Supporting information for:

Markovnikov-selective double hydrosilylation of challenging terminal aryl alkynes under cobalt and iron catalysis

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1. General remarks

All manipulations, except work-up and purification of final products, were conducted under argon atmosphere using standard Schlenk techniques. Catalytic tests and syntheses of geminal bis(silanes) were carried out in Schlenk-bomb flask reaction vessels. THF, THF-d_8, dioxane and toluene were purified by distillation from potassium or sodium with benzophenone as indicator. Methylene chloride and acetonitrile were distilled from calcium hydride. Other solvents and all reagents were used as received from commercial suppliers. Geminal bis(silanes) were purified by column chromatography using silica stationary phase (230-240 mesh size). 2-Chloro-1-methyl-1*H*-benzimidazole (**A**) and 2-(1-methylhydrazinyl)-1*H*-benzimidazole (**B**) intermediates for ligands **L4** and **L5** were synthesized according to literature procedures.[1, 2] Complexes: **Co-L1**, **Fe-L1**, **Fe-L2** and **Fe-L5** were prepared as reported previously.[3, 4]

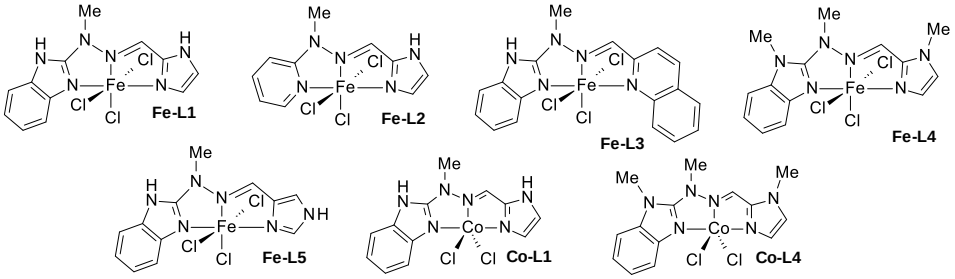


Figure S1. Cobalt(II) and iron(III) complexes used in this study.

^{1}H NMR spectra for determination of the yield catalytic tests in optimisation process were recorded on Bruker UltraShield 300 MHz operating at 300 MHz for ^{1}H NMR measurements. GC-MS analyses of samples from catalytic test runs were conducted using Bruker Scion 436-GC with a Bruker Scion SQ mass detector. NMR spectra of synthesised compounds and for monitoring of modifications of ligand **L1** and **Fe-L1** and **Co-L1** complexes upon addition of $NaHBEt_3$ were recorded on Bruker Avance 600 MHz operating at 600 MHz for ^{1}H NMR, 193 MHz for ^{11}B NMR, at 150 MHz for ^{13}C{^{1}H} NMR and at 119 MHz for ^{29}Si{^{1}H} NMR. NMR spectra of synthesised compounds were recorded on: Bruker Ascend™ 400 MHz operating at 400 MHz ^{1}H NMR, at 377 MHz for ^{19}F NMR, at 101 MHz for ^{13}C{^{1}H} NMR and at 79 MHz for ^{29}Si{^{1}H} NMR; NMR Varian VNMR-S 400 MHz operating at 79 MHz for ^{29}Si NMR. HRMS-ESI were recorded on Impact HD QTOF Bruker spectrometer. ESI-MS analyses were performed using Mas ZQ Water spectrometer. EI-MS analysis was performed using 320 MS/450 GC Bruker apparatus. Elemental analyses for C, H, and N were carried out using an Elementar Analyser Vario EL III. Infrared spectra were recorded on a FT-IR IFS 66/s. SEM analysis of postreaction samples was performed on QUANTA 250 FEG apparatus.

2. General procedures for catalytic double hydrosilylation

All solutions and mixtures were prepared in a Schlenk-bomb flask equipped with magnetic stirring bar which, prior to putting any material inside, was evacuated and, when under vacuum, its walls were heated thoroughly with a heat gun. After cooling down, the vessel was backfilled with argon, what was followed with two more cycles of gas evacuation and backfilling with argon. Addition of any material was conducted under the protective flow of argon.

Method A – when silane and alkyne are both liquids.
Co-L1 (1.8 mg, 5 μmol) and THF (0.5 ml) were added to the Schlenk-bomb flask placed over a working magnetic stirrer. To such obtained mixture a solution of $NaHBEt_3$ in toluene was added and stirring was continued at ambient temperature for 15 min. Next, alkyne (0.5 mmol) and silane (1.0 mmol) were added and the reaction vessel was placed in preheated oil bath (100 °C) to continue stirring for 3 h. After that time heating was removed and the reaction mixture was allowed to cool down to ambient temperature, followed by filtration through silica pad which was washed with a mixture of hexane (2 mL) and ethyl acetate (1 mL). Combined filtrates were evaporated *in vacuo* leaving an oil residue to which a mixture of hexane (2 mL) and ethyl acetate (1 mL) was added. Resulting suspension was filtrated through silica pad, which was washed with a mixture of hexane (6 mL) and ethyl acetate (3 mL). Combined filtrates were evaporated *in vacuo* giving a crude product in a form of an oil, which was further purified by column chromatography on silica (230-240 mesh size) using hexane as eluent. Fractions containing the pure product were combined and volatiles were removed *in vacuo* yielding the desired compound.

Method B – when at least one substrate (silane or alkyne) is solid.
A solution of alkyne (0.5 mmol) and silane (1.0 mmol) in THF (0.3 mL) was prepared. In a separate Schlenk-bomb flask a mixture of **Co-L1** (1.8 mg, 5 μmol) in THF (0.4 ml) was activated by adding a solution of $NaHBEt_3$ in toluene (35 μL, 1 M, 35 μmol), followed by stirring at ambient temperature for 15 min. Next, the solution of activated complex was added to the mixture of substrates and the reaction vessel was placed in preheated oil bath (100 °C) to continue stirring for 3 h. After that time heating was removed and the reaction mixture was allowed to cool down to ambient temperature, followed by filtration through silica pad which was washed with a mixture of hexane (2 mL) and ethyl acetate (1 mL). Combined filtrated were evaporated *in vacuo* leaving an oil residue to which a

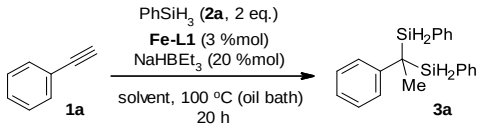
mixture of hexane (2 mL) and ethyl acetate (1 mL) was added. Resulting suspension was filtrated through silica pad, which was washed with a mixture of hexane (6 mL) and ethyl acetate (3 mL). Combined filtrated were evaporated *in vacuo* giving a crude product in a form of an oil, which was further purified by column chromatography on silica (230-240 mesh size) using hexane as eluent. Fractions containing the pure product were combined and volatiles were removed *in vacuo* yielding the desired compound.

Method C – for synthesis of mixed geminal-bis(silanes).
A mixture of **Co-L1** (0.9 mg, 2.5 μmol), phenylacetylene (55 μL, 0.5 mmol) and silane 1 (0.5 mmol) in THF (0.5 ml) was prepared in the Schlenk-bomb flask and stirred at ambient temperature for 15 min. Next, a solution of $NaHBEt_3$ in toluene (5 μL, 1 M, 5 μL) was added and the reaction vessel was placed in preheated oil bath (40 °C if silane 1 was primary/secondary or 60 °C if silane 1 was tertiary) to continue stirring for 20 h. After that time the flask was removed from the heating bath and allowed to cool down for 5 min. Next, a solution, prepared 15 min. prior in inert conditions, from **Co-L1** (1.8 mg, 5 μmol), THF (0.5 ml) and $NaHBEt_3$ (35 μL, 1 M in toluene, 35 μmol) was added to the original reaction vessel, followed by addition of silane 2 (0.5 mmol). The flask was subsequently put in preheated oil bath (100 °C) and reaction mixture was stirred for 20 h. After that time heating was removed and the reaction mixture was allowed to cool down to ambient temperature, followed by filtration through silica pad which was washed with a mixture of hexane (2 mL) and ethyl acetate (1 mL). Combined filtrates were evaporated *in vacuo* leaving an oil residue to which a mixture of hexane (2 mL) and ethyl acetate (1 mL) was added. Resulting suspension was filtrated through silica pad, which was washed with a mixture of hexane (6 mL) and ethyl acetate (3 mL). Combined filtrates were evaporated *in vacuo* giving a crude product in a form of an oil, which was further purified by column chromatography on silica (230-240 mesh size) using hexane as eluent. Fractions containing the pure product were combined and volatiles were removed *in vacuo* yielding the desired compound.

3. Optimization of phenylacetylene double hydrosilylation using phenylsilane

Initial reaction optimisation experiments were aiming for improving the yield of *gem*-bis(silane) **3a**, which was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as internal standard. Reactions were carried analogously to the *Method A* from the section above, using initially 3 mol% of **Fe-L1** as a precatalyst. Solvent screening showed that THF was better reaction medium than dioxane, acetonitrile, methylene chloride and toluene (Table S1).

Table S1. Solvent screening.

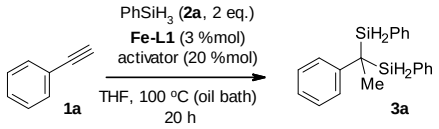


Entry	Solvent	NMR yield of **3a** (%)
1	THF	28
2	Dioxane	15
3	Toluene	0
4[a]	Dichloromethane	0
5	Acetonitrile	0

[a] Reaction carried at 60 °C.

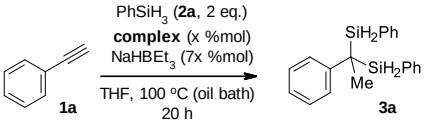
A set of potential activators was tested, among which triethylborohydrides served best, giving comparable results between sodium, potassium and lithium salts (Table S2). Lowering the loading of **Fe-L1** from 3 %mol to 1 %mol was beneficial for **3a** formation while further decrease in the amount of the iron complex resulted in worse yield of **3a** (Table S3). In case of **Co-L1** decrease in loading from 3 %mol to 1 %mol did not exert significant change (Table S3). Experiments carried out with 1 %mol of **Fe-L1** confirmed that lowering the temperature causes decrease in the yield of **3a** formation (Table S4). Control experiments confirmed that neither $FeCl_3$ or $CoCl_2$ without **L1**, nor **L1** without these halides or $NaHBEt_3$ on its own are capable of enabling double hydrosilylation of phenylacetylene (Table S5). Catalytic system composed of $FeCl_3$ and **L1** allowed for formation of **3a**, however with somewhat lower yield than in case of **Fe-L1** (Table S5). Using **Co-L1** and **Fe-L1** together gave better results than for any of them used on their own (Table S6). Two-stage one-pot procedure involving 1 %mol of **Co-L1** and 0.5 %mol of **Fe-L1** in the first stage and another 0.5 %mol of **Fe-L1** in the second stage worked better than approach aiming for using solely **Co-L1** in the first stage for monohydrosilylation of phenylacetylene, followed by second stage with only **Fe-L1** to enable second hydrosilylation process. Changing of the order of use of precatalyst, *i.e*. 0.5 %mol of **Fe-L1** in the first stage and 1 %mol of **Co-L1** with 0.5 %mol of **Fe-L1** in the second stage, worked less efficient (Table S6). Shortening of the reaction time from 20 h to 12 h resulted in slight yield decrease for **3a**.

Table S2. Activator screening.



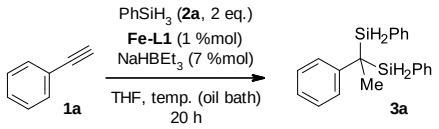
Entry	Activator	NMR yield of **3a** (%)
1	$NaHBEt_3$	28
2	$LiHBEt_3$	27
3	$KHBEt_3$	21
4	EtMgBr	0
5	*t*-BuONa	0

Table S3. Studies on precatalyst loading.



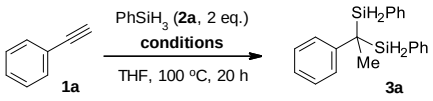
Entry	**Complex**/x	NMR yield of **3a** (%)
1	**Fe-L1**/3	28
2	**Fe-L1**/2	36
3	**Fe-L1**/1	43
4	**Fe-L1**/0.5	34

Table S4. Investigations on reaction temperature.



Entry	Temperature (°C)	NMR yield of **3a** (%)
1	100	43
2	80	29
3	60	9

Table S5. Control experiments.

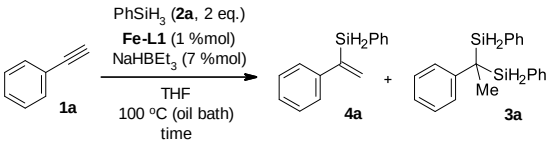


Entry	Conditions	NMR yield of **3a** (%)
1	$FeCl_3$ (3 %mol), $NaHBEt_3$ (20 %mol)	0
2	$CoCl_2$ (3 %mol), $NaHBEt_3$ (20 %mol)	0
3	**L1** (3 %mol), $NaHBEt_3$ (20 %mol)	0
4	$FeCl_3$ (3 %mol), **L1** (3 %mol), $NaHBEt_3$ (20 %mol)	21
5	$NaHBEt_3$ (20 %mol)	0

4. Kinetic experiments

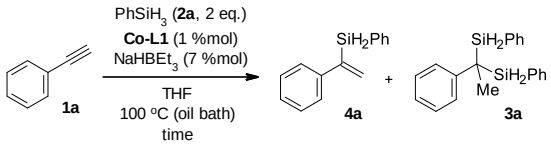
In order to gain better insight regarding the nature of the two consecutive hydrosilylation reactions taking place in double hydrosilylation of phenylacetylene as well to compare **Fe-L1** and **Co-L1** we have conducted a series of kinetic experiments that have showed us that **Co-L1** is more active than **Fe-L1** in the first hydrosilylation step, while for the second one activity of these two complexes are similar (Tables 6 to 9).

Table S6. Kinetic experiments on double hydrosilylation of phenylacetylene using **Fe-L1**.



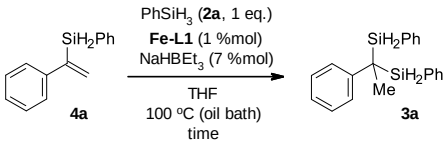
Entry	Time (min)	NMR yield of **4a** (%)	NMR yield of **3a** (%)
1	5	13	0
2	15	18	0
3	30	24	0
4	60	38	0
5	120	39	0
6	300	21	19
7	480	13	24
8	720	0	39

Table S7. Kinetic experiments on double hydrosilylation of phenylacetylene using **Co-L1**.



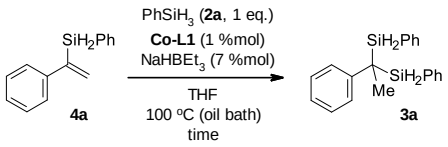
Entry	Time (min)	NMR yield of **4a** (%)	NMR yield of **3a** (%)
1	5	39	26
2	15	24	38
3	30	2	58
4	60	2	59
5	300	0	64
6	480	0	60
7	720	0	62

Table S8. Kinetic experiments on catalytic hydrosilylation of **4a** using **Fe-L1**.



Entry	Time (min)	NMR yield of **3a** (%)
1	5	52
2	15	59
3	360	64
4	480	64
5	720	65

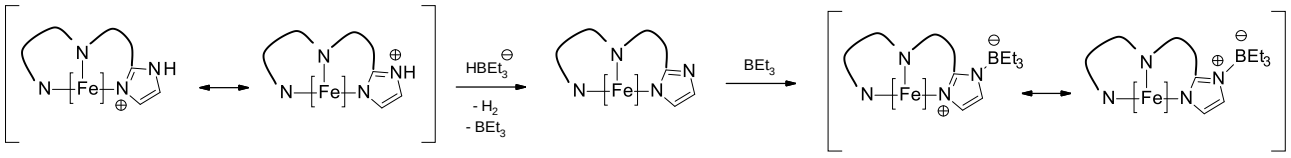
Table S9. Kinetic experiments on catalytic hydrosilylation of **4a** using **Co-L1**.



Entry	Time (min)	NMR yield of **3a** (%)
1	5	57
2	15	66
3	360	69
4	480	62
5	720	66

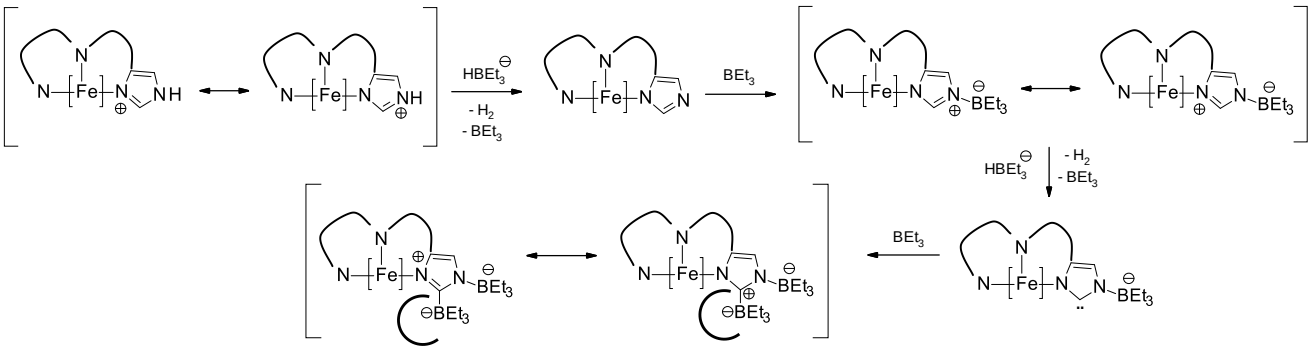
5. NMR experiments

Our precatalyst screening revealed that presence of NH units in the structure of the metal complex is an important factor regarding catalytic activity. We came out with hypothesis that this is the case due to reactions with $NaHBEt_3$ that may take place at these sites (Schemes S1 and S2). First NH might serve as proton source to react with $[HBEt_3]^-$ what would lead to liberation of H_2 and BEt_3 (Scheme S2). Nitrogen atom, after deprotonation, could then bind BEt_3 Lewis acid produced in previous reaction what should lead to change in overall electron properties of the ligand and probably also the conformational dynamics within the ligand framework.



Scheme S1. Illustration of possible reactions between the imidazole containing ligand and $NaHBEt_3$ – imidazole side of **L1**.

Moreover, such hypothesis agrees with the results obtained for **Fe-L5** with differently oriented imidazole ring. In case of this complex after NH deprotonation and binding of BEt_3 to the nitrogen atom should lead to increase acidity of C-H being between nitrogen atoms – resembling imidazolium salts serving as *N*-heterocyclic carbene precursors (Scheme S2). Hence C-H deporotonation at this position should be possible that could be followed by binding of liberated BEt_3 to the carbon atom. As a consequence a strong steric crowding would be build up around metal centre making it much more difficult to operate as a catalyst in hydrosilylation process (Scheme S3).



Scheme S2. Illustration of possible reactions between the imidazole containing ligand and $NaHBEt_3$ – imidazole side of **L5**.

In order to verify this hypothesis about reactions between $NaHBEt_3$ and the ligand we have conducted a series of NMR experiments – all of which were carried at ambient temperature with samples prepared in protective atmosphere of argon using dry THF-d_8.

First, we have investigated the process of $NaHBEt_3$ addition to ligand **L1**. Monitoring of this process by ^{1}H NMR showed that $NaHBEt_3$ acts as a base and deprotonates NH groups (Figure S2).

Another thing we sought to confirm along the way was formation of B-N bond. In order to do that we have measured the ^{11}B NMR spectrum of a **L1** sample after addition of $NaHBEt_3$ (Figure S3). This allowed us to observe a sharp signal at –0.13 ppm that we assign to the BEt_3 bonded to the nitrogen atom (Figure S3).[5]

Next, we have conducted a set of similar experiments on **Fe-L1** and **Co-L1**. As complexes **Fe-L1** and **Co-L1** ~~is~~ are paramagnetic their ^{1}H NMR spectra are illegible and no information about the fate of NH upon addition of $NaHBEt_3$ can be derived. However, ^{1}H NMR spectroscopy allowed us to observe appearance of broad signals in the high field region that we tentatively assign to [Fe-H] and [Co-H] species (Figures S4 and S5). In order to verify if formation of B-N bond takes place upon addition of $NaHBEt_3$ to **Fe-L1** and **Co-L1** we have measured ^{11}B NMR spectra (Figures S6 and S7). After adding of 1 equivalent of $NaHBEt_3$ to **Fe-L1** full consumption of $[HBEt_3]^-$ could be seen and a signal at 53.53 ppm appeared, which remained present when more $NaHBEt_3$ was added, only slightly changing its position. Based on literature data we tentatively interpret this signal as resulting from N-BEt_2 unit.[5] ^{11}B NMR spectrum after addition of 3 equivalents of $NaHBEt_3$ displayed one more signal at 71.94 ppm that we interpret as a result of equilibrium between $[HBEt_3]^-$, BEt_3 and $[Et_3B\text{-}H\text{-}BEt_3]^-$.[6] After addition of 7 equivalents of $NaHBEt_3$ this signal migrated, as expected, towards higher field region. Along with that two more signals appeared at 1.19 ppm and –0.41 ppm that we interpret as resulting from N-B units from BEt_3 binding to nitrogen atoms after their deprotonation (Figure S6). Addition of $NaHBEt_3$ to **Co-L1** also led to species giving signals at 1.19 ppm and –0.41 ppm in ^{11}B NMR (Figure S7).

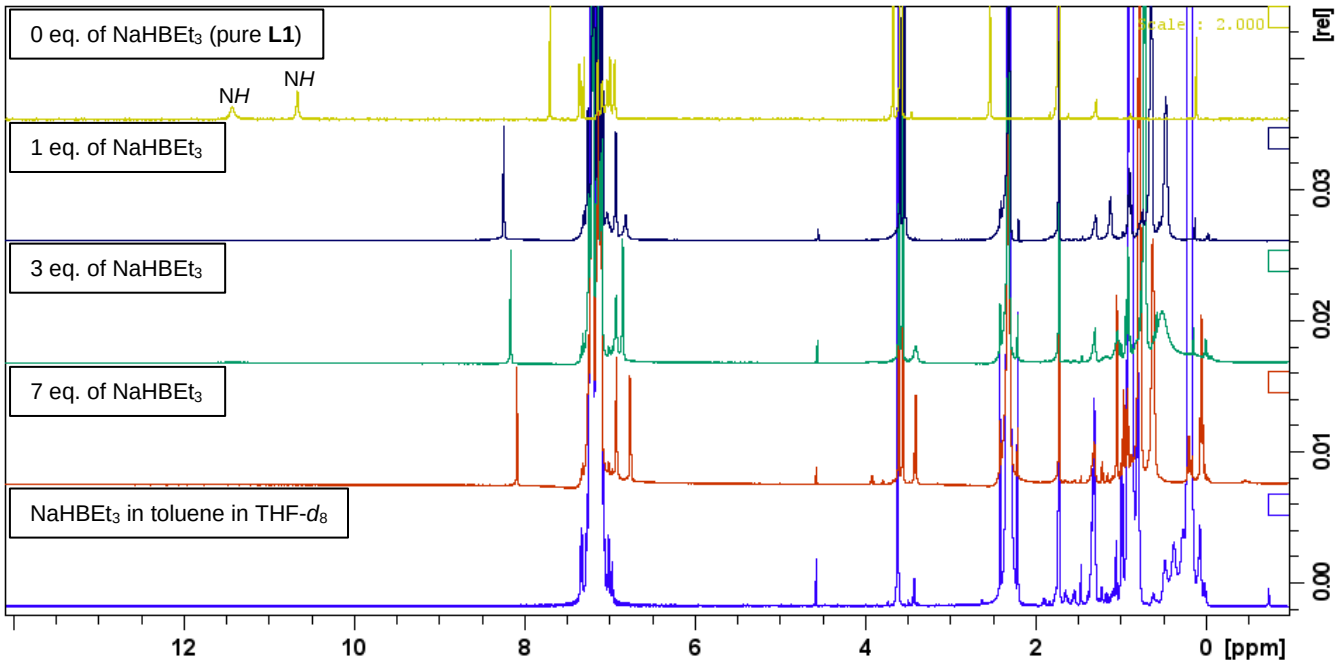


Figure S2. ^{1}H NMR studies on **L1 (**dissolved in THF-d_8) upon addition of NaHBEt$_3$ (1M solution in toluene).

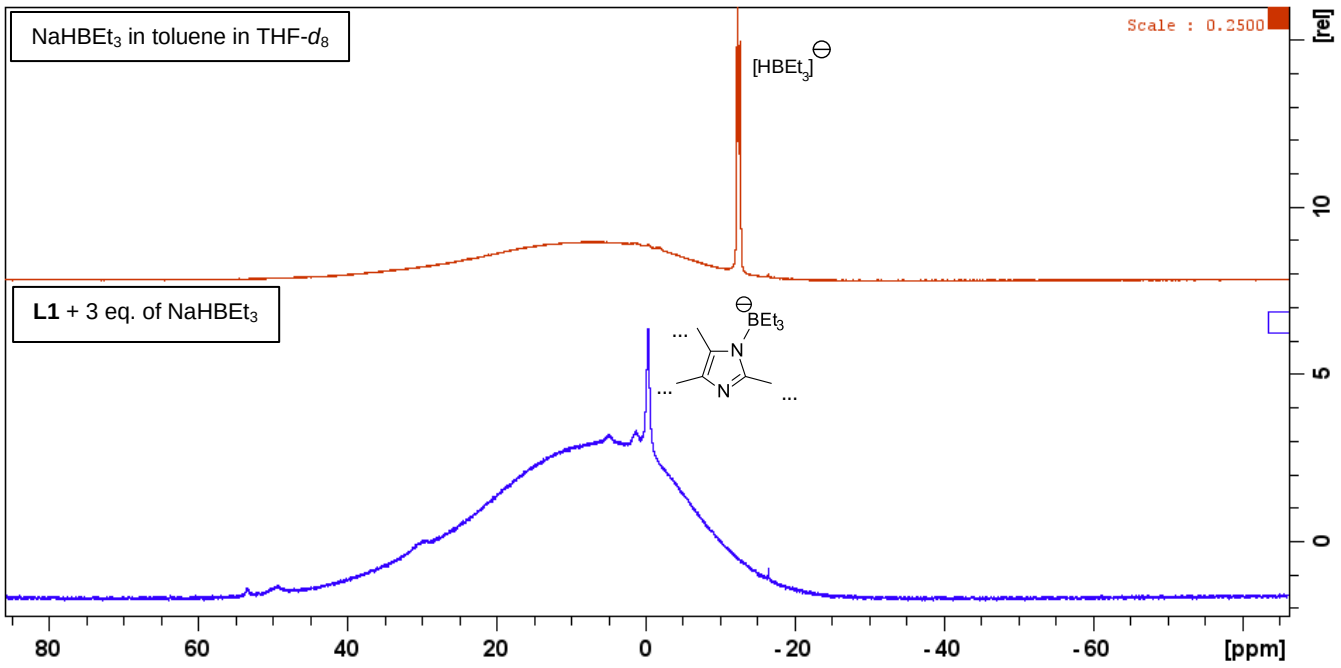


Figure S3. ^{11}B NMR studies on **L1 (**dissolved in THF-d_8) upon addition of NaHBEt$_3$ (1M solution in toluene).

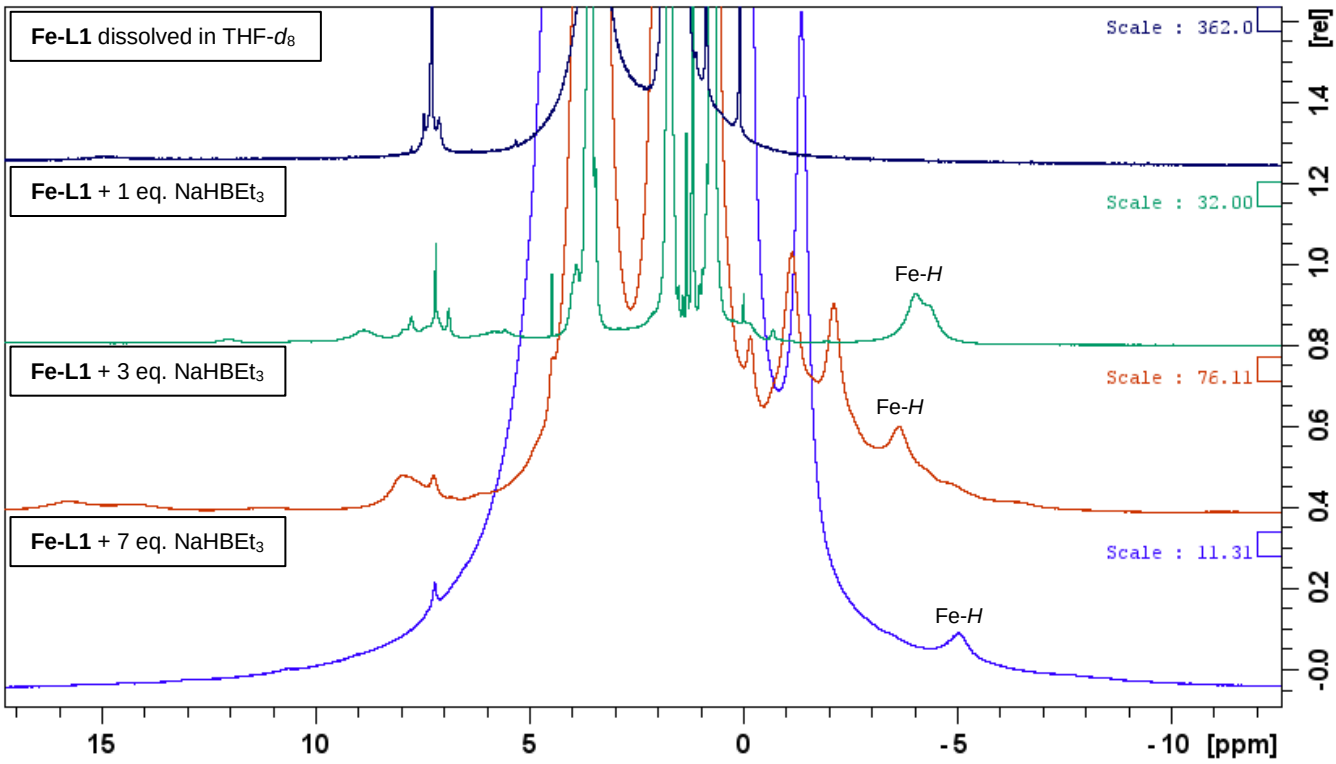


Figure S4. ^{1}H NMR studies on **Fe-L1** (dissolved in THF-d_8) upon addition of NaHBEt$_3$ (1M solution in THF).

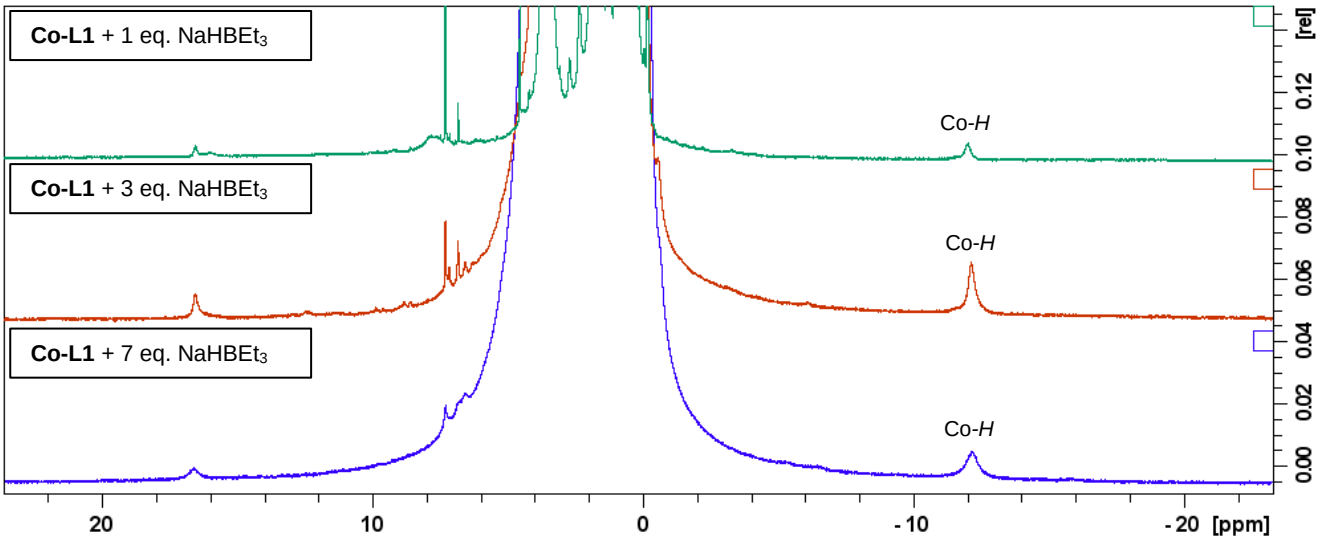


Figure S5. ^{1}H NMR studies on **Co-L1** upon addition of NaHBEt$_3$ (1M solution in THF).

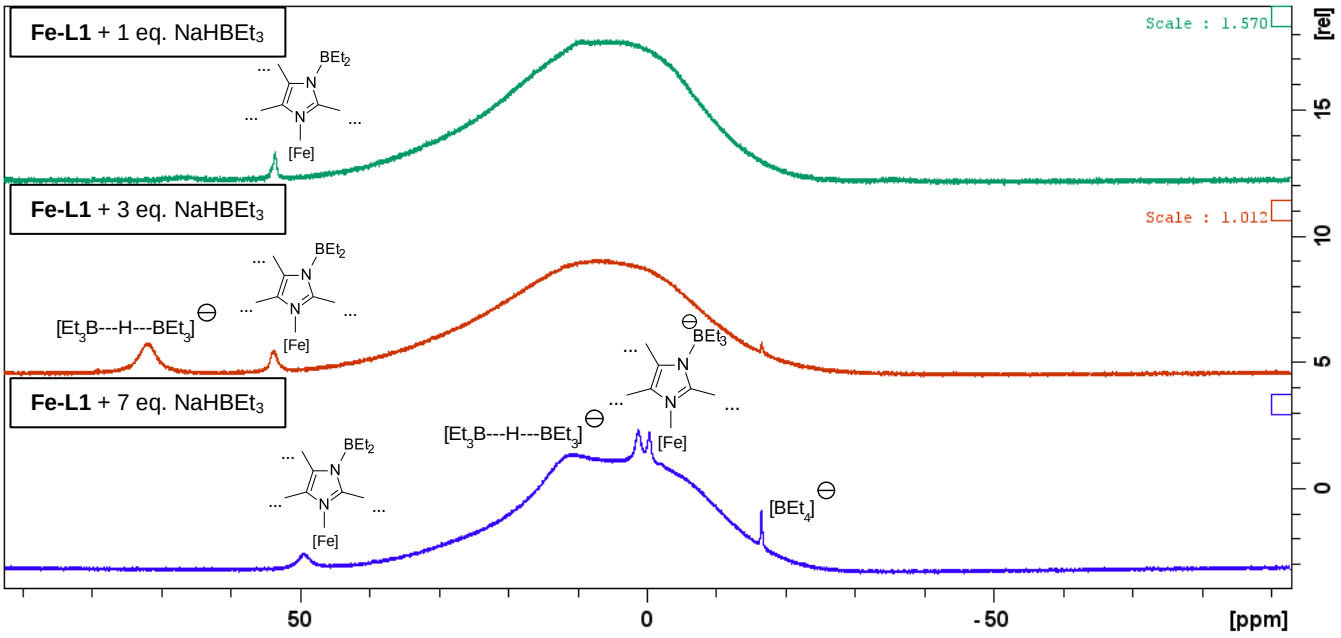


Figure S6. ^{11}B NMR studies on **Fe-L1** (dissolved in THF-d_8) upon addition of $NaHBEt_3$ (1M solution in THF).

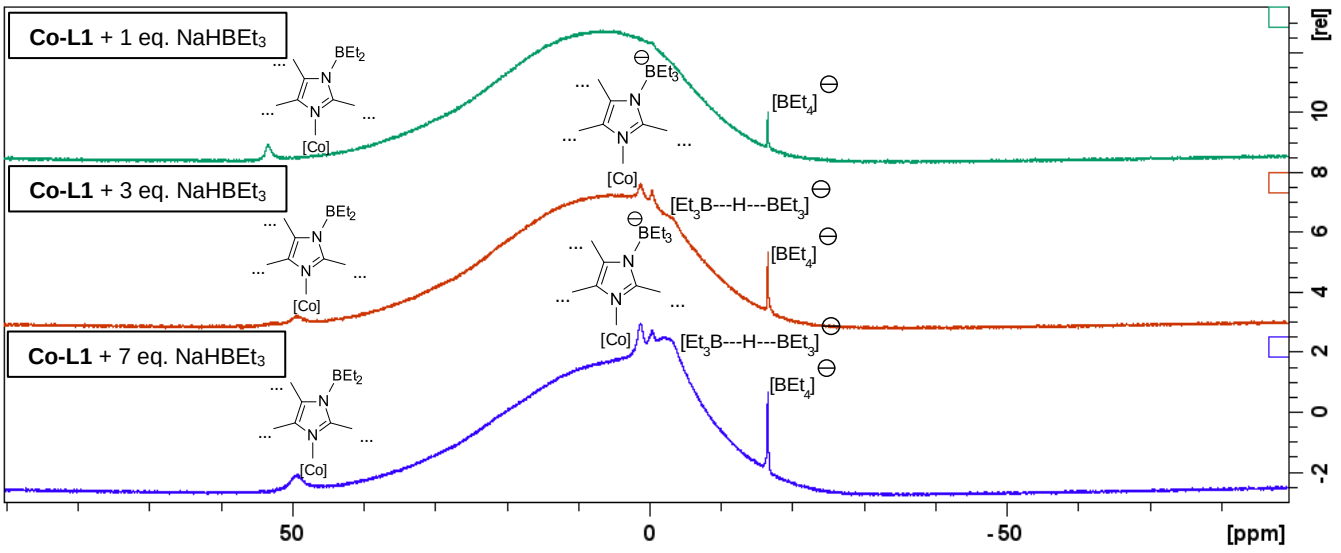


Figure S7. ^{11}B NMR studies on **Co-L1** (dissolved in THF-d_8) upon addition of $NaHBEt_3$ (1M solution in THF).

6. SEM analysis of postreaction mixtures

In order to verify if **Fe-L1** or **Co-L1** could be a source of nanoparticles that could have influence the hydrosilylation processes respective postreaction mixtures were analyzed using SEM technique. This confirmed that **Fe-L1** and **Co-L1** are not being transformed into nanoparticles (Figures S8 and S9).

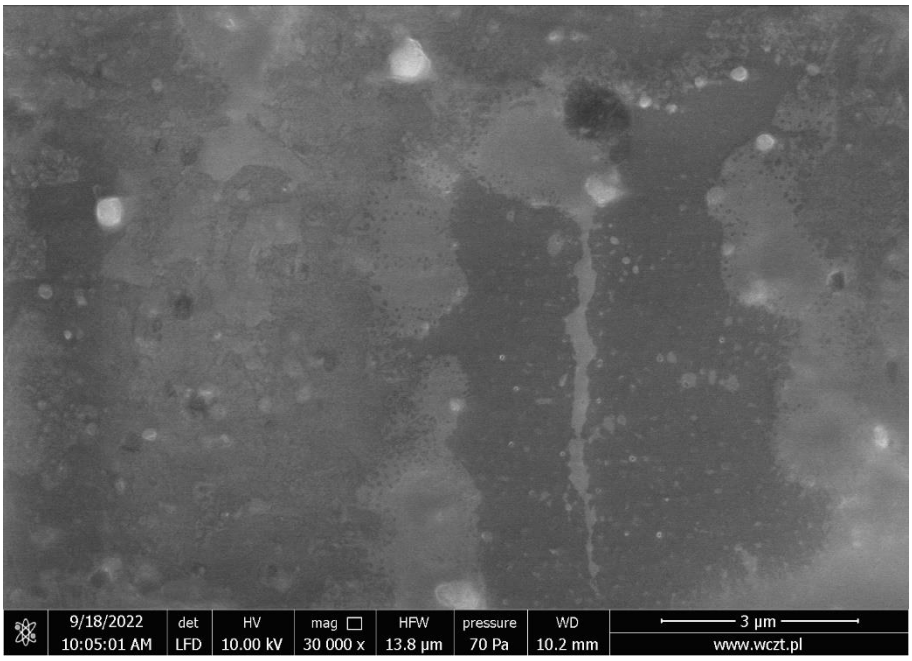


Figure S9. SEM image of a sample from postreaction mixture of phenylacetylene double hydrosilylation using **Fe-L1**.

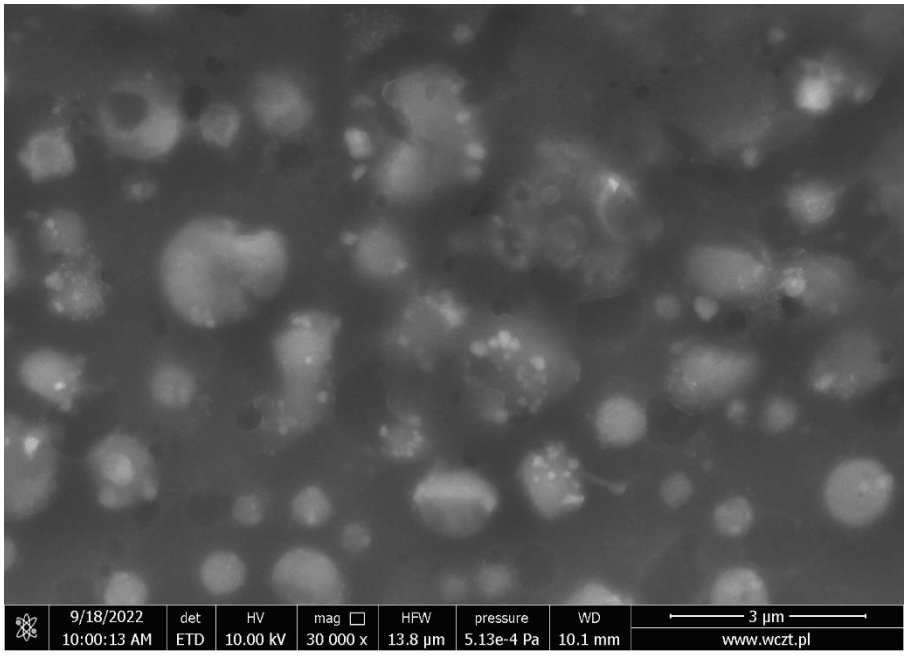
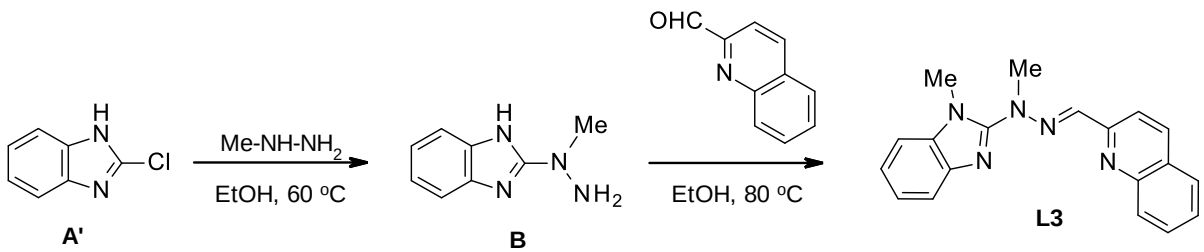


Figure S9. SEM image of a sample from postreaction mixture of phenylacetylene double hydrosilylation using **Co-L1**.

7. Synthesis of hydrazone ligands L3 and L4

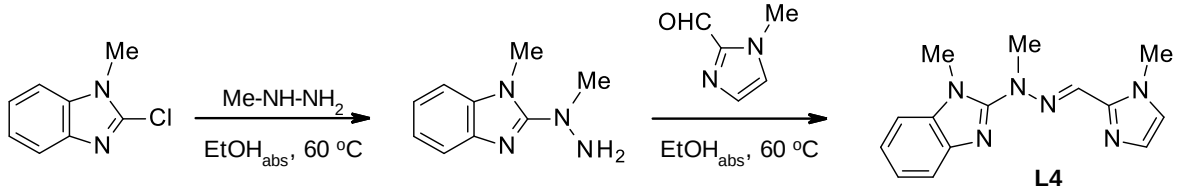
Ligand L3



Ligand **L3** was prepared in two-steps *via* substitution of 2-chloro-1*H*-benzimidazole **A'** with excess of 1-methylhydrazine[4] followed by condensation of obtained arylhydrazine **B** with quinoline-2-carboxaldehyde.

Arylhydrazine **B** (0.80 g, 4.93 mmol) was dissolved in 10 mL of anhydrous EtOH and obtained solution was added to the round-bottom flask with a magnetic stirring bar which was previously evacuated and filled with argon. While stirring the quinoline-2-carboxaldehyde (0.78 g, 4.97 mmol) was added and the reaction was continued for 2 h at 80˚C. Next, the reaction mixture was cooled to room temperature and concentrated under vacuum. The mixture was left in the freezer until the precipitate appeared. The resulting precipitate of ligand **L3** was filtered on a Büchner funnel, washed with EtOH (2x5 mL) and dried under vacuum (1.12 g, yield = 75%).
^{1}H NMR ($(CD_3)_2SO$, 600 MHz): δ 12.08 (s, 1H), 8.54 (d, *J* = 8.5 Hz, 1H), 8.41 (d, *J* = 8.7 Hz, 1H), 8.02 – 7.97 (m, 2H), 7.95 (s, 1H), 7.77 (ddd, *J* = 8.2, 6.7, 1.5 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.42 – 7.33 (m, 2H), 7.10 – 7.03 (m, 2H), 3.72 (s separating into two s, 3H); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ 154.7, 153.6, 147.6, 142.6, 137.3, 136.8, 134.3, 130.4, 128.7, 128.3, 127.8, 127.1, 121.3, 120.8, 118.6, 116.8, 110.3, 32.2; **IR** (cm^{-1}): 3418 (N-H); 3062 (C-H); 2899 (N-CH_3), 2848; 1513 (C=C), 1504, 1483; 1385 (C-N), 1362; 1142 (C-H), 1122, 1069, 1055; 798 (C-H), 786; **ESI-MS**(+) *m*/*z* (%): 302 (100) [*M*+H]$^+$; **Elemental analysis**, calc. for $C_{18}H_{15}N_5$: C, 71.74; H, 5.02; N, 23.24; found: C, 72.15; H, 5.10; N, 23.13%.

Ligand L4

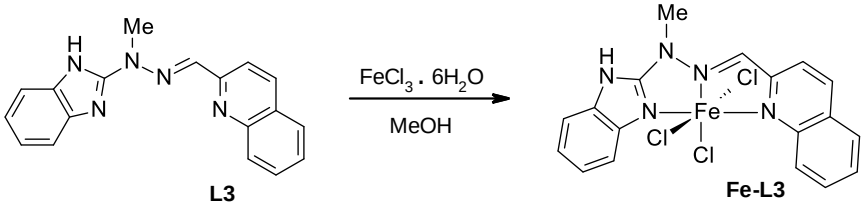


Ligand **L4** was prepared in two-steps, *via* substitution of 2-chloro-1-methyl-1*H*-benzimidazole **A** with excess of 1-methylhydrazine followed by condensation of the obtained arylhydrazine **C** with 1-methyl-2-imidazolecarboxaldehyde.

A 100 mL two-necked flask with a magnetic stirring bar was evacuated and backfilled with argon (three cycles). Substrate 2-chloro-1-methyl-1*H*-benzimidazole (300 mg, 1.80 mmol) and 8 ml of anhydrous EtOH was added to the flask. The mixture was stirred and heated at 60˚C. Next, the fivefold surplus of 1-methylhydrazine (0.47 mL, 8.93 mmol) was added dropwise to the mixture. After 24 h heating was removed and reaction mixture was allowed to cool down to ambient temperature. Next, the reaction mixture was concentrated and the product was extracted into the dichloromethane (3x100 mL). Organic layers were combined, washed with brine and dried with anhydrous Na_2SO_4. After filtration, the organic solvent was evaporated *in vacuo*. The product was subjected to further purification by flash column chromatography on alumina with dichloromethane:methanol (9:1 v:v) solvent system to obtain the anticipated product (268 mg, 1.52 mmol, yield = 85%).
Intermediate hydrazine derivative **C** (86.3 mg, 0.49 mmol) was dissolved in 4 mL of an anhydrous EtOH in the protective atmosphere of argon. While stirring the 1-methyl-2-imidazolecarboxaldehyde (53.9 mg, 0.49 mmol) was added. After 24 h at 60˚C, the reaction mixture was cooled to room temperature and concentrated under vacuum. The obtained ligand **L4** was extracted with dichloromethane (3x100 mL), washed with brine and dried over anhydrous Na_2SO_4. Organic solvent was removed *in vacuo* and final product was purified *via* flash column chromatography on alumina with ethyl acetate:hexane (1:1 v:v) solvent system (89.6 mg, yield = 68.2%).
^{1}H NMR ($(CD_3)_2SO$, 600 MHz): δ 7.83 (s separating into two s, 1H), 7.46 – 7.37 (m, 2H), 7.26 (s separating into two s, 1H), 7.16 – 7.11 (m, 2H), 7.01 (d, *J* = 1.1 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.61 (s separating into two s, 3H); **^{13}C{^{1}H} NMR** ($(CD_3)_2SO$, 151 MHz) δ 153.6, 142.3, 140.5, 136.3, 130.2, 128.6, 124.4, 121.6, 120.9, 117.2, 109.3, 34.7, 34.4, 32.4; **IR** (KBr, cm^{-1}): 3056 (C-H); 1490 (C=C); 1417 (C-N); 1317 (C=N), 1289; 1137 (C-H), 1080; 713 (C-H); **ESI-MS**(+) *m*/*z* (%): 269 (100) [*M*+H]$^+$, 291 (30) [*M*+Na]$^+$; **Elemental analysis**, calc. for $C_{14}H_{16}N_6$: C, 62.67; H, 6.01; N, 31.32; found: C, 62.15; H, 6.10; N, 31.13%.

8. Synthesis of precatalysts

Complex **Fe-L3** [Fe(**L3**)Cl_3]:

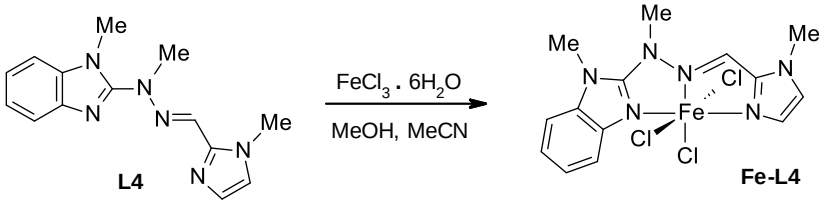


L3 **Fe-L3**

Ligand **L3** (40.0 mg, 0.13 mmol) and $FeCl_3 \cdot 6H_2O$ (35.9 mg, 0.133 mmol) were dissolved in 15 mL CH_3OH. The reaction mixture was magnetically stirred for 24h at room temperature to give a brown solution. The reaction mixture was concentrated and Et_2O was added. The precipitate was obtained, filtered *via* suction filtration, washed with Et_2O (2x5 mL) and dried under vacuum (46.4 mg, yield = 88.9%).

IR (KBr cm^{-1}): 3617 (N-H), 3421; 3041 (C-H); 1614 (C=C), 1596, 1548; 1474 (C-N), 1461; 1143 (C-H), 1056; 788 (C-H), 764; **ESI-MS**(+) *m/z* (%): 303 (100) [**L3**+H]$^+$, 427 (20) [Fe(**L3**)Cl_2]$^+$; **Elemental analysis**, calc. for [Fe($C_{18}H_{15}N_5$)Cl_3]: C, 46.64; H, 3.26; N, 15.11; found: C, 46.88; H, 3.32; N, 15.23%.

Complex **Fe-L4** [Fe(**L4**)Cl_3]:

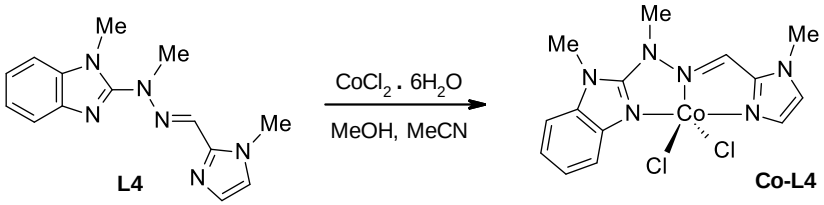


L4 **Fe-L4**

Ligand **L4** (26.8 mg, 0.10 mmol) and $FeCl_3 \cdot 6H_2O$ (27.3 mg, 0.10 mmol) were dissolved in 15 mL of CH_3OH/CH_3CN mixture (1:1, v:v). The reaction mixture was stirred for 48 h at room temperature to give dark-green solution. The reaction mixture was concentrated and 10 mL of Et_2O was added. The precipitate was obtained, filtered, washed with Et_2O (2x5 mL) and dried under vacuum (42.3 mg, yield = 98.2%).

IR (KBr, cm^{-1}): 3164 (C-H), 3013; 2898 (CH_3); 1612 (C=C), 1533, 1496; 1475 (C-N), 1411; 1281 (C=N); 1166 (C-H), 1131; 993 (C-H), 871, 829, 735; **ESI-MS**(+) *m/z* (%): 269 (100) [**L4**+H]+, 359 (30) [Fe(**L4**)Cl]$^+$; **Elemental analysis**, calc. for [Fe($C_{14}H_{16}N_6$)Cl_3]: C, 39.06; H, 3.75; N, 19.52; found: C, 38.98; H, 3.68; N, 19.63%.

Complex Co-**L4** [Co(**L4**)Cl_2]:

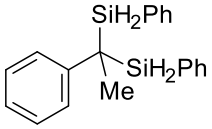


L4 **Co-L4**

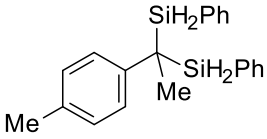
Ligand **L4** (30.0 mg, 0.11 mmol) and $CoCl_2 \cdot 6H_2O$ (26.6 mg, 0.11 mmol) were dissolved in 15 mL of CH_3OH/CH_3CN mixture (1:1, v:v). The reaction mixture was magnetically stirred for 48h at room temperature to give green solution. The reaction mixture was concentrated and Et_2O was added. The precipitate was obtained, filtered *via* suction filtration and washed with Et_2O (2x5 mL) and dried under vacuum (38.7 mg, yield = 88.4%).

IR (KBr, cm^{-1}): 3106 (C-H), 3027; 2769 (CH_3); 1619 (C=C), 1533, 1490; 1454 (C-N), 1425; 1281 (C=N); 1188 (C-H), 1109; 999 (C-H), 965, 821, 756; **ESI-MS**(+) *m/z* (%): 362 (100) [Co(**L4**)Cl]$^+$; **Elemental analysis**, calc. for [Co($C_{14}H_{16}N_6$)Cl_2]: C, 42.23; H, 4.05; N, 21.11; found: C, 42.38; H, 3.98; N, 21.06%.

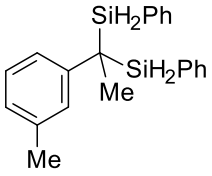
9. Synthesis of geminal bis(silanes)



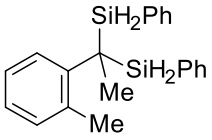
(1-Phenylethane-1,1-diyl)bis(phenylsilane) (3a) was synthesized according to *Method A* and obtained as colourless oil (91 mg, yield = 58%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H, Ar-*H*), 7.35 – 7.26 (m, 10H, Ar-*H*), 7.25 – 7.20 (m, 2H, Ar-*H*), 7.19 – 7.12 (m, 1H, Ar-*H*), 4.67 (d, $^{2}J_{HH}$ = 6.7 Hz, 2H, 2xSiH*H*), 4.56 (d, $^{2}J_{HH}$ = 6.7 Hz, 2H, 2xSiH*H*), 1.54 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 143.5, 136.3, 130.5, 130.0, 128.6, 127.8, 126.8, 124.4, 17.4, 17.3; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –20.19; **HRMS** (ESI) *m*/*z*: calc. for $C_{20}H_{22}NaSi_2^+$ ([*M*+Na]$^+$): 341.1153, found: 341.1154.



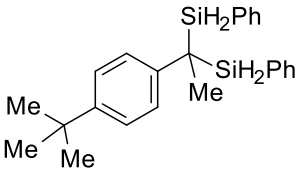
(1-(4-Methylphenyl)ethane-1,1-diyl)bis(phenylsilane) (3b) was synthesized according to *Method A* and obtained as colourless oil (109 mg, yield = 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H, Ar-*H*), 7.36 – 7.32 (m, 4H, Ar-*H*), 7.32 – 7.26 (m, 4H, Ar-*H*), 7.15 – 7.09 (m, 4H, Ar-*H*), 4.63 (d, $^{2}J_{HH}$ = 6.7 Hz, 2H, 2xSiH*H*), 4.53 (d, $^{2}J_{HH}$ = 6.7 Hz, 2H, 2xSiH*H*), 2.36 (s, 3H, ArCH_3), 1.52 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 140.3, 136.3, 133.8, 130.8, 130.7, 129.9, 129.3, 127.8, 126.7, 21.0, 17.4, 16.7; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –20.30; **HRMS** (ESI) *m*/*z*: calc. for $C_{21}H_{24}NaSi_2^+$ ([*M*+Na]$^+$): 355.1309, found: 355.1314.



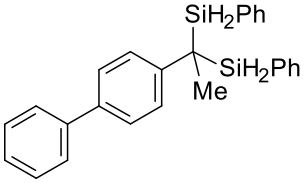
(1-(3-Methylphenyl)ethane-1,1-diyl)bis(phenylsilane) (3c) was synthesized according to *Method A* and obtained as colourless oil (89 mg, yield = 54%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H, Ar-*H*), 7.36 – 7.26 (m, 8H, Ar-*H*), 7.22 – 7.16 (m, 1H, Ar-*H*), 7.06 – 7.00 (m, 2H, Ar-*H*), 6.99 – 6.95 (m, 1H, Ar-*H*), 4.65 (d, $^{2}J_{HH}$ = 6.8 Hz, 2H, 2xSiH*H*), 4.54 (d, $^{2}J_{HH}$ = 6.8 Hz, 2H, 2xSiH*H*), 2.32 (s, 3H, ArCH_3), 1.53 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 143.4, 137.9, 136.3, 130.7, 129.9, 128.4, 127.8, 127.6, 125.2, 123.8, 21.8, 17.4, 17.1; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –20.19; **HRMS** (ESI) *m*/*z*: calc. for $C_{21}H_{24}NaSi_2^+$ ([*M*+Na]$^+$): 355.1309, found: 355.1325.



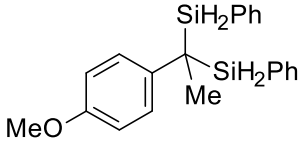
(1-(2-Methylphenyl)ethane-1,1-diyl)bis(phenylsilane) (3d) was synthesized according to *Method A* and obtained as colourless oil (66 mg, yield = 40%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H, Ar-*H*), 7.35 – 7.31 (m, 4H, Ar-*H*), 7.30 – 7.25 (m, 4H, Ar-*H*), 7.18 – 7.14 (m, 1H, Ar-*H*), 7.13 – 7.06 (m, 3H, Ar-*H*), 4.76 (d, $^{2}J_{HH}$ = 6.8 Hz, 2H, 2xSiH*H*), 4.61 (d, $^{2}J_{HH}$ = 6.8 Hz, 2H, 2xSiH*H*), 2.61 (s, 3H, ArCH_3), 1.68 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 141.9, 136.1, 132.1, 131.2, 129.9, 127.9, 126.9, 126.3, 125.0, 23.8, 22.1, 16.3; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –22.43; **HRMS** (ESI) *m*/*z*: calc. for $C_{21}H_{24}NaSi_2^+$ ([*M*+Na]$^+$): 355.1309, found: 355.1317.



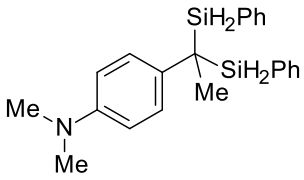
(1-(4-*tert*-butylethylphenyl)ethane-1,1-diyl)bis(phenylsilane) (3e) was synthesized according to *Method A* and obtained as colourless oil (116 mg, yield = 62%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H, Ar-*H*), 7.27 – 7.26 (m, 2H, Ar-*H*), 7.26 – 7.24 (m, 4H, Ar-*H*), 7.24 – 7.20 (m, 4H, Ar-*H*), 7.12 – 7.09 (m, 2H, Ar-*H*), 4.58 (d separating into two d, $^{2}J_{HH}$ = 6.7 Hz, 2H, 2xSiH*H*), 4.50 (d, $^{2}J_{HH}$ = 6.7 Hz, 2H, 2xSiH*H*), 1.47 (s, 3H, C(SiH_2Ph)$_2$CH_3), 1.31 (s, 9H, C(CH_3)$_3$); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 147.3, 140.2, 136.3, 130.8, 129.9, 127.8, 126.4, 125.4, 34.4, 31.6, 17.4, 16.6; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –20.54. **HRMS** (ESI) *m*/*z*: calc. for $C_{24}H_{30}NaSi_2^+$ ([*M*+Na]$^+$): 397.1778, found: 397.1786.



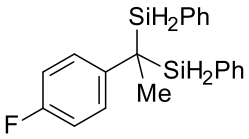
(1-([1,1'-biphenyl]-4-yl)ethane-1,1-diyl)bis(phenylsilane) (3f) was synthesized according to *Method B* and obtained as colourless oil that solidified overtime (86 mg, yield = 44%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 2H, Ar-*H*), 7.60 – 7.55 (m, 2H, Ar-*H*), 7.51 – 7.46 (m, 2H, Ar-*H*), 7.43 – 7.35 (m, 7H, Ar-*H*), 7.33 – 7.27 (m, 6H, Ar-*H*), 4.71 (d, $^{2}J_{HH}$ = 6.7 Hz, 2H, 2xSiH*H*), 4.59 (d, $^{2}J_{HH}$ = 6.7 Hz, 2H, 2xSiH*H*), 1.58 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 142.9, 140.9, 137.0, 136.3, 130.5, 128.9, 127.9, 127.2, 127.1, 126.9, 17.4, 17.3; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –20.23; **HRMS** (ESI) *m*/*z*: calc. for $C_{26}H_{26}NaSi_2^+$ ([*M*+Na]$^+$): 417.1465, found: 417.1479.



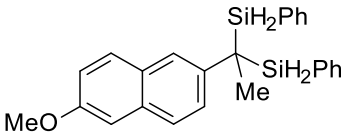
(1-(4-Metoxyphenyl)ethane-1,1-diyl)bis(phenylsilane) (3g) was synthesized according to *Method A* and obtained as colourless oil (112 mg, yield = 67%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H, Ar-*H*), 7.36 – 7.26 (m, 8H, Ar-*H*), 7.17 – 7.11 (m, 2H, Ar-*H*), 6.89 – 6.83 (m, 2H, Ar-*H*), 4.64 (d, $^{2}J_{HH}$ = 6.7 Hz, 2H, 2xSiH*H*), 4.53 (d, $^{2}J_{HH}$ = 6.7 Hz, 2H, 2xSiH*H*), 3.83 (s, 3H, OCH_3), 1.51 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 156.8, 136.3, 135.3, 130.6, 129.9, 127.8, 127.7, 111.1, 55.4, 17.6, 16.1; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –20.50; **HRMS** (ESI) *m*/*z*: calc. for $C_{21}H_{24}NaOSi_2^+$ ([*M*+Na]$^+$): 371.1258, found: 355.1258.



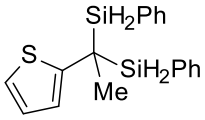
(1-(4-[Dimethylamino]phenyl)ethane-1,1-diyl)bis(phenylsilane) (3h) was synthesized according to *Method B* and obtained as colourless oil (58 mg, yield = 32%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 6H, Ar-*H*), 7.31 – 7.25 (m, 4H, Ar-*H*), 7.11 (appd, 2H, $^{3}J_{HH}$ = 8.8 Hz, Ar-*H*), 6.73 (appd, 2H, $^{3}J_{HH}$ = 8.8 Hz, Ar-*H*), 4.60 (d, $^{2}J_{HH}$ = 6.6 Hz, 2H, 2xSiH*H*), 4.51 (d, $^{2}J_{HH}$ = 6.6 Hz, 2H, 2xSiH*H*), 2.96 (s, 6H, N(CH_3)$_2$), 1.50 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 148.0, 136.3, 131.2, 131.1, 129.8, 127.8, 127.4, 113.4, 41.0, 17.5, 15.5; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –20.91; **HRMS** (ESI) *m*/*z*: calc. for $C_{22}H_{28}Si_2^+$ ([*M*+H]$^+$): 362.1755, found: 362.1764.



(1-(4-Fluorophenyl)ethane-1,1-diyl)bis(phenylsilane) (3i) was synthesized according to *Method A* and obtained as colourless oil (96 mg, yield = 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H, Ar-*H*), 7.33 – 7.26 (m, 8H, Ar-*H*), 7.17 – 7.12 (m, 2H, Ar-*H*), 7.02 – 6.96 (m, 2H, Ar-*H*), 4.65 (d, $^{2}J_{HH}$ = 6.7 Hz, 2H, 2xSiH*H*), 4.53 (d, $^{2}J_{HH}$ = 6.7 Hz, 2H, 2xSiH*H*), 1.52 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 160.4 (d, $^{1}J_{CF}$ = 244.1 Hz), 139.1 (d, $^{4}J_{CF}$ = 3.1 Hz), 130.2, 130.1, 128.1 (d, $^{3}J_{CF}$ = 7.6 Hz, ^{Ar}C), 127.9, 115.3 (d, $^{2}J_{CF}$ = 21.2 Hz), 17.7, 16.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ – 119.43 (m); **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –20.03 (d, $^{6}J_{SiF}$ = 1.6 Hz); **HRMS** (ESI) *m*/*z*: calc. for $C_{20}H_{21}FNaSi_2^+$ ([*M*+Na]$^+$): 359.1058, found: 359.1073.

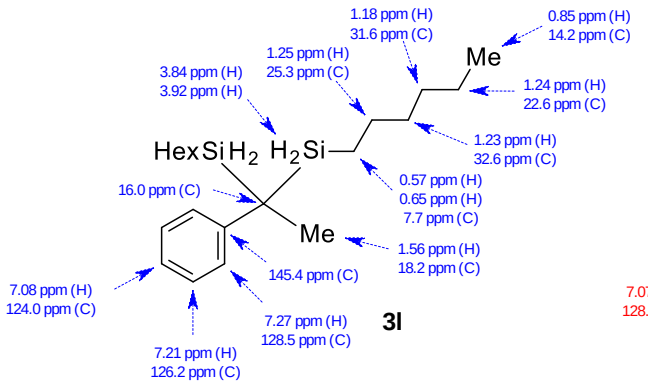


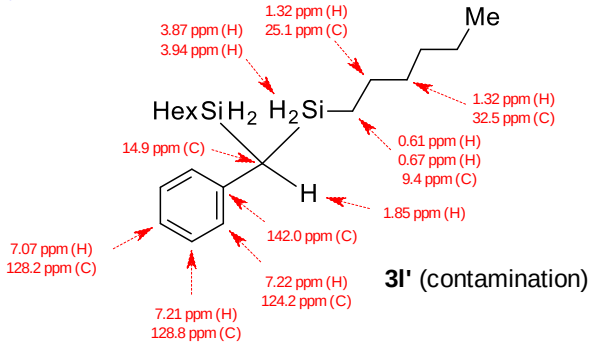
(1-(6-Methoxynaphth-2-yl)ethane-1,1-diyl)bis(phenylsilane) (3j) was synthesized according to *Method B* and obtained as colourless oil that solidified overtime (132 mg, yield = 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.77 (m, 1H, Ar-*H*), 7.64 – 7.60 (m, 1H, Ar-*H*), 7.51 – 7.47 (m, 1H, Ar-*H*), 7.47 – 7.40 (m, 2H, Ar-*H*), 7.39 – 7.34 (m, 2H, Ar-*H*), 7.33 – 7.28 (m, 4H, Ar-*H*), 7.26 – 7.22 (m, 3H, Ar-*H*), 7.16 – 7.12 (m, 2H, Ar-*H*), 4.72 (d, $^{2}J_{HH}$ = 6.6 Hz, 2H, 2xSiH*H*), 4.59 (d, $^{2}J_{HH}$ = 6.6 Hz, 2H, 2xSiH*H*), 3.96 (s, 3H, OCH_3),1.64 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 157.2, 138.8, 136.3, 132.0, 130.5, 130.0, 129.5, 129.2, 127.9, 126.9, 126.8, 124.2, 118.8, 105.6, 55.4, 17.6, 17.5; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –20.66; **HRMS** (ESI) *m*/*z*: calc. for $C_{25}H_{26}NaOSi_2^+$ ([*M*+Na]$^+$): 421.1414, found: 421.1424.



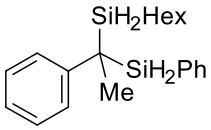
(1-(2-Thienyl)ethane-1,1-diyl)bis(phenylsilane) (3k) was synthesized according to *Method A* and obtained as colourless oil (54 mg, yield = 37%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 6H, Ar-*H*), 7.34 – 7.28 (m, 4H, Ar-*H*), 7.10 – 7.07 (m, 1H, Ar^S-*H*), 7.00 – 6.96 (m, 1H, Ar^S-*H*), 6.75 – 6.70 (m, 1H, Ar^S-*H*), 4.63 (d, $^{2}J_{HH}$ = 7.0 Hz, 2H, 2xSiH*H*), 4.55 (d, $^{2}J_{HH}$ = 7.0 Hz, 2H, 2xSiH*H*), 1.58 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 149.5, 136.3, 130.2, 130.1, 127.9, 127.3, 122.5, 121.8, 19.5, 15.8; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –20.40; **HRMS** (ESI) *m*/*z*: calc. for $C_{18}H_{21}SSi_2^+$ ([*M*+H]$^+$): 325.0897, found: 325.0897.

(1-Phenylethane-1,1-diyl)bis(hexylsilane) (3l)

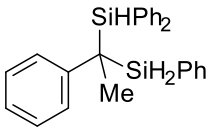




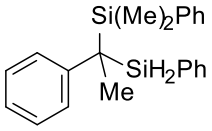
3l was synthesized according to *Method A* and obtained as colourless oil (62 mg, yield = 28% - due to contamination, please see Figure S10 below). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H, Ar-*H*), 7.25 – 7.18 (m, 2H, Ar-*H*), 7.10 – 7.05 (m, 2H, Ar-*H*), 3.95 – 3.90 (m, 2H, 2xSiH*H*), 3.86 – 3.83 (m, 2H, 2xSiH*H*), 1.84 (tt, $^{3}J_{HH}$ = 5.0 Hz, $^{3}J_{HH}$ = 3.2 Hz, 0.25 H, PhC*H*(SiH$_2$Hex)$_2$ – contam.), 1.56 (s, 3H, C(SiH$_2$Hex)$_2$CH_3), 1.35 – 1.16 (m, 16H, 2x(CH_2)$_4$), 0.85 (t, $^{3}J_{HH}$ = 7.0 Hz, 6H, 2xCH$_2$CH_3), 0.72 – 0.55 (m, 4H, 2xSiH$_2$CH_2); **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$) δ 145.4, 142.0 (contam.), 128.8 (contam.), 128.5, 128.2 (contam.), 126.2, 124.2 (contam.), 124.0, 32.6, 32.5 (contam.) 31.6, 25.3, 25.1 (contam.) 22.6, 18.2, 16.0, 14.9 (contam.), 14.2, 9.4 (contam.), 7.7; **^{29}Si{^{1}H} NMR** (119 MHz, $CDCl_3$) δ –16.51, –25.27 (contam.); **HRMS** (ESI) *m*/*z*: calc. for $C_{20}H_{38}NaSi_2^+$ ([*M*+Na]$^+$): 357.2404, found: 357.2420; calc. for $C_{19}H_{36}NaSi_2^+$ (contam., [*M*+Na]$^+$): 343.2248, found: 343.2255.



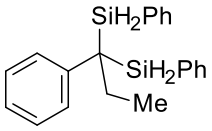
1-(hexylsilyl)-1-phenyl-1-(phenylsilyl)ethane (9a) was synthesized according to *Method C* and obtained as colourless oil (33 mg, yield = 20%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 1H, Ar-*H*), 7.35 – 7.30 (m, 2H, Ar-*H*), 7.30 – 7.24 (m, 4H, Ar-*H*), 7.24 – 7.20 (m, 2H, Ar-*H*), 7.15 – 7.09 (m, 1H, Ar-*H*), 4.56 (d, $^{2}J_{HH}$ = 6.7 Hz, 1H, SiH*H*Ph), 4.50 (d, $^{2}J_{HH}$ = 6.7 Hz, 1H, SiH*H*Ph), 4.01 (m, 1H, SiH*H*Hex), 3.90 (m, 1H, SiH*H*Hex), 1.55 (s, 3H, CH_3), 1.34 – 1.13 (m, 8H, (CH_2)$_4$), 0.87 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, CH$_2$CH_3), 0.69 – 0.52 (m, 2H, SiH$_2$CH_2); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 144.5, 136.2, 130.9, 129.9, 128.6, 127.8, 126.5, 124.2, 32.6, 31.6, 25.3, 22.6, 17.7, 16.7, 14.2, 7.5; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –17.40, –19.23; **HRMS** (ESI) *m*/*z*: calc. for $C_{20}H_{30}NaSi_2^+$ ([*M*+Na]$^+$): 349.1778, found: 349.1783.



1-(diphenylsilyl)-1-phenyl-1-(phenylsilyl)ethane (9b) was synthesized according to *Method C* and obtained as colourless oil (113 mg, yield = 58%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H, Ar-*H*), 7.48 – 7.41 (m, 1H, Ar-*H*), 7.40 – 7.34 (m, 5H, Ar-*H*), 7.30 – 7.22 (m, 5H, Ar-*H*), 7.20 – 7.16 (m, 4H, Ar-*H*), 7.15 – 7.10 (m, 3H, Ar-*H*), 5.21 (s, 1H, Si*H*Ph_2), 4.67 (d, $^{2}J_{HH}$ = 6.8 Hz, 1H, SiH*H*Ph), 4.46 (d separating into two d, $^{2}J_{HH}$ = 6.8 Hz, 1H, SiH*H*Ph), 1.58 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 143.3, 136.4, 136.3, 136.2, 133.0, 132.9, 130.4, 130.0, 129.8, 129.8, 129.7, 128.4, 128.0, 127.8, 127.7, 127.4, 124.4, 19.2, 16.8; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –8.58, –21.20; **HRMS** (ESI) *m*/*z*: calc. for $C_{26}H_{26}NaSi_2^+$ ([*M*+Na]$^+$): 417.1465, found: 417.1474.



1-(dimethylphenylsilyl)-1-phenyl-1-(phenylsilyl)ethane (9c) was synthesized according to *Method C* and obtained as colourless oil that solidified overtime (124 mg, yield = 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 1H, Ar-*H*), 7.35 – 7.28 (m, 5H, Ar-*H*), 7.26 – 7.18 (m, 6H, Ar-*H*), 7.14 – 7.08 (m, 3H, Ar-*H*), 4.78 (d separating into two d, $^{2}J_{HH}$ = 6.4 Hz, 1H, SiH*H*Ph), 4.49 (d, $^{2}J_{HH}$ = 6.4 Hz, 1H, SiH*H*Ph), 1.46 (s separating into two s, 3H, CCH_3), 0.40 (s, 3H, SiCH_3), 0.38 (s, 3H, SiCH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 144.0, 136.9, 136.2, 135.0, 130.9, 129.6, 129.2, 128.1, 127.7, 127.4, 127.3, 124.0, 19.9, 17.2, –3.7, –4.4; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –0.25, –24.80; **HRMS** (ESI) *m*/*z*: calc. for $C_{22}H_{26}NaSi_2^+$ ([*M*+Na]$^+$): 369.1465, found: 369.1479.



(1-Phenylpropane-1,1-diyl)bis(phenylsilane) (10) A mixture of **Co-L1** (0.9 mg, 2.5 μmol), 1-phenylpropyne (58 mg, 0.5 mmol) and phenylsilane (62 μL,0.5 mmol) in THF (0.5 ml) was prepared in the Schlenk-bomb flask and stirred at ambient temperature for 15 min. Next, a solution of $NaHBEt_3$ in toluene (10 μL, 1 M, 10 μL) was added and the reaction vessel was placed in preheated oil bath (40 °C) to continue stirring for 20 h. After that time the flask was removed from the heating bath and allowed to cool down for 5 min. Next, a solution, prepared 15 min. prior in inert conditions, from **Co-L1** (1.8 mg, 5 μmol), THF (0.5 ml) and $NaHBEt_3$ (35 μL, 1 M in toluene, 35 μmol) was added to the original reaction vessel, followed by addition of phenylsilane (62 μL,0.5 mmol). The flask was subsequently put in preheated oil bath (100 °C) and reaction mixture was stirred for 20 h. After that time heating was removed and the reaction mixture was allowed to cool down to ambient temperature, followed by filtration through silica pad which was washed with a mixture of hexane (2 mL) and ethyl acetate (1 mL). Combined filtrates were evaporated *in vacuo* leaving an oil residue to which a mixture of hexane (2 mL) and ethyl acetate (1 mL) was added. Resulting suspension was filtrated through silica pad, which was washed with a mixture of hexane (6 mL) and ethyl acetate (3 mL). Combined filtrates were evaporated *in vacuo* giving a crude product in a form of an oil, which was further purified by column chromatography on silica (230-240 mesh size) using hexane as eluent. Fractions containing the pure product were combined and volatiles were removed *in vacuo* yielding the desired compound as colourless oil (30 mg, yield = 18%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H, Ar-*H*), 7.36 – 7.32 (m, 4H, Ar-*H*), 7.31 – 7.26 (m, 6H, Ar-*H*), 7.24 – 7.21 (m, 2H, Ar-*H*), 7.18 – 7.13 (m, 1H, Ar-*H*), 4.64 (s, 4H, 2xSiH_2), 2.08 (q, $^{3}J_{HH}$ = 7.4 Hz, 2H, CH_2), 1.11 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, CH_3); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 142.3, 136.4, 130.9, 129.9, 128.5, 127.8, 127.8, 124.5, 24.1, 24.1, 11.6; **^{29}Si{^{1}H} NMR** (79 MHz, $CDCl_3$) δ –22.89; **EI-MS**(+) *m*/*z* (%): 332 (8) [M]$^+$, 225 (22) [M-PhSiH_2]$^+$, ; **Elemental analysis**, calc. for $C_{21}H_{24}Si_2$: C, 75.84; H, 7.27; found: C, 75.42; H, 7.39%.

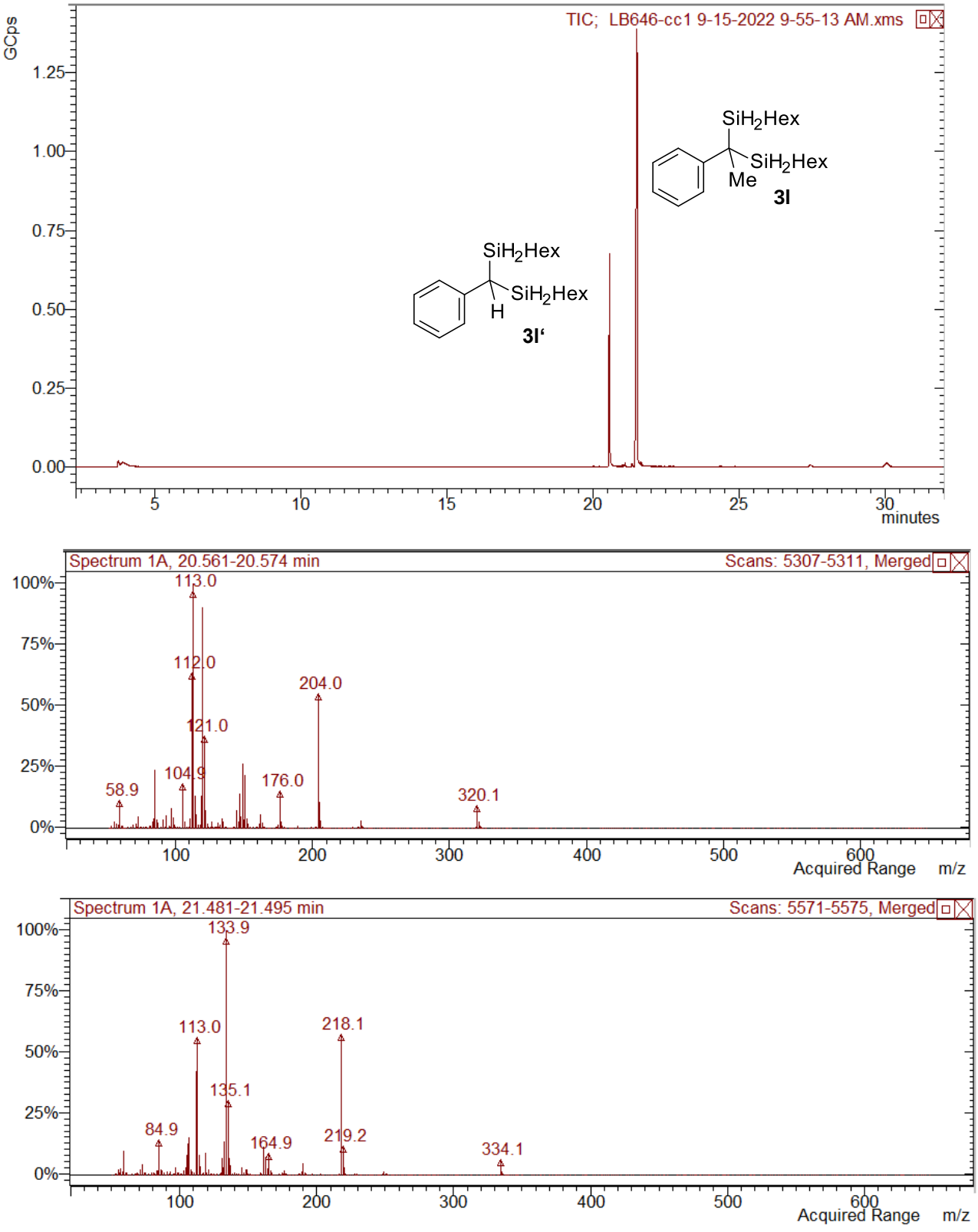
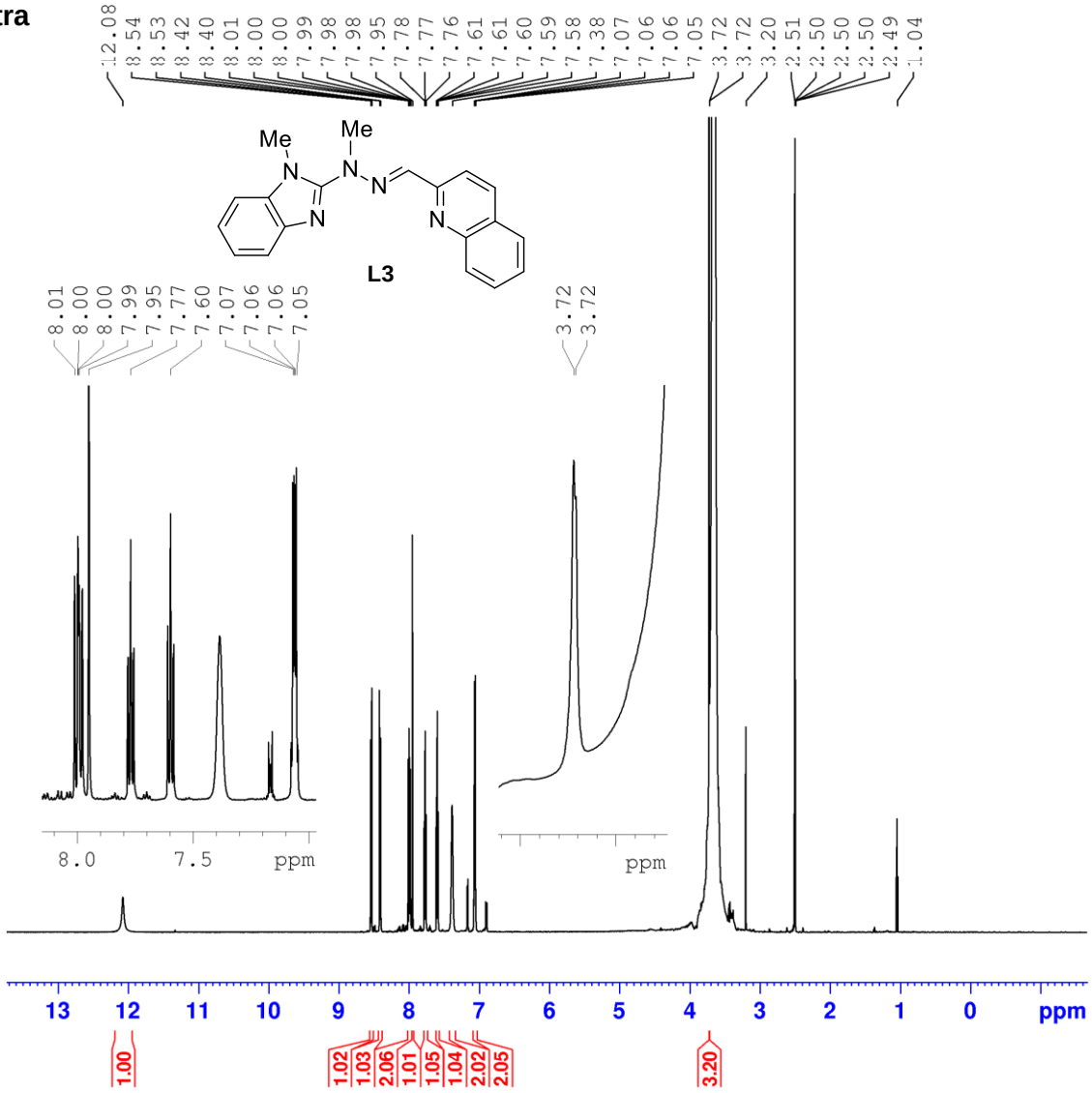


Figure S10. GC-MS data for **3l** product, documenting inseparable contamination **3l‘**.

10. NMR spectra



BRUKER

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DW                42.000 usec
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TE                298.0 K
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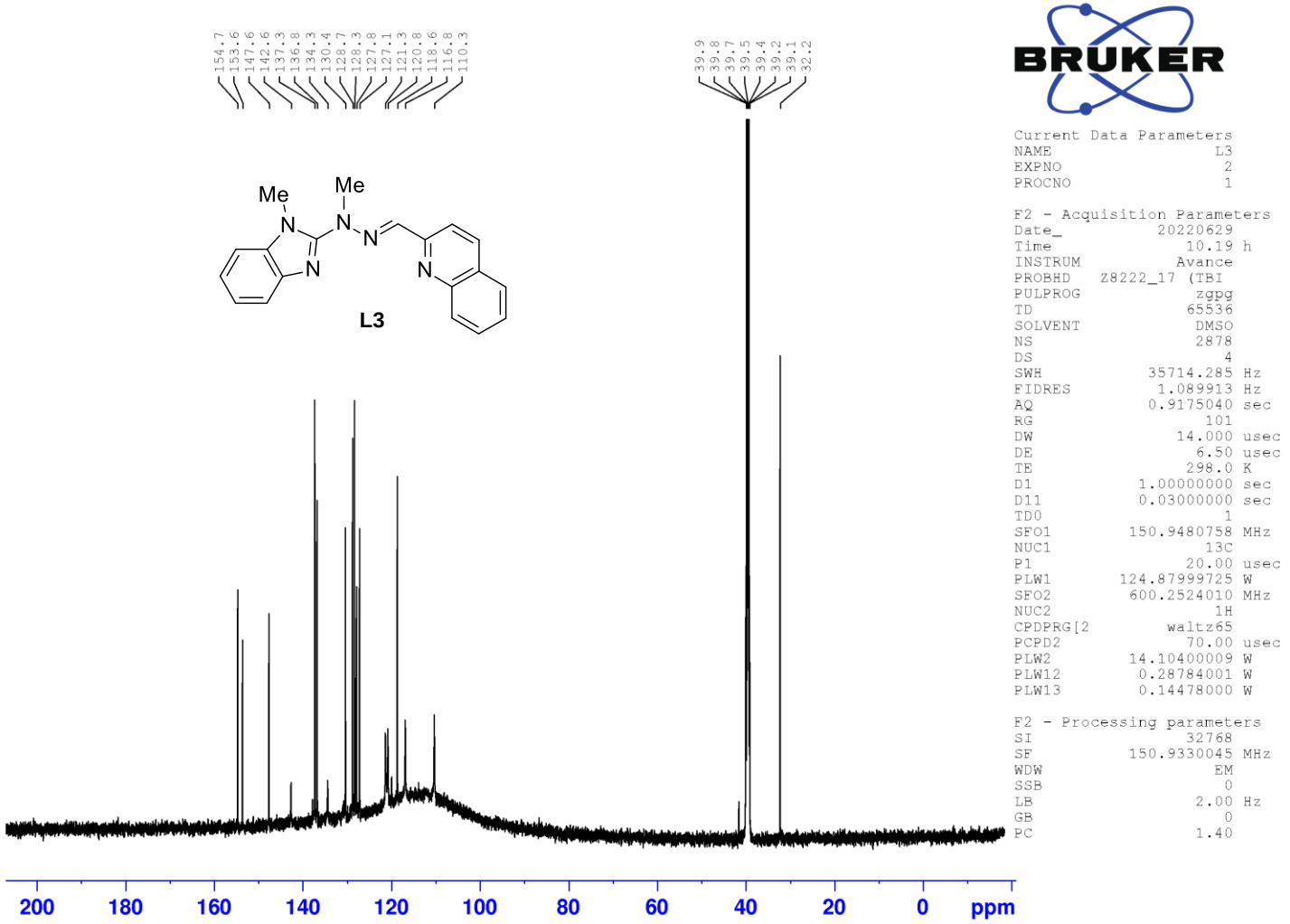

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PROCNO                 1

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NUC2                1H
CPDPRG[2         waltz65
PCPD2             70.00 usec
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PLW13        0.14478000 W

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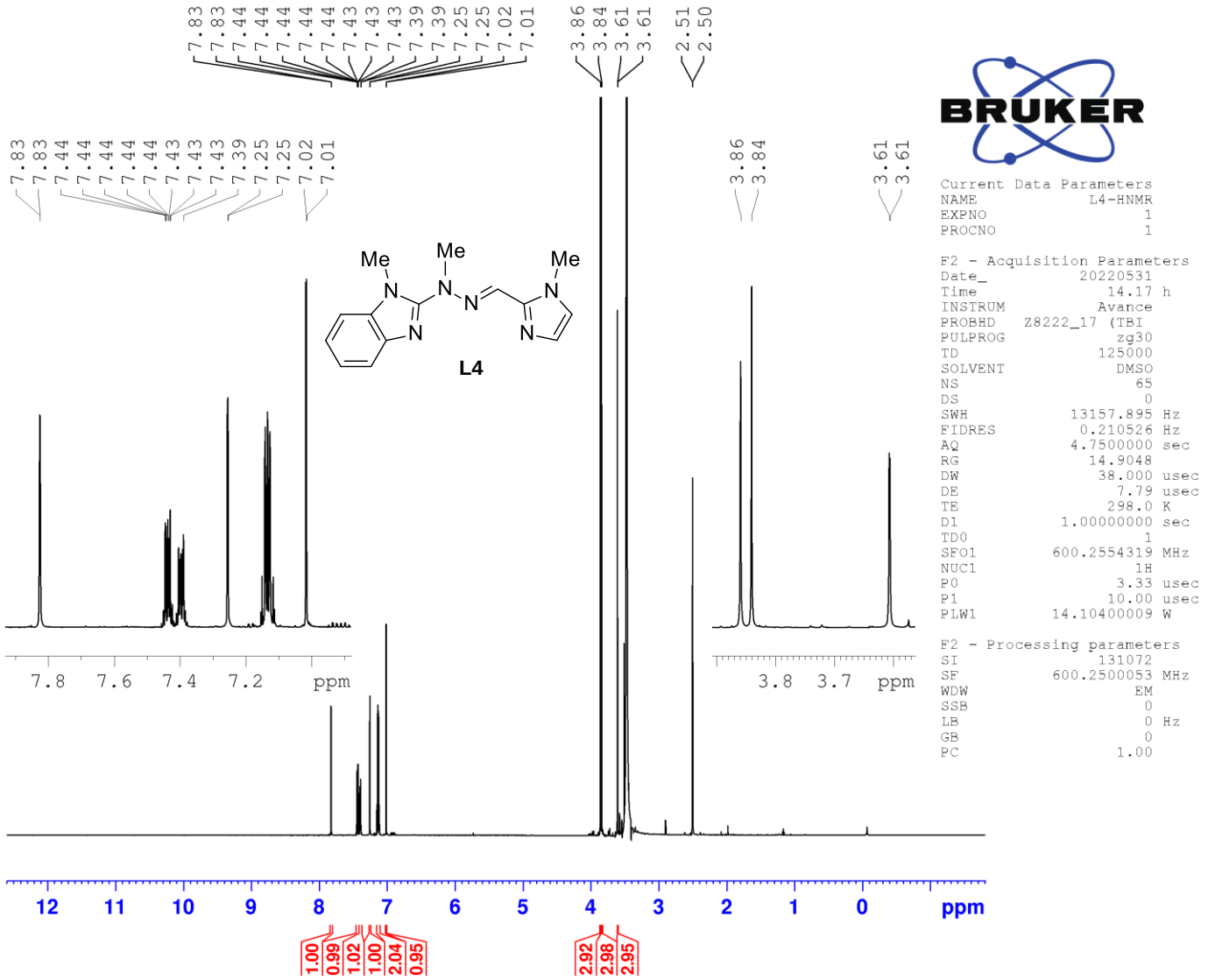

BRUKER

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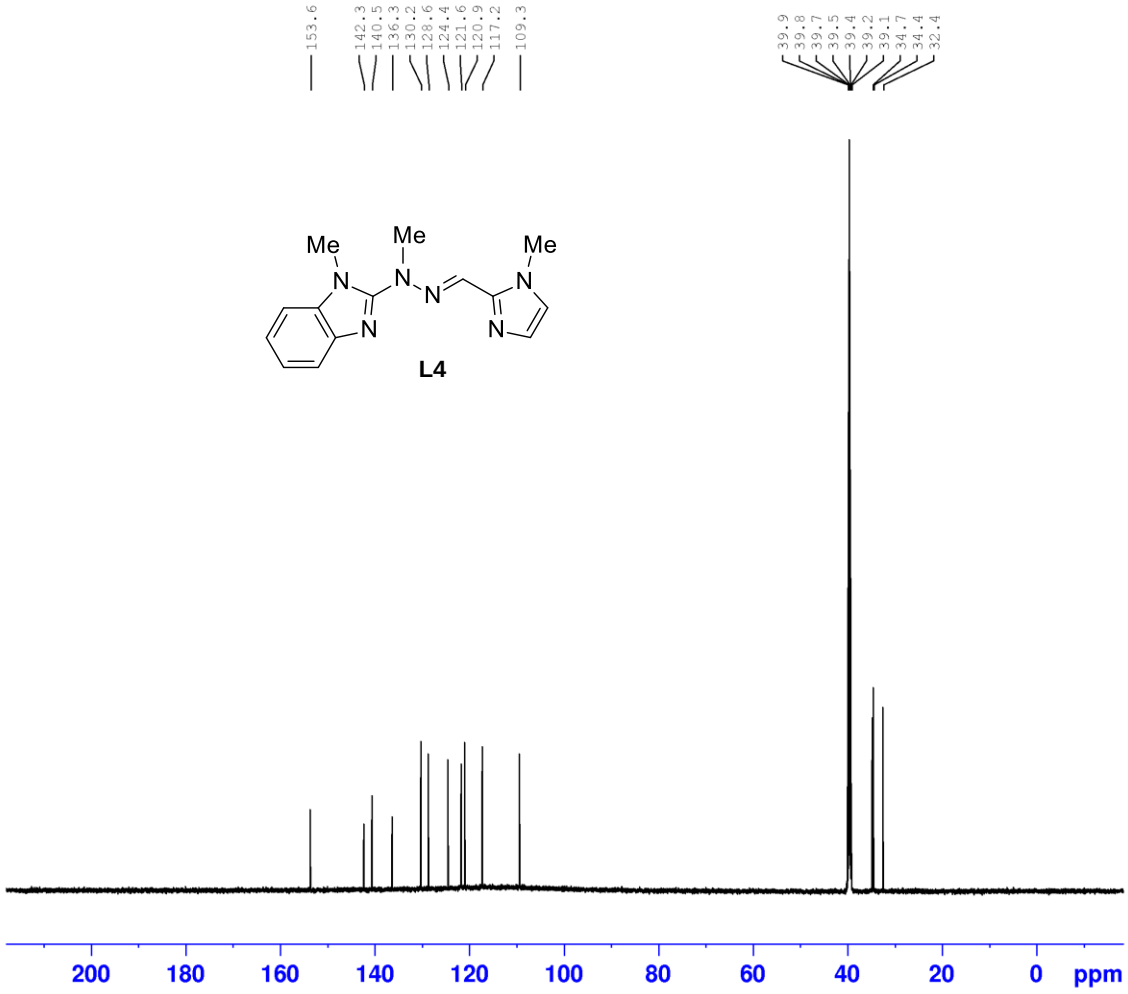

BRUKER

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PROCNO                      1

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NUC2                      1H
CPDPRG[2              waltz65
PCPD2                 70.00 usec
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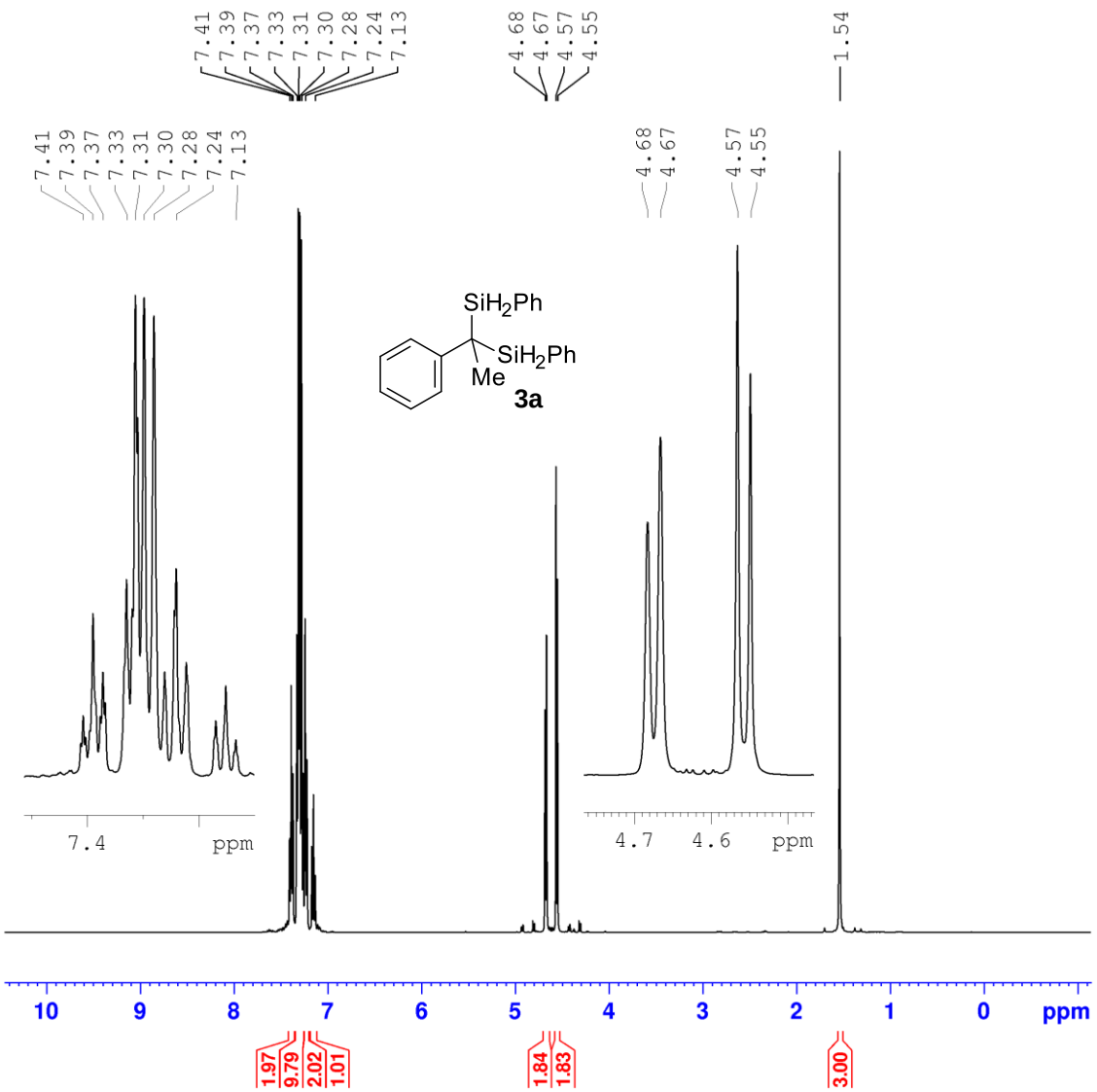


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PROCNO                    1

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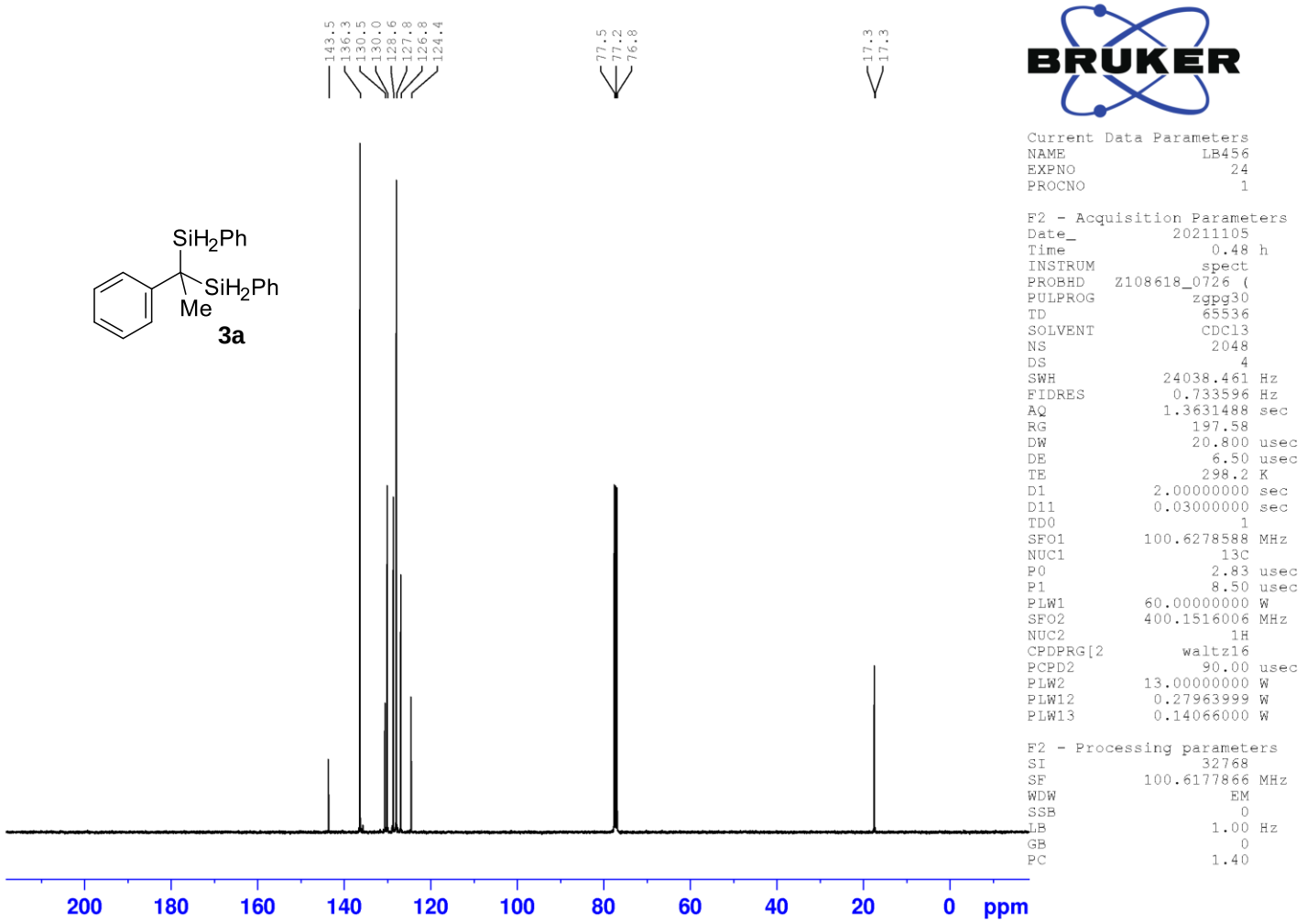


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DS                       4
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AQ               1.3631488 sec
RG                  197.58
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NUC2                   1H
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PLW13           0.14066000 W

F2 - Processing parameters
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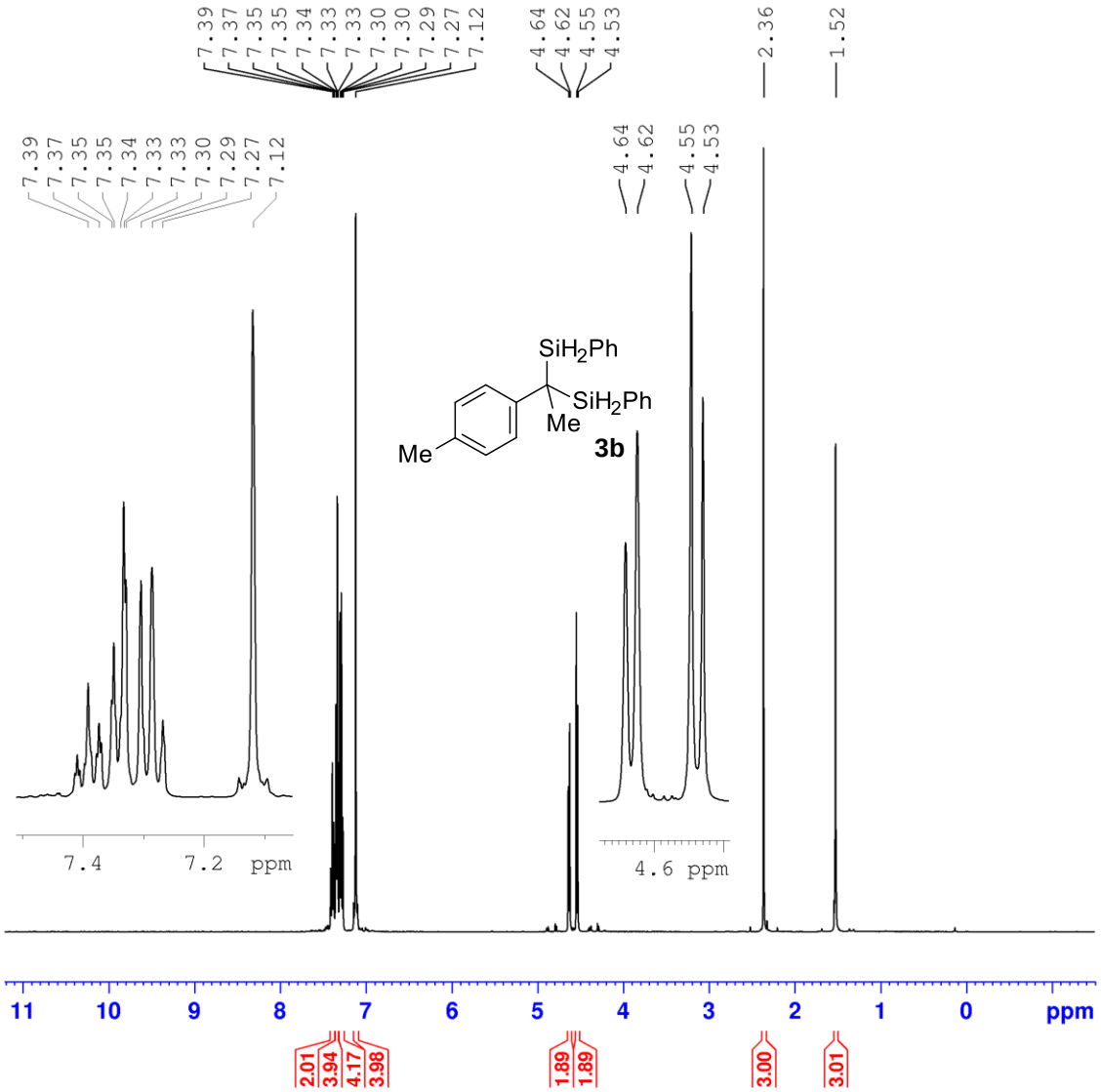
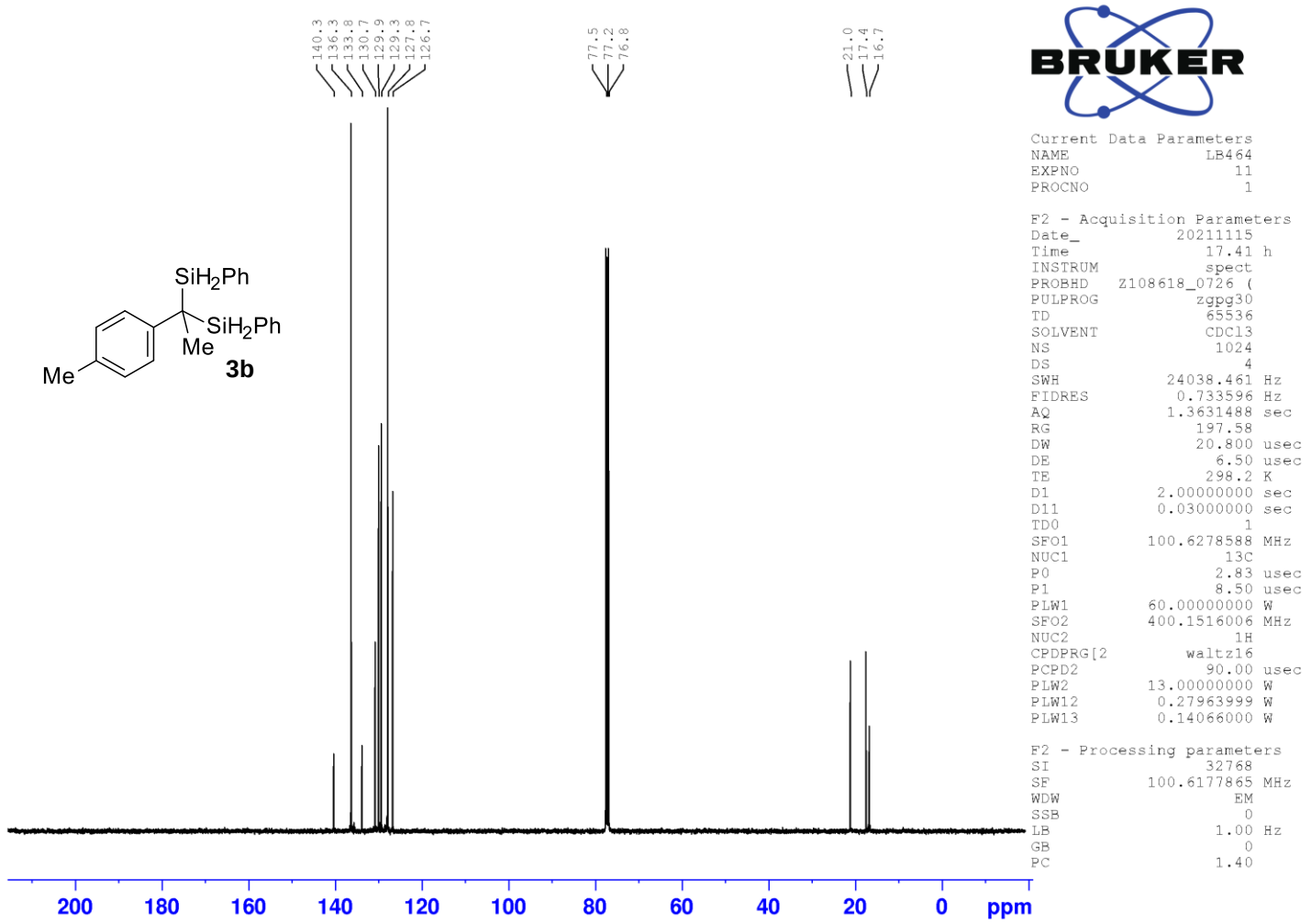
GB                       0
PC                    1.40
```




```
Current Data Parameters
NAME                  LB464
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211115
Time                 16.40 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH               8012.820 Hz
FIDRES               0.244532 Hz
AQ                4.0894465 sec
RG                    88.29
DW                  62.400 usec
DE                   6.50 usec
TE                  298.1 K
D1             1.00000000 sec
TD0                     1
SFO1           400.1524711 MHz
NUC1                   1H
P0                   4.40 usec
P1                  13.20 usec
PLW1           13.00000000 W

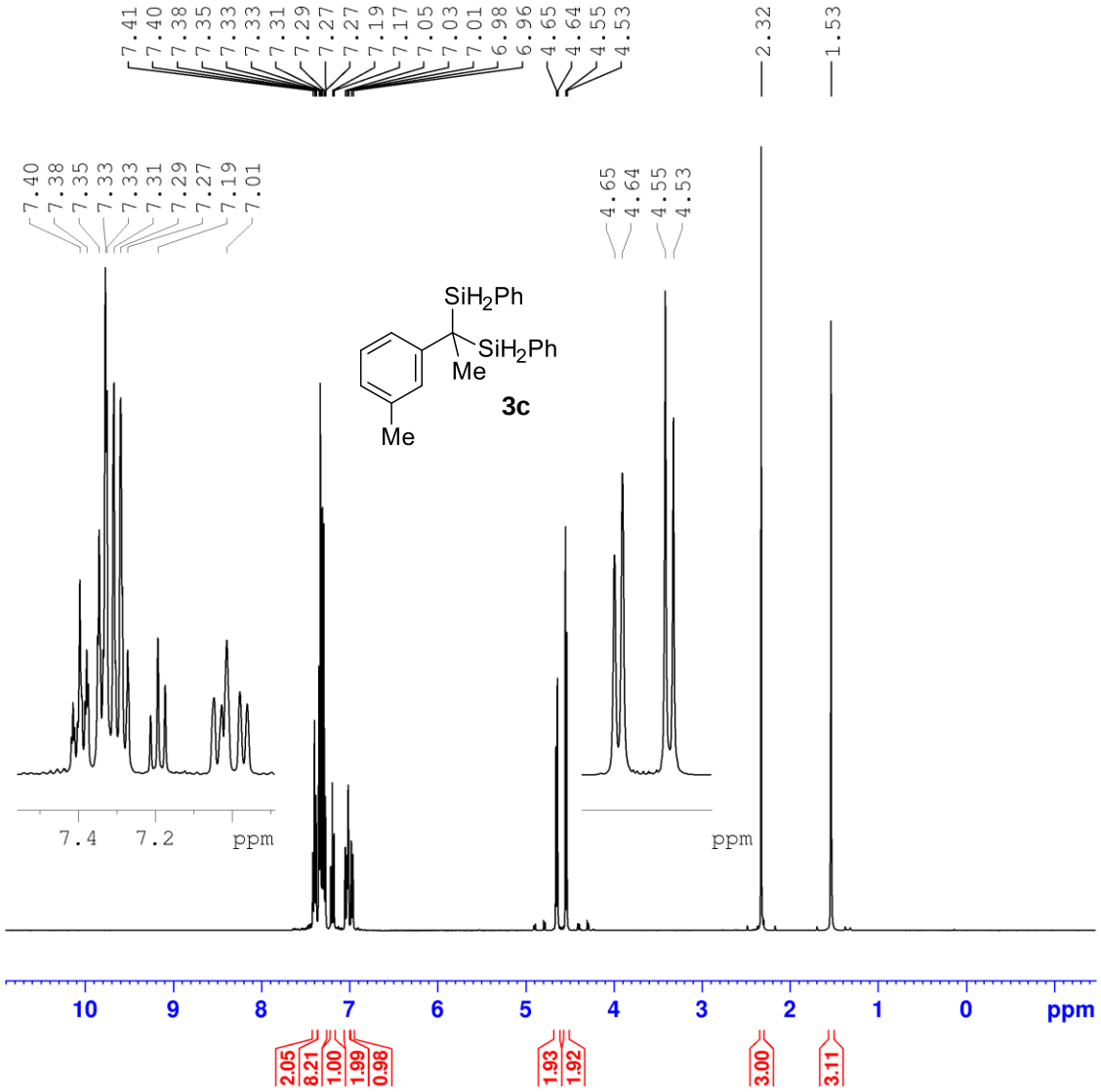
F2 - Processing parameters
SI                  65536
SF             400.1500000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




```
Current Data Parameters
NAME                  LB464
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211115
Time                 17.41 h
INSTRUM                spect
PROBHD    Z108618_0726 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                1.3631488 sec
RG                   197.58
DW                  20.800 usec
DE                   6.50 usec
TE                  298.2 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1
SFO1           100.6278588 MHz
NUC1                   13C
P0                   2.83 usec
P1                   8.50 usec
PLW1           60.00000000 W
SFO2           400.1516006 MHz
NUC2                   1H
CPDPRG[2            waltz16
PCPD2                90.00 usec
PLW2           13.00000000 W
PLW12           0.27963999 W
PLW13           0.14066000 W

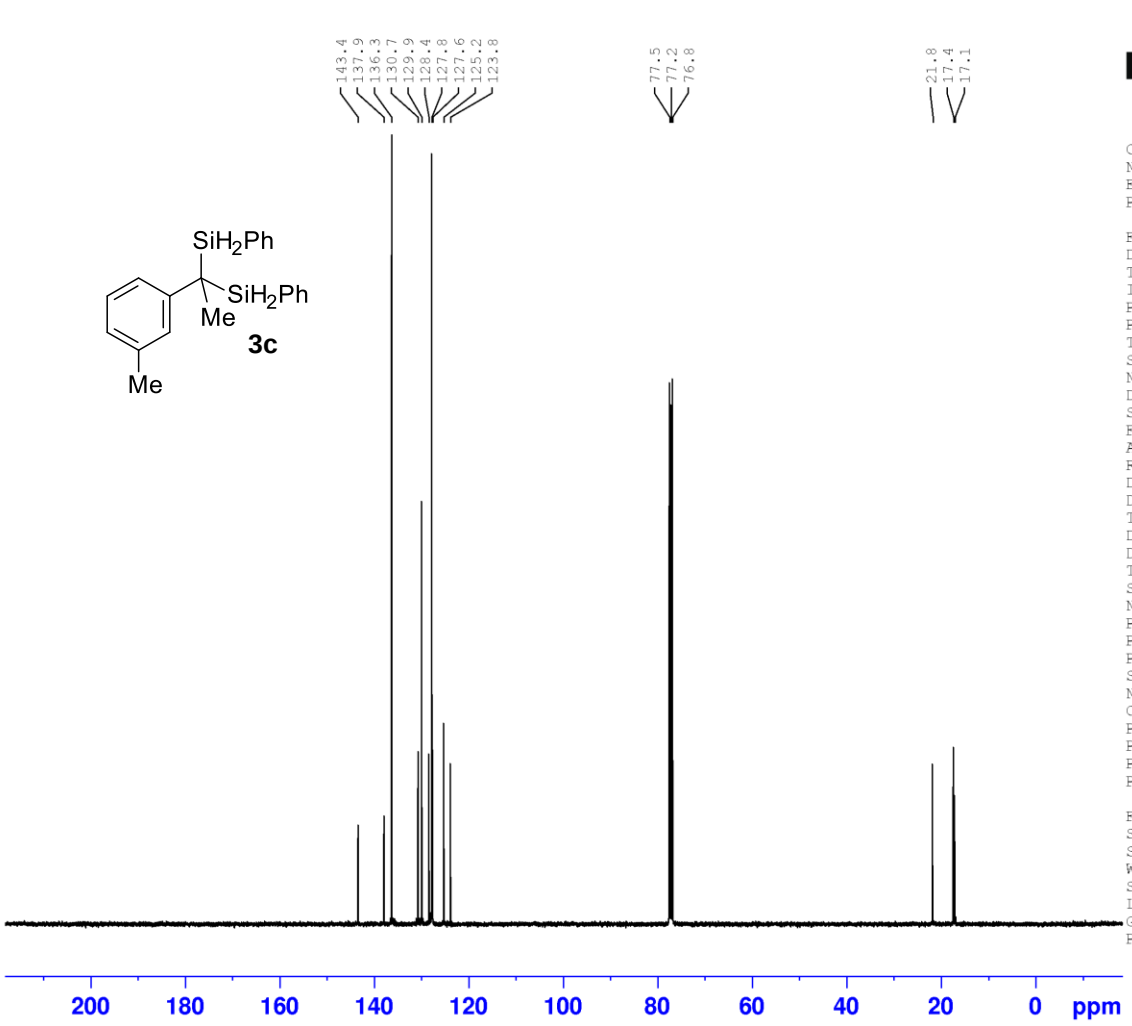
F2 - Processing parameters
SI                   32768
SF             100.6177865 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```




```
Current Data Parameters
NAME                  LB470
EXPNO                    23
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211115
Time                 18.52 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH               8012.820 Hz
FIDRES               0.244532 Hz
AQ                4.0894465 sec
RG                    88.29
DW                   62.400 usec
DE                    6.50 usec
TE                   298.1 K
D1              1.00000000 sec
TD0                     1
SFO1           400.1524711 MHz
NUC1                   1H
P0                    4.40 usec
P1                   13.20 usec
PLW1           13.00000000 W

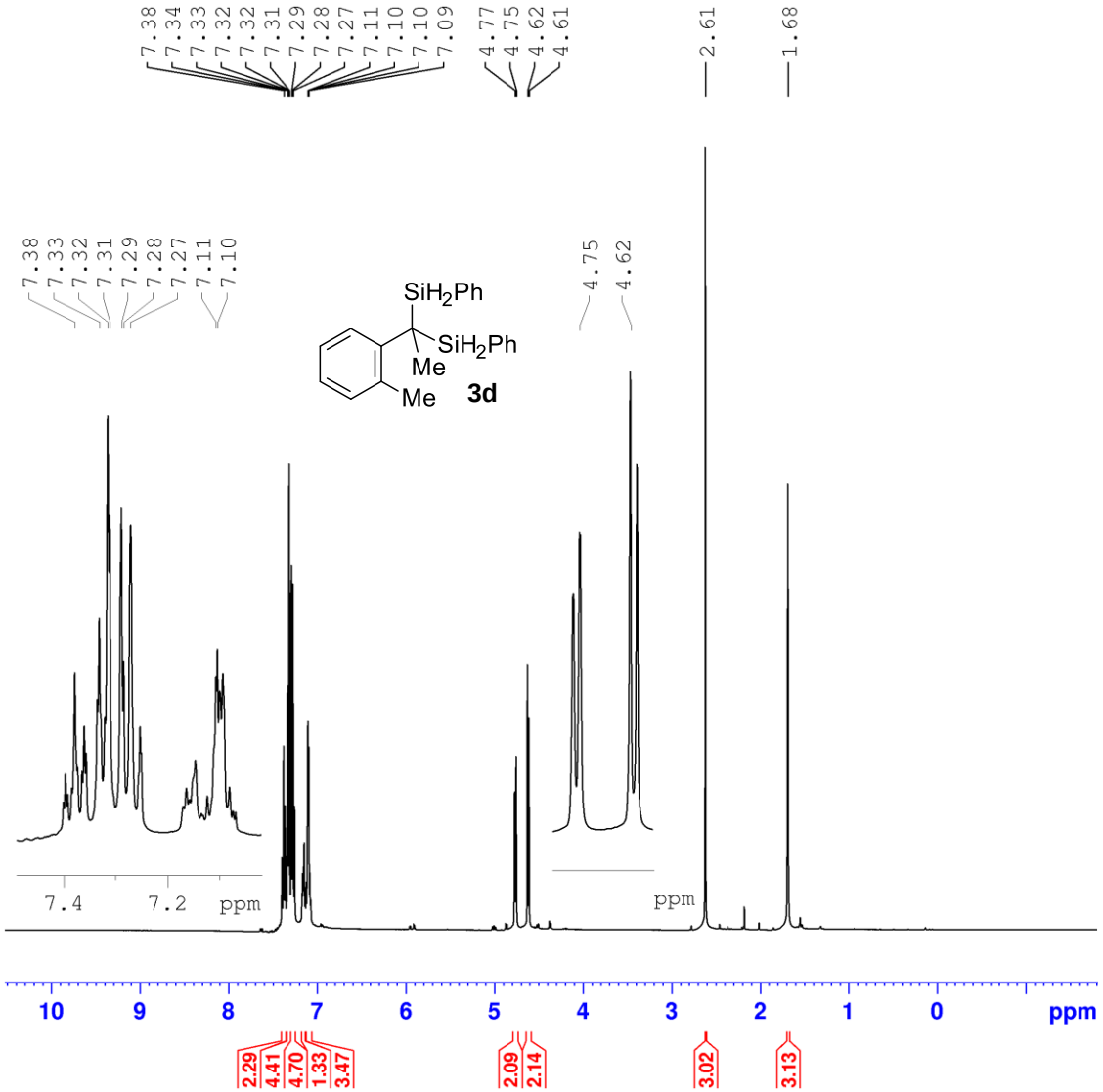
F2 - Processing parameters
SI                  65536
SF             400.1500000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




```
Current Data Parameters
NAME                  LB470
EXPNO                    24
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211115
Time                 19.51 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ               1.3631488 sec
RG                  197.58
DW                  20.800 usec
DE                   6.50 usec
TE                  298.1 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1
SFO1           100.6278588 MHz
NUC1                    13C
P0                   2.83 usec
P1                   8.50 usec
PLW1           60.00000000 W
SFO2           400.1516006 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                90.00 usec
PLW2           13.00000000 W
PLW12           0.27963999 W
PLW13           0.14066000 W

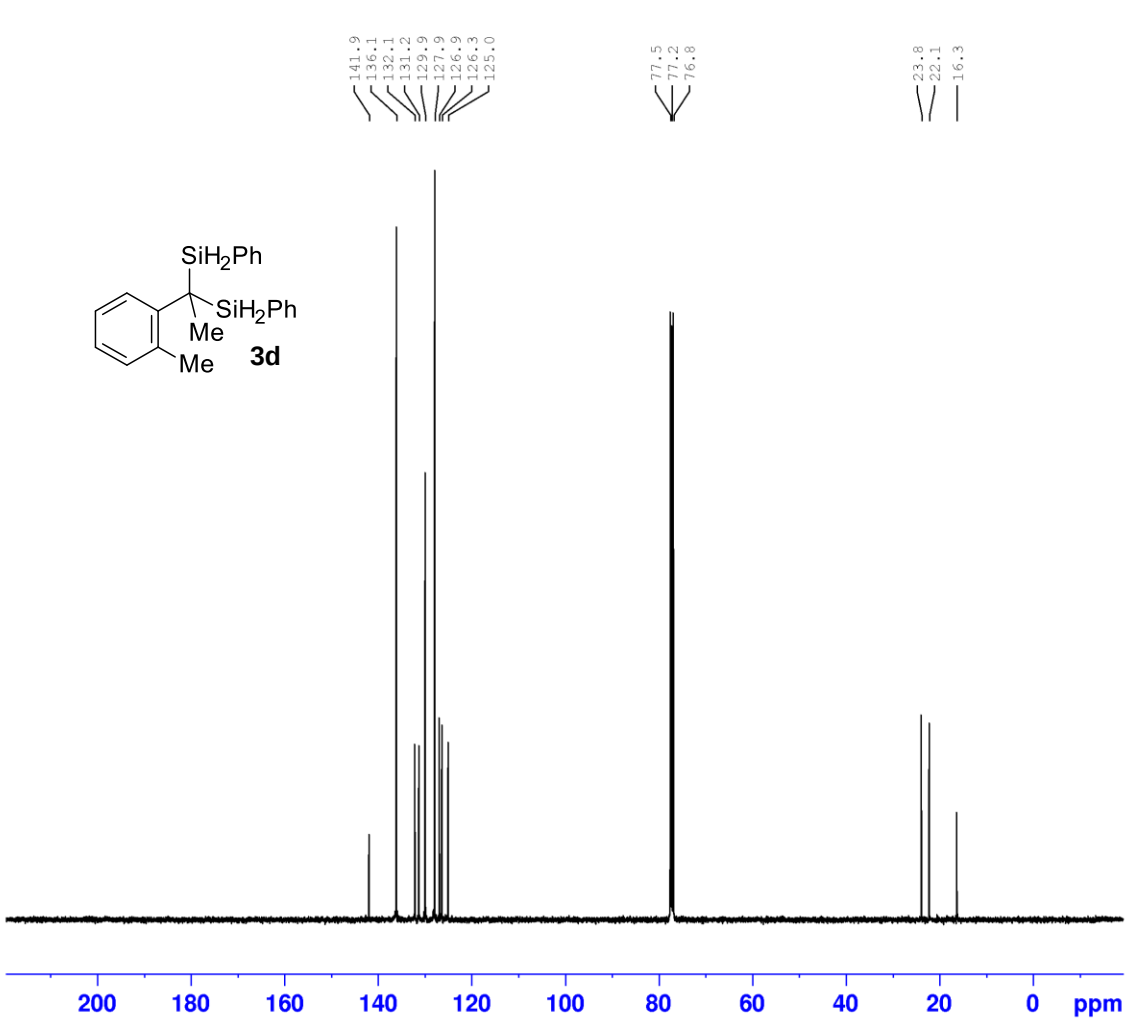
F2 - Processing parameters
SI                    32768
SF             100.6177871 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```




```
Current Data Parameters
NAME                  LB469
EXPNO                    23
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211115
Time                  17.46 h
INSTRUM               spect
PROBHD    Z108618_0726 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                8012.820 Hz
FIDRES                0.244532 Hz
AQ                 4.0894465 sec
RG                    99.28
DW                   62.400 usec
DE                    6.50 usec
TE                   298.1 K
D1                1.00000000 sec
TD0                       1
SFO1             400.1524711 MHz
NUC1                     1H
P0                    4.40 usec
P1                   13.20 usec
PLW1             13.00000000 W

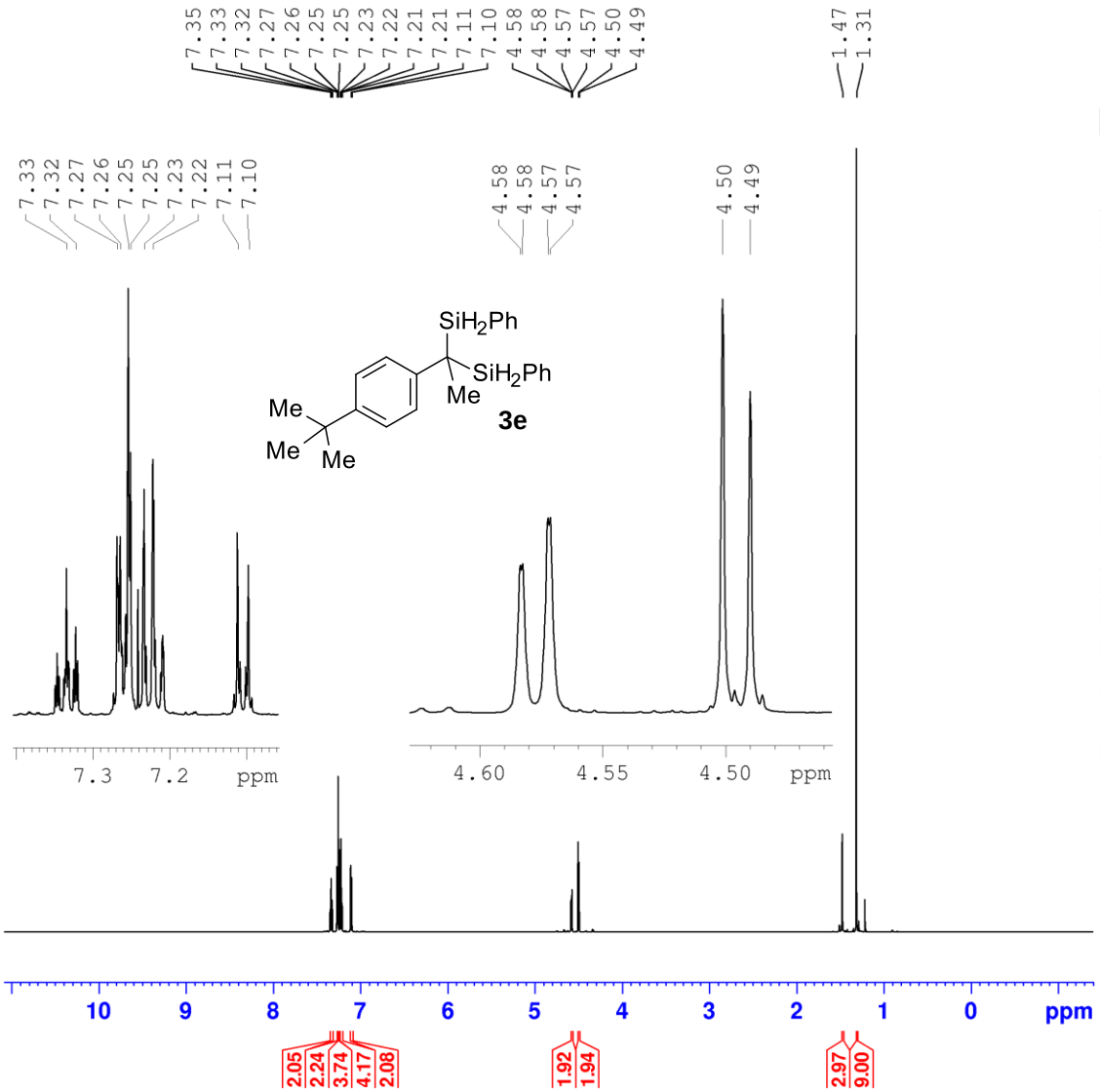
F2 - Processing parameters
SI                    65536
SF               400.1500000 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```




```
Current Data Parameters
NAME                  LB469
EXPNO                    24
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211115
Time                 18.46 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG            zgpg30
TD                  65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              24038.461 Hz
FIDRES           0.733596 Hz
AQ               1.3631488 sec
RG                  197.58
DW                  20.800 usec
DE                   6.50 usec
TE                  298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1
SFO1          100.6278588 MHz
NUC1                   13C
P0                    2.83 usec
P1                    8.50 usec
PLW1          60.00000000 W
SFO2          400.1516006 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2                90.00 usec
PLW2          13.00000000 W
PLW12          0.27963999 W
PLW13          0.14066000 W

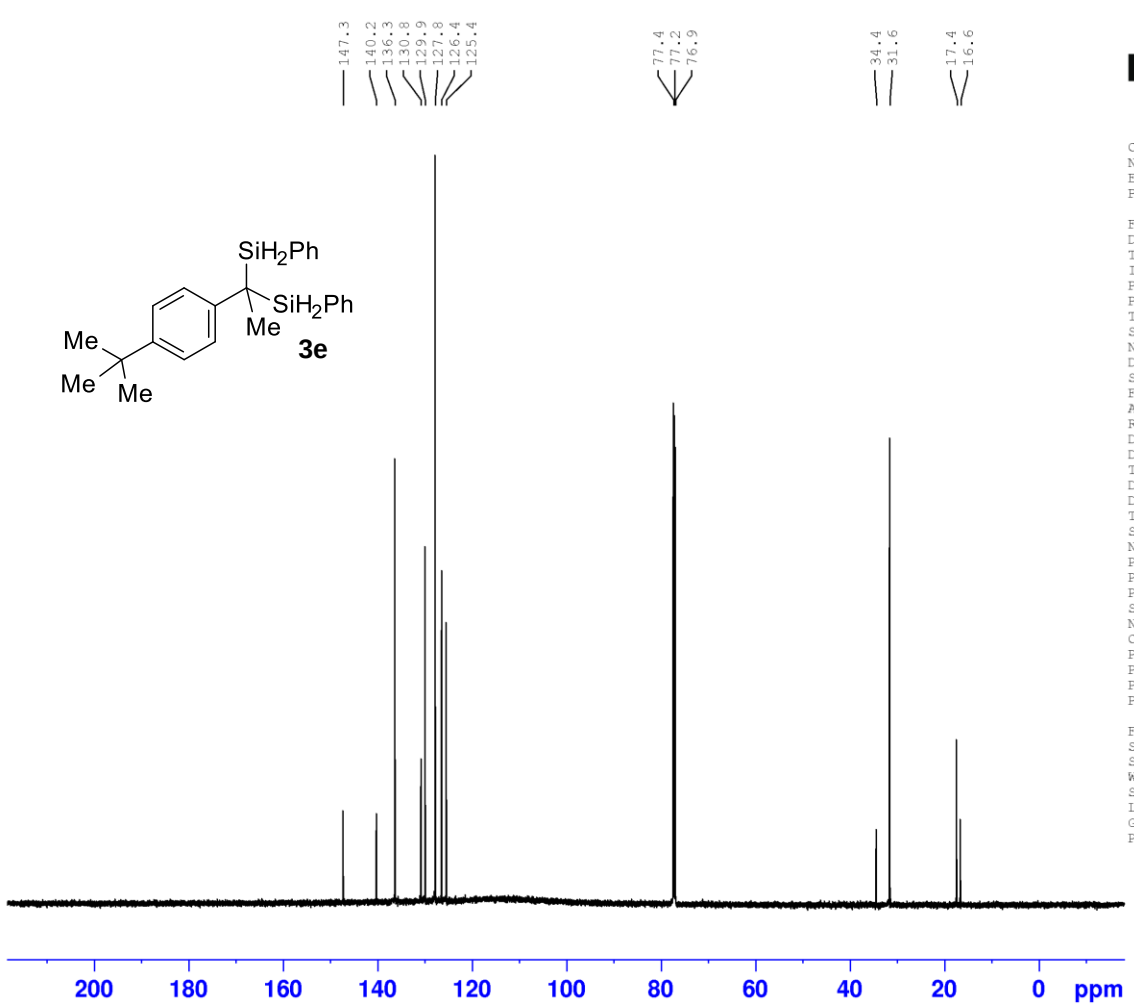
F2 - Processing parameters
SI                    32768
SF            100.6177866 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



```
Current Data Parameters
NAME      PP_LB555-wydzial chemii
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220511
Time              12.13 h
INSTRUM           Avance
PROBHD   Z8222_17 (TBI
PULPROG             zg30
TD                107142
SOLVENT             CDCl3
NS                    32
DS                     0
SWH             9615.385 Hz
FIDRES          0.179489 Hz
AQ              5.5713840 sec
RG               2.14629
DW                52.000 usec
DE                11.29 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1
SFO1          600.2536696 MHz
NUC1                  1H
P0                 3.33 usec
P1                10.00 usec
PLW1          14.10400009 W

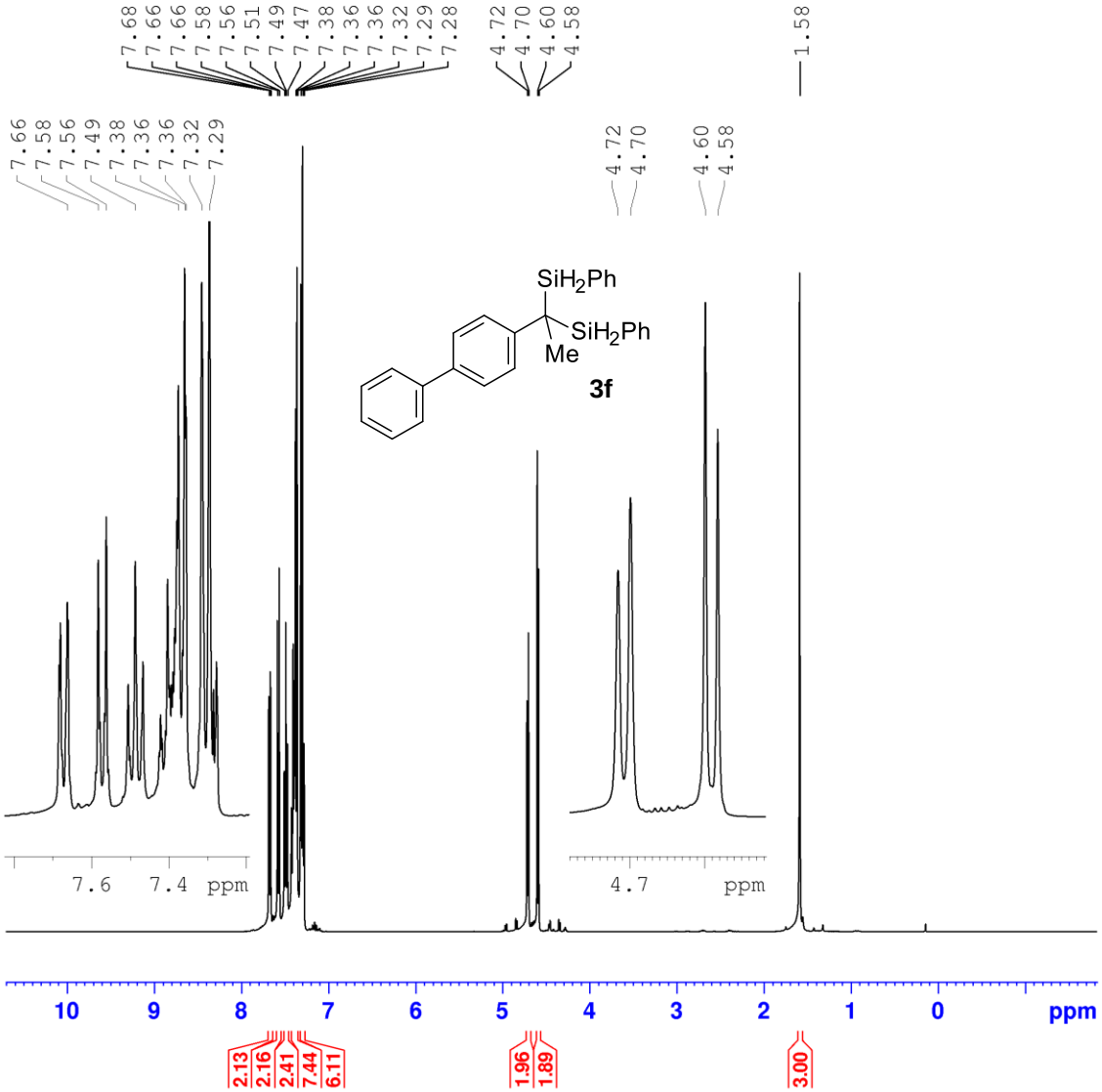
F2 - Processing parameters
SI                 65536
SF            600.2500264 MHz
WDW                   EM
SSB                    0
LB                     0 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME      PP_LB555-wydzial chemii
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220511
Time              13.01 h
INSTRUM           Avance
PROBHD   Z8222_17 (TBI
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                1408
DS                4
SWH           35714.285 Hz
FIDRES         1.089913 Hz
AQ            0.9175040 sec
RG                101
DW              14.000 usec
DE               6.50 usec
TE              298.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0               1
SFO1        150.9480758 MHz
NUC1              13C
P0               6.67 usec
P1              20.00 usec
PLW1       124.87999725 W
SFO2        600.2524010 MHz
NUC2              1H
CPDPRG[2        waltz65
PCPD2            70.00 usec
PLW2        14.10400009 W
PLW12        0.28784001 W
PLW13        0.14478000 W

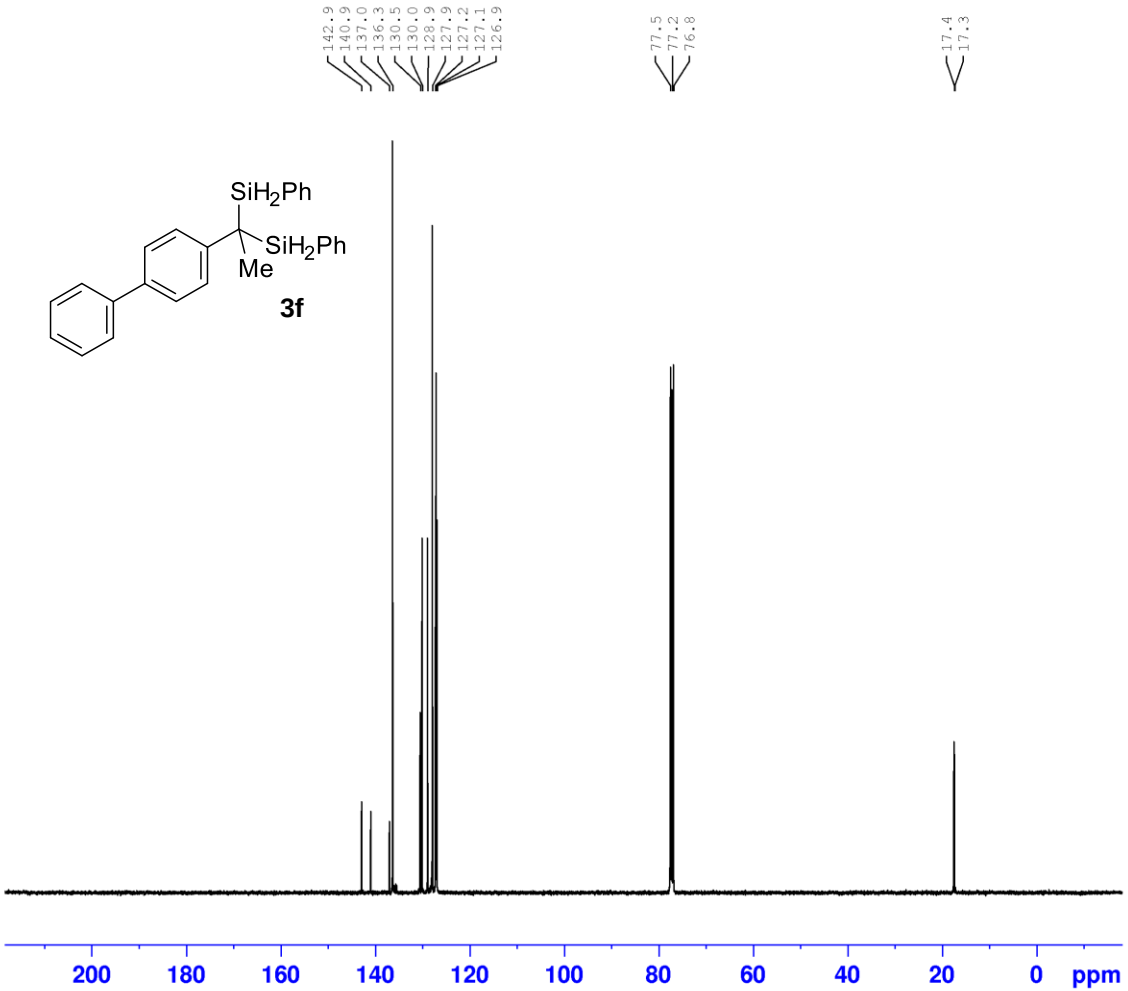
F2 - Processing parameters
SI               32768
SF          150.9329632 MHz
WDW                EM
SSB                0
LB              0.80 Hz
GB                 0
PC              1.40
```




```
Current Data Parameters
NAME                  LB467
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211104
Time                 18.46 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH               8012.820 Hz
FIDRES               0.244532 Hz
AQ                4.0894465 sec
RG                    88.29
DW                  62.400 usec
DE                   6.50 usec
TE                  298.1 K
D1              1.00000000 sec
TD0                     1
SFO1           400.1524711 MHz
NUC1                   1H
P0                   4.40 usec
P1                  13.20 usec
PLW1           13.00000000 W

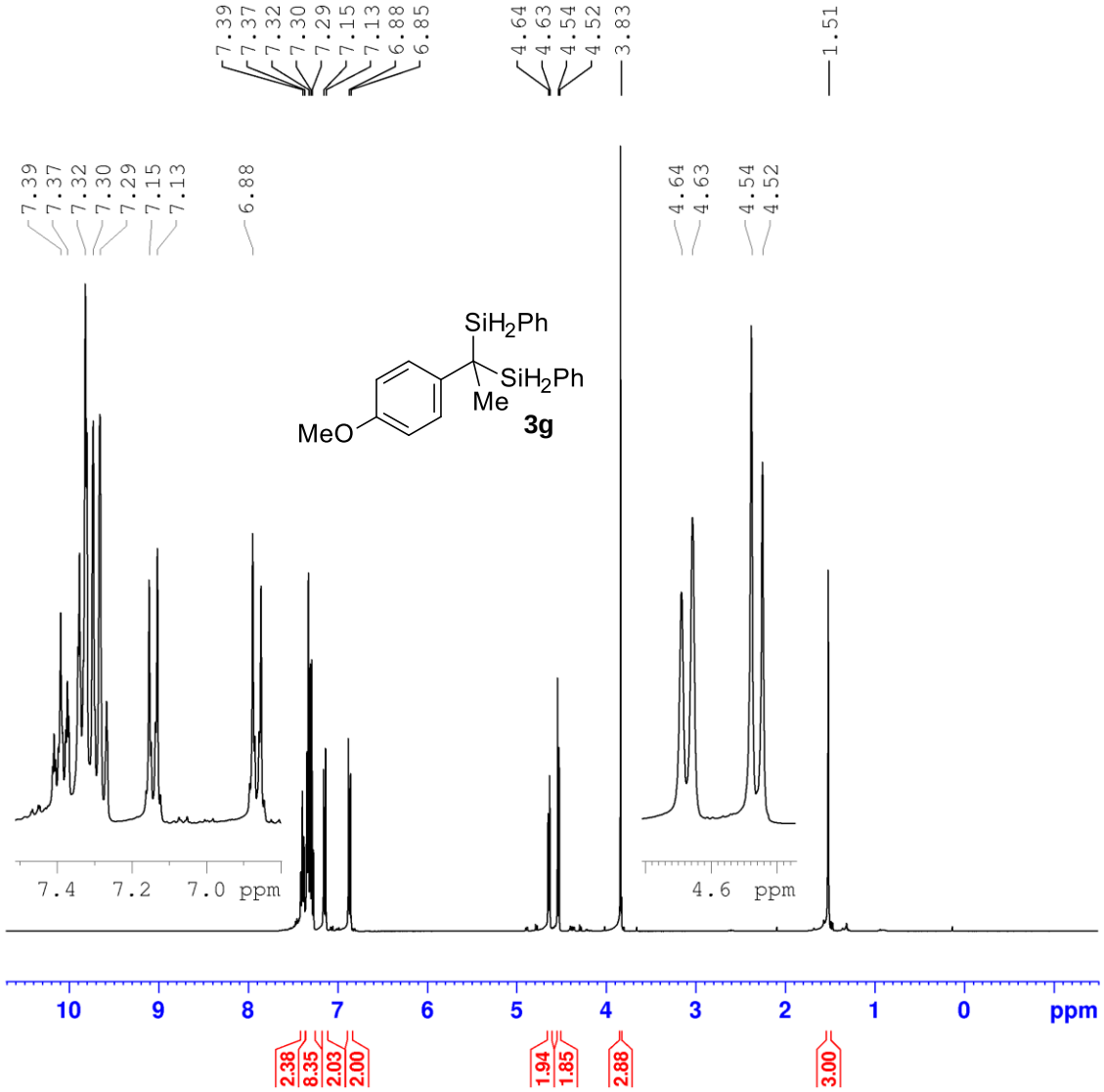
F2 - Processing parameters
SI                  65536
SF             400.1500000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




```
Current Data Parameters
NAME                  LB467
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211104
Time                 20.44 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    2048
DS                       4
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ               1.3631488 sec
RG                  197.58
DW                  20.800 usec
DE                   6.50 usec
TE                  298.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1
SFO1          100.6278588 MHz
NUC1                  13C
P0                   2.83 usec
P1                   8.50 usec
PLW1           60.00000000 W
SFO2          400.1516006 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2                90.00 usec
PLW2           13.00000000 W
PLW12           0.27963999 W
PLW13           0.14066000 W

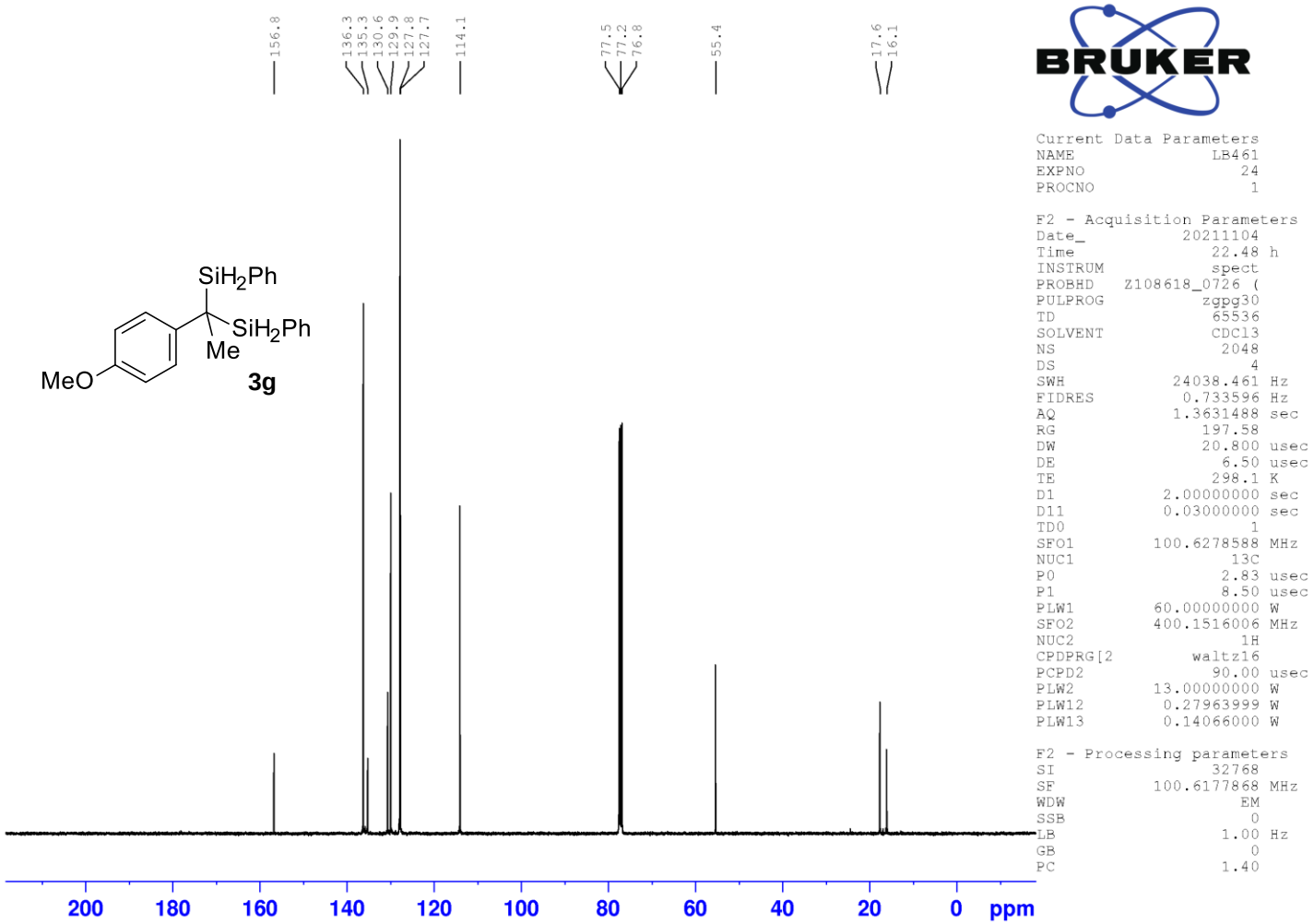
F2 - Processing parameters
SI                   32768
SF            100.6177873 MHz
WDW                  EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```




```
Current Data Parameters
NAME                  LB461
EXPNO                    23
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211104
Time                 20.50 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH               8012.820 Hz
FIDRES               0.244532 Hz
AQ                4.0894465 sec
RG                    88.29
DW                  62.400 usec
DE                   6.50 usec
TE                  298.1 K
D1              1.00000000 sec
TD0                     1
SFO1           400.1524711 MHz
NUC1                   1H
P0                   4.40 usec
P1                  13.20 usec
PLW1           13.00000000 W

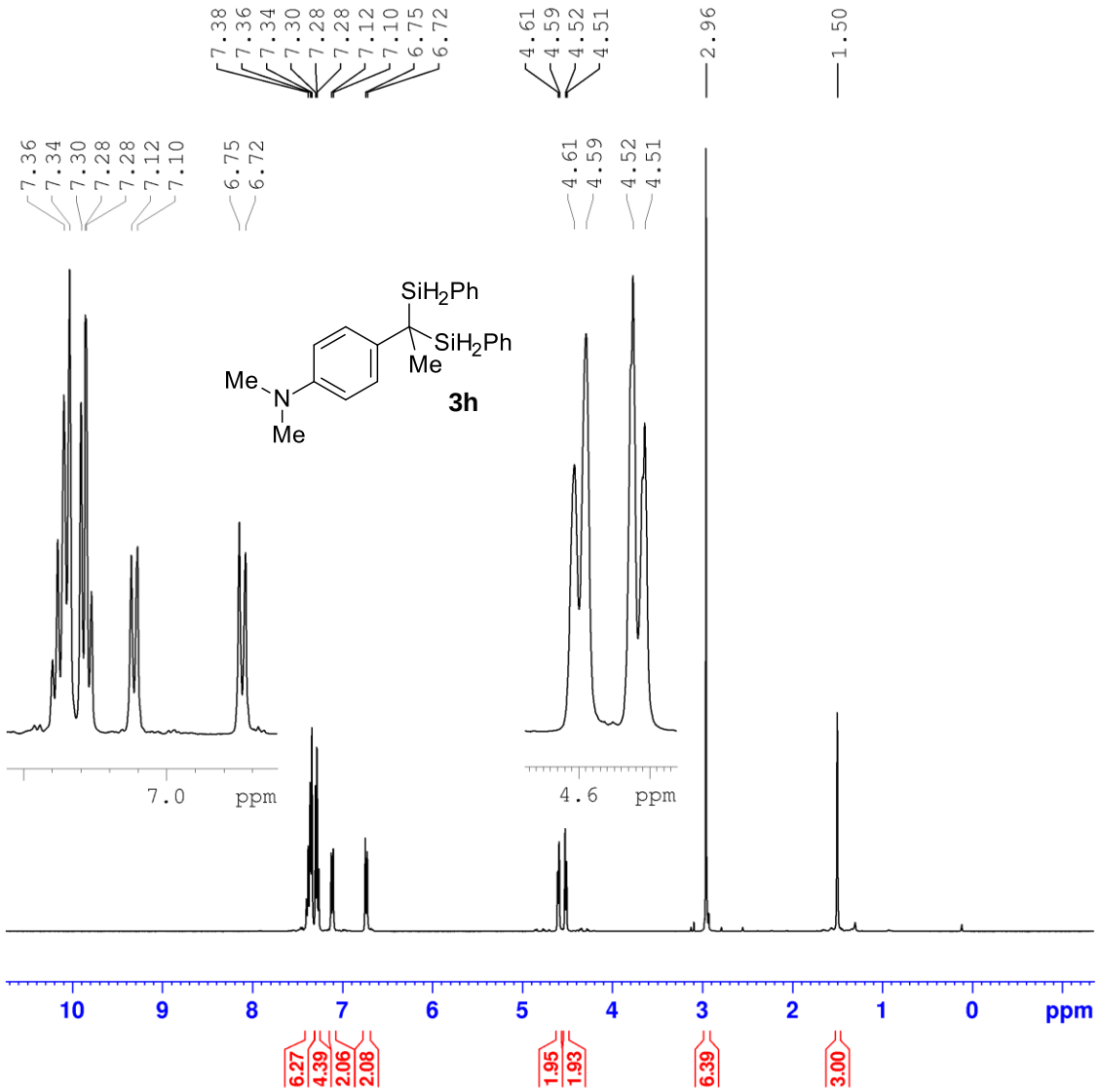
F2 - Processing parameters
SI                  65536
SF             400.1500000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




```
Current Data Parameters
NAME                  LB461
EXPNO                    24
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211104
Time                  22.48 h
INSTRUM               spect
PROBHD    Z108618_0726 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2048
DS                        4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                1.3631488 sec
RG                   197.58
DW                   20.800 usec
DE                    6.50 usec
TE                   298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1
SFO1          100.6278588 MHz
NUC1                   13C
P0                    2.83 usec
P1                    8.50 usec
PLW1          60.00000000 W
SFO2          400.1516006 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2          13.00000000 W
PLW12          0.27963999 W
PLW13          0.14066000 W

F2 - Processing parameters
SI                    32768
SF            100.6177868 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



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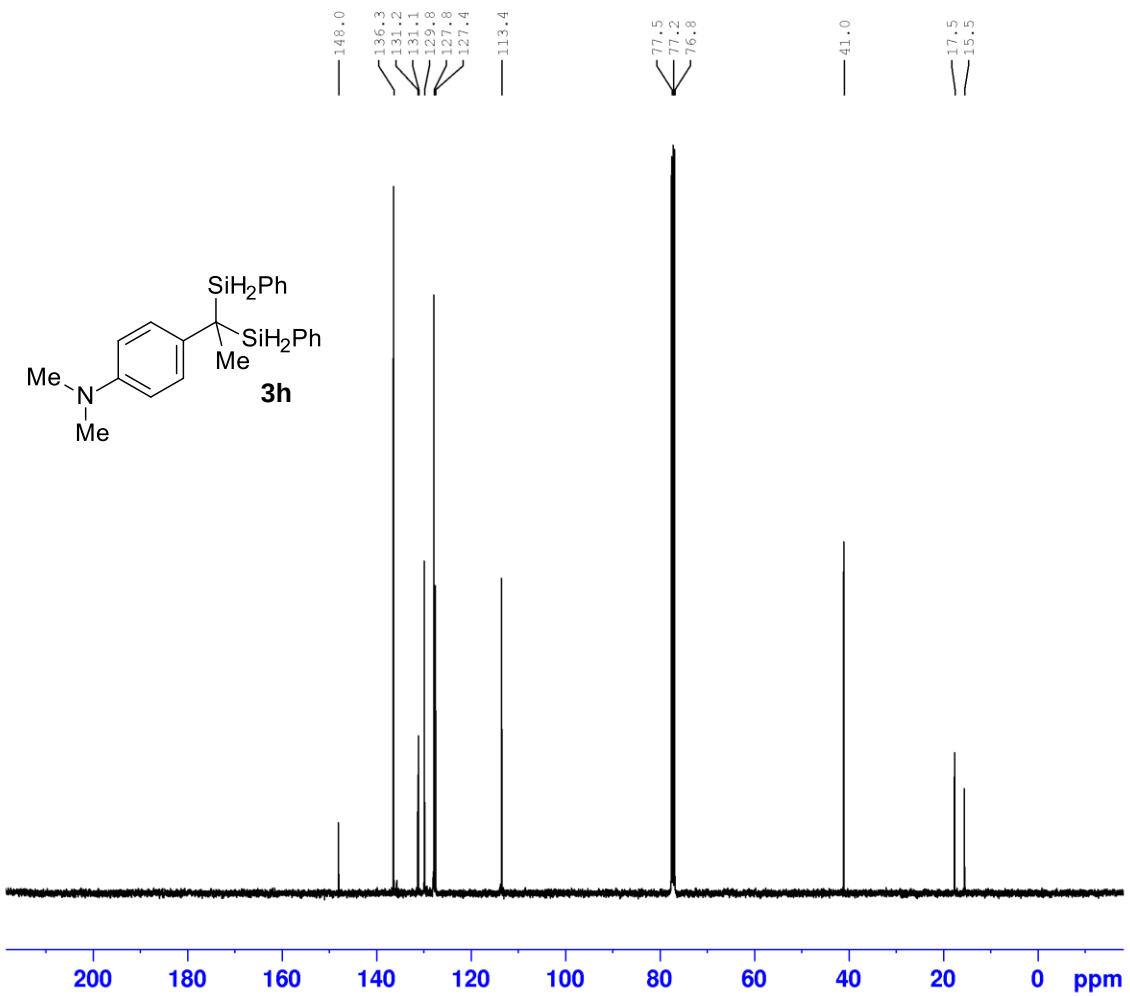
```
Current Data Parameters
NAME                  LB472
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211201
Time                 16.26 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH               8012.820 Hz
FIDRES               0.244532 Hz
AQ                4.0894465 sec
RG                   128.09
DW                   62.400 usec
DE                    6.50 usec
TE                   298.2 K
D1              1.00000000 sec
TD0                     1
SFO1           400.1524711 MHz
NUC1                   1H
P0                    4.40 usec
P1                   13.20 usec
PLW1           13.00000000 W

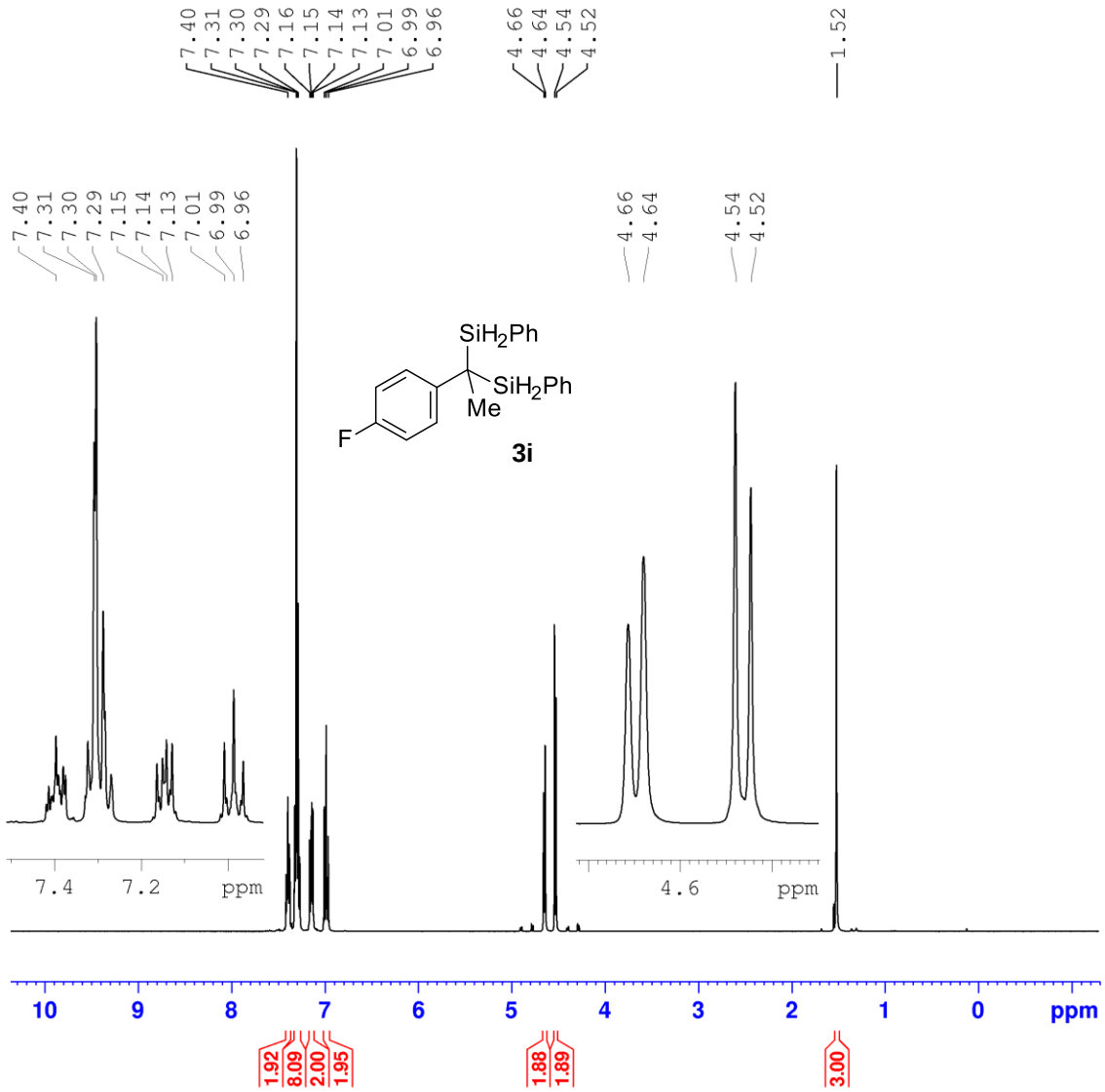
F2 - Processing parameters
SI                  65536
SF             400.1500000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




```
Current Data Parameters
NAME                  LB472
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211201
Time                 17.26 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ               1.3631488 sec
RG                  197.58
DW                  20.800 usec
DE                   6.50 usec
TE                  298.1 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1
SFO1           100.6278588 MHz
NUC1                   13C
P0                   2.83 usec
P1                   8.50 usec
PLW1           60.00000000 W
SFO2           400.1516006 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2           13.00000000 W
PLW12           0.27963999 W
PLW13           0.14066000 W

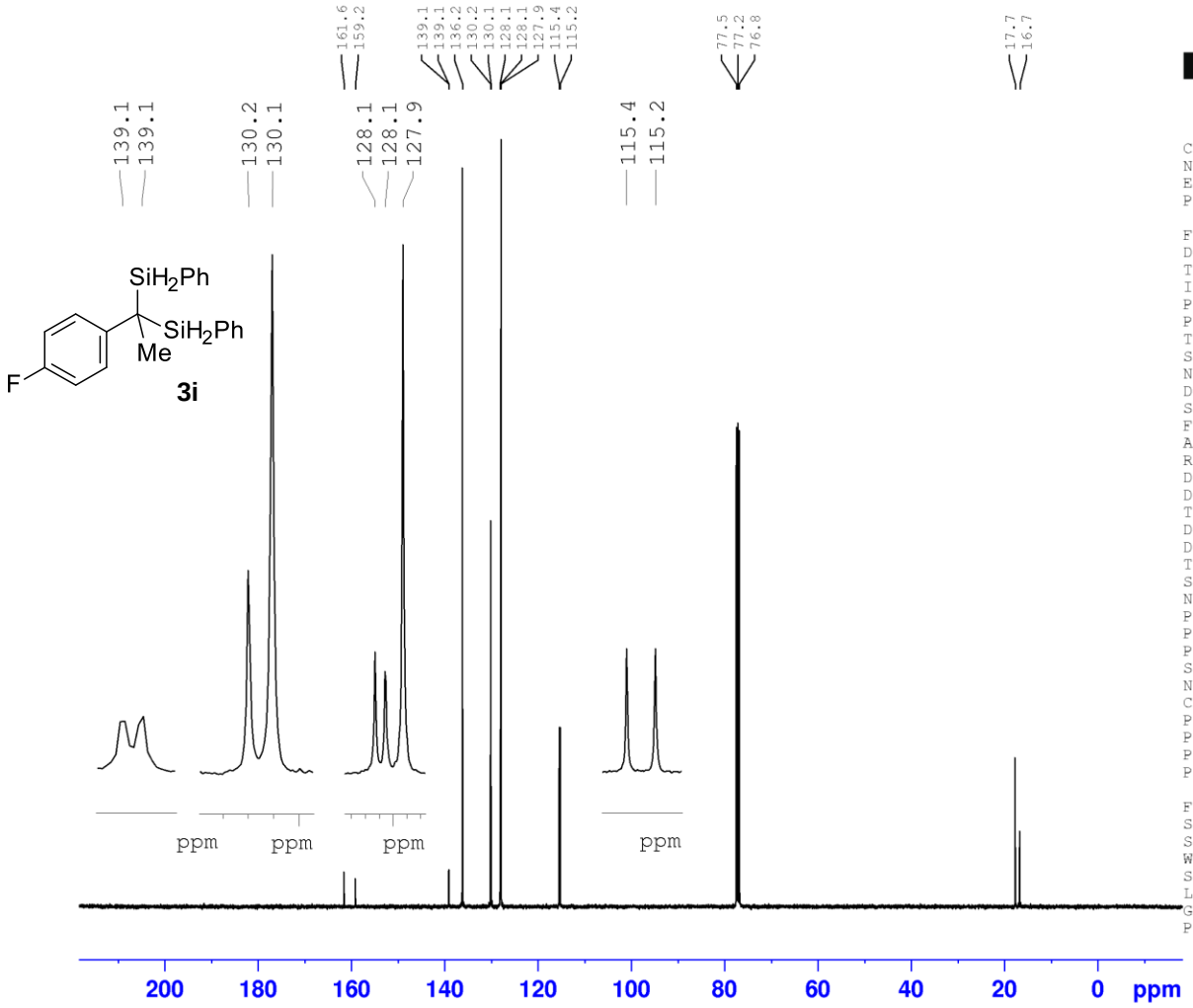
F2 - Processing parameters
SI                   32768
SF             100.6177853 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```




```
Current Data Parameters
NAME                  LB483
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211209
Time                  16.43 h
INSTRUM               spect
PROBHD    Z108618_0726 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                8012.820 Hz
FIDRES                0.244532 Hz
AQ                 4.0894465 sec
RG                    99.28
DW                   62.400 usec
DE                    6.50 usec
TE                   298.1 K
D1                1.00000000 sec
TD0                       1
SFO1             400.1524711 MHz
NUC1                     1H
P0                    4.40 usec
P1                   13.20 usec
PLW1             13.00000000 W

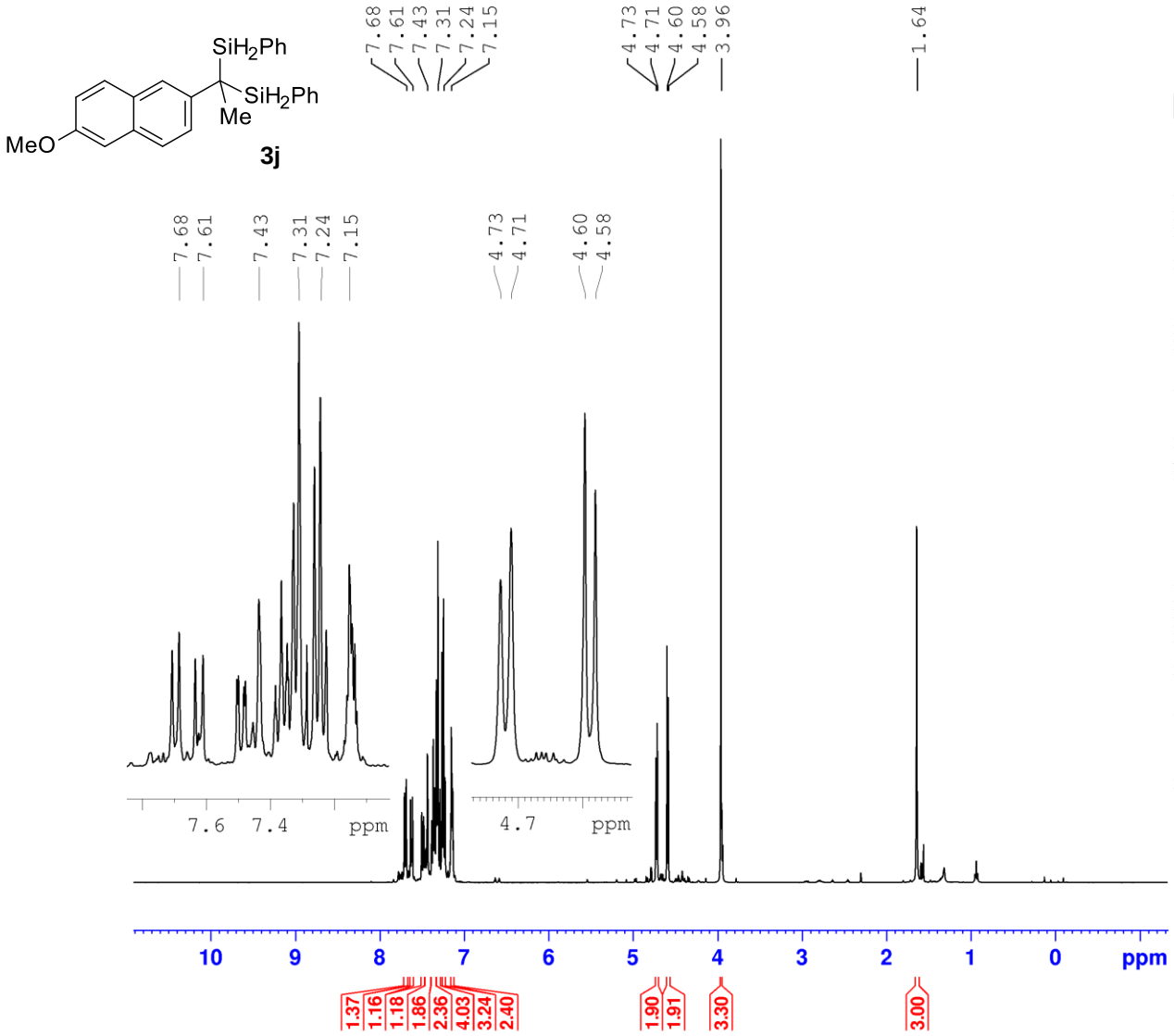
F2 - Processing parameters
SI                    65536
SF               400.1500000 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```




```
Current Data Parameters
NAME                  LB483
EXPNO                    12
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211209
Time                  17.48 h
INSTRUM               spect
PROBHD    Z108618_0726 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                1.3631488 sec
RG                   197.58
DW                   20.800 usec
DE                    6.50 usec
TE                   298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1
SFO1          100.6278588 MHz
NUC1                    13C
P0                    2.83 usec
P1                    8.50 usec
PLW1          60.00000000 W
SFO2          400.1516006 MHz
NUC2                    1H
CPDPRG[2          waltz16
PCPD2                90.00 usec
PLW2          13.00000000 W
PLW12          0.27963999 W
PLW13          0.14066000 W

F2 - Processing parameters
SI                    32768
SF            100.6177856 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



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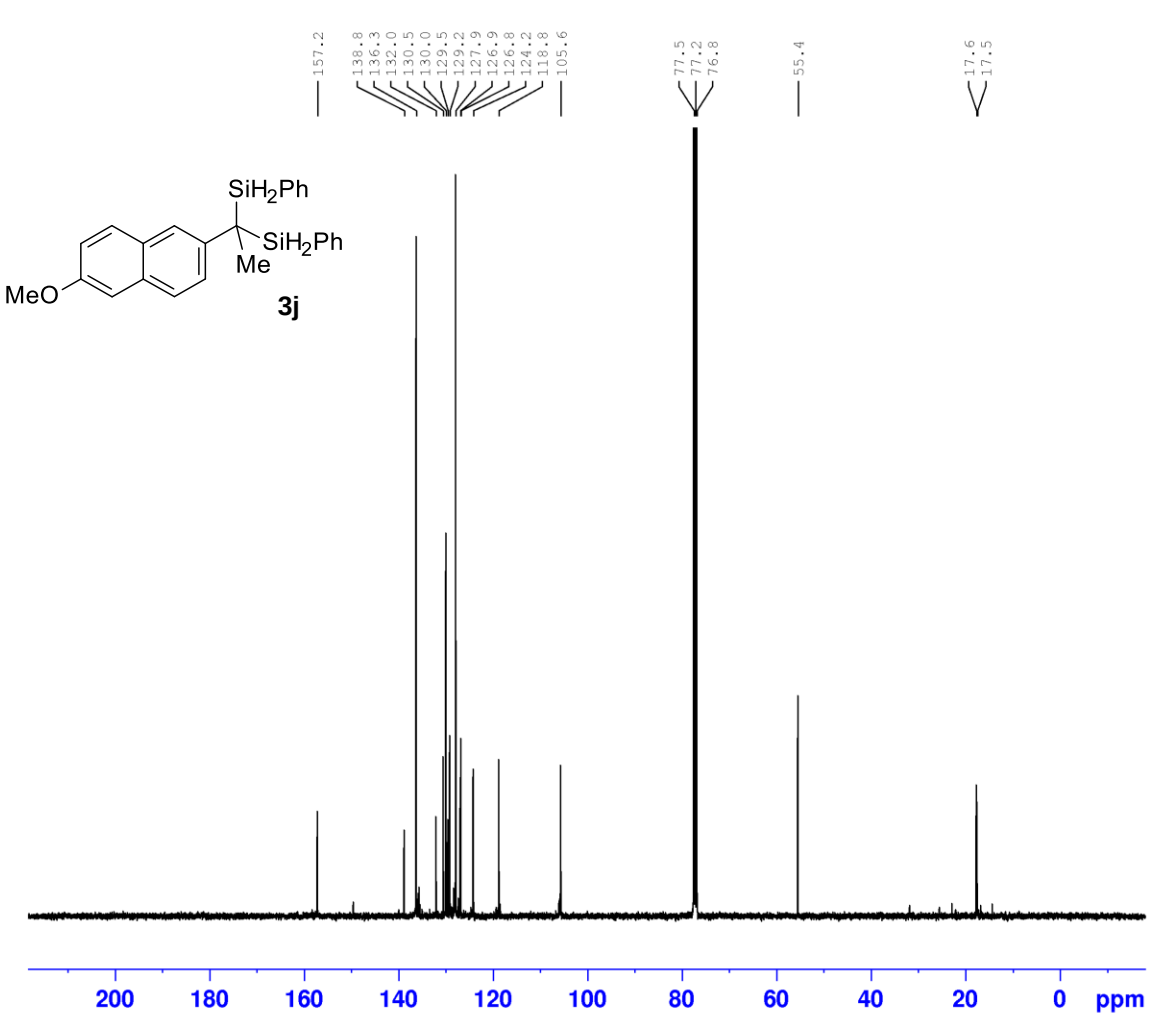
```
Current Data Parameters
NAME                  LB476
EXPNO                    23
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211201
Time                 17.32 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH               8012.820 Hz
FIDRES               0.244532 Hz
AQ                4.0894465 sec
RG                    99.28
DW                  62.400 usec
DE                   6.50 usec
TE                  298.1 K
D1             1.00000000 sec
TD0                     1
SFO1           400.1524711 MHz
NUC1                   1H
P0                   4.40 usec
P1                  13.20 usec
PLW1           13.00000000 W

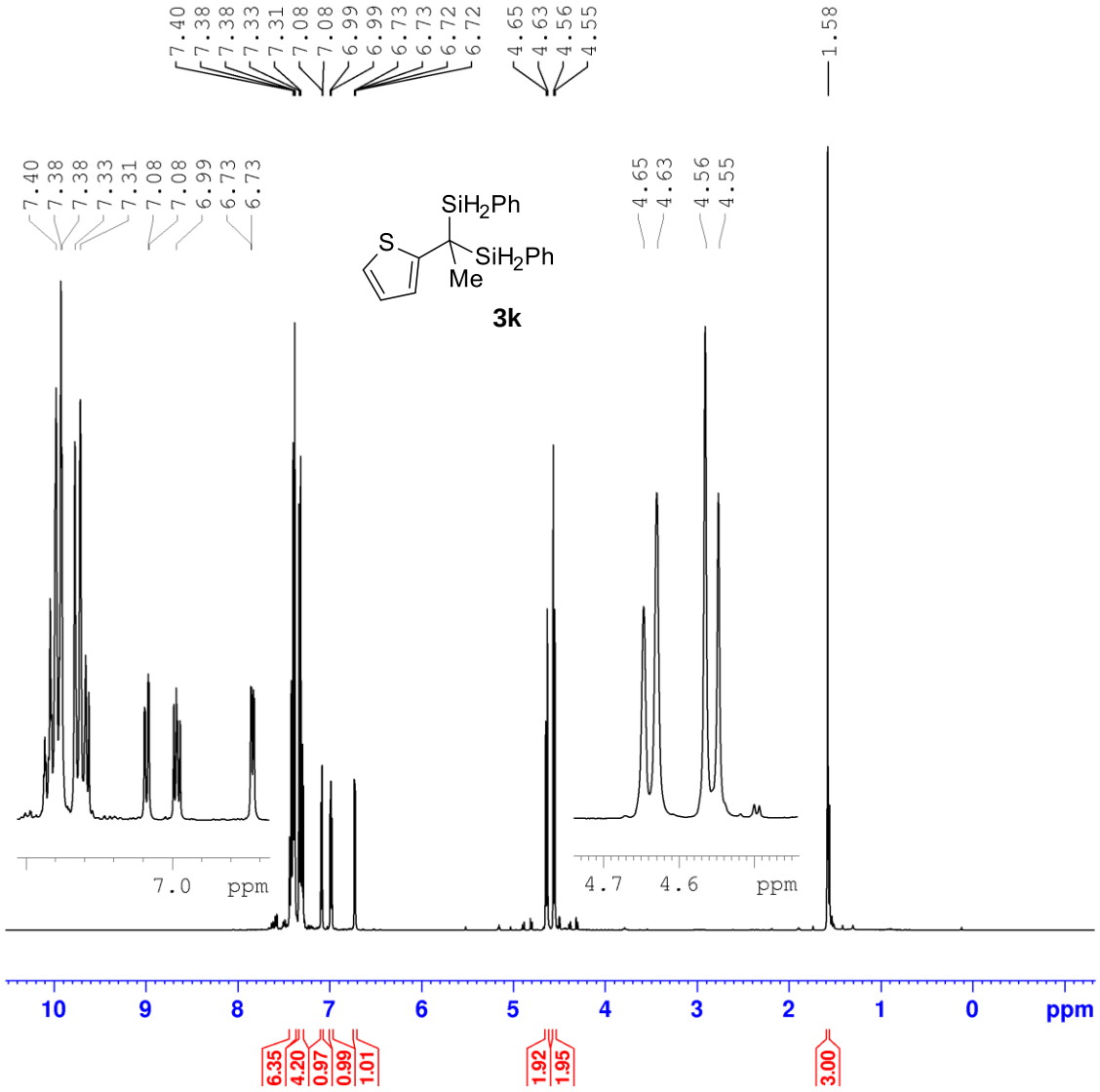
F2 - Processing parameters
SI                  65536
SF             400.1500000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




```
Current Data Parameters
NAME                  LB476
EXPNO                    24
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211201
Time                 18.31 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                1.3631488 sec
RG                   197.58
DW                   20.800 usec
DE                    6.50 usec
TE                   298.1 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1
SFO1            100.6278588 MHz
NUC1                    13C
P0                    2.83 usec
P1                    8.50 usec
PLW1            60.00000000 W
SFO2            400.1516006 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                90.00 usec
PLW2            13.00000000 W
PLW12            0.27963999 W
PLW13            0.14066000 W

F2 - Processing parameters
SI                    32768
SF              100.6177862 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.40
```

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Current Data Parameters
NAME                  LB465
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211108
Time                 20.42 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH               8012.820 Hz
FIDRES            0.244532 Hz
AQ                4.0894465 sec
RG                  128.09
DW                  62.400 usec
DE                   6.50 usec
TE                  298.2 K
D1              1.00000000 sec
TD0                     1
SFO1           400.1524711 MHz
NUC1                   1H
P0                   4.40 usec
P1                  13.20 usec
PLW1           13.00000000 W

F2 - Processing parameters
SI                  65536
SF             400.1500000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```
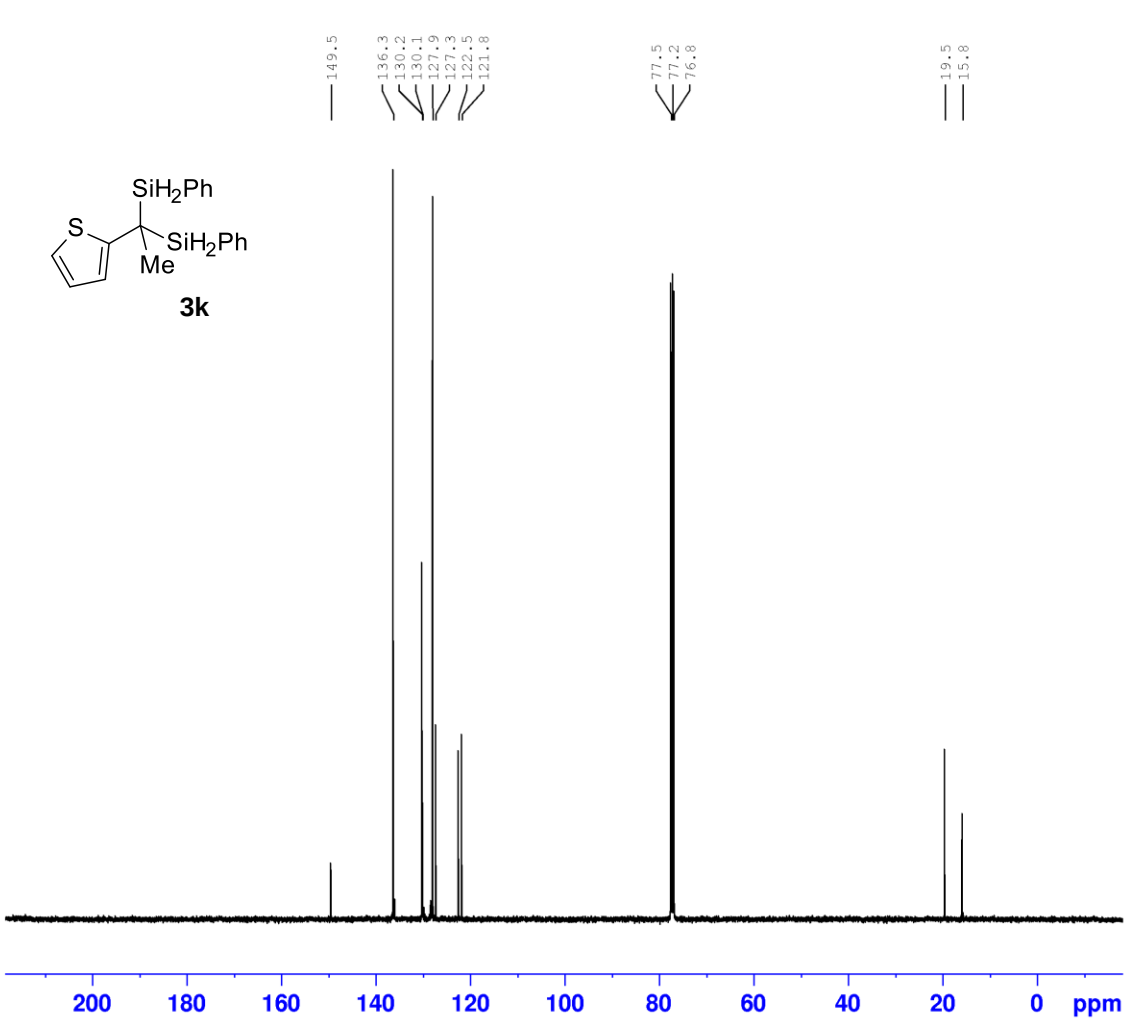
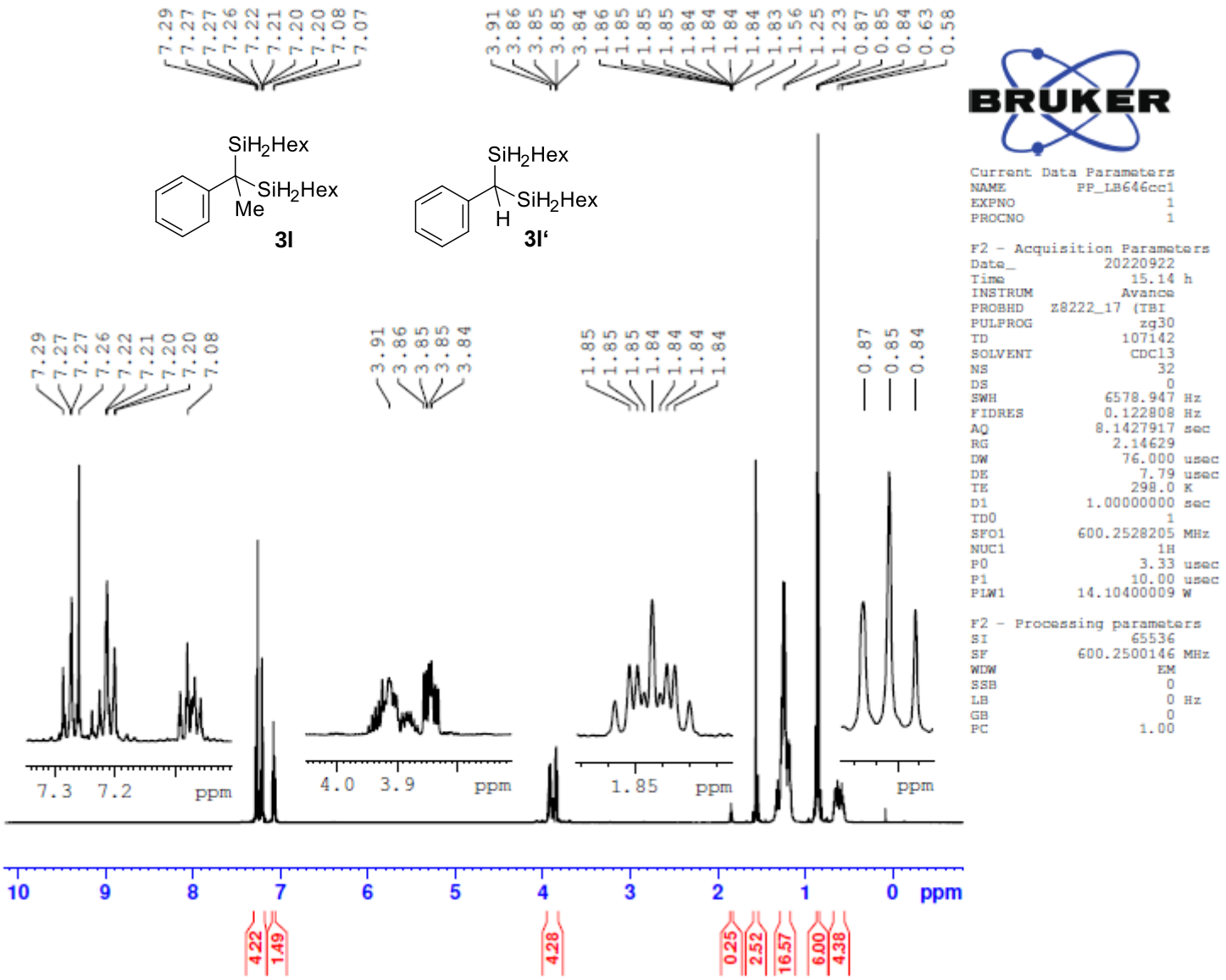



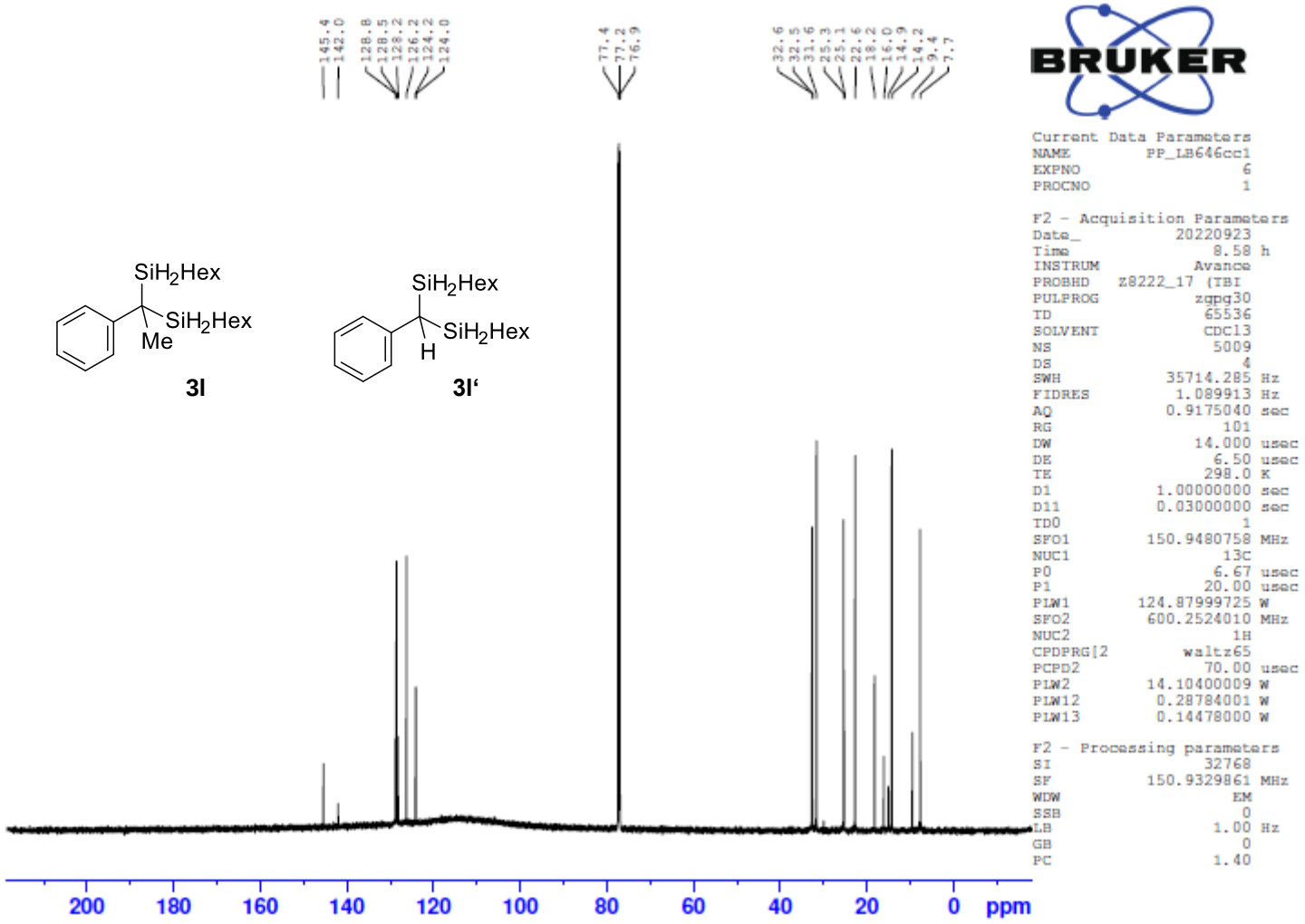

```
Current Data Parameters
NAME                  LB465
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20211108
Time                 21.42 h
INSTRUM               spect
PROBHD    Z108618_0726 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ               1.3631488 sec
RG                  197.58
DW                  20.800 usec
DE                   6.50 usec
TE                  298.2 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1
SFO1           100.6278588 MHz
NUC1                   13C
P0                   2.83 usec
P1                   8.50 usec
PLW1            60.00000000 W
SFO2           400.1516006 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2            13.00000000 W
PLW12            0.27963999 W
PLW13            0.14066000 W

F2 - Processing parameters
SI                   32768
SF             100.6177855 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



Current Data Parameters
NAME PP_LB646cc1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220922
Time 15.14 h
INSTRUM Avance
PROBHD Z8222_17 (TBI
PULPROG zg30
TD 107142
SOLVENT CDCl3
NS 32
DS 0
SWH 6578.947 Hz
FIDRES 0.122808 Hz
AQ 8.1427917 sec
RG 2.14629
DW 76.000 usec
DE 7.79 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.2528205 MHz
NUC1 1H
P0 3.33 usec
P1 10.00 usec
PLW1 14.10400009 W

F2 - Processing parameters
SI 65536
SF 600.2500146 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00



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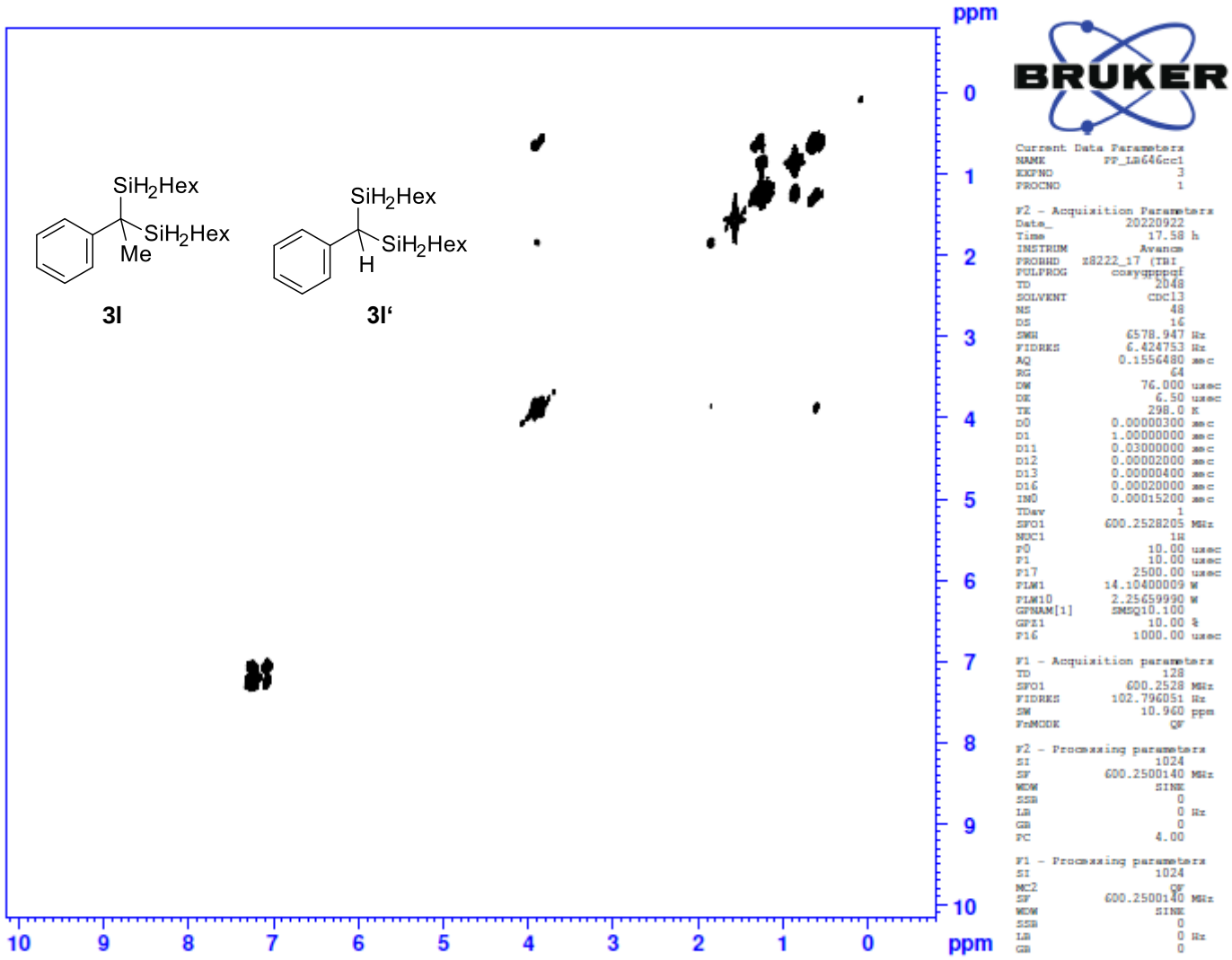
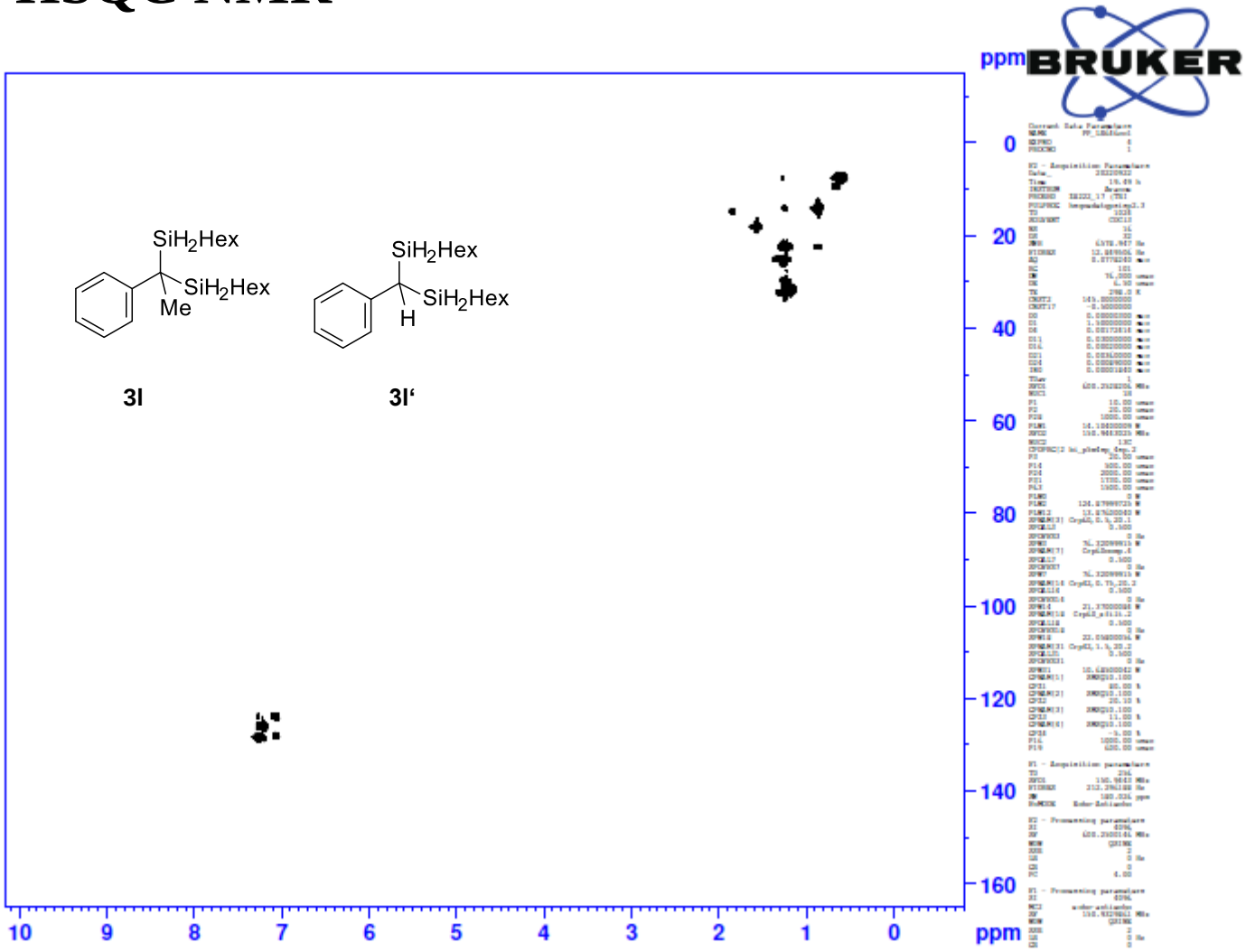
```
Current Data Parameters
NAME         PP_LB646cc1
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220923
Time                8.58 h
INSTRUM           Avance
PROBHD   z8222_17 (TBI
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 5009
DS                    4
SWH           35714.285 Hz
FIDRES         1.089913 Hz
AQ             0.9175040 sec
RG                  101
DW                14.000 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                   1
SFO1         150.9480758 MHz
NUC1                13C
P0                 6.67 usec
P1                20.00 usec
PLW1        124.87999725 W
SFO2         600.2524010 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2             70.00 usec
PLW2         14.10400009 W
PLW12         0.28784001 W
PLW13         0.14478000 W

F2 - Processing parameters
SI                 32768
SF           150.9329861 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{1}H-^{1}H COSY NMR

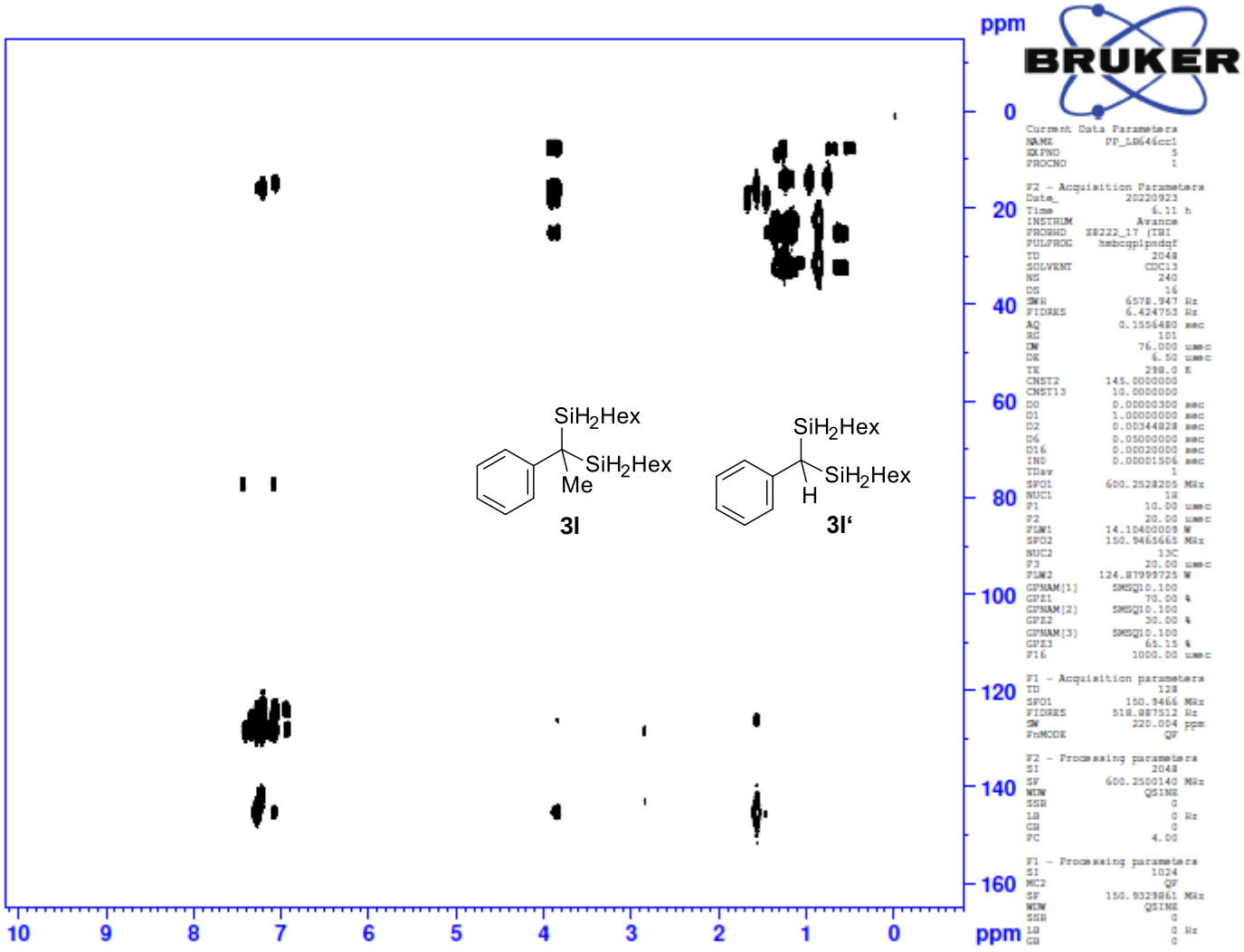


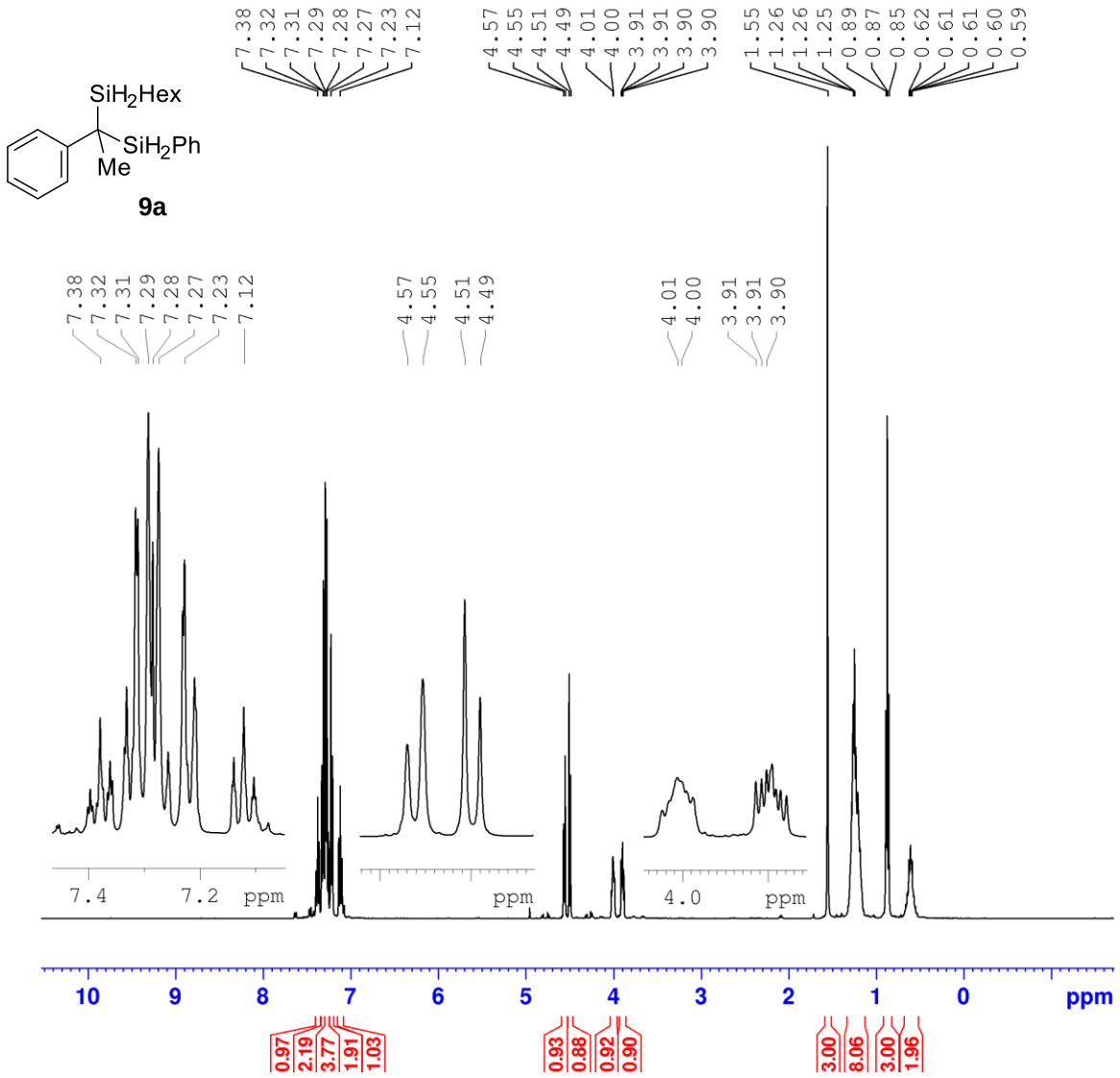

```
Current Data Parameters
NAME          FF_LB646cc1
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20220922
Time                17.58 h
INSTRUM              Avance
PROBHD    z8222_17 (TBI
PULPROG       cosygpppqf
TD                    2048
SOLVENT              CDCl3
NS                      48
DS                      16
SWH                6578.947 Hz
FIDRES             6.424753 Hz
AQ                 0.1556480 sec
RG                        64
DW                   76.000 usec
DE                    6.50 usec
TE                   298.0 K
D0                0.00000300 sec
D1                1.00000000 sec
D11               0.03000000 sec
D12               0.00002000 sec
D13               0.00000400 sec
D16               0.00020000 sec
IN0               0.00015200 sec
TDav                      1
SFO1           600.2528205 MHz
NUC1                    1H
P0                   10.00 usec
P1                   10.00 usec
P17                2500.00 usec
PLW1          14.10400009 W
PLW10          2.25659990 W
GPNAM[1]       SMSQ10.100
GPZ11                10.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                      128
SFO1              600.2528 MHz
FIDRES          102.796051 Hz
SW                  10.960 ppm
FnMODE                   QF

F2 - Processing parameters
SI                      1024
SF             600.2500140 MHz
WDW                   SINE
SSB                      0
LB                       0 Hz
GB                       0
PC                    4.00

F1 - Processing parameters
SI                      1024
MC2                     QF
SF             600.2500140 MHz
WDW                   SINE
SSB                      0
LB                       0 Hz
GB                       0
```

^{1}H-^{13}C HSQC NMR

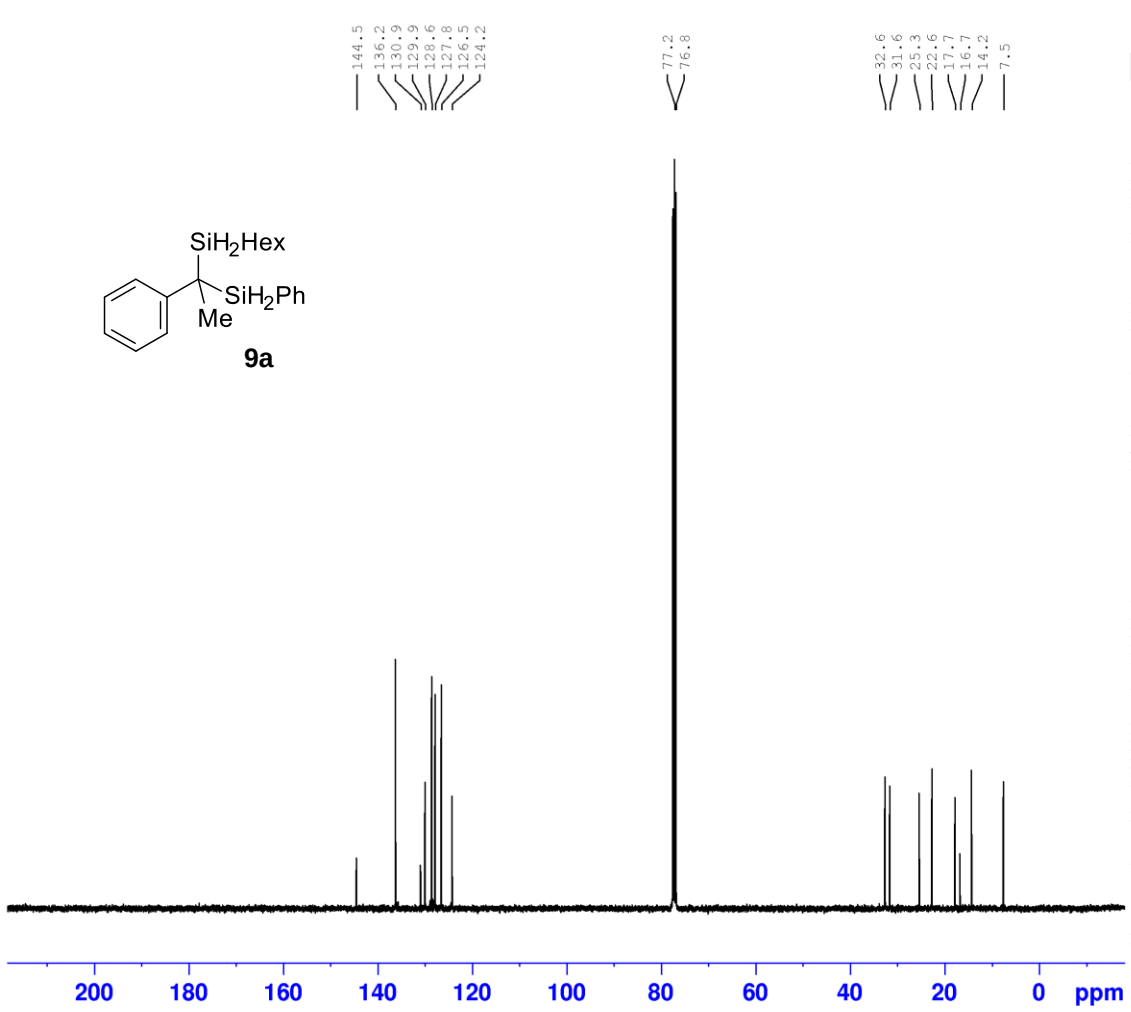


^{1}H-^{13}C HMBC NMR

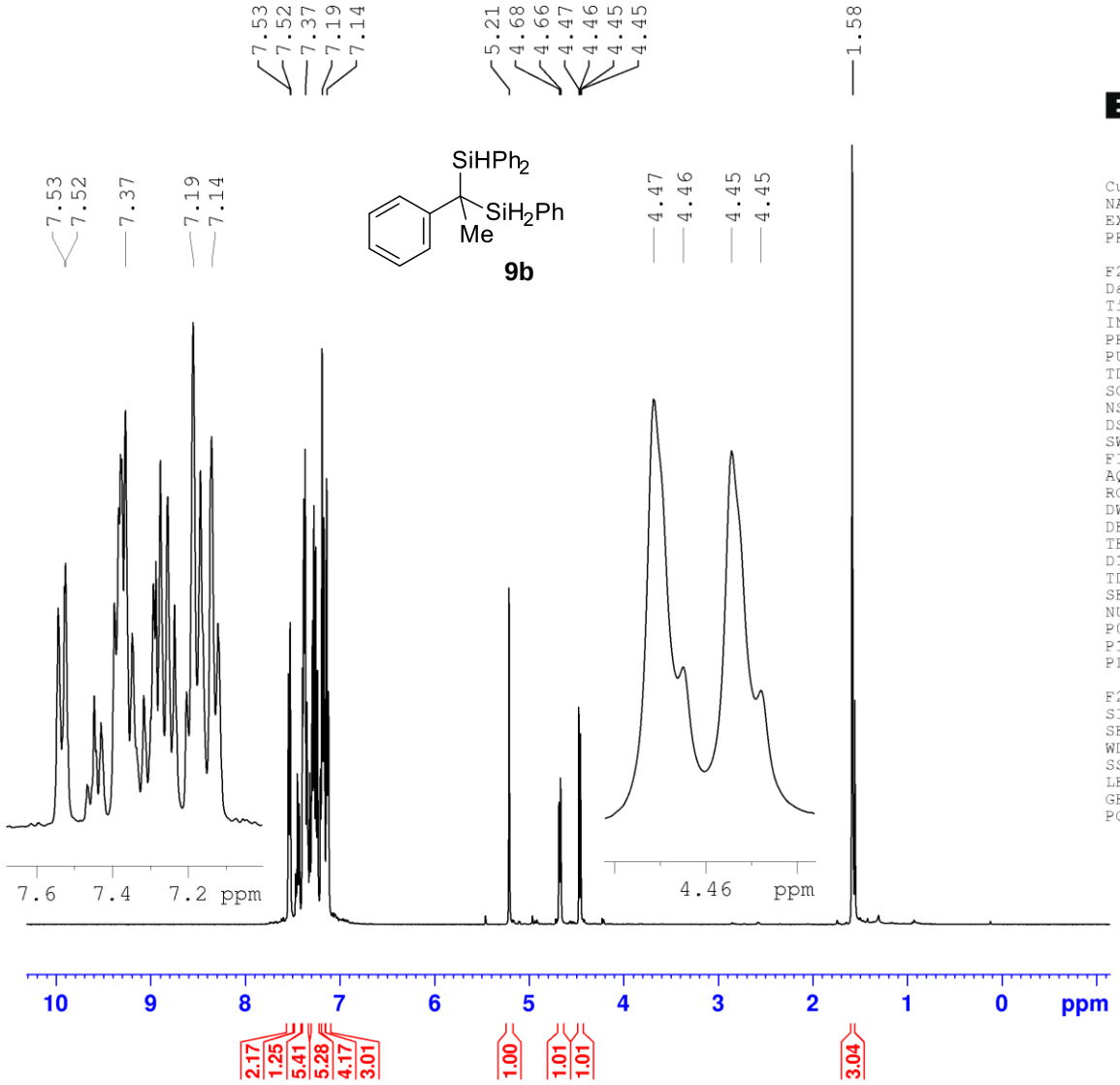





```
Current Data Parameters
NAME                  LB540
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220321
Time                  9.34 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                8012.820 Hz
FIDRES                0.244532 Hz
AQ                 4.0894465 sec
RG                    143.52
DW                    62.400 usec
DE                     6.50 usec
TE                    298.1 K
D1                 1.00000000 sec
TD0                       1
SFO1             400.1524711 MHz
NUC1                     1H
P0                     4.40 usec
P1                    13.20 usec
PLW1              13.00000000 W

F2 - Processing parameters
SI                    65536
SF               400.1500000 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```




```
Current Data Parameters
NAME                  LB540
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220321
Time                 13.12 h
INSTRUM               spect
PROBHD    Z108618_0726 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                1.3631488 sec
RG                   197.58
DW                   20.800 usec
DE                    6.50 usec
TE                   298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1
SFO1          100.6278588 MHz
NUC1                    13C
P0                    2.83 usec
P1                    8.50 usec
PLW1          60.00000000 W
SFO2          400.1516006 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2          13.00000000 W
PLW12          0.27963999 W
PLW13          0.14066000 W

F2 - Processing parameters
SI                    32768
SF            100.6177839 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.40
```



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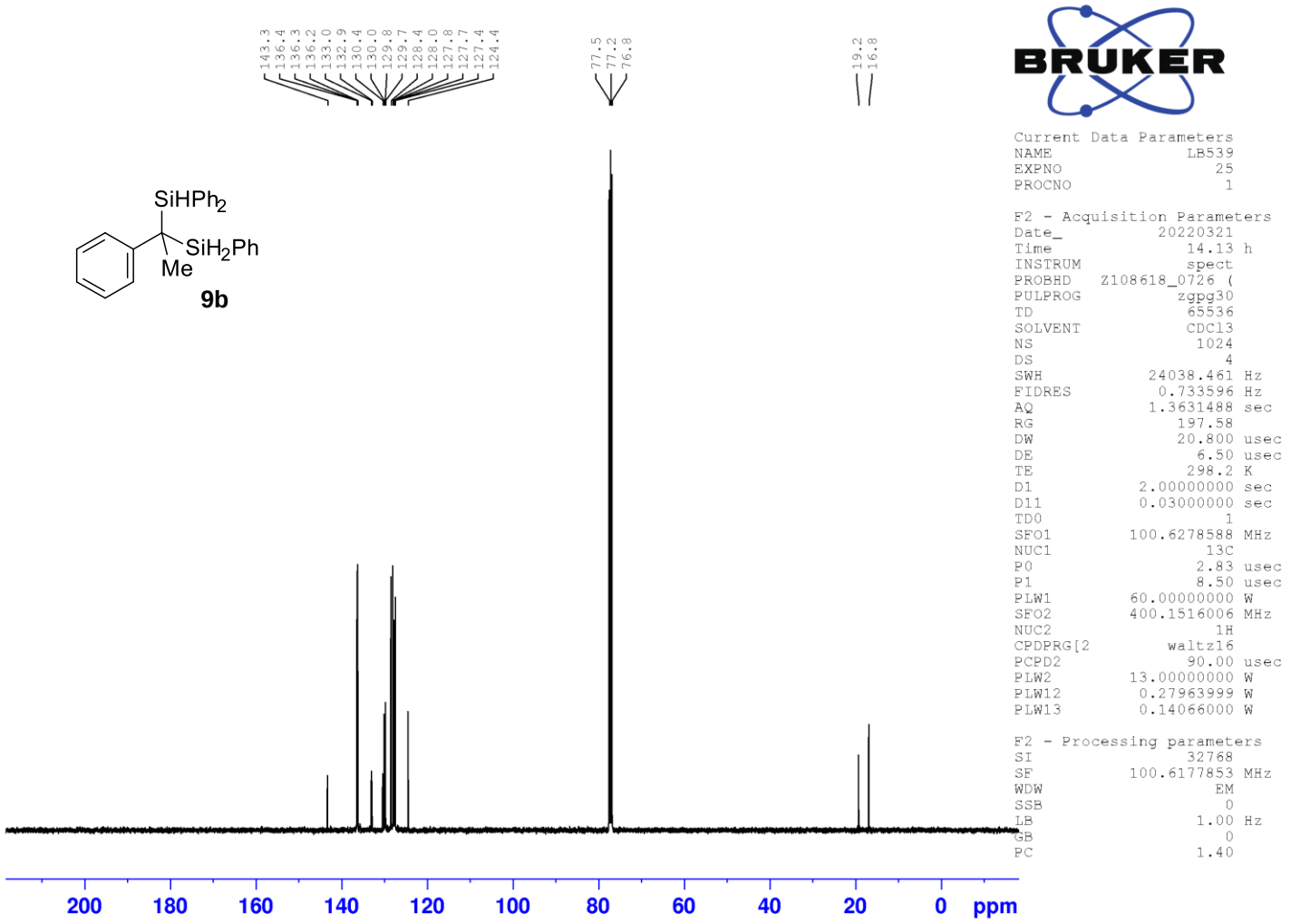
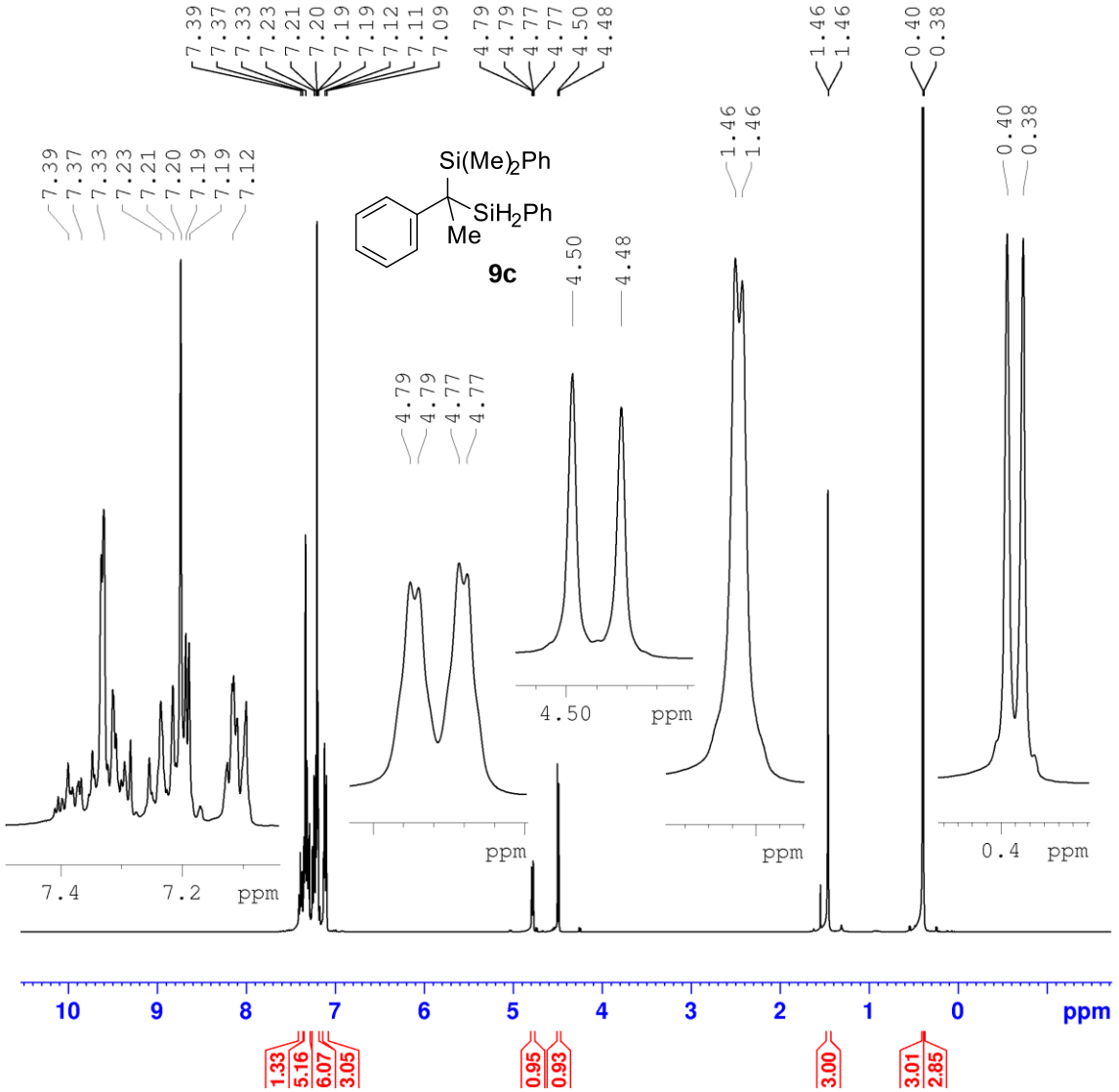
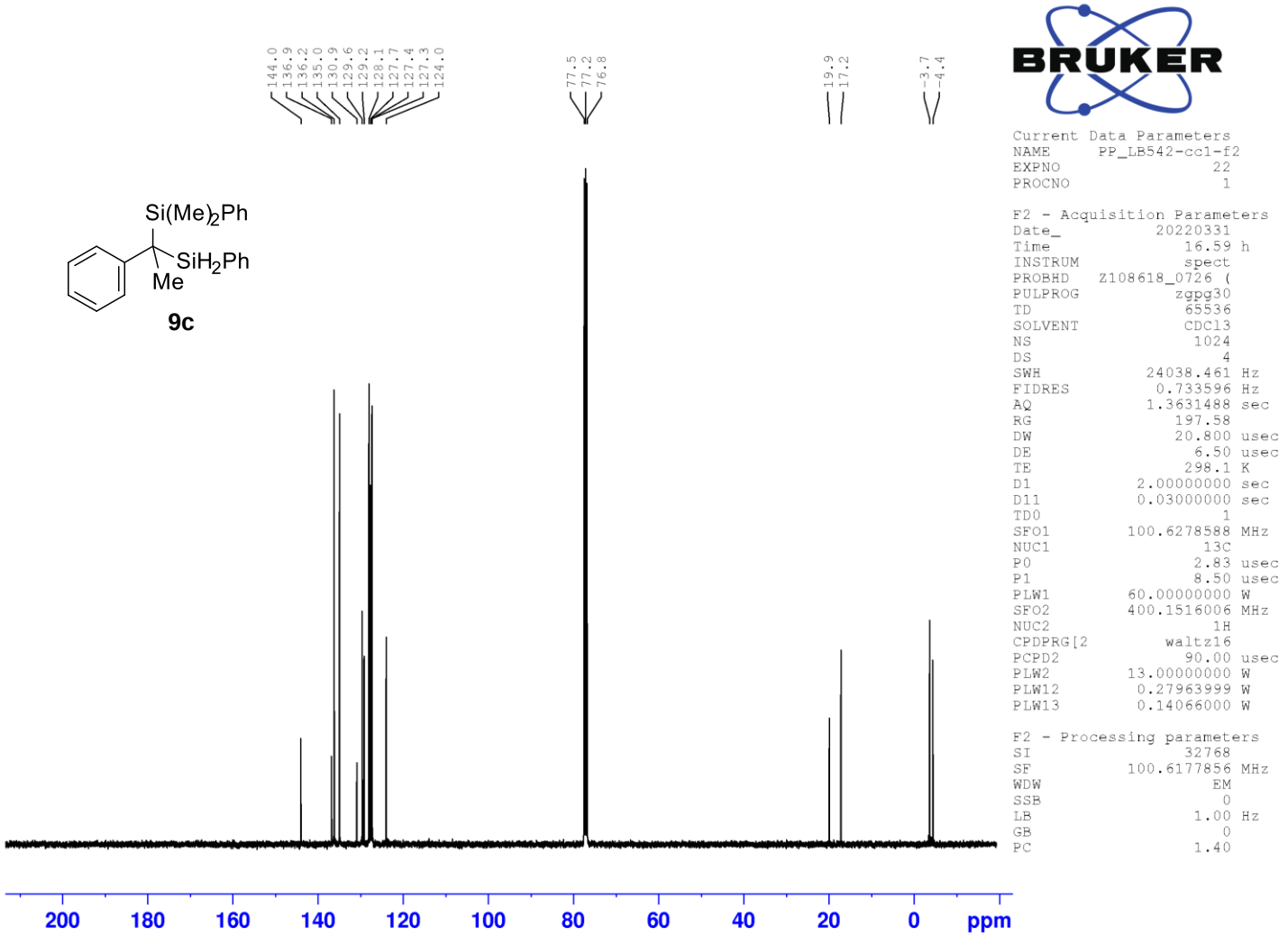
```
Current Data Parameters
NAME                  LB539
EXPNO                    24
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220321
Time                  9.40 h
INSTRUM              spect
PROBHD    Z108618_0726 (
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH               8012.820 Hz
FIDRES               0.244532 Hz
AQ                4.0894465 sec
RG                   128.09
DW                   62.400 usec
DE                    6.50 usec
TE                   298.1 K
D1             1.00000000 sec
TD0                      1
SFO1           400.1524711 MHz
NUC1                    1H
P0                    4.40 usec
P1                   13.20 usec
PLW1          13.00000000 W

F2 - Processing parameters
SI                   65536
SF             400.1500000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



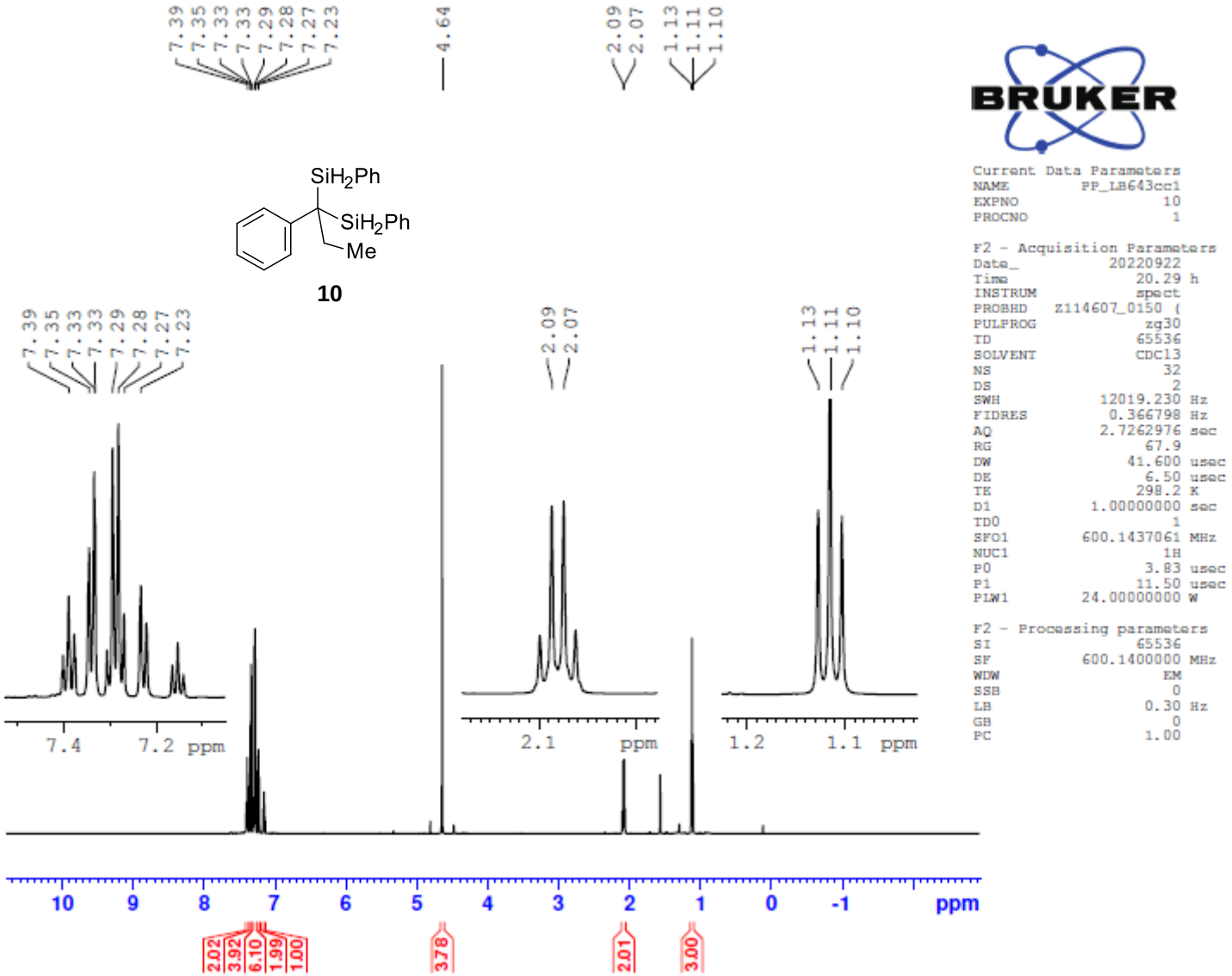

```
Current Data Parameters
NAME                  LB539
EXPNO                    25
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220321
Time                 14.13 h
INSTRUM                spect
PROBHD    Z108618_0726 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                1.3631488 sec
RG                   197.58
DW                   20.800 usec
DE                    6.50 usec
TE                   298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1
SFO1          100.6278588 MHz
NUC1                   13C
P0                    2.83 usec
P1                    8.50 usec
PLW1          60.00000000 W
SFO2          400.1516006 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2          13.00000000 W
PLW12          0.27963999 W
PLW13          0.14066000 W

F2 - Processing parameters
SI                    32768
SF            100.6177853 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



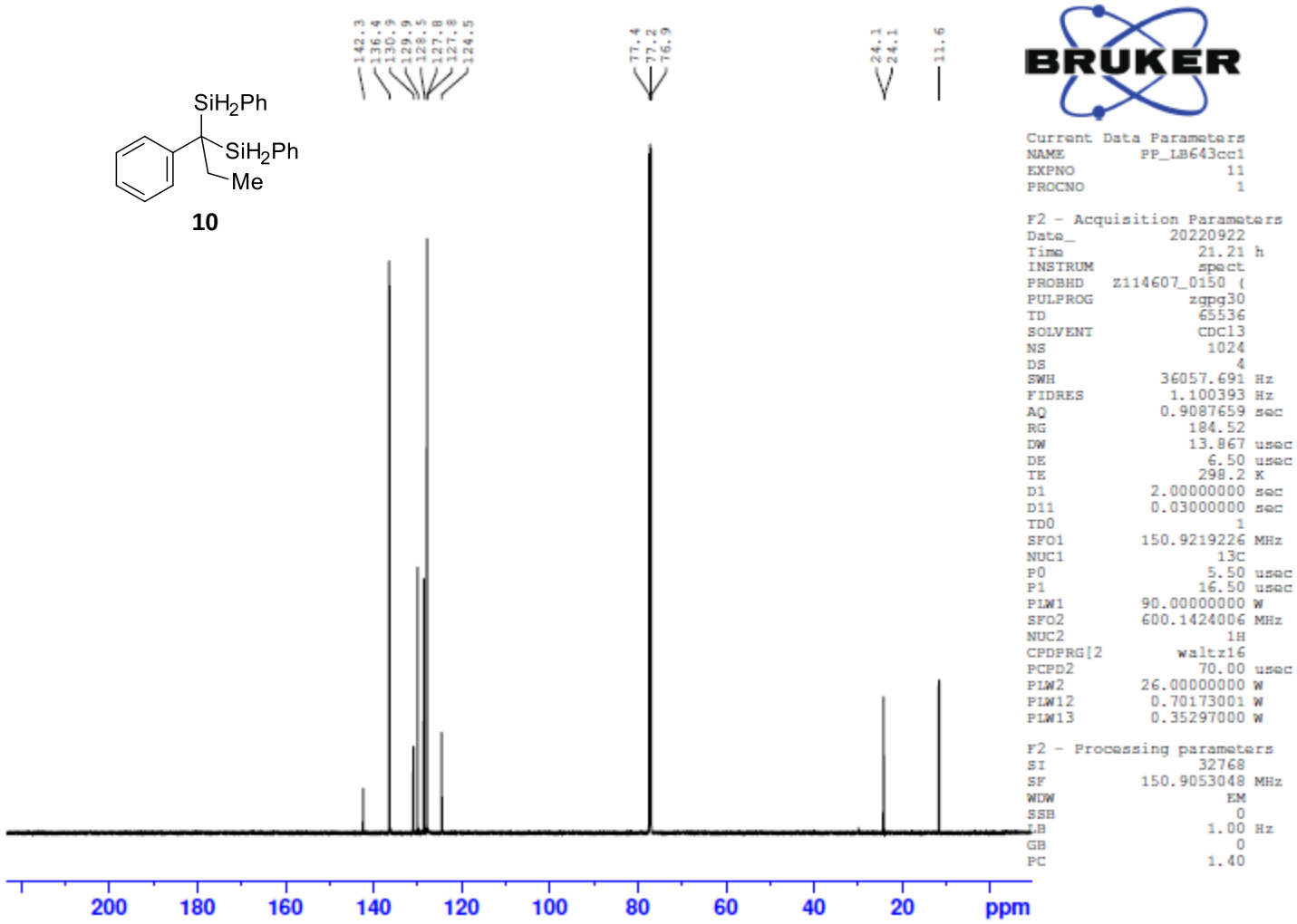

```
Current Data Parameters
NAME      PP_LB542-cc1-f2
EXPNO                  24
PROCNO                  1

F2 - Acquisition Parameters
Date_            20220331
Time                17.03 h
INSTRUM             spect
PROBHD    Z108618_0726 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH              8012.820 Hz
FIDRES           0.244532 Hz
AQ               4.0894465 sec
RG                  112.78
DW                  62.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.00000000 sec
TD0                     1
SFO1           400.1524711 MHz
NUC1                   1H
P0                   4.40 usec
P1                  13.20 usec
PLW1           13.00000000 W

F2 - Processing parameters
SI                  65536
SF             400.1500000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




```
Current Data Parameters
NAME      PP_LB542-cc1-f2
EXPNO                  22
PROCNO                  1

F2 - Acquisition Parameters
Date_           20220331
Time              16.59 h
INSTRUM             spect
PROBHD   Z108618_0726 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             1.3631488 sec
RG                197.58
DW                20.800 usec
DE                 6.50 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1        100.6278588 MHz
NUC1                13C
P0                 2.83 usec
P1                 8.50 usec
PLW1         60.00000000 W
SFO2        400.1516006 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2         13.00000000 W
PLW12         0.27963999 W
PLW13         0.14066000 W

F2 - Processing parameters
SI                32768
SF          100.6177856 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```




```
Current Data Parameters
NAME         PP_LB643cc1
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220922
Time              20.29 h
INSTRUM             spect
PROBHD    Z114607_0150 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH           12019.230 Hz
FIDRES            0.366798 Hz
AQ                2.7262976 sec
RG                   67.9
DW                  41.600 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.00000000 sec
TD0                    1
SFO1          600.1437061 MHz
NUC1                  1H
P0                   3.83 usec
P1                  11.50 usec
PLW1          24.00000000 W

F2 - Processing parameters
SI                 65536
SF            600.1400000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



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```
Current Data Parameters
NAME         PP_LB643cc1
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220922
Time              21.21 h
INSTRUM             spect
PROBHD   Z114607_0150 (
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           36057.691 Hz
FIDRES         1.100393 Hz
AQ            0.9087659 sec
RG               184.52
DW               13.867 usec
DE                6.50 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1        150.9219226 MHz
NUC1                13C
P0                 5.50 usec
P1                16.50 usec
PLW1         90.00000000 W
SFO2        600.1424006 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2         26.00000000 W
PLW12         0.70173001 W
PLW13         0.35297000 W

F2 - Processing parameters
SI                32768
SF          150.9053048 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

11. References

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