MECHANISTIC STUDIES OF THE SILYL-HECK REACTION

by

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I would like to thank Dr. Donald Watson for the opportunity to perform undergraduate research and for the constant guidance he has provided. I also wish to thank the Watson research group for their continuous assistance and advice throughout my undergraduate career. I am also grateful for fellowship support from the ACS Division of Organic Chemistry SURF Program, the Chemistry and Biochemistry Alumni Undergraduate Fellowship Program, the Undergraduate Research Program, and Mr. David Plastino. Lastly, I am tremendously thankful for the kind support of my family and friends, without whom this work would not have been possible.

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ABSTRACT

Mechanistic studies of the silyl-Heck reaction were performed. The precatalyst for the reaction was characterized by NMR and X-ray crystallography. NMR experiments were conducted to determine the viability of oxidative addition of the palladium complex across the Si–I bond of iodotrimethylsilane. Variable Temperature NMR experiments were used to confirm the existence of ligand dissociation equilibria between palladium phosphine complexes. VT NMR experiments were also used to determine productive intermediates in the silyl-Heck reaction. A side product formed in the reactions with iodotrimethylsilane was elucidated as a palladium hydride complex. This compound was prepared independently and characterized by NMR and X-ray crystallography. Studies were performed to determine the source of the palladium hydride complex and various sources of hydriodic acid were ruled out. Perdeuterated iodotrimethylsilane was synthesized and used in NMR experiments to rule out the possibility of palladium hydride formation by β-hydride elimination.

GENERAL EXPERIMENTAL DETAILS

Toluene, benzene, and Et_2O were dried on alumina according to published procedures. [1] Pentane was purchased in anhydrous septum sealed bottles and sparged with nitrogen before use. Iodotrimethylsilane, purchased from Aldrich or Gelest, was handled under nitrogen and stored over copper beads in a storage flask with a Teflon valve. *tert*-Butyldiphenylphosphine (*t*$BuPh_2P$) was purchased commercially or prepared according to literature procedures.[2] The dry crystalline ligand was found to be air stable; exposing *t*$BuPPh_2$ to air for one month at RT only resulted in trace oxidation by ^{31}P NMR. All hot glassware was oven dried for a minimum of four hours. Reactions were heated and stirred in temperature-controlled oil baths. All other substrates and reagents were purchased in highest analytical purity from commercial suppliers and used as received. "Double manifold" refers to a standard Schlenk-line gas manifold equipped with nitrogen and vacuum (ca. 100 mtorr).

Chapter 1

INTRODUCTION TO THE SILYL-HECK REACTION

Cross coupling reactions mediated by transition metal catalysts constitute important methods for the construction of chemical bonds in organic synthesis.[3] Palladium catalysts are particularly useful in their ability to enact these transformations, and various protocols have been developed that utilize these reagents.[4] The Heck reaction was the first of these to be developed, and employs a palladium catalyst to couple activated (pseudo)halides with alkenes (Figure 1). The Heck reaction provides a robust and versatile approach to carbon-carbon bond formation, and has many applications in the regio- and stereoselective construction of diverse carbon frameworks.[4]

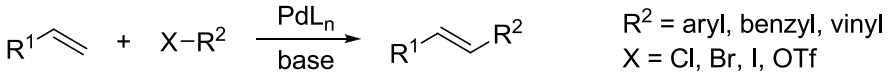


Figure 1 Heck Reaction

Organosilanes are ubiquitous reagents in organic chemistry due to their low cost, low toxicity, high stability, and versatility.[5] The main applications of vinyl and allyl silanes are as nucleophiles in organic synthesis. The synthetic importance of vinyl silanes is mainly as partners in Hiyama cross-coupling reactions.[6] The primary

applications of allyl silanes include allylation and crotylation reactions.[7] Examples of Hiyama coupling[8] and Hosomi-Sakurai crotylation[9] reactions are shown in Figure 2.

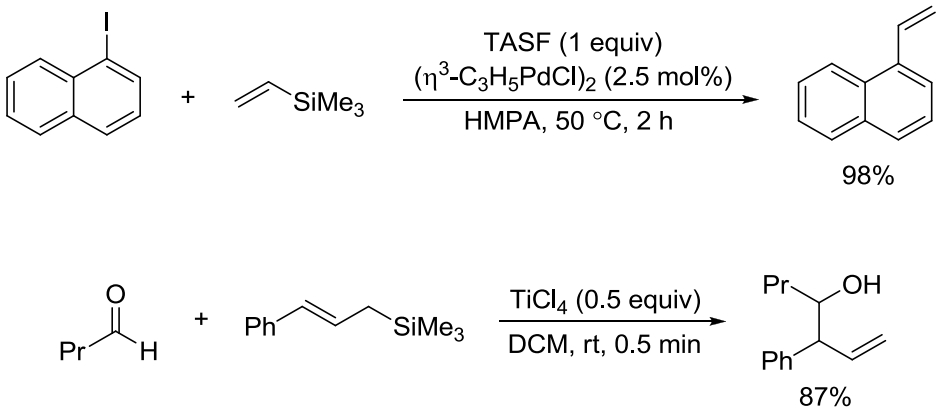


Figure 2 Synthetic Utility of Vinyl and Allyl Silanes

The incorporation of silicon-containing moieties is thus an important task in organic synthesis. The Watson group has thus developed a protocol for the palladium catalyzed silylation of styrenes as an efficient route to (*E*)-vinyl silanes using iodotrimethylsilane as a coupling partner (Figure 3).[10] In this reaction, the palladium bis(phosphine) catalyst is first generated *in situ* and undergoes reactivity analogous to the Heck reaction to achieve carbon–silicon bond formation.

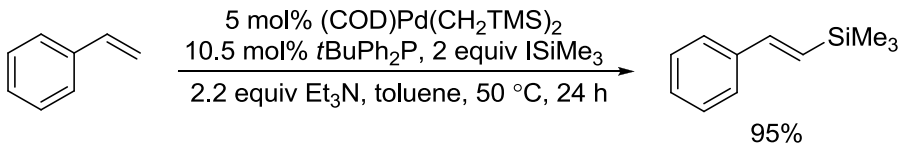


Figure 3 Silyl-Heck Reaction to Form Vinyl Silanes

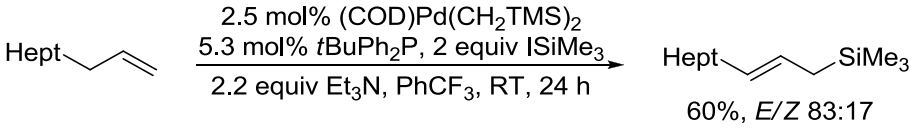


Figure 4 Silyl-Heck Reaction to Form Allyl Silanes

Depending on the existence of β-hydrogens in the substrate, this reaction is capable of efficiently and selectively delivering either vinyl or allyl silanes from terminal alkenes. This is an indication that β-hydride elimination is a fundamental step of this transformation. It is believed that allyl/vinyl selectivity in these reactions is due to steric influences. For substrates lacking substitution at the γ position of the alkene, the bulky steric characteristics of the trimethylsilyl group cause β-hydride elimination to occur towards the opposite side, thereby selectively giving allyl silanes.

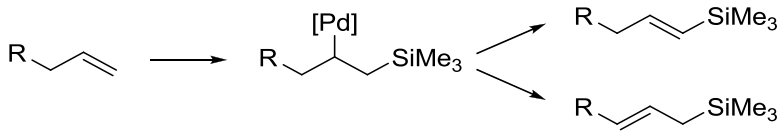


Figure 5 Role of β-Hydride Elimination in Determining Vinyl or Allyl Silane Formation

This hypothesis is supported by findings reported by the Watson group.[10] For substrates with increased substitution at the γ position of the alkene, the steric environments of the two sides of the alkyl chain are more similar. In this case, β-hydride elimination is found to occur in both directions. In Figure 6, the Silyl-Heck reaction of 4-phenyl-1-butene is compared to that of the same compound with a silyl

protected alcohol at the γ position. The silyl-Heck reaction with 4-phenyl-1-butene gives the allyl silane product with an E-allyl to Z-allyl ratio of 87:13, but no vinyl product is observed. When a similar substrate with increased substitution is used, the E-allyl and E-vinyl isomers of product are formed in a 68:32 ratio.

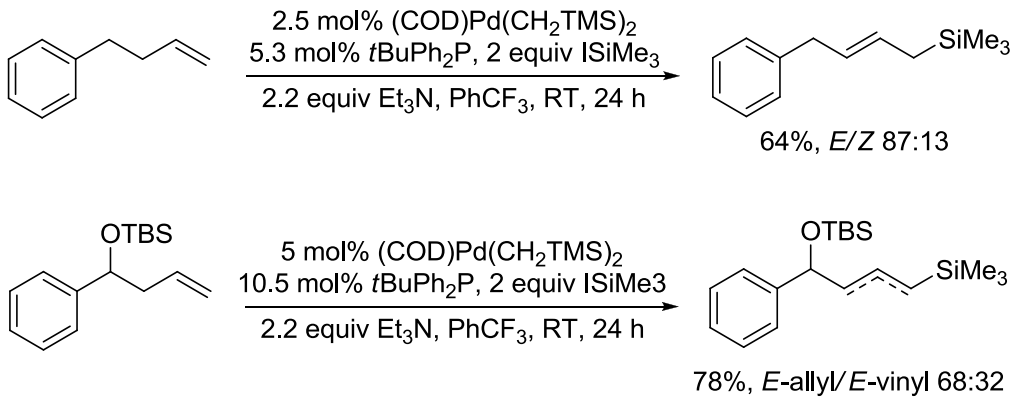


Figure 6 Effect of Substrate Substitution on Product Isomer Distribution

The *tert*-butyldimethylsilyl group is a sterically encumbered moiety that leads to formation of vinyl silane. The formation of both silane isomers can be attributed to the similar steric characteristics at both possible sites of β-hydride elimination. The increased steric bulk at the γ position also causes Z-isomer to not form as part of the product isomer distribution in the silyl-Heck reaction.

Chapter 2

MECHANISM OF THE SILYL-HECK REACTION

In an effort to improve the efficiency and better understand the mechanistic details of the silyl-Heck reaction, elementary steps in the putative catalytic cycle were studied. Although similar mechanisms have been proposed in the literature,[11] to date no mechanistic studies have been performed. The mechanistic proposals in the literature are based on the well-known mechanism of the Heck reaction.

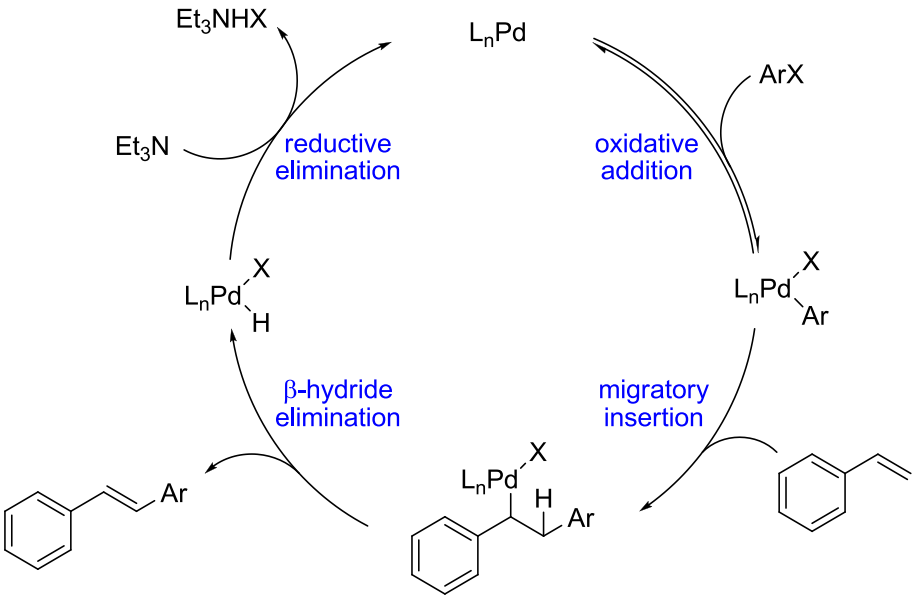


Figure 7 Catalytic Cycle of the Heck Reaction

The Heck reaction follows the catalytic pathway shown in Figure 7. The palladium catalyst first undergoes oxidative addition to an activated carbon–halogen bond, such as an aryl–halogen bond. Alkenes can subsequently perform migratory insertion into the palladium–carbon bond. This intermediate will then undergo β-hydride elimination to furnish the cross-coupled product. Elimination also forms a palladium hydride intermediate, which through reductive elimination regenerates the palladium catalyst.

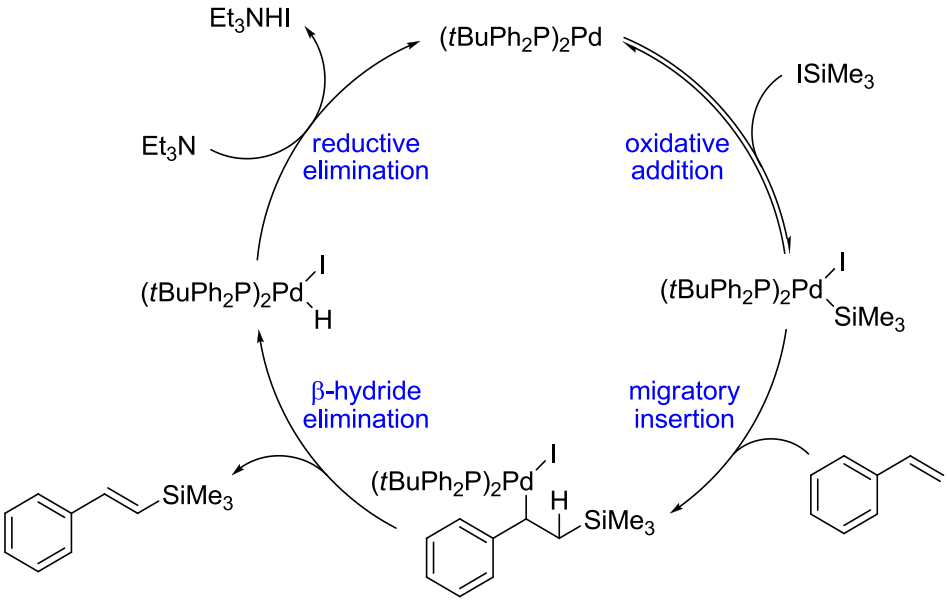
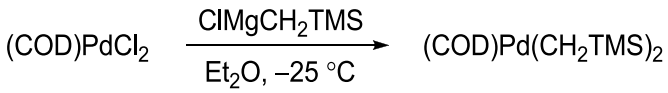


Figure 8 Putative Catalytic Pathway for the Silyl-Heck Reaction

The silyl-Heck reaction is believed to proceed in a manner that is mechanistically analogous to the Heck reaction (Figure 8). The palladium catalyst is capable of performing oxidative addition to the silicon–iodine bond of

iodotrimethylsilane. Similar to the Heck reaction, an alkene can insert into the palladium–silicon bond. After insertion, β-hydride elimination furnishes silylated product and a palladium hydride complex. The palladium complex undergoes reductive elimination to form palladium(0), which then reenters the catalytic cycle.

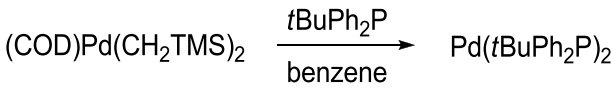
I began to study the mechanism of the silyl-Heck reaction by synthesizing what was then believed to be the active catalyst for the reaction. The synthesis of the palladium precatalyst was a procedure developed in our laboratory, similar to published procedures.[12]



Synthesis of Palladium Precatalyst. A Schlenk flask equipped with a stir bar was attached to a double manifold, flame dried, and allowed to cool to room temperature under vacuum. The vessel was refilled with nitrogen and charged with (COD)$PdCl_2$ (2.0 g, 7.0 mmol). The septum was replaced, and the flask was evacuated and refilled with nitrogen three times. Et_2O (80 mL) was added. The suspension was cooled to –25 °C and (trimethylsilyl)methylmagnesium chloride (16.12 mL, 1.0 M in Et_2O) was added dropwise with rigorous stirring. The reaction was allowed to stir at –25 °C for 1.5 h and quenched with acetone (0.6 mL). After stirring for five minutes, the septum was replaced with a glass stopper under positive nitrogen pressure, and the solvent was evaporated to dryness at –25 °C *in vacuo*. The flask was refilled with nitrogen, and the glass stopper was replaced with a septum. Pentane (40 mL) was added, the

resulting suspension was shaken at –25 °C, and the pentane layer was transferred via cannula filtration to a second Schlenk flask (dry, nitrogen filled) at 0 °C. This extraction procedure was repeated with an additional 40 mL of pentane. The combined extracts were then evaporated to dryness *in vacuo* at 0 °C to yield 2.72 g (quantitative) of the palladium precursor as a white solid. The compound can be handled briefly at RT and is air stable, but decomposes at RT after about 1 h. The compound can be stored indefinitely at temperatures at or below 0 °C.

The palladium bis(phosphine) complex could be readily prepared from the precatalyst, a reaction that is presumed to occur *in situ* in the silyl-Heck reaction.



Synthesis of Palladium Bis(phosphine) Complex. In a glovebox, (COD)Pd(CH_2TMS)$_2$ (0.30 g, 0.77 mmol), *t*BuPh_2P (0.37 g, 1.54 mmol), and benzene (5.0 mL) were added to a 1 dram vial. The reaction was stirred for 7 h, at which point the solution was filtered through glass wool and dried overnight to give a brown solid (0.458 g, quantitative). X-ray quality crystals were obtained by slow evaporation of a benzene solution over 7 d.

A drastic downfield shift in the ^{31}P NMR spectrum indicated ligation of the phosphine to the palladium. The ^{1}H NMR also showed the disappearance of peaks corresponding to cyclooctadiene and a modest downfield shift. X-ray quality crystals

were also produced, providing further evidence of the synthesis of the palladium bis(phosphine) complex.

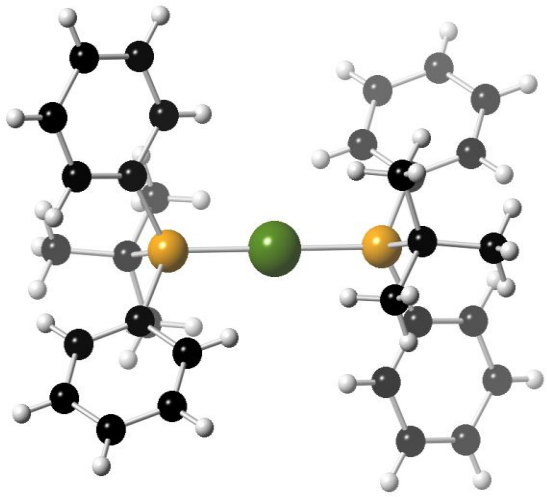


Figure 9 Crystal Structure of Palladium Bis(phosphine) Complex

Notably, the palladium bis(phosphine) complex functions as an effective catalyst in the silyl-Heck reaction. No difference in yield was observed between reactions using the preformed catalyst and those with catalyst generation *in situ*. This suggests that the palladium bis(phosphine) complex is an effective precatalyst in this reaction.

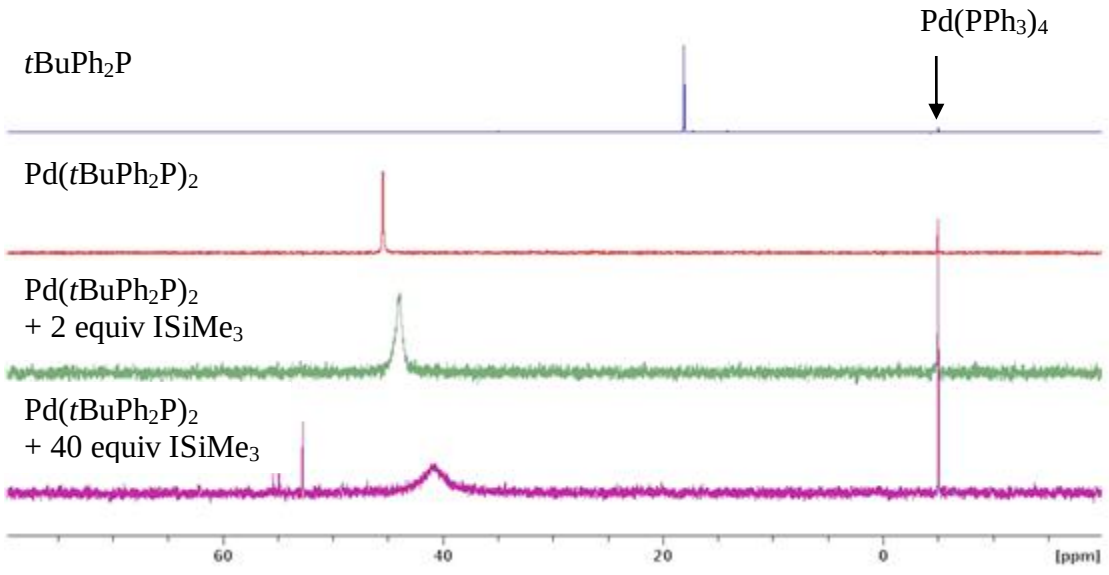


Figure 10 ^{31}P NMR Experiment of Palladium Bis(phosphine) with Added Iodotrimethylsilane

Once the palladium bis(phosphine) complex was fully characterized, the oxidative addition step within the proposed catalytic pathway was probed. ^{1}H and ^{31}P NMR analysis of stoichiometric reactions were used to determine the viability of this process. Triphenylphosphine was used as an internal standard in these experiments, with the shift defined as −5 ppm. An upfield shift is observed when iodotrimethylsilane is added to the palladium bis(phosphine) complex. This was indicative of the appearance of one or more new peaks corresponding to the oxidative addition product or other intermediates. It is believed that a single peak is observed instead of many because the interconversion of complexes may be rapid on an NMR timescale, resulting in an average of the peaks in the NMR spectrum. In order to

determine the structure of the compounds formed in this reaction, Variable Temperature NMR would be used in later experiments.

^{31}P NMR Experiment of Palladium Bis(phosphine) with Added Iodotrimethylsilane. In a glovebox, Pd(*t*BuPh$_2$P)$_2$ (0.025 g, 0.042 mmol) and benzene (1.00 mL) were added to an NMR tube. The sample was inverted until the solution was homogeneous and a flame sealed pipet tip containing triphenylphosphine solution in benzene was added to the NMR tube. The sample was taken outside a glovebox, analyzed by ^{31}P NMR, and brought back into a glovebox. Iodotrimethylsilane (12.1 μL, 0.084 mmol, 2.0 equiv) was added to the NMR tube. The sample was analyzed by ^{31}P NMR again and brought back into a glovebox. Iodotrimethylsilane (229 μL, 1.60 mmol, 38 equiv) was added to the NMR tube to bring the total equivalency of ISiMe$_3$ to 40 equivalents. The sample was analyzed a final time by NMR.

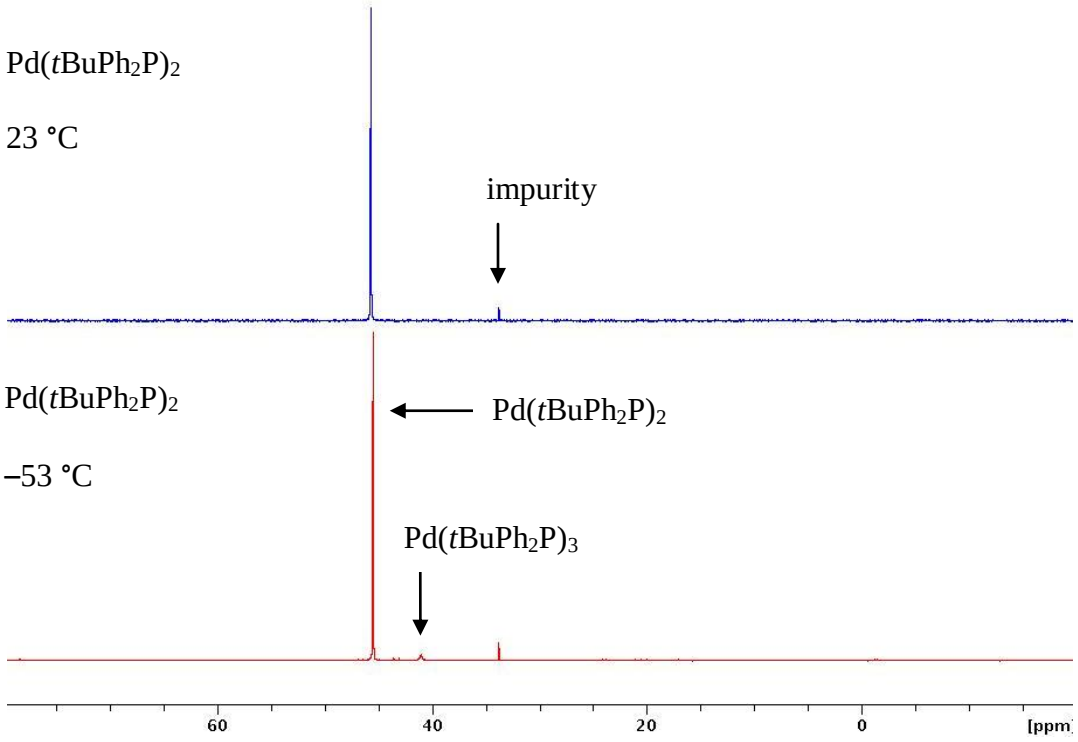


Figure 11 ^{31}**P Variable Temperature NMR Experiment of Palladium Bis(phosphine) Complex**

Variable Temperature NMR experiments were also carried out on the palladium bis(phosphine) complex. At room temperature, the ^{31}P NMR shows only one peak (Figure 11, blue spectrum). However, at lower temperatures, this peak resolves into a major and minor peak (Figure 11, red spectrum). It was hypothesized that the minor peak corresponded to the palladium tris(phosphine) complex, Pd(*t*BuPh$_2$P)$_3$. In order to test this supposition, NMR experiments were conducted in which phosphine was added to the preformed palladium bis(phosphine) complex.

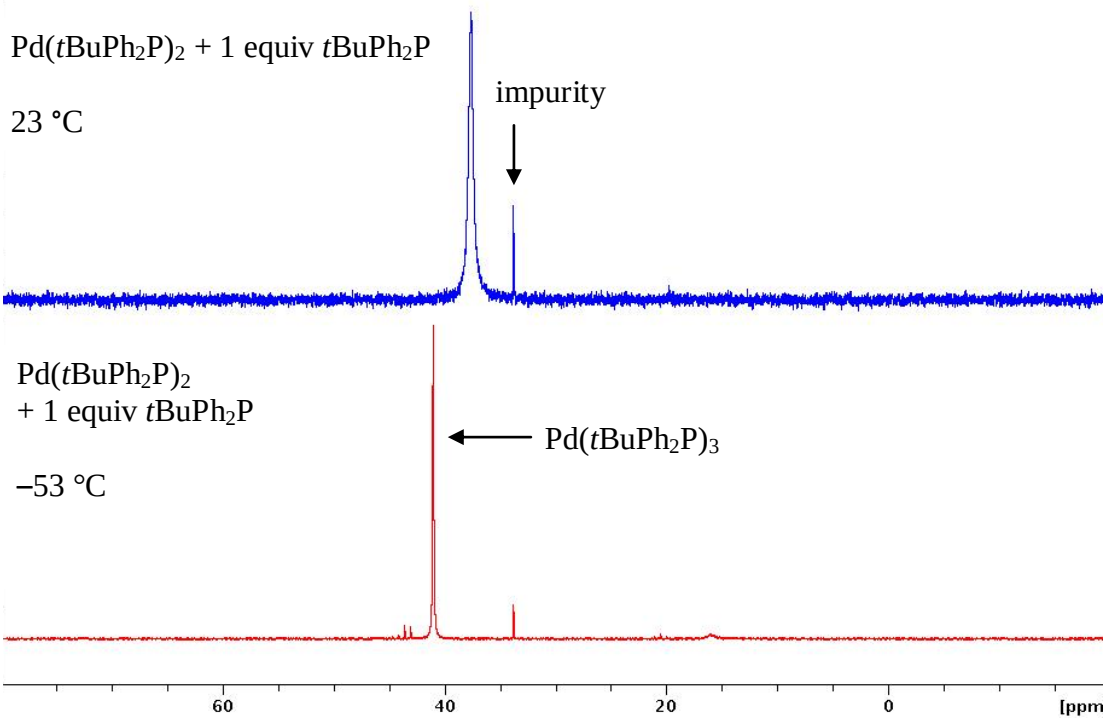


Figure 12 **^{31}P NMR Variable Temperature NMR Experiment of Palladium Bis(phosphine) with Added Phosphine**

Upon adding an equivalent of phosphine to the palladium complex, an upfield shift was observed at room temperature. Analysis of this solution at low temperature resulted in a single peak with the same chemical shift as the minor peak from the analysis of the palladium bis(phosphine) complex. This showed that the peak corresponds to the palladium tris(phosphine) complex. Figure 13 shows a direct comparison of the low temperature spectra of the palladium bis(phosphine) complex without and with added phosphine. The figure clearly shows that the minor peak of the low temperature spectrum of the bis(phosphine) complex overlaps with the major peak of the experiment with added phosphine.

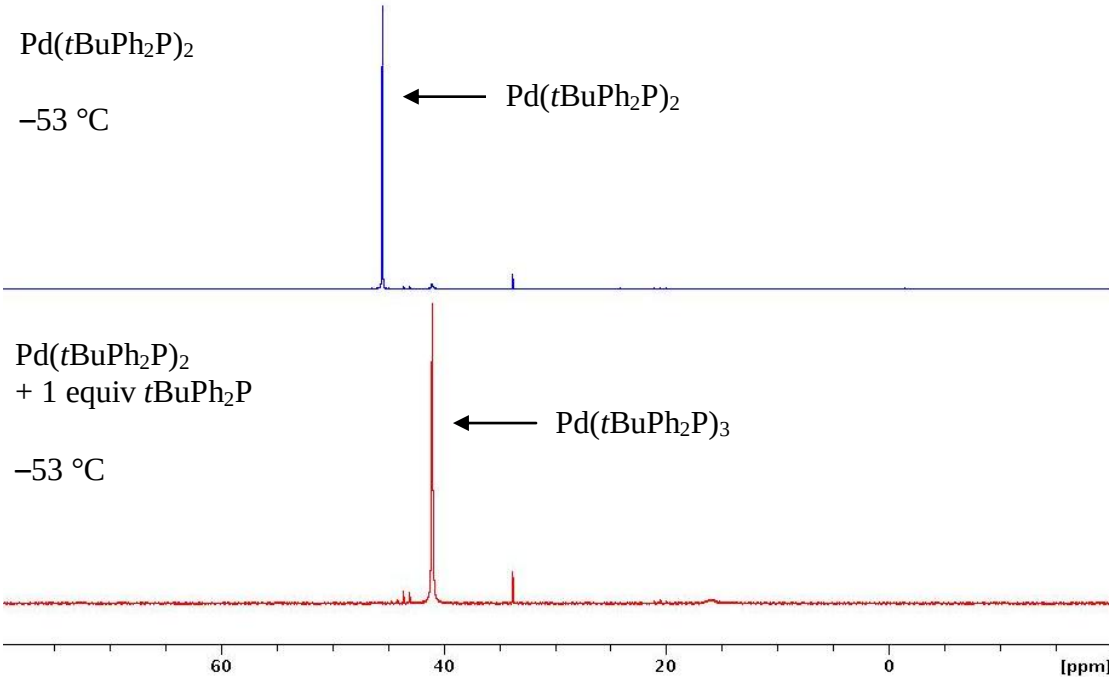
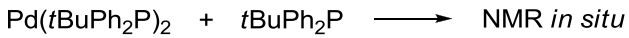


Figure 13 **^{31}P NMR Variable Temperature NMR Experiment of Palladium Bis(phosphine) Complex with Added Phosphine**



^{31}P NMR Experiment of Palladium Bis(phosphine) with Added Phosphine. In a glovebox, Pd(*t*BuPh$_2$P)$_2$ (0.025 g, 0.042 mmol, 1.0 equiv) and benzene (1.00 mL) were added to an NMR tube. A second sample was prepared with Pd(*t*BuPh$_2$P)$_2$ (0.025 g, 0.042 mmol, 1.0 equiv), *t*BuPh$_2$P (0.010 g, 0.042 mmol, 1.0 equiv) and benzene (1.00 mL) in another NMR tube. The samples were inverted until the solution was homogeneous. The samples were taken outside a glovebox and analyzed by ^{31}P NMR at various temperatures.

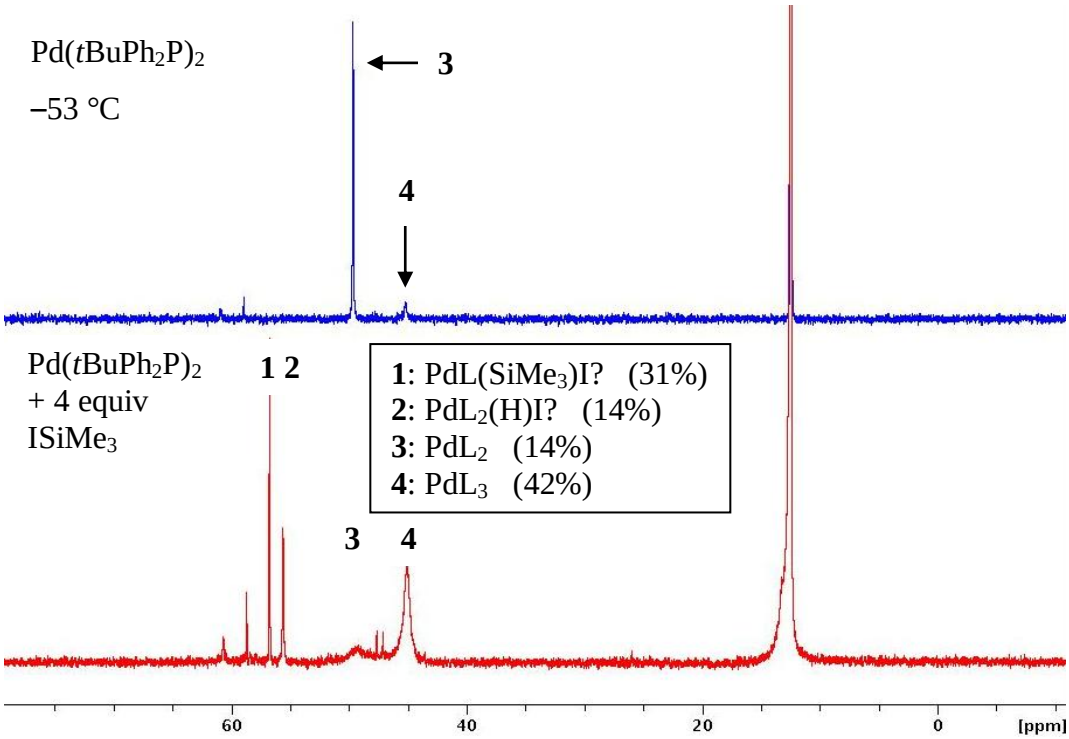


Figure 14 **^{31}P Variable Temperature NMR Experiment of Palladium Bis(phosphine) Complex with Added Iodotrimethylsilane**

Variable Temperature NMR experiments were then conducted on the palladium bis(phosphine) complex with added iodotrimethylsilane. During the ^{31}P Variable Temperature NMR experiments, a flame-sealed internal standard of *t*Bu$_2$MeP was added to the sample. This phosphine was chosen for its low freezing point so that it would not solidify at lower temperatures. The spectra were shifted such that the peak for tBu$_2$MeP was at 12.5 ppm.[13]

The major products of the reaction are believed to be the oxidative addition product, the palladium hydride complex, and the palladium bis- and tris(phosphine) complexes. Figure 15 outlines the putative pathway for formation of these

compounds. As was discovered in previous experiments, there exists a dissociative equilibrium between the palladium bis- and tris(phosphine) complexes. This dissociative mechanism may also account for the formation of a mono(phosphine) palladium complex. The mono(phosphine) complex is then capable of performing oxidative addition into the silicon–iodide bond of iodotrimethylsilane. Formation of the palladium hydride complex will be discussed in the next chapter.

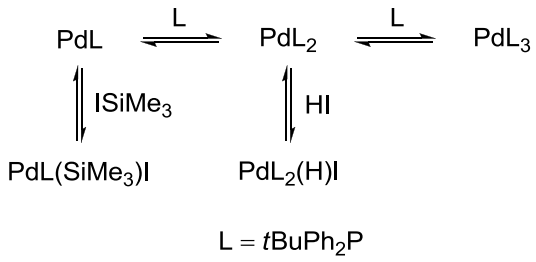


Figure 15 Reaction Equilibria for Palladium Bis(phosphine) and Iodotrimethylsilane Solution

Oxidative addition is not believed to occur to the palladium bis(phosphine) complex due to the sterically encumbered nature of the hypothetical product. The combination of two bulky phosphine ligands with a trimethylsilyl moiety in a square planar arrangement is an extremely sterically demanding complex that is likely to be high in energy. Oxidative addition is therefore believed to occur to the mono(phosphine) palladium complex. This hypothesis is supported by the findings of a colleague, Jesse M^{c}Atee, who has isolated and characterized an oxidative addition product with one phosphine ligated to palladium. The crystal structure, shown in

Figure 16, uses a slightly more electron rich phosphine ligand and provides further confirmation for the viability of the oxidative addition step.

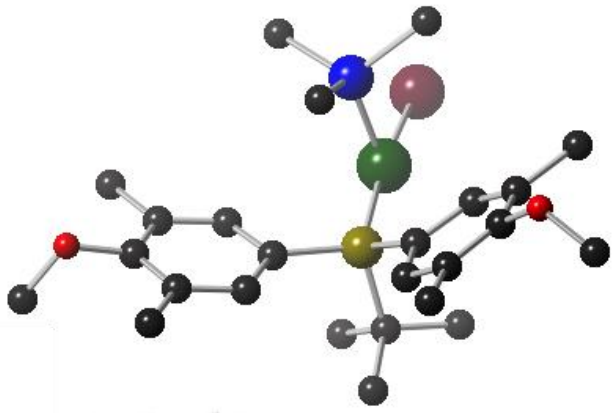


Figure 16 Oxidative Addition Product from Mono(phosphine) Palladium

$$Pd(t\text{BuPh}_2\text{P})_2 + \text{ISiMe}_3 \longrightarrow \text{NMR } \textit{in situ}$$

^{31}P Variable Temperature NMR Experiment of Palladium Bis(phosphine) with Iodotrimethylsilane. In a glovebox, $Pd(t\text{BuPh}_2\text{P})_2$ (0.021 g, 0.036 mmol) and toluene-d_8 (1.00 mL) were added to an NMR tube. The sample was inverted until the solution was homogeneous and a flame sealed pipet tip containing $t\text{Bu}_2\text{MeP}$ was added to the NMR tube. The sample was taken outside a glovebox, analyzed by ^{31}P NMR at various temperatures, and brought back into a glovebox. Iodotrimethylsilane (13.6 μL, 0.144 mmol, 4.0 equiv) was added to the NMR tube and the sample was analyzed by ^{31}P NMR again at various temperatures.

Chapter 3

PALLADIUM HYDRIDE FORMATION

The NMR experiments that were performed provided strong evidence for ligand exchange and oxidative addition mechanisms. We also sought to understand the formation of palladium hydride complex. The peak height for the complex was observed to increase after adding iodotrimethylsilane and drying the reaction. Through repeated addition of iodotrimethylsilane to the palladium bis(phosphine) complex and drying, I was able to isolate this compound. Indeed, the ^{31}P NMR shift of the isolated compound was responsible for the peak in the room temperature NMR experiments as well. The ^{1}H NMR looked similar to the bis(phosphine) complex, but contained another resonance: a triplet at –10.2 ppm.

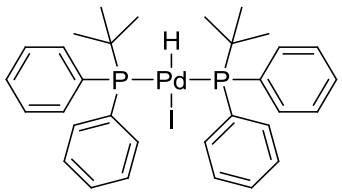
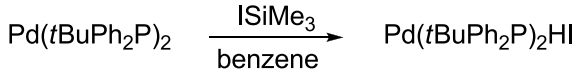


Figure 17 Palladium Hydride Complex



Synthesis of Palladium Hydride Complex. In a glovebox, Pd(*t*BuPh$_2$P)$_2$ (0.150 g, 0.254 mmol, 1 equiv), benzene (1.00 mL), and Me$_3$SiI (145 μL, 4 equiv) were added to a 1 dram vial and stirred for 4 h. The solution was then filtered through glass wool and dried overnight. Me$_3$SiI (145 μL, 4 equiv) and benzene (1.00 mL) were again added. The reaction was stirred for 48 h and then dried overnight. The resulting solid was washed with pentane (3 mL), taken up in benzene, filtered, and dried. X-ray crystals were obtained after 4 d by layering pentane on a benzene solution in an NMR tube.

Crystals were again prepared for X-ray analysis that confirmed the structure of the palladium complex. As one would expect, the phosphine ligands adopt a *trans* conformation due to the large steric nature of these substituents.

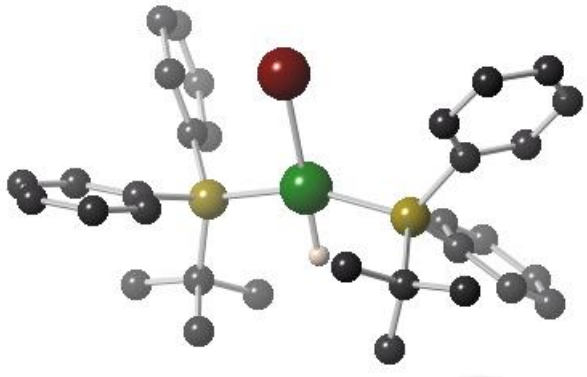


Figure 18 Crystal Structure of Palladium Hydride Complex

The palladium hydride complex was being formed through simple addition of iodotrimethylsilane to the palladium precatalyst. We sought to determine the pathway of formation of this compound to understand more intimate details of the mechanism. The mode of formation of this complex was also deemed important in case it would become a significant byproduct or otherwise interfere with the selectivity or efficiency of the silyl-Heck reaction.

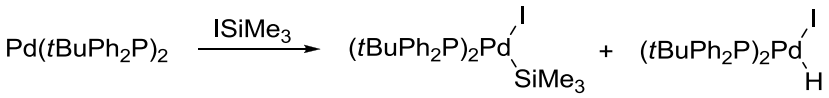


Figure 19 Generation of Palladium Hydride Complex

One straightforward pathway to the production of the palladium hydride complex is oxidative addition of the palladium bis(phosphine) complex into hydriodic acid. The relatively small amount of palladium hydride complex generated could thus be due to a minute amount of hydriodic acid in the reaction.

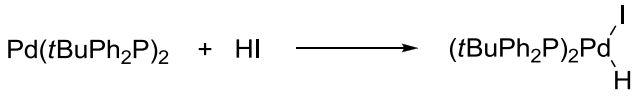


Figure 20 Addition of HI to Palladium Bis(phosphine) Complex

Thus, we sought to determine the possible sources of hydriodic acid in the reaction. The first possibility was that hydriodic acid was present in the iodotrimethylsilane. However, when freshly vacuum transferred iodotrimethylsilane was used in stoichiometric reactions, the palladium hydride complex still formed. This indicated that hydriodic acid contamination of the iodotrimethylsilane was not responsible for formation of the palladium hydride complex.

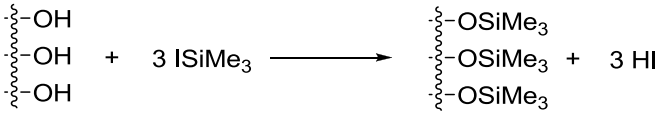


Figure 21 Silylation of Glassware by Iodotrimethylsilane

Another possible source of hydriodic acid that was explored was the glassware itself. At the molecular level, glassware contains pendant hydroxyl groups. In the presence of a reactive electrophile such as iodotrimethylsilane, the nucleophilicity of this functional group is capable of displacing a halogen, thus forming hydriodic acid *in situ*. In order to determine if this reaction was releasing hydriodic acid that was forming the palladium hydride complex, silylation of the glassware prior to the reaction was explored. When I used silylated glassware in the reactions, the formation of the palladium hydride complex continued to be observed. This indicated that silylation of glassware may not the source of hydriodic acid in the experiment.

Chapter 4

NMR STUDIES WITH DEUTERATED ANALOGS

After ruling out sources of hydriodic acid in the reaction, other mechanistic pathways to generate the palladium hydride complex that was observed in the NMR experiments were probed. Another possible source of palladium hydride is β-hydride elimination of the palladium silane intermediate as shown in Figure 22.

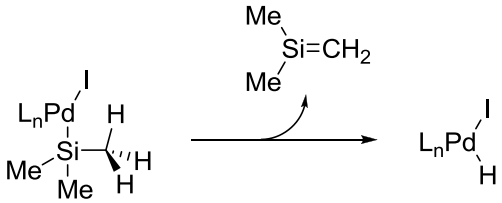


Figure 22 β-Hydride Elimination to form Palladium HI Complex

This study took advantage of the fact that iodotrimethylsilane is the proton source for formation of the palladium hydride. In order to probe this mechanistic possibility, we sought to synthesize the perdeuterated analog of iodotrimethylsilane. Therefore, if elmination was the active pathway for formation of the palladium hydride complex, then reaction of the palladium bis(phosphine) complex with deuterated iodotrimethylsilane would yield the palladium deuteride complex. As before, the ^{1}H NMR spectrum would contain an indicative resonance as a triplet at –

10.2 ppm. If the product of this reaction lacked this peak in the ^{1}H NMR spectrum, but it appeared by ^{2}H NMR, it was reasoned this would be a strong indication that palladium hydride complex formation is due to β-hydride formation.

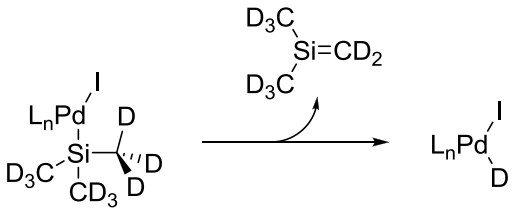
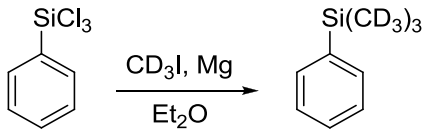


Figure 23 Theorized β-Hydride Elimination to Form Palladium Deuteride Complex

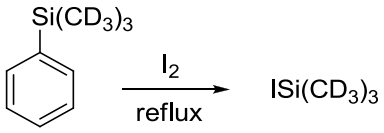
We thus set out to prepare perdeuterated iodotrimethylsilane according to literature procedures.[14] The synthetic route to this compound involves a Grignard addition of iodomethane-d_3 to trichlorophenyl silane. Once the silane is methylated, it can be refluxed with iodine to cleave the phenyl group and install the iodide. The perdeuterated compound can then be distilled from antimony to give purified product.



Synthesis of Trimethylphenylsilane-d_9. An oven-dried 3-neck 250 mL round bottom flask equipped with stir bar and reflux condenser was brought into a glovebox and magnesium shavings (3.66 g, 150.7 mmol, 3.85 equiv) were added. The system

was closed with septa, brought out of a glovebox, and put under nitrogen on a manifold. Ether (70 mL) and CD_3I (8.04 mL, 129.2 mmol, 3.30 equiv) were added and the solution was allowed to cool to room temperature. The solution was then cooled to 0 °C and a solution of $PhSiCl_3$ (6.27 mL, 39.15 mmol, 1 equiv) in Et_2O (30 mL) was added via cannula and the solution was stirred overnight. Water (45 mL) was added very slowly and the solution was filtered through glass wool, extracted with Et_2O (40 mL). The organic layer was washed with water (2 x 40 mL) and brine (40 mL), dried over $MgSO_4$, and the solvent was removed via rotary evaporation to give a pale yellow oil (5.78 g, 93%).

The methylation of the trichlorosilane with deuterated iodomethane was replicated. The Grignard reaction proceeded smoothly and was readily scalable. The second step of the sequence involves refluxing the methylated silane in iodine. The perdeuterated iodotrimethylsilane was then distilled from antimony in low yield.



Synthesis of Iodotrimethylsilane-d_9. An oven-dried 15-mL 3-neck round bottom flask equipped with stirbar and reflux condenser was attached to a double manifold and allowed to cool under vacuum. I_2 (5.57 g, 22.0 mmol, 1.1 equiv) was added and the system was purged with N_2 three times. $PhSiMe_3$ (3.18 g, 20.0 mmol, 1.0 equiv) was then added and the system was heated to 165 °C for 29 h. The solution was then

cooled to room temperature and transferred to an oven-dried 10-mL round bottom flask containing Sb (0.50 g, 4.10 mmol, 0.20 equiv). The solution was then distilled at 165 °C into a high pressure reaction vessel to give a clear liquid (0.44 g, 11% yield). The solution was immediately taken into a glovebox and put over copper beads.

The perdeuterated iodotrimethylsilane was synthesized in low yield, and could then be used in NMR experiments. When perdeuterated iodotrimethylsilane was reacted with the palladium bis(phosphine) complex, the palladium hydride complex and *not* the palladium deuteride complex was formed. This was a clear indication that β-hydride elimination was not the active mechanism for generation of the palladium hydride in the original experiments. As the palladium hydride was not produced by β-hydride elimination, it is thought that the proton source was from silylation of the glassware. Although the reactions run using silylated J. Young NMR tubes produced a small amount the palladium hydride complex, it is believed to have come from silylation of pipets and other glassware used to manipulate the material.

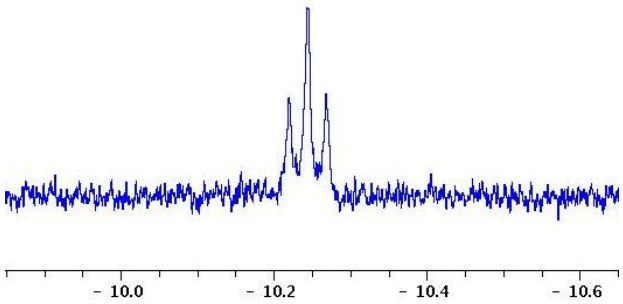


Figure 24 Triplet Indicating Palladium Hydride Complex Formation

Formation of the palladium hydride complex was determined by ^{1}H NMR. The spectrum shows a distinct triplet in the upfield region, consistent with the palladium hydride species. The ^{2}H NMR of the solution showed no formation of palladium deuteride complex, providing further evidence that the β-hydride mechanism was not operative in the reaction.

Chapter 5

CONCLUSION

In summary, mechanistic studies of the silyl-Heck reaction were performed. The precatalyst for the reaction was characterized by NMR and X-ray crystallography. NMR experiments were conducted to determine the viability of oxidative addition of the palladium complex across the Si–I bond of iodotrimethylsilane. Variable Temperature NMR experiments were used to confirm the existence of ligand dissociation equilibria between palladium phosphine complexes. VT NMR experiments were also used to determine productive intermediates in the silyl-Heck reaction. A side product formed in the reactions with iodotrimethylsilane was elucidated as a palladium hydride complex. This compound was prepared independently and characterized by NMR and X-ray crystallography. Studies were performed to determine the source of the palladium hydride complex and various sources of hydriodic acid were ruled out. Perdeuterated iodotrimethylsilane was synthesized and used in NMR experiments to rule out the possibility of palladium hydride formation by β-hydride elimination.

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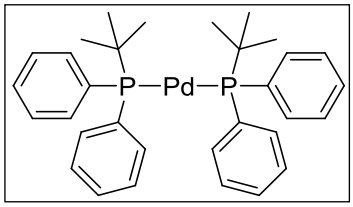
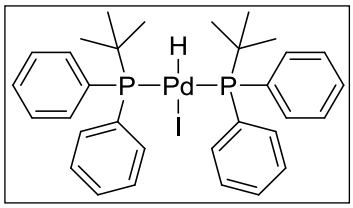
SPECTRAL DATA

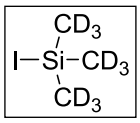
NMR Description	Nucleus	Spectrum
Figure 10, *t*BuPh$_2$P	^{31}P	1
Figure 10, Pd(*t*BuPh$_2$P)$_2$	^{31}P	2
Figure 10, Pd(*t*BuPh$_2$P)$_2$ + 2 equiv ISiMe$_3$	^{31}P	3
Figure 10, Pd(*t*BuPh$_2$P)$_2$ + 40 equiv ISiMe$_3$	^{31}P	4
Figure 11, Pd(*t*BuPh$_2$P)$_2$, 23 °C	^{31}P	5
Figure 11/13, Pd(*t*BuPh$_2$P)$_2$, –53 °C	^{31}P	6
Figure 12, Pd(*t*BuPh$_2$P)$_2$ + 1 equiv *t*BuPh$_2$P, 23 °C	^{31}P	7
Figure 12/13, Pd(*t*BuPh$_2$P)$_2$ + 1 equiv *t*BuPh$_2$P, –53 °C	^{31}P	8
Figure 14, Pd(*t*BuPh$_2$P)$_2$, –53 °C	^{31}P	9
Figure 14, Pd(*t*BuPh$_2$P)$_2$ + 4 equiv ISiMe$_3$, –53 °C	^{31}P	10
Pd(*t*BuPh$_2$P)$_2$	^{1}H	11
Pd(*t*BuPh$_2$P)$_2$	^{31}P	12
Pd(*t*BuPh$_2$P)$_2$(H)I	^{1}H	13
Pd(*t*BuPh$_2$P)$_2$(H)I	^{31}P	14
ISi(CD$_3$)$_3$	^{1}H	15
ISi(CD$_3$)$_3$	^{2}H	16



Pd(*t*BuPh$_2$P)$_2$: ^{1}H NMR (400 mHz, toluene-d$_8$) δ 8.09 (br s, 8 H), 7.13 (m, 12 H), 1.37 (br s, 18 H); ^{31}P NMR (162 mHz, toluene-d$_8$) δ 45.9 (s).

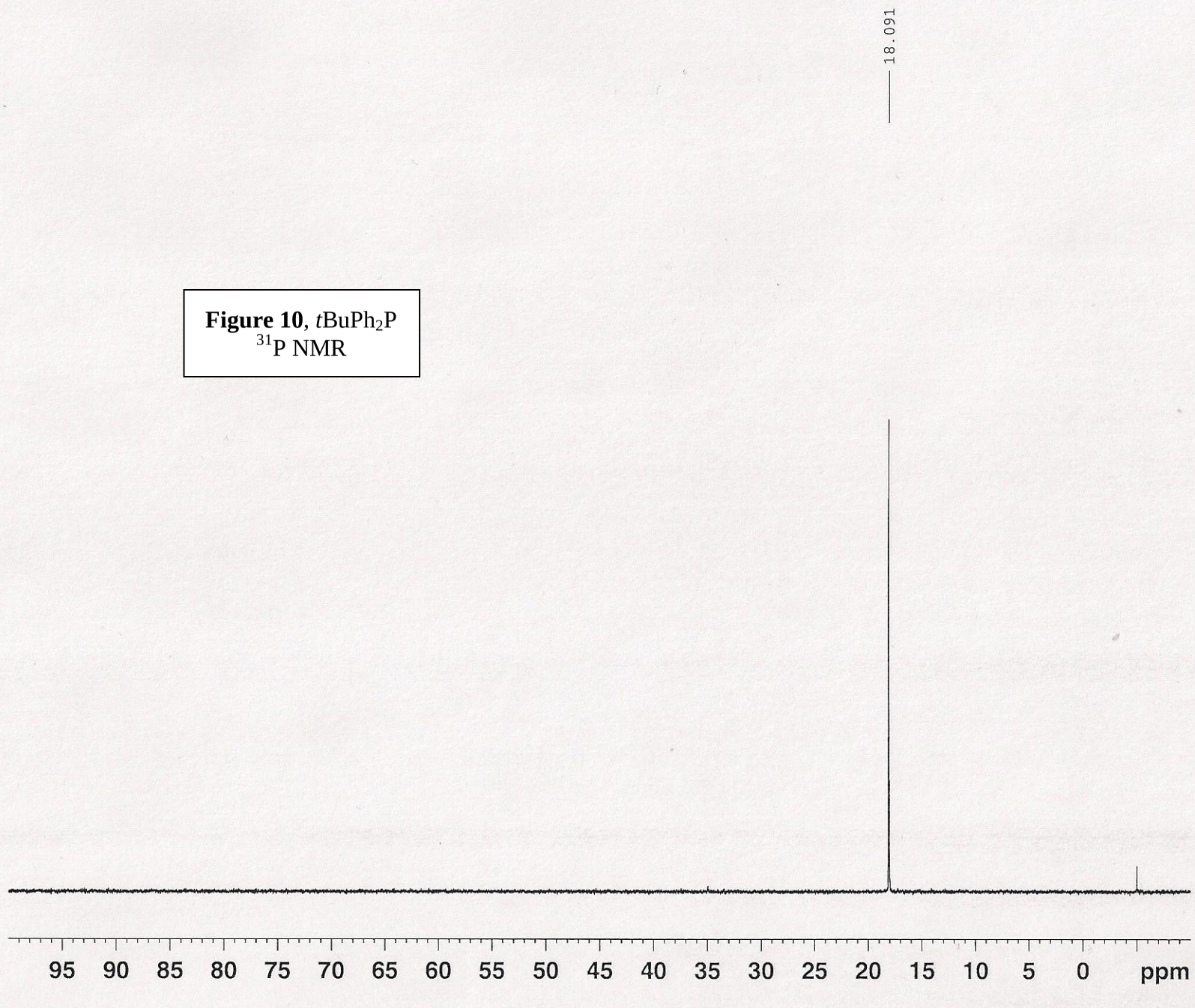


Pd(*t*BuPh$_2$P)$_2$(H)I: ^{1}H NMR (400 mHz, C_6D_6) δ 7.98 (d, *J* = 9.2 Hz, 8 H), 7.08 (m, *J* = 7.6 Hz, 12 H), 1.32 (t, *J* = 7.6 Hz, 18 H), –10.14 (t, *J* = 10.0 Hz, 1 H); ^{31}P NMR (162 mHz, C_6D_6) δ 52.5 (s).



ISi(CD$_3$)$_3$: ^{2}H NMR (61 mHz, C_6H_6) δ 0.41 (s, 9 D).

Figure 10, *t*BuPh$_2$P
^{31}P NMR



Spectrum 1

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DS                       4
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RG                 20642.5
DW                   7.700 usec
DE                   7.50 usec
TE                  297.8 K
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d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                      1

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PL1                   0.00 dB
SFO1          161.9755899 MHz

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PL12                16.00 dB
PL13                16.00 dB
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F2 - Processing parameters
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LB                     1.00 Hz
GB                        0
PC                     1.40
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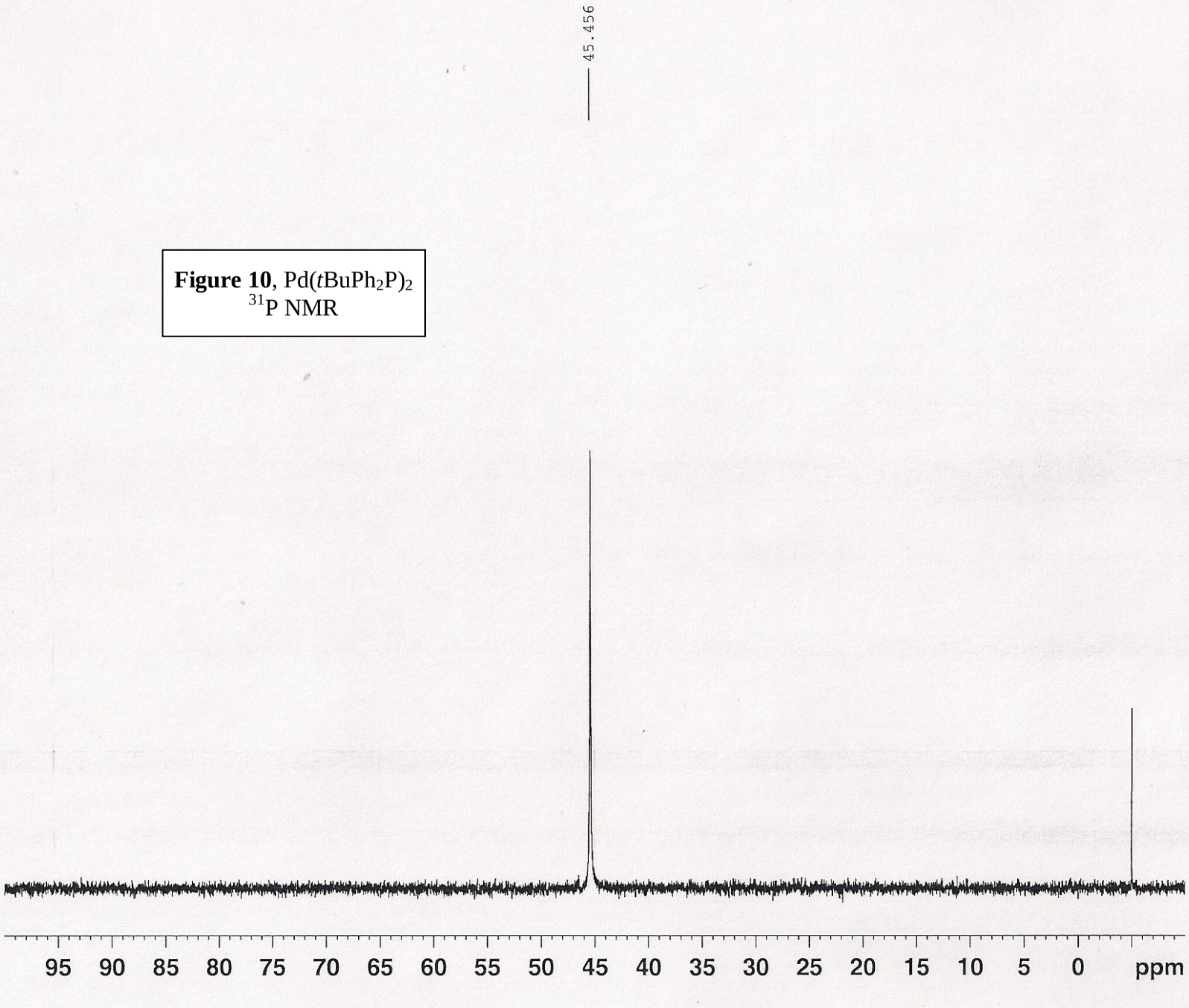
Figure 10, Pd(tBuPh$_2$P)$_2$
^{31}P NMR

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RG              20642.5
DW                7.700 usec
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TE                297.7 K
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d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

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PL1                0.00 dB
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======== CHANNEL f2 ========
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F2 - Processing parameters
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SF          161.9836240 MHz
WDW                  EM
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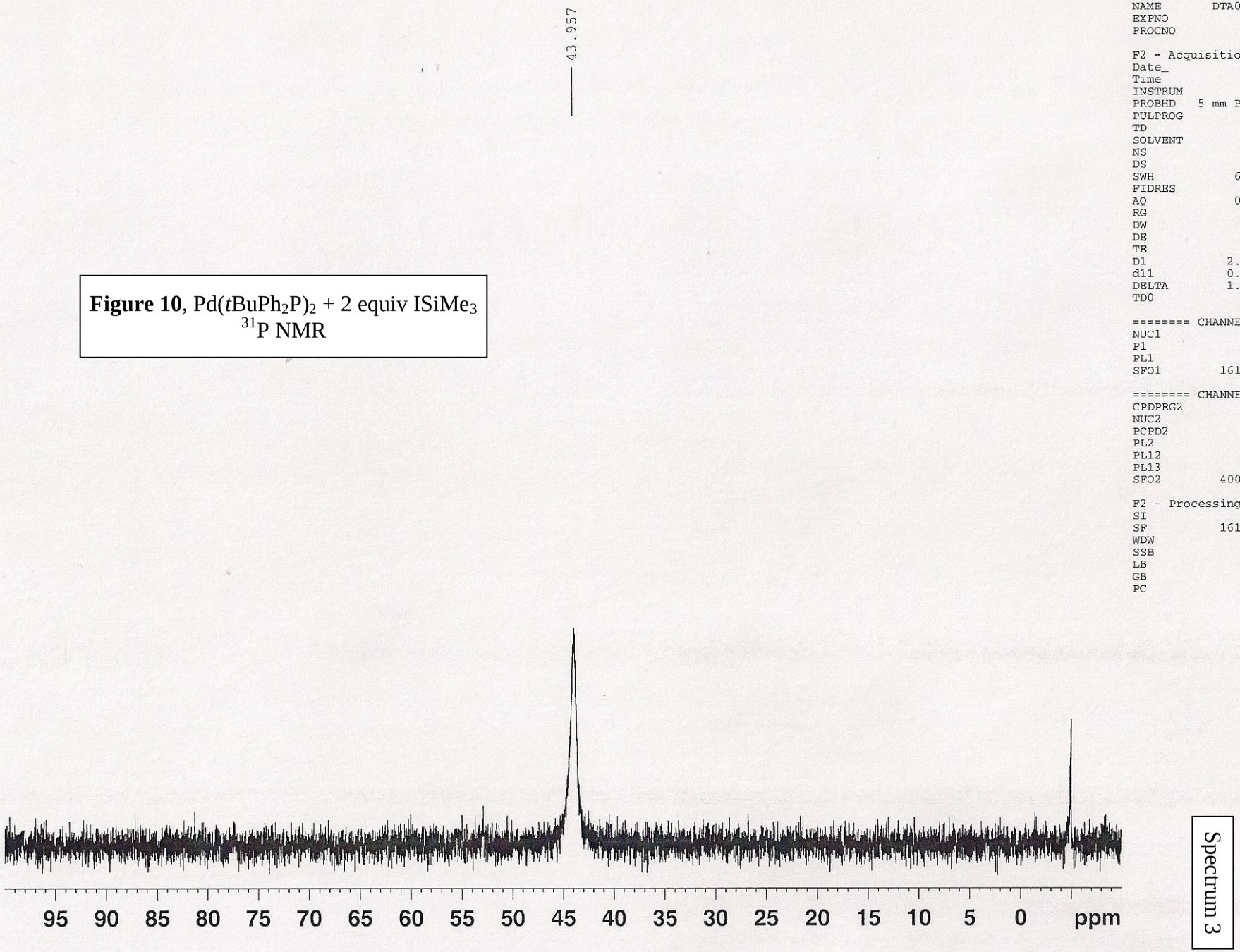
Spectrum 2

Figure 10, Pd(tBuPh$_2$P)$_2$ + 2 equiv ISiMe$_3$
^{31}P NMR

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RG               20642.5
DW                7.700 usec
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d11          0.03000000 sec
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TD0                   1

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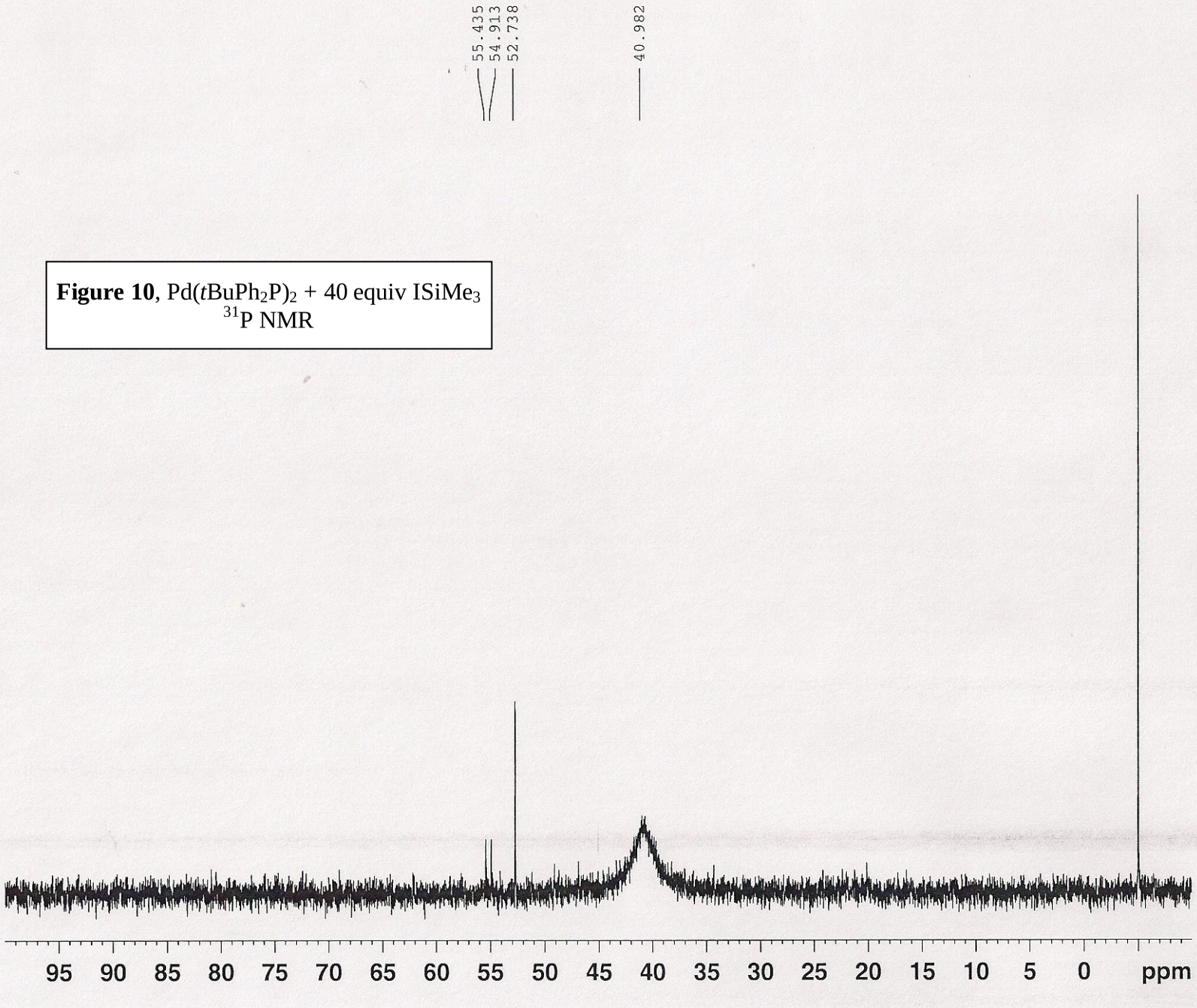
Spectrum 3

Figure 10, Pd(tBuPh$_2$P)$_2$ + 40 equiv ISiMe$_3$
^{31}P NMR

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PCPD2              100.00 usec
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PL12                16.00 dB
PL13                16.00 dB
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F2 - Processing parameters
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WDW                     EM
SSB                      0
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PC                    1.40
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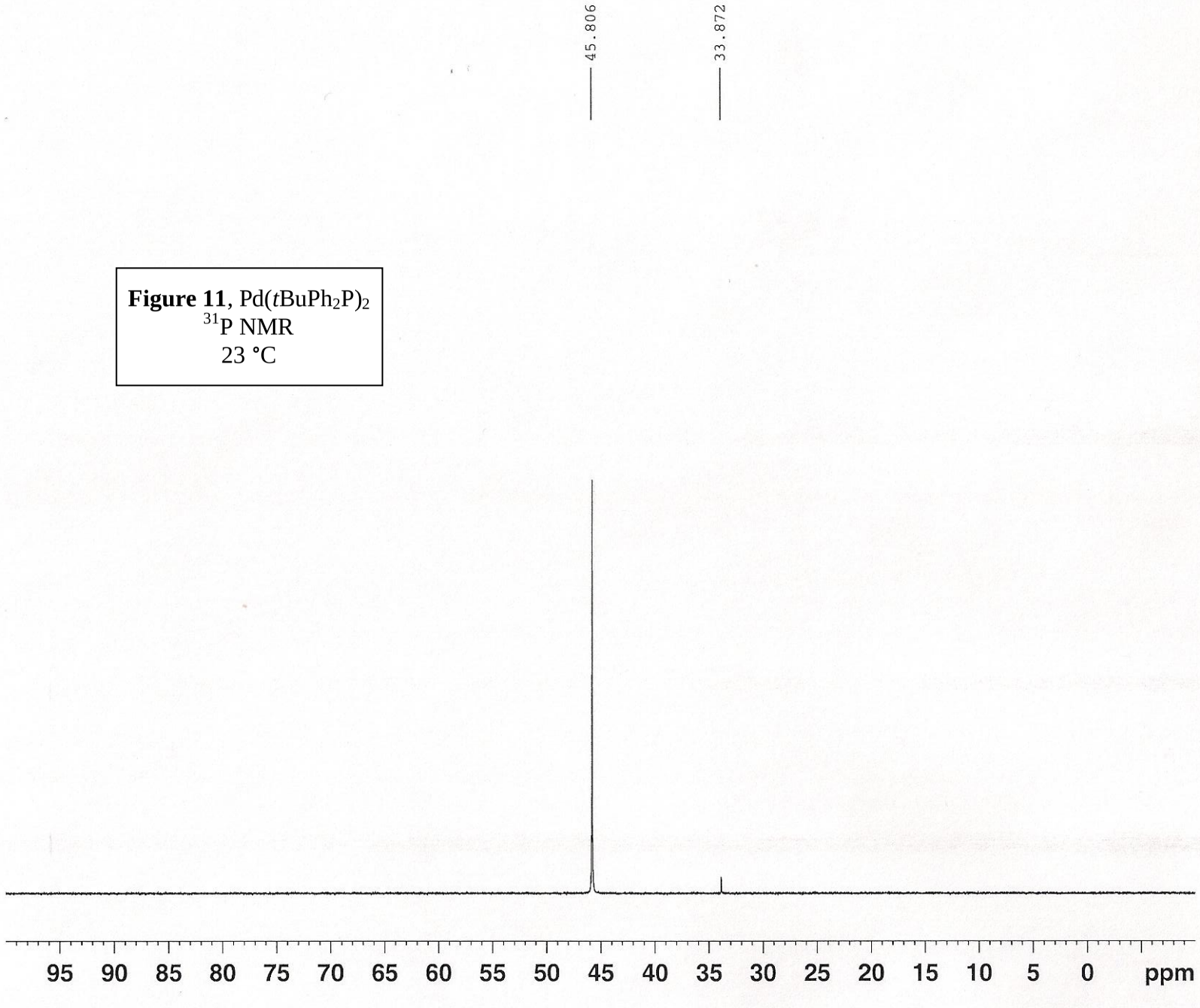
Spectrum 4

Figure 11, Pd(tBuPh$_2$P)$_2$
^{31}P NMR
23 °C

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PROCNO                 1

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SOLVENT             Tol
NS                   32
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FIDRES         0.978127 Hz
AQ            0.5112308 sec
RG                  203
DW                7.800 usec
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TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
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P1                8.00 usec

F2 - Processing parameters
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WDW                  EM
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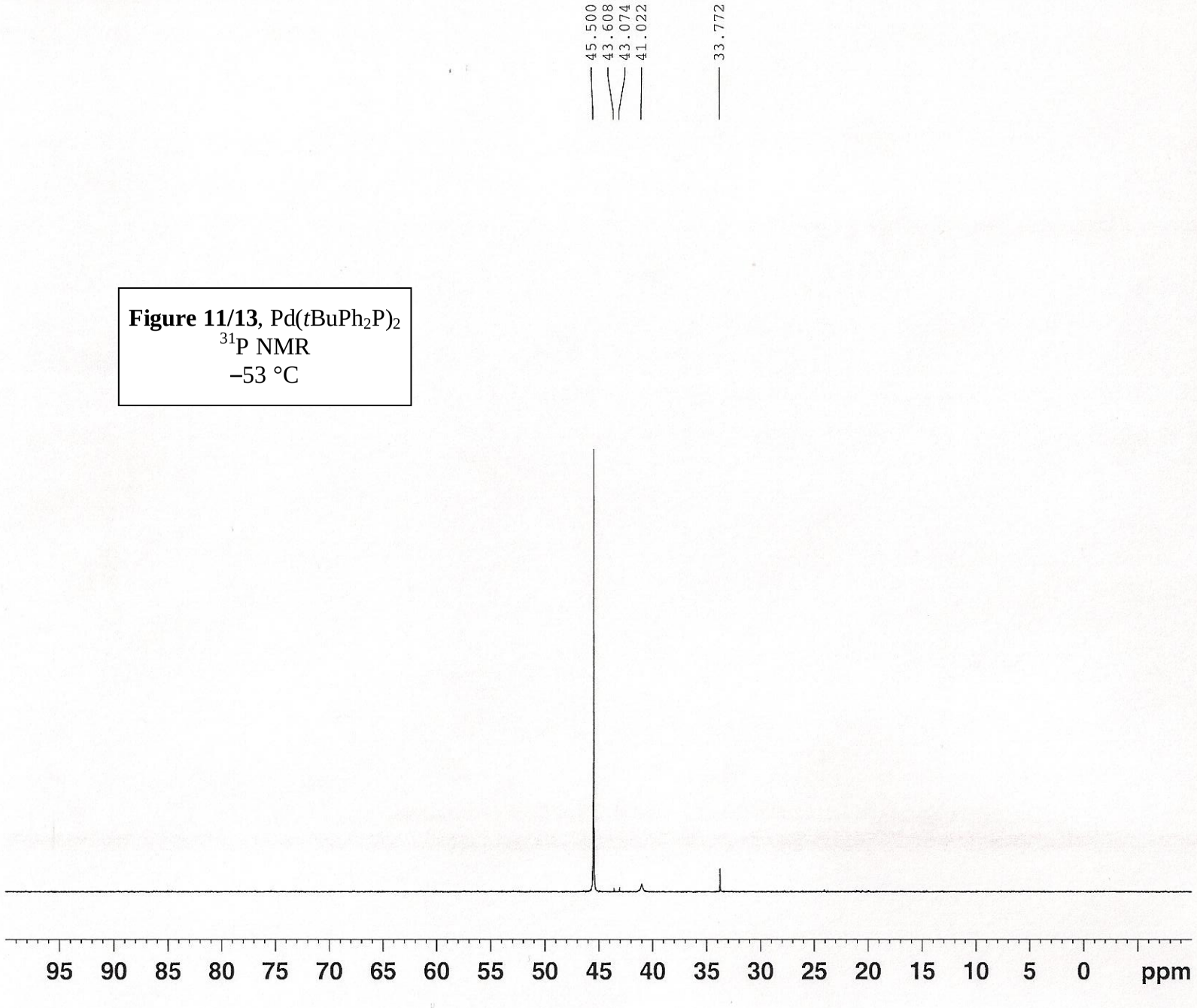
Spectrum 5

Figure 11/13, Pd(tBuPh$_2$P)$_2$
^{31}P NMR
–53 °C

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======== CHANNEL f1 ========
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NUC1                       31P
P1                       8.00 usec

F2 - Processing parameters
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SF                 161.9836890 MHz
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LB                       1.00 Hz
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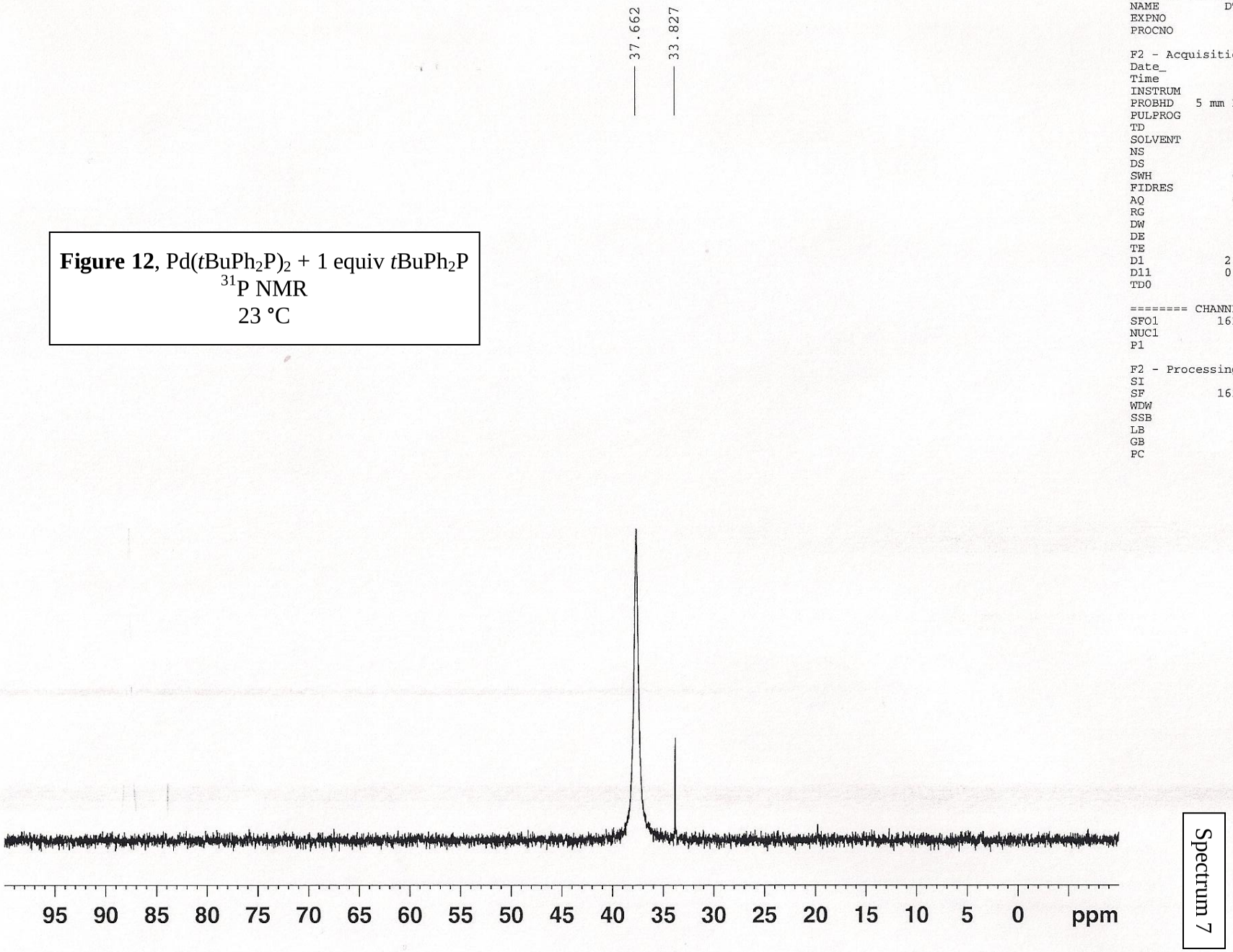
Spectrum 6

Figure 12, Pd(tBuPh$_2$P)$_2$ + 1 equiv tBuPh$_2$P
^{31}P NMR
23 °C

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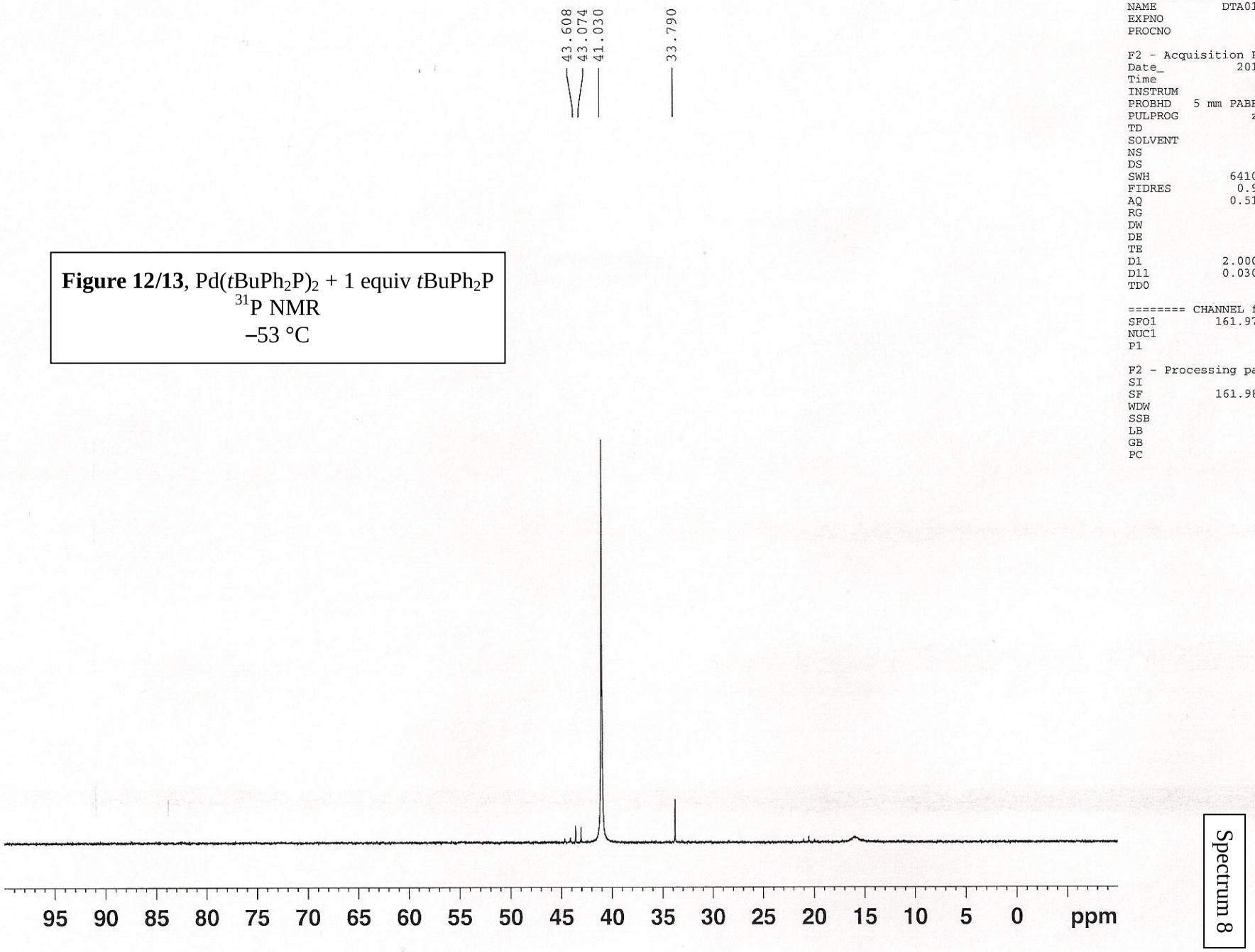
PULPROG          zgpg30
TD                65536
SOLVENT             Tol
NS                   32
DS                    4
SWH           64102.562 Hz
FIDRES         0.978127 Hz
AQ            0.5112308 sec
RG                  203
DW                7.800 usec
DE                6.50 usec
TE               300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        161.9755899 MHz
NUC1               31P
P1                8.00 usec

F2 - Processing parameters
SI                32768
SF          161.9836950 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00
```

Spectrum 7

Figure 12/13, Pd(tBuPh$_2$P)$_2$ + 1 equiv tBuPh$_2$P
^{31}P NMR
–53 °C



Spectrum 8

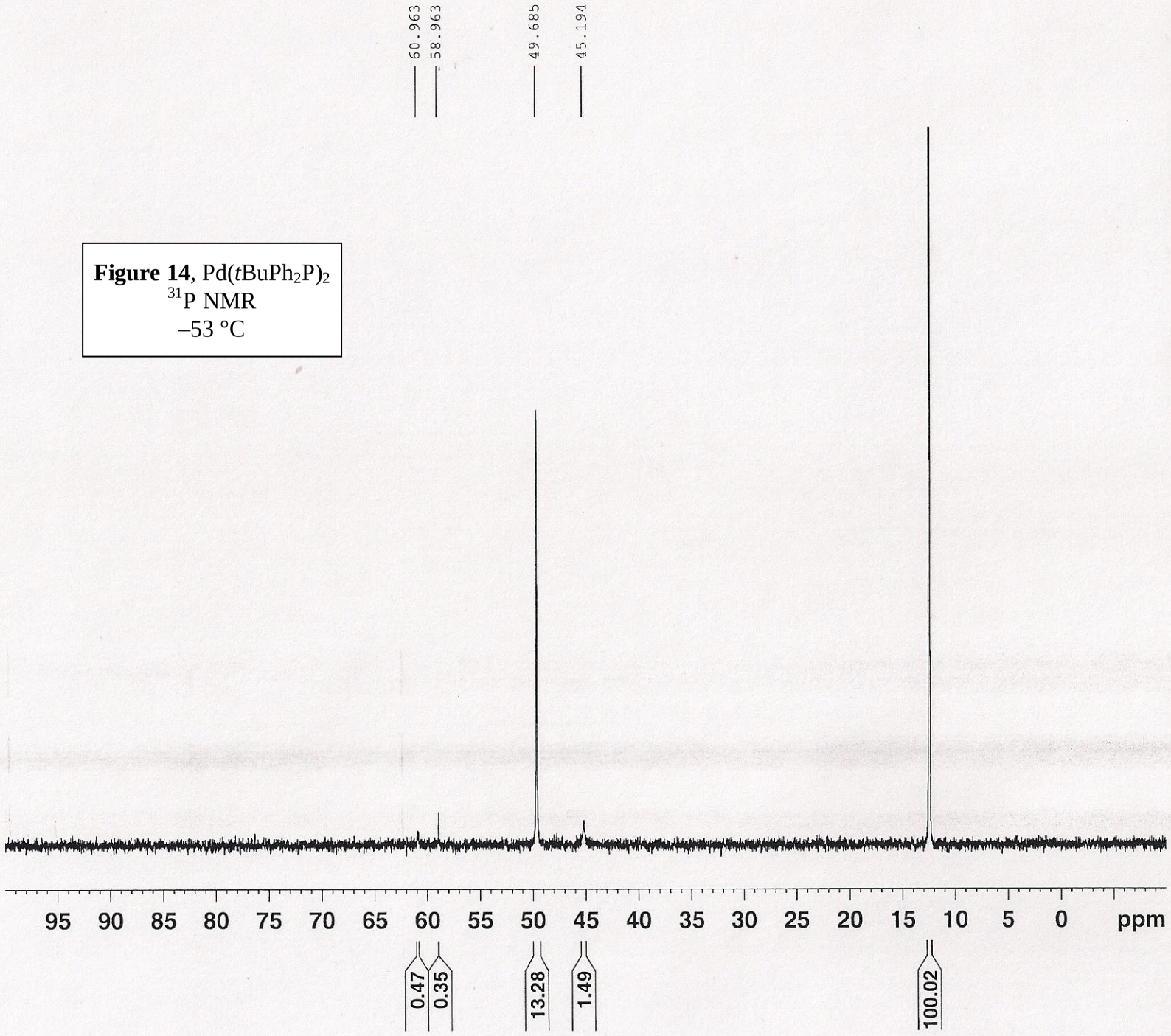
```
Current Data Parameters
NAME          DTA01180B4
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120124
Time               17.21
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT             Tol
NS                   32
DS                    4
SWH           64102.562 Hz
FIDRES         0.978127 Hz
AQ            0.5112308 sec
RG                  203
DW                7.800 usec
DE                6.50 usec
TE                220.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        161.9755899 MHz
NUC1              31P
P1                8.00 usec

F2 - Processing parameters
SI                32768
SF          161.9836890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Figure 14, Pd(tBuPh$_2$P)$_2$
^{31}P NMR
–53 °C




```
Current Data Parameters
NAME      DTA01191A2-P-dec
EXPNO                    1
PROCNO                   1

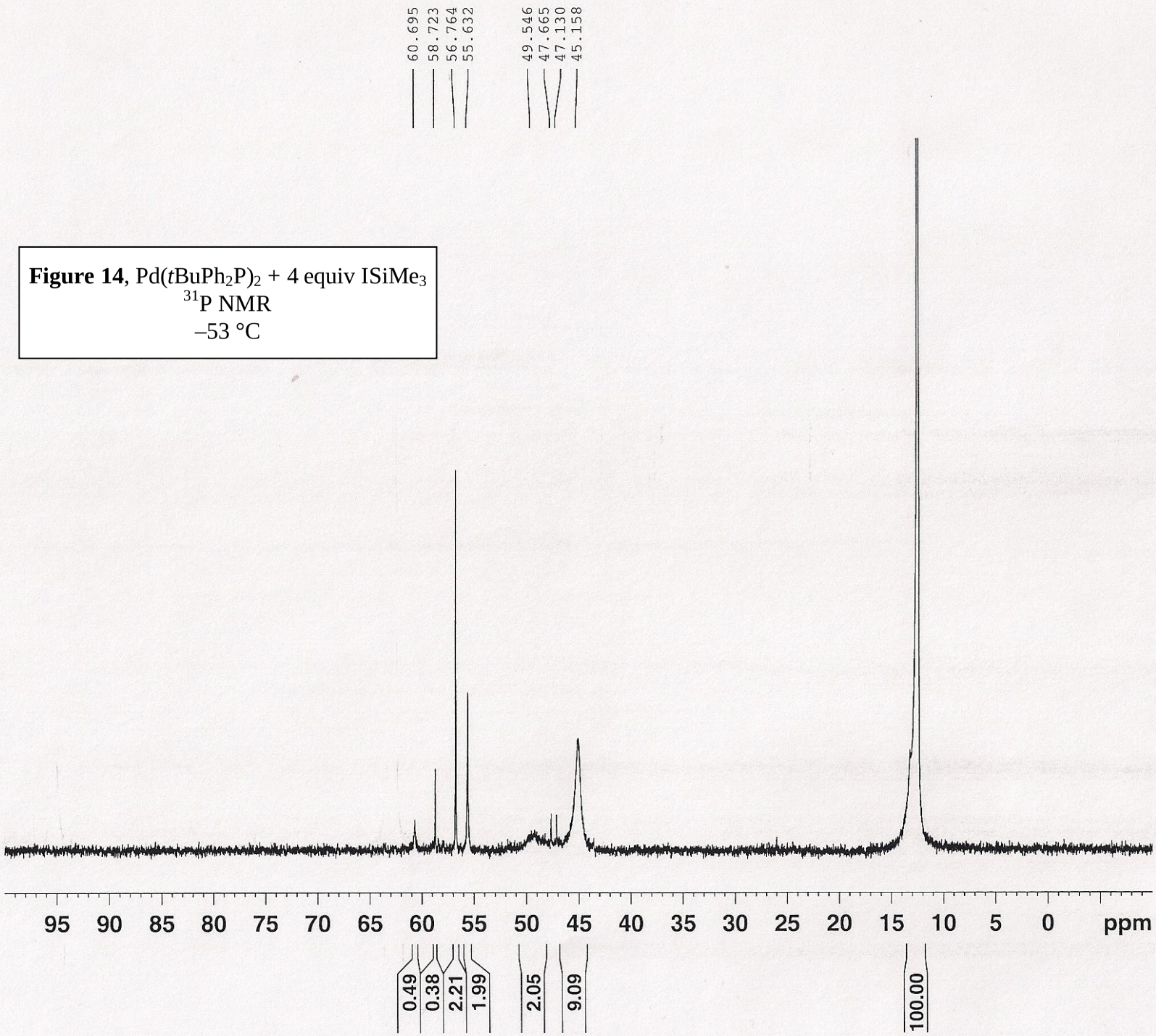
F2 - Acquisition Parameters
Date_             20120420
Time                 14.06
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                65536
SOLVENT             Tol
NS                   32
DS                    4
SWH           64102.562 Hz
FIDRES         0.978127 Hz
AQ            0.5112308 sec
RG                  203
DW                7.800 usec
DE                6.50 usec
TE                218.5 K
D1           5.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        161.9755899 MHz
NUC1                31P
P1                8.00 usec

F2 - Processing parameters
SI                32768
SF          161.9829444 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Spectrum 9

Figure 14, Pd(tBuPh$_2$P)$_2$ + 4 equiv ISiMe$_3$
^{31}P NMR
–53 °C



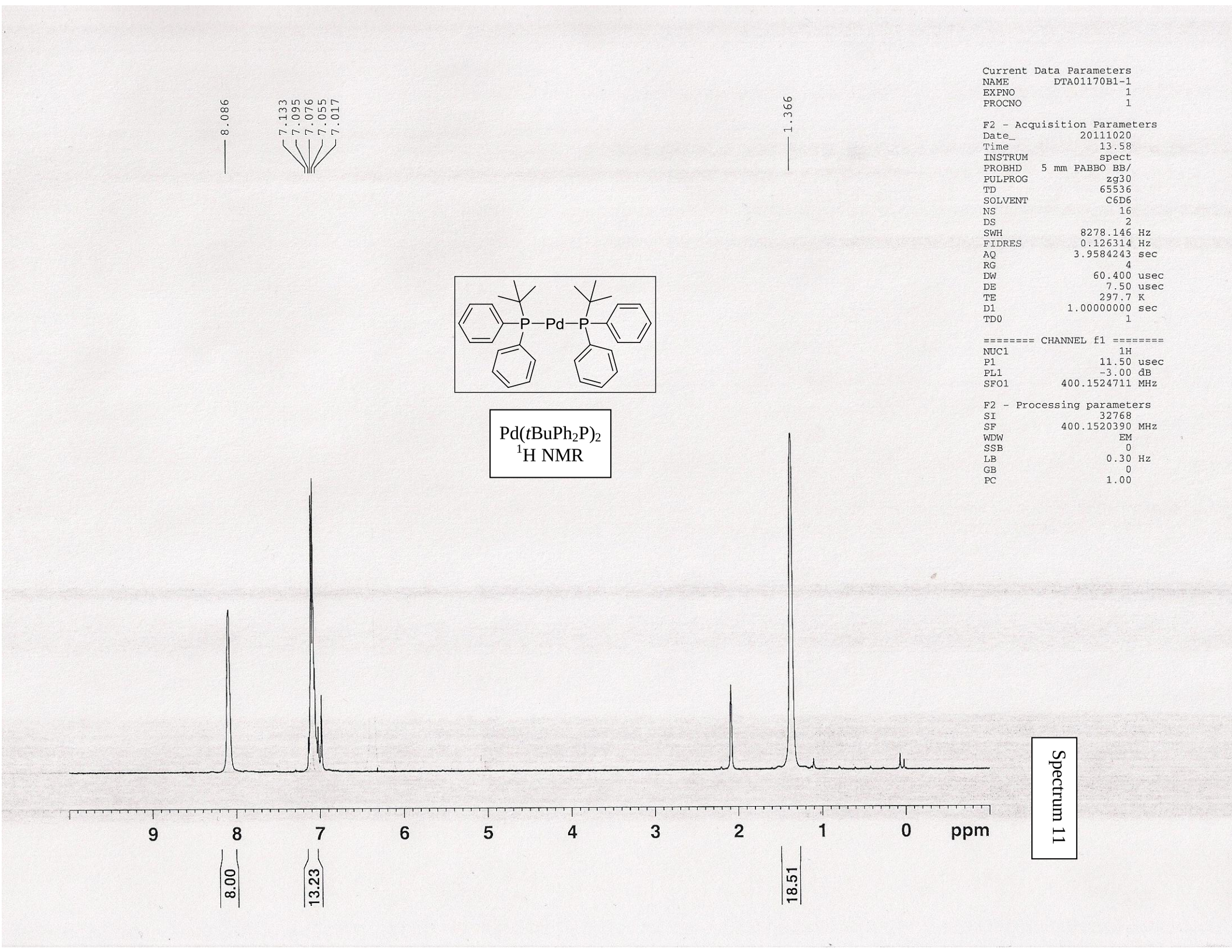

```
Current Data Parameters
NAME      DTA01191A3-P-dec
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120420
Time                 14.54
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT                Tol
NS                      32
DS                       4
SWH              64102.562 Hz
FIDRES           0.978127 Hz
AQ               0.5112308 sec
RG                     203
DW                 7.800 usec
DE                 6.50 usec
TE                 219.9 K
D1              5.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          161.9755899 MHz
NUC1                   31P
P1                  8.00 usec

F2 - Processing parameters
SI                   32768
SF            161.9830383 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

Spectrum 10



Current Data Parameters

NAME	DTA01170B1-1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

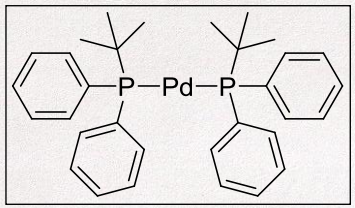
Date_	20111020
Time	13.58
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	C6D6
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	4
DW	60.400 usec
DE	7.50 usec
TE	297.7 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	11.50 usec
PL1	-3.00 dB
SFO1	400.1524711 MHz

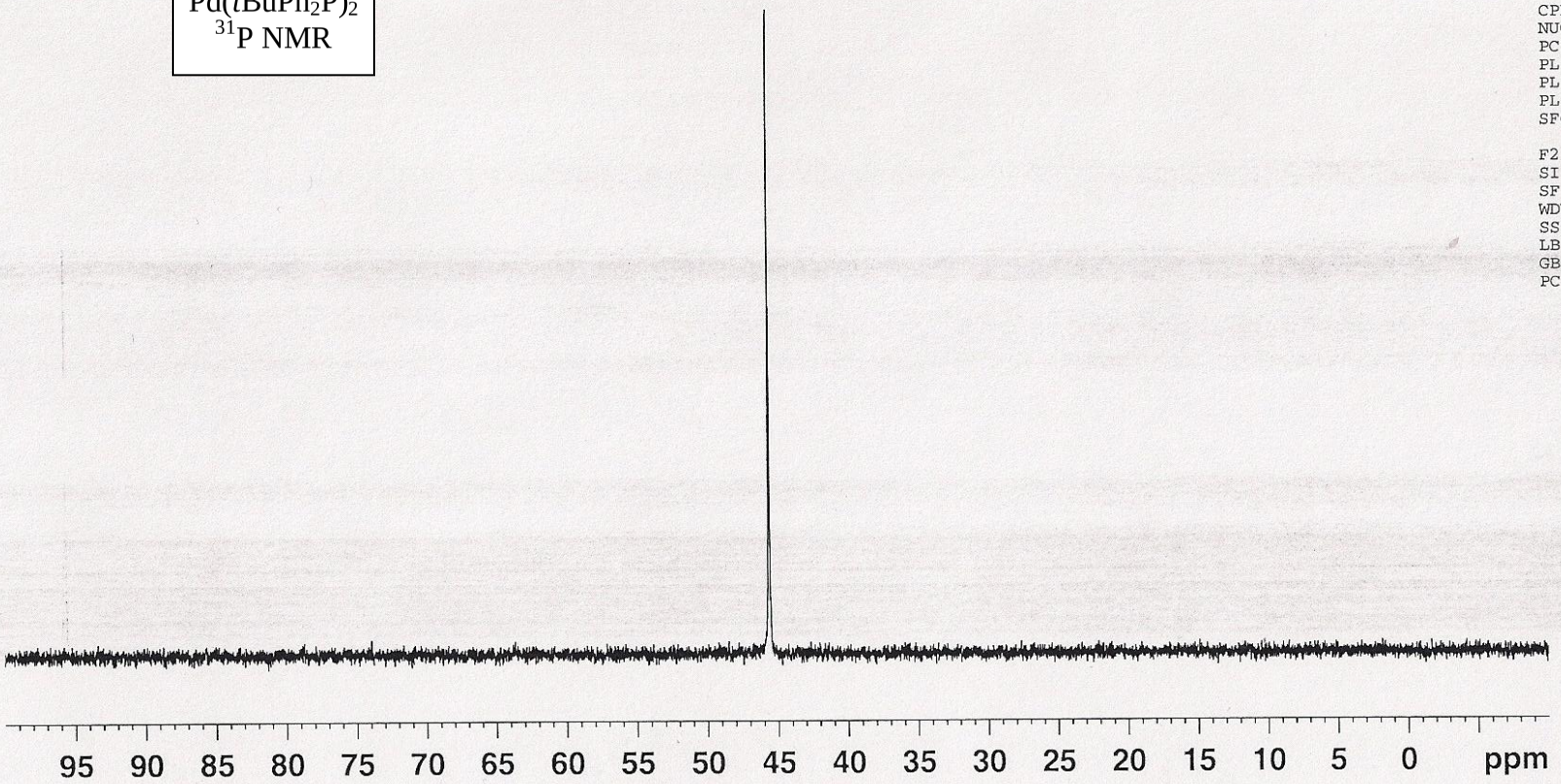
F2 - Processing parameters

SI	32768
SF	400.1520390 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



Pd(tBuPh$_2$P)$_2$
^{31}P NMR

45.922




```
Current Data Parameters
NAME        DTA01170B1-2
EXPNO                  1
PROCNO                 1

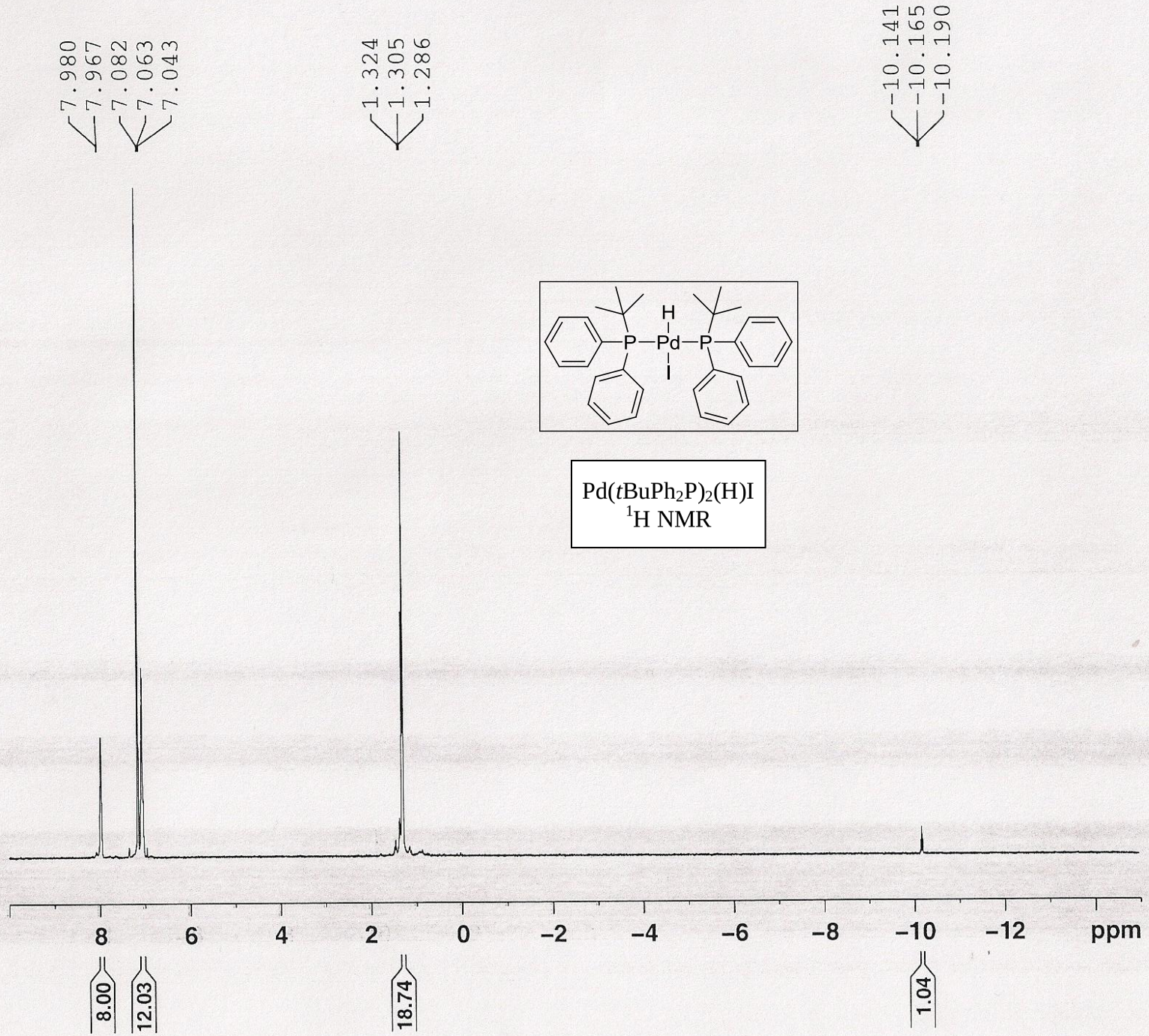
F2 - Acquisition Parameters
Date_           20111020
Time               13.55
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT             Tol
NS                   53
DS                    4
SWH           64935.066 Hz
FIDRES         0.990830 Hz
AQ             0.5046772 sec
RG                 22800
DW                 7.700 usec
DE                 7.50 usec
TE                297.9 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 31P
P1                10.00 usec
PL1                0.00 dB
SFO1        161.9755899 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2               120.00 dB
PL12               16.00 dB
PL13               16.00 dB
SFO2        400.1516006 MHz

F2 - Processing parameters
SI                 32768
SF          161.9836890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Spectrum 12



Pd(*t*BuPh$_2$P)$_2$(H)I
^{1}H NMR

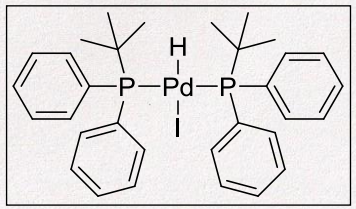
```
Current Data Parameters
NAME      DTA01142B3-crystal-re
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20110725
Time                 16.03
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT              C6D6
NS                     16
DS                      2
SWH             11990.407 Hz
FIDRES          0.182959 Hz
AQ              2.7328513 sec
RG                    512
DW                 41.700 usec
DE                  7.50 usec
TE                 297.5 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 11.50 usec
PL1                -3.00 dB
SFO1         400.1500000 MHz

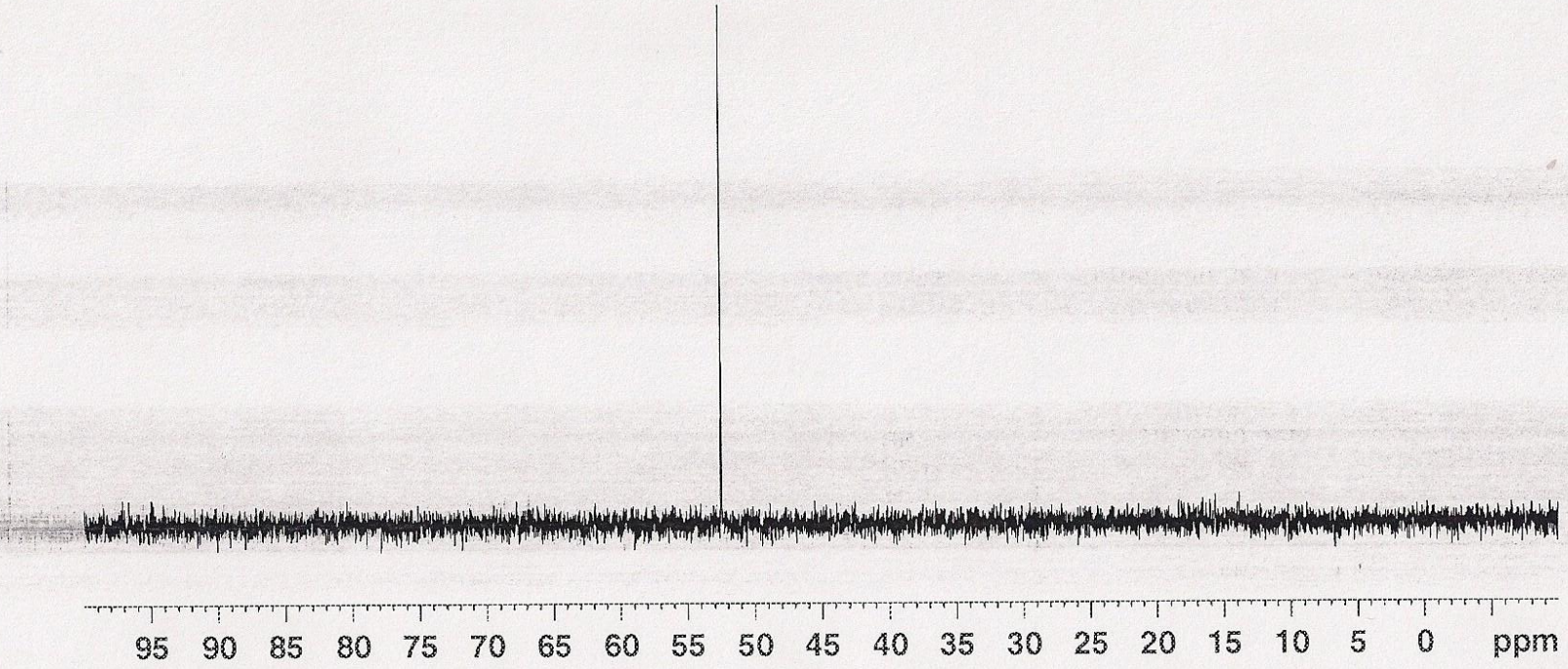
F2 - Processing parameters
SI                  32768
SF           400.1499914 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

Spectrum 13



Pd(*t*BuPh$_2$P)$_2$(H)I
^{31}P NMR

52.49

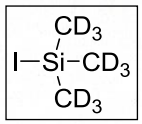



```
Current Data Parameters
NAME      DTA01142B3-crystal-
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20110722
Time                 13.57
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT            Acetone
NS                       102
DS                         4
SWH              64935.066 Hz
FIDRES            0.990830 Hz
AQ                0.5046272 sec
RG                  20642.5
DW                    7.700 use
DE                    7.50 use
TE                   297.7 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                        1
SFO1          161.9755899 MHz
NUC1                    31P
P1                    10.00 use
PLW1           -1.00000000 W
SFO2          400.1516006 MHz
NUC2                    1H
CPDPRG[2          waltz16
PCPD2              100.00 use
PLW2           -1.00000000 W
PLW12          -1.00000000 W
PLW13          -1.00000000 W

F2 - Processing parameters
SI                     32768
SF            161.9836890 MHz
WDW                       EM
SSB
LB                     1.00 Hz
GB
PC                     1.40
```

Spectrum 14



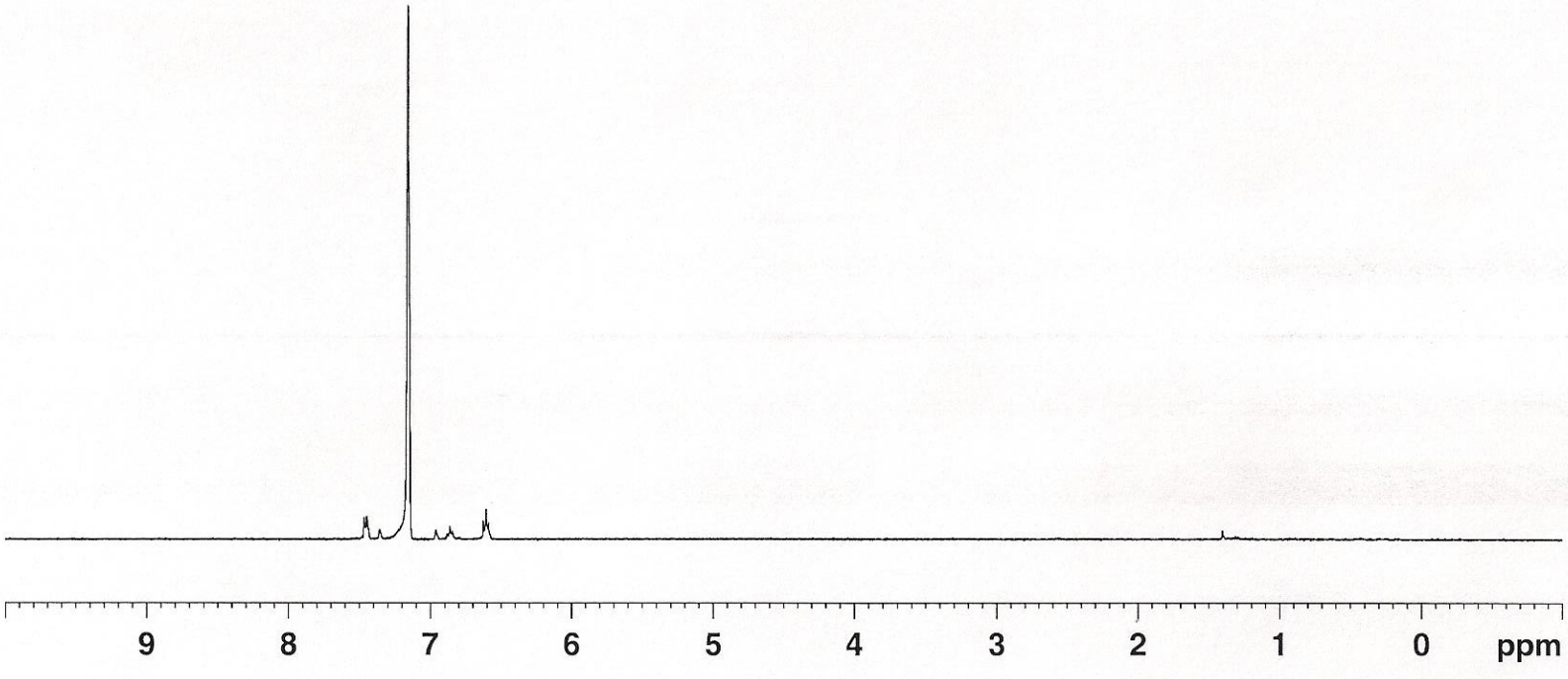
$ISi(CD_3)_3$
^1H NMR

```
Current Data Parameters
NAME      DTA01192A1-C6D6
EXPNO                   1
PROCNO                  1

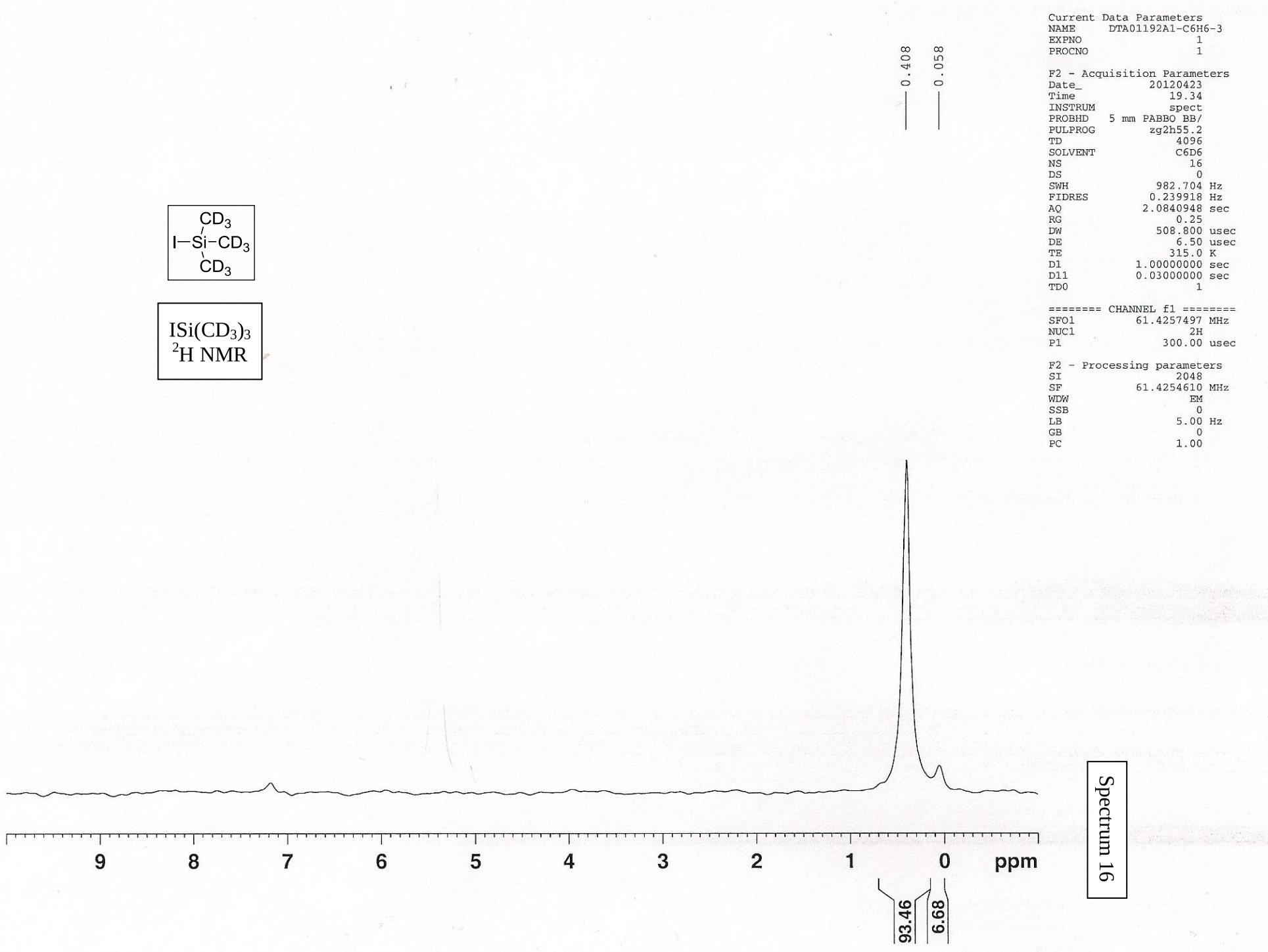
F2 - Acquisition Parameters
Date_           20120423
Time               19.26
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            C6D6
NS                   16
DS                    4
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   203
DW                62.400 usec
DE                16.52 usec
TE                300.0 K
D1             1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         400.1524711 MHz
NUC1                 1H
P1                14.80 usec

F2 - Processing parameters
SI                 65536
SF           400.1499951 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



Spectrum 15


0.408
0.058
Current Data Parameters
NAME DTA01192A1-C6H6-3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120423
Time 19.34
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg2h55.2
TD 4096
SOLVENT C6D6
NS 16
DS 0
SWH 982.704 Hz
FIDRES 0.239918 Hz
AQ 2.0840948 sec
RG 0.25
DW 508.800 usec
DE 6.50 usec
TE 315.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 61.4257497 MHz
NUC1 2H
P1 300.00 usec
F2 - Processing parameters
SI 2048
SF 61.4254610 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.00
CD3
I—Si—CD3
CD3
ISi(CD3)3
2H NMR
9
8
7
6
5
4
3
2
1
0
ppm
93.46
6.68
Spectrum 16