SUPPORTING INFORMATION

for

Salen-type nickel(II) complexes in distinct selective hydrosilylation of alkenes under mild conditions

Bartłomiej Szarłan[a,b], Jakub Robaszkiewicz[a,b], Maciej Kubicki[a], Piotr Pawluć[a,b], Maciej Zaranek[b]

[a] Faculty of Chemistry,
[b] Center for Advanced Technologies,
Adam Mickiewicz University in Poznań,
Uniwersytetu Poznańskiego 8[a] and 10[b]
61-614 Poznań, Poland

Contents:

Contact with authors:

B. Szarłan	bartlomiej.szarlan@amu.edu.pl
J. Robaszkiewicz	jrobaszkiewicz@amu.edu.pl
M. Kubicki	maciej.kubicki@amu.edu.pl
M. Zaranek	m.zaranek@amu.edu.pl
P. Pawluć	piotr.pawluc@amu.edu.pl

1. General remarks

All reactions were performed in oven-dried glassware under argon atmosphere. THF was purified by the MBraun SPS-8400 system and degassed before use. Phenylsilane was purified by distillation under reduced pressure over calcium hydride. Styrene was distilled under reduced pressure. Other reagents were used as supplied:

- *Sigma-Aldrich*: 3-methylstyrene, 4-methylstyrene, 2-methylstyrene, 4-chlorostyrene, 4-bromostyrene, 4-(trifluoromethyl)styrene, 2-methoxystyrene
- *Sigma*: styrene, 4-*tert*-butylstyrene, 1-octene, 4-methoxystyrene, allylbenzene, 4-vinylcyclohexene, *N*,*N*-dimethylallylamine, trierhoxyvinylsilane, *rac*-*trans*-1,2-diamino-cyclohexane
- *Merck*: allyl glycidyl ether
- *Fluorochem*: 4-fluorostyrene
- *Acros*: trimethylvinylsilane, 1,2-diaminobenzene
- *Alfa Aesar*: 1,2-diaminoethane
- *Thermo Fisher*: nickel(II) acetate
- *Apollo Scientific*: salicylaldehyde

^{1}H and ^{13}C NMR spectra were recorded using Bruker Avance Neo 300 MHz spectrometer and referenced to the residual solvent peak. GC-MS analyses were carried out on Agilent 8860 GC-MSD System. High-resolution mass spectrometry was performed on a Bruker Impact HD ESI-QTOF spectrometer.

Diffraction data were collected by the ω-scan technique, at 130(1) K for compound 1 on Rigaku SuperNova four-circle diffractometer equipped with a mirror-monochromatic enhanced Cu-Kα radiation (λ= 1.54184 Å) with Atlas CCD detector. For compound 2 at 100(1) K, using graphite-monochromated MoKα radiation (λ=0.71073 Å), on Rigaku XCalibur four-circle diffractometer with Eos CCD detector[1].

For compound 3 data were collected by the ω- and ϕ-scan technique, at room temperature, on Bruker D8 Quest four-circle diffractometer equipped with a microfocus source Incoatec ImS DII MoKα radiation (λ=0.71073 Å)[2]. For 1 and 2 the data were corrected for Lorentz-polarization as well as for absorption effects [1]. For 3 the frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm [3]. Data were corrected for absorption effects using the Multi-Scan method (SADABS) [4]. Precise unit-cell parameters were determined by a least-squares fit of the reflections of the highest intensity, chosen from the whole experiment. The structures were solved with SHELXT [5] and refined with the full-matrix least-squares procedure on F2 by SHELXL [6] using Olex2 software[7]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined as 'riding model' with isotropic displacement parameters set at 1.2 times Ueq of appropriate carrier atoms.

2. General Procedure for synthesis of ligands

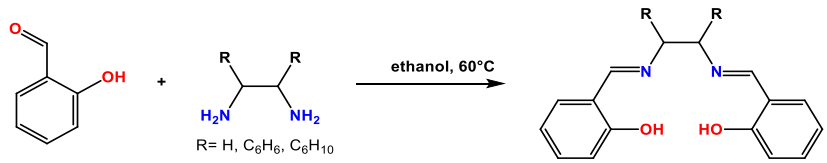


Figure S1 General procedure for ligand synthesis

An oven-dried two-neck round-bottom flask equipped with a reflux condenser was flushed with argon. **Absolute ethanol** (50 mL) was added and heated up to 60 °C, then, **salicylaldehyde** (20 mmol, 2.44 g, 2.09 mL) was added followed by **diamine** (10 mmol). Immediate precipitation of flaky crystals was observed. The reaction was carried out for the next 18h, after which it was cooled to r.t. The precipitate was filtered and washed with **cold ethanol** (3x10 mL). The residue was dried under vacuum. The purity of the products was sufficient to abandon further purification.

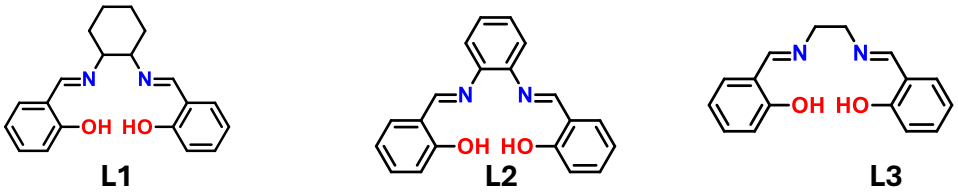


Figure S2 Structures of ligands

L1, *rac*-*N*,*N*'-bis(salicylidene)-*trans*-1,2-diaminocyclohexane, 74%

Elem. Anal. [%] Calcd. C: 74.51, H: 6.88, N: 8.69, O:9.92; found C 74.45, H: 6.94, N: 8.66, O: 10.17

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 13.24 (s, 2H), 8.19 (s, 2H), 7.16 (ddd, 2H, *J* = 8.3, 7.3, 1.8 Hz), 7.07 (dd, 2H, *J* = 7.7, 1.7 Hz), 6.81 (dd, 2H, *J* = 8.3, 1.1 Hz), 6.71 (td, 2H, *J* = 7.5, 1.1 Hz), 1.76-1.93 (m, 4H), 1.55-1.73 (m, 2H), 1.34-1.46 (m, 2H)

L2, *N*,*N*'-bis(salicylidene)-1,2-diaminobenzene, 65%

Elem. Anal. [%] Calcd. C: 75.90, H: 5.10, N: 8.86, O: 10.11; found C: 75.84, H: 5.37, N: 8.81, O: 10.37

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 12.90 (wide s, 2H) 8.56 (s, 2H), 7.23-7.34 (m, 6H), 7.12-7.20 (m, 2H), 6.97 (ddd, 2H, *J* = 8.2, 1.1, 0.5 Hz), 6.84 (td, 2H, *J* = 7.5, 1.1 Hz)

L3, *N*,*N*'-bis(salicylidene)-1,2-diaminoethane, 78%

Elem. Anal. [%] Calcd. C: 71.62, H: 6.01, N: 10.44, O: 11.93; found C: 71.98, H: 6.25, N: 10.5, O: 12.24

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 13.21 (s, 2H), 8.36 (s, 2H), 7.29 (ddd, 2H, *J* = 8.25, 7.22, 1.71 Hz), 7.23 (d, 2H, *J* = 8.35 Hz), 6.94 (ddt, 2H, *J* = 8.28, 1.05, 0.50 Hz), 6.86 (ddd, 2H, *J* = 7.68, 7.27, 1.11 Hz), 3.94 (s, 4H)

3. General Procedure for synthesis of precatalysts

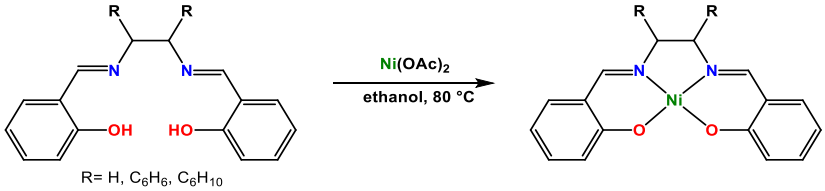


Figure S3 General procedure for precatalysts synthesis

Into an oven-dried two-neck round-bottom flask equipped with reflux condenser **ligand** (5 mmol) and **nickel(II) acetate** (5 mmol) were added. The flask was then evacuated and the air was replaced with argon. **Absolute ethanol** (12mL) was added and the reaction was stirred for 18 hours after which the brown precipitate was filtered, washed with **cold ethanol** (3x10mL), and dried under vacuum. SCXRD-quality crystals were grown from dichloromethane by layer diffusion with toluene as the nonsolvent.

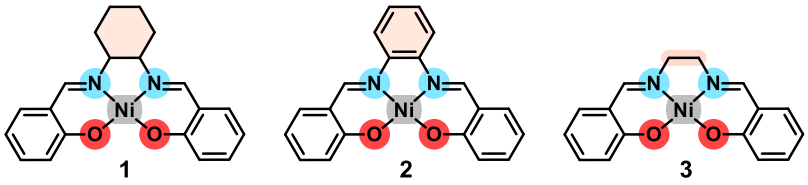
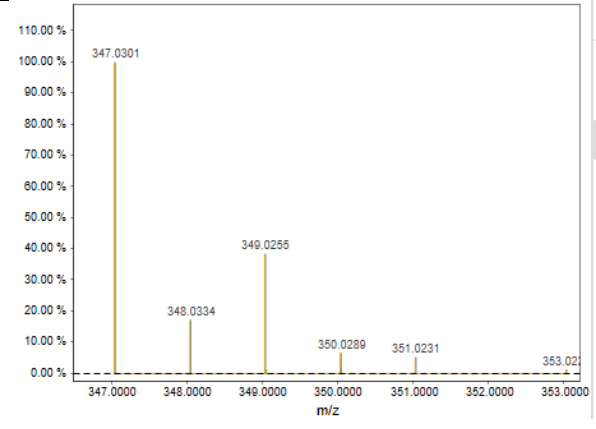
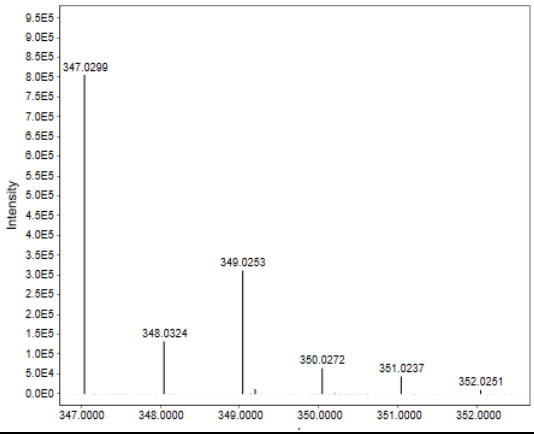


Figure S4 Structures of precatalysts

1, [NiL1], 62%, **Elem. Anal. [%]**: Calcd. C: 63.37, H: 5.32, N: 7.39; Found: C: 63.45, H: 5.27, N: 7.31

HRMS (ESI-qTOF):

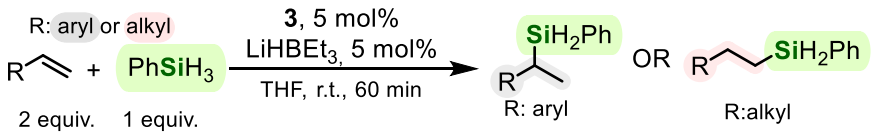
Calculated for $[M+Na]^+$ 347.0301	Found 347.0299
	

2, [NiL2], 57%, **Elem. Anal. [%]**: Calcd. C: 64.40, H: 3.78, N: 7.51; Found: C: 64.86, H: 3.79, N: 7.60

3, [NiL3], 64%, **Elem. Anal. [%]**: Calcd. C: 59.13, H: 4.34, N: 8.62; Found: C: 58.89, H: 4,29, N: 8.54

The complexes are poorly soluble in organic solvents and recording meaningful NMR spectra was impossible. Note: under catalytic reaction conditions, the complexes dissolve only upon addition of the activator.

4. General procedure for catalytic hydrosilylation of alkenes



Into an oven- and vacuum-dried Schlenk flask, the **precatalyst** (0.05 mmol, 16.3 mg of **3**) was added. The reaction flask was then evacuated, and the air was replaced with argon. Subsequently, the **alkene** (2 mmol), **silane** (1 mmol), and **THF** (0.35 mL) were added. The reaction mixture was stirred using a magnetic stirrer, and the **activator** (0.05 mmol, 0.05 mL of 1M THF solution) was introduced. The reaction was carried out for 1 hour at room temperature. After completion, the solvent was removed under reduced pressure. The residue was dissolved in **hexane** and filtered. The remaining precipitate was thoroughly washed with hexane (3 × 15 mL). The filtrates were combined and concentrated to yield the desired product by evaporation of hexane and excess of olefin.

5. X-ray diffraction data of 1, 2, and 3

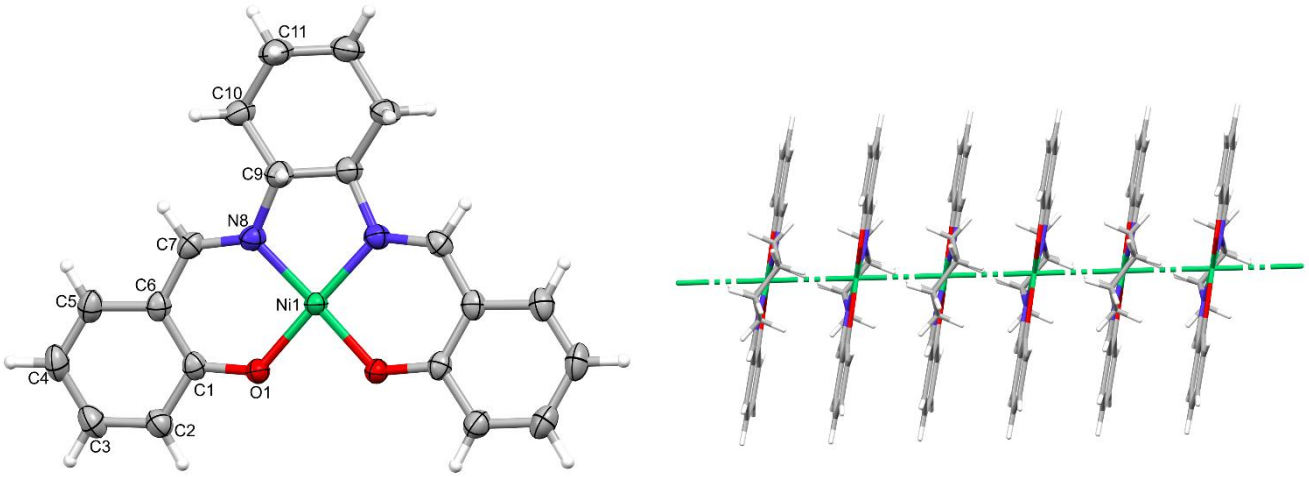


Figure S5. Structure of [NiL1], **1**

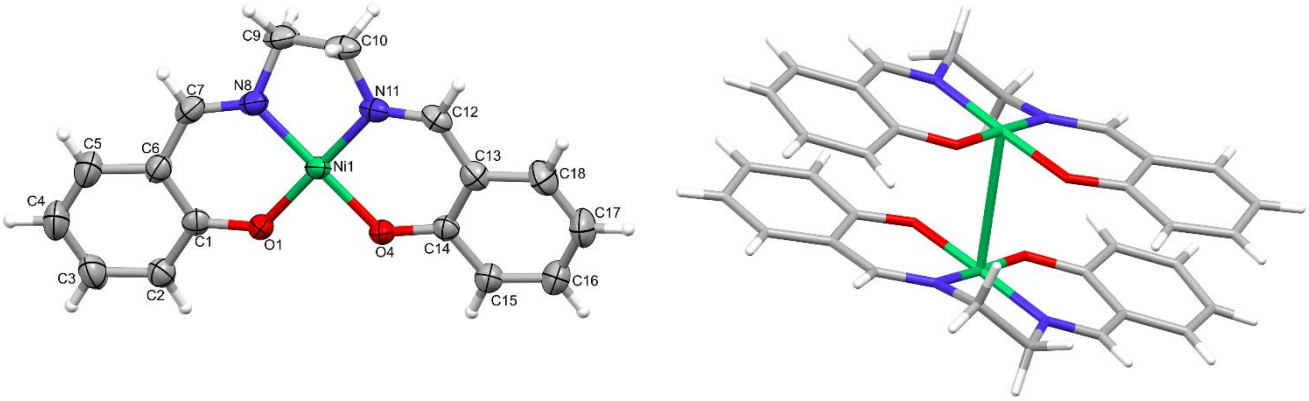


Figure S6. Structure of [NiL3], **3**

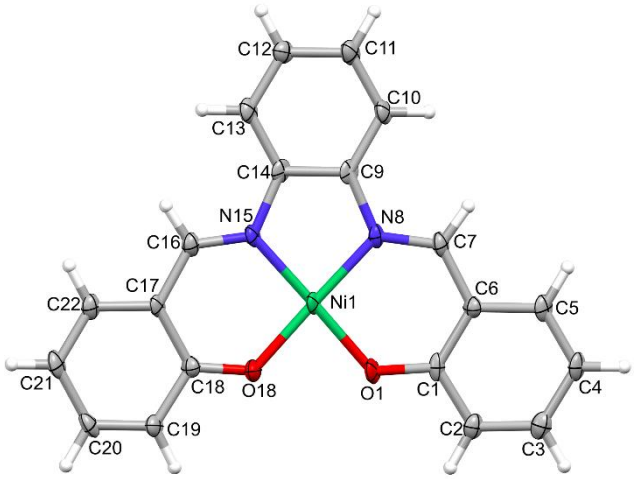


Figure S7. Structure of [NiL2], **2**

Table S1. Crystal data, data collection and structure refinement

Compound	**1**	**2**	**3**
Formula	$C_{20}H_{20}N_2NiO_2$	$C_{20}H_{14}N_2NiO_2$	$C_{16}H_{14}N_2NiO_2$
Formula weight	379.09	373.04	325.00
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	Pnna	$P2_12_12_1$	Pbca
a(Å)	6.81550(11)	5.3195(2)	7.4766(3)
b(Å)	13.6335(2)	16.6342(8)	13.8147(6)
c(Å)	17.8897(3)	17.1790(7)	26.1363(11)
V(Å^3)	1662.30(5)	1520.08(11)	2699.5(2)
Z	4	4	8
D_x(g cm^{-3})	1.515	1.630	1.599
F(000)	792	768	1344
μ(mm^{-1})	1.811	1.293	2.122
Reflections:			
collected	12095	10076	25804
unique (R_{int})	1698 (0.0240)	3275 (0.0673)	2665 (0.0532)
with I>2σ(I)	1578	2891	2363
R(F) [I>2σ(I)]	0.0330	0.0570	0.0428
wR(F^2) [I>2σ(I)]	0.0962	0.1280	0.1057
R(F) [all data]	0.0350	0.0665	0.0504
wR(F^2) [all data]	0.0979	0.1349	0.1089
Goodness of fit	1.128	1.065	1.162
max/min $\Delta\rho$ (e·Å^{-3})	0.61/-0.23	0.91/-1.08	0.33/-0.38
CCDC deposition number	2394784	2394785	2394786

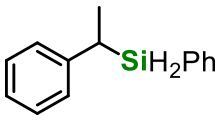
Table S2. Suppl. Relevant geometric parameters (Å, °) with s.u.'s in parentheses. Symmetry codes: [i] ½-x, 1-y,z; [ii] -x,1-y,1-z; [iii] 1-x,1-y,1-z.

	1	2	3
Ni1-O1	1.8481(11)	1.844(4)	1.8533(15)
Ni1-N8	1.8561(14)	1.859(5)	1.8456(19)
Ni1-N15		1.855(5)	
Ni1-N11			1.8516(19)
Ni1-O18		1.836(4)	
Ni1-O14			1.8465(15)
O1-Ni1-O1^i	83.66(7)		
O1-Ni1-O18		84.03(19)	
O1-Ni1-O14			85.39(7)
O1-Ni1-N8	95.19(6)	95.0(2)	93.97(8)
O1-Ni1-N8^i	175.34(5)		
O1-Ni1-N15		178.8(2)	
O1-Ni1-N11			178.38(7)

N8-Ni1-N15 N8-Ni1-N11		86.1(2)	 86.20(9)
N8-Ni1-O18 N8-Ni1-O14		178.3(2)	 178.52(8)
N15-Ni1-O18 N11-Ni1-O14		94.89(19)	 94.48(8)
Ni1···Ni1[ii] Ni1···Ni1[iii]	3.421		 3.199

6. Analytical data of isolated hydrosilylation products

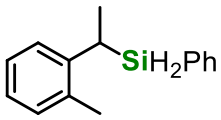
7a, Phenyl(1-phenylethyl)silane, Yield= 90% (94:6)



^{1}H HMR (300 MHz, $CDCl_3$): δ [ppm]: 7.48-7.39 (m, 3H, Ar-H), 7.38-7.32 (m, 2H, Ar-H), 7.31-7.27 (m, 2H, Ar-H), 7.20-7.12 (m, 3H, Ar-H) 4.38-4.37 (d, J=2.38, 2H, SiH2), 2.71-2.60 (m, 1H, CH),1.52-1.49 (d, J=7.3, 3H, CH3)

^{13}CNMR (75 MHz, $CDCl_3$): δ [ppm]: 144.68, 135.79, 131.52, 129.89, 128.52, 127.99, 127.26, 125.16, 25.52, 16.51.

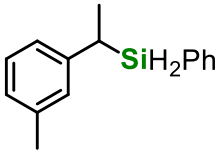
7b, Phenyl(1-(o-tolyl)ethyl)silane, Yield = 30% (67:33)



^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 4.36-4.29(m, 2H, SiH_2), 2.24(s, 3H, CH_3), 1.50-1.46(d, J=7.41 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 143.31, 136.01, 135.64, 132.00, 130.56, 130.19, 128.29, 126.66, 126.42, 125.24, 21.20, 20.47, 17.00.

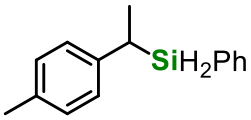
7c, Phenyl(1-(m-tolyl)ethyl)silane, Yield= 66% (77:23)



^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 4.38-4.34(m, 2H, SiH_2), 2.68-2.57(m, 2H, CH), 2.34(s, 3H, CH_3), 1.50-1.47(d, J=7.5 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 144.88, 138.25, 136.06, 131.94, 130.12, 128.66, 128.34, 128.22, 126.22, 124.53, 25.64, 21.86, 16.80.

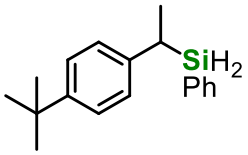
7d, Phenyl(1-(p-tolyl)ethyl)silane, Yield= 90% (75:25)



^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 4.37-3.33(m, 2H, SiH_2), 2.66-2.56(m, 1H,CH), 2.34(s, 1H, CH_3), 1.48-1.44(d, J=7.65, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 141.52, 135.77, 134.51, 131.70, 129.84, 129.23, 127.98, 127.13, 76.73, 24.94, 21.08, 16.70.

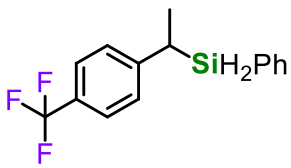
7e, (1-(4-(tert-butyl)phenyl)ethyl)(phenyl)silane, Yield= 73% (97:3)



^{1}H HMR (300 MHz, $CDCl_3$): δ [ppm]: 7.47-7.37 (m, 3H, Ar-H), 7.36-7.27 (m, 4H, Ar-H), 7.11-7.04 (m, 2H, Ar-H), 4.37-4.3 (m, 2H, SiH_2), 2.67-2.57 (m, 1H, CH), 1.48-1.45 (d, *J*= 7.87, 3H, CH_3) 1.34 (s, 9H, CH_3)

^{13}CNMR (75 MHz, $CDCl_3$): δ [ppm]: 147.90, 141.49, 135.79, 131.81, 129.83, 127.97, 126.87, 125.40, 34.44, 31.57, 24.80, 16.53.

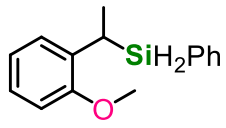
7f, Phenyl(1-(4-(trifluoromethyl)phenyl)ethyl)silane, Yield= 86% (100:0)



^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 7.52-7.48 (m, 2H, Ar-H), 7.43-7.39(m, 3H, Ar-H), 7.36-7.33(m, 2H, Ar-H), 7.20-7.15(m, 2H, Ar-H), 4.37-4.30(m, 2H, SiH_2), 2.74-2.66(m, 2H, CH), 1.52-1.46(d, J=7.29 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]:: 135.74, 130.17, 128.12, 127.37, [126.35, 122.75; *d*, *J*=272 Hz left of -CF_3 *q*], 125.38 (q, $^2J_{CF}$=3.8 Hz), 25.95, 16.16.

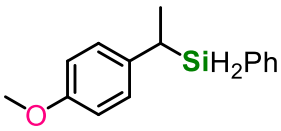
7g, (1-(2-methoxyphenyl)ethyl)(phenyl)silane, Yield= 67% (86:14)



^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 4.22-4.15(m, 2H, SiH_2), 3.60(s, 3H, OCH_3), 2.97-2.85(m, 1H, CH), 1.36-1.31(d, J=7.41 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 156.09, 135.52, 133.33, 132.61, 129.46, 127.71, 126.79, 125.80, 120.66, 110.00, 55.04, 17.87, 15.78.

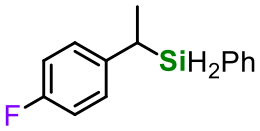
7h, (1-(4-methoxyphenyl)ethyl)(phenyl)silane, Yield= 65% (88:12)



^{1}H HMR (300 MHz, $CDCl_3$): δ [ppm]: 7.35-7.29 (m, 3H, Ar-H), 7.25-7.21 (m, 2H, Ar-H), 6.96- 6.91 (m, 2H, Ar-H), 6.73-7.70 (m, 2H, Ar-H), 4.23-4.22 (d, *J*= 3.25, 2H, Si-H), 2.53-2.41 (m, 1H, CH), 1.41-1.33 (d, *J*=7.5, 3H, CH_3)

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 157.31, 136.66, 135.78, 131.72, 129.84, 128.12, 127.98, 114.00, 55.38, 24.39, 16.89.

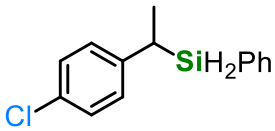
7j, (1-(4-fluorophenyl)ethyl)(phenyl)silane, Yield= 90% (87:13)



^{1}H HMR (300 MHz, $CDCl_3$): δ [ppm]: 7.43-7.38 (m, 3H, Ar-H), 7.37-7.32 (m, 2H, Ar-H), 7.08-7.00 (m, 2H, Ar-H), 6.99-6.91 (m, 2H, Ar-H), 4.34-4.33 (d, *J*= 3.06, 2H, SiH_2, 2.69-2.55 (m, 1H, CH), 1.47-1.45 (d, *J*= 8.35, 3H, CH_3)

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 160.82 (d, $^1J_{CF}$=242 Hz), 140.24, 140.20, 135.76, 131.21, 129.99, 128.50, 128.40, 128.04, 115.38, 115.09, 24.76, 16.75.

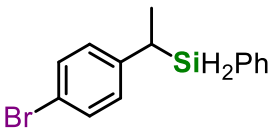
7k, (1-(4-chlorophenyl)ethyl)(phenyl)silane, Yield= 99% (100:0)



^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 7.43-7.37(m, 3H, Ar-H), 7.25-7.21(m, 2H, CH), 7.12-7.09(m, 2H, Ar-H), 6.93-6.88(d, J= 8.7 Hz, 2H, Ar-H), 4.5-3.90(m, 2H, SiH_2), 2.54-2.46(m, 1H, CH), 1.39-1.31(d, J=7.32 Hz, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 143.17, 135.67, 130.97, 130.59, 129.96, 128.47, 128.42, 127.98, 25.02, 16.37.

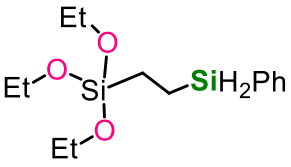
7l, (1-(4-bromophenyl)ethyl)(phenyl)silane, Yield= 86% (94:6)



^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 7.34-7.29(m, 3H, Ar-H), 7.28-7.20(m, 4H, Ar-H), 6.89-6.82(d, J=8.46 Hz, 2H, Ar-H), 4.55-3.88(m, 2H, SiH_2), 2.54-2.44(m, 1H, CH), 1.36-1.30(d, J=7.47, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 143.79, 135.78, 131.51, 130.97, 130.08, 128.95, 128.10, 118.68, 25.21, 16.40.

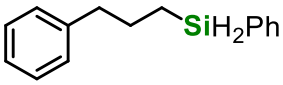
7m, Triethoxy(2-(phenylsilyl)ethyl)silane, Yield= 73% (0:100)



^{1}H HMR (300 MHz, $CDCl_3$): δ [ppm]: 7.59-7.57 (m, 2H, Ar-H), 7.40-7.32 (m, 3H, Ar-H), 4.32-4.30 (t, *J*= 3.55, 2H, SiH_2), 3.85-3.78 (q, *J*= 7.05, 6H, CH_2), 1.25-1.20 (t, *J*= 7.50, 9H, CH_3), 1.04-0.95 (m, 2H, CH_2), 0.74-.067 (m, 2H,CH_2)

^{13}C HMR (75 MHz, $CDCl_3$):δ [ppm]: 135.38, 132.66, 129.68, 128.09, 58.58, 18.43, 4.51, 1.95.

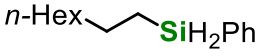
7n, Phenyl(3-phenylpropyl)silane, Yield= 96% (0:100)



^{1}H HMR (300 MHz, $CDCl_3$): δ [ppm]: 7.48-7.45 (m, 2H, Ar-H), 7.31-7.23 (m, 3H, Ar-H), 7.22-7.16 (m, 2H, Ar-H), 7.12-7.05 (m, 3H, Ar-H), 4.23-4.21 (t, *J*= 3.70, 2H, SiH_2), 2.61-2.56 (t, *J*=7.39, 2H, CH_2), 1.75-1.65 (m, 2H, $SiCH_2$), 0.94-0.85 (m, 2H, CH_2)

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 142.20, 135.34, 132.54, 129.69, 128.63, 128.39, 128.12, 125.89, 39.09, 27.13, 9.88.

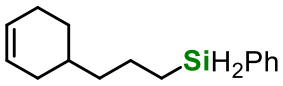
7o, Octyl(phenyl)silane, Yield= 85% (0:100)



^{1}H HMR (300 MHz, $CDCl_3$): δ [ppm]: 7.60-7.57 (m, 2H, Ar-H), 7.39-7.35 (m, 3H, Ar-H), 4.32-4.29 (t, *J*= 3.69, 2H, SiH_2), 1.53-1.42 (m, 2H, $SiCH_2$), 1.40-1.34 (m, 2H, CH_3CH_2), 1.30-1.23 (m, 8H, $CH_3CH_2C_4H_8$), 0.99-0.93 (m, 2H, $CH_2CH_2SiH_2$), 0.91-0.87 (t, *J*= 6.16, 3H, CH_3)

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 135.36, 132.98, 129.61, 128.09, 33.00, 32.05, 29.39, 25.23, 22.83, 14.27, 10.17.

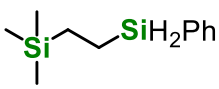
7p, (2-(cyclohex-3-en-1-yl)ethyl)(phenyl)silane, Yield= 77% (0:100)



^{1}H HMR (300 MHz, $CDCl_3$): δ [ppm]: 7.64-7.58 (m, 2H, Ar-H), 7.43-7.35 (m, 3H, Ar-H), 5.67 (s, 2H, CH_2=CH_2), 4.34-4.31 (t, *J*=3.6, 2H, SiH_2), 2.23-2.04 (m, 3H,), 1.86-1.74 (m, 1H), 1.73-1.62 (m, 1H), 1.61-1.51 (m, 1H), 1.50-1.39 (m, 2H), 1.28-1.15 (m, 1H), 1.04-0.94 (m, 2H)

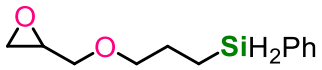
^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 135.33, 132.82, 129.65, 128.11, 127.20, 126.66, 36.24, 31.94, 31.66, 28.57, 25.40, 7.32.

7q, Trimethyl(2-(phenylsilyl)ethyl)silane, Yield= 83% (0:100)



^{1}H HMR (300 MHz, $CDCl_3$): δ [ppm]: 7.67- 7.60 (m, 2H, Ar-H), 7.46-7.36 (m, 3H, Ar-H), 4.35-4.33 (t, *J*=3.57, 2H, SiH_2), 0.93-0.86 (m, 2H, CH_2), 0.63-0.57 (m, 2H, CH_2), 0.34 (s, 3H, CH_3)
^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 135.38, 133.05, 129.64, 128.10, 10.77, 2.85, -1.99.

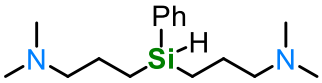
7r, (3-(Oxiran-2-ylmethoxy)propyl)(phenyl)silane, Yield=21% (0:100)



^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 7.52-7.46(m, 2H, Ar-H), 7.32-7.26(m, 3H, Ar-H), 4.27-4.20(m, 2H, SiH_2), 3.64-3.57(m, 1H, CH), 3.46-3.36(m, 2H, CH), 3.30-3.25(m, 1H, CH), 3.08-3.03(m, 1H, CH), 2.73-2.69(m, 1H, CH), 2.54-2.50(m, 1H, CH), 1.73-1.61(m, 2H, CH), 0.96-0.86(m, 2H,CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm]: 135.21, 132.38, 129.61, 128.02, 73.41, 71.46, 50.86, 44.34, 25.22, 6.48.

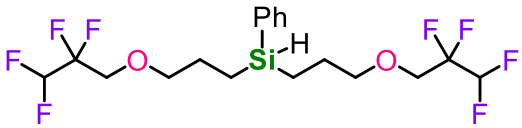
7s, 3,3'-(phenylsilanediyl)bis(N,N-dimethylpropan-1-amine), Yield= 84% (0:100)



^{1}H HMR (300 MHz, $CDCl_3$): δ [ppm]: 7.54-7.50 (m, 2H, Ar-H), 7.35-7.31 (m, 3H, Ar-H), 4.31-4.26 (m, 1H, SiH), 2.30-2.20 (m, 4H, CH_2), 2.16 (s, 12H, CH_3), 1.58-1.48 (m, 2H, CH_2), 0.87- 0.8 (m, 2H, CH_2)

^{13}C NMR (300 MHz, $CDCl_3$): δ [ppm]: 135.47, 135.19, 134.70, 129.35, 127.95, 62.88, 45.50, 22.67, 9.61.

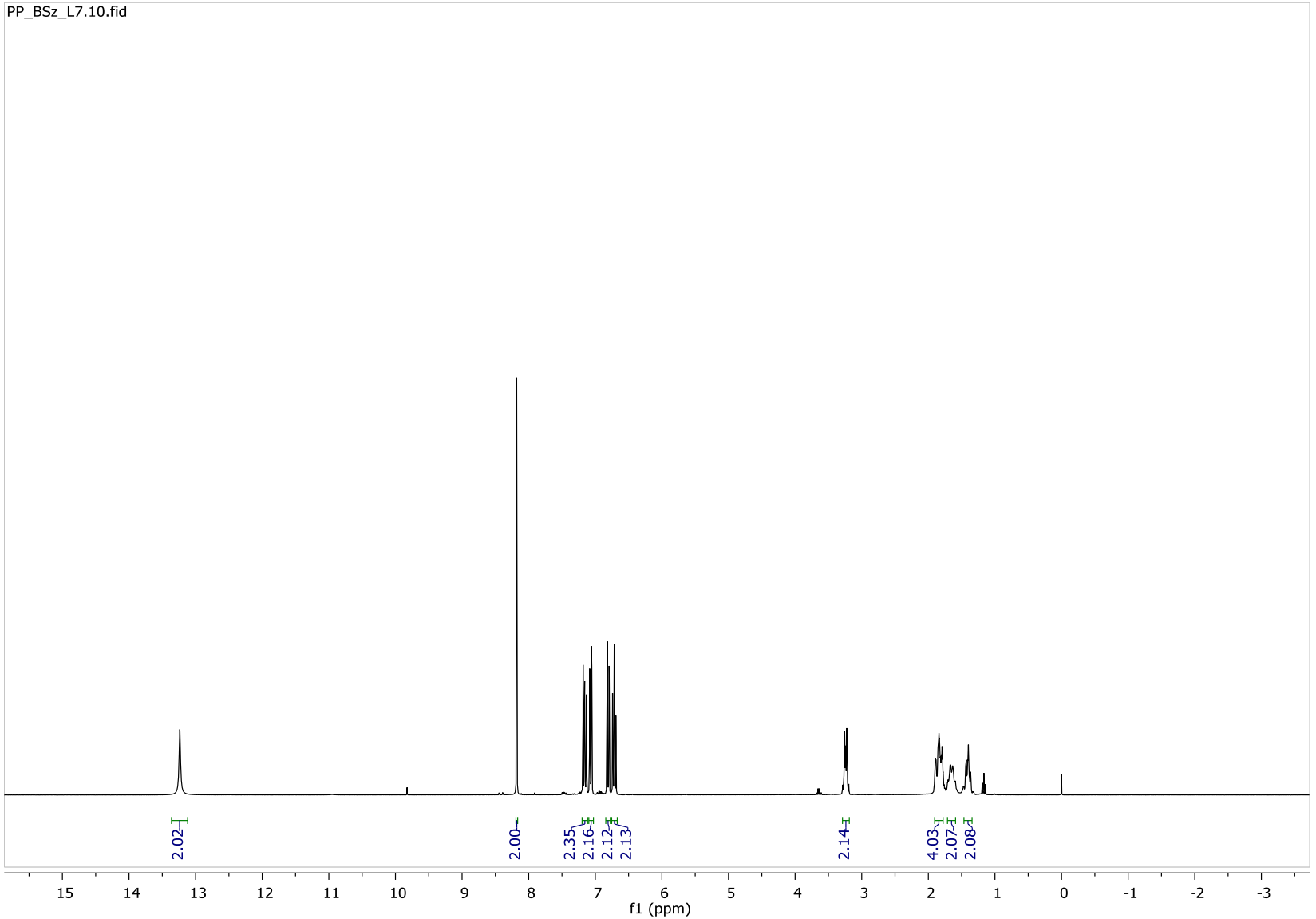
7t, Phenylbis(3-(2,2,3,3-tetrafluoropropoxy)propyl)silane, Yield= 72% (0:100)



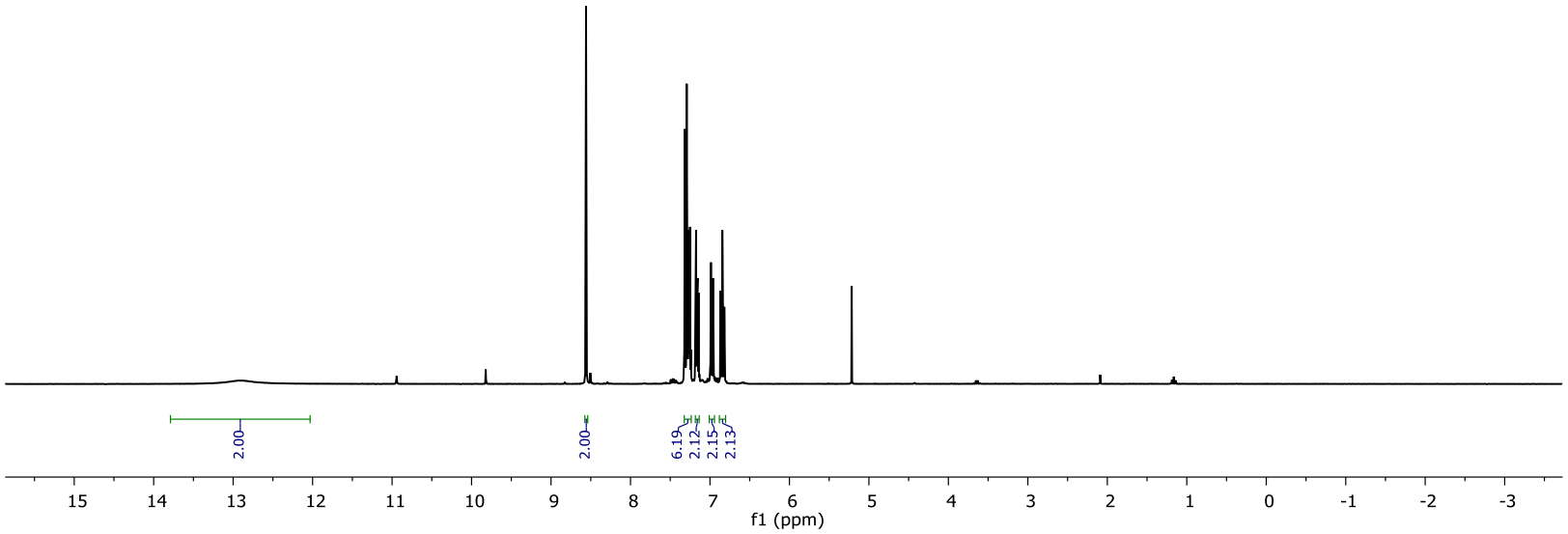
^{1}H HMR (300 MHz, $CDCl_3$): δ [ppm]: 7.05-6.98 (m, 2H, Ar-H), 6.90-6.83 (m, 3H, Ar-H) 5.57-5.18 (tt, J_1= 5.12, 1H, CF_2-H), 3.8-3.78 (t, *J*= 3.42, 1H, Si-H), 3.28-3.19 (t, *J*= 13.09, 2H, CH_2), 3.01-2.98, *J*= 7.34, 2H, CH_2), 1.20- 1.10 (m, 2H, CH_2), 0.40- 0.33 (m, 2H, CH_2)

^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm]: 135.23, 134.70, 129.72, 128.20, 115.21 (tt, $^{1}J_{CF}$=249 Hz, $^{2}J_{CF}$=26 Hz), 109.30 (tt, $^{1}J_{CF}$=249 Hz, $^{2}J_{CF}$=33 Hz), 74.90, 67.95 (tt, $^{2}J_{CF}$=28 Hz, $^{3}J_{CF}$=1 Hz), 24.49, 7.92.

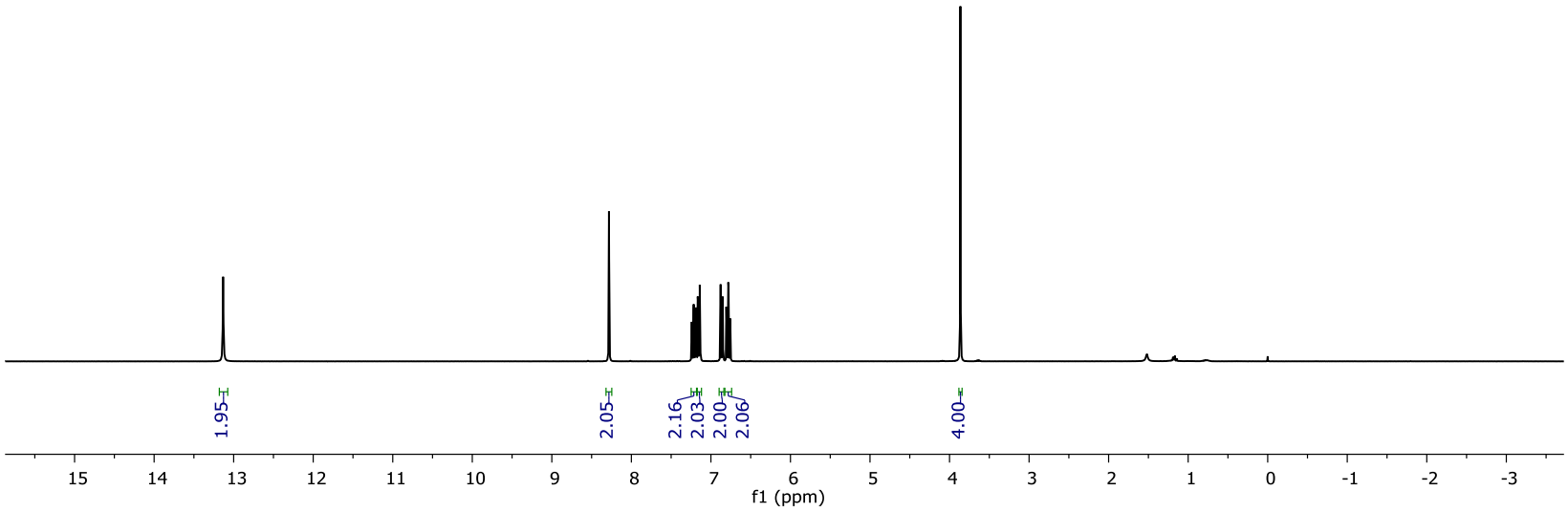
L1


PP_BSz_L7.10.fid
2.02
2.00
2.35
2.16
2.12
2.13
2.14
4.03
2.07
2.08
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

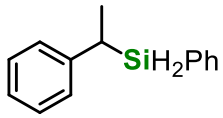
L2

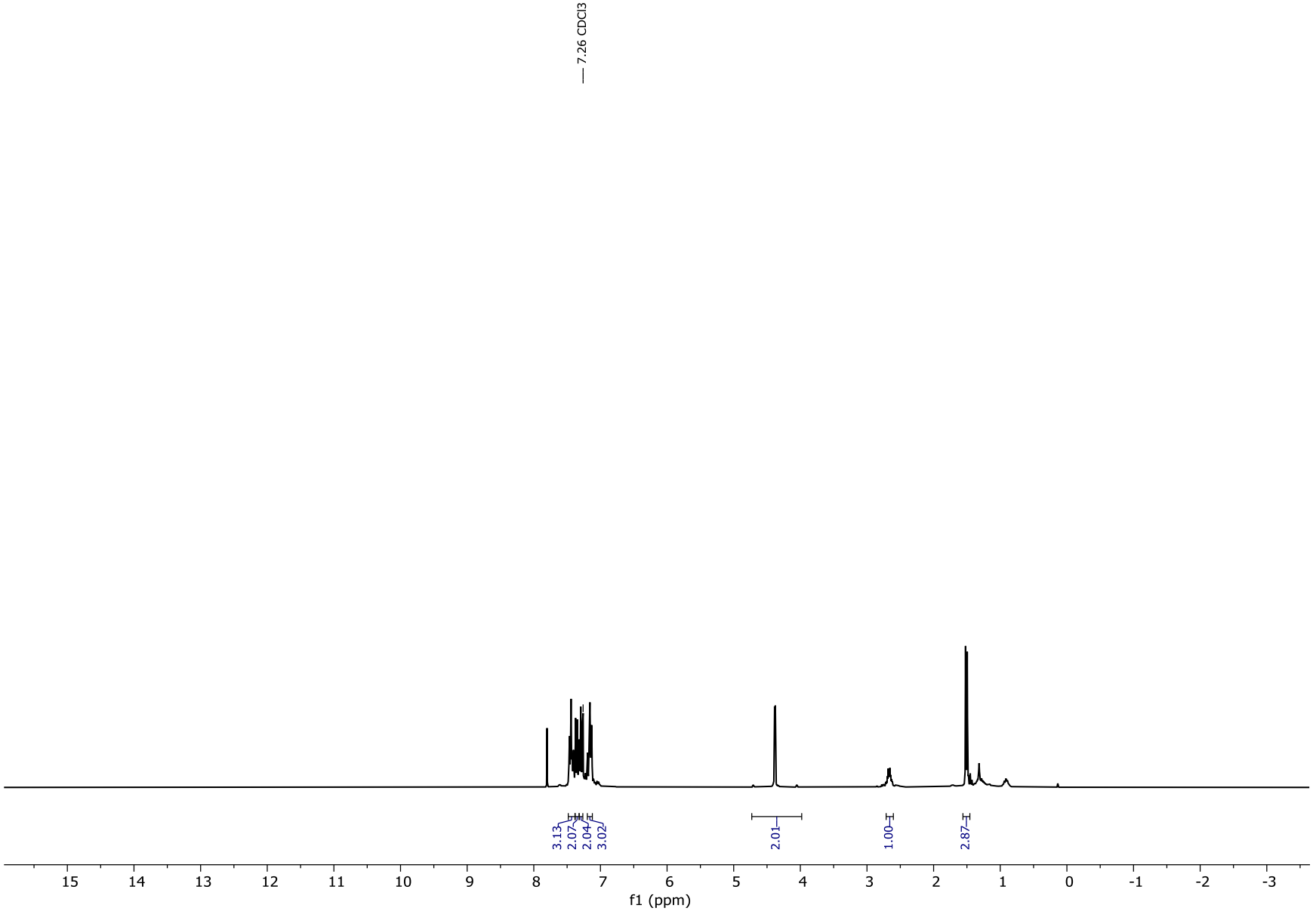


L3

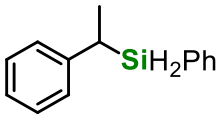

1.95
2.05
2.16
2.03
2.00
2.06
4.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

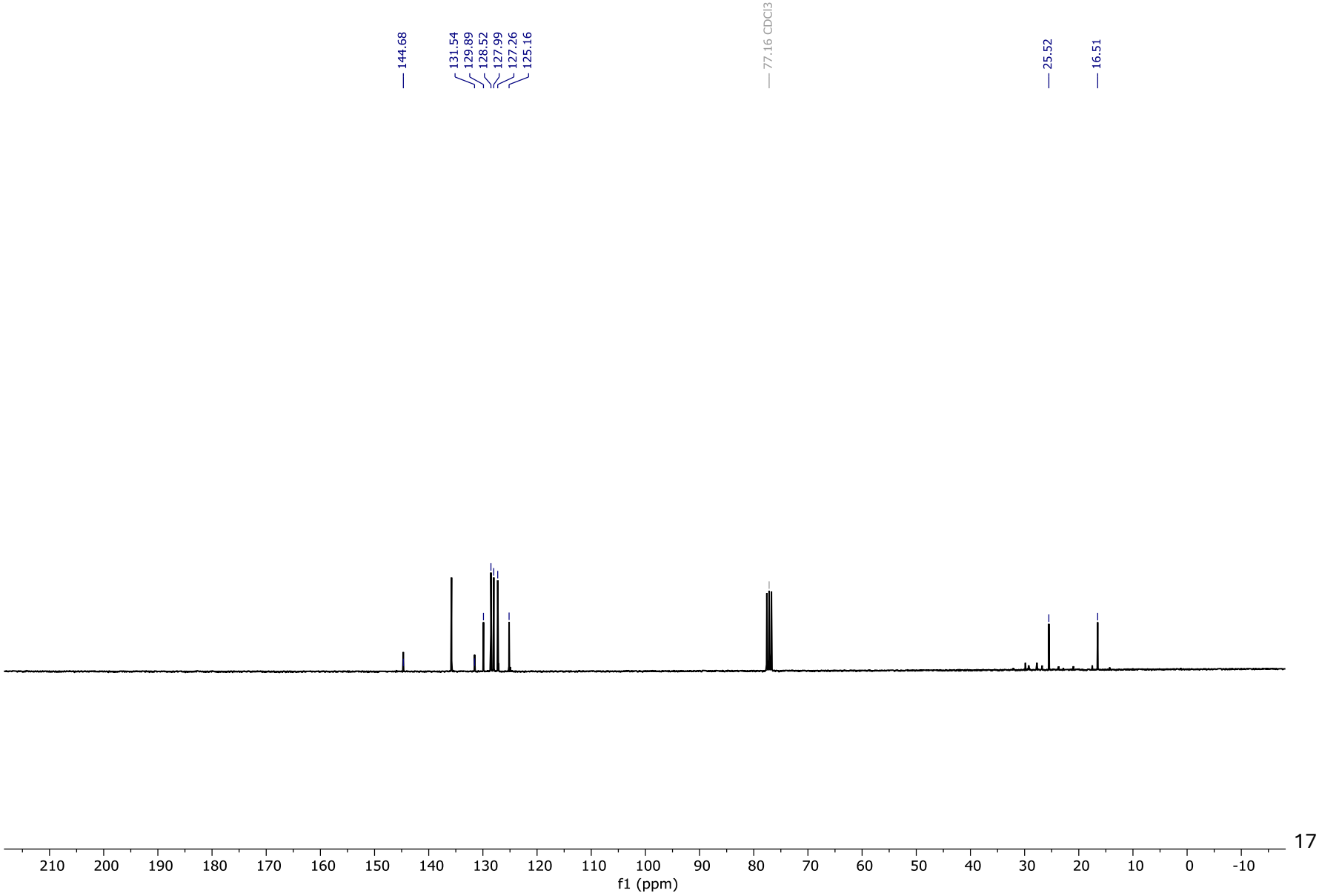
7a


SiH2Ph

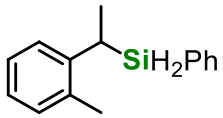

7.26 CDCl3
3.13
2.07
2.04
3.02
2.01
1.00
2.87
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

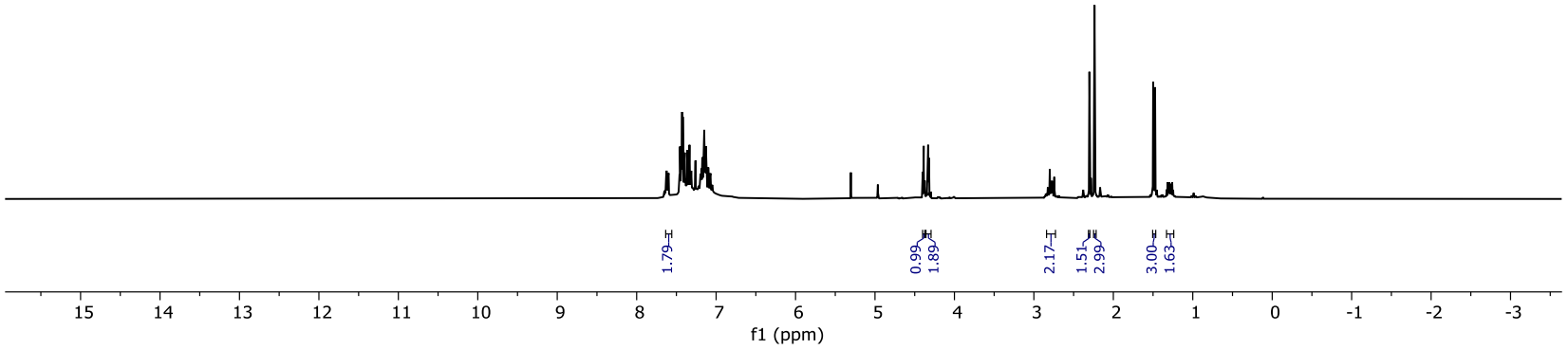
7a


SiH2Ph

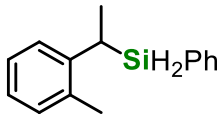

144.68
131.54
129.89
128.52
127.99
127.26
125.16
77.16 CDCl3
25.52
16.51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

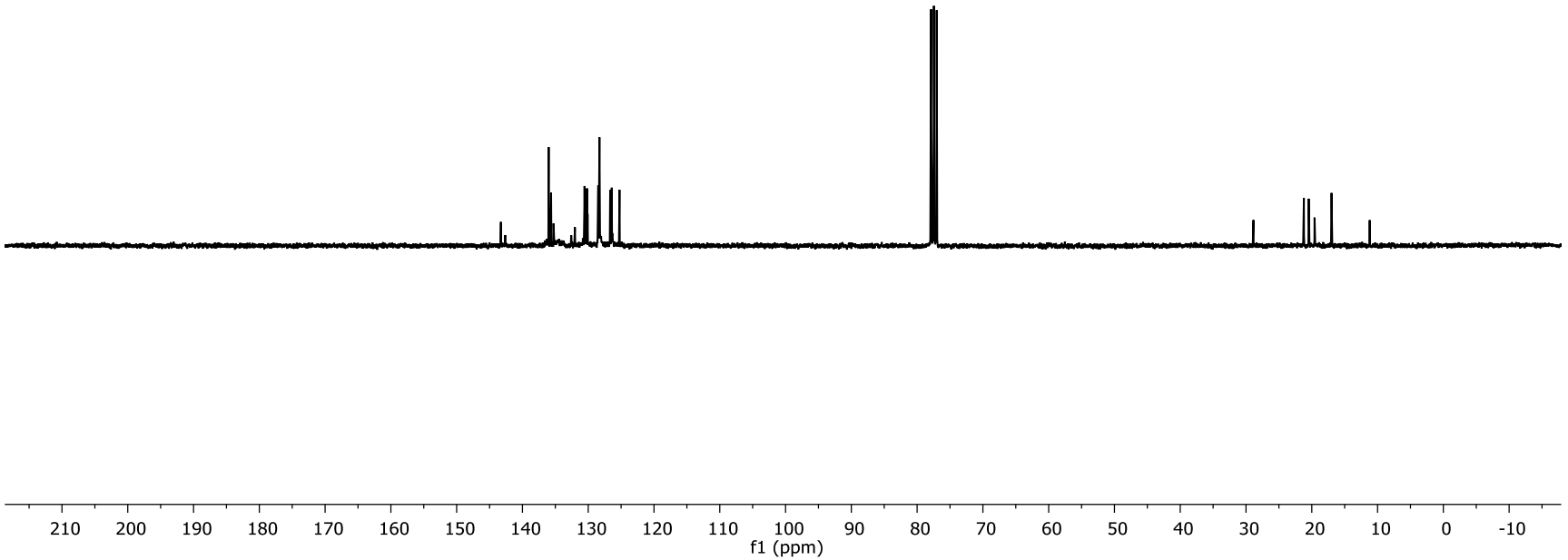
7b


SiH2Ph

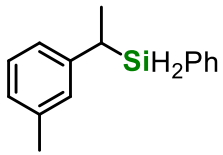

1.79
0.99
1.89
2.17
1.51
2.99
3.00
1.63
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

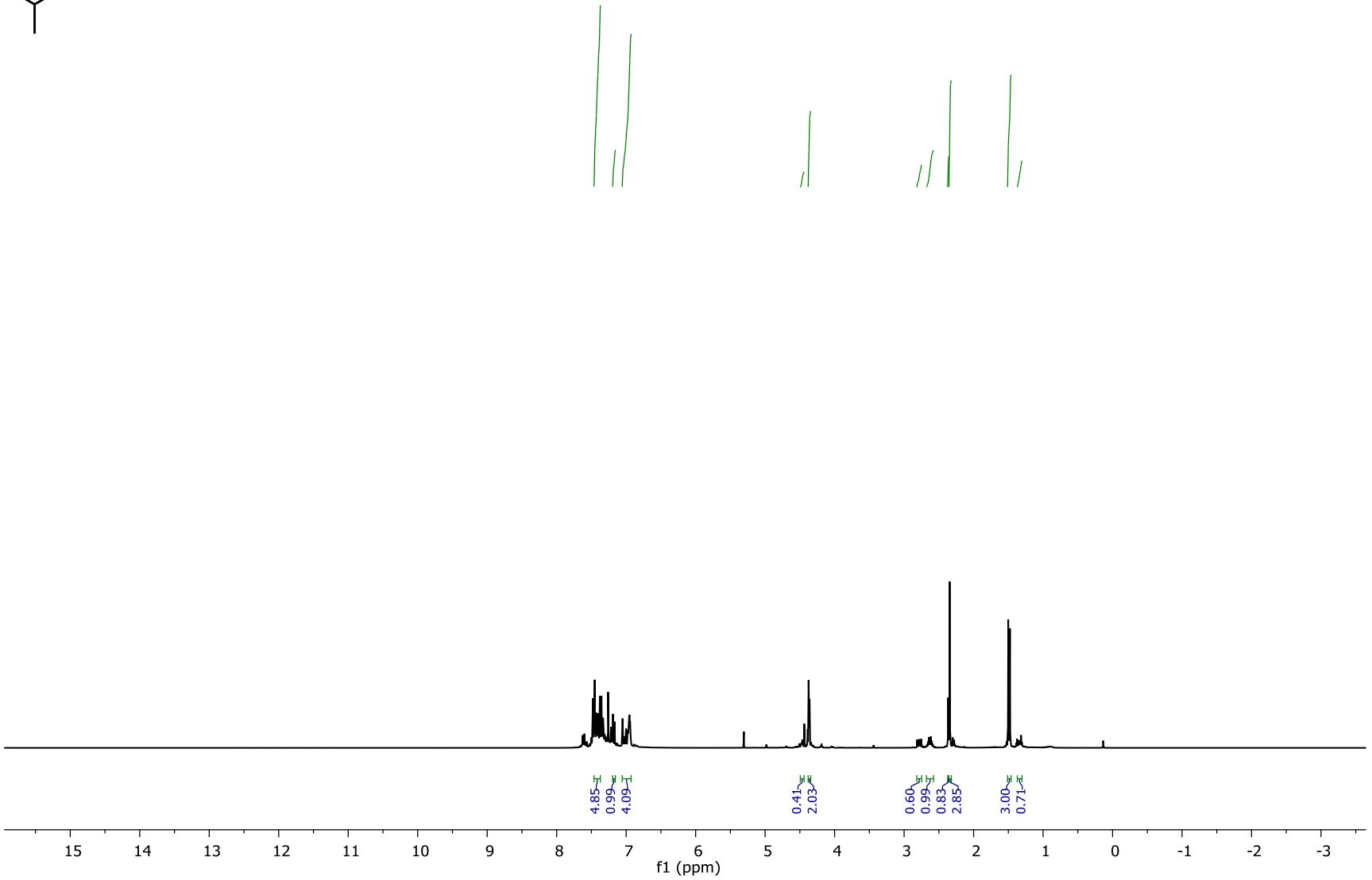
7b


SiH2Ph

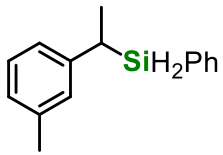

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7c


SiH2Ph

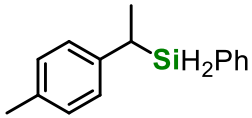

4.85
0.99
4.09
0.41
2.03
0.60
0.99
0.83
2.85
3.00
0.71
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

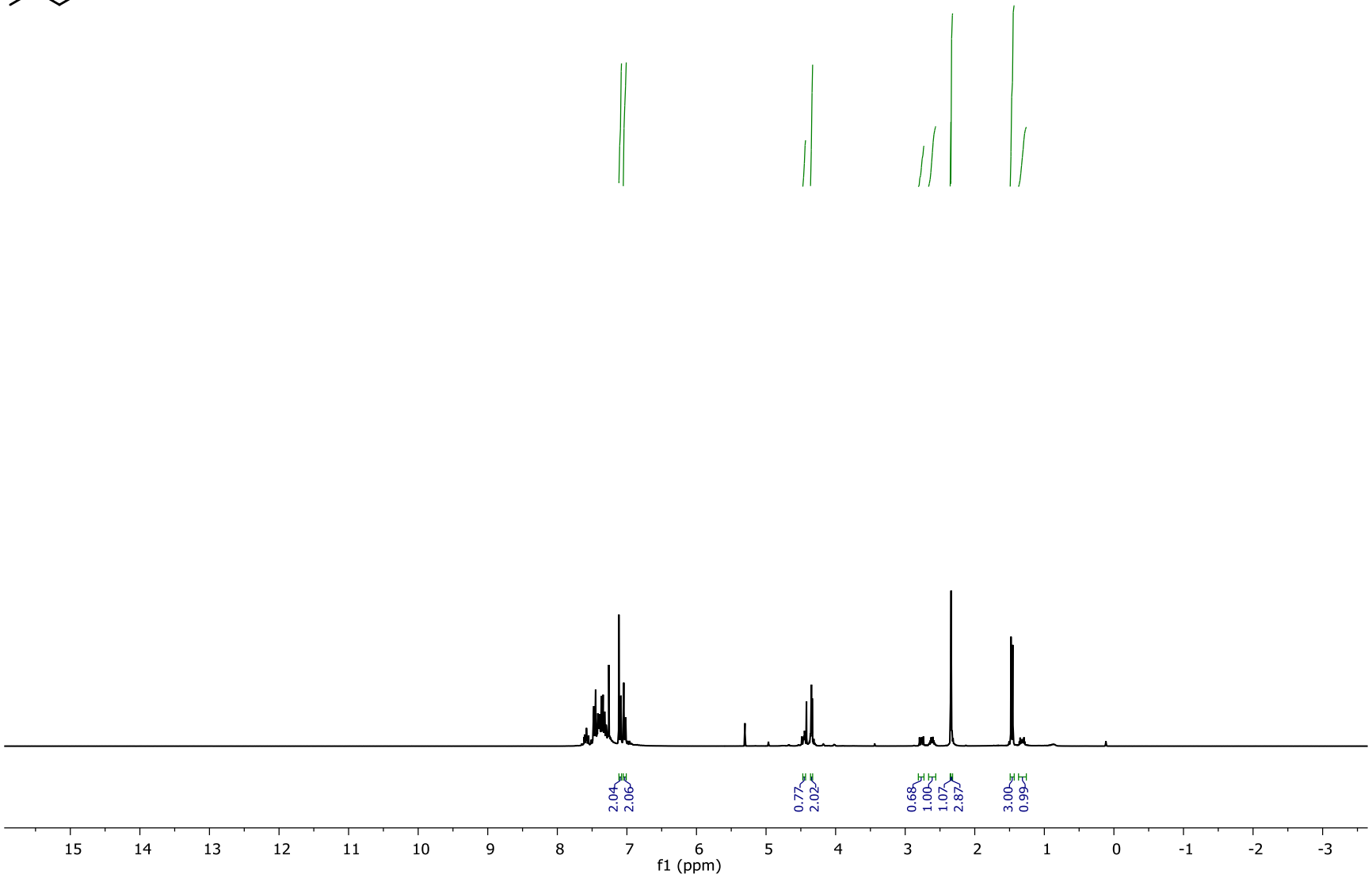
7c


SiH2Ph

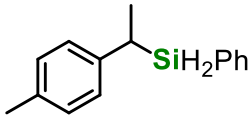
144.88
138.25
136.06
131.94
130.12
128.66
128.34
128.22
126.22
124.53
25.64
21.86
16.80
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7d


SiH2Ph

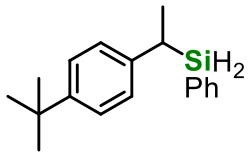

2.04
2.06
0.77
2.02
0.68
1.00
1.07
2.87
3.00
0.99
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

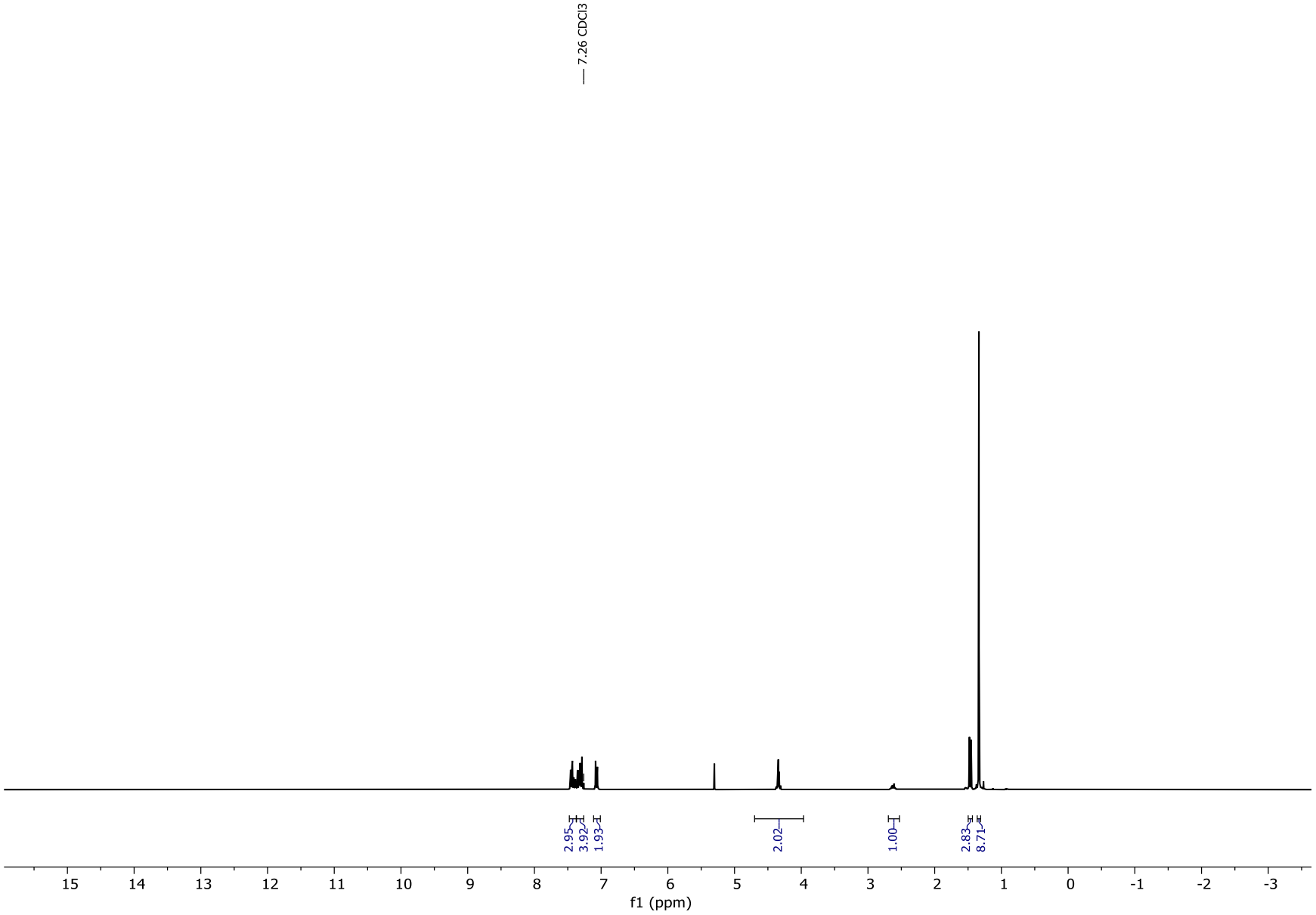
7d


SiH2Ph

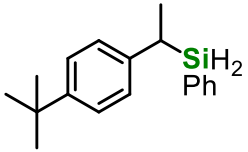
141.52
135.77
134.51
131.70
129.84
129.23
127.98
127.13
76.73
24.94
21.08
16.70
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

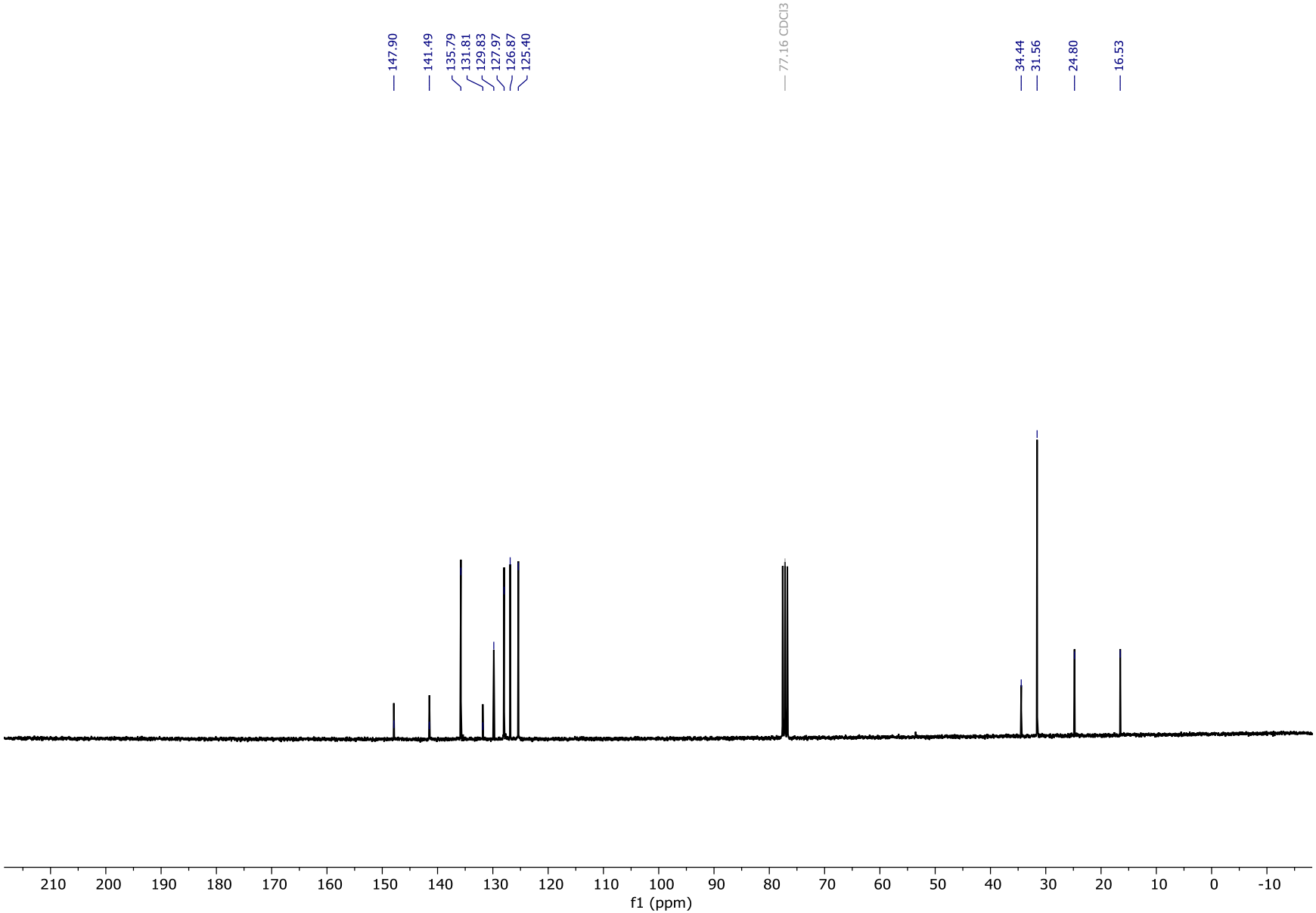
7e


SiH2
Ph

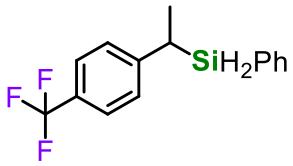

7.26 CDCl3
2.95
3.92
1.93
2.02
1.00
2.83
8.71
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

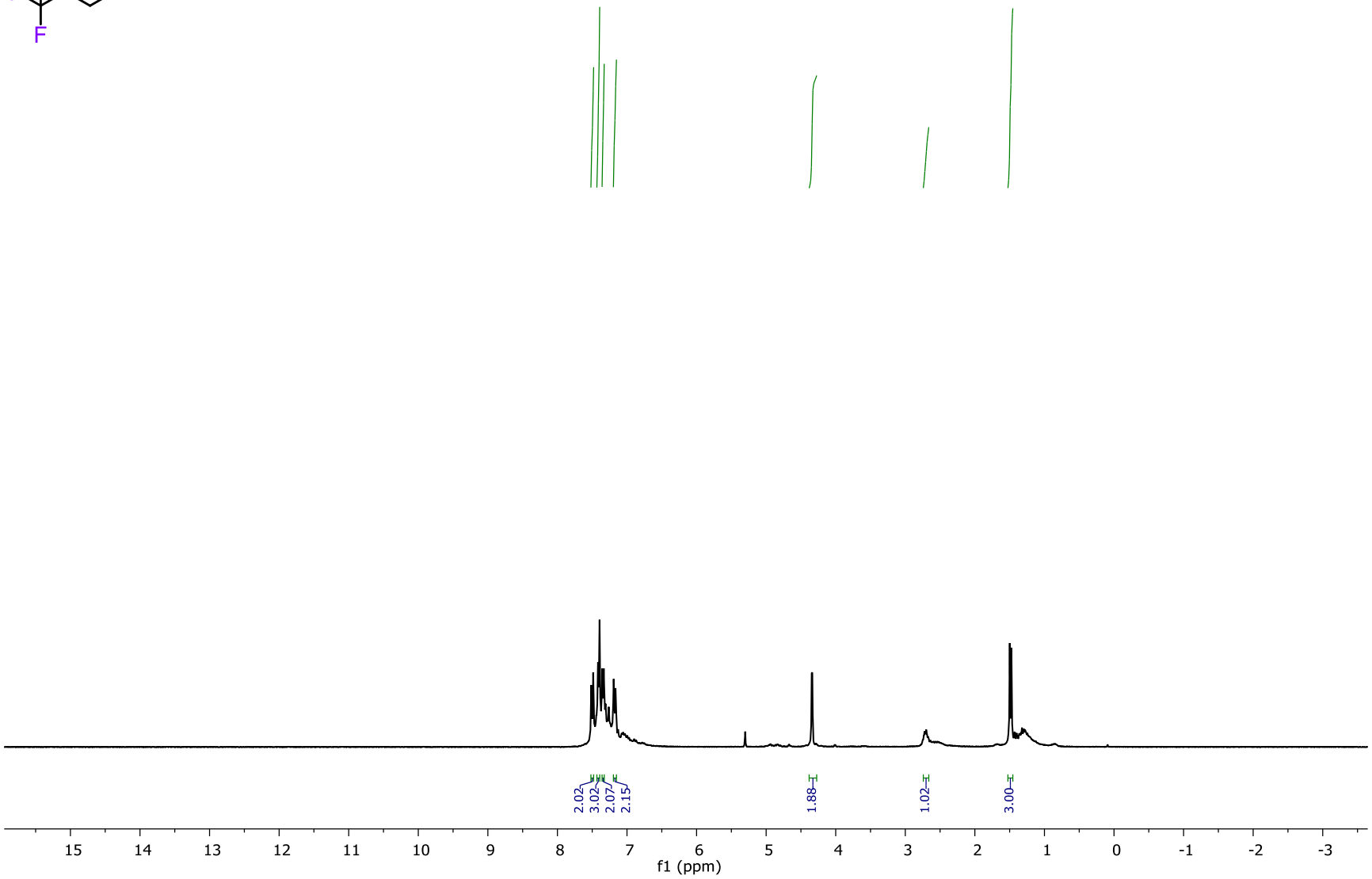
7e


SiH2
Ph

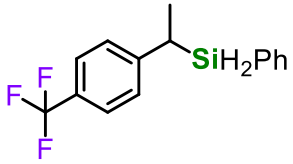

147.90
141.49
135.79
131.81
129.83
127.97
126.87
125.40
77.16 CDCl3
34.44
31.56
24.80
16.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

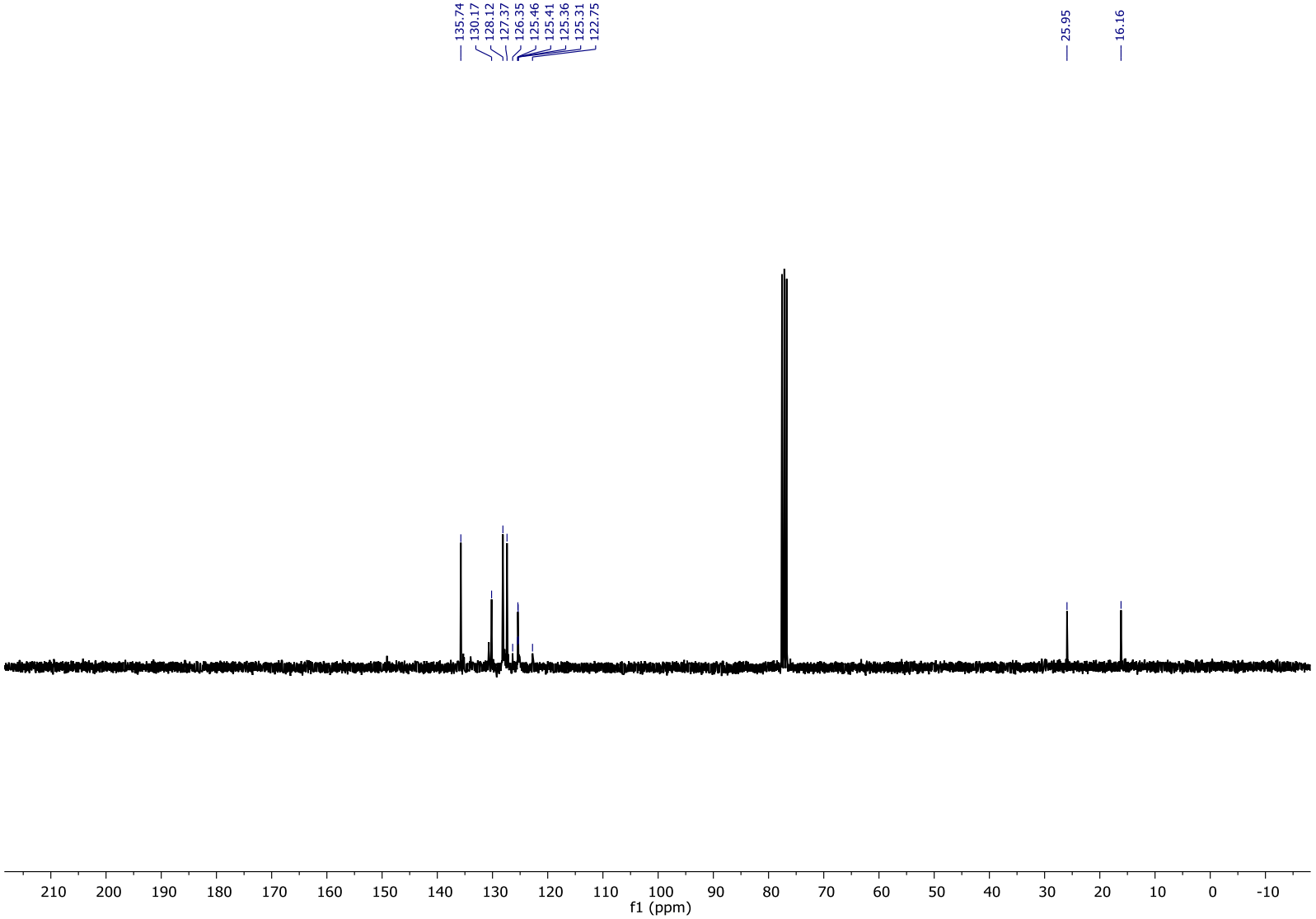
7f


F
F
F
SiH2Ph

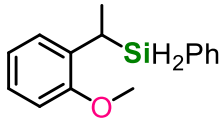

2.02
3.02
2.07
2.15
1.88
1.02
3.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

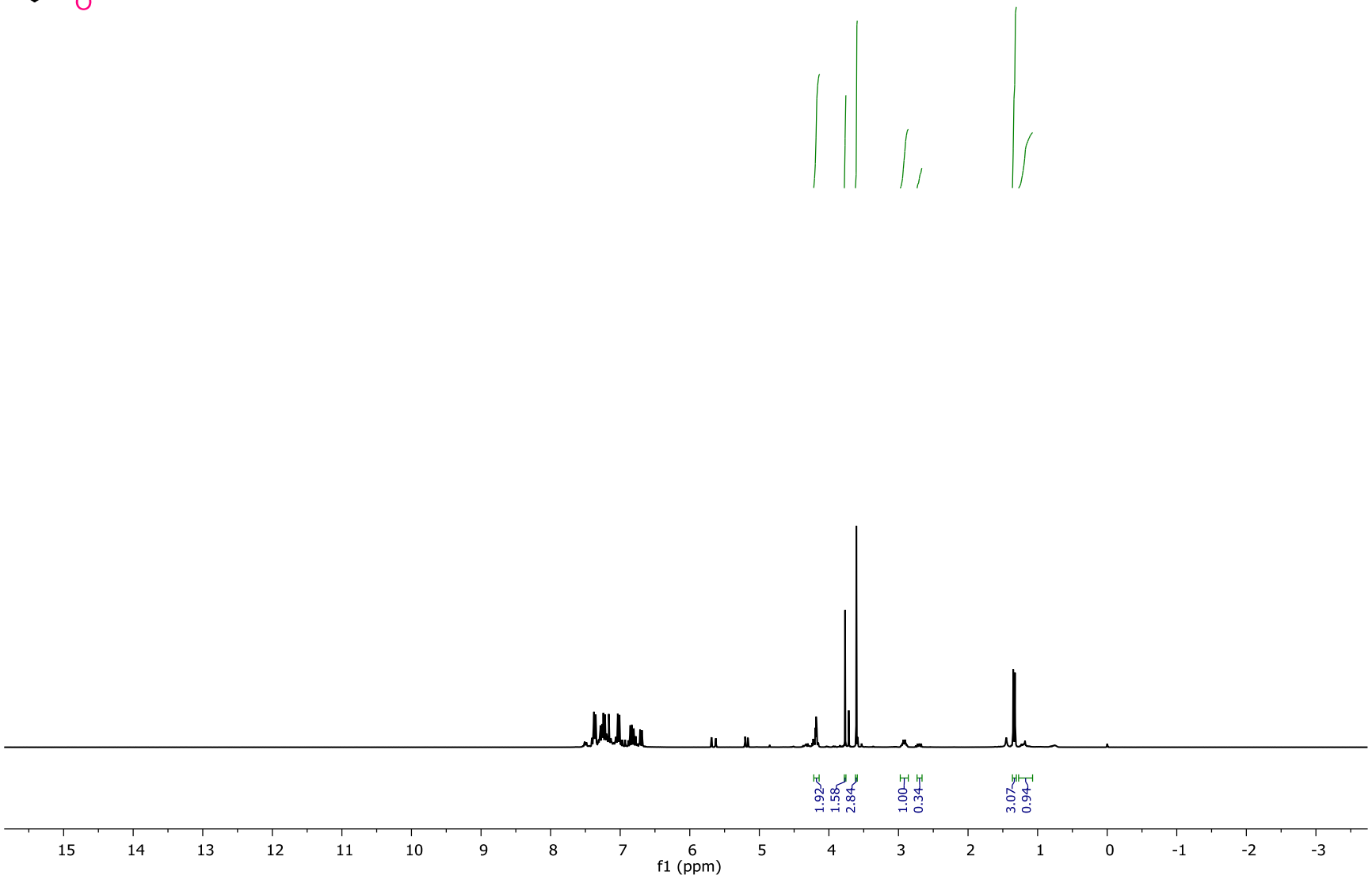
7f


SiH2Ph
F
F
F

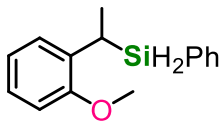

135.74
130.17
128.12
127.37
126.35
125.46
125.41
125.36
125.31
122.75
25.95
16.16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7g


SiH2Ph
O

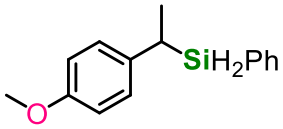

1.92
1.58
2.84
1.00
0.34
3.07
0.94
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

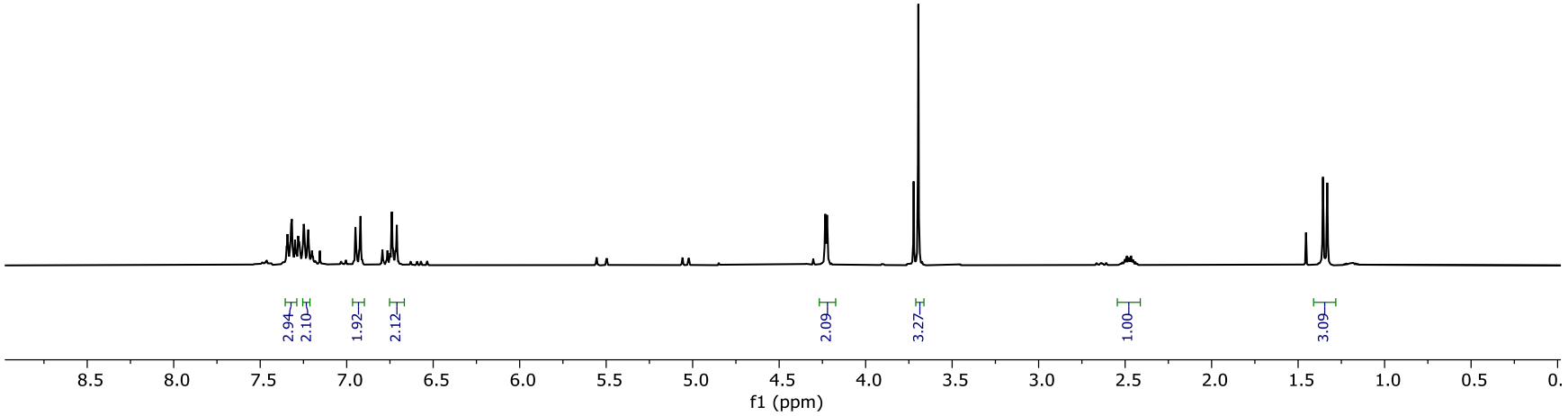
7g


SiH2Ph
O

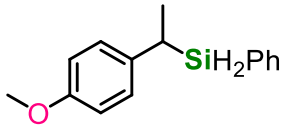
156.09
135.52
133.33
132.61
129.46
127.71
126.79
125.80
120.66
110.00
55.04
17.87
15.78
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

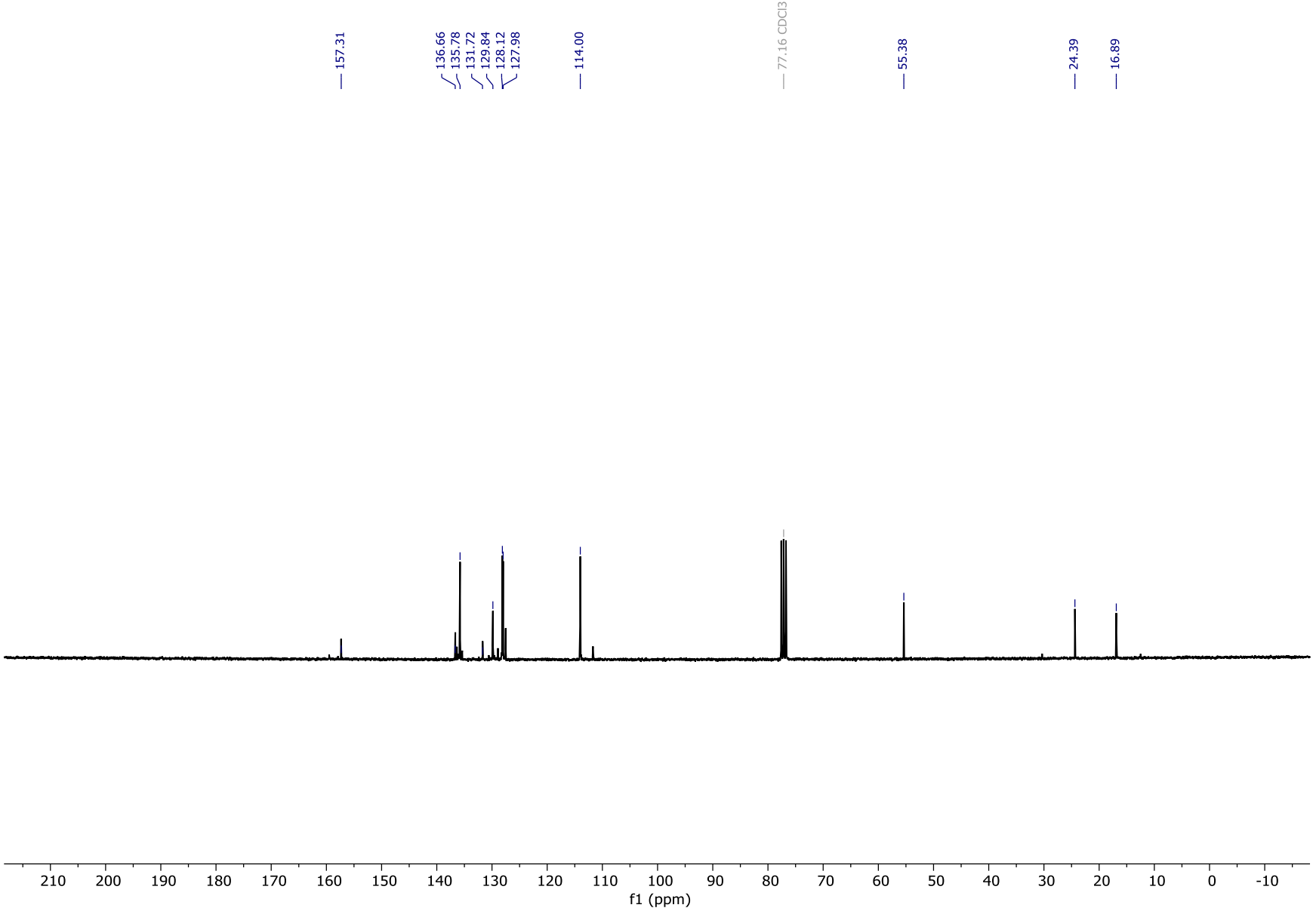
7h


SiH2Ph
O

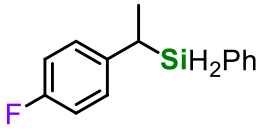

2.94
2.10
1.92
2.12
2.09
3.27
1.00
3.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

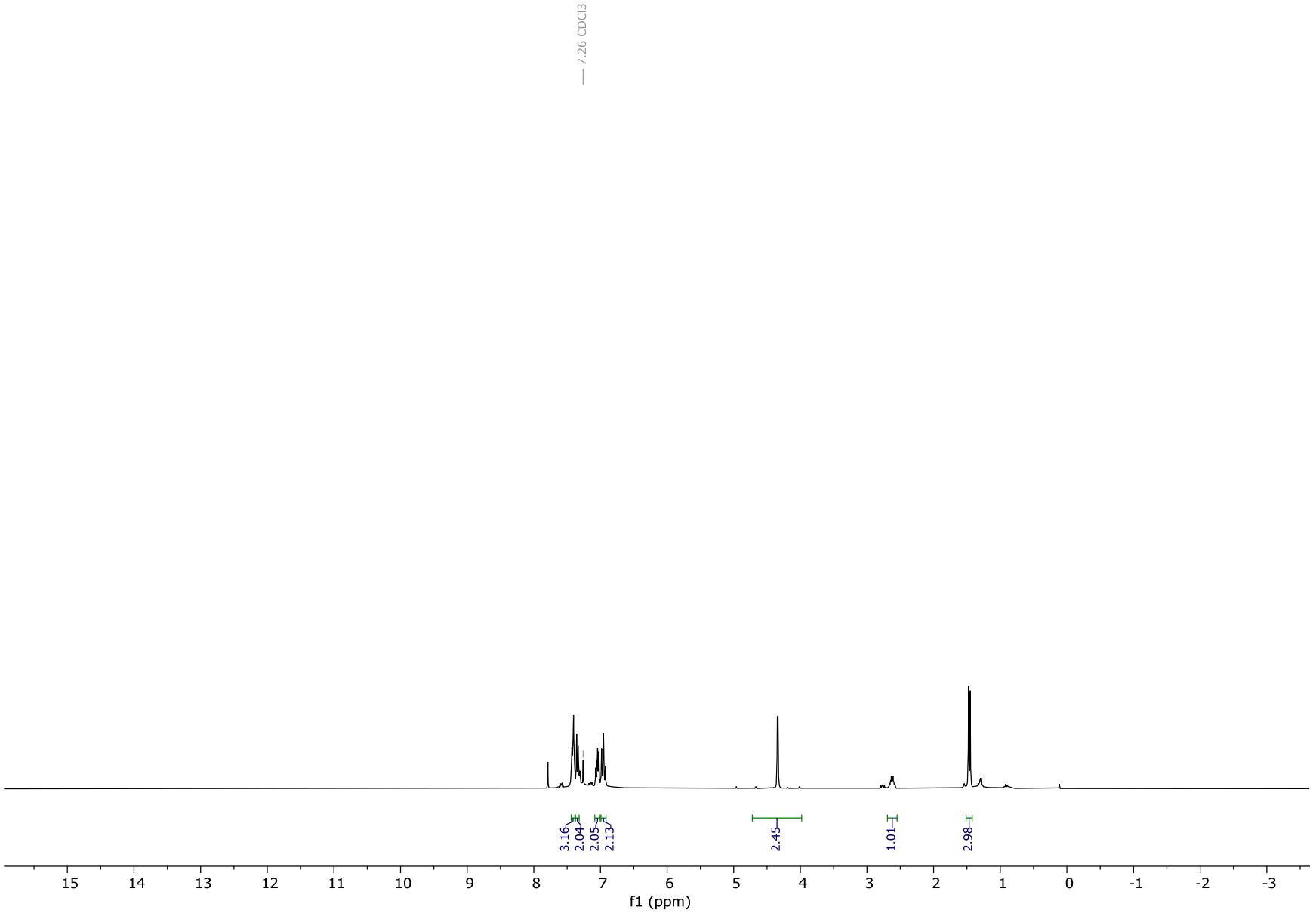
7h


SiH2Ph
O

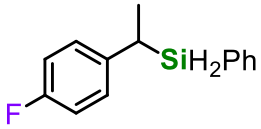

157.31
136.66
135.78
131.72
129.84
128.12
127.98
114.00
77.16 CDCl3
55.38
24.39
16.89
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

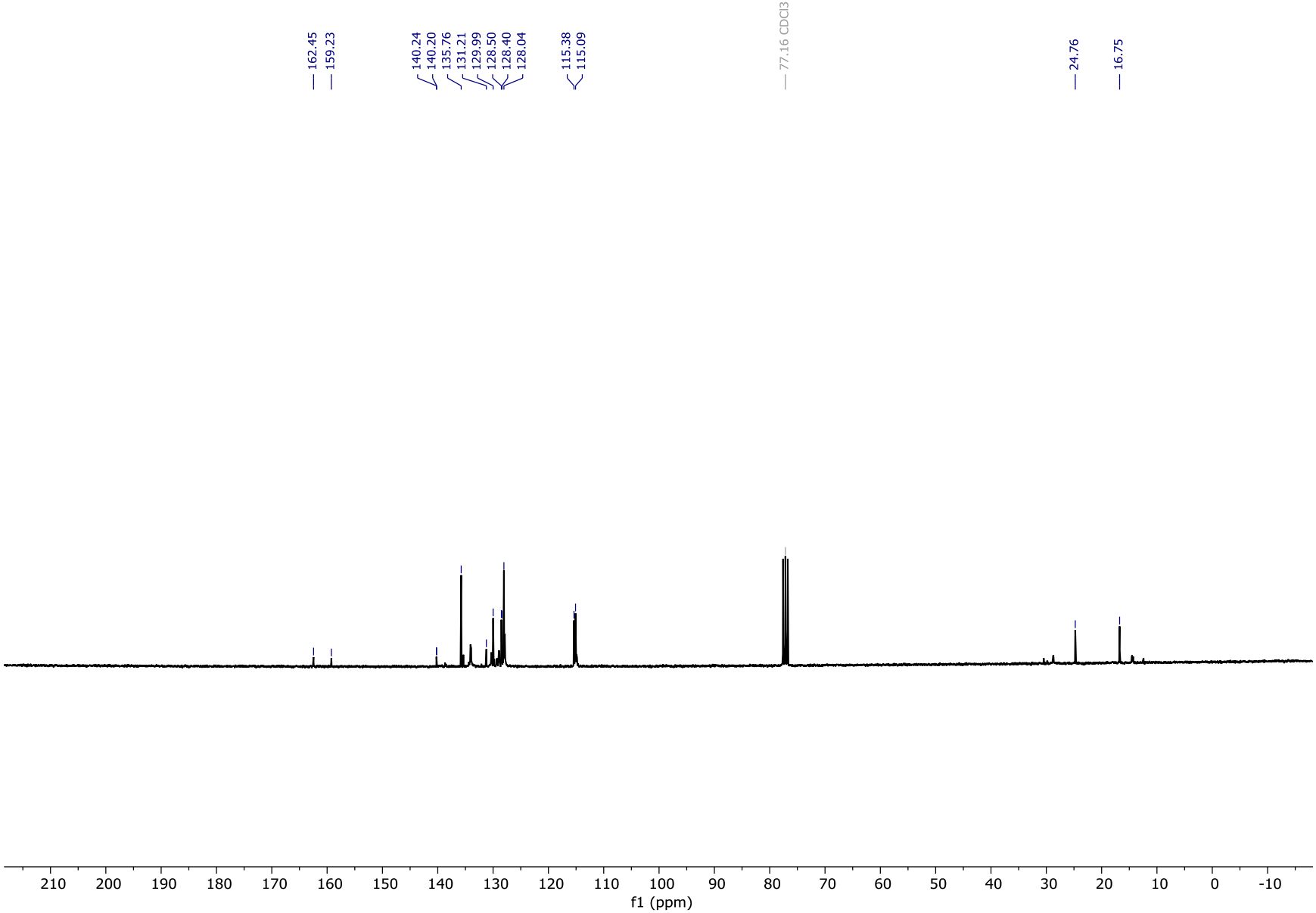
7j


SiH2Ph
F

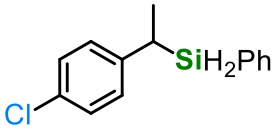

7.26 CDCl3
3.16
2.04
2.05
2.13
2.45
1.01
2.98
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

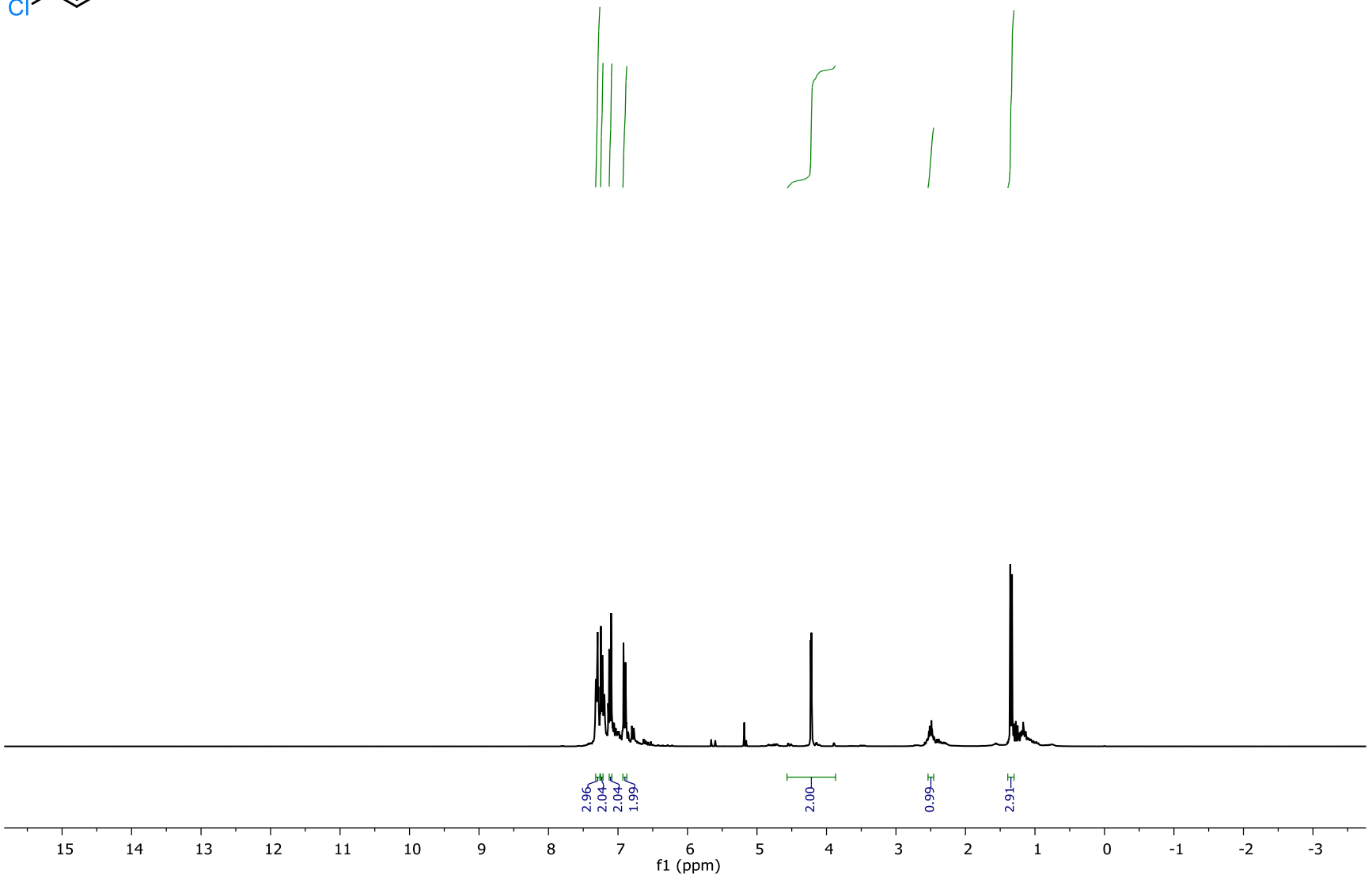
7j


SiH2Ph
F

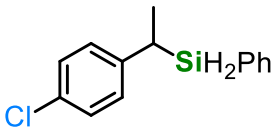

162.45
159.23
140.24
140.20
135.76
131.21
129.99
128.50
128.40
128.04
115.38
115.09
77.16 CDCl3
24.76
16.75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7k


SiH2Ph
Cl

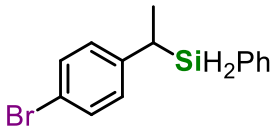

2.96
2.04
2.04
1.99
2.00
0.99
2.91
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

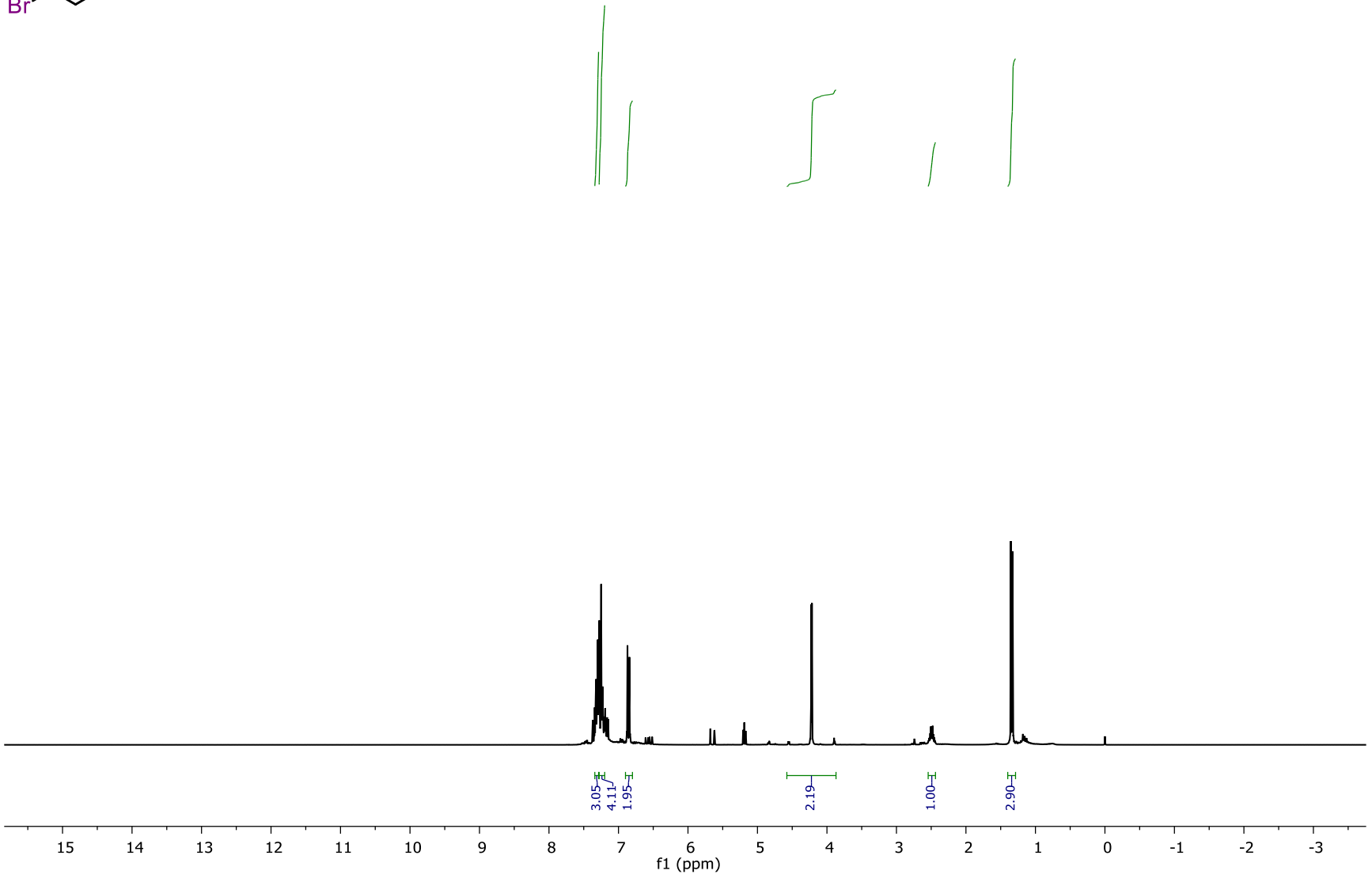
7k


SiH2Ph
Cl

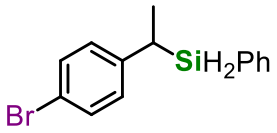
143.17
135.67
130.97
130.59
129.96
128.47
128.42
127.98
25.02
16.37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7l


SiH2Ph
Br

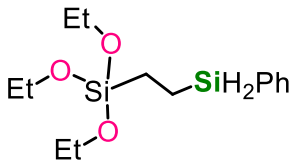

3.05
4.11
1.95
2.19
1.00
2.90
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

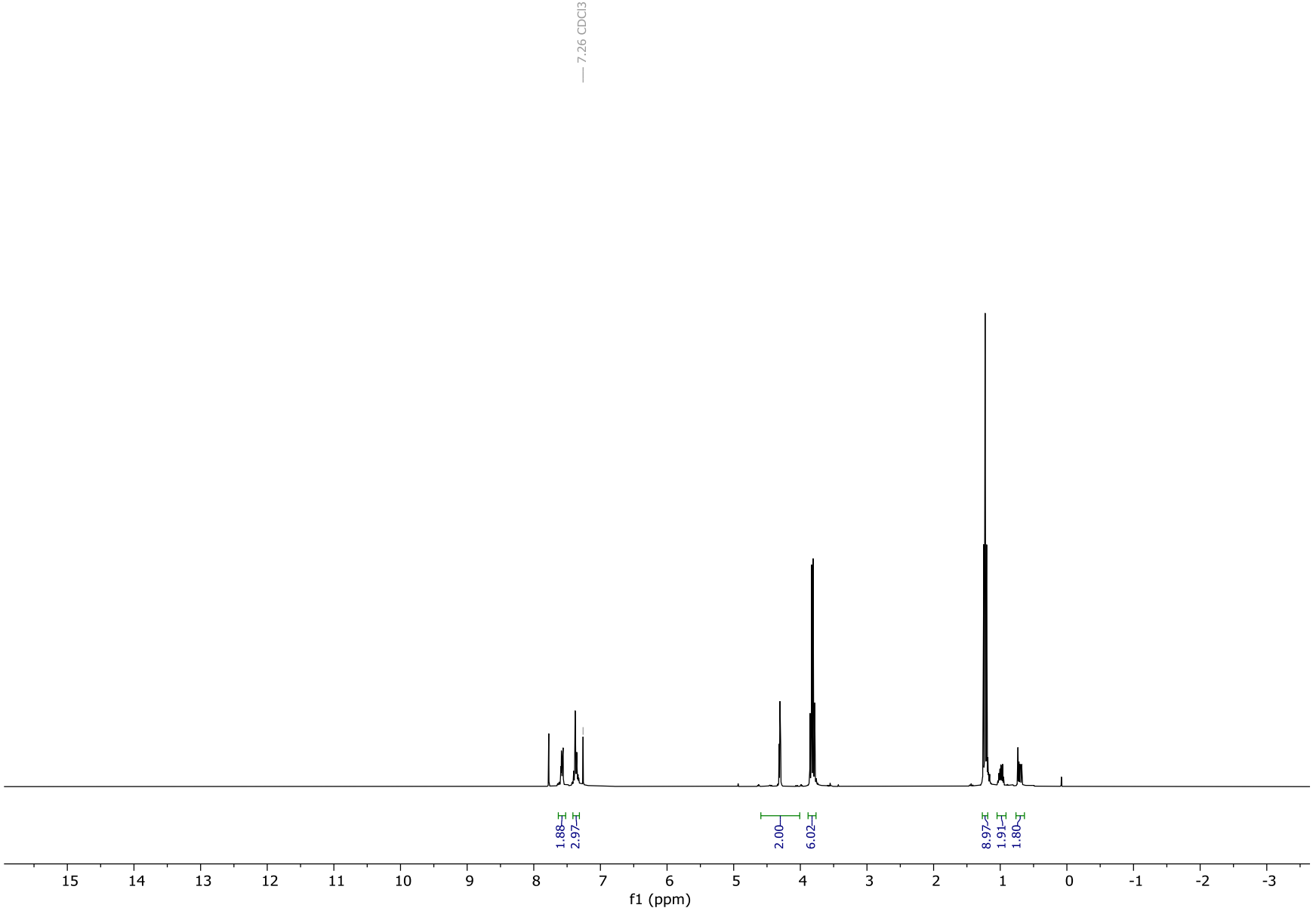
7l


SiH2Ph
Br

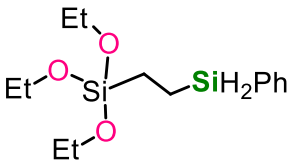
143.79
135.78
131.51
130.97
130.08
128.95
128.10
118.68
25.21
16.40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

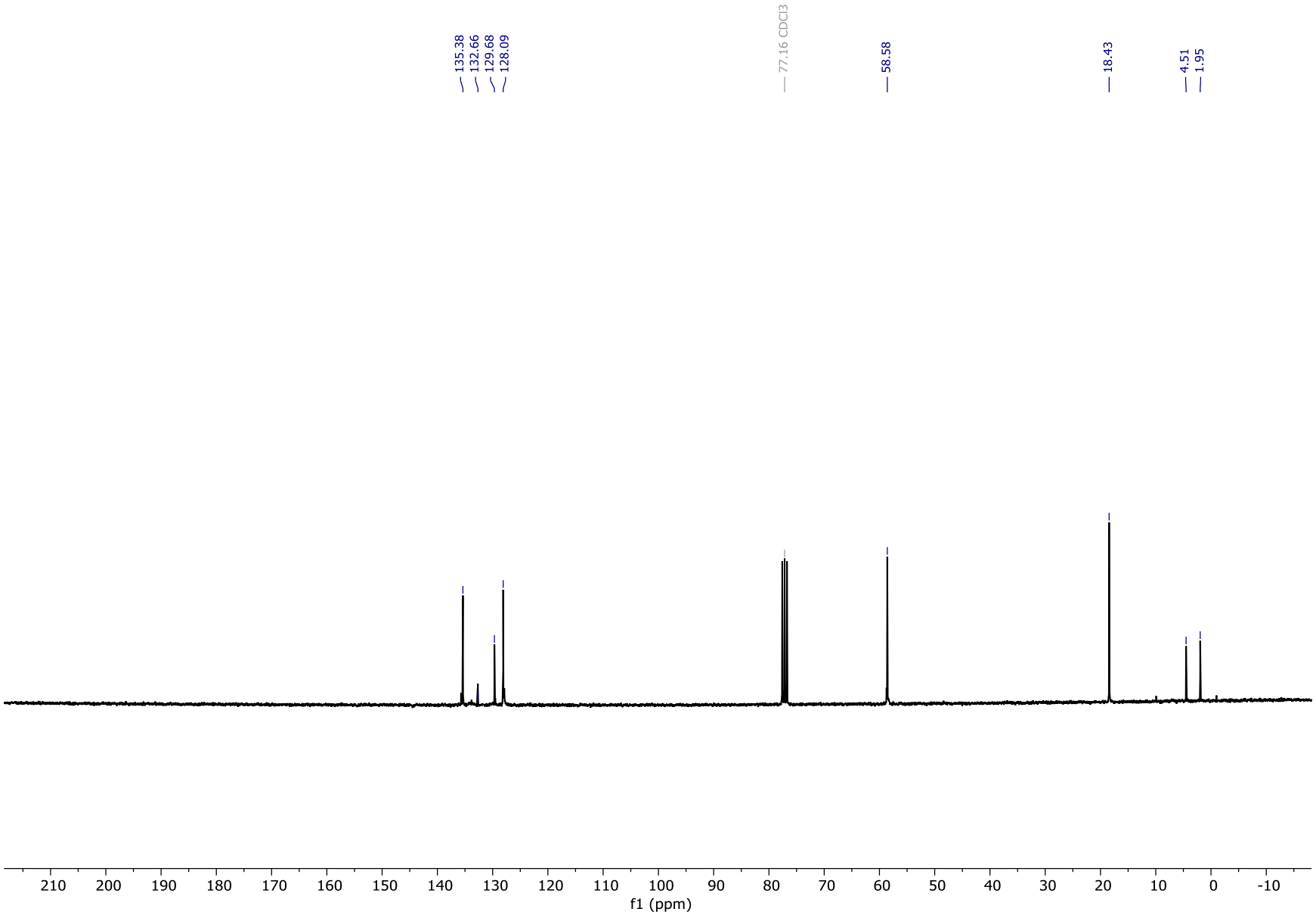
7m


Et
O
Et
O
Si
SiH2Ph
O
Et

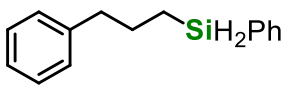

7.26 CDCl3
1.88
2.97
2.00
6.02
8.97
1.91
1.80
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

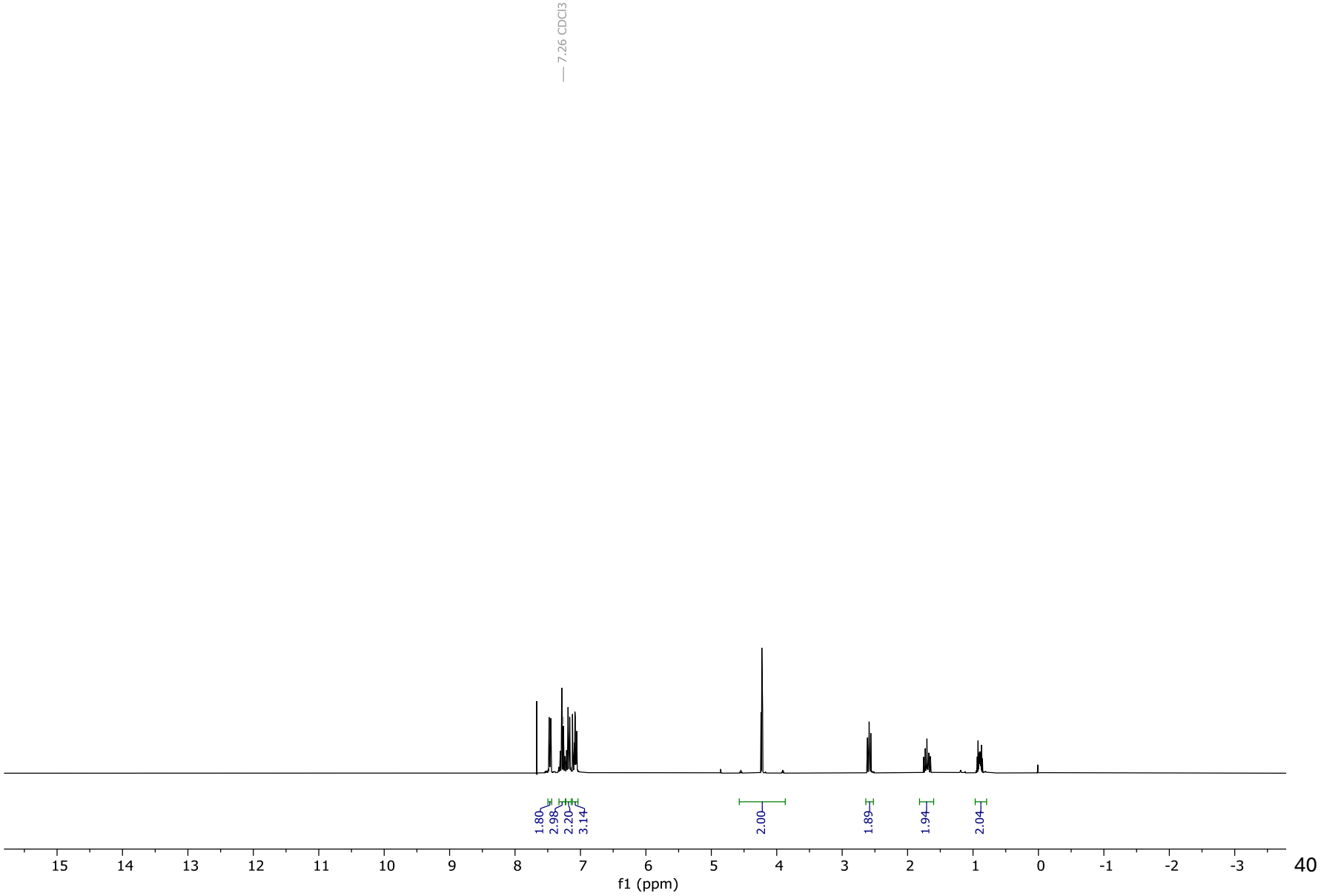
7m


Et
O
Et
O
Si
SiH2Ph
O
Et

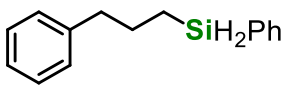

135.38
132.66
129.68
128.09
77.16 CDCl3
58.58
18.43
4.51
1.95
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

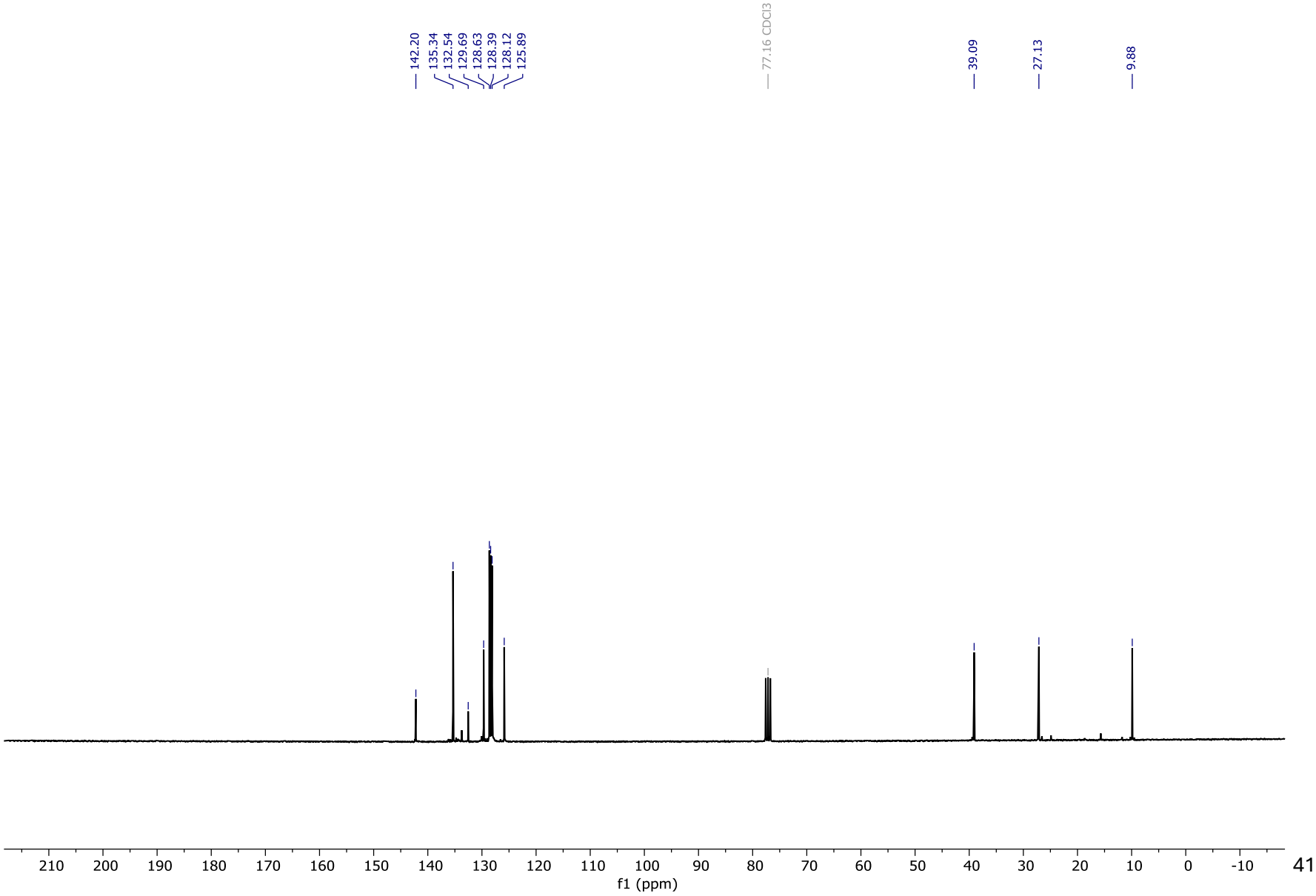
7n


SiH2Ph

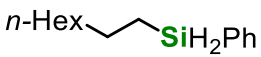

7.26 CDCl3
1.80
2.98
2.20
3.14
2.00
1.89
1.94
2.04
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

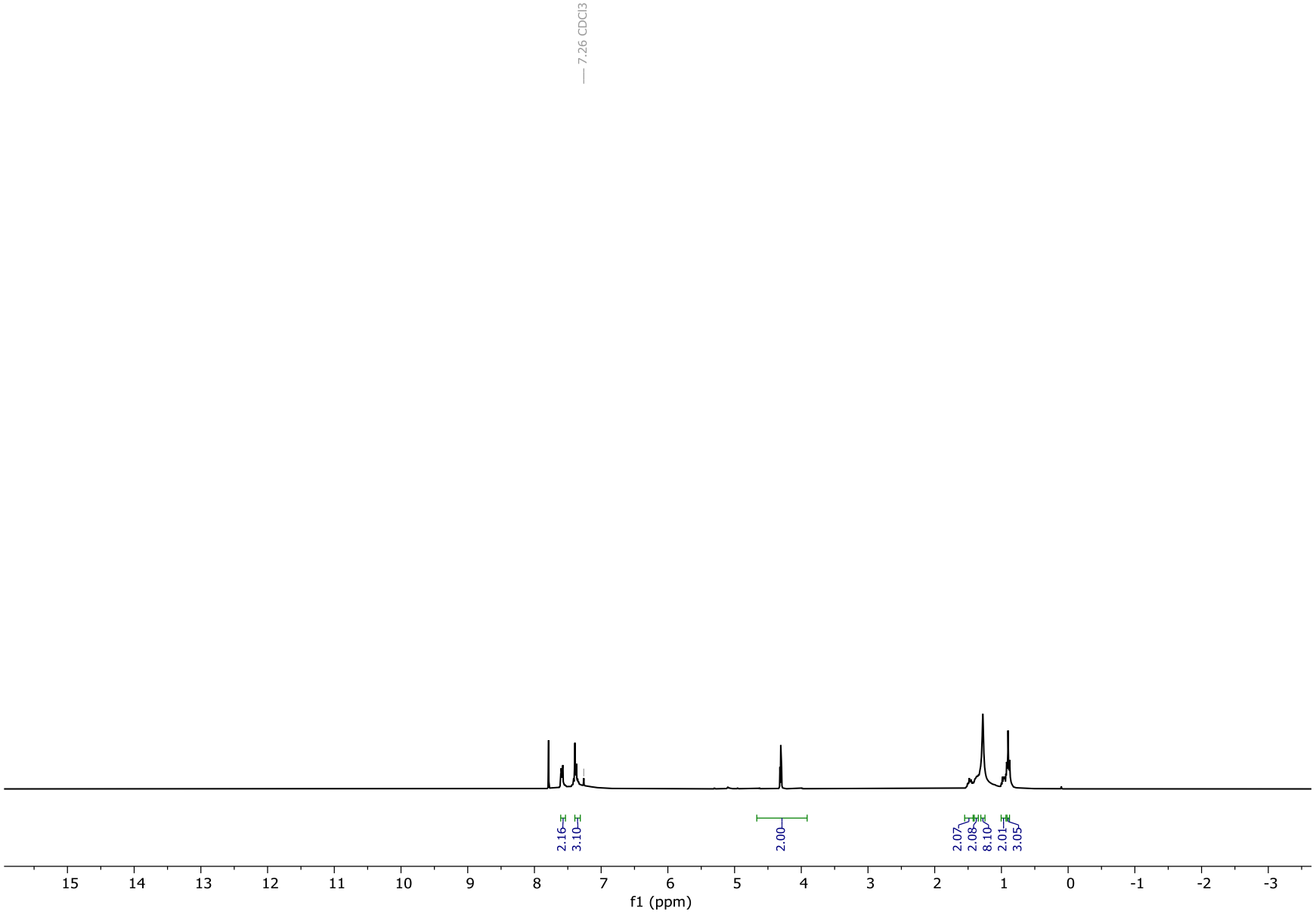
7n


SiH2Ph

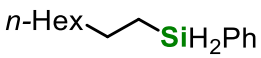

142.20
135.34
132.54
129.69
128.63
128.39
128.12
125.89
77.16 CDCl3
39.09
27.13
9.88
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

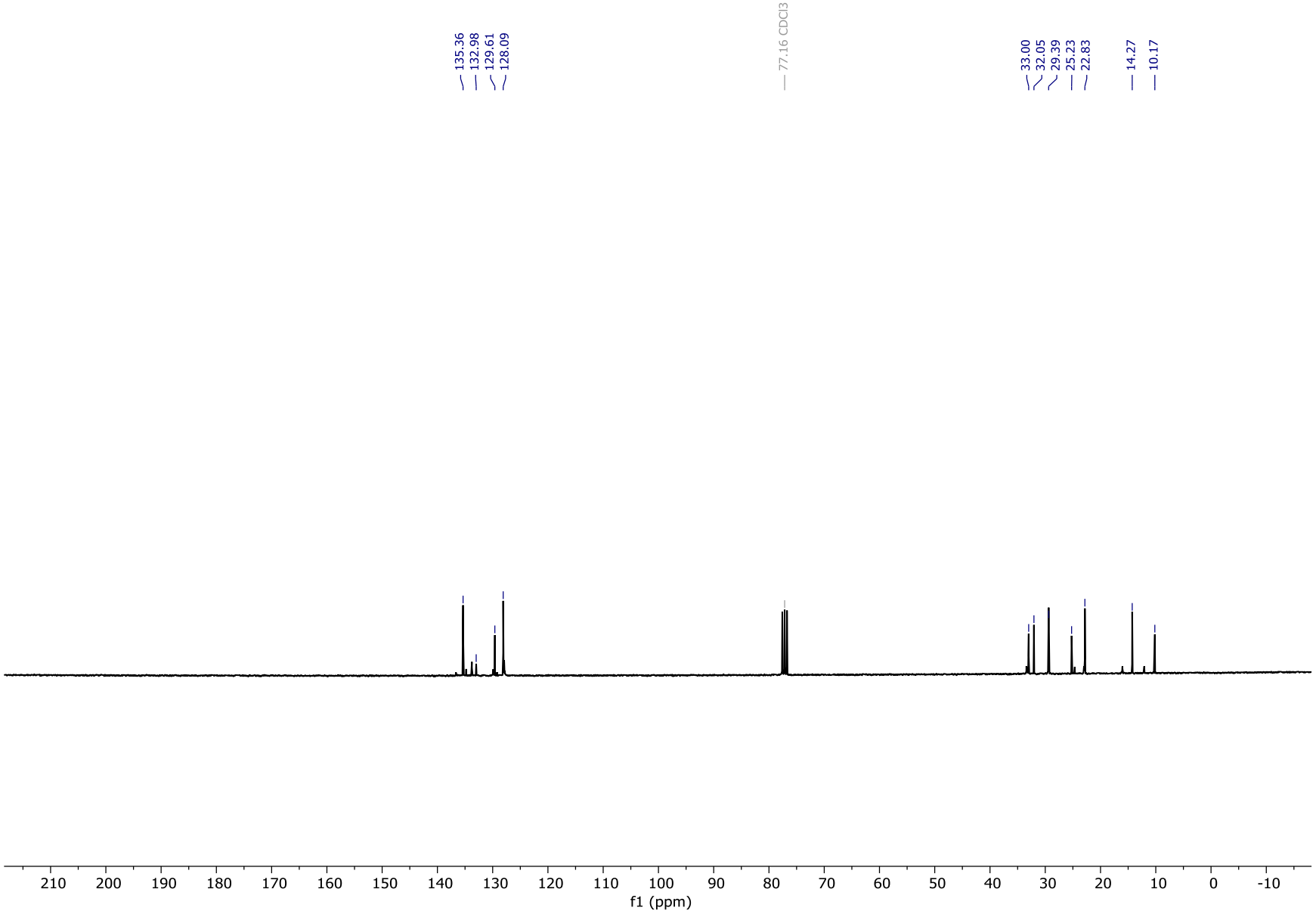
7o


n-Hex
SiH2Ph

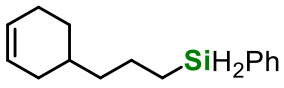

7.26 CDCl3
2.16
3.10
2.00
2.07
2.08
8.10
2.01
3.05
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

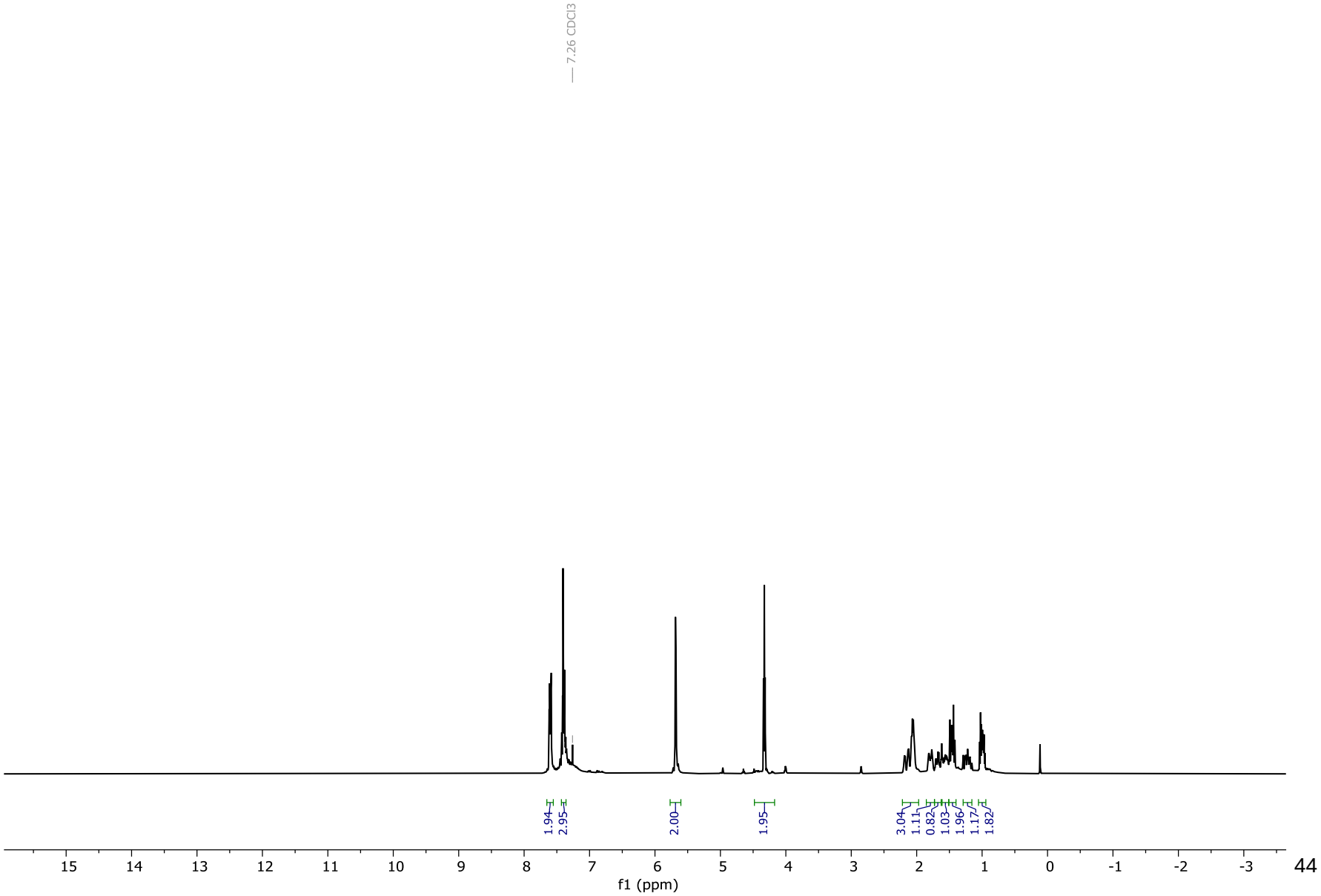
7o


n-Hex
SiH2Ph

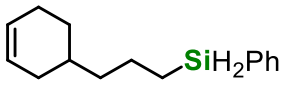

135.36
132.98
129.61
128.09
77.16 CDCl3
33.00
32.05
29.39
25.23
22.83
14.27
10.17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

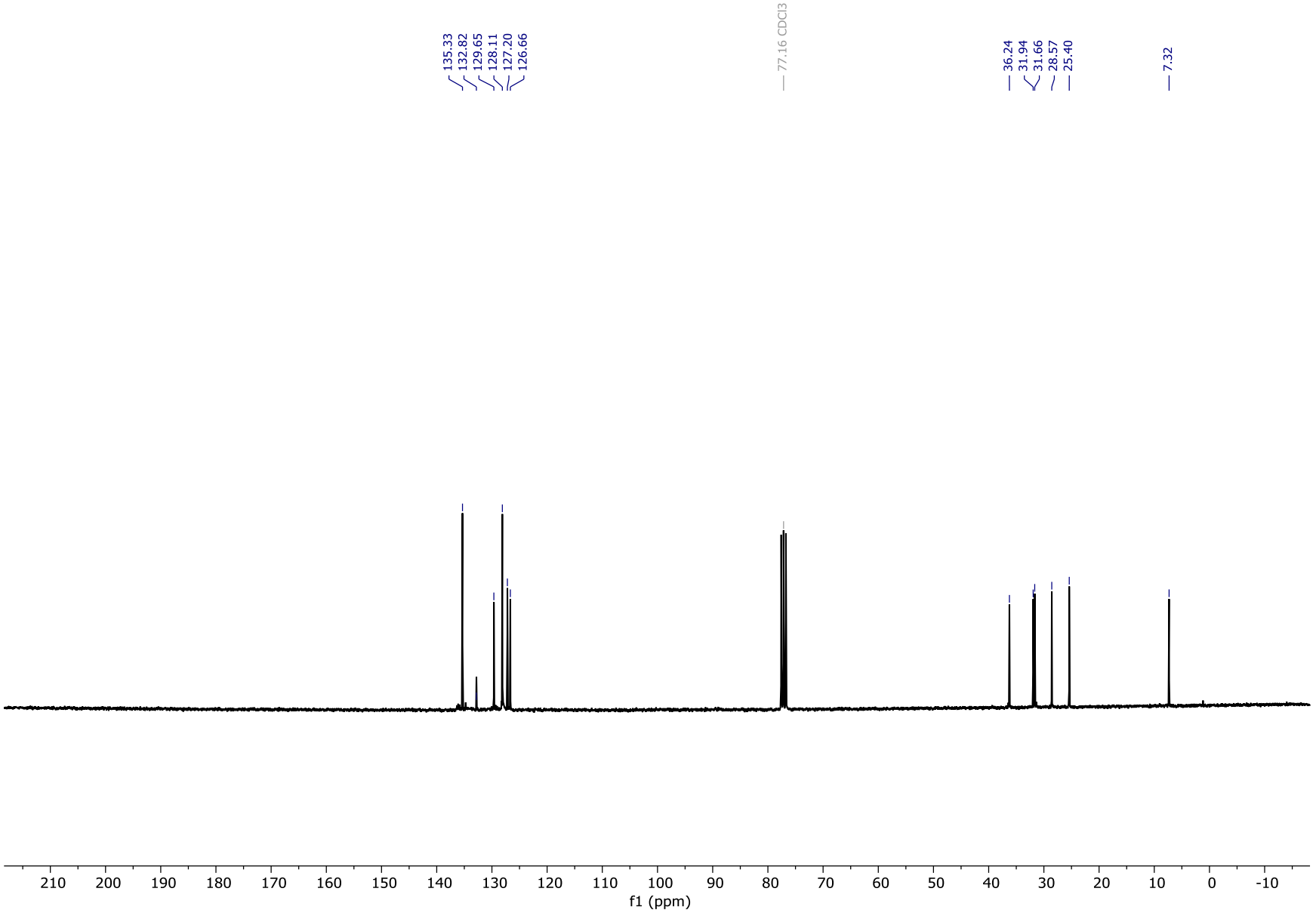
7p


SiH2Ph

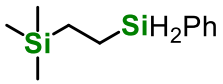

7.26 CDCl3
1.94
2.95
2.00
1.95
3.04
1.11
0.82
1.03
1.96
1.17
1.82
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

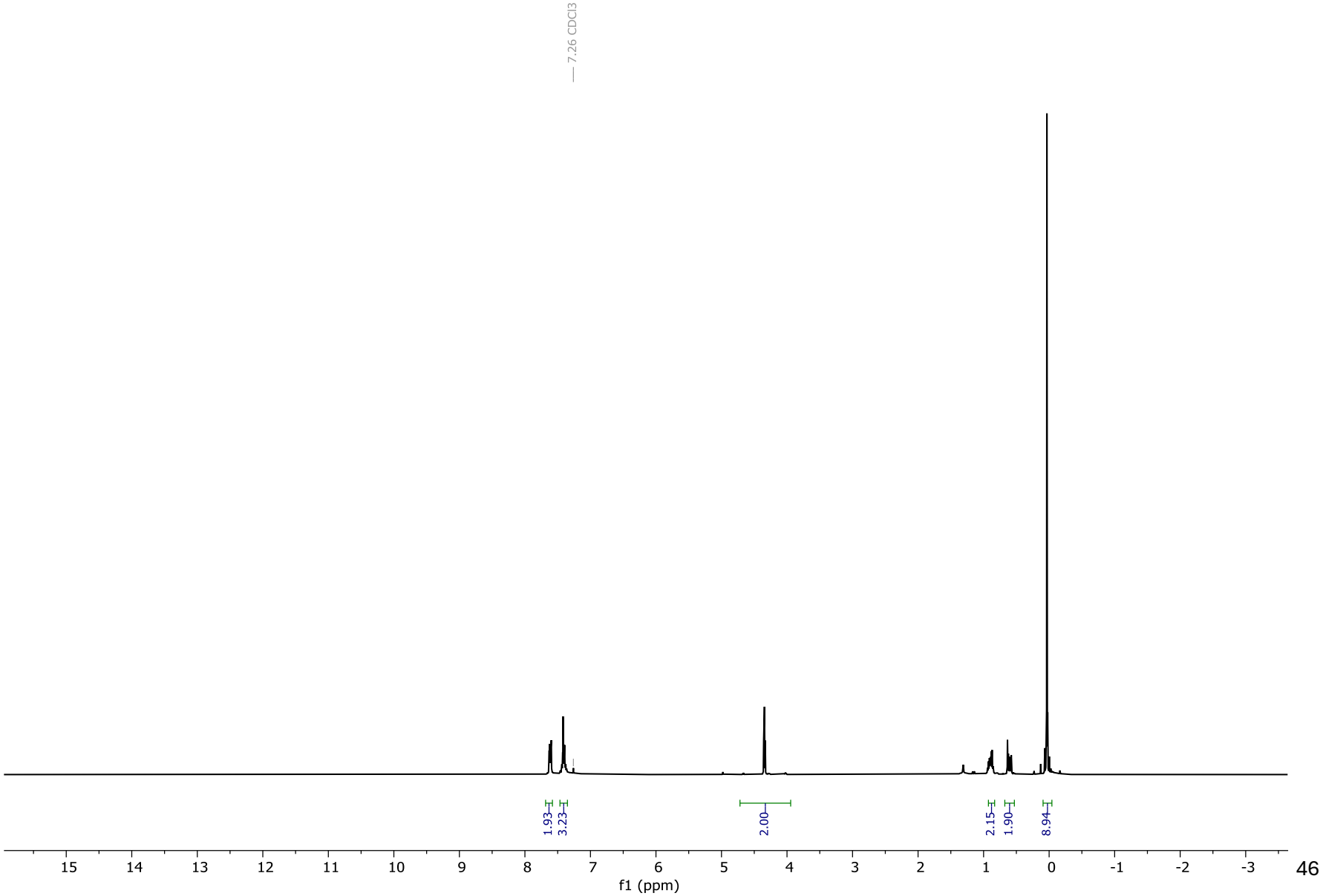
7p


SiH2Ph

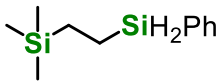

135.33
132.82
129.65
128.11
127.20
126.66
77.16 CDCl3
36.24
31.94
31.66
28.57
25.40
7.32
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

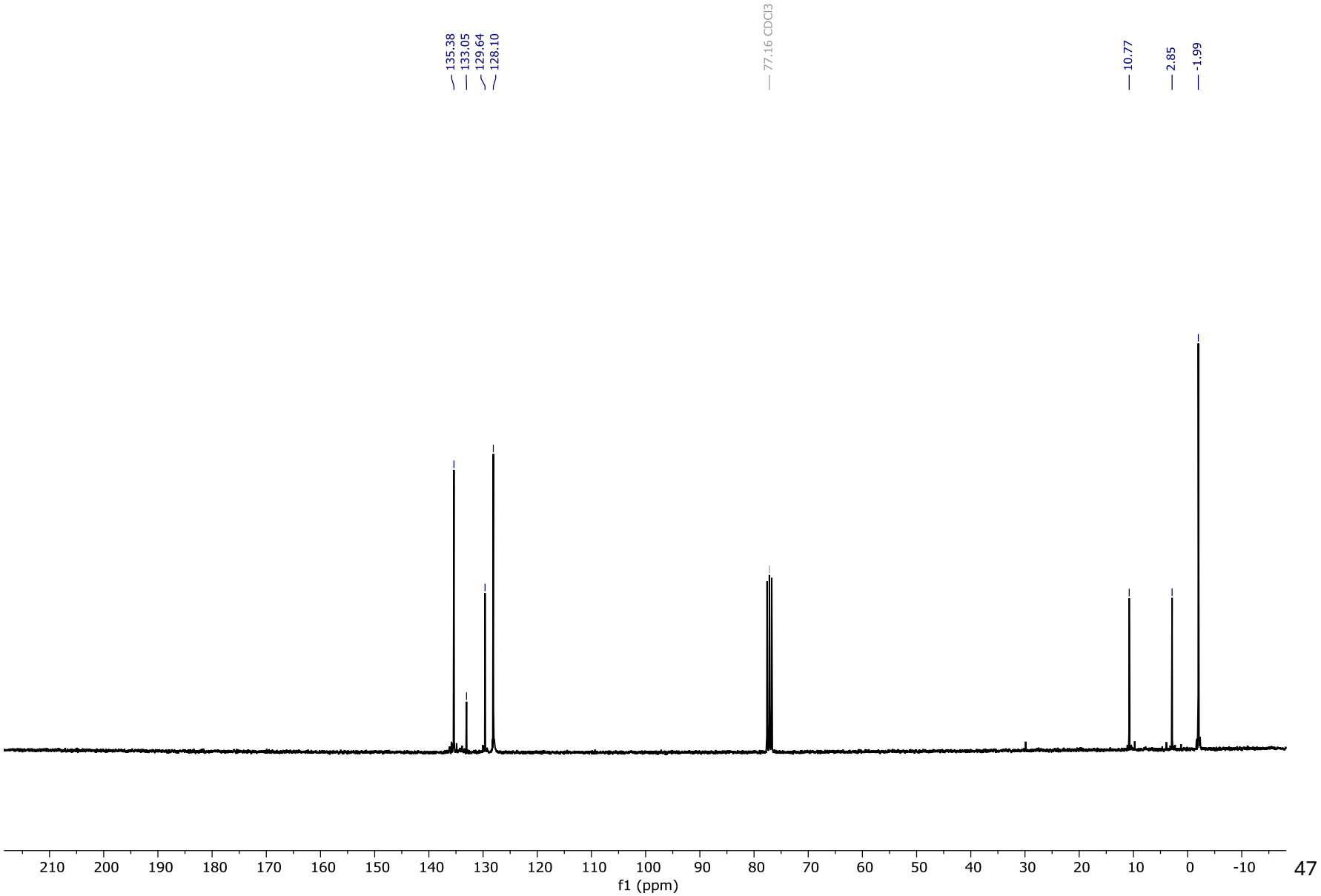
7q


Si
SiH2Ph

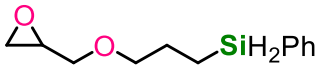

7.26 CDCl3
1.93
3.23
2.00
2.15
1.90
8.94
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

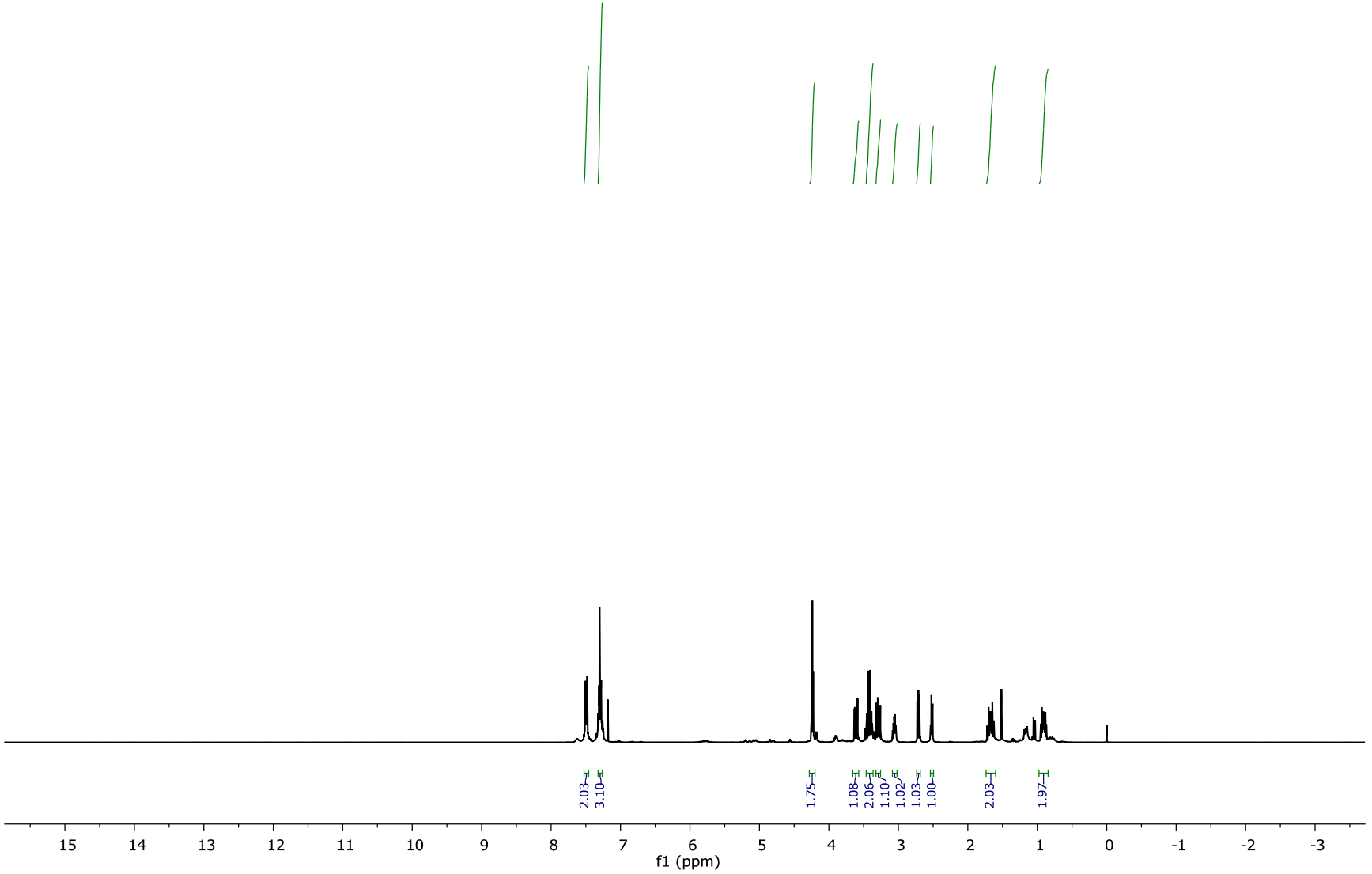
7q


Si
SiH2Ph

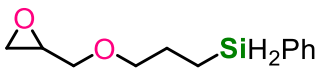

135.38
133.05
129.64
128.10
77.16 CDCl3
10.77
2.85
-1.99
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7r


O
O
SiH2Ph

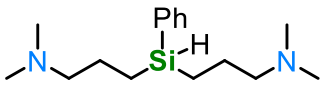

2.03
3.10
1.75
1.08
2.06
1.10
1.02
1.03
1.00
2.03
1.97
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

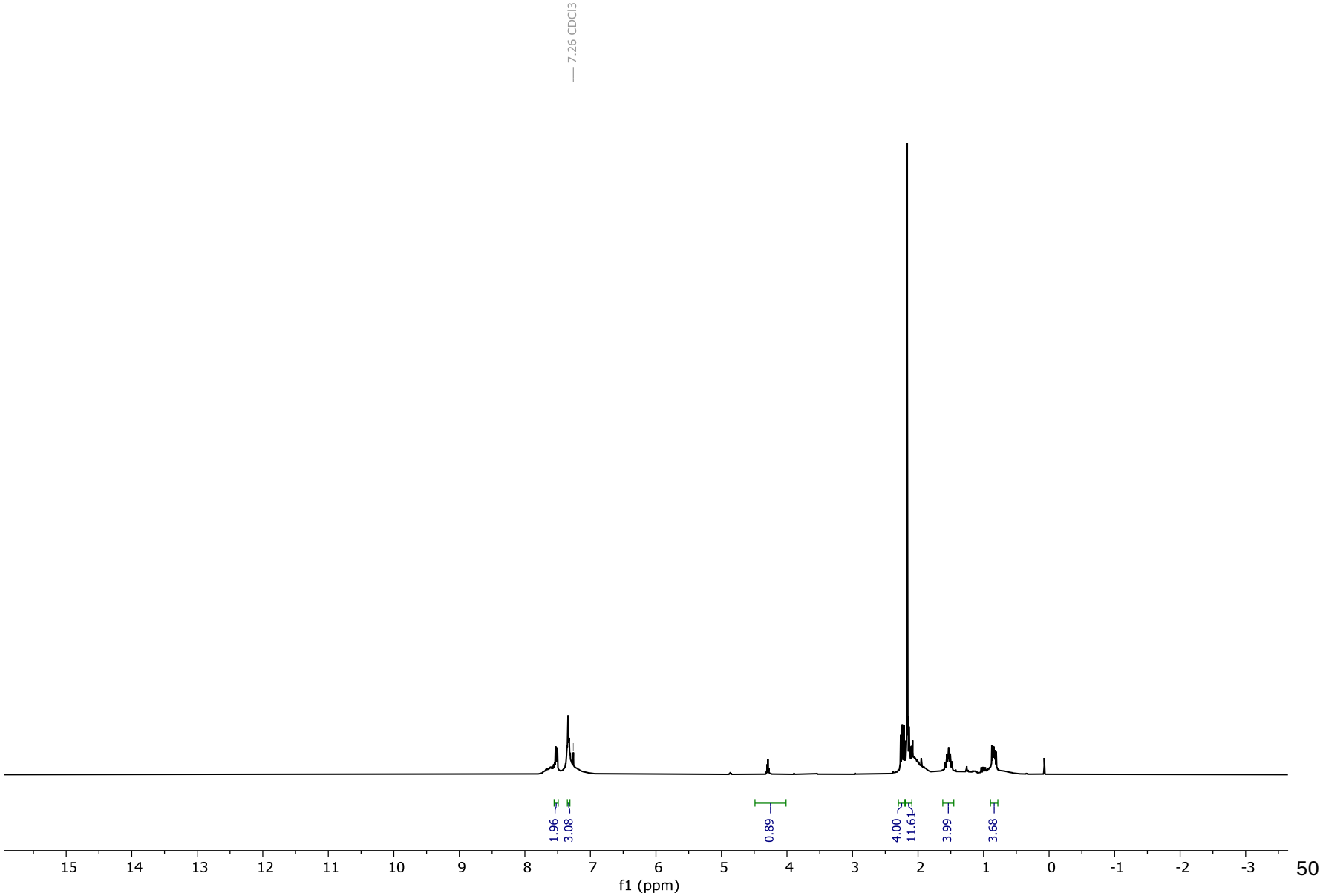
7r


O
O
SiH2Ph

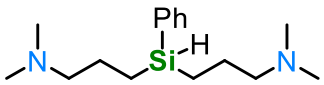
135.21
132.38
129.61
128.02
73.41
71.46
50.86
44.34
25.22
6.48
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

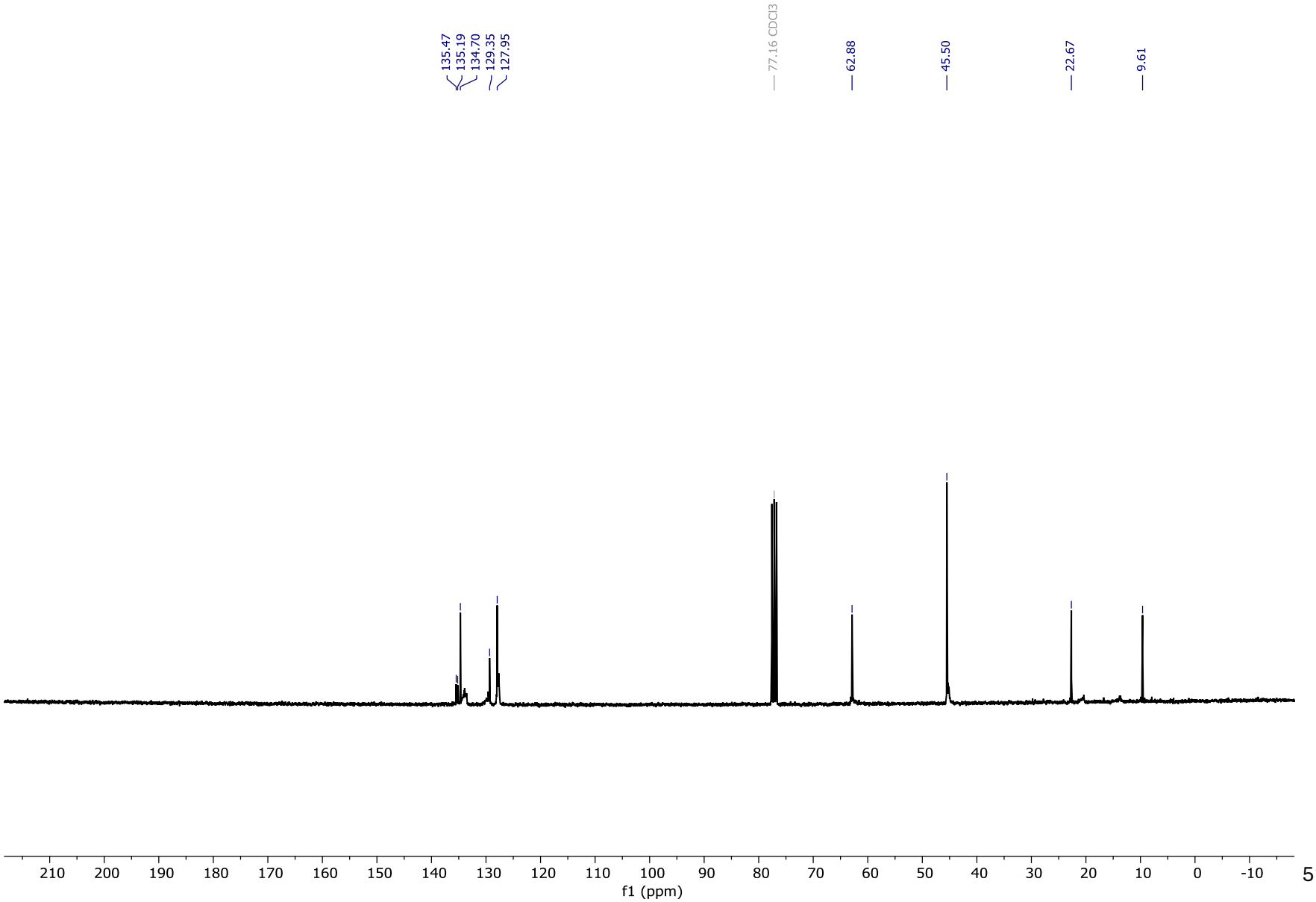
7s


Ph
H
Si
N
N

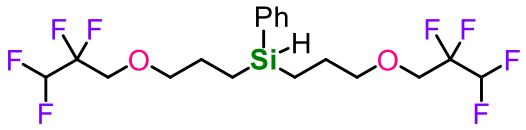

7.26 CDCl3
1.96
3.08
0.89
4.00
11.61
3.99
3.68
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

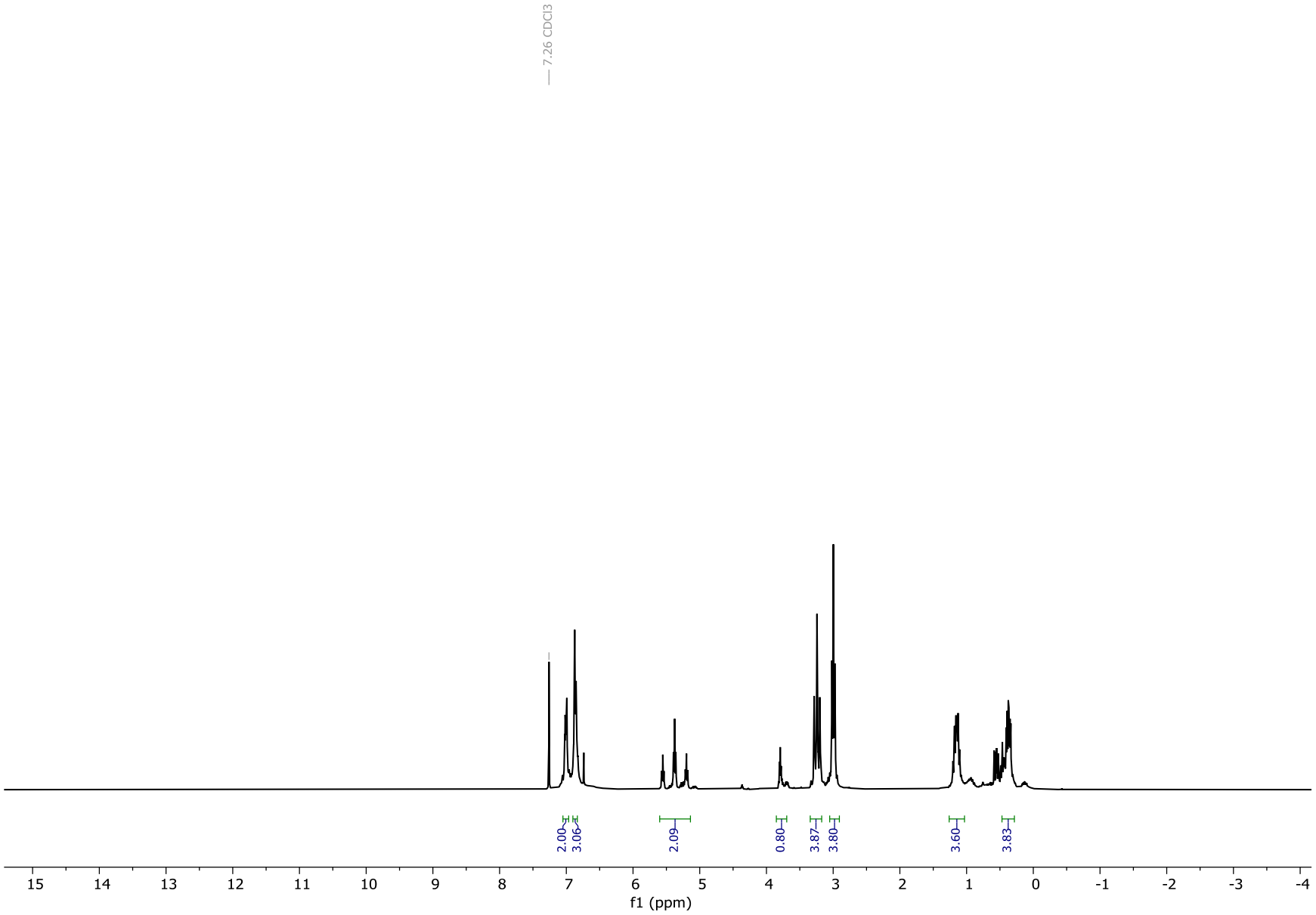
7s


Ph
H
Si
N
N

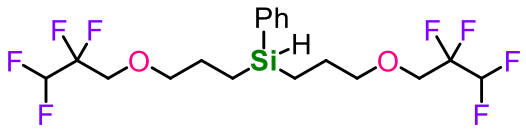

135.47
135.19
134.70
129.35
127.95
77.16 CDCl3
62.88
45.50
22.67
9.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7t

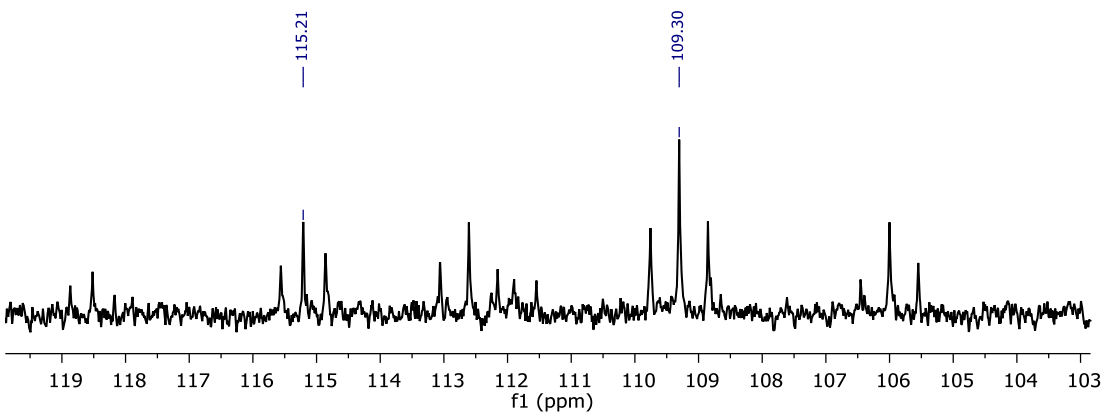

Ph
F F
F
F
O
Si
H
O
F F
F
F

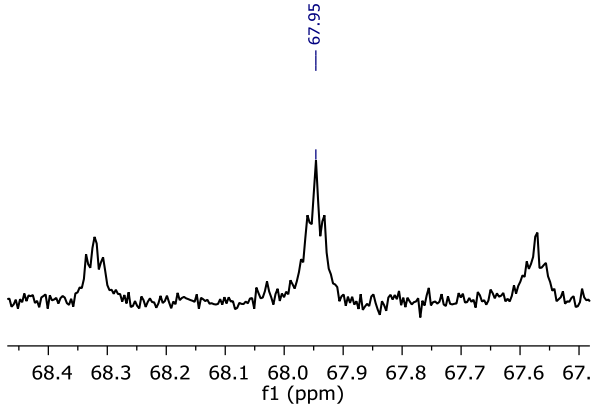

7.26 CDCl3
2.00
3.06
2.09
0.80
3.87
3.80
3.60
3.83
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

7t


Ph
F F
F
F
O
Si
H
O
F F
F
F

135.23
134.70
129.72
128.20
115.21
109.30
77.16 CDCl3
74.90
67.95
24.49
7.92
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


115.21
109.30
119 118 117 116 115 114 113 112 111 110 109 108 107 106 105 104 103
f1 (ppm)


67.95
68.4 68.3 68.2 68.1 68.0 67.9 67.8 67.7 67.6 67.
f1 (ppm)

7. References

1. CrysAlisPRO. CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd. 2014.
2. Bruker (2023). Apex5., Bruker AXS Inc., Madison, Wisconsin, USA.
3. SAINT V8.40B, Bruker AXS LLC, 2019
4. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination J. Appl. Cryst. 2015, 48, 3-10.
5. G. M. Sheldrick, SHELXT – Integrated space-group and crystal-structure determination. Acta Crystallogr. 2015, A71, 3-8.
6. G. M. Sheldrick, Crystal structure refinement with SHELXL. Acta Crystallogr. 2015, C71, 3-8.
7. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst 2009, 42, 339—341.