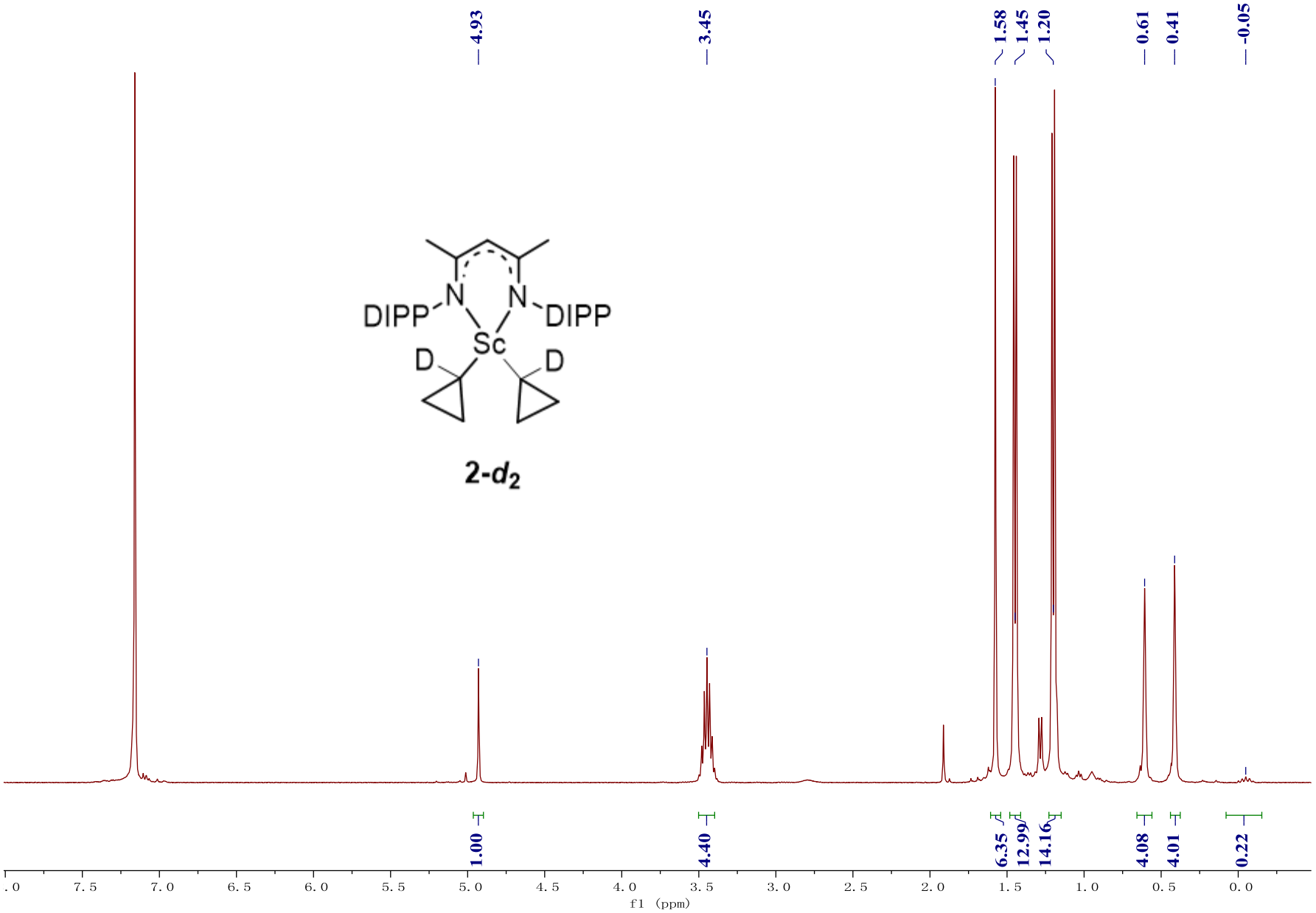


Fig. S24 ^{1}H NMR spectrum of **2-*d*$_2$** (400 MHz, C_6D_6, 25 ^{o}C).

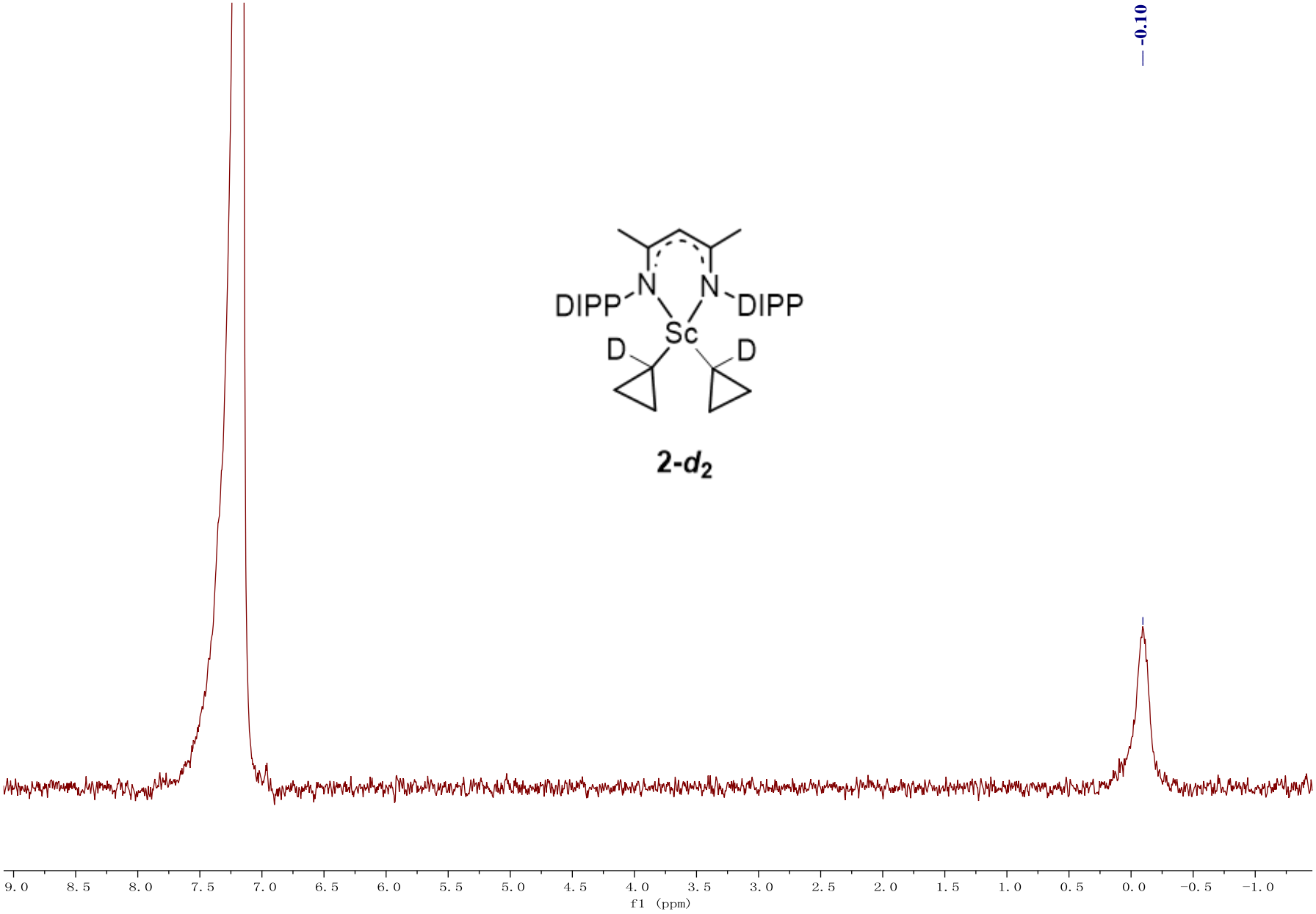


Fig. S25 ^{2}H NMR spectrum of **2-*d*$_2$** (60 MHz, C_6H_6, 25 ^{o}C). C_6D_6 as the reference.

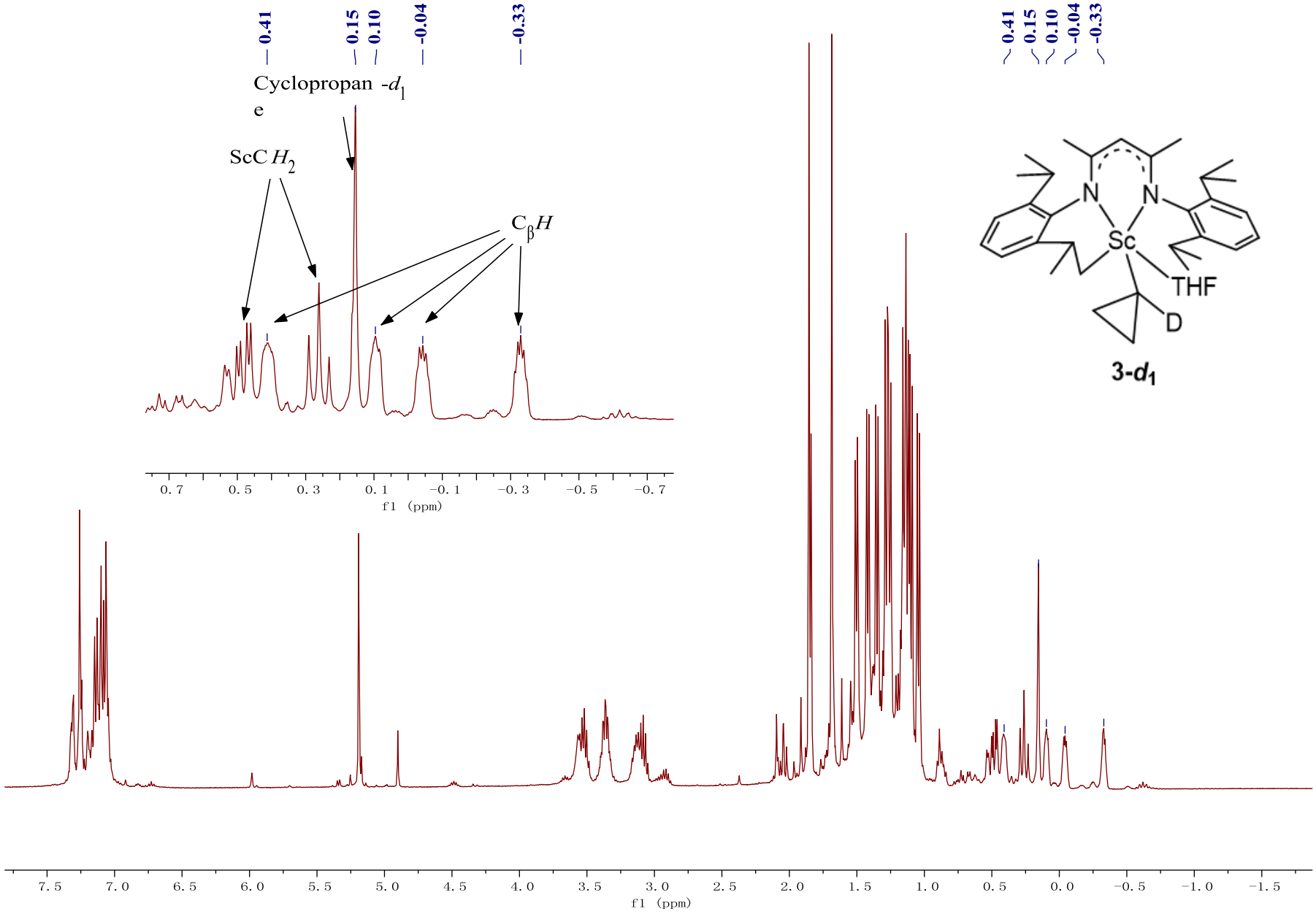


Fig. S26 ^{1}H NMR spectral monitoring of the thermolysis of **2-*d*$_2$** into **3-*d*$_1$** in THF-d_8/C_6D_6 at 65 ºC in 24 h (400 MHz, 25 ºC).

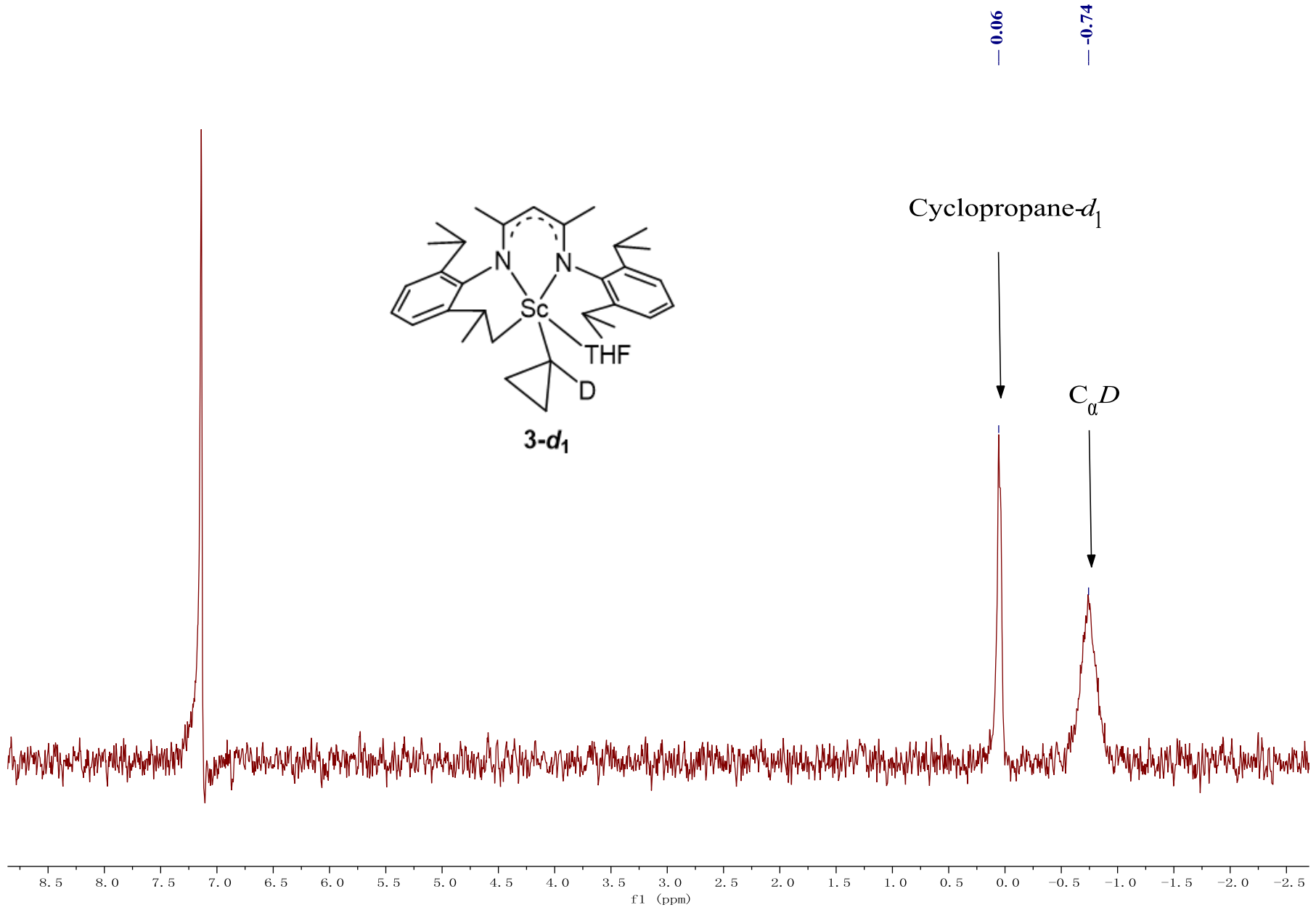
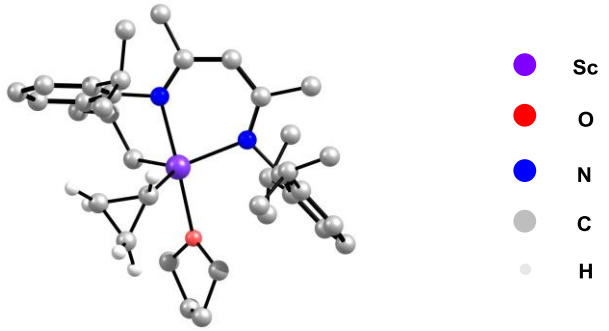


Fig. S27 ^{2}H NMR spectral monitoring of the thermolysis of **2-*d*$_2$** into **3-*d*$_1$** in THF /C_6H_6 at 65 ºC in 24 h (400 MHz, 25 ºC).

Computational data.

1- Cartesian coordinates and SCF energies of optimized structures.

- Complex **3** (E(RPBE1PBE) = -1632.74893187 au)



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6	3.568328000	11.685793000	6.997910000
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6	4.780304000	12.488133000	5.081675000
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6	5.690957000	12.785118000	7.295236000
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6	4.972896000	5.092417000	9.306916000
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1	5.823045000	9.254349000	7.172841000
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1	0.878161000	6.411834000	5.003609000
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1	3.093792000	8.379217000	13.243664000
1	1.920473000	7.073499000	13.469506000
1	3.268416000	6.859708000	12.331100000
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1	5.037354000	7.946076000	11.019062000
1	6.504550000	5.625752000	10.804311000
1	4.836751000	5.553346000	11.422446000
1	5.744134000	5.121469000	8.521250000
1	4.715595000	4.040099000	9.491023000
1	3.581781000	5.939492000	7.819130000
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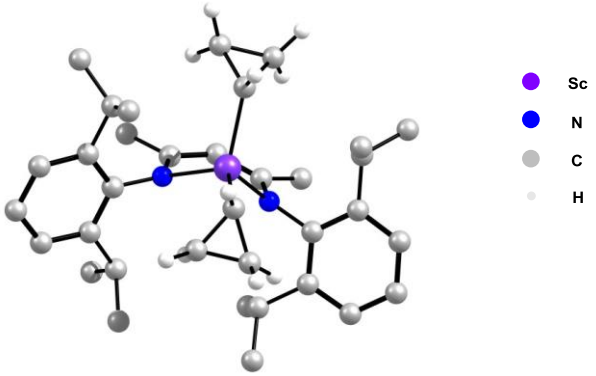
- Complex **2** (E(RPBE1PBE) = -1518.48876008 au)



21	0.068441000	-1.053038000	-0.586067000
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6	-2.459755000	-0.383070000	2.775371000
6	-1.279665000	-0.287008000	1.853014000
6	-0.003858000	-0.396770000	2.433056000
6	1.261004000	-0.125420000	1.880553000
6	2.415684000	-0.024009000	2.833085000
6	-2.765894000	0.281988000	0.082045000
6	-3.650831000	-0.677591000	-0.454078000
6	-4.886975000	-0.250121000	-0.946293000
6	-5.253885000	1.089440000	-0.909250000
6	-4.368958000	2.026460000	-0.388880000
6	-3.116009000	1.650266000	0.102773000
6	-2.170227000	2.717178000	0.622894000
6	-1.902896000	3.784193000	-0.438246000
6	-2.681186000	3.361710000	1.912051000
6	-3.278918000	-2.142976000	-0.529578000
6	-4.336871000	-3.055496000	0.086285000
6	-2.959583000	-2.554925000	-1.967362000
6	2.729207000	0.492514000	0.100363000
6	2.881299000	1.867177000	-0.187684000
6	4.120843000	2.312991000	-0.654152000

6	5.174268000	1.429073000	-0.862419000
6	4.990131000	0.072532000	-0.629992000
6	3.772201000	-0.421886000	-0.153986000
6	3.574866000	-1.915294000	0.001788000
6	3.351416000	-2.562943000	-1.367090000
6	4.710574000	-2.599932000	0.757557000
6	1.721487000	2.831875000	-0.019021000
6	1.597813000	3.338174000	1.419072000
6	1.779878000	3.998563000	-1.000142000
6	0.245713000	-0.679606000	-2.701594000
6	-0.491188000	0.661416000	-2.699596000
6	0.917096000	0.575376000	-3.182539000
6	0.110887000	-3.174144000	-0.010138000
6	0.814513000	-3.748561000	1.203278000
6	-0.664478000	-3.849152000	1.102431000
1	-3.978937000	-4.096401000	0.100881000
1	-4.568848000	-2.761798000	1.121519000
1	-5.279061000	-3.037489000	-0.484173000
1	-3.851167000	-2.477887000	-2.610115000
1	-2.184332000	-1.911398000	-2.412709000
1	-2.598315000	-3.594093000	-2.001712000
1	-5.576871000	-0.987437000	-1.364131000
1	-6.227273000	1.405033000	-1.291837000
1	-4.654397000	3.081386000	-0.370102000
1	-2.360962000	-2.287954000	0.057980000
1	-1.212717000	2.225462000	0.851803000
1	-1.490920000	3.345894000	-1.359200000
1	-2.823413000	4.324584000	-0.708025000
1	-1.186211000	4.529748000	-0.062042000
1	-3.641184000	3.876555000	1.747233000
1	-2.834007000	2.620824000	2.709787000
1	-1.961199000	4.107761000	2.283691000
1	-0.069890000	-1.343230000	-3.505764000
1	1.080093000	0.694667000	-4.249597000
1	1.700006000	1.022679000	-2.574532000
1	-1.290668000	0.846770000	-3.409392000
1	-0.661718000	1.161879000	-1.741622000
1	-3.104926000	-1.219828000	2.466773000
1	-2.148191000	-0.533053000	3.814414000
1	-3.081015000	0.520345000	2.712884000
1	2.960653000	0.918326000	2.680748000
1	2.083558000	-0.085565000	3.874927000
1	3.136486000	-0.832345000	2.638669000
1	-0.001386000	-0.607803000	3.493381000
1	2.656057000	-2.076654000	0.582344000
1	5.655947000	-2.573339000	0.193095000

1	4.894562000	-2.126820000	1.734690000
1	4.465188000	-3.658526000	0.933715000
1	4.251948000	-2.472815000	-1.995727000
1	3.110107000	-3.630936000	-1.255841000
1	2.522743000	-2.084087000	-1.914251000
1	5.807478000	-0.624716000	-0.828175000
1	6.134873000	1.798697000	-1.228683000
1	4.262735000	3.372220000	-0.873952000
1	0.763959000	4.051962000	1.508820000
1	1.406178000	2.519574000	2.126507000
1	2.519451000	3.853702000	1.733140000
1	1.898467000	3.647448000	-2.036117000
1	0.853288000	4.586763000	-0.947039000
1	2.610078000	4.685952000	-0.774537000
1	0.806690000	2.257486000	-0.239403000
1	0.215372000	-3.830468000	-0.880720000
1	-1.095983000	-4.829793000	0.924402000
1	-1.254869000	-3.231534000	1.776023000
1	1.395886000	-4.659627000	1.094922000
1	1.215810000	-3.060330000	1.943928000

2- Main NBO delocalizations (second order perturbation of the Fock matrix in NBO basis) for complex **2**.

As an assessment of the energies involved, the delocalization of σ-C-C and σ-C-H are compared to the delocalization of the σ-C-C into the σ-C-C* that are observed in any cyclopropyl derivative.