2-(3-Cyanopropyldimethylsilyl)ethyl as Polar Sulfur Protection Group

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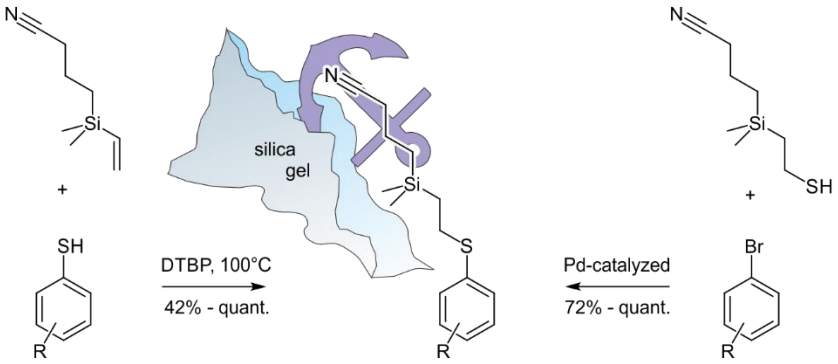


Abstract Organosulfur compounds are ubiquitous in synthetic chemistry, in biology and in material chemistry. The reactivity of free sulfhydryls requires their masking in many synthetic strategies. To facilitate the isolation of protected thiols by chromatography, we propose 2-(3-cyanopropyldimethylsilyl)ethyl as polar protection group analogue of 2-(trimethylsilyl)ethyl. The masked thiophenol can be obtained in two synthetically complementing ways. Either an already existing thiophenol can be protected, or the protected thiol group is introduced by a cross-coupling reaction. In both cases the required reagents are available straight forwardly from inexpensive starting materials. Thiol protection and thiol introduction both tolerate a large variety of functional groups and substitution patterns, and the protected thiophenols are stable in a broad range of reaction conditions. The stability of the protected derivatives in cross-coupling reactions and the mild reaction conditions for the release of the protection group further emphasizes the potential of the methodology.

Key words Thiol, protection groups, cross-coupling, easy to purify, polarity

Thiol (sulfhydryl) groups are ubiquitous as important functional groups e.g. in biology, materials chemistry, or molecular devices. Due to their rich and unique chemistry, they are often involved in highly functional areas of proteins. An example is the formation of disulfides under rather mild conditions. The formation of disulfide bonds between thiols exposed by the amino acid cysteine contributes crucially to the stability of the tertiary structure of folded proteins.[1] The importance of sulfur containing scaffolds for biological activity is also reflected in their frequent appearance in natural products,[2] medicinal chemistry[3] and sulfur comprising proteins.[4]

The importance of sulfhydryl groups arises from the unique chemistry of sulfur (e.g. nucleophilicity, affinity to metals, rich redox chemistry),[5] reflected in a broad range of reactivity. While nature profits extensively from the rich diversity of reactivity of sulfur, this becomes challenging in many reaction strategies in synthetic organic chemistry. Examples are the tendency of free thiols to form disulfides and other oxidation products under more oxidative conditions.[6,7] Another issue is the strong affinity of thiols to metals and metal ions being responsible for the poisoning of various catalytic systems.[8]

Our own interest in masking the thiol group is related to its role as anchor group immobilizing molecules on noble metal surfaces. We developed numerous single molecule devices integrated in physical experiments with thiol-metal bonds. While the thiol-gold bond might have intrinsic challenges due to the variety of atomistic realizations on Au(111) surfaces, it remains the workhorse in single molecule electronics.[9] In particular, the combination of reliable electronic contact and mechanical stability with enough mobility enabling e.g. the formation of self-assembled monolayers makes the thiol anchor group very appealing for the purpose. The examples of single molecule experiments range from terminally thiol-functionalized rigid rods[10-15] and shape persistent macrocycles[16,17] over mechano-sensitive structures[18,19] to three-dimensional objects, spatially oriented by three parallel immobilizing thiol-gold bonds.[20-25] In many cases, the syntheses of these functional molecules required the protection of the sulfhydryl groups.

So far, known protected aryl thiols can be categorized in five main groups: *S*-aryl thioates (e.g. acetyl),[26-31] arylalkylsulfides and arylheteroalkylsulfides,[32-36] *S*-aryl carbonothioates and S-aryl carbamothioates,[37-39] arylbenzylsulfides,[40-42] and silicon comprising[43-46] aryl sulfides. Particularly appealing is the ethyl silane sulfur protection group (PG)[43,47-49] due to its wide range of tolerated reaction conditions. On the other hand are trialkyl arylthiosilanes considerably less stable than their oxygen analogues and thus synthetically less useful.

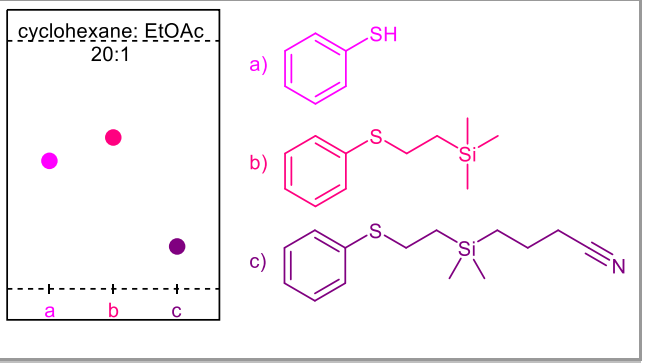
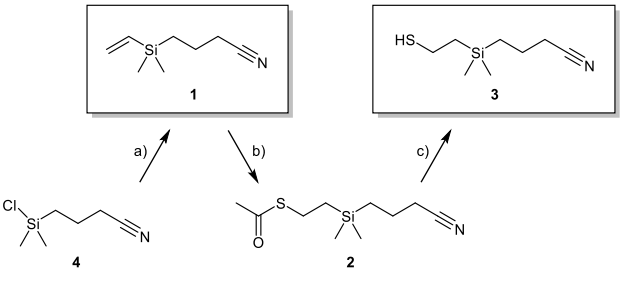


Figure 1 Thin layer chromatography (TLC) of a) benzenethiol (R_f = 0.52), b) 2-(trimethylsilyl)ethyl thiophenol (R_f = 0.61) and c) 2-(3-cyanopropyl-dimethylsilyl)ethyl thiophenol (R_f = 0.17) shows the enhanced polarity of the protection group reported here, which eases the isolation of the protected compound by flash column chromatography.

Ideal protection groups are on the one hand, stable under a wide range of reaction conditions, but on the other hand they remain removable under mild conditions, allowing a large variety of functional groups to be present. In addition, the protected and the deprotected compound should provide polarity features enabling their separation by chromatography.

Here we report 2-(3-cyanopropyldimethylsilyl)ethyl (**Figure 1, c)** as promising polar protection group of arylthiols. The object of the study is an analogue of the popular 2-(trimethylsilyl) ethyl protection group (**Figure 1, b**)[43] but with optimized polarity features to facilitate separation by chromatography. The concept to enhance the polarity of a silyl-protection group with an exposed nitrile group is borrowed from Höger and Bonrad, who reported the potential of 3-cyanopropyldimethylsilyl as protection groups of alkynes in 2000.[50] The peripheral nitrile group facilitates separation of the protected derivatives by flash column chromatography, while the trialkyl-silyl core structure provides similar stability features and deprotection conditions as the classical analogues. As displayed in **Figure 1**, the polarity of the 2-(3-cyanopropyldimethylsilyl) ethyl protected thiophenol is increased considerably compared to the 2-(trimethylsilyl)ethyl analogue.

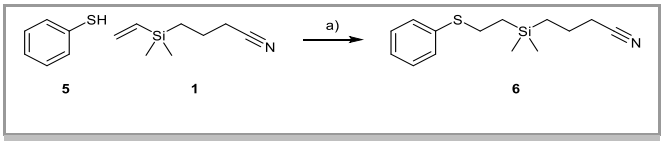
An appealing aspect of this protection group is that it cannot only be introduced with 3-cyanopropyldimethyl vinylsilane (**1**) to mask an exposed aryl or alkyl thiol, but also with 2-(3-cyano-propyldimethylsilyl)ethanthiol (**3**) in a masked thiol introducing cross coupling reaction, substituting a suitable leaving group. As displayed in **Scheme 1**, the required reagent (**3**) is obtained via 2-(3-cyanopropyldimethylsilyl)ethyl ethanethioate (**2**).



Scheme 1 Preparation of reagents **1** and **3**. a) Vinylmagnesiumbromide, THF, 10 °C, 30 min., 78%. b) a) Thioacetic acid, AIBN, 60 °C, 2 h., 91%. c) K_2CO_3, MeOH, H_2O, Et_2O, room temperature, 2 h, then citric acid, 75%.

The protection of the thiols was investigated first. The reagent **1** introducing the protection group was prepared with a similar protocol reported for the synthesis of vinyl trimethylsilane[51,52] (**Scheme 1**). However, according to gas chromatography-mass spectrometry (GC-MS), the reaction was completed after the addition of vinylmagnesium bromide at 10 °C to a solution of chloro-(3-cyanopropyl)dimethylsilane (CPDMS-Cl, **4**) in THF, and subsequent heating was not required. Product **1** was obtained as colorless oil in 78% yield after vacuum distillation.

The thiol-ene addition between vinylsilanes and thiophenols with azobis(isobutyronitrile) (AIBN) as radical initiator is well known[43] and the protected thiophenols are usually obtained in excellent yields. Here in our case, di-*tert*-butyl peroxide (DTBP) was favored as radical initiator, because it is liquid at room temperature and thus it is better suited for the selected neat reaction conditions.[53-55] The radical reaction between **1** and parent thiophenol **5** (**Scheme 2**) provided protected thiophenol **6** in very good 93% yield on a half gram scale, and in even better 99% isolated yield on a 5 g scale.



Scheme 2 Protection of benzenethiol (**5**) with protection group precursor **1**. a) DTBP, neat, 100 °C, 1 h, 93% (0.5 g), 99% (5.0 g).

The reaction conditions introducing the protection group tolerate a variety of functional groups (**Figure 2**). There are however general trends. Liquid thiophenols (e.g. **6**, **20,** and **21**) react faster and the masked derivatives are obtained in higher yields than for solid thiophenols (**13**, **14**, **16**, **17** and **18**). Steric hindrance in the investigated thiophenols requires elongated reaction periods (e.g. **7** and **10** *vs.* **6**, **8** and **9**). Strongly polarizing substituents tend to slow the reaction down. (**13**, **14**, **15, 16, 17** or **19**). Aniline **13** required 150°C as reaction temperature, the reaction was extremely slow otherwise. The protocol also works in excellent yields with aliphatic thiols, as demonstrated with 1-octanethiol (**21**) as representative example.

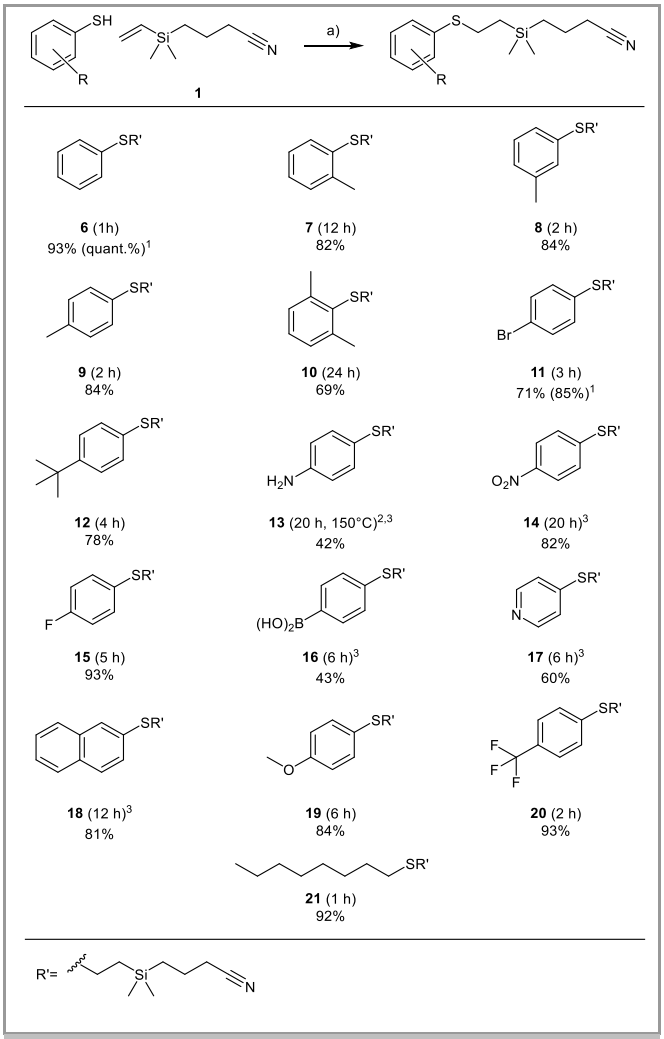


Figure 2 Reaction scope of thioaryl derivatives protection (including a thioalkyl model compound) with the reagent **1**. a) 1.2 eq. **1**, DTBP, 100 °C, 1-20 h.[1] 5 g Scale. [2] extremely slow reaction at 100 °C. [3] For reactions of solid compounds 2.4 eq. **1** were used.

As alternative approach to protected thiophenol derivetives, a cross-coupling protocol for the introduction of the masked thiol was considered. For the synthesis of 2-(3-cyanopropyldimethyl-silyl)ethan-thiol (**3**) a route developed by Schwan *et al*[48] was used (**Scheme 1**). Freshly distilled thioacetic acid was stirred with **1** and AIBN as radical initiator at 60 °C for 2 h. Compound **2** was obtained as light yellow oil in 91% yield after vacuum distillation. Thioacetate **2** was hydrolyzed with K_2CO_3 in a solvent mixture of MeOH, H_2O, and Et_2O. After addition of citric acid to protonate the thiolate, 2-(3-cyanopropyldimethylsilyl)ethanthiol (**3**) was isolated by fractional vacuum distillation in 75% yield as a colorless oil.

To substitute arylbromides with thiol **3** a reaction protocol of Itoh and Mase was adapted.[34] The reported procedure uses $Pd_2(dba)_3$(2.5mol%) as a pre-catalyst and Xantphos (5 mol%) as ligand. The similar polarities of dba and compound **6** motivated the search for an alternative palladium source. By using $(Ph_3P)_4Pd$ or $(Ph_3P)_2PdCl_2$ as catalysts the same yield were obtained without purification issues. For the cross-coupling protocol $(Ph_3P)_2PdCl_2$ was chosen as pre-catalyst due to the lower price and larger tolerance to oxygen impurities compared to $(Ph_3P)_4Pd$.

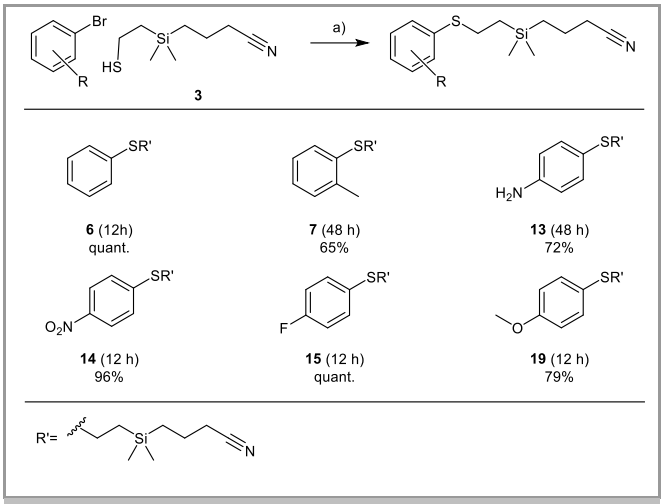
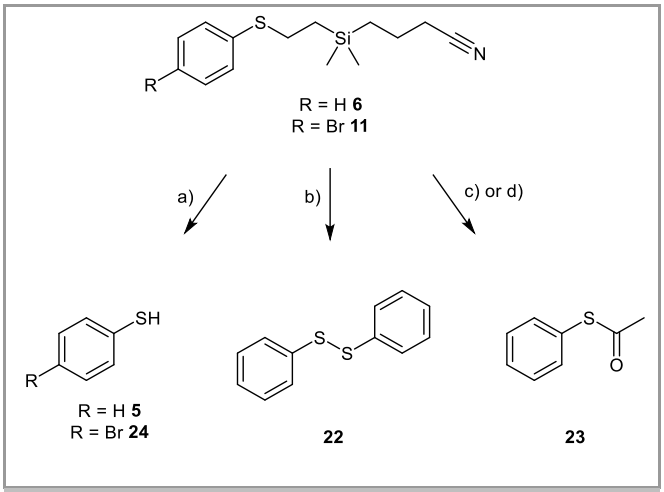


Figure 3 Reaction scope of masked thiol introduction by a cross-coupling protocol with reagent **3**. a) 1.2 eq. **3**, $(Ph_3P)_2PdCl_2$ (2.5 mol%), Xantphos (5 mol%), *i*Pr_2NEt, dioxane, 110°C.

The protected thioaryls **6**, **14**, **15**, and **19** were all obtained with this protocol within 12 h reaction time in good to excellent yields (**Figure 3**). The syntheses of **7** and **13** required repeated addition of $(Ph_3P)_2PdCl_2$ and Xantphos until complete disappearance of the starting material was observed by GC-MS after 48 h. The steric hindrance of the neighboring methyl group in compound **7** and the electron donating amine group in **13** was not only reflected in reduced reaction rates, but also in smaller isolated yields. While model compound **7** was obtained in better yields by the radical reaction between 2-methyl benzenethiol and **1** (82% *vs.* 65%), the cross-coupling reaction appears to be the better strategy for aniline **13** (72% *vs.* 42%).

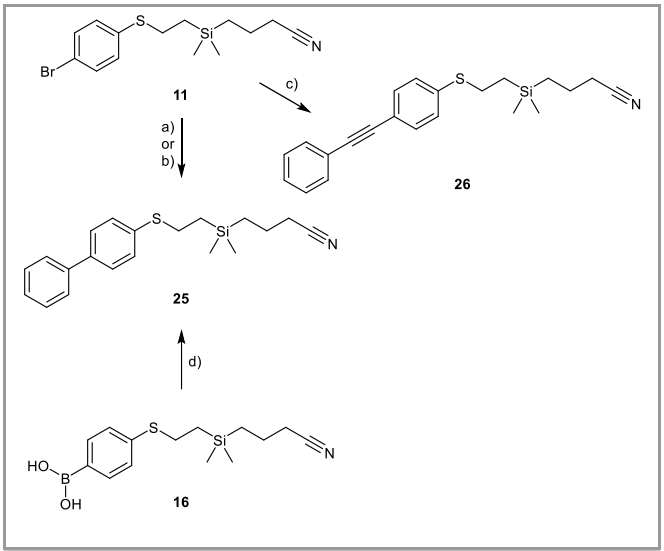


Scheme 3 Release of the PG demonstrated with compound **6,** providing benzenethiol (**5**), 1,1'-disulfanediyldibenzene (**22**), and S-phenyl ethanethioate (**23**). Procedure a) was further studied with **11** yielding in 4-bromobenzenethiol (**24**). a) TBAF, THF, room temperature, 4 h, 42% (**5**), 90% (**24**). b) TBAF, THF, room temperature, 4 h, then pyridine, I_2, 30 min., 95%. c) TBAF, THF, room temperature, 4 h, then AcCl, 8 h, 83% d) $AgBF_4$, AcCl, DCM, room temperature, 12 h, 89%.

To remove the PG four different procedures were investigated, using **6** as model compound (**Scheme 3**). In the first approach, benzenethiol (**5**) was deprotected by TBAF in THF at room temperature. Unfortunately, benzenethiol (**5**) is not suited as model compound due to its challenging isolation features. While the deprotection reaction proceeded quantitatively according to

reaction monitoring by gas chromatography, purification of **5** by column chromatography, acid-base extraction, and distillation resulted only in fractions comprising impurities. Finally, a pure fraction of **5** was isolated in mediocre 42% yield by extraction in Et_2O with $NaHCO_3$. As more representative example, the derivative **11** was exposed to the same reaction conditions and the corresponding less volatile thiophenol derivative **24** was isolated in 90% yield. However, thiol **24** was also quickly oxidizing to the corresponding disulfide in the presence of oxygen. To facilitate the isolation of the released thiophenols, their *in-situ* transformation to the corresponding disulfides or acetyl-protected derivatives was investigated. Both derivatives are appealing due to their potential as precursors of self-assembled monolayers. To favor disulfide formation, iodine and pyridine were added to the TBAF deprotection reaction mixture and indeed, 1,1'-disulfanediyldibenzene (**22**) was isolated in excellent 95% yield. Also, the capture of the thiophenol as S-phenyl ethanethioate (**23**) by addition of acetylchloride to the deprotection reaction mixture was successful (83%). In an alternative protocol, **6** was treated with $AgBF_4$ and AcCl in DCM at room temperature for 12 h, providing the ethanethioate **23** in 89% yield.

With our research topic geared towards rigid structures exposing thiophenols as anchor groups, the stability of the protected thiophenols in cross-coupling reactions was of particular interest. Especially *Suzuki* cross-coupling conditions are known to be troublesome for a variety of thiophenol PGs.[29] As displayed in **Scheme 4**, 2-(3-cyanopropyldimethylsilyl)ethyl protected thiophenol derivatives have been engaged successfully in both, *Suzuki* and *Sonogashira* reactions. To explore the limit of the PG stability, bromine substituted thiophenol **11** was selected as starting material, requiring considerably higher reaction temperatures than corresponding iodine analogues. In the case of the *Suzuki* reaction the stability of the PG was studied as subunit of both reaction partners, the halide and the boronic acid. Biphenyl **25** was assembled first, starting with compound **11** and, in a second approach, using the boronic acid **16** as starting material. The reaction of compound **11** with phenylboronic acid was investigated with two catalytic systems, $(Ph_3P)_2PdCl_2$ and SPhos Pd G2 (2 mol% respectively), with the second giving slightly better yields (90% *vs*. 92%). Consequently the same catalyst (SPhos Pd G2, 2 mol%) was used to couple boronic acid **16** with iodobenzene, yielding again **25** in good 87% isolated yield and demonstrating the suitability of iodoaryls as reaction partners in the presence of the PG. Compound **11** was also engaged in a *Sonogashira* reaction with phenylacetylene, using a mixture of THF and piperidine as solvent, and the combination of CuI (6 mol%) and $(Ph_3P)_2PdCl_2$ (5 mol%) as catalytic system.[56] Also under these cross coupling conditions the PG proved to be perfectly stable and the desired tolane **26** was isolated in 91% yield.



Scheme 4 Stability of the PG in cross-coupling reactions. Assembly of biphenyl **25** in a *Suzuki* reaction with either bromine **11** or boronic acid **16**, and the synthesis of tolane **26** in a *Sonogashira* reaction. a) Phenylboronic acid, K_2CO_3, $(Ph_3P)_2PdCl_2$ (2 mol%), toluene, H_2O, 80 °C, 3 h, 90%. b) Phenylboronic acid, K_2CO_3, SPhos Pd G2 (2 mol%), toluene, H_2O, 80 °C, 3 h, 92%. c) Phenylacetylene, CuI (6 mol%), $(Ph_3P)_2PdCl_2$ (5 mol%), THF, piperidine, 80 °C, 3 h, 91%. d) Iodobenzene, K_2CO_3, SPhos Pd G2 (2 mol%), toluene, H_2O, 80 °C, 12 h, 87%.

Of particular interest, with respect to a new protection group, is its behavior under typical reaction conditions. Without claiming to be comprehensive, a variety of 29 different reaction conditions were investigated and are summarized in **Table 1**. In particular the stability of the PG in aqueous conditions, in the presence of bases, nucleophiles, electrophiles, and redox agents was investigated. In each test reaction 50 mg of compound **6** were dissolved in 5 mL of solvent (water/EtOH 4:1, THF, EtOH or DCM) and the mixture was stirred at -78 °C, room temperature or 100 °C. As color code of **Table 1** a dark green background signals stability for a period of seven days, a light green background indicates no signs of degradation within 3 days, while a dark red background expresses that the masked thiophenol did not survive the first hour. The pale red background indicates challenging stability features and individual details are given as footnote of **Table 1**. In 20 cases compound **6** was stable for at least 7 days under the conditions employed (dark green background), and in four cases (LDA, *t*BuOK, OsO_4 and Br_2) for at least 3 days (light green background). Under conditions using electrophiles and reducing agents the 2-(3-cyanopropyldimethylsilyl) ethan thiol protection group seems to be especially stable, as in none of the tested conditions decomposition or side reactions were observed. Under strongly acidic or basic aqueous conditions at 100°C compound **6** was not stable at all. *n*BuLi and Me_2CuLi reacted partially with compound **6**, but full decomposition was not observed. *m*CPBA oxidised ~50% of the protected thiophenol to the corresponding sulfone. If 2.5 eq *m*CPBA were used, full conversion to the corresponding sulfone was observed.

In summary, 2-(3-cyanopropyldimethylsilyl)ethyl is investigated as polar protection group of thiophenols, still keeping the reactivity features of the parent TMS-ethyl protection group. The new PG can be introduced by simple protocols either from the corresponding vinylsilane **1** masking a free thiophenol, or as sulfur introducing reagent **3** substituting a halide atom in a cross-

coupling protocol. In both cases, the required reagent is available from inexpensive commercial starting materials in good yields. A variety of substituents and substitution patterns are tolerated and the protected thiophenol is stable in a wide window of reaction conditions. Furthermore, the PG is suited for cross-coupling reactions, as typical Pd-catalyzed *Suzuki* and *Sonogashira* reactions were performed in good yields. The 2-(3-cyanopropyldimethylsilyl)ethyl protection group is released by mild reaction conditions, comparable to the ones used for the deprotection of the parent TMS-ethyl. The increased polarity of the presented PG considerably facilitates isolation of protected thiophenol derivatives by chromatographic methods.

Table 1 Stability of the 2-(3-cyanopropyldimethylsilyl)ethyl thiophenol protection group

Aqueous:	pH=1, 100 °C[1, a]	pH=1, room temp.[2,d]	pH=4, room temp. [2,d]	pH=9, room temp. [2,d]	pH=12, room temp.[2,d]	pH=12, 100 °C[1,a]
Bases:	LDA [6,c]	Pyridine [3,d]	*t*BuOK [3,c]			
Nucleophiles:	*n*BuLi[6,b]	*i*PrMgCl [6,d]	Me_2CuLi[6,b]	NaOEt [4,d]	NH_3 [3,d]	
Electrophiles:	AcCl [5,d]	AcH [3,d]	CH_3I [3,d]	AcOH [5,d]	Ac_2O [5,d]	
Reduction:	Raney Ni, H_2 [4,d]	Pd/C, H_2 [4,8,d]	Fe, HCl [4,7,d]	$LiAlH_4$ [3,d]	$NaBH_4$ [4,d]	$NaBH_3CN$ [4,d]
Oxidation:	OsO_4 [3,c]	MnO_2 [5,d]	*m*CPBA[5,b]	Br_2 [5,c]		

Conditions for the stability measurements were as follows: 50 mg of the masked thiophenol **6** and 1.0 eq. reagent in 5.0 mL solvent were stirred at room temperature under argon, GC-MS measurements were made after 1h, 10 h, 24 h, 3 days and 7 days. [1] 4 mL water + 1 mL EtOH, 100 °C [2] 4 mL water + 1 mL EtOH [3] THF [4] EtOH [5] DCM [6] THF, -78°C [7] 10 eq. Fe, 0.5 mL HCl conc.[8] 0.1 eq. Pd/C [a] Stable for less than 1 h, [b] partially stable (*n*BuLi: ~35% decomp. within first hour increase to ~50% decomp. after 7 days. Me_2CuLi: ~15% decomp. within first hour then stable in that range., *m*CPBA: ~50% of the protected thiophenol is oxidized to the corresponding sulfone within the first hour then stable in that range.) [c] stable for at least 3 days, [d] stable for at least 7 days.

All chemicals were directly used for synthesis without further purification unless stated otherwise. Dry solvents were used with crown cap as purchased from Sigma-Aldrich . NMR solvent was obtained from CIL Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). All NMR experiments were performed on Bruker Avance III or III HD, two or four-channel NMR spectrometer operating at 500.13 MHz proton frequency. The instrument was equipped with direct observe BBFO 5 mm probes, with self-shielded z-gradient. The experiments were performed at 298 K. All chemical shifts (δ) are reported in ppm relative to the used solvent and coupling constants, (J) are given in Hertz (Hz). Multiplicities are written as: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublet, m = multiplet. A Shimadzu GC–MS-QP2010 SE gas chromatograph system, with a ZB-5HT inferno column (30 m × 0.25 mm × 0.25 mm), at 1 mL/min He-flow rate (split = 20:1) with a Shimadzu mass detector (EI 70 eV) was used. For column chromatography SilicaFlash® P60 from SILICYCLE was used with a particle size of 40–63 µm (230–400 mesh). High-resolution mass spectra (HRMS) were measured with a Bruker Maxis 4G ESI-TOF instrument or on a Waters Micromass AutoSpec Ultima (EI-Sector).

3-Cyanopropyl dimethyl vinylsilane (1) (954114-30-8)[57]**:** A 2 L three-neck round-bottom flask was equipped with a dropping funnel, a reflux condenser and a thermometer, heated out and then flushed with argon. CPDMS-Cl (100 mL, 611 mmol, 1.0 eq) was dissolved in dry THF (300 mL) and a solution of vinylmagnesium chloride in THF (420 mL, 1.6 M, 672 mmol, 1.1 eq) was added drop-wise over 30 min at 5-10 °C. The reaction was finished according to GC-MS after the addition and the cold mixture was diluted with TBME (450 mL). The mixture was poured into ice-cold water (250 mL) (slightly exothermic) and acidified with aq. HCl 1M (~125 mL). The organic layer was separated and extracted with H_2O (450 mL) and brine (450 mL), dried over Na_2SO_4 and concentrated under reduced pressure to a yellow oil. The crude mixture was purified by vacuum distillation (82-94 °C at 5 x 10^{-1} mbar). Compound **1** (72.9 g, 475 mmol, 78%) was obtained as colorless liquid.

Density (24 °C): 0.839 g/mL

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 6.14 (dd, *J*=20.3 Hz, 14.7 Hz, 1H), 5.98 (dd, *J*=14.7 Hz, 3.8 Hz, 1H), 5.71 (dd, *J*=20.3 Hz, 3.8 Hz, 1H), 2.34 (t, *J*=7.0 Hz, 2H), 1.70 – 1.61 (m, 2H), 0.75 – 0.68 (m, 2H), 0.09 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 138.7, 132.6, 120.4, 21.2, 21.2, 15.5, -3.4.

DEPT-135 (126 MHz, CD_2Cl_2): δ = 138.7, 132.6, 21.2, 21.2, 15.5, -3.4.

HRMS (EI, 70 eV): *m/z* calcd for $C_7H_{12}NSi$ $[M\text{-}CH_3]^+$ 138.07335; found: 138.07332.

The spectra data of this compound were identical to those reported in the literature.

2-(3-Cyanopropyldimethylsilyl)ethyl ethanethioate (2): 1 (30.0 g, 196 mmol, 1.0 eq) was added to an argon-flushed and dried one-neck round-bottom flask equipped with a reflux condenser. Freshly distilled thioacetic acid (17 mL, 235 mmol, 1.2 eq) and AIBN (328 mg, 1.96 mmol, 0.01 eq) were added to the reaction mixture which then was heated to 60°C with a preheated oil bath for 2 h. After full conversion according to GC-MS, the reaction was cooled to room temperature and the reflux condenser was replaced with a short distillation bridge. Compound **2** (41.1 g, 179 mmol, 91%) was obtained after distillation (137-157 °C, 4-7 x 10^{-1} mbar) as light yellow liquid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.90 – 2.85 (m, 2H), 2.36 (t, *J*=7.0 Hz, 2H), 2.28 (s, 3H), 1.69 – 1.62 (m, 2H), 0.92 – 0.86 (m, 2H), 0.73 – 0.67 (m, 2H), 0.05 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 196.3, 120.3, 31.0, 25.6, 21.3, 21.0, 16.5, 15.2, -3.5.

DEPT-135 (126 MHz, CD_2Cl_2): δ = 31.0, 25.6, 21.3, 21.0, 16.5, 15.2, -3.5.

HRMS (ESI, MeOH): *m/z* calcd for $C_{10}H_{19}NNaOSSi$ $[M+Na]^+$ 252.0849; found: 252.0850.

2-(3-Cyanopropyldimethylsilyl)ethan thiol (3): In an argon-flushed and dried one-neck round-bottom flask a suspension of K_2CO_3 (27.2 g, 197 mmol, 1.1 eq) in MeOH (170 mL) and H_2O (80 mL) was degassed with argon for 30 minutes. **2** (41.0 g, 179 mmol, 1.0 eq) in Et_2O (80 mL) was added and the reaction mixture was stirred for 2 h. After full conversion according to GC-MS, the reaction mixture was carefully quenched with citric acid (38.2 g, 197 mmol, 1.1 eq.) in small portions. TBME (250 mL) was added and the reaction mixture was transferred into a separating funnel. The separated organic layer was washed with aq. citric acid solution (1%, 2 x 150 mL), dried over Na_2SO_4 and concentrated to a yellow oil. Compound **3** (25.1 g, 134 mmol, 75%) was obtained as colorless liquid after two consecutive fractional distillations (88-93 °C, 8.8 x 10^{-3} mbar).

Density (24 °C):0.932 g/mL

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.64 – 2.55 (m, 2H), 2.35 (t, *J*=7.0 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.55 (t, *J*=6.9 Hz, 1H), 1.00 – 0.94 (m, 2H), 0.71 – 0.65 (m, 2H), 0.03 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 120.3, 22.0, 21.3, 21.1, 21.0, 15.3, -3.5.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 22.0, 21.3, 21.1, 21.0, 15.3, -3.5.

HRMS (ESI, MeOH): *m/z* calcd for $C_8H_{17}NNaSSi$ $[M+Na]^+$ 210.0743; found: 210.0743.

General protocol 1 for the protection of free thiols in a radical reaction:

A microwave tube was charged with thiol (500 mg, 1.00 eq.), **1** (1.2 eq. for liquid starting material or 2.4 eq for solid starting material) and di-tert-butyl peroxide (0.15 eq.). The mixture was purged with argon. The tube was sealed and stirred at 100 °C. After full conversion according to GC-MS, the reaction was cooled to room temperature and the reaction mixture was diluted with EtOAc (50 mL) and washed with aqueous NaOH solution (1M, 50 mL). The aqueous layer was extracted with EtOAc (50 mL) again. The combined organic layers were washed with brine (50 mL) and dried over Na_2SO_4. The mixture was concentrated under reduced pressure and subjected to column chromatography.

General protocol 2 for the palladium-catalyzed carbon−sulfur bond formation:

To a dry and argon-flushed Schlenktube (25 mL) bromide (500 mg, 1.0 eq.), *i*Pr_2NEt (2.0 eq) and dioxane (6.0 mL) were added and degassed by bubbling argon through the reaction mixture for 10 minutes. **3** (1.2 eq.) was added and degassed for another 5 minutes. $(Ph_3P)_2PdCl_2$ (2.5 mol%) and Xantphos (5.0 mol%) were added together and the reaction mixture was stirred at 110 °C. After full conversion according to GC-MS, the reaction was cooled to room temperature and the reaction mixture was diluted with EtOAc (50 mL) and washed with H_2O (50 mL) and brine (50 mL) and dried over Na_2SO_4. The mixture was concentrated under reduced pressure and subjected to column chromatography.

4-(Dimethyl(2-(phenylthio)ethyl)silyl)butanenitrile (6):

Protocol1: (500 mg scale) Compound **6** (1.10 g, 4.18 mmol, 93%) was isolated as light yellow liquid, CC (100 g SiO_2, cyclohexane: ethyl acetate (Cy:EtOAc) 99:1 -> 90:10).

(5.00 g scale) Compound **6** (11.9 g, 45.2 mmol, quant.) was isolated as light yellow liquid. CC (340 g SiO_2, Cy:EtOAc 99:1 -> 91:9)

Protocol2: Compound **6** (829 mg, 3.15 mmol, quant) was isolated as light yellow liquid, CC (100 g SiO_2, Cy:EtOAc 98:2 -> 82:18).

R_f = 0.17 (Cy:EtOAc 20:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.32 – 7.27 (m, 4H), 7.20 – 7.15 (m, 1H), 3.00 – 2.94 (m, 2H), 2.34 (t, *J*=7.0 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.00 – 0.93 (m, 2H), 0.73 – 0.67 (m, 2H), 0.06 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 137.7, 129.4, 129.3, 126.2, 120.3, 29.7, 21.3, 21.1, 15.7, 15.2, -3.5.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 129.4, 129.3, 126.2, 29.7, 21.3, 21.1, 15.7, 15.2, -3.5.

HRMS (ESI, MeOH): *m/z* calcd for $C_{14}H_{21}NNaSSi$ $[M+Na]^+$ 286.1056; found: 286.1060.

4-(Dimethyl(2-(o-tolylthio)ethyl)silyl)butanenitrile (7):

Protocol1: Compound **7** (891 mg, 3.21 mmol, 82%) was isolated as light yellow liquid, CC (340 g SiO_2, Cy:EtOAc 99:1 -> 92:8).

Protocol2: $(Ph_3P)_2PdCl_2$ (2.5 mol%) and Xantphos (5.0 mol%) were added 4 times over a reaction time of 48 h. Compound **7** (525 mg, 1.89 mmol, 65%) was isolated as light yellow liquid, CC (100 g SiO_2, Cy:EtOAc 99:1 -> 90:10).

R_f = 0.18 (Cy:EtOAc 20:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.26 – 7.22 (m, 1H), 7.16 (m, 2H), 7.10 – 7.05 (m, 1H), 3.03 – 2.87 (m, 2H), 2.40 – 2.30 (m, 5H), 1.70 – 1.59 (m, 2H), 1.03 – 0.94 (m, 2H), 0.76 – 0.66 (m, 2H), 0.07 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 137.7, 137.0, 130.5, 128.0, 126.9, 125.9, 120.3, 28.9, 21.3, 21.1, 20.6, 15.5, 15.3, -3.4.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 130.5, 127.9, 126.9, 125.9, 28.9, 21.3, 21.1, 20.6, 15.5, 15.3, -3.4.

HRMS (ESI, MeOH): *m/z* calcd for $C_{15}H_{23}NNaSSi$ $[M+Na]^+$ 300.1213; found: 300.1209.

4-(Dimethyl(2-(m-tolylthio)ethyl)silyl)butanenitrile (8):

Protocol1: Compound **8** (938 mg, 3.38 mmol, 84%) was isolated as light yellow liquid, CC (340 g SiO_2, Cy:EtOAc 100:0 -> 92:8).

R_f = 0.17 (Cy:EtOAc 20:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.18 (t, *J*=7.6 Hz, 1H), 7.13 (m, 1H), 7.10 (m, 1H), 6.99 (m, 1H), 3.00 – 2.94 (m, 2H), 2.37 – 2.31 (m, 5H), 1.70 – 1.59 (m, 2H), 0.99 – 0.92 (m, 2H), 0.74 – 0.66 (m, 2H), 0.07 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 139.3, 137.4, 129.9, 129.2, 127.1, 126.2, 120.3, 29.6, 21.6, 21.3, 21.1, 15.8, 15.3, -3.4.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 129.9, 129.2, 127.1, 126.2, 29.6, 21.6, 21.3, 21.1, 15.8, 15.3, -3.4.

HRMS (ESI, MeOH): *m/z* calcd for $C_{15}H_{23}NNaSSi$ $[M+Na]^+$ 300.1213; found: 300.1209.

4-(Dimethyl(2-(p-tolylthio)ethyl)silyl)butanenitrile (9):

Protocol1: Compound **9** (947 mg, 3.41 mmol, 84%) was isolated as light yellow liquid, CC (340 g SiO_2, Cy:EtOAc 99:1 -> 90:10).

R_f = 0.18 (Cy:EtOAc 20:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.24 – 7.19 (m, 2H), 7.14 – 7.09 (m, 2H), 2.97 – 2.88 (m, 2H), 2.38 – 2.29 (m, 5H), 1.68 – 1.58 (m, 2H), 0.98 – 0.89 (m, 2H), 0.73 – 0.64 (m, 2H), 0.05 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 136.5, 133.8, 130.2, 130.1, 120.3, 30.4, 21.3, 21.3, 21.1, 15.9, 15.3, -3.5.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 130.2, 130.1, 30.4, 21.3, 21.3, 21.1, 15.9, 15.3, -3.5.

HRMS (ESI, MeOH): *m/z* calcd for $C_{15}H_{23}NNaSSi$ $[M+Na]^+$ 300.1213; found: 300.1209.

4- ((2- ((2,6- Dimethylphenyl) thio) ethyl) dimethylsilyl) butanenitrile (10):

Protocol1: Compound **10** (701 mg, 2.40 mmol, 69%) was isolated as light yellow liquid, CC (340 g SiO_2, Cy:EtOAc 98:2 -> 88:12).

R_f = 0.23 (Cy:EtOAc 10:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.10 (s, 3H), 2.71 – 2.65 (m, 2H), 2.53 (s, 6H), 2.32 (t, *J*=7.0 Hz, 2H), 1.64 – 1.55 (m, 2H), 0.89 – 0.83 (m, 2H), 0.68 – 0.61 (m, 2H), 0.00 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 143.6, 134.3, 128.6, 128.5, 120.3, 31.2, 22.4, 21.3, 21.1, 16.5, 15.2, -3.5.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 128.6, 128.5, 31.2, 22.4, 21.3, 21.1, 16.5, 15.2, -3.5.

HRMS (ESI, MeOH): *m/z* calcd for $C_{16}H_{25}NNaSSi$ $[M+Na]^+$ 314.1369; found: 314.1369.

4-((2-((4-Bromophenyl)thio)ethyl)dimethylsilyl)butanenitrile (11):

Protocol1: (500 mg scale) Compound **11** (610 mg, 1.78 mmol, 71%) was isolated as light yellow liquid, CC (100 g SiO_2, Cy:EtOAc 98:2 -> 81:19).

(3.00 g scale) Compound **11** (4.39 g, 12.8 mmol, 85%) was isolated as light yellow liquid, CC (680 g SiO_2, Cy:EtOAc 98:2 -> 82:18).

R_f = 0.29 (Cy:EtOAc 10:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.45 – 7.37 (m, 1H), 7.20 – 7.16 (m, 1H), 3.00 – 2.90 (m, 1H), 2.35 (t, *J*=6.9, 1H), 1.68 – 1.59 (m, 1H), 0.98 – 0.90 (m, 1H), 0.73 – 0.66 (m, 1H), 0.06 (s, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 137.1, 132.4, 130.9, 120.3, 119.8, 29.9, 21.3, 21.1, 15.7, 15.2, -3.5.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 132.4, 130.9, 29.9, 21.3, 21.1, 15.7, 15.2, -3.5.

HRMS (ESI, MeOH): *m/z* calcd for $C_{14}H_{20}BrNNaSSi$ $[M+Na]^+$ 364.0161; found: 364.0158.

4- ((2- ((4- (Tert- butyl) phenyl) thio) ethyl) dimethylsilyl) butanenitrile (12):

Protocol1: Compound **12** (723 mg, 2.26 mmol, 78%) was isolated as colorless liquid, CC (50 g SiO_2, Cy:EtOAc 98:2 -> 82:18).

R_f = 0.29 (Cy:EtOAc 10:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.36 – 7.29 (m, 2H), 7.28 – 7.21 (m, 2H), 2.97 – 2.92 (m, 2H), 2.34 (t, *J*=7.0 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.30 (s, 9H), 0.98 – 0.93 (m, 2H), 0.72 – 0.67 (m, 2H), 0.06 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 149.7, 134.0, 129.5, 126.5, 120.3, 34.9, 31.6, 30.1, 21.3, 21.1, 15.9, 15.3, -3.4.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 129.5, 126.5, 31.6, 30.1, 21.3, 21.1, 15.9, 15.3, -3.4.

HRMS (ESI, MeOH): *m/z* calcd for $C_{18}H_{29}NNaSSi$ $[M+Na]^+$ 342.1682; found: 342.1680.

4-((2-((4-Aminophenyl)thio)ethyl)dimethylsilyl)butanenitrile (13):

Protocol1: Reaction temperature was 150 °C. Compound **13** (419 mg, 1.51 mmol, 42%) was isolated as yellow liquid, CC (340 g SiO_2, Cy:EtOAc 90:10 ->0:100).

Protocol2: $(Ph_3P)_2PdCl_2$ (2.5 mol%) and Xantphos (5.0 mol%) were added 4 times over a reaction time of 48 h. Compound **13** (586 mg, 2.10 mmol, 72%) was isolated as yellow liquid, CC (100 g SiO_2, Cy:EtOAc 90:10 ->0:100).

R_f = 0.21 (Cy:EtOAc 1:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.22 – 7.17 (m, 2H), 6.64 – 6.60 (m, 2H), 3.77 (s, 2H), 2.84 – 2.77 (m, 2H), 2.32 (t, *J*=7.0 Hz, 2H), 1.65 – 1.54 (m, 2H), 0.93 – 0.84 (m, 2H), 0.69 – 0.61 (m, 2H), 0.01 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 146.8, 134.3, 123.9, 120.3, 115.8, 32.5, 21.3, 21.1, 16.1, 15.2, -3.5.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 134.3, 115.8, 32.5, 21.3, 21.1, 16.1, 15.2, -3.5.

HRMS (ESI, MeOH): *m/z* calcd for $C_{14}H_{23}N_2SSi$ $[M+H]^+$ 279.1346; found: 279.1343

4-(Dimethyl(2-((4-nitrophenyl)thio)ethyl)silyl)butanenitrile (14):

Protocol1: Compound **14** (784 mg, 2.54 mmol, 82%) was isolated as yellow liquid, CC (340 g SiO_2, Cy:EtOAc 98:2 ->82:18).

Protocol2: Compound **14** (731 mg, 2.371 mmol, 96%) was isolated as yellow liquid, CC (100 g SiO_2, Cy:EtOAc 98:2 ->82:18).

R_f = 0.17 (Cy:EtOAc 10:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 8.13 – 8.09 (m, 2H), 7.34 – 7.30 (m, 2H), 3.11 – 3.04 (m, 2H), 2.37 (t, *J*=6.9 Hz, 2H), 1.71 – 1.62 (m, 2H), 1.06 – 0.99 (m, 2H), 0.78 – 0.71 (m, 2H), 0.10 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 148.9, 145.4, 126.6, 124.4, 120.2, 28.3, 21.3, 21.0, 15.1, 15.0, -3.5.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 126.6, 124.4, 28.3, 21.3, 21.0, 15.1, 15.03, -3.5.

HRMS (ESI, MeOH): *m/z* calcd for $C_{14}H_{20}N_2NaO_2SSi$ $[M+Na]^+$ 331.0907; found: 331.0907

4-((2-((4-Fluorophenyl)thio)ethyl)dimethylsilyl)butanenitrile (15):

Protocol1: Compound **15** (999 mg, 3.55 mmol, 93%) was isolated as light yellow liquid, CC (340 g SiO_2, Cy:EtOAc 98:2 ->83:17).

Protocol2: Compound **15** (796 mg, 2.83 mmol, quant.) was isolated as light yellow liquid, CC (100 g SiO_2, Cy:EtOAc 98:2 ->81:19).

R_f = 0.18 (Cy:EtOAc 10:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.35 – 7.30 (m, 2H), 7.04 – 6.99 (m, 2H), 2.95 – 2.88 (m, 2H), 2.34 (t, *J*=6.9 Hz, 2H), 1.66 – 1.58 (m, 2H), 0.95 – 0.89 (m, 2H), 0.71 – 0.65 (m, 2H), 0.04 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 162.2 (d, $J_{C,F}$ = 245.0 Hz), 132.5 (d, $J_{C,F}$ = 7.9 Hz), 120.4, 116.4 (d, $J_{C,F}$ = 21.8 Hz), 31.2, 21.4, 21.2, 16.0, 15.3, -3.4.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 132.5 (d, $J_{C,F}$ = 7.9 Hz), 116.4 (d, $J_{C,F}$ = 21.8 Hz), 31.2, 21.4, 21.2, 16.0, 15.3, -3.4.

HRMS (ESI, MeOH): *m/z* calcd for $C_{14}H_{20}FNNaSSi$ $[M+Na]^+$ 304.0962; found: 304.0960

(4- ((2- ((3-Cyanopropyl) dimethylsilyl) ethyl) thio) phenyl) boronic acid (16):

Protocol1: Compound **16** (388 mg, 1.26 mmol, 43%) was isolated as white solid, CC (100 g SiO_2, Cy:EtOAc 90:10 -> 0:100).

R_f = 0.22 (Cy:EtOAc 1:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 8.14 – 8.10 (m, 2H), 7.40 – 7.35 (m, 2H), 3.11 – 3.05 (m, 2H), 2.37 (t, *J*=7.0 Hz, 2H), 1.71 – 1.62 (m, 2H), 1.07 – 1.01 (m, 2H), 0.78 – 0.71 (m, 2H), 0.11 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 144.3, 136.4, 126.8, 120.3, 28.3, 21.3, 21.1, 15.5, 15.2, -3.4. The resonance of the aryl-carbon atom with the boron substituent was not detectable in the ^{13}C NMR spectrum, probably because of line broadening due to the short relaxation time and the quadrupole moment of ^{11}B.[58]

DEPT-135 (126 MHz, CD_2Cl_2) δ = 136.4, 126.8, 28.3, 21.3, 21.1, 15.5, 15.24, -3.4.

HRMS (ESI, MeOH): *m/z* calcd for $C_{14}H_{22}BNNaO_2SSi$ $[M+Na]^+$ 330.1126; found: 330.1127

4-(Dimethyl(2-(pyridin-4-ylthio)ethyl)silyl)butanenitrile (17):

Protocol1: Compound **17** (321 mg, 1.21 mmol, 60%) was isolated as yellow liquid, CC (340 g SiO_2, Cy 100%).

R_f = 0.07 (Cy 100%)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 8.38 – 8.33 (m, 2H), 7.11 – 7.07 (m, 2H), 3.06 – 2.99 (m, 2H), 2.37 (t, *J*=6.9 Hz, 2H), 1.70 – 1.61 (m, 2H), 1.04 – 0.98 (m, 2H), 0.77 – 0.71 (m, 2H), 0.10 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 150.0, 149.7, 121.1, 120.2, 27.0, 21.3, 21.1, 15.2, 15.0, -3.5.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 149.7, 121.1, 27.0, 21.3, 21.1, 15.2, 15.0, -3.5.

HRMS (ESI, MeOH): *m/z* calcd for $C_{13}H_{21}N_2SSi$ $[M+H]^+$ 265.1189; found: 265.1189

4-(Dimethyl(2-(naphthalen-2-ylthio)ethyl)silyl)butanenitrile (18):

Protocol1: Compound **18** (780 mg, 2.49 mmol, 81%) was isolated as light yellow liquid, CC (340 g SiO_2, Cy:EtOAc 99:1 -> 90:10).

R_f = 0.15 (Cy:EtOAc 20:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.81 (dq, J=7.7 Hz, 0.8 Hz, 1H), 7.77 (dd, J=8.2 Hz, 0.8 Hz, 2H), 7.72 (dd, J=1.9 Hz, 0.8 Hz, 1H), 7.48 (ddd, J=8.1 Hz, 6.7 Hz, 1.4 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.43 – 7.39 (m, 1H), 3.13 – 3.06 (m, 2H), 2.34 (t, J=7.0 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.05 – 0.99 (m, 2H), 0.77 – 0.69 (m, 2H), 0.09 (s, 7H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 135.4, 134.4, 132.1, 128.8, 128.2, 127.6, 127.4, 127.1, 126.6, 126.0, 120.3, 29.5, 21.3, 21.1, 15.7, 15.2, -3.4.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 128.8, 128.2, 127.6, 127.4, 127.1, 126.6, 126.0, 29.5, 21.3, 21.1, 15.7, 15.2, -3.4.

HRMS (ESI, MeOH): *m/z* calcd for $C_{18}H_{23}NNaSSi$ $[M+Na]^+$ 336.1213; found: 336.1210.

4- ((2- ((4- Methoxyphenyl) thio) ethyl) dimethylsilyl) butanenitrile (19):

Protocol1: Compound **19** (878 mg, 2.99 mmol, 84%) was isolated as light yellow liquid, CC (340 g SiO_2, Cy:EtOAc 98:2 ->84:16).

Protocol2: Compound **19** (622 mg, 2.12 mmol, 79%) was isolated as light yellow liquid, CC (100 g SiO_2, Cy:EtOAc 98:2 ->82:18).

R_f = 0.19 (Cy:EtOAc 10:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.34 – 7.29 (m, 2H), 6.87 – 6.83 (m, 2H), 3.78 (s, 3H), 2.90 – 2.83 (m, 2H), 2.33 (t, *J*=7.0 Hz, 2H), 1.65 – 1.56 (m, 2H), 0.94 – 0.85 (m, 2H), 0.71 – 0.63 (m, 2H), 0.03 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 159.4, 133.4, 127.5, 120.3, 115.0, 55.8, 31.9, 21.3, 21.1, 16.1, 15.2, -3.5.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 133.4, 115.0, 55.8, 31.9, 21.3, 21.1, 16.1, 15.2, -3.5.

HRMS (ESI, MeOH): *m/z* calcd for $C_{15}H_{23}NNaOSSi$ $[M+Na]^+$ 316.1162; found: 316.1163.

4- (Dimethyl (2- ((4-(trifluoromethyl) phenyl) thio) ethyl) silyl) butanenitrile (20):

Protocol1: Compound **20** (836 mg, 2.52 mmol, 93%) was isolated as light yellow liquid, CC (100 g SiO_2, Cy:EtOAc 98:2 -> 82:18).

R_f = 0.21 (Cy:EtOAc 10:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.54 – 7.51 (m, 2H), 7.37 – 7.34 (m, 2H), 3.07 – 3.00 (m, 2H), 2.36 (t, *J*=6.9 Hz, 2H), 1.70 – 1.61 (m, 2H), 1.03 – 0.96 (m, 2H), 0.76 – 0.70 (m, 2H), 0.09 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 143.7 (q, $J_{C,F}$ = 1,5 Hz), 127.7, 127.4 (q, $J_{C,F}$ = 32 Hz), 126.1 (q, $J_{C,F}$ = 3.8 Hz), 125.0 (q, $J_{C,F}$ = 271 Hz), 120.3, 28.7, 21.3, 21.1, 15.4, 15.2, -3.5.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 127.7, 126.1 (q, $J_{C,F}$ = 3.8 Hz), 28.7, 21.3, 21.1, 15.4, 15.2, -3.5.

HRMS (ESI, MeOH): *m/z* calcd for $C_{15}H_{20}F_3NNaSSi$ $[M+Na]^+$ 354.0930; found: 354.0934.

4-(Dimethyl(2-(octylthio)ethyl)silyl)butanenitrile (21):

Protocol1: Compound **21** (932 mg, 3.11 mmol, 92%) was isolated as light yellow liquid, CC (400 g SiO_2, Cy:EtOAc 20:1).

R_f = 0.18 (Cy:EtOAc 20:1), $KMnO_4$ dip

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 2.56 – 2.52 (m, 2H), 2.52 – 2.48 (m, 2H), 2.37 – 2.33 (m, 2H), 1.69 – 1.61 (m, 2H), 1.60 – 1.52 (m, 2H), 1.41 – 1.24 (m, 10H), 0.91 – 0.85 (m, 5H), 0.71 – 0.66 (m, 2H), 0.04 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 120.3, 32.4, 32.4, 30.2, 29.8, 29.8, 29.5, 27.8, 23.2, 21.3, 21.2, 16.3, 15.3, 14.4, -3.4.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 32.4, 32.4, 30.2, 29.8, 29.8, 29.5, 27.8, 23.2, 21.3, 21.2, 16.3, 15.3, 14.4, -3.4.

HRMS (ESI, MeOH): *m/z* calcd for $C_{16}H_{33}NNaSSi$ $[M+Na]^+$ 322.1995; found: 322.1990.

Benzenethiol (5) (108-98-5)**:**

To a round- bottom flask equipped with a magnetic stirrer compound **6** (500 mg, 1.90 mmol, 1.0 eq.) and THF (25 mL) were added. TBAF (3.8 mL, 3.80 mmol, 2.0 eq.) was added and the reaction mixture was stirred at room temperature for 4 h. After full conversion according to GC-MS the reaction was quenched with TFA (292 µL, 3.80 mmol, 2.0 eq.). The reaction mixture was diluted with Et_2O (100 mL) and washed with aq. citric acid solution (1%, 100 mL), and water (2 x 100 mL). The organic layer was the washed with a sat. Na_2CO_3 solution (3 x 100 mL). The combined sat. Na_2CO_3 solutions were acidified with conc. HCl and extracted with Et_2O (3 x 100 mL) and the three combined organic layers (not the first) were dried over Na_2SO_4 and concentrated. To remove remaining Et_2O the compound was distilled. Compound **5** (88.1 mg, 800 µmol, 42%) was isolated as light yellow liquid,

R_f = 0.52 (Cy:EtOAc 20:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.30 – 7.27 (m, 2H), 7.26 – 7.22 (m, 2H), 7.18 – 7.14 (m, 1H), 3.54 (s, 1H).

The spectra data of this compound was identical to those reported in the literature.

1,2-Diphenyldisulfane (22) (882-33-7)**:**

To a round- bottom flask equipped with a magnetic stirrer compound **6** (500 mg, 1.90 mmol, 1.0 eq.) and THF (25 mL) were added. TBAF (3.8 mL, 3.80 mmol, 2.0 eq.) was added and the reaction mixture was stirred at room temperature for 4 h. After full conversion according to GC-MS pyridine (170 µL, 2.09 mmol, 1.1 eq.) was added to the reaction, followed by a solution of I_2 (290 mg, 1.14 mmol, 0.60 eq.) in THF (5.0 mL). The reaction mixture was stirred for another 30 min. The mixture was diluted with EtOAc (100 mL) and washed with aq. citric acid solution (1%, 100 mL), sat. $Na_2S_2O_3$ (100 mL) and brine (100 mL), and dried over Na_2SO_4. The mixture was concentrated under reduced pressure and subjected to column chromatography. Compound **22** (196 mg, 898 µmol, 95%) was isolated as light yellow solid, CC (50 g SiO_2, Cy:EtOAc 98:2 ->86:14).

R_f = 0.57 (Cy:EtOAc 10:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.55 – 7.50 (m, 4H), 7.35 – 7.30 (m, 4H), 7.27 – 7.23 (m, 2H).

The spectra data of this compound was identical to those reported in the literature.

S-Phenyl ethanethioate (23) (934-87-2)**:**

To a round- bottom flask equipped with a magnetic stirrer compound **6** (500 mg, 1.90 mmol, 1.0 eq.) and THF (25 mL) were added. TBAF (3.8 mL, 3.80 mmol, 2.0 eq.) was added and the reaction mixture was stirred at room temperature for 4 h. After full conversion according to GC-MS to the reaction acetyl chloride (542 µL, 7.60 mmol, 4.0 eq.) was added and the reaction was stirred for 8 h. The reaction mixture was diluted with EtOAc (100 mL) and washed with water (100 mL) and brine (100 mL), and dried over Na_2SO_4. The mixture was concentrated under reduced pressure and subjected to column chromatography. Compound **23** (240 mg, 1.58 mmol, 83%) was isolated as light yellow liquid, CC (50 g SiO_2, Cy:EtOAc 98:2 ->90:10).

Or: To a round- bottom flask equipped with a magnetic stirrer compound **6** (500 mg, 1.90 mmol, 1.0 eq.) and acetyl chloride (542 µL , 7.6 mmol, 4.0 eq) in DCM (25 mL) were added. $AgBF_4$ (740 mg, 3.80 mmol, 2.0 eq.) was added as well and stirred at room temperature for 12 h. The reaction mixture was diluted with EtOAc (100 mL) and washed with water (100 mL) and brine (100 mL), dried over Na_2SO_4. The mixture was concentrated under reduced pressure and subjected to column chromatography. Compound **23** (256 mg, 1.68 mmol, 89%) was isolated as light yellow liquid, CC (50 g SiO_2, Cy:EtOAc 98:2 ->90:10).

R_f = 0.41 (Cy:EtOAc 10:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.43 (s, 5H), 2.41 (s, 3H).

The spectra data of this compound was identical to those reported in the literature.

4-Bromobenzenethiol (24) (106-53-6)**:**

To a round- bottom flask equipped with a magnetic stirrer compound **11** (500 mg, 1.46 mmol, 1.0 eq.) and THF (25 mL) were added. TBAF (7.3 mL, 7.30 mmol, 5.0 eq.) was added and the reaction mixture was stirred at room temperature for 1 h. After full conversion according to GC-MS the reaction was quenched with TFA (225 µL, 2.92 mmol, 2.0 eq.). The reaction mixture was diluted with EtOAc (100 mL) and washed with aq. citric acid solution (1%, 100 mL), water (100 mL) and brine (100 mL), and dried over Na_2SO_4. The mixture was concentrated under reduced pressure and subjected to column chromatography. Compound **24** (249 mg, 1.32 mmol, 90%), was isolated as light yellow solid, CC (340 g SiO_2, Cy:EtOAc 95:5 ->66:34).

R_f = 0.13 (Cy:EtOAc 4:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = δ 7.39 – 7.34 (m, 2H), 7.19 – 7.14 (m, 2H), 3.56 (s, 1H).

The spectra data of this compound was identical to those reported in the literature.

4- ((2- ([1,1'- Biphenyl] -4-ylthio) ethyl) dimethylsilyl) butanenitrile (25):

To a dry and argon-flushed Schlenktube compound **11** (500 mg, 1.46 mmol, 1.0 eq), phenylboronicacid (275 mg, 2.10 mmol, 1.5 eq) and K_2CO_3 (611 mg, 4.38 mmol, 3.0 eq) were added and placed under vacuum for 5 min. Then dry toluene (10 mL) and H_2O (2.5 mL) were added and the mixture degassed by passing argon through for further 5 min. SPhos Pd G2 (21.0 mg, 29.2 µmol, 0.02 eq) was added and the mixture was heated to

80 °C for 3 h. After full conversion according to GC-MS to the reaction mixture was diluted with CH_2Cl_2 (100 mL) and washed with H_2O (100 mL) and brine (100 mL) and dried over Na_2SO_4. The mixture was concentrated under reduced pressure and subjected to column chromatography. Compound **25** (455 mg, 1.34 mmol, 92%) was isolated as yellow liquid, CC (100 g SiO_2, Cy:EtOAc 98:2 ->82:18).

Or: An oven dried and argon flushed Schlenktube was charged with compound **16** (240 mg, 781 µmol, 1.2 eq), iodobenzene (136 mg, 651 µmol, 1.0 eq) and K_2CO_3 (273 mg, 1.95 mmol, 3.0 eq) and placed under vacuum for 5 min. Then dry Toluene (5 mL) and H_2O (1.25 mL) were added and the mixture degassed by passing argon through for further 5 min. SPhos Pd G2 (9.38 mg, 13.0 µmol, 0.02 eq) was added and the mixture was heated to 80 °C for 3 h. The solution was diluted with CH_2Cl_2 (100 mL) and washed with H_2O (100 mL) and brine (100 mL) and dried over Na_2SO_4. The mixture was concentrated under reduced pressure and subjected to column chromatography. Compound **25** (193 mg, 568 µmol, 87%) was isolated as yellow liquid, CC (50 g SiO_2, Cy:EtOAc 98:2 ->82:18).

R_f = 0.24 (Cy:EtOAc 10:1)

H NMR (500 MHz, CD_2Cl_2) δ = 7.62 – 7.58 (m, 2H), 7.57 – 7.53 (m, 2H), 7.46 – 7.42 (m, 2H), 7.40 – 7.37 (m, 2H), 7.35 (ddt, *J*=8.6 Hz, 7.0 Hz, 1.0 Hz, 1H), 3.06 – 2.99 (m, 2H), 2.35 (t, *J*=6.9 Hz, 2H), 1.70 – 1.60 (m, 2H), 1.05 – 0.98 (m, 2H), 0.77 – 0.68 (m, 2H), 0.08 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 140.3, 138.4, 136.4, 129.0, 128.8, 127.4, 127.3, 126.7, 119.7, 29.2, 20.8, 20.5, 15.2, 14.7, -4.0.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 129.0, 128.8, 127.4, 127.3, 126.7, 29.2, 20.8, 20.5, 15.2, 14.7, -4.0.

HRMS (ESI, MeOH): *m/z* calcd for $C_{20}H_{25}NNaSSi$ $[M+Na]^+$ 362.1369; found: 362.1366.

4- (Dimethyl (2- ((4- (phenylethynyl) phenyl) thio) ethyl) silyl) butanenitrile (26):

An oven dried and argon-flushed Schlenktube was charged with compound **11** (500 mg, 1.46 mmol, 1.0 eq), dry THF (3 mL) and piperidine (1 mL) and the yellow mixture was degassed with argon for 10 min. Then phenylacetylene (245 µL, 2.19 mmol, 1.5 eq.) was added and the reaction mixture was again bubbled with argon for 5 min. Then $(Ph_3P)_2PdCl_2$ (51.2 mg, 73.0 µmol, 0.05 eq.) and CuI (17.0 mg, 87.6 µmol, 0.06 eq.) were added. The exothermic mixture was degassed with argon for an additional 5 min. The yellow suspension was stirred at 80 °C for 3 h. After full conversion according to GC-MS to the reaction mixture was diluted with EtOAc (50 mL) and washed with H_2O (50 mL) and brine (50 mL) and dried over Na_2SO_4. The mixture was concentrated under reduced pressure and subjected to column chromatography. Compound **26** (481 mg, 1.32 mmol, 91%) was isolated as yellow liquid, CC (340 g SiO_2, Cy:EtOAc 98:2 ->83:17).

R_f = 0.21 (Cy:EtOAc 10:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.54 – 7.51 (m, 2H), 7.47 – 7.44 (m, 2H), 7.38 – 7.34 (m, 3H), 7.28 – 7.25 (m, 2H), 3.05 – 2.97 (m, 2H), 2.36 (t, *J*=7.0 Hz, 2H), 1.70 – 1.60 (m, 2H), 1.02 – 0.96 (m, 2H), 0.77 – 0.68 (m, 2H), 0.08 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ = 139.0, 132.4, 132.0, 129.0, 128.9, 128.3, 123.8, 120.5, 120.3, 90.0, 89.6, 29.2, 21.3, 21.1, 15.6, 15.2, -3.5.

DEPT-135 (126 MHz, CD_2Cl_2) δ = 132.4, 132.0, 129.0, 128.9, 128.3, 29.2, 21.3, 21.1, 15.5, 15.2, -3.5.

HRMS (ESI, MeOH): *m/z* calcd for $C_{22}H_{25}NNaSSi$ $[M+Na]^+$ 386.1369; found: 386.1369.

Trimethyl(2-(phenylthio)ethyl)silane (b) (17988-59-9)**:**

A microwave tube was charged with thiophenol (0.46 mL, 4.49 mmol, 1.00 eq.), vinyltrimethylsilane (0.81 mL, 5.39 mmol, 1.2 eq.) and di-tert-butyl peroxide (0.12 mL, 0.673 mmol, 0.15 eq.). The mixture was purged with argon. The tube was sealed and stirred for 1 h at 100 °C. After full conversion according to GC-MS, the reaction mixture was cooled to room temperature, diluted with EtOAc (50 mL) and washed with aqueous NaOH solution (1M, 50 mL). The aqueous layer was extracted with EtOAc (50 mL) again. The combined organic layers were washed with brine (50 mL) and dried over Na_2SO_4. The mixture was concentrated under reduced pressure and subjected to column chromatography.

Compound **b** (888 mg, 4.22 mmol, 94%) was isolated as colorless liquid, CC (100 g SiO_2, Cy:EtOAc 100:0 ->85:15).

R_f = 0.61 (Cy:EtOAc 20:1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.33 – 7.26 (m, 4H), 7.19 – 7.14 (m, 1H), 3.02 – 2.94 (m, 2H), 0.97 – 0.91 (m, 2H), 0.06 (s, 9H).

The spectra data of this compound was identical to those reported in the literature.

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

YES (this text will be updated with links prior to publication)

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Supporting Information

The order of the items in the supporting information file follows the order of their discussion in the main manuscript.

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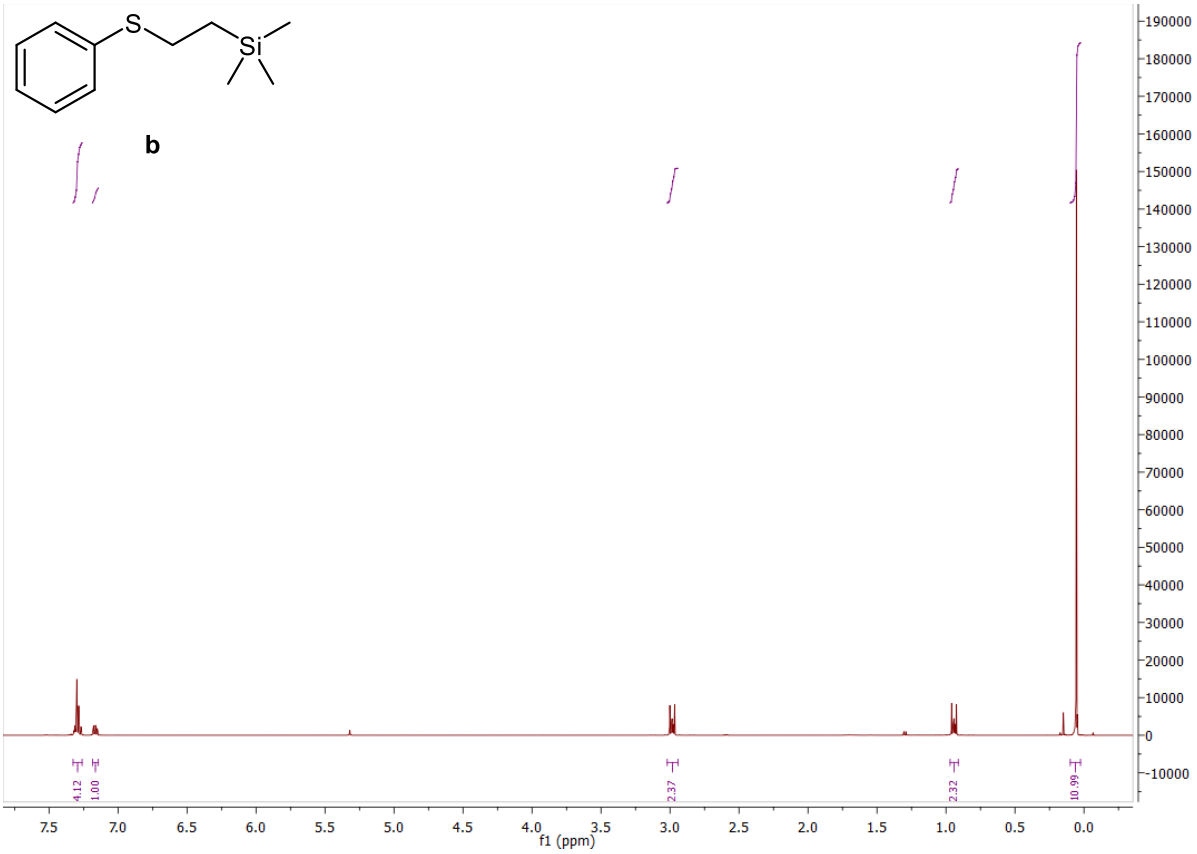
1. Compound **b**



The spectra data of this compound was identical to those reported in the literature. (CAS: 17988-59-9)

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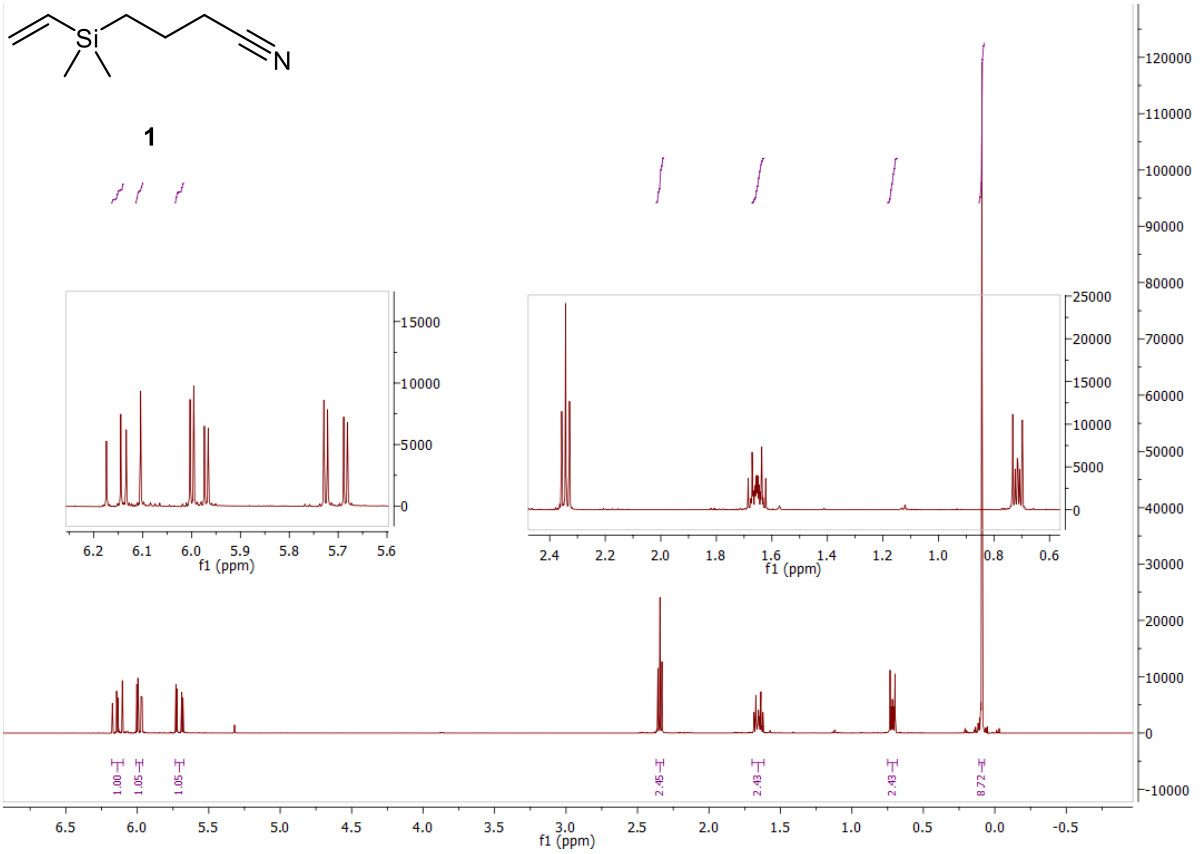

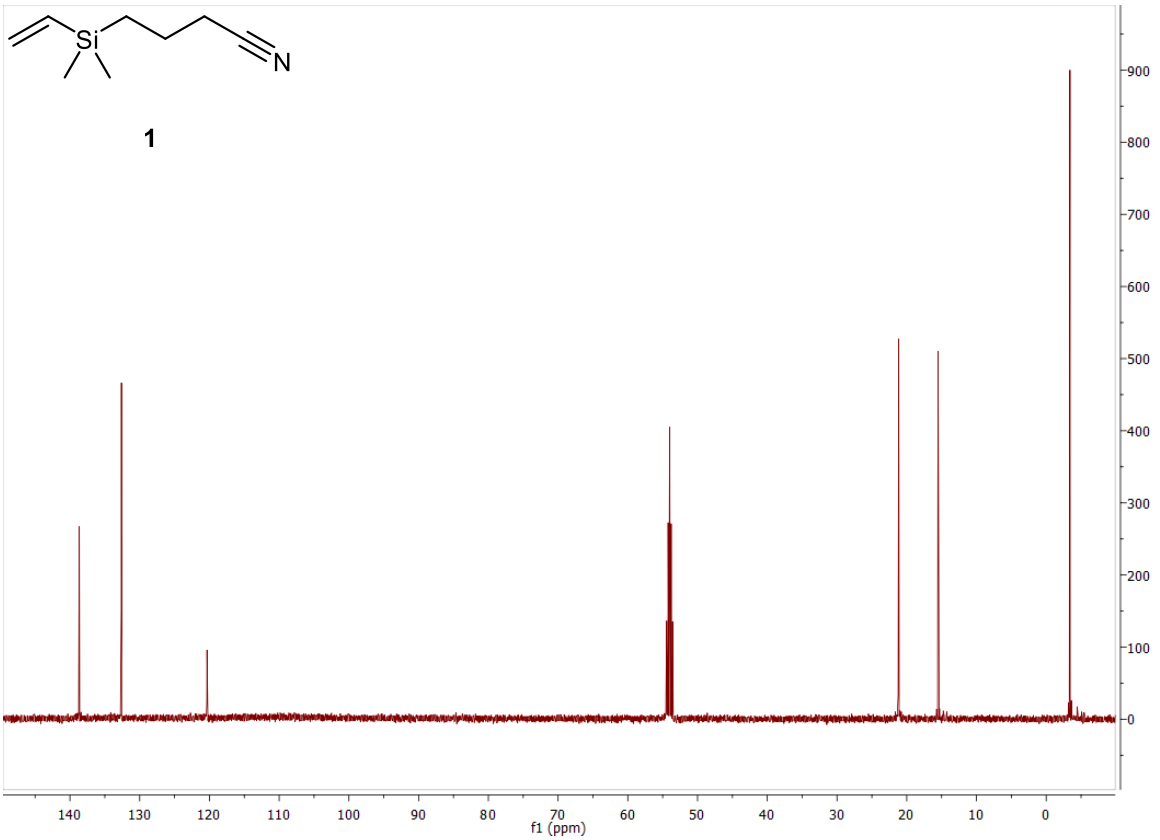

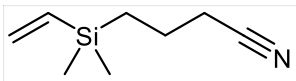

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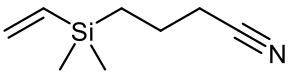

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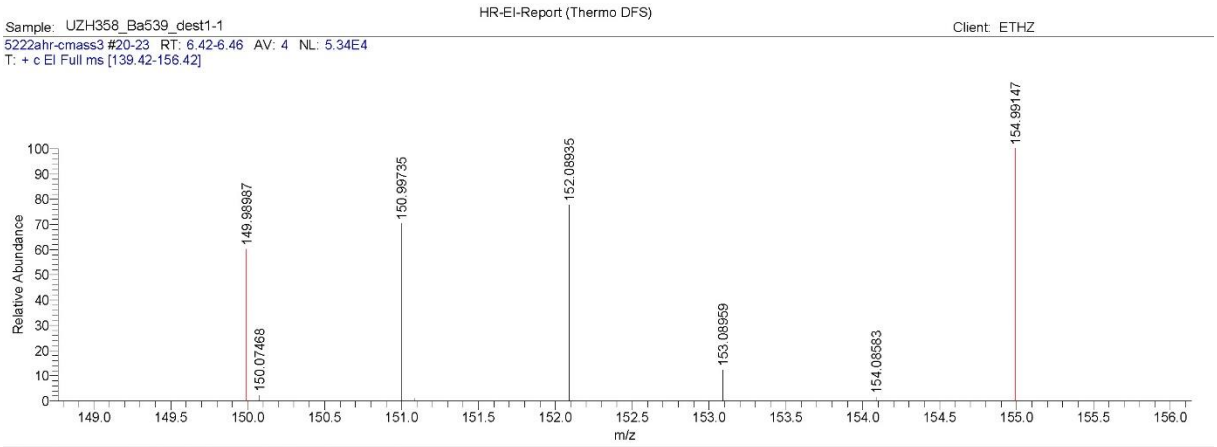

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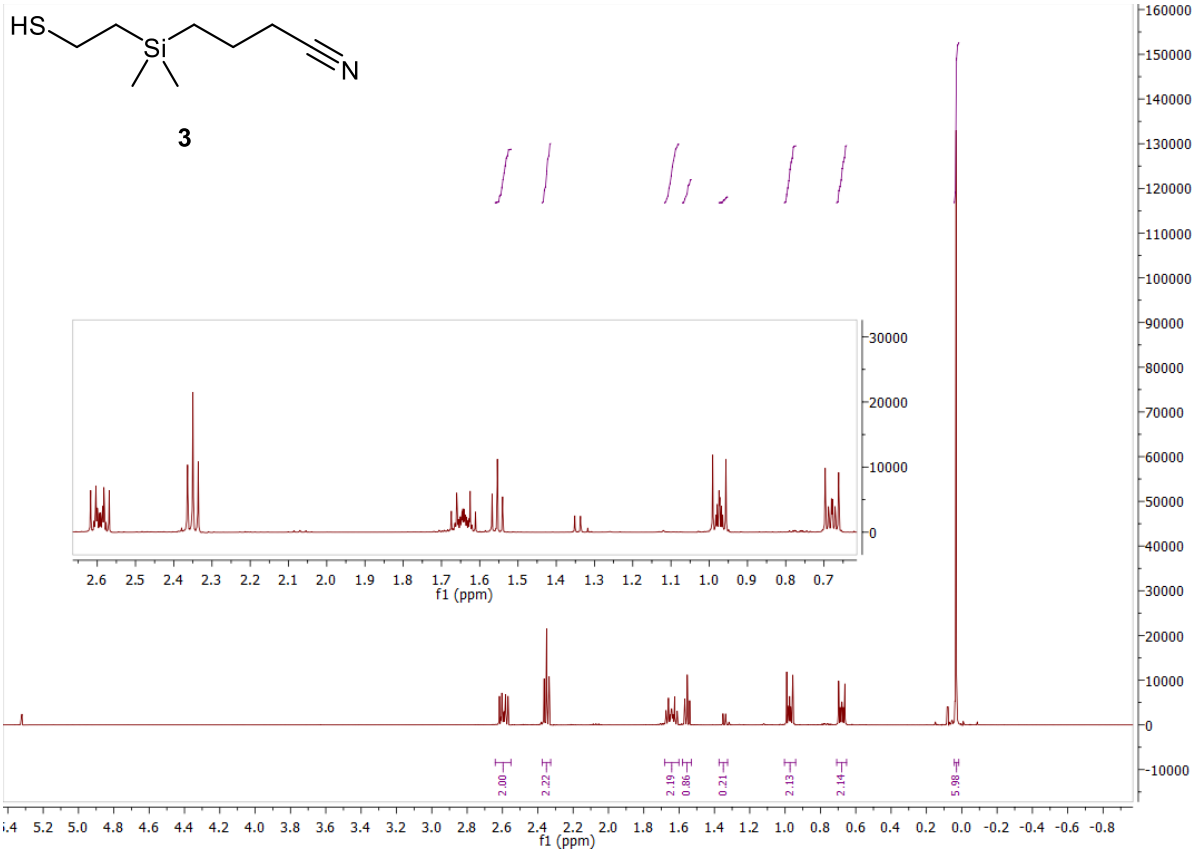
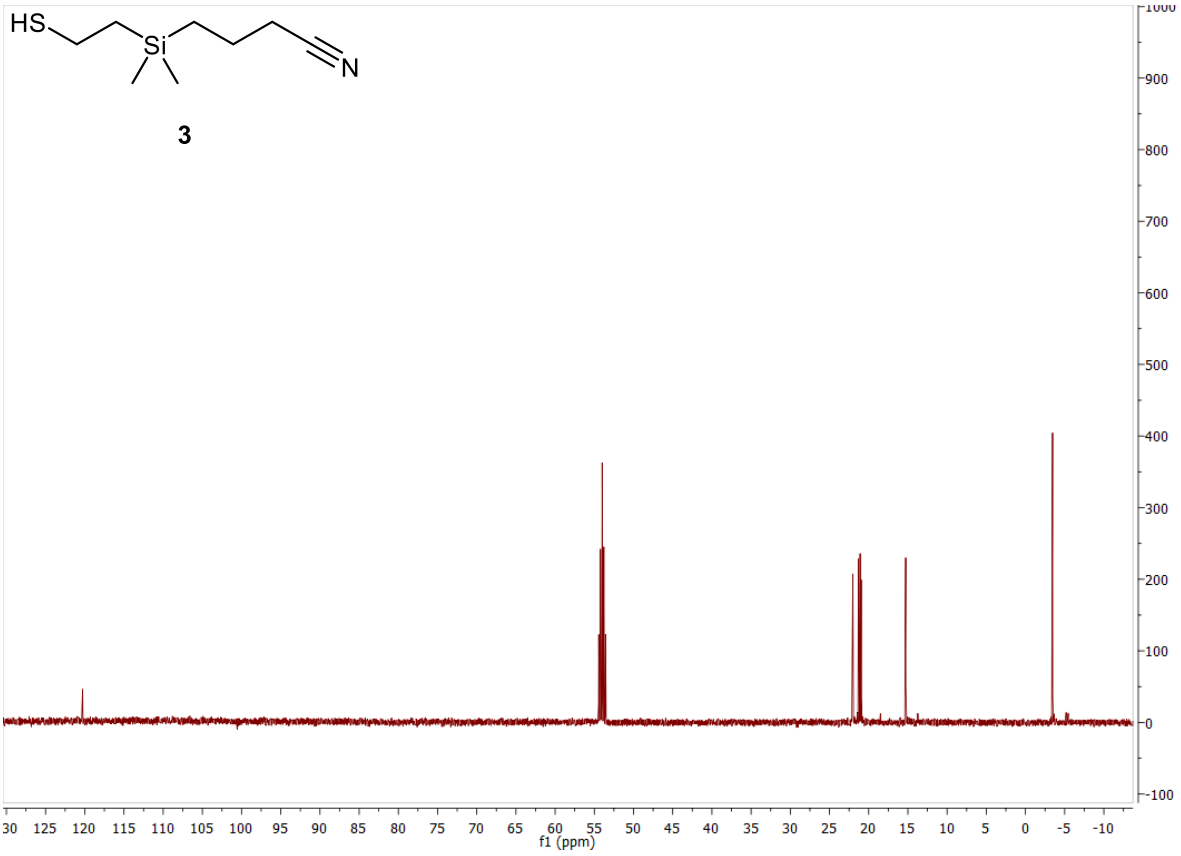
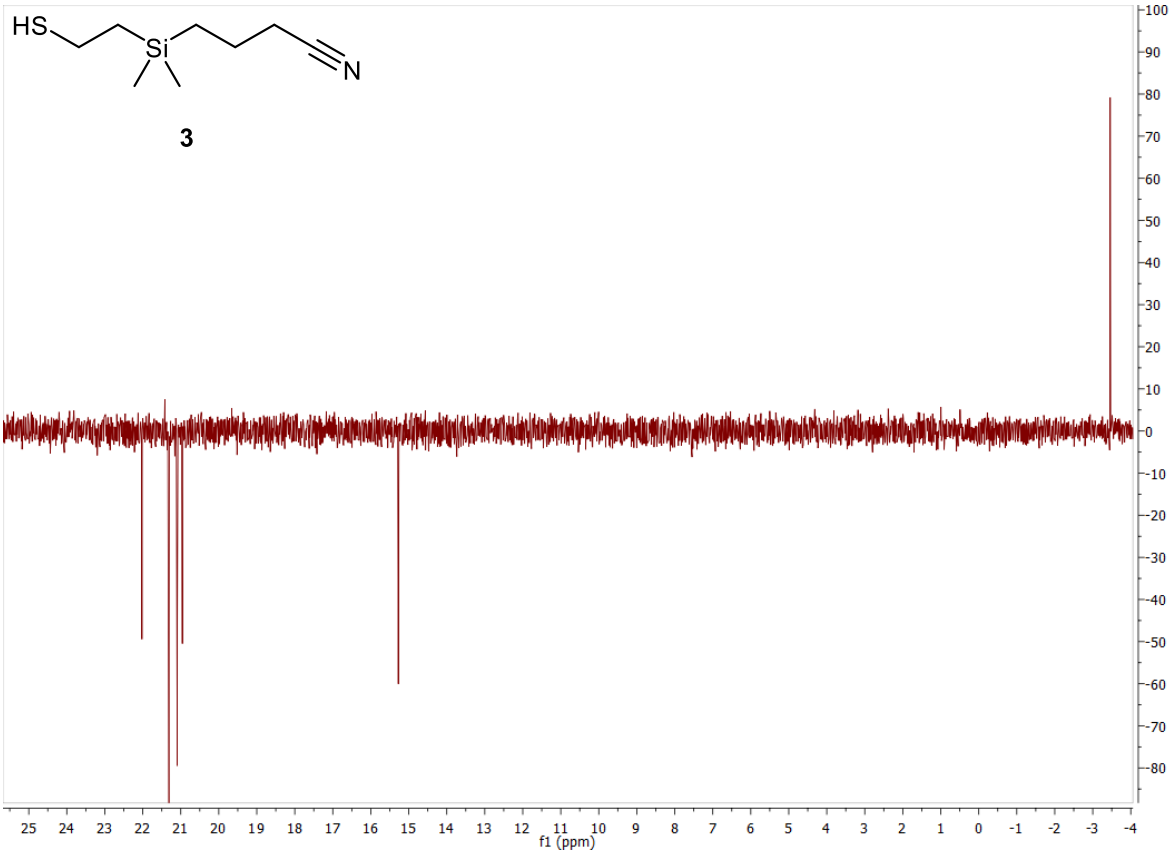
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
152.08935	41470.5	100.00	152.08905	1.97	$C_{10}H_2O_2N_7$
			152.08900	2.27	$C_8H_{14}NSi$

The spectra data of this compound was identical to those reported in the literature. (CAS: 954114-30-8)[1]

3. Compound **3**:

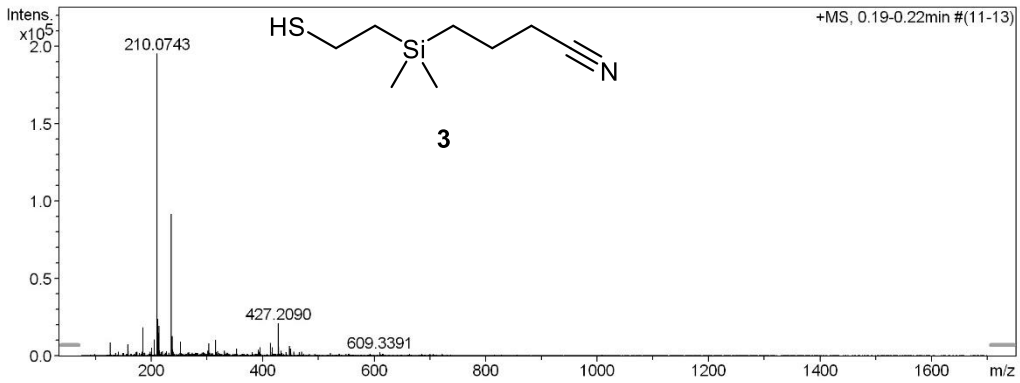




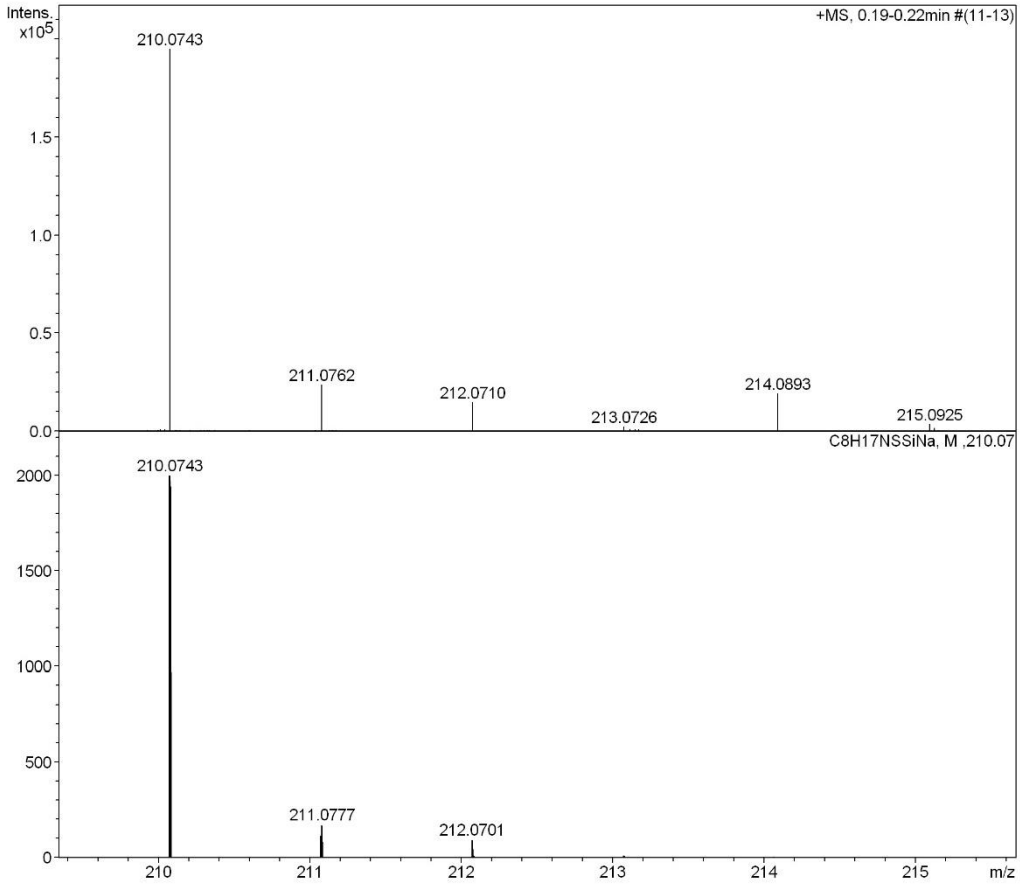

HS
Si
N
3
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba556**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	21 Direct_pos_low.m



3



High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	z
210.0743	1	C 8 H 17 N Na S Si	100.00	210.0743	-0.0	-0.1	14.8	1.5	even	1+

Mass list

#	m/z	I %	I
1	126.0736	4.3	8443
2	136.1122	0.8	1495
3	141.0010	1.3	2533
4	149.0231	0.7	1435
5	150.1283	0.9	1697
6	158.0273	3.7	7160
7	158.9639	1.5	2873
8	173.0784	1.1	2084
9	174.1596	1.4	2655
10	179.0333	0.7	1457
11	183.0782	1.3	2502
12	183.0996	0.7	1341
13	185.1146	9.4	18389
14	186.1179	0.8	1487
15	188.0919	1.0	1934
16	197.1152	0.7	1339
17	198.1852	1.3	2486
18	201.1023	2.6	5041
19	205.0598	5.3	10361
20	205.1192	0.8	1502
21	210.0743	100.0	194936
22	211.0762	12.1	23539
23	212.0710	7.6	14778
24	213.0726	1.2	2312
25	214.0893	9.8	19143
26	215.0925	1.7	3388
27	215.1251	0.8	1526
28	217.1049	1.1	2229
29	220.1666	1.4	2778
30	225.1090	1.0	1923
31	226.9513	1.4	2777
32	231.1171	1.0	1926
33	236.0714	46.9	91421
34	237.0745	6.4	12536
35	238.0674	2.0	3958
36	239.0884	1.3	2528
37	251.1612	0.8	1615
38	252.0845	4.8	9285
39	253.0873	0.8	1500
40	265.1400	0.8	1643
41	265.1766	1.0	1975
42	267.1567	1.1	2087
43	273.1450	0.9	1752
44	273.1673	0.9	1692
45	273.1892	0.8	1490
46	277.2137	0.7	1416
47	279.2291	1.0	1936
48	281.1731	0.8	1517
49	283.1506	0.8	1493
50	291.1931	0.9	1851
51	293.2079	1.0	1855
52	293.2439	1.1	2224
53	294.9383	0.9	1701
54	299.1616	0.7	1406
55	301.1407	1.6	3169
56	301.2114	0.7	1362
57	303.1774	4.1	8014
58	305.2079	1.0	1994
59	309.2039	0.7	1447
60	315.1928	5.2	10228
61	316.1957	1.2	2343
62	317.1713	0.7	1315

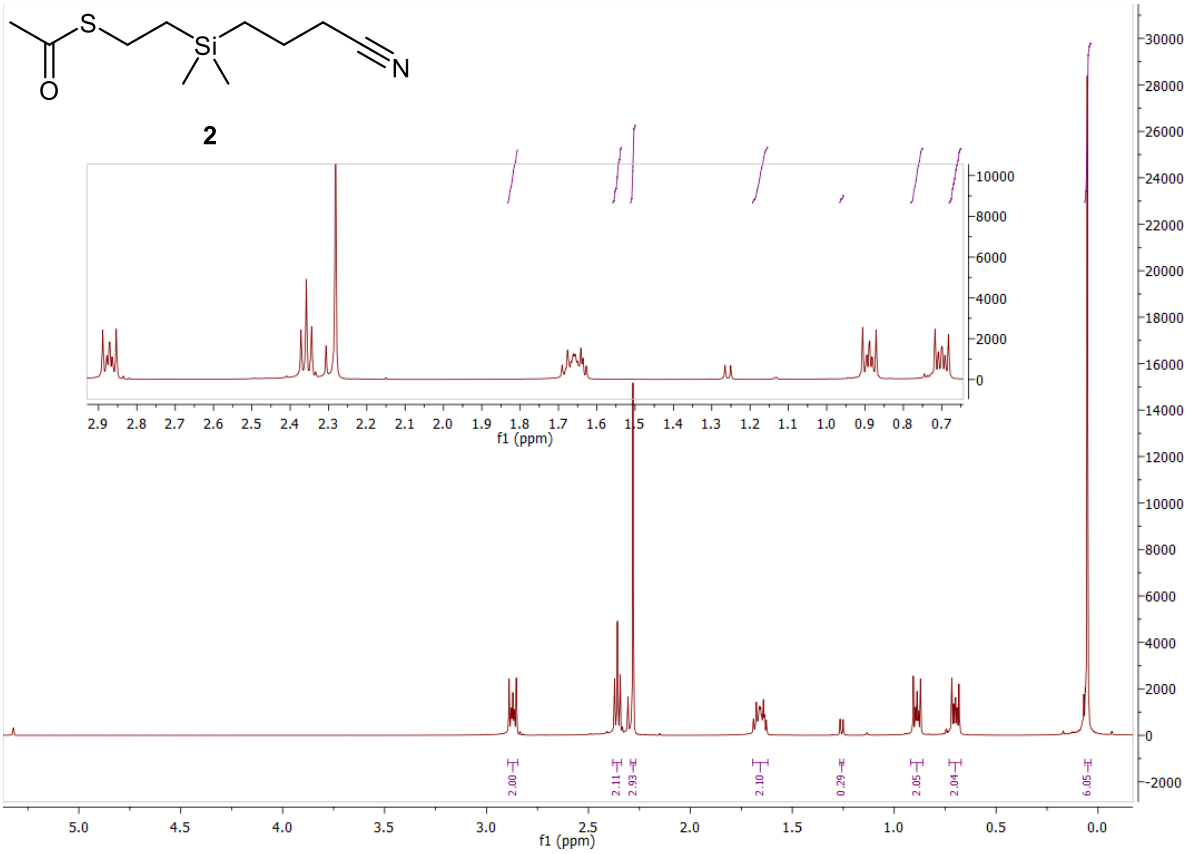
High Resolution Mass Spectrometry Report

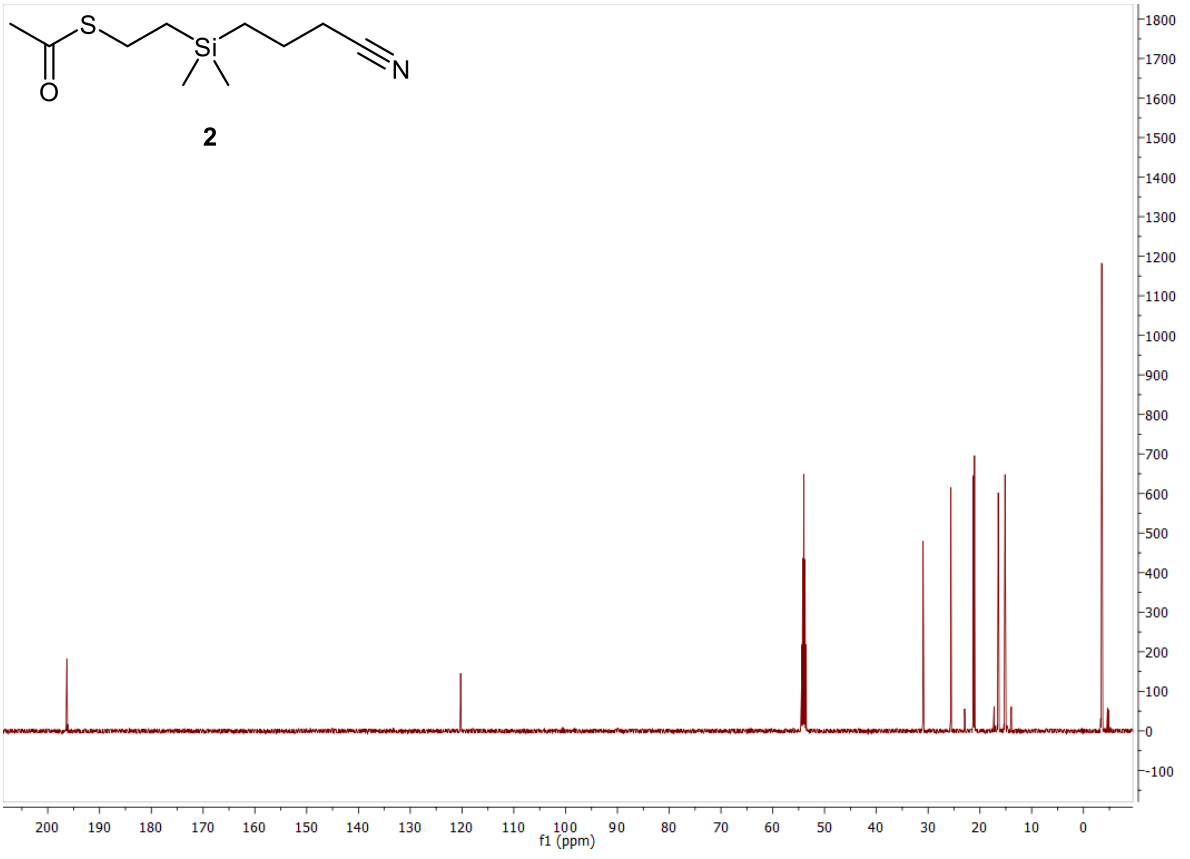
#	m/z	I %	I
63	319.2237	1.5	2857
64	321.2044	0.8	1587
65	331.1873	1.6	3079
66	331.2081	1.0	1922
67	335.1363	1.0	1933
68	335.2193	0.7	1288
69	337.1982	1.0	1883
70	353.2660	2.2	4328
71	381.2975	1.2	2325
72	391.2091	1.9	3638
73	393.2960	1.4	2677
74	395.1434	2.7	5330
75	395.1816	1.2	2410
76	395.3628	1.9	3721
77	396.1455	0.7	1392
78	413.1932	2.2	4244
79	413.2661	4.2	8240
80	414.2686	1.1	2240
81	417.3446	2.7	5341
82	418.3483	0.7	1380
83	423.1574	0.7	1412
84	427.2090	10.7	20910
85	428.2127	2.9	5714
86	429.2148	0.7	1294
87	433.1033	1.6	3182
88	433.3801	0.7	1451
89	441.2965	1.1	2237
90	447.3448	3.2	6181
91	448.3486	0.7	1376
92	449.1536	0.9	1768
93	449.3760	2.3	4480
94	450.3782	0.9	1794
95	455.2394	1.3	2478
96	465.3702	1.1	2082
97	469.3278	1.3	2607
98	521.3821	0.7	1446
99	592.5403	0.7	1347
100	609.3391	1.2	2261

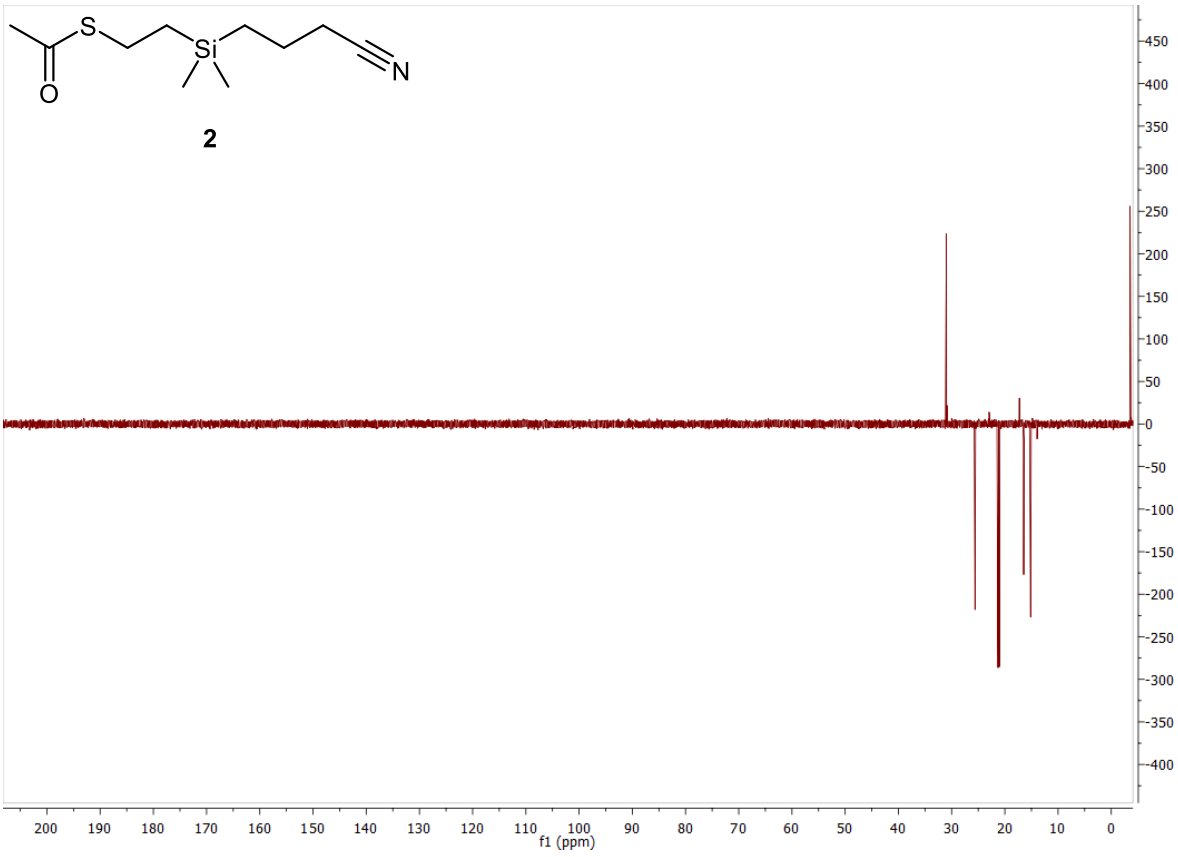
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV

4. Compound **2**:

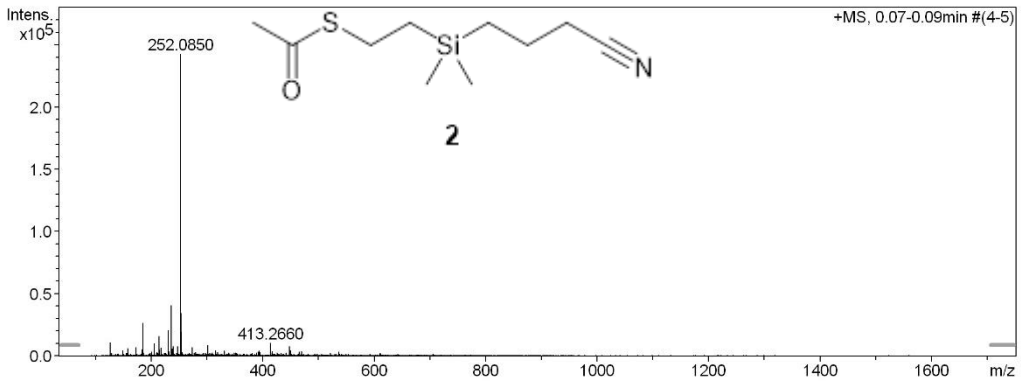




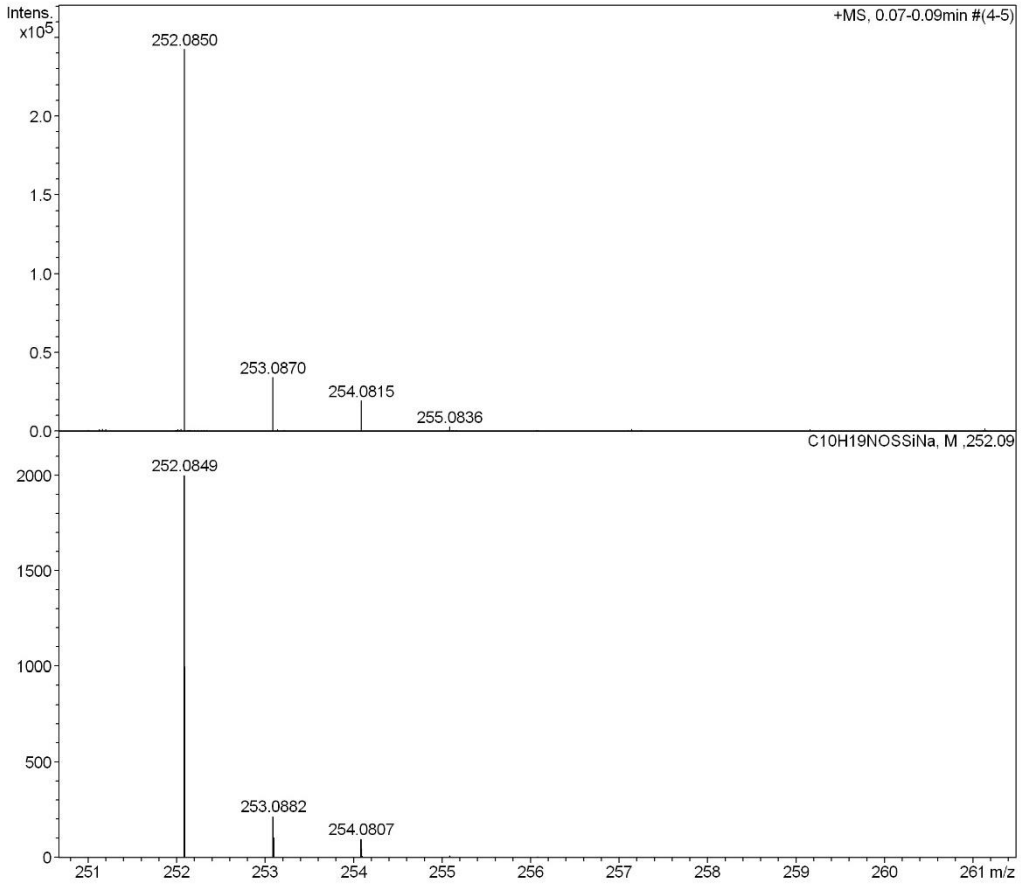

S
Si
N
O
2
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba554**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	21 Direct_pos_low.m



2



High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	z
252.0850	1	C 10 H 19 N Na O S Si	100.00	252.0849	-0.1	-0.3	15.9	2.5	even	1+

Mass list

#	m/z	I %	I
1	126.0735	4.4	10756
2	129.0526	0.7	1805
3	139.0502	0.7	1730
4	141.0001	0.7	1658
5	149.0232	1.8	4282
6	155.0474	0.9	2112
7	157.0834	0.9	2125
8	158.0268	2.5	5937
9	163.1322	0.7	1715
10	173.0781	2.8	6801
11	181.0836	0.7	1686
12	183.0781	2.1	5132
13	183.0994	0.7	1600
14	185.1147	10.8	26265
15	186.1179	1.0	2395
16	195.0993	0.6	1441
17	198.1854	0.8	1917
18	201.1029	1.3	3136
19	205.0598	4.0	9730
20	209.1146	0.8	1871
21	210.0739	1.1	2584
22	211.0938	0.8	1867
23	213.1092	0.7	1680
24	214.0892	6.5	15671
25	215.0911	0.9	2252
26	215.1251	1.9	4622
27	217.1047	2.5	6089
28	223.0939	0.7	1773
29	225.1086	0.8	1984
30	230.1028	8.4	20403
31	231.1050	1.4	3498
32	232.0992	0.9	2271
33	236.0713	16.6	40307
34	237.0748	2.3	5593
35	238.0676	1.0	2360
36	239.0885	3.2	7638
37	239.1250	0.6	1559
38	241.1409	0.7	1765
39	245.0786	0.9	2098
40	247.1290	3.0	7285
41	248.1311	0.7	1587
42	252.0850	100.0	242245
43	253.0870	14.1	34150
44	254.0815	8.0	19350
45	255.0836	1.2	2857
46	261.1284	0.7	1686
47	268.0587	0.8	1838
48	273.1671	2.7	6658
49	277.1776	0.6	1548
50	277.2139	0.8	1980
51	279.1584	0.9	2164
52	279.2292	1.1	2679
53	281.1722	0.6	1550
54	283.2246	0.7	1601
55	293.2450	0.8	1906
56	297.2394	0.8	1898
57	301.1405	3.4	8267
58	305.2445	0.8	2029
59	309.2039	0.9	2173
60	315.1923	1.7	4211
61	319.2235	1.1	2573
62	331.1880	0.7	1797

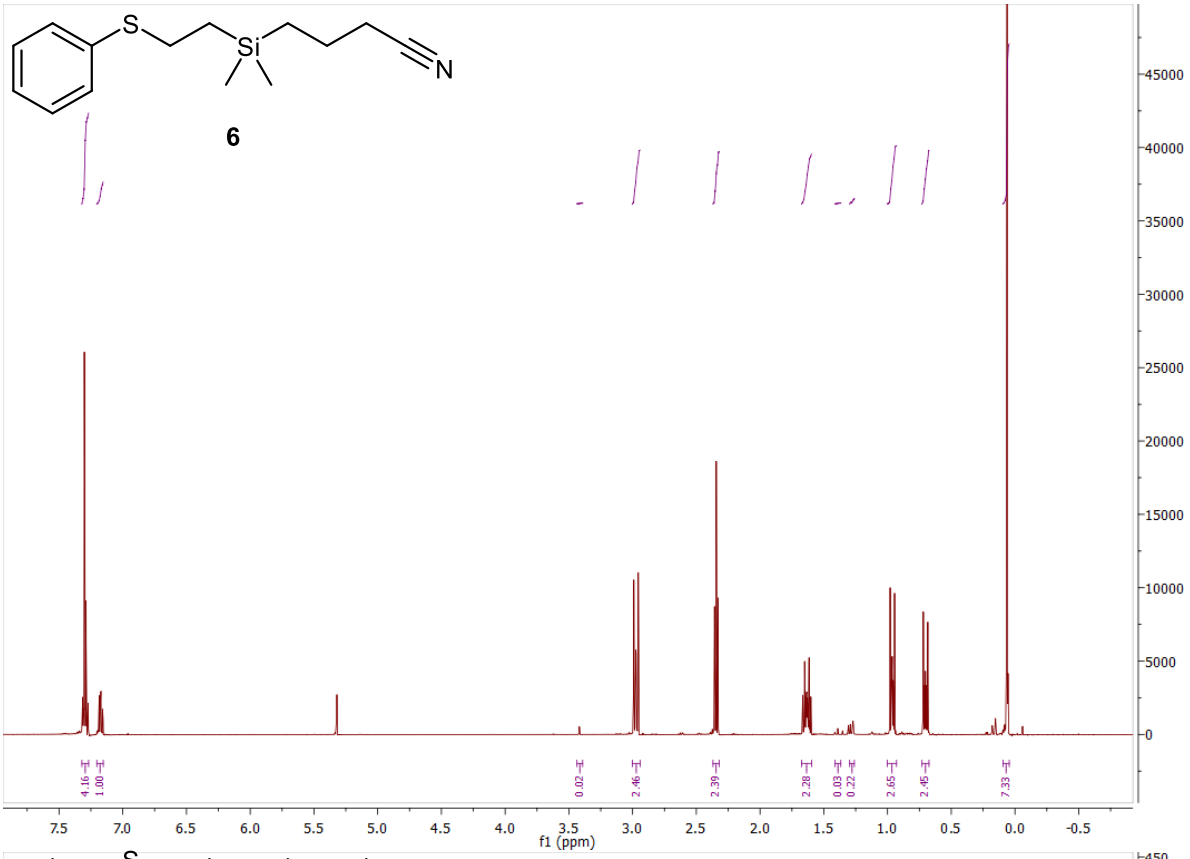
High Resolution Mass Spectrometry Report

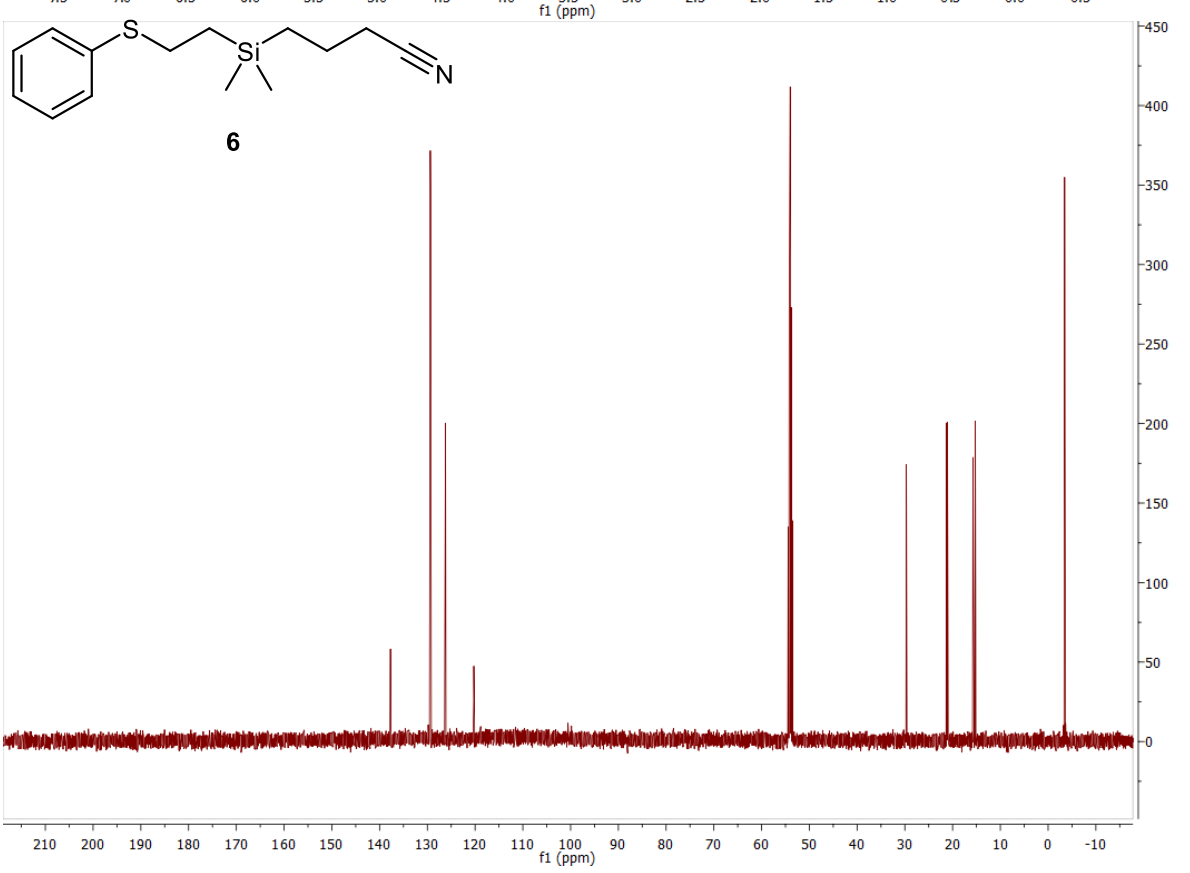
#	m/z	I %	I
63	331.2087	1.6	3839
64	339.1782	0.9	2224
65	345.2395	0.6	1441
66	348.9898	0.9	2219
67	350.9869	1.0	2330
68	353.2663	0.8	2000
69	355.2813	0.7	1659
70	365.2672	0.6	1523
71	367.2088	0.6	1536
72	379.2815	0.6	1421
73	381.2973	0.7	1786
74	389.2512	1.0	2334
75	391.2089	1.3	3044
76	391.2832	1.0	2474
77	393.2975	1.6	3843
78	395.3627	1.1	2575
79	413.2660	4.1	10053
80	414.2698	0.9	2284
81	417.3446	1.5	3543
82	421.3289	0.6	1527
83	425.3627	0.9	2236
84	433.1016	0.8	1843
85	441.2970	1.0	2425
86	447.3447	3.0	7365
87	448.3484	1.0	2481
88	449.3738	1.7	4134
89	463.3742	0.6	1509
90	465.3706	1.3	3174
91	469.3289	1.5	3663
92	481.1809	0.6	1567
93	481.3655	0.7	1658
94	493.3503	0.7	1678
95	497.3581	0.6	1510
96	521.3800	0.8	1967
97	536.1653	1.3	3218
98	537.1675	0.7	1624
99	610.1854	0.8	1989
100	705.5185	0.6	1426

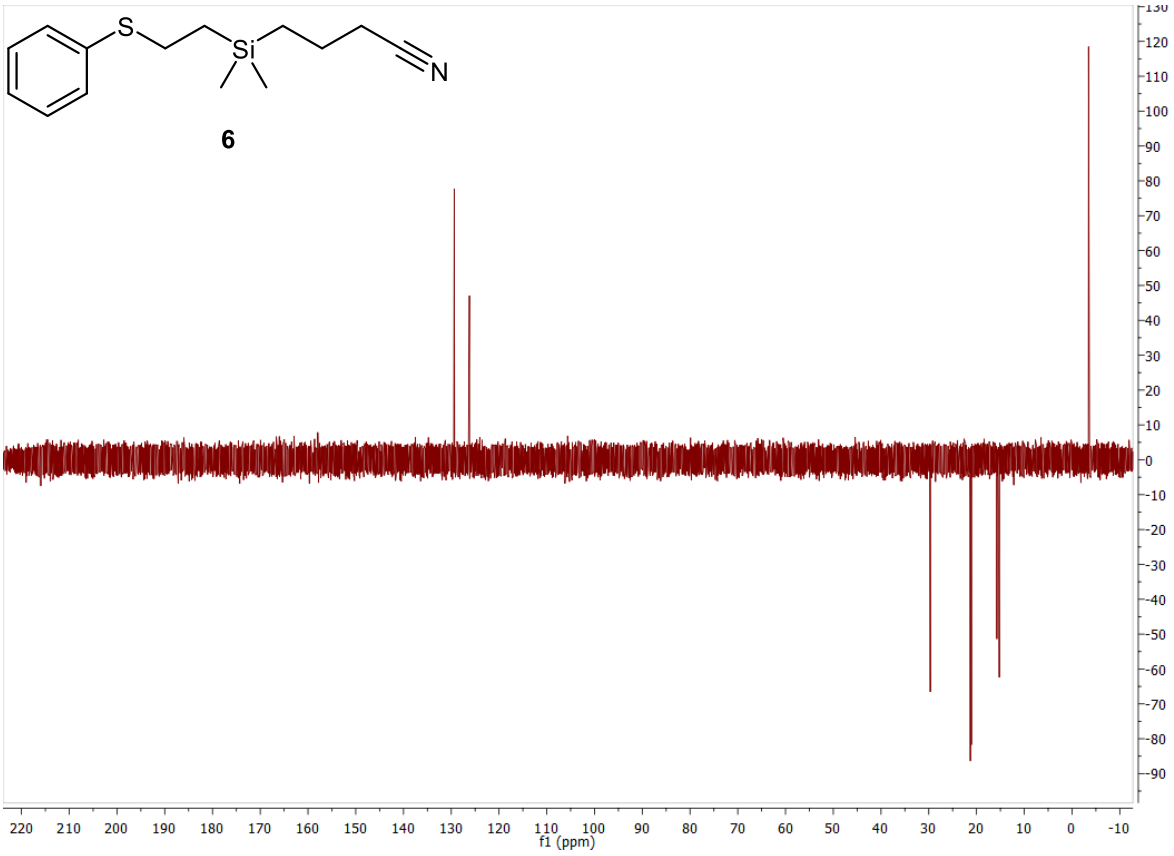
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV

5. Compound **6**:

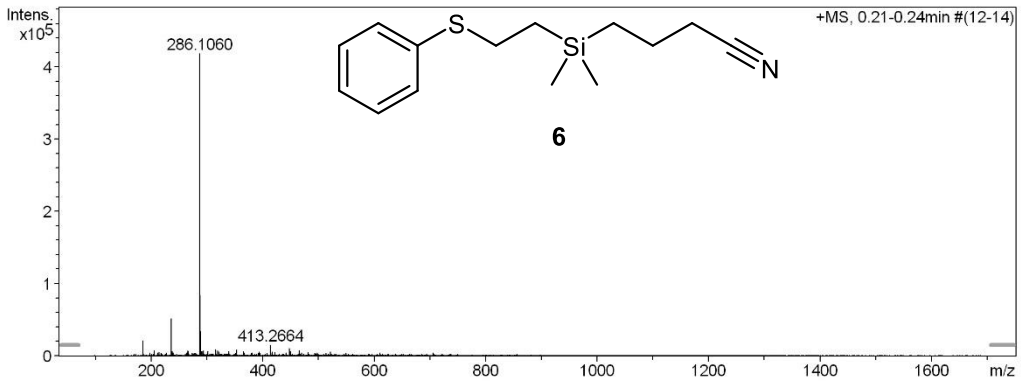

S
Si
N
6
4.16
1.00
0.02
2.46
2.39
2.28
0.03
0.22
2.65
2.45
7.33
f1 (ppm)


S
Si
N
6
f1 (ppm)

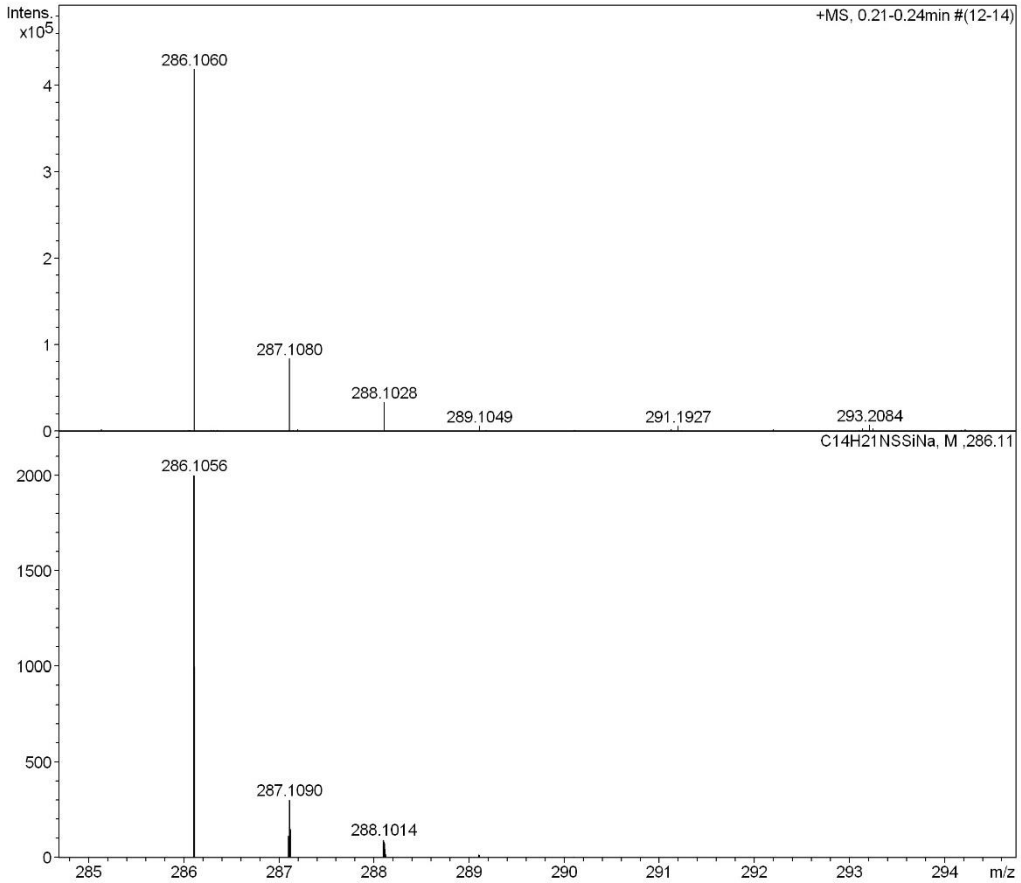

S
Si
N
6
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / / Ba523**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m



6



High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^- Conf	z
286.1060	1	C 14 H 21 N Na S Si	100.00	286.1056	-0.4	-1.4	11.9	5.5	even	1+

Mass list

#	m/z	I %	I
1	169.0471	0.5	2265
2	185.1147	4.9	20664
3	197.0785	1.0	4273
4	205.0597	1.7	7202
5	211.0940	1.0	4185
6	214.0897	1.1	4640
7	217.1049	0.8	3361
8	225.1087	0.6	2520
9	226.9512	1.0	4351
10	236.0715	12.3	51512
11	237.0744	1.5	6111
12	239.0889	0.9	3874
13	261.1295	0.7	2774
14	264.1235	0.9	3869
15	265.1188	1.5	6473
16	265.1395	0.5	2265
17	265.1768	0.5	2244
18	266.1723	1.5	6304
19	273.1681	0.8	3269
20	277.2141	0.8	3332
21	279.2290	0.8	3456
22	286.1060	100.0	417877
23	287.1080	20.0	83634
24	288.1028	8.0	33473
25	289.1049	1.4	5825
26	291.1927	1.4	5869
27	293.1356	0.7	2859
28	293.2084	1.6	6650
29	293.2440	0.6	2685
30	299.1948	0.5	2201
31	301.1409	1.4	5885
32	301.2115	0.8	3181
33	305.2455	0.7	2998
34	307.1876	0.6	2342
35	309.2042	0.6	2574
36	311.1464	0.7	2863
37	315.1927	2.1	8784
38	319.2239	1.6	6545
39	321.2403	1.2	5212
40	325.1619	0.5	2293
41	327.2272	0.5	2223
42	331.1869	0.7	2761
43	331.2081	0.7	2929
44	335.1817	0.6	2520
45	335.2196	0.7	2831
46	339.1774	1.5	6120
47	351.1787	0.5	2205
48	351.2499	0.8	3432
49	353.1931	0.6	2332
50	353.2658	1.9	8083
51	365.1055	1.5	6360
52	365.2677	1.0	4032
53	367.2093	0.9	3969
54	367.2452	0.8	3238
55	379.2821	0.8	3550
56	381.2970	1.0	4277
57	385.2923	0.5	2183
58	391.2086	0.8	3422
59	393.2981	1.3	5521
60	395.2405	0.6	2707
61	395.2767	0.9	3600
62	407.3129	0.9	3614

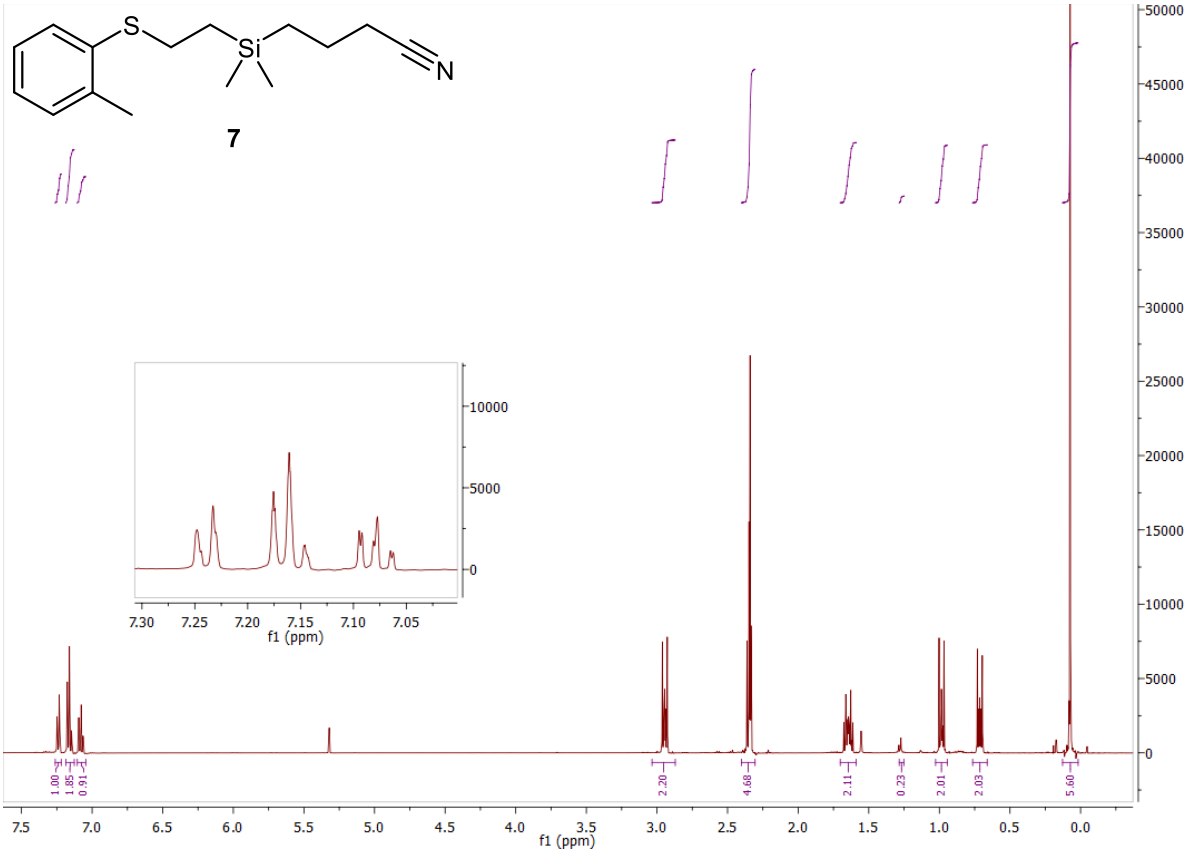
High Resolution Mass Spectrometry Report

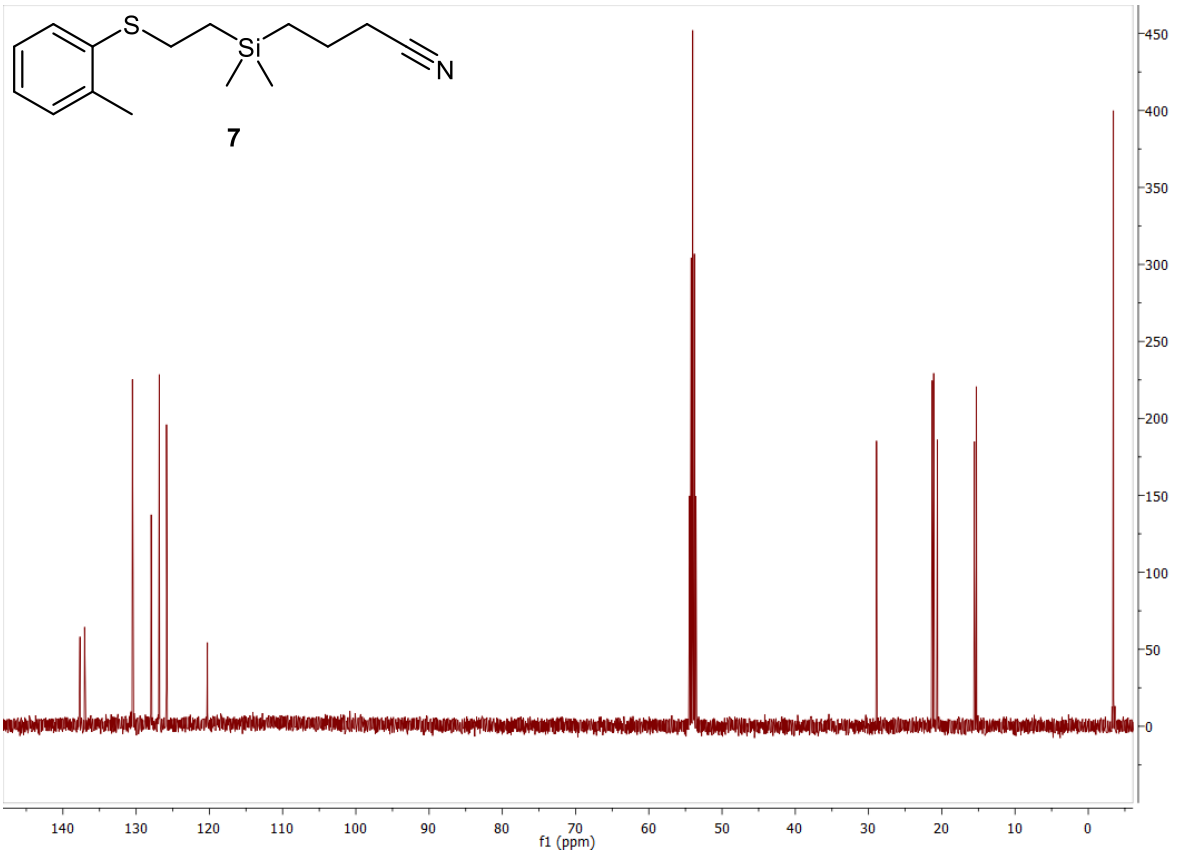
#	m/z	I %	I
63	413.2664	3.5	14707
64	414.2695	1.0	4032
65	417.3448	1.2	5120
66	421.3295	1.2	4955
67	429.3188	0.6	2572
68	435.3442	0.7	2851
69	441.2973	0.9	3848
70	447.3445	2.5	10240
71	448.3479	0.6	2427
72	449.3742	1.4	6055
73	453.2819	0.5	2230
74	465.3699	1.8	7329
75	466.3728	0.6	2400
76	467.2982	0.6	2697
77	469.3287	1.0	4257
78	473.3453	0.7	2919
79	481.3141	1.1	4570
80	481.3652	1.1	4696
81	493.3496	0.9	3556
82	495.3296	0.6	2563
83	497.3588	0.9	3823
84	509.3435	0.6	2333
85	513.3547	0.8	3346
86	517.3700	0.6	2438
87	521.3813	1.4	5706
88	529.3493	0.6	2530
89	545.3440	0.6	2421
90	549.2211	0.6	2654
91	549.4127	0.9	3568
92	553.4602	0.5	2189
93	561.3391	0.6	2348
94	561.3970	0.6	2622
95	609.3586	0.9	3864
96	637.3928	0.6	2617
97	685.4360	0.6	2355
98	705.5815	1.0	3995
99	721.5761	0.7	2822
100	735.5076	0.5	2189

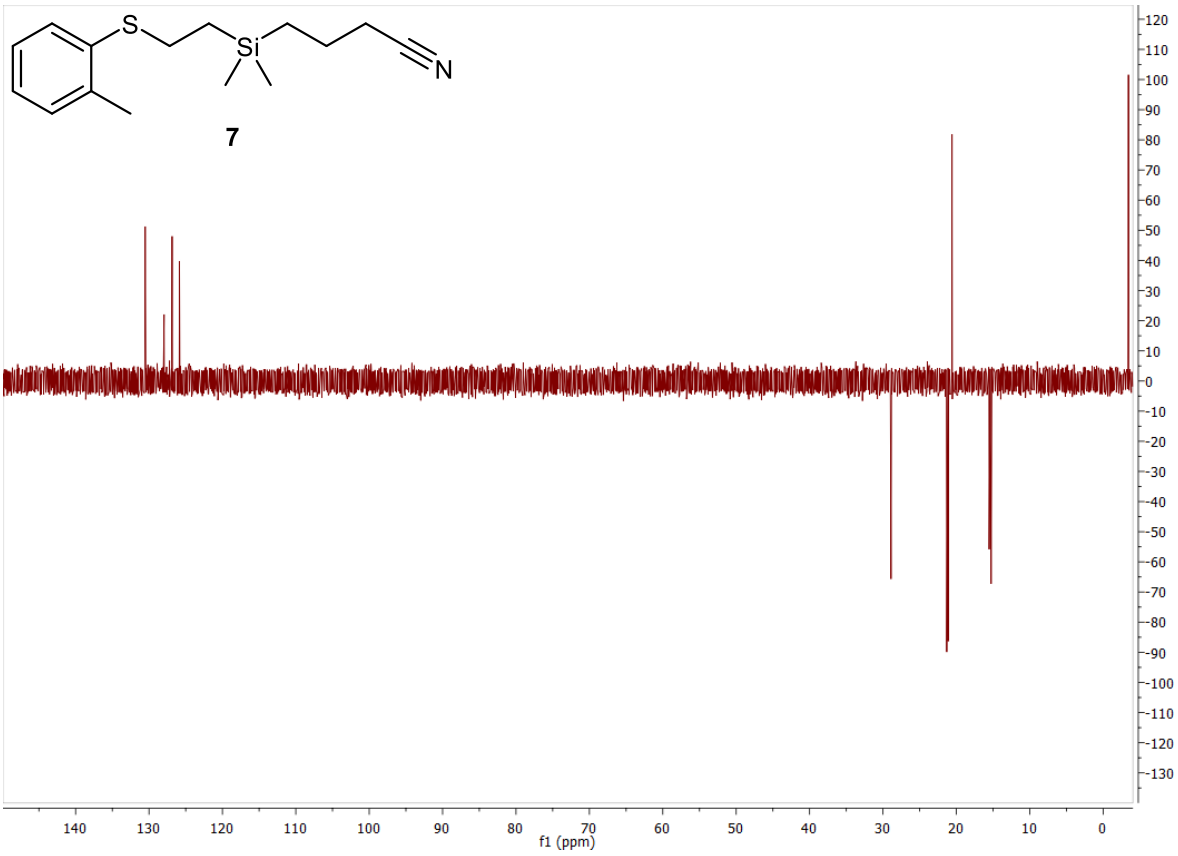
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV

6. Compound **7**:

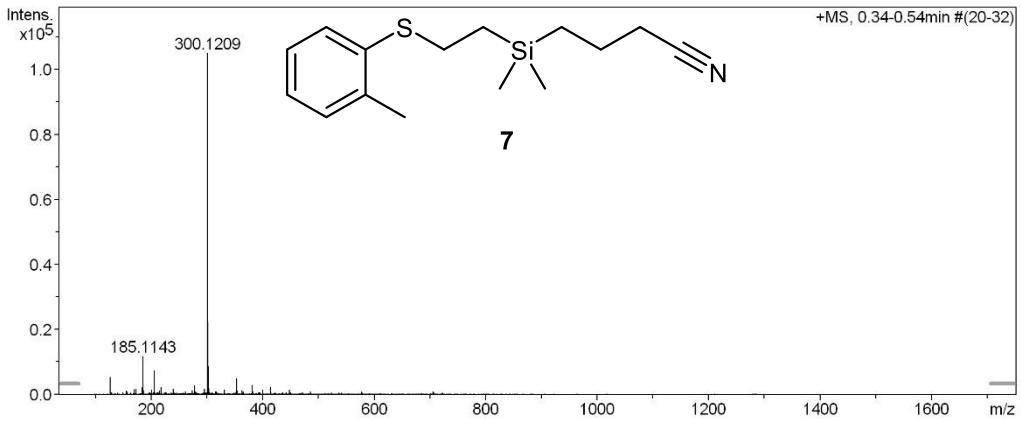




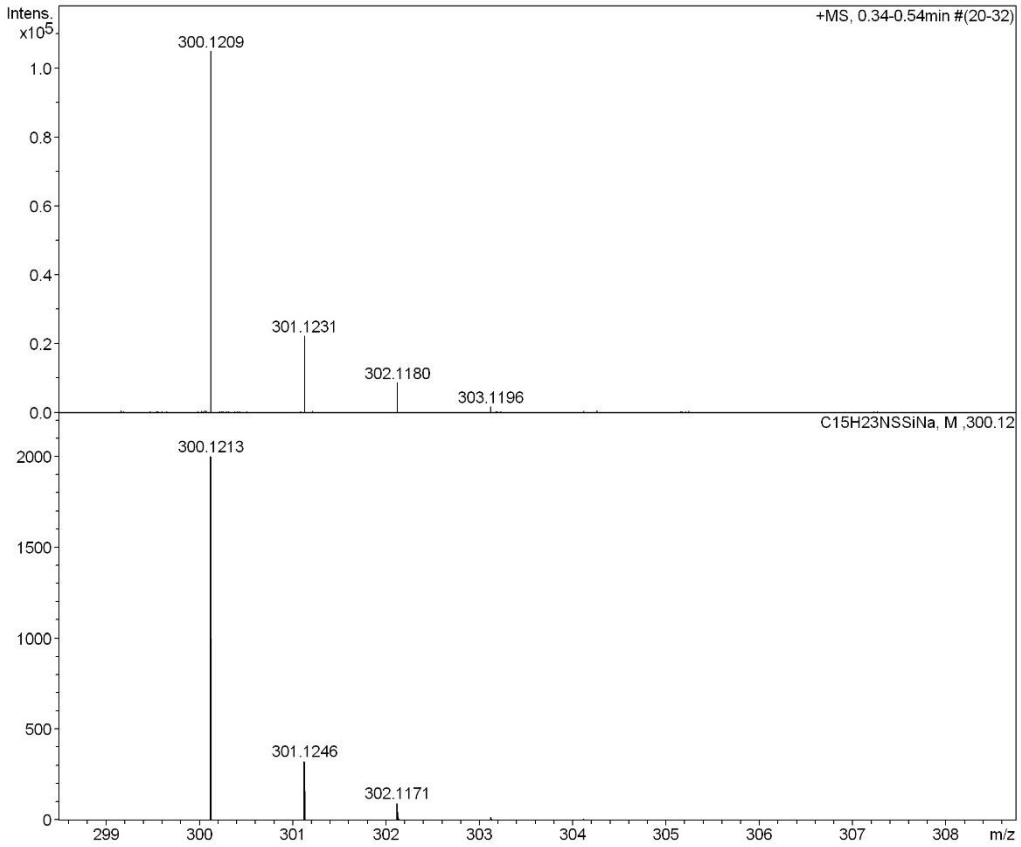

S
Si
N
7
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba507 chr1#1**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	21 Direct_pos_low.m



7



High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^- Conf	z
300.1209	1	C 15 H 23 N Na S Si	100.00	300.1213	0.4	1.3	11.5	5.5	even	1+

Mass list

#	m/z	I %	I
1	126.0738	4.9	5182
2	127.0755	0.6	591
3	129.0529	0.5	560
4	139.0504	0.4	393
5	149.0231	0.5	564
6	155.0467	1.0	1064
7	157.0832	0.8	804
8	163.1330	0.5	483
9	169.0467	0.5	550
10	169.1446	1.4	1455
11	173.0780	1.6	1684
12	183.0634	0.6	599
13	183.0773	2.0	2149
14	185.0775	0.4	445
15	185.1143	11.1	11634
16	186.1181	1.2	1230
17	195.0990	0.4	408
18	197.0777	0.5	557
19	201.1024	1.3	1324
20	203.0518	0.6	578
21	205.0595	7.1	7421
22	206.0625	0.6	593
23	209.1146	0.4	393
24	211.0931	0.6	595
25	213.1090	0.5	488
26	213.1459	0.5	478
27	215.1248	0.9	978
28	217.1041	2.1	2156
29	218.0774	0.4	440
30	225.1092	0.6	656
31	227.1257	0.4	428
32	236.0714	0.4	416
33	239.0885	1.6	1651
34	239.1243	0.6	631
35	241.0678	0.4	452
36	245.0783	0.4	467
37	257.1359	0.5	483
38	261.1304	0.7	723
39	273.1662	1.2	1229
40	277.2134	0.4	465
41	278.1383	2.6	2695
42	279.1413	0.7	765
43	279.2286	0.6	660
44	281.1712	0.4	392
45	293.2080	0.4	434
46	295.1649	1.5	1584
47	297.2398	0.4	425
48	299.1604	0.5	498
49	300.0233	0.4	393
50	300.0582	0.5	571
51	300.0762	0.4	459
52	300.1209	100.0	104853
53	301.1231	21.2	22256
54	301.2107	0.4	398
55	302.1180	8.2	8645
56	303.1196	1.7	1754
57	304.1183	0.4	385
58	304.2605	0.6	633
59	305.2437	0.4	437
60	309.2039	0.5	558
61	315.1924	0.9	971
62	316.0946	0.6	668

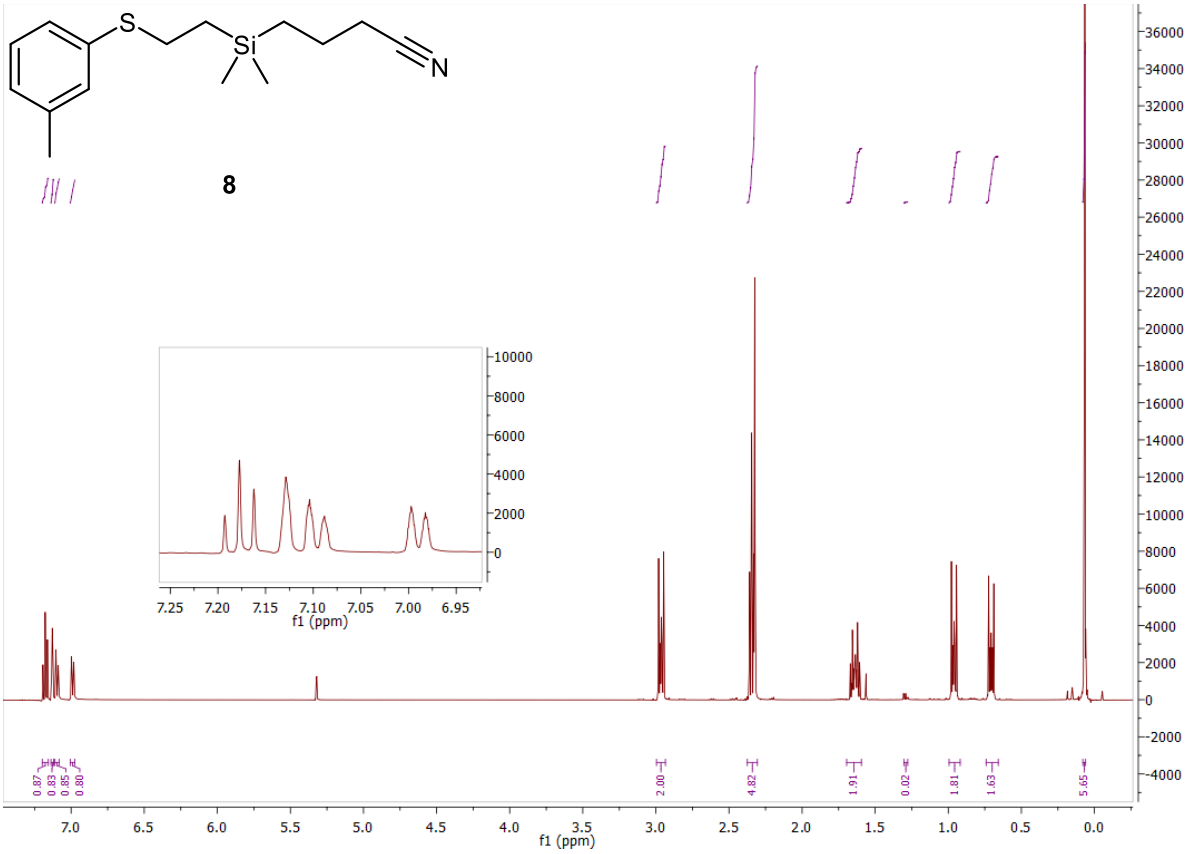
High Resolution Mass Spectrometry Report

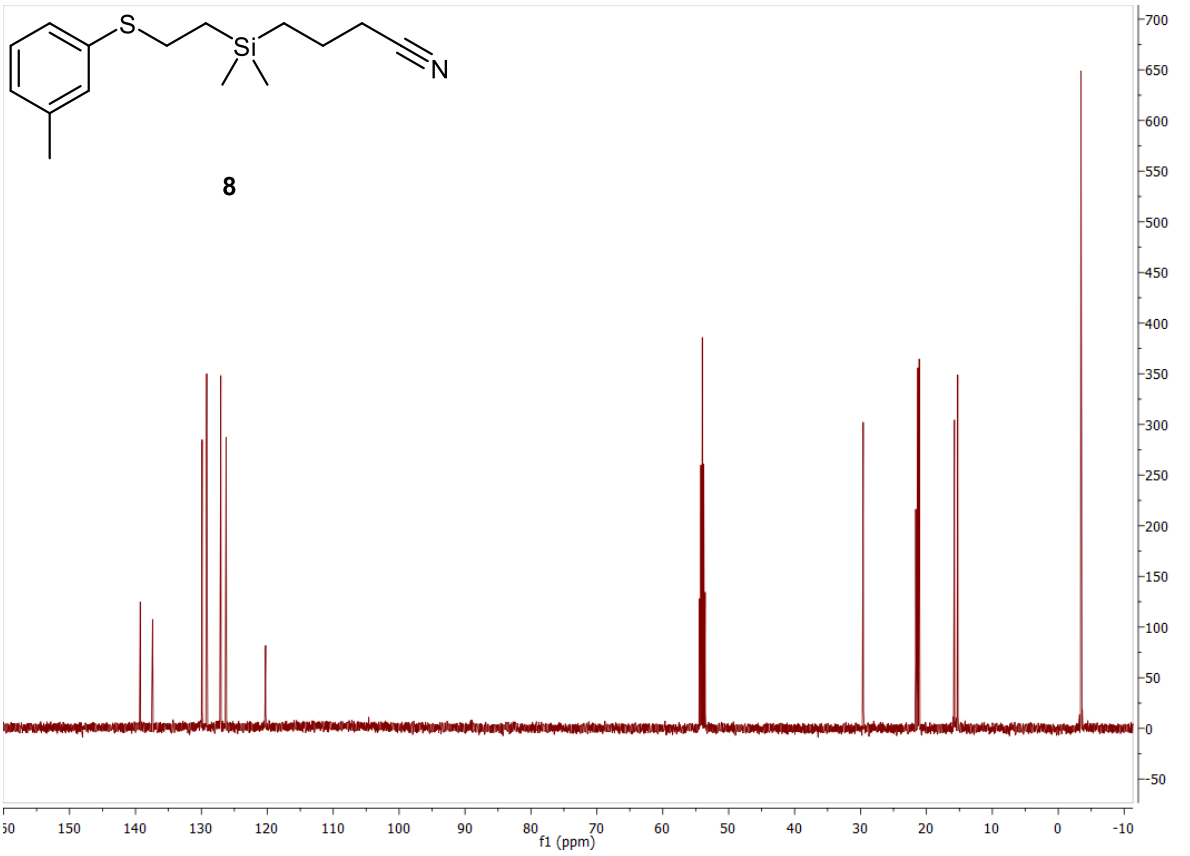
#	m/z	I %	I
63	316.1158	0.9	903
64	331.1876	1.3	1311
65	331.2068	0.6	615
66	348.9894	0.5	475
67	350.9859	0.4	454
68	353.2657	4.5	4758
69	354.2682	1.0	1017
70	363.1563	1.2	1251
71	364.1588	0.4	392
72	365.1048	0.7	762
73	365.2695	0.4	390
74	381.1668	1.5	1582
75	381.2969	2.6	2777
76	382.3000	0.7	718
77	391.2837	0.4	461
78	393.2961	0.5	570
79	395.1822	0.6	602
80	399.1776	1.3	1392
81	413.1277	1.1	1123
82	413.2659	2.2	2272
83	414.2677	0.6	611
84	421.3287	0.4	390
85	435.1097	0.6	618
86	441.2975	0.6	582
87	447.3450	1.3	1366
88	448.3462	0.4	420
89	449.3725	0.6	595
90	469.3286	0.4	452
91	472.1148	0.4	386
92	485.3292	0.7	777
93	523.3218	0.4	402
94	536.1654	0.5	525
95	541.1208	0.4	444
96	577.2526	0.8	794
97	578.2553	0.4	442
98	705.5829	0.9	967
99	706.5859	0.5	485
100	721.5753	0.4	446

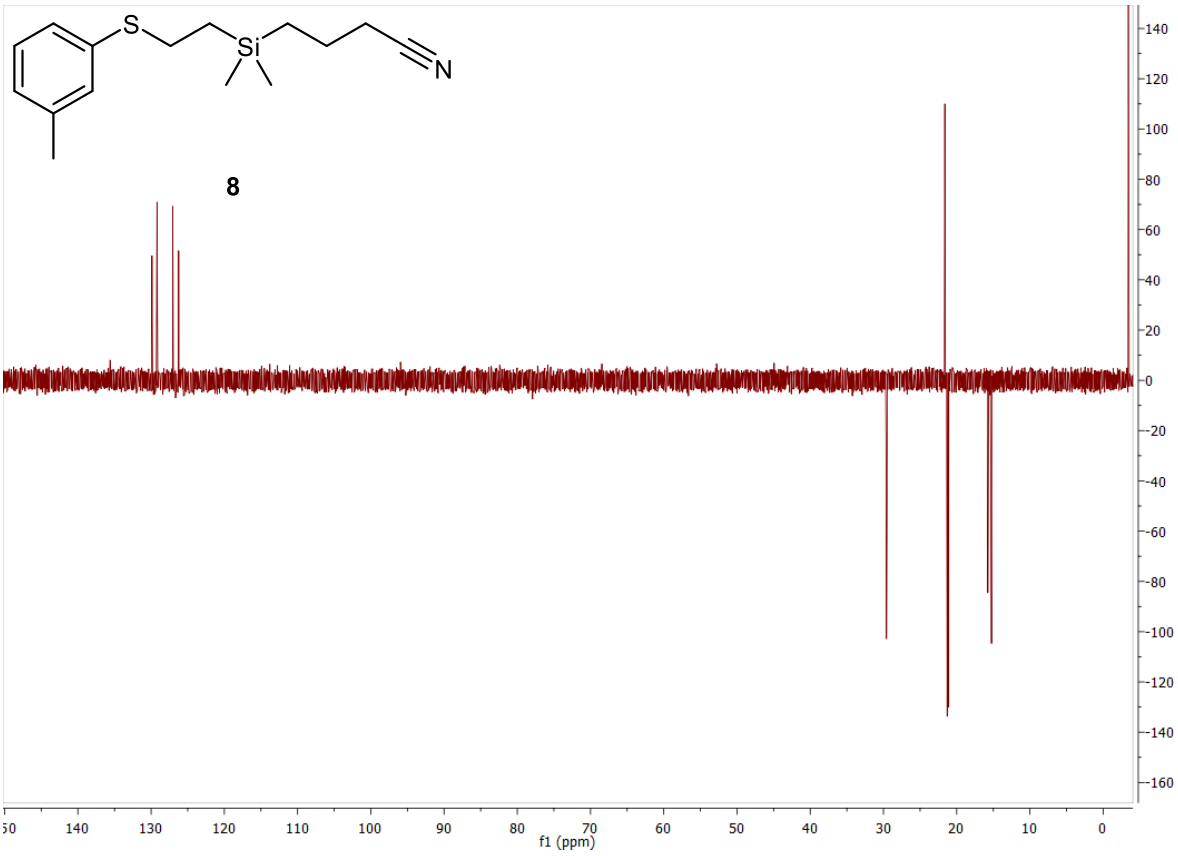
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV

7. Compound **8**:






S
Si
N
8
140
120
100
80
60
40
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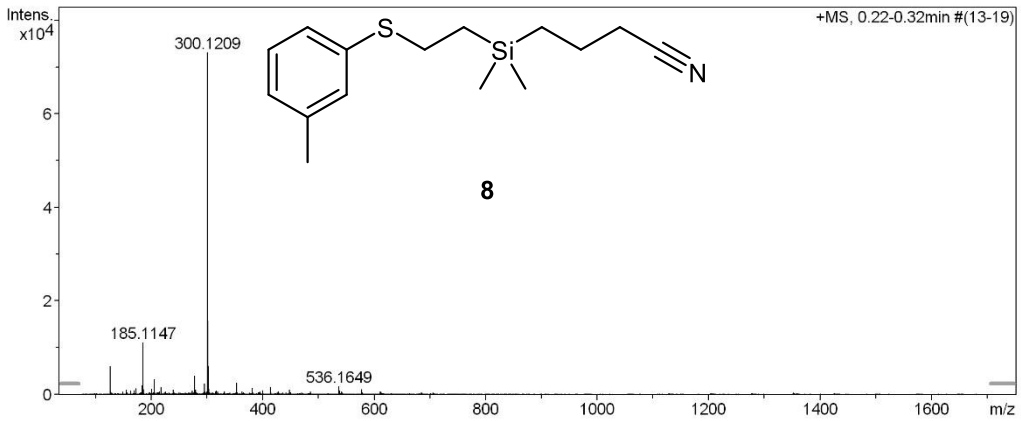
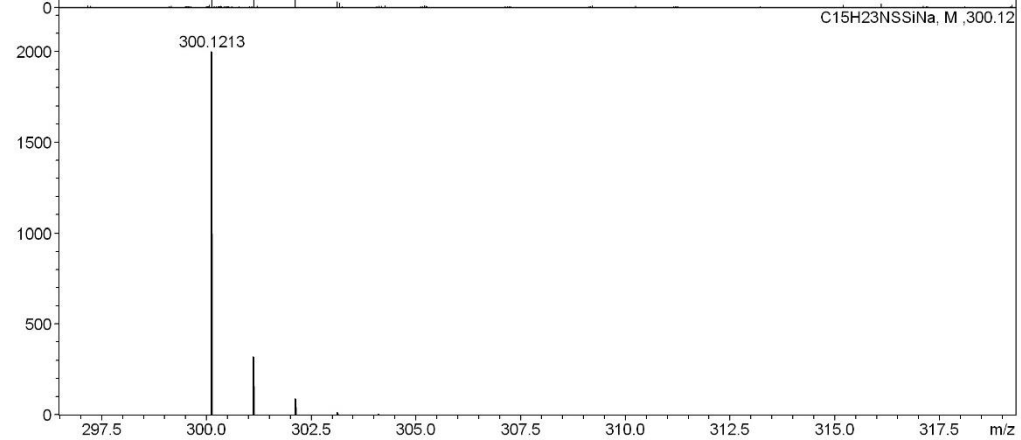
0
-20
-40
-60
-80
-100
-120
-140
-160
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba512 chr1#2**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	21 Direct_pos_low.m



8



High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^- Conf	z
300.1209	1	C 15 H 23 N Na S Si	100.00	300.1213	0.4	1.3	11.1	5.5	even	1+

Mass list

#	m/z	I %	I
1	126.0739	8.2	5951
2	127.0164	0.4	300
3	127.0747	0.8	578
4	129.0529	0.5	342
5	149.0235	0.7	525
6	155.0468	1.3	943
7	157.0836	0.5	386
8	163.1333	1.0	754
9	169.1451	1.2	869
10	173.0783	1.7	1255
11	180.1593	0.4	328
12	181.0836	0.6	408
13	183.0631	0.6	444
14	183.0778	2.6	1923
15	183.0987	0.8	558
16	185.1147	15.1	11004
17	186.1177	1.4	1022
18	197.0776	0.5	365
19	201.1026	1.6	1189
20	203.0531	0.6	440
21	205.0596	4.4	3216
22	206.0621	0.5	334
23	211.0935	0.6	436
24	213.1094	0.4	313
25	213.1451	0.6	436
26	215.1246	0.9	646
27	217.1047	2.1	1505
28	223.0944	0.5	349
29	223.1313	0.4	292
30	225.1092	0.7	507
31	231.1204	0.4	312
32	239.0885	1.3	981
33	239.1248	0.7	542
34	241.1412	0.4	319
35	251.1600	0.5	357
36	261.1284	0.5	333
37	267.1549	0.6	444
38	271.1523	0.5	350
39	273.1668	1.0	703
40	277.2148	0.5	394
41	278.1388	5.5	3987
42	279.1418	1.3	984
43	280.1368	0.6	430
44	281.1701	0.4	294
45	293.2098	0.4	324
46	295.1654	3.2	2323
47	296.1670	0.7	518
48	297.1661	0.5	356
49	297.2390	0.4	309
50	300.0706	0.7	529
51	300.1209	100.0	73001
52	301.1233	21.4	15598
53	302.1181	8.2	6014
54	303.1204	1.6	1135
55	303.1770	1.2	889
56	304.2620	0.5	375
57	305.2082	0.5	351
58	309.2042	0.5	356
59	310.2373	0.4	292
60	315.1922	0.7	503
61	316.0951	1.0	762
62	319.2228	0.7	498

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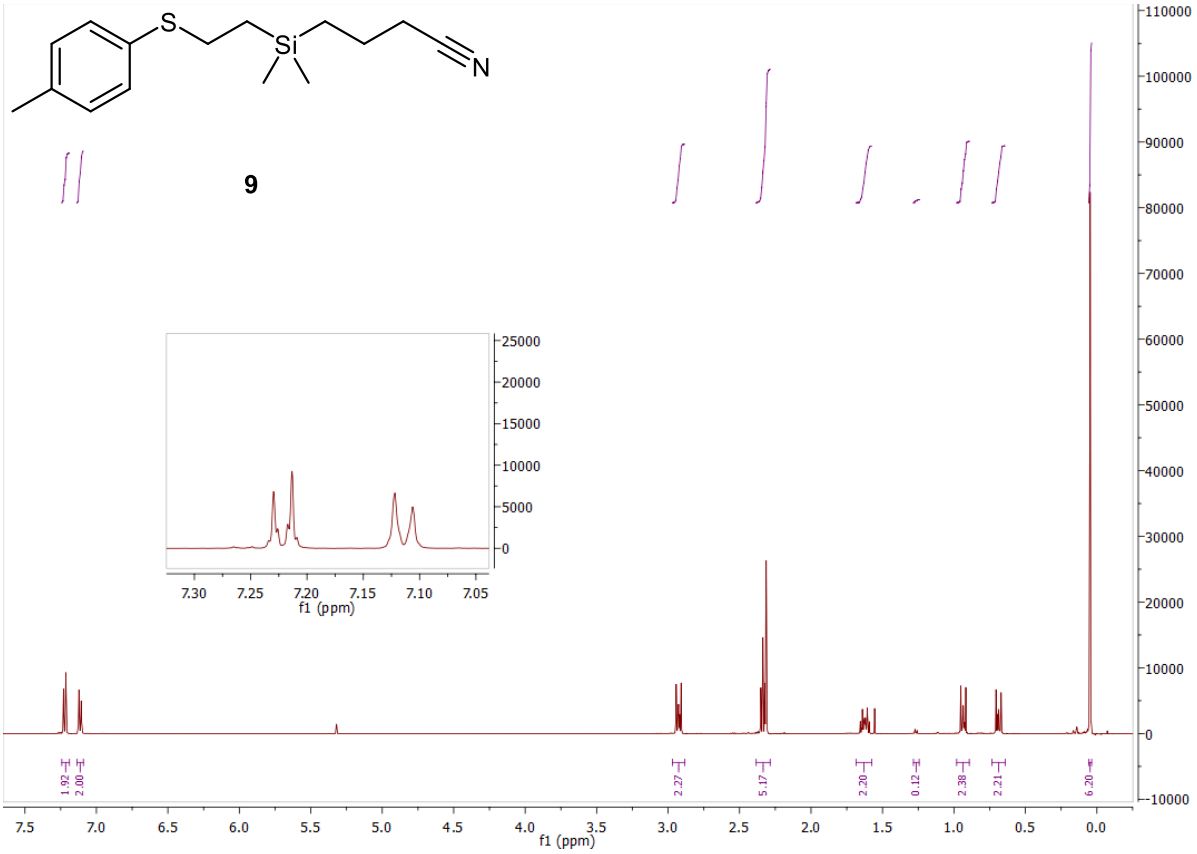
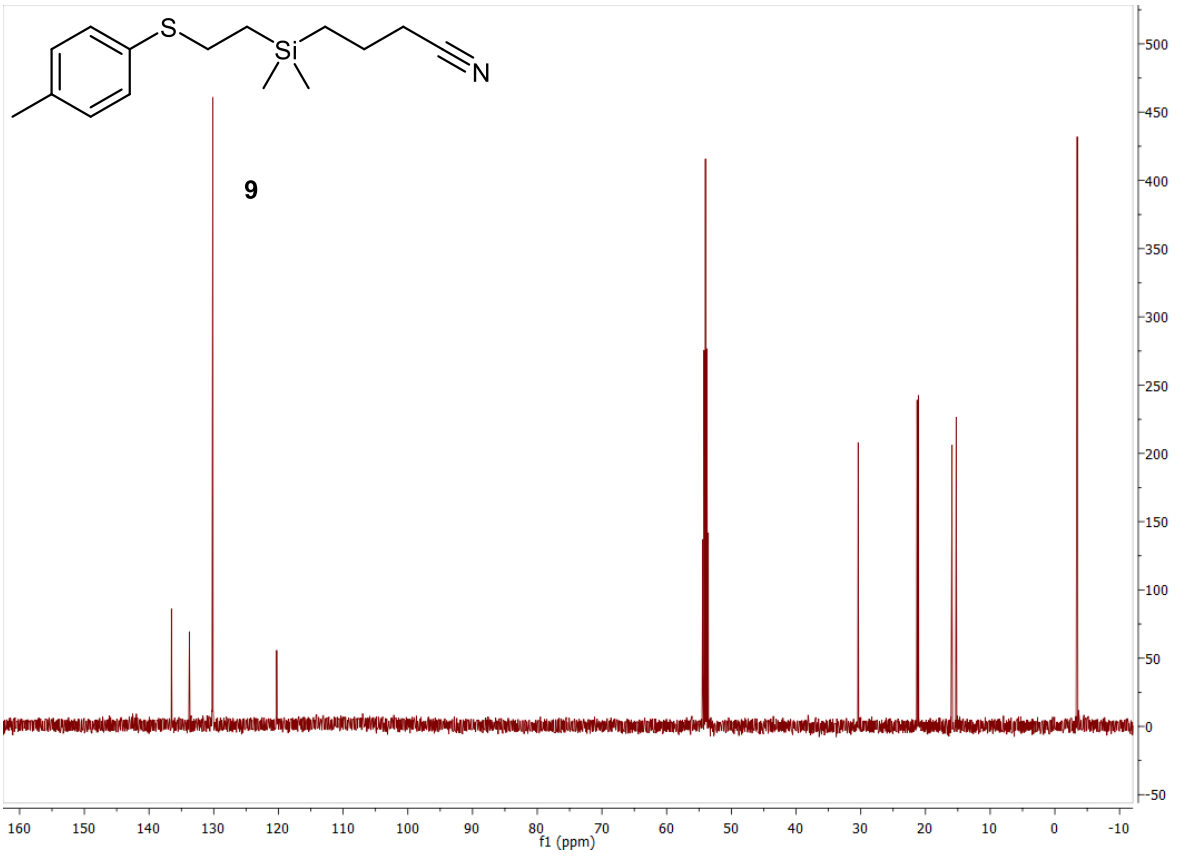
#	m/z	I %	I
63	331.1859	0.9	639
64	331.2084	0.8	548
65	353.2658	3.3	2394
66	354.2685	0.6	464
67	363.1573	0.7	499
68	365.1055	0.5	398
69	365.2650	0.5	355
70	381.1668	1.1	815
71	381.2973	1.8	1328
72	382.2996	0.5	362
73	391.2832	0.6	454
74	393.2970	0.6	462
75	395.1813	0.7	516
76	399.1771	1.2	851
77	413.1290	0.9	684
78	413.1922	0.5	332
79	413.2662	2.2	1604
80	414.2704	0.6	453
81	425.3630	0.4	309
82	427.2093	0.9	670
83	428.2113	0.4	282
84	441.2975	0.4	313
85	447.3445	1.3	955
86	448.3502	0.5	354
87	449.3767	0.5	400
88	485.3284	0.7	491
89	536.1649	2.3	1714
90	537.1660	1.1	815
91	538.1629	0.9	685
92	541.1196	0.7	545
93	542.1241	0.5	333
94	577.2537	1.4	995
95	578.2554	0.6	436
96	610.1837	0.8	563
97	611.1831	0.7	496
98	612.1833	0.5	329
99	685.2055	0.4	315
100	705.5860	0.4	320

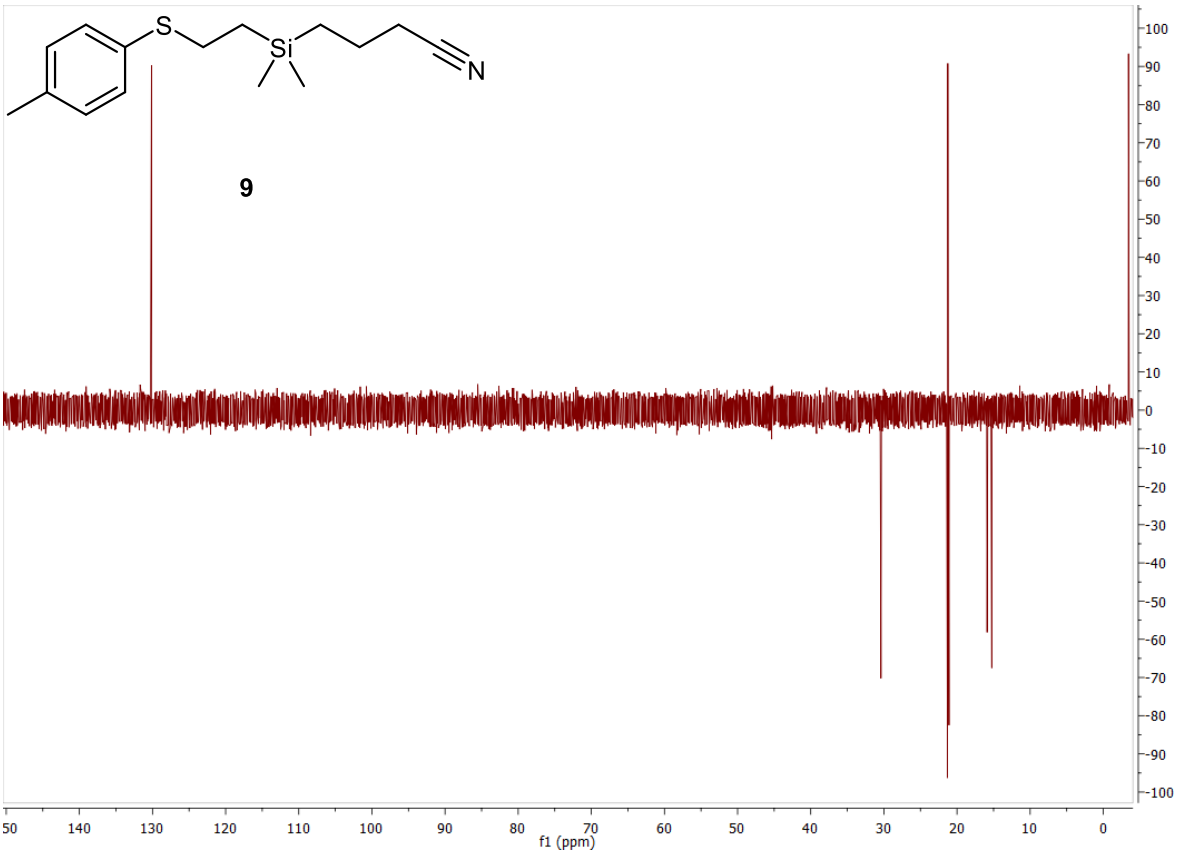
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV

8. Compound **9**:

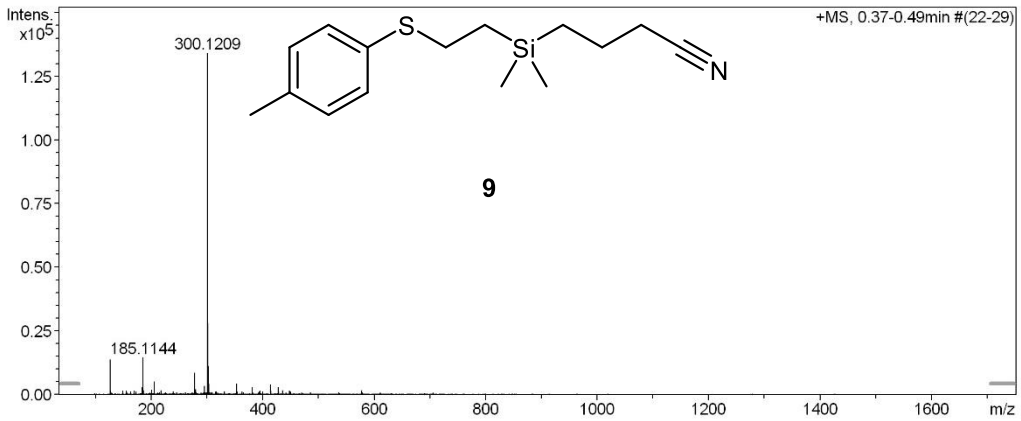




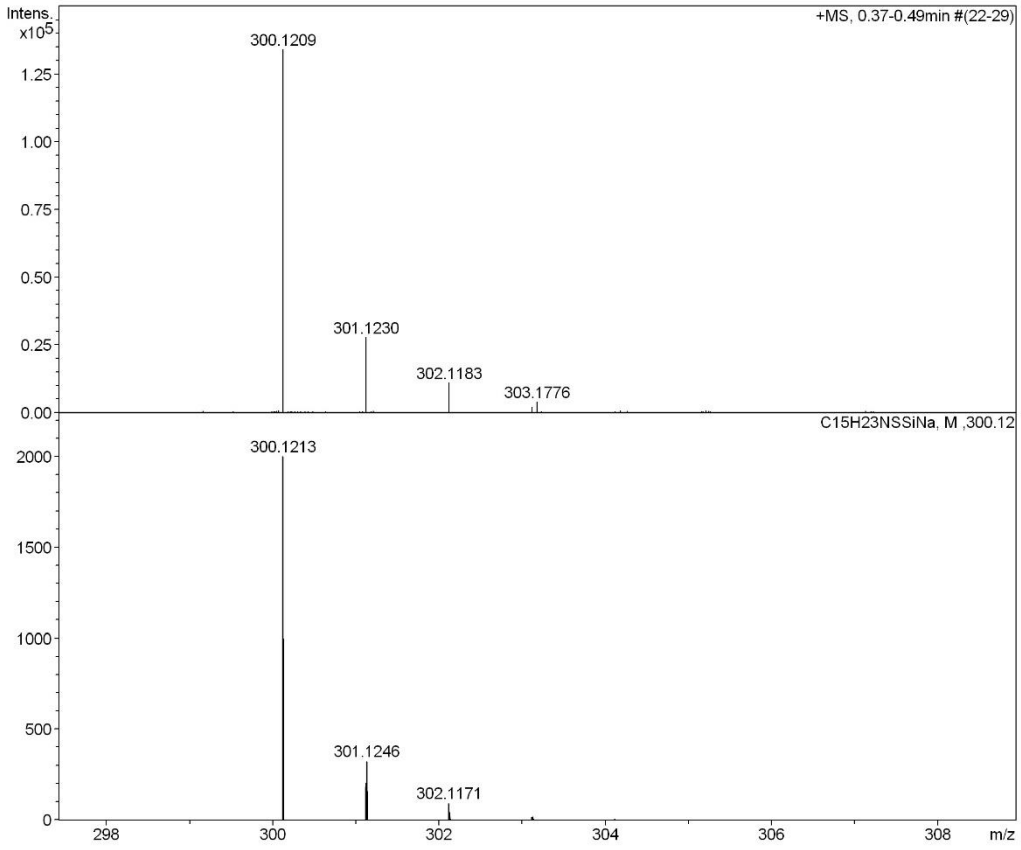

S
Si
N
9
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba510 chr1#1**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	21 Direct_pos_low.m



9



High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^- Conf	z
300.1209	1	C 15 H 23 N Na S Si	100.00	300.1213	0.4	1.2	12.8	5.5	even	1+

Mass list

#	m/z	I %	I
1	98.0435	0.3	452
2	126.0739	10.2	13651
3	127.0757	1.0	1342
4	128.0706	0.3	463
5	129.0529	0.4	512
6	149.0231	0.9	1259
7	155.0466	1.0	1297
8	157.0835	0.4	536
9	163.1322	0.9	1236
10	169.1444	0.9	1263
11	173.0782	0.9	1153
12	183.0775	2.1	2773
13	183.0993	0.5	704
14	185.1144	10.8	14471
15	186.1179	1.1	1446
16	197.0776	0.4	528
17	201.1030	1.3	1765
18	203.0523	0.3	465
19	205.0596	3.7	4896
20	211.0932	0.5	636
21	215.1247	0.6	822
22	217.1043	1.1	1482
23	225.1093	0.6	798
24	239.0883	0.9	1219
25	239.1248	0.4	541
26	245.0781	0.5	729
27	251.1608	0.3	421
28	257.1357	0.3	436
29	261.1296	0.5	705
30	265.1403	0.3	464
31	267.1554	0.3	423
32	271.1505	0.3	448
33	273.1661	0.6	814
34	275.1467	0.3	437
35	277.2130	0.4	493
36	278.1385	6.3	8441
37	279.1408	1.4	1895
38	279.2292	0.4	496
39	280.1353	0.6	847
40	281.1369	0.3	434
41	289.1613	0.4	561
42	293.2073	0.4	503
43	295.1652	2.4	3165
44	296.1676	0.5	675
45	297.2390	0.4	602
46	299.1601	0.4	486
47	300.0455	0.5	609
48	300.0711	0.5	682
49	300.1209	100.0	133918
50	300.2968	0.3	426
51	301.1230	20.8	27813
52	301.2103	0.3	464
53	302.1183	8.3	11067
54	303.1199	1.5	2012
55	303.1776	3.0	4036
56	304.1169	0.3	447
57	304.1813	0.6	741
58	304.2604	0.4	593
59	305.2078	0.5	706
60	305.2444	0.4	480
61	307.1271	0.5	609
62	309.2052	0.6	747

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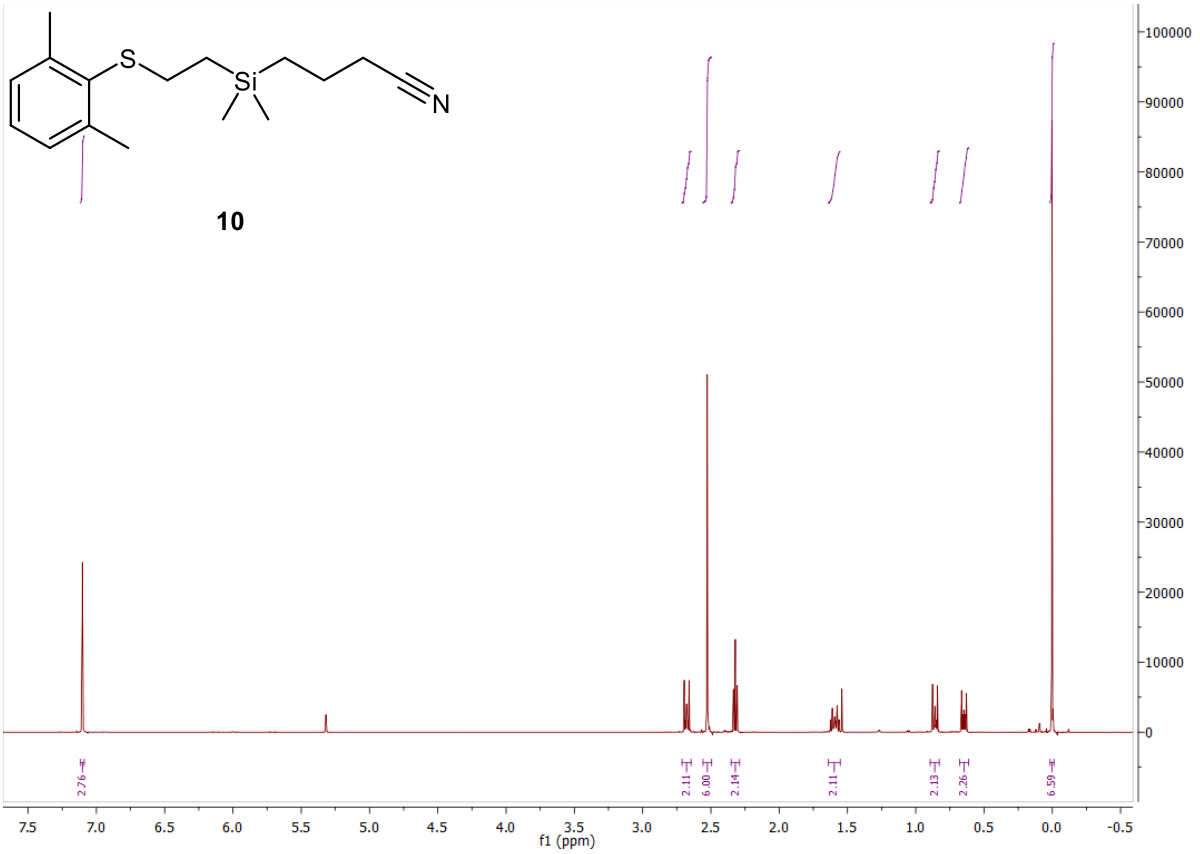
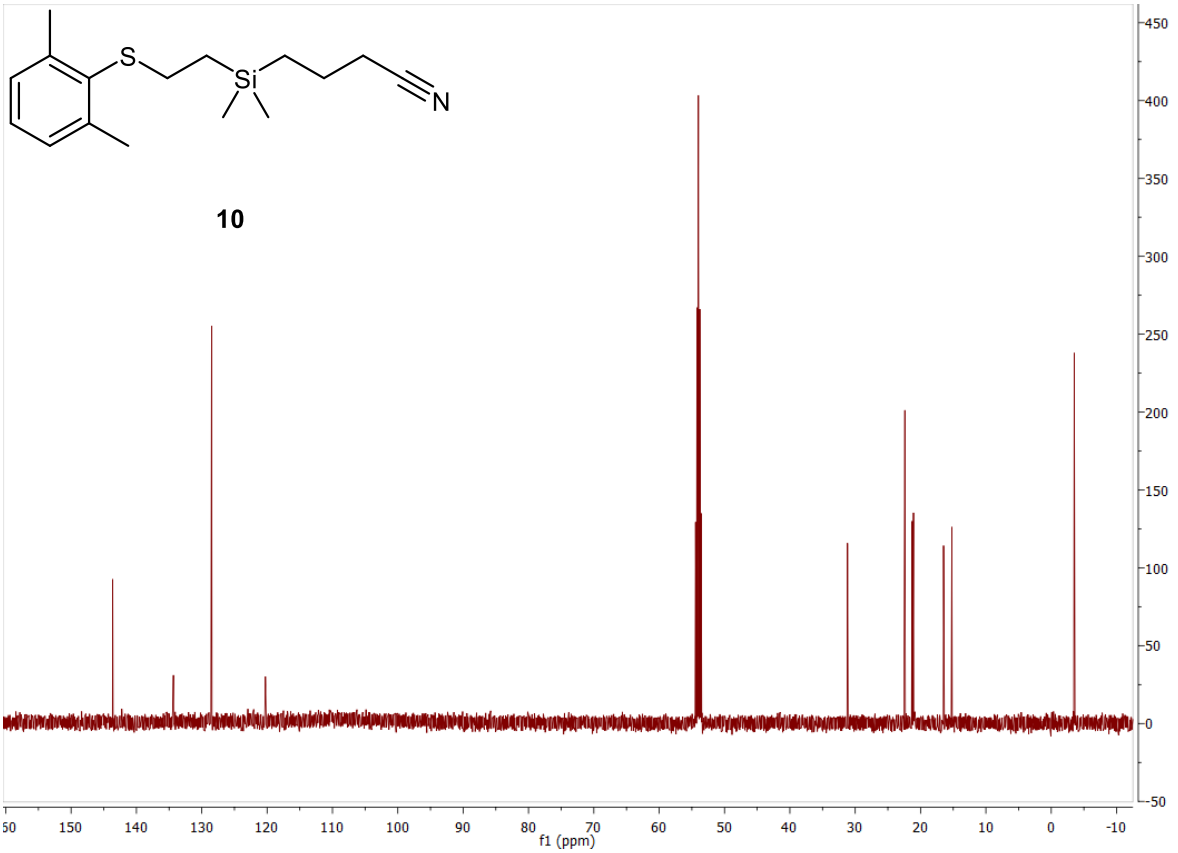
#	m/z	I %	I
63	315.1921	0.6	870
64	316.0946	0.9	1242
65	319.2241	0.4	549
66	325.2333	0.3	455
67	331.1875	0.8	1131
68	331.2071	0.5	683
69	353.2657	3.1	4173
70	354.2687	0.8	1013
71	363.1561	0.7	933
72	365.1055	0.6	773
73	365.2710	0.5	672
74	381.1668	1.1	1535
75	381.2970	2.0	2629
76	382.2999	0.5	649
77	391.2835	0.5	627
78	393.2960	0.7	935
79	395.1805	1.0	1363
80	399.1775	0.9	1201
81	413.1279	2.9	3837
82	413.1929	0.5	622
83	413.2660	1.7	2298
84	414.1311	1.0	1339
85	414.2701	0.5	679
86	427.2091	2.1	2764
87	428.2119	0.7	917
88	435.1097	1.2	1575
89	436.1103	0.3	458
90	441.2970	0.4	496
91	447.3451	1.0	1354
92	449.3732	0.7	894
93	469.3274	0.4	578
94	485.3283	0.6	857
95	536.1653	0.6	822
96	577.2526	1.1	1466
97	578.2558	0.6	756
98	579.2534	0.3	466
99	610.1827	0.4	543
100	705.5835	0.4	512

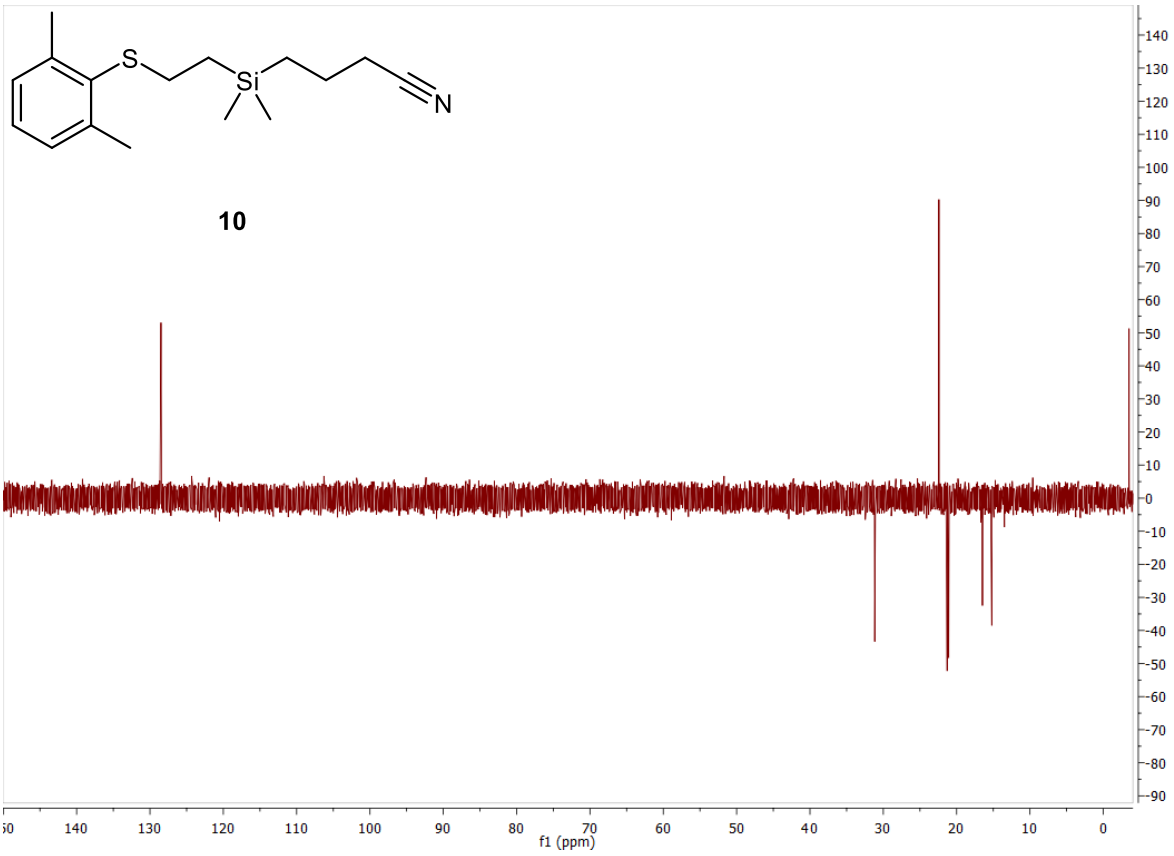
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV

9. Compound **10**:

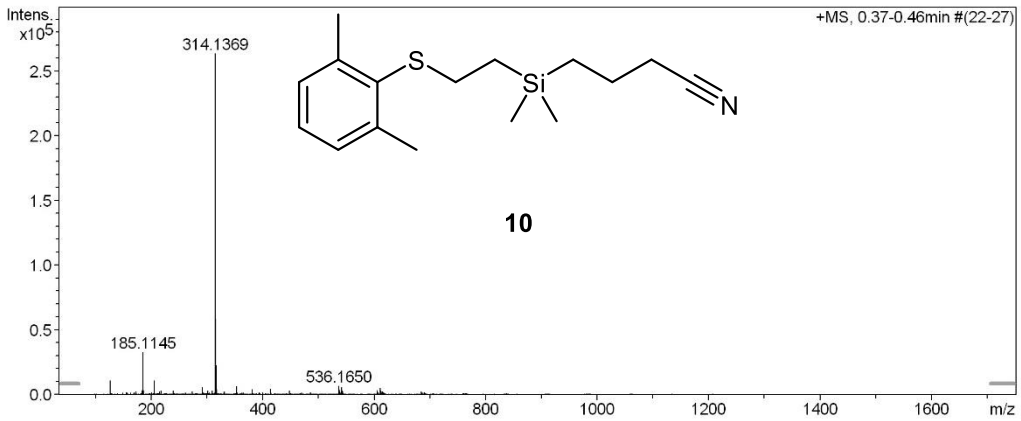


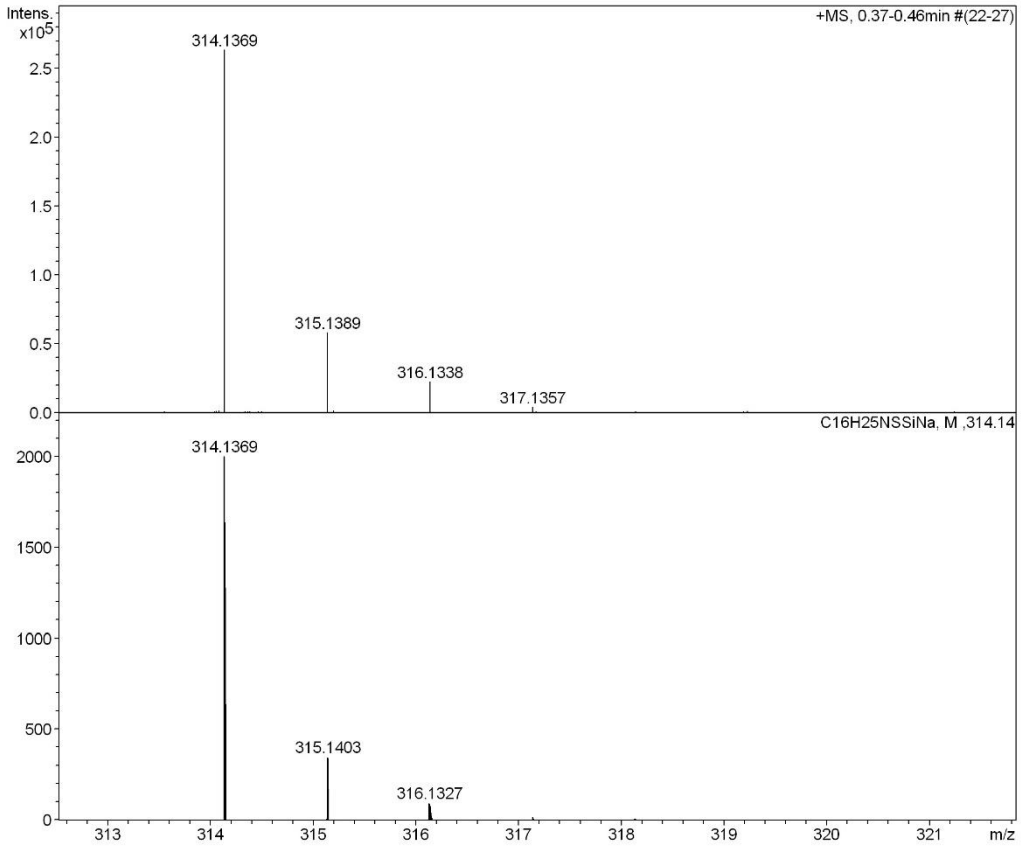



S
Si
N
10
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba508 chr1#2**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	21 Direct_pos_low.m





10

High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^- Conf	z
314.1369	1	C 16 H 25 N Na S Si	100.00	314.1369	0.0	0.1	12.4	5.5	even	1+

Mass list

#	m/z	I %	I
1	126.0739	4.0	10459
2	127.0752	0.4	937
3	149.0229	0.4	971
4	155.0468	0.5	1447
5	157.0834	0.4	1084
6	163.1326	0.5	1215
7	169.1448	0.6	1661
8	173.0781	0.9	2283
9	183.0780	1.1	2935
10	185.1145	12.3	32339
11	186.1178	1.2	3095
12	197.0781	0.3	679
13	201.1031	0.6	1483
14	203.0524	0.3	885
15	205.0594	4.1	10728
16	206.0621	0.3	835
17	209.1148	0.3	677
18	211.0938	0.3	920
19	215.1247	0.7	1743
20	217.1041	1.0	2597
21	225.1080	0.3	917
22	239.0881	1.0	2756
23	245.0778	0.3	846
24	261.1297	0.4	1025
25	273.1664	0.9	2304
26	279.2293	0.3	821
27	281.1721	0.3	793
28	292.1543	2.0	5323
29	293.1571	0.5	1285
30	293.2075	0.3	812
31	294.1515	0.3	717
32	297.2393	0.3	786
33	299.1613	0.3	726
34	300.1203	0.3	894
35	301.1399	1.0	2610
36	301.2106	0.3	718
37	304.2601	0.4	961
38	309.1811	1.1	2817
39	310.1836	0.3	912
40	314.0539	0.5	1231
41	314.0845	0.5	1283
42	314.1369	100.0	263279
43	315.1389	22.1	58179
44	315.1925	0.5	1413
45	316.1338	8.4	22206
46	317.1357	1.5	3909
47	317.1676	0.3	721
48	318.1348	0.3	854
49	319.2242	0.4	929
50	330.1099	0.7	1917
51	331.1872	0.7	1896
52	331.2066	0.5	1291
53	348.9897	0.3	727
54	350.9874	0.3	774
55	353.2655	2.4	6219
56	354.2692	0.5	1215
57	363.1567	0.5	1249
58	365.1052	0.5	1218
59	381.1666	0.7	1815
60	381.2969	1.4	3780
61	382.3000	0.3	873
62	393.2975	0.6	1520

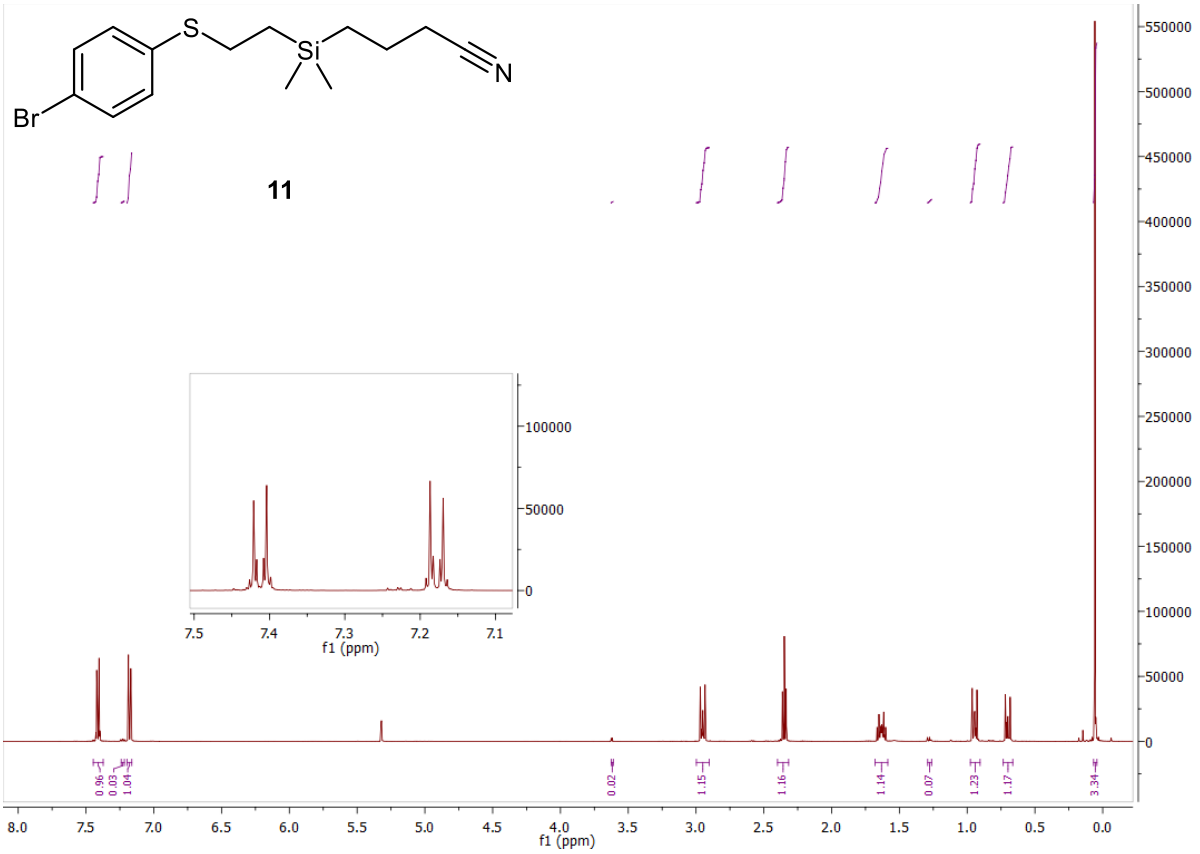
High Resolution Mass Spectrometry Report

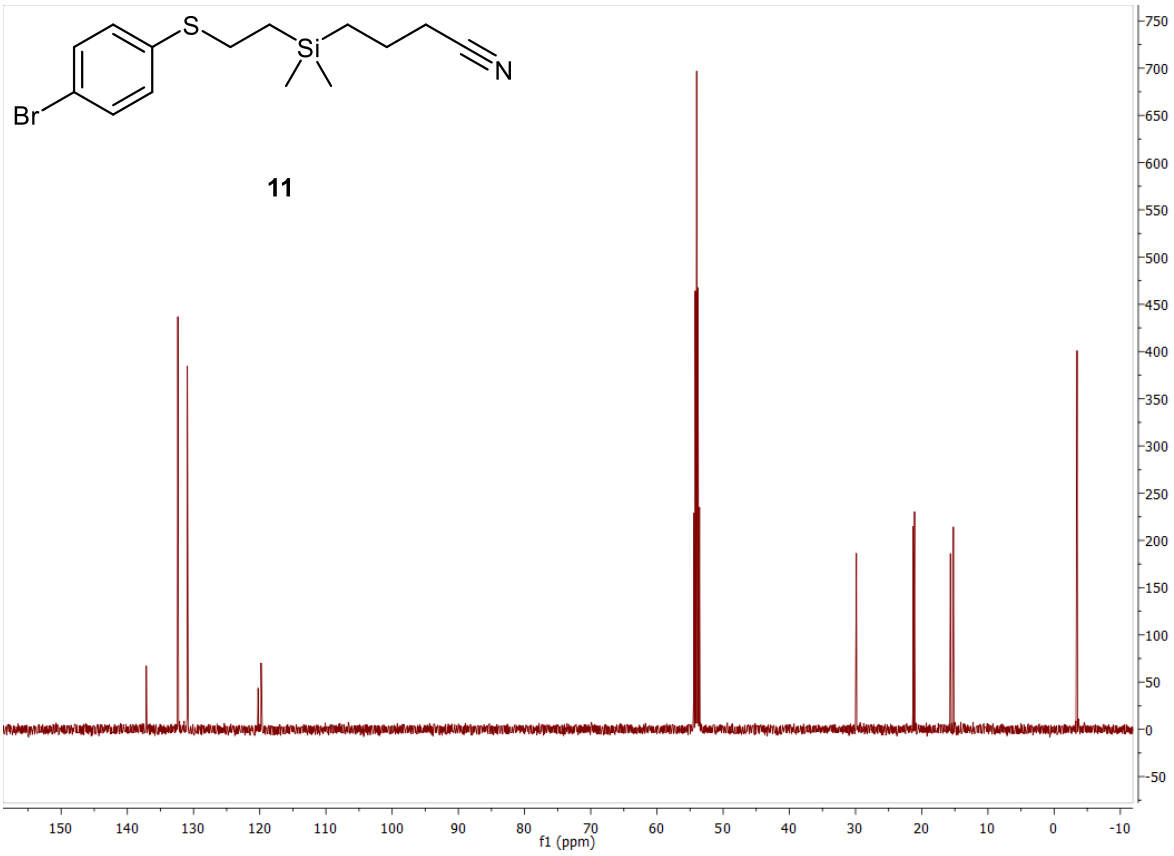
#	m/z	I %	I
63	399.1778	0.6	1539
64	413.2661	1.5	4012
65	414.2698	0.5	1305
66	421.3295	0.3	725
67	441.2979	0.4	940
68	447.3449	1.0	2531
69	448.3477	0.3	730
70	449.3686	0.3	826
71	467.1034	0.3	825
72	469.3275	0.4	997
73	485.3287	0.6	1544
74	536.1650	2.4	6248
75	537.1662	1.2	3235
76	538.1636	0.8	2188
77	539.1647	0.4	970
78	541.1207	2.0	5165
79	542.1219	1.0	2582
80	543.1196	0.9	2335
81	544.1204	0.3	679
82	605.2848	1.2	3176
83	606.2881	0.6	1635
84	607.2831	0.3	829
85	610.1836	1.8	4768
86	611.1851	1.0	2664
87	612.1827	0.7	1884
88	613.1810	0.4	938
89	615.1393	0.9	2432
90	616.1403	0.6	1532
91	617.1378	0.5	1335
92	684.2027	0.8	2061
93	685.2027	0.4	1163
94	686.2025	0.4	1086
95	689.1597	0.6	1646
96	690.1581	0.5	1243
97	691.1579	0.3	851
98	705.5820	0.3	897
99	758.2210	0.4	930
100	763.1751	0.3	797

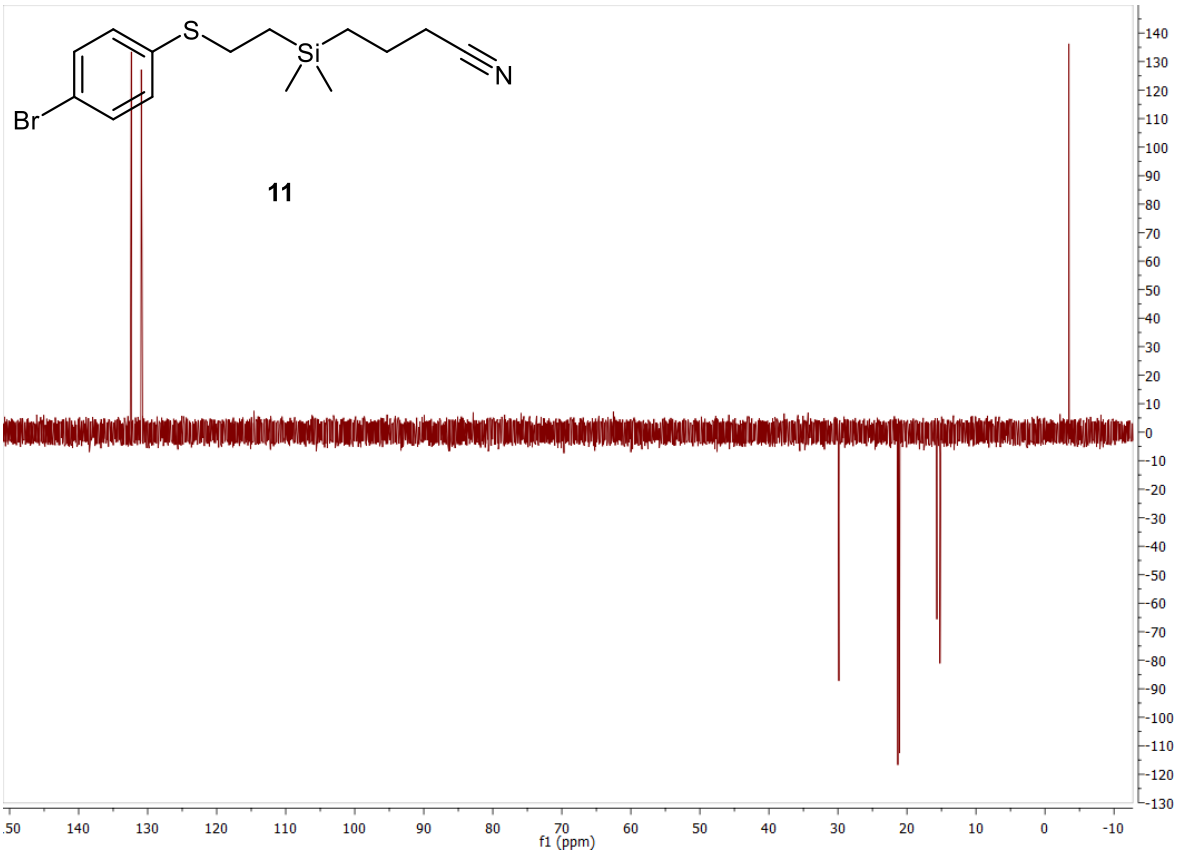
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV

10. Compound **11**:

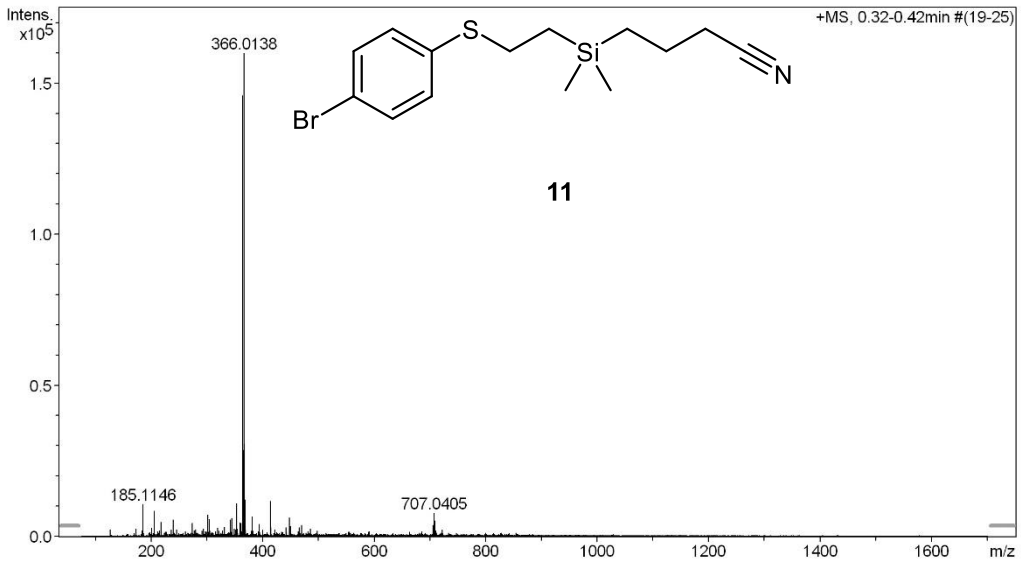




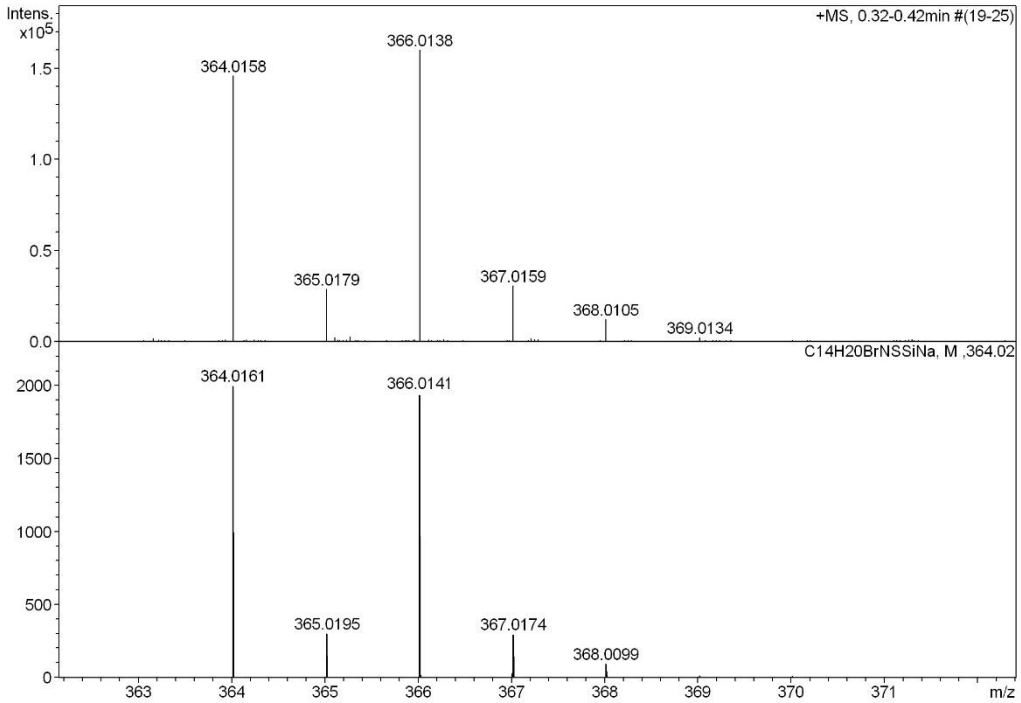

Br
S
Si
N
11
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
.50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba465 chr1#2**	Instrument	maXis 4G
Comment	0.9 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m



11



High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	z
364.0158	1	C 14 H 20 Br N Na S Si	100.00	364.0161	0.3	0.8	15.4	5.5	even	1+

Mass list

#	m/z	I %	I
1	126.0732	1.4	2271
2	173.0787	1.5	2396
3	183.0775	1.2	1923
4	185.1146	6.6	10590
5	197.0784	0.8	1320
6	201.1023	1.7	2706
7	205.0597	5.2	8388
8	211.0934	1.0	1598
9	215.1250	1.2	1874
10	217.1044	2.9	4626
11	225.1092	0.9	1411
12	227.1247	0.9	1390
13	236.0715	1.3	2042
14	239.0884	3.4	5487
15	245.0777	1.4	2209
16	261.1277	1.0	1537
17	273.1667	2.7	4337
18	277.2129	1.2	1874
19	279.2285	1.4	2309
20	291.1923	1.1	1826
21	293.2082	1.5	2409
22	297.2392	1.0	1571
23	299.1611	0.9	1377
24	301.1403	4.5	7163
25	302.1441	0.9	1451
26	304.2603	3.6	5689
27	305.2078	0.8	1296
28	305.2448	1.1	1762
29	305.2626	0.8	1352
30	309.2036	0.9	1370
31	315.1909	1.0	1547
32	319.2237	1.8	2805
33	321.2387	1.1	1747
34	328.0716	1.2	1972
35	331.1881	1.1	1735
36	331.2081	1.9	3087
37	339.1770	0.8	1333
38	342.0333	3.4	5456
39	343.0356	1.0	1524
40	344.0317	3.7	5972
41	345.0339	0.8	1351
42	348.9886	1.5	2379
43	350.9864	1.4	2210
44	353.2652	6.7	10748
45	354.2693	1.5	2405
46	359.0602	2.8	4517
47	361.0578	2.7	4372
48	363.1565	1.0	1668
49	364.0158	91.2	145823
50	365.0179	17.9	28613
51	365.1046	1.3	2082
52	365.2679	1.6	2533
53	366.0138	100.0	159820
54	367.0159	19.1	30520
55	367.2082	0.9	1474
56	368.0105	7.6	12156
57	369.0134	1.3	2133
58	379.2813	1.1	1714
59	379.9886	0.8	1322
60	381.1663	1.3	2084
61	381.2967	4.0	6471
62	381.9873	0.9	1482

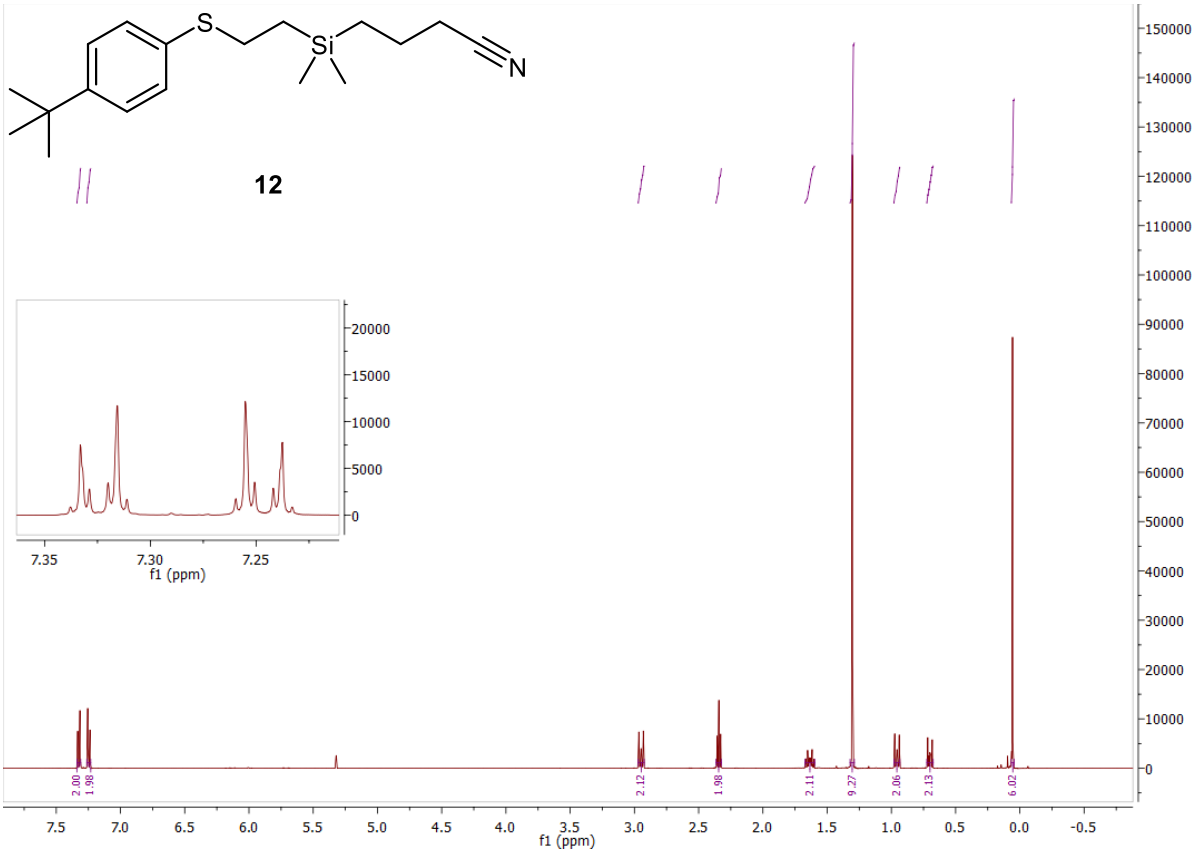
High Resolution Mass Spectrometry Report

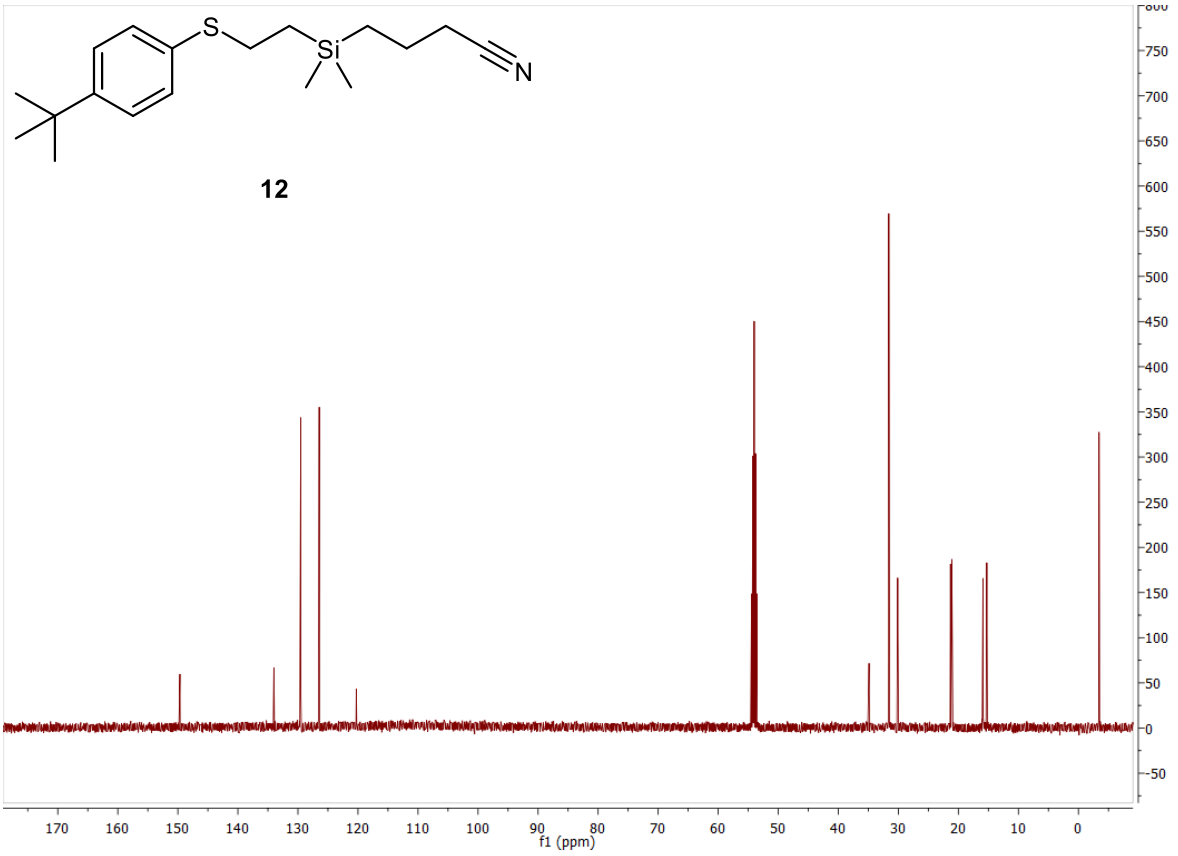
#	m/z	I %	I
63	382.3000	1.1	1702
64	391.2828	1.0	1665
65	393.2972	2.5	4005
66	394.3002	0.8	1241
67	399.1765	1.3	2108
68	407.3126	0.8	1355
69	413.2655	7.2	11553
70	414.2687	1.8	2931
71	421.3282	1.5	2322
72	433.3792	0.9	1390
73	435.3442	0.8	1290
74	441.2967	1.8	2871
75	442.2991	0.8	1240
76	447.3445	3.9	6198
77	448.3480	1.2	1963
78	449.3736	2.1	3420
79	463.3762	1.0	1573
80	465.3695	1.8	2838
81	469.3288	2.3	3726
82	481.3130	0.8	1217
83	481.3630	1.0	1566
84	485.3279	1.5	2404
85	497.3582	1.1	1702
86	553.3883	0.9	1451
87	555.5114	0.9	1508
88	589.4783	0.9	1436
89	591.4943	1.0	1619
90	663.4574	0.9	1401
91	685.4349	1.0	1613
92	705.0418	2.3	3636
93	705.5806	1.8	2870
94	706.0451	1.1	1724
95	706.5850	1.0	1576
96	707.0405	4.8	7722
97	708.0412	2.0	3248
98	709.0379	3.2	5180
99	710.0407	1.2	1981
100	721.5745	1.3	2028

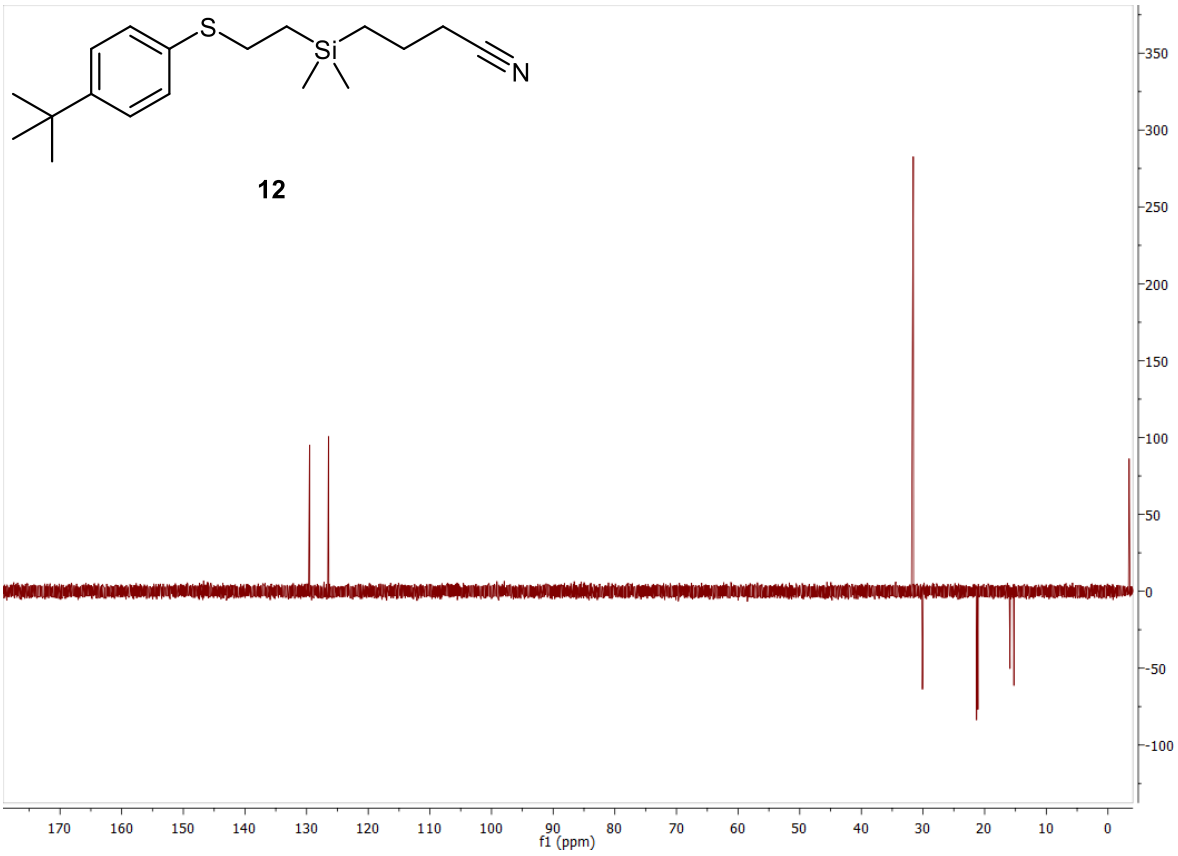
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV

11. Compound **12**:






S
Si
N
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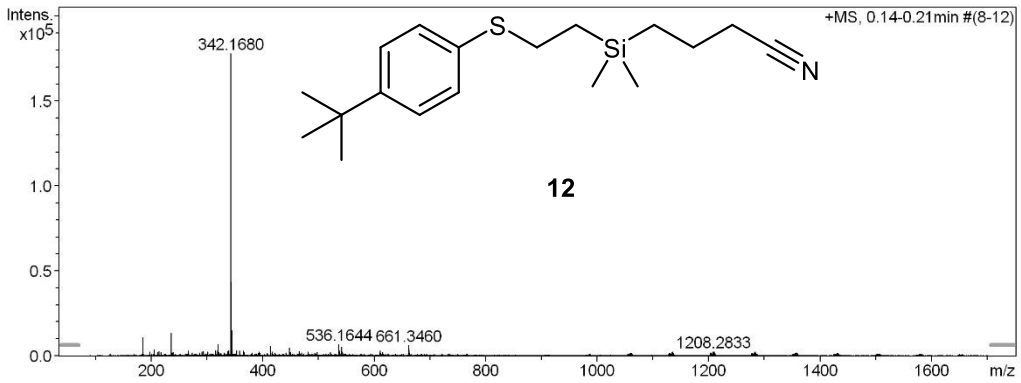
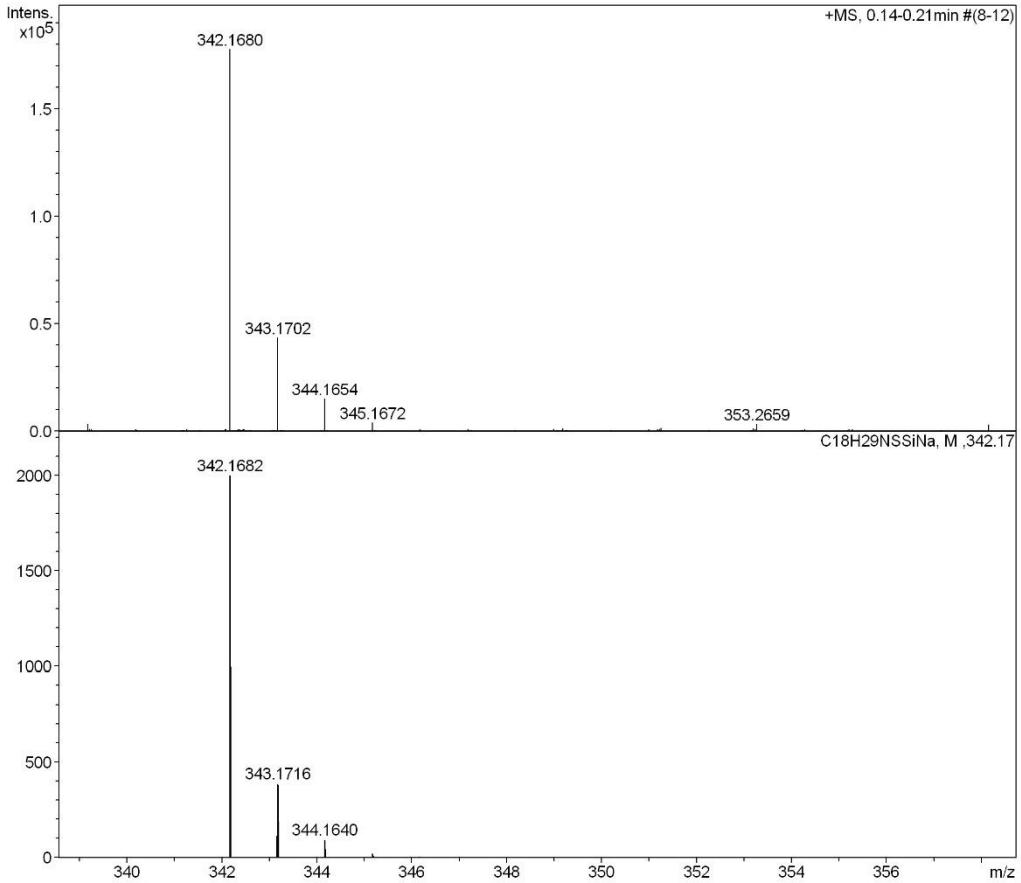
350
300
250
200
150
100
50
0
-50
-100
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / / Ba544**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m



12



High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^- Conf	z
342.1680	1	C 18 H 29 N Na S Si	100.00	342.1682	0.2	0.6	14.1	5.5	even	1+

Mass list

#	m/z	I %	I
1	185.1144	6.1	10811
2	197.0779	1.3	2273
3	205.0597	2.1	3693
4	211.0934	1.1	1918
5	214.0895	1.4	2564
6	217.1040	1.1	1995
7	225.1096	0.7	1279
8	236.0711	7.5	13266
9	237.0744	1.0	1782
10	239.0883	1.2	2050
11	266.1720	1.7	2995
12	273.1660	1.0	1753
13	286.1053	0.9	1583
14	291.1921	1.3	2369
15	293.1351	0.7	1285
16	293.2079	1.5	2725
17	301.1406	1.4	2433
18	315.1923	1.7	3038
19	319.2242	1.6	2914
20	320.1856	3.8	6727
21	321.1879	1.1	1886
22	321.2390	1.0	1738
23	325.1616	0.8	1371
24	331.1877	0.8	1414
25	331.2077	1.0	1694
26	337.2116	1.5	2714
27	339.1778	1.8	3278
28	342.1680	100.0	177632
29	343.1702	24.5	43451
30	344.1654	8.4	14947
31	345.1672	2.1	3768
32	353.2659	1.8	3133
33	358.1417	1.6	2896
34	365.1048	1.7	2931
35	365.2682	0.9	1534
36	367.2085	1.2	2084
37	367.2449	0.8	1478
38	381.2961	1.0	1843
39	391.2092	0.8	1338
40	393.2972	1.3	2343
41	395.2400	0.7	1326
42	395.2769	0.7	1331
43	407.3122	0.9	1553
44	413.2657	3.2	5648
45	414.2690	0.9	1513
46	417.3450	1.4	2409
47	421.3292	1.0	1745
48	441.2972	1.0	1697
49	447.3440	2.6	4570
50	449.3731	1.1	2004
51	465.3696	1.5	2608
52	469.3284	0.9	1662
53	481.3128	0.9	1625
54	481.3635	1.3	2303
55	493.3494	0.7	1326
56	497.3579	1.1	1907
57	521.3799	1.1	1962
58	536.1644	3.6	6472
59	537.1658	1.8	3148
60	538.1629	1.3	2380
61	541.1201	3.0	5299
62	542.1214	1.3	2394

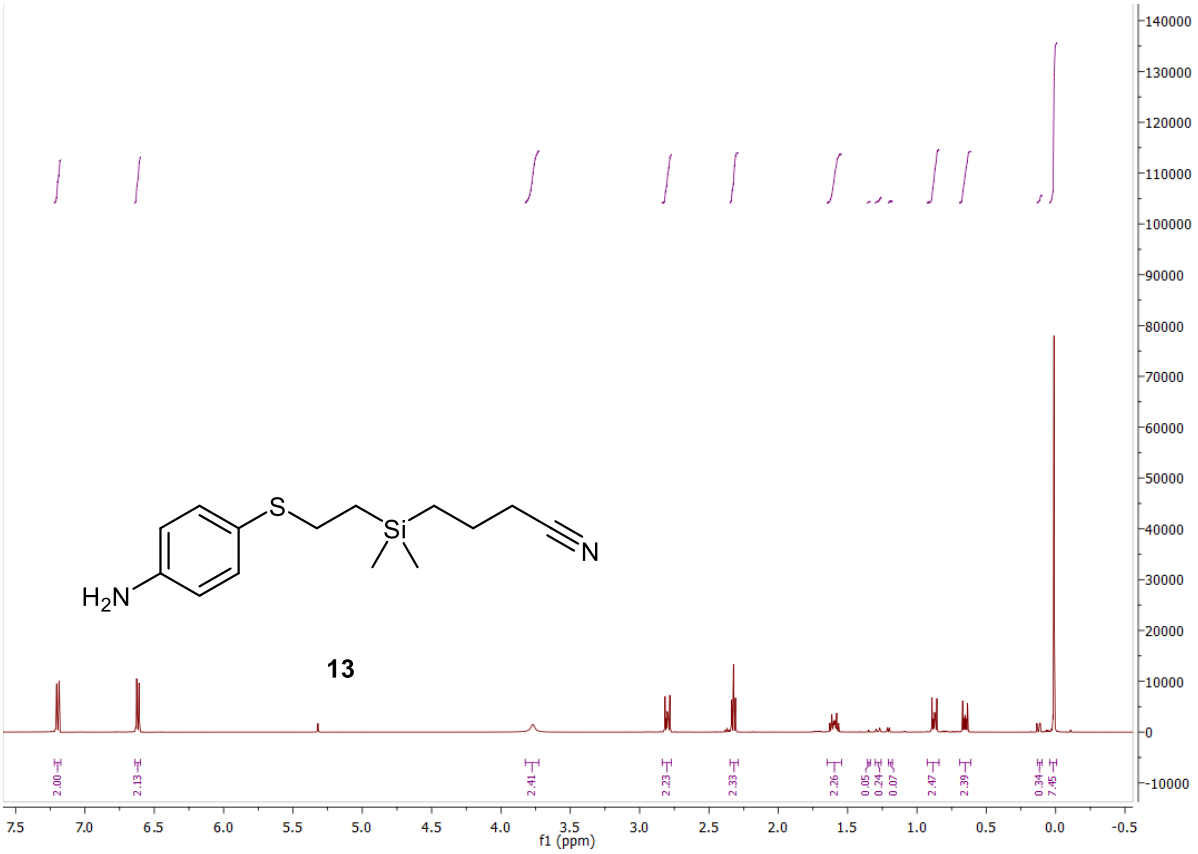
High Resolution Mass Spectrometry Report

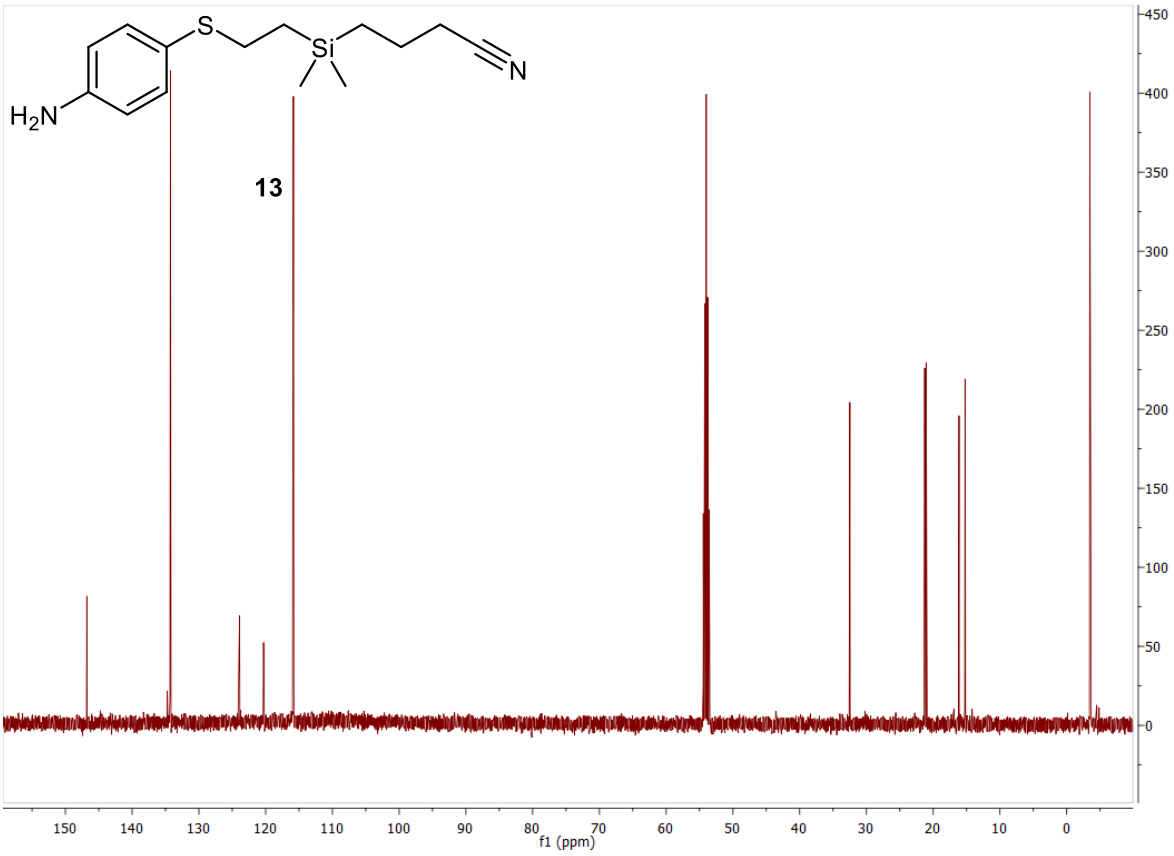
#	m/z	I %	I
63	543.1195	0.9	1645
64	609.3590	0.9	1656
65	610.1839	1.7	2967
66	611.1855	0.9	1542
67	612.1813	0.7	1284
68	615.1386	1.1	1879
69	661.3460	3.3	5936
70	662.3488	2.0	3599
71	663.3469	1.0	1835
72	1059.2482	0.7	1314
73	1060.2486	0.8	1442
74	1061.2467	0.8	1413
75	1129.3089	0.8	1378
76	1130.3082	0.8	1460
77	1133.2643	1.0	1818
78	1134.2666	1.1	1992
79	1135.2637	1.2	2169
80	1136.2627	0.9	1512
81	1202.3258	0.9	1591
82	1203.3273	1.0	1700
83	1204.3253	0.9	1582
84	1207.2800	1.1	2011
85	1208.2833	1.4	2419
86	1209.2807	1.3	2229
87	1210.2809	1.0	1829
88	1277.3445	0.9	1533
89	1278.3443	0.8	1480
90	1281.3021	1.0	1789
91	1282.2998	1.2	2093
92	1283.3005	1.3	2241
93	1284.2962	1.0	1860
94	1355.3198	0.8	1338
95	1356.3192	0.9	1670
96	1357.3145	1.0	1852
97	1358.3133	0.9	1527
98	1430.3313	0.8	1427
99	1431.3320	0.9	1552
100	1432.3320	0.7	1268

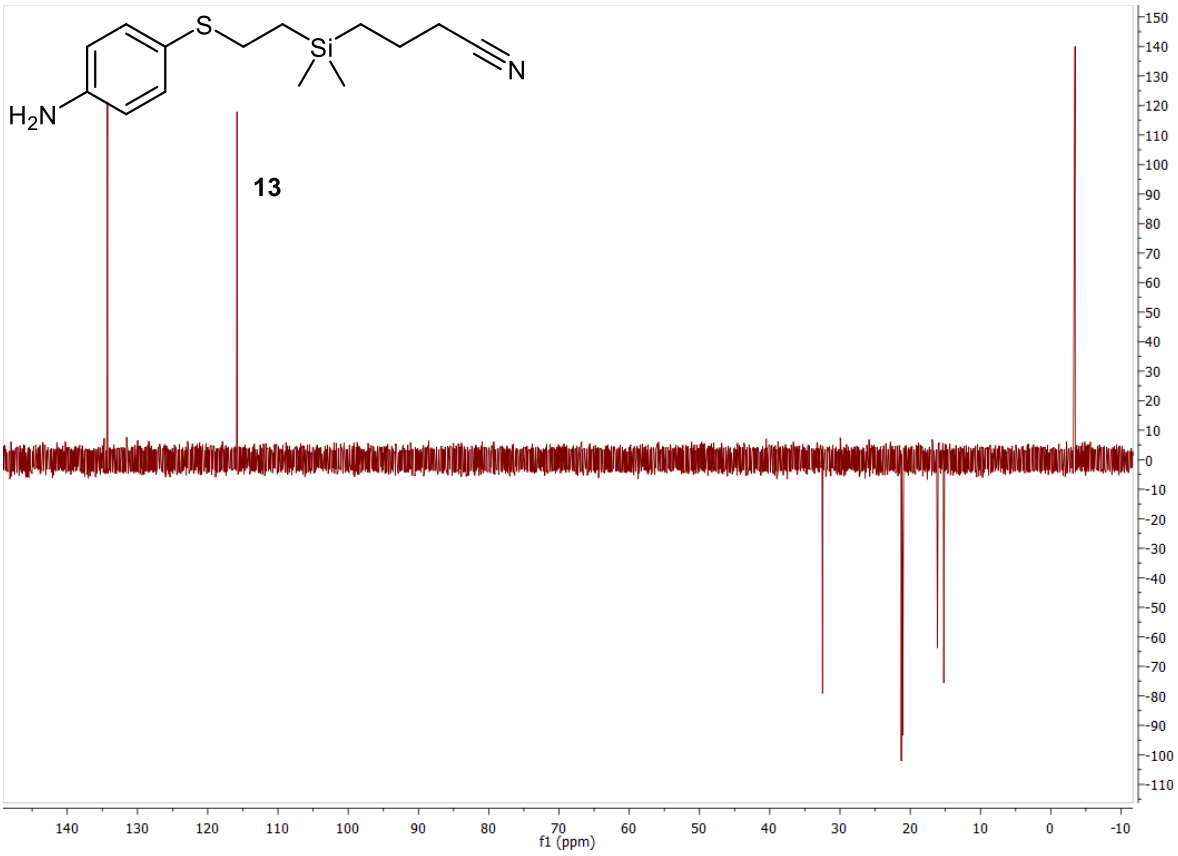
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV

12. Compound **13**:

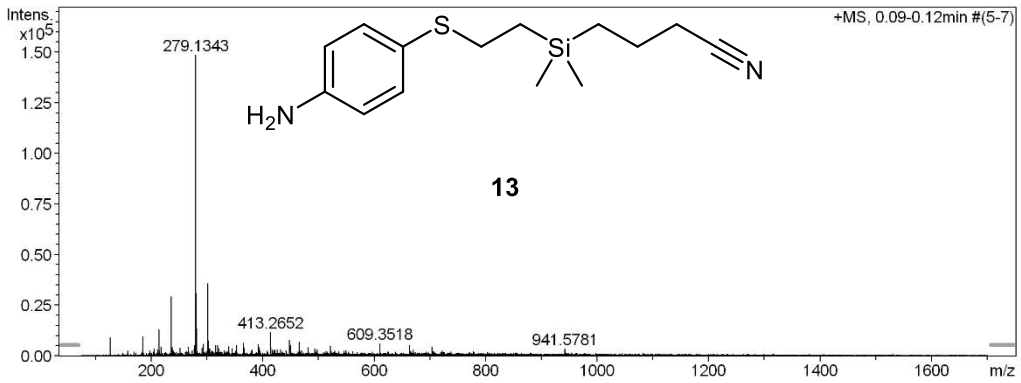




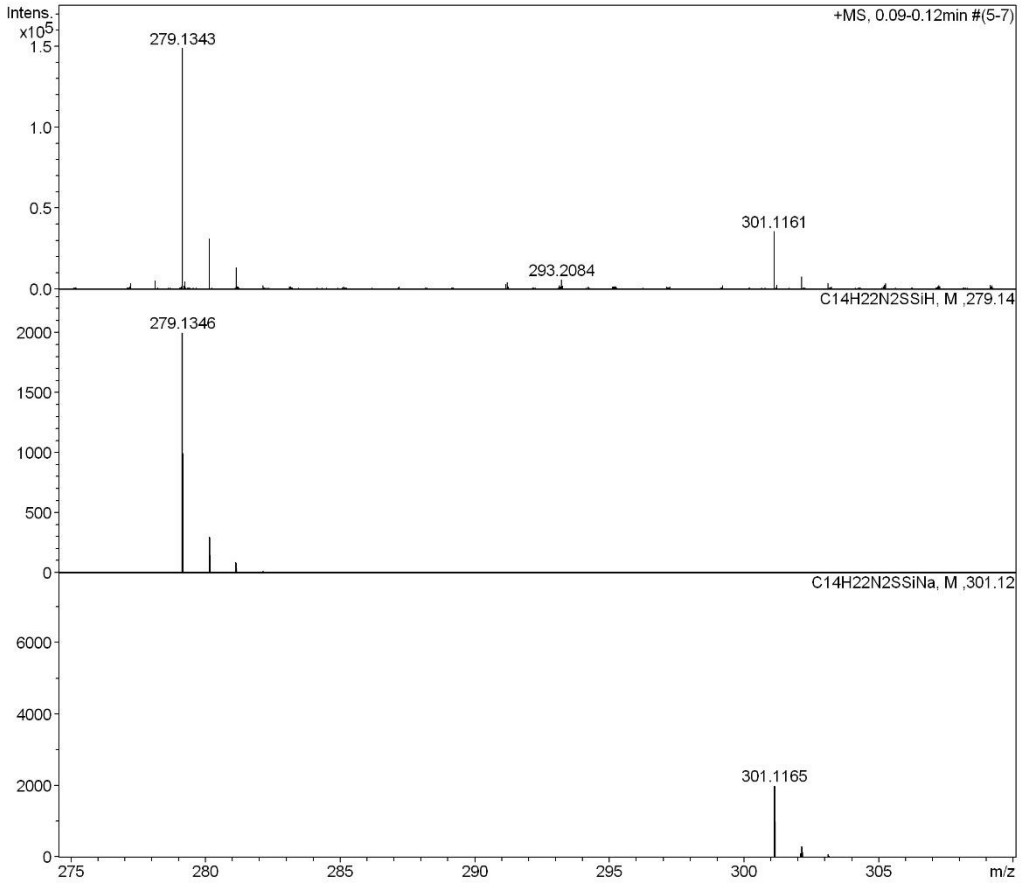

S
Si
N
H2N
13
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / / Ba545**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m



13



High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^- Conf	z
279.1343	1	C 14 H 23 N 2 S Si	100.00	279.1346	0.3	1.1	7.4	5.5	even	1+
301.1161	1	C 14 H 22 N 2 Na S Si	100.00	301.1165	0.5	1.5	4.4	5.5	even	

Mass list

#	m/z	I %	I
1	126.0732	6.0	8848
2	158.0275	1.6	2316
3	183.0775	1.4	2027
4	185.1147	6.4	9501
5	197.0776	1.8	2709
6	205.0597	2.3	3393
7	211.0936	2.0	3032
8	214.0895	8.7	12942
9	215.0926	1.6	2329
10	217.1049	2.9	4273
11	236.0713	19.7	29191
12	237.0744	2.8	4099
13	239.0882	1.8	2671
14	251.1031	2.6	3834
15	263.0813	1.4	2070
16	266.1721	2.9	4298
17	273.1668	1.8	2615
18	277.2143	2.4	3582
19	278.1265	3.4	4995
20	279.1343	100.0	148433
21	279.2291	3.0	4396
22	280.1364	20.8	30893
23	281.1317	8.9	13195
24	282.1340	1.4	2133
25	291.1337	2.0	2921
26	291.1924	2.6	3852
27	293.1346	1.5	2221
28	293.2084	3.9	5821
29	299.1941	1.5	2219
30	301.1161	24.0	35590
31	301.2102	1.7	2533
32	302.1185	5.0	7485
33	303.1130	2.4	3554
34	305.2078	1.5	2264
35	305.2448	2.3	3387
36	309.1308	1.6	2411
37	309.2038	1.5	2242
38	311.1453	1.4	2018
39	315.1918	3.5	5214
40	319.2237	3.4	5087
41	321.2398	2.5	3661
42	325.1608	1.4	2027
43	331.2083	1.7	2537
44	335.2180	1.5	2163
45	339.1776	3.1	4558
46	345.1421	2.4	3553
47	351.2499	1.6	2411
48	353.1921	1.5	2189
49	353.2654	3.5	5251
50	365.1051	4.2	6259
51	365.2704	2.0	3008
52	367.2078	2.6	3928
53	367.2441	1.8	2706
54	379.2809	1.7	2496
55	381.2968	2.0	2933
56	391.2077	1.9	2801
57	391.2836	3.7	5499
58	393.2983	2.8	4103
59	395.2389	1.6	2432
60	395.2762	1.6	2424
61	395.3622	1.8	2679

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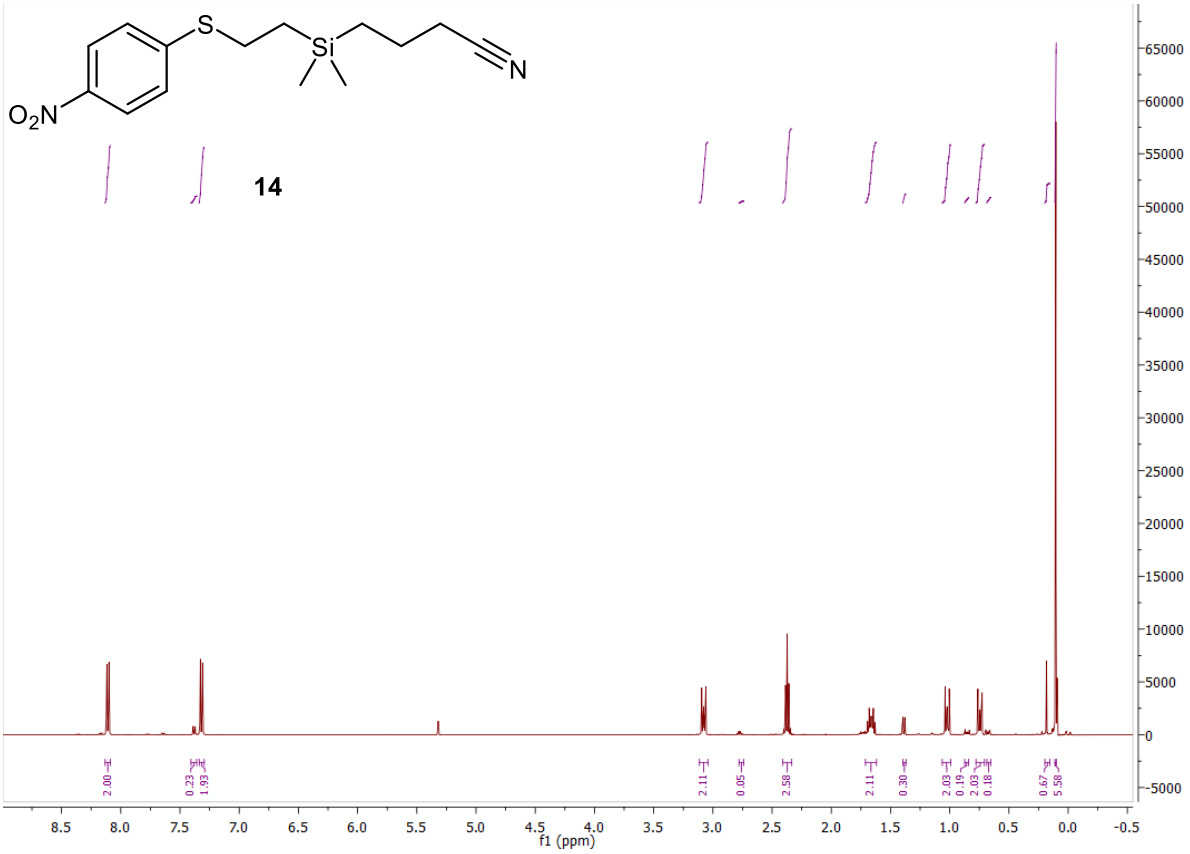
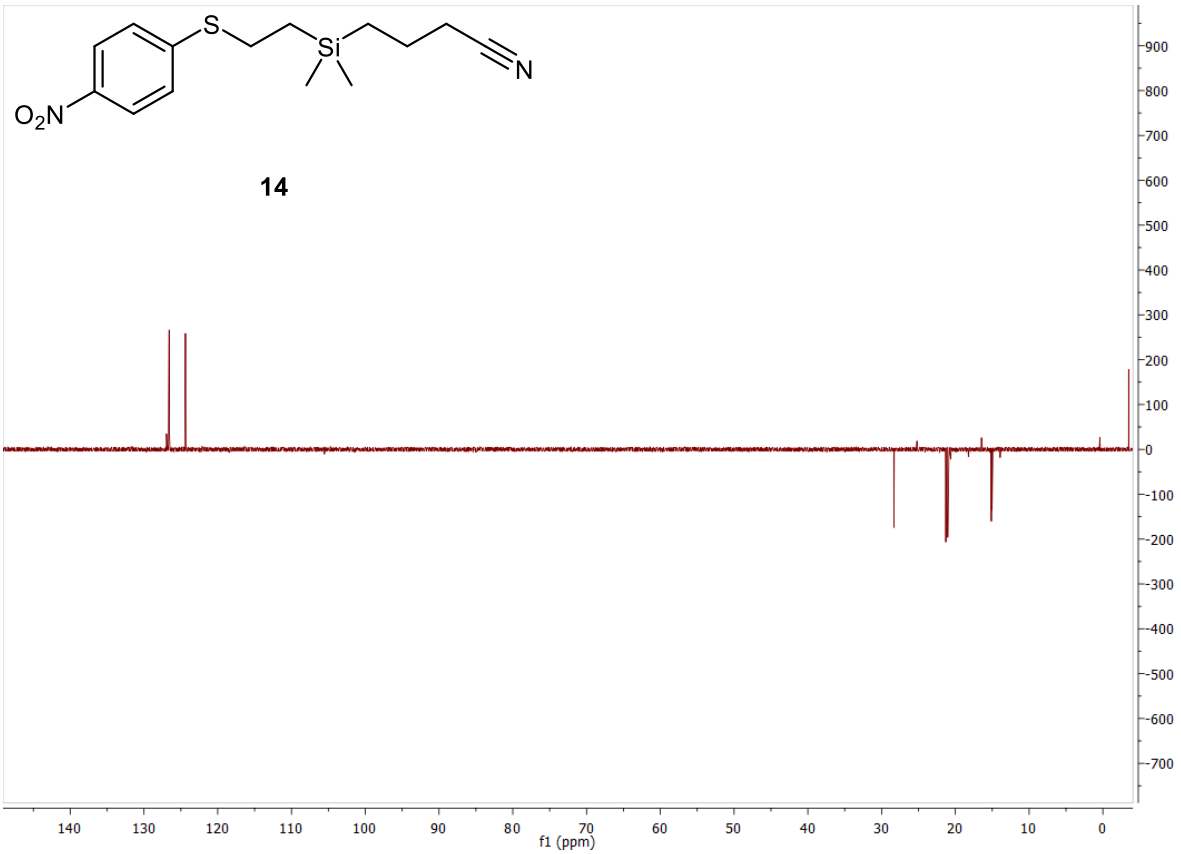
#	m/z	I %	I
62	407.3128	1.6	2378
63	413.2652	7.7	11454
64	414.2695	2.6	3832
65	417.3445	2.0	3033
66	419.3148	1.7	2534
67	421.3300	2.1	3176
68	425.3640	1.9	2872
69	432.2314	2.0	2900
70	441.2972	1.8	2702
71	447.3443	5.1	7615
72	448.3478	1.5	2257
73	449.3729	3.6	5352
74	465.3695	4.6	6788
75	466.3749	1.6	2338
76	469.3265	1.8	2625
77	481.3137	2.0	2999
78	481.3641	2.7	3977
79	493.3488	2.2	3285
80	497.3595	2.1	3145
81	513.3529	1.5	2278
82	516.4256	1.4	2025
83	521.3797	3.2	4732
84	522.3830	1.4	2066
85	529.3477	1.7	2516
86	536.1652	1.4	2063
87	545.3436	1.7	2497
88	549.4112	1.9	2757
89	561.3392	1.5	2182
90	609.3518	4.1	6090
91	625.3182	1.4	2045
92	663.2498	3.4	5066
93	664.2520	1.6	2390
94	669.4119	1.9	2859
95	703.4898	2.9	4280
96	705.4924	1.4	2072
97	721.5175	1.6	2356
98	777.5216	1.4	2149
99	941.5781	2.3	3436
100	942.5817	1.8	2681

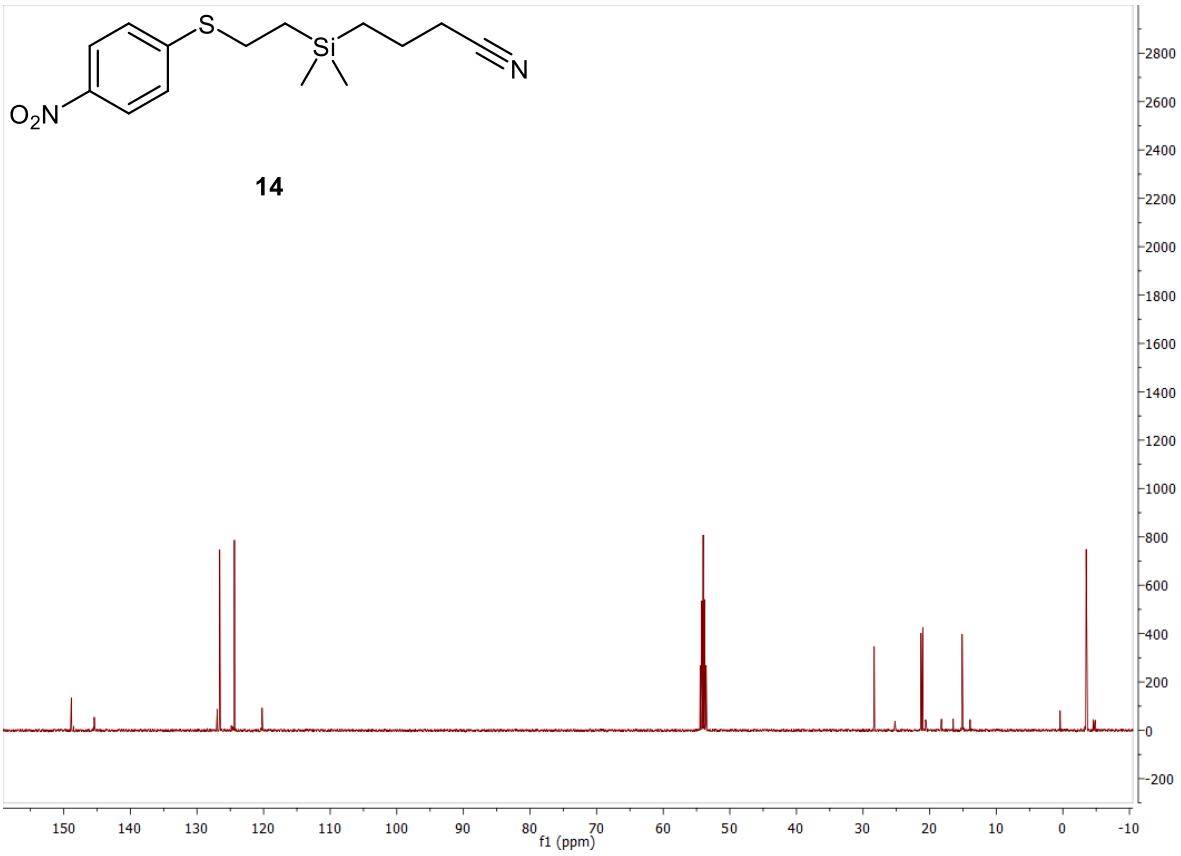
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV

13. Compound **14**:

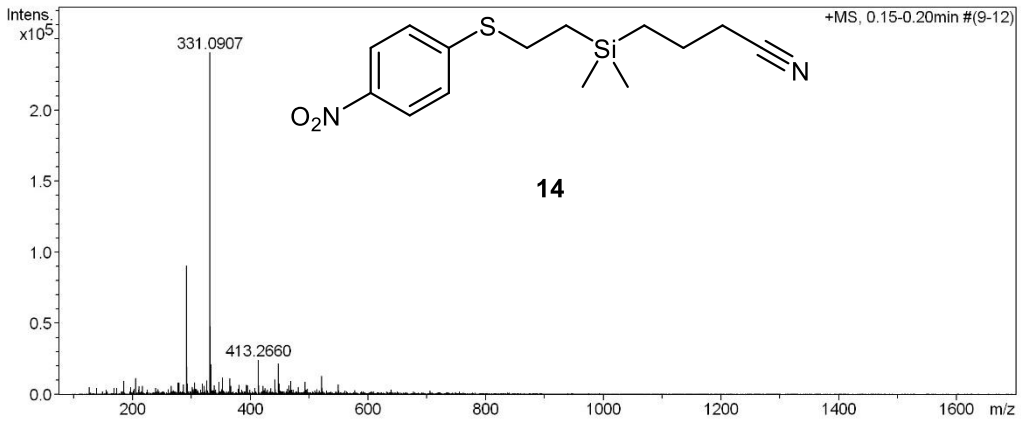


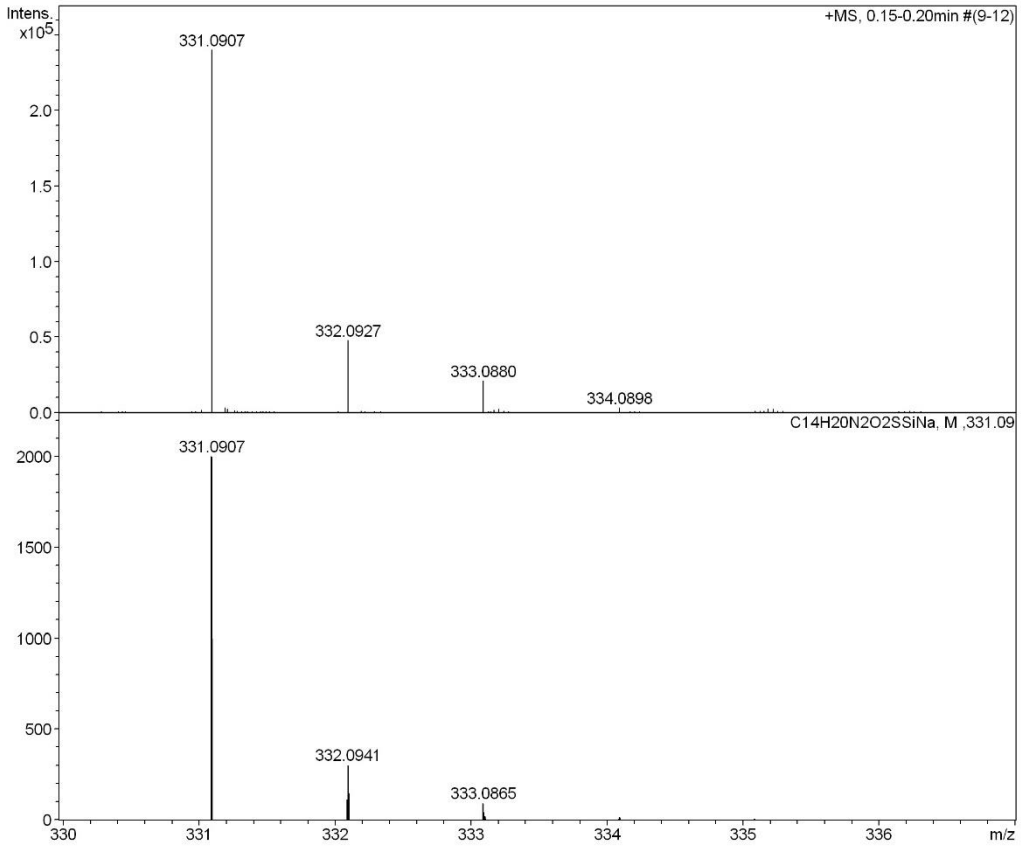



S
Si
N
O_2N
14
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba513 PDC 1#2**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	21 Direct_pos_low.m





14

High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^- Conf	z
331.0907	1	C 14 H 20 N 2 Na O 2 S Si	100.00	331.0907	-0.1	-0.2	12.7	6.5	even	1+

Mass list

#	m/z	I %	I
1	126.0738	2.0	4835
2	139.0504	1.9	4466
3	155.0535	1.2	2959
4	169.0470	1.4	3344
5	169.1444	1.8	4321
6	173.0783	1.8	4293
7	185.1144	3.9	9388
8	197.0782	2.0	4768
9	203.0521	1.6	3855
10	205.0597	4.7	11386
11	210.1099	1.3	3177
12	211.0938	2.3	5410
13	217.1044	2.4	5708
14	225.1090	1.3	3091
15	239.0883	1.9	4602
16	243.0834	1.5	3491
17	261.1302	1.4	3294
18	266.1721	2.5	5921
19	269.1492	1.2	2784
20	277.2134	3.3	7847
21	279.2288	3.5	8333
22	286.1762	2.8	6726
23	291.1316	37.5	90080
24	291.1927	1.7	4117
25	291.2287	1.2	2959
26	292.1331	8.0	19142
27	293.1306	3.2	7611
28	293.2082	2.9	6995
29	293.2447	1.4	3419
30	301.1401	2.1	5149
31	303.2290	1.5	3576
32	305.2449	3.4	8121
33	307.1072	1.6	3825
34	307.2599	1.2	2946
35	309.1080	1.4	3248
36	309.1298	1.4	3262
37	309.2030	1.3	3032
38	315.1919	1.2	2989
39	319.2240	3.2	7656
40	321.2392	2.4	5794
41	325.1611	1.3	3018
42	326.1346	4.0	9597
43	327.1376	1.1	2527
44	331.0907	100.0	240044
45	331.1873	1.4	3364
46	332.0927	19.9	47792
47	333.0880	8.7	20916
48	334.0898	1.4	3275
49	337.2349	1.1	2717
50	339.1773	2.5	6110
51	341.2652	1.3	3158
52	347.0638	3.6	8523
53	351.2504	1.5	3584
54	353.1930	1.3	3116
55	353.2658	4.9	11826
56	365.1049	4.6	10934
57	365.2723	1.9	4631
58	367.2088	2.0	4848
59	367.2451	2.5	5949
60	379.2814	1.6	3820
61	381.1666	1.2	2814
62	381.2974	2.7	6492

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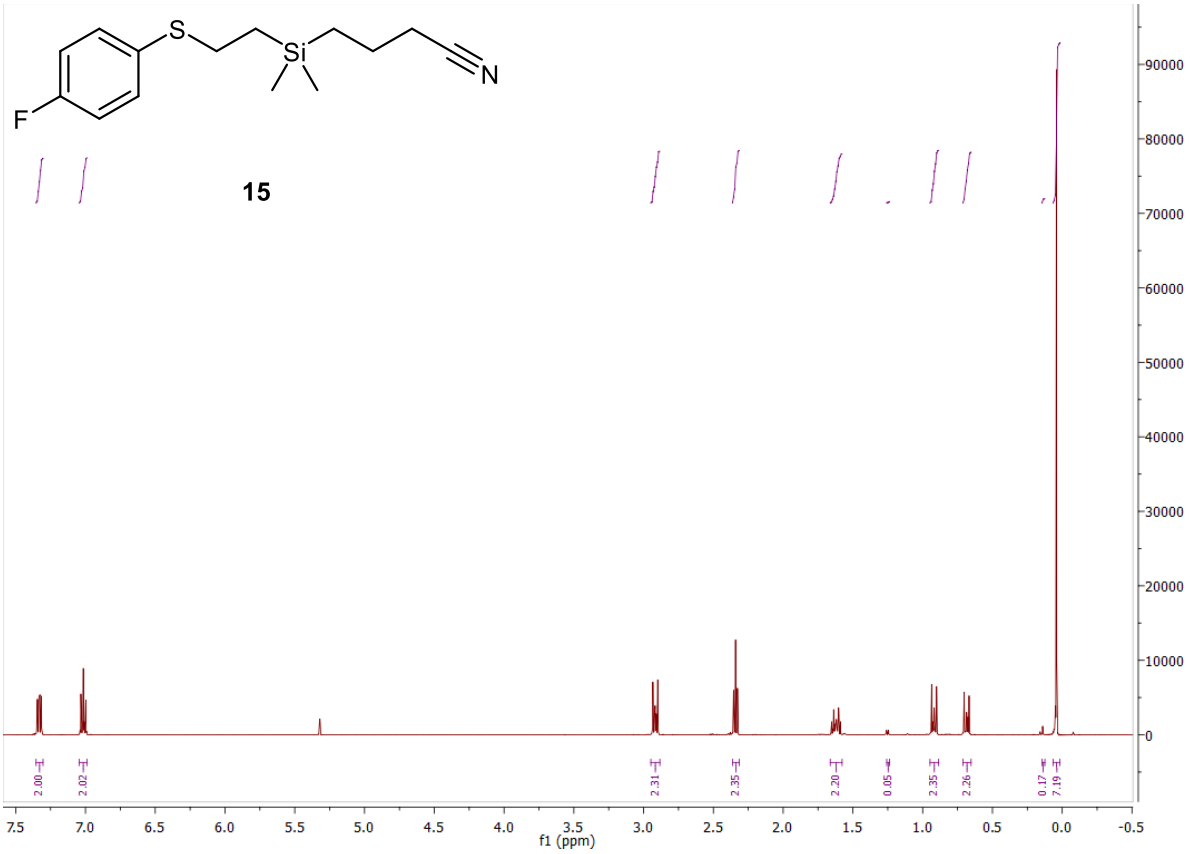
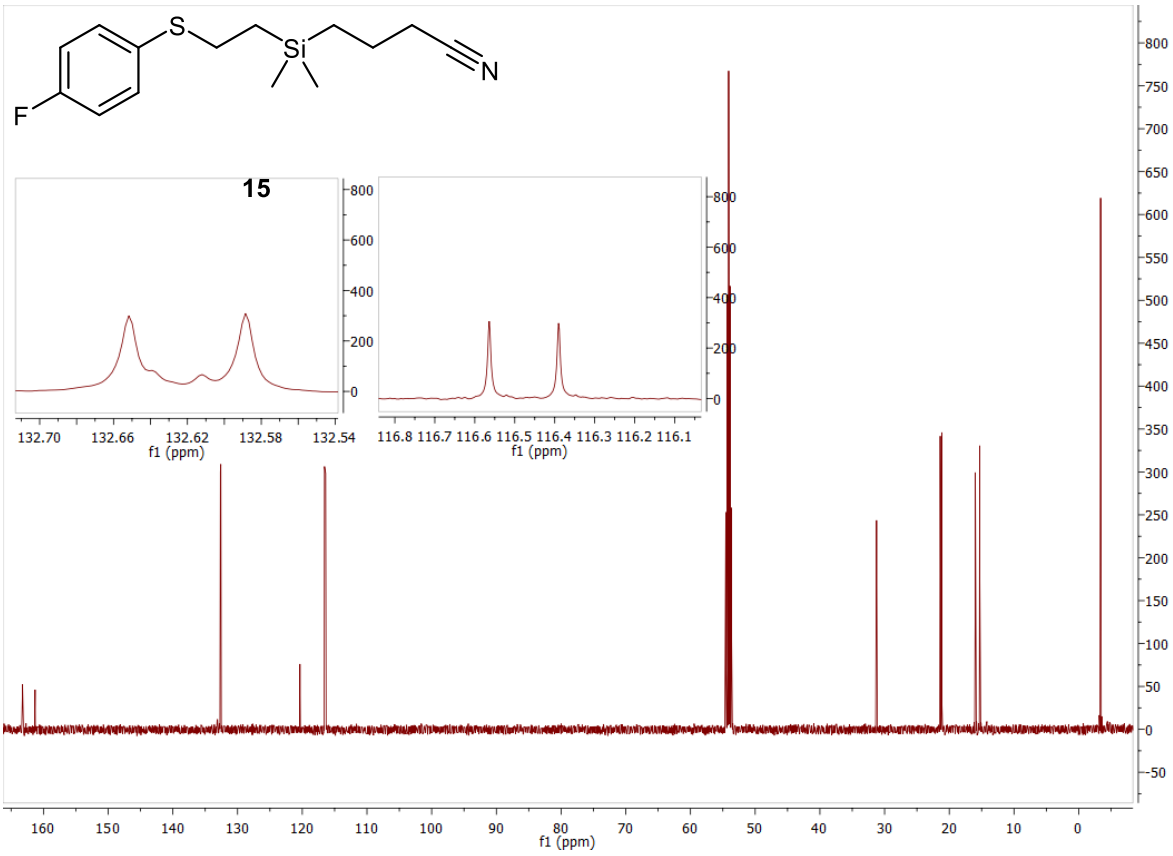
#	m/z	I %	I
63	385.2920	1.3	3078
64	393.2985	2.7	6522
65	395.2403	1.3	3191
66	395.2760	2.6	6258
67	399.1764	1.3	3035
68	407.3124	1.8	4347
69	413.2660	9.9	23884
70	414.2689	2.6	6345
71	421.3285	2.4	5779
72	423.3088	1.2	2803
73	425.2144	1.7	4199
74	429.3181	1.3	3049
75	435.3435	1.7	4007
76	441.2970	4.2	10138
77	442.2996	1.4	3322
78	447.3444	9.0	21629
79	448.3476	3.0	7184
80	449.3708	3.1	7448
81	463.3376	1.5	3611
82	463.3743	1.5	3553
83	465.3693	2.5	6108
84	467.2981	1.1	2624
85	469.3286	3.9	9367
86	470.3313	1.3	3077
87	473.3439	1.2	2947
88	481.3130	1.5	3550
89	481.3648	2.0	4746
90	493.3498	3.6	8610
91	494.3527	1.2	2916
92	495.3297	1.2	2868
93	497.3587	1.5	3718
94	513.3533	1.4	3378
95	521.3805	5.3	12751
96	522.3842	1.9	4585
97	549.4122	2.9	6864
98	550.4158	1.1	2549
99	577.4425	1.1	2634
100	639.1915	1.2	2979

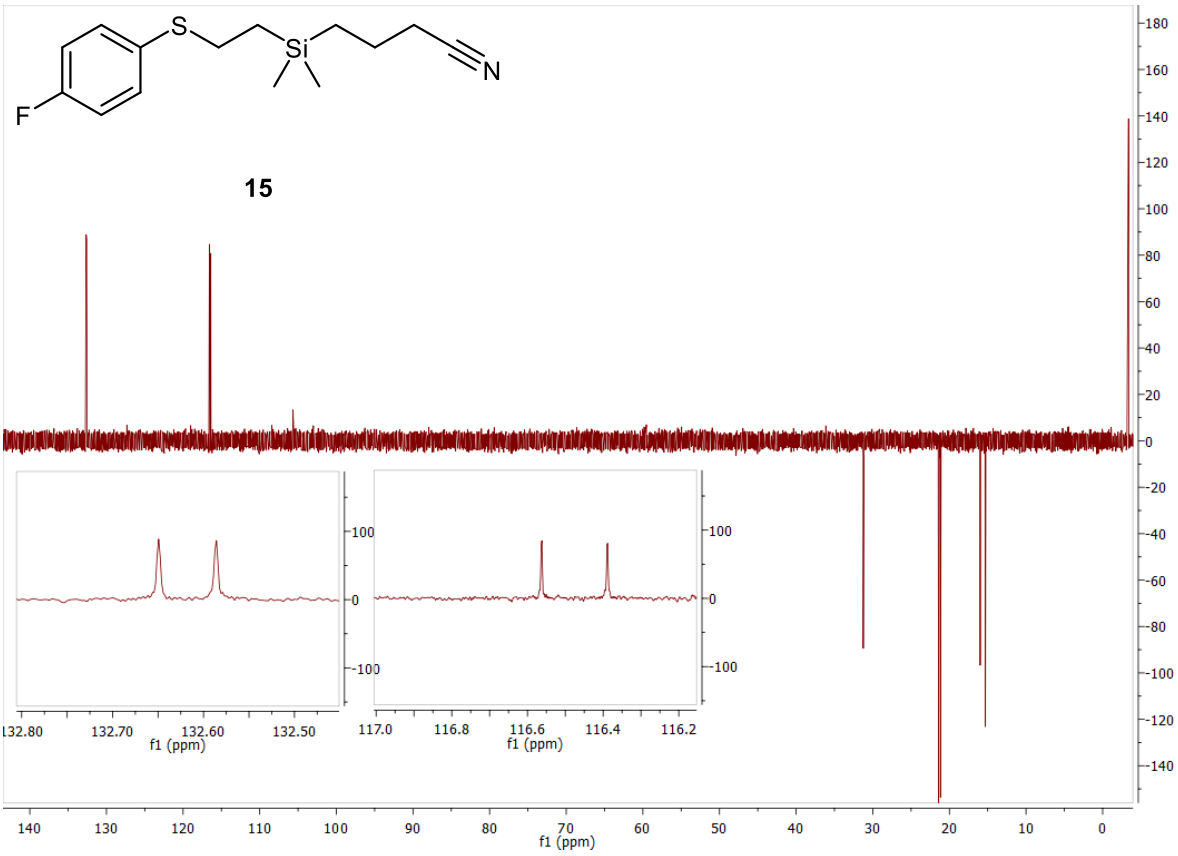
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV

14. Compound **15**:

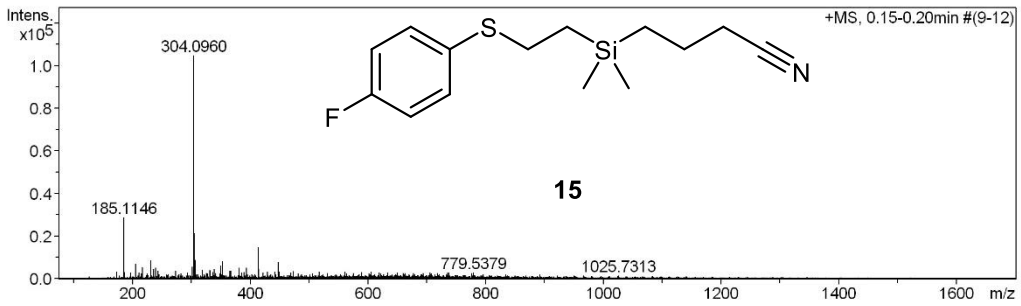


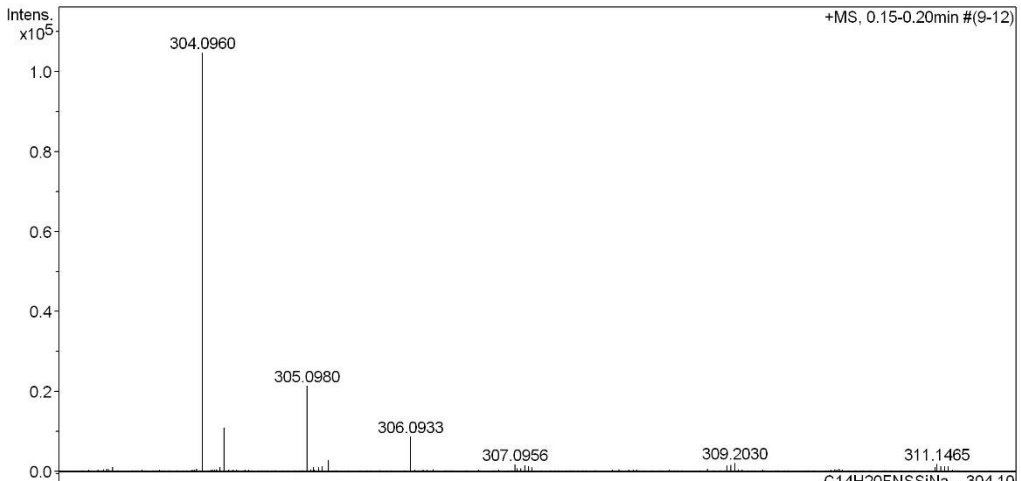


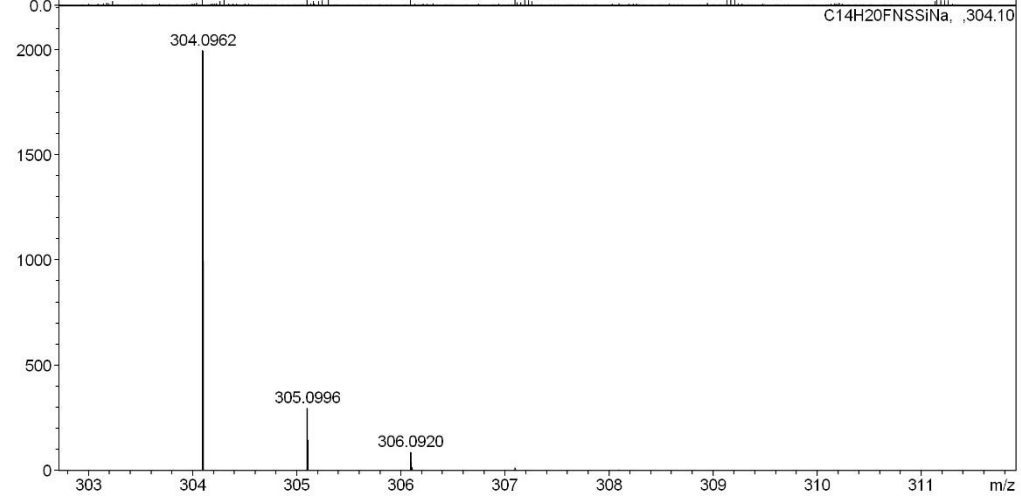

S
Si
N
F
15
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
100
0
-100
132.80
132.70
132.60
132.50
f1 (ppm)
117.0
116.8
116.6
116.4
116.2
f1 (ppm)
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba591 chr1_1**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m







High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	z
304.0960	1	C 14 H 20 F N Na S Si	100.00	304.0962	0.2	0.7	10.0	5.5	even	1+

Mass list

#	m/z	I %	I
1	173.0784	3.1	3214
2	185.1146	27.4	28676
3	186.1178	2.9	3022
4	197.0780	2.6	2757
5	205.0597	6.5	6762
6	211.0944	2.6	2672
7	215.1250	2.1	2224
8	217.1044	5.0	5260
9	225.1094	2.2	2298
10	231.1353	8.0	8359
11	236.0716	4.1	4251
12	239.0884	4.7	4952
13	243.0982	3.4	3569
14	245.0778	1.9	2025
15	261.1304	2.0	2126
16	273.1664	3.6	3758
17	279.2289	2.1	2148
18	282.1136	2.2	2290
19	293.2084	2.6	2734
20	301.1405	5.3	5561
21	304.0960	100.0	104617
22	304.2996	10.4	10864
23	305.0980	20.4	21307
24	305.3029	2.7	2838
25	306.0933	8.2	8605
26	309.2030	2.0	2051
27	319.1296	3.9	4039
28	319.2239	2.2	2255
29	321.2397	1.9	1978
30	325.1619	2.3	2433
31	326.3776	2.2	2261
32	327.1582	2.2	2276
33	331.2087	3.8	3996
34	332.3302	3.5	3686
35	336.1212	2.9	2985
36	339.1777	4.3	4451
37	341.2656	2.4	2482
38	348.9900	2.2	2263
39	349.1408	5.8	6053
40	353.1938	1.9	1938
41	353.2656	7.6	7991
42	365.1053	3.6	3725
43	365.2670	2.5	2620
44	367.2093	3.5	3614
45	381.2973	4.7	4968
46	385.2915	2.6	2679
47	389.2501	2.7	2871
48	393.2973	4.8	4997
49	402.3570	2.1	2151
50	407.3128	2.0	2136
51	413.2658	14.0	14595
52	414.2698	4.1	4311
53	421.3286	2.6	2762
54	429.3182	3.1	3200
55	435.3445	2.0	2094
56	441.2972	3.1	3263
57	447.2925	2.5	2581
58	447.3442	7.5	7796
59	448.3477	2.3	2412
60	449.3605	3.0	3090
61	469.3273	2.7	2844
62	473.3442	3.3	3425

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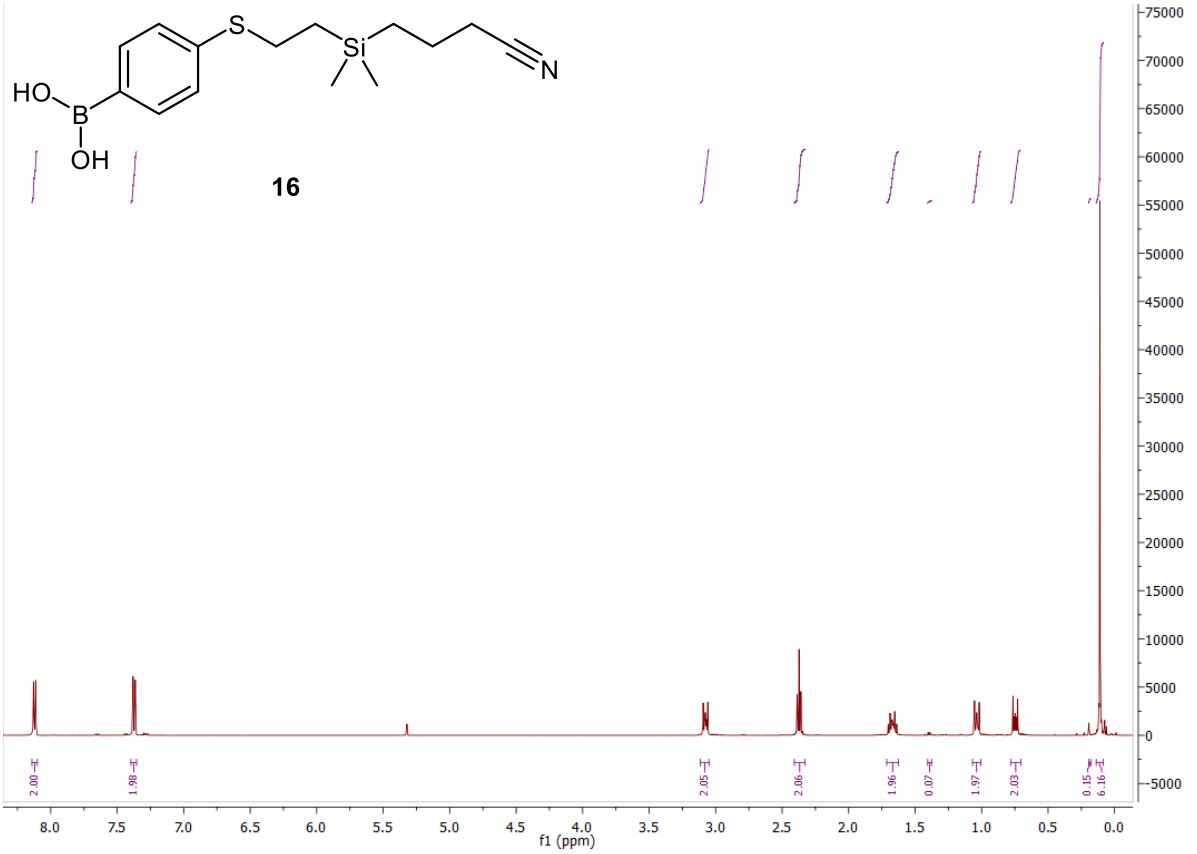
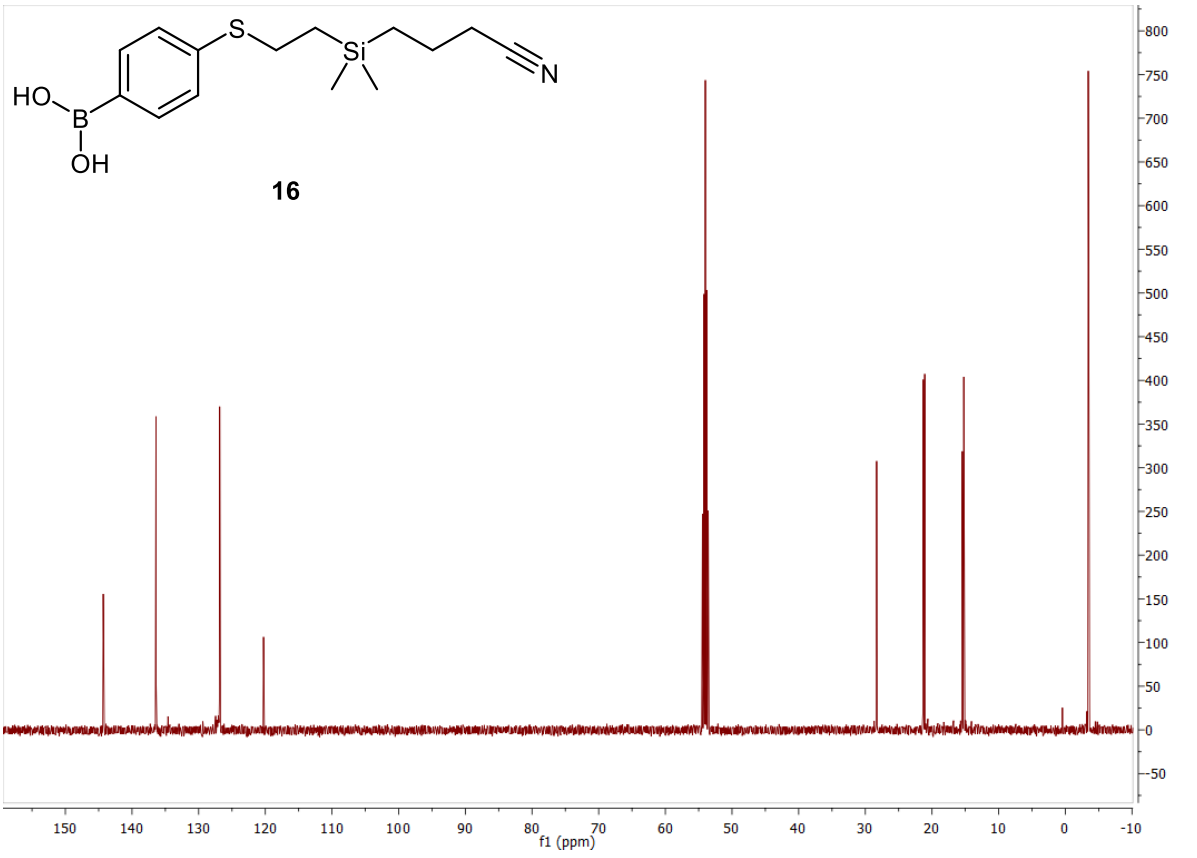
#	m/z	I %	I
63	481.3131	2.2	2340
64	487.3594	1.9	1995
65	505.3343	2.1	2212
66	517.3708	3.1	3292
67	531.3856	2.4	2530
68	553.3857	1.9	2017
69	561.3961	3.0	3169
70	563.3762	2.2	2312
71	575.4094	2.4	2505
72	585.2031	2.0	2055
73	589.4191	2.8	2887
74	601.4647	2.1	2211
75	605.4216	3.1	3286
76	619.4367	2.6	2720
77	621.4185	2.2	2304
78	626.4294	2.0	2075
79	633.4450	2.6	2772
80	647.4549	2.0	2054
81	649.4505	2.7	2786
82	659.5051	2.4	2465
83	663.4606	2.5	2603
84	669.4653	1.8	1914
85	677.4719	2.4	2491
86	679.4606	2.0	2044
87	691.4825	1.9	1982
88	693.4751	2.4	2508
89	705.4967	1.9	2020
90	705.5812	2.6	2757
91	706.4854	1.9	1946
92	707.4891	2.2	2285
93	717.5490	2.5	2579
94	721.4964	1.9	2038
95	733.5469	1.8	1928
96	735.5119	2.6	2760
97	737.5008	2.7	2833
98	775.5891	2.4	2509
99	779.5379	2.7	2835
100	795.5430	1.9	2036

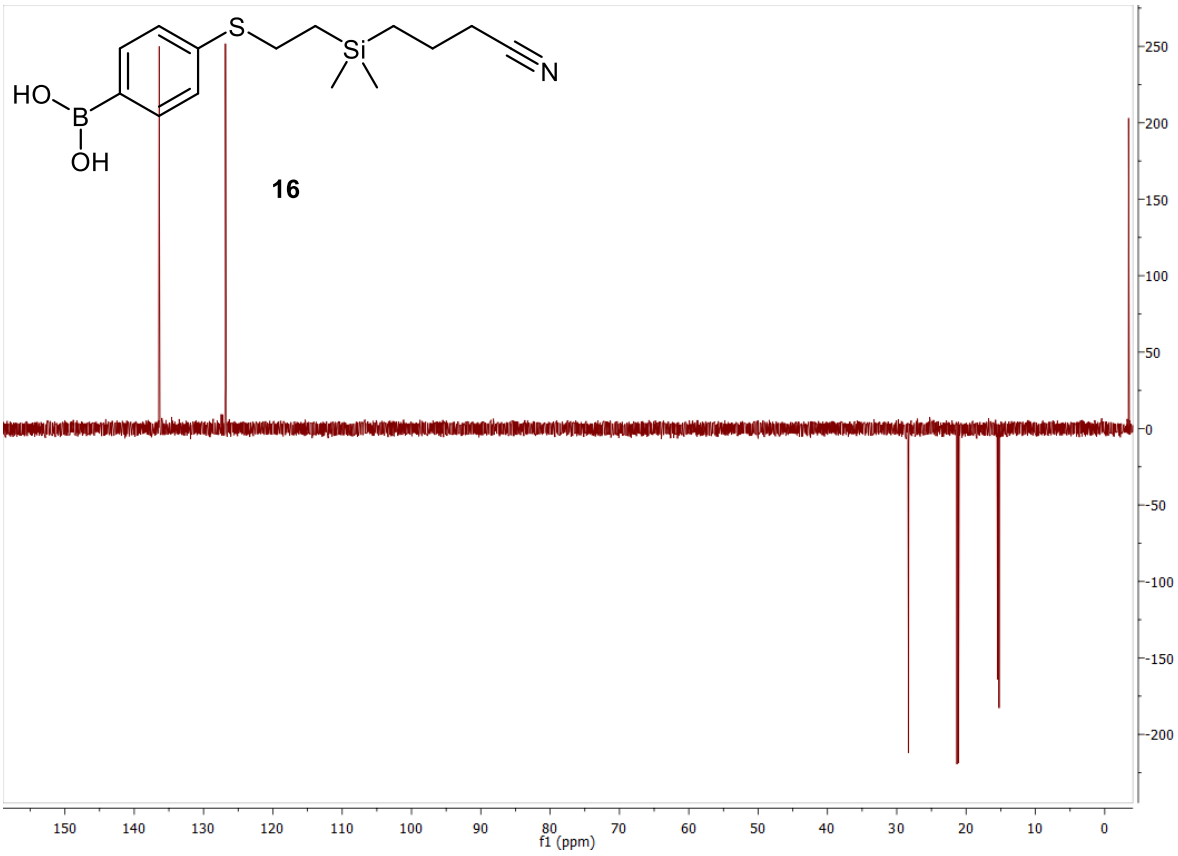
Acquisition Parameter

General	Fore Vacuum	2.69e+000 mBar	High Vacuum	1.01e-007 mBar	Source Type	ESI
	Scan Begin	75 m/z	Scan End	1700 m/z	Ion Polarity	Positive
Source	Set Nebulizer	0.4 Bar	Set Capillary	3600 V	Set Dry Gas	4.0 l/min
	Set Dry Heater	180 °C	Set End Plate Offset	-500 V		
Quadrupole	Set Ion Energy (MS only)	4.0 eV				
Coll. Cell	Collision Energy	8.0 eV	Set Collision Cell RF	350.0 Vpp		
Ion Cooler	Set Ion Cooler Transfer Time	75.0 µs	Set Ion Cooler Pre Pulse Storage Time	10.0 µs		

15. Compound **16**:

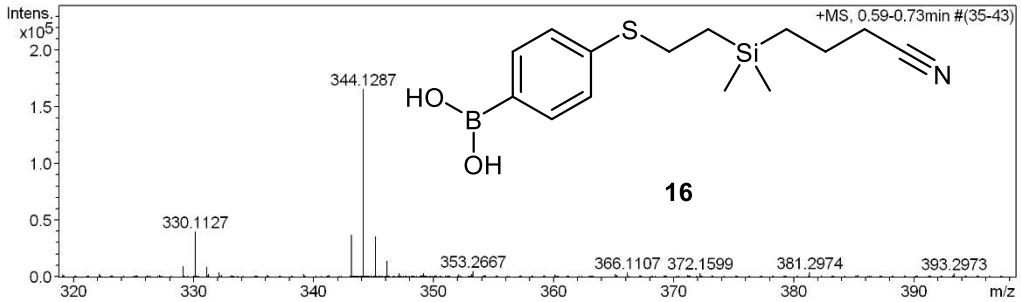


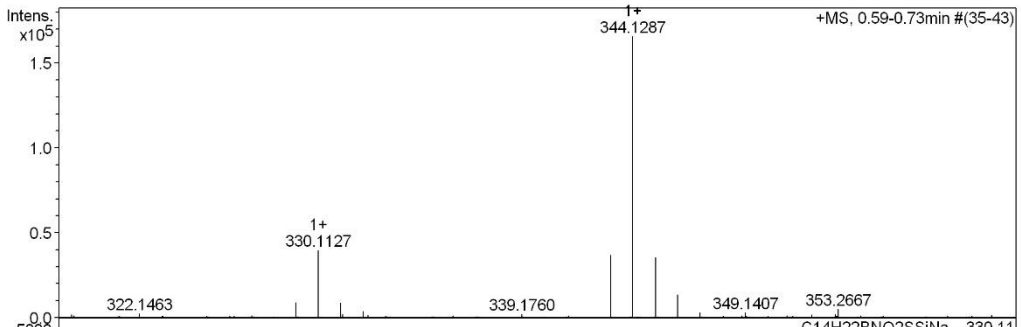


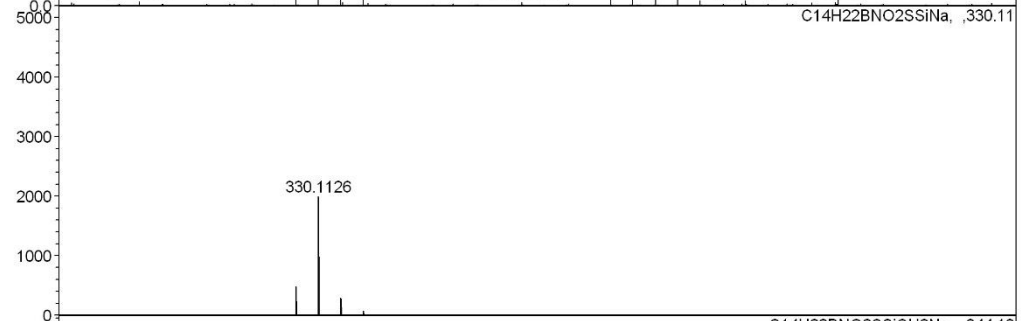

HO
B
OH
S
Si
N
16
250
200
150
100
50
0
-50
-100
-150
-200
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

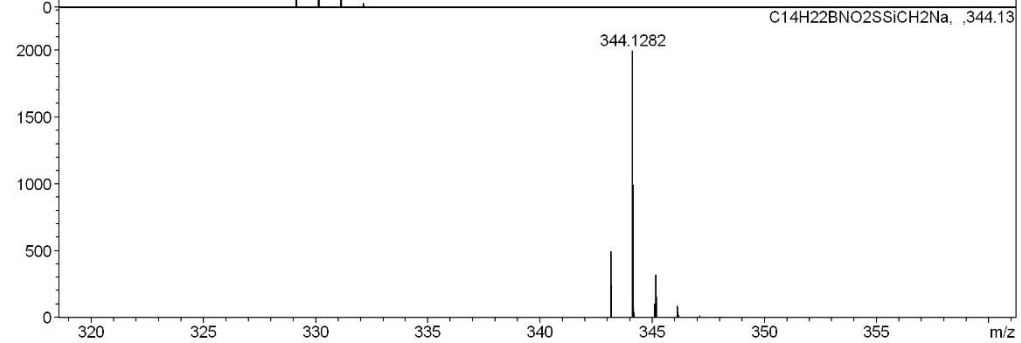
High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba524 chr1_1**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m









High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	z
330.1127	1	C 14 H 22 B N Na O 2 S Si	100.00	330.1129	-0.1	-0.2	6.2	5.5	even	1+
344.1287	1	C 15 H 24 B N Na O 2 S Si	100.00	344.1285	-0.1	-0.4	15.5	5.5	even	

Mass list

#	m/z	I %	I
1	173.0785	1.2	1937
2	185.1149	10.3	17034
3	186.1184	1.1	1891
4	197.0783	0.7	1176
5	205.0601	4.3	7091
6	211.0945	0.7	1209
7	215.1252	0.9	1445
8	217.1046	2.0	3346
9	225.1091	0.8	1283
10	226.9514	1.3	2147
11	231.1355	2.3	3726
12	236.0716	2.4	4029
13	239.0888	1.8	2931
14	242.2840	4.7	7741
15	243.0986	1.0	1730
16	243.2876	0.9	1548
17	245.0787	0.7	1170
18	259.1304	0.8	1353
19	261.1298	0.8	1356
20	273.1672	1.2	2052
21	277.2138	0.7	1161
22	279.1353	0.8	1352
23	279.2297	1.4	2387
24	286.1052	2.0	3292
25	291.1318	5.0	8316
26	292.1338	1.2	1909
27	293.2082	0.7	1187
28	293.2449	0.7	1201
29	294.9381	0.8	1247
30	297.2395	0.9	1434
31	301.1406	2.0	3243
32	301.2107	1.0	1602
33	302.1005	0.9	1471
34	303.2292	0.7	1168
35	304.0959	1.6	2654
36	304.2997	2.3	3870
37	305.2446	0.7	1143
38	319.1307	1.1	1813
39	322.1463	1.3	2209
40	327.1586	0.7	1161
41	329.1160	5.4	8963
42	330.1127	24.0	39622
43	331.1146	5.3	8710
44	331.2083	1.2	1959
45	332.1104	2.3	3834
46	332.3305	0.8	1388
47	339.1760	1.3	2126
48	341.2659	0.7	1236
49	343.1318	22.2	36725
50	344.1287	100.0	165256
51	345.1305	21.4	35419
52	346.1260	8.2	13595
53	347.1276	1.7	2827
54	349.1407	1.7	2830
55	352.0947	1.1	1758
56	353.1451	1.3	2130
57	353.2667	2.9	4788
58	354.2694	0.7	1151
59	360.1018	0.9	1544
60	365.1066	1.3	2128
61	366.1107	2.0	3366

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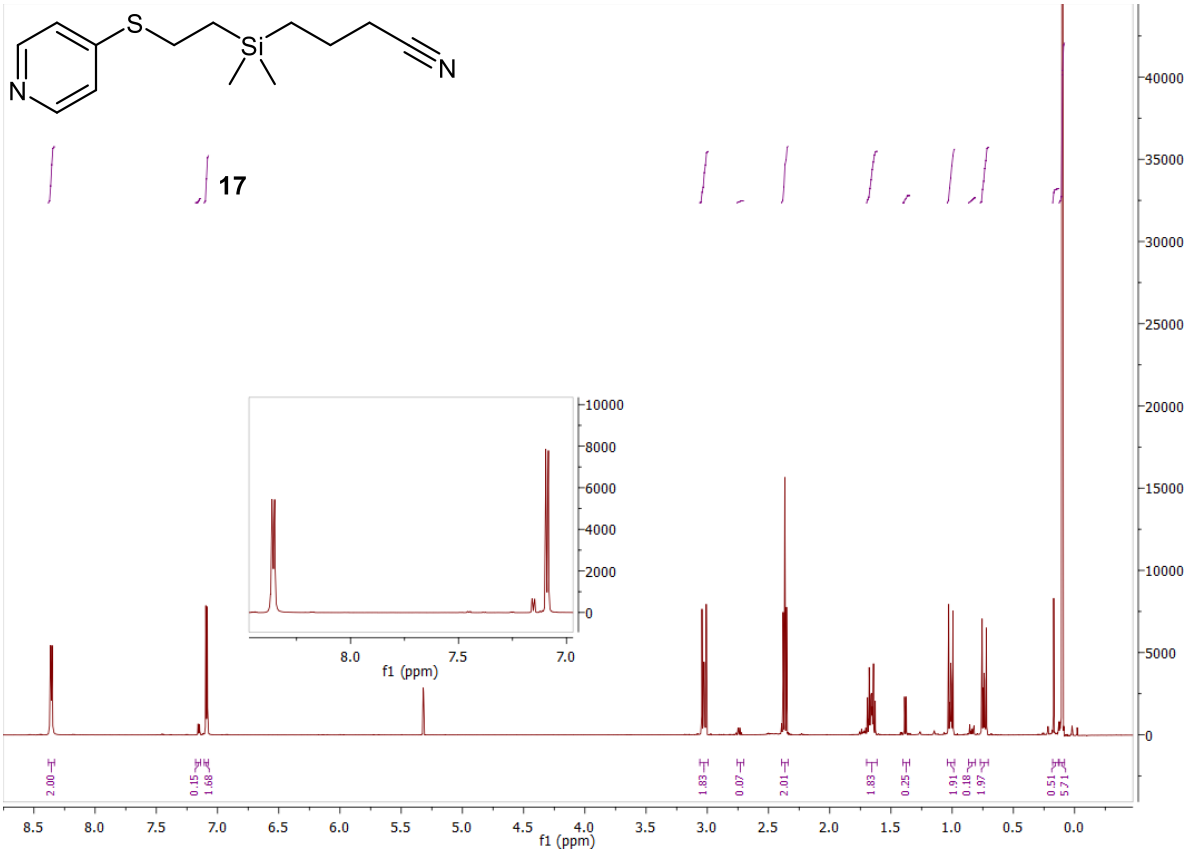
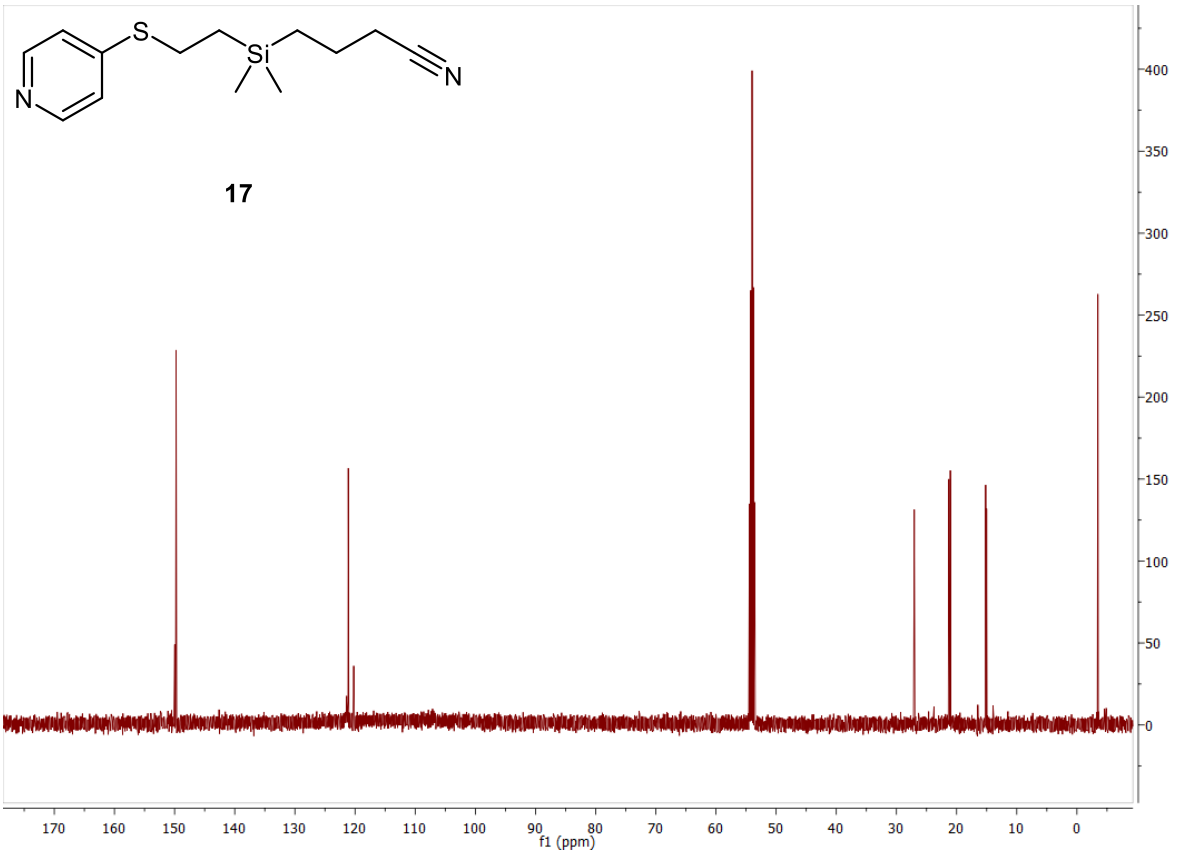
#	m/z	I %	I
62	371.1632	0.7	1179
63	372.1599	1.8	3021
64	381.2974	2.1	3482
65	385.2918	0.7	1214
66	393.2973	1.7	2781
67	413.2663	4.9	8020
68	414.2693	1.3	2189
69	421.3283	0.9	1563
70	429.3186	0.9	1425
71	433.3800	0.9	1436
72	441.2971	1.2	1941
73	447.3449	2.7	4493
74	448.3481	0.8	1404
75	449.3733	1.1	1898
76	463.3743	0.7	1169
77	465.3702	0.7	1117
78	469.3281	2.4	4035
79	470.3320	0.7	1197
80	473.3464	0.9	1544
81	517.3691	0.9	1502
82	536.1646	0.7	1231
83	541.1209	1.2	1911
84	542.1230	0.7	1138
85	545.3947	0.8	1261
86	561.3965	0.8	1362
87	575.4015	0.8	1389
88	603.4362	0.9	1425
89	605.4235	0.9	1491
90	619.4354	0.7	1220
91	624.3710	0.8	1335
92	633.4430	0.7	1141
93	649.4502	0.7	1134
94	663.4615	0.8	1251
95	677.4762	0.8	1274
96	703.5315	0.7	1211
97	705.5827	3.5	5856
98	706.5845	1.6	2610
99	707.4860	0.7	1134
100	721.5714	0.7	1151

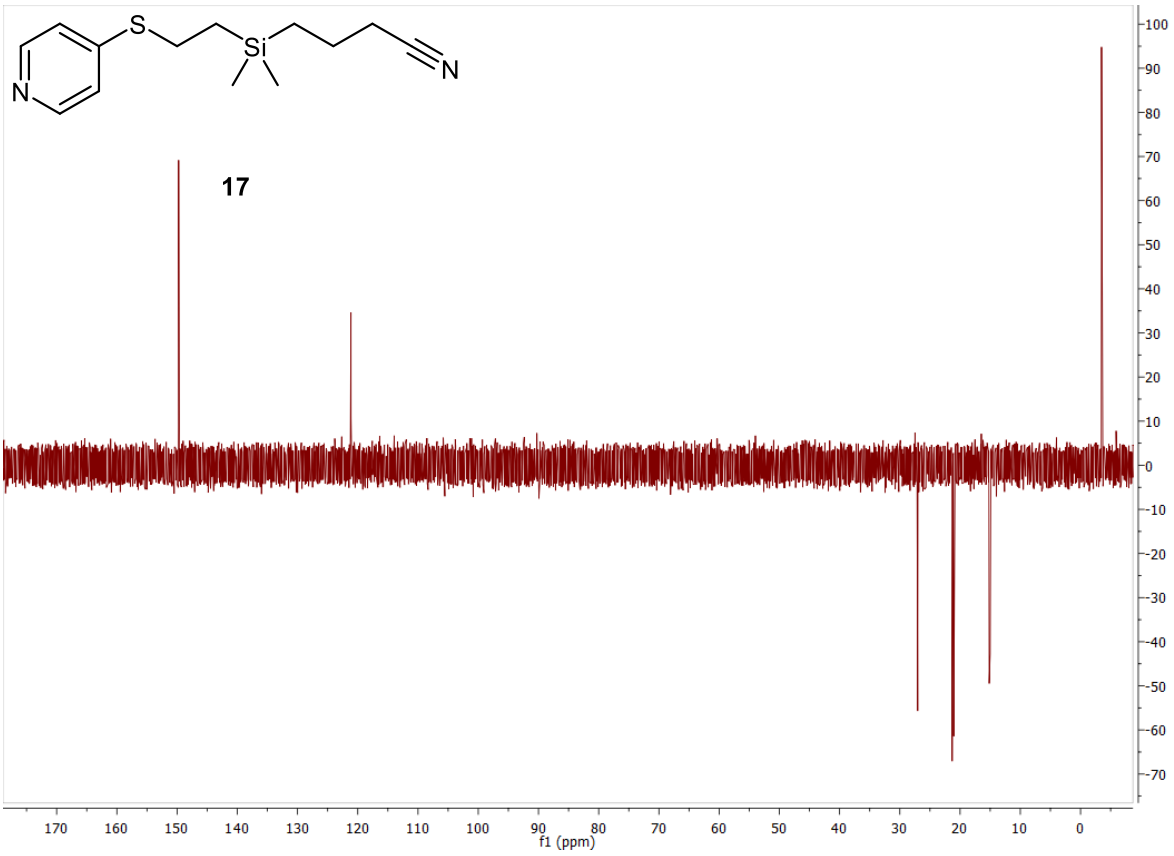
Acquisition Parameter

General	Fore Vacuum	2.68e+000 mBar	High Vacuum	1.01e-007 mBar	Source Type	ESI
	Scan Begin	75 m/z	Scan End	1700 m/z	Ion Polarity	Positive
Source	Set Nebulizer	0.4 Bar	Set Capillary	3600 V	Set Dry Gas	4.0 l/min
	Set Dry Heater	180 °C	Set End Plate Offset	-500 V		
Quadrupole	Set Ion Energy (MS only)	4.0 eV				
Coll. Cell	Collision Energy	8.0 eV	Set Collision Cell RF	350.0 Vpp		
Ion Cooler	Set Ion Cooler Transfer Time	75.0 µs	Set Ion Cooler Pre Pulse Storage Time	10.0 µs		

16. Compound **17**:

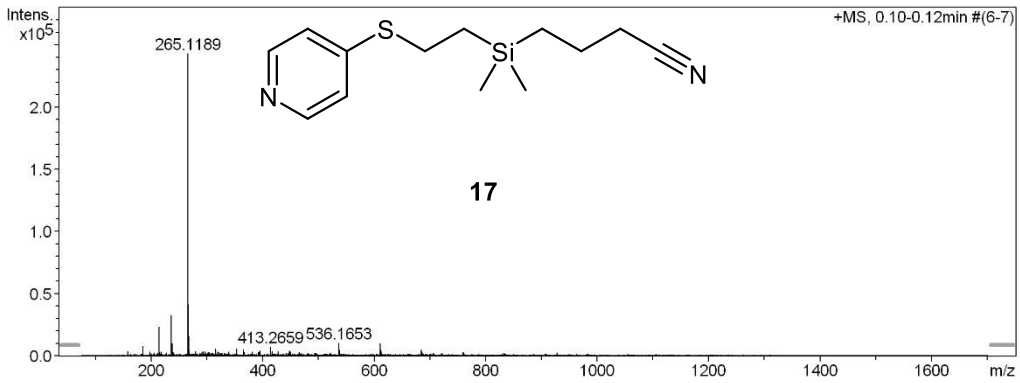




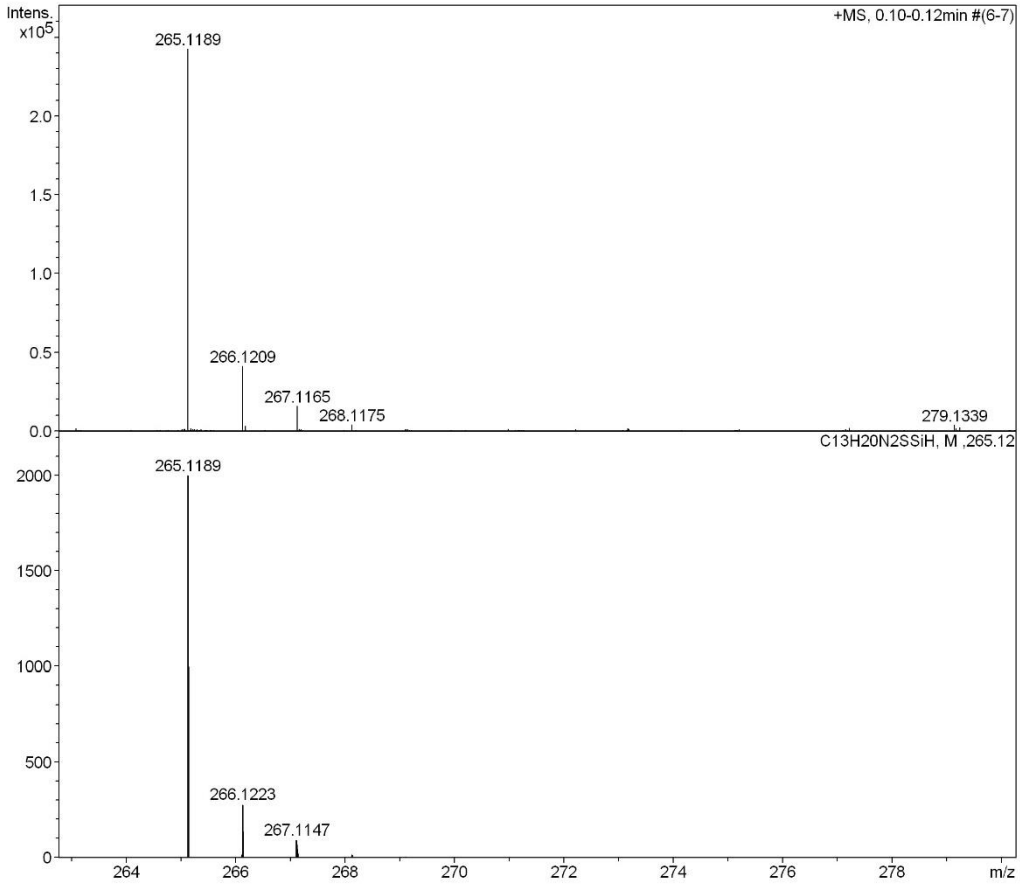

S
Si
N
N
17
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / / Ba540**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m



17



High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^- Conf	z
265.1189	1	C 13 H 21 N 2 S Si	100.00	265.1189	-0.0	-0.1	24.8	5.5	even	1+

Mass list

#	m/z	I %	I
1	158.0267	1.5	3531
2	185.1145	3.2	7820
3	197.0779	1.3	3076
4	198.1856	0.7	1771
5	205.0598	1.0	2402
6	211.0946	0.7	1794
7	214.0894	9.6	23199
8	215.0923	1.1	2616
9	217.1049	1.2	2950
10	226.9511	0.9	2253
11	236.0713	13.4	32535
12	237.0866	4.0	9780
13	238.0901	0.9	2092
14	239.0867	1.1	2593
15	265.1189	100.0	242582
16	266.1209	17.0	41130
17	266.1720	1.3	3178
18	267.1165	6.5	15789
19	268.1175	1.7	4003
20	273.1669	0.7	1693
21	277.2125	0.7	1750
22	279.1339	1.5	3703
23	279.2287	0.9	2160
24	287.1016	0.8	1864
25	291.1929	1.1	2775
26	293.2085	1.5	3705
27	293.2445	0.7	1715
28	297.0908	1.3	3072
29	299.1940	0.7	1617
30	301.1410	1.0	2311
31	301.2110	0.9	2109
32	303.1767	1.1	2680
33	305.2449	0.9	2192
34	307.1879	0.7	1708
35	309.2034	0.9	2092
36	310.2361	0.8	1910
37	315.1931	2.3	5623
38	319.2238	1.3	3242
39	321.2398	1.1	2571
40	325.1617	0.7	1818
41	327.2271	0.8	1837
42	331.2087	0.8	1990
43	335.2177	0.7	1722
44	337.1979	0.7	1744
45	339.1769	1.2	3018
46	353.2659	2.2	5311
47	365.1058	2.2	5281
48	365.2682	0.8	2031
49	367.2087	1.2	2932
50	367.2447	0.8	1927
51	381.2984	1.3	3047
52	391.2084	1.2	2933
53	391.2831	1.0	2375
54	393.2962	1.3	3040
55	395.2769	0.8	1970
56	395.3632	1.8	4263
57	413.2659	2.9	6990
58	414.2686	0.9	2197
59	417.3451	1.5	3678
60	419.2403	0.7	1636
61	421.3283	0.7	1617
62	425.3655	0.7	1711

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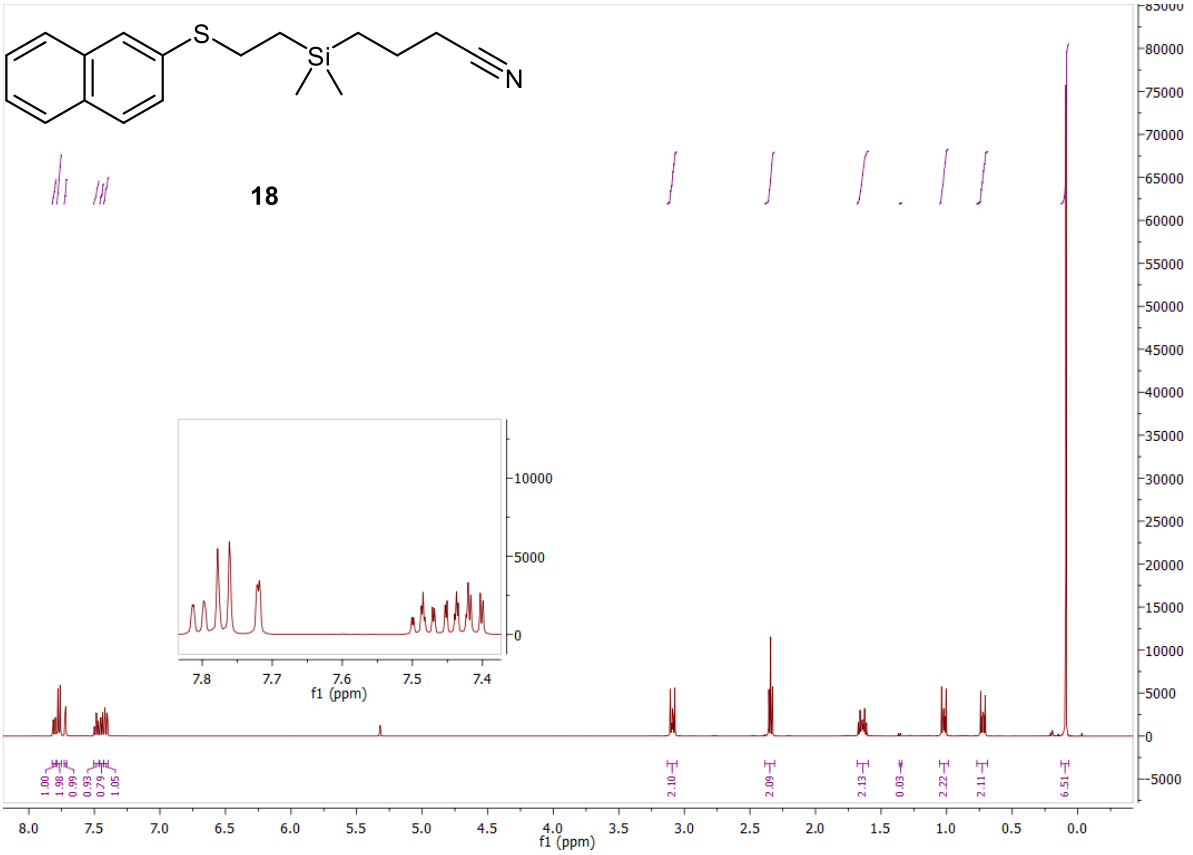
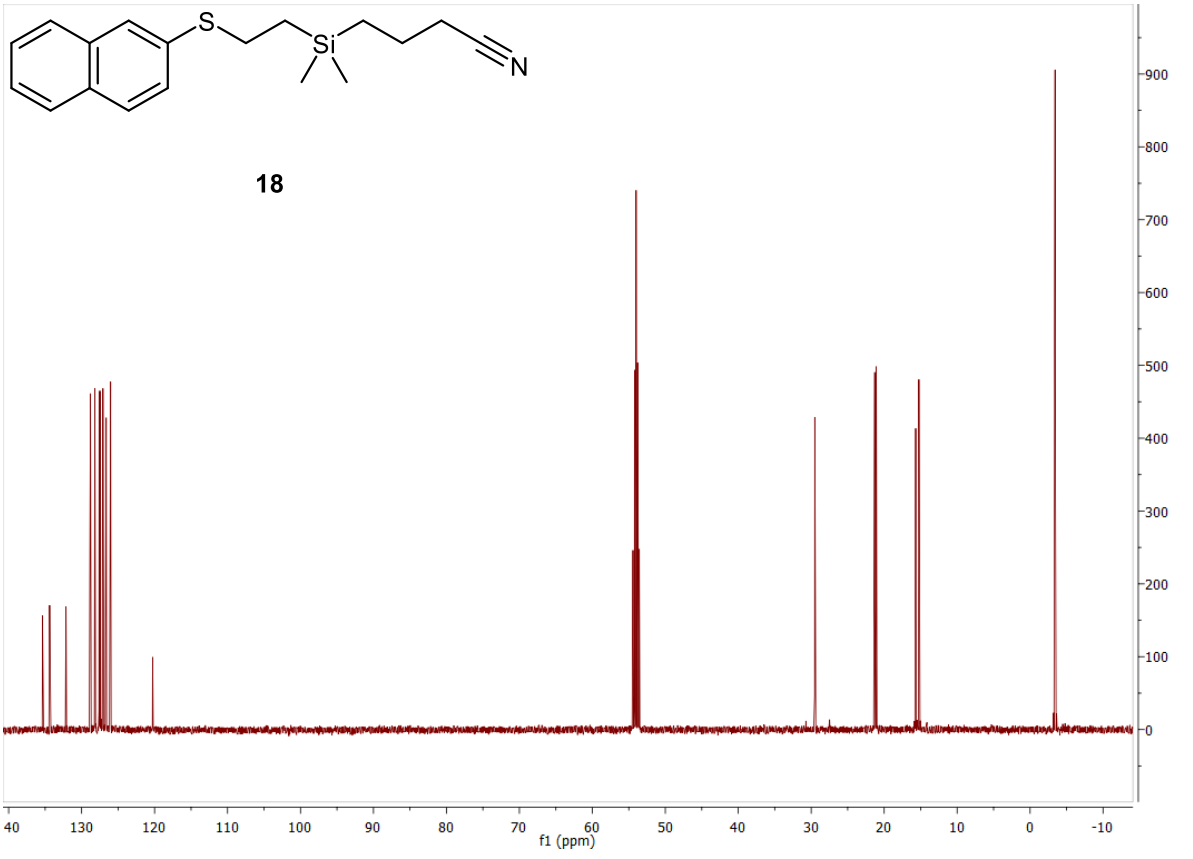
#	m/z	I %	I
63	427.2089	1.5	3579
64	435.3448	0.7	1650
65	441.2966	0.9	2142
66	445.1208	0.8	2047
67	447.3450	1.7	4082
68	449.3744	1.3	3049
69	462.1446	0.7	1670
70	465.3690	1.2	2913
71	469.3273	0.8	1901
72	481.3122	0.9	2103
73	481.3649	0.8	1932
74	493.3484	0.8	1865
75	495.3288	0.8	1978
76	497.3599	0.7	1659
77	511.3440	0.7	1753
78	521.3815	1.0	2332
79	536.1653	4.1	10017
80	537.1658	2.0	4947
81	538.1641	1.7	4224
82	539.1647	0.7	1740
83	541.1207	0.7	1644
84	609.3393	0.9	2098
85	609.3618	1.1	2720
86	610.1834	4.0	9660
87	611.1849	2.1	5079
88	612.1819	1.5	3628
89	684.2014	1.9	4612
90	685.2042	1.3	3211
91	686.2026	0.8	2055
92	700.6251	0.7	1734
93	705.5832	0.9	2125
94	721.5766	0.8	1985
95	758.2208	1.2	2852
96	759.2201	1.2	2818
97	760.2203	0.8	1827
98	832.2380	0.8	1909
99	834.7397	0.7	1744
100	927.5660	1.0	2452

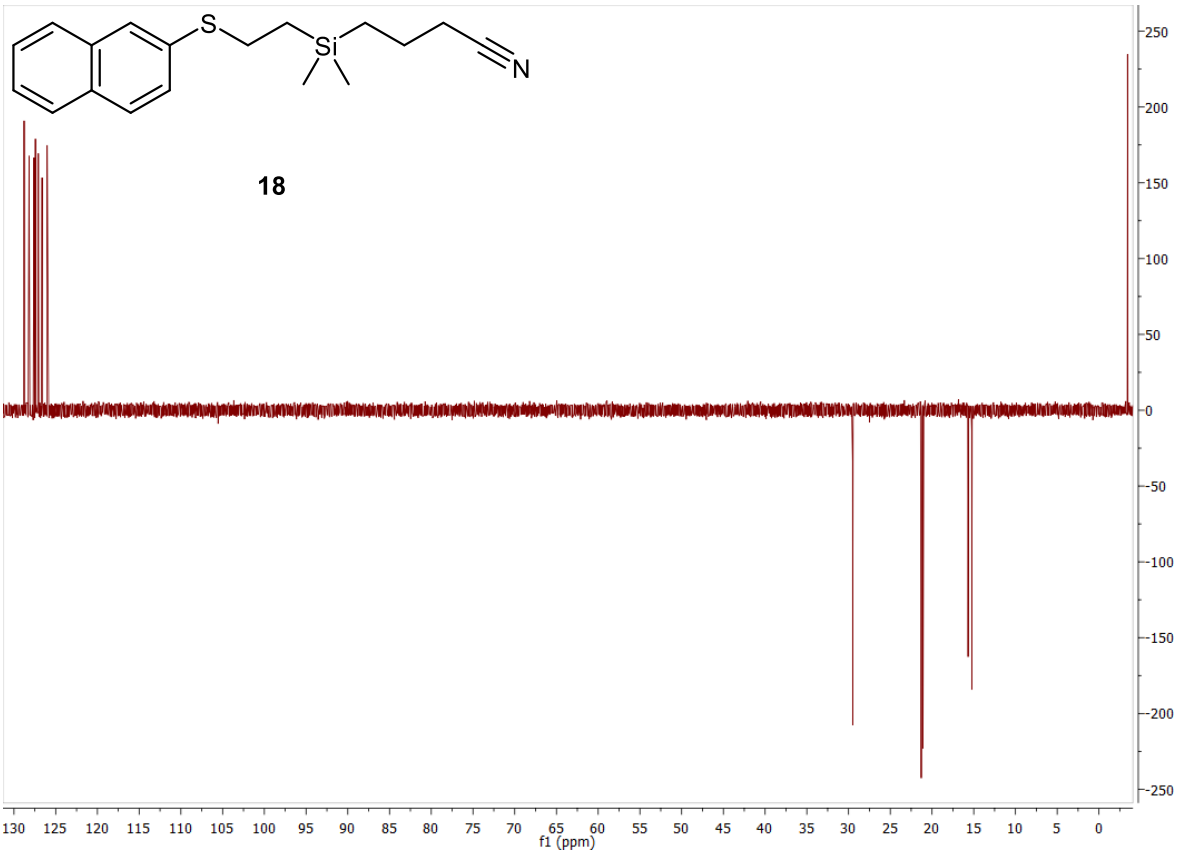
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV

17. Compound **18**:

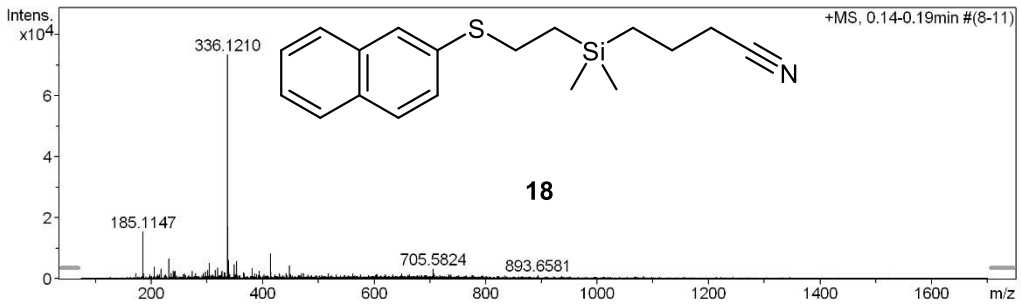


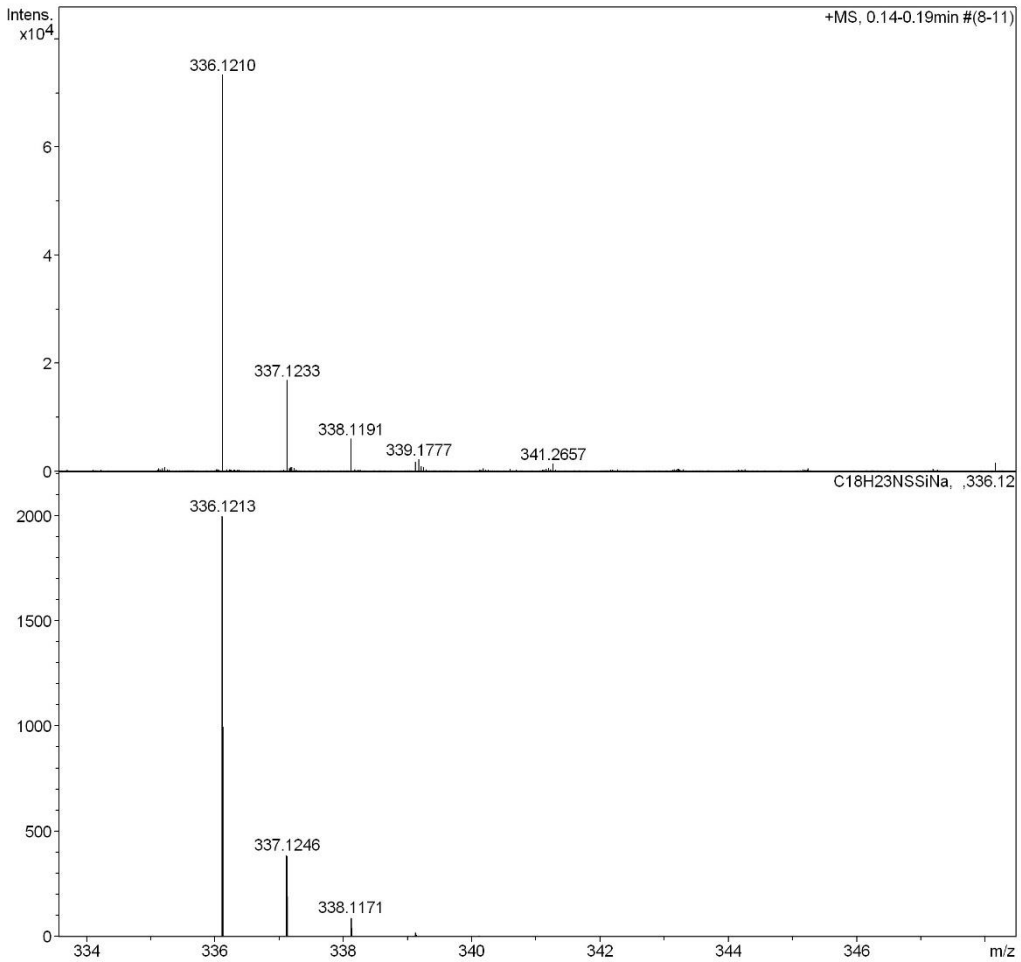



S
Si
N
18
250
200
150
100
50
0
-50
-100
-150
-200
-250
130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba582 chr1_2**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m





High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	z
336.1210	1	C 18 H 23 N Na S Si	100.00	336.1213	0.3	0.8	19.3	8.5	even	1+

Mass list

#	m/z	I %	I
1	173.0788	2.4	1787
2	185.1147	20.8	15277
3	186.1182	2.2	1623
4	197.0785	1.9	1397
5	205.0600	5.3	3856
6	211.0941	1.8	1350
7	215.1256	1.9	1404
8	217.1048	4.5	3274
9	225.1100	1.7	1226
10	231.1352	9.0	6621
11	232.1385	1.5	1092
12	236.0712	2.4	1780
13	239.0886	3.6	2623
14	242.2837	3.1	2307
15	243.0985	3.5	2545
16	257.1135	1.7	1228
17	259.1300	2.2	1618
18	261.1288	1.6	1162
19	273.1671	3.2	2341
20	279.2286	2.3	1681
21	293.2082	2.5	1807
22	297.1482	3.0	2173
23	297.2397	1.6	1178
24	301.1409	3.9	2863
25	304.2996	7.1	5183
26	305.3027	1.6	1162
27	309.2029	1.7	1255
28	314.1385	3.6	2670
29	319.1302	4.7	3462
30	323.1881	1.5	1105
31	325.1611	1.5	1080
32	326.1749	2.6	1906
33	326.3770	2.1	1526
34	327.1581	3.4	2514
35	331.1656	2.8	2052
36	331.2088	2.9	2107
37	332.3307	2.6	1888
38	336.1210	100.0	73322
39	337.1233	23.0	16843
40	338.1191	8.2	6035
41	339.1202	2.3	1670
42	339.1777	3.1	2242
43	341.2657	2.0	1457
44	348.1566	2.3	1652
45	348.9889	1.9	1390
46	349.1406	6.3	4649
47	350.9873	1.7	1233
48	352.0957	2.1	1546
49	353.1451	2.0	1468
50	353.1934	1.6	1177
51	353.2661	7.9	5788
52	354.2702	1.5	1085
53	365.1054	2.8	2049
54	365.2679	1.6	1187
55	367.2080	2.1	1535
56	381.2971	4.6	3389
57	385.2915	2.3	1654
58	389.2512	2.0	1448
59	393.2969	3.4	2509
60	402.3574	2.0	1464
61	407.3125	1.6	1154
62	413.2659	11.2	8201

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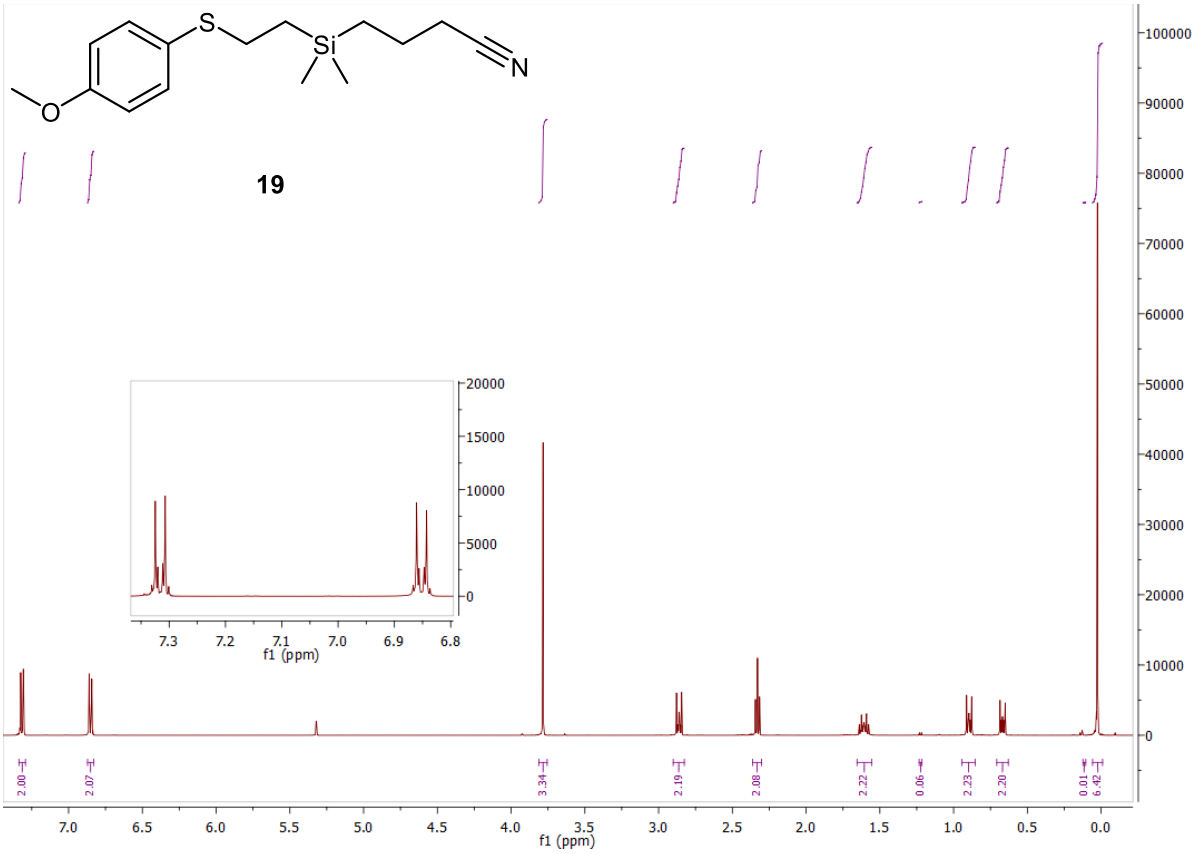
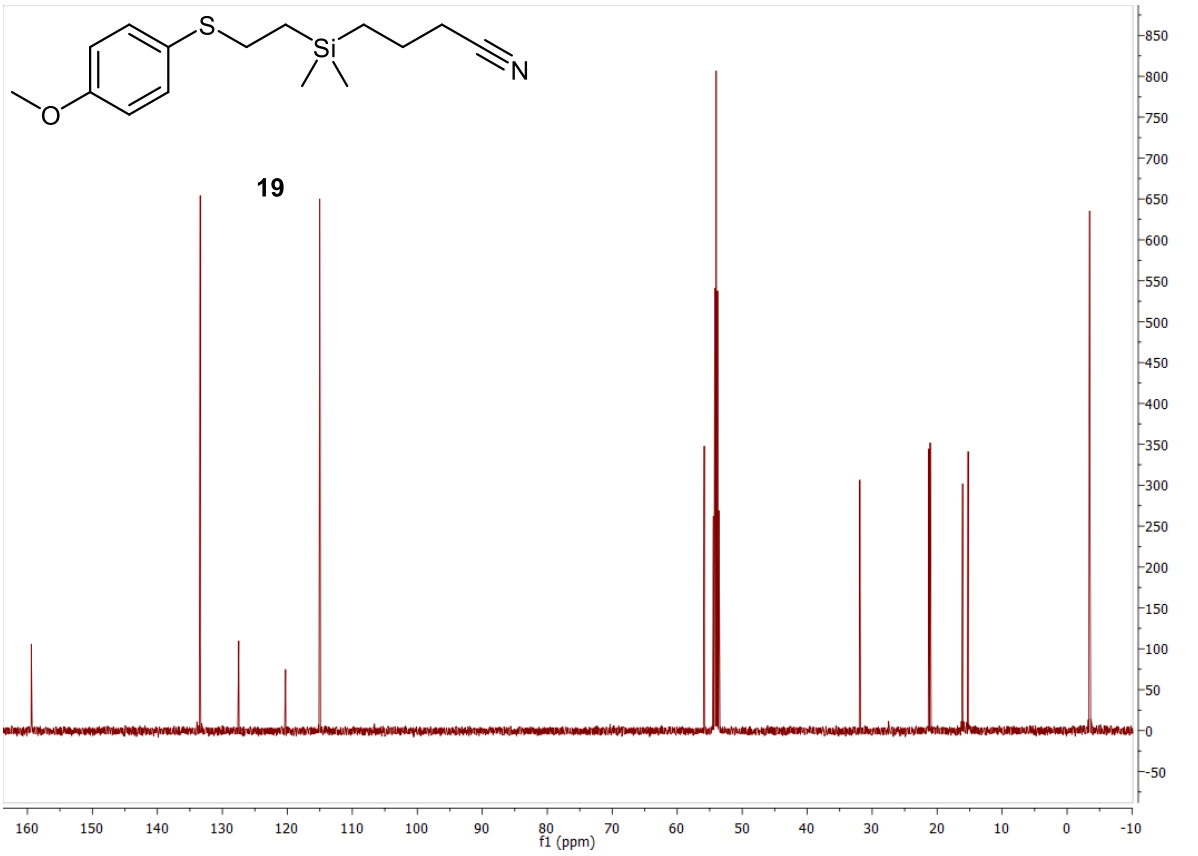
#	m/z	I %	I
63	414.2691	3.1	2273
64	421.3276	2.0	1468
65	429.3172	2.4	1793
66	430.3881	1.7	1211
67	441.2970	2.4	1796
68	447.3446	5.9	4358
69	448.3476	2.1	1503
70	449.3696	1.9	1422
71	463.3756	1.5	1117
72	469.3276	2.5	1829
73	473.3447	2.5	1807
74	481.3134	1.8	1355
75	487.3609	1.5	1129
76	505.3355	1.6	1175
77	517.3712	2.2	1615
78	531.3858	1.8	1329
79	561.3985	2.3	1661
80	575.4099	1.8	1306
81	601.4641	1.5	1122
82	603.4306	1.9	1404
83	605.4216	1.9	1371
84	619.4369	1.8	1331
85	633.4480	2.0	1459
86	649.2523	2.1	1522
87	649.4496	2.0	1451
88	659.5070	1.6	1138
89	663.4628	1.9	1383
90	677.4797	1.6	1141
91	685.4346	1.5	1097
92	691.4836	1.6	1162
93	693.4746	1.5	1066
94	705.5028	1.7	1213
95	705.5824	4.3	3160
96	706.5837	2.3	1652
97	717.5499	1.5	1078
98	733.5400	1.9	1371
99	737.5037	1.7	1239
100	776.5810	1.6	1148

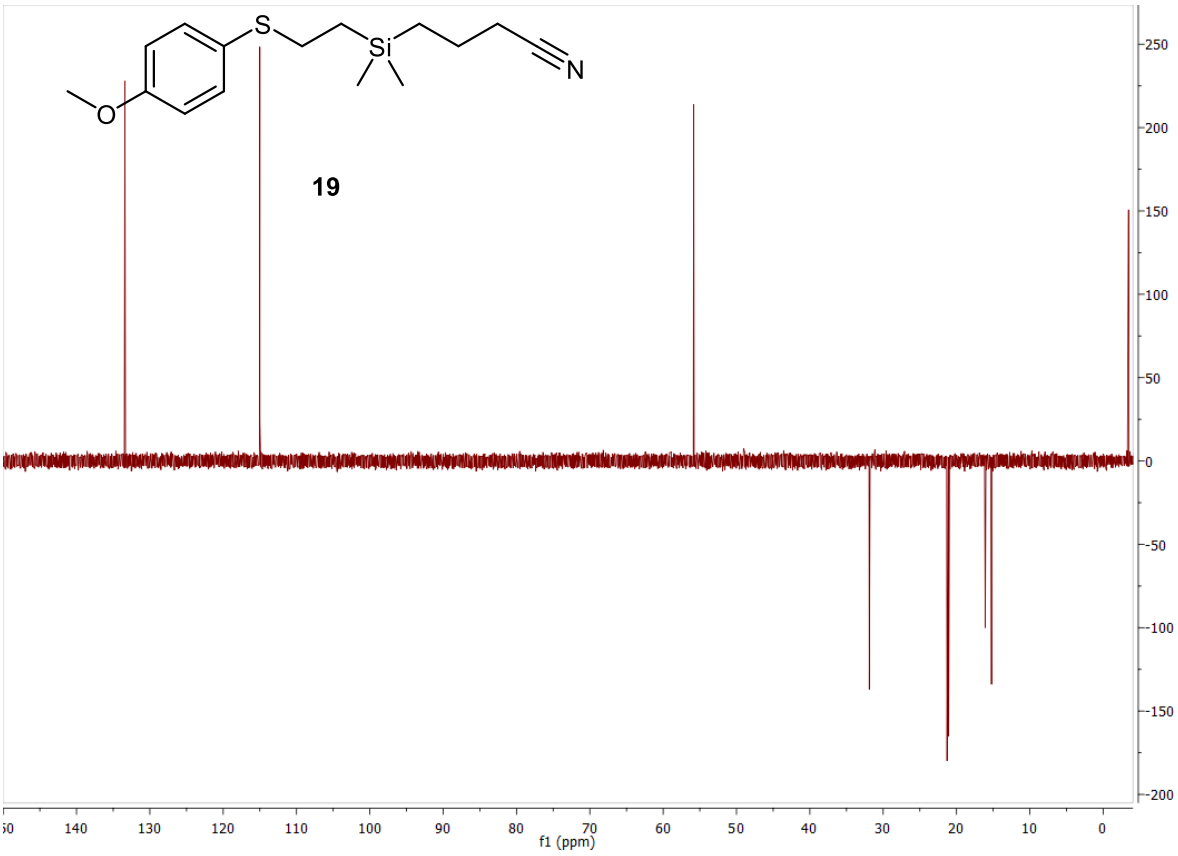
Acquisition Parameter

General	Fore Vacuum	2.69e+000 mBar	High Vacuum	1.01e-007 mBar	Source Type	ESI
	Scan Begin	75 m/z	Scan End	1700 m/z	Ion Polarity	Positive
Source	Set Nebulizer	0.4 Bar	Set Capillary	3600 V	Set Dry Gas	4.0 l/min
	Set Dry Heater	180 °C	Set End Plate Offset	-500 V		
Quadrupole	Set Ion Energy (MS only)	4.0 eV				
Coll. Cell	Collision Energy	8.0 eV	Set Collision Cell RF	350.0 Vpp		
Ion Cooler	Set Ion Cooler Transfer Time	75.0 µs	Set Ion Cooler Pre Pulse Storage Time	10.0 µs		

18. Compound **19**:

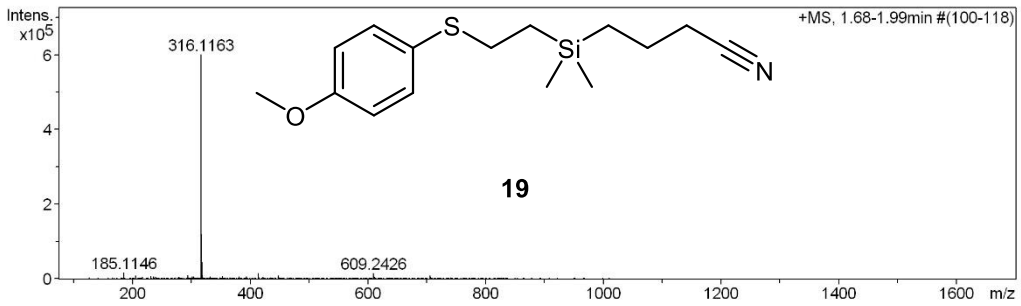




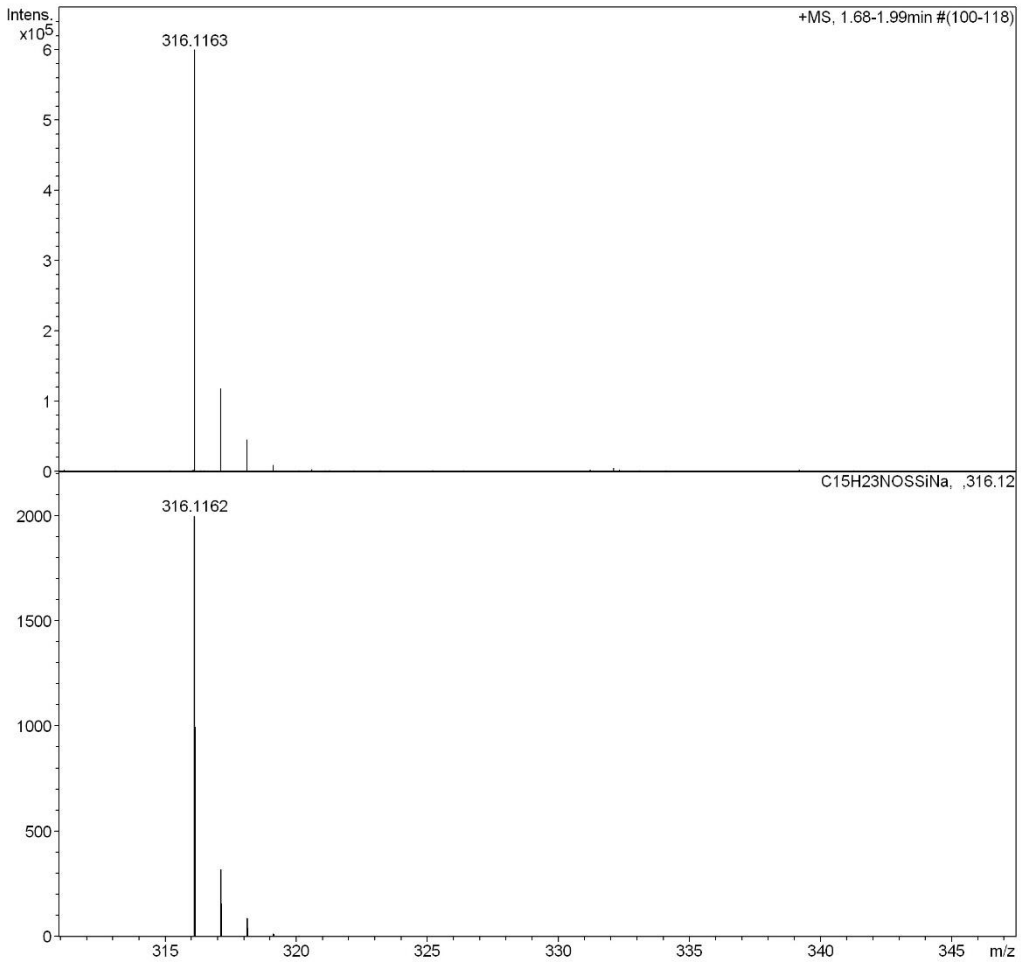

S
Si
N
O
19
250
200
150
100
50
0
-50
-100
-150
-200
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba595 chr1_1**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m



19



High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	z
316.1163	1	C 15 H 23 N Na O S Si	100.00	316.1162	-0.1	-0.4	19.2	5.5	even	1+

Mass list

#	m/z	I %	I
1	126.0735	0.4	2168
2	165.0533	0.3	1993
3	173.0786	0.3	1688
4	180.5297	0.3	2091
5	185.1146	2.5	15177
6	186.1183	0.3	1540
7	197.0782	0.3	1748
8	205.0598	1.4	8100
9	211.0941	0.3	1621
10	217.1044	0.6	3325
11	225.1090	0.3	1660
12	226.9509	0.4	2163
13	231.1350	1.1	6865
14	234.9856	0.6	3354
15	236.0710	0.9	5097
16	239.0884	0.6	3747
17	243.0984	0.3	1508
18	245.0777	0.3	1517
19	245.1504	0.2	1479
20	257.1139	0.3	1880
21	259.1296	0.3	1610
22	261.1287	0.3	1520
23	273.1671	0.3	2093
24	277.2133	0.3	1981
25	279.2286	0.6	3835
26	293.2081	0.4	2177
27	293.2445	0.3	1582
28	294.1337	1.6	9700
29	295.1363	0.4	2370
30	297.2394	0.3	1820
31	301.1405	0.8	5002
32	301.2109	0.4	2480
33	303.2288	0.3	1625
34	304.2991	0.8	4875
35	305.1186	0.2	1464
36	305.2442	0.3	1993
37	307.2600	0.2	1480
38	309.2031	0.3	1522
39	311.1599	0.4	2248
40	313.1074	0.2	1415
41	316.0661	0.4	2101
42	316.1163	100.0	599499
43	317.1182	19.7	118268
44	318.1132	7.5	44935
45	319.1154	1.5	8792
46	319.2240	0.3	1553
47	320.1125	0.3	1706
48	320.5951	0.4	2443
49	321.2393	0.3	1698
50	331.2084	0.4	2165
51	332.0895	0.8	4736
52	332.3302	0.3	2051
53	339.1773	0.3	1820
54	341.2652	0.2	1438
55	344.1278	0.3	1580
56	348.9897	0.3	1608
57	349.1407	0.5	3132
58	353.1452	0.5	2740
59	353.2656	1.0	6150
60	354.2692	0.2	1409
61	365.1053	0.4	2619
62	365.2673	0.4	2377

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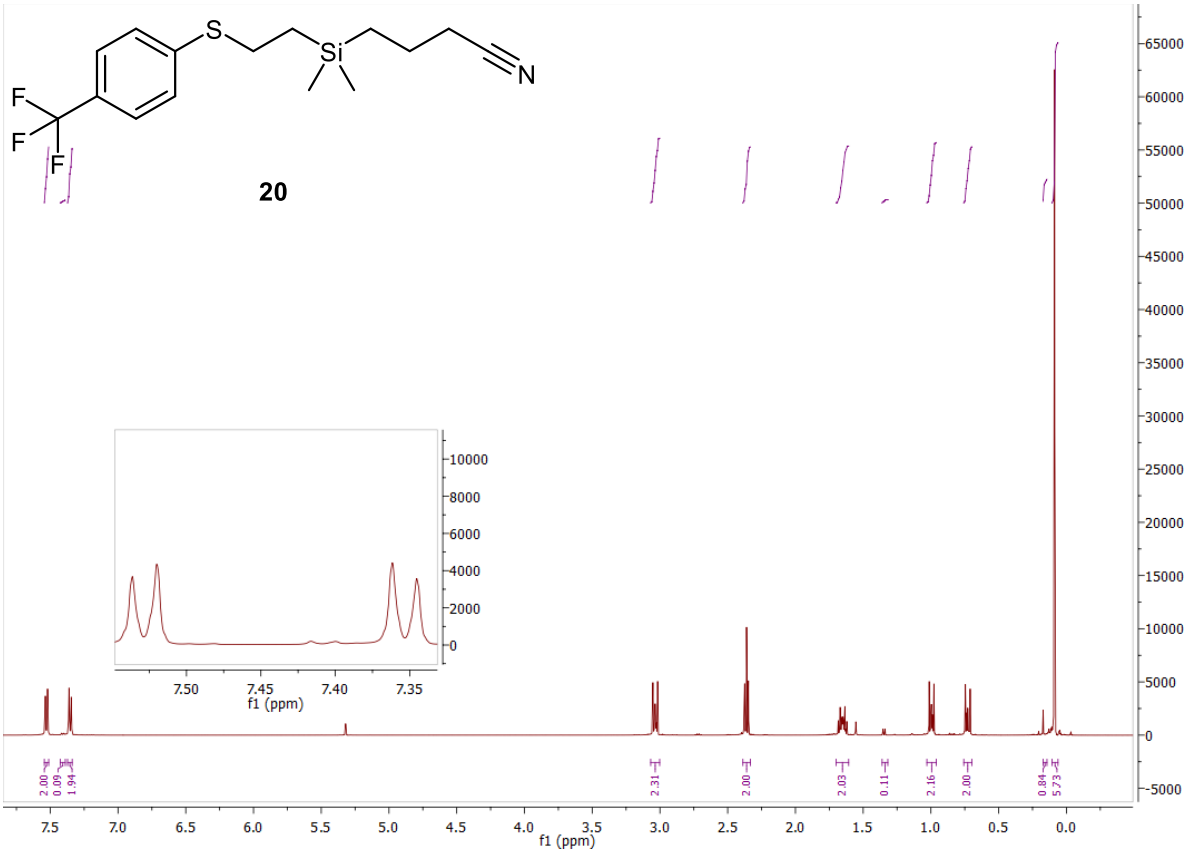
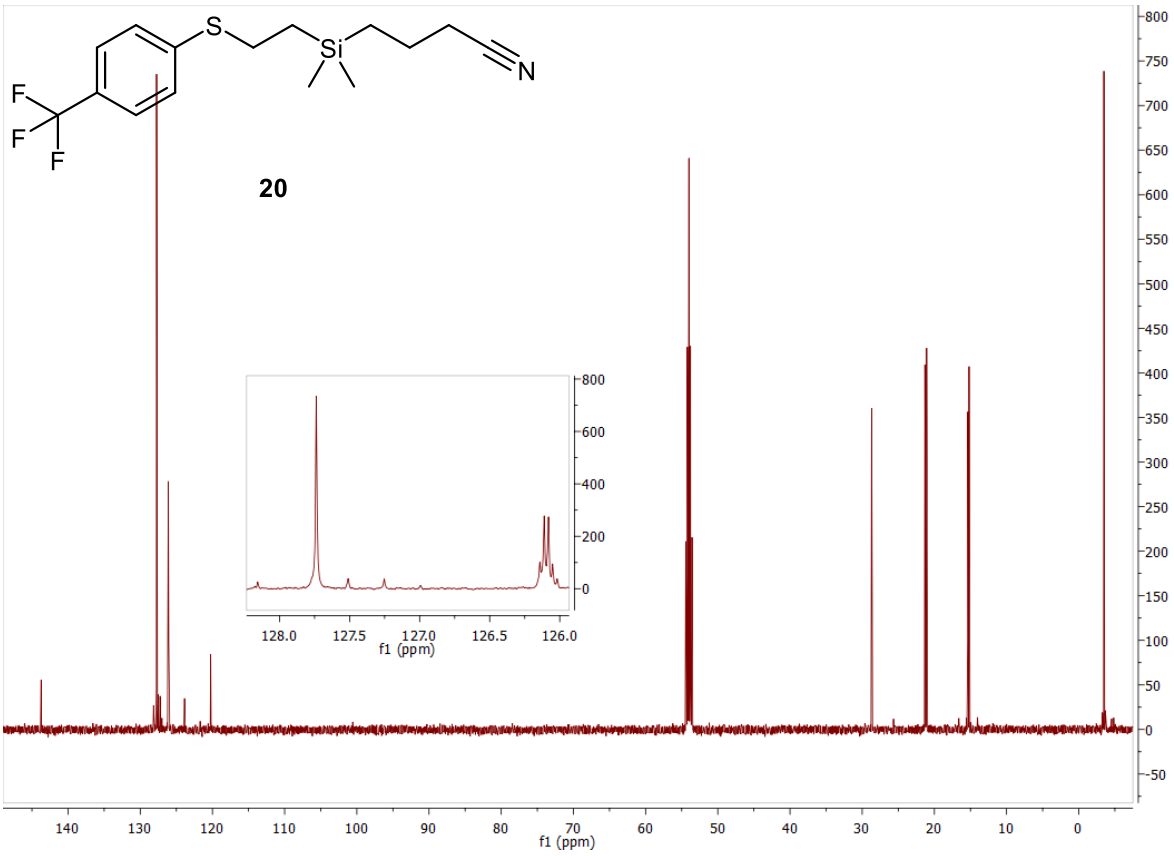
#	m/z	I %	I
63	381.2971	0.8	4620
64	384.1031	0.2	1433
65	385.2921	0.2	1405
66	393.0616	0.5	3131
67	393.2970	0.8	4741
68	407.3130	0.4	2309
69	413.2658	2.4	14133
70	414.2691	0.6	3896
71	421.3283	0.6	3354
72	429.3179	0.3	1517
73	433.3791	0.3	1721
74	435.3439	0.4	2130
75	441.2968	0.5	3113
76	447.3440	1.3	7790
77	448.3477	0.4	2256
78	449.3613	0.5	2964
79	463.3751	0.4	2151
80	469.3283	0.5	3175
81	473.3436	0.3	1671
82	477.3900	0.3	1516
83	495.3296	0.2	1404
84	513.1916	0.3	1701
85	517.3702	0.3	1561
86	555.5105	0.2	1471
87	561.3958	0.3	1571
88	589.4201	0.2	1412
89	601.4639	0.2	1406
90	605.4215	0.2	1495
91	609.2426	2.5	14818
92	610.2446	1.1	6572
93	611.2417	0.6	3696
94	633.4410	0.2	1488
95	649.4500	0.2	1466
96	663.4589	0.3	1651
97	705.5818	1.2	7464
98	706.3929	0.4	2303
99	706.5852	0.6	3639
100	740.4708	0.4	2235

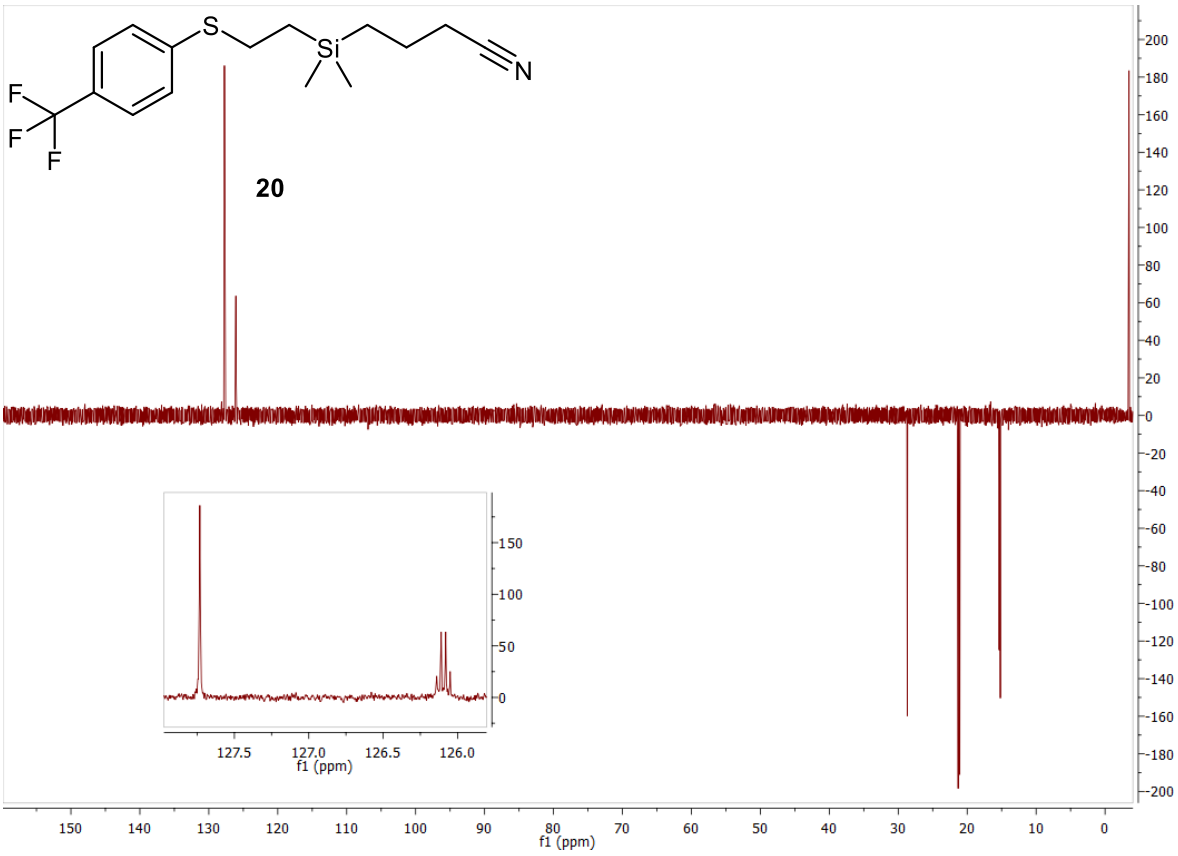
Acquisition Parameter

General	Fore Vacuum	2.68e+000 mBar	High Vacuum	1.01e-007 mBar	Source Type	ESI
	Scan Begin	75 m/z	Scan End	1700 m/z	Ion Polarity	Positive
Source	Set Nebulizer	0.4 Bar	Set Capillary	3600 V	Set Dry Gas	4.0 l/min
	Set Dry Heater	180 °C	Set End Plate Offset	-500 V		
Quadrupole	Set Ion Energy (MS only)	4.0 eV				
Coll. Cell	Collision Energy	8.0 eV	Set Collision Cell RF	350.0 Vpp		
Ion Cooler	Set Ion Cooler Transfer Time	75.0 µs	Set Ion Cooler Pre Pulse Storage Time	10.0 µs		

19. Compound **20**:

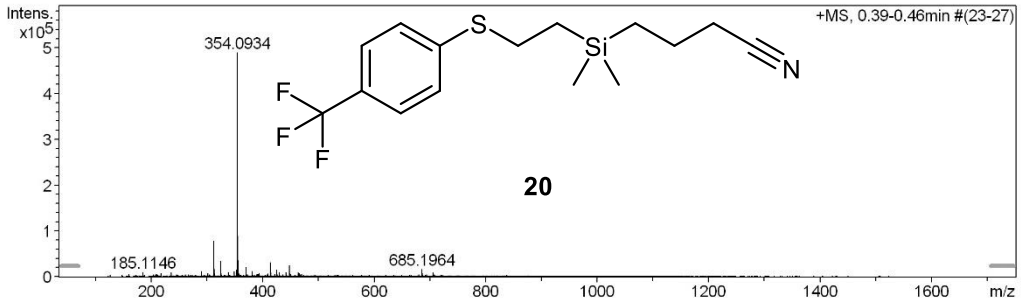




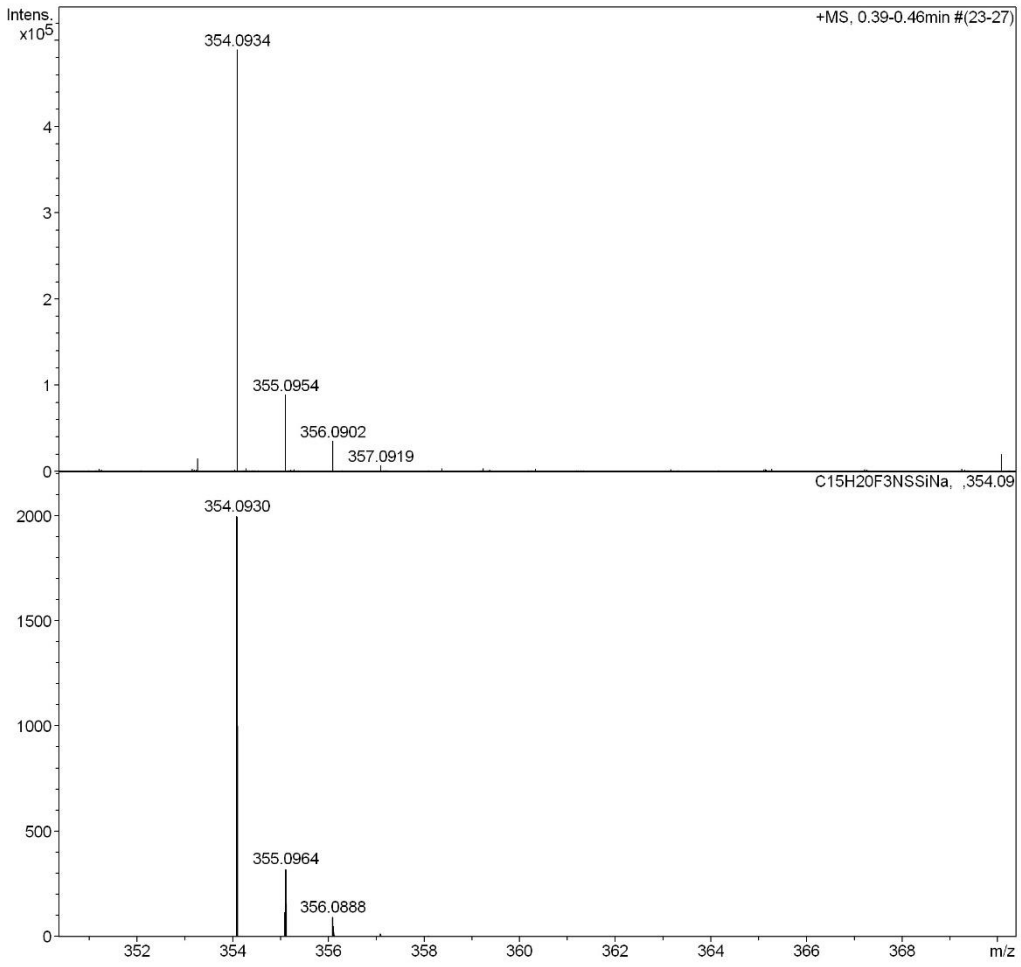

S
Si
N
F
F
F
20
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba547 chr1#2**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m



20



High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	z
354.0934	1	C 15 H 20 F 3 N Na S Si	100.00	354.0930	-0.4	-1.0	26.1	5.5	even	1+

Mass list

#	m/z	I %	I
1	126.0731	0.7	3278
2	147.1603	0.7	3229
3	159.1605	1.1	5235
4	173.0781	0.6	2832
5	185.1146	2.0	9638
6	187.1549	0.6	3152
7	203.0800	0.8	4150
8	208.0742	1.0	4683
9	209.0754	1.2	5735
10	211.0719	0.7	3287
11	217.1045	1.6	7700
12	236.0710	1.6	8039
13	245.0506	0.8	3866
14	247.0472	0.6	3011
15	255.0793	0.7	3357
16	261.1296	0.8	3940
17	266.1724	0.8	3957
18	270.0926	0.6	2921
19	279.2288	0.7	3230
20	290.1023	2.4	11566
21	295.1931	0.7	3209
22	301.1406	1.6	7948
23	304.2996	0.8	3975
24	305.2449	0.7	3461
25	312.1045	15.9	77500
26	313.1067	3.3	16129
27	314.1014	1.3	6392
28	324.1245	7.0	34117
29	325.1268	1.4	7080
30	326.1224	0.7	3568
31	331.2088	0.8	3711
32	332.1108	0.7	3185
33	338.1188	2.0	9980
34	341.2658	0.7	3242
35	349.1370	2.1	10153
36	353.2658	3.0	14566
37	354.0934	100.0	488697
38	354.2695	0.7	3530
39	355.0954	18.2	88748
40	356.0902	7.2	35325
41	357.0919	1.3	6530
42	358.3679	0.7	3555
43	359.2399	0.7	3285
44	360.3230	0.6	3103
45	365.2675	0.6	2973
46	370.0667	4.1	20083
47	371.0690	0.9	4248
48	372.0643	0.8	3882
49	381.2972	2.4	11607
50	382.3005	0.6	2881
51	385.2923	0.7	3242
52	389.2512	0.8	3965
53	390.0634	1.0	4879
54	391.2834	1.1	5410
55	393.2975	1.6	7667
56	405.0388	0.6	2802
57	407.3131	0.8	3806
58	409.2919	1.3	6263
59	413.2660	6.3	30645
60	414.2694	1.7	8204
61	421.3287	1.1	5384
62	425.2142	3.0	14624

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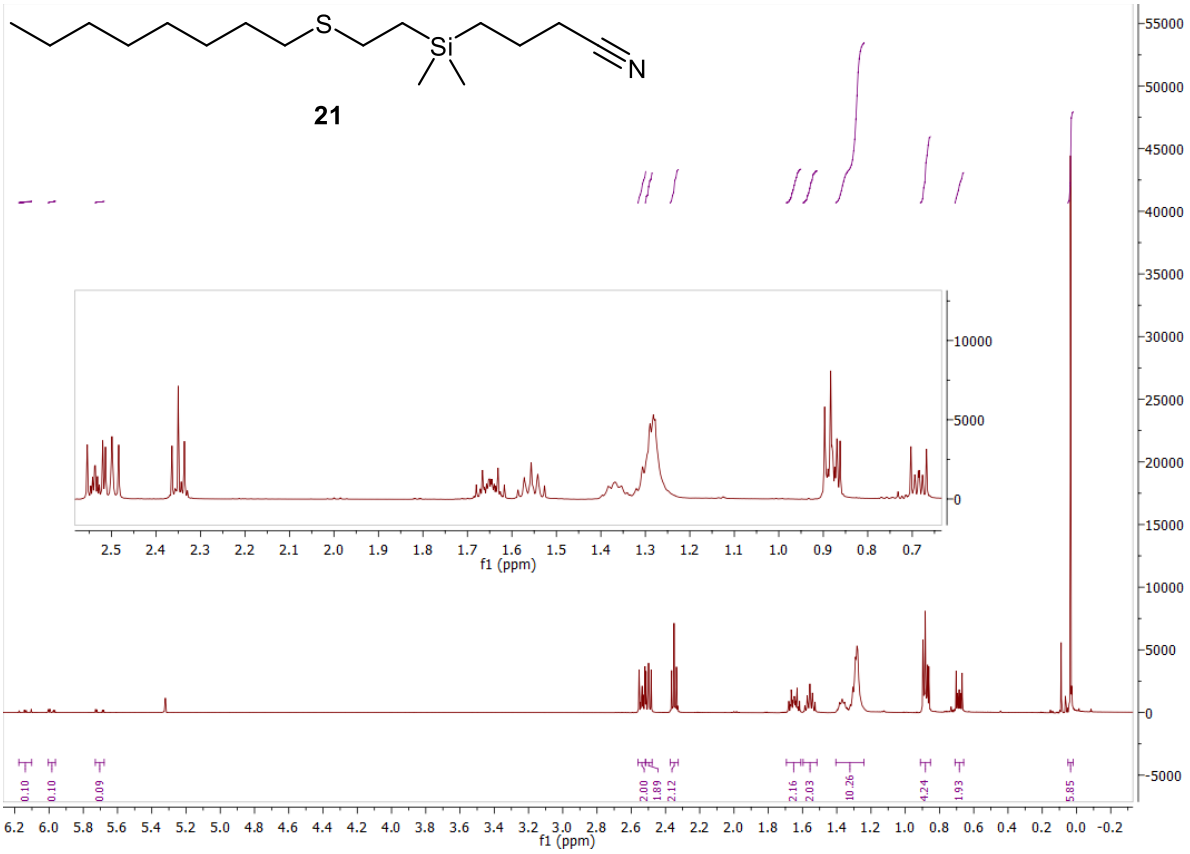
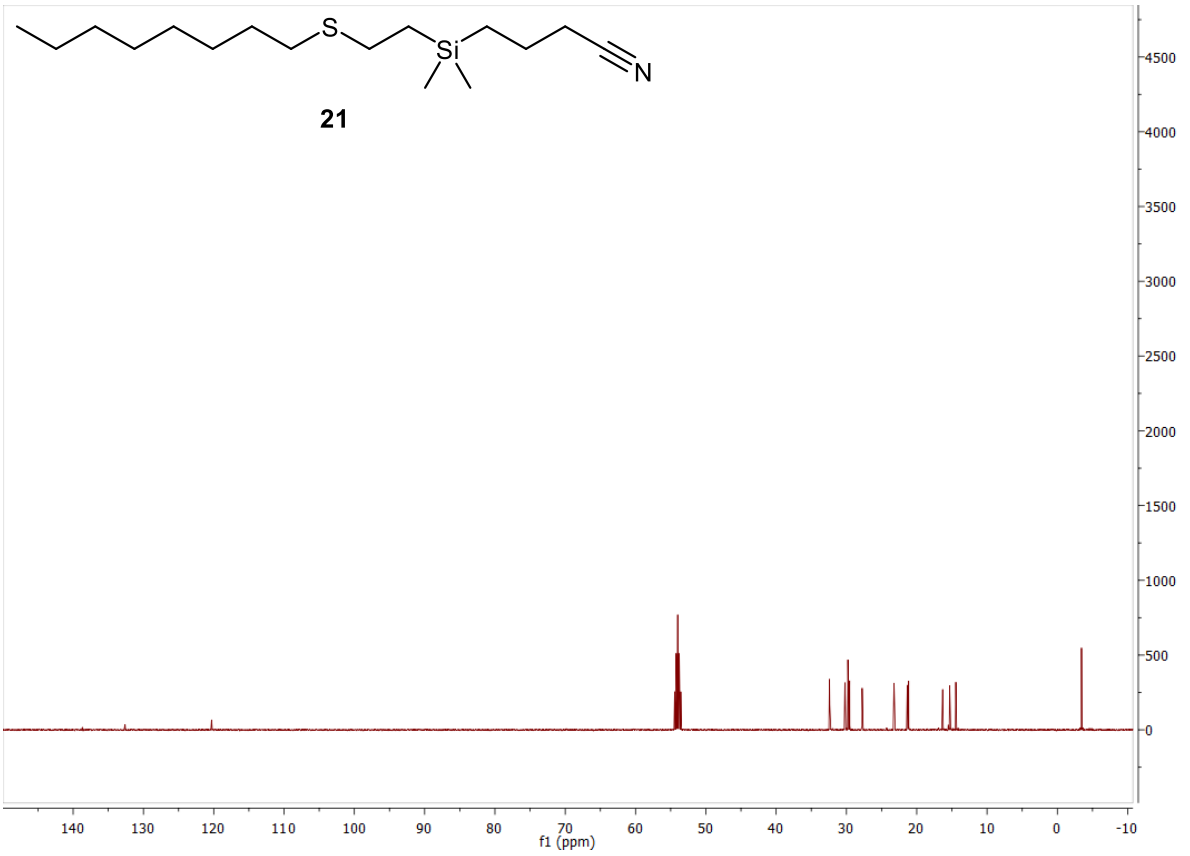
#	m/z	I %	I
63	425.3625	0.9	4407
64	426.2175	0.8	3680
65	429.2400	2.0	9812
66	429.3182	0.7	3341
67	430.2433	0.6	3056
68	435.3438	0.8	3744
69	441.1886	0.9	4168
70	441.2967	1.9	9229
71	442.2998	0.6	3037
72	447.2928	0.6	3108
73	447.3444	5.1	24867
74	448.3475	1.4	6948
75	449.3588	1.1	5519
76	457.2712	0.7	3393
77	463.3185	1.7	8323
78	463.3743	0.7	3439
79	464.3218	0.6	2904
80	465.3154	1.4	6983
81	467.3099	0.9	4285
82	469.3274	1.1	5307
83	473.3445	0.7	3443
84	493.3462	0.6	2882
85	517.3708	0.6	2958
86	529.4945	0.6	2823
87	535.3967	0.7	3326
88	577.3708	0.7	3613
89	621.3977	0.7	3197
90	663.4608	0.6	3018
91	665.4236	0.7	3370
92	679.4397	0.8	3949
93	685.1964	3.3	15896
94	686.1989	1.5	7247
95	687.1957	0.7	3586
96	693.4659	0.8	3871
97	705.5818	1.7	8072
98	706.5852	0.8	3731
99	707.4860	0.6	2941
100	721.5574	0.7	3340

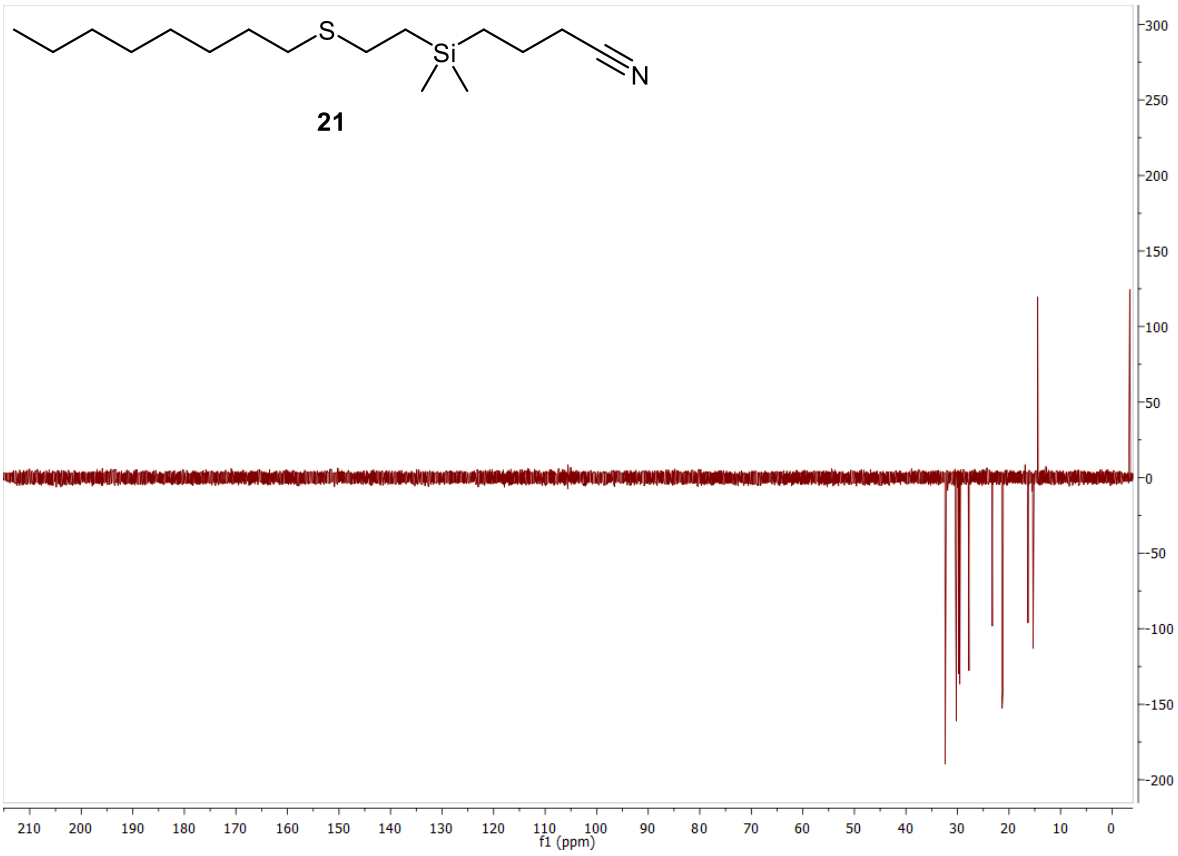
Acquisition Parameter

General	Fore Vacuum	2.69e+000 mBar	High Vacuum	1.06e-007 mBar	Source Type	ESI
	Scan Begin	75 m/z	Scan End	1700 m/z	Ion Polarity	Positive
Source	Set Nebulizer	0.4 Bar	Set Capillary	3600 V	Set Dry Gas	4.0 l/min
	Set Dry Heater	180 °C	Set End Plate Offset	-500 V		
Quadrupole	Set Ion Energy (MS only)	4.0 eV				
Coll. Cell	Collision Energy	8.0 eV	Set Collision Cell RF	350.0 Vpp		
Ion Cooler	Set Ion Cooler Transfer Time	75.0 µs	Set Ion Cooler Pre Pulse Storage Time	10.0 µs		

20. Compound **21**:

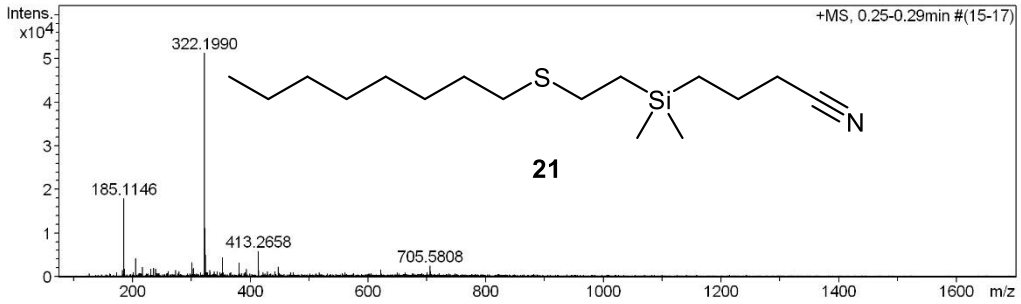


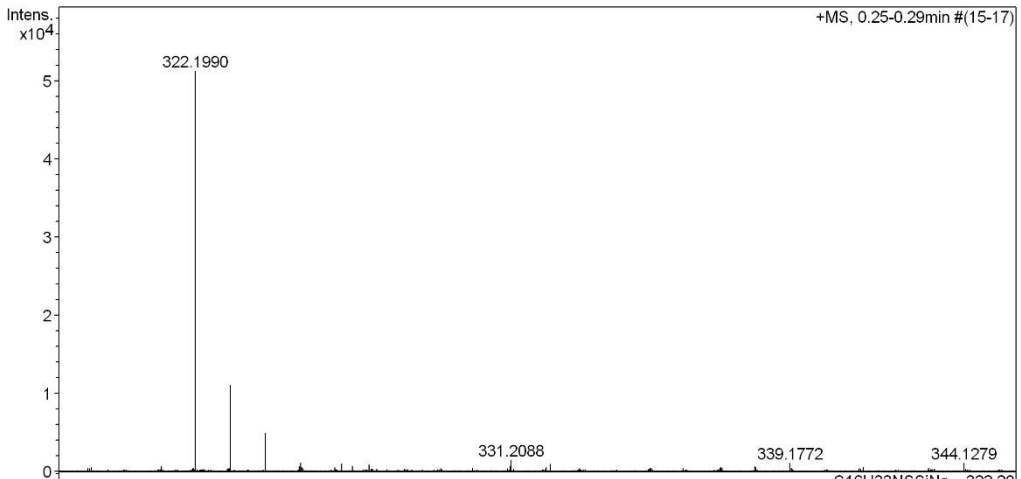


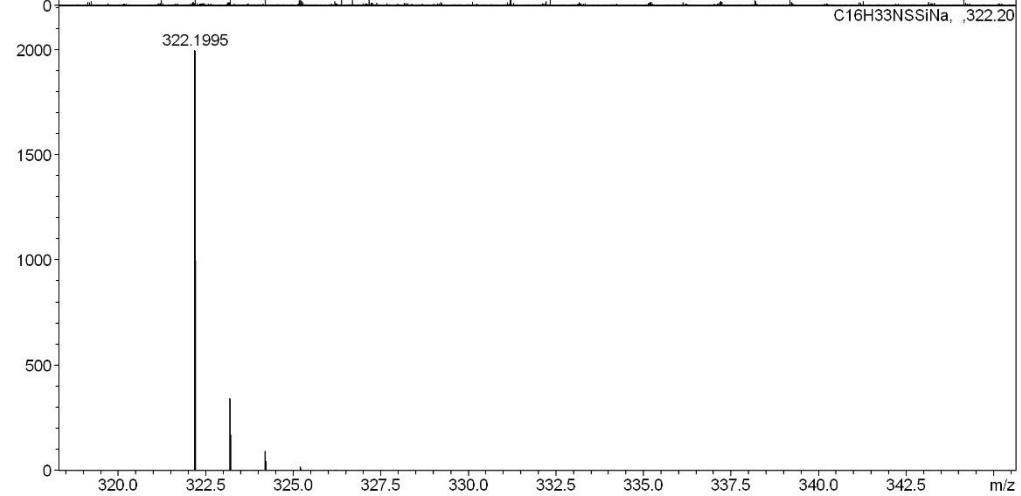

S
Si
N
21
300
250
200
150
100
50
0
-50
-100
-150
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba590chr1_1**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m







High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	z
322.1990	1	C 16 H 33 N Na S Si	100.00	322.1995	0.6	1.7	12.7	1.5	even	1+

Mass list

#	m/z	I %	I
1	126.0736	1.3	643
2	161.1056	1.3	656
3	173.0779	1.8	924
4	183.0777	2.9	1473
5	185.1146	34.9	17842
6	186.1178	3.5	1810
7	201.1027	2.0	1002
8	205.0596	8.1	4150
9	211.0940	1.5	780
10	213.1094	1.6	819
11	215.1254	1.4	714
12	217.1043	4.1	2115
13	223.1295	1.4	695
14	227.1254	1.3	683
15	231.1348	3.5	1785
16	236.0710	3.7	1899
17	239.0884	3.5	1774
18	241.1400	1.5	776
19	243.0990	1.3	691
20	245.0776	1.3	662
21	245.1508	1.4	732
22	257.1134	1.4	692
23	259.1291	1.5	770
24	261.1298	2.4	1245
25	273.1670	2.8	1441
26	277.2132	1.3	658
27	279.2295	2.3	1172
28	293.2079	1.2	636
29	297.2391	1.3	671
30	300.2169	6.3	3212
31	301.1400	3.6	1840
32	301.2171	1.8	927
33	304.2992	3.6	1864
34	309.2024	1.4	722
35	315.1907	1.8	925
36	321.2392	1.3	681
37	322.1990	100.0	51197
38	323.2012	21.6	11034
39	324.1963	9.7	4955
40	325.1994	2.1	1052
41	326.3774	1.9	989
42	326.6785	1.3	662
43	327.1589	1.7	859
44	327.1766	1.2	640
45	331.1875	1.3	670
46	331.2088	2.8	1408
47	332.3293	1.9	948
48	338.1731	1.2	631
49	339.1772	2.1	1061
50	344.1279	2.1	1062
51	349.1408	1.9	959
52	351.1949	1.5	750
53	353.1449	4.0	2046
54	353.2659	8.6	4406
55	354.2699	1.8	898
56	365.1042	1.5	785
57	365.2697	1.5	747
58	367.2081	1.9	954
59	381.2970	6.1	3105
60	382.3003	1.4	705
61	385.2922	1.6	819
62	389.2493	1.4	717

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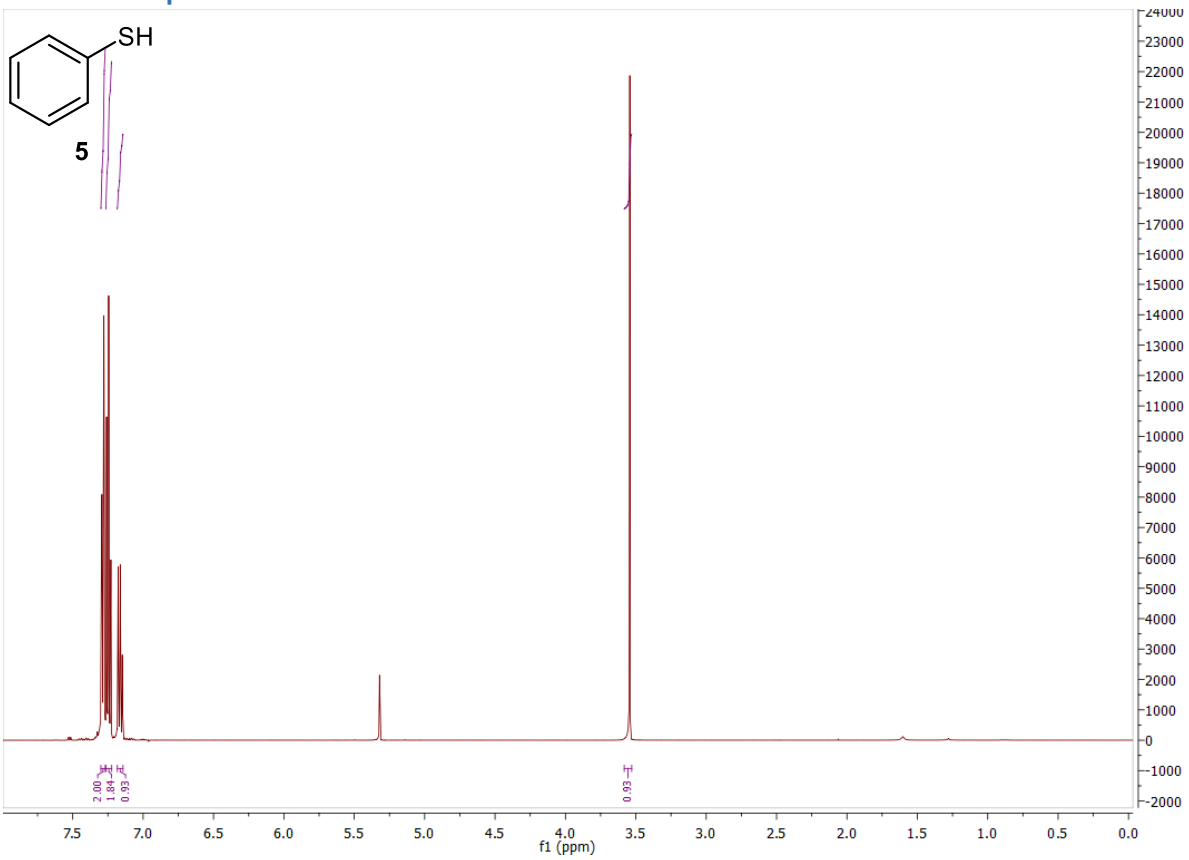
#	m/z	I %	I
63	391.2836	2.1	1057
64	393.2977	3.4	1718
65	399.1446	1.3	643
66	413.2658	11.4	5812
67	414.2695	2.7	1391
68	421.3291	1.7	845
69	425.3616	1.3	676
70	429.3186	2.1	1066
71	435.3454	1.3	646
72	441.2963	2.1	1090
73	447.3446	4.3	2204
74	448.3478	1.7	861
75	449.3568	1.5	767
76	449.3712	1.5	769
77	469.3269	2.1	1061
78	473.3433	2.0	999
79	501.3751	1.3	663
80	512.4145	1.4	718
81	517.3710	1.7	891
82	556.4391	1.5	783
83	561.3961	1.7	865
84	575.3915	1.6	807
85	575.4108	1.3	682
86	601.4660	1.3	689
87	605.4239	1.6	823
88	621.4092	3.0	1535
89	622.4141	1.3	684
90	649.4471	1.6	840
91	663.4569	1.7	854
92	675.5048	1.4	703
93	677.4779	1.4	713
94	691.5031	1.6	800
95	700.6254	2.0	1045
96	705.5808	4.9	2508
97	706.5856	2.5	1256
98	721.5750	1.6	794
99	737.4999	1.2	626
100	747.5606	1.3	642

Acquisition Parameter

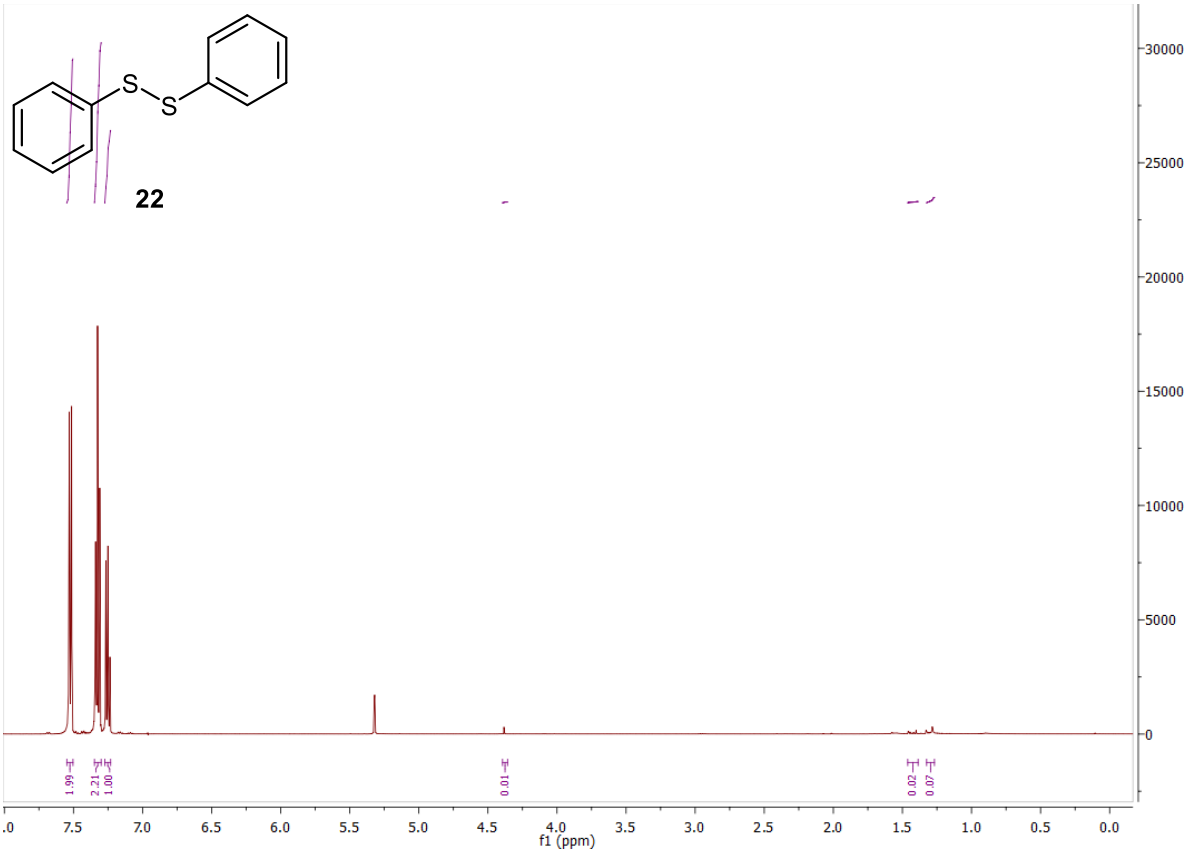
General	Fore Vacuum	2.69e+000 mBar	High Vacuum	1.02e-007 mBar	Source Type	ESI
	Scan Begin	75 m/z	Scan End	1700 m/z	Ion Polarity	Positive
Source	Set Nebulizer	0.4 Bar	Set Capillary	3600 V	Set Dry Gas	4.0 l/min
	Set Dry Heater	180 °C	Set End Plate Offset	-500 V		
Quadrupole	Set Ion Energy (MS only)	4.0 eV				
Coll. Cell	Collision Energy	8.0 eV	Set Collision Cell RF	350.0 Vpp		
Ion Cooler	Set Ion Cooler Transfer Time	75.0 µs	Set Ion Cooler Pre Pulse Storage Time	10.0 µs		

21. Compound **5**:



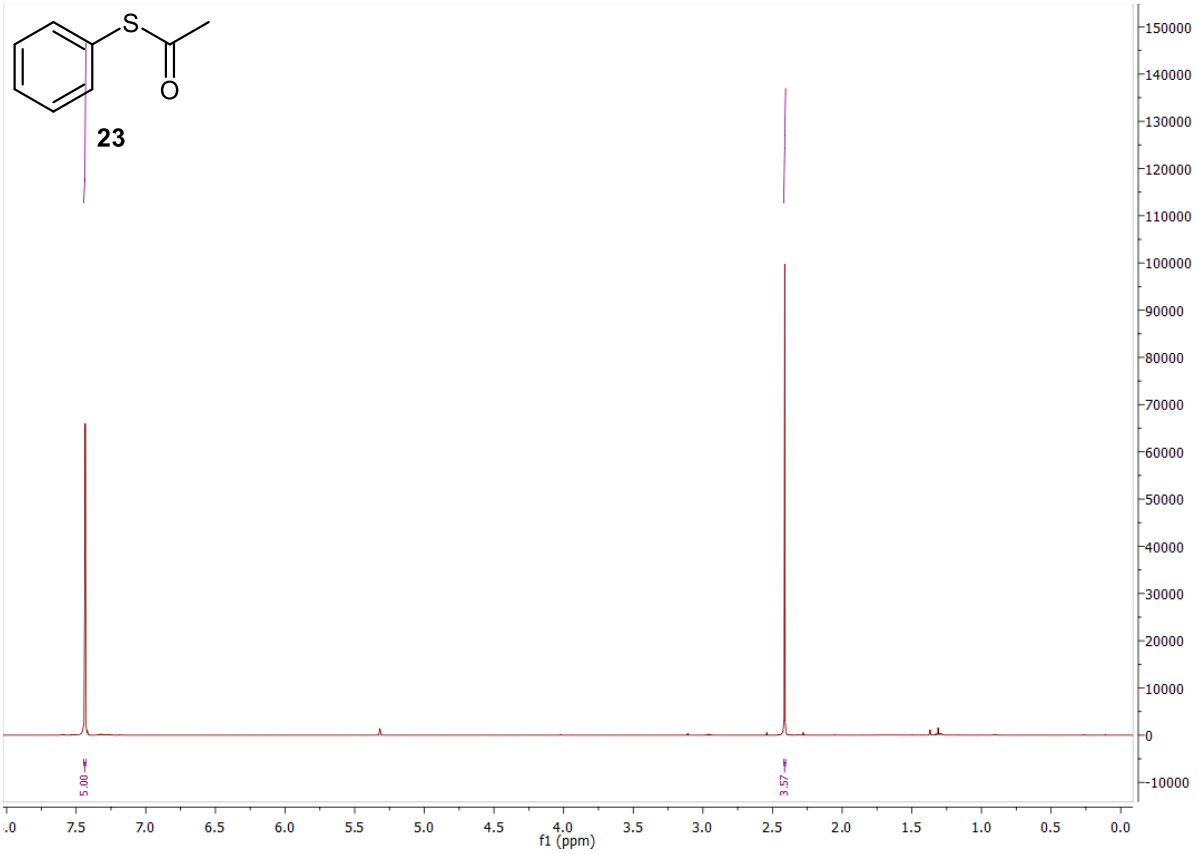
The spectra data of this compound was identical to those reported in the literature. (CAS: 108-98-5)

22. Compound **22**:



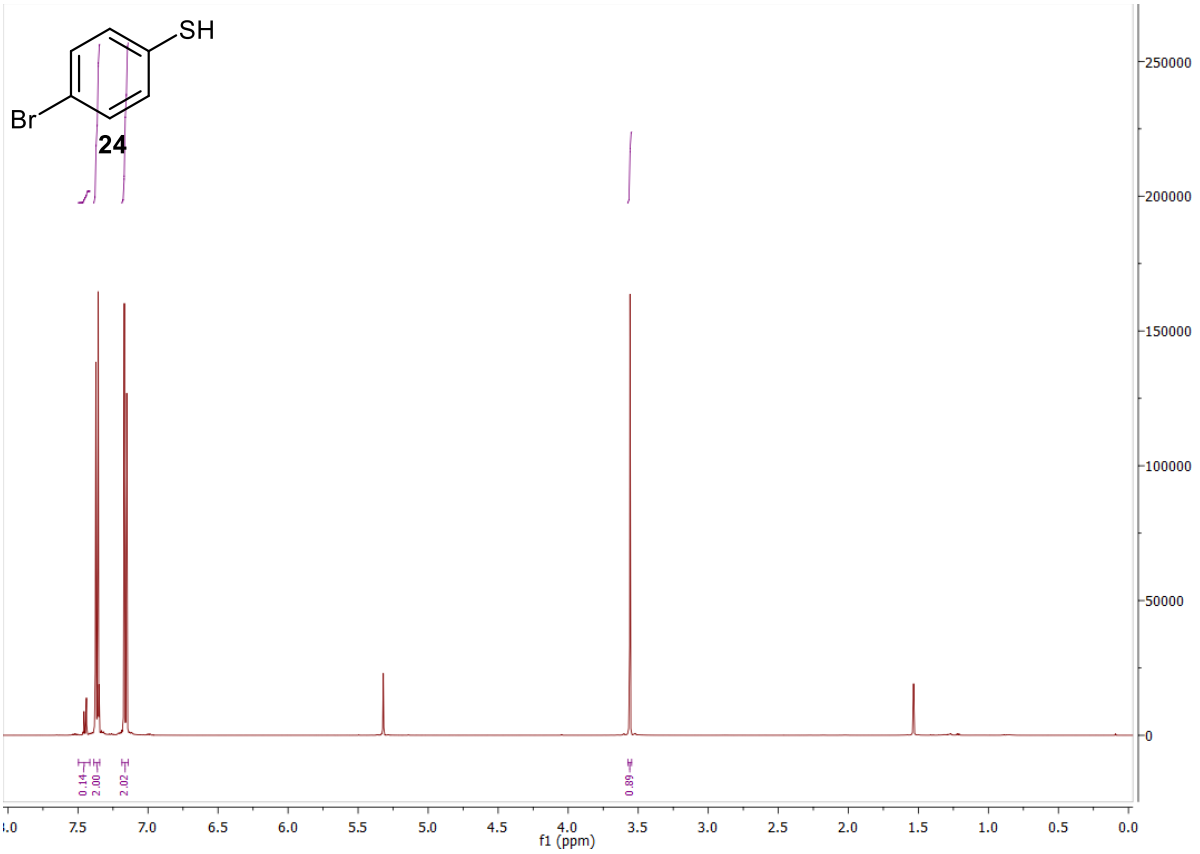
The spectra data of this compound was identical to those reported in the literature. (CAS: 882-33-7)

23. Compound **23**:



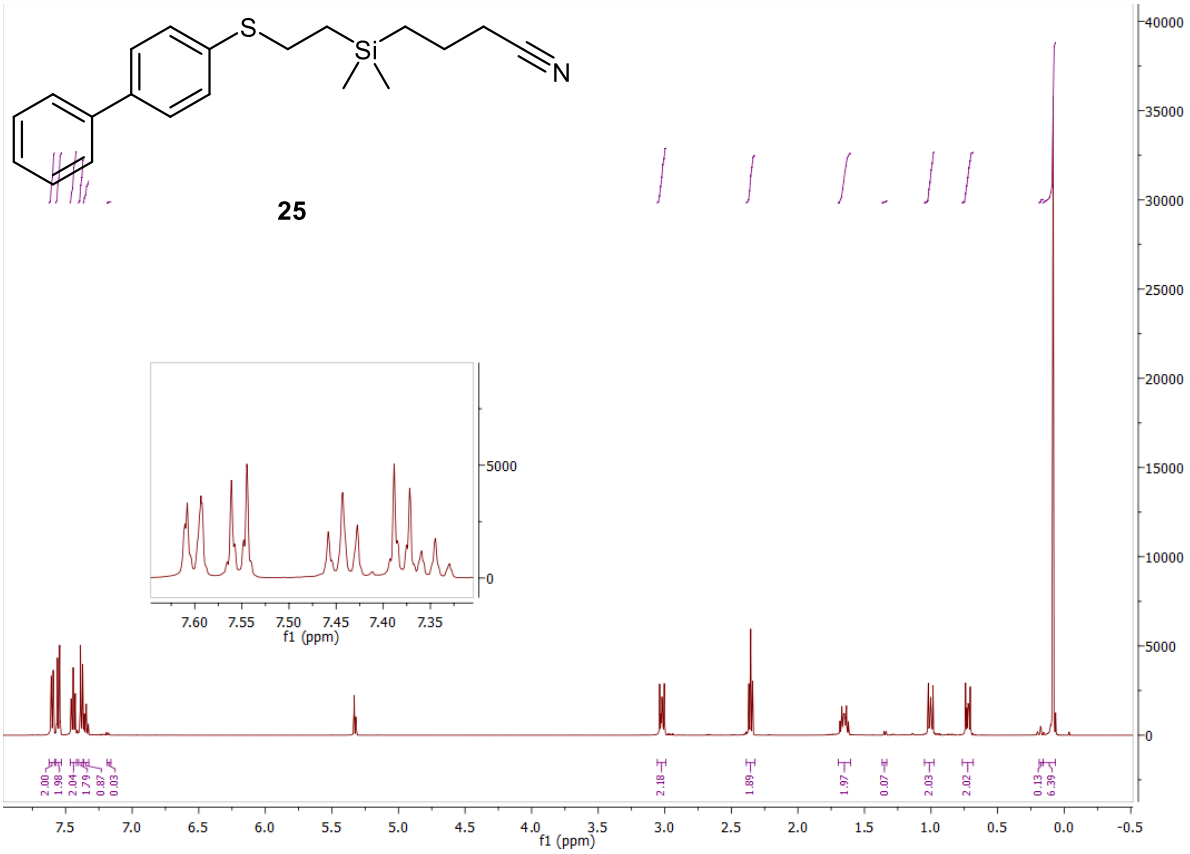
The spectra data of this compound was identical to those reported in the literature. (CAS: 934-87-2)

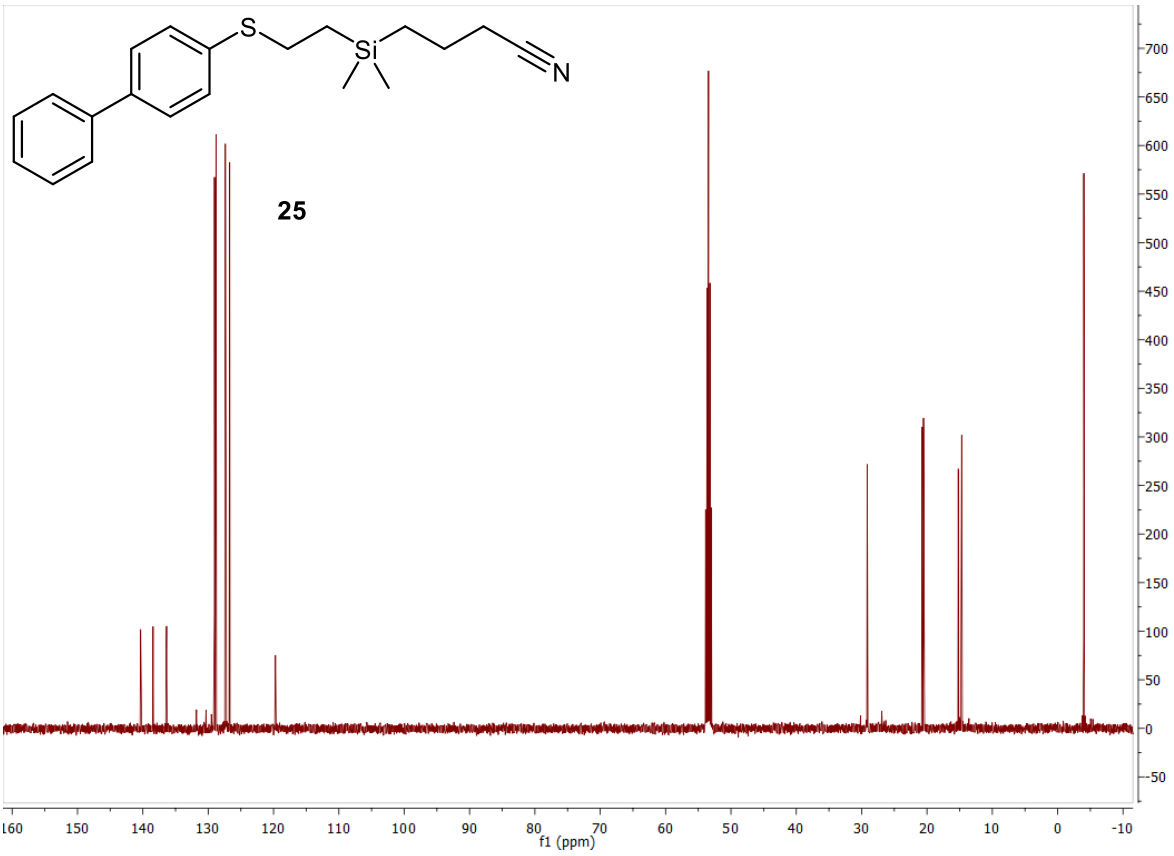
24. Compound **24**:

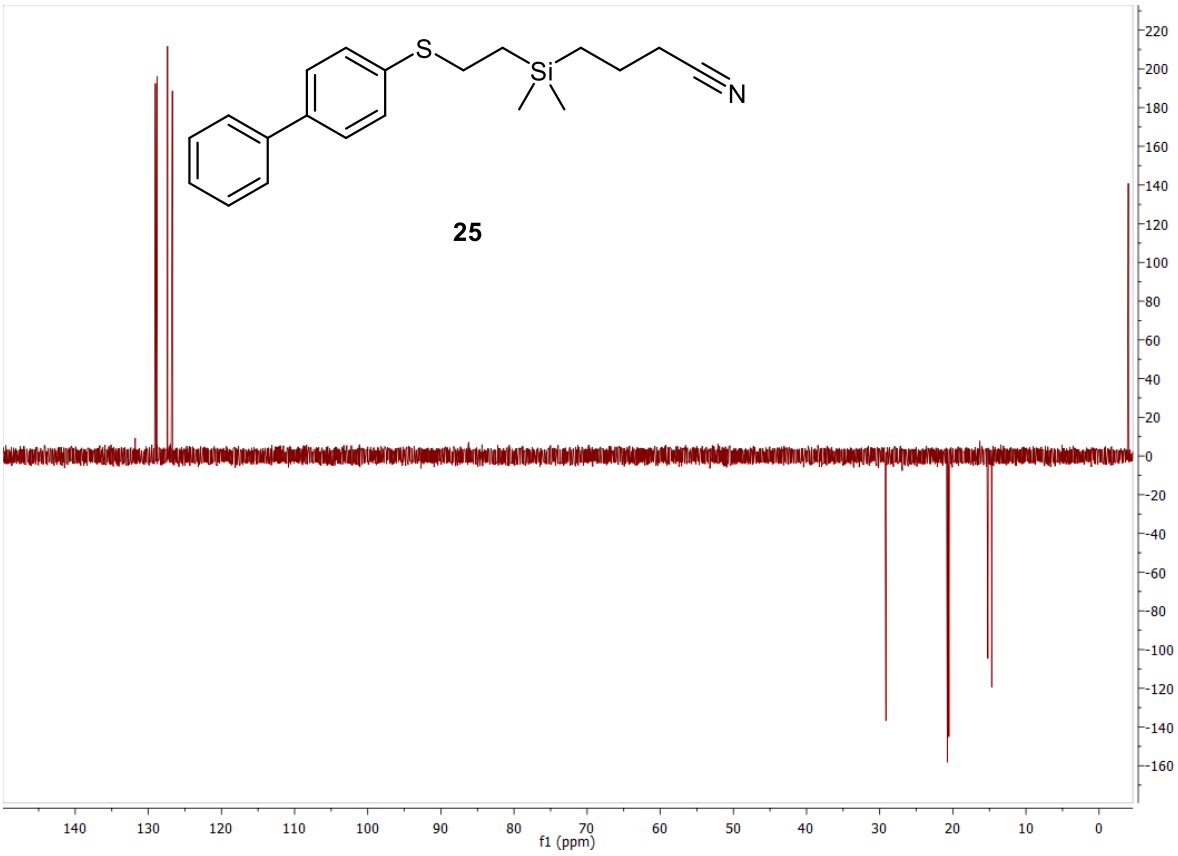


The spectra data of this compound was identical to those reported in the literature. (CAS: 106-53-6)

25. Compound **25**:

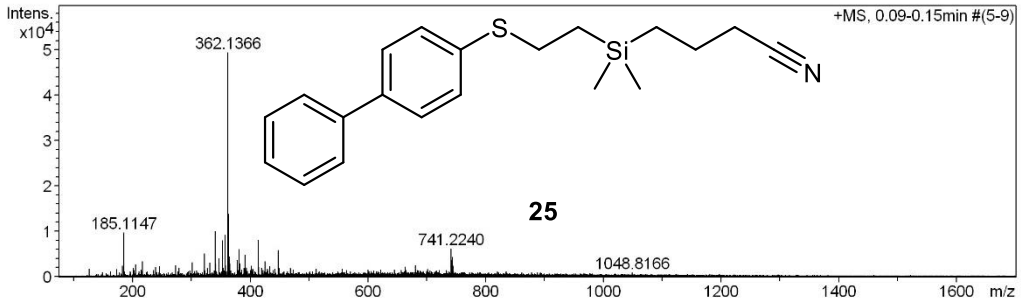


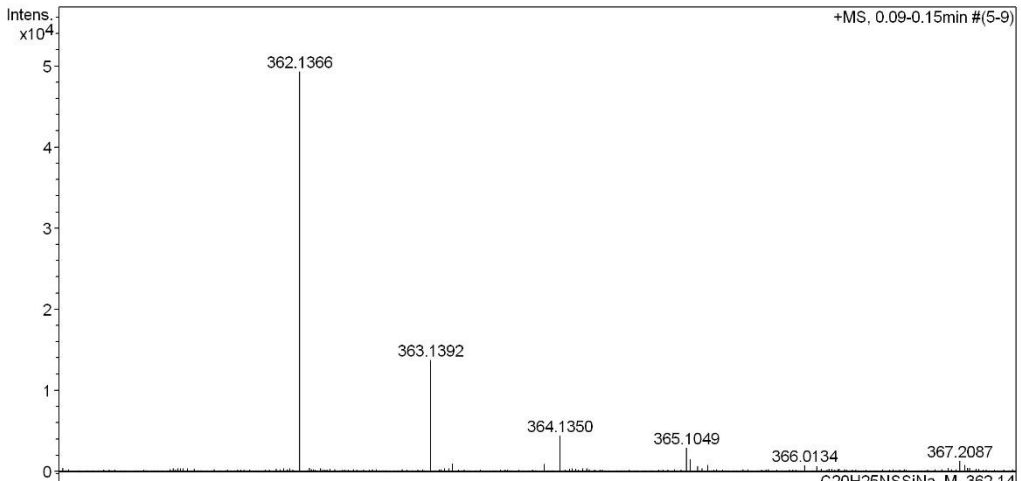


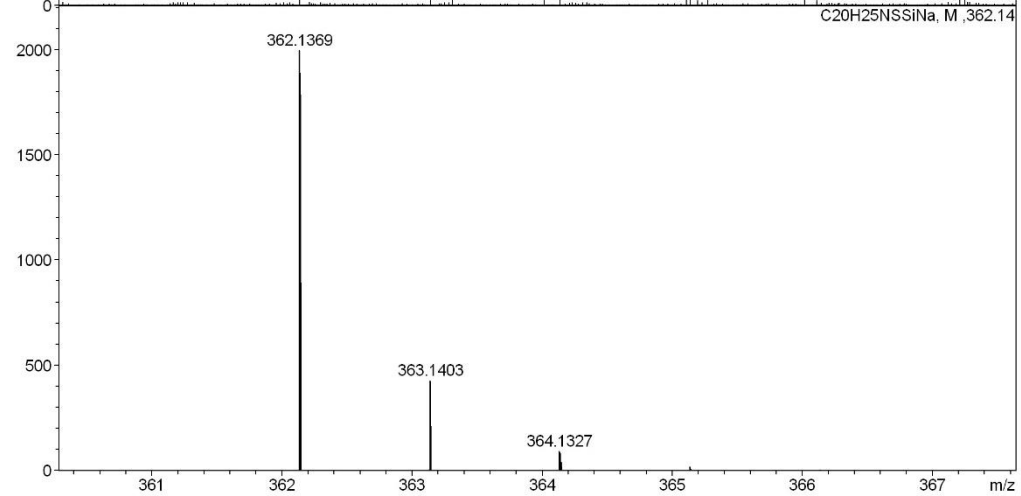

S
Si
N
25
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba573 chr1-1**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m







High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^- Conf	z
362.1366	1	C 20 H 25 N Na S Si	100.00	362.1369	0.3	0.9	13.8	9.5	even	1+

Mass list

#	m/z	I %	I
1	126.0733	3.6	1772
2	173.0782	3.3	1607
3	183.0781	4.8	2341
4	185.1147	19.5	9624
5	201.1019	3.9	1901
6	203.0522	2.8	1362
7	205.0597	5.5	2694
8	214.0889	3.0	1481
9	217.1049	6.8	3364
10	236.0714	2.8	1378
11	239.0885	4.1	2000
12	246.1274	4.6	2249
13	273.1674	4.9	2428
14	279.1587	3.2	1600
15	279.2291	3.9	1943
16	297.2393	2.6	1260
17	301.1403	6.2	3074
18	305.2443	2.4	1186
19	309.2052	2.5	1252
20	321.1816	2.9	1443
21	322.1905	10.3	5094
22	323.1937	2.7	1336
23	327.0775	3.7	1813
24	331.2084	6.1	3011
25	339.1762	2.5	1256
26	340.1544	20.3	10014
27	341.1566	5.7	2829
28	341.2663	3.3	1624
29	347.2009	8.0	3930
30	353.1458	3.2	1571
31	353.2660	16.0	7904
32	354.2693	3.8	1884
33	355.2819	2.5	1237
34	357.1812	18.6	9181
35	358.1838	5.0	2478
36	362.1366	100.0	49281
37	363.1392	27.9	13731
38	364.1350	8.9	4390
39	365.1049	5.9	2912
40	365.1349	3.1	1514
41	367.2087	2.6	1275
42	378.1103	7.5	3701
43	379.1131	2.8	1361
44	379.2812	2.5	1235
45	381.2972	12.2	5989
46	382.3010	3.1	1548
47	383.1404	5.9	2915
48	385.2923	3.1	1548
49	389.2509	3.7	1802
50	391.2839	9.5	4677
51	392.2868	2.8	1400
52	393.2968	4.0	1983
53	400.1671	2.9	1431
54	402.0760	4.8	2373
55	402.3573	3.2	1568
56	405.1220	3.2	1573
57	413.2656	16.2	8001
58	414.2685	4.2	2080
59	419.3148	3.9	1911
60	421.3289	2.9	1405
61	425.3627	6.7	3324
62	429.2404	2.7	1343

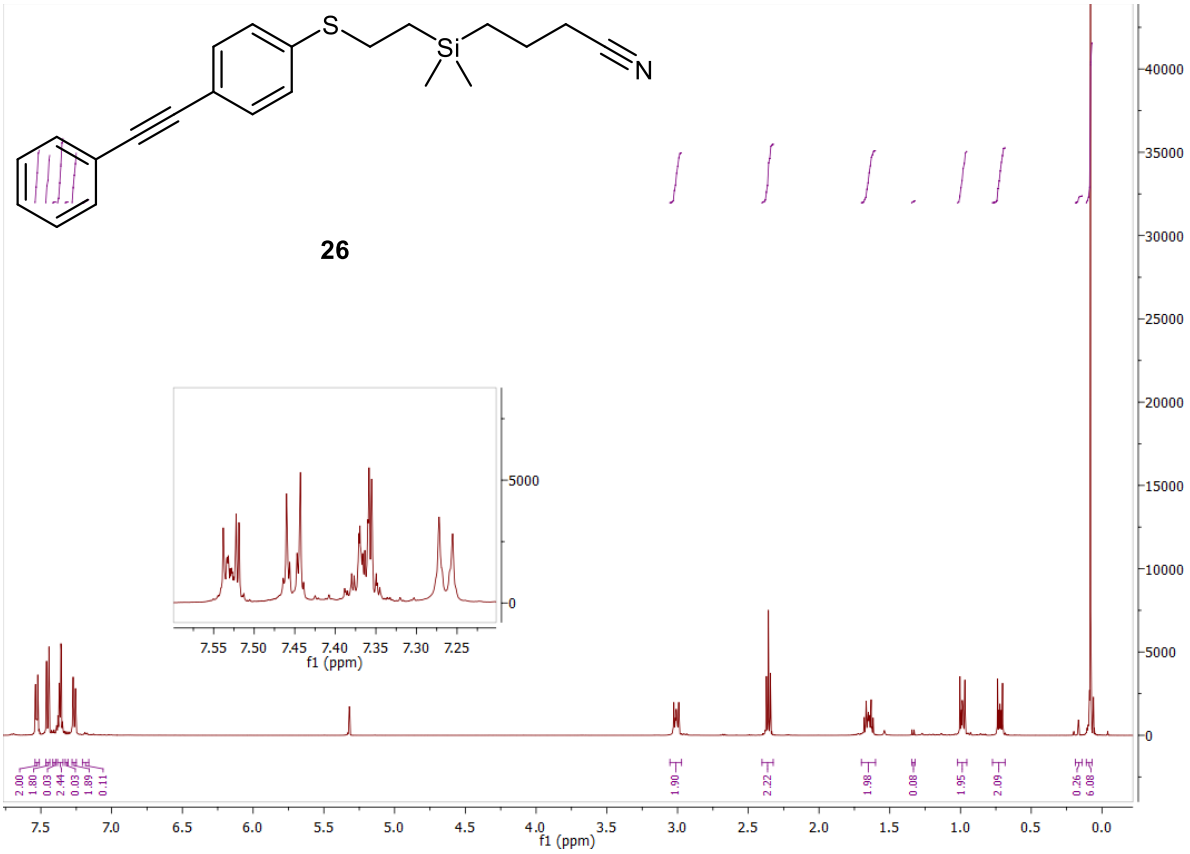
High Resolution Mass Spectrometry Report

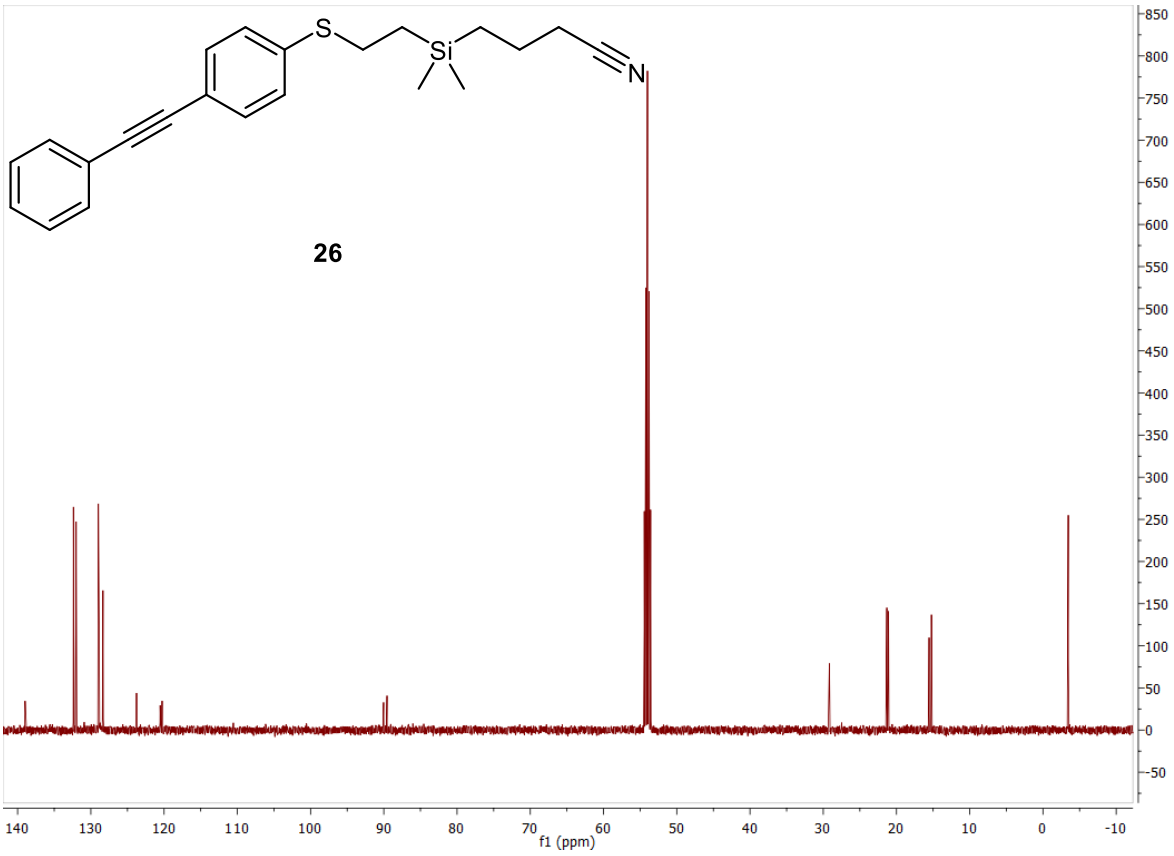
#	m/z	I %	I
63	429.3173	3.5	1743
64	430.3884	2.6	1289
65	433.1024	4.5	2233
66	439.2036	2.8	1383
67	441.2966	3.4	1689
68	447.3447	11.8	5800
69	448.3483	3.2	1579
70	449.3630	3.6	1781
71	468.3890	3.7	1847
72	469.3293	3.3	1618
73	473.3442	3.0	1480
74	512.4161	3.5	1713
75	556.4415	3.4	1694
76	563.3764	2.8	1397
77	600.4678	3.1	1526
78	610.1845	2.7	1327
79	621.4186	3.0	1486
80	644.4935	3.0	1476
81	656.5824	2.8	1365
82	663.4535	4.3	2117
83	664.4568	2.9	1406
84	680.4802	4.9	2424
85	681.4858	2.7	1347
86	684.2030	2.9	1422
87	685.4364	2.6	1292
88	688.5214	2.7	1316
89	699.5927	2.5	1217
90	701.2845	3.2	1599
91	705.5824	2.7	1331
92	716.5429	2.5	1252
93	721.4798	2.8	1374
94	721.5710	2.4	1186
95	732.5479	2.9	1448
96	733.5514	2.4	1197
97	741.2240	12.5	6150
98	742.2265	7.4	3666
99	743.2231	8.8	4320
100	744.2246	4.8	2383

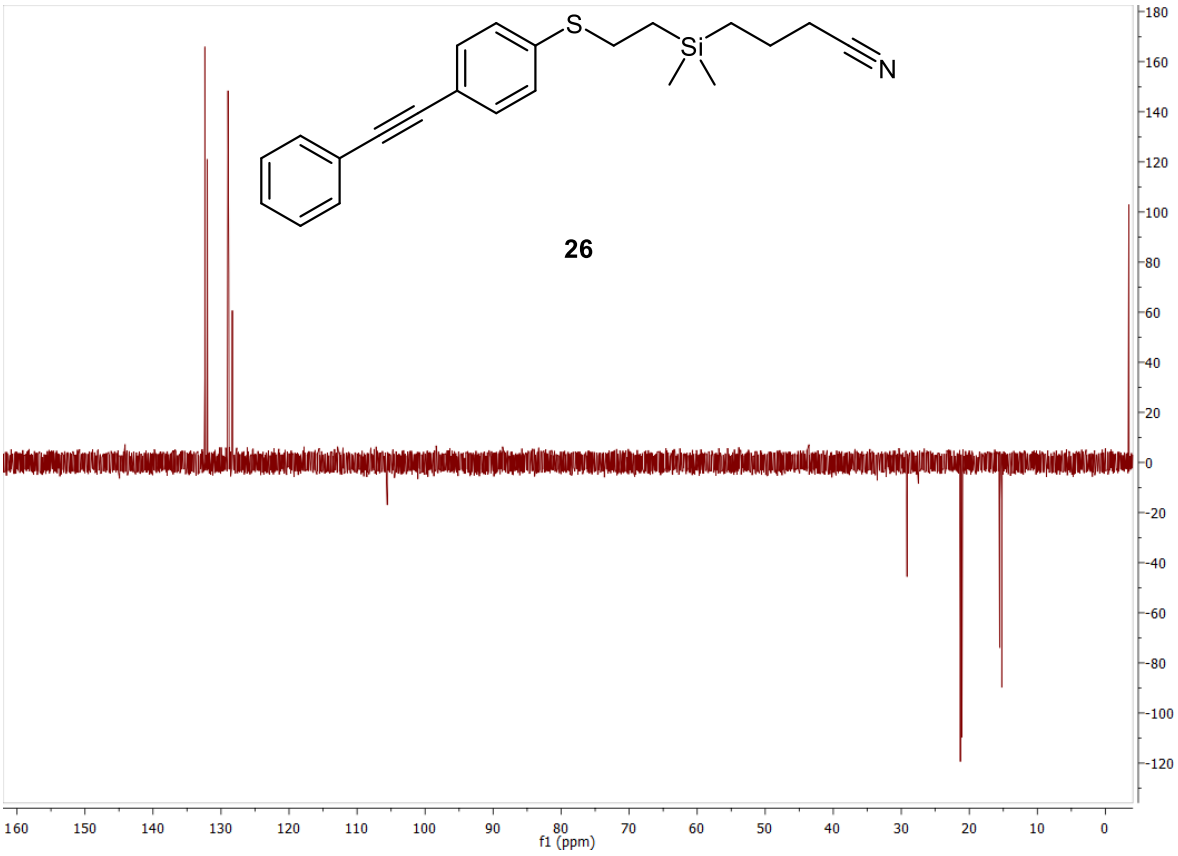
Acquisition Parameter

General	Fore Vacuum	2.80e+000 mBar	High Vacuum	9.59e-008 mBar	Source Type	ESI
	Scan Begin	75 m/z	Scan End	1700 m/z	Ion Polarity	Positive
Source	Set Nebulizer	0.4 Bar	Set Capillary	3600 V	Set Dry Gas	4.0 l/min
	Set Dry Heater	180 °C	Set End Plate Offset	-500 V		
Quadrupole	Set Ion Energy (MS only)	4.0 eV				
Coll. Cell	Collision Energy	8.0 eV	Set Collision Cell RF	350.0 Vpp		
Ion Cooler	Set Ion Cooler Transfer Time	75.0 µs	Set Ion Cooler Pre Pulse Storage Time	10.0 µs		

26. Compound **26**:

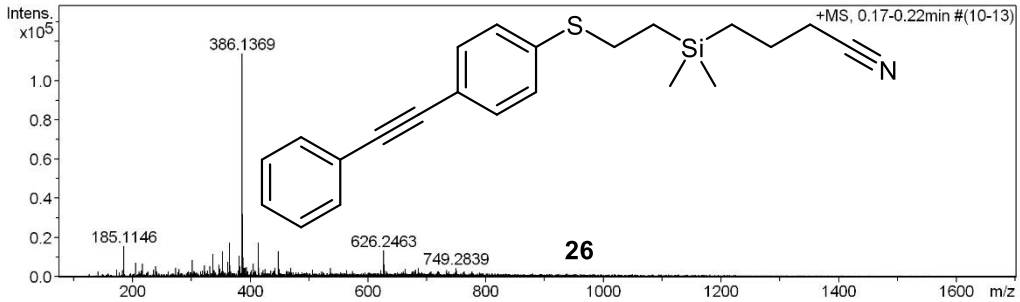


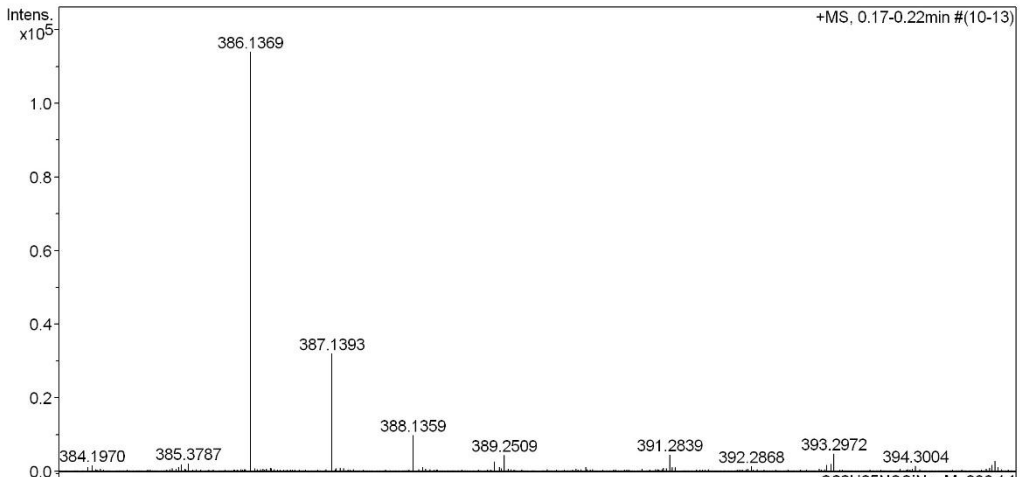


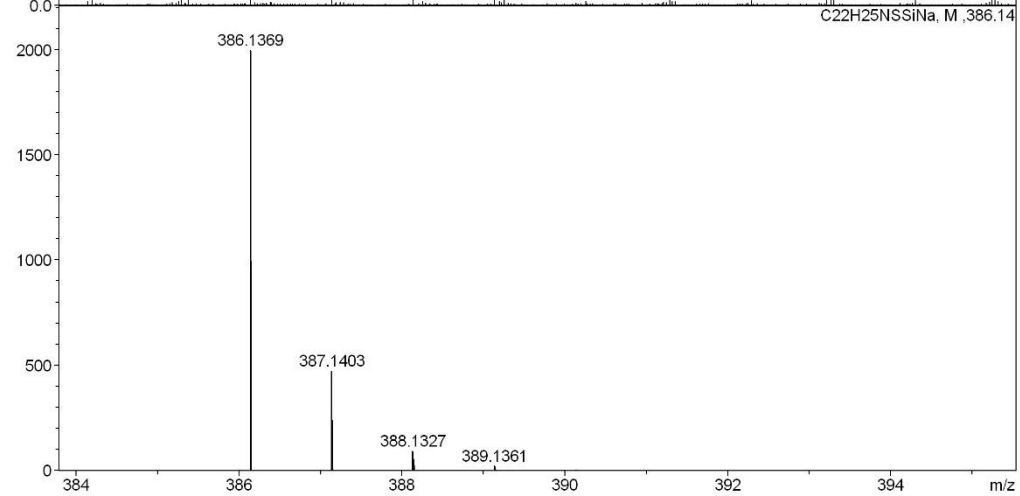

S
Si
N
26
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

High Resolution Mass Spectrometry Report

Sample Name	**Linda Bannwart / Ba574 chr1-1**	Instrument	maXis 4G
Comment	10 ug/mL in MeOH, analyzed in MeOH	Method	22 Direct_pos_mid.m







High Resolution Mass Spectrometry Report

Measured m/z vs. theoretical m/z

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^- Conf	z
386.1369	1	C 22 H 25 N Na S Si	100.00	386.1369	0.0	0.0	20.2	11.5	even	1+

Mass list

#	m/z	I %	I
1	173.0788	3.1	3546
2	183.0779	2.7	3114
3	185.1146	13.6	15445
4	205.0597	6.2	7068
5	211.0943	2.3	2602
6	215.1254	2.6	2937
7	217.1047	5.7	6453
8	226.9512	2.2	2541
9	236.0712	3.1	3494
10	239.0886	4.7	5344
11	241.0683	2.3	2597
12	261.1299	2.2	2537
13	273.1668	3.9	4455
14	279.2291	3.3	3786
15	294.9386	2.5	2837
16	301.1406	7.4	8471
17	301.2114	2.5	2886
18	304.2602	2.5	2850
19	305.1552	2.1	2434
20	315.1927	2.3	2589
21	319.2244	2.7	3050
22	321.2388	2.2	2551
23	322.1907	5.0	5688
24	323.1941	2.2	2482
25	327.0780	2.6	3009
26	331.2078	4.6	5249
27	336.1235	10.0	11321
28	337.1255	3.1	3491
29	339.1785	2.5	2872
30	347.2009	5.2	5964
31	349.0596	3.4	3914
32	350.9871	2.2	2525
33	353.2659	11.3	12910
34	354.2697	2.4	2758
35	362.1368	6.5	7365
36	364.1548	15.1	17156
37	365.1052	4.9	5585
38	365.1571	5.0	5661
39	366.0123	2.2	2519
40	367.2085	2.1	2402
41	379.2817	2.6	3007
42	381.1815	9.4	10691
43	381.2974	8.7	9901
44	382.1838	3.1	3549
45	382.3002	2.2	2558
46	383.1401	4.5	5109
47	386.1369	100.0	113754
48	387.1393	28.1	31911
49	388.1359	8.6	9773
50	389.1356	2.3	2584
51	389.2509	3.9	4401
52	391.2839	4.0	4548
53	393.2972	4.2	4753
54	395.2762	2.5	2824
55	402.1105	2.8	3190
56	405.1220	5.7	6486
57	407.3133	2.8	3184
58	409.2564	2.2	2512
59	413.2662	15.1	17151
60	414.2692	3.6	4105
61	421.3283	2.8	3216
62	425.3621	3.2	3619

High Resolution Mass Spectrometry Report

#	m/z	I %	I
63	435.3438	2.6	2965
64	439.2028	2.2	2551
65	441.2242	2.7	3046
66	441.2975	3.8	4369
67	447.2921	3.4	3857
68	447.3451	11.4	12917
69	448.3477	3.4	3914
70	449.3669	3.3	3775
71	461.1847	2.4	2685
72	463.3750	2.4	2690
73	465.3704	2.1	2418
74	469.3278	3.8	4367
75	505.3348	3.0	3410
76	521.3801	2.1	2437
77	536.1651	3.8	4295
78	563.3762	2.9	3299
79	573.4205	2.3	2637
80	621.4183	2.9	3289
81	626.2463	11.7	13267
82	627.2479	5.5	6204
83	628.2489	2.6	2973
84	631.4806	2.2	2527
85	659.5121	2.1	2397
86	663.4519	3.5	3982
87	675.5041	2.1	2425
88	677.4886	2.2	2522
89	679.4591	2.4	2704
90	680.4791	3.1	3519
91	685.4345	3.7	4251
92	707.4920	2.1	2445
93	717.5494	2.2	2514
94	719.5419	2.4	2739
95	733.5511	2.9	3274
96	737.5019	2.3	2602
97	749.2839	3.8	4289
98	750.2859	2.6	2977
99	763.5414	2.2	2447
100	776.5862	2.3	2563

Acquisition Parameter

General	Fore Vacuum	2.79e+000 mBar	High Vacuum	9.56e-008 mBar	Source Type	ESI
	Scan Begin	75 m/z	Scan End	1700 m/z	Ion Polarity	Positive
Source	Set Nebulizer	0.4 Bar	Set Capillary	3600 V	Set Dry Gas	4.0 l/min
	Set Dry Heater	180 °C	Set End Plate Offset	-500 V		
Quadrupole	Set Ion Energy (MS only)	4.0 eV				
Coll. Cell	Collision Energy	8.0 eV	Set Collision Cell RF	350.0 Vpp		
Ion Cooler	Set Ion Cooler Transfer Time	75.0 µs	Set Ion Cooler Pre Pulse Storage Time	10.0 µs		

References

(1) Jun, C.-H.; Kim, H.-S.; Park, J.-W. WO2007120014 (A1), **2007**.