Octakis(3-azidopropyl)octasilsesquioxane: A Versatile Nanobuilding Block for the Efficient Preparation of Highly Functionalized Cube-Octameric Polyhedral Oligosilsesquioxane Framew...

ARTICLE *in* CHEMISTRY - A EUROPEAN JOURNAL · MARCH 2010

Impact Factor: 5.73 · DOI: 10.1002/chem.200902422 · Source: PubMed

4 AUTHORS, INCLUDING:

Beatriz Trastoy
University of Maryland, Baltimore
10 PUBLICATIONS **135** CITATIONS
SEE PROFILE

Maria Eugenia Pérez-Ojeda
Spanish National Research Council
16 PUBLICATIONS **258** CITATIONS
SEE PROFILE

Jose Luis Chiara
Spanish National Research Council
102 PUBLICATIONS **1,588** CITATIONS
SEE PROFILE

CHEMISTRY
A EUROPEAN JOURNAL

FULL PAPER

DOI: 10.1002/chem.200((will be filled in by the editorial staff))

Octakis(3-azidopropyl)octasilsesquioxane: A Versatile Nano-Building Block for the Efficient Preparation of Highly Functionalized Cube-Octameric POSS Frameworks by "Click" Assembly

Beatriz Trastoy,[a] M. Eugenia Pérez-Ojeda, [b] Roberto Sastre, [b] and Jose Luis Chiara*[a]

Abstract: A one-step synthesis of octakis(3-azidopropyl)octasilsesquioxane from commercially available octakis(3-aminopropyl)octasilsesquioxane has been developed by a highly efficient diazo-transfer reaction under very mild conditions. Nonaflyl azide is shown to be a safer, cheaper and more efficient reagent for this transformation than the better known and generally used diazo-transfer reagent triflyl azide. Octakis(3-azidopropyl)octasilsesquioxane is an excellent nanobulding block that can be readily octafunctionalized with a diversity of simple and highly functionalized terminal alkynes by copper(I)-catalyzed 1,3-dipolar azide-alkyne cycloaddition under very mild conditions to provide new functional nanocages keeping a perfect 3-D cubic symmetry. The mildness, simplicity and efficiency of this approach have been demonstrated in the preparation of a glyco-POSS conjugate and a BODIPY-POSS cluster.

Keywords: azides • silsesquioxanes • click chemistry • carbohydrates • dyes/pigments

Introduction

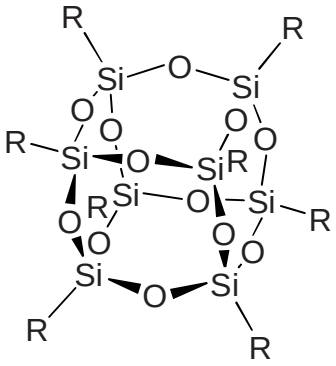
Fully condensed polyhedral oligosilsesquioxanes (POSS) are unique nanometer-sized hybrid inorganic–organic materials of chemical composition $(RSiO_{1.5})_n$, which can be readily synthesized by hydrolytic condensation of trifunctional organosilicon monomers $RSiX_3$ (R = organic group; X = halogen or alkoxide group).[1] Thanks to their rigid inorganic core, POSS are endowed with a considerable chemical and thermal stability. Although this family of compounds has been known for more than 60 years,[2] until the past decade the majority of commonly available POSS derivatives lacked sufficient functionality for most chemical applications. The discovery of new spontaneous self-assembly reactions[3-5] that provide ready access to a variety of novel POSS frameworks, the development of general and efficient methodologies for the synthetic manipulation of their pendant organic groups (see below), and the recent commercial availability of a wide range of simple monomers on a multigram scale[6] are contributing to the steep development of POSS chemistry in the last decades. Applications in areas as diverse as polymers, composite materials, dendrimers, optical materials, liquid crystals, drug carriers, metal catalysts, and cosmetics have been described over the past several years, especially in the patent literature.[7] The most promising POSS monomers are the highly symmetrical and topologically ideal cube-octameric frameworks (T_8), of general formula type $(RSiO_{1.5})_8$. Among these, octahydridooctasilsesquioxane (**1**),[8-10] the simplest T_8 compound, together with octavinyloctasilsesquioxane (**2**),[5,11,12] octaphenyloctasilsesquioxane (**3**),[3,5,13] and octakis(3-aminopropyl)octasilsesquioxane (**4**)[14-17] have been the most useful precursors to a variety of highly functionalized T_8 products (Figure 1). Key to all potential uses of these POSS basic monomers is the ease with which their pendant organic functionality can be altered in a controlled and highly efficient way to produce new molecules suitable for further functionalization. Since these T_8 molecules contain eight points for functionalization and partial transformation produce complex mixtures of products that are generally difficult to separate, it is critical that the reaction chosen for this task proceeds in a highly efficient way. A relatively wide range of derivatization reactions are suited for this purpose, although care must be taken to avoid strongly acidic, basic or oxidizing environments that can compromise the stability of the POSS cage. Transition metal-catalyzed reactions such as hydrosilylation,[18-25] olefin cross-metathesis,[24,26-28] and Heck,[24,29-33] Suzuki,[24,32] or Sonogashira[24,32] couplings; acylation[16,34-37] and Michael addition[16,38] reactions of amines; electrophilic aromatic substitution reactions;[32,39-43] and radical addition of thiols[44,45] or R_2PH[46-48] to olefins, have been used for this purpose with great success. Surprisingly, the 1,3-dipolar Huisgen cycloaddition of azides to alkynes,[49] a paradigmatic example of "click reaction"[50] that has proven to be a robust and reliable method for the efficient

[a] B. Trastoy, Dr. J. L. Chiara
Instituto de Química Orgánica General, CSIC
Juan de la Cierva, 3; E-28006 Madrid, Spain
Fax: (+) 34-915644853
E-mail: jl.chiara@iqog.csic.es

[b] M. Eugenia Pérez-Ojeda, Prof. Dr. Roberto Sastre
Instituto de Ciencia y Tecnología de Polímeros, CSIC
Juan de la Cierva, 3; E-28006 Madrid, Spain

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

functionalization of a wide variety of molecules under mild conditions, has been very scarcely used in POSS chemistry because of the lack of appropriately functionalized POSS derivatives.[51]



1, R = H
2, R = CH=CH$_2$
3, R = Ph
4, R = (CH$_2$)$_3$NH$_2$
5, R = (CH$_2$)$_3$N$_3$

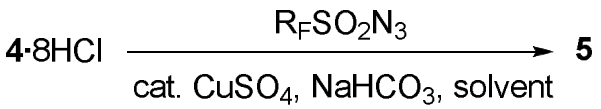
Figure 1. Simple octafunctionalized POSS T_8 monomers.

In this paper, we report on the synthesis of the new octaazide-POSS **5** (Figure 1) with a perfect 3-D cubic symmetry and an initial screening of reaction conditions for its octafunctionalization with a variety of alkynes by copper(I)-catalyzed[52,53] 1,3-dipolar azide-alkyne cycloaddition reaction (CuAAC).

Results and Discussion

We prepared compound **5** from the corresponding octaamino-POSS **4** using an efficient diazo-transfer reaction. Compound **4** is commercially available as its octahydrochloride salt[6] and can be easily obtained in multigram quantities from an inexpensive organosilicon precursor.[14,15,34] We examined two different diazo-transfer reagents for the synthesis of **5**: trifluromethanesulfonyl (triflyl) azide, which has been profusely used for the preparation of organic azides from the corresponding primary amines, mostly in carbohydrate chemistry;[54-56] and nonafluorobutanesulfonyl (nonaflyl) azide,[57,58] which at the onset of our work had never been used before for the synthesis of organic azides.[59] Triflyl azide is potentially explosive, it has a relatively poor shelf life and it must be prepared just before use from triflic anhydride and sodium azide as a solution in dichloromethane[54,60] or toluene.[61] In contrast, nonaflyl azide is stable at room temperature, can be safely distilled and kept as a neat reagent at 4 ºC for later use without decomposition, and is easily obtained from the much cheaper and readily available nonaflyl fluoride.[57,58] In an initial screening of reaction conditions (Table 1), we identified two factors as most critical to obtain an optimal yield of **5**. The first is the procedure employed for the required neutralization of **4**•8HCl to the free amine, which is known to be difficult to accomplish without compromising the Si/O framework.[16] In situ neutralization by incorporation of an excess of aqueous $NaHCO_3$ in the diazo-transfer reaction (Table 1, entries 2–6) afforded better yields than the previously described[16] pre-treatment of **4**•8HCl with Amberlite IRA-400/OH resin in methanol (Table 1, entry 1). The second factor affecting the yield is the reaction solvent. Homogenous solvent mixtures containing water, a simple alcohol and an apolar organic solvent were needed to solubilize all reaction components. Toluene was used as the apolar organic solvent in the case of triflyl azide (Table 1, entries 1–5),[61] while diethyl ether was required instead to dissolve the nonaflyl reagent (Table 1, entry 6). Mixtures containing ethanol or isopropanol as the alcohol component afforded the best yields (Table 1, entries 3, 4, and 6). In gram-scale preparations of **5**, the order of addition of reagents was also of importance. When $NaHCO_3$ was added to an aqueous solution of **4**•8HCl and $CuSO_4$•H_2O, a blue precipitate appeared, which was probably formed by a mixture of **4**/Cu(II) complexes. Under these conditions, yields usually halved due to the persistent heterogeneous nature of the reaction. Precipitation can be largely avoided by adding $NaHCO_3$ last and in small portions under very good stirring. Eventually, nonaflyl azide proved to be the reagent of choice for this transformation, both for its higher efficiency and for its much lower cost. Under the optimized conditions (Table 1, entry 6), compound **5** was obtained in gram amounts as a viscous liquid in 60-73% yield after chromatographic purification, which accounts for an excellent >94% yield per amino group in the diazo-transfer reaction. The structure of **5** was unambiguously confirmed from its HRMS, FT-IR, and NMR spectral data (Figure 2). Thus, a strong IR band at 2099 cm^{-1} characteristic of the azide group, a single set of resonances in the ^1H and ^{13}C NMR spectra, and a narrow singlet resonance in the ^{29}Si NMR spectrum, revealed the perfect 3-D cubic symmetry of this compound.

Table 1. Synthesis of octa-azide POSS **5** from octa-amino POSS **4**•8HCl by diazotransfer reaction.[a]



Entry	R_F	Solvent (v/v ratio)	Yield (%)[b]
1[c]	CF_3	Toluene/MeOH/H_2O (7.8:11:0.2)	17–20
2	CF_3	Toluene/MeOH/H_2O (7.8:11:0.2)	28–30
3	CF_3	Toluene/EtOH/H_2O (7.8:11:0.2)	50–54
4	CF_3	Toluene/*i*PrOH/H_2O (7.8:11:0.2)	55
5	CF_3	Toluene/*t*BuOH/H_2O (7.8:11:0.2)	42
6	$CF_3(CF_2)_3$	Et_2O/EtOH/H_2O (1:3:1)	60–73

[a] Reaction conditions: **4**•8HCl (1 mol-equiv), $RFSO_2N_3$ (R_F = CF_3, ca. 36 mol-equiv; R_F = $(CF_2)_3CF_3$, 24 mol-equiv), $CuSO_4$•$5H_2O$ (0.5 mol-equiv), $NaHCO_3$ (32 mol-equiv), rt, 16 h. [b] Yield of pure product after chromatography. [c] Compound **4** was added to the reaction as a solution in MeOH prepared by stirring a suspension of **4**•8HCl in this solvent with an excess of Amberlite IRA-400/OH at 0 ºC.

Very recently, Ge et al.[51c] have described a different synthesis of **5** by nucleophilic substitution reaction of octakis(3-chloropropyl)octasilsesquioxane with NaN_3. However, comparison of the reported spectral data[62] with those measured under the same conditions for our sample of **5** (see Figure 2 and Experimental Section), revealed some significant differences. First, Ge et al. observed a considerable broadening of the ^1H NMR signals (cf. Figure 1 of ref. [51c]), as opposed to well resolved multiplets (Figure 2c) in our case. Second, the ^{13}C and ^{29}Si NMR signals of the Si–CH_2 moiety (the most sensitive to cage structural modifications) appeared in their case, respectively, at ca. 1 ppm downfield and 2 ppm upfield shifted from those measured for our sample of **5**, which were observed at 9.0 ppm and –67.0 ppm, respectively. Moreover, since the authors did not report any mass spectral data for **5**, the

identity of their compound could not be unambiguously ascertained. Most likely, these substantial spectral differences are a consequence of a structural divergence between the products prepared by the two routes. Given the known propensity of POSS cages to suffer cleavage and rearrangement under nucleophilic attack,[63] it is probable that the azide anion has caused cage expansion (to T_{10} and T_{12}) or even degradation to a mixture of oligomers under the harsh thermal conditions (DMF, 120 ºC, 2 days) employed by the authors in the substitution reaction. In fact, in an interesting study of cage rearrangements of silsesquioxanes that included octakis(3-chloropropyl)octasilsesquioxane, Marsmann[63] observed that the T_8 to T_{10} rearrangement results in a ca. 2 ppm upfield shift of the ^{29}Si resonance, which is precisely the same shift observed between the sample of **5** prepared by diazo-transfer reaction in this work and that obtained by nucleophilic substitution.[64]

Since azides are potentially explosive,[65] we have evaluated the safety profile of octa-azide **5** by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).[66] This study showed that a slow thermal decomposition of compound **5** started at 237 ºC, well above the temperature required to perform the thermal cycloadditions (see below), exhibiting no characteristics of explosive behaviour, with a weight loss of only ca. 27% in approximately the same temperature range as the DSC exotherm. Thus, gram quantities of **5** can be safely prepared and stored for later use without any special precautions.

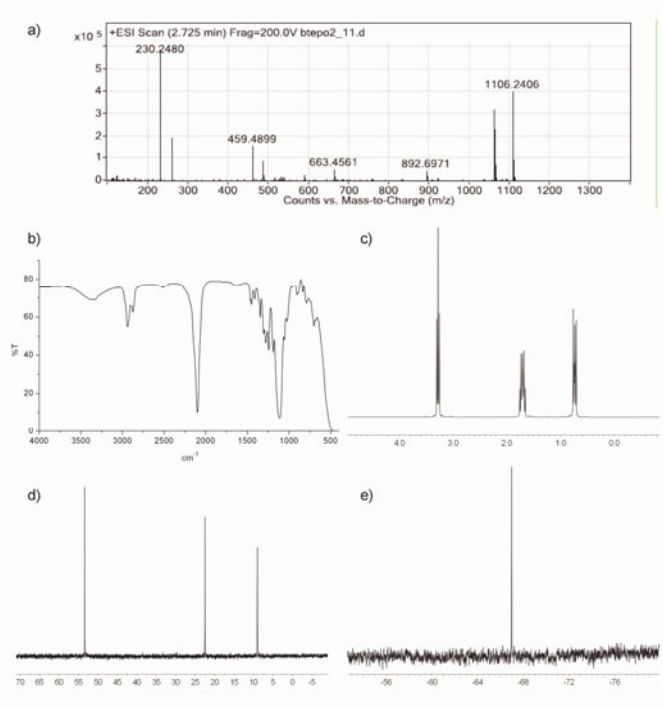
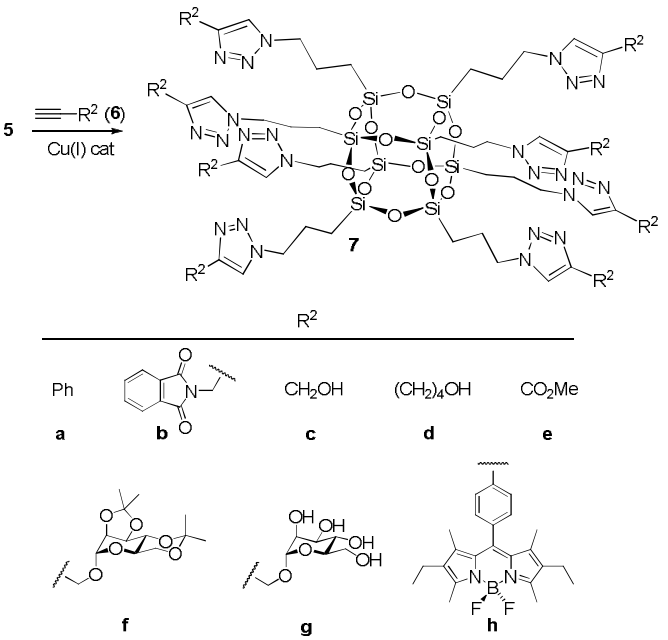


Figure 2. a) ESI-MS (H_2O/MeOH containing 0.1% HCO_2NH_4), 1106.2406 $[M + NH_4]^+$, 1061.2084 $[(M - N_2) + H]^+$; b) FT-IR (thin film); c) ^{1}H NMR ($CDCl_3$); d) ^{13}C NMR ($CDCl_3$); and e) ^{29}Si NMR ($CDCl_3$) spectra of octa-azide POSS **5**.

With an optimized procedure in our hands for the efficient preparation of octa-azide-POSS **5** in gram-scale, we studied next its octafunctionalization with simple alkynes by CuAAC (Scheme 1). Using phenyl acetylene as a model, different copper catalyst and solvent systems were assayed for the synthesis of the corresponding octatriazolyl-POSS product **7a** (Table 2, entries 1–4). Although all reaction conditions examined afforded excellent yields of **7a** with complete regioselectivity using a 5% molar copper catalyst with respect to alkyne, reaction times varied widely. Slow reactions were observed when the cycloaddition was performed at room temperature under homogeneous conditions in toluene using the soluble catalysts $(EtO)_3P{\bullet}CuI$[67] or the recently described [(IPr)CuCl][68,69] (IPr = *N*,*N*'-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and [Cu($C18_6$tren)]Br[70,71] ($C18_6$tren = tris(2-dioctadecylaminoethyl)amine) in the presence of base (Table 2, entries 1–3), with reaction times diminishing in this same order. However, the fastest reaction and the highest yield (96% isolated yield, which represents >99% per azide group) was obtained with the $CuSO_4{\bullet}H_2O$/sodium ascorbate precatalyst system[53] using a biphasic CH_2Cl_2/water solvent mixture[72] at room temperature (Table 2, entry 6). The study was extended to other simple alkynes **6b-e** and the process was found to tolerate a broad range of functional groups and reaction conditions affording the corresponding octatriazolyl-POSS products **7b-e** regioselectively and in good yield (lowest yield = 61%, which represents 94% per azide group). In those cases where the optimal room temperature conditions using the $CuSO_4{\bullet}H_2O$/sodium ascorbate system resulted in sluggish reactions (Table 2, entry 5), the soluble Cu(I) catalysts performed very efficiently under microwave heating in homogenous conditions, with greatly reduced reaction times (Table 2, entries 6–13). The hexane-soluble [Cu($C18_6$tren)]Br catalyst is particularly attractive in the case of hydrophilic alkynes (Table 2, entries 7–10), allowing a straightforward work-up of the crude reaction mixture by a simple hexane/MeOH liquid-liquid extraction, which completely removed the copper catalyst in the hexane fraction affording the pure product in the MeOH phase, free from copper impurities. Besides, this was the most efficient of the three soluble Cu(I) catalysts tested. As already observed for their precursor **5**, all new octatriazolyl-POSS products **7** prepared in this work showed a single set of signals in ^{1}H and ^{13}C NMR and one singlet in the ^{29}Si NMR spectra,[73] as expected for a perfect 3-D cubic molecular symmetry.



Scheme 1. Synthesis of octatriazolyl-POSS compounds **7** by CuAAC reaction of **5** with terminal alkynes.

Table 2. Synthesis of octa-triazolyl POSS **7a-h** from octa-azide-POSS **5** by CuAAC reaction.

Entry	Alkyne	Catalyst	Base	Solvent (v/v ratio)	T (°C)	t (h)	Product	Yield (%)
1	**6a**	$(EtO)_3P$·CuI	*i*Pr_2NEt	Toluene	25	70	**7a**	90
2		[(IPr)CuCl]	*i*Pr_2NEt	Toluene	25	48		90
3		[Cu($C18_6$tren)]Br	*i*Pr_2NEt	Toluene	25	20		92
4		$CuSO_4$·$5H_2O$/sodium ascorbate	none	CH_2Cl_2/H_2O (1:1)	25	1		96
5	**6b**	$CuSO_4$·$5H_2O$/sodium ascorbate	none	CH_2Cl_2/H_2O (1:1)	25	18	**7b**	61
6		[Cu($C18_6$tren)]Br	*i*Pr_2NEt	Toluene	80 (MW)	3		89
7	**6c**	[Cu($C18_6$tren)]Br	*i*Pr_2NEt	Toluene	80 (MW)	3	**7c**	67
8				THF/H_2O (2:1)	25	24		77
9	**6d**	[Cu($C18_6$tren)]Br	*i*Pr_2NEt	Toluene	80 (MW)	3	**7d**	71
10				THF/H_2O (2:1)	25	24		80
11	**6e**	[Cu($C18_6$tren)]Br	*i*Pr_2NEt	Toluene	80 (MW)	3	**7e**	88
12	**6f**	$(EtO)_3P$·CuI	*i*Pr_2NEt	Toluene	80 (MW)	9	**7f**	63
13		[Cu($C18_6$tren)]Br	*i*Pr_2NEt	Toluene	80 (MW)	3		78
14		$CuSO_4$·$5H_2O$/sodium ascorbate	none	CH_2Cl_2/H_2O (1:1)	25	2		85
15	**6h**	$CuSO_4$·$5H_2O$/sodium ascorbate	none	CH_2Cl_2/H_2O (1:1)	25	4.5	**7h**	70

Armed with the required methodology for the synthesis of octaazido-POSS **5** and its efficient derivatization with simple alkynes by CuAAC reaction, we proceeded to apply it to the preparation of more complex functional nanoplatforms. The assembly of a multivalent POSS glycoconjugate[74] (**7g**) and a POSS-fluorophore cluster[75] (**7h**) were selected for this study. Synthetic multivalent glycoconjugates are interesting constructs for the study of carbohydrate-protein recognition processes and have a number of other potential practical applications including the prevention of early adhesion of pathogens to host epithelial cells, the neutralization of viruses and toxins, the preparation of vaccines, and carbohydrate-guided targeted drug delivery.[77-79] On the other hand, multimeric fluorescent molecules have been used as chemosensors for H^+ or metal ions, biological probes, optical brighteners, light harvesting devices or as potential compounds for organic light-emitting diodes.[80,81] Glyco-POSS **7f** was readily assembled from **5** by CuAAC reaction with acetal-protected propargyl α-D-mannopyranoside **6f**[82] under homogenous or biphasic conditions (Table 2, entries 12–14). As observed with the simple alkynes, the best yield was obtained with $CuSO_4$·$5H_2O$ /sodium ascorbate in a CH_2Cl_2/H_2O mixture at room temperature (Table 2, entry 14). Deprotection of **7f** under mildly acidic conditions by treatment with trifluoroacetic acid in THF/H_2O (4:1) at room temperature proceeded without affecting the stability of the POSS cage to afford the free octamannoside glyco-POSS **7g** in 90% isolated yield. Likewise, reaction of **5** with the ethynylphenyl functionalized boron dipyrromethene (BODIPY) fluorescent dye **6h**,[83,84] using $CuSO_4$•$5H_2O$/sodium ascorbate in CH_2Cl_2/H_2O provided the fluorophore cluster **7h** in very good yield (Table 2, entry 15). The kinetics and thermodynamics of the complexation reaction of **7g** and other similarly prepared glyco-POSS compounds with model lectins and the photophysical properties of fluorophore cluster **7h** are currently being evaluated in collaboration with other groups and will be reported in due course.

Conclusion

In conclusion, we have developed a one-step synthesis of octakis(3-azidopropyl)octasilsesquioxane (**5**) from commercially available octakis(3-aminopropyl)octasilsesquioxane (**4**) by a highly efficient diazo-transfer reaction under very mild conditions. We have found that nonaflyl azide is a safer, cheaper and more efficient diazo transfer reagent than the better known and commonly used triflyl azide. Compound **5**, showing eight azide groups, is an excellent nanobulding block that can be efficiently and regioselectively octafunctionalized with a diversity of simple and complex terminal

alkynes by copper(I)-catalyzed 1,3-dipolar azide-alkyne cycloaddition (CuAAC) under very mild conditions to provide new functional nanocages **7** in high yield, keeping a perfect 3-D cubic symmetry. A screening of different CuAAC reaction conditions revealed that both, the $CuSO_4$•$5H_2O$/sodium ascorbate precatalyst system in aqueous solvents at room temperature and the recently described [Cu(C18$_6$tren)]Br catalyst in organic solvents under microwave irradiation provided the best yields and shortest reaction times. The mildness, simplicity, efficiency, and versatility of this approach have been demonstrated in the preparation of a glyco-POSS conjugate and a BODIPY-POSS cluster. We believe that this methodology opens ample possibilities for the efficient and controlled assembly of new hybrid organic/inorganic nanomaterials with a high degree of symmetry and with carefully tailored functional properties.

Experimental Section

General methods. All melting points were measured with a Reicher Jung Thermovar micro-melting apparatus. Infrared (FT-IR) spectra were measured as KBr pellets or oils between KBr plates using a Perkin Elmer Spectrum One spectrophotometer and are reported in cm^{-1}. Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR or ^{13}C NMR) spectra were recorded on a BRUKER AMX-300 (300 and 75 MHz, respectively), a Varian INOVA 300 (300 and 75 MHz, respectively), a Varian INOVA 400 (400 and 100 MHz, respectively) or a Varian UNITY 500 (500 and 125 MHz, respectively) spectrometers. Silicon-29 nuclear magnetic resonance spectra were measured on a Varian INOVA 400 spectrometer (79.5 MHz). Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual peaks of the deuterated NMR solvent used or to internal tetramethylsilane. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances, b = broad), integration, coupling constants in hertz (Hz), and assignment. Proton and carbon-13 assignments are based on DQ-COSY, HSQC, and HMBC correlation experiments. Thin layer chromatography (TLC) was performed with Merck Silica Gel 60 F254 plates. The chromatograms were viewed under UV light and/or by treatment with a solution of ammonium molybdate (50 g) and cerium(IV) sulphate (1 g) in 5 % aqueous H_2SO_4 (1 L) followed by charring on a hot plate. For detection of azides, the chromatograms were first dipped in a 1% (w/v) solution of Ph_3P in EtOAc, dried at rt, then dipped in a 1% or 5% (w/v) solution of ninhydrin in 95% aqueous EtOH, and finally charred on a hot plate.[85] Column chromatography was performed with Merck silica gel, grade 60, 230–400 mesh. Mass spectra were recorded on a MALDI Voyager-DE PRO time-of-flight (TOF) spectrometer (Applied Biosystems), using a 2,5-dihydroxybenzoic acid matrix, or in an Agilent/HP 1100 LC/MSD spectrometer using ESI or APCI sources. High resolution mass spectra (HRMS) were recorded on an Agilent 6520 Q-TOF instrument with a ESI source. Elemental analyses were determined in a Heraus CHN-O analyser. Anhydrous solvents were prepared according to standard methods by distillation over drying agents or via elution through a Pure Solv™ column drying system[86] from Innovative Technology, Inc. All other solvents were of HPLC grade and were used as provided. All reactions were carried out with magnetic stirring and, if air or moisture sensitive, in oven-dried glassware under argon. Microwave irradiation experiments were performed with a single-mode Discover System from CEM Corporation, using standard Pyrex tubes (10 or 35 mL capacity) sealed with a rubber cap. Copper(I) catalysts $(EtO)_3P$•CuI,[87] [(IPr)CuCl] (IPr = N,N'-bis(2,6-diisopropylphenyl)imidazol-2-ylidene),[88] and [Cu(C18$_6$tren)]Br (C18$_6$tren = tris(2-dioctadecylaminoethyl)amine)[70] were prepared following described procedures.

Octakis(3-azidopropyl)octasilsesquioxane (5). *Method A: With triflyl azide. a) Synthesis of a toluene solution of triflyl azide.* To a solution of sodium azide (1.06 g, 16.32 mmol) in water (2.6 mL) was added toluene (2.6 mL) and the mixture was cooled to 0 ºC. Triflic anhydride (1.4 mL, 8.16 mmol) was then added dropwise under vigorous stirring (30 min addition time) and the stirring was continued for 2 h at 10 ºC. A saturated aqueous solution of $NaHCO_3$ was added dropwise until gas evolution had ceased and the two phases were separated. The aqueous layer was extracted with toluene (2 × 2.6 mL). The combined organic layers containing trifyl azide were used in the subsequent diazo transfer reaction. *b) Diazo transfer reaction.* To a solution of octakis(3-aminopropyl)octasilsesquioxane octahydrochloride (**4**·8HCl)[16] (200 mg, 0.22 mmol), $NaHCO_3$ (592 mg, 7.04 mmol) and $CuSO_4$·$5H_2O$ (4 mg, 0.34 mmol) in water (0.2 mL) at 0 ºC was added the stock solution of triflyl azide in toluene prepared above (7.8 mL) followed by *i*PrOH (11 mL) to obtain a homogeneous mixture. After vigorously stirring at room temperature for 12 h, the mixture was concentrated at reduced pressure, and the crude was partitioned between EtOAc (25 mL) and a saturated aqueous solution of EDTA (15 mL). The phases were separated, the aqueous solution was extracted with EtOAc (3 × 10 mL), the combined organic layers were washed with brine, dried (Na_2SO_4) and the solvent was removed at reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc 15:1) to obtain **5** as a colorless viscous oil (130 mg, 54%). When this reaction was run on 1.0–2.0 g of starting octaamino-POSS **4**, the yield dropped to only 30-32%.

Method B: With nonaflyl azide. a) Synthesis of nonaflyl azide.[58] To a solution of NaN_3 (8.0 g, 123 mmol) in MeOH (220 mL) was added perfluorobutanesulfonyl fluoride (20 mL, 111 mmol). After stirring at 20 ºC for 12 h, the mixture was poured onto ice-water. If a stable emulsion is formed, it can be broken by filtration through a layer of Na_2SO_4 to give two layers. The colorless oily layer of perfluorobutansulfonyl azide was separated, dried over Na_2SO_4 and used without further purification for the diazo-transfer reaction (22 g, 60%). The pure reagent can be kept at 4 ºC for several weeks without decomposition. *b) Diazo transfer reaction.* To a solution of octakis(3-aminopropyl)octasilsesquioxane octahydrochloride (**4**·8HCl)[16] (2.0 g, 1.70 mmol) in water (2 mL) at 0 ºC were added in sequence EtOH (90 mL), a solution of perfluorobutansulfonyl azide (13.30 g, 40.9 mmol) in Et_2O (30 mL), a solution of Cu_2SO_4·$5H_2O$ (213 mg, 0.852 mmol) in water (2 mL), and a solution of $NaHCO_3$ (4.58 g, 54.6 mmol) in water (26 mL). The reaction mixture was vigorously stirred at 0 ºC for 1 h and at room temperature for 24 h. The mixture was concentrated at reduced pressure, CH_2Cl_2 (150 mL) was added, and the resultant solution was washed with a saturated aqueous solution of $NaHCO_3$ (4 × 100 mL) to remove the nonafluorobutanesulfonamide. The organic layer was separated, dried over Na_2SO_4, and concentrated at reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc 15:1) to afford **5** as a colorless viscous oil (1.250 g, 67%). R_f = 0.6 (silica gel, hexane/EtOAc 5:1). IR (film) ν = 2939, 2875, 2099 (s, N_3), 1304, 1278, 1243, 1188, 1111 (s), 699 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.46–1.00 (m, 16H, SiCH_2), 1.42–1.99 (m, 16H, SiCH$_2$CH_2), 3.28 (t, 16H, *J* = 6.9 Hz, SiCH$_2$CH$_2$CH_2N$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 9.0 (SiCH$_2$), 22.5 (SiCH$_2$CH$_2$), 53.4 (SiCH$_2$CH$_2$CH$_2$N$_3$). ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ –67.0. MS API-ESI (*m/z*): 1112 [M+Na$^+$]. HRMS (ESI) calcd for $C_{24}H_{52}N_{25}O_{12}Si_8$ 1106.2381 [M + NH_4^+], found 1106.2396.

Octakis[3-(4'-phenyl-1'*H*-1',2',3'-triazol-1'-yl)propyl]octasilsesquioxane (7a). *Method A.* To a solution of azido-POSS **5** (20 mg, 0.018 mmol) and phenylacetylene (20 µL, 0.182 mmol) in toluene (1 mL), was added $(EtO)_3P$•CuI (3 mg, 0.008 mmol) and *i*Pr$_2$NEt (66 µL, 0.378 mmol). After stirring for 70 h at rt, the solvent was removed at reduced pressure, the crude was dissolved in CH_2Cl_2 and the product was precipitated with Et_2O to afford **7a** (30 mg, 90 %) as a white powder.

Method B. To a solution of azido-POSS **5** (20 mg, 0.018 mmol) and phenylacetylene (20 µL, 0.182 mmol) in toluene (1 mL), was added [(IPr)CuCl] (3 mg, 0.009 mmol) and *i*Pr$_2$NEt (66 µL, 0.378 mmol). After stirring for 48 h at rt, the solvent was removed at reduced pressure, the crude was dissolved in CH_2Cl_2 and the product was precipitated with Et_2O to afford **7a** (30 mg, 90 %) as a white powder.

Method C. To a solution of azido-POSS **5** (20 mg, 0.018 mmol) and phenylacetylene (20 µL, 0.182 mmol) in toluene (1 mL), was added [Cu(C18$_6$tren)]Br (17 mg, 0.009 mmol) and *i*Pr$_2$NEt (66 µL, 0.378 mmol). After stirring for 20 h at rt, the solvent was removed at reduced pressure, the crude was dissolved in CH_2Cl_2 and the product was precipitated with Et_2O to afford **7a** (31 mg, 92 %) as a white powder.

Method D. To a solution of azido-POSS **5** (20 mg, 0.018 mmol) and phenylacetylene (20 µL, 0.182 mmol) in CH_2Cl_2 (0.5 mL), was added a solution of $CuSO_4$·$5H_2O$ (2.5 mg, 0.010 mmol) and sodium ascorbate (9 mg, 0.045 mmol) in water (0.5 mL). After stirring for 1 h at rt, a saturated aqueous EDTA solution (1 mL) was added, the mixture was vigorously stirred for 30 min, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried over Na_2SO_4, the solvent was removed at reduced pressure, the crude was dissolved in CH_2Cl_2 and the product was precipitated with Et_2O to afford **7a** (33 mg, 96%) as a white powder. M.p. (from Et_2O): 207–209 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.61–0.65 (m, 16H, SiCH_2), 2.00–2.04 (m, 16H, SiCH$_2$CH_2), 4.35 (t, 16H, *J* = 6.7 Hz, SiCH$_2$CH$_2$CH_2N$_3$), 7.26–7.38 (m, 24H, Ar), 7.82 (d, 16H, *J* = 7.4 Hz, Ar), 7.95 (s, 8H, 1,2,3-triazole). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 8.8 (SiCH$_2$), 24.7 (SiCH$_2$CH$_2$), 52.4 (SiCH$_2$CH$_2$CH$_2$N$_3$), 120.4 (*C*H 1,2,3-triazole), 125.8 (2*C*H, Ph), 128.3 (*C*H, Ph), 129.0 (2*C*H, Ph), 130.8 (C, Ph), 148.1 (C, 1,2,3-triazole). ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ = –67.2. HRMS (ESI): calcd for $C_{88}H_{97}N_{22}O_{12}Si_8$ [M + H$^+$] 1905.5872, found 1905.5816.

Octakis[(3-(4'-((1",3"-dioxoisoindolin-2"-yl)methyl)-1'*H*-1',2',3'-triazol-1'-yl)propyl)]octasilsesquioxane (7b). *Method C.* To a solution of azido-POSS **5** (20 mg, 0.018 mmol) and *N*-propargyl phthalimide (33 mg, 0.178 mmol) in toluene (1 mL), was added [Cu(C18$_6$tren)]Br (17 mg, 0.009 mmol) and *i*Pr$_2$NEt (66 µL, 0.378 mmol). After heating for 3 h at 80 ºC under microwave irradiation, a white precipitate was formed. The reaction mixture was dissolved in MeOH and precipitated with $CHCl_3$ to afford **7b** as a white powder (34.2 mg, 74 %).

Method D. To a solution of azido-POSS **5** (20 mg, 0.018 mmol) and *N*-propargyl phthalimide (33 mg, 0.178 mmol) in CH_2Cl_2 (1 mL), was added a solution of $CuSO_4$·$5H_2O$ (2.5 mg, 0.010 mmol) and sodium ascorbate (9 mg, 0.045 mmol) in water (1 mL). After stirring for 18 h at rt, a saturated aqueous EDTA solution (1 mL) was

added, the mixture was vigorously stirred for 30 min, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried over Na_2SO_4, the solvent was removed at reduced pressure and the crude was dissolved in MeOH and precipitated with $CHCl_3$ to afford **7b** as a white powder (28 mg, 61%). M.p. (from $CHCl_3$): 163–166 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.46–0.50 (m, 16H, SiCH_2), 1.74–1.78 (m, 16H, SiCH$_2$CH_2), 4.21 (t, 16H, *J* = 6.7 Hz, SiCH$_2$CH$_2$CH_2), 7.77–7.83 (m, 32H, Ar), 8.03 (s, 8H, 1,2,3-triazole). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 7.9 (Si*C*H$_2$), 23.3 (SiCH$_2$*C*H$_2$), 32.9 (*C*H$_2$N-phtalimido), 51.2 (SiCH$_2$CH$_2$*C*H$_2$), 123.1 (*C*H, 1,2,3-triazole; 2*C*H phthalimido), 131.5 (2*C*, phthalimido), 134.4 (2*C*H, phthalimido), 142.2 (*C*, 1,2,3-triazole), 167.2 (*C*=O, phthalimido). ^{29}Si NMR (79.5 MHz, DMSO-d_6) δ = –66.6. HRMS (ESI): calcd for $C_{112}H_{105}N_{32}O_{28}Si_8$ [M + H$^+$] 2569.5930, found 2569.5841.

Octakis[(3-(4'-(hydroxymethyl)-1'*H*-1',2',3'-triazol-1'-yl)propyl)]octasilsesquioxane (7c). *Method C.* To a solution of azido-POSS **5** (20 mg, 0.018 mmol) and propargyl alcohol (11 µL, 0.189 mmol) in toluene (1.0 mL), was added [Cu(C18$_6$tren)]Br (17 mg, 0.009 mmol) and *i*Pr$_2$NEt (66 µL, 0.378 mmol). After heating for 3 h at 80 ºC under microwave irradiation, a white precipitate was formed. The precipitate was dissolved in MeOH (2 mL), the solution was extracted with hexane (3 × 3 mL), and the methanol layer was concentrated at reduced pressure to afford **7c** as a colorless oil (18.5 mg, 67%). Using THF/H_2O (2 : 1) instead of toluene in this procedure gave **7c** in 77 % yield, after stirring the reaction for 25 h at rt. ^{1}H NMR (400 MHz, CD_3OD) δ = 0.59–0.63 (m, 16H, SiCH_2), 1.92–1.98 (m, 16H, SiCH$_2$CH_2), 4.39 (t, 16H, *J* = 6.8 Hz, SiCH$_2$CH$_2$CH_2), 4.69 (s, 16H, CH_2OH), 7.93 (s, 8H, 1,2,3-triazole). ^{13}C NMR (100 MHz, CD_3OD) δ = 9.5 (Si*C*H$_2$), 25.2 (SiCH$_2$*C*H$_2$), 53.4 (SiCH$_2$CH$_2$*C*H$_2$), 56.6 (*C*H$_2$OH), 124.5 (*C*H, 1,2,3-triazole), 149.2 (*C*, 1,2,3-triazole). HRMS (ESI): calcd for $C_{48}H_{81}N_{24}O_{20}Si_8$ [M + H$^+$] 1537.4213, found 1537.4253.

Octakis[3-(4'-(4"-hydroxybutyl)-1'*H*-1',2',3'-triazol-1'-yl]propyl)silsesquioxane (7d). *Method C.* To a solution of azido-POSS **5** (20 mg, 0.018 mmol) and 5-hexyn-1-ol (21 µL, 0.190 mmol) in toluene (1 mL), was added [Cu(C18$_6$tren)]Br (17 mg, 0.009 mmol) and *i*Pr$_2$NEt (66 µL, 0.378 mmol). After heating for 3 h at 80 ºC under microwave irradiation, a white precipitate was formed. The precipitate was dissolved in MeOH (2 mL), the solution was extracted with hexane (3 × 5 mL), and the methanol layer was concentrated at reduced pressure to afford **7d** (24 mg, 71%) as a colorless oil. Using THF/H_2O (2 : 1) instead of toluene in this procedure gave **7d** in 80% yield after stirring the reaction for 25 h at rt. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.45 (bs, 16H, SiCH_2), 1.39–1.47 (m, 16H, CH$_2$CH$_2$CH_2CH$_2$OH), 1.53–1.63 (m, 16H, CH$_2$CH_2CH$_2$CH$_2$OH), 1.75 (bs, 16H, SiCH$_2$CH_2), 2.55–2.60 (m, 16H, CH_2CH$_2$CH$_2$CH$_2$OH), 3.37 (bs, 16H, CH$_2$CH$_2$CH$_2$CH_2OH), 4.22 (bs, 16H, SiCH$_2$CH$_2$CH_2), 4.39 (bs, 16H, CH$_2$CH$_2$CH$_2$CH$_2$O*H*), 7.79 (s, 8H, 1,2,3-triazole). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 9.2 (Si*C*H$_2$, data obtained from the HSQC spectrum), 24.1 (SiCH$_2$*C*H$_2$), 25.5 (*C*H$_2$CH$_2$CH$_2$CH$_2$OH), 26.3 (CH$_2$*C*H$_2$CH$_2$CH$_2$OH), 32.7 (CH$_2$CH$_2$*C*H$_2$CH$_2$OH), 51.7 (SiCH$_2$CH$_2$*C*H$_2$), 61.1 (CH$_2$CH$_2$CH$_2$*C*H$_2$OH), 122.3 (*C*H, 1,2,3-triazole), 147.6 (*C*, 1,2,3-triazole). HRMS (ESI): calcd for $C_{72}H_{129}N_{24}O_{20}Si_8$ [M + H$^+$] 1873.7969, found 1873.7951.

Octakis[3-(4'-(methoxycarbonyl)-1'*H*-1',2',3'-triazol-1'-yl)propyl]octasilsesquioxane (7e). *Method C.* To a solution of azido-POSS **5** (20 mg, 0.018 mmol) and methyl propiolate (16 µL, 0.180 mmol) in toluene (1 mL), was added [Cu(C18$_6$tren)]Br (17 mg, 0.009 mmol) and *i*Pr$_2$NEt (66 µL, 0.378 mmol). After heating for 8 h at 80 ºC under microwave irradiation, a white precipitate was formed. The reaction mixture was dissolved in MeOH and precipitated by addition of $CHCl_3$ to afford **7e** (28 mg, 88%) as a white powder. M.p. (from $CHCl_3$): 125–127 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.54–0.59 (m, 16H, SiCH_2), 1.97–2.02 (m, 16H, SiCH$_2$CH_2), 3.93 (s, 24H, COOCH_3), 4.42 (t, 16H, *J* = 6.7 Hz, SiCH$_2$CH$_2$CH_2), 8.24 (s, 8H, 1,2,3-triazole). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 8.3 (Si*C*H$_2$), 23.7 (SiCH$_2$*C*H$_2$), 52.2 (SiCH$_2$CH$_2$*C*H$_2$), 52.4 (*C*OOCH$_3$), 127.9 (*C*H, 1,2,3-triazole), 139.8 (*C*, 1,2,3-triazole), 161.1 (*C*OOCH$_3$). ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ = –67.4. HRMS (ESI): calcd for $C_{56}H_{81}N_{24}O_{28}Si_8$ [M + H$^+$] 1761.3806, found 1761.3796.

Octakis{3-[4'-((2",3":4",6"-di-O-isopropylidene-α-D-mannopyranos-1"-yl)methyl)-1'*H*-1',2',3'-triazol-1'-yl]propyl}octasilsesquioxane (7f). *Method A.* To a solution of azido-POSS **5** (35 mg, 0.032 mmol) and propargyl 2,3:4,6-di-*O*-isopropylidene-α-D-mannopyranoside (**6f**)[82] (86 mg, 0.288 mmol) in THF (1 mL), was added $(EtO)_3P{\cdot}CuI$ (5 mg, 0.014 mmol) and *i*Pr$_2$NEt (91 µL, 0.522 mmol). After stirring for 9 h at 80 ºC under microwave irradiation, the solvent was removed at reduced pressure and the residue was purified by flash column chromatography (CH_2Cl_2/MeOH 10:1) to afford **7f** (70 mg, 63%) as a white powder.

Method C. To a solution of azido-POSS **5** (51 mg, 0.047 mmol) and propargyl 2,3:4,6-di-*O*-isopropylidene-α-D-mannopyranoside (**6f**)[82] (144 mg, 0.483 mmol) in toluene (5 mL), was added [Cu(C18$_6$tren)]Br (43 mg, 0.024 mmol) and *i*Pr$_2$NEt (135 µL, 0.775 mmol). After stirring for 8 h at 80 ºC under microwave irradiation, a white precipitate was formed. The solvent was removed at reduced pressure and the residue was purified by flash column chromatography (CH_2Cl_2/MeOH 10:1) to afford **7f** (127 mg, 78%) as a white powder.

Method D. To a solution of azido-POSS **5** (20 mg, 0.018 mmol) and propargyl 2,3:4,6-di-*O*-isopropylidene-α-D-mannopyranoside (**6f**)[82] (53 mg, 0.178 mmol) in CH_2Cl_2 (0.5 mL), was added a solution of $CuSO_4{\cdot}5H_2O$ (2.5 mg, 0.010 mmol) and sodium ascorbate (9 mg, 0.045 mmol) in water (0.5 mL). After stirring for 2 h at rt, a saturated aqueous EDTA solution (1 mL) was added, the mixture was vigorously stirred for 30 min, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 2 mL). The organic layers were combined, dried over Na_2SO_4, and the solvent was removed at reduced pressure. The crude was purified by flash column chromatography (CH_2Cl_2/MeOH 10:1) to afford **7f** (53 mg, 85%) as a white powder. M.p. (from CH_2Cl_2): 118–122 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.57–0.61 (m, 16H, Si-CH_2CH$_2$CH$_2$), 1.25 (s, 24 H, C(CH$_3$)$_2$), 1.34 (s, 24 H, C(CH$_3$)$_2$), 1.45 (s, 24 H, C(CH$_3$)$_2$), 1.47 (s, 24 H, C(CH$_3$)$_2$), 1.92–2.03 (m, 16 H, SiCH$_2$CH_2CH$_2$), 3.51–3.60 (m, 8 H, H-5"), 3.66–3.67 (m, 8 H, H-4"), 3.70 (t, 8H, *J* = 10.5 Hz, H-6a"), 3.82 (dd, 8 H, *J* = 5.6, 10.5 Hz, H-6b"), 4.05 (dd, 8 H, *J* = 5.4, 7.8 Hz, H-3"), 4.11 (d, 8 H, *J* = 5.4 Hz, H-2"), 4.27 (t, 16 H, *J* = 7.1 Hz, SiCH$_2$CH$_2$CH_2), 4.60 (d, 8H, *J* = 12.2 Hz, CH_2O-C-1"), 4.77 (d, 8H, *J* = 12.2 Hz, CH_2O-C-1"), 5.09 (s, 1H, H-1"), 7.72 (s, 8H, CH of 1,2,3-triazole). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 8.9 (Si*C*H$_2$CH$_2$CH$_2$), 19.0 (C(*C*H$_3$)$_2$), 24.2 (SiCH$_2$*C*H$_2$CH$_2$), 26.4 (C(*C*H$_3$)$_2$), 28.4 (C(*C*H$_3$)$_2$), 29.3 (C(*C*H$_3$)$_2$), 52.4 (SiCH$_2$CH$_2$*C*H$_2$), 60.5 (*C*H$_2$O-C-1"), 61.8 (C-5"), 62.2 (C-6"), 72.8 (C-4"), 75.0 (C-3"), 76.1 (C-2"), 97.2 (C-1"), 99.9 (*C*(CH$_3$)$_2$), 109.7 (*C*(CH$_3$)$_2$), 123.6 (CH of 1,2,3-triazole), 143.9 (C of 1,2,3 triazole). ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ = –67.3. MALDI-TOF (hydroxybenzoic acid matrix) *m/z*: 3496 [M+Na$^+$]. HRMS (ESI): calcd for $C_{144}H_{226}N_{24}O_{60}Si_8$ [(M + 2H)$^{2+}$] 1737.6762, found 1737.6858 (M+2H)$^{+2}$.

Octakis{3-[4'-((α-D-mannopyranos-1"-yl)methyl)-1'*H*-1',2',3'-triazol-1'-yl]propyl}octasilsesquioxane (7g). To a solution of glyco-POSS **7f** (54 mg, 0.015 mmol) in THF/H_2O (4:1) (2 mL) was added trifluoroacetic acid (25 µL, 0.324 mmol). After stirring for 3 h at rt, **7g** was isolated as a white precipitate (38 mg, 90%). M.p. (from H_2O): 112–116 ºC. ^{1}H RMN (500 MHz, D_2O) δ = 0.32–0.44 (m, 16H, Si-CH_2CH$_2$CH$_2$), 1.74–1.78 (m, 16 H, SiCH$_2$CH_2CH$_2$), 3.47–3.78 (m, 48 H, H-2", H-3", H-4", H-5", H-6a", H-6b"), 4.14–4.30 (m, 16 H, SiCH$_2$CH$_2$CH_2), 4.61–4.68 (m, 16H, CH_2CCH), 4.8 (s, 8H, H-1"), 7.9 (bs, 8H, 1,2,3-triazole). ^{13}C RMN (125 MHz, DMSO-d_6) δ = 10.7 (SiCH_2CH$_2$CH$_2$, data obtained from HSQC spectrum), 25.2 (SiCH$_2$*C*H$_2$CH$_2$), 53.46 SiCH$_2$CH$_2$*C*H2), 61.0 (OCH$_2$-triazole), 62.3 (C-6"), 68.1 (C-4"), 71.4 (C-2"), 71.9 (C-3"), 74.5 (C-5"), 100.7 (C-1"), 126.4 (CH in triazole), 144.97 (C in triazole). MALDI-TOF (2,5-dihydroxybenxoic acid matrix) *m/z*: 2855 [M+Na]$^+$. HRMS (ESI): calcd for $C_{97}H_{161}N_{23}NaO_{60}Si_8$ [M + Na]$^+$ 2855.8258, found 2855.8253.

Octakis{3-[4'-(4"-(2"',8"'-diethyl-5"',5"'-difluoro-1"',3"',7"',9"'-tetramethyldipyrrolo[1"',2"'-c:2"',1"'f][1"',3"',2"']diazaborinin-4"'-ium-5"'-uid-10"'-yl)phenyl)-1'*H*-1',2',3'-triazol-1'-yl]propyl}octasilsesquioxane (7h): *Method D.* To a solution of azido-POSS **5** (20 mg, 0.018 mmol) and 4,4-difluoro-8-(4'-ethynylphenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene (**6h**)[83] (72 mg, 0,178 mmol) in CH_2Cl_2 (0.9 mL), was added a solution of $CuSO_4{\cdot}5H_2O$ (2.5 mg, 0.010 mmol) and sodium ascorbate (9 mg, 0.045 mmol) in water (0.6 mL). After stirring for 4.5 h at rt, a saturated aqueous EDTA solution (1 mL) was added, the mixture was vigorously stirred for 30 min, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The organic layers were combined, dried over Na_2SO_4, and the solvent was removed at reduced pressure. The crude was purified by flash column chromatography (hexane/EtOAc 5:1) to afford **7h** (54 mg, 70%) as a red powder. M.p. (from CH_2Cl_2): 290 ºC (decomposition). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.68–0.75 (m, 16H, Si-CH_2CH$_2$CH$_2$), 0.93 (t, 48H, *J* = 7.4 Hz, 16×(CH_3CH$_2$), 1.30 (s, 48 H, 16×CH_3-C), 2.13–2.18 (m, 16 H, SiCH$_2$CH_2CH$_2$), 2.25 (q, 32 H, *J* = 7.4, 16×CH_2CH$_3$), 2.51 (s, 48 H, 16×CH_3-C), 4.46 (t, 16H, *J* = 6.9 Hz, SiCH$_2$CH$_2$CH_2), 7.32 (d, 16H, J_{AB} = 8.2 Hz, 2×C*H* Ar), 8.01 (d, 16H, J_{AB} = 8.2, 2×C*H* Ar), 8.15 (s, 8H, in 1,2,3-triazole). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 8.7 (Si*C*H$_2$CH$_2$CH$_2$), 11.9 (CH$_3$), 12.5 (CH$_3$), 14.6 (CH$_3$-*C*H$_2$), 17.0 (CH$_3$-*C*H$_2$), 24.1 (SiCH$_2$*C*H$_2$CH$_2$), 52.4 (SiCH$_2$CH$_2$*C*H$_2$), 120.7 (CH in 1,2,3-triazole), 126.1 (CH phenyl), 129.0 (CH phenyl), 130.1, 131.2, 133.1, 135.8, 137.9, 139.2 (C in 1,2,3-triazole), 147.1, 154.0. ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ = –67.1. MALDI-TOF (2,5-dihydroxybenzoic acid matrix) *m/z*: 4304 [M – F]$^+$.

Acknowledgements

We thank the Ministry of Education and Science of Spain for financial support (project CTQ-2006-15515-C02-02/BQU) and for a FPU predoctoral fellowship to B. T. Thanks are due also to Dr. M. Luisa Jimeno for assistance in the measurement of ^{29}Si NMR spectra, Dr. Roberto Alcázar-Montero for the DSC and TGA study, and Prof. Felix Sánchez and Dr. Marta Iglesias for a kind gift of the [(IPr)CuCl] catalyst.

[1] For reviews, see: a) Lickiss, P. D.; Rataboul, F. *Adv. Organomet. Chem.* **2008**, *57*, 1–116; b) Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199–236.

[2] Scott, D. W. *J. Am. Chem. Soc.* **1946**, *68*, 356–358.

[3] Bassindale, A. R.; Liu, Z.; MacKinnon, I. A.; Taylor, P. G.; Yang, Y.; Light, M. E.; Horton, P. N.; Hursthouse, M. B. *Dalton Trans.* **2003**, 2945–2949.

[4] Bassindale, A. R.; Chen, H.; Liu, Z.; MacKinnon, I. A.; Parker, D. J.; Taylor, P. G.; Yang, Y.; Light, M. E.; Horton, P. N.; Hursthouse, M. B. *J. Organomet. Chem.* **2004**, *689*, 3287–3300.

[5] Dare, E. O.; Liu, L.-K.; Peng, J. *Dalton Trans.* **2006**, 3668–3671.

[6] Hybrid Plastics Inc. (http://www.hybridplastics.com) is the main supplier of POSS products. POSS is a registered trademark of this company.

[7] For reviews on practical applications of POSS molecules, see ref. [1a] and the following: a) Bourbigot, S.; Duquesne, S.; Jama, C. *Macromol. Symp.* **2006**, *233*, 180–190; b) Kannan, R. Y.; Salacinski, H. J.; Butler, P. E.; Seifalian, A. M. *Acc. Chem. Res.* **2005**, *38*, 879–884; c) Laine, R. M. *J. Mater. Chem.* **2005**, *15*, 3725–3744; d) Li, G.; Pittman, C. U., Jr. *Macromol. Containing Met. Met.-Like Elem.* **2005**, *4*, 79–131; e) Joshi, M.; Butola, B. S. *J. Macromol. Sci., Polym. Rev.* **2004**, *C44*, 389–410; f) Phillips, S. H.; Haddad, T. S.; Tomczak, S. J. *Curr. Opin. Solid State Mater. Sci.* **2004**, *8*, 21–29; g) Pittman, C. U., Jr.; Li, G.-Z.; Ni, H. *Macromol. Symp.* **2003**, *196*, 301–325; h) Provatas, A.; Matisons, J. G. *Trends Polym. Sci.* **1997**, *5*, 327–332.

[8] Muller, R.; Dathe, C.; Heinrich, L. *J. Prakt. Chem.* **1959**, *9*, 71–74.

[9] Frye, C. L.; Collins, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 5586–5588.

[10] Agaskar, P. A. *Inorg. Chem.* **1991**, *30*, 2707–2708.

[11] Andrianov, K. A.; Petrovnina, N. M.; Vasileva, T. V.; Shklover, V. E.; Dyachenko, B. I. *Zh. Obshch. Khim.* **1978**, *48*, 2692–2695.

[12] Harrison, P. G.; Hall, C. *Main Group Met. Chem.* **1997**, *20*, 515–529.

[13] Olsson, K. *Ark. Kemi* **1958**, *13*, 367–378.

[14] Gravel, M.-C.; Laine, R. M. *Polym. Prepr.* **1997**, *38*, 155–156.

[15] Feher, F. J.; Wyndham, K. D. *Chem. Commun.* **1998**, 323–324.

[16] Feher, F. J.; Wyndham, K. D.; Soulivong, D.; Nguyen, F. *J. Chem. Soc., Dalton Trans.* **1999**, 1491–1498.

[17] Seckin, T.; Gueltek, A.; Koeytepe, S. *Turk. J. Chem.* **2005**, *29*, 49–59.

[18] Herren, D.; Buergy, H.; Calzaferri, G. *Helv. Chim. Acta* **1991**, *74*, 24–26.

[19] Bassindale, A. R.; Gentle, T. E. *J. Mater. Chem.* **1993**, *3*, 1319–1325.

[20] Said, M. A.; Roesky, H. W.; Rennekamp, C.; Andruh, M.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem. Int. Ed.* **1999**, *38*, 661–664.

[21] Bassindale, A. R.; Gentle, T. *J. Organomet. Chem.* **1996**, *521*, 391–393.

[22] Kim, K.-M.; Chujo, Y. *Polym. Bull.* **2001**, *46*, 15–21.

[23] Dittmar, U.; Hendan, B. J.; Floerke, U.; Marsmann, H. C. *J. Organomet. Chem.* **1995**, *489*, 185–94.

[24] Cheng, G.; Vautravers, N. R.; Morris, R. E.; Cole-Hamilton, D. J. *Org. Biomol. Chem.* **2008**, *6*, 4662–4667.

[25] Jaffres, P.-A.; Morris, R. E. *J. Chem. Soc., Dalton Trans.* **1998**, 2767–2770.

[26] Itami, Y.; Marciniec, B.; Kubicki, M. *Chem. Eur. J.* **2004**, *10*, 1239–1248.

[27] Sulaiman, S.; Bhaskar, A.; Zhang, J.; Guda, R.; Goodson, T., III; Laine, R. M. *Chem. Mater.* **2008**, *20*, 5563–5573.

[28] Feher, F. J.; Soulivong, D.; Eklund, A. G.; Wyndham, K. D. *Chem. Commun.* **1997**, 1185–1186.

[29] Brick, C. M.; Tamaki, R.; Kim, S. G.; Asuncion, M. Z.; Roll, M.; Nemoto, T.; Ouchi, Y.; Chujo, Y.; Laine, R. M. *Macromolecules* **2005**, *38*, 4655–4660.

[30] Sellinger, A.; Tamaki, R.; Laine, R. M.; Ueno, K.; Tanabe, H.; Williams, E.; Jabbour, G. E. *Chem. Commun.* **2005**, 3700–3702.

[31] Lo, M. Y.; Zhen, C.; Lauters, M.; Jabbour, G. E.; Sellinger, A. *J. Am. Chem. Soc.* **2007**, *129*, 5808-5809.

[32] Roll, M. F.; Asuncion, M. Z.; Kampf, J.; Laine, R. M. *ACS Nano* **2008**, *2*, 320–326.

[33] Lo, M. Y.; Ueno, K.; Tanabe, H.; Sellinger, A. *Chem. Rec.* **2006**, *6*, 157–168.

[34] Gravel, M. C.; Zhang, C.; Dinderman, M.; Laine, R. M. *Appl. Organomet. Chem.* **1999**, *13*, 329–336.

[35] Tanaka, K.; Kitamura, N.; Naka, K.; Chujo, Y. *Chem. Commun.* **2008**, 6176–6178.

[36] Kaneshiro, T. L.; Wang, X.; Lu, Z.-R. *Mol. Pharmaceutics* **2007**, *4*, 759–768.

[37] McCusker, C.; Carroll, J. B.; Rotello, V. M. *Chem. Commun.* **2005**, 996–998.

[38] Naka, K.; Fujita, M.; Tanaka, K.; Chujo, Y. *Langmuir* **2007**, *23*, 9057–9063.

[39] Olsson, K.; Gronwall, C. *Ark. Kemi* **1961**, *17*, 529–540.

[40] Tamaki, R.; Tanaka, Y.; Asuncion, M. Z.; Choi, J.; Laine, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 12416–12417.

[41] Kim, S. G.; Choi, J.; Tamaki, R.; Laine, R. M. *Polymer* **2005**, *46*, 4514–4524.

[42] Takahashi, K.; Sulaiman, S.; Katzenstein, J. M.; Snoblen, S.; Laine, R. M. *Aust. J. Chem.* **2006**, *59*, 564–570.

[43] He, C.; Xiao, Y.; Huang, J.; Lin, T.; Mya, K. Y.; Zhang, X. *J. Am. Chem. Soc.* **2004**, *126*, 7792–7793.

[44] Koenig, H. J.; Marsmann, H. C.; Letzel, M. C. *Organosilicon Chem. V, [Sci. Contrib. Eur. Silicon Days], 1st* **2003**, 425–428.

[45] Gao, Y.; Eguchi, A.; Kakehi, K.; Lee, Y. C. *Org. Lett.* **2004**, *6*, 3457–3460.

[46] Ropartz, L.; Foster, D. F.; Morris, R. E.; Slawin, A. M. Z.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 1997–2008.

[47] Ropartz, L.; Morris, R. E.; Foster, D. F.; Cole-Hamilton, D. J. *J. Mol. Catal. A: Chem.* **2002**, *182-183*, 99–105.

[48] Ropartz, L.; Morris, R. E.; Schwarz, G. P.; Foster, D. F.; Cole-Hamilton, D. J. *Inorg. Chem. Commun.* **2000**, *3*, 714–717.

[49] Meldal, M.; Tornoe, C. W. *Chem. Rev.* **2008**, *108*, 2952–3015.

[50] Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021.

[51] a) Binder, W. H.; Petraru, L.; Sachenshofer, R.; Zirbs, R. *Monastsh. Chem.* **2006**, *137*, 835–841; b) Ak, M.; Gacal, B.; Kiskan, B.; Yagci, Y.; Toppare, L. *Polymer* **2008**, *49*, 2202–2210; c) Ge, Z.; Wang, D.; Zhou, Y.; Liu, H.; Liu, S. *Macromolecules* **2009**, *42*, 2903–2910.

[52] Tornoe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057–3064.

[53] Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 2596–2599.

[54] Vasella, A.; Witzig, C.; Chiara, J. L.; Martinlomas, M. *Helv. Chim. Acta* **1991**, *74*, 2073–2077.

[55] Alper, P. B.; Hung, S.-C.; Wong, C.-H. *Tetrahedron Lett.* **1996**, *37*, 6029–6032.

[56] Nyffeler, P. T.; Liang, C.-H.; Koeller, K. M.; Wong, C.-H. *J. Am. Chem. Soc.* **2002**, *124*, 10773–10778.

[57] Volkov, N. D.; Nazaretyan, V. P.; Yagupol'skii, L. M. *Zh. Org. Khim.* **1982**, *18*, 519–525.

[58] Zhu, S.-Z. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2077–2081.

[59] For a former single example of primary amine to azide transformation using this reagent, see: Yekta, S.; Prisyazhnyuk, V.; Reissig, H.-U. *Synlett* **2007**, 2069–2072.

[60] Cavender, C. J.; Shiner, V. J., Jr. *J. Org. Chem.* **1972**, *37*, 3567–3569.

[61] Titz, A.; Radic, Z.; Schwardt, O.; Ernst, B. *Tetrahedron Lett.* **2006**, *47*, 2383–2385.

[62] ^{1}H NMR ($CDCl_3$): δ = 0.61–0.84 (2H, Si–CH_2), 1.54–1.83 (2H, Si–CH_2CH_2), 3.24–3.47 (2H, Si–$CH_2CH_2CH_2N_3$); ^{13}C NMR ($CDCl_3$): δ = 9.8 (Si–CH_2), 22.8 (Si–CH_2CH_2), 53.6 (Si–$CH_2CH_2CH_2N_3$); ^{29}Si NMR ($CDCl_3$): δ = –69.1 (*Si*–CH_2).

[63] Rikowski, E.; Marsmann, H. C. *Polyhedron* **1997**, *16*, 3357–3361.

[64] While this manuscript was in preparation, Kawakami and co-workers communicated that the treatment of octakis(3-chloropropyl)octasilsesquioxane with NaN_3 in DMF, using milder reaction conditions (60 ºC, 16 h) than those employed by Ge et al. (ref. [51c]), did produced the expected cage rearrangement to afford a difficult to separate mixture of T_8 (**5**), T_{10} (major product), and T_{12} POSS cages: Ervithayasuporn, V.; Wang, X.; Kawakami, Y. *Chem. Commun.* **2009**, 5130–5132.

[65] Braese, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem. Int. Ed.* **2005**, *44*, 5188–5240.

[66] See the Supporting information.

[67] Perez-Balderas, F.; Ortega-Munoz, M.; Morales-Sanfrutos, J.; Hernandez-Mateo, F.; Calvo-Flores, F. G.; Calvo-Asin, J. A.; Isac-Garcia, J.; Santoyo-Gonzalez, F. *Org. Lett.* **2003**, *5*, 1951–1954.

[68] Jurkauskas, V.; Sadighi, J. P.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2417–2420.

[69] Diez-Gonzalez, S.; Correa, A.; Cavallo, L.; Nolan, S. P. *Chem. Eur. J.* **2006**, *12*, 7558–7564.

[70] Barre, G.; Taton, D.; Lastecoueres, D.; Vincent, J.-M. *J. Am. Chem. Soc.* **2004**, *126*, 7764–7765.

[71] Candelon, N.; Lastecoueres, D.; Diallo, A. K.; Ruiz Aranzaes, J.; Astruc, D.; Vincent, J.-M. *Chem. Commun.* **2008**, 741–743.

[72] Lee, B.-Y.; Park, S. R.; Jeon, H. B.; Kim, K. S. *Tetrahedron Lett.* **2006**, *47*, 5105–5109.

[73] POSS compounds with free hydroxy groups (**7c**, **7d**, and **7g**) showed a marked broadening of most ^{1}H and ^{13}C NMR resonances at room temperature (see Supporting information), which we attribute to aggregation effects. This broadening was even more pronounced in the case of ^{29}Si NMR spectra, so that no signal could be distinguished for these compounds under the measurement conditions (25 ºC). A similar broadening of NMR spectra has been observed before for other polyhydroxylated POSS products (see ref. [15] and [16]).

[74] For previous examples of POSS glycoconjugates, see ref. [16] and [45].

[75] For recent examples of synthesis of POSS derivatives for optical aplications, see ref. [27], [30], [31], [33], [43], and [76]. A POSS derivative partially functionalized with a BODIPY dye has been prepared recently as an uncharacterized heterogeneous mixture of products (ref. [37]).

[76] Vautravers, N. R.; Andre, P.; Slawin, A. M. Z.; Cole-Hamilton, D. J. *Org. Biomol. Chem.* **2009**, *7*, 717–724.

[77] Lundquist, J. J.; Toone, E. J. *Chem. Rev.* **2002**, *102*, 555–578.

[78] Kiessling, L. L.; Gestwicki, J. E.; Strong, L. E. *Angew. Chem. Int. Ed.* **2006**, *45*, 2348–2368.

[79] Pieters, R. J. *Org. Biomol. Chem.* **2009**, *7*, 2013–2025.

[80] Dirksen, A.; De Cola, L. *C. R. Chim.* **2003**, *6*, 873–882.

[81] Lo, S.-C.; Burn, P. L. *Chem. Rev.* **2007**, *107*, 1097–1116.

[82] Ferrandiz-Huertas, C.; Isac-Garcia, J.; Perez-Balderas, F.; Santoyo-Gonzalez, F. *Synthesis* **2005**, 939–944.

[83] Ulrich, G.; Ziessel, R. *J. Org. Chem.* **2004**, *69*, 2070–2083.

[84] Azov, V. A.; Schlegel, A.; Diederich, F. *Angew. Chem. Int. Ed.* **2005**, *44*, 4635–4638.

[85] Punna, S., Finn, M. G. *Synlett* **2004**, 99–100.

[86] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

[87] Ziegler, F. E.; Fowler, K. W.; Rodgers, W. B.; Wester, R. T. *Organic Syntheses*; Wiley: New York, 1993; Collect. Vol. VIII, p 586.

[88] Kaur, H.; Zinn, F. K.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2004**, *23*, 1157–1160.

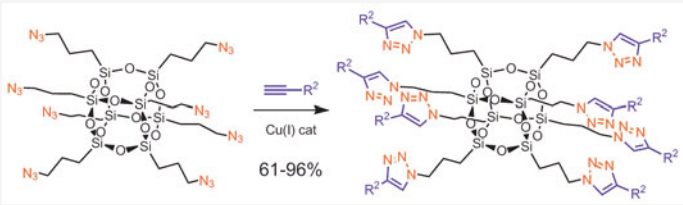
Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Entry for the Table of Contents

Catch Phrase

*Beatriz Trastoy, M. Eugenia Pérez-Ojeda, Roberto Sastre, and Jose Luis Chiara** ……..… Page – Page

Octakis(3-azidopropyl)octasilsesquioxane: A Versatile Nano-Building Block for the Efficient Preparation of Highly Functionalized Cube-Octameric POSS Frameworks by "Click" Assembly



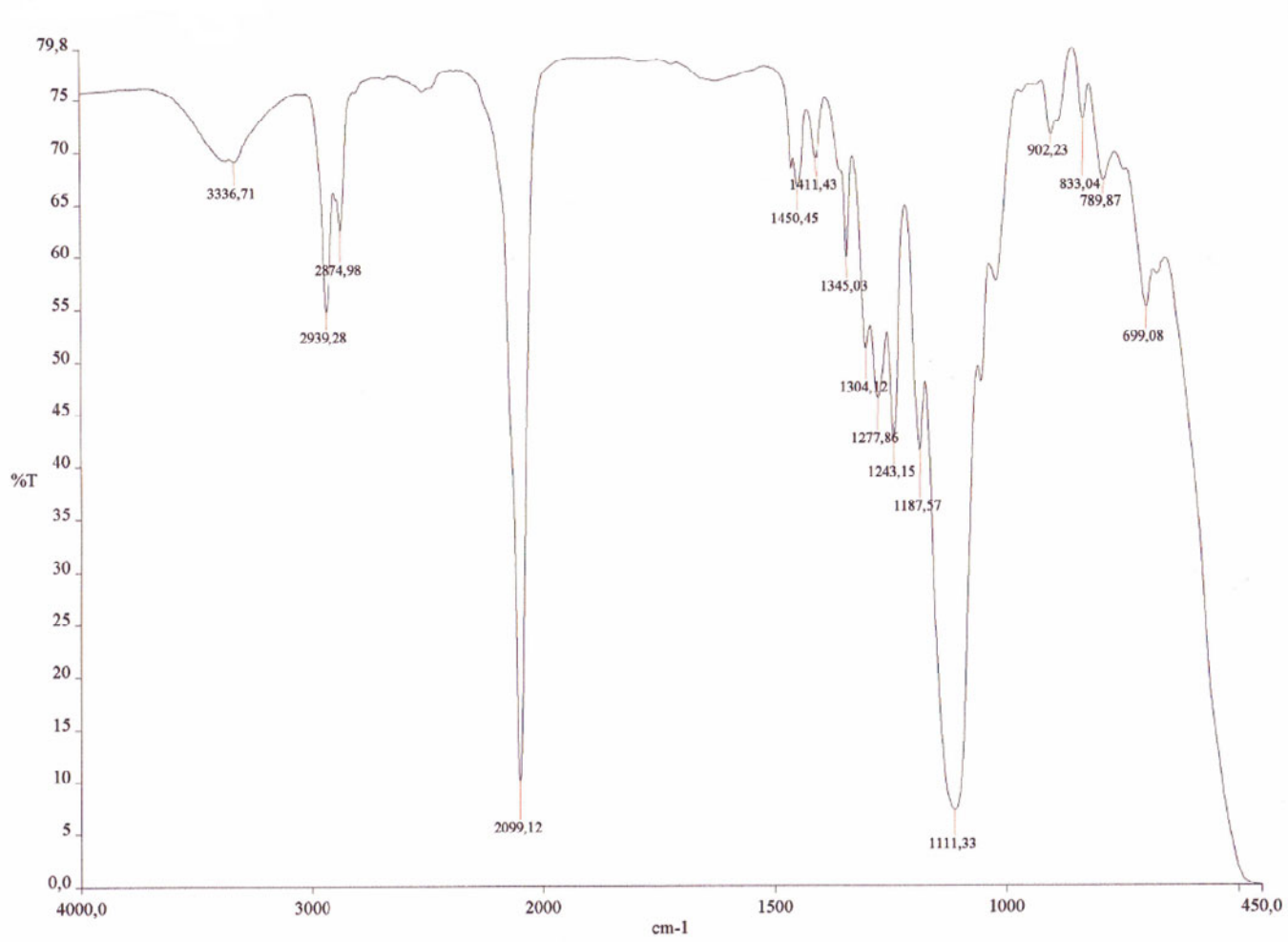
Clickable nanobuilding block: A one-step synthesis of an octa-azide silsesquioxane with perfect 3-D cubic symmetry has been realized from a commercially available silsesquioxane using an efficient diazo-transfer reaction under very mild conditions. This compound is an excellent nanobulding block that can be readily octafunctionalized with a diversity of simple and highly functionalized terminal alkynes by copper(I)-catalyzed 1,3-dipolar azide-alkyne cycloaddition to provide new functional nanocages keeping a perfect 3-D cubic symmetry.

Supporting information

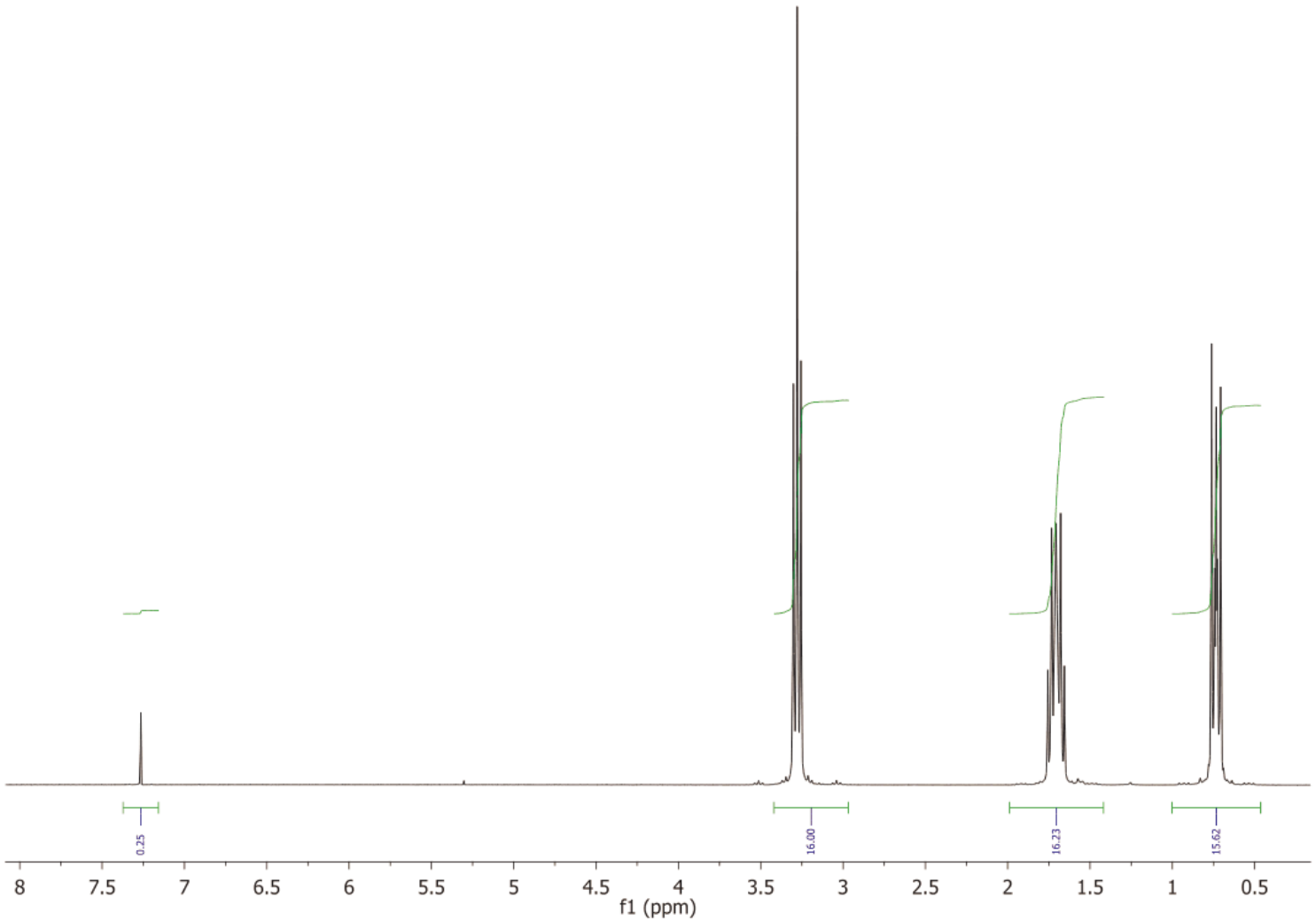
Octakis(3-azidopropyl)octasilsesquioxane: A Versatile Nano-Building Block for the Efficient Preparation of Highly Functionalized Cube-Octameric POSS Frameworks by "Click" Assembly

Beatriz Trastoy,[a] M. Eugenia Pérez-Ojeda,[b] Roberto Sastre,[b] and Jose Luis Chiara*[a]

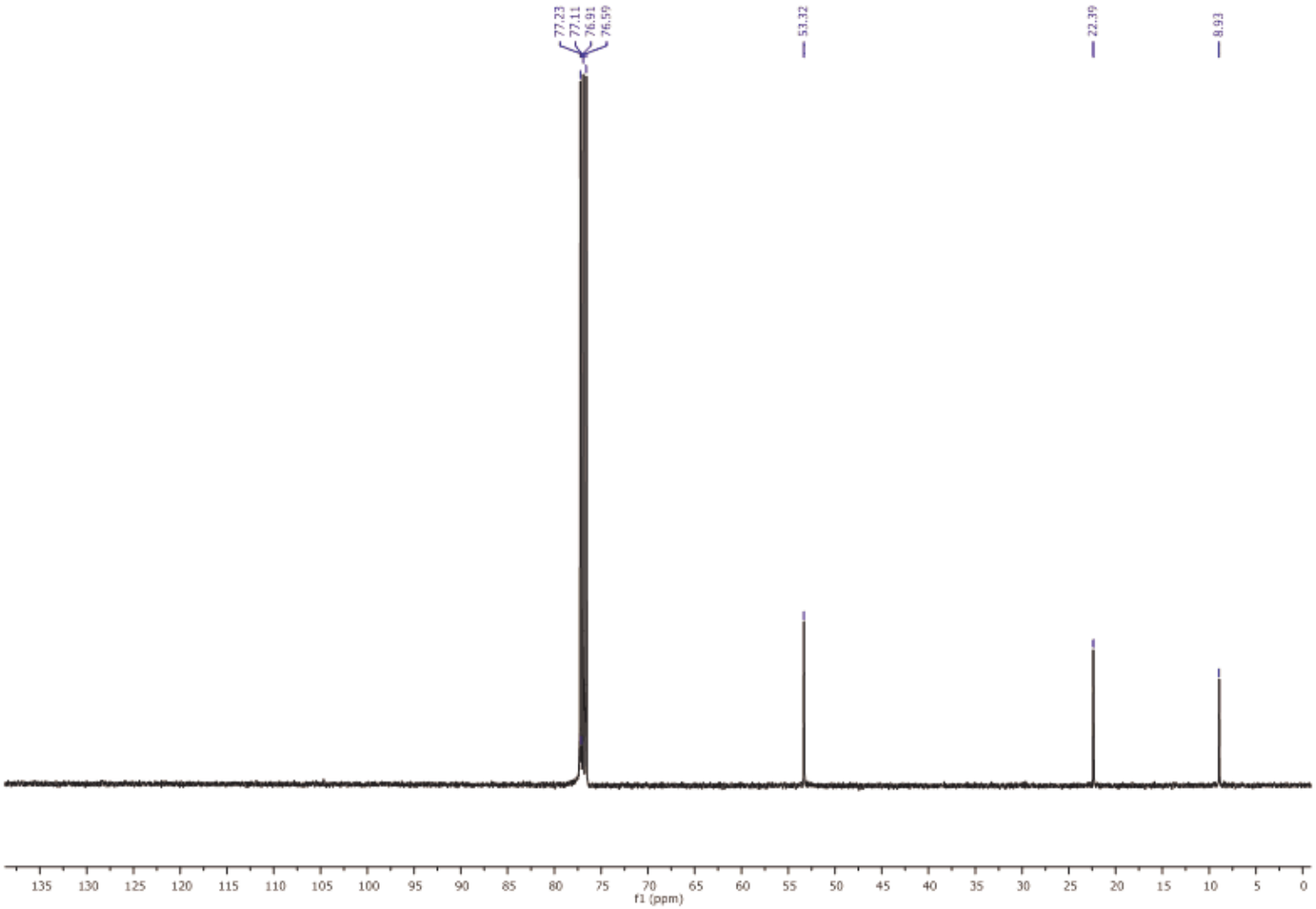
[a] Instituto de Química Orgánica General, and [b] Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva, 3; E-28006 Madrid, Spain



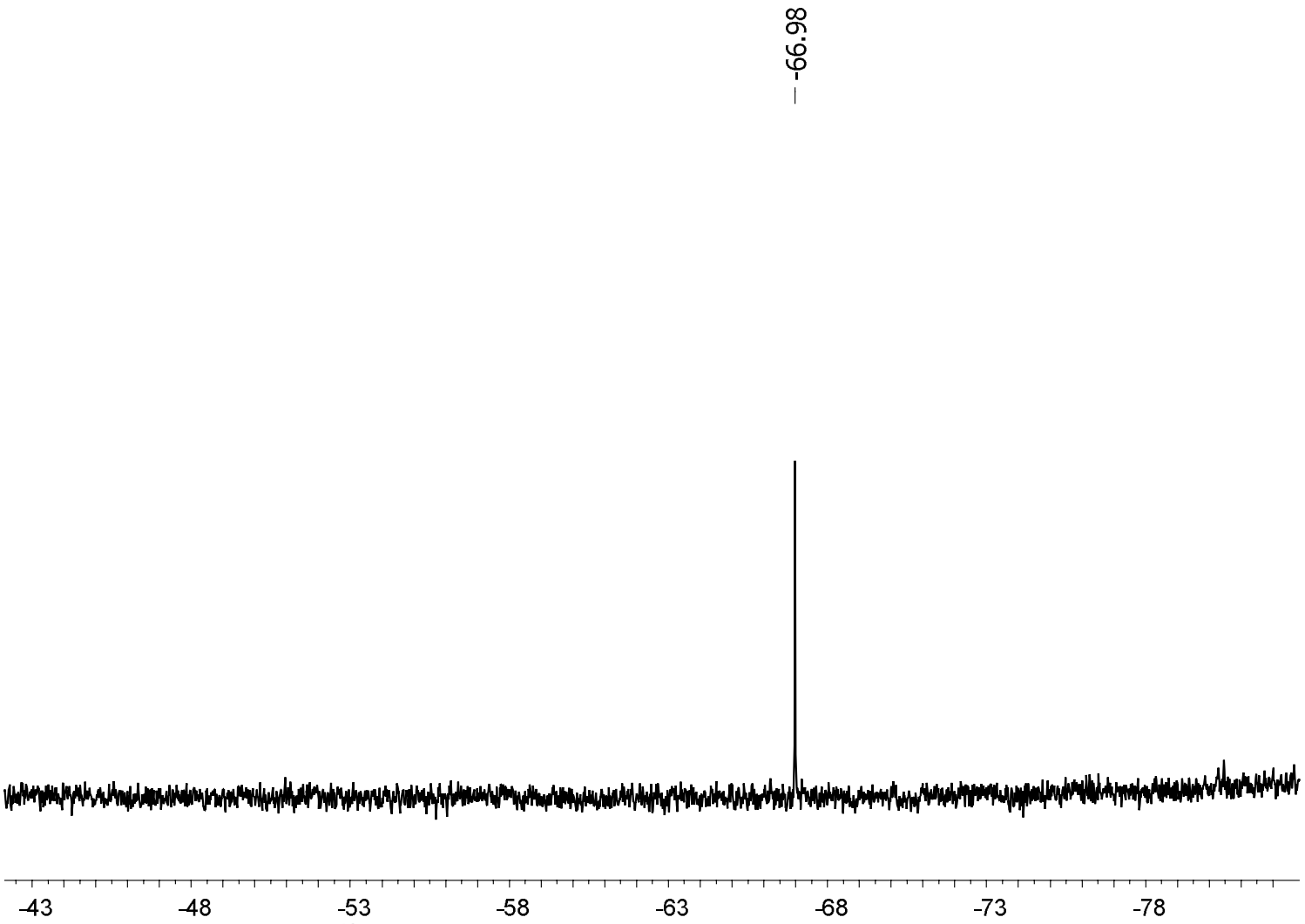
FT-IR (thin film) spectrum of compound **5**



^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **5**



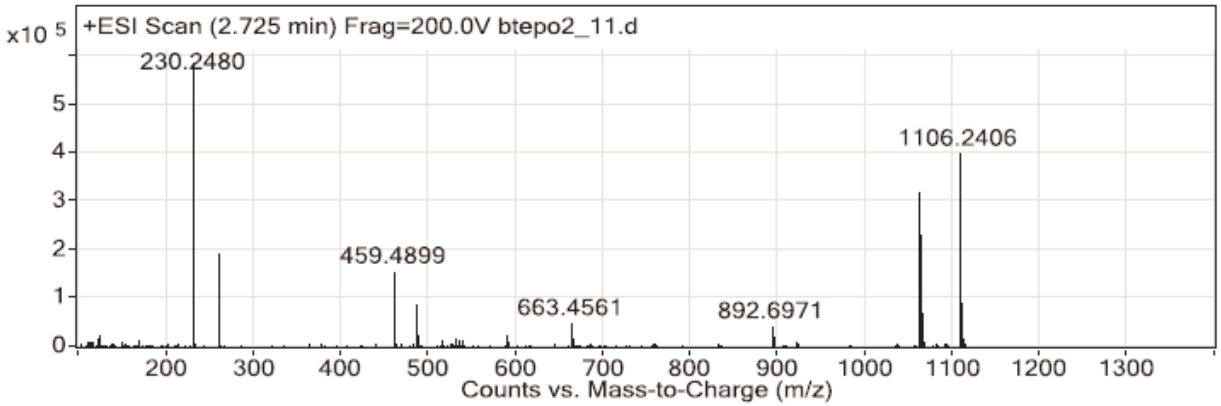
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **5**



^{29}Si NMR ($CDCl_3$, 79.5 MHz) spectrum of compound **5**

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	Esi



Peak List

m/z	z	Abund
230.2480	1	583880
258.2795	1	192275
459.4899	1	154020
1061.2084	1	318720
1062.2086	1	230916
1063.2077	1	168542
1106.2406	1	396828
1107.2416	1	296899
1108.2405	1	211735
1109.2409	1	91031

--- End Of Report ---

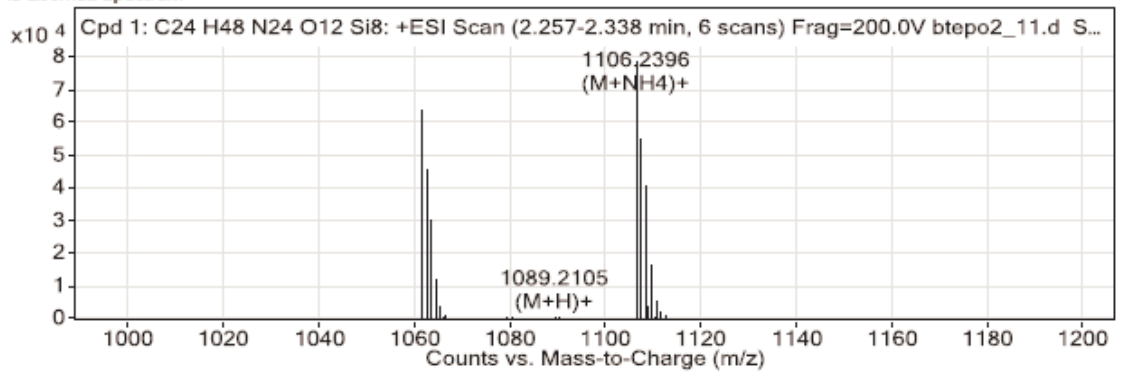
ESI-MS spectrum (H_2O/MeOH, 0.1% HCO_2NH_4) of compound **5**

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C24 H48 N24 O12 Si8	2.338	1088.2057	78718	C24 H48 N24 O12 Si8	1088.2038	1.79

Compound Label	RT	Algorithm	Mass
Cpd 1: C24 H48 N24 O12 Si8	2.338	Find By Formula	1088.2057

MS Zoomed Spectrum

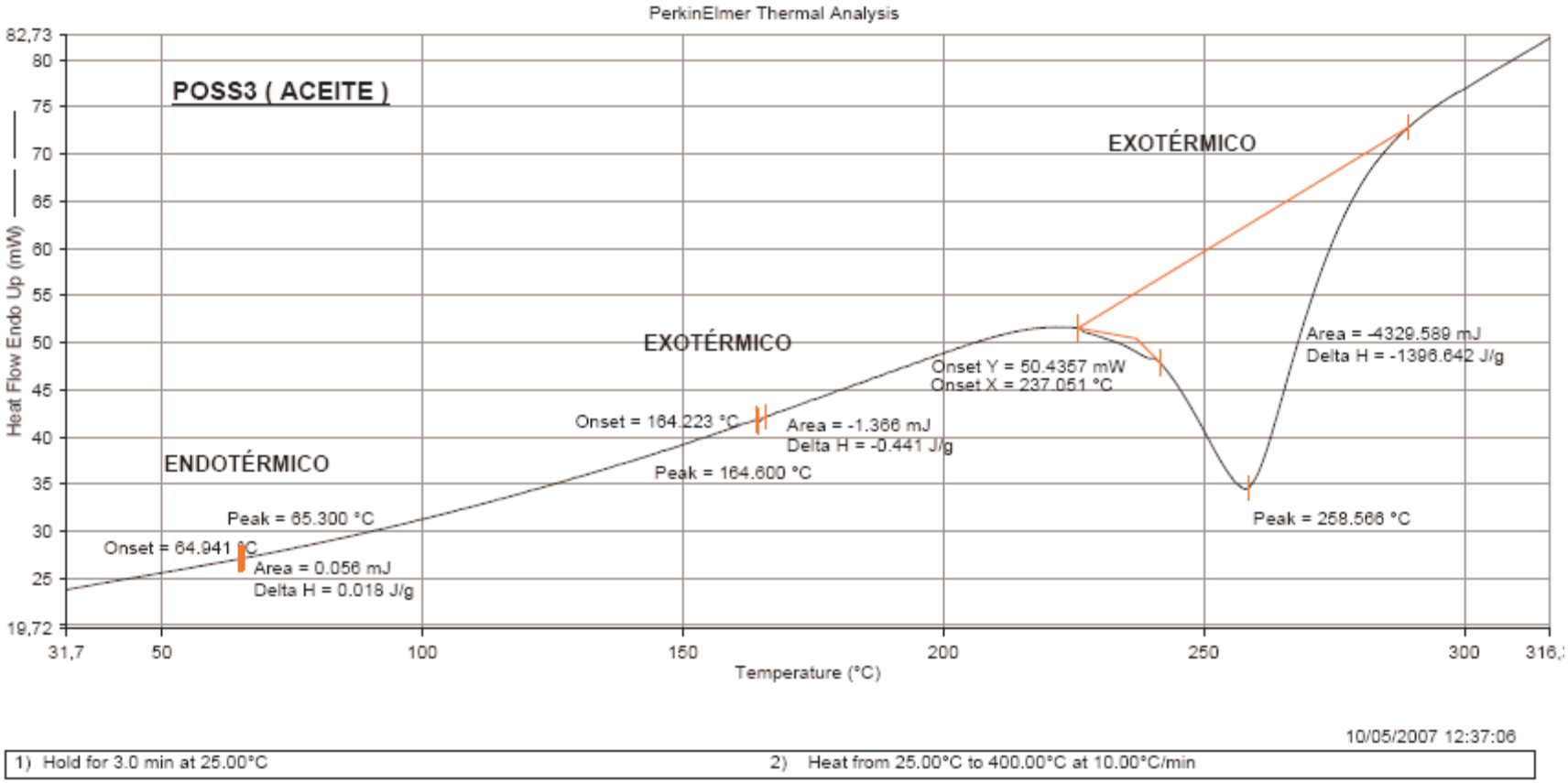


MS Spectrum Peak List

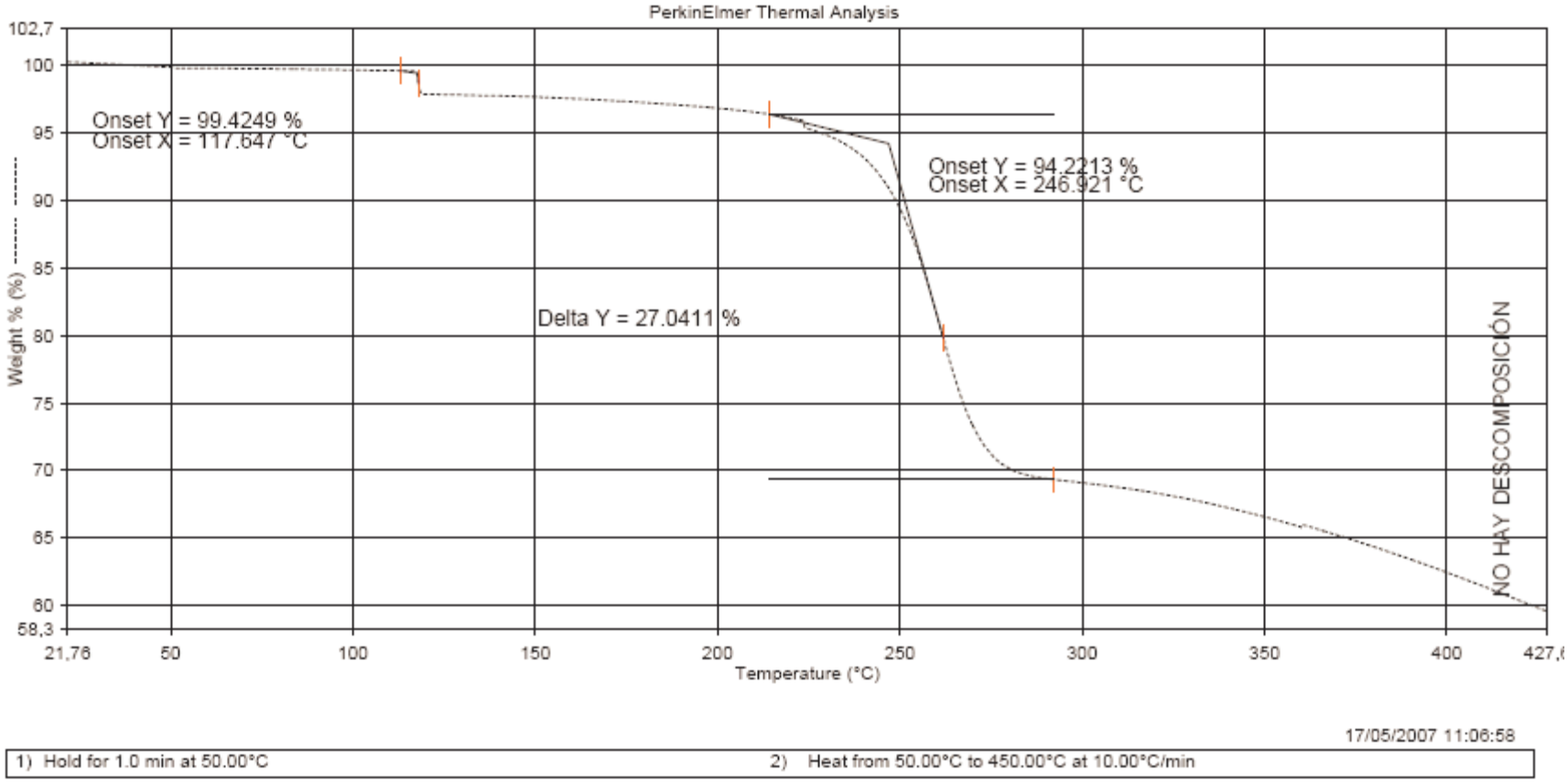
m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
1089.2105	1089.211	-0.45	1	1046	C24 H49 N24 O12 Si8	(M+H)+
1106.2396	1106.2376	1.81		78718	C24 H52 N25 O12 Si8	(M+NH4)+
1106.3712				1213		
1107.2401	1107.2382	1.73		54823	C24 H52 N25 O12 Si8	(M+NH4)+
1107.3608				1516		
1108.2386	1108.2369	1.5		41030	C24 H52 N25 O12 Si8	(M+NH4)+
1108.3542				4326		
1109.2387	1109.2367	1.82		16513	C24 H52 N25 O12 Si8	(M+NH4)+
1110.2376	1110.2357	1.74		6136	C24 H52 N25 O12 Si8	(M+NH4)+
1111.2157				2553		

--- End Of Report ---

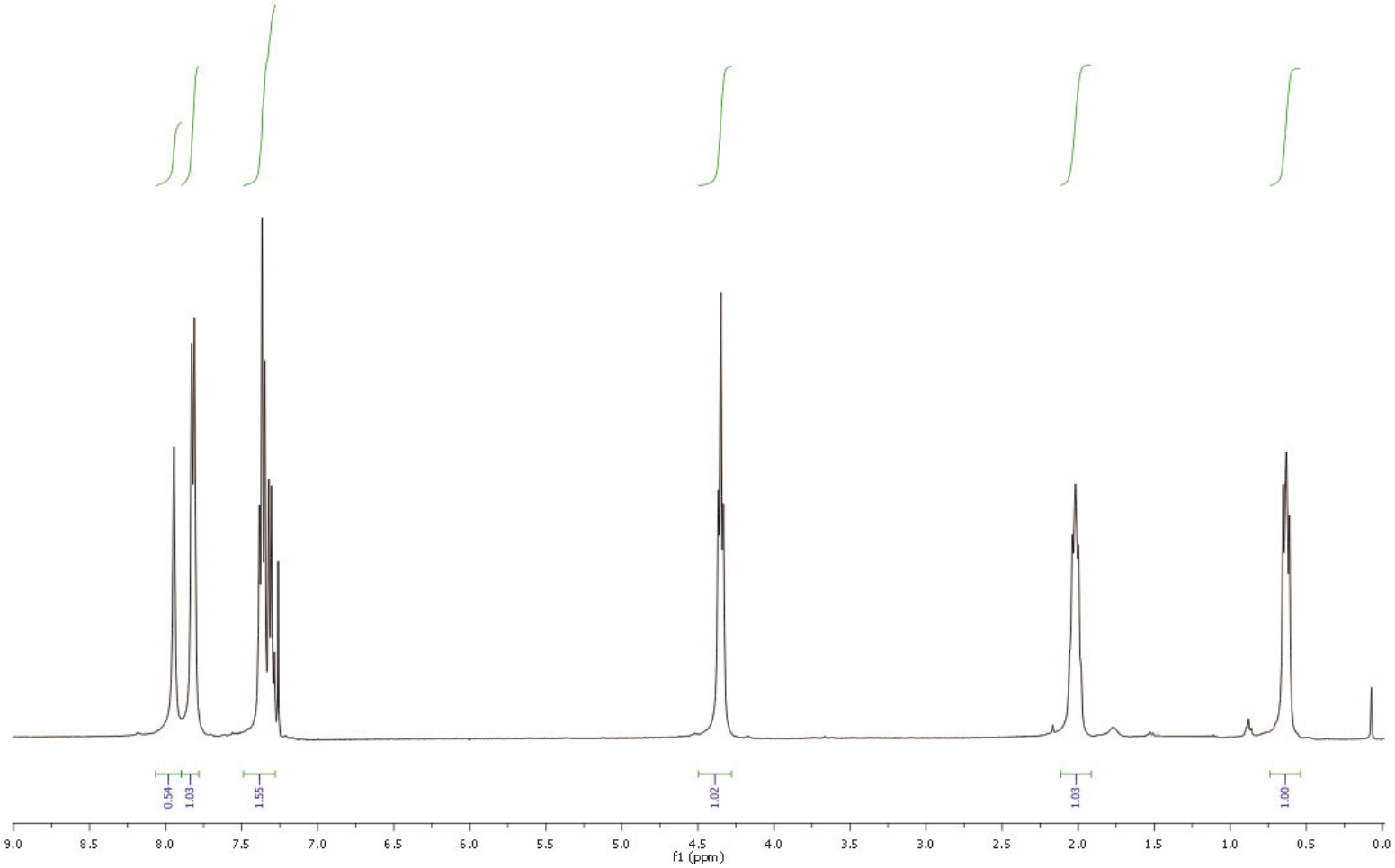
HRMS (ESI+) spectrum of compound **5**



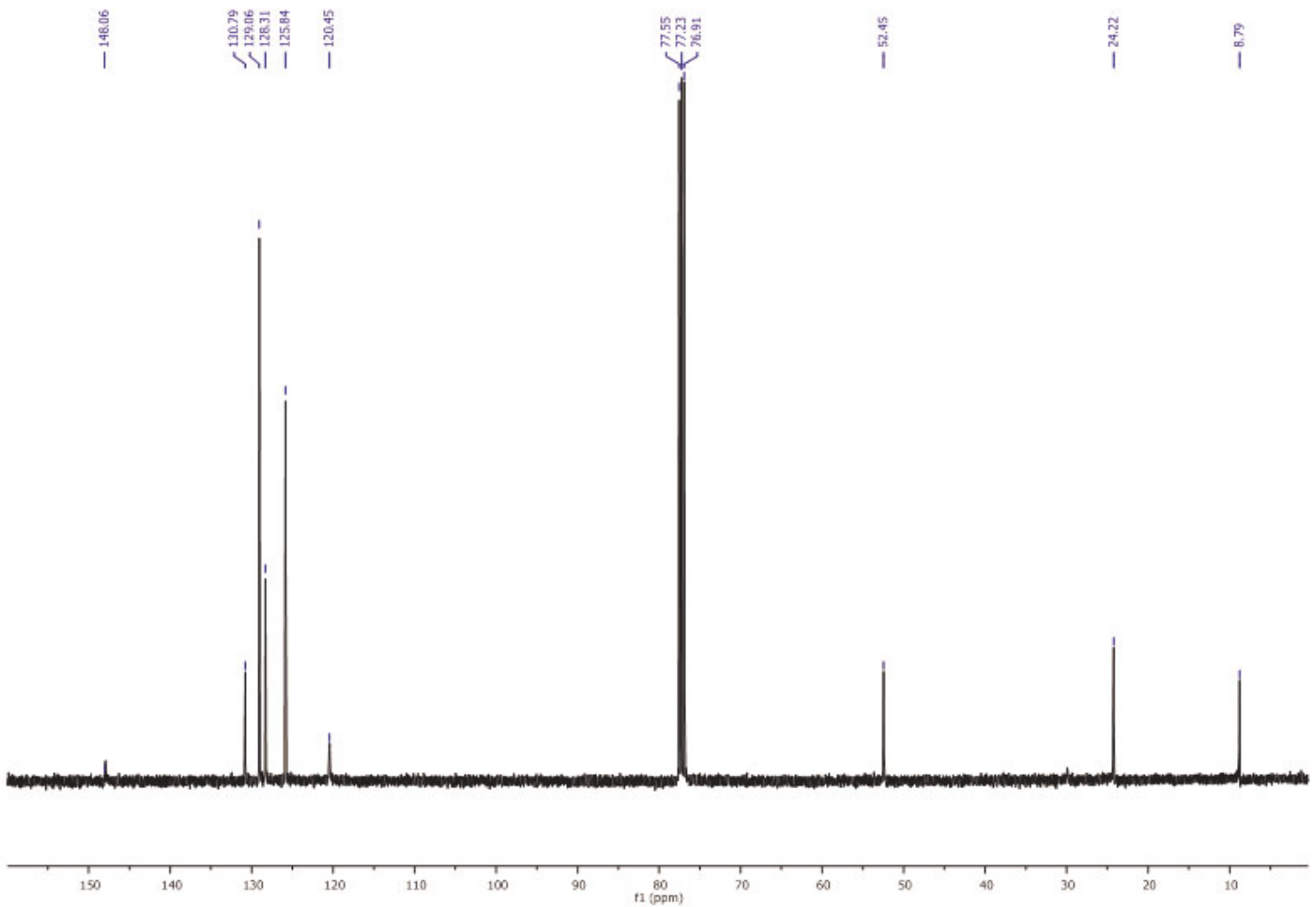
Thermogravimetric analysis study of compound **5**



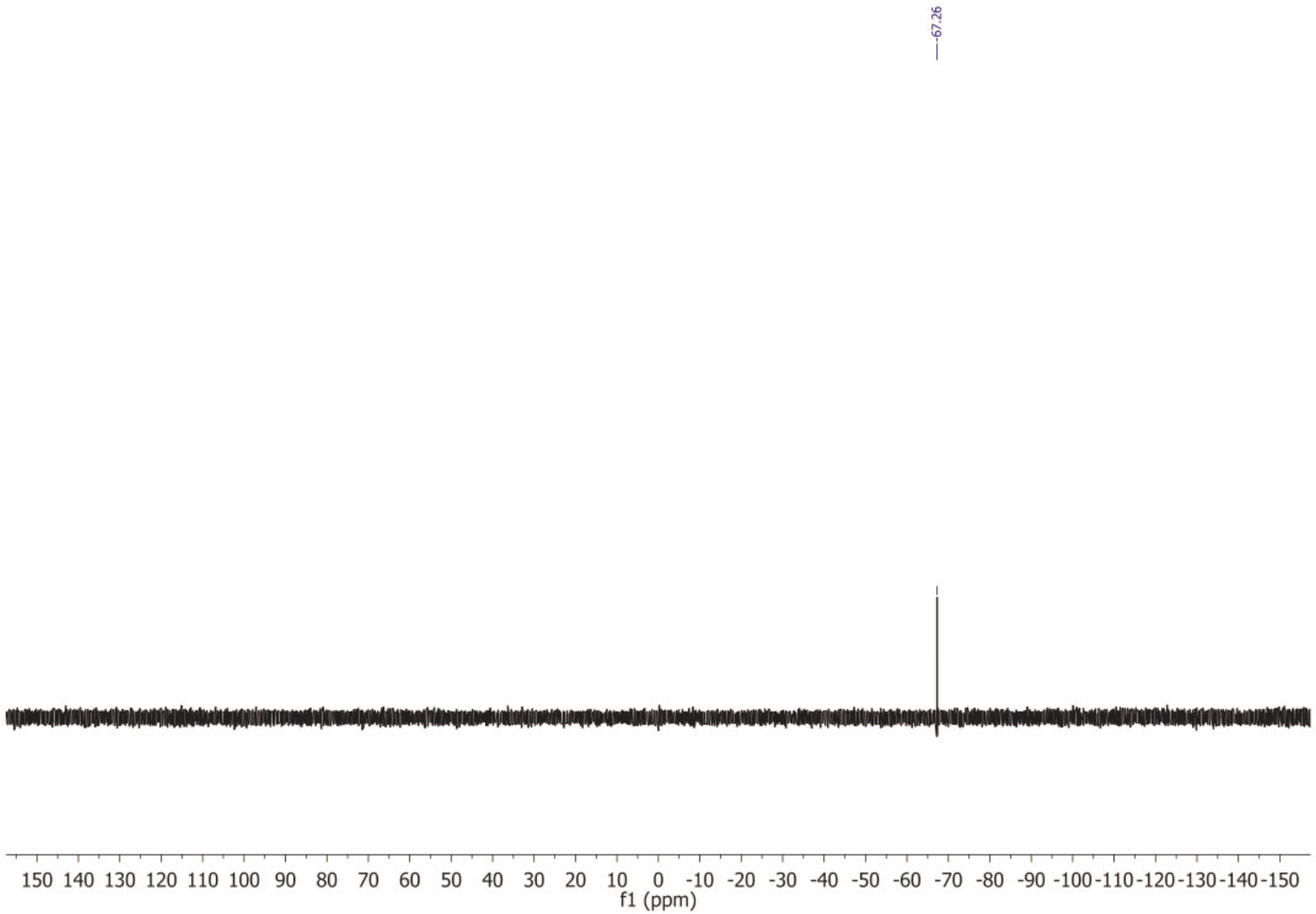
Differential scanning calorimetry study of compound **5**



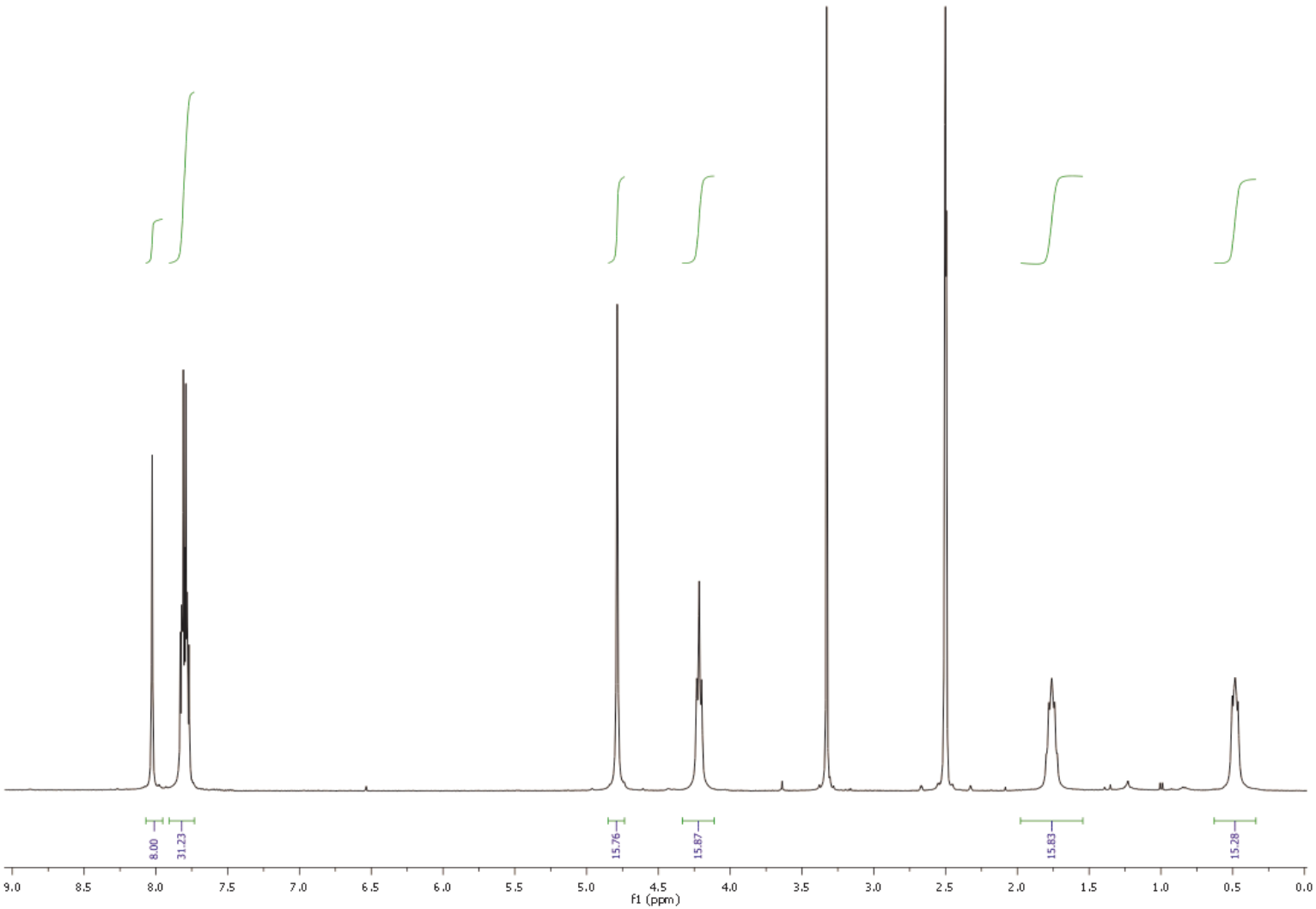
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **7a**



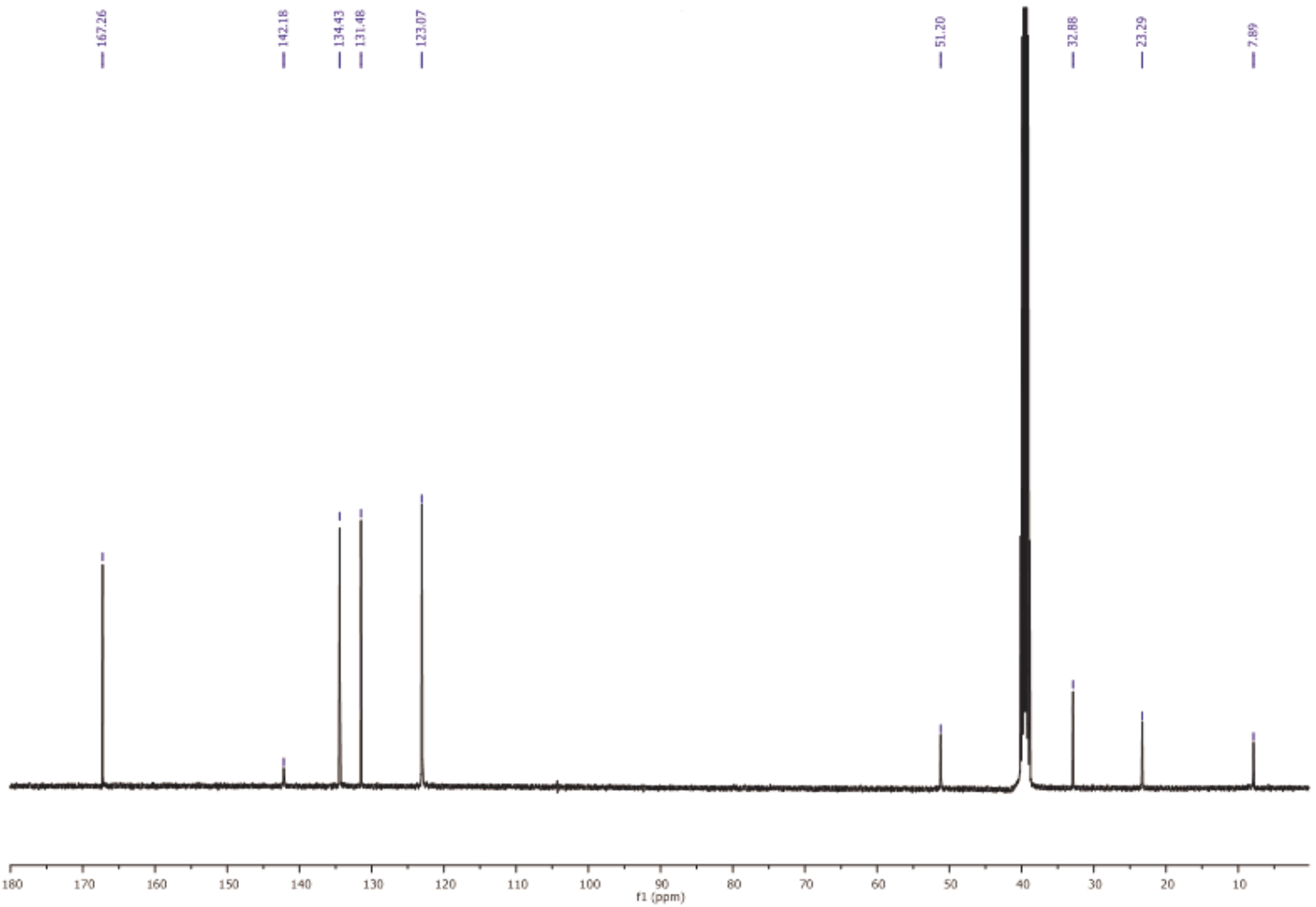
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **7a**



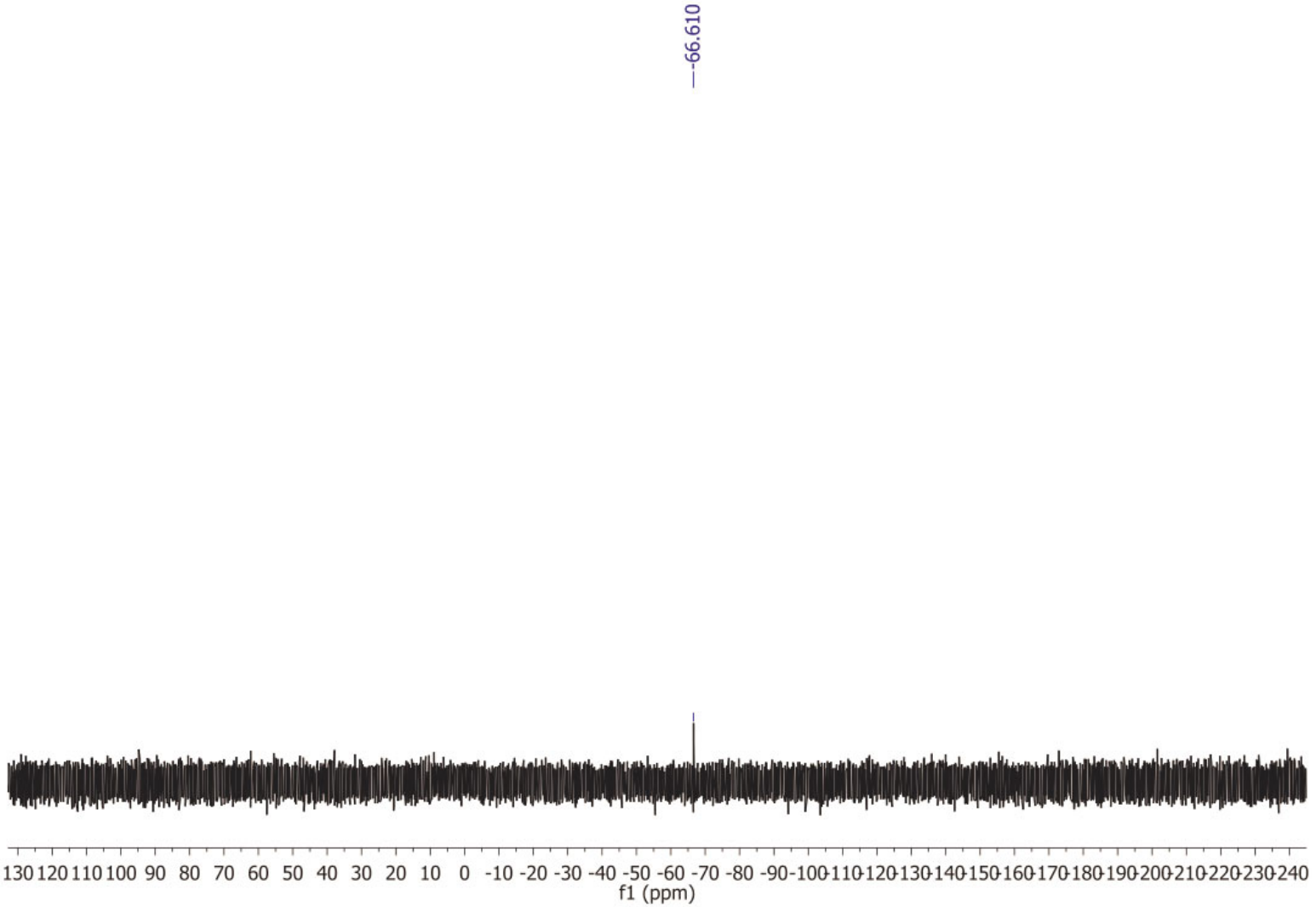
^{29}Si NMR ($CDCl_3$, 79.5 MHz) spectrum of compound **7a**



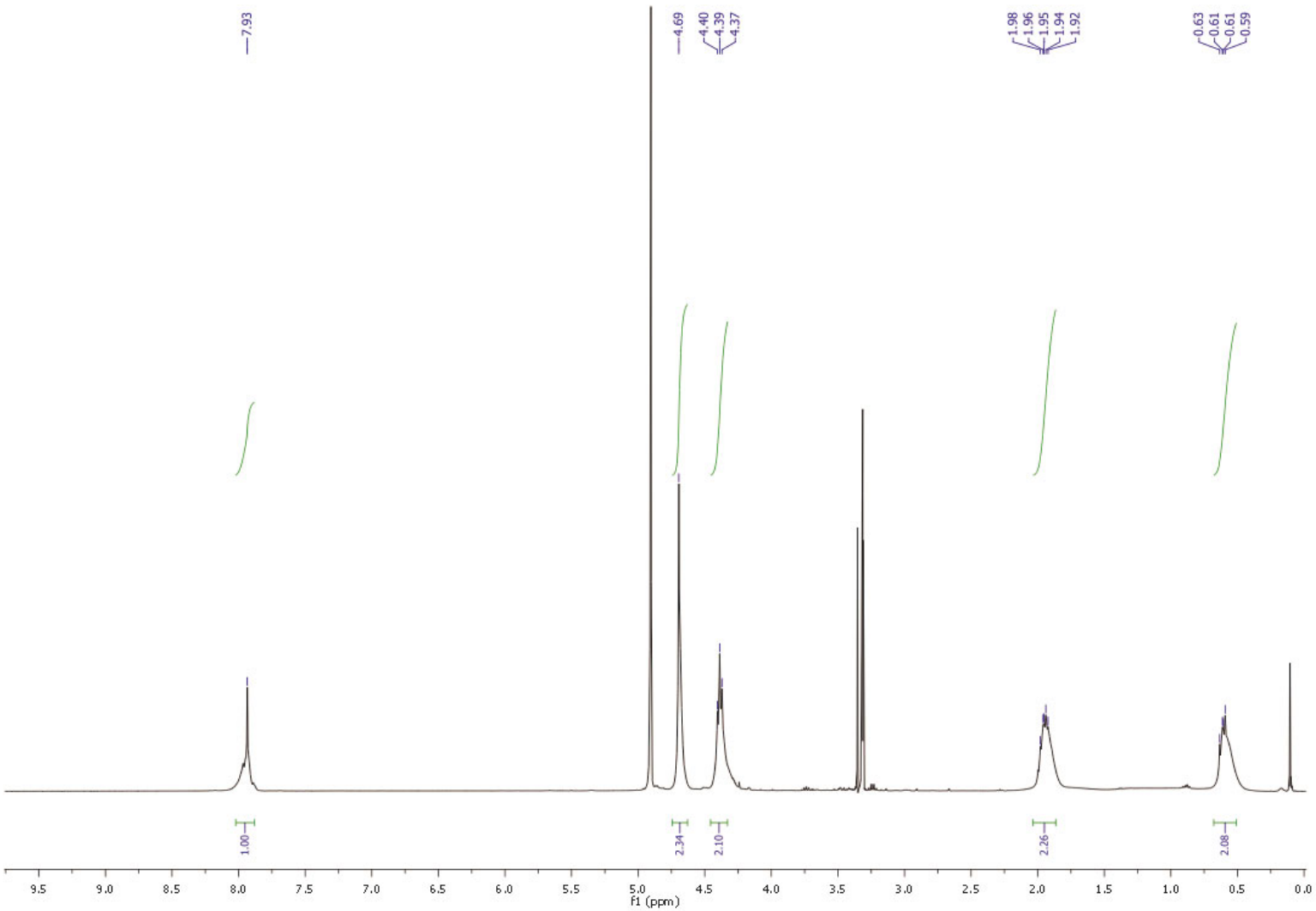
^{1}H NMR (DMSO-d_6, 400 MHz) spectrum of compound **7b**



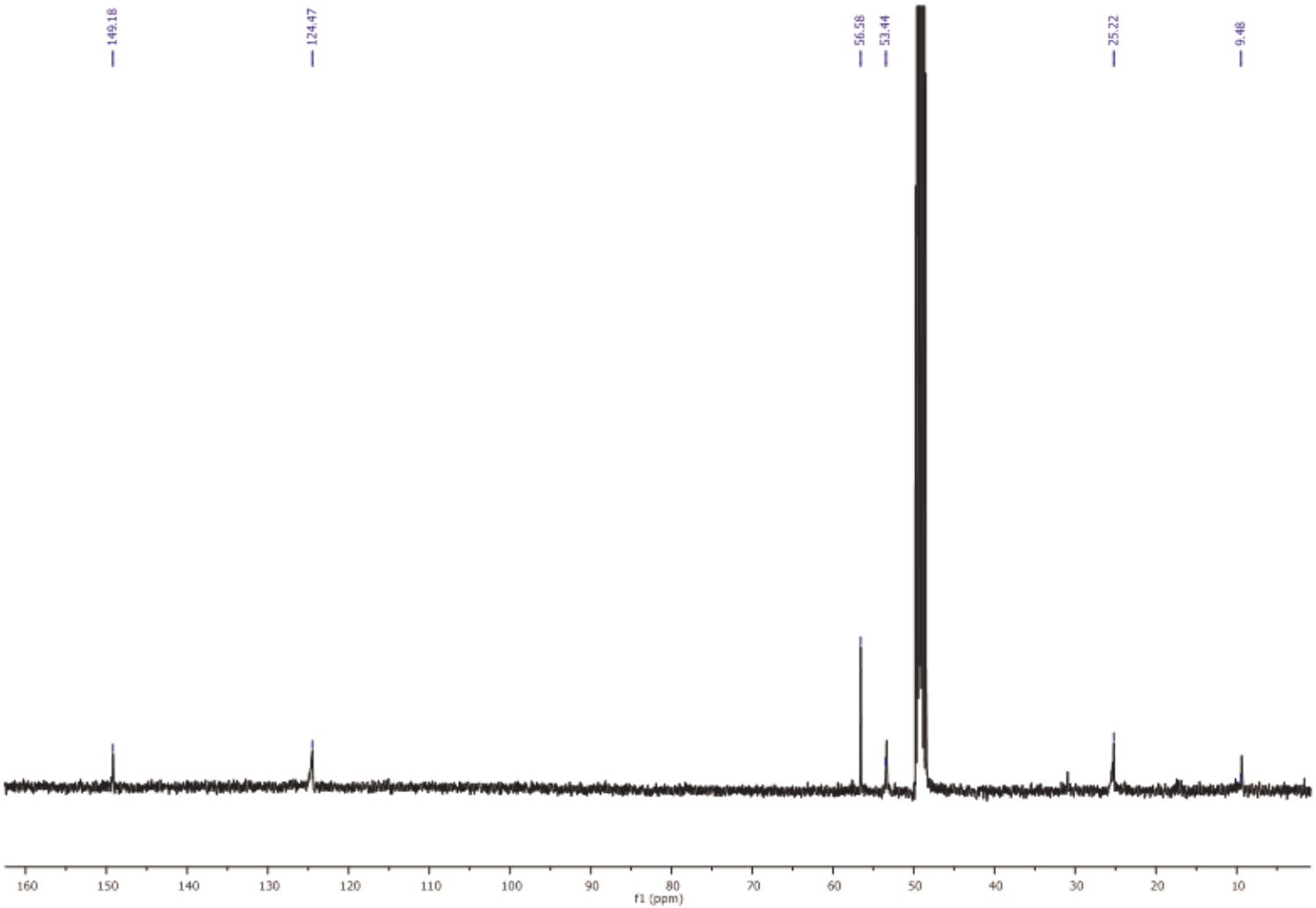
^{13}C NMR (DMSO-d_6, 100 MHz) spectrum of compound **7b**



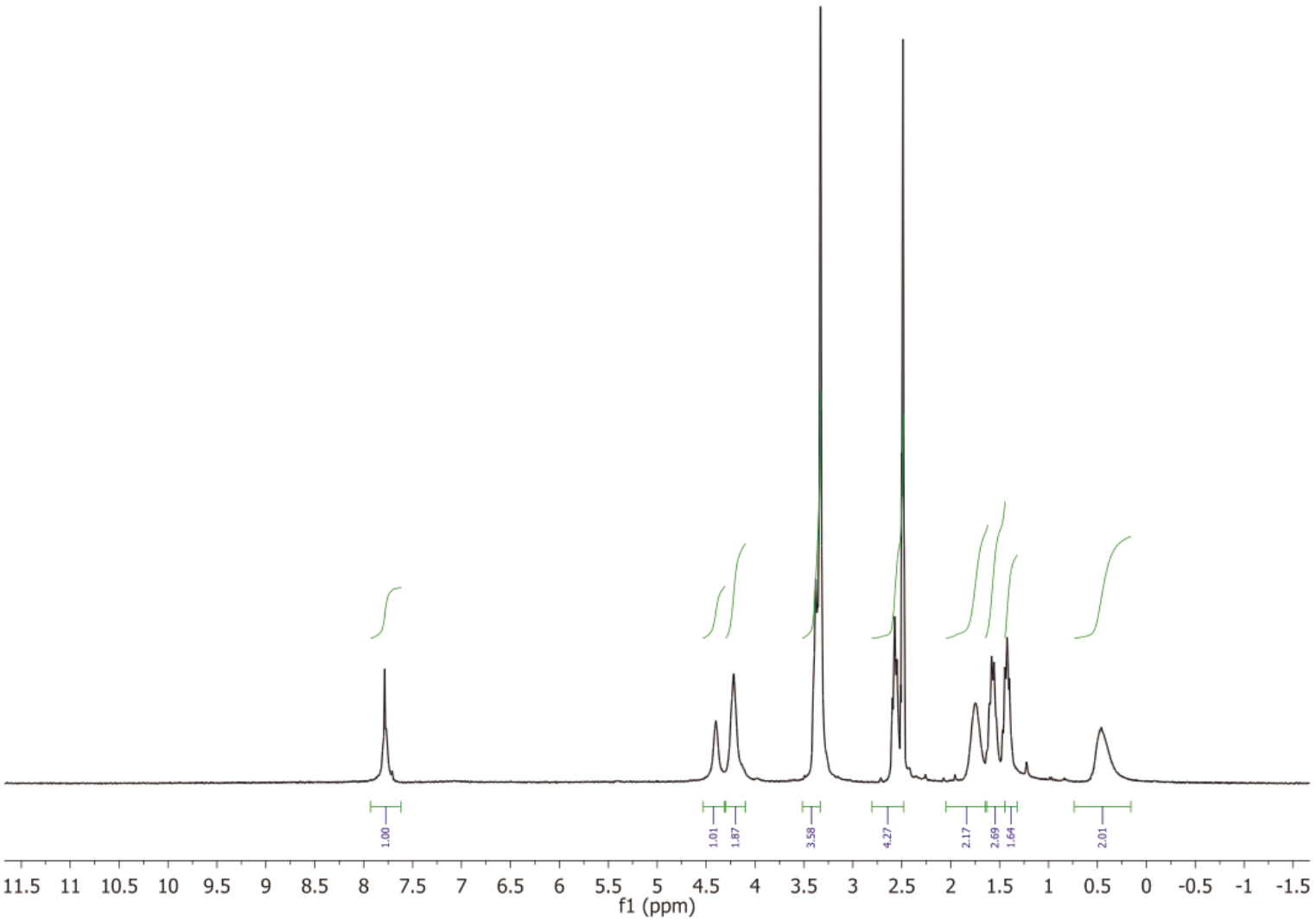
^{29}Si NMR (DMSO-d_6, 79.5 MHz) spectrum of compound **7b**



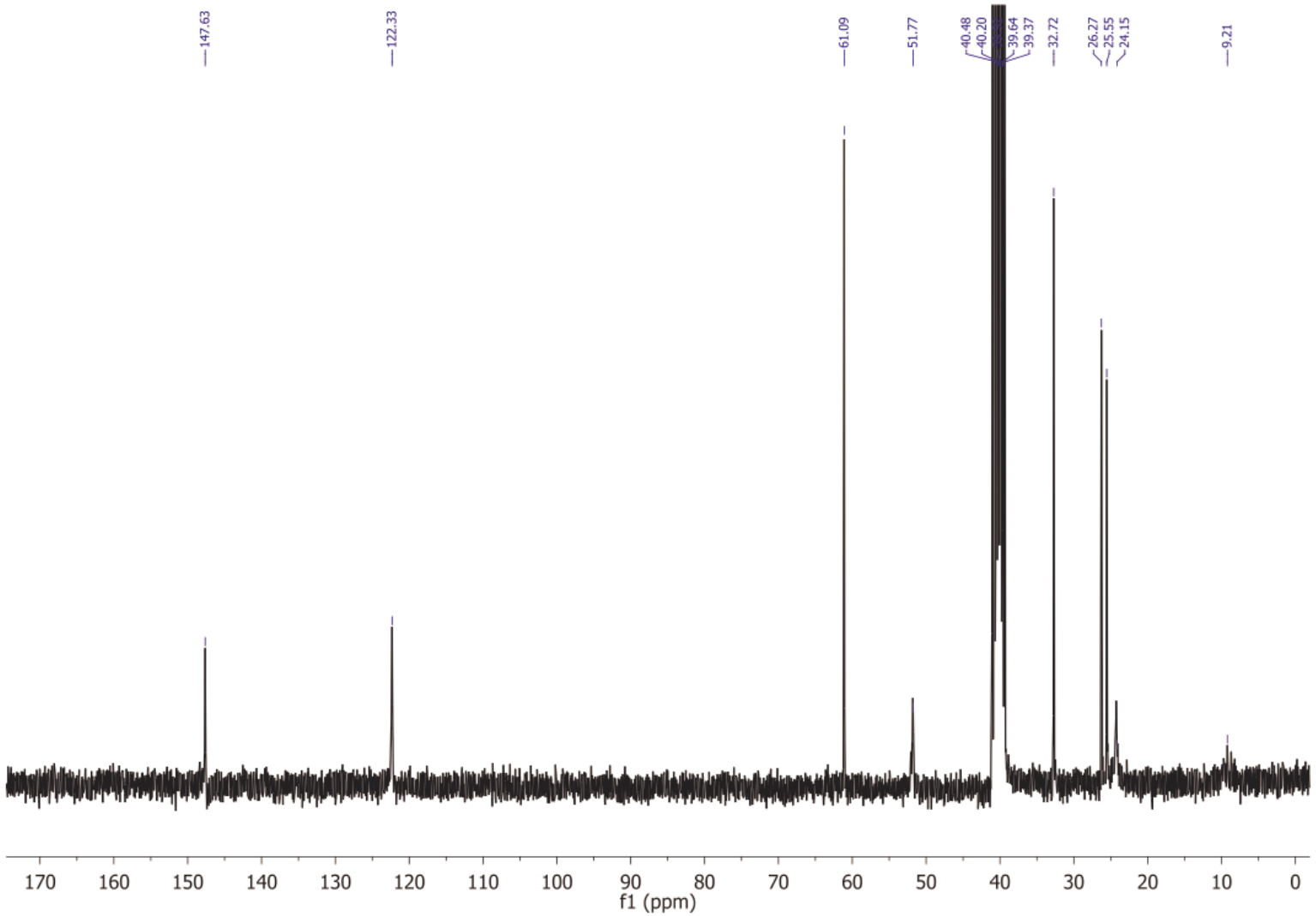
^{1}H NMR (CD_3OD, 400 MHz) spectrum of compound **7c**



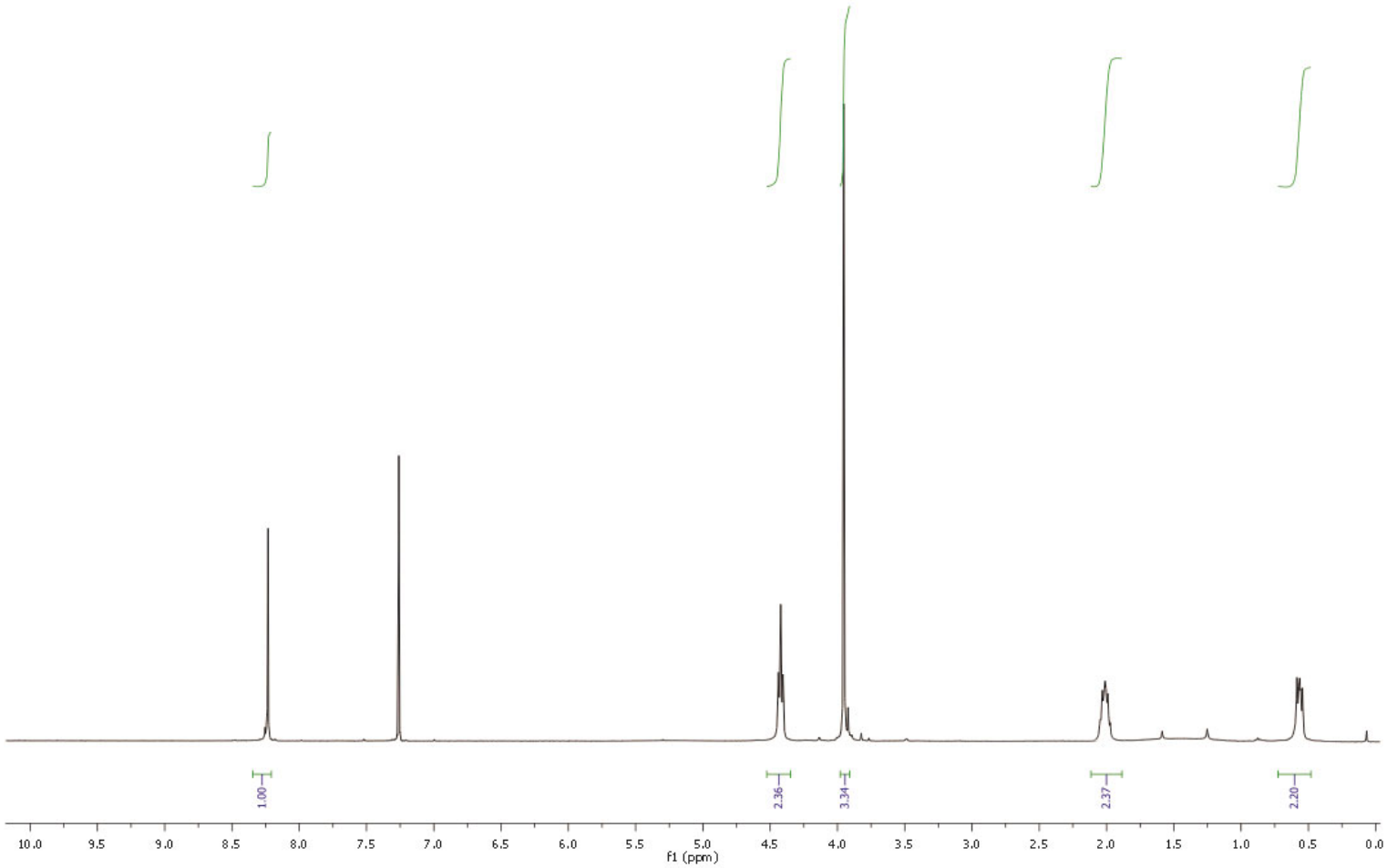
^{13}C NMR (CD_3OD, 100 MHz) spectrum of compound **7c**



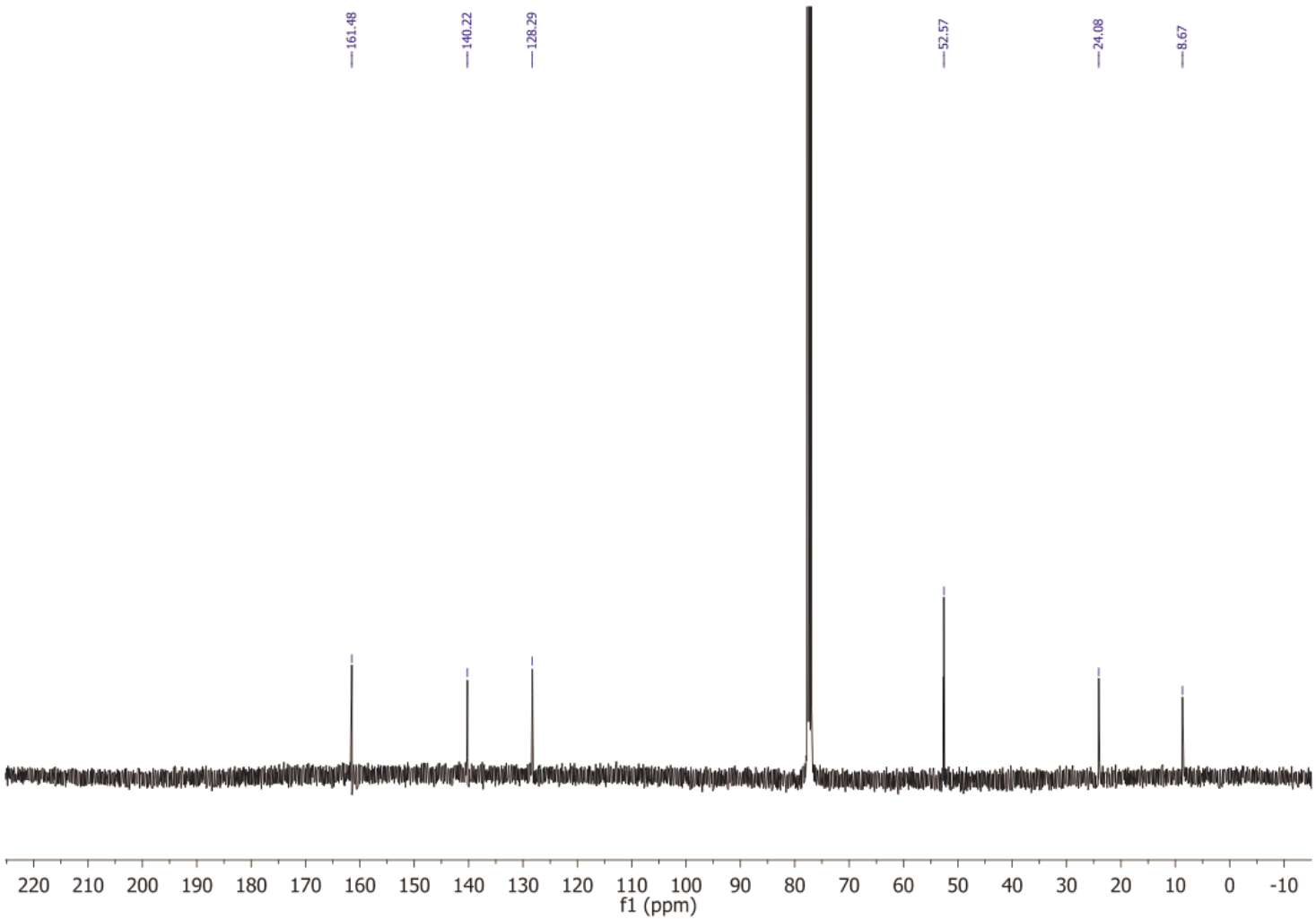
^{1}H NMR (DMSO-d_6, 400 MHz) spectrum of compound **7d**



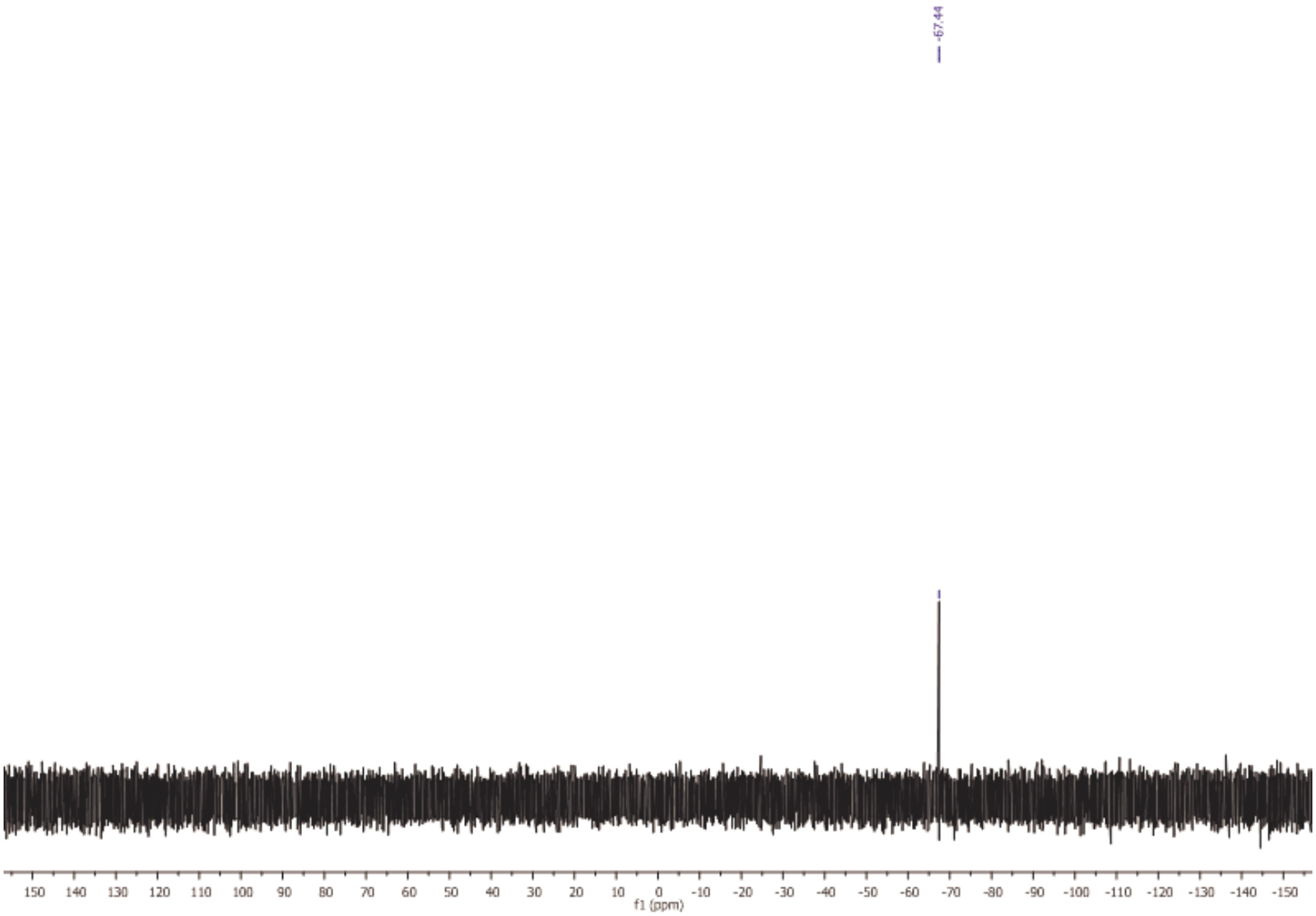
^{13}C NMR (DMSO-d_6, 100 MHz) spectrum of compound **7d**



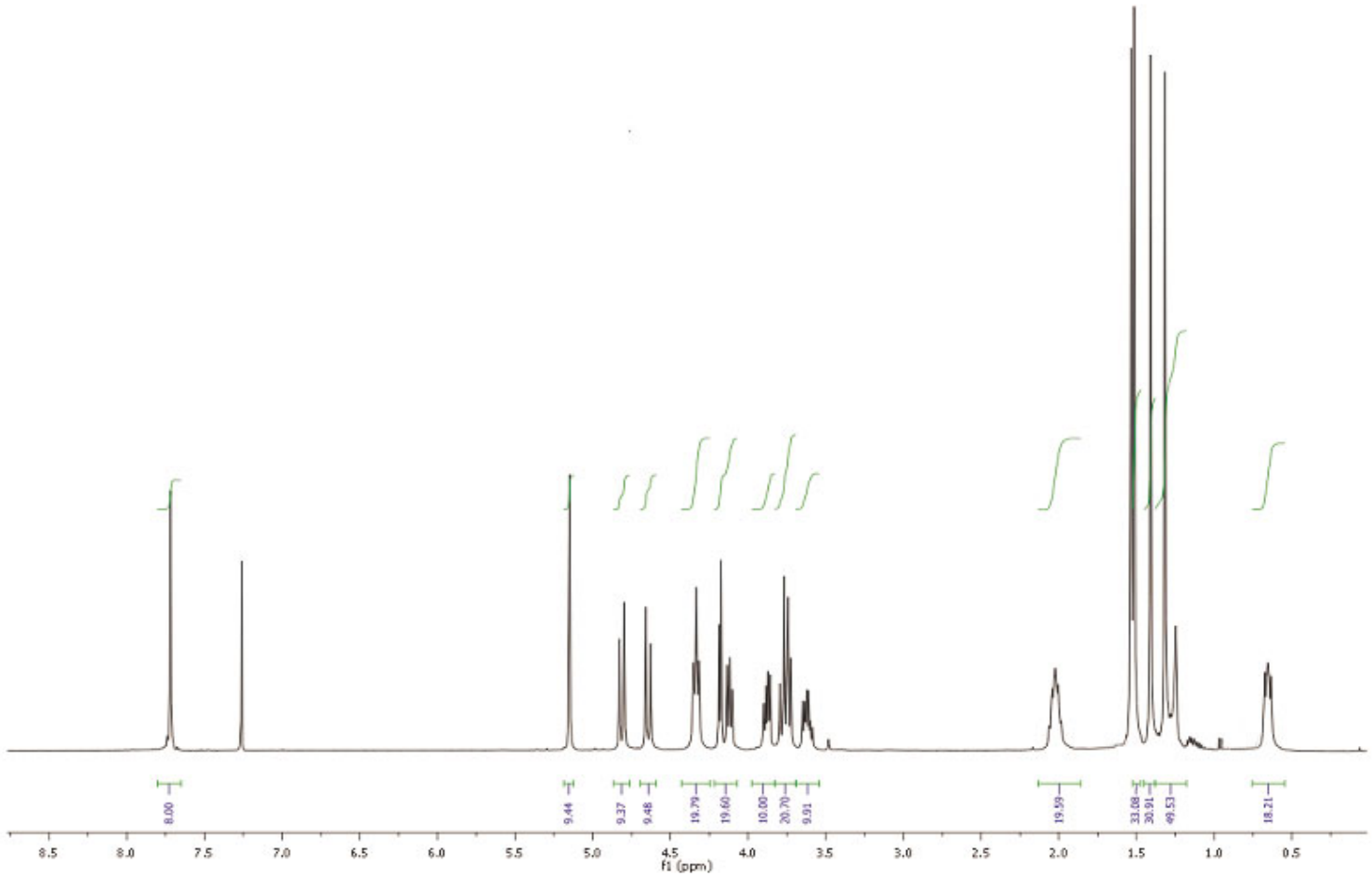
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **7e**



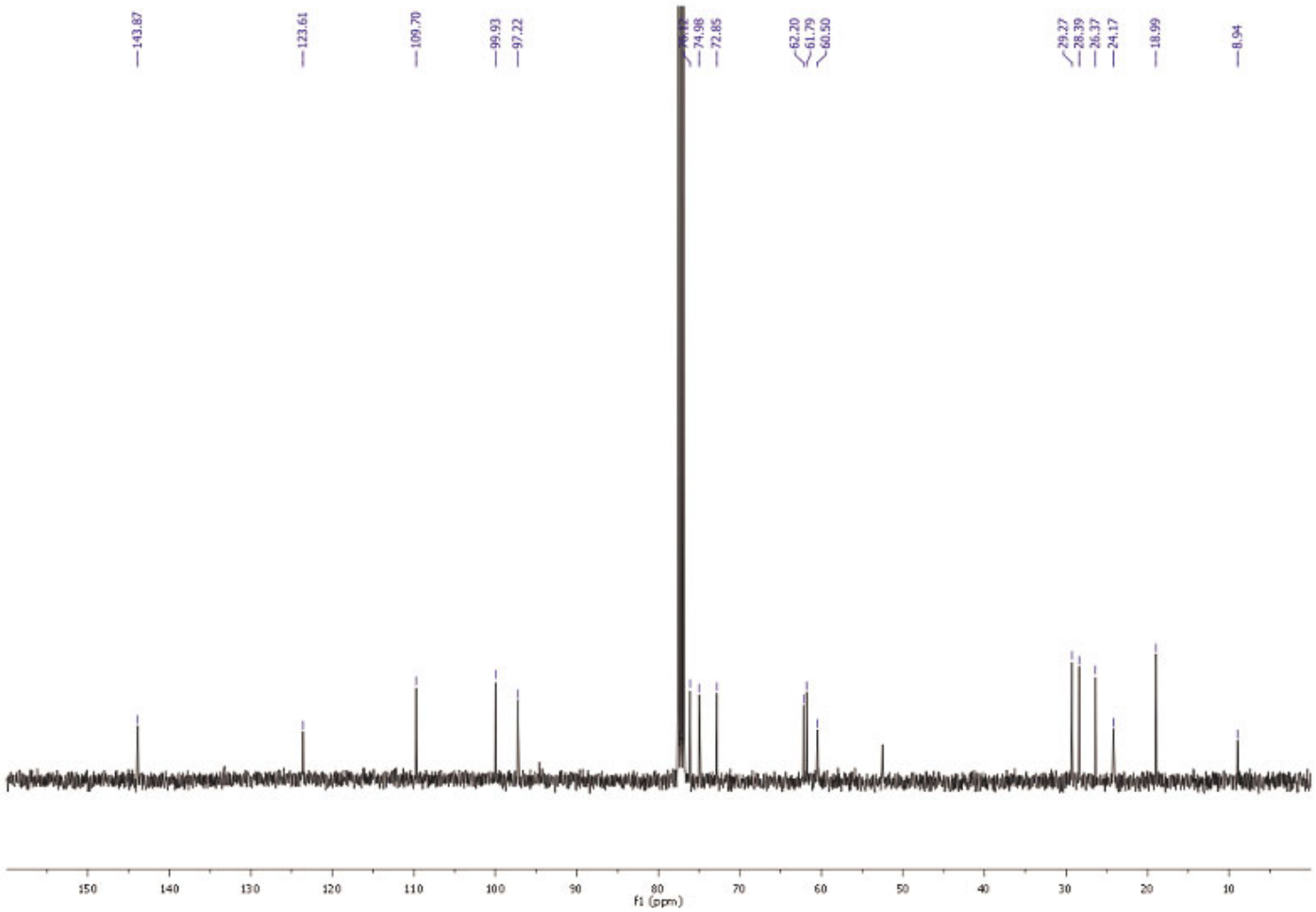
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **7e**



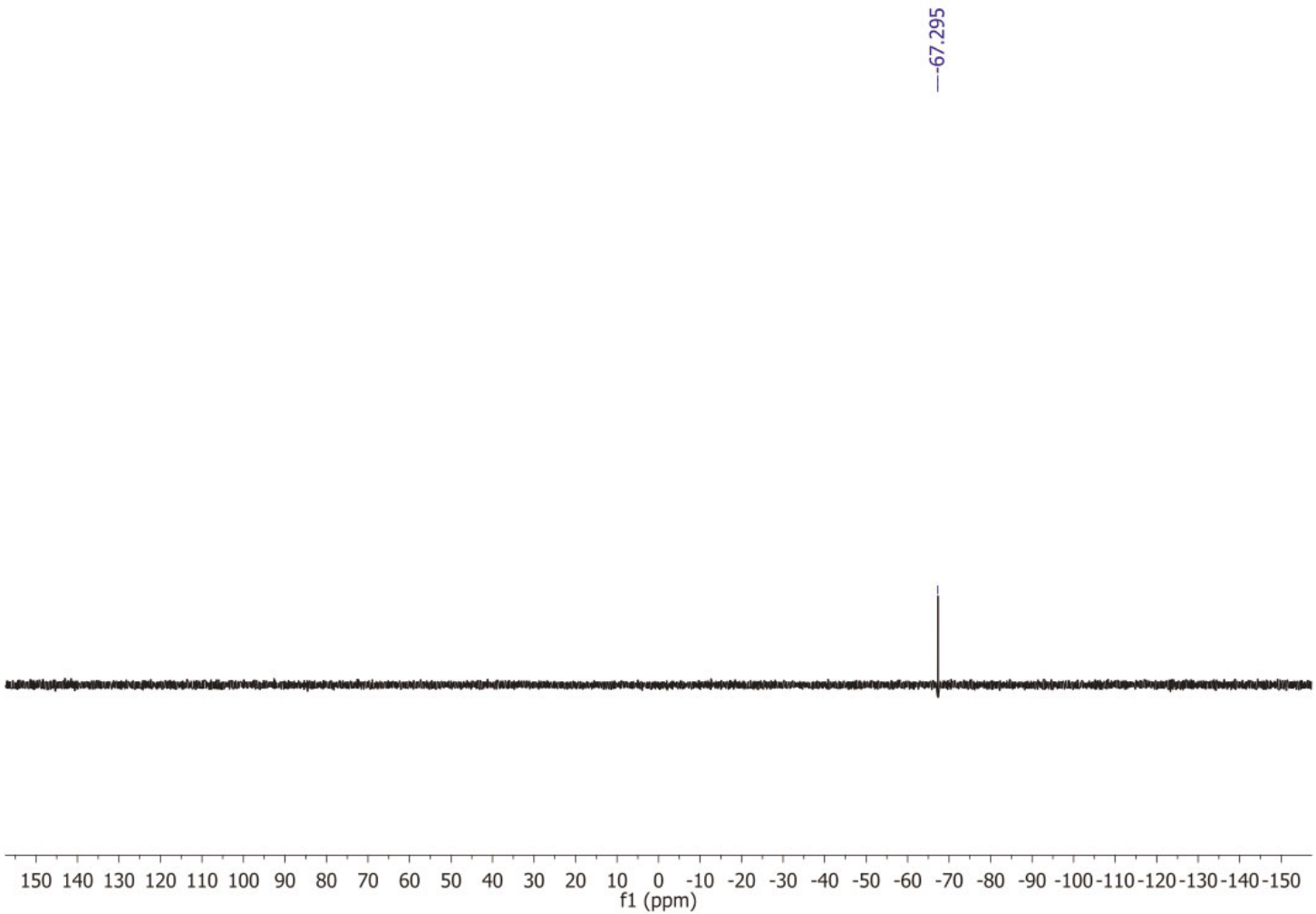
^{29}Si NMR ($CDCl_3$, 79.5 MHz) spectrum of compound **7e**



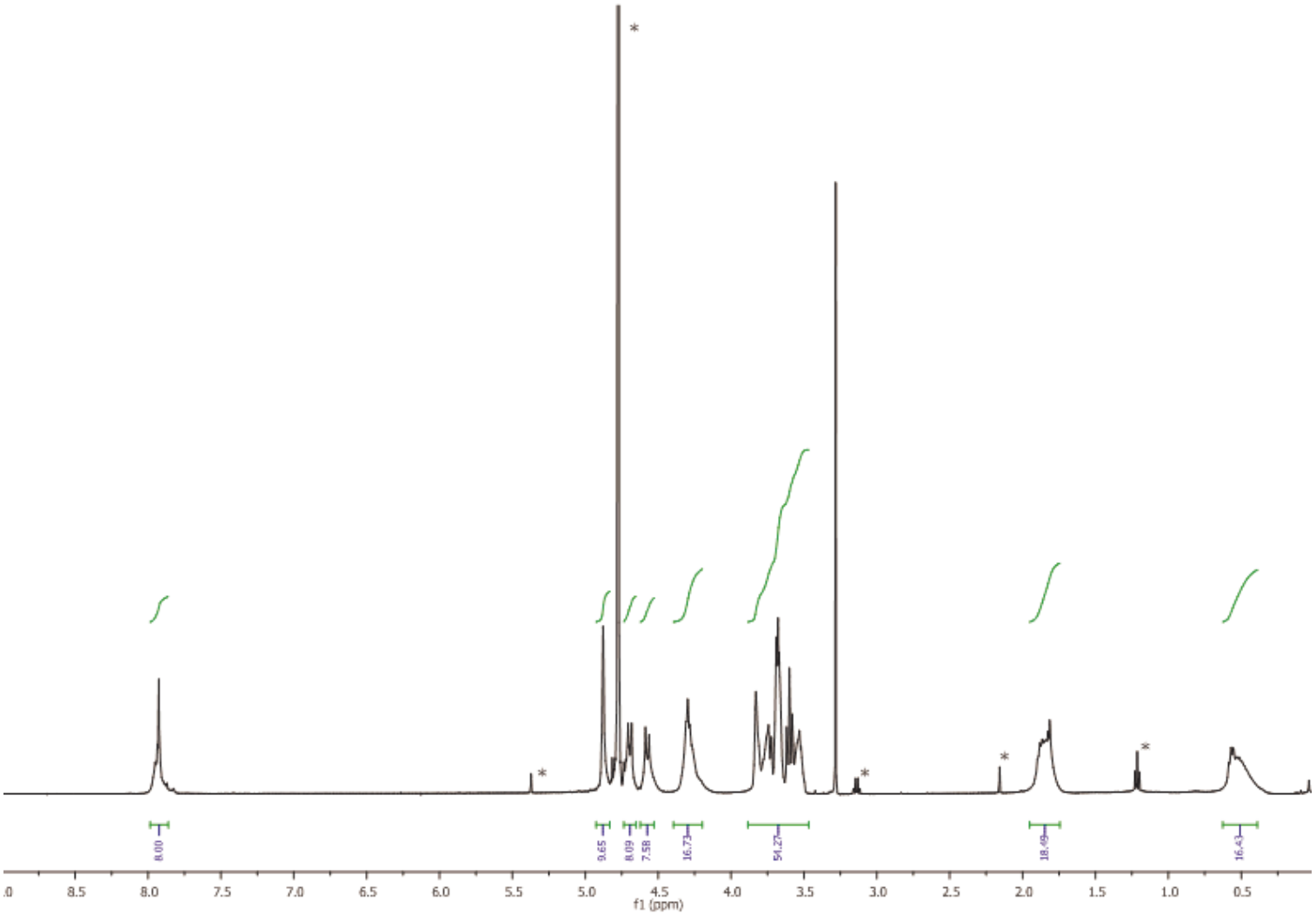
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **7f**



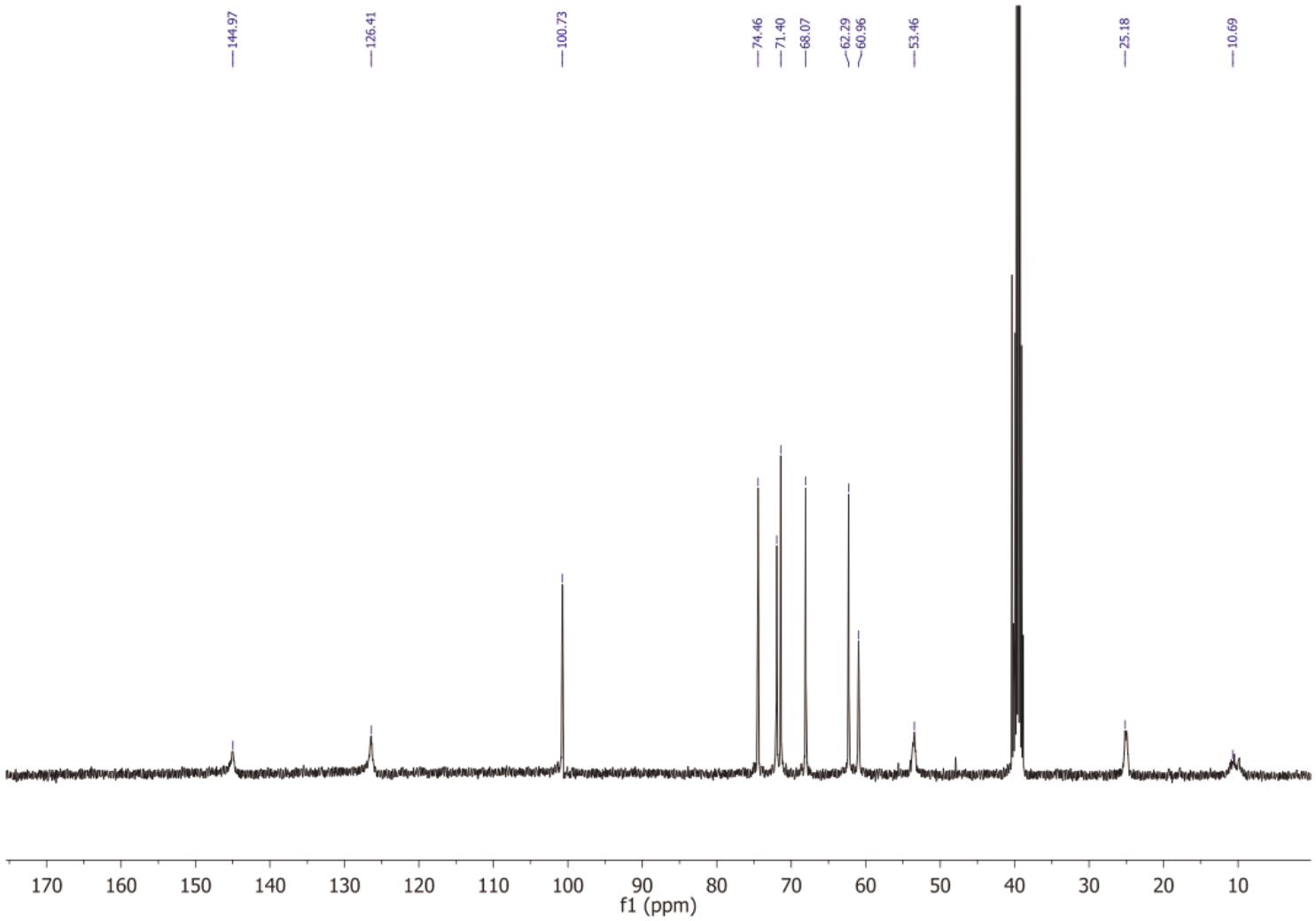
^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **7f**



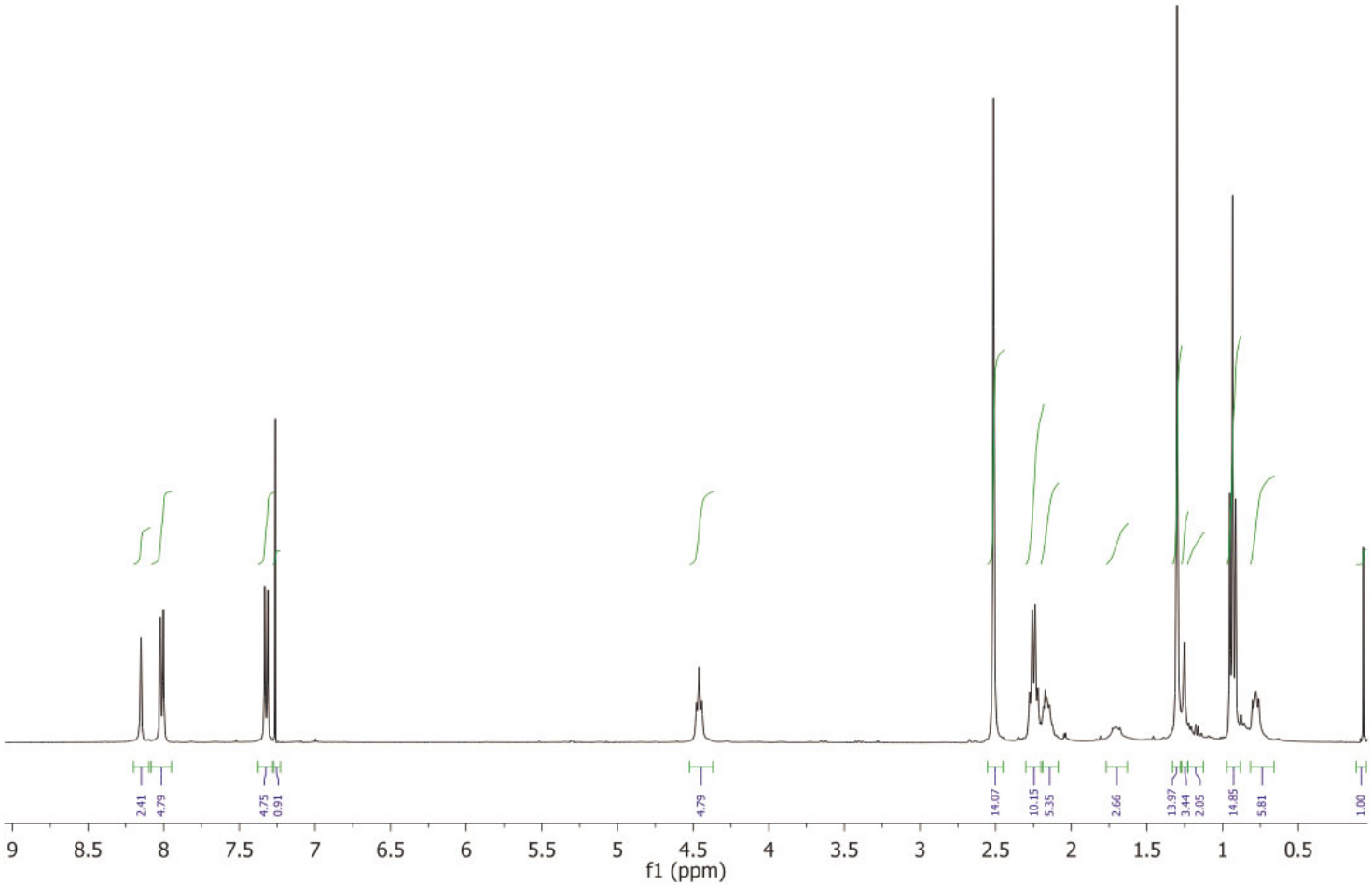
^{29}Si NMR ($CDCl_3$, 79.5 MHz) spectrum of compound **7f**



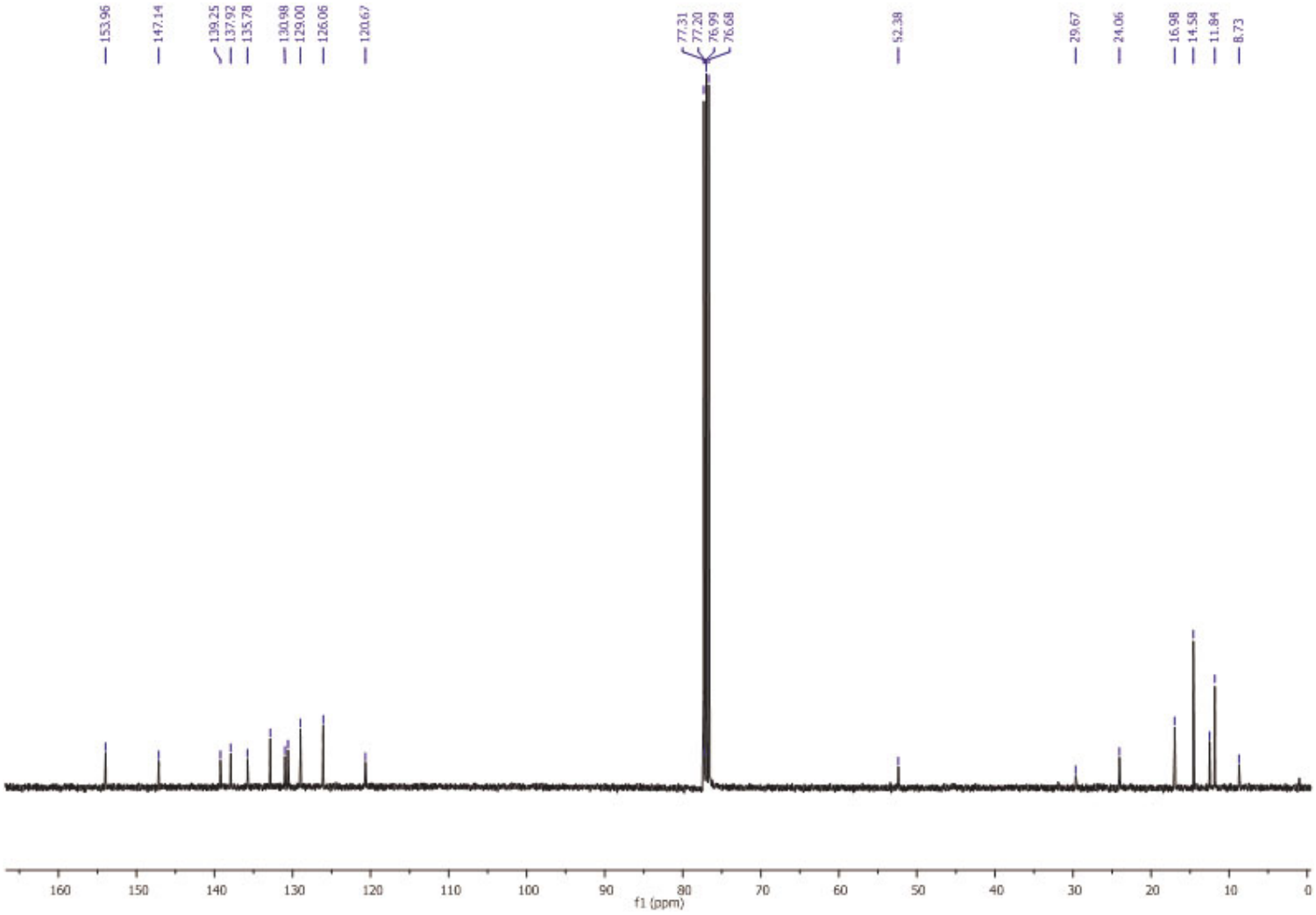
^{1}H NMR (D_2O, 400 MHz) spectrum of compound **7g**



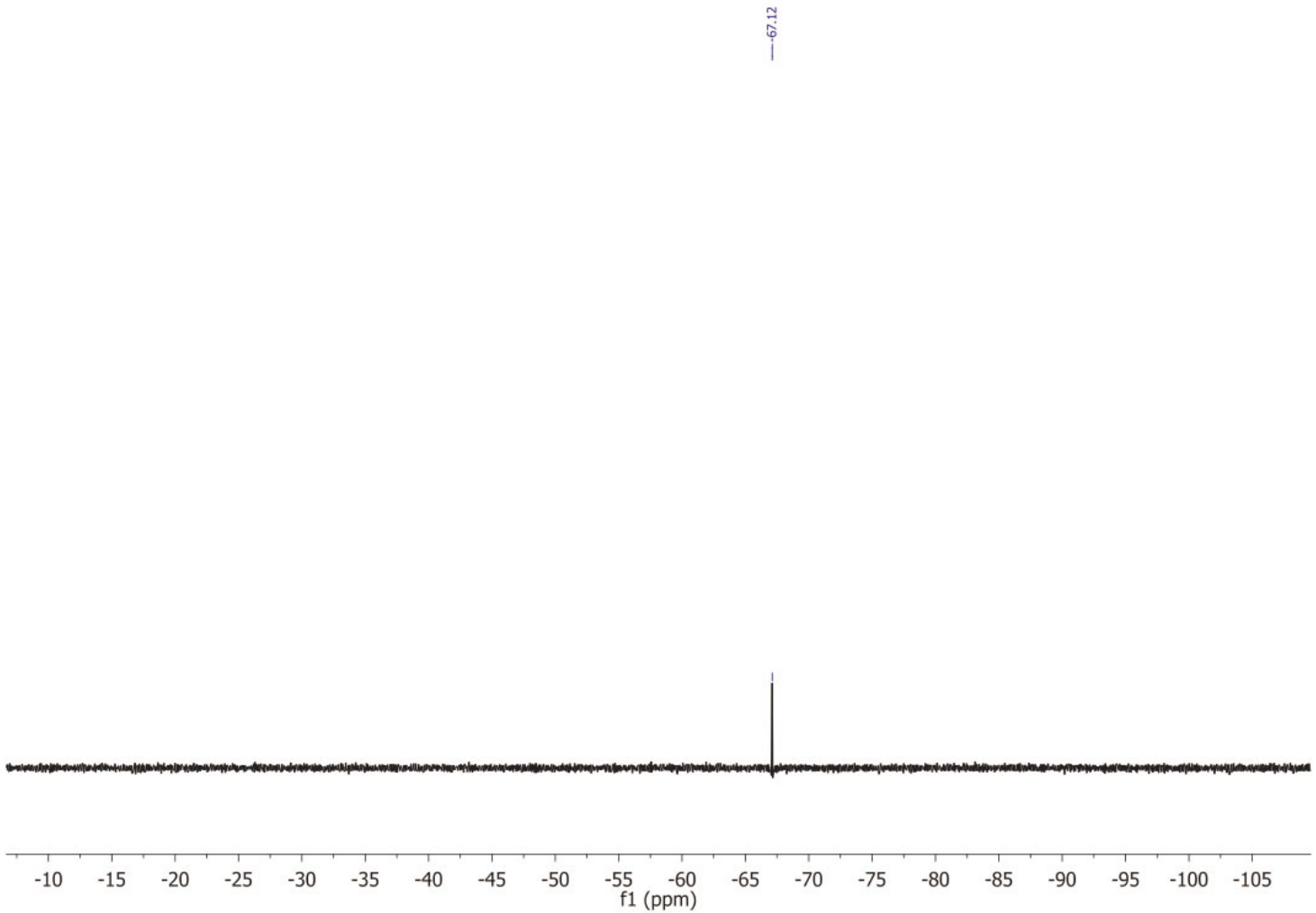
^{13}C NMR (DMSO-d_6, 100 MHz) spectrum of compound **7g**



^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **7h**



^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **7h**



^{29}Si NMR ($CDCl_3$, 79.5 MHz) spectrum of compound **7h**