Synthesis and Testing of Hydrolysis Resistant Siloxane Surfactants as Additives for Pool Fire Suppression - Phase II

SERDP Exploratory Development (SEED) Project # WP18–1519

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14. ABSTRACT

Perfluoroalkyl surfactants are the key ingredients in aqueous film forming foams (AFFF) which are used by the Department of Defense and others to fight hydrocarbon (Class B) pool fires. Perfluoroalkyl surfactants work extremely well for this application, however there are growing concerns about these materials because they are highly persistent in the environment and may be toxic to plants and animals or increase their risk to certain diseases. The objective of this project was to explore hydrolysis-resistant siloxane surfactants as replacements of perfluoroalkyl surfactants found in current aqueous film forming foam (AFFF) concentrates used in fire-fighting by the Department of Defense (DoD). The new, stable siloxane surfactants produced in this research will contain only the elements carbon, silicon, hydrogen and oxygen. Foams containing the new surfactants will extinguish small-scale, unleaded gasoline pool fire in 45 seconds or less as dictated by MIL-F-24385F.

15. SUBJECT TERMS

Fire fighting, Foam, Surfactants, Siloxanes, Fuels, Surface tension, Hydrolysis, Amines, Carbohydrates, Phosphorus, Silicon, Fluorine, Nucleophilic substitution, Nuclear magnetic resonance, Fire safety, Organic synthesis

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List of Acronyms

AFFF	Aqueous film forming foam
APG	Alkyl polyglucoside
ASAP	Atmospheric solids analysis probe
CAFS	Compressed air foam system
CMC	Critical micelle concentration
dgbe	Diethylene glycol monobutyl ether
DoD	Department of defense
F^3	Fire fighting foams
g	grams
gpm	Gallons per minute
Kg	kilogram
L	liter
Me	methyl
Mil spec	Military specification
mL	milliliter
mN/m	Millinewton per meter
MS	Mass spectrometry
NAWCWDCL	Naval Air Warfare Center Weapons Division China Lake
NMR	Nuclear magnetic resonance
NRL	Naval Research Laboratory
PFOA	Perfluorooctanoic acid
PFOS	perfluorooctanesulfonate
Ph	phenyl
psi	Pounds per square inch
rt	Room temperature
SERDP	Strategic Environmental Research and Development Program
TBDMS	Tert-butyldimethylsilyl
*t*Bu	*Tertiary*-butyl
TMS	trimethylsilyl

Keywords

Fire fighting, Foam, Surfactants, Siloxanes, Fuels, Surface tension, Hydrolysis, Amines, Carbohydrates, Phosphorus, Silicon, Fluorine, Nucleophilic substitution, Nuclear magnetic resonance, Fire safety, Organic synthesis

Disclaimer

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ABSTRACT

1.1 Objective: Perfluoroalkyl surfactants are the key ingredients in aqueous film forming foams (AFFF) which are used by the Department of Defense and others to fight hydrocarbon (Class B) pool fires. Perfluoroalkyl surfactants work extremely well for this application, however there are growing concerns about these materials because they are highly persistent in the environment and may be toxic to plants and animals or increase their risk to certain diseases. The objective of this project was to explore hydrolysis-resistant siloxane surfactants as replacements of perfluoroalkyl surfactants found in current aqueous film forming foam (AFFF) concentrates used in fire-fighting by the Department of Defense (DoD). The new, stable siloxane surfactants produced in this research will contain only the elements carbon, silicon, hydrogen and oxygen. Foams containing the new surfactants will extinguish small-scale, unleaded gasoline pool fire in 45 seconds or less as dictated by MIL-F-24385F.

1.2 Technical Approach: In previous work, it was discovered that the inexpensive 3-aminopropylmethylbis(trimethylsiloxy)silane (APS) can be converted into surfactants with a positive spreading coefficient on cyclohexane. However, these surfactants could not extinguish a heptane pool fire themselves but could extinguish such fires in synergistic mixtures with other hydrocarbon surfactants such as alkyl polyglucosides. There were obvious stability issues with these simple siloxane surfactants, with apparent hydrolysis or other chemical changes occurring at the siloxane head group. This chemical reactivity was most likely the result of the water-labile trimethylsiloxy groups of the siloxane head. The hydrolysis of the siloxane would probably be enhanced when applied on pool fires and the thermal stress they cause. Therefore, we will synthesize new siloxane surfactants with hydrolysis-resistance by adding methyl groups to the terminal silicon atoms. Thus, surfactants with trisiloxane head groups terminating in bis(ethyldimethylsiloxy), bis(isopropyldimethylsiloxy) and bis(*tert*-butyldimethylsiloxy) will be synthesized. We will quantify the effects of changes to the surfactant chemical structures on surfactant/fuel diffusion at fuel-aqueous interface, micelle diffusion, and bubble coalescence rate at foam-fuel interface, in addition to the foam dynamics and fire extinction for heptane and gasoline fuels at bench-scale. For leading surfactant candidates, we will scale-up synthesis to generate 200 mL of surfactant and conduct 28 ft^2 MilSpec gasoline pool fire testing.

1.3 Benefits: This new technology could help the DoD eliminate perfluoroalkyl surfactants from AFFF concentrates since these compounds appear to be persistent in the environment. Eliminating perfluoroalkyl surfactant use could also mitigate future legal issues since it is not clear what their biological effects really are. Using hydrolysis-resistant siloxane surfactants, it may be possible to extinguish fires with smaller quantities of chemicals than previous AFFF formulations.

Executive Summary

Introduction: The triservices of the DoD use enormous quantities of highly flammable substances, particularly high vapor pressure hydrocarbon liquids (such as gasoline, diesel and jet fuel) which pose serious risks of fire. Even though personnel have excellent training with appropriate procedures and safeguards in place to minimize the risks of fire from these substances, fires can and do happen. Extinguishing such hydrocarbon pool fires as fast as possible must be accomplished in order to minimize damage to infrastructure, vehicles and equipment as well as keep personnel safe from harm on ships or airfields. Fire-fighting foams (F^3) were developed to combat hydrocarbon liquid pool fires as early as 1902 and these are referred to as Class B foams. F^3 are based on surfactants (surface active agents) that can be added to water, typically at the nozzle of a hose by a mixing head inlet, which create a thick foam spray, Figure 1. The F^3 is sprayed onto the pool fire, similar to a wide blanket, and in this way the fire is covered over with a stable mass of small air-filled bubbles.

Figure 1 Navy personnel in full fire suits to fight high temperature jet fuel fire with film forming foam (AFFF).

The burning fuel is thus starved from atmospheric oxygen and is extinguished. Because the aqueous foam is composed mostly of air, it is light and able to rest on top of the hydrocarbon, for example gasoline, whose density is typically less than water (e.g. octane: d = 0.7 g / mL) but also has a very low surface tension of 20.7 mN/m, Table 1. Gasoline is a much harder fuel to form a film on than diesel on account of its lower surface tension.

Table 1 Surface tensions of various DoD hydrocarbon fuels.

FUEL	Surface tension mN/m (24 C)
Diesel	28.3
Jet	26.7
gasoline	20.7

Not all surfactants work well as F^3 and many types have been tried. The best surfactants for F^3 are the perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) and related perfluoroalkyl brethren, whose fire-fighting applications were discovered and developed by the US Navy, Figure 2.

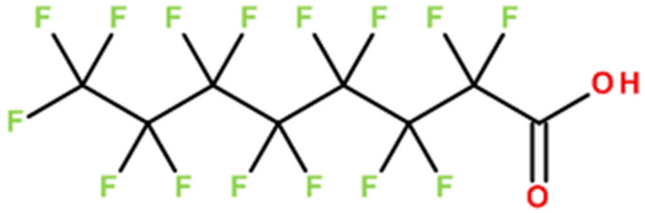


Figure 2 Chemical structure of perfluorooctanoic acid (PFOA), a typical ingredient that is used in AFFF concentrates that is highly effective at putting out liquid hydrocarbon pool fires.

These perfluoroalkyl surfactants maintain good quality foams and also have the unique property of being both hydrophobic *and* oleophobic. This means that the perfluoroalkyl surfactants are resistance to dissolve in both water and non-polar liquids such as the hydrocarbon fuels, Figure 3.

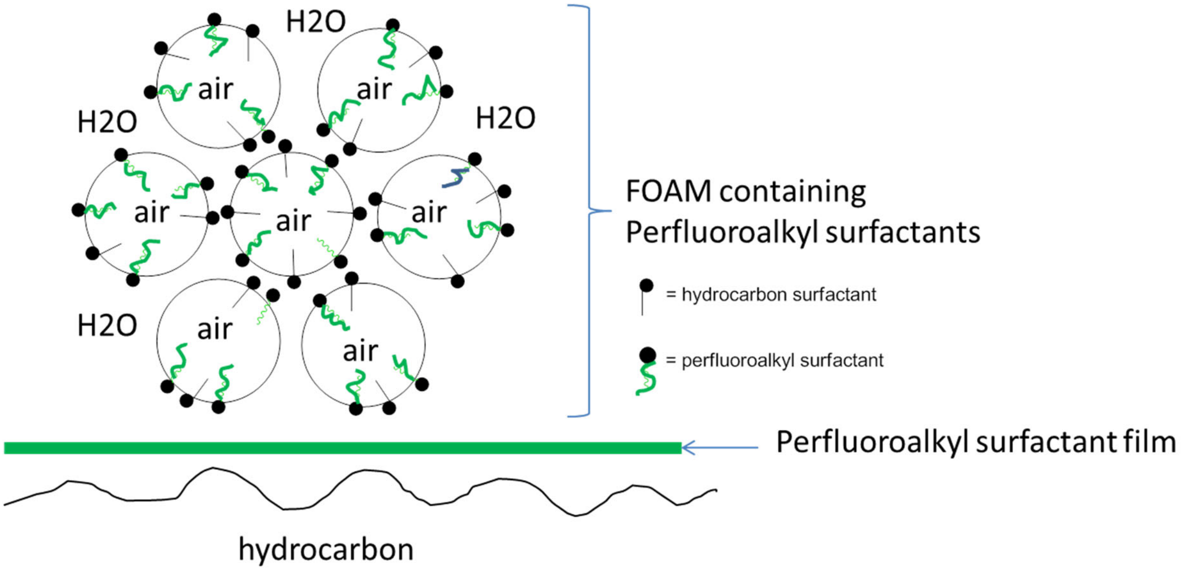


Figure 3 Perfluoroalkyl surfactants foam on the surface of fuel.

Objectives: The objective of this project WP18–1519 was to explore hydrolysis-resistant siloxane surfactants as replacements of perfluoroalkyl surfactants found in current aqueous film forming foam (AFFF) concentrates used in fire-fighting by the Department of Defense (DoD). The new, stable siloxane surfactants produced in this research will contain only the elements carbon, silicon, hydrogen and oxygen. Foams containing the new surfactants will extinguish small-scale, unleaded gasoline pool fire in 45 seconds or less as dictated by MIL-F-24385F.

Technical Approach: Silicon is the second most abundant element in the Earth's crust and so new surfactants made from this element might be environmentally-friendly materials. Siloxanes have the defining feature that each pair of silicon atoms are separated by an oxygen atom. Siloxanes can undergo cleavage at any silicon-oxygen bond by hydrolysis. In this project, siloxanes will be designed and synthesized with particular alkyl substituents in order to increase their hydrolytic stability. The hydrolytically stable siloxanes will be further derivatized into structures with surfactant properties. The surfactant properties of these new silicon-containing materials will be measured such as surface and interfacial tensions against cyclohexane, specified by MIL-F-24385F. Silicon-based surfactants with spreading coefficient > +3 mN/m will be tested for extinguishing small-scale hydrocarbon pool fires.

Results and Discussion: New siloxane surfactants were synthesized by a four-step route starting from an inexpensive, commercially available silane and silanol reagents, Figure 4. The new siloxanes had tert-butyldimethylsilyl rather than trimethylsilyl groups as the terminus. For water solubility of the new siloxanes, it was critical to incorporate the proper number of aldonic acid substituents, Figure 5.

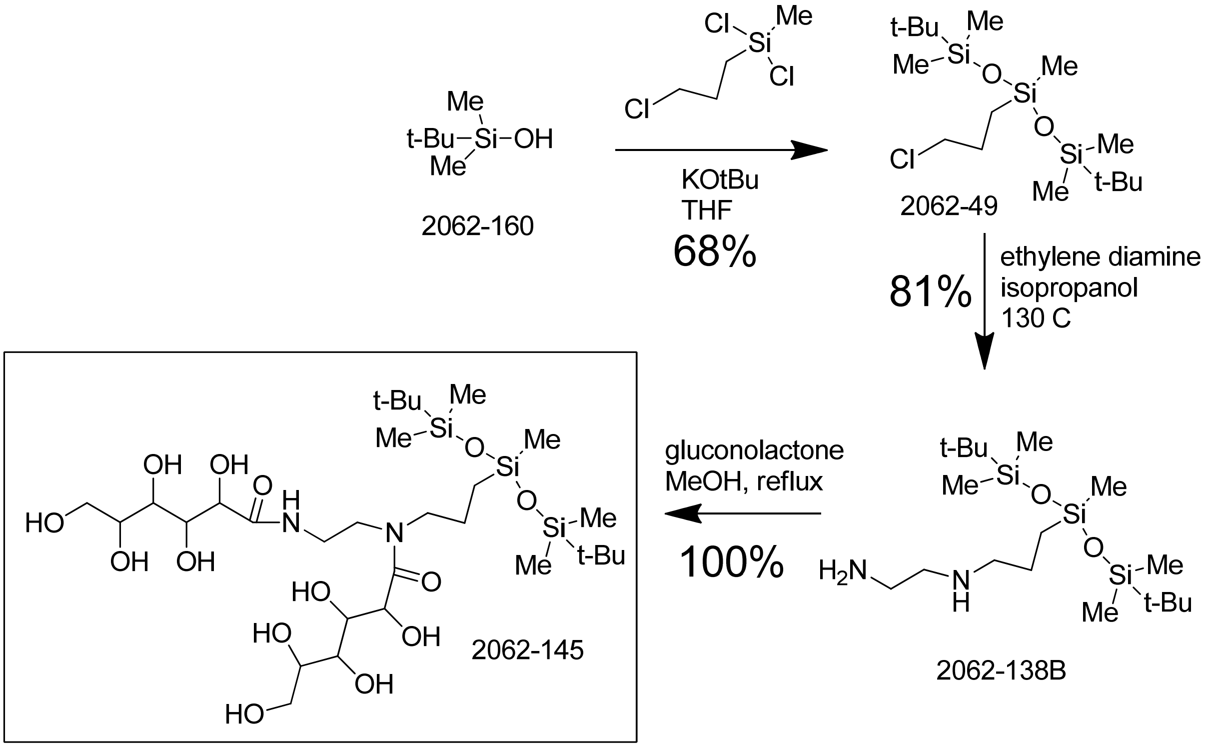


Figure 4 Three step chemical synthesis of a hydrolysis-resistant siloxane surfactant 2062–145.

Figure 5 Water solubility of the new surfactants was dependent on the number of aldonic acid substituents present in the molecules.

The stability to hydrolysis was tested by dissolving two structurally similar siloxane surfactants in water, Figure 6. After 29 days, the siloxane surfactant capped with tert-butyldimethylsilyl groups continued to make foam when shaken indicating surfactant properties were intact. In contrast, the siloxane surfactant capped with trimethylsilyl groups no longer produced any foam when shaken and had obviously lost surfactant activity.

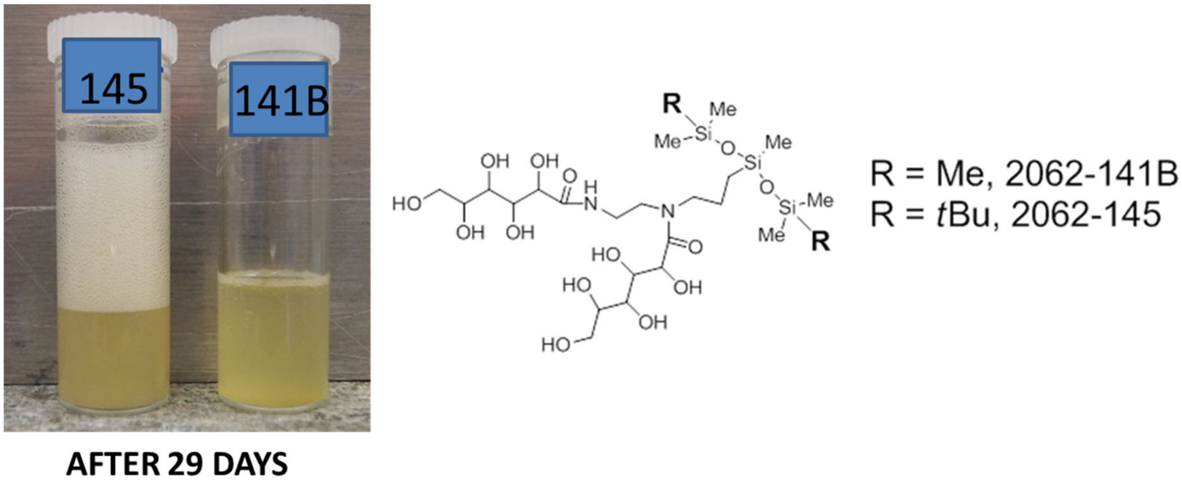
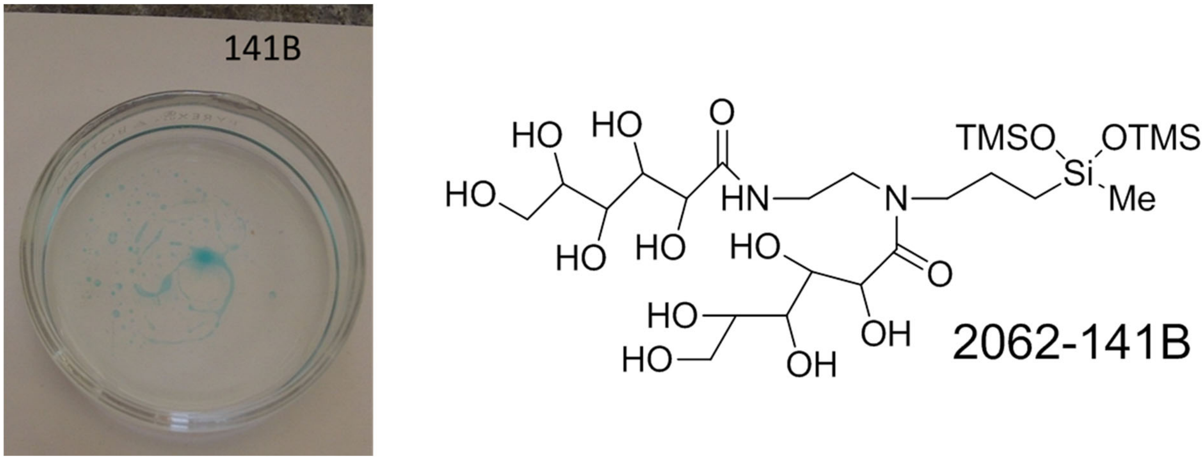


Figure 6 Test of hydrolysis resistance of two new siloxane surfactants.

Surface tension measurements showed that the new siloxane surfactants had critical micelle concentrations around 25 mN/m or less which was consistent with hydrocarbon surfactants. Certain derivative of the new siloxane surfactants displayed spreading behavior when their aqueous solutions were deposited on the surface of a pool of cyclohexane, Figure 7.



2062-141B

Figure 7 Spreading behaviour of one of the new siloxane surfactants 2026–141B on cyclohexanes.

One of the new hydrolysis-resistant siloxane surfactants was tested for extinguishment of a 20 square inch pool fire using F24 jet fuel. A compressed air foam system (CAFS) was assembled for delivery of the surfactant mixture to the pool fire, Figure 8. The applications rate of foam to the small pool fire was carefully controlled with good consistency to obtain reproducible results.

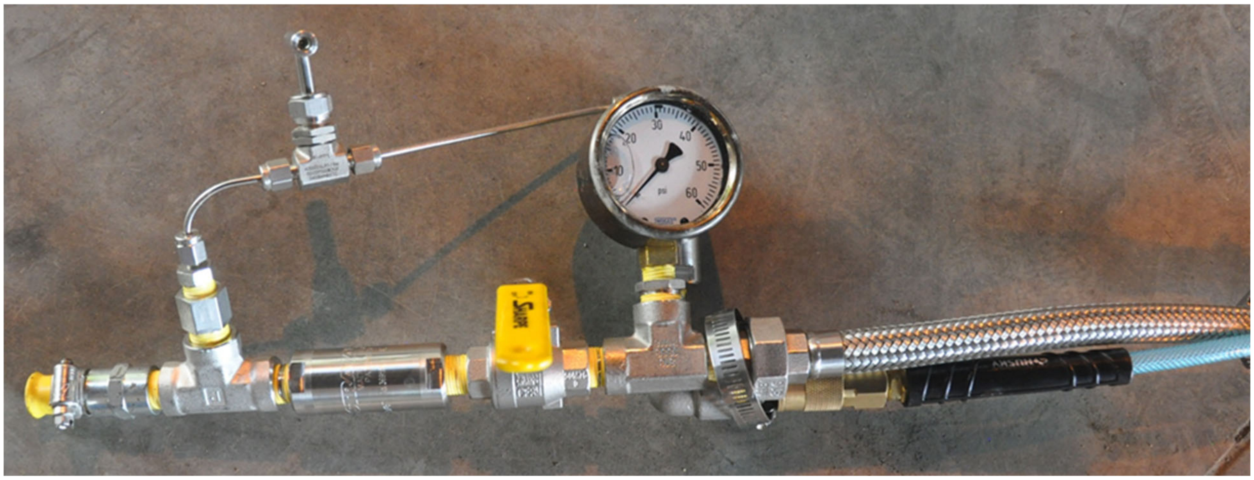


Figure 8 The CAFS adapter for delivery of surfactant solutions to the hydrocarbon pool fires.

The surfactant mixture was composed of one of the new hydrolysis-resistant siloxane surfactants 2062–145, a commercial alkylpolyglucoside (Glucopon 225DK) and diethyleneglycol monobutyl ether in water, Figure 9. The ratio of ingredients in the experimental surfactant mixture is shown in Table 2.

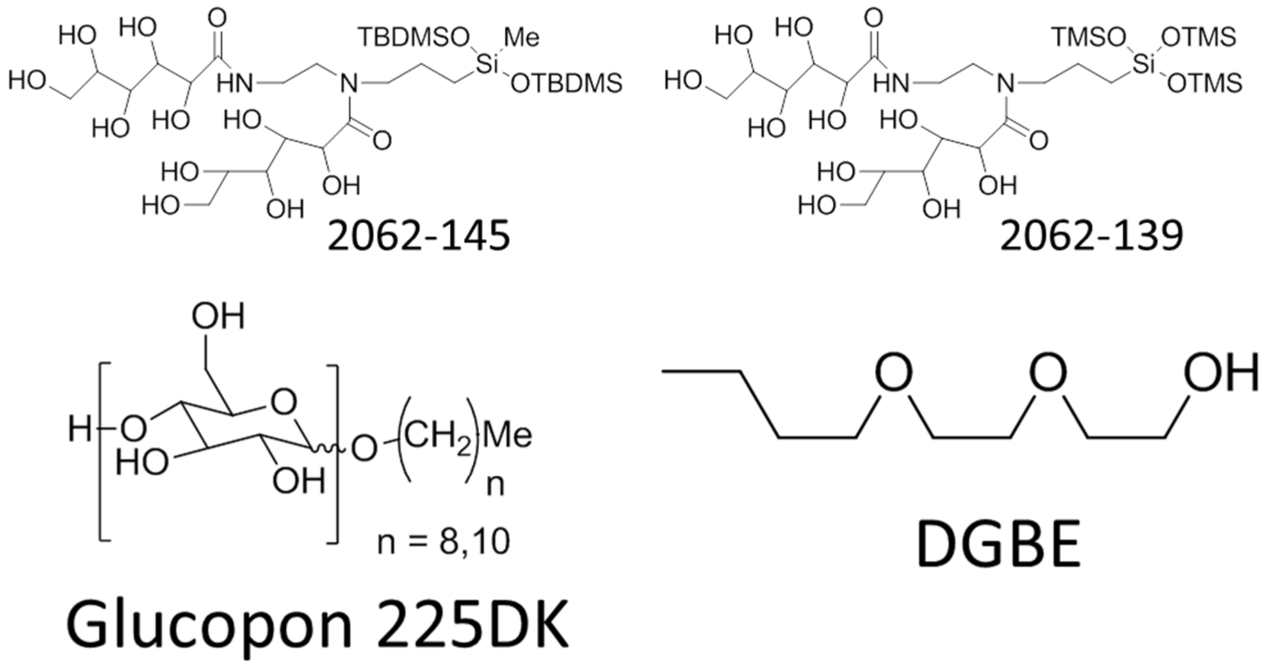


Figure 9 Fire fighting surfactant mixtures made from new siloxane surfactants, a hydrocarbon surfactant (225DK) and diethylene glycol monobutyl ether (DGBE) in water.

Table 2 Composition of experimental surfactant solutions used in pool fire testing.

Component	Quantity	Ratio additive to total solution (g/Kg)
DGBE	41.4 mL	5
Glucopon 225DK	24 grams	3
2062–145 or 2062–139	16 grams	2
Distilled H_2O	8 L	

The fire extinguishment results showed that the experimental mixture containing the hydrolysis-resistant surfactant required 61 seconds, or four times longer application time to reach 100% extinction versus military specification AFFF solution which required only 11 seconds, Table 3. It was also shown that the hydrolysis-resistant surfactant was a vital component in the experimental mixture because in its absence the mixture of glucopon 225DK and DGBE was unable to extinguish the fire, Figure 10. Remarkably, the siloxane surfactant mixture composed of 2062–139 was able to extinguish the fire in 11 seconds just like the AFFF solution, albeit at a slightly higher application rate.

Table 3 Extinguishment results from 20 square inch F24 pool fire.

Agent	Nozzle type	Agent Flow Rate (GPM)	100% out (Sec.) average of 3 runs

Mil Spec C6 AFFF 3%	FN025	0.153	11
145/225DK/DGBE	CAFS	0.161	61
225DK/DGBE	CAFS	0.161	NE[a]
139/225DK/DGBE	CAFS	0.161	11

[a] NE = no extinguishment; only two runs were made

Figure 10 Photograph during extinguishment test with the 2062–145/225DK/DGBE mixture showing the CAFS nozzle in action to put out the 20 square inch F24 pool fire.

Implication for Future Research and Benefits: Unfortunately there as not enough time to fire test all of the many siloxane surfactants made during the project. Certainly additional funding would allow for a complete extinguishment data set for the all of the reported compounds. Although preliminary data indicate that siloxane surfactants 2062–145 and 2062–139 are useful in hydrocarbon pool fire extinguishment on small scale. The siloxane surfactant 2062–139 should be synthesized at large scale and studied further urgently. It would be important to obtain data with these new surfactants on the military specification 28 square foot pan fire. An analytical studies of the hydrolysis of the tert-butyldimethylsilyl capped siloxane surfactants would be an important follow on study. There are many other siloxane surfactants with alternate structures which could be derivatized with tert-butyldimethylsilyl groups such as PEO-siloxanes and many others. Considering all the careful experiments and expensive instruments that are necessary for collecting tensiometry data, maybe a simple empirical test of a large number of a variety of surfactants agents pool fires by an automated system (e.g. robots) might be a useful method to identify new lead surfactants. There are so many more surfactants available today as opposed to the early days (1960's) of foam fire-fighting research that a cheap and fast screen might uncover surfactant phenomenon that one could not predict beforehand.

Objective

The objective of this limited-scope research project was to explore an innovative approach in using hydrolysis-resistant siloxane surfactants as replacements for perfluoroalkyl surfactants found in current aqueous film forming foam (AFFF) concentrates used by Department of Defense (DoD) for pool fire suppression. Foams containing the new surfactants will be formulated to extinguish small-scale, unleaded gasoline pool fire in 45 seconds or less as dictated by MIL-F-24385F. In addition, the hydrolysis-resistant siloxane surfactants may have low acute toxicity to fish and be biodegradable according to measurements of chemical oxygen demand and biological oxygen demand of microorganisms.

Background

The triservices of the DoD use enormous quantities of highly flammable substances, particularly high vapor pressure hydrocarbon liquids (such as gasoline, diesel and jet fuel) which pose serious risks of fire. Even though personnel have excellent training with appropriate procedures and safeguards in place to minimize the risks of fire from these substances, fires can and do happen. Extinguishing such fires as fast as possible must be accomplished in order to minimize damage to infrastructure, vehicles and equipment as well as keep personnel safe from harm on ships or airfields. Fire-fighting foams (F^3) were developed to combat hydrocarbon liquid pool fires as early as 1902 and these are referred to as Class B foams. F^3 are based on surfactants (surface active agents) that can be added to water, typically at the nozzle of a hose by a mixing head inlet, which create a thick foam spray, Figure 11. The F^3 is sprayed onto the pool fire, similar to a wide blanket, and in this way the fire is covered over with a stable mass of small air-filled bubbles.

Figure 11 Navy fire crew extinguishing hydrocarbon pool fire at a test facility with aqueous film forming foam (AFFF).

The burning fuel is thus starved from atmospheric oxygen and is extinguished. Because the aqueous foam is composed mostly of air, it is light and able to rest on top of the hydrocarbon, for example gasoline, whose density is typically less than water (e.g. octane: d = 0.7 g / mL) but also has a very low surface tension of 20.7 mN/m, Table 4. Gasoline is a much harder fuel to form a film on than diesel on account of its lower surface tension.

Table 4 Surface tensions of various DoD hydrocarbon fuels.

FUEL	Surface tension mN/m (24 C)
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Not all surfactants work well as F^3 and many types have been tried.[1] The best surfactants for F^3 are the perfluorooctanesulfonate (PFOS), Figure 13, and perfluorooctanecarboxylate (PFOA), and related perfluoroalkyl brethren, which were discovered and developed by the US Navy, Figure 13.

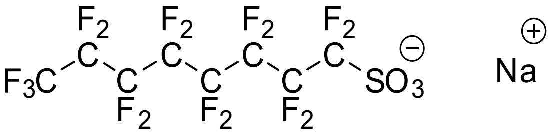


Figure 12 Chemical structure of sodium perfluorooctanesulfonate (PFOS), a typical ingredient that is used in AFFF concentrates that is highly effective at putting out liquid hydrocarbon fires.

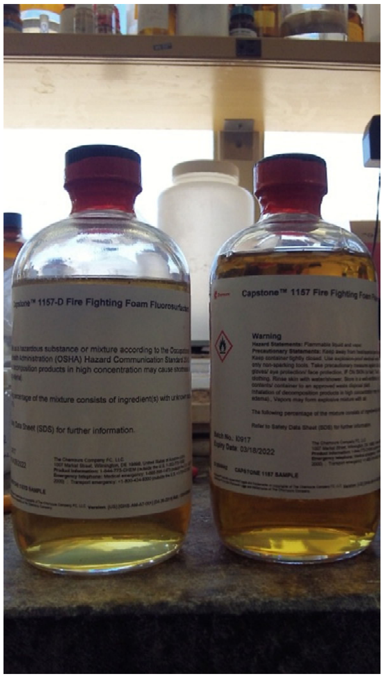


Figure 13 Samples of Capstone 1157 and 1157D courtesy of Chemours, the manufacturer of AFFF, these are the primary fluorosurfactants without additives used in many mil-spec AFFF formulations.

These perfluoroalkyl surfactants maintain good quality foams and also have the unique property of being both hydrophobic *and* oleophobic. This means that the perfluoroalkyl surfactants are resistance to dissolve in both water and non-polar liquids such as the hydrocarbon fuels, Figure 14.[2]

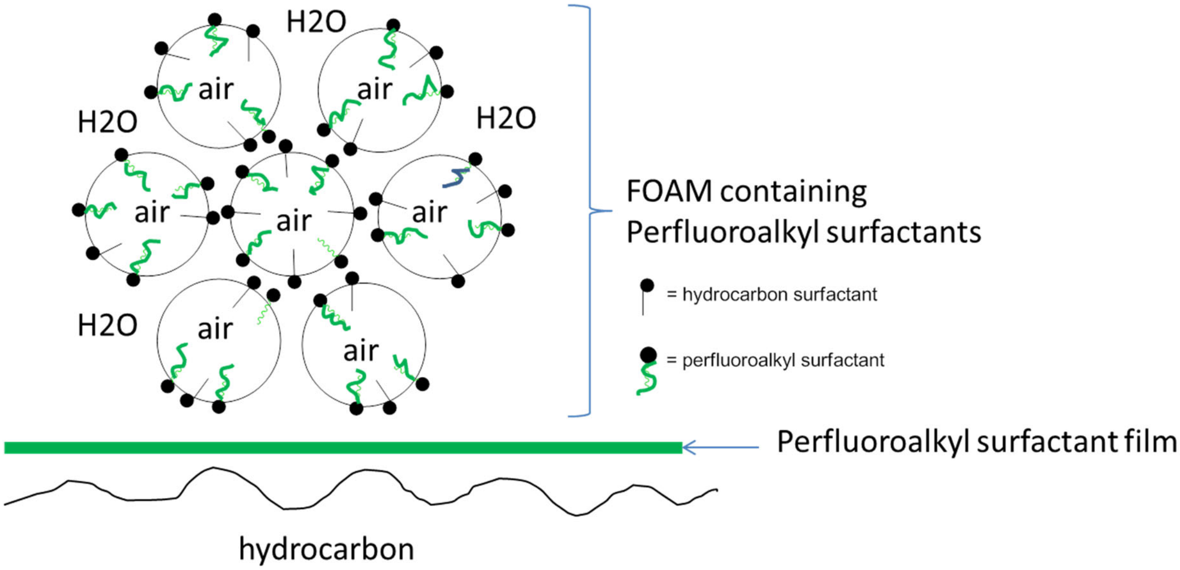


Figure 14 Perfluoroalkylsurfactant foam on surface of fuel.

The recent studies by Hinnant *et al.* on the properties of perfluoroalkylsulfonates are important to consider.[3] These authors hypothesize that a barrier to the vapor of the hydrocarbon pool is made because the perfluoroalkyl surfactant at the lamella interface is strongly oleophobic. These authors also demonstrated that foams made from oleophobic perfluoroalkyl surfactants have longer lifetimes than those made from hydrocarbon surfactants when placed on the surface hydrocarbon solvents.[4] What this means then is that the perfluoroalkyl surfactant F^3 when sprayed onto a burning pool fire of gasoline will not be broken down quickly when coming in contact with the flammable liquid or its vapor headspace. As the foam does break down, a film of the hydrocarbon insoluble perfluoroalkyl surfactant is left on top of the flammable liquid, covering it up and starving it of more oxygen preventing further combustion.[5] This is the reason they are called aqueous film forming foams (AFFF). Table 5 below shows that AFFF concentrates are a mixture of ingredients where the perfluoroalkyl surfactant, in this case Chemguard FS157, is just a minor (5.8%) but critical component. The other ingredients, such as non-ionic surfactants (APG = alkylpolyglycosides), help to maintain a robust foam along with other additives and solvents.

Table 5 Typical ingredients of an AFFF concentrate.

Ingredient	**Purpose**	**Percentage**
water	solvent	60.0
Corrosion inhibitor	Corrosion inhibitor	0.1
Chemguard FS-157 (fluorosurfactant)	Film former	5.8
APG	foamer	17.5
Buffer	buffer	0.1
Diethylene glycol monobutyl ether	solvent	8.7
Ethylene glycol	solvent	5.8
Urea	stabilizer	2.0

Organofluorine compounds are extremely rare in nature, in fact only a handful of fluorine containing natural products (e.g. fluoroacetic acid, fluoroacetone and fluorocitrate) have ever been isolated and reported.[6] Thus, anthropogenic perfluoroalkyl substances released into the environment are highly resistant to biodegradation as microorganism either cannot take up these substances and/or their enzymes will not recognize these substances and break them down. This has caused perfluoroalkyl substances to have accumulated in the biosphere since the 1960's to such an extent that there may be no place on the Earth's surface not contaminated (ppm level) with these materials. In fact, these issues prompted 3M Company to begin phase out manufacture of perfluoroalkyl surfactants in 2003. Although perfluoroalkyl surfactants are excellent for F^3, it may be possible to identify new F^3 made from surfactants that pose less of a burden on the environment but do the same job.

Looking at the composition of the Earth's crust, one sees that silicon is second only to oxygen in natural abundance. It was conceived that if one could instantaneously create a flexible blanket of lightweight foam made of glass and air, that would make a perfect suffocating material to throw on a gasoline pool fire which was both impervious to the hydrocarbon liquid as well as thermally stable to the heat from its flame. A step in this direction was recently reported by Vinogradov *et al.*[7] who made an F^3 composed of water soluble silicates. The technology is interesting, while a water solution of soluble sodium silicate and sodium dodecylsulfate was sprayed, some acetic acid is dosed into the solution at the nozzle, Figure 15. The change in pH neutralizes the sodium silicate causing precipitation of insoluble silicate (SiO_2) while in the air. The net result was to literally cover the burning area with a thick layer of amorphous silica gel. These researchers did not attempt to put out hydrocarbon pool fires with their technology. Silica gel is dense and heavy and so would not likely form a surface layer on a hydrocarbon pool. While their technology may be useful in certain situations such as forest fires, the cleanup of the resulting silica gel mess on airbases and ships could be difficult and even dangerous. The silica gel will not wash away with water and will have to be manually dislodged with tools. In addition, the silica gel can form dust which is a respiratory hazard (e.g. silicosis) so personnel would require protective breathing gear. The benefit of their technology is that the silica gel F^3 is non-toxic and highly biodegradable since it is only composed of a common hydrocarbon surfactant and silica gel which is essentially inert.

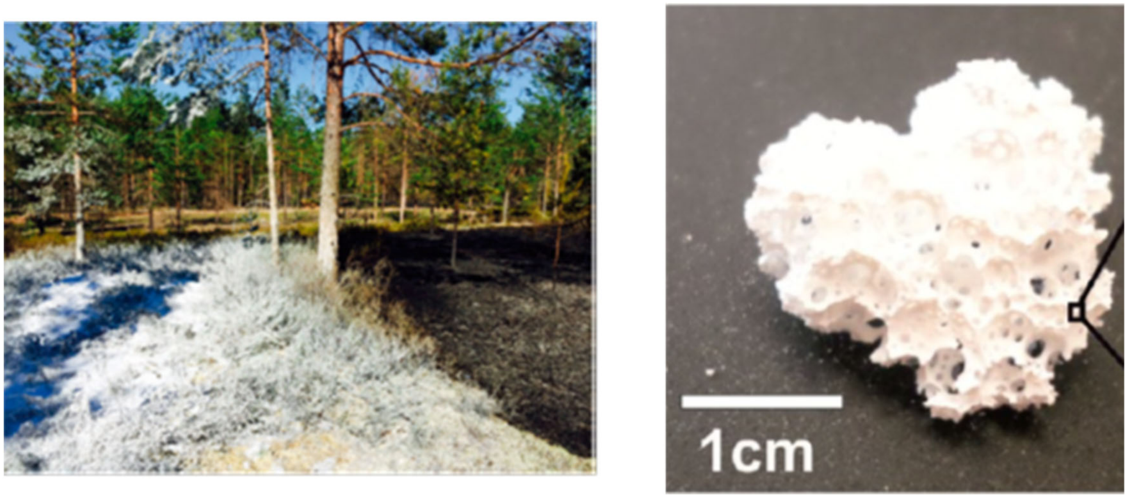
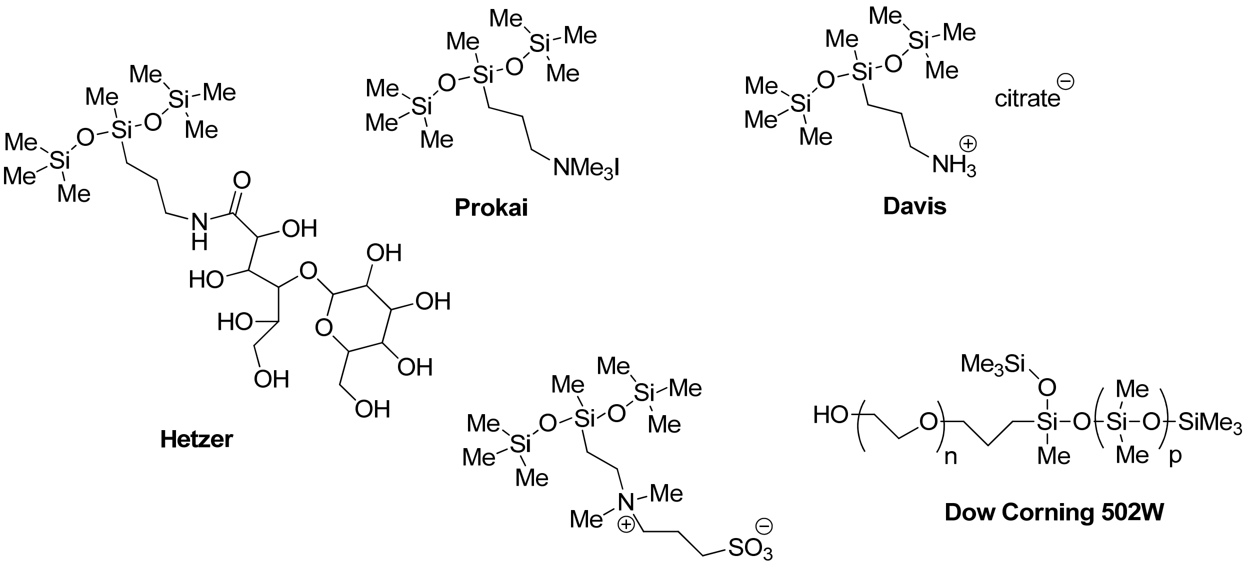


Figure 15 Vinogradov et al. demonstrated fire fighting with a foam that created massive quantities of a silica gel to cover the fire.

A previous installment of this SEED project WP18–1519 was carried out in FY18 (March 2018–March 2019) and was entitled "Surfactants with Organosilicate Nanostructures for Use as Fire-Fighting Foams (F^3)". In this earlier project, an attempt was made to synthesize polyhedral oligomeric silsesquioxanes (POSS) with surfactant properties which could be useful as additives in pool fire fighting foams. There is a detailed report of this earlier project on the SERDP website so a review is not necessary here. In brief, a derivative made from POSS was a rather poor surfactant based on surface tension analyses and the synthesis was also complex. So it was decided to pivot away from POSS derivatives and focus on siloxane surfactants because several groups have had some success incorporating them in foams for pool fire extinction.

There have been some interesting results of siloxane surfactants as replacements for fluorine-containing surfactants in fire fighting foams and some of their structures are shown in Figure 16. The trialkylammoniumpropylmethyldisiloxane (**Prokai**) was patented by Union Carbide and when combined with a protein foam was described as forming a foam blanket on gasoline.[8] The citrate salt of 3-aminopropylmethyldisiloxane (**Davis**) was shown to have very low surface tension on cyclohexane, however when used on its own in a heptane pool fire extinction test failed to put out the fire.[9] The lactobionamidopropyldisiloxane (**Hetzer**) when combined with the commercial alkylpolyglucoside Glucopon 215 was able to extinguish a 4.6 m^2 F-34 pool fire (e.g. diesel fuel) in ~ 60 seconds while AFFF put out a similar fire in about 45 seconds.[10] Scientists at the Naval Research Laboratory found that a mixture of alkylpolyglucoside Glucopon 225DK and **Dow Corning 502W** surfactant was able to extinguish heptane pool fires almost as quickly as control AFFF.[11]



Prokai

Davis

Hetzer

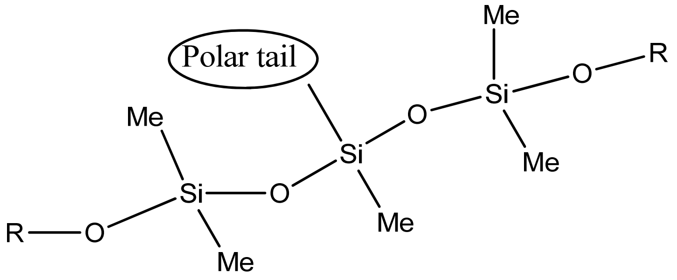
SA Snow et al

Dow Corning 502W

Figure 16 Siloxane-containing surfactants as possible fluorine-free, fire-fighting foams.

Closer examination of these siloxane-based surfactants shows that their hydrophobic siloxane head groups all share a common structural feature, the siloxane is capped or terminated by trimethyl silyl groups. Siloxanes are known to suffer from hydrolysis which can be accelerated by non-neutral pH. SA Snow *et al.* showed that sulfobetaine-siloxane surfactants would slowly hydrolyze yielding bis(trimethylsilyl)ether (TMS–O–TMS) in water at room temperature.[12] In addition, it is likely that an increase in temperature, such as exposure to a burning hydrocarbon pool fire, might further accelerate hydolysis of trimethylsilyl capped siloxanes. Any such hydrolysis of the siloxane surfactant would cause the loss of potency of the surfactant, increased surface tension and causing premature decomposition of the foam and decrease extinction time or prevent extinction of a hydrocarbon pool fire altogether. Therefore, siloxane surfactants with structures that would make the siloxane portion less susceptible to hydrolysis could lead to more stable and effective fire fighting foams.

The hydrophobic siloxane head group could be made more water resistant by adding more hydrocarbon substituents. For example, a 2011 patent taught the creation of hydrolysis-resistant siloxane surfactants from trisiloxanes which were capped with *tert*-butyldimethylsilyl (**1**) or isopropyldimethylsilyl (**2**) groups instead of trimethylsilyl (**3**), Figure 17.[13]



1 R = Me
2 R = *tert*-butyl
3 R = isopropyl

Figure 17 Hydrophobic siloxane head group structures.

The 2011 patent described that the hydrolysis resistant siloxane surfactants remained unchanged after 5 weeks incubation at any pH between 4–11, while the trimethyl-capped siloxane surfactant underwent significant hydrolysis and loss of spreading ability at pH above and below 7 in the same time period. Presumably the increase in bulky aliphatic groups on the trisiloxane presents steric hindrance to ready attack on the silicon atoms by water.

Materials and Methods

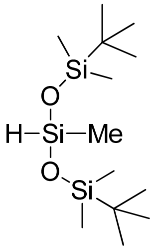
Chemicals and Reagents

3-Chloropropylmethyldichlorosilane, 3-aminopropyltris(trimethylsiloxy)silane, 3-aminopropylmethylbis(trimethylsiloxy)silane, 3-chloropropyltrichlorosilane, methyldichlorosilane, tris(trimethylsiloxy)silane and trichlorosilane were purchased from Gelest, Morrisville PA. Glucopon® 225DK was a gift from the Naval Research Laboratory. Karstedt's catalyst, triethylchlorosilane, triethylenetetramine, diethylenetriamine, ethylene diamine, allyl bromide, dimethylaminoethanol, dimethylamine, 1,3-propanesultone, 4-dimethylaminopyridine, pyridine, *tert*-butyldimethylchlorosilane, γ–gluconic acid lactone, anhydrous cyclohexane and all other reagents were purchased from Sigma-Aldrich, Milwaukee WI and used as received. The FD&C Blue #1 powder was a gift from Hilton Davis, LLC.

Chemical Characterization

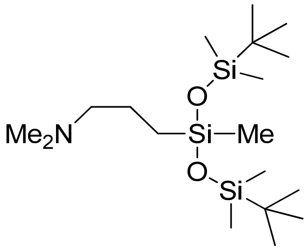
Thin-layer chromatography was performed on aluminum foil backed, silica gel 60 plates containing uv-indicator and visualized by ultraviolet lamp (λ_{254}) as well as dipping in an ethanol solution of 10 wt% phosphomolybdic acid ($H_3PMo_{12}O_{40}$) followed by heating. NMR experiments were carried out on a JEOL ECZ 400 MHz instrument (^1H = 400 MHz; ^{13}C = 100 MHz; ^{29}Si = 79 MHz) and the free-induction decay data were worked up using ACD/NMR Processor (Advanced Chemistry Development, Inc.). The silicon-29 NMR pulse sequence incorporated population transfer (proton decoupled distortionless enhancement by polarization transfer (DEPT)) to enhance the signal to noise ratio.[14] The silicon-29 NMR spectra were referenced to tetramethylsilane (0 ppm) by the NMR tube interchange technique.[15] Certain synthesized products were sent to Atlantic Microlab, Inc. (Norcross, GA) for combustion analyses.

Synthesis of Hydrolysis-resistant Siloxane Surfactants



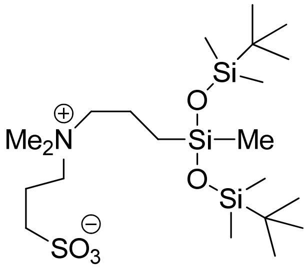
Methylbis(*tert*-butyldimethylsiloxy)silane [2040–103]

A round-bottomed flask (50 mL) equipped with magnetic stirring bar and reflux condenser was filled with *tert*-butyldimethylsilyl chloride (10 g, 66 mmol, 2 equiv), dichloromethylsilane (3.82 g, 3.47 mL, 33 mmol) and diethyl ether (25 mL). The mixture was stirred at rt while H_2O (5 g, 270 mmol) was added dropwise through the condenser. Afterwards the mixture was gently refluxed for 24 h. The reaction mixture was cooled to rt and partitioned between H_2O and hexanes. The organic layer was washed in sequence with H_2O followed by brine. The organic layer was separated and dried over anhydrous $MgSO_4$ and then the solvent was rotary evaporated (60 torr, 45 °C bath). The crude product was fractionally distilled at reduced pressure (10 torr) to obtain the pure product as a colorless viscous liquid (bp 100–120 °C). The mass of product was 5.51 g (86%). ^{1}H NMR ($CDCl_3$; 400 MHz, δ, ppm): 4.67 (m, 1H), 0.87 (s, 18H), 0.1 (s, 3H), 0.05 (s, 12H); ^{13}C NMR ($CDCl_3$; 100 MHz, δ, ppm): 25.69, 18.14, 1.67, – 3.11; ^{29}Si NMR ($CDCl_3$; 79 MHz, δ, ppm): 12.44, – 36.68. Elemental analysis calculated for $C_{18}H_{46}O_3Si_4$: C, 51.12; H, 10.96. Found: C, 51.33; H, 11.20.



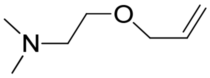
3-(N,N-Dimethylamino)propylmethylbis(*tert*-butyldimethylsiloxy)silane [2062–168]

A round-bottomed flask (25 mL) equipped with magnetic stirring bar, reflux condenser and nitrogen-bubbler was filled with methylbis(*t*-butyldimethylsiloxy)silane (3.46 g, 10 mmol), N,N-dimethylallylamine (850 mg, 10 mmol, 1 equiv) and degassed toluene (10 mL). In one portion, Karstedt's catalyst (200 μL) was added to the reaction mixture which was then refluxed for 24 h. The reaction mixture was dark in color after the heating procedure. The mixture was cooled to rt and the solvent and volatiles were removed by rotary evaporation. The crude product was purified by reduced pressure fractional distillation (10 torr) to obtain the product as a colorless oil (bp 130–160 °C). The mass of product was 3.28 g (76%). ^{1}H NMR (CDCl$_3$; 400 MHz, δ, ppm): 2.25-2.17 (m, 8H), 1.54–1.42 (m, 2H), 0.84 (s, 18H), 0.46–0.38 (m, 2H), 0.03 to – 0.02 (m, 15H); ^{13}C NMR (CDCl$_3$; 100 MHz, δ, ppm): 63.37, 45.53, 25.75, 21.35, 18.14, 15.35, 0.17, – 2.85; ^{29}Si NMR (CDCl$_3$; 79 MHz, δ, ppm): 10.23, – 22.36.



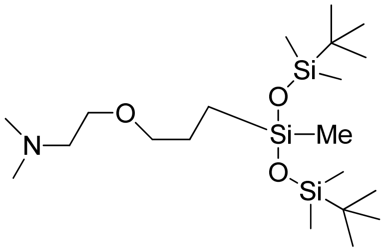
3-((3-(1,5-di-*tert*-butyl-1,1,3,5,5-pentamethyltrisiloxan-3-yl)propyl)dimethylammonio)propane-1-sulfonate [2062–71B]

A round-bottomed flask (25 mL) equipped with magnetic stirring bar and reflux condenser was filled with amine (3.28 g, 7.6 mmol, 1 equiv), 1,3-propanesultone (930 mg, 7.6 mmol) and anhydrous toluene (10 mL). The mixture was heated to 100 °C for 1 h. During this time a semi-solid precipitated from the reaction mixture. Afterwards the mixture was cooled to rt and diluted with hexanes (10 mL). The white solids were collected by suction filtration on a medium porosity glass fritted filter funnel. The mass of product was 2.99 g (76%). Crystals suitable for X-ray analysis were obtained by recrystallization of the product from MeCN. ^{1}H NMR (CDCl$_3$; 400 MHz, δ, ppm): 3.66 (m, 2H), 3.20 (m, 2H), 3.13 (s, 6H), 2.85 (t, J = 6.86 Hz, 2H), 2.2 (m, 2H), 1.66 (m, 2H), 0.81 (s, 18H), 0.42 (m, 2H), 0.03 (s, 3H), – 0.01 (s, 12H); ^{13}C NMR (CDCl$_3$; 100 MHz, δ, ppm): 66.80, 64.05, 50.65, 47.75, 25.70, 19.59, 18.09, 16.98, 14.03, – 0.19, – 2.80; ^{29}Si NMR (CDCl$_3$; 79 MHz, δ, ppm): 11.99, – 24.46. Elemental analysis calculated for $C_{21}H_{51}NO_5SSi_3$: C, 49.08; H, 10.00; N, 2.73; S, 6.24. Found: C, 48.98; H, 9.95; N, 2.77; S, 6.29.



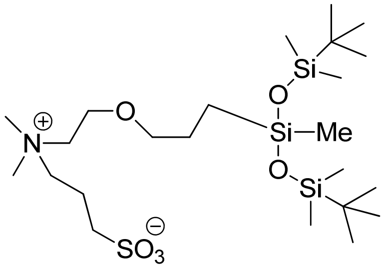
2-(allyloxy)-N,N-dimethylethanamine [2062–61]

A two-necked, round-bottomed flask (1 L) equipped with magnetic stirring bar was filled with N,N-dimethylaminoethanol (44.35 g, 50 mL, 0.5 mol) and anhydrous THF (500 mL). One neck of the flask was protected by a nitrogen bubbler while potassium *tert*-butoxide (67.2 g, 0.6 mol, 1.2 equiv) was added through the second neck in about 15 min. The neck was stoppered and the mixture stirred at rt until all the solids dissolved. The bubbler was removed and an addition funnel was equipped and filled with allyl bromide (62.55 g, 45 mL, 0.51 mol, 1.02 equiv). The bubbler was placed at the top of the addition funnel. The alkyl halide was added dropwise to the reaction mixture over a period of 1 h. Once the addition was complete, the addition funnel was replaced with a condenser and the mixture was heated at a gentle reflux for 18 h. The mixture was cooled to rt and partitioned between diethyl ether (200 mL) and H_2O (200 mL). The organic phase was separated and then washed with H_2O (100 mL) followed by brine (100 mL). The organic layer was dried over anhydrous $MgSO_4$ and then the solvent was rotary evaporated (60 torr, rt bath). The crude product was distilled at atmospheric pressure collecting the product (bp 90–135 °C) and discarding the early distillate which contained by-product *tert*-butanol. The mass of product was 42.7 g (66%). ^{1}H NMR ($CDCl_3$; 400 MHz, δ, ppm): 5.87–5.75 (m, 1H), 5.2–5.03 (m, 2H), 3.89 (dt, J = 5.72 and 1.37 Hz, 2H), 3.4 (t, J = 5.95 Hz, 2H), 2.40 (t, J = 5.72 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR ($CDCl_3$; 100 MHz, δ, ppm): 134.89, 117.04, 72.15, 68.05, 58.95, 45.90.



2-(3-(1,5-di-*tert*-butyl-1,1,3,5,5-pentamethyltrisiloxan-3-yl)propoxy)-N,N-dimethylethanamine [2062–108]

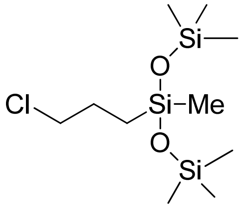
A round-bottomed flask (25 mL) equipped with magnetic stirring bar, reflux condenser and nitrogen-bubbler was filled with methylbis(t-butyldimethylsiloxy)silane (5.51 g, 15.9 mmol), 2-(allyloxy)-N,N-dimethylethanamine (2.05 g, 15.9 mmol, 1 equiv) and degassed toluene (10 mL). In one portion, Karstedt's catalyst (300 μL) was added to the reaction mixture which was then refluxed for 24 h. The reaction mixture was dark in color after the heating procedure. The mixture was cooled to rt and the solvent and volatiles were removed by rotary evaporation. The crude product was purified by reduced pressure fractional distillation (0.1 torr) to obtain the product as a thick, colorless oil (bp 80–110 °C). The mass of product was 3.49 g (46%). ^{1}H NMR ($CDCl_3$; 400 MHz, δ, ppm): 3.49 (t, J = 5.95 Hz, 2H), 3.37 (t, J = 7.09 Hz, 2H), 2.48 (t, J = 5.95 Hz, 2H), 2.25 (s, 6H), 1.59 (m, 2H), 0.84 (s, 18H), 0.43 (m, 2H), 0.02 to – 0.01 (m, 15H).



3-((2-(3-(1,5-di-*tert*-butyl-1,1,3,5,5-pentamethyltrisiloxan-3-yl)propoxy)ethyl)dimethylammonio)propane-1-sulfonate [2062–111B]

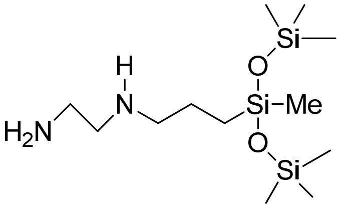
A round-bottomed flask equipped with magnetic stirring bar and reflux condenser was filled with amine (4.71 g, 9.9 mmol, 1.1 equiv), 1,3-propanesultone (1.1 g, 9 mmol) and anhydrous toluene (10 mL). The mixture was heated to 60 °C for 4 h. Afterwards the mixture was allowed to stir overnight at rt. The next day, the reaction mixture was thick with a precipitate. The reaction mixture was diluted with hexanes (10 mL) and pelleted by centrifugation. The supernantant was decanted and the white solid was kept under dynamic vacuum (12 h) to remove traces of solvent.

The mass of product was 4.55 g (77%). ^{1}H NMR (CDCl$_3$; 400 MHz, δ, ppm): 3.83–3.71 (m, 4H), 3.63 (m, 2H), 3.34 (t, *J* = 6.86 Hz, 2H), 3.2 (s, 6H), 2.83 (t, *J* = 6.86 Hz, 2H), 2.2 (m, 2H), 1.52 (m, 2H), 0.81 (s, 18H), 0.37 (m, 2H), – 0.02 (s, 15H); ^{13}C NMR (CDCl$_3$; 100 MHz, δ, ppm): 74.42, 65.30, 64.65, 63.49, 51.54, 47.89, 25.73, 23.34, 19.60, 18.10, 13.85, – 0.20, – 2.84; ^{29}Si NMR (CDCl$_3$; 79 MHz, δ, ppm): 10.60, – 22.88. Elemental analysis calculated for $C_{23}H_{55}NO_6SSi_3$: C, 49.51; H, 9.93; N, 2.51. Found: C, 49.24; H, 10.05; N, 2.54.



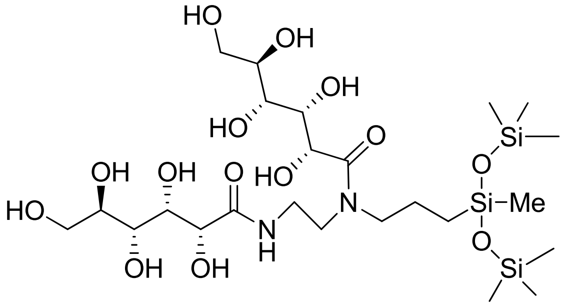
3-(3-chloropropyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane [2062–133A]

A round-bottomed flask (500 mL) equipped with magnetic stirring bar was filled with 3-chloropropylmethyldichlorosilane (38.2 g, 31 mL, 199 mmol) and chlorotrimethylsilane (86.45 g, 100.5 mL, 796 mmol, 4 equiv). A reflux condenser was equipped to the flask and on top of the condenser was fitted an addition funnel. The funnel was filled with isopropanol (71.69 g, 1.19 mol, 6 equiv) which was added in a gentle stream over 20 min. Next, the addition funnel was filled with water (21.42 g, 1.19 mol, 6 equiv) and this was added dropwise over 30 min. Once everything was together, the mixture was vigorously stirred at room temperature for 18 h. The next day, the mixture was partitioned between Et$_2$O and water. The organic layer was separated and washed with water, then brine and finally dried over anhydrous MgSO$_4$. The solvent was rotary evaporated and the residue was distilled at reduced pressure (bp 40–105 °C, 10 torr) to give the product as a colorless oil (24 g, 35%).



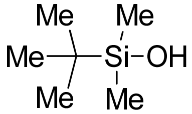
N^1-(3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propyl)ethane-1,2-diamine [2062–141]

A heavy-walled, screw-top, glass pressure vessel was equipped with a magnetic stirring bar and filled with 3-(3-chloropropyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (12 g, 36 mmol), 1,2-ethylenediamine (10.68 g, 178 mmol, 5 equiv) and isopropanol (10 g). The pressure vessel was sealed and the mixture was heated and stirred in a 130 °C oil bath. After 2 h, the mixture was cooled to room temperature and partitioned between Et$_2$O and water. The organic layer was separated and washed with water, then brine and finally dried over anhydrous MgSO$_4$. The solvent was rotary evaporated and the residue was distilled at reduced pressure (bp 105-112 °C, 0.1 torr) to give the product as a colorless oil (7.73 g, 59%).



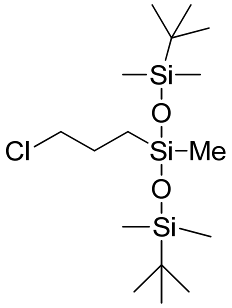
N^1-(3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propyl)ethane-1,2-diamine-1,2-bis-D-gluconamide [2062–141B]

A round-bottomed flask (25 mL) equipped with magnetic stirring bar was charged with N^1-(3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propyl)ethane-1,2-diamine (2.68 g, 7.4 mmol), δ-gluconolactone (2.64, 14.8 mmol) and MeOH (10 mL). The mixture was refluxed under a nitrogen bubbler for 1 h. Afterwards, the solvent was rotary evaporated leaving a residue. The residue was stored high vacuum to remove the remaining traces of solvent. The final product was a brittle, glass-like foam (5 g, 99%). Elemental analysis calculated for $C_{25}H_{54}N_2O_{14}Si_3$: C, 42.46; H, 8.02; N, 4.13. Found: C, 42.39; H, 8.17; N, 4.18.



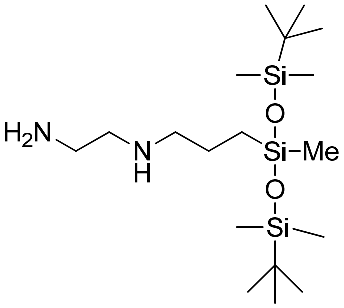
***Tert*-butyldimethylsilanol [2062–160]**

A round-bottomed flask (3 L) equipped with magnetic stirring bar was filled with *tert*-butyldimethylsilyl chloride (100 g, 663 mmol) and THF (1 L). The mixture was cooled in an ice bath and vigorously stirred while a solution of 28% ammonium hydroxide (388.39 mL, 3.1 mol) in H_2O (693.45 mL) was added dropwise over 2 h. Afterwards, the cooling bath was removed and the mixture was stirred at room temperature overnight. The next day, the reaction mixture was extracted with Et_2O (1 L X 3). The organic layers were separated and collected and washed with brine (1 L). The organic layer was separated and dried over anhydrous magnesium sulfate (25 g) and then filtered and rotary evaporated (10 torr, bath = 50 °C) to remove the volatile solvents. The resulting oil required no further purification (80 g, 90%).



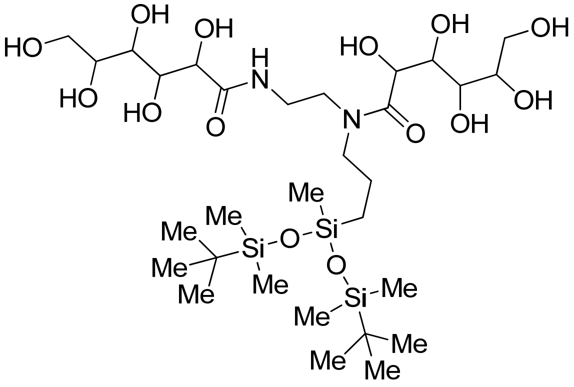
3-chloropropylmethylbis(*tert*-butyldimethylsilyl)silane [2062–137]

A round-bottomed flask (2 L) equipped with magnetic stirring bar was filled with *tert*-butyldimethylsilanol (122.98 g, 929 mmol, 2.18 equiv) and anhydrous THF (500 mL). The mixture was protected with an anhydrous nitrogen bubbler and then cooled in an ice bath. Once cold, freshly pulverized potassium *tert*-butoxide (104.05 g, 929 mmol, 2.18 equiv) was added into the reaction mixture in one portion. The solids were allowed to dissolve almost completely in 30 min. Next, an addition funnel was equipped and filled with 3-chloropropylmethyldichlorosilane (81.79 g, 66.49 mL, 426 mmol, 1 equiv). While maintaining the reaction flask in an ice bath, the dichlorosilyl compound was added dropwise into the reaction mixture. Copious white solids (KCl) precipitated during the addition. Once complete, the cooling bath was removed and the mixture was stirred at room temperature. The reaction mixture was partitioned between Et_2O (2 L) and H_2O (2 L). The organic layer was separated and washed with H_2O (1 L) and then brine (1 L). The organic layer was separated and dried over anhydrous Magnesium sulfate (25 g) and then filtered and rotary evaporated (10 torr, bath = 50 °C) to remove the volatile solvents. Afterwards, the oily residue was fractionally distilled under reduced pressure (0.1 torr) to obtain the product as a colorless oil (112.31 g, 68 %).



N-(3-(methyl-bis(*tert*-butyldimethylsiloxy)silan-3-yl)ethane-1,2-diamine [2062–138]

A BüchiGlas steel miniclave (300 mL) equipped with a magnetic stirring bar was filled with 3-chloropropylmethylbis(*tert*-butyldimethylsilyl)silane (112.32 g, 292 mmol), ethylene diamine (87.6 g, 98.43 mL, 1.46 mol, 5 equiv) and isopropanol (60 mL). The mixture was sealed and stirred in an oil bath set to 130 °C for 4 h. After this time, thin-layered chromatography showed the reaction was complete. The reaction mixture was partitioned between Et_2O (1 L) and H_2O (1 L). The organic layer was separated and washed again with H_2O (1 L) and then with brine (1 L). The organic layer was separated and rotary evaporated (10 torr, 60 °C bath) to remove solvent and volatiles. The oily residue was fractionally distilled at reduced pressure (0.1 torr) to isolate the product (bp 80–135 °C) as a thick, colorless oil (96.84 g, 81 %).

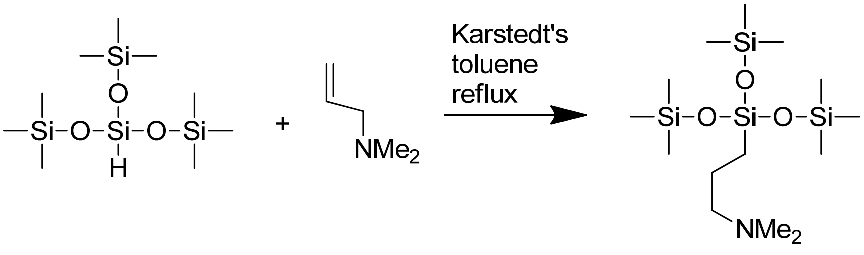


N-(3-(methyl-bis(*tert*-butyldimethylsiloxy)silan-3-yl)ethane-1,2-diamine bis(gluconamide) [2062–145]

A round-bottomed flask (1 L) equipped with magnetic stirring bar was filled with N-(3-(methyl-bis(*tert*-butyldimethylsiloxy)silan-3-yl)ethane-1,2-diamine (96.84 g, 237 mmol, 1 equiv) and anhydrous MeOH (500 mL). The mixture was agitated briefly to dissolve all of the starting material. Afterwards, δ–gluconolactone (84.4 g, 474 mmol, 2 equiv) was added in one portion to the vigorously stirred mixture. The reaction was refluxed under an anhydrous nitrogen bubbler for 2.5 h. Next, the mixture was cooled to room temperature and then rotary evaporated (60 torr, 50 °C) to remove the majority of the solvent. Then the mixture was rotary evaporated under stronger vacuum (10 torr, 50 °C) to remove most of the remaining solvent. Finally, the sample was placed under high vacuum (0.1 torr, 50 °C) to remove the last traces of solvent. The resulting orange, brittle, foamy-like product did not require further purification (181.13 g, 100%).

Results and Discussion

In support of our colleagues at NRL (SERDP WP-20 1507) it was necessary to prepare alkylaminosiloxanes (e.g. 2062–120) such as shown in Figure 18. The synthesis hinges upon the hydrosilation between a substituted silane and a substituted allylamine catalyzed by a platinum catalyst known as Karstedt's catalyst, Figure 19. The reaction was run multiple times on many occasions but could never be made to go to completion, always giving ~60% yield of product after separation of unreacted silane. Later in the project obtaining this and other substituted silane starting materials became a challenge. The commercial suppliers only offered ten to twenty-five grams lots of silanes of interest and then they ran out of material for purchase. In addition, any surfactant that is made must be prepared on a minimum of ten gram scale in order to obtain meaningful extinction testing data. Thus, the above issues made it prudent to change the synthesis strategy to reagents readily available in bulk.



2062-120

Figure 18 Hydrosilation reaction of silane and allylamine catalyzed by platinum catalyst.

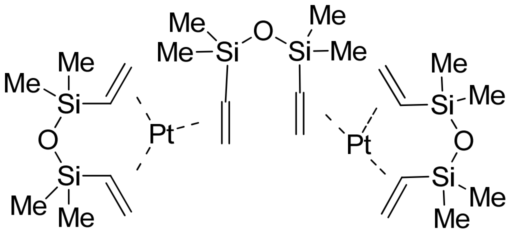


Figure 19 The Karstedt's platinum catalyst.

A literature report by Lane and Speier described how the aminosiloxane 2062-120 could be synthesized by the curious reaction shown in Figure 20.[16] In their reaction, trimethylamine is alkylated by the chloroalkylsiloxane to form a quaternary ammonium salt intermediate. Because there is a large excess of trimethylamine present in the reaction, the quaternary ammonium intermediate acts as an alkylating agent transferring a methyl group to trimethylamine and forming tetramethylammonium chloride. The report contained the experimental conditions for their reaction which they ran on nearly two molar scale and achieved an 88% yield of 2062–120. So this report provided some hope that large quantities of aminoalkylsiloxanes could be made on large scale without the difficult hydrosilation reaction.

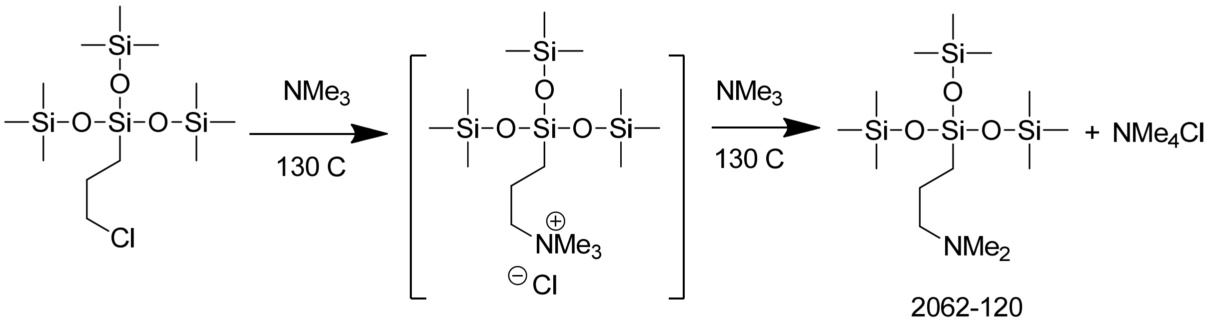


Figure 20 Dimethylamination of the chloropropyltetrasiloxane using trimethylamine found in the literature.

Large quantities of 3-chloropropyltrichlorosilane (500 grams) could be obtained from Gelest. The compound could be converted into the tetrasiloxane 2062–104 by controlled hydrolysis with chlorotrimethylsilane, Figure 21.[17] In the second step, the 3-chloropropyltris(trimethylsiloxy)silane (2062–104) was reacted with excess dimethylamine in a BüchiGlas steel autoclave at 130 °C to obtain the aminoalkyltetrasiloxane 2062–120 after removal of the by-product dimethylamine hydrochloride, Figure 22.[18] The pressure vessel was necessary since dimethylamine (bp 7 °C) is a gas at ambient conditions. Each of these two steps ran at ~80% yield with the added benefit that the reaction could be run at much larger scales. In fact, the amination reaction gave forty grams of 2062–120 the very first time it was run. In comparison, it was never possible to generate this quantity of product by the hydrosilation method. The 3-chloropropyltrichlorosilane compound is probably manufactured by hydrosilation of allyl chloride with trichlorosilane.[19] Thus, the alternative method leverages industry's hydrosilation capabilities and capacities to great advantage.

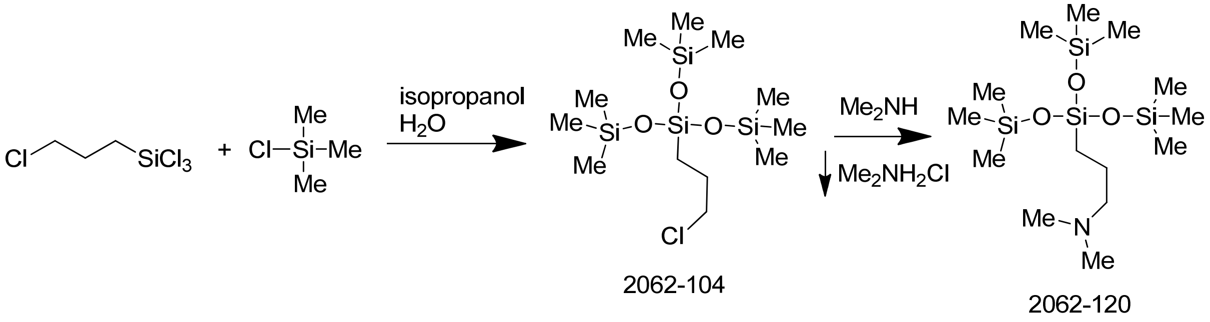


Figure 21 Two-step synthesis of the dimethylaminopropyltetrasiloxane using dimethylamine.

Figure 22 Stainless steel Buchiglas miniclave, a high pressure autoclave used in the amination reaction.

The synthesis of the trisiloxane 2062–133A from 3-chloropropylmethyldichlorosilane and trimethylsilyl chloride could be accomplished by the controlled hydrolysis method shown earlier, Figure 23. Surprisingly, the yield of 2062–133A in this case was only 35%. There was a considerable amount of by-product where only one trimethylsiloxane group (2062–133B) had been incorporated. Fortunately, these two reaction products could be separated by reduced pressure fraction distillation.

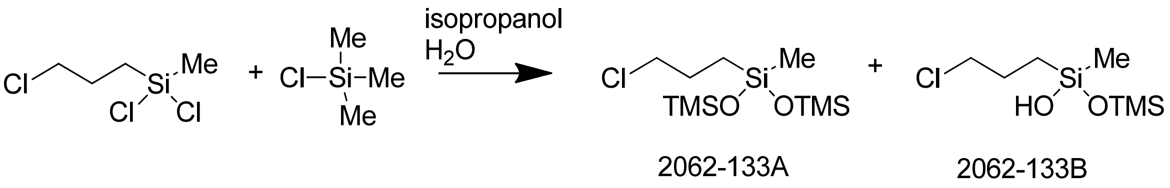


Figure 23 Controlled hydrolysis/silation with trimethylsilyl chloride in a mixture of water and isopropanol.

The first target of a hydrolysis resistant siloxane group was a tetrasiloxane with three *tert*-butyldimethylsiloxy groups, tris(*tert*-butyldimethylsiloxane)silane (2062–79). This compound was mentioned in a patent but was made by a method involving specialized reagents that were inconvenient to obtain. Instead, it was found that 2062–79 could be made very easily by the reaction of trichlorosilane with *tert*-butyldimethylsilanol in hexanes solvent with pyridine as base, Figure 24.[20] The by-product pyridine hydrochloride that had precipitated could be removed by filtration and the product 2062–79 was distilled at reduced pressure. The product was a viscous liquid which was contrary to the US patent that reported a solid.[21] Further research showed there must have been an error in translation as the earlier or original German patent did mention this compound was a liquid.[22]

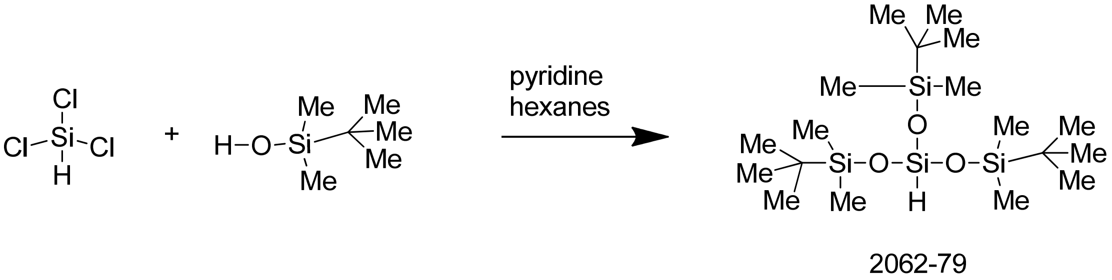


Figure 24 Relatively simple synthesis of tris(t-butyldimethylsiloxy)silane from trichlorosilane and the silanol.

Unfortunately, an attempt at the hydrosilation reaction of tris(*tert*-butyldimethylsiloxy)silane 2062–79 with N,N-dimethylallylamine failed and the only product recovered was *tert*-butyldimethylsilanol, Figure 25. As mentioned previously, the hydrosilation reaction is somewhat capricious and the hypothesis for this failed reaction was that the high degree of steric bulk made for an even poorer reaction for tris(*tert*-butyldimethylsiloxy)silane.

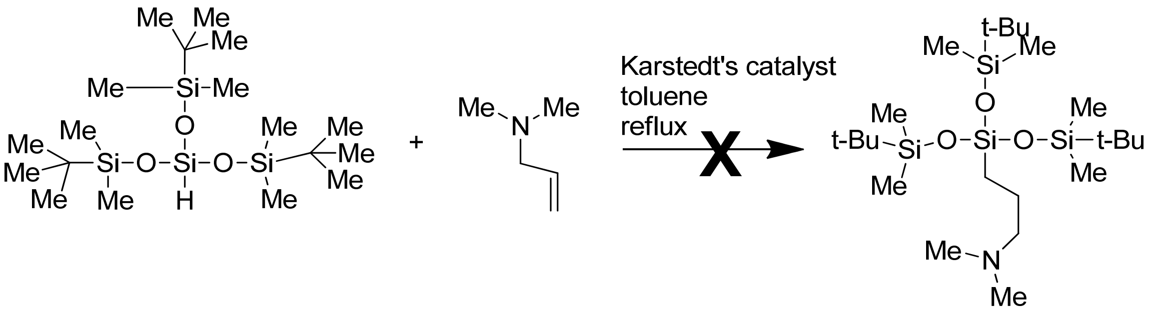


Figure 25 Failure to obtain the desired product from the platinum-catalyzed hydrosilation.

Therefore, it was decided to try the synthetic approach through the 3-chloropropyltrichlorosilane intermediate which would give the 3-chloropropyltris(*tert*-butyldimethylsiloxy)silane intermediate. However, the usual conditions to generate the siloxane bonds with *tert*-butyldimethylsilanol or *tert*-butyldimethylsilyl chloride all failed to give the desired product, Figure 26. Attempts to generate the analogous tetrasiloxane using triethylsilyl chloride, isomeric with *tert*-butyldimethylsilyl chloride, but contrary to a recent literature report, this reaction also failed under the typical hydrolysis conditions, Figure 27.[23] Even when a stronger base such as potassium *tert*-butoxide was employed to generate the potassium *tert*-butyldimethylsilanolate, the only product that was observed was the trisiloxane 2062–136, Figure 28. The current hypotheses for these unsuccessful results are that great steric bulk is placed around the central silicon atom making complete reaction very difficult or impossible.

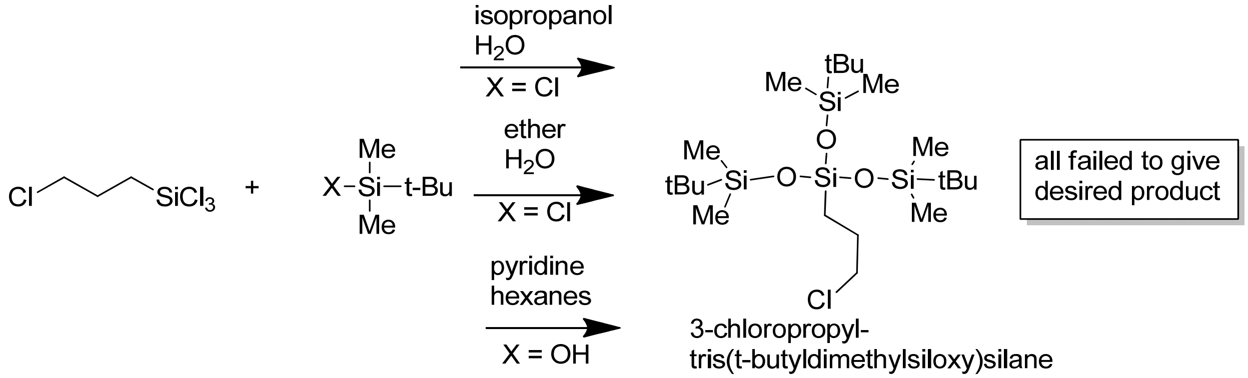


Figure 26 The simple standards methods for siloxane synthesis were unsuccessful.

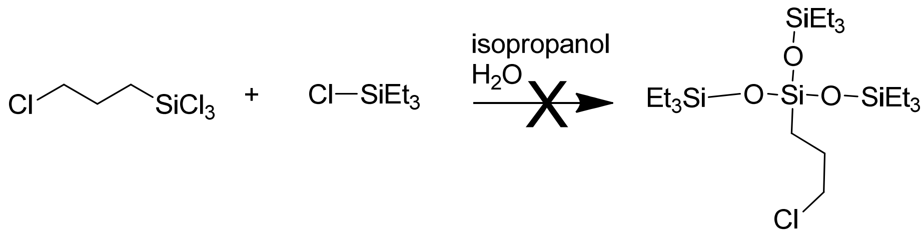
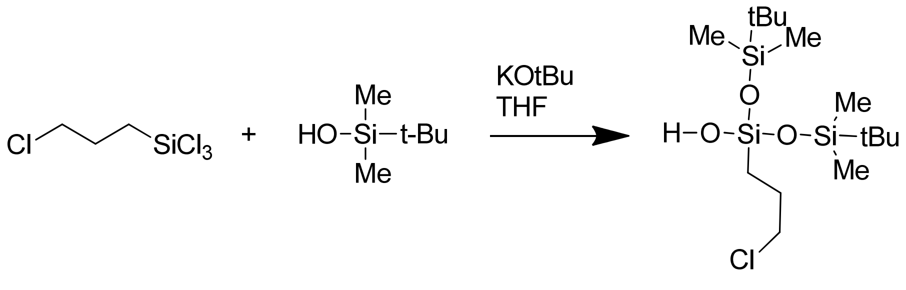


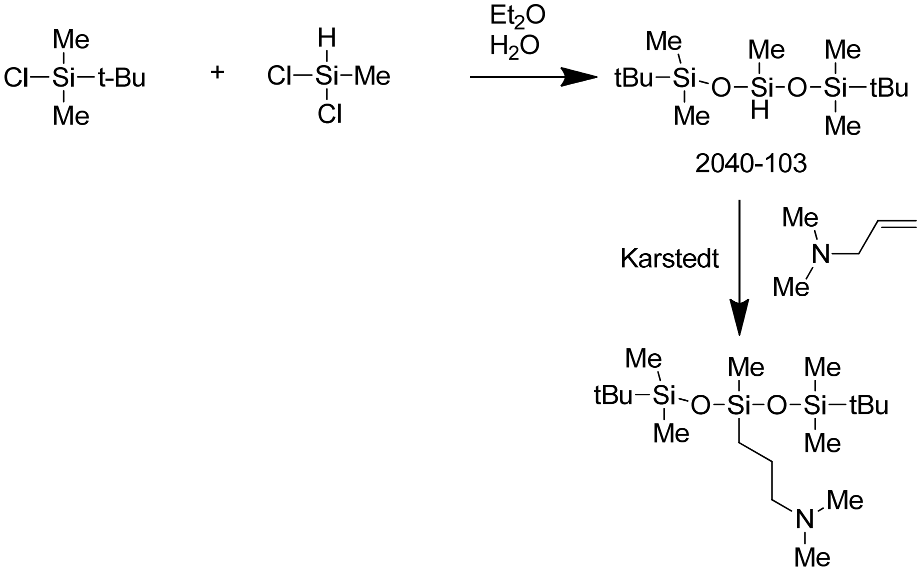
Figure 27 Even the less sterically hindered triethylsilyl chloride would not generate the desired tetrasiloxane.



2062-136

Figure 28 Tert-butyldimethylsilanol was too bulky to achieve complete siloxylation.

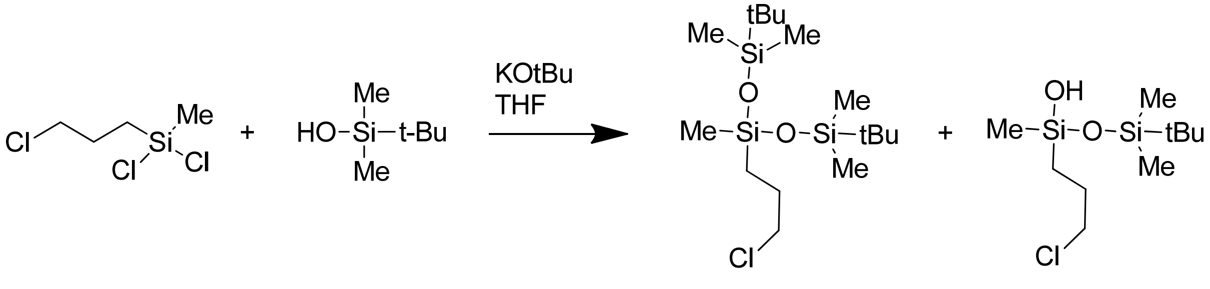
Given the difficulties in preparing the hydrolysis resistant tetrasiloxane 3-chloropropyltris(*tert*-butyldimethylsiloxy)silane, it was decided to try to synthesize a hydrolysis resistant disiloxane since the latter might have less of a steric issue. The synthesis of methylbis(*tert*-butyldimethylsiloxy)silane (2040–103) had appeared in a recent patent already.[24] It was found that diethyl ether could be substituted for diisopropyl ether in the controlled hydrolysis reaction of *tert*-butyldimethylsilyl chloride and methyldichlorosilane. The desired product 2040–103 could be purified by distillation and was obtained in ~50% yield, Figure 29. This silane 2040–103 would undergo the platinum-catalyzed hydrosilation reaction with N,N-dimethylallylamine to give the aminosiloxane 2062–158 in modest yield after separation of unreacted silane 2040–103 by distillation. Evidently the steric bulk of the silane with only two *tert*-butyldimethylsilyl groups was not so severe in this example of hydrosilation.[25]



2062-158

Figure 29 Bis(t-butyldimethylsiloxy)silane would undergo the hydrosilation reaction with N,N-dimethylallylamine.

But in order to avoid the hydrosilation reaction which would eventually become a bottleneck during scale-up, the 3-chloropropylmethyldichlorosilane was obtained from Gelest in large quantities (500 grams). The latter was reacted with potassium *tert*-butyldimethylsilanolate that was generated *in situ* by the deprotonation of *tert*-butyldimethylsilanol with the strong, non-nucleophilic base potassium *tert*-butoxide. This reaction gave a modest yield of the desired trisiloxane compound 2062–49 which has not been reported in the literature, Figure 30. In addition, there was always obtained the 'incomplete' siloxane 2062–149 where only one siloxane bond had formed. The two products were easily separated by silica gel column chromatography, the silanol 2062–149 being more polar than the trisiloxane 2062–49. Later, it was shown that separation of the two products could be performed by reduced pressure, fractional distillation to greatly increase throughput. The reaction gave a yield of about 60% of the desired trisiloxane 2062–49 but all attempts to drive the reaction to completion with excess silanolate have failed.

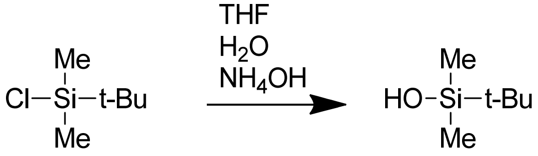


2062-49

2062-149

Figure 30 The trisiloxane incorporating t-butyldimethylsilyl groups was synthesized using the strong base potassium tert-butoxide.

Another challenge that came about during this time was that obtaining *tert*-butyldimethylsilanol (2062–160) from commercial sources was becoming an issue. It was only available in ten to twenty-five grams sizes from Gelest or Aldrich and their supplies were quickly exhausted. Rather than lose precious project time waiting for the product to become available, its preparation was carried out. In the event, the hydrolysis of readily available *tert*-butyldimethylsilyl chloride catalyzed by ammonium hydroxide was an excellent method to prepare the silanol quickly and in good yield, Figure 31.[26]



$$\mathrm{Cl{-}Si(Me)_2{-}t\text{-}Bu} \xrightarrow{\mathrm{THF,\ H_2O,\ NH_4OH}} \mathrm{HO{-}Si(Me)_2{-}t\text{-}Bu}$$

2062-160

Figure 31 T-Butyldimethylsilanol was easily made by hydrolysis of the silyl chloride.

The chloropropylsiloxanes must be further functionalized before they can have surfactant character. As an exploration of reactivity, the simple amination of the 3-chloropropyltris(trimethylsiloxy)silane (2062–104) was attempted using excess ammonia in a screw-cap, glass pressure tub, Figure 32. The glass vessel required cooling in order to condense the gaseous ammonia (bp –33 °C). After about five hours, there appeared to be some resonances corresponding to product in the proton NMR spectrum of a reaction aliquot. Evidently more time was needed and/or higher temperature to complete the reaction but unfortunately the vessel burst and this reaction was not pursued further. In the future, this reaction must be run in the BüchiGlas steel autoclave since it can handle much higher pressures. This particular aminopropylsiloxane 2062–164 product is commercially available but only in small quantities not sufficient for preparing adequate amounts of surfactants for testing.

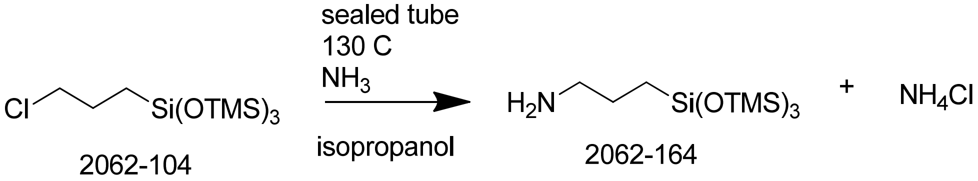


Figure 32 The simple amination with ammonia appeared to react as desired.

There was a patent from Dow in the early 1960's that taught one could react 3-chloropropyltris(trimethylsiloxy)silane (2062–104) with excess ethylene diamine to generate the mono-alkylated product.[27] One equivalent of the ethylene diamine becomes the by-product hydrochloric acid to become the corresponding hydrochloride salt. This reaction was repeated with 2062–104 only that some isopropanol was included as a solvent and the reaction was carried out in a glass pressure vessel, Figure 33. The reaction was complete in a few hours since the starting material 2062–104 was no longer present by thin-layer chromatographic analysis. After a diethyl ether/aqueous work-up, the expected product 2062–129C was isolated by distillation in good yield. This diamine had been prepared and exploited by several Chinese groups in the synthesis of surfactants.[28,29]

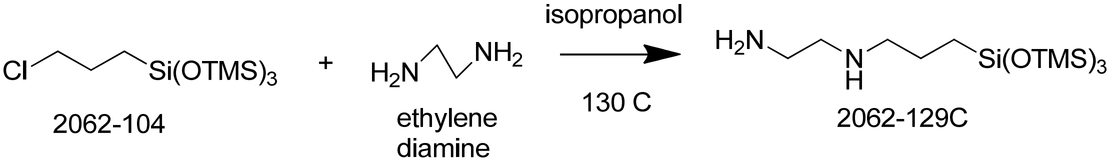


Figure 33 Amination of the chloropropyltetrasiloxane with ethylene diamine.

The reaction of diaminotetrasiloxane 2062–129C with one molar equivalent of δ–gluconolactone forms the mono-gluconamide (2062–135) at the more reactive primary amino group, Figure 34. However, the reaction of this diamine with two equivalents of δ–gluconolactone (2062–139) had not been reported previously. This might become of interest when the siloxane group structure has more lipophilic character to balance. The monogluconamide 2062–135 has some water solubility although the sample did not completely dissolve, but it did product some foaming behaviour when shaken, Figure 35. However, the bisgluconamide 2062–139 had excellent water solubility and was completely soluble in water and made strong foam when vigorously shaken.

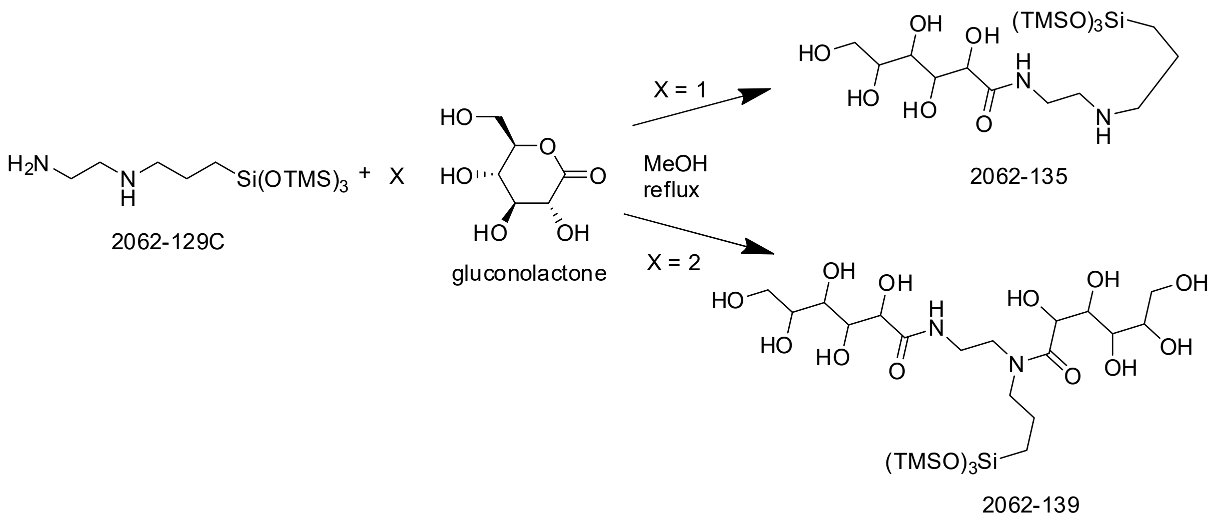


Figure 34 The diaminoalkyltetrasiloxane could be derivatized with sugar acid lactones.

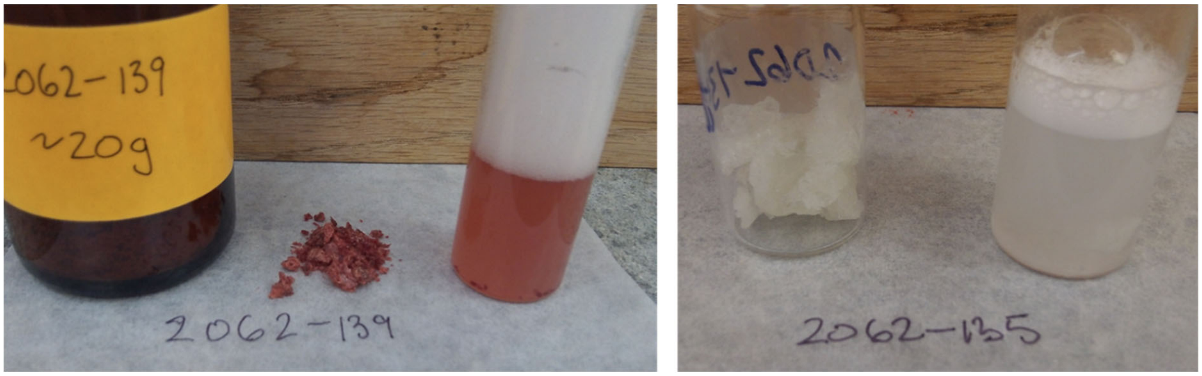


Figure 35 The mono- and bis-gluconamides of diaminoalkylsiloxane 2062–129C and their empirical solubility in water after vigorous shaking.

Along the same lines, the bis(gluconamide) of the diaminodisiloxane 2062–141 was synthesized, Figure 36. The monogluconamide 2082–2 had been previously reported by Han and Zhang.[30] It was immediately obvious that the bisgluconamide 2062–141B was much more water soluble than the monogluconamide, Figure 37. The bisgluconamide made a more transparent solution as compared to the monogluconamide, Figure 38.

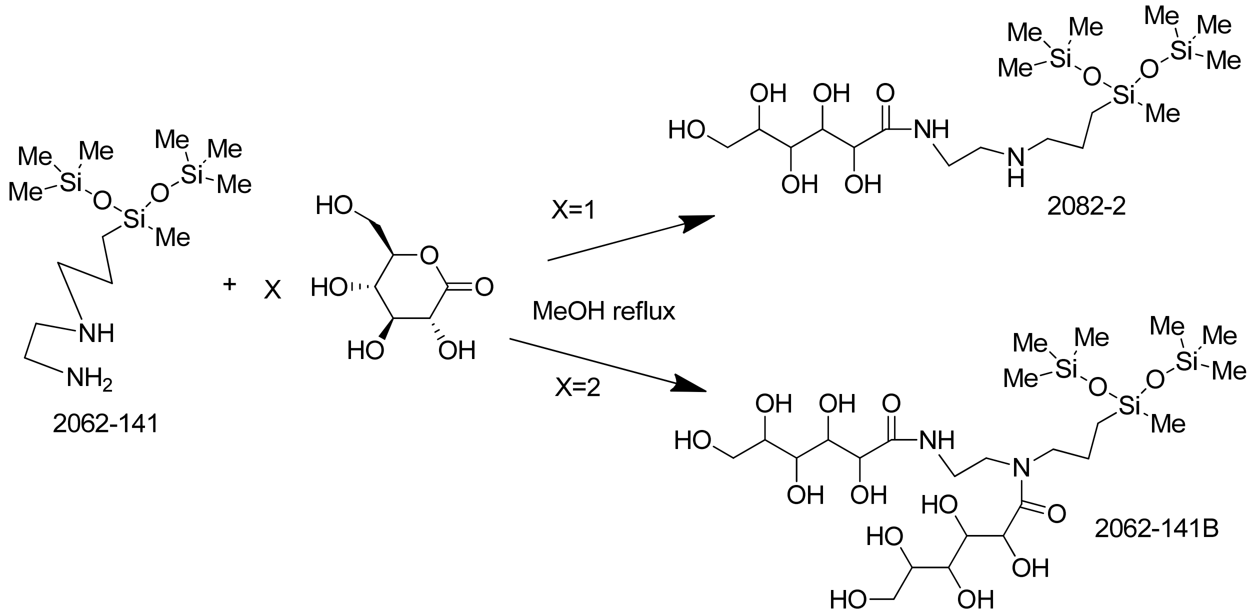


Figure 36 Chemical synthesis of the mono- and bis-gluconamides from the diaminoalkylsiloxanes 2062–141.

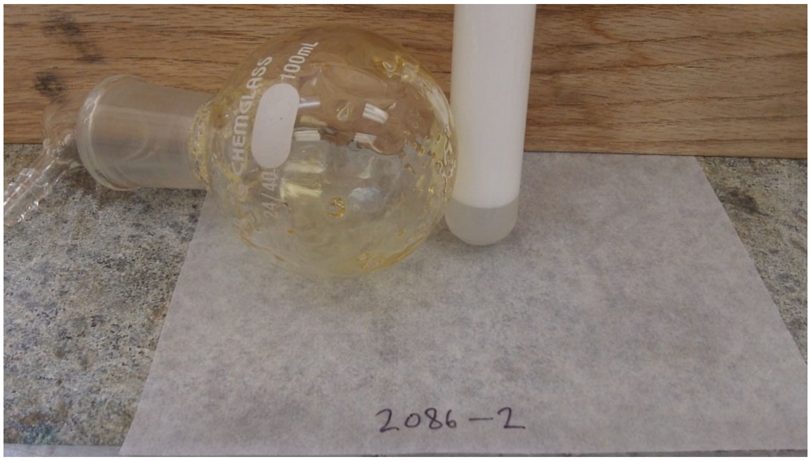


Figure 37 The monogluconamide 2086–2 was soluble in water and made strong foam when shaken.

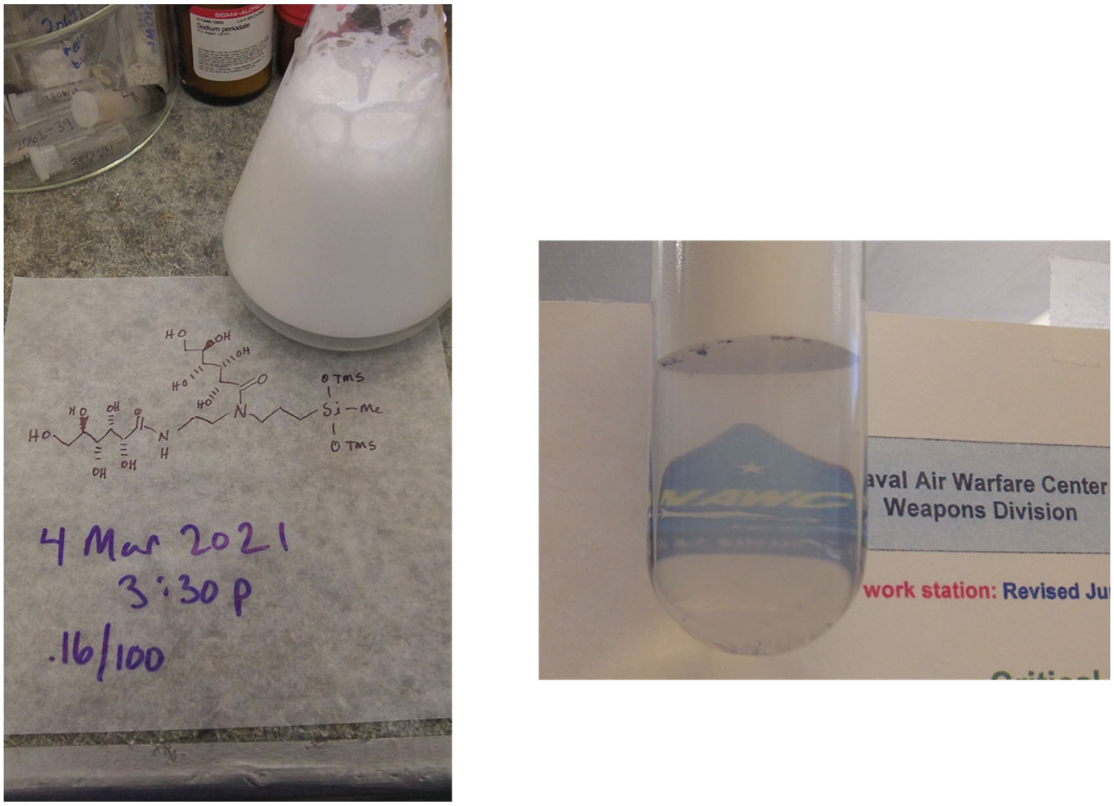


Figure 38 The bis(gluconamide) 2062–141B was soluble in water and generated a foaming solution when vigorously shaken. It appeared to have empirically better water solubility than 2082–2.

Although, combustion analysis and NMR confirmed that the bis(gluconamides) 2062–139 and 2062–141B had been synthesized, it was decided to obtain MS data to further confirm the products as drawn. Professor Laszlo Prokai at the University of North Texas Health Science Center kindly provided us with negative-ion mode ASAP® MS data on bis(gluconamide) 2062–141B.[31,32] These MS data show that the molecular ion has lost one proton under these ionization conditions and therefore the original compound must have two gluconamides, one bonded to each nitrogen atom, Figure 39. There are also three water loss events of the M-H ion which makes sense since there are ten hydroxyl groups present in the molecule, Figure 40.

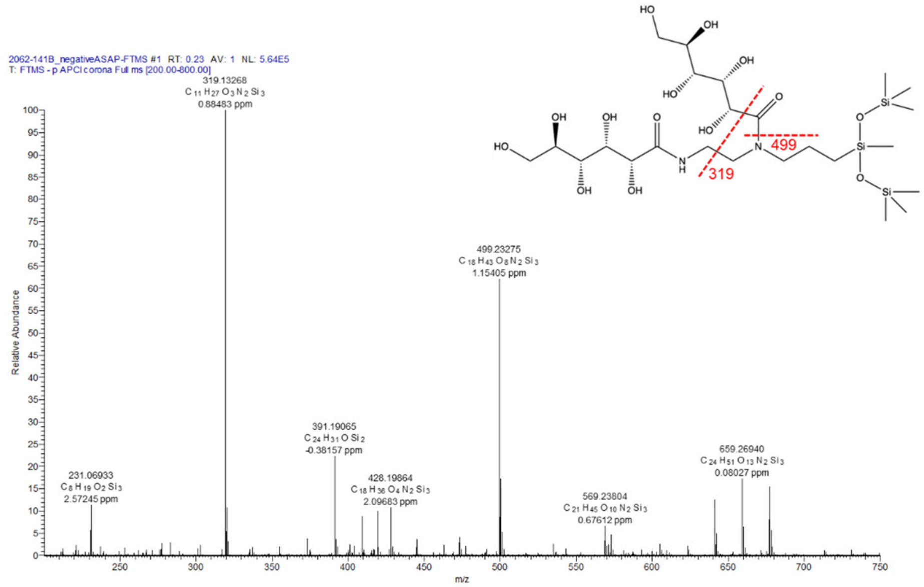


Figure 39 Negative-ion mode of ASAP mass spectrum of the 2062–141B confirming structure.

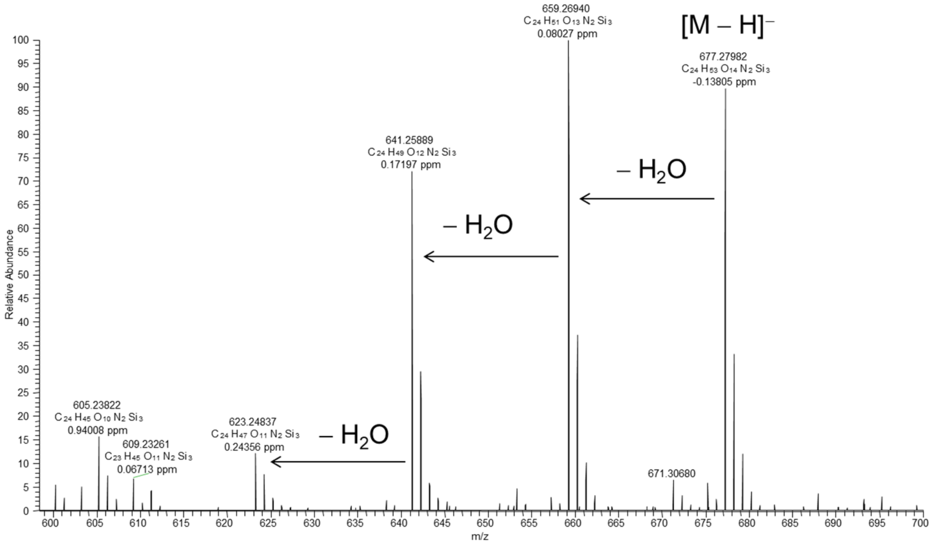


Figure 40 Close up view of the ASAP mass spectrum of the 2062–141B, the molecular ion has lost one proton by the MS ionization method.

While waiting for the MS data, it was decided to make the bis(gluconamide) of ethylene diamine (2062–143) as a comparison, Figure 41.[33] This was done without issue by a similar procedure only that the product precipitated during the reaction. The product 2062–143 was soluble in water but did not generate any foam when shaken. The compound was a white powder that was insoluble in common organic solvents including deuterochloroform and dimethylsulfoxide-*d*$_6$ in which the above 2062–141B was soluble for NMR experiments. Thus, preparing 2062–143 helped to show that its functionalization with the siloxane had a tremendous impact in creating a surfactant from an otherwise strictly water soluble compound.

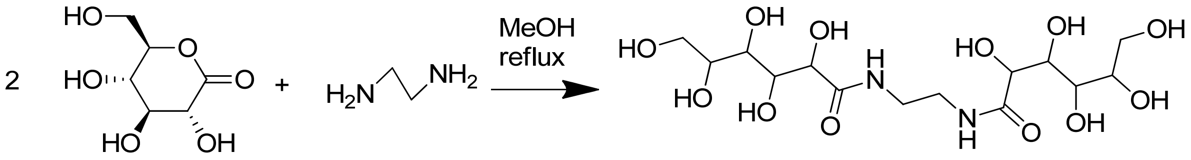


Figure 41 Synthesis of the bis(gluconamide) of ethylene diamine (2062–143), the compound had no surfactant qualities.

The ethylene diamine functionalization was next performed on the 3-chloropropylmethylbis(tert-butyldimethylsiloxy)silane 2062–49, Figure 42. Typical conditions were to employ five molar equivalents of ethylene diamine, the excess amine necessary to react and sequester the hydrogen chloride by-product. The reaction was successful and the unreported product 2062–138B and residual ethylene diamine could be separated by reduced pressure fractional distillation.

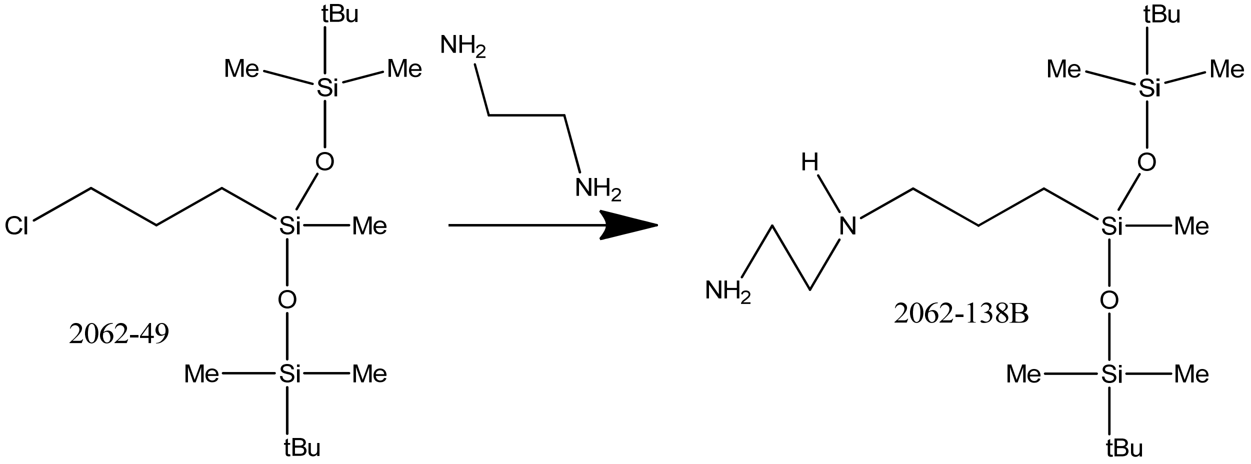


Figure 42 Amination of the tert-butyldimethylsilyl analog with ethylene diamine.

The new diaminoalkylsiloxane 2062–138B was not soluble in water but simply floated on the surface since its density was less than water. However, when 2062–138B was suspended in water and then neutralized with two molar equivalents of organic acids it became soluble. Two different acidic sugar derivatives, ascorbic acid and lactobionic acid, were used in this test of solubility to determine whether the diamine could be brought into a water solution, Figures 43 and 44. Each of the two amino groups become ionized resulting in the bisammonium salt of 2062-138B. The initial results were positive in that neutralization of the diamine with two equivalents of either organic acid made a water soluble mixture of a material with surfactant-like character (foaming on shaking). The bislactobionate of 2062–138B was stable even after storage at room temperature for forty-eight days, Figure 46. Although the bisascorbate of 2062–138B was a fine white color when made initially and had good foaming properties. However, after this solution was stored at room temperature for fifty days, the mixture no longer made any foam and had a dark orange-brown color, Figure 45. It is hypothesized that this decomposition had nothing to do with the dialkylaminosiloxane 2062–138B but entirely due to oxidation of the ascorbate ions as ascorbic acid is not stable in aqueous solutions.[34]

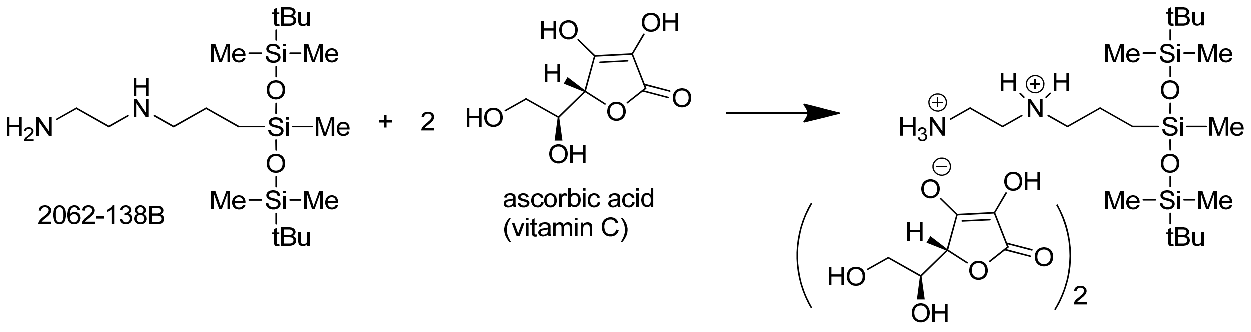


Figure 43 The diaminoalkyltrisiloxane with tert-butyldimethylsilyl groups would dissolve in water when neutralized with two equivalents to ascorbic acid.

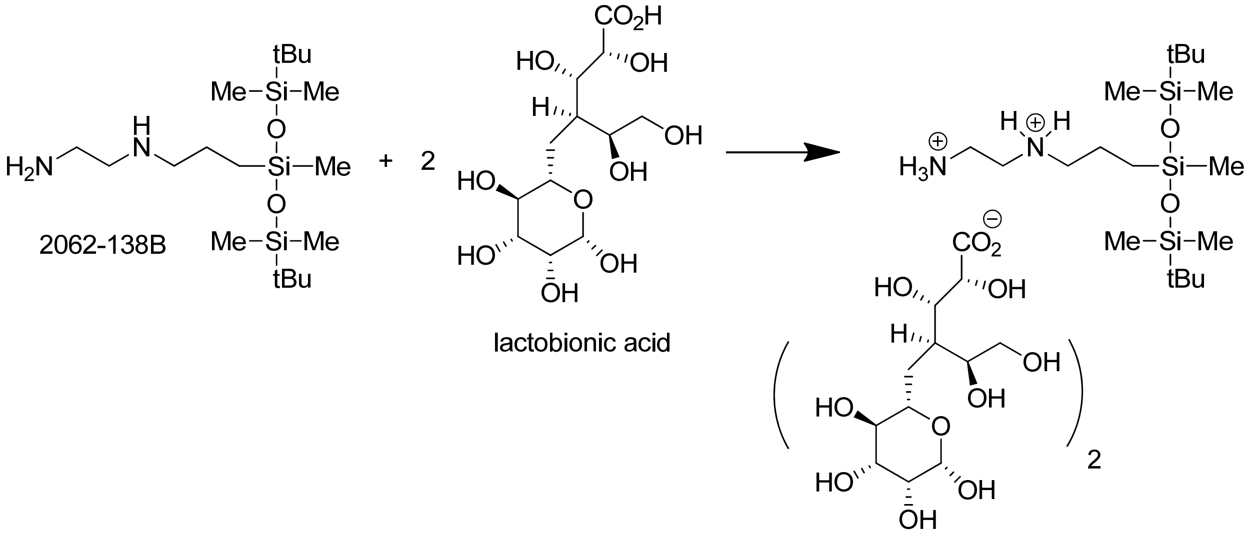


Figure 44 The diaminoalkyltrisiloxane with tert-butyldimethylsilyl groups would dissolve in water when neutralized with two equivalents of lactobionic acid.

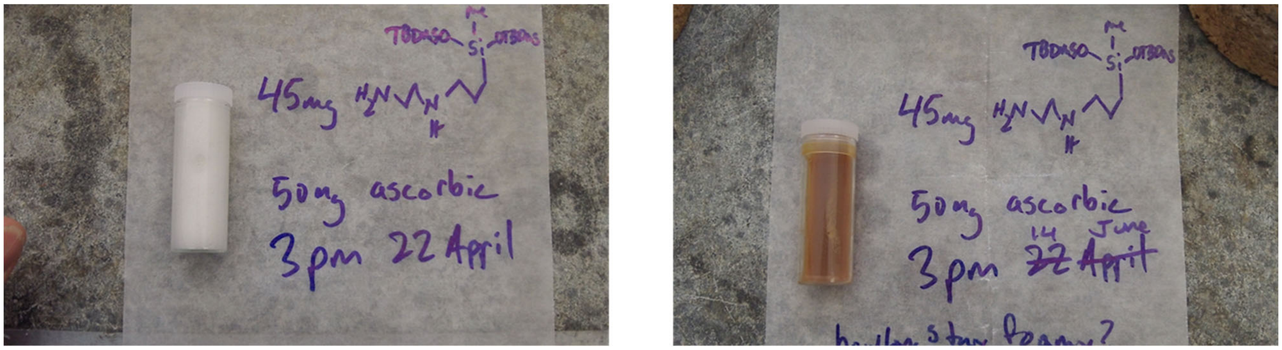


Figure 45 The salt made from 2062–138B and ascorbic acid was soluble in water and made a foaming solution when shaken (LEFT). However the sample was not stable to long periods of storage and underwent decomposition and no longer foamed (50 days) (RIGHT).

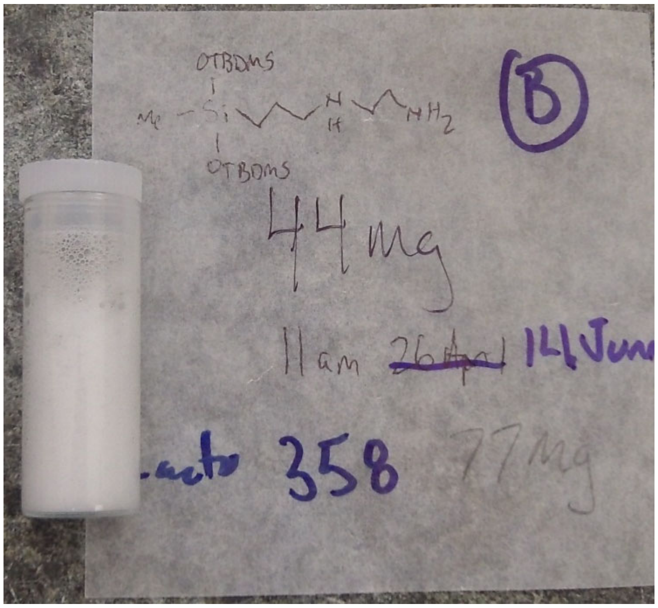


Figure 46 After 48 days the surfactant made from the 2062–138B and lactobionic acid had not decomposed but remained a surfactant when vigorously shaken.

This diaminoalkylsiloxane 2062–138B was then reacted in the same manner with one or two equivalents of δ-gluconolactone, Figure 47. Both the mono-gluconamide 2062–172 and di-gluconamide 2062–145 were brittle foamy solid materials. The mono-gluconamide 2062–172 was not soluble in water even after a prolonged period of time, Figure 48.

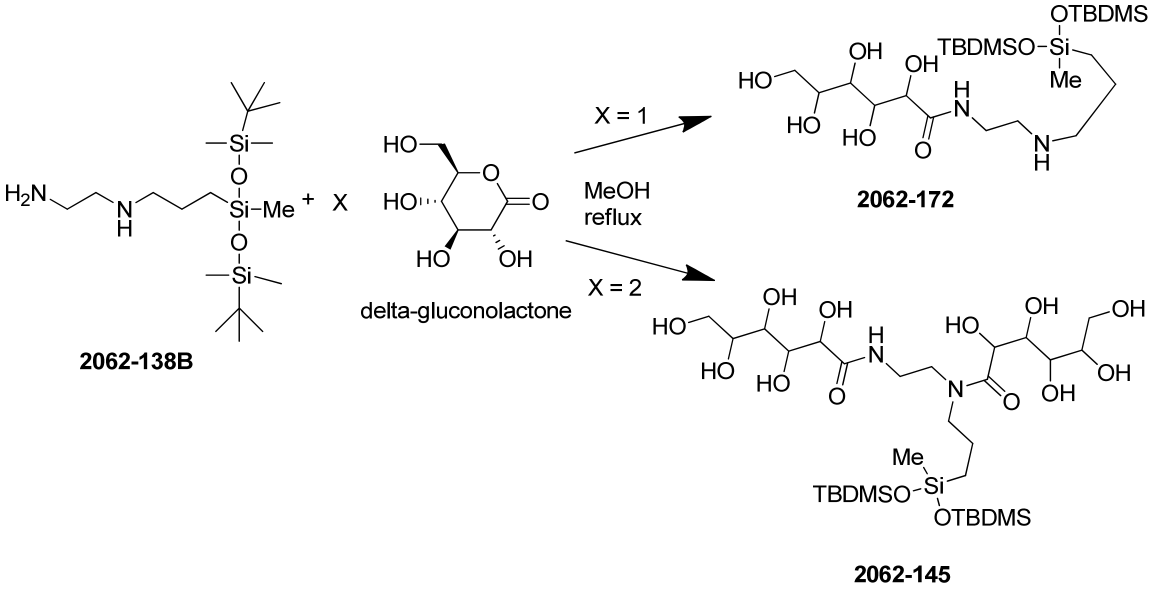


Figure 47 Synthesis of mono- and di-gluconamides from diamine 2062–138B.

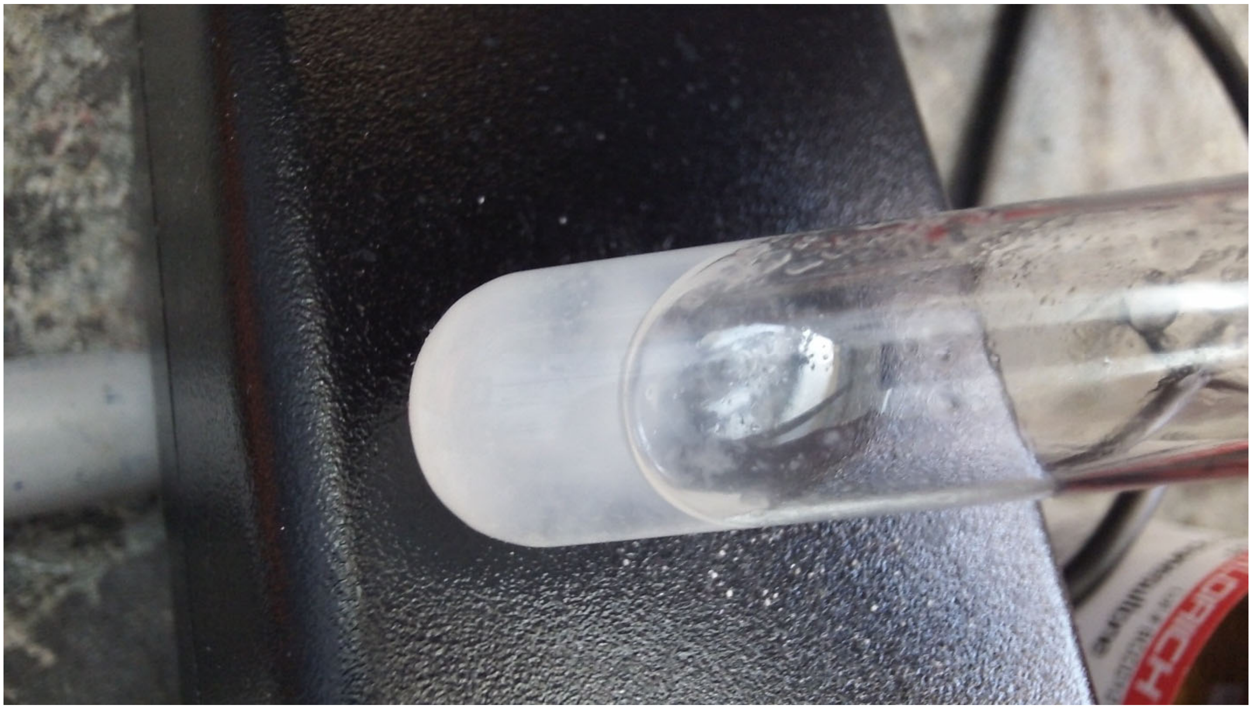


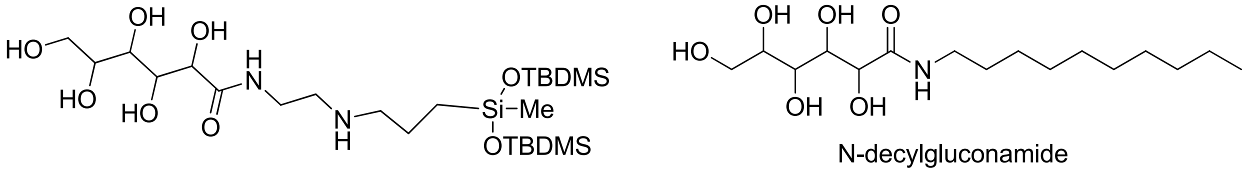
Figure 48 The monogluconamide 2062–172 would not dissolve in water but remained a suspension for one month.

In contrast, the bis-gluconamide 2062–145 would slowly but completely dissolve in water and the solution generated foam when shaken up as expected for an aqueous surfactant mixture,

Figure 49. The hypothesis drawn from these two compounds was that at least two sugars were necessary to overcome the very lipophilic siloxane headgroup and provide enough water solubility.

Figure 49 The bisgluconamide 2062–145 would slowly and completely dissolve in water and gave an apparent surfactant solution that foamed when shaken vigorously.

The bisgluconamide 2062–145 had structural similarities to N-alkylgluconamides which have been shown to have surfactant properties, Figure 50.[35] However, in this case there was not enough water solublizing character with just one aldonamide substituent.



2062-172

N-decylgluconamide

Figure 50 Structural similarities between gluconamidosiloxanes and the known surfactant class, N-alkylgluconamides.

A similar series of steps was used to prepare a trisiloxane capped with phenyl groups, Figure 51, since the resulting siloxane would also have water-resistant similar to *tert*-butyl groups. In the first step, the commercial 3-chloropropylmethyldichlorosilane was reacted with potassium phenyldimethylsilanolate to form the trisiloxane 2062–176. Although trisiloxane 2062–176 had been reported by Huang et al., the synthesis described here was simpler and gave the product in good yield.[36] In the second step, excess ethylene diamine was reacted with the trisiloxane 2062–176 in a pressure tube at 130 °C. After purification, the diaminoalkylsiloxane 2062–194 was reacted with two molar equivalents of gluconolactone in refluxing methanol to give the final product surfactant 2062–197. Although the surfactant 2062–197 incorporated two hydrophobic phenyl groups in the trisiloxane head group, the molecule would dissolve in water owing to the two sugar groups and the surfactant created moderate foaming when its aqueous solution was vigorously shaken, Figure 52.

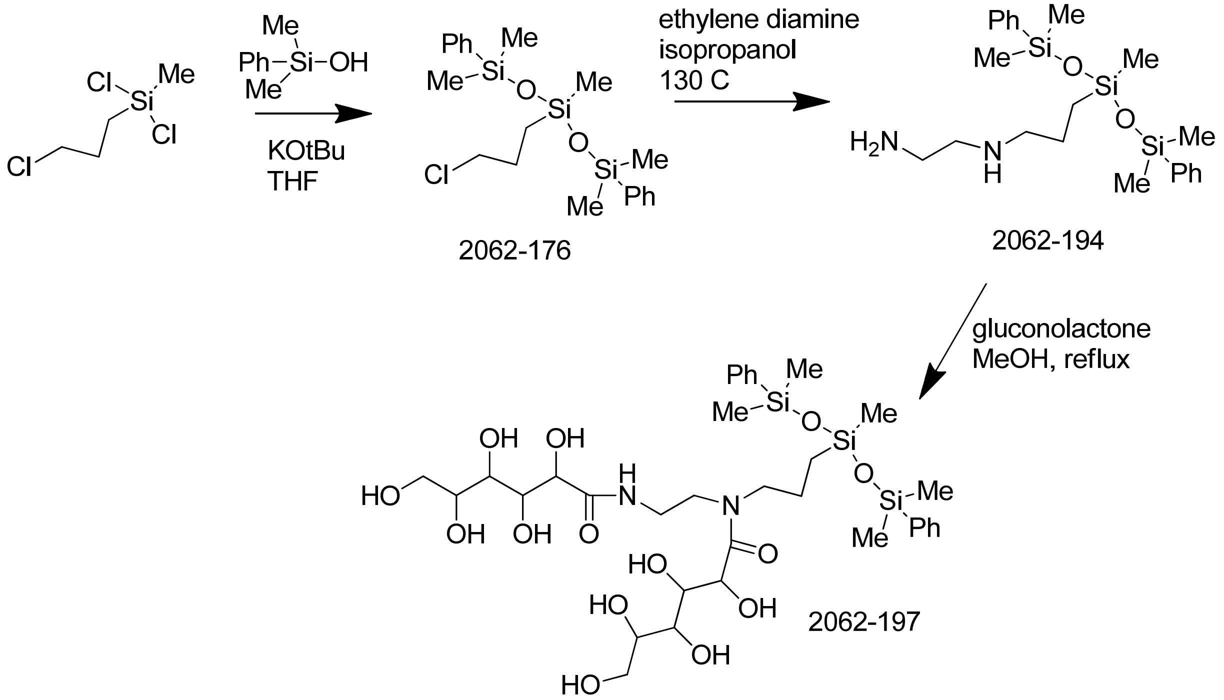


Figure 51 Three step synthesis of the phenyldimethylsilyl surfactant analog.

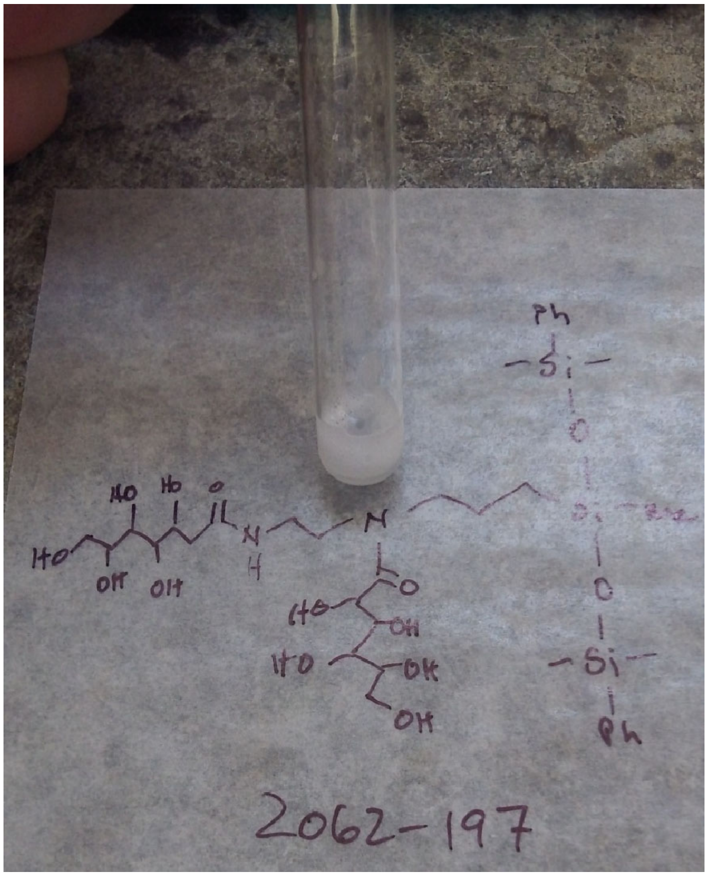


Figure 52 The phenyldimethylsilyl surfactant analog 2062–197 was soluble in water and made foam when shaken.

The alkylation chemistry of the chloropropylsiloxanes was expanded further using polyaminoalkanes other than ethylenediamine. Reaction of the chloropropylsiloxane 2062–49 with excess diethylenetriamine gave the triaminoalkylsiloxane 2062–154, Figure 53. The latter compound was reacted with three equivalents of δ-gluconolactone in refluxing methanol. The product from this reaction was the trisgluconamidoalkylsiloxane 2062–156. The product 2062–156 was now readily soluble in water and the resulting solution generated foam when shaken, Figure 54. The increased water solubility makes sense since there was a greater proportion of hydrophilic sugar groups in the molecule to offset the lipophilic bis-*tert*-butyldimethylsilyl capped siloxane head group.

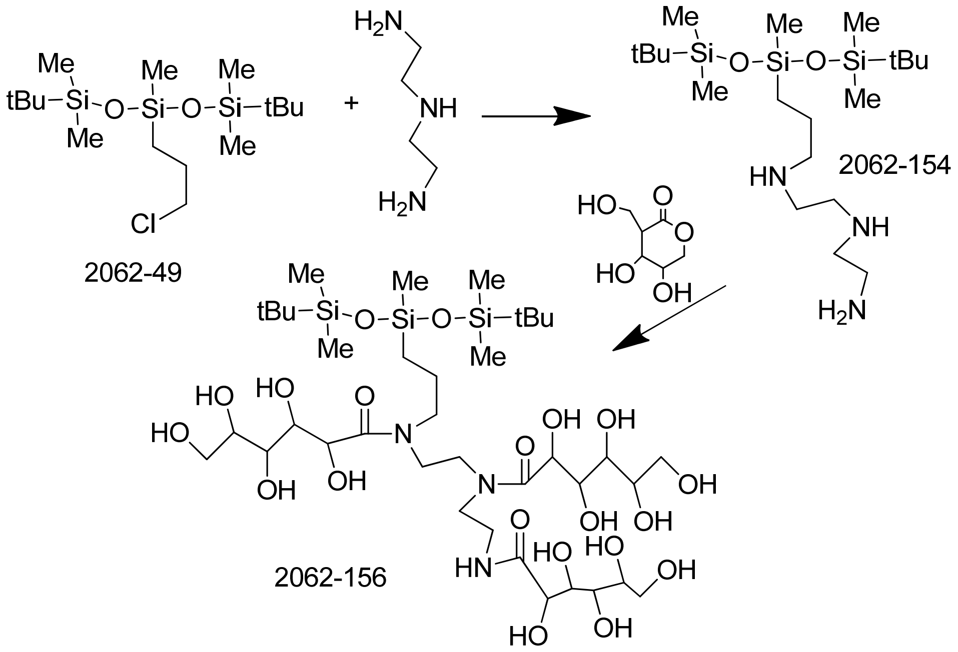


Figure 53 The reaction sequence could be extended to diethylenetriamine to generate a tris(gluconamido)siloxane surfactant.

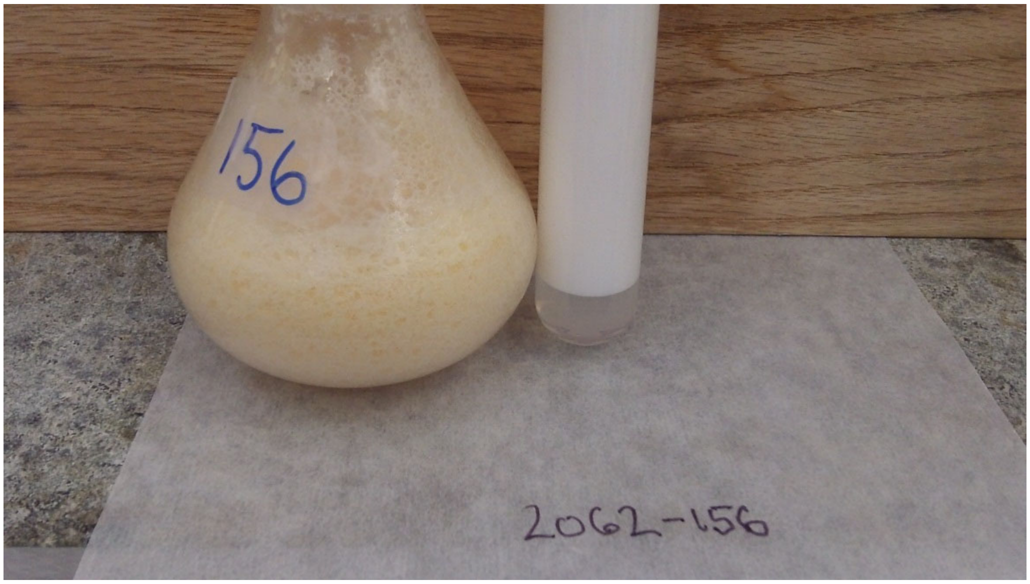


Figure 54 Trisgluconamido 2062–156 was a brittle solid material that dissolved in water easily and generated a foaming solution when shaken.

Even the alkylation of triethylenetetramine with 2062–49 was successful which gave the corresponding tetraminoalkylsiloxane 2062–165, Figure 55. At this time, the glucosamidation of the tetramine has not been carried out but there is no reason to believe that the reaction would not work. Unfortunately, the triethylenetetramine starting material is quite expensive and available in only small quantities from several vendors.

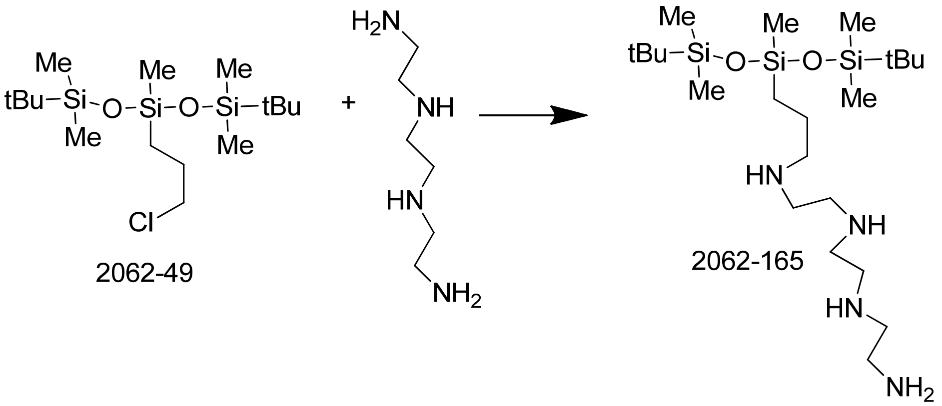


Figure 55 Preliminary results showed that triethylenetetramine would undergo the alkylation of 3-chloropropylsiloxanes.

The term 'betaine' was once reserved for the natural product N,N,N-trimethylglycine inner salt, Figure 56. Siloxane surfactants with betaine structures (anion and cation in a single molecule) were reported by researchers at Dow.[37] This seemed like a good strategy for functionalization of the dimethylaminoalkylsiloxane 2062–158, Figure 57. A molar equivalent mixture of the dimethylaminoalkylsiloxane 2062–158 and 1,3-propanesultone were heated to 60 °C in toluene. The product could be isolated by diluting with hexanes and filtering the solid product. The yield was high for this reaction which gave product sulfobetaine 2062–71B. It was possible to form single crystals of the compound by recrystallization from acetonitrile. X-ray crystallography courtesy of Greg Imler at NRL showed that the compound indeed had the structure as drawn, Figure 58. Several months after the compound had been synthesized, it was discovered that the compound had already appeared in a 2012 patent.[38] The patent taught that this compound (example #8 in the patent) was soluble in water and they could obtain a surface tension measurement. However, empirical testing of the sample prepared during this project showed it had very little if any solubility in water, Figure 59.

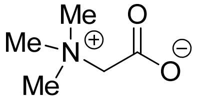


Figure 56 The chemical structure of N,N,N-trimethyleneglycine which is sometimes referred to as betaine.

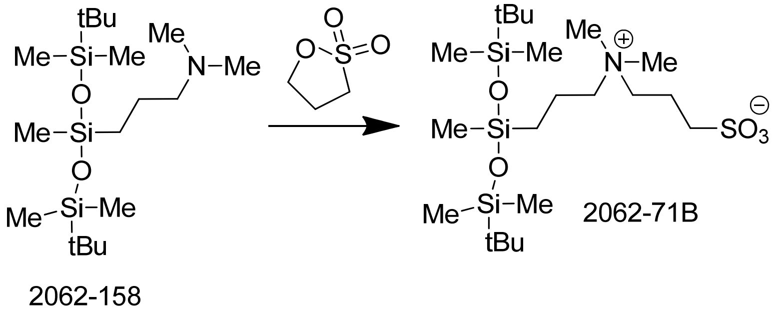


Figure 57 The tert-butyldimethylsilyl sulfo betaine structure was made in one step by reaction of the amine with 1,3-propanesultone.

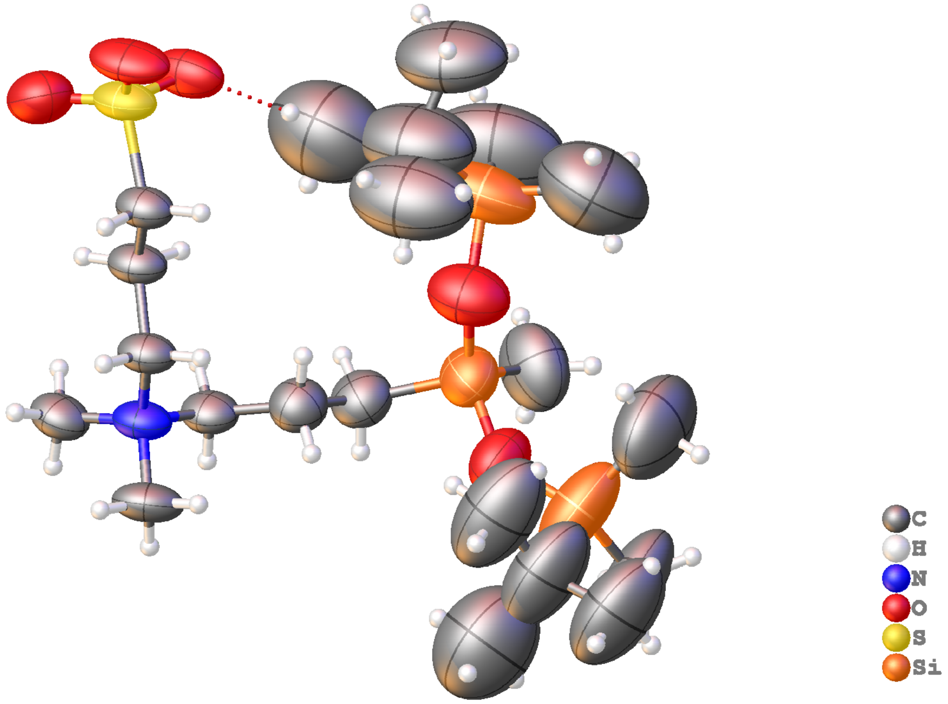


Figure 58 X-ray crystal structure of 2062–71B (solution courtesy of Greg Imler, NRL).

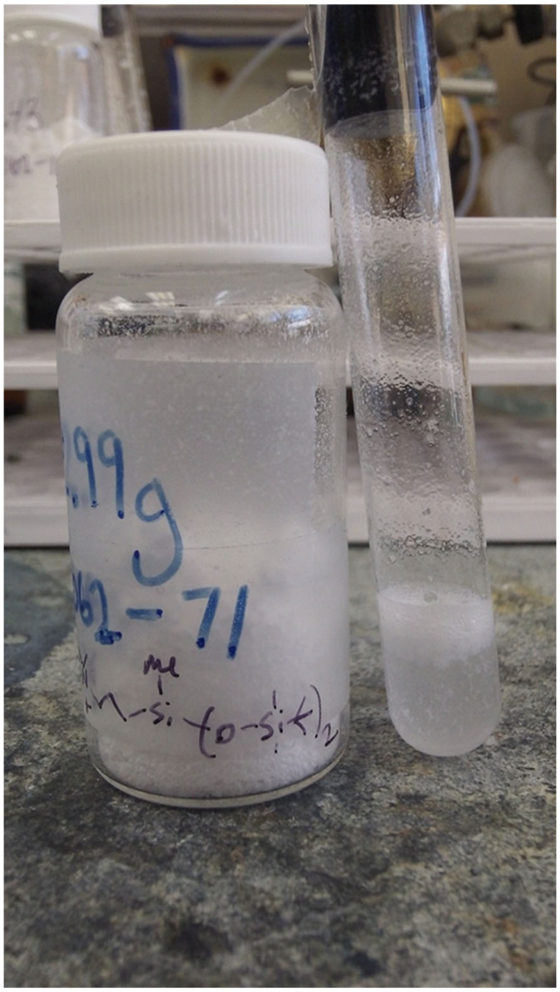


Figure 59 The sulfobetaine 2062–71B was a crystalline solid with very little solubility in water.

In an effort to improve the solubility of structures similar to 2062–71B, the addition of an ethylene oxide unit into the linker between the siloxane and betaine was made, Figure 60. In the first step dimethylaminoethanol was etherified with allyl bromide using potassium *tert*-butoxide, instead of sodium hydride as was done previously.[39] The product ether 2062–61 underwent the hydrosilation reaction with trisiloxane 2040–103 reasonably well. The product dimethylaminoethyloxypropylsiloxane 2062–108 underwent alkylation reaction with 1,3-propanesultone in the same fashion as before to give the desired sulfobetaine 2062–111B. Although the product was a solid, it could not be recrystallized from typical organic solvents. The water solubility of the compound did not appear to be significantly improvement over 2062–71B and the compound 2062–111B did not dissolve sufficiently in water based on empirical tests, Figure 61. It was also noteworthy that the compound 2062–111B had an excellent combustion analysis, indicating the siloxane head group was stable to the presence of the sulfate ion.

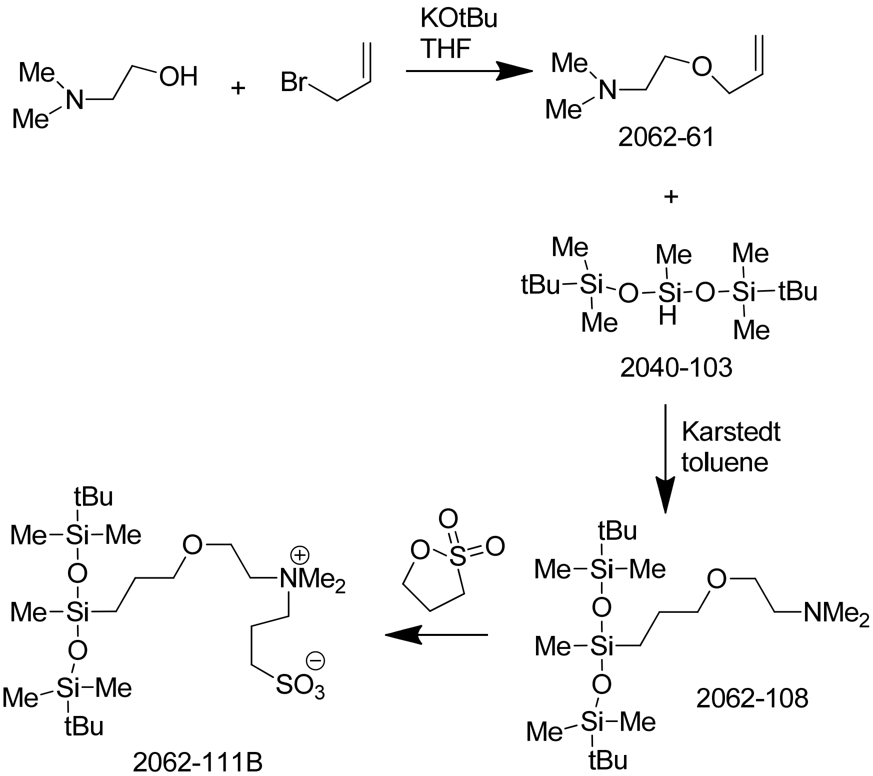


Figure 60 Multi-step organic synthesis of the unknown sulfobetaine 2062–111B.

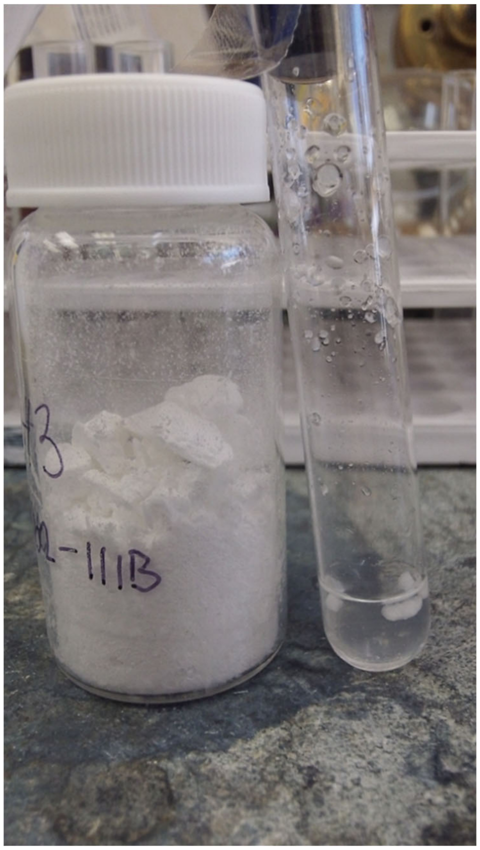


Figure 61 The sulfobetaine 2062–111B was a solid that had little solubility in water.

Pyridinium salts can be made fairly easily by reaction of pyridines with alkylating agents and can have surfactant properties.[40] Reaction of 3-chloropropyltris(trimethylsiloxy)silane with pyridine has been reported to generate a pyridinium-salt which was a surfactant-like molecule.[41] The synthesis could be repeated as reported by refluxing an excess of pyridine with 3-chloropropyltris(trimethylsiloxy)silane in acetonitrile for several days to form 2062–148, Figure 62. The pyridinium salt 2062–148 was a solid that was easily soluble in water and made foam when shaken, Figure 63. It was hypothesized that a similar reaction with 4-dimethylaminopyridine (DMAP) might react faster owing to the added electron density of the pyridine nitrogen atom. Indeed, the reaction between 3-chloropropyltris(trimethylsiloxy)silane and DMAP was complete after just eight hours reflux. The 4-dimethylpyridinium salt 2062–159 was a solid and also soluble in water and made foam when shaken, Figure 64. It was supposed that the second tertiary nitrogen atom in 2062–159 could be further functionalized, for example alkylation, but there was not enough time to pursue further chemistry.

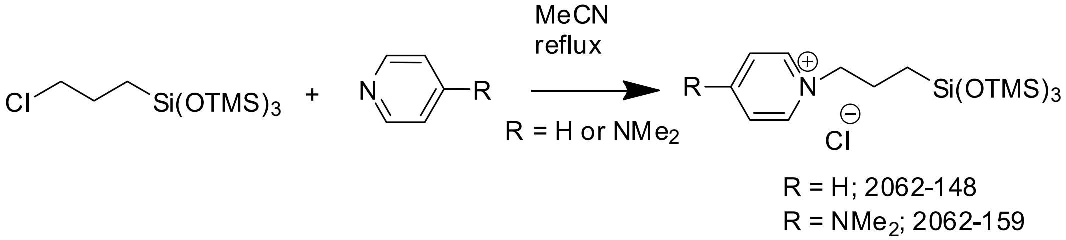


Figure 62 Pyridinium salts could be made by reaction of pyridines with the chloropropylsiloxanes.

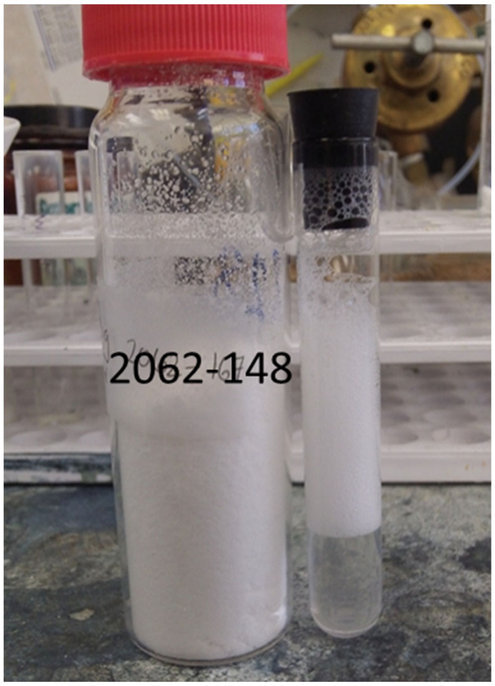


Figure 63 The pyridinium salt 2062–148 was a highly water soluble solid that generated strong foam when shaken.

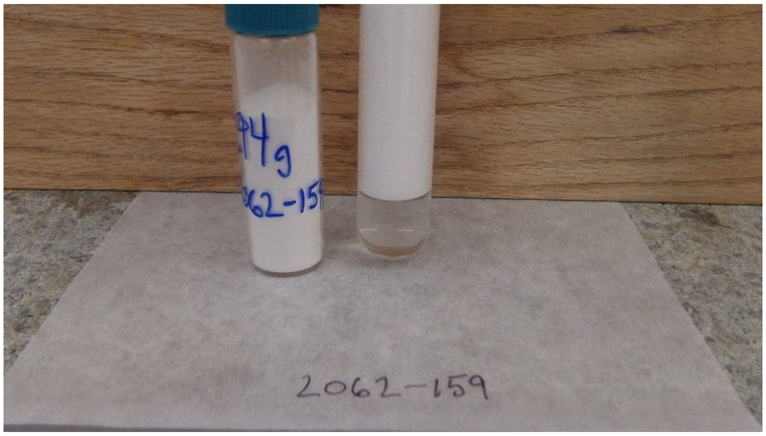


Figure 64 The 4-dimethylaminopyridinium salt 2062–159 had good solubility in water and strong foam created when shaken.

A similar reaction was carried out on the 3-chloropropylsiloxane 2062–49 with 4-dimethylaminopyridine, Figure 65. The crude product containing the excess DMAP could be slurried with toluene which dissolved the DMAP and left the desired product insoluble. The purified product 2062–173 was soluble in water but not quite as readily as the 2062–159 analog. The compound 2062–173 had surfactant qualities since the solution generated foam when shaken vigorously, Figure 66.

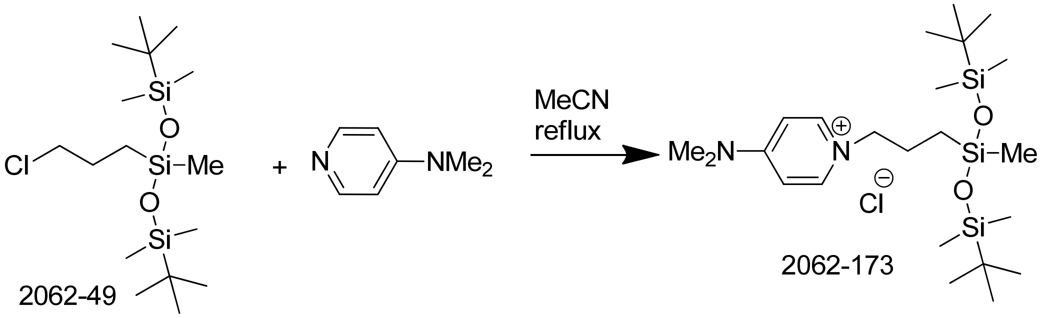


Figure 65 The tert-butyldimethylsilyl analog of the 4-dimethylaminopyridinium salt was also synthesized.

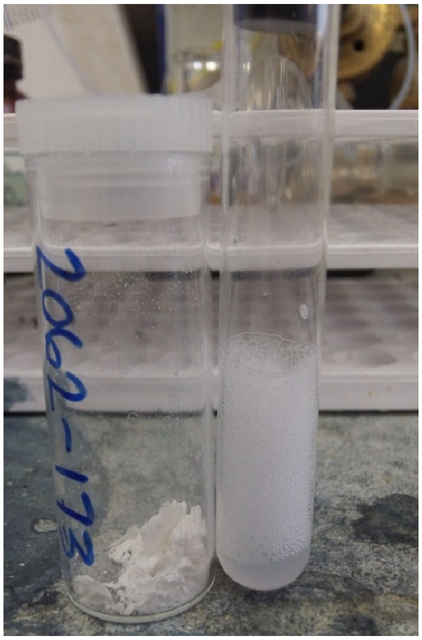


Figure 66 The 4-dimethylaminopyridinium salt of 3-chloropropylsiloxane 2062–49 was a solid that was soluble in water and made foam when shaken.

Triphenylphosphine was sulfonated on a single benzene ring with a 20% solution of sulfur trioxide in concentration sulfuric acid (oleum) following literature procedures, Figure 67.[42] The product sodium triphenylphosphinemonosulfonate (2062–199) was isolated and ^{31}P NMR spectra showed only single peak at – 5.4 ppm clearly indicating that the phosphorus atom had not been oxidized. The oxidation of 2040–199 was straightforward using a 30% solution of hydrogen peroxide in water. After evaporation of the water, the product sodium triphenylphosphineoxidemonosulfonate (2040–200) was highly water soluble but could be recrystallized from a mixture of methanol and acetonitrile. The crystals were not stable to air storage because they were hygroscopic. The ^{31}P NMR spectra showed only a single peak at 34.8 ppm indicating the phosphorus atom was completely oxidized.[43] Although 2062–199 and 2062–200 were solids, they could be dissolved in water. Interestingly, the product 2062–199 appeared to have surfactant like properties as its mixture in water made fairly stable foam behaviour, Figure 68.

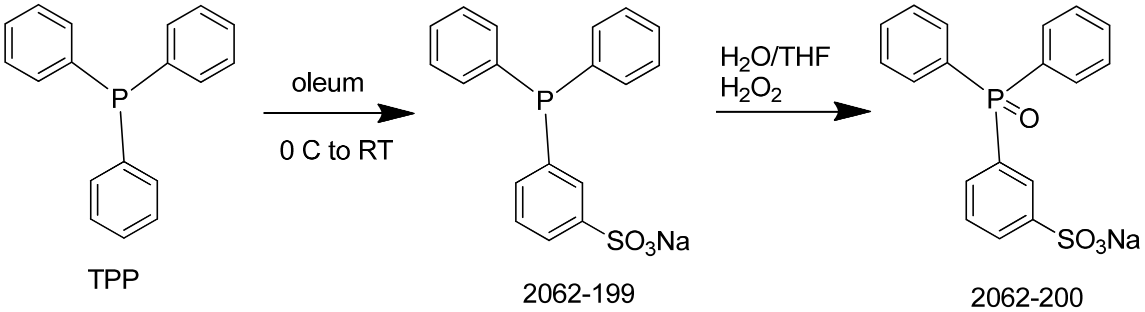


Figure 67 Synthesis of sodium mono-sulfonated triphenylphosphine (2062–199) and sodium monosulfonated triphenylphosphine oxide (2062–200).

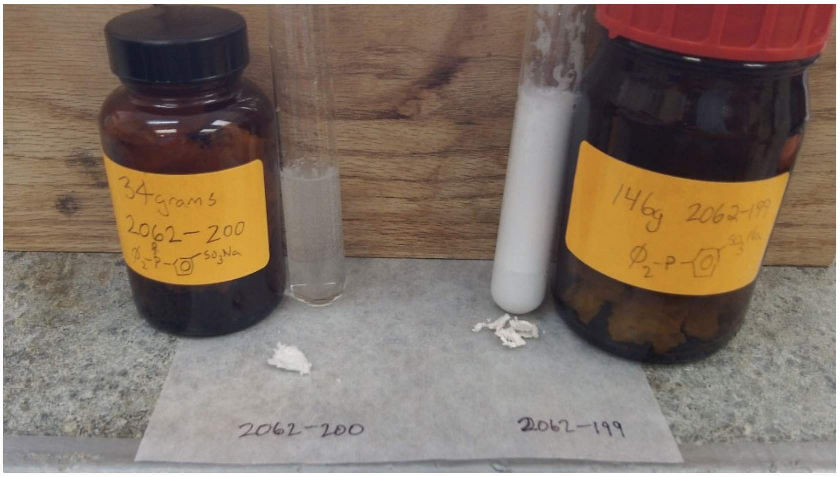


Figure 68 The oxide 2062–200 was highly water soluble and showed little surfactant properties, however the phosphine 2062–199 was less soluble in water and made foaming solution when shaken.

Although the phosphine 2062–199 showed some water solubility, it had a very cloudy appearance that suggested particulates were present. The aqueous solubility of 2062–199 has been reported to be 12.5 grams/L but this was found to be a little too high. The phosphine 2062–199 (0.25 and 0.5 grams) was dissolved in 100 mL of water at lesser concentrations. Each solution had a characteristic milky appearance, however each of these solution would pass rapidly through a medium porosity glass filter frit (15 µm pore size) with some vacuum (60 torr), Figure 69.[44] This empirical test suggested that there would be no issue with such cloudy mixture moving through small orifices such as spray nozzles in fire fighting apparati.

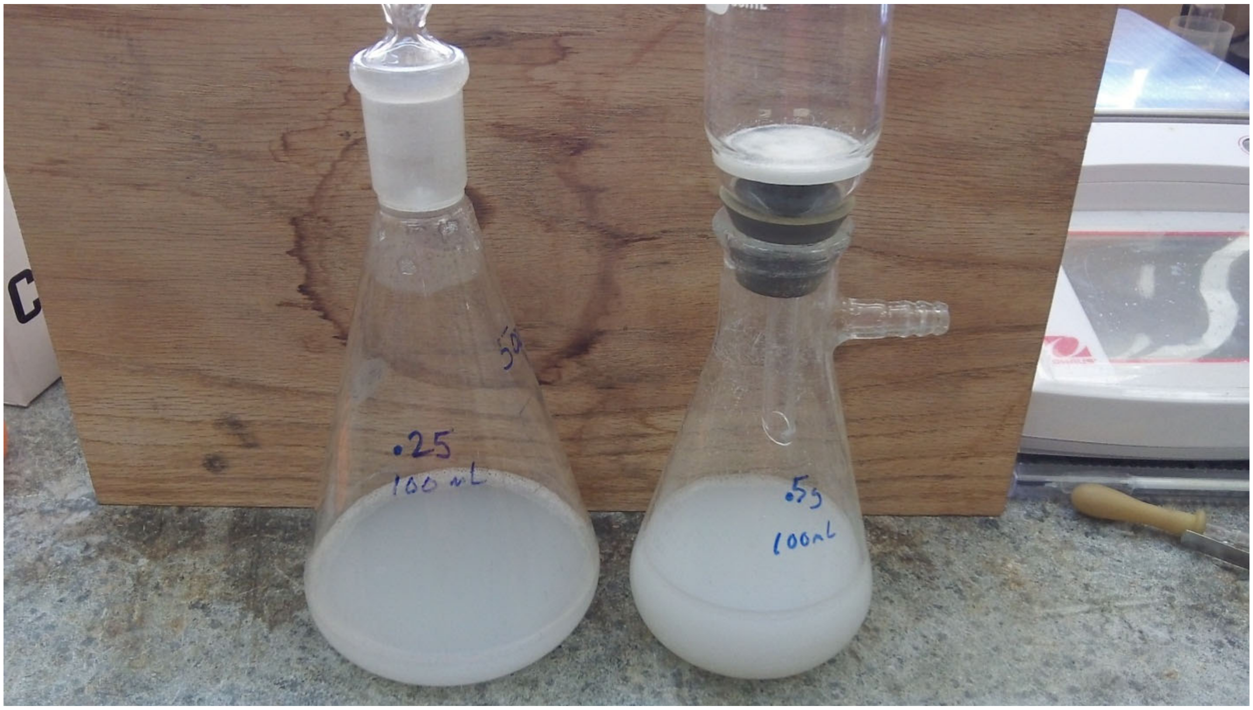
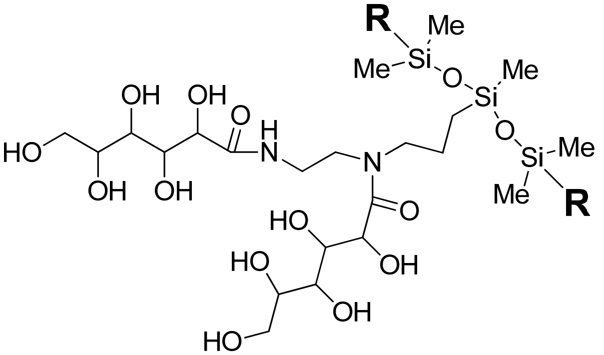


Figure 69 The aqueous solutions of phosphine 2062–199 were cloudy in appearance but would pass through a filter frit without issue.

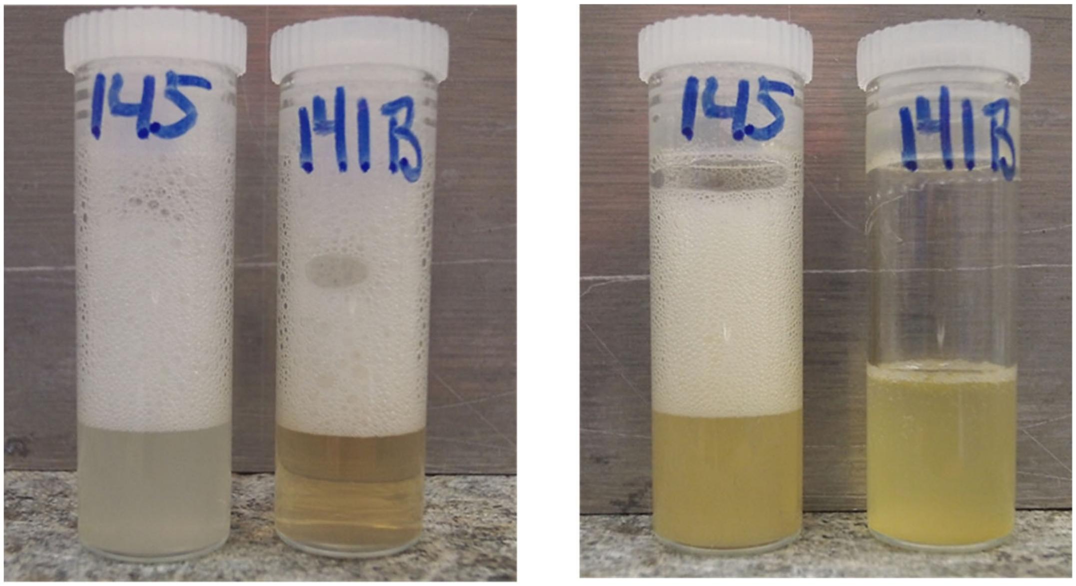
One of the primary hypotheses of the proposal was that hydrolysis-resistant siloxane surfactant would have improved stability in aqueous solution over ‘typical’ siloxane surfactants which are terminated with the trimethylsiloxy group. The synthesis strategy found during this project allowed for the synthesis of both of these kinds of siloxane surfactants, Figure 70.



R = Me, 2062-141B
R = *t*Bu, 2062-145

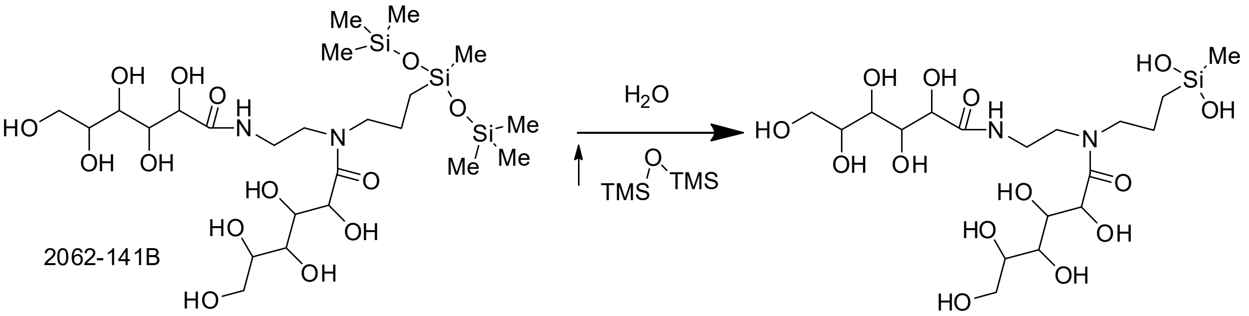
Figure 70 Two structural analogs of glucosamidoalkylsiloxane surfactants, one has trimethylsilyl termination while the other has tert-butyldimethylsilyl termination.

Therefore, a simple empirical test of the stability of two of the simplest members of each group was made. An equimolar quantity of 2062–141B and 2062–145 were dissolved in an equal volume of water and the two samples were simply stored under ambient conditions for an extended period of time. As can be seen in Figure 71, at the beginning of the test both surfactant solutions generated copious foaming after vigorous shaking. After twenty-nine days the siloxane surfactant terminated with tert-butyldimethylsiloxy groups 2062–145 continued to make a foaming solution when shaken while the siloxane surfactant terminated with trimethylsiloxy groups 2062–141B had virtually no ability to generate foam when shaken. It is hypothesized that the 2062–141B surfactant underwent hydrolysis at the siloxane head group as researchers at Dow had already shown with sulfobetaine siloxane surfactants. The hydrolysis products of 2062–141B no longer had the proper chemical structure consistent with a surfactant and thus could no longer generate the typical aerated foam, Figure 72.



Time Zero After 29 days

Figure 71 Empirical stability comparison of aqueous solutions of surfactants 2062–145 and 2062–141B after storage at room temperature.



2062-141B

Figure 72 Postulated hydrolysis reaction of 2062–141B losing trimethylsilyl ether in the process.

Surfactants are compounds containing both hydrophobic and hydrophilic portions which can decrease the surface tension of water, Figure 73. Deionized water has a surface tension of >71 mN/m at room temperature. If a surfactant were dissolved in deionized water, then the surface tension measured would be lower <71 mN/m. If several measurements of surface tension versus surfactant concentration were made, then the concentration at which the surface tension no longer decreases but levels out and micelle formation occurs. This point is called the critical micelle concentration (CMC). If the compounds made in this study behave as surfactants, then one should observe a 'hockey stick' type curve in the surface tension measurements in water.

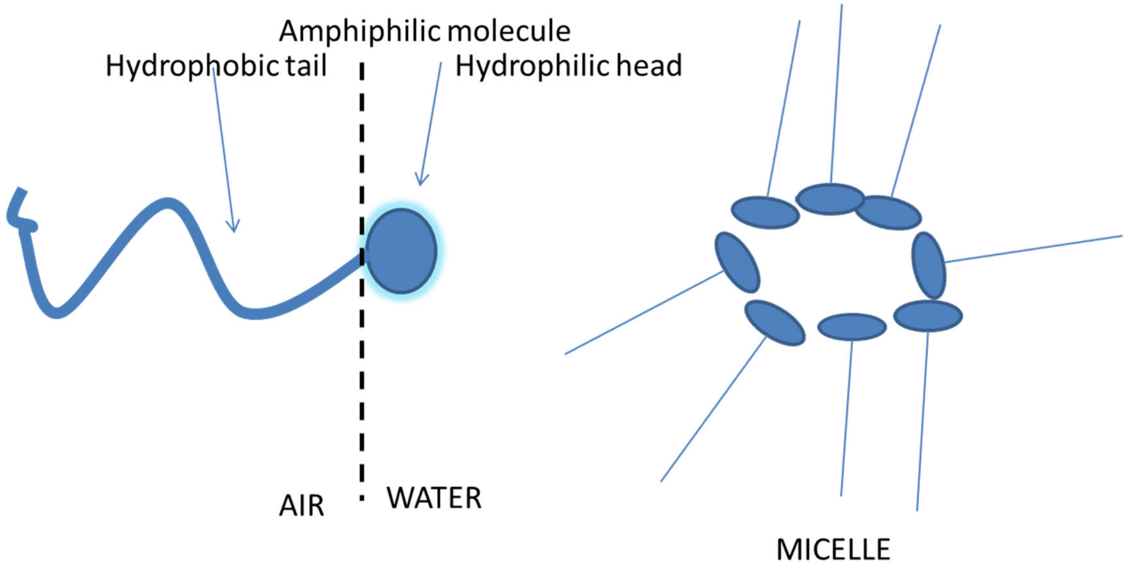
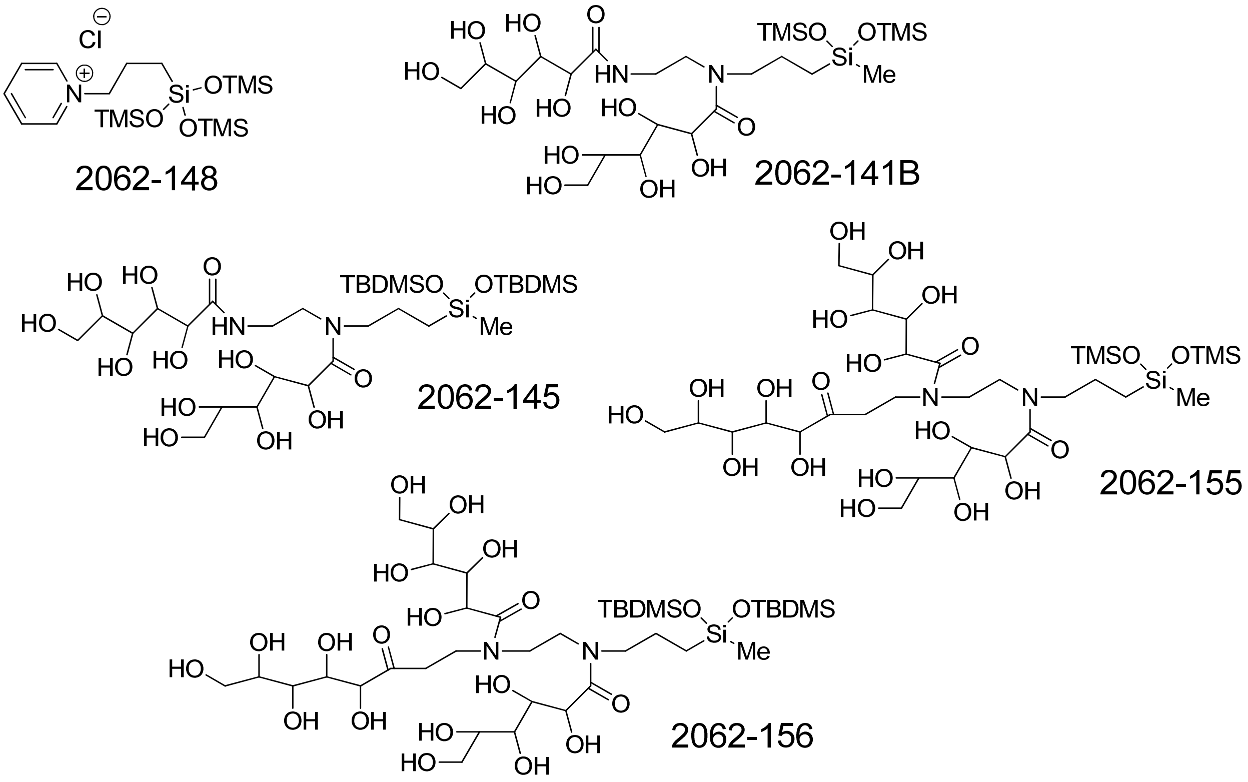


Figure 73 General structure of surfactant in water solution and behaviour when at the CMC.

Although instrumentation for conducting surface tension measurements were available on site, it was difficult to find colleagues to perform these analyses at China Lake. Fortunately, Art Snow Ph. D. at NRL kindly made time from his research endeavors to carry out these important measurements for the project. The surface tension measurements were made by the Wilhelmy plate method and the general procedure for the analysis followed the descriptions of Professor Christopher Rulison.[45] The surface tension data Art Snow collected at NRL is presented in this section of the report. The structure of these six siloxane surfactants, compounds 2062–: 139, 141B, 145, 155, 156, and 148, which were measured are shown in Figure 74. The surface tension curves for the compounds are shown in Figure 75–78.



2062-148

2062-141B

2062-145

2062-155

2062-156

Figure 74 Chemical structures of the siloxane surfactants tested for surface tension.

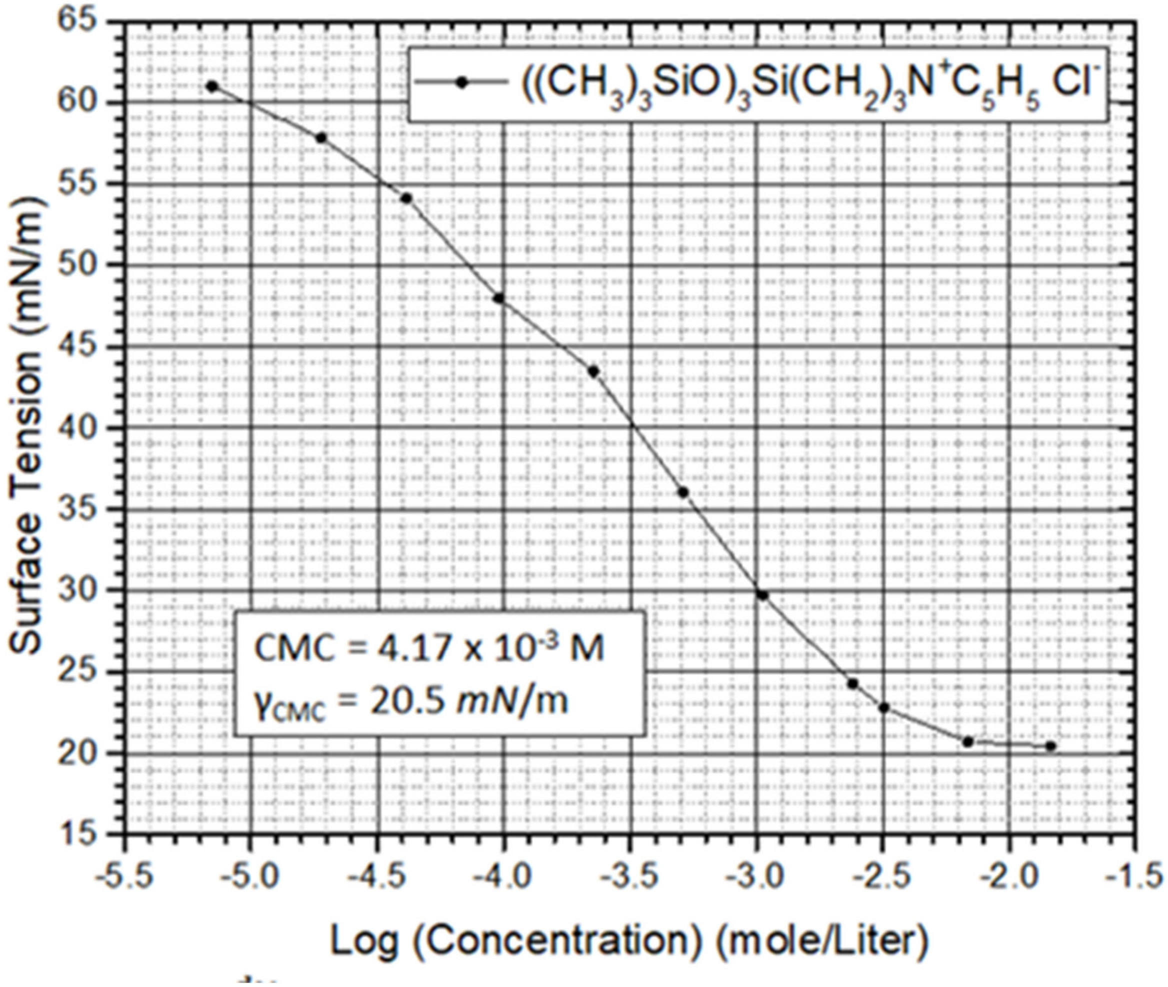


Figure 75 Surface tension data (mole/L) for surfactant 2062–148.

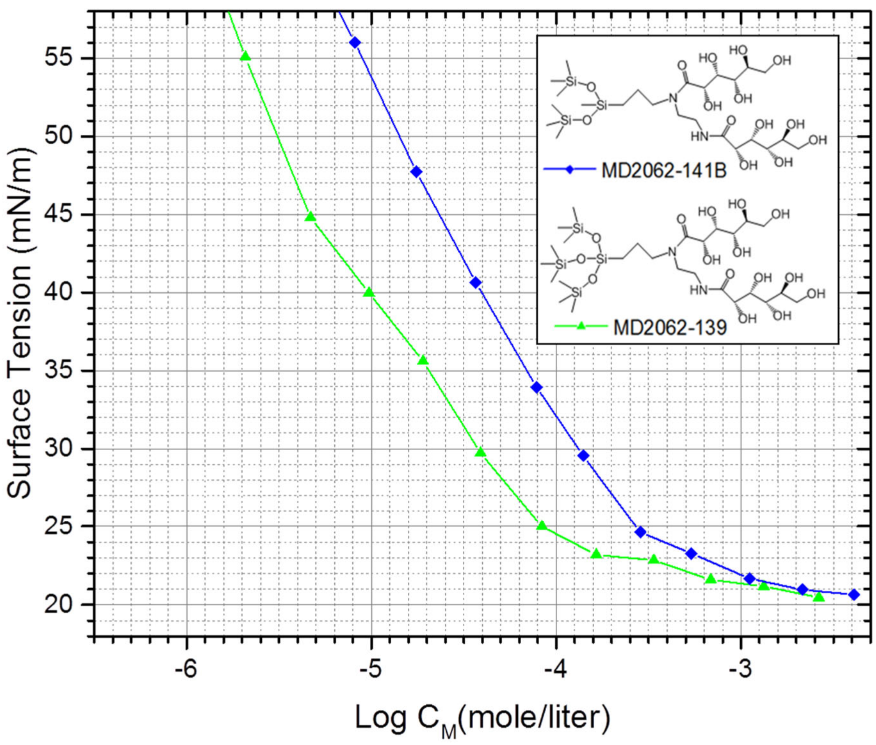


Figure 76 Surface tension data (mole/Liter) of 2062–141B and 2062–139.

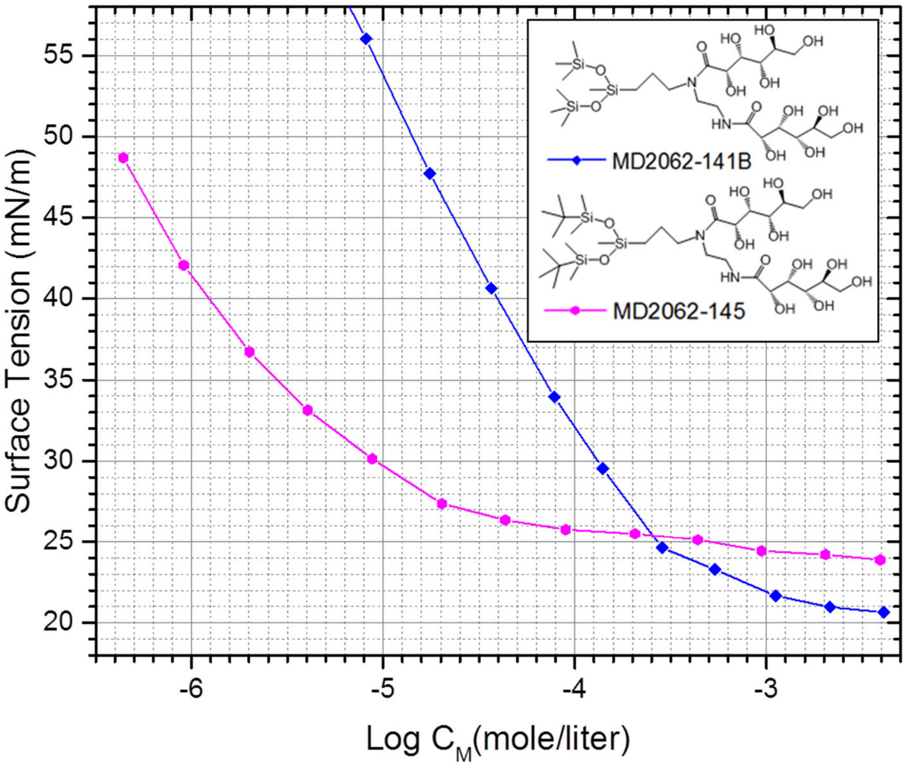


Figure 77 Surface tension data (mole/L) of 2062–141B and 2062–145.

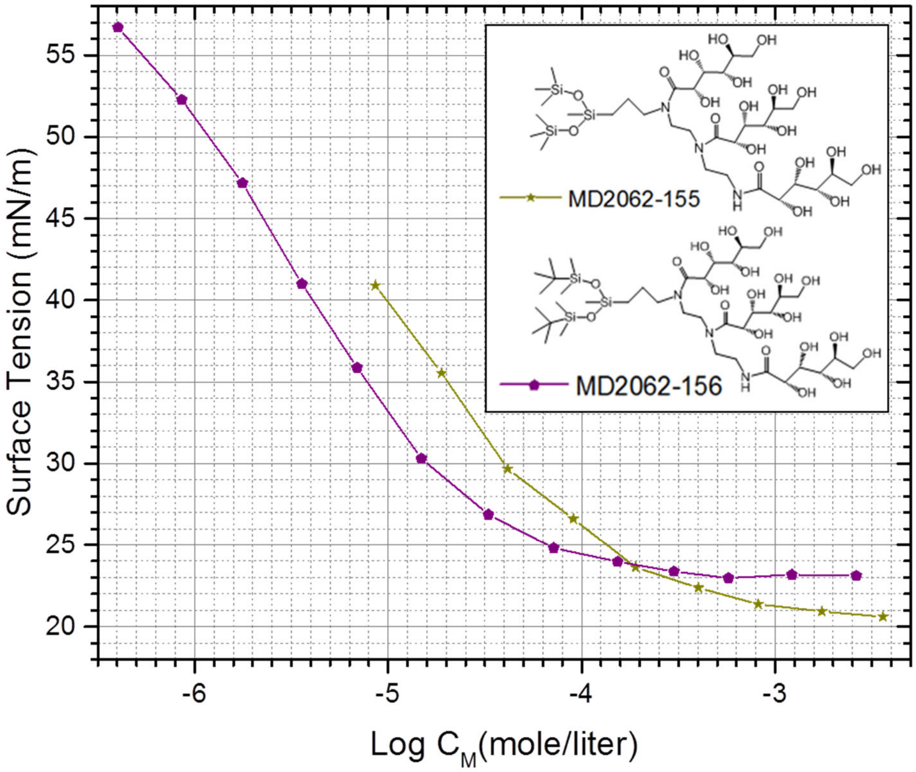
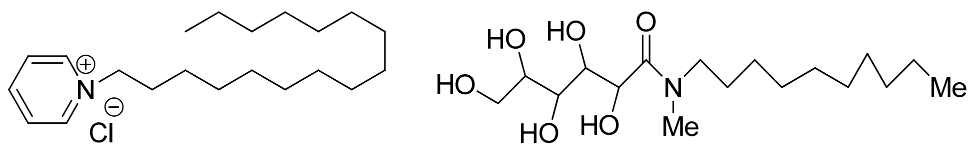


Figure 78 Surface tension data (mole/L) for 2062–155 and 2062–156.

The surface tension measurements confirm the empirical observations that each of the compounds behaves as a surface tension depressing agent or surfactant in water, Table 6. The surfactants had surface tension at the CMC (γ_{CMC}) between 26.4 and 20.5 mN/m. The ratio of surfactant to water (g/Kg) at CMC was between 0.019 and 5.25 for the surfactants tested. The value for the pyridinium salt 2062–148 was surprisingly high (5.25 g/Kg), at least one of magnitude higher than the other surfactants test. However, this value for 2062–148 was similar to other pyridinium salt surfactants such as cetylpyridinium chloride (CPC) with CMC ~0.34g/Kg, Figure.[46] The molarity (M) of the nonionic siloxane surfactants were in the range of 0.26×10^{-4} and 3.8×10^{-4}. These nonionic siloxane surfactants were more powerful surfactants than their hydrocarbon analogs such as N-decyl-N-methylgluconamide (DMGA) (γ_{CMC} = 36.1 mN/m and CMC = 0.45 g/Kg), Figure 79.[47]

Table 6 Surface tension and CMC data for aqueous solutions of project surfactants.

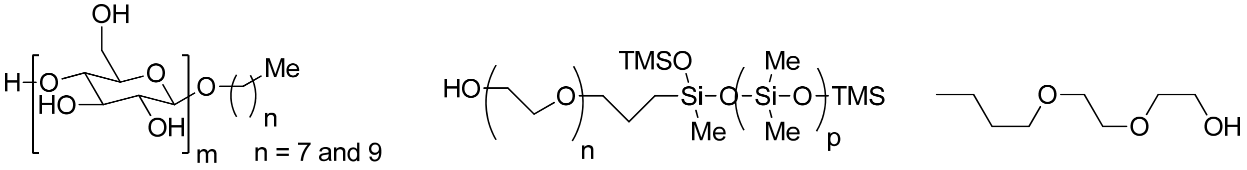
Surfactant (2062–)	γ_{CMC} (mN/m)	CMC (g/Kg)	CMC (M)	Molecular weight
139	23.4	0.079	1.0×10^{-4}	753
141B	22.3	0.26	3.8×10^{-4}	679
145	26.4	0.019	0.26×10^{-4}	763
155	22.0	0.24	2.7×10^{-4}	900
156	24.0	0.033	0.32×10^{-4}	984
148	20.5	5.25	4.17×10^{-3}	452.3



CPC DMGA

Figure 79 Hydrocarbon analog structures of siloxane surfactants.

The ability of a surfactant solution to spread on the surface of hydrocarbons may be critical to a successful non-fluorinated film foaming and ultimately extinguishment of hydrocarbon pool fires. The current military specification (MIL-F-24385F) for AFFF requires that the fire-fighting foam must have a positive spreading coefficient on the surface of cyclohexane (24.95 mN/m at 20 °C).[48] Often this measurement can be made by interfacial surface tension instrumentation, however, in this short SEED project there was not sufficient opportunity to come up to speed on these analytical techniques. Therefore, a simple empirical approach was taken by carefully applying droplets of the aqueous solutions of the surfactants onto cyclohexane (~3 mL) contained in a low-profile Petri dish.[49] As mentioned earlier, several groups have already shown that siloxane surfactants work best in fire fighting foam applications when combined with a hydrocarbon surfactant and solvent. Our colleagues at the Naval Research Laboratory found positive results with a mixture of DOWSIL 502W, Glucopon 225DK and diethyleneglycol monobutyl ether (DGBE) in suppression of heptane pool fires, Figure 80.[50]



BASF Glucopon 225DK Dow Corning DOWSIL 502W DGBE

Figure 80 Synergistic combination of siloxane and hydrocarbon surfactants effective for extinguishing heptane pool fires discovered by scientists at the Naval Research Laboratory.

The exact chemical explanation why each surfactant alone can't extinguish the same heptane pool fire is not clear at this time. Since there was a sample of Glucopon 225DK available courtesy of our NRL colleagues, mixtures of the siloxane surfactants from this project, 225DK and DGBE were studied in spreading on cyclohexane. The aqueous solution of the surfactants were dyed by adding blue #1 powder (~5 mg), a common food coloring, to help in visualization since the solutions were generally clear and nearly colorless. A digital camera was used in an attempt to document as best as possible the dynamic nature of the experiment since the surface of the liquid was at the mercy of the air currents in the laboratory. To obtain familiarity with the experiment, the results of settings droplets of an aqueous solution of 502W/225DK/DGBE onto cyclohexane is shown in Figure 81. One can see the sharp blue spheres are where droplets of the aqueous solution have penetrated and fallen through the layer of cyclohexane. But there was also a droplet which spread out on the surface of the cyclohexane which became very light blue in the process. This spreading phenomenon is the desired effect that the siloxane surfactant will impart to the surfactants solutions.

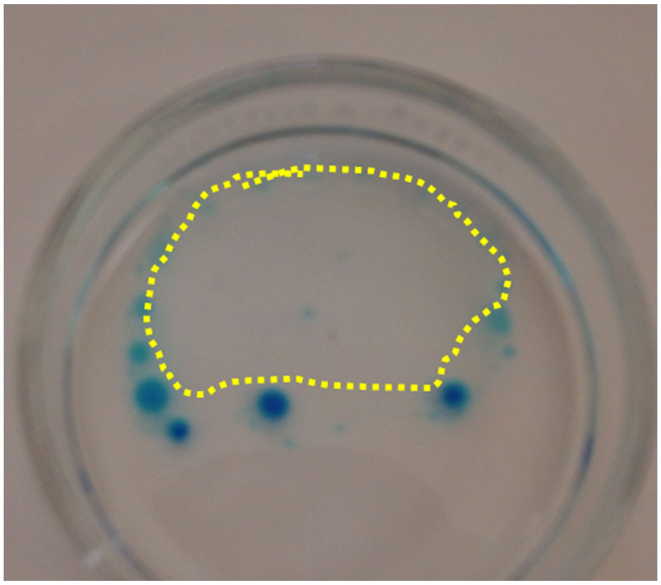
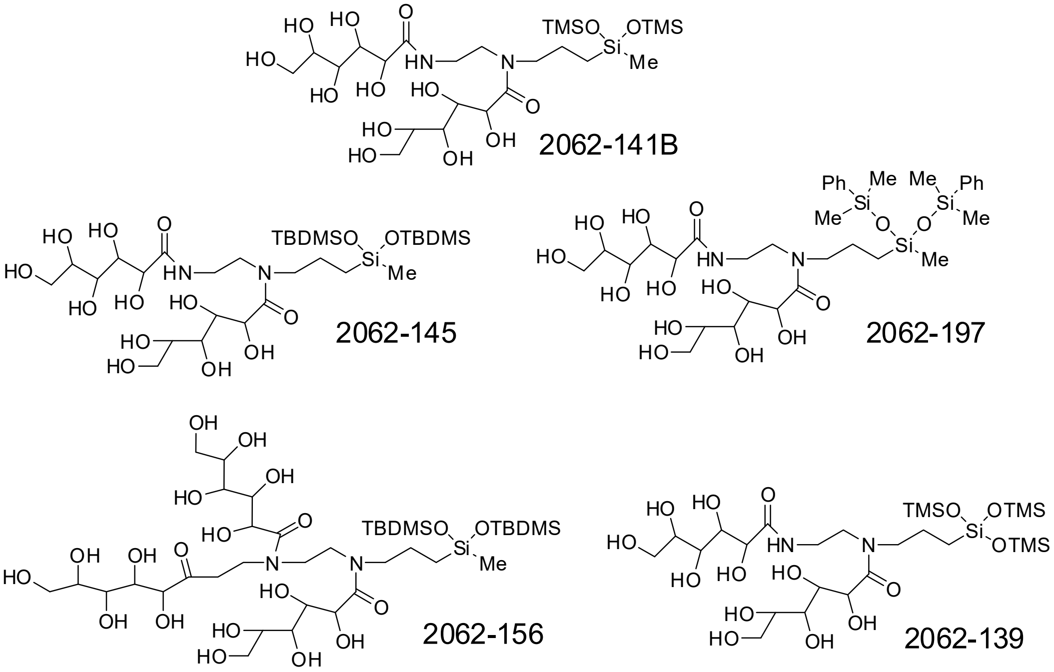


Figure 81 Behaviour of droplets of aqueous 502W/225DK/DGBE on cyclohexane, the spreading of a droplet was light blue in color and difficult to see but was annotated on the photograph.

Five of the siloxane surfactants made during the project were tested for spreading on cyclohexane were 2062–: 139, 141B, 145, 156, and 197, Figure 82. The results of the spreading experiments are shown in Figure 83.



2062-141B

2062-145

2062-197

2062-156

2062-139

Figure 82 Chemical structures of siloxane surfactants tested for spreading on cyclohexane.

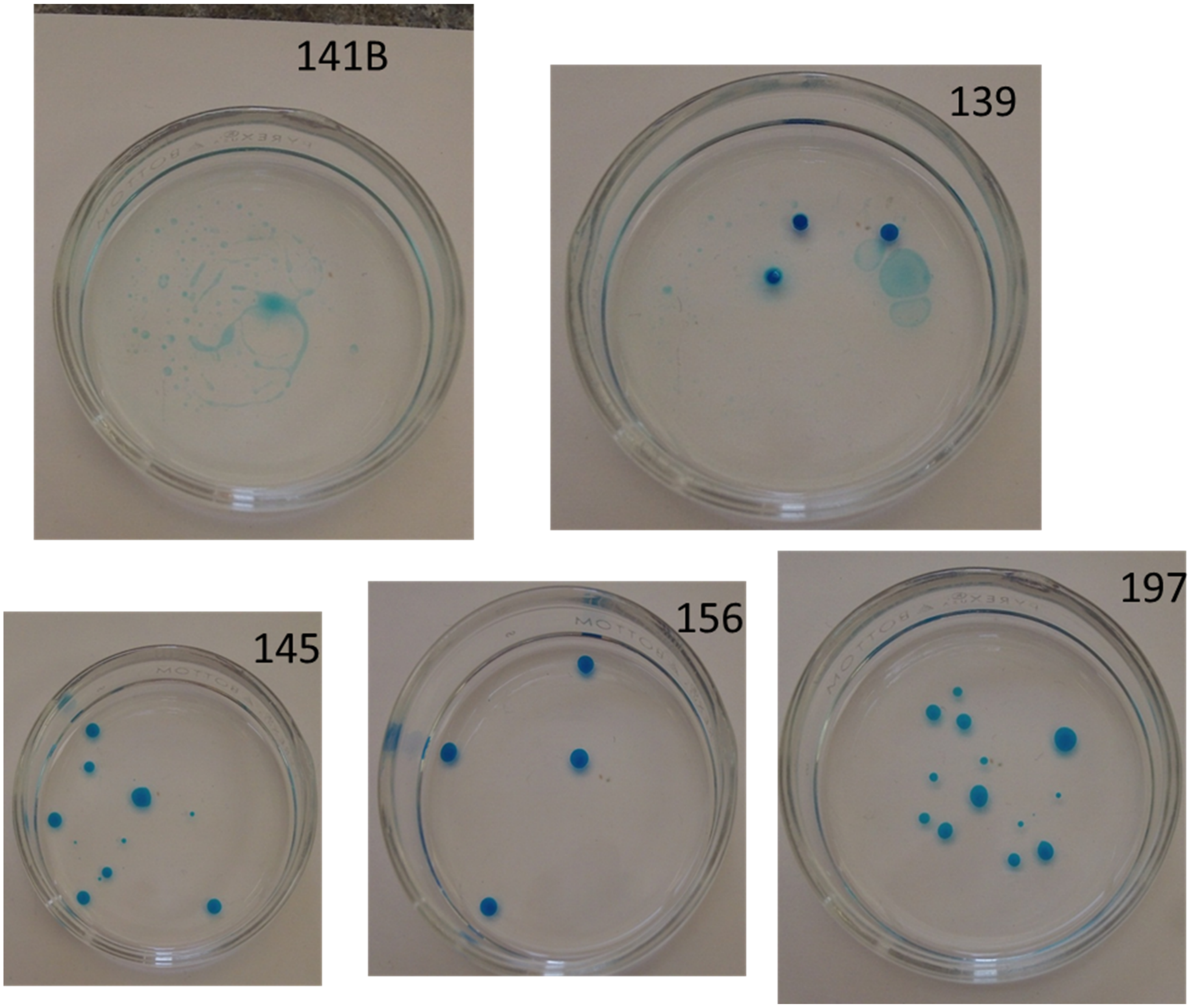


Figure 83 Spreading behaviour of droplets of aqueous solutions of siloxane surfactants 2062–X/225DK/DGBE on cyclohexane in a Petri dish.

As can be seen from the photographs, the siloxane surfactants which appeared show spreading were 2062–139 and 2062–141B which were both trimethylsilyl terminated siloxanes. In contrast, the other three siloxanes with *tert*-butyldimethylsilyl or phenyldimethylsilyl terminations did not display spreading behaviour in this experiment.

For fire extinction tests, it was decided to test the simplest hydrolysis resistant siloxane surfactant to synthesize and so the scale-up of 2062–145 was carried out. Technically this was only a three step synthesis, however since the *tert*-butyldimethylsilanol was not commercially available in bulk quantities, its preparation had to be taken into account. Thus, the overall synthesis of this surfactant required four synthetic steps. The yields for these steps after scale-up are shown in the Figure 84 and the overall yield of the synthesis was 49% and gave 180 grams of product with which to experiment. In addition, the tetrasiloxane 2062–139 was also synthesized at larger scale (~96 grams). A photograph of these two products is shown in Figure 85.

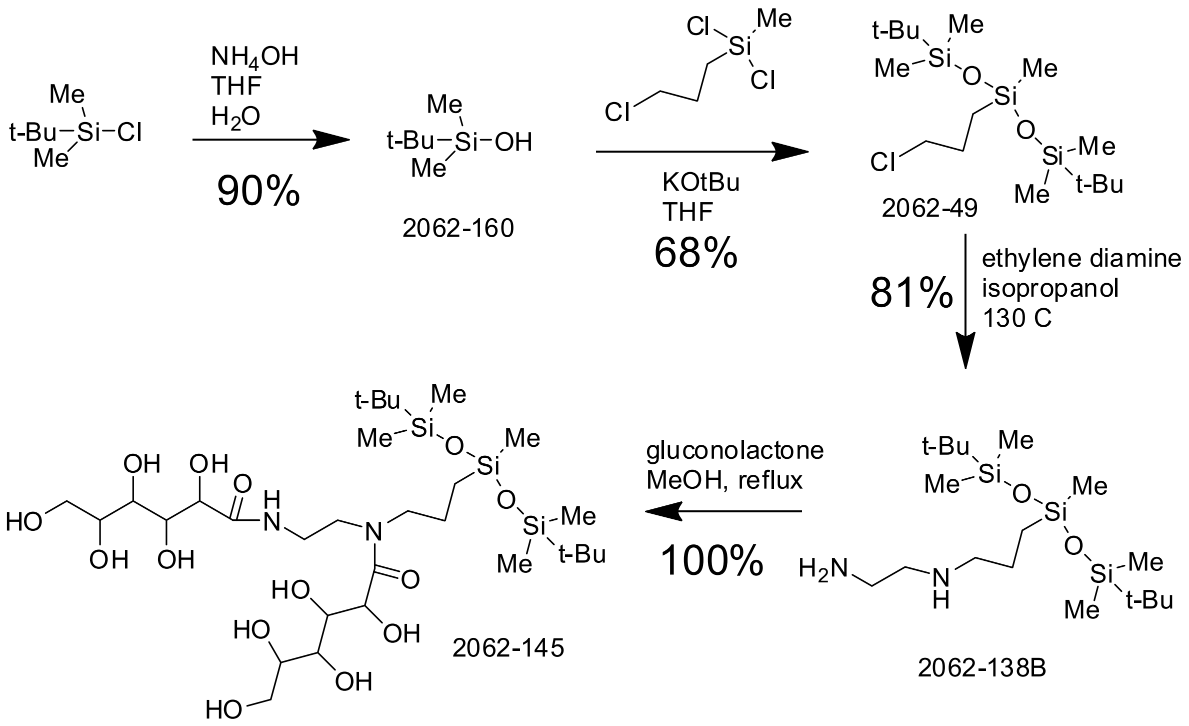


Figure 84 Overall synthetic process and yields to scale-up 180 grams of siloxane surfactant 2062–145.

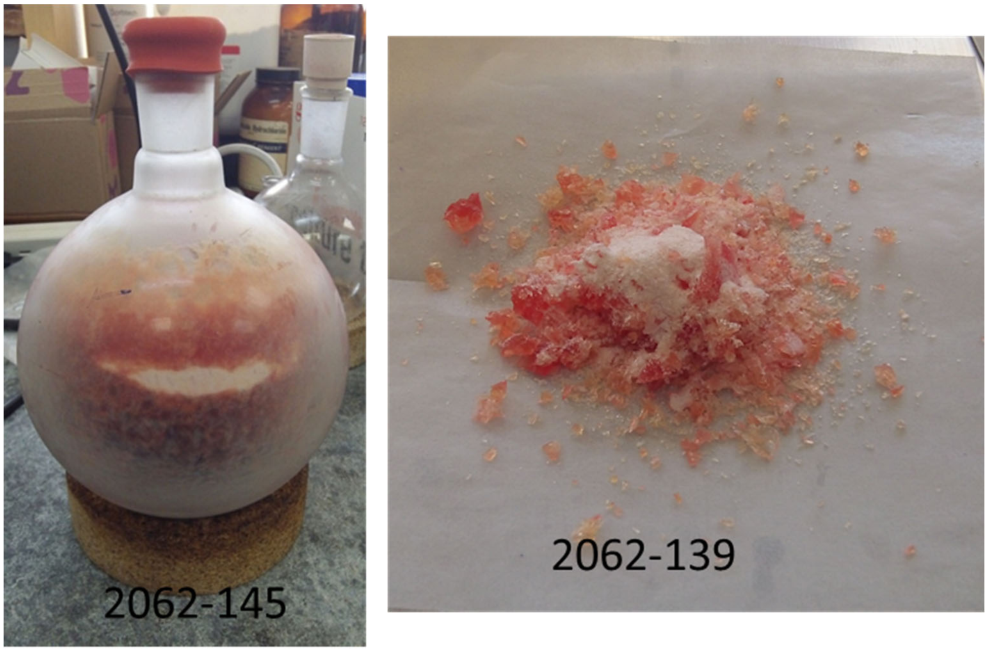


Figure 85 Over 180 grams of hydrolysis-resistant siloxane surfactant 2062–145 and 96 grams of tetrasiloxane surfactant 2062–139 were synthesized for fire-extinction testing.

An important chemical detail discovered during the scale-up campaign was that the quality of the potassium *tert*-butoxide base was critical for optimal yield of the 3-chloropropylmethylbis(*tert*-butyldimethylsilyl)silane. Potassium *tert*-butoxide is not only hygroscopic but can also react with carbon dioxide, Figure 86.[51] It is hypothesized that samples of this base when stored under ambient conditions for long periods of time had undergone significant CO_2-absorption.

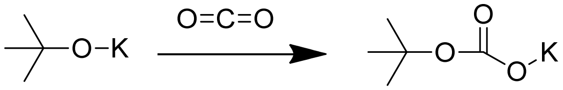


Figure 86 When stored under ambient conditions, potassium tert-butoxide may undergo slow absorption of carbon dioxide from the atmosphere becoming a less effective base.

The hydrocarbon pool fire extinguishment testing was carried out by Eric Sievert, Jason Lint and Ross Davidson from Fire Science of the Combustion Science Branch at NAWCWDCL. They have access to a large burn room which is an enclosed building with an air scrubbing system and an oil/water system to allow for indoor pool fire testing under a controlled environment. The facilities were equipped with appropriate personal protective safety equipment (e.g. Building air-scrubber, breathing apparatus, firefighting ensembles) specific to firefighting. The military specifications (Mil Spec) for testing AFFF solutions indicates a twenty-eight square foot pan fire of gasoline with an agent application rate of 2 gallons per minute (GPM) for the tests. Such a large pan would necessarily require large volumes of surfactant solution and thus large quantities of experimental surfactants. In the effort to keep the quantities of materials lower, a 20 inch diameter/2.18 square foot pan was selected for the testing in this project, Figure 87. The 20 inch diameter/2.18 square foot pan was jacketed with a secondary pan fitted with inlet/outlet for cooling water, so the inner pan was filled with fuel while the outer pan was filled with water. The jacketed 20 inch diameter/2.18 square foot pan with cooling was important since a standard metal pan will become warped (e.g. ‘potato chipped’) over time from the enormous heat emitted from hydrocarbon pool fires. The jacketed pan was also set inside a larger forty-five inch diameter pan to contain any resulting splashes during testing.

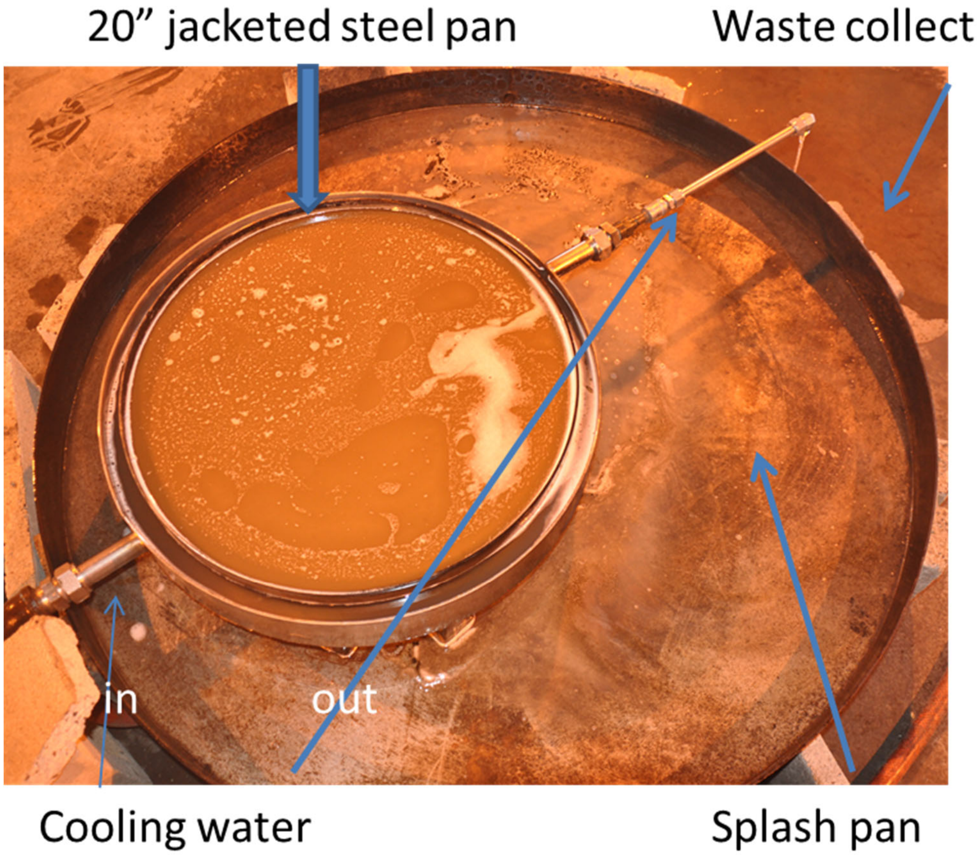


Figure 87 Twenty inch diameter/2.18 square foot jacketed steel pan used in pool fire extinguishment testing.

Another deviation from the military specification was that jet fuel (F24) was used as the hydrocarbon pool fire rather than gasoline, since the latter is probably the most difficult hydrocarbon fuel to extinguish. The F24 jet fuel is similar to JP8 only that it does not contain the stabilizers and other additives.[52] An inexpensive and widely available five gallon paint pot (e.g. www.amazon.com) was adapted and used to generate and deliver foam in the pool fire extinguishment tests Figure 88. The air regulated paint pot had air inlet which was pressured with regulated shop air to push unaerated foam solution through the outlet line from the paint pot to the nozzle. There are air pressure gauges both on the paint pot, to measure safe working pressures, as well as the shop air supply line to measure max pressure into the paint pot. An in-line regulator between the paint pot tank and the agent supply line was also in place to accurately control and measure the pressures and foam flow rates at the nozzle

Figure 88 An inexpensive, air regulated generic five gallon pressure paint pot was adapted and used to generate and apply surfactant solutions in pool fire testing.

Although the paint pot had an internal mixing paddle, it was not necessary to use any internal mixing since the siloxane surfactant solutions were clear, stable solutions without phase separation and free from particulates. The foam solutions prior to being dumped into the paint pot were thoroughly mixed by hand and were used immediately to prevent any potential settling. The hose coming from the paint pot was 1/2" diameter steel braided hose. It was decided to purchase BETE standard brass fan nozzles (NF-04 and NF-025) both with a 30° spray angle which were fitted to the end of the hose with coupling adapters and a shutoff ball valve, Figure 89. The liquid filled, bourdon tube pressure gauge was a special calibrated unit that read to ± 1 pounds/in^2 (psi) manufactured by WIKA. This pressure gauge allowed for more precise control of the flow rate at the nozzle.

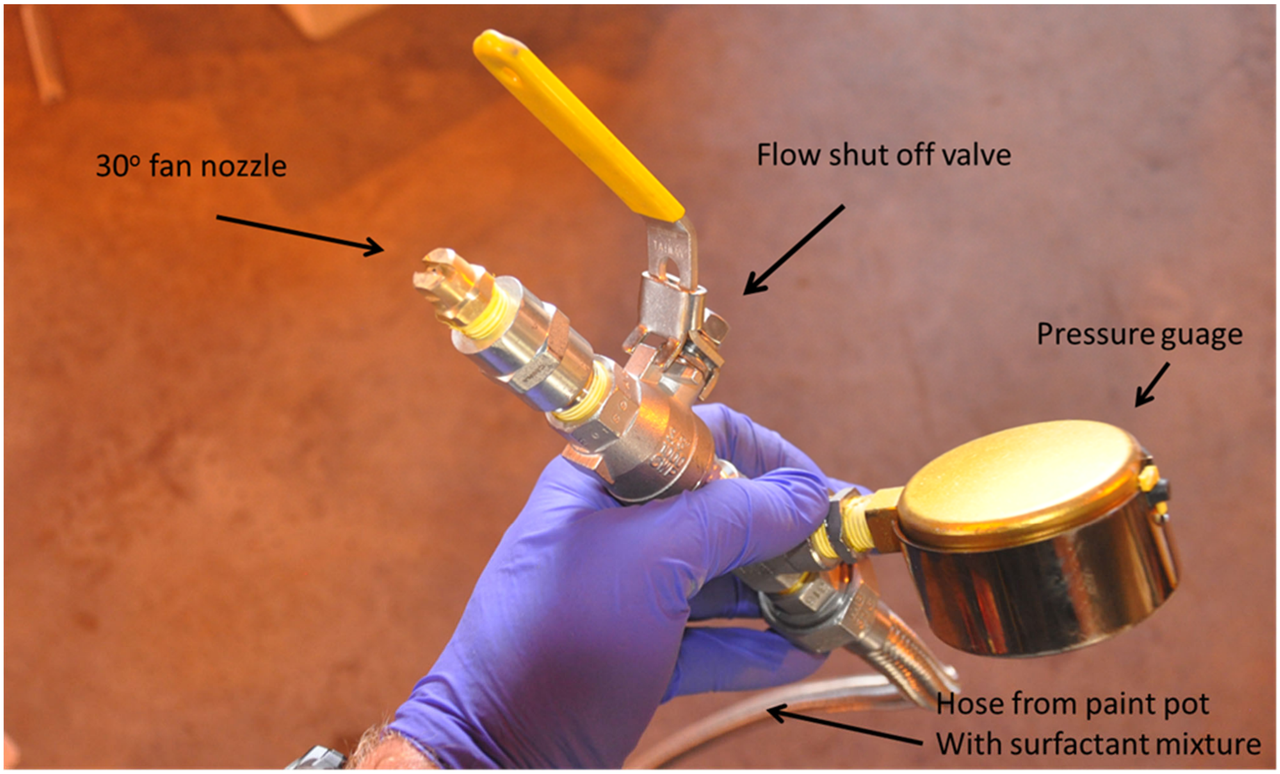


Figure 89 The simple fan nozzle (NF025) for surfactant solution delivery to pool fire.

The foam application rate must be matched to the size of the pan fire so in this case scaling down was necessary. This comparison was made using the data (e.g. application rate) already given for the twenty-eight square foot pan fire data found in the military specification for AFFF. The BETE fan nozzle was carefully chosen after calculating the proper scaled-down flow rate based on twenty square inch pan fire, Tables 7 and 8. The target flow rate for the scaled down pan size was determined to be ~ 0.153 gallons per minute (GPM). This was important because using a nozzle with higher flow rate could lead to false positive results. Nozzle NF04 was used for higher flow rate tests, tests ES1#3 and ES1#4, and nozzle NF025 was used in all other tests. The flow rates of the individual BETE nozzles and specific nozzle configuration, e.g. CAFS, Screen Tip (ST), was tested and proven reliable by matching the working gauge pressures near the nozzle while timing the liquid fill rate in graduated cylinders (1 L).

Table 7 BETE NF025 fan nozzle tested flow rates from the manufacturer's specifications.

		NF025 Nozzle Gallons per minute @ psi						
Nozzle Configuration	K factor	11	12	13	14	15	16	Equiv. orifice Diam. (in)
Simple Fan Nozzle	0.0632	0.14	0.20	0.25	0.28	0.35	0.40	0.040

Simple Fan Nozzle Only	0.0395	.149	.153	.158	.161	.173	Not Tested	0.040
Fan Nozzle/CAFS & w/ST	0.0395	Not Tested	Not Tested	Not Tested	.148	.153	.161	0.040

Table 8 BETE NF04 fan nozzle tested flow rates from the manufacturer's specifications.

		NF04 Nozzle Gallons per minute @ psi						
Nozzle Configuration	K factor	20	21	22	22.5	23	23.5	Equiv. orifice Diam.
Simple Fan Nozzle	0.0632	0.142	0.147	0.150	0.151	0.153	0.155	0.052”

An 8 L solution of the hydrolysis-resistant siloxane surfactant 2062–145 was made for testing. In addition to the siloxane, there was also DGBE and the hydrocarbon surfactant BASF glucopon 225DK in the mixture, Table 9. There was no issue in dissolving the three components in water which resulted in a clear solution that was free from any particulate matter, Figure 90.

Table 9 Composition of experimental siloxane surfactant solutions used in pool fire testing.

Component	Quantity	Ratio additive to total solution (g/Kg)
DGBE	41.4 mL	5
Glucopon 225DK	24 grams	3
2062–145 or 2062–139	16 grams	2
Distilled H_2O	8 L	

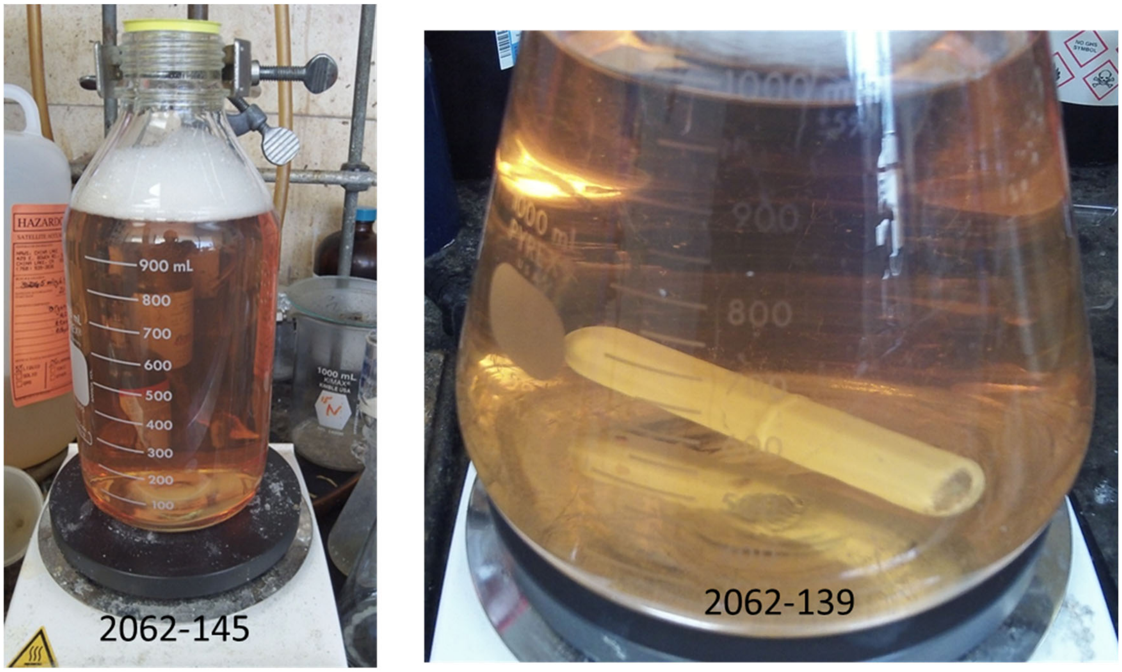


Figure 90 The siloxane surfactant mixture 2062–145/225DK/DGBE (left) and 2062–139/225DK/DGBE (right) after dissolving in 1 L water, the concentrates would then be delivered to Fire Science where they were brought up to a total of 8 L with water before loading into the paint can chamber.

The standard procedure for the F24 pool fire tests was to fill the pan with water then add a layer of JP8 on top of the water layer. The F24 layer was carefully measured to be 3/8" deep and gave a ¼" freeboard or free space above the layers of liquid, Figure 91. The fuel was then ignited with a torch and the fuel was allowed to become fully involved. Once fully involved a 10 second pre-burn time was observed before foam solution was applied. The instant foam solution touched the pool fire was time zero by stopwatch. The time when 90% as well as 100% of the pool fire was extinguished were both recorded. Because of the preliminary nature of the project, burnback experiments were not performed at this time.

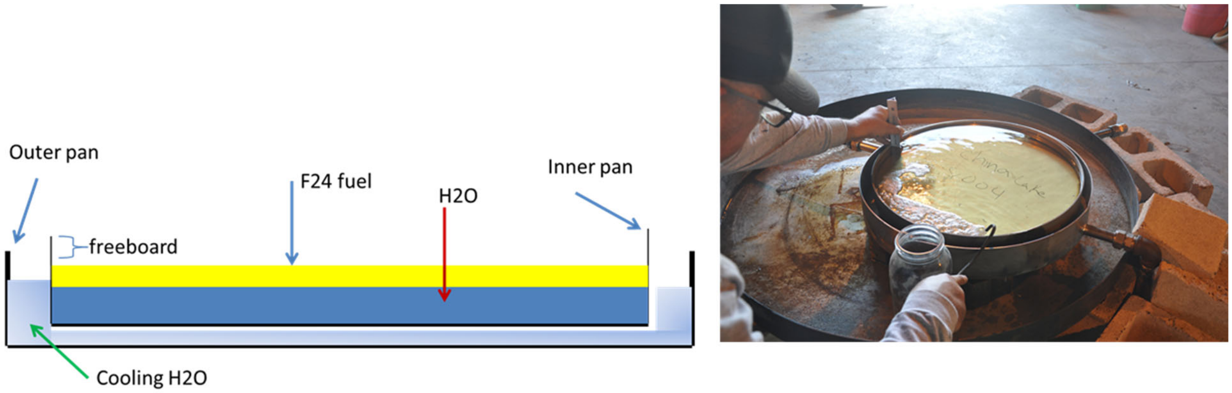


Figure 91 Schematic representation of the hydrocarbon pool fire setup (left) and carefully filling the inner fire pan with F24 fuel to the freeboard level (right).

In other experiments, the surfactant solutions were applied to the pool fire by a low flow compressed air foam systems (CAFS). The CAFS has the advantage that it can generate foams with a range of consistencies from the same surfactant solution based on the addition of supplemental air.[53] The CAFS used the NF024 nozzle with an additional water faucet style screen at the tip. The CAFS assembly is shown in Figure 92.

There is an additional hose to bring compressed air to the nozzle assembly and the air is mixed with the surfactant solution just before the outlet tip of the assembly. There are two check valves, one each for the air and surfactant lines to prevent any backflow in the system. There was also a valve on the compressed air line to adjust airflow into the mixing chamber to change the foam characteristics. The mixing chamber was simply made by extending the 1/8th" 316L stainless steel into the center of the stainless steel pipe tee fitting and bent forward so that the air would be dispersed directly into the surfactant solution and toward the nozzle opening, Figure 93.

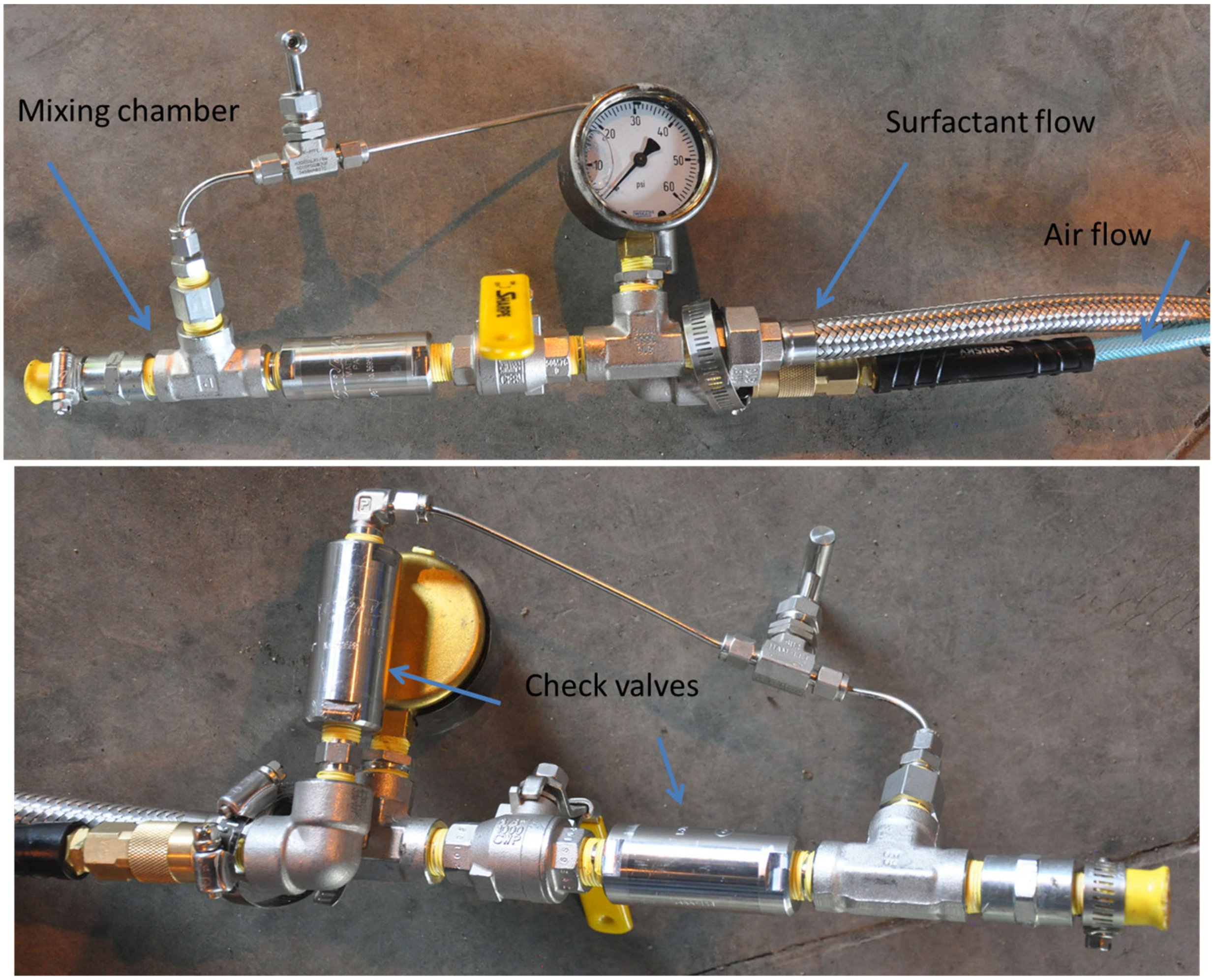


Figure 92 Front and rear views of the CAFS adapter for delivery of surfactant solution to pool fires.

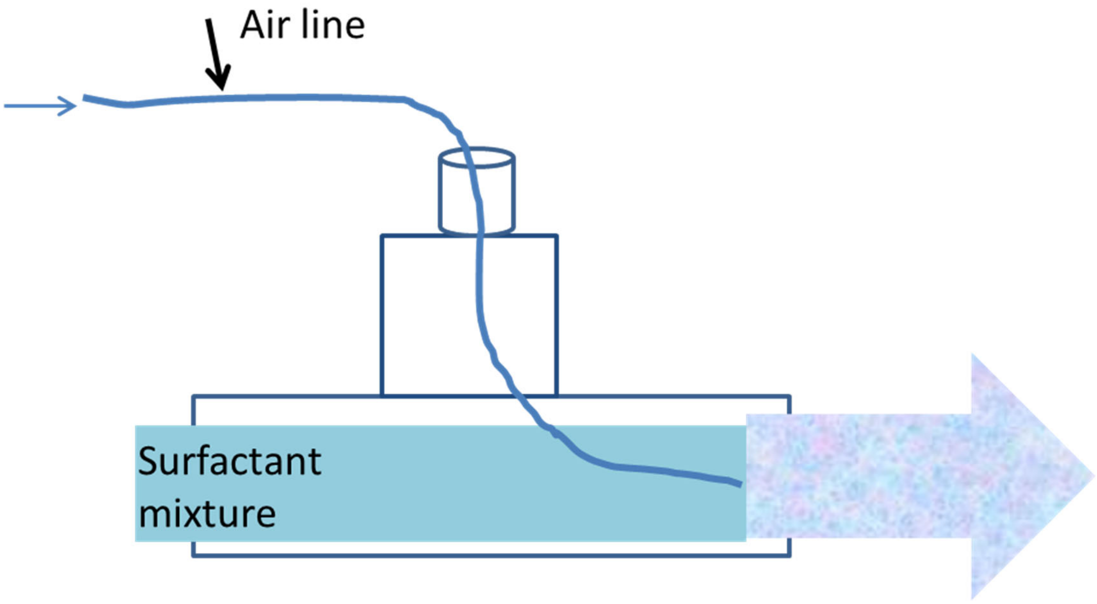


Figure 93 Schematic representation of the mixing chamber of the CAFS nozzle which helps to further aerate the surfactant mixture creating smaller bubbles and better quality foam.

The low-flow CAFS system developed by Fire Science produced foam expansion with the experimental foams that were slightly lower (2.58/1) but consistent with the foam expansion of the Mil Spec AFFF foam (3.09/1) expansion tests, Table 10. One can see that there was an improvement in the quality of the agent foam and its expansion when the CAFS was used. It was also shown that the siloxane 2062–145 had a positive improvement on the expansion ratio of the foam (2.58/1) in contrast to the mixture without the siloxane (2.31/1).

Table 10 Average foam expansion ratios.

Agent and Specific Nozzle Hardware	Foam Expansion Ratio
AFFF w/o CAFS and with Spray Tip (ST)	2.98/1
AFFF w/ CAFS and ST	3.09/1
145/225DK/DGBE w/o CAFS and w/ ST	2.29/1
145/225DK/DGBE w/ CAFS and ST	2.58/1
225DK/DGBE w/ CAFS and ST	2.31/1

Foam expansion and flow rates were measured by timing 100% of the nozzles agent stream flowing into a pre-weighed 1000 mL graduated cylinder cut flush at the 1000 mL gradient, Figure 94. The flow rate was calculated by dividing the agent weight (grams) by the time it took to fill the graduated cylinder (sec). Foam expansion ratio was calculated by dividing the agent weight (grams) by 1000 mL.

Figure 94 Foam expansion test of surfactant 2062–145/225DK/DGBE with 1 L graduate cylinder.

The data collected from the 20” diameter pan fire with F24 fuel with various surfactant solutions included: nozzle type, agent flow rate in gallons per minute (GPM), time to 90% extinguished (seconds), time to complete extinguishment (seconds), application rate (AR) in gallons per minute per square foot (GPM/ft^2), application density (AR/60x(100% extinguish time in seconds)), temperature of the Burnroom (Fahrenheit), relative humidity of the Burnroom and temperature of the surfactant solution (Centigrade). The data for the extinguishment testing is collected in Table 11. Tests 1–4 were baseline experiments using commercial Mil Spec C6 AFFF and the simple fan nozzle NF025 pictured in Figure 92. The AFFF tests showed the agent had no trouble completely extinguishing the F24 pool fire in fifteen seconds or less. When the flow rate was increased slightly to 0.175 GPM, the fire was put out a few seconds faster than the slower rate of 0.153 GPM. There were two flow rates (0.175 and 0.153 GPM) used in the AFFF experiments and the higher rate reached extinguishment slightly faster.

Table 11 20" Pan fire extinguishment testing data with F24 fuel.

Test Number	Agent	Nozzle type	Agent Flow Rate (GPM)	90% out (Sec.)	100% out (Sec.)	Application Rate (**AR**) *GPM/sq. ft.*	Application Density *AR*FF*	Room Temp °F Humidity (%)	Agent Temp °C
T1 Baseline	Mil Spec C6 AFFF 3%	FN025	0.153	12.5	15	0.07	0.017	102.1/12%	37.8
T2 Baseline	Mil Spec C6 AFFF 3%	FN025	0.173	6	7	0.079	0.009	104.8/12.2%	34.2
T3 Baseline	Mil Spec C6 AFFF 3%	FN025	0.153	6.5	9	0.07	0.01	89.2/21.7	32.8
T4 Baseline	Mil Spec C6 AFFF 3%	FN025	0.153	7	9	0.07	0.01	94.5/21.2%	34.2
ES1#1	145/225DK/DGBE	FN025	0.153	220	232	0.07	0.27	98.4/14.3%	34.8
ES1#2	145/225DK/DGBE	FN025	0.158	148	150	0.072	0.18	99.5/18.6%	33.5
ES1#3	145/225DK/DGBE	FN04	0.306	113	113	0.14	0.263	81.9/21.8%	28.1
ES1#4	145/225DK/DGBE	FN04	0.306	59	63	0.14	0.147	81.5/21.4%	28.1
ES1#5	145/225DK/DGBE	CAFS	0.153	150	158	0.07	0.184	93.8/21.2%	32.6
ES1#6	145/225DK/DGBE	CAFS	0.161	65	70	0.073	0.085	94.7/16.7%	32.6
ES1#7	145/225DK/DGBE	CAFS	0.161	40	51	0.073	0.062	95.5/15.4%	32.7
ES1#8	145/225DK/DGBE	CAFS	0.161	51	62	0.073	0.075	96.2/19.6%	33
ES2#9	225DK/DGBE	CAFS	0.161	0	0	0.073	0.324	86.9/29.3	30.5
ES2#10	225DK/DGBE	CAFS	0.161	0	0	0.073	0.324	90.6/29.6	30.5
ES4#15	145/2062-200/225DK/DGBE	CAFS	0.161	0	0	0.073	0.292	95.0/17.1	32.3
ES4#16	145/2062-200/225DK/DGBE	CAFS	0.161	0	0	0.073	0.292	96.8/14.9	32.3
ES5#17	139/225DK/DGBE	CAFS	0.161	9	11.7	0.073	0.014	95.2/14.1	33.7
ES5#18	139/225DK/DGBE	CAFS	0.161	9	10.3	0.073	0.012	99.5/14	33.8
ES5#19	139/225DK/DGBE	CAFS	0.153	8	10.5	0.07	0.012	99.8/14.9	33.8
ES5#20	139/225DK/DGBE	CAFS	0.161	11	12.09	0.073	0.014	100.1/16.1	33.9

Test numbers ES1#1–ES1#8 were the experimental surfactant mixture of 2062–145/glucopon 225DK/DGBE. In runs ES1#1 and ES1#2, the agent was delivered by the NF025 nozzle at about the same agent flow rate (0.153 GPM) as the AFFF runs. As one can see, ES1#1 the fire was not put out until 232 seconds (nearly four minutes). Experience has shown that the surfactant solution had little effect on the fire and the fire may have burned out near the end due to lack of fuel. In experiment ES1#2, the fire was put out faster at 150 seconds (2 ½ minutes) but this was due to a more aggressive firefighting agent application with which the surfactant solution was applied to the fire. In ES1#2, although the application rate and aggressive tactics was essentially the same as in ES1#1, the surfactant solution was delivered at closer range to push the thinning fuel over to one side of the pan, allowing the side walls of the pan to cool. This application technique reduced the severity of the re-flash and allowed the fuel to cool below its flash point. The agent had no real effect on the fire. Although the pan size was rated for a surfactant application rate of 0.15 GPM, it was decided to increase the flow rate for the 2062–145/glucopon 225DK/DGBE mixture to observe any changes. In tests ES1#3 and ES1#4, the surfactant flow rate was doubled to 0.306 gallons per minute by the use of the Simple Fan BETE nozzle NF04 to see if that would have a positive effect on extinguishment. Indeed, the 100% extinguishment times were improved at 63 and 113 seconds (1–1.5 minutes), Figure 95.

Figure 95 Photograph during ES1#3 test with flowrate doubled, showing the fire fighter had to employ multiple tactics with the NF04 nozzle to put the fire out. One can see the very fine spray created from the simple fan DETE NF04 nozzle which did not create very much foam from the nozzle.

During these initial experiments ES1#1–ES1#4 it was noted that the surfactant solution coming out of the Simple Fan BETE NF04/NF025 nozzles did not have a well formed or thick foam quality. Although the AFFF solution had similar consistency when used with the NF025 simple fan nozzle, it had no trouble putting out the fire indicating how well fluorinated surfactants work in firefighting foams. In an effort to improve the quality of the foam that was delivered to the pool fire, it was decided to try applying the 2062–145/glucopon 225DK/DGBE with the low flow CAFS nozzle (NF025) with a Screen Tip to help generate bubbles. The screen tip was a simple plastic sink faucet screen glued in place with 5 minute urethane epoxy into a molded plastic cylinder secured over the NF025 nozzle. In test ES1#5, the flow rate was brought back down to the 0.153 GPM rate for the 20” diameter pan. The fire was extinguished in 158 seconds (2.6 minutes). It was noted that the introduction of the CAFS systems improved the firefighting capability of the agent by improving the generation and quality of the bubbles. The fire test team noted that if the flow rate was increased slightly by 1 psi that fire extinguishment would be obtainable. Therefore, the flow rate was increased a small amount (1 psi) to 0.161 GPM to compensate. This slight increase in flow rate had a dramatic impact on bubble quality, generation and accumulation. Fire extinguishment as can be seen in tests ES1#6–ES1#8, where the 100% extinguishment times were 70, 51 and 62 seconds, respectively, Figure 96. The experimental surfactant solution, CAFS nozzle with screen tip and slightly elevated flow rate made for fairly reproducible extinguishment times of about 1 minute. To determine the impact that the siloxane surfactant had on the surfactant mixture, the final two runs ES1#9 and ES1#10 used the surfactant mixture made from 225DK/DGBE without the siloxane present. Even by delivering this mixture of surfactant with CAFS and the ST to the pool fire, there was no extinguishment of the pool fire in either of the runs even up to four minutes application time. These final two experiments clearly demonstrated that the siloxane surfactant 2062–145 had a real and positive impact on the firefighting ability of the foam mixtures.

Figure 96 Photograph during ES1#6 test showing the CAFS nozzle in action, the fire fighter could stand in one spot and put out the fire with the better quality foam created by the CAFS nozzle.

The phosphine oxide 2062–200 was also tested as an additive with the surfactant mixture with 2062–145. The ratio of the ingredients for the test with the phosphine oxide are shown in Table 12. Two runs were made (ES4#15 and ES4#16) and it was found that this mixture failed to extinguish the fire in over four minutes in either run. This was a curious result in that the expectation was that there would be extinguishment in around 60 seconds if the phosphine oxide additive was not active and simply a spectator. Instead, it appeared that the phosphine oxide 2062–200 caused the whole mixture to become useless at fire extinction. It was noted that this particular surfactant mixture was made up and stored at ambient temperature for three days before use.

Table 12 Ingredients of surfactant mixture with phosphine oxide 2062-200.

Ingredient	amount
2062–200	34 g
2062–145	16 g
Glucopon 225DK	24 g
DGBE	41 mL
Water	8 L

Also tested with the tetrasiloxane surfactant 2062–139 which had trimethylsilyl termination of the siloxane. This surfactant dissolved in water slowly but completely and was made into a solution with 225DK and DGBE, Table 13 and Figure 97. Remarkably, this surfactant mixture was able to extinguish the fire with an average of just over 11 seconds between three separate runs, ES5#17, ES5#18 and ES5#20. The flow rate for the 2062–139 mixture was slightly higher (0.161 GPM) than the milspec tests (0.153 GPM). But the difference in application rates was very small (5%). Be that as it may, the extinction times of the 2062–139 and AFFF experiments were both the same (11 seconds), Figure 98. In fact, one run was made (ES5#19) with the 2062–139 mixture at 0.153 GPM application rate and the fire was put out in 10.5 seconds.

Table 13 Ingredients of surfactant mixture with 2062–139.

ingredient	amount
2062–139	16 g
Glucopon 225DK	24 g
DGBE	41 mL
water	8 L

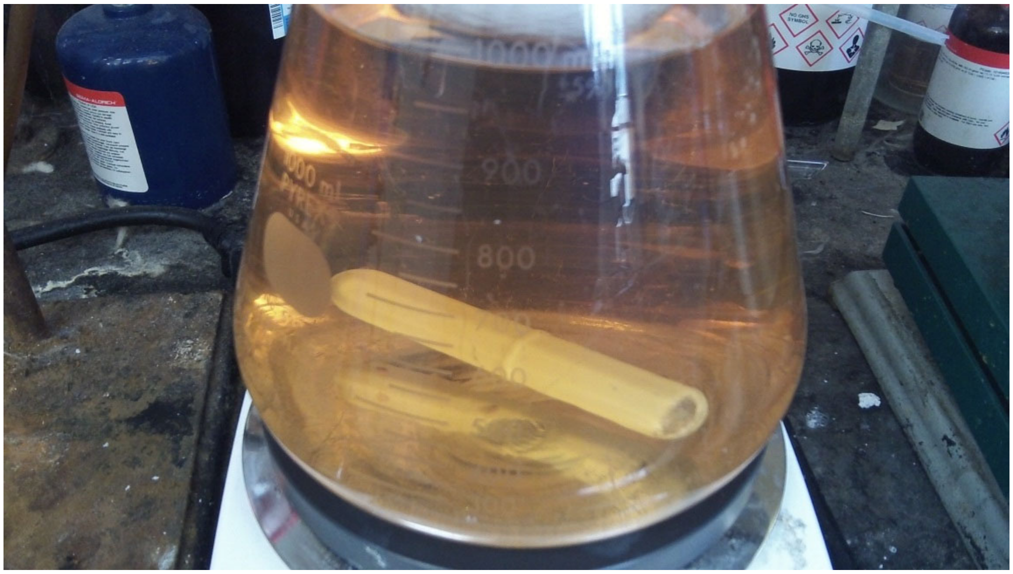


Figure 97 The surfactant mixture made from 2062–139/225DK/DGBE was a completely soluble composition in water.

Figure 98 Fire extinguishment experiment with 2062–139/225DK/DGBE in water. The mixture was able to extinguish the 20 square inch F24 pool fire in an average of 11 seconds.

Conclusions and Implications for Future Research

Several siloxane surfactants with new and unreported structures were synthesized during this SEED project. These new siloxanes had structures which incorporated tert-butyldimethylsilyl (TBDMS) groups as the terminating group of the siloxane portion. The chemical synthesis route to make these new siloxanes was fairly simple. The key part of the synthesis was the derivatization with polyalkylamines. The polyaminoalkylsiloxane could be reacted with the proper amount of aldonic acids to make the siloxane surfactants water soluble. The empirical studies of hydrolysis showed that the TBDMS siloxane surfactants had greatly improved stability to water in comparison with the trimethylsilyl analogs. Since the chemical synthesis was rather simple, a large quantity of the new siloxane surfactant 2062–145 was made. A simple CAFS fire fighting nozzle was assembled with flow rates matched to the small pool fire size. The CAFS nozzle gave good quality foam which enabled for the testing of the surfactant mixtures. A fluorine-free, surfactant mixture made from 2062–145, an alkylpolyglucoside (Glucopon 225DK) and organic solvent (DGBE) in water was able to extinguish a 20 in^2 diameter F24 pool fire in about 60 seconds. This result was about four times slower than the extinguishing rate of AFFF (15 seconds) so there is certainly room for improvement. But excellent fire extinction results were found with the trimethylsilyl terminated siloxane surfactant 2062–139. The 20 square inch F24 pool fire could be extinguished in an average of 11 seconds using a surfactant mixture incorporating 2062–139, which was the same time as in the case with AFFF. The quantities of each surfactant in the mixtures were chosen arbitrarily and process development could lead to a ratio that extinguishes faster. It would be interesting to test the 2062–145 and 2062–139 mixtures on the milspec 28 ft^2 pool fire of jet fuel or even gasoline. Compound 2062–139 can be made in just two chemical process steps and should be scaled up and studied further as a hydrocarbon pool fire fighting additive urgently. Unfortunately, there was not enough time left on the project to continue testing all of the other siloxane surfactants made during the project. There could be other surfactants among those made here with equal or better results in the pool fire tests. There are several SERDP projects looking at siloxanes as additives in hydrocarbon pool fire fighting. These other SERDP projects may find the results described here interesting for the design of siloxanes with better stability and fire fighting properties.

Literature Cited

[1] Perri, J. M.; Sloviter, B. 'All purpose fire extinguishing foams', Technical Report 6130, November 1952.

[2] Dlugogorski, B. Z.; Kennedy, E. M.; Schaefer, T. H.; Vitali, J. A. in 'What properties matter in fire fighting foams?' www.solbergfoam.com.

[3] Hinnant, K. M. et al. *Fire Safety Journal* **2017**, 91, 653–661.

[4] Hinnant, K. M. et al. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2017**, *522*, 1–17.

[5] Moran, H. E.; Burnett, J. C.; Leonard, J. T. Suppression of fuel evaporation by aqueous films of fluorochemical surfactant solutions, Naval Research Laboratory Memo Report 7247, Washington DC, 1971.

[6] Harper, D. B.; O'Hagan, D. *Natural Product Reports* **1994**, 123–133.

[7] Vinogradov, A. V. et al. *ACS Appl. Mater. Interfaces* **2016**, *8*, 294−301.

[8] Rosen, M. R.; Prokai, B. Method of extinguishing fires and compositions thereof containing cationic silicone surfactants. U.S. Patent 3,677,347, Jul 18, 1972.

[9] Davis, MC. Surfactants with Organosilicate Nanostructures for Use as Fire-Fighting Foam (F^3) SERDP Exploratory Development (SEED) Project # WP18–1519; SERDP Final Report, 16 July 2019.

[10] Hetzer, R. H. and Kümmerlen, F. "*Siloxane-based AFFF: Testing of Experimental Foam Concentrates*", National Fire Protection Association Symposia (SupDet 2016), Quincy, MA, March 2 2016.

[11] R. Ananth, A. W. Snow, K. Hinnant, S. L. Giles, Siloxane and glucoside surfactant formulation for fire-fighting foam applications, US Patent 20190321670A1, 24 October 2019.

[12] Snow, S. A.; Fenton, W. N.; Owen, M. J. *Langmuir* **1990**, *6*, 385–391.

[13] G. A. Policello, M. D. Leatherman, W. Peng ; S. K. Rajaraman, S. Xia, US Patent US 2011/0251067 A1, 13 October 2011.

[14] D. Uhrín, S. Uhrínová, E. Eichler, J–R. Brisson, *J. Mag. Res. A* **1995**, *115*, 119–122.

[15] F. Uhlig and H. C. Marsmann, *^{29}Si NMR Some Practical Aspects*, Gelest Incorporated technical literature.

[16] T. H. Lane and J. L. Speier, *J. Org. Chem.* **1976**, *41*, 2714–2716.

[17] Y. Huang, L. Meng, M. Guo, P. Zhao, H. Zhang, S. Chen, J. Zhang, and S. Feng, *Langmuir* **2018**, *34*, 4382–4389; JW Ryan, GK Menzie and JL Speier, *J. Am. Chem. Soc.* **1960**, *82*, 3601–3604.

[18] T. H. Lane and J. L. Speier, *J. Org. Chem.* **1976**, *41*, 2714–2716; KW Michael and YA Peters, Tris-trimethylsiloxy amines, US Patent 3,719,697, 6 March 1973.

[19] R. Sonnenschein and C. Batz-Sohn, US Patent 20020008011, 28 March 2001.

[20] A. V. Arzumanyan et al., *Green Chemistry* **2018**, *20*, 1467–1471.

[21] H. J. Vahlensieck and H. J. Koetzsch, US Patent US 4,824,982, 25 April 1989.

[22] H. J. Kötzsch and H. J. Vahlensieck, German Patent DE 3303707, 2 April 1983.

[23] J. Tan, M. Lin, and Z. Ye, *Journal of Solution Chemistry* **2018**, *47*, 2082–2093.

[24] G. A. Policello, M. D. Leatherman, W. Peng, S. Rajaraman and Z. Xia, US Patent 9,935,842, 3 May 2011.

[25] M. D. Leatherman, G. A. Policello, W. N. Peng, L. Zheng, R. Wagner, S. K. Rajaraman, Z. Xia, US Patent 2009/0176893A1, 9 July 209.

[26] F. Ibba, P. Capurro, S. Garbarino, M. Anselmo, L. Moni, and A. Basso, *Organic Letters* **2018**, *20*, 1098–1101.

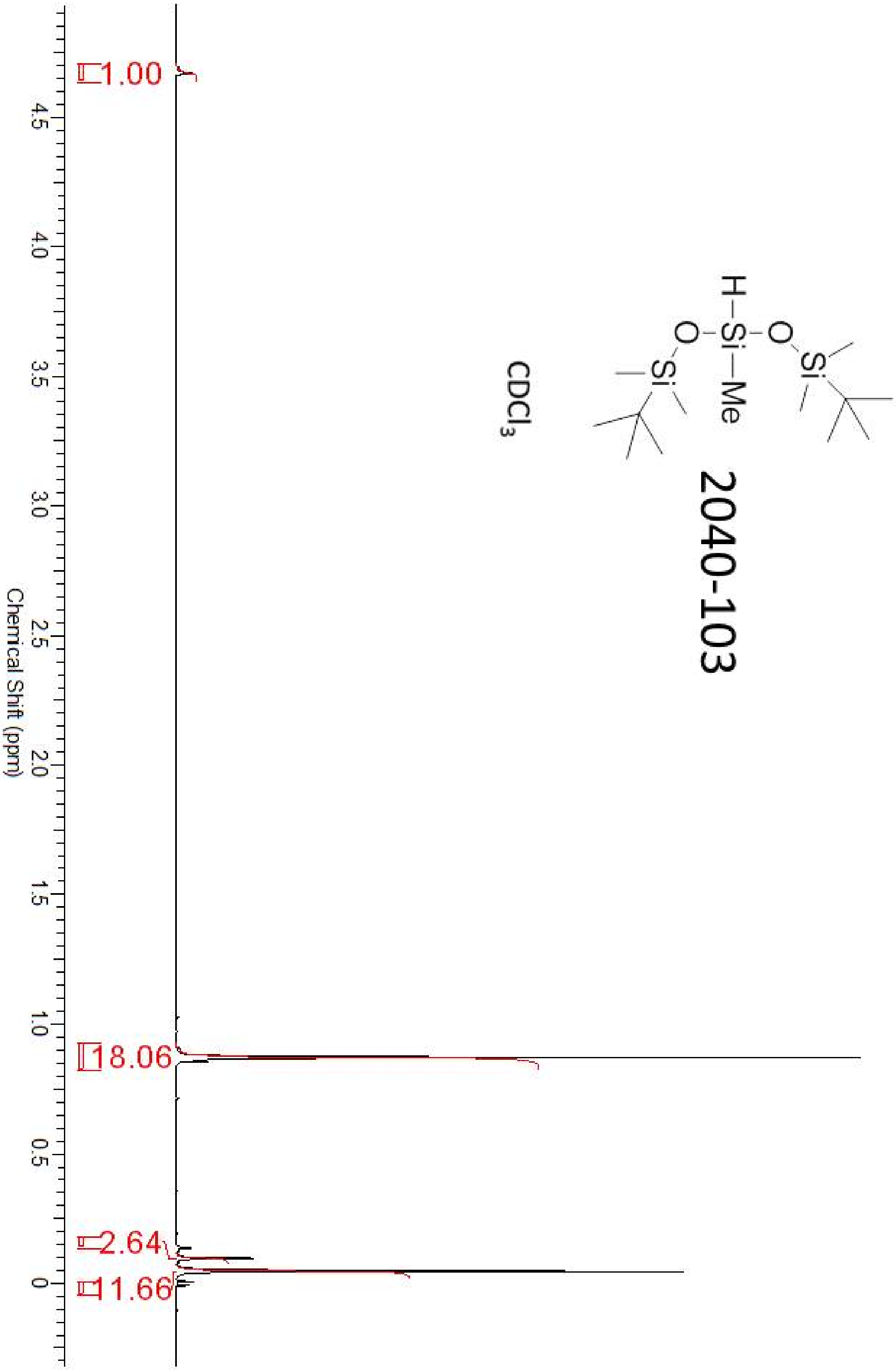
[27] Organosiloxane compounds, British Patent GB 914,460, 29 August 1961.
[28] F. Han and G. Zhang, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2004**, *237*, 79–85.
[29] G. Wang, P. Li, Z. Du, W. Wang and G. Li, *Langmuir* **2015**, *31*, 8235–8242.
[30] F. Han and G-Y. Zhang, *Tenside, Surfactants, Detergents* **2003**, *40*, 332–337.
[31] K. Isaac-Olivé, L. Aranda-Lara, BE Ocampo-Garcia, CL Santos-Cuevas, NP Jimenez-Mancilla, MA Luna-Gutierrez, B Nagarajan, N Sabnis, S, Raut, L Prokai, AG Lacko, *Nanoscale* **2019**, *11*, 541–551.
[32] CN McEwen, RG McKay, BS Larsen, *Anal. Chem.* **2005**, *77*, 7826–7831.
[33] H. U. Geyer, *Chem. Ber.* **1964**, *97*, 2271–2275.
[34] *Ascorbic acid: chemistry, metabolism, and uses*. PA Seib and BM Tolbert, Eds. American Chemistry Society, Washington, DC, 1982.
[35] CL Mehltretter and JC Rankin, Gluconamides, US Patent 2,662,073, 12 August 1953; M Monsigny, Aldonic acid amide for biodegradable surfactants, French Patent 2,523,962, 30 September 1983; U Hees and M Weuthen, Use of gluconamide derivatives as surfactants in compositions for cleaning hard surfaces, German Patent 4,406,160, 31 August 1995.
[36] Y. Huang, M. Guo, S. Feng, *Langmuir* **2019**, *35*, 9785–9793.
[37] S. A. Snow, W. N. Fenton, and M. J. Owen, *Langmuir* **1990**, *6*, 385–391.
[38] M. D. Leatherman, G. A. Policello, W. N. Peng, L. Zheng, R. Wagner, S. K, Rajaraman and X. Zijun, US Patent 8,263,669, 11 September 2012.
[39] H. J. Cho, J. Y. Ko, D. H. Lee, C. M. Park, and S. C. Ji, Korean patent KR 1249352, 2 April 2013.
[40] P. Madaan, VK Tyagi, *Journal of Oleo Science* **2008**, *57*, 197–215.
[41] L. Fang, J. Tan, Y. Zheng, G. Yang, J. Yu and S. Feng, *J. Molec. Liquids* **2017**, *231*, 134–141.
[42] A. Karschin, W. Klaui, W. Peters and B. Spingler, *Eur. J. Inorg. Chem.* **2010**, 942–946; F. Joo, J. Kovacs, A. Katho, A.C. Benyei, T. Decuir and D.J. Darensbourg, *Inorg. Synth.* **1998**, *32*, 2–4.
[43] M.L. Tulchinsky and A.G. Abatjoglou, US 8,394,978, 12 March 2013.
[44] https://adamschittenden.com/technical/frits/frit.size, accessed 9 August 2021.
[45] *The DuNouy Ring Method, Wilhelmy Plate Method, Pedant Drop Method, and Bubble Pressure Method for Surface Tension Measurement-A Comparison of Methods and Capabilities*, Christopher Rulison, Ph. D., Principal Scientist, Augustine Scientific, https://docplayer.net/58315784-Dr-christopher-rulison-principal-scientist-augustine-scientific.html, accessed 30 July 2021.
[46] JE Morozova, VV Syakaev, *et al. Soft Matter* **2017**, *13*, 2004–2013.
[47] B Burczyk, KA Wilk, A Sokoowski and L Syper, *J. Colloid Interface Sci.* **2001**, *240*, 552–558.
[48] MIL-F-24385F Fire Extinguishing Agent Aqueous Film Forming Foam (AFFF) Liquid Concentrate, For Fresh and Seawater, 7 January 1992.
[49] RH Hetzer, F Kümmerlen, K Wirz and D Blunk, *Fire testing a new fluorine-free AFFF based on a novel class of environmentally sound high performance siloxane surfactants*, Fire Safety Proceedings of the 11th International Symposium, 1261–1270, 2014; DOI: 10.3801/IAFSS.FSS.11-1261.
[50] R Ananth, AW Snow, KM Hinnant, SL Giles, JP Farley, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2019**, *579*, 123686.
[51] G. Kaupp, D. Matthies, C. De Vrese, *Chemiker-Zeitung* **1989**, *113*, 219–20.

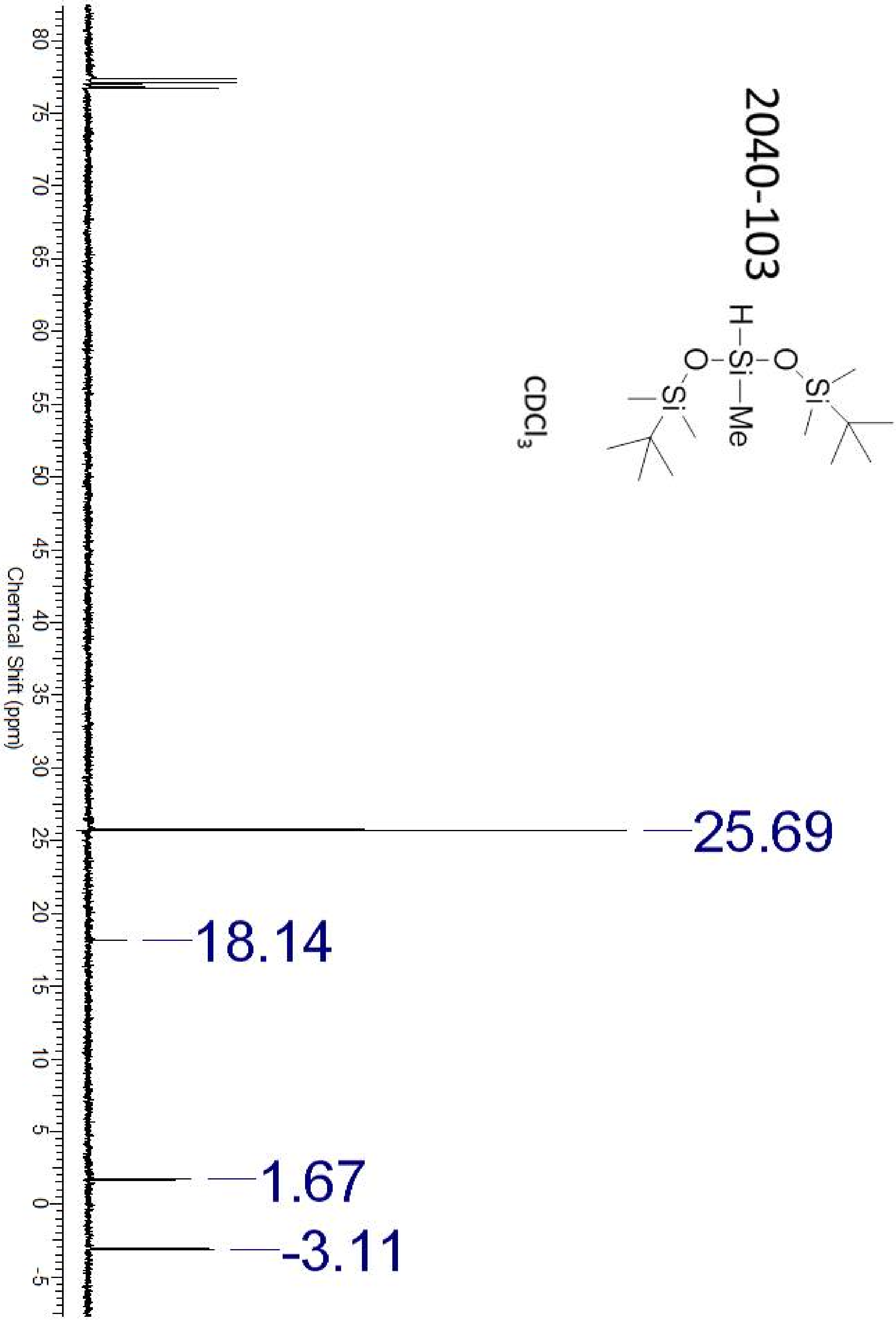
[52] STANAG 3747, Guide Specifications (Minimum Quality Standards) For Aviation Turbine Fuels (F24, F27, F34, F35, F37, F40 and F44)-AFLP-3747 Edition C, 16 August 2017.
[53] MA Cummins, Foam generating fire fighting device. US Patent 4,318,433, 9 March 1982.

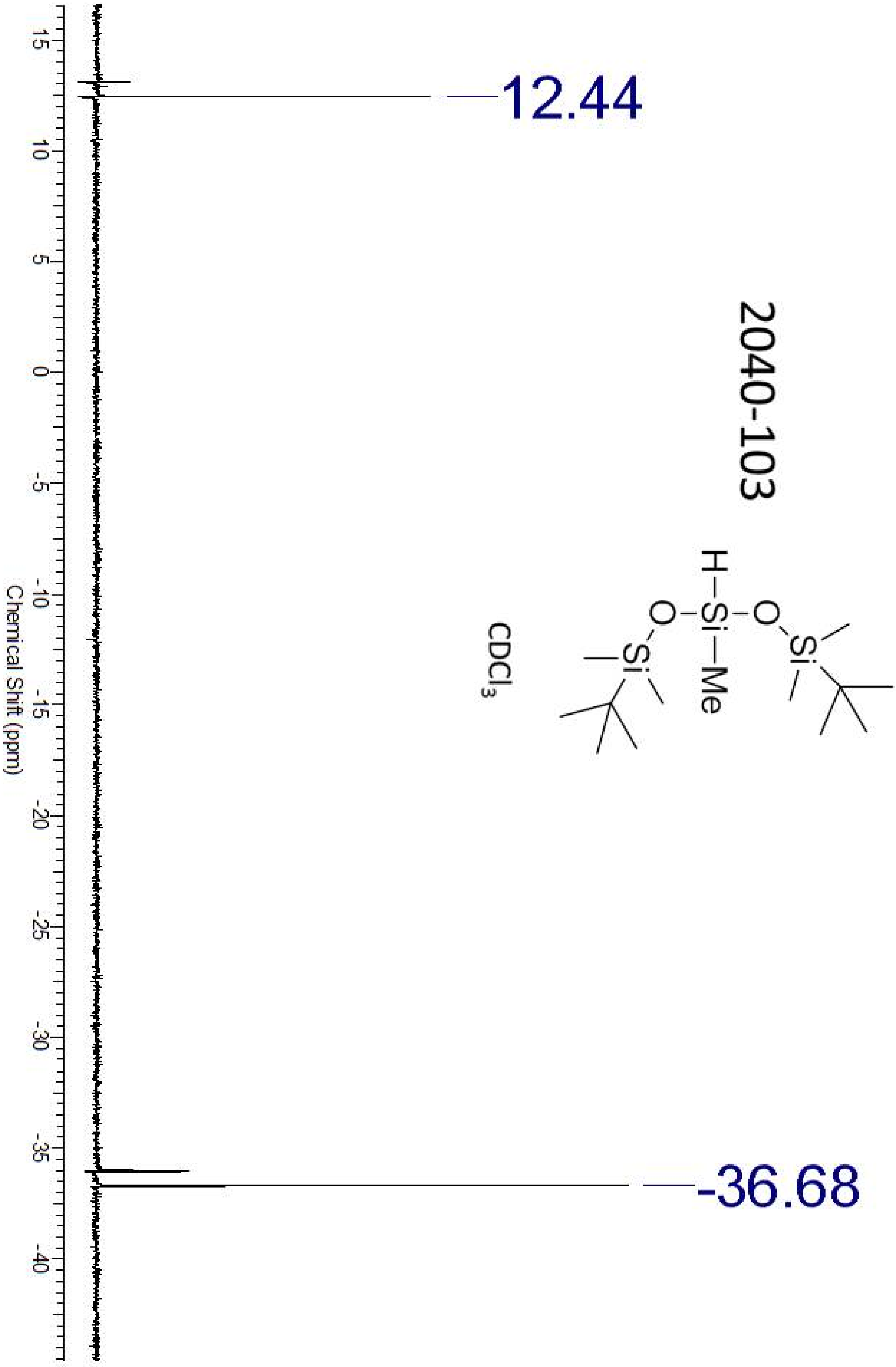
Appendices

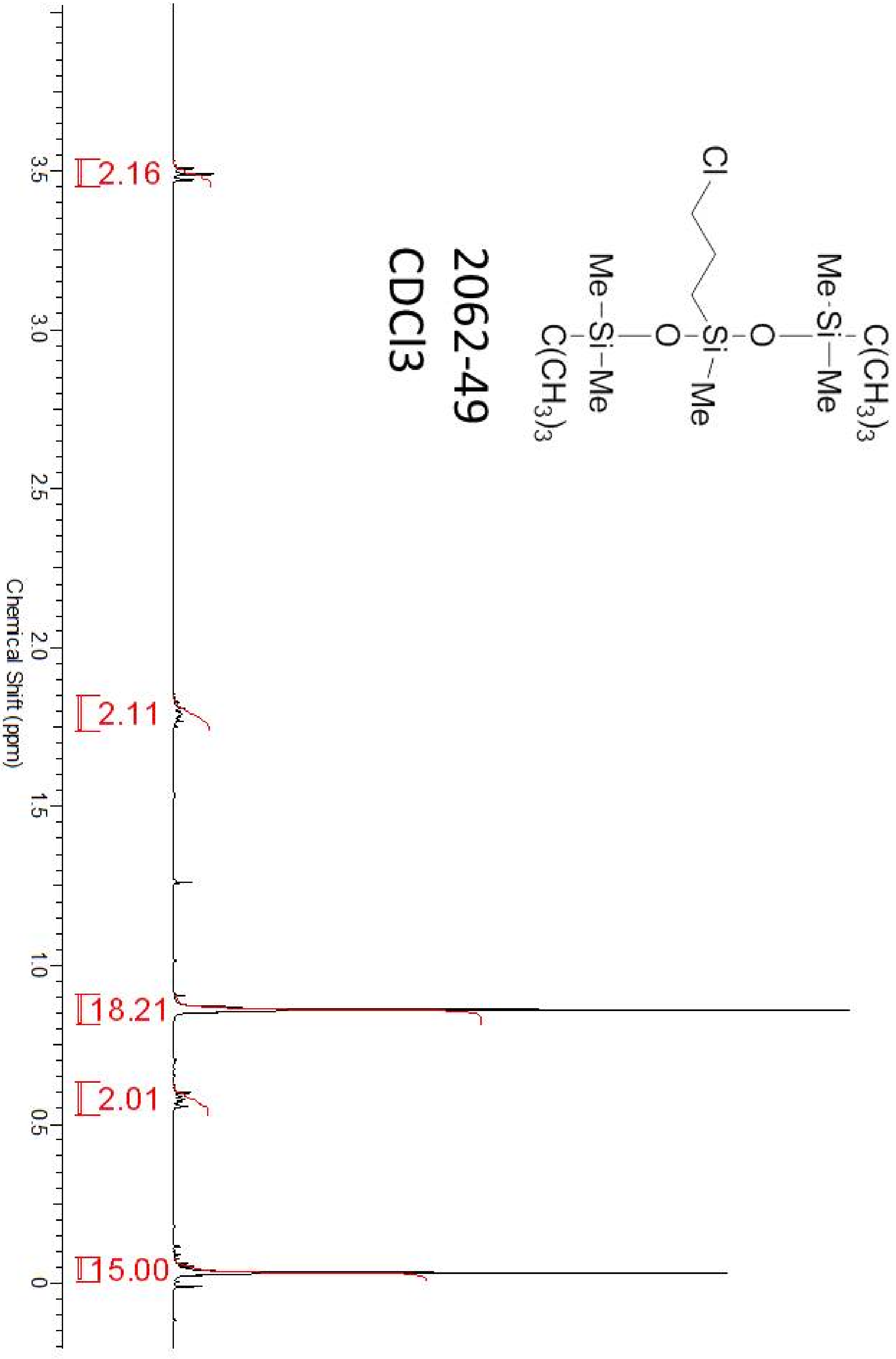
Appendix A. NMR data

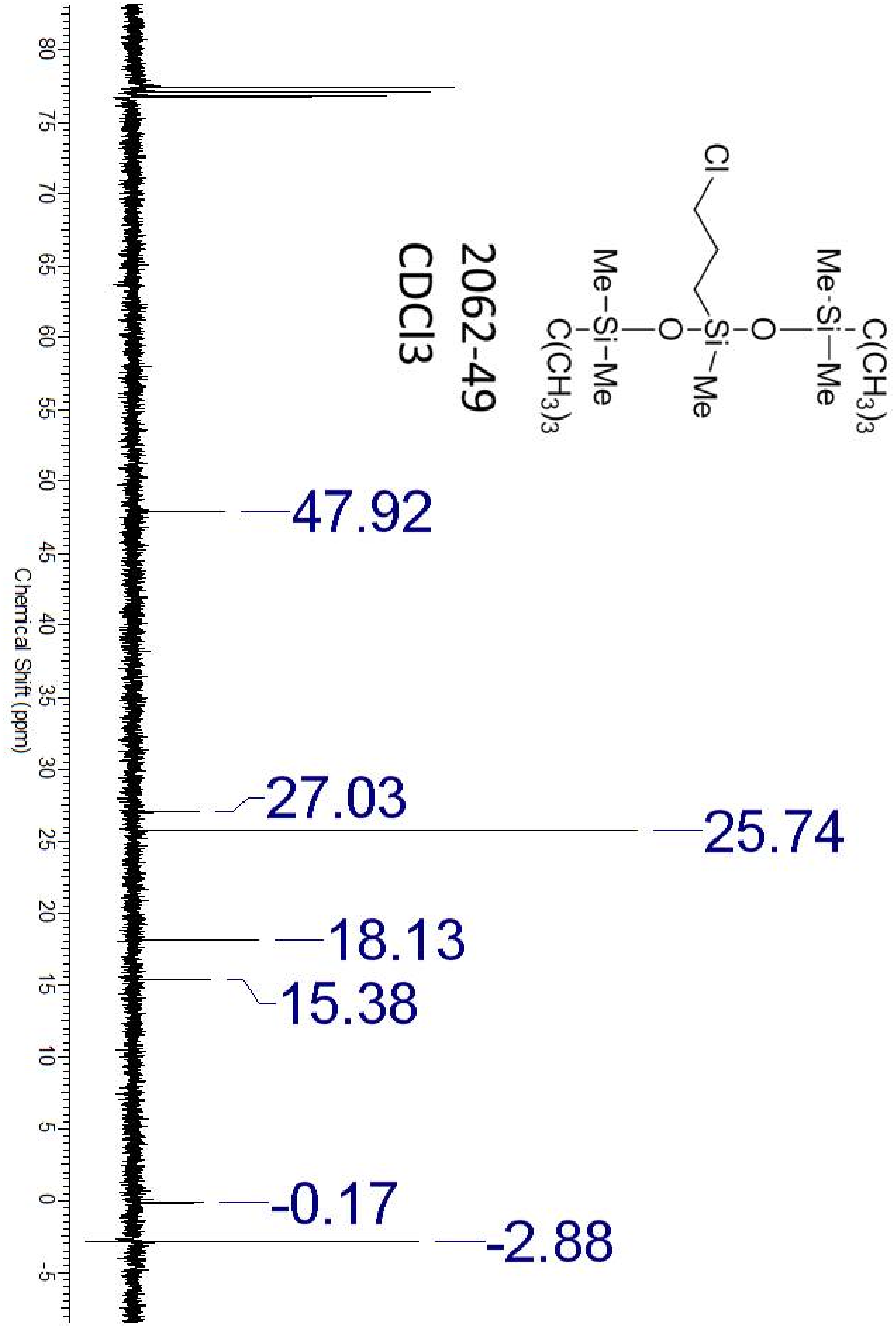
The NMR data for the surfactants and reaction intermediates of this report are not listed in their order of appearance in the text. Instead, the NMR data is listed in numerical order based on research lab book and page number. For each compound the ^{1}H spectra is shown first followed by ^{13}C and in certain cases ^{29}Si and ^{31}P.

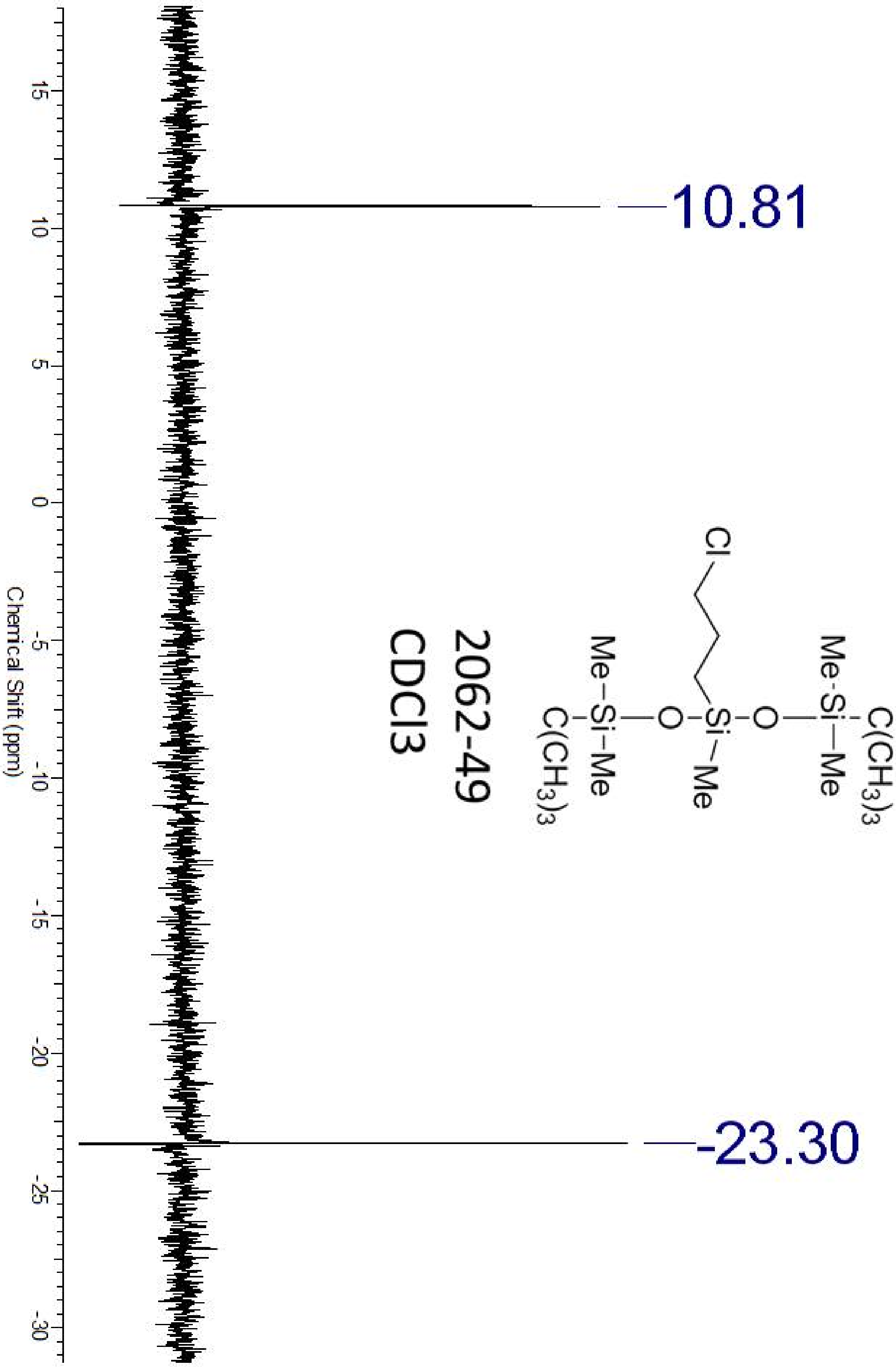

2040-103
CDCl3
H
Si
Me
O
O
Si
Si
1.00
18.06
2.64
11.66
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

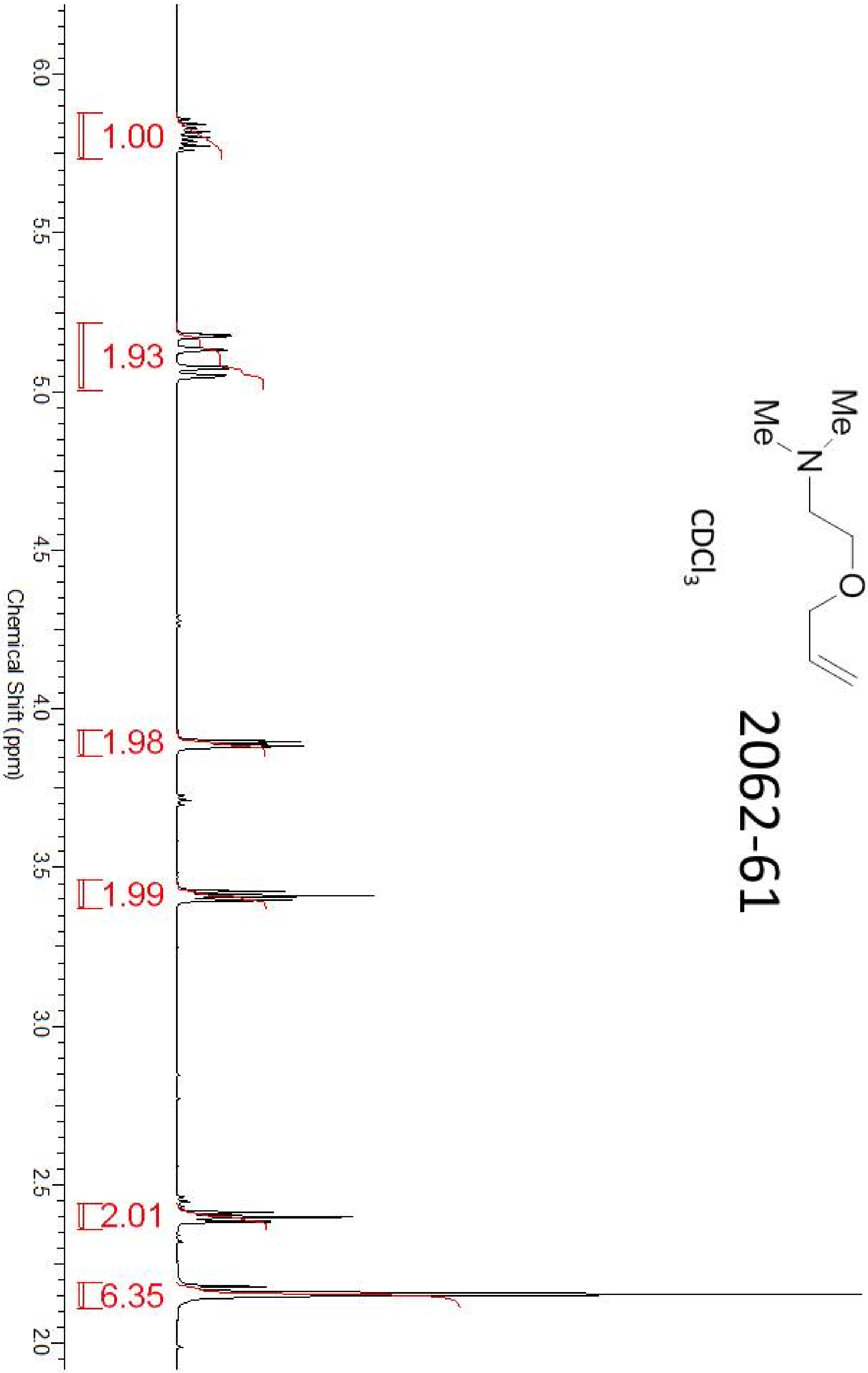

2040-103
H–Si–Me
O
Si
CDCl3
25.69
18.14
1.67
-3.11
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
Chemical Shift (ppm)


12.44
-36.68
2040-103
H–Si–Me
O
O
Si
Si
CDCl3
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
Chemical Shift (ppm)

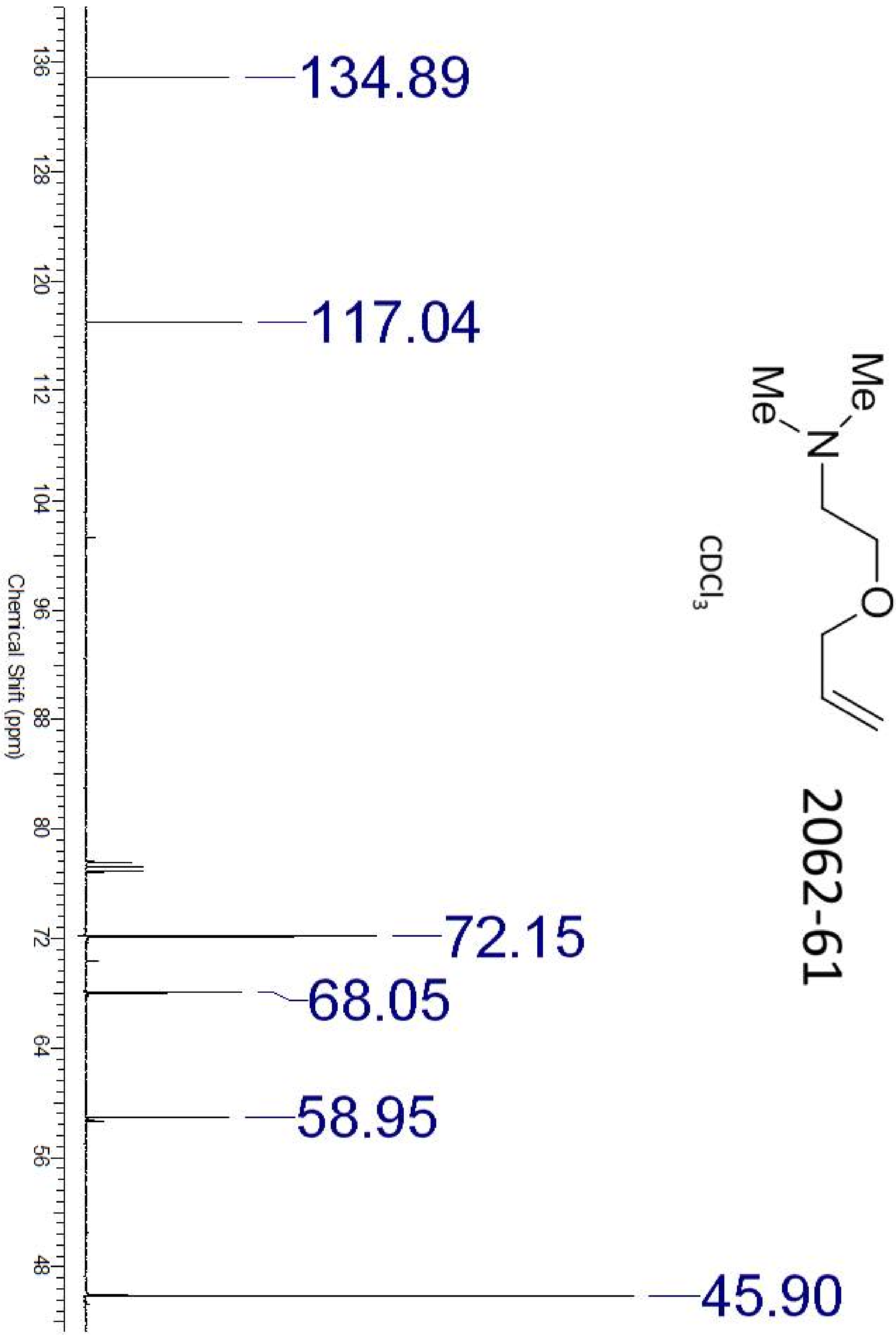

2062-49
CDCl3
Cl
Me-Si-Me
C(CH3)3
O
Si
Me
O
Me-Si-Me
C(CH3)3
2.16
2.11
18.21
2.01
15.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


Cl
Me-Si-O-Si-O-Si-Me
Me
C(CH3)3
2062-49
CDCl3
47.92
27.03
25.74
18.13
15.38
-0.17
-2.88
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
Chemical Shift (ppm)


10.81
-23.30
Cl
Me-Si-Me
C(CH3)3
O
Si
Me
2062-49
CDCl3
15
10
5
0
-5
-10
-15
-20
-25
-30
Chemical Shift (ppm)


Me
Me
N
O
CDCl3
1.00
1.93
1.98
1.99
2.01
6.35
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)

2062-61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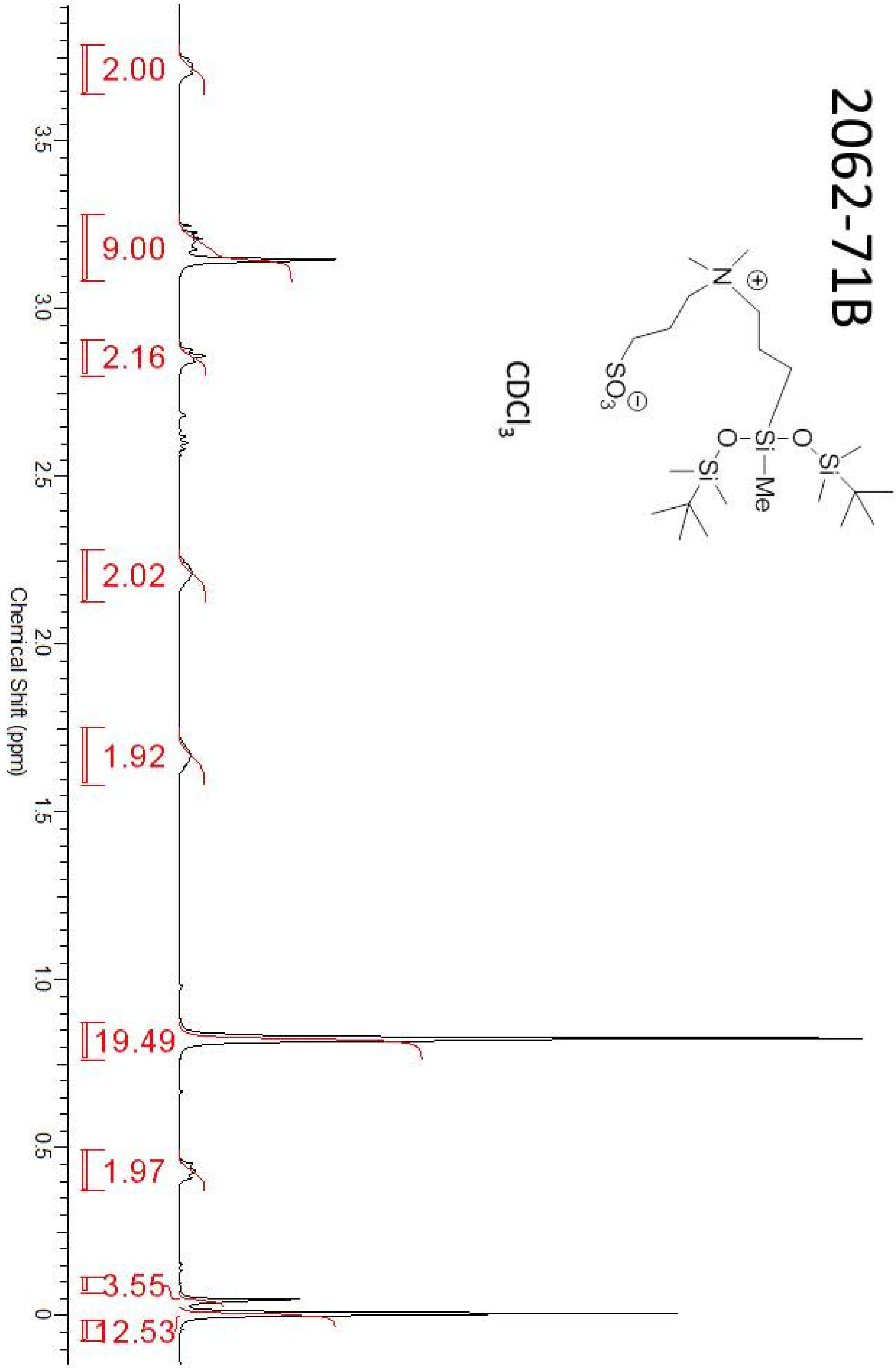
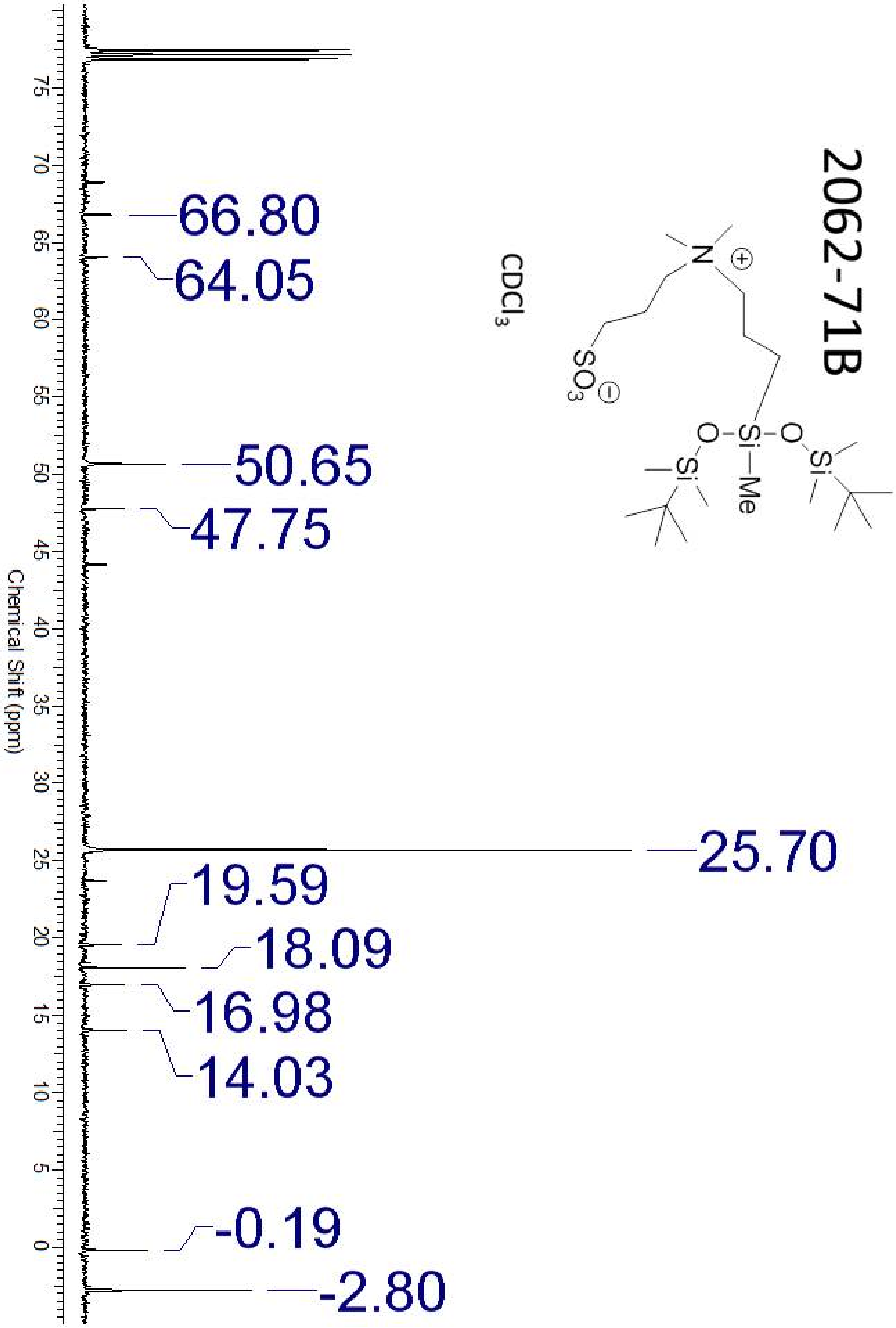
CDCl3
Me
Me
N
O
134.89
117.04
72.15
68.05
58.95
45.90
136
128
120
112
104
96
88
80
72
64
56
48
Chemical Shift (ppm)


2062-71B
N
⊕
SO3
⊖
O
Si
Me
O
Si
O
Si
CDCl3
2.00
9.00
2.16
2.02
1.92
19.49
1.97
3.55
12.53
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)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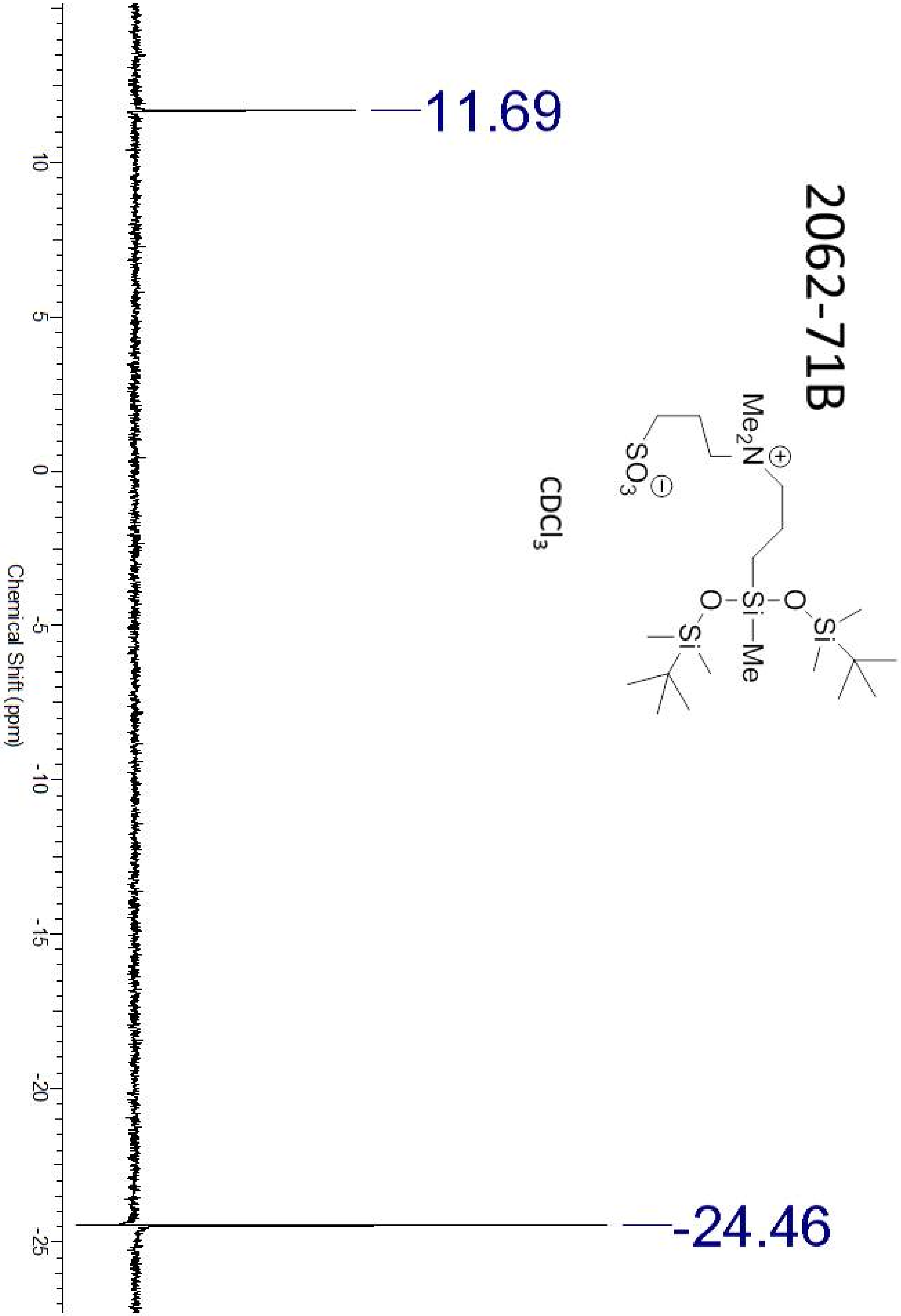
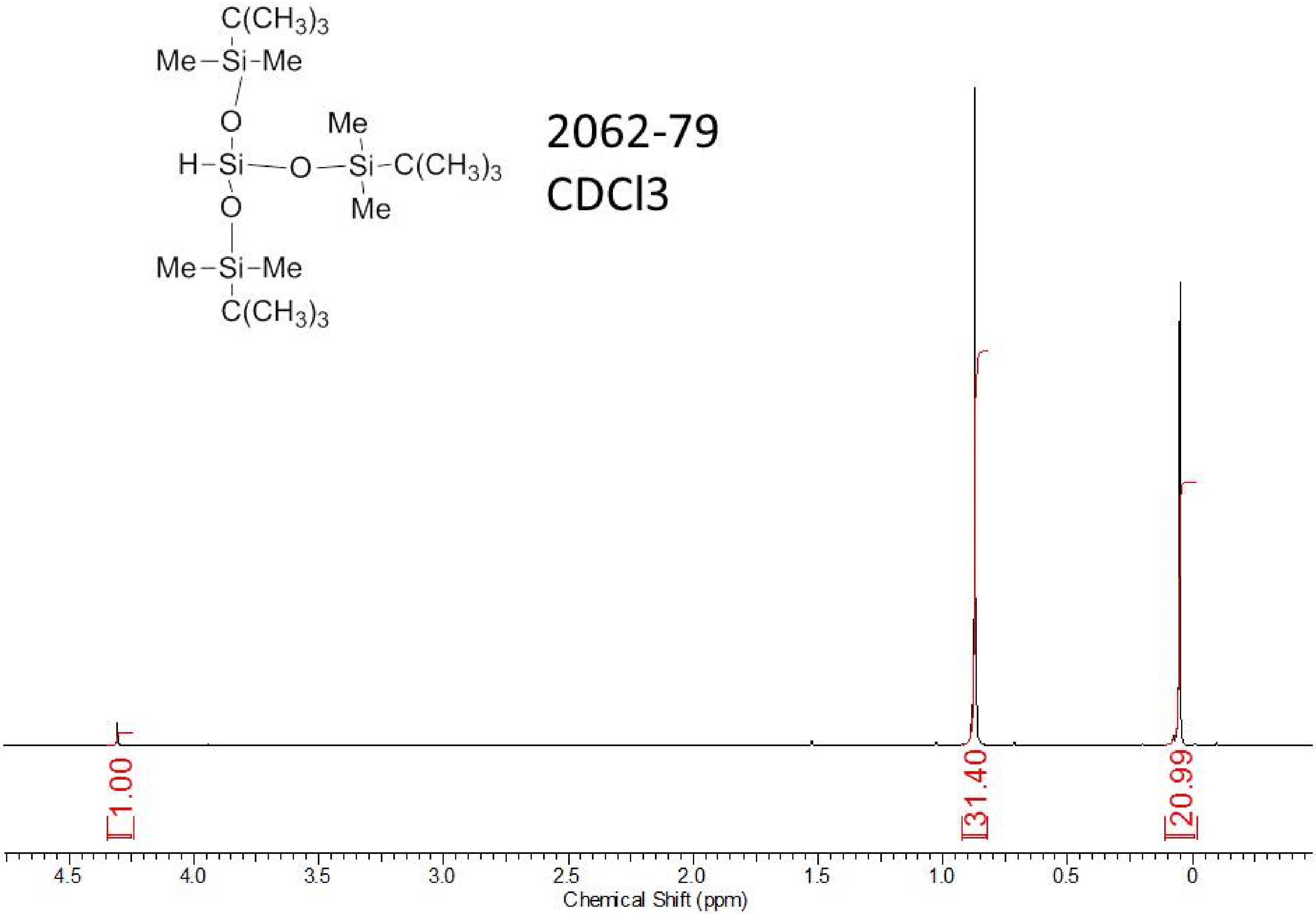
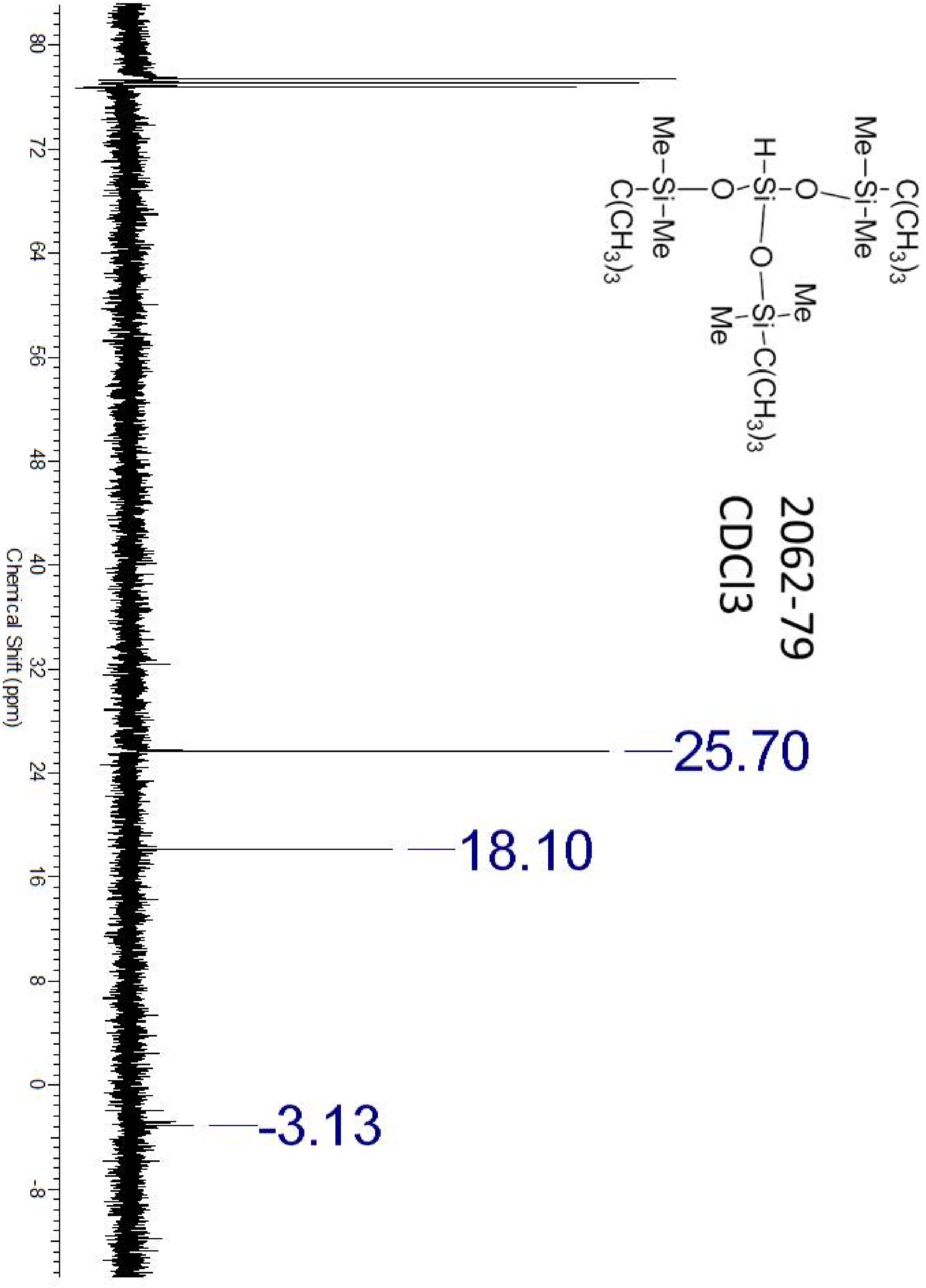
⊕
SO3
⊖
Si
O
Me
CDCl3
66.80
64.05
50.65
47.75
25.70
19.59
18.09
16.98
14.03
-0.19
-2.80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
Chemical Shift (ppm)


2062-71B

CDCl$_3$


2062-79
CDCl3
C(CH3)3
Me–Si–Me
O
H–Si–O–Si–C(CH3)3
Me
Me
O
Me–Si–Me
C(CH3)3
1.00
31.40
20.99
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)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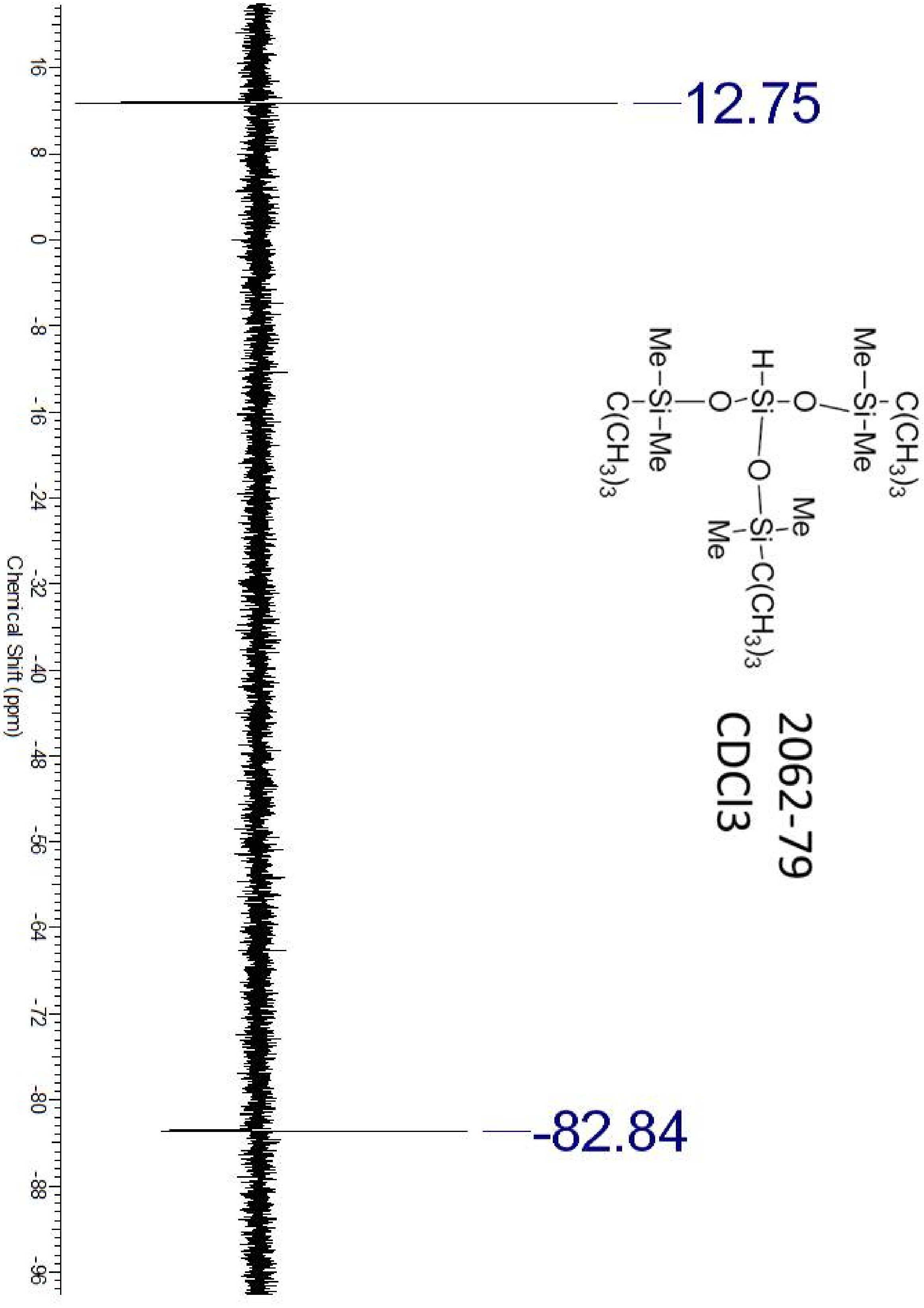
CDCl3
C(CH3)3
Me–Si–Me
O
H–Si–O–Si–C(CH3)3
Me
Me
O
Me–Si–Me
C(CH3)3
25.70
18.10
-3.13
80
72
64
56
48
40
32
24
16
8
0
-8
Chemical Shift (ppm)


12.75
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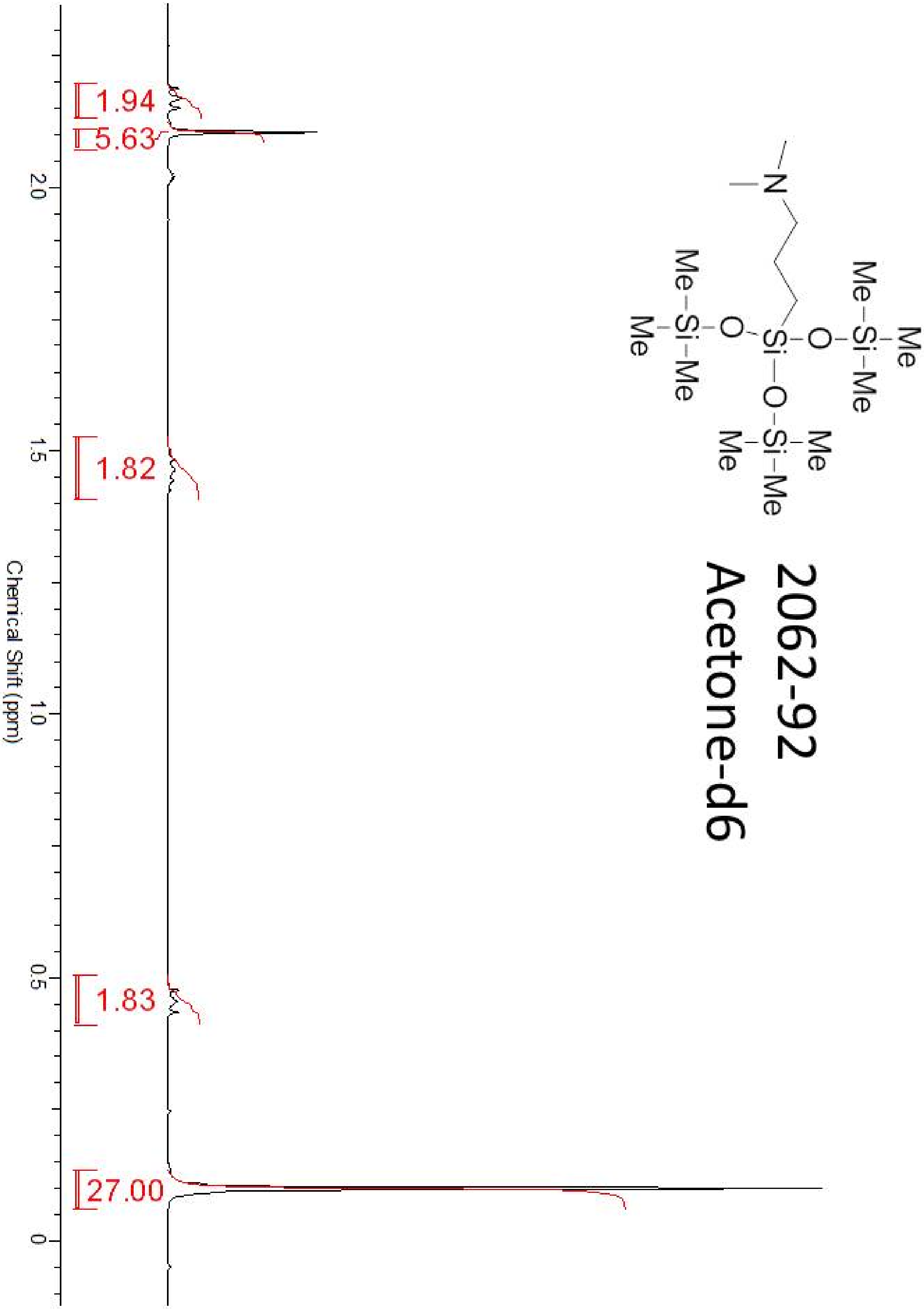
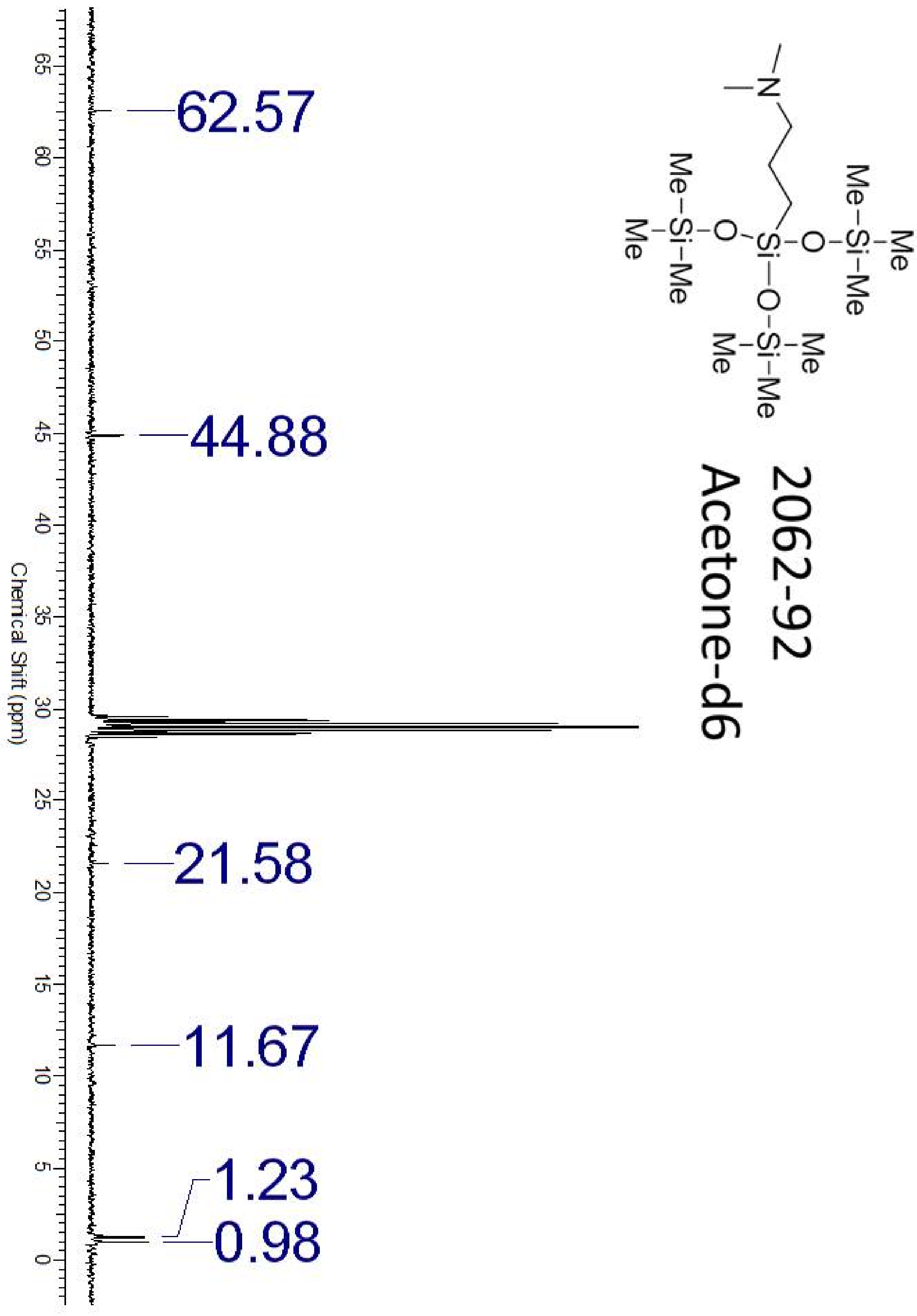
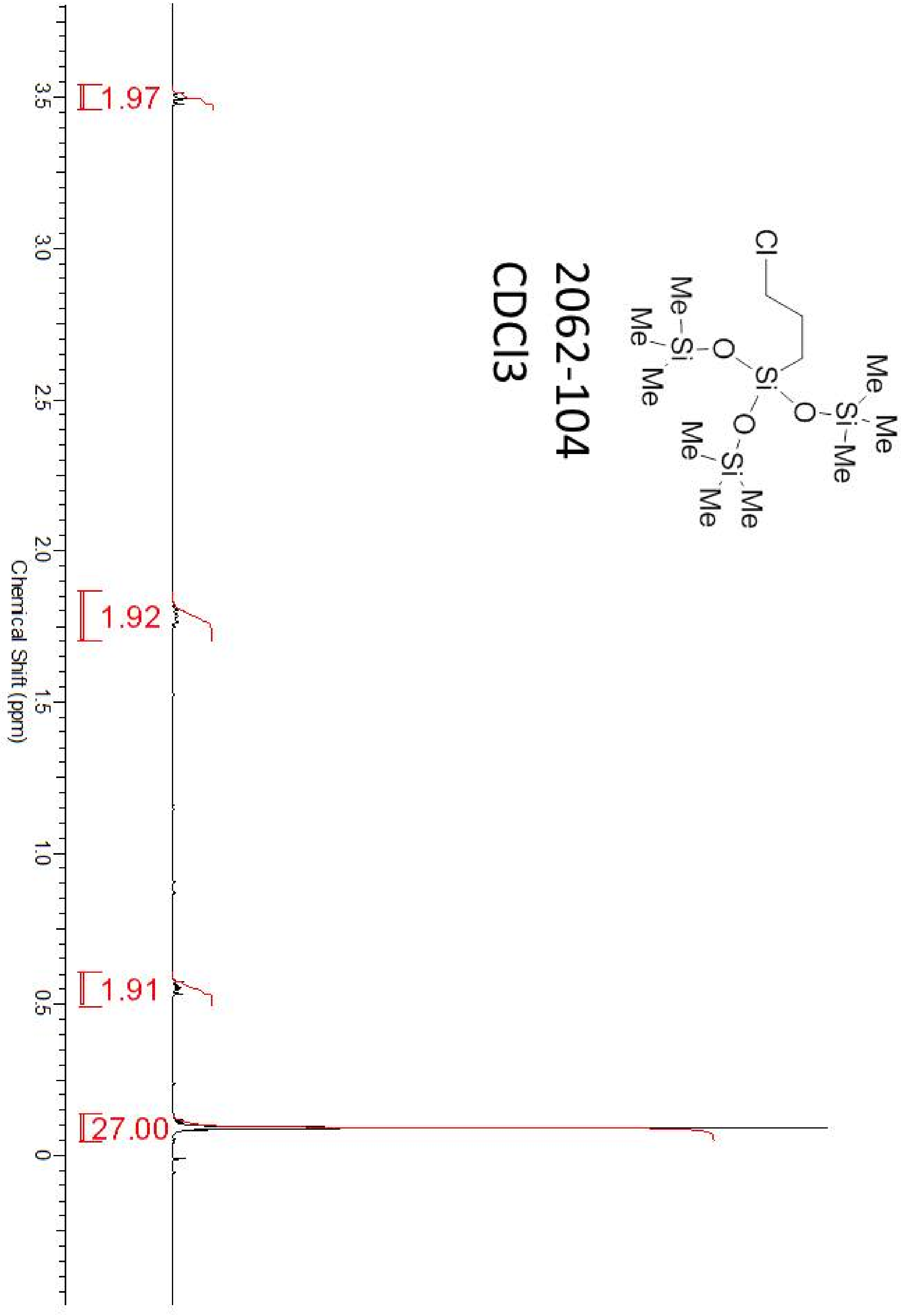
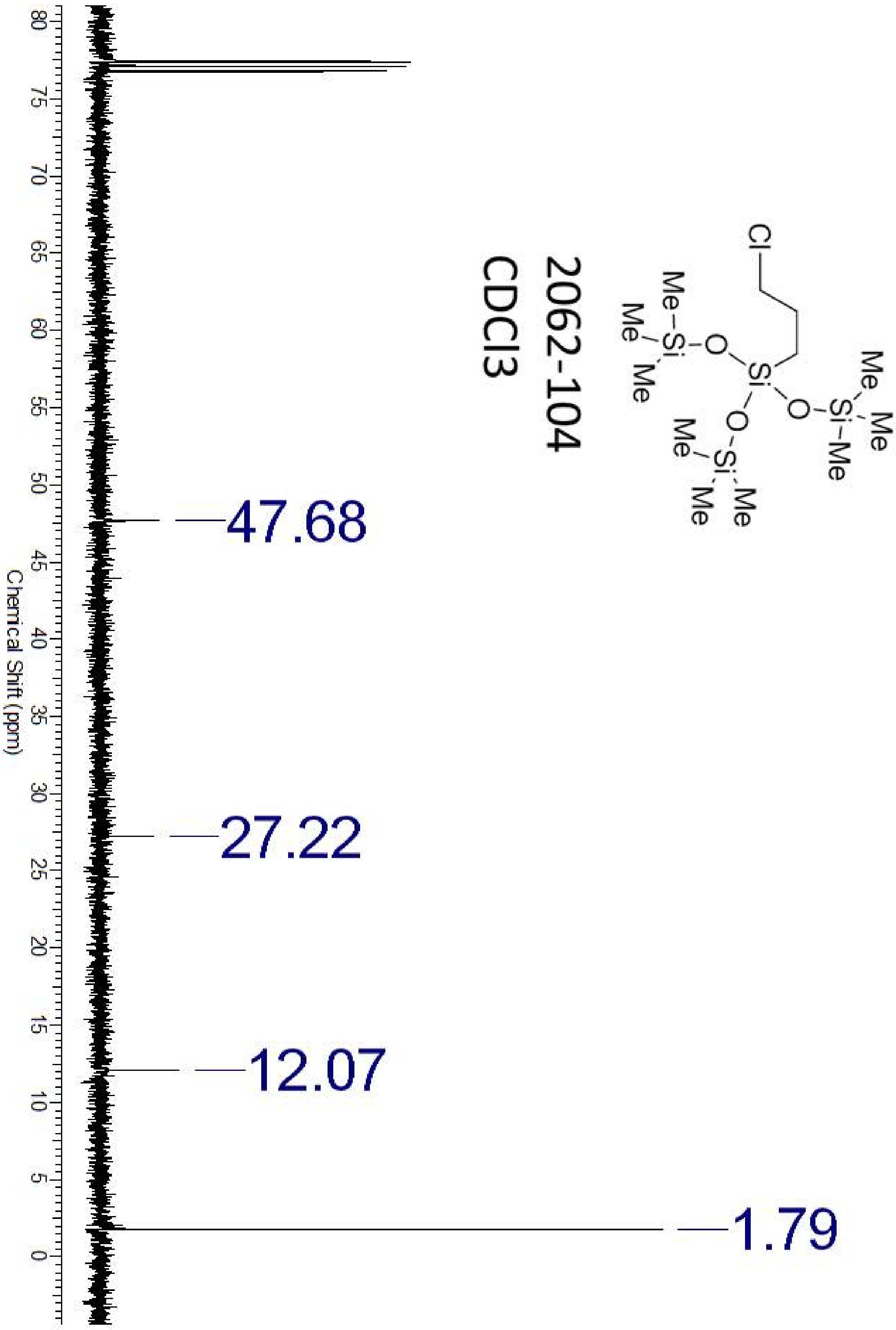
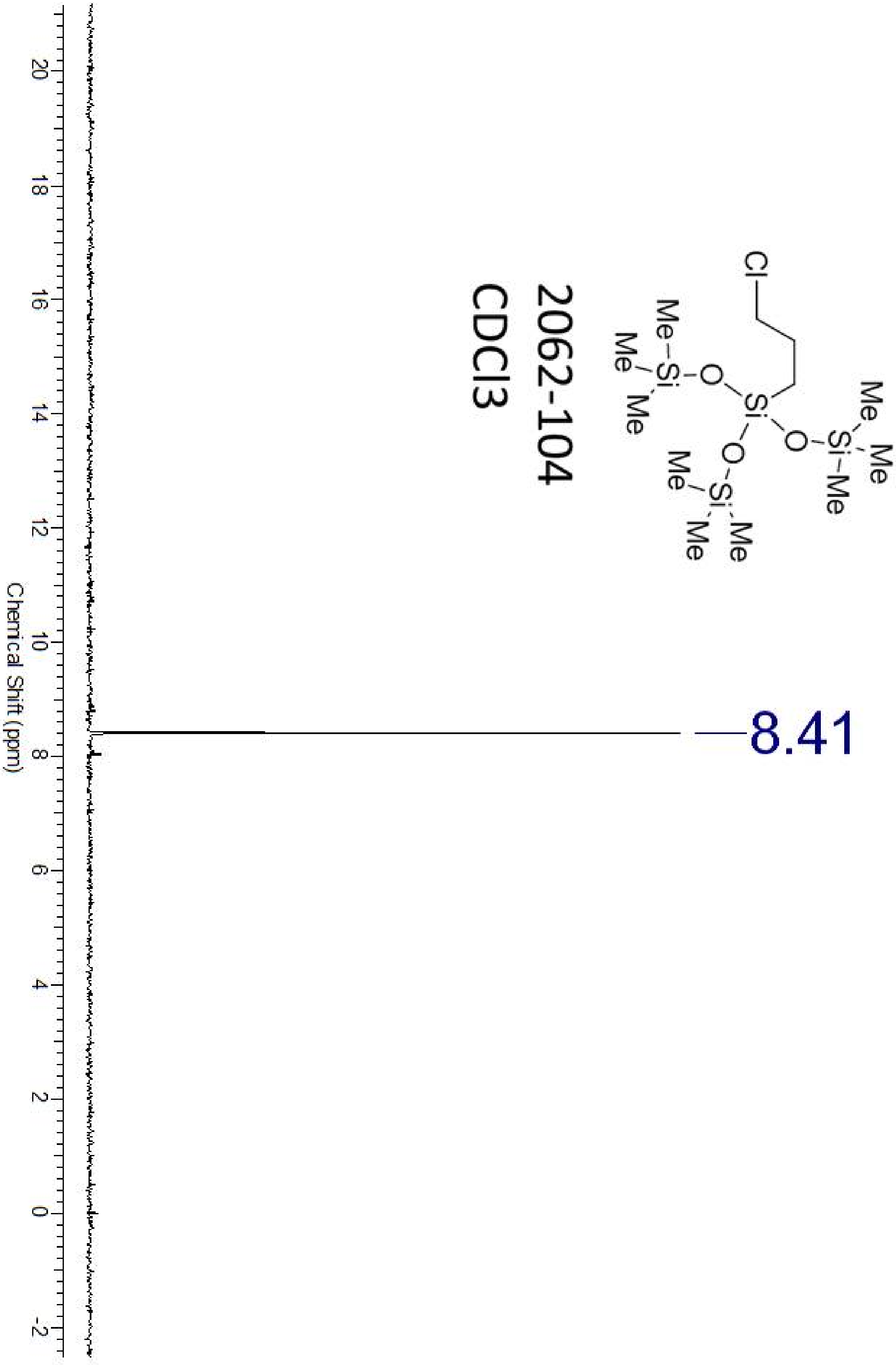
16
8
0
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
-88
-96
Chemical Shift (ppm)
C(CH3)3
Me–Si–Me
O
H–Si–O–Si–C(CH3)3
Me
Me
O
Me–Si–Me
C(CH3)3
2062-79
CDCl3

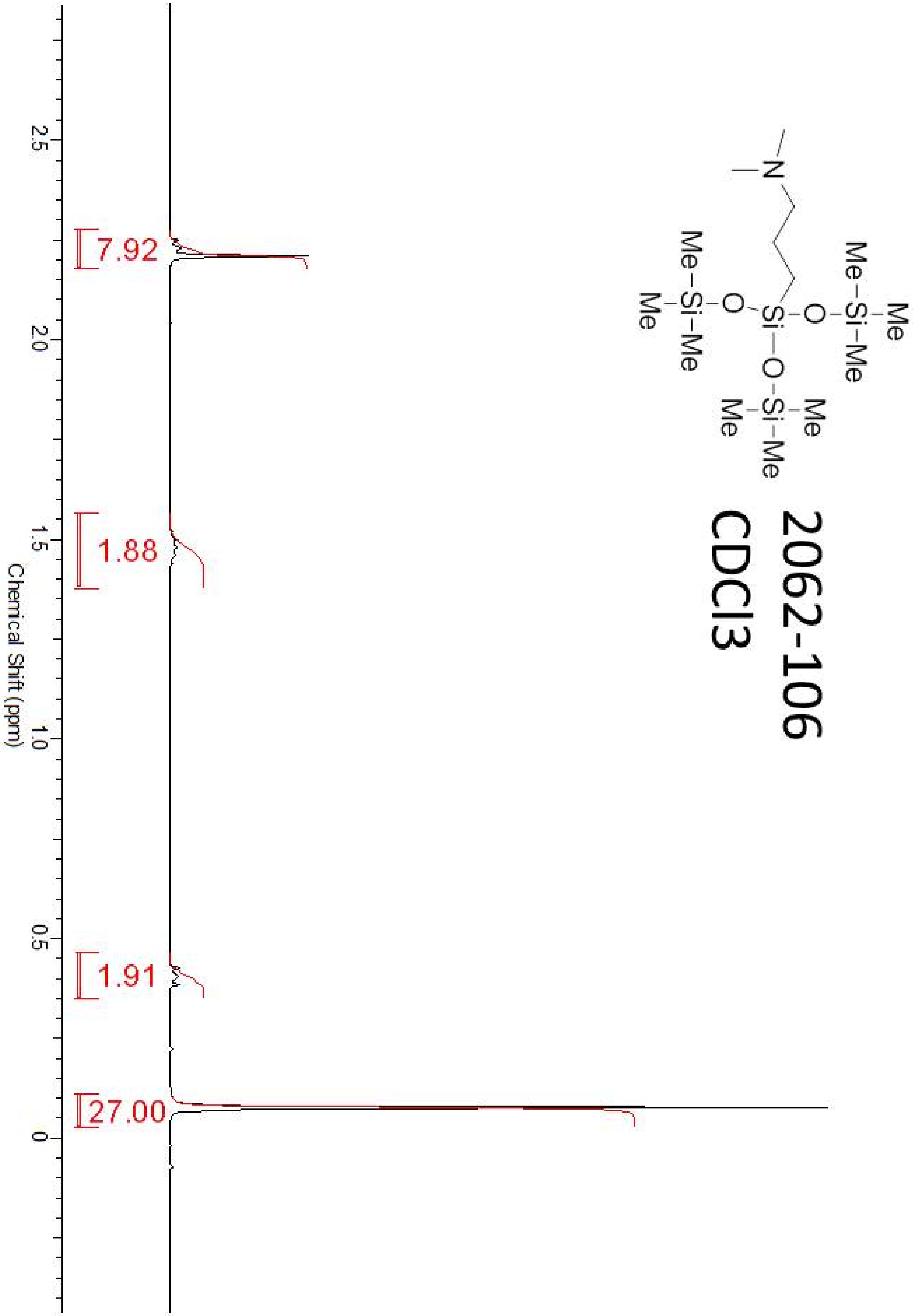

2062-92
Acetone-d6
Me
Me–Si–Me
O
N
Si–O–Si–Me
O
Me–Si–Me
Me
1.94
5.63
1.82
1.83
27.00
Chemical Shift (ppm)
2.0
1.5
1.0
0.5
0


2062-92
Acetone-d6
Me
Me–Si–Me
O
N
Si–O–Si–Me
Me
Me
O
Me–Si–Me
Me
62.57
44.88
21.58
11.67
1.23
0.98
65
60
55
50
45
40
35
30
25
20
15
10
5
0
Chemical Shift (ppm)


2062-104
CDCl3
Cl
Si
O
Me
Si
1.97
1.92
1.91
27.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


2062-104
CDCl3
Cl
Si
O
Me
Si
Me
47.68
27.22
12.07
1.79
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
Chemical Shift (ppm)


Cl
Me
Me
Si
Me
O
Si
O
Si
Me
Me
Me
O
Si
Me
Me
2062-104
CDCl3
8.41
20
18
16
14
12
10
8
6
4
2
0
-2
Chemical Shift (ppm)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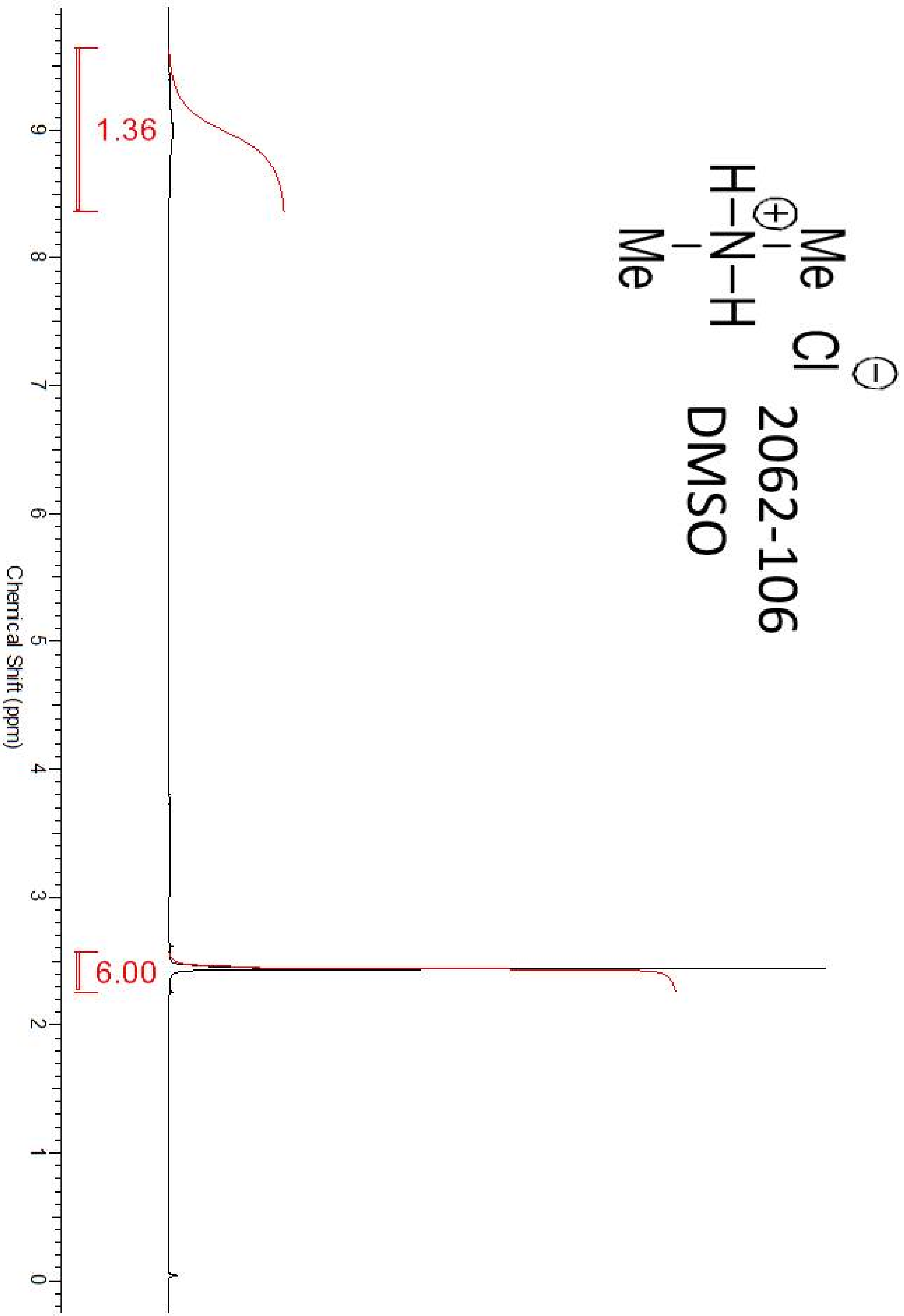
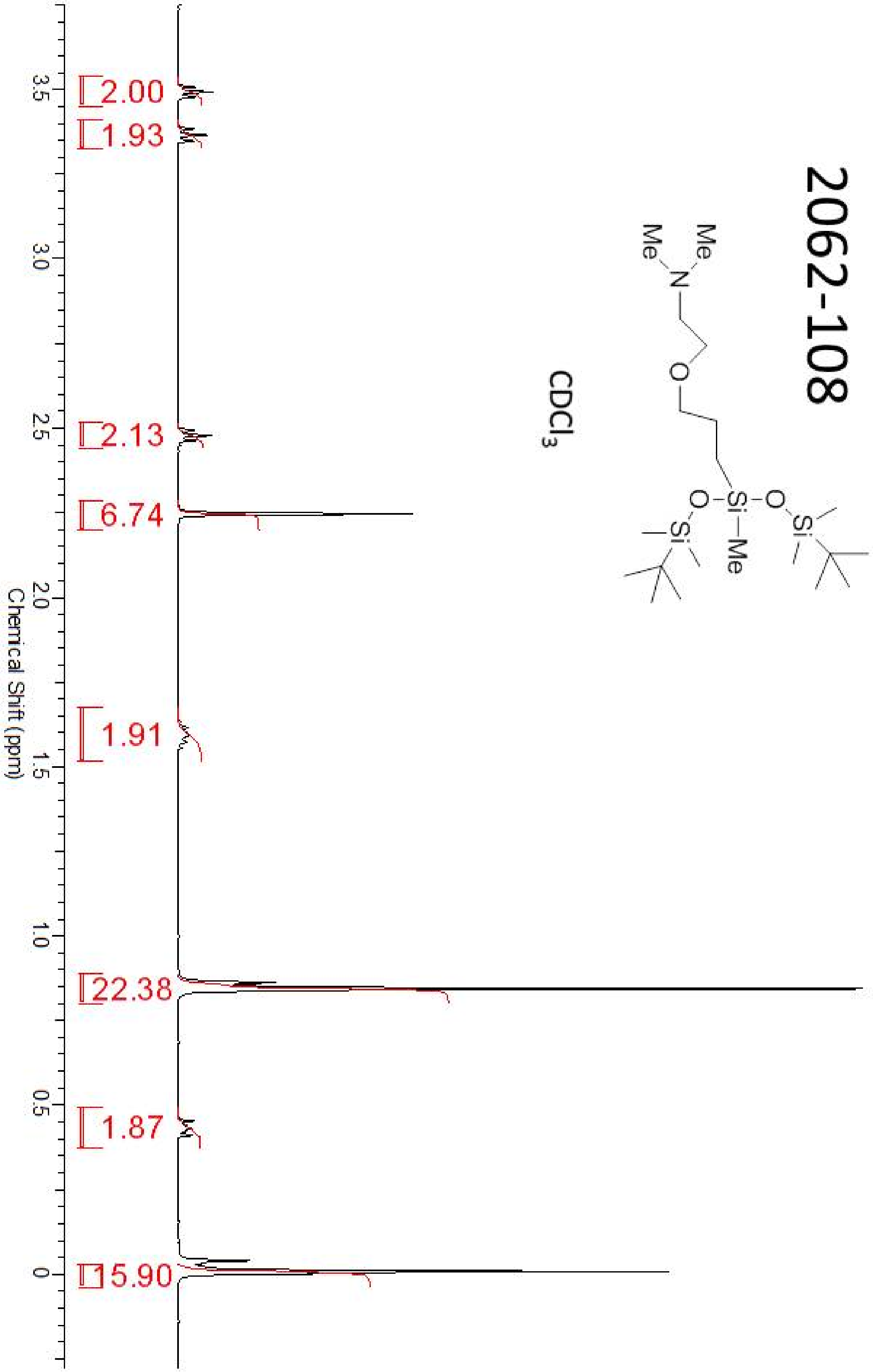
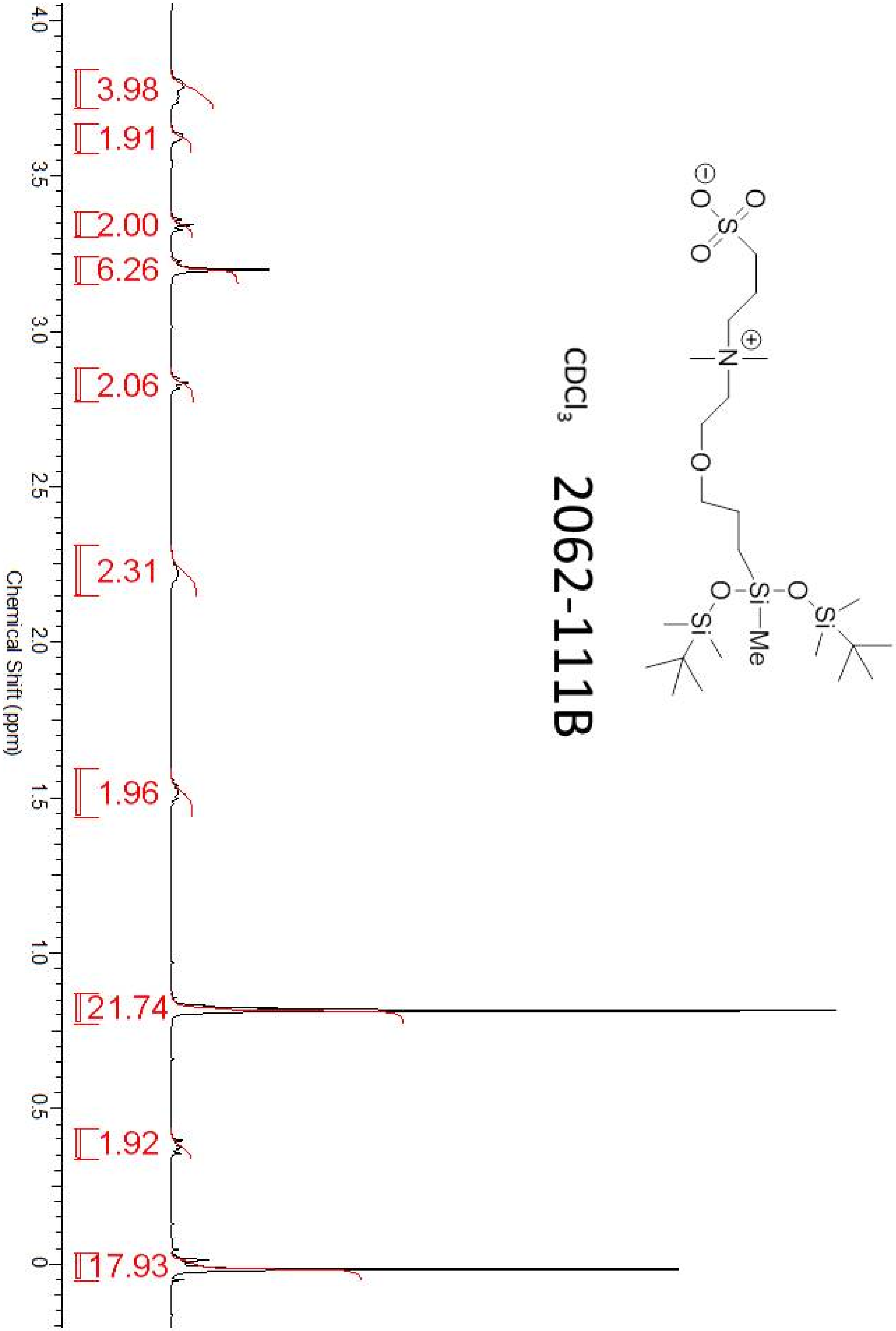
CDCl3
Me–Si–Me
Me
O
Si
O
Me–Si–Me
Me
N
7.92
1.88
1.91
27.00
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

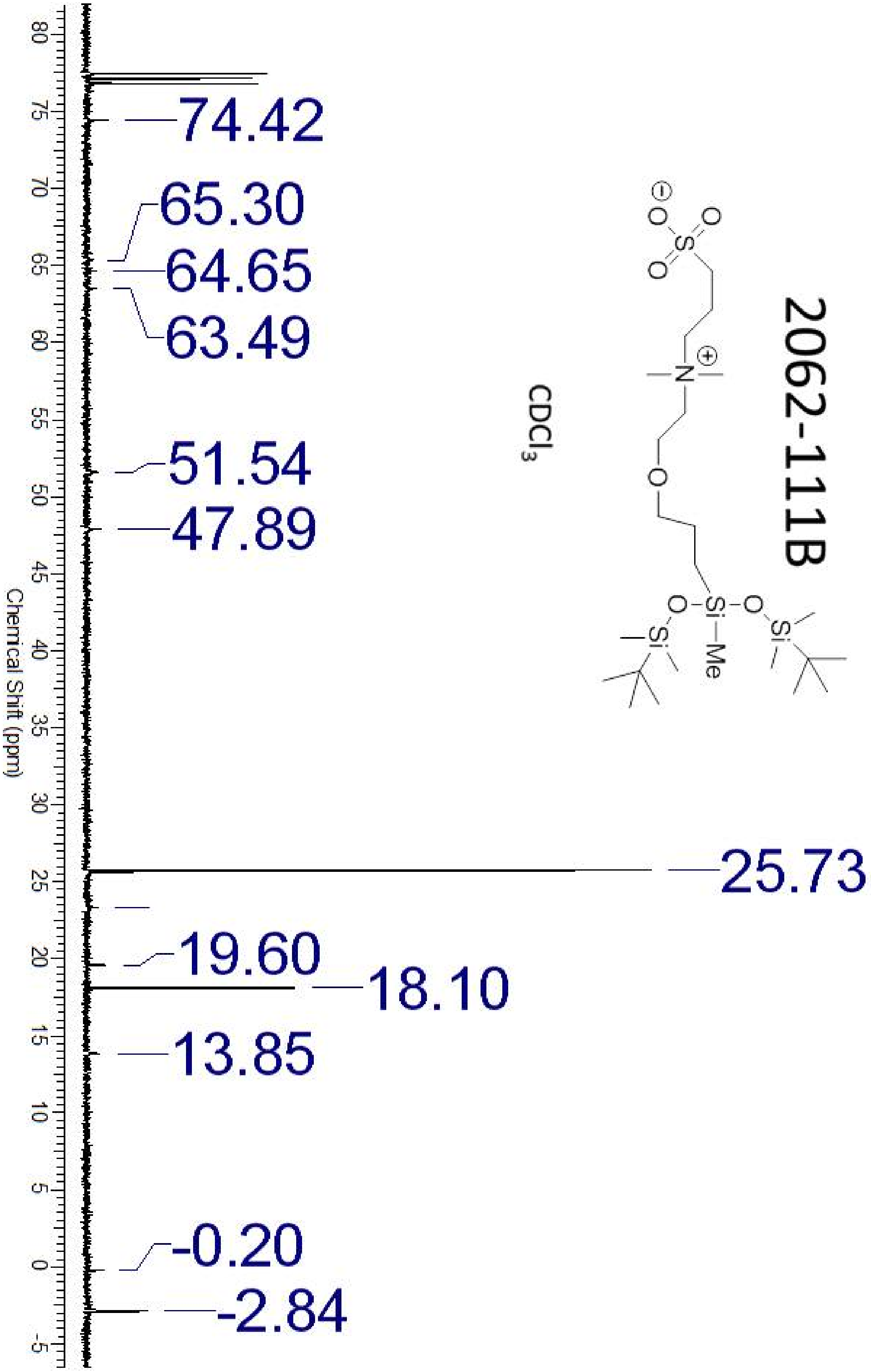

2062-106
DMSO
Me
H
N
H
Me
Cl
1.36
6.00
Chemical Shift (ppm)
9
8
7
6
5
4
3
2
1
0

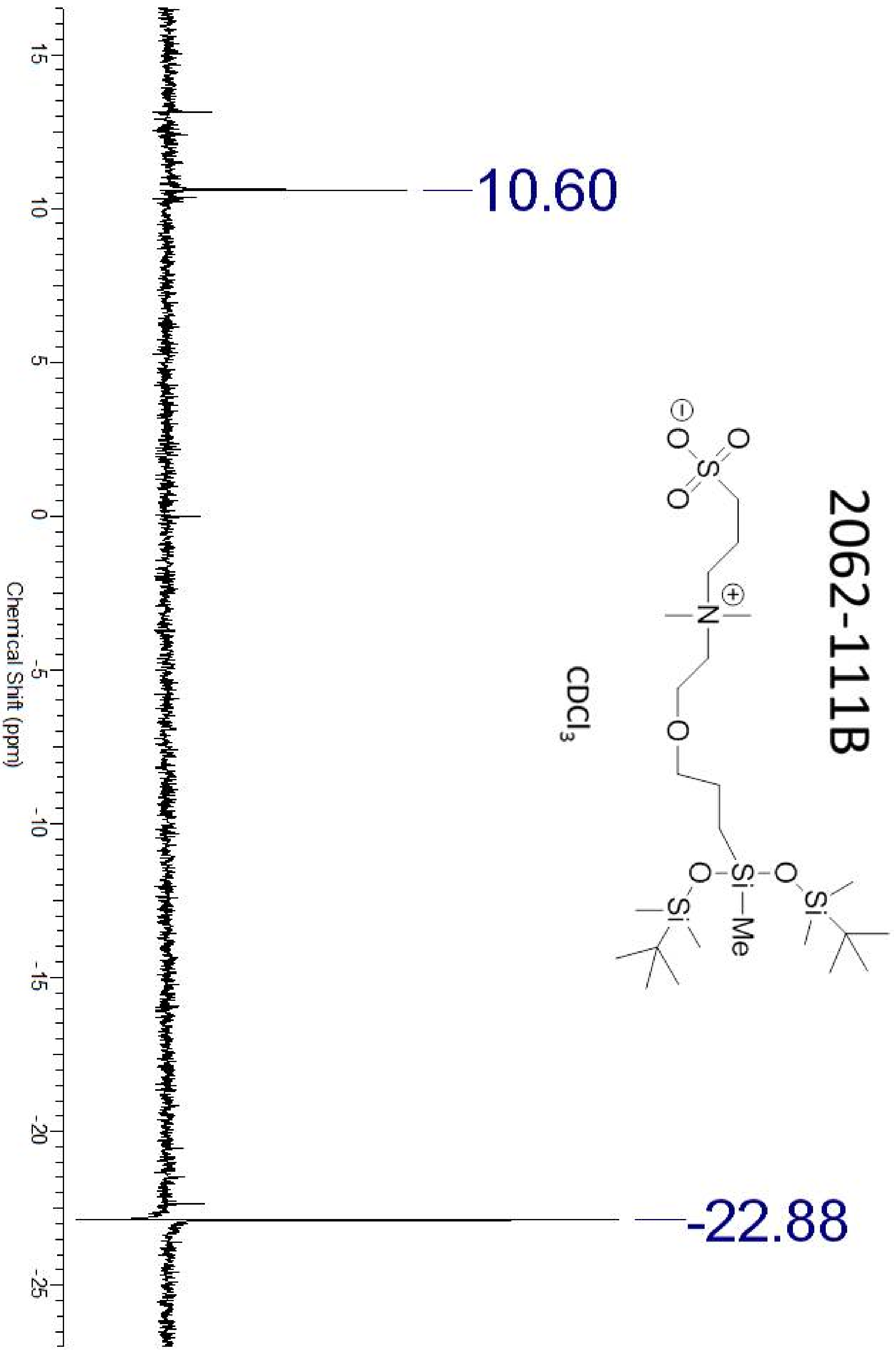

2062-108
Me
Me
N
O
Si
O
O
Si
Si
Me
CDCl3
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
2.00
1.93
2.13
6.74
1.91
22.38
1.87
15.90

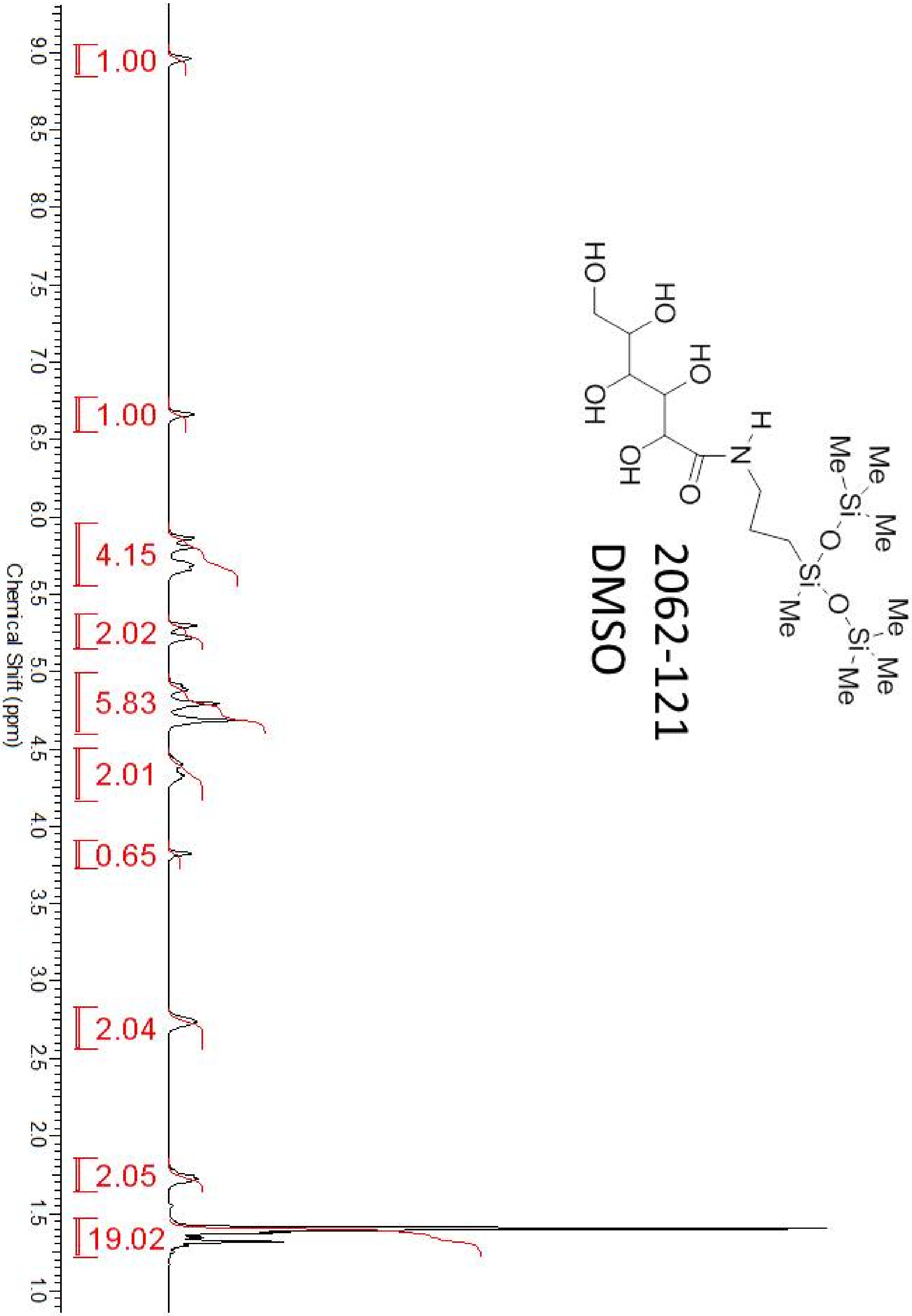


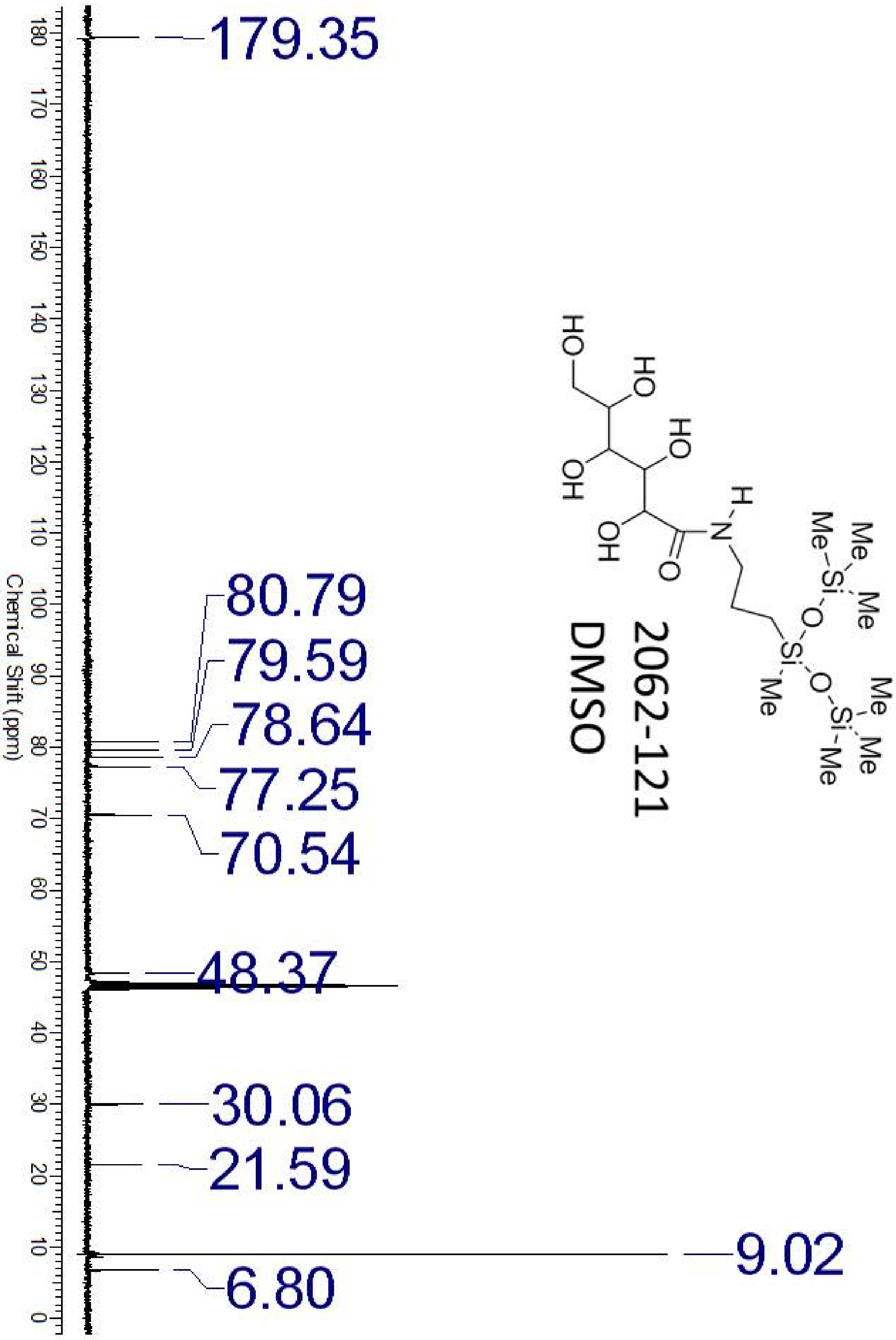
2062-111B

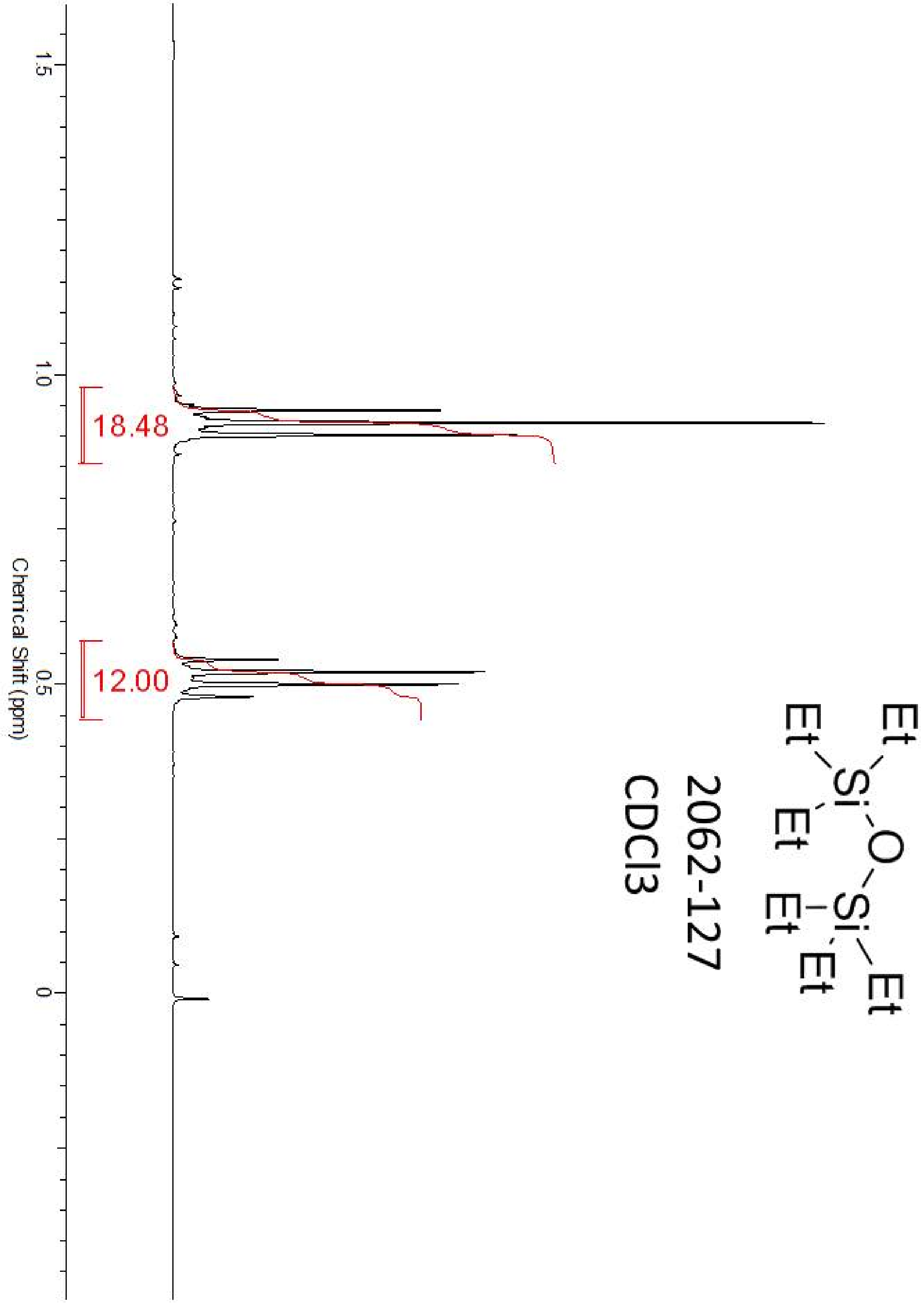
$CDCl_3$

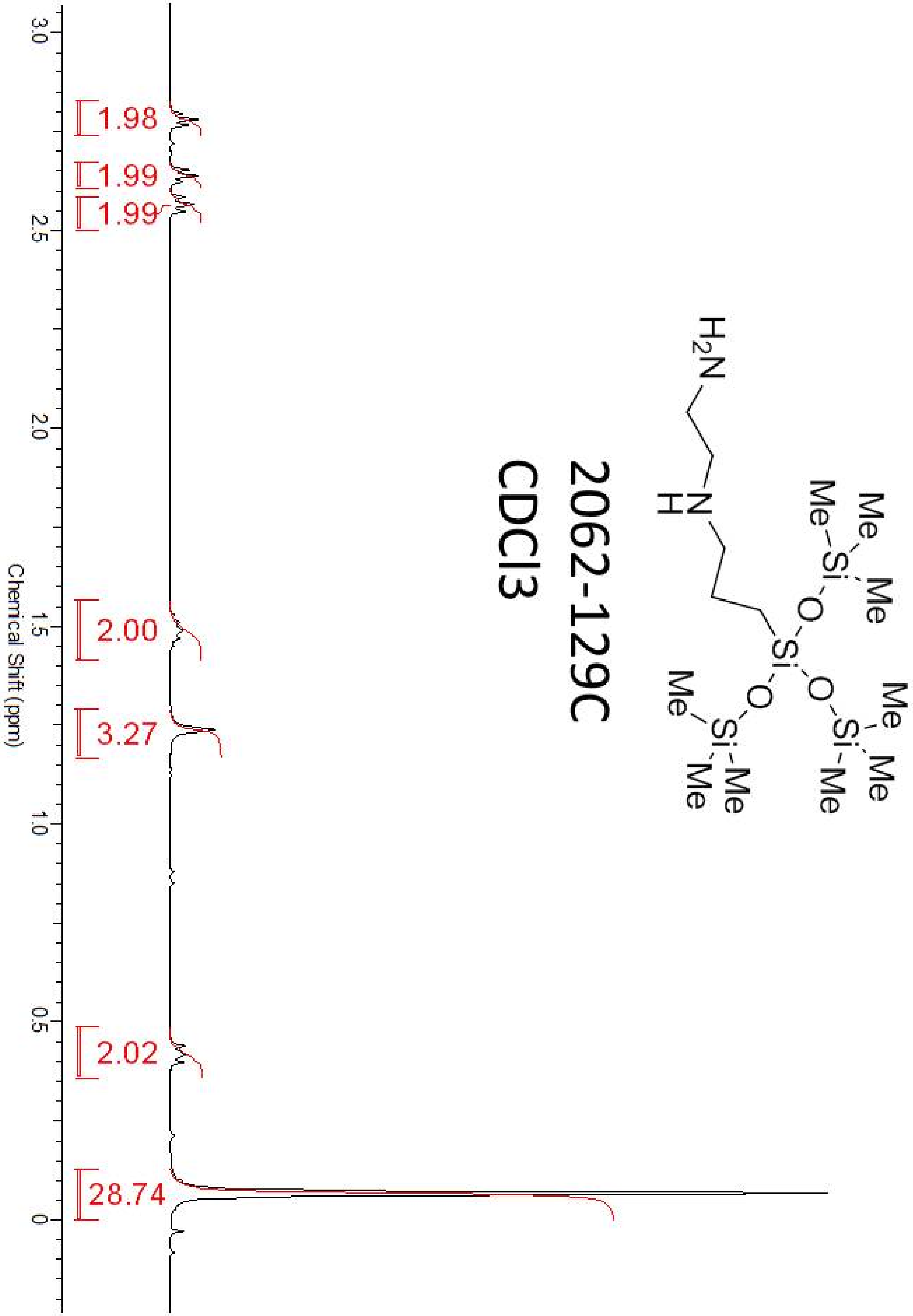

2062-111B
CDCl3
74.42
65.30
64.65
63.49
51.54
47.89
25.73
19.60
18.10
13.85
-0.20
-2.84
Chemical Shift (ppm)
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
Si
Me
O
N
S

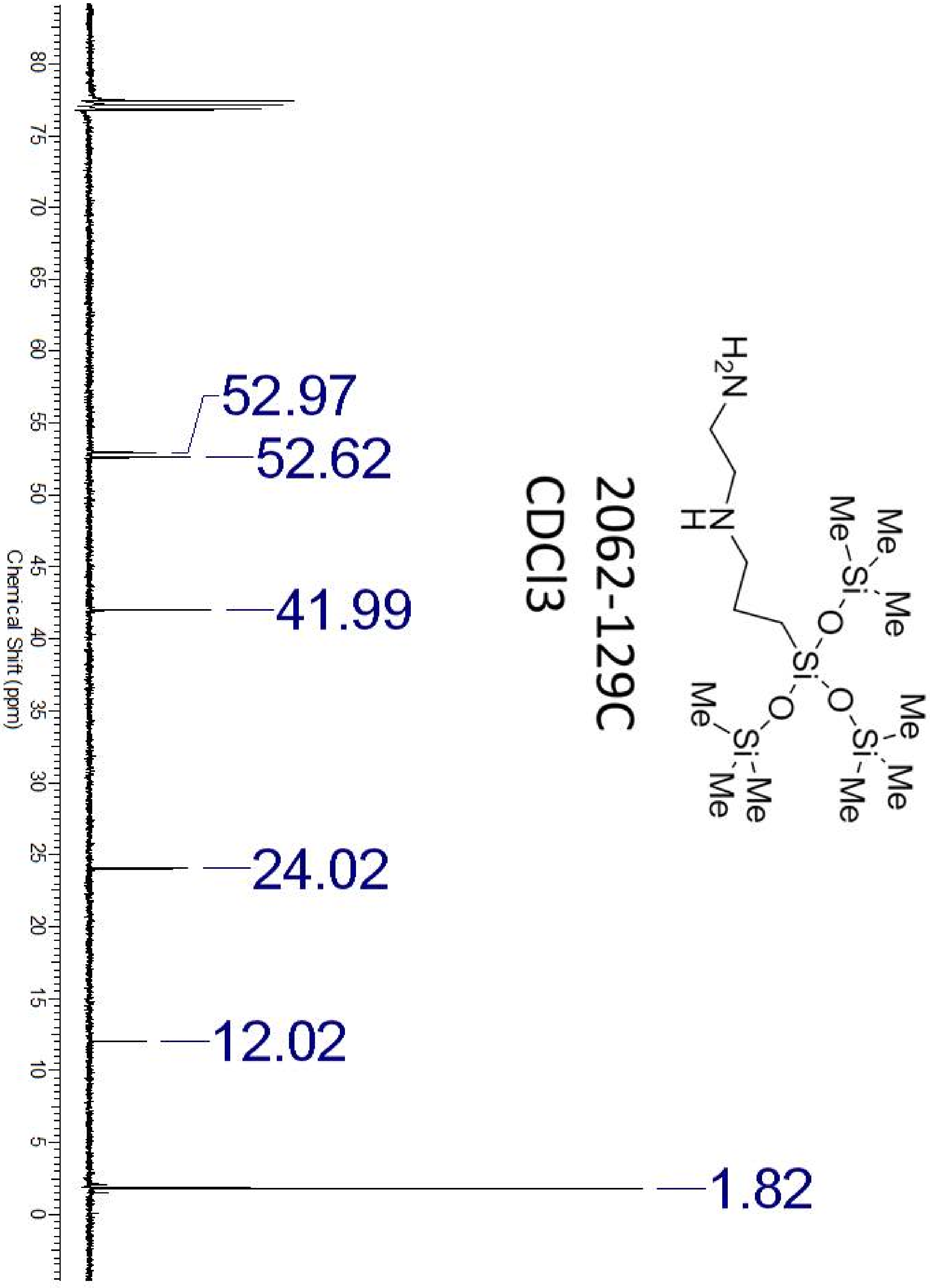

2062-111B
CDCl3
Me
10.60
-22.88
15
10
5
0
-5
-10
-15
-20
-25
Chemical Shift (ppm)

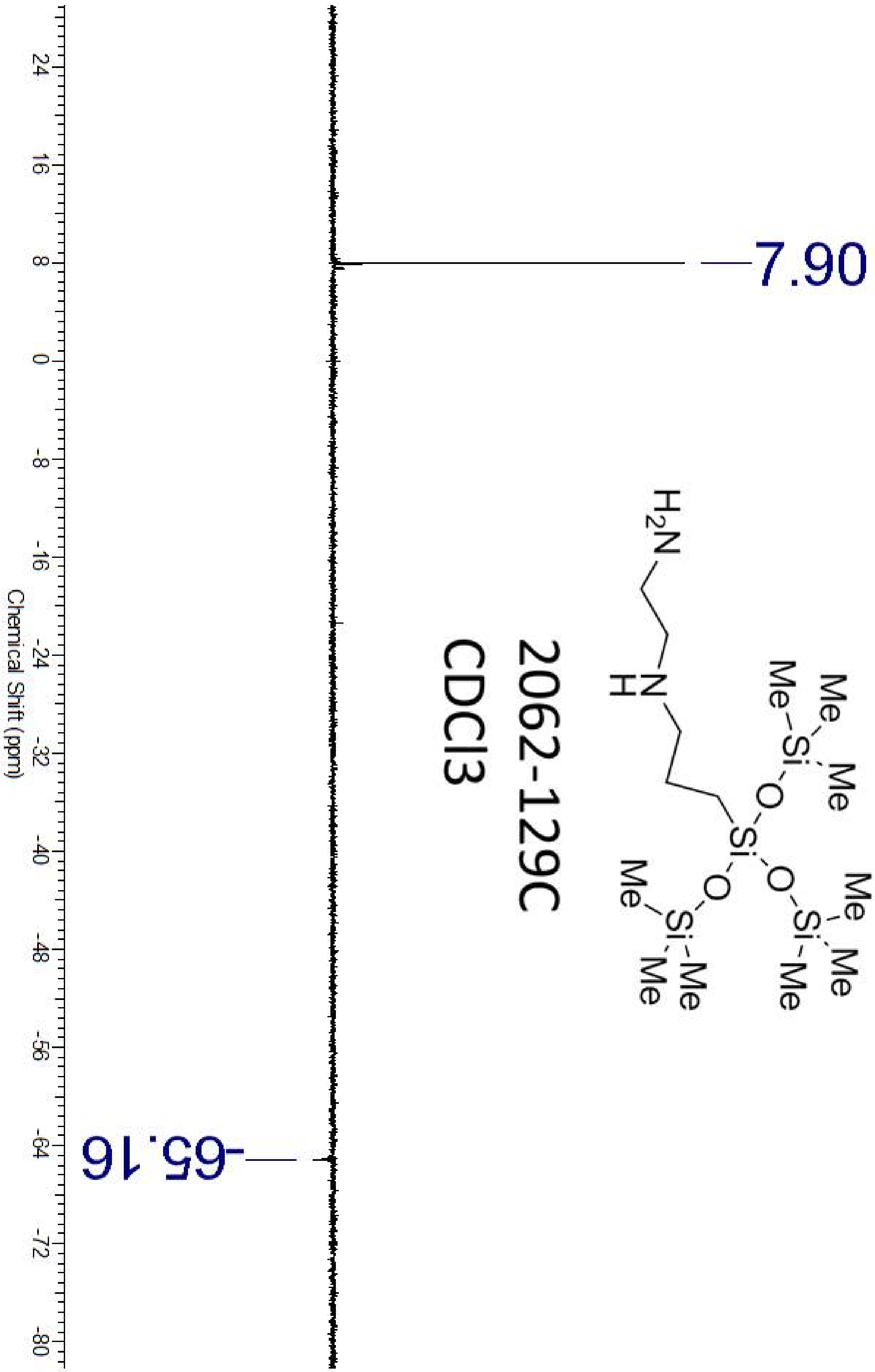

2062-121
DMSO
HO
HO
HO
OH
OH
O
H
N
Me
Me
Si
O
Si
Me
O
Si
Me
Me
Me
1.00
1.00
4.15
2.02
5.83
2.01
0.65
2.04
2.05
19.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

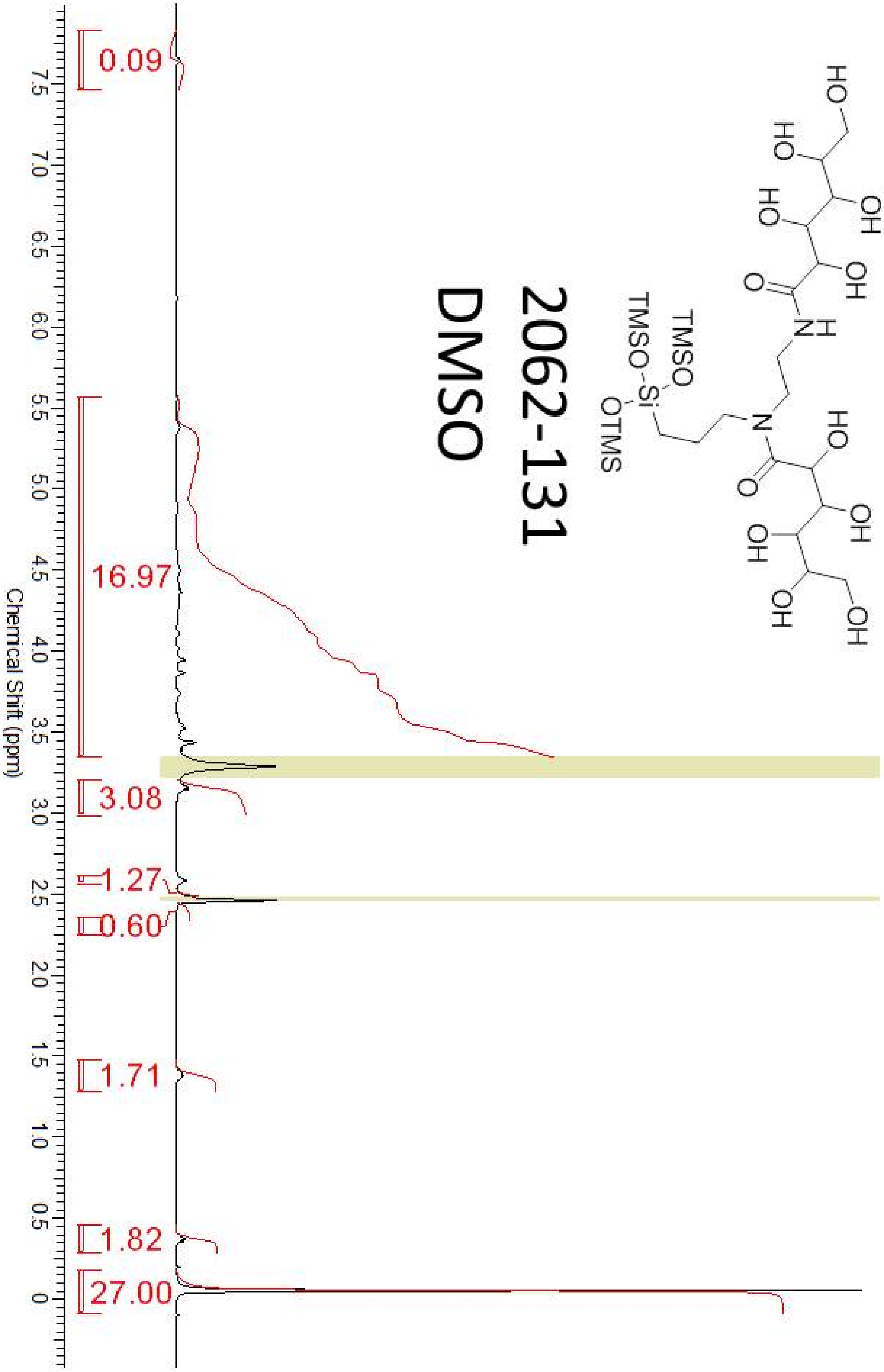

179.35
80.79
79.59
78.64
77.25
70.54
48.37
30.06
21.59
9.02
6.80
Chemical Shift (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
HO
OH
OH
HO
OH
O
N
H
Me
Me
Si
O
Si
Me
O
Si
Me
Me
Me
Me
2062-121
DMSO

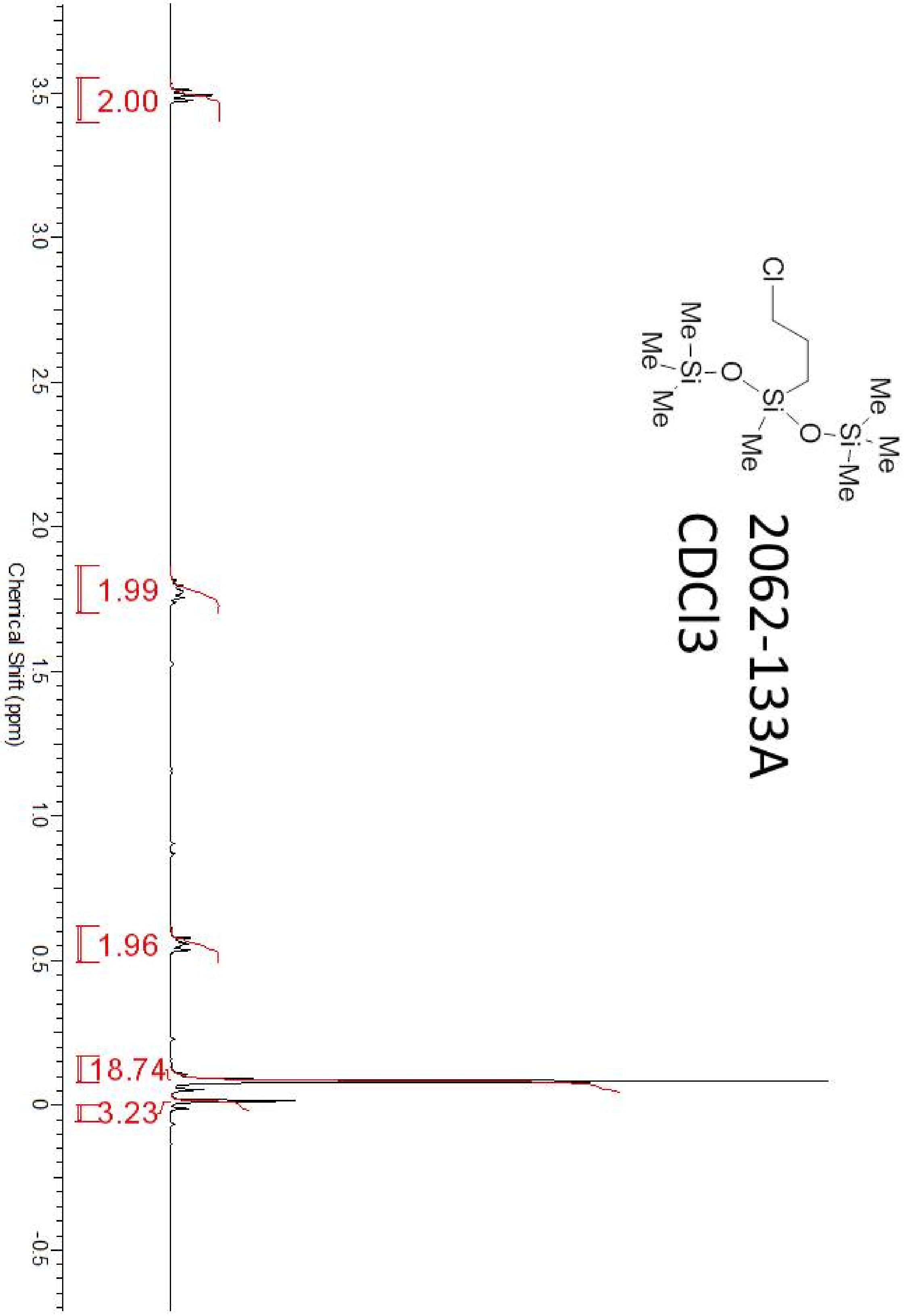

Et
Et
Si
O
Si
Et
Et
Et
Et
2062-127
CDCl3
18.48
12.00
1.5
1.0
0.5
0
Chemical Shift (ppm)

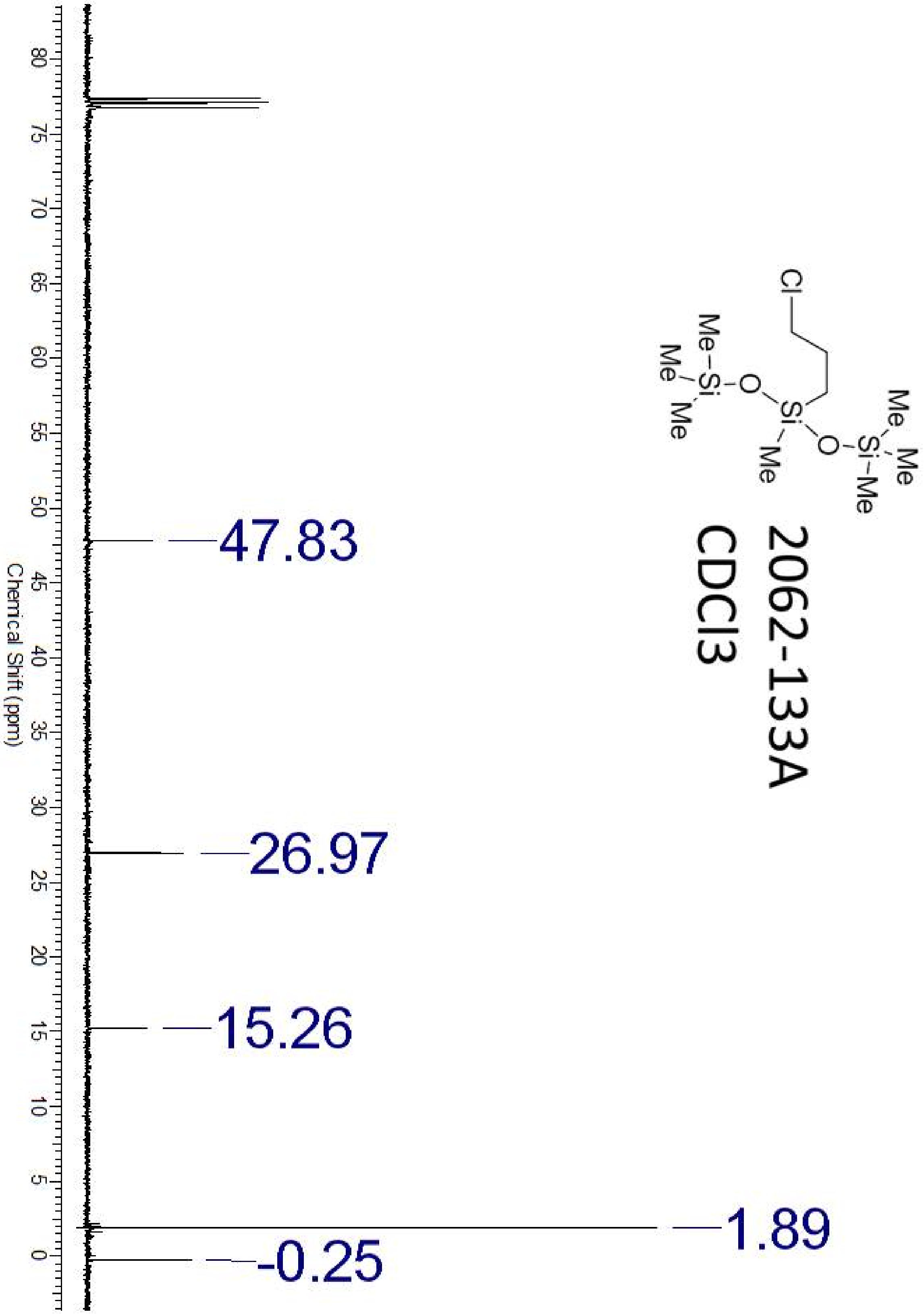

2062-129C
CDCl3

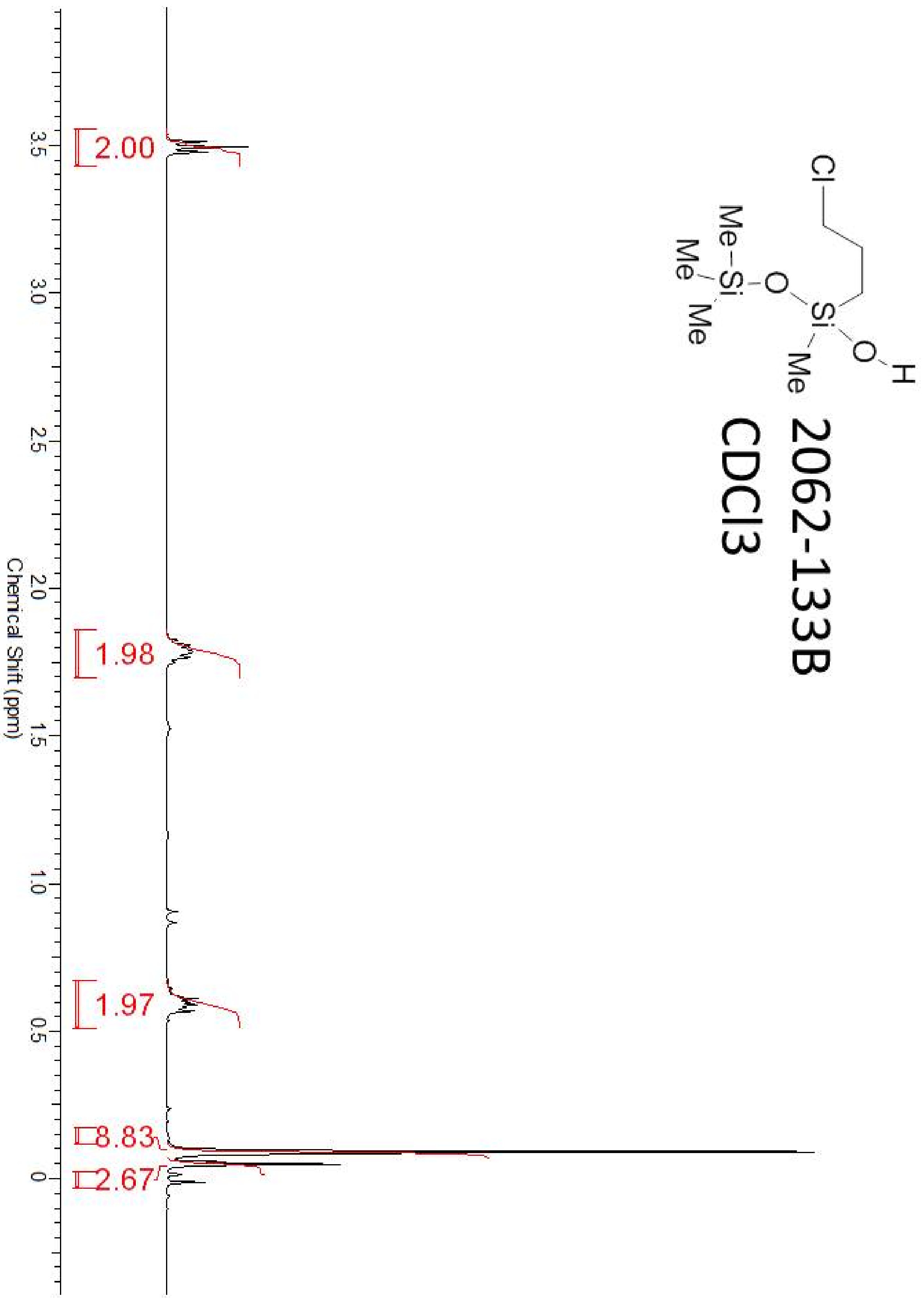

2062-129C
CDCl3
H2N
N
H
Si
O
Me
52.97
52.62
41.99
24.02
12.02
1.82
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
Chemical Shift (ppm)

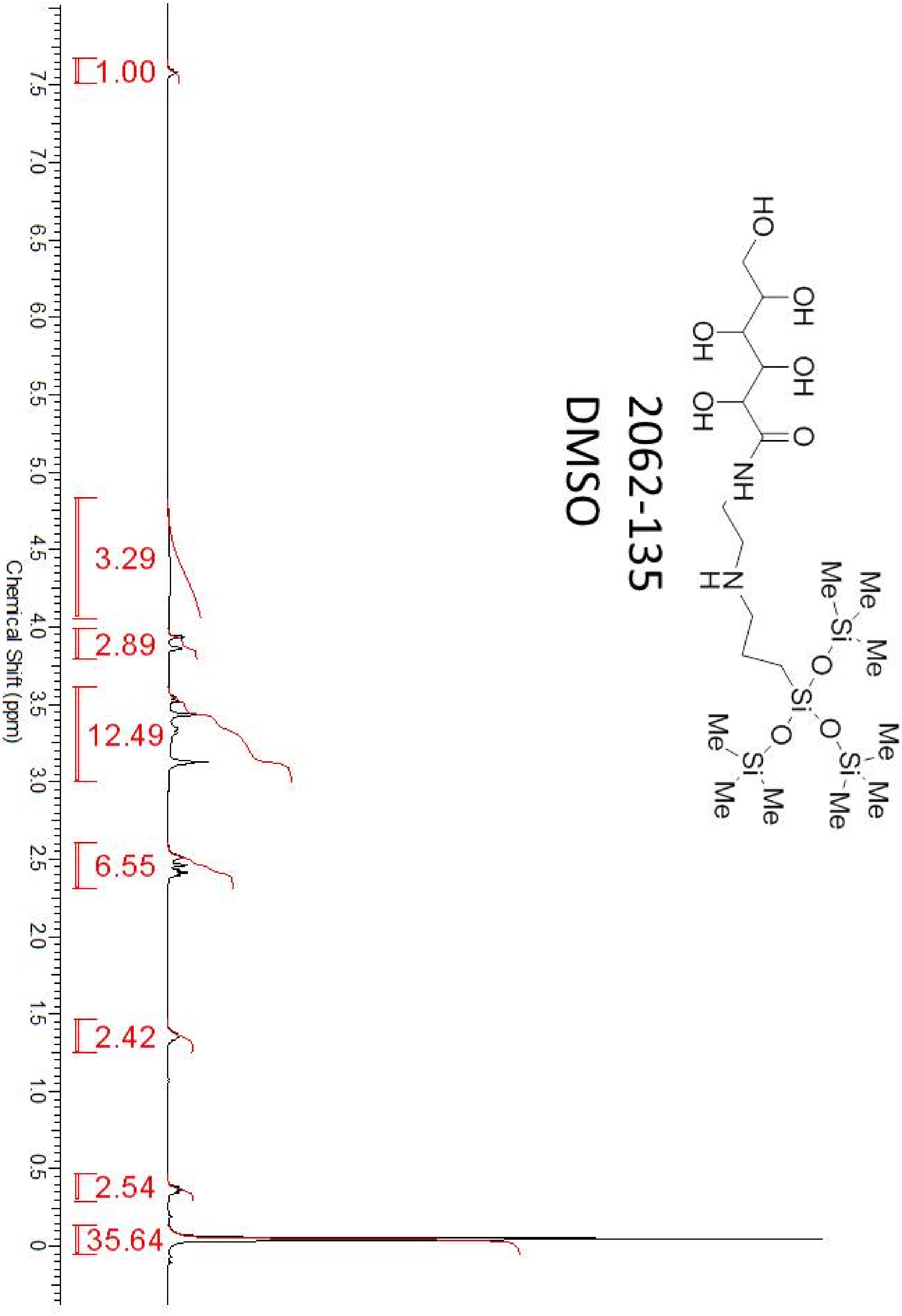

7.90
-65.16
24
16
8
0
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
Chemical Shift (ppm)
H2N
N
H
Me
Me
Si
O
Si
O
Si
Me
Me
Me
O
Si
Me
Me
Me
Me
2062-129C
CDCl3


2062-131
DMSO
HO
OH
O
N
H
TMSO
TMSO
Si
OTMS
0.09
16.97
3.08
1.27
0.60
1.71
1.82
27.00
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
0
Chemical Shift (ppm)


2062-133A
CDCl3
Cl
Me
Si
O
Me
Si
Me
Me
O
Si
Me
Me
Me
2.00
1.99
1.96
18.74
3.23
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)

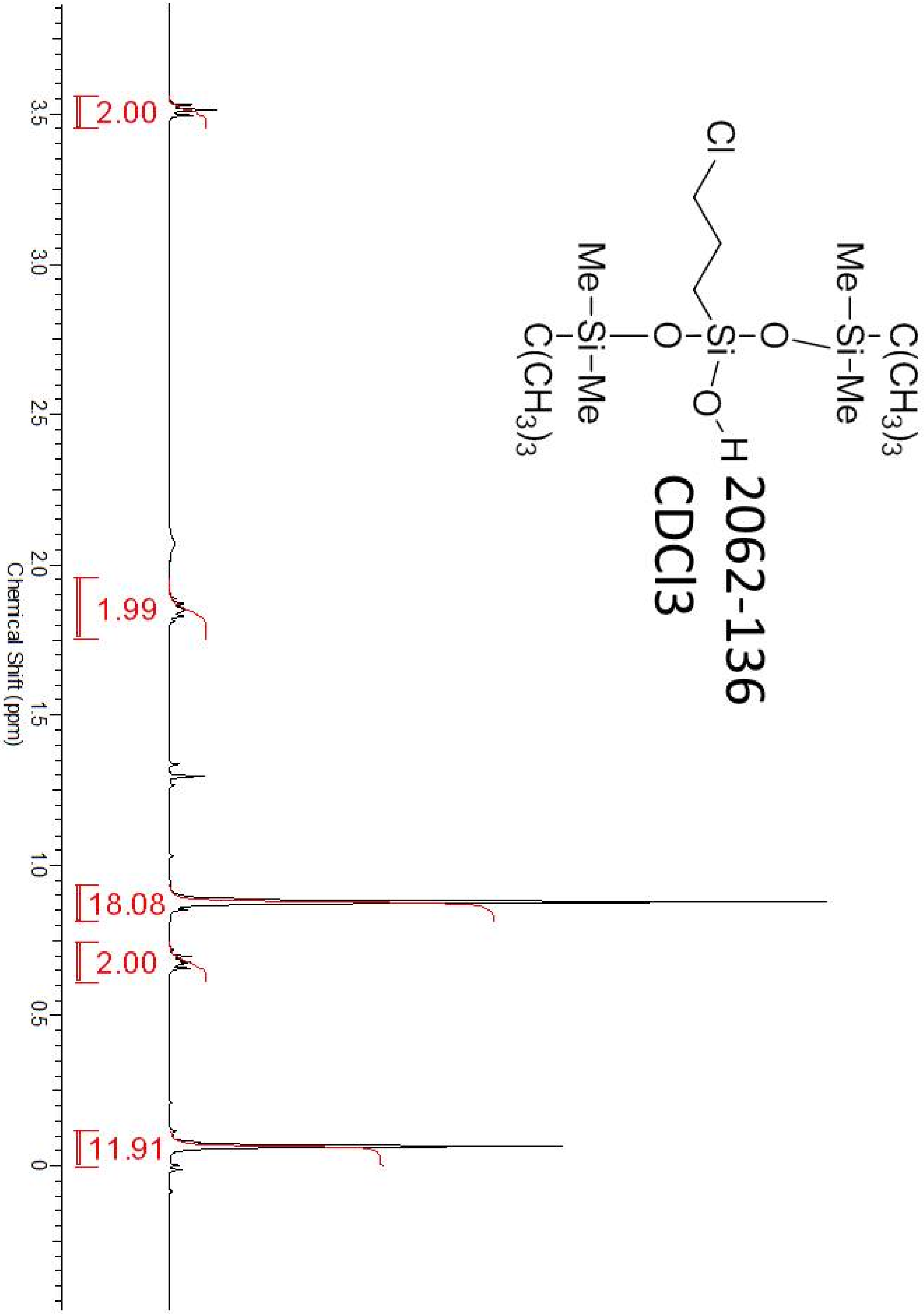

2062-133A
CDCl3
Cl
Si
O
Me
Me
Me
Si
Me
O
Si
Me
Me
Me
47.83
26.97
15.26
1.89
-0.25
Chemical Shift (ppm)
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0

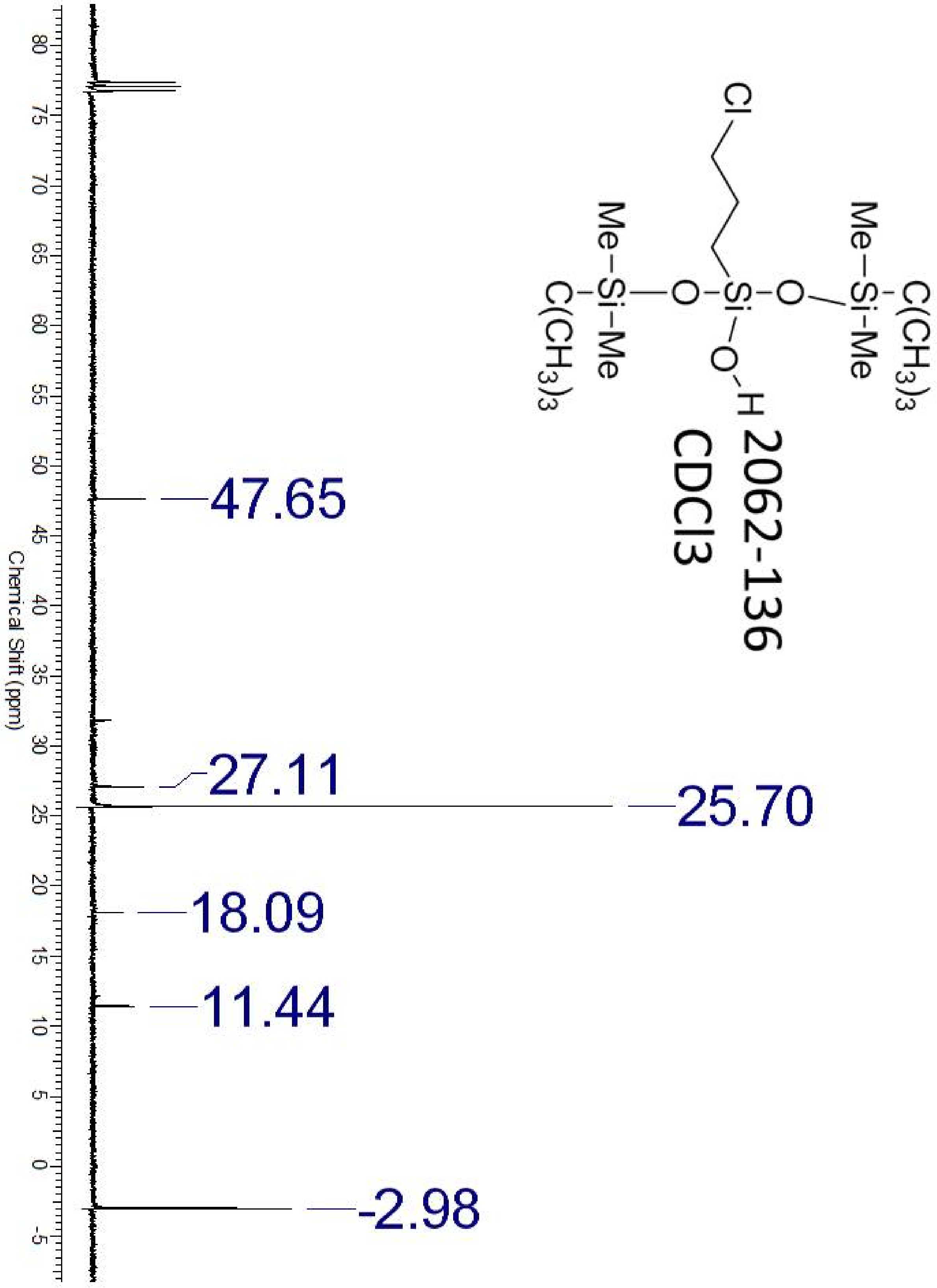

2062-133B
CDCl3
Cl
Si
O
H
Me
O
Me–Si
Me
Me
2.00
1.98
1.97
8.83
2.67
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

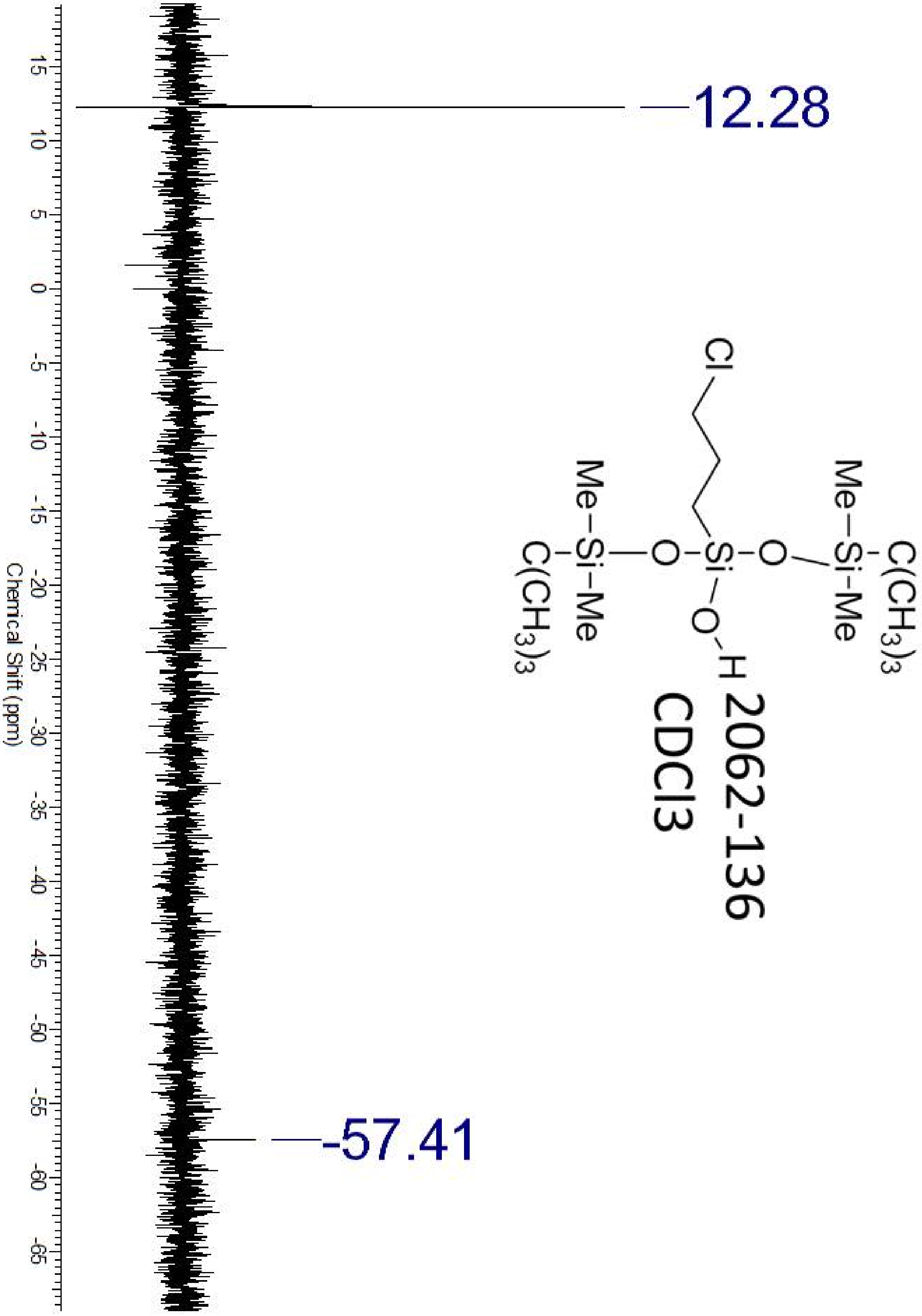


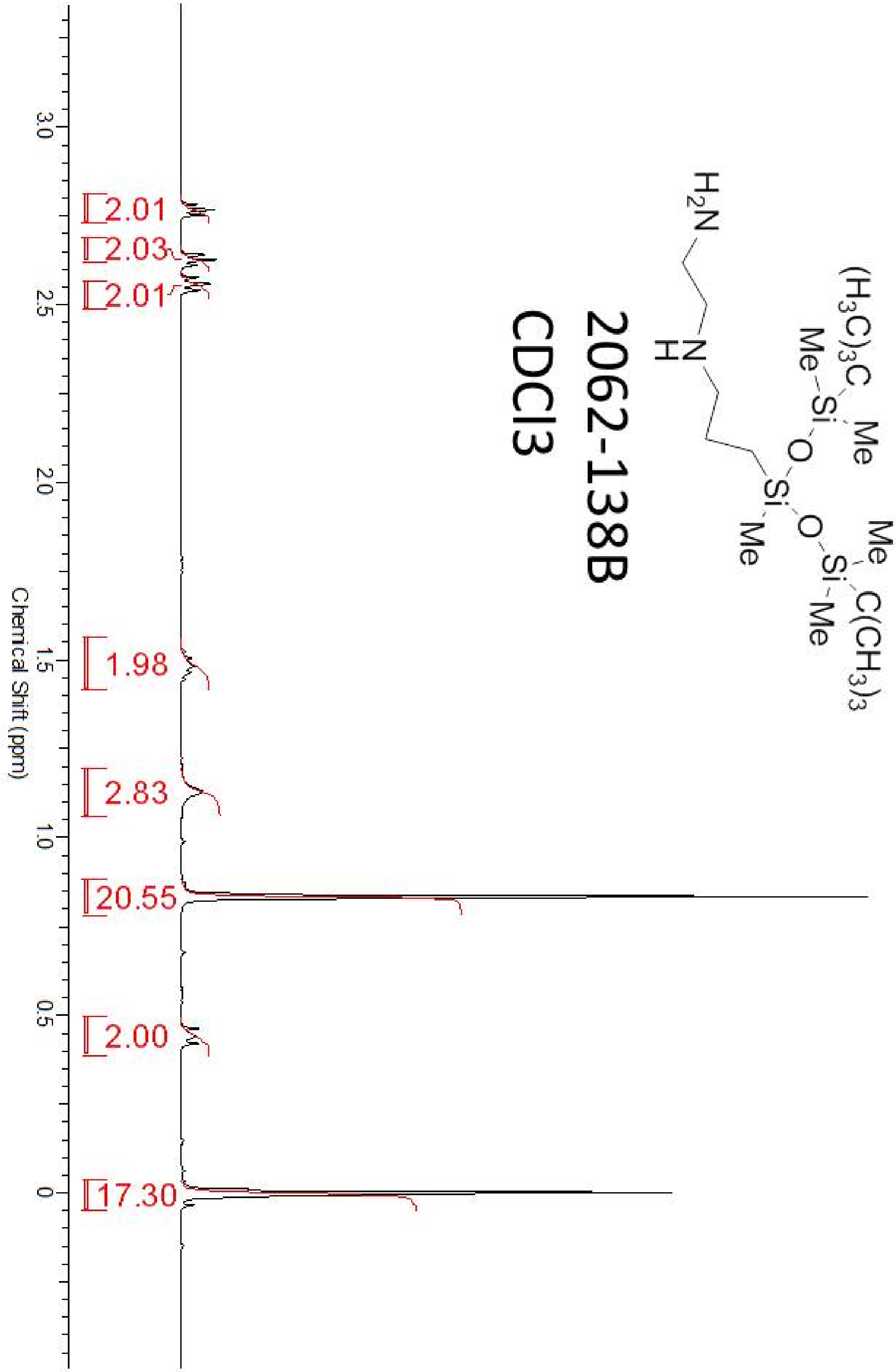
2062-135

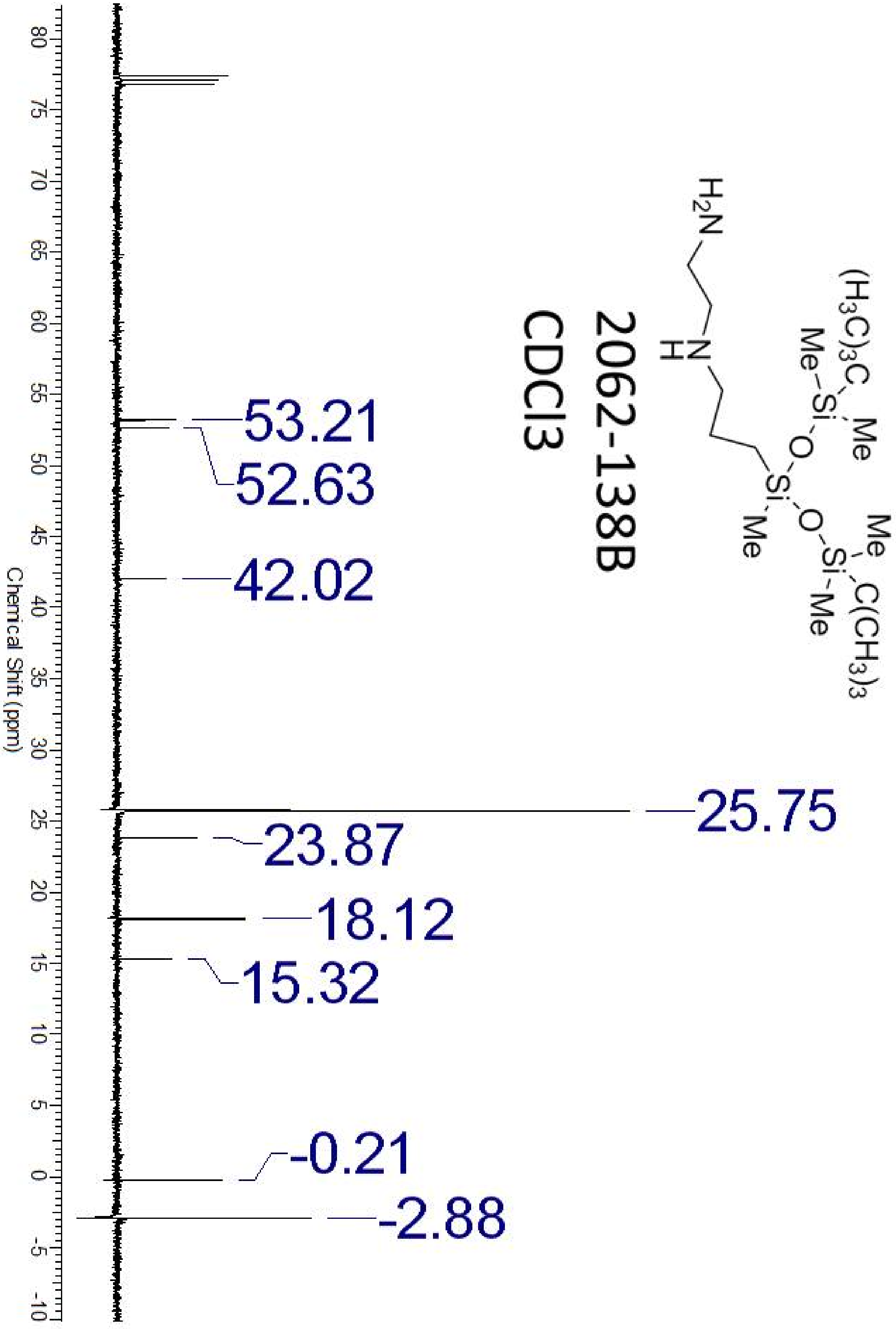
DMSO

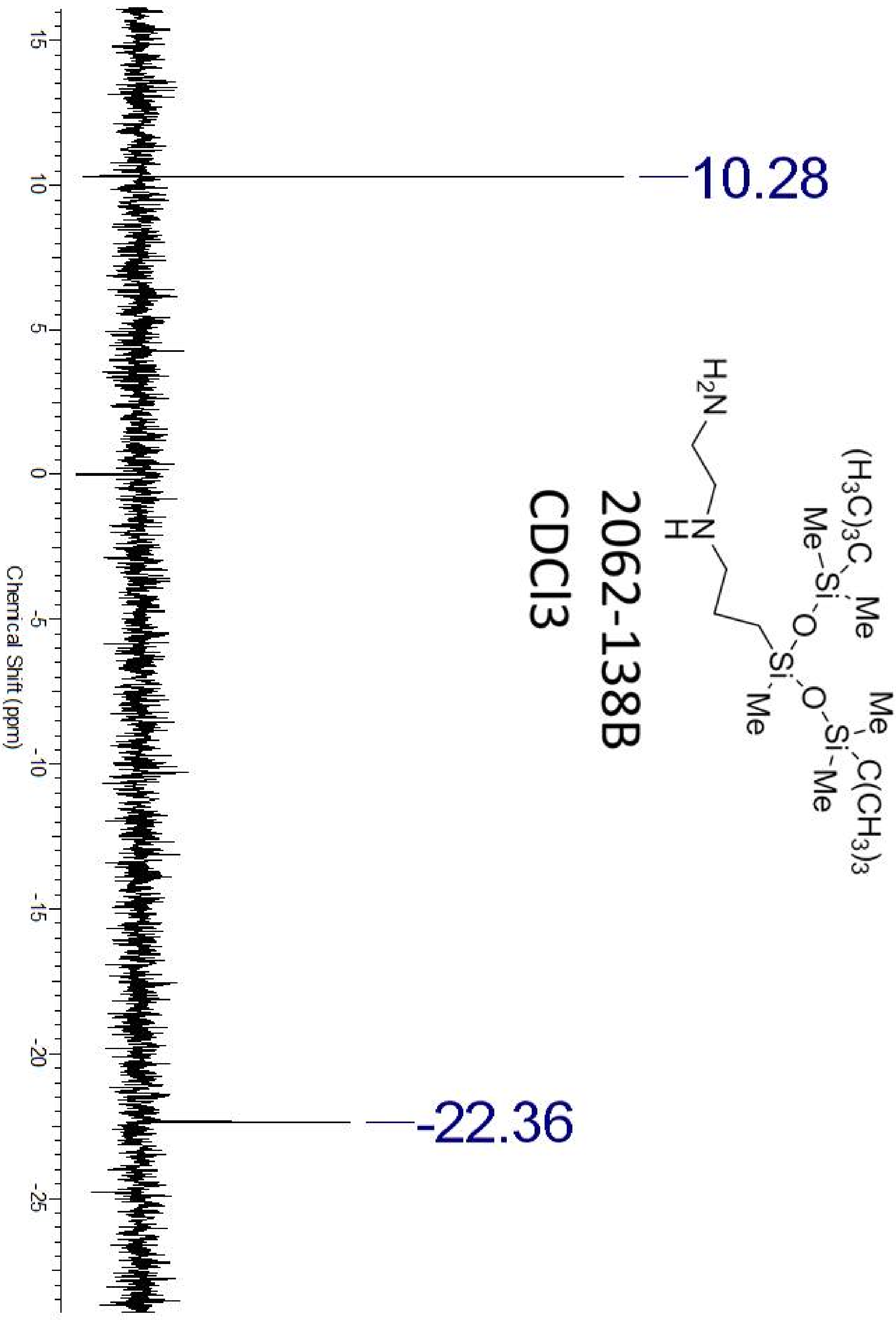

2062-136
CDCl3
Cl
Si
O
H
Me–Si–Me
C(CH3)3
2.00
1.99
18.08
2.00
11.91
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

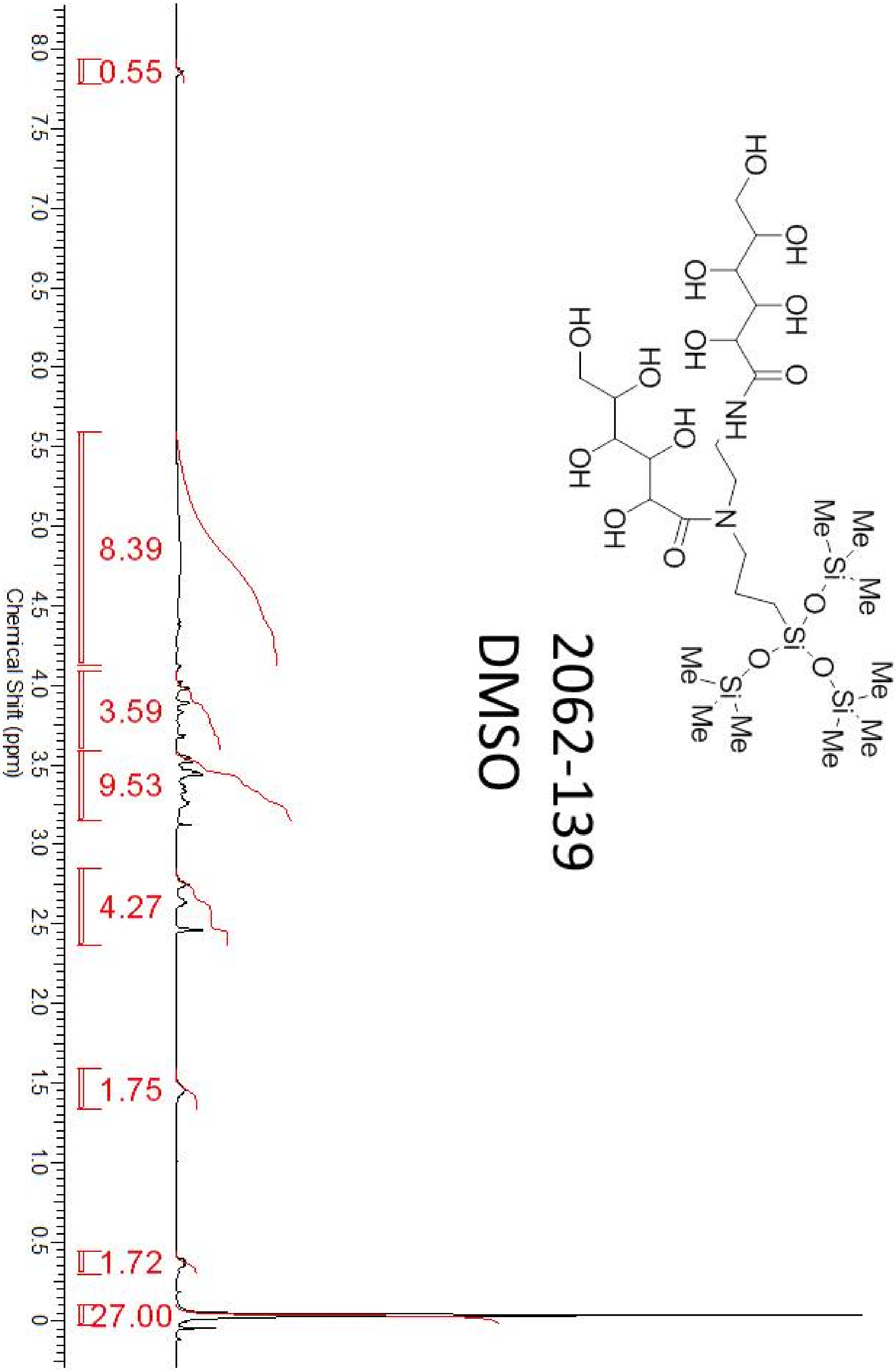

2062-136
CDCl3
Cl
Me
Si
Me
C(CH3)3
O
Si
O
H
O
Me
Si
Me
C(CH3)3
47.65
27.11
25.70
18.09
11.44
-2.98
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
Chemical Shift (ppm)


12.28
-57.41
Cl
Me–Si–Me
C(CH3)3
O
Si
O–H
2062-136
CDCl3
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
Chemical Shift (ppm)

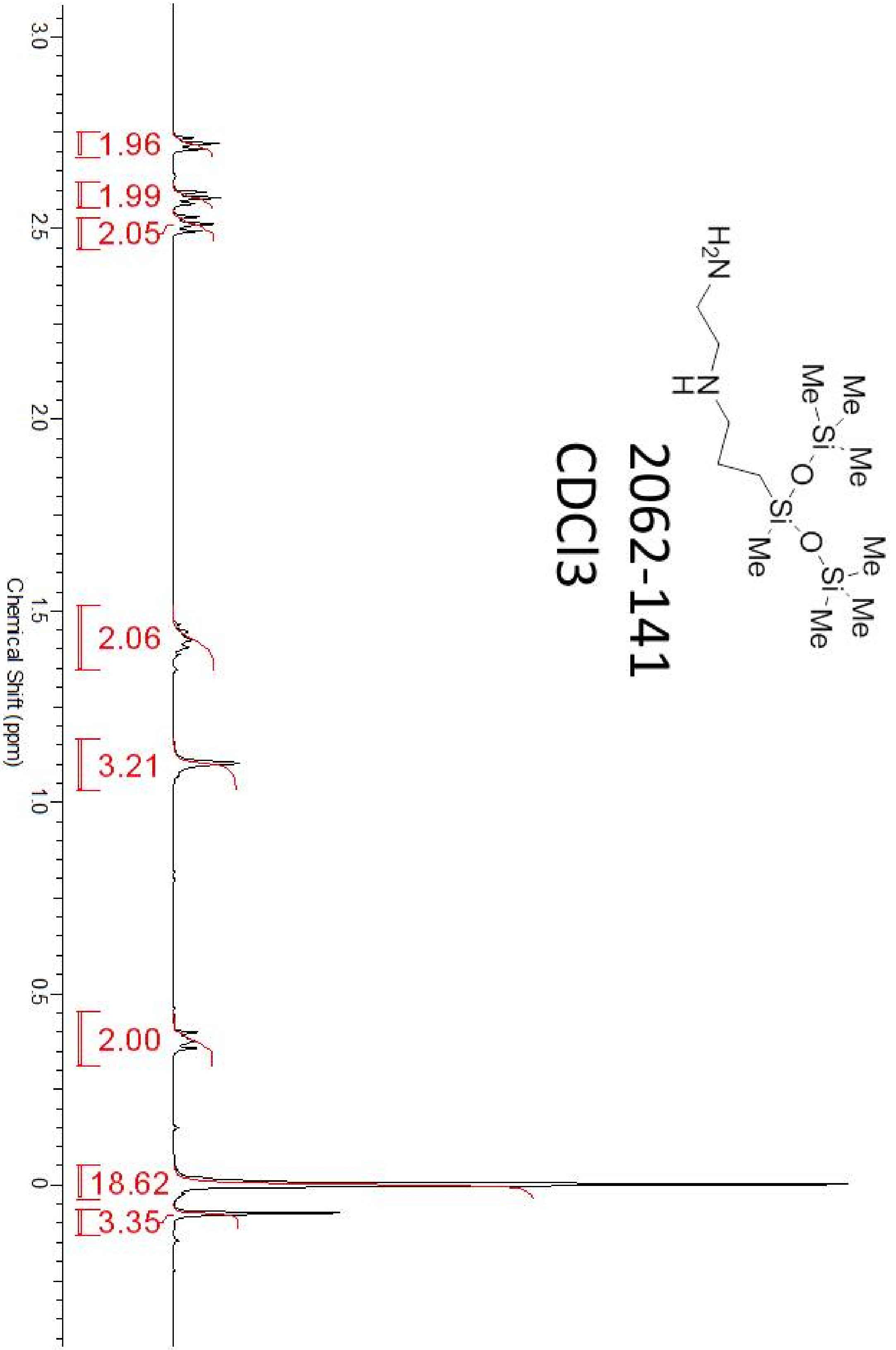

(H3C)3C
Me
Me
Si
O
Si
Me
O
Me
Si
Me
C(CH3)3
H2N
N
H
2062-138B
CDCl3
2.01
2.03
2.01
1.98
2.83
20.55
2.00
17.30
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

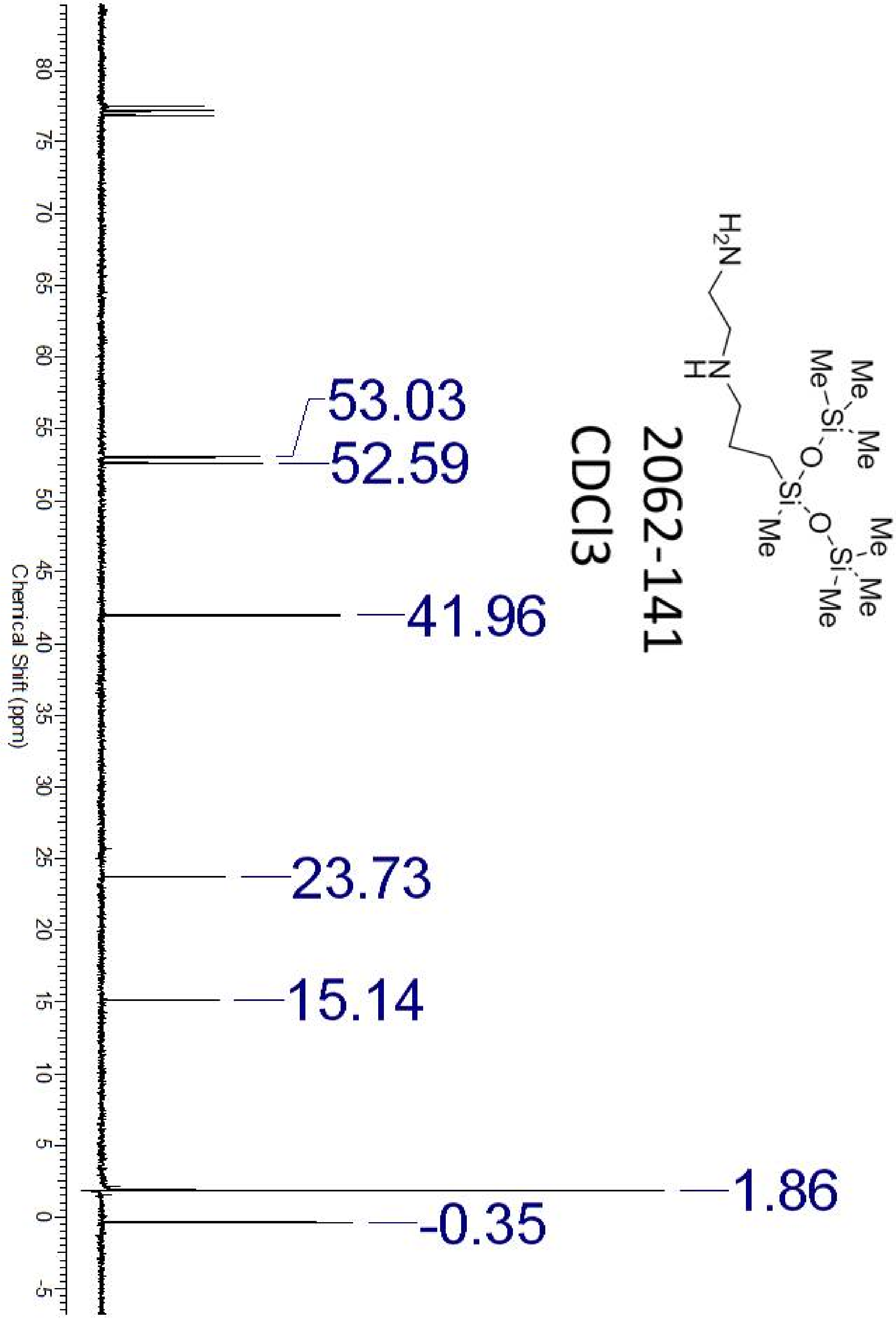

2062-138B
CDCl3
H2N
N
H
(H3C)3C
Me
Me
Si
O
Si
Me
O
Si
Me
Me
C(CH3)3
53.21
52.63
42.02
25.75
23.87
18.12
15.32
-0.21
-2.88
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
Chemical Shift (ppm)

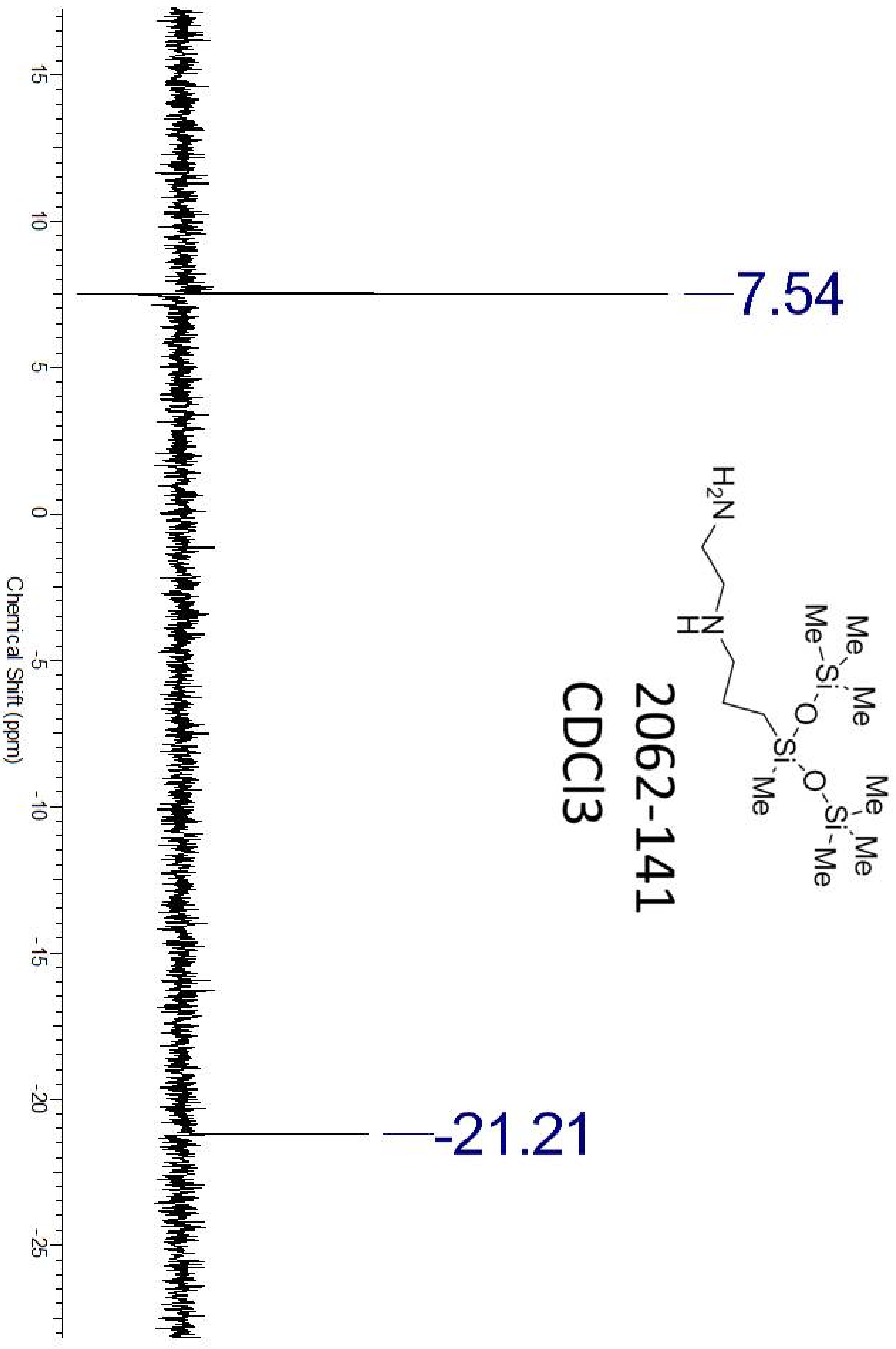

10.28
-22.36
H_2N
N
H
$(H_3C)_3C$
Me
Me
Si
O
Si
Me
O
Si
Me
Me
$C(CH_3)_3$
2062-138B
CDCl3
15
10
5
0
-5
-10
-15
-20
-25
Chemical Shift (ppm)

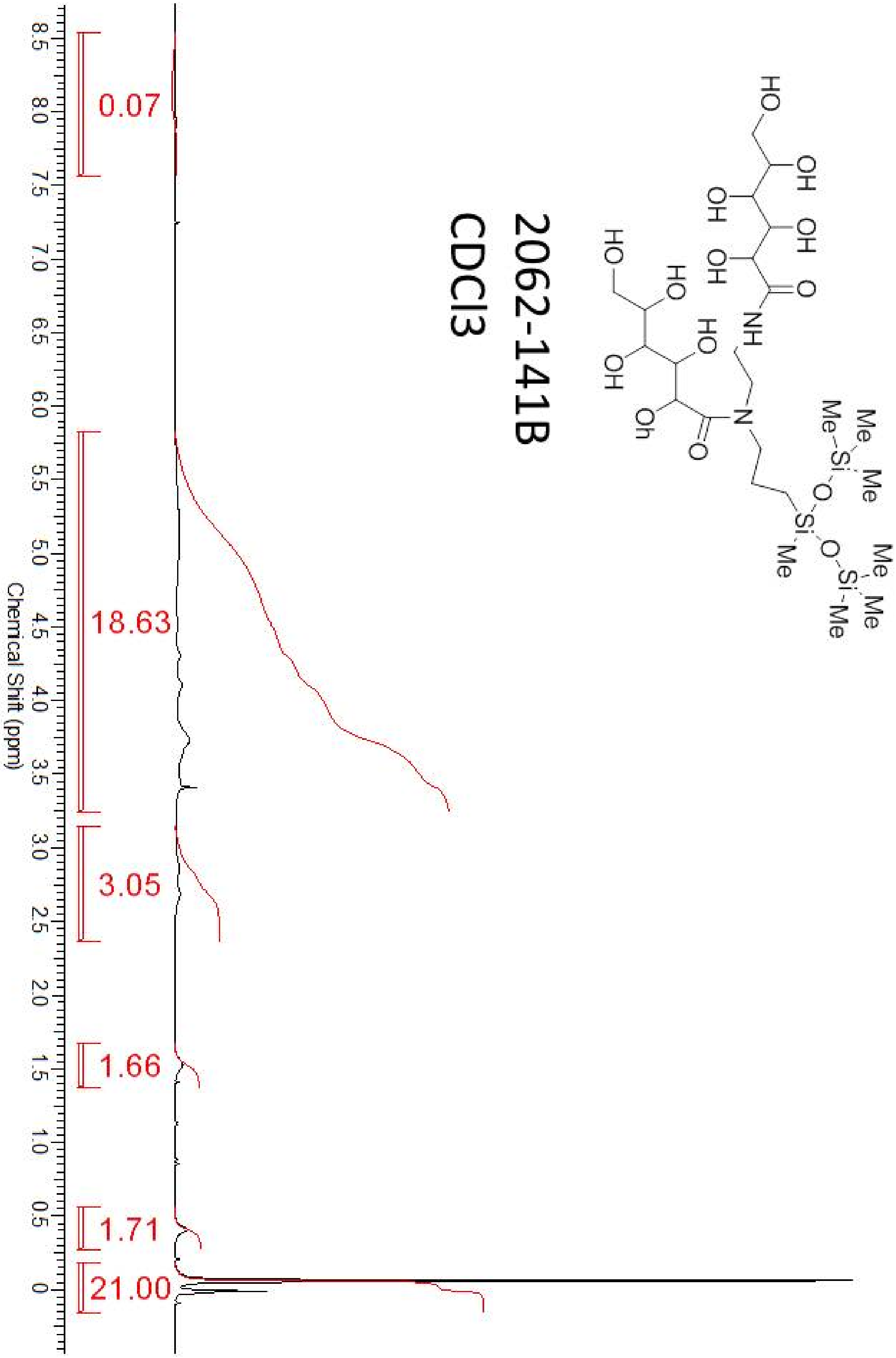


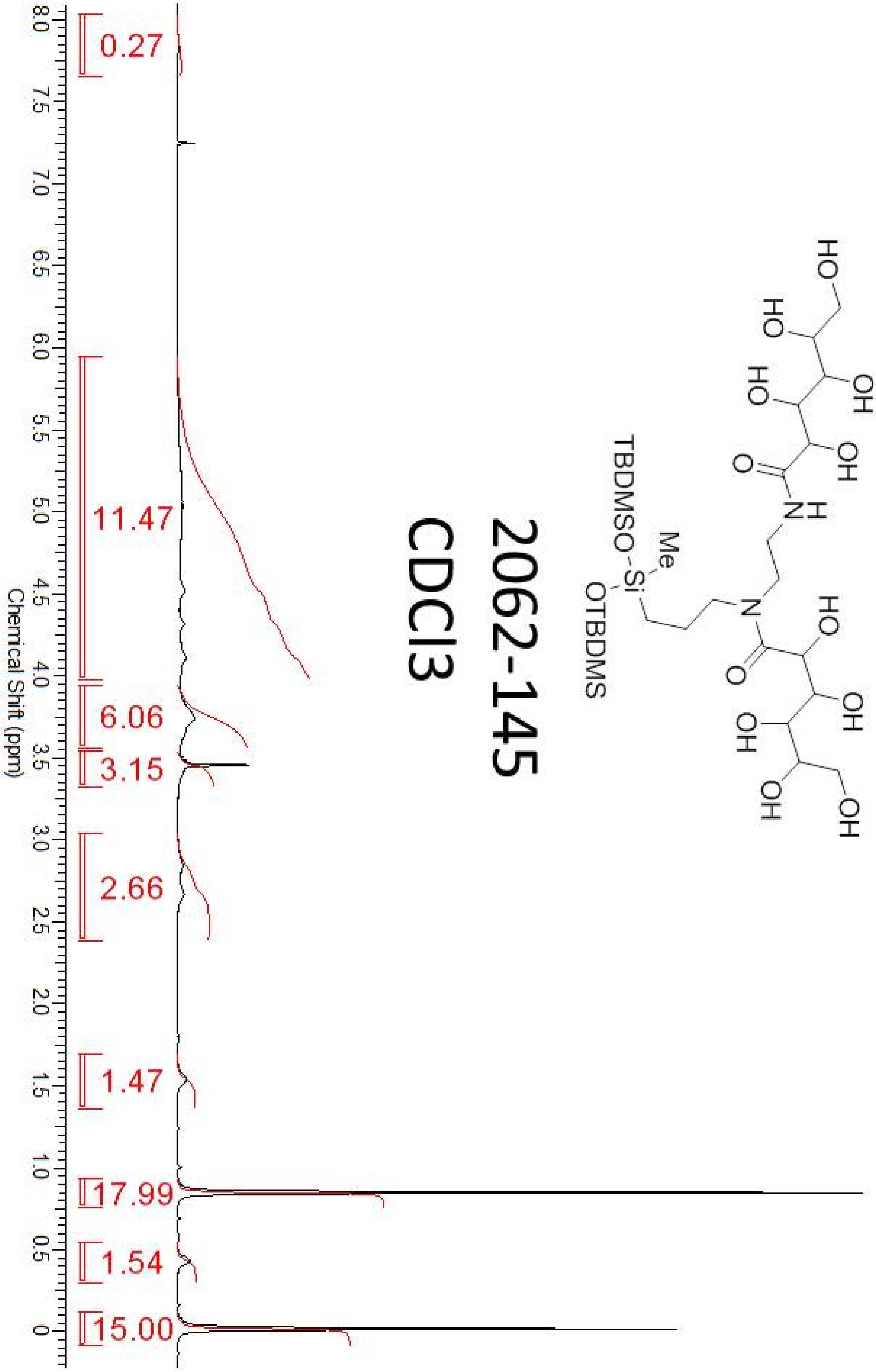
2062-139
DMSO

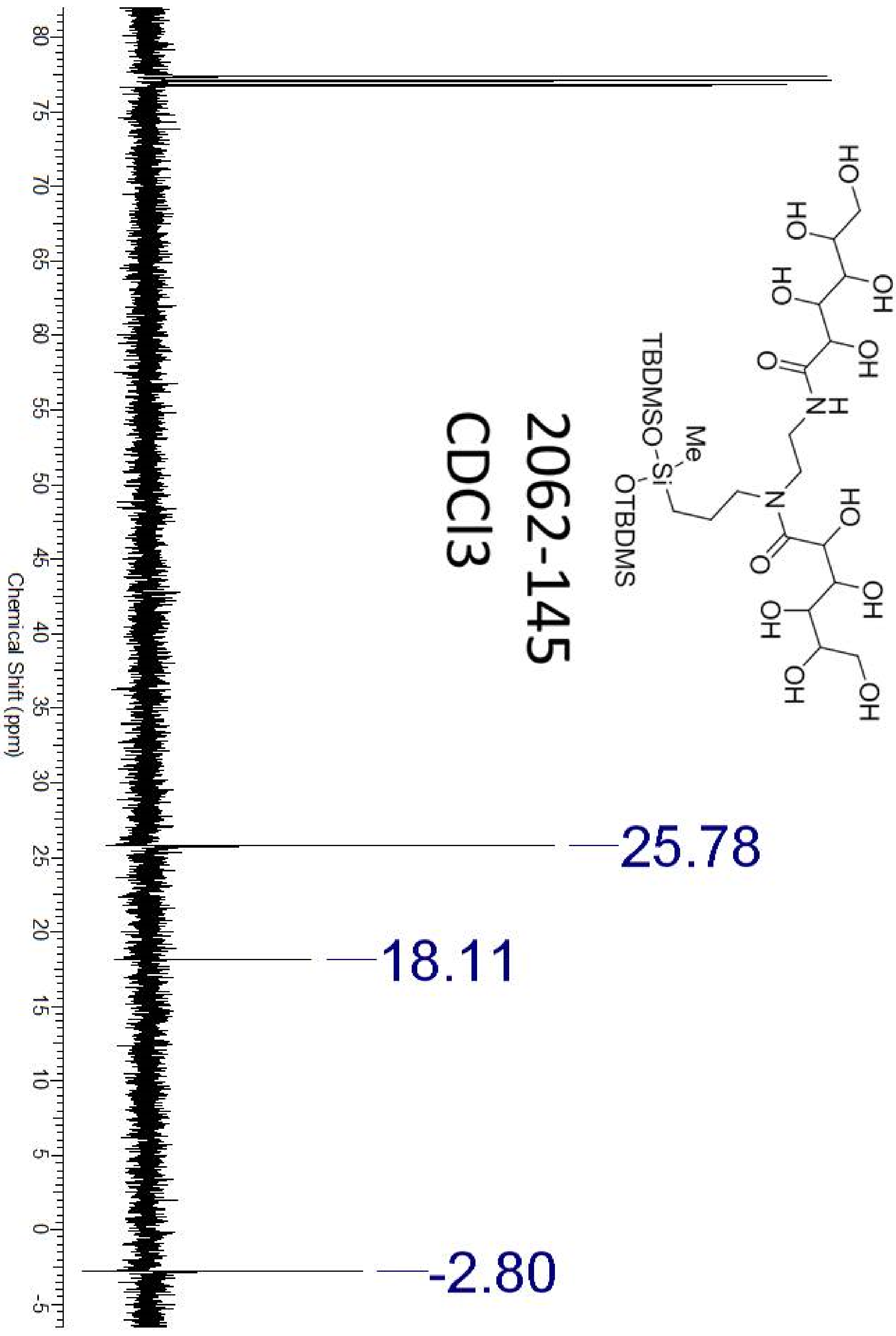

2062-141
CDCl3
H2N
N
H
Me
Me
Si
O
Si
Me
O
Si
Me
Me
Me
Me
1.96
1.99
2.05
2.06
3.21
2.00
18.62
3.35
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

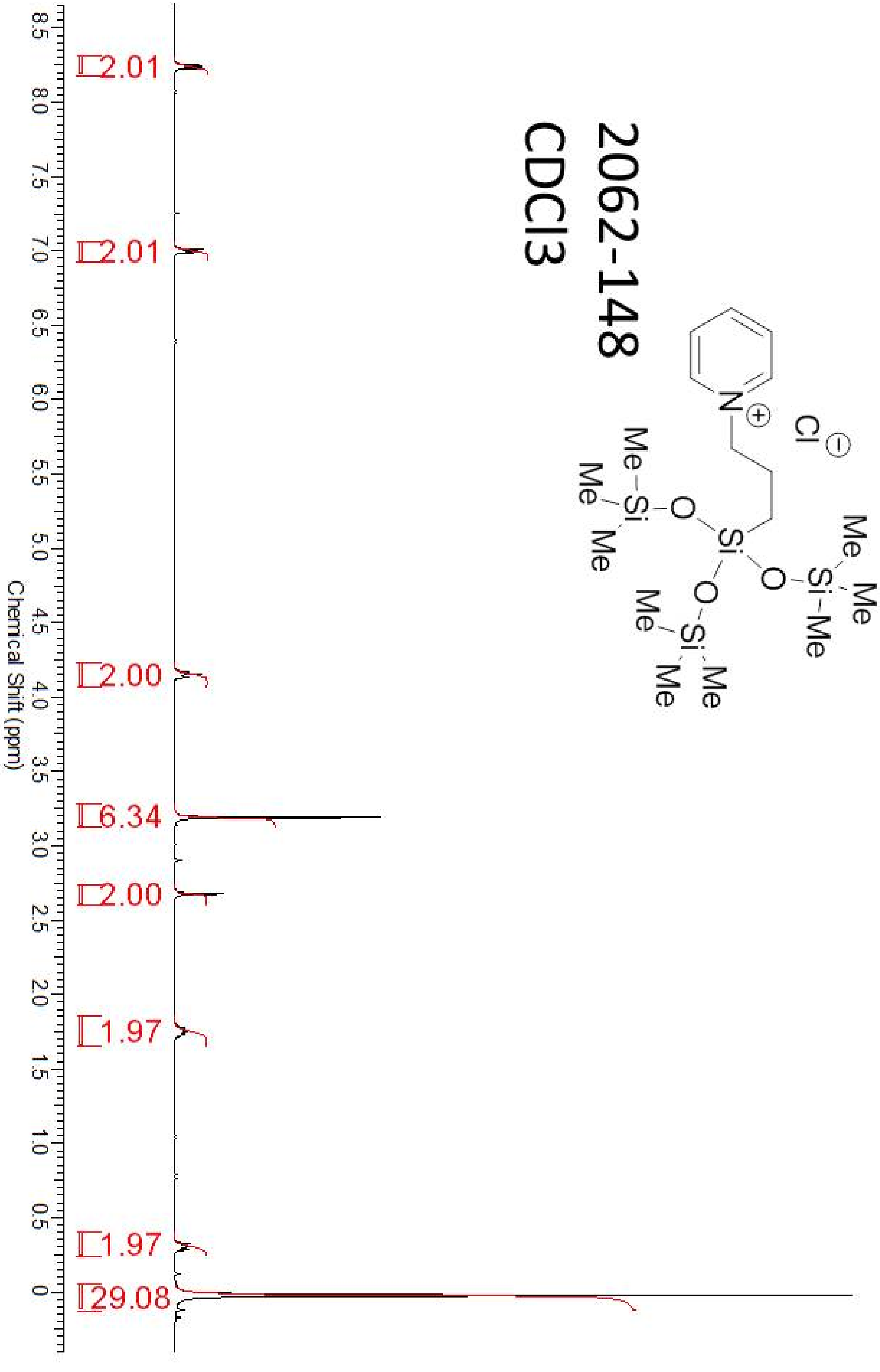

2062-141
CDCl3
H2N
N
H
Me
Me
Me
Si
O
Si
Me
O
Si
Me
Me
Me
53.03
52.59
41.96
23.73
15.14
1.86
-0.35
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
Chemical Shift (ppm)

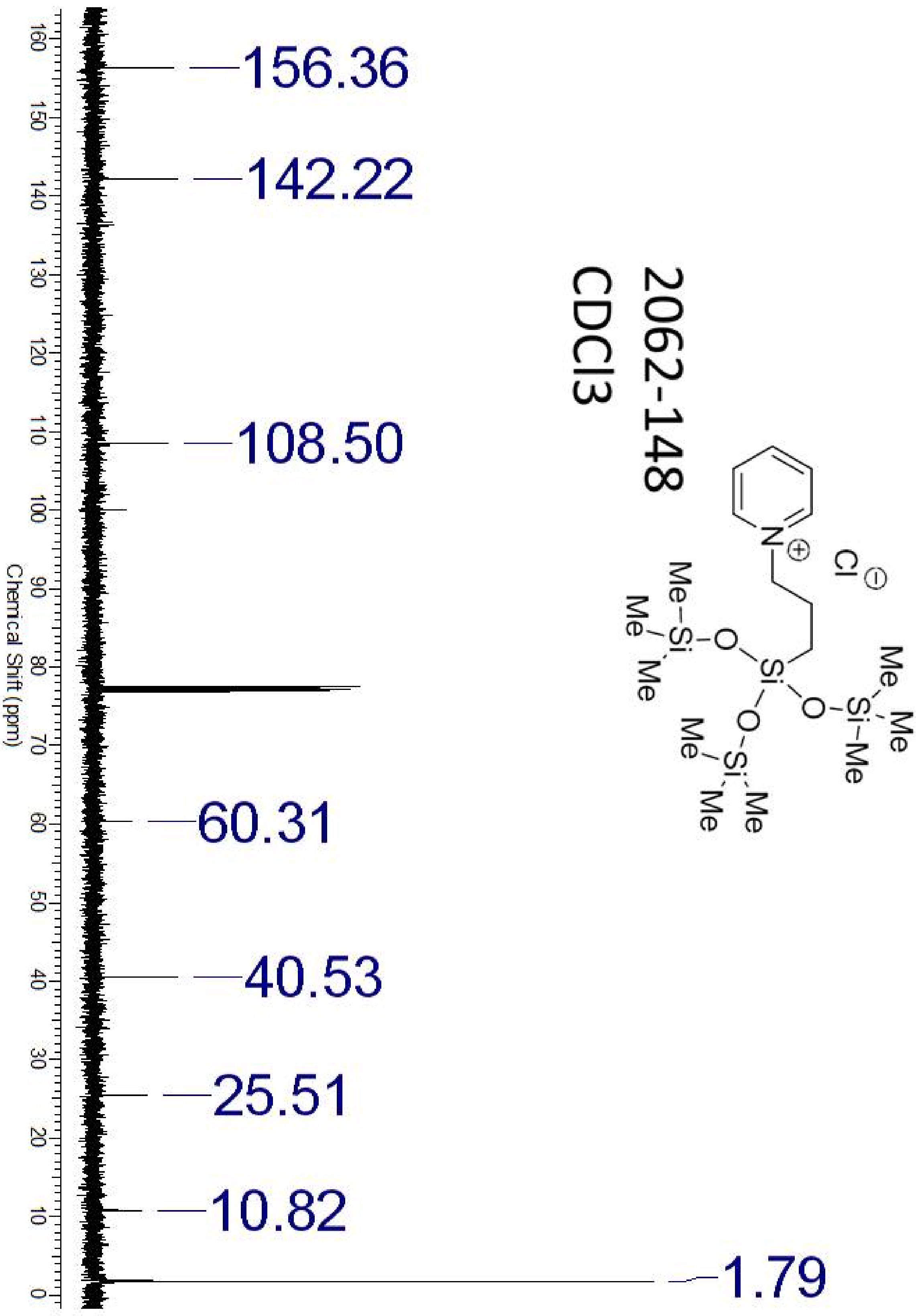

7.54
-21.21
15
10
5
0
-5
-10
-15
-20
-25
Chemical Shift (ppm)
H2N
N
H
Me
Me
Me
Si
O
Si
Me
O
Me
Si
Me
Me
2062-141
CDCl3

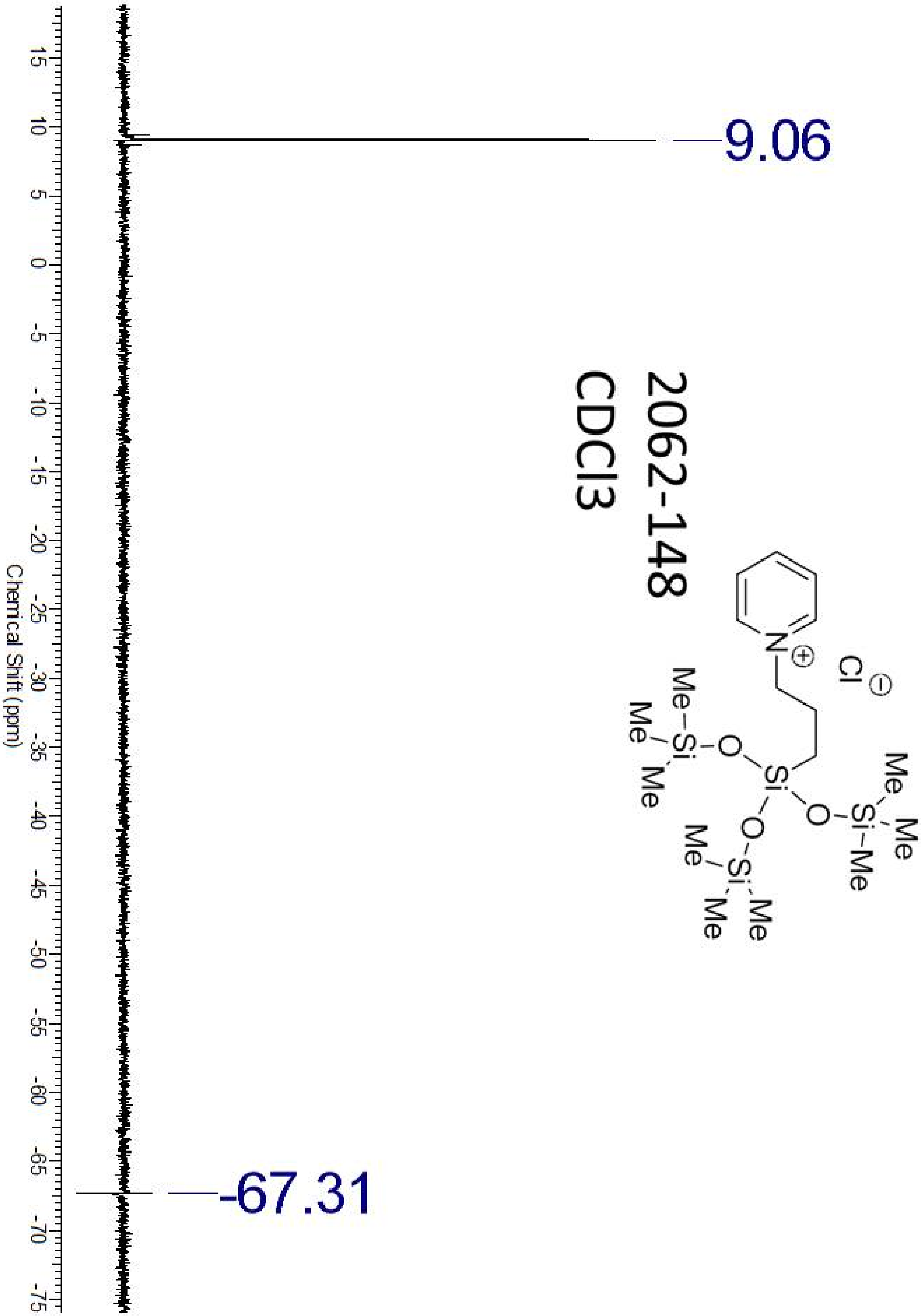

2062-141B
CDCl3
HO
OH
OH
OH
OH
O
NH
HO
HO
HO
OH
Oh
O
N
Me
Me
Me
Si
O
Si
Me
O
Me
Me
Si
Me
0.07
18.63
3.05
1.66
1.71
21.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

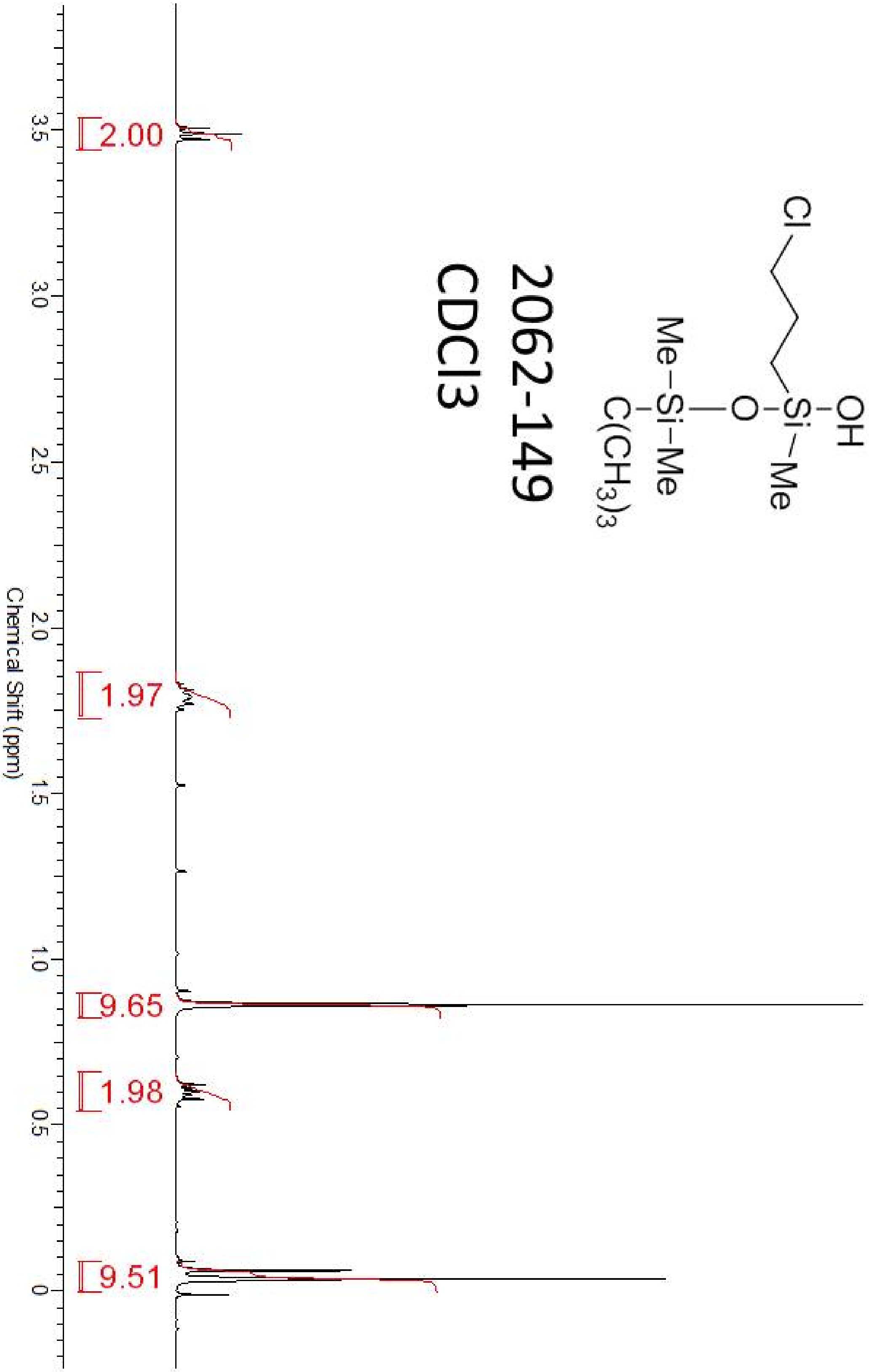

2062-145
CDCl3
HO
OH
HO
OH
HO
OH
O
H
N
N
O
HO
OH
OH
OH
HO
Me
TBDMSO
Si
OTBDMS
0.27
11.47
6.06
3.15
2.66
1.47
17.99
1.54
15.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

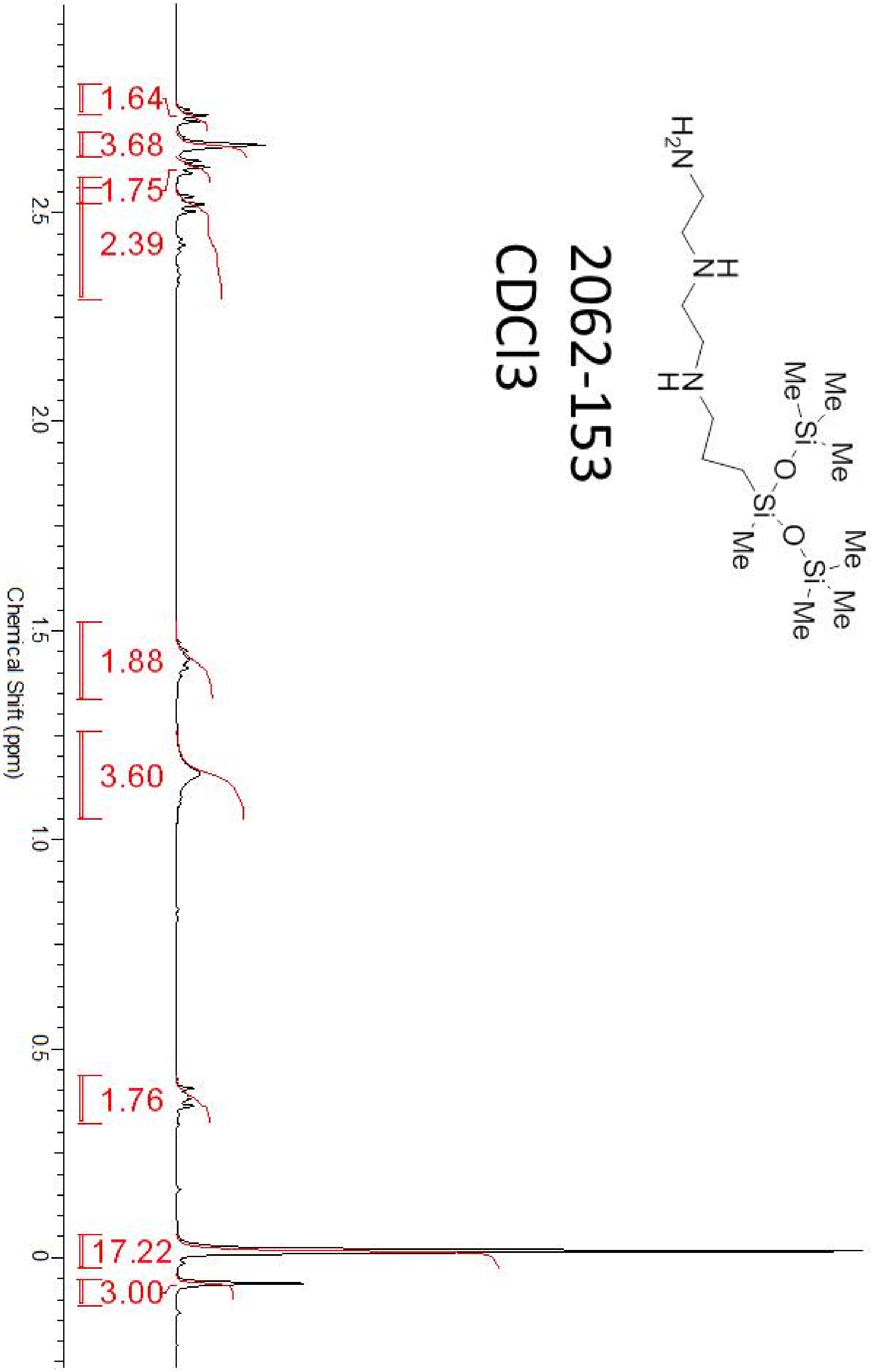

2062-145
CDCl3
25.78
18.11
-2.80
Chemical Shift (ppm)
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
TBDMSO
Si
Me
OTBDMS
N
H
O
OH
HO

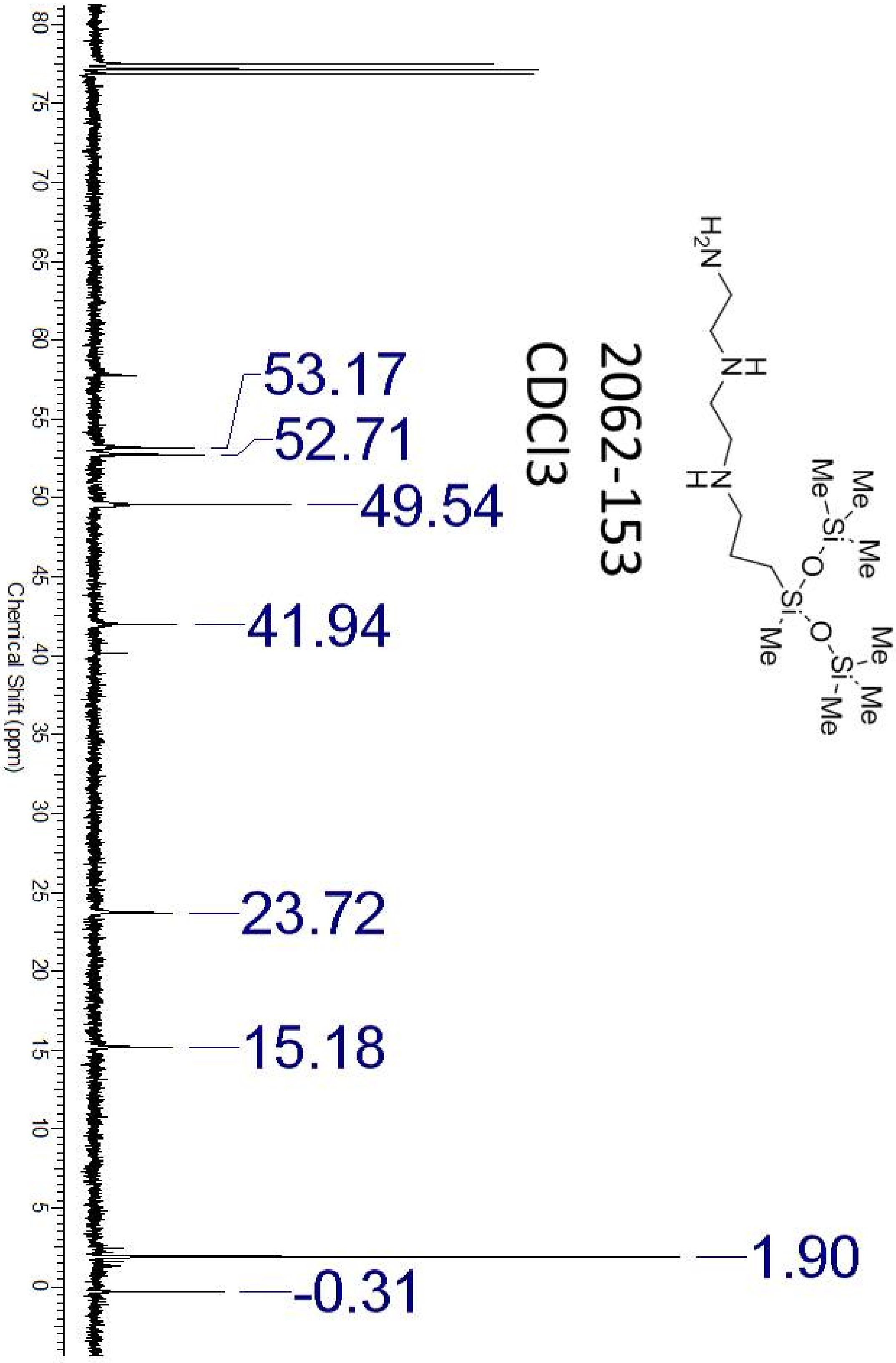

2062-148
CDCl3
N⊕
Cl⊖
Si
O
Me
2.01
2.01
2.00
6.34
2.00
1.97
1.97
29.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

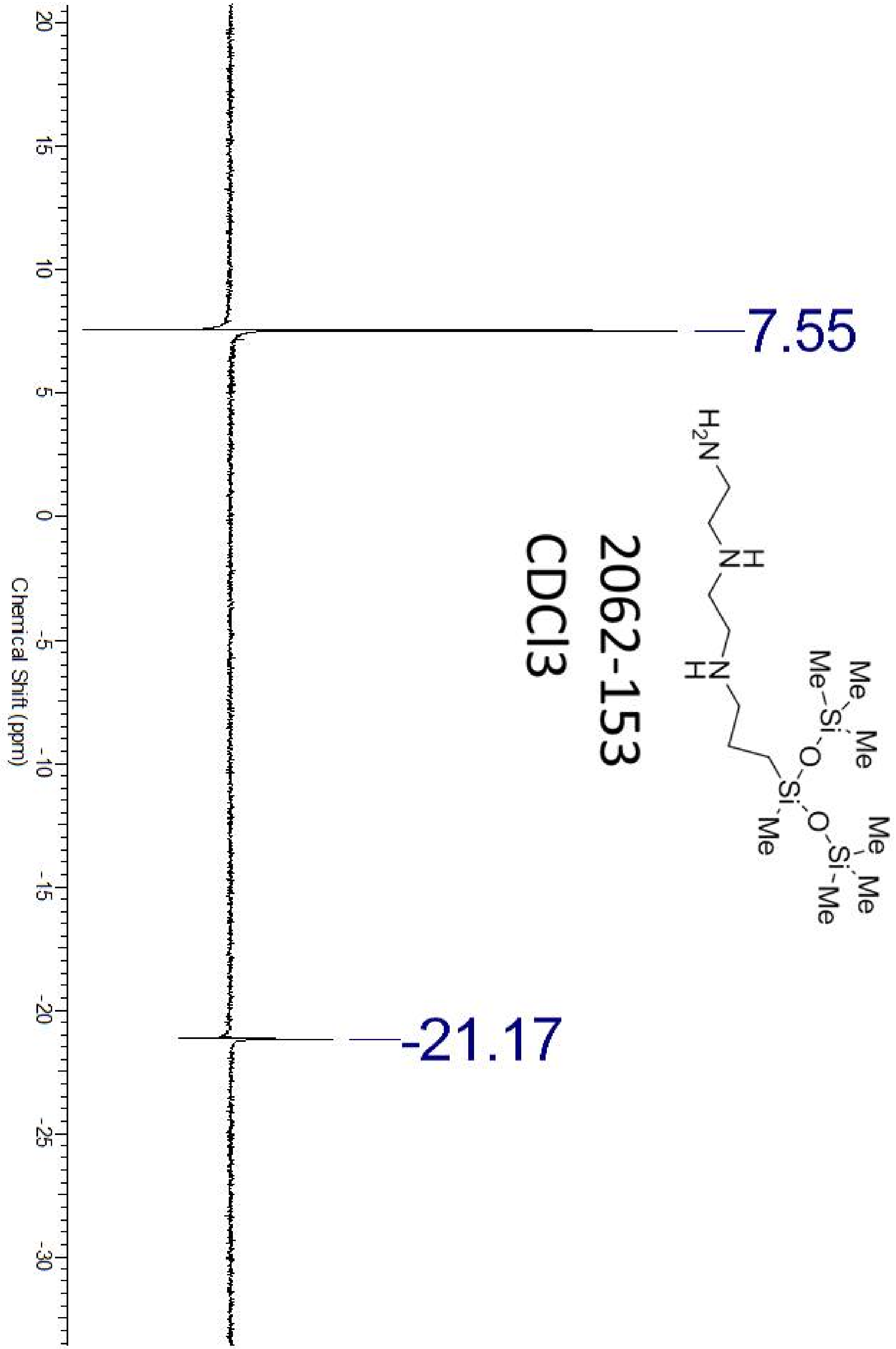

2062-148
CDCl3
156.36
142.22
108.50
60.31
40.53
25.51
10.82
1.79
Chemical Shift (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
⊕
Cl
⊖
Si
O
Me
Me–Si
Si–Me

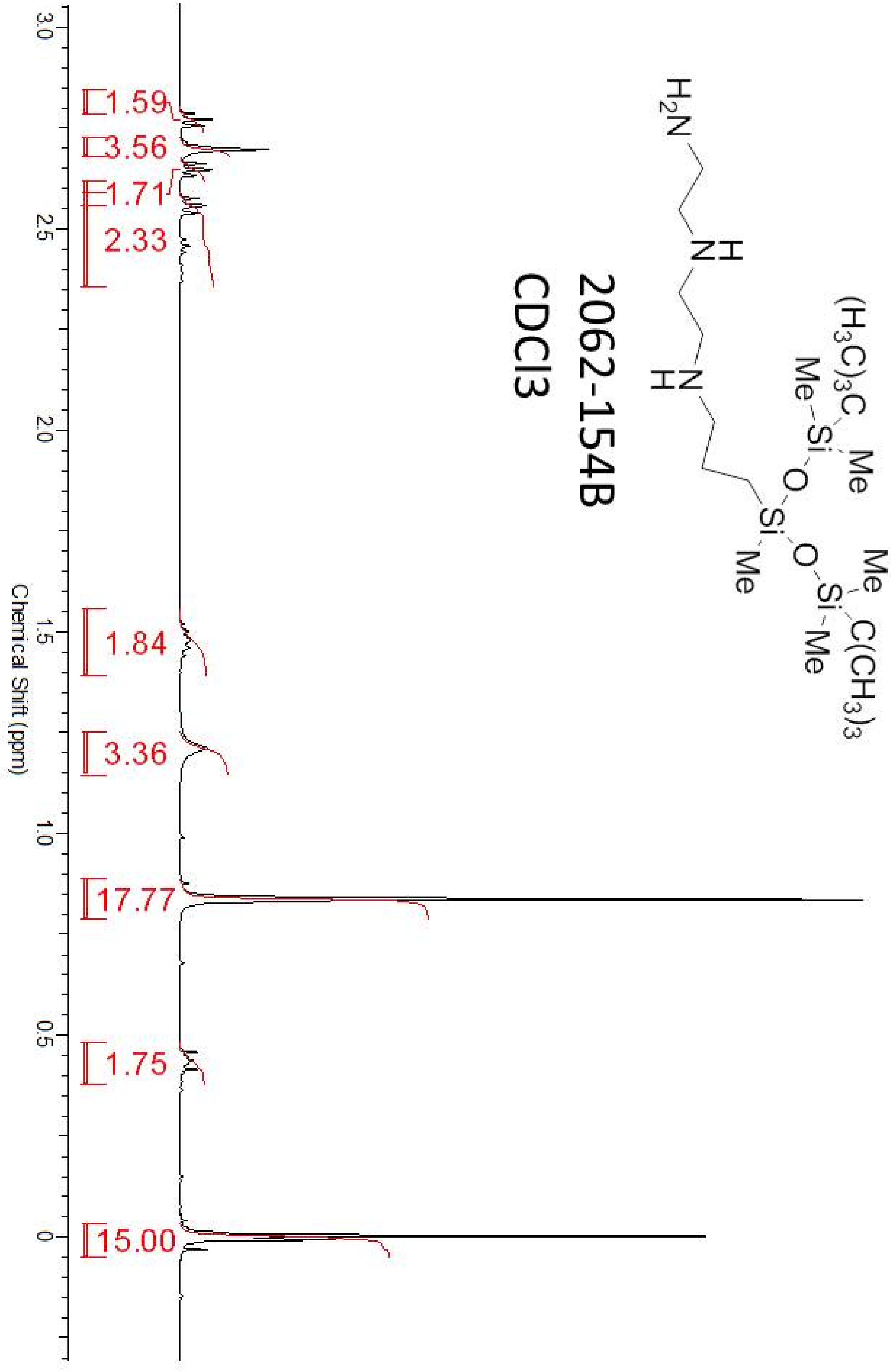

9.06
-67.31
2062-148
CDCl3
N
Cl
Si
O
Me
Chemical Shift (ppm)
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75

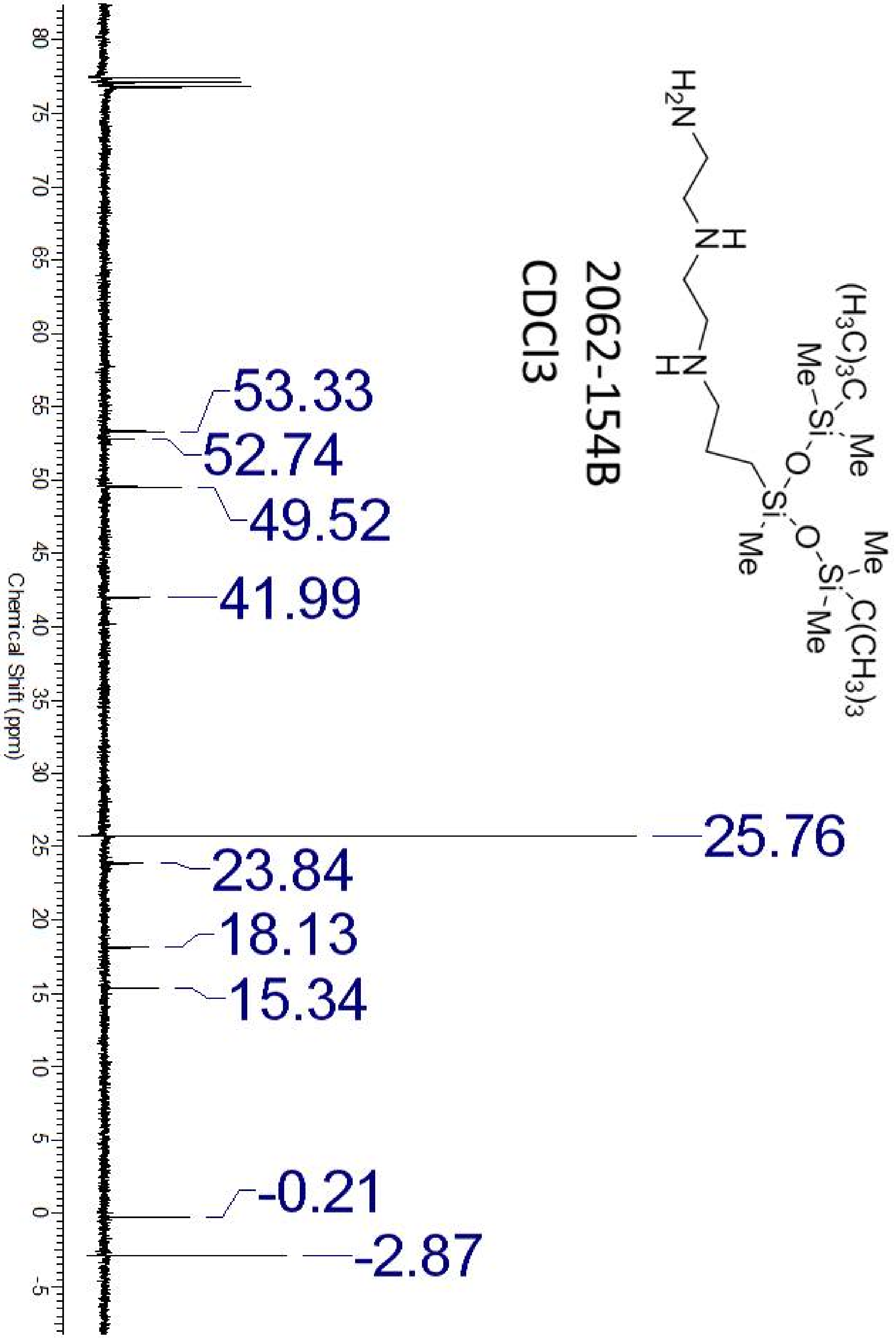

Cl
OH
Si
Me
O
Me
Si
Me
C(CH3)3
2062-149
CDCl3
2.00
1.97
9.65
1.98
9.51
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

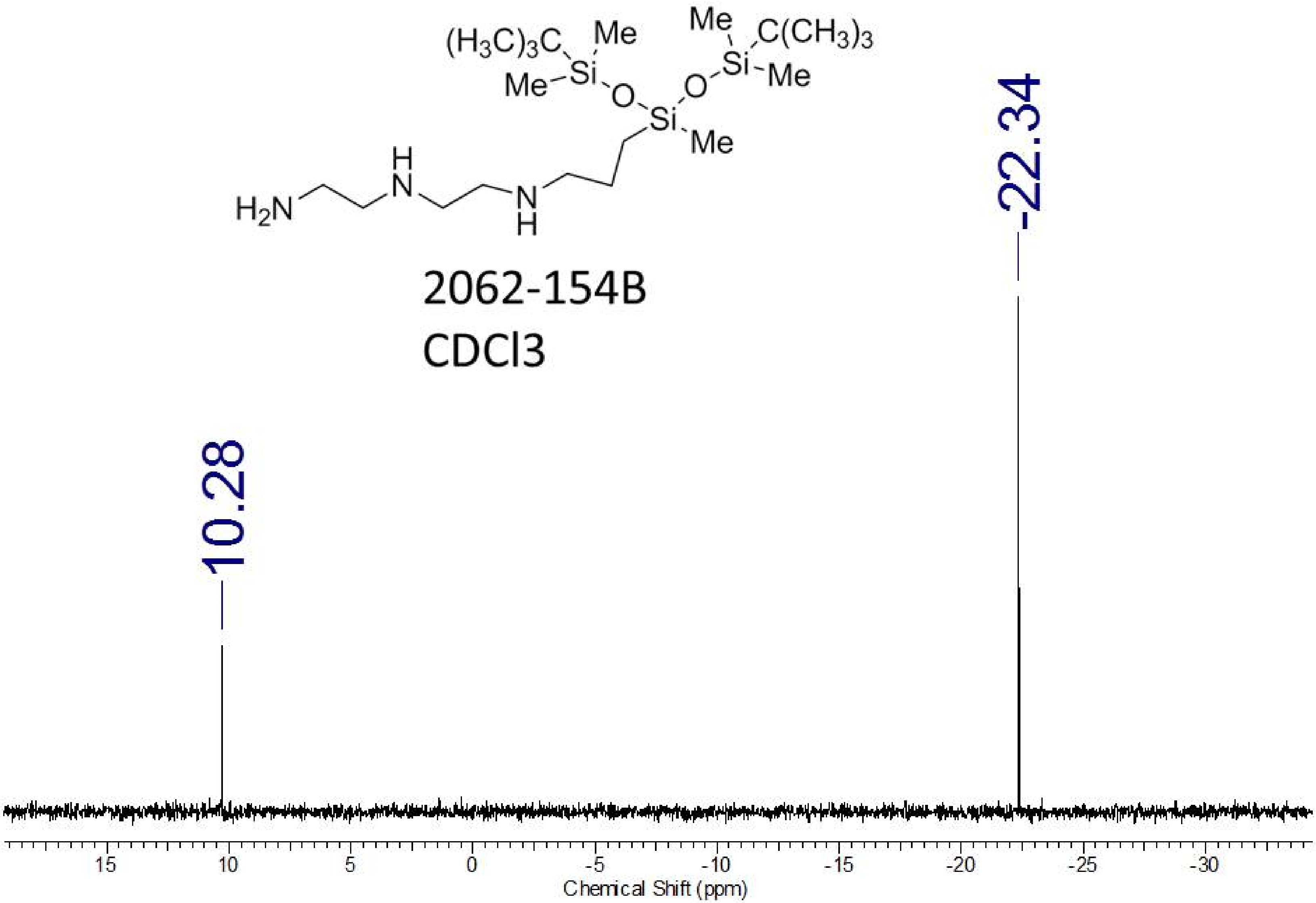

2062-153
CDCl3
H2N
H
N
H
Me
Me
Me
Si
O
Si
Me
O
Si
Me
Me
Me
1.64
3.68
1.75
2.39
1.88
3.60
1.76
17.22
3.00
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

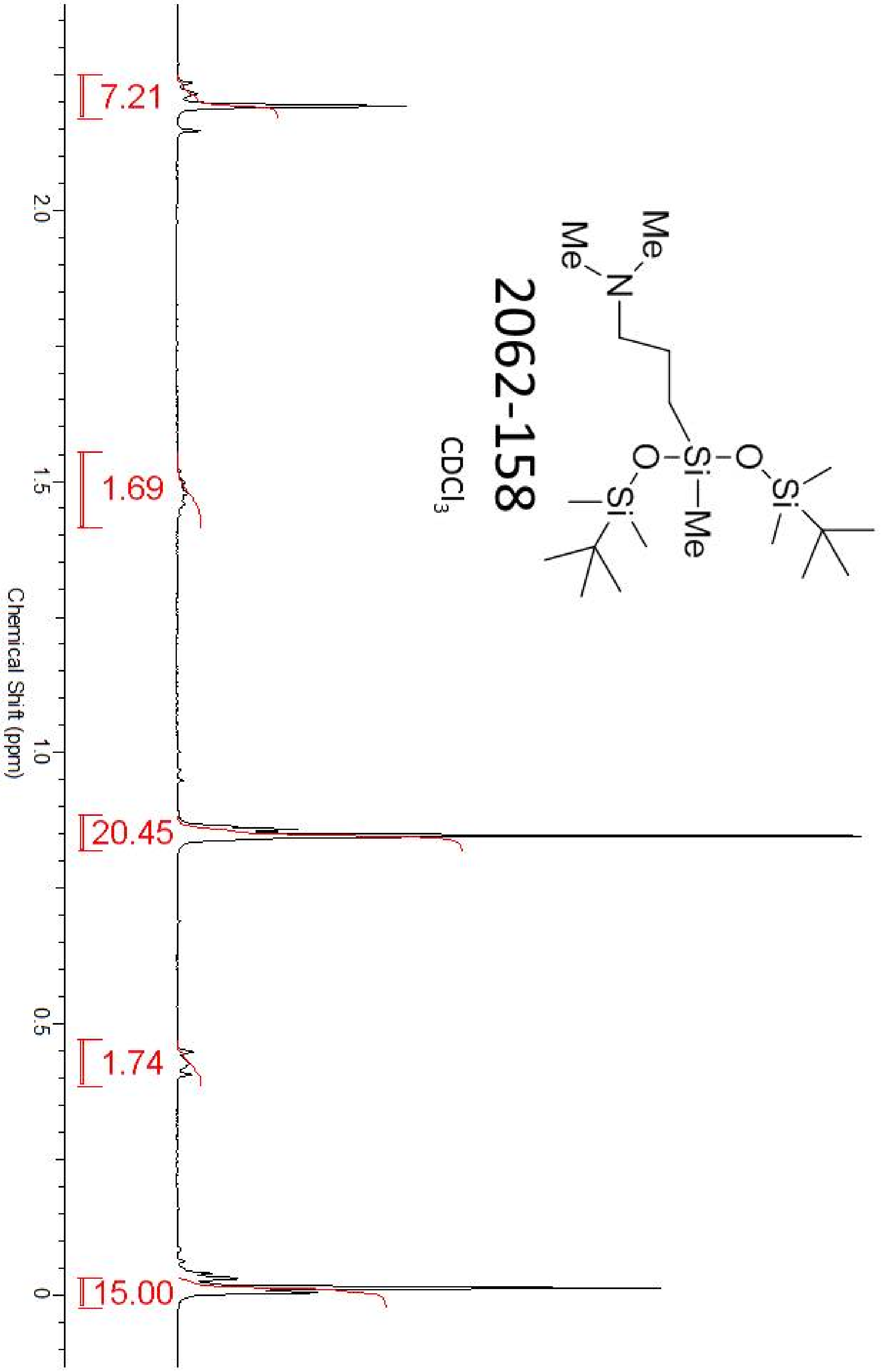

2062-153
CDCl3
53.17
52.71
49.54
41.94
23.72
15.18
1.90
-0.31
Chemical Shift (ppm)
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
H2N
N
H
Me
Si
O

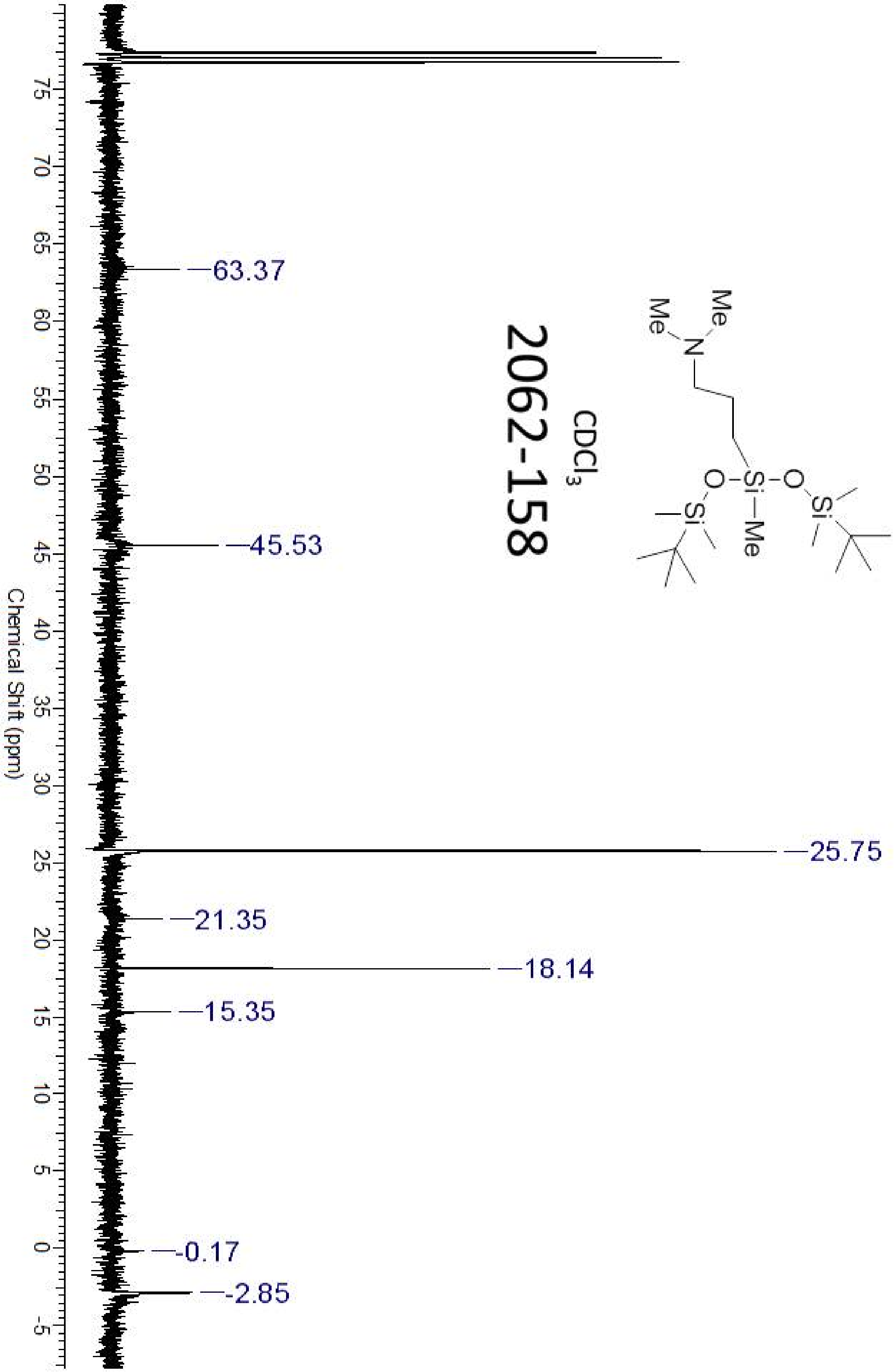

7.55
-21.17
2062-153
CDCl3
H2N
H
N
H
N
Me
Me
Me
Si
O
Si
Me
O
Me
Si
Me
Me
20
15
10
5
0
-5
-10
-15
-20
-25
-30
Chemical Shift (ppm)

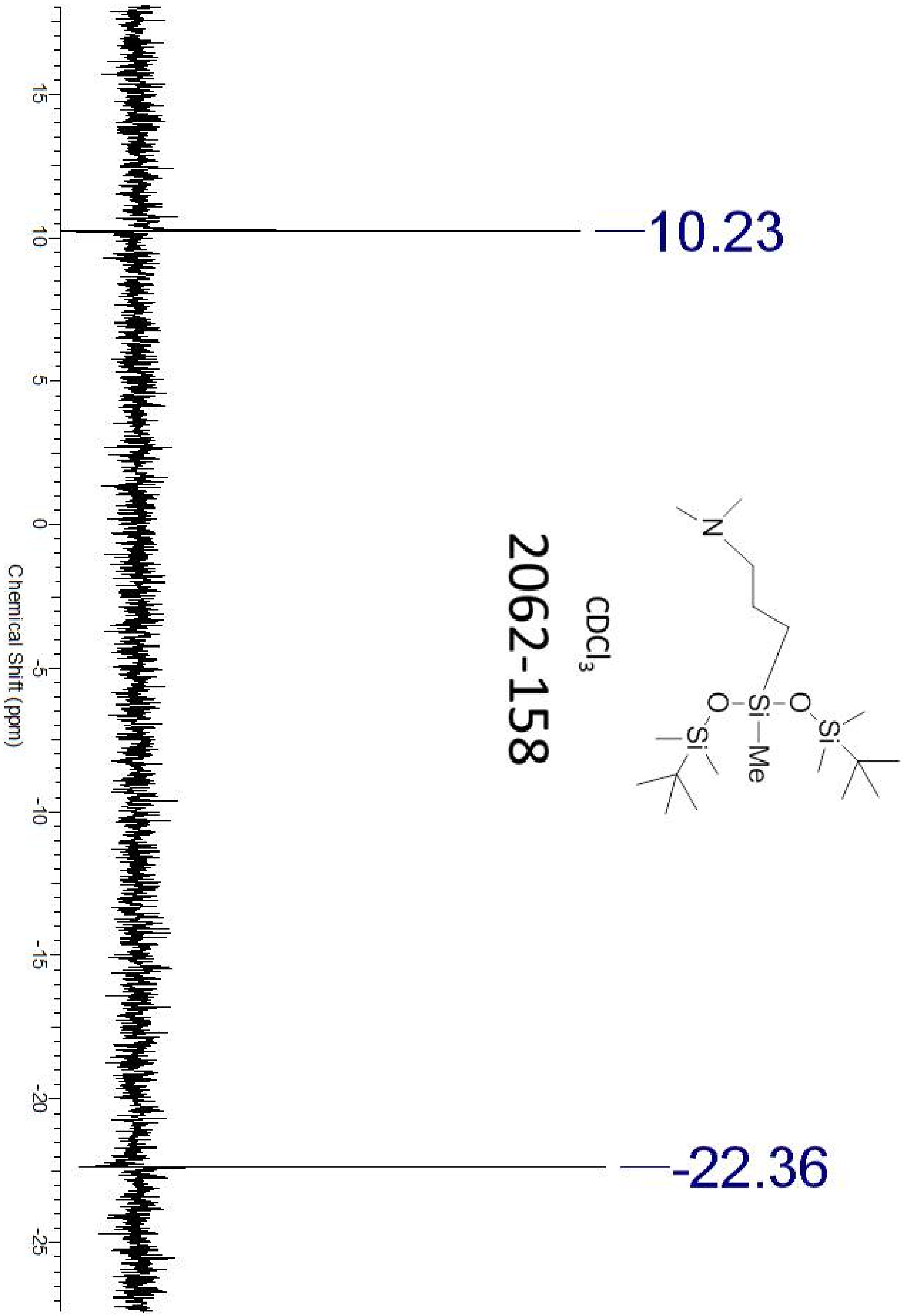

2062-154B
CDCl3
H2N
H
N
N
H
(H3C)3C
Me
Me
Si
O
Si
Me
O
Me
Si
Me
C(CH3)3
1.59
3.56
1.71
2.33
1.84
3.36
17.77
1.75
15.00
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

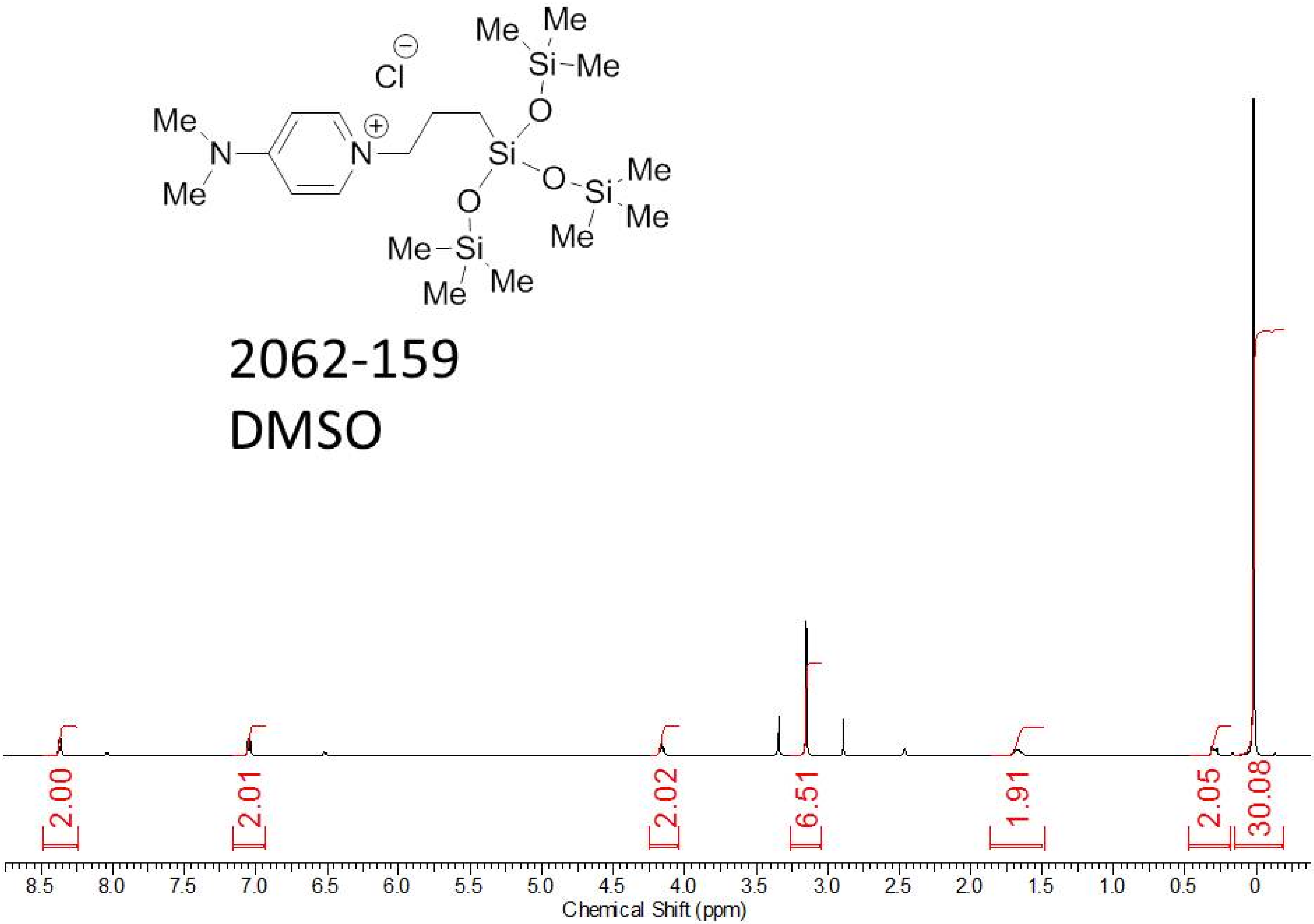

2062-154B
CDCl3
H_2N
H
N
H
N
$(H_3C)_3C$
Me
Me
Si
O
Si
Me
O
Si
Me
Me
$C(CH_3)_3$
53.33
52.74
49.52
41.99
25.76
23.84
18.13
15.34
-0.21
-2.87
Chemical Shift (ppm)
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5

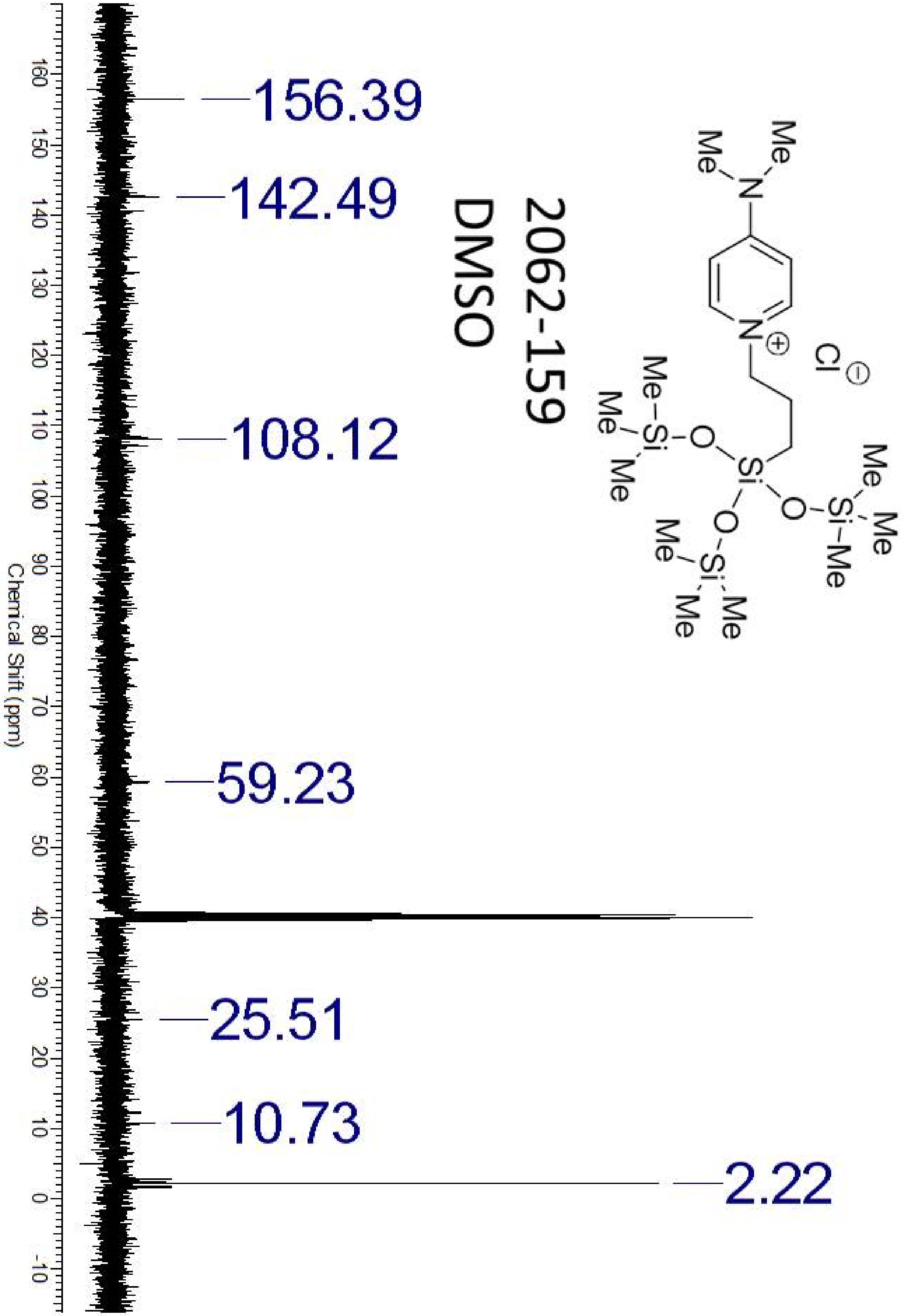

(H3C)3C
Me
Me
Si
O
Si
Me
O
Me
Si
C(CH3)3
Me
H2N
H
N
N
H
2062-154B
CDCl3
10.28
-22.34
15
10
5
0
-5
-10
-15
-20
-25
-30
Chemical Shift (ppm)

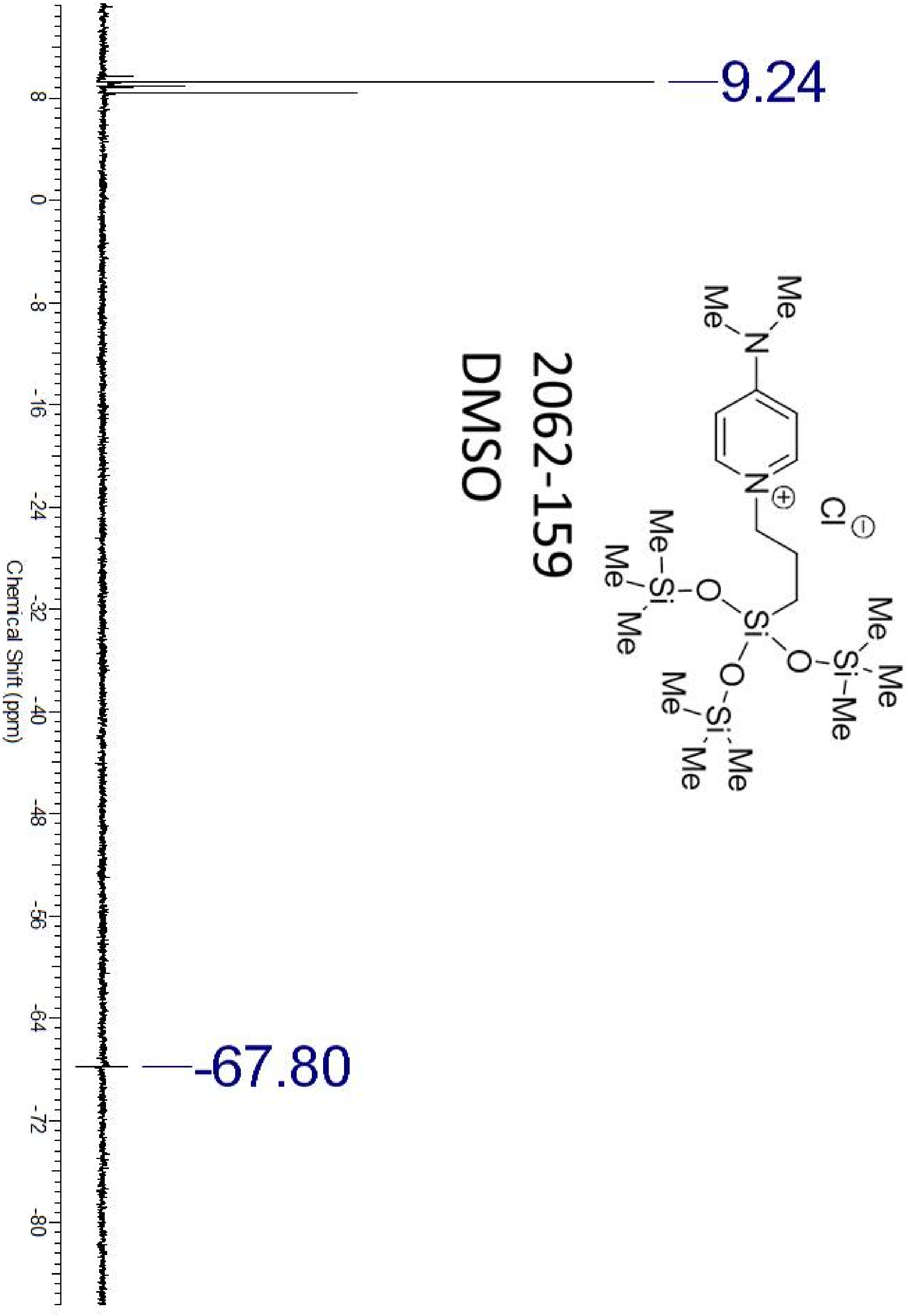

2062-158
CDCl$_3$
Me
Me
N
Si
O
O
Si
Si
Me
7.21
1.69
20.45
1.74
15.00
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

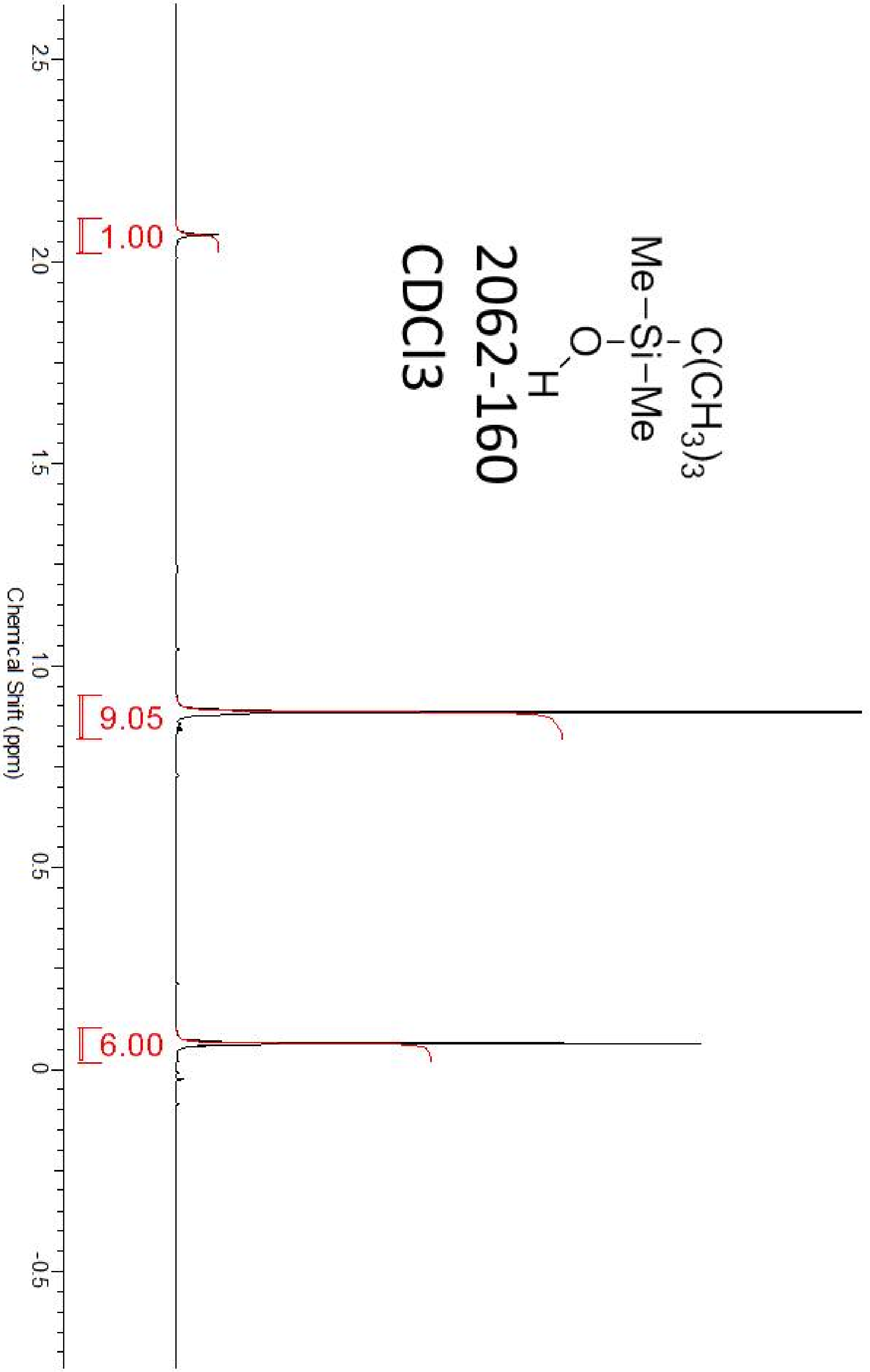

2062-158
CDCl3
Me
Me
N
Si
O
O
Si
Si
Me
63.37
45.53
25.75
21.35
18.14
15.35
-0.17
-2.85
Chemical Shift (ppm)
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5

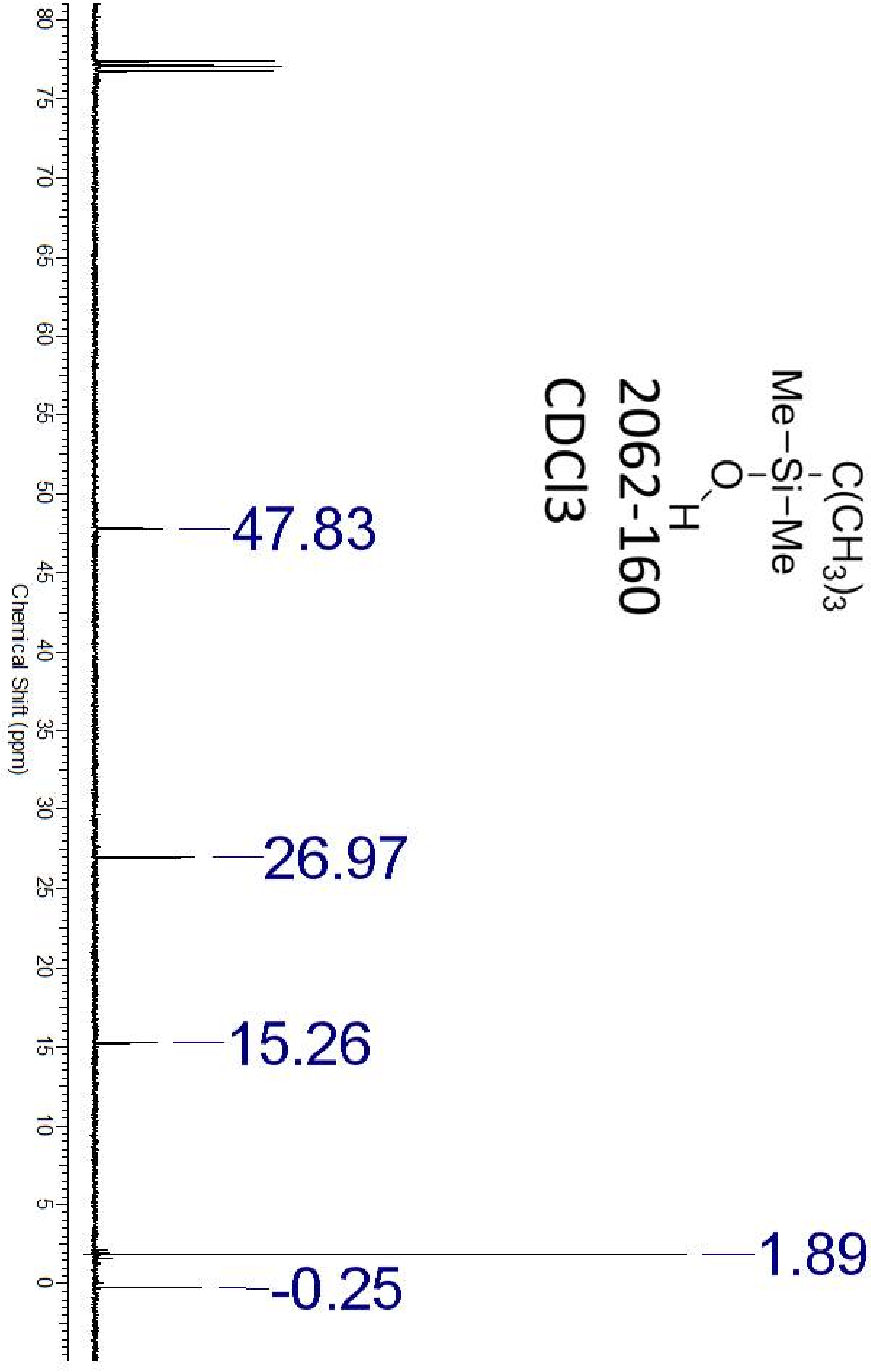

10.23
-22.36
CDCl3
2062-158
N
Si
O
Si
O
Si
Me
15
10
5
0
-5
-10
-15
-20
-25
Chemical Shift (ppm)

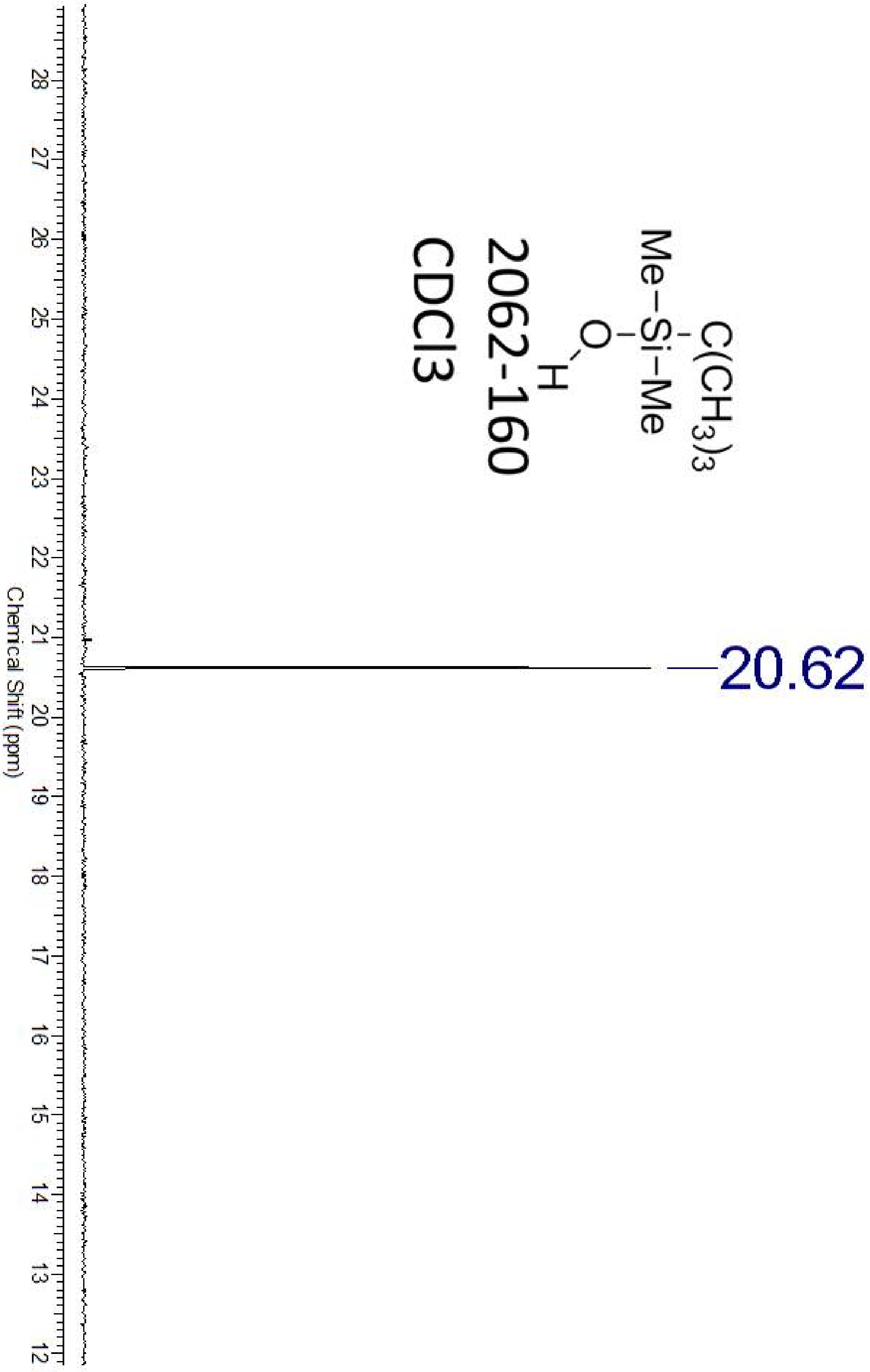

Cl
Me
N
Me
N
Si
O
Si
Me
O
Si
Me
O
Si
Me
2062-159
DMSO
2.00
2.01
2.02
6.51
1.91
2.05
30.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


2062-159
DMSO
156.39
142.49
108.12
59.23
25.51
10.73
2.22
Chemical Shift (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Me
N
N
Cl
Si
O
Me–Si
Si–Me

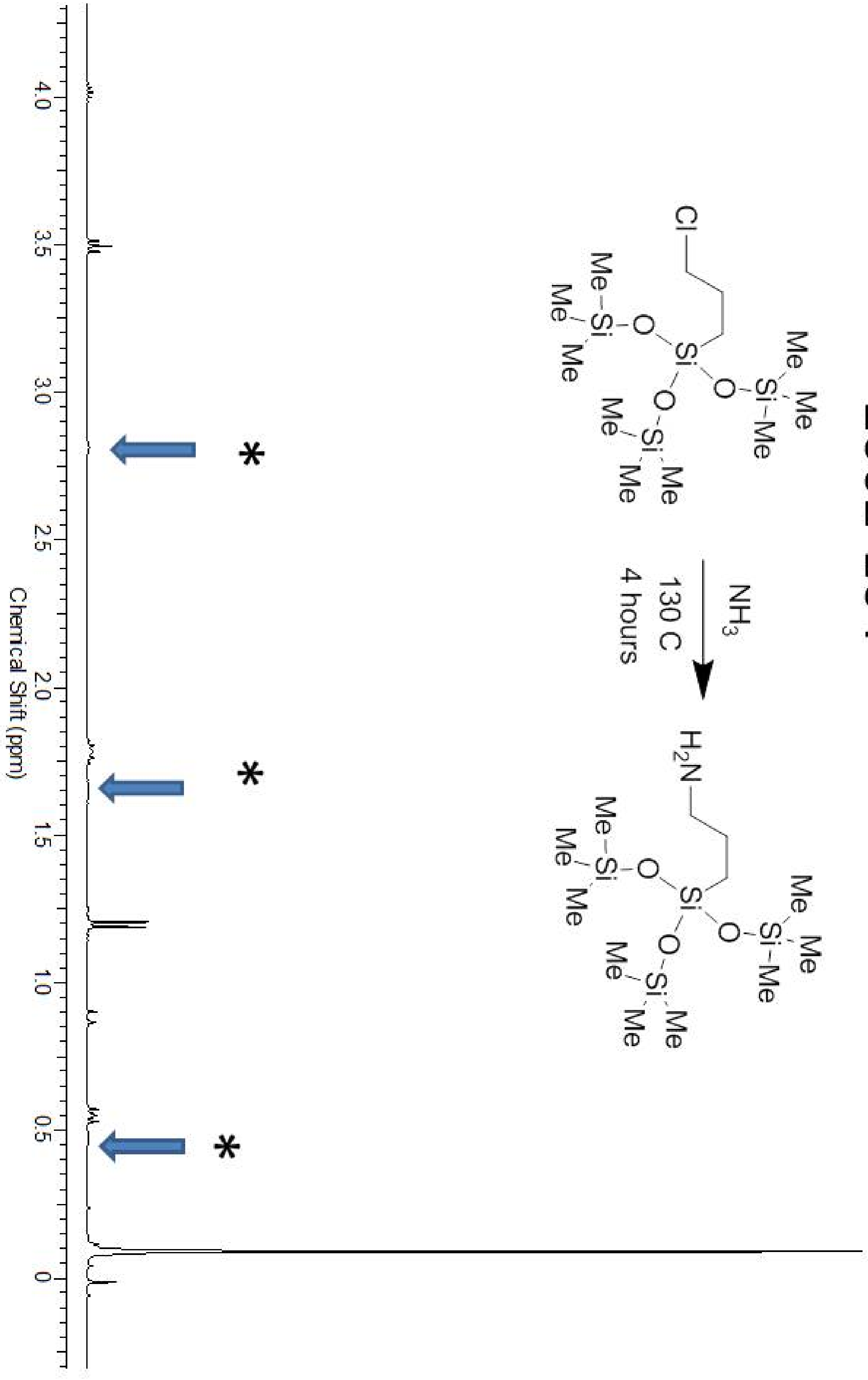

9.24
-67.80
2062-159
DMSO
Chemical Shift (ppm)
8
0
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
Me
Me
N
N
⊕
Cl
⊖
Si
O
Si
Me

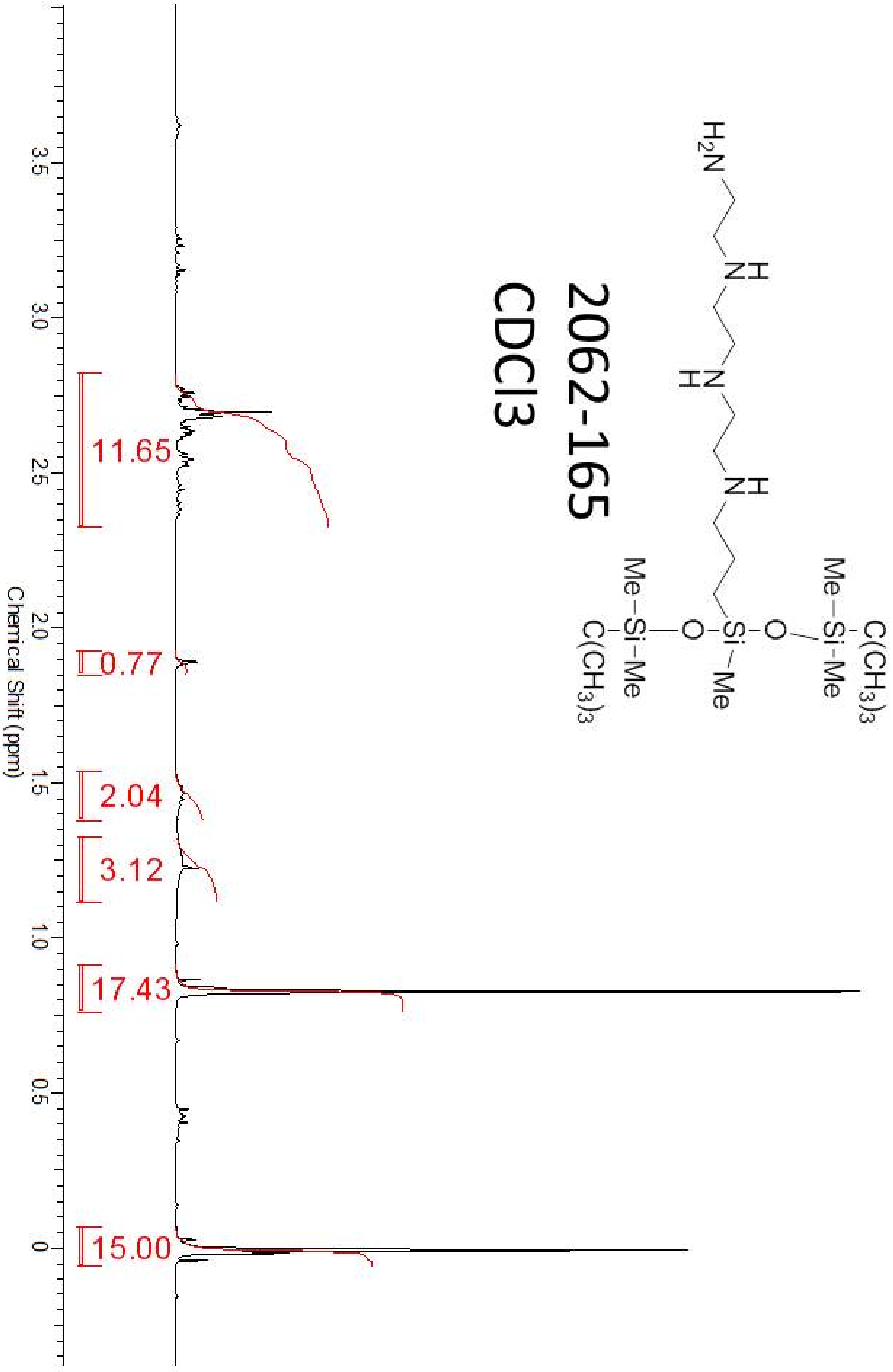

C(CH3)3
Me–Si–Me
O
H
2062-160
CDCl3
1.00
9.05
6.00
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)

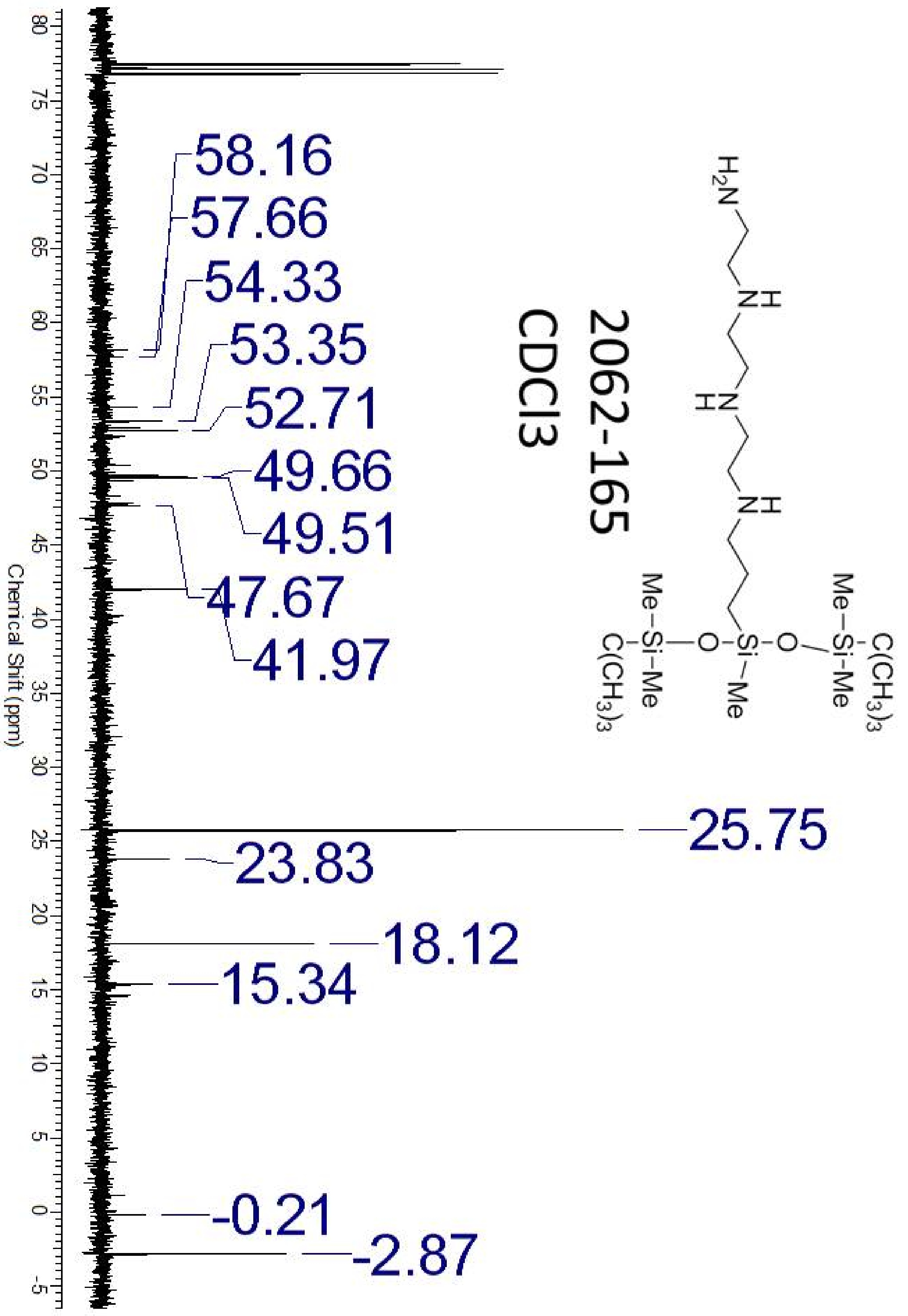

C(CH3)3
Me–Si–Me
O
H
2062-160
CDCl3
47.83
26.97
15.26
1.89
-0.25
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
Chemical Shift (ppm)

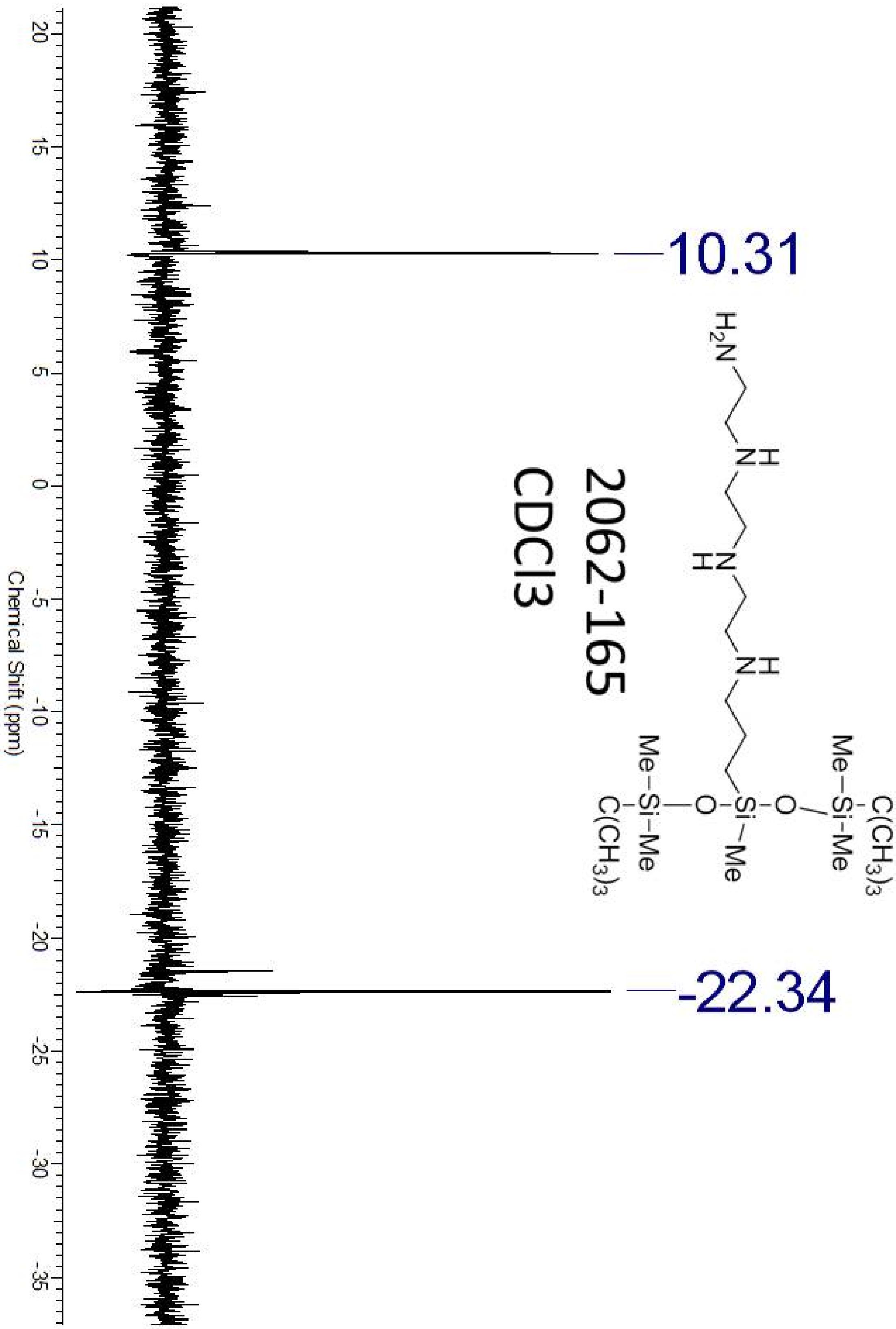

C(CH3)3
Me–Si–Me
O
H
2062-160
CDCl3
20.62
Chemical Shift (ppm)
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12

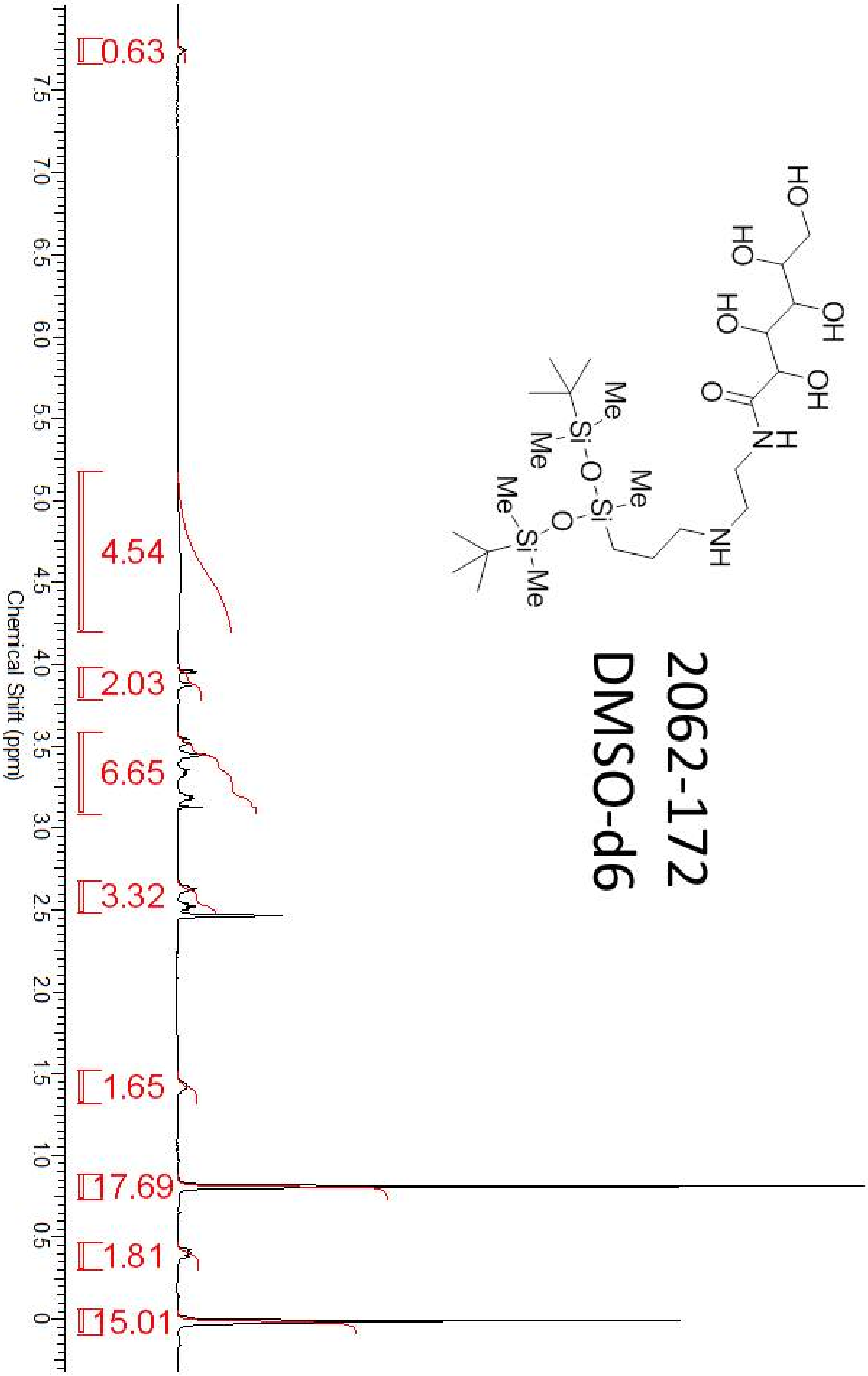
2062-164

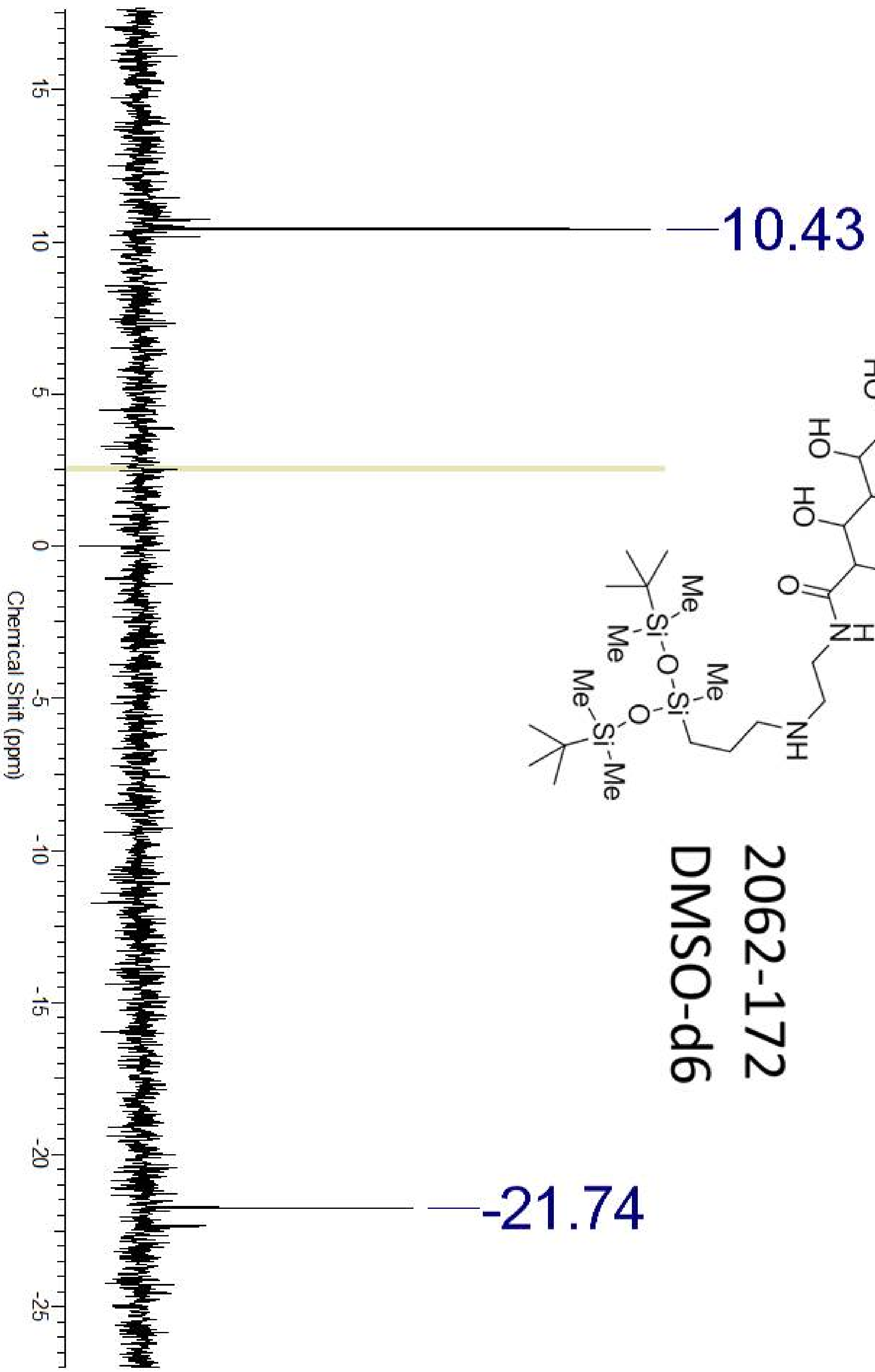

Cl
Me
Me
Si–Me
O
Si
O
Me–Si
Me
Me
O
Me
Si
Me
Me
NH$_3$
130 C
4 hours
H$_2$N
*
*
*
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

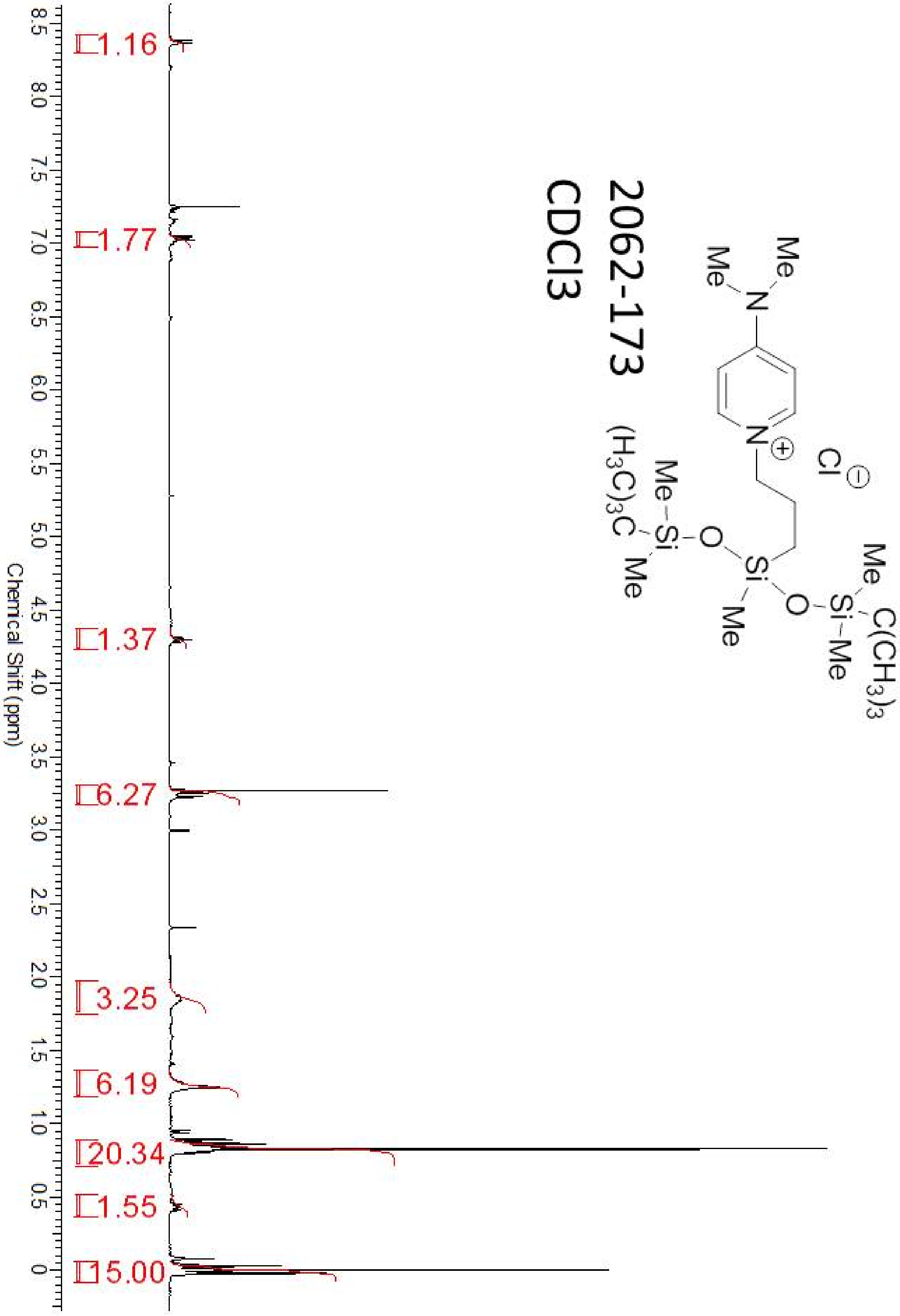

2062-165
CDCl3
H2N
H
N
H
N
H
N
Me–Si–C(CH3)3
O
Si
Me
O
Me–Si–Me
C(CH3)3
11.65
0.77
2.04
3.12
17.43
15.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

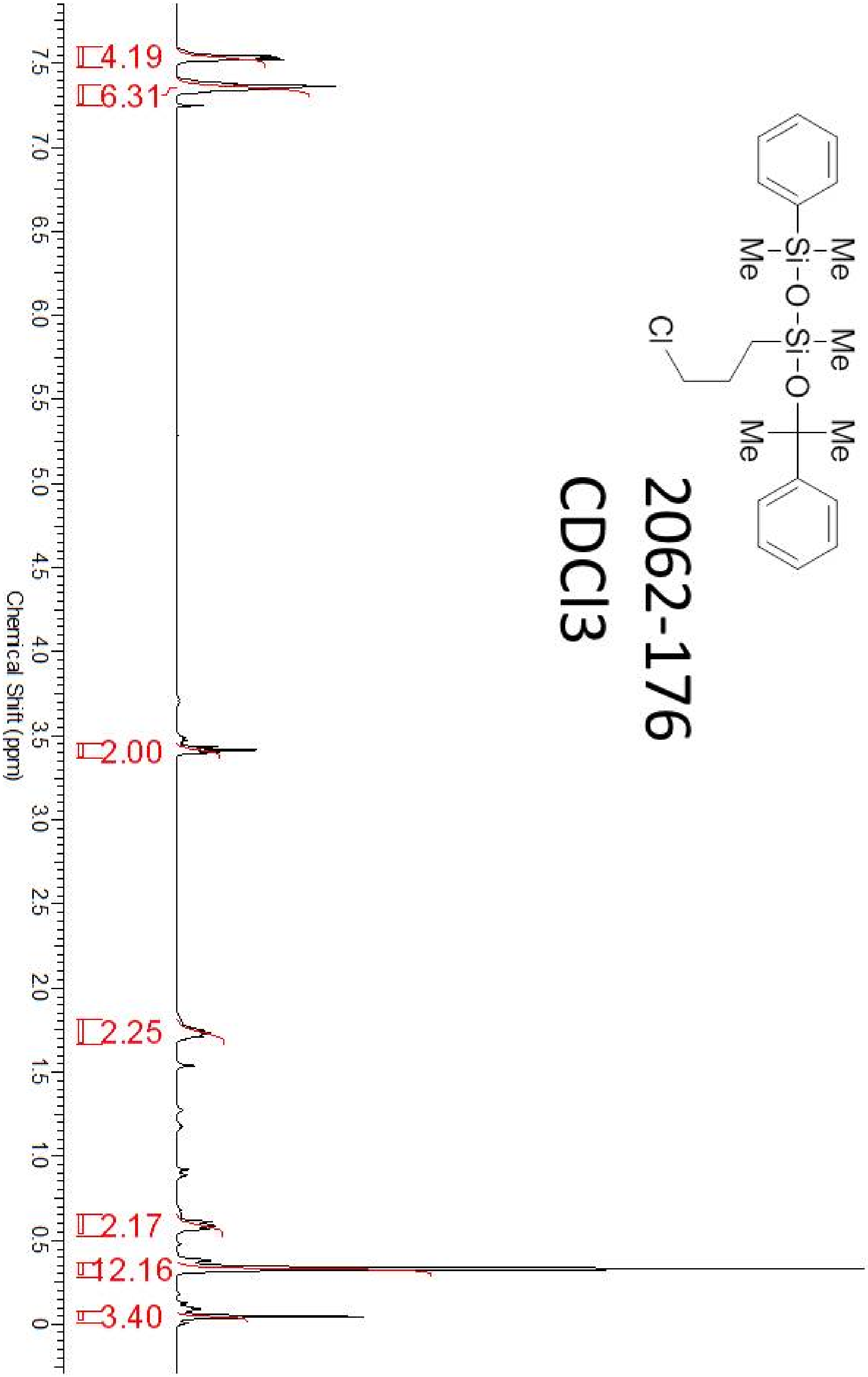

2062-165
CDCl3
58.16
57.66
54.33
53.35
52.71
49.66
49.51
47.67
41.97
25.75
23.83
18.12
15.34
-0.21
-2.87
Chemical Shift (ppm)
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
H_2N
H
N
H
N
H
N
Me
Si
Me
O
O
Me–Si–Me
Me–Si–Me
$C(CH_3)_3$
$C(CH_3)_3$

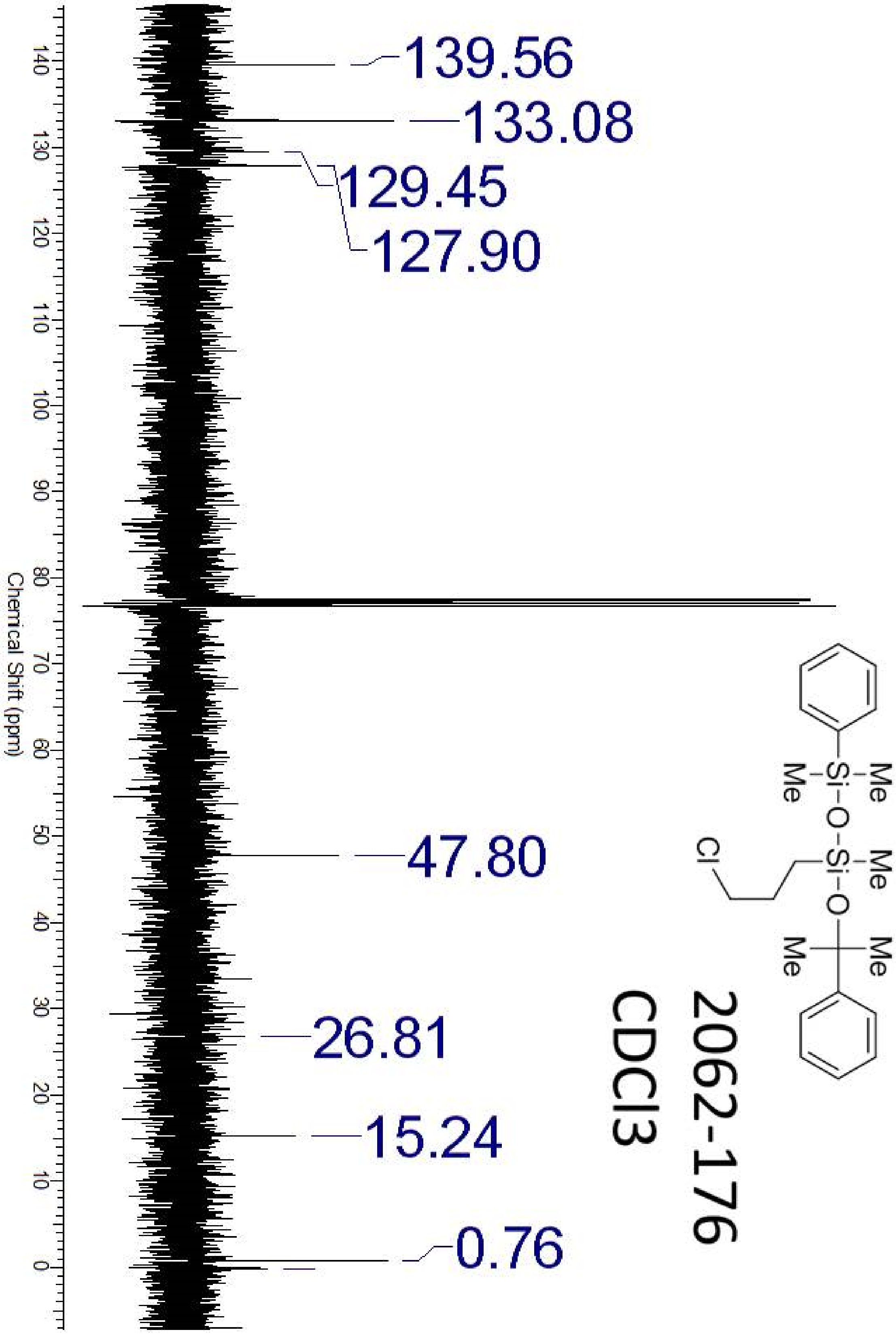

10.31
-22.34
2062-165
CDCl3
H2N
H
N
Me–Si–Me
C(CH3)3
O
Si
Me
Chemical Shift (ppm)
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35

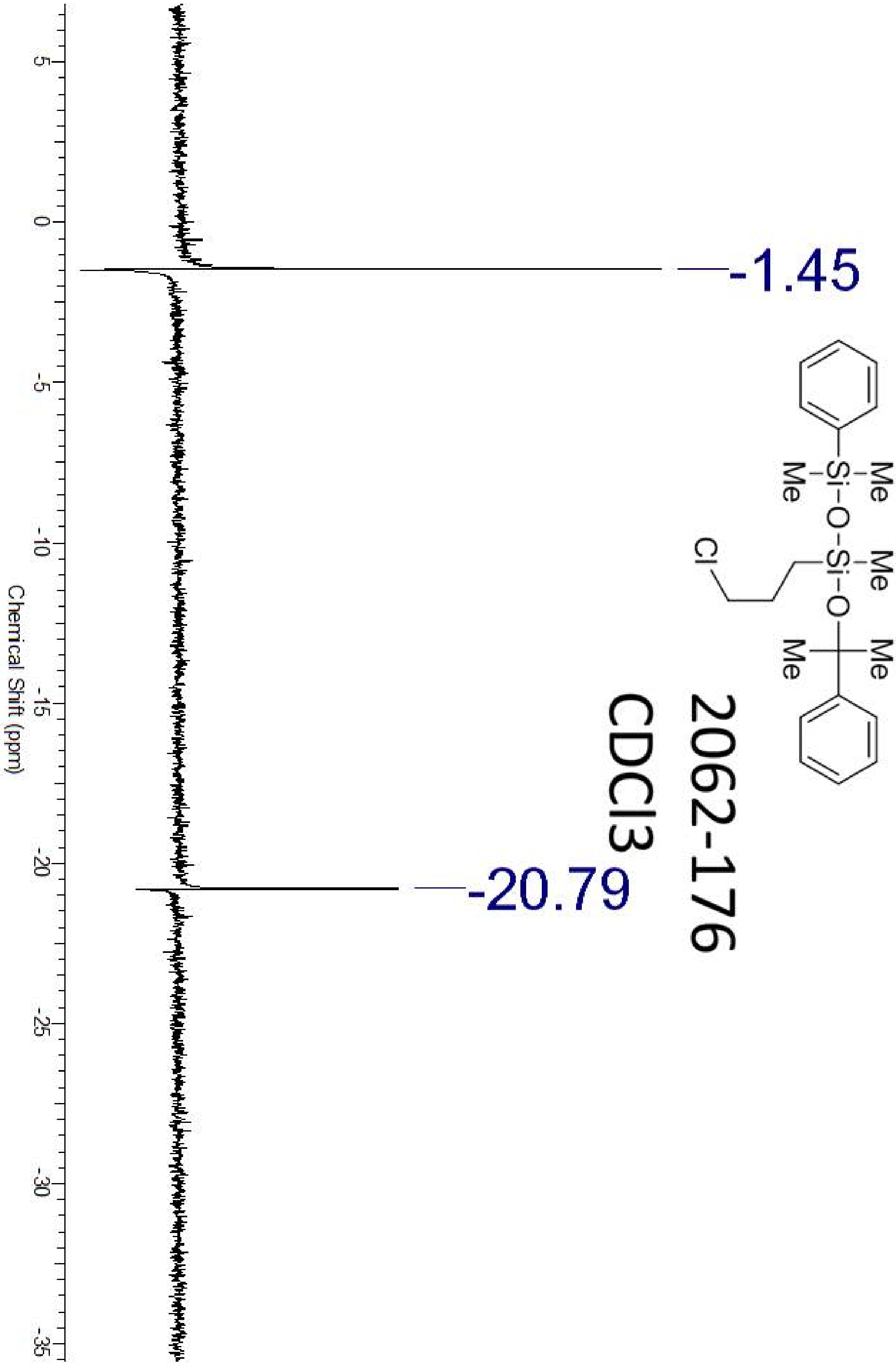

2062-172
DMSO-d6
HO
HO
OH
HO
OH
O
H
N
NH
Me
Si
Me
O
Me
Si
O
Me
Si
Me
Me
0.63
4.54
2.03
6.65
3.32
1.65
17.69
1.81
15.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

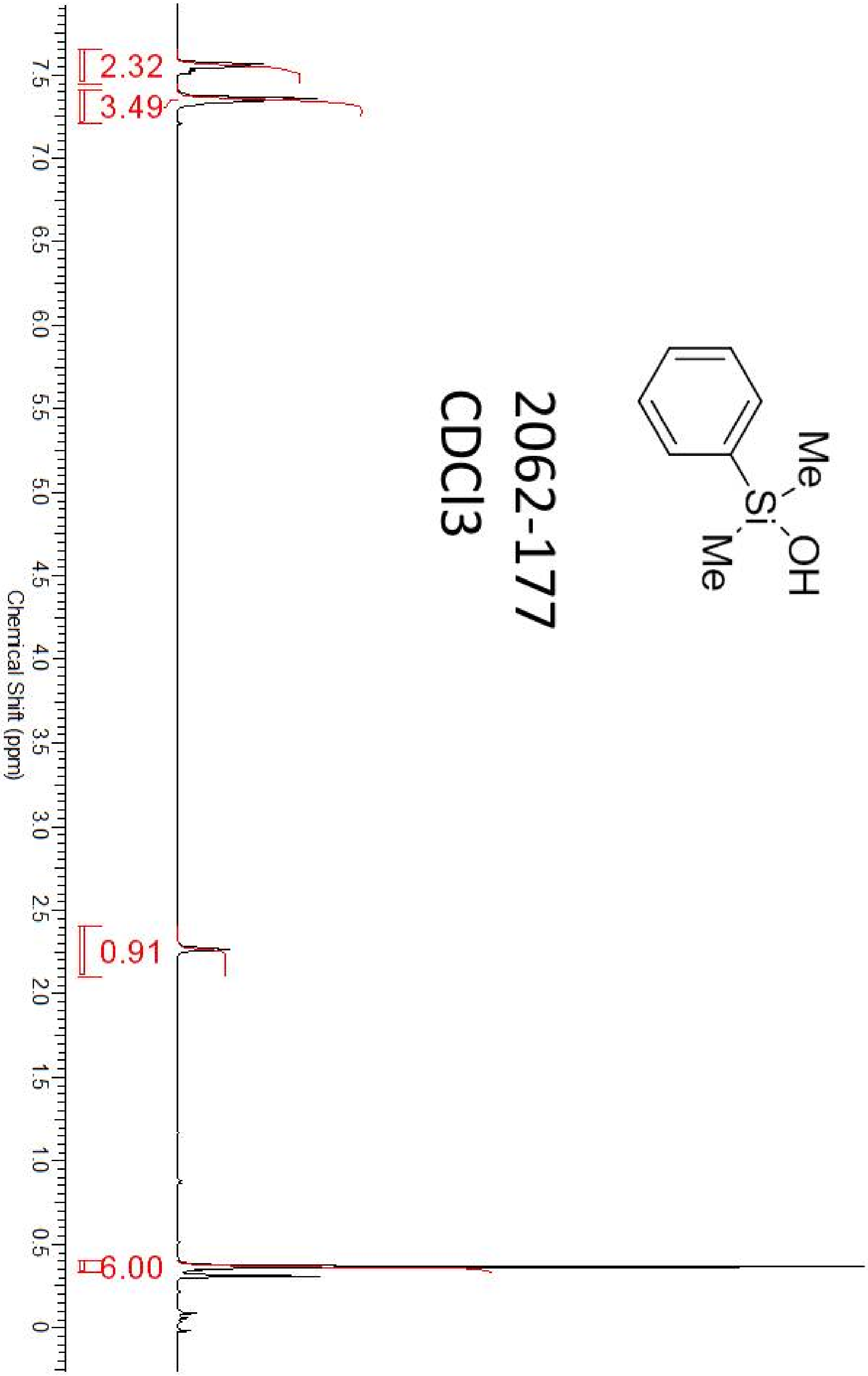

10.43
-21.74
2062-172
DMSO-d6
15
10
5
0
-5
-10
-15
-20
-25
Chemical Shift (ppm)
HO
OH
O
H
N
NH
Me
Si
O

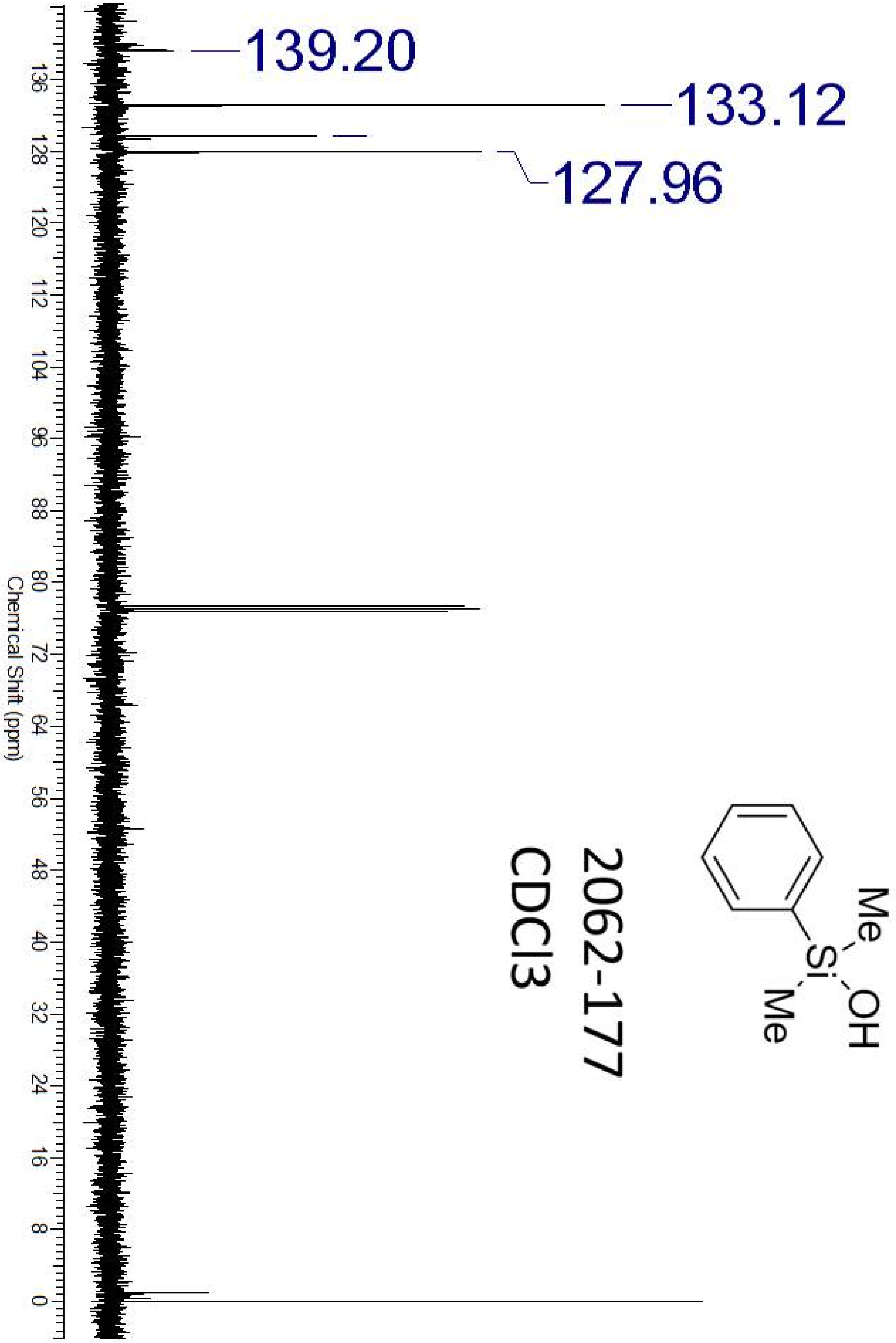

2062-173
CDCl3
Me
Me
N
N
Cl
Si
O
O
Si
Me
Me
C(CH3)3
Me
Si
Me
(H3C)3C
Me
1.16
1.77
1.37
6.27
3.25
6.19
20.34
1.55
15.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

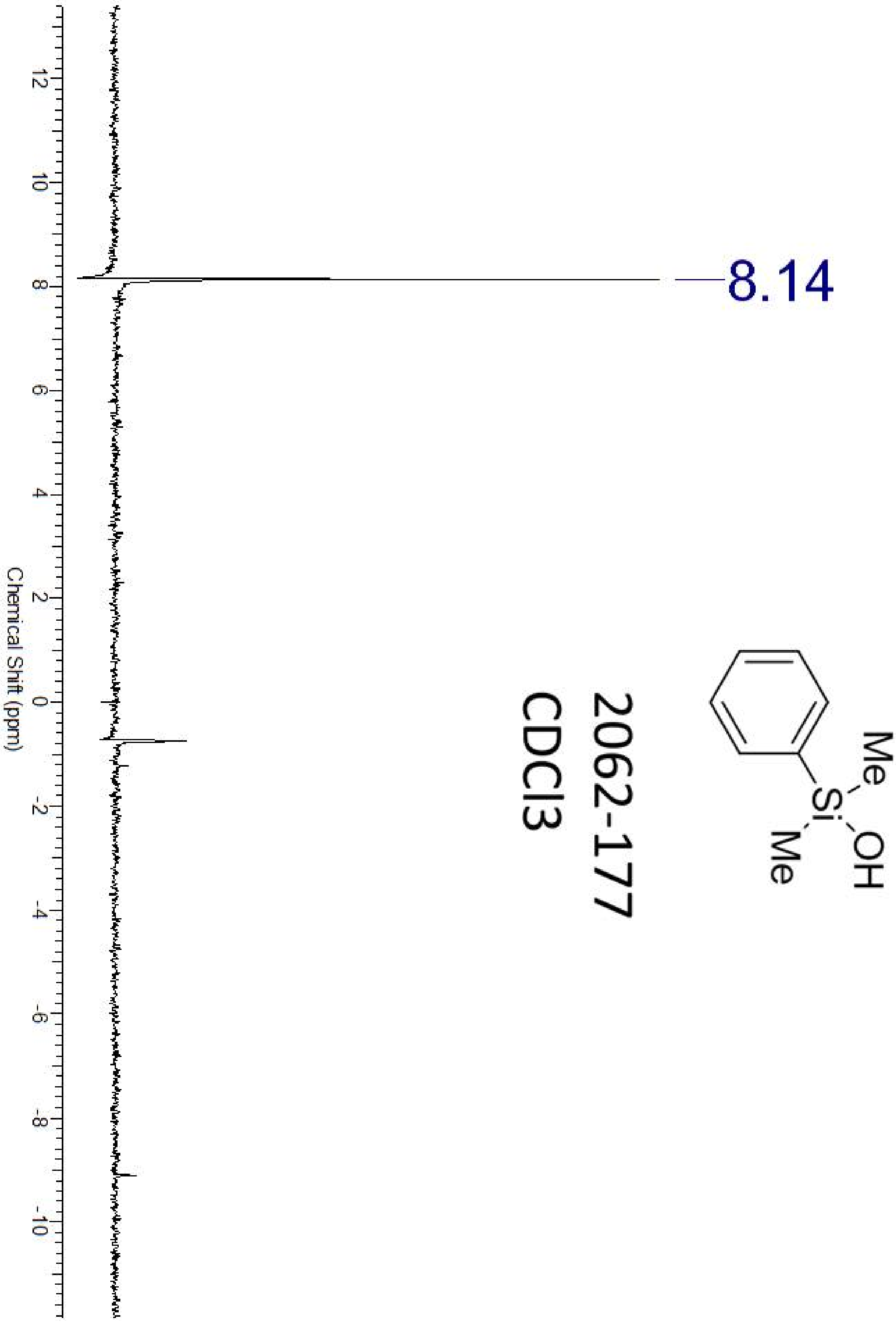

2062-176
CDCl3
Me
Si
O
Cl
4.19
6.31
2.00
2.25
2.17
12.16
3.40
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

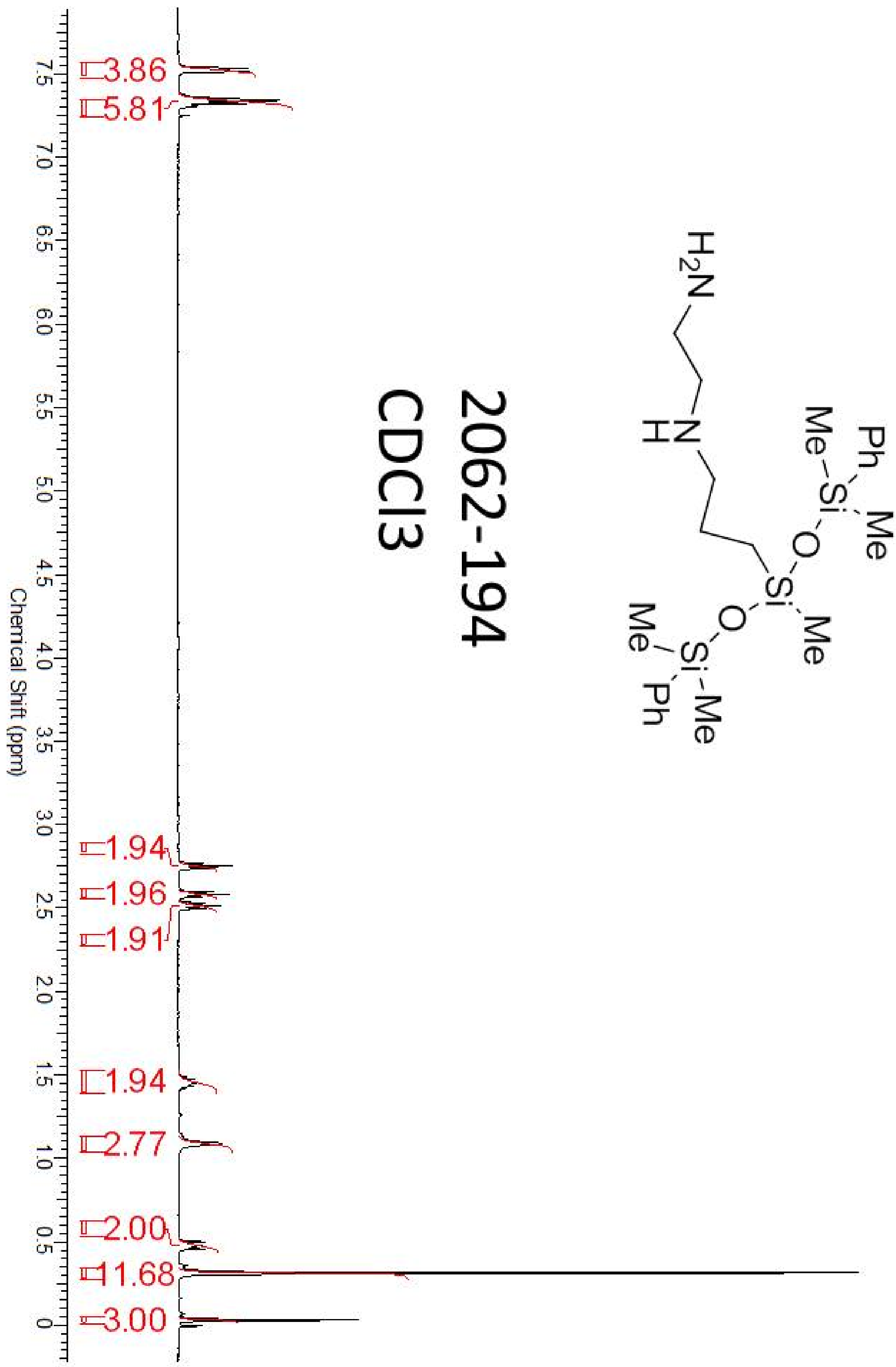

139.56
133.08
129.45
127.90
47.80
26.81
15.24
0.76
Chemical Shift (ppm)
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Me
Si
Me
O
Cl
Si
Me
O
Me
Me
2062-176
CDCl3

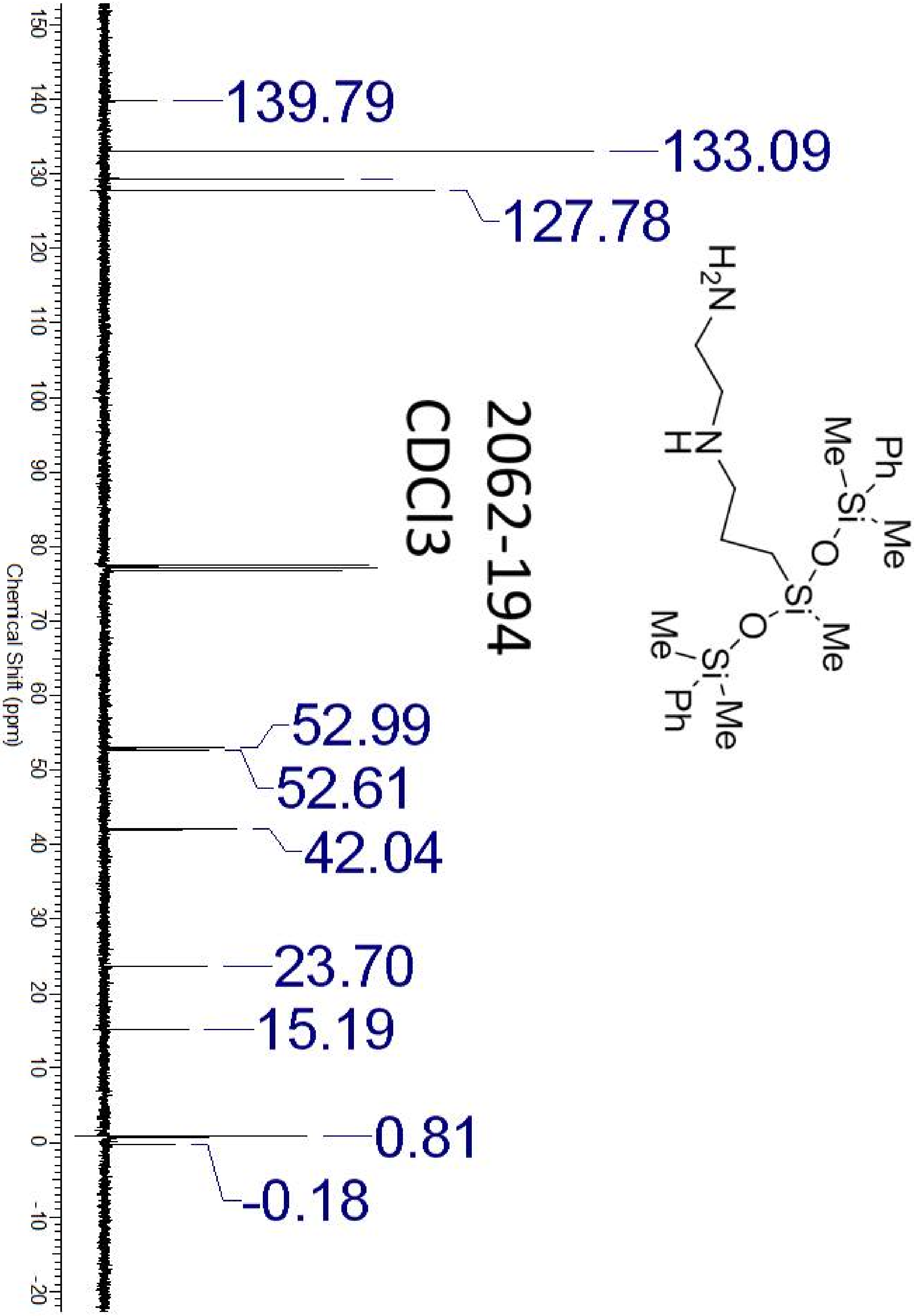

-1.45
-20.79
Me
Si
O
Me
Si
Cl
O
Me
Me
Me
Me
2062-176
CDCl3
5
0
-5
-10
-15
-20
-25
-30
-35
Chemical Shift (ppm)

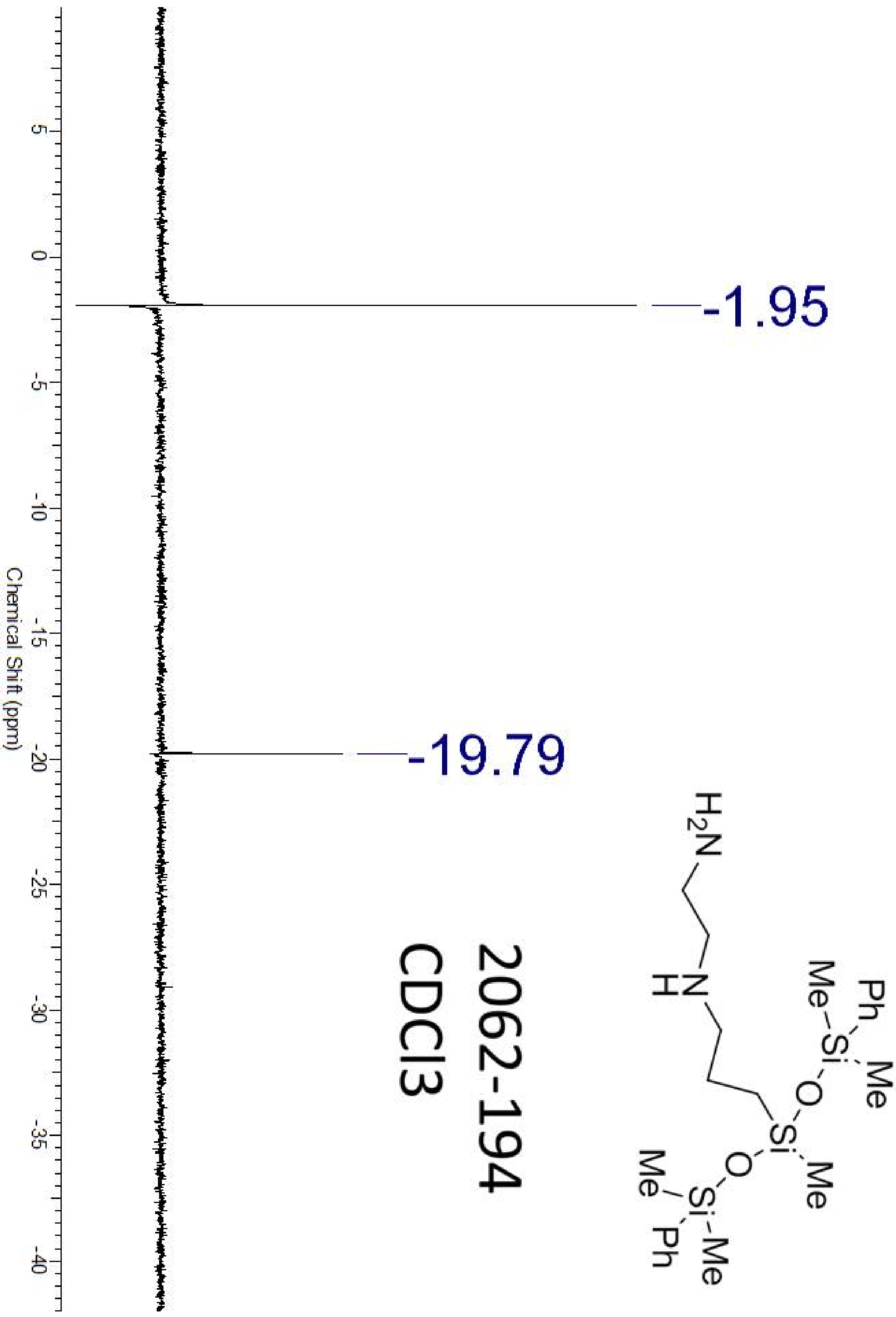

Me
Si
OH
Me
2062-177
CDCl3
2.32
3.49
0.91
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


139.20
133.12
127.96
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)
Me
Si
OH
Me
2062-177
CDCl3

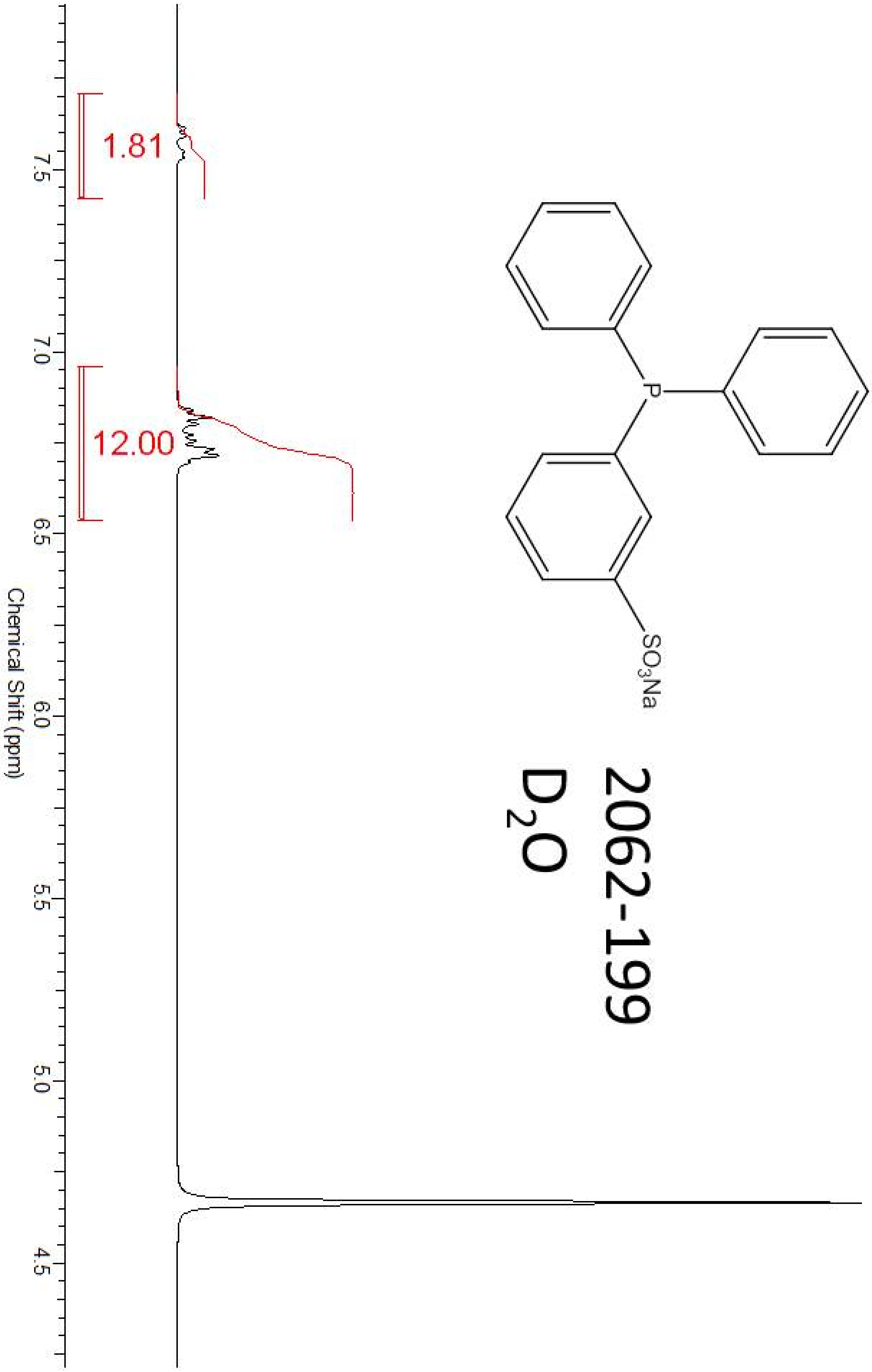

8.14
Me
Si
OH
Me
2062-177
CDCl3
12
10
8
6
4
2
0
-2
-4
-6
-8
-10
Chemical Shift (ppm)

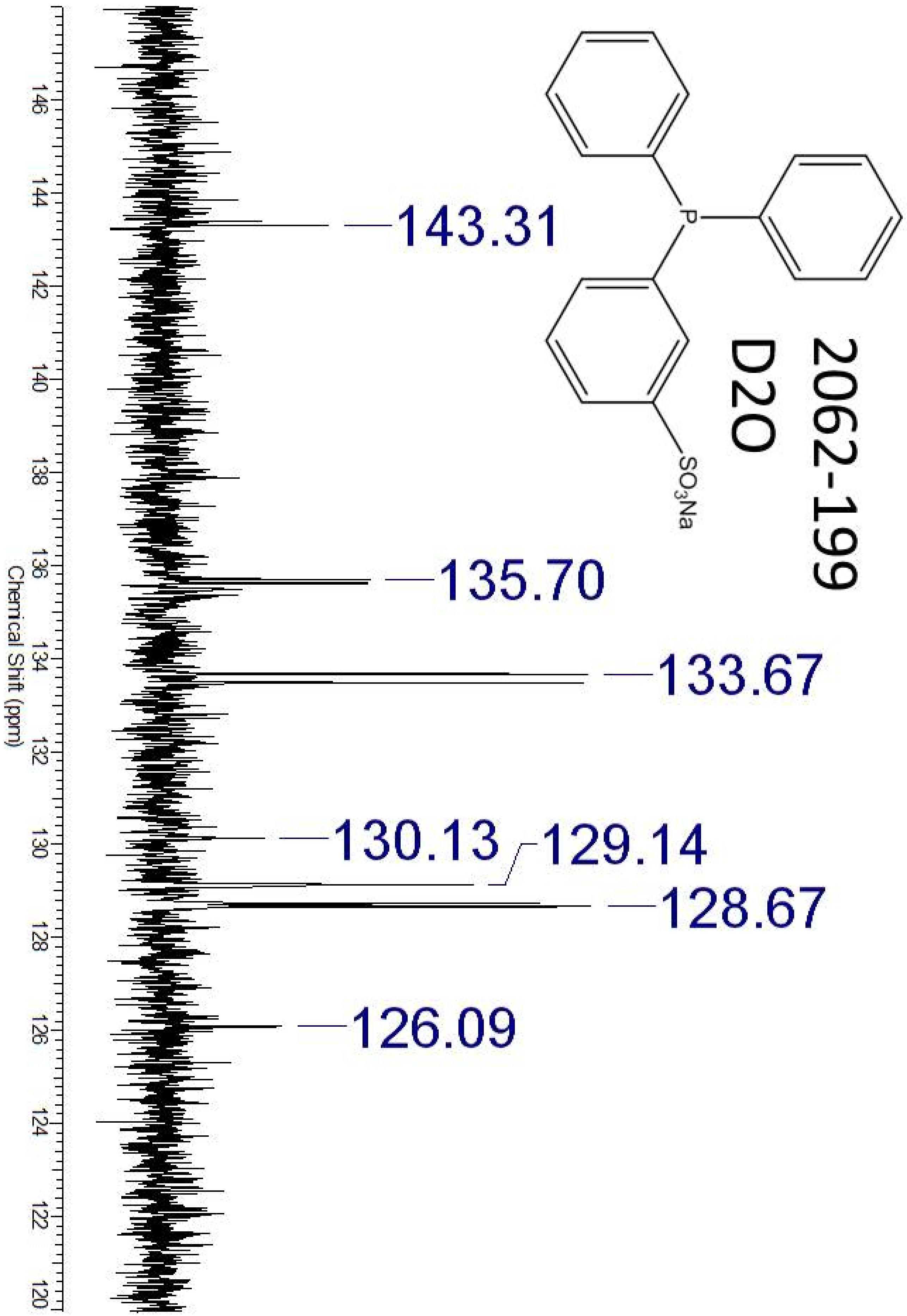

2062-194
CDCl3
H2N
N
H
Ph
Me
Me
Si
O
Si
Me
O
Si
Me
Me
Ph
3.86
5.81
1.94
1.96
1.91
1.94
2.77
2.00
11.68
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

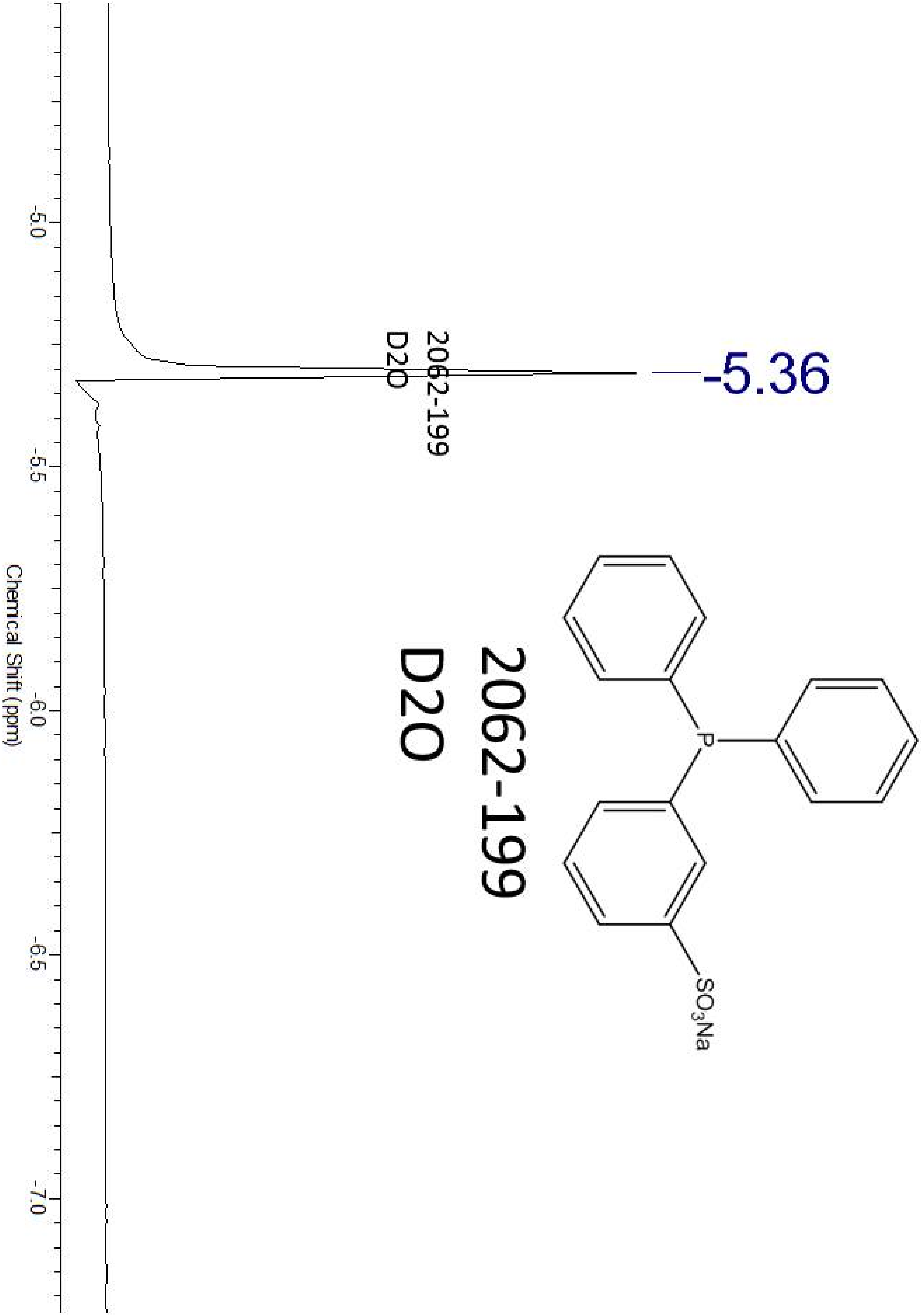

139.79
133.09
127.78
52.99
52.61
42.04
23.70
15.19
0.81
-0.18
2062-194
CDCl3
H2N
N
H
Si
O
Me
Ph
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
Chemical Shift (ppm)

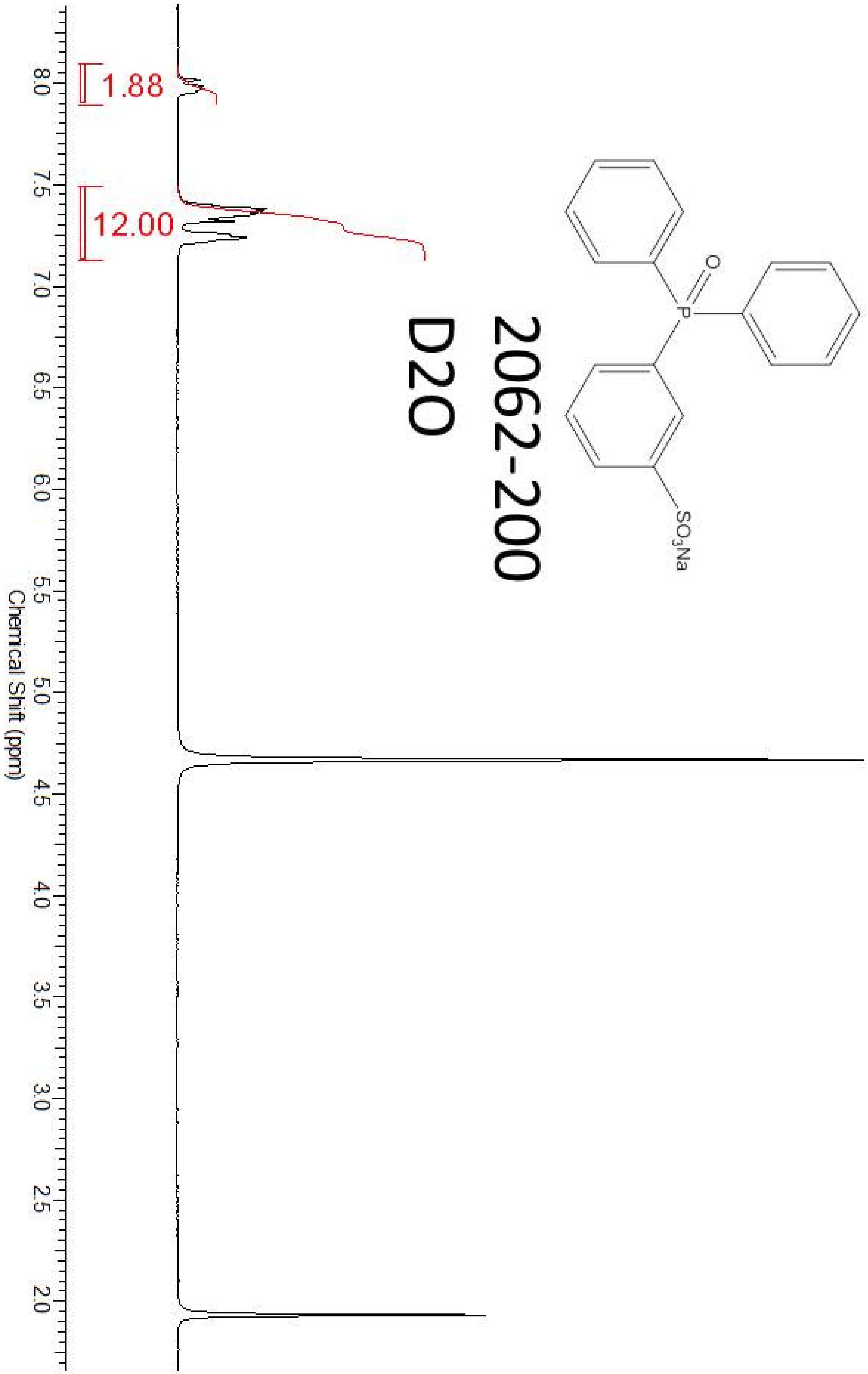


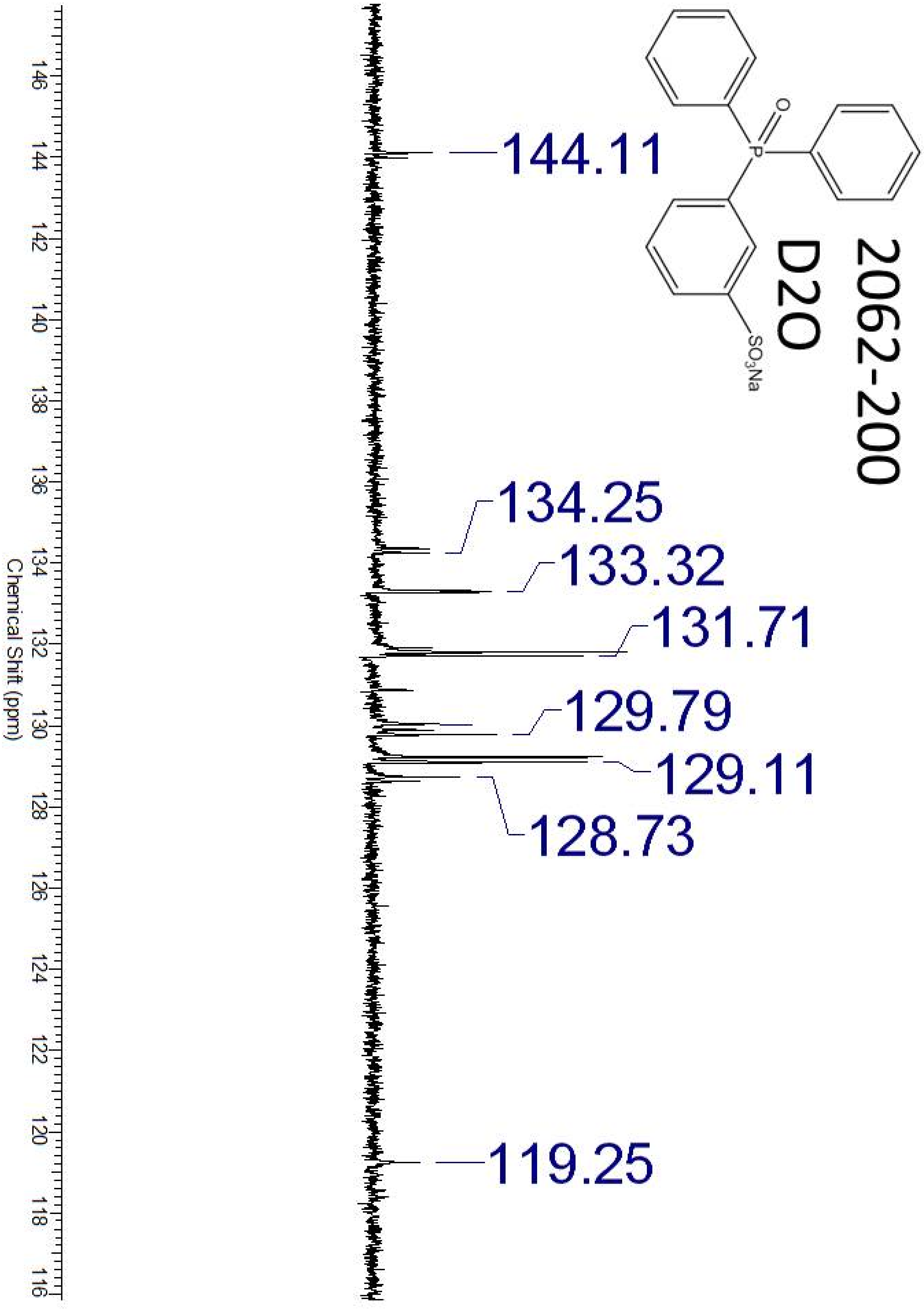
-1.95
-19.79
2062-194
CDCl3
5
0
-5
-10
-15
-20
-25
-30
-35
-40
Chemical Shift (ppm)
H2N
N
H
Si
O
Me
Ph

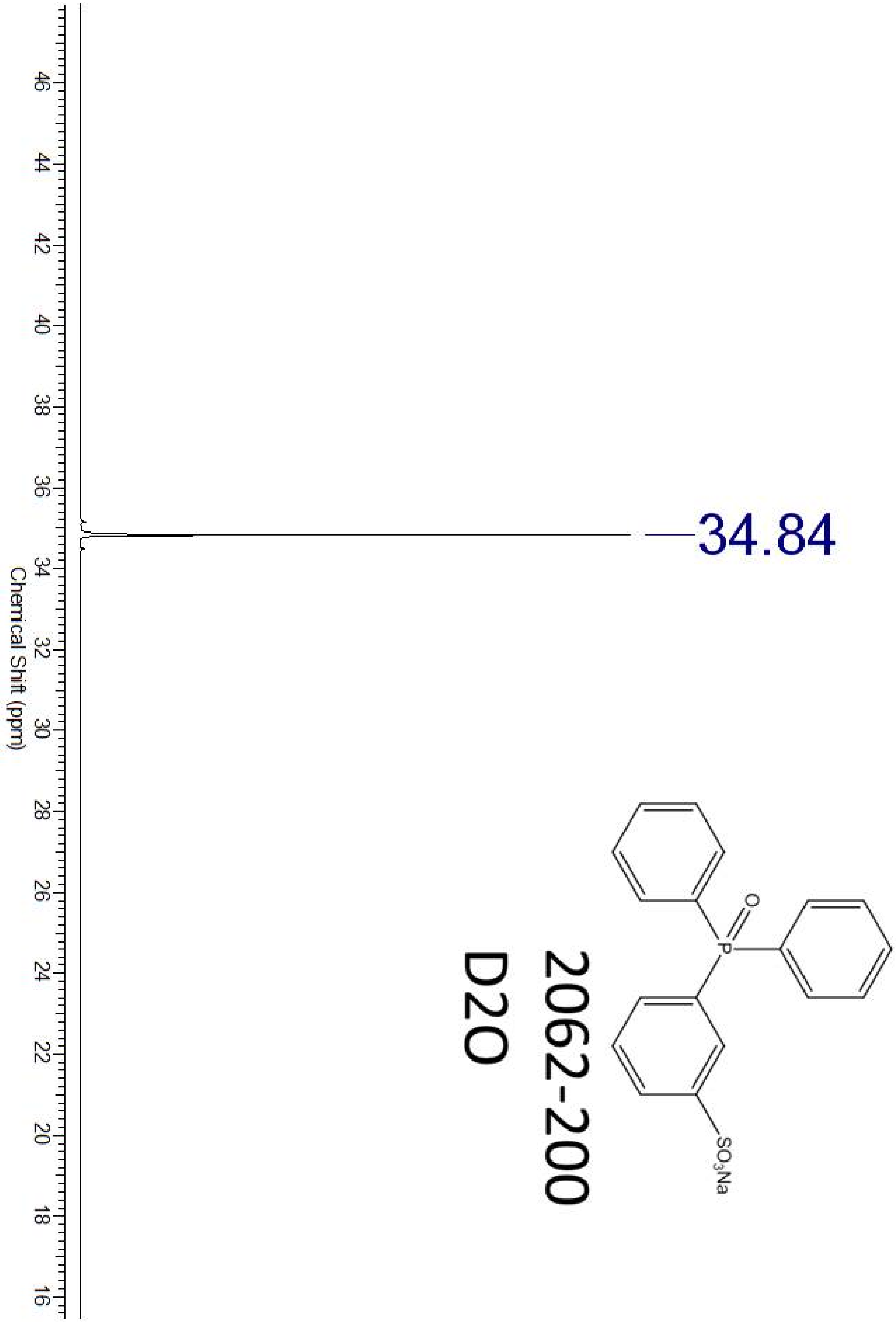

2062-199
D2O
P
SO3Na
1.81
12.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
Chemical Shift (ppm)

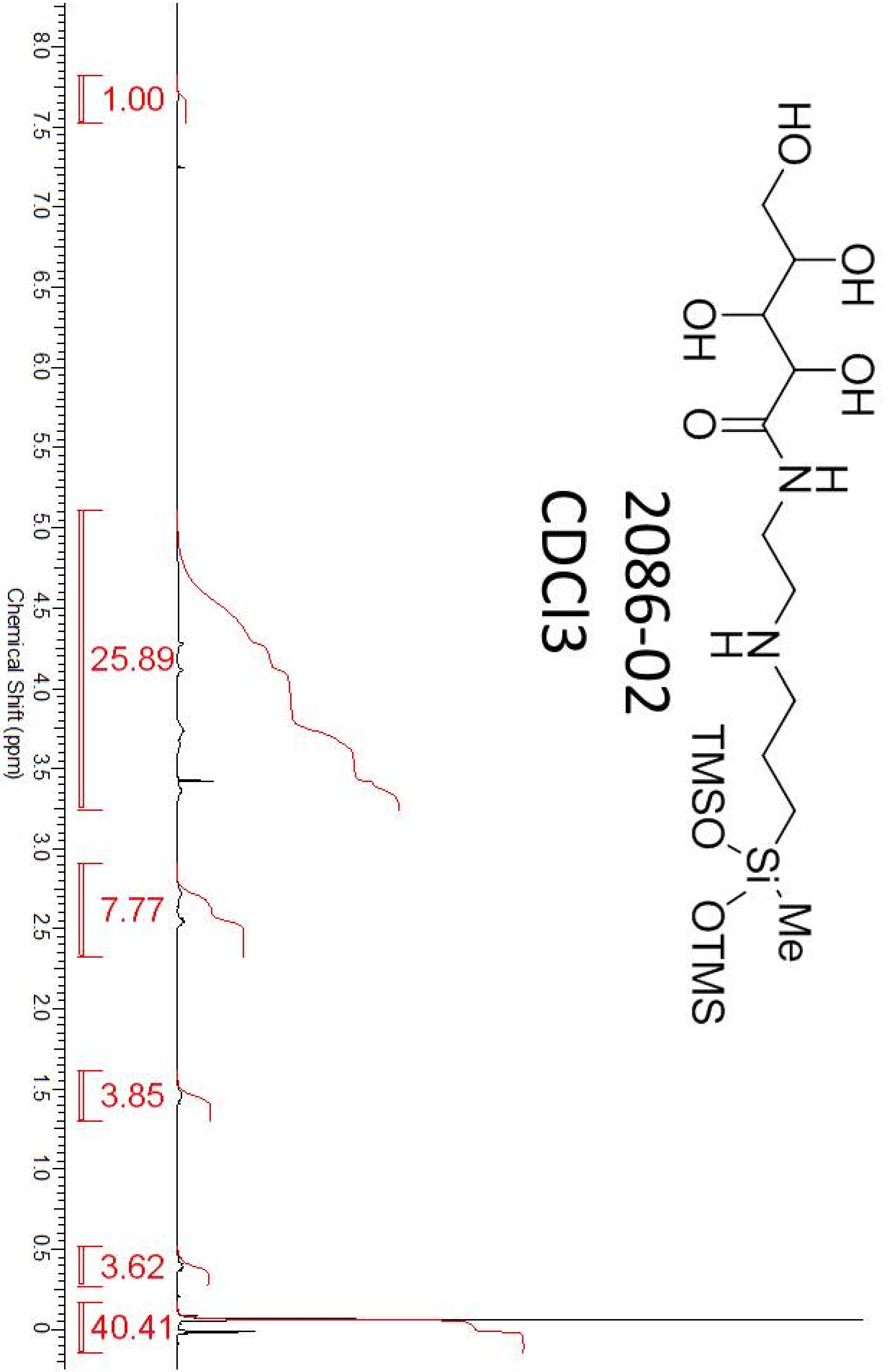

2062-199
D2O
P
SO3Na
143.31
135.70
133.67
130.13
129.14
128.67
126.09
146
144
142
140
138
136
134
132
130
128
126
124
122
120
Chemical Shift (ppm)

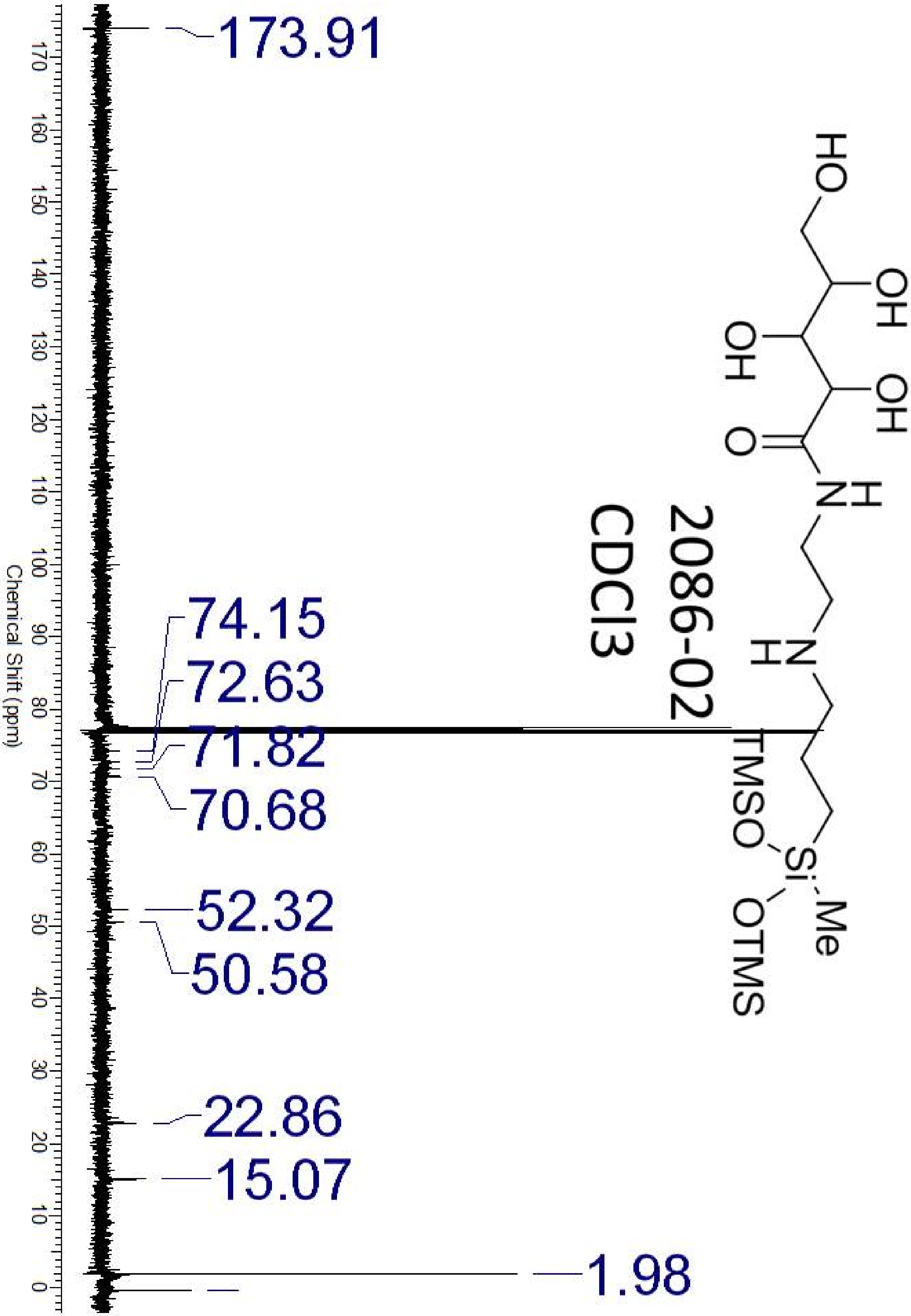

-5.36
2062-199
D2O
P
SO3Na
-5.0
-5.5
-6.0
-6.5
-7.0
Chemical Shift (ppm)

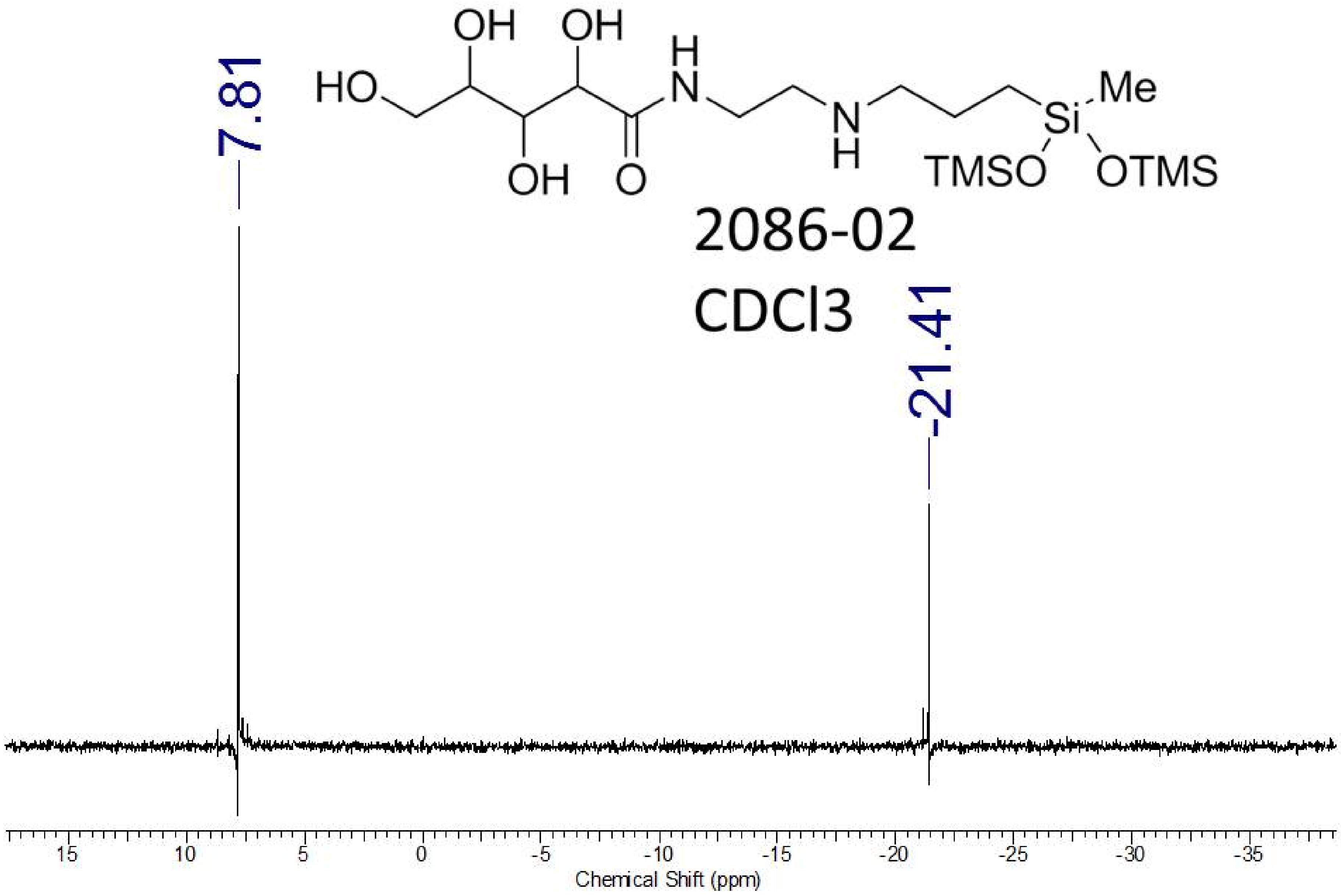

2062-200
D2O
O
P
SO3Na
1.88
12.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)


2062-200
D2O
O
P
SO3Na
144.11
134.25
133.32
131.71
129.79
129.11
128.73
119.25
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
Chemical Shift (ppm)


46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
Chemical Shift (ppm)
34.84
O
P
SO3Na
2062-200
D2O


HO
OH
OH
OH
O
H
N
N
H
TMSO
Si
Me
OTMS
2086-02
CDCl3
1.00
25.89
7.77
3.85
3.62
40.41
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
0
Chemical Shift (ppm)


173.91
74.15
72.63
71.82
70.68
52.32
50.58
22.86
15.07
1.98
2086-02
CDCl3
HO
OH
OH
OH
O
H
N
N
H
TMSO
Si
Me
OTMS
Chemical Shift (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.81
-21.41
HO
OH
OH
OH
O
H
N
N
H
Si
Me
TMSO
OTMS
2086-02
CDCl3
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
Chemical Shift (ppm)