Doctoral Dissertation

Cobalt(II) complexes with Schiff base ligands as new pre-catalysts for hydrosilylation of alkenes and alkynes

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A doctoral dissertation submitted in the form of a thematically coherent series of scientific articles published in scientific journals, prepared in the field of science, in the discipline of chemical science.

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~My sincere thanks

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A special thanks to Centre For Advanced Technologies, Adam Mickiewicz University Poznań, in which I had an opportunity to conduct my studies.

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Curriculum vitae

Personal Information

Name / Surname	Maciej Skrodzki
Date of birth	10.10.1993
Place of birth	Poznań
Citizenship	Polish

Educational Career

10.2012 – 09.2015	Adam Mickiewicz University in Poznań, General Chemistry – First cycle studies - *Bachelor*
10.2015 – 06.2017	Adam Mickiewicz University in Poznań, General Chemistry – Second cycle studies - *Master of sciences*
09.2017	Adam Mickiewicz University in Poznań - Faculty of Chemistry – *PhD candidate*

Scientific resume

Articles included in the doctoral dissertation.

Appendix **A1** Bocian A*., **Skrodzki M***., Kubicki M., Gorczyński A., Pawluć P., Patroniak V.; *The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins. Appl. Catal. A-Gen.* **2020**, 602, 117665. [IF= 5.72, MNiSW= 100, Cited by 6(5), *equally contributed]

Appendix **A2** **Skrodzki M**., Patroniak V., Pawluć P.; *Schiff Base Cobalt(II) Complex-catalysed Highly Markovnikov-Selective Hydrosilylation of Alkynes. Org. Lett*. **2021**, 23, 663-667. [IF= 6.00, MNiSW= 140, Cited by 13(12)]

Appendix **A3** **Skrodzki M**., Ortega Garrido V, Csaky A. G., Pawluć P.; *Searching for highly active cobalt catalysts bearing Schiff base ligands for Markovnikov-selective hydrosilylation of alkynes with tertiary silanes. J. Catal.* **2022**, 441, 116-121. [IF= 8.05, MNiSW= 140, Cited by 0]

Appendix **A4** **Skrodzki M**., Witomska S., Pawluć P.; *Sodium triethylborohydride as a catalyst for the dehydrogenative silylation of terminal alkynes with hydrosilanes. Dalton Trans*., **2018**, 47, 5948. [IF= 4.57, MNiSW= 140, Cited by 23(22)]

Summary:

IF = 24.34

MNiSW = 520

Citations = 42 (39 *self-citations excluded*)

Articles not included in the doctoral dissertation.

1. Britton L., **Skrodzki M**., Nichol G.S., Dominey A.P., Pawluć P., Docherty J.H., Thomas S.P.; *Manganese-catalysed C(sp^2)-H Borylation of Furan and Thiophenes Derivatives. ACS Catal*. **2021**, 11, 6857-6864. [IF= 13.08, MNiSW= 200, Cited by 3]

2. **Skrodzki M**., Witomska S., Zaranek M., Pawluć P.; *Direct Dehydrogenative Coupling of Alcohols with Hydrosilanes Promoted by Sodium tri(sec-butyl)borohydride. Catalysts*, **2018**, 8, 618. [IF= 4.50, MNiSW= 100, Cited by 7]

3. Zaranek M., **Skrodzki M**., Szudkowska-Frątczak J., Dodot M., Kownacki I., Orwat B., Pawluć P.: *Iridium-catalysed desilylative acylation of 1-alkenylsilanes, J. Mol. Catal. A: Chem.,* **2017**, 426, 75-78. [IF= 5.06, MNiSW= 70, Cited by 6]

Total **IF** = 46.98

Total **MNiSW** = 890

Total **Citations** = 58 (55 *self-citations excluded*)

h-index = 5

Source: Google Scholar, access: 03.07.2022

Achievements

1) Authorship and co-authorship of 7 scientific articles in top peer-revived journals.

2) Rector's and pro-quality scholarship holder during PhD studies.

3) An Award for "Outstanding Poster Presentation" at the "*19th International Symposium on Silicon Chemistry / 10th European Silicon Days"* conference.

4) Second cycle studies graduation with *Maxima Cum Laude* title.

Internships

06-10.2019 **Edinburgh, Scotland**	University of Edinburgh. Supervisor: S. P. Thomas. Project title: Manganese-catalysed C(sp^2)-H Borylation of Furan and Thiophene Derivatives.
02.2019 **Tarragona, Spain**	Centra Tecnologic de la Quimica de Catalunya (CTQC), Supervisor: B. Tylkowski. Theoretical and practical application of confocal Raman spectroscopy
06-07.2015 **Montpellier, France**	Ecole Nationale Supérieure de Chimie de Montpellier. AM2N Group, Supervisor: F. Monnier. Project title: Hydroamination of alkynes in presence of copper catalysts.
08-09.2014 **Płock, Poland**	PKN Orlen – Theoretical and practical aspects of crude oil refinery

Research Projects

02.2022 Principal investigator	Preludium grant no. 2019/33/N/ST4/00049 financed by Polish National Science Centre *Cobalt catalysed hydrogenation of alkenes and alkynes*
10.2017 – 07.2020 Investigator	OPUS grant no. 2016/23/B/ST5/00177 financed by Polish National Science Centre *New catalysts for hydrometallation of alkenes and alkynes*

List of conferences

International Conferences

09.2021 Evora, **Portugal**	*International Symposium on Synthesis and Catalysis 2021* "Schiff Base Cobalt(II) Complex-catalysed Highly Markovnikov-Selective Hydrosilylation of Alkynes" Flash poster presentation
06.2021 Toulouse, **France**	*19th International Symposium on Silicon Chemistry / 10th European Silicon Days* "Schiff Base Cobalt(II) Complex-catalysed Selective Hydrosilylation of Alkynes" Poster presentation - Award for "Outstanding Poster Presentation"
09.2018 Świeradów-Zdrój, **Poland**	*18th International Seminar of PhD Students on Organometallic and Coordination Chemistry* "Sodium Triethylborohydride as a catalyst for the dehydrogenative silylation of terminal alkynes with hydrosilanes" Oral presentation
07.2018 Florence, **Italy**	*28th International Conference on Organometallic Chemistry* "Dehydrogenative Silylation of Terminal Alkynes with Hydrosilanes in the Presence of Sodium Triethylborohydride as Catalyst" *Poster presentation*
06.2018 Poznań, **Poland**	*Chemistry Beyond Nature* "Acylation of Vinylsilanes – Synthetical and Mechanistic Aspects" *Oral and poster presentation*

Domestic Conferences

11.2021 *XXV Ogólnopolskie Sympozjum Naukowe Naukowego Koła Chemików Uniwersytetu im. Adama Mickiewicza w Poznaniu*

Poznań

„Aktywność Katalityczna Kompleksów Kobaltu(II) z zasadami Schiffa w Reakcji Hydrosililowania Alkenów i Alkinów”

Oral presentation

03.2019 XXII Ogólnopolskie Sympozjum Naukowe Naukowego Koła Chemików Uniwersytetu im. Adama Mickiewicza w Poznaniu

Poznań

„Nowe katalizatory reakcji hydrosililowania alkenów i alkinów”

Oral presentation

03.2018 XXI Ogólnopolskie Sympozjum Naukowe Naukowego Koła Chemików Uniwersytetu im. Adama Mickiewicza w Poznaniu

Poznań

„W poszukiwaniu pereł – aktywacja wiązania C-H”

Oral presentation

10.2017 XX Ogólnopolskie Sympozjum Naukowe Naukowego Koła Chemików Uniwersytetu im. Adama Mickiewicza w Poznaniu

Poznań

„Leki małocząsteczkowe w walce z drobnoustrojami”

Oral presentation

05.2017 X Wrocławskie Studenckie Sympozjum Chemiczne

Wrocław „O zmniejszaniu przypadkowości, czyli biomimetyka w czystej postaci”

Oral presentation

05.2017 XLVI Ogólnopolska Szkoła Chemii „Potęga Pierwiastków”

Warszawa „Acylowanie winylosilanów – aspekty syntetyczna i mechanistyczne”

Oral presentation

03.2017 XIX Ogólnopolskie Sympozjum Naukowe Naukowego Koła Chemików Uniwersytetu im. Adama Mickiewicza w Poznaniu

Poznań

„O zmniejszaniu przypadkowości, czyli biomimetyka w czystej postaci”

Oral presentation

05.2016 XLIV Ogólnopolska Szkoła Chemii „Poznaj Naszą Chemię”

Poznań „Powrót do epoki żelaza”

Poster presentation

12.2015 I Wielkopolskie Sympozjum Chemii Bioorganicznej, Organicznej i Biomateriałów BioOrg 2015

Poznań

„Hydroaminowanie alkinów katalizowane związkami miedzi(I)”

Poster presentation

11.2015 *XLIII Ogólnopolska Szkoła Chemii „Chemia Wydobyta Wiedzą”*

Wrocław „Hydroaminowanie alkinów katalizowane związkami miedzi(I)”

Poster presentation

10.2015 XVII Ogólnopolskie Sympozjum Naukowe Naukowego Koła Chemików Uniwersytetu im. Adama Mickiewicza w Poznaniu

Poznań

„Hydroaminowanie alkinów katalizowane związkami miedzi(I)”

Oral presentation

05.2015 VI Wrocławskie Studenckie Sympozjum Chemiczne

Wrocław „Reakcje w reaktorze mikrofalowym jako nowoczesna metoda preparatyki chemicznej „

Oral presentation

04.2015 *XLII Ogólnopolska Szkoła Chemii „Chemia Wydobyta Wiedzą”*

Rzeszów „Acylowanie Winylosilanów – aspekty syntetyczne i mechanistyczne”

Poster presentation

03.2015 XVI Ogólnopolskie Sympozjum Naukowe Naukowego Koła Chemików Uniwersytetu im. Adama Mickiewicza w Poznaniu

Poznań

„Zupa gotowa w pięć minut, czyli reakcje w reaktorze mikrofalowym”

Oral presentation

10.2014 **Poznań**

XV Ogólnopolskie Sympozjum Naukowe Naukowego Koła Chemików Uniwersytetu im. Adama Mickiewicza w Poznaniu

„Destylacja rurowo wieżowa, czyli przerób ropy naftowej”

Oral presentation

03.2014 **Poznań**

XIV Ogólnopolskie Sympozjum Naukowe Naukowego Koła Chemików Uniwersytetu im. Adama Mickiewicza w Poznaniu

„Teoria pola krystalicznego. Główne geometrie związków kompleksowych oraz ich rozszczepienia”

Oral presentation

Summary:	Count	Oral Presentation	Poster Presentation
International	5	2	4
Domestic	16	12	4
Total	21	15	8

Abstract

Hydrosilylation is one of the most important catalytic reactions used on a large industrial scale for the synthesis and modification of silicon compounds. Catalysts commonly used in this process are platinum compounds, however, high price of platinum, negative impact on the environment connected to mining, deposits depletion and impossibility of the catalyst's reuse in technological processes - all have prompted the search for cheaper alternative solutions based on other elements showing similar effectiveness. One idea proposed to solve this problem was to use catalytic systems based on the first-row transition elements (*3d* metals), such as iron or cobalt, that are more abundant in nature. What is more, in the times of multistep and complex ligands, it is essential to develop a rational coordination environment of metal centres. The research work presented in this doctoral dissertation, consisting of a cycle of four papers (A1-A4), is a combination of these two ideas – the use of abundant and sustainable 3*d* metals with simple Schiff base ligands as catalysts for the hydrosilylation reaction.

The first article from the series presented as the basis for conferment of the Doctor of Philosophy degree presents syntheses, structures and catalytic activities of five cobalt(II) complexes with Schiff base ligands. The complexes were applied as pre-catalysts in hydrosilylation of alkenes with primary, secondary, and tertiary silanes. The study has shown that pentacoordinated cobalt(II) chloride complex with benzimidazole/2*H*-imidazole-based ligand, when activated by lithium triethylborohydride, acts as a good catalyst for β-selective hydrosilylation of vinylarenes by primary and secondary silanes in mild conditions and at low catalyst loading.

The second and third papers chosen as the basis of the dissertation describe the catalytic activity of cobalt(II) chloride complexes with benzimidazole/2*H*-imidazole and pyrimidine/2*H*-imidazole-based ligands in the hydrosilylation of alkynes. The above-mentioned complexes, activated by lithium triethylborohydride, have been found to act as effective catalysts for regioselective hydrosilylation of alkynes by primary, secondary, and tertiary silanes. NMR investigation has proven extremely high selectivity of this process toward *syn*-*α*-addition. These catalytic systems were applied to both alkyl- and aryl-substituted internal and terminal alkynes, showing good functional group compatibility (amine, halide, ether, nitrile etc.). The effectiveness of the catalytic process at extremely

low catalyst loading (as low as 500 ppm) in a reaction catalysed by Co(II)/pyrimidine/2*H*-imidazole has pointed out the uniqueness of the developed system.

The last selected article from the cycle presents the first example of sodium triethylborohydride-catalysed C(sp)–H bond silylation. The reaction of aromatic and aliphatic terminal alkynes with hydrosilanes and hydrosiloxanes led to the products of dehydrogenative coupling. Surprisingly, the competitive hydrosilylation of alkynes did not occur as a side-reaction. This observation suggested the need for complex analysis of the reaction pathway on which the metal pre-catalysts are activated by alkali metal borohydrides.

Streszczenie pracy

Hydrosililowanie to jeden z najważniejszych procesów przemysłowych, a swoje zastosowanie znajduje w syntezie oraz modyfikacji związków krzemoorganicznych. Najczęściej stosowanymi katalizatorami tej reakcji są związki platyny. Cena platyny, jej zmniejszające się zasoby, negatywny wpływ na środowisko związany z wydobyciem tego metalu oraz niski stopień jej recyklingu skłaniają naukowców do poszukiwania alternatywnych metali do syntezy katalizatorów. Nowe katalizatory, z założenia, mają być oparte na metalach tańszych, jednocześnie wykazując podobną aktywność katalityczną. Alternatywą taką są metale przejściowe pierwszego szeregu. Żelazo czy kobalt są szeroko rozpowszechnione w przyrodzie, a zatem tanie. Innym ważnym aspektem jest otoczenie koordynacyjne metalu centralnego. Zdarza się, że wieloetapowy proces syntezy zaawansowanych strukturalnie ligandów dorównuje, lub nawet przewyższa cenę platyny. Z tego powodu ważne jest, aby nowe kompleksy metali – katalizatory, posiadały racjonalnie dopasowane ligandy. Moja rozprawa doktorska łączy te dwie idee – zastosowania metali tanich, szeroko rozpowszechnionych w przyrodzie oraz prostych ligandów typu zasad Schiffa do syntezy katalizatorów reakcji hydrosililowania.

Pierwsza praca opisuje projektowanie oraz syntezę pięciu kompleksów kobaltu(II) z ligandami typu Schiffa. Kompleksy zostały przebadane jako pre-katalizatory w reakcji hydrosililowania alkenów z silanami pierwszo- drugo- oraz trzeciorzędowymi. Badania wykazały, że pięciokoorynacyjny kompleks chlorku kobaltu(II) z ligandem benzimidazol/2*H*-imidazol, aktywowany przez trietylohydroboran litu, jest wydajnym i selektywnym katalizatorem hydrosililowania winyloarenów przez pierwszo- i drugorzędowe silany, jednocześnie będąc aktywnym w niskich stężeniach i łagodnych warunkach reakcji.

Druga i trzecia praca opisuje aktywność katalityczną kompleksów kobaltu(II) z ligandami – benzimidazol/2*H*-imidazol oraz pirymidyna/2*H*-imidazol w reakcji hydrosililowania alkinów. Kompleksy te, aktywowane przez trietylohydroboran litu zostały zastosowane jako wydajne katalizatory hydrosililowania alkinów z silanami pierwszo-, drugo oraz trzeciorzędowymi. Badania magnetycznego rezonansu jądrowego dowiodły niemalże wyłączną *syn* addycję silanu. Opracowane układy katalityczne mogą być stosowane zarówno dla alkinów alifatycznych, aromatycznych, wewnętrznych i terminalnych, jak i tych z grupami funkcyjnymi (gr. aminowa, estrowa, halogenkowa,

nitrylowa). Wyjątkowo niskie stężenie katalizatora Co(II)/pirymidyna/2*H*-imidazol (0.05–2 % mol) świadczy o bezsprzecznej unikalności tego układu katalitycznego.

Ostatnia praca prezentuje pierwszy przypadek zastosowania trietylohydroboranu sodu jako katalizatora reakcji dehydrogenującego sililowania wiązania C(sp)-H. Reakcje aromatycznych oraz alifatycznych alkinów z wodorosilanami i wodorosiloksanami w obecności trietylohydroboranu sodu prowadzą do selektywnego otrzymania produktów dehydrogenującego sprzęgania. Co ciekawe, w podanych warunkach reakcji, żaden z produktów hydrosililowania nie został wykryty. W przypadku aktywacji kompleksów metali przejściowych poprzez trialkilohydroborany, powyższe obserwacje uświadamiają potrzebę dogłębnych badań.

Abbreviations

API	amine-pyridine-diimine
Cy	cyclohexyl
dvtms	1,1,3,3-tetramethyl-1,3-divinyldisiloxane
ESI-MS	Mass spectrometry with electrospray ionization
Et	ethyl
GC	gas chromatography
GC-MS	gas chromatography coupled with mass spectrometry
IPO	iminopyridine-oxazoline
*i*Pr	isopropyl
Me	methyl
Mes	mesityl
ox	oxazoline
PDI	pyridinediimine
Ph	phenyl
PyBox	(2,6-bisoxazoline)pyridine
*t*Bu	*tert*-butyl
THF	tetrahydrofuran
UV	ultraviolet (light)

1. Overview of the literature

1.1 General introduction

Silicon compounds represent a very wide area of worldwide industry. Silicon and its compounds can be found in multipurpose products used in everyday life, as well as in cutting edge special purpose technologies: from ceramics, electronics, photovoltaics, silicone rubbers to optics, medicine, pharmacy, reagents and fine chemicals[1–6]. Two of the most important and interesting compounds are siloxanes and silicones. Siloxanes are organosilicon compounds with silicon-oxygen-silicon backbone with *R* group connected to silicon, where *R* stands for hydrogen atom or organic groups or chains. Polymers of siloxanes, such as poly(dimethylsiloxane) or poly(diphenylsiloxane), are named silicones[7]. They can be synthesised in many variations and may exhibit different properties. The presence of organic groups paves the way for a diversity of modifications. Silicones and siloxanes have become known as components oils and greases, emulsions, antifoams, rubbers, caulks and resins[8,9]. Because of good biocompatibility, low skin irritation potential, UV resistance, and water vapour permeability they are applied in modern healthcare and cosmetics[10–14]. The fast technological pace and consumerism induce the pressure on the search for newer and more cost-efficient technologies to meet the increasing demands for synthesis and modification of such compounds. One of the most straightforward reactions for the synthesis and modification of siloxanes and silanes is hydrosilylation.

1.1 Hydrosilylation

The reaction of addition of silicon hydrides to unsaturated π bonds (i.e., carbon-carbon, carbon-oxygen, or carbon-nitrogen unsaturated bonds) is known as hydrosilylation. The variety of unsaturated compounds and hydrosilanes opens the possibility of syntheses of a diversity of products. The catalytic approach to hydrosilylation offers control of regio- or stereoselectivity of this process. The catalytic hydrosilylation of alkenes usually results in the formation of one of two possible products, while

hydrosilylation of alkynes may results in the formation of one of three possible products (*Figure 1.1*).

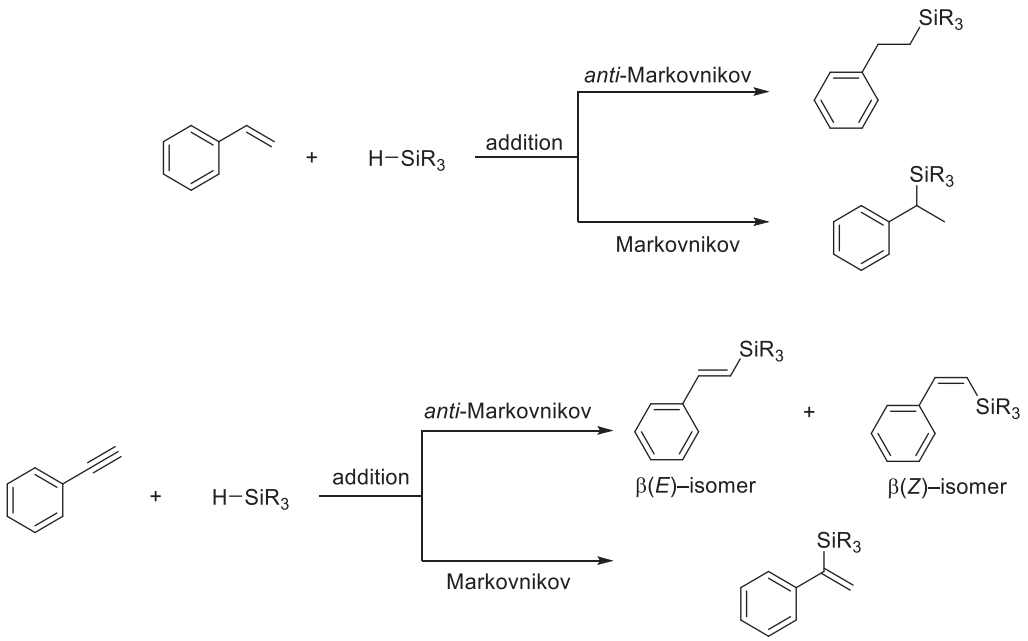


Figure 1.1 Possible outcome of hydrosilylation of terminal alkenes and alkynes

The first example of hydrosilylation is historically connected to the experiments performed by Sommer[15] in 1947. In the presence of a peroxide used as a radical initiator, Sommer successfully carried out a reaction of addition of trichlorosilane to 1-octene. Despite the high industrial potential, the real impact of the reaction of hydrosilylation was unappreciated. The tables were turned with the discovery of the first metal pre-catalyst of hydrosilylation by Speier[16] in 1957. The application of hexachloroplatinic acid was a springboard for further development of platinum catalysts for hydrosilylation. The subsequent major catalyst discovery took place in 1973, when Karstedt[17] treated 1,1,3,3-tetramethyl-1,3-divinyldisiloxane with H_2PtCl_6 obtaining a catalytically active complex shown in *Figure 1.2*.

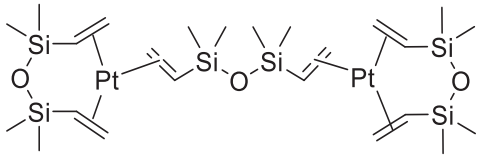


Figure 1.2 The structure of Karstedt's catalyst.

The mechanistic investigation of hydrosilylation was undertaken by Chalk and Harrod in 1965. The mechanism they proposed provides a classical pathway for oxidative addition and reductive elimination steps in hydrosilylation[18] (*Figure 1.3*). Later, Chalk and Harrod's report became the foundation for mechanistic investigation involving other transition metal catalysts. The modified Chalk-Harrod mechanism was proposed to explain the formation of vinylsilane by the insertion of an alkene into the metal-silyl bond.

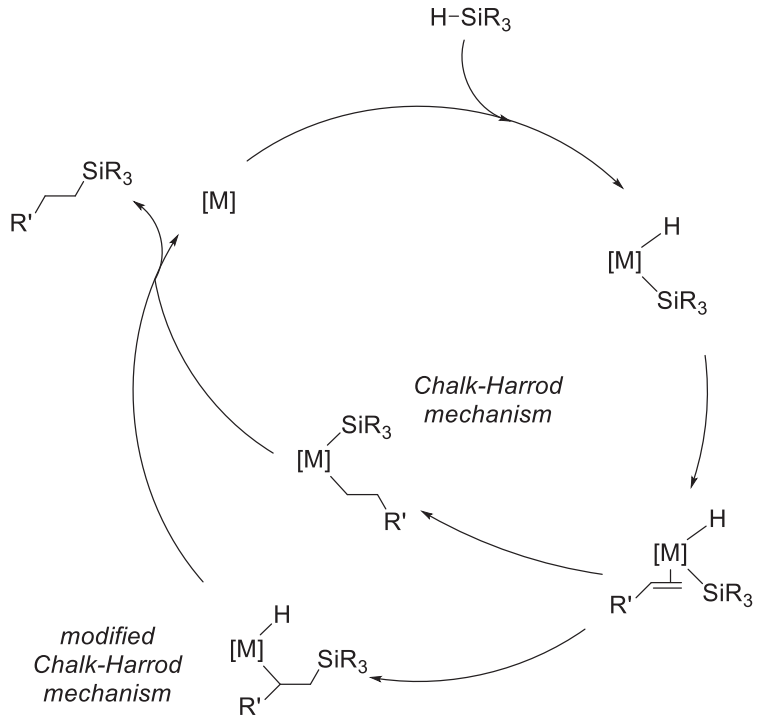


Figure 1.3 Chalk-Harrod mechanism for alkene hydrosilylation

1.2 Noble metal catalysts

Since the late 1970s, Speier's and Karstedt's catalysts have been applied in a majority of industrial hydrosilylation processes as well as on the laboratory scale. In the last decades, the idea of discovery of newer, more active, and selective platinum catalysts had crystallised as the challenge for scientists all over the world[19,20]. In the articles published by Marco[21–25], carbene-platinum catalysts with characteristic "*Karstedt-like*" *dvtms* parts (*Figure 1.4*) have been proposed. These catalysts have been applied in hydrosilylation of aliphatic alkenes and an alkyne (1-octyne) with tertiary silanes and siloxanes ($BuMe_2SiH$, $(EtO)_3SiH$, $(Me_3SiO)Me_2SiH$, Et_3SiH, $(Me_3SiO)_2MeSiH$, Me_2PhSiH, Ph_3SiH). The reactions occurred with high yield and high β-selectivity (up to 96% and 100% β-addition product in

the reactions with alkenes, and up to >99% yield and 15:1 β/α ratio in the reactions with alkynes). Platinum carbene catalysts were found to exhibit properties superior to those of Karstedt's catalyst in terms of activity, selectivity, and functional group tolerance (epoxides, ketones, esters). The downside of the mentioned hydrosilylation system is the side reaction of isomerisation of terminal alkenes into unreactive internal ones.

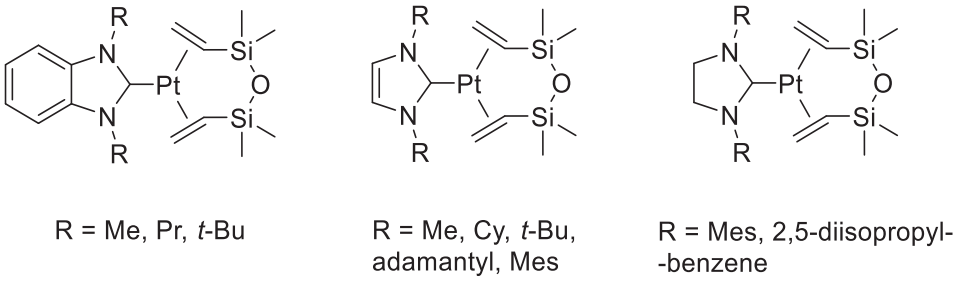


Figure 1.4 Three generations of "Karstedt like" hydrosilylation complexes.

Among all extensively studied noble metal catalysts for hydrosilylation, a significant attention was paid to palladium ones. Despite the well-known tendency of Pd(II) to undergo reduction to palladium black[26], many palladium catalysts have been proven to be highly effective in hydrosilylation[27–32]. The need for stabilization of such catalysts by multidentate ligands, e.g., phosphines, paved the way for introducing chiral ligands, and thus catalysis of hydrosilylation in the stereoselective manner[33–35]. Special attention has been also paid to complexes including rhodium[36–40], iridium[41–44] or ruthenium[45–48].

1.3 Earth abundant metal catalysts

While the noble-metal-catalysed reactions took a special place in scientific research, recently an uptrend toward utilization of earth abundant metals as catalysts has been established. The sustainable and economical aspects of application of base metals have prompted extensive research on iron and cobalt based hydrosilylation catalysts.

1.3.1 Iron catalysts

Iron is one of the most abundant metals in the Earth's crust. Iron salts and oxides are cheap and readily available. Its proximity to ruthenium, a versatile metal centre for catalysts, have attracted the attention of scientists. A variety of oxidation and spin states give iron a great catalytic potential[49,50]. Despite aforementioned upsides, the area of homogenous iron catalysis is an interplay of fragile compromises between stability, activity and selectivity[51,52]. Although this challenge has been taken up by many scientific groups, iron-catalysed hydrosilylation is still an open field of research.

One of the first reports on iron-catalysed hydrosilylation describes the catalytic activity of iron-carbonyl complexes[53,54]. For instance, $Fe_3(CO)_{12}$ complex has been applied to hydrosilylation of styrene and its *para*-substituted derivatives, such as 4-methylstyrene, 4-chlorostyrene and 4-vinylanisole, with triethylsilane. Despite recognised great pioneering value, the use of this catalytic system is limited to styrenes and requires a threefold excess of alkene and the reaction is carried out in benzene.

The breakthrough in iron-catalysed hydrosilylation was the discovery of Fe complexes with tridentate nitrogen ligands. The first iron pyridinediimine complex was reported by Chirik[55] in 2004. The steric hindrance and redox potential of the ligand had positive impact on the reactivity of such catalyst. Under mild conditions and low catalyst loading, alkenes underwent hydrosilylation with phenylsilane and diphenylsilane, affording mainly an *anti*-Markovnikov products. Further development of the Chirik's Fe-PDI complexes (*Figure 1.5)* improved their catalytic properties[56–60]. For example, complex $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ exhibited superior catalytic activity in *anti*-Markovnikov hydrosilylation (25000 TON, 100000 h^{-1} TOF), and could be applied in the reaction with triethylsilane, triethoxysilane or 1,1,1,3,5,5,5-heptamethyltrisiloxane.

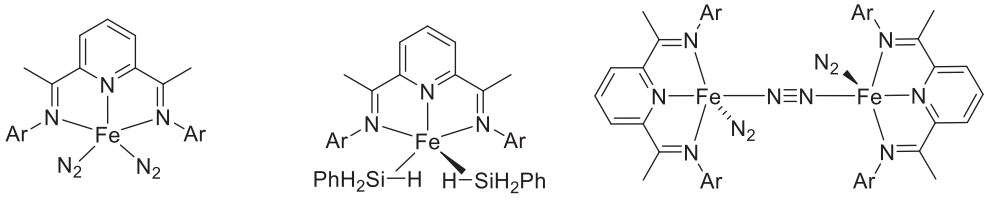


Figure 1.5 The evolution of Chirik's Fe-PDI complexes

The low dissociation energy of N_2 ligand acts as a double-edged sword. On the one hand, it guarantees high activity, but on the other hand, such complex is highly vulnerable to moisture and air presence. Bench stable complexes activated *in situ* directly in the reaction mixture make an effective alternative. Shelf-stable and easily operational Fe-PDI complexes have been reported by the Thomas' group[61–63] (*Figure 1.6*). According to their studies, the direct activation of iron pre-catalyst with Grignard's reagent or sodium butoxide led to good silane conversion, equalling the results obtained for Fe-PDI-dinitrogen complexes.

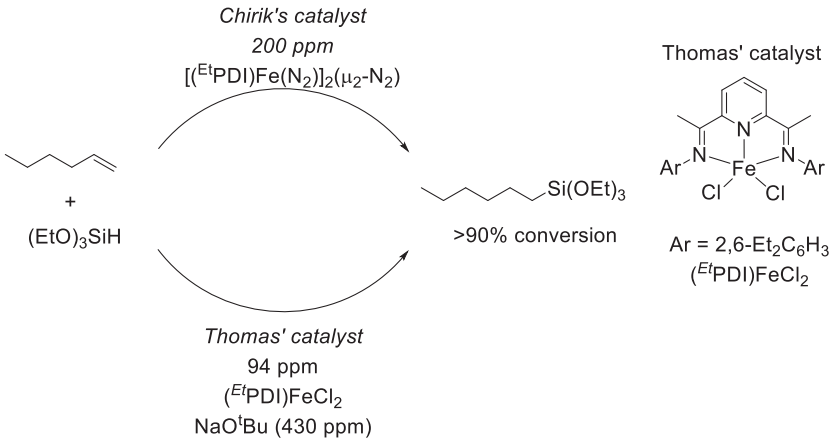


Figure 1.6 Comparison of activities of Fe-PDI-N_2 and bench stable $FeCl_2$-PDI complexes.

Later developments of iron-catalysed hydrosilylation include the introduction of other bidentate or tridentate nitrogen-based ligands, such as phenanthroline[64–66], iminobipyridine[67,68] or terpyridine[69,70].

1.3.2 Cobalt Catalysts

While numerous studies have been conducted on iridium and rhodium-catalysed hydrosilylation, the first metal of the 9th group – cobalt – emerged as an eco-friendly and sustainable alternative[71–73]. One of the earliest cobalt-catalysed hydrosilylation of alkenes has been reported by Chalk and Harrod[74]. $Co_2(CO)_8$ was found to be active in the *anti*-Markovnikov hydrosilylation of terminal aliphatic alkenes with $(MeO)_3SiH$, Et_3SiH and

$PhCl_2SiH$. Later, the cobalt-carbonyl complexes have been applied in hydrosilylation of aryl alkenes[75,76] and alkynes[77,78]. The general concept of ligands for Co-catalysed hydrosilylation was evolving until 2016, when the PDI and similar nitrogen-based tridentate ligands were applied to cobalt.

After unprecedented success of PDI ligands in iron-catalysed hydrosilylation, Chirik synthesised bench stable pyridinediimine cobalt(II) complex as a catalyst for alkene hydrosilylation[79,80]. The complex is *in situ* activated by the substrates – silanes - that are known reducing agents. The work of RajanBabu reports the use of ($^{i\text{Pr}}$PDI)$CoCl_2$ as pre-catalyst for hydrosilylation of terminal alkenes and dienes with phenylsilane, diphenylsilane and methylphenylsilane[81]. Later, Ge and Huang have independently described the moderate activity of ($^{\text{Ph}}$PDI)$Co(acac)_2$, (APDI)$Co(acac)_2$, (PyBox)$Co(acac)_2$ and (IPO)$CoCl_2$ (activated by $NaHBEt_3$) complexes in diene hydrosilylation[82,83]. Application of the aforementioned pre-catalysts led to 27%, 33%, 49% and 72% yield of 1,2-Markovnikov addition product, respectively (*Figure 1.7*). Our group have also contributed to development of such pre-catalysts[84]. The pyridine-hydrazone-imidazole cobalt(II) complex, activated by $NaHBEt_3$ catalysed hydrosilylation of alkenes with primary and secondary silanes and siloxanes with moderate to very good conversions. Despite the pioneering value of this investigation, and along with low pre-catalyst loading, the fact that the reaction had to be conducted in high temperatures and a narrow substrate scope determined a low application value of the proposed catalytic system.

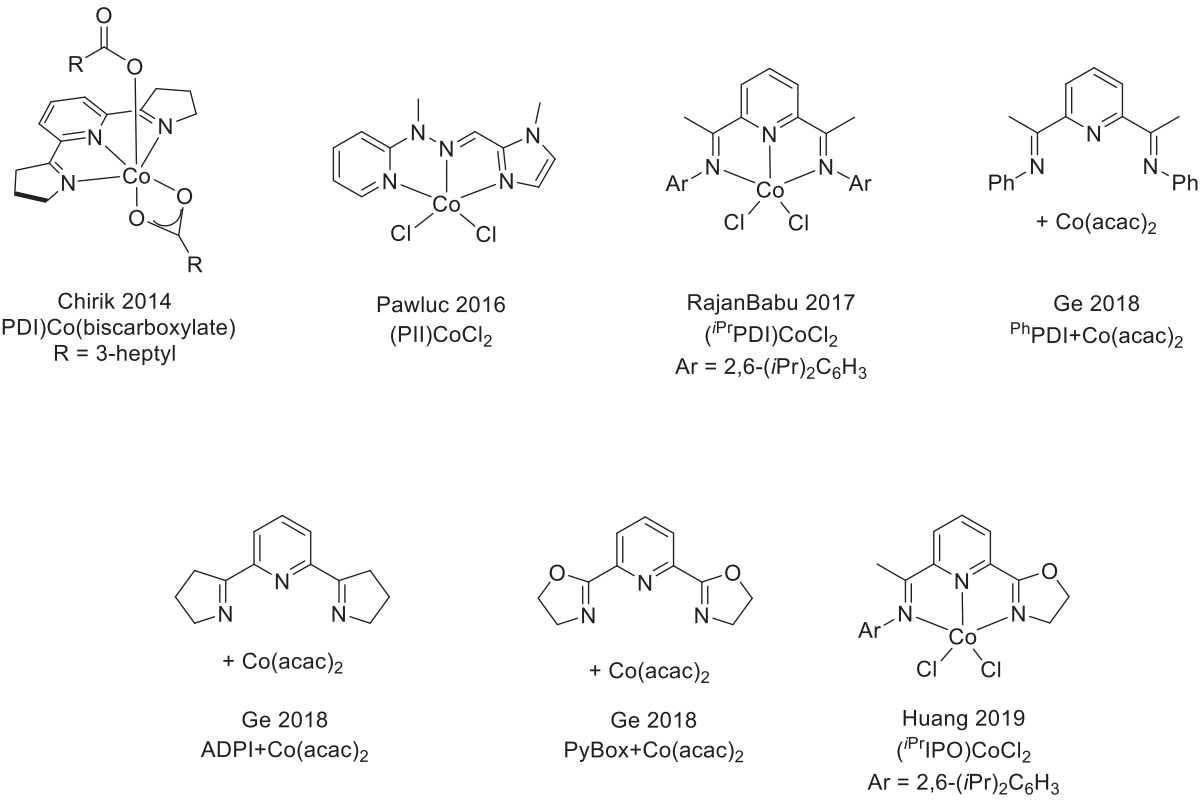
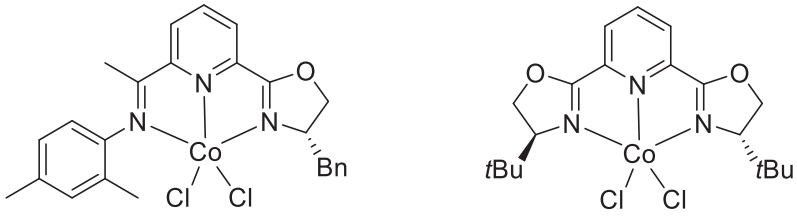


Figure 1.7 Pre-catalysts for alkenes and dienes hydrosilylation with NNN-tridentate motif

A number of cobalt catalysts have been proven to be active in hydrosilylation of alkynes. For instance, Deng's group have designed a carbene-Cobalt complex, providing a convenient pathway to synthesize β-(*E*)-vinylsilanes[85]. Later, Thomas' and Ge's groups have proposed catalytic systems comprising cobalt(II) complexes with ^{mes}PDI ligands, which afforded β-(*E*)-vinylsilanes or β-(*Z*)-vinylsilanes, depending on the activator type and addition of phenol [86,87]. Although many reports on the catalytic activity of cobalt complexes have been published, most of them concerned the synthesis of anti-Markovnikov addition products. Markovnikov-selective catalytic systems based on cobalt were hardly known before 2016.

The Markovnikov-selective cobalt-catalysed hydrosilylation of alkynes, involving nitrogen-based tridentate ligands, was reported in 2016 by groups of Lu and Huang[88,89] (*Figure 1.8*). The application of such complexes activated by $NaHBEt_3$ resulted in general in formation of Markovnikov addition product. The catalytic systems proposed by the above

authors promote regioselective transformation, compatible with secondary silanes and tolerate various functional groups.

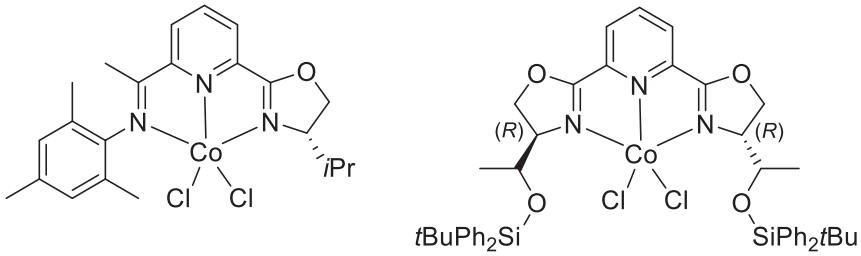


Lu 2016
$(IPO)CoCl_2$

Huang 2016
$(PyBox)CoCl_2$

Figure 1.8 Structures of the first NNN cobalt(II) pre-catalysts for Markovnikov hydrosilylation of alkynes

The articles from 2016 were the springboards for further development and evolution of nitrogen-based tridentate cobalt(II) complexes for alkyne hydrosilylation. For example, Lu and Huang designed and developed the processes to obtain chiral products[90,91]. Lu's work describes a one-pot hydrosilylation/hydrogenation in the presence of $(IPO)CoCl_2$, $NaHBEt_3$ as an activator, alkyne, diphenylsilane and hydrogen. On the other hand, Huang reported the enantioselective hydrosilylation with $(PyBox)CoCl_2$ complex, activated by $NaHBEt_3$ (*Figure 1.9*).



Lu 2017
$(IPO)CoCl_2$

Huang 2018
$(PyBox)CoCl_2$

Figure 1.9 The second NNN-Co(II) generation catalysts of Lu and Huang for the synthesis of chiral silyl products

The mechanistic approach, based on the modified Chalk-Harrod cycle, has been proposed by Huang[92] (*Figure 1.10* ***A***), in which the cobalt pre-catalyst reacts with an activator to generate cobalt-hydride. After subsequent reaction with hydrosilane, the

cobalt-silyl species initiate the catalytic cycle. The alkyne molecule is coordinated to the metal centre. The migratory insertion of coordinated alkyne into silyl-cobalt bond occurs regioselectively, to avoid steric obstacle of the [Co] complex. The last step involves the reaction with hydrosilane molecule, release of α-vinylsilane, and regeneration of the catalyst. Despite a great mechanistic value, the described mechanistic investigation assumed the formation of *syn*-addition products. No information was given about the *anti*-addition products, whose traces are usually observed. An alternative catalytic cycle has been proposed by Lu[93] (*Figure 1.10* ***B***). The first steps involve generation of active cobalt species and migratory insertion of alkyne into the cobalt-silyl bond. The *anti*-addition products are occasionally formed when Crabtree-Ojima type isomerisation takes place. The last part of catalytic cycle proposed by Lu, similarly to the Huang's cycle, includes the reaction with hydrosilane molecule, release of α-vinylsilane and regeneration of the catalyst.

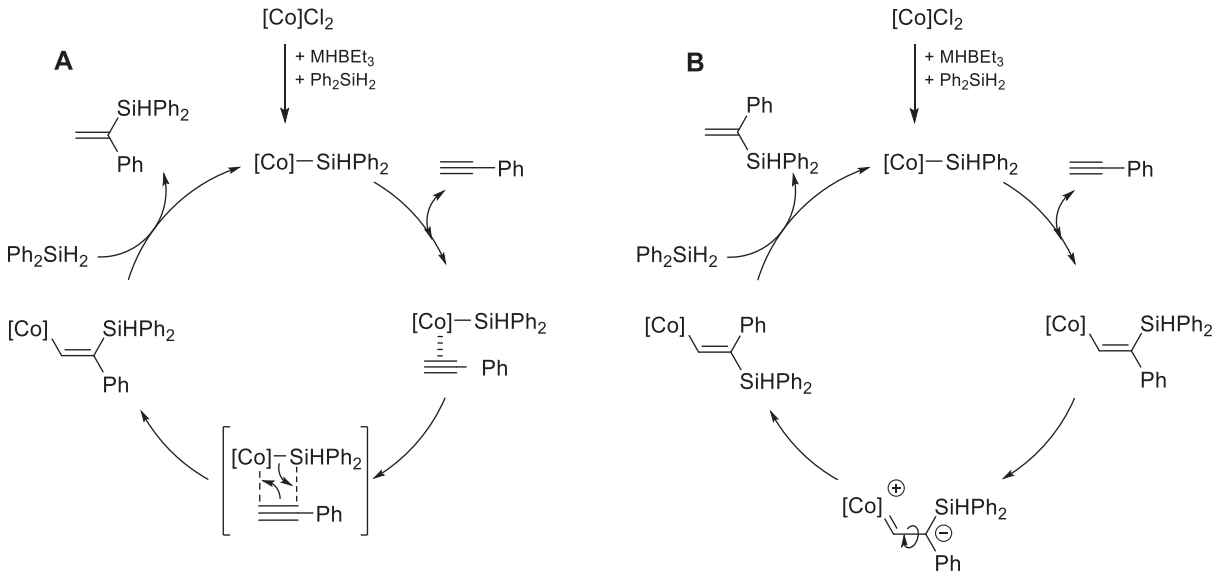
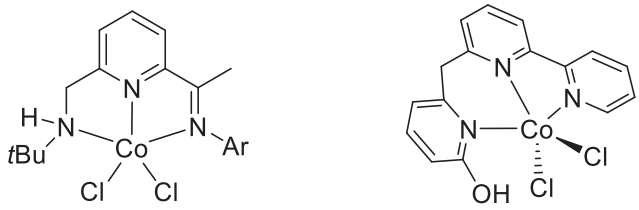


Figure 1.10 Huang's (**A**) and Lu's (**B**) proposed catalytic cycles describing hydrosilylation of alkynes, explaining the formation of *syn*-addition and *anti*-addition products

A few other catalytic systems have been also described as highly selective and effective in Markovnikov-selective hydrosilylation of alkynes (*Figure 1.11*). Reports of Yang describe a shelf-stable (API)$CoCl_2$ pre-catalyst. Presented complex, after activation by $NaHBEt_3$, catalysed hydrosilylation of alkenes with various functional groups with primary silanes[94]. This catalytic system also tolerated secondary and tertiary silanes; however, an increased time as well as increased catalyst and activator loadings were necessary. Chen has proposed a cobalt pre-catalyst bearing a 2-(2-(6-hydroxypyridyl)methyl)-bipyridine ligand - (N^CNN)$CoCl_2$ - for hydrosilylation of a wide range of aryl alkynes and conjugated diynes[95,96].



Yang 2018
(API)$CoCl_2$
Ar = mes

Chen 2019
(N^CNN)$CoCl_2$

Figure 1.11 Structures of (API)$CoCl_2$ and (N^CNN)$CoCl_2$ – pre-catalysts proposed for Markovnikov selective alkyne hydrosilylation

Although a variety of hydrosilylation catalysts have been proposed, actually, there is a shortage of well-tailored catalysts based on earth-abundant metals. There are only a few catalytic systems reported as compatible with primary and secondary silanes. What is more, there is a great challenge of selective and efficient hydrosilylation catalysis with tertiary silanes and siloxanes[97–99] (*Figure 1.12*). According to the current state of knowledge, there are no NNN-tridentate cobalt complexes that are well tuned for tertiary silanes.

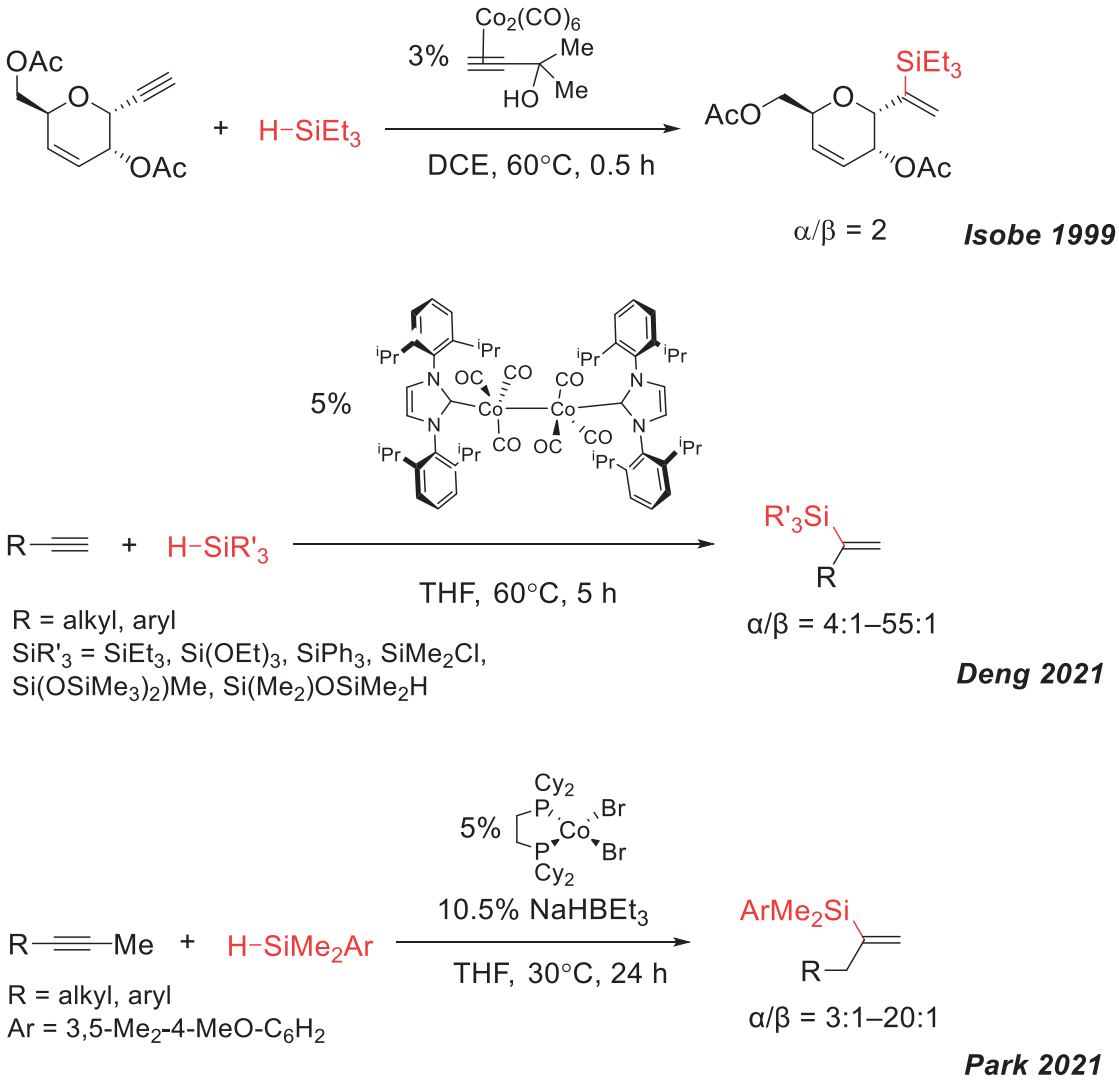


Figure 1.12 Catalysts for α-selective alkyne hydrosilylation with tertiary silanes.

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2. Aims of the study

Increasing demand of industry for silicon-based materials, such as silane coupling agents and functionalised silicones, induce a great pressure on scientists. One of the most atom-economical transformations involved in the syntheses of such compounds is hydrosilylation. For many years much attention has been paid to designing noble metal catalysts for this reaction. Scientists all over the world have taken part in the pursuit of development of noble metal hydrosilylation catalysts, slowly losing sense of purpose. While the correlation between cost of platinum complexes and the silicones has been generally recognised, the aspects of inflating prices of noble metals, deposits depletion, their toxicity and environmental pollution caused by mining have usually been omitted. Therefore, from the economic and sustainable development points of view, utilisation of earth abundant metals is favourable. Nevertheless, in the times of heavy and multistep synthesised ligands, it is crucial to introduce new, sustainable, rational and possibly simple coordination environment.

Among many earth abundant metals, cobalt poses an interesting alternative to the known noble metal catalysts. In recent years, cobalt compounds have been reported as efficient and selective catalysts for hydrosilylation of alkenes and alkynes. Cobalt catalysts stand out among the other base-metal ones, e.g., those of iron or nickel. Although application of these metals is cost-efficient, the overall prices of their complexes are still high, as the complexity of ligands, such as heavy molecular phosphines or pincer ligands, is significant. To compete with well-known noble-metal catalysts, new complexes should bear simple and therefore cheap ligands, while maintaining high activity and selectivity.

One of the main aims of the studies, undertaken as the basis of the doctoral dissertation, was to design and synthesise a library of cobalt complexes with structurally simple tridentate Schiff base type ligands. The selection of Schiff base ligands was driven by the shortage of cobalt catalysts with simple and cost-efficient coordination structure. What is more, the hydrazone linker acts as a good spacer creating coordination pocket for metal ions. The synthesised complexes were assessed as catalysts for the reaction of hydrosilylation of alkenes and alkynes with primary, secondary and tertiary silanes. Another objective of the studies was the evaluation of catalytic activity of the activator, e.g. alkali metal borohydride, in the reaction without a transition metal catalyst.

The design, synthesis and characterization of ligands and cobalt complexes are presented in supplementary articles **A1** and **A3**. The superior activity of the obtained complexes in hydrosilylation of alkenes, presented in **A1**, has prompted further research on their activity towards hydrosilylation of alkynes, which in fact is presented in article **A2**. Article **A3** presents further investigation of the relation between the structure and catalytic activity of Schiff base cobalt complexes with particular emphasis on the reactivity of alkynes with tertiary silanes, commonly perceived as hardly reactive in *3d* transition metal catalysed reactions. The last article, **A4**, presents the evolution of the blind test, which has shown unexpected catalytic activity of alkali metal borohydrides in dehydrogenative silylation of terminal alkynes with hydrosilanes.

The doctoral dissertation submitted as the basis for conferment of a Doctor of Philisophy degree is based on the following articles:

Appendix **A1** Bocian A*., **Skrodzki M***., Kubicki M., Gorczyński A., Pawluć P., Patroniak V.; *The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins. Appl. Catal. A-Gen.* **2020**, 602, 117665. [IF= 5.72, MNiSW= 100, Cited by 6(5), *equally contributed]

Appendix **A2** **Skrodzki M**., Patroniak V., Pawluć P.; *Schiff Base Cobalt(II) Complex-catalysed Highly Markovnikov-Selective Hydrosilylation of Alkynes. Org. Lett*. **2021**, 23, 663-667. [IF= 6.00, MNiSW= 140, Cited by 13(12)]

Appendix **A3** **Skrodzki M**., Ortega Garrido V, Csaky A. G., Pawluć P.; *Searching for highly active cobalt catalysts bearing Schiff base ligands for Markovnikov-selective hydrosilylation of alkynes with tertiary silanes. J. Catal.* **2022**, 441, 116-121. [IF= 8.05, MNiSW= 140, Cited by 0]

Appendix **A4** **Skrodzki M**., Witomska S., Pawluć P.; *Sodium triethylborohydride as a catalyst for the dehydrogenative silylation of terminal alkynes with hydrosilanes. Dalton Trans*., **2018**, 47, 5948. [IF= 4.57, MNiSW= 140, Cited by 23(22)]

3. Discussion of the results of the study

3.1 Hydrosilylation of alkenes

The catalytic activities of newly proposed cobalt complexes are presented in article **A1**, "*The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins*". Firstly, in the collaboration with Prof. V. Patroniak group from the Adam Mickiewicz University, the ligands were synthesised in a two-step process involving the substitution of haloarene with N-methylhydrazine, followed by condensation of the obtained compound with imidazolecarboxaldehyde. The synthetic pathway of ligand *L1* is shown in *Figure 3.1*.

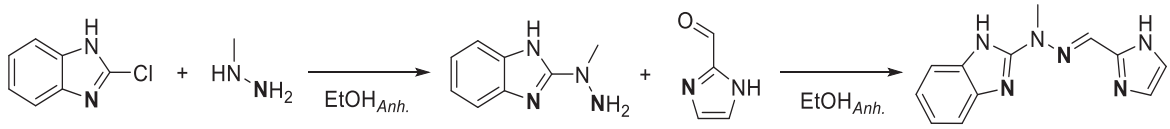


Figure 3.1 Synthesis of (*E*)-2-(2-((1H-imidazol-2-yl)methylene)-1-methylhydrazinyl)-1H-benzo[d]imidazole

According to this procedure, 5 N_3-tridentate ligands have been synthesised (*Figure 3.2*), bearing in their structure fragments of benzimidazole (L^1-L^3), pyridine (L^4, L^5), methylhydrazine (L^1-L^5), 2-imidazolecarboxaldehyde (L^1, L^5), 1-methyl-2-imidazolecarboxaldehyde (L^3), or 4-imidazolecarboxaldehyde (L^2, L^4).

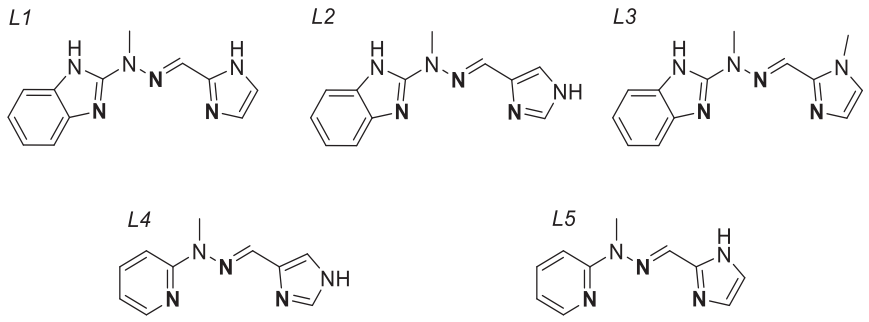


Figure 3.2 Structures of ligands (*L1-L5*)

Secondly, the complexation reaction of ligands L^1 - L^5 with cobalt(II) chloride, was performed at the equimolar ratio of reagents (*Figure 3.3*). This straightforward method, afforded cobalt(II) complexes in yields ranging from 63% to 99%. All of the obtained cobalt complexes are shelf-stable, and no visible degradation is observed in 12 months after synthesis.

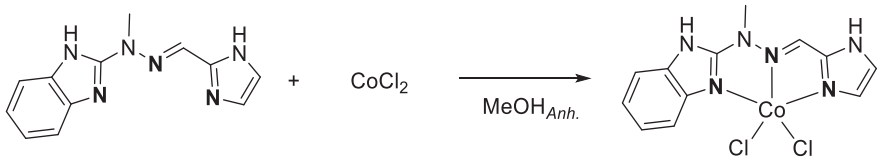


Figure 3.3 Synthesis of $Co(L^1)Cl_2$

The complexes were subjected to ESI-MS. The X-ray diffraction structures were solved by Prof. M. Kubicki from the Adam Mickiewicz University. Complexes **1**, **2** and **4** [$Co(L^1)Cl_2$, $Co(L^2)Cl_2$ and $Co(L^4)Cl_2$] belong to the *open* species, in which the metal to ligand ratio is in particular 1:1, however, complex **4** had an additional solvent (MeOH) molecule associated to the cobalt ion. Analysis of the crystal of complex **3** [$Co(L^3)Cl_2$], has shown *closed* structure, with two ligand molecules coordinated to one cobalt ion (*Figure 3.4*). From the catalytic point of view, synthesis of the *open* structure is more preferable. The accessibility of reagents to the metallic centre define the properties of catalysts due to easy substitution of chloride with hydride and possible reductive elimination of HCl or H_2 leading to cobalt(0) or cobalt(I) species. Thus, the *open* ones are expected to excel *closed* ones, because the centres of the latter are hindered.

The catalytic studies of cobalt complexes were performed in accordance with the Nakazawa protocol, in which alkali metal borohydrides were employed as activators[100]. The active forms of the catalysts were thus generated *in-situ* from cobalt(II) precursors (**1**-**5**). In the model reaction of hydrosilylation of styrene with phenylsilane, all activated complexes showed catalytic activity. The outcome of each reaction was dependent on the applied Schiff base scaffold, as well as on the type of metal ion in borohydride. In the presence of an alkali metal borohydride, the silane undergoes redistribution, which is why the screening of catalysts was needed to find the optimum conditions.

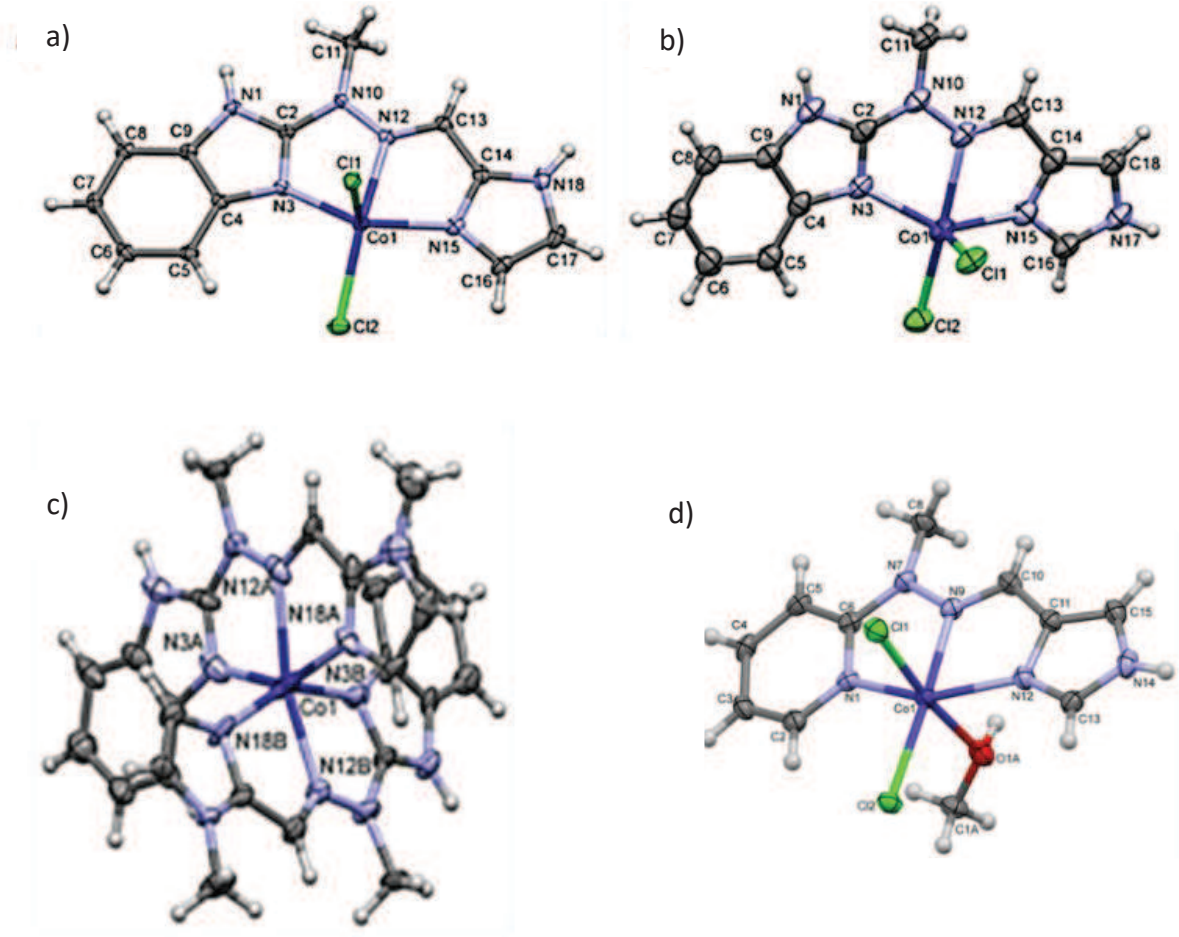


Figure 3.4 Acquired X-Ray structures of complexes: a) **1** $Co(L^1)Cl_2]$, b) **2** $[Co(L^2)Cl_2]$, c) **3** $[Co(L^3)Cl_2]$, d) **4** $[Co(L^4)Cl_2]$

In a typical procedure of hydrosilylation, phenylsilane and styrene were used in the 1 : 1 ratio, and a 3 mol % of cobalt pre-catalyst was activated with 12 mol % activator. The post-reaction mixtures were analysed by GC and GC-MS methods. The use of pyridinic

complexes, **4** and **5**, activated by $NaHBEt_3$ allowed for a total conversion of phenylsilane at 80°C. Although a high conversion was achieved, the post-reaction mixture did not contain the expected compounds, but double hydrosilylation products, higher order products, and diphenylsilane - a result of phenylsilane redistribution. On the other hand, the use of the complexes with benzimidazole moiety – **1**, **2** and **3**, activated by $NaHBEt_3$ at 80°C, resulted in 100%, 53% and 29% conversion of phenylsilane, respectively. Only in the post-reaction mixture obtained after hydrosilylation in the presence of complexes **1** and **2**, the *alpha* or *beta* hydrosilylation products were detected. As expected, the lowest activity and selectivity were achieved when using the *closed* precursor – **3**. The decision to use $LiHBEt_3$ as the activator had a crucial consequences for further studies. While the conversion of phenylsilane in the presence of complexes **2**, **3**, **4**, **5** as catalysts dropped below 50%, the reaction with **1** resulted in total conversion of $PhSiH_3$, maintaining decent β-selectivity (>78% of β-addition product). Lowering of the reaction temperature resulted in cessation of silane redistribution. Lowering of the catalyst loading to 0.25 mol % had a positive impact on selectivity. In the optimised conditions: 1 equivalent of phenylsilane, 1 equivalent of styrene, 0.25 mol % of cobalt(II) pre-catalyst **1**, 0.75 mol % of $LiHBEt_3$, 0.5M THF solution, 20 hours at room temperature, the conversion of silane reached 98% and the selectivity of products β:α = 98:2.

The optimised conditions were applied to the hydrosilylation reactions of styrene derivatives and aliphatic alkenes with various silanes. The reaction with 2-vinylnaphthalene or styrene with phenyl- and diphenylsilane proceeded smoothly to give the expected β-addition products quantitatively. The presence of both, electron withdrawing and donating groups at phenyl ring, such as 4-OMe and 4-Br did not significantly lower the conversion of phenylsilane and diphenylsilane. Also, the use of styrenes bearing electron donating groups, 4-metylstyrene and 4-*tert*-butylstyrene, provided very good conversions. Moreover, the hydrosilylation with Ph_2SiH_2, in comparison to that with $PhSiH_3$, yielded only β-addition products (*Figure 3.5*).

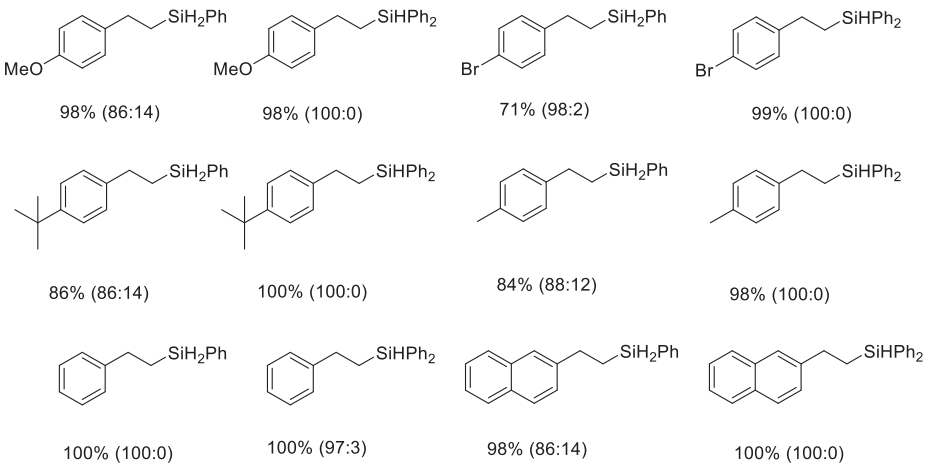


Figure 3.5 Products of hydrosilylation of vinylarenes with phenylsilane and diphenylsilane. The conversions of silane and selectivity (in parentheses) of β:α addition are given.

The above-mentioned reaction system is compatible with vinyl arenes. Unfortunately, the aliphatic alkenes, such as hex-1-ene or 3,3-dimethylbut-1-ene are incompatible and no conversion of silane was observed. Another limitation is intolerance of tertiary silane ($PhMe_2SiH$), and secondary aliphatic silane (Et_2SiH_2).

Despite the narrow spectrum of substrates, the above-described catalytic system with simple benzimidazole-imine-2*H*-imidazole cobalt(II) complex and lithium triethylborohydride, is effective in transformation of vinyl arenes and primary or secondary silanes to 1-silyl-2-arylethanes.

3.2 Hydrosilylation of alkynes

The hydrosilylation of alkynes is presented in the articles entitled "*Schiff Base Cobalt(II) Complex-Catalysed Highly Markovnikov-Selective Hydrosilylation of Alkynes*" **A2** and "*Searching for highly active cobalt catalysts bearing Schiff base ligands for Markovnikov-selective hydrosilylation of alkynes with tertiary silanes"* **A3**.

The former article is devoted to the assessment of catalytic activity of a cobalt(II) complex with a simple benzimidazole-imine-2*H*-imidazole ligand, which exhibited superior properties in selective hydrosilylation of alkenes. Optimization studies were performed for

the temperature of the process, solvent, activator, and catalyst loading. In the model reaction, phenylacetylene was hydrosilylated with diphenylsilane at the molar ratio of 1 : 1 in the presence of 3 mol % of pre-catalyst **1** and 9 mol % of $LiHBEt_3$, as 2M THF solution. The reaction mixture was stirred and heated for 20 hours in a Schlenk flask. The post-reaction mixture was analysed with GC and GC-MS. The results of the screening confirmed the optimal choice of the solvent. Although conversion of substrates in toluene or dioxane was high, selectivity of hydrosilylation was low. The use of both $NaHBEt_3$ and NaO^tBu led to lower selectivity, whereas the presence of the latter activator significantly decreased the conversion of diphenylsilane. As a result of the optimization, the pre-catalyst and activator loadings and the temperature were set at 0.1 mol % and 0.3 mol % and 40°C, respectively. In these conditions, diphenylsilane underwent transformation to vinylsilane with >99% conversion, and 99:1 selectivity of α to β addition products (*Figure 3.6*).

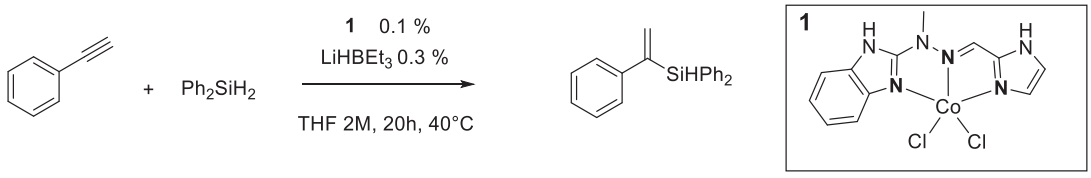


Figure 3.6 Optimized conditions for phenylacetylene hydrosilylation with diphenylsilane

After the optimization studies, the reactivity of various alkynes was examined (*Figure 3.7*). The reactions with phenylacetylene bearing substituents in -*para* position, such as 4-*tert*-butylphenylacetylene, 4-ethynylanisole and 4-ethynylaniline proceeded with superb selectivity (99:1 - α:β) and yield. Cyclopropylacetylene, cyclohexylacetylene and cyclohexenylacetylene were hydrosilylated smoothly, however, the selectivity of the reactions was slightly lower for the first two compounds: 97:3 and 94:6 α:β, respectively. The reaction with 4-Bromophenylacetylene resulted in moderate conversion and a higher catalyst loading was necessary (0.5 mol %). The terminal aliphatic alkynes, 3-phenylprop-1-yne and oct-1-yne, were hydrosilylated and no traces of β-addition products were detected. The same outcome was observed for the reaction with internal alkynes: oct-4-yne and diphenylacetylene. The ^1H NMR analysis proved the structure of products - (*E*)-silylalkenes. The presence of 3-ethynylthiophene was tolerated within reaction conditions, and the hydrosilylation with diphenylsilane yielded only α-vinylsilane formation. The competitive hydrosilylation of carbon-heteroatom bond in 4-ethynylbenzonitrile and

butynyl benzoate did not occur, which proves the chemoselectivity of the proposed catalytic system toward C-C bonds. The methyl substituent in *-ortho*, *-meta* or *-para* positions did not affect the selectivity. Because of the presence of alkali metal borohydride, the alcohols are incompatible, since reactions of compounds with unprotected OH group lead to dehydrogenative coupling with hydrosilanes. On the other hand, protected alcohols, such as silyl ethers, gave the expected product in moderate yield (72%). Reaction of 1-phenylprop-1-yne resulted in a mixture of 1,2 and 2,1 addition products, presumably due to a narrow steric hindrance of the methyl group. The reactions with 4-bromophenylacetylene, cyclohexylacetylene, oct-4-yne, 4-methylphenylacetylene and 4-ethynylbenzonitrile required an increased pre-catalyst loading (0.5 mol %).

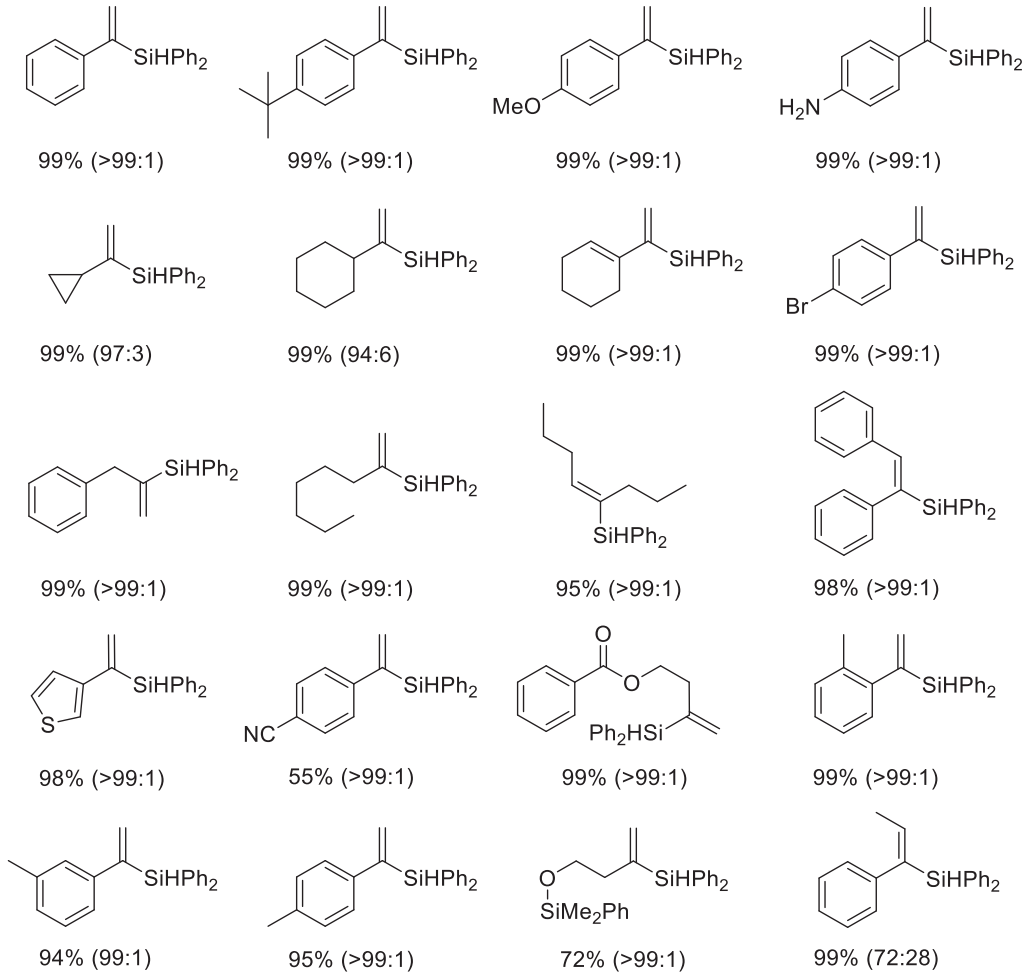


Figure 3.7 The reactivities of various alkynes in the reaction with diphenylsilane in the presence of pre-catalyst **1**. The isolation yields are given, regioselectivity is shown in parentheses.

The scalability of hydrosilylation was also evaluated. For this purpose, 4 mmol of diphenylsilane was used in the reaction with phenylacetylene in the presence of 0.1 mol % of pre-catalyst **1** and 0.3 mol % of $LiHBEt_3$. The product of this reaction was isolated in 98% yield (1.12 g) with the selectivity of α to β addition 99:1.

The studies reported in the paper "*Schiff Base Cobalt(II) Complex- catalysed Highly Markovnikov-Selective Hydrosilylation of Alkynes*" were undertaken to assess the activity of pre-catalyst **1** in hydrosilylation of primary and tertiary silanes. The optimization of the reaction conditions was performed for a systems comprising phenylsilane and phenylacetylene. In this reaction, the effective loading of the pre-catalyst turned out to be half as much as in the reaction with diphenylsilane. Despite high conversions and the absence of β-addition products, the side products of subsequent alkyne α-hydrosilylation (αα) were observed (*Figure 3.8*).

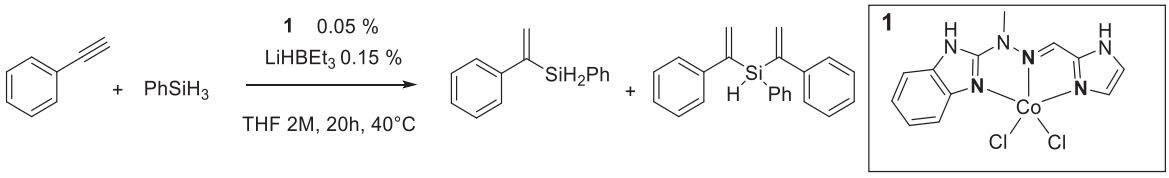


Figure 3.8 Optimised conditions for phenylacetylene hydrosilylation with phenylsilane

The scope of substrates was investigated (*Figure 3.9*). The conversion of phenylsilane in the reaction with phenylacetylene was calculated as 98%. Most of the chosen unsaturated substrates, such as 4-*tert*-butylacetylene; 4-ethynylanisole; 4-ethynylaniline; cyclopropylacetylene and 3-phenylprop-1-yne, reacted well, and the conversion of phenylsilane was above 93%. 4-Bromophenylacetylene reacted with moderate conversion - 38%. This particular reaction was expected to have the lowest conversion, as the reaction with diphenylsilane required fivefold excess of pre-catalyst **1**. The results of this reaction suggest a negative impact of electron withdrawing groups, such as *bromo* and presumably other halides, leading to significantly lower conversions, and imply the necessity of increasing the pre-catalyst loading. The differently substituted methylphenylacetylenes have undergone the reaction smoothly, and the position of the substituent did not have an impact on conversion. However, the selectivities of the reactions with 2-

methylphenylacetylene and 3-methylphenylacetylene were slightly lower (both 91:9 of α:αα) than that of the reaction with 4-methylphenylacetylene (97:7 of α:αα).

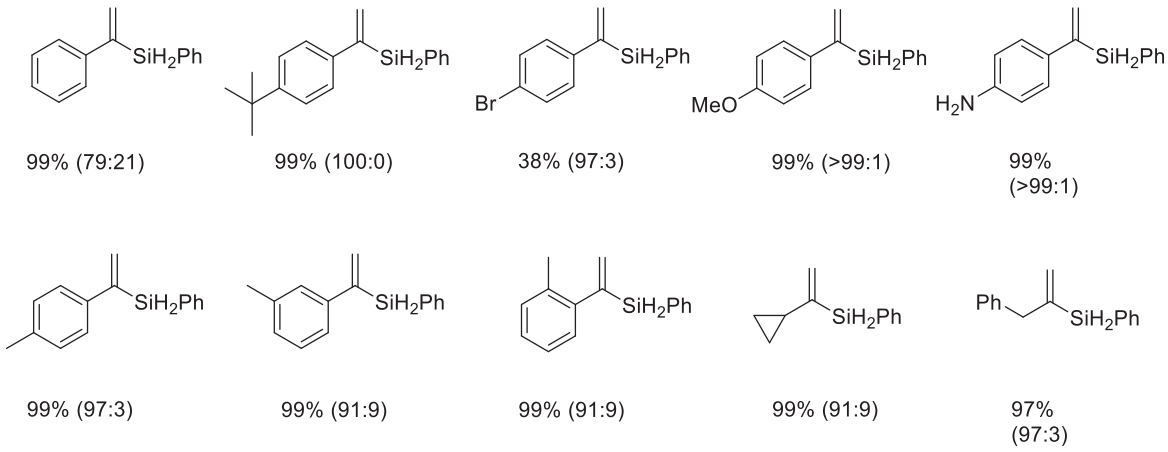


Figure 3.9 The reactivity of various alkynes in the reaction with phenylsilane. The GC-calculated conversions and α:αα selectivity are given

As mentioned above, pre-catalyst **1** was also examined in the hydrosilylation of alkynes with tertiary silanes, which are the most challenging hydrosilanes. The catalytic system based on complex **1** as the pre-catalyst and $LiHBEt_3$ as the activator was found to be active in hydrosilylation of aryl alkynes and cyclopropylacetylene with dimethylphenylsilane, however, increased pre-catalyst loading and temperature were necessary. The optimized conditions comprised 0.5 mol % of **1**, 1.5 mol % of $LiHBEt_3$ and a temperature elevated to 60 °C. Analysis of the post-reaction mixture has shown the presence of an α-addition product as well as traces of the β-addition one.

Under the optimised conditions, the substrate scope was investigated. In the reaction with phenylacetylene, 94% conversion of dimethylphenylsilane and 91:9 selectivity of α- over β-addition products were obtained. The use of alkyl substituents, such as in 4-*tert*-butylphenylacetylene, 4-methylphenylacetylene, 3-methylphenylacetylene or 2-methylphenylacetylene, resulted in the conversion of silane ranging from 92% to 99%. Cyclopropylacetylene, 4-ethynylanisole, 4-bromophenylacetylene, and 4-ethynylaniline were tolerated, however, the reactions with the two latter compounds resulted in lower conversions of dimethylphenylsilane (*Figure 3.10*). The α-selectivity of the aforementioned reactions was superior to that of β-addition and ranged from 99:1 to 91:9.

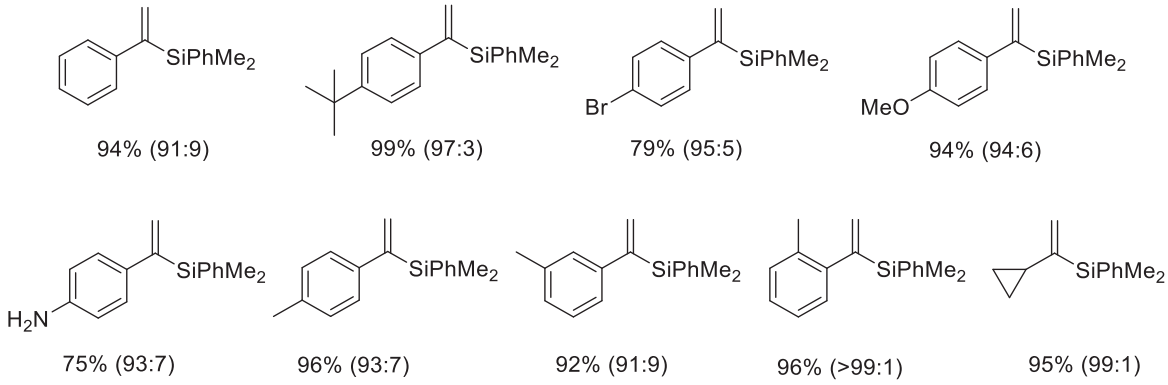


Figure 3.10 The reactivities of various alkynes in the reaction with dimethylphenylsilane. Isolated yield and α:β selectivity are given

To examine the mode of the silane addition to phenylacetylene, ^{1}H NMR deuterium labelling experiments were performed (*Figure 3.11*). The reaction of D1-phenylacetylene and diphenylsilane afforded *syn*-addition product, and no *anti*-addition products were observed. The results of this experiment suggest a reaction pathway based on the modified Chalk-Harrod mechanism described by Huang.

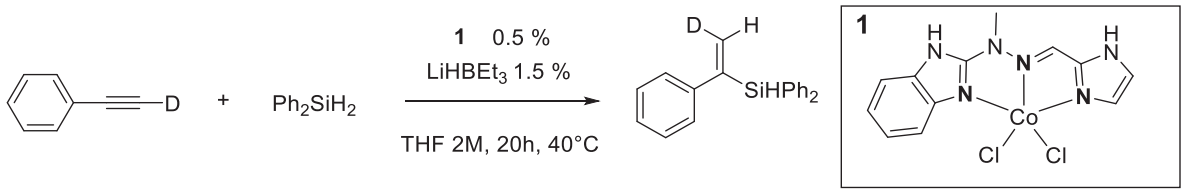


Figure 3.11 Deuterium-labelled studies on the nature of cobalt-catalysed addition of diphenylsilane to alkyne

Presented studies on the activity of cobalt(II) complex with benzimidazole-imine-2*H*-imidazole ligand activated by $LiHBEt_3$ indicate a high potential in hydrosilylation of alkynes with primary, secondary and tertiary silanes. The low catalyst loading (500 ppm) supported with mild reaction conditions, substrate tolerance and superb selectivity are very unique even amongst noble metal catalysts.

The continuation of studies on cobalt pre-catalysts for alkyne hydrosilylation is presented in article "*Searching for highly active cobalt catalysts bearing Schiff base ligands for Markovnikov-selective hydrosilylation of alkynes with tertiary silanes"*. In this article particular attention was paid to the reactivity of tertiary silanes which are the most challenging substrates in cobalt-catalysed alkyne hydrosilylation. For this purpose, 9 ligands were synthesised (*L*^{4} – *L*^{12}) in accordance with the idea of high activity Co(II) pre-catalysts with hydrazone Schiff base motifs (*Figure 3.12*).

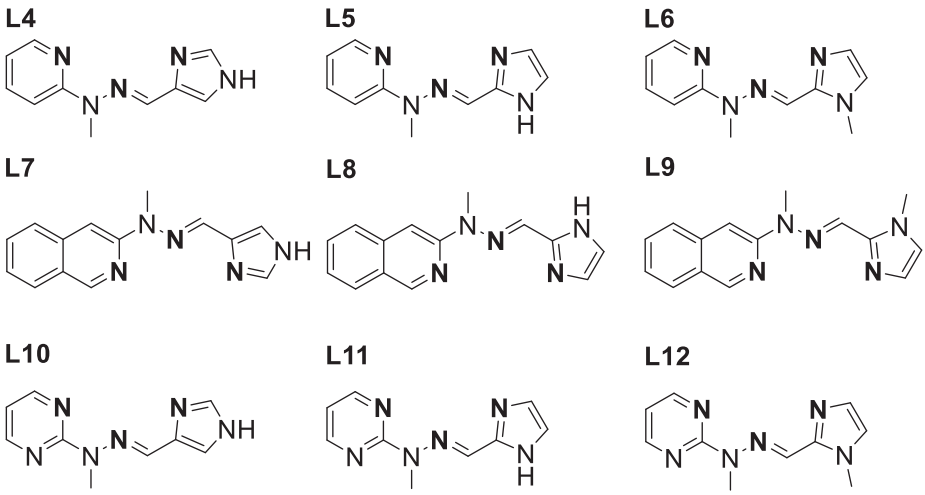


Figure 3.12 The structures of L^{4} – L^{12} ligands

The activity of *in situ* synthesised complexes were examined in the reaction of diphenylsilane and phenylacetylene in 1:1 ratio. In the reaction setup, 1 mol % of a ligand and 1 mol % of anhydrous cobalt(II) chloride were mixed together and further dried under reduced pressure. The reagents and solvent (1M THF) were then placed into Schlenk flask under inert atmosphere. After the addition of $LiHBEt_3$, as activator, reaction was stirred in the room temperature over 20 hours. The post-reaction mixtures were analysed by GC.

The outcome of the catalysts screening is shown in *Figure 3.13*. Moderate conversions of silane, ranging from 26% to 58%, were observed in the presence of 1*Me*-imidazol-2-yl moiety (L^{6}, L^{9}, L^{12}). The selectivity of the aforementioned reactions were unsatisfactory. On the other hand, higher conversions were observed for the reactions with 1*H*-imidazol-4-yl derivatives (L^{4}, L^{7}, L^{10}). The selectivity of the reactions with L^{4} and L^{10} were directed toward α-addition, whereas the reaction with L^{7} showed no selectivity. The

highest conversions and selectivity were noted for the reactions involving ligands with 1*H*-imidazol-2-yl motifs (L^5, L^8, L^{11}). Results of the initial trials indicate the strong impact of imidazole side of ligands on efficiency and selectivity of the reaction. Further investigation of the optimal loading has shown that the use of L^{11} brought higher activity and selectivity than the presence of L^5 and L^8. The optimum conditions of the reaction with diphenylsilane are following: the use of 0.05 mol % of anhydrous $CoCl_2$, 0.05 mol % of L^{11}, 0.15 mol % of $LiHBEt_3$ and a temperature of 40°C. Similar optimization was performed for dimethylphenylsilane to give the optimum conditions as the use of 0.25 mol % of anhydrous $CoCl_2$, 0.25 mol % of L^{11}, 0.75 mol % of $LiHBEt_3$ and a temperature of 60°C.

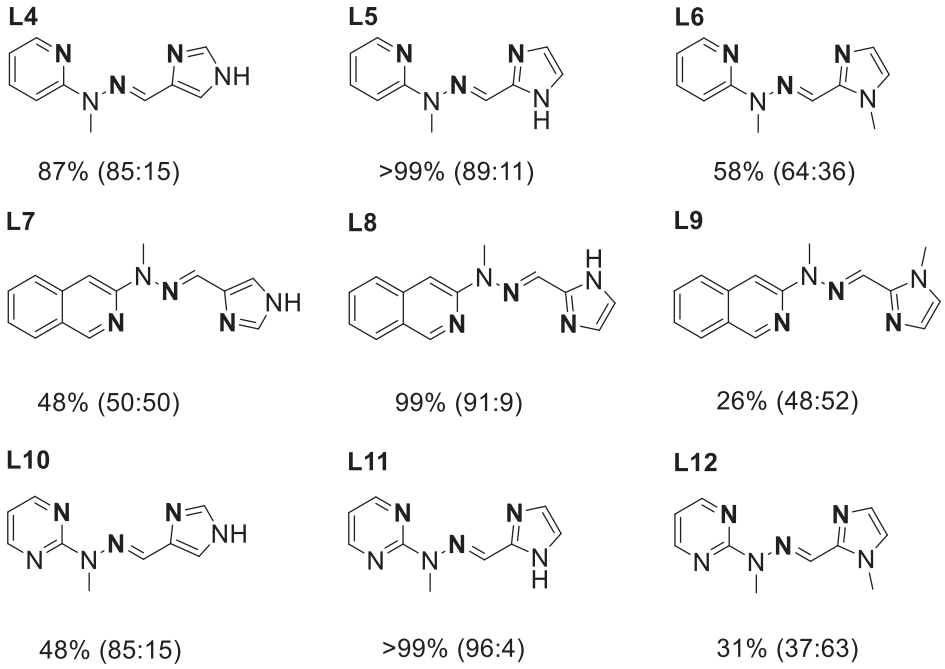
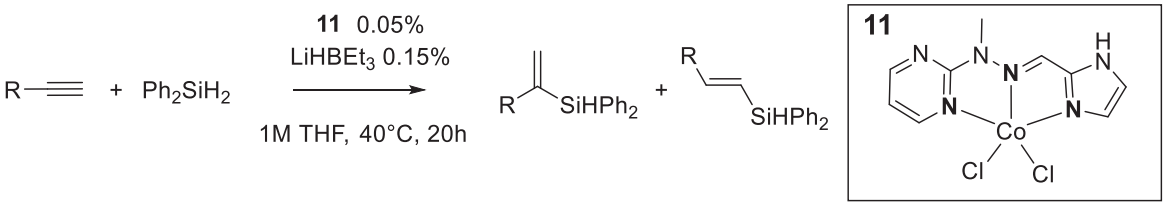


Figure 3.13 The outcome of application of various hydrazone Schiff base ligands in the hydrosilylation of phenylacetylene with diphenylsilane. The conversions of silane and selectivity of α:β addition products are given

In the optimized conditions, a series of tests were performed with various alkynes and diphenylsilane (*Table 3.14*). For the repeatability of the results, the complex **11** [$Co(L^{11})Cl_2$] was synthesised again and applied to further reactions. Phenylacetylene reacted with diphenylsilane with a 100% yield. No traces of β-addition products were observed. Phenylacetylenes bearing alkyl substituents, such as 4-methylphenylcetyene; 2-methylphenylacetylene; 3-methylphenylacetylene and 4-*tert*-butylphenylacetylene, underwent the reaction with quantitative conversion. The conversion of diphenylsilane in

all reactions were >99%. Phenylacetylene with halide substituents - 4-fluorophenylacetylene and 4-bromophenylacetylene also reacted with a quantitative conversion of diphenylsilane. Heteroaromatic 2-ethynylthiophene was compatible with tertiary silanes, however, 2-ethynylpyridine, even in the presence of 2 mol % of pre-catalyst **11**, yielded vinylsilane products only in 23% with selectivity of 69:31 of α- to β-addition.



R	Silane	Silane Conversion [%][a]	Selectivity *α/β*
Phenyl	Ph_2SiH_2	>99 (95)	100:0
(4-Me)C_6H_4		>99	96:4
(2-Me)C_6H_4		99	99:1
(3-Me)C_6H_4		99	94:6
(4-*t*Bu)C_6H_4		>99 (92)	99:1
(4-F)C_6H_4		>99 (96)	97:3
(4-Br)C_6H_4[b]		99	97:3
2-thienyl		>99	100:0
2-pyridyl[d]		23	69:31
(4-NH_2)C_6H_4		>99	100:0
(4-CN)C_6H_4[b]		69	97:3
n-hexyl		>99	93:7
cyclopropyl		>99	100:0
cyclohexyl[b]		95	84:16
cyclohexen-1-yl		>99	92:8
(4-NMe_2)C_6H_4		>99 (98)	95:5
(4-MeO)C_6H_4		>99 (96)	100:0
Phenyl[c]	Et_2SiH_2	>99	100:0[c]

Table 3.14 Conditions: Alkyne 0.5 mmol, silane 0.5 mmol, 0.05 mol % of complex **1**, 0.015 mol % $LiHBEt_3$, 1M solution of silane in THF, 40°C, 20 hours. [a]Calculated by GC with mesitylene (0.166 mmol) as internal standard. [b]0.5 mol % of complex **1**, 1.5 mol % $LiHBEt_3$, 60°C. Isolated yields of the reaction products are given in parentheses. [c]Mixture of diethyl(1-phenylvinyl)silane and diethylbis(1-phenylvinyl)silane in 87:13 ratio. [d]2 mol % of complex **11**

The substrates bearing a reactive group at the phenyl ring, such as 4-ethynylaniline, 4-ethynylbenzonitrile, 4-ethynylanisole, 4-ethynyl-N,N-dimethylaniline reacted with good

yields and selectivity. The aliphatic and cycloaliphatic substrates were tolerated, however, the selectivity in the reaction with cyclohexylacetylene was slightly lower than reactions with cyclopropylacetylene and cyclohexenylacetylene. Diethylsilane, in the reaction with phenylacetylene, underwent total conversion and no traces of β-addition were found. The above protocol was also applied to hydrosilylation of internal alkynes - phenyl(trimethylsilyl)acetylenes (*Figure 3.15*). These compounds are usually transformed by ruthenium catalysts. So far, only a few catalytic systems have been reported for the hydrosilylation of terminal[89] and internal silylacetylenes[85], most of which promoted the formation of geminal bis(silyl)alkene products. To the best of my knowledge, there is only one example of cobalt-catalysed alkyne hydrosilylation leading to such products known in the literature[101]. In our procedure, the pre-catalyst loading was set at 2 mol % of **11** and 6 mol % of $LiHBEt_3$. All 1-(phenyl)-2-trimethylsilylacetylenes were transformed to (*E*)-1-aryl-1,2-bis(silyl)ethenes in yields ranging from 72% to 97%.

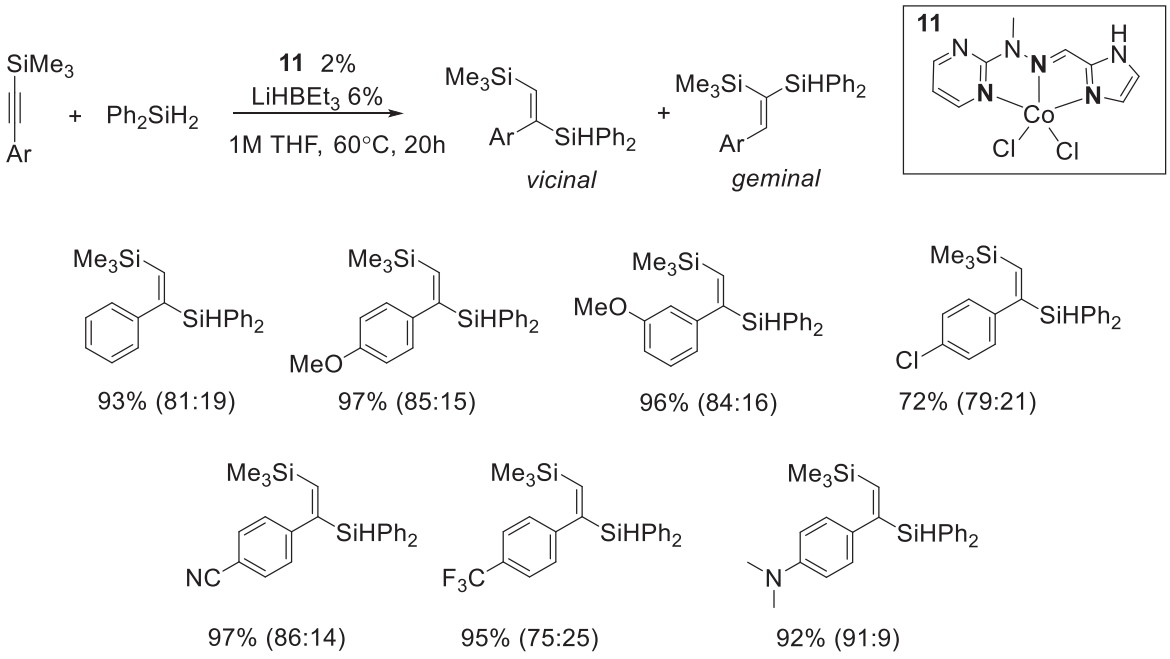
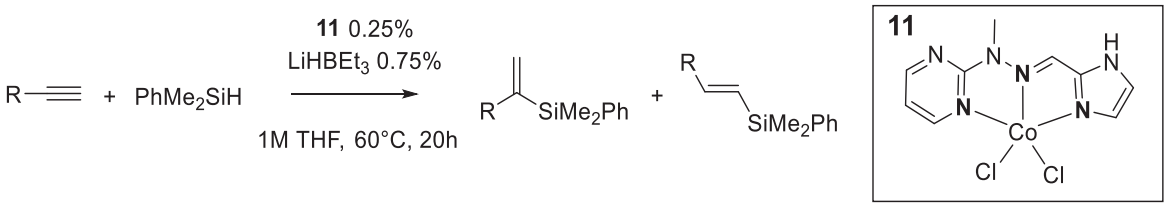


Figure 3.15 The reactivity of 1-aryl-2-trimethylsilylacetylenes in the reaction with diphenylsilane. Isolated yields and 1,2- to 1,1-bis(silyl)ethenes selectivity are given.

The results of hydrosilylation of alkynes with dimethylphenylsilane catalysed by **11** are shown in *Table 3.16*. Phenylacetylene and its alkyl derivatives reacted with good conversion and selectivity, however, lower conversion of dimethylphenylsilane was observed for the reaction with 4-*tert*-butylphenylacetylene.



R	Silane Conversion[a] [%]	Selectivity *α/β*
Phenyl	98	96:4
(4-Me)C_6H_4	98	94:6
(4-*t*Bu)C_6H_4	78	93:7
(2-Me)C_6H_4	89	98:2
(3-Me)C_6H_4	94	93:7
(4-MeO)C_6H_4	97	94:6
(4-NH_2)C_6H_4	88	96:4
(4-NMe_2)C_6H_4	>99 (95)	99:1
(4-F)C_6H_4	>99 (98)	97:3
cyclopropyl	100	98:2
cyclohexen-1-yl	100	88:12
2-thienyl	30	85:15

Table 3.16 Conditions: Alkyne 0.5 mmol, $PhMe_2SiH$ 0.5mmol, 0.25 mol % of complex **1**, 0.75 mol % $LiHBEt_3$, 1M solution of silane in THF, 60°C, 20 hours. [a]Calculated by GC with mesitylene (0.166 mmol) as internal standard. Isolated yields of the selected reaction products are given in parentheses.

Alkynes such as 4-ethynylanisole, 4-ethynyl-*N*,*N*-dimenthylaniline, 4-fluorophenylacetylene and 4-ethynylaniline reacted well, however, the yield of the reaction with the latter one was under 90%. The reactions with cyclopropylacetylene and cyclohexenylacetylene resulted in total conversion of silane with good selectivity of 98:2 and 88:12 of α:β addition, respectively. The reaction with 2-ethynylthiophene was less efficient, as the conversion was calculated as 30%.

To examine the spectrum of tolerance of developed catalytic system, various tertiary silanes were tested (*Figure 3.17*). A shortened optimization protocol indicated 2 mol % of **11** and 6 mol % of $LiHBEt_3$ as the best conditions. Phenylacetylene and its derivatives reacted with triethylsilane, triphenylsilane, triethoxysilane, pentamethyldisiloxane, methyldiphenylsilane and diethoxymethylsilane. Various alkynes were suitable for reactions with pentamethyldisiloxane, giving yields ranging from 92% to 98%, and selectivity of α- to β- addition from 98:2 to 71:29. Similar outcome was observed in the reaction with methyldiphenylsilane. In addition to trials with phenylacetylene derivatives,

cyclopropylacetylene and hex-1-yne reacted well, and yielded α-vinylsilanes in 87% and 97%, respectively.

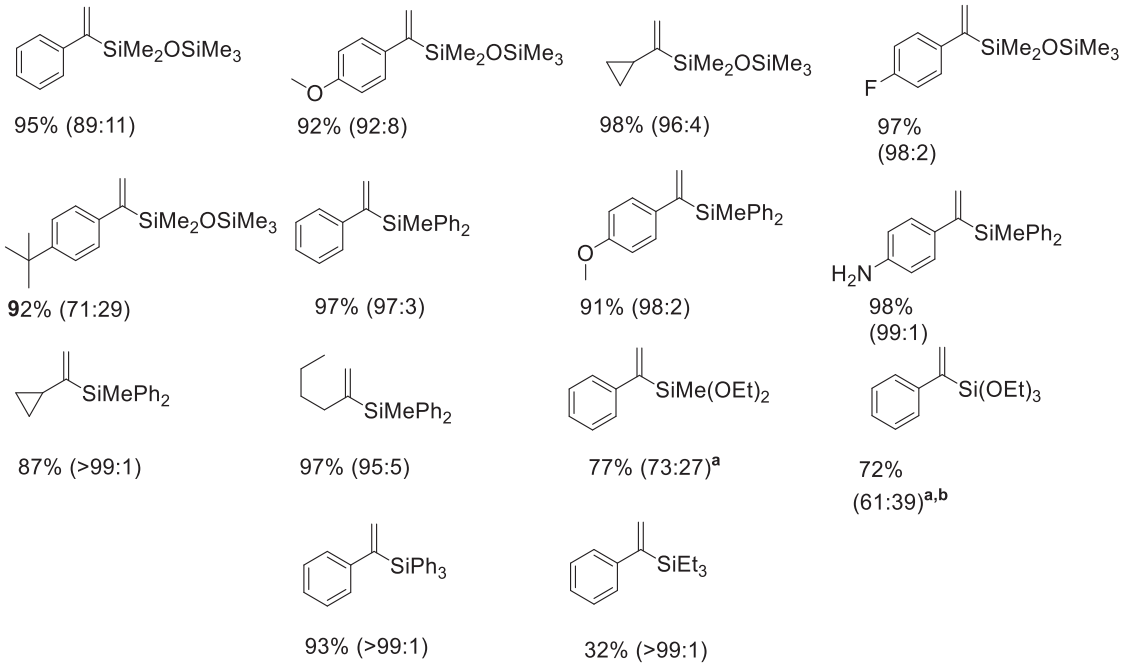


Figure 3.17 Scope of hydrosilylation of alkynes with various silanes. Isolation yields are given. [a]Not isolated. [b]Reaction with twofold excess of silane.

Moderate yields and selectivity were observed for the reaction of phenylacetylene with diethoxymethylsilane and triethoxysilane, however, triphenylsilane underwent effective and selective conversion to corresponding α-vinylsilanes. The transformation of triethylsilane turned out to be the most challenging. Despite superb selectivity, analysis of the post-reaction mixture indicated the formation of 1-(triethylsilyl)-1-phenylethene in only 32% yield.

The study reported in A3 deeply explores the impact of the ligand structure on the cobalt-catalysed alkyne hydrosilylation. Based on the conducted experiments, it can be concluded that the efficiency and regioselectivity are driven mostly by the imidazole side of the ligand but the role of the activator in the pre-catalyst activity and reaction selectivity is not entirely clear. It can be assumed that the borohydride interacts with the imidazole fragment acting as a base and deprotonates the NH group. Further interactions with free borane can electronically and sterically stabilize the imidazole ring. The catalytic system, in which **11** acts as a pre-catalyst, can be applied to many alkynes, both aryl and alkyl, as well

as internal and terminal ones. Very low pre-catalyst loading (0.05 – 2 mol %) and functional group tolerance indicates its high activity and uniqueness. It is worth mentioning that the new catalytic system proposed outperforms the so far known cobalt-based ones.

3.3 Silylation of alkynes

The studies reported in the paper **A4 "***Sodium triethylborohydride as a catalyst for the dehydrogenative silylation of terminal alkynes with hydrosilanes"*, concerned dehydrogenative coupling of terminal alkynes with hydrosilanes. Particular attention has been paid to alkali metal borohydrides, which play a role of activators in the transition-metal-catalysed reactions. Earlier, $NaHBEt_3$ has been reported as a catalyst for Markovnikov-selective hydrosilylation of styrene derivatives with hydrosilanes[102]. Above-mentioned applications were an inspiration for a study of the interaction between hydrosilanes, alkynes and sodium triethylborohydride.

Initial examinations were carried out for a system comprising phenylacetylene and diphenylsilane. Reaction of these two compounds in the presence of 10 mol % of $NaHBEt_3$ at 60°C in toluene resulted in 2% conversion of silane. The increase in temperature to 80°C and then to 100°C increased the conversion up to 79%. Further elevation of the temperature had a negative impact on selectivity as it promoted polymerization of phenylacetylene. Changes in the catalyst loading into 5 mol % and 20 mol % did not improve the conversion of substrates. Application of $LiHBEt_3$ or $KHBEt_3$ resulted in 39% and 28% conversion, respectively. The optimised conditions (*Figure 3.18*) were applied to the reactions with various alkynes and silanes.

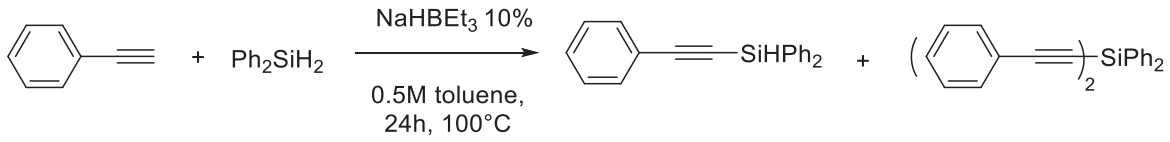


Figure 3.18 Optimised conditions for dehydrogenative coupling of terminal alkynes with silanes

Phenylacetylene was reacted with various primary and secondary silanes, (*Figure 3.19*) and their conversions ranged from 54% to 79%. Tertiary silanes were not compatible

with the reaction conditions, however, the reaction of phenylacetylene with 1,1,1,3,5,5,5-heptamethyltrisiloxane afforded a single product in 32% isolated yield. Despite moderate conversions of phenylsilane and diphenylsilane in the reactions with 4-tertbutylphenylacetylene, 4-ethynylanisole, and 4-bromophenylacetylene, no traces of double silylated product were detected. The alkyl and cycloalkyl alkynes, such as 3,3-dimethylbut-1-yne, cyclohexylacetylene, cyclohexenylacetylene or oct-1-yne were tolerated. The reaction of the latter compound with phenylsilane showed no selectivity, as analysis of post-reaction mixture indicated 51 to 49 of single to double silylated products.

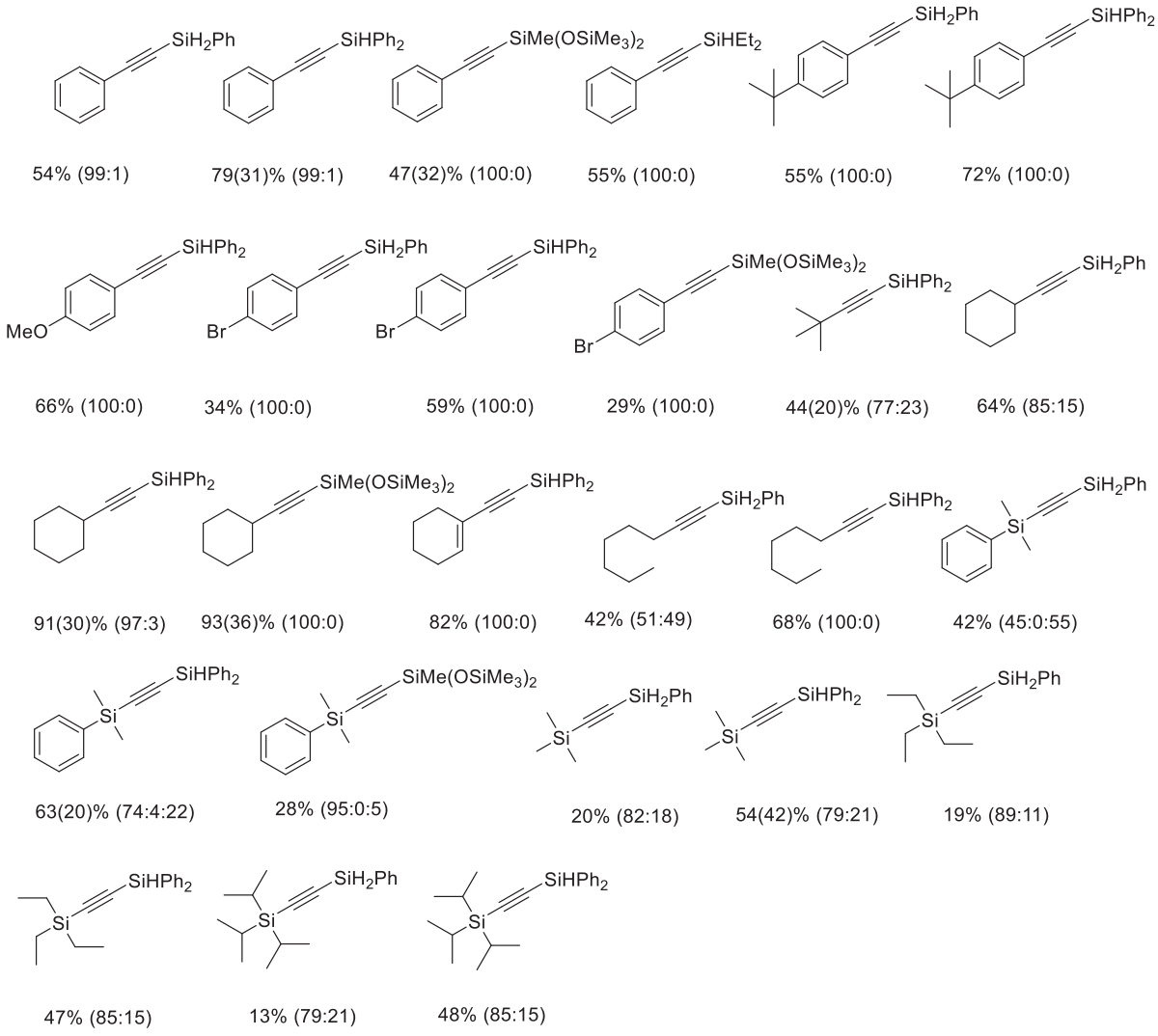


Figure 3.19 Products of dehydrogenative coupling of alkynes with silanes. The conversions of silane and selectivity of single to double silylation are given. Isolated yields in parentheses.

Silylation of ethynylsilanes – (dimethylphenylsilyl)acetylene, (trimethylsilyl)acetylene, (triethylsilyl)acetylene, (triisopopylsilyl)acetylene, were less successful as the conversion of phenylsilane and diphenylsilane ranged from 19% to 63%, however, in all cases the formation of single silylation product was privileged. Apart from the presence of double silylation products in reactions with (dimethyl(phenyl)silyl)acetylene, a homocoupling of alkyne was noted. In *Figure 3.19,* yields of homocoupling products are included as the third position in parentheses where relevant.

The proposed mechanism of this transformation is shown in *Figure 3.20*. $NaHBEt_3$ undergoes dissociation under the reaction conditions. Then, sodium hydride reacts with terminal alkyne forming sodium acetylide and releasing a hydrogen molecule. Sodium acetylide interacts with hydrosilane releasing the product and leading to recovery of sodium hydride. Deuterium labelled experiments with independent use of D_1-phenylacetylene and D_2-diphenylsilane confirmed the formation of hydrogen deuteride.

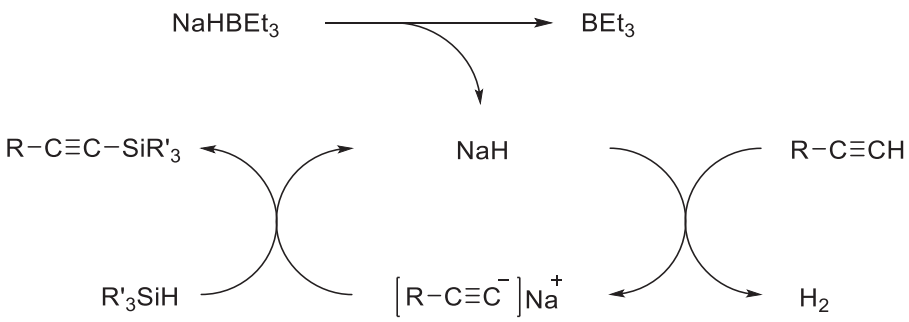


Figure 3.20 Proposed mechanism for dehydrogenative silylation of terminal alkynes with hydrosilanes in the presence of $NaHBEt_3$

Article **A4** delivers a deeper insight into the catalytic properties of metal borohydrides. Sodium triethylborohydride, commonly used as an *in situ* activator, can independently catalyse the reaction of dehydrogenative coupling of alkynes with primary and secondary silanes, as well as with hydrosiloxanes. Despite average yields, the method proposed provided a straightforward and inexpensive way to synthesise 1,2-(bis)silylethynes and alkynylsiloxanes.

4. Conclusions

From among structurally similar complexes presented in **Article 1**, the pentacoordinated cobalt(II) chloride complex with benzimidazole/2*H*-imidazole-based ligand, activated by lithium triethylborohydride, was determined as the most active catalyst of hydrosilylation of alkenes. The reactions performed in the presence of this catalyst afforded β-addition products selectively. The scope of the reaction includes primary- and secondary silanes as well as various vinylarenes. Mild reaction conditions and low catalyst loading are attractive features of the designed and developed catalytic system proposed in **A1**. The study presented in **A1** has shown that similar coordination motifs do not necessarily lead to the isostructural group of catalytically active cobalt(II) coordination compounds, which is an important finding that should be taken into account in designing of new catalysts in general.

In the studies reported in **Article 2**, the aforementioned cobalt(II) chloride complex with benzimidazole/2*H*-imidazole ligand, activated by lithium triethylborohydride, was tested in hydrosilylation of alkynes. It has shown good catalytic performance with primary, secondary and tertiary silanes. Similarly, mild reaction conditions and low catalyst loading, down to 1000 ppm are very attractive features. The functional group tolerance – amine, halide, ester, nitrile – and extremely high selectivity toward *syn*-*α*-addition products are unique features of the developed method. This catalytic system excelled the other known cobalt(II) complexes with NNN-donor ligands in terms of activity and selectivity.

The continued search for the most active alkyne hydrosilylation catalysts has been described **Article 3**. Nine cobalt pre-catalysts of similar structures were assessed in hydrosilylation of phenylacetylene with diphenylsilane. The results showed a strong impact of 2*H*-imidazole moiety on the catalytic activity. From among 3 compounds with the same backbone, Co(II)/pyrimidine/2*H*-imidazole activated by lithium triethylborohydride turned out to be the most active and has led to selective formation of α-vinylsilanes. The tolerance of primary, secondary and tertiary silanes as well as various functional group in alkyne molecule proved the versatility of the developed catalytic system. It is worth noting that the optimised catalyst loading for the reaction involving phenylacetylene and phenylsilane was determined as 500 ppm.

Article 4 describes the activity of sodium triethylborohydride as a highly selective, inexpensive and commercially available catalyst for the silylation of aromatic and aliphatic alkynes with hydrosilanes. Although the substrate scope is limited, this particular method can be applied to the synthesis of alkynylsilanes containing SiH_2Ph and $SiHPh_2$ groups, unsymmetrically substituted bis(silyl)ethynes, and, what is important, alkynylsiloxanes which are interesting substrates in cross coupling reactions. It is necessary to mention that alkali metal borohydrides are widely used as activators in metal-catalysed transformations. These observations induce investigation on the reaction pathway every time the metal borohydrides are used.

Published Articles - Appendix

Appendix **A1** Bocian A*., **Skrodzki M***., Kubicki M., Gorczyński A., Pawluć P., Patroniak V.; *The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins. Appl. Catal. A-Gen.* **2020**, 602, 117665. [IF= 5.71, MNiSW= 100, Cited by 6(5), *equally contributed]

Appendix **A2** **Skrodzki M**., Patroniak V., Pawluć P.; *Schiff Base Cobalt(II) Complex-catalysed Highly Markovnikov-Selective Hydrosilylation of Alkynes. Org. Lett*. **2021**, 23, 663-667. [IF= 6.00, MNiSW= 140, Cited by 13(12)]

Appendix **A3** **Skrodzki M**., Ortega Garrido V, Csaky A. G., Pawluć P.; *Searching for highly active cobalt catalysts bearing Schiff base ligands for Markovnikov-selective hydrosilylation of alkynes with tertiary silanes. J. Catal.* **2022**, 441, 116-121. [IF= 7.92, MNiSW= 140, Cited by 0]

Appendix **A4** **Skrodzki M**., Witomska S., Pawluć P.; *Sodium triethylborohydride as a catalyst for the dehydrogenative silylation of terminal alkynes with hydrosilanes. Dalton Trans*., **2018**, 47, 5948. [IF= 4.39, MNiSW= 140, Cited by 21(20)]

Appendix **A1**

Bocian A*., **Skrodzki M***., Kubicki M., Gorczyński A., Pawluć P., Patroniak V.; *The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins. Appl. Catal. A-Gen.* **2020**, 602, 117665.

*equally contributed]

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The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins

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ABSTRACT

Environmental and economic aspects render the search for new nonprecious metal hydrosilylation catalysts an up-to-date challenge. Cobalt stands as an interesting alternative to the benchmark platinum-based species, nonetheless its relative infancy necessitates further studies, particularly regarding the structure of organic ligands that decorate the catalytically active metallic centre. As a continuation of our previous communication, we synthesized and characterized a series of new cobalt(II) chloride bench-stable precatalysts coordinated to a small library of structurally similar Schiff base ligands. Thus the synthesized species were evaluated for their ability to act as olefin hydrosilylation catalysts in the presence of alkali metal triethylborohydrides. From the crystal engineering point of view, it was observed that the number and arrangement of the Schiff base non-coordinating hydrogen bond donors affects the composition of formed complexes, resulting in predominant formation of either [Co**L**Cl_2] 'open' or [Co$\mathbf{L}_2$]$^{2+}$ 'closed' species or a mixture of these. This affects their catalytic properties, with the benzimidazole/2H-imidazole 'open' system being the most efficient in terms of hydrosilylation selectivity and lowest catalyst loading. All in all, our work shows that seemingly similar coordination motifs do not necessarily lead to the isostructural group of catalytically open cobalt(II) coordination compounds, which is an important factor to consider in the design of new catalysts in general.

1. Introduction

Transition-metal catalysed hydrofunctionalization of carbon-carbon multiple bonds with Si-H is a widely utilized chemical reaction to get functionalized molecules and materials of importance in both academia and industry [1,2]. Though historically and practically these processes have been catalysed by platinum species [3,4], recent progress in this area clearly implies that earth abundant transition metals can stand up to the challenge of outperforming the expensive Pt compounds [5–7]. Cobalt has been recognized as one of such candidates, offering not only great abundance and low biotoxicity, but also rich redox properties and coordination chemistry that allows tuning its final catalytic efficiency [8–10]. Although initial reports [11–14] have shown that low-valent cobalt carbonyl compounds can act as hydrosilylation precatalysts, their tunability and thus poor catalytic efficiency were impairing factors. As a solution, various ligand environments were studied and some notable recent examples encompass N-heterocyclic carbenes [15,16] β-diketiminate arenes [17] or carboxylate/isocyanide mixtures [18].

Specifically, the tridentate scaffolds have been found one of the most promising ligands to alter activity, selectivity and fidelity of the catalyst. [4,19,20] The underpinnings were laid by the group of Chirik and co-workers [21] who have shown that NNN-pyridinediimine (PDI) ligands can form robust iron alkene hydrosilylation catalysts, and this finding was later transferred to general use of such scaffold for the design of new cobalt precatalysts. For example, the same group has recently demonstrated [22] that PDI-Co–bis(carboxylates) form bench stable alkene hydrosilylation precatalysts with high anti-Markovnikov selectivity and broad functional group tolerance. Extension for enantioselective variants of the reaction with NNN-oxazoline-imino-pyridine ligands has also been demonstrated [23,24]. Interestingly, the use of NNN-bipyridineimine ligand was shown to affect the olefin/ketone chemoselectivities in a facile manner via external reaction conditions [25]. Recent progress also allowed for efficient and selective hydrosilylations of alkenes [8,26–29].

Changes in the ligand donor atoms has been also found to be an effective strategy for activity improvement with CCC-pincer-bis

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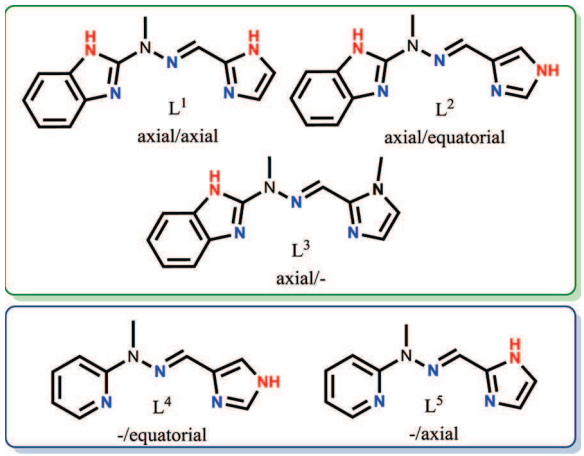


Fig. 1. Schematic representation of ligands used in this work; green frame denotes the family of benzimidazole-scaffolded ligands whereas blue frame shows the family of pyridine-scaffolded coordinating agents.

(carbene) [30], diphosphine ketone [31] or PNN-phosphine-iminopyridine [32–34] cobalt complexes displaying switchable regio- and chemoselectivities. Design of pyridine/quinoline-oxazoline ligands that furnish tetrahedrally coordinated cobalt species are also of interest for regio- and enantioselective Markovnikov 1,2-hydrosilylation of conjugated dienes. [35]

We have shown previously [36] that the cobalt(II) complex with meridional, NNN-Schiff base ligand might act as a precatalyst in hydrosilylation reactions, specifically inducing hydrosilylation and dehydrogenative silylation of olefins in the presence of sodium triethylborohydride, which depends on the choice of the hydrosilane. We have recently published [37] a small library of structurally similar ligands (Fig. 1) and reported differences in the observed catalytic and biological properties in a series of Fe(II/III) complexes.

Taking into account the above-discussed and well-known influence of the subtle structural ligand changes on the hydrosilylation activities, the aim of our study was to establish the effect of selected ligands making complexes with cobalt(II) chloride and establish if non-coordinating N-donor atoms influence the structure of the cobalt complexes and their hydrosilylation efficiency.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were purchased form commercial sources and used as received.

Elemental analyses for C, H, and N were carried out using an Elementar Analyser Vario EL III. Infrared spectra were recorded on an iS50 FT-IR, Thermo Scientific Nicolet. Electrospray ionisation mass spectroscopy (ESI-MS) was performed using Mas ZQ Water spectrometer.

2.2. Synthesis of ligands

The five ligands chosen above were prepared according to the synthetic procedure reported previously [37].

2.3. Synthesis of complexes

In complexes **1**-**5** the molar ratio of the ligand to the corresponding salt was 1:1. To a solution of $\mathbf{L^1}$- $\mathbf{L^4}$ in hot MeOH, $\mathbf{L^5}$ in DCM, a methanolic solution of $CoCl_2{\cdot}6H_2O$ was added. The mixture was stirred for 24 h at room temperature. The solvents were subsequently evaporated under vacuum to minimal amount and an excess of Et_2O was added.

Table 1
Synthetic parameters of synthesized cobalt complexes.

No.	Ligand mg	$CoCl_2{\cdot}6H_2O$ mg	Colour	Yield[a]		Crystals from
				mg	%	
1	100.0	99.1	green	153.9	99.8	PhMe
2	100.0	99.1	sea-blue	129.8	84.2	Et_2O
3	100.0	93.6	lime-green	137.2	63.2	iPr_2O
4	100.0	118.4	green	169.0	93.8	iPr_2O
5	100.0	118.4	dark green	118.0	71.7	–

The obtained precipitate was filtered off, washed twice with Et_2O (10 ml in total) and air dried. Yields based on the ligands are shown in Table 1. Crystals suitable for X-ray characterization were grown by vial-to-vial diffusion of different external solvents into the methanolic solution of complexes at 4 °C. The data are compiled in Table 1.

1 $[Co\mathbf{L^1}Cl_2]$

ESI-MS(+) *m/z* (%): 241 (30) $[H\mathbf{L^1}]^+$, 334 (100) $[Co\mathbf{L^1}Cl]^+$. Anal. calc. for $[Co(C_{12}H_{12}N_6)Cl_2]$: C: 37.14, H: 3.64, N: 21.65 %; found: C: 37.00, H: 3.92, N: 21.35 %. IR: ν (CH)−$_{ar}$ 3166; ν (CC) 1575; ν(CN==) 1473, 1436, 1319; ρ(C−H) 1150, 1104, 1050, 1006, γ(C−H) 966, 808, 744 cm^{-1}.

Crystallized compounds **1** and **1a** differ in the co-crystallized solvent lattice molecules.

2 $[Co\mathbf{L^2}Cl_2]$

ESI-MS(+) *m/z* (%): 241 (30) $[H\mathbf{L^2}]^+$, 334 (85) $[Co\mathbf{L^2}Cl]^+$, 538 (50) $[Co\mathbf{L^2}(\mathbf{L^2}\text{-H})]^+$.Anal. calc. for $[Co(C_{12}H_{12}N_6)Cl_2]$: C: 38.94, H: 3.27, N: 22.71 %; found: C: 38.43, H: 3.44, N: 22.00 %. IR: ν(NH) 3306; ν(CH)−−$_{ar}$ 3125; ν(CC) 1583; ν(CN) 1463, 1434; ρ(CH===−) 1136, 1074, 1045, 999; γ(C−H)$_{ar}$ 966, 804, 766, 710 cm^{-1}.

Crystallized compounds **2** and **2a** differ in the cobalt(II) chemical compositions, being 1:1 (M:L) 'open' or 1:2 (M:L) 'closed' species respectively. Please note, however, that in **2a**, cobalt is also present in the form of $[CoCl_4]^{2-}$, therefore the initial synthetic 1:1 stoichiometry is still maintained.

3 $[Co(\mathbf{L^3})_2][CoCl_4]$

ESI-MS(+) *m/z* (%): 255 (10) $[H\mathbf{L^3}]^+$, 348 (100) $[Co\mathbf{L^3}Cl]^+$, 566 (50) $[Co\mathbf{L^3}(\mathbf{L^3}\text{-H})]^+$. Anal. calc. for $[Co(C_{13}H_{14}N_6)_2]CoCl_4$: C: 35.63, H: 4.60, N: 19.18 %; found: C: 35.58, H: 4.47, N: 19.06 %. IR: ν(NH) 3443; ν(CH)−−$_{ar}$ 3118; ν(CC) 1573; ν(CN==) 1473, 1463, 1421, ρ(C−H) 1192, 1055, 1041, 1005; γ(C−H)$_{ar}$ 969, 756, 745 cm^{-1}.

4 $[Co\mathbf{L^4}Cl_2(MeOH)]$

ESI-MS(+) *m/z* (%): 295 (100) $[Co\mathbf{L^4}Cl]^+$. Anal. calc. for $[Co(C_{10}H_{11}N_5)Cl_2(CH_3OH)]$: C: 36.39, H: 4.16, N: 19.29 %; found: C: 36.25, H: 4.18, N: 18.98 %. IR: ν(NH) 3213; ν(CH)−−$_{ar}$ 3130; ν(CC)=$_{py}$, ν(CN=)$_{py}$ 1598, 1568, 1557, 1480, 1425, 1379, 1314; γ(CH−)$_{ar}$ 990, 893, 847, 781, 763 cm^{-1}.

5 $[Co\mathbf{L^5}Cl_2]$

ESI-MS(+) *m/z* (%): 202 (20) $[H\mathbf{L^5}]^+$, 295 (100) $[Co\mathbf{L^5}Cl]^+$. Anal. calc. for $[Co(C_{10}H_{11}N_5)Cl_2]$: C: 36.28, H: 3.35, N: 21.15 %; found: C: 35.61, H: 3.66, N: 20.45 %. IR: ν(NH) 3501; ν(CH)−−$_{ar}$ 3150; ν(CC)=$_{py}$, ν(C =N)$_{py}$ 1584, 1438, 1393, 1315; γ(C−H)$_{ar}$ 850, 746 cm^{-1}.

2.4. X-ray crystallography

Diffraction data were collected by the ω-scan technique at room temperature (**1**) or at 130(1)K (**2**, **2a**) on a Rigaku SuperNova four-circle diffractometer with an Atlas CCD detector and mirror-monochromated CuK_α radiation (λ = 1.54178 Å), and at 100(1) K (**1a**, **3**) or 130(1) K (**5**) on a Rigaku XCalibur four-circle diffractometer with an EOS CCD detector and graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The data were corrected for Lorentz-polarization as well as for absorption effects [38]. Precise unit-cell parameters were determined by a least-squares fit of the reflections of the highest intensity,

chosen from the whole experiment. The structures were solved with SHELXT-2013 [39] and refined with the full-matrix least-squares procedure on F^2 by SHELXL-2013 [40]. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in idealized positions and refined as 'riding model' with isotropic displacement parameters set at 1.2 (1.5 for CH_3) times U_{eq} of appropriate carrier atoms. In **1a**, **2a** and **3** diffused residual density was found, which could not be modelled as reasonable solvent molecules, so the SQUEEZE procedure [41] was applied in these cases. In turn in **1** the disordered methanol molecule with half-occupation was modelled.

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-1869192 – CCDC 1869197. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk.

2.5. Hydrosilylation studies

All reactions were performed in flame-dried Schlenk flask under argon atmosphere. THF was purified by distillation over sodium and benzophenone, under argon atmosphere. Other solvents were dried by distillation over calcium hydride.

Gas chromatography was performed on a Bruker Scion 436-GC with a 30 m Agilent VF5-ms 0.53 mm Megabore column and a TCD detector. The temperature program was as follows: 60 °C (3 min), 20 °C/min, 280 °C (20 min). Decane was used as a reference. GC–MS analyses were performed on a Bruker Scion 436-GC with a 30 m Varian DB-5 0.25 mm capillary column and a Scion SQ-MS mass spectrometry detector. The temperature program was as follows: 60 °C (3 min), 10 °C/min, 250 °C (15 min). NMR analyses were performed on a Bruker Fourier 300 MHz or 400 MHz spectrometer.

2.6. General procedure of alkene hydrosilylation

Portions of 1.0 mmol of silane, 0.5 ml of THF, 1.0 mmol of alkene, 0.1 ml of decane and precatalyst were placed in previously evacuated Schlenk bomb flask fitted with a plug valve. A reference sample was taken. Next, 1 M solution of $LiHBEt_3$ in THF was added, the reaction vessel was closed and heated to a given temperature upon stirring. After a specified time, the reaction mixture was cooled down to room temperature and analysed using GC and GC–MS. Selected products of hydrosilylation were isolated by precipitation of the catalyst with hexane followed by filtration through syringe filter. The filtrate was then concentrated under reduced pressure.

3. Results and discussion

3.1. Synthesis and characterization

The group of five hydrazone Schiff base ligands $\mathbf{L^1}$–$\mathbf{L^5}$ was successfully synthesized in a two-step synthetic protocol, derived from 2-chlorobenzimidazole (ligands $\mathbf{L^1}$–$\mathbf{L^3}$) or 2-bromopyridine (ligands $\mathbf{L^4}$ and $\mathbf{L^5}$). [37] Their distinct feature is the N_3-tridentate meridional binding subunit with varying number (0–2) and topology (axial vs. equatorial) of NH donor hydrogen bonds (Fig. 1). The choice of the appropriate binding group also affects the basicity of the ligand, as expressed by comparison of the pKa values: pyridine (5.2) > benzimidazole (5.5) > imidazole (6.95) [42], which would mean that the benzimidazole/imidazole family $\mathbf{L^1}$-$\mathbf{L^3}$ is more basic and thus more stable complexes should be formed. In addition, complexes based on the 2H-imidazole are also considered to be more basic than 4H-imidazoles [43] and therefore the following order of basicity can be constructed: ($\mathbf{L^4} > \mathbf{L^5}$) > > ($\mathbf{L^2} > \mathbf{L^1} \sim > \mathbf{L^3}$).

With the aim of forming bench stable, cobalt(II) hydrosilylation precatalysts, the ligands were coordinated with equimolar amounts of cobalt(II) chlorides, precipitated and recrystallized. Two kinds of coordination compounds were obtained, that can be referred to as 1:1 'open' or 1:2 'closed' ones, depending on whether catalytically active metallic centre is coordinated by one or two Schiff base ligands (see X-ray description). The type of coordination is very important from the catalytic point of view, since the activity of the latter ones is predicted to be hampered. Ligands $\mathbf{L^1}$, $\mathbf{L^4}$ and $\mathbf{L^5}$ lead to predominant formation of 1:1, open species, whereas $\mathbf{L^3}$ to 1:2 closed complexes. Interestingly, mixed axial/equatorial arrangement of NH bonds in $\mathbf{L^2}$ resulted in isolation of two cobalt complexes, each belonging to one of the above distinguished groups.

In solution however, one cannot exclude that speciation of complexes occurs, which is however amenable to the applied cone voltage [44] and do not constitute definitive proofs. Under similar ESI-MS conditions, the following 'closed' $[CoL_2]^{2+}$ to 'open' $[CoLCl]^{+}$ signal ratio was observed, expressed as the % of the intensity of the 'closed' system, related to the 100 % intensity of the 'open' signal: **1** (~20 %), **2** (~25 %), **3** (~50 %), **4** (~10 %), **5** (~25 %). Indeed, the highest signal ratio was observed for **3**, which constitutes the most basic $\mathbf{L^3}$ ligand system. This is in line with the results found in the solid state, bearing in mind however, that this does indicate the selective formation of such species (in $\mathbf{L^2}$ 1:1 open systems crystallized as well). In addition, similarity of the ESI signal-distribution of compound **5** to **1, 2** and **4** implies a predominant formation of an 'open' 1:1 cobalt complex in **5**, for which no X-ray is provided. It is important however to note that in case of the borohydride-mediated hydrosilylation process, cobalt(II) chloride complexes function only as precatalysts and undergo structural changes to the catalytically active hydride species. Solution speciation of the latter ones can therefore differ from the speciation of compounds **1**-**5** and *in situ-operando* techniques would be needed to gain detailed insight into this manner.

3.2. Description of crystal structures

Six X-ray structures were acquired in total, with perspective view of 5 of them depicted in Fig. 2. Relevant geometrical parameters of the complexes are listed in Table 2, while the hydrogen-bond data – in Table S1. Crystal data, data collection and structure refinement is

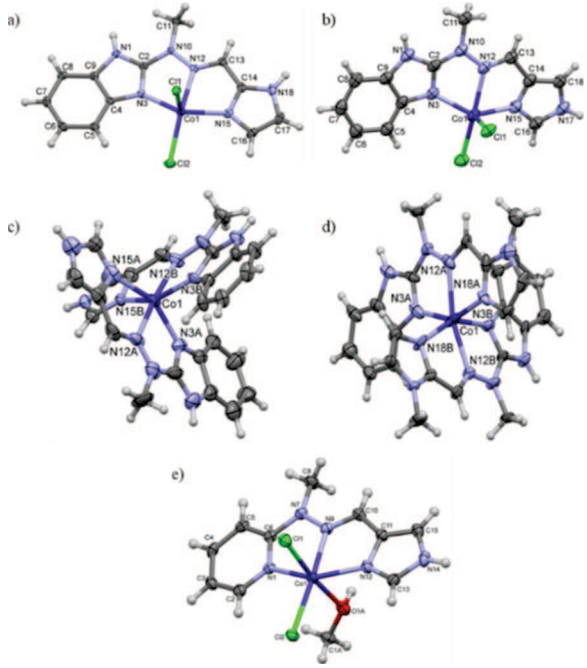


Fig. 2. Perspective view of complexes **1a** (a), **2** (b), **2a** (c), **3** (d), **4** (e); ellipsoids are drawn at the 50 % probability level, hydrogen atoms are shown as spheres of arbitrary radii. Counterions are not shown for clarity reasons.

Table 2
Relevant geometrical data (Å, º); "angles" are three largest angles around Co center, A, B and C denote mean planes of benzimidazole or pyridine ring, chain linker and imidazole ring, respectively.

	1	1a	2	2a (A)	2a (B)	3	4
Co1-N3	2.103(6)	2.085(2)	2.064 [38]	2.056 [38]2.103 [38]	2.037 [38] 2.101(10)	2.034(5) 2.074(10)	2.123 [38]
Co1-N12	2.237 [38]	2.215(2)	2.180(5)	2.126 [38]2.153 [38]	2.085(11) 2.179 [38]	2.193(11) 2.121(9)	2.112 [38]
Co1-N18 (N15)	2.096 [38]	2.082(2)	2.083 [38]	2.176 [38]2.131 [38]	2.140(13) 2.221 [38]	2.127(9) 2.276(10)	2.130 [38]
Co1-Cl1	2.313 [38]	2.3473 [38]	2.3576(14)				2.4795(9)
Co1-Cl2	2.339(2)	2.3119 [38]	2.2851(15)				2.3559(9)
Co1-O1							2.227(2)
C2-N1-C9	107.3 [38]	106.2(2)	106.9 [38]	109.0 [38]109.0 [38]	105.4(10) 109.0 [38]	109.4(12) 107.3(9)	117.9 [38]
C2-N3-C4	106.1(6)	104.52(19)	105.7 [38]	106.0(6) 105.9(6)	105.5(10) 106.0(6)	113.9(10) 101.7(9)	
C13-N12-N10	125.9 [38]	124.7(2)	124.5(5)	127.3 [38]127.4 [38]	120.6(11) 127.2 [38]	122.9(11) 124.7(10)	123.3 [38]
C14-N15-C16	107.4 [38]	105.7(2)	106.1(5)	105.5(6) 105.5(6)	105.6(13) 105.4(6)	128.3(15) 107.4(9)	105.4 [38]
C16-N18-C17	105.7 [38]	107.8(2)	109.4 [38]	106.9 [38]106.9 [38]	107.4(12) 106.9 [38]	110.2(11) 104.5(9)	108.2 [38]
angles	156.5(2) 140.2 [38] 108.58(9)	156.62(6) 141.47 [38]108.23 [38]	163.60(12) 139.02 [38] 105.36(13)	173.6 [38]151.0 [38]150.8 [38]	173.8 [38] 152.9(5) 148.3 [38]	164.3 [38]150.3 [38] 147.8(5)	173.62(6) 171.49 [38] 150.45(11)
A/B	4.3(5)	5.34(19)	2.6 [38]	5.7(11) 6.7(10)	6.0(11) 4.0(12)	3.7(10) 3.4 [38]	4.7(2)
B/C	5.8(6)	6.80(18)	1.7 [38]	1.8(14) 2.9(10)	4.0(10) 0.5(14)	3.3(10) 6.5 [38]	8.5(2)
A/C	6.9(5)	7.76(12)	3.6 [38]	6.2(10)7.5 [38]	8.7 [38] 4.2(10)	5.5 [38] 8.1(6)	11.07(14)
A/A'				82.2 [38]	81.8 [38]	87.7(2)	

gathered in Table S2. Two types of the complexes can be distinguished: neutral ones of the general formula [Co**L**$Cl_2(MeOH)_x$] (**1** and **2** where x = 0; **4** where x = 1 and additional coordinated methanol molecule is observed), and +2 charged $[CoL_2]^{2+}$ (**2a**, **3**), in which only Schiff base ligand molecules are involved in coordination. Charge of the latter structures is compensated by $CoCl_4^{2-}$ (**2a**, **3**) and Cl- (**2a**) counterions, therefore the initial synthetic stoichiometry is maintained. All N-heterocyclic ligands are tridentate, with three nitrogen atoms involved in coordination, and are almost planar, as may be seen by analysing the dihedral angles between planar fragments of the molecules (Table 2). Complexes **1** and **2** are 5-coordinated, in a distorted tetragonal pyramid fashion (three ligand nitrogen and one chloride approximately coplanar, second Cl- in apical position, cf. Fig. 2a, b), while the other complexes are six coordinated, by 6 nitrogen atoms from two **L** molecules in **2a** and **3**, and three ligand nitrogen, two Cl- and methanol oxygen in **4**. In these cases the coordination scheme is a distorted octahedron. Complexes **1** and **1a** are isostructural; they probably contain different solvent molecules. In structure **1** (apparently of worse quality) we were able to model the disordered methanol molecule without any restraints, which improved the quality of the model. It is also interesting when compared with structure **4**, where the MeOH molecule actively coordinates to the cobalt metallic centre, and in **4** it prefers to constitute part of the crystal lattice. In **1a**, even though the quality of the structure looks better, we were not able to reasonably model the diffused electron density, and the attempts using the model of **1** led to significantly worse refinements, therefore SQUEEZE procedure was used in this case. The crystal structure of these complexes show that the solvent takes part in hydrogen bonding (Fig. 3, Table S1), so we might assume that in **1a** totally disordered water molecules take part in formation of the crystal lattice.

It should be noted that in **1** and **2**, where Schiff base ligands differ only in arrangement of the imidazole NH position, the apical chloride anions are involved in hydrogen bonding: in **1** the N—H···Cl interactions close the dimeric rings, which are further connected by hydrogen bonds with the solvent molecules (Fig. 3 right), in **2** such rings are also

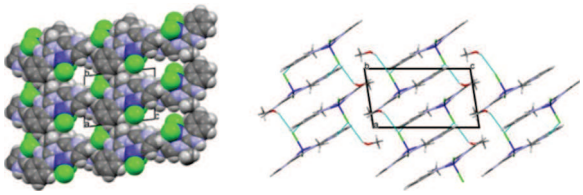


Fig. 3. The van der Waals radii representation of the crystal structure of **1a** (without solvent); (Bottom) Hydrogen bonds (blue dashed lines) in the structure of **1**; MeOH solvent molecules are involved in the network.

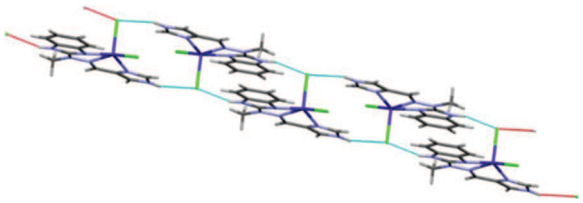


Fig. 4. The chain of dimers in **2** connected by N—H···Cl hydrogen bonds.

closed, but they are further expanded by N—H···Cl bonds into chains (Fig. 4).

In **4**, which differs from **2** in the change of benzimidazole to pyridine rings in the ligand, thanks to the presence of an additional hydrogen bond donor offered by coordinated methanol molecule, both Cl^- ions take part in hydrogen bonds (Fig. 5 left, Table S1). Three-molecule rings are formed, which further expand into the fully three-dimensional, hydrogen-bonded structure (Fig. 5 right).

Crystal lattices of coordination compounds that belong to the $[CoL_2]^{2+}$ group differ significantly from the [Co**L**$Cl_2(MeOH)_x$] group due to the presence of an additional ionic component.

Structure of **2a** is unique due to very complicated character; this compound crystallizes in the trigonal R3 space group, with a degree of pseudosymmetry. Its unit cell contains 18 double-charged $[CoL_2]^{2+}$

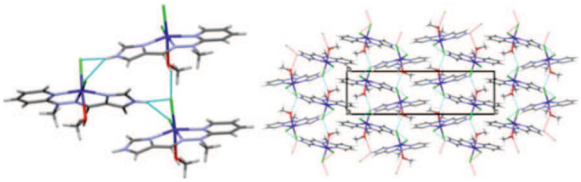


Fig. 5. (Left) Three-membered hydrogen-bonded ring in **4**; (right) crystal architecture of **4**; hydrogen bonds are shown as dashed lines.

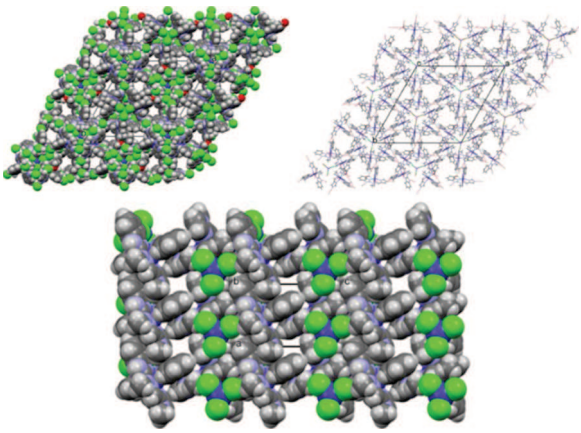


Fig. 6. Voids (channels along [001]) in the crystal structure of **2a**; (middle) crystal structure of **2a** as seen along the three-fold axis (z); (bottom) Van der Waals representation of structure **3**.

complexes, 3 $[CoCl_4]^{2-}$ anions and 10 chloride anions; additionally we have identified 18 methanol molecules and the regions of diffused electron density (17.6 % of the unit cell volume [45]), which could not be modelled (Fig. 6 top left). All these components are connected by electrostatic interactions between charged fragments and by a network of hydrogen bonds into the three-dimensional architecture (Fig. 6 top right)

The crystal structure of **3** also contains voids, the channels along the [010] direction (Fig. 6 bottom), which sum up to 17.5 % of the unit cell volume [45]; its architecture is mainly determined by electrostatic interactions between cations and anions.

3.3. Catalytic activity of Co(II) complexes in olefin hydrosilylation

Activation of the synthesized cobalt complexes was performed in accordance with the protocol of Nakazawa et al. [46] using alkali metal triethylborohydrides. Thus, the active cobalt catalysts were generated *in-situ* from bench-stable cobalt(II) precursors, which has recently been a commonly employed strategy.[4] All the Co(II) complexes showed catalytic activity in the model reaction of hydrosilylation of styrene with phenylsilane (marked as the abbreviation **H** in the Table 3) when activated by sodium or lithium triethylborohydrides, however, competitive phenylsilane redistribution to diphenylsilane (marked as the abbreviation **R** in the Table 3) was also observed under given conditions in most cases (Scheme 1). The results vary significantly depending on the chosen Schiff base scaffold, which can be to a certain extent corroborated by the structures determined in the solid and solution states. The conditions for effective addition of phenylsilane to styrene in the presence of cobalt(II) complexes and $MHBEt_3$ were optimized *via* catalytic screening of the substrate conversion, together with evaluation of selectivity by GC and GC–MS methods. In a typical procedure, styrene, phenylsilane and the cobalt precatalyst (1:1:0.03 M ratio) were dissolved in dry THF, then 0.12 equiv. of triethylborohydride was added and the reaction mixture was heated and stirred at 80 ˚C or stirred at room temperature for 20 h using Schlenk techniques (Table 4).

Pyridinic complexes **4** and **5** showed catalytic activity at 80 ˚C in the presence of $NaHBEt_3$, with moderate selectivity. The formation of significant amounts of diphenylsilane (26–39 %), as the product of competitive phenylsilane redistribution was observed (Table 3, entries 1 and 4). The reactions performed with lithium triethylborohydride resulted in conversions not exceeding 50 %, however with only single hydrosilylation step taking place, resulting in alpha and beta products detected in the reaction mixture, exclusively alpha for catalyst **4**. High selectivity towards *α*-hydrosilylation products in the presence of alkali metal trialkylborohydrides at elevated temperatures can be connected with intrinsic catalytic activity of the latter in the Markovnikov-selective hydrosilylation, recently discovered by our group. [47]

From among the benzimidazole-based cobalt(II) precursors tested, **1** (3 mol%) activated by 4 equivalents of $NaHBEt_3$ or $LiHBEt_3$ showed the highest activity and selectivity (93–96 %) towards hydrosilylation reaction (Table 3, entries 9–10). After several attempts we found that a catalytic system consisting of **1** and $LiHBEt_3$ promoted hydrosilylation also at room temperature to yield predominantly the β-addition product, although higher-order addition products were also detected in the reaction mixture (Table 3, entry 11). In addition, the presence of THF as a solvent appears to be necessary to ensure higher selectivity to give β-hydrosilylation product at room temperature (Table 3, entry 12). When **1** is compared to the remaining cobalt complexes from this group, either reduced activity and selectivity (**2**) or competitive phenylsilane redistribution process were observed (**3**). The latter one is the least active system from all studied cobalt(II) precatalysts, with no hydrosilylation observed in the presence of $NaHBEt_3$. This observation can be explained when remembering that in the solid state, this system forms closed $[CoL_2]^{2+}$ species therefore rendering them catalytically inert. Certain degree of activity can be explained by the presence of $[CoCl_4]^{2-}$ counteranion, which also depends on the triethylborohydride salt (Table 3, entries 13 and 14).

The best precatalysts turned out to be the pentacoordinated neutral complex **1** containing a tridentate Schiff base ligand and two chloride anions $[CoLCl_2]$. Its high performance is probably due to the easier substitution of chloride ligands with hydrides and generation of the active form of the cobalt catalyst. This would be a result of a subtle interplay between the basicity of the ligand as well as thus-derived propensity towards formation of 'open' species. Indeed, the most basic ligand $\mathbf{L_3}$ forms predominantly 'closed' species, therefore its activity is worse than one would expect.

The mechanism proposed involves the activation of cobalt(II) complex with alkali metal borohydride to give cobalt-hydride intermediates. Depending on the type of cobalt(II) complex activation, hydrosilylation is possible according to the classical Chalk-Harrod mechanism [11] (where active species - Co(0) complexes are generated by elimination of molecular hydrogen) or σ-bond metathesis (SBM), in which there is no change in the cobalt oxidation state. SBM relies on the insertion of alkene into cobalt-hydrogen bond followed by the proper metathesis of σ bonds with hydrosilane leading to regeneration of the initial complex cobalt-hydride complex. To further verify the catalytic efficiency of the developed system, catalyst loading experiments were carried out using the model reaction of styrene and $PhSiH_3$. To our delight, lowering the precatalyst **1** loading to 0.25 mol% and $LiHBEt_3$ to 0.75 mol% did not significantly affect their catalytic activity and the reaction took place effectively within 20 h (98 % silane conversion) with increasing selectivity of the hydrosilylation process (98 % of β-hydrosilylation product) (Table 3, entry 13). The increase in hydrosilylation selectivity as catalyst loading (both Co precursor and borohydride) decreases may be due to the lower content of lithium triethylborohydride in the reaction mixture, which promotes competitive redistribution of phenylsilane. Such a low loading of the cobalt precatalyst in the olefin hydrosilylation reaction has been very rare reported in literature [23,32,48], with one of the lowest (50 ppm) reported so far belonging to silyl-donor-functionalized NHC Co(II) complexes [15].

Table 3
Catalytic activity of cobalt(II) complexes with tridentate Schiff base ligands activated by alkali metal trialkylborohydrides in hydrosilylation of styrene with phenylsilane.

Entry	Catalyst	T[°C]	$MHBEt_3$	Phenylsilane Conversion[d]	Hydrosilylation Selectivity α:β:higher-order products	Selectivity H/R
1	**5**	80	$NaHBEt_3$	100	0:0:100	61:39
2		80	$LiHBEt_3$	47	57:43:0	54:46
3		RT	$LiHBEt_3$	34	62:38:0	73:27
4	**4**	80	$NaHBEt_3$	100	0:0:100	74:26
5		80	$LiHBEt_3$	46	100:0:0	65:35
6		RT	$LiHBEt_3$	26	100:0:0	37:63
7	**2**	80	$NaHBEt_3$	53	81:19:0	80:20
8		80	$LiHBEt_3$	15	86:14:0	92:8
9	**1**	80	$NaHBEt_3$	100	32:50:18	96:4
10		80	$LiHBEt_3$	100	6:78:16	93:7
11		RT	$LiHBEt_3$	100	4:77:18	100:0
12		RT	$LiHBEt_3$	100	16:59:25	100:0[b]
13		**RT**	**$LiHBEt_3$**	**98**	**2:98:0**	**100:0[c]**
14	**3**	80	$NaHBEt_3$	29	0:0:100	40:60
15		80	$LiHBEt_3$	48	83:17:0	30:70

Reaction conditions: [Co]:[$MHBEt_3$]:[styrene]:[$PhSiH_3$] = 0.03:0.12:1:1, THF (0.5 M), 20 h; [a] Reaction performed with 1 mol% **1** and 4 mol% $LiHBEt_3$; [b] Reaction performed without THF, [c] Reaction conditions: [**1**]:[$LiHBEt_3$]:[styrene]:[$PhSiH_3$] = 0.25:0.75:100:100, THF (0.5 M), 20 h, [d]calculated by GC with decane as internal standard.

With the slightly modified conditions in hand, we subsequently examined the scope of hydrosilylation with other olefins and various silanes since it is known that hydrosilanes of diverse reactivity and degree of substitution are remarkably different in the activation of precatalysts for Co-catalyzed hydrosilylation.[7] The presence of functional groups at the phenyl ring, either electron-donating or electron-withdrawing, did not significantly affect the reactivity of styrene derivatives in the reaction with phenylsilane and diphenylsilane (Table 4, entries 1–8). All the reactions with phenylsilane occurred with high selectivity towards β-hydrosilylation products (86–98 %). Moreover, we have found that hydrosilylation of substituted styrenes with Ph_2SiH_2 proceeded smoothly to give β-addition products in almost quantitative yields. Similarly as for styrene derivatives, hydrosilylation of 2-vinylnaphthalene (Table 4, entries 9–10) led to the *β*-addition products as predominant under given conditions, in good yield. Unfortunately, the reaction of styrene with diethylsilane proceeded with low silane conversion (21 %). Tertiary silanes ($PhMe_2SiH$, Et_3SiH or $Me_3SiOSiMe_2H$) did not hydrosilylate styrene or other olefin under the applied conditions.

Similarly, hex-1-ene and 3,3-dimethylbut-1-ene seem to be inactive in the reaction with primary and secondary silanes in the presence of **1**/$LiHBEt_3$ catalytic system. Unfortunately, increasing the reaction temperature to 80 °C and the precatalyst loading up to 3 mol% did not improve the reaction of tertiary silanes with styrene as well as the reaction of aliphatic olefins with phenylsilane, which implies that insufficient activity for this group of compounds is the inherent nature of the catalyst. It is also worth noting that although dehydrogenative silylation in similar N3-Co(II)Cl_2 systems can be observed [36,49] it was not the case here in any studied system.

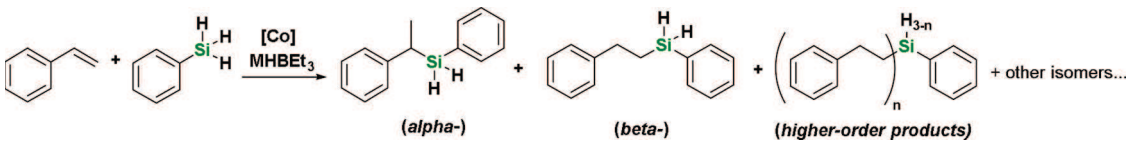
Table 4
Catalytic activity of **1**/$LiHBEt_3$ system in hydrosilylation of olefins.

Entry	olefin	Silane	Silane Conversion[c]	Hydrosilylation Selectivity β α:	Selectivity H/R
1		$PhSiH_3$	98	86:14	100:0
2		Ph_2SiH_2	98	100:0	100:0
3		$PhSiH_3$	71	98:2	100:0
4		Ph_2SiH_2	99	100:0	100:0
5		$PhSiH_3$	86	86:14	100:0
6		Ph_2SiH_2	100	100:0	100:0
7		$PhSiH_3$	84	88:12	100:0
8		Ph_2SiH_2	98	100:0	100:0
9		$PhSiH_3$	98	86:14	100:0
10		Ph_2SiH_2	100	100:0	100:0
11		Ph_2SiH_2	100 (96)[a]	100:0	100:0
12		$PhSiH_3$	100 (98)[b]	97:3	100:0
13		Et_2SiH_2	21	80:20	100:0
14		$PhMe_2SiH$	0	–	–
15		Et_3SiH	0	–	–
16		$PhSiH_3$	0	–	–
17		Ph_2SiH_2	0	–	–
18		$PhSiH_3$	0	–	–
19		Ph_2SiH_2	0	–	–

Reaction conditions: [**1**]:[$LiHBEt_3$]:[olefin]:[$PhSiH_3$] = 0.25:0.75:100:100, THF (0.5 M), 20 h, RT; [a] isolated yield of (2-phenylethyl)diphenylsilane; [b] isolated yield of (2-phenylethyl)phenylsilane; [c]Calculated by GC with decane as internal standard.

4. Conclusions

A series of structurally similar Schiff base ligands allows formation of bench-stable cobalt(II) precatalysts, whose structure and catalytic activity depend on the benzimidazole/ pyridine/ imidazole frameworks. The pentacoordinated cobalt(II) chloride complex with benzimidazole/2H-imidazole-based ligand, when activated by lithium triethylborohydride, has been found to act as a good catalyst for hydrosilylation of vinylarenes by primary and secondary silanes. Mild reaction conditions, low catalyst loading and high selectivity towards β-hydrosilylation products are attractive features of the developed catalytic system. It is worth noting that no competitive silane redistribution or olefin dehydrogenative silylation has been observed under applied conditions. Our work shows that seemingly similar coordination motifs



Scheme 1. Hydrosilylation of styrene in the presence of [Co(II)]/$MHBEt_3$ catalytic system.

do not necessarily lead to the isostructural group of catalytically open cobalt(II) coordination compounds, which is an important factor to consider in the design of new catalysts in general.

CRediT authorship contribution statement

Aleksandra Bocian: Conceptualization, Methodology, Formal analysis, Investigation, Writing - review & editing. **Maciej Skrodzki:** Conceptualization, Methodology, Formal analysis, Investigation, Writing - review & editing. **Maciej Kubicki:** Formal analysis, Writing - review & editing. **Adam Gorczyński:** Conceptualization, Formal analysis, Investigation, Visualization, Writing - original draft, Writing - review & editing. **Piotr Pawluć:** Supervision, Project administration, Writing - review & editing. **Violetta Patroniak:** Supervision, Writing - review & editing.

Declaration of Competing Interest

There are no conflicts to declare.

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ELECTRONIC SUPPLEMENTARY INFORMATION for

The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins

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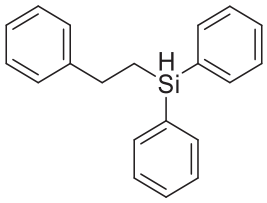
Table of contents:

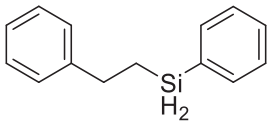
1. Analytical data of isolated products

1.1. Phenethyldiphenylsilane **1**; colourless oli, yield: 277 mg (96%)



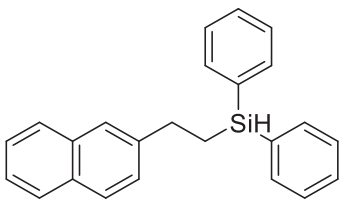
^{1}H NMR (300MHz, $CDCl_3$): δ7.63-7.51 (m, 4H), 7.40-7.30 (m, 6H), 7.25-7.20 (m, 2H), 7.19-7.08 (m, 3H), 4.96-4.78 (t, 1H), 2.85-2.58 (m, 2H), 1.53-1.43 (m, 2H)
^{13}C NMR (75 MHz, $CDCl_3$): δ144.39, 135.18, 134.09, 129.68, 128.37, 128.07, 127.86, 125.74, 30.44, 14.28
Conforms to the literature analytical data.[1]

1.2. Phenethyl(phenyl)silane **2**; colourless oli, yield: 208 mg (98%)



^{1}H NMR (300MHz, $CDCl_3$): δ7.61-7.55 (m, 2H), 7.42-7.36 (m, 3H), 7.33-7.28 (m, 2H), 7.23-7.19 (m, 3H), 4.41-4.25 (t, 2H), 2.84-2.73 (m, 2H), 1.37-1.28 (m, 2H)
^{13}C NMR (75 MHz, $CDCl_3$): δ144.01, 135.28, 132.16, 129.68, 128.40, 128.07, 127.92, 125.84, 31.12, 12.14
Conforms to the literature analytical data.[2]

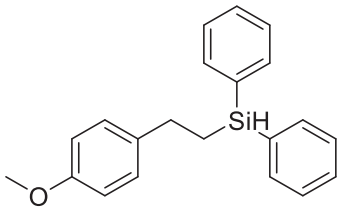
1.3 (2-(naphthalen-2-yl)ethyl)diphenylsilane; crude product – *not isolated*



^{1}H NMR (300MHz, $CDCl_3$): δ7.86-7.74 (m, 3H), 7.66-7.60 (m, 4H), 7.49-7.33 (m, 10H), 4.97-4.93 (t, 1H), 3.05-2.87 (m, 2H), 1.75-1.57 (m, 2H)

Conforms to the literature analytical data.[3]

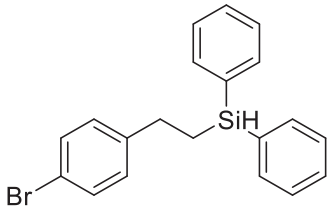
1.4 (4-methoxyphenethyl)diphenylsilane; crude product – *not isolated*



^{1}H NMR (300MHz, $CDCl_3$): δ7.63-7.57 (m, 4H), 7.43-7.36 (m, 6H), 7.15-7.09 (m, 2H), 6.86-6.80 (m, 2H), 4.95-4.87 (t, 1H), 3.82-3.77 (s, 3H), 2.80-2.69 (m, 2H), 1.55-1.47 (m, 2H)

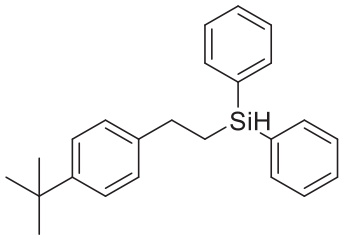
Conforms to the literature analytical data.[3]

1.5 (4-bromophenethyl)diphenylsilane; crude product – *not isolated*



^{1}H NMR (300MHz, $CDCl_3$): δ7.61-7.55 (m, 4H), 7.46-7.35 (m, 8H), 7.09-7.02 (m, 2H), 4.94-4.87 (s, 1H), 2.79-2.68 (m, 2H), 1.54-1.44 (m, 2H)

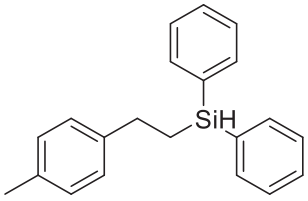
1.6 (4-(tert-butyl)phenethyl)diphenylsilane; crude product – *not isolated*



^{1}H NMR (300MHz, $CDCl_3$): δ7.66-7.55 (m, 4H), 7.43-7.36 (m, 6H), 7.34-7.29 (d, 2H), 7.18-7.11 (d, 2H), 4.95-4.91 (t, 1H), 2.84-2.70 (m, 2H), 1.58-1.48 (m, 2H), 1.36-1.31 (s, 9H)

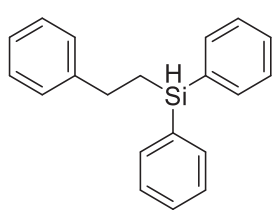
Conforms to the literature analytical data.[4]

1.7 (4-methylphenethyl)diphenylsilane; crude product – *not isolated*



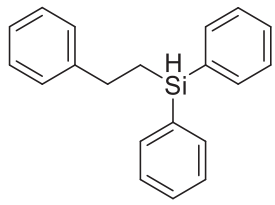
^{1}H NMR (300MHz, $CDCl_3$): δ7.64-7.56 (m, 4H), 7.44-7.36 (m, 6H), 7.12-7.08 (s, 4H), 4.94-4.88 (t, 1H), 2.82-2.70 (m, 2H), 2.35-2.33 (s, 3H), 1.55-1.46 (m, 2H)

Conforms to the literature analytical data.[4]

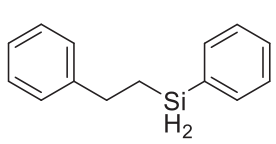

H
Si

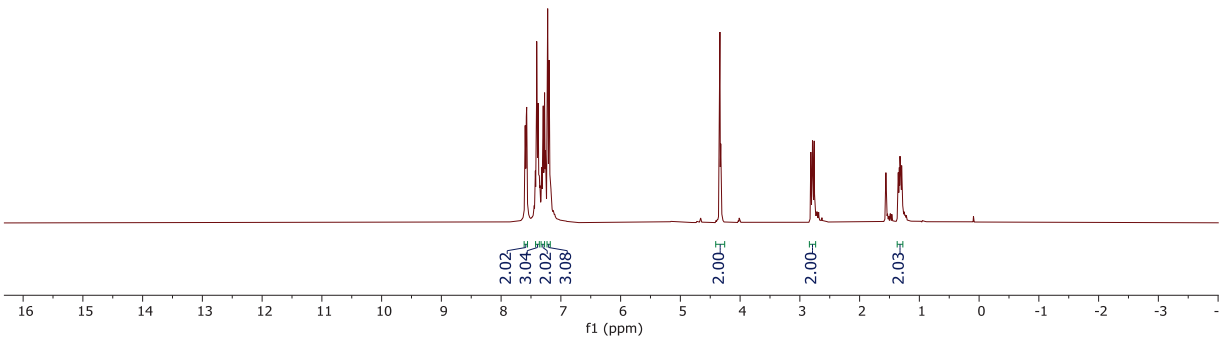
4.03
6.08
2.04
2.79
1.00
1.93
2.18
f1 (ppm)

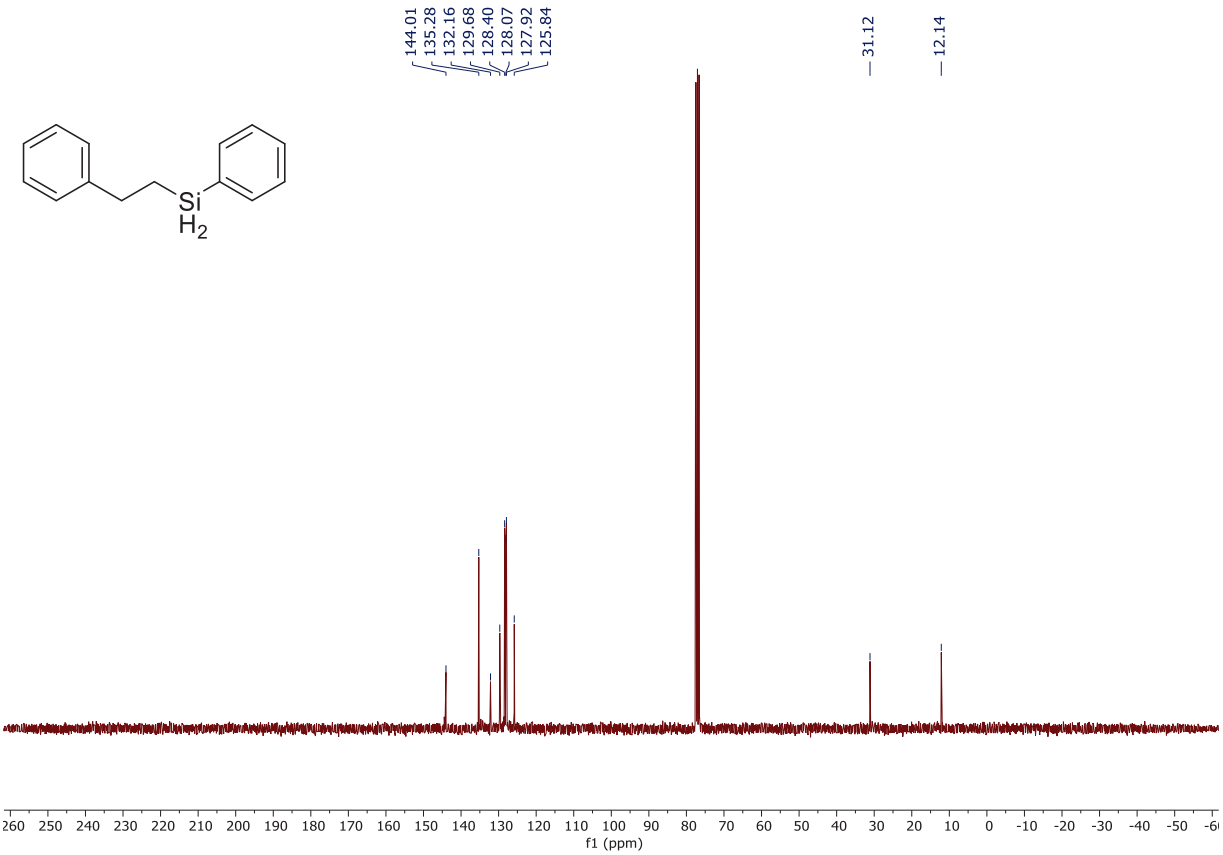

144.39
135.18
134.09
129.68
128.37
128.07
127.86
125.74
30.44
14.28

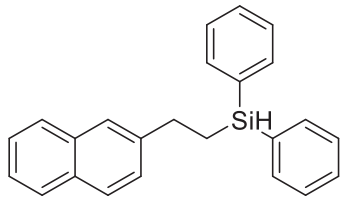

H
Si

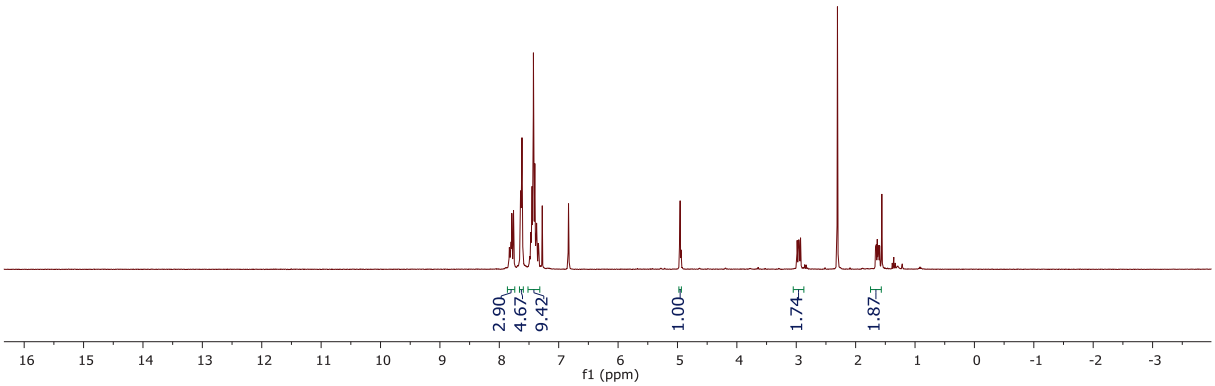
f1 (ppm)

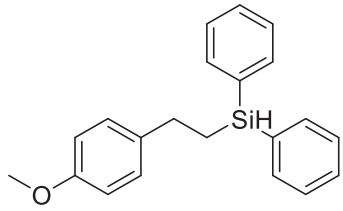

Si
H2

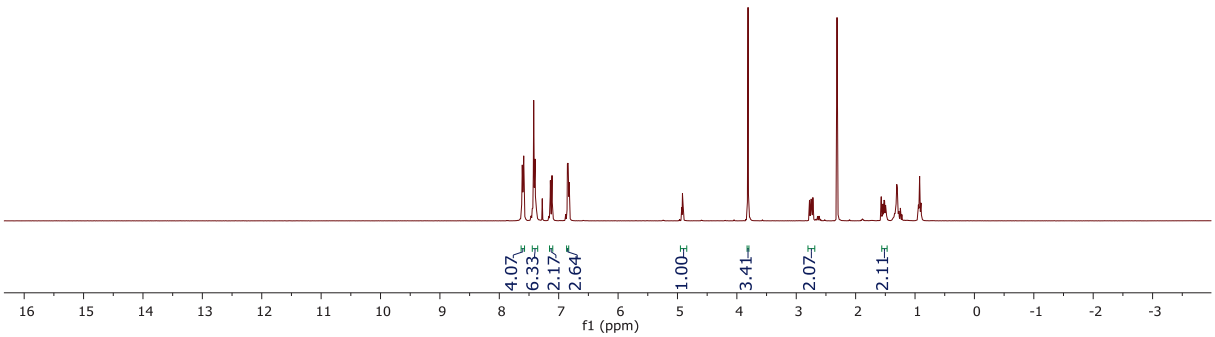

2.02
3.04
2.02
3.08
2.00
2.00
2.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


144.01
135.28
132.16
129.68
128.40
128.07
127.92
125.84
31.12
12.14
Si
H2
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)


SiH


2.90
4.67
9.42
1.00
1.74
1.87
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


SiH
O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6.33
2.17
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1.00
3.41
2.07
2.11
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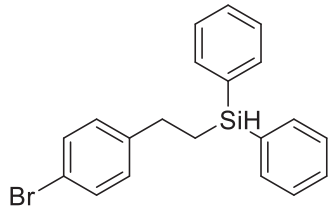
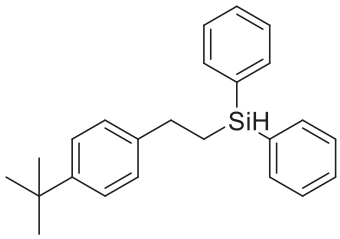
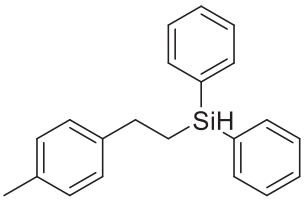
f1 (ppm)

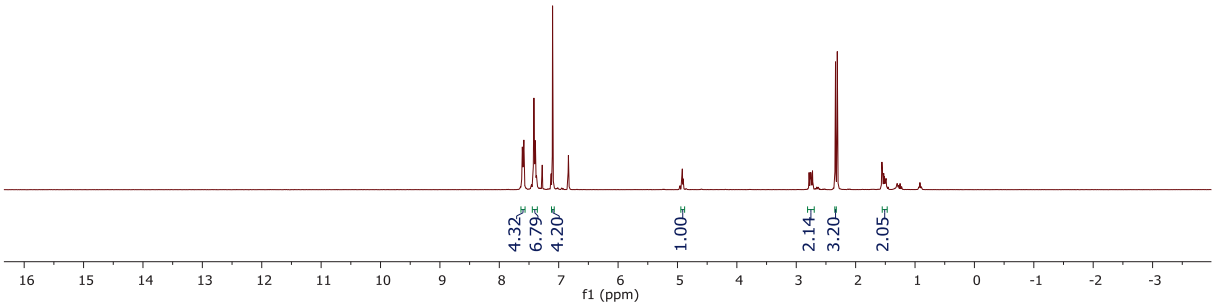

SiH
Br

4.24
8.77
2.29
1.00
2.13
2.19
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


SiH

4.07
6.03
2.11
2.10
1.00
1.90
2.57
9.37
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


SiH


4.32
6.79
4.20
1.00
2.14
3.20
2.05
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

2. **Table S1. Hydrogen bond data** (Å, º)

D	H	A	D-H	H···A	D···A	D-H···A
1						
N1	H1	Cl2^{i}	0.86	2.41	3.177(7)	149
N15	H15	O1A	0.86	1.94	2.771(15)	163
O1A	H1A	Cl1^{ii}	0.82	2.81	3.253(16)	116
1a						
N1	H1	Cl1^{iii}	0.88	2.37	3.145(2)	147
2						
N1	H1	Cl1^{iv}	0.88	2.29	3.108(4)	154
N17	H17	Cl^{v}	0.88	2.52	3.210(4)	136
3						
N1A	H1A	Cl2^{vi}	0.88	2.32	3.182(9)	167
N17A	H17A	Cl1	0.88	2.32	3.199(11)	177
N1B	H1B	O1S	0.88	1.87	2.748(14)	171
N17B	H17B	Cl2A	0.88	2.39	3.145(8)	144
N1C	H1C	O1	0.88	1.84	2.709(14)	172
N1D	H1D	Cl3^{vii}	0.88	2.29	3.142(9)	164
N17D	H17D	Cl1^{viii}	0.88	2.28	3.159(11)	175
O1	H1	Cl3	0.84	2.24	3.027(13)	156
O1S	H1S	Cl2	0.84	2.29	3.087(13)	159
4						
N1A	H1A	Cl4C^{ix}	0.88	2.34	3.197(12)	166
5						
N14	H14	Cl2^{x}	0.88	2.38	3.117(3)	141
O1A	H1A	Cl1^{ix}	0.84	2.36	3.094(2)	147

Symmetry codes: ^{i} 2-x,1-y,1-z; ^{ii} x,1+y,z; ^{iii} –x,1-y,1-z; ^{iv}2-x,1-y,1-z; ^{v} 1-x,2-y,1-z; ^{vi} 2/3-y,1/3+x-y,1/3+z; ^{vii} 1/3-y,-1/3+x-y,-1/3+z; ^{viii} -1/3+x,1/3+y,1/3+z; ^{ix} x,-1+y,z;

Table S2. Crystal data, data collection and structure refinement.

Compound	**1**	**1a**	**2**	**2a**	**3**	**4**
Formula	$C_{12}H_{12}Cl_2CoN_6 \cdot 1/2(CH_3OH)$	$C_{12}H_{12}Cl_2CoN_6$ (+ solvent)	$C_{12}H_{12}Cl_2CoN_6$	$6(C_{24}H_{24}CoN_{12})^{2+} \cdot Cl_4Co^{2-} \cdot 10Cl^- \cdot 6CH_3OH)$ 10 +solvent	$C_{26}H_{28}CoN_{12}^{2+} \cdot Cl_4Co^{2-} \cdot$ + solvent	$C_{11}H_{15}Cl_2CoN_5O$
Formula weight	383.13	370.11	370.11	3984.36	768.26	363.11
Crystal system	triclinic	triclinic	monoclinic	trigonal	triclinic	monoclinic
Space group	P-1	P-1	$P2_1/c$	R3	P-1	$P2_1/c$
a(Å)	7.3390(8)	7.1631(9)	8.2811(3)	33.4583(12)	9.1843(16)	8.4966(8)
b(Å)	9.2816(10)	9.1376(8)	10.4308(4)	33.4583(12)	12.6894(9)	6.9222(6)
c(Å)	12.7849(7)	12.6825(14)	16.4512(9)	16.2030(8)	17.4156(15)	23.938(2)
α(°)	80.998(7)	81.820(8)	90	90	69.898(7)	90
β(°)	79.208(7)	79.328(10)	93.178(4)	90	86.868(10)	93.728(9)
γ(°)	74.600(9)	74.562(9)	90	120	87.032(9)	90
V(Å^3)	819.50(14)	782.53(15)	1418.84(11)	15708.5(14)	1902.0(4)	1405.0(2)
Z	2	2	4	3	2	4
D_x(g cm^{-3})	1.565	1.571	1.733	1.264	1.341	1.717
F(000)	392	374	748	6141	780	740
μ(mm^{-1})	11.276	1.439	12.970	6.398	1.187	1.604
Reflections:						
collected	5308	5178	5284	12444	13147	5175
unique (R_{int})	2936 (0.056)	3110 (0.023)	2547 (0.050)	8144 (0.024)	6663 (0.084)	2830 (0.030)
with I>2σ(I)	2334	2621	2190	7391	2999	2375
R(F) [I>2σ(I)]	0.098	0.034	0.068	0.107	0.133	0.046
wR(F^2) [I>2σ(I)]	0.275	0.071	0.161	0.257	0.248	0.116
R(F) [all data]	0.114	0.044	0.075	0.113	0.239	0.056
wR(F^2) [all data]	0.289	0.076	0.166	0.261	0.278	0.125
Goodness of fit	1.09	1.03	1.04	1.14	1.17	1.08
max/min Δρ (e·Å^{-3})	1.24/-0.72	0.38/-0.34	1.23/-0.59	1.94/-1.52	2.69/-1.59	0.94/-0.61

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Appendix **A2**

Skrodzki M., Patroniak V., Pawluć P.; *Schiff Base Cobalt(II) Complex-catalysed Highly Markovnikov-Selective Hydrosilylation of Alkynes*. *Org. Lett*. **2021**, 23, 663-667.

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Letter

Schiff Base Cobalt(II) Complex-Catalyzed Highly Markovnikov-Selective Hydrosilylation of Alkynes

Maciej Skrodzki, Violetta Patroniak, and Piotr Pawluć*

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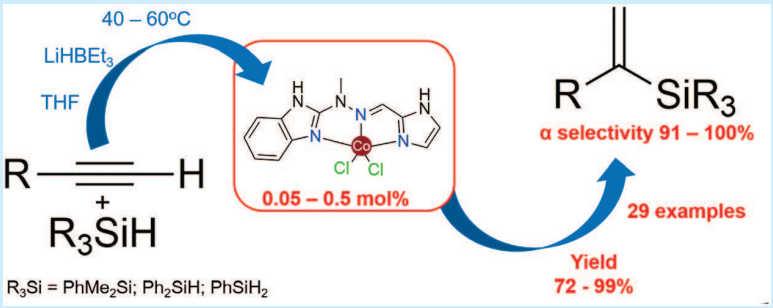

ABSTRACT: A bench-stable cobalt(II) complex, with 3N-donor socket-type benzimidazole-imine-2*H*-imidazole ligand is reported as a precatalyst for regioselective hydrosilylation of terminal alkynes. Both aromatic and aliphatic alkynes could be effectively hydrosilylated with primary, secondary, and tertiary silane to give α-vinylsilanes in high yields with excellent Markovnikov selectivity and extensive functional-group tolerance. Catalyst loading varies within 0.5−0.05 mol %, which is one of the most efficient reported so far in the literature on cobalt-catalyzed alkyne hydrosilylation.

Organosilicon compounds are particularly interesting and powerful tools in organic chemistry. Vinylsilanes, which belong to this group, are applied in the syntheses of natural products,[1] cross coupling reactions,[2] and stereocontrolled reactions,[3] especially in hydrogenation processes.[4] Among all the synthetic pathways for obtaining vinylsilanes, the noble metal-catalyzed hydrosilylation of alkynes and 1,3-dienes has been generally accepted as the most effective route.[5−10] One of the main problems in hydrosilylation of internal and terminal alkynes is the control of regio- and stereoselectivity. Development of newer and more sophisticated catalysts, in terms of structure, that would help to solve this problem has been the challenge for a number of research groups.[11]

From the environmental and economic point of view, compounds based on earth abundant metals are more desirable as catalysts than those based on noble metals. On the other hand, in the era of molecular-heavy and complex ligands, it is essential to develop a rational and sustainable coordination environment. New, simple ligands must be designed to compete with multistep synthesized ones in terms of activity, chemo- regio-, and stereoselectivity. Complexes of first row transition metals, such as Fe or Co, have been proven to be efficient and selective in the reaction of hydrosilylation of alkynes,[12−23] providing β-(*E*/*Z*)-vinylsilanes or α-vinylsilanes. Although these catalysts show high catalytic activity, obtaining α-vinylsilanes as a result of hydrosilylation of alkynes is still challenging and rarely reported, and is usually achieved with cobalt(II) precatalysts.[24−30]

For this purpose, as illustrated in Scheme 1, Huang's and Lu's research groups have developed efficient systems based on pyridine-bis(oxazoline) (PyBox)[24] or iminopyridine-oxazoline (IPO)[25] 3N tridentate pincer ligands, whereas Yang's[26] and Jin's[27] groups have proposed structurally simpler (amine)-pyridine-imine ligands. Regiocontrol in Markovnikov hydrosilylation of terminal alkynes can be also achieved using $Co(OAc)_2{\cdot}4H_2O$/2,2′-bipyridine catalytic system.[28] To the best of our knowledge, all these catalytic systems are active in reactions of terminal alkynes involving primary and secondary silanes.

Recently we have synthesized a series of new cobalt(II) chloride precatalysts coordinated to structurally similar hydrazone Schiff base ligands, easily obtained in a two-step synthetic protocol.[31] These complexes are air- and moisture-stable, and are operationally simple and easy to handle on the laboratory bench. The synthesized cobalt(II) complexes have been evaluated for their ability to act as olefin hydrosilylation

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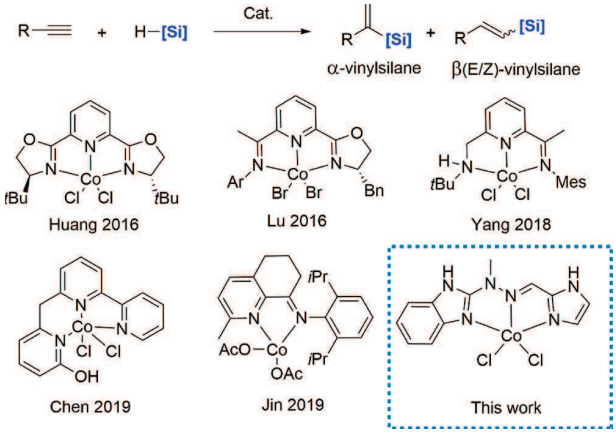
Scheme 1. Cobalt(II) Based Precatalysts for α-Selective Alkyne Hydrosilylation



catalysts in the presence of alkali metal trialkylborohydrides. The cobalt(II) chloride complex containing benzimidazole-imine-2*H*-imidazole ligand (complex **1**, Scheme 1) has been selected as the most efficient in terms of hydrosilylation activity and selectivity toward β-addition. Successful use of complex **1** as a catalyst for hydrosilylation of olefins prompted us to investigate its catalytic activity in the reaction with alkynes. Herein we describe highly selective hydrosilylation of internal and terminal alkynes with primary, secondary, and tertiary silanes in the presence of Schiff base cobalt(II) complex.

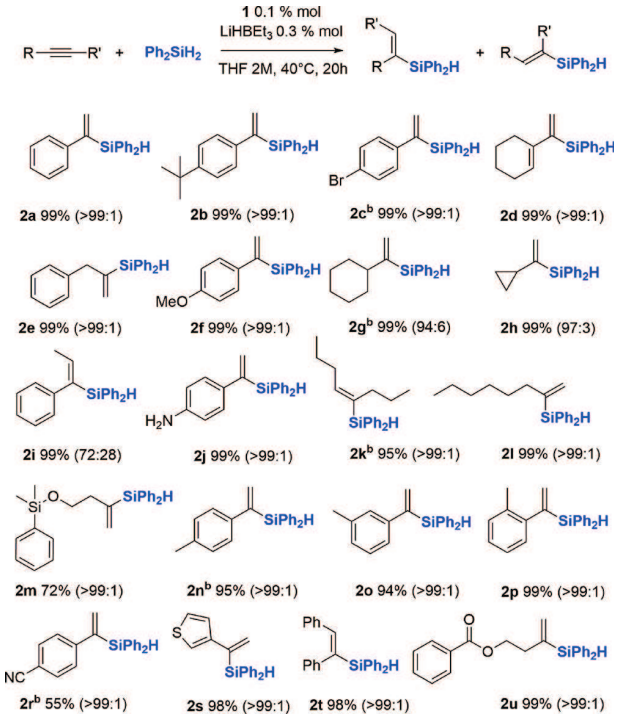
For the optimization reaction (Table 1), phenylacetylene and diphenylsilane were chosen as model substrates. To minimize the amount of wastes, the reaction setup was based on an equimolar ratio of alkyne to silane. The initial reaction was carried out in the presence of 3 mol % of precatalyst **1** with 9 mol % of sodium triethylborohydride in toluene as an activator. The concentration of silane was set to 2 M in THF at the temperature of boiling solvent (Table 1, entry 1). High conversion of diphenylsilane and regioselectivity toward α-addition were observed. To satisfy our aims we also investigated the reaction with $LiHBEt_3$ in THF as an activator. Fortunately, the use of the alternative reducing agent led to increased selectivity toward Markovnikov product, while maintaining high conversion of diphenylsilane (Table 1, entry 2). Experiments with toluene and dioxane as solvents (Table 1, entry 3–4) were successful, but resulted in yielding a mixture of 95% of α-vinylsilane and 5% of β-vinylsilane. Encouraged by these results we tried to lower the concentrations of cobalt precatalyst and borohydride activator. In our investigation, the catalyst loading was lowered from 3 mol % to 0.1 mol %, preserving its activity and selectivity (Table 1, entry 7). Reaction of phenylacetylene with diphenylsilane was completed in 1h at 40 °C. Further decreases in the catalyst loading (0.05 mol % of **1** and 0.15 mol % $LiHBEt_3$) resulted in a slightly lower diphenylsilane conversion (85%), even at elevated temperatures. Having optimized the conditions for hydrosilylation of phenylacetylene with diphenylsilane, the reaction scope was explored by using a variety of terminal and internal alkynes. In addition, the influence of functional groups, i.e., electron-donating and electron-withdrawing substituents to phenyl ring, was investigated. In most experiments, the yields of the reaction products were quantitative, and selectivities toward α-addition products exceeded 99% (Scheme 2).

Table 1. Optimization Protocol for Hydrosilylation of Phenylacetylene with Diphenylsilane[a]

entry	solvent	temp. [°C]	cat. **1** loading [mol %]	Ph_2SiH_2 conversion[b] [%]	selectivity[b] (α:β)
1[d]	THF	70	3	>99	95:5
2	THF	70	3	>99	99:1
3	toluene	70	1	>99	95:5
4	dioxane	70	1	>99	95:5
5	THF	40	1	>99	99:1
6[e]	THF	40	1	52	87:13
7	THF	40	0.5	>99	98:2
8[c]	THF	40	0.1	>99	99:1
9[c]	THF	RT	0.1	85	95:5
10	THF	60	0.05	85	99:1

[a]Conditions: Ph_2SiH_2 (0.5 mmol), phenylacetylene (0.5 mmol), precatalyst (0.05–3 mol %), $LiHBEt_3$ (0.15–9 mol %), 20h, solvent 0.25 mL, unless stated otherwise. [b]Calculated by GC with decane as internal standard. [c]1 h. [d]Reaction with $NaHBEt_3$ (9 mol %). [e]Reaction with *t*-BuONa (2 mol %).

Scheme 2. Range of Alkynes in Hydrosilylation with Diphenylsilane[a]



[a]Conditions: alkyne (1 mmol), diphenylsilane (1 mmol), complex **1** (0.1 mol %), $LiHBEt_3$ (0.3 mol %). Ratio of α to β-addition products determined using GC. Isolation yields. [b]Reaction performed at 60 °C with 0.5% mol **1** and 1.5% mol $LiHBEt_3$.

The reactions with alkynes effectively occurred in the presence 0.1 mol % catalyst **1** and 0.3 mol % $LiHBEt_3$ concentration at 40 °C but required a relatively long time (20 h). Phenylacetylene reacted with diphenylsilane to give the corresponding α-vinylsilane with 99% isolated yield (**2a**). To check the impact of different substituents, the reactions

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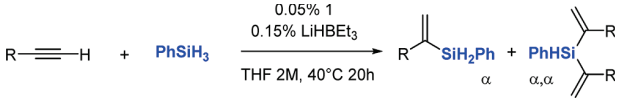
involving para-substituted phenylacetylene were performed. 4-*tert*-Butylphenylacetylene, 4-ethynylanisole, and 4-ethynylaniline reacted with 99:1 selectivity (α/β-vinylsilane), with a 99% isolated yield (**2b**, **2f**, **2j**).

Halide substituents such as 4-bromophenylacetylene underwent the reaction with excellent yield, employing increased catalyst loading (**2c**). Cycloaliphatic alkynes, ethynylcyclohexane, cyclohexenyleacetylene, and cyclopropylacetylene, were also smoothly hydrosilylated according to our protocol (**2d**, **2g**, **2h**). However, despite excellent conversions of cycloaliphatic alkynes, trace amounts of β-addition products were observed (3−6%). Aliphatic alkynes, 3-phenylprop-1-yne and oct-1-yne, were transformed easily to the corresponding α-vinylsilanes, and no β-addition products were observed (**2e**, **2l**). Symmetrical internal alkynes, 4-octyne and diphenylacetylene, underwent hydrosilylation with total conversion of diphenylsilane (**2k**, **2t**), giving selectively the corresponding (*E*)-silylalkenes. Interestingly, the reaction with 1-phenylprop-1-yne resulted in a mixture of α and β-addition products (in favor of α), presumably due to a low steric hindrance of a methyl group (**2i**). Heteroaromatic thiophene moiety was tolerated, and the reaction proceeded smoothly to yield single α-vinylsilane isomer (**2s**). It is worth noting that the reactive groups such as nitrile and ester were compatible with the hydrosilylation conditions (**2r**, **2u**). We also examined the impact of a methyl group substituted to phenyl ring. In contrast to 4-ethynyltoluene, which required elevated temperature and increased catalyst loading (**2n**), 2-ethynyltoluene and 3-ethynyltoluene were transformed easily (**2o**, **2p**) to the corresponding α-vinylsilanes. Masked alcohol, (but-3-yn-1-yloxy)dimethyl(phenyl)silane, appeared to be less reactive and gave the corresponding product with 72% yield (**2m**).

To highlight the utility of this procedure for the synthesis of α-vinylsilane, we conducted the synthesis on a gram-scale under the optimized conditions. The hydrosilylation of phenylacetylene (4 mmol) with Ph_2SiH_2 (4 mmol) in the presence of 0.1 mol % **1** and 0.3 mol % $LiHBEt_3$ afforded 1.12 g of diphenyl(1-phenylvinyl)silane (**2a**) in 98% isolated yield with 99:1 α/β selectivity.

Our next aim was to investigate the reactivity of primary silane in the reaction with terminal alkynes. The reaction of phenylacetylene with phenylsilane catalyzed by **1** activated with $LiHBEt_3$ under standard conditions (0.1 mol % of **1**, 0.3 mol % of $LiHBEt_3$, 40 °C, 20 h) results in a mixture of Markovnikov addition product, phenyl(1-phenylvinyl)silane, and a product of subsequent hydrosilylation of the latter, phenyldi(1-phenylvinyl)silane. During optimization of the reaction conditions (SI), we found that the lowering of catalyst **1** loading to 0.05 mol % resulted in the total conversion of substrates and did not substantially affect hydrosilylation selectivity. Further lowering of the catalyst **1** loading to 0.005 mol % resulted in a decrease in phenylsilane conversion; however, the catalyst still remained very active (TOF as high as 8000 h^{-1}). In all cases only Markovnikov addition products were detected, and no trace amounts of β-addition products were observed. In the optimized conditions (0.05 mol % of **1**, 0.15 mol % of $LiHBEt_3$, 40 °C, 20 h), the substrate scope of the Markovnikov-selective hydrosilylation was investigated with a range of electronically different terminal alkynes (Table 2). Aromatic and aliphatic alkynes underwent successful hydrosilylation with phenylsilane in excellent yields and regioselectivity; however, small amounts of double addition products (α,α-divinylsilanes) were observed. Phenylacetylene derivatives with electron-donating groups such as methoxy, amine, and methyl reacted smoothly (99% yields), whereas the presence of electron-withdrawing 4-bromo-substituent decreased the reaction yield (38%). Cyclopropylacetylene and 3-phenyl-prop-1-yne also underwent successful hydrosilylation in good yields. In all cases, exclusive formation of α-addition products was observed and no β-vinylsilanes were detected.

Table 2. Scope of Alkynes in Hydrosilylation with Phenylsilane[a]



entry	R	yield [%] (isolated)	selectivity $\alpha:\beta$	selectivity $\alpha:\alpha,\alpha$
1	Ph (**3a**)	99 (98)	>99:1	79:21
2	4-*t*-BuC_6H_4	99	>99:1	100:0
3	4-BrC_6H_4	38	>99:1	97:3
4	4-MeOC_6H_4	99	>99:1	>99:1
5	4-$NH_2C_6H_4$	99	>99:1	>99:1
6	4-MeC_6H_4	99	>99:1	97:3
7	3-MeC_6H_4 (**3g**)	99 (94)	>99:1	91:9
8	2-MeC_6H_4 (**3h**)	99 (99)	>99:1	91:9
9	Cyclopropyl	99	>99:1	91:9
10	$PhCH_2$	93	>99:1	97:3

[a]Conditions: alkyne (1 mmol), phenylsilane (1 mmol), **1** (0.05 mol %), $LiHBEt_3$ (0.15 mol %), 40 °C, 20 h. Product ratio and reaction yield determined by GC.

Complex **1** was found to successfully catalyze hydrosilylation of alkynes with tertiary silane−dimethylphenylsilane. To the best of our knowledge, Markovnikov hydrosilylation of terminal alkynes with tertiary silanes is very scarce using cobalt catalysis. A single example of regioselective hydrosilylation of phenylacetylene with $PhMe_2SiH$ (84% yield, $\alpha:\beta$ = 88:12) has been reported recently.[25] In our experiments, dimethylphenylsilane underwent quantitative reactions with terminal alkynes; however, the reaction required higher concentration of the catalyst (0.5 mol %) and elevated temperature (60 °C) in comparison with the protocol developed for primary and secondary silanes. Applying the optimized conditions, we examined the impact of alkyne structure on silane conversion and hydrosilylation selectivity (Scheme 3). Phenylacetylene was hydrosilylated easily by dimethylphenylsilane with 91% selectivity toward α-addition product (**4a**). The presence of alkyl substituents at the phenyl ring led to increased selectivity toward α-addition, irrespective of their position (**4b**, **4f−h**). Bromo, amino and methoxy groups were tolerated, however, hydrosilylation of 4-bromophenylacetylene and 4-aminophenylacetylene (**4c** and **4e**) proceeded with lower yields (75−79%) than the other compounds. Cyclopropylacetylene underwent hydrosilylation with excellent yield and selectivity (**4i**), but 3-phenylprop-1-yne was not reactive in the reaction with dimethylphenylsilane.

Our protocol seems to be the first effective cobalt complex-catalyzed Markovnikov-selective hydrosilylation of aromatic and cycloaliphatic alkynes with $PhMe_2SiH$. Unfortunately, increasing the reaction temperature and the precatalyst loading did not afford positive results for the reaction of other tertiary silanes such as triphenylsilane, triethoxysilane, or triethylsilane with terminal alkynes, which implies that it is the inherent

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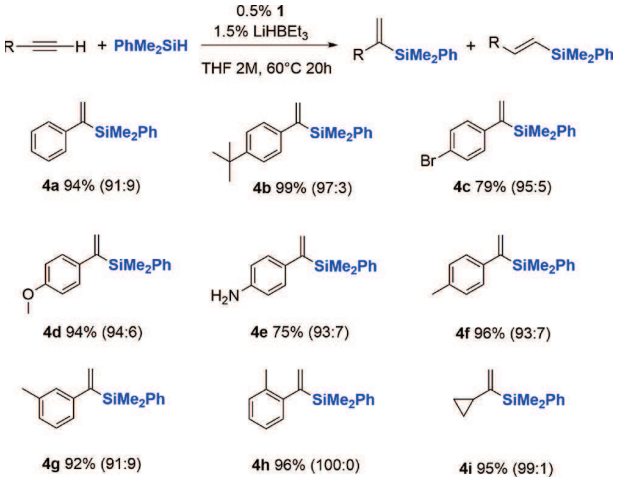
Scheme 3. Range of Alkynes in Hydrosilylation with Dimethylphenylsilane[a]

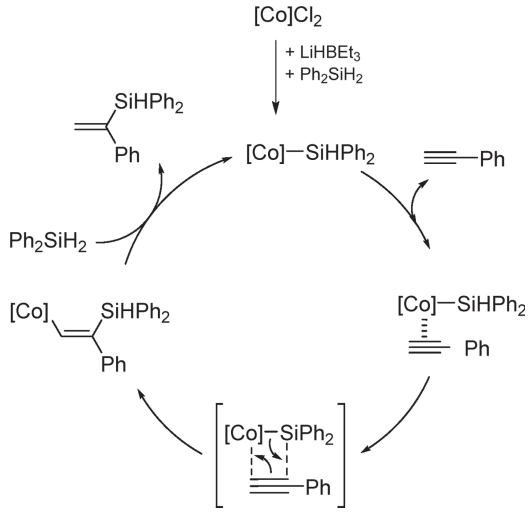


[a]Conditions: alkyne (1 mmol), dimethylphenylsilane (1 mmol), **1** (0.5 mol %), $LiHBEt_3$ (1.5 mol %), THF, 60 °C, 20 h. Isolated yields. Regioselectivity α:β-(E) determined by ^{1}H NMR.

nature of the catalyst to be insufficiently active for this group of compounds.

To understand the nature of silane addition to alkyne, NMR studies with deuterium labeled phenylacetylene were performed. Reaction of D_1-phenylacetylene and diphenylsilane afforded *syn*-addition product, and no *anti*-addition products were observed (SI). On the basis of deuterium labeling experiments and the previously reported data,[30] we propose the following simplified mechanism for cobalt-catalyzed α-selective alkyne hydrosilylation (Scheme 4). Cobalt(II) precatalyst reacts with borohydride and silane to form in situ cobalt(I)-silyl intermediate. Following this, migratory insertion of alkyne into Co−Si bond takes place to produce vinylcobalt species, which can undergo reaction with silane to afford α-vinylsilane and regenerate the catalytically active cobalt-silyl intermediate. Alternatively, Co(0) pathway of Markovnikov-selective hydrosilylation, recently proposed for 3N pincer−cobalt complex on the basis of DFT calculations, can be considered.[32]

Scheme 4. Proposed Mechanism for Cobalt-Catalyzed α-Selective Alkyne Hydrosilylation



In conclusion, a pentacoordinated cobalt(II) chloride complex with benzimidazole/2*H*-imidazole-based ligand, activated by lithium triethylborohydride, has been found to act as a good catalyst for regioselective hydrosilylation of alkynes by primary, secondary, and tertiary silanes. Mild reaction conditions, low catalyst loading, functional group tolerance (amine, halide, ester, nitrile, etc.), and extremely high selectivity toward α-hydrosilylation products are unique features of the developed methodology. We believe that the possibility of using tertiary silane makes it more universal than the previously reported catalytic systems based on cobalt complexes with 3N-donor ligands.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03721.

Experimental details, characterization data, and copies of ^{1}H NMR, ^{13}C NMR, and IR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

For

Schiff Base Cobalt(II) Complex-Catalyzed Highly Markovnikov-Selective Hydrosilylation of Alkynes

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EXPERIMENTAL PROCEDURES

1.1. General remarks:

All reactions were performed in flame-dried glassware under argon atmosphere. THF was purified by distillation over sodium and benzophenone, under argon atmosphere. Other solvents were dried by distillation over calcium hydride.

Gas chromatography was performed on a Bruker Scion 436-GC with a 30 m Agilent VF5-ms 0.53 mm Megabore column and a TCD detector. The temperature program was as follows: 60 °C (3 min), 20 °C/min, 280 °C (20 min). Decane was used as a reference. GC-MS analyses were performed on a Bruker Scion 436-GC with a 30 m Varian DB-5 0.25 mm capillary column and a Scion SQ-MS mass spectrometry detector. The temperature program was as follows: 60 °C (3 min), 10 °C/min, 250 °C (15 min). NMR analyses were performed on a Bruker Fourier 300 MHz or 400 MHz spectrometer.

FT-IR spectra were recorded on a Nicolet iS50 (Thermo Scientific) Fourier transform spectrophotometer equipped with a diamond ATR unit. In all cases, 16 scans at a resolution of 2 cm^{-1} were collected, to record the spectra in the range of 4000-400 $cm^{-1.}$

HRMS Spectra were recorded on a QTOF type mass spectrometer (Impact HD, Bruker) in positive ion mode.

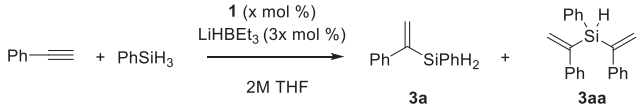
1.2. General procedure of alkyne hydrosilylation:

General procedure for hydrosilylation of alkynes **A**: To a flame-dried Schlenk bomb flask charged with argon, precatalyst (0.1 mol %), THF (0.5 mL), silane (1.0 mmol), and alkyne (1.0 mmol) were placed. Mixture was then heated to 40°C with stirring in oil bath. After 10 minutes $LiHBEt_3$ was added (0.3 mol %), and reaction vessel was then closed. After 20 hours, hexane was added to reaction mixture. Solution was then filtered through silica plug, and concentrated on rotavapor. The crude mixture was purified by evaporating volatiles on vacuum line followed by extraction with hexane. Regioselectivity was monitored by ^1H NMR.

General procedure for hydrosilylation of alkynes **B**: To a flame-dried Schlenk bomb flask charged with argon, precatalyst (0.5 mol %), THF (0.5 mL), silane (1.0 mmol), and alkyne (1.0 mmol) were placed. Mixture was then heated to 60°C with stirring in oil bath. After 10 minutes $LiHBEt_3$ was added (1.5 mol %), and reaction vessel was then closed. After 20 hours, hexane was added to reaction mixture. Solution was then filtered through silica plug, and concentrated on rotavapor. The crude mixture was purified by evaporating volatiles on vacuum line followed by extraction with hexane. Regioselectivity was monitored by ^1H NMR.

General procedure for hydrosilylation of alkynes **C**: To a flame-dried Schlenk bomb flask charged with argon, precatalyst (0.05 mol %), THF (0.5 mL), silane (1.0 mmol), and alkyne (1.0 mmol) were placed. Mixture was then heated to 40°C with stirring in oil bath. After 10 minutes $LiHBEt_3$ was added (0.15 mol %), and reaction vessel was then closed. After 20 hours, hexane was added to reaction mixture. Solution was then filtered through silica plug, and concentrated on rotavapor. The crude mixture was purified by evaporating volatiles on vacuum line followed by extraction with hexane. Regioselectivity was monitored by ^1H NMR..

1.3. Optimization of hydrosilylation of phenylacetylene with phenylsilane[a]

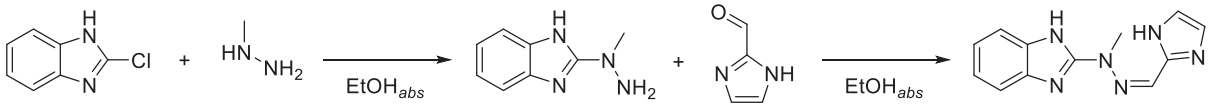


Entry	Catalyst **1** loading [mol%]	Time [h]	Temp. [°C]	Phenylsilane Conversion[b] [%]	Selectivity[c] (**3a**/**3aa**)
1	0.1	20	40	>99	78:22
2	0.05	20	40	>99	79:21
3[d]	0.05	20	40	>99	91:9
4	0.05	20	20	91	79:21
5	0.025	20	40	>99	84:16
6	0.01	20	40	>99	86:14
7	0.01	0.166	40	14	94:6
8	0.005	20	40	85	89:11
9	0.005	0.5	40	20	92:8

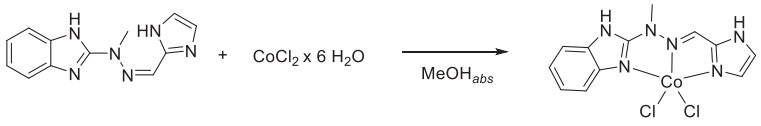
[a]Conditions: phenylacetylene (1 mmol), phenylsilane (1 mmol). [b,c]Calculated by GC with decane as internal standard.

[d]Reaction with 1.5 mmol of phenylsilane.

1.4. Ligand(**L**) and complex **1** synthesis:



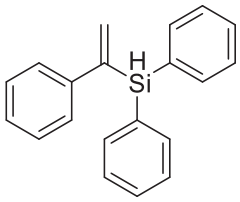
Ligand was synthesized according to reported procedure[1]. 2-chlorobenzimidazole (8.00 g 0.05 mol) was placed under argon atmosphere in two-necked round-bottomed flask. Methylhydrazine (11.9 g, 0.25 mol), in five-fold excess, was dissolved in anhydrous ethanol and was added to the reaction mixture, which was heated in heating mantle to 80°C and stirred for 20 h. The white, crystalline product was filtered on Büchner funnel and dried under vacuum. Yield 68.2% (5.8 g, 0.036 mol). Then condensation of 2-imidazolecarboxyaldehyde with 2-(1-methylhydrazine)benzimidazole was performed. At two-necked round-bottomed flask 2-(1- methylhydrazine)benzimidazole (1 g, 6.16 mmol) placed under argon atmosphere. The 4-imidazolecarboxyaldehyde (0.591 g, 6.16 mmol) was dissolved in anhydrous ethanol and was added to the reaction mixture. Reaction mixture was stirred for 24 h at 60°C. Yellow clear solution was cooled to room temperature. Precipitate, was then filtered by vacuum filtration, washed with anhydrous ethanol and dried under vacuum to give 1.24 g (5.16 mmol) of **L**. The supernatant was concentrated to minimal amount of volume and the next part of precipitate was obtained 0.140 g (0.58 mmol). Total yield is 91% (1.38 g, 5.74 mmol).



Complex **1** was synthesized according to reported procedure[2]. To a solution of **L** (100.0 mg) in hot MeOH, the methanolic solution of $CoCl_2 \cdot 6H_2O$ (99.1 mg) was added. Mixture was stirred for 24 h at room temperature. Solvents were subsequently evaporated under vacuum to minimal amount. Then, excess of Et_2O was added. Precipitate was filtered and washed twice with Et_2O and air dried, affording 153.9 mg (99.8% yield) of complex **1**.

2. Analytical data of isolated products

2.1.(2a) Diphenyl(1-phenylvinyl)silane – prepared from phenylacetylene (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (colorless oil, 285.9 mg - >99%).

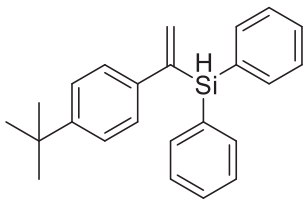


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 – 7.45 (m, 4H), 7.36 – 7.23 (m, 8H), 7.21-7.12 (m, 3H), 6.23 – 6.19 (d, 1H, *J* = 1.7 Hz), 5.63 - 5.59 (d, 1H, *J* = 2.4 Hz), 5.31 (s, 1H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 145.9, 142.9, 135.8, 133.1, 132.2, 129.9, 128.5, 128.1, 127.1, 126.8

Corresponds to previously reported data [3]

2.2.(2b) (1-(4-(*tert*-butyl)phenyl)vinyl)diphenylsilane - prepared from (4-*tert*-butyl)phenylacetylene (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 340.5 mg - >99%).

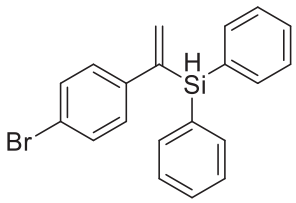


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 – 7.46 (m, 4H), 7.36 – 7.17 (m, 10H), 6.23 – 6.19 (dd, 1H, *J* = 2.3 Hz), 5.58 - 5.53 (d, 1H, *J* = 2.4 Hz), 5.32 (s, 1H), 1.20 (s, 9H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 150.1, 145.1, 139.8, 135.8, 133.3, 131.5, 139.8, 128.1, 126.3, 125.4, 34.5, 31.3

Corresponds to previously reported data [3]

2.3. (2c) (1-(4-bromophenyl)vinyl)diphenylsilane - prepared from (4-bromo)phenylacetylene (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 365.0 mg - >99%).

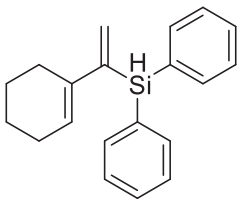


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 – 7.53 (m, 4H), 7.47 – 7.34 (m, 8H), 7.24-7.16 (m, 2H), 6.29 – 6.26 (d, 1H, *J* = 1.7 Hz), 5.74 - 5.70 (d, 1H, *J* = 2.2 Hz), 5.38 (s, 1H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 144.9, 141.9, 135.8, 132.7, 132.6, 131.5, 130.0, 128.4, 128.2, 121.1

Corresponds to previously reported data [3]

2.4.(2d) (1-cyclohex-1-enylvinyl)diphenylsilane - prepared from cyclohexylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 146.2 mg - >99%).

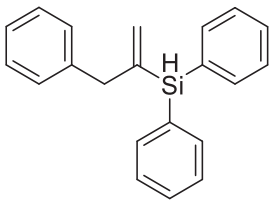


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 – 7.53 (m, 4H), 7.41 – 7.34 (m, 6H), 5.99 (s, 1H), 5.96 – 5.91 (t, 1H), 5.38 – 5.34 (d, 1H, *J* = 2.2 Hz), 5.33 - 5.30 (s, 1H), 2.29-2.20 (m, 2H), 2.10 – 2.01 (m, 2H), 1.75 – 1.65 (m, 2H), 1.60 – 1.52 (m, 2H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 145.9, 138.5, 135.8, 135.5, 133.9, 129.5, 127.9, 127.0, 26.0, 26.0, 22.3, 22.2

Corresponds to previously reported data [4]

2.5.(2e) Diphenyl(3-phenylprop-1-en-2-yl)silane - prepared from 3-phenylprop-1-yne (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 298,0 mg - >99%).

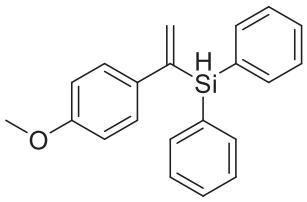


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 – 7.41 (m, 4H), 7.33 – 7.24 (m, 6H), 7.19 - 7.09 (m, 3H), 7.01 – 6.96 (d, 2H), 5.68 – 5.65 (d, 1H, *J* = 1.1 Hz), 5.49 - 5.46 (d, 1H, *J* = 1.3 Hz), 4.92 (s, 1H), 3.44 (s, 2H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 145.8, 139.3, 135.7, 132.9, 131.2, 129.75, 129.5, 128.3, 128.0, 126.1, 43.0

HRMS (ESI): calculated for $[C_{21}H_{20}SiNa]^+$ requires 323.1226 m/z, found 323.1226 m/z

2.6.(2f) (1-(4-methoxyphenyl)vinyl)diphenylsilane - prepared from 4-ethynylanisole (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 313.8 mg - >99%).

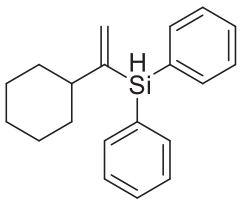


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 – 7.57 (m, 4H), 7.45 – 7.31 (m, 8H), 6.86 – 6.80 (d, 2H), 6.28 – 6.25 (d, 1H, *J* = 1.8 Hz), 5.64 - 5.61 (d, 1H, *J* = 2.1 Hz), 5.42 (s, 1H), 3.77 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 144.7, 135.8, 133.2, 129.8, 128.1, 127.8, 113.8, 55.3

Corresponds to previously reported data [3]

2.7.(2g) (1-cyclohexylvinyl)diphenylsilane - prepared from cyclohexylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 146.2 mg - >99%).

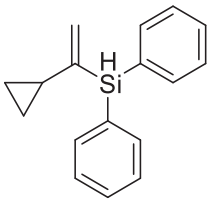


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 – 7.56 (m, 4H), 7.46 – 7.36 (m, 6H), 5.94 – 5.92 (m, 1H), 5.46 – 5.42 (d, 1H, *J* = 2.3 Hz), 5.18 (s, 1H), 2.25-2.15 (m, 1H), 1.81 – 1.71 (m, 4H), 1.31 – 1.17 (m, 4H), 1.20 – 1.09 (m, 2H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 152.0, 135.7, 133.9, 129.5, 128.0, 127.9, 42.9, 33.2, 26.7, 26.2

Corresponds to previously reported data [4]

2.8.(2h) (1-cyclopropylvinyl)diphenylsilane - prepared from cyclopropylacetylene (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 249.8 mg - >99%).

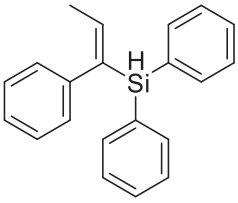


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 – 7.57 (m, 4H), 7.45 – 7.34 (m, 6H), 5.65 – 5.62 (d, 1H, *J* = 1.8 Hz), 5.28 - 5.25 (d, 1H, *J* = 2.4 Hz), 5.01 (s, 1H), 1.59 – 1.50 (m, 1H), 0.73 – 0.64 (m, 2H), 0.57 – 0.51 (m, 2H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.7, 135.5, 133.1, 129.5, 127.5, 127.8, 125.8, 16.4, 7.3

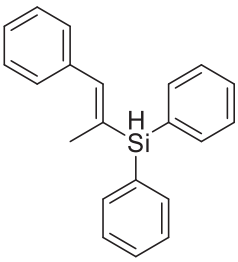
Corresponds to previously reported data [5]

2.9.(2i) (*E*)-diphenyl(1-phenylprop-1-en-1-yl)silane (*major product)* - prepared from 1-phenylprop-1-yne (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 146.2 mg - >99%).



Major product

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 – 7.61 (m, 1H), 7.59 – 7.50 (m, 3H), 7.47 – 7.32 (m, 7H), 7.30 – 7.21 (m, 2H), 7.21 – 7.12 (m, 1H), 7.06 – 7.01 (m, 1H), 6.95 (s, 0.26H *minor*), 6.41 – 6.22 (q, 0.74H *major*), 5.32 (s, 0.28H minor), 5.22 (s, 0.72H *major*), 2.09 (s, 0.8H *minor*), 1.81 – 1.69 (d, 2.20H *major*)

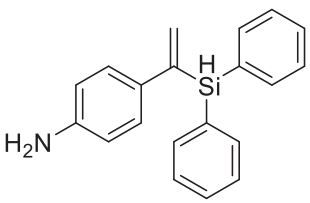


Minor product

^{13}C NMR (75 MHz, $CDCl_3$): δ 142.8, 142.1, 141.1, 139.04, 137.9, 135.8, 135.8, 133.6, 133.2, 129.8, 129.6, 129.1, 128.5, 128.1, 128.1, 128.1, 127.9, 127.0, 125.8, 17.5, 16.4

Corresponds to previously reported data [3]

2.10.(2j) 4-(1-(diphenylsilyl)vinyl)aniline - prepared from (4-ethynyl)aniline (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (brown oil, 300.9 mg - >99%).

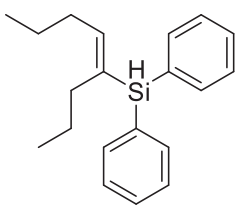


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 – 7.55 (m, 4H), 7.42 – 7.32 (m, 6H), 7.25 - 7.19 (m, 2H), 6.62 – 6.56 (m, 2H), 6.25 – 6.22 (dd, 1H, *J* = 2.3 Hz), 5.55 - 5.52 (d, 1H, *J* = 2.4 Hz), 5.39 (s, 1H), 3.63 (s, 2H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 145.7, 144.6, 135.8, 133.4, 133.0, 129.7, 129.2, 128.0, 127.7, 115.0

Corresponds to previously reported data [3]

2.11.(2k) (*E*)-oct-4-en-4-yldiphenylsilane - prepared from oct-4-yne (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 280.3 mg - 95%).

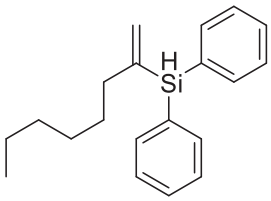


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 – 7.55 (m, 4H), 7.42 – 7.35 (m, 4H), 5.96 – 5.90 (t, 1H), 6.28 – 6.25 (d, 1H, *J* = 1.8 Hz), 5.10 (s, 1H), 2.26-2.14 (m, 4H), 1.48 – 1.38 (h, 2H), 1.38 – 1.28 (h, 2H), 0.97 – 0.90 (t, 3H), 0.88 – 0.81 (t, 3H),

^{13}C NMR (75 MHz, $CDCl_3$): δ 146.7, 135.7, 135.1, 134.3, 129.4, 127.9, 32.6, 30.9, 23.1, 22.6, 14.3, 14.0

Corresponds to previously reported data [3]

2.12.(2l) Oct-1-en-2-yldiphenylsilane - prepared from okt-1-yne (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 146.2 mg - >99%).

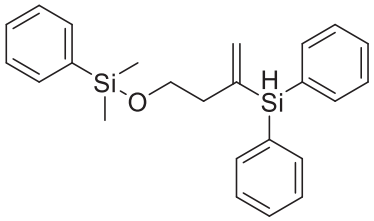


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 – 7.51 (m, 4H), 7.45 – 7.31 (m, 6H), 5.93 – 5.80 (b, 1H), 5.50 – 5.43 (d, 1H, *J* = 2.8 Hz), 5.07 (s, 1H), 2.28-2.17 (t, 2H), 1.46 – 1.34 (m, 2H), 1.27 – 1.17 (m, 6H), 0.89 – 0.79 (m, 3H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 146.6, 135.7, 133.4, 129.6, 129.5, 128.0, 37.0, 31.7, 29.0, 28.8, 22.6, 14.1

Corresponds to previously reported data [4]

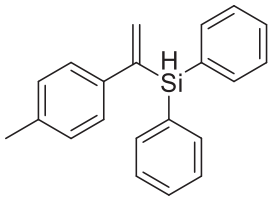
2.13.(2m) ((3-(diphenylsilyl)but-3-en-1-yl)oxy)dimethyl(phenyl)silane - (but-3-yn-1-yloxy)--dimethyl(phenyl)silane (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (colorless oil, 140.1 mg – 72%).



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 – 7.50 (m, 5H), 7.45 – 7.33 (m, 10H), 5.99 – 5.83 (m, 1H), 5.56 (s, 1H), 5.09 (s, 1H), 3.68 – 3.58 (t, 2H), 2.55 – 2.45 (t, 1H), 0.35 – 0.26 (s, 6H)

HRMS (ESI): calculated for $[C_{24}H_{28}Si_2ONa]^+$ requires 411.1571 m/z, found 411.1575 m/z

2.14.(2n) Diphenyl(1-(*p*-tolyl)vinyl)silane - prepared from (4-methyl)phenylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 142.8 mg - 95%).

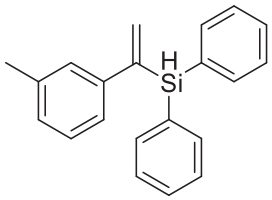


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 – 7.53 (m, 4H), 7.41 – 7.31 (m, 7H), δ7.24 – 7.22 (m, 1H), 7.08 – 7.03 (m, 2H), 6.29 – 6.23 (dd, 1H, *J* = 2.1 Hz), 5.66 – 5.59 (d, 1H, *J* = 2.2 Hz), 5.37 (s, 1H), 2.29 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 145.5, 139.9, 136.8, 135.8, 133.2, 131.37, 129.8, 129.1, 128.1, 126.6, 21.1

Corresponds to previously reported data [3]

2.15.(2o) Diphenyl(1-(*m*-tolyl)vinyl)silane - prepared from (3-methyl)phenylacetylene (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 281,3 mg - 94%).

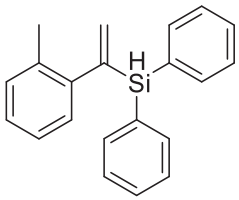


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 – 7.60 (m, 4H), 7.48 – 7.38 (m, 6H), δ7.23 – 7.17 (m, 3H), 7.10 – 7.06 (m, 1H), 6.33 – 6.31 (dd, 1H, *J* = 2.5 Hz), 5.73 – 5.71 (d, 1H, *J* = 2.5 Hz), 4.74 (s, 1H), 2.24 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 148.0, 143.4, 135.7, 134.6, 133.8, 132.9, 130.1, 129.8, 128.1, 128.0, 126.4, 125.5, 20.4

Corresponds to previously reported data [3]

2.16.(2p) Diphenyl(1-(*o*-tolyl)vinyl)silane - prepared from (2-methyl)phenylacetylene (1.0 mmol) and diphenylsilane (1.0 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 298,5 mg - >99%).

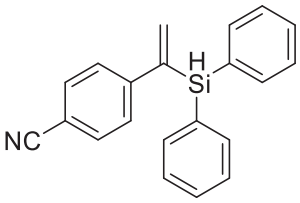


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 – 7.57 (m, 4H), 7.48 – 7.37 (m, 6H), δ7.19 – 7.06 (m, 3H), 6.98 – 6.95 (d, 1H), 6.01 – 5.98 (d, 1H, *J* = 3.1 Hz), 5.95 – 5.93 (d, 1H, *J* = 3.1 Hz), 5.26 (s, 1H), 2.24 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 148.0, 143.4, 135.7, 134.5, 133.3, 132.9, 130.1, 129.8, 128.0, 128.0, 126.4, 125.4, 20.4

Corresponds to previously reported data [3]

2.17.(2r) 4-(1-(diphenylsilyl)vinyl)benzonitrile - prepared from 4-ethynylbenzonitrile (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **B** at 40ºC. Purified by extraction with *n*-hexane followed by filtration through silica plug. Mixture required further purification by column chromatography on silica gel (hexane:ethyl acetate = 2:1). Volatiles were removed under lower pressure affording pure product (yellow oil, 85.3 mg - 55%).

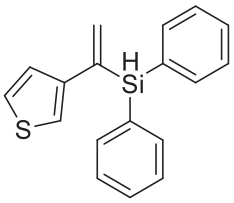


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 – 7.51 (m, 6H), 7.45 – 7.34 (m, 8H), 6.34 – 6.27 (dd, 1H, *J* = 2.0, 0.6 Hz), 5.84 – 5.79 (d, 1H, *J* = 2.1 Hz), 5.40 – 5.33 (s, 1H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.9, 145.3, 135.7, 134.5, 132.2, 132.0, 130.2, 128.2, 127.4, 118.9, 110.6

Corresponds to previously reported data [3]

2.18.(2s) Diphenyl(1-(thiophen-3-yl)vinyl)silane - prepared from 3-ethynylthiophene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (brown oil, 144.2 mg – 98%).

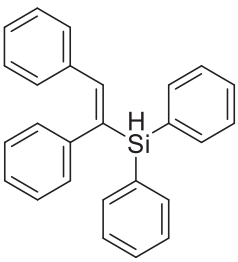


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 – 7.58 (m, 4H), 7.43 – 7.35 (m, 6H), 7.16 – 7.12 (m, 1H), 6.96 – 6.91 (m, 1H), 6.90 – 6.85 (m, 1H), 6.35 (s, 1H), 5.52– 5.47 (d, 1H, *J* = 1.6 Hz), 5.42 (s, 1H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 146.4, 137.9, 135.8, 134.7, 134.3, 132.4, 130.0, 129.6, 128.1, 127.5, 126.0, 124.2

Corresponds to previously reported data [3]

2.19.(2t) (*E*)-(1,2-diphenylvinyl)diphenylsilane - prepared from diphenylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 176.8 mg - 98%).

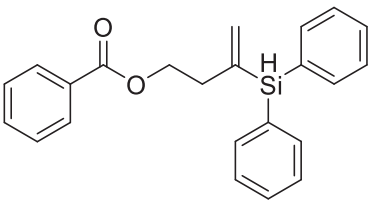


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 – 7.54 (m, 4H), 7.46 – 7.36 (m, 6H), 7.42 – 7.33 (m, 6H), 7.24 – 7.15 (m, 3H), 7.13 – 7.08 (m, 3H), 7.04 – 6.98 (m, 5H), 5.28 (s, 1H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 142.9, 141.6, 140.2, 136.9, 135.9, 133.0, 129.8, 129.7, 128.6, 128.1, 128.0, 127.9, 127.5, 126.2

Corresponds to previously reported data [3]

2.20.(2u) 3-(diphenylsilyl)but-3-en-1-yl benzoate - prepared from butyn-3-yl benzoate (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (colourless, 178.2 mg – 99%).

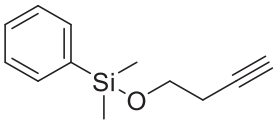


^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 – 7.95 (m, 2H), 7.61 – 7.51 (m, 5H), 7.45 – 7.32 (m, 8H), 6.07 – 6.01 (d, 1H, *J* = 1.4 Hz), 5.65 – 5.57 (d, 1H, *J* = 2.3 Hz), 5.15 (s, 1H), 4.43 – 4.31 (t, 2H), 2.76 – 2.67 (t, 2H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 142.2, 135.6, 132.8, 132.6, 132.5, 130.3, 129.9, 129.6, 128.3, 128.1, 63.8, 35.8

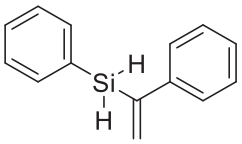
HRMS (ESI): calculated for $[C_{23}H_{22}SiO_2Na]^+$ requires 381.1281 m/z, found 381.1289 m/z

2.21. (but-3-yn-1-yloxy)dimethyl(phenyl)silane - But-3-yn-1-ol was silylated with dimethylphenylsilane according to reported procedure[6]. (but-3-yn-1-yloxy)dimethyl(phenyl)silane was purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under reduced pressure.



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 – 7.54 (m, 2H), 7.42 – 7.33 (m, 3H), 3.78 – 3.68 (t, 2H), 2.47– 2.37 (td, 2H), 2.00 – 1.93 (t, 1H), 0.40 (s, 6H)

2.22.(3a) Phenyl(1-phenylvinyl)silane– prepared from phenylsilane (1.0 mmol) and phenylacetylene (1.0 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 206.3 mg – 98%).

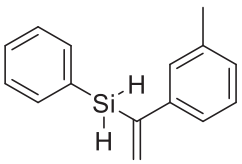


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 – 7.51 (m, 2H), 7.37 – 7.27 (m, 6H), 7.25 – 7.17 (m, 2H), 6.23 – 6.18 (d, 1H, *J* = 2.4 Hz), 5.81 – 5.77 (d, 1H, *J* = 2.3 Hz), 4.80 (s, 2H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 144.2, 142.3, 135.6, 131.4, 131.2, 129.9, 128.6, 128.2, 127.3, 126.5

Corresponds to previously reported data [7]

2.23.(3g) Phenyl(1-(*m*-tolyl)vinyl)silane – prepared from phenylsilane (1.0 mmol) and 3-ethynyltoluene (1.0 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 210.3 mg – 94%).

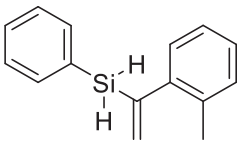


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 – 7.58 (m, 2H), 7.46 – 7.34 (m, 3H), 7.25 – 7.16 (m, 3H), 7.12 – 7.04 (m, 1H), 6.27 – 6.23 (d, 1H, *J* = 2.5 Hz), 5.87 – 5.79 (d, 1H, *J* = 2.4 Hz), 4.86 (s, 2H), 2.40– 2.34 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 144.3, 142.3, 138.1, 135.6, 131.1, 129.9, 128.4, 128.1, 127.1, 123.7, 21.5

Corresponds to previously reported data [7]

2.24.(3h) Phenyl(1-(*o*-tolyl)vinyl)silane – prepared from phenylsilane (1.0 mmol) and 2-ethynyltoluene (1.0 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 223.9 mg – 99%).

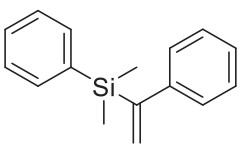


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 – 7.53 (m, 2H), 7.44 – 7.32 (m, 3H), 7.19 – 7.08 (m, 3H), 7.02 – 6.89 (m, 1H), 5.95 – 5.91 (d, 1H, *J* = 2.0 Hz), 5.90 – 5.86 (d, 1H, *J* = 1.9 Hz), 4.71 (s, 2H), 2.25 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 146.5, 143.1, 135.6, 133.0, 130.1, 129.9, 128.0, 127.9, 126.6, 125.6, 20.3

Corresponds to previously reported data [7]

2.25.(4a) Dimethyl(phenyl)(1-phenylvinyl)silane – prepared from dimethyl(phenyl)silane (1.0 mmol) and phenylacetylene (1.0 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 225.0 mg – 94%).

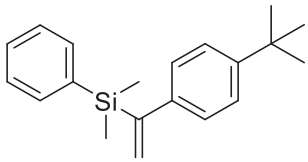


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 – 7.51 (m, 2H), 7.41 – 7.32 (m, 3H), 7.25 – 7.17 (m, 3H), 7.12 (m, 2H), 6.04 – 5.95 (d, 1H, *J* = 2.8 Hz), 5.72 – 5.63 (d, 1H, *J* = 2.9 Hz), 0.41 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 153.3, 146.5, 140.6, 136.4, 131.5, 131.4, 130.4, 130.1, 129.2, 128.7, 0.0

Corresponds to previously reported data [8]

2.26.(4b) (1-(4-(*tert*-butyl)phenyl)vinyl)dimethyl(phenyl)silane - prepared from dimethyl(phenyl)silane (1.0 mmol) and 1-(*tert*-butyl)-4-ethynylbenzene (1.0 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 291.5 mg – 99 %).

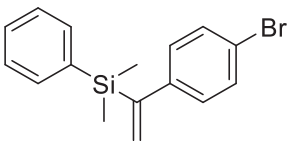


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 – 7.54 (m, 2H), 7.46 – 7.35 (m, 3H), 7.32 – 7.24 (m, 2H), 7.17 – 7.02 (m, 2H), 6.11 – 6.00 (d, 1H, *J* = 2.8 Hz), 5.72 – 5.62 (d, 1H, *J* = 2.9 Hz), 1.32 (s, 9H), 0.50 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 152.3, 151.5, 143.0, 140.8, 136.2, 131.2, 130.8, 130.0, 128.6, 127.2, 36.6, 33.5, 0.0

Corresponds to previously reported data [10]

2.27.(4c) (1-(4-bromophenyl)vinyl)dimethyl(phenyl)silane - prepared from dimethyl(phenyl)silane (1.0 mmol) and 1-bromo-4-ethynylbenzene (1.0 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 251.7 mg – 79%).

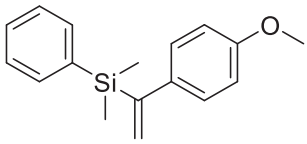


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 – 7.49 (m, 2H), 7.41 – 7.29 (m, 5H), 7.01 – 6.96 (m, 2H), 6.01 – 5.92 (d, 1H, *J* = 2.7, 0.6 Hz), 5.74 – 5.66 (d, 1H, *J* = 2.8 Hz), 0.40 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 152.6, 145.6, 140.3, 136.5, 133.7, 132.0, 131.7, 131.0, 130.4, 122.9, 0.0

Corresponds to previously reported data [8]

2.28.(4d) (1-(4-methoxyphenyl)vinyl)dimethyl(phenyl)silane – prepared from dimethyl(phenyl)silane (1.0 mmol) and 4-ethynylanisole (1.0 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 251.7 mg – 94%).

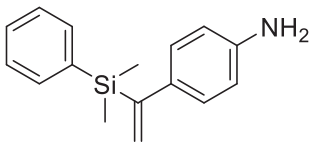


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 – 7.54 (m, 2H), 7.40 – 7.33 (m, 3H), 7.13 – 7.05 (m, 2H), 6.82 – 6.75 (m, 2H), 6.03 – 5.96 (d, 1H, *J* = 2.8 Hz), 5.65 – 5.59 (d, 1H, *J* = 2.8 Hz), 3.77 (s, 3H), 0.42 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 160.6, 152.1, 140.7, 138.6, 136.2, 131.2, 130.2, 130.1, 130.0, 115.7, 57.4, 0.0

Corresponds to previously reported data [8]

2.29.(4e) 4-(1-(dimethyl(phenyl)silyl)vinyl)aniline – prepared form dimethyl(phenyl)silane (1.0 mmol) and 4-ethynylaniline (1.0 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 189.4 mg – 75%).

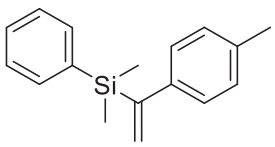


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 – 7.52 (m, 2H), 7.41 – 7.32 (m, 3H), 7.02 – 6.96 (m, 2H), 5.59 – 5.54 (m, 2H), 6.00 – 5.96 (d, 1H, *J* = 2.8 Hz), 5.58 – 5.55 (d, 1H, *J* = 2.8 Hz), 3.78 – 3.45 (b, 2H), 0.42 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 151.8, 147.1, 140.9, 136.3, 136.1, 131.0, 129.9, 129.9, 129.0, 117.0, 0.0

HRMS (ESI): calculated for $[C_{16}H_{20}SiN]^+$ requires 254.1360 m/z, found 254.1365 m/z

2.30.(4f) dimethyl(phenyl)(1-(*p*-tolyl)vinyl)silane - prepared from dimethyl(phenyl)silane (1.0 mmol) and 4-ethynyltoluene (1.0 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 243.4 mg – 96%).

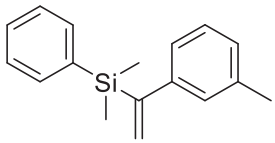


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 – 7.53 (m, 2H), 7.43 – 7.32 (m, 3H), 7.10 – 6.99 (m, 4H), 6.05 – 5.95 (d, 1H, *J* = 2.8 Hz), 5.71 – 5.61 (d, 1H, *J* = 2.9 Hz), 2.31 (s, 3H), 0.44 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 152.8, 143.4, 140.7, 138.3, 136.3, 131.3, 131.1, 130.9, 130.0, 129.0, 23.3, 0.0

Corresponds to previously reported data [9]

2.31.(4g) dimethyl(phenyl)(1-(*m*-tolyl)vinyl)silane – prepared from dimethyl(phenyl)silane (1.0 mmol) and 3-ethynyltoluene (1.0 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (yellow oil, 231.3 mg – 92%).

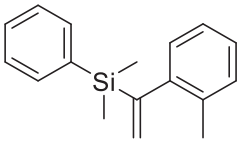


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 – 7.53 (m, 2H), 7.24 – 7.17 (m, 3H), 7.10 – 6.99 (m, 2H), 6.91 – 6.84 (m, 2H), 6.02 – 6.98 (d, 1H, *J* = 3.0 Hz), 6.67 – 5.63 (d, 1H, *J* = 3.0 Hz), 2.07 (s, 3H), 0.39 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 153.3, 146.4, 140.6, 139.9, 136.4, 131.3, 130.2, 130.1, 129.9, 129.4, 126.3, 23.8, 0.00

HRMS (ESI): calculated for $[C_{17}H_{20}SiNa]^+$ requires 275.1226 m/z, found 275.1226 m/z

2.32.(4h) dimethyl(phenyl)(1-(*o*-tolyl)vinyl)silane – prepared from dimethyl(phenyl)silane (1.0 mmol) and 2-ethynyltoluene (1.0 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (orange oil, 243.3 mg – 96%).

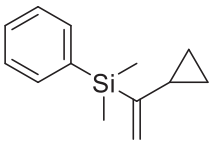


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 – 7.44 (m, 2H), 7.24 – 7.18 (m, 3H), 7.08 – 6.99 (m, 3H), 6.94 – 6.88 (m, 1H), 5.72 – 5.69 (d, 1H, *J* = 3.4 Hz), 5.67 – 5.63 (d, 1H, *J* = 3.4 Hz), 2.06 (s, 3H), 0.32 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 152.3, 143.9, 137.7, 134.3, 134.1, 130.0, 129.6, 129.1, 127.7, 127.7, 125.9, 125.0, 20.2, -3.0

Corresponds to previously reported data [11]

2.33.(4i) (1-cyclopropylvinyl)dimethyl(phenyl)silane – prepared from dimethyl(phenyl)silane (1.0 mmol) and cyclopropylacetylene (1.0 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (pale yellow oil, 193.1 mg – 95%).

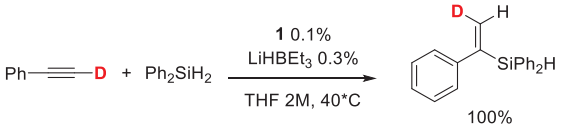


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 – 7.52 (m, 2H), 7.28 – 7.20 (m, 3H), 5.54 – 5.45 (m, 1H), 5.35 – 5.26 (d, 1H, *J* = 2.6 Hz), 1.35 – 1.22 (quint, 1H), 0.46 – 0.41 (m, 4H), 0.38 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 151.8, 138.4, 134.0, 128.9, 127.7, 121.6, 15.4, 6.9, -2.9

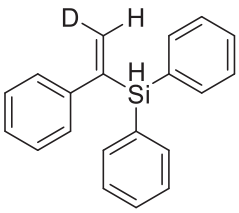
Corresponds to previously reported data [12]

3. Deuterium labelled experiment



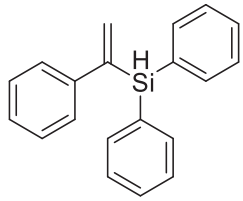
3.1 Hydrosililation of D_1-phenylaceylene with diphenylsilane.

To a flame-dried Schlenk bomb flask charged with argon, precatalyst (1 mol %), THF (1.0 mL), diphenylsilane (0.5 mmol), and D_1-phenylacetylene (0.5 mmol) were placed. Mixture was then heated to 40°C with stirring. After 10 minutes $LiHBEt_3$ was added (0.3 mol %), and reaction vessel was then closed. After 1 hour, hexane was added to reaction mixture. Solution was then filtered through silica plug, and concentrated on rotavapor. The crude mixture was purified by evaporating volatiles on vacuum line followed by extraction with hexane. Regioselectivity was monitored by ^1H NMR.

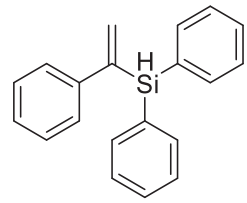


^1H NMR (300 MHz, $CDCl_3$): δ7.52 – 7.46 (m, 4H), 7.36 – 7.24 (m, 8H), 7.21-7.11 (m, 3H), **[6.23 – 6.19 *Not observed*],** 5.63 - 5.56 (s, 1H,), 5.37 – 5.28 (s, 1H)

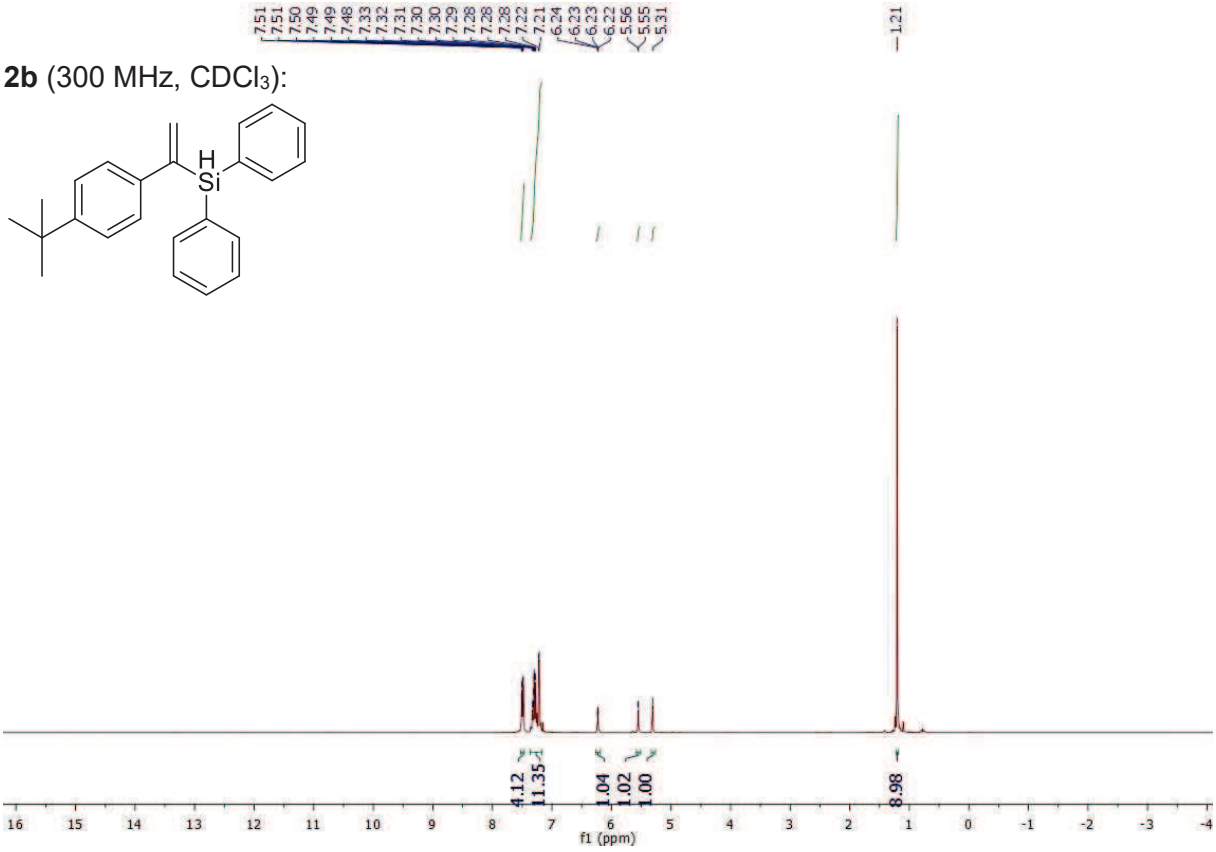
2a (300 MHz, $CDCl_3$):



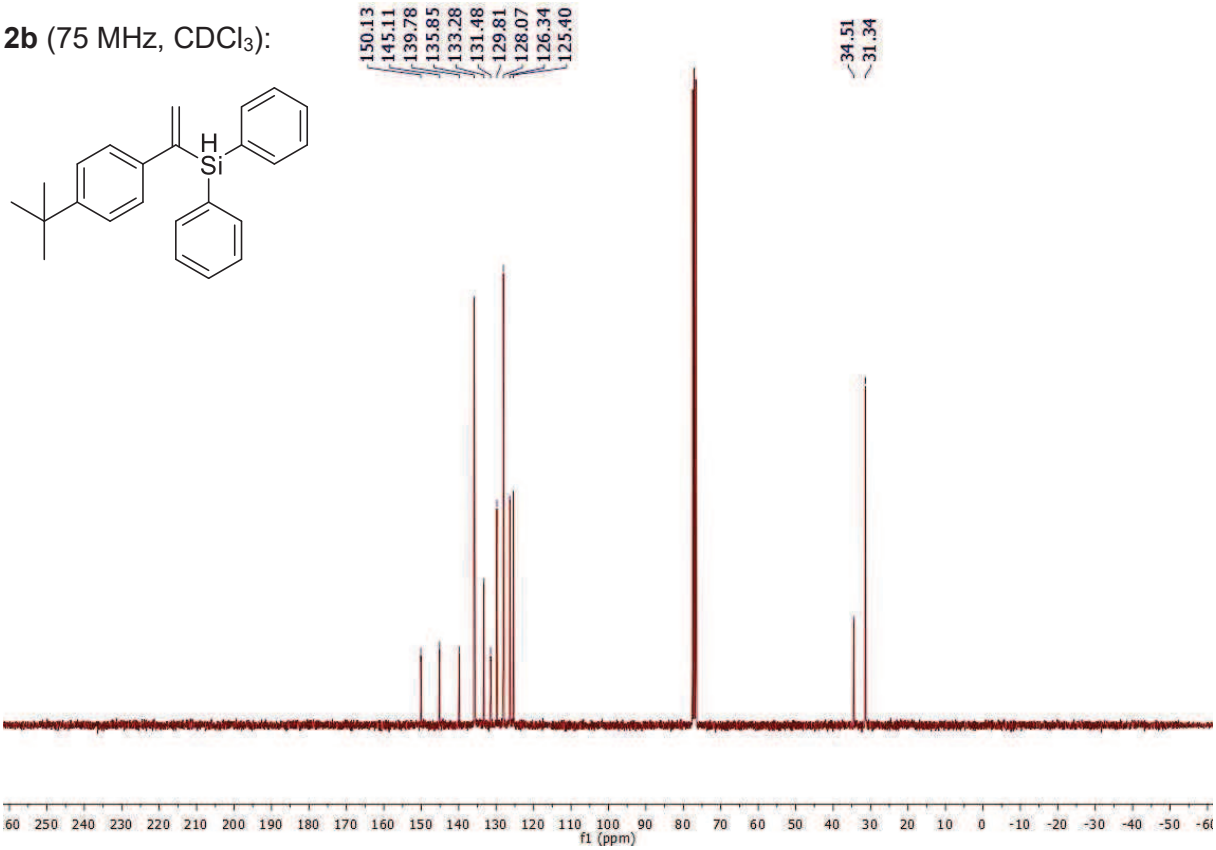
2a (75 MHz, $CDCl_3$):



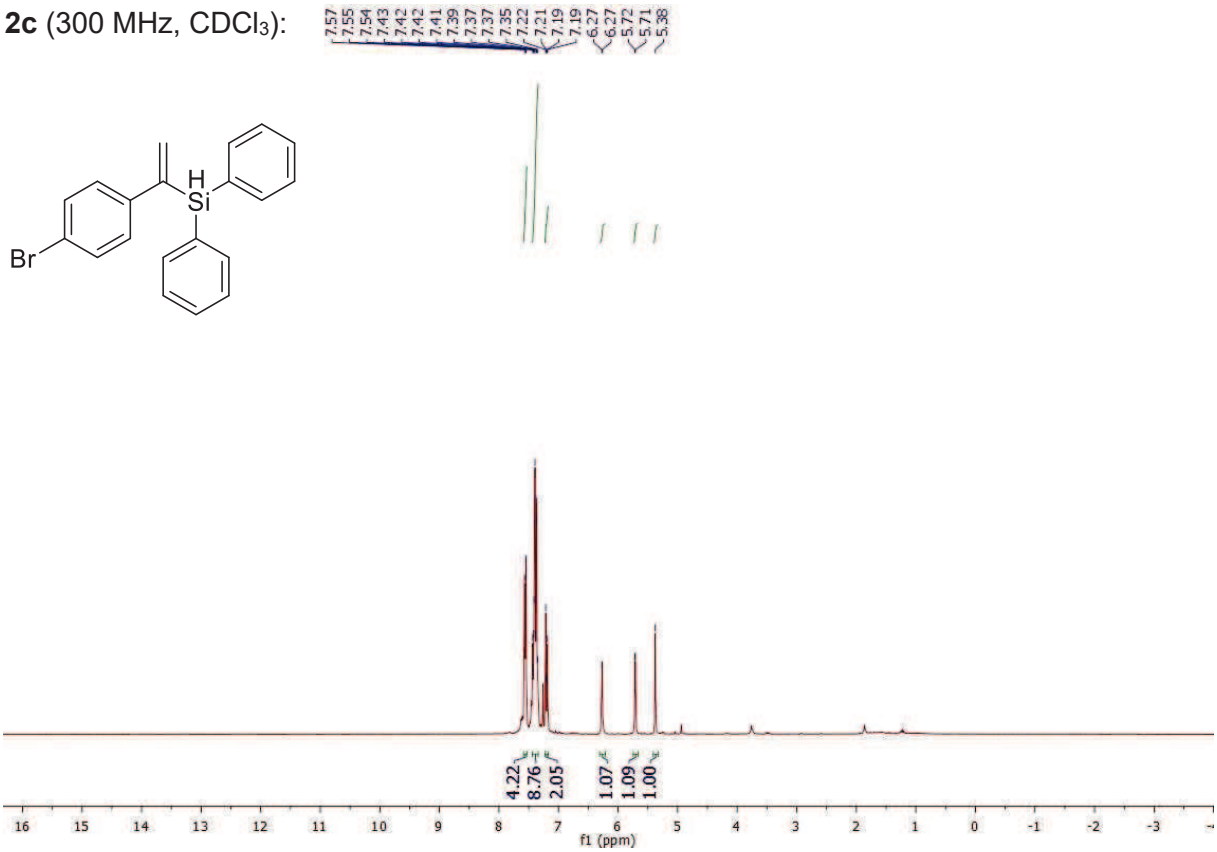
2b (300 MHz, $CDCl_3$):



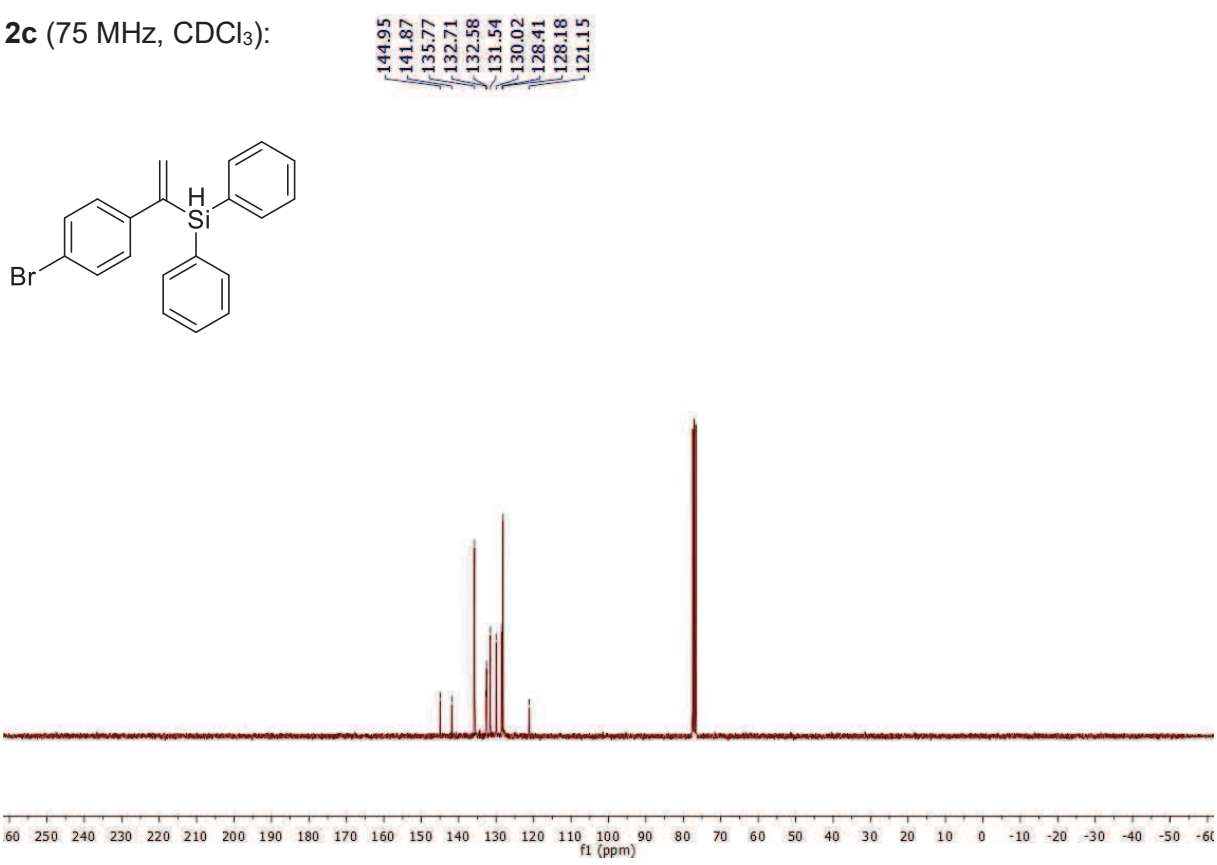
2b (75 MHz, $CDCl_3$):



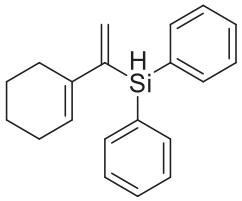
2c (300 MHz, $CDCl_3$):



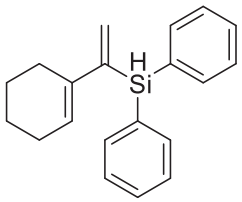
2c (75 MHz, $CDCl_3$):



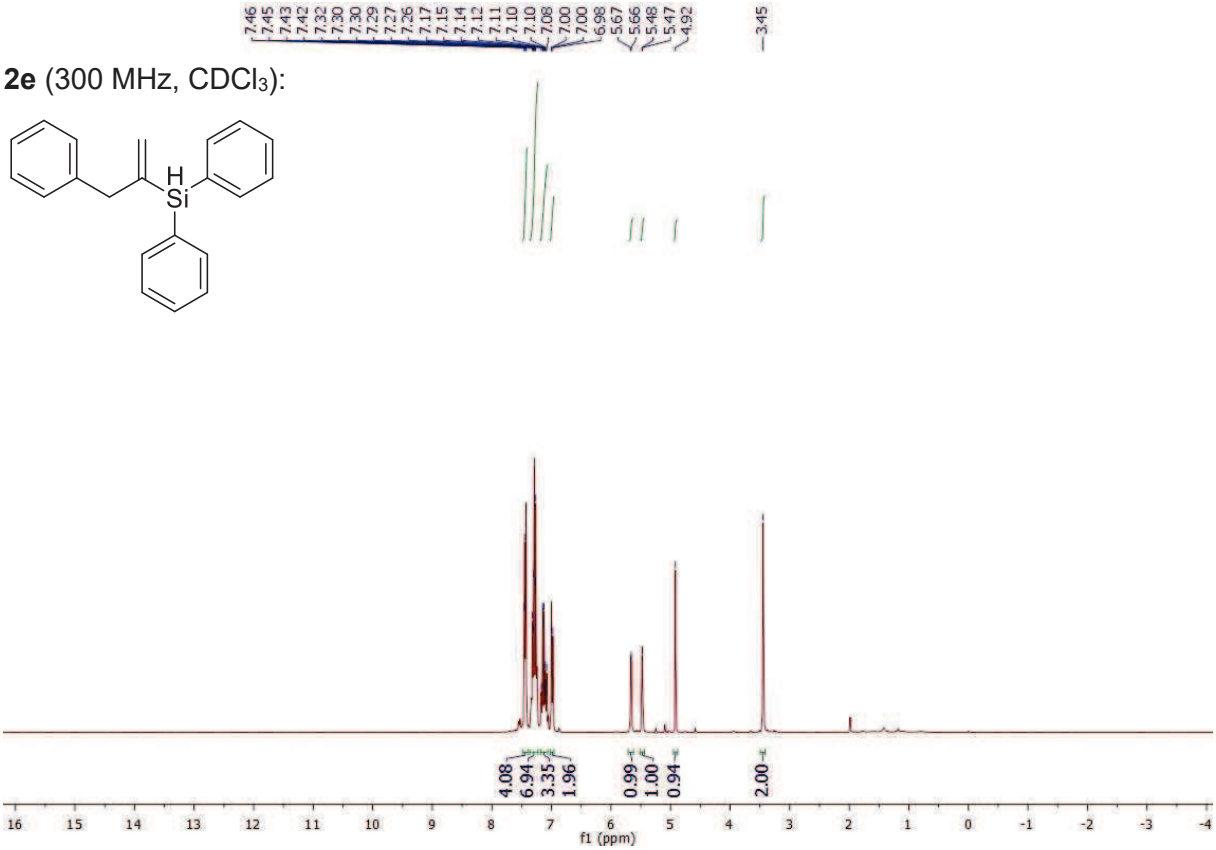
2d (300MHz, $CDCl_3$):



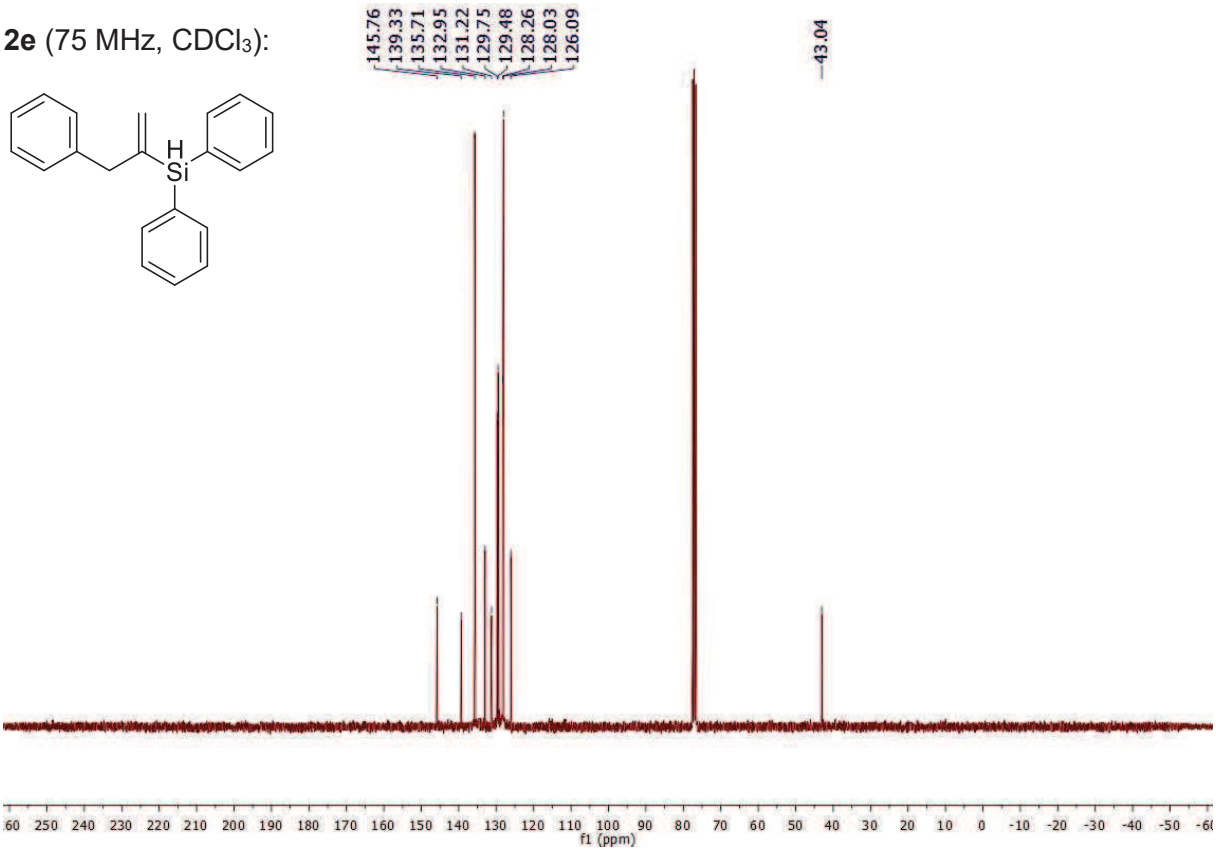
2d (75 MHz, $CDCl_3$):

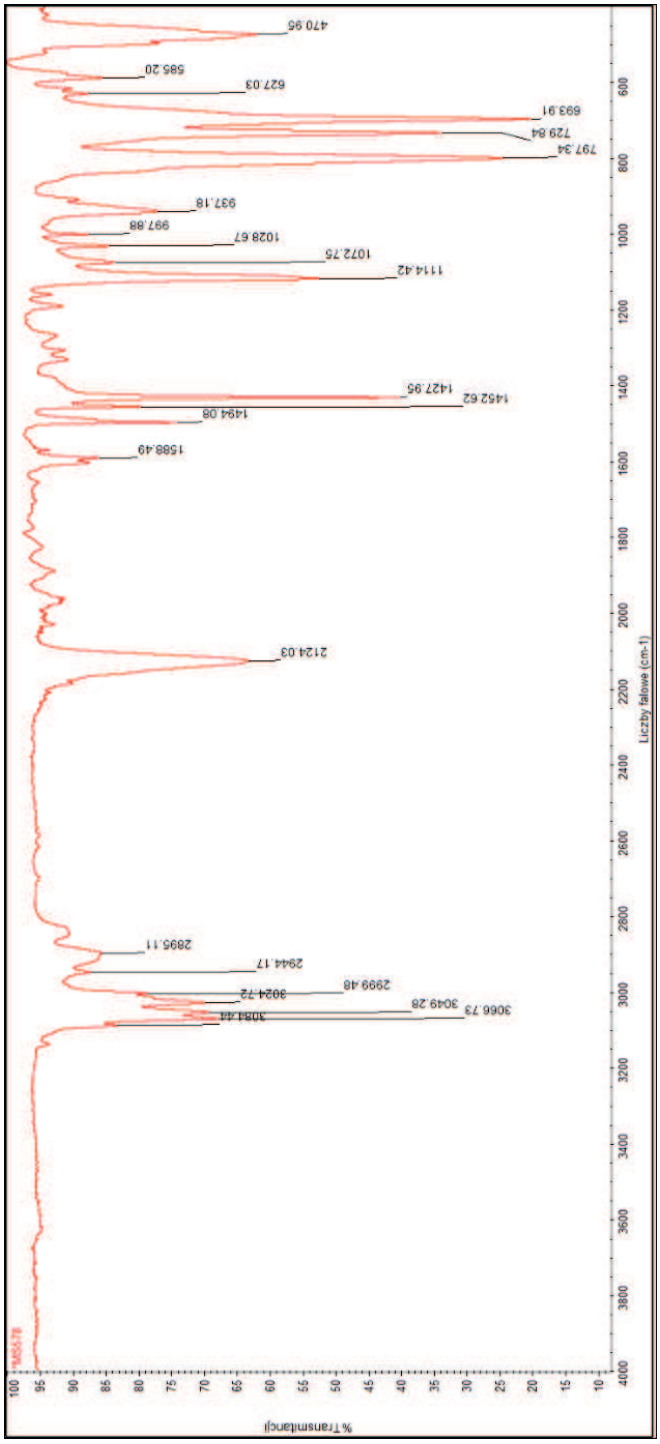


2e (300 MHz, $CDCl_3$):



2e (75 MHz, $CDCl_3$):

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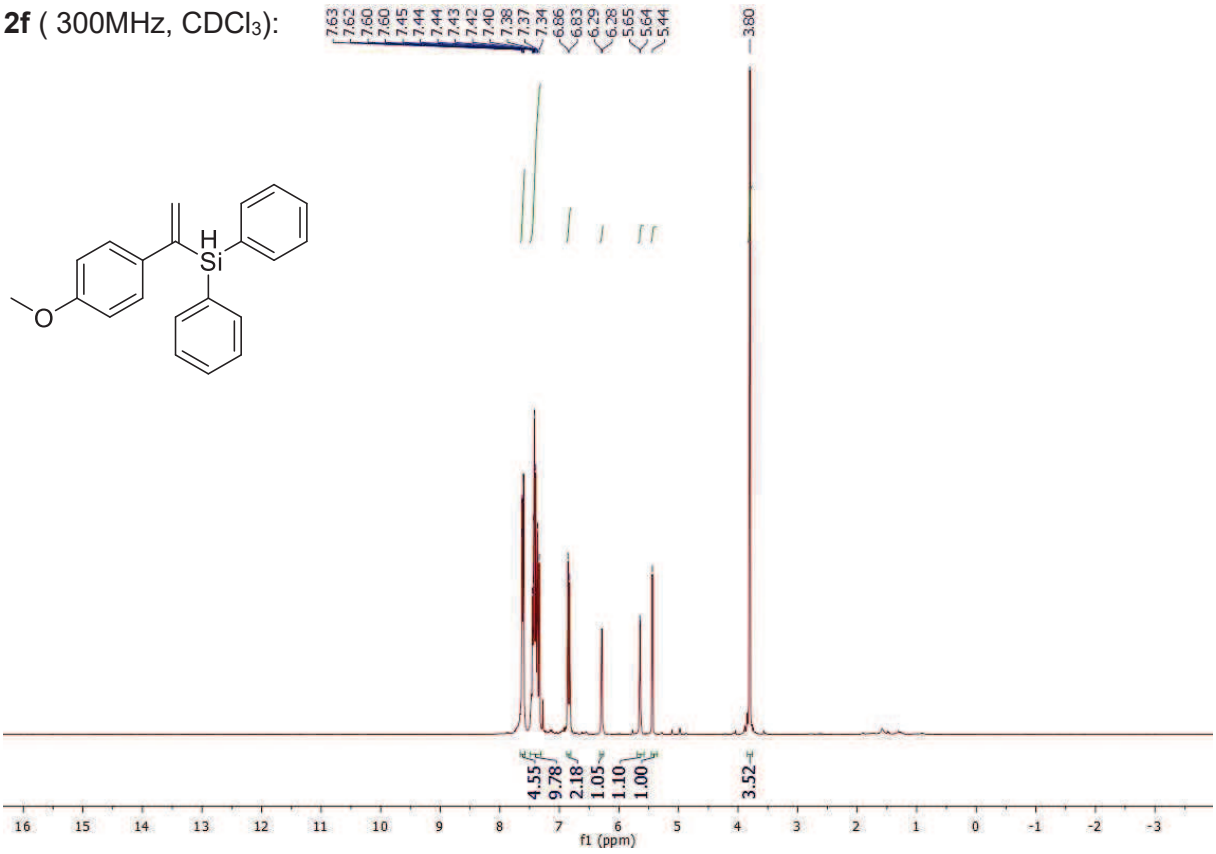
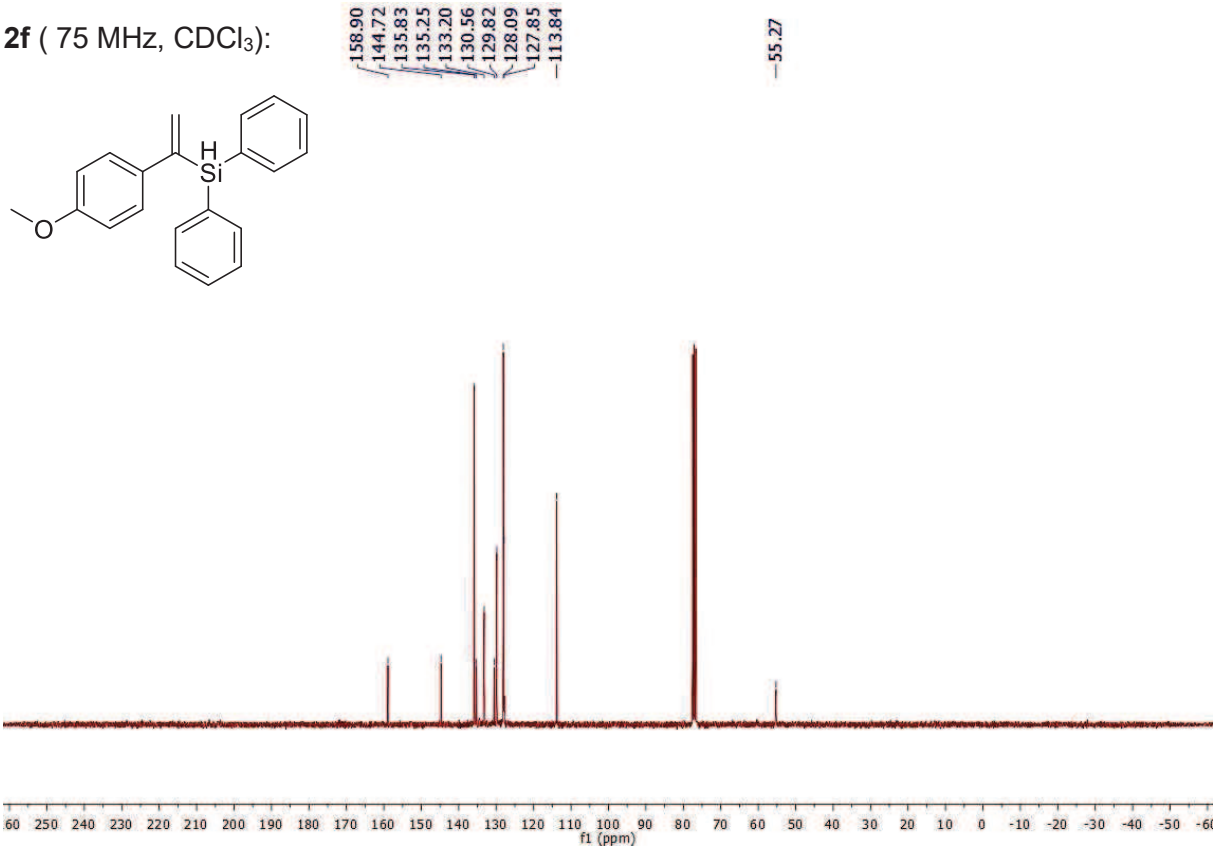
585.20
627.03
693.91
729.84
797.34
937.18
997.88
1028.67
1072.75
1114.42
1427.95
1452.62
1494.08
1588.49
2124.03
2895.11
2944.17
2999.48
3024.72
3049.28
3066.73
3084.44
%Transmitancji
Liczby falowe (cm-1)

2e

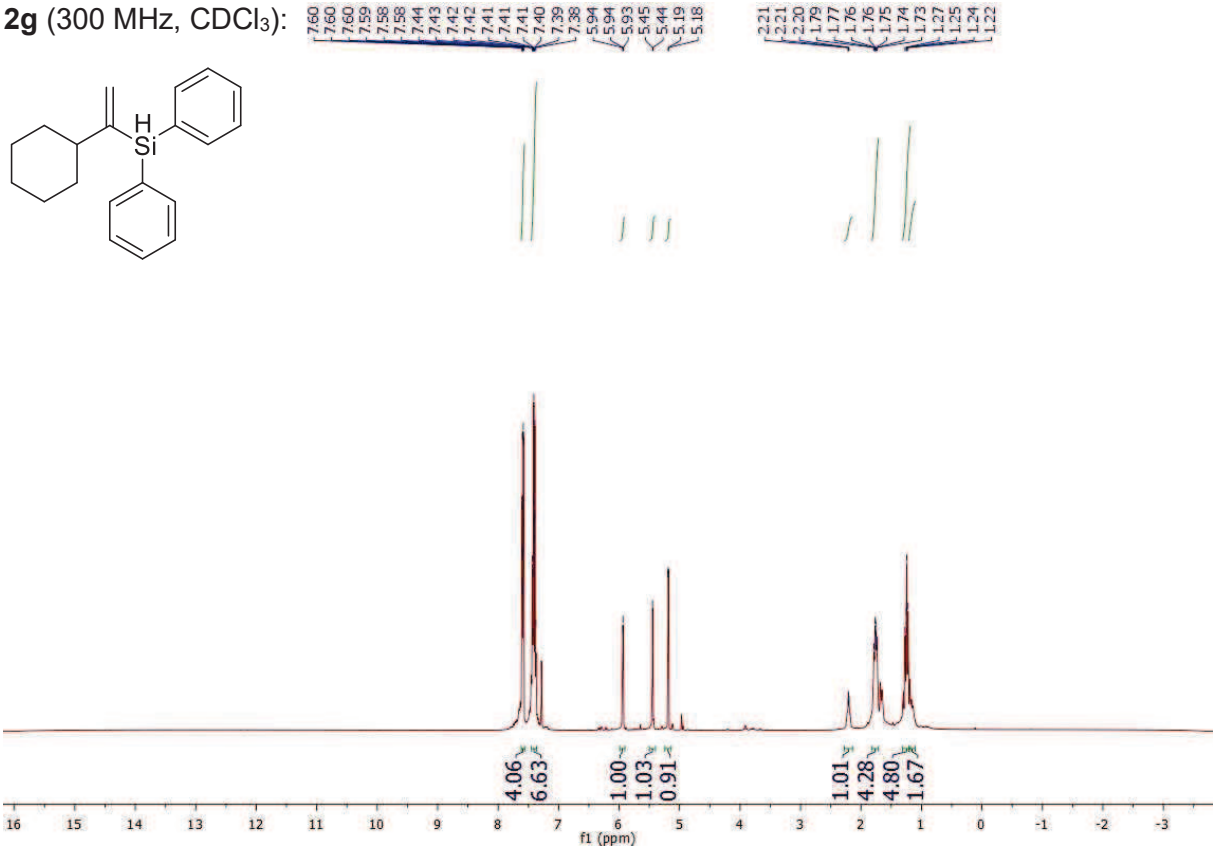
2f (300MHz, $CDCl_3$):



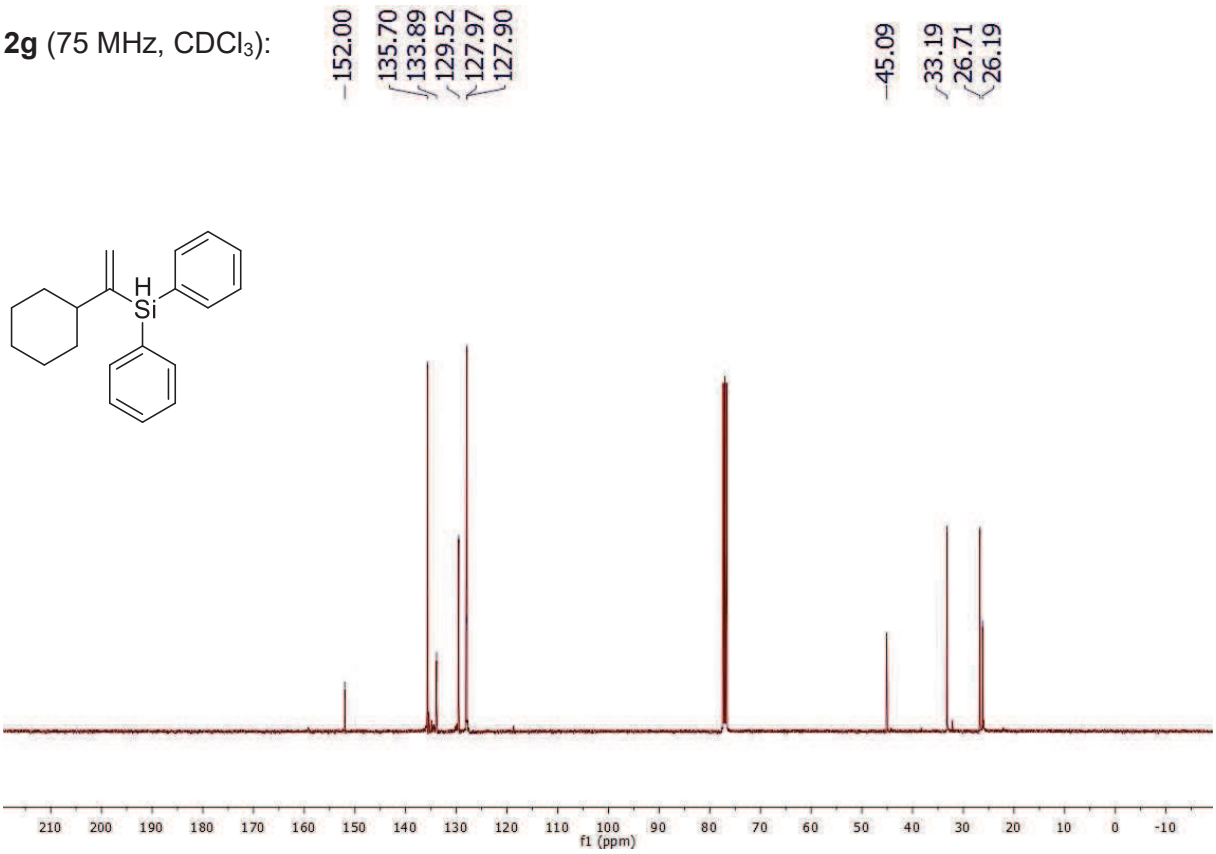
2f (75 MHz, $CDCl_3$):



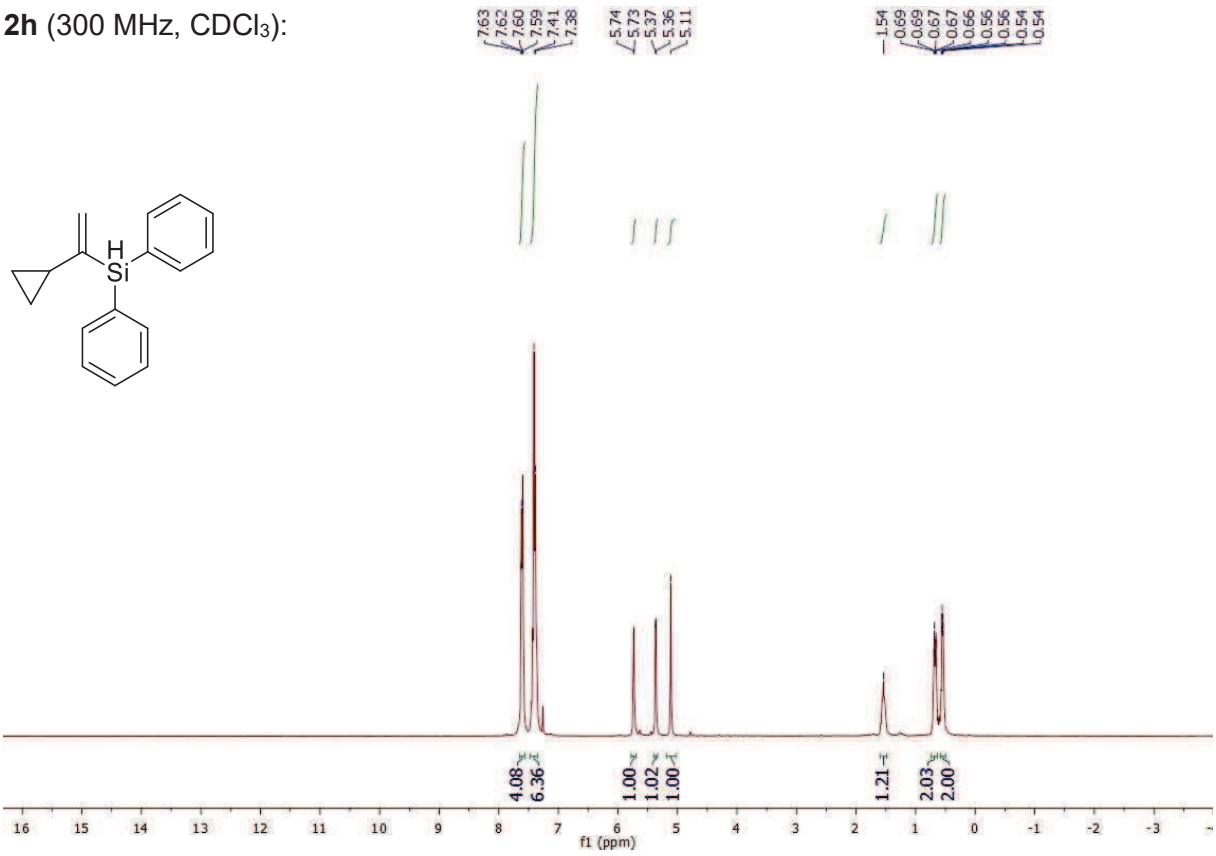
2g (300 MHz, $CDCl_3$):



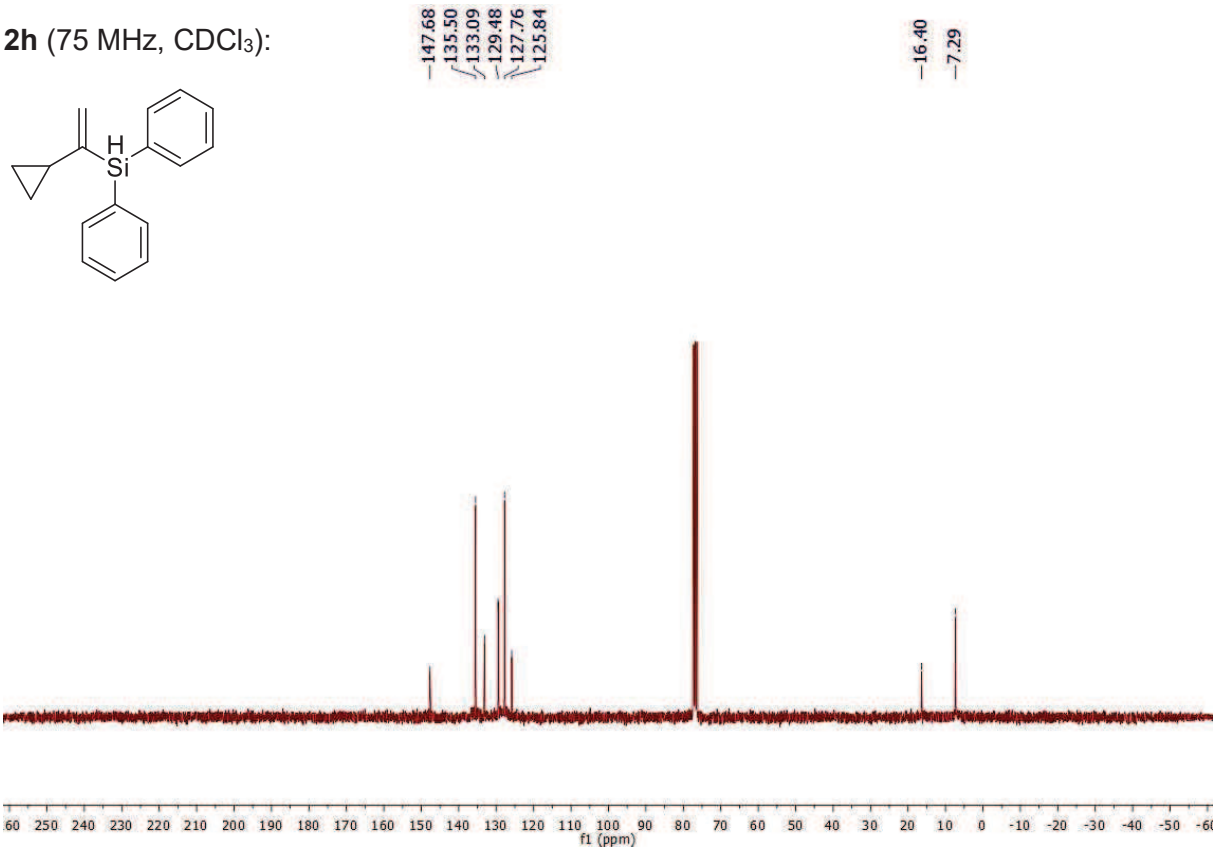
2g (75 MHz, $CDCl_3$):



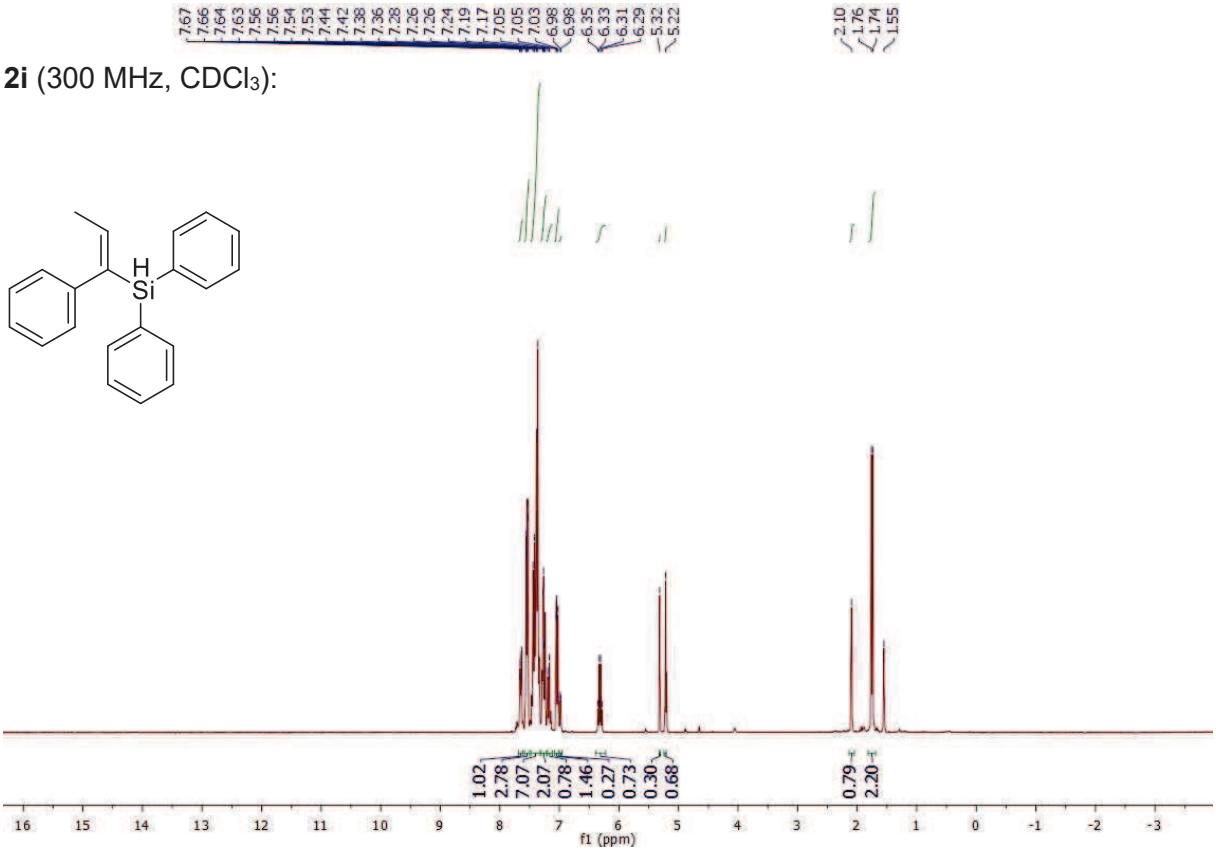
2h (300 MHz, $CDCl_3$):



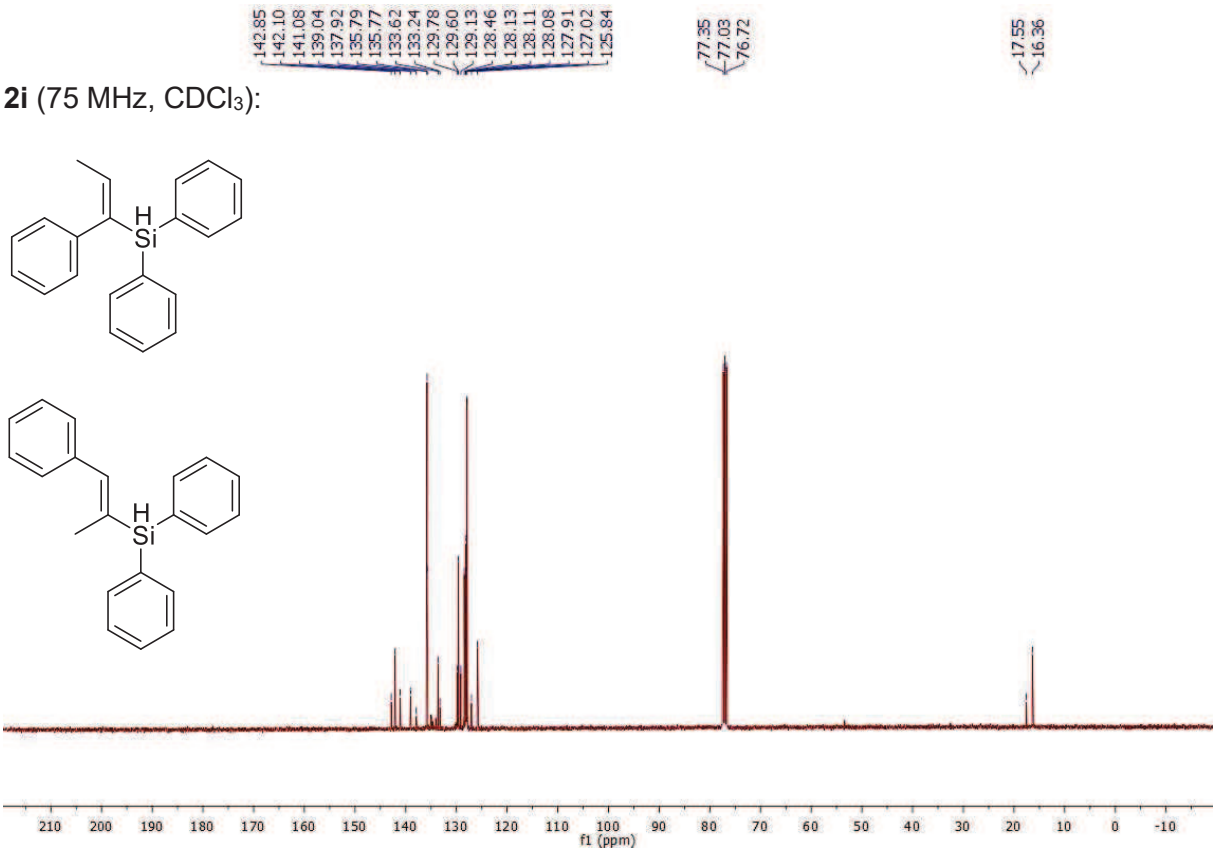
2h (75 MHz, $CDCl_3$):



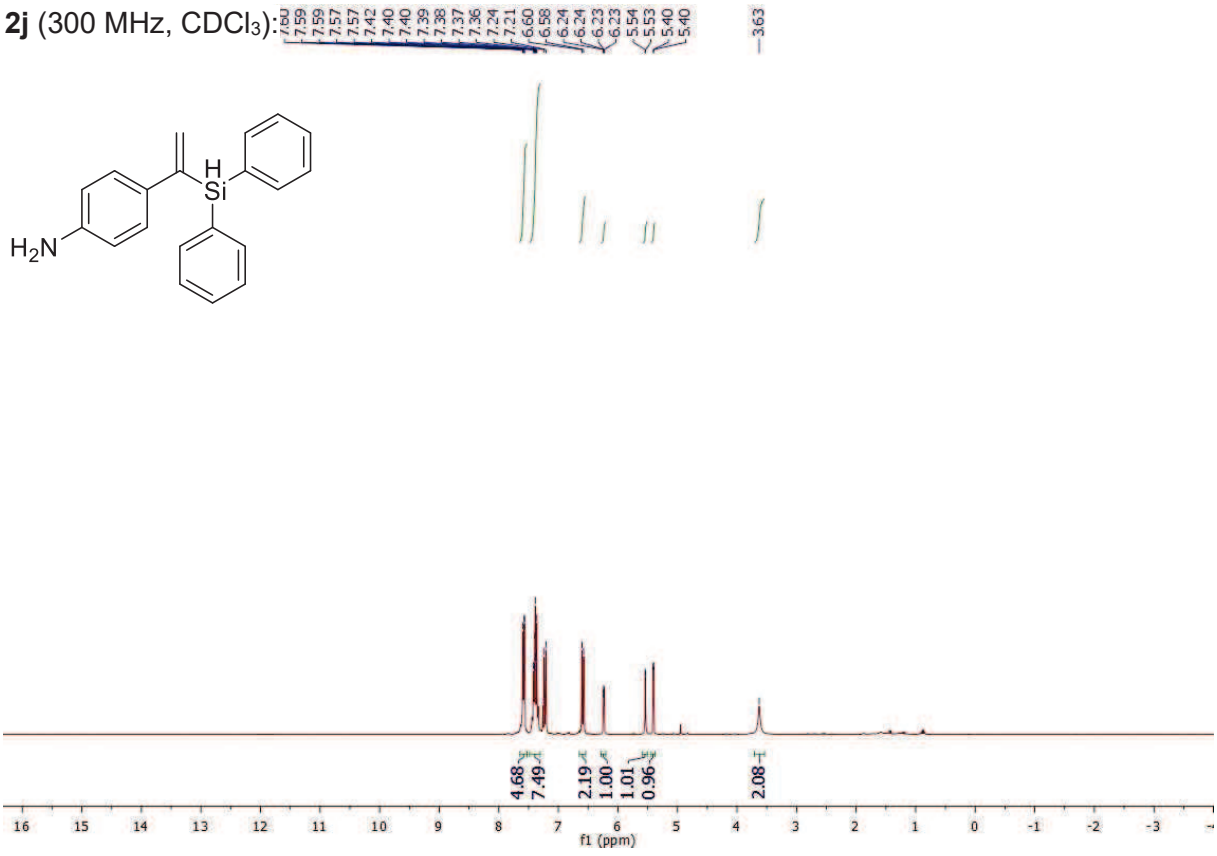
2i (300 MHz, $CDCl_3$):



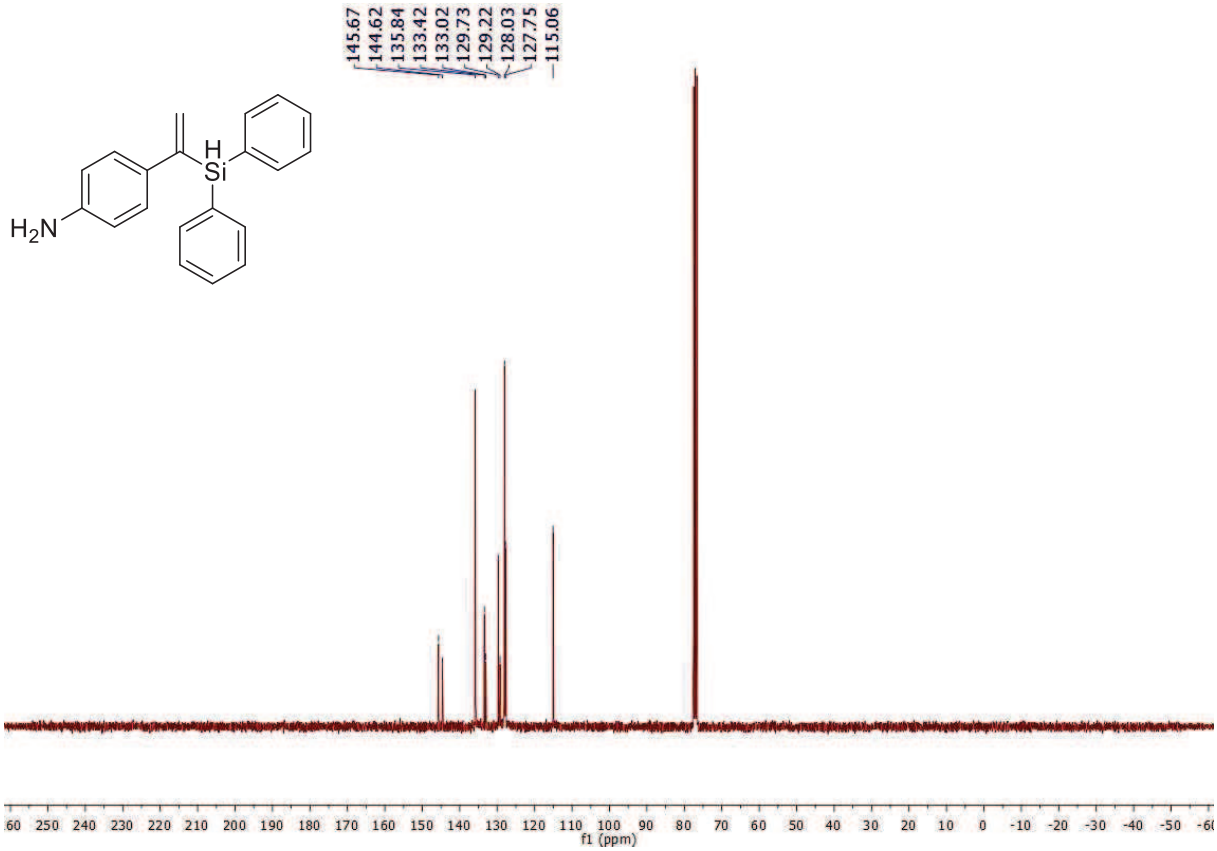
2i (75 MHz, $CDCl_3$):



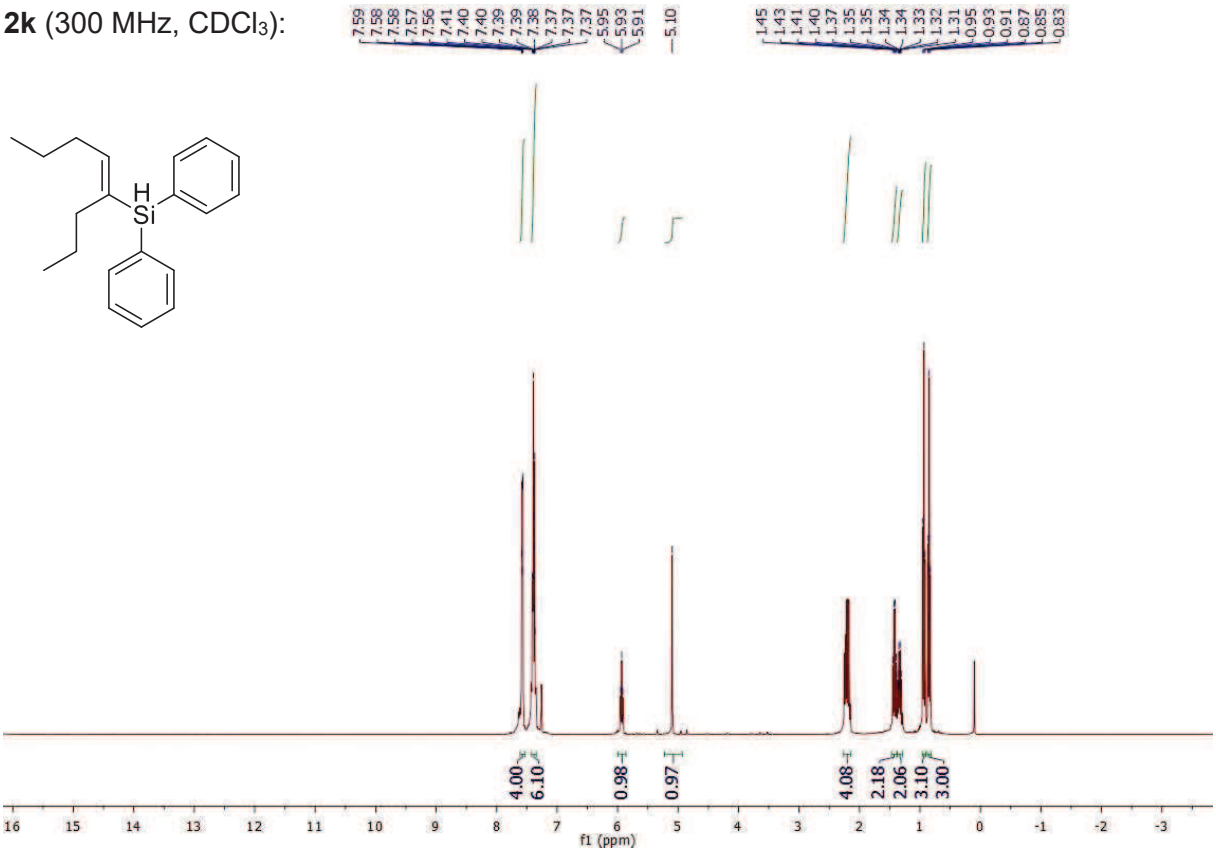
2j (300 MHz, $CDCl_3$):



2j (75 MHz, $CDCl_3$):



2k (300 MHz, $CDCl_3$):



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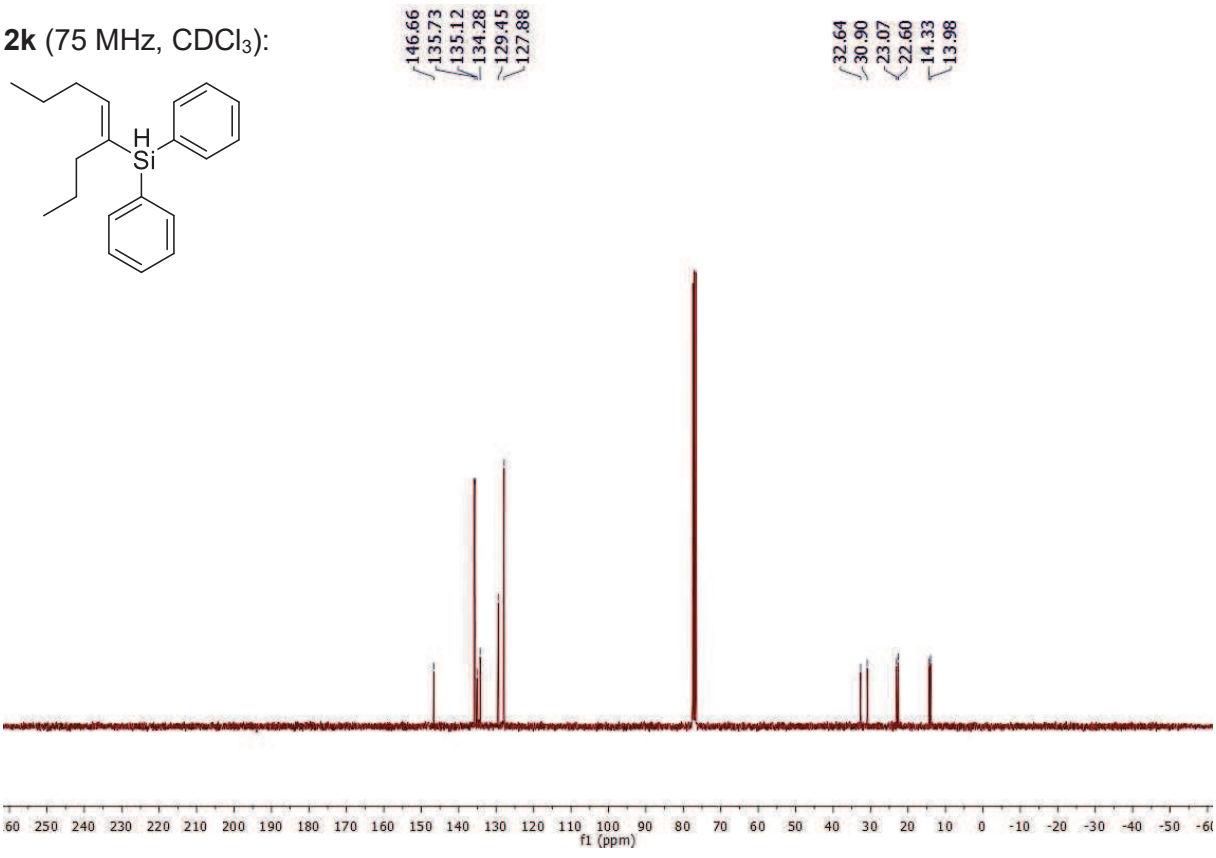
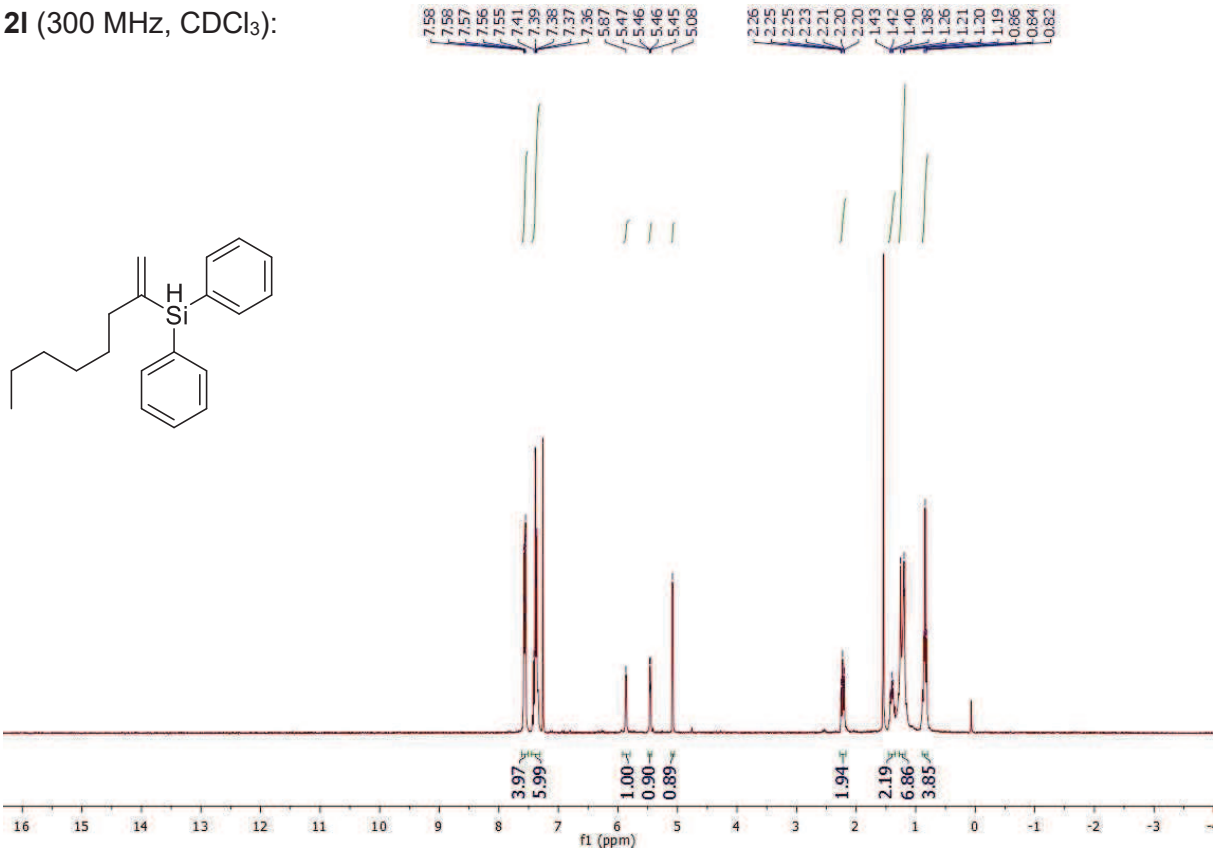
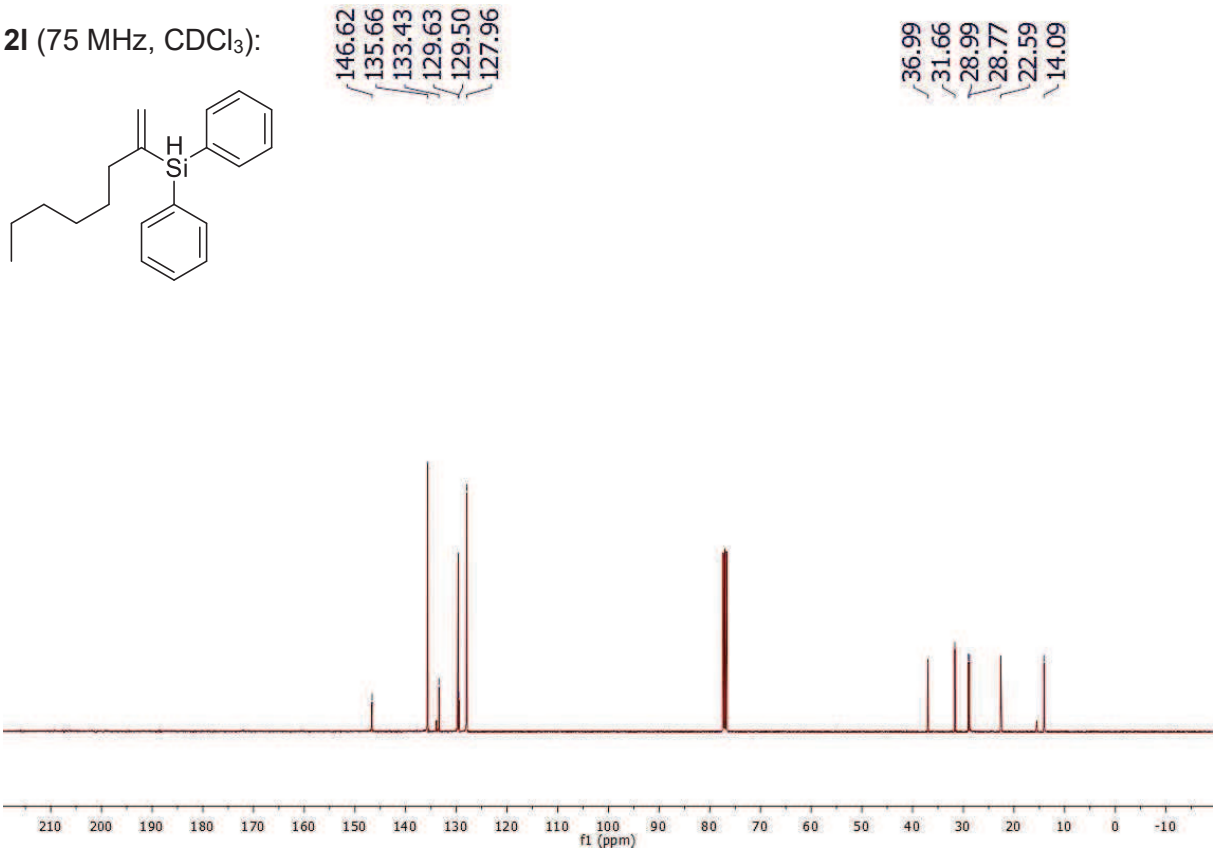


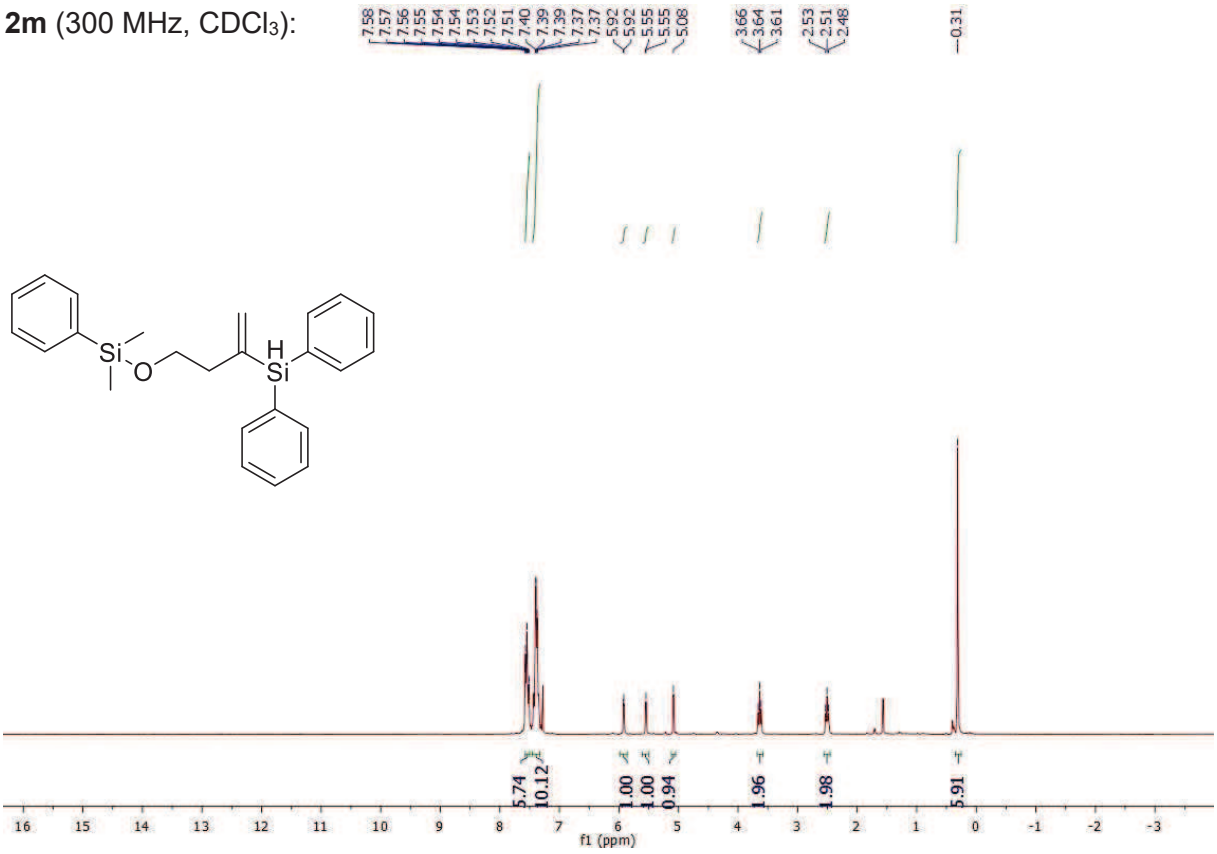
2l (300 MHz, $CDCl_3$):



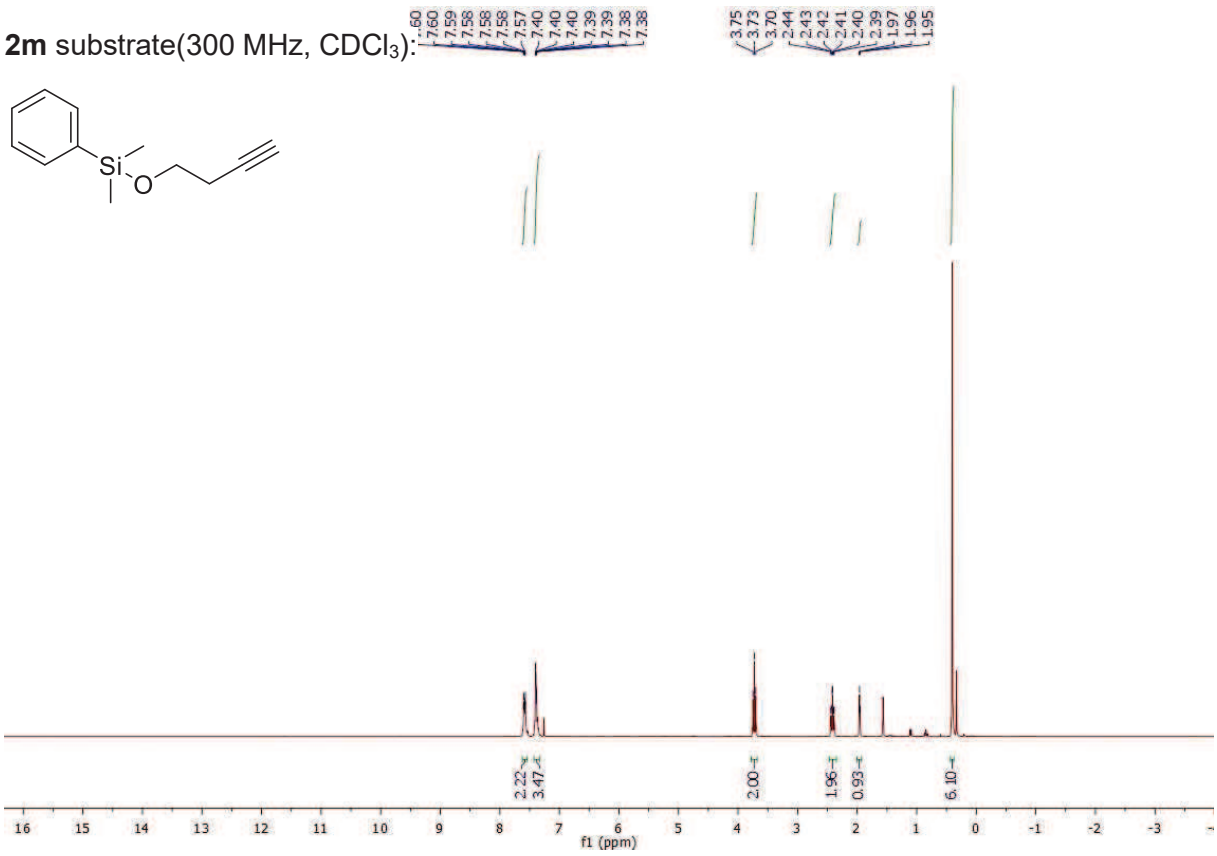
2l (75 MHz, $CDCl_3$):

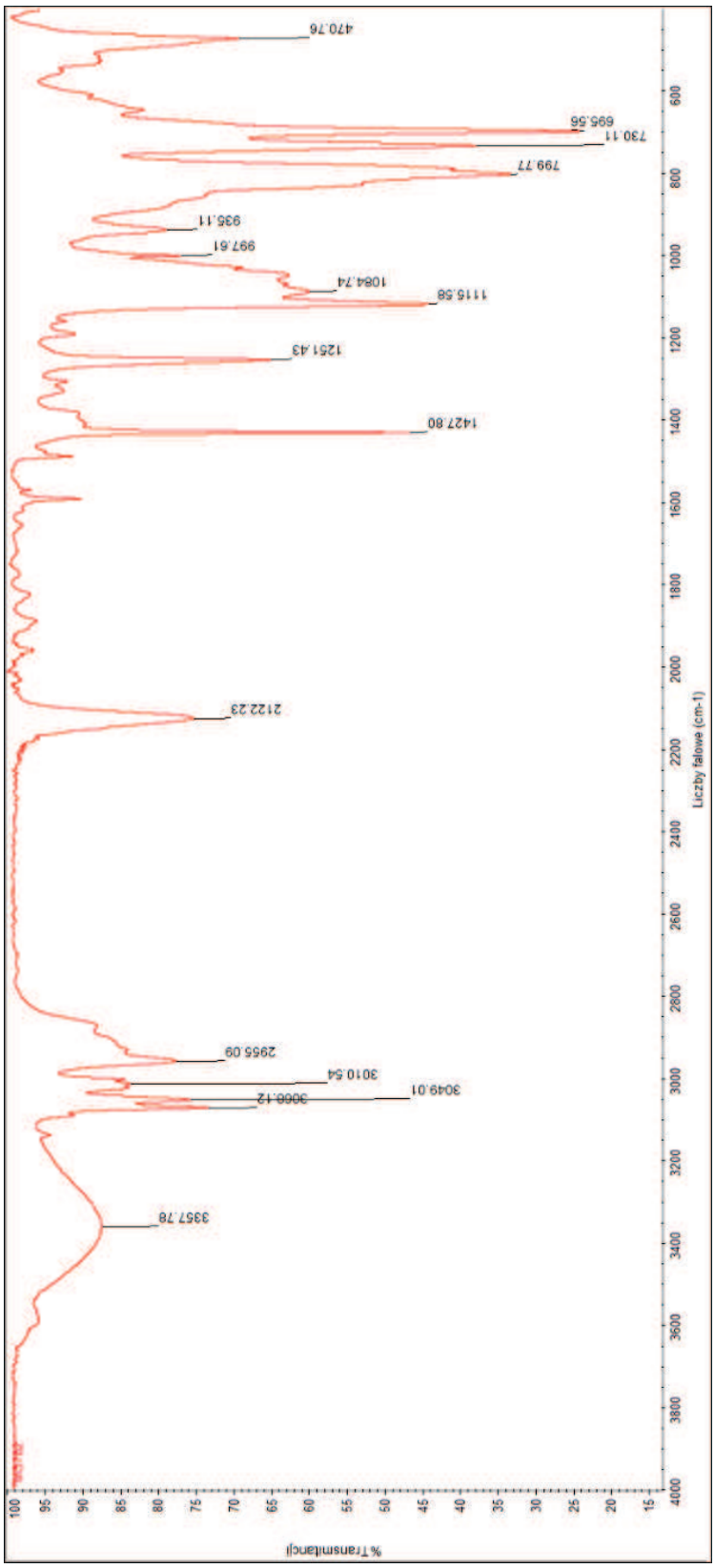


2m (300 MHz, $CDCl_3$):



2m substrate(300 MHz, $CDCl_3$):




470.76
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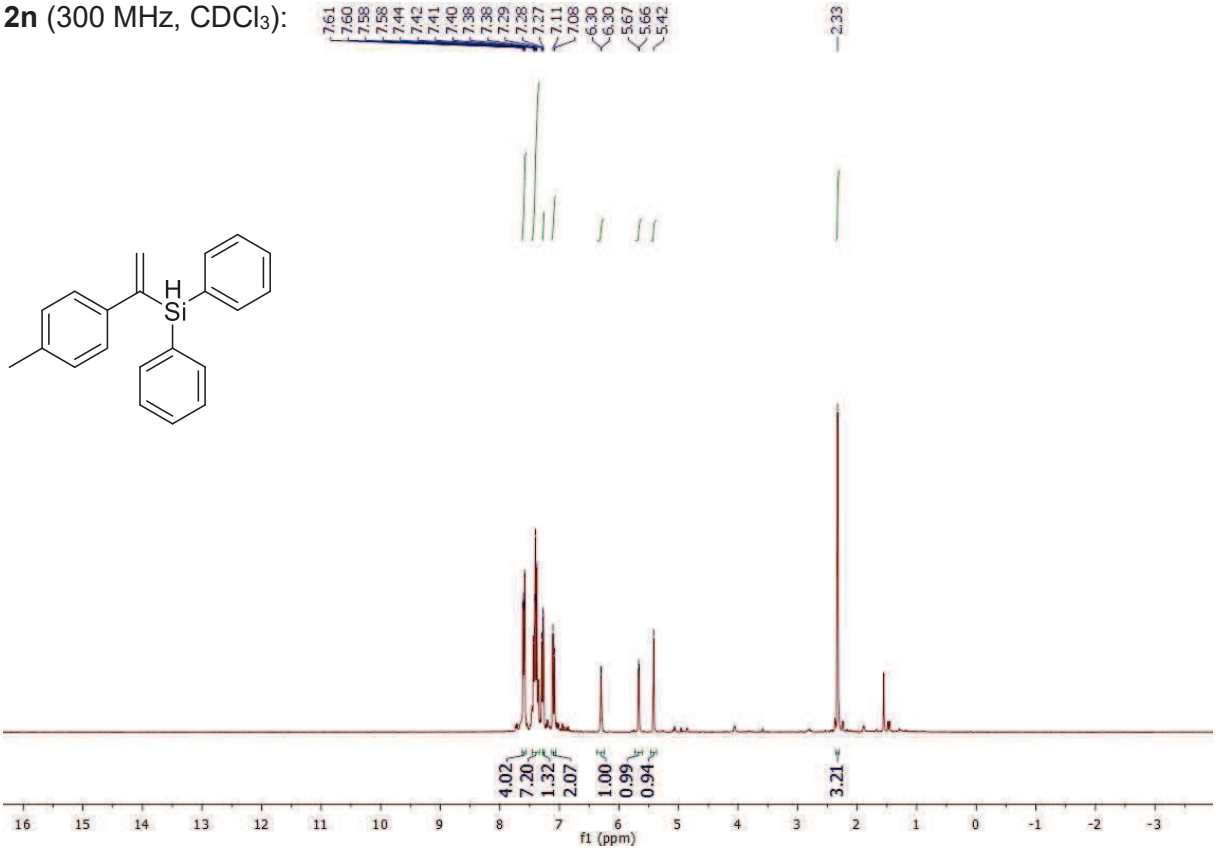
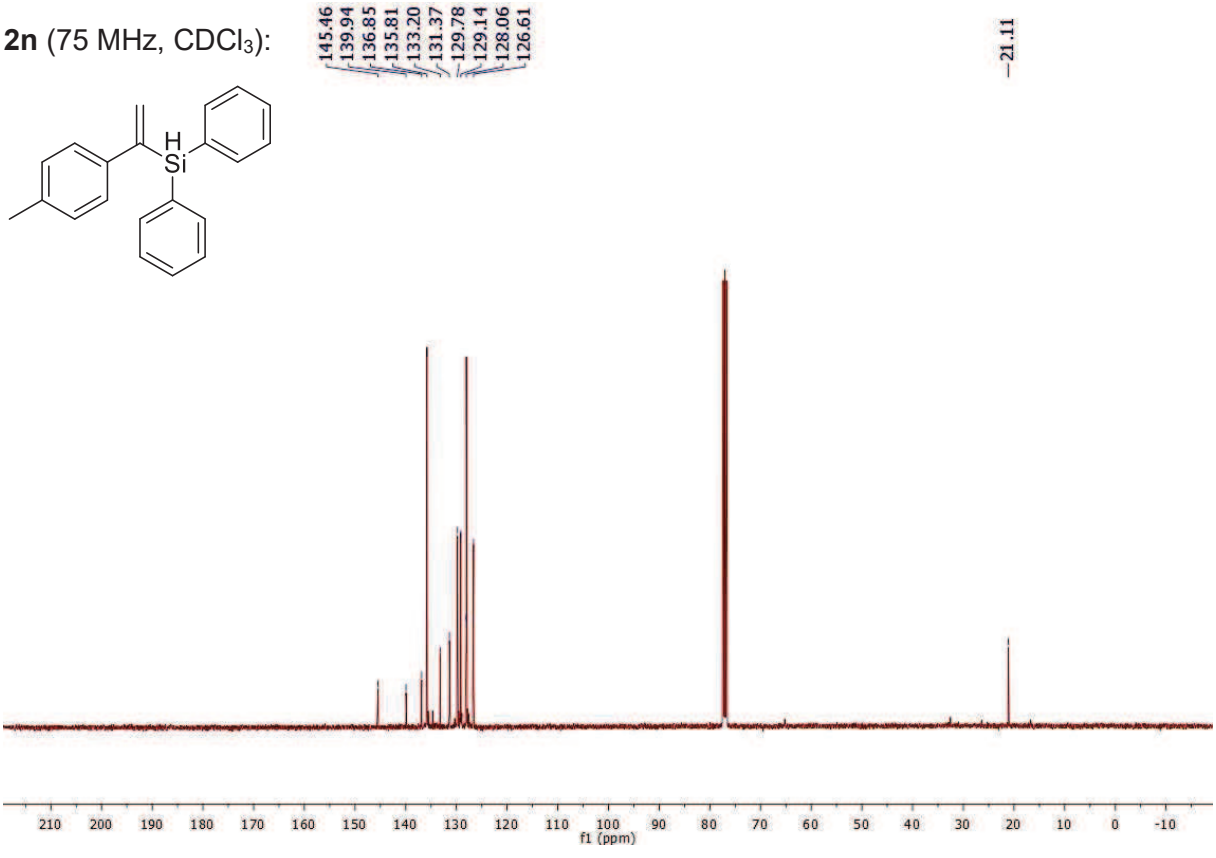
997.61
1084.74
1115.58
1251.43
1427.80
2122.23
2955.09
3010.54
3049.01
3066.12
3357.78
%Transmitancji
Liczby falowe (cm-1)

2m

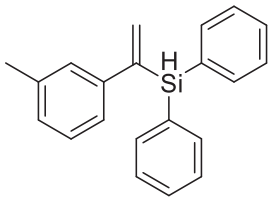
2n (300 MHz, $CDCl_3$):



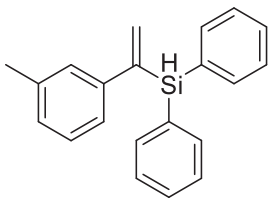
2n (75 MHz, $CDCl_3$):



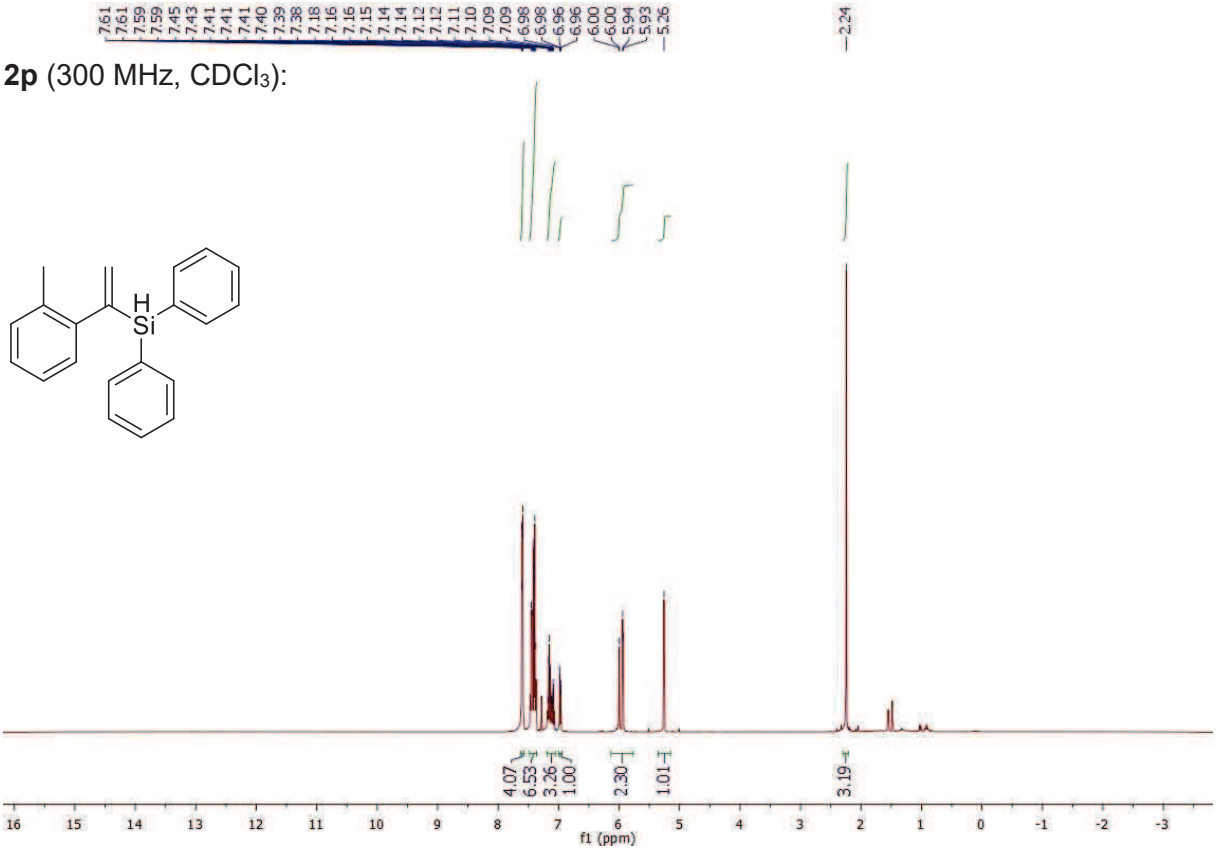
2o (300 MHz, $CDCl_3$):



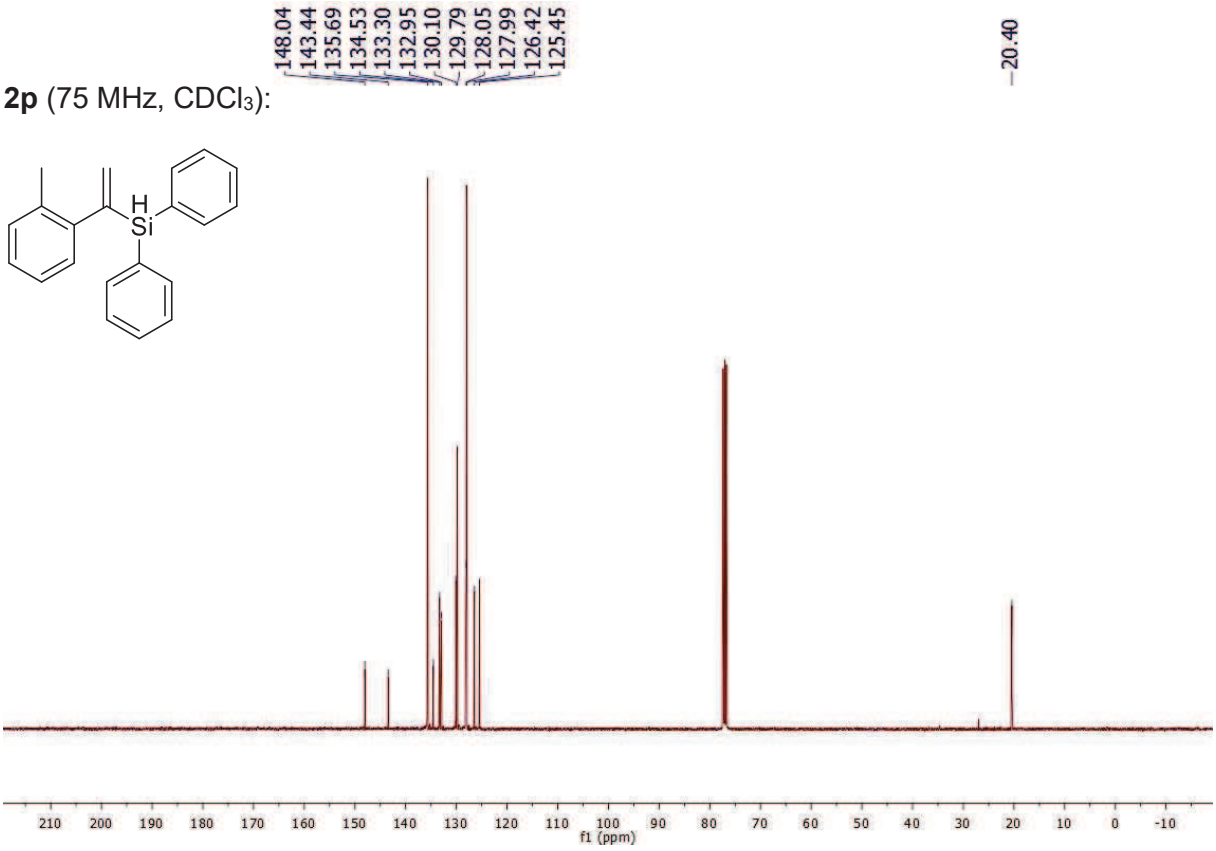
2o (75 MHz, $CDCl_3$):



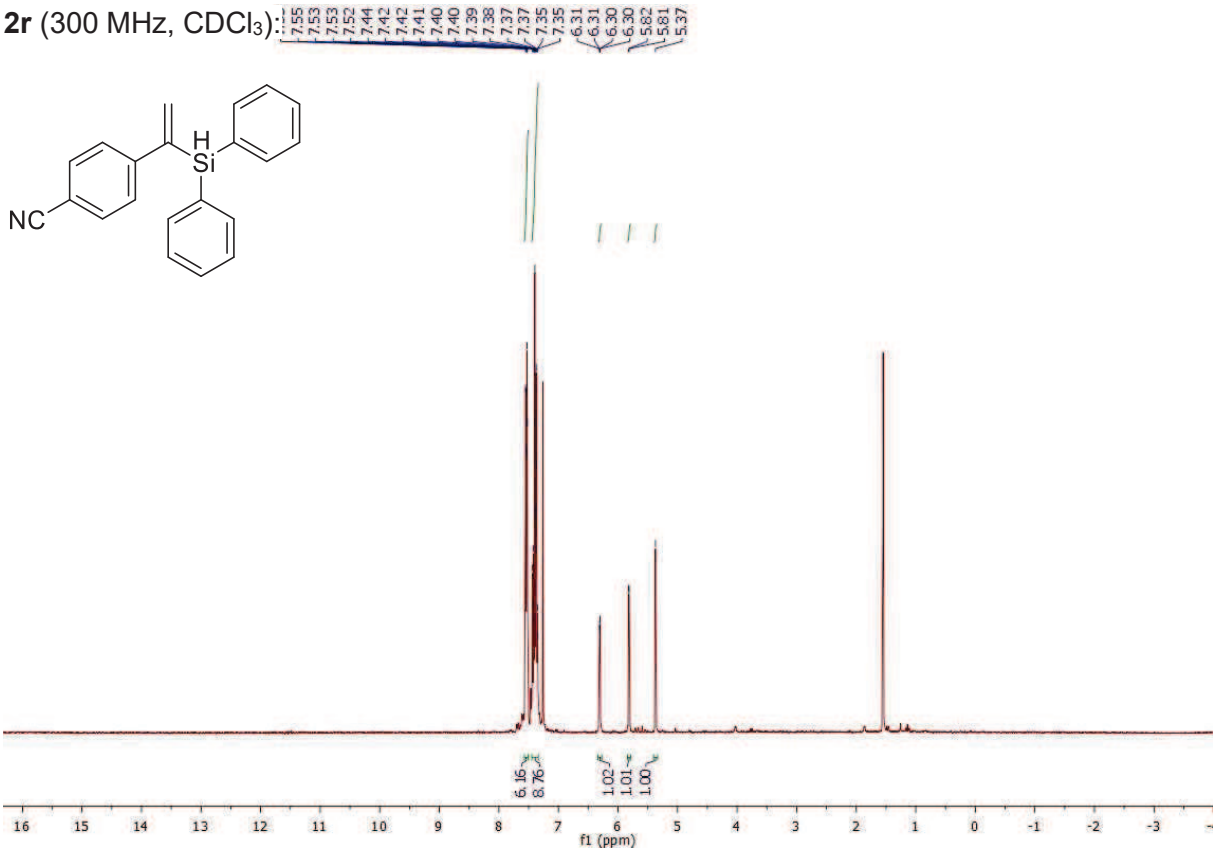
2p (300 MHz, $CDCl_3$):



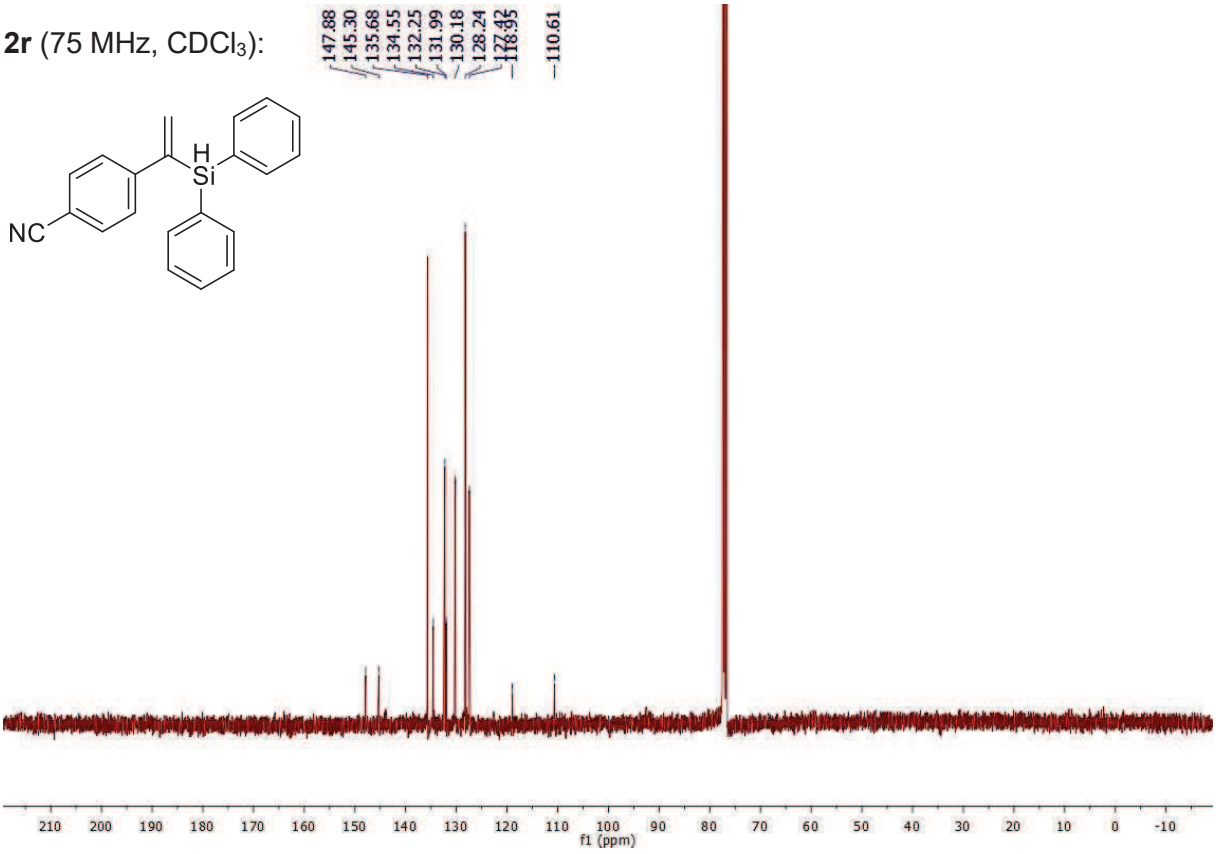
2p (75 MHz, $CDCl_3$):



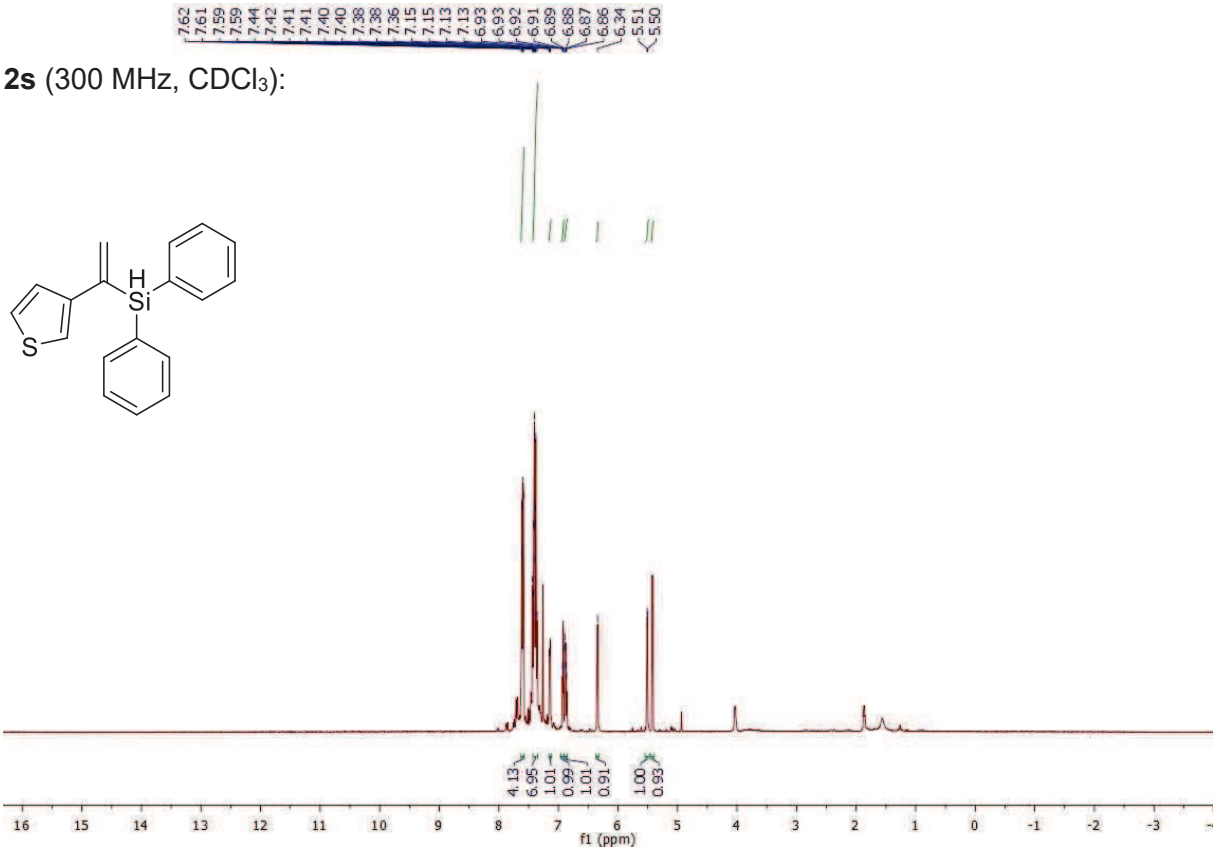
2r (300 MHz, $CDCl_3$):



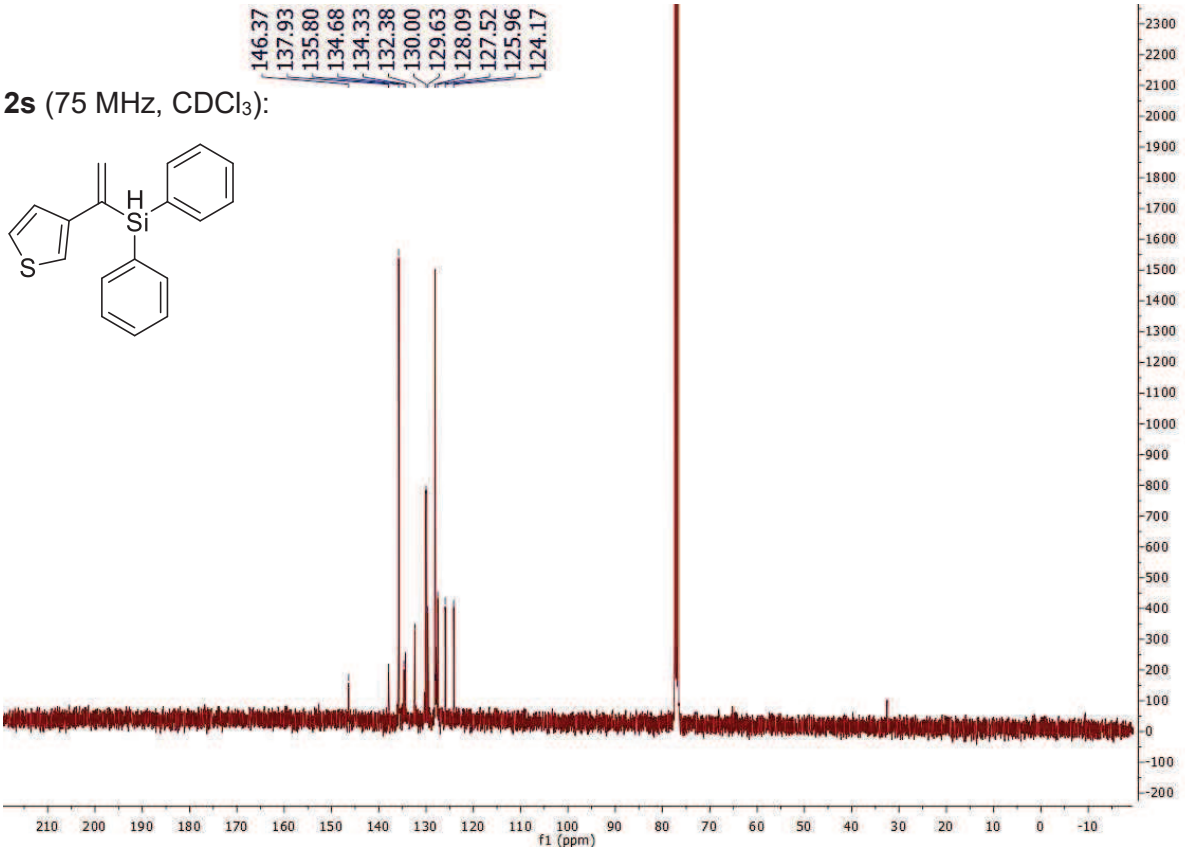
2r (75 MHz, $CDCl_3$):



2s (300 MHz, $CDCl_3$):



2s (75 MHz, $CDCl_3$):



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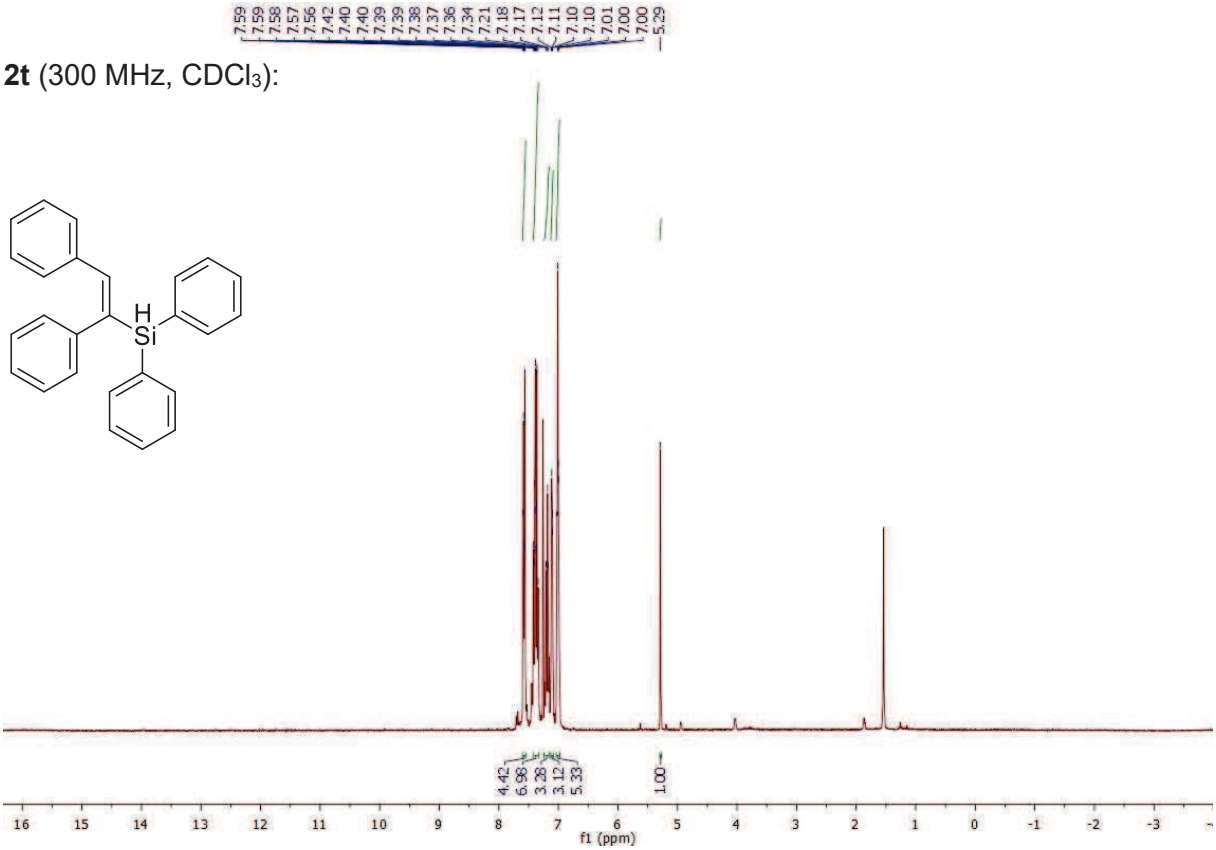

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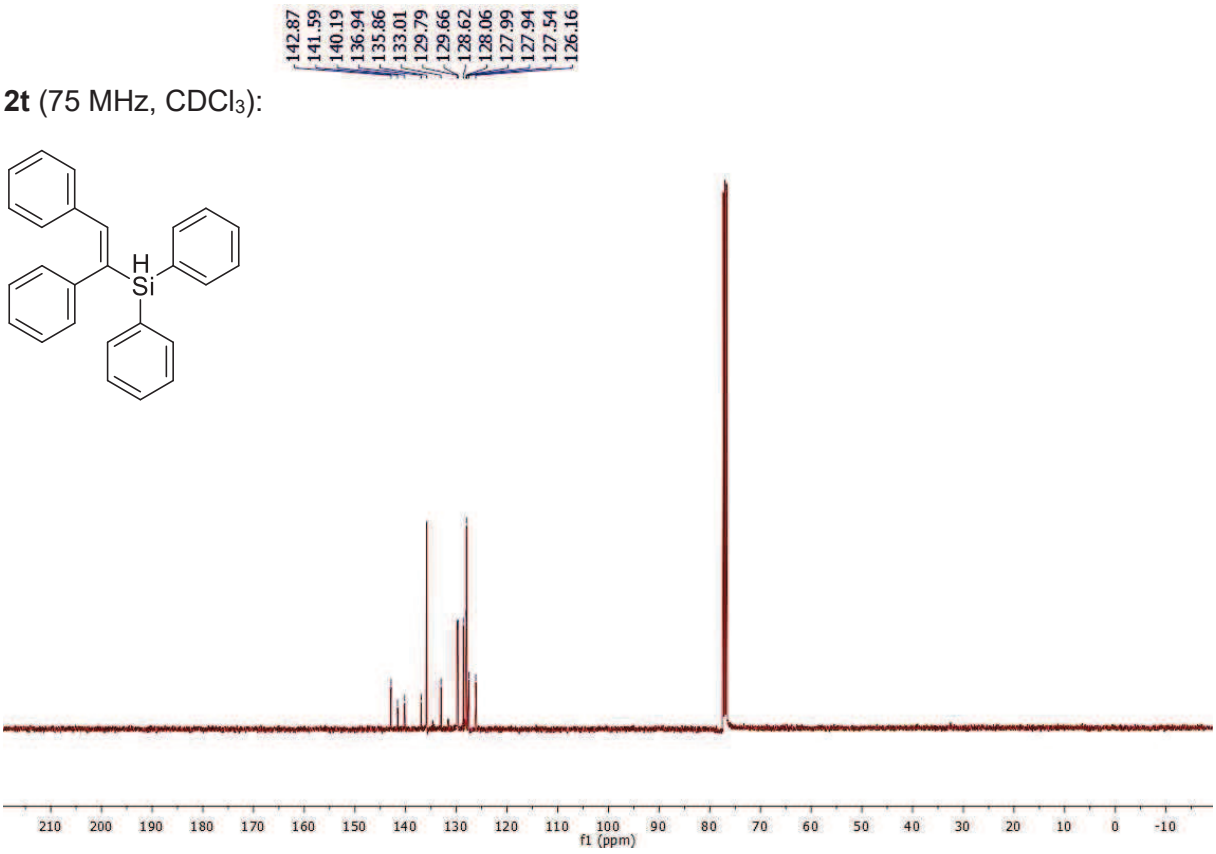
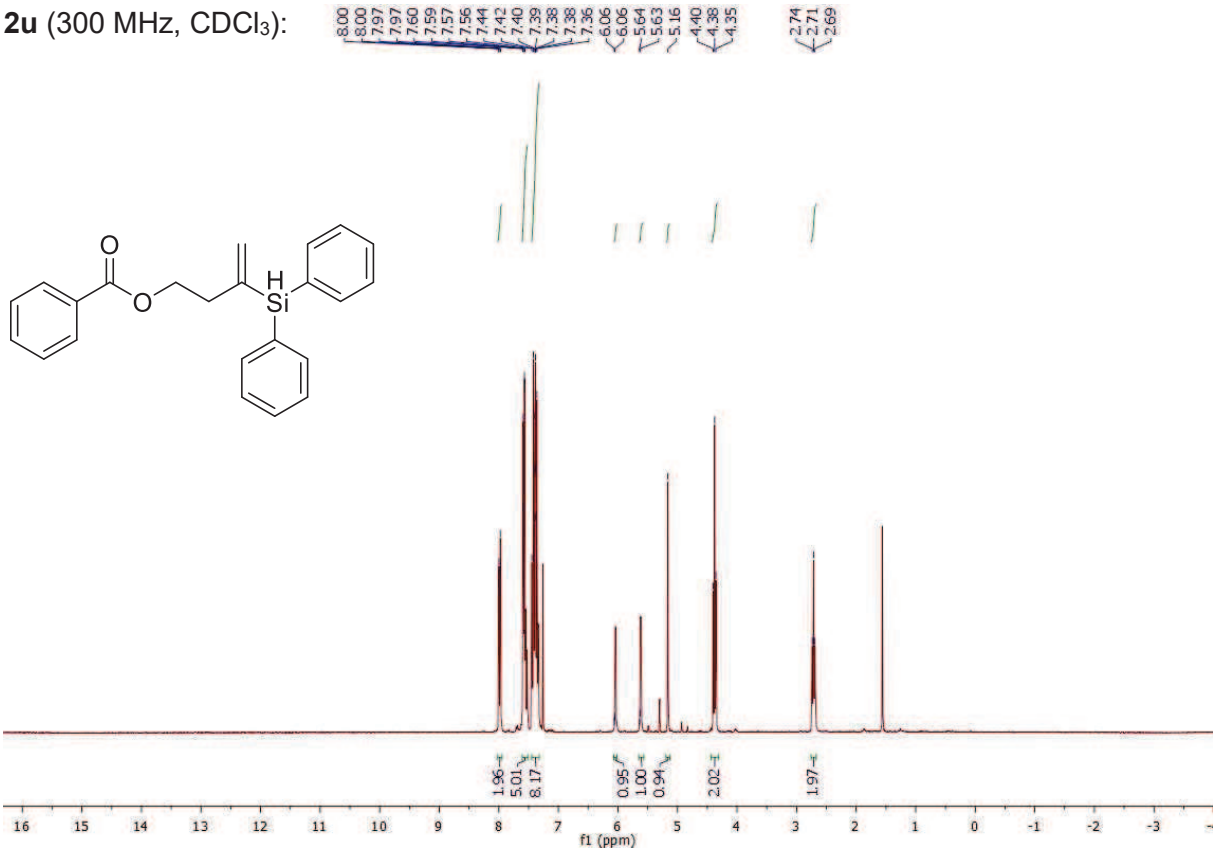
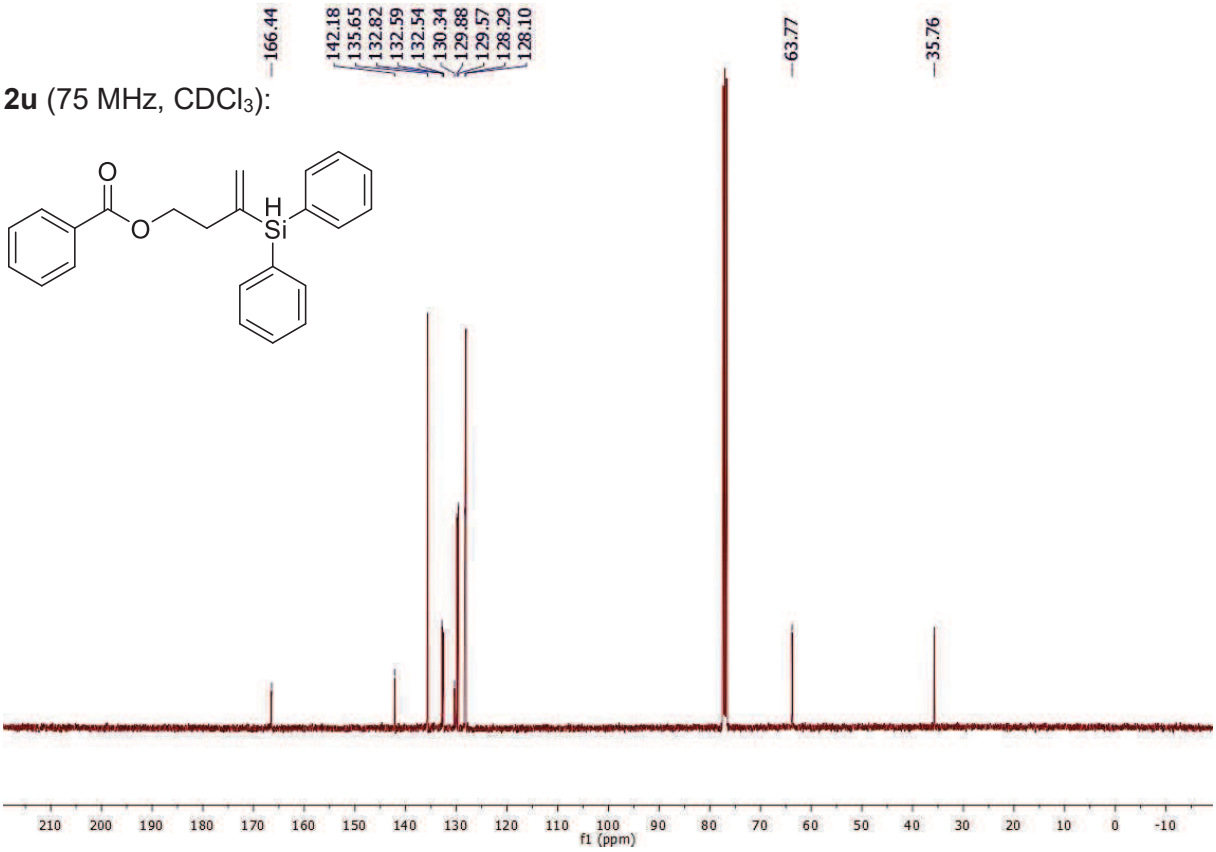
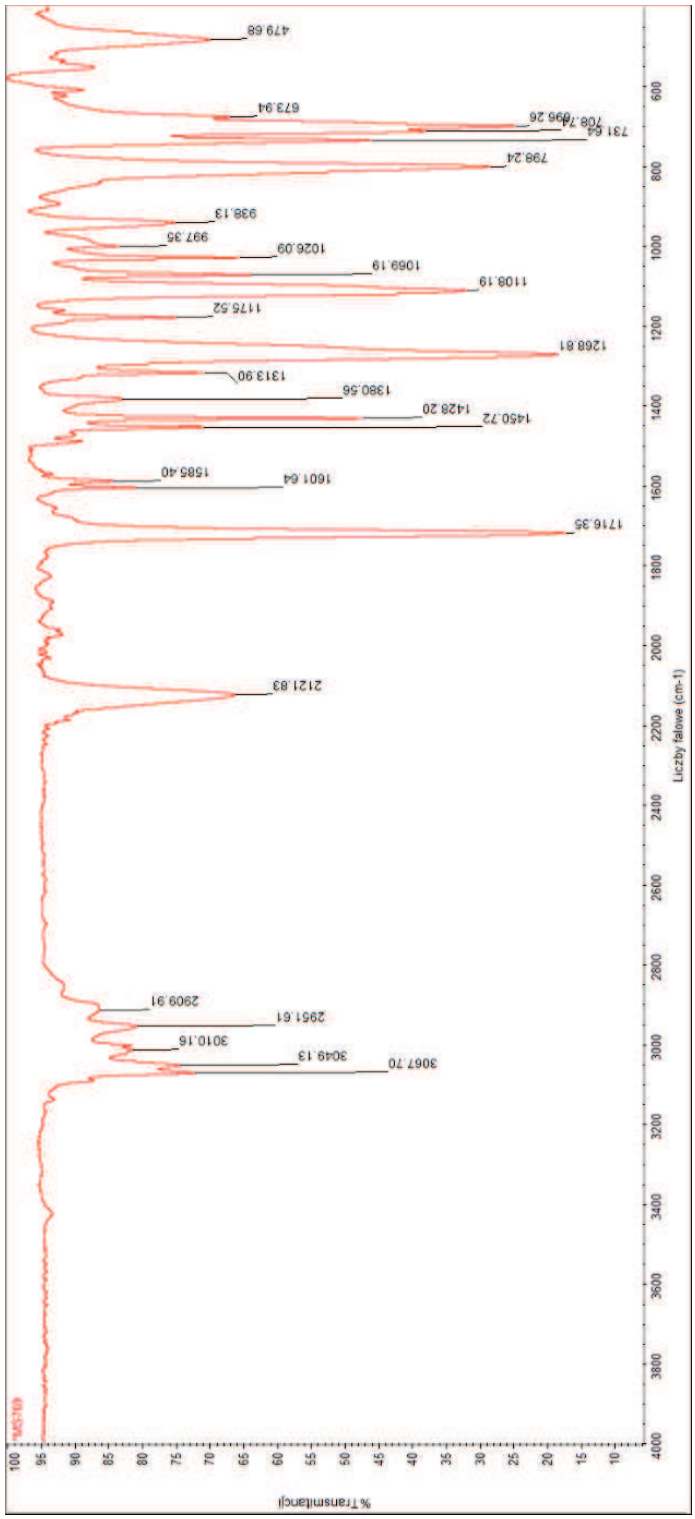


2u (300 MHz, $CDCl_3$):



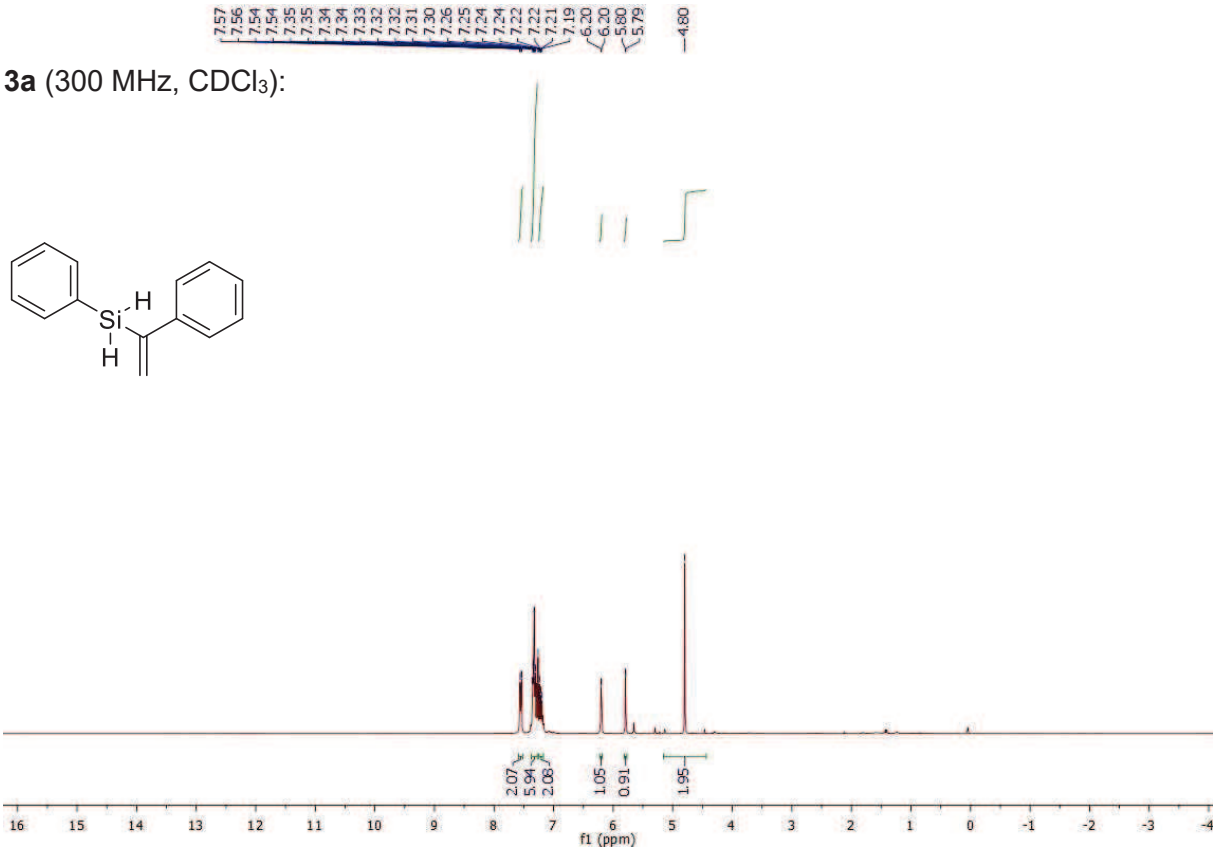
2u (75 MHz, $CDCl_3$):



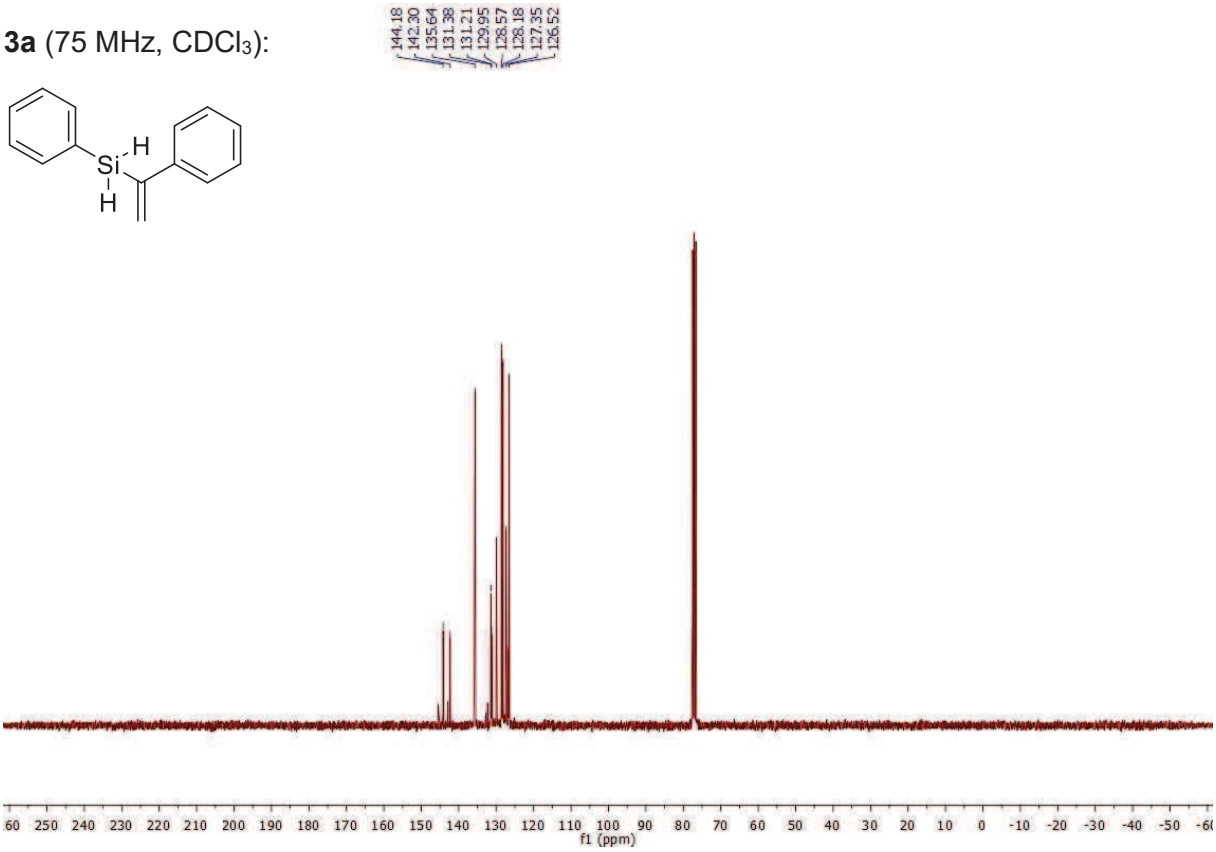

479.68
673.94
708.74
731.64
798.24
938.13
997.35
1026.09
1069.19
1108.19
1175.52
1268.81
1313.90
1380.56
1428.20
1450.72
1585.40
1601.64
1716.35
2121.83
2909.91
2951.61
3010.16
3049.13
3067.70
%Transmitancji
Liczby falowe (cm-1)

2u

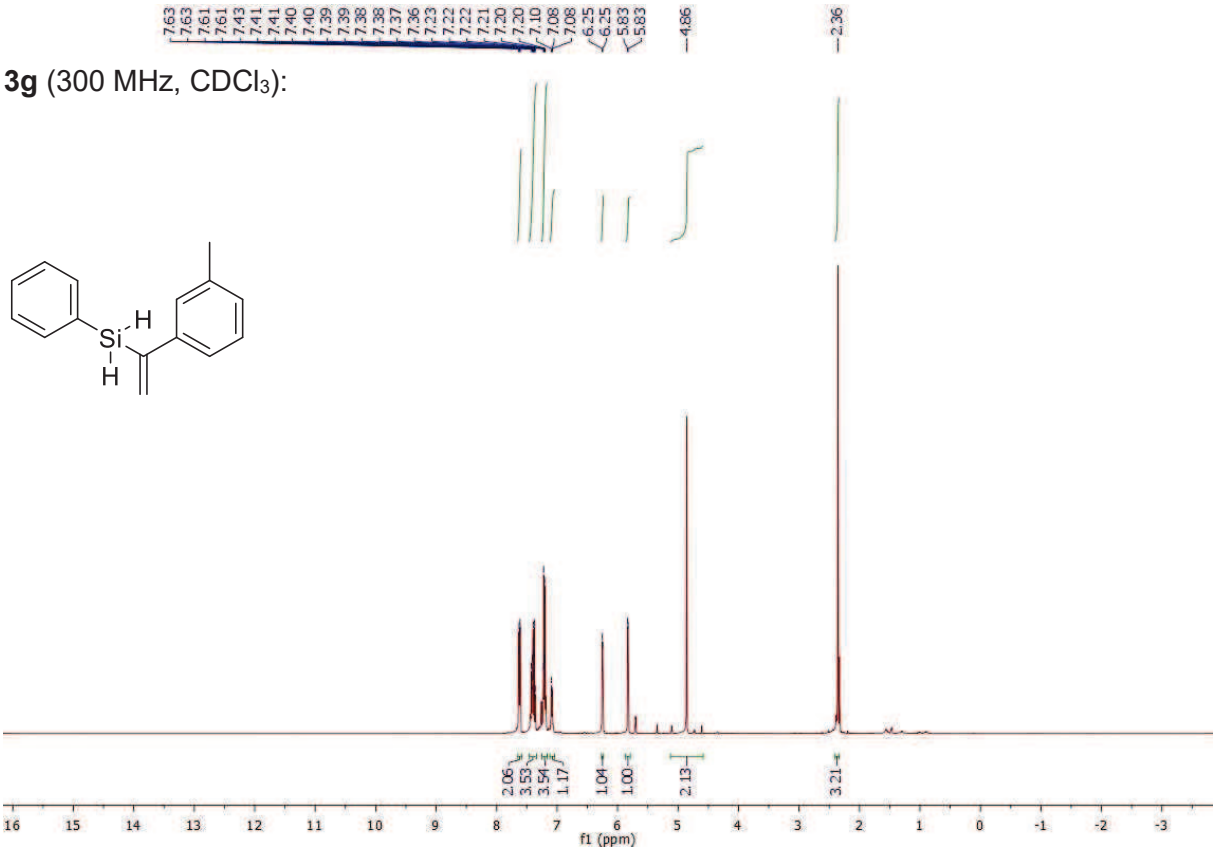
3a (300 MHz, $CDCl_3$):



3a (75 MHz, $CDCl_3$):



3g (300 MHz, $CDCl_3$):



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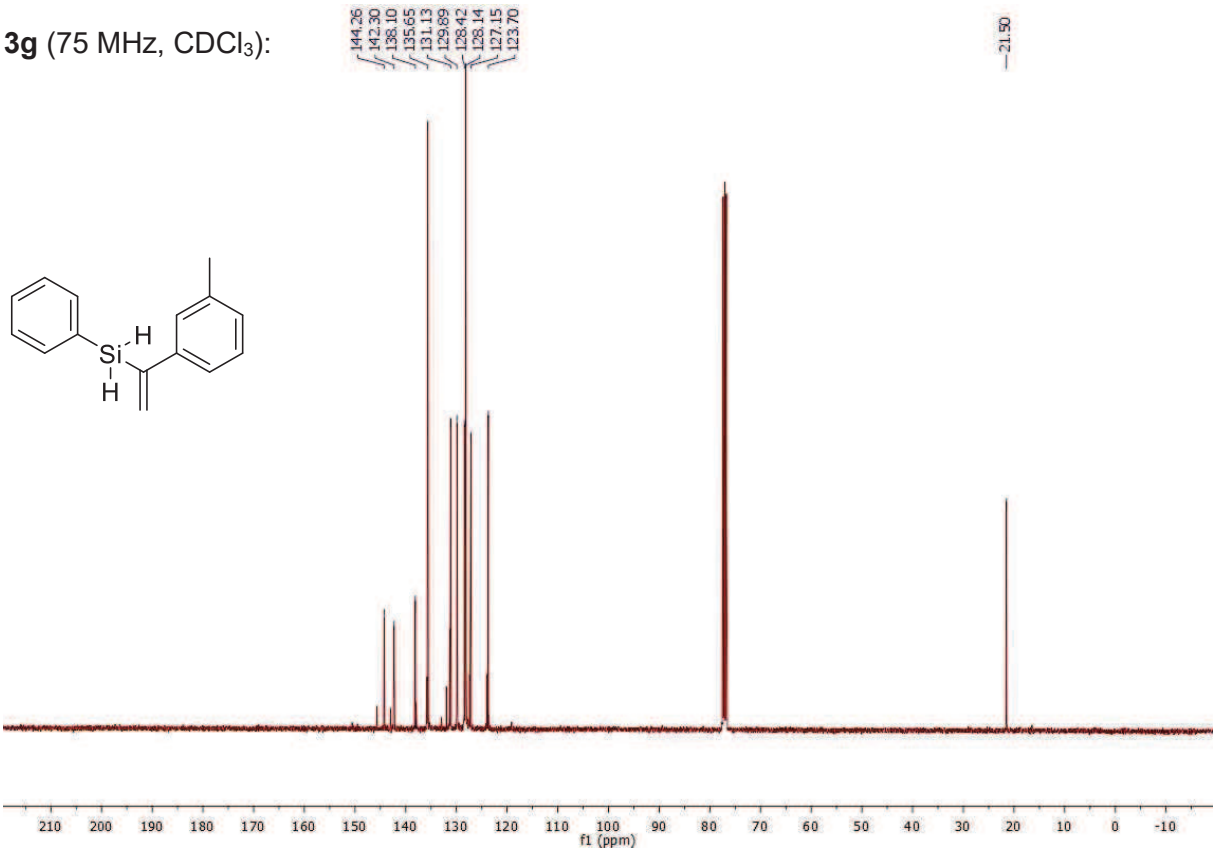
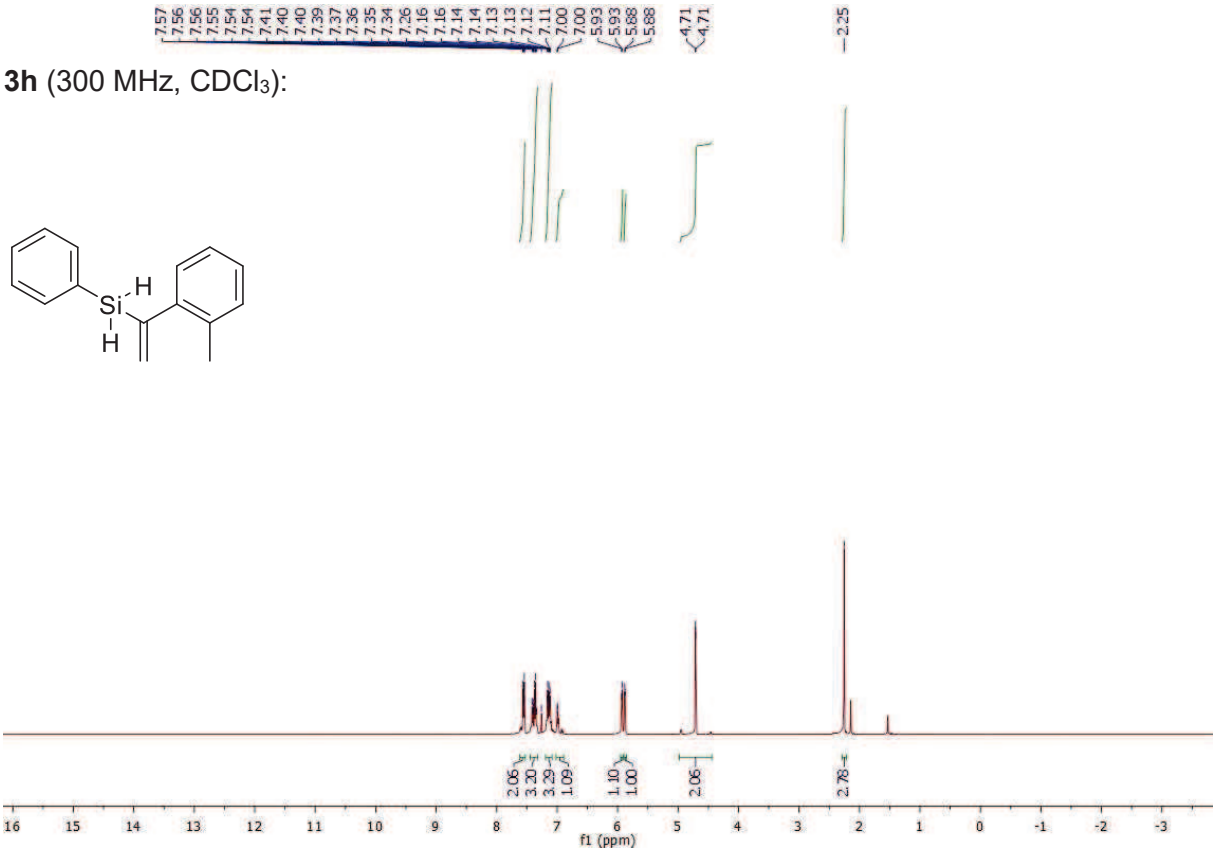
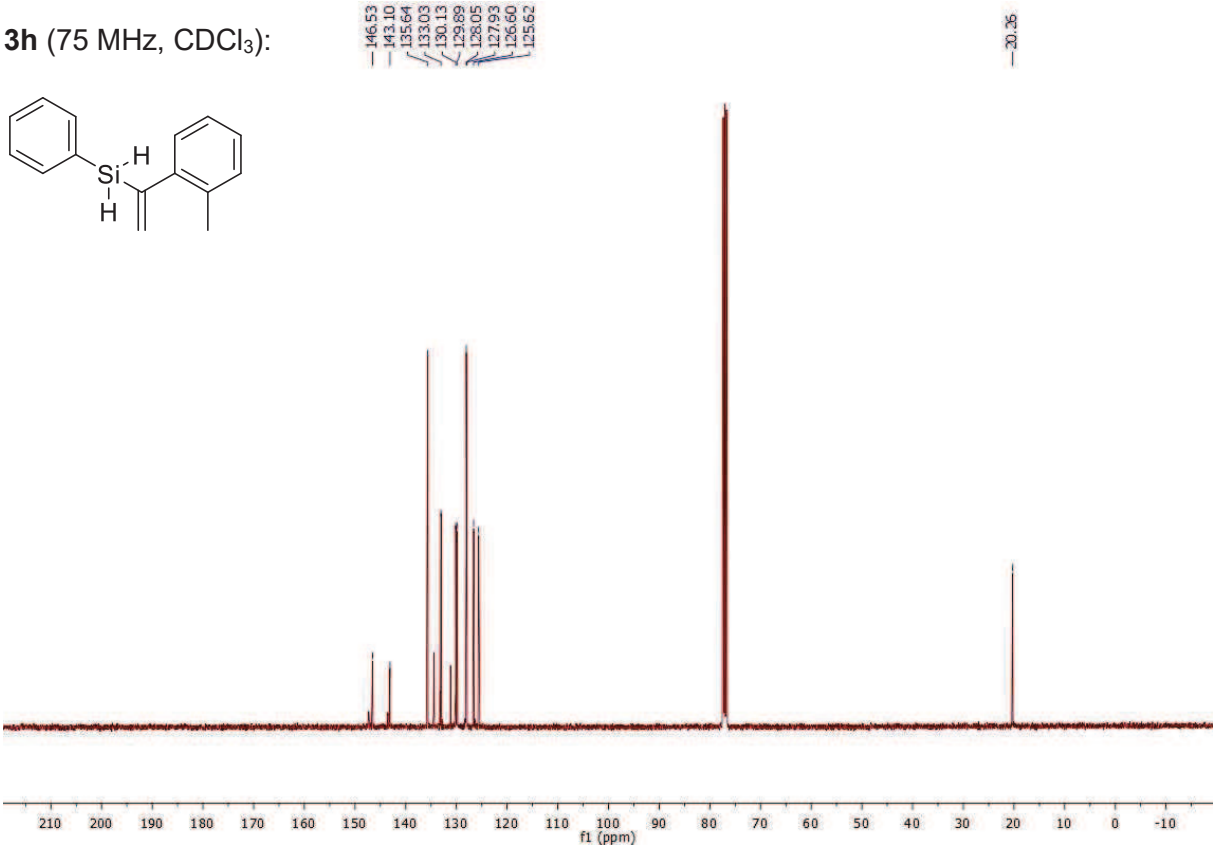


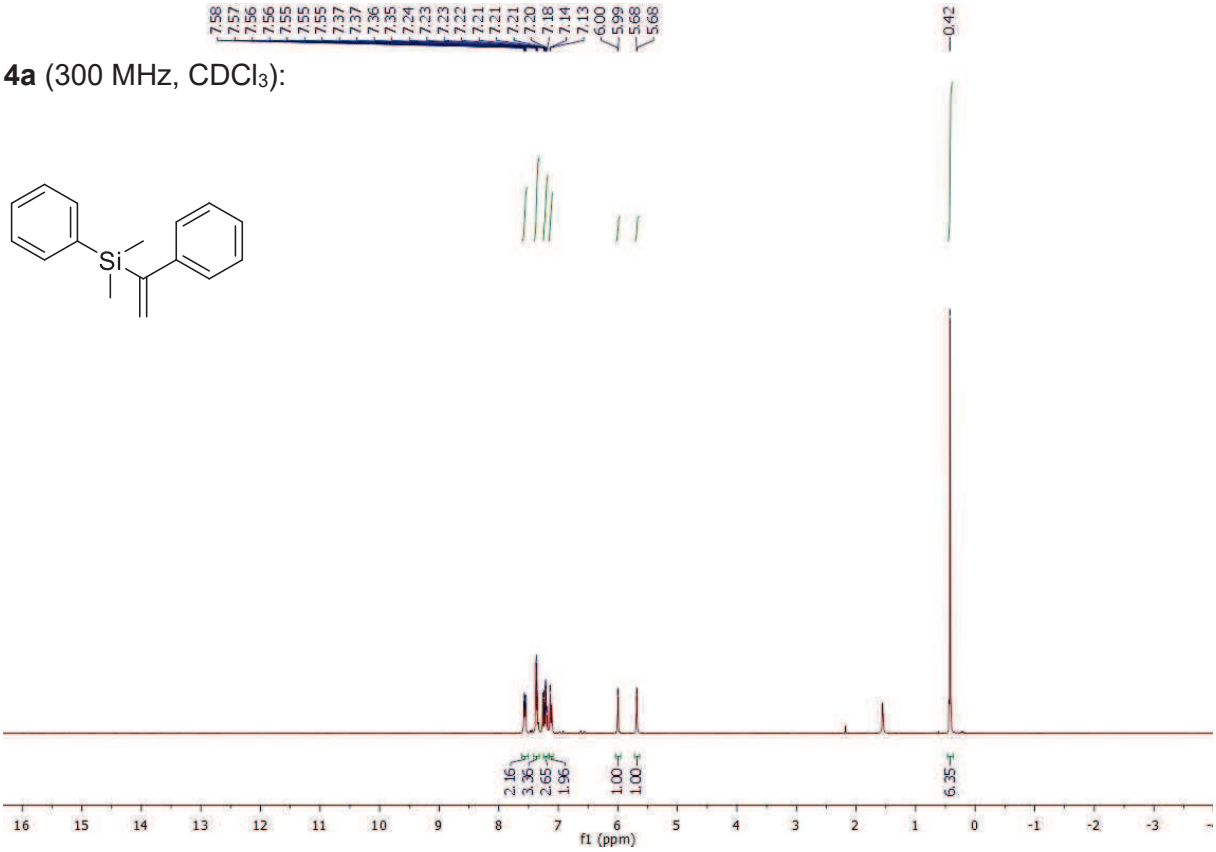
3h (300 MHz, $CDCl_3$):



3h (75 MHz, $CDCl_3$):



4a (300 MHz, $CDCl_3$):



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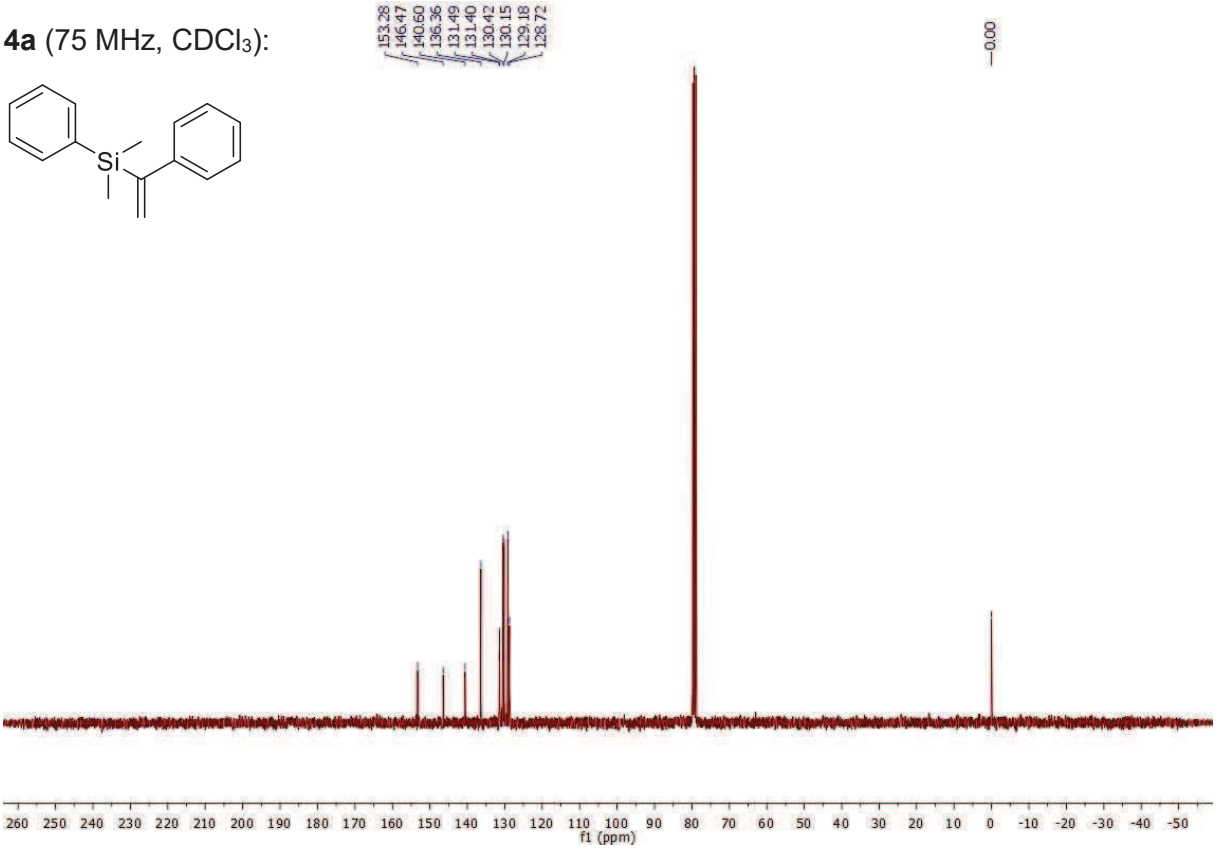

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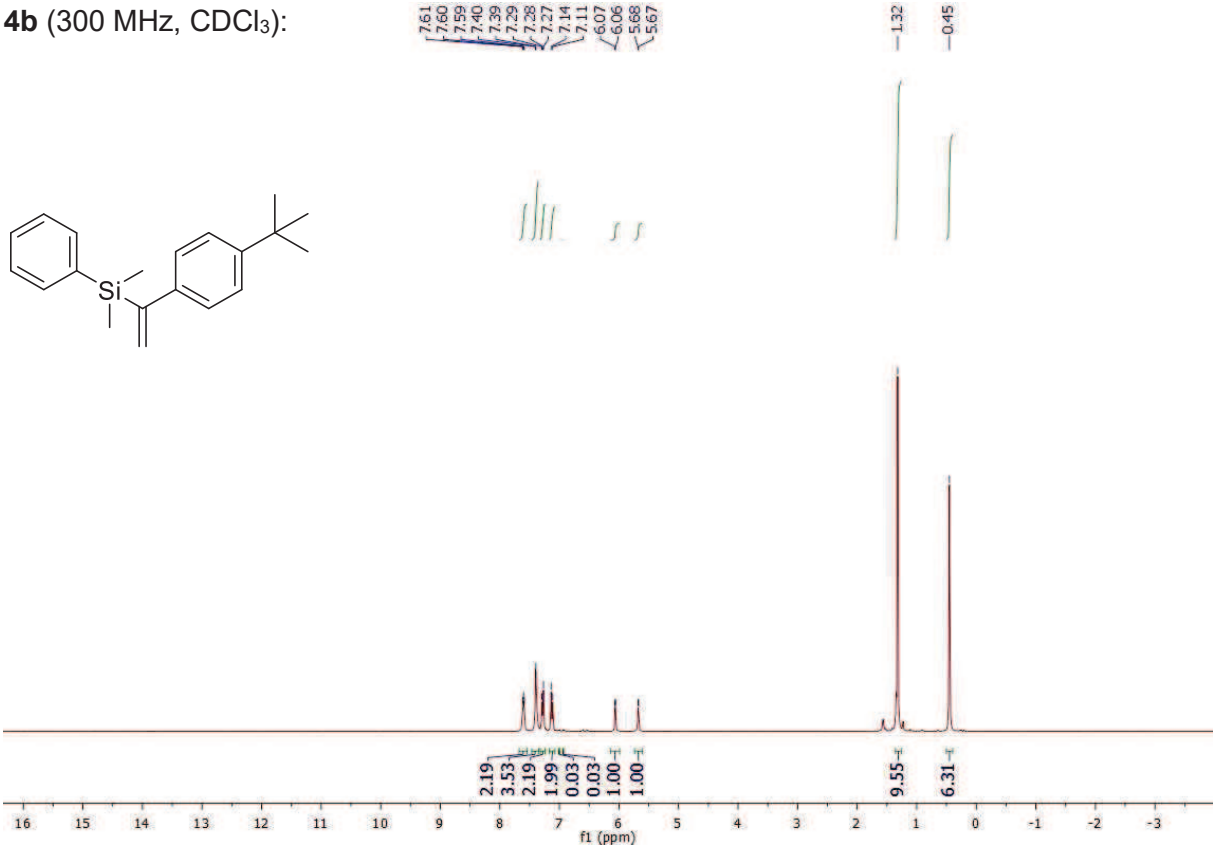

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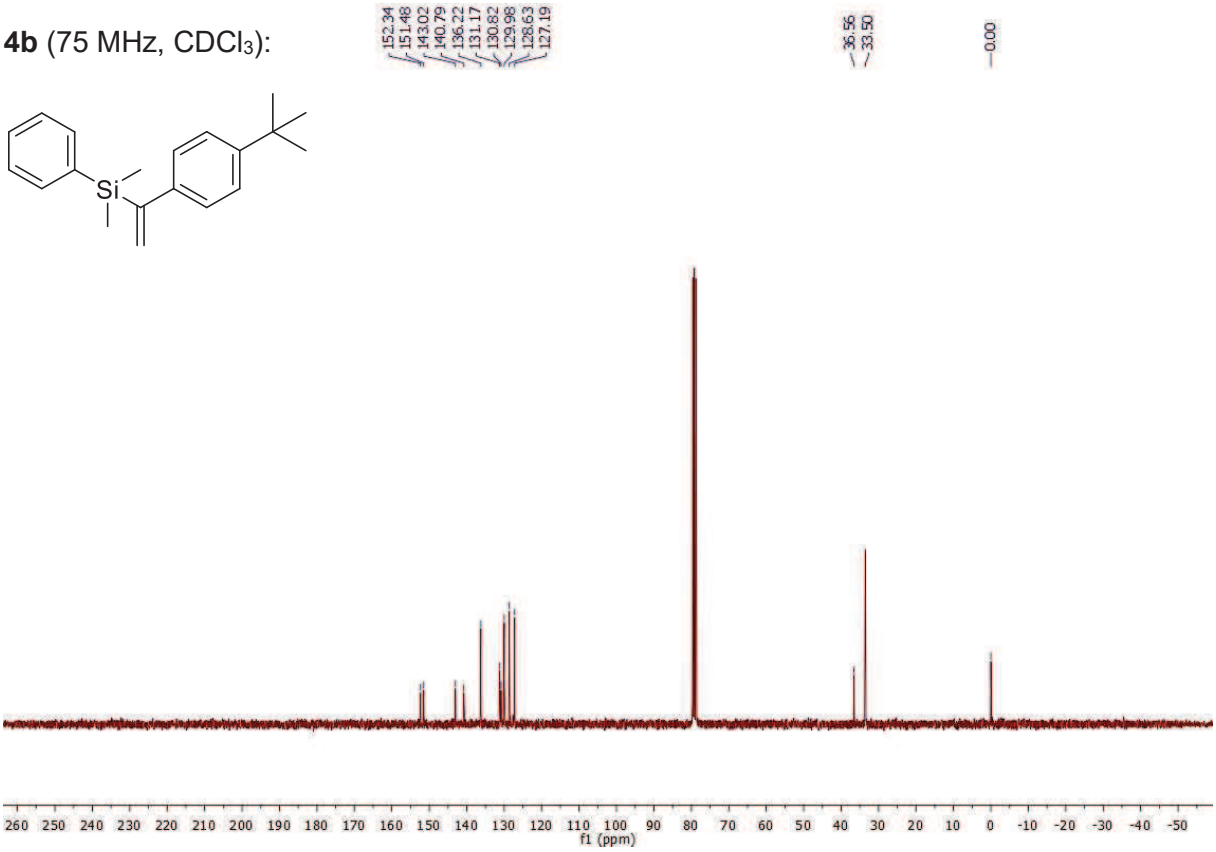

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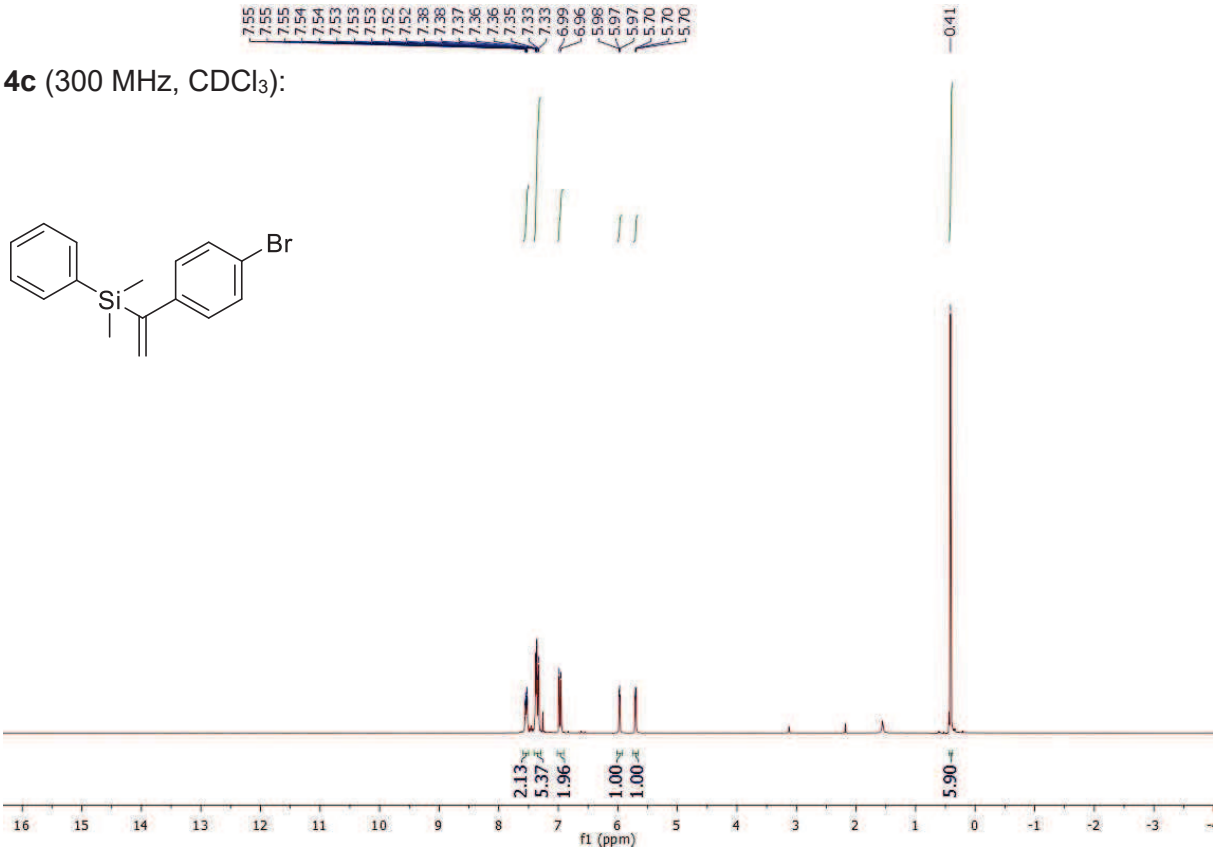

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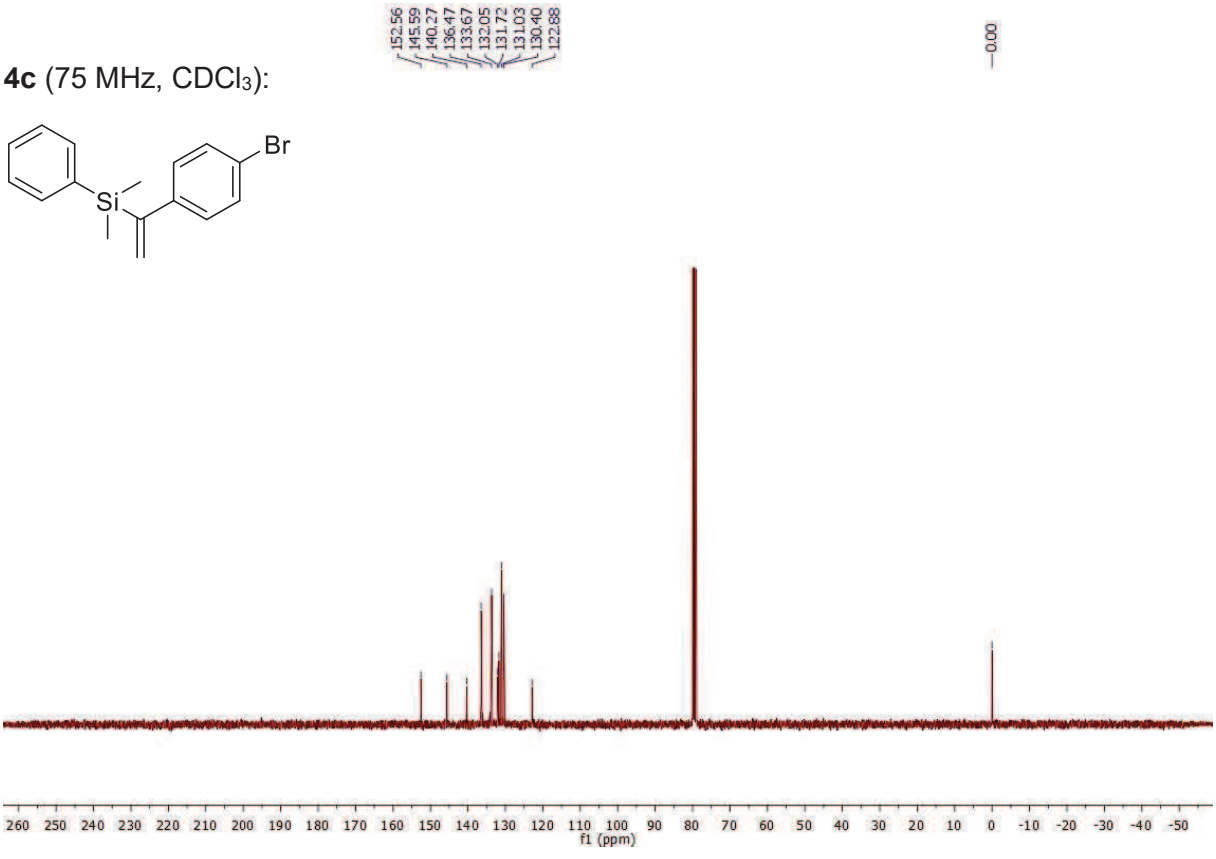

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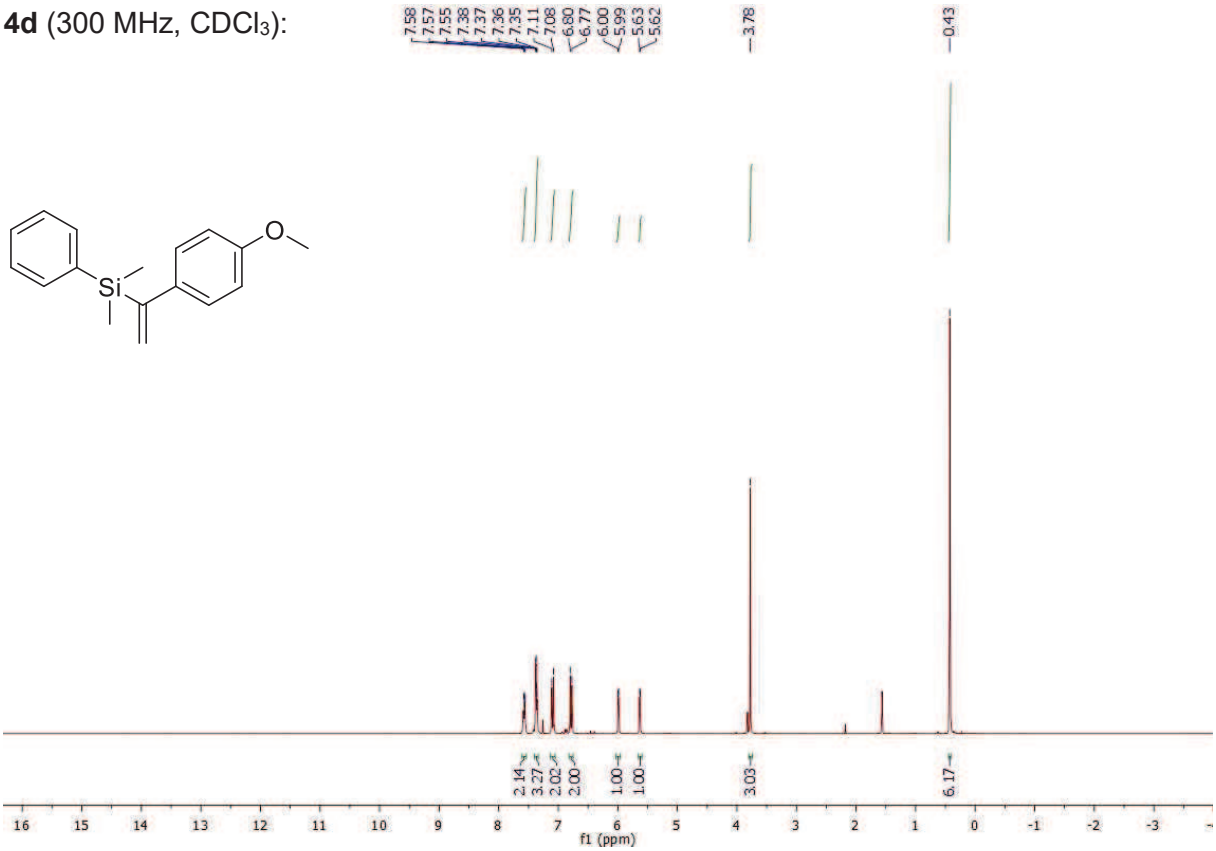
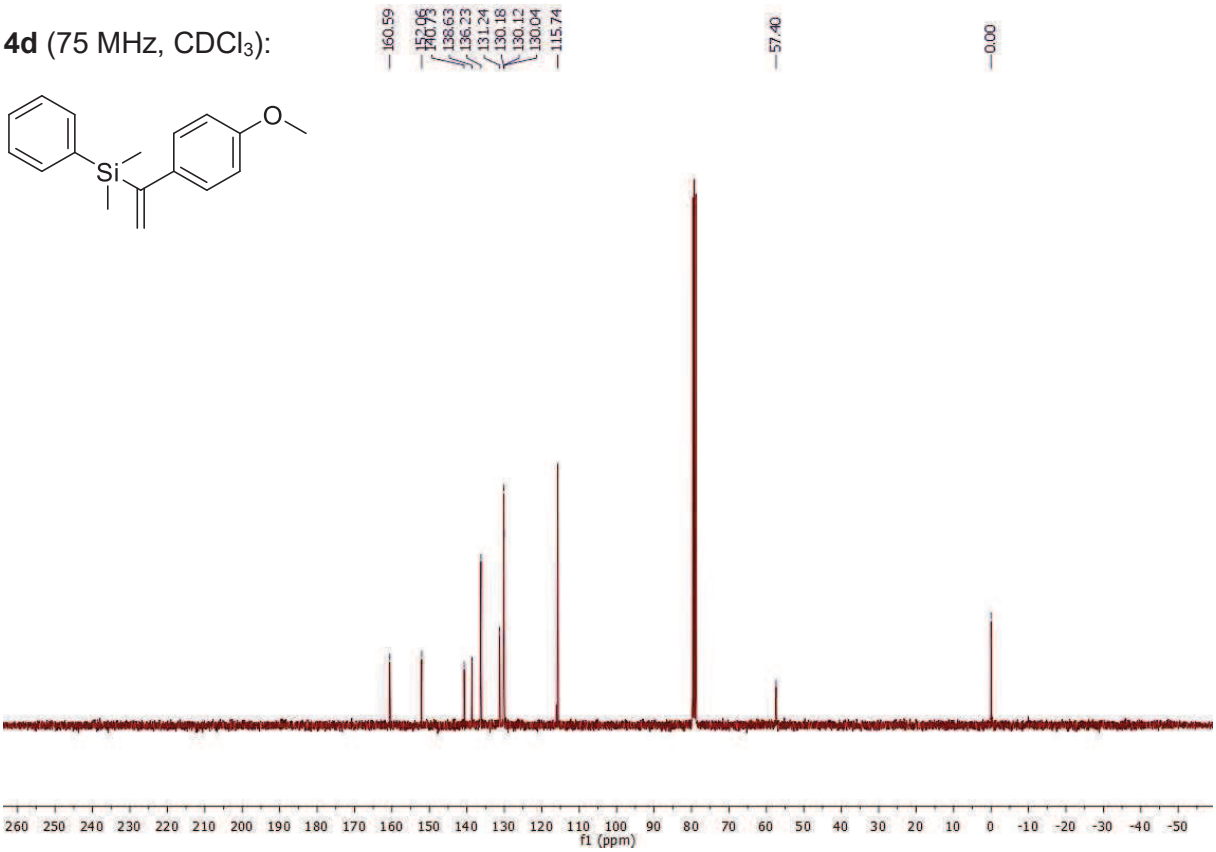


4d (75 MHz, $CDCl_3$):



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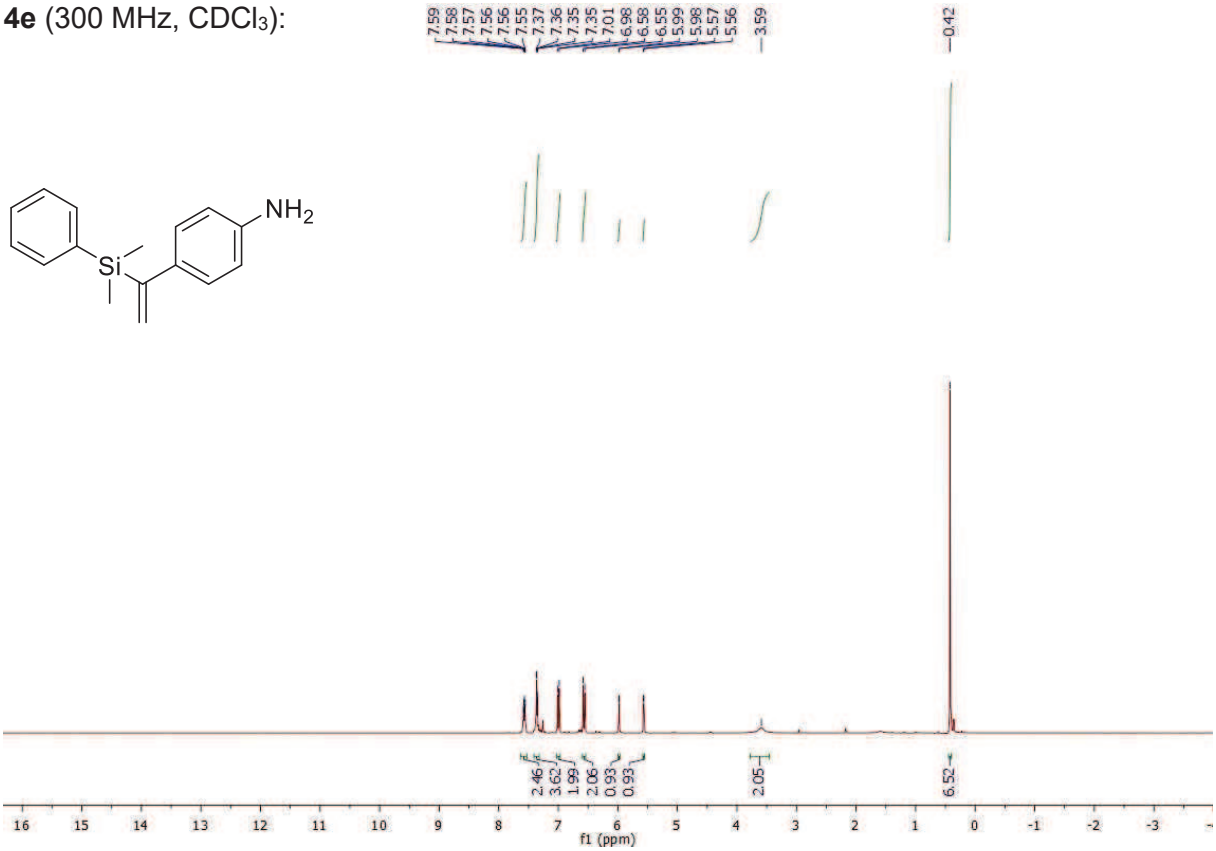

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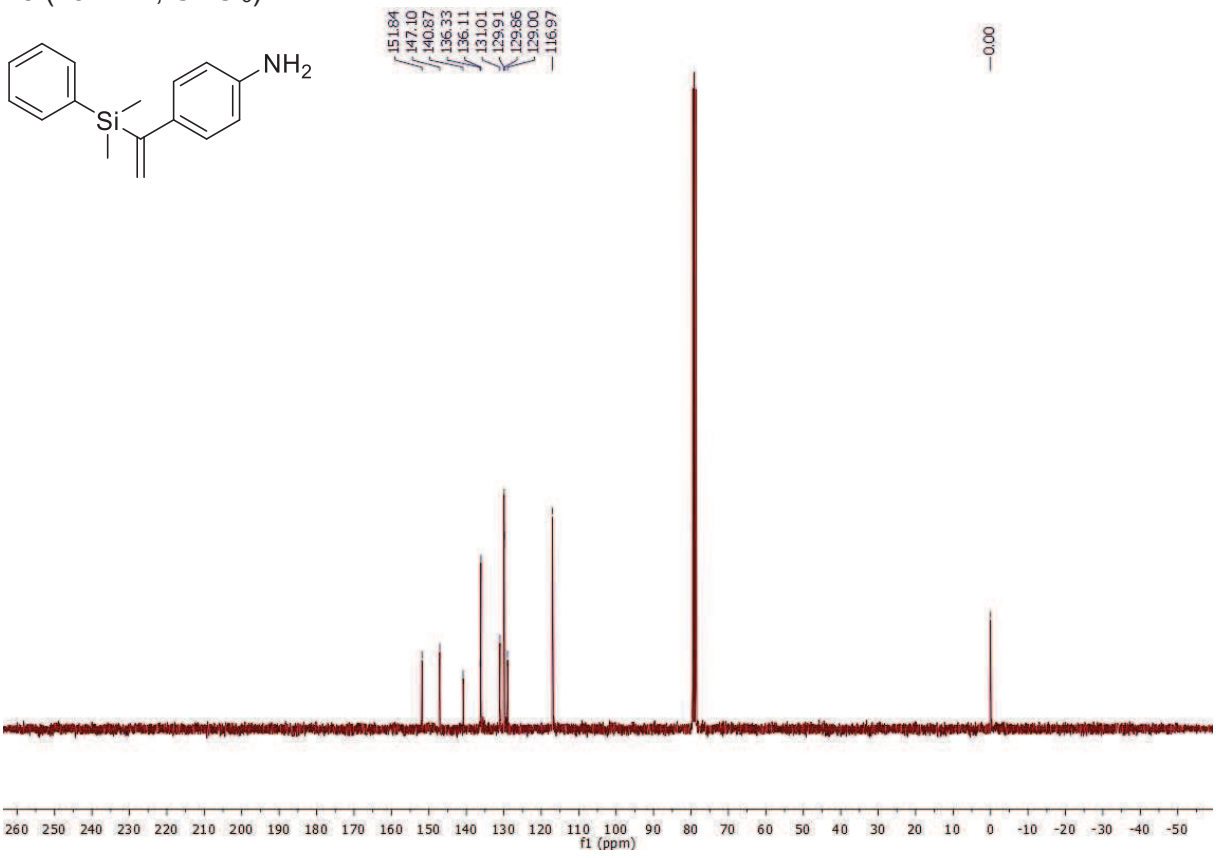
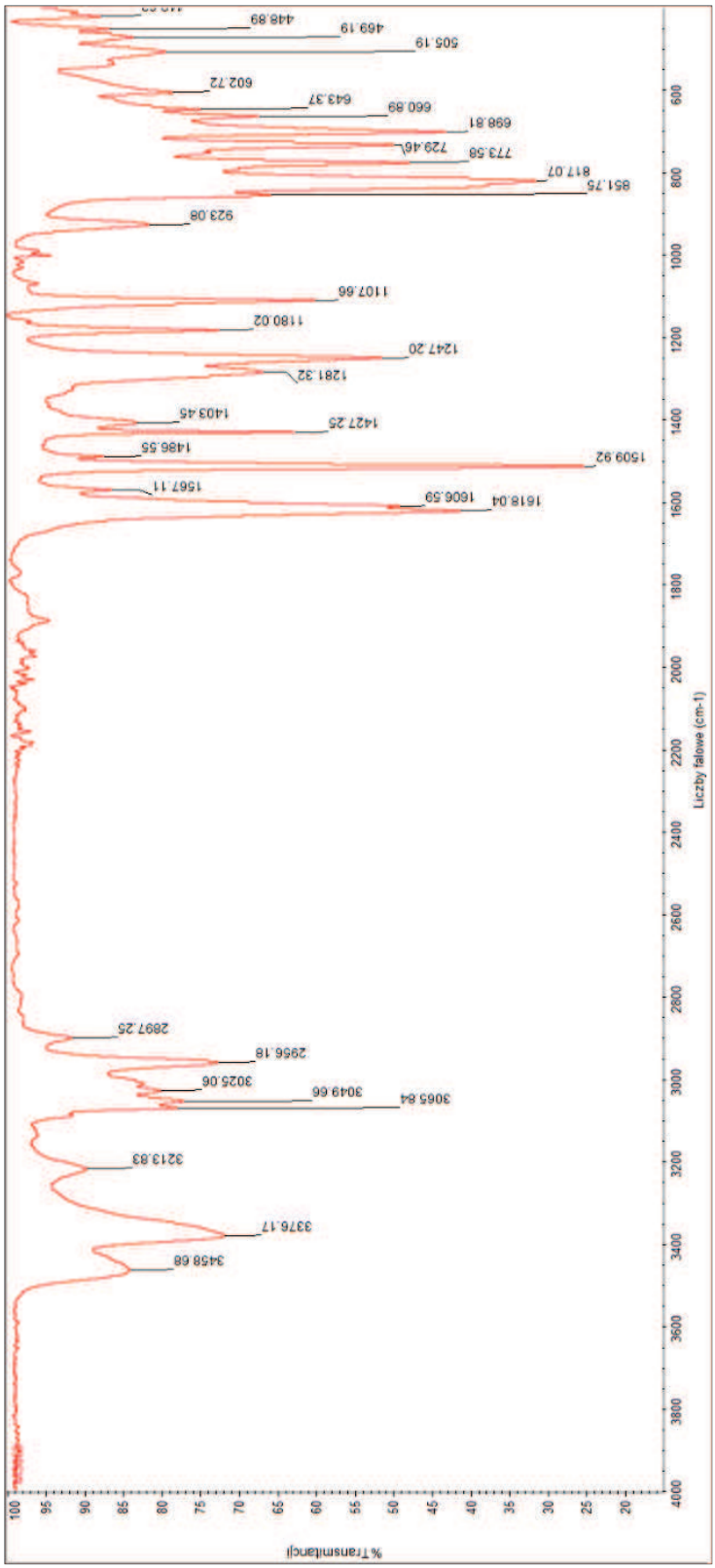
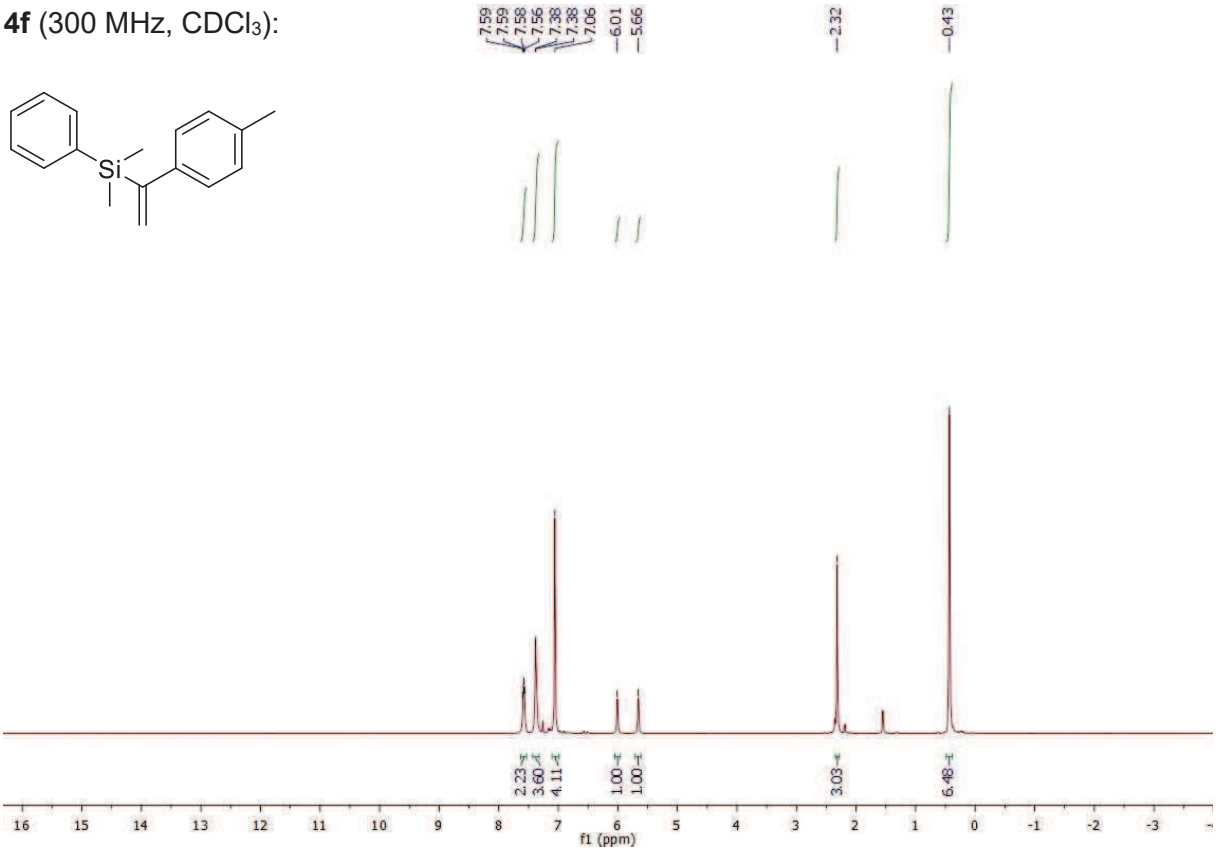


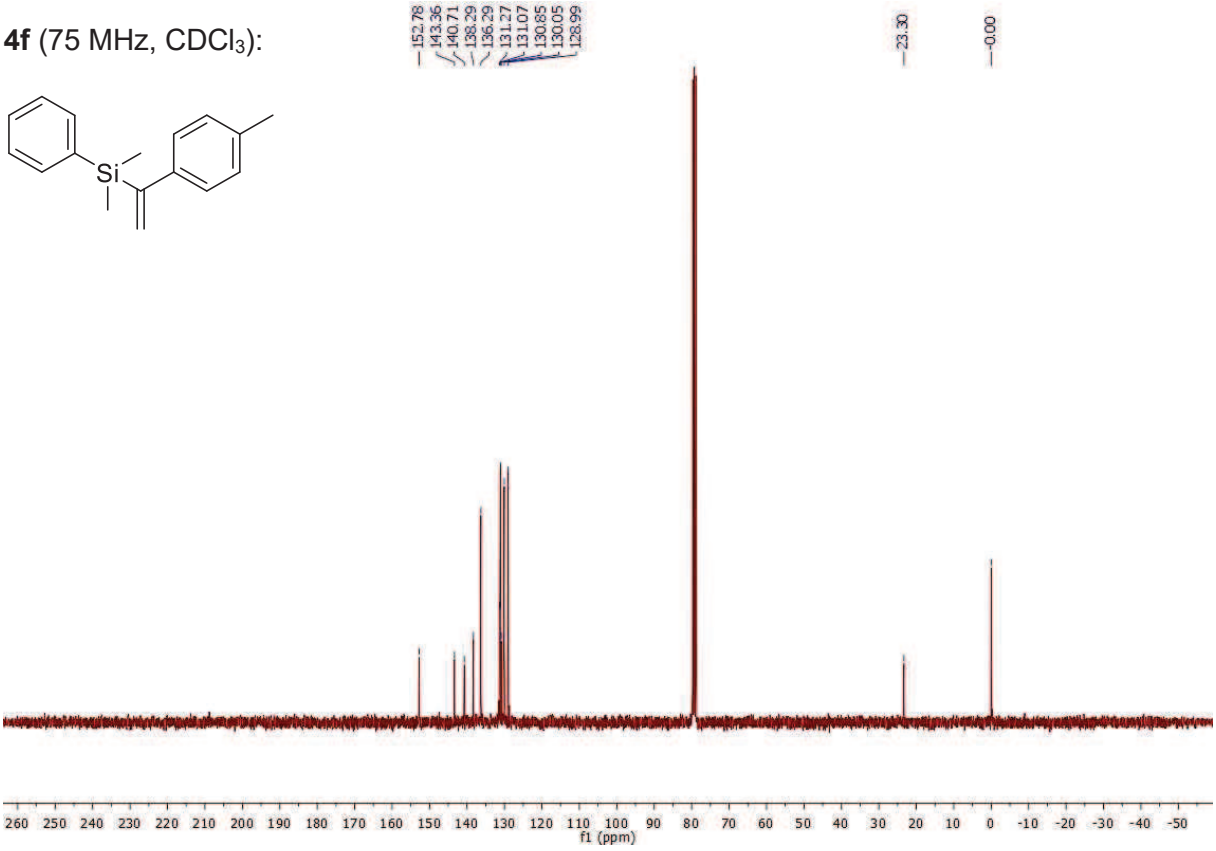

%Transmitancji
Liczby falowe (cm-1)
448.89
469.19
505.19
602.72
643.37
660.89
698.81
729.46
773.58
817.07
851.75
923.08
1107.66
1180.02
1247.20
1281.32
1403.45
1427.25
1486.55
1509.92
1567.11
1606.59
1618.04
2897.25
2956.18
3025.06
3049.66
3065.84
3213.83
3376.17
3458.68

4e

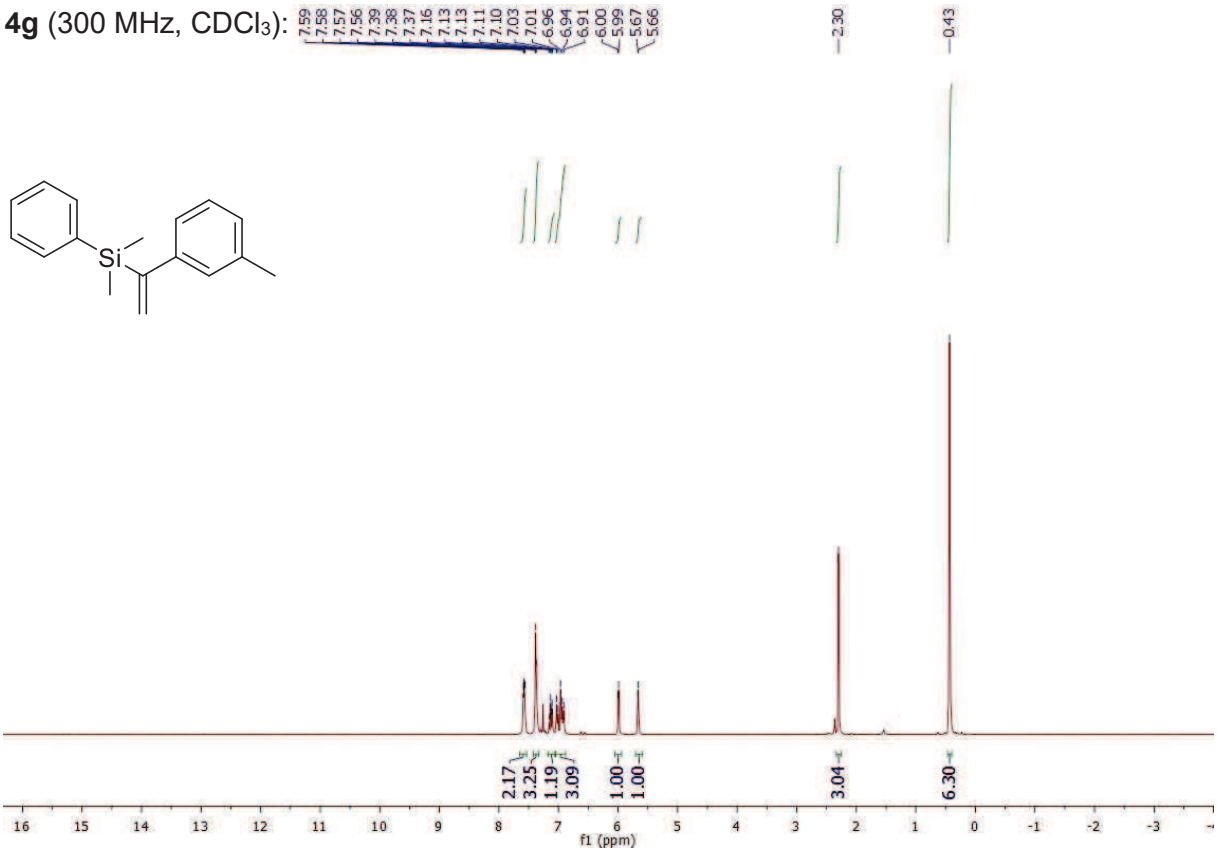
4f (300 MHz, $CDCl_3$):



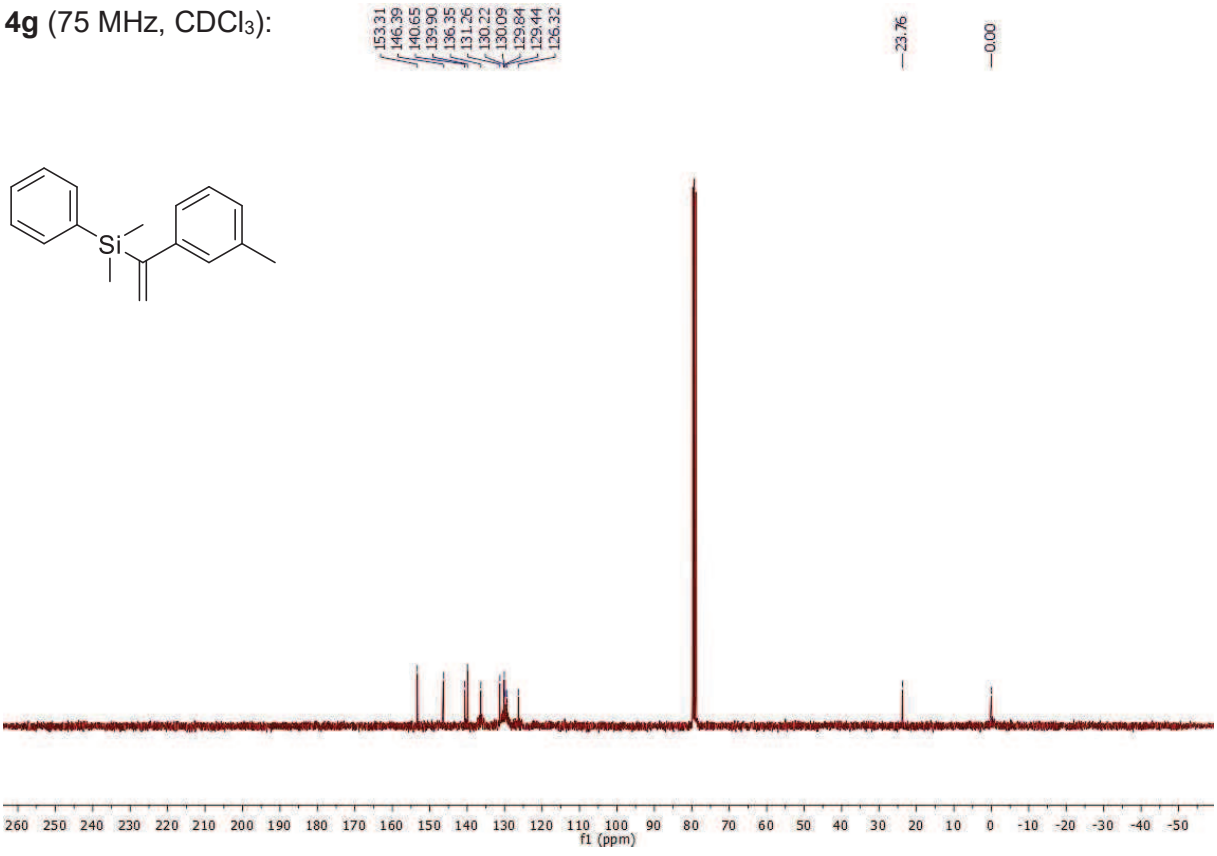
4f (75 MHz, $CDCl_3$):



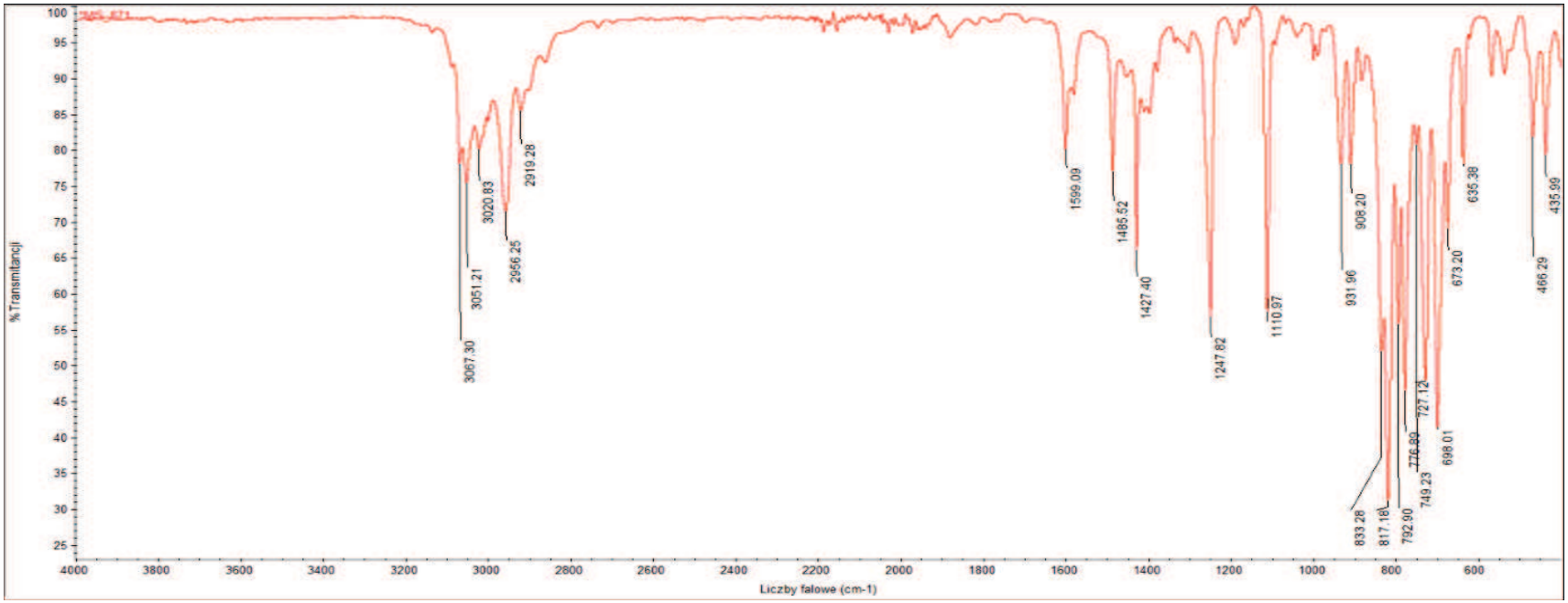
4g (300 MHz, $CDCl_3$):



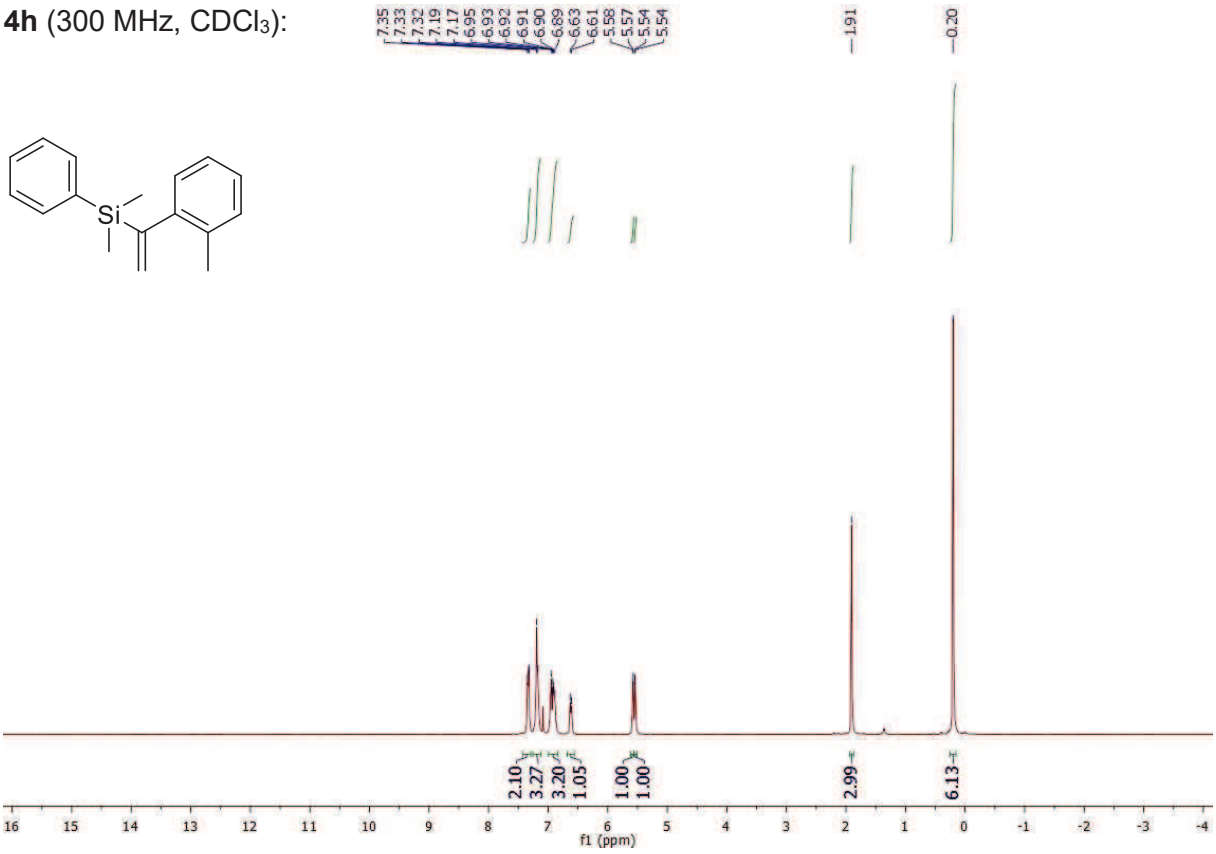
4g (75 MHz, $CDCl_3$):



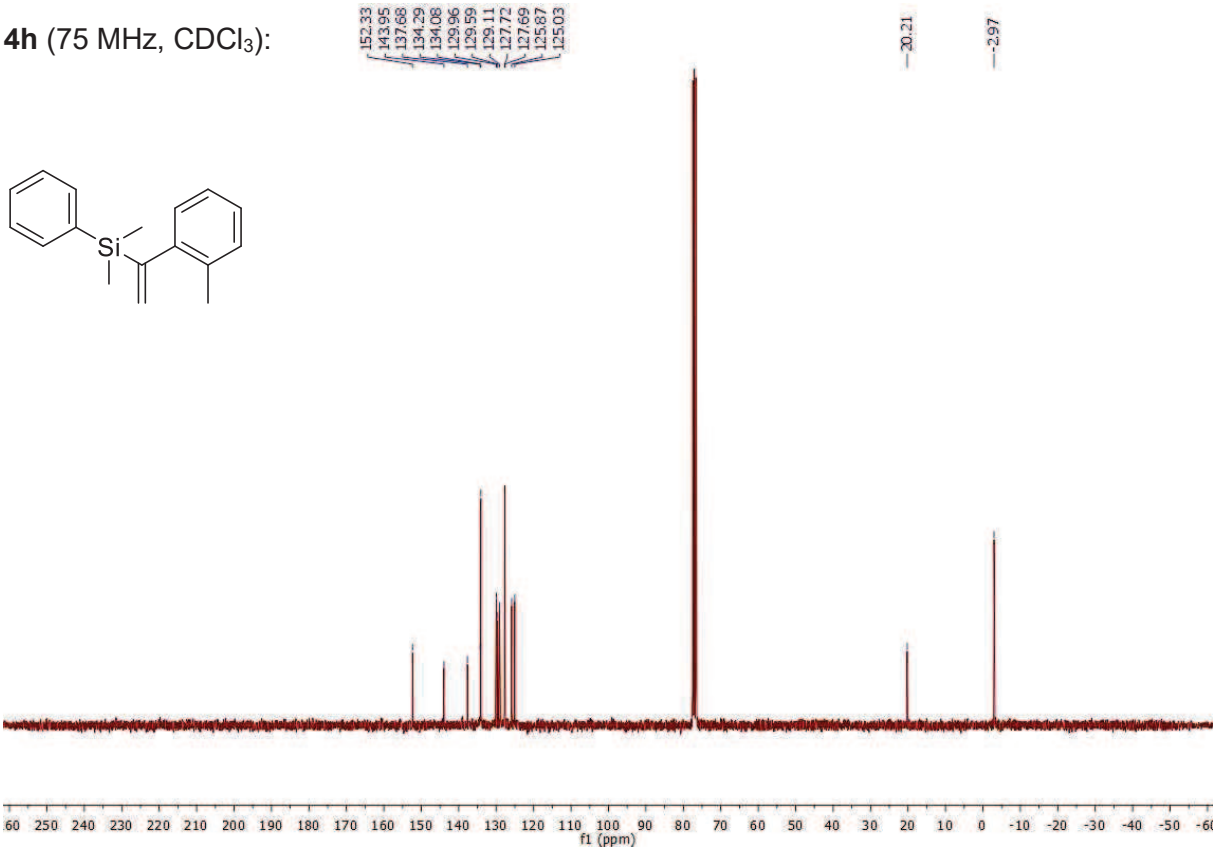
4g


%Transmittancji
Liczby falowe (cm-1)
3067.30
3051.21
3020.83
2956.25
2919.28
1599.09
1485.52
1427.40
1247.82
1110.97
931.96
908.20
833.28
817.18
792.90
776.80
749.23
727.12
698.01
673.20
635.38
466.29
435.99

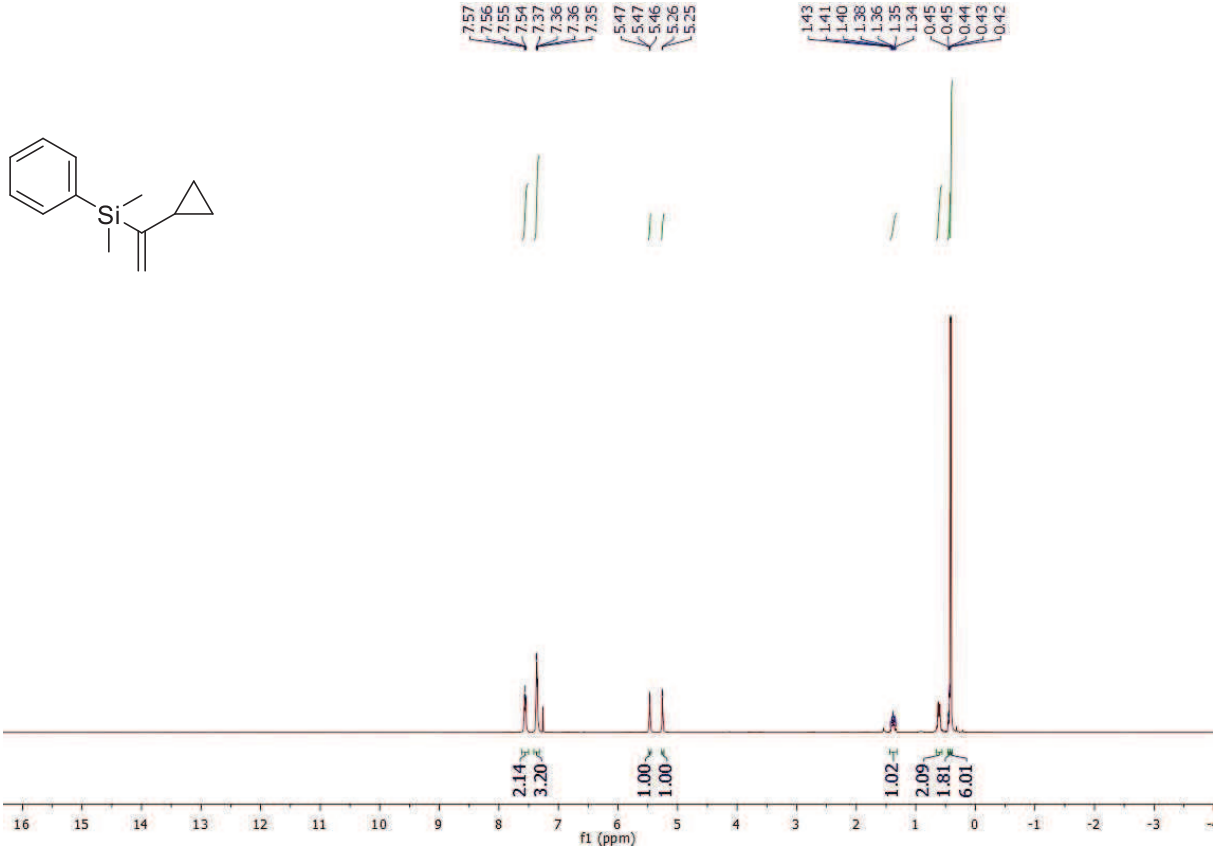
4h (300 MHz, $CDCl_3$):



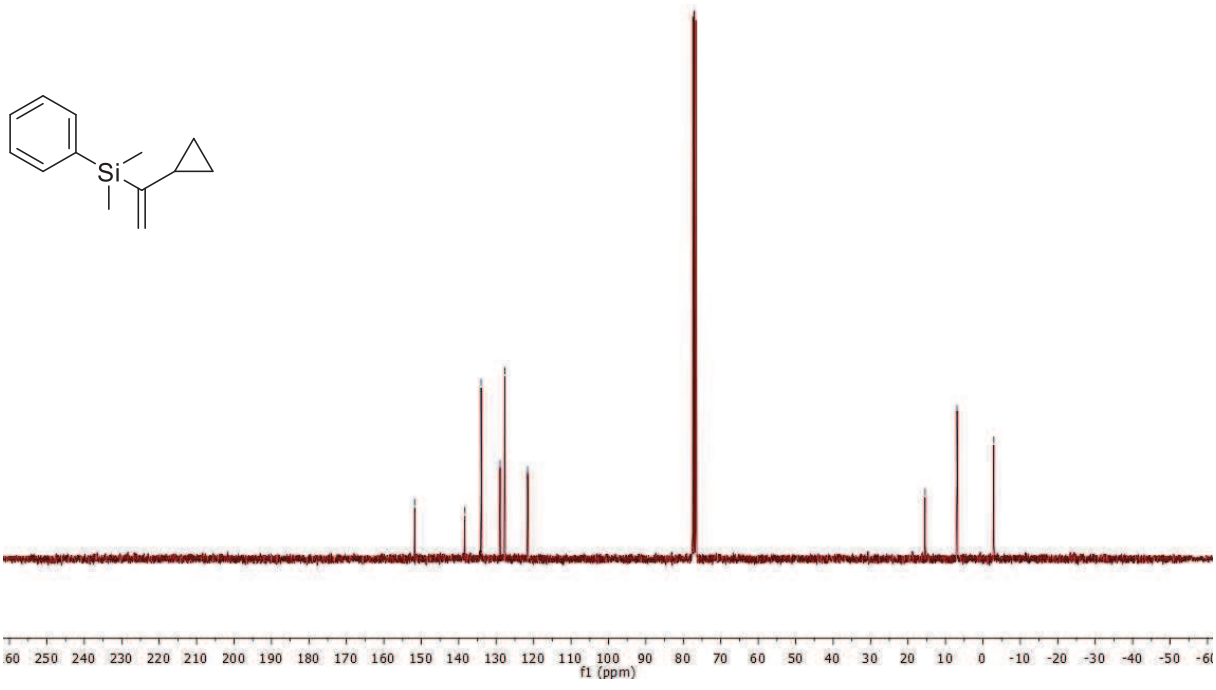
4h (75 MHz, $CDCl_3$):

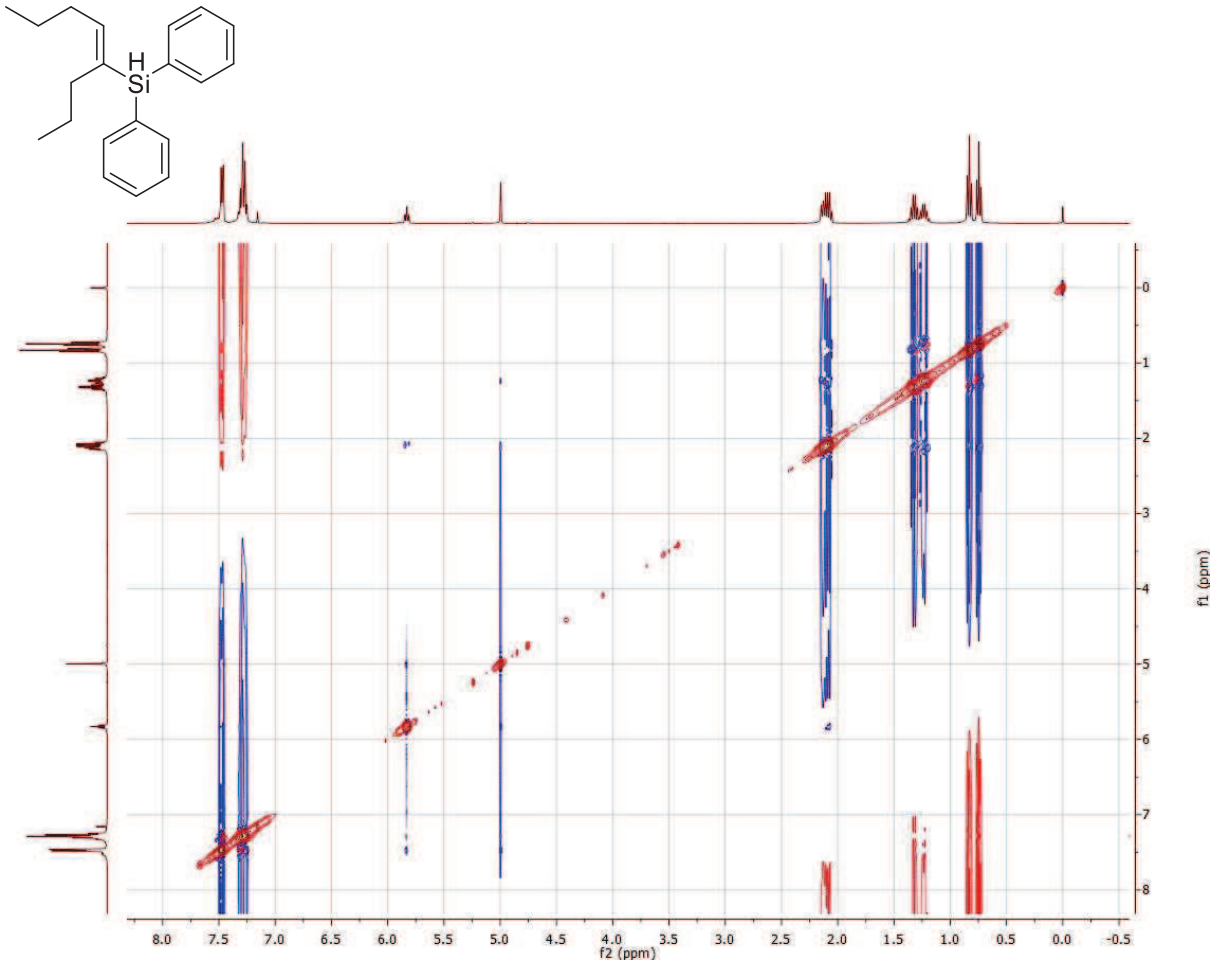


4i (300 MHz, $CDCl_3$):

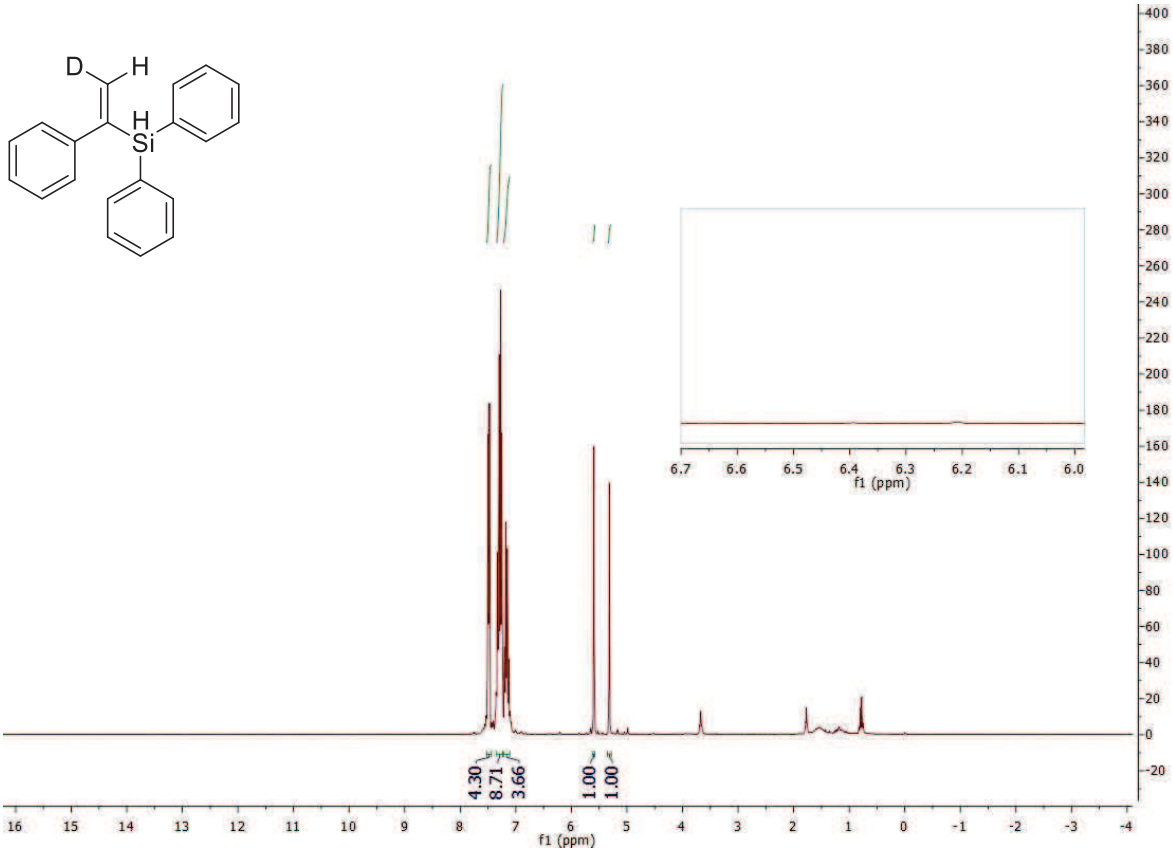


4i (75 MHz, $CDCl_3$):





Deuterium labelled experiment (300 MHz, $CDCl_3$):



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Appendix **A3**

Skrodzki M., Ortega Garrido V, Csaky A. G., Pawluć P.; *Searching for highly active cobalt catalysts bearing Schiff base ligands for Markovnikov-selective hydrosilylation of alkynes with tertiary silanes. J. Catal*. **2022**, 441, 116-121.

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Searching for highly active cobalt catalysts bearing Schiff base ligands for Markovnikov-selective hydrosilylation of alkynes with tertiary silanes

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ABSTRACT

The search for simple and easy-to-synthesize ligands for bench stable cobalt (pre)catalysts that would ensure high activity and selectivity in alkyne hydrosilylation reactions is an interesting current challenge. Herein, we report that a cobalt(II) complex bearing pyrimidine-imine-2*H*-imidazole ligand activated by $LiHBEt_3$ exhibits not only high catalytic activity, but also unprecedented tolerance towards tertiary silanes in highly regioselective Markovnikov hydrosilylation of aliphatic and aromatic terminal alkynes to give α-vinylsilanes. In addition, a variety of 1-aryl-2-(trimethylsilyl)acetylenes have been hydrosilylated efficiently by diphenylsilane in the presence of $[Co(L)Cl_2]/LiHBEt_3$ catalytic system to yield (*E*)-1-aryl-1,2-bis(silyl)ethenes with high selectivity. Such selectivity is very rarely observed for cobalt-catalyzed hydrosilylation of silylacetylenes.

1. Introduction

Vinylsilanes are versatile reagents in organic and organometallic chemistry. Due to their stability, low toxicity and ease of handling, they have been extensively applied in organic synthesis, fine chemistry and materials science [1]. From among all the synthetic pathways for such compounds, direct addition of Si-H to alkynes is perceived as the most efficient and atom economical [2]. Initially, the field of metal-catalyzed hydrosilylation of alkynes was overwhelmed by noble metals [3] such as Ru, Pt and Ir. The reactions involving catalysts based on these metals are efficient and selective, however, the low natural abundance of such metals and increasing market demand resulted in enormous peak in price. Due to the fact that the price of noble metals determines the subsequent price of the catalyst, development of new precious metal catalysts is becoming increasingly economically questionable. To this end hydrosilylation catalysts based on earth abundant metals are more desirable from the economic and environmental points of view [4]. On the other hand, scientists should also reconsider developing multistep synthetized and complex ligands. New catalysts should bear simple and rational coordinating environment, simultaneously maintaining high efficiency and selectivity.

Cobalt catalysis offers a sustainable alternative to the commonly used noble metal catalysts [5]. In the last decade, cobalt complexes have been reported as effective catalysts in the synthesis of β-(*E*) [6], β-(*Z*) [7] and α-vinylsilanes [8]. Despite extensive research, the field of α-selective hydrosilylation of alkynes with ligand simplification has not yet been fully examined. Jin's [9] and von Wangelin's [10] groups have developed systems based on $Co(OAc)_2$ and simple, bidentate ligands. Although characterized by high conversion and selectivity, the hydrosilylation involving secondary and tertiary silanes was neither satisfactory nor accessible. Subsequently, Chen's [11] group described the complex of $CoBr_2$ with N^CNN tridentate ligand as active in the hydrosilylation of alkynes and 1,3-diynes with diphenylsilane.

Tertiary silanes are very challenging substrates in cobalt-catalyzed alkyne Markovnikov hydrosilylation (Scheme 1). Apart from noble metal catalysts, in 1999 Isobe [12] described a single example of hydrosilylation of dihydropyranyl-substituted alkyne with triethylsilane with poor selectivity (α/β = 2) in the presence of $Co_2(CO)_6/HC{\equiv}CCMe_2OH$ complex. After two decades, Deng's [13] and Park's [14] groups developed new cobalt catalysts for efficient alkyne Markovnikov hydrosilylation with tertiary silanes. Despite excellent results and impressive selectivity (α/β up to 55:1), the Deng catalyst, based on dicobalt carbonyl *N*-heterocyclic carbene complex $[(IPr)_2Co_2(CO)_6]$ (IPr = 1,3-di(2,6-diisopropylphenyl)-imidazol-2-ylidene), requires 10 mol % of cobalt loading. Park and co-workers have described the use of a cobalt hydride catalytic

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E-mail address: piotrpaw@amu.edu.pl (P. Pawluć).

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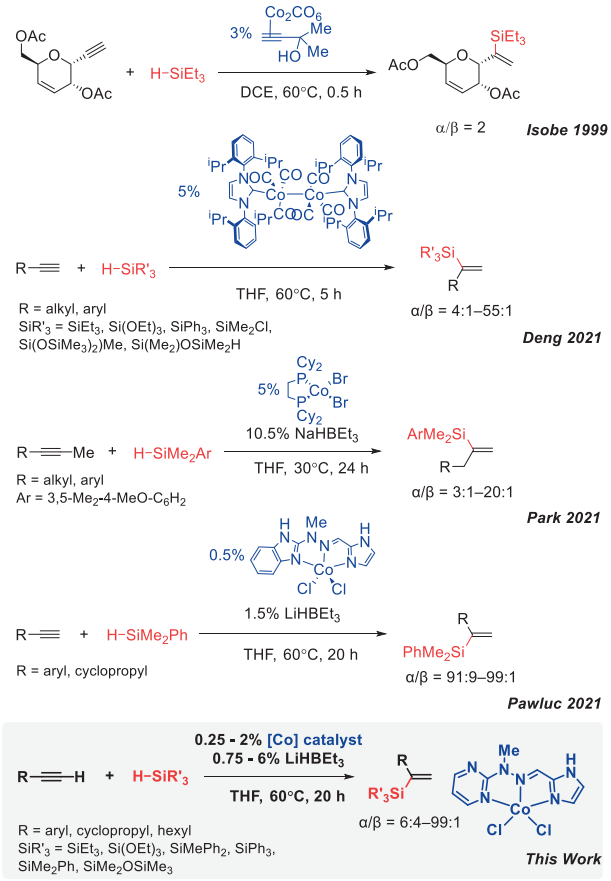
0021-9517/



Scheme 1. Co complexes for α-selective hydrosilylation of alkynes with tertiary silanes.

system generated from [(bis(dicyclohexylphosphino)ethane)$CoBr_2$] complex and $NaHBEt_3$ for regioselective migratory hydrosilylation of 2-alkynes to furnish α-vinylsilanes with excellent regioselectivity (α/β up to 20:1). However, the application of.

commercially unavailable dimethyl(3,5-dimethyl-4-methoxy phenyl)silane and relatively high (pre)catalyst loading (5–7.5 mol %) somewhat limits its versatility.

Our previously reported catalytic system [15], based on cobalt (II) complex with a simple Schiff base ligand: benzimidazole-imine-2*H*-imidazole, catalyzed Markovnikov hydrosilylation of terminal alkynes with $HSiMe_2Ph$ with high selectivity (91–99% of α-isomer). The hydrazone Schiff base ligand can be easily obtained in a two-step synthetic protocol from commercially available substrates. Although this is the most active catalytic system reported to date (0.5 mol % Co complex activated by 1.5 mol % $LiHBEt_3$), its further application for reactions with other tertiary silanes was unsuccessful.

Inspired by the results of the study with using Schiff bases as optimal ligands in the selective hydrosilylation of alkynes, we decided to look for a more universal coordination environment for cobalt(II) ions, which would create a catalyst tolerant to a wide variety of tertiary silanes. Herein, we describe the application of structurally simple ligands which, after coordination with cobalt (II) chloride, allow high activity and selectivity in the hydrosilylation reactions of terminal and internal alkynes to be maintained.

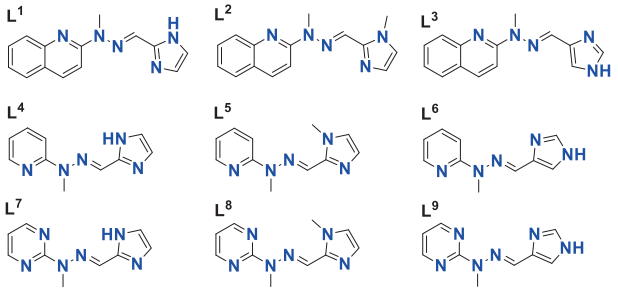
2. Results and disscusion

A series of *in situ* formed Co(II) complexes with hydrazone Schiff base ligands **L^1-L^9** (Scheme 2) were evaluated with regard to their activity and selectivity in model hydrosilylation reaction of phenylacetylene with diphenylsilane. Schiff base ligands are easily obtained through a two-step synthetic protocol (SI).

In order to check the selectivity of the hydrosilylation reaction, catalytic tests were carried out using equimolar amounts of phenylacetylene and diphenylsilane. For this purpose, anhydrous $CoCl_2$ and ligands were placed in a Schlenk flask, dried under reduced pressure and stirred in THF for an hour before the experiment. The reaction of phenylacetylene and diphenylsilane was carried out in the presence of 1 mol % of ligand (L^1-L^9), 1 mol % of anhydrous $CoCl_2$ and threefold excess of an activator ($LiHBEt_3$), at room temperature for 20hs, under argon atmosphere. The results are summarized in Table 1. The results obtained by employing the ligands with the 1Me-imidazol-2-yl motif (L^2, L^5, L^8) show diphenylsilane conversions ranging from 26% to 58% without specified selectivity. Subsequently investigated Schiff base motifs containing 1*H*-imidazol-4-yl derivatives (L^3, L^6, L^9) showed higher activity (48–87%), and selectivity towards α-selective hydrosilylation (for L^6 and L^9) products under similar reaction conditions, while the reaction in the presence of L^3 was non-selective. The efficiency and regioselectivity are mostly driven by the imidazole side of the ligand. However, the role of the activator on the activity and selectivity is not entirely clear. The borohydride seems to interact with the imidazole fragment acting as a base and deprotonating the NH groups. Further interactions with free borane can electronically and sterically stabilize the imidazole ring. The cobalt complexes containing 1*H*-imidazol-2-yl scaffold (L^1, L^4, L^7) seemed to be the most active and selective systems. Thus, the (pre)catalysts containing $CoCl_2$ and ligands **L^1**, **L^4** and **L^7** were chosen for further investigation.

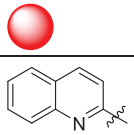
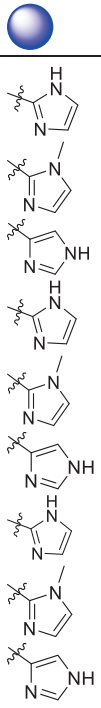
Catalytic activity and selectivity of all three systems remained unchanged when salt/ligand loadings were lowered to 0.5 mol % (Table 2, entry 1–3). Further lowering of the catalyst loading to 0.1 mol % was successful only for the $CoCl_2$ and pyrimidine ligand L^7 mixture, activated by $LiHBEt_3$ (entry 4–6). The use of the other borohydrides tested, i.e. $KHBEt_3$, NaHB(*sec*-Bu)$_3$ and $NaHBEt_3$, led to total conversion of diphenylsilane with slightly lower selectivity (entry 7–9), whereas the use of sodium *tert*-butoxide resulted in 54% of conversion of silane (entry 10). This phenomenon might be connected to the size of borohydride counterion (α/β selectivity $LiHBEt_3$ > $NaHBEt_3$ > $KHBEt_3$). Elevated temperature (40 °C) was found to be effective with a lower catalyst loading of 0.05 mol % (entry 13), which is one of the most efficient catalytic systems reported so far in the literature on cobalt-catalyzed alkyne hydrosilylation. Unfortunately, 0.01 mol % of catalyst loading, at an elevated temperature, was enough for only 58% conversion of diphenylsilane.

On the basis of these results, we synthesized a cobalt(II) complex with ligand **L^7** (synthesis and characterization is described in the Supporting Information) and we used the complex [Co(L^7)Cl_2], in which L^7 is (*E*)-2-(2-((1*H*-imidazol-2-yl)methylene)-1-methylhydrazinyl)pyrimidine, for further research (complex **1**). Com-



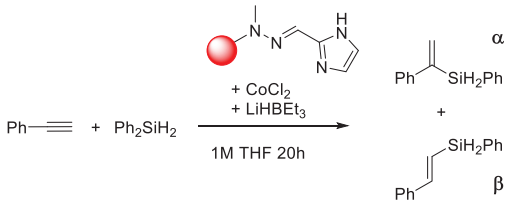
Scheme 2. Structures of Schiff base ligands.

Table 1
Hydrosilylation of phenylacetylene with diphenylsilane in the presence of $CoCl_2$/hydrazone Schiff base ligand activated by lithium triethylborohydride.

entry			Conversion of Ph_2SiH_2	α/β ratio
L^1			99	91:9
L^2			26	48:52
L^3			48	50:50
L^4			>99	89:11
L^5			58	64:36
L^6			87	85:15
L^7			**>99**	**96:4**
L^8			31	37:63
L^9			48	85:15

[a]Conditions: Phenylacetylene 1 mmol, Ph_2SiH_2 1 mmol, Schiff base ligand 1 mol %, $CoCl_2$ 1 mol %, $LiHBEt_3$ 3 mol %, 1 M solution of silane in THF, room temperature, 20 h. [b]Calculated by GC with mesitylene (0.166 mmol) as internal standard.

Table 2
Optimization of conditions for hydrosilylation of phenylacetylene with diphenylsilane[a].



entry	$CoCl_2$ & Ligand [mol %]	Conversion of Ph_2SiH_2 [%]	α/β ratio
1	**L^1** 0.5%	98	97:3
2	**L^4** 0.5%	>99	94:6
3	**L^7** 0.5%	>99	96:4
4	**L^1** 0.1%	13	64:36
5	**L^4** 0.1%	32	72:28
6	**L^7** 0.1%	97	94:6
7[c]	**L^7** 0.1%	>99	89:11
8[d]	**L^7** 0.1%	>99	84:16
9[e]	**L^7** 0.1%	>99	95:5
10[f]	**L^7** 0.1%	54	76:24
11 [g]	**L^7** 0.1%	>99	72:28
12	**L^7** 0.05%	97	98:2
13 [h]	**L^7** 0,05%	>99	>99:1
14 [h]	**L^7** 0,01%	58	98:1

[a] Conditions: Phenylacetylene 1–5 mmol, Ph_2SiH_2 1–5 mmol, anhydrous $CoCl_2$ *n* mol %, ligand *n* mol %, $LiHBEt_3$ *3n* mol %, 1 M solution of silane in THF, room temperature, 20 h. [b]Calculated by GC with mesitylene (0.166 mmol) as internal standard. Reactions with [c]$KHBEt_3$/[d]NaHB(*sec*-Bu)$_3$/[e]$NaHBEt_3^f$/NaO^tBu/[e]Red-Al as an activator (instead of $LiHBEt_3$). [h]Reaction heated to 40 °C.

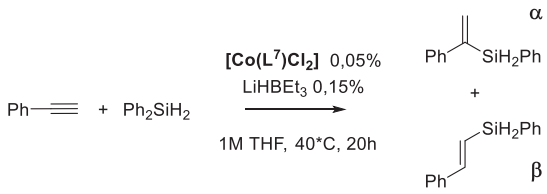
plex **1** was air- and moisture-stable, operationally simple and easy to handle on the laboratory bench.

Hydrosilylation of other aliphatic and aromatic alkynes with diphenylsilane has been performed under established reaction conditions (Table 3). Application of alkyl-substituted phenylacetylenes led to the synthesis of α-vinylsilanes with good regioselectivity (**2b**-**2e**) (α/β > 94:6). Halogenated aryl alkynes such as 4-fluorophenylacetylene (**2f**) or 4-bromophenylacetylene (**2 g**) were hydrosilylated effectively with good selectivity (97%) towards α-addition products.

Despite the high conversion of 2-ethynylthiophene (**2 h**), another heteroaromatic substrate – 2-ethynylpyridine (**2i**) reacted with diphenylsilane only with 23% conversion and moderate selectivity, even using a ten times higher concentration of the cobalt (pre)catalyst and activator. Reactive groups, such as amine (**2j**), dimethylamine (**2p**), methoxy (**2r**) or nitrile (**2 k**) were tolerated, affording products in good yields. Aliphatic and cycloaliphatic alkynes, such as hex-1-yne (**2 l**), ethynylcyclopropane (**2 m**), cyclohexylacetylene (**2n**) and 1-ethynylcyclohexene (**2o**) showed reactivity similar to aromatic alkynes, except for the reaction of diphenylsilane with cyclohexylacetylene, where a slightly lower selectivity (α/β = 84:16) was observed. It should be noted that to achieve total conversion of substrates, the reactions with cyclohexyl-acetylene, 4-bromophenylacetylene and 4-ethynylbenzonitrile required higher catalyst loading (0.5 mol % complex **1** and 1.5 mol % $LiHBEt_3$). The reaction of phenylacetylene with an equimolar amount of diethylsilane resulted in total conversion of silane, however, a mixture of Markovnikov addition product - diethyl(1-phenylvinyl) silane, and a product of subsequent hydrosilylation of the latter - diethyldi(1-phenylvinyl)silane was detected in 87:13 ratio. Selected products were isolated and characterized using ^1H and ^{13}C NMR.

Our main target was to investigate the catalytic activity of cobalt(II) complex in the Markovnikov hydrosilylation of alkynes with tertiary silanes. For this purpose, reactions of dimethylphenylsilane with various aromatic and cycloaliphatic alkynes (Table 4) were performed. As we established in our previous work,[15] to provide complete conversion, tertiary silanes

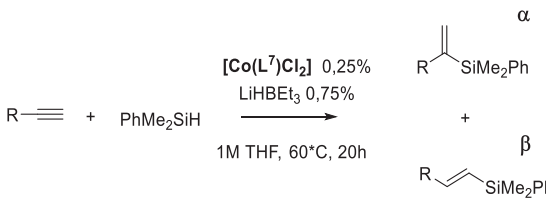
Table 3
Scope of alkynes in the hydrosilylation with secondary silanes.[a].



Entry	R	Silane	Silane Conver-sion [%][b]	Selecti-vity α/β
2a	Phenyl	Ph_2SiH_2	>99 (95)	100:0
2b	(4-Me)C_6H_4		>99	96:4
2c	(2-Me)C_6H_4		99	99:1
2d	(3-Me)C_6H_4		99	94:6
2e	(4-*t*Bu)C_6H_4		>99 (92)	99:1
2f	(4-F)C_6H_4		>99 (96)	97:3
2g[c]	(4-Br)C_6H_4		99	97:3
2 h	2-thienyl		>99	100:0
2i[c]	2-pyridyl		23	69:31
2j	(4-NH_2)C_6H_4		>99	100:0
2k[c]	(4-CN)C_6H_4		69	97:3
2 l	*n*-hexyl		>99	93:7
2 *m*	cyclopropyl		>99	100:0
2n[c]	cyclohexyl		95	84:16
2o	cyclohexen-1-yl		>99	92:8
2p	(4-NMe_2)C_6H_4		>99 (98)	95:5
2r	(4-MeO)C_6H_4		>99 (96)	100:0
2s[e]	Phenyl	Et_2SiH_2	>99	100:0[d]

[a] Conditions: Alkyne 0.5 mmol, silane 0.5 mmol, 0.05 mol % of complex **1**, 0.015 mol % $LiHBEt_3$, 1 M solution of silane in THF, 40 °C, 20 h. [b]Calculated by GC with mesitylene (0.166 mmol) as internal standard. [c]0.5 mol % of complex **1**, 1.5 mol % $LiHBEt_3$, 60 °C. Isolated yields of the reaction products are given in parentheses. [d]Mixture of diethyl(1-phenylvinyl)silane and diethyldi(1-phenylvinyl)silane in 87:13 ratio. [e]2 mol % of complex **1**.

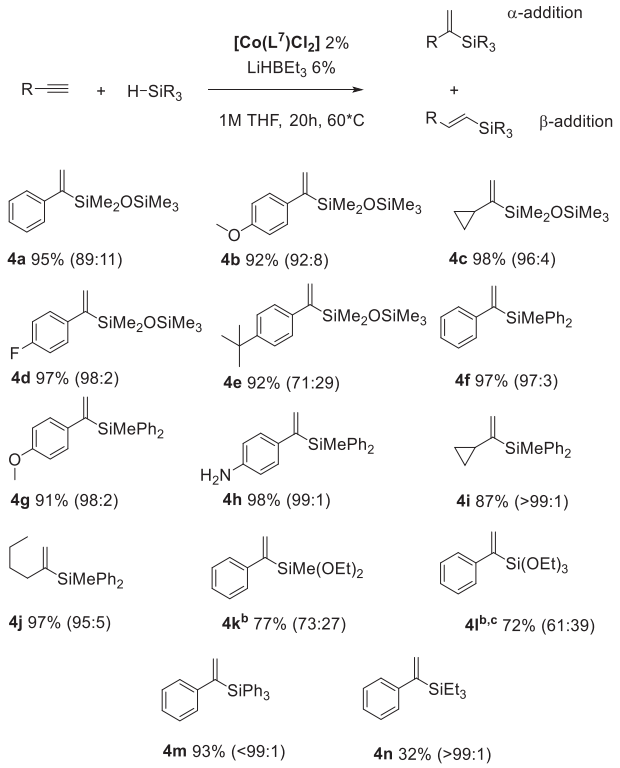
Table 4
Scope of alkynes in the hydrosilylation with dimethylphenylsilane[a].



Entry	R	Silane Conversion [%]	Selectivity α/β
3a	Phenyl	98	96:4
3b	(4-Me)C_6H_4	98	94:6
3c	(4-*t*Bu)C_6H_4	78	93:7
3d	(2-Me)C_6H_4	89	98:2
3e	(3-Me)C_6H_4	94	93:7
3f	(4-MeO)C_6H_4	97	94:6
3 g	(4-NH_2)C_6H_4	88	96:4
3 h	(4-NMe_2)C_6H_4	>99 (95)	99:1
3i	(4-F)C_6H_4	>99 (98)	97:3
3j	cyclopropyl	100	98:2
3 k	cyclohexen-1-yl	100	88:12
3 l	2-thienyl	30	85:15

[a] Conditions: Alkyne 0.5 mmol, $PhMe_2SiH$ 0.5 mmol, 0.25 mol % of complex **1**, 0.75 mol % $LiHBEt_3$, 1 M solution of silane in THF, 60 °C, 20 h. [b]Calculated by GC with mesitylene (0.166 mmol) as internal standard. Isolated yields of the selected reaction products are given in parentheses.

require elevated temperature (60 °C). Based on catalytic tests of the reaction of phenylacetylene with dimethylphenylsilane, we determined the optimal catalyst loading as 0.25 mol % of complex **1**, which is not achievable for previously reported cobalt-based catalysts. Phenylacetylene and its alkyl-substituted derivatives (**3a**-**e**) reacted with excellent selectivity and good yields. However, slightly worse selectivity in the reaction with 3-ethynyltoluene



Scheme 3. Reactivity of tertiary silanes in the reactions with terminal alkynes.[a]. [a]Conditions: Alkyne 0.5 mmol, silane 0.5 mmol, 2 mol % of complex **1**, 6 mol % $LiHBEt_3$, 1 M solution of silane in THF, 60 °C, 20 h. Ratio of α- to β-addition products in parentheses, determined by ^1H NMR. Isolation yields. [b]Not isolated, conversions calculated by GC with mesitylene as internal standard. [c]Reaction with twofold excess of silane.

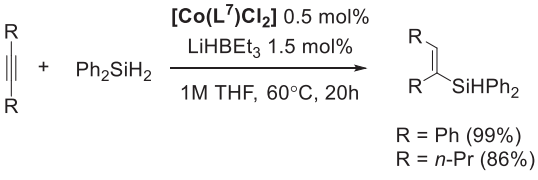
was observed. Methoxy, amino, dimethylamino, and fluoro substituents (**3f**-**3i**) were tolerated and functionalized aryl acetylenes reacted with good conversion and with selectivity α/β not less than 94:6. Cycloaliphatic alkynes such as cyclopropylacetylene (**3j**) and 1-ethynylcyclohexene (**3 k**) were smoothly hydrosilylated under the given conditions, however, the reaction with the latter resulted in generation of an increased amount of β-(*E*) addition product (α/β = 88:12). The reaction with 2-ethynylthiophene (**3 l**) was less successful in terms of substrate conversion and reaction selectivity.

We broadened the reaction scope by applying various tertiary silanes (Scheme 3) such as triethylsilane, triethoxysilane, methyldiphenylsilane, triphenylsilane, diethoxymethylsilane and pentamethyldisiloxane (**4a-n**), from which α-vinylsilanes bearing different silyl groups were synthesized in moderate to good yields. The best results were achieved by applying 2 mol% of complex **1**, at 60 °C for 20 h. Outstanding selectivities were obtained in the reactions of both aromatic and aliphatic alkynes with methyldiphenylsilane and triphenylsilane (**4f**-**4i**, **4 m**) (α/β > 97:3). Triethylsilane reacted with phenylacetylene affording only one product (**4n**). Although the obtained selectivity was excellent, the conversion of silane was only 32%. Triethoxysilane and diethoxymethylsilane reacted with moderate conversions (**4 k**, **4 l**) and selectivities lower than that obtained using the other silanes. The decreased Markovnikov selectivity observed for the reactions of alkoxysilanes can be attributed to the steric, less demanding nature of ethoxylsilyl groups. Unsurprisingly, the Si-O bond cleavages with simultaneous formation of cyclic siloxanes were observed under the applied conditions. This phenomenon is a common issue in the reaction of alkoxysilanes in the presence of strong bases and nucleophiles [16]. Contrary to alkoxysilanes, pentamethyldisiloxane proved to be an effective partner for the catalytic hydrosilylation of aromatic and aliphatic alkynes (**4a-4e**), however, the Markovnikov selectivity was strictly dependent on the alkyne used and varied within the range 71–98%.

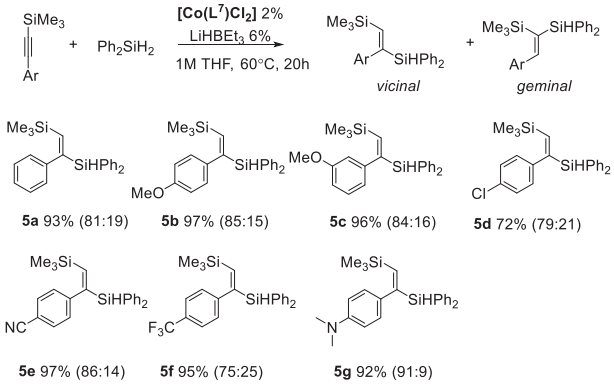
The reaction of D_1-phenylacetylene and diphenylsilane afforded *syn*-addition product, and no anti-addition products were observed (SI). On the basis of deuterium labeling experiments and the previously reported data[5b] we assume that the hydrosilylation of alkynes catalyzed by complex **1** in the presence of $LiHBEt_3$ proceed *via* cobalt(I)-silyl intermediate. Alternatively, Co(0) pathway of Markovnikov-selective hydrosilylation, recently proposed for 3 *N* pincer cobalt complex on the basis of DFT calculations can be considered [17].

Internal alkynes could also be hydrosilylated under our cobalt-catalyzed conditions. Symmetrical internal alkynes: oct-4-yne and diphenylacetylene underwent hydrosilylation with diphenylsilane with good yield (86–99%), selectively giving the corresponding (*E*)-silylalkenes (Scheme 4). The reaction occurred with 0.5 mol % complex **1** and 1.5 mol% $LiHBEt_3$ at 60 °C for 20 h. Unfortunately, increasing the reaction temperature, time and the precatalyst loading did not afford positive results for the reaction with tertiary silanes.

To emphasize the applicability of our catalytic system, we investigated the hydrosilylation of 1-phenyl-2-(trimethylsilyl)acetylenes (Scheme 5). The most common approach to the hydrosilylation of silylacetylenes involves ruthenium catalysts [18].



Scheme 4. Hydrosilylation of symmetrical internal alkynes with diphenylsilane.



Scheme 5. Hydrosilylation of 1-aryl-2-(trimethylsilyl)ethynes with diphenylsilane. [a]Conditions: Alkyne 0.5 mmol, Ph_2SiH_2 0.5 mmol, 2 mol % of complex **1**, 6 mol % $LiHBEt_3$, 1 M solution of silane in THF, 60 °C, 20 h. Ratio of *vicinal* to *geminal* products determined by ^1H NMR. Isolated yields.

Silylacetylenes are challenging substrates for cobalt complex-catalyzed hydrosilylation. So far, only few catalytic systems have been reported for the hydrosilylation of terminal [8b] and internal silylacetylenes [6g], most of which promoted the formation of geminal bis(silyl)alkene products. The application of our catalytic system $[Co(L^7)Cl_2]/LiHBEt_3$ indicated formation of isomeric (bis) silylated products - (*E*)-1-aryl-1,2-bis(silyl)ethenes in good yields (72–97%), which constitute a group of useful synthons [19]. To the best of our knowledge, there is only one example in the literature of cobalt-catalyzed alkyne hydrosilylation leading to such products [20]. 1-Phenyl-2-(trimethylsilyl)acetylene and its derivatives were reacted with diphenylsilane in the presence of 2 mol% of complex **1** over 20 h at 60 °C. The reaction of diphenylsilane with 1-phenyl-2-(trimethylsilyl)acetylene led to (*E*)-1-phenyl-1-diphenylsilyl-2-(trimethylsilyl)ethene (**5a**) as a predominant product with 93% yield (selectivity 81:19 of *1,2- (vicinal)* to *1,1-* (*geminal*) product). A similar selectivity was observed for *p*- and *m*-substituted derivatives on the phenyl ring, irrespective of the nature of the substituents (**5b**-**5 g**). The highest selectivity was achieved for an electron donating dimethylamino group (*vic*: *gem* = 91:9), and the lowest for an electron withdrawing *p*-trifluoromethyl substituent (*vic*: *gem* = 75:25).

3. Conclusions

In summary, a new bench stable and easily synthesized (pre)-catalyst for cobalt-catalyzed Markovnikov hydrosilylation of alkynes has been developed. A pentacoordinated cobalt(II) chloride complex with pyrimidine/2*H*-imidazole-based ligand, activated by lithium triethylborohydride, has been found to act as a good catalyst for regioselective hydrosilylation of terminal alkynes by secondary and tertiary silanes as well as internal alkynes by diphenylsilane. The catalytic system is applicable to both alkyl- and aryl-substituted alkynes showing good functional group compatibility (amine, halide, ether, nitrile etc.) and broad scope on tertiary silanes. Low catalyst loading (0.05–2 mol %) and high selectivity towards α-hydrosilylation products make it more universal than the previously reported catalytic systems based on cobalt complexes with 3 *N*-donor ligands.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We would like to dedicate our article to professor Pierre Dixneuf in recognition of his outstanding achievements in the field of homogeneous catalysis.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2022.05.002.

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SUPPORTING INFORMATION

For

Searching for Highly Active Cobalt Catalysts Bearing Schiff Base Ligands for Markovnikov-selective Hydrosilylation of Alkynes with Tertiary Silanes

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CONTENTS:

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EXPERIMENTAL PROCEDURES

1.1. General remarks:

All reactions were performed in flame-dried glassware under argon atmosphere. THF was purified by distillation over sodium and benzophenone, under argon atmosphere. Other solvents were dried by distillation over calcium hydride.

Gas chromatography was performed on a Bruker Scion 436-GC with a 30 m Agilent VF5-ms 0.53 mm Megabore column and a TCD detector. The temperature program was as follows: 60 °C (3 min), 20 °C/min, 280 °C (20 min). Decane was used as a reference. GC-MS analyses were performed on a Bruker Scion 436-GC with a 30 m Varian DB-5 0.25 mm capillary column and a Scion SQ-MS mass spectrometry detector. The temperature program was as follows: 60 °C (3 min), 10 °C/min, 250 °C (15 min). NMR analyses were performed on a Bruker Fourier 300 MHz or 400 MHz spectrometer.

FT-IR spectra were recorded on a Nicolet iS50 (Thermo Scientific) Fourier transform spectrophotometer equipped with a diamond ATR unit. In all cases, 16 scans at a resolution of 2 cm^{-1} were collected, to record the spectra in the range of 4000-400 $cm^{-1.}$

HRMS Spectra were recorded on a QTOF type mass spectrometer (Impact HD, Bruker) in positive ion mode.

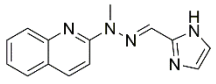
1.2. General procedure of alkyne hydrosilylation:

General procedure for hydrosilylation of alkynes **A**: A flame-dried Schlenk bomb flask was charged with argon, to which precatalyst (0.05 mol %), THF (0.5 mL), silane (0.5 mmol), and alkyne (0.5 mmol) were added. . The mixture was then heated to 40°C upon stirring in an oil bath. After 10 minutes $LiHBEt_3$ was added (0.15 mol %), and the reaction vessel was closed. After 20 hours, hexane was added to the reaction mixture. The solution was then filtered through a silica plug, and concentrated on a rotavapor. The crude mixture was purified by evaporating volatiles on vacuum line, followed by extraction with hexane. Regioselectivity was monitored by ^1H NMR.

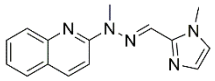
General procedure for hydrosilylation of alkynes **B**: A flame-dried Schlenk bomb flask was charged with argon, to which precatalyst (0.25 mol %), THF (0.5 mL), silane (0.5 mmol), and alkyne (0.5 mmol) were added. The mixture was then heated to 40°C upon stirring in an oil bath. After 10 minutes $LiHBEt_3$ was added (0.75 mol %), and the reaction vessel was closed. After 20 hours, hexane was added to the reaction mixture. The solution was then filtered through a silica plug, and concentrated on a rotavapor. The crude mixture was purified by evaporating volatiles on vacuum line, followed by extraction with hexane. Regioselectivity was monitored by ^1H NMR.

General procedure for hydrosilylation of alkynes **C**: A flame-dried Schlenk bomb flask was charged with argon, to which precatalyst (2 mol %), THF (0.5 mL), silane (1.0 mmol), and alkyne (1.0 mmol) were added. The mixture was then heated to 60°C upon stirring in an oil bath. After 10 minutes $LiHBEt_3$ was added (6 mol %), and the reaction vessel was closed. After 20 hours, hexane was added to the reaction mixture. The solution was then filtered through a silica plug, and concentrated on a rotavapor. The crude mixture was purified by evaporating volatiles on vacuum line, followed by extraction with hexane. Regioselectivity was monitored by ^1H NMR.

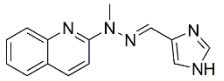
1.3. Ligand structures and General procedure for ligand (**L**) synthesis:



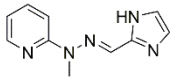
L[1] (*E*)-2-(2-((1*H*-imidazol-2-yl) methylene)-1-methylhydrazinyl)quinoline



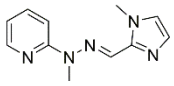
L[2] (*E*)-2-(1-methyl-2-((1-methyl-1*H*-imidazol-2-yl) methylene)hydrazinyl)quinoline



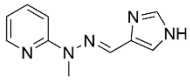
L[3] (*E*)-2-(2-((1*H*-imidazol-4-yl) methylene)-1-methylhydrazinyl)quinoline



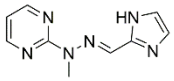
L[4] (*E*)-2-(2-((1*H*-imidazol-2-yl) methylene)-1-methylhydrazinyl)pyridine



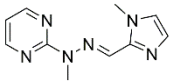
L[5] (*E*)-2-(1-methyl-2-((1-methyl-1*H*-imidazol-2-yl) methylene)hydrazinyl)pyridine



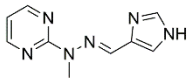
L[6] (*E*)-2-(2-((1*H*-imidazol-4-yl) methylene)-1-methylhydrazinyl)pyridine



L[7] (*E*)-2-(2-((1*H*-imidazol-2-yl) methylene)-1-methylhydrazinyl)pyrimidine

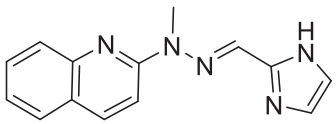


L[8] (*E*)-2-(1-methyl-2-((1-methyl-1*H*-imidazol-2-yl) methylene)hydrazinyl)pyrimidine



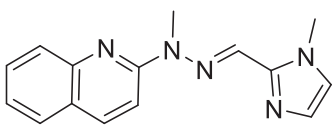
L[9] (*E*)-2-(2-((1*H*-imidazol-4-yl) methylene)-1-methylhydrazinyl)pyrimidine

Chloroarene (0.05 mol) was placed under argon atmosphere in a two-necked round-bottomed flask. Methylhydrazine (0.25 mol), in five-fold excess, was dissolved in anhydrous ethanol and added to the reaction mixture, which was heated in a heating mantle to 80°C and stirred for 20 h. The product was concentrated, precipitated with Et_2O, filtered off on a Büchner funnel and dried under vacuum. Then condensation of imidazolecarboxyaldehyde with (1-methylhydrazine)arene was performed. In a two-necked round-bottomed flask (1-methylhydrazine)arene (0.01 mol) was placed under argon atmosphere. Imidazolecarboxyaldehyde (0.01 mol) was dissolved in anhydrous ethanol and added to the reaction mixture. The reaction mixture was stirred for 24 h at 80°C. The solution was then cooled to room temperature. The precipitate was filtered off by vacuum filtration equipment, washed with cold anhydrous ethanol and dried under vacuum to give **L**. The supernatant was concentrated to minimal volume and a subsequent part of the precipitate was obtained.



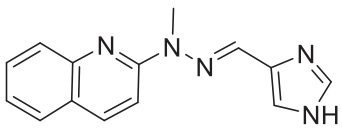
L[1] - ^{1}H NMR (300 MHz, CDCl3): δ 7.96 – 7.90 (1H, d), 7.83 – 7.73 (2H, t), 7.69 – 7.66 (1H, s), 7.65 – 7.60 (1H, d), 7.57 – 7.49 (1H, t), 3.73 – 3.67 (3H, s)

^{13}C NMR (300 MHz, CD_3OD): δ 155.9, 146.6, 144.9, 137.3, 129.2, 127.1, 126.6, 124.8, 124.7, 123.3, 111.2, 28.4



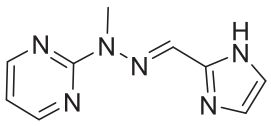
L[2] - ^{1}H NMR (300 MHz, CDCl3): δ 8.03 – 7.99 (1H, d), 7.89 – 7.86 (1H, s), 7.85 – 7.81 (1H, d), 7.79 – 7.74 (1H, d), 7.71 – 7.67 (1H, d), 7.64 – 7.58 (1H, d), 7.35 – 7.31 (1H, t), 7.13 – 7.09 (1H, s), 6.97 – 6.92 (1H, s), 4.11 – 4.06 (3H, s), 3.84 – 3.79 (3H, s)

^{13}C NMR (300 MHz, CD_3OD): δ 155.9, 146.9, 143.5, 137.6, 129.7, 128.9, 128.4, 127.3, 124.5, 123.6, 110.8, 35.9, 29.2



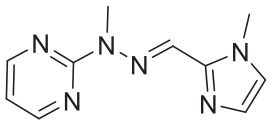
L³ - ^{1}H NMR (300 MHz, CD_3OD): δ 8.21 – 8.04 (2H, q), 7.88 – 7.82 (1H, s), 7.80 -7.68 (3H, m), 7.62 – 7.55 (1H, t), 7.39 – 7.27 (2H, m), 3.81 – 3.72 (3H, s)

^{13}C NMR (300 MHz, CD_3OD): δ 146.8, 137.1, 129.1, 127.1, 126.3, 124.4, 122.9, 111.3, 28.3



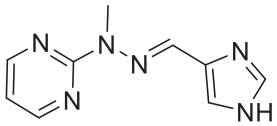
L⁷ - ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 – 8.38 (2H, d), 7.88 – 7.83 (1H, s), 7.18 – 7.00 (2H, b), 6.80 – 6.72 (1H, t), 3.72 – 3.66 (3H, s)

^{13}C NMR (300 MHz, $CDCl_3$): δ 159.7, 157.9, 145.0, 129.9, 113.2, 30.4



L⁸- ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 – 8.48 (2H, d), 7.94 -7.88 (1H, s), 6.94 – 6.90 (1H, s), 6.81 – 6.75 (1H, t), 4.17 – 4.12 (3H, s), 3.71 – 3.69 (3H, s)

^{13}C NMR (300 MHz, $CDCl_3$): δ 158.1, 131.5, 130.5, 128.9, 123.8, 113.4, 35.5, 30.3

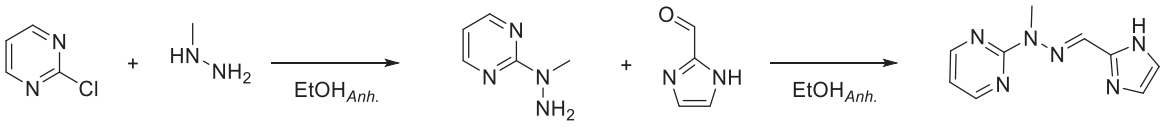


L⁹ - ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 – 8.38 (2H, d), 7.77 – 7.74 (1H, s), 7.66 – 7.62 (1H, s), 7.32 – 7.27 (1H, s), 6.70 – 6.77 (1H, t), 3.70 – 3.66 (3H, s)

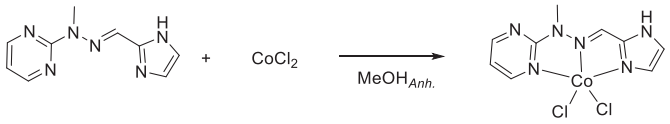
^{13}C NMR (300 MHz, $CDCl_3$): δ 159.9, 157.9, 137.2, 128.5, 112.8, 30.2

Synthesis and characterization of ligands **L⁴**, **L⁵**, **L⁶** are known and described.[1]

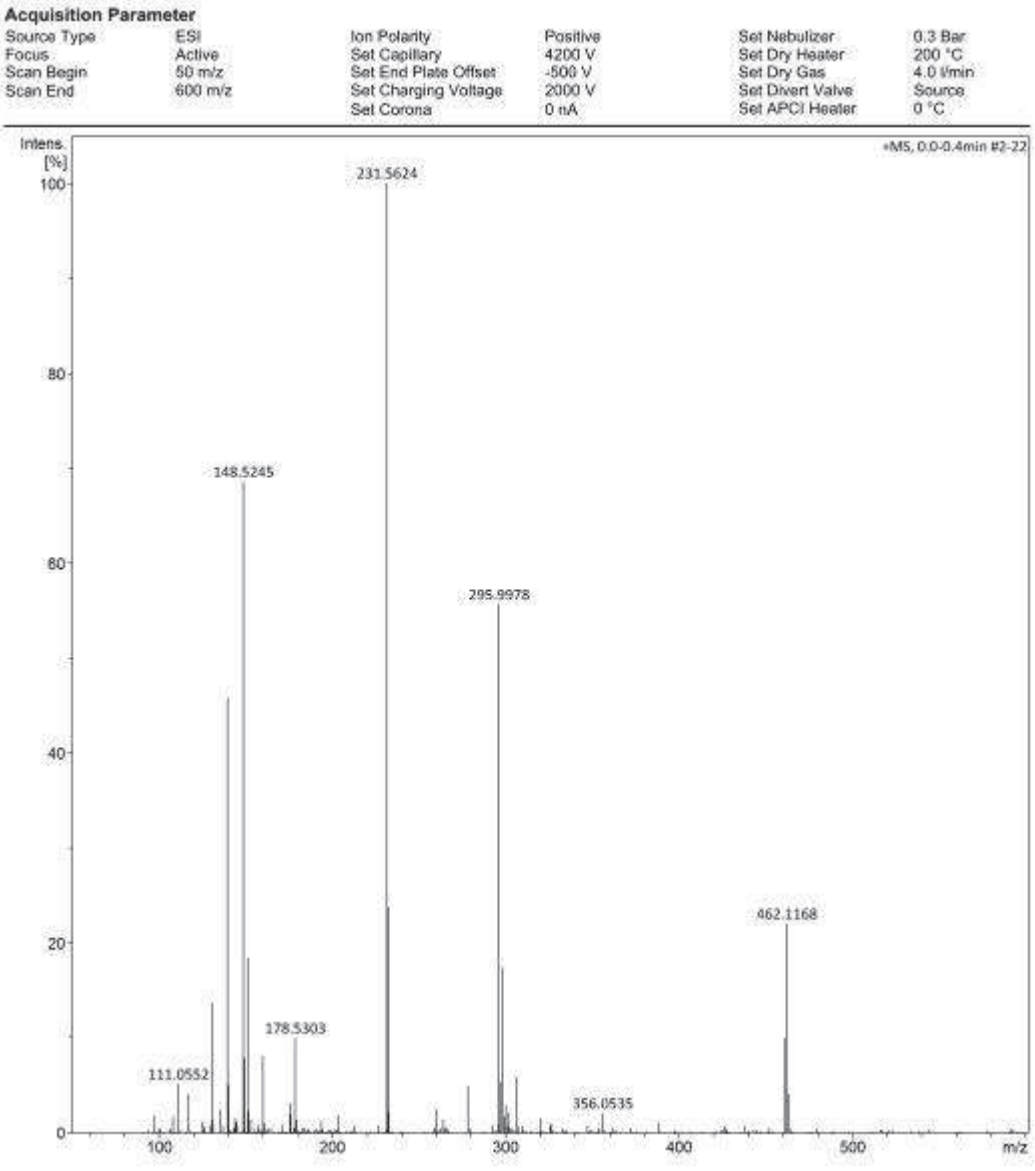
1.4. Ligand (**L⁷**) and complex **[Co(L⁷)Cl₂]** synthesis:

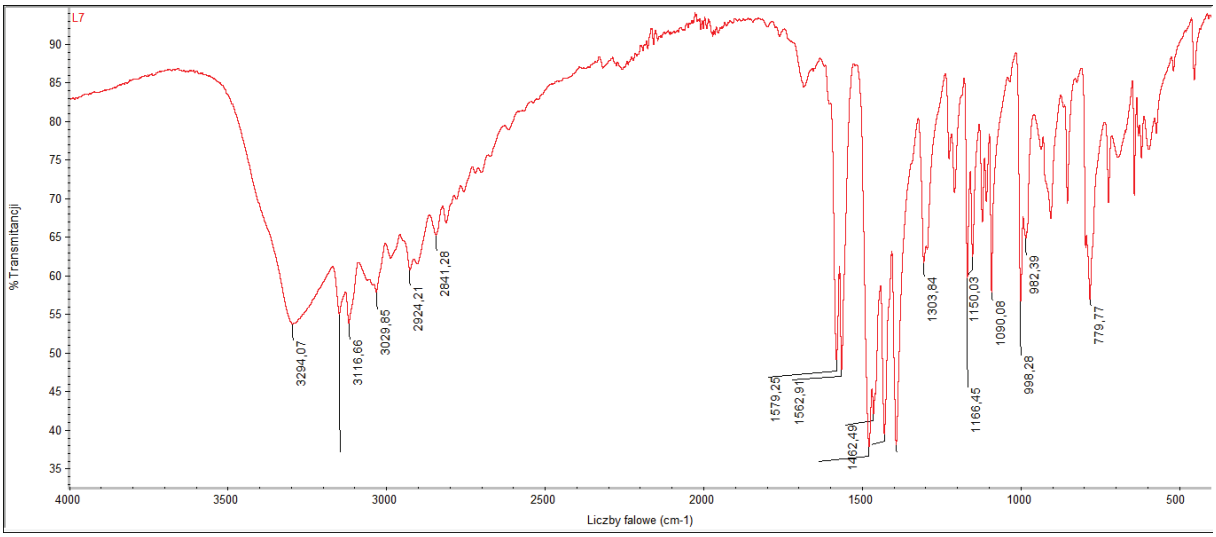


2-Chloropirymidine (5.73 g 0.05 mol) was placed under argon atmosphere in a two-necked round-bottomed flask. Methylhydrazine (11.9 g, 0.25 mol), in five-fold excess, was dissolved in anhydrous ethanol and added to the reaction mixture, which was heated in a heating mantle to 80°C and stirred for 20 h. The pale orange, crystalline product was filtered off on a Büchner funnel and dried under vacuum. Yield 53% (3.29 g, 0.026 mol). Then condensation of 2-imidazolecarboxyaldehyde with 2-(1-methylhydrazine)pyrimidine was performed. A two-necked round-bottomed flask was charged with 2-(1-methylhydrazine)pyrimidine (1 g, 8.05 mmol) under argon atmosphere. 4-Imidazolecarboxyaldehyde (0.772 g, 8.05 mmol) was dissolved in anhydrous ethanol and was added to the reaction mixture. The reaction mixture was stirred for 24 h at 60°C. Yellow clear solution was cooled to room temperature. The precipitate, was then filtered off by vacuum filtration, washed with anhydrous ethanol and dried under vacuum to give 0.833 g (4.12 mmol) of **L⁷**. The supernatant was concentrated to minimal volume and a subsequent part of the precipitate was obtained 0.253 g (1.25 mmol). Total yield is 67% (1.09 g, 5.37 mmol).

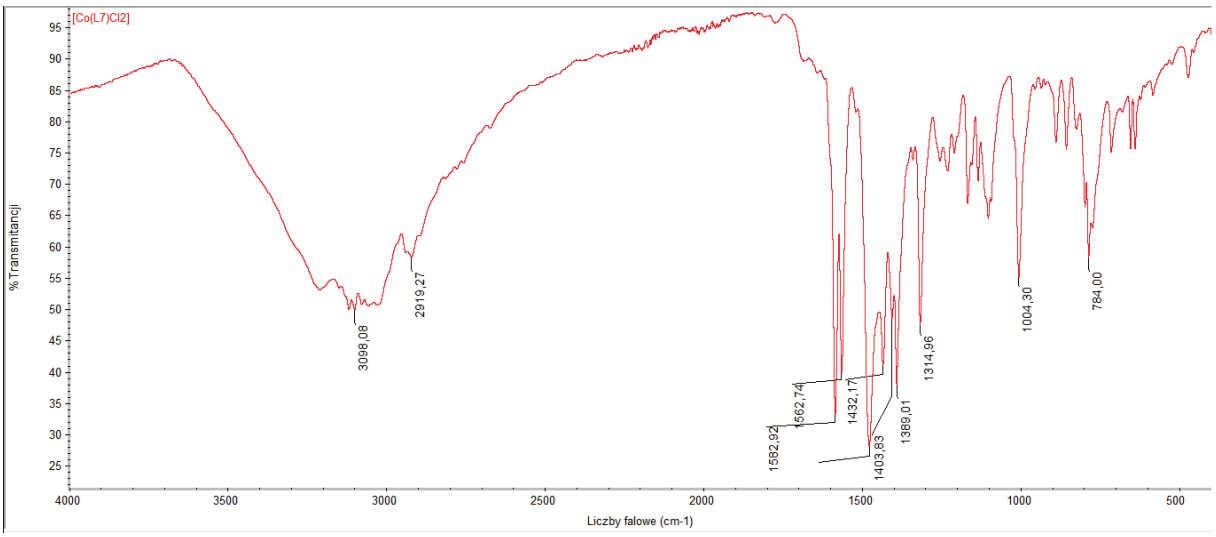


To a solution of **L**[7] (100.0 mg 4.95 mmol) in hot MeOH, the methanolic solution of anhydrous $CoCl_2$ (64.3 mg 4.95 mmol) was added. The mixture was stirred for 24 h at room temperature. The solvents were subsequently evaporated under vacuum to minimal volume. Then, excess of acetone was added. The precipitate was filtered off and washed twice with acetone and air dried, affording 146.2 mg (89% yield) of complex **[Co(L[7])Cl$_2$]**





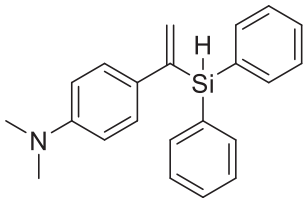
L^{7} IR spectra (cm^{-1}): 3294, 3116, 3029, 2924, 2841, 1579, 1562, 1462, 1303, 1166, 1150, 1090, 988, 779



[Co(L^{7})Cl$_2$] IR spectra (cm^{-1}): 3098, 2919, 1582, 1562, 1432, 1403, 1389, 1314, 1004, 784

2. Analytical data of isolated products

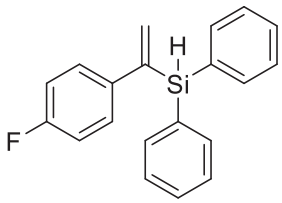
2.1. (2p) 4-(1-(diphenylsilyl)vinyl)aniline– prepared from 4-ethynyl-N,N-dimethylaniline (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (160.4.0 mg - 98%). Corresponds to reported data. [2]



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 – 7.70 (4H, m), 7.51 – 7.43 (8H, m), 6.80 – 6.73 (2H, d), 6.41 – 6.34 (1H, dd, *J* = 2.44, 1.08 Hz), 5.67 – 5.64 (1H, d, *J* = 2.44 Hz), 5.59 – 5.54 (1H, s), 3.02 – 2.98 (3H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 149.8, 144.5, 135.9, 133.6, 130.9, 129.7, 128.6, 128.1, 127.6, 112.6, 40.6

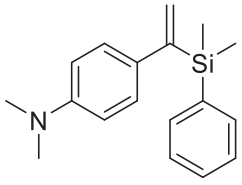
2.2. (2f) (1-(4-fluorophenyl)vinyl)diphenylsilane - prepared from (4-Fluoro)phenylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (145.9 mg - 96%). Corresponds to reported data. [2]



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 – 7.43 (4H, m), 7.35 – 7.18 (8H, m), 6.90 – 6.80 (2H, t), 6.17 – 6.12 (1H, d, *J* = 2.38 Hz), 5.62 – 5.57 (1H, d, *J* = 2.39 Hz), 5.31 – 5.26 (1H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.8, 160.6, 144.9, 139.0, 135.8, 132.8, 130.0, 128.2, 115.5, 115.2

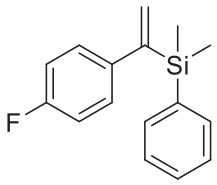
2.3. (3h) 4-(1-(dimethylphenylsilyl)vinyl)aniline– prepared from 4-ethynyl-N,N-dimethylaniline (0.5 mmol) and dimethylphenylsilane (0.5 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (133.5 mg - 95%). Corresponds to reported data. [3]



^{1}H NMR (300 MHz, $CDCl_3$): 7.53 – 7.43 (2H, m), 7.28 – 7.21 (3H, m), 7.05 – 6.96 (2H, m), 6.56 – 6.47 (2H, m), 5.93 – 6.87 (1H, d, *J* = 2.79 Hz), 5.48 – 5.42 (1H, d, *J* = 2.82 Hz), 2.82 – 2.74 (3H, s), 0.36 – 0.28 (6H, s)

^{13}C NMR (75 MHz, $CDCl_3$): 151.4, 141.0, 136.0, 133.9, 130.8, 129.7, 129.6, 128.3, 114.2, 42.5, 0.0

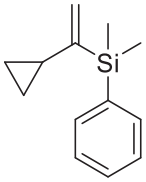
2.4. (3i) (1-(4-fluorophenyl)vinyl)(dimethyl)phenylsilane - prepared from (4-Fluoro)phenylacetylene (1.0 mmol) and dimethylphenylsilane (1.0 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (125.3 mg – 98%).



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 – 7.51 (2H, m), 7.40 – 7.32 (3H, m), 7.09 – 7.02 (2H, m), 6.95 – 6.86 (2H, m), 5.98 – 5.93 (1H, d, *J* = 2.73 Hz), 5.70 - 5.65 (1H, d, *J* = 2.76 Hz), 0.43 – 0.39 (6H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8, 162.5, 152.4, 142.5, 142.4, 140.0, 136.4, 131.6, 130.6, 130.3, 117.2, 0.0

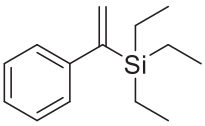
2.5. (3j) ((cyclopropyl)vinyl)(dimethyl)phenylsilane - prepared from cyclopropylacetylene (0.5 mmol) and dimethylphenylsilane (0.5 mmol) according to general procedure **B**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording pure product (93.9 mg – 93%). Corresponds to reported data. [4]



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 -7.53 (2H, m), 7.40 – 7.32 (3H, m), 5.48 – 5.45 (1H, dd, *J* = 2.55, 1.36 Hz), 5.27 – 5.22 (1H, d, *J* = 2.68 Hz), 1.44 – 1.33 (1H, dt), 0.65 – 0.56 (2H, m), 0.46 – 0.40 (8H, m)

^{13}C NMR (75 MHz, $CDCl_3$): δ 151.7, 138.3, 134.0, 128.9, 127.7, 121.6, 6.9

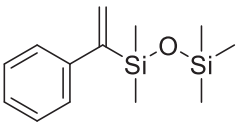
2.6. (4o) triethyl(1-phenylvinyl)silane - prepared from phenylacetylene (1.0 mmol) and triethylsilane (1.0 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (69.5 mg - 32%). Corresponds to reported data. [5]



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 – 7.63 (2H, m), 7.54 – 7.44 (3H, m), 6.89 – 6.85 (1H, d, *J* = 3.09 Hz), 5.59 – 5.56 (1H, d, *J* = 3.10 Hz), 0.96 – 0.89 (9H, t), 0.71 – 0.62 (6H, q)

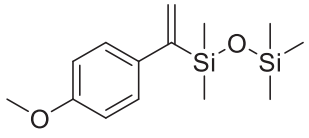
^{13}C NMR (75 MHz, $CDCl_3$): δ 150.4, 145.5, 128.8, 128.0, 126.6, 126.0, 7.3, 3.3

2.7. (4a) 1,1,1,3,3-pentamethyl-3-(1-phenylvinyl)disiloxane - prepared from pentamethyldisiloxane (0.5 mmol) and phenylacetylene (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (118,8 mg - 95%)



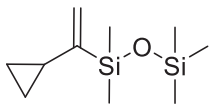
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 – 7.40 (3H, m), 7.23 – 7.20 (2H, m), 5.92 – 5.86 (1H, d, *J* = 2.99 Hz), 5.70 – 5.64 (1H, d, *J* = 2.96 Hz), 0.25 – 0.22 (6H, s), 0.08 – 0.05 (9H, s)

2.8. (4b) 1-(1-(4-methoxyphenyl)vinyl)-1,1,3,3,3-pentamethyldisiloxane - prepared from pentamethyldisiloxane (0.5 mmol) and (4-methoxy)phenylacetylene (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (128.9 mg - 92%).



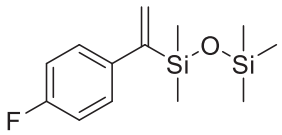
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 – 7.25 (2H, m), 6.93 – 6.86 (3H, m), 5.92 – 5.86 (1H, d, *J* = 2.98 Hz), 5.65 – 5.60 (1H, d, *J* = 2.96 Hz), 3.87 – 3.82 (3H, s), 0.28 – 0.23 (6H, s), 0.12 – 0.09 (9H, s

2.9. (4c) 1-(1-cyclopropylvinyl)-1,1,3,3,3-pentamethyldisiloxane - prepared from pentamethyldisiloxane (0.5 mmol) and cyclopropylacetylene (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (105.1mg - 98%).



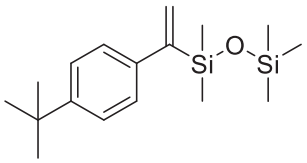
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.38 – 5.35 (1H, dd), 5.26 – 5.23 (1H, d), 2.21 – 2.10 (1H, m), 1.93 – 1.784 (2H, m), 1.51 – 1.33 (2H, m), 0.19 – 0.17 (6H, s), 0.11 – 0.09 (9H, s)

2.10. (4d) 1-(1-(4-fluorophenyl)vinyl)-1,1,3,3,3-pentamethyldisiloxane - prepared from pentamethyldisiloxane (0.5 mmol) and (4-Fluoro)phenylacetylene (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (130.2 mg - 98%).



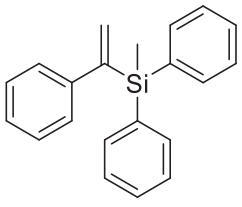
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 – 7.12 (2H, m), 6.99 – 6.95 (2H, m), 5.88 – 5.82 (1H, dd, *J* = 2.77, 1.31 Hz), 5.67 – 5.62 (1H, d, *J* = 2.81 Hz), 0.26 – 0.19 (6H, s), 0.08 – 0.03 (9H, s)

2.11. (4f) 1-(1-(4-(tert-butyl)phenyl)vinyl)-1,1,3,3,3-pentamethyldisiloxane - prepared from pentamethyldisiloxane (0.5 mmol) and (4-(tert-butyl))phenylacetylene (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (141.1mg - 92%).



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 – 7.33 (2H, m), 7.29 – 7.28 (2H, m), 5.95 – 5.92 (1H, d, *J* = 2.96 Hz), 5.68 – 5.65 (1H, d, *J* = 2.99 Hz), 1.36 – 1.35 (9H, s), 0.28 – 0.26 (6H, s), 0.10 – 0.08 (9H, s)

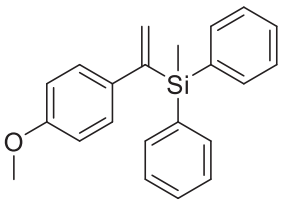
2.12. (4g) methyldiphenyl(1-phenylvinyl)silane– prepared from phenylacetylene (0.5 mmol) and methyldiphenylsilane (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (145.1 mg - 97%).



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 – 7.51 (4H, m), 7.43 – 7.32 (7H, m), 7.22 – 7.15 (4H, m), 6.19 – 6.13 (1H, d, *J* = 2.82 Hz), 5.62 – 5.55 (1H, d, *J* = 2.84 Hz), 0.69 – 0.64 (3H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 148.7, 143.8, 136.0, 135.2, 129.4, 128.1, 127.8, 127.0, 126.6, -3.4

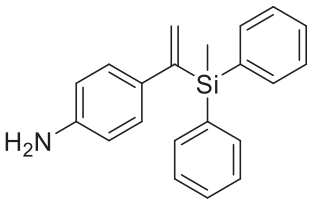
2.13. (4h) (1-(4-methoxyphenyl)vinyl)(methyl)diphenylsilane – prepared from 4-methoxyphenylacetylene (0.5 mmol) and methyldiphenylsilane (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (149.8 – 91%).



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 – 7.52 (4H, m), 7.41 – 7.35 (6H, m), 7.17 -7.09 (2H, m), 6.79 – 7.73 (2H, d), 6.16 – 6.08 (1H, dd, *J* = 2.77, 1.49 Hz), 5.54 – 5.48 (1H, dd, *J* = 2.80, 1.56 Hz), 3.78 – 3.75 (3H, s), 0.69 – 0.65 (3H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 147.9, 136.5, 136.3, 135.4, 130.7, 129.6, 128.4, 128.1, 113.8, 55.2, -3.0

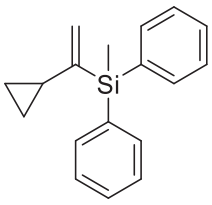
2.14. (4i) 4-(1-(methyldiphenylsilyl)vinyl)aniline – prepared from 4-ethynyl-N,N-dimethylaniline (0.5 mmol) and methyldiphenylsilane e (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (153.9 mg – 98%).



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 – 7.50 (4H, m), 7.43 – 7.30 (6H, m), 7.06 – 7.00 (2H, m), 6.56 – 6.51 (2H, m), 6.15 – 6.05 (1H, d, *J* = 2.73 Hz), 5.46 – 5.36 (1H, d, *J* = 2.77 Hz), 3.64 – 3.53 (2H, s), 0.69 – 0.65 (3H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.5, 145.1, 136.5, 135.2, 133.9, 129.4, 129.2, 128.0, 127.8, 114.9, -3.2

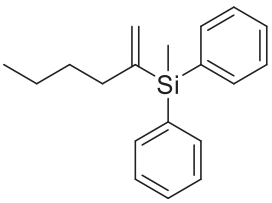
2.15. (4j) (1-cyclopropylvinyl)(methyl)diphenylsilane – prepared from cyclopropylacetylene (0.5 mmol) and methyldiphenylsilane (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (114.4 mg - 87%)



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 – 7.52 (4H, m), 7.40 – 7.34 (6H, m), 5.60 – 5.56 (1H, dd, *J* = 2.43, 1.27 Hz), 5.25 – 5.22 (1H, d, *J* = 2.44 Hz), 1.48 – 1.39 (1H, dt), 0.73 – 0.68 (3H, s), 0.67 – 0.59 (2H, m), 0.52 – 0.46 (2H, m)

^{13}C NMR (75 MHz, $CDCl_3$): δ 149.9, 136.1, 135.1, 129.2, 127.7, 123.8, 15.6, 7.7, -3.8

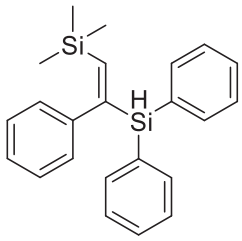
2.16. (4k) hex-1-en-2-yl(methyl)diphenylsilane – prepared from hex-1-yne (0.5 mmol) and methyldiphenylsilane (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (135.8 mg - 97%). Corresponds to reported data. [6]



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 – 7.49 (4H, m), 7.40 – 7.32 (6H, m), 5.87 – 5.80 (1H, d, *J* = 2.91 Hz), 5.42 – 5.36 (1H, d, *J* = 2.82 Hz), 2.22 - 2.12 (3H, t), 1.41 – 1.17 (4H, m), 0.86 – 0.77 (3H, t), 0.68 – 0.63 (3H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 148.4, 136.2, 135.0, 129.2, 128.2, 127.7, 35.7, 31.0, 22.4, 13.9, -3.9

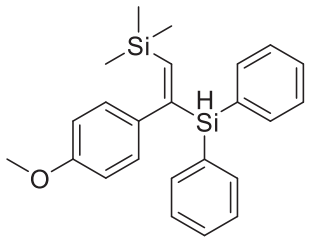
2.17. (5a) (E)-(2-(diphenylsilyl)-2-phenylvinyl)trimethylsilane - prepared from 1-Phenyl-2-trimethylsilylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (166.5 mg - 93%). Corresponds to reported data. [7]



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 – 7.48 (4H, m), 7.41- 7.33 (6H, m) 7.19 – 7.14 (3H, m), 6.99 – 6.94 (2H, m), 6.63 – 6.59 (1H, s), 5.33 – 5.32 (0.15H, s), 5.20 – 5.17 (0.85H, s), -0.13 - -0.16 (9H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 160.5, 159.0, 151.4, 144.5, 135.8, 133.3, 129.7, 127.9, 127.7, 126.3, 0.0

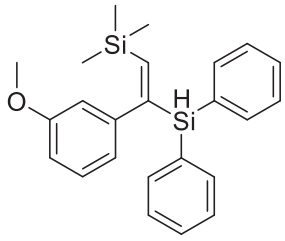
2.18. (5b) (E)-(2-(diphenylsilyl)-2-(4-methoxyphenyl)vinyl)trimethylsilane - prepared from ((4-methoxyphenyl)ethynyl)trimethylsilane (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (188.4 mg - 97%)



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 – 7.48 (4H, m), 7.40 – 7.33 (7H, m), 6.90 – 6.87 (2H, m), 6.75 – 6.72 (2H, m), 6.59 – 6.57 (1.H, s), 5.19 – 5.16 (1H, s), 3.77 – 3.7., 5 (3H, s) -0.12 - -0.15 (9H, s),

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5, 158.2, 151.3, 136.9, 135.8, 133.5, 129.6, 128.5, 128.8, 127.9, 113.2, 55.1, -0.1

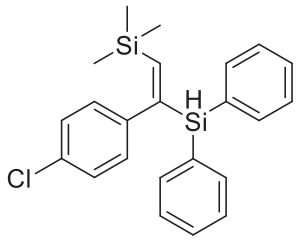
2.19. (5c) (E)-(2-(diphenylsilyl)-2-(3-methoxyphenyl)vinyl)trimethylsilane - prepared from ((3-methoxyphenyl)ethynyl)trimethylsilane (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (187.0mg - 96%)



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 – 750 (3H, m), 7.40 – 7.32 (7H, m), 7.13 – 7.07 (1H, t), 6.73 – 6.68 (1H, dd), 6.61 – 6.60 (1H, s), 6.59 – 6.56 (1H, d), 5.20 – 5.15 (1H, s), 6.64 – 3.62 (3H, s), -0.10 - -0.13 (9H, s)

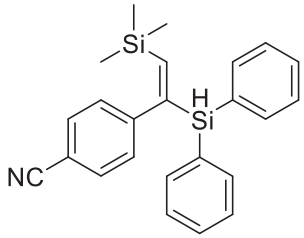
^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 158.8, 151.2, 145.8, 135.8, 133.3, 129.7, 128.8, 127.9, 120.3, 112.9, 112.3, 55.0, 0.0

2.20. (5d) (E)-(2-(4-chlorophenyl)-2-(diphenylsilyl)vinyl)trimethylsilane - prepared from ((4-chlorophenyl)ethynyl)trimethylsilane (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (141.3mg - 72%)



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 – 7.53 (3H, m), 7.50 – 7.47 (4H, m), 7.19 – 7.12 (5H, m), 6.90 - 6.85 (2H, m), 5.20 – 5.11 (1H, s), -0.13 - -0.15 (9H, s)

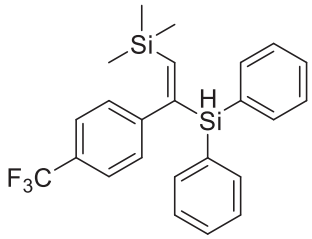
2.21. (5e) (E)-4-(1-(diphenylsilyl)-2-(trimethylsilyl)vinyl)benzonitrile - prepared from 4-((trimethylsilyl)ethynyl)benzonitrile (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (186.1mg - 97%)



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 – 7.46 (6H, m), 7.41 – 7.35 (7H, m), 7.04 – 7.01 (2H, d), 6.69 – 6.67 (1H, s), 5.17 – 5.14 (1H, s), -0.14 - -0.16 (9H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 157.6, 152.8, 149.7, 135.6, 132.2, 131.6, 130.0, 128.45, 128.1, 119.0, 110.0, 0.0

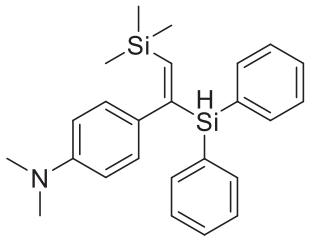
2.22. (5f) (E)-(2-(diphenylsilyl)-2-(4-(trifluoromethyl)phenyl)vinyl)trimethylsilane - prepared from trimethyl((4-(trifluoromethyl)phenyl)ethynyl)silane (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (202.5 mg - 95%)



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 – 7.50 (4H, m), 7.47 – 7.41 (6H, m), 7.40 – 7.36 (4H, m), 7.10 – 7.04 (2H, d), 6.71 – 6.68 (1H, s), 5.21 – 5.18 (1H, s), -0.11 - -0.15 (9H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.3, 157.9, 152.5, 148.3, 135.7, 134.3, 133.9, 132.5, 129.9, 128.0, 124.7, 0.0

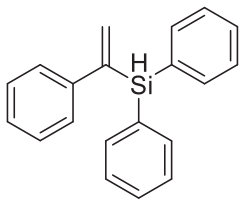
2.23. (5g) (E)-4-(1-(diphenylsilyl)-2-(trimethylsilyl)vinyl)-N,N-dimethylaniline - prepared from N,N-dimethyl-4-((trimethylsilyl)ethynyl)aniline (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (184.7 mg - 92%)



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 – 7.49 (4H, m), 7.38 – 7.33 (6H, m), 6.90 – 6.86 (2H, d), 6.60 – 6.56 (2H, d), 6.51 – 6.50 (1H, s), 2.91 – 2.90 (6H, s), -0.10 - -0.12 (9H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 150.4, 149.3, 135.8, 133.9, 132.9, 129.5, 128.6, 127.9, 112.0, 40.6, -0.3

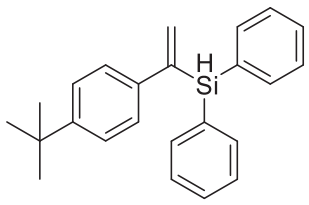
2.24. (2a) diphenyl(1-phenylvinyl)silane - prepared from phenylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (135.9 mg - 95%). Corresponds to reported data. [4]



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 – 7.56 (4H, m), 7.46 – 7.35 (10H, m), 7.27 – 7.23 (1H, m), 6.34 – 6.28 (1H, dd, J = 2.47, 0.99 Hz), 5.75 – 5.68 (1H, d, J = 2.52 Hz), 5.44 – 5.40 (1H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 145.9, 142.9, 135.7, 133.0, 132.1, 129.8, 128.4, 128.0, 127.0, 126.7

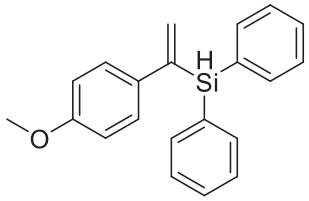
2.25. (2e) (1-(4-(tert-butyl)phenyl)vinyl)diphenylsilane - prepared from (4-(tert-butyl))phenylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (157.6 mg - 92%). Corresponds to reported data. [4]



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 – 7.55 (4H, m), 7.43 – 7.35 (7H, m), 7.31 – 7.28 (3H, m), 6.34 – 6.29 (1H, dd, J = 2.51, 1.17 Hz), 5.66 – 5.62 (1H, d, J = 2.39 Hz), 5.42 – 5.36 (1H, s), 1.13 – 1.28 (9H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 150.1, 145.1, 139.7, 135.8, 133.2, 131.1, 129.7, 128.0, 126.3, 125.3, 34.4, 31.3

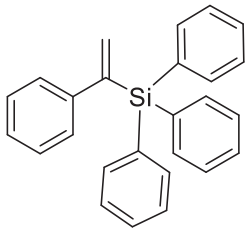
2.26. (2r) (1-(4-methoxyphenyl)vinyl)diphenylsilane - prepared from phenylacetylene (0.5 mmol) and diphenylsilane (0.5 mmol) according to general procedure **A**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (151.7 mg - 96%). Corresponds to reported data. [4]



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 – 7.54 (4H, m), 7.40 – 7.29 (8H, m), 6.84 – 6.77 (2H, d, J = 2.42, 0.98 Hz), 6.27 – 6.21 (1H, dd, J = 2.44, 0.79 Hz), 5.63 – 5.58 (1H, d), 5.41 – 5.36 (1H, s), 3.78 – 3.76 (3H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 144.7, 135.8, 135.2, 134.3, 133.2, 130.5, 129.7, 128.0, 113.8, 55.2

2.27. (4n) triphenyl(1-phenylvinyl)silane - prepared from (4-methoxy) phenylacetylene (0.5 mmol) and triphenylsilane (0.5 mmol) according to general procedure **C**. Purified by extraction with *n*-hexane followed by filtration through silica plug. Volatiles were removed under lower pressure affording product (168.6 mg - 93%). Corresponds to reported data. [5]



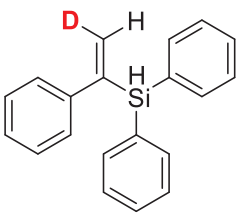
^{1}H NMR (300 MHz, $CDCl_3$): δ 7/53 – 7.47 (6H, m), 7.43 – 7.38 (4H, m), 7.36 – 7.31 (6H, m), 7.19 – 7.16 (4H, s), 6.30 – 6.27 (1H, d, *J* = 2.72 Hz), 5.71 – 5.68 (1H, d, *J* = 2.74 Hz)

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.2, 143.9, 136.4, 134.2, 133.9, 129.5, 128.1, 127.8, 127.4, 126.7

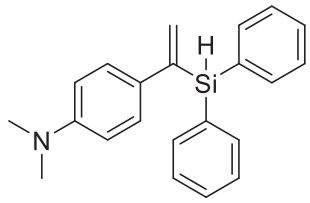
3. Deuterium labelled experiment

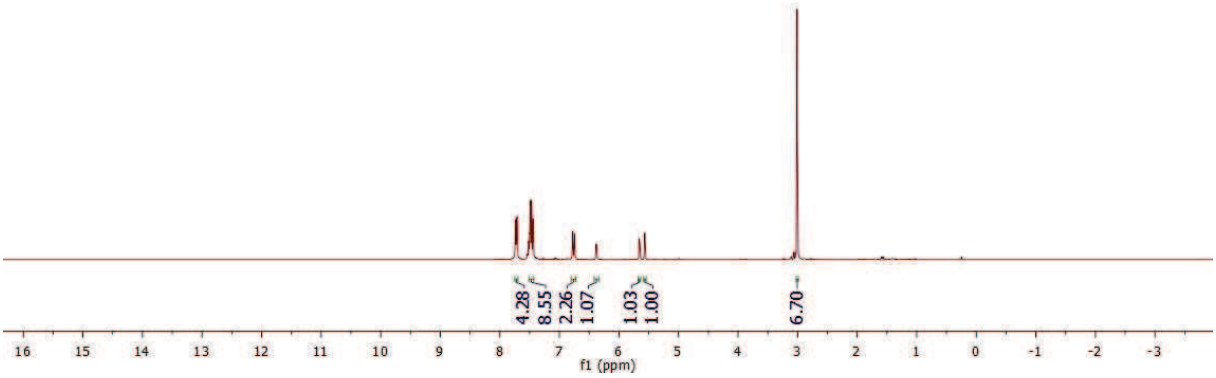
3.1 Hydrosililation of D_1-phenylaceylene with diphenylsilane.

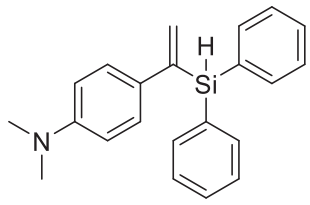
To a flame-dried Schlenk bomb flask charged with argon, precatalyst (0.1 mol %), THF (0.5 mL), diphenylsilane (0.5 mmol), and D_1-phenylacetylene (0.5 mmol) were placed. Mixture was then heated to 40°C with stirring. After 10 minutes $LiHBEt_3$ was added (0.3 mol %), and reaction vessel was then closed. After 20 hours, diethyl ether was added to reaction mixture. Solution was then filtered through silica plug, and concentrated on rotavapor. The crude mixture was purified by evaporating volatiles on vacuum line followed by extraction with hexane. Regioselectivity was monitored by ^{1}H NMR.



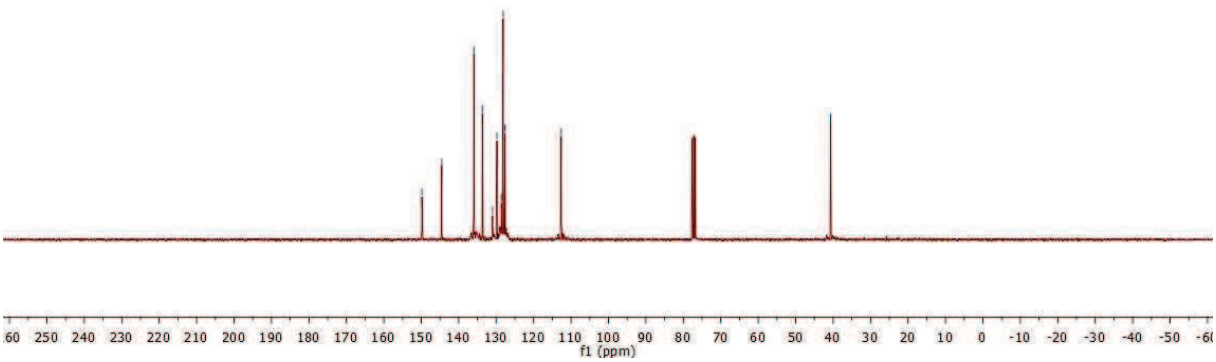
^{1}H NMR (300 MHz, $CDCl_3$): δ7.60– 7.55 (m, 4H), 7.44 – 7.32 (m, 10H), 7.24-7.21 (m, 3H), **[6.34 – 6.28 *Not observed*],** 5.69 - 5.67 (s, 1H,), 5.42 – 5.38 (s, 1H)

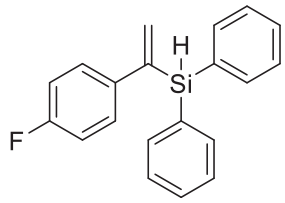

H
Si
N

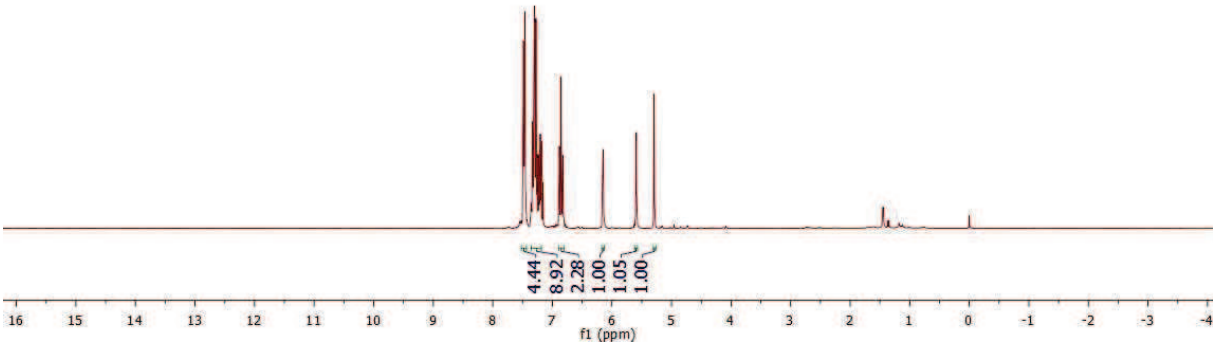

4.28
8.55
2.26
1.07
1.03
1.00
6.70
f1 (ppm)

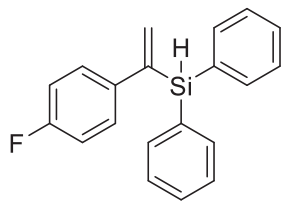

H
Si
N


149.83
144.52
135.96
133.69
130.96
129.79
128.61
128.13
127.64
112.61
40.66

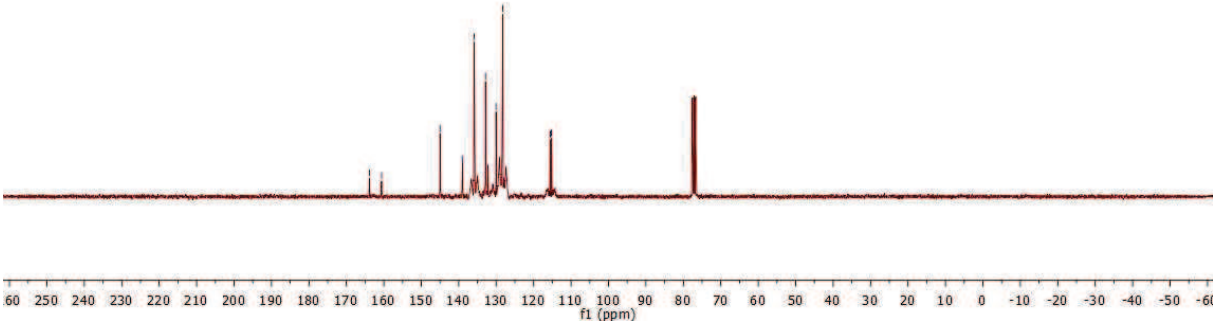

f1 (ppm)

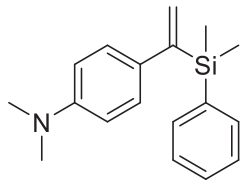

H
Si
F


4.44
8.92
2.28
1.00
1.05
1.00
f1 (ppm)


H
Si
F

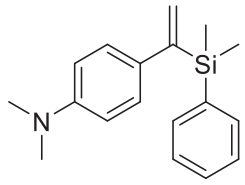

163.86
160.60
144.98
139.04
135.66
132.86
130.04
128.23
115.52
115.23

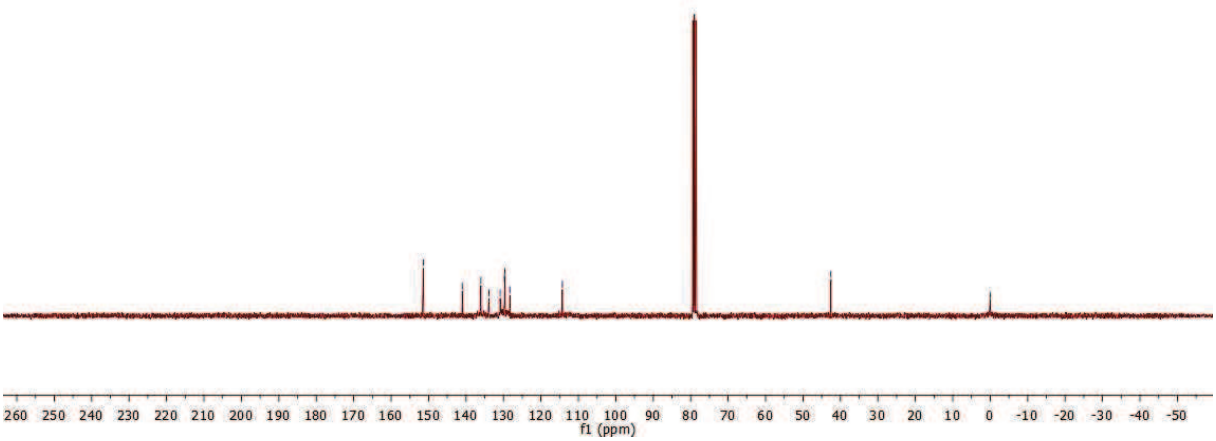

f1 (ppm)

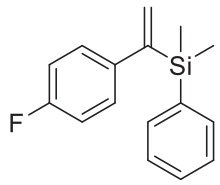

Si
N

2.08
3.13
2.04
2.06
0.99
1.00
6.11
6.15
f1 (ppm)

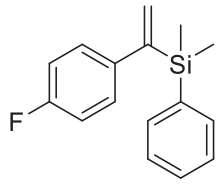

151.41
141.01
136.04
133.90
130.88
129.76
129.62
128.30
114.29
42.56
0.01


Si
N

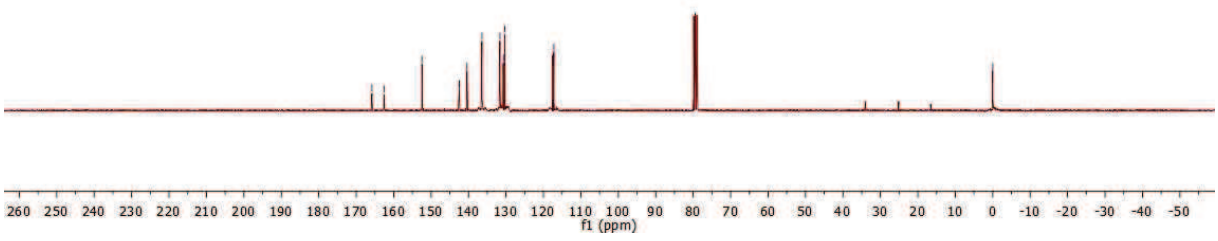

f1 (ppm)

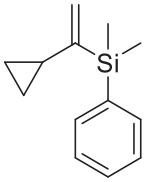

Si
F

1.93
3.10
2.04
2.08
1.00
1.01
5.88
f1 (ppm)

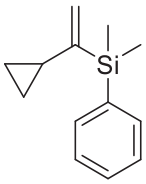

Si
F


165.82
162.58
152.45
142.53
142.48
140.42
136.43
131.62
130.69
130.33
117.21
0.00

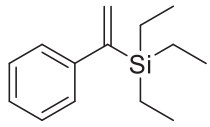

f1 (ppm)

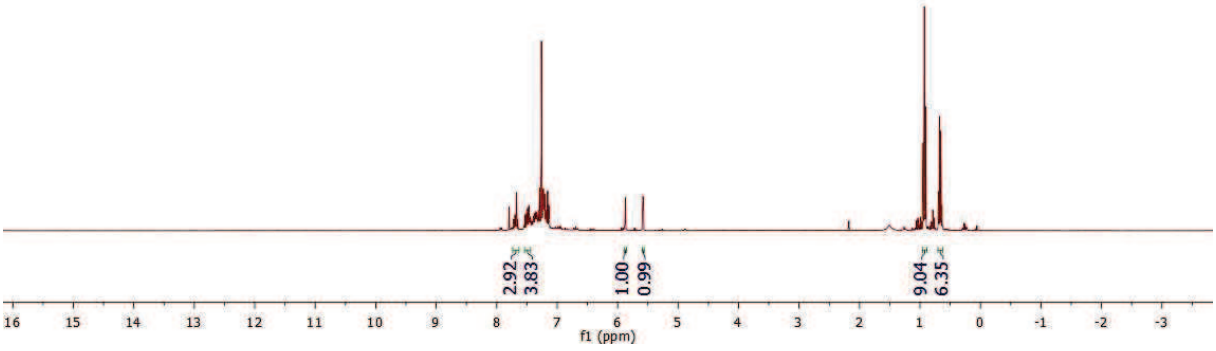

Si

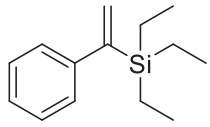
2.10
3.21
0.96
1.00
1.03
2.12
8.03
f1 (ppm)


Si

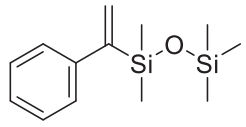
151.77
138.37
134.02
128.94
127.72
121.60
6.90
f1 (ppm)

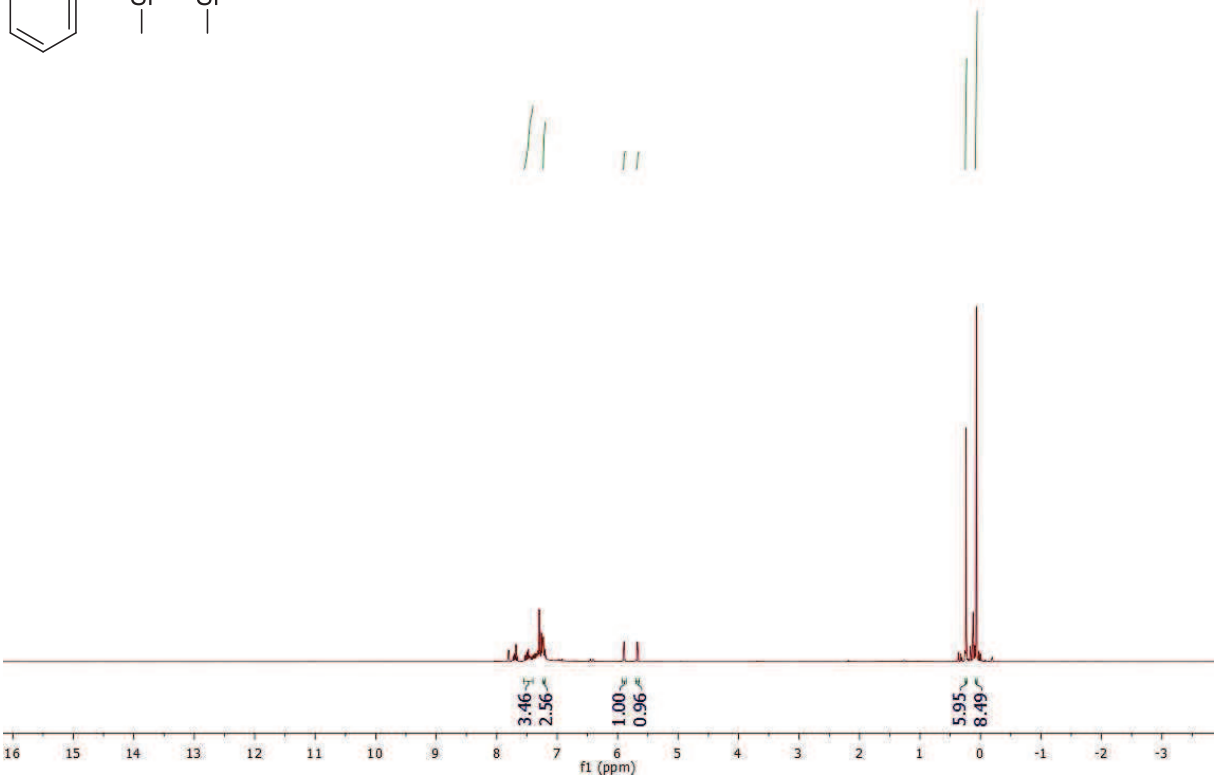

Si

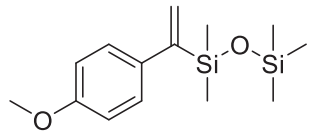

2.92
3.83
1.00
0.99
9.04
6.35
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Si

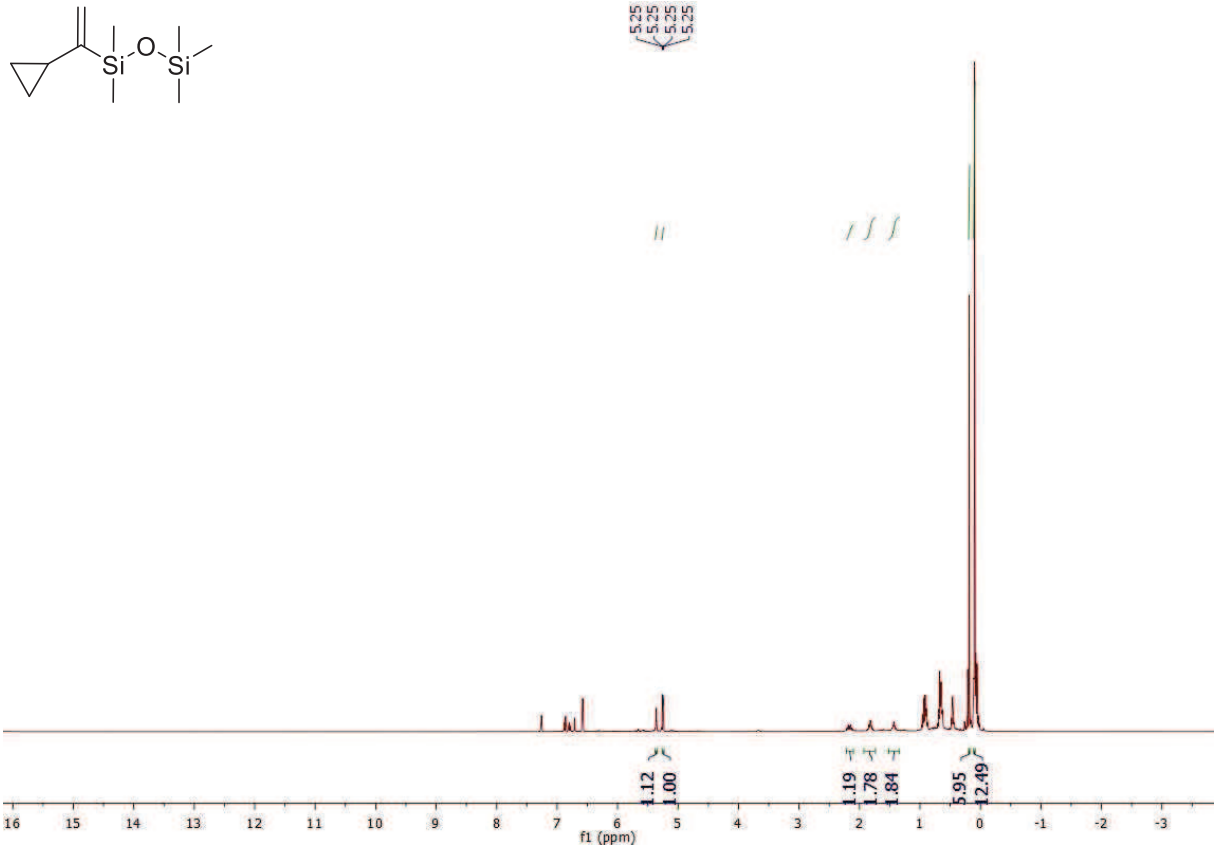
150.47
145.53
128.82
128.08
126.66
126.09
7.30
3.31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

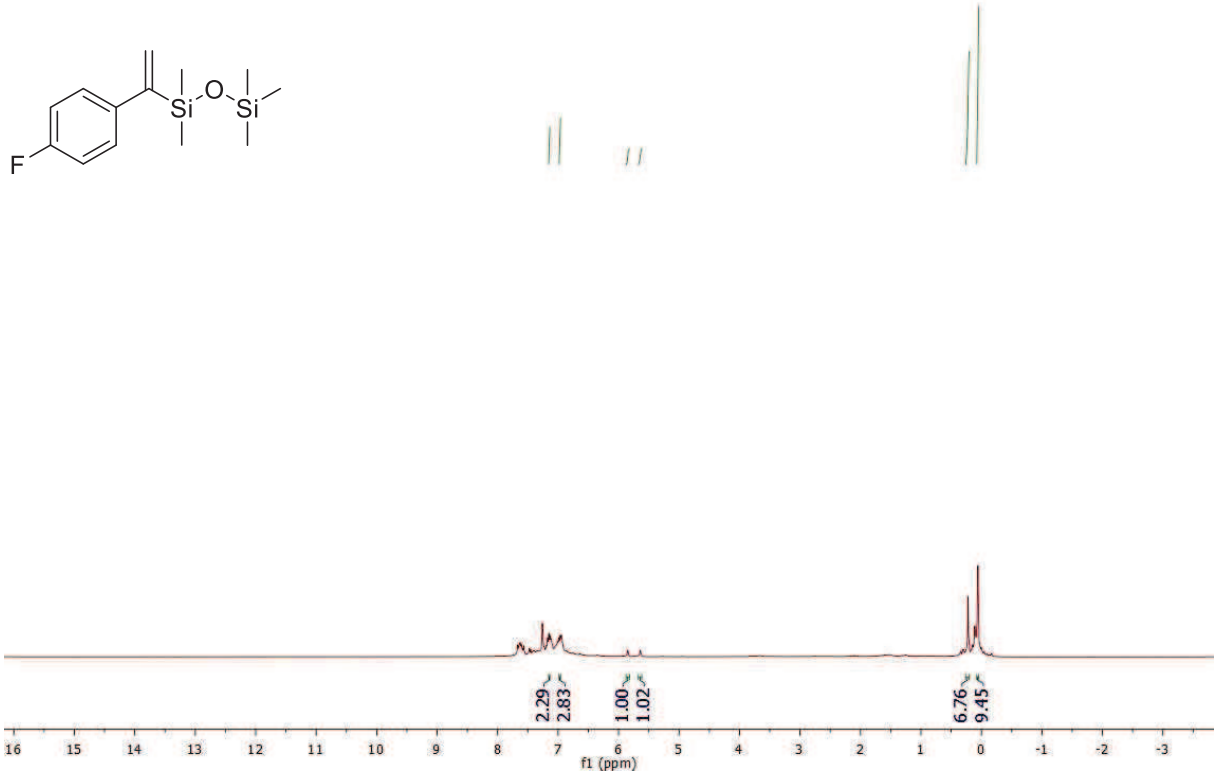

Si
O
Si

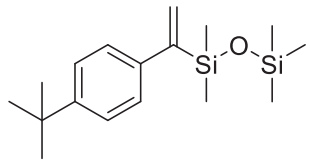

3.46
2.56
1.00
0.96
5.95
8.49
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

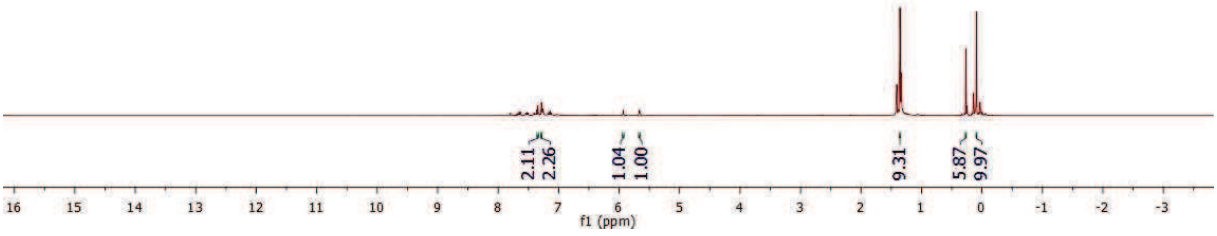

Si
O
Si
O

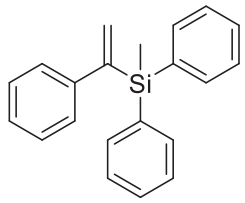
2.43
3.32
1.00
0.93
6.21
6.19
9.88
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Si
O
Si
5.25
5.25
5.25
5.25
1.12
1.00
1.19
1.78
1.84
5.95
12.49
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

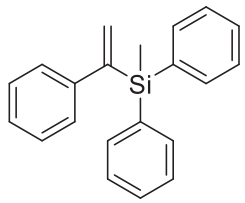

F
Si
O
Si
2.29
2.83
1.00
1.02
6.76
9.45
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Si
O
Si

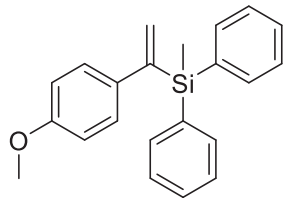

2.11
2.26
1.04
1.00
9.31
5.87
9.97
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


Si

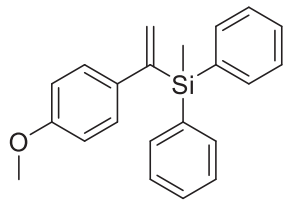
4.56
7.13
4.88
1.00
1.02
3.09
f1 (ppm)


Si

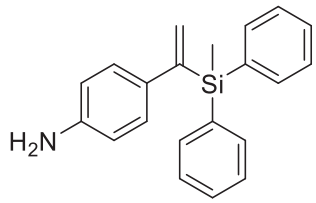
148.77
143.84
136.06
135.21
129.40
128.18
127.88
127.08
126.62
-3.46
f1 (ppm)


Si
O

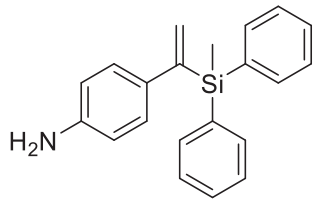
4.83
6.69
2.05
2.04
1.02
1.00
2.92
3.00
f1 (ppm)


Si
O

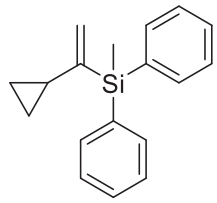
158.82
147.95
136.50
136.30
135.43
130.76
129.64
128.40
128.16
113.87
55.29
-3.05
f1 (ppm)


Si
H2N

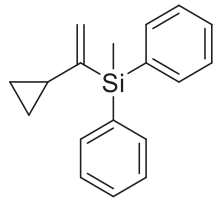
4.11
6.77
1.92
1.86
1.00
1.00
1.78
2.85
f1 (ppm)


Si
H2N

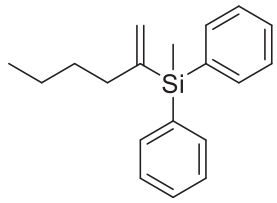
147.59
145.17
136.50
135.22
133.94
129.47
129.26
128.08
127.82
114.93
-3.25
f1 (ppm)


Si

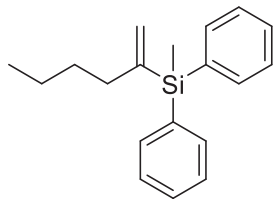
4.36
6.38
1.00
1.01
1.02
3.02
2.68
2.01
f1 (ppm)


Si

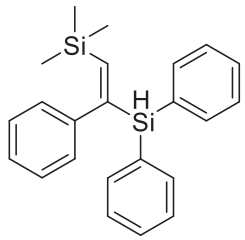
149.91
136.11
135.14
129.25
127.76
123.80
15.63
7.74
-3.89
f1 (ppm)

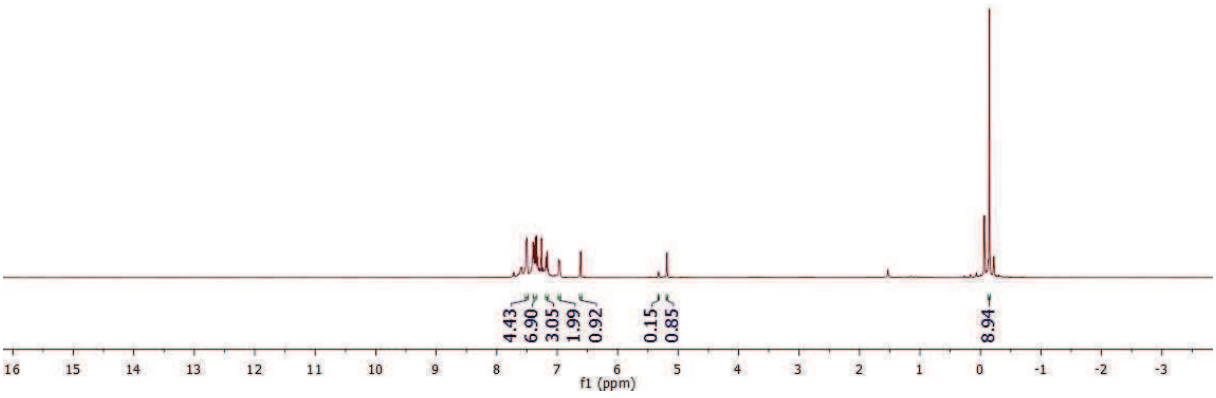

Si

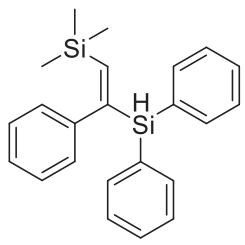
4.37
6.84
1.00
1.00
2.10
4.58
3.05
3.08
f1 (ppm)


Si

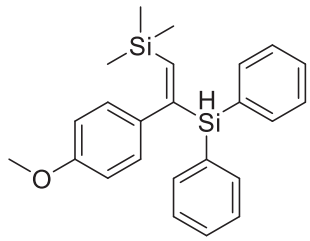
148.46
136.23
135.06
129.20
128.26
127.75
35.71
31.01
22.49
13.93
-3.92
f1 (ppm)

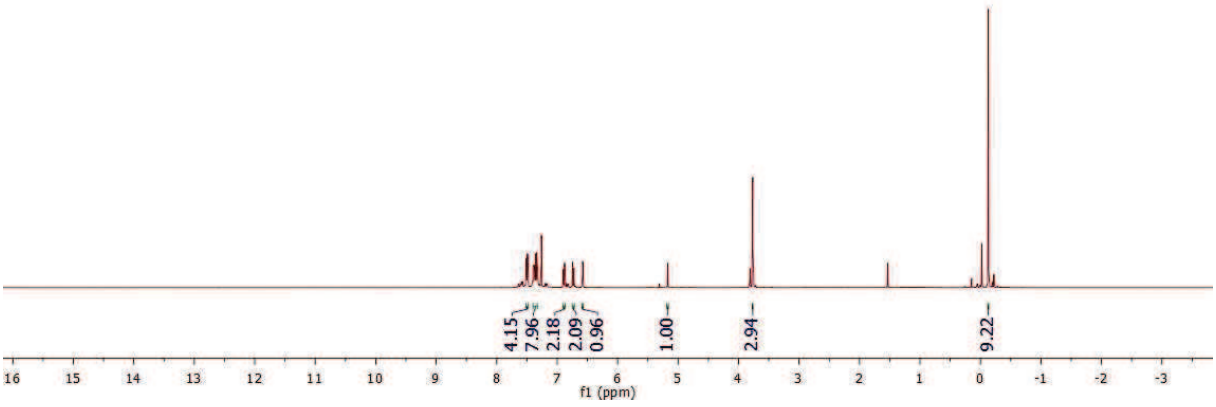

Si
H
Si

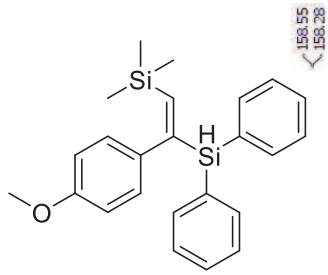

4.43
6.90
3.05
1.99
0.92
0.15
0.85
8.94
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Si
H
Si

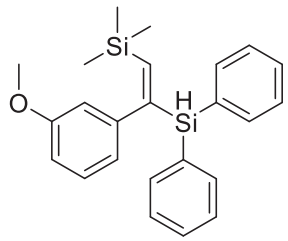
160.55
159.07
151.43
144.51
135.82
133.35
129.71
127.97
127.79
126.29
0.08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

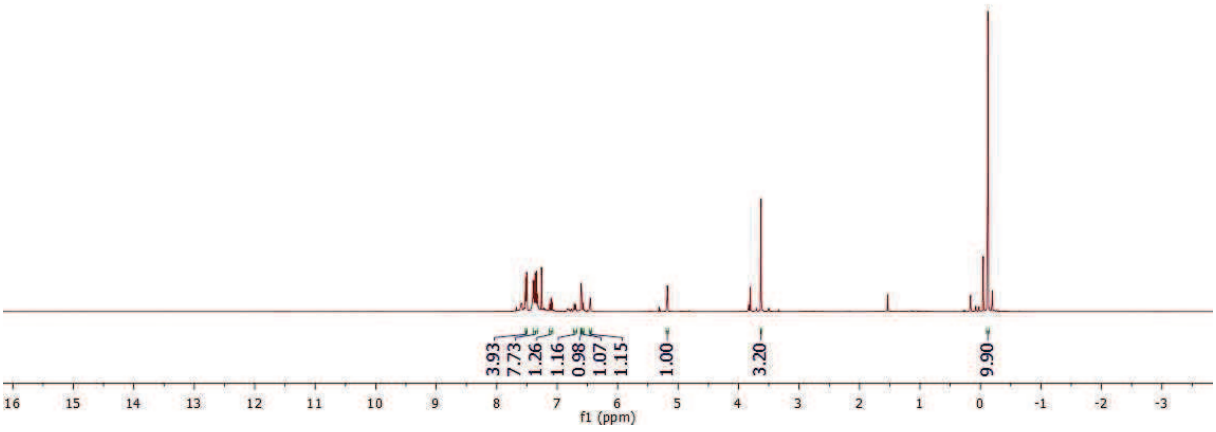

Si
H
Si
O

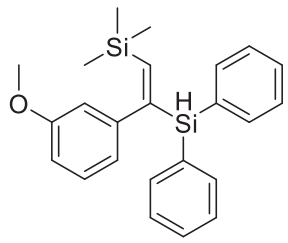

4.15
7.96
2.18
2.09
0.96
1.00
2.94
9.22
f1 (ppm)


Si
H
Si
O

158.55
158.28
151.37
136.91
135.81
133.52
129.65
128.85
127.95
113.20
55.17
0.16
f1 (ppm)

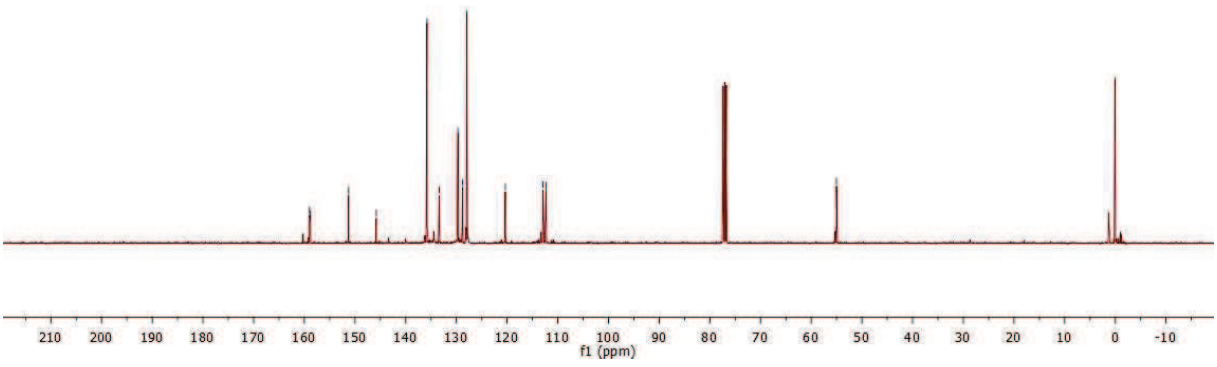

Si
O
H
Si

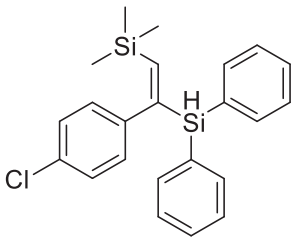

3.93
7.73
1.26
1.16
0.98
1.07
1.15
1.00
3.20
9.90
f1 (ppm)

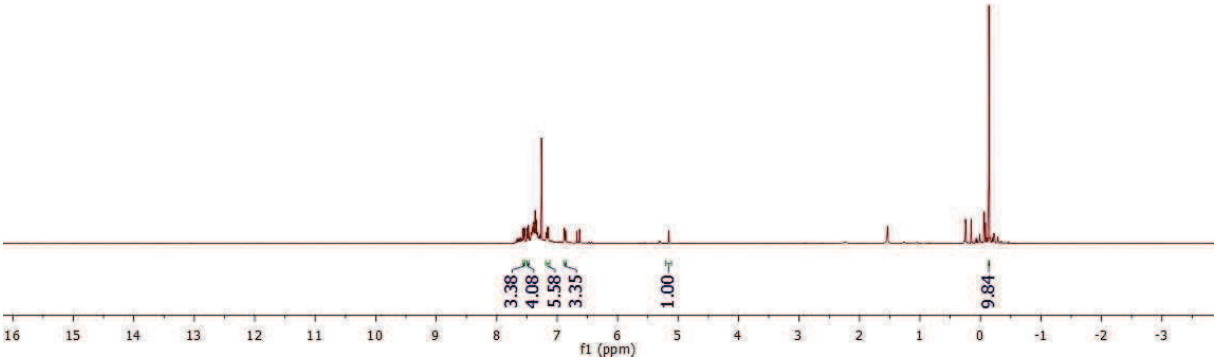

Si
O
H
Si

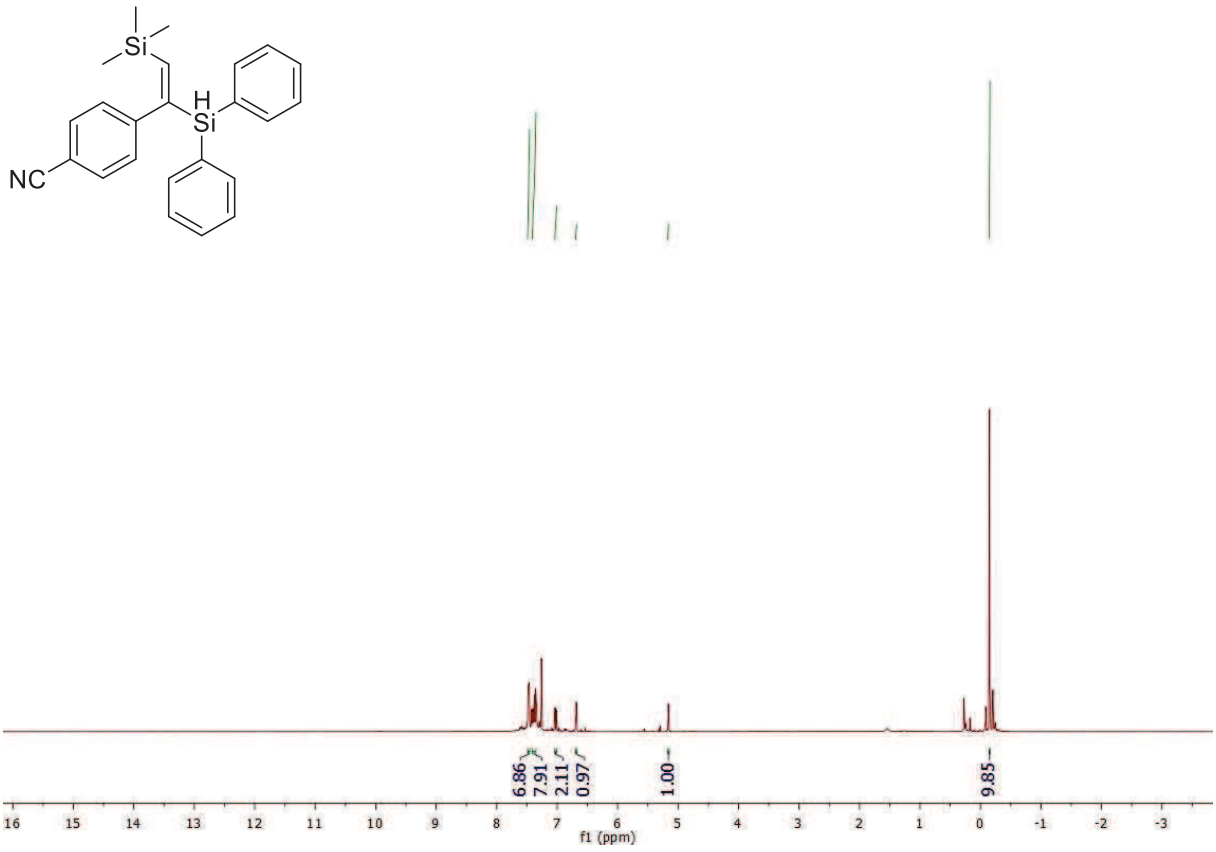

158.99
158.81
151.27
145.83
135.80
133.36
129.70
128.80
127.95
120.35
112.92
112.31

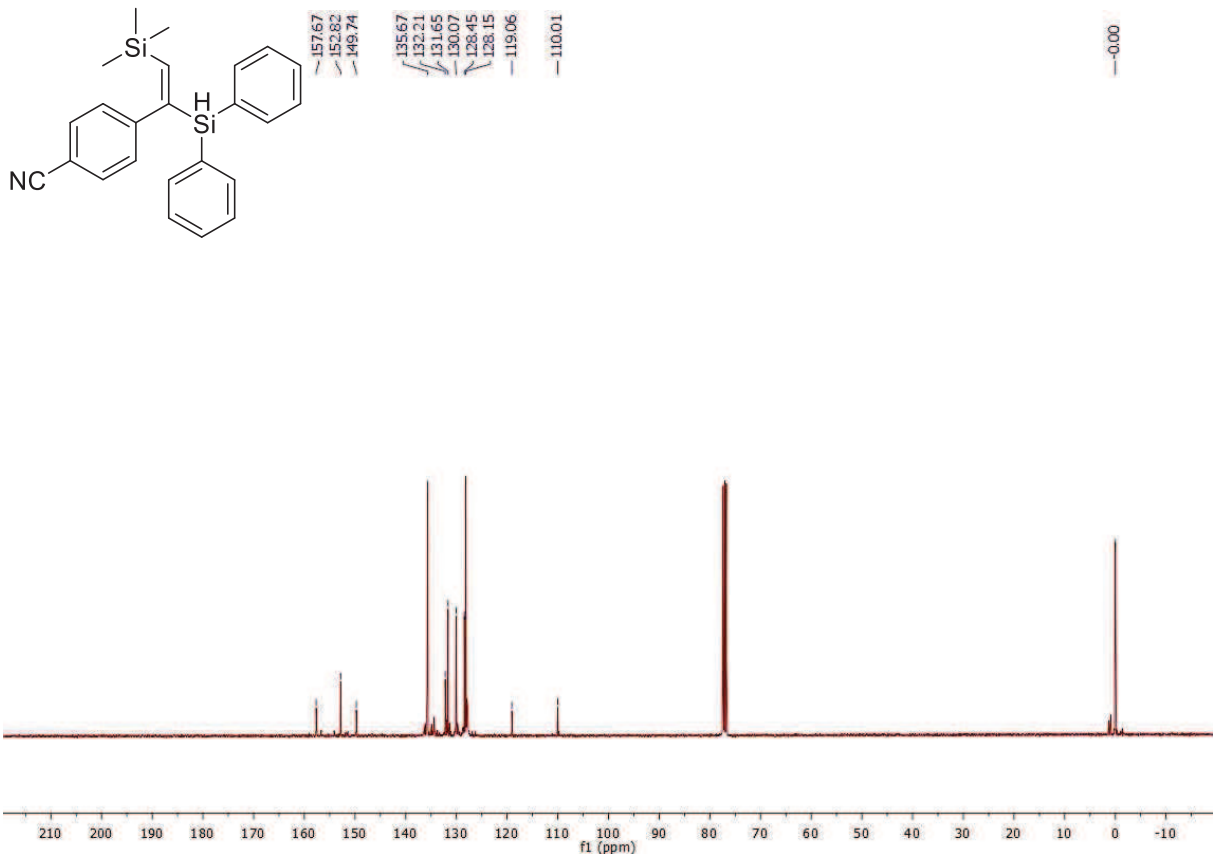

55.03
0.07

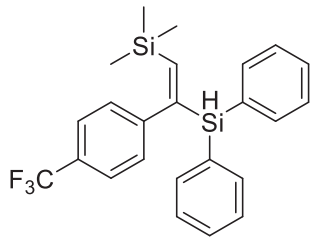

f1 (ppm)

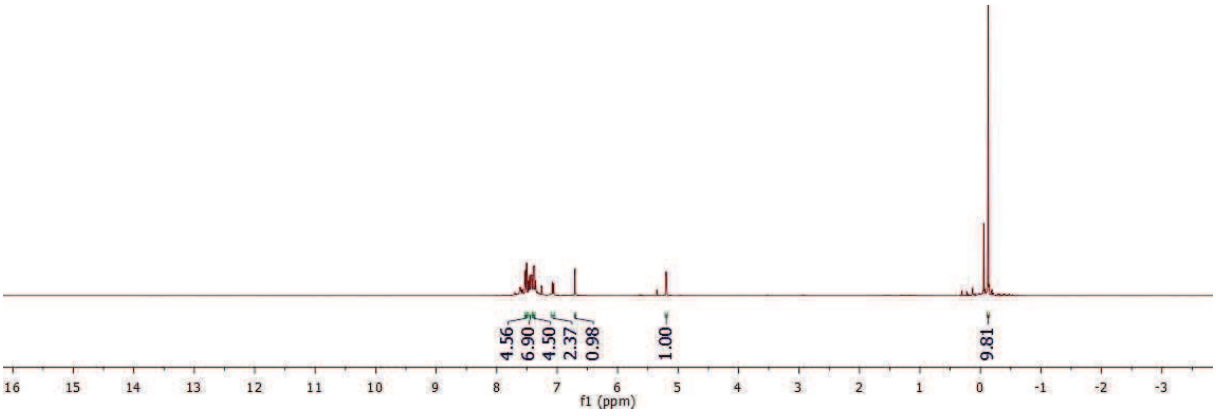

Si
H
Si
Cl

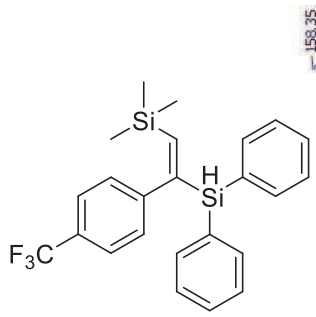

3.38
4.08
5.58
3.35
1.00
9.84
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


Si
H
Si
NC
6.86
7.91
2.11
0.97
1.00
9.85
f1 (ppm)

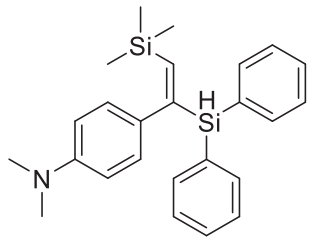

Si
H
Si
NC
157.67
152.82
149.74
135.67
132.21
131.65
130.07
128.45
128.15
119.06
110.01
0.00
f1 (ppm)

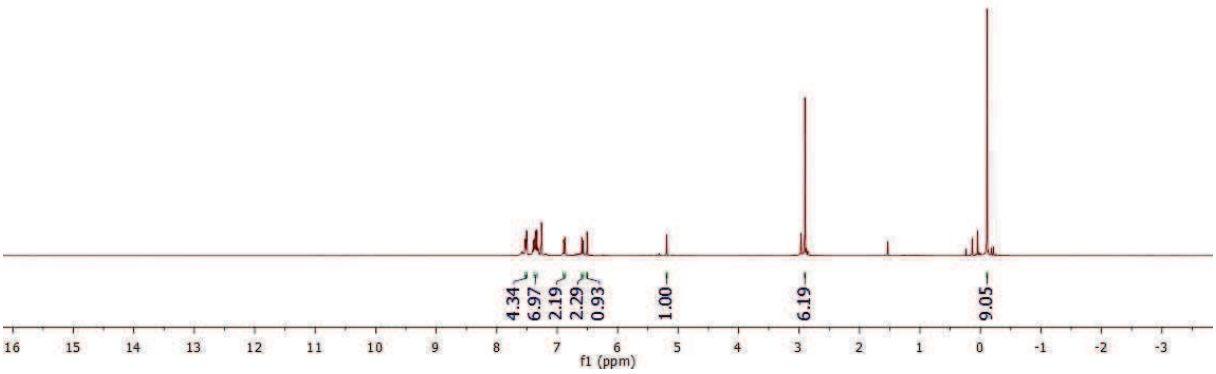

Si
H
Si
F3C


4.56
6.90
4.50
2.37
0.98
1.00
9.81
f1 (ppm)

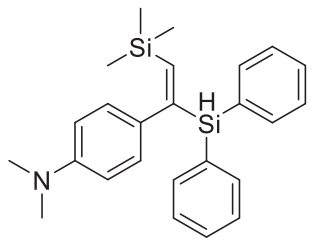

Si
H
Si
F3C

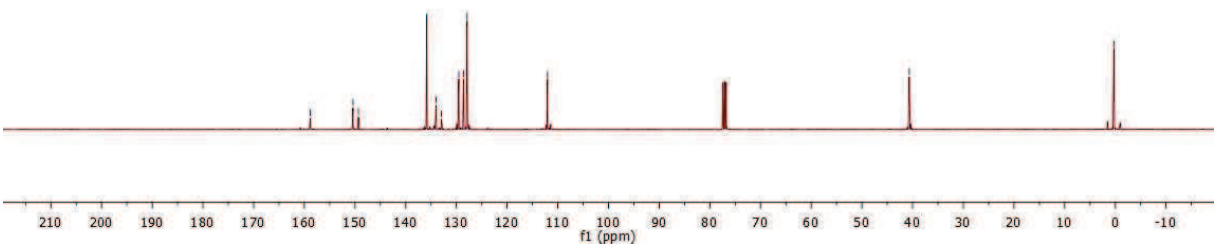
158.35
157.93
152.55
148.35
135.72
134.35
133.99
132.58
129.94
128.08
124.75
0.01
f1 (ppm)

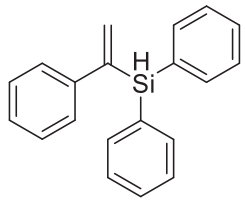

Si
H
Si
N

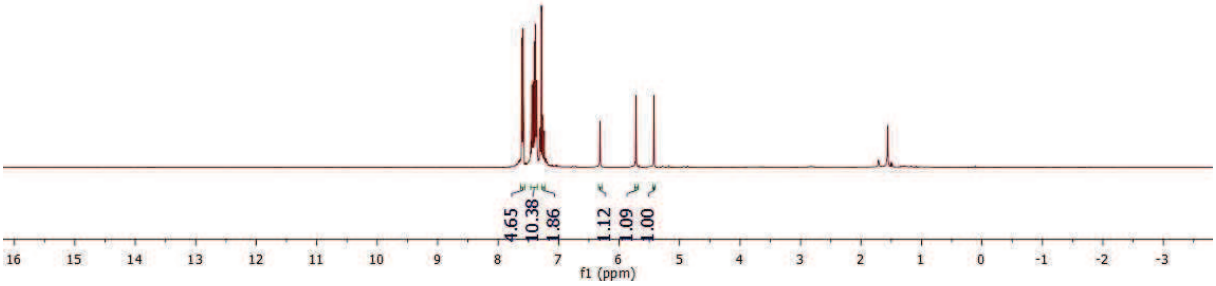

4.34
6.97
2.19
2.29
0.93
1.00
6.19
9.05
f1 (ppm)

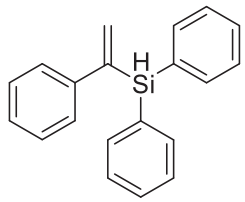

158.81
150.40
149.34
135.87
133.98
132.95
129.52
128.61
127.90
112.03
40.67
0.30


Si
H
Si
N

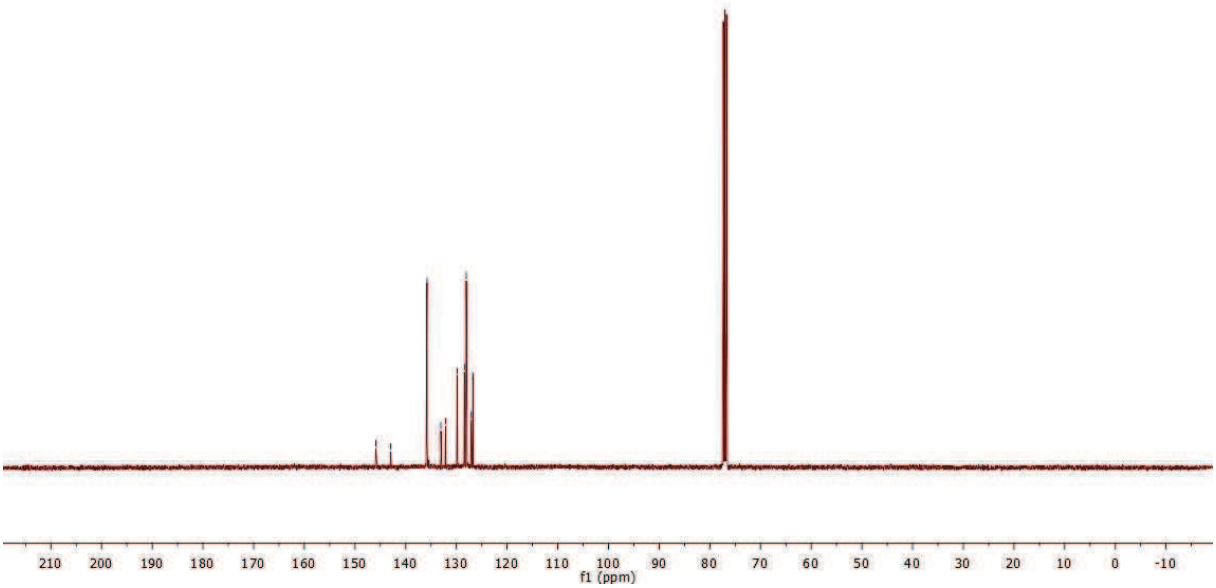

f1 (ppm)

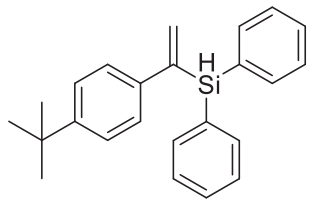

H
Si


4.65
10.38
1.86
1.12
1.09
1.00
f1 (ppm)

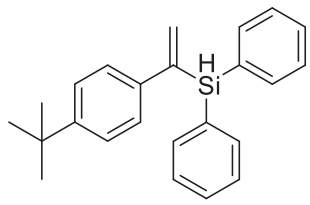

H
Si


145.90
142.94
135.79
133.06
132.16
129.82
128.42
128.06
127.09
126.74

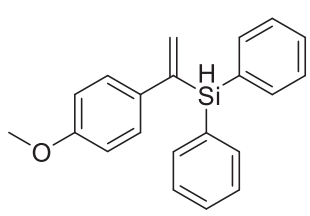

f1 (ppm)


H
Si

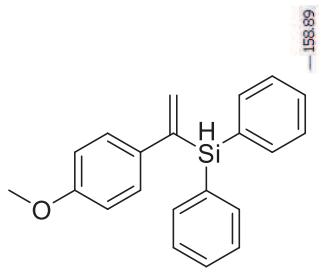
4.51
7.46
3.46
1.06
1.07
1.00
9.51
f1 (ppm)


H
Si

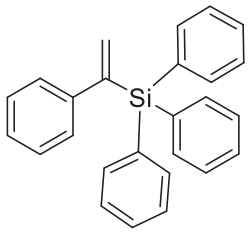
150.11
145.17
139.79
135.82
133.28
131.41
129.77
128.04
126.33
125.36
34.48
31.31
f1 (ppm)

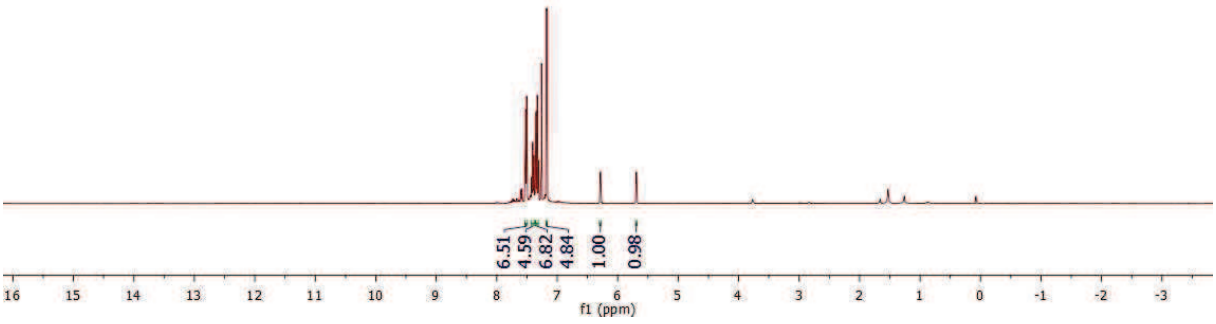

H
Si
O

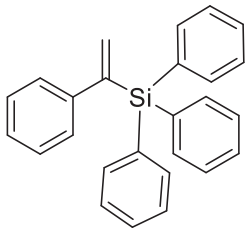
4.05
8.82
2.09
1.00
1.00
0.94
3.02
f1 (ppm)


H
Si
O

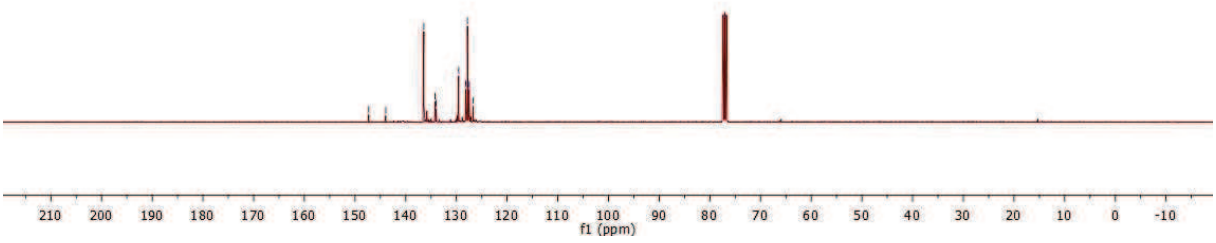
158.89
144.78
135.80
135.28
134.37
133.20
130.50
129.78
128.05
113.83
55.24
f1 (ppm)


Si


6.51
4.59
6.82
4.84
1.00
0.98
f1 (ppm)


Si


147.29
143.93
136.42
134.22
133.98
129.55
128.15
127.83
127.48
126.74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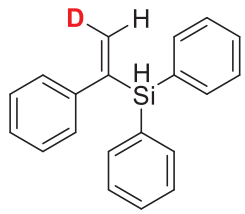
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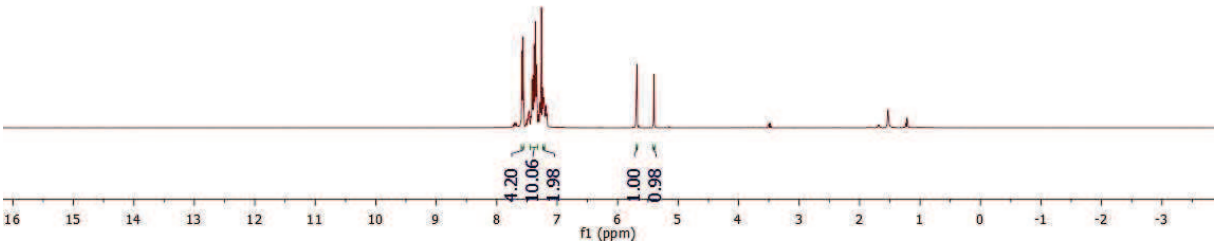
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-3
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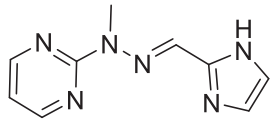

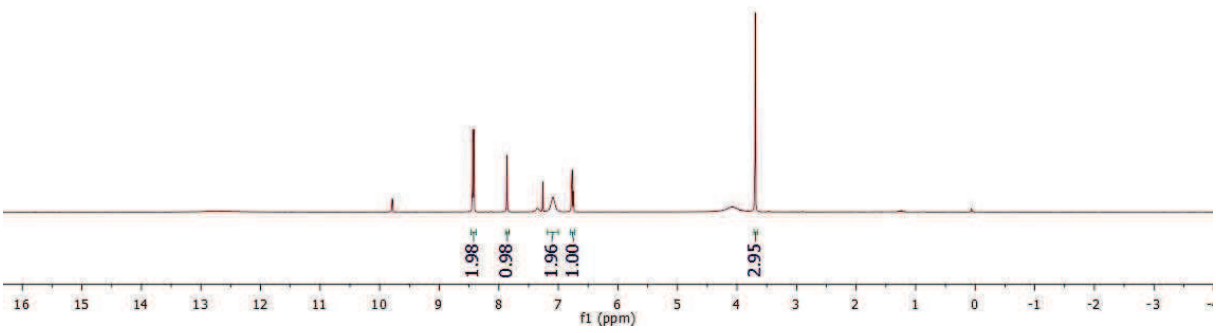
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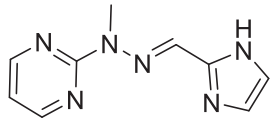

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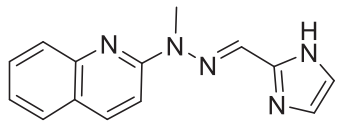

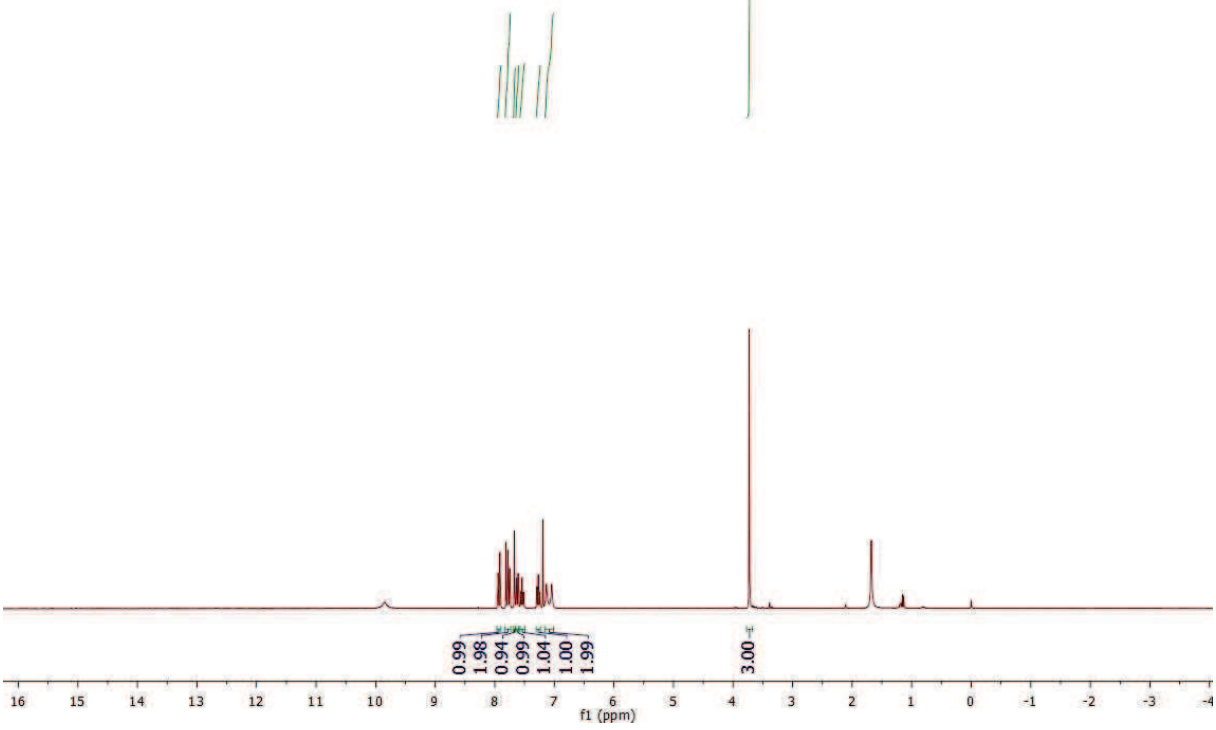
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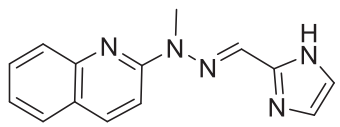

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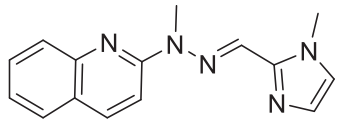

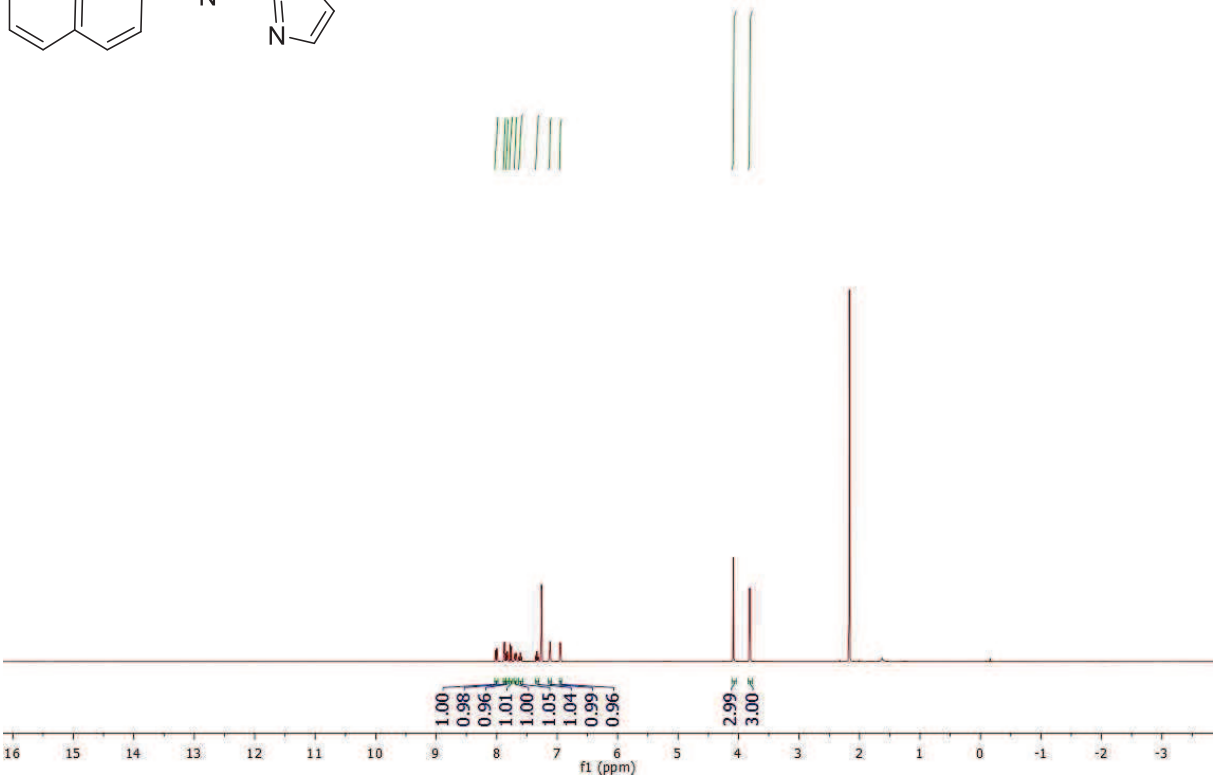
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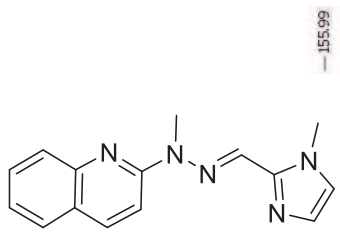

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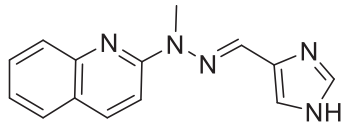
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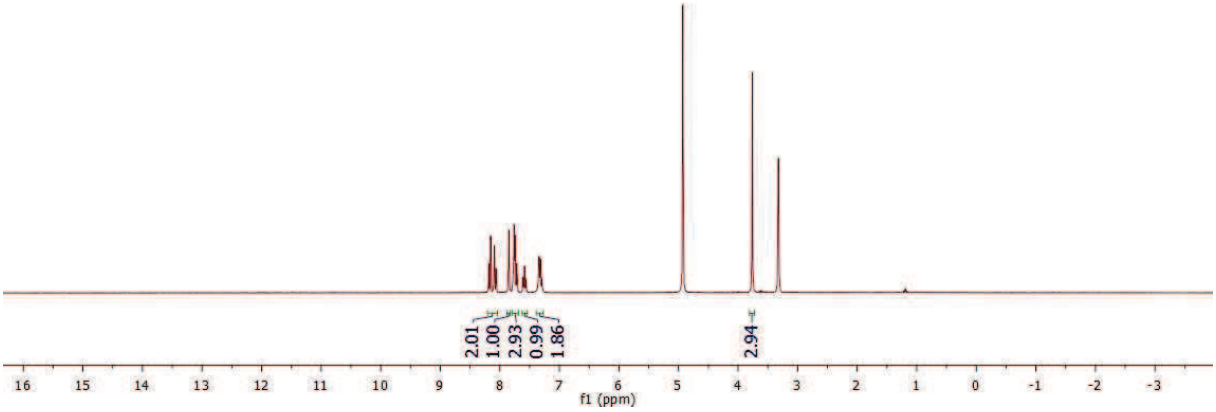
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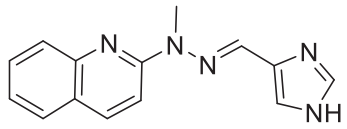
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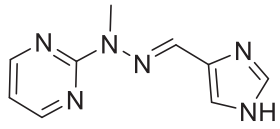
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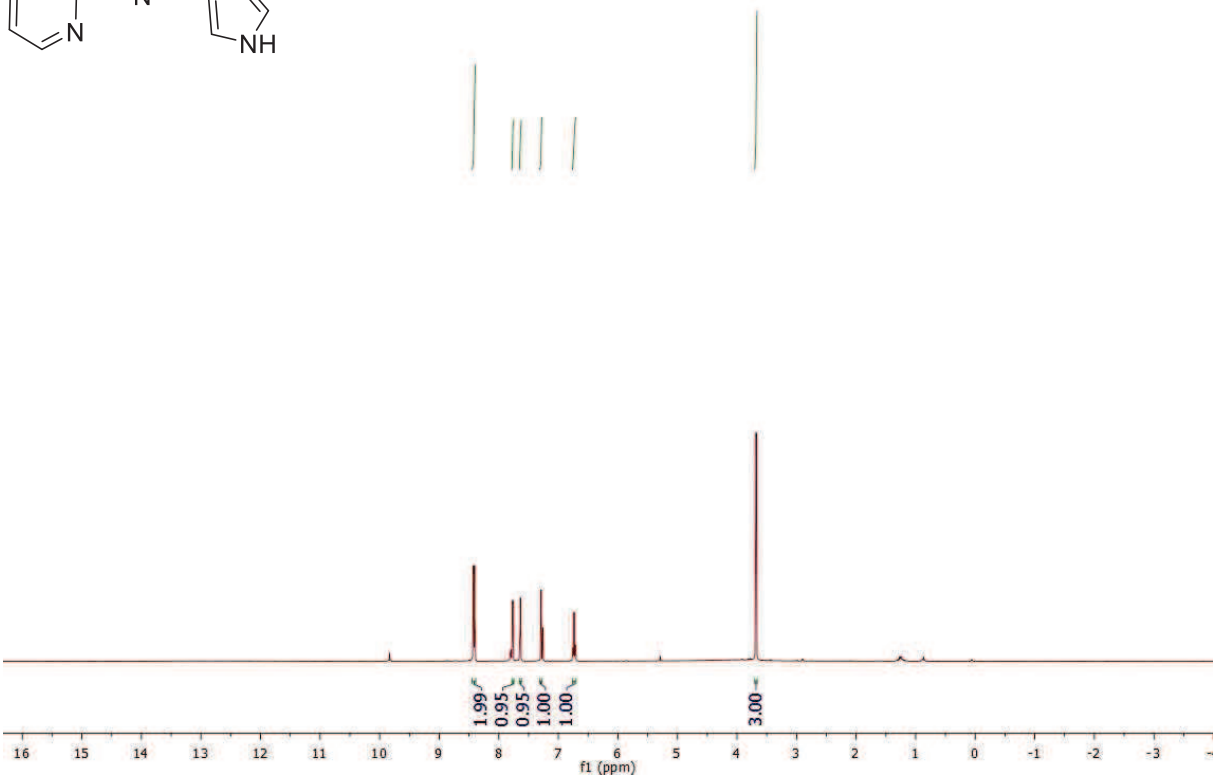
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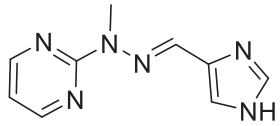
f1 (ppm)


N
N
N
N
NH

159.91
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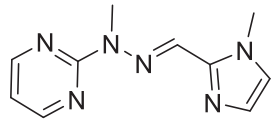
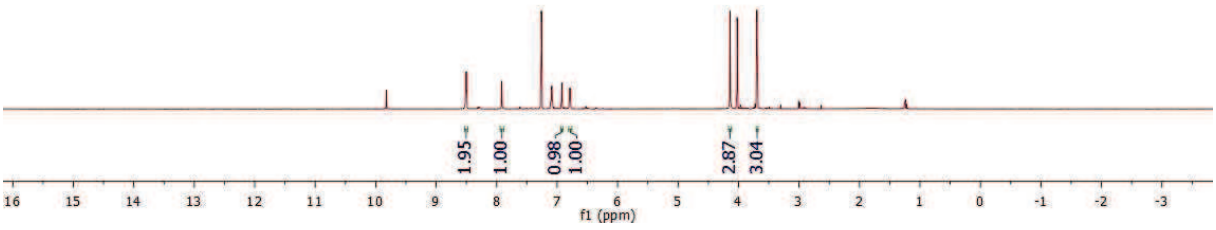
f1 (ppm)

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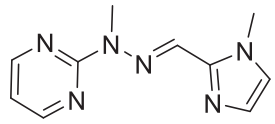
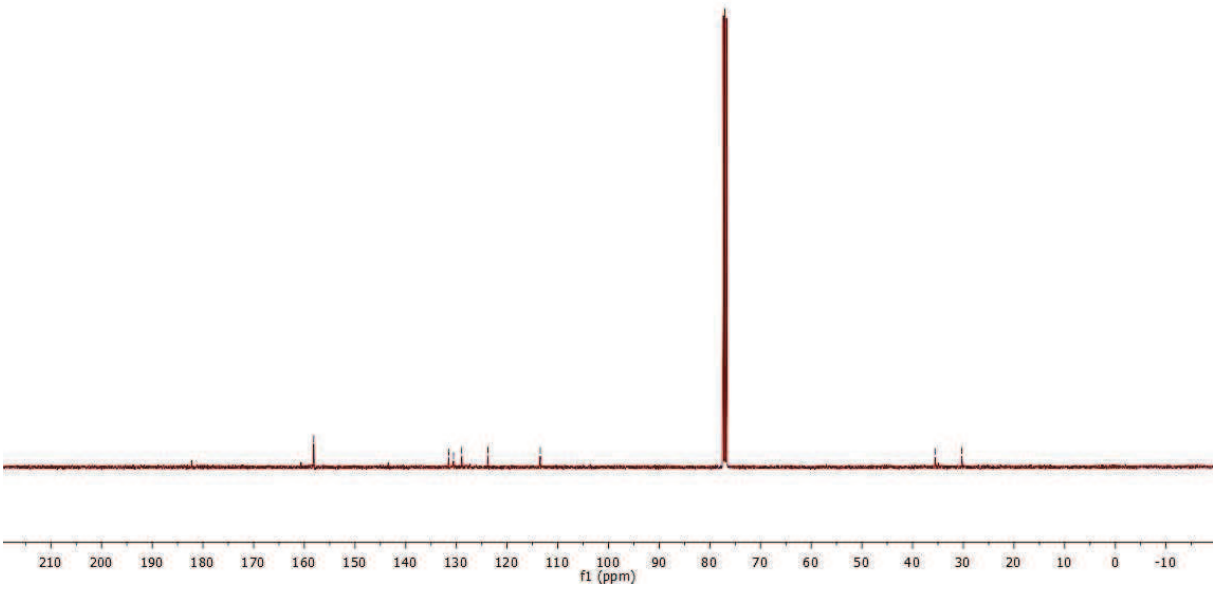
30.32

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Cited literature:

[1] Bocian, A.; Szymańska, M.; Brykczyńska, D.; Kubicki, M.; Wałęsa-Chorab, M.; Fik-Jaskółka M.A.; Gorczyński, A.; Patroniak, V. *Molecules*, **2019**, 24, 3173.
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[4] Skrodzki, M.; Patroniak, V.; Pawluć, P., *Org. Lett*. **2021**, *23*, 663.
[5] Wang, D.; Lai, Y.; Wang, P.; Leng, X.; Xiao, J.; Deng, L., *J. Am. Chem. Soc.* **2021**, 143, 32, 12847–12856
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Appendix **A4**

Skrodzki M., Witomska S., Pawluć P.; *Sodium triethylborohydride as a catalyst for the dehydrogenative silylation of terminal alkynes with hydrosilanes. Dalton Trans*., **2018**, 47, 5948.

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Sodium triethylborohydride as a catalyst for the dehydrogenative silylation of terminal alkynes with hydrosilanes†‡

Maciej Skrodzki,[a,b] Samanta Witomska[a,b] and Piotr Pawluć *[a,b]

The first example of sodium triethylborohydride-catalyzed C(sp)–H bond silylation is reported. The reaction of aromatic and aliphatic alkynes with aromatic hydrosilanes and hydrosiloxanes proceeded in a highly selective manner to afford dehydrocoupling products. Competitive hydrosilylation of the terminal alkyne did not occur as a side-reaction. In view of the above it is remarkable that $NaHBEt_3$ is commonly used as a reducing agent generating active transition-metal catalysts *in situ* in other hydrosilylation reactions.

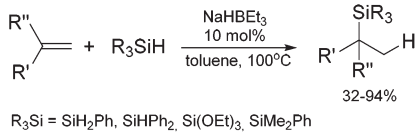
Introduction

Alkynylsilanes are versatile starting materials that are used not only as protected forms of terminal alkynes but also in carbon–carbon and carbon–heteroatom bond formation reactions.[1–3] The preparation of silylalkynes is routinely achieved by the deprotonation of terminal alkynes with strong bases, followed by addition of silyl electrophiles *e.g.* halosilanes,[4–6] siloxanes,[7,8] silylamines[9,10] or silyl triflates.[11]

Catalytic dehydrogenative silylation of terminal alkynes with hydrosilanes appears to be a method more convenient for the synthesis of silylalkynes due to reagent availability, atom economy, and waste reduction.[12–17] However, the necessity of the use of precious metal catalysts and competitive hydrosilylation reactions remains a fundamental limitation for these transformations. On the other hand, highly basic compounds such as metal alkoxides,[18] MgO,[18] KNH_2,[19] $LiAlH_4$,[20] and even metal hydroxides[21] have shown catalytic activity in the dehydrocoupling of terminal alkynes with hydrosilanes. However, in contrast to metal alkoxides and hydroxides, the application of metal hydrides as catalysts is limited to only a handful of examples.

Recently, we have reported that sodium triethylborohydride can be used as a highly selective and commercially available catalyst for the hydrosilylation of resonance-stabilized alkenes with hydrosilanes, which does not provide pathways for dehydrogenative processes.[22] The hydrosilylation of selected alkenes, in particular styrenes, vinylsilanes and allyl glycidyl ether, with aromatic and alkoxy hydrosilanes proceeded in a highly regioselective manner to afford Markovnikov products (Scheme 1) according to an unusual anionic mechanism. It is significant that several protocols use $NaHBEt_3$ as a reducing agent generating active catalysts *in situ* in other hydrosilylation reactions.

Hydroborane adducts and $NaHBEt_3$ have been recently demonstrated to catalyze the hydroboration of alkynes and alkenes with pinacolborane to afford alkenyl and alkyl boronic esters, respectively.[23] On the other hand, lithium diamidodihydridoaluminates promote the hydroboration of aldehydes and ketones[24] and simple aluminum hydrides (*e.g.* $LiAlH_4$ and DIBAL-H) have been recently reported as catalysts for the selective hydroboration of alkenes[25] and alkynes[26] which are conceptually related to hydrosilylation chemistry. Triethylborohydrides of lithium and sodium were also found to be good catalysts for the hydrosilylation of C=O and C=N bonds.[27] It is significant that many protocols use metal borohydrides *e.g.* $NaHBEt_3$ as reducing agents generating active transition-metal catalysts *in situ* in other alkyne hydrosilylation reactions;[28–31] however, it has never been used alone as a catalyst for the (hydro)silylation of alkynes.



Scheme 1 Regioselective hydrosilylation of olefins in the presence of $NaHBEt_3$.

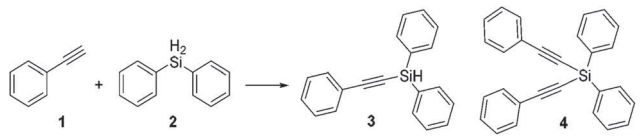
[a]*Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland*
[b]*Center for Advanced Technologies, Adam Mickiewicz University in Poznań, Umultowska 89c, 61-614 Poznań, Poland. E-mail: piotr.pawluc@amu.edu.pl*
†Dedicated to Professor Jacek Gawroński on the occasion of his 75th birthday.
‡Electronic supplementary information (ESI) available. See DOI: 10.1039/c8dt00684a

The successful use of $NaHBEt_3$ as a highly selective catalyst for the α-hydrosilylation of olefins prompted us to investigate its catalytic activity in the reaction with alkynes. Unexpectedly, we have found that the application of $NaHBEt_3$ as a catalyst in the reaction of terminal alkynes with hydrosilanes promoted the dehydrocoupling pathway instead of alkyne hydrosilylation. Herein, we wish to report a new transition metal-free catalytic system for the highly selective dehydrogenative silylation of terminal alkynes with hydrosilanes, providing an efficient route to differently substituted silylalkynes.

Results and discussion

We started the study with the silylation of phenylacetylene **1** using H_2SiPh_2 under our previously reported $NaHBEt_3$-catalyzed olefin hydrosilylation conditions. The reaction of equimolar amounts of alkyne **1** and H_2SiPh_2 performed in toluene at 100 °C yielded exclusively the mono-silylation product ((ethynylphenyl)diphenylsilane **3**) in 79% yield after 24 h (Table 1, entry 5). The structure of compound **3** was confirmed by ^1H and ^{13}C NMR spectroscopy of the isolated product (see the ESI‡). While the reaction mixture was heated in toluene-d8, the appearance of a new signal (s, 4.50 ppm) was detected in the ^1H NMR spectrum, which can be assigned to the hydrogen molecule, in line with literature data.[32] Additional experiments performed with phenylacetylene and deuterated diphenylsilane as well as deuterated phenylacetylene and diphenylsilane confirmed the formation of hydrogen deuteride (HD) (1 : 1 : 1 triplet, 4.26 ppm) under the same conditions (see the ESI‡).

Table 1 Screening of the reaction conditions



Entry	[1] : [2]	Catalytic system[a]	t/h	T/°C	Conversion of **2**[b]	Selectivity[c]
1	1 : 1	10% $NaHBEt_3$	24	60	2%	—
2	1 : 1	10% $NaHBEt_3$	24	80	52%	99% **3**
3	1 : 1	10% $NaHBEt_3$	2	100	35%	99% **3**
4	1 : 1	10% $NaHBEt_3$	6	100	58%	99% **3**
5	1 : 1	10% $NaHBEt_3$	24	100	79%	99% **3**
6	1 : 1	10% $NaHBEt_3$	24	120	100%	99% **3**
7	1 : 1	5% $NaHBEt_3$	24	100	70%	99% **3**
8	1 : 1	10% $NaHBEt_3$	48	100	83%	99% **3**
9	1 : 1	20% $NaHBEt_3$	24	100	72%	99% **3**
10	2 : 1	10% $NaHBEt_3$	24	100	84%	99% **3**
11	1 : 1	10% $KHBEt_3$	24	100	28%	97% **3**
12	1 : 1	10% $LiHBEt_3$	24	100	39%	98% **3**
13	1 : 1	Without $NaHBEt_3$	24	100	0	—

[a] 0.5 M solution of **2** in toluene unless stated otherwise. [b] Determined by GC with decane as an internal standard. [c] Determined by GC and ^1H NMR spectroscopy of isolated **3**.

The influence of temperature and catalyst loading was tested for the model reaction. A decrease in the catalyst loading to 5 mol% lowered the conversion of H_2SiPh_2 to 70% after 24 h (entry 7), whereas an increase in the catalyst concentration to 20 mol% did not affect significantly the silane conversion (entry 9). Increasing the reaction temperature to 120 °C resulted in complete conversion of silane after 24 h; however, under the conditions used a rapid polymerization of phenylacetylene took place. On the other hand, the silylation reaction performed at a lower temperature (80 °C) caused a decrease in silane conversion to 52% after 24 h (entry 2) and a further decrease in temperature led to a drastic reduction of silane conversion (entry 1).

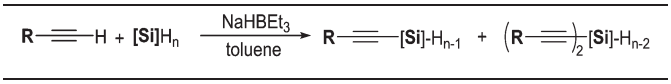
Formation of the bis-silylated product **4** was observed only in trace amounts (less than 1%) in most cases. It is worth noting that lithium triethylborohydride, while being far better in the hydrosilylation of ketones and imines,[27] exhibited the activity of only half of that of $NaHBEt_3$ under the same conditions (entry 12). The use of potassium triethylborohydride led to only 28% conversion of diphenylsilane, however, with good selectivity towards mono-silylation (entry 11). The use of two-fold excess of alkyne **1** leads to a slightly higher H_2SiPh_2 conversion (84%), and interestingly, the reaction proceeds almost exclusively towards the single mono-silylation product **3** (entry 10). In all cases, no side hydrosilylation by-products have been observed.

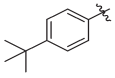
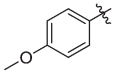
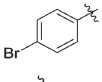
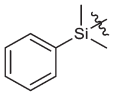
Under the optimized conditions, we then examined the scope and limitations of the proposed method by determining the range of substituted alkynes and hydrosilanes. In a typical procedure, the substrates and catalyst (10 mol%) were dissolved in toluene (0.5 M concentration) and heated in a Schlenk bomb flask fitted with a plug valve, at 100 °C for 24 h under an argon atmosphere. The results are presented in Table 2.

The results provided evidence that $NaHBEt_3$ can be applied as a catalyst for the silylation of various terminal alkynes, *e.g.*, aryl-substituted alkynes, aliphatic alkynes and alkynylsilanes with hydrosilanes bearing preferentially aromatic substituents. The representative products of the reactions that proceeded with good yields were isolated and proven to be dehydrocoupling products (see the ESI‡).

Simple phenylacetylene **1** reacted with phenylsilane, diphenylsilane and diethylsilane to form selectively mono-substituted products with moderate yields; nonetheless the reaction failed completely for the tertiary silanes such as dimethylphenylsilane and triethylsilane. Surprisingly, the reaction of **1** with 1,1,1,3,5,5,5-heptamethyltrisiloxane proceeded successfully to afford 3-ethynylphenyl-1,1,1,3,5,5,5-heptamethyltrisiloxane as a single product in 32% isolated yield. The presence of functional groups at the phenyl ring, either electron-donating or electron-withdrawing, did not significantly affect the reactivity of phenylacetylene derivatives. Electron-donating groups such as *p*-*t*Bu gave rise to the corresponding products (entries 7 and 8) in moderate to good 55–72% yields. The introduction of the *p*-MeO group into the phenyl ring caused a decrease in the conversion of silanes (entries 9 and 10).

Table 2 Results of dehydrogenative coupling of alkynes with hydrosilanes in the presence of $NaHBEt_3$

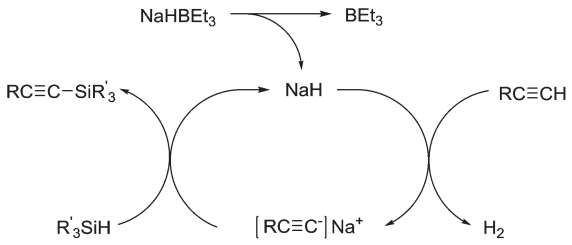


Entry	Alkyne	Silane	Silylacetylene yield[a] [%] (isolated)	Selectivity[b] [mono] : [di]
1		H_3SiPh	54	99 : 1
2		H_2SiPh_2	79 (31)	99 : 1
3		$HSiMe(OSiMe_3)_2$	47 (32)	100 : 0
4		H_2SiEt_2	55	100 : 0
5		$HSiMe_2Ph$	0	—
6		$HSiEt_3$	0	—
7		H_3SiPh	55	100 : 0
8		H_2SiPh_2	72	100 : 0
9		H_3SiPh	38	—
10		H_2SiPh_2	66	100 : 0
11		H_3SiPh	34	47 : 0
12		H_2SiPh_2	59	100 : 0
13		$HSiMe(OSiMe_3)_2$	29	100 : 0
14		H_2SiPh_2	44 (20)	77 : 23
15		H_3SiPh	64	85 : 15
16		H_2SiPh_2	91 (30)	97 : 3
17		$HSiMe(OSiMe_3)_2$	93 (36)	100 : 0
18		H_2SiPh_2	82	100 : 0
19		H_3SiPh	42	51 : 49
20		H_2SiPh_2	68	100 : 0
21		H_3SiPh	42	45 : 0 : (55)[c]
22		H_2SiPh_2	63 (20)	74 : 4 : (22)[c]
23		$HSiMe(OSiMe_3)_2$	28	95 : 0 : (5)[c]
24		H_3SiPh	20	82 : 18
25		H_2SiPh_2	54 (42)	79 : 21
26		H_3SiPh	19	89 : 11
27		H_2SiPh_2	47	85 : 15
28		H_3SiPh	13	79 : 21
29		H_2SiPh_2	48	85 : 15

[a] Reaction conditions: 0.5 M hydrosilane in toluene, 100 °C, [HSi] : [alkyne] : [$NaHBEt_3$] = 1 : 1 : 0.10. [b] Calculated by GC analysis using decane as an internal standard. [c] In parentheses the amount of symmetrical bis(silyl)acetylene related to silylacetylene determined by GC and ^{1}H NMR spectroscopy.

Phenylacetylene substituted with the electron-withdrawing group such as *p*-Br led to the corresponding products with 29–59% yields (entries 11–13).

Contrary to olefin hydrosilylation, not only aromatic acetylenes but also simple aliphatic substrates *i.e.* 1-octyne, 3,3-dimethylbut-1-yne, ethynylcyclohexane or 1-ethynylcyclohex-1-ene can be used with this catalytic system. If 1-octyne was used, both single and double substitution products were formed, depending on the hydrosilane substrate. The reaction with diphenylsilane led to the formation of a mono-substituted product (entry 20), while phenylsilane gave equimolar amounts of single and double substitution products (entry 19). The $NaHBEt_3$-catalyzed dehydrocoupling proceeded more efficiently for alicyclic substrates: ethynylcyclohexane and 1-ethynylcyclohex-1-ene to afford the corresponding 1-cyclohex(en)yl-2-silylethynes in high yields (64–93%).



Scheme 2 The proposed mechanism of dehydrogenative coupling of alkynes with hydrosilanes.

Silylation of ethynylsilanes (entries 21–29) was less effective (13–63% yield). Both aromatic silanes and hydrosiloxanes can be employed for the silylation of ethynylsilanes to afford unsymmetrically substituted bis(silyl)ethynes. However, when using ethynyldimethyl-phenylsilane as a substrate in the reaction with aromatic silanes, significant amounts of the symmetrical silylation by-product (bis(dimethylphenylsilyl)ethyne) were detected (entries 21 and 22). In all cases, no side hydrosilylation by-products were observed. Interestingly, internal alkynes (*e.g.* diphenylacetylene, 1-phenyl-1-propyne and trimethylsilylacetylene) do not undergo the competitive hydrosilylation reaction with diphenylsilane and phenylsilane that might be expected for internal alkynes under given conditions.

The postulated mechanism of the $NaHBEt_3$-catalyzed dehydrogenative silylation reaction is similar to those reported for alkyne silylation catalyzed by other complex metal hydrides[18] and assumes the generation of an acetylide anion as an intermediate (Scheme 2).

It has been established that $HBEt_3^-$ has one of the lowest standard enthalpies of dissociation from among many other borohydrides.[33] Thus, sodium hydride generated by the initial dissociation of triethylhydroborate would react with alkyne to give sodium acetylide with the evolution of molecular hydrogen. In the next step sodium acetylide would then react with hydrosilane to form the dehydrocoupling product with the regeneration of sodium hydride. A possible role of trialkylborane released as a result of the initial dissociation of trialkylhydroborate should also be considered. Boron, which in this compound is a strong Lewis acid, can facilitate the removal of the hydride anion during the substitution, acting similarly to perfluorinated triphenylborane in the mechanism of transfer hydrosilylation.[34]

Conclusions

In conclusion, sodium triethylborohydride can be used as a highly selective, inexpensive and commercially available catalyst for the silylation of aromatic and aliphatic alkynes with

hydrosilanes, which does not provide pathways for hydrosilylation processes. Although the substrate scope is limited, this particular method can be applied to the synthesis of alkynylsilanes containing SiH_2Ph and $SiHPh_2$ groups, unsymmetrically substituted bis(silyl)ethynes and, what is important – alkynylsiloxanes which are interesting substrates in cross-coupling reactions. It is remarkable that $NaHBEt_3$, reported here as a single catalyst, is widely used for the *in situ* reduction of other hydrosilylation precatalysts.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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SUPPORTING INFORMATION

for

Sodium triethylborohydride as a catalyst for dehydrogenative silylation of terminal alkynes with hydrosilanes

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Experimental procedures

1.1 General remarks

All reactions were performed in oven-dried glassware under argon atmosphere. Toluene was purified by MBraun SPS-8400 system and degassed after collection. Other solvents were dried by distillation over calcium hydride.

Gas chromatography was performed on a Bruker Scion 436-GC with a 30 m Agilent VF5-ms 0.53 mm Megabore column and a TCD detector. The temperature program was as follows: 60 °C (3 min), 20 °C/min, 280 °C (20 min). Decane was used as a reference. GC-MS analyses were performed on a Bruker Scion 436-GC with a 30 m Varian DB-5 0.25 mm capillary column and a Scion SQ-MS mass spectrometry detector. The temperature program was as follows: 60 °C (3 min), 10 °C/min, 250 °C (15 min). NMR analyses were performed on a Bruker Fourier 300 spectrometer.

1.2 General procedure of dehydrogenative silylation catalyzed by $NaHBEt_3$

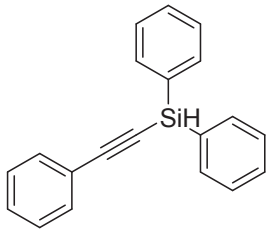
0.5 mmol of silane, 1 mL of toluene, 0.5 mmol of alkyne, and 0.1 mL of decane were placed in previously evacuated Schlenk bomb flask fitted with a plug valve. A reference sample was taken. Next, 0.05 mL of 1M solution of $NaHBEt_3$ (0.05 mmol) in toluene was added, reaction vessel was closed and heated at 100 °C with stirring.

After specified time, reaction mixture was cooled down to the room temperature and analyzed using GC and GC-MS.

Products of dehydrogenative silylation were isolated by first evaporating toluene on a rotary evaporator, then extraction with 1 mL of hexane followed by column chromatography of concentrated extract (SiO_2, hexane as eluent).

Analytical data of isolated products

2.1. Diphenyl(phenylethynyl)silane **1**; colorless oil, yield: 87 mg (31%)



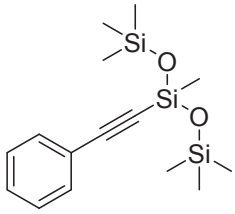
^{1}H NMR (300MHz, $CDCl_3$): δ7.78-7.66 (m, 4H), 7.60-7.51 (m, 2H), 7.48-7.28 (m, 9H), 5.3 (s, 1H)

^{13}C NMR (75 MHz, $CDCl_3$): δ135.24, 132.24, 132.18, 130.16, 129.17, 128.33, 128.17, 122.52, 109.56, 87.15

MS (70 eV): m/z (%): 206 (100), 284 (82), 129 (66), 205 (56), 207 (54), 105 (53), 181 (46), 178 (27), 180 (26), 204 (26), 283 (23), 285 (22), 103 (21), 130 (16), 53 (16), 179 (14), 208 (13), 182 (12), 106 (11), 155 (11).

Conforms to the literature analytical data.[1]

1.2. 1,1,1,3,5,5,5-heptamethyl-3-(phenylethynyl)trisiloxane **2**; colorless oil, yield: 103 mg (32%)



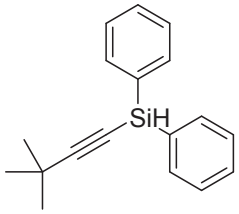
^{1}H NMR (300MHz, $CDCl_3$): 7.34-7.25 (m, 2H), 7.17-7.06 (m,3H), 0.07 (s,3H), 0.00 (s,18H)

^{13}C NMR (75 MHz, $CDCl_3$): 130.25, 127.02, 126.52, 121.07, 99.97, 90.75, 0.06, 0.00

MS (70 eV): m/z (%): 307 (100), 159 (47), 308 (34),73 (25),309 (14),146 (12).

HRMS (ESI TOF) calcd for $C_{15}H_{26}O_2Si_3Na$: 345,1138, found: 345,1132

1.3. (3,3-dimethylbut-1-yn-1-yl)diphenylsilane **3**; colorless oil, yield: 53 mg (20%)



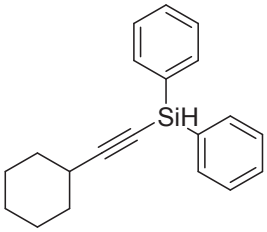
^{1}H NMR (300MHz, $CDCl_3$): δ7.70-7.61 (m, 4H), 7.43-7.32 (m, 6H), 5.12 (s, 1H), 1.31 (s, 9H)

^{13}C NMR (75 MHz, $CDCl_3$): δ135.09, 133.06, 129.84, 128.00, 121.08, 75.16, 30.79, 28.54

MS (70 eV): m/z (%): 207 (100), 186 (99), 171 (52), 105 (49), 129 (45), 208 (31), 181 (23), 187 (22), 145 (21), 53 (20), 130 (20), 143 (18), 264 (17), 172 (15), 221 (13), 121 (12), 51 (11), 84 (11), 183 (11), 188 (11), 67 (10).

Conforms to the literature analytical data.[2]

1.4. *(cyclohexylethynyl)diphenylsilane* **4**; colorless oil, yield: 87 mg (30%)



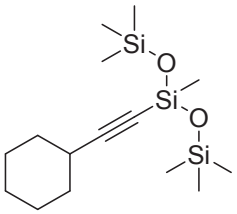
^{1}H NMR (300MHz, $CDCl_3$):7.72-7.59 (m, 4H), 7.45-7.30 (m, 6H), 5.25-5.03 (s, 1H), 2.61-2.44 (m, 1H), 1.92-1.68 (m, 4H), 1.62-1.25 (m, 6H)

*^{13}C NMR (75 MHz, $CDCl_3$):*135.10, 133.01, 129.88, 128.02, 116.96, 76.94, 32.38, 30.26, 25.83, 24.76

MS (70 eV): m/z (%): 212 (100), 105 (95), 183 (56), 181 (54), 207 (53),208 (44), 106 (34), 53 (33), 131 (30), 209 (30), 189 (27), 129 (26), 133 (24), 107 (24), 134 (24), 130 (23), 144 (21), 213 (20), 79 (19), 169 (18), 182 (18), 190 (17), 155 (16), 121 (15), 157 (13), 171 (12), 132 (12), 103 (11), 222 (11), 158 (10), 55 (10).

Conforms to the literature analytical data.[3]

1.5. *3-(cyclohexylethynyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane* **5**; colorless oil, yield: 118 mg (36%)



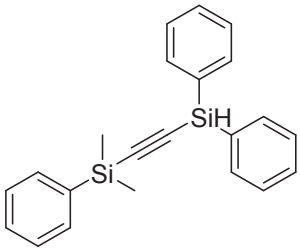
^{1}H NMR (300MHz, $CDCl_3$): 2.44-2.32 (m, 1H), 1.87-1.63)m, 4H), 1.54-1.22(m, 6H), 0.20-0.08 (m, 21H)

^{13}C NMR (75 MHz, $CDCl_3$): 106.85, 81.10, 30.57, 27.96, 24.12, 23.05, 0.21, 0.00

MS (70 eV): m/z (%): 313 (100), 73 (92), 207 (75), 231 (41), 314 (34), 208 (18), 315 (17), 133 (15), 83 (13), 189 (11), 59 (11), 191 (11), 232 (11), 74 (10), 209 (10).

HRMS (ESI TOF) calcd for $C_{15}H_{32}O_2Si_3Na$: 351,1608, found: 351,1598

1.6. *((Diphenylsilyl)ethynyl)dimethyl(phenyl)silane* **6**; colorless oil, yield: 68 mg (20%)

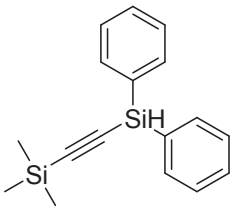


^{1}H NMR (300MHz, $CDCl_3$): 7.74-7.64 (m, 6H), 7.46-7.35 (m, 9H), 5.21 (s, 1H), 0.51 (s, 6H)

*^{13}C NMR (75 MHz, $CDCl_3$):*137.27, 136.21, 135.87, 135.33, 134.77, 132.85, 131.15, 130.59, 129.13, 128.95, 118.52, 109.18, 0.00

MS (70 eV): m/z (%): 105 (100), 197 (87), 327 (77), 135 (63), 264 (48), 86 (42), 78 (36), 57 (35), 209 (33), 106 (33), 77 (31), 342 (31), 23 (30), 206 (30), 249 (29), 119 (29), 283 (26), 59 (24), 266 (23), 107 (22), 198 (22), 51 (22), 73 (22), 158 (20), 147 (20), 181 (20), 328 (20), 195 (18), 165 (17), 132 (17), 259 (17), 159 (16), 109 (16), 91 (16), 146 (15), 152 (15), 180 (15), 87 (14), 211 (14), 97 (13), 186 (13), 343 (13), 341 (12), 50 (12), 171 (12), 60 (12), 129 (12),163 (12), 81 (12), 149 (11), 288 (10), 136 (10).

1.7. *((diphenylsilyl)ethynyl)trimethylsilane,* **7**; colorless oil, yield: 118 mg (42%)



^{1}H NMR (300MHz, $CDCl_3$): 7.75-7.65 (m, 4H), 7.48-7.39 (m, 6H), 5.19 (s, 1H), 0.28 (s, 9H)

^{13}C NMR (75 MHz, $CDCl_3$): 135.42, 132.25, 130.33, 128.34, 120.11, 106.22, 0.00

MS (70 eV): m/z (%): 135 (100), 265 (85), 202 (74), 187 (73), 105 (56), 197 (29), 73 (27), 280 (27),245 (26), 266 (23), 181 (22), 207 (20), 53 (19), 203 (19), 129 (17), 188 (16), 107 (14), 159 (12),143 (12), 221 (11), 131 (11), 51 (10), 182 (10), 195 (10), 136 (10).

Conforms to the literature analytical data[4]

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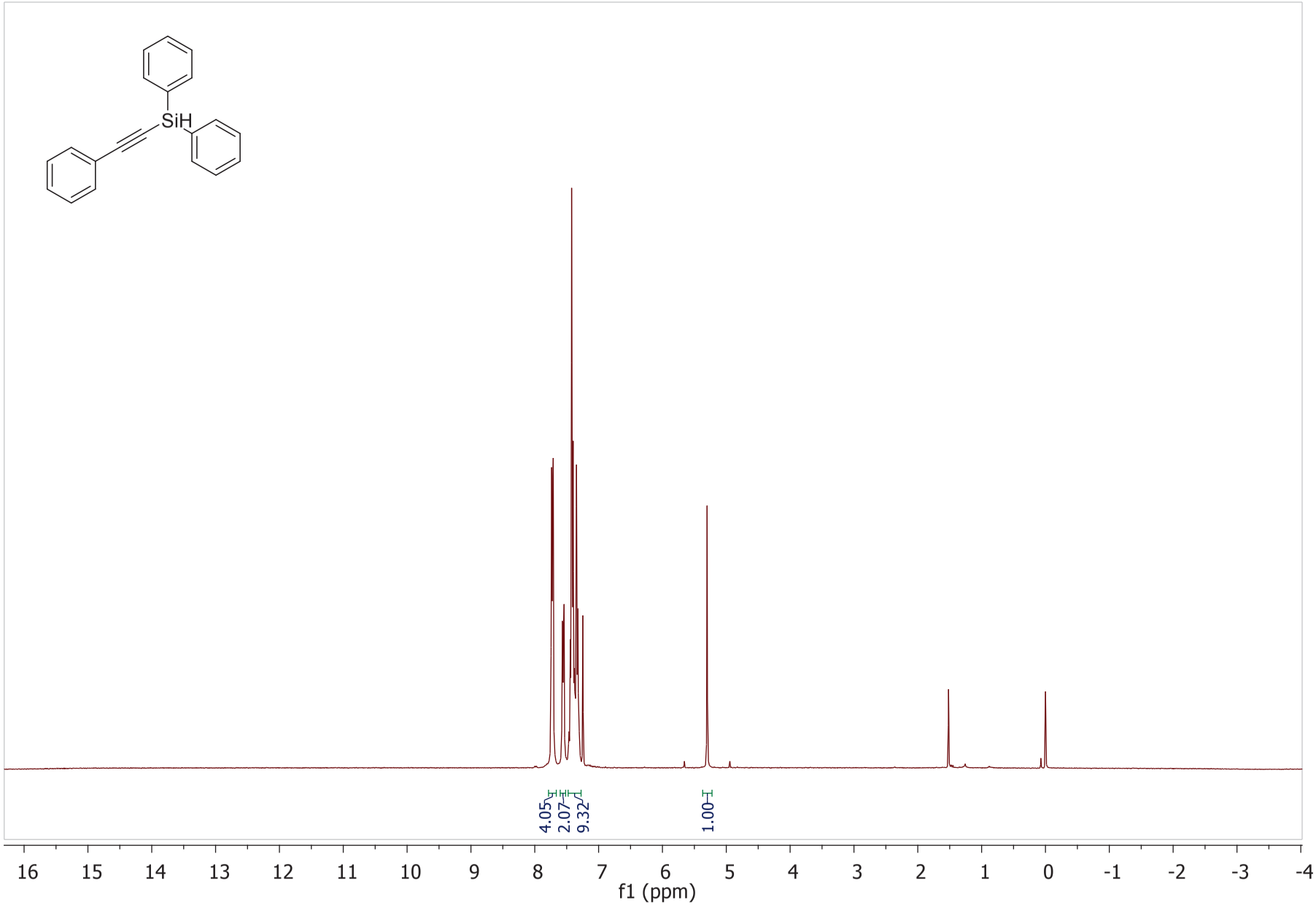
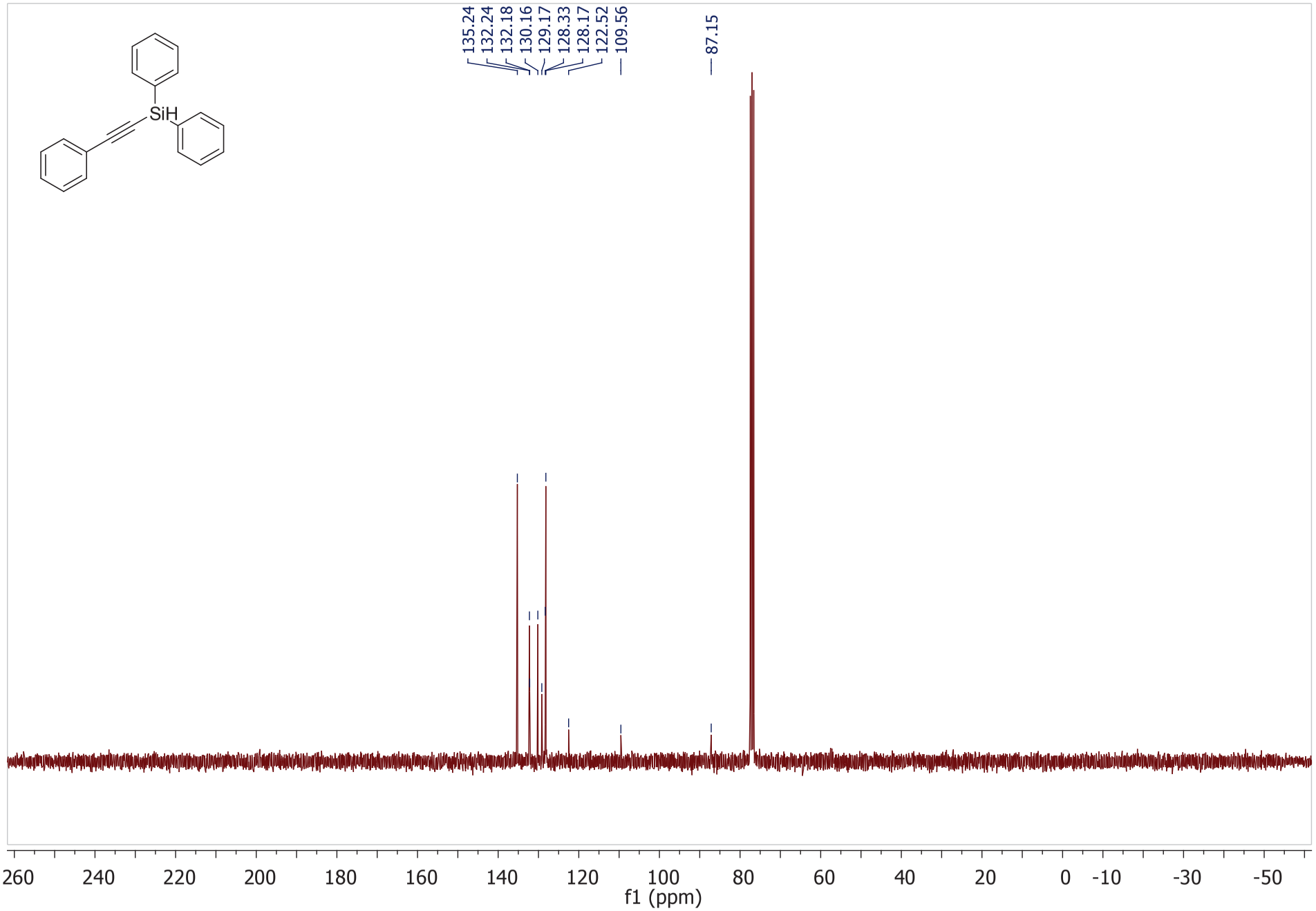
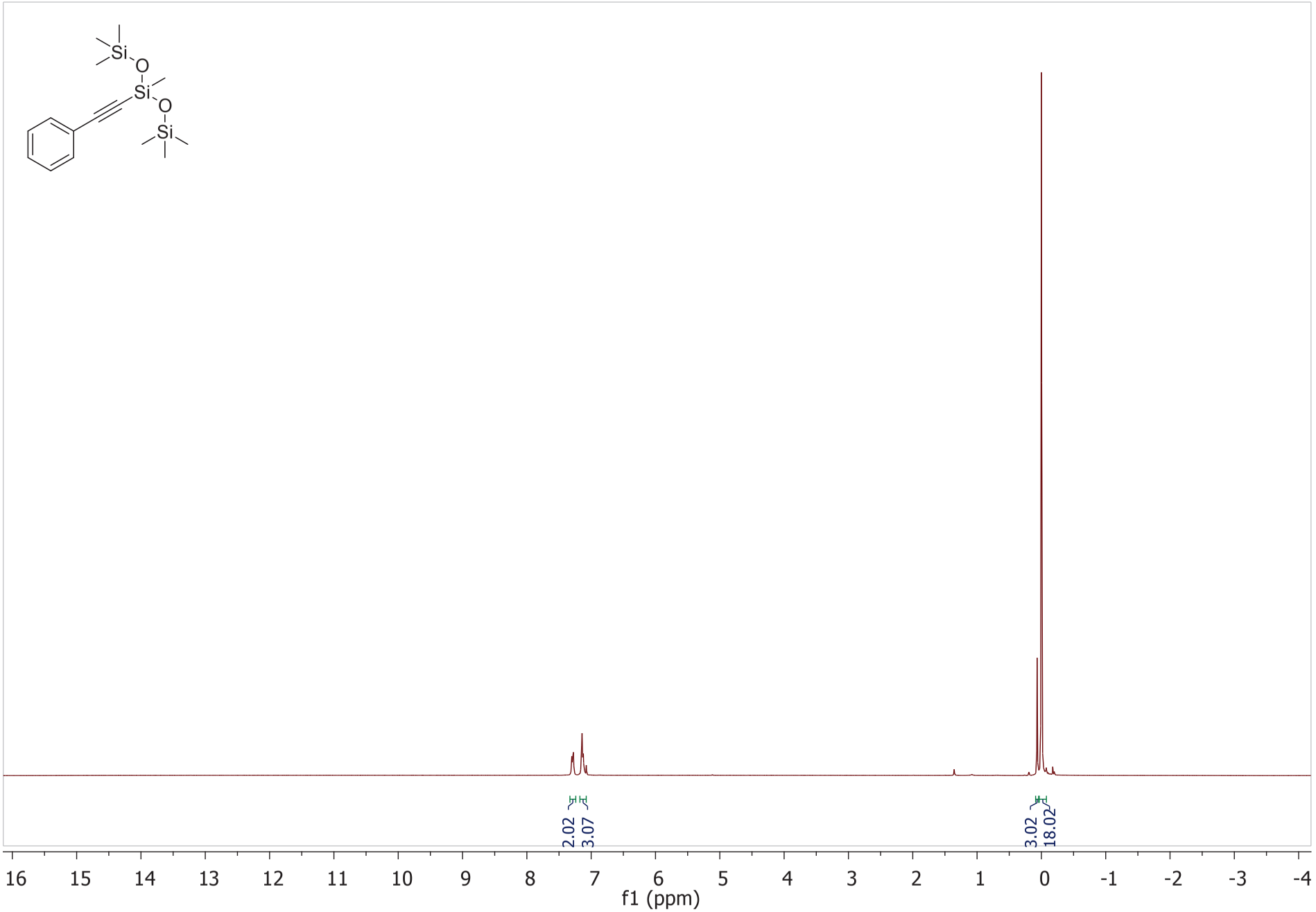
2. **Spectra of products**




SiH
135.24
132.24
132.18
130.16
129.17
128.33
128.17
122.52
109.56
87.15
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
f1 (ppm)


Si
O
Si
O
Si
2.02
3.07
3.02
18.02
16
15
14
13
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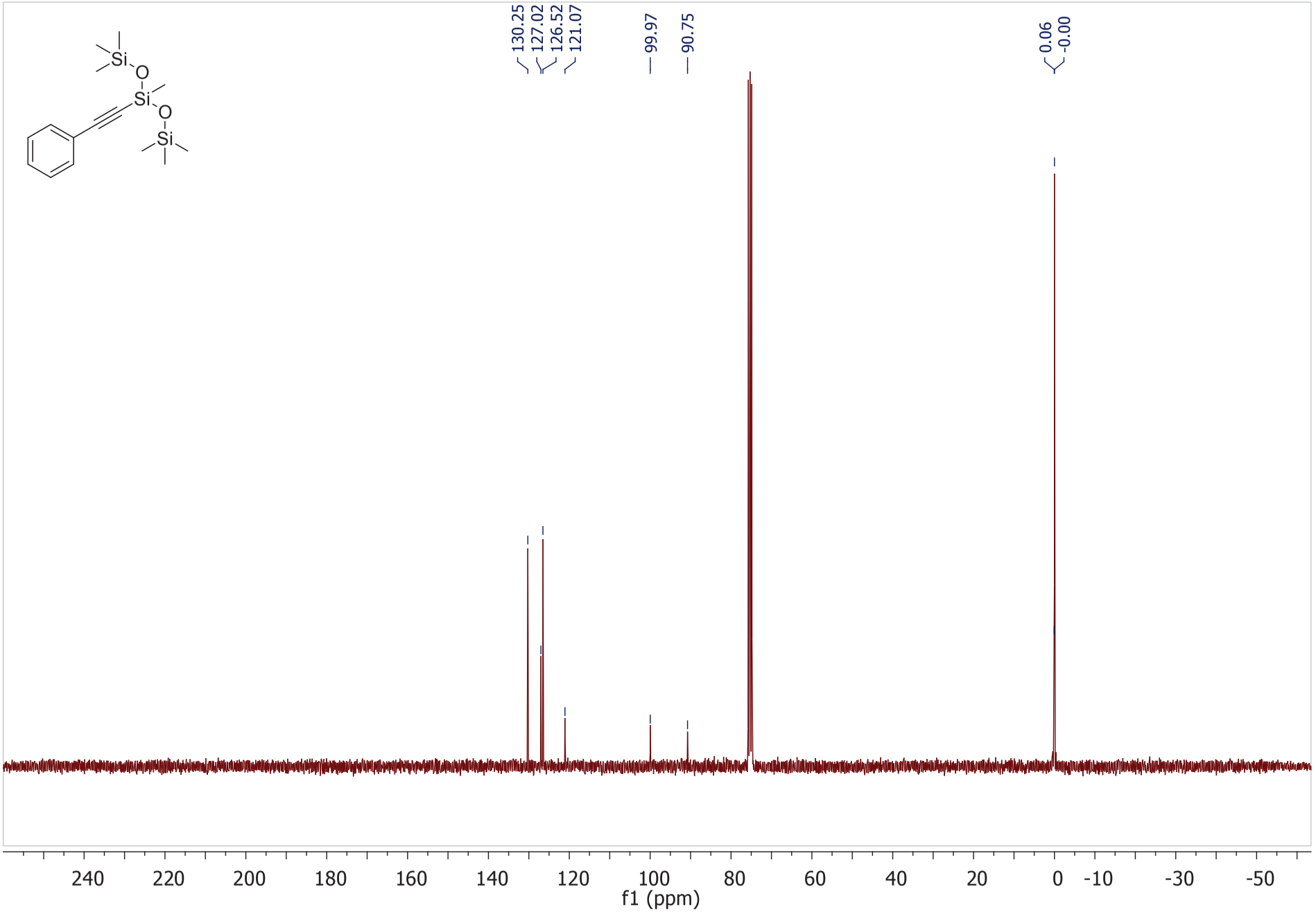
-2
-3
-4
f1 (ppm)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127.02
126.52
121.07
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90.75
0.06
-0.00
Si
O
Si
O
Si
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180
160
140
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100
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60
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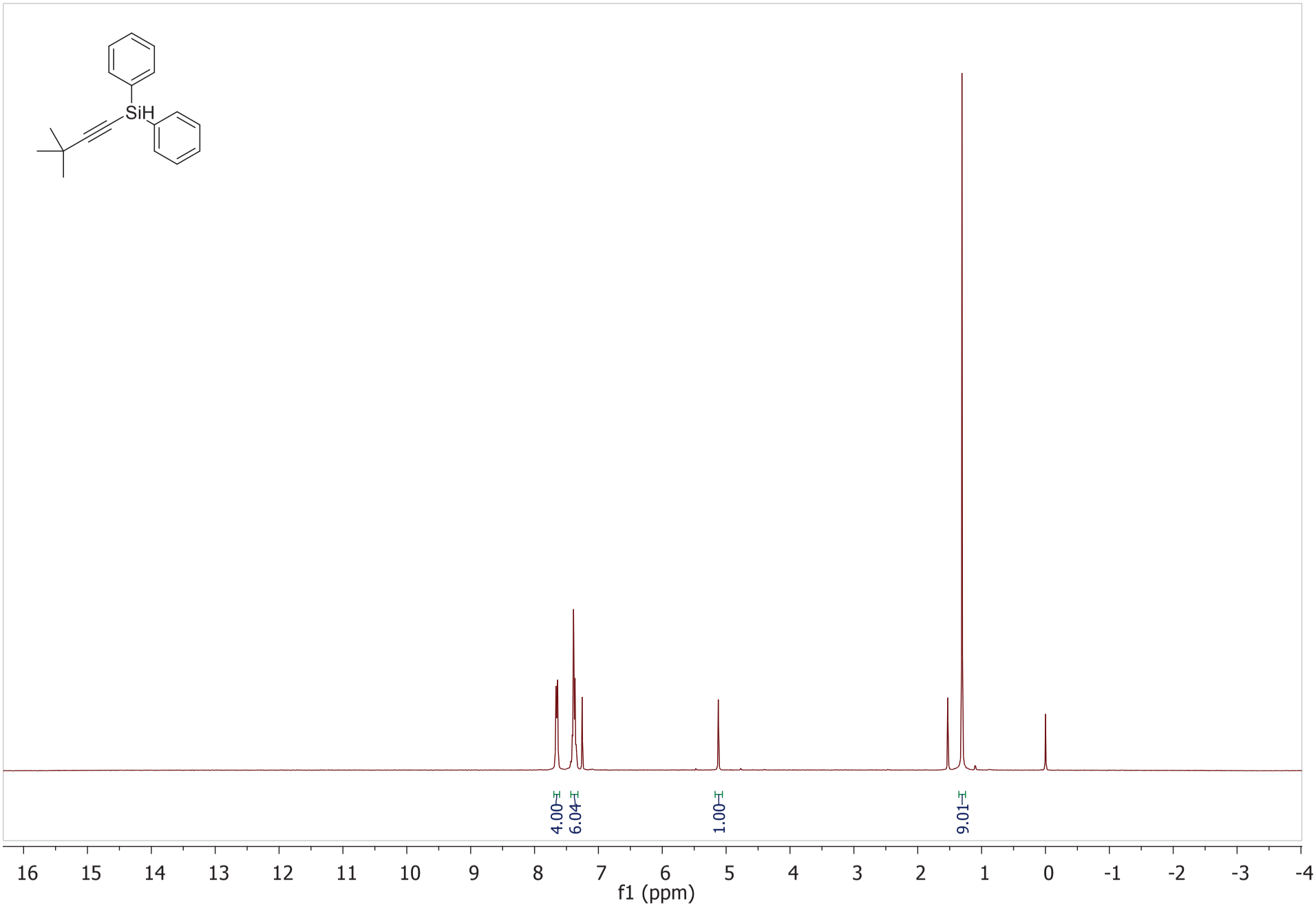
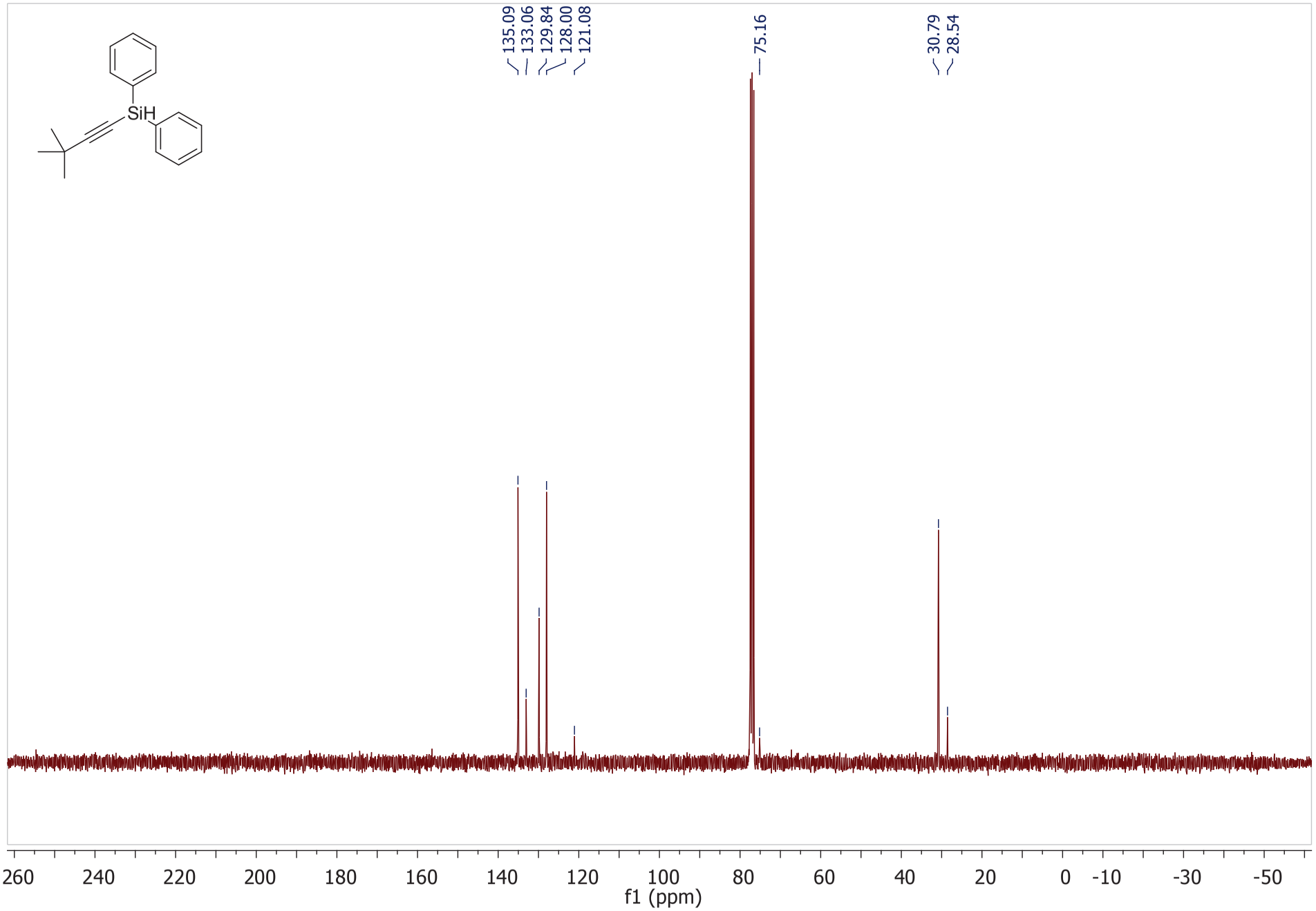
20
0
-10
-30
-50
f1 (ppm)


SiH
4.00
6.04
1.00
9.01
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


135.09
133.06
129.84
128.00
121.08
75.16
30.79
28.54
SiH
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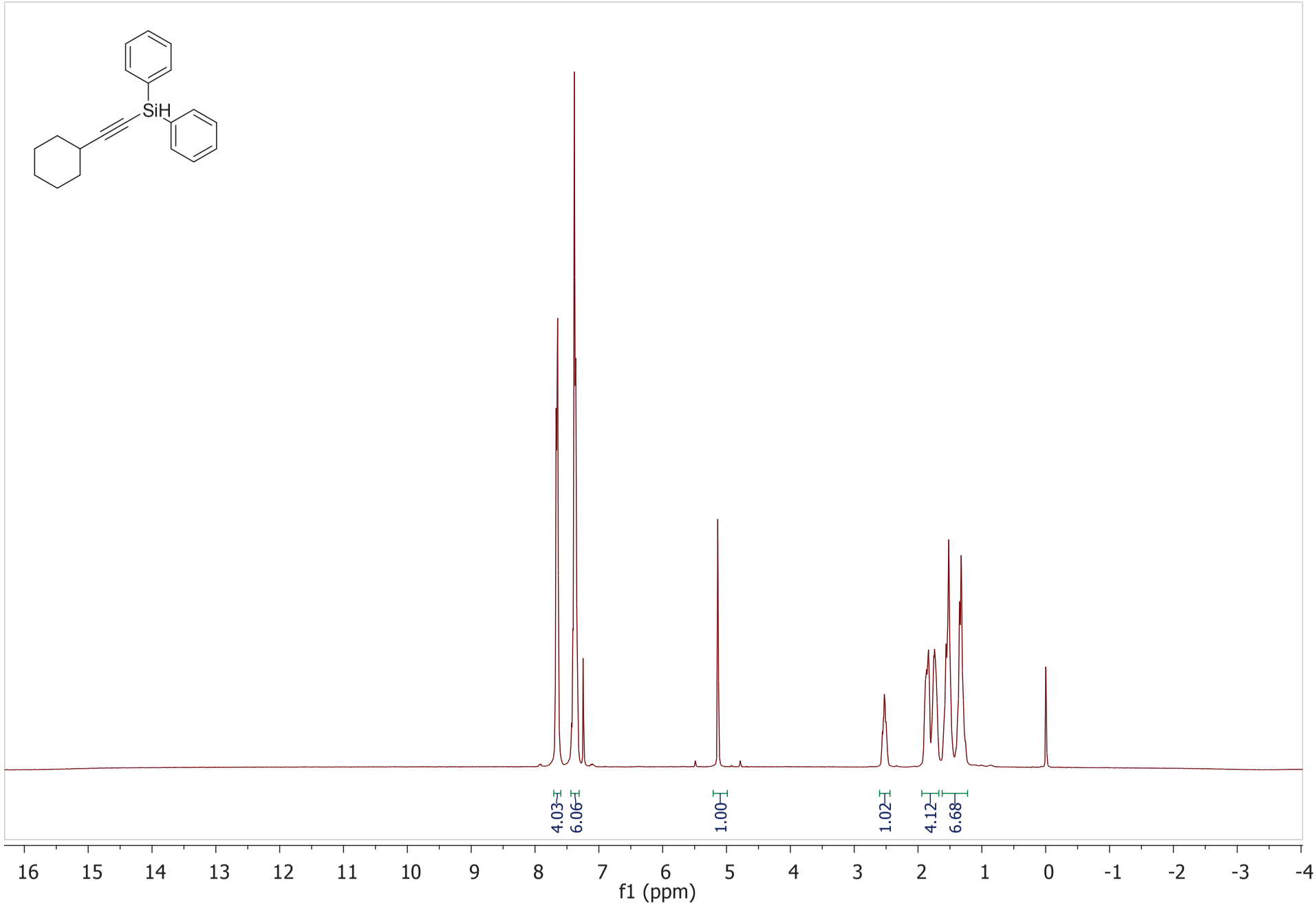
200
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
f1 (ppm)


SiH
4.03
6.06
1.00
1.02
4.12
6.68
16
15
14
13
12
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8
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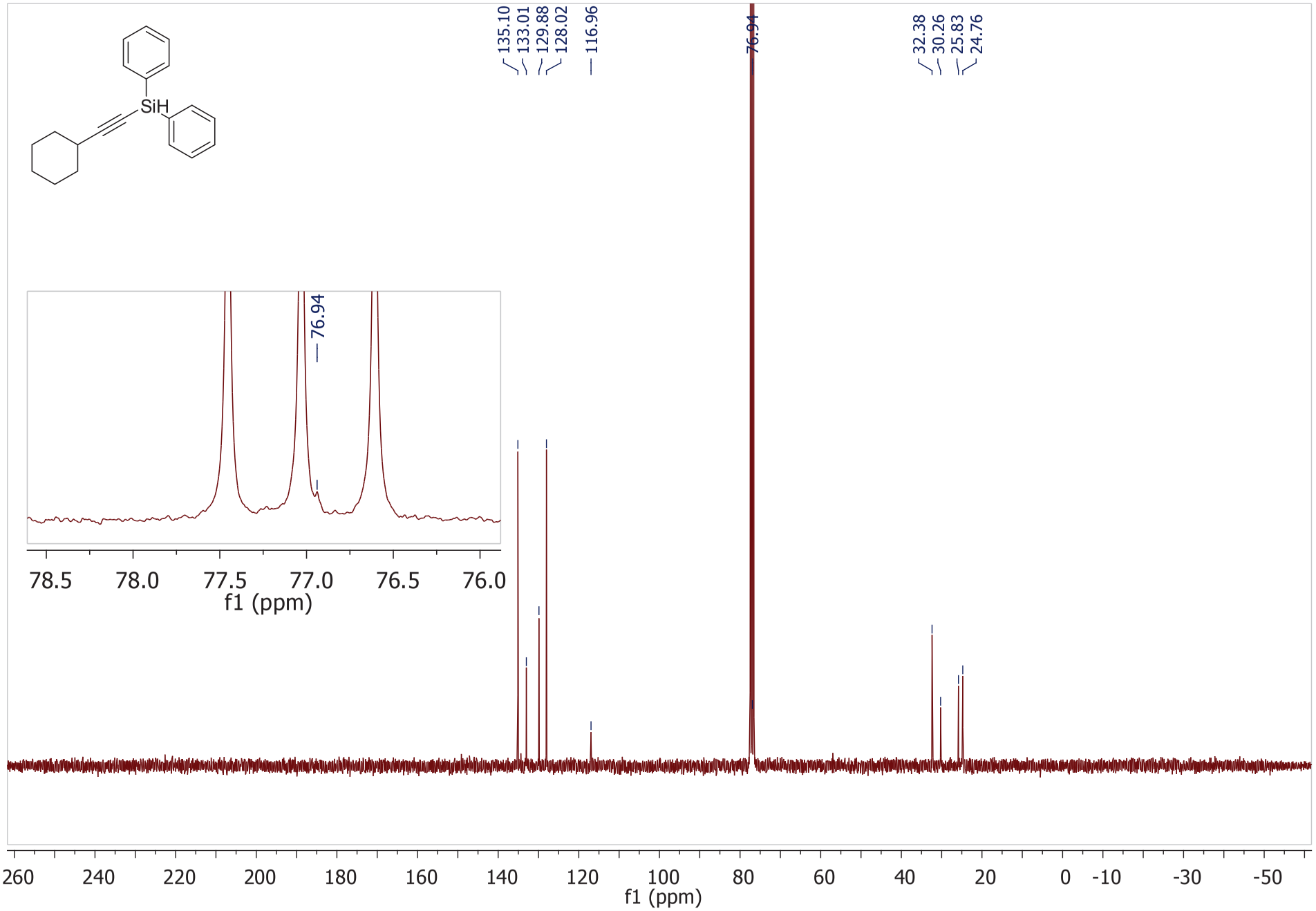
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)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128.02
116.96
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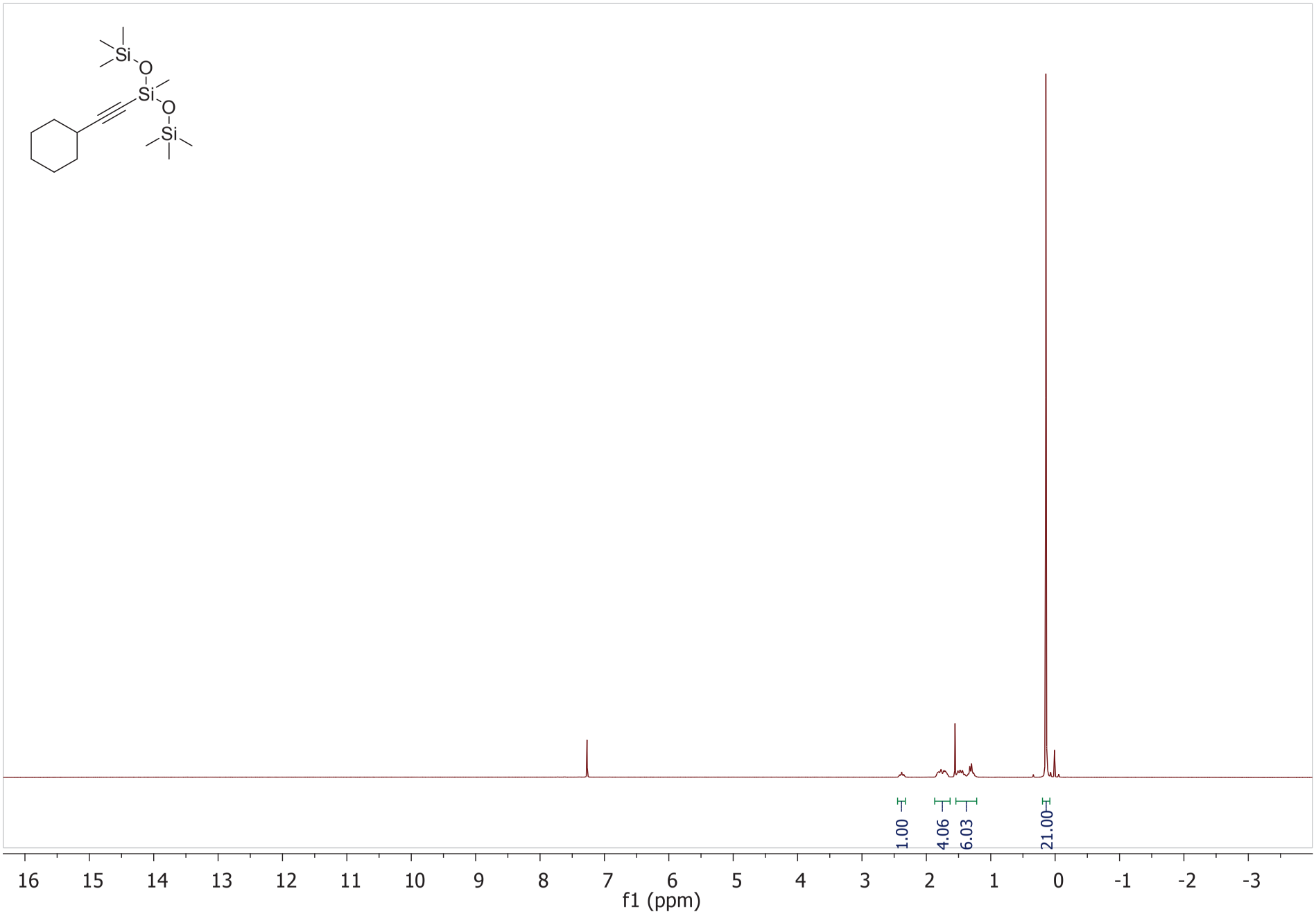
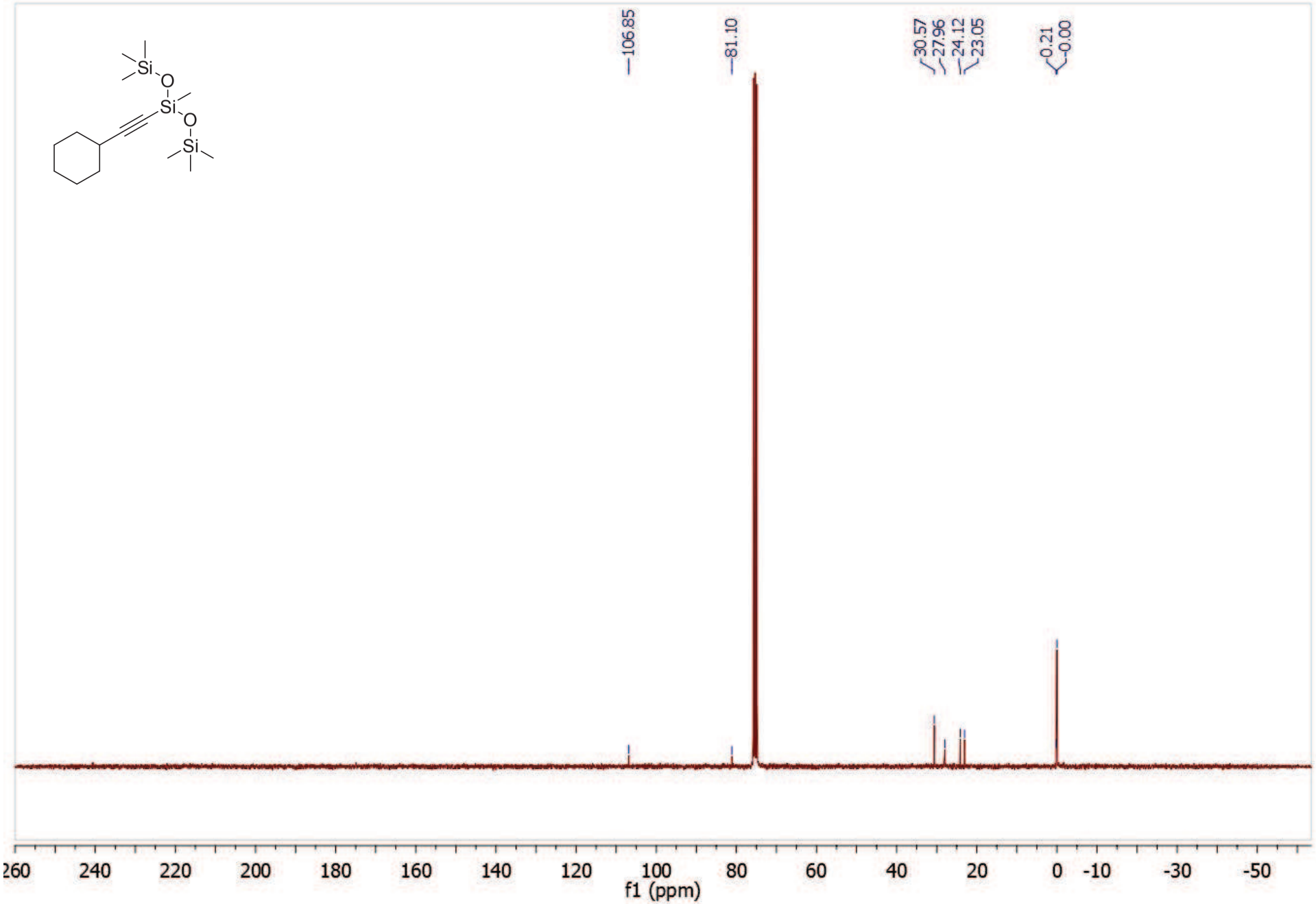
32.38
30.26
25.83
24.76
76.94
78.5
78.0
77.5
77.0
76.5
76.0
f1 (ppm)
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
f1 (ppm)


Si
O
Si
O
Si
1.00
4.06
6.03
21.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


106.85
81.10
30.57
27.96
24.12
23.05
0.21
0.00
Si
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Si
O
Si
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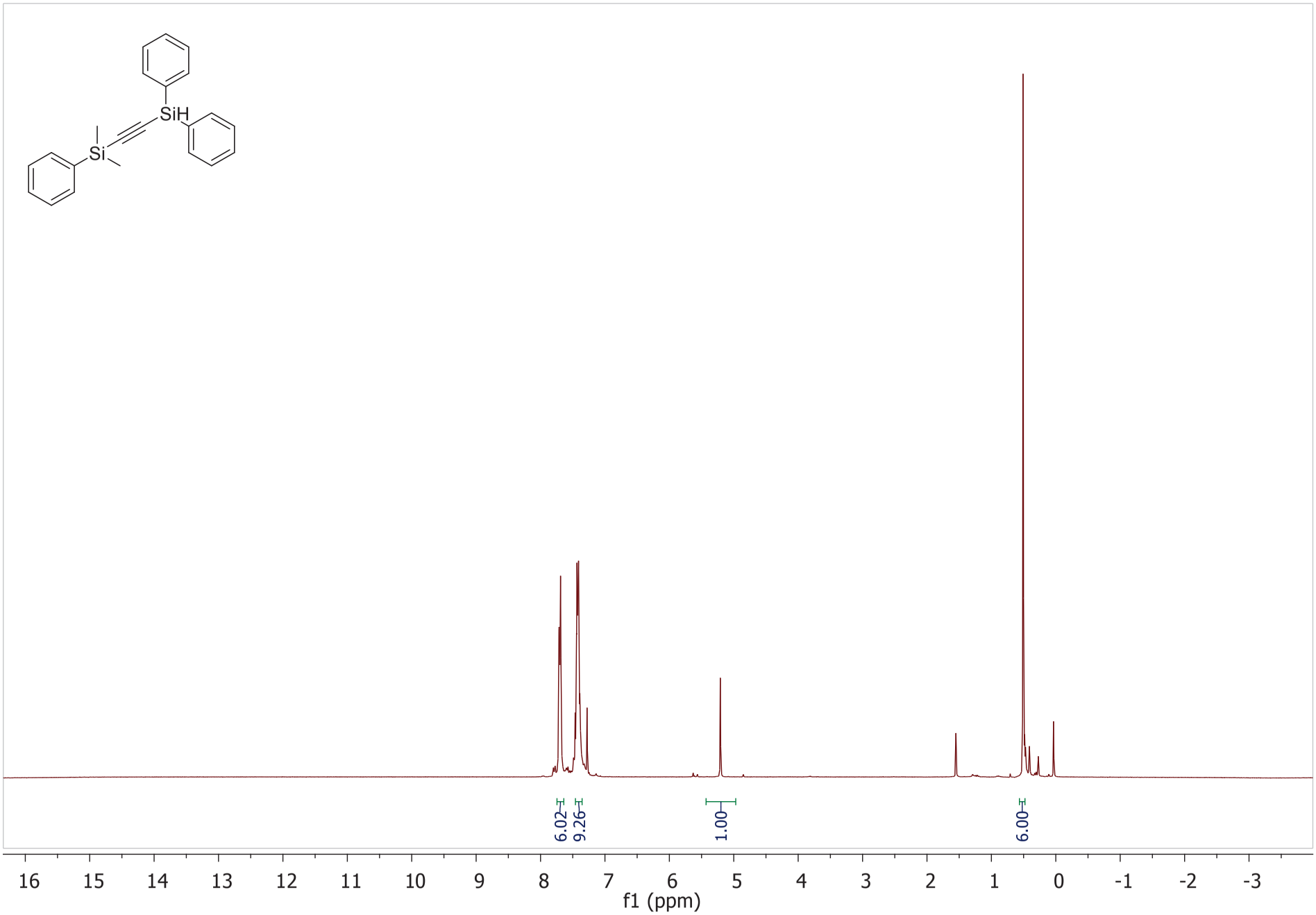
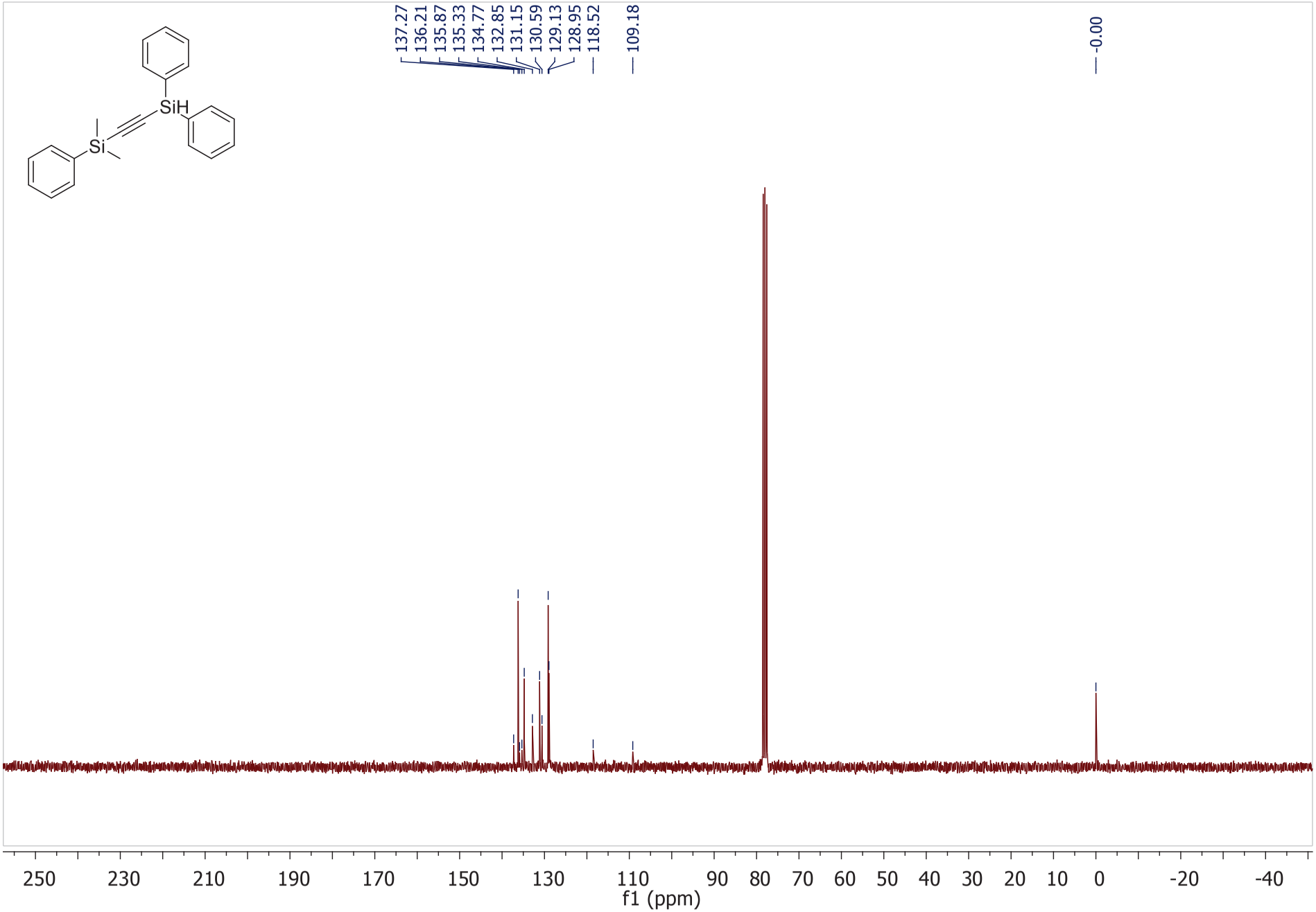
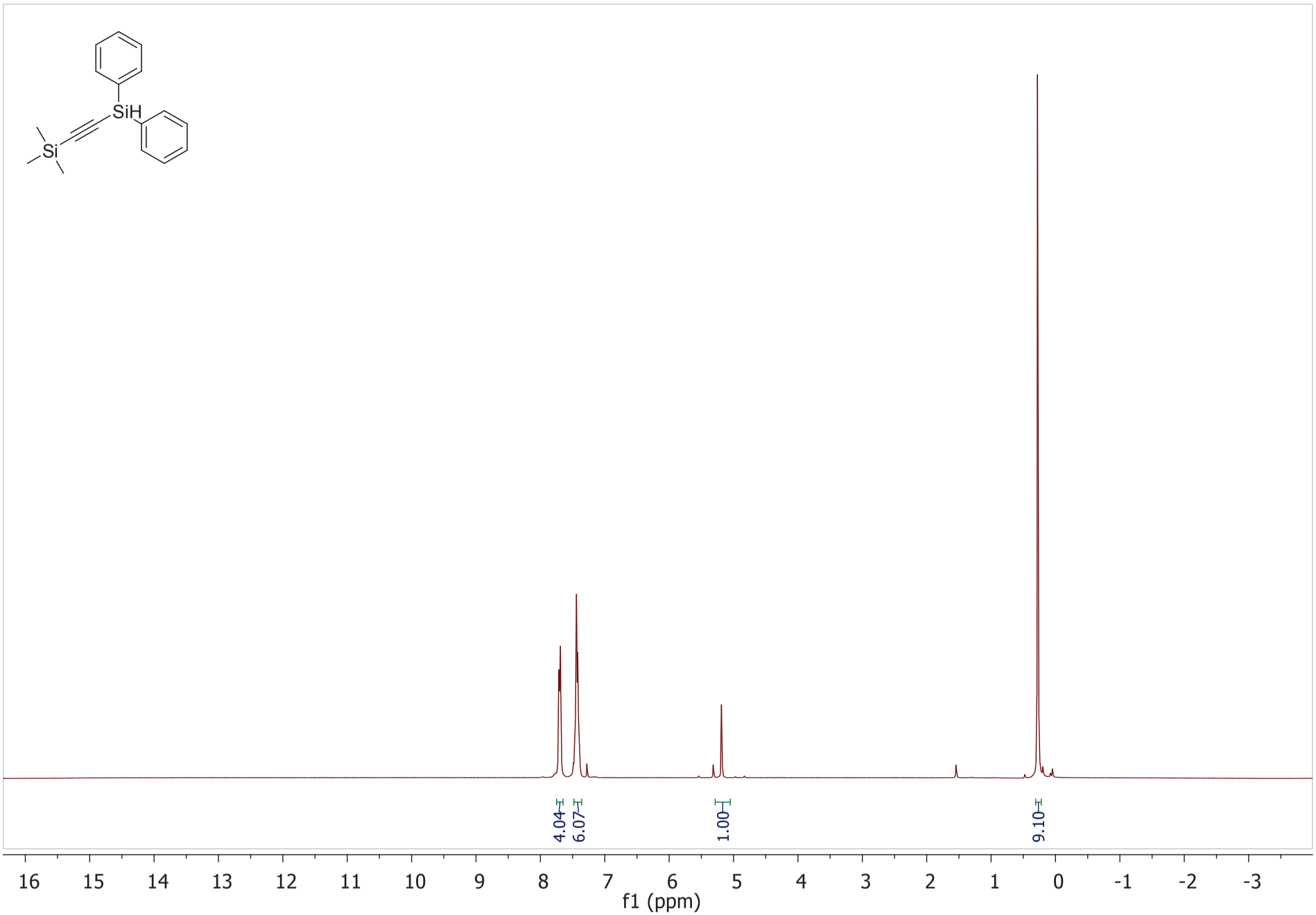
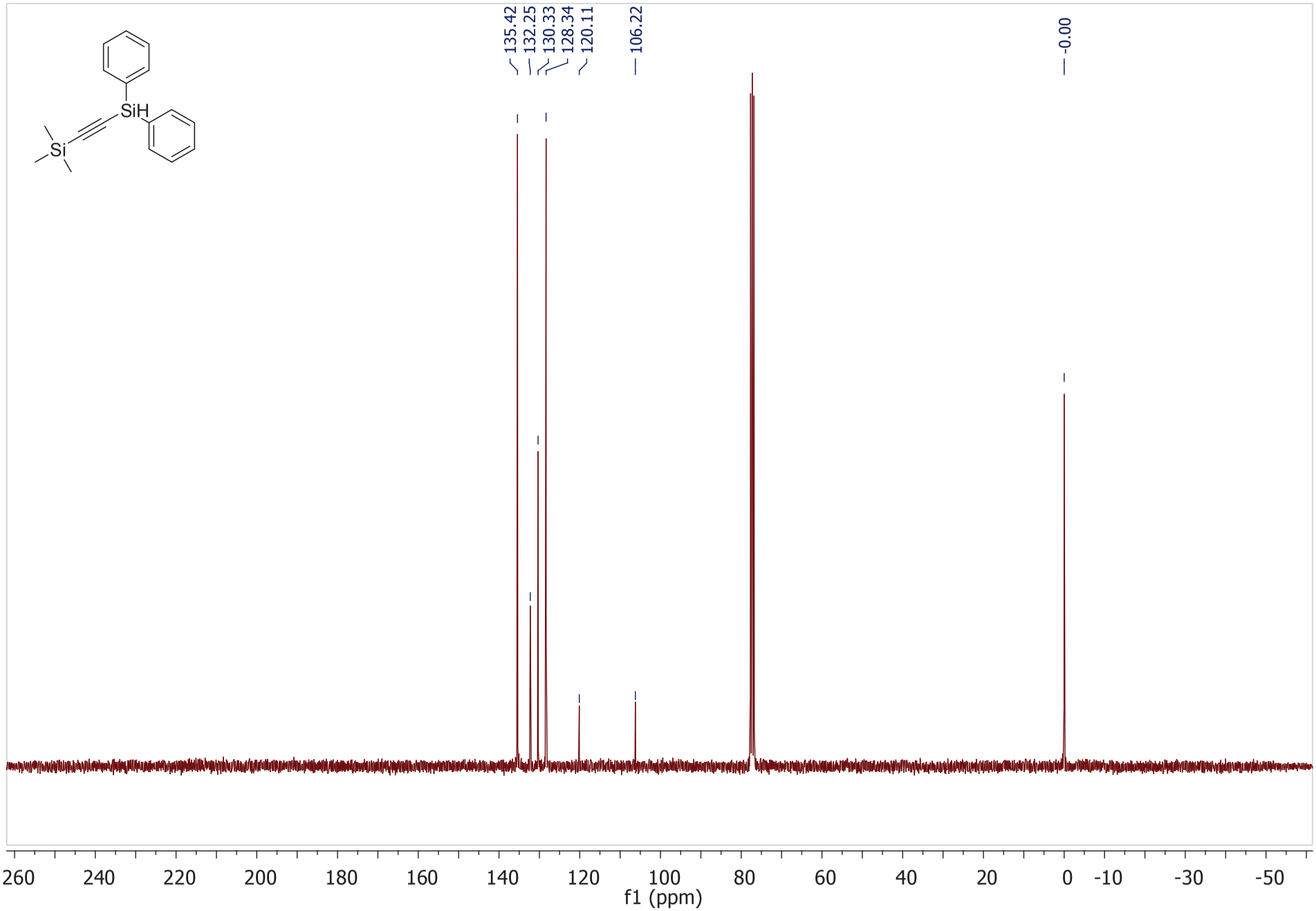
200
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
f1 (ppm)


SiH
Si
6.02
9.26
1.00
6.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


137.27
136.21
135.87
135.33
134.77
132.85
131.15
130.59
129.13
128.95
118.52
109.18
-0.00
SiH
Si
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
-40
f1 (ppm)


SiH
Si
4.04
6.07
1.00
9.10
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


SiH
Si
135.42
132.25
130.33
128.34
120.11
106.22
-0.00
260
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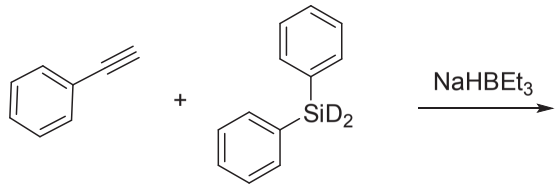
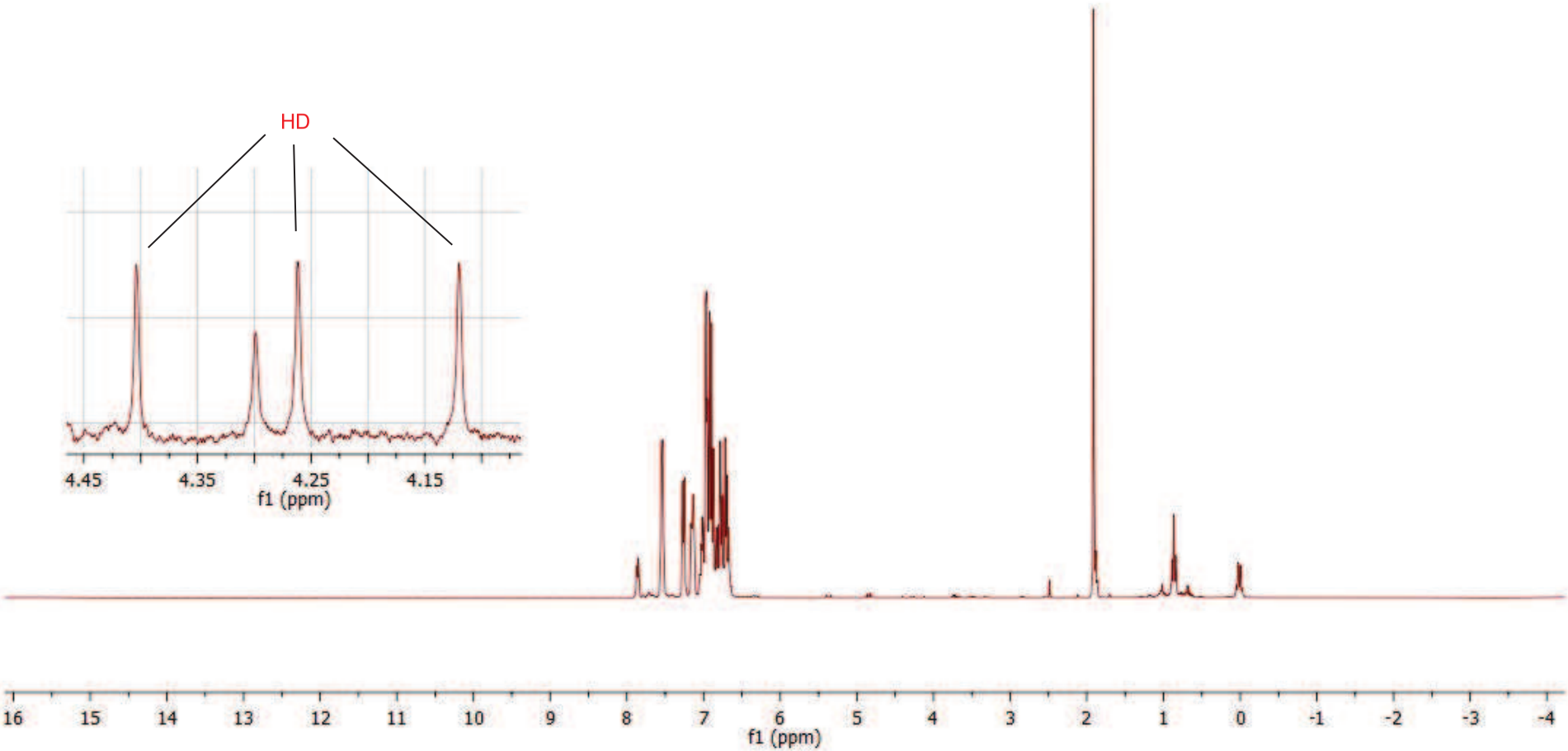
200
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
f1 (ppm)


+
SiD2
NaHBEt3


HD
4.45
4.35
4.25
4.15
f1 (ppm)
16
15
14
13
12
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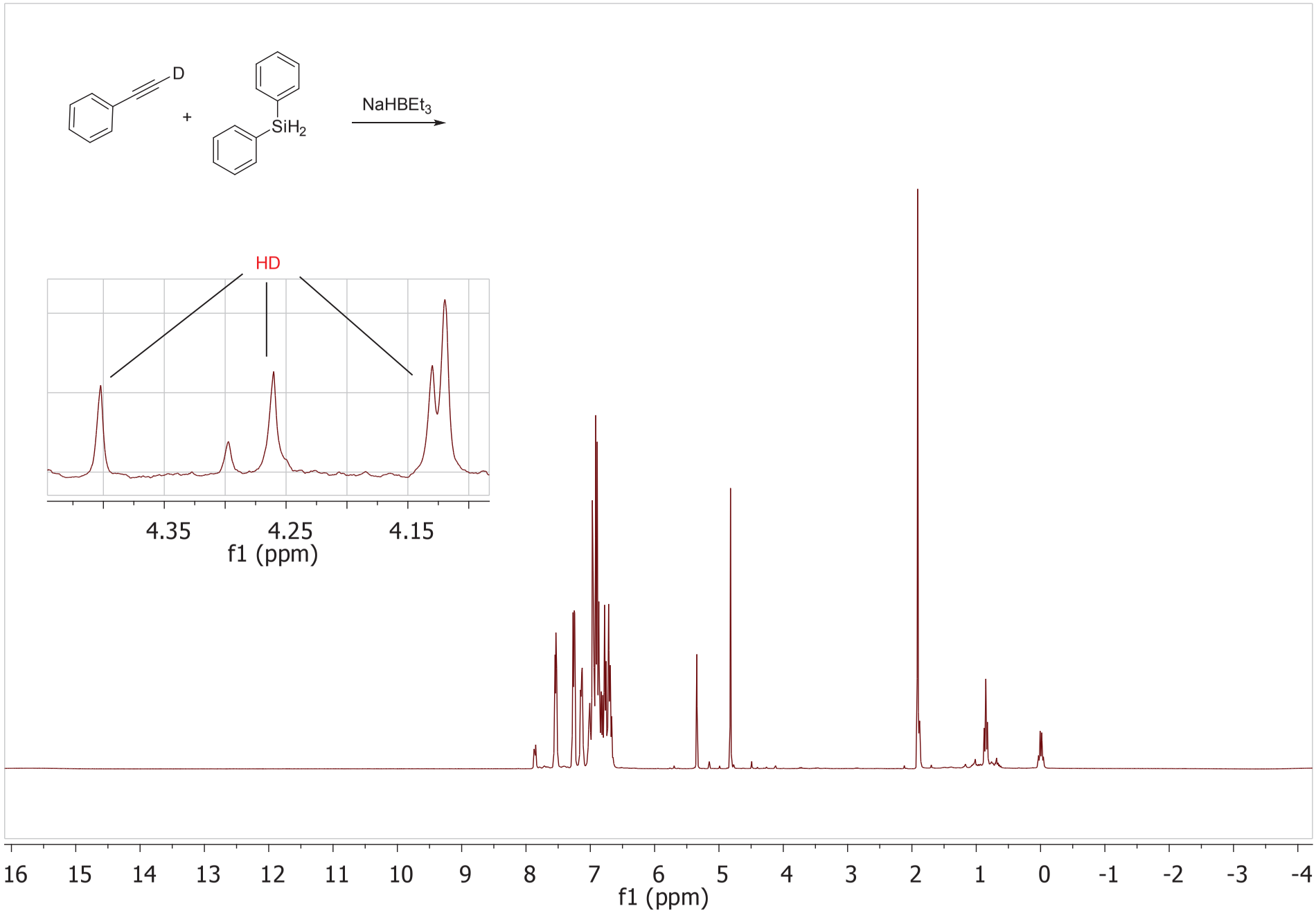
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


D
+
SiH2
NaHBEt3
HD
4.35
4.25
4.15
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

28.06.2022

Maciej Skrodzki

Faculty of Chemistry

Uniwersytetu Poznańskiego 8

Declaration

I declare, that in the following articles:

Bocian A., Skrodzki M., Kubicki M., Gorczyński A., Pawluć P., Patroniak V.; *The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins. Appl. Catal. A-Gen.* 2020, 602, 117665. **(A1)**

Skrodzki M., Patroniak V., Pawluć P.; *Schiff Base Cobalt(II) Complex-Catalyzed Highly Markovnikov-Selective Hydrosilylation of Alkynes. Org. Lett*. 2021, 23, 663-667. **(A2)**

Skrodzki M., Ortega Garrido V, Csaky A. G., Pawluć P.; *Searching for highly active cobalt catalysts bearing Schiff base ligands for Markovnikov-selective hydrosilylation of alkynes with tertiary silanes. J. Catal.* 2022, 441, 116-121. **(A3)**

Skrodzki M., Witomska S., Pawluć P.; *Sodium triethylborohydride as a catalyst for the dehydrogenative silylation of terminal alkynes with hydrosilanes. Dalton Trans.*, 2018, 47, 5948. **(A4)**

Which are parts of the doctoral dissertation entitled:

Cobalt(II) complexes with Schiff base ligands as new pre-catalysts for hydrosilylation of alkenes and alkynes

My own contribution in these articles includes:

- Catalysts screening and optimization (A1-A4)
- Synthesis of ligand and catalyst (A2)
- Analysis of postreaction mixtures (A1-A4)
- Synthesis, isolation and characterization of products (A1-A4)
- Registration and interpretation of NMR spectra (A1-A4)
- Mechanistic investigations, including reactions with deuterated substrates (A2-A4)
- Manuscript writing (A2-A4)
- Manuscript reviving and editing (A1)
- Preparation the Supporting Information (A1-A4)

Maciej Skrodzki

Poznan, 29.06.2022

prof. dr hab. Piotr Pawluć

Faculty of Chemistry AMU

Supervisor's declaration

I declare, that in the following articles:

Bocian A., Skrodzki M., Kubicki M., Gorczyński A., Pawluć P., Patroniak V.; *The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins. Appl. Catal. A-Gen.* 2020, 602, 117665.

Skrodzki M., Patroniak V., Pawluć P.; *Schiff Base Cobalt(II) Complex-Catalyzed Highly Markovnikov-Selective Hydrosilylation of Alkynes. Org. Lett*. 2021, 23, 663-667.

Skrodzki M., Ortega Garrido V, Csaky A. G., Pawluć P.; *Searching for highly active cobalt catalysts bearing Schiff base ligands for Markovnikov-selective hydrosilylation of alkynes with tertiary silanes. J. Catal.* 2022, 441, 116-121.

Skrodzki M., Witomska S., Pawluć P.; *Sodium triethylborohydride as a catalyst for the dehydrogenative silylation of terminal alkynes with hydrosilanes. Dalton Trans.*, 2018, 47, 5948.

Which are the parts of the doctoral dissertation entitled:

Cobalt(II) complexes with Schiff base ligands as new pre-catalysts for hydrosilylation of alkenes and alkynes

My own contribution in these articles includes:

- Direct supervision on PhD candidate's work
- Discussion on results and conceptualisation of work
- Manuscript writing and editing
- Correspondence with editors and reviewers

.....

prof. dr hab. Piotr Pawluć

23.06.2022

Dr Aleksandra Bocian

Polna 25a

64-020 Czempiń

Declaration

I declare, that in the following article:

Bocian A., Skrodzki M., Kubicki M., Gorczyński A., Pawluć P., Patroniak V.; *The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins. Appl. Catal. A-Gen.* 2020, 602, 117665.

Which is a part of the doctoral dissertation entitled:

Cobalt(II) complexes with Schiff base ligands as new pre-catalysts for hydrosilylation of alkenes and alkynes

My own contribution includes:

- synthesis of cobalt's complexes
- analysis and interpretation of compound's measurements
- writing a part of manuscript based on cobalt's complexes

A. Bocian

.....

Name Surname

24.06.2022

Dr. Adam Gorczyński

Faculty of Chemistry, Adam Mickiewicz University,

Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland

Declaration

I declare, that in the following article:

Bocian A., Skrodzki M., Kubicki M., Gorczyński A., Pawluć P., Patroniak V.; *The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins. Appl. Catal. A-Gen.* **2020**, 602, 117665.

Which is a part of the doctoral dissertation entitled:

Cobalt(II) complexes with Schiff base ligands as new pre-catalysts for hydrosilylation of alkenes and alkynes

My own contribution includes:

- conceptualization of the design of ligand/cobalt coordination compounds and partial structure/properties correlation of observed catalytic results
- preparation of the original manuscript draft and subsequent revisions related to the ligand/complexes sections

Signed by /
Podpisano przez:

Adam Paweł
Gorczyński

Date / Data: 2022-06-24 11:34

……..

Name Surname

Poznań, 19.06.2022

Maciej Kubicki

Faculty of Chemistry,

Adam Mickiewicz University

Poznań, Poland

Declaration

I declare, that in the following article(s):

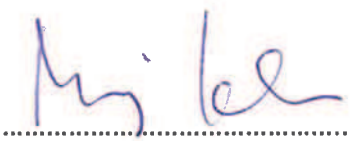
Bocian A., Skrodzki M., Kubicki M., Gorczyński A., Pawluć P., Patroniak V.; *The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins. Appl. Catal. A-Gen.* **2020**, 602, 117665.

Which is a part of the doctoral dissertation entitled:

Cobalt(II) complexes with Schiff base ligands as new pre-catalysts for hydrosilylation of alkenes and alkynes

My own contribution include(s):

Determination of the solid-state structure of the three complexes, and description of these structures.



Maciej Kubicki

24.06.2022

Violetta Patroniak

Faculty of Chemistry

Uniwersytetu Poznańskiego 8

61-614 Poznań

Declaration

I declare, that in the following articles:

Bocian A., Skrodzki M., Kubicki M., Gorczyński A., Pawluć P., Patroniak V.; *The effect of Schiff base ligands on the structure and catalytic activity of cobalt complexes in hydrosilylation of olefins. Appl. Catal. A-Gen.* **2020**, 602, 117665.

Skrodzki M., Patroniak V., Pawluć P.; *Schiff Base Cobalt(II) Complex-Catalyzed Highly Markovnikov-Selective Hydrosilylation of Alkynes. Org. Lett.* 2021, 23, 663-667.

Which are parts of the doctoral dissertation entitled:

Cobalt(II) complexes with Schiff base ligands as new pre-catalysts for hydrosilylation of alkenes and alkynes

I certify that my contribution consisted of conceptualization of this articles and editioral proofreading.

.....

Prof. dr hab. Violetta Patroniak

20.06.2022

Víctor Ortega Garrido

Grupo de Síntesis Orgánica y Bioevaluación, Instituto Pluridisciplinar. Universidad Complutense, Paseo de Juan XXIII, 1, 28040 Madrid.

Declaration

I declare, that in the following article(s):

Skrodzki M., Ortega Garrido V, Csaky A. G., Pawluć P.; *Searching for highly active cobalt catalysts bearing Schiff base ligands for Markovnikov-selective hydrosilylation of alkynes with tertiary silanes. J. Catal.* **2022**, 441, 116-121.

Which is a part of the doctoral dissertation entitled:

Cobalt(II) complexes with Schiff base ligands as new pre-catalysts for hydrosilylation of alkenes and alkynes

My own contribution include(s):

-Synthesis, purification and characterization of Shiff base ligands

-Preparation of cobalt(II) complexes

.....

Victor Ortega Garrido

19.06.2022

Prof. Dr. Aurelio G. Csáky

Instituto Pluridisciplinar

Universidad Complutense de Madrid

Paseo de Juan XXIII, 1

28040 – Madrid

Spain

Declaration

I declare, that in the following article(s):

Skrodzki M., Ortega Garrido V, Csaky A. G., Pawluć P.; *Searching for highly active cobalt catalysts bearing Schiff base ligands for Markovnikov-selective hydrosilylation of alkynes with tertiary silanes. J. Catal.* **2022**, 441, 116-121.

Which is a part of the doctoral dissertation entitled:

Cobalt(II) complexes with Schiff base ligands as new pre-catalysts for hydrosilylation of alkenes and alkynes

My own contribution include(s):

- General mechanistic discussion

…….

Aurelio G. Csáky

28.06.2022

Samanta Witomska

Center of Advanced Technologies

Adam Mickiewicz University

Uniwersytetu Poznańskiego 10

61-614 Poznań

Declaration

I declare, that in the following article:

Skrodzki M., Witomska S., Pawluć P.; *Sodium triethylborohydride as a catalyst for the dehydrogenative silylation of terminal alkynes with hydrosilanes. Dalton Trans.*, 2018, 47, 5948.

Which is a part of the doctoral dissertation entitled:

Cobalt(II) complexes with Schiff base ligands as new pre-catalysts for hydrosilylation of alkenes and alkynes

My own contribution includes:

- initial catalytic tests (reactions of phenylacetylene with phenylsilane)
- co-interpreting of results
- revision of the manuscript

Witomska

.....

Samanta Witomska