Expeditious Approach to 3,3'-Bis-Silyl BINOLs, Biphenols, and 3,3'-Bis-Silyl Phosphoramidites Enabled by Catalytic C–H Silylation with a Traceless Acetal Directing Group.

by

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Abstract

Expeditious Approach to 3,3'-Bis-Silyl BINOLs, Biphenols, and 3,3'-Bis-Silyl Phosphoramidites Enabled by Catalytic C–H Silylation with a Traceless Acetal Directing Group.

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The University of Texas at Arlington, 2021

Supervising Professor: Dr. Junha Jeon

The research described in this dissertation is on two different projects namely i) Syntheses of 3,3'-bis-functionalized BINOL and biphenol compounds, ii) Syntheses of 3,3'-bis-silyl-BINOL-based phosphoramidites.

The first chapter reports attempts at developing a unified strategy to access a range of 3,3' bis-substituted BINOLs. This approach to access the 3,3'-functionalized BINOLs centers on the use of dioxasilines as a key intermediate generated through C-H activation catalytic reductive 3,3'-bis-silylation with a traceless acetal directing group. Dioxasilines successfully undergo nucleophilic addition to achieve various species of 3,3'-bis-silyl BINOLs with good yields. The scope is also expanded to a variety of silanes and biphenols. Furthermore, dioxasilines can also be subjected to Hiyama-Denmark coupling to accomplish 3,3'-bis-arylation of BINOL. Moreover, 3,3'-bis-silyl BINOLs can undergo gold-catalyzed direct arylation which allows for further modifications. Despite multiple trials and modifications, arylations using previously mentioned methods did not produce adequate yields. More importantly, this adduct is subjected to stereoisomers analysis to confirm the circumvention of the racemization issue previously reported

as one of the most common challenges of BINOL's derivatization. This approach gives easy access to an array of 3,3'-bis-functionalized BINOL to be used in asymmetric syntheses.

The second chapter describes the development of the strategy to access the 3,3'-bis-silyl-BINOL-based phosphoramidites. There are two reported methods to form phosphoramidite. The first bond formation (P-C or P-N) dictates the reagents and reaction conditions. This research finds that only the one of those two methods is applicable to our 3,3'-bis-silyl BINOLs. P-N bond initial formation followed by the addition of deprotonated 3,3'-bis-silyl BINOLs utilizes a milder condition, so the desilylation can be minimized. X-ray crystal structures of several resulted phosphoramidites are acquired to confirm the structures. This method creates a library of phosphoramidite ligands which has not been easily accessed before yet may have significant impact on stereoselectivities.

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Additional work performed while pursuing my Ph.D. that does not appear in this thesis has been published in:

1. Asgari, P.; Dakarapu, U. S.; **Nguyen, H. H**.; Jeon, J., Aryne cycloaddition reactions of benzodioxasilines as aryne precursors generated by catalytic reductive ortho-CH silylation of phenols with traceless acetal directing groups. *Tetrahedron.* **2017,** *73* (29), 4052-4061.

2. Parenky, A. C.; Souza, N. G.; **Nguyen H, H**.; Jeon, J.; Choi, H., Decomposition of Carboxylic PFAS by Persulfate Activated by Silver under Ambient Conditions. *Journal of Environmental Engineering.* **2020,** *146* (10), 06020003.

Chapter 1

Syntheses of 3,3’-bis-functionalized BINOL and Biphenol compounds

1.1. Introduction

1.1.a. Silicon and Organosilanes.

Silicon, which is categorized as semiconductor and has both metal and nonmetal properties, makes up in average about 30% of the lithosphere by weight.[1] Oxygen and silicon, which are the most abundant elements in the corresponding order, bond strongly with each other to form silica or silicate.[1] Silicon has zero to minimal contribution in the atmosphere and hydrosphere. The biosphere contains silicon in various amounts among all organisms at different stages of their evolution.[2] Nevertheless, although its importance in the survival of most species is universally highlighted, the nuances regarding the biochemical process of silicon are still being discovered.[2] Silicon plays important roles in vertebrates as an essential micronutrient. In humans, it has been found to support healthy bone development and preservation.[3-5]

Silicon and carbon share various similarities which can be observed in Group IV elements.[1, 6] Nevertheless, numerous significant differences influence the characteristics of their bond formations.[6] Due to its size and the low-lying 3d orbitals, silicon has the capability to form 5- and 6-coordination complexes, which leads to unique reactivity and stereochemistry possibilities.[1] Moreover, silicon bonds exhibit more polarization than their carbon bonds' counterparts.[1] A silicon-carbon bond shows a partial negative charge positioned on the carbon. [1] Furthermore, the shortened bond lengths and enhanced bond dissociation energies of certain silicon bonds might reflect to the back-bonding involving the 3d orbitals.[1] Therefore, these properties expand silicon chemistry to vast and unique territories.

Organosilanes have many applications which are essential to modern society. For example, in the materials industry, they are the main components in surface coating, polymers, surfactants,

adhesive, battery, and integrated circuit.[2, 7, 8] Moreover, organosilanes have been studied and used for many innovative medical technologies such as drug discovery and delivery.[2-4]

Organosilicon chemistry not only benefits from diverse, inexpensive, low toxicity, and high stability starting reagents, but also possesses a vast established fundamental knowledge as one of the most well-studied topics in the 21st century. Therefore, organosilicon chemistry has a large repertoire of reactions, many of which have become essential in organic syntheses. Organosilanes play versatile roles in many reactions such as protecting groups, Lewis acid catalysts, reducing agents,[9, 10] and nucleophiles[11, 12]. In addition, they serve as coupling partners in many important reactions such as Hiyama cross-coupling reaction, the important Denmark-modified version, and many more variations of metal catalyzed cross-coupling reactions. [11, 13-16] Furthermore, the higher Si-O bond dissociation energy compared to Si-H and Si-C bonds offers the driving force for the generation of silyl ether from alkoxides known as Brook rearrangement.[17, 18] The retro-Brook rearrangement, which is reverse process, can also be achieved with some adjustments in the reaction condition. [19, 20] The discovery of this equilibrium has allowed many useful transformations such as silyl enol ether, 2,3-disubstituted thiophenes synthesis,[21] anion relay chemistry,[22, 23] and trifluoromethylation.[24] Innovations in organosilicon chemistry are still under investigation and continue to facilitate numerous total syntheses.

1.1.b. Introduction to 3,3'-functionalization of BINOL.

1.1.b.1. Introduction to BINOL and its derivatives.

BINOL or 1,1'-binaphthalene-2,2'-diol is a highly aromatic diol compound which exhibits axial chirality (Figure 1.1). This axial chirality which distinguishes between two enantiomers, (*R*)-BINOL and (*S*)-BINOL, grants it powerful influence over the stereochemical outcomes of many reactions as either catalyst or ligand. Synthesized first in 1926 by Pummerer, BINOL was first

used as an auxiliary ligand to achieve the successful enantioselective reduction of prochiral carbonyl compounds by Noyori in 1979.[25, 26]

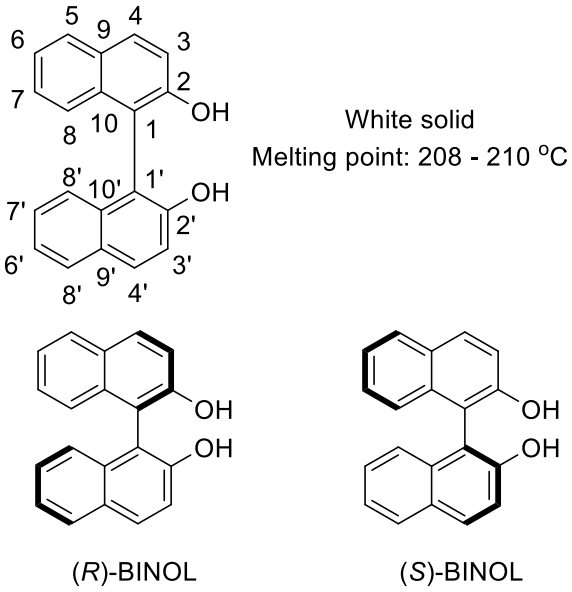


Figure 1.1. BINOL's physical properties and enantiomers.[25, 27]

Inducing the formation of the correct enantiomers or diastereomers is extremely crucial in drug development. BINOL and its derivatives have facilitated an enormous set of stereoselective reactions including various methods of carbon-carbon bond formation and catalytic heteroatom-transfer.[25, 27, 28] For example, BINOL derivatives have played a critical role in syntheses of HIV treatment drugs such as Enfavirenz and Maraviroc (Figure 1.2).[29, 30]

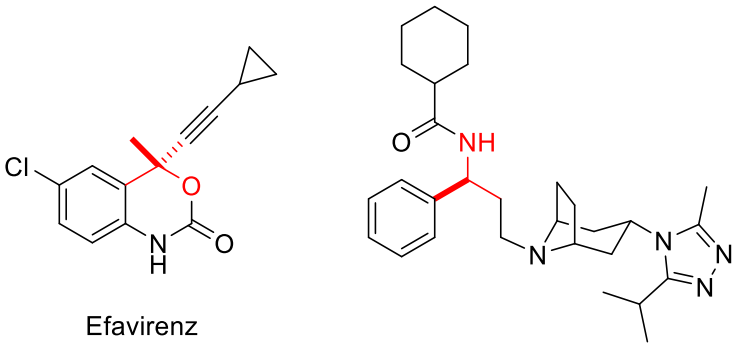


Figure 1.2. Enfavirenz and Maraviroc.

Nevertheless, BINOLs have been found to undergo racemization under extreme heating conditions.[31, 32] Furthermore, acidic and basic conditions can assist this process by reducing the temperature required for the conversion (Table 1.1).[31] Similar conditions should be avoided in modifications of BINOL derivatives in order to reserve its stereochemical integrity.

Solvent	Condition	Temperature (°C)
Naphthalene		195
Diphenyl ether		220
Dioxane – water	HCl (1.2 M)	100
Butanol	KOH (0.67 M)	118

Table 1.1. Racemization conditions.

1.1.b.2. Stoichiometric methods.

Among BINOL derivatives, the 3,3'-bis-substituted BINOL derivatives show dominant stereoselectivity due to the proximity of the substituents to the reactive site. Developed by Cram and co-workers as early as 1978, one of the most prominent synthetic strategies consists of deprotonation of a protected BINOL by an organolithium reagent and addition of an electrophile such as sulfur, halogen, and silicon compounds (Figure 1.3).[31, 33] Furthermore, the scope of electrophiles has been expanded with many useful functional group installations such as boron, carbonyl, and alcohol.[31] Nevertheless, these strategies face many challenges such as a

stoichiometric use of reagents, multiple purification steps of various intermediates, and possibility of racemization of the BINOL.

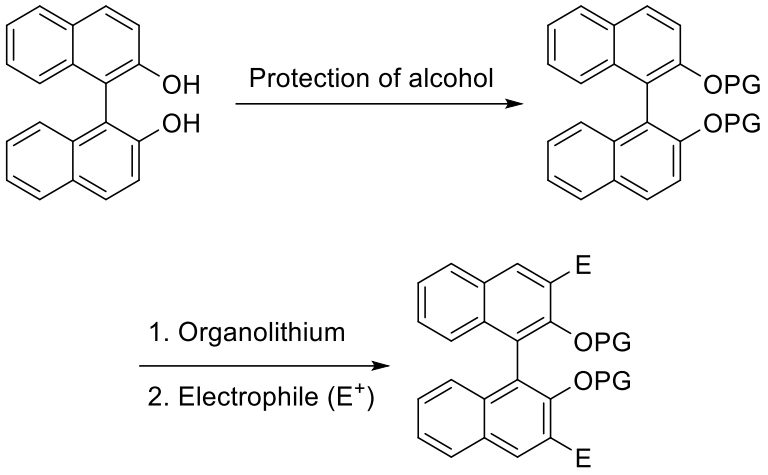


Figure 1.3. Stoichiometric 3,3' functionalization of BINOL method.

1.1.b.3. Catalytic method.

Most recently, Clark and co-workers have developed an efficient three-step synthesis of 3,3'-bis-aryl-BINOLs which took advantage of the Hartwig's silane-directed 3,3'-bis-borylation and an *in situ* Suzuki coupling reaction.[28] Although this method is superior due to its catalytic nature, there is still a need for an innovative environmentally benign method with more versatile intermediates during the synthesis (Figure 1.4).

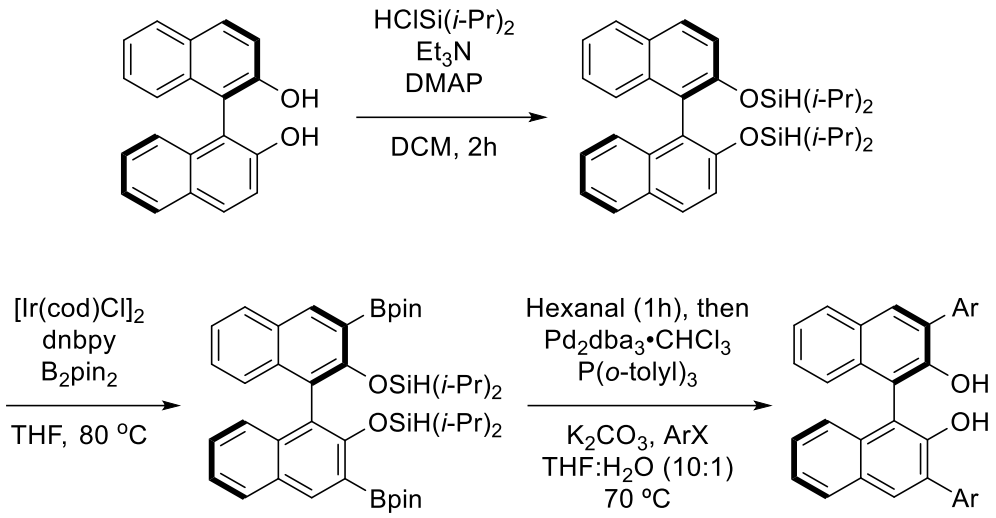


Figure 1.4. Catalytic efficient three-step synthesis of 3,3'-bis-aryl-BINOLs.

1.1.b.4. 3,3'silylation of BINOL

The 3,3'-bis-silyl-BINOL derivatives not only have been utilized as powerful stereoselective ligands but can also serve as an intermediate for further modifications such as cross-coupling reactions. The most cited method of 3,3'-bis-silyl groups installation is a variation of Cram's stoichiometric method developed by Snieckus and co-workers by using chlorosilane as the electrophile.[31, 34] Yamamoto's group reported another noteworthy method by utilizing 1,3-rearrangement of 3,3'-bis-bromo silyl ether form of BINOL (Figure 1.5).[35] Nevertheless, these strategies face many challenges such as a stoichiometric use of reagents, multiple purification steps of various intermediates, and possibility of racemization of the BINOL.

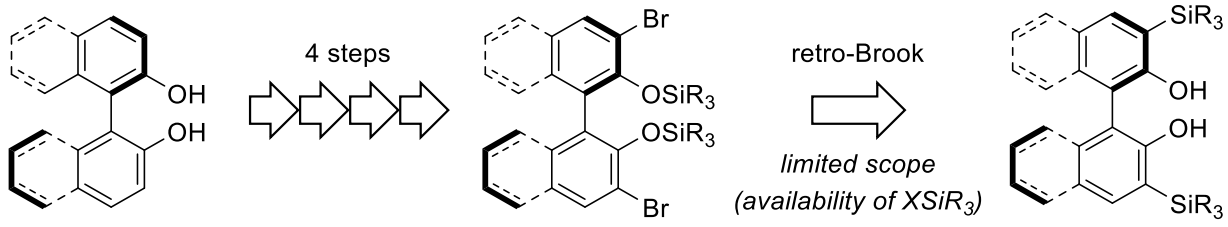


Figure 1.5.1,3-rearrangement of 3,3'-bis-bromo silyl ether of BINOL.

Other motivations for pursuing the effective generation of these derivatives are their capabilities to participate in various cross-coupling reactions. The Hiyama-Denmark reaction will grant access to the 3,3'-bis-aryl-BINOL derivatives.[16, 36] Moreover, recently Lloyd-Jones group published an innovative method involving Au-catalyzed coupling of unfunctionalized arenes with aryltrimethylsilane.[37] One of the biggest advantages of this strategy is to preserve potentially reactive, yet useful functional groups in the final products. Moreover, trifilated compounds can undergo the modified Ni-catalyzed coupling reported by the Yu's group to form BINAP derivatives.[38]

1.1.c. Introduction to C-H activation catalytic reductive ortho silylation with a traceless acetal directing group.

Recently, our group published our research on a catalytic reductive *ortho*-C-H silylation of phenols with a traceless acetal directing groups to form unique cyclic organosilanes, dioxasilines.[39] This method features an Ir-catalyzed ester hydrosilylation and Rh-catalyzed ortho-C-H silylation in a one-pot process with readily available phenyl acetates as starting materials (Figure 1.6). Previous silylation methods suffers from utilization of stoichiometric amount of reagents, limited functional group tolerance, moderate yields, low selectivity, and difficult installation and removal of directing groups. These processes transform the acetylated phenols to benzodioxasiline through directed *ortho*-C-H activation with excellent yield. Our group also demonstrates multiple methods to modify this intermediate into different useful products.

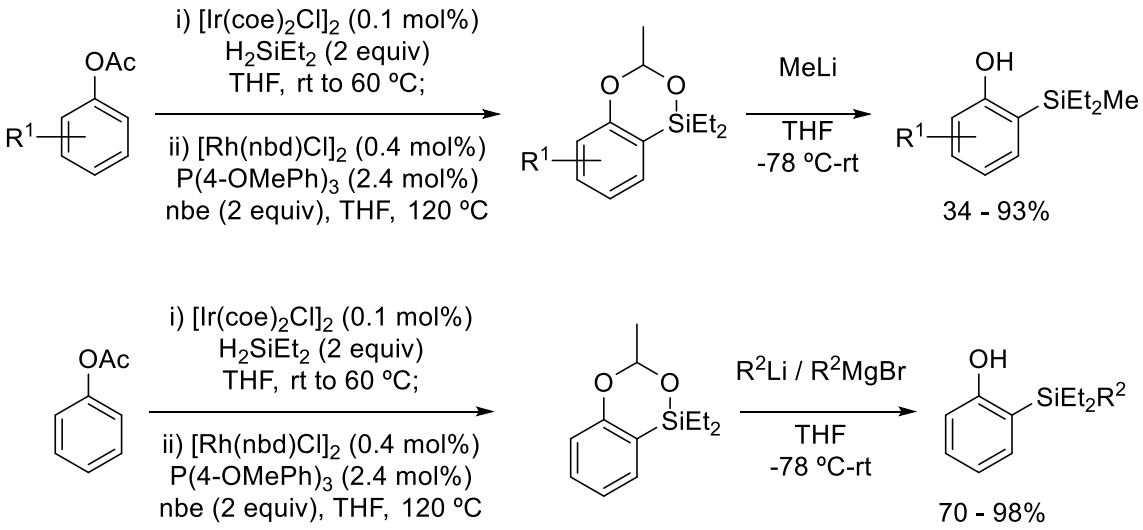


Figure 1.6. Catalytic reductive *ortho*-C-H silylation of phenols

1.2. Strategy for synthesis of 3,3'-bis-silylation of BINOL.

1.2.a. Proposed strategy.

The bis-acetylated BINOL synthesized from BINOL would undergo hydrosilylation with $[Ir(coe)_2Cl]_2$ and dialkyldihydrosilanes to form the bis-silyl acetal, which can be subjected to the C–H activation process catalyzed by $[Rh(nbd)Cl]_2$ and P(4-MeOPh)$_3$ as ligand. The resulting dioxasiline can be further treated with a series of nucleophiles (e.g., Grignards reagents, organolithium reagents, and oxygen nucleophiles) to yield the 3,3'-bis-silyl BINOL derivatives (Figure 1.7).

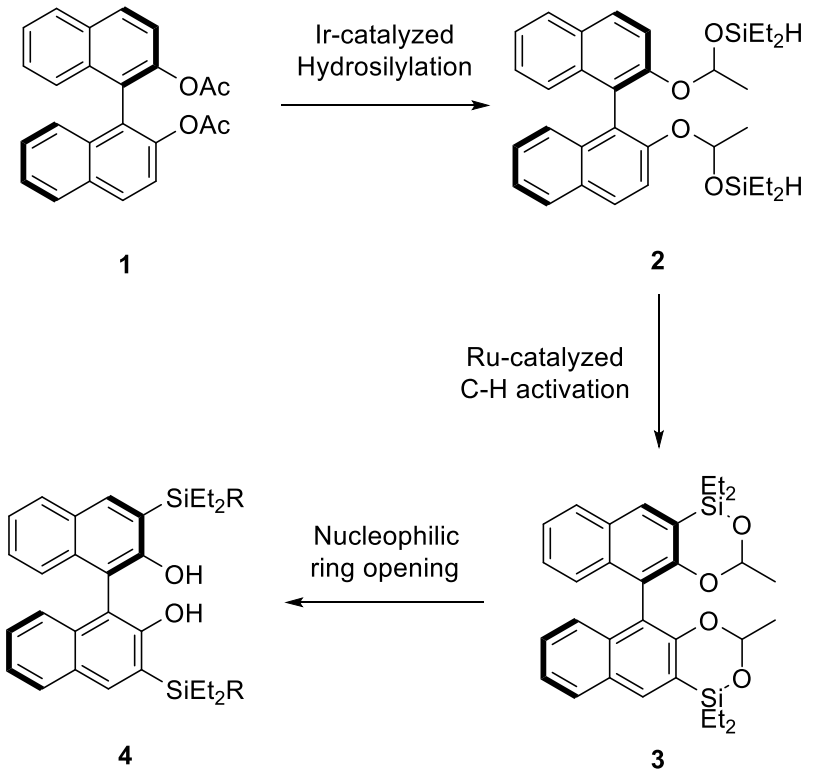


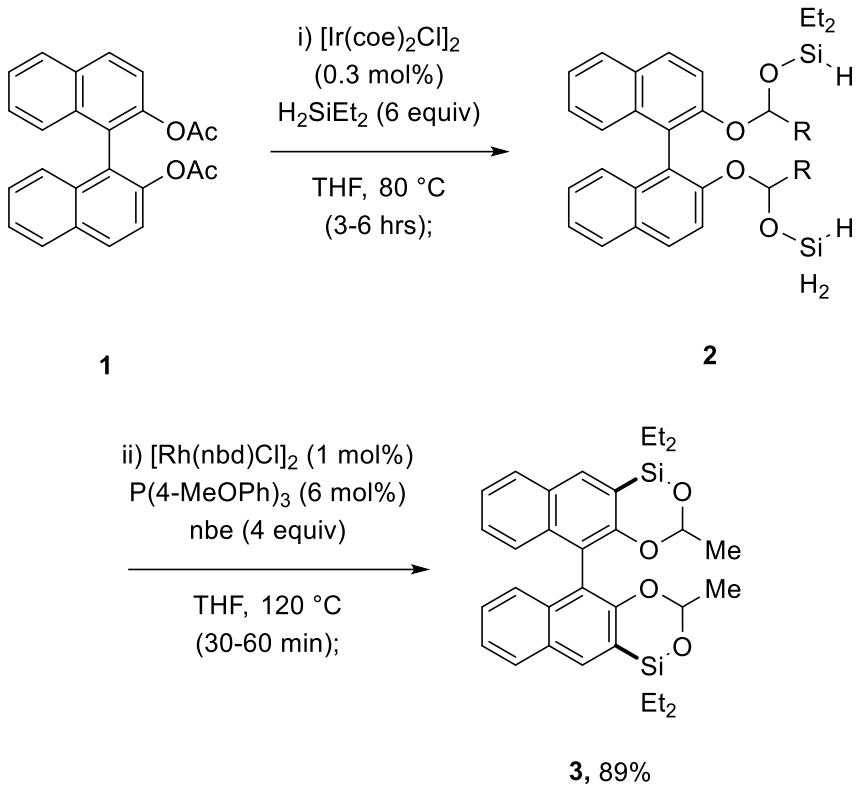
Figure 1.7. Proposed strategy for 3,3'-bis-silylation of BINOL.

1.2.b. Initial studies.

Initial research has shown that the bis-acetylation of BINOL yielded desired product with excellent yield. Furthermore, the one-pot process involving sequential Ir-catalyzed ester hydrosilylation and Rh-catalyzed C–H silylation produced the dioxasilines in excellent yield (89%). Moreover, a ring-opening addition of various nucleophiles has been carried out with either organomagnesium or organolithium reagents. These reactions produced from good to moderate yields (35 to 87%) in one-pot reaction without any purification from dioxasilines.

1.2.c. Optimization.

1.2.c.1. Optimization of reaction time.



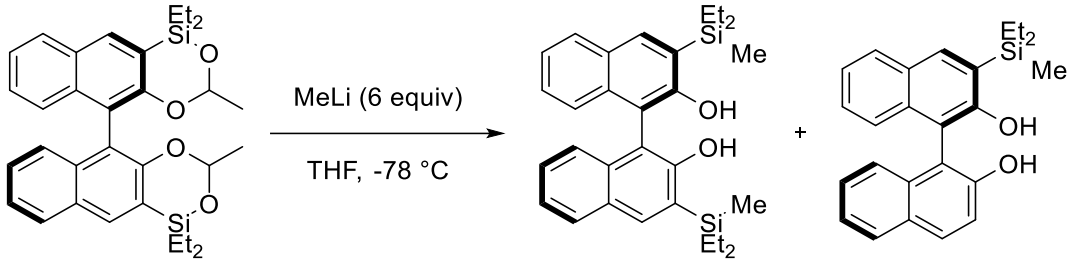
[a]Conditions: (i) [1,1'-binaphthalene]-2,2'-diyl diacetate **1** (0.4 mmol), $[Ir(coe)_2Cl]_2$ (0.3 mol %), H_2SiEt_2 (6 equiv), THF (1M), 80 °C, 3-6 h. (ii) $[Rh(nbd)Cl]_2$ (1 mol%), $P(4\text{-}OMePh)_3$ (6 mol%), nbe (4 equiv), THF (1M), 120 °C, 30-60 min.

Figure 1.8. Synthesis of bis-dioxasilines.[a]

Our approach to expeditious synthesis of 3,3'-bis-silyl-BINOLs/biphenols and 3,3'-bis-silyl BINOLs/biphenols-based phosphoramidites initially centered on development of catalytic dual C–H silylation of bis-acetyl (*R*)-BINOL **1** with a traceless directing group. Dual Ir-catalyzed ester hydrosilylation of **1** to afford bis-silyl acetal **2** is generally completed in 3-6 h in THF at 80 °C with 0.3 mol% of catalyst, and the succeeding, two-fold *ortho*-C–H silylations of **2** under Rh catalysis to provide bis-cyclic silyl acetal **3** (i.e., bis-dioxasilines) were completed within 30 min in THF at 120 °C in a closed vessel. The resulting dioxasilines **3** in an inconsequential

diastereomeric mixture (ca. 1.6:1.6:1:1.6) were indeed chromatographically stable and can be stored for a few weeks (Figure 1.8).

Two-fold nucleophilic addition of a variety of nucleophiles to **3** was accomplished in one-pot and within 5 minutes in most cases, to produce diverse 3,3'-bis-silyl-BINOLs **4** with moderate to good yields (10 examples, **4a-f**, **m-q**, 35-87% yields, 3 steps, Table 1.4). However, longer reaction time gave predominantly mono-desilylation products when the reaction is done in one-pot. For example, mono-desilylated product **5** was produced with 95% yield after 30 minutes (Table 1.2). The reduction in the yield of the desired product **4** over time confirmed this hypothesis although the two products have never been isolated together due to their vastly different polarities.



3 **4a** **4'a**

Time (minute)	**4a**	**4'a**
5	83%	
15	35%	
30		95%

Table 1.2. Formation of desilylated product **5** over prolonged reaction time.

1.2.c.2. Optimization of anions.

Among the nucleophiles, organolithiums were generally found to be optimal for the ring-opening of the dioxasilines **3**, because of the rapid product formation and minimal desilylation. Specifically, alkyl nucleophiles varying steric hindrance were introduced by using their

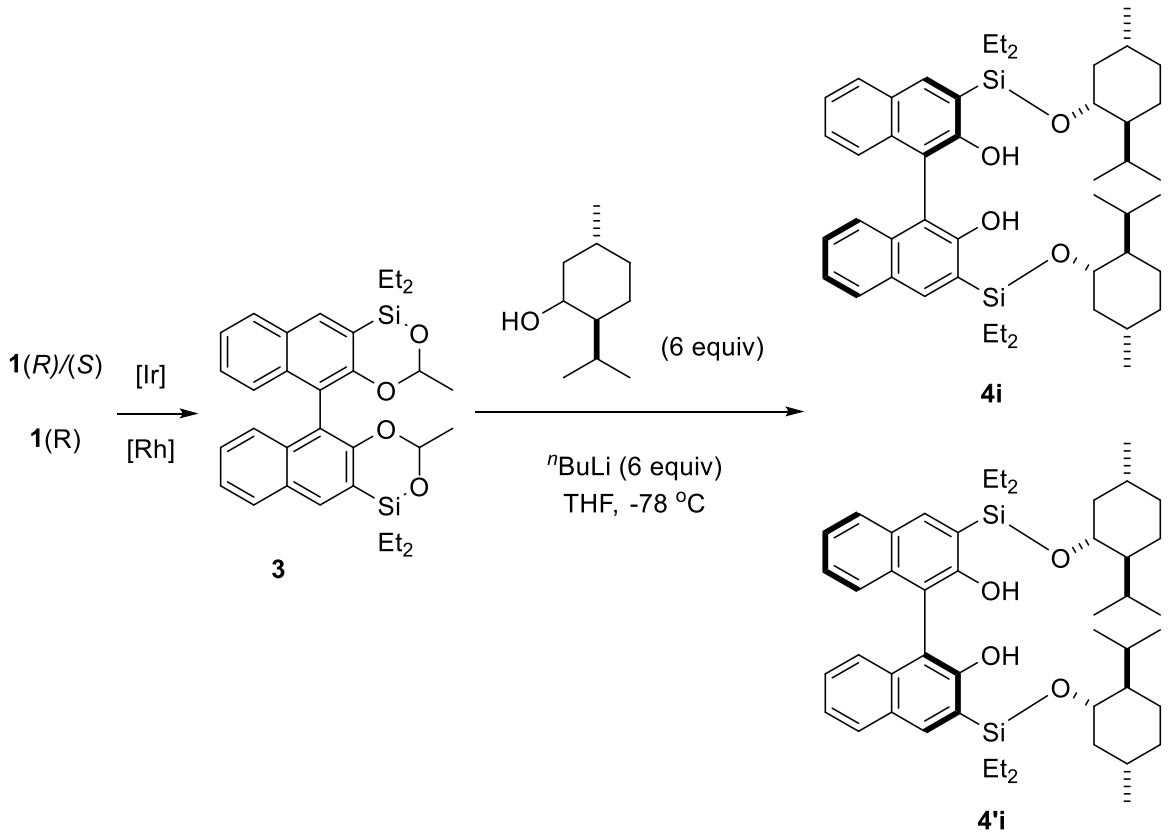
corresponding organolithium reagents to produce compounds **4a-c** with good yields (Table 1.4.a). Vinyl and allyl Grignard nucleophiles provided 3,3'-bis-silyl BINOLs **4d-e** with moderate to good yields (Table 1.4.b). Addition of lithium acetylide to **3** furnished 3,3'-bis-diethylalkynylsilyl BINOL **4f** (Table 1.4.b). We then examined hydride and heteroatomic nucleophiles (Table 1.4.c). 3,3'-Bis-hydrodiethylsilyl BINOL **4g** was generated using LAH as the hydride nucleophile. Oxygen nucleophiles also underwent reaction with diminishing yields of **4h** and **4i**, because of competing desilylation. A key to success of the reaction with electronically and sterically varied aryl and heteroaromatic organolithium reagents was timely addition of the corresponding anions to the dioxasiline **3**, because of the distinctive life-times of the reagents (Table 1.4.d and 1.4.e). Successful examples include lithio-benzene, 3,5-dimethylbenzene, 3,5-ditrifluoromethylbenzene, furan, benzofuran, thiophene, benzothiophene, and indole, leading to corresponding 3,3'-bisarylsilyl and 3,3'-bis-heteroaromatic silyl BINOLs **4j-r** with moderate yields (3 steps) (Table 1.4). The facile introduction of the heterocycles to the BINOL scaffold not only can alter steric and electronic nature, but also can provide an additional metal binding element that controls stereofidelity and/or reactivity of catalytic transformations. However, the mesityllithium failed to add to **3** where either no reaction was observed or significant desilylation was detected upon forcing conditions.

1.2.c.3. Optimization of dioxasilines.

While most reactions (from **1** to **4**) can be done in a one-pot fashion, the reactions with LAH, methoxy, phenyl, and indole nucleophiles required a semi-purification of the dioxasiline intermediates **3** (i.e., filtration through a plug of silica gel) to minimize mono-desilylation. Reactions with purified compound **3** and methyllithium over an hour did not produce any desilylated product which might indicate that desilylation in one-pot reactions might be caused by

the leftover catalysts and by-products.

1.2.c.4. Racemization negation.



Starting material	**4i : 4'i**
1 (*R*)	1 : 0
1 (*R*) + (*S*)	1 : 1

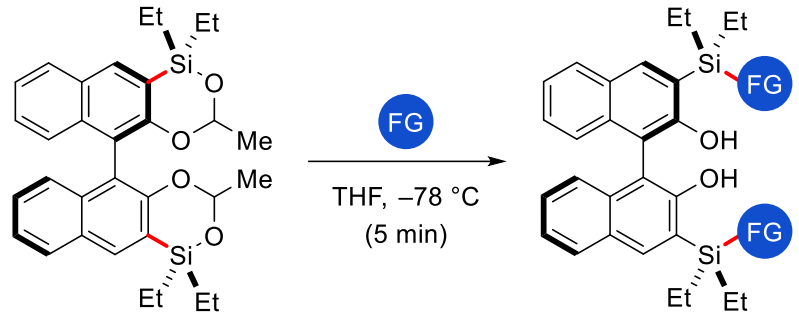
Table 1.3. L-menthol addition with **1** (*R*) and racemic mixture of **1**.

Racemization has been an issue with previous syntheses of these compounds, so it is important for us to confirm that our products are not mixtures. After multiple failed attempts of HPLC separation of product **4a**, we resorted to the method of comparative analytical resolution of the products of L-menthol anion addition (**4i**). NMR analysis of the purified product mixtures'

spectra showed that while the racemic mixture of BINOL produced an equal mixture of two diastereomers, (*R*)-BINOL only generated one product which matched one of the diastereomers (Table 1.3).

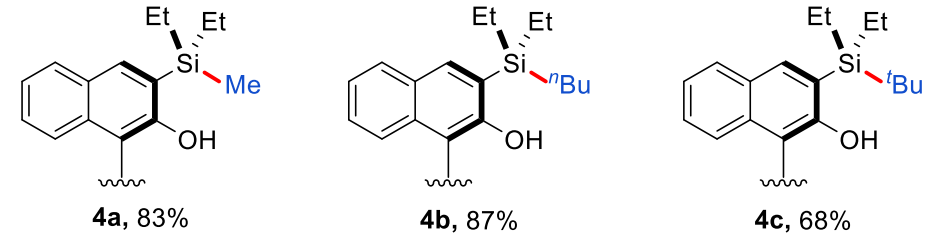
1.2.d. Substrate scope of 3,3'-bis-silylation of BINOL.

Optimization process has led to the success and improvement of the nucleophilic addition to form 3,3'-bis-silylated BINOL derivatives. Thus, various nucleophiles have been demonstrated to be compatible with this process (Table 1.4).



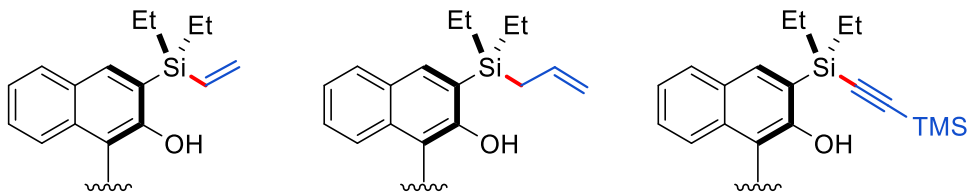
3 **4**

a. alkyl substituents



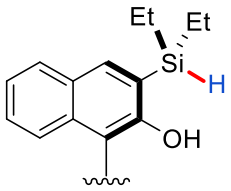
4a, 83% **4b,** 87% **4c,** 68%

b. vinyl, allyl, and alkynyl substituents

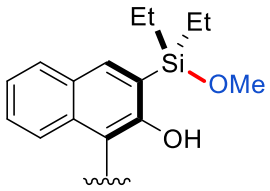


4d, 85% **4e,** 63% **4f,** 61%

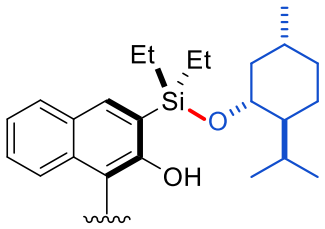
c. hydrogen and heteroatomic substituents



4g, 61%

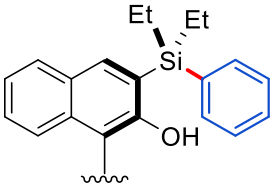


4h, 30%

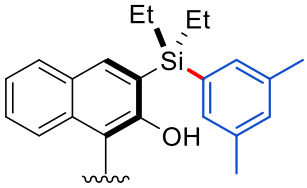


4i, 42%

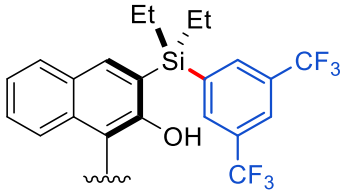
d. aryl substituents



4j, 61%

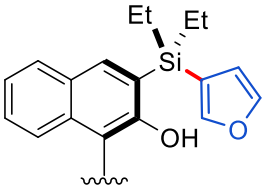


4k, 47%

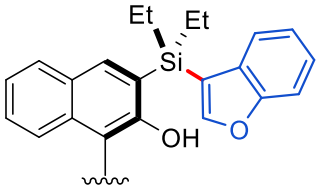


4l, 46%

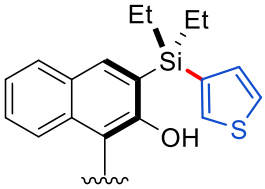
e. heterocyclic substituents



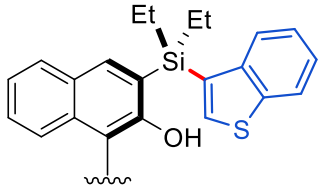
4m, 59%



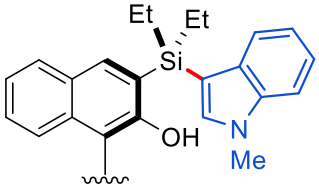
4o, 57%



4p, 57%



4q, 50%



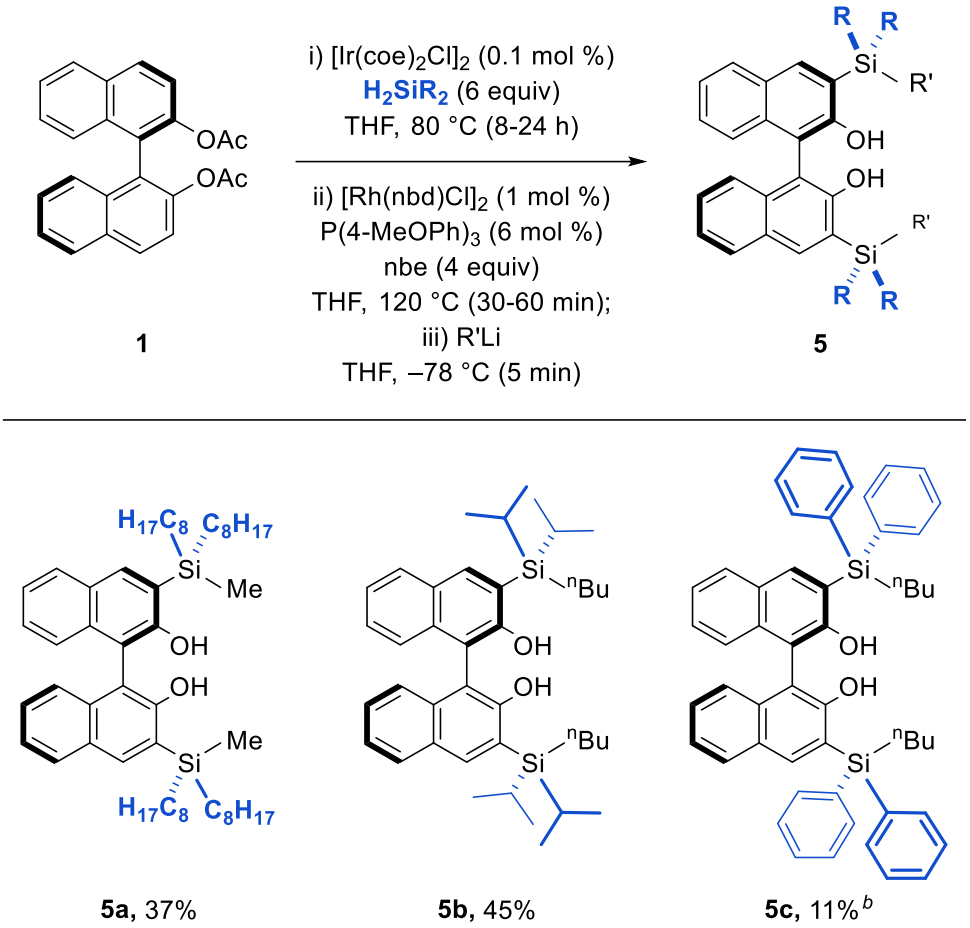
4r, 68%

[a]Conditions: FG (6 equiv), THF (2M), -78 °C, 5 min.

Table 1.4. Substrate scope of 3,3'-bis-silylation of BINOL[a].

1.2.e. Silane scope of 3,3'-bis- silylation of BINOL.

Sterically and electronically different silane agents were examined to expand the scope of the reaction. Dihydrodiisopropylsilane [H_2Si^iPr] and dihydrodiphenylsilane [H_2SiPh_2] were commercially available. Dihydrodioctylsilane [$H_2Si(oct)_2$] was prepared through reduction of the corresponding dichlorosilanes using LAH. Dihydrodioctylsilane [$H_2Si(oct)_2$] and dihydrodiisopropylsilane [H_2Si^iPr] slowed down the ester hydrosilylation step significantly under the standard Ir catalysis conditions. They produced desired product with moderate yield **5a,b** (Table 1.5). Under the identical conditions, dihydrodiphenylsilane [H_2SiPh_2] reacted with **1** very fast, but the reaction produced disiloxane byproducts quickly, which resulted in low yield in C–H silylation. The electron-donating nature of the phenyl groups might contribute to formation of the byproducts.



[a]Conditions: (i) [1,1'-binaphthalene]-2,2'-diyl diacetate **13** (0.4 mmol), $[Ir(coe)_2Cl]_2$ (0.3 mol %), H_2SiR_2 (6 equiv), THF (1M), 80 °C, 8-24 h. (ii) $[Rh(nbd)Cl]_2$ (1 mol%), $P(4\text{-}OMePh)_3$ (6 mol%), nbe (4 equiv), THF (1M), 120 °C, 30-60 min. (iii) ^{n}BuLi (6 equiv), THF (2M), -78 °C, 5 min. [b]NMR yield.

Table 1.5. Silane scope of 3,3'-bis- silylation of BINOL[a].

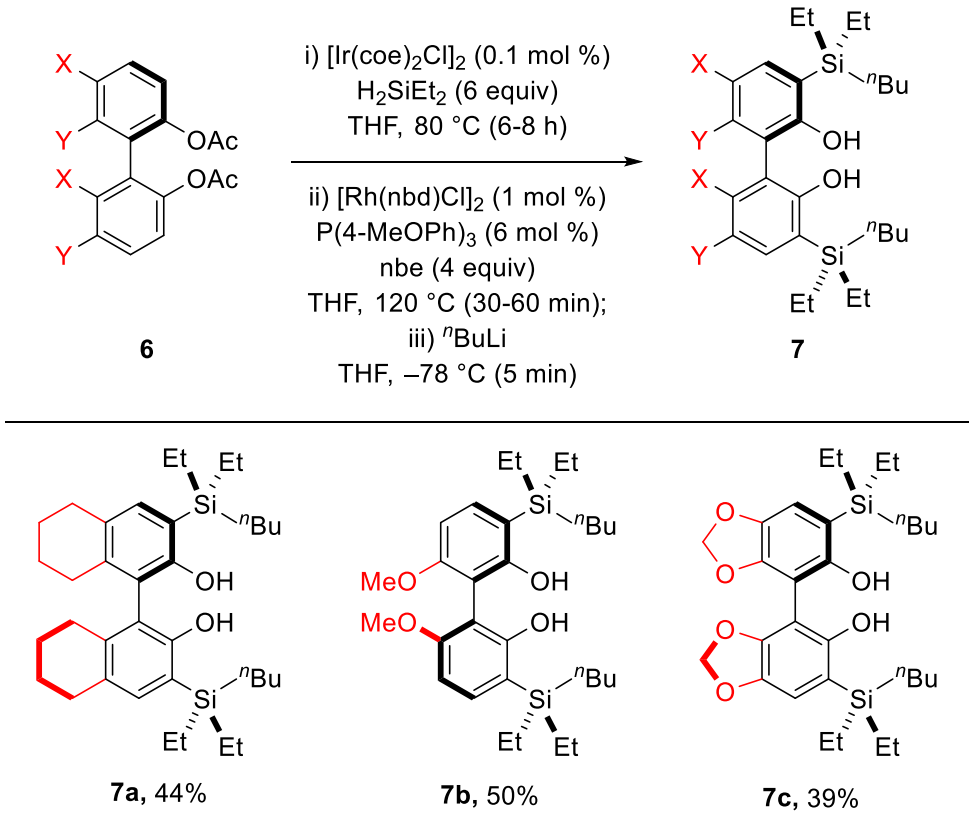
1.3. Strategy for synthesis of 3,3'-bis-silyl biphenols.

1.3.a. Optimization of 3,3'-bis-silyl biphenols.

Next, we expanded the scope of 3,3'-bis-silyl biphenol scaffold through catalytic C–H silylation of axially chiral biphenols with a traceless acetal directing group. Generally, slower

reaction kinetics was observed, compared with most of the substrates in BINOL's cases. NMR and TLC analysis were used to monitor the reactions' completion. Specifically, the hydrosilylation and C-H activation required more time and was less efficient than BINOL, while the nucleophilic addition completion time remains very fast.

1.3.b. Substrate scope of 3,3'-bis-silylation of biphenols.



[a]Conditions: (i) [1,1'-binphenyl]-2,2'-diyl diacetate **6** (0.4 mmol), $[Ir(coe)_2Cl]_2$ (0.3 mol %), H_2SiEt_2 (6 equiv), THF (1M), 80 °C, 6-8 h. (ii) $[Rh(nbd)Cl]_2$ (1 mol%), $P(4\text{-}OMePh)_3$ (6 mol%), nbe (4 equiv), THF (1M), 120 °C, 30-60 min. (iii) $^{n}BuLi$(6 equiv), THF (2M), -78 °C, 5 min.

Table 1.6. Substrate scope of 3,3'-bis-silylation of biphenols[a].

The substrates such as H8-BINOL and 6,6'-dimethoxy-1,1'- biphenyl-2,2’-diol are commercially available. However, both 6,6'-dimethoxy-1,1'- biphenyl-2,2’-diol and bis-dibenzodioxole-2,2’-diol can be synthesized using copper-catalyzed Ullmann coupling procedure.[40] In this study, we used *n*-butyllithium as a nucleophile to dioxasilines (e.g., H8-BINOL, 6,6'-dimethoxy-1,1'- biphenyl-2,2’-diol, and bis-dibenzodioxole-2,2’-diol) to provide the corresponding 3,3’-bis-silyl biphenols (**7a-c)** in moderate yields (Table 1.6).

1.4. Summary of 3,3’-functionalization of BINOL and biphenols.

3,3’-functionlization of BINOL and biphenols have been successfully achieved with moderate to good yields. The process was found to be compatible with various nucleophiles and silanes. This process is efficient, selective, and immune to racemization. These compounds might be valuable in asymmetric catalysis. Thus, this method can streamline the syntheses of similar derivatives with tunable substituents to provide customizable selectivity for new syntheses.

Chapter 2

Synthesis of 3,3'-bis-functionalized BINOL-based Phosphoramidites

2.1. Introduction.

2.1.a. Importance of phosphoramidite.

Phosphorus ligands have been wildly popular in asymmetric transformation.[41, 42] Many of mono- and bidentate phosphorus ligands possess TADDOL, spirobiindanediol, BINOL, and biphenol backbones.[42] A large number of these chrial monodentate phosphorous ligands consisting of phosphites and phosphoramidites has been explored in various metal-catalyzed reactions such as hydrogenation,[43, 44] hydrovinylation,[45, 46] hydrosilylation,[47] intramolecular Heck reaction,[48] hydroformylation,[49] allylic alkylation,[50] amination,[51] and etherification.[52] Since the introduction of the monodentate chiral phosphoramidite (also known as Monophos) by Feringa and cowokers in 1994, BINOL-based and biphenol-based phosphoamidites have increasingly gained popluarity due to their crucial roles in achieving high enantioselectivity in many asymmtric reactions.[41] Moreover, these ligands are flexible with the modification processes, which expands their applications in catalysis. The 3,3'-positions of BINOL-based phosphorus ligands were found to have great influence on the catalystic effect on selectivity.

2.1.b. Properties of phosphoramidite.

Phosphoramidite has the most applications among the three known types of phosphorus amides (phosphoramidite, phosphordiamide and phosphortriamide).[42] The unshared pair of electrons which the phosphorus and nitrogen atoms each possess can be the metal-binding sites of phosphoramidite.[42] Furthermore, X-ray analysis of phosphoramidite finds that the phosphorus atom has a pseudotetrahedral geometry or adopts tetrahedral geometry within metal complexes whereas the nitrogen atom often adopts trigonal planar geometry.[42] Phosphoramidite ligands are π-acceptors and σ-donors. These electronic properties can be adjusted by fine-tuning the substituents at different locations within the molecules. For example, modifications at the

phosphorus atom can affect the strength of the π-accepting feature while alterations of the substituents at the nitrogen and oxygen atom can change the donating properties of the ligands.[42]

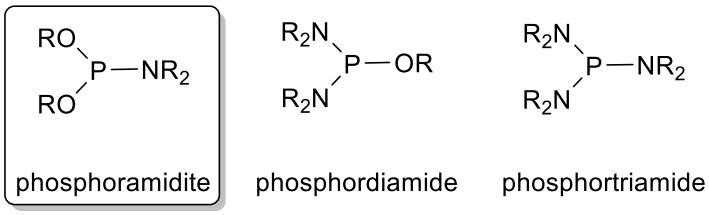


Figure 2.1. Common phosphorus amides.

2.1.c. Synthetic strategies of phosphoramidite.

There are two main synthetic routes that enable access to phosphoramidite. They differ in the order of bond formations which can play an important role in the flexible modification of the substituents. The formation of P-O bonds before P-N bond is more widely utilized, but the P-N bond preceding the P-O bonds formation is found to be more desirable in case of more sterically hindered amines. [41, 42]

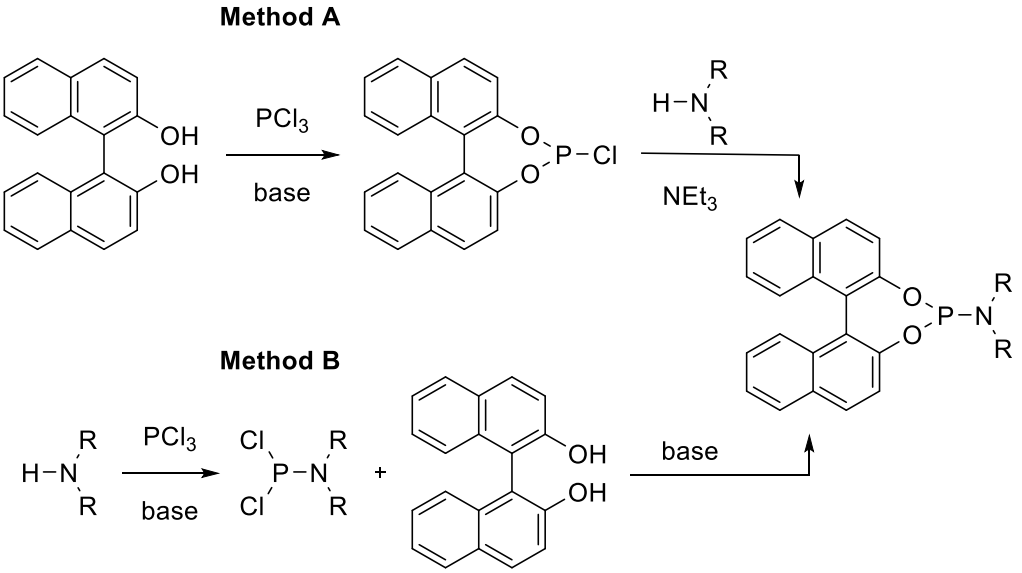


Figure 2.2. Syntheses of BINOL-based phosphoramidites.

2.2. Strategy for syntheses of 3,3'-silyl-BINOL-based phosphoramidites.

2.2.a. Initial studies.

Upon establishing preparation of axially chiral 3,3'-bis-silyl BINOLs we explored the phosphoramidation step to afford 3,3'-bis-silyl BINOL-based phosphoramidites. Initial attempt to this step involved a reaction of **4a** with PCl_3 under basic conditions, to form phosphorochloridite, then formation of a P–N bond to form **8a** (**Method A).** However, the reaction ultimately failed to produce the corresponding phosphoramidite **8a**, because of the significant desilylation of 3,3'-bis-silyl-BINOL. The steric hinderance of the amines, the sensitivity of the silyl groups, and the tendency of racemization under basic condition of BINOL render this method detrimental for the formation of phosphoramidite.

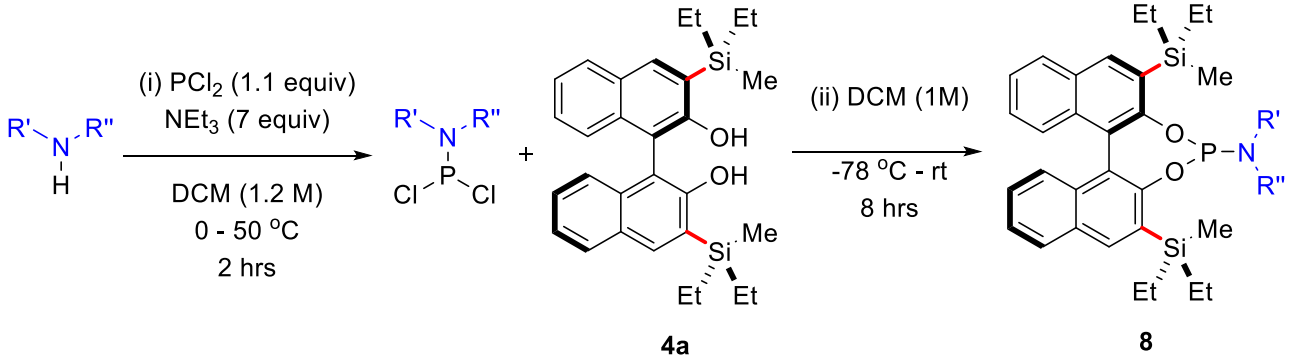
2.2.b. Optimization.

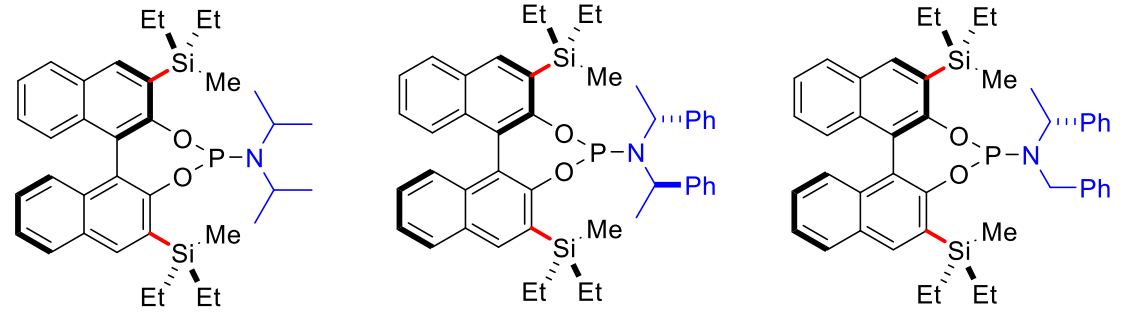
Alternatively, we started with making a P–N bond first by a reaction of secondary amine with PCl_3 to afford the corresponding dichlorophosphinamine, then forming the P–O bonds under buffered conditions (**Method B**). This method successfully generated 3,3'-bis-silyl BINOL-based phosphoramidite **8a** with moderate yield, mainly because of the reduced reactivity by steric bulk of the 3,3'-bis-silyl moieties. X-ray crystallography confirmed the structure of **8a**. Despite the complex NMR spectrum of this molecule, possibly due to the rotamers, X-ray structure of this molecule was obtained which helped better understand the overall topological conformation of the two silyl groups within the ligands (Table 2.1).

2.2.c. Scope of 3,3'-silyl-BINOL-based phosphoramidites.

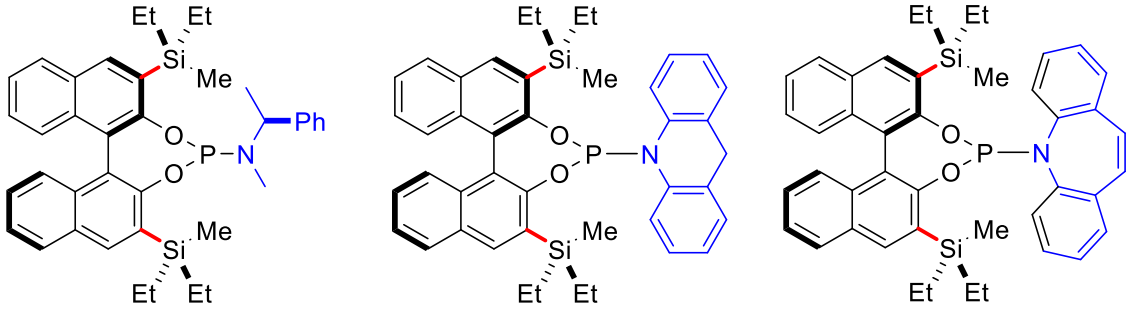
We expanded the substrate scope of this sequential traceless hydrosilyl acetal-directed dual C–H silylation/phosphoramidation. 3,3'-Bis-silyl BINOL-based phosphoramidites derivatives were

successfully synthesized with moderate to good yield (6 examples, 55-76% yields, Table 2.1). Moreover, X-ray crystallography was used to confirm the structures of **8a**, **8e**, and **8f**.





8a, 67% **8b**, 62% **8c**, 76%



8d, 58% **8e**, 61% **8f**, 55%

[a]Conditions: (i) R'R''NH (1.2 mmol), PCl_3 (1.1 equiv), NEt_3 (7 equiv), DCM (1.2 M), 0-50 °C, 2 h. (ii) **4a** (1 equiv), DCM (1M), -78°C-rt, 8 h.

Table 2.1. Scope of 3,3'-silyl-BINOL-based phosphoramidites[a].

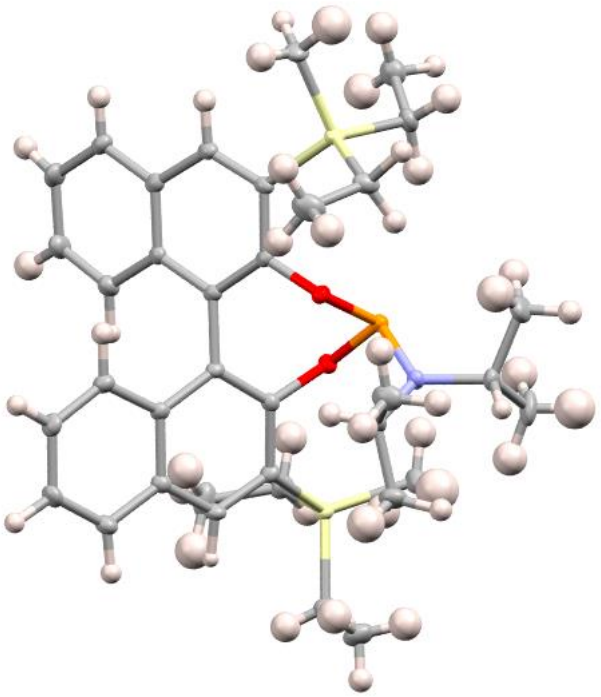


Figure 2.3. Structure of **8a** obtained by X-ray crystallography.

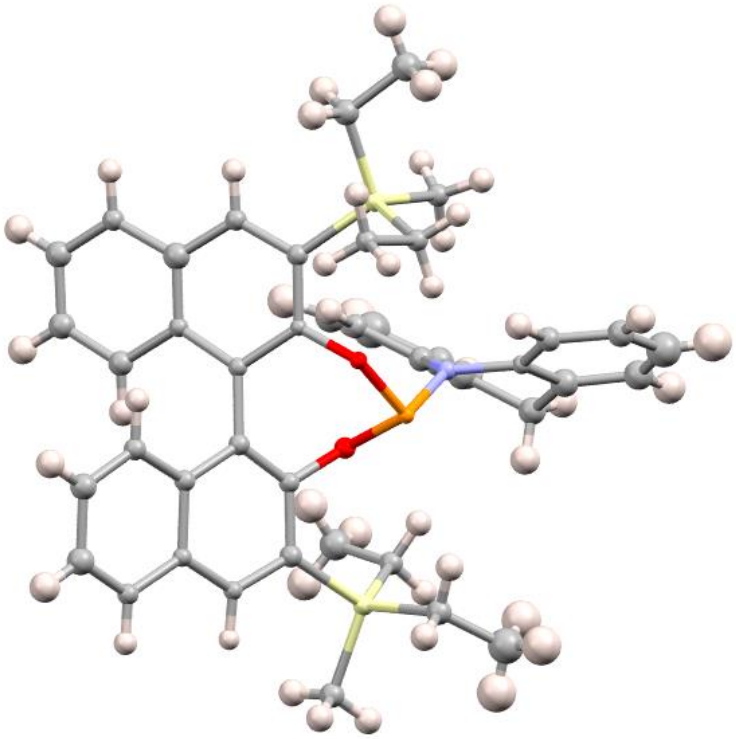


Figure 2.4. Structure of **8e** obtained by X-ray crystallography.

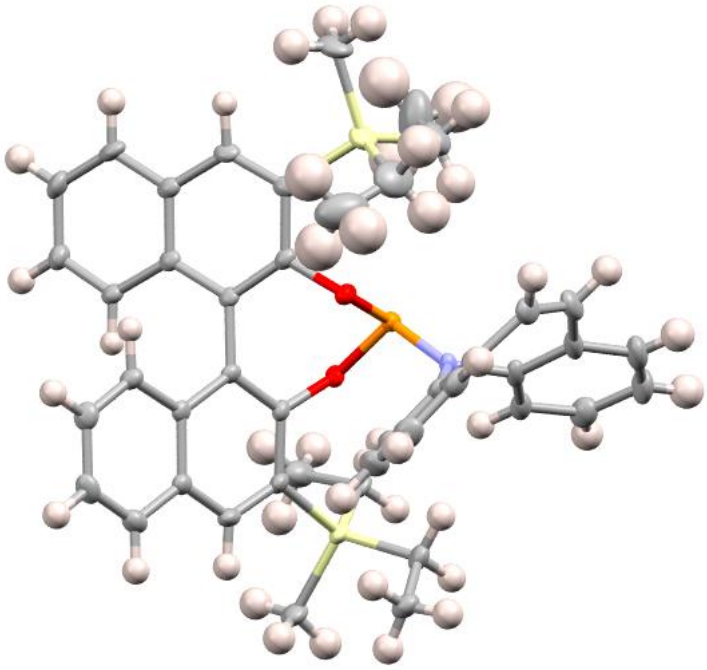


Figure 2.4. Structure of **8f** obtained by X-ray crystallography.

The steric hindrance of the amines might contribute to the decrease in yields. Moreover, purification of the base and amine is the key for the yield improvement of this reaction.

2.3. Summary of synthesis of 3,3'-silyl-BINOL-based phosphoramidites.

Syntheses of phosphoramidite with tunable 3,3'-silyl-BINOLs are valuable yet seemingly unknown. The This process can streamline the syntheses of 3,3'-functionalized BINOL-based phosphoramidites. These molecules might be utilized as ligands to improve the selectivity in many asymmetry syntheses.

Appendix A: List of Abbreviations

δ: chemical shift (ppm)

μL: microliter

Ac: acetate

Ar: aryl group or substituent, general

Bn: benzyl

Bu: butyl

^{t}Bu: tert-butyl

C: Celsius

calcd: calculated

cat.: catalyst, catalytic amount

cf: compare

DCM: dichloromethane

Eq.: equation

equiv.: equivalent

Et: ethyl

THF: tetrahydrofuran

g: gram

GCMS: gas chromatography mass spectrometry

h: hours

HRMS: high resolution mass spectrometry

Hz: hertz

IR: infrared spectroscopy

J: coupling constant, NMR spectroscopy

M: molar

[M+]: molecular ion

Me: methyl

min.: minutes

mg: milligram

MHz: megahertz

mL: milliliter

mmol: millimole

MW: molecular weight

n/a: not applicable

NMR: nuclear magnetic resonance spectroscopy

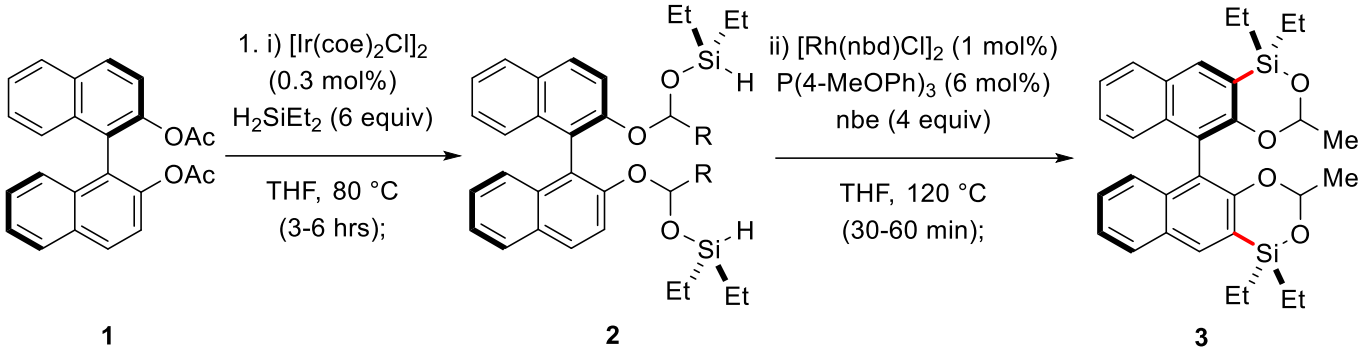
Appendix B: Experimental Procedures

Chapter 1

I. Materials and Methods

Reactions requiring anhydrous conditions were performed under an atmosphere of nitrogen or argon in flame or oven-dried glassware. Anhydrous toluene and dichloromethane (DCM) were distilled from CaH_2. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium and benzophenone. All other solvents and reagents from commercial sources were used as received. NMR spectra were recorded on a 500 or 300 MHz NMR spectrometer. ^{1}H NMR chemical shifts are referenced to benzene (7.16 ppm) and chloroform (7.26 ppm). ^{13}C NMR chemical shifts are referenced to C_6D_6 (128.06 ppm) and $CDCl_3$ (77.23 ppm). The following abbreviations are used to describe multiplets: s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), m (multiplet), nfom (nonfirst-order multiplet), and br (broad). The following format was used to report peaks: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^{1}H NMR assignments are indicated by structure environment (e.g., CH_aH_b). ^{1}H NMR and ^{13}C NMR were processed with the iNMR software program. Infrared (IR) spectra were recorded using neat (for liquid compound) or a thin film from a concentrated DCM solution. Absorptions are reported in cm^{-1}. Only the most intense and/or diagnostic peaks are reported. MPLC refers to medium pressure liquid chromatography (25−200 psi) using hand-packed columns of silica gel (20−45 μm, spherical, 70 Å pore size), an HPLC pump, and a differential refractive index detector. High-resolution mass spectra (HRMS) were recorded in atmospheric-pressure chemical ionization and time-of-flight (APCI/TOF) mode. Samples were introduced as solutions in a mixed solution of methanol and DCM. Analytical TLC experiments were performed on an F254 plate with 250 μm thickness. Detection was performed by UV light or potassium phosphomolybdic acid, potassium permanganate, and p-anisaldehyde staining.

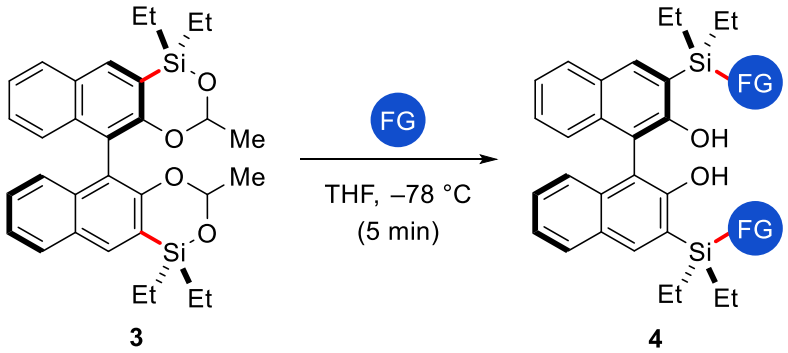
I. General Procedure for C-H Silylation to Prepare 1,1,1',1'-tetraethyl-3,3'-dimethyl-1*H*,1'*H*-5,5'-binaphtho[2,3-*c*][1,5,2]dioxasiline.



(i) $[Ir(coe)_2Cl]_2$ (1.1 mg, 1.2 μmol, 0.3 mol %) and [1,1'-binaphthalene]-2,2'-diyl diacetate **1** (148.2 mg, 0.4 mmol) were added to a flame-dried, nitrogen-purged septum-capped vial. The mixture was dissolved with THF (0.4 mL, 1.0 M), and diethylsilane (0.31 mL, 2.4 mmol) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner under a N_2 atmosphere [note: diethylsilane (bp 56 °C and density 0.686 g/mL) is volatile]. The reaction mixture was stirred for 3-12 h at 60 °C. Volatiles were removed in vacuo to afford silyl acetals, which were directly used for subsequent reactions without further purification.

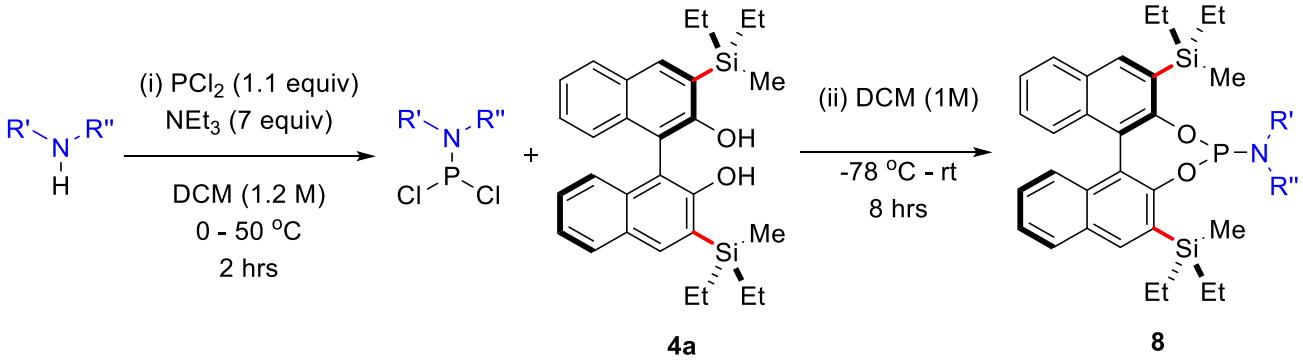
(ii) $[Rh(nbd)Cl]_2$ (1.84 mg, 4 μmol, 1 mol %), tris(4-methoxyphenyl)phosphine (8.45 mg, 12 μmol, 6 mol %), norbornene (150 mg, 1.6 mmol), and THF (0.4 mL, 1 M) were added to the crude silyl acetals (0.4 mmol). The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at 120 °C for 1 hour. The resulting 1,1,1',1'-tetraethyl-3,3'-dimethyl-1*H*,1'*H*-5,5'-binaphtho[2,3-*c*][1,5,2]dioxasiline were directly used for a subsequent reaction without further purification. For analytical purposes, volatiles were removed in vacuo, and the resulting mixture was dissolved with pentane, filtered through a pad of Celite®, and concentrated in vacuo. The crude product was purified by MPLC (hexanes/EtOAc =60:1, 6 mL/min, retention time 5-10 min).

II. General Procedure for Nucleophilic Opening of Dioxasilines.



Lithium nucleophile was generated by treatment of the corresponding molecule or its halide form (1.4 mmol) with *n*-BuLi (0.52 mL, 2 M in THF, 1.3 mmol) in THF (2.8 mL) at –78 °C for 30 min. The crude dioxasiline **4** (1 mmol) was added into the reaction mixture, which was stirred at –78 °C for 5 min. The reaction was quenched by adding saturated aqueous ammonium chloride solution. The mixture was extracted with diethyl ether. The combined organic layer was washed with water and brine and dried over anhydrous sodium sulfate. The volatiles were removed **in vacuo,** and the crude mixture was purified by MPLC to afford 3,3'-bis-substituted BINOL derivative (hexanes/EtOAc = 80:1, 6 mL/min, retention time 5-20 min).

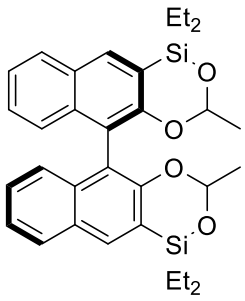
III. General Procedure for phosphoamidites.



Solution of phosphorus trichloride (30mg, 0.22 mmol) in DCM (1 mL, 0.22 M) was prepared. Solution of amine (0.22 mmol) and triethyl amine (1.2 mmol) in DCM (1 mL, 1.2 M) was prepared and cooled to 0 ^{o}C. The phosphorus trichloride solution was added to the solution of amines via cannula transfer slowly. The mixture was heated for 2 hour at 50 ^{o}C. The reaction mixture was then cooled to -78 ^{o}C before a solution of 3,3'-bis(diethyl(methyl)silyl)-[1,1'-binaphthalene]-2,2'-diol in DCM (1mL) was added. The reaction mixture was stirred for 8 hours at room temperature. The volatiles were removed in vacuo, and the crude material was purified by MPLC to afford 3,3'-bis-substituted BINOL derivative (hexanes/EtOAc = 80:1, 6mL/min, retention time 10-30 min).

Appendix C

Spectral data of the compounds



1,1,1',1'-Tetraethyl-3,3'-dimethyl-1H,1'H-5,5'-binaphtho[2,3-c][1,5,2]dioxasiline (3)

Yield: 0.4 mmol scale, 193 mg, 89%. 4 sets of diastereomers = 1.56:1.56:1.0:1.56.

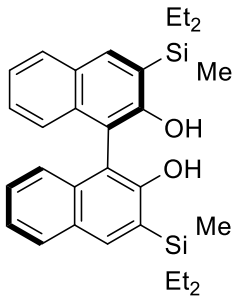
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.01-7.98 (m, 2H, Ar-*H*), 7.89 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.88 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.36 (dd, *J* = 8.0, 8.0 Hz, 1H, Ar-*H*), 7.35 (dd, *J* = 8.0, 8.0 Hz, 1H, Ar-*H*), 7.30-7.21 (m, 3H, Ar-*H*), 7.13 (dd, *J* = 8.3, 8.3 Hz, 1H, Ar-*H*), 5.53 (q, *J* = 5.0 Hz, 0.55 H, OC*H*Me), 5.47 (q, *J* = 5.0 Hz, 0.55 H, OC*H*Me), 5.40 (q, *J* = 5.0 Hz, 0.35 H, OC*H*Me), 5.32 (q, *J* = 5.0 Hz, 0.55 H, OC*H*Me), 1.37 (d, *J* = 5.0 Hz, 1.65H, OCHCH_3), 1.33 (d, *J* = 5.0 Hz, 1.65H, OCHCH_3), 1.19 (d, *J* = 5.0 Hz, 1.65H, OCHCH_3), 1.19-1.14 (m, 6H, $SiCH_2CH_3$), 1.12 (d, *J* = 5.0 Hz, 1.05H, OCHCH_3), and 1.09-0.84 [m, 14H, $SiCH_2CH_3$ and $Si(CH_2CH_3)_2$].

^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.3, 158.19, 158.09, 157.92, 135.39, 135.33, 135.01, 134.86, 134.76, 134.73, 129.84, 129.80, 129.76, 129.72, 128.35, 128.27, 127.13, 127.05, 126.81, 126.78, 126.4, 126.05, 126.01, 125.5, 124.13, 124.05, 123.99, 123.95, 122.7, 122.4, 121.9, 121.6, 119.21, 119.15, 119.04, 118.97, 97.6, 96.84, 96.68, 96.3, 23.84, 23.75, 23.59, 23.48, 7.3, 7.14, 7.12, 7.10, 7.08, 6.99, 6.97, 6.91, 6.60, 6.55, 6.52, and 6.51.

IR (neat): 2958 (m), 1619 (w), 1586 (w), 1391 (m), 1232 (m), 1088 (s), 1043 (m), 931 (s), 734 (s), and 702 (s) cm^{-1}.

TLC: Rf = 0.4 in 20:1 hexanes: EtOAc.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{32}H_{39}O_4Si_2)^+$: 543.2381. Found: 543.2360.



3,3'-bis(diethyl(methyl)silyl)-[1,1'-binaphthalene]-2,2'-diol (4a)

Yield: 0.2 mmol scale, 80.8 mg, 83%.

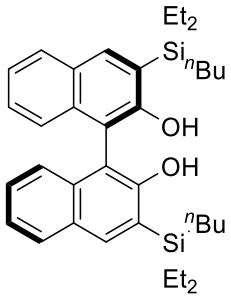
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.09 [s, 2H, C*H(4,4')*], 7.91 [d, *J* = 7.8 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.36 [ddd, *J* = 8.0, 6.8, 1.2 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.30 [ddd, *J* = 8.3, 6.8, 1.4 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.11 [d, *J* = 8.3 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 5.24 (s, 2H, O*H*), 0.90–1.04 [m, 20H, Si(CH_2CH_3)$_2$], 0.41 [s, 6H, SiCH_3].

^{13}C-NMR (500 MHz; $CDCl_3$): δ 157, 138, 134, 129, 128, 127, 126, 124, 123, 109, 7.39, 7.36, 5.23, 5.14, 5.84.

IR (**neat**): 3500 (m), 2951 (m), 2872 (m), 1616 (m), 1581 (m), 1355 (m), 1303 (m), 1251 (m), 1042 (m), 788 (s), 748 (s), 687 (m) cm^{-1}.

TLC: Rf = 0.4 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{30}H_{38}NaO_2Si_2)^+$: 509.2303. Found: 509.2301.



3,3'-bis(butyldiethylsilyl)-[1,1'-binaphthalene]-2,2'-diol (4b)

Yield: 0.2 mmol scale, 99.3 mg, 87%.

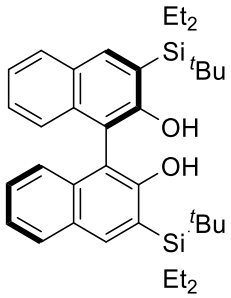
^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.09 [s, 2H, C*H(4,4')*], 7.92 [d, *J* = 8.0 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.37 [ddd, *J* = 7.9, 6.8, 1.0 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7,30 [ddd, *J* = 8.3, 6.9, 1.2 Hz, C*H(6,6')* or C*H(7,7')*], 7.13 [d, *J* = 8.3 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 5.24 (s, 2H, O*H*), 1.36-1.38 (m, 8H, $SiCH_2CH_2CH_2CH_3$), 1.03-1.06 [m, 12H, $Si(CH_2CH_3)_2$], and 0.97-1.00 (m, 12H, $SiCH_2CH_2CH_2CH_3$ and $Si(CH_2CH_3)_2$], and 0.89-0.92 [m, 6H, $SiCH_2CH_2CH_2CH_3$].

^{13}C-NMR ($CDCl_3$, 500 MHz;): δ 157, 139, 134, 129, 128, 127, 126, 124, 123, 109, 26.8, 26.4, 13.9, 11.5, 7.78, 3,90.

IR (**neat**): 3500 (m), 2953 (s), 2923 (s), 2872 (m), 1580 (m), 1355 (m), 1179 (m), 1144 (m), 1042 (m), 777 (s), 721 (m) cm^{-1}.

TLC: Rf = 0.5 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{36}H_{50}NaO_2Si_2)^+$: 593.3242. Found: 593.3245.



3,3'-bis(*tert*-butyldiethylsilyl)-[1,1'-binaphthalene]-2,2'-diol (4c)

Yield: 0.2 mmol scale, 77.6 mg, 68%.

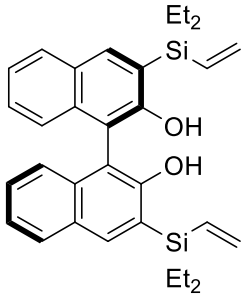
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.10 [s, 2H, C*H(4,4')*], 7.92 [d, *J* = 7.9 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.37 [ddd, *J* = 7.9, 6.9, 1.0 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.37 [ddd, *J* = 8.2, 6.9, 1.2 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.13 [d, *J* = 8.3 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 5.25 (s, 2H, O*H*), 1.04–1.23 [m, 20H, $Si(CH_2CH_3)_2$], 0.98 [s, 18H, $SiC(CH_3)_3$].

^{13}C-NMR (126 MHz; $CDCl_3$): δ 157.4, 140.1, 134.3, 129.3, 128.7, 127.7, 125.1, 124.0, 123.7, 109.9, 28.0, 18.6, 8.36, 8.30, 2.29, 2.14.

IR (**neat**): 3500 (m), 2952 (m), 2928 (m), 2876 (m), 2854 (m), 1578 (m), 1355 (m), 1181 (m), 1144 (m), 1041 (m), 1013 (m), 821 (m), 750 (m), 717 (s), 674 (m) cm^{-1}.

TLC: Rf = 0.5 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{36}H_{50}NaO_2Si_2)^+$: 593.3242. Found: 593.3239.



3,3'-bis(diethyl(vinyl)silyl)-[1,1'-binaphthalene]-2,2'-diol (4d)

Yield: 0.2 mmol scale, 87 mg, 85%.

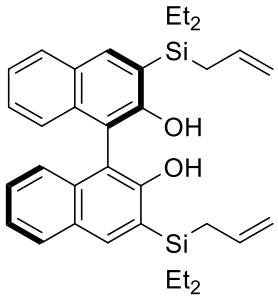
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.10 [s, 2H, C*H(4,4')*], 7.88 [d, *J* = 8.0 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.35 [ddd, *J* = 8.0, 6.7, 1.2 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.29 [ddd, *J* = 8.0, 6.7, 1.2 Hz, 2H, C*H(6,6')* or C*H(7,7'*)], 7.09 [d, *J* = 8.0 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 6.46 (dd, *J* = 14.8, 20.5 Hz, 2H, SiC*H*=CH2), 6.19 (dd, J = 14.8, 3.7 Hz, 2H, SiCH=C$H_{cis}H_{trans}$), 5.90 (dd, *J* = 20.5, 3.7 Hz, 2H, SiCH=C$H_{cis}H_{trans}$), 5.24 (s, 2H, ArO*H*), and 1.02 [m, 20H, Si(CH_2CH_3)$_2$].

^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.1, 139.7, 135.8, 134.5, 133.8, 129.5, 128.8, 127.9, 125.7, 124.1, 123.9, 109.8, 7.9, 7.8, 4.2, and 4.1.

IR (neat): 3485 (br, w), 3422 (br, w), 2955 (m), 1573 (m), 1444 (m), 1207 (s), 1129 (s), 1007 (s), and 736 (s) cm^{-1}.

TLC: Rf = 0.3 in 20:1 hexanes: EtOAc.

HRMS (APCI /TOF): Calcd for (M+H) $^{+}$ $(C_{32}H_{39}O_2Si_2)^{+}$: 511.2483. Found: 511.2467.



3,3'-bis(allyldiethylsilyl)-[1,1'-binaphthalene]-2,2'-diol (4e)

Yield: 0.2 mmol scale, 67.8 mg, 63%.

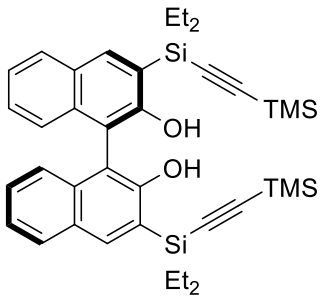
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.10 [s, 2H, C*H(4,4')*], 7.91 [d, *J* = 7.9 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.38 [ddd, *J* = 7.9, 6.9, 1.1 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.32 [ddd, *J* = 8.3, 6.9, 1.3 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.14 [d, *J* = 8.3 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 5.88 (dddd, J = 16.89, 9.99, 8.14, 8.14 Hz, 2H, $SiCH_2CH$=CH_2), 5.27 (s, 2H, O*H*), 4.95 (dd, J = 16.91, 2.06 Hz, 2H, $SiCH$=$CH_{cis}H_{trans}$), 4.84(dd, *J* = 10.04, 2.18 Hz, 2H, $SiCH$=$CH_{cis}H_{trans}$), 2.04 (d, J = 8.11 Hz, 4H, $SiCH_2CH$=CH_2), 1.05 [m, 20H, $Si(CH_2CH_3)_2$].

^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.0, 139.2, 135.4, 134.4, 129.4, 128.7, 127.8, 125.6, 124.1, 123.9, 113.2, 109.6.

IR (neat): 3500 (m), 2952 (m), 2873 (m), 1580 (m), 1355 (m), 1143 (m), 777 (m), 749 (s), 7.15 (m) cm^{-1}.

TLC: Rf = 0.3 in 20 :1 hexanes: EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^{+}$ $(C_{36}H_{38}NaO_2Si_2)^{+}$: 561.2616. Found: 561.268.



3,3'-bis(diethyl((trimethylsilyl)ethynyl)silyl)-[1,1'-binaphthalene]-2,2'-diol (4f)

Yield: 0.2 mmol scale, 79.4 mg, 61%.

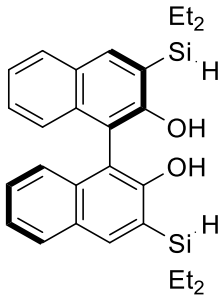
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.50 [s, 2H, C*H(4,4')*], 7.95 [d, *J* = 8.1 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.39 [ddd, *J* = 7.9, 6.9, 1.0 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.32 [ddd, *J* = 8.3, 6.9, 1.3 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.11 [d, *J* = 8.4, 4H, C*H(5,5')* or C*H(8,8'*)], 5.38 (s, 2H, O*H*), 1.12–0.94 [m, 20H, Si(CH_2CH_3)$_2$], and 0.34 [s, 9H, C(CH_3)$_3$].

^{13}C-NMR (500 MHz; $CDCl_3$): δ 156.7, 140.8, 134.7, 129.4, 129.0, 128.0, 124.1, 123.9, 123.6, 118.3, 110.4, 109.9, 7.93, 7.86, 5.98, 5.82, 0.188.

IR (**neat**): 3500 (br, s), 2956 (m), 2874 (m), 1583 (m), 1571 (m), 1355 (m), 1201 (m), 1144 (m), 1214 (m), 842 (s), 728 (s), 709 (m) cm^{-1}

TLC: Rf = 0.4 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{38}H_{50}NaO_2Si_2)^+$: 673.2780. Found: 673.2781.



3,3'-bis(diethylsilyl)-[1,1'-binaphthalene]-2,2'-diol (4g)

Yield: 0.2 mmol scale, 55.9 mg, 61%.

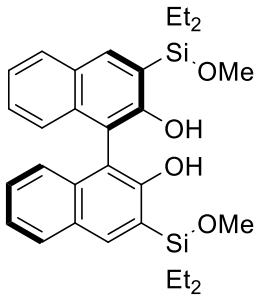
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.20 [s, 2H, C*H(4,4')*], 7.91 [d, *J* = 7.7 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.37 [ddd, *J* = 8.1, 6.8, 1.3 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.32 [ddd, *J* = 8.3, 6.8, 1.4 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.12 [d, *J* = 8.2, 2H, C*H(5,5')* or C*H(8,8')*], 5.23 (s, 2H, O*H*), 4.41 (q, *J* = 3.4 Hz, 2H, Si*H*), 1.09–1.06 [m, 12H, Si(CH_2CH_3)$_2$], and 0.93-1.05 [m, 8H, Si(CH_2CH_3)$_2$].

^{13}C-NMR (500 MHz; $CDCl_3$): δ 156.8, 140.1, 134.6, 129.4, 128.7, 127.9, 124.9, 124.1, 123.9, 109.6, 8.63, 8.60, 3.75, 3.56.

IR (**neat**): 3633 (m), 2952 (m), 2872 (m), 2019 (m), 1582 (m), 1355 (m), 1144 (m), 1045 (m), 985 (m), 810 (s), 750 (m), 685 (m) cm^{-1}.

TLC: Rf = 0.3 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{28}H_{34}NaO_2Si_2)^+$: 481.1990. Found: 481.1997.



3,3'-bis(diethyl(methoxy)silyl)-[1,1'-binaphthalene]-2,2'-diol (4h)

Yield: 0.2 mmol scale, 31.1 mg, 30%.

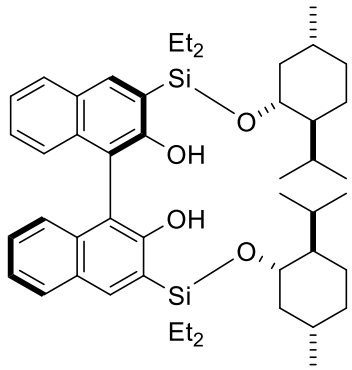
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.05 [s, 2H, C*H(4,4')*], 7.88 [d, *J* = 7.7 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.32 [ddd, *J* = 7.9, 6.8, 1.1 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.32 [ddd, *J* = 8.3, 6.8, 1.4 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.15 [d, *J* = 8.7, 2H, C*H(5,5')* or C*H(8,8')*], 6.95 (s, 2H, O*H*), 3.67 (s, 6H, SiOC*H*$_3$), and 1.03–1.10 [m, 20H, Si(CH_2CH_3)$_2$].

^{13}C-NMR (500 MHz; $CDCl_3$): δ 156.8, 137.6, 135.1, 128.9, 128.6, 127.6, 124.6, 123.4, 123.2, 112.7, 51.35, 6.98, 6.90, 5.65, 5.50.

IR (**neat**): 3523 (m), 3299 (br, w), 3054 (s), 2875 (m), 1617(m), 1582 (m), 1412 (m), 1355 (m), 1199 (m), 1143 (m), 1070 (m), 751 (s), 707 (s) cm^{-1}

TLC: Rf = 0.4 in 20:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{36}H_{38}NaO_2Si_2)^+$: 613.2201. Found: 613.2293.



3-(diethyl(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)silyl)-3'-(diethyl(((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)silyl)-[1,1'-binaphthalene]-2,2'-diol (4i)

Yield: 0.2 mmol scale, 64.4 mg, 42%.

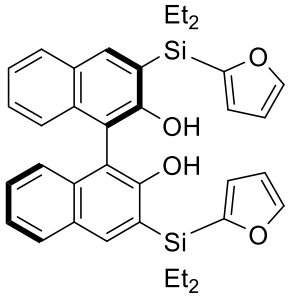
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.07 [s, 2H, C*H(4,4')*], 7.86 [d, *J* = 7.7 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.30 [ddd, *J* = 8.0, 6.8, 1.2 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.25 [ddd, *J* = 8.1, 6.7, 1.3 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.15 [d, *J* = 8.4, 4H, C*H(5,5')* or C*H(8,8')*], 6.96 (s, 2H, O*H*), 3.70 (ddd, *J* = 10.4, 10.4, 4.3 Hz, 2H, SiOC*H*), 2.27 [ddddd, *J* = 13.9, 13.9, 6.9, 6.9, 3.9 Hz, 2H, C*H*(CH(CH_2)$_2$], 2.00 (m, 2H, C*H*CH_3), 1.58-1.64 [m, 4H, Alkyl-*H*,], 1.35 [m, 2H, C*H*(CH_3)$_2$], 1.23 (m, 2H, Alkyl-*H*), 1.13 (m, 2H, Alkyl-*H*), 1.02-1.08 [m, 20H, CH(C*H*$_3$)$_2$ and Si(C*H*$_2$$CH_3$)$_2$], 0.93 (m, 2H, Alkyl-*H*), 0.85-0.88 (m, 12H, Si(CH_2C*H*$_3$)$_2$], 0.82 (m, 2H, Alkyl-*H*), 0.71 [d, *J* = 6.9 Hz, 6H, CHC*H*$_3$].

^{13}C-NMR (500 MHz; $CDCl_3$): δ 156.9, 137.6, 135.1, 128.9, 128.6, 127.3, 124.7, 124.4, 123.2, 112.8, 74.0, 50.2, 45.2, 34.5, 31.9, 25.3, 23.0, 22.4, 21.5, 16.0, 7.4, 7.2, 6.8, 6.6.

IR (**neat**): 3520 (w), 3268 (m, br), 2953 (s), 2872 (m), 1580 (m), 1446 (m), 1355 (m), 1203 (m), 1145 (m), 1044 (s), 749 (m), 730 (m), 708 (m) cm^{-1}

TLC: Rf = 0.4 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{48}H_{70}O_4NaSi_2)^+$: 789.4705. Found: 789.4711.



3,3'-bis(diethyl(furan-2-yl)silyl)-[1,1'-binaphthalene]-2,2'-diol (4m)

Yield: 0.2 mmol scale, 69.7 mg, 59%.

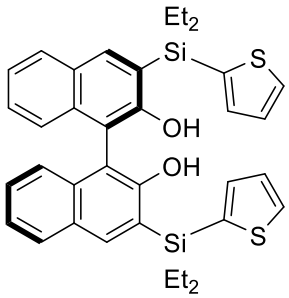
^{1}H-NMR ($CDCl_3$,500 MHz): δ 7.97 [s, 2H, C*H(4,4')*], 7.83 [d, *J* = 7.5 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.78 (d, *J* = 1.6 Hz, Furan-*H(3)* or Furan-*H(5)*], 7.33 [ddd, *J* = 8.0, 6.8, 1.3 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.29 [ddd, *J* = 8.2, 6.8, 1.4 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.10 [d, *J* = 8.2, 2H, C*H(5,5')* or C*H(8,8')*], 6.86 [d, *J* = 3.2 Hz, 2H, Furan-*H(3)* or Furan-*H(5)*], 6.50 [dd, *J* = 3.2, 1.6 Hz, Furan-*H(4)*], 5.26 (s, 2H, O*H*), 1.19 [m, 8H, $Si(CH_2CH_3)_2$], and 1.06 [m, 12H, $Si(CH_2CH_3)_2$].

^{13}C-NMR (500 MHz; $CDCl_3$): δ 157.1, 156.8, 147.2, 140.2, 134.5, 129.4, 128.9, 127.9, 124.3, 123.9, 123.8, 122.0, 109.7, 109.6, 7.79, 7.77, 4.46, 4.46.

IR (**neat**): 3500 (m), 2950 (m), 2872 (m), 1580 (m), 1355 (m), 1201 (m), 1142 (m), 1042 (m), 786 (s), 746 (s), 686 (m) cm^{-1}.

TLC: Rf = 0.4 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{36}H_{38}NaO_4Si_2)^+$: 613.2201. Found: 613.2293.



3,3'-bis(diethyl(thiophen-2-yl)silyl)-[1,1'-binaphthalene]-2,2'-diol (4p)

Yield: 0.2 mmol scale, 69.6 mg, 57%.

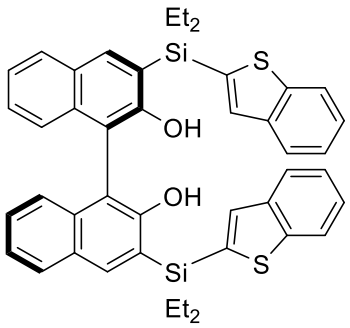
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.03 [s, 2H, C*H(4,4')*], 7.83 [dd, *J* = 7.5, 1.5 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.69 (dd, *J* = 4.6, 0.9 Hz, 2H, SC*H*), 7.46 [dd, *J* = 3.4, 0.9 Hz, 2H, SC(Si)C*H*], 7.36-7.29 [m, 4H, C*H(6,6')* or C*H(7,7')*], 7.28 (dd, *J* = 4.6, 3.4 Hz, 2H, SCHC*H*), 7.13 [dd, *J* = 8.1, 1.6 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 5.29 (s, 2H, O*H*), 1.33-1.24 [m, 8H, Si(C$H_2$$CH_3$)$_2$], and 1.11 [t, *J* = 7.8 Hz, 6H, Si(CH_2CH_3)].

^{13}C-NMR ($CDCl_3$,500 MHz): δ 157.0, 140.2, 136.0, 135.6, 134.7, 131.3, 129.4, 129.0, 128.3, 128.1, 125.1, 124.13, 123.97, 109.9, 8.0, 5.64, and 5.55.

IR (**neat**): 3500 (m), 2957 (m), 2857 (m), 1614 (m), 1571 (m), 1357 (m), 1214 (m), 1143 (m), 1000 (m), 714 (m) cm^{-1}.

TLC: Rf = 0.4 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{36}H_{38}NaO_2S_2Si_2)^+$: 645.1744. Found: 645.1753.



3,3'-bis(benzo[*b*]thiophen-2-yldiethylsilyl)-[1,1'-binaphthalene]-2,2'-diol (4q)

Yield: 0.2 mmol scale, 72.3 mg, 50%.

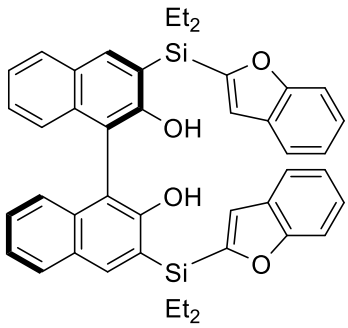
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.12 [s, 2H, C*H(4,4')*], 7.92 [d, *J* = 7.5 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.83-7.87 [m, 4H, Thianaphthene-*H(7,4)*], 7.67 [s, 2H, Thianaphthene-*H(3)*], 7.30-7.40 [m, 8H, C*H(6,6')*, C*H(7,7')*, and Thianaphthene-*H(6,5)*], 7.17 [d, *J* = 7.9 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 5.34 (s, 2H, O*H*), 1.29-1.40 [m, 8H, Si(CH_2CH_3)$_2$], and 1.13-1.17 [m, 12H, Si(CH_2CH_3)].

^{13}C NMR ($CDCl_3$, 500 MHz): 156.9, 144.0, 141.1, 140.2, 138.1, 134.6, 132.9, 129.4, 128.9, 128.2, 124.5, 124.4, 124.1, 124.0, 123.9, 123.7, 122.3, 109.9, 7.90, 5.36, 5.26.

IR (**neat**): 3500 (m), 2953 (m), 2872 (m), 1580 (m), 1355 (m), 1143 (m), 1017 (m), 979 (m), 754 (s), 685 (s) cm^{-1}.

TLC: Rf = 0.4 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{44}H_{42}KO_2S_2Si_2)^+$: 761.1796. Found: 761.1704.



3,3'-bis(benzofuran-2-yldiethylsilyl)-[1,1'-binaphthalene]-2,2'-diol (4o)

Yield: 0.2 mmol scale, 69.7 mg, 57%.

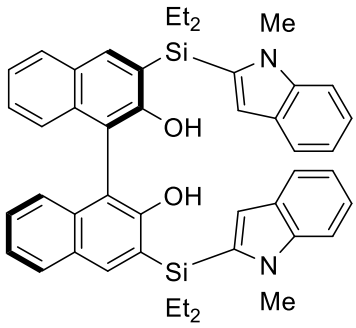
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.08 [s, 2H, C*H(4,4')*], 7.81 [d, *J* = 7.4 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.65 [dd, *J* = 8.2 Hz, 2H, Benzofuran-*H(7)*], 7.60 [d, *J* = 8.2 Hz, 2H, Benzofuran-*H(4)*], 7.32 [m, 6H, C*H(6,6')* or C*H(7,7')* and Benzofuran-*H(5)* or *H(6)*], 7.25 [t, *J* = 7.3 Hz, 2H, Benzofuran-*H(5)* or *H(6)*], 7.21 [s, 2H, Benzofuran-*H(3)*], 7.14 [d, J = 7.6 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 5.31 (s, 2H, O*H*), 1.23-1.33 [m, 8H, Si(CH_2CH$_3$)$_2$], 1.11–1.14 [m, 12H, Si(CH$_2$CH_3)$_2$].

^{13}C-NMR ($CDCl_3$,500 MHz): δ 160.5, 158.4, 156.8, 140.3, 134.6, 128.9, 124.5, 124.0, 123.9, 123.7, 123.4, 123.3, 122.5, 121.2, 118.6, 111.6, 109.8, 7.79, 4.42, 4.33.

IR (**neat**): 3500 (m), 2955 (m), 2874 (m), 1614 (m), 1581 (m), 1442 (m), 1356 (m), 1253 (m), 1143 (m), 790 (m), 752 (s), 717 (s) cm^{-1}

TLC: Rf = 0.4 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{44}H_{42}NaO_4Si_2)^+$: 713.2514. Found: 713.2532.



3,3'-bis(diethyl(1-methyl-1H-indol-2-yl)silyl)-[1,1'-binaphthalene]-2,2'-diol (4r)

Yield: 0.2 mmol scale, 97.5 mg, 68%.

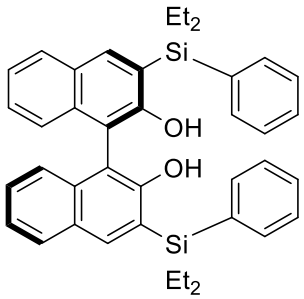
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.06 [s, 2H, C*H(4,4')*], 7.86 [dd, *J* = 7.3, 1.8 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.73 [d, *J* = 7.9 Hz, 2H, Indole-*H(7)* or Indole-*H(4)*], 7.4 [t, *J* = 8.3 Hz, 2H, Indole-*H(5)* or Indole-*H(6)*], 7.34-7.40 [m, 4H, C*H(6,6')* or C*H(7,7');* and Indole-*H(5)* or Indole-*H(6)*], 7.32 [ddd, *J* = 8.2, 7.0, 1.1, 2H, C*H(6,6')* or C*H(7,7')*], 7.17-7.20 [m, 4H, Indole-*H(7)* or Indole-*H(4)*; and C*H(5,5')* or C*H(8,8')*, 6.98 [s, 2H, Indole-*H(3)*], 5.31 (s, 2H, O*H*), 3.83 (s, 6H, NCH_3), 1.31-1.51 [m, 8H, Si(CH_2CH$_3$)$_2$], 1.10–1.15 [m, 12H, Si(CH$_2$CH_3)$_2$].

^{13}C-NMR (126 MHz; $CDCl_3$): δ 156.8, 140.5, 139.9, 137.4, 129.4, 128.9, 128.7, 128.1, 125.1, 124.0, 123.9, 122.1, 120.9, 119.3, 113.5, 110.2, 109.4, 33.4, 7.91, 7.88, 4.91, 4.78.

IR (**neat**): 3500 (m), 3035 (m), 2874 (m), 1581 (m), 1417 (m), 1298 (m), 1221 (m), 1143 (m), 790 (m), 752 (s), 717 (s) cm^{-1}.

TLC: Rf = 0.4 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{46}H_{49}N_2O_2Si_2)^+$: 717.3327. Found: 717.3323.



3,3'-bis(diethyl(phenyl)silyl)-[1,1'-binaphthalene]-2,2'-diol (4j)

Yield: 0.2 mmol scale, 74.5 mg, 61%.

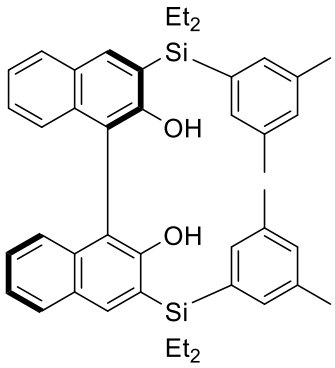
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.04 [s, 2H, C*H(4,4')*], 7.84 [d, *J* = 7.8 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.64 (dd, *J* = 7.3, 1.7, 4H, CH_{meta}), 7.40 (m, 6H, CH_{ortho} and CH_{para}), 7.34 [ddd, *J* = 8.0, 6.9, 1.1, 2H, C*H(6,6')* or C*H(7,7')*], 7.30 [ddd, *J* = 8.4, 6.9, 1.5, 2H, C*H(6,6')* or C*H(7,7')*], 7.13 [d, *J* = 8.2, 2H, C*H(5,5')* or C*H(8,8')*], 5.22 (s, 2H, O*H*), 1.36–1.21 [m, 8H, Si(CH_2CH$_3$)$_2$], 1.10–1.07 [m, 12H, Si(CH$_2$CH_3)$_2$].

^{13}C-NMR (126 MHz; $CDCl_3$): δ 157.1, 140.1, 136.7, 134.5, 129.4, 129.1, 128.8, 127.9, 127.8, 125.4, 124.0, 123.8, 109.9, 7.88, 7.84, 4.18, 4.15.

IR (**neat**): 3500 (m), 2953 (m), 2874 (m), 1580 (m), 1378 (m), 1356 (m), 1302 (m), 1144 (m), 1007 (m), 777 (m), 724 (s), 664 (s) cm^{-1}

TLC: Rf = 0.3 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{40}H_{42}NaO_2Si_2)^+$: 633.2616. Found: 633.2627.



3,3'-bis((3,5-dimethylphenyl)diethylsilyl)-[1,1'-binaphthalene]-2,2'-diol (4k)

Yield: 0.2 mmol scale, 62.7 mg, 47%.

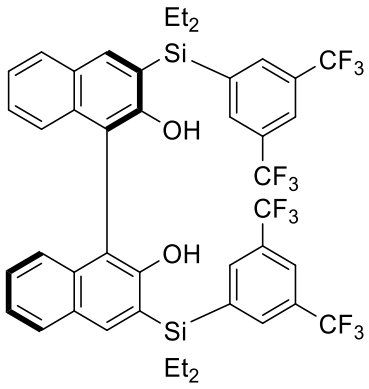
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.08 [s, 2H, C*H(4,4')*], 7.88 [d, *J* = 7.9 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.35 [ddd, *J* = 7.9, 6.8, 1.2 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.31 [ddd, *J* = 8.3, 6.8, 1.4 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.21 (s, 4H, CH_{ortho}), 7.16 [d, *J* = 8.2 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.03 (s, 2H, CH_{para}), 5.23 (s, 2H, O*H*), 2.32 [s, 12H, $(CH_3)_{meta}$], 1.19–1.32 [m, 8H, $Si(CH_2CH_3)_2$], 1.06–1.09 [m, 12H, $Si(CH_2CH_3)_2$].

^{13}C-NMR ($CDCl_3$, 500 MHz): δ 157.1, 140.0. 137.0, 136.4, 134.5, 132.5, 130.9, 129.4, 128.8, 127.8, 125.5, 124.1, 123.8, 109.9, 21.6, 7.93, 7.88, 4.23.

IR (**neat**): 3500 (m), 2952 (m), 2872 (m), 1580 (m), 1571 (m), 1355 (m), 1141 (m), 846 (m), 750 (s), 722 (s), 475 (m) cm^{-1}

TLC: Rf = 0.4 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{44}H_{50}NaO_2Si_2)^+$: 689.3242. Found: 689.3247.



3,3'-bis((3,5-bis(trifluoromethyl)phenyl)diethylsilyl)-[1,1'-binaphthalene]-2,2'-diol (4l)

Yield: 0.2 mmol scale, 81.3 mg, 46%.

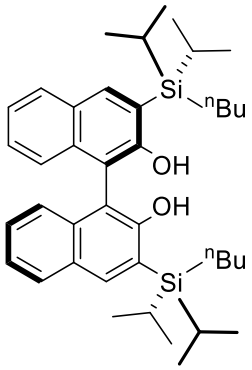
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.12 [s, 2H, C*H(4,4')*], 7.98 (s, 4H, CH_{ortho}), 7.91 [dd, *J* = 8.0, 0.39 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.85 (s, 2H, CH_{para}), 7.41 [ddd, *J* = 7.9, 7.0, 0.94 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.35 [ddd, *J* = 8.3, 7.1, 1.3, 2H, C*H(6,6')* or C*H(7,7')*], 7.11 [dd, *J* = 8.3, 0.4, 2H, C*H(5,5')* or C*H(8,8')*], 5.14 (s, 2H, O*H*), 1.25-1.40 [m, 8H, Si(CH_2CH$_3$)$_2$], and 1.11-1.07 [m, 12H, Si(CH$_2$CH_3)$_2$].

^{13}C-NMR (126 MHz; $CDCl_3$): δ 156.6, 140.9, 140.2, 134.6, 134.3, 131.1-130.3 [131.1: 130.8: 130.5: 130.3 (1:3:3:1)], 129.4, 129.0, 128.7, 124.9, 124.4, 123.8, 123.1, 122.9, 122.7, 110, 7.55, 7.51, 3.66, 3.60.

IR (**neat**): 3500 (w), 2958 (w), 2878 (w), 1582 (w), 1357 (s), 1180 (m), 1124 (s), 906 (m), 726 (s), 705 (s), 680 (s), 440 (m) cm^{-1}.

TLC: Rf = 0.4 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{44}H_{39}F_{12}O_2Si_2)^+$: 883.2291. Found: 883.2250.



3,3'-bis(butyldiisopropylsilyl)-[1,1'-binaphthalene]-2,2'-diol (5a)

Yield: 0.2 mmol scale, 56.4 mg, 45%.

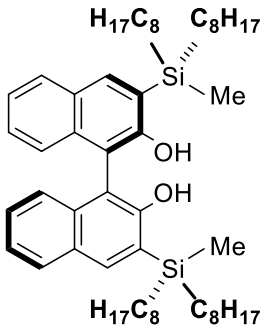
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.15 [s, 2H, C*H(4,4')*], 7.94 [d, *J* = 8.0 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.39 [ddd, *J* = 8.0, 6.8, 1.1 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.32 [ddd, *J* = 8.3, 6.9, 1.3 Hz, C*H(6,6')* or C*H(7,7')*], 7.15 [d, *J* = 8.3 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 5.27 (s, 2H, O*H*), 1.42-1.51[m, 12H, SiC*H*$(CH_3)_2$ and $SiCH_2CH_2CH_2CH_3$], 1.06-1.16 [m, 28H, $SiCH(CH_3)_2$ and $SiCH_2CH_2CH_2CH_3$], 0.96 [t, 6H, $SiCH_2CH_2CH_2CH_3$].

^{13}C-NMR ($CDCl_3$, 500 MHz;): δ 157.3, 139.8, 134.3, 129.4, 128.7, 127.7, 125.4, 124.0, 123.7, 109.7, 27.4, 27.1, 19.0, 18.9, 18.7, 18.6, 13.9, 11.9, 11.8, 9.88.

IR (**neat**): 3500 (s), 2954 (s), 2925 (s), 2863 (s), 1580 (m), 1356 (m), 1180 (m), 1144 (m), 882 (m), 750 (m), 685 (m) cm^{-1}.

TLC: Rf = 0.4 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+K)^+$ $(C_{40}H_{58}KO_2Si_2)^+$: 665.3607. Found: 665.3609.



3,3'-bis(methyldioctylsilyl)-[1,1'-binaphthalene]-2,2'-diol (5b)

Yield: 0.2 mmol scale, 60.9 mg, 37%.

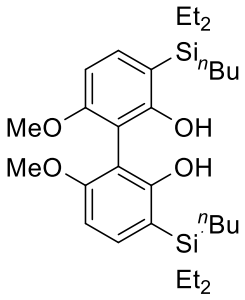
^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.05 [s, 2H, C*H(4,4')*], 7.88 [d, *J* = 8.1 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 7.35 [ddd, *J* = 8.0, 6.8, 1.1 Hz, 2H, C*H(6,6')* or C*H(7,7')*], 7.27 [ddd, *J* = 8.3, 6.8, 1.3 Hz, C*H(6,6')* or C*H(7,7')*], 7.09 [d, *J* = 8.3 Hz, 2H, C*H(5,5')* or C*H(8,8')*], 5.20 (s, 2H, O*H*), 1.23-1.31 [m, 56H, $Si(C_7H_{14}CH_3)_2$], 0.84-0.90 [m, 12H, $Si(C_7H_{14}CH_3)_2$], 0.39 [s, 6H, $SiCH_3$].

^{13}C-NMR ($CDCl_3$, 500 MHz;): δ 138.6, 134.3, 129.4, 128.6, 127.8, 127.6, 124.1, 123.7, 109.5, 33.9, 33.8, 32.1, 29.5, 29.4, 24.3, 24.2, 22.8, 14.3.

IR (**neat**): 3500 (w), 2955 (m), 2921 (s), 2853 (m), 1582 (w), 1464 (w), 1204 (w), 1070 (w), 1043 (w), 749 (w) cm^{-1}.

TLC: Rf = 0.3 in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{54}H_{86}NaO_2Si_2)^+$: 845.6059. Found: 845.6063.



3,3'-bis(butyldiethylsilyl)-6,6'-dimethoxy-[1,1'-biphenyl]-2,2'-diol (7b)

Yield: 0.2 mmol scale, 55.2 mg, 50%.

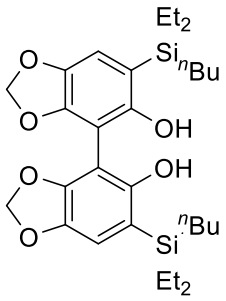
^{1}H-NMR ($CDCl_3$,500 MHz): δ 7.39 [d, *J* = 8.2 Hz, 2H, C*H(5,5')*], 6.62 [d, *J* = 8.2 Hz , 2H, C*H(4,4')*], 5.20 (s, 2H, O*H*), 3.76 (s, 6H, OCH_3), 1.28-1.35 [m, 8H, SiCH$_2$CH_2CH_2CH$_3$), 0.97-1.00 [m, 12H, Si(CH$_2$CH_3)$_2$], 0.81-0.90 (m, 18H, SiCH_2CH$_2$CH$_2$CH_3 and Si(CH_2CH$_3$)$_2$].

^{13}C-NMR (126 MHz; $CDCl_3$): δ 160.5, 159.1, 137.5, 115.2, 105.9, 103.4, 55.9. 26.9, 26.4, 14.0, 11.8, 7.81, 4.12.

IR (**neat**): 3500 (m), 2953 (m), 2872 (m), 1587 (m), 1463 (m), 1278 (m), 1095 (s), 717 (s) cm^{-1}

TLC: Rf = 0.4 in 20:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{30}H_{50}NaO_4Si_2)^+$: 553.3140. Found: 553.3147.



6,6'-bis(butyldiethylsilyl)-[4,4'-bibenzo[*d*][1,3]dioxole]-5,5'-diol (7c)

Yield: 0.4 mmol scale, 43.6 mg, 39%.

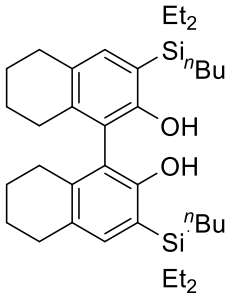
^{1}H-NMR ($CDCl_3$,500 MHz): δ 6.87 [s, 2H, C*H(4,4')*], 5.96 [dd, *J* = 21, 1.2 Hz , 4H, OCH_2O], 5.13 (s, 2H, O*H*), 1.26-1.37 [m, 8H, SiCH$_2$CH_2CH_2CH$_3$), 0.97 [t, *J* = 7.6 Hz, 12H, Si(CH$_2$CH_3)$_2$], 0.81-0.89 (m, 18H, SiCH_2CH$_2$CH$_2$CH_3 and Si(CH_2CH$_3$)$_2$].

^{13}C-NMR (126 MHz; $CDCl_3$): δ 153.3, 147.1, 141.7, 115.7, 114.7, 101.8, 101.6, 26.9, 26.3, 13.9, 11.8, 7.78, 4.11.

IR (**neat**): 3500 (w), 2953 (s), 2872 (m), 1581 (m), 1302 (m), 1204 (m), 1013 (m), 793 (s), 750 (s) cm^{-1}.

TLC: Rf = 0.3 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+K)^+$ $(C_{30}H_{46}KO_6Si_2)^+$: 597.2465. Found: 597.2459.



3,3'-bis(butyldiethylsilyl)-5,5',6,6',7,7',8,8'-octahydro-[1,1'-binaphthalene]-2,2'-diol (7a)

Yield: 0.4 mmol scale, 51.0 mg, 44%.

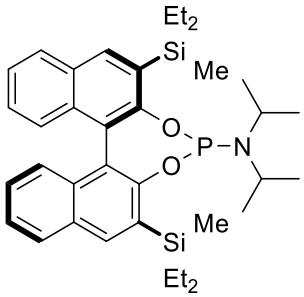
^{1}H-NMR ($CDCl_3$,500 MHz): δ 7.14 [s, 2H, C*H(4,4')*], 4.75 (s, 2H, O*H*), 2.77 [t, *J* = 5.8 Hz, 4H, C(5,5')CH_2], 2.23 [m, 4H, C(6,6')CH_2], 1,77 [p, *J* = 6 Hz, C(5,5')CH_2CH_2 or C(6,6')CH_2CH_2], 1.70 [p, *J* = 6 Hz, C(5,5')CH_2CH_2 or C(6,6')CH_2CH_2], 1.30-1.37 [m, 8H, $SiCH_2CH_2CH_2CH_3$), 0.98-1.01 [m, 12H, $Si(CH_2CH_3)_2$], 0.97-1.00 (m, 18H, $SiCH_2CH_2CH_2CH_3$ and $Si(CH_2CH_3)_2$].

^{13}C-NMR (126 MHz; $CDCl_3$): δ 156.4, 138.5, 137.6, 129.4, 120.1, 117.9, 29.4, 27.3, 26.9, 26.5, 23.2, 23.1, 14.0, 11.7, 7.88, 4.06.

IR (**neat**): 3500 (m), 2922 (s), 1588 (m), 1387 (m), 1317 (m), 1186 (m), 1005 (m), 715 (m) cm^{-1}.

TLC: Rf = 0.4 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+Na)^+$ $(C_{36}H_{58}NaO_2Si_2)^+$: 601.3868. Found: 601.3832.



2,6-bis(diethyl(methyl)silyl)-*N*,*N*-diisopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (8a)

Yield: 1 mmol scale, 412.6 mg, 67%.

^{1}H-NMR (C_6D_6, 500 MHz): δ 8.16 [s, 1H, C*H(4,4')*], 8.15 [s, 1H, C*H(4,4')*], 7.77 [d, *J* = 8.2 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 7.72 [d, *J* = 8.1 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 7.38 [d, *J* = 8.6 Hz, 1H, C*H(5,5')* or C*H(8,8')*], 7.17 [m, 1H, C*H(5,5')* or C*H(8,8')*], 7.11 [ddd, *J* = 7.9, 6.8, 1.1 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 7.10 [ddd, *J* = 7.9, 6.8, 1.1 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 6.88 [ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 6.84 [ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 0.91-1.22 [m, 34H, Si(CH_2CH_3)$_2$ and NC*H*(CH_3)$_2$], 0.58 [s, 3H, SiCH_3], 0.56 [s, 3H, SiCH_3].

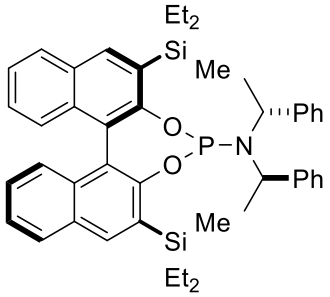
^{13}C-NMR (C_6D_6, 500 MHz): δ 138.34, 137.01, 134.94, 134.77, 131.42, 130.59, 130.53, 130.50, 128.74, 128.38, 128.36, 127.30, 126.97, 126.93, 126.85, 124.72, 124.67, 123.37, 121.88, 121.85, 30.48, 30.23, 7.96, 7.93, 7.84, 7.43, 6.49, 6.44, 6.41, 6.36, 6.32, -3.44, -4.71, -4.74.

^{31}P-NMR (C_6D_6, 300 MHz): δ 154.

IR (**neat**): 2952 (m), 2872 (m), 1384 (m), 1197 (m), 1173 (m), 1122 (m), 963 (s), 783 (s), 746 (s) cm^{-1}.

TLC: Rf = 0.3 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{38}H_{59}NO_2PSi_2)^+$: 648.3816. Found: 648.3897.



2,6-bis(diethyl(methyl)silyl)-*N*,*N*-bis((*R*)-1-phenylethyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (8b)

Yield: 1 mmol scale, 458.7 mg, 62%.

^{1}H-NMR (C_6D_6, 500 MHz): δ 8.23 [s, 1H, C*H(4,4')*], 8.12 [s, 1H, C*H(4,4')*], 7.75 [d, *J* = 8.1 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 7.66 [d, *J* = 8.1 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 7.40 [d, *J* = 8.5 Hz, 1H, C*H(5,5')* or C*H(8,8')*], 7.05-7.19 [m, 13H, N(CHCH$_3$C$_6$*H*$_5$)$_2$, C*H(6,6')* or C*H(7,7')*, and C*H(5,5')* or C*H(8,8')*], 6.90 [ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 6.84 [ddd, *J* = 8.2, 6.8, 1.1 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 4.40 [m, 2H, N(C*H*CH$_3$C$_6$H$_5$)$_2$], 0.79-1.36 [m, 26H, Si(C*H*$_2$C*H*$_3$)$_2$ and N(CHC*H*$_3$C$_6$H$_5$)$_2$], 0.67 [s, 3H, SiC*H*$_3$], 0.11 [s, 3H, SiC*H*$_3$].

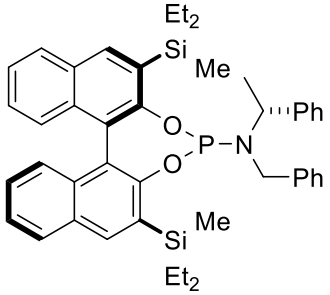
^{13}C-NMR (C_6D_6, 500 MHz): δ 154.6, 154.4, 154.3, 143.7, 138.5, 136.7, 135.0, 134.9, 131.5, 131.4, 130.5, 130.4, 129.1, 128.7, 128.4, 128.3,127.3, 127.2. 127.0, 126.9, 124.8, 124.7, 123.8, 123.7, 121.3, 56.3, 56.2, 56.1, 34.0, 34.9, 31.9, 29.4, 27.2, 25.6, 23.1, 20.9, 14.4, 11.7, 8.14, 8.04, 8.00, 7.91, 6.55, 6.53, 6.47, 6.43, 6.31, 5.92, -4.46, -4.92.

^{31}P-NMR (C_6D_6, 300 MHz): δ 153.

IR (**neat**): 2952 (m), 2872 (m), 1384 (m), 1219 (m), 1091 (m), 975 (s), 784 (s), 748 (s), 698 (m) cm^{-1}.

TLC: Rf = 0.3 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{46}H_{55}NO_2PSi_2)^+$: 740.3503. Found: 740.3323.



***N*-benzyl-2,6-bis(diethyl(methyl)silyl)-*N*-((*R*)-1-phenylethyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (8c)**

Yield: 1 mmol scale, 551.8 mg, 76%.

^{1}H-NMR (C_6D_6, 500 MHz): δ 8.21 [s, 1H, C*H(4,4')*], 8.14 [s, 1H, C*H(4,4')*], 7.73 [d, *J* = 8.0 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 7.68 [d, *J* = 8.1 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 7.32 [d, *J* = 8.7 Hz, 1H, C*H(5,5')* or C*H(8,8')*], 7.30 [d, *J* = 7.6 Hz, 1H, C*H(5,5')* or C*H(8,8')*], 6.83-6.99 [m, 12H, N(CHCH$_3$C$_6$*H*$_5$)(CH$_2$C$_6$*H*$_5$) and C*H(6,6')* or C*H(7,7')*], 6.83 [ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 4.42 [m, 1H, N(CHCH$_3$C$_6$H$_5$)(C*H*$_2$C$_6$H$_5$)], 4.19 [m, 1H, N(CHCH$_3$C$_6$H$_5$)(C*H*$_2$C$_6$H$_5$)], 3.87 [m, 1H, N(C*H*CH$_3$C$_6$H$_5$)(CH$_2$C$_6$H$_5$)], 0.69-1.80 [m, 26H, Si(C*H*$_2$C*H*$_3$)$_2$ and N(CHC*H*$_3$C$_6$H$_5$)(CH$_2$C$_6$H$_5$)], 0.63 [s, 3H, SiC*H*$_3$], 0.33 [s, 3H, SiC*H*$_3$].

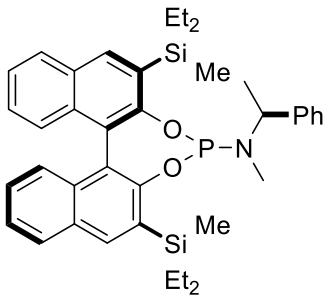
^{13}C-NMR (C_6D_6, 500 MHz): δ 154.0, 138.6, 138.0, 134.9, 134.8, 131.5, 130.5, 130.4, 129.2, 128.7, 128.6, 128.4, 127.7, 127.4, 127.3, 127.2, 127.0, 126.9, 124.9, 124.7, 124.1, 124.0, 121.6, 121.5, 57.5, 57.4, 50.0, 49.9, 34.9, 34.8, 31.9, 27.2, 25.6, 23.5, 23.4, 23.1, 20.9, 14.4, 8.06, 8.04, 8.01, 6.62, 6.58, 6.20, 6.13, -4.47.

^{31}P-NMR (C_6D_6, 300 MHz): δ 145.

IR (**neat**): 2952 (m), 2872 (m), 1385 (m), 1217 (m), 1091 (m), 975 (m), 784 (s), 748 (s), 699 (m) cm^{-1}.

TLC: Rf = 0.3 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{45}H_{53}NO_2PSi_2)^+$: 726.3347. Found: 726.3367.



2,6-bis(diethyl(methyl)silyl)-*N*-methyl-*N*-((*S*)-1-phenylethyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (8d)

Yield: 1 mmol scale, 376.8 mg, 58%.

^{1}H-NMR (C_6D_6, 500 MHz): 8.18 [s, 1H, C*H(4,4')*], 8.13 [s, 1H, C*H(4,4')*], 7.75 [d, *J* = 8.0 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 7.73 [d, *J* = 8.0 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 7.38 [d, *J* = 8.4 Hz, 1H, C*H(5,5')* or C*H(8,8')*], 7.08-7.26 [m, 8H, $CH_3NCHCH_3C_6H_5$, C*H(6,6')* or C*H(7,7')*, and C*H(5,5')* or C*H(8,8')*], 6.89 [ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 6.86 [ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 4.40 [m, 1H, $CH_3NCHCH_3C_6H_5$], 0.79-1.36 [m, 26H, $Si(CH_2CH_3)_2$ and $CH_3NCHCH_3C_6H_5$], 0.60 [s, 3H, $SiCH_3$], 0.45 [s, 3H, $SiCH_3$].

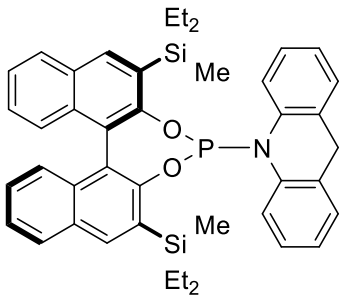
^{13}C-NMR (C_6D_6, 500 MHz): δ 154.8, 154.6, 143.3, 143.2, 138.4, 137.8, 134.9, 134.7, 131.5, 130.6, 130.5, 130.4, 128.7, 128.6, 128.5, 127.5, 127.3, 127.2, 127.0, 126.9, 124.8, 124.7, 123.7, 123.6, 121.9, 121.8, 34.9, 34.8, 31.0, 27.3, 25.7, 20.9, 8.09, 8.05, 8.02, 7.99, 6.51, 6.47, 6.21, 6.06, -4.69.

^{31}P-NMR (C_6D_6, 300 MHz): δ 147.

IR (**neat**): 2952 (m), 2873 (m), 1384 (m), 1199 (m), 1006 (m), 976 (m), 785 (s), 748 (s) cm^{-1}.

TLC: Rf = 0.3 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{39}H_{49}NO_2PSi_2)^+$: 650.3034. Found: 650.3052.



10-(2,6-bis(diethyl(methyl)silyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-9,10-dihydroacridine (8e)

Yield: 1 mmol scale, 424.6 mg, 61%.

^{1}H-NMR ($CDCl_3$,500 MHz): δ 8.29 [s, 1H, C*H(4,4')*], 8.05 [s, 1H, C*H(4,4')*], 7.81 [d, *J* = 8.1 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 7.67 [d, *J* = 8.1 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 7.32 [d, *J* = 6.2 Hz, 1H, C*H(5,5')* or C*H(8,8')*], 7.30 [d, *J* = 6.5 Hz, 1H, C*H(5,5')* or C*H(8,8')*], 7.19 [ddd, *J* = 8.0, 6.8, 1.0 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 7.11 [ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 6.98 [m, 2H, 9,10-dihydro-acridine*H(3,4,5,6,7,8)*], 6.98 [m, 2H, 9,10-dihydro-acridine*H(4,5)*], 6.90 [ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 6.88 [ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H, C*H(6,6')* or C*H(7,7')*], 6.64 [m, 1H, 9,10-dihydro-acridine*H(3,4,5,6,7,8)*], 6.27 [m, 1H, 9,10-dihydro-acridine*H(3,4,5,6,7,8)*], 3.98 [m, 1H, 9,10-dihydro-acridine*H(9)*], 3.61 [m, 1H, 9,10-dihydro-acridine*H(9)*], 0.71-1.80 [m, 20H, Si(CH_2CH_3)$_2$], 0.50 [s, 3H, SiCH_3], 0.24 [s, 3H, SiCH_3].

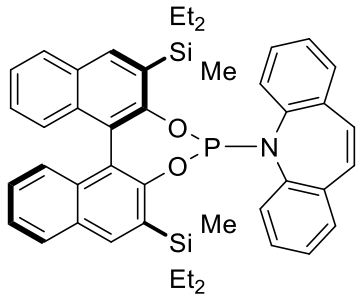
^{13}C-NMR (C_6D_6, 500 MHz): δ 154.56, 154.47, 153.65, 138.92, 138.51, 134.78, 134.79, 131.74, 130.79, 130.67, 130.47, 128.79, 128.55, 127.48, 127.34, 127.14, 125.25, 125.01, 123.81, 123.76, 122.39, 34.99, 33.72, 31.98, 27.24, 25.65, 23.06, 20.91, 14.37, 7.88, 7.82, 7.63, 7.60, 6.33, 6.29, 6.24, 6.22, 6.07, 5.88, -4.82, -5.01, -5.05.

^{31}P-NMR (C_6D_6, 300 MHz): δ 136.

IR (**neat**): 2952 (m), 2873 (m), 1305 (m), 1131(m), 1003 (m), 982 (s), 791 (s), 751 (s) cm^{-1}.

TLC: Rf = 0.3 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+K)^+$ $(C_{43}H_{46}KNO_2PSi_2)^+$: 734.2436. Found: 734.2453.



5-(2,6-bis(diethyl(methyl)silyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-5H-dibenzo[*b*,*f*]azepine (8f)

Yield: 1 mmol scale, 389.4 mg, 55%.

^{1}H-NMR (C_6D_6, 500 MHz): δ 8.19 [s, 1H, C*H(4,4')*], 8.06 [s, 1H, C*H(4,4')*], 7.79 [d, J = 8.0 Hz, 1H, iminostilbene-*H(4,6)*], 7.77 [d, J = 8.0 Hz, 1H, iminostilbene-*H(4,6)*], 7.64 [d, *J* = 8.5 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 7.14 [d, J = 8.1 Hz, 2H, iminostilbene-*H(1,9)*], 7.11 [d, *J* = 8.5 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 7.06 [ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H, iminostilbene-*H(2,3)* or *H(7,8)*], 6.98 [t, *J* = 8.0 Hz, 1H, iminostilbene-*H(2,3)* or *H(7,8)*], 6.90 [dd, *J* = 7.7, 1.4 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 6.85 [dd, *J* = 7.6, 1.5 Hz, 1H, C*H(5,5')* or C*H(8, 8')*], 6.77-6.84 [m, 4H, C*H(6,6')* and C*H(7,7')*], 6.64 [d, J = 8.1 Hz, 2H, iminostilbene-*H(10,11)*], 6.57 [ddd, *J* = 8.5, 7.4, 1.1 Hz, 1H, iminostilbene-*H(2,3)* or *H(7,8)*], 6.46 [t, *J* = 8.5 Hz, 1H, iminostilbene-*H(2,3)* or *H(7,8)*], 0.84-1.80 [m, 20H, Si(CH_2CH_3)$_2$], 0.66 [s, 3H, SiCH_3], 0.47 [s, 3H, SiCH_3].

^{13}C-NMR (C_6D_6, 500 MHz): δ 153.8, 153.5, 143.5, 141.9, 138.1, 137.3, 135.9, 135.2, 134.6, 134.5, 132.2, 131.2, 130.8, 130.3, 130.0, 129.8, 129.3, 128.7, 128.6, 128.4, 128.3, 127.0, 126.7,

126.6, 126.5, 126.2, 124.9, 124.6, 123.5, 121.8, 7.98, 7.91, 7.84, 7.03, 6.82, 6.24, 6.20, 6.17, -4.00, -4.85, -4.87.

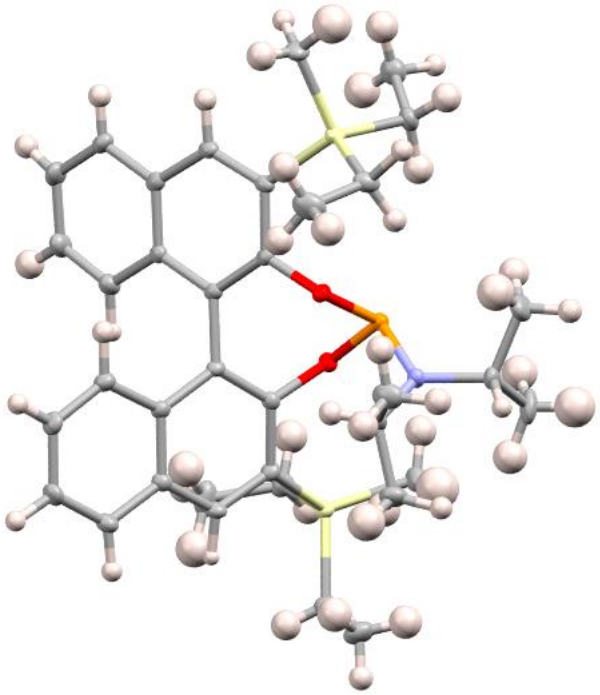
^{31}P-NMR (C_6D_6, 300 MHz): δ 136.

IR (**neat**): 2952 (m), 2872 (m), 1486 (m), 1384 (m), 1198 (m), 1091 (m), 966 (s), 796 (s), 748 (s) cm^{-1}.

TLC: Rf = 0.3 in 40:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{44}H_{47}NO_2PSi_2)^+$: 708.2877. Found: 708.2886.

Table SI-1-8a Crystal data and structure refinement for 2,6-bis(diethyl(methyl)silyl)-N,N diisopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (8a)



Empirical formula: $C_{36}H_{50}NO_2PSi_2$

Formula weight: 510.80

Cell setting: orthorhombic

Crystal system monoclinic

Space group H-M: 'P 21 21 21'

Space group Hall: 'P 2xab;2ybc;2zac'

a/Å 7.957

b/Å 19.9437

c/Å 22.0739

α/° 90

β/° 90

γ/° 90

Volume/$Å^3$: 3502.952

Z: 4

F(000): 1328

ρ_{cal}cg/cm^3:1.1679

μ/mm^{-1} 0.178

Radiation MoKα (λ = 0.71073)

2Θ range for data collection/° 2.11 to 28.24

Index ranges $-10 \leq h \leq 10$, $-26 \leq k \leq 26$, $-29 \leq l \leq 28$

Reflections collected: 35164

Independent reflections 11030 [Rint = 0.0244, Rsigma = 0.0192]

Data/restraints/parameters: 6829/0/579

Goodness-of-fit on F^2: 1.14

Final R indexes [I>=3σ (I)] R1 = 0.0301, wR2 = 0.0286

Final R indexes [all data] R1 = 0.0301, wR2 = 0.0286

Largest diff. peak/hole / e $Å^{-3}$ 1.06/-0.53

Table SI-2-8a Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for 2,6-bis(diethyl(methyl)silyl)-N,N diisopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (8a). Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

[Atom Element x y z Ueq]

P1 P 0.06870(5) 0.04079(2) 0.217422(17) 0.01456(11)

Si1 Si 0.01540(6) 0.17068(2) 0.385155(17) 0.01494(11)

Si2 Si -0.01760(5) -0.00202(2) 0.037656(18) 0.01575(11)

O1 O -0.02379(14) 0.10367(5) 0.25480(4) 0.0158(3)

O2 O 0.10659(14) 0.07961(5) 0.15173(4) 0.0153(3)

N1 N 0.26757(17) 0.03460(7) 0.23912(6) 0.0170(4)

C1 C 0.3398(2) 0.19676(12) 0.43867(9) 0.0296(6)

H7 H 0.364(3) 0.1515(12) 0.4447(10) 0.045(7)

H8 H 0.401(3) 0.2151(9) 0.4677(8) 0.024(5)

H1 H 0.372(3) 0.2101(13) 0.4007(11) 0.049(7)

C2 C 0.1527(2) 0.21304(10) 0.44342(7) 0.0201(5)

H10 H 0.144(3) 0.2565(11) 0.4451(10) 0.037(6)

H9 H 0.105(2) 0.1993(8) 0.4816(7) 0.008(4)

C3 C 0.0752(2) 0.20234(8) 0.30697(6) 0.0155(4)

C4 C 0.02400(19) 0.17075(7) 0.25175(6) 0.0135(4)

C5 C 0.0089(2) 0.20452(7) 0.19731(6) 0.0135(4)

C6 C -0.07900(19) 0.17282(8) 0.14469(6) 0.0135(4)

C7 C -0.02563(19) 0.11197(7) 0.12249(6) 0.0138(4)

C8 C -0.0945(2) 0.08058(8) 0.06981(6) 0.0148(4)

C9 C -0.1103(2) -0.07413(9) 0.08158(8) 0.0230(5)

H32 H -0.056(3) -0.1163(10) 0.0656(9) 0.036(5)

H31 H -0.077(3) -0.0605(10) 0.1256(9) 0.038(5)

C10 C -0.3000(2) -0.08223(11) 0.07608(10) 0.0290(6)

H2 H -0.342(3) -0.0469(13) 0.0896(11) 0.053(8)

H29 H -0.353(2) -0.1213(9) 0.1039(8) 0.020(5)

H30 H -0.325(3) -0.0920(11) 0.0340(10) 0.043(6)

C11 C -0.2482(3) 0.26994(11) 0.38333(11) 0.0347(7)

H50 H -0.178(3) 0.3021(13) 0.4081(11) 0.056(7)

H3 H -0.368(3) 0.2832(11) 0.3919(9) 0.037(6)

H51 H -0.238(3) 0.2740(12) 0.3424(12) 0.053(7)

C12 C -0.2104(2) 0.19706(9) 0.39826(8) 0.0214(5)

H48 H -0.285(3) 0.1680(11) 0.3740(10) 0.046(6)

H49 H -0.235(3) 0.1852(10) 0.4400(10) 0.035(6)

C13 C 0.0329(3) 0.07817(9) 0.39593(8) 0.0255(5)

H4 H -0.017(3) 0.0619(9) 0.4351(9) 0.034(5)

H6 H 0.142(4) 0.0638(14) 0.3875(12) 0.076(9)

H5 H -0.038(3) 0.0529(11) 0.3700(9) 0.040(6)

C14 C 0.1347(2) 0.26734(8) 0.30210(7) 0.0166(5)

H11 H 0.167(2) 0.2920(9) 0.3370(7) 0.011(4)

C15 C 0.14354(19) 0.30210(8) 0.24628(7) 0.0158(4)

C16 C 0.07630(19) 0.27118(8) 0.19320(6) 0.0141(4)

C17 C 0.3955(2) 0.08825(9) 0.22891(7) 0.0194(5)

H15 H 0.338(2) 0.1249(10) 0.2133(8) 0.024(5)

C18 C 0.5201(3) 0.06813(11) 0.17882(9) 0.0309(6)

H14 H 0.591(3) 0.0271(11) 0.1903(9) 0.030(5)

H12 H 0.604(3) 0.1036(12) 0.1743(9) 0.038(6)

H13 H 0.478(3) 0.0543(10) 0.1411(9) 0.033(5)

C19 C 0.4872(3) 0.10727(10) 0.28671(8) 0.0283(5)

H16 H 0.407(3) 0.1217(11) 0.3148(10) 0.048(6)

H17 H 0.571(3) 0.1427(12) 0.2768(10) 0.058(7)

H18 H 0.564(2) 0.0710(9) 0.3016(7) 0.021(5)

C20 C 0.3333(2) -0.03180(8) 0.25950(8) 0.0202(5)

H19 H 0.457(2) -0.0267(9) 0.2616(7) 0.017(4)

C21 C 0.2670(3) -0.05115(11) 0.32191(10) 0.0358(7)

H21 H 0.294(3) -0.0129(12) 0.3544(10) 0.048(7)

H22 H 0.317(4) -0.0912(14) 0.3322(12) 0.068(8)

H20 H 0.146(3) -0.0585(12) 0.3156(11) 0.052(7)

C22 C 0.3016(3) -0.08782(10) 0.21392(10) 0.0363(7)

H23 H 0.176(3) -0.0974(10) 0.2089(9) 0.037(6)

H24 H 0.362(2) -0.1291(10) 0.2257(8) 0.024(5)

H25 H 0.351(3) -0.0724(13) 0.1742(12) 0.057(7)

C23 C -0.22531(19) 0.20346(8) 0.11807(7) 0.0142(4)

C24 C -0.3087(2) 0.25959(9) 0.14491(8) 0.0208(5)

H42 H -0.270(2) 0.2784(9) 0.1816(8) 0.016(4)

C25 C -0.4530(2) 0.28444(9) 0.11951(8) 0.0259(5)

H41 H -0.516(3) 0.3196(10) 0.1388(9) 0.035(5)

C26 C -0.5201(2) 0.25718(9) 0.06569(8) 0.0255(5)

H40 H -0.615(3) 0.2704(9) 0.0486(8) 0.023(5)

C27 C -0.4428(2) 0.20282(8) 0.03920(7) 0.0194(5)

H39 H -0.489(2) 0.1846(9) 0.0039(8) 0.022(5)

C28 C -0.2965(2) 0.17407(8) 0.06537(7) 0.0161(4)

C29 C -0.2248(2) 0.11380(8) 0.04197(7) 0.0163(4)

H38 H -0.276(2) 0.0948(9) 0.0052(8) 0.021(5)

C30 C -0.0926(3) -0.00633(10) -0.04306(7) 0.0242(5)

H26 H -0.056(3) 0.0273(11) -0.0650(9) 0.036(6)

H27 H -0.213(3) -0.0082(9) -0.0490(8) 0.020(5)

H28 H -0.044(3) -0.0485(13) -0.0644(11) 0.063(7)

C31 C 0.2178(2) -0.00809(9) 0.03864(8) 0.0234(5)

H34 H 0.253(2) -0.0160(9) 0.0801(9) 0.023(5)

H33 H 0.248(2) -0.0530(9) 0.0177(8) 0.020(5)

C32 C 0.3077(3) 0.05281(11) 0.01104(10) 0.0341(7)

H35 H 0.277(3) 0.0578(11) -0.0312(10) 0.038(6)

H36 H 0.424(3) 0.0471(11) 0.0128(9) 0.047(6)

H37 H 0.290(3) 0.0946(11) 0.0334(10) 0.036(6)

C33 C 0.0805(2) 0.30810(8) 0.13789(7) 0.0178(4)

H46 H 0.033(2) 0.2870(9) 0.1013(8) 0.021(5)

C34 C 0.1451(2) 0.37174(9) 0.13598(7) 0.0204(5)

H45 H 0.146(2) 0.3937(9) 0.0999(8) 0.018(5)

C35 C 0.2099(2) 0.40259(9) 0.18849(8) 0.0206(5)

H44 H 0.252(2) 0.4477(10) 0.1850(8) 0.017(4)

C36 C 0.2106(2) 0.36834(8) 0.24227(7) 0.0193(5)

H43 H 0.255(2) 0.3855(9) 0.2797(8) 0.018(4)

Table SI-3-8a Anisotropic Displacement Parameters (Å2×103) for 2,6-bis(diethyl(methyl)silyl)-*N*,*N* diisopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (8a). The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

[Atom Element U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}]

P1 P 0.01544(19) 0.01313(19) 0.01511(17) -0.00057(16) -0.00229(15) 0.00003(15)

Si1 Si 0.0172(2) 0.0163(2) 0.01127(17) -0.00021(18) -0.00038(16) 0.00076(15)

Si2 Si 0.0173(2) 0.0155(2) 0.01444(18) 0.00031(19) -0.00189(16) -0.00323(16)

O1 O 0.0200(6) 0.0136(5) 0.0139(5) -0.0010(5) 0.0009(4) 0.0006(4)

O2 O 0.0163(5) 0.0161(6) 0.0135(5) 0.0028(5) -0.0021(4) -0.0002(4)

N1 N 0.0177(7) 0.0138(7) 0.0195(6) -0.0014(6) -0.0034(5) 0.0022(5)

C1 C 0.0206(9) 0.0423(13) 0.0261(10) -0.0006(9) -0.0058(8) -0.0028(9)

C2 C 0.0210(9) 0.0243(10) 0.0152(8) 0.0003(7) -0.0013(6) -0.0027(7)

C3 C 0.0155(7) 0.0183(8) 0.0126(6) 0.0016(7) 0.0008(6) -0.0005(6)

C4 C 0.0115(7) 0.0137(7) 0.0155(6) 0.0001(6) 0.0015(6) -0.0008(6)

C5 C 0.0137(7) 0.0151(7) 0.0115(6) 0.0020(7) -0.0003(6) -0.0029(5)

C6 C 0.0134(7) 0.0149(7) 0.0121(6) -0.0033(6) -0.0002(6) 0.0012(5)

C7 C 0.0140(7) 0.0161(7) 0.0114(6) -0.0013(6) -0.0003(6) 0.0028(5)

C8 C 0.0172(8) 0.0150(7) 0.0121(7) -0.0031(6) 0.0018(6) -0.0017(5)

C9 C 0.0259(10) 0.0151(9) 0.0280(9) -0.0007(7) -0.0016(7) 0.0017(7)

C10 C 0.0268(10) 0.0273(11) 0.0329(11) -0.0032(9) 0.0022(8) 0.0025(8)

C11 C 0.0247(10) 0.0330(11) 0.0465(12) 0.0093(9) 0.0075(10) 0.0123(10)

C12 C 0.0173(8) 0.0265(9) 0.0203(8) -0.0022(7) 0.0004(6) 0.0033(7)

C13 C 0.0355(11) 0.0203(9) 0.0206(8) 0.0008(8) 0.0001(8) 0.0031(6)

C14 C 0.0182(8) 0.0182(8) 0.0135(7) -0.0015(7) -0.0002(6) -0.0045(6)

C15 C 0.0146(8) 0.0166(8) 0.0162(7) 0.0002(6) 0.0008(6) -0.0020(6)

C16 C 0.0109(7) 0.0165(8) 0.0148(7) 0.0007(6) -0.0004(6) -0.0010(6)

C17 C 0.0186(8) 0.0155(8) 0.0239(8) -0.0037(7) -0.0021(6) 0.0022(6)

C18 C 0.0289(10) 0.0358(11) 0.0280(9) -0.0105(10) 0.0046(8) -0.0007(8)

C19 C 0.0243(9) 0.0307(10) 0.0298(9) -0.0050(9) -0.0064(8) -0.0054(8)

C20 C 0.0207(9) 0.0159(8) 0.0240(8) 0.0046(7) -0.0036(6) 0.0027(6)

C21 C 0.0508(14) 0.0240(11) 0.0328(10) 0.0126(10) 0.0041(10) 0.0140(9)

C22 C 0.0495(14) 0.0189(10) 0.0404(12) 0.0110(10) -0.0107(10) -0.0054(9)

C23 C 0.0155(7) 0.0130(7) 0.0141(7) -0.0014(6) 0.0000(6) 0.0018(6)

C24 C 0.0195(8) 0.0182(8) 0.0247(9) 0.0009(7) -0.0023(7) -0.0032(7)

C25 C 0.0220(9) 0.0206(9) 0.0351(9) 0.0066(7) -0.0048(7) -0.0047(7)

C26 C 0.0203(9) 0.0228(9) 0.0336(9) 0.0053(8) -0.0079(8) 0.0017(7)

C27 C 0.0178(8) 0.0225(8) 0.0180(7) -0.0007(7) -0.0044(6) 0.0030(7)

C28 C 0.0159(8) 0.0180(8) 0.0145(7) -0.0030(7) 0.0003(6) 0.0034(6)

C29 C 0.0192(8) 0.0170(8) 0.0128(7) -0.0024(7) -0.0014(6) -0.0001(6)

C30 C 0.0324(10) 0.0226(9) 0.0176(8) 0.0034(8) -0.0036(7) -0.0070(7)

C31 C 0.0187(8) 0.0249(9) 0.0266(9) 0.0014(7) 0.0001(7) -0.0093(7)

C32 C 0.0246(11) 0.0385(13) 0.0393(12) -0.0079(9) 0.0077(9) -0.0069(9)

C33 C 0.0171(8) 0.0213(8) 0.0151(7) 0.0002(7) -0.0017(6) -0.0006(6)

C34 C 0.0237(9) 0.0208(9) 0.0166(8) -0.0008(7) 0.0007(6) 0.0057(6)

C35 C 0.0209(8) 0.0152(9) 0.0256(8) -0.0042(7) 0.0002(7) 0.0005(7)

C36 C 0.0221(9) 0.0177(8) 0.0181(8) -0.0028(7) 0.0005(6) -0.0035(6)

Table SI-4-8a Bond Lengths for 2,6-bis(diethyl(methyl)silyl)-*N*,*N* diisopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (8a).

[Atom Atom Length/Å]

P1 N1 1.6581(16)

Si1 C2 1.8867(17)

Si1 C3 1.8984(14)

Si1 C12 1.8943(17)

Si1 C13 1.8655(18)

Si2 C8 1.8952(16)

Si2 C9 1.8847(18)

Si2 C30 1.8810(17)

Si2 C31 1.8771(16)

O1 C4 1.3925(17)

O2 C7 1.3927(17)

N1 C17 1.494(2)

N1 C20 1.493(2)

C1 H7 0.94(2)

C1 H8 0.88(2)

C1 H1 0.91(2)

C1 C2 1.527(2)

C2 H10 0.88(2)

C2 H9 0.964(16)

C3 C4 1.431(2)

C3 C14 1.384(2)

C4 C5 1.3830(19)

C5 C6 1.496(2)

C5 C16 1.436(2)

C6 C7 1.376(2)

C6 C23 1.440(2)

C7 C8 1.430(2)

C8 C29 1.375(2)

C9 H32 1.00(2)

C9 H31 1.04(2)

C9 C10 1.523(2)

C10 H2 0.84(2)

C10 H30 0.97(2)

C11 H50 1.01(2)

C11 H3 1.01(2)

C11 H51 0.92(2)

C11 C12 1.520(3)

C12 H48 0.99(2)

C12 H49 0.97(2)

C13 H4 1.01(2)

C13 H6 0.93(3)

C13 H5 0.95(2)

C14 H11 0.949(16)

C14 C15 1.416(2)

C15 C16 1.428(2)

C15 C36 1.428(2)

C16 C33 1.426(2)

C17 H15 0.930(19)

C17 C18 1.539(3)

C17 C19 1.518(2)

C18 H14 1.03(2)

C18 H12 0.98(2)

C18 H13 0.94(2)

C19 H16 0.94(2)

C19 H17 1.00(2)

C19 H18 1.003(17)

C20 H19 0.991(16)

C20 C21 1.525(3)

C20 C22 1.525(3)

C21 H22 0.92(2)

C21 H20 0.98(2)

C22 H23 1.02(2)

C22 H24 0.987(19)

C22 H25 1.01(2)

C23 C24 1.430(2)

C23 C28 1.420(2)

C24 H42 0.944(18)

C24 C25 1.371(2)

C25 H41 0.97(2)

C25 C26 1.411(2)

C26 H40 0.88(2)

C26 C27 1.377(2)

C27 H39 0.935(18)

C27 C28 1.420(2)

C28 C29 1.427(2)

C29 H38 0.984(17)

C30 H26 0.87(2)

C30 H27 0.97(2)

C30 H28 1.04(2)

C31 H34 0.97(2)

C31 H33 1.036(18)

C31 C32 1.536(3)

C32 H35 0.96(2)

C32 H36 0.93(2)

C32 H37 0.98(2)

C33 H46 0.986(18)

C33 C34 1.370(2)

C34 H45 0.909(18)

C34 C35 1.410(2)

C35 H44 0.97(2)

C35 C36 1.370(2)

C36 H43 0.962(18)

Table SI-5-8a Bond Angles for 2,6-bis(diethyl(methyl)silyl)-*N*,*N* diisopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (8a).

[Atom Atom Atom Angle/°]

C2 Si1 C3 109.01(7)

C2 Si1 C12 108.72(8)

C2 Si1 C13 108.20(9)

C3 Si1 C12 106.51(8)

C3 Si1 C13 115.23(8)

C12 Si1 C13 109.03(9)

C8 Si2 C9 110.14(7)

C8 Si2 C30 106.96(8)

C8 Si2 C31 111.96(8)

C9 Si2 C30 109.18(9)

C9 Si2 C31 109.60(8)

C30 Si2 C31 108.94(9)

P1 N1 C17 123.60(11)

P1 N1 C20 119.16(11)

C17 N1 C20 116.25(14)

H7 C1 H8 100.4(18)

H7 C1 H1 111.0(19)

H7 C1 C2 113.2(14)

H8 C1 H1 112.9(19)

H8 C1 C2 113.6(14)

H1 C1 C2 106.0(15)

Si1 C2 C1 115.03(13)

Si1 C2 H10 115.3(15)

Si1 C2 H9 104.0(9)

C1 C2 H10 106.9(16)

C1 C2 H9 112.6(10)

H10 C2 H9 102.5(17)

Si1 C3 C4 123.81(11)

Si1 C3 C14 117.89(11)

C4 C3 C14 116.33(13)

O1 C4 C3 117.37(12)

O1 C4 C5 119.08(12)

C3 C4 C5 123.40(13)

C4 C5 C6 120.64(13)

C4 C5 C16 118.24(13)

C6 C5 C16 121.11(12)

C5 C6 C7 120.32(14)

C5 C6 C23 121.03(14)

C7 C6 C23 118.59(13)

O2 C7 C6 118.48(12)

O2 C7 C8 117.62(12)

C6 C7 C8 123.87(14)

Si2 C8 C7 124.14(11)

Si2 C8 C29 119.66(11)

C7 C8 C29 116.20(14)

Si2 C9 H32 106.6(12)

Si2 C9 H31 100.9(12)

Si2 C9 C10 115.32(13)

H32 C9 H31 115.3(17)

H32 C9 C10 108.1(13)

H31 C9 C10 110.7(13)

C9 C10 H2 106.2(16)

C9 C10 H30 107.5(14)

H2 C10 H30 116(2)

H50 C11 H3 104.9(18)

H50 C11 H51 115.5(19)

H50 C11 C12 112.3(12)

H3 C11 H51 104.3(19)

H3 C11 C12 113.2(12)

H51 C11 C12 106.4(13)

Si1 C12 C11 114.83(13)

Si1 C12 H48 108.9(13)

Si1 C12 H49 105.5(14)

C11 C12 H48 108.9(12)

C11 C12 H49 113.7(12)

H48 C12 H49 104.3(18)

Si1 C13 H4 113.5(11)

Si1 C13 H6 110.0(13)

Si1 C13 H5 113.7(12)

H4 C13 H6 116.8(18)

H4 C13 H5 96.5(17)

H6 C13 H5 105(2)

C3 C14 H11 121.0(10)

C3 C14 C15 122.90(14)

H11 C14 C15 116.1(10)

C14 C15 C16 118.96(14)

C14 C15 C36 121.71(14)

C16 C15 C36 119.26(14)

C5 C16 C15 119.19(13)

C5 C16 C33 122.73(13)

C15 C16 C33 118.08(14)

N1 C17 H15 106.6(11)

N1 C17 C18 111.12(14)

N1 C17 C19 112.33(14)

H15 C17 C18 104.9(11)

H15 C17 C19 110.5(11)

C18 C17 C19 111.08(15)

C17 C18 H14 112.7(12)

C17 C18 H12 108.7(12)

C17 C18 H13 119.0(14)

H14 C18 H12 103.5(18)

H14 C18 H13 100.1(17)

H12 C18 H13 111.7(18)

C17 C19 H16 108.1(14)

C17 C19 H17 108.6(13)

C17 C19 H18 112.8(9)

H16 C19 H17 111.9(18)

H16 C19 H18 114.9(16)

H17 C19 H18 100.3(16)

N1 C20 H19 105.7(10)

N1 C20 C21 112.09(14)

N1 C20 C22 113.13(15)

H19 C20 C21 109.1(9)

H19 C20 C22 105.7(10)

C21 C20 C22 110.69(15)

C20 C21 H22 106.8(16)

C20 C21 H20 104.8(13)

H22 C21 H20 110(2)

C20 C22 H23 111.4(11)

C20 C22 H24 110.8(11)

C20 C22 H25 106.4(12)

H23 C22 H24 110.8(15)

H23 C22 H25 109.9(17)

H24 C22 H25 107.4(16)

C6 C23 C24 122.57(14)

C6 C23 C28 118.78(14)

C24 C23 C28 118.51(14)

C23 C24 H42 121.0(10)

C23 C24 C25 120.16(16)

H42 C24 C25 118.7(10)

C24 C25 H41 121.3(13)

C24 C25 C26 121.47(16)

H41 C25 C26 117.2(13)

C25 C26 H40 124.6(12)

C25 C26 C27 119.46(15)

H40 C26 C27 115.8(12)

C26 C27 H39 119.0(10)

C26 C27 C28 120.75(15)

H39 C27 C28 120.3(10)

C23 C28 C27 119.56(14)

C23 C28 C29 118.98(14)

C27 C28 C29 121.36(14)

C8 C29 C28 123.05(14)

C8 C29 H38 119.7(10)

C28 C29 H38 117.2(10)

Si2 C30 H26 112.7(14)

Si2 C30 H27 116.4(11)

Si2 C30 H28 109.8(12)

H26 C30 H27 106.6(19)

H26 C30 H28 104.6(18)

H27 C30 H28 106.0(17)

Si2 C31 H34 108.0(10)

Si2 C31 H33 106.4(9)

Si2 C31 C32 114.15(13)

H34 C31 H33 102.3(14)

H34 C31 C32 111.6(10)

H33 C31 C32 113.5(10)

C31 C32 H35 110.4(13)

C31 C32 H36 110.3(12)

C31 C32 H37 114.5(13)

H35 C32 H36 107.8(19)

H35 C32 H37 110.3(18)

H36 C32 H37 103.1(19)

C16 C33 H46 118.2(10)

C16 C33 C34 120.89(14)

H46 C33 C34 120.9(10)

C33 C34 H45 118.4(11)

C33 C34 C35 121.08(15)

H45 C34 C35 120.5(11)

C34 C35 H44 118.0(11)

C34 C35 C36 119.76(16)

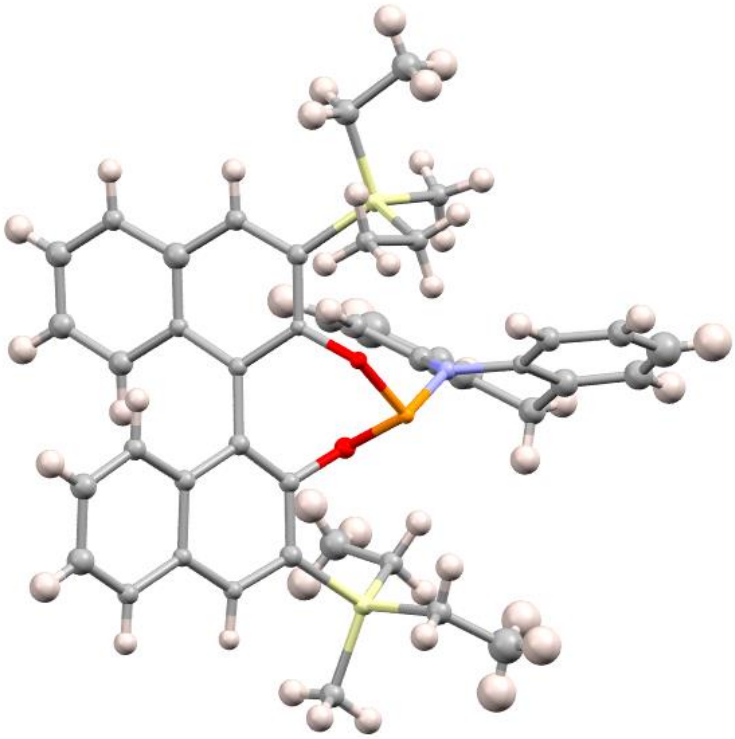
H44 C35 C36 122.3(11)

C15 C36 C35 120.91(15)

C15 C36 H43 114.4(11)

C35 C36 H43 124.7(11)

Table SI-1-8e Crystal data and structure refinement for 10-(2,6-bis(diethyl(methyl)silyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-9,10-dihydroacridine (8e).



Empirical formula: $C_{43}H_{56}NO_2PSi_2$

Formula weight: 696.00

Cell setting: monoclinic

Crystal system monoclinic

Space group H-M: 'P 1 21 1'

Space group Hall: 'P 2yb'

a/Å 11.3036

b/Å 47.9522

c/Å 14.6236

α/° 90

β/° 90

γ/° 90

Volume/$Å^3$: 7926.467

Z: 8

F(000): 2960

ρ_{cal}cg/cm^3: 1.1664

μ/mm^{-1}: 0.165

Radiation MoKα (λ = 0.71073)

2Θ range for data collection/° 1.89 to 32.83

Index ranges -17 ≤ h ≤ 9, -72 ≤ k ≤ 57, -21 ≤ l ≤ 21

Reflections collected: 39289

Independent reflections 16518 [Rint = 0.0762, Rsigma = 0.1539]

Data/restraints/parameters: 6829/0/579

Goodness-of-fit on F^2: 1.44

Final R indexes [I>=3σ (I)] R1 = 0.0830, wR2 = 0.0618

Final R indexes [all data] R1 = 0.0830, wR2 = 0.0618

Largest diff. peak/hole / e $Å^{-3}$ 1.8702/ -0.59

Table SI-2-8e Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for 10-(2,6-bis(diethyl(methyl)silyl)dinaphtho[2,1-

***d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-9,10-dihydroacridine (8e). Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.**

[Atom Element x y z Ueq]

P1 P 0.84552(17) 0.68054(4) 1.41126(14) 0.0158(4)

Si1 Si 0.56041(19) 0.57053(4) 1.01826(15) 0.0175(5)

Si2 Si 1.16856(19) 0.67317(5) 1.52013(15) 0.0177(5)

O1 O -0.4731(4) 0.33178(9) 0.0282(3) 0.0099(10)

O2 O 0.2487(4) 0.41401(9) 0.4817(3) 0.0089(10)

N1 N -0.2531(5) 0.30703(12) 0.0322(4) 0.0126(13)

C1 C -0.6843(6) 0.27480(14) 0.0967(5) 0.0094(15)

C2 C 0.6603(7) 0.68073(18) 0.7117(6) 0.028(2)

C3 C 0.9413(7) 0.64643(15) 1.1157(5) 0.0160(17)

C4 C 0.9310(6) 0.58536(15) 0.7421(5) 0.0115(15)

C5 C 1.1865(7) 0.62384(17) 1.4082(6) 0.025(2)

C6 C -0.5593(6) 0.31009(14) 0.0240(5) 0.0098(15)

C7 C 0.1404(6) 0.43198(14) 0.3139(5) 0.0087(14)

C8 C 0.0798(6) 0.41002(15) 0.1690(5) 0.0153(16)

C9 C 1.1699(7) 0.71081(17) 1.4820(6) 0.0211(19)

C10 C 0.5426(7) 0.62086(15) 0.9062(5) 0.0147(16)

C11 C -0.1488(6) 0.32042(15) -0.0112(5) 0.0162(16)

C12 C 1.2593(7) 0.61986(16) 0.7854(5) 0.0201(18)

C13 C -0.7895(8) 0.23619(19) 0.1686(7) 0.034(2)

C14 C 0.5601(7) 0.68647(20) 0.7720(6) 0.031(2)

C15 C -0.0389(6) 0.30942(15) 0.0082(5) 0.0147(16)

C16 C 0.6887(6) 0.43625(15) 0.5042(5) 0.0133(16)

C17 C -0.6601(6) 0.27551(14) -0.0712(5) 0.0139(16)

C18 C 0.8171(7) 0.59685(15) 0.7148(5) 0.0150(16)

C19 C 0.7437(7) 0.60081(18) 0.4265(6) 0.028(2)

C20 C -0.0114(8) 0.39927(19) 0.1076(6) 0.034(2)

C21 C -0.6122(6) 0.30087(15) 0.1029(5) 0.0140(16)

C22 C 0.2555(6) 0.42886(15) 0.2847(5) 0.0128(16)

C23 C -0.0411(7) 0.50965(18) 0.5020(7) 0.032(2)

C24 C 0.7330(6) 0.65954(14) 1.0833(5) 0.0124(15)

C25 C -0.7532(3) 0.34777(11) 0.39048(15) 0.0122(16)

C26 C 0.8486(6) 0.65206(15) 1.0506(5) 0.0109(15)

C27 C 0.7387(7) 0.72838(18) 1.4546(6) 0.025(2)

C28 C 0.0461(6) 0.42154(15) 0.2542(5) 0.0139(16)

C29 C 1.0033(6) 0.63791(16) 1.2831(5) 0.0153(16)

C30 C 1.1510(7) 0.60485(17) 1.3375(6) 0.0239(19)

C31 C 0.4095(7) 0.58089(17) 1.0625(6) 0.025(2)

C32 C -0.0558(7) 0.50995(16) 0.3347(6) 0.0242(19)

C33 C 0.8575(7) 0.59510(16) 0.4565(5) 0.0195(18)

C34 C 1.1326(6) 0.64955(14) 1.4187(5) 0.0091(15)

C35 C 1.0379(6) 0.65526(15) 1.3550(5) 0.0126(16)

C36 C -0.5896(6) 0.31428(15) 0.1933(5) 0.0149(16)

C37 C 0.5732(7) 0.42544(17) 0.5264(6) 0.026(2)

C38 C -0.4763(6) 0.31508(14) 0.2307(4) 0.0096(15)

C39 C 0.6034(7) 0.59547(17) 0.9210(6) 0.0205(18)

C40 C 0.7280(7) 0.60577(16) 0.7850(6) 0.0184(17)

C41 C -0.1343(7) 0.26467(16) 0.0644(5) 0.0173(17)

C42 C 0.6761(7) 0.63336(16) 0.7776(5) 0.0182(17)

C43 C 0.9872(6) 0.51462(16) 0.9581(5) 0.0145(17)

H1 H 0.687629 0.694613 0.669394 0.0331

H2 H 1.249179 0.618603 1.449042 0.0299

H3 H 1.09009 0.717159 1.473626 0.0254

H4 H 1.19642 0.722397 1.531461 0.0254

H5 H 0.475072 0.62501 0.943668 0.0176

H6 H 1.284262 0.630176 0.838253 0.0241

H7 H 1.318794 0.621129 0.738756 0.0241

H8 H 1.186358 0.627471 0.762844 0.0241

H9 H -0.822186 0.227295 0.221677 0.0409

H10 H 0.52081 0.704183 0.768265 0.0373

H11 H -0.679605 0.267444 -0.129378 0.0166

H12 H 0.726248 0.601307 0.36226 0.0334

H13 H -0.055874 0.517931 0.5607 0.0381

H14 H 0.670896 0.662051 1.039314 0.0149

H15 H 0.412205 0.59975 1.084396 0.0301

H16 H 0.352632 0.579501 1.013948 0.0301

H17 H 0.387122 0.56868 1.11153 0.0301

H18 H -0.084727 0.518554 0.279786 0.029

H19 H 0.919865 0.592983 0.41246 0.0234

H20 H 0.219012 0.404017 0.079025 0.0232

H21 H 0.633917 0.660547 1.211619 0.0253

H22 H 0.095013 0.427831 0.380205 0.0134

H23 H -0.77789 0.227785 -0.055952 0.0233

H24 H 0.996762 0.641755 0.860477 0.024

H25 H 1.188163 0.587247 0.863947 0.0233

H26 H 1.314295 0.580445 0.831394 0.0233

H27 H -0.075349 0.372376 -0.141956 0.0245

H28 H -0.424763 0.268635 0.024911 0.0222

H29 H 0.549958 0.65512 1.363339 0.0271

H30 H 0.423937 0.662623 1.33564 0.0271

H31 H 1.123717 0.543049 0.951531 0.0293

H32 H 0.612242 0.606261 0.627733 0.0299

H33 H 0.024466 0.477892 0.268942 0.0328

H34 H 0.116094 0.353741 -0.12656 0.0293

H35 H 0.807817 0.654325 0.913139 0.0273

H36 H 1.253685 0.56101 0.563424 0.0336

H37 H 1.285625 0.590444 0.597419 0.0336

H38 H 1.159551 0.635931 0.968974 0.0245

H39 H 0.468867 0.611755 1.340001 0.0298

H40 H 0.397999 0.621654 1.253759 0.0298

H41 H 0.534655 0.616484 1.246911 0.0298

H42 H 1.207852 0.540385 1.259988 0.0319

H43 H -0.527604 0.33898 0.43572 0.0175

H44 H 0.998716 0.457944 1.090505 0.0416

H45 H 1.120286 0.638442 1.125617 0.029

H46 H -0.120119 0.540447 0.421925 0.0374

H47 H 0.521482 0.768072 1.573033 0.0461

H48 H 0.583252 0.753135 1.650694 0.0461

H49 H 0.504915 0.543752 0.402947 0.0411

H50 H 0.139344 0.314164 -0.029704 0.0257

H51 H -0.243676 0.415532 0.236664 0.032

H52 H 0.672675 0.515768 0.401759 0.0334

H53 H 0.630761 0.525021 0.974084 0.0265

H54 H 0.522766 0.521185 1.030482 0.0265

H55 H -0.022092 0.29235 0.133383 0.0221

H56 H 0.044721 0.27585 0.059915 0.0221

H57 H 0.475472 0.68301 1.063413 0.0207

H58 H 0.440976 0.653048 1.097976 0.0207

H59 H -0.405211 0.218743 0.051926 0.0265

H60 H -0.639496 0.286355 -0.277129 0.0455

H61 H -0.724115 0.30952 -0.251665 0.0455

H62 H 0.720462 0.559233 1.241919 0.0619

H63 H 0.583239 0.558573 1.226529 0.0619

H64 H 0.664387 0.536637 1.177704 0.0619

H65 H -0.052528 0.227426 0.088967 0.0335

H66 H -0.094673 0.429671 0.337833 0.025

H67 H 1.002632 0.684437 1.738141 0.0283

H68 H 1.14048 0.683777 1.726561 0.0283

H69 H 1.065597 0.706603 1.676167 0.0283

H70 H 0.491477 0.721264 1.271635 0.0286

H71 H 0.629039 0.718869 1.282778 0.0286

H72 H 0.574271 0.725703 1.186872 0.0286

H73 H 1.374044 0.662533 1.514568 0.0248

H74 H 1.345752 0.67793 1.606572 0.0248

H75 H 1.315686 0.646187 1.595714 0.0248

H76 H -0.837235 0.205194 0.076786 0.025

H77 H 0.456738 0.671671 0.872841 0.0219

H78 H -0.20283 0.391914 0.117899 0.0425

H79 H 1.042967 0.550336 1.167428 0.0377

H80 H -0.224902 0.200432 0.086858 0.0324

H81 H 1.099094 0.526704 0.782303 0.0252

H82 H 1.161802 0.518719 0.69034 0.0252

H83 H 1.237353 0.524451 0.778252 0.0252

H84 H -0.521921 0.302368 -0.10722 0.0086

H85 H -0.24317 0.351616 -0.074269 0.0293

H86 H 0.989275 0.798076 1.330188 0.0454

H87 H 0.765232 0.471046 0.442032 0.0311

H88 H 0.698394 0.452718 0.372245 0.0311

H89 H 0.782068 0.651354 0.677702 0.0236

H90 H 1.061547 0.580738 0.541759 0.0227

H91 H 1.243157 0.520317 1.063798 0.0344

H92 H 0.862544 0.432302 0.532819 0.0394

H93 H 0.470417 0.506577 0.891954 0.0473

H94 H 0.407708 0.535616 0.900632 0.0473

H95 H 0.525319 0.532885 0.844531 0.0473

H96 H -0.825978 0.322522 0.150668 0.0137

H97 H 0.577497 0.611006 0.46937 0.0335

H98 H 0.032417 0.476532 0.635372 0.0303

H99 H 0.302342 0.478447 0.484944 0.0191

H100 H 1.272079 0.571874 1.373286 0.0296

H101 H 0.534235 0.714987 1.590665 0.036

H102 H 0.47681 0.729035 1.517344 0.036

H103 H 0.32273 0.525629 0.449142 0.0377

H104 H -0.719611 0.270366 0.236414 0.0199

H105 H 0.975763 0.669992 1.586159 0.0283

H106 H 1.055094 0.648724 1.632196 0.0283

H107 H 0.614098 0.697494 1.455094 0.0246

H108 H 0.955853 0.594371 1.170588 0.0201

H109 H -0.496706 0.364477 -0.119769 0.0426

H110 H -0.537102 0.367252 -0.221918 0.0426

H111 H -0.631453 0.362933 -0.144634 0.0426

H112 H 0.264132 0.680133 1.096506 0.0531

H113 H 0.295389 0.674365 1.199222 0.0531

H114 H 0.324765 0.703396 1.15547 0.0531

H115 H 0.27338 0.386998 0.646531 0.0428

H116 H 0.229814 0.384736 0.739558 0.0428

H117 H 0.717575 0.505076 0.629157 0.0465

H118 H 0.705907 0.448795 0.839975 0.0404

H119 H -0.687717 0.315749 -0.406439 0.0339

H120 H -0.618557 0.340113 -0.358984 0.0339

H121 H -0.550614 0.313464 -0.39212 0.0339

H122 H 0.558745 0.453548 0.247111 0.0316

H123 H 0.593734 0.457632 0.150516 0.0316

H124 H 1.252304 0.737216 1.388588 0.0426

H125 H 1.32015 0.708909 1.399811 0.0426

H126 H 1.203476 0.710117 1.341992 0.0426

H127 H 0.493718 0.497452 0.196361 0.0471

H128 H 0.414273 0.483157 0.122039 0.0471

H129 H 0.383291 0.479855 0.225969 0.0471

H130 H 0.847756 0.533386 0.714662 0.0283

H131 H 1.052889 0.785239 1.183611 0.0471

H132 H -0.35555 0.319376 -0.262446 0.0265

H133 H -0.328428 0.313695 -0.161842 0.0265

H134 H 0.601995 0.38711 0.176223 0.0378

H135 H 0.541965 0.393483 0.270576 0.0378

H136 H 0.479833 0.373526 0.200551 0.0378

H137 H 0.062644 0.459158 0.781095 0.0463

H138 H -0.002717 0.432131 0.758237 0.0463

H139 H 0.885872 0.786956 1.475324 0.0414

H140 H 0.950195 0.759869 1.505903 0.0414

H141 H 1.457802 0.562273 0.585696 0.0416

H142 H 1.440829 0.572548 0.686617 0.0416

H143 H 1.405192 0.542056 0.659477 0.0416

H144 H 0.884834 0.709652 1.215087 0.0299

H145 H 0.130735 0.35747 0.621472 0.0595

H146 H 0.050779 0.370094 0.698667 0.0595

H147 H 0.058249 0.38477 0.603048 0.0595

H148 H 0.406782 0.398049 0.012988 0.0534

H149 H 0.395902 0.42824 -0.000152 0.0534

H150 H 1.182116 0.47626 1.121758 0.0596

H151 H 0.719741 0.784236 1.581431 0.0457

H152 H 0.767568 0.486734 1.009605 0.0355

H153 H 0.824204 0.458292 0.980566 0.0355

H154 H 0.751509 0.574247 1.090453 0.0309

H155 H 0.669605 0.594755 1.1355 0.0309

H156 H 0.995468 0.741328 1.126878 0.0469

H157 H -0.282715 0.273495 -0.248927 0.037

H158 H -0.383971 0.266073 -0.179832 0.037

H159 H -0.414121 0.271814 -0.282762 0.037

H160 H 0.66692 0.461259 0.682482 0.0654

H161 H 0.390727 0.444327 0.669912 0.0609

H162 H 0.321626 0.468645 0.717667 0.0609

H163 H 0.360228 0.442422 0.774302 0.0609

H164 H 0.485383 0.395027 0.599864 0.0364

H165 H -0.260904 0.369107 0.396916 0.0842

H166 H -0.139507 0.354162 0.38002 0.0842

H167 H -0.221945 0.361421 0.297165 0.0842

H168 H -0.193087 0.252474 0.291079 0.1328

H169 H -0.288564 0.259549 0.365291 0.1328

H170 H -0.314422 0.265557 0.261829 0.1328

H171 H -0.968681 0.345688 0.240329 0.0158

H172 H -0.354202 0.328434 0.528749 0.07

H173 H -0.361935 0.29684 0.507763 0.07

H174 H -0.175175 0.301038 0.260151 0.0655

H175 H -0.128087 0.293334 0.350833 0.0655

H176 H 0.047063 0.432831 0.91904 0.1212

H177 H 0.108332 0.407148 0.872601 0.1212

H178 H 0.181734 0.434124 0.89378 0.1212

H179 H -0.204061 0.308271 0.612478 0.0685

H180 H -0.160046 0.291167 0.52769 0.0685

H181 H -0.140448 0.323511 0.53138 0.0685

H182 H 0.558394 0.407597 -0.083897 0.0879

H183 H 0.596483 0.434118 -0.028557 0.0879

H184 H 0.625078 0.404305 0.009477 0.0879

Table SI-3-8e Bond Lengths for 10-(2,6-bis(diethyl(methyl)silyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-9,10-dihydroacridine (8e).

[Atom Atom Length/Å]

P1 N2 1.715(5)

P2 N1 1.732(6)

P3 N3 1.729(5)

P4 N4 1.736(6)

Si1 C31 1.891(8)

Si1 C39 1.922(9)

Si1 C90 1.915(10)

Si1 C159 1.915(9)

Si2 C9 1.889(10)

Si2 C34 1.911(7)

Si2 C104 1.881(7)

Si2 C131 1.892(9)

Si3 C97 1.869(9)

Si3 C112 1.932(6)

Si3 C134 1.950(10)

Si3 C146 1.919(8)

Si3 H84 1.3099

Si4 C50 1.895(8)

Si4 C60 1.892(9)

Si4 C94 1.924(7)

Si4 C103 1.918(10)

Si4 H21 1.1715

Si5 C57 1.906(9)

Si5 C73 1.885(9)

Si5 C74 1.920(8)

Si5 C111 1.841(10)

Si6 C115 1.915(7)

Si6 C141 1.926(10)

Si6 C148 1.856(9)

Si6 C155 1.890(11)

Si7 C55 1.904(9)

Si7 C136 1.904(10)

Si7 C150 1.887(10)

Si7 C163 1.904(10)

Si8 C100 1.893(7)

Si8 C165 1.875(10)

Si8 C168 1.930(12)

Si8 C169 1.812(11)

O1 C6 1.426(7)

O2 C46 1.435(7)

O3 C77 1.382(9)

O4 C4 1.370(8)

O5 C64 1.399(10)

O6 C35 1.414(7)

O7 C38 1.454(8)

N1 C11 1.485(9)

N1 C56 1.425(7)

O8 C22 1.400(8)

N2 C27 1.437(10)

N2 C53 1.457(10)

C1 C21 1.496(8)

C1 C49 1.414(10)

C1 C130 1.432(10)

C2 C14 1.462(12)

C2 C118 1.386(13)

C2 H1 0.9609

N3 C43 1.468(9)

N3 C92 1.462(10)

C3 C26 1.442(10)

C3 C44 1.522(10)

C3 C82 1.417(11)

C4 C18 1.456(10)

C4 C74 1.410(10)

N4 C37 1.475(10)

N4 C69 1.453(11)

C5 C30 1.432(13)

C5 C34 1.383(11)

C5 H2 0.9596

C6 C21 1.372(10)

C6 C112 1.486(9)

C7 C22 1.377(10)

C7 C28 1.467(10)

C7 C51 1.508(9)

C8 C20 1.460(11)

C8 C28 1.415(10)

C8 C45 1.424(10)

C9 C142 1.556(12)

C9 H3 0.9601

C9 H4 0.9604

C10 C39 1.415(11)

C10 C91 1.383(11)

C10 H5 0.9601

C11 C15 1.379(10)

C11 C113 1.388(13)

C12 H6 0.9591

C12 H7 0.9597

C12 H8 0.9594

C13 C106 1.431(13)

C13 C130 1.408(13)

C13 H9 0.9598

C14 C107 1.362(12)

C14 H10 0.9588

C15 C87 1.463(11)

C15 C93 1.477(11)

C16 C37 1.442(11)

C16 C116 1.562(11)

C16 C121 1.370(11)

C17 C49 1.415(10)

C17 C112 1.398(8)

C17 H11 0.96

C18 C40 1.500(12)

C18 C63 1.465(10)

C19 C33 1.386(11)

C19 C124 1.392(12)

C19 H12 0.9602

C20 C108 1.428(13)

C21 C36 1.492(10)

C22 C115 1.419(10)

C23 C47 1.445(13)

C23 C84 1.430(13)

C23 H13 0.9614

C24 C26 1.436(10)

C24 C50 1.427(9)

C24 H14 0.96

C25 C61 1.391(8)

C25 C105 1.369(5)

C26 C71 1.408(11)

C27 C68 1.426(13)

C27 C132 1.394(12)

C28 C101 1.398(10)

C29 C35 1.398(10)

C29 C44 1.544(11)

C29 C48 1.439(11)

C30 C48 1.376(11)

C30 C127 1.500(13)

C31 H15 0.9594

C31 H16 0.9601

C31 H17 0.9599

C32 C66 1.370(13)

C32 C84 1.412(13)

C32 H18 0.9592

C33 C72 1.468(11)

C33 H19 0.9602

C34 C35 1.446(10)

C36 C38 1.393(10)

C36 C78 1.457(10)

C37 C164 1.408(13)

C38 C100 1.406(9)

C39 C64 1.429(11)

C40 C42 1.452(13)

C40 C64 1.366(12)

C41 C56 1.415(10)

C41 C93 1.569(11)

C41 C99 1.387(14)

C42 C91 1.489(11)

C42 C118 1.434(12)

C43 C62 1.400(11)

C43 C83 1.428(13)

C44 C77 1.305(11)

C45 C115 1.385(10)

C45 H20 0.9598

C46 C51 1.417(8)

C46 C55 1.356(11)

C47 C96 1.388(12)

C47 C125 1.446(12)

C48 C133 1.475(9)

C49 C52 1.455(13)

C50 C77 1.476(10)

C50 H21 0.9598

C51 C96 1.470(10)

C51 H22 0.9594

C52 C106 1.367(12)

C52 H23 0.9601

C53 C147 1.433(13)

C53 C153 1.407(12)

C54 C71 1.387(11)

C54 C75 1.480(11)

C54 H24 0.9606

C55 C125 1.432(13)

C56 C59 1.448(11)

C57 H25 0.9596

C57 H26 0.9608

C58 C67 1.393(11)

C58 C113 1.410(11)

C58 H27 0.9607

C59 C95 1.455(13)

C59 H28 0.9607

C60 H29 0.9599

C60 H30 0.9613

C61 C78 1.461(10)

C61 C80 1.447(10)

C62 C120 1.411(13)

C62 H31 0.96

C63 C65 1.446(11)

C63 C72 1.391(12)

C65 C124 1.404(12)

C65 H32 0.9607

C66 C96 1.444(13)

C66 H33 0.9609

C67 C87 1.408(13)

C67 H34 0.9594

C68 C151 1.531(12)

C68 C157 1.351(12)

C69 C70 1.403(11)

C69 C126 1.424(12)

C70 C89 1.427(13)

C70 C116 1.454(12)

C71 H35 0.9601

C72 C119 1.434(12)

C73 C152 1.541(12)

C73 H36 0.9605

C73 H37 0.9597

C74 C119 1.411(10)

C75 C82 1.378(11)

C75 H38 0.96

C76 H39 0.9605

C76 H40 0.9602

C76 H41 0.9597

C78 C123 1.460(10)

C79 C109 1.409(12)

C79 C127 1.397(13)

C79 H42 0.9587

C80 C100 1.413(10)

C80 H43 0.9603

C81 C83 1.450(13)

C81 C156 1.350(14)

C81 H44 0.9601

C82 H45 0.9601

C83 C158 1.504(13)

C84 H46 0.9608

C85 C128 1.464(14)

C85 C157 1.453(13)

C85 H47 0.959

C85 H48 0.9605

C86 C89 1.379(13)

C86 C129 1.387(13)

C86 H49 0.9584

C87 H50 0.9611

C88 C101 1.388(12)

C88 C108 1.387(13)

C88 H51 0.9605

C89 H52 0.9604

C90 C122 1.483(13)

C90 H53 0.9593

C90 H54 0.9594

C91 C107 1.441(13)

C92 C117 1.363(13)

C92 C144 1.436(12)

C93 H55 0.9592

C93 H56 0.9605

C94 H57 0.9591

C94 H58 0.9614

C95 C110 1.338(12)

C95 H59 0.9602

C97 C140 1.567(13)

C97 H60 0.9621

C97 H61 0.9597

C98 C159 1.568(14)

C98 H62 0.9591

C98 H63 0.9613

C98 H64 0.9598

C99 C110 1.400(13)

C99 H65 0.9593

C101 H66 0.9605

C102 C131 1.564(13)

C102 H67 0.9601

C102 H68 0.9601

C102 H69 0.9582

C103 H70 0.9603

C103 H71 0.9601

C103 H72 0.9608

C104 H73 0.9598

C104 H74 0.9603

C104 H75 0.9596

C105 C167 1.465(8)

C106 H76 0.9581

C107 H77 0.9609

C108 H78 0.9586

C109 C133 1.375(11)

C109 H79 0.9588

C110 H80 0.9579

C111 H81 0.9605

C111 H82 0.9609

C111 H83 0.961

C112 H84 0.9597

C113 H85 0.9592

C114 C145 1.386(14)

C114 C147 1.425(13)

C114 H86 0.9599

C116 H87 0.9601

C116 H88 0.9602

C117 C139 1.417(13)

C117 C158 1.548(12)

C118 H89 0.9602

C119 H90 0.9596

C120 C156 1.432(14)

C120 H91 0.9606

C121 C137 1.374(14)

C121 H92 0.9603

C122 H93 0.959

C122 H94 0.9606

C122 H95 0.96

C123 C167 1.401(9)

C123 H96 0.96

C124 H97 0.9604

C125 H98 0.9604

C126 C129 1.373(13)

C126 H99 0.9598

C127 H100 0.96

C128 C132 1.424(12)

C128 H101 0.9589

C128 H102 0.9601

C129 H103 0.959

C130 H104 0.9599

C131 H105 0.9598

C131 H106 0.961

C132 H107 0.9606

C133 H108 0.9601

C134 H109 0.9594

C134 H110 0.96

C134 H111 0.9593

C135 H112 0.9599

C135 H113 0.9601

C135 H114 0.9596

C136 C154 1.501(14)

C136 H115 0.9596

C136 H116 0.9601

C137 C149 1.440(14)

C138 C144 1.393(13)

C138 C162 1.363(14)

C138 H117 0.9602

C139 C162 1.451(15)

C139 H118 0.9606

C140 H119 0.9604

C140 H120 0.9577

C140 H121 0.9603

C141 C143 1.538(13)

C141 H122 0.9599

C141 H123 0.9598

C142 H124 0.9596

C142 H125 0.9602

C142 H126 0.9596

C143 H127 0.9616

C143 H128 0.9608

C143 H129 0.9597

C144 H130 0.9593

C145 C160 1.397(14)

C145 H131 0.9598

C146 C161 1.560(13)

C146 H132 0.9584

C146 H133 0.9594

C147 C151 1.498(12)

C148 H134 0.9595

C148 H135 0.9601

C148 H136 0.9593

C149 C164 1.404(14)

C150 H137 0.961

C150 H138 0.9603

C151 H139 0.9599

C151 H140 0.9594

C152 H141 0.9599

C152 H142 0.959

C152 H143 0.9618

C153 C160 1.404(13)

C153 H144 0.9588

C154 H145 0.9583

C154 H146 0.9596

C154 H147 0.9605

C155 C173 1.554(16)

C155 H148 0.9587

C155 H149 0.9612

C156 H150 0.9605

C157 H151 0.9614

C158 H152 0.9605

C158 H153 0.9592

C159 H154 0.9606

C159 H155 0.9592

C160 H156 0.9606

C161 H157 0.9597

C161 H158 0.959

C161 H159 0.9593

C162 H160 0.958

C163 H161 0.9603

C163 H162 0.9606

C163 H163 0.9592

C164 H164 0.9602

C165 H165 0.9616

C165 H166 0.9583

C165 H167 0.9606

C166 C169 1.526(17)

C166 H168 0.9558

C166 H169 0.9647

C166 H170 0.9605

C167 H171 0.9603

C168 C171 1.543(14)

C168 H172 0.9585

C168 H173 0.9619

C169 H174 0.9596

C169 H175 0.9609

C170 H176 0.9665

C170 H177 0.9577

C170 H178 0.9601

C171 H179 0.9597

C171 H180 0.9604

C171 H181 0.96

C173 H182 0.9608

C173 H183 0.9569

C173 H184 0.9574

Table SI-4-8e Bond Angles for 10-(2,6-bis(diethyl(methyl)silyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-9,10-dihydroacridine (8e).

[Atom Atom Atom Angle/°]

C31 Si1 C39 108.5(4)

C31 Si1 C90 107.8(4)

C31 Si1 C159 108.2(4)

C39 Si1 C90 113.4(4)

C39 Si1 C159 107.2(4)

C90 Si1 C159 111.6(4)

C9 Si2 C34 109.9(3)

C9 Si2 C104 108.9(4)

C9 Si2 C131 110.2(4)

C34 Si2 C104 108.7(3)

C34 Si2 C131 108.9(4)

C104 Si2 C131 110.3(4)

C97 Si3 C112 106.3(3)

C97 Si3 C134 109.3(4)

C97 Si3 C146 110.4(4)

C97 Si3 H84 120.23

C112 Si3 C134 110.1(3)

C112 Si3 C146 111.3(3)

C112 Si3 H84 26.57

C134 Si3 C146 109.4(4)

C134 Si3 H84 119.33

C146 Si3 H84 84.84

C50 Si4 C60 110.9(3)

C50 Si4 C94 108.3(3)

C50 Si4 C103 109.5(3)

C50 Si4 H21 24.45

C60 Si4 C94 107.4(4)

C60 Si4 C103 113.9(4)

C60 Si4 H21 87.01

C94 Si4 C103 106.6(4)

C94 Si4 H21 112.51

C103 Si4 H21 127

C57 Si5 C73 106.4(4)

C57 Si5 C74 111.5(4)

C57 Si5 C111 111.0(4)

C73 Si5 C74 109.9(4)

C73 Si5 C111 109.2(4)

C74 Si5 C111 108.8(4)

C115 Si6 C141 111.4(3)

C115 Si6 C148 106.8(3)

C115 Si6 C155 107.7(4)

C141 Si6 C148 112.0(4)

C141 Si6 C155 111.1(4)

C148 Si6 C155 107.6(4)

C55 Si7 C136 111.5(4)

C55 Si7 C150 108.9(4)

C55 Si7 C163 106.9(4)

C136 Si7 C150 107.9(4)

C136 Si7 C163 111.5(4)

C150 Si7 C163 110.1(4)

C100 Si8 C165 108.8(4)

C100 Si8 C168 107.0(4)

C100 Si8 C169 113.9(4)

C165 Si8 C168 107.8(5)

C165 Si8 C169 108.8(5)

C168 Si8 C169 110.4(5)

P2 N1 C11 114.8(5)

P2 N1 C56 127.7(5)

C11 N1 C56 115.0(6)

P1 N2 C27 115.5(5)

P1 N2 C53 127.8(5)

C27 N2 C53 114.9(6)

C21 C1 C49 118.5(6)

C21 C1 C130 120.6(6)

C49 C1 C130 120.9(6)

C14 C2 C118 119.1(8)

C14 C2 H1 120.35

C118 C2 H1 120.58

P3 N3 C43 113.6(5)

P3 N3 C92 127.2(5)

C43 N3 C92 115.9(6)

C26 C3 C44 116.3(7)

C26 C3 C82 118.7(7)

C44 C3 C82 124.9(7)

O4 C4 C18 119.8(6)

O4 C4 C74 117.0(6)

C18 C4 C74 122.9(7)

P4 N4 C37 111.5(5)

P4 N4 C69 126.4(5)

C37 N4 C69 116.6(6)

C30 C5 C34 121.4(7)

C30 C5 H2 119.46

C34 C5 H2 119.17

O1 C6 C21 119.7(6)

O1 C6 C112 116.5(5)

C21 C6 C112 123.7(5)

C22 C7 C28 117.7(6)

C22 C7 C51 119.5(6)

C28 C7 C51 122.8(6)

C20 C8 C28 119.2(6)

C20 C8 C45 119.4(7)

C28 C8 C45 121.3(6)

Si2 C9 C142 116.1(6)

Si2 C9 H3 109.5

Si2 C9 H4 109.48

C142 C9 H3 109.46

C142 C9 H4 109.46

H3 C9 H4 101.86

C39 C10 C91 123.0(7)

C39 C10 H5 118.39

C91 C10 H5 118.64

N1 C11 C15 117.5(7)

N1 C11 C113 118.9(6)

C15 C11 C113 123.5(7)

H6 C12 H7 109.58

H6 C12 H8 109.6

H7 C12 H8 109.55

C106 C13 C130 120.5(8)

C106 C13 H9 119.68

C130 C13 H9 119.82

C2 C14 C107 120.9(8)

C2 C14 H10 119.52

C107 C14 H10 119.6

C11 C15 C87 116.6(8)

C11 C15 C93 120.0(7)

C87 C15 C93 123.3(7)

C37 C16 C116 117.0(6)

C37 C16 C121 118.8(7)

C116 C16 C121 124.2(7)

C49 C17 C112 121.8(6)

C49 C17 H11 119.13

C112 C17 H11 119.09

C4 C18 C40 120.9(7)

C4 C18 C63 115.5(7)

C40 C18 C63 123.4(7)

C33 C19 C124 119.4(8)

C33 C19 H12 120.35

C124 C19 H12 120.28

C8 C20 C108 117.2(8)

C1 C21 C6 117.1(6)

C1 C21 C36 120.5(6)

C6 C21 C36 122.1(6)

O8 C22 C7 118.8(6)

O8 C22 C115 116.1(6)

C7 C22 C115 125.1(6)

C47 C23 C84 117.8(8)

C47 C23 H13 121.23

C84 C23 H13 120.98

C26 C24 C50 123.5(7)

C26 C24 H14 118.28

C50 C24 H14 118.21

C61 C25 C105 123.9(4)

C3 C26 C24 119.2(7)

C3 C26 C71 120.9(6)

C24 C26 C71 119.9(7)

N2 C27 C68 120.5(7)

N2 C27 C132 120.2(8)

C68 C27 C132 119.3(8)

C7 C28 C8 117.5(6)

C7 C28 C101 122.5(7)

C8 C28 C101 120.0(7)

C35 C29 C44 118.7(7)

C35 C29 C48 116.4(6)

C44 C29 C48 124.9(7)

C5 C30 C48 121.8(8)

C5 C30 C127 118.8(7)

C48 C30 C127 119.2(7)

Si1 C31 H15 109.46

Si1 C31 H16 109.44

Si1 C31 H17 109.42

H15 C31 H16 109.51

H15 C31 H17 109.53

H16 C31 H17 109.47

C66 C32 C84 122.2(8)

C66 C32 H18 118.75

C84 C32 H18 119.01

C19 C33 C72 121.4(7)

C19 C33 H19 119.33

C72 C33 H19 119.32

Si2 C34 C5 121.4(6)

Si2 C34 C35 122.9(4)

C5 C34 C35 115.2(6)

O6 C35 C29 118.8(6)

O6 C35 C34 116.0(5)

C29 C35 C34 125.2(6)

C21 C36 C38 121.1(6)

C21 C36 C78 120.8(6)

C38 C36 C78 118.0(6)

N4 C37 C16 118.2(7)

N4 C37 C164 121.8(7)

C16 C37 C164 120.0(7)

O7 C38 C36 114.8(5)

O7 C38 C100 119.5(6)

C36 C38 C100 125.6(6)

Si1 C39 C10 121.8(6)

Si1 C39 C64 122.7(7)

C10 C39 C64 115.5(8)

C18 C40 C42 118.7(8)

C18 C40 C64 122.9(8)

C42 C40 C64 118.4(8)

C56 C41 C93 113.9(7)

C56 C41 C99 120.6(7)

C93 C41 C99 125.4(7)

C40 C42 C91 117.1(7)

C40 C42 C118 125.2(7)

C91 C42 C118 117.7(8)

N3 C43 C62 120.1(8)

N3 C43 C83 117.6(6)

C62 C43 C83 122.1(8)

C3 C44 C29 114.5(7)

C3 C44 C77 121.3(7)

C29 C44 C77 124.2(7)

C8 C45 C115 121.2(7)

C8 C45 H20 119.36

C115 C45 H20 119.44

O2 C46 C51 115.5(5)

O2 C46 C55 118.6(6)

C51 C46 C55 125.8(6)

C23 C47 C96 121.9(8)

C23 C47 C125 118.0(8)

C96 C47 C125 120.0(8)

C29 C48 C30 119.7(7)

C29 C48 C133 120.3(6)

C30 C48 C133 120.1(6)

C1 C49 C17 121.6(7)

C1 C49 C52 119.4(7)

C17 C49 C52 118.9(7)

Si4 C50 C24 121.3(5)

Si4 C50 C77 123.6(5)

Si4 C50 H21 30.34

C24 C50 C77 115.0(6)

C24 C50 H21 131.64

C77 C50 H21 106.54

C7 C51 C46 123.7(5)

C7 C51 C96 120.5(6)

C7 C51 H22 47.6

C46 C51 C96 115.7(6)

C46 C51 H22 97.83

C96 C51 H22 129.21

C49 C52 C106 119.1(8)

C49 C52 H23 120.37

C106 C52 H23 120.53

N2 C53 C147 117.5(6)

N2 C53 C153 121.4(8)

C147 C53 C153 121.1(8)

C71 C54 C75 120.5(8)

C71 C54 H24 119.81

C75 C54 H24 119.73

Si7 C55 C46 126.3(6)

Si7 C55 C125 116.5(6)

C46 C55 C125 117.2(8)

N1 C56 C41 121.5(6)

N1 C56 C59 119.5(6)

C41 C56 C59 118.9(6)

Si5 C57 H25 109.41

Si5 C57 H26 109.35

H25 C57 H26 106.44

C67 C58 C113 124.3(8)

C67 C58 H27 117.82

C113 C58 H27 117.85

C56 C59 C95 118.1(7)

C56 C59 H28 120.86

C95 C59 H28 121.08

Si4 C60 H29 109.42

Si4 C60 H30 109.33

H29 C60 H30 104.99

C25 C61 C78 119.8(6)

C25 C61 C80 122.2(6)

C78 C61 C80 118.0(6)

C43 C62 C120 118.7(8)

C43 C62 H31 120.6

C120 C62 H31 120.67

C18 C63 C65 118.8(7)

C18 C63 C72 120.5(7)

C65 C63 C72 120.7(7)

O5 C64 C39 115.9(7)

O5 C64 C40 118.5(7)

C39 C64 C40 125.6(9)

C63 C65 C124 118.9(7)

C63 C65 H32 120.57

C124 C65 H32 120.54

C32 C66 C96 120.0(8)

C32 C66 H33 120.07

C96 C66 H33 119.89

C58 C67 C87 116.0(8)

C58 C67 H34 122.11

C87 C67 H34 121.93

C27 C68 C151 117.0(7)

C27 C68 C157 120.0(7)

C151 C68 C157 123.0(8)

N4 C69 C70 118.1(7)

N4 C69 C126 119.2(7)

C70 C69 C126 122.6(9)

C69 C70 C89 115.8(8)

C69 C70 C116 121.7(8)

C89 C70 C116 122.5(8)

C26 C71 C54 119.5(7)

C26 C71 H35 120.19

C54 C71 H35 120.28

C33 C72 C63 117.7(8)

C33 C72 C119 121.7(8)

C63 C72 C119 120.6(8)

Si5 C73 C152 112.2(6)

Si5 C73 H36 109.44

Si5 C73 H37 109.48

C152 C73 H36 109.5

C152 C73 H37 109.44

H36 C73 H37 106.58

Si5 C74 C4 123.8(5)

Si5 C74 C119 118.0(6)

C4 C74 C119 118.2(7)

C54 C75 C82 118.7(7)

C54 C75 H38 120.61

C82 C75 H38 120.68

H39 C76 H40 109.41

H39 C76 H41 109.46

H40 C76 H41 109.48

O3 C77 C44 122.3(7)

O3 C77 C50 113.5(6)

C44 C77 C50 124.0(7)

C36 C78 C61 118.9(6)

C36 C78 C123 123.0(6)

C61 C78 C123 118.1(6)

C109 C79 C127 121.9(8)

C109 C79 H42 119.1

C127 C79 H42 118.99

C61 C80 C100 123.0(7)

C61 C80 H43 118.42

C100 C80 H43 118.55

C83 C81 C156 119.2(9)

C83 C81 H44 120.41

C156 C81 H44 120.42

C3 C82 C75 121.5(7)

C3 C82 H45 119.27

C75 C82 H45 119.2

C43 C83 C81 117.9(8)

C43 C83 C158 119.3(8)

C81 C83 C158 122.8(8)

C23 C84 C32 119.3(8)

C23 C84 H46 120.39

C32 C84 H46 120.33

C128 C85 C157 114.3(8)

C128 C85 H47 109.44

C128 C85 H48 109.3

C157 C85 H47 109.67

C157 C85 H48 109.51

H47 C85 H48 104.08

C89 C86 C129 120.2(9)

C89 C86 H49 119.93

C129 C86 H49 119.91

C15 C87 C67 122.2(7)

C15 C87 H50 118.79

C67 C87 H50 119.06

C101 C88 C108 119.2(8)

C101 C88 H51 120.42

C108 C88 H51 120.4

C70 C89 C86 121.9(8)

C70 C89 H52 119.13

C86 C89 H52 118.99

Si1 C90 C122 116.6(7)

Si1 C90 H53 109.46

Si1 C90 H54 109.43

C122 C90 H53 109.46

C122 C90 H54 109.46

H53 C90 H54 101.38

C10 C91 C42 119.7(8)

C10 C91 C107 122.0(7)

C42 C91 C107 118.1(7)

N3 C92 C117 119.7(8)

N3 C92 C144 119.2(8)

C117 C92 C144 121.0(8)

C15 C93 C41 112.7(6)

C15 C93 H55 109.64

C15 C93 H56 109.51

C41 C93 H55 109.43

C41 C93 H56 109.37

H55 C93 H56 106

Si4 C94 H57 109.54

Si4 C94 H58 109.43

H57 C94 H58 109.9

C59 C95 C110 119.7(8)

C59 C95 H59 120.26

C110 C95 H59 120.06

C47 C96 C51 119.9(7)

C47 C96 C66 118.6(8)

C51 C96 C66 121.4(7)

Si3 C97 C140 114.5(6)

Si3 C97 H60 109.42

Si3 C97 H61 109.54

C140 C97 H60 109.47

C140 C97 H61 109.53

H60 C97 H61 103.81

C159 C98 H62 109.53

C159 C98 H63 109.39

C159 C98 H64 109.53

H62 C98 H63 109.44

H62 C98 H64 109.56

H63 C98 H64 109.38

C41 C99 C110 119.7(8)

C41 C99 H65 120.07

C110 C99 H65 120.25

Si8 C100 C38 123.9(5)

Si8 C100 C80 120.0(5)

C38 C100 C80 116.0(6)

C28 C101 C88 121.9(7)

C28 C101 H66 119.07

C88 C101 H66 119.03

C131 C102 H67 109.33

C131 C102 H68 109.36

C131 C102 H69 109.43

H67 C102 H68 109.46

H67 C102 H69 109.62

H68 C102 H69 109.62

Si4 C103 H70 109.54

Si4 C103 H71 109.56

Si4 C103 H72 109.49

H70 C103 H71 109.44

H70 C103 H72 109.38

H71 C103 H72 109.4

Si2 C104 H73 109.44

Si2 C104 H74 109.44

Si2 C104 H75 109.48

H73 C104 H74 109.46

H73 C104 H75 109.52

H74 C104 H75 109.48

C25 C105 C167 117.3(4)

C13 C106 C52 121.6(9)

C13 C106 H76 119.26

C52 C106 H76 119.13

C14 C107 C91 121.8(7)

C14 C107 H77 118.96

C91 C107 H77 119.24

C20 C108 C88 122.1(8)

C20 C108 H78 133.15

C88 C108 H78 104.46

C79 C109 C133 120.5(8)

C79 C109 H79 119.78

C133 C109 H79 119.69

C95 C110 C99 123.0(9)

C95 C110 H80 118.57

C99 C110 H80 118.42

Si5 C111 H81 109.63

Si5 C111 H82 109.59

Si5 C111 H83 109.61

H81 C111 H82 109.35

H81 C111 H83 109.34

H82 C111 H83 109.31

Si3 C112 C6 122.6(4)

Si3 C112 C17 121.3(5)

Si3 C112 H84 37.63

C6 C112 C17 116.1(5)

C6 C112 H84 107.75

C17 C112 H84 123.99

C11 C113 C58 117.2(7)

C11 C113 H85 121.3

C58 C113 H85 121.48

C145 C114 C147 123.5(9)

C145 C114 H86 118.18

C147 C114 H86 118.33

Si6 C115 C22 122.4(5)

Si6 C115 C45 120.6(5)

C22 C115 C45 116.7(6)

C16 C116 C70 111.8(7)

C16 C116 H87 109.56

C16 C116 H88 109.47

C70 C116 H87 109.46

C70 C116 H88 109.39

H87 C116 H88 107.06

C92 C117 C139 120.1(8)

C92 C117 C158 119.3(8)

C139 C117 C158 120.6(8)

C2 C118 C42 122.4(7)

C2 C118 H89 118.67

C42 C118 H89 118.96

C72 C119 C74 121.0(7)

C72 C119 H90 119.56

C74 C119 H90 119.42

C62 C120 C156 118.9(9)

C62 C120 H91 120.47

C156 C120 H91 120.68

C16 C121 C137 122.3(8)

C16 C121 H92 118.88

C137 C121 H92 118.84

C90 C122 H93 109.47

C90 C122 H94 109.43

C90 C122 H95 109.45

H93 C122 H94 109.5

H93 C122 H95 109.55

H94 C122 H95 109.42

C78 C123 C167 118.6(6)

C78 C123 H96 120.66

C167 C123 H96 120.76

C19 C124 C65 121.8(8)

C19 C124 H97 119.12

C65 C124 H97 119.09

C47 C125 C55 120.2(8)

C47 C125 H98 119.94

C55 C125 H98 119.82

C69 C126 C129 118.2(8)

C69 C126 H99 121.01

C129 C126 H99 120.75

C30 C127 C79 118.1(7)

C30 C127 H100 120.97

C79 C127 H100 120.94

C85 C128 C132 120.4(8)

C85 C128 H101 109.51

C85 C128 H102 109.39

C132 C128 H101 109.58

C132 C128 H102 109.47

H101 C128 H102 95.72

C86 C129 C126 121.3(8)

C86 C129 H103 119.38

C126 C129 H103 119.35

C1 C130 C13 118.3(7)

C1 C130 H104 120.75

C13 C130 H104 120.93

Si2 C131 C102 114.2(6)

Si2 C131 H105 109.45

Si2 C131 H106 109.37

C102 C131 H105 109.56

C102 C131 H106 109.55

H105 C131 H106 104.21

C27 C132 C128 121.3(8)

C27 C132 H107 119.41

C128 C132 H107 119.25

C48 C133 C109 120.0(7)

C48 C133 H108 119.94

C109 C133 H108 120.01

Si3 C134 H109 109.39

Si3 C134 H110 109.39

Si3 C134 H111 109.41

H109 C134 H110 109.52

H109 C134 H111 109.58

H110 C134 H111 109.53

H112 C135 H113 109.47

H112 C135 H114 109.51

H113 C135 H114 109.5

Si7 C136 C154 118.8(7)

Si7 C136 H115 109.5

Si7 C136 H116 109.46

C154 C136 H115 109.45

C154 C136 H116 109.42

H115 C136 H116 98.19

C121 C137 C149 120.2(9)

C144 C138 C162 120.8(10)

C144 C138 H117 119.77

C162 C138 H117 119.39

C117 C139 C162 118.4(8)

C117 C139 H118 120.86

C162 C139 H118 120.75

C97 C140 H119 109.36

C97 C140 H120 109.41

C97 C140 H121 109.36

H119 C140 H120 109.64

H119 C140 H121 109.42

H120 C140 H121 109.64

Si6 C141 C143 116.9(6)

Si6 C141 H122 109.52

Si6 C141 H123 109.51

C143 C141 H122 109.43

C143 C141 H123 109.48

H122 C141 H123 100.87

C9 C142 H124 109.46

C9 C142 H125 109.41

C9 C142 H126 109.44

H124 C142 H125 109.48

H124 C142 H126 109.54

H125 C142 H126 109.49

C141 C143 H127 109.54

C141 C143 H128 109.58

C141 C143 H129 109.65

H127 C143 H128 109.27

H127 C143 H129 109.36

H128 C143 H129 109.43

C92 C144 C138 118.9(8)

C92 C144 H130 120.57

C138 C144 H130 120.57

C114 C145 C160 117.1(9)

C114 C145 H131 121.51

C160 C145 H131 121.42

Si3 C146 C161 113.2(6)

Si3 C146 H132 109.56

Si3 C146 H133 109.48

C161 C146 H132 109.44

C161 C146 H133 109.36

H132 C146 H133 105.57

C53 C147 C114 116.5(8)

C53 C147 C151 119.9(8)

C114 C147 C151 123.6(8)

Si6 C148 H134 109.41

Si6 C148 H135 109.39

Si6 C148 H136 109.43

H134 C148 H135 109.5

H134 C148 H136 109.57

H135 C148 H136 109.52

C137 C149 C164 118.7(9)

Si7 C150 H137 109.43

Si7 C150 H138 109.47

H137 C150 H138 105.45

C68 C151 C147 110.8(7)

C68 C151 H139 109.36

C68 C151 H140 109.5

C147 C151 H139 109.48

C147 C151 H140 109.49

H139 C151 H140 108.15

C73 C152 H141 109.53

C73 C152 H142 109.56

C73 C152 H143 109.43

H141 C152 H142 109.56

H141 C152 H143 109.33

H142 C152 H143 109.4

C53 C153 C160 118.2(9)

C53 C153 H144 120.95

C160 C153 H144 120.86

C136 C154 H145 109.44

C136 C154 H146 109.39

C136 C154 H147 109.31

H145 C154 H146 109.65

H145 C154 H147 109.57

H146 C154 H147 109.47

Si6 C155 C173 117.8(8)

Si6 C155 H148 109.5

Si6 C155 H149 109.35

C173 C155 H148 109.67

C173 C155 H149 109.46

H148 C155 H149 99.53

C81 C156 C120 123.1(10)

C81 C156 H150 118.68

C120 C156 H150 118.27

C68 C157 C85 124.6(9)

C68 C157 H151 117.68

C85 C157 H151 117.71

C83 C158 C117 109.7(7)

C83 C158 H152 109.49

C83 C158 H153 109.49

C117 C158 H152 109.36

C117 C158 H153 109.55

H152 C158 H153 109.26

Si1 C159 C98 115.3(6)

Si1 C159 H154 109.43

Si1 C159 H155 109.49

C98 C159 H154 109.4

C98 C159 H155 109.54

H154 C159 H155 103.03

C145 C160 C153 123.3(9)

C145 C160 H156 118.41

C153 C160 H156 118.33

C146 C161 H157 109.3

C146 C161 H158 109.41

C146 C161 H159 109.36

H157 C161 H158 109.58

H157 C161 H159 109.56

H158 C161 H159 109.61

C138 C162 C139 120.3(9)

C138 C162 H160 119.82

C139 C162 H160 119.88

Si7 C163 H161 109.48

Si7 C163 H162 109.44

Si7 C163 H163 109.52

H161 C163 H162 109.39

H161 C163 H163 109.51

H162 C163 H163 109.48

C37 C164 C149 120.0(8)

C37 C164 H164 120.07

C149 C164 H164 119.96

Si8 C165 H165 109.45

Si8 C165 H166 109.59

Si8 C165 H167 109.46

H165 C165 H166 109.48

H165 C165 H167 109.29

H166 C165 H167 109.57

C169 C166 H168 109.82

C169 C166 H169 109.27

C169 C166 H170 109.48

H168 C166 H169 109.43

H168 C166 H170 109.79

H169 C166 H170 109.04

C105 C167 C123 122.2(6)

C105 C167 H171 118.84

C123 C167 H171 118.92

Si8 C168 C171 111.4(7)

Si8 C168 H172 109.59

Si8 C168 H173 109.4

C171 C168 H172 109.54

C171 C168 H173 109.36

H172 C168 H173 107.45

Si8 C169 C166 117.4(8)

Si8 C169 H174 109.52

Si8 C169 H175 109.46

C166 C169 H174 109.32

C166 C169 H175 109.34

H174 C169 H175 100.44

H176 C170 H177 109.11

H176 C170 H178 108.92

H177 C170 H178 109.66

C168 C171 H179 109.5

C168 C171 H180 109.53

C168 C171 H181 109.41

H179 C171 H180 109.46

H179 C171 H181 109.49

H180 C171 H181 109.43

C155 C173 H182 109.01

C155 C173 H183 109.34

C155 C173 H184 109.22

H182 C173 H183 109.67

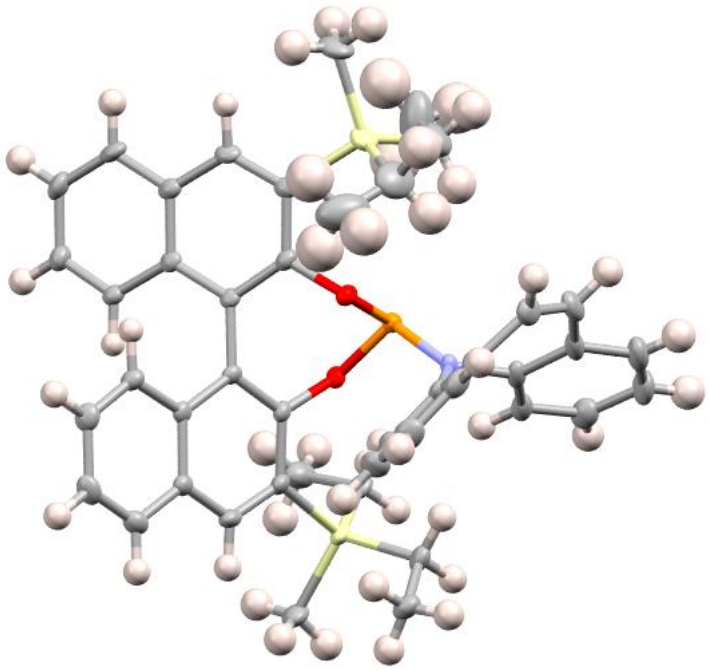
H182 C173 H184 109.62

H183 C173 H184 109.96

Si4 H21 C50 125.22

Si3 H84 C112 115.8

Table SI-1-8f Crystal data and structure refinement for 5-(2,6 bis(diethyl(methyl)silyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-5H-dibenzo[*b*,*f*]azepine (8f).



Empirical formula: $C_{44}H_{46}NO_2PSi_2$

Formula weight: 708.00

Cell setting: orthorhombic

Space group H-M: 'P 21 21 21'

Space group Hall: 'P 2xab;2ybc;2zac'

a/Å 8.2733

b/Å 20.8121

c/Å 22.2982

α/° 90

β/° 90

γ/° 90

Volume/$Å^3$: 3839.41

Z: 4

F(000): 1504

ρ_{cal}cg/cm^3: 1.2248

μ/mm^{-1}: 0.172

Radiation MoKα (λ = 0.71073)

2Θ range for data collection/° 2.07 to 28.3

Index ranges -11 ≤ h ≤ 11, -27 ≤ k ≤ 27, -29 ≤ l ≤ 29

Reflections collected: 9526

Independent reflections 40836 [Rint = 0.0692, Rsigma = 0.0592]

Data/restraints/parameters: 6457/0/ 451

Goodness-of-fit on F^2: 1.19

Final R indexes [I>=3σ (I)] R1 0.0410, wR2 = 0.0332

Final R indexes [all data] R1 = 0.0410, wR2 = 0.0332

Largest diff. peak/hole / e $Å^{-3}$ 0.5113/ -0.40

Table SI-2-8f Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for 5-(2,6 bis(diethyl(methyl)silyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-5H-dibenzo[*b*,*f*]azepine (8f). Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

[Atom Element x y z Ueq]

P1 P 0.72990(7) 0.39762(3) 0.23576(3) 0.01790(17)

Si1 Si 0.95197(8) 0.26972(3) 0.09916(3) 0.0234(2)

Si2 Si 0.66038(10) 0.47820(3) 0.39757(3) 0.0352(2)

O1 O 0.84842(19) 0.41400(6) 0.29332(6) 0.0197(5)

O2 O 0.80247(18) 0.32570(7) 0.21689(6) 0.0191(5)

N1 N 0.8102(2) 0.45501(8) 0.19142(8) 0.0195(6)

C1 C 0.9312(3) 0.20254(10) 0.38258(9) 0.0193(7)

C2 C 1.0409(3) 0.27647(10) 0.17744(9) 0.0216(7)

C3 C 0.9556(3) 0.30076(10) 0.22783(9) 0.0173(6)

C4 C 0.7036(3) 0.47935(11) 0.14521(10) 0.0231(7)

C5 C 0.9853(3) 0.34696(11) 0.05717(10) 0.0277(8)

C6 C 0.8933(3) 0.16013(12) 0.42703(10) 0.0252(8)

C7 C 0.9092(3) 0.31333(10) 0.33833(9) 0.0160(7)

C8 C 1.2556(3) 0.27874(10) 0.35167(9) 0.0210(7)

C9 C 0.7336(3) 0.24563(10) 0.10109(10) 0.0277(7)

C10 C 1.1779(3) 0.27819(9) 0.29447(9) 0.0164(6)

C11 C 1.0134(3) 0.29696(10) 0.28606(9) 0.0161(6)

C12 C 0.6379(3) 0.43674(12) 0.10401(11) 0.0266(8)

C13 C 0.7465(3) 0.39395(10) 0.39302(9) 0.0207(7)

C14 C 0.9860(3) 0.54787(11) 0.21413(10) 0.0249(8)

C15 C 0.7899(3) 0.28743(10) 0.43650(9) 0.0207(7)

C16 C 1.1043(3) 0.44535(12) 0.18823(10) 0.0237(7)

C17 C 0.9684(3) 0.48295(11) 0.19647(10) 0.0211(7)

C18 C 0.8055(3) 0.18008(12) 0.47781(11) 0.0294(8)

C19 C 0.8332(3) 0.37175(10) 0.34229(9) 0.0184(7)

C20 C 1.2723(3) 0.25984(10) 0.24422(9) 0.0196(7)

C21 C 1.1977(3) 0.25700(10) 0.18754(10) 0.0257(8)

C22 C 0.8800(3) 0.26785(10) 0.38575(9) 0.0176(6)

C23 C 0.7303(3) 0.35152(10) 0.43946(10) 0.0211(7)

C24 C 0.7122(3) 0.59119(11) 0.18878(12) 0.0321(8)

C25 C 1.4139(3) 0.26239(11) 0.35781(11) 0.0255(8)

C26 C 0.6586(3) 0.54415(11) 0.14447(11) 0.0290(8)

C27 C 0.8506(3) 0.59197(11) 0.22000(11) 0.0308(8)

C28 C 1.2771(3) 0.53346(13) 0.21637(11) 0.0351(9)

C29 C 1.0635(4) 0.20415(12) 0.05913(10) 0.0354(9)

C30 C 0.5916(4) 0.49084(15) 0.47680(12) 0.0443(11)

C31 C 0.5283(3) 0.45756(13) 0.06093(12) 0.0348(9)

C32 C 1.4378(3) 0.24387(11) 0.25226(10) 0.0253(8)

C33 C 1.1409(3) 0.57113(12) 0.22463(11) 0.0317(9)

C34 C 0.7551(3) 0.24251(12) 0.48223(9) 0.0263(8)

C35 C 1.5072(3) 0.24492(11) 0.30723(11) 0.0265(8)

C36 C 0.4864(4) 0.48838(15) 0.34602(14) 0.0510(11)

C37 C 1.2592(3) 0.47023(12) 0.19804(11) 0.0335(9)

C38 C 1.1642(3) 0.36294(12) 0.04619(11) 0.0320(9)

C39 C 0.5505(3) 0.56443(13) 0.09986(13) 0.0389(9)

C40 C 0.4865(3) 0.52238(14) 0.05857(13) 0.0408(10)

C41 C 0.7004(4) 0.17857(12) 0.12614(12) 0.0422(10)

C42 C 0.8229(5) 0.53891(13) 0.37601(15) 0.0620(14)

C45 C 0.3669(5) 0.43856(18) 0.3502(2) 0.0881(18)

C46 C 0.9887(5) 0.52245(18) 0.39047(18) 0.0783(16)

H1 H 0.993123 0.188229 0.348714 0.0232

H2 H 0.929309 0.345251 0.019494 0.0332

H3 H 0.935014 0.381682 0.078502 0.0332

H4 H 0.926979 0.116135 0.423654 0.0303

H5 H 1.194745 0.290908 0.38653 0.0252

H6 H 0.673127 0.276819 0.123505 0.0333

H7 H 0.688535 0.249042 0.061545 0.0333

H8 H 0.668462 0.392267 0.105288 0.0319

H9 H 1.092248 0.401521 0.175579 0.0284

H10 H 0.78105 0.150011 0.509177 0.0352

H11 H 1.259083 0.240715 0.154314 0.0308

H12 H 0.67684 0.365463 0.475387 0.0254

H13 H 0.638969 0.626003 0.196546 0.0385

H14 H 1.462818 0.262718 0.396848 0.0305

H15 H 0.86152 0.625303 0.249484 0.0369

H16 H 1.38288 0.550963 0.223261 0.0421

H17 H 1.029164 0.202601 0.01803 0.0425

H18 H 1.177534 0.212541 0.060765 0.0425

H19 H 1.041014 0.163709 0.078078 0.0425

H20 H 0.673242 0.475644 0.503898 0.0532

H21 H 0.573205 0.535799 0.483582 0.0532

H22 H 0.493067 0.467542 0.483487 0.0532

H23 H 0.481979 0.427596 0.033088 0.0417

H24 H 1.501631 0.232107 0.218034 0.0304

H25 H 1.153935 0.614658 0.238021 0.038

H26 H 0.695225 0.25599 0.516901 0.0315

H27 H 1.619155 0.233856 0.311851 0.0317

H28 H 0.436457 0.529305 0.353119 0.0612

H29 H 0.524894 0.491151 0.30548 0.0612

H30 H 1.352593 0.443611 0.192102 0.0402

H31 H 1.172468 0.40393 0.026693 0.0384

H32 H 1.220291 0.364409 0.083854 0.0384

H33 H 1.211546 0.330461 0.021178 0.0384

H34 H 0.520236 0.608925 0.098079 0.0467

H35 H 0.413468 0.537608 0.02829 0.0489

H36 H 0.586315 0.170164 0.124945 0.0507

H37 H 0.756177 0.147168 0.10236 0.0507

H38 H 0.7377 0.176267 0.166843 0.0507

H39 H 0.814623 0.548493 0.334007 0.0744

H40 H 0.797026 0.580006 0.393053 0.0744

H41 H 0.267104 0.453456 0.333225 0.1057

H42 H 0.403382 0.401346 0.328689 0.1057

H43 H 0.350315 0.427571 0.391585 0.1057

H44 H 1.059214 0.55626 0.377284 0.0939

H45 H 0.99927 0.517061 0.433047 0.0939

H46 H 1.017475 0.483131 0.370643 0.0939

Table SI-3-8f Anisotropic Displacement Parameters (Å2×103) for 5-(2,6 bis(diethyl(methyl)silyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-5H-dibenzo[*b*,*f*]azepine (8f). The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

[Atom Element U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}]

P1 P 0.0194(3) 0.0156(3) 0.0187(3) 0.0011(2) 0.0027(2) 0.0020(2)

Si1 Si 0.0343(4) 0.0238(3) 0.0120(3) 0.0050(3) 0.0007(3) 0.0016(3)

Si2 Si 0.0500(5) 0.0268(4) 0.0289(4) 0.0115(3) 0.0045(4) -0.0077(3)

O1 O 0.0265(9) 0.0153(8) 0.0172(8) -0.0010(6) 0.0027(7) 0.0012(6)

O2 O 0.0229(9) 0.0179(8) 0.0164(8) 0.0024(6) -0.0024(6) 0.0007(6)

N1 N 0.0175(11) 0.0174(9) 0.0237(10) 0.0017(8) 0.0008(8) 0.0069(8)

C1 C 0.0221(13) 0.0218(12) 0.0140(11) -0.0014(10) 0.0001(9) -0.0006(9)

C2 C 0.0285(14) 0.0210(12) 0.0153(10) 0.0032(10) 0.0024(10) 0.0049(9)

C3 C 0.0229(13) 0.0140(10) 0.0149(11) 0.0002(9) -0.0010(9) 0.0024(8)

C4 C 0.0158(13) 0.0233(12) 0.0304(13) -0.0011(10) 0.0003(10) 0.0120(10)

C5 C 0.0312(15) 0.0314(14) 0.0204(12) 0.0011(11) -0.0031(10) 0.0087(10)

C6 C 0.0317(15) 0.0225(13) 0.0215(12) -0.0001(10) -0.0023(11) 0.0045(10)

C7 C 0.0176(12) 0.0183(11) 0.0121(10) -0.0028(9) -0.0027(9) -0.0020(8)

C8 C 0.0233(14) 0.0230(12) 0.0165(10) -0.0033(10) 0.0003(10) -0.0003(9)

C9 C 0.0401(15) 0.0289(13) 0.0141(10) 0.0003(11) -0.0052(11) -0.0020(10)

C10 C 0.0203(12) 0.0107(10) 0.0183(11) -0.0033(9) 0.0011(9) 0.0028(8)

C11 C 0.0192(12) 0.0138(10) 0.0152(10) -0.0034(9) 0.0026(9) 0.0014(8)

C12 C 0.0213(13) 0.0279(13) 0.0305(13) 0.0003(10) 0.0007(11) 0.0110(11)

C13 C 0.0184(12) 0.0253(11) 0.0184(10) -0.0030(10) -0.0018(9) -0.0063(9)

C14 C 0.0269(14) 0.0228(13) 0.0250(12) -0.0039(10) 0.0039(10) 0.0060(10)

C15 C 0.0192(13) 0.0279(13) 0.0150(10) -0.0017(10) -0.0015(9) -0.0007(9)

C16 C 0.0225(14) 0.0279(13) 0.0208(12) 0.0011(10) 0.0024(10) 0.0027(10)

C17 C 0.0199(13) 0.0230(12) 0.0205(12) -0.0028(10) 0.0010(9) 0.0077(9)

C18 C 0.0359(16) 0.0302(14) 0.0220(12) -0.0019(12) -0.0009(11) 0.0112(10)

C19 C 0.0206(12) 0.0204(12) 0.0143(10) -0.0042(9) -0.0011(9) 0.0018(9)

C20 C 0.0235(13) 0.0152(10) 0.0200(11) 0.0003(10) 0.0035(9) 0.0034(8)

C21 C 0.0356(16) 0.0237(12) 0.0177(11) 0.0065(10) 0.0092(10) 0.0025(10)

C22 C 0.0161(12) 0.0218(12) 0.0149(10) -0.0026(9) -0.0037(8) -0.0006(9)

C23 C 0.0218(13) 0.0264(12) 0.0152(11) -0.0018(10) 0.0000(10) -0.0079(9)

C24 C 0.0300(15) 0.0178(12) 0.0486(15) 0.0052(11) 0.0045(13) 0.0072(11)

C25 C 0.0233(14) 0.0258(13) 0.0272(13) -0.0058(10) -0.0064(10) 0.0009(10)

C26 C 0.0214(13) 0.0268(13) 0.0388(15) 0.0057(11) 0.0034(11) 0.0148(11)

C27 C 0.0400(16) 0.0172(13) 0.0351(15) -0.0006(11) 0.0059(12) 0.0072(10)

C28 C 0.0234(15) 0.0450(17) 0.0369(14) -0.0132(13) -0.0022(11) 0.0060(12)

C29 C 0.0528(18) 0.0367(15) 0.0166(12) 0.0089(13) 0.0037(12) -0.0004(11)

C30 C 0.049(2) 0.0503(19) 0.0334(15) 0.0126(14) 0.0057(13) -0.0200(14)

C31 C 0.0251(15) 0.0448(17) 0.0345(14) -0.0029(12) -0.0033(12) 0.0068(12)

C32 C 0.0222(13) 0.0220(13) 0.0318(14) -0.0007(10) 0.0059(10) 0.0018(10)

C33 C 0.0413(17) 0.0276(14) 0.0261(14) -0.0087(12) -0.0004(12) 0.0079(11)

C34 C 0.0272(14) 0.0393(15) 0.0124(11) -0.0019(11) 0.0030(10) 0.0020(9)

C35 C 0.0146(12) 0.0234(12) 0.0414(15) -0.0035(9) -0.0025(11) 0.0028(11)

C36 C 0.057(2) 0.0429(18) 0.053(2) 0.0190(15) -0.0027(16) -0.0070(14)

C37 C 0.0220(14) 0.0428(16) 0.0355(14) 0.0021(12) 0.0028(12) -0.0002(12)

C38 C 0.0334(16) 0.0420(16) 0.0207(13) 0.0002(12) 0.0026(11) 0.0044(11)

C39 C 0.0303(15) 0.0370(15) 0.0494(17) 0.0085(12) -0.0016(14) 0.0176(14)

C40 C 0.0305(17) 0.0483(18) 0.0435(17) 0.0087(14) -0.0108(13) 0.0166(14)

C41 C 0.054(2) 0.0317(15) 0.0413(16) 0.0041(13) 0.0154(14) -0.0003(12)

C42 C 0.090(3) 0.0276(17) 0.068(2) -0.0023(17) 0.014(2) -0.0084(15)

C45 C 0.081(3) 0.068(3) 0.115(4) -0.014(2) -0.041(3) 0.032(2)

C46 C 0.096(3) 0.071(2) 0.068(3) -0.033(2) 0.028(2) -0.018(2)

Table SI-4-8f Bond Lengths for 5-(2,6 bis(diethyl(methyl)silyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-5H-dibenzo[*b*,*f*]azepine (8f).

[Atom Atom Length/Å]

P1 N1 1.6872(18)

Si1 C2 1.899(2)

Si1 C5 1.881(2)

Si1 C9 1.876(3)

Si1 C29 1.875(3)

Si2 C13 1.894(2)

Si2 C30 1.875(2)

Si2 C36 1.855(3)

Si2 C42 1.906(3)

O1 C19 1.407(2)

O2 C3 1.390(3)

N1 C4 1.448(3)

N1 C17 1.435(3)

C1 C6 1.363(3)

C1 C22 1.427(3)

C1 H1 0.9596

C2 C3 1.420(3)

C2 C21 1.378(3)

C3 C11 1.386(3)

C4 C12 1.388(3)

C4 C26 1.401(3)

C5 C38 1.536(3)

C5 H2 0.9606

C5 H3 0.959

C6 C18 1.409(3)

C6 H4 0.9594

C7 C11 1.489(3)

C7 C19 1.373(3)

C7 C22 1.438(3)

C8 C10 1.428(3)

C8 C25 1.360(3)

C8 H5 0.9603

C9 C41 1.527(3)

C9 H6 0.9602

C9 H7 0.9602

C10 C11 1.429(3)

C10 C20 1.418(3)

C12 C31 1.391(3)

C12 H8 0.9591

C13 C19 1.417(3)

C13 C23 1.369(3)

C14 C17 1.416(3)

C14 C27 1.454(3)

C14 C33 1.389(3)

C15 C22 1.415(3)

C15 C23 1.424(3)

C15 C34 1.413(3)

C16 C17 1.381(3)

C16 C37 1.399(3)

C16 H9 0.9608

C18 C34 1.368(3)

C18 H10 0.9605

C20 C21 1.409(3)

C20 C32 1.420(3)

C21 H11 0.9594

C23 H12 0.9594

C24 C26 1.459(3)

C24 C27 1.340(3)

C24 H13 0.96

C25 C35 1.415(3)

C25 H14 0.9602

C26 C39 1.402(3)

C27 H15 0.9596

C28 C33 1.384(3)

C28 C37 1.388(3)

C28 H16 0.9599

C29 H17 0.9593

C29 H18 0.9604

C29 H19 0.9593

C30 H20 0.9596

C30 H21 0.9608

C30 H22 0.9597

C31 C40 1.393(3)

C31 H23 0.9599

C32 C35 1.352(3)

C32 H24 0.9607

C33 H25 0.9607

C34 H26 0.9602

C35 H27 0.9599

C36 C45 1.435(5)

C36 H28 0.9595

C36 H29 0.9597

C37 H30 0.9594

C38 H31 0.9608

C38 H32 0.9598

C38 H33 0.9594

C39 C40 1.376(3)

C39 H34 0.9607

C40 H35 0.9602

C41 H36 0.9604

C41 H37 0.9597

C41 H38 0.9607

C42 C46 1.451(6)

C42 H39 0.9599

C42 H40 0.9604

C45 H41 0.9595

C45 H42 0.9604

C45 H43 0.9608

C46 H44 0.9611

C46 H45 0.9592

C46 H46 0.9595

Table SI-5-8f Bond Angles for 5-(2,6 bis(diethyl(methyl)silyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-5H-dibenzo[*b*,*f*]azepine (8f).

[Atom Atom Atom Angle/°

C2 Si1 C5 109.68(10)

C2 Si1 C9 111.83(10)

C2 Si1 C29 107.54(11)

C5 Si1 C9 112.43(11)

C5 Si1 C29 108.28(10)

C9 Si1 C29 106.87(12)

C13 Si2 C30 107.10(10)

C13 Si2 C36 111.38(10)

C13 Si2 C42 109.53(12)

C30 Si2 C36 109.43(13)

C30 Si2 C42 111.05(11)

C36 Si2 C42 108.37(12)

P1 N1 C4 115.08(14)

P1 N1 C17 126.82(15)

C4 N1 C17 118.06(17)

C6 C1 C22 120.9(2)

C6 C1 H1 119.62

C22 C1 H1 119.51

Si1 C2 C3 124.13(18)

Si1 C2 C21 119.50(16)

C3 C2 C21 116.4(2)

O2 C3 C2 116.54(18)

O2 C3 C11 120.00(19)

C2 C3 C11 123.3(2)

N1 C4 C12 119.14(19)

N1 C4 C26 120.43(19)

C12 C4 C26 120.3(2)

Si1 C5 C38 113.88(15)

Si1 C5 H2 109.41

Si1 C5 H3 109.49

C38 C5 H2 109.45

C38 C5 H3 109.57

H2 C5 H3 104.65

C1 C6 C18 120.8(2)

C1 C6 H4 119.61

C18 C6 H4 119.61

C11 C7 C19 121.17(19)

C11 C7 C22 121.53(19)

C19 C7 C22 117.3(2)

C10 C8 C25 121.4(2)

C10 C8 H5 119.26

C25 C8 H5 119.31

Si1 C9 C41 115.23(18)

Si1 C9 H6 109.44

Si1 C9 H7 109.44

C41 C9 H6 109.53

C41 C9 H7 109.49

H6 C9 H7 103.01

C8 C10 C11 123.0(2)

C8 C10 C20 117.4(2)

C11 C10 C20 119.66(19)

C3 C11 C7 121.4(2)

C3 C11 C10 117.9(2)

C7 C11 C10 120.75(19)

C4 C12 C31 120.9(2)

C4 C12 H8 119.53

C31 C12 H8 119.61

Si2 C13 C19 122.33(15)

Si2 C13 C23 121.35(17)

C19 C13 C23 116.3(2)

C17 C14 C27 123.3(2)

C17 C14 C33 118.3(2)

C27 C14 C33 118.42(19)

C22 C15 C23 119.27(19)

C22 C15 C34 119.67(19)

C23 C15 C34 121.0(2)

C17 C16 C37 121.1(2)

C17 C16 H9 119.46

C37 C16 H9 119.44

N1 C17 C14 120.1(2)

N1 C17 C16 120.18(19)

C14 C17 C16 119.6(2)

C6 C18 C34 119.7(2)

C6 C18 H10 120.11

C34 C18 H10 120.15

O1 C19 C7 117.56(18)

O1 C19 C13 117.47(18)

C7 C19 C13 124.91(19)

C10 C20 C21 118.6(2)

C10 C20 C32 119.6(2)

C21 C20 C32 121.8(2)

C2 C21 C20 123.1(2)

C2 C21 H11 118.49

C20 C21 H11 118.38

C1 C22 C7 122.70(19)

C1 C22 C15 118.01(19)

C7 C22 C15 119.22(19)

C13 C23 C15 122.4(2)

C13 C23 H12 118.74

C15 C23 H12 118.86

C26 C24 C27 128.3(2)

C26 C24 H13 115.84

C27 C24 H13 115.88

C8 C25 C35 120.6(2)

C8 C25 H14 119.7

C35 C25 H14 119.67

C4 C26 C24 123.9(2)

C4 C26 C39 117.8(2)

C24 C26 C39 118.23(19)

C14 C27 C24 127.1(2)

C14 C27 H15 116.45

C24 C27 H15 116.43

C33 C28 C37 119.3(2)

C33 C28 H16 120.47

C37 C28 H16 120.26

Si1 C29 H17 109.44

Si1 C29 H18 109.38

Si1 C29 H19 109.43

H17 C29 H18 109.5

H17 C29 H19 109.58

H18 C29 H19 109.5

Si2 C30 H20 109.5

Si2 C30 H21 109.44

Si2 C30 H22 109.5

H20 C30 H21 109.44

H20 C30 H22 109.53

H21 C30 H22 109.43

C12 C31 C40 119.3(2)

C12 C31 H23 120.21

C40 C31 H23 120.45

C20 C32 C35 121.4(2)

C20 C32 H24 119.25

C35 C32 H24 119.37

C14 C33 C28 122.2(2)

C14 C33 H25 118.94

C28 C33 H25 118.9

C15 C34 C18 120.9(2)

C15 C34 H26 119.53

C18 C34 H26 119.55

C25 C35 C32 119.6(2)

C25 C35 H27 120.13

C32 C35 H27 120.25

Si2 C36 C45 114.3(2)

Si2 C36 H28 109.46

Si2 C36 H29 109.45

C45 C36 H28 109.47

C45 C36 H29 109.45

H28 C36 H29 104.22

C16 C37 C28 119.6(2)

C16 C37 H30 120.24

C28 C37 H30 120.14

C5 C38 H31 109.41

C5 C38 H32 109.46

C5 C38 H33 109.55

H31 C38 H32 109.42

H31 C38 H33 109.45

H32 C38 H33 109.53

C26 C39 C40 122.0(2)

C26 C39 H34 119.04

C40 C39 H34 118.96

C31 C40 C39 119.7(2)

C31 C40 H35 120.08

C39 C40 H35 120.26

C9 C41 H36 109.51

C9 C41 H37 109.55

C9 C41 H38 109.49

H36 C41 H37 109.46

H36 C41 H38 109.38

H37 C41 H38 109.43

Si2 C42 C46 117.0(2)

Si2 C42 H39 109.49

Si2 C42 H40 109.46

C46 C42 H39 109.52

C46 C42 H40 109.48

H39 C42 H40 100.66

C36 C45 H41 109.53

C36 C45 H42 109.5

C36 C45 H43 109.48

H41 C45 H42 109.49

H41 C45 H43 109.45

H42 C45 H43 109.37

C42 C46 H44 109.39

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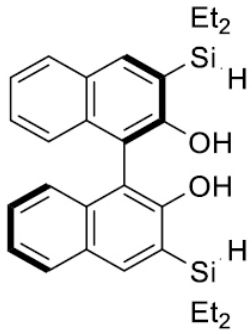
H44 C46 H45 109.44

H44 C46 H46 109.42

H45 C46 H46 109.58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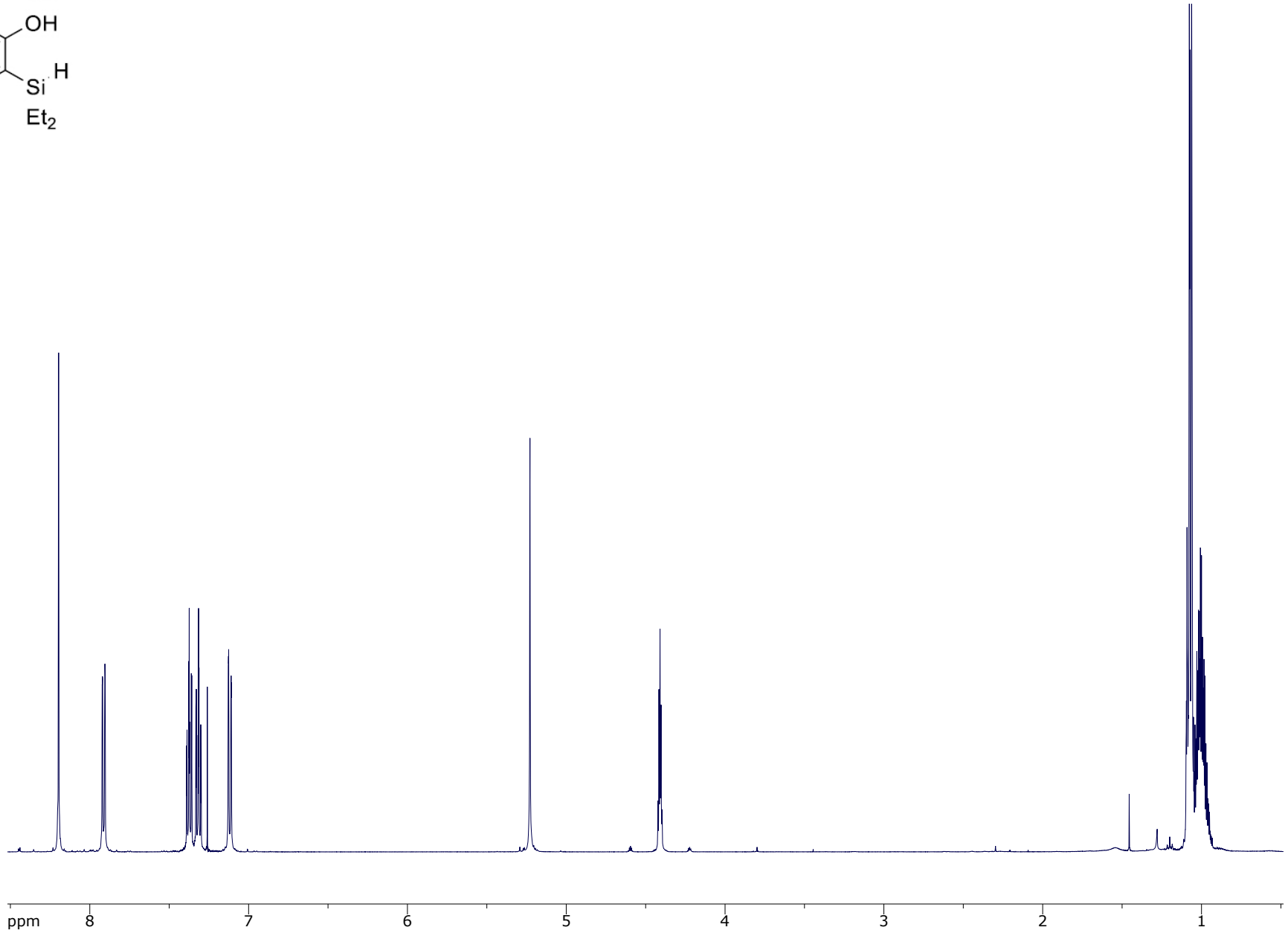
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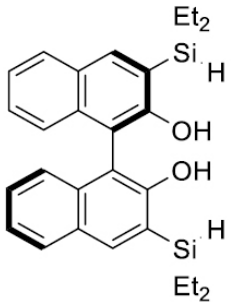
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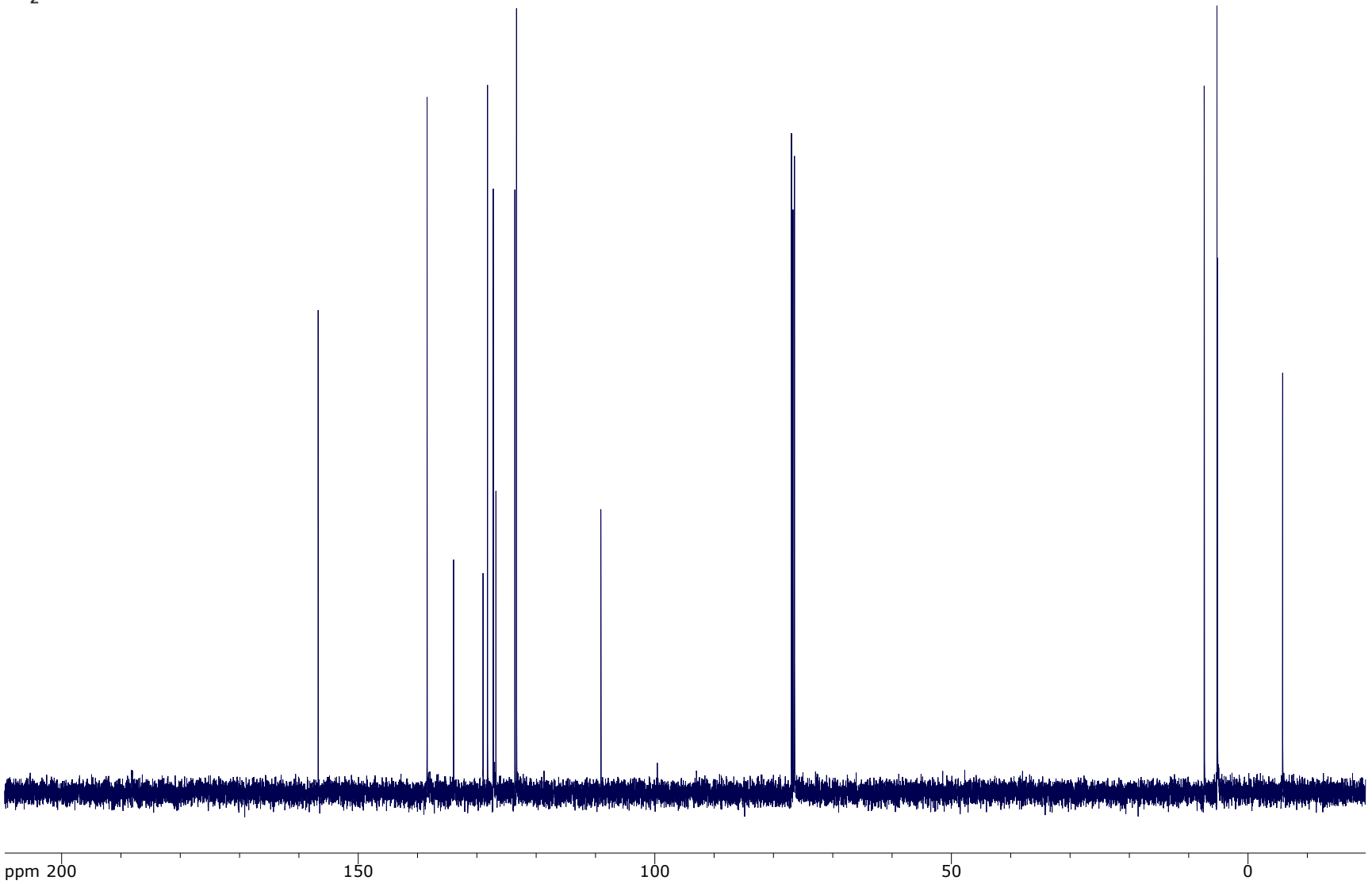
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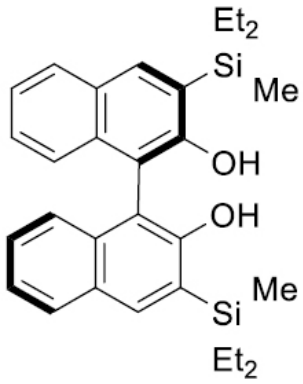
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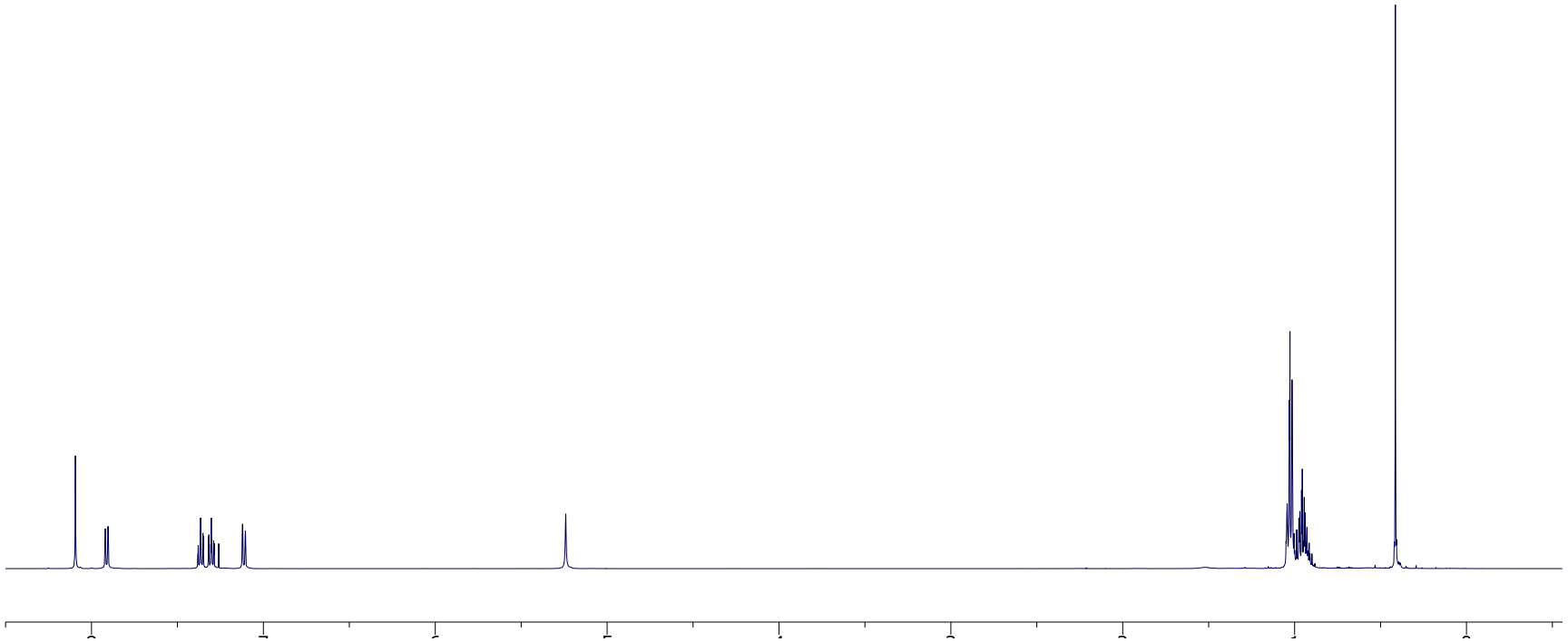
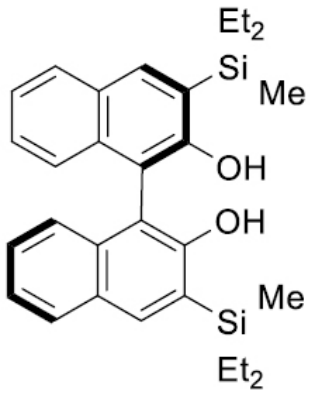
Si
Et2

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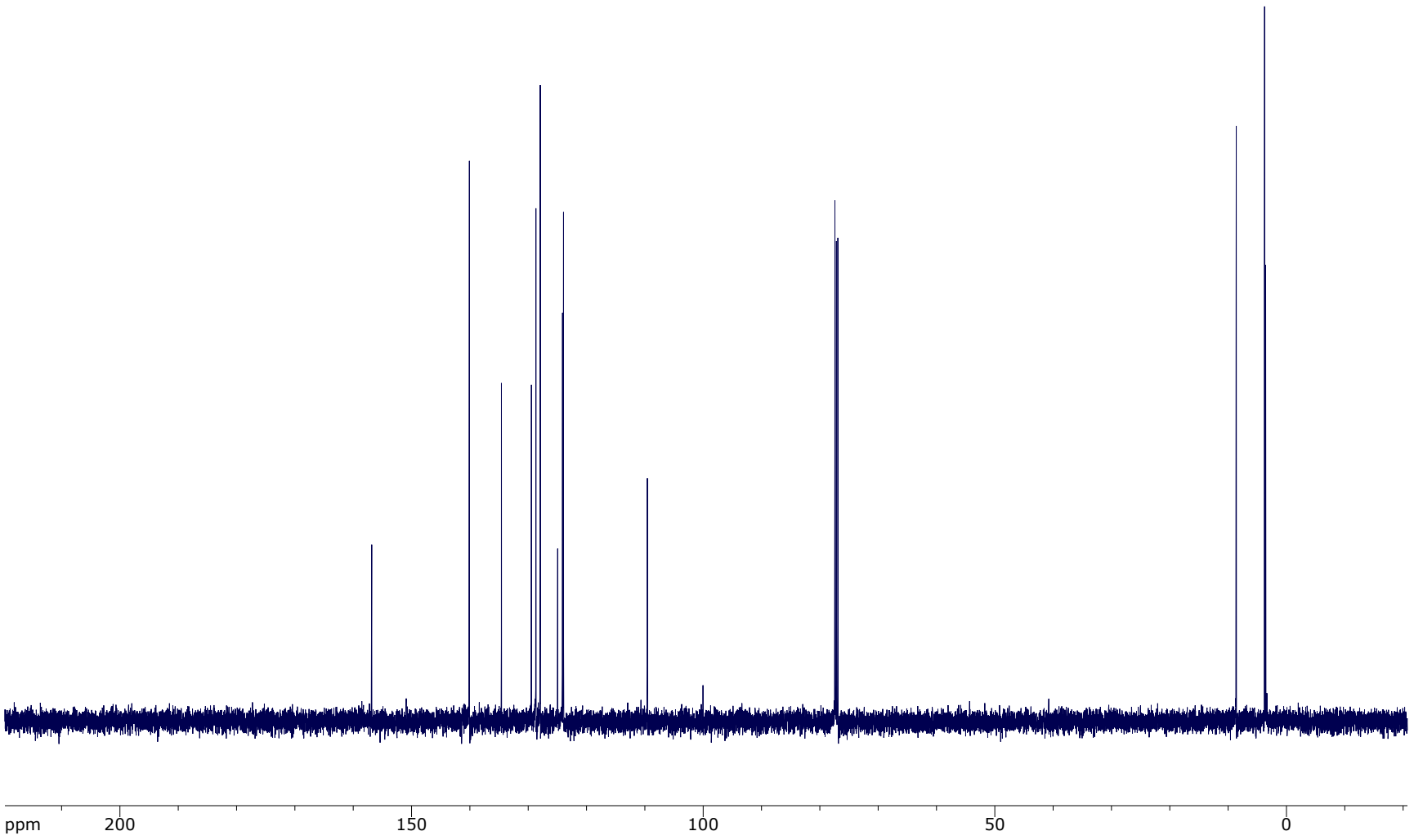
Si
Et2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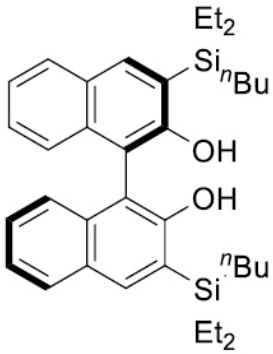
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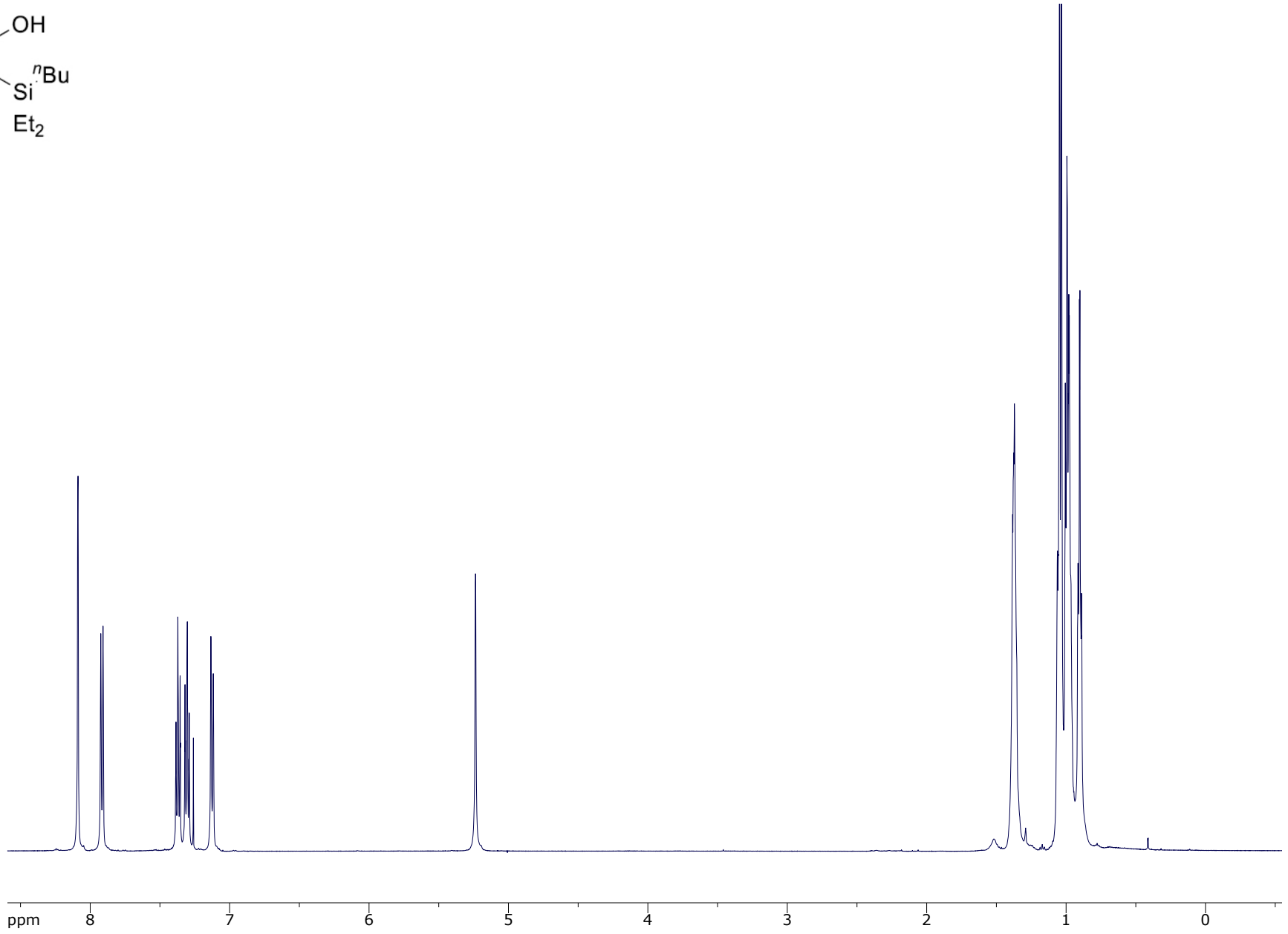
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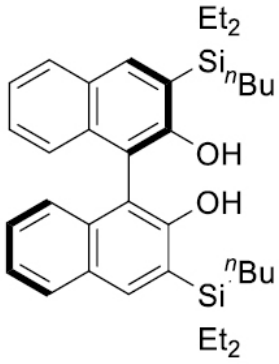
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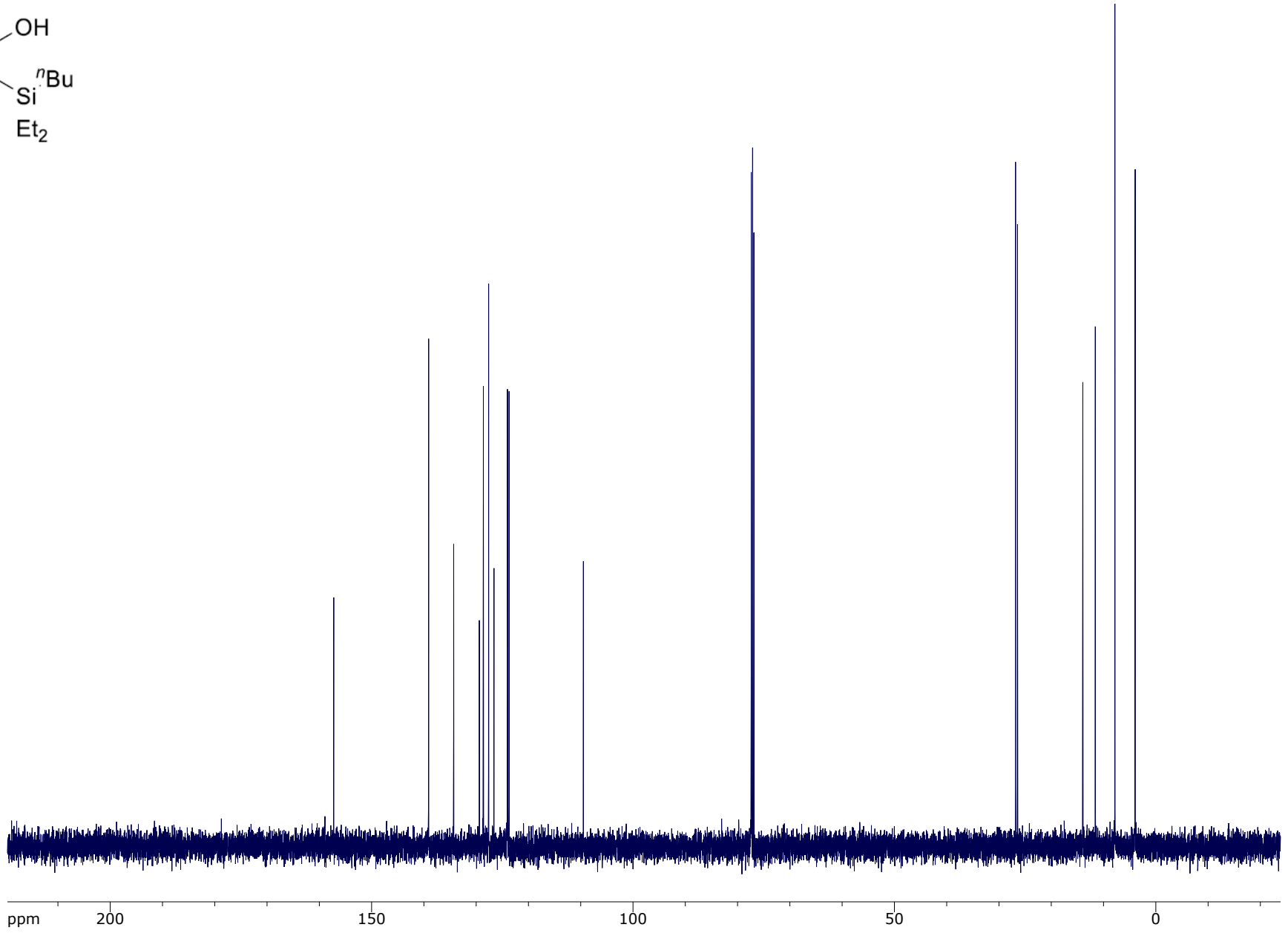
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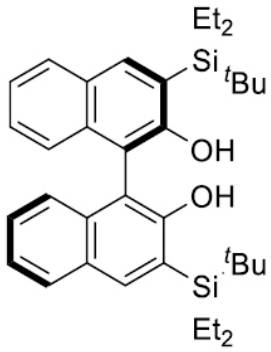
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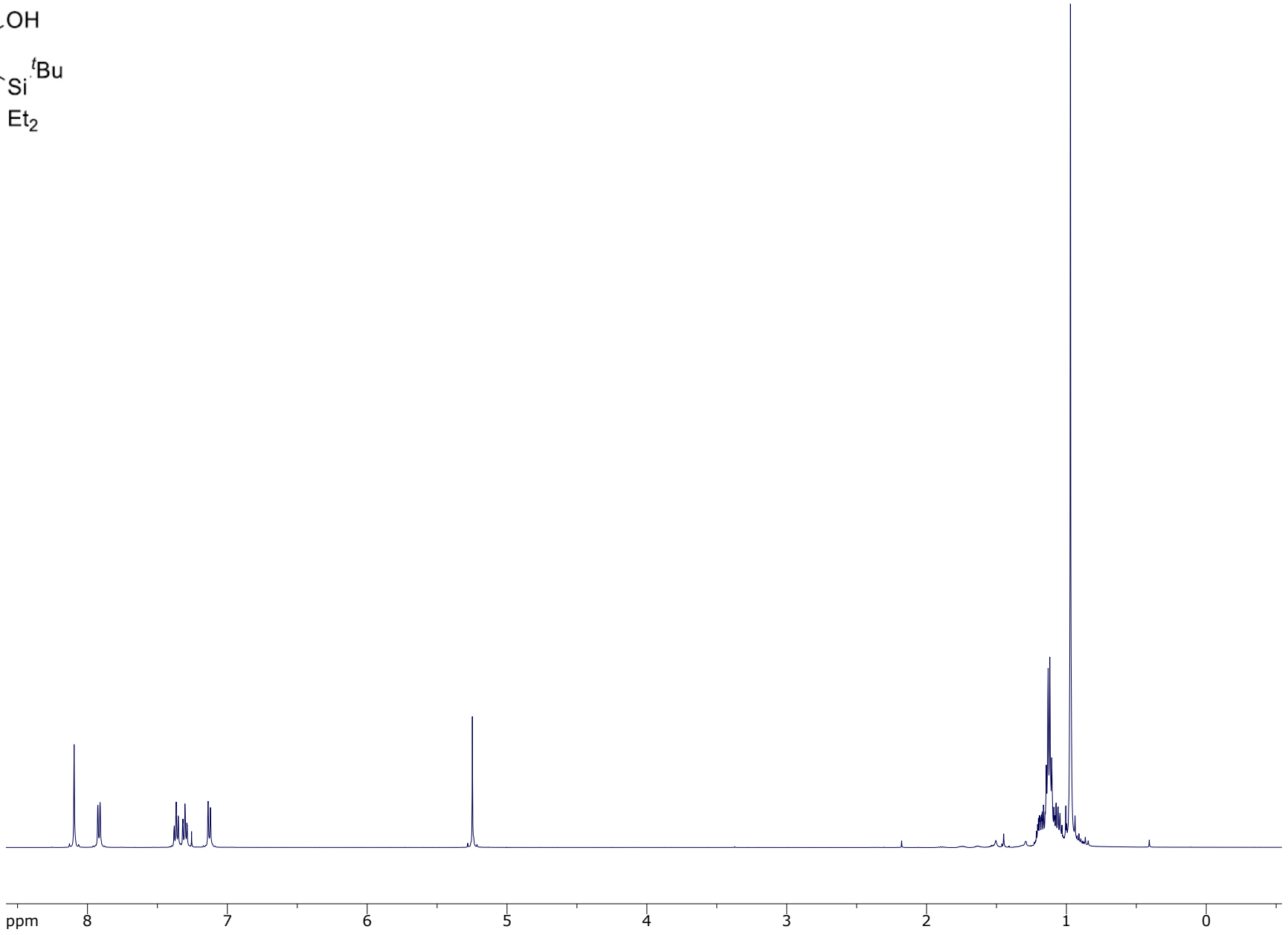
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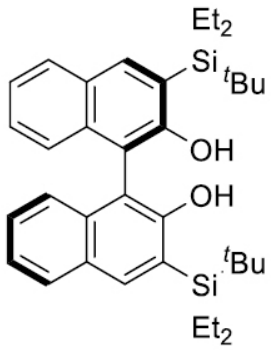
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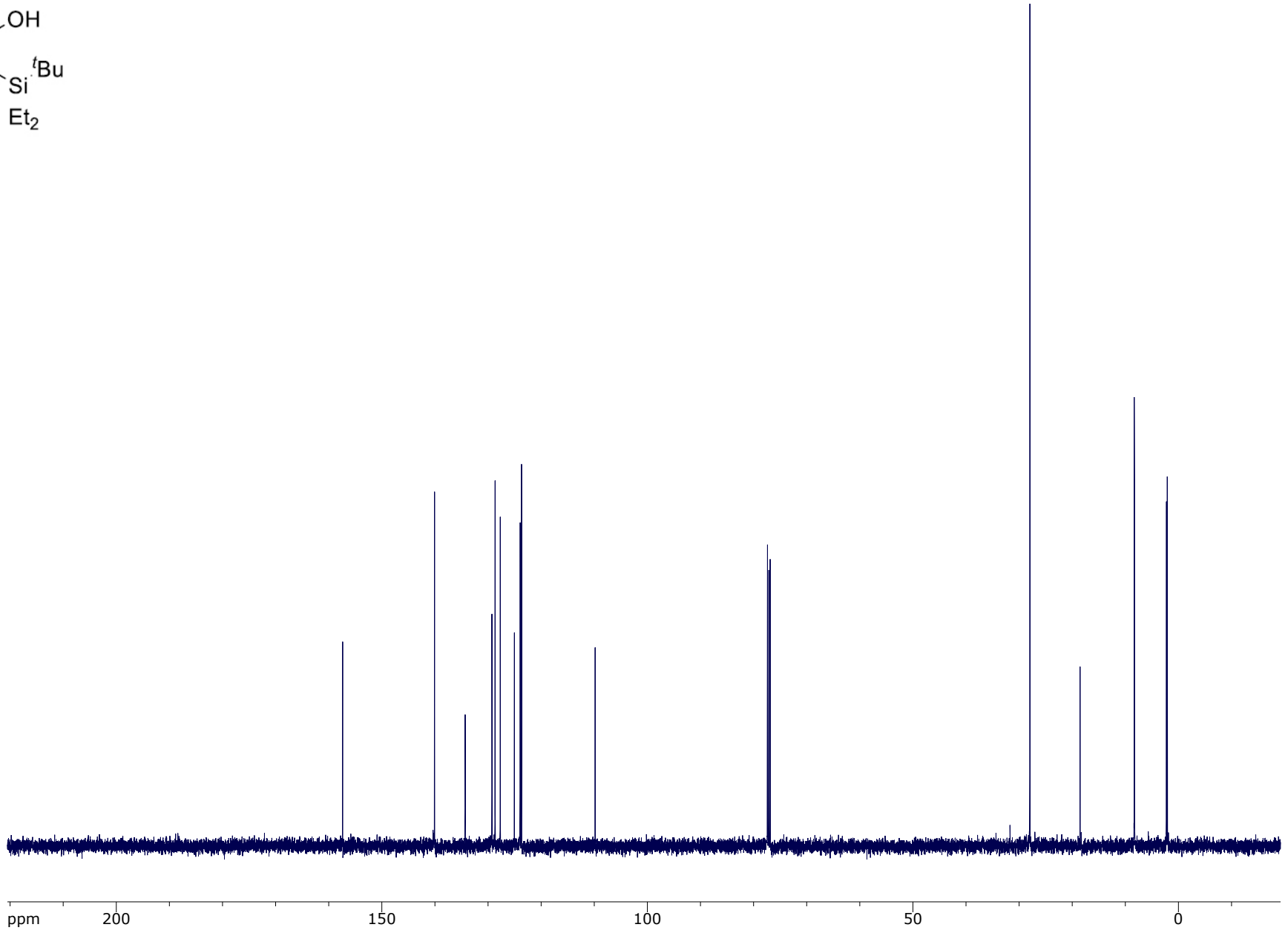
Si
Et2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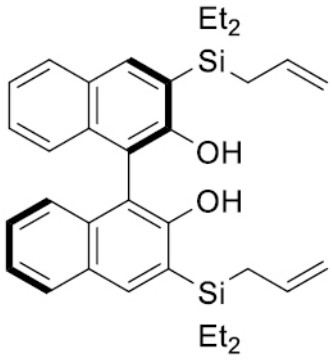
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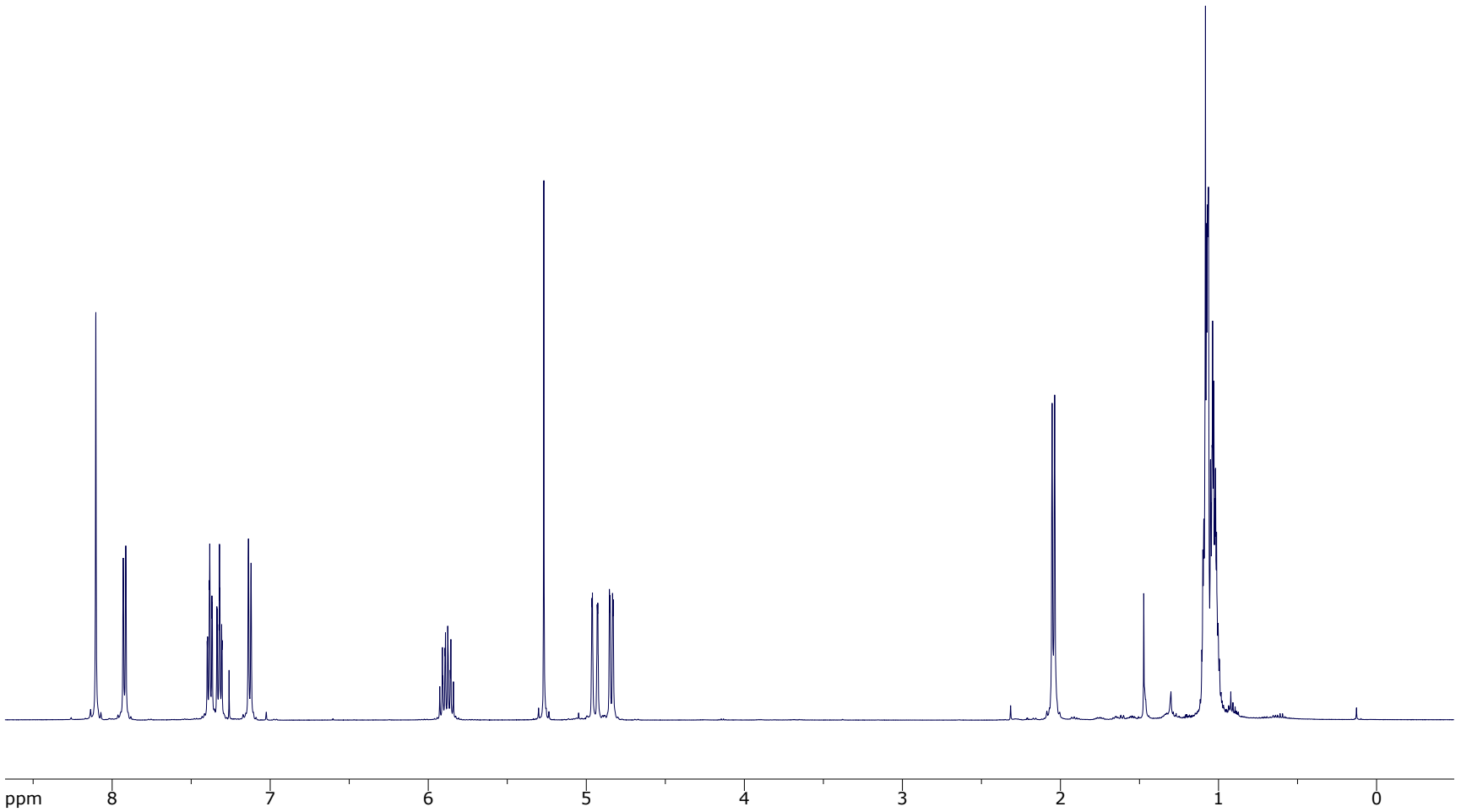
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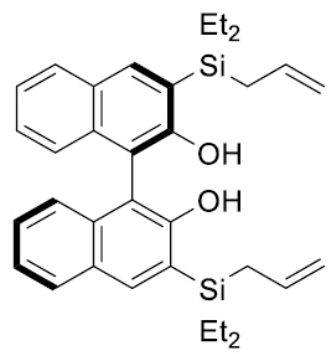
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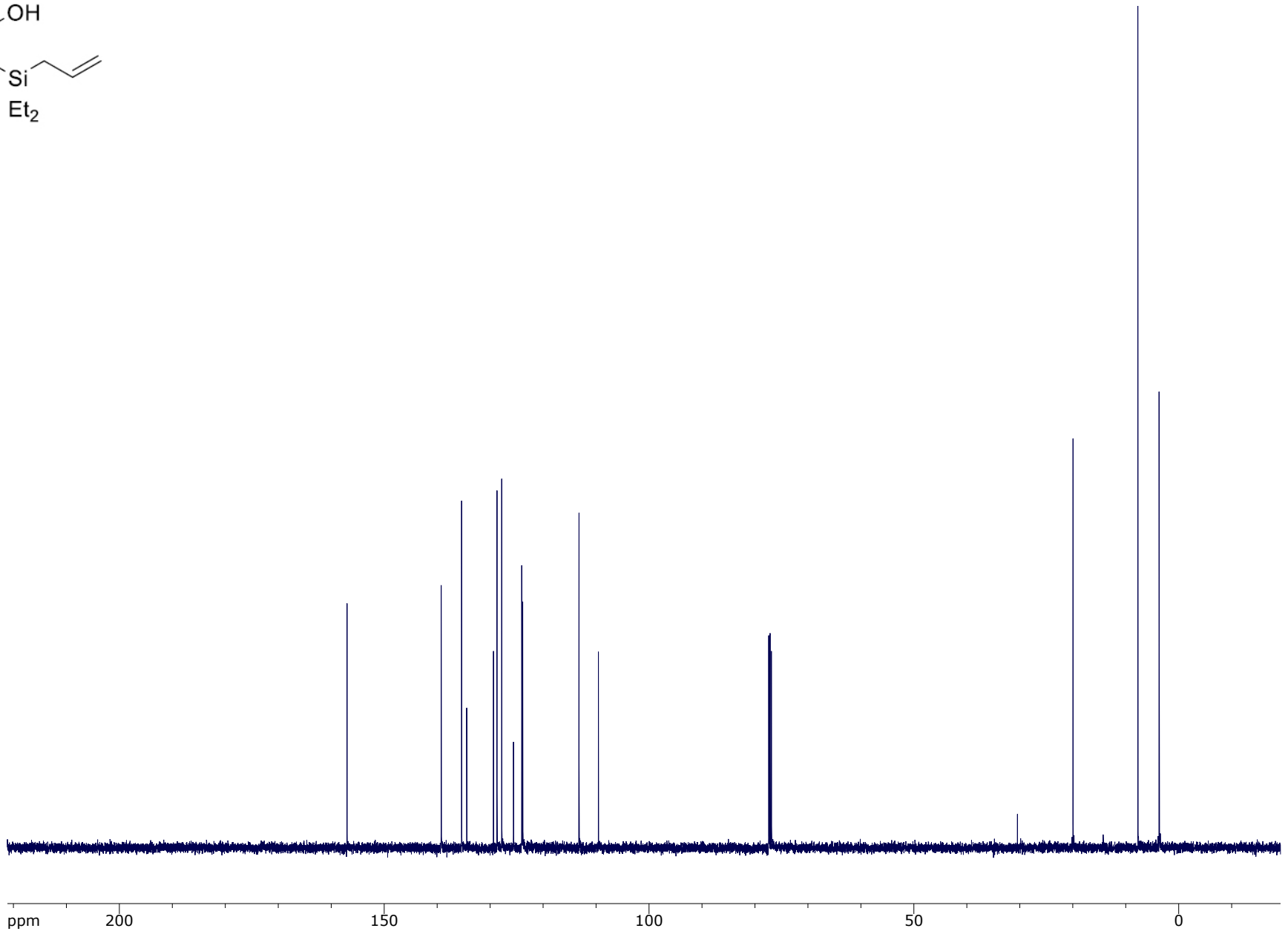
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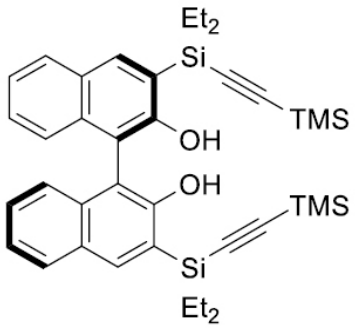
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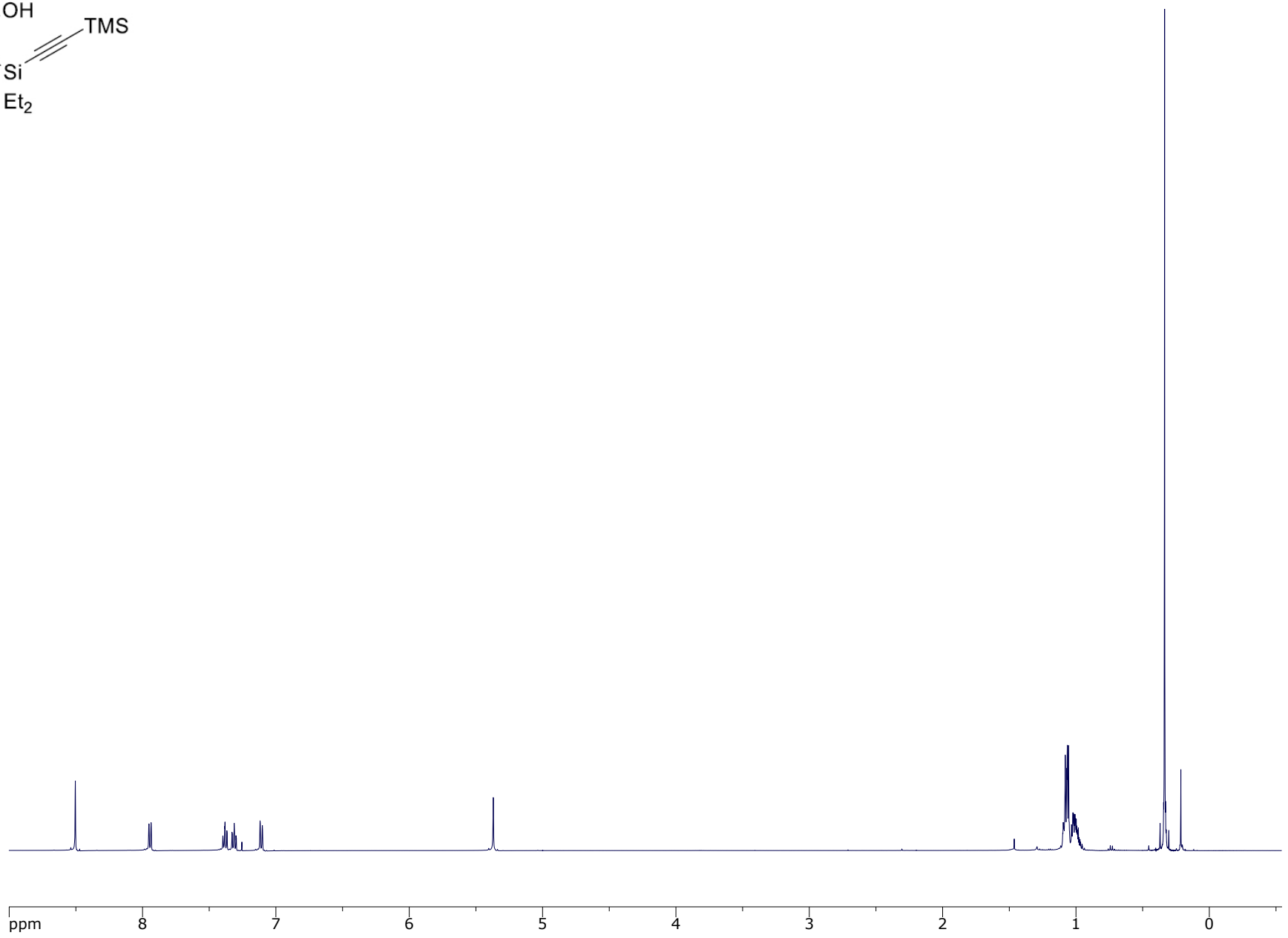
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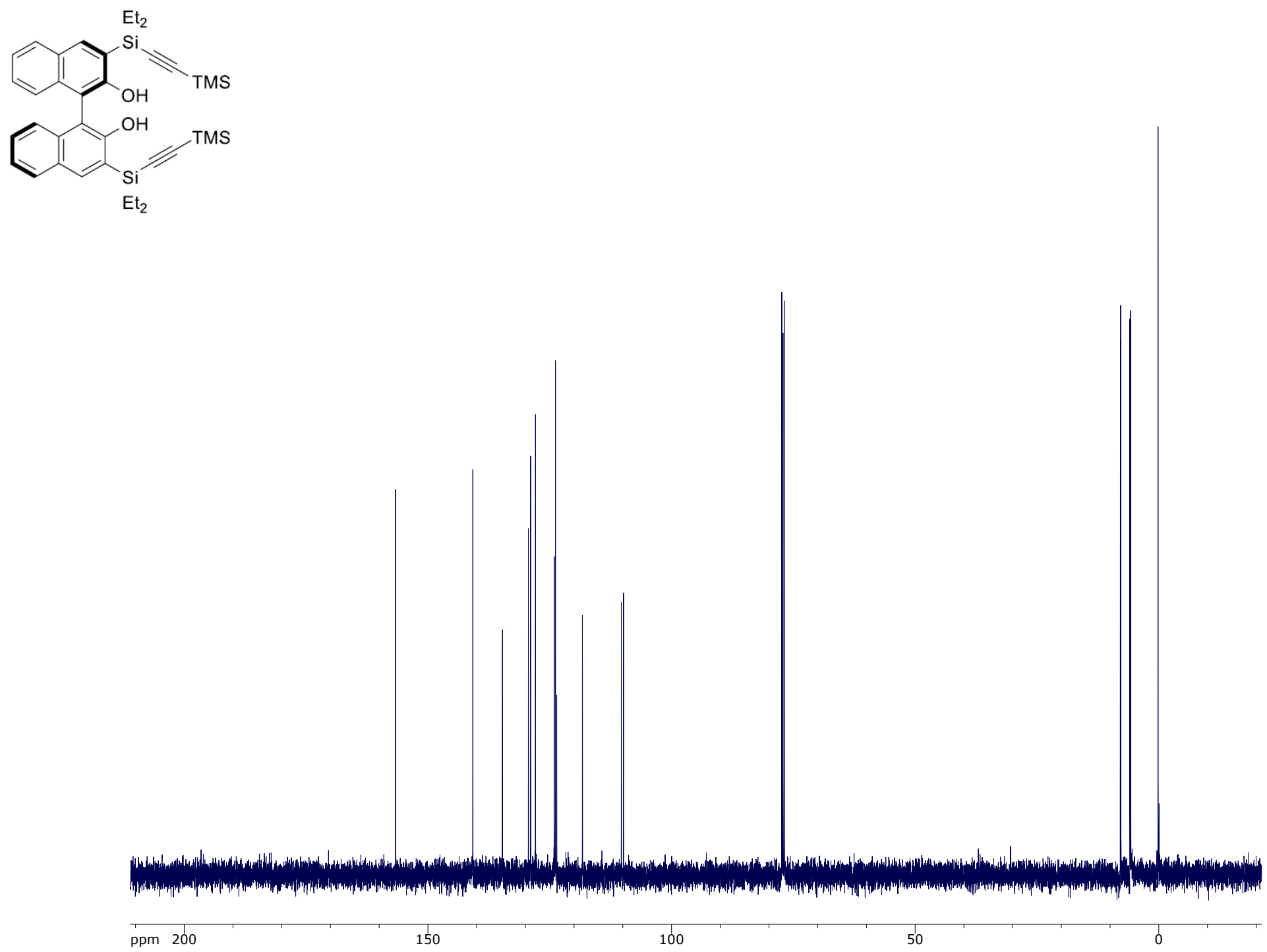
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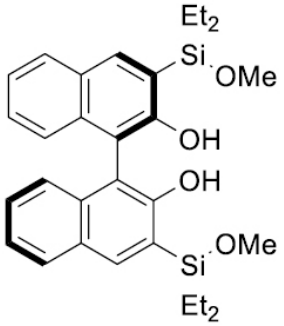
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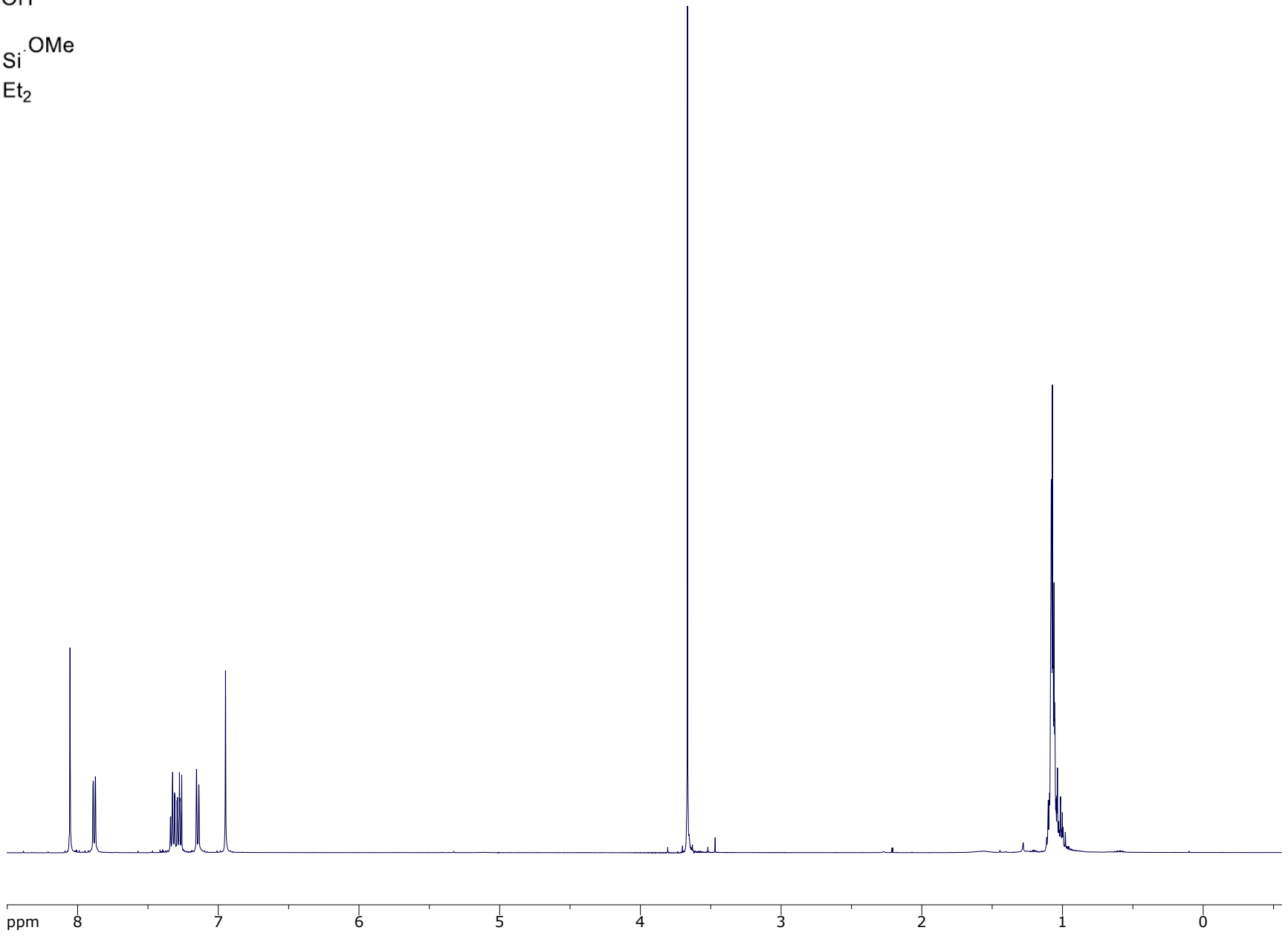
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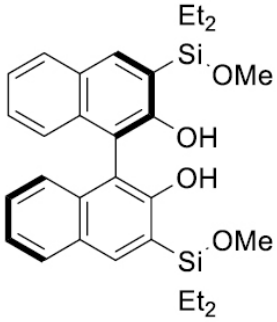
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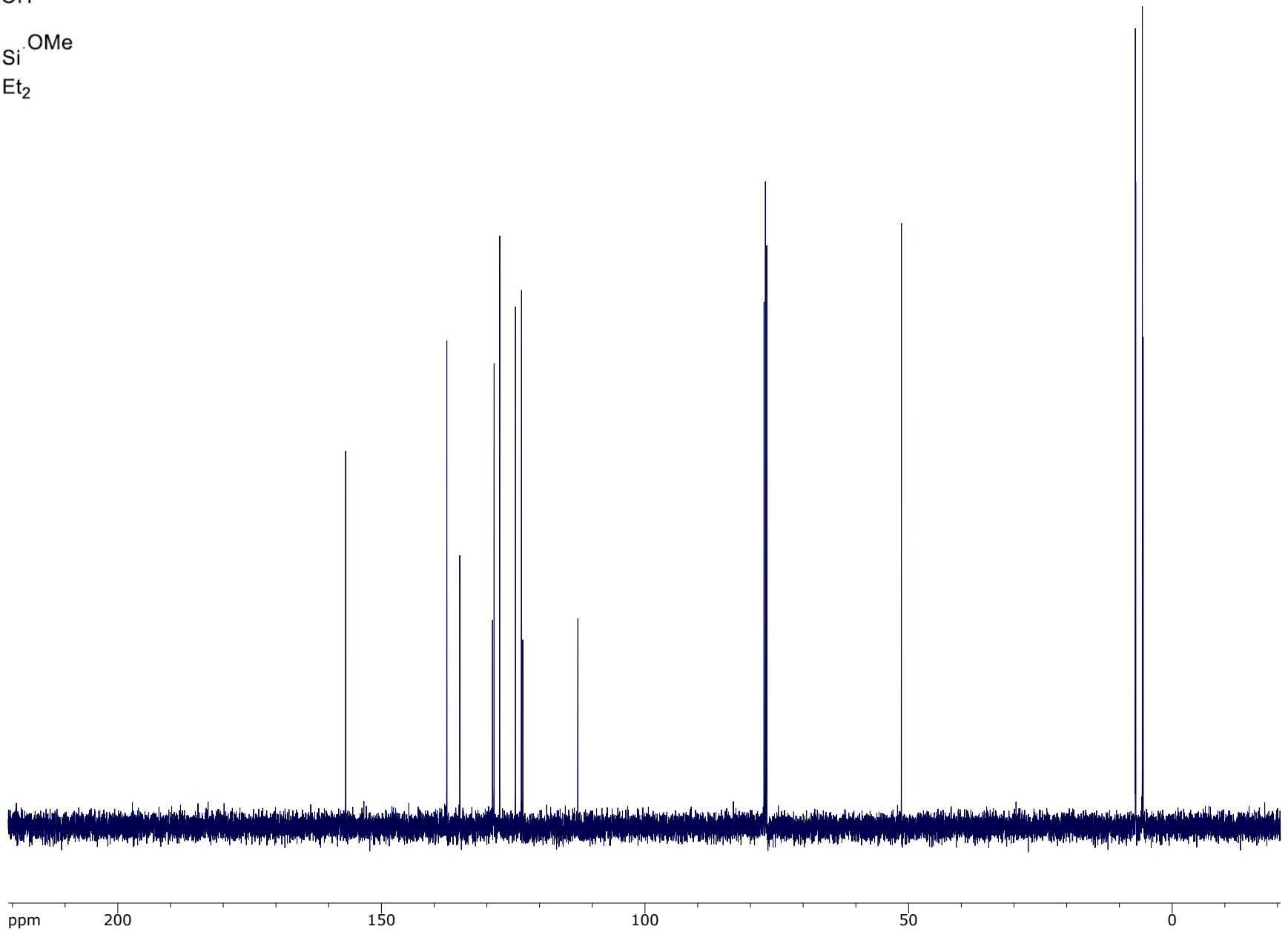
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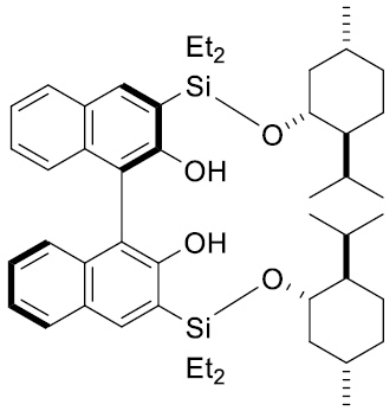
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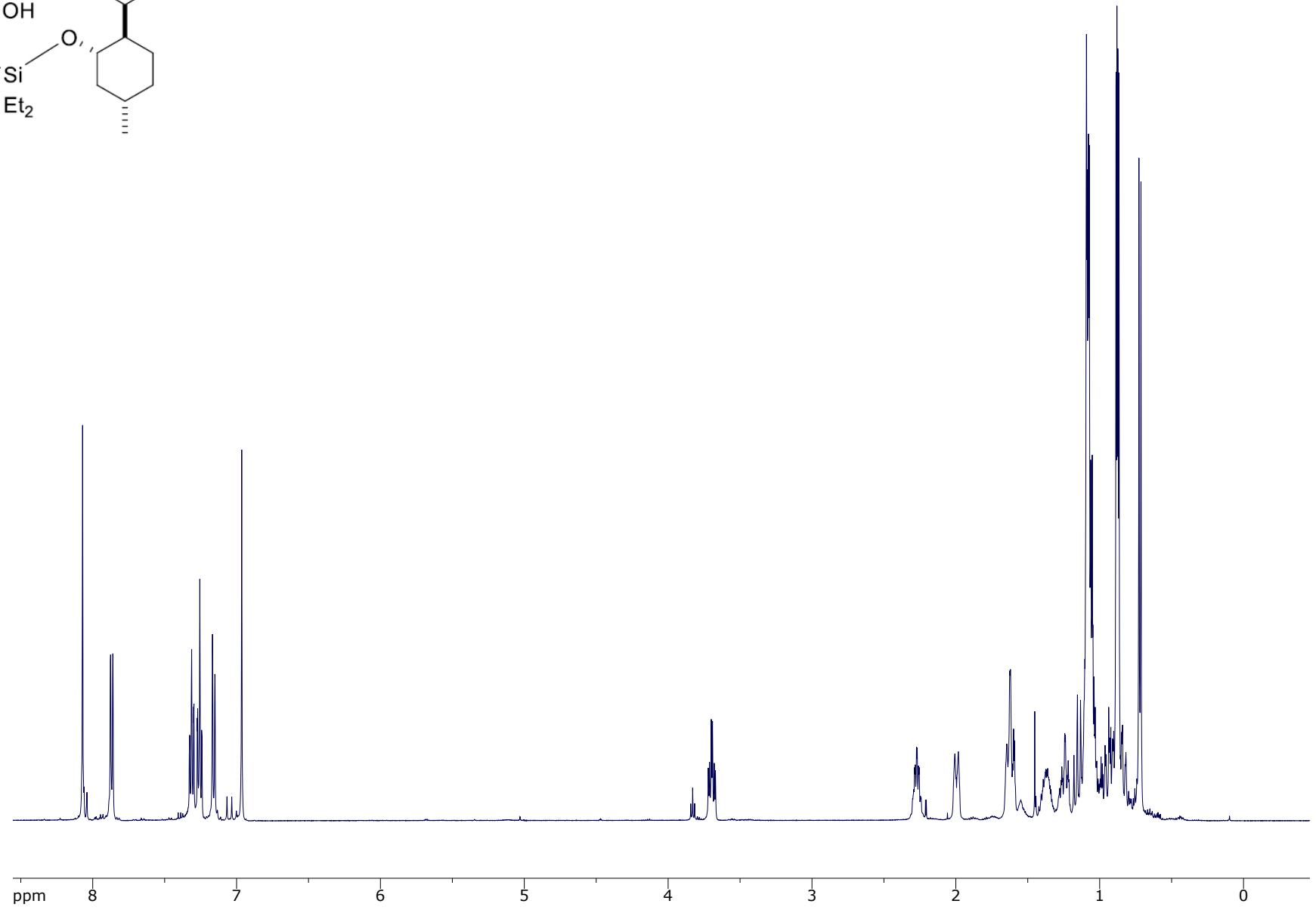
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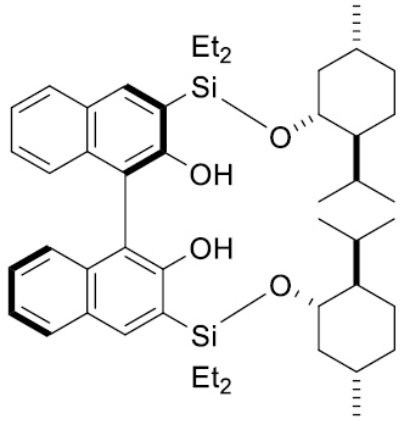
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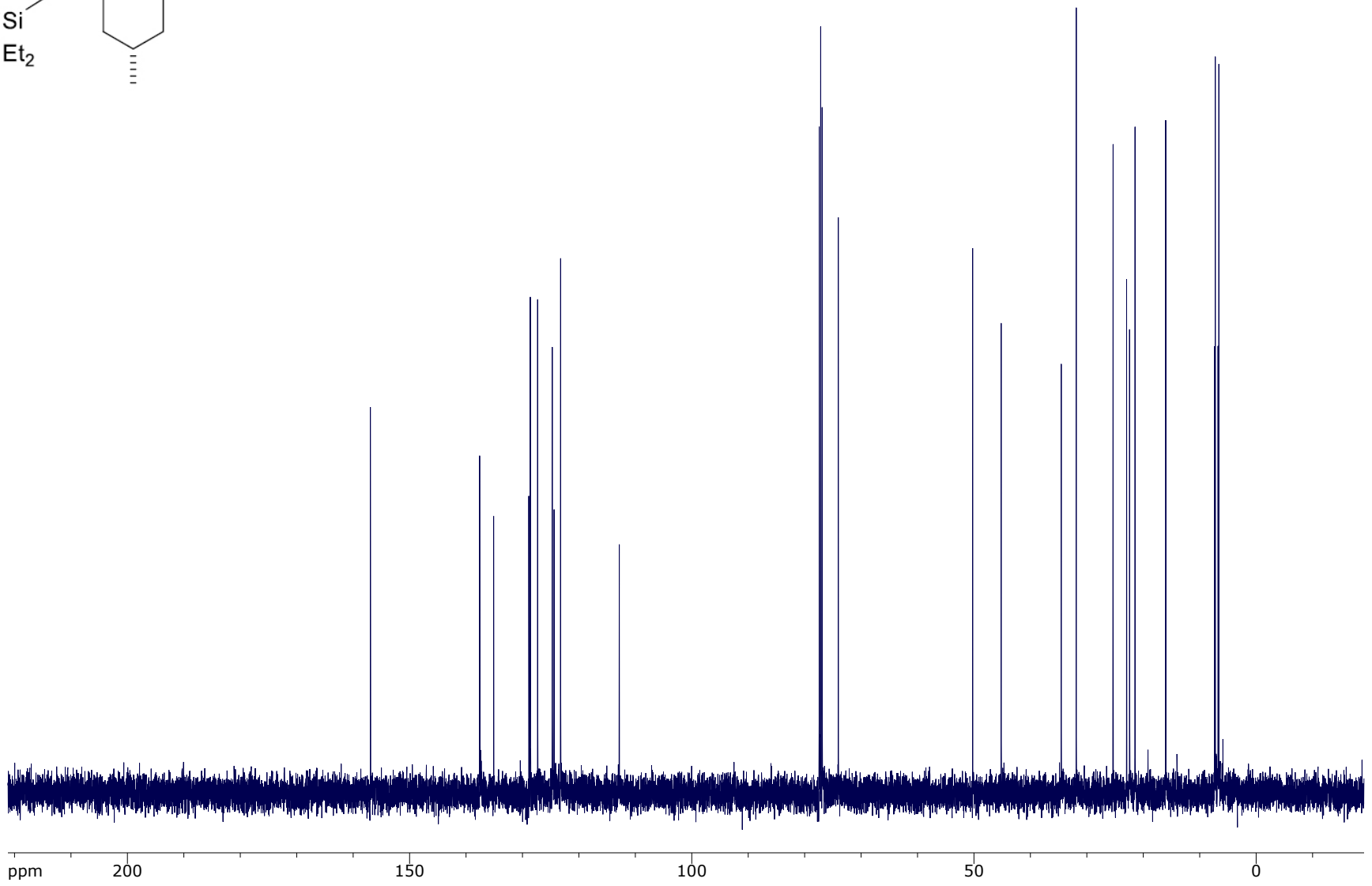
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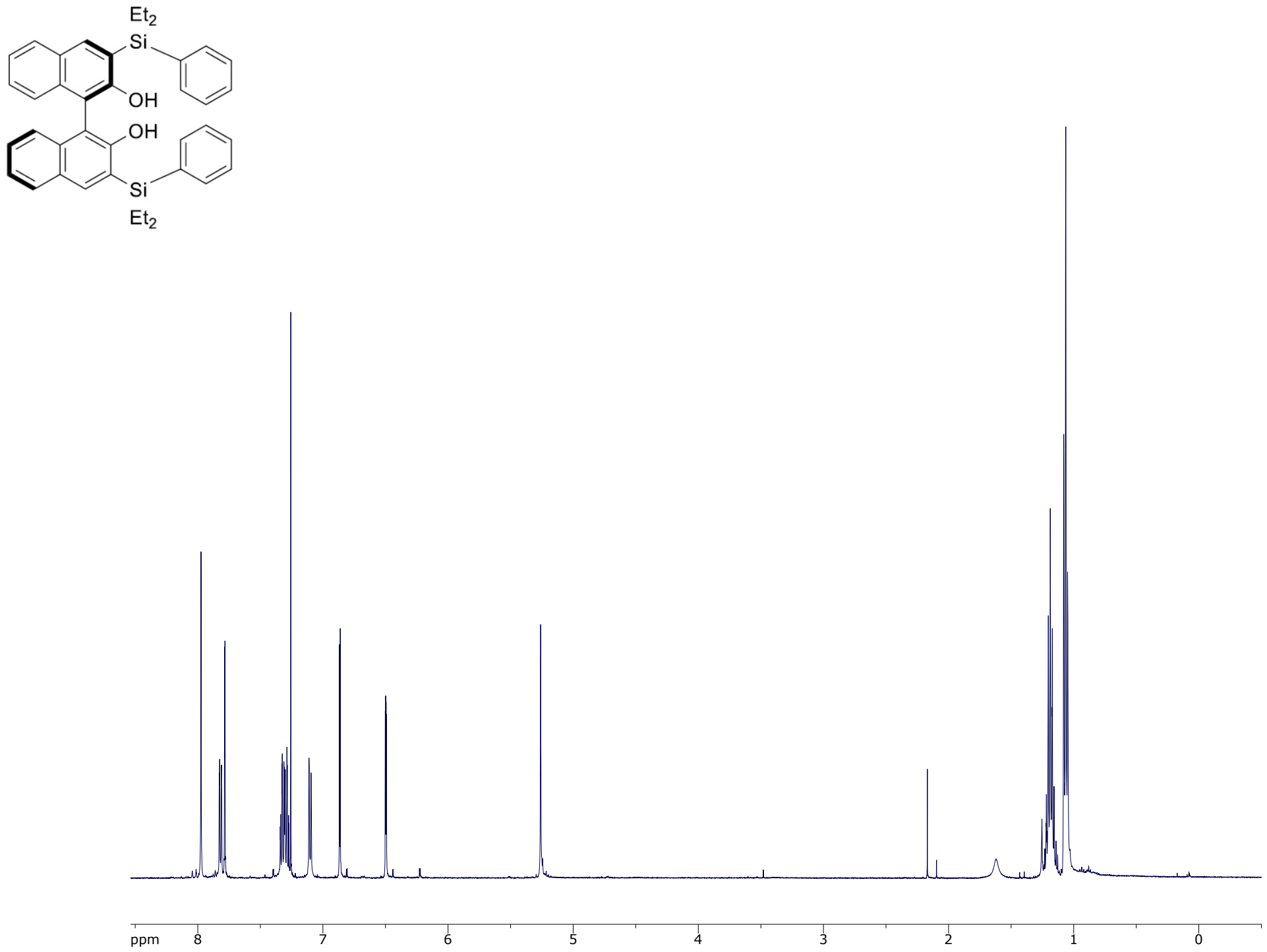
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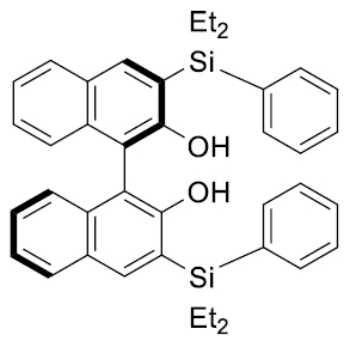
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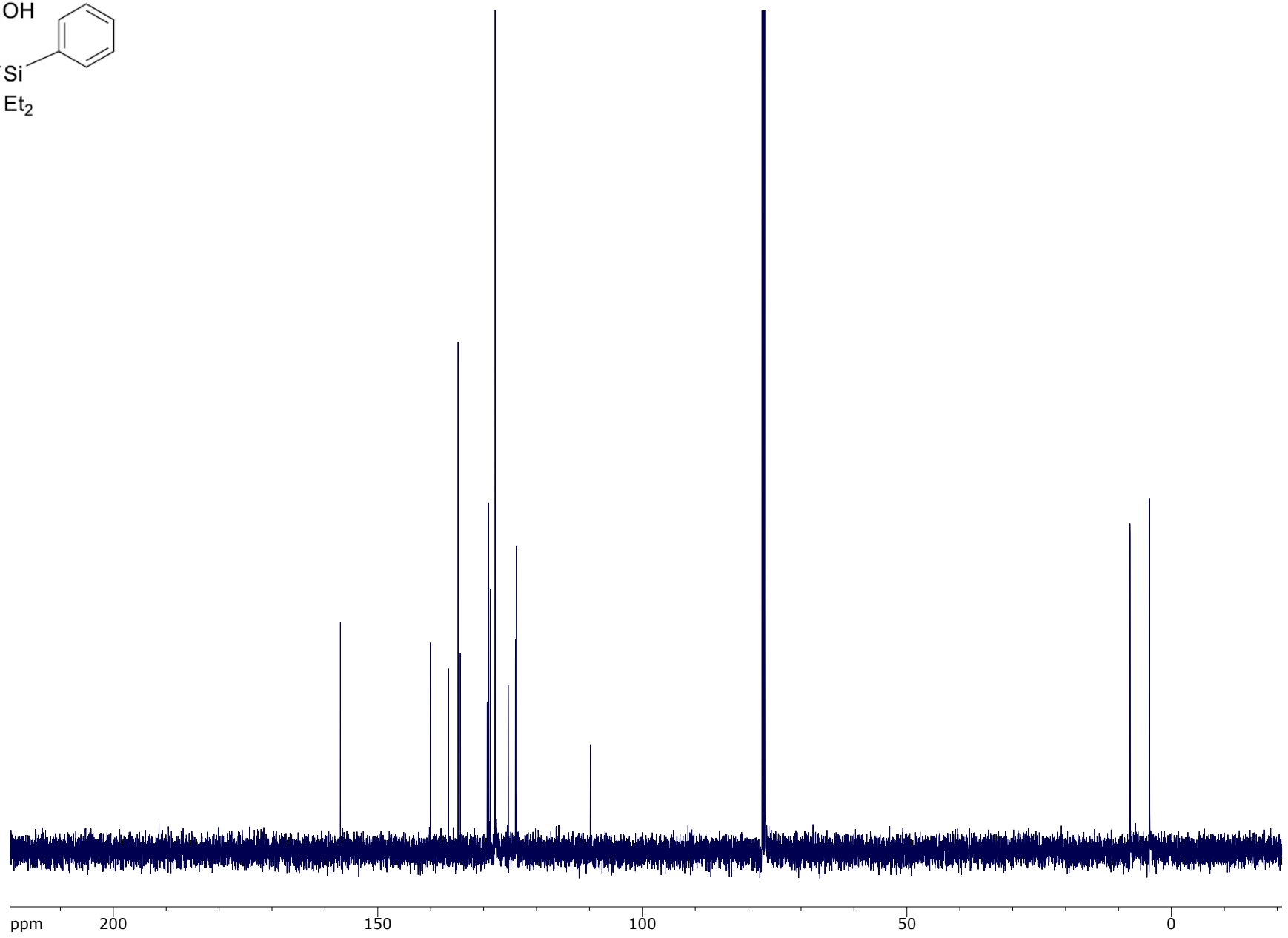
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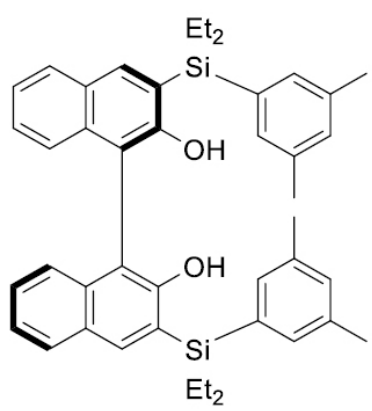
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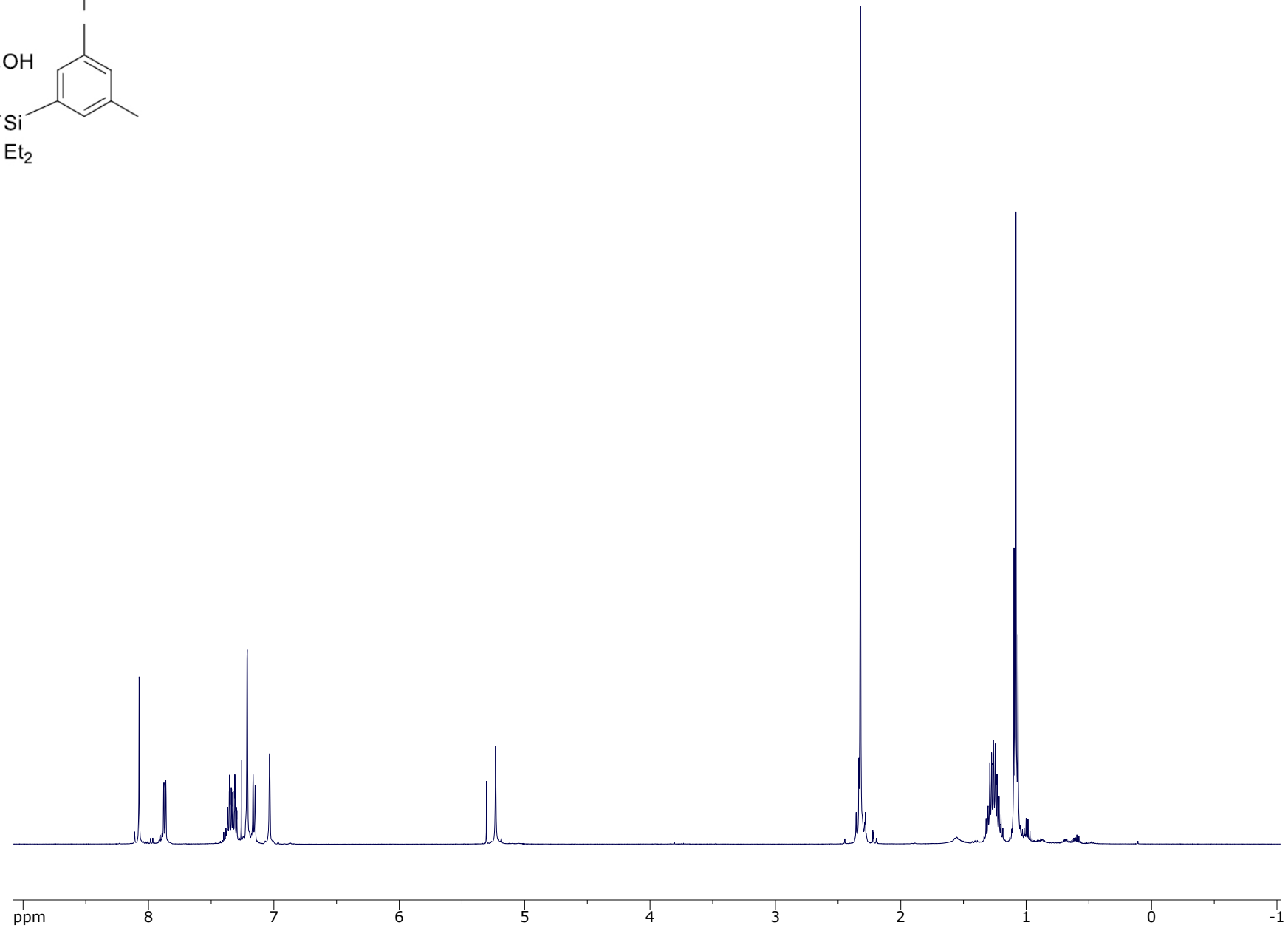
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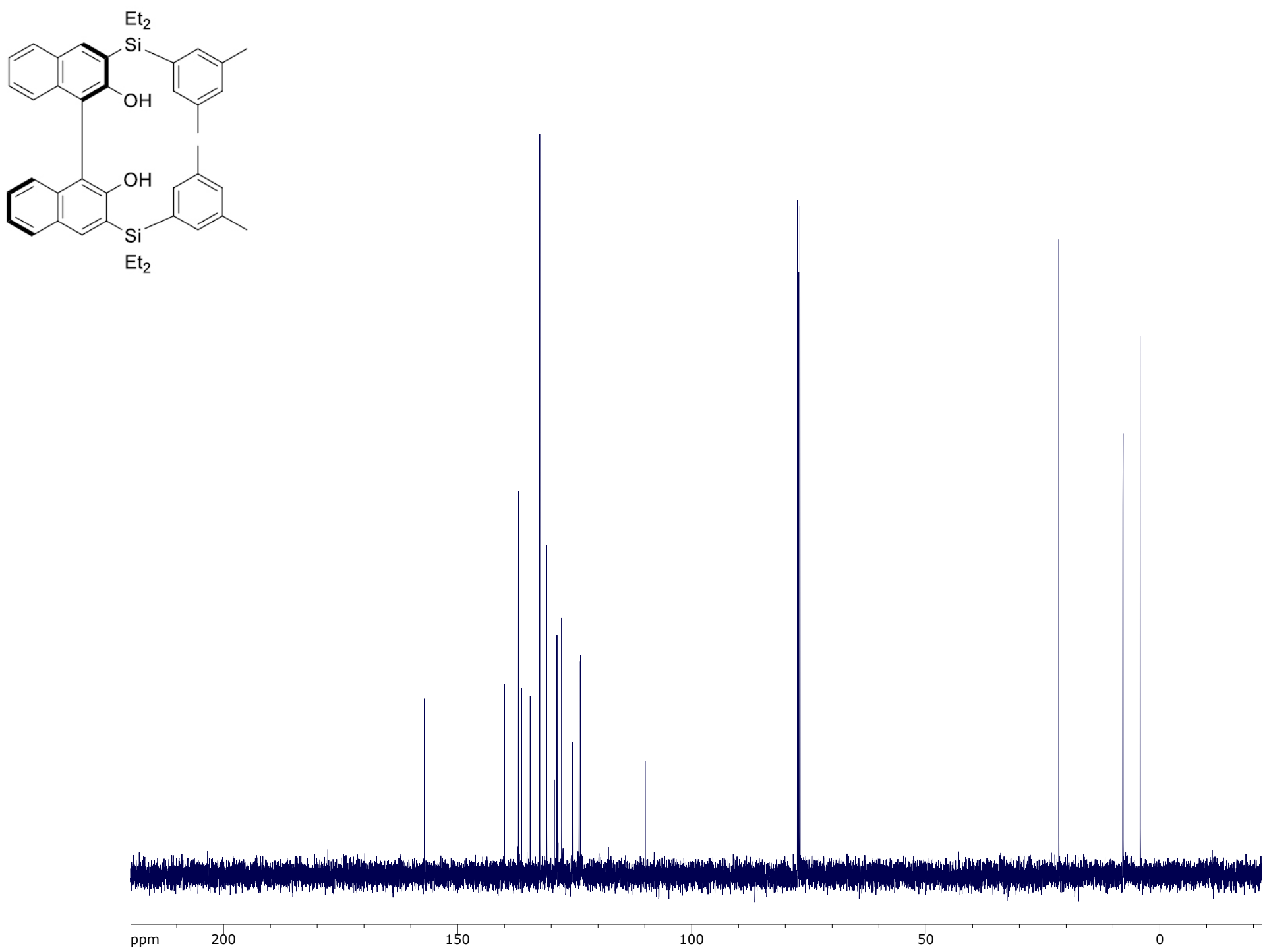
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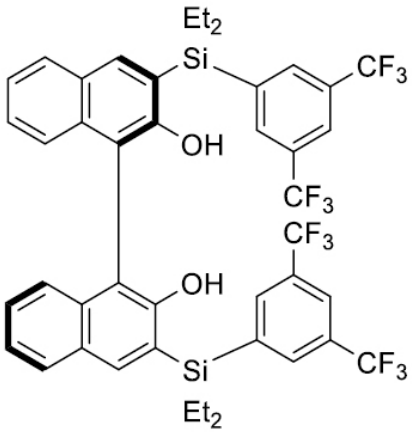
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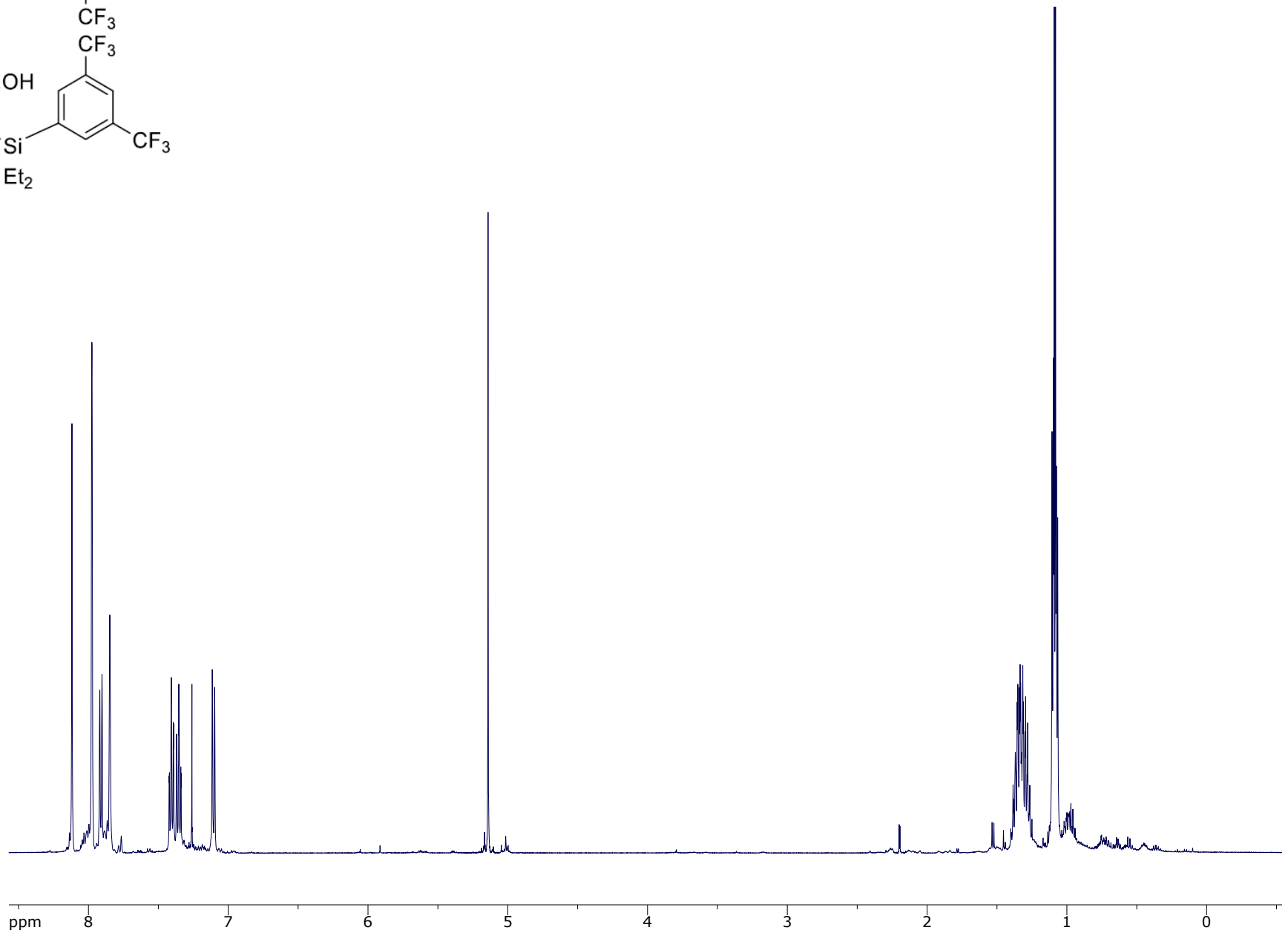
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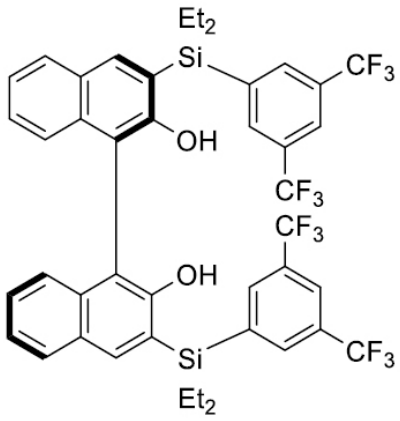
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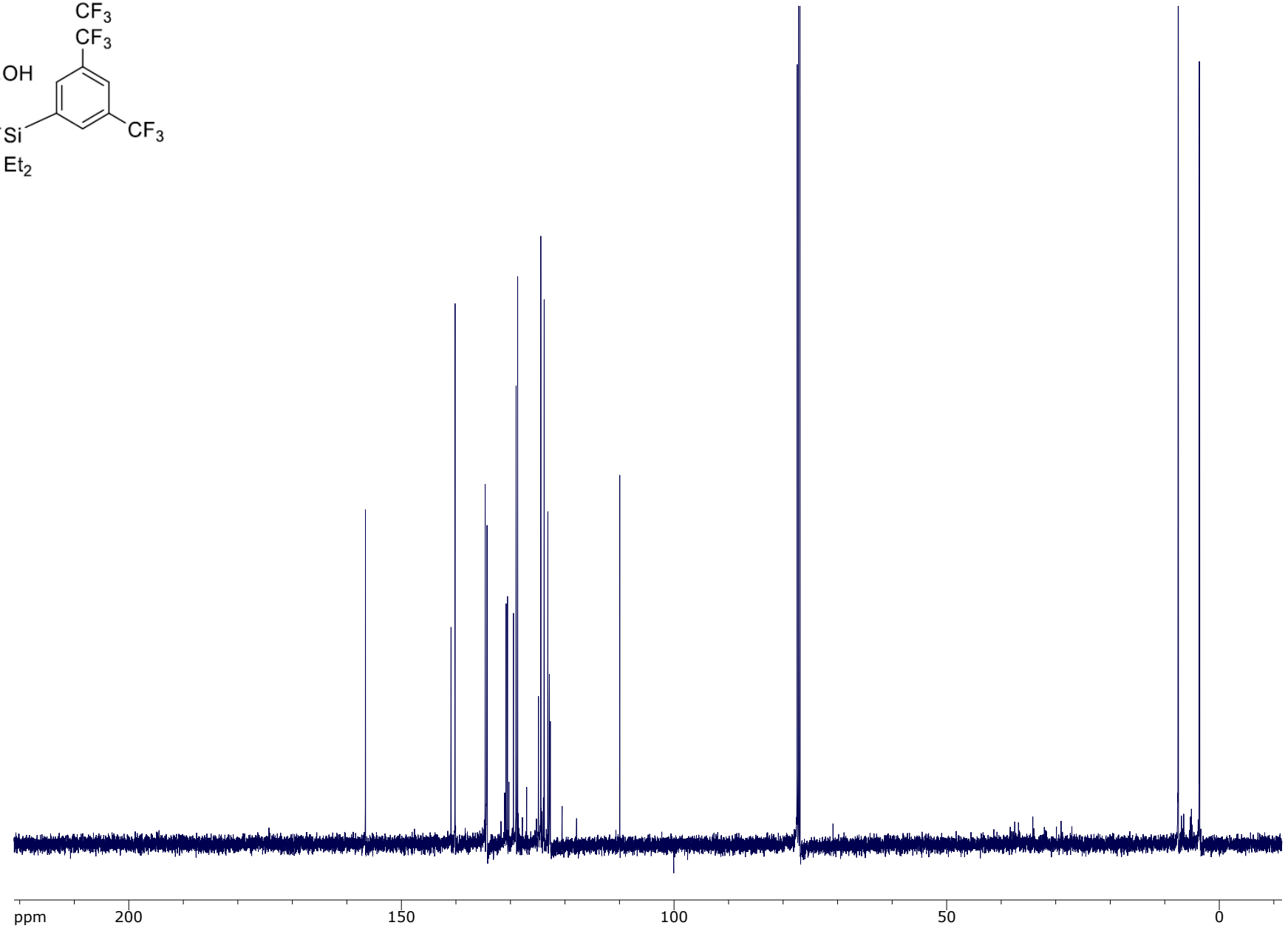
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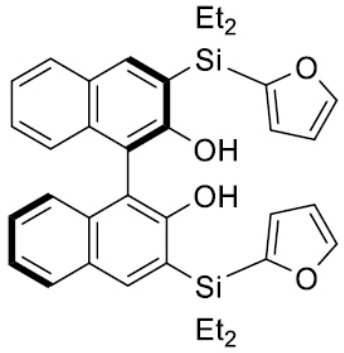
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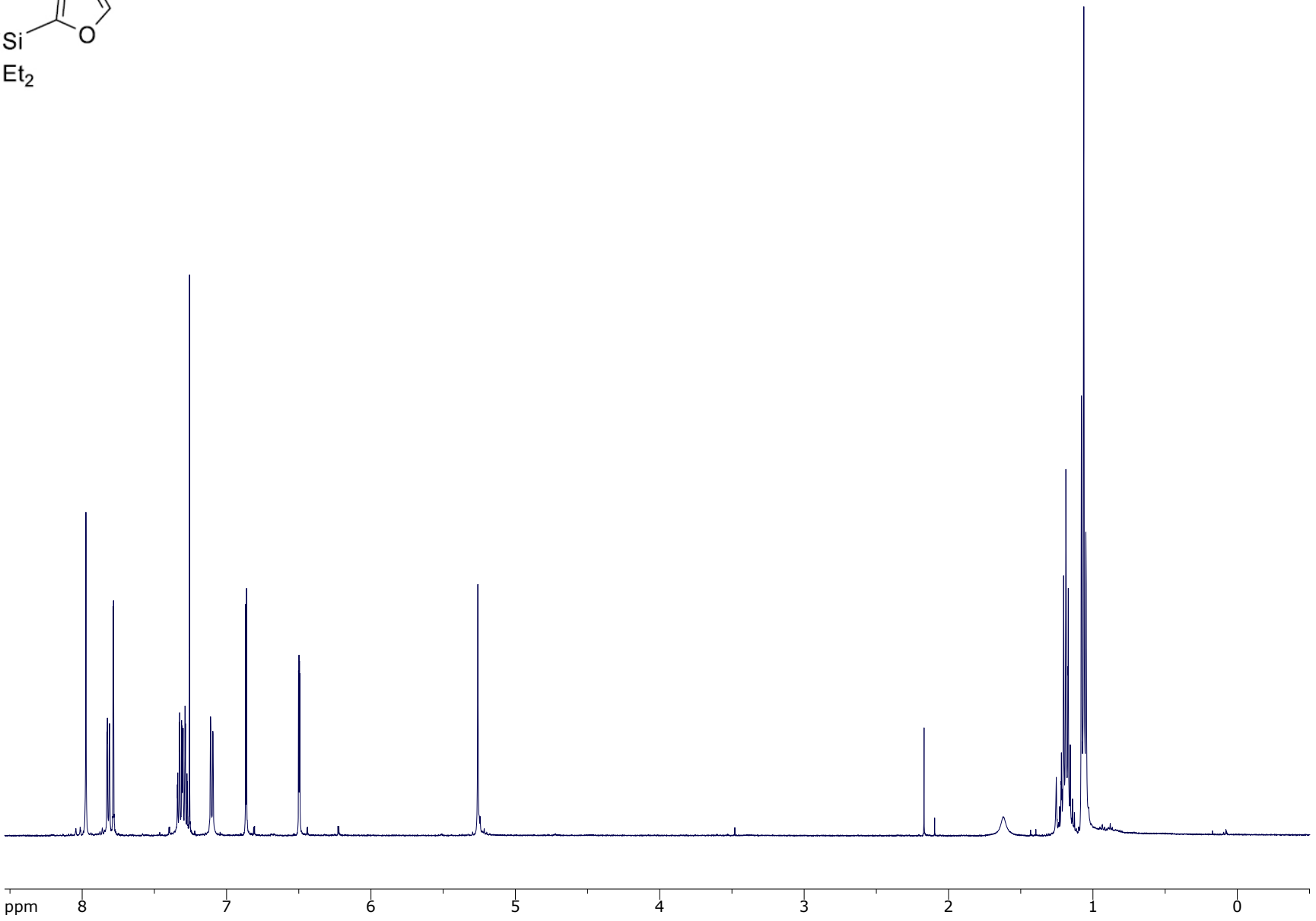
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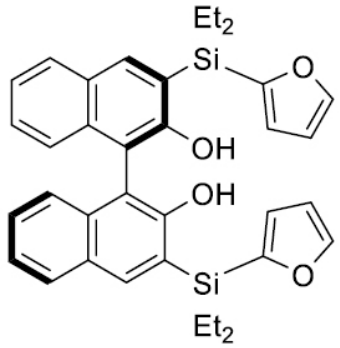
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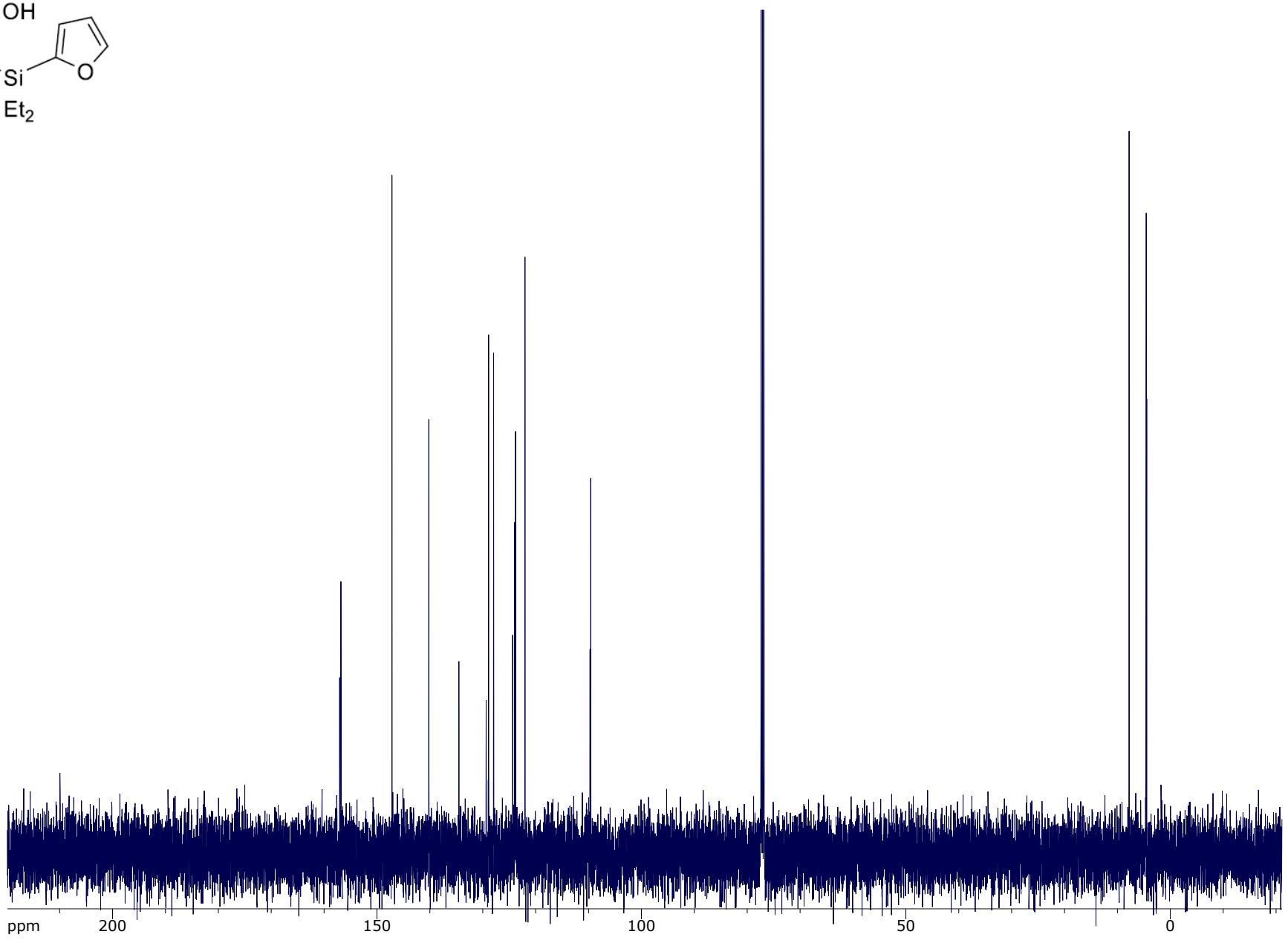
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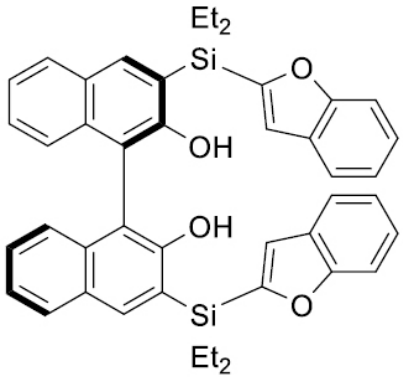
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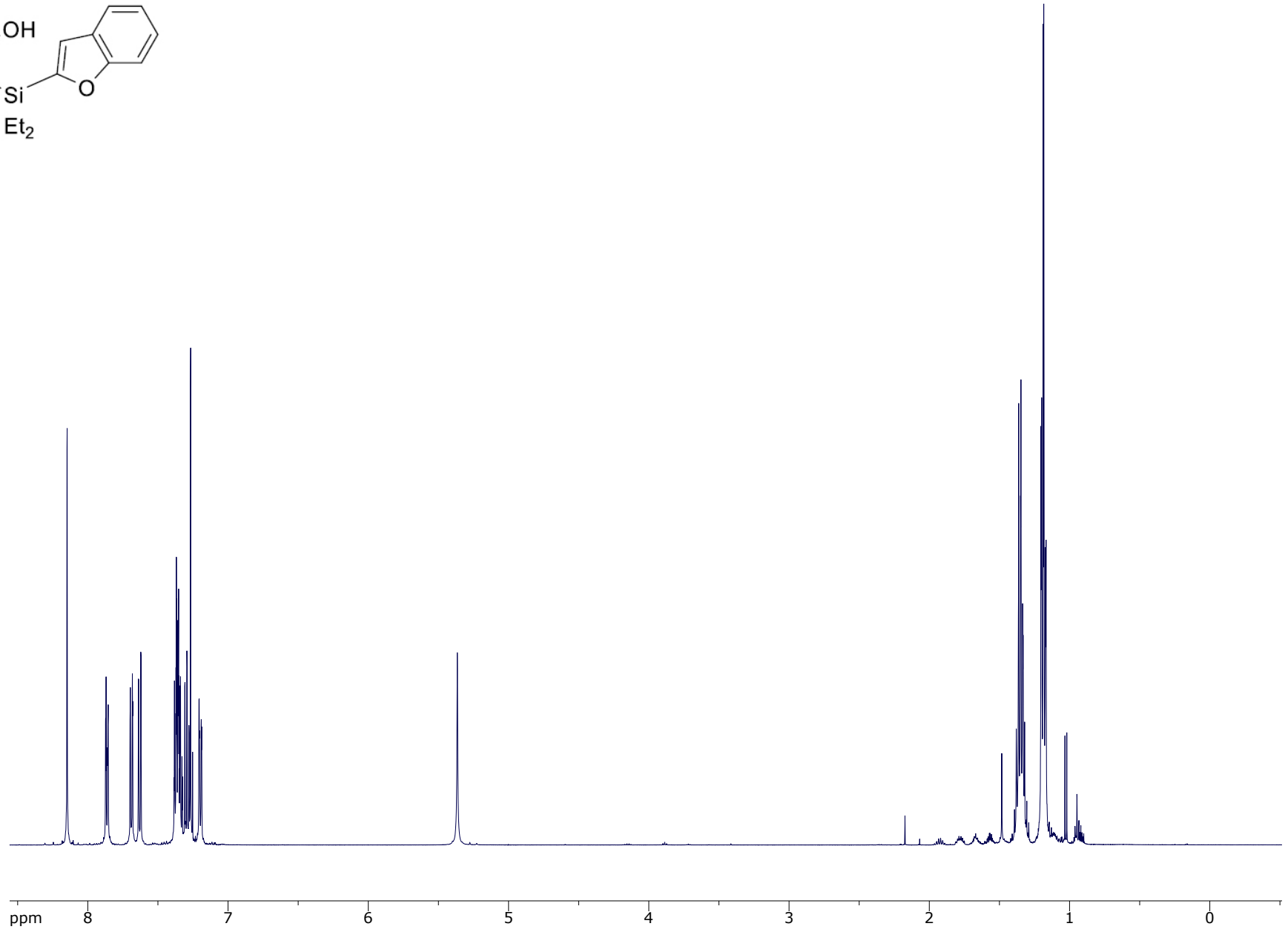
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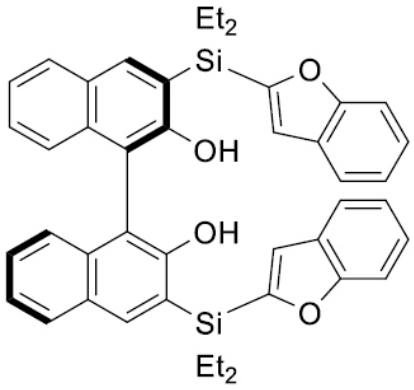
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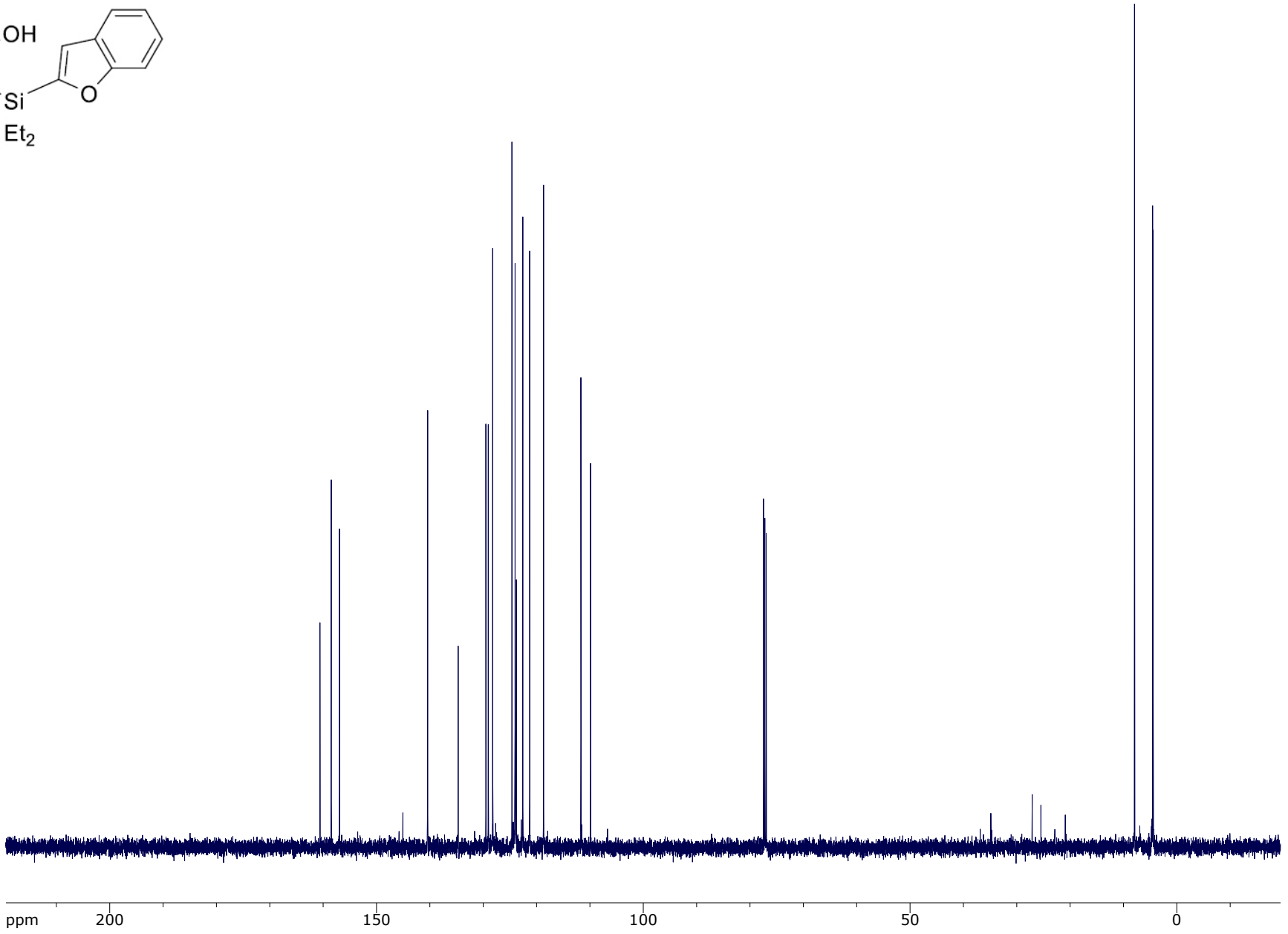
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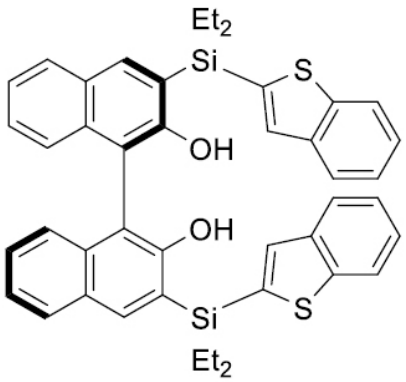
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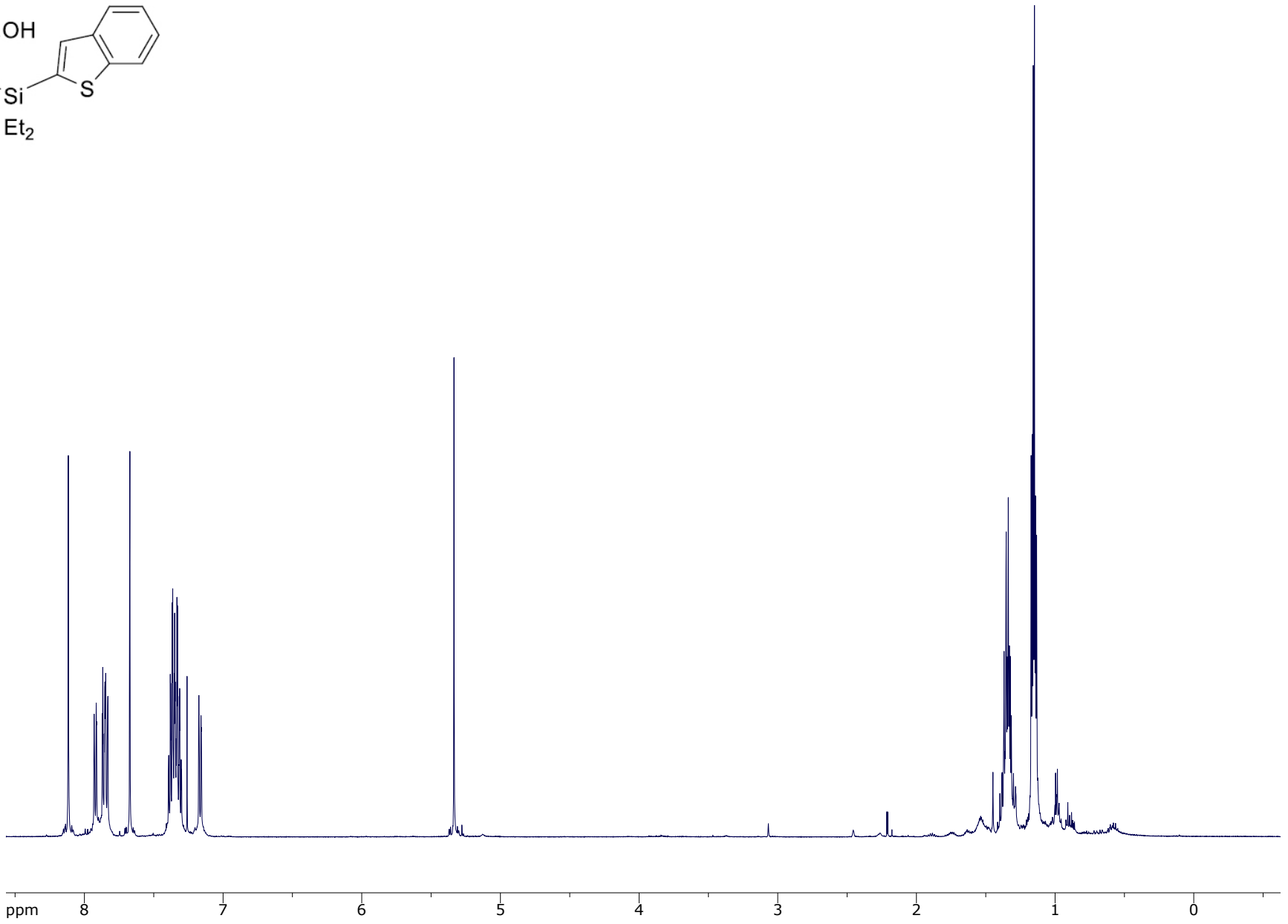
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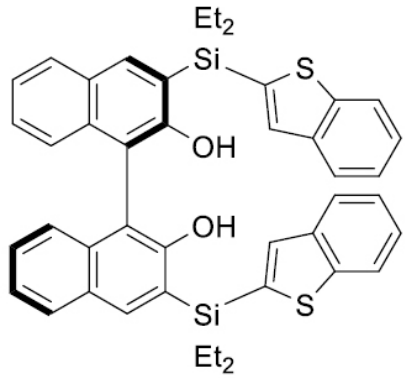
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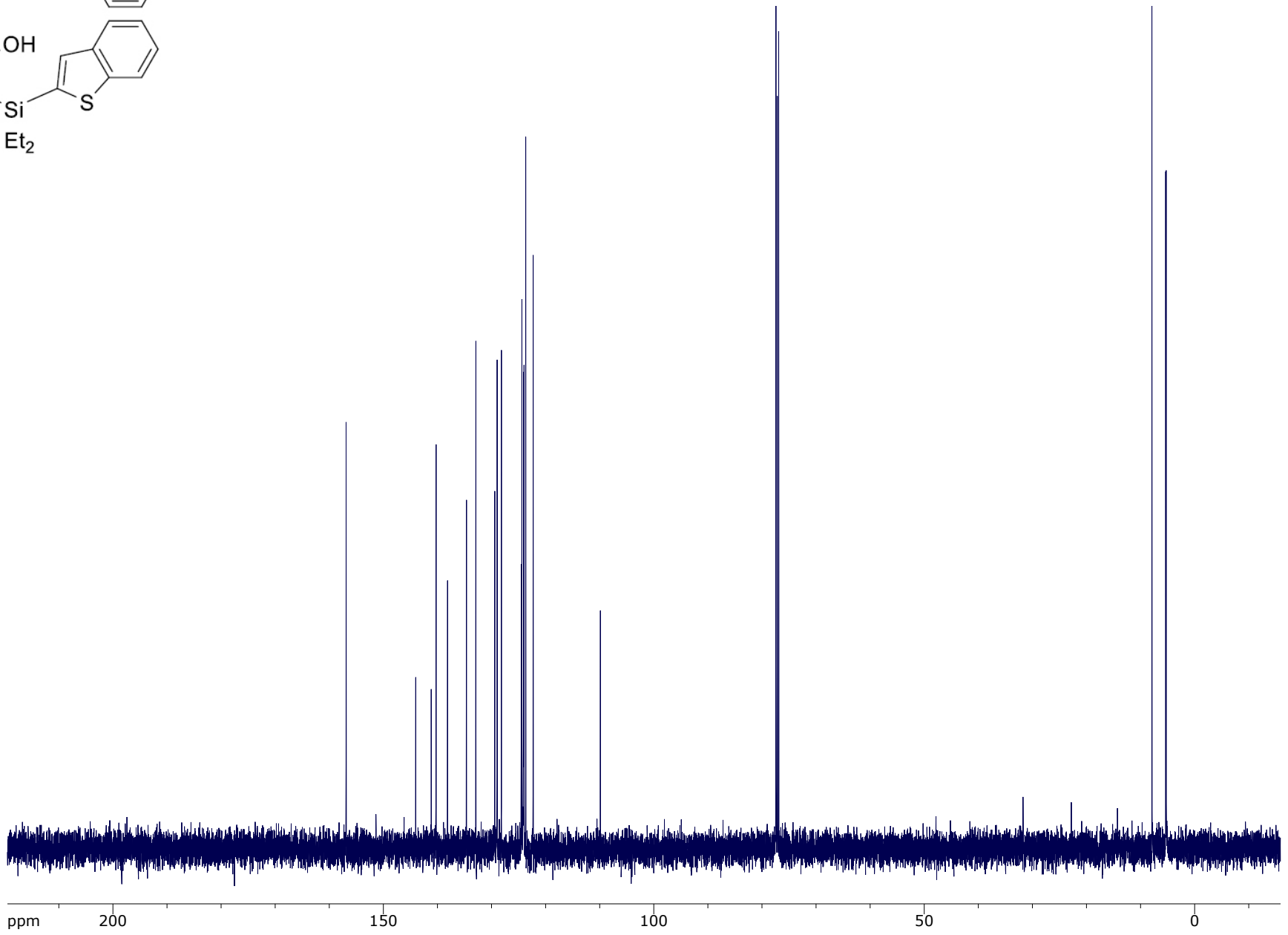
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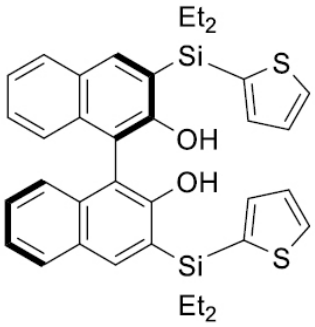
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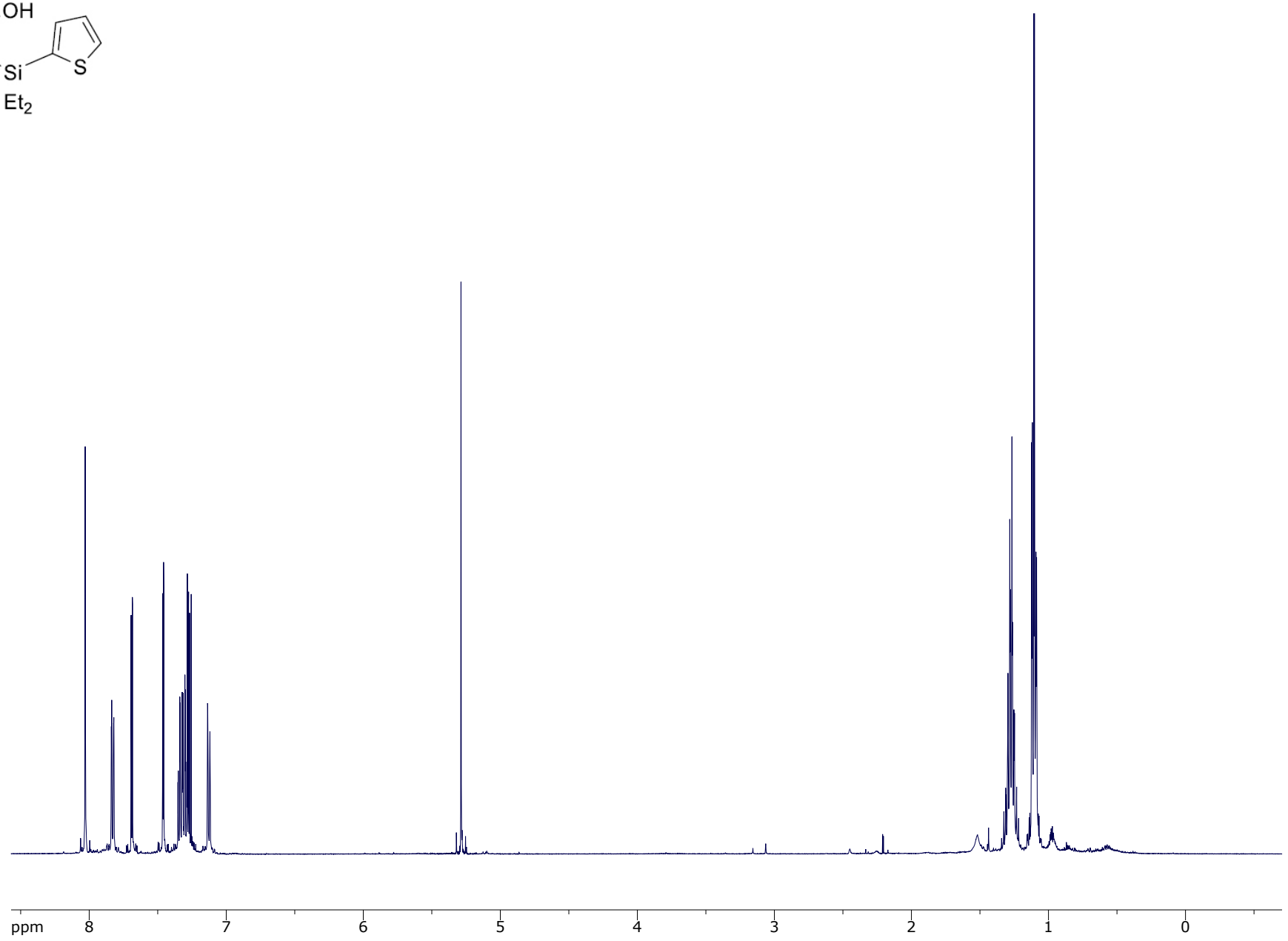
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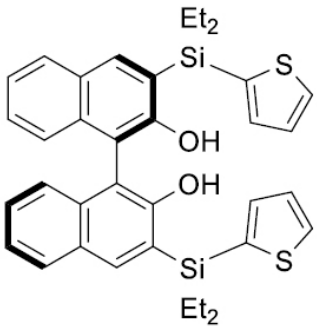
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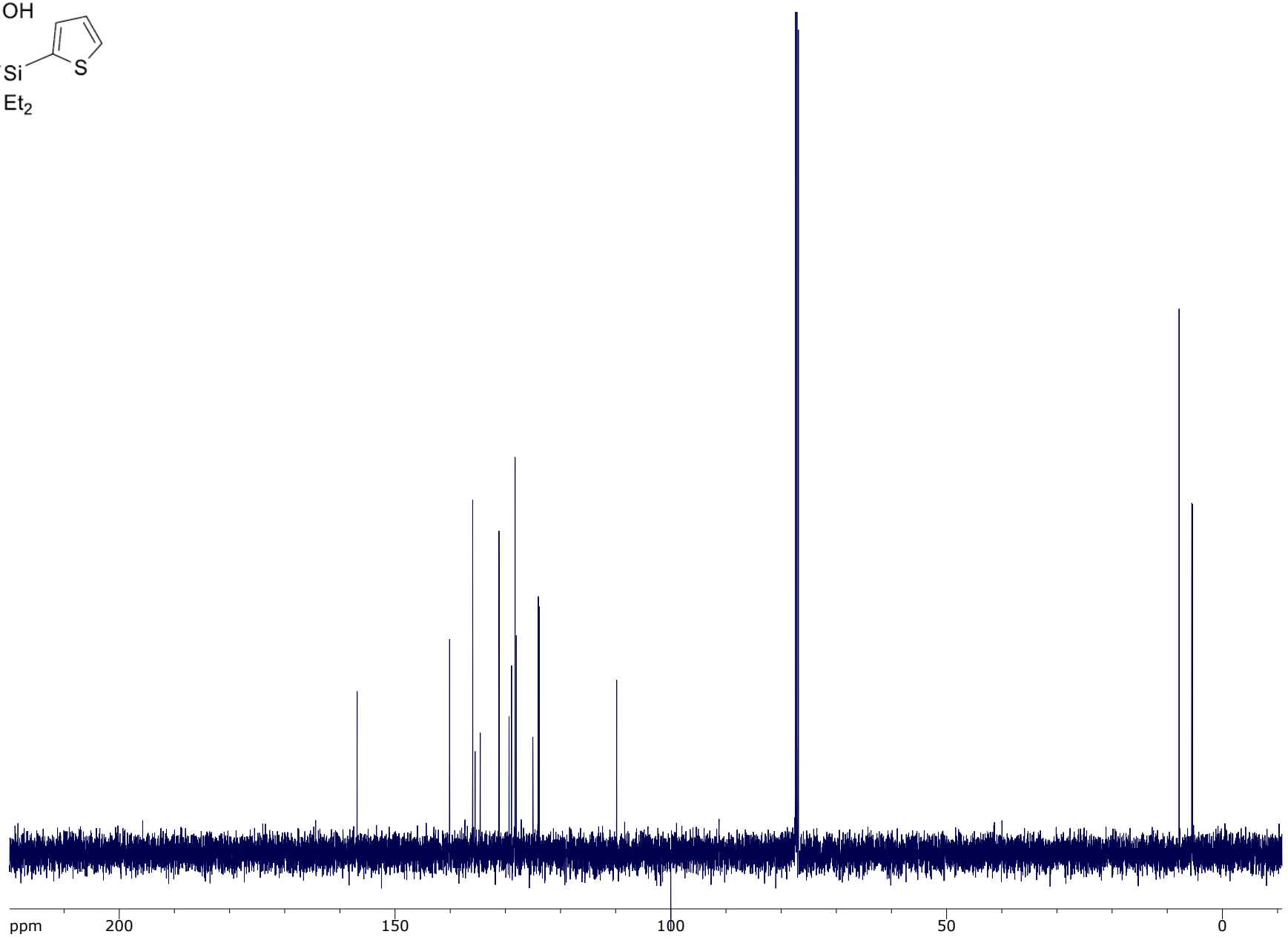
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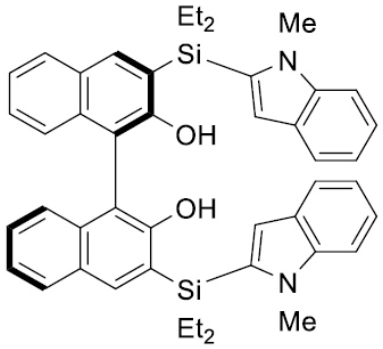
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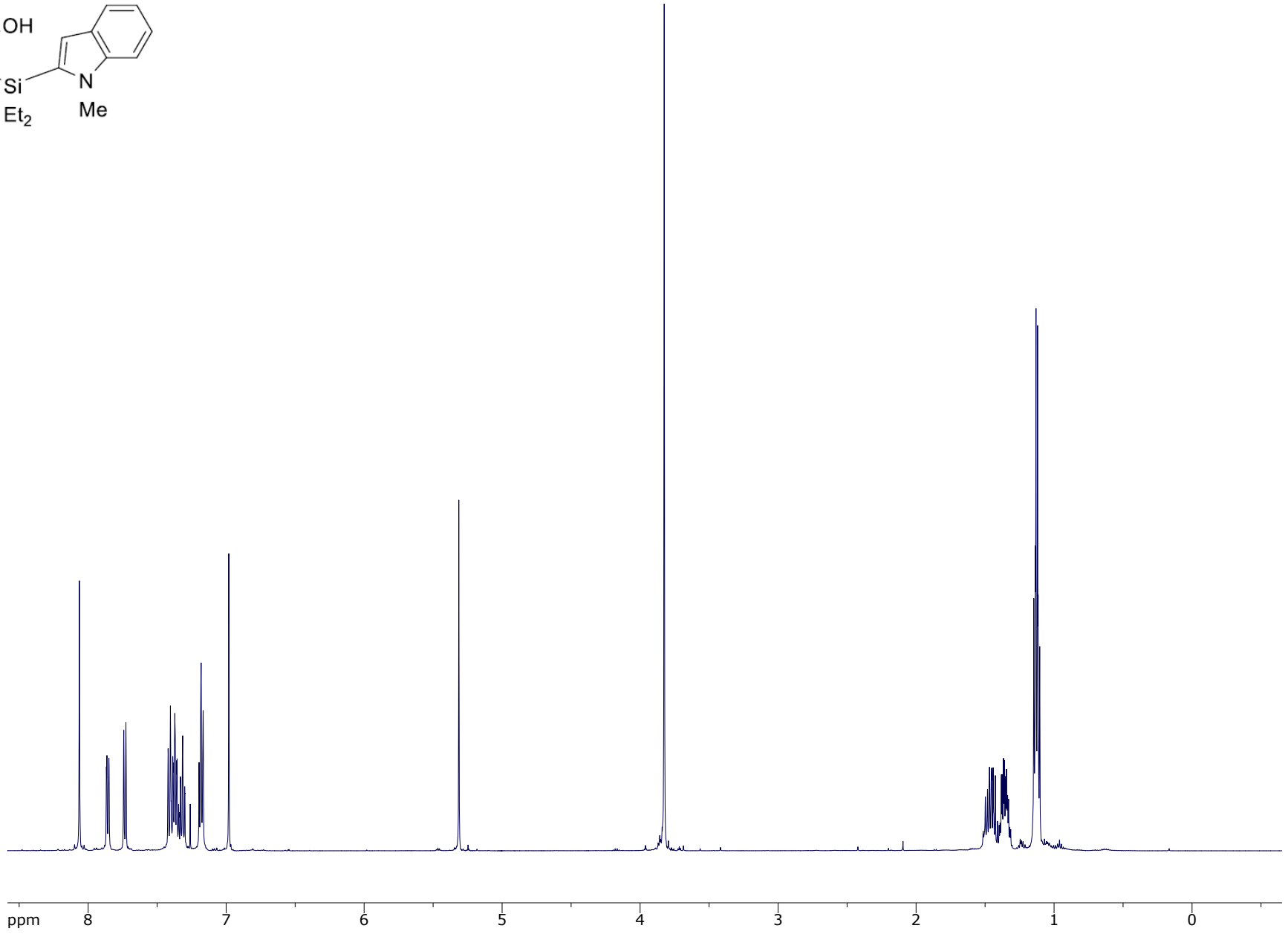
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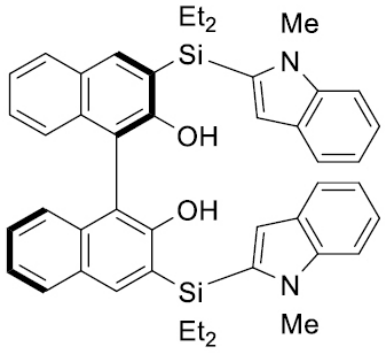
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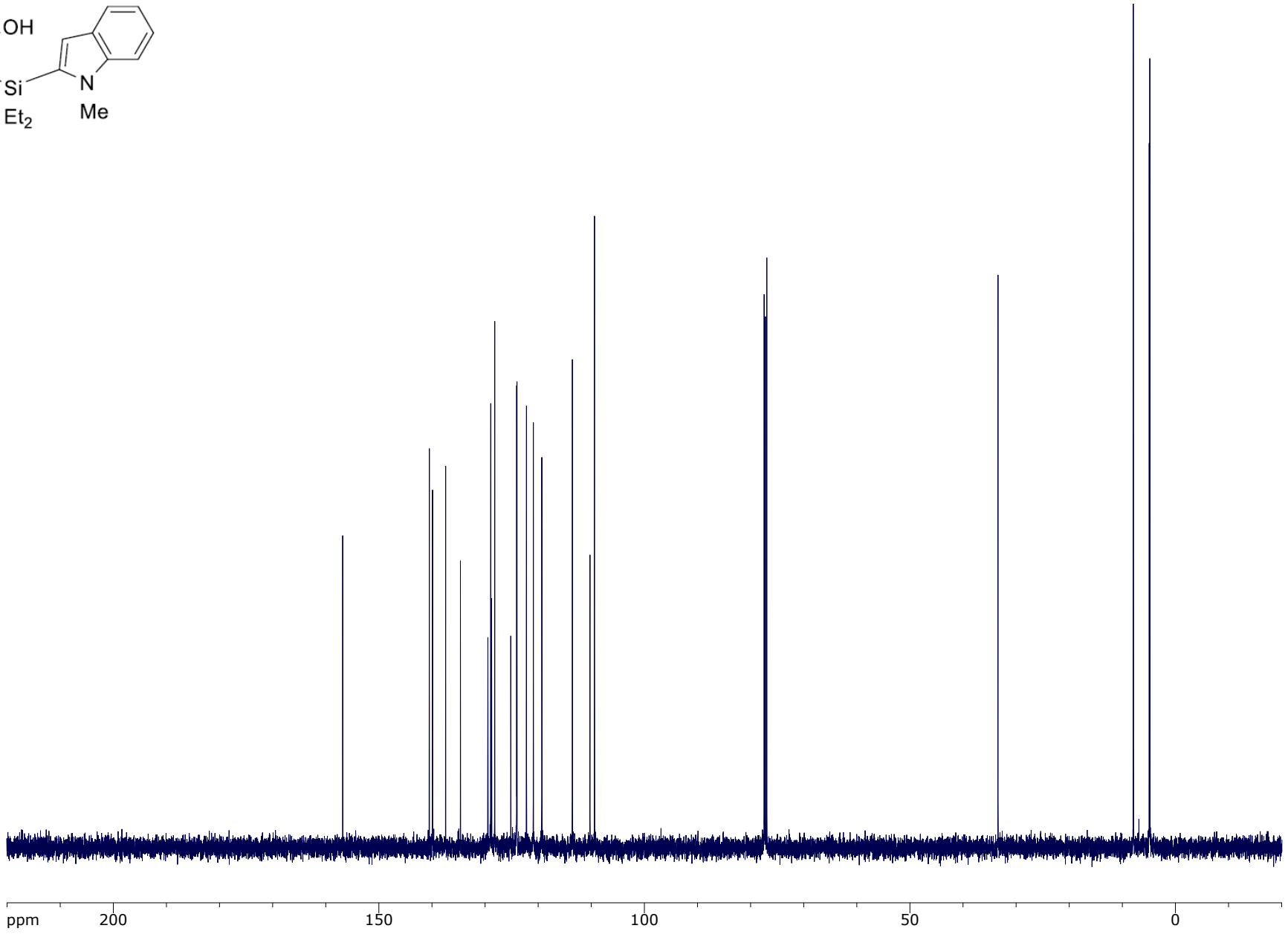
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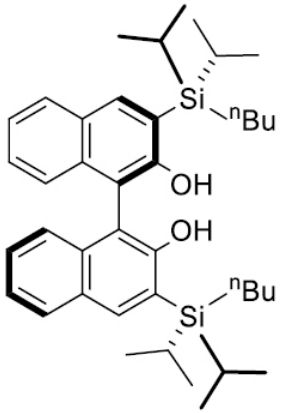
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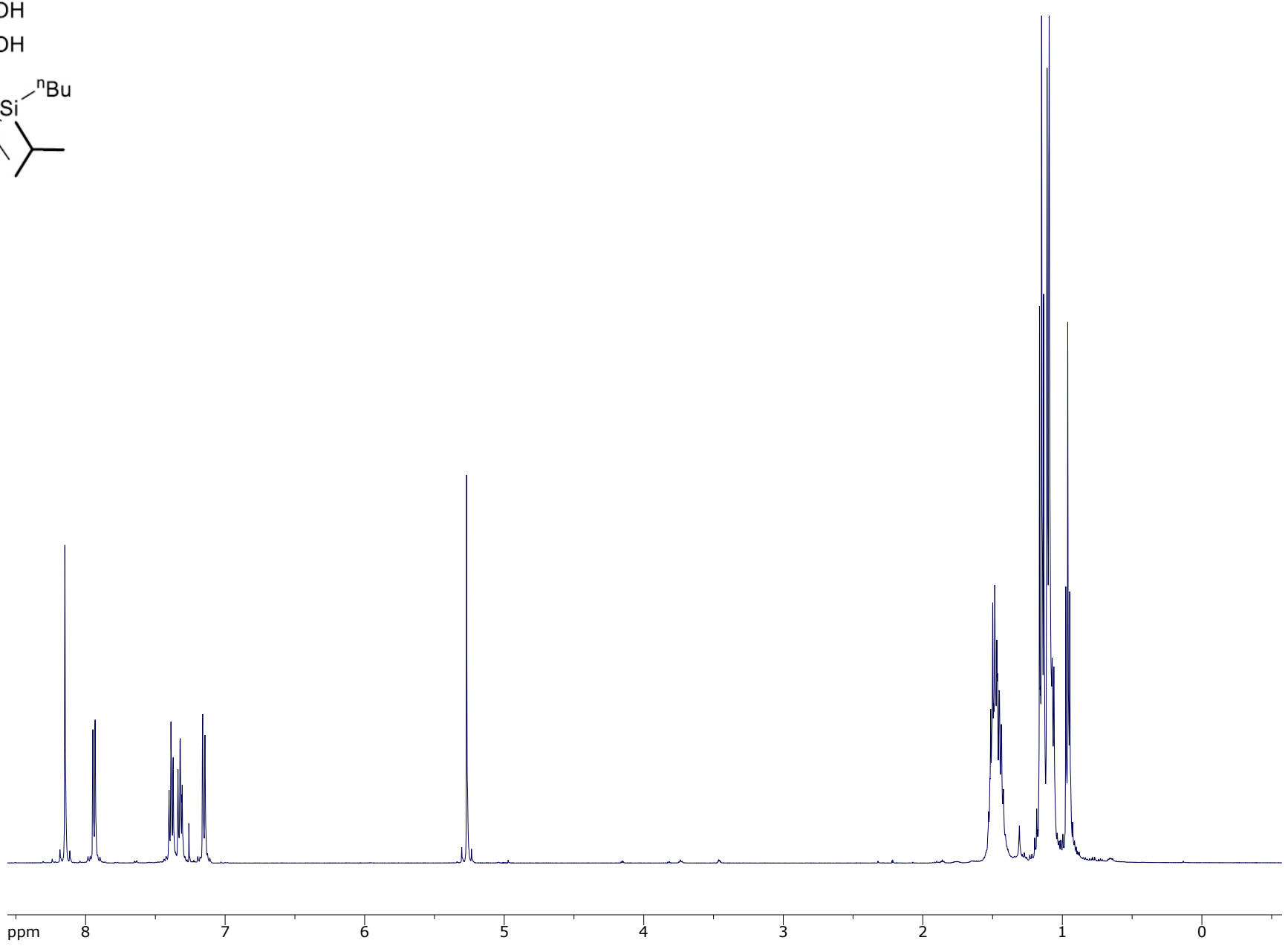
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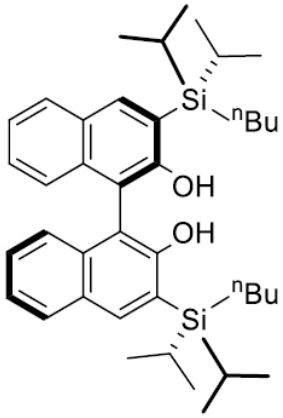
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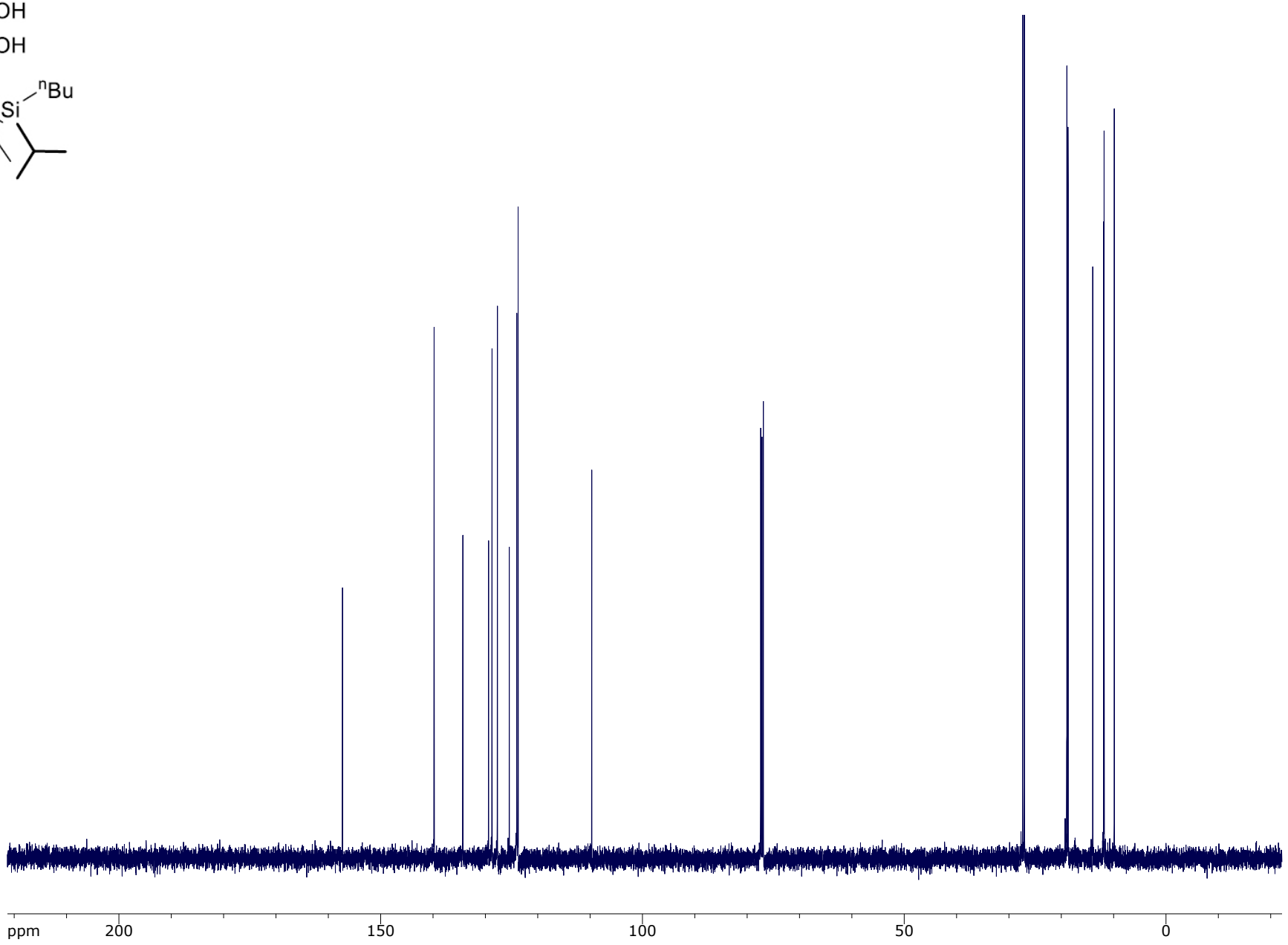
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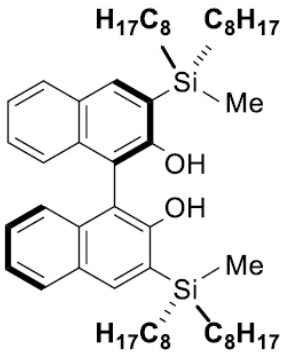
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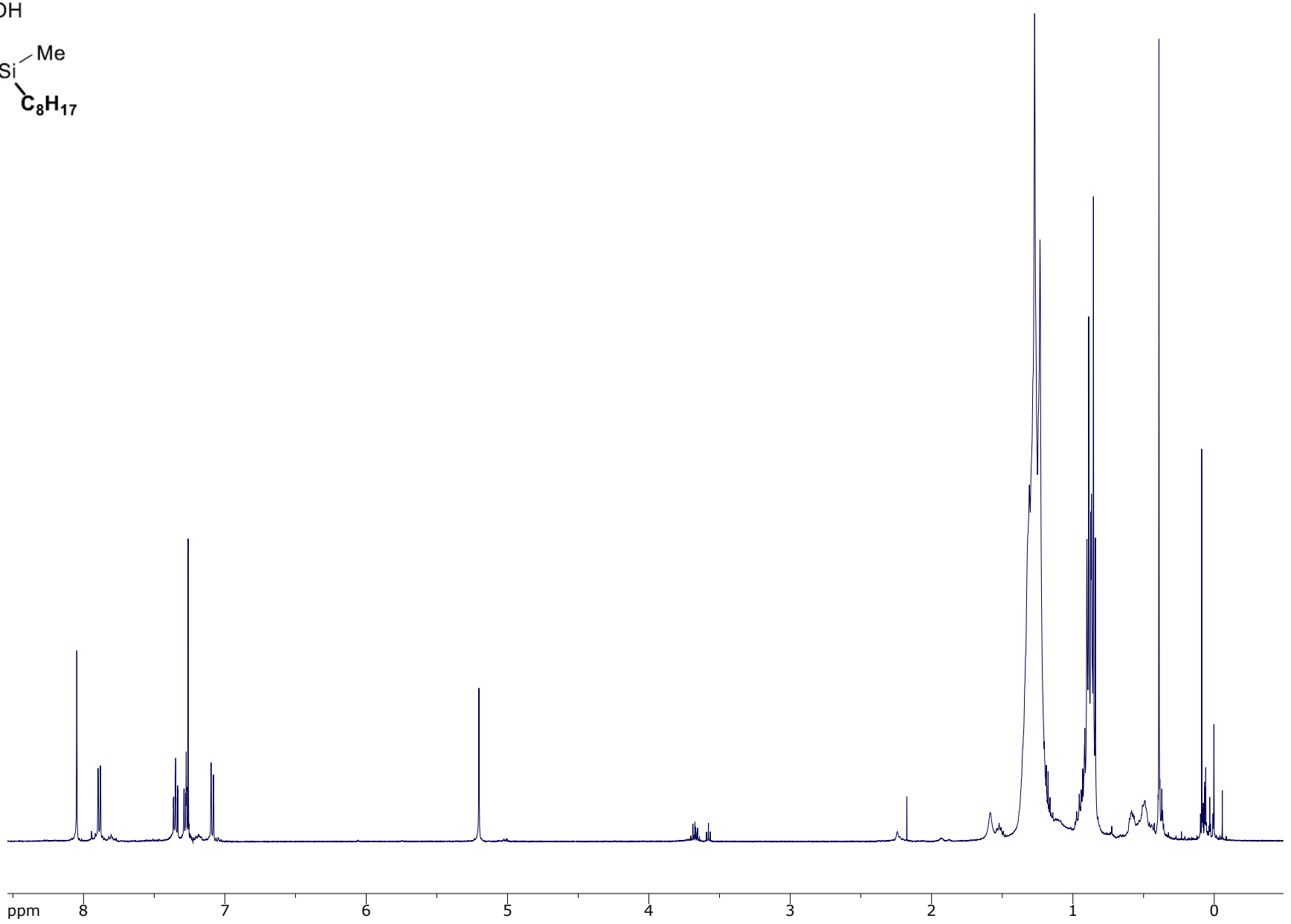
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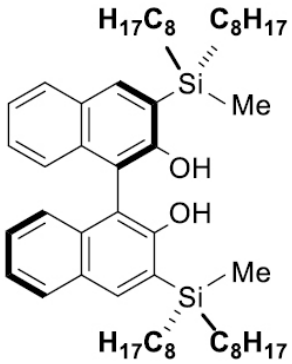
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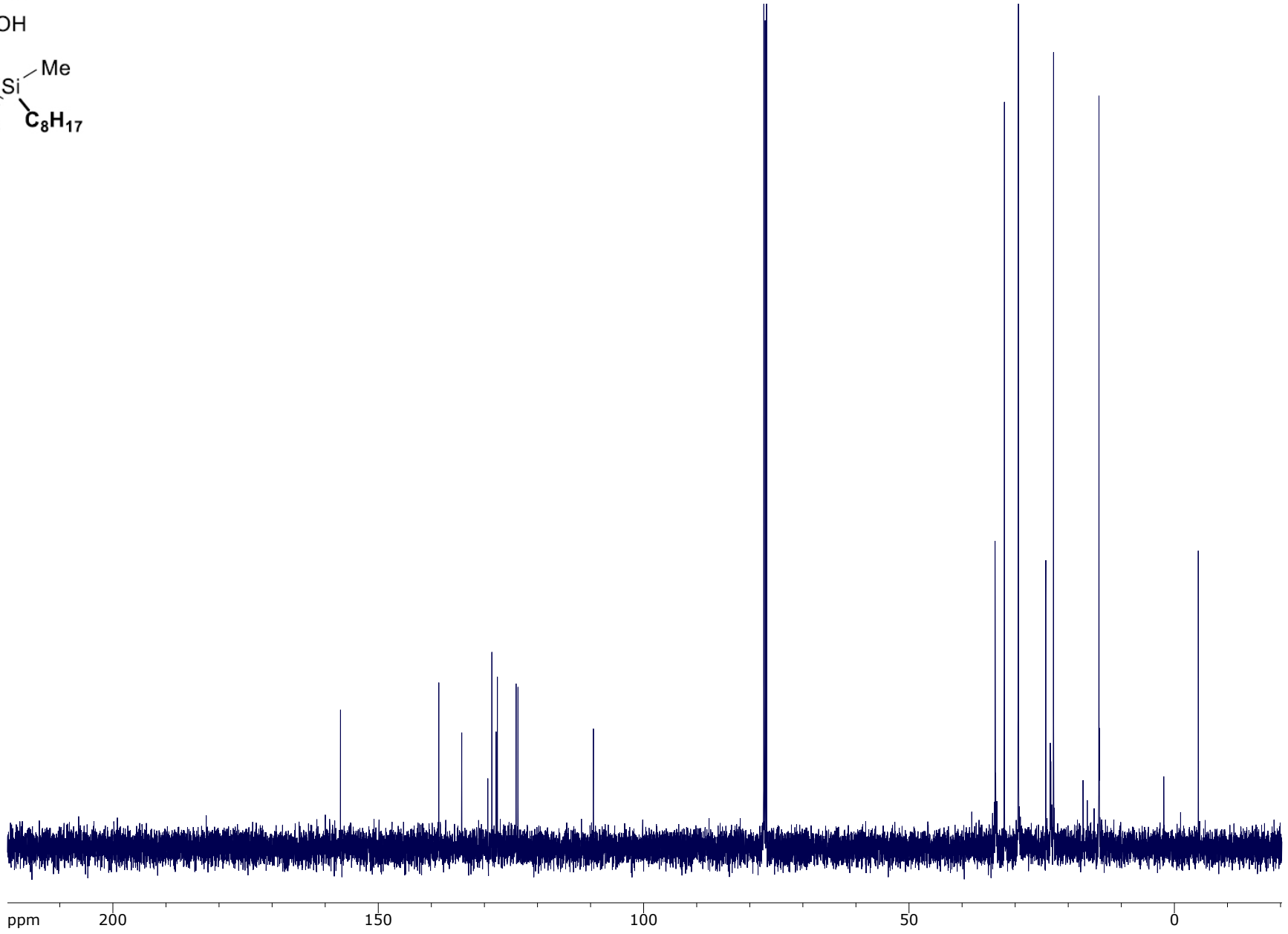
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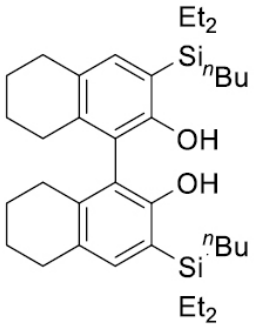
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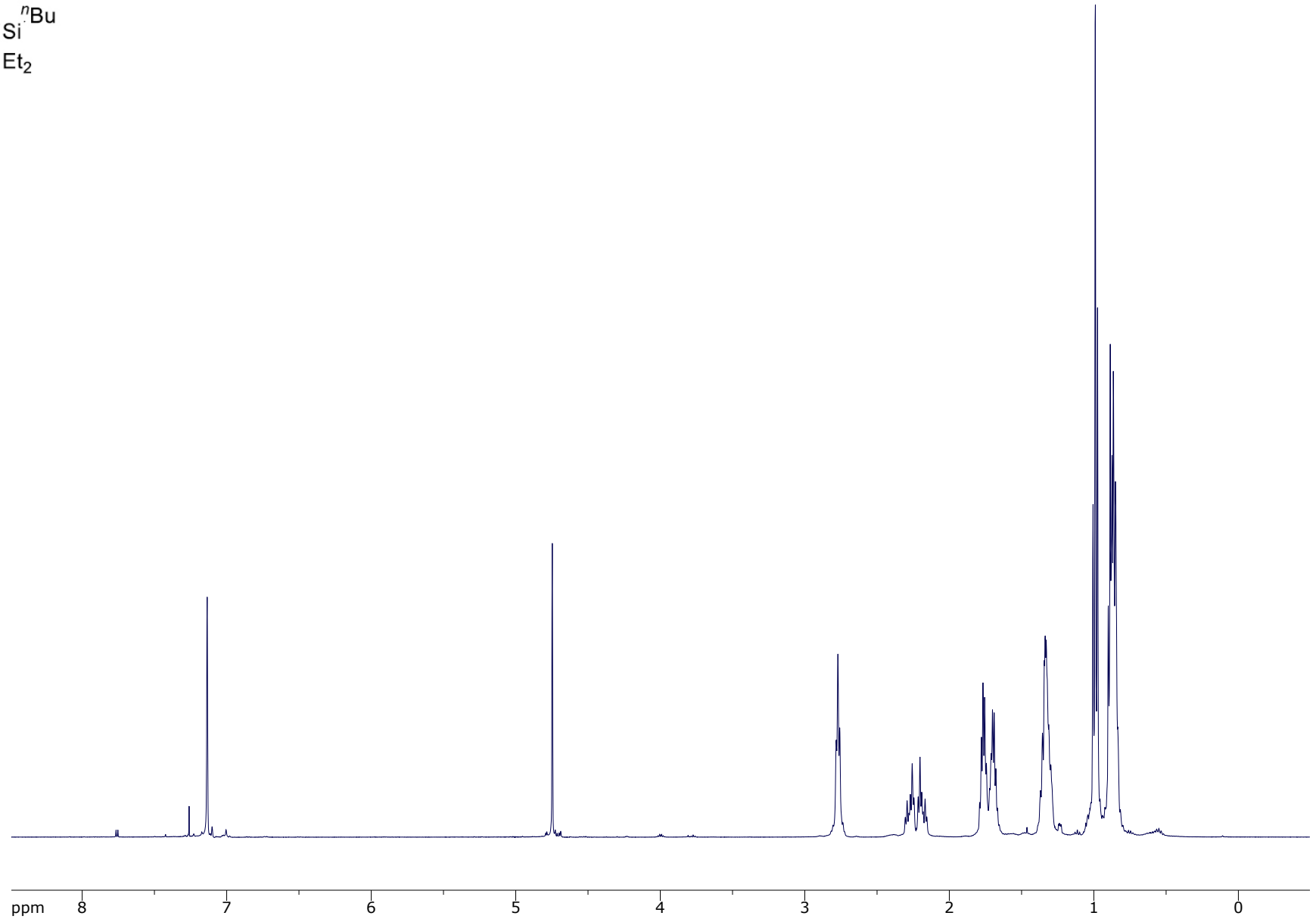
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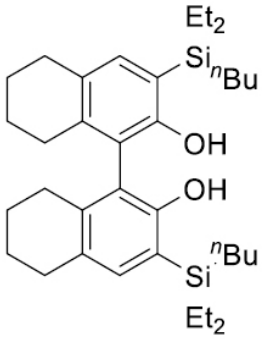
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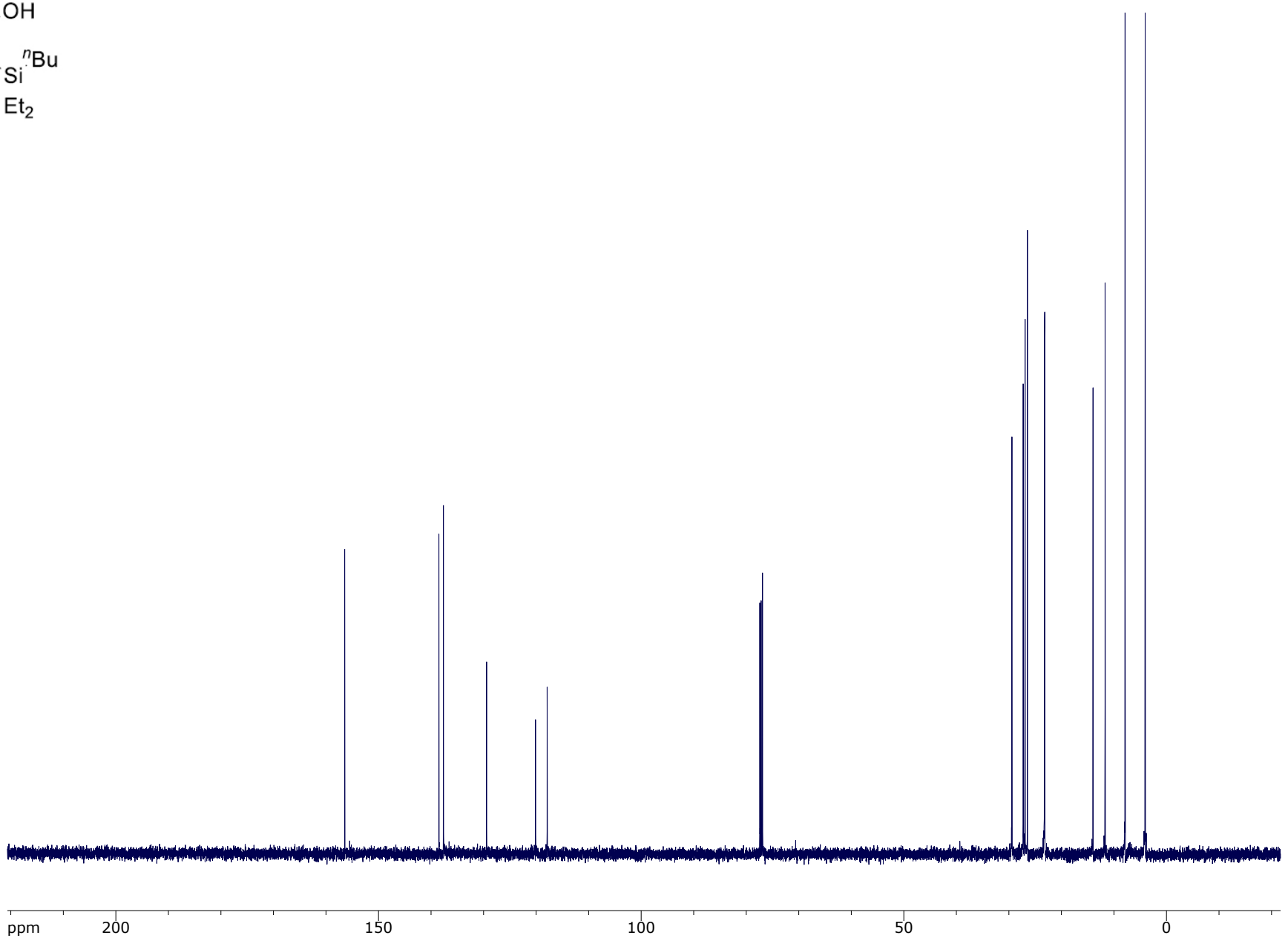
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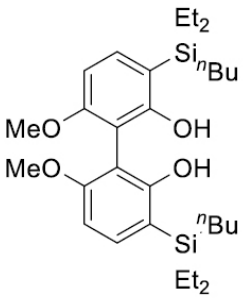
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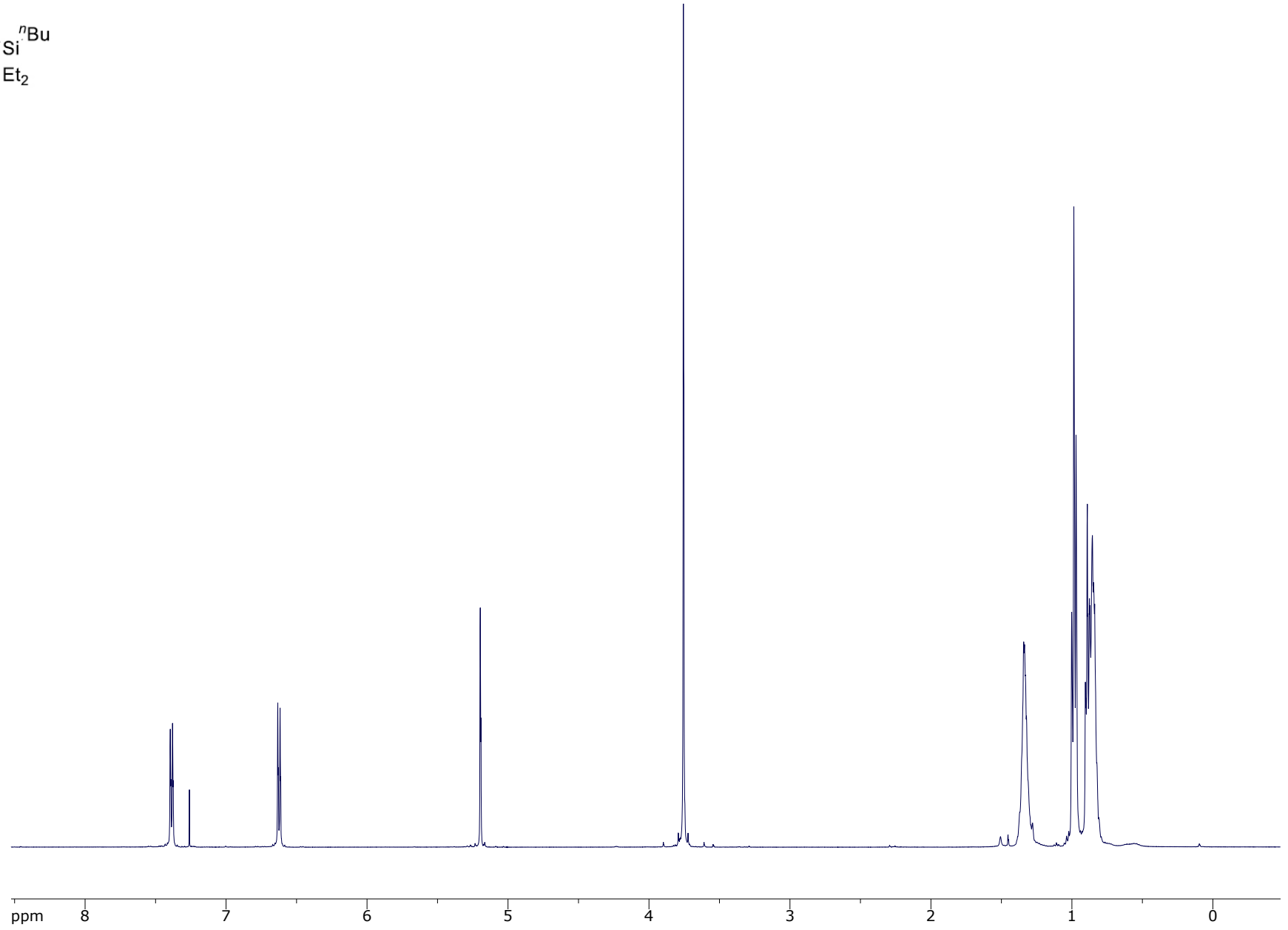
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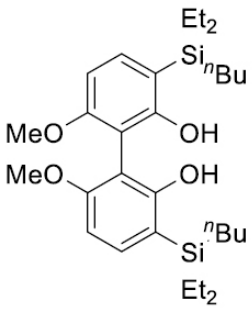
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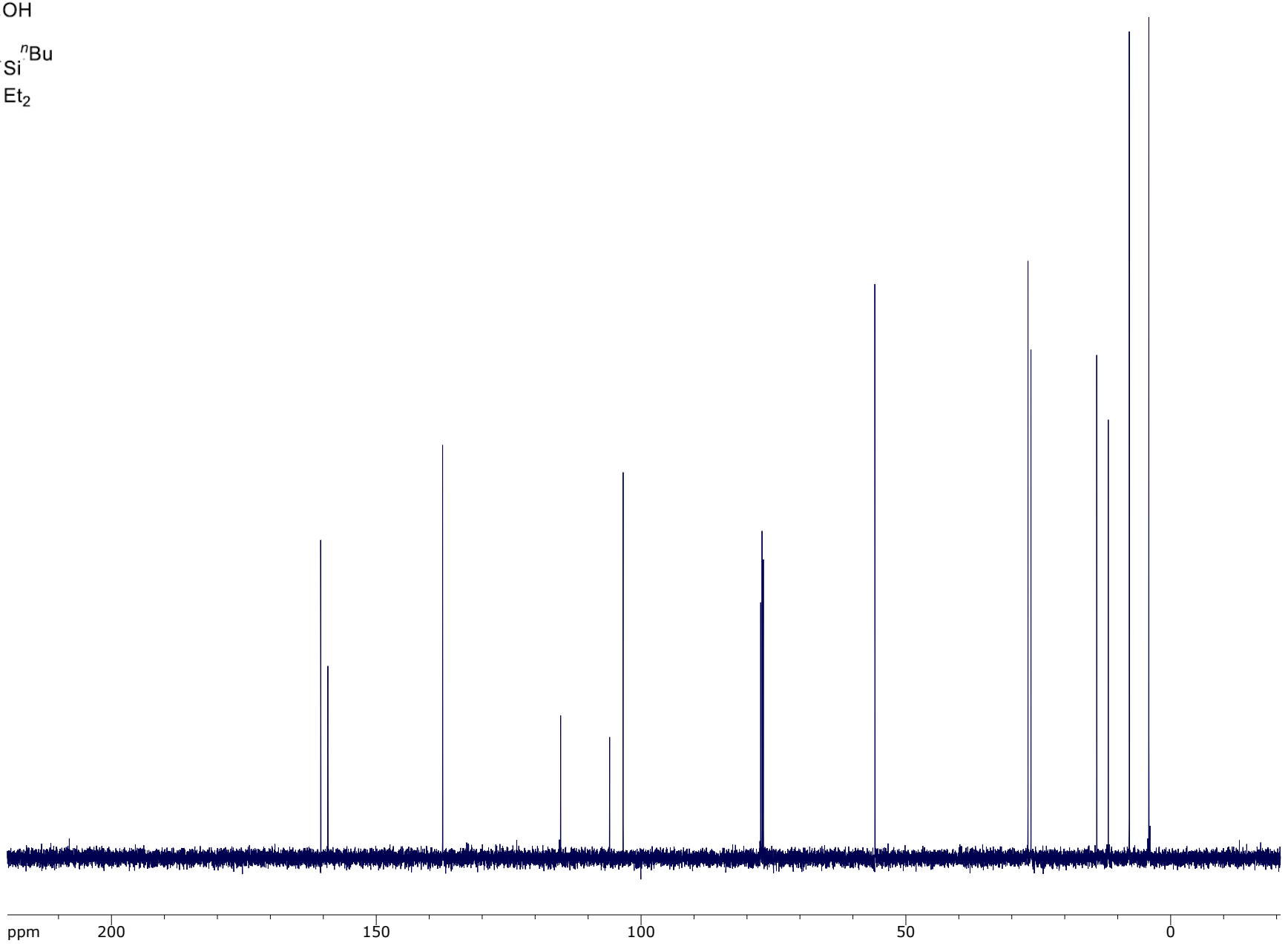
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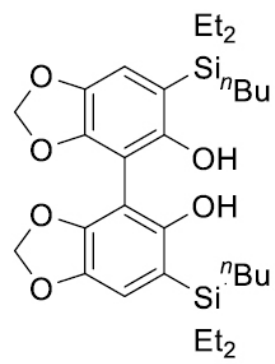
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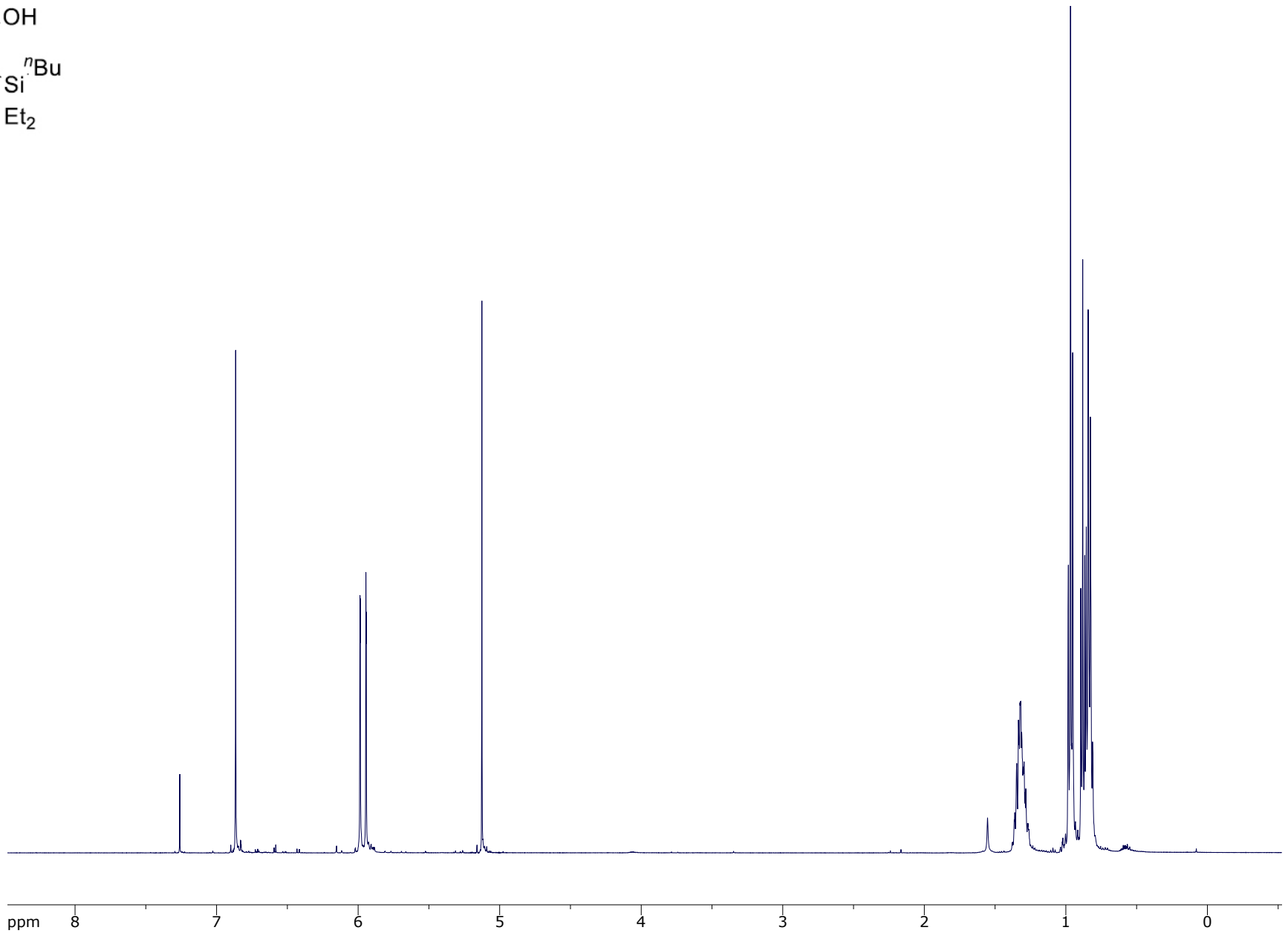
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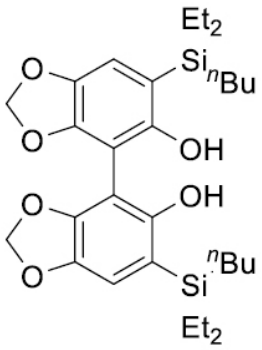
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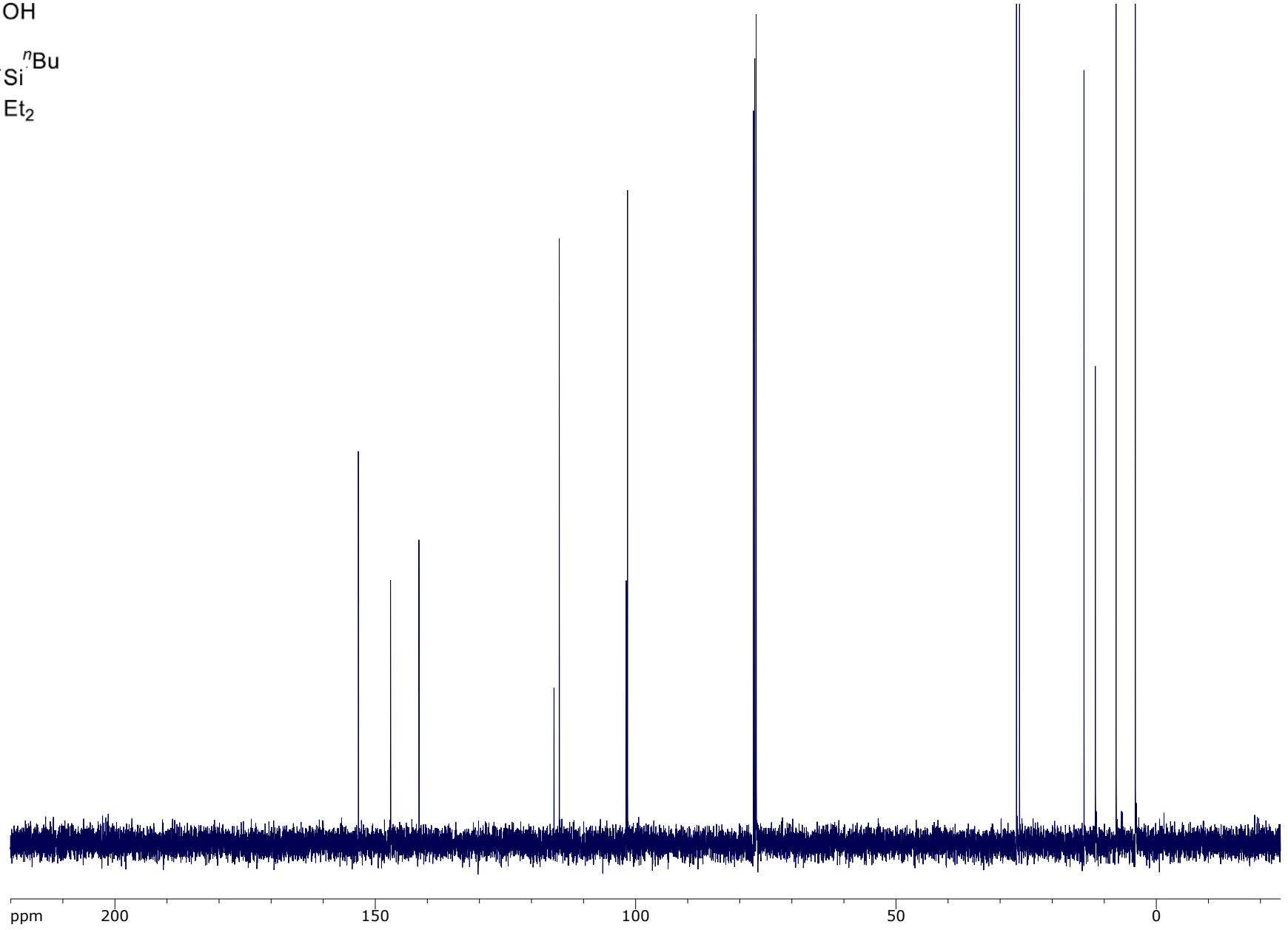
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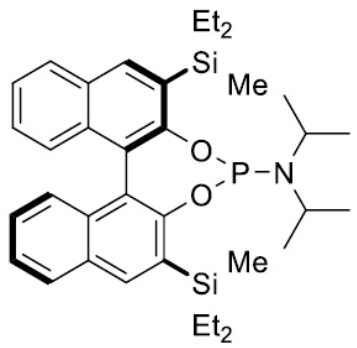
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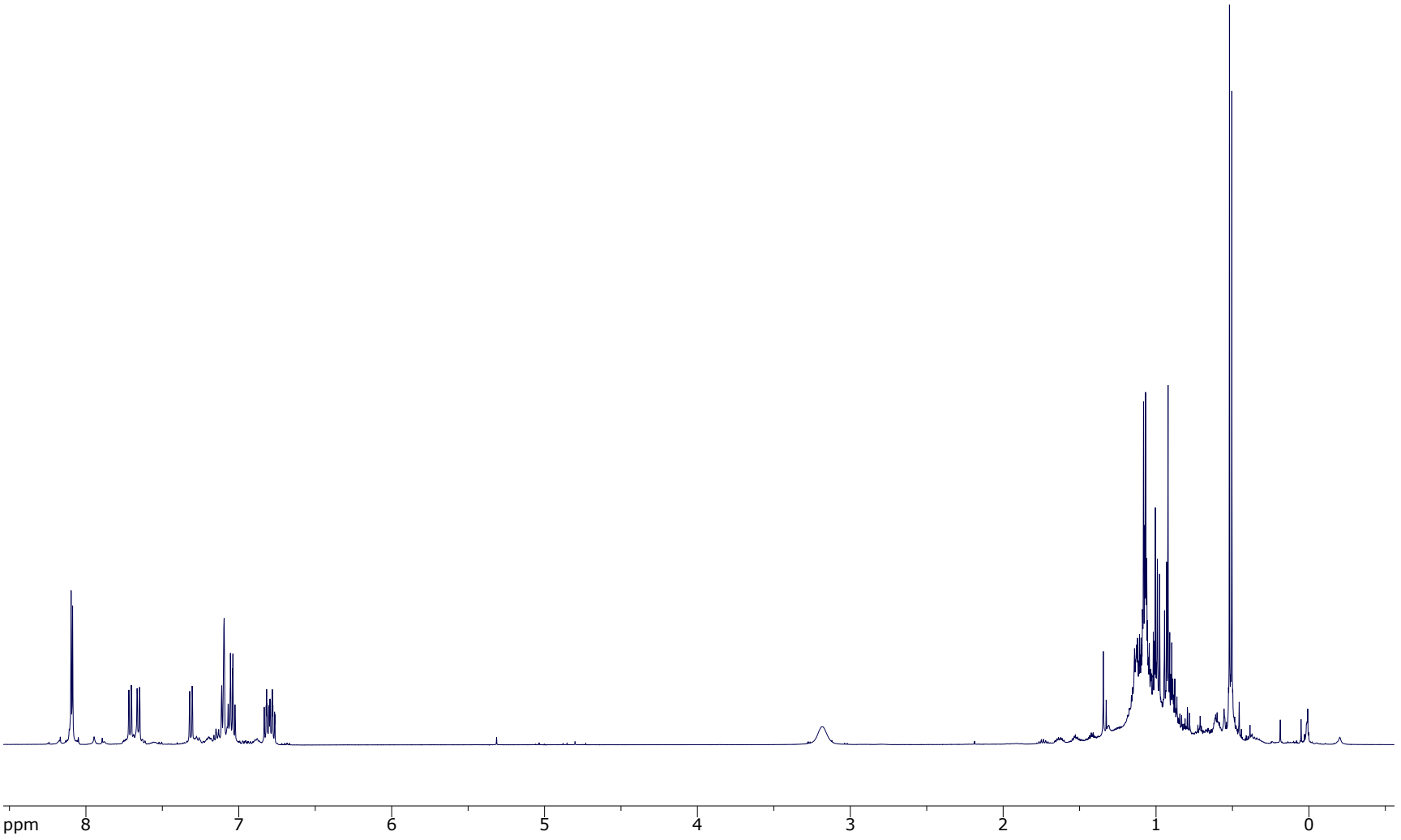
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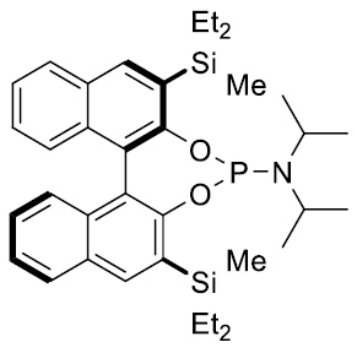
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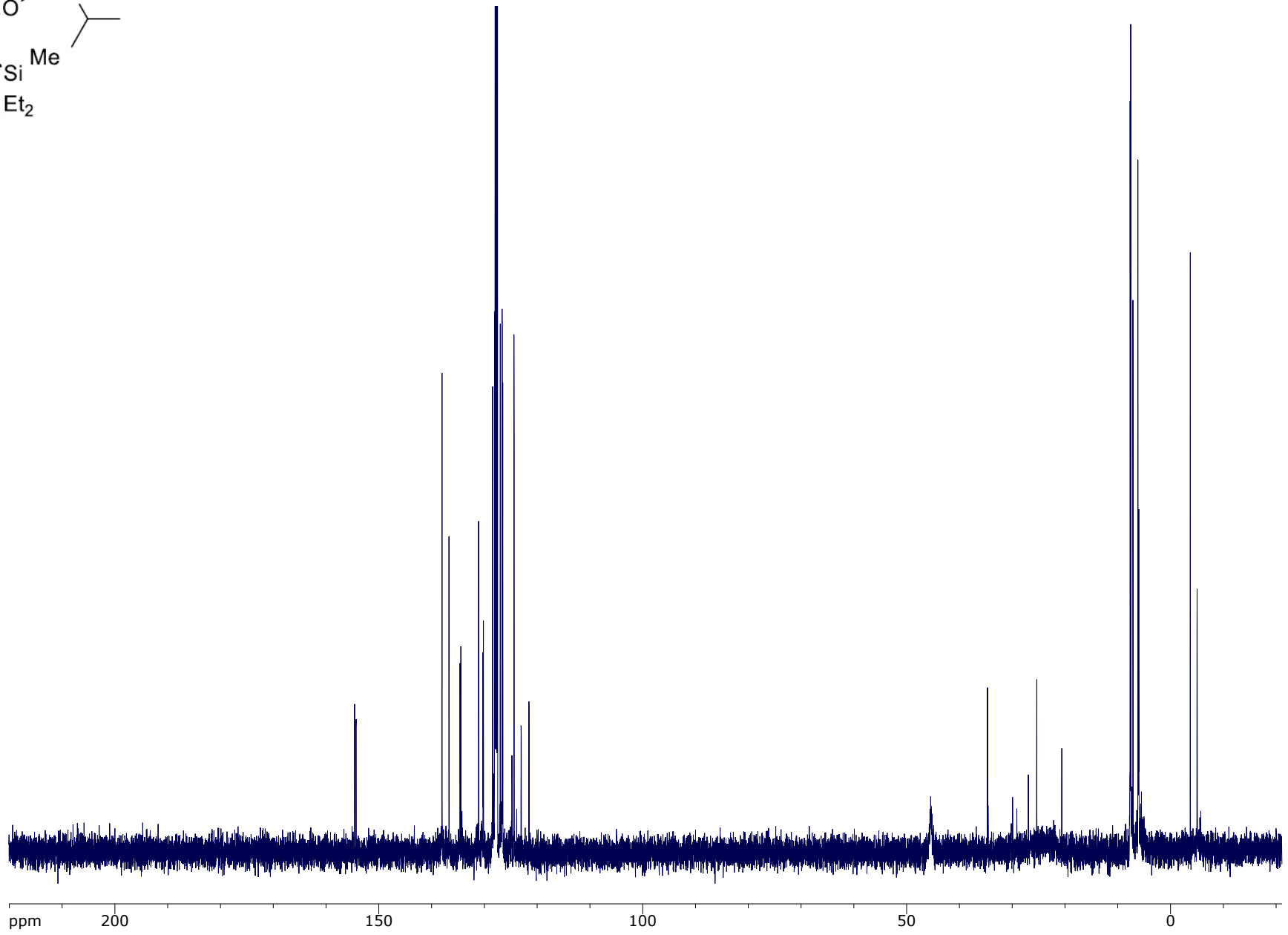
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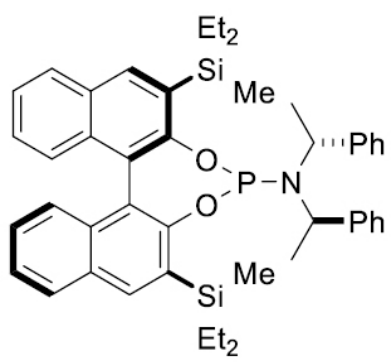
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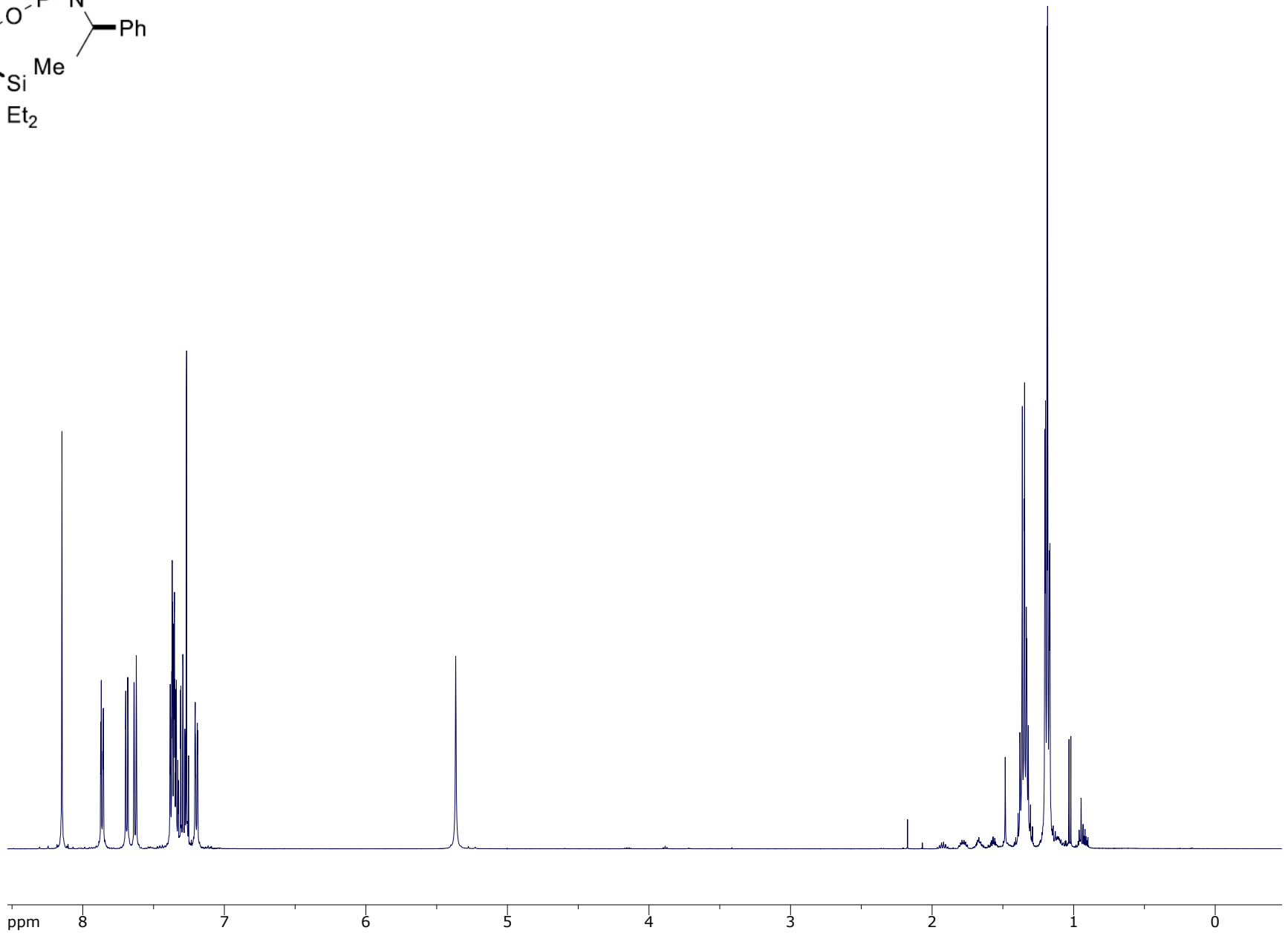
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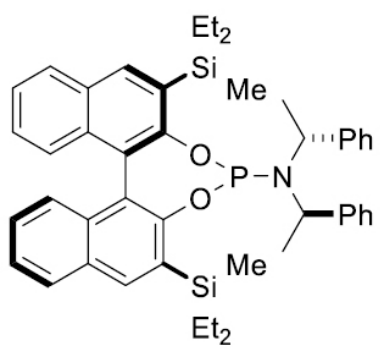
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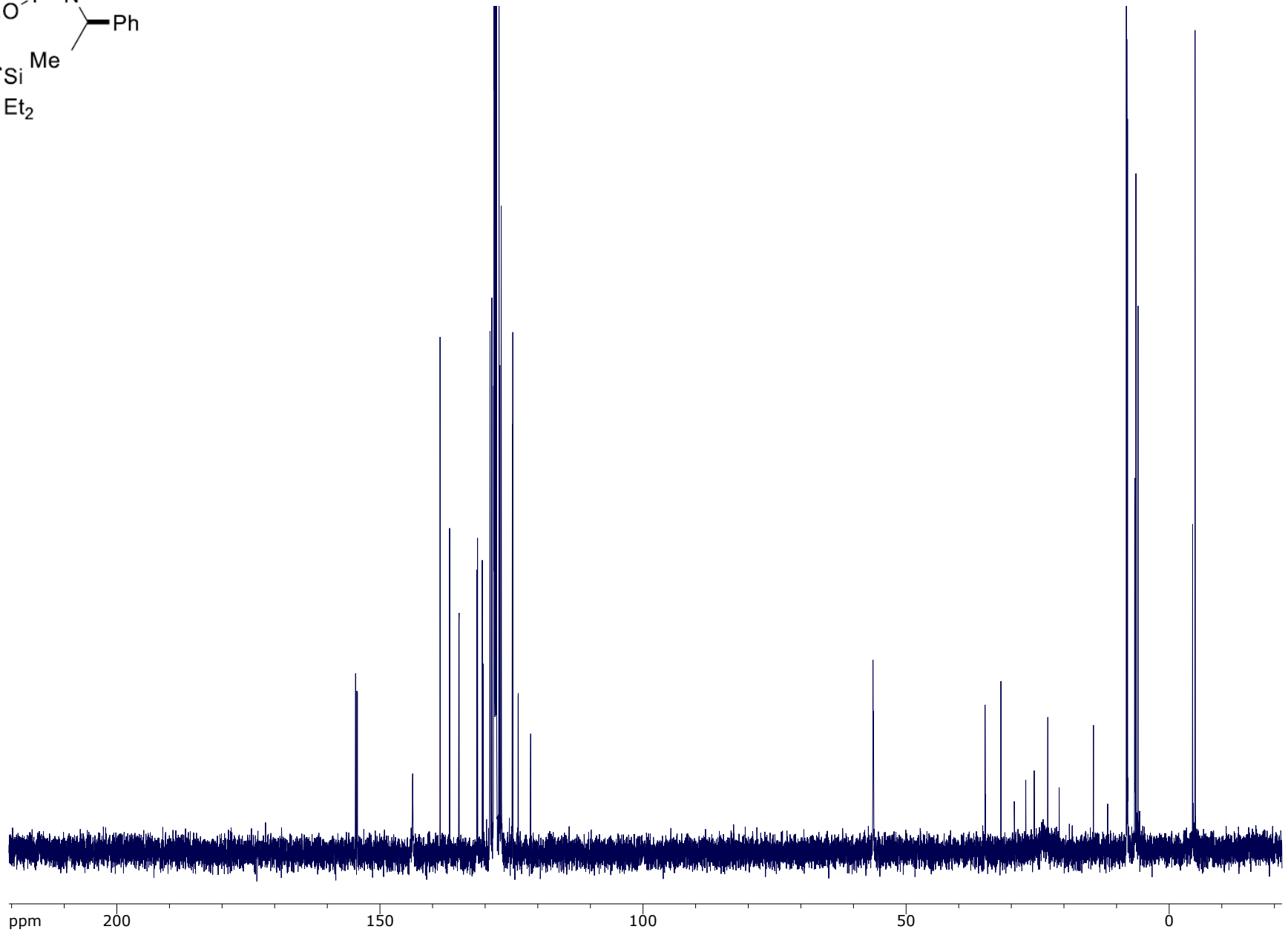
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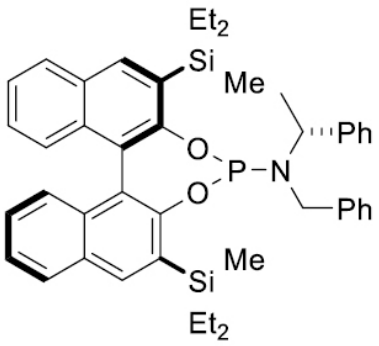
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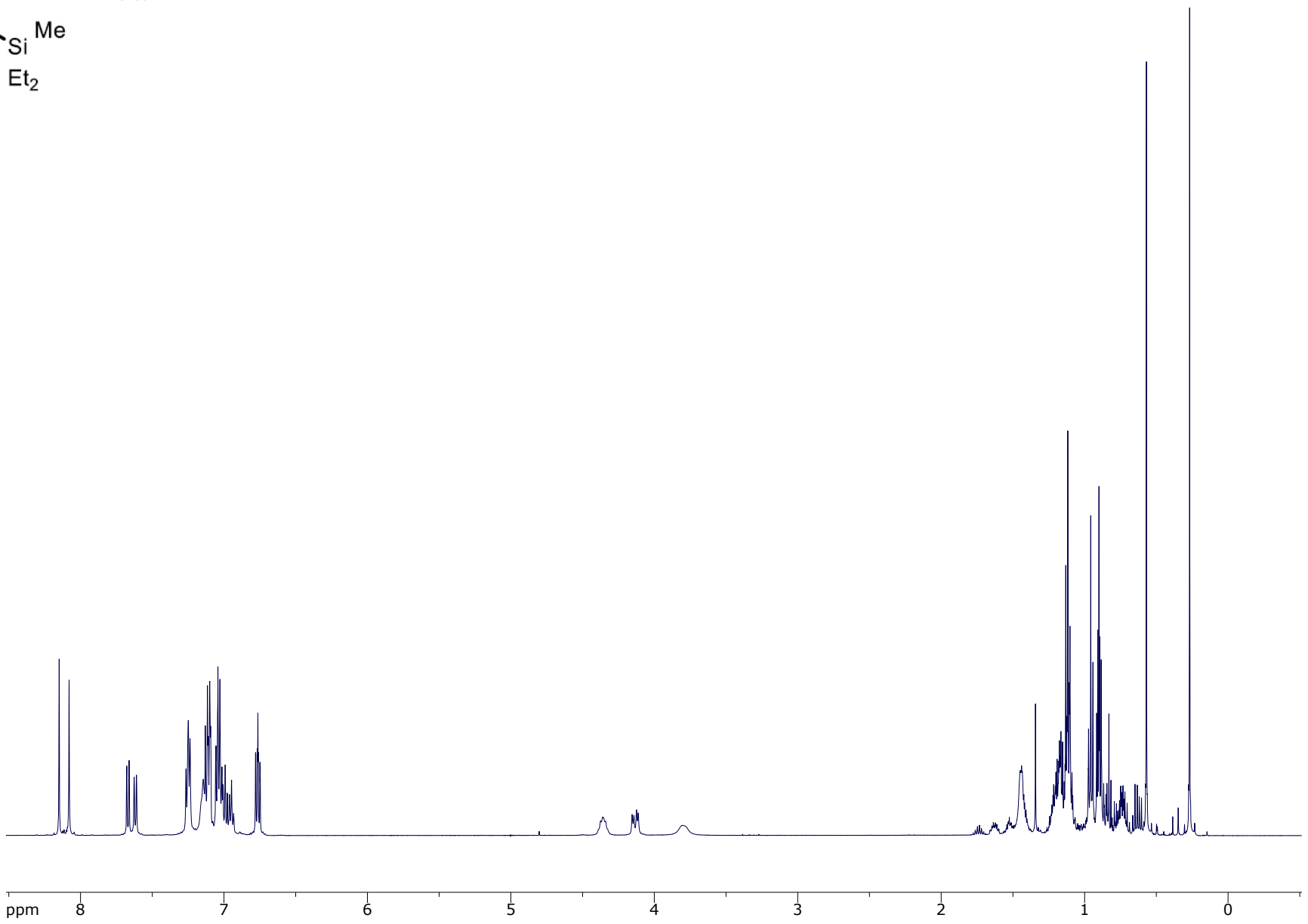
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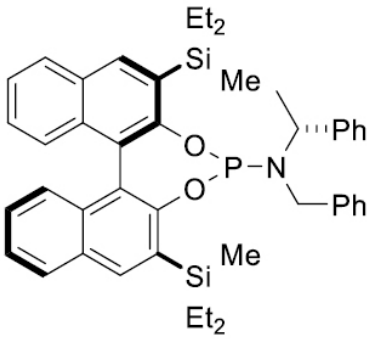
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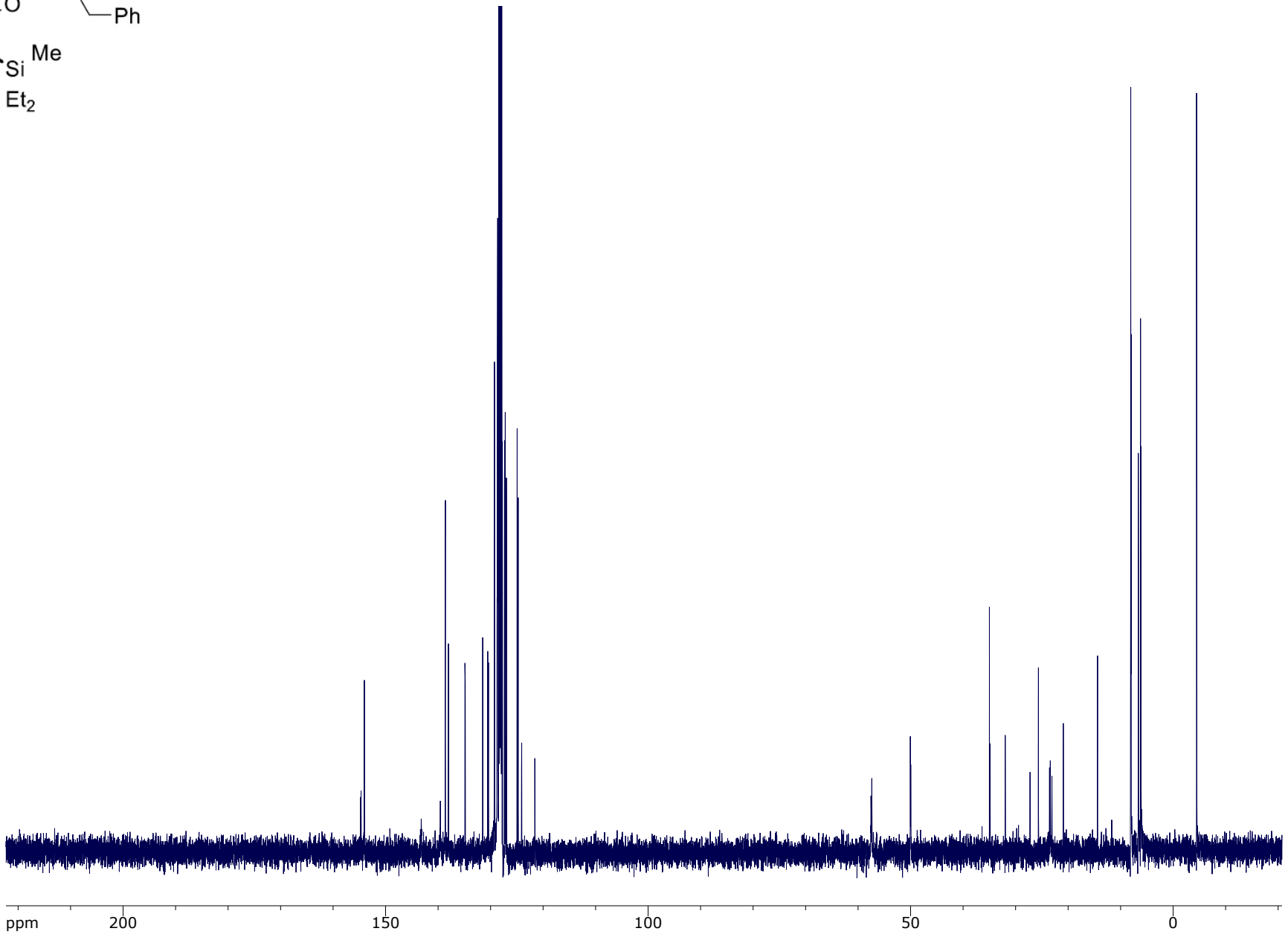
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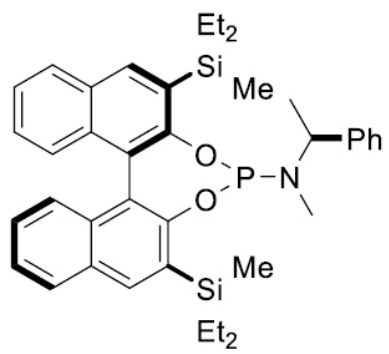
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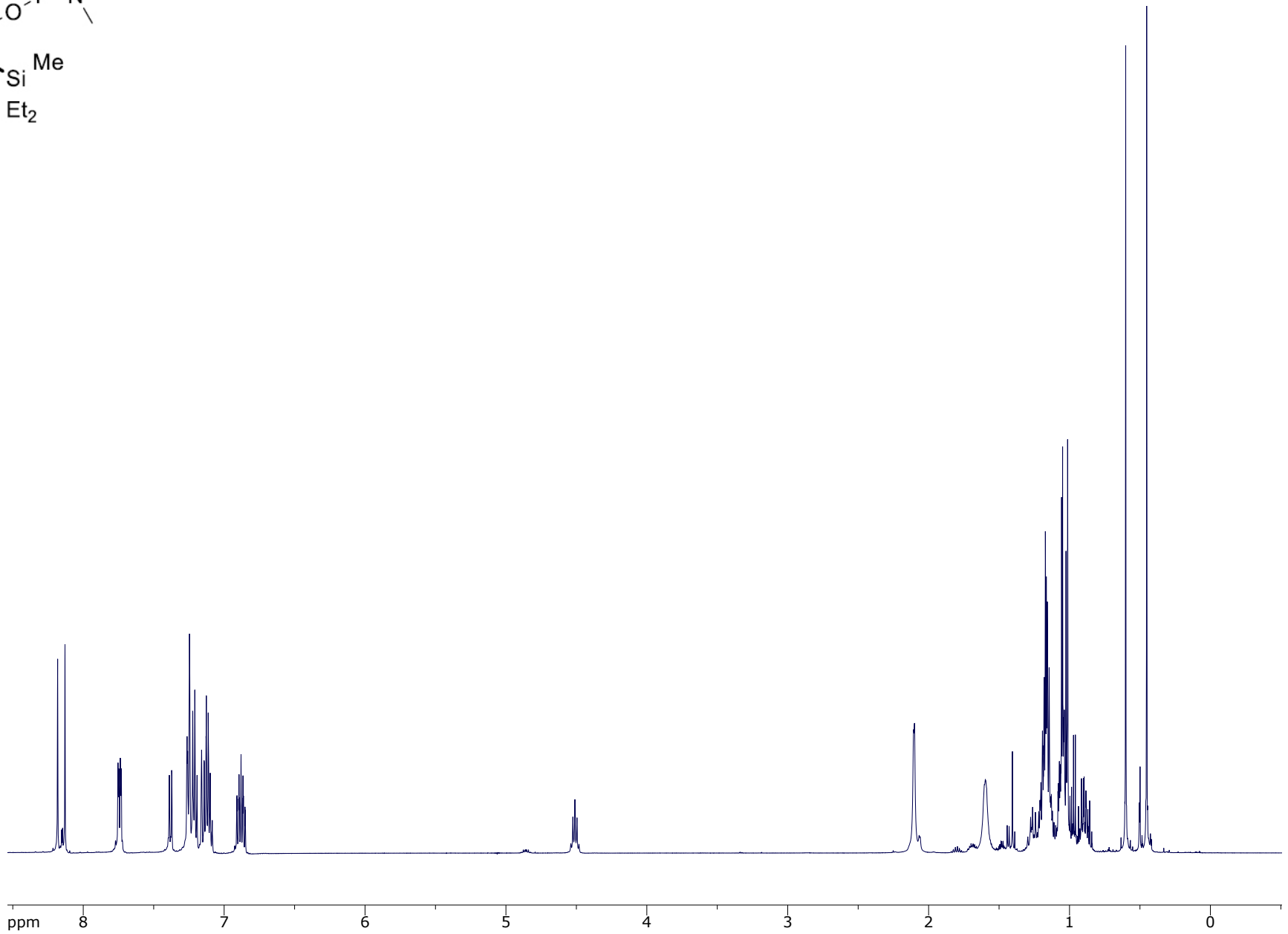
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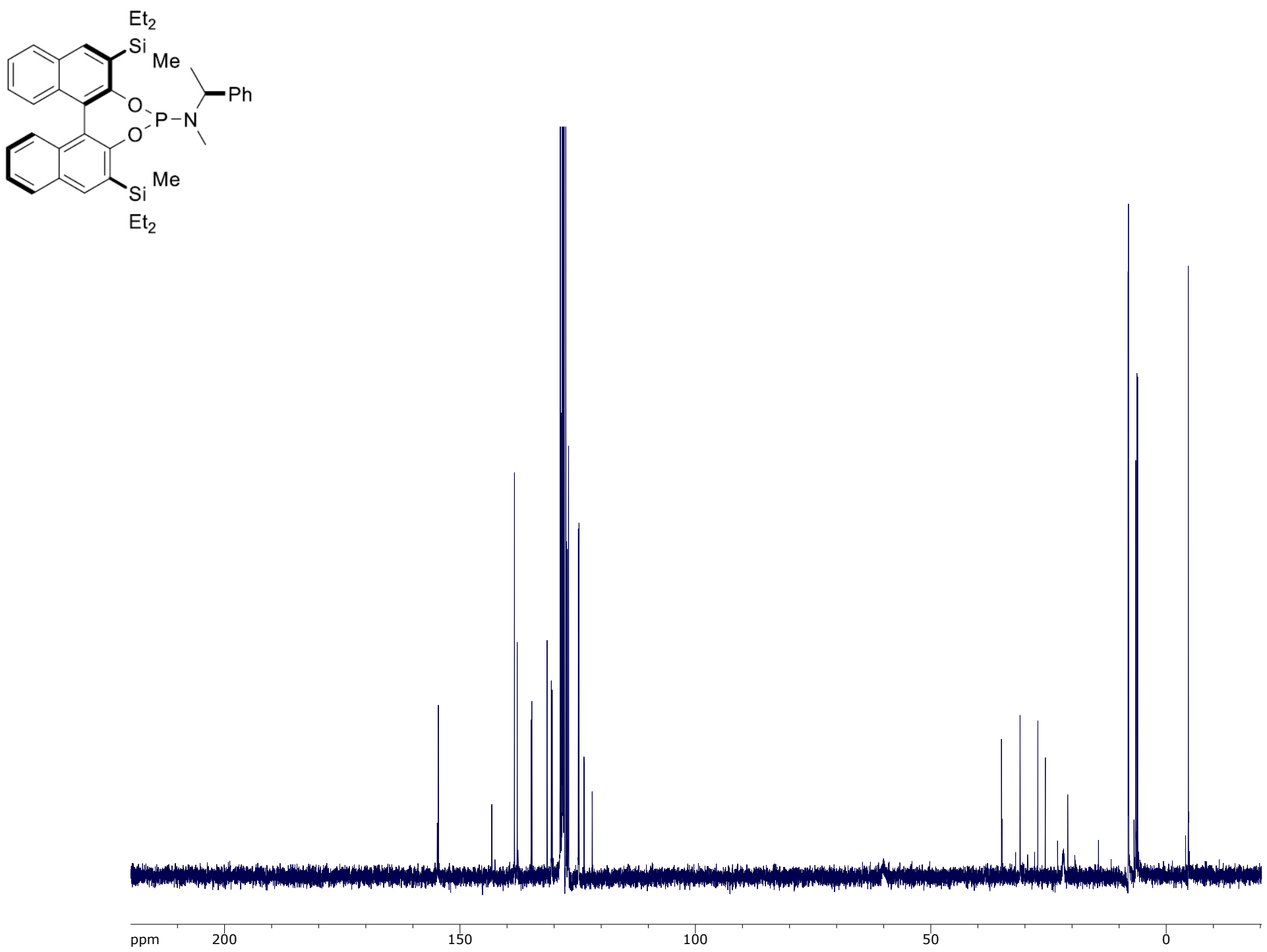
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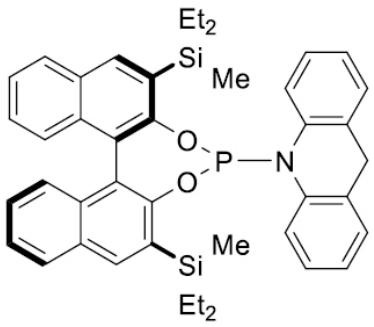
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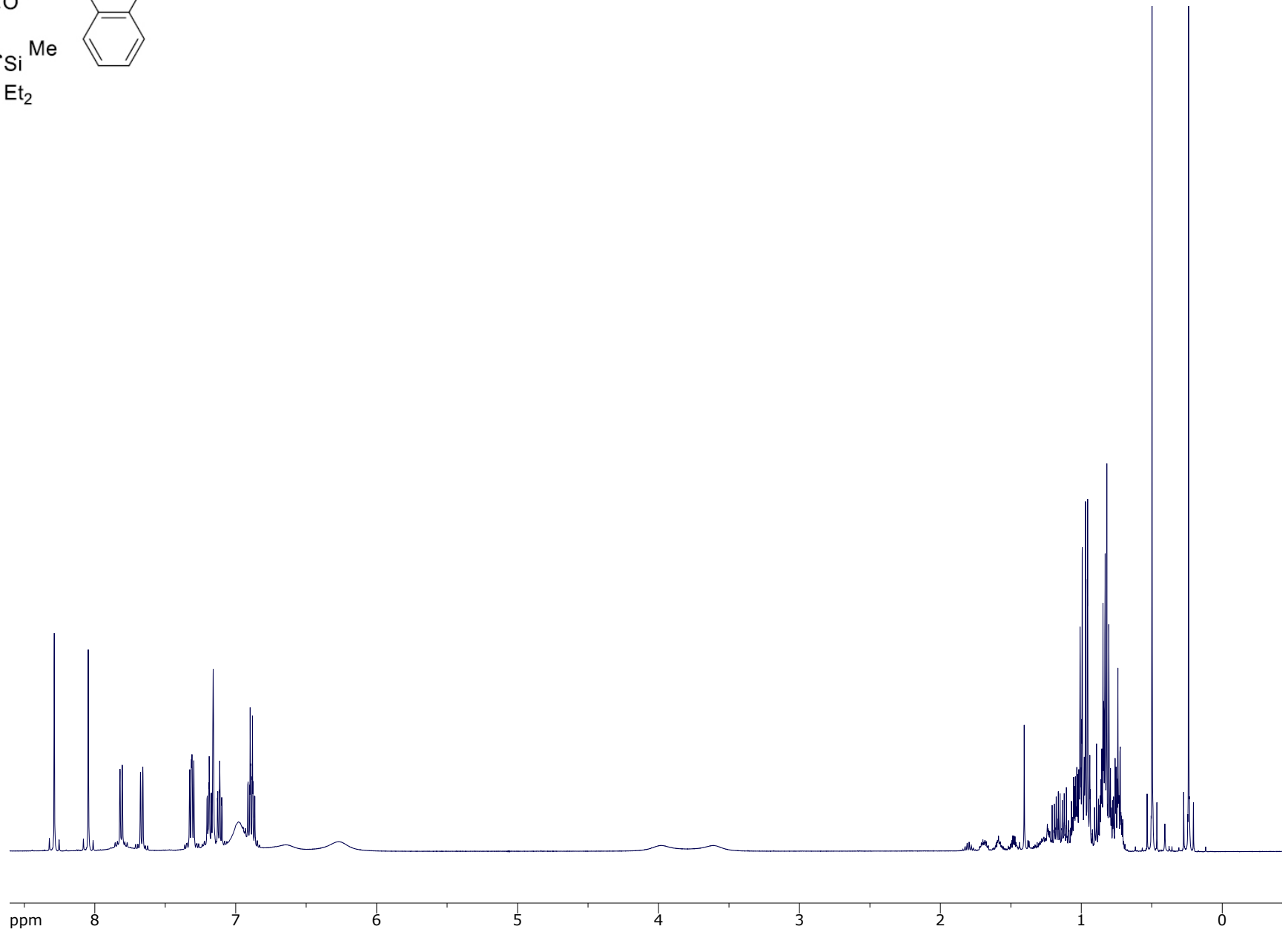
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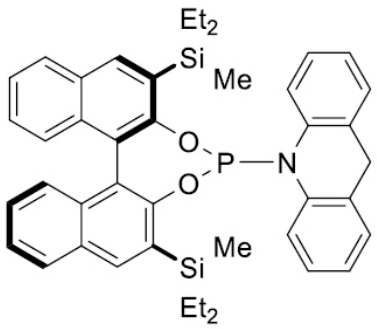
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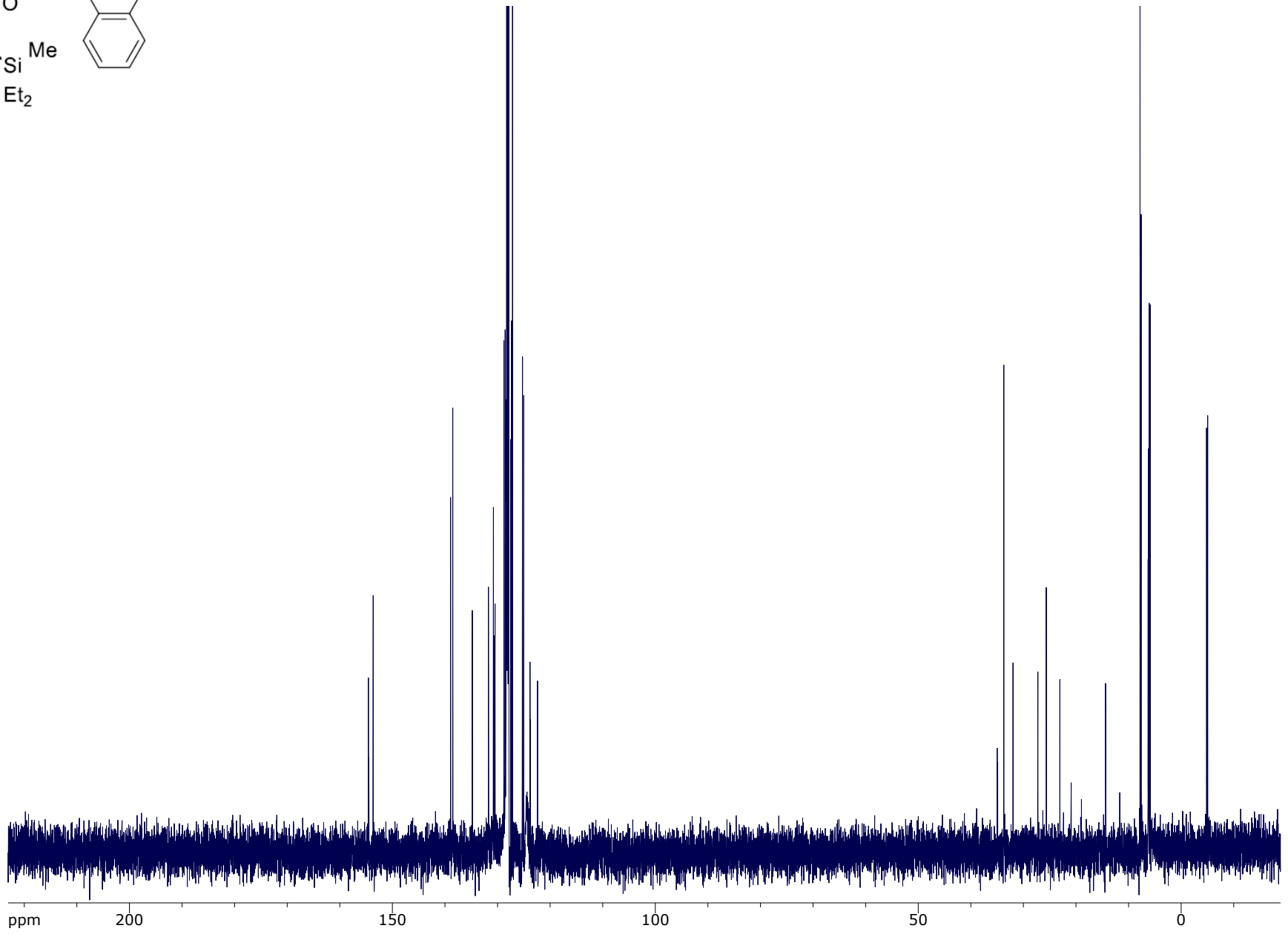
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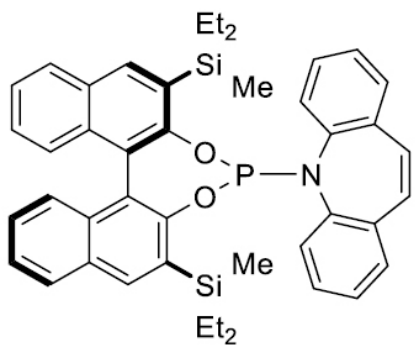
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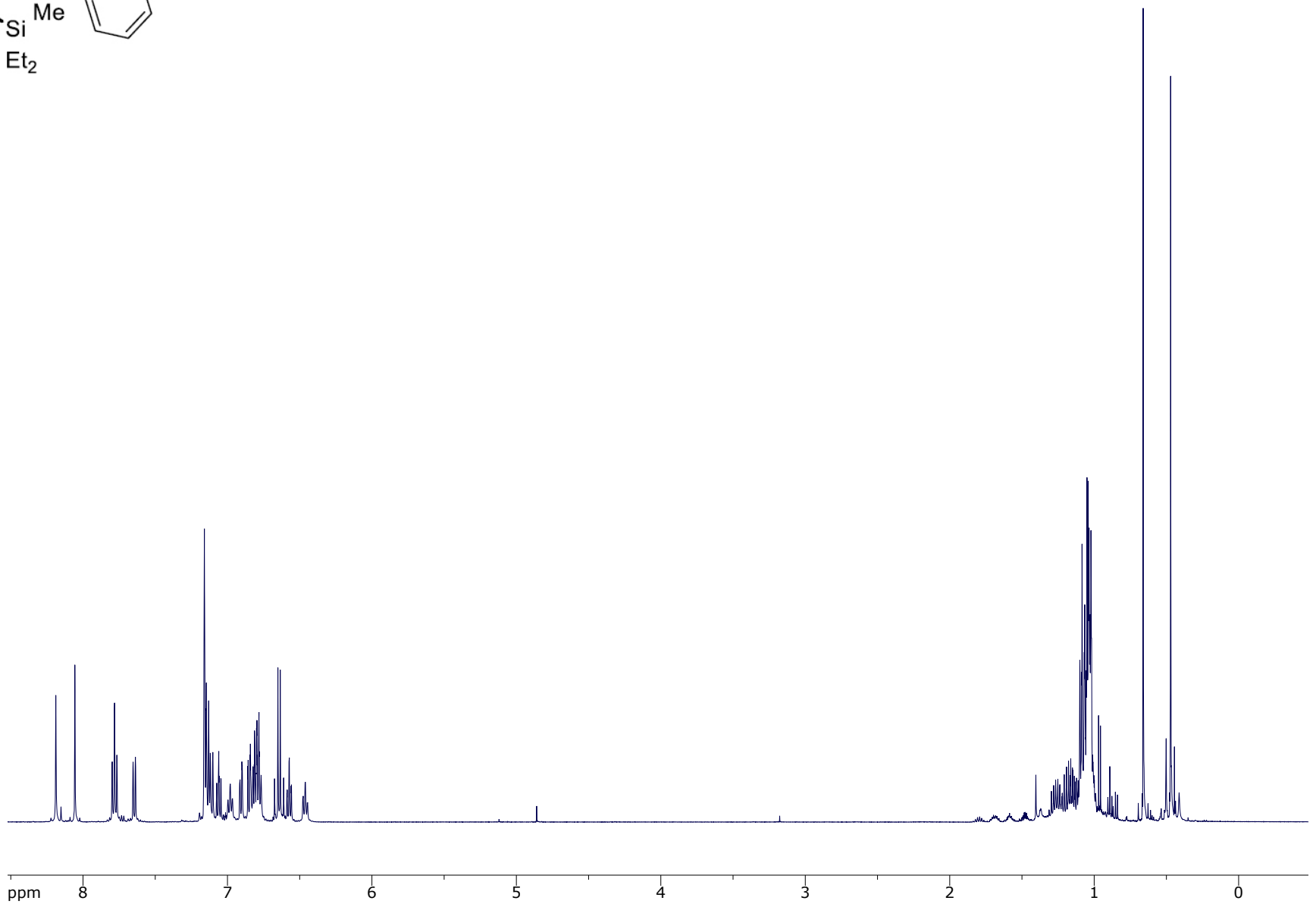
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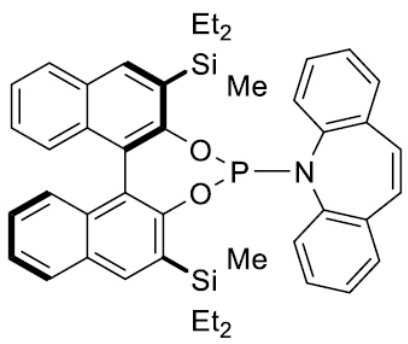
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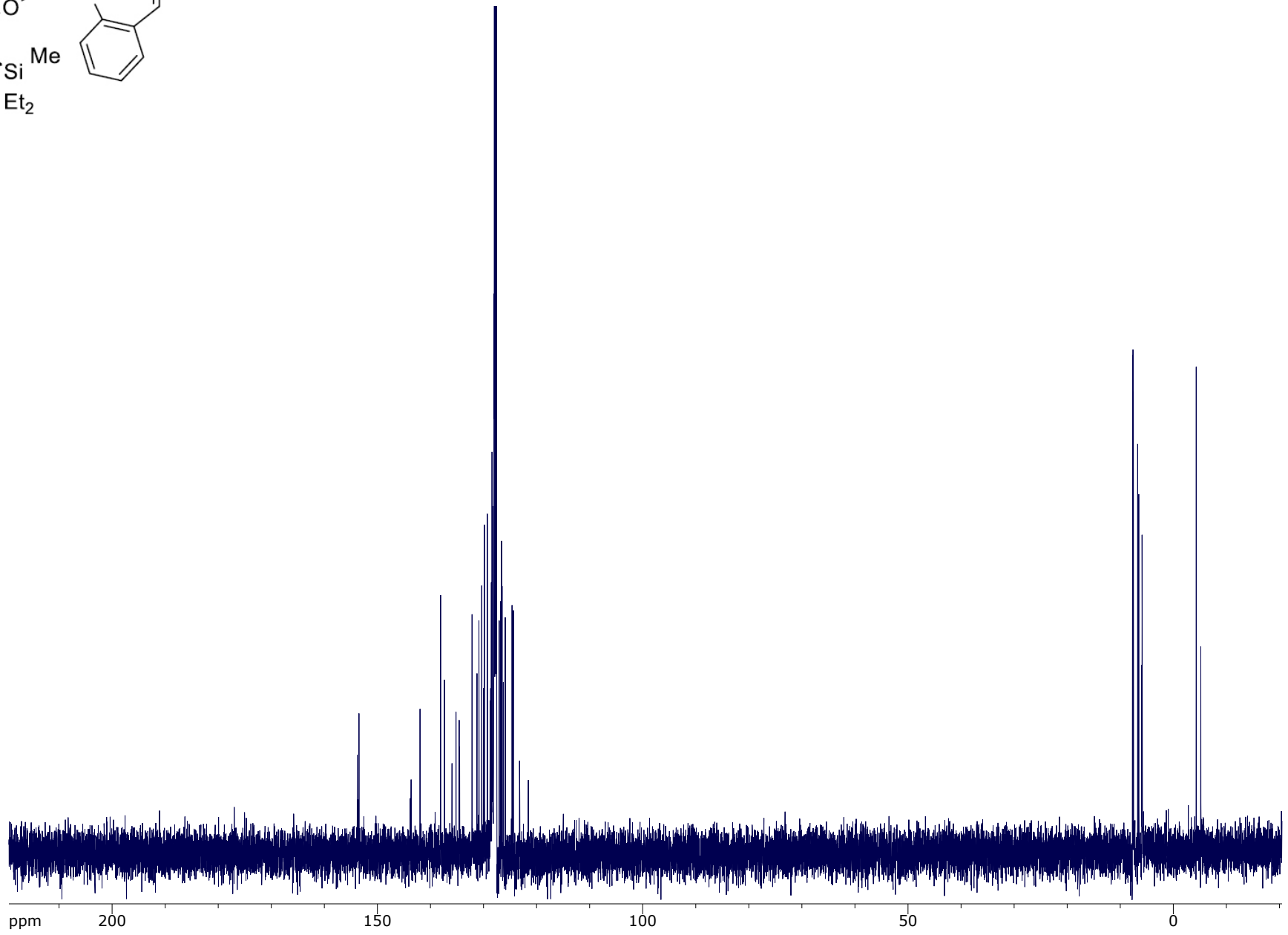
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