

NI-CATALYZED CROSS-COUPLING REACTIONS
OF PHENOL-DERIVED ELECTROPHILES

by

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DEDICATION

To all my family and friends who have encouraged and supported me throughout the pursuit of this doctorate.

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ABSTRACT

Herein we present in three parts our work on a variety of Ni-catalyzed cross-coupling reactions using phenol-derived electrophiles. The first part details an efficient Ni-catalyzed Stille cross-coupling of C—O electrophiles through a combination of computational and experimental methods. These allowed for the investigation of the mechanism and showed the formation of a novel 8-centered transition state involving KF. Chloride inhibits the reaction through forming a low-energy Ni(II)-chloride species during oxidative addition that has a high activation barrier towards transmetalation. This methodology was shown effective for a wide variety of C—O electrophiles and organostannanes including several difficult bond constructions. The second part explores the development of a chemoselective Ni-catalyzed Suzuki cross-coupling that is selective for C—O bonds in the presence of C—Cl bonds. This selectivity is unusual since organohalides typically undergo oxidative addition with Ni(0) and Pd(0) at similar or faster rates to phenol-derived electrophiles. We were able to pair computational and experimental investigations to develop a reliable strategy and understand the likely origin of this unique selectivity. Stoichiometric experiments showed that small phosphines, like PMe_3 and PPhMe_2 , are unique in their ability to facilitate the selective reaction at C—O bonds in the presence of C—Cl bonds. Computational investigations show the electronic and steric properties of these small ligands are crucial for a close interaction between nickel and a sulfonyl oxygen during oxidative addition, the step where selectivity is determined. The third part looked at the use of aryl methyl ethers as an electrophile under Ni-catalyzed Suzuki-Miyaura and Kumada cross-coupling conditions. Three ligands bearing chelating arms were synthesized, two known and one new, to explore the respective scopes and how these ligands compare to more commonly used ligands such as PCy_3 or ICy . We saw no success under Suzuki-Miyaura conditions but found the hydroxyphosphine ligands facilitated the Ni-catalyzed Kumada cross-coupling of Ar-OMe, which had not been reported. Further investigations proved the hydroxyphosphines had no apparent benefit over commercial ligand as far as yield, scope, or mild reaction conditions.

CHAPTER ONE

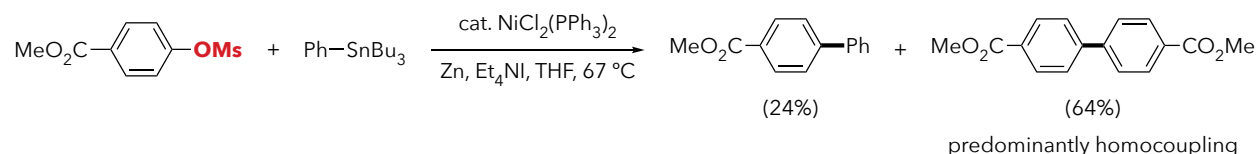
INTRODUCTION

Organic chemistry is a field with many synthetic tools. Arguably one of the most utilized tools is that of late transition metal catalyzed cross-coupling reactions. Transition metal catalyzed cross-coupling reactions are valuable tools to form new C—C bonds more efficiently, simplifying the synthesis of complex molecules. The importance of transition metal catalyzed cross-coupling reactions was recognized when the 2010 Nobel Prize in Chemistry was awarded to Richard Heck, Ei-ichi Negishi, and Akira Suzuki.¹ Palladium has long been the catalyst of choice for the lion's share of cross-coupling reactions including the cross-coupling reactions discussed in this document, the Stille, Suzuki-Miyaura, and Kumada cross-coupling reactions. While Pd is an effective catalyst in a variety of cross-coupling reactions, it struggles to oxidatively add into less reactive electrophiles effectively and is largely limited to reactions of aryl halides and aryl triflates. Both palladium and nickel are group ten metals and because of this they behave similarly in many of the same elementary reactions. Nickel lies directly above palladium in the periodic table, which gives nickel reactivity that cannot be obtained with palladium. Nickel is more earth-abundant than palladium (eighth most abundant transition metal versus one of the five rarest metals),² and is more cost effective. Perhaps the most attractive reason to study nickel as a catalyst is due to its ability to catalyze cross-coupling reactions with less reactive electrophiles including various phenol-derived electrophiles.³ Phenol-derived electrophiles display greater synthetic application as directing groups⁴ than aryl halides. This greater synthetic utility combined with the increased availability and lowered cost of phenols make them a desirable electrophile.⁵

Palladium and nickel are similar in many ways but there are a few key differences to identify. Due to the position of nickel on the periodic table it is a slightly harder element that has a smaller atomic radius than palladium. Nickel is also less electronegative than palladium making it undergo oxidative addition more readily. This easier oxidative addition allows nickel to react with cross-coupling electrophiles that are considerably less reactive with palladium as the catalyst. These differences give nickel the ability to oxidatively add into less reactive bonds that would either be unreactive with palladium or require more forceful reaction conditions. Nickel can oxidatively add into C—O bonds that typically are less reactive towards oxidative addition.³ The application of nickel catalysts gives an opportunity for the cross-coupling of C—O bonds under more mild conditions. This has allowed recent developments in the nickel catalysis of phenol derivatives as useful electrophiles in Suzuki-Miyaura,⁶ Negishi,⁷ and Kumada reactions⁸ among various other cross-coupling reactions.⁵

The Stille coupling is a common cross-coupling reaction that works well with aryl halide electrophiles. However, a Ni-catalyzed Stille coupling using non-triflate phenolic derivatives had not been developed prior to our work. This cross-coupling uses an organostannane and an aryl halide or pseudohalide to form a new C—C bond. A common application of the Stille coupling is in the synthesis of natural products.⁹ The reaction conditions tolerate a wide variety of functional groups on the electrophile and nucleophile making this cross-coupling reaction one of the more versatile cross-coupling methods. The palladium catalyzed Stille coupling works quite well with aryl halides and aryl triflates⁸ but the coupling of less-reactive phenolic derivatives is more limited in scope.¹⁰ An initial attempt at developing a Ni-catalyzed Stille cross-coupling of phenolic electrophiles was attempted by Percec, but homocoupling was the major product obtained (Scheme 1).^{7a} This result, attributed to sluggish transmetalation, delayed further exploration into the Ni-

catalyzed Stille cross-coupling of phenolic derivatives until our group revisited this reaction in recent years.¹¹



Scheme 1. Percec's Ni-catalyzed Stille coupling with aryl mesylates resulting in homocoupling.

The use of nickel as a catalyst has many advantages but there are still several challenges. One challenge of nickel catalysis is controlling chemo- and site-selectivity in the presence of multiple (pseudo)halides with similar reactivity. Previous to the work in this document, the nickel catalyzed chemoselective coupling of non-triflate phenol derivatives had not been published. For many years, published work showed the presence of aryl halides prohibited reaction at C—O bonds due to the greater reactivity of aryl halides (Figure 1).

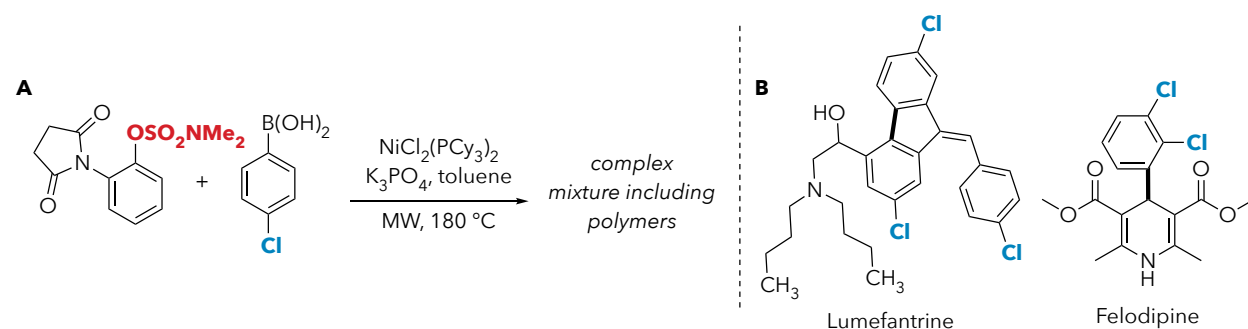
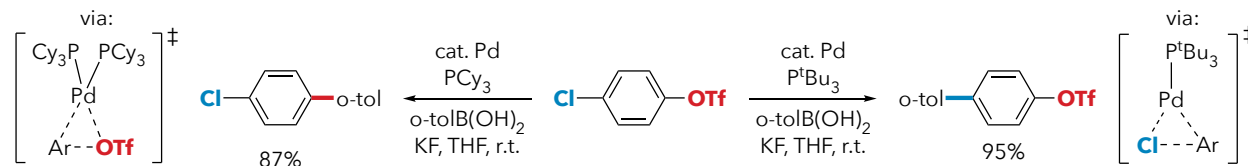


Figure 1. (A) One relevant example showing the intolerance of aryl halides in cross coupling of phenolic electrophiles¹² and (B) two pharmacologically relevant compounds where selectivity during cross coupling could result in a more efficient synthesis.¹³

The lack of a viable path to obtain selectivity with a nickel catalyst becomes an issue when the target molecule contains aryl halides (Figure 1). The use of different phosphines in several studies have resulted in orthogonal selectivity between aryl halides and aryl triflates in palladium-catalyzed Suzuki-Miyaura coupling.^{14,15,16,17,18} These studies suggest that a large factor in

determining whether the coupling takes place at a C—Cl bond or a C—OTf bond is the bulkiness of the phosphine, which impacts the coordination number of Pd during oxidative addition (Scheme 2).

Fu 2000 and Schoenebeck/Houk 2010

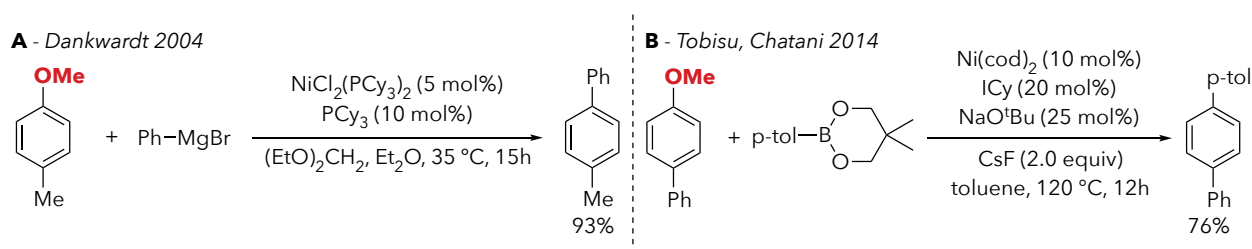


Scheme 2. Previous investigations into palladium catalyzed chemoselective Suzuki-Miyaura cross-coupling reactions.¹⁶ The transition states shown were determined through DFT calculations.²⁰

Additional experimental¹⁹ and computational^{20,21} studies on the Pd-catalyzed cross-coupling of aryl triflates in the presence of aryl chlorides also suggest the ligation state of palladium during oxidative addition influences the selectivity of the reaction.^{19,20,21} When a less hindered ligand such as PCy₃ is used a PdL₂ species is favored, this bisligated species is more electron-rich and prefers to react at the C—OTf bond due to more effective interactions with the C—OTf bond that is much more polarized when compared with the C—Cl bond. With a less sterically hindered ligand such as P(*t*Bu)₃, palladium prefers to be monoligated (PdL) resulting in palladium being less electron-rich and reacting preferentially at the C—Cl bond because of the smaller distortion energy of these bonds.²⁰ The origins of selectivity in Pd-catalyzed Suzuki-Miyaura couplings between C—Cl and C—OTf bonds is well studied, but the role ligands play on controlling the selectivity between different electrophiles in Ni-catalyzed cross-couplings is much less studied. We undertook the first mechanistic study of a ligand-controlled Ni-catalyzed Suzuki-Miyaura cross-coupling.

Phenols are widely available and can be readily transformed into effective electrophiles. Bulkier phenol-derived electrophiles, such as sulfamates, tosylates, and mesylates often work quite well with a nickel catalyst in various cross-coupling reactions but current methods to synthesize

these electrophiles often result in one equivalent of halogen waste being generated. Many aryl methyl ethers can be readily generated through breaking lignin down into small fragments and are commercially available, bypassing this synthetic step. While aryl methyl ethers have an advantage over many other phenol-derived electrophiles by not resulting in loss of a halogen equivalent, they are also significantly less reactive. Because of this, aryl methyl ethers can be carried through multiple synthetic steps and can even serve as protecting groups²² in multi-step synthetic reactions. The use of aryl methyl ethers in Ni-catalyzed cross-coupling reactions has been documented under Kumada coupling conditions and under more forceful Suzuki-Miyaura coupling conditions (Scheme 3).^{5h,6f,8a,8d,23}



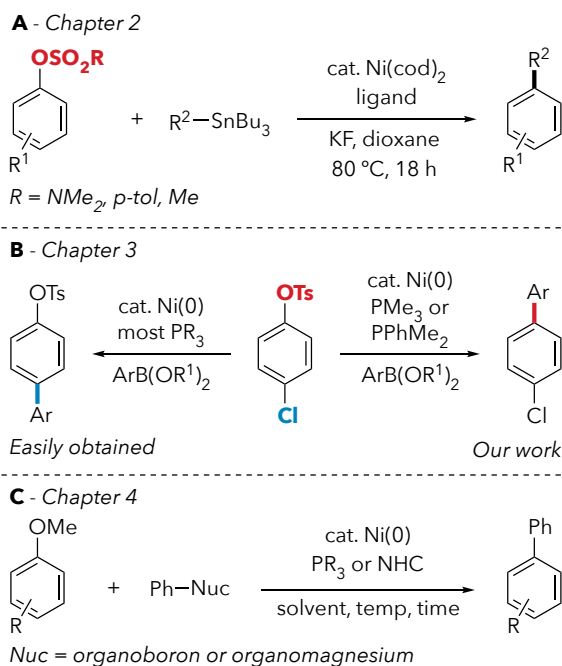
Scheme 3. Examples of Ni-catalyzed cross-coupling with aryl methyl ethers – (A) Kumada conditions improved by Dankwardt^{8d} and (B) Suzuki conditions developed by Tobisu and Chatani.^{23f}

The work in this dissertation is divided into three areas of methodology development: the Ni-catalyzed Stille cross-coupling of aryl sulfamates, the Ni-catalyzed chemoselective Suzuki-Miyaura cross-coupling of aryl tosylates over aryl chlorides, and the Ni-catalyzed cross-coupling of aryl methyl ethers. While these three projects involve different electrophiles and types of cross-couplings, they are all catalyzed by nickel, the electrophiles are all phenolic in nature, and they are all cross-coupling reactions. The overall goal of this research was to explore Ni-catalyzed cross-coupling methods to establish efficient and reliable methods to create new bonds from phenol-derived electrophiles. The first project (Scheme 4A) was explored through a combination of

catalytic, stoichiometric, and computational studies that established the methodology and explained why previous attempts at developing a Ni-catalyzed Stille cross-coupling with phenolic electrophiles had been unsuccessful. The success of the second project (Scheme 4B) was achieved through extensive mechanistic studies, both computational and experimental, to understand the origins of selectivity in a Ni-catalyzed Suzuki-Miyaura coupling and the effect ligands play on the selectivity of the oxidative addition step. The third project (Scheme 4C) was explored through synthesizing and using various ligands that had not been reported for the Ni-catalyzed Suzuki-Miyaura or Kumada couplings of aryl methyl ethers and screening reaction variables to obtain the best product yield. Overall, these projects increase the knowledge of Ni-catalyzed cross-couplings and have the potential for making synthetic chemistry more efficient through eliminating steps to obtain the target or using more readily available

electrophiles.

Chapter 2 details the development of the first efficient, Ni-catalyzed Stille coupling of phenol-derived electrophiles. Through the course of this project, we established a broad scope and examined the transmetalation step of this system. These investigations showed the importance of KF and the inhibitory effect of a chloride source in this reaction. Chapter 3 discusses the investigation and development of a Ni-catalyzed chemoselective Suzuki-Miyaura



Scheme 4. General reaction schemes for each project.

cross-coupling using small phosphine ligands. This reaction was highly selective for reaction at

the C—OTs bond when small tri- or dimethyl phosphines were used. DFT computations suggest this unique selectivity does not arise from the typical origin of metal ligation state. Chapter 4 delves into the development of Ni-catalyzed cross-couplings of Ar-OMe through the use of ligands bearing anionic arms. These are arms that bear a group that can be deprotonated under basic conditions resulting in them becoming anionic. Three ligands bearing anionic arms were synthesized, and two of these were used successfully in the Kumada coupling of Ar-OMe.

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CHAPTER TWO

NICKEL-CATALYZED STILLE CROSS-COUPPLING OF C—O ELECTROPHILES

Contribution of Authors and Co-Authors

Manuscript in Chapter Two.

Author: John E. A. Russell

Contributions: Prepared compounds of interest. Synthesized reagents and prepared compounds of interest. Conducted mechanistic studies. Helped revise the manuscript and SI.

Co-Author: Emily D. Entz

Contributions: Helped continue optimization of reaction conditions and synthesize reagents. Prepared compounds of interest. Helped revise the manuscript and SI.

Co-Author: Ian M. Joyce

Contributions: Worked on early optimization and helped synthesize reagents.

Co-Author: Sharon R. Neufeldt

Contributions: Conceptualization, data curation, formal analysis, funding acquisition, computational experiments, project administration, supervision, visualization, writing – original draft; writing – review and editing.

Manuscript Information

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Nickel-Catalyzed Stille Cross Coupling of C–O Electrophiles

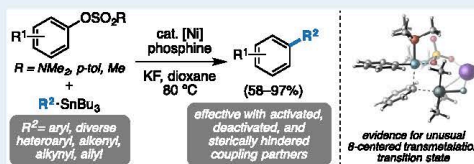
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Supporting Information

ABSTRACT: Aryl sulfamates, tosylates, and mesylates undergo efficient Ni-catalyzed cross coupling with diverse organostannanes in the presence of relatively unhindered alkylphosphine ligands and KF. The coupling is valuable for difficult bond constructions, such as aryl–heteroaryl, aryl–alkenyl, and aryl–alkynyl, using nontriflate phenol derivatives. A combination of experimental and computational studies implicates an unusual mechanism for transmetalation involving an 8-centered cyclic transition state. This reaction is inhibited by chloride sources due to slow transmetalation of organostannanes at a Ni(II)–chloride intermediate. These studies help to explain why prior efforts to achieve Ni-catalyzed Stille coupling of phenol derivatives were unsuccessful.

KEYWORDS: cross-coupling, DFT, nickel, phenol derivatives, transmetalation



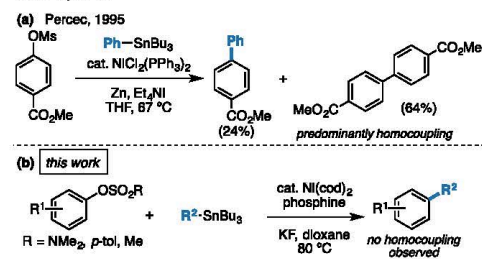
Phenol-derived electrophiles have numerous advantages over aryl halides as cross-coupling partners including synthetic utility as directing groups as well as the low cost and high availability of phenols.¹ Highly activated phenol derivatives like aryl triflates are difficult to carry through multiple synthetic steps because of their tendency toward hydrolysis. However, recent developments in nickel catalysis have enabled less labile phenol derivatives such as sulfonates, sulfamates, carbamates, and esters to be used in Suzuki–Miyaura,² Negishi,³ Kumada,^{3a,4} and other cross couplings.¹ Despite these advances, the Ni-catalyzed Stille coupling of phenol derivatives has remained elusive since Percec’s early report that homocoupling dominates in the reaction of aryl mesylates with PhSnBu₃ using NiCl₂(PPh₃)₂ as a precatalyst (Scheme 1a).^{3a,5} The poor efficiency of cross coupling was attributed to slow transmetalation from tin to nickel.

The palladium-catalyzed Stille coupling of aryl halides and triflates is a powerful C–C bond-forming strategy.⁶ Although other methods—especially Suzuki–Miyaura couplings—are

often preferred because of tin’s toxicity, the Stille coupling remains important due to the stability and high functional group tolerance of organostannanes.^{7,8} Nevertheless, when using more inert phenol-derived electrophiles, the Pd-catalyzed Stille reaction is limited to unhindered electron-deficient or -neutral aryl sulfonates and a small scope of organostannanes.⁹ Because Ni is more reactive than Pd with C–O bonds,¹ we reasoned that Ni catalysis should enable more efficient and general Stille coupling of nontriflate phenol derivatives if the problem of slow transmetalation can be overcome. Here we report that Ni(0) catalyzes the cross coupling of diverse aryl sulfamates and sulfonates with aryl-, heteroaryl-, alkenyl-, alkynyl-, and allylstannanes (Scheme 1b). Moreover, we provide evidence for a novel transmetalation mechanism and an explanation for an inhibitory effect of chloride in this system.

We first examined the reaction between **1** and PhSnBu₃ in the presence of Ni(cod)₂, PCy₃, and KF in 1,4-dioxane (Table 1). Aryl sulfamates are synthetically valuable C–O electrophiles because they are also effective directing groups for ortho metalation.¹⁰ The ligand PCy₃ was chosen on the basis of its efficacy in Ni-catalyzed Suzuki–Miyaura couplings of aryl sulfamates.¹¹ KF was added because fluoride is known to accelerate Pd-catalyzed Stille couplings.^{6,12,13} A poor yield of **2** was observed after 18 h at 60 °C (entry 1), but increasing the reaction temperature to 80 °C improves the yield of **2** to 60% (entry 2). None of the homocoupled product **3** was detected. Interestingly, the addition of LiCl shuts down reactivity (entry 3) even though chloride salts are commonly included in Pd-catalyzed Stille couplings.^{6,14} Gratifyingly, nearly quantitative conversion to **2** was achieved with several

Scheme 1. Ni-Catalyzed Stille Coupling of Phenol-Derived Electrophiles

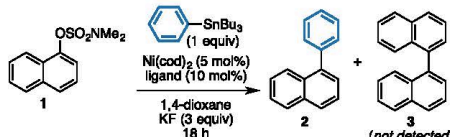


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Table 1. Optimization of the Ni-Catalyzed Stille Coupling



entry	ligand	temp. (°C)	additive	2 (%) ^a
1	PCy ₃	60		27
2	PCy ₃	80		60
3	PCy ₃	80	LiCl (3 equiv)	n.d.
4	PBu ₃	80		88
5	PPhEt ₂	80		≥99
6	PPhMe ₂	80		96
7	PPh ₂ Me	80		≥99
8	PPh ₃	80		52
9 ^b	PPhEt ₂	80		n.d.

^aGC yield calibrated against undecane as an internal standard. n.d. = not detected. Average of two runs. ^bWithout KF.

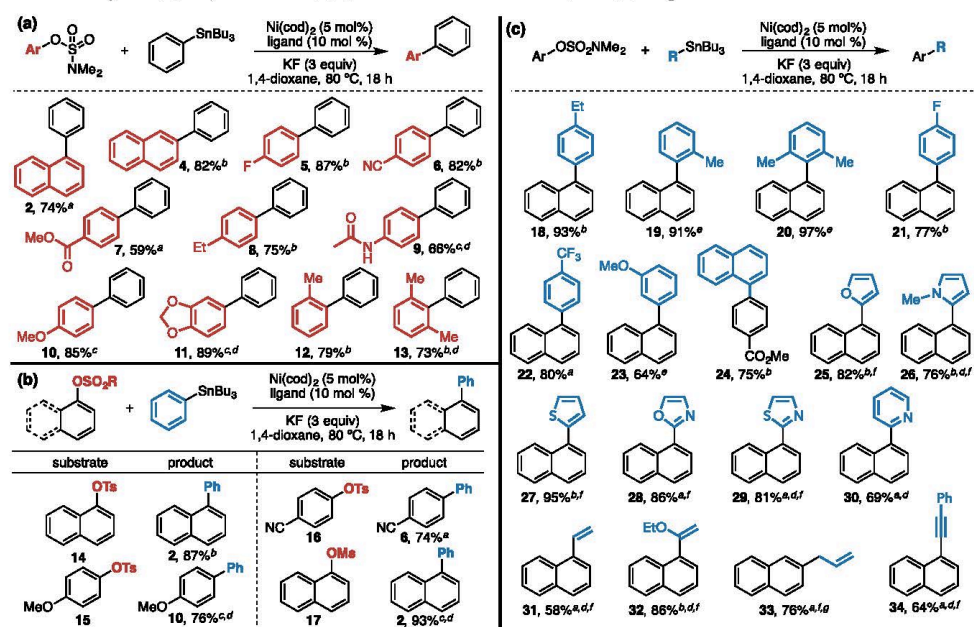
less sterically hindered mono-, di-, and trialkylphosphines (entries 4–7). At least one alkyl substituent on the phosphine is needed for high conversion: the use of PPh₃ gives only a moderate yield (entry 8). No reaction is observed in the absence of KF (entry 9).

With several optimal ligands in hand (PBu₃, PPhEt₂, PPhMe₂, PPh₂Me), the scope of aryl sulfamates was examined

(Scheme 2a). Activated (2 and 4–7) and deactivated (8–13) aryl sulfamates undergo efficient cross coupling. Steric hindrance on the electrophile is well tolerated (12 and 13), as are fluorides,¹⁵ nitriles,¹⁶ esters,^{1,2d,e} amides,¹⁷ and acetals¹⁸—functional groups that are also known to undergo activation by Ni(0) (5–7, 9, and 11). In addition to aryl sulfamates, both activated (14 and 16) and deactivated (15) aryl tosylates, as well as naphthyl mesylate 17, readily undergo the Ni-catalyzed Stille coupling (Scheme 2b).

Diverse organostannanes are effective coupling partners, including aryl tributylstannanes bearing electron-donating (18–20) and -withdrawing (21–23) substituents or containing fused aromatic rings (24) (Scheme 2c). This reaction is effective for constructing diverse C–C bonds that are largely inaccessible from nontriflate phenol derivatives by other cross-coupling methods. For example, 2-(tributylstannyl) oxygen-, nitrogen-, and sulfur-containing five- and six-membered heteroaryl nucleophiles undergo efficient cross coupling (25–30). In contrast, the analogous Suzuki–Miyaura coupling of nontriflate phenol derivatives has not been demonstrated with most of the corresponding organoboron reagents.¹⁹ Alkenyl stannanes (31 and 32) are readily coupled to afford products complementary to the Ni-catalyzed Heck reaction of nontriflate phenolic electrophiles,²⁰ a reaction that is limited to alkyl- or aryl-substituted alkenes and does not include enol ethers. The use of allyl- and alkenyltributyl stannanes permits allylation and alkenylation of phenol-derived electrophiles (33 and 34).^{21,22}

Scheme 2. Scope of (a) Aryl Sulfamates, (b) Other Phenol Derivatives, and (c) Organostannanes



^aLigand = PPhMe₂. ^bLigand = PPhEt₂. ^cLigand = PBu₃. ^dWith 10 mol % Ni(cod)₂ and 20 mol % ligand. ^eLigand = PPh₂Me. ^fBHT added during isolation. ^gProduct comprises ~9:1 ratio of 33 to the isomerized alkene 2-(1-propen-1-yl)naphthalene.

As described above, during reaction optimization we found that 3 equiv of LiCl completely inhibits this Ni-catalyzed reaction (see Table 1 entry 3). Further exploration revealed that even a substoichiometric quantity of LiCl severely impairs catalysis (Table 2, compare entries 1 and 2). The inhibitory

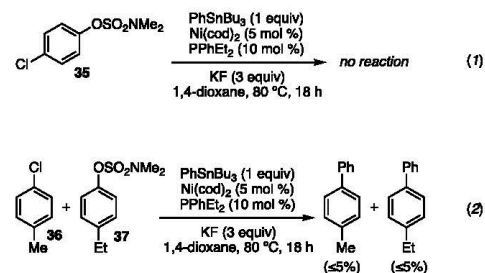
Table 2. Inhibition of Catalysis by Chloride Sources

entry	additive(s)	2 (%) ^a
1	none	≥99 ^b
2	LiCl (10 mol %)	13 ^b
3	LiCl (10 mol %) + 12-crown-4 (20 mol %)	13 ^b
4	12-crown-4 (20 mol %)	≥99 ^b
5	NBu ₄ Cl (10 mol %)	10 ^b
6	KCl (10 mol %)	42 ^b
7	ZnCl ₂ (10 mol %)	n.d.

^aGC yield calibrated against undecane as an internal standard. n.d. = not detected. ^bAverage of two runs.

effect of LiCl is observed even when Li⁺ is sequestered by a crown ether (entry 3), suggesting that inhibition is due to chloride rather than Li⁺. The crown ether itself does not inhibit catalysis (entry 4). To further explore this phenomenon, additional chloride salts were evaluated as additives. Indeed, NBu₄Cl, KCl, and ZnCl₂ were all found to impair catalysis even at low loadings (10 mol %, entries 5–7).

Consistent with catalyst inhibition by chloride sources, no reaction is observed using a chloro-substituted aryl sulfamate 35 (eq 1). An exogenous aryl chloride 36 also inhibits the Ni-



catalyzed Stille coupling of aryl sulfamate 37 (eq 2). Interestingly, cross coupling of the aryl chloride does not take place either, even though aryl chlorides are excellent coupling partners in other types of Ni-catalyzed cross couplings.²⁵ We hypothesize that the Ni(II)–chloride species formed upon oxidative addition of an aryl chloride²⁴ or by anion exchange between a Ni(II)–sulfamate and exogenous Cl[−] is relatively inert toward transmetalation with PhSnBu₃.²⁵ Consequently, the catalyst is deactivated by aryl chlorides or chloride salts. This hypothesis could also help to explain why the use of NiCl₂(PPh₃)₂ leads to slow transmetalation with organostannanes, as described by Percec and co-workers.^{3a}

To explore this hypothesis, DFT calculations were performed to compare possible mechanisms for transmetalation from tin to nickel using PMe₃ and PhSnMe₃ as

computationally convenient models (Figure 1a).^{26,27} We focused on transmetalation at Ni(II) because recent studies on related Suzuki–Miyaura couplings of aryl sulfamates support a Ni(0)/(II) catalytic cycle in which any Ni(I) species exist as unproductive off-cycle intermediates.^{19a,28,29} Complex 38 represents the species resulting from oxidative addition of an aryl sulfamate at Ni(0).³⁰ In Mechanism A, 38 reacts directly with PhSnMe₃ and transmetalation proceeds through a 6-centered cyclic transition state (TSA). In Mechanism B, 38 is intercepted by a pentavalent tin fluoride species formed from the reaction of PhSnMe₃ with KF.^{12b,h,i} Transmetalation takes place through a novel 8-centered transition state with K⁺ acting as a bridge between fluoride and oxygen (TSB). Mechanism C represents a possible path in the presence of chloride salts: this mechanism proceeds through formation of Ni(II)–chloride complex 39C followed by transmetalation through a 4-centered cyclic transition state TSC. Finally, Mechanism D proceeds through formation of a Ni(II)–fluoride complex 39D (by anion exchange using KF) and involves F...Sn bond formation in the 4-centered transition state TSD.^{31,32}

The calculations suggest that, in the absence of chloride, transmetalation proceeds through Mechanism B or D. Both mechanisms justify the requirement for KF in the catalytic conditions and are characterized by relatively low free energies of activation (15.0 kcal/mol for TSB measured from 38; 20.4 kcal/mol for TSD measured from 39D). In contrast, Mechanism A's barrier is much higher (27.8 kcal/mol for TSA). The relevance of Mechanism D depends on whether a Ni(II)–fluoride species (39D) forms rapidly under the reaction conditions. To explore this possibility, we turned to stoichiometric oxidative addition studies. Aryl sulfamate 42 reacts with Ni(cod)₂ and PPhEt₂ in 1,4-dioxane to give complex 43 (Figure 1B).^{27b} When 43 is heated with KF in 1,4-dioxane for 1 h, no significant changes are observed by ³¹P, ¹⁹F, ¹H, or ¹³C NMR, suggesting that sulfamate-for-fluoride anion exchange does not take place under these conditions.³³ As such, Mechanism D appears improbable, and Mechanism B is more likely to operate under the catalytic conditions.

Further support for the relevance of Mechanism B, involving a bridging K⁺ during transmetalation, is provided by experimental evaluation of different counterions for fluoride (Table 3). Whereas 1 undergoes cross coupling in quantitative yield when KF is the fluoride source, LiF and NaF are completely ineffective for this transformation. The poor results with Li⁺ and Na⁺ counterions could also relate to worse solubility of these salts. However, even the highly soluble salt CsF gives considerably lower yields than KF, suggesting that Cs⁺ may not be as effective as K⁺ at forming a bridge during transmetalation.

DFT predicts that transmetalation at a Ni(II)–chloride (Mechanism C) is considerably slower than transmetalation through either Mechanism B or Mechanism D (ΔG[‡] for TSC = 24.3 kcal/mol measured from 39C). Accordingly, these calculations are consistent with inhibition by LiCl if a Ni(II)–chloride species forms rapidly under the reaction conditions. This possibility was also investigated through stoichiometric studies. In contrast to the observed lack of reactivity between 43 and KF, 43 is almost completely transformed into a new complex upon heating with LiCl in 1,4-dioxane for 1 h. The new complex is spectroscopically identical to the product formed upon reaction of aryl chloride 45 with Ni(cod)₂/PPhEt₂, corresponding to trans Ni(II)–chloride complex 44. When complex 44 is heated with PhSnBu₃ and KF in 1,4-



couplings of aryl triflates, chloride sources have an inhibitory effect in this system due to the formation of Ni(II)–chloride intermediates that are slow to participate in transmetalation.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b00744.

Experimental procedures, characterization data, NMR spectra, crystallographic data, computational details, energies and Cartesian coordinates of minimum energy calculated structures (PDF)

NMR spectra (PDF)

X-ray crystallographic data for 43 (CIF)

X-ray crystallographic data for 44 (CIF)

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■ Notes

The authors declare no competing financial interest.

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- (27) (a) The use of PMe₃ provides ~25% yield of **46** in the catalytic cross-coupling of substrate **42** with PhSnBu₃ (see SI). (b) Substrate **42** undergoes catalytic cross coupling with PhSnBu₃ in the presence of Ni(cod)₂, PPhEt₂, and KF to provide **46** in quantitative yield (see SI).
- (28) However, the involvement of odd-electron Ni species cannot be ruled out without a more in-depth mechanistic study.
- (29) Catalysis by Ni(I) was tentatively ruled out in a Ni-catalyzed Stille coupling of Ar—NMe₃⁺ electrophiles (see ref 13).
- (30) Sulfamate can bind in a κ^1 or κ^2 fashion; based on experimental evidence its hapticity in an oxidative addition complex seems to depend on the size of the phosphine ligand. Compare complex **43** (κ^1 sulfamate with two PPhEt₂ ligands) to ArNi(PCy₃)(κ^2 -OSO₂NMe₂) in: Hooker, L. V.; Neufeldt, S. R. Ligand state of nickel during C—O bond activation with monodentate phosphines. *Tetrahedron* **2018**, *74*, 6717.
- (31) A 4-centered cyclic transition state involving Ni—fluoride has been proposed for the Ni-catalyzed Stille coupling of Ar—NMe₃⁺ electrophiles (see ref 13).
- (32) “Open” (noncyclic) transmetalation transition states could not be located computationally. With palladium, these are considered most relevant in highly polar solvents in the absence of strongly coordinating anions, a scenario unlike the system currently under study.
- (33) Similarly, when **42** is stirred with Ni(cod)₂, PPhEt₂, and KF in 1,4-dioxane overnight, the only product observed by NMR is the nickel sulfamate complex **43** (there is no evidence for formation of a nickel fluoride species, see SI).

CHAPTER THREE

SMALL PHOSPHINE LIGANDS ENABLE SELECTIVE OXIDATIVE

ADDITION OF Ar—O OVER Ar—Cl BONDS AT NICKEL (0)

Contribution of Authors and Co-Authors

Manuscript in Chapter Three

Co-First Author: John E. A. Russell

Contributions: Conducted stoichiometric oxidative addition studies to explore the selectivity with various ligands. Synthesized compounds and catalysts of interest. Wrote the SI and helped revise figures and manuscript.

Co-First Author: Emily D. Entz

Contributions: Conducted catalytic studies. Synthesized compounds of interest. Wrote the SI and helped revise figures and manuscript.

Co-Author: Leidy V. Hooker

Contributions: Greatly helped with early investigations, optimizations, and rational.

Co-Author: Sharon R. Neufeldt

Contributions: Conceptualization, data curation, formal analysis, funding acquisition, computational experiments, project administration, supervision, visualization, writing – original draft; writing – review and editing.

Manuscript Information

Emily E. Entz, John E. A. Russell, Leidy V. Hooker, Sharon R. Neufeldt

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Small Phosphine Ligands Enable Selective Oxidative Addition of Ar–O over Ar–Cl Bonds at Nickel(0)

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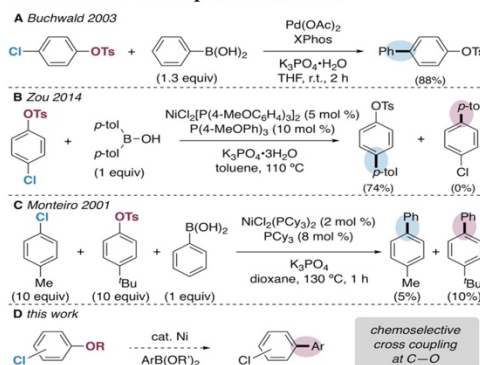
ABSTRACT: Current methods for Suzuki–Miyaura couplings of nontriflate phenol derivatives are limited by their intolerance of halides including aryl chlorides. This is because Ni(0) and Pd(0) often undergo oxidative addition of organohalides at a similar or faster rate than most Ar–O bonds. DFT and stoichiometric oxidative addition studies demonstrate that small phosphines, in particular PMe₃, are unique in promoting preferential reaction of Ni(0) with aryl tosylates and other C–O bonds in the presence of aryl chlorides. This selectivity was exploited in the first Ni-catalyzed C–O-selective Suzuki–Miyaura coupling of chlorinated phenol derivatives where the oxygen-containing leaving group is not a fluorinated sulfonate such as triflate. Computational studies suggest that the origin of divergent selectivity between PMe₃ and other phosphines differs from prior examples of ligand-controlled chemodivergent cross-couplings. PMe₃ effects selective reaction at tosylate due to both electronic and steric factors. A close interaction between nickel and a sulfonyl oxygen of tosylate during oxidative addition is critical to the observed selectivity.

INTRODUCTION

The Suzuki–Miyaura cross-coupling reaction is among the most widely used strategies for C–C bond formation in organic synthesis. This transformation is traditionally catalyzed by palladium and employs aryl halides or arenes substituted by highly labile fluorinated sulfonates (especially triflates) as electrophilic coupling partners.¹ However, recent advances in nickel-catalyzed cross-couplings have facilitated the use of more robust phenol derivatives such as aryl sulfamates, tosylates, mesylates, carbamates, and esters.² The ability to exploit less labile phenol derivatives as alternatives to aryl halides has several advantages. First, phenols can be cheaper or more accessible than organohalides. Second, many phenol derivatives can be carried through multiple synthetic steps, including those involving Pd-catalysis (e.g., Scheme 1A).³ Third, some phenol derivatives can direct other synthetic steps prior to their use in cross-coupling, such as *ortho* metalation, catalytic C–H functionalization, and electrophilic aromatic substitution.^{4,5}

Despite numerous reports of Ni-catalyzed cross-coupling of robust phenol derivatives, a critical limitation of current methods is that aryl halides such as chloride are not tolerated. This is because organohalides tend to react with Ni(0) at a similar or faster rate than Ar–O bonds.^{6,7} Efforts to achieve Ni-catalyzed Suzuki–Miyaura coupling of chlorophenol derivatives have rarely been reported, but the few existing examples demonstrate preferential coupling of the chloride (e.g., Scheme 1B), poor yields, and/or low selectivity to form a mixture of products (e.g., Scheme 1C).^{8–10} This functional group

Scheme 1. Ni- and Pd-Catalyzed Suzuki–Miyaura Couplings of Non-Triflate Chlorophenol Derivatives



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incompatibility severely limits the utility of phenol-derived electrophiles, as myriad biologically relevant synthetic targets contain halogens. For example, about 40% of drugs currently on the market or in clinical trials and about 50% of molecules in high-throughput screening are halogenated.¹¹ Among these, a large percentage (~38%) are chlorinated.¹² As such, development of methods for selective cross-coupling of chlorinated phenol derivatives via C–O cleavage (Scheme 1D) could streamline access to pharmacologically relevant targets.

Herein, we demonstrate that small phosphine ligands for Ni(0), especially PMe_3 , facilitate selective oxidative addition of Ar–OTs bonds in the presence of Ar–Cl bonds. This selectivity is accurately predicted by DFT calculations, and a series of stoichiometric studies confirm that methylphosphines are unique in enabling this C–O-selective oxidative addition. By using a Ni/ PMe_3 catalytic system, we provide proof-of-principle for a highly selective Suzuki–Miyaura cross-coupling of chloroaryl tosylates through C–O cleavage.^{10,13,14} Our DFT studies suggest that trimethylphosphine's unique effect on selectivity can be attributed to a combination of electronic and steric factors. In particular, trimethylphosphine's small size enables a close stabilizing interaction between a sulfonyl S=O and Ni during oxidative addition at C–OTs.

RESULTS AND DISCUSSION

DFT Calculations With PMe_3 . We conducted density functional theory (DFT) calculations on oxidative addition at Ni(0) to gather insight into the effect of ligands on this step.¹⁵ Our initial DFT studies examined the reaction of $\text{Ni}(\text{PMe}_3)_2$ with 4-chlorophenyl tosylate (**1**). We chose to focus on aryl tosylates because they are generally reactive toward Ni(0) but are often inert toward other reaction conditions including Pd-catalysis (e.g., Scheme 1A). PMe_3 was chosen as a model phosphine ligand due to its computational simplicity. Previous DFT studies suggested that bis-phosphine ligated nickel is likely favored over monoligated analogues during oxidative addition when dispersion is considered,¹⁶ so two PMe_3 ligands were included in these calculations. Geometry optimizations were conducted using the functional MN15L,¹⁷ and energies were further refined with MN15L using a larger basis set and 1,4-dioxane as an implicit solvent (see SI for details).

Surprisingly, our initial calculations predict that the oxidative addition of C–OTs at $\text{Ni}(\text{PMe}_3)_2$ should be significantly faster than the oxidative addition of C–Cl (Figure 1). Transition

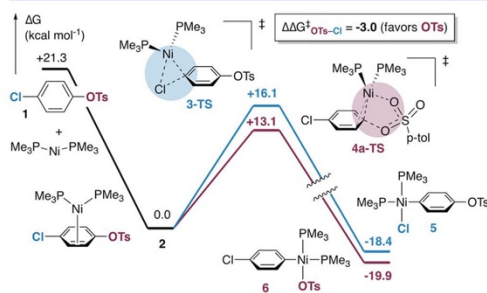


Figure 1. Free energy profile for oxidative addition of the C–O and C–Cl bonds of **1** at $\text{Ni}(\text{PMe}_3)_2$.

structure **4a-TS** is ~ 3.0 kcal mol^{-1} lower in energy than **3-TS**, suggesting that selective cross-coupling at tosylate might occur with Ni/ PMe_3 . We initially assumed that this prediction reflected error in the DFT energies, since it contradicts literature results with PCy_3 ,^{8a} 1,2-bis(diphenylphosphino)ethane,^{8b} and triarylphosphines^{8f}—ligands that are more conventional for catalysis. To our knowledge, PMe_3 had not been experimentally evaluated in Ni-catalyzed Suzuki–Miyaura cross-couplings.^{18–20}

DFT Calculations Using PCy_3 and PPh_3 . We next calculated oxidative addition transition structures with the more experimentally relevant phosphine ligands PCy_3 and PPh_3 (Figure 2). In contrast to the calculations with PMe_3 ,

R	reaction at chloride		reaction at tosylate		$\Delta\Delta G^\ddagger_{\text{OTs-Cl}}$
	$\Delta G^\ddagger$ (kcal mol^{-1})		$\Delta G^\ddagger$ (kcal mol^{-1})		
Me	16.1		13.1		-3.0
Ph	12.6		14.6		2.0
Cy	10.2		9.0		-1.2

Figure 2. Calculated free energies of activation (in kcal mol^{-1}) for oxidative addition with PMe_3 , PPh_3 , and PCy_3 , measured from the preceding π complex.

oxidative addition at $\text{Ni}(\text{PPh}_3)_2$ is predicted to be faster at chloride than tosylate ($\Delta\Delta G^\ddagger = 2.0$ kcal mol^{-1}). $\text{Ni}(\text{PCy}_3)_2$ favors reaction at tosylate but only by 1.2 kcal mol^{-1} (compared to 3.0 kcal mol^{-1} with PMe_3). These predictions are consistent with experimental reports using PCy_3 ^{8a} or triarylphosphines in catalysis^{8f} and contrast with our DFT results using PMe_3 .

Several additional DFT methods were evaluated with each of the ligands PMe_3 , PCy_3 , and PPh_3 . Most methods predict the same trend in preference for oxidative addition of tosylate ($\text{PMe}_3 > \text{PCy}_3 > \text{PPh}_3$; see SI for details). With the majority of methods tested, $\text{Ni}(\text{PMe}_3)_2$ is predicted to favor reaction at tosylate, while $\text{Ni}(\text{PPh}_3)_2$ is usually predicted to react at chloride. As such, DFT calculations suggest that the small phosphine PMe_3 is more likely to facilitate the desired chemoselectivity than traditional ligands like PCy_3 and PPh_3 .

Stoichiometric Oxidative Addition Studies. Stoichiometric oxidative addition studies with PCy_3 , PPh_3 , and PMe_3 were undertaken and the results were compared to the DFT predictions. When $\text{Ni}(\text{cod})_2$ and PCy_3 (1:2) are combined in 1,4-dioxane, a new signal appears in the ^{31}P NMR spectrum assigned to a $\text{Ni}(0)/\text{PCy}_3$ adduct (46.0 ppm, Figure 3A). Free PCy_3 (9.9 ppm) is also still detectable after 2 h. Upon addition of 1-chloronaphthalene (**7**), a new signal grows in within 2 h (11.9 ppm) corresponding to the oxidative addition adduct **9** (Figure 3B). A smaller signal at 12.9 ppm was identified as the $\text{Ni}(\text{II})$ -2-naphthyl adduct resulting from oxidative addition of 2-chloronaphthalene, which is a contaminant in commercial **7**.²¹ Alternatively, addition of aryl tosylate **8** leads to a new signal at 10.9 ppm corresponding to **10** (Figure 3C). Finally, when a $\text{Ni}(\text{cod})_2/\text{PCy}_3$ solution is combined with a mixture of **7** and **8** (1.0 equiv each), signals for both **9** and **10** appear in a 1.5:1 ratio (Figure 3D).²² These results show that $\text{Ni}(0)/\text{PCy}_3$ has a slight preference for oxidative addition of Ar–OTs in an intermolecular competition.

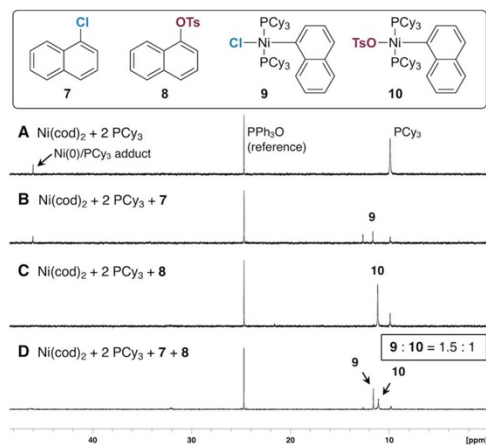


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR studies on oxidative addition at Ni/PCy_3 (reaction conditions = 2 h at room temperature in 1,4-dioxane).

The analogous experiments using PPh_3 demonstrate much higher selectivity for oxidative addition of C–Cl. In a competition reaction between **7** and **8** with $\text{Ni}(\text{cod})_2/\text{PPh}_3$ (1:2), the only oxidative addition adduct detected results from reaction at chloride (see SI for details). These results are consistent with the trends predicted by DFT as well as Zou's catalytic studies using a triarylphosphine (Scheme 1B).^{8f}

In stark contrast to PCy_3 and PPh_3 , the combination of a mixture of **7** and **8** with a 1:2 solution of $\text{Ni}(\text{cod})_2/\text{PMe}_3$ gives preferential oxidative addition at C–OTs (Figure 4). The putative oxidative addition adducts **11** and **12** are formed in about a 1:6.3 ratio based on ^{31}P NMR integrations. Taken together, the results of the intermolecular competition studies with the three ligands are consistent with the DFT-predicted

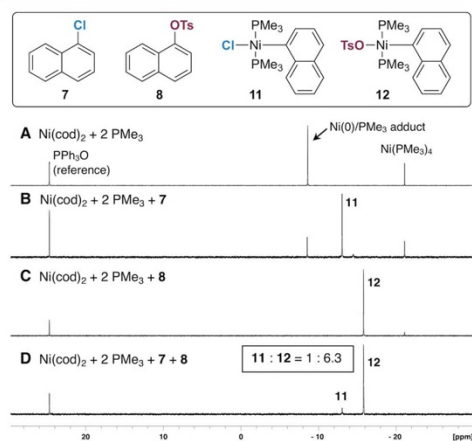


Figure 4. $^{31}\text{P}\{^1\text{H}\}$ NMR studies on oxidative addition at Ni/PMe_3 (reaction conditions = 2 h at room temperature in 1,4-dioxane).

trend in preference for oxidative addition at C–OTs ($\text{PMe}_3 > \text{PCy}_3 > \text{PPh}_3$).

A variety of additional phosphine ligands were evaluated for their effect on oxidative addition selectivity (Table 1). The

Table 1. Ligand Effect on Selectivity of Oxidative Addition

$\text{7} + \text{8} \xrightarrow[\text{1,4-dioxane, r.t., 2 h}]{\text{Ni(cod)}_2 \text{ (1 equiv)}, \text{PR}_3 \text{ (2 equiv)}} \text{A} + \text{B}$		
entry	ligand	A : B
1	PPh_3	>99 : 1
2	$\text{P}(\text{C}_6\text{H}_4\text{-OMe})_3$	>99 : 1
3	$\text{P}(\text{C}_6\text{H}_4\text{-F})_3$	>99 : 1
4	PPhMe_2	1 : 5.7
5	PPhEt_2	2.2 : 1
6	PPh_2Me	1 : 1
7	PCy_3	1.5 : 1
8	$\text{P}(\text{n-Bu})_3$	1.1 : 1
9	$\text{P}(\text{i-Bu})_3$	2.9 : 1
10 ^a	PCy_2	>99 : 1
11	PEt_3	1.8 : 1
12	PMe_3	1 : 6.3

^aWith 1 equiv of bisphosphine relative to nickel.

results show a trend that triarylphosphines strongly favor reaction at chloride (entries 1–3), while most alkyl phosphines give a mixture of products (entries 4–12). The best selectivity for reaction at tosylate is obtained with PMe_3 (entry 12), but PPhMe_2 gives similar selectivity (entry 4). Interestingly, the analogous ethyl phosphines PPhEt_2 and PEt_3 slightly favor reaction at chloride instead of tosylate (entries 5 and 11), suggesting that the small size of a methyl group on phosphine is important.

We next evaluated the selectivity when competing 1-chloronaphthalene **7** against a variety of other 1-naphthyl derivatives for oxidative addition at $\text{Ni}(\text{0})/\text{PMe}_3$ (Table 2). Excitingly, reaction of an aryl triflate (entry 1) as well as the more robust phenol derivatives mesylate (entry 3) and sulfamate (entry 4) are preferred over reaction of naphthyl chloride when using PMe_3 . The use of PCy_3 or PPh_3 results in a slight preference for reaction of triflate over chloride, but

Table 2. Selectivity of Ni/PR_3 for Reaction of Various Phenol Derivatives in Competition with 1-Chloronaphthalene

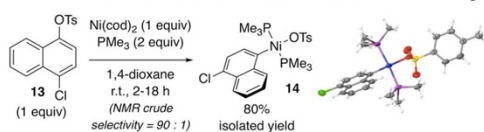
$\text{7} + \text{OR} \xrightarrow[\text{1,4-dioxane, r.t., 2 h}]{\text{Ni(cod)}_2 \text{ (1 equiv)}, \text{PMe}_3 \text{ (2 equiv)}} \text{A} + \text{B}$		
entry	–OR	A : B
1	–OTf	1:88.6
2	–OTs	1:6.3
3	–OMs	1:10.0
4	–OSO ₂ NMe ₂	1:4.6
5	–OCONEt ₂	>99:1
6	–OPiv	>99:1

^aThe reported amounts of A include the $\text{Ni}(\text{Cl})(2\text{-naphthyl})$ product resulting from the 2-chloronaphthalene contaminant in **7**, when detected.

oxidative addition of chloride is preferred over all other types of C–O bonds depicted in Table 2 with these ligands.

The chemoselectivity of oxidative addition with PMe_3 was further evaluated in an intramolecular competition. A 1:2 solution of $\text{Ni}(\text{cod})_2/\text{PMe}_3$ was combined with chloronaphthyl tosylate **13** (Scheme 2). Tentative assignment of product

Scheme 2. Chemoselective Oxidative Addition with PMe_3



signals was made by analogy to the reaction of $\text{Ni}(\text{cod})_2/\text{PMe}_3$ with **7** or **8**. The product resulting from reaction at tosylate is favored over the putative nickel chloride adduct by about 90:1, suggesting that tosylate selectivity can be even stronger in an intramolecular versus intermolecular competition.²³ The major oxidative addition adduct **14** was isolated in 80% yield and its identity was confirmed by X-ray crystallography.

Taken together, these stoichiometric studies indicate that PMe_3 and PPhMe_2 are unique in providing good selectivity for oxidative addition of aryl tosylates over aryl chlorides at $\text{Ni}(0)$.

Catalytic Studies on Chemoselective Cross-coupling. Trimethylphosphine was investigated as a ligand for a chemoselective Ni-catalyzed Suzuki–Miyaura coupling of chloroaryl tosylates. Initial conditions were modeled after previously reported cross-couplings of aryl tosylates.^{8a,24} Substrate **1**, 4-methoxyphenylboronic acid (**15**), and K_3PO_4 were combined with $\text{Ni}(\text{cod})_2$ and PMe_3 in 1,4-dioxane (Table 3). Excitingly, heating to 80 °C led to formation of products **17** and **18** in about a 1:13 ratio favoring C–OTs cleavage (entry 1). However, the yield of **18** is fair and mass balance is poor under these conditions. Moreover, PMe_3 and $\text{Ni}(\text{cod})_2$ are both highly air-sensitive, and PMe_3 is a volatile liquid that is difficult to measure accurately in small volumes. This latter feature of PMe_3 proved to be particularly problematic for reproducibility, as the reaction outcome is sensitive to the $\text{PMe}_3/\text{Ni}(\text{cod})_2$ ratio. The best ratio is $\text{PMe}_3/\text{Ni} \approx 2:1$ (9–10 mol % of PMe_3 , entries 1 and 3), but a higher or lower ratio gives worse yield of **18** and/or worse mass balance (entries 2, 4, and 5).

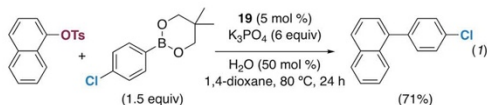
For this reason, we synthesized the $\text{Ni}(\text{II})$ precatalyst **19**. This precatalyst ensures a phosphine/nickel ratio of 2:1. Use of **19** together with boronic ester **16** led to much better mass balance and better reproducibility (entry 6). Finally, addition of a small quantity of water (0.5 equiv) enabled high yield of **18** with excellent mass balance (entry 7). Use of the chloride analogue of the precatalyst (**20**) gave similar results (entry 8).²⁵ The reaction could be set up on the benchtop by using the semistable precatalyst **21** and sparging the reaction mixture briefly with N_2 prior to heating, although the yield of **18** was somewhat eroded (entry 9).²⁶ For comparison, a variety of other phosphine ligands were also evaluated in this catalytic system. Consistent with the stoichiometric studies, PPhMe_2 gave comparable results to PMe_3 , albeit with slightly lower selectivity and yield (entry 10). All other phosphines evaluated in this catalytic reaction favored reaction at chloride or gave poor selectivity and/or yield (see SI).

Table 3. Optimization of a Chemoselective Suzuki–Miyaura Cross-Coupling of 4-Chlorophenyl Tosylate^a

entry	[B]	[Ni]	PMe_3 (mol %)	1 (%)	17 (%)	18 (%)
1	15	$\text{Ni}(\text{cod})_2$	10%	9	4	54
2	15	$\text{Ni}(\text{cod})_2$	6%	27	7	39
3	15	$\text{Ni}(\text{cod})_2$	9%	12	6	62
4	15	$\text{Ni}(\text{cod})_2$	12%	3	4	55
5	15	$\text{Ni}(\text{cod})_2$	15%	14	10	38
6	16	19		37	3	60
7 ^b	16	19		5	2	88 (72) ^c
8 ^b	16	20		1	2	83
9 ^{b,d}	16	21		21	3	61 (57) ^c
10 ^{b,e}	16	22		9	5	73

^aGC yields calibrated against undecane as the internal standard. Average of two runs. Small quantities of diarylation observed in all cases (~3–10%). PMP = *para*-methoxyphenyl. ^bWith H_2O (50 mol %). ^cIsolated yield in parentheses. ^dSet up on benchtop. ^eWith 4 mol % of the mono-THF adduct of precatalyst **22**.

The generality of the Ni/PMe_3 catalytic system was further explored with a modest scope of boronic ester coupling partners and chlorophenol derivatives (Table 4). Unsurprisingly, the high selectivity for reaction at tosylate was unaffected by the electronics of the arylboronic ester (entries 1–6), although in some cases, larger amounts of diarylated products were detected (entries 1 and 6).²⁷ High selectivity for reaction at tosylate was retained using chloroaryl tosylates with different substitution patterns (**33** and **35**). However, *ortho*-chlorophenyl tosylate **31** gives diarylation as the major product (**32**).²⁸ 4-Chlorophenyl dimethylsulfamate and triflate also provide **18** as the major product, resulting from oxidative addition of the C–O bond (entries 8–9). A considerable amount of unproductive substrate decomposition occurred when using the aryl triflate **30**.²⁹ An aryl tosylate was successfully cross-coupled with a chloro-substituted boronic ester (eq 1). However, the attempted cross-coupling of



heteroaryl substrates or boronic esters was unproductive and led to recovery of starting material or a complex mixture of products (see SI).³⁰ We anticipate that the generality of this chemoselective cross-coupling can be improved in the future by better understanding the mechanisms of catalyst deactivation or conversion to less-selective catalytic species.³¹

Computational Analysis of Selectivity Origin. Previous examples of ligand-controlled chemoselective cross-coupling

A

	NBO charge at nickel ^a	HOMO energy
$\text{Me}_3\text{P}-\text{Ni}-\text{PMe}_3$	-0.37(-0.30)	-3.27 eV
$\text{Cy}_3\text{P}-\text{Ni}-\text{PCy}_3$	-0.47(-0.24)	-2.79 eV
$\text{Ph}_3\text{P}-\text{Ni}-\text{PPh}_3$	-0.23(-0.04)	-3.47 eV

^aThe charge in parentheses is when NiL_2 is distorted into a transition state geometry.

B

NBO charge at carbon:

Figure 6. (A) Calculated NBO charges and HOMO energies for optimized $\text{Ni}(\text{PR}_3)_2$ structures, (B) NBO charges at carbon in chlorophenyl tosylate.³⁹

coupling of chloroaryl triflates (Figure 5A).^{32b} However, this electronic explanation is unsatisfying in the current system when considering PCy_3 , which is usually thought of as more electron-donating than either PPh_3 or PMe_3 .⁴⁰ $\text{Ni}(\text{PCy}_3)_2$ has a higher-energy HOMO than PMe_3 and a more negatively charged metal center, yet PCy_3 effects only poor selectivity between tosylate and chloride. As such, ligand electronics are not sufficient to explain the unique selectivity observed with PMe_3 , especially when compared to other electron-rich alkyl phosphines like PCy_3 .

To understand the difference between the behaviors of PMe_3 and PCy_3 , we more carefully examined the calculated oxidative addition transition structures using these ligands (Figure 7). With both of these ligands, insertion of $\text{Ni}(0)$ into $\text{C}-\text{Cl}$ proceeds through a concerted 3-centered transition structure in which nickel interacts with the departing chloride (3-TS and 38-TS). In contrast, 3-centered concerted transition structures for tosylate activation could not be located. Instead, $\text{C}-\text{O}$ cleavage occurs through a nucleophilic displacement mechanism: nickel does not interact significantly with the departing oxygen. During reaction at tosylate, nickel has a closer association with the *ortho* carbon of the substrate: the $\text{Ni}\cdots\text{C}_{\text{ortho}}$ distances range from 2.10–2.31 Å in the transition structures for oxidative addition at $\text{C}-\text{OTs}$ (4a-TS, 4b-TS,

37a-TS, and 37b-TS) compared to 2.33–2.37 Å for reaction at $\text{C}-\text{Cl}$ (3-TS and 38-TS, $\text{Ni}\cdots\text{C}_{\text{ortho}}$ distances not labeled). Oxidative addition of tosylate can occur through a conformation in which the $\text{S}=\text{O}$ bonds point away from nickel, referred to as a “dissociation” mechanism (4b-TS and 37b-TS), or through a conformation in which one of the sulfonyl oxygens interacts with nickel, referred to as a “5-centered” mechanism⁴¹ (4a-TS and 37a-TS). With PMe_3 , this $\text{Ni}\cdots\text{O}=\text{S}$ interaction results in a lower energy structure compared to the dissociation mechanism. However, with PCy_3 , the two mechanisms for reaction at tosylate are energetically similar.

The geometries and energetics of these transition structures are consistent with a steric argument for the different selectivity seen with PMe_3 compared to PCy_3 . If reaction at tosylate is desired, then PCy_3 has the advantage of being more electron-donating than PMe_3 (see discussion above). However, PMe_3 is also electron-donating—albeit perhaps not as strongly as PCy_3 —and it has the added advantage of minimal sterics. The reason why *small ligand size promotes reaction at tosylate is because of the possibility for a close stabilizing interaction between a sulfonyl $\text{S}=\text{O}$ and Ni during the 5-centered transition state (4a-TS)*. This interaction is also possible with PCy_3 (37a-TS), but it is less stabilizing due to a longer $\text{Ni}\cdots\text{O}=\text{S}$ distance (2.52 vs 2.33 Å). Apparently, PCy_3 sterically shields nickel from having a close interaction with oxygen. As a result, the 5-centered mechanism with PCy_3 is not more facile than the dissociation mechanism. In contrast, the 5-centered mechanism with PMe_3 is about 3 kcal mol^{−1} lower in energy than both the corresponding dissociation mechanism and the mechanism for reaction at chloride.

We conducted a distortion-interaction analysis on the relevant PMe_3 - and PCy_3 -containing transition structures to gather further evidence for the role of ligand sterics on selectivity. This type of analysis, also called an activation-strain analysis, involves dissecting the activation energy ($\Delta E^\ddagger$) into a distortion (ΔE_{dist}) and an interaction term (ΔE_{int}) (Figure 8A).⁴² The distortion term is typically a positive value (unfavorable) and represents the energy penalty for distorting

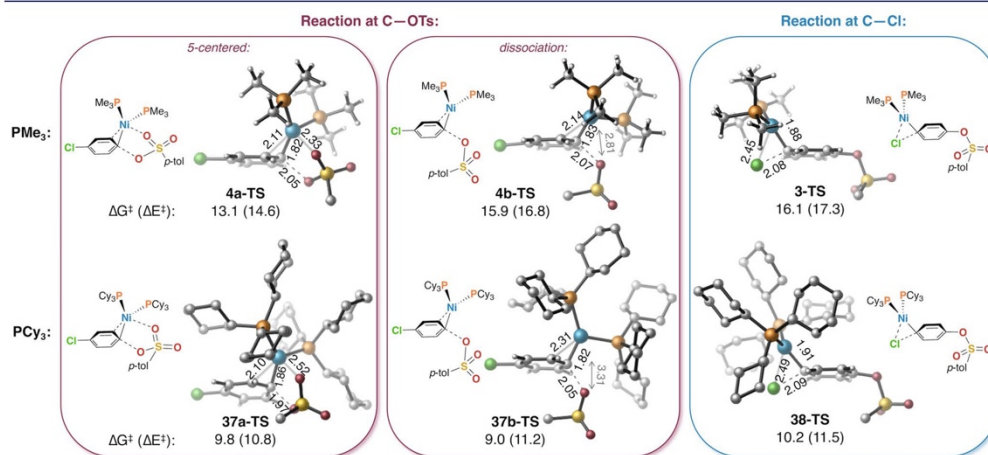


Figure 7. Oxidative addition transition structures using $\text{Ni}(\text{PMe}_3)_2$ and $\text{Ni}(\text{PCy}_3)_2$. Most of the carbons and hydrogens of tosylate, as well as the hydrogens on PCy_3 , are hidden for clarity (see SI for complete structures).

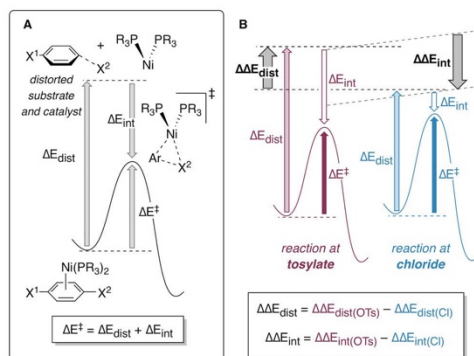


Figure 8. (A) Definition of distortion and interaction energy. (B) Selectivity is determined by the difference in distortion energy ($\Delta\Delta E_{\text{dist}}$) and interaction energy ($\Delta\Delta E_{\text{int}}$) when comparing oxidative addition at tosylate vs chloride.

the reactants into the transition state geometry. The interaction term is usually attractive (a negative value) and represents the favorable interaction between substrate and catalyst due to factors like orbital mixing, electron correlation, and Coulombic pairing of opposite charges. The relationship between distortion and interaction is defined as $\Delta E^\ddagger = \Delta E_{\text{dist}} + \Delta E_{\text{int}}$. Distortion and interaction energies of the transition structures were measured from the lowest-energy preceding π complexes.

With both PCy_3 and PMe_3 , the reaction at tosylate involves greater distortion energy than the reaction at chloride (compare total ΔE_{dist} values in Table 5). This is due to

Table 5. Distortion-Interaction Analysis of Relevant PMe_3 - and PCy_3 -Containing Transition Structures

	TS	ΔE_{dist}			$\Delta\Delta E_{\text{dist}}$	ΔE_{int}	$\Delta\Delta E_{\text{int}}$	$\Delta E^\ddagger$	$\Delta\Delta E^\ddagger$
		cat.	subst.	total					
PMe_3	4a-TS	5.2	57.4	62.6	45.0	-48.0	-47.7	14.6	-2.7
	3-TS	1.3	16.3	17.6		-0.3		17.3	
	37a-TS	1.3	47.4	48.7	41.9	-37.9	-42.6	10.8	-0.7
PCy_3	37b-TS	2.6	52.8	55.4		-44.2		11.2	
	38-TS	-3.9	10.7	6.8		4.7		11.5	

greater distortion of both the substrate and the catalyst. The substrate is more distorted during reaction at tosylate because of nickel's more extensive interaction with the arene π system (both the *ipso* and the *ortho* carbons) as well as distortion of several bond angles in the departing tosylate group. The larger catalyst distortion energies during reaction at tosylate reflect the more constrained geometry of NiL_2 . During reaction at chloride, the ligands have more room to spread out because Ni is further away from the substrate aryl ring. In fact, the catalyst distortion energy is actually slightly negative (favorable) during insertion of $\text{Ni}(\text{PCy}_3)_2$ into C-Cl (38-TS), reflecting a relaxation of the P-Ni-P bond angle in the TS compared to the preceding π complex (122° in 38-TS vs 115° in the corresponding π complex). Although distortion energy favors reaction at chloride for both ligands, interaction energy

strongly favors (is more negative) reaction at tosylate. This can be rationalized by (1) the stronger Coulombic attraction between Ni and the electron-deficient carbon of C-OTs and (2) the ability for another oxygen of S=O to interact with Ni during a 5-centered mechanism.

Selectivity of oxidative addition depends on the differences between the distortion and interaction energies for the reaction at the two possible sites. These differences are defined as $\Delta\Delta E_{\text{dist}} = \Delta E_{\text{dist}}(\text{OTs}) - \Delta E_{\text{dist}}(\text{Cl})$ and $\Delta\Delta E_{\text{int}} = \Delta E_{\text{int}}(\text{OTs}) - \Delta E_{\text{int}}(\text{Cl})$ (Figure 8B). $\Delta\Delta E_{\text{dist}}$ is always a positive value, and a larger $\Delta\Delta E_{\text{dist}}$ signifies a more powerful influence of distortion energy in favor of reaction at chloride. Conversely, $\Delta\Delta E_{\text{int}}$ is always negative. A more negative value of $\Delta\Delta E_{\text{int}}$ indicates a more powerful influence of interaction energy in favor of reaction at tosylate.

If a reaction at tosylate is desired, the dissociation mechanism with $\text{Ni}(\text{PCy}_3)_2$ (37b-TS) has a larger distortion disadvantage than either of the 5-centered mechanisms 37a-TS or 4a-TS (compare the values of $\Delta\Delta E_{\text{dist}}$ in Table 5). This may be due to the larger bending of tosylate out-of-plane of the arene in 37b-TS. However, this bending also leads to a large interaction energy advantage for the dissociation mechanism ($\Delta\Delta E_{\text{int}}$), likely due to better orbital overlap between nickel's HOMO and the C-OTs σ^* (the Ni-C-O bond angle is 117° in 37b-TS compared to 107° in 37a-TS and 101° in 4a-TS). The effects of $\Delta\Delta E_{\text{dist}}$ and $\Delta\Delta E_{\text{int}}$ nearly cancel each other out for 37b-TS, and this dissociation mechanism for reaction at tosylate using PCy_3 is only slightly lower in energy than that of the reaction at chloride. The 5-centered mechanism with PCy_3 (37a-TS) has a much smaller distortion disadvantage than either 37b-TS or 4a-TS due to the earliness of the transition structure 37a-TS.⁴³ However, 37a-TS also has less of an interaction energy advantage than the corresponding transition structure using PMe_3 (4a-TS). This is because the stabilizing $\text{Ni}\cdots\text{O}=\text{S}$ interaction in 37a-TS is less significant, as evidenced by the longer distance. In fact, when the intrinsic reaction coordinate for 37a-TS is followed, the $\text{Ni}\cdots\text{O}$ distance remains longer than that of 4a-TS until well after the transition state (when the breaking C $\cdots\text{O}$ Ts bond is elongated to 2.55 Å). As a result, the effects of $\Delta\Delta E_{\text{dist}}$ and $\Delta\Delta E_{\text{int}}$ again nearly cancel out and 37a-TS has a similar energy barrier as that for the reaction at chloride (38-TS). In contrast, the 5-centered mechanism with $\text{Ni}(\text{PMe}_3)_2$ has a stronger interaction between Ni and O=S, resulting in a value of $\Delta\Delta E_{\text{int}}$ for 4a-TS that outweighs the influence of distortion energy ($\Delta\Delta E_{\text{dist}}$) and makes the reaction at tosylate more facile than the reaction at chloride.

CONCLUSION

Prior Ni-catalyzed Suzuki-Miyaura cross-couplings of non-triflate phenol derivatives do not tolerate aryl chlorides: a feature that limits their synthetic utility. We have shown that DFT calculations accurately predict the following ligand trend for the reaction of tosylate over chloride at $\text{Ni}(0)$: $\text{PMe}_3 > \text{PCy}_3 > \text{PPh}_3$. In stoichiometric studies evaluating a wider range of phosphine ligands, we demonstrate that methylphosphines are uniquely capable of promoting the chemoselective oxidative addition of aryl tosylates in the presence of aryl chlorides. Good to excellent selectivity for the reactions of aryl triflates, mesylates, and sulfamates over aryl chlorides was also observed. This selectivity was exploited to demonstrate proof-of-principle for a C-O-selective Suzuki-Miyaura coupling of chlorinated phenol derivatives. We anticipate that a

detailed understanding of catalyst decomposition mechanisms will lead to improvements of the scope of the catalytic process.

It appears that the unique behavior of methyl phosphines compared to that of other phosphines does not relate to the catalyst's ligation state by ancillary ligands and thus differs from prior examples of ligand-controlled chemodivergent cross-couplings. Computational analysis suggests that the unusual selectivity of $\text{Ni}(\text{PMe}_3)_2$ for insertion into C–OTs is due to both electronic and steric factors. In contrast to the effect of triarylphosphines, the use of an alkyl phosphine results in an electron-rich active catalyst that can more effectively donate into the more electrophilic carbon of C–OTs. Furthermore, the small size of PMe_3 allows for a close interaction between Ni and a sulfonyl oxygen of tosylate during a 5-centered oxidative addition mechanism. This interaction helps to stabilize the buildup of positive charge at nickel during its oxidation from $\text{Ni}(0)$ to $\text{Ni}(II)$ and is less significant with bulkier alkyl phosphines. Notably, the differences observed between PMe_3 and PCy_3 caution against relying on PMe_3 as a computational model for more complex alkylphosphines.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c06995>.

Experimental and computational details, NMR spectra, crystallographic details, and calculated energies (PDF)
Cartesian coordinates of minimum-energy calculated structures (ZIP)
X-ray crystallographic data for 14 (CIF)

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Notes

The authors declare no competing financial interest.

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- (22) When detected, the small amount of the Ni(II)(2-naphthyl) chloride adduct, resulting from oxidative addition of the contaminant 2-chloronaphthalene, was included in obtaining the ratio of reaction at C–Cl vs C–O in all stoichiometric studies we report.
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- (27) Interestingly, diarylation tended to be more problematic when using older batches of Ni(II) precatalyst, even though the precatalysts were stored in a glovebox at -25°C .
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CHAPTER FOUR

NICKEL CATALYZED CROSS-COUPPLINGS OF ARYL METHYL ETHERS

Introduction

I. Introduction to Cross-Coupling Reactions and Phenol-Derived Electrophiles.

Cross-coupling occurs between an electrophile and a nucleophile resulting in a new C—C or C—heteroatom bond through the action of a transition metal catalyst. The transition metal catalyzed cross-coupling reaction is a common and valuable strategy to form new bonds, simplifying the synthesis of complex molecules. Transition metal catalyzed cross-coupling reactions take many different appearances in the form of different nucleophiles, two varieties are the focus of this report. Aryl halides are historically the preferred electrophilic coupling partner but as more research has occurred, phenol-derived electrophiles have gained prominence. Phenol-derived electrophiles display several advantages as the electrophilic cross-coupling partner when compared to aryl halides. Among these advantages are the low cost and wide availability of phenols, the precursor to phenol-derived electrophiles. The variety of available phenol-derived electrophiles spans a spectrum of reactivity with a phenol being the least reactive and triflate being the most reactive (Figure 1).¹ Many of these phenol-derived electrophiles can be carried through multiple synthetic steps, or they can direct other synthetic steps. Aryl ethers, especially aryl methyl ethers (Ar-OMe), are among the least reactive phenol-derived electrophiles (Figure 1). However, one advantage aryl methyl ethers have over the more reactive phenol-derived electrophiles is the greater atom economy of the leaving group. Furthermore, unlike many other phenol-derived electrophiles, many Ar-OMe reagents are commercially available.

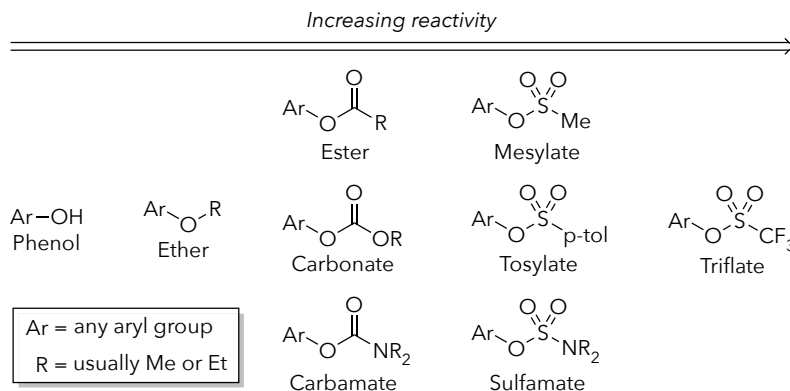


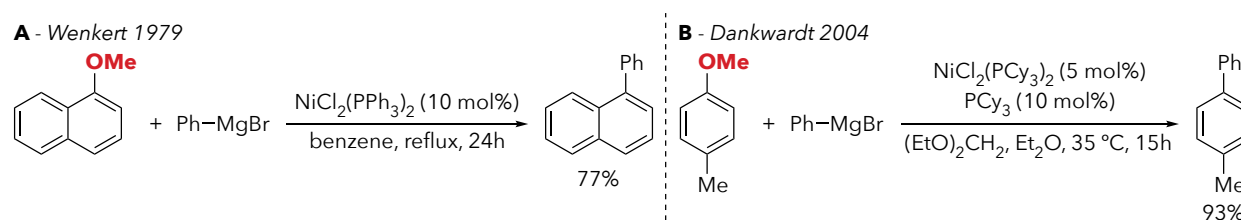
Figure 1. Relative reactivity of phenols and phenol derivatives in cross-coupling reactions.

II. An Overview of Nickel Catalysis of Cross-Coupling Reactions of Aryl Methyl Ethers.

Nickel has a long history as a catalyst in cross-coupling reactions. However, when it was discovered that palladium could also catalyze cross-coupling reactions, development and understanding of nickel catalysis slowed down until recently.² The resurgence of nickel has been driven partially due to nickel being seen as a cheaper, more earth-abundant alternative to palladium. Nickel is also able to catalyze cross-coupling reactions using electrophiles that are largely unreactive under palladium catalysis.^{1,3} This ability of nickel to react with more inert phenolic electrophiles has led to nickel being studied for new cross-coupling applications.

Wenkert, in 1979, developed the first Ni-catalyzed Kumada-Tamao-Corriu-type cross-coupling of aryl ethers with Grignard reagents (Scheme 1a).⁴ However, this reaction did not garner significant interest until many years later, partially due to the development of aryl triflates as competent phenol-derived electrophiles for similar couplings. Due to low-valent nickel possessing unique reactivity in the activation of typically unreactive C_(ar)—O bonds, the Kumada coupling of aryl methyl ethers has reemerged as a focus of active research over the past 20 years. The first major advancement since Wenkert's initial work was achieved by Dankwardt in the early 21st century (Scheme 1b). Dankwardt improved on Wenkert's conditions, which used PPh₃ as a ligand for the nickel catalyst, by exploring alkylphosphine ligands such as PCy₃ and PⁱPr₃. This

significantly improved the yields and scope of the reaction.⁵ The original conditions developed by Wenkert resulted in a scope largely limited to fused aromatic rings,⁴ whereas Dankwardt expanded this scope to include a wider variety of aryl methyl ethers.⁵ In the years following Dankwardt's work, other trialkylphosphines⁶ were studied in addition to N-heterocyclic carbene (NHC) ligands bearing bulky aryl groups such as 2,6-diisopropylphenyl.⁷ These studies have shown the ligands that result in the best yields and the broadest scope typically have the three following traits: significant steric bulk, monodenticity, and strong σ -donating ability.



Scheme 1. (a) Wenkert's pioneering conditions for the cross-coupling of aryl ethers. (b) An example of reaction improvements reported by Dankwardt.

In 2008, Tobisu and Chatani explored the Ni-catalyzed cross-coupling of aryl ethers with organoboron reagents.⁸ Consistent with the ligand trends observed with the Kumada coupling of aryl methyl ethers, they found the Ni(cod)₂/PCy₃ catalytic system was suitable for this application (Scheme 2a).⁹ Although they were able to develop a Ni-catalyzed Suzuki-Miyaura cross-coupling of Ar-OMe that showed exceptional functional group tolerance, anisole derivatives remained inert under their best conditions. Further developments on the Ni-catalyzed Suzuki-Miyaura cross-coupling of aryl ethers with organoboron reagents showed that NHC ligands substituted with bulky alkyl groups (e.g. cyclohexyl groups, aka ICy) (Scheme 2b) tend to work better than phosphine ligands mostly due to their better σ -donating ability.¹⁰ Unlike the improved conditions for the Kumada coupling of aryl methyl ethers, the Suzuki conditions are mostly restricted to naphthalene derivatives or higher π -extended aromatic substrates, which has hindered further reaction

development.¹¹ The limitations in the electrophile scope under Suzuki conditions are often attributed to a high energy barrier during oxidative addition.

III. Computational Studies of Cross-Coupling Reactions with Phenol-Derived Electrophiles.

There have been many different computational investigations regarding the oxidative addition of nickel into C—O bonds.¹² These different investigations each add a little more information about the oxidative addition step: the magnitude of the energy barrier and how this barrier is affected by reaction conditions. In general, the disparity in reactivity between methoxynaphthalene derivatives and simpler aromatic ethers such as anisole or anisole derivatives have resulted in the best Suzuki-Miyaura coupling of Ar-OMe being limited to extended π -electron systems and aryl groups with electron withdrawing groups. Naphthalene derivatives have extended π -electron systems which allow for the dearomatization of one arene ring while retaining aromaticity in the other during π -complexation which is prior to the rate determining step (oxidative addition).^{12b} Oxidative addition for the cross-coupling of Ar-OMe typically occurs through a 3-centered transition state from the preceding π -complex. Overall, this has the effect of lowering the energy barrier for the rate determining step, making it easier to obtain the oxidative addition product when compared to simpler aromatic systems. This difference is observed experimentally with the different yields between using methoxynaphthalene derivatives and anisole derivatives.^{4,5,9,10,11}

An early computational investigation into the Ni-catalyzed Suzuki-Miyaura coupling of aryl carbamates and sulfamates found that for both phenol-derived electrophiles the oxidative addition step was the rate determining step (RDS).^{12a} Cornella, Gómez-Bengoa, and Martin reported an experimental and theoretical study that entailed exploring the oxidative addition step into the C_{ar}—OMe bond.^{12b} They were able to show the Ni-catalyzed cleavage of C—OMe bonds

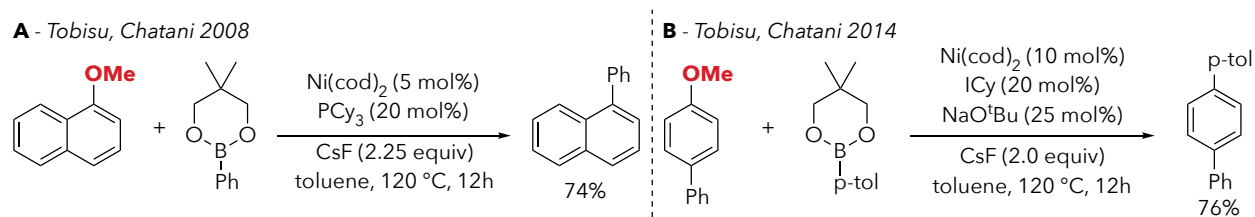
can proceed through different pathways depending on what nickel source is used. Their initial computations were also able to show that oxidative addition was the RDS and was preceded by a π -complexation event, previous to which nickel was bisligated. However, they also explored the cleavage of C—OMe bonds in the presence of silanes and showed that in this case the catalytically active species was a Ni(I)-silane and the RDS was migratory insertion into the naphthalene backbone oxidative addition was not a mechanistic step. Additional studies conducted by other groups investigating the Ni-catalyzed cleavage of C—OMe bonds showed in many cases that oxidative addition is the RDS preceded by a π -complexation step.^{12d,f,g,h,k,l} However two investigations under Kumada conditions that after the π -complex is formed, transmetalation occurs prior to oxidative addition or at least a non-typical mechanism is at play.^{12c,e} Wang and Uchiyama showed the order of transmetalation and oxidative addition were also swapped in the presence of organolithium and organozinc reagents.¹²ⁱ While many of the computational investigations support a monoligated nickel species as the catalyst in the lowest energy pathways, when dispersion is accounted for in the calculations, the lowest energy transition states often involve a bisligated nickel species.^{12j,13}

Further studies following the Martin report investigated the role of various additives in aiding the oxidative addition step. These show through computational studies that the presence of a Lewis acid can interact with the etheric oxygen weakening the C—O bond, this in turn has the effect of making the oxidative addition of nickel into the inert C—OMe bond less energy demanding,^{12c,h,i,k,l} the role of the Lewis acid can be fulfilled by the organometallic nucleophile. Grignard reagents are exceptional at stabilizing the transition state and helping the etheric oxygen act as a leaving group, but organoaluminum reagents are also able to play a cooperative role with nickel to facilitate the oxidative addition into the C—OMe bond. The combined data obtained from

these theoretical investigations indicate that the RDS is oxidative addition of nickel into the C—OMe bond preceded by a π -complexation event. The activation barrier can be decreased under Kumada conditions through the application of Lewis acids, this has the effect of stabilizing the oxidative addition transition state but this has not been found to be the case under Suzuki conditions. While much is known about the Ni-catalyzed cleavage of C—OMe bonds through the oxidative addition step, with only a handful of the studies being conducted on cross-coupling reactions, this information has thus far not been translated into expanding the scope beyond the current limitations.

IV. Expanding the Scope of the Nickel Catalyzed Cross-Coupling of Aryl Methyl Ethers.

The initial development of the Ni-catalyzed cross-coupling of aryl methyl ethers reported by Wenkert was largely limited to methoxynaphthalene derivatives, and other Ar-OMe attempted resulted in very low yields.⁴ Pursuant improvements on the Wenkert conditions conducted by several groups expanded the viable scope through exploring various ligands and further optimizing reaction conditions.^{5,7,14} The result of these studies and improvements expanded the viable scope of the reaction to include electron-neutral anisole derivatives and sterically demanding aryl methyl ethers as the electrophilic coupling partner. Thus, current methods for coupling Grignard reagents with aryl methyl ethers have very few scope limitations.



Scheme 2. (a) The pioneering work by Tobisu and Chatani of the Ni-catalyzed Suzuki-Miyaura cross-coupling of aryl ethers. (b) Further improvements to the cross-coupling of aryl ethers with organoboron nucleophiles.

Tobisu and Chatani first developed the Ni-catalyzed cross-coupling of aryl methyl ethers with organoboron reagents in 2008, but the scope was limited almost exclusively to methoxynaphthalene derivatives and PCy₃ used as the ligand (Scheme 2A).^{9a} This very limited scope was expanded to include anisole derivatives that had electron withdrawing substituents with ICy¹⁰ as the ligand (Scheme 2B). However, the scope of the reaction was still limited, likely due to the different reactivity between methoxynaphthalene derivatives and many anisole derivatives.

V. Mechanistic Studies on Oxidative Addition into C—O Bonds.

The lack of a viable strategy resulting in the efficient cross-coupling of less reactive aryl methyl ethers has led to further exploration into the Suzuki-Miyaura cross-coupling of aryl ethers stalling out until more can be understood about the nature of this problem and why it appears prevalent in Ni-catalyzed cross-coupling of low-reactivity electrophiles.¹⁵ Previous work by Nakamura provides one explanation for why the same difference in reactivity observed between methoxynaphthalene and anisole is less pronounced when using the corresponding aryl-chlorides and -bromides. Their work suggests that ligand exchange (π -complexation) is the first irreversible step and oxidative addition follows immediately, so the ability of the substrate to form a π -arene metal complex could change how the reaction progressed (Figure 2A).¹⁶ These investigations have little relevance for the coupling of Ar-OMe because of the greater reactivity of aryl halides. Studies exploring the Ni-catalyzed cleavage of less reactive C—O bonds show the π -complexation event is associated with only a small energy increase followed by a rate determining step (Figure 2B).¹² The difference in reactivity between π -extended systems and simpler aromatic systems is most often observed with aryl ethers,^{3,4,7,9} aryl fluorides,^{15a} aryl amides,^{15f} aryl esters,^{15d,e,g,h} and phenols.^{15b,c}

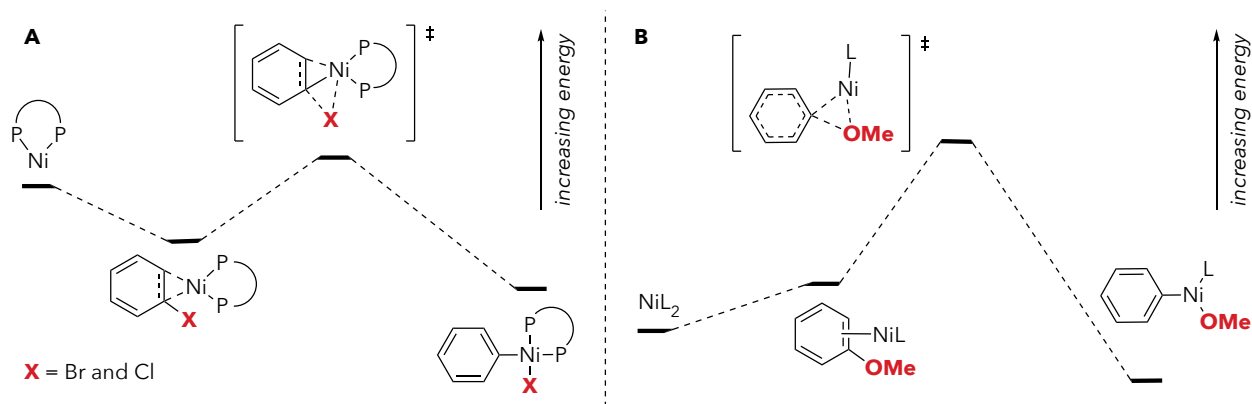


Figure 2. General energy diagrams for the insertion of nickel into aryl halide bonds^{16a} (**A**) and aryl methyl ether (**B**) bonds.^{12b}

A closer look at the literature suggests the extent of this disparate reactivity is at least partially dependent on the nature of the ligand. Recall that under the original Wenkert conditions with PPh_3 as the ligand, the reaction scope was limited to naphthyl ethers. However, later development by Dankwardt widened the scope to include phenyl ethers when different ligands bearing alkyl groups were used (e.g. PCy_3 , PCy_2Ph , P^iPr_3 , and IPr).^{5,6,7} Occasionally when Grignard reagents or other really reactive nucleophiles are employed in a cross-coupling reaction, it is possible to have transmetalation occur prior oxidative addition while the Suzuki cross-coupling follows the traditional order with oxidative addition occurring before transmetalation. This switching of the steps could help explain the observed dependence on the identity of the nucleophile, Grignard reagents appear to allow for a wider Ar-OMe scope than when organoboron reagents are used. The first report of a Ni-catalyzed Kumada cross-coupling of aryl methyl ethers displayed a significant difference in reactivity between naphthyl and phenyl ethers, but Dankwardt's work along with others seem to have remedied this problem.^{5,6,7} This survey of literature suggests the low reactivity of certain electrophiles arises from the high activation barrier of oxidative addition. This high activation barrier can be overcome by the application of a sufficiently reactive nucleophile like a

Grignard reagent or using a more advantageous ligand such as PCy₃, IPr, or ICy to expand the reaction scope beyond methoxynaphthalene derivatives and other electrophiles with extended π -systems.

VI. Background for Ligand Development.

The previous literature investigating the oxidative addition of nickel into C—OMe bond yields helpful information regarding how this process occurs and what decreases the activation barrier. The information gleaned from previous experimental and computational studies on the coupling of Ar-OMe and the corresponding oxidative addition step provide a solid base of precedent for this work. Finding a way to overcome this widespread disparity in reactivity among the less-reactive electrophiles would significantly facilitate the further development of Ni-catalyzed aromatic transformations. One possible way to overcome this challenge is to generate a more electron-rich active nickel species through exploring new ligands and tuning their electronic nature. Another way would be to develop ligands with pendant arms that could act as a directing group to guide nickel into the C—OMe bond or this pendant arm could chelate to a Lewis acid and draw electron density away from the C—OMe bond lowering the energy barrier. It is widely accepted that the nature of the ligand plays a large role in Pd-catalyzed cross-coupling reactions and tremendous work has been put into studying ligand design.¹⁷ Unfortunately, this work is not readily applicable to nickel catalysis, especially with aryl ether electrophiles.⁹ In fact, several ligands capable of promoting Pd-catalyzed Suzuki-Miyaura cross-coupling are largely ineffective in the Ni-catalyzed Suzuki-Miyaura cross-coupling of aryl ethers (Figure 3).⁹ However, a study looking at various NHC ligands revealed that ICy allowed for a larger scope of electrophiles including aryl methyl ethers that do not contain a fused ring structure. Unfortunately, electron-rich anisole derivatives still proved challenging.¹⁰ One potential solution would be to further tune and

develop ligands to effectively generate an anionic nickel species or a Ni-ate species that would facilitate the oxidative addition into C_(ar)—O bonds with a lower activation barrier.

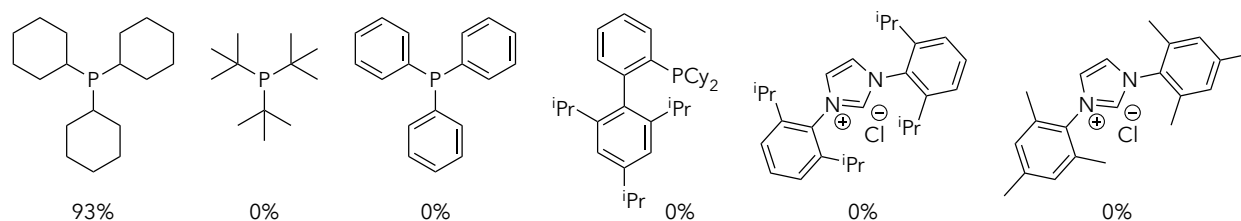


Figure 3. Examples of ligands effective for Pd-catalyzed Suzuki-Miyaura cross-coupling of aryl methyl ethers with more reactive electrophiles that are ineffective for the Ni-catalyzed version, the only exception is PCy₃.^{9a} Same reaction conditions as Scheme 2a.

Published results show that NHC ligands tend to work better than phosphine ligands for the cross-coupling of Ar-OMe under Suzuki conditions. Hydroxyphosphine ligands also show promise for facilitating the cross-coupling of low-reactivity electrophiles through the generation of an anionic nickel species. Hydroxyphosphine ligands (Figure 4A) have found a niche in Kumada-Tamao-Corriu (Kumada) reactions¹⁸ but display characteristics that could be helpful in overcoming the high oxidative addition energy barrier under Suzuki conditions.

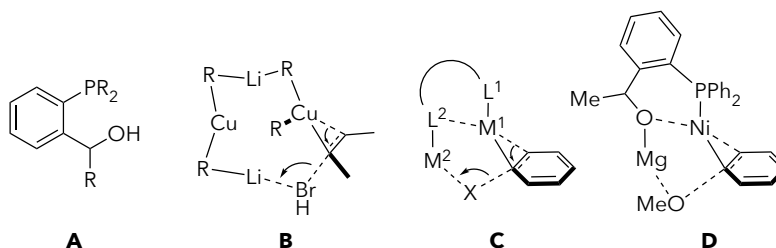
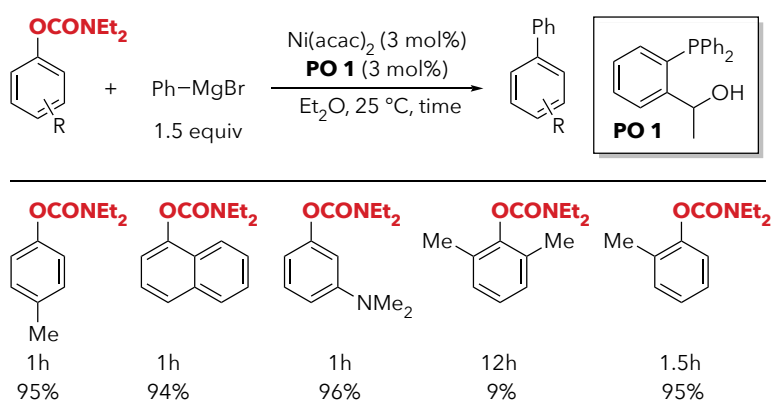


Figure 4. A general hydroxyphosphine ligand and likely modes of push-pull type C(sp²)—X bond oxidative addition.

These ligands allow for a bimetallic, push-pull design that promotes cross-coupling. In the context of this project, a bimetallic push-pull system occurs when magnesium coordinates to and pulls electron density away from the leaving group, allowing nickel to approach and undergo oxidative addition more readily. The precedent for this push-pull mechanism originates from a mechanistic

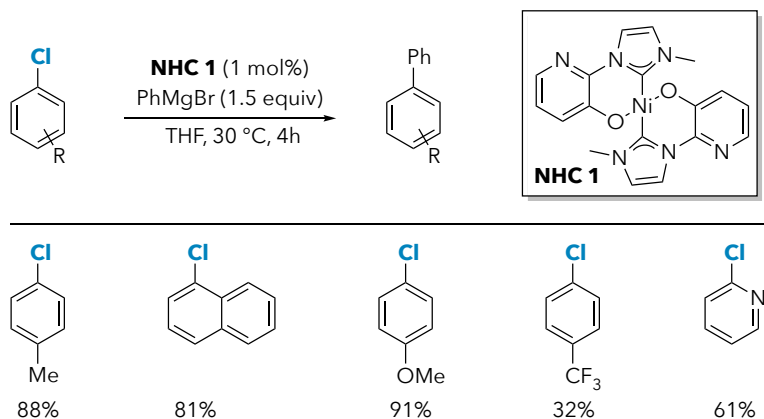
study of the oxidative addition of lithium diorganocuprate(I) into an alkenyl bromide: both theory and experiments suggest that d^{10} Cu(I) and cationic Li(I) cooperate to activate the C—Br bond in the transition state (TS) **B** (Figure 4).¹⁸ A similar scenario, **C**, is expected for Ni(0) with a hydroxyphosphine ligand that is able to simultaneously coordinate to a group-10 metal (M1) and a Lewis acidic metal (M2); this coordination to a group-10 metal did not happen with the diorganocuprate (Figure 4B).



Scheme 3. Select examples of Ni-catalyzed Kumada cross-coupling of aryl carbamates with a hydroxyphosphine ligand.

This bimetallic mechanism (Figure 4D) involving nickel and magnesium was supported by computations. The lowest energy transition state has magnesium coordinated to both the substrate and ligand oxygens (Figure 4D). The hydroxyphosphine ligands are less sterically demanding than PCy₃ yet they promote the Ni-catalyzed cross-coupling of Grignard reagents with aryl carbamates and other low-reactivity electrophiles (Scheme 3).¹⁸ Computations regarding the application of hydroxyphosphine ligands to cross-coupling reactions indicate that the pendant group is helping to direct nickel to activate the C—OMe bond through chelation with a Lewis acid.¹⁸ Hydroxyphosphine ligands also have the ability to generate anionic nickel once the hydroxy arm is deprotonated. While these ligands appear to increase the reactivity of certain electrophiles when compared to more standard ligands under the same conditions, hydroxyphosphine ligands had not

been explored with aryl ethers or under Suzuki-Miyaura (SM) cross-coupling conditions. Following the development of hydroxyphosphine and the literature showing the effectiveness of NHC ligands, an NHC ligand bearing a hydroxy pendant arm was developed by the Anantharaman group.¹⁹ They were able to turn their **NHC-OH** ligands into a bis-NHC-O/Ni complex and display the catalytic reactivity with aryl chlorides (Scheme 4). Due to the hydroxy arm, **NHC-OH** and the corresponding NHC-O/Ni complex could make nickel anionic or could chelate Lewis acids to facilitate oxidative addition.



Scheme 4. Select examples of Ni-catalyzed Kumada cross-coupling of aryl chlorides with the hydroxy-NHC/Ni complex (**NHC 1**).

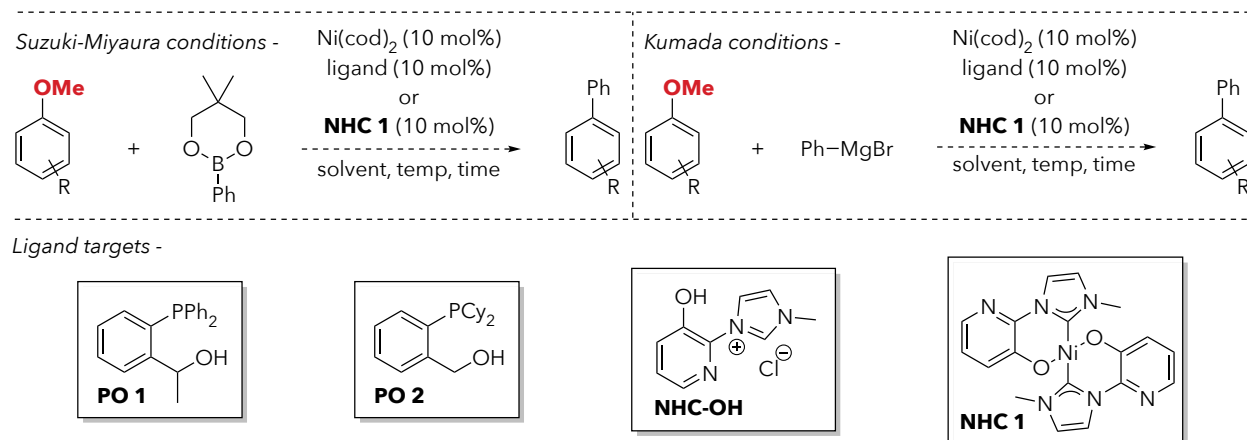
VII. Project Goals and Hypotheses.

The previous studies on the Ni-catalyzed Suzuki and Kumada couplings supplied excellent indications regarding which ligands tend to work well (e.g. PCy₃ and ICy). However, none of these ligands adequately overcome the energy barrier of oxidative addition, which limits the scope of the electrophile that can be used in the Ni-catalyzed cross-coupling reaction. Ligands bearing anionic arms pose a potential solution to lower this energy barrier and expand the scope through two different pathways. These ligands could facilitate the generation of an anionic nickel species or could participate in the push-pull system described above and thereby weaken the C_(ar)—O

bond. Our hypothesis was two-fold: An anionic ligand can be used (1) to generate an anionic nickel species or (2) to synthesize a ligand bearing a pendant arm with the potential to coordinate to a Lewis acid and direct nickel into the C—OMe bond. Ligand targets were informed by previous attempts in the Ni-catalyzed cross-coupling of Ar-OMe and the literature reports of ligands bearing hydroxyl arms being used in Ni-catalyzed cross-coupling reactions.^{18,19}

Results and Discussion

There are some examples in the literature of ligand bearing anionic arms participating in cross-coupling reactions.^{18,19} The ligands reported by Nakamura and Anantharaman provide an excellent starting point for our investigations into the cross-coupling of Ar-OMe under Suzuki conditions with the goal of expanding the scope. Initially, we synthesized the hydroxyphosphine ligand developed by Nakamura (**PO 1** in Scheme 5) before exploring novel hydroxyphosphine ligands.¹⁸ Relying on previous studies in the literature of cross-coupling Ar-OMe,^{9,10} we identified a novel ligand (**PO 2** in Scheme 5) that has increased steric bulk relative to **PO 1** and should therefore favor the oxidative addition of nickel into the C—OMe bond.



Scheme 5. General reaction schemes for Suzuki and Kumada cross-coupling reactions (top) and the ligand or complex targets (bottom).

Previous literature exploring Kumada cross-coupling with documented hydroxyphosphine ligands did not report any attempts at using aryl ethers as the electrophile. However, due to the reactivity they observed with aryl carbamates in addition to the computational studies supporting a bimetallic push-pull system, we hypothesized that hydroxyphosphine ligands could facilitate the cross-coupling of Ar-OMe under Kumada and Suzuki conditions. Thus, the hydroxyphosphine ligands provided a starting point for ligand tuning to optimize the product formation (Scheme 5).

Because of the apparent success NHCs have at promoting the cross-coupling of Ar-OMe under Suzuki conditions, a third ligand target that is an NHC bearing a hydroxymethyl-substituted pyridine ring was also proposed (Scheme 5). The presence of the hydroxymethyl substituent allows the NHC ligand to participate in the push-pull system of the hydroxyphosphine ligands. Moreover, the hydroxy arm could be deprotonated and make nickel anionic. The hydroxy-NHC (**NHC-OH**, Scheme 5) we chose to study was the one reported by Anantharaman in their efficient catalysis of the Kumada cross-coupling of aryl chlorides.¹⁹ There is no precedent for this particular ligand promoting the oxidative addition of nickel into C_(ar)—O bonds, but it could make nickel more anionic due to the oxygen arms similarly to the hydroxyphosphine ligands. After synthesizing the desired ligands, they were used under the best literature conditions for the Ni-catalyzed Suzuki-Miyaura cross-coupling of Ar-OMe.²⁰ We started our investigation by following the best literature conditions but substituting **PO 1** as the ligand (Table 1 entry 1). When initially there was no yield observed with the hydroxyphosphine ligand, the reaction conditions were varied²¹ to try to obtain the desired product (Table 1), and the other targeted ligands **PO 2** and the bis-NHC-O/Ni complex were also tested. Prior literature reports suggested the Lewis acidity of magnesium could play a role in the overall reactivity of ligands bearing an anionic arm.^{18b} Other literature provides computational evidence for the presence of Lewis acids facilitating the oxidative addition of nickel

into C—OMe bonds and cooperating in the process.^{12c,h,i,j,k} Because of this, we explored the addition of various Lewis acids (Table 1 entries 2-5) and other additives (Table 1 entries 6-8) in an effort to generate a similar push-pull type system for oxidative addition to that suggested in literature.¹⁸ However, our experimental results showed the addition of Lewis acids under Suzuki conditions did not lead to the cross-coupling product (Table 1 entries 2-5 and 9-12).²² The results from the various Lewis acids screens suggest these ligands were not able to sufficiently stabilize the transition state leading to oxidative addition; the activation barrier for the RDS was not significantly lowered by these ligands under the conditions shown in Table 1.

Often when NHC ligands are reported in the literature of Ar-OMe cross-couplings, they are stirred with a base (NaO^tBu in this case) to generate the free carbene before adding to the reaction. Due to this, in some of our investigations with **NHC-OH**, we stirred our ligand with Ni(cod)₂ and NaO^tBu prior to adding the remainder of the reactants (Table 1 entry 11), but we saw no yield in our system. **PO 1** was treated to the same prestir with Ni(cod)₂ and NaO^tBu to deprotonate the hydroxyl group. However, no product was observed in that case either, suggesting either deprotonation did not occur or the donating effect of the anionic group was not sufficient (Table 1 entry 12). Wang and Uchiyama provide computational support for PhMgBr donating a Ph group to Ni⁰ forming a reactive Ni-ate species.^{12e} Because of the precedent, we attempted stirring the nickel, ligand, and a sub-stoichiometric amount PhMgBr for 15 minutes (Table 1 entries 13 and 14) to investigate the possible formation of a reactive Ni-ate species before adding the remainder of the reagents. This attempt also did not result in formation of product. Under the conditions shown in Table 1 entries 13 and 14, the most likely reason for lack of product formation is that a sub-stoichiometric amount PhMgBr was not able to adequately promote the desired push-pull mechanism

Table one shows the results of a variety of additives and bases, but none of the conditions shown resulted in the desired product with any of the ligands. Additional variations on these reaction conditions are provided in the experimental section but also do not afford product. With these negative results, and keeping in mind that these ligands and complexes with the exception of **NHC-OH** were reported for Kumada reactions, we next turned to exploring the cross-coupling of Ar-OMe with the more reactive Grignard nucleophile PhMgBr, as shown in Table 2.

Table 1. Optimization and exploration of Ni-catalyzed Suzuki-Miyaura cross-coupling of Ar-OMe with hydroxyphosphine and hydroxy-NHC ligands.

Entry	Additive (equiv)	Base (equiv)	Ligand	Ni source	1 (%)	2 (%)	3 (%)
1	None	CsF (3.0)	PO 1	Ni(cod) ₂	>99	NR	48
2	MgBr ₂ (2.0)	K ₃ PO ₄ (3.0)	PO 1	Ni(cod) ₂	>99	NR	52
3	LiBr (2.0)	K ₃ PO ₄ (3.0)	PO 1	Ni(cod) ₂	>99	NR	49
4	ZnBr ₂ (2.0)	K ₃ PO ₄ (3.0)	PO 1	Ni(cod) ₂	>99	NR	46
5	AlCl ₃ (2.0)	K ₃ PO ₄ (3.0)	PO 1	Ni(cod) ₂	>99	NR	44
6	KF (2.0)	K ₃ PO ₄ (3.0)	PO 1	Ni(cod) ₂	>99	NR	51
7	NaO ^t Bu (2.0)	K ₃ PO ₄ (3.0)	PO 1	Ni(cod) ₂	>99	NR	47
8	CsF (2.0)	K ₃ PO ₄ (3.0)	PO 1	Ni(cod) ₂	>99	NR	48
9	MgBr ₂ (2.0)	NaOH (5.0)	PO 1	Ni(cod) ₂	>99	NR	43
10	MgBr ₂ (2.0)	K ₃ PO ₄ (3.0)	NHC-OH	Ni(cod) ₂	>99	NR	50
11	MgBr ₂ (2.0)	K ₃ PO ₄ (3.0)	NHC-OH ^a	Ni(cod) ₂	>99	NR	48
12	ZnBr ₂ (2.0)	K ₃ PO ₄ (5.0)	PO 1 ^a	Ni(cod) ₂	>99	NR	46
13	H ₂ O (5.0)	K ₃ PO ₄ (5.0)	NA	NHC 1 ^b	>99	NR	54
14	None	K ₃ PO ₄ (5.0)	NA	NHC 1 ^b	>99	NR	50
15	None	K ₃ PO ₄ (5.0)	PO 2	Ni(cod) ₂	>99	NR	2
16	H ₂ O (1.0)	K ₃ PO ₄ (5.0)	PO 2	Ni(cod) ₂	>99	NR	25
17	H ₂ O (5.0)	CsF (5.0)	PO 2	Ni(cod) ₂	>99	NR	39

^aLigand and Ni(cod)₂ were stirred in toluene with NaO^tBu (30 mol%) for 2 hours before adding to the reaction vial. ^b**NHC 1** was stirred with PhMgBr (30 mol%) for 20 minutes before adding to the reaction vial.

Since **PO 1**, **PO 2**, and **NHC 1** had been used under Kumada conditions in the literature to couple other electrophiles but not aryl methyl ethers. We initially started the investigation with the more reactive nucleophile largely using the best literature conditions except substituting Ni(cod)₂

for Ni(acac)₂ (Scheme 3 and multiple entries in Table 2). Gratifyingly, the desired product was formed in calibrated GC yields up to 89% under Kumada conditions. Since all ligands and complexes shown in table 2 (**PO 1**, **PO 2**, **NHC-OH**, and **NHC 1**) allowed for the formation new C—C bonds from Ar-OMe, the next task was to determine if these ligands would allow for better reactivity than that seen with more conventional ligands (Table 2). Our experimental results show that the **NHC-OH** ligand (Table 2 entries 1 and 2) and the bis-NHC-O/Ni complex (Table 2 entries 3-6) both work but not as well as the hydroxyphosphine ligands (See SI for more data with the NHC ligands). Gratifyingly, both versions of the hydroxyphosphine ligand (PO 1 and PO 2) facilitated moderate to high yield in the coupling of 1-methoxynaphthalene with phenylmagnesium bromide. Entry 7 in Table 2 shows a 58% calibrated yield that increases to 71% when the temperature is raised to 60 °C (Table 2 entry 8), but the yield deteriorates as the temperature is increased further (Table 2 entry 9).

Table 2. Optimization and exploration of Ni-catalyzed Kumada cross-coupling of Ar-OMe with hydroxyphosphine and hydroxy-NHC ligands.

Entry	Solvent	Ligand	Ni source	Temp	1 (%)	2 (%)	3 (%)
1	THF	NHC-OH	Ni(cod) ₂	30 °C	93	<5	27
2	toluene	NHC-OH	Ni(cod) ₂	30 °C	72	41	82
3	THF	NA	NHC 1	30 °C	87	13	23
4	toluene	NA	NHC 1	30 °C	42	49	32
5	CPME	NA	NHC 1	30 °C	87	13	28
6	dioxane	NA	NHC 1	30 °C	99	2	20
7	toluene	PO 1	Ni(cod) ₂	30 °C	35	58	48
8	toluene	PO 1	Ni(cod) ₂	60 °C	27	71	47
9	toluene	PO 1	Ni(cod) ₂	80 °C	26	65	48
10	THF	PO 1	Ni(cod) ₂	60 °C	71	28	47
11	dioxane	PO 1	Ni(cod) ₂	60 °C	66	33	39
12	CPME	PO 1	Ni(cod) ₂	60 °C	74	25	38
13	toluene	PO 2	Ni(cod) ₂	60 °C	<2	89	8

When compared to a selection of other solvents, toluene resulted in the best product yield (Table 2 entries 10-12). **PO 2** results in high yields when used under the optimized conditions for **PO 1** (Table 2 entry 13), likely due to the increased electron donating ability of the cyclohexyl groups. Optimization of this reaction with hydroxyphosphine ligands resulted in the reaction giving moderate to high yields at a temperature of 60 °C. Both hydroxyphosphine ligands resulted in moderate to high yields of the cross-coupled product under Kumada conditions.

To determine if the observed reactivity was due to the anionic pendant arm or not, the reaction results were compared to commercial PPh_3 and PCy_3 ligands (Table 3). **PO 1** and **PO 2** both resulted in better yields than PPh_3 (Table 3 entries 2-4) suggesting the hydroxyphosphine ligands do facilitate Ni-catalyzed cross-coupling of Ar-OMe better than the original Wenkert conditions. Unfortunately, **PO 1** and **PO 2** both performed worse than the inexpensive, commercially available PCy_3 at 24 hours and the optimized temperature (Table 3 entries 1, 2 and 4). This suggests the potential benefit of the anionic arm is not greater than the benefit derived from the alkyl groups. We further explored the reactivity of **PO 2** and PCy_3 by comparing the yield at lower temperatures (Table 3 entries 5 and 6), shorter reaction times (Table 3 entries 7 and 8), and with less reactive substrates (Table 3 entries 9-12) but in all cases, commercial PCy_3 performed at least as well as the novel ligand suggesting that under these conditions, the presence of a hydroxyl arm is no better than three alkyl groups.

Based on the previous literature, bulkier ligands like PCy_3 tend to result in a better yield of the cross-coupling product.^{9,10} To explore if turning one alkyl ring into an aryl ring for **PO 2** is responsible for the decreased performance, we compared **PO 2** to a series of commercial ligands (PPh_2Cy , PPhCy_2 , and PCy_3). As shown in Table 3, the observed yield does not appear to heavily depend on the number of alkyl groups on the phosphine (entries 13-17). Nearly quantitative GC

yields are obtained for the series of commercial ligands (>99%) whereas **PO 2** only resulted in a yield of 69% but when the ligand loading of **PO 2** was increased to 20 mol%, a >99% GC yield was obtained.

Table 3. Comparing the reactivity of hydroxyphosphine ligands to commercial, monodentate phosphine ligands.

Reaction scheme: Anisole (1) + Ph-MgBr (1.5 equiv) $\xrightarrow[\text{toluene, 60 } ^\circ\text{C, time}]{\text{Ni(cod)}_2 \text{ (10 mol\%)}, \text{ligand (mol\%)}}$ 1-phenylnaphthalene (2) + biphenyl (3)

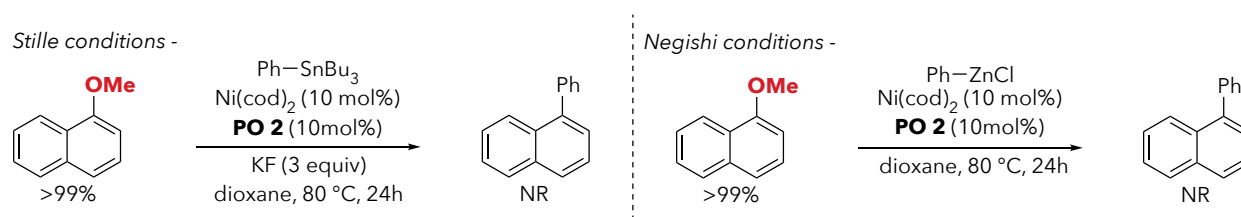
Entry	Ligand (mol%)	Temp	Time	1 (%)	2 (%)	3 (%)
1	PCy ₃ (20)	60 °C	24h	<1	>99	24
2	PO 2 (10)	60 °C	24h	<1	>99	27
3	PPh ₃ (20)	60 °C	24h	37	61	38
4	PO 1 (10)	60 °C	24h	19	74	45
5	PCy ₃ (20)	25 °C	24h	<1	>99	22
6	PO 2 (10)	25 °C	24h	5	92	22
7	PCy ₃ (20)	60 °C	1h	<1	99	29
8	PO 2 (10)	60 °C	1h	6	85	26
9 ^a	PCy ₃ (20)	60 °C	24h	15	84	30
10 ^b	PCy ₃ (20)	60 °C	24h	61	27	20
11 ^a	PO 2 (10)	60 °C	24h	84	15	25
12 ^b	PO 2 (10)	60 °C	24h	98	2	24
13	PCy ₃ (20)	60 °C	3h	<1	>99	25
14	PPhCy ₂ (20)	60 °C	3h	<1	>99	18
15	PPh ₂ Cy (20)	60 °C	3h	2	>99	24
16	PO 2 (20)	60 °C	3h	2	>99	19
17	PO 2 (10)	60 °C	3h	4	69	39

^aAnisole was used as the aryl ether. ^b2,6-dimethylanisole was used as the aryl ether.

The ligand loading results of **PO 2** suggest the benefits of a second phosphine attached to nickel outweigh the influence of possible Lewis acid chelation arising from the pendant arm. Additionally, the ligand comparison results show that just one alkyl group present on the phosphine is enough to facilitate a high yield under our conditions (Table 3) and **PO 2** performs comparably at the same loading. As seen in these results, when **PO 2** and similar commercial ligands are compared at the same ligand loading, similar yields are obtained. However, these results are not consistent with what would be expected if **PO 2** binds to nickel in a bidentate fashion similar to what is shown in

Figure 4. These results indicate that a Ni:phosphine ratio of 1:2 is more advantages than the presence of a pendant arm. Additional studies including comparing PCy₃ with **PO 2** at the same ligand loading at room temperature and also with a variety of less reactive Ar-OMe are needed to fully understand these results.

Following up on these results of our novel **PO 2** being outperformed by commercial ligands, we explored the coupling of Ar-OMe under other coupling conditions. To our knowledge, there have not been any reports for the Ni-catalyzed Stille or Negishi cross-coupling of Ar-OMe, and an advancement in this area would be notable. We set up the corresponding reactions with **PO 2** (Scheme 6) under conditions that have been successful with other phenolic electrophiles to test the reactivity with Ar-OMe. Our hypothesis was that since these nucleophiles are typically seen as more reactive than organoboron reagents, they would potentially allow for the cross-coupling of Ar-OMe. Unfortunately, there was no reaction observed and primarily starting material was observed in the GC chromatograph (Scheme 6). At this point in the development of hydroxyphosphine ligands, they appear to primarily be effective under Kumada conditions. This suggests two possibilities: (1) the presence of an organomagnesium reagent causes transmetalation to occur before oxidative addition or (2) organomagnesium can participate in the expected bimetallic mechanism while other nucleophiles cannot effectively fulfill this role. Importantly, this role in the bimetallic mechanism apparently cannot be filled by the addition of a Lewis acid, either.



Scheme 6. Reactions of an Ar-OMe under either Stille or Negishi conditions using **PO 2**.

As far as our investigations went, ligands bearing coordinating hydroxyl arms are not capable of facilitating the Ni-catalyzed cross-coupling of Ar-OMe under Suzuki-Miyaura conditions. This is displayed by the results in Table 1. When these ligands were applied to Ni-catalyzed Kumada conditions, they were found to be capable of facilitating the cross-coupling of Ar-OMe (Table 2). These ligands were effective at facilitating the Ni-catalyzed cross-coupling Ar-OMe under Kumada conditions in better yields than PPh_3 but unfortunately were less effective than PCy_3 (Table 3). After comparing **PO 2** to the commercial phosphine ligands PPh_2Cy , PPhCy_2 , and PCy_3 , we concluded that the hydroxymethyl substituent does not play a significant role in the performance of **PO 2**. Possible reasons for the observed lack of reactivity under Suzuki-Miyaura conditions include the deprotonated hydroxyl group was not able to coordinate to nickel or the coordination of an anionic group did not make the active nickel species sufficiently more nucleophilic to overcome the energy barrier but additional studies are needed to better understand the results described herein.

Conclusion

The purpose of this project was to develop an efficient Ni-catalyzed Suzuki-Miyaura cross-coupling of Ar-OMe that overcame the significant energy barrier leading to oxidative addition to widen the scope of this coupling reaction beyond the current limitations. There were two hypotheses going into this project: (1) generating an anionic nickel species through the application of a hydroxyphosphine ligand or some other anionic bidentate ligand would facilitate oxidative addition of nickel into the C—OMe bond, and (2) ligands bearing pendant arms could chelate to a Lewis acid, directing nickel to the C—OMe bond and facilitating oxidative addition. Our aim was to develop an effective Ni-catalyzed cross-coupling reaction of aryl methyl ethers through

developing ligands that would address the two points of our hypothesis and reduce the barrier of oxidative addition into the C—OMe bond. We were successful at synthesizing the targeted ligands bearing hydroxy pendant arms. When these ligands were tested under Suzuki-Miyaura conditions however, they were not able to facilitate the formation of the cross-coupled product. Why these ligands were not able to promote the cross-coupled product under Suzuki-Miyaura conditions remains unclear, but it is possible the coordination of the hydroxy group to nickel was disfavored, and added Lewis acids were not able to fill the chelating role. Under Kumada conditions, all the synthesized ligands and complexes led to the formation of the desired product, likely due to the more reactive nature of the organomagnesium reagents. Additionally, previously published computational results using hydroxyphosphine ligands under Kumada conditions suggest that the Grignard reagent chelates to both the hydroxymethyl substituent and the methyl ether, thereby facilitating oxidative addition. Unfortunately, PCy₃ and other commercial ligands resulted in better yields than the hydroxyphosphine ligands. Our investigations also suggested that a Ni:P ratio of 1:2 is more advantageous than the presence of the hydroxy arm and the benefit it could provide as seen by the results of the ligand comparisons.

Further exploration into this project should mainly be directed towards ligand development. Following up on the work with hydroxyphosphine ligands in this report, future investigations could include the synthesis of trialkyl-hydroxyphosphine ligands to have a better comparison to PCy₃. Additional studies would explore why PCy₃ and PCy₂Ph result in better reaction yields than **PO 2**, since the yields do not appear to be strictly due to the substituents on phosphorous. Another type of ligand that could yield promising results would be a hydroxydiphosphine-type ligand (Figure 5). A ligand of this type could allow for two electron donating phosphorus atoms to be bound to the nickel atom leaving the pendant arm available for coordination to a Lewis acid. Ligands bearing

a semi-labile pendant arm in addition to atoms other than phosphorus able to bind to nickel (maybe an NHC) would be of interest as well (Figure 5).

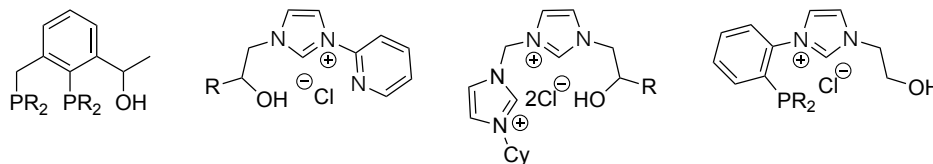


Figure 5. Examples of bidentate ligands with the potential of an anionic pendant arm.

Pursuing ligand of this type would allow for nickel to remain bound to two electron donating atoms throughout the catalytic cycle as suggested in the computations^{12j} while facilitating the coordination of a Lewis acid to draw electron density away from the C_{ar}—OMe bond. A better understanding of the commercial ligands compared to **PO 2** could be to look at their yields with less reactive Ar-OMe such as simple anisole derivatives or at lower temperatures. Other areas of investigation could include looking into the use of stronger bases and a pre-stir of the ligand and catalyst with various Lewis acids to form the hydroxyphosphine/Ni complex and set up the push-pull mechanism.¹⁸ It would be intriguing to synthesize hydroxyphosphine/Ni complexes and use them as the catalyst in further exploration in the cross-coupling of Ar-OMe. This would ensure the hydroxy arm is deprotonated and favored to follow the push-pull system described in the literature.

This work, while not able to achieve our initial aim, provides a consistent synthesis of hydroxyphosphine ligands. The comparison of a novel hydroxyphosphine ligand to a series of commercial ligands under Kumada conditions is also presented. These hydroxyphosphine ligands could make nickel anionic once deprotonated, or they could act as a directing group by chelating through a Lewis acid. Both outcomes could make oxidative addition more attainable to a wider variety of Ar-OMe electrophiles. Experimentally, however, the hydroxyphosphine ligands are

ineffective under Suzuki-Miyaura conditions described herein at promoting the cross-coupling of Ar-OMe.

Experimental Section

General Materials and Methods. NMR spectra was recorded on a Bruker Ascend Avance NEO 400 MHz (400.132 MHz for ^1H , 100.623 MHz for ^{13}C , or 161.967 MHz for ^{31}P) spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent used as an internal reference [^1H : CHCl_3 (7.26 ppm); ^{13}C CDCl_3 (77.16 ppm)].²³ ^{31}P chemical shifts are reported in ppm relative to phosphoric acid. Multiplicities are reported as follows: doublet of doublets (dd), triplet of doublets (td), quartet (q), multiplet or multiple overlapping signals (m). GC data were collected using a Shimadzu GC-2010 Plus with a flame ionization detector equipped with a SH-Rxi-5ms capillary column (15 m x 0.25 mm ID x 0.25 μm df).

Phenylboronic acid, LiCl, LiBr, ZnBr_2 , NaI, NH_4F , CsF, Cs_2CO_3 , NaF, 1-methylimidazole, 2-chloro-3-pyridinol, *p*-toluenesulfonic acid monohydrate, ethylene glycol, CPME, 2-bromobenzaldehyde, Mg turnings, 2-bromotoluene, PCy_3 , 4-methylanisole, and 2,6-dimethylanisole were obtained from Oakwood Chemical and used as received. Lithium aluminum hydride, neopentyl glycol, $\text{Ni}(\text{cod})_2$, potassium phosphate, aluminum chloride, calcium chloride, potassium fluoride, sodium *tert*-butoxide, sodium bromide, potassium *tert*-butoxide, 1-chloronaphthalene, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and 1,2-dibromoethane were obtained from Acros Organics as used as received. DCM, MgSO_4 , EtOAc, hexanes, Et_2O , NaOH, NaCl, MgBr_2 , NH_4Cl , KCl, MeCN, EtOH, and Na_2SO_4 were obtained from Fisher Chemical and used as received. Potassium diphenylphosphide, KBr, MgCl_2 , ZnCl_2 , $\text{Mg}(\text{ClO}_4)_2$, AlEt_3 , and AlMe_3 were obtained from Sigma-

Aldrich and used as received. Chlorodicyclohexylphosphine, 2'-fluoroacetophenone, 1-methoxynaphthalene, PPh₂Cy, anisole, NaBf₄, and Li₂CO₃ were obtained from TCI America and used as received. Tributylphenylstannane, PPh₃, NaCN, NaOEt, K₂CO₃, and MgO were obtained from Alfa Aesar and used as received. PPhCy₂ was obtained from Strem Chemicals and used as received. CDCl₃ was obtained from Cambridge Isotope Laboratories and used as received. 1,4-dioxane and phenylmagnesium bromide (1.6M in CPME, **4**) were obtained from Acros in ACROSeal bottles (extra dry) and used as received. *n*-butyl lithium (2.5M in hexanes) and *t*-butyl lithium (1.7M in pentane) were obtained from Sigma-Aldrich in Sure/Seal bottles and used as received. THF and toluene were obtained from Fisher Chemical and degassed and dried with a JC Meyer solvent system prior to use. **PO 1**,^{18b} **NHC-OH**,¹⁹ **NHC 1**,¹⁹ 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**5**),²⁴ (PPh₃)₂NiCl₂,²⁵ chlorophenylzinc,²⁶ 2-(2-bromophenyl)-1,3-dioxolane,²⁷ and 1-[2-(diphenylphosphino)phenyl]ethenone,²⁸ dicyclohexyl[2-(1,3-dioxolan-2-yl)phenyl]phosphine²⁹ and 2-(dicyclohexylphosphino)-benzaldehyde (**6**)²⁹ were synthesized by literature procedures.

General Procedure for Suzuki-Miyaura Cross-Coupling of Aryl Methyl Ethers. In a nitrogen atmosphere glovebox, the base (3.0 equiv or 5.0 equiv), **1** (14.5 μ L, 0.1 mmol, 1.0 equiv), **5** (28.5 mg, 0.15 mmol, 1.5 equiv), and any indicated additives were combined in a one-dram vial equipped with a stir bar. In a second vial was prepared a stock solution of Ni(cod)₂ and the appropriate ligand in toluene (0.033 *mM* with respect to nickel) or **NHC 1** in toluene (0.033 *mM* with respect to nickel). 300 μ L of the nickel stock solution was added to the reaction vial (0.01 mmol of nickel, 10 mol%). The vial was sealed with a cap with a PTFE-lined septum and removed from the glovebox. The reactions were stirred at 120 °C for 24 h unless otherwise indicated. Undecane (10.5 μ L, 0.5 equiv) was then added as an internal GC standard and the vial was diluted to the top with

Et₂O and mixed well. As aliquot of the reaction mixture was filtered through celite and analyzed by GC.

Table 4. Extra optimization results for **NHC-OH** under the Suzuki conditions with various additives.

Entry	Additive (equiv)	Base (equiv)	Ligand	1 (%)	2 (%)	3 (%)
1	Mg(ClO ₄) ₂ (2.0)	K ₃ PO ₄ (3.0)	NHC-OH	>99	NR	NR
2	MgO (2.0)	K ₃ PO ₄ (3.0)	NHC-OH	>99	NR	NR
3	MgBr ₂ (2.0)	K ₃ PO ₄ (3.0)	NHC-OH	>99	NR	NR
4	MgCl ₂ (2.0)	K ₃ PO ₄ (3.0)	NHC-OH	>99	NR	NR
5	Mg(ClO ₄) ₂ (2.0)	NaO ^t Bu (3.0)	NHC-OH	>99	NR	NR
6	MgO (2.0)	NaO ^t Bu (3.0)	NHC-OH	>99	NR	NR
7	MgBr ₂ (2.0)	NaO ^t Bu (3.0)	NHC-OH	>99	NR	NR
8	MgCl ₂ (2.0)	NaO ^t Bu (3.0)	NHC-OH	>99	NR	NR
9	ZnBr ₂ (2.0)	NaO ^t Bu (3.0)	NHC-OH	>99	NR	NR
10	AlCl ₃ (2.0)	NaO ^t Bu (3.0)	NHC-OH	>99	NR	NR
11	Mg(ClO ₄) ₂ (2.0)	K ₃ PO ₄ (3.0)	NHC-OH ^a	>99	NR	NR
12	MgO (2.0)	K ₃ PO ₄ (3.0)	NHC-OH ^a	>99	NR	NR
13	MgBr ₂ (2.0)	K ₃ PO ₄ (3.0)	NHC-OH ^a	>99	NR	NR
14	MgCl ₂ (2.0)	K ₃ PO ₄ (3.0)	NHC-OH ^a	>99	NR	NR
15	None	K ₃ PO ₄ (5.0)	NHC-OH ^{ab}	>99	NR	NR

^aLigand and Ni(cod)₂ were stirred in toluene with NaO^tBu (30 mol%) for 2 hours before adding to the reaction vial.

^bBoronic ester was stirred with nBuLi (1.0 equiv) for 5 minutes before placing in the freezer.

Table 5. Extra optimization results of the Suzuki conditions using **NHC 1** as the nickel source and testing various additives.

Entry	Additive (equiv)	Base (equiv)	Ni source	1 (%)	2 (%)	3 (%)
1	Mg(ClO ₄) ₂ (2.0)	K ₃ PO ₄ (3.0)	NHC 1	>99	NR	NR
2	MgO (2.0)	K ₃ PO ₄ (3.0)	NHC 1	>99	NR	NR
3	MgBr ₂ (2.0)	K ₃ PO ₄ (3.0)	NHC 1	>99	NR	NR
4	MgCl ₂ (2.0)	K ₃ PO ₄ (3.0)	NHC 1	>99	NR	NR
5	None	K ₃ PO ₄ (3.0)	NHC 1	>99	NR	NR

~Table 5 continued on the next page~

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6	H ₂ O (5.0)	K ₃ PO ₄ (5.0)	NHC 1 ^a	>99	NR	54
7	None	K ₃ PO ₄ (5.0)	NHC 1 ^a	>99	NR	50
8	None	K ₃ PO ₄ (5.0)	NHC 1	>99	NR	62
9	AlMe ₃ (2.0)	K ₃ PO ₄ (5.0)	NHC 1	>99	NR	52
10	AlEt ₃ (2.0)	K ₃ PO ₄ (5.0)	NHC 1	>99	NR	74

^aNHC 1 was stirred with PhMgBr (30 mol%) for 20 minutes before adding to the reaction vial.

Table 6. Vials displaying the use of PMe₃ nickel precatalysts that were effective for obtaining chemoselective cross-coupling of aryl-OTs over aryl-Cl.

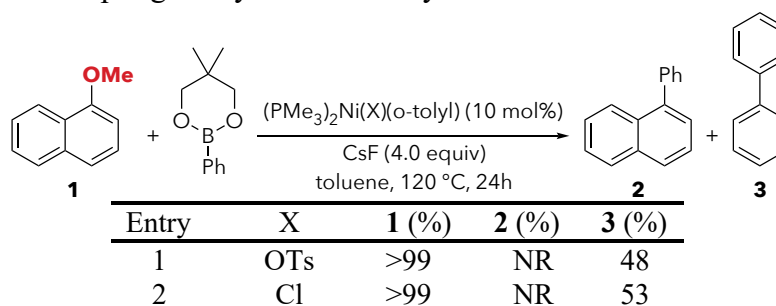
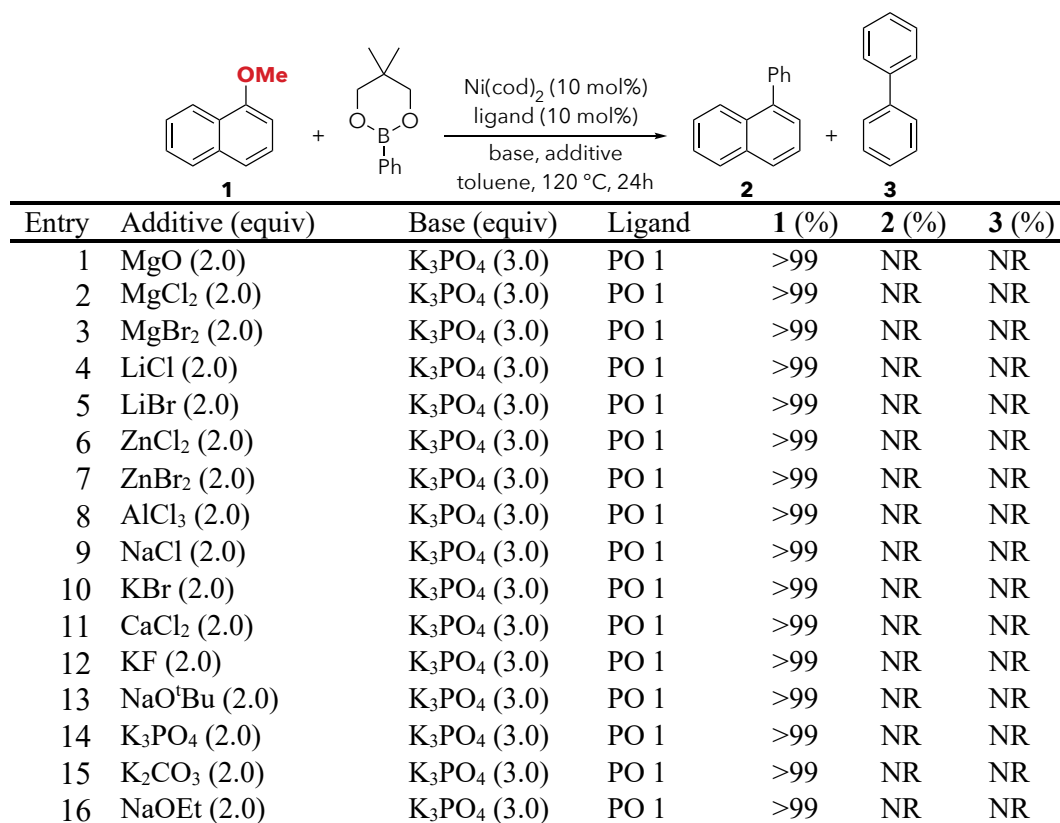


Table 7. Extra optimization results for NHC-OH under the Suzuki conditions with various additives.



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17	NaI (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
18	NaBF ₄ (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
19	NH ₄ F (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
20	NaBr (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
21	NH ₄ Cl (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
22	KCl (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
23	NaCN (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
24	CsF (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
25	KO ^t Bu (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
26	Cs ₂ CO ₃ (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
27	NaF (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
28	Mg(ClO ₄) ₂ (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
29	Li ₂ CO ₃ (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
30	AlEt ₃ (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
31	[(CH ₃) ₂ CHO] ₃ B (2.0)	K ₃ PO ₄ (3.0)	PO 1	>99	NR	NR
32	None	K ₃ PO ₄ (3.0)	PO 1 ^a	>99	NR	NR
33	MgBr ₂ (2.0)	K ₃ PO ₄ (3.0)	PO 1 ^a	>99	NR	NR
34	None	K ₃ PO ₄ (5.0)	PO 1	>99	NR	NR
35	MgBr ₂ (2.0)	K ₃ PO ₄ (5.0)	PO 1	>99	NR	NR
36	MgO (2.0)	K ₃ PO ₄ (5.0)	PO 1	>99	NR	NR
37	None	NaOH (5.0)	PO 1	>99	NR	NR
38	MgBr ₂ (2.0)	NaOH (5.0)	PO 1	>99	NR	NR
39	MgO (2.0)	NaOH (5.0)	PO 1	>99	NR	NR
40	MgO (2.0)	K ₃ PO ₄ (5.0)	PO 1 ^a	>99	NR	NR
41	MgCl ₂ (2.0)	K ₃ PO ₄ (5.0)	PO 1 ^a	>99	NR	NR
42	ZnBr ₂ (2.0)	K ₃ PO ₄ (5.0)	PO 1 ^a	>99	NR	NR
43	None	K ₃ PO ₄ (5.0)	PO 1 ^{ab}	>99	NR	NR
44	None	K ₃ PO ₄ (5.0)	PO 1	>99	NR	80
45	AlMe ₃ (2.0)	K ₃ PO ₄ (5.0)	PO 1	>99	NR	78
46	AlEt ₃ (2.0)	K ₃ PO ₄ (5.0)	PO 1	>99	NR	81
47	None	K ₃ PO ₄ (5.0)	PO 2	>99	NR	2
48	H ₂ O (1.0)	K ₃ PO ₄ (5.0)	PO 2	>99	NR	25
49	H ₂ O (1.0)	NaO ^t Bu (5.0)	PO 2	>99	NR	30
50	H ₂ O (1.0)	KO ^t Bu (5.0)	PO 2	>99	NR	18
51	H ₂ O (1.0)	CsF (5.0)	PO 2	>99	NR	23
52	H ₂ O (1.0)	KF (5.0)	PO 2	>99	NR	24
53 ^c	H ₂ O (1.0)	CsF (5.0)	PO 2	>99	NR	19
54	H ₂ O (5.0)	CsF (5.0)	PO 2	>99	NR	39

^aLigand and Ni(cod)₂ were stirred in toluene with NaO^tBu (30 mol%) for 2 hours before adding to the reaction vial.

^bBoronic ester was stirred with nBuLi (1.0 equiv) for 5 minutes before placing in the freezer. ^cAlso had MgBr₂ (2.0 equiv) in the reaction.

General Procedure for Kumada Cross-Coupling of Aryl Methyl Ethers. In a nitrogen atmosphere

glovebox, **1** (14.5 μ L, 0.1 mmol, 1.0 equiv), **4** (93.8 μ L, 0.15 mmol, 1.5 equiv), and any indicated

additives were combined in a one-dram vial equipped with a stir bar. In a second vial was prepared a stock solution of Ni(cod)₂ and the appropriate ligand in toluene (0.033 *mM* with respect to nickel) or **NHC 1** in toluene (0.033 *mM* with respect to nickel). 300 μ L of the nickel stock solution was added to the reaction vial (0.01 mmol of nickel, 10 mol%). The vial was sealed with a cap with a PTFE-lined septum and removed from the glovebox. The reactions were stirred at 60 °C for 24 h unless otherwise indicated. Undecane (10.5 μ L, 0.5 equiv) was then added as an internal GC standard and the vial was diluted to the top with Et₂O and mixed well. An aliquot of the reaction mixture was filtered through celite and analyzed by GC.

Table 8. Additional optimization results using **NHC 1** or **NHC-OH**.

Reaction scheme: 1-methoxynaphthalene (**1**) + Ph-MgBr $\xrightarrow[\text{solvent, temp, time}]{\text{Ni(cod)}_2 \text{ (10 mol\%)} \text{ or ligand (10 mol\%)} \text{ or NHC 1 (10 mol\%)}}$ 1-phenylnaphthalene (**2**) + 1-phenylnaphthalene (**3**)

Entry	Solvent	Ligand	Ni source (mol%)	Temp	Time	1 (%)	2 (%)	3 (%)
1	THF	NHC-OH	Ni(cod) ₂ (10)	30 °C	24h	93	<5	27
2	THF	NA	NHC 1 (10)	30 °C	24h	33	67	34
3	toluene	NHC-OH	Ni(cod) ₂ (10)	30 °C	24h	72	41	82
4	toluene	NA	NHC 1 (10)	30 °C	24h	13	85	69
5	toluene	NA	NHC 1 (10)	30 °C	24h	64	35	43
6	toluene	NA	NHC 1 (10)	25 °C	24h	76	23	44
7 ^a	toluene	NA	NHC 1 (10)	30 °C	24h	73	19	30
8	toluene	NA	NHC 1 (10)	30 °C	24h	66	25	44
9 ^b	toluene	NA	NHC 1 (10)	30 °C	24h	40	40	56
10	toluene	NA	NHC 1 (10)	30 °C	2h	91	8	34
11	toluene	NA	NHC 1 (10)	30 °C	4h	75	14	34
12	toluene	NA	NHC 1 (10)	30 °C	8h	76	24	36
13	toluene	NA	NHC 1 (10)	30 °C	12h	61	39	42
14	toluene	NA	NHC 1 (10)	30 °C	24h	62	36	39
15	toluene	NA	NHC 1 (10)	30 °C	48h	44	50	40
16	toluene	NA	NHC 1 (2.5)	30 °C	24h	39	27	50
17	toluene	NA	NHC 1 (5.0)	30 °C	24h	37	27	48
18	toluene	NA	NHC 1 (10.0)	30 °C	24h	42	49	32
19	toluene	NA	NHC 1 (15.0)	30 °C	24h	47	43	30
20	toluene	NA	NHC 1 (20.0)	30 °C	24h	52	39	29
21	THF	NA	NHC 1 (10)	30 °C	24h	87	13	23

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22	toluene	NA	NHC 1 (10)	30 °C	24h	39	48	32
23	CPME	NA	NHC 1 (10)	30 °C	24h	87	13	28
24	dioxane	NA	NHC 1 (10)	30 °C	24h	99	2	20
25	DCM	NA	NHC 1 (10)	30 °C	24h	>99	<1	41
26	toluene	NA	NHC 1 (10)	30 °C	24h	55	23	42
27	toluene	NA	NHC 1 (10)	60 °C	24h	41	24	41
28	toluene	NA	NHC 1 (10)	80 °C	24h	39	25	41
29	toluene	NA	NHC 1 (10)	100 °C	24h	37	26	39
30	toluene	NA	NHC 1 (10)	30 °C	24h	54	23	40
31	toluene	NA	NHC 1 (10)	30 °C	72h	53	22	40
32	toluene	NA	NHC 1 (10)	30 °C	24h	69	17	42
33	toluene	NA	NHC 1 (10)	30 °C	24h	45	26	53
34 ^c	toluene	NA	NHC 1 (10)	30 °C	24h	93	6	26
35 ^d	toluene	NA	NHC 1 (10)	30 °C	24h	>99	<1	15

^a1.0 equiv of PhMgBr was used. ^b2.0 equiv of PhMgBr was used. ^cAlMe₃ (2.0 equiv) was added. ^dAlEt₃ (2.0 equiv) was added.

Table 9. Additional optimization results with the hydroxyphosphine ligands.

Reaction scheme: 1-methylnaphthalene (1) + Ph-MgBr $\xrightarrow[\text{solvent, temp, time}]{\text{Ni(cod)}_2 (10 \text{ mol\%}), \text{ligand (mol\%)}}$ 1-phenylnaphthalene (2) + biphenyl (3)

Entry	Solvent	Ligand (mol%)	Temp	Time	1 (%)	2 (%)	3 (%)
1	toluene	PO 1 (10)	30 °C	24h	35	58	48
2 ^a	toluene	PO 1 (10)	30 °C	24h	96	13	20
3 ^b	toluene	PO 1 (10)	30 °C	24h	>99	<1	13
4	toluene	PO 1 (10)	25 °C	24h	49	51	42
5	toluene	PO 1 (10)	60 °C	24h	27	71	47
6	toluene	PO 1 (10)	80 °C	24h	26	65	48
7	toluene	PO 1 (10)	100 °C	24h	36	57	47
8	toluene	PO 1 (10)	30 °C	24h	34	58	40
9	toluene	PO 1 (10)	60 °C	24h	29	69	40
10	toluene	PO 1 (12)	60 °C	24h	26	69	38
11	toluene	PO 1 (15)	60 °C	24h	27	71	35
12	toluene	PO 1 (20)	60 °C	24h	27	72	34
13	toluene	PO 1 (10)	60 °C	24h	22	66	52
14	THF	PO 1 (10)	60 °C	24h	71	28	47
15	dioxane	PO 1 (12)	60 °C	24h	66	33	39
16	CPME	PO 1 (15)	60 °C	24h	74	25	38
17	Et ₂ O	PO 1 (20)	60 °C	24h	44	60	42
18	toluene	PO 1 (10)	60 °C	24h	25	68	50
19	toluene	PO 1 (10)	40 °C	24h	26	63	49

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20	toluene	PO 1 (10)	50 °C	24h	29	65	49
21	toluene	PO 1 (10)	70 °C	24h	23	67	50
22	toluene	PO 1 (10)	60 °C	2h	32	68	48
23	toluene	PO 1 (10)	60 °C	6h	26	72	51
24	toluene	PO 1 (10)	60 °C	10h	26	70	47
25	toluene	PO 1 (10)	60 °C	24h	24	75	49
26	toluene	PO 1 (10)	60 °C	48h	24	72	47
27	toluene	PO 2 (10)	60 °C	24h	<2	89	8
28 ^c	toluene	PO 1 (10)	60 °C	24h	90	9	13

^aAlMe₃ (2.0 equiv) was added. ^bAlEt₃ (2.0 equiv) was added. ^c o-tolylphenyl MgBr (1.5 equiv) was used.

Table 10. Additional reactions exploring the performance of various ligands.

Entry	Ligand (mol%)	Temp	Time	1 (%)	2 (%)	3 (%)
1	PCy ₃ (20)	60 °C	2h	<1	>99	25
2	PCy ₃ (20)	60 °C	6h	<1	90	22
3	PCy ₃ (20)	60 °C	8h	<1	>99	25
4	PCy ₃ (20)	60 °C	24h	<1	>99	24
5	PO 2 (10)	60 °C	2h	<1	85	26
6	PO 2 (10)	60 °C	6h	<1	90	26
7	PO 2 (10)	60 °C	8h	<1	94	26
8	PO 2 (10)	60 °C	24h	<1	>99	27
9	PPh ₃ (20)	60 °C	24h	37	61	38
10	PO 1 (10)	60 °C	24h	19	74	45
11	PCy ₃ (20)	25 °C	24h	<1	>99	22
12	PO 2 (10)	25 °C	24h	5	92	22
13	PCy ₃ (20)	60 °C	30min	<1	96	4
14	PCy ₃ (20)	60 °C	1h	<1	99	29
15	PCy ₃ (20)	60 °C	1.5h	<1	98	30
16	PCy ₃ (20)	60 °C	2h	<1	98	27
17	PCy ₃ (20)	60 °C	2.5h	<1	97	27
18	PCy ₃ (20)	60 °C	3h	<1	95	27
19	PO 2 (10)	60 °C	30min	13	94	30
20	PO 2 (10)	60 °C	1h	6	85	26
21	PO 2 (10)	60 °C	1.5h	5	86	27
22	PO 2 (10)	60 °C	2h	<1	82	26
23	PO 2 (10)	60 °C	2.5h	<1	81	25
24	PO 2 (10)	60 °C	3h	<1	84	25
25	PCy ₃ (20)	60 °C	24h	<1	>99	23

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26	PCy ₃ (10)	60 °C	24h	<1	95	29
27	PPhCy ₂ (20)	60 °C	24h	<1	>99	17
28	PPhCy ₂ (10)	60 °C	24h	<1	>99	20
29	PCy ₃ (20)	60 °C	24h	<1	>99	27
30	PPhCy ₂ (20)	60 °C	24h	<1	>99	17
31	PPh ₂ Cy (20)	60 °C	24h	<1	>99	23
32	PCy ₃ (20)	60 °C	3h	<1	>99	25
33	PCy ₃ (10)	60 °C	3h	<1	96	30
34	PPhCy ₂ (20)	60 °C	3h	<1	>99	18
35	PPhCy ₂ (10)	60 °C	3h	<1	97	23
36	PPh ₂ Cy (20)	60 °C	3h	2	>99	24
37	PPh ₂ Cy (10)	60 °C	3h	<1	>99	25
38	PO 2 (20)	60 °C	3h	2	>99	19
39	PO 2 (10)	60 °C	3h	4	69	39

Synthesis of (2-(Dicyclohexylphosphino)phenyl)methanol **PO 2**. Synthesized by a modified literature procedure.^{18b} In a nitrogen atmosphere glovebox, LiAlH₄ (28.1 mg, 0.74 mmol, 1.5 equiv) and THF (5mL) were added to an oven-dried 25 mL round bottom flask and **6** was dissolved in 3 mL of THF in a 20 mL vial and sealed with a rubber septum. The round bottom flask was removed from the glovebox and cooled to 0 °C while stirring under nitrogen. While stirring at 0 °C, **6** was added dropwise over 10 minutes with nitrogen pressure. Then the reaction mixture was stirred for 30 minutes at 0 °C before diluting with another 5 mL of THF, treating successively with degassed H₂O (0.1 mL), degassed 15% aq. NaOH (0.1 mL), and degassed H₂O (0.3 mL). The RBF containing the reaction mixture was brought back into the glovebox and filtered through a short silica plug under vacuum and washed with Et₂O (5 mL) and DCM (1.5 mL). After this, the filtrate was transferred to a 20 mL vial, capped loosely, placed in a vacuum chamber which was sealed, the chamber was removed from the glovebox, and all volatiles were removed under hi-vac. Once all volatiles were removed, the product was purified by KugelRohr. This was achieved by bringing the vacuum chamber with the crude product inside back into the glovebox, the crude product was transferred into a 50 mL RBF, sealed with a rubber septum, removed from the glovebox, and

attached to the KugelRohr after flushing the system with nitrogen. Once the distillation was complete, the RBF containing the product was removed, quickly sealed with a rubber septum, and transferred into the glovebox. Once inside the glovebox, the product was dissolved in DCM (3 mL) and filtered through a short silica plug under vacuum to remove any phosphine oxides. The filtrate was transferred to a 20 mL vial, capped loosely, placed in a vacuum chamber which was sealed, removed from the glovebox, and placed under hi-vac to remove all volatiles. **PO 2** was obtained as a viscous opaque oil was obtained after all volatiles were removed to result in a 80% yield of 121.7 mg. ^1H NMR (400 MHz, CDCl_3 , δ): 7.51-7.45 (m, 1H), 7.37-7.26 (multiple signals, 3H), 4.86 (dd, $J = 7.3, 1.4$ Hz, 2H), 3.05 (q, $J = 7.3$ Hz, 1H), 2.01-1.88 (multiple signals, 3H), 1.65 (td, $J = 46.5, 12.1$ Hz, 8H), 1.38-0.97 (multiple signals, 11H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , δ): 147.1 (d, $J_{\text{CP}} = 24.0$ Hz), 132.4 (d, $J_{\text{CP}} = 17.9$ Hz), 132.3 (d, $J_{\text{CP}} = 3.3$ Hz), 128.3, 127.8 (d, $J_{\text{CP}} = 7.4$ Hz), 126.3, 64.2 (d, $J_{\text{CP}} = 18.3$ Hz), 32.9 (d, $J_{\text{CP}} = 10.1$ Hz), 29.7 (d, $J_{\text{CP}} = 16.2$ Hz), 28.2 (d, $J_{\text{CP}} = 7.6$ Hz), 26.3 (d, $J_{\text{CP}} = 12.5$ Hz), 26.1 (d, $J_{\text{CP}} = 8.0$ Hz), 24.8; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , δ): -15.3.

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21. All optimization with the hydroxyphosphine ligands were conducted with the triaryl-hydroxyphosphine ligand due to the easier synthesis and more stable nature of the ligand.
22. It is worth noting that Tobisu and Chatani think the coordination of an ether oxygen to a Lewis acid, MgI_2 is unlikely based on their experimental observations.^{12f}
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CHAPTER FIVE

CONCLUSION

This body of research shows that nickel is an effective catalyst to obtain new C—C bonds in multiple cross-coupling systems using C—O electrophiles that are largely inaccessible electrophiles under palladium catalysis. Chapter 2 explored the development of a Ni-catalyzed Stille cross-coupling of phenol-derived electrophiles through catalytic and stoichiometric experimental studies, supported by computational studies. We were able to provide strong experimental evidence for nickel being able to catalyze the cross-coupling of aryl sulfamates under Stille coupling conditions. Additionally, we were able to show this methodology supports coupling organostannanes with aryl tosylates and aryl mesylates. Our Ni-catalyzed system shows promise for constructing difficult bonds from aryl sulfamates and organostannanes, specifically aryl-heteroaryl, aryl-alkenyl, and aryl-alkynyl bonds that were largely inaccessible from other cross-coupling methods employing non-triflate phenol derivatives. This work overcame the limitations of homocoupling, thus enabling Stille cross-coupling at a variety of phenolic derived sites. In addition, computational studies provided insight into why this system was successful in comparison to previous studies.

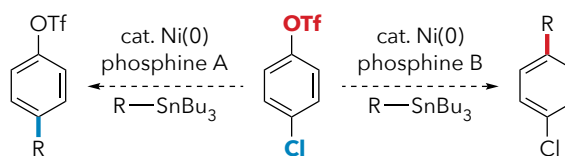
Through computational studies, we were able to study the transmetalation step of the catalytic cycle to learn how our system worked and possible reasons why previous attempts were unsuccessful. The DFT studies showed that when a chloride source is present in the reaction, a Ni(II)-chloride species is generated resulting in an energy barrier of $\Delta G^\ddagger = 24.3$ kcal/mol to reach the required transition state. However, when no chloride is present, the most favored pathway is through an eight-centered transition state involving KF and the organostannane resulting in an

energy barrier of $\Delta G^\ddagger = 15.0$ kcal/mol. This data suggests transmetalation is significantly slower when a Ni(II)-chloride species is involved due to the increased energy barrier of the transition state. Experimental results using Ni(II)-Cl and Ni(II)-sulfamate oxidative addition complexes as catalysts allowed us to explore this inhibitory effect further.

Experimental results confirmed that chloride could replace sulfamate and result in a more stable nickel complex that would prevent transmetalation. The importance of KF was also confirmed experimentally supporting the eight-centered transition state found by DFT. When the fluoride counterion was changed, the product yield was greatly reduced or completely inhibited. These experimental results combined with computational results provide a possible explanation of why Percec's attempt at developing a Ni-catalyzed Stille cross-coupling of aryl mesylates was unsuccessful, resulting primarily in homocoupling.¹

Our work showed the avoidance of chloride sources, the inclusion of KF, and the application of mono-, di-, or trialkylphosphine ligands resulted in a wide variety of aryl sulfamates and organostannanes undergoing cross-coupling in excellent yields. The computations suggested the presence of chloride in the reaction leads to a stable Ni(II) oxidative addition complex which inhibits transmetalation. Our computational studies suggest KF is crucial in transmetalation because of the formation of an eight-centered transition state. Experimental results confirmed the importance of KF for this reaction through exploring various fluoride counterions and the absence of KF.

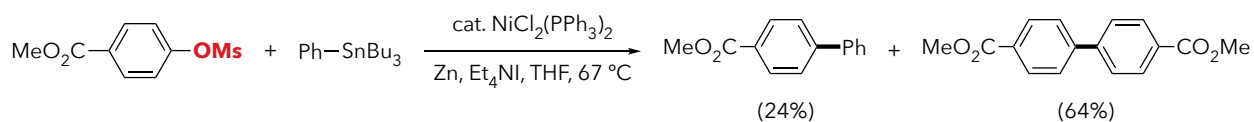
We successfully developed a system that tolerated a wide variety of substrates and explored the mechanism. Through the course of the project a couple of areas of further exploration



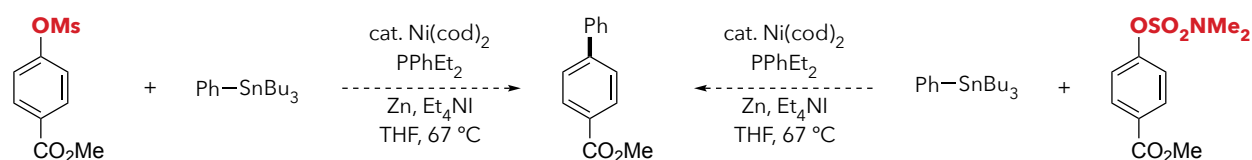
Scheme 1. Proposed chemoselective Ni-catalyzed Stille coupling.

arose that were out of the project scope at the time. It would be intriguing to further investigate the observed inhibitory effect of chloride and if it extends to other halides or to triflate. The inhibitory effect of chloride comes from forming a stable Ni(II)-chloride complex during oxidative addition making the activation barrier for transmetalation prohibitive. This could provide further insight into the inhibitory effect, especially if more reactive halides or triflate doesn't hinder product formation. Assuming that triflate does not inhibit the transmetalation step, it would be interesting to see if a triflate could outcompete chloride for binding with nickel, preventing the Ni(II)-chloride species from forming. From the experimental results in chapter 2, we know that once the Ni(II)-chloride species is formed it cannot be displaced by sulfamate. However, since chloride and triflate are more similar in their reactivities, it is conceivable that triflate might be able to displace chloride, allowing the catalytic cycle to proceed. If the inhibitory effect could be overcome, it is conceivable that a triflate-selective Ni-catalyzed Stille cross-coupling could be developed, adding to the toolbox of Ni-catalyzed chemoselectivity (Scheme 1).

A - Percec's conditions



B - Combined conditions



Scheme 2. (A) Percec's conditions leading to homocoupling of the aryl mesylate and (B) a proposed combination of conditions to further study why no homocoupling was observed in our work.

Another possible topic for further study would be revisiting Percec's¹ results and switching the $\text{NiCl}_2(\text{PPh}_3)_2$ catalyst to our $\text{Ni}(\text{cod})_2/\text{PPhEt}_2$ catalyst but otherwise keeping their conditions the

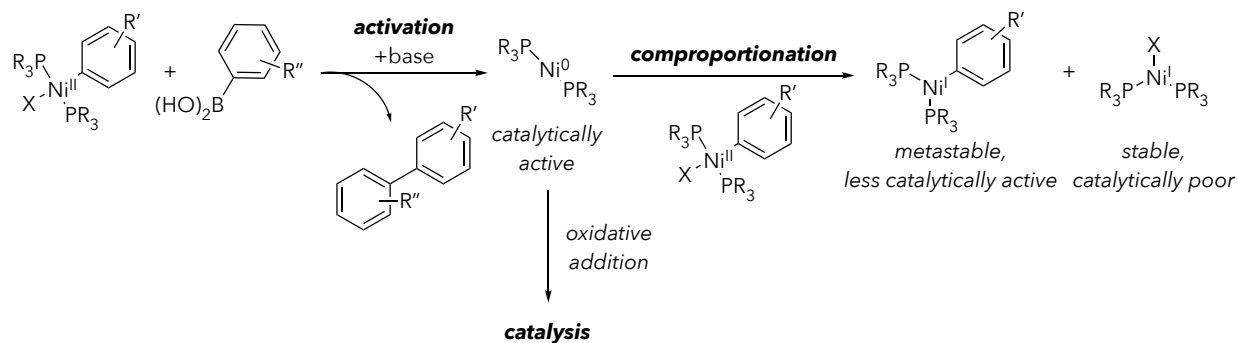
same (Scheme 2). This could provide further experimental insight into why they obtained homocoupling as the major product and allow for further understanding the importance of the fluoride ion in facilitating Ni-catalyzed Stille cross-coupling.

Chapter 3 explored chemoselectivity of chloroaryl tosylates in Ni-catalyzed Suzuki-Miyaura cross-coupling. This investigation showed that coupling at the tosylate site was favored over chloride due to a combination of ligand sterics and electronics unique to small phosphine ligands. Through a combination of DFT calculations and experiments, stoichiometric and catalytic, we identified a variety of ligands that resulted in excellent selectivity of C—OTs bonds in the presence of C—Cl bonds. Our studies focused on the oxidative addition step of the catalytic cycle since chemoselectivity is usually determined during this step due to oxidative addition being the rate determining step.

To our knowledge, this work demonstrates the first experimentally evaluated use of PMe_3 in Ni-catalyzed Suzuki-Miyaura cross-coupling reactions. We were surprised by the initial DFT calculations that showed that PMe_3 resulted in selective reaction at the C—OTs bond in the presence of C—Cl bonds. DFT studies predicted a preference for reaction at tosylate in the following order, $\text{PMe}_3 > \text{PCy}_3 > \text{PPh}_3$. This order was substantiated by stoichiometric oxidative addition studies that evaluated a selection of phosphine ligands with a variety of electronic and steric properties. Triaryl phosphines promote exclusive reaction at C—Cl bonds while tri- and dimethyl phosphines are the only types of phosphines that promote selective reaction at tosylate in this system. Further DFT calculations suggest that unlike other literature examples of chemoselective cross-couplings, our system does not appear to rely on the ligation state of nickel. Instead, selectivity in our Ni-catalyzed system likely is controlled through a combination of electronic and steric factors that are typical of small phosphine ligands.

After exploring the origin of selectivity through computations and experiments, we demonstrated this tosylate-selective Suzuki-Miyaura reaction catalyzed by Ni/PMe₃ tolerated a variety of boronic ester coupling partners and aryl tosylates. This scope maintained excellent selectivity for reaction at the C—OTs bond. We successfully developed a reliable pathway to a Ni-catalyzed Suzuki-Miyaura cross-coupling of aryl tosylates in the presence of aryl chlorides with high selectivity but there are a few areas that could be improved or explored further.

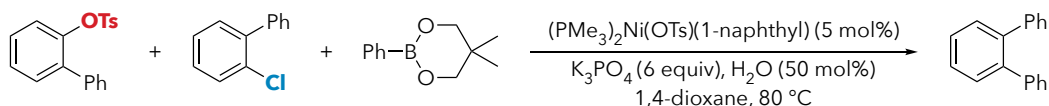
Throughout the development of our chemoselective Ni-catalyzed Suzuki-Miyaura cross-coupling, there were reproducibility issues that would be fixed by synthesizing a fresh batch of the desired precatalyst. Further investigation into the precatalyst decomposition pathway would be advantageous to better understand nickel precatalysts. Literature precedent suggests the catalytically active Ni(0) species and an unactivated Ni(II) precatalyst could undergo comproportionation resulting in a low-reactivity Ni(I) species (Scheme 3).² The proposed investigation would likely entail EPR studies comparing freshly synthesized precatalyst to an older batch and explore various aryl substituents and the effect they have on catalyst decomposition.



Scheme 3. Comproportionation of Ni(II) and Ni(0) to form Ni(I) as suggested in previous literature.

Another unanswered question from this work stems from the observation of one of the chloroaryl tosylates resulting in diarylation as the major product, the *o*-chlorophenyl tosylate. Understanding why this occurs could help increase the knowledge of our chemoselective system

and the catalytic cycle. We hypothesize that after finishing the reductive elimination step of the catalytic cycle, nickel is still closely associated with the substrate due to π -complexation and therefore prefers to undergo oxidative addition with the C—Cl bond instead of dissociating completely to react with a new C—OTs bond. Previous experimental and computational studies suggest that after reductive elimination, the π -complexation can persist and nickel will walk to the next reactive site instead of dissociating and forming a new π -complex.³ One potential reason diarylation was only observed with the *o*-chlorophenyl tosylate is likely due to the proximity of the second reactive site meaning nickel would not have to walk very far to undergo oxidative addition. This is supported by previous studies that also suggest that continuing π -complexation of nickel to the substrate after reductive elimination is not thermodynamically favorable for cross-coupling reactions of polyhaloarenes.^{3a} To confirm if this is the case, time trials of this reaction would need to be performed to determine if one product is indeed forming faster than the other and then watching how the product ratios track. Another way to investigate the hypothesis of the π -complexation favoring nickel oxidatively adding into the C—Cl bond after cross-coupling with C—OTs, would be to perform an intermolecular competition reaction of both monoarylated products (Scheme 4); a reaction occurring primarily at the C—OTs bond would indicate a π -complex between the catalyst and substrate leads to diarylation. Understanding this diarylation process in our chemoselective method would help understand the catalytic cycle and how it changes with different substitution patterns of the substrate.

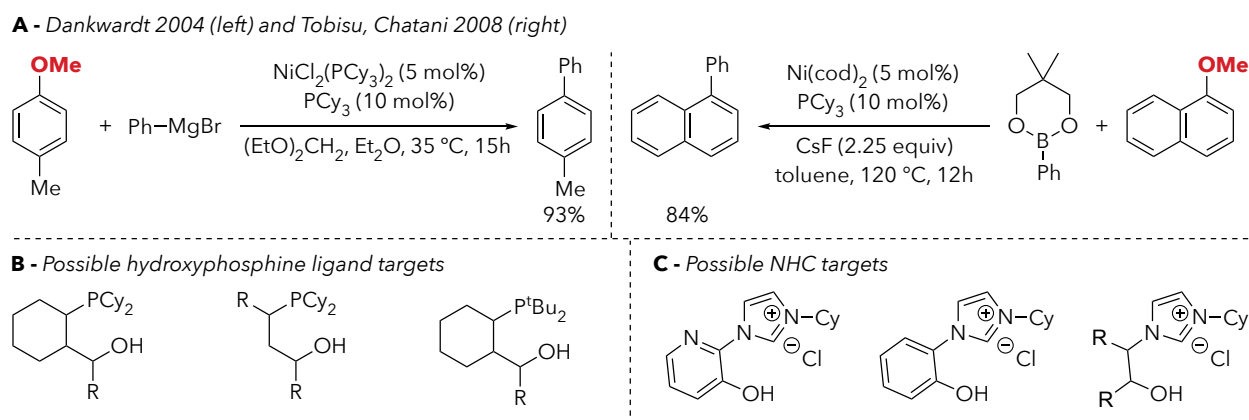


Scheme 4. Showing the application of authentic monoarylated products to from the diarylated product to determine if π -complexation is responsible for the observed diarylation.⁴

Chapter 4 detailed the exploration of Ni-catalyzed cross-coupling reactions using aryl methyl ethers as the electrophile. We started our investigation by synthesizing ligands bearing anionic arms, hydroxyphosphine and NHC ligands, that would add electron density to nickel allowing it to add into the electron-dense C—OMe bond more effectively. Initially, our goal was to use these ligands to facilitate the coupling of Ar-OMe under relatively mild Suzuki-Miyaura conditions. Unfortunately none of the ligands we synthesized were able to promote any cross-coupling of Ar-OMe with organoboron reagents. Our secondary goal was to show the first use of hydroxyphosphine ligands or hydroxy-NHC ligands in the Ni-catalyzed Kumada cross-coupling of Ar-OMe. While the bis-NHC-O/Ni complex facilitated low yields of the cross-coupled product, the two hydroxyphosphine ligands promoted the formation of the desired product in moderate to high yields. However, while determining if the observed yield was due to the anionic arm on the hydroxyphosphine ligand, we found commercial PCy₃ was at least as good as the best performing hydroxyphosphine ligand. Even though the application of hydroxyphosphine ligands proved to be no better at promoting the Ni-catalyzed Kumada cross-coupling of Ar-OMe than PCy₃, we were able to establish that hydroxyphosphine ligands were capable at promoting the formation of the cross-coupled product from Ar-OMe. Additionally, we established a reliable pathway to synthesize a novel dialkylaryl-hydroxyphosphine ligand in moderate yields. Our initial goal was not met but that leaves the door open for various future avenues of research into this field of study.

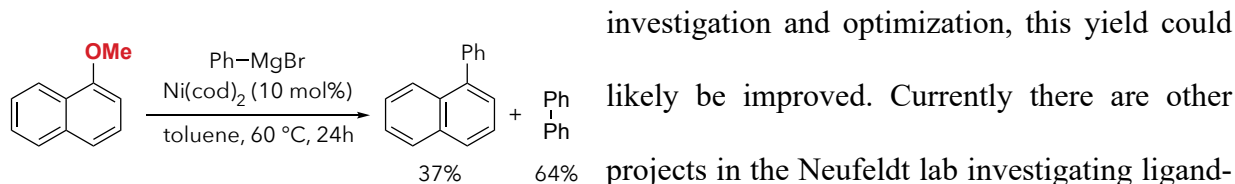
The focus of this project was the synthesis and application of different ligands of the phosphine and NHC varieties bearing an anionic arm to obtain better reactivity of aryl methyl ethers. These arms would ideally be able to increase the electron density around nickel. While we were successful at synthesizing a few different ligands, they were not able to promote cross-coupling under Suzuki and or Kumada conditions in comparison to PCy₃. Literature shows that

PCy₃ works well under Kumada conditions⁵ and exhibits some reactivity under Suzuki conditions⁶ (Scheme 5A). Therefore, it would be intriguing to develop a synthesis of trialkylhydroxyphosphine ligands that bear significant steric bulk and show excellent σ -donating ability (Scheme 5B). The further exploration and development of NHC ligands bearing various anionic arms could also lead to a solution to the low reactivity of aryl methyl ethers (Scheme 5C).



Scheme 5. (A) Examples of PCy₃ working with nickel to efficiently couple Ar-OMe under Kumada and Suzuki conditions. Possible hydroxyphosphine ligand (B) and NHC targets (C).

A final area of further investigation arises from the results with either very little added ligand or no ligand at all (Scheme 6). These reactions resulted in a low yield suggesting that there could be the potential to develop a Ni-catalyzed Kumada cross-coupling of Ar-OMe in the absence of any added ligand which has not been reported in the literature. To rule out other reaction pathways, a reaction was run under the same conditions but without any nickel and no product was observed. Unfortunately, the yield without any added ligand is poor (<40%), but with further



Scheme 6. Preliminary ligand-free results.

investigation and optimization, this yield could likely be improved. Currently there are other projects in the Neufeldt lab investigating ligand-free catalysis, these projects could inform how a

Ni-catalyzed Kumada coupling of Ar-OMe could be developed and improved. Developing a ligand-free Ni-catalyzed Kumada cross-coupling of Ar-OMe would contribute to the small body of work already established⁷ by using a less-reactive electrophile.

The research described herein focused on studying Ni-catalyzed cross-coupling reactions of phenolic electrophiles. All three of these projects explored different cross-coupling reactions, each with a different phenol-derived electrophile displaying a range of reactivity. Through these investigations we often paired experimental work with computational studies to help explain what was observed. The first two projects relied heavily on computational work to explain some of our observations and the final project was explored through experimental work. This body of work established the first efficient Ni-catalyzed Stille cross-coupling of phenolic electrophiles, the first highly selective Ni-catalyzed Suzuki cross-coupling of aryl tosylates in the presence of aryl chlorides, and the investigation of the Ni-catalyzed cross-coupling of Ar-OMe. All three projects leave some questions and avenues for further development.

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APPENDICES

APPENDIX A

CHAPTER TWO SUPPLEMENTAL

Supporting Information

for

Ni-Catalyzed Stille Cross Coupling of C—O Electrophiles

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I. Experimental Details

A. General Materials and Methods

NMR spectra were recorded at 298 K on a Bruker DRX 500 MHz (500.233 MHz for ^1H , 125.795 MHz for ^{13}C , 202.487 MHz for ^{31}P , 470.639 MHz for ^{19}F) or a Bruker DPX 300 MHz (282.425 MHz for ^{19}F) spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference [^1H : CHCl_3 (7.26 ppm) or $\text{C}_6\text{D}_5\text{H}$ (7.16 ppm); ^{13}C : CDCl_3 (77.16 ppm) or C_6D_6 (128.06 ppm)].¹ ^{31}P chemical shifts are reported in ppm relative to phosphoric acid, with Ph_3PO used as an internal reference (25.55 ppm in C_6D_6). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublets of doublets (ddd), triplet (t), quartet (q), quintet (quint), multiplet or multiple overlapping signals (m), and broad resonance (br). GC data were collected using a Shimadzu GC-2010 Plus with a flame ionization detector equipped with a SH-Rxi-5ms capillary column (15 m x 0.25 mm ID x 0.25 μm df). HRMS data were collected on an Agilent 6538 UHD-QTOF or a Bruker MicroTOF. Melting points were measured using a Thomas-Hoover “Uni-Melt” capillary melting point apparatus.

PCy_3 , PBU_3 , Mg turnings, Bu_3SnCl , LiCl , Ph_3PO , 1-naphthol, 4-fluorophenol, 4-hydroxybenzonitrile, methyl 4-hydroxybenzoate, 4-acetamidophenol, 4-methoxyphenol, 1-bromo-4-ethylbenzene, 2-bromo-*m*-xylene, 1-bromo-4-fluorobenzene, 3-bromoanisole, 1-bromonaphthalene, 2-tributylstannylthiazole, 2-tributylstannylpyridine, tributyl(vinyl)stannane, 1-ethoxytributylstannane, allyltributylstannane, and 2,6-di-*tert*-butyl-4-methylphenol (BHT) were obtained from Oakwood Chemical and used as received unless otherwise noted. PPhEt_2 and PPh_2Cy were obtained from TCI America and used as received. PPhMe_2 , NaH (60% dispersion in oil), *N,N*-dimethylsulfamoyl chloride, TsCl, dibromoethane, KF, undecane, 2-naphthol, 4-ethylphenol, and 4-chlorotoluene (**36**) were obtained from Acros and used as received. 1,4-Dioxane, dimethoxyethane (DME), and pyridine were obtained from Acros in ACROSeal bottles (extra dry) and used as received. PPh_2Me , PPh_3 , Et_3N , sesamol, 2-(tributylstannyl)furan, 1-methyl-2-(tributylstannyl)pyrrole, 2-(tributylstannyl)thiophene, 2-(tributylstannyl)oxazole, and 12-crown-4 were obtained from Alfa Aesar and used as received. Et_2O , hexanes, EtOAc , MgSO_4 , HCl, NaHCO_3 , NaCl, and NaOH were obtained from Fisher Chemical and used as received unless otherwise noted. Benzene was obtained from Beantown Chemical or Riedel-de Haën and used as received. PhSnBu_3 and tributyl(phenylethynyl)tin were obtained from Sigma-Aldrich and used as received. PPhCy_2 was obtained from Strem and used as received. THF was obtained from Fisher Chemical and degassed and dried with a JC Meyer solvent system prior to use. $\text{Ni}(\text{cod})_2$ was obtained from Alfa Aesar or Acros and used as received. Aryl sulfamate **1** and the aryl sulfamate precursors to compounds **10**, **12**, and **13** were prepared according to a literature procedure.² Aryl sulfamates **37** and **42** were prepared according to a literature procedure.³ Aryl mesylate **174**, the aryl tributylstannane

¹ Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.

² Quasdorf, K. W.; Riener, M.; Petrova, K. V.; Garg, N. K. *J. Am. Chem. Soc.* **2009**, *131*, 17748.

³ Hooker, L. V.; Neufeldt, S. R. *Tetrahedron* **2018**, *74*, 6717.

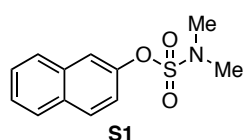
⁴ Mori, A.; Mizusaki, T.; Ikawa, T.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *Chem. Eur. J.* **2007**, *13*, 1432.

precursors to **19** and **22**⁵, and aryl sulfamate **35**⁶ were prepared according to literature procedures. CDCl₃ and C₆D₆ were obtained from Cambridge Isotope Laboratories and used as received. Flash column chromatography was performed on SiliCycle silica gel 60 (40–63 μm particle size) and thin layer chromatography was performed on SiliCycle TLC plates pre-coated with extra hard silica gel 60 F₂₅₄.

B. Synthesis of Starting Materials

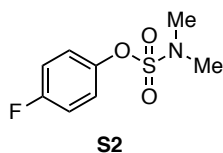
i. Synthesis of Aryl Sulfamate Precursors to **4**, **5**, **6**, **7**, **8**, **9**, and **11**

General Procedure. Aryl sulfamates were prepared according to a modified literature procedure:² NaH (1.2 equiv, 60% dispersion in oil) was cooled to 0 °C in a pear-shaped flask. A solution of the substituted phenol (1 equiv) in DME was added dropwise by cannula to the NaH. The resulting homogeneous solution was warmed to rt for 10 min and then cooled to 0 °C. A solution of *N,N*-dimethylsulfamoyl chloride (1.0–1.25 equiv) in DME was added dropwise by cannula to the reaction vessel. The reaction was warmed to rt, stirred overnight, and then quenched with several drops of H₂O. DME was removed by rotary evaporation, and the solid residue was then dissolved in Et₂O (50 mL) and H₂O (15 mL) and transferred to a separatory funnel. The layers were separated, and the organic layer was washed with 1 M KOH (15 mL), then H₂O (15 mL). The combined aqueous layers were then extracted with Et₂O (3 x 20 mL), washed with brine (15 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by recrystallization.



Naphthalen-2-yl dimethylsulfamate (S1, precursor to 4): Aryl sulfamate **S1** was prepared according to the general procedure using NaH (431 mg, 10.78 mmol, 1.20 equiv), 2-naphthol (1.29 g, 8.97 mmol, 1.00 equiv), *N,N*-dimethylsulfamoyl chloride (1.2 mL, 11.2 mmol, 1.25 equiv), and DME (30 mL). The crude solid was

recrystallized from hexanes yielding **S1** as a light tan powder (1.29 g, 57% yield). Spectral data are consistent with those previously reported.⁷



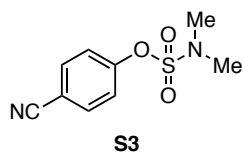
4-Fluorophenyl dimethylsulfamate (S2, precursor to 5): Aryl sulfamate **S2** was prepared according to the general procedure using NaH (440 mg, 11.00 mmol, 1.23 equiv), 4-fluorophenol (1.34 g, 8.97 mmol, 1.00 equiv), *N,N*-dimethylsulfamoyl chloride (1.0 mL, 9.33 mmol, 1.04 equiv), and DME (30 mL). The crude solid was

recrystallized from a 4:1 solution of hexanes and ethyl acetate yielding **S2** as a white powder (453 mg, 23% yield); ¹⁹F NMR (282 MHz, CDCl₃, δ): –115.2. Spectral data are consistent with those previously reported.⁶

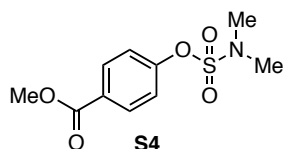
⁵ Gligorich, K. M.; Cummings, S. A.; Sigman, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 14193.

⁶ Molander, G. A.; Shin, I. *Org. Lett.* **2013**, *15*, 2534.

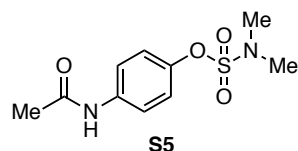
⁷ Leowanawat, P.; Zhang, N.; Percec, V. *J. Org. Chem.* **2012**, *77*, 1018.



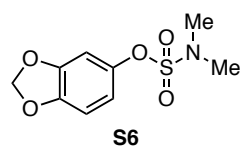
4-Cyanophenyl dimethylsulfamate (S3, precursor to 6): Aryl sulfamate **S3** was prepared according to the general procedure using NaH (431 mg, 10.78 mmol, 1.20 equiv), 4-hydroxybenzonitrile (1.08 g, 9.06 mmol, 1.00 equiv), *N,N*-dimethylsulfamoyl chloride (1.0 mL, 9.33 mmol, 1.03 equiv), and DME (30 mL). The crude solid was recrystallized from a 4:1 solution of hexanes and EtOAc yielding **S3** as a pale pink solid (1.36 g, 67% yield). Spectral data are consistent with those previously reported.⁸



Methyl 4-((*N,N*-dimethylsulfamoyl)oxy)benzoate (S4, precursor to 7): Aryl sulfamate **S4** was prepared according to the general procedure using NaH (435 mg, 10.87 mmol, 1.20 equiv), methyl 4-hydroxybenzoate (1.34 g, 8.97 mmol, 1.00 equiv), *N,N*-dimethylsulfamoyl chloride (1.0 mL, 9.33 mmol, 1.04 equiv), and DME (30 mL). The crude solid was recrystallized from a 1:1 solution of hexanes and EtOAc yielding **S4** as a white crystalline solid (1.23 g, 53% yield). Spectral data are consistent with those previously reported.⁸



4-Acetamidophenyl dimethylsulfamate (S5, precursor to 9): Aryl sulfamate **S5** was prepared according to the general procedure using NaH (432 mg, 10.76 mmol, 1.20 equiv), 4-acetamidophenol (1.36 g, 9.00 mmol, 1.00 equiv), *N,N*-dimethylsulfamoyl chloride (1.2 mL, 11.2 mmol, 1.24 equiv), and DME (30 mL). The crude solid was recrystallized from a 1:1 solution of hexanes and EtOAc yielding **S5** as a pale pink powder (218.4 g, 9.4% yield); m.p. 102–105 °C [uncorrected, measured against benzoic acid (111–114 °C)]; ¹H NMR (500 MHz, CDCl₃, δ): 7.52 (d, *J* = 8.9 Hz, 2H), 7.45–7.30 (br s, 1H), 7.22 (d, *J* = 8.9 Hz, 2H), 2.97 (s, 6H), 2.17 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃, δ): 168.4, 146.3, 136.6, 122.5, 121.0, 38.9, 24.7; HRMS (ESI/Q-TOF) *m/z*: [M + H]⁺ Calcd for C₁₀H₁₅N₂O₄S 259.0742; Found 259.0722.



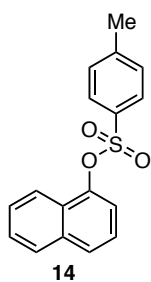
Benzo[d][1,3]dioxol-5-yl dimethylsulfamate (S6, precursor to 11): Aryl sulfamate **S6** was prepared according to the general procedure using NaH (438 mg, 10.95 mmol, 1.22 equiv), sesamol (1.24 g, 8.97 mmol, 1.00 equiv), *N,N*-dimethylsulfamoyl chloride (1.0 mL, 9.33 mmol, 1.04 equiv), and DME (30 mL). The crude solid was recrystallized from a 1:1 solution of hexanes and isopropanol yielding **S6** as a white powder (1.67 g, 76% yield). Spectral data are consistent with those previously reported.⁹

⁸ Leowanawat, P.; Zhang, N.; Resmerita, A.-M.; Rosen, B. M.; Percec, V. *J. Org. Chem.* **2011**, 76, 9946.

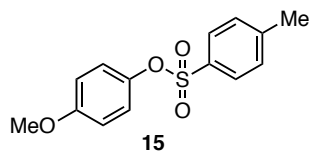
⁹ Yue, H.; Guo, L.; Liu, X.; Rueping, M. *Org. Lett.* **2017**, 19, 1788.

ii. Synthesis of Aryl Tosylates **14**, **15**, and **16**

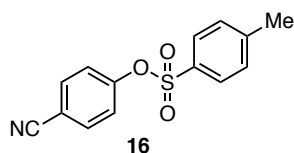
General Procedure. Aryl tosylates were prepared according to a modified literature procedure:¹⁰ Substituted phenol (1 equiv) and TsCl (1.8 equiv) were added to a 100 mL round bottom flask with pyridine and stirred under nitrogen at 45 °C overnight. The reaction mixture was allowed to cool to room temperature before adding H₂O (5 mL) to the reaction mixture and stirring at room temperature for 2.5 h. The reaction mixture was then diluted with 25 mL benzene and 10 mL H₂O and transferred to a separatory funnel. The aqueous and organic layers were separated, and the organic layer was extracted with 10% aqueous HCl (2 x 25 mL), saturated aqueous NaHCO₃ (1 x 25 mL) and brine (1 x 25 mL). The organic layer was dried over MgSO₄, filtered, concentrated, and purified by recrystallization.



Naphthalen-1-yl 4-methylbenzenesulfonate (14): Aryl tosylate **14** was prepared according to the general procedure using 1-naphthol (1.00 g, 3.47 mmol, 1.00 equiv), TsCl (2.38 g, 6.24 mmol, 1.8 equiv), and pyridine (10.0 mL). The crude solid was recrystallized from hexanes yielding **14** as a pale pink solid (1.51 g, 73% yield). Spectral data are consistent with those previously reported.¹¹



4-Methoxyphenyl 4-methylbenzenesulfonate (15): Aryl tosylate **15** was prepared according to the general procedure using 4-methoxyphenol (862 mg, 3.47 mmol, 1.00 equiv), TsCl (2.38 g, 6.24 mmol, 1.80 equiv), and pyridine (10.0 mL). The crude solid was recrystallized from hexanes yielding **15** as a white solid (1.39 g, 72% yield). Spectral data are consistent with those previously reported.¹¹



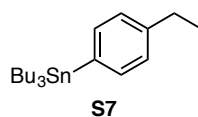
4-Cyanophenyl 4-methylbenzenesulfonate (16): Aryl tosylate **16** was prepared according to the general procedure using 4-hydroxybenzoate (827 mg, 3.47 mmol, 1.00 equiv), TsCl (2.38 g, 6.24 mmol, 1.80 equiv), and pyridine (10.0 mL). The crude solid was recrystallized from hexanes yielding **16** as a white solid (1.29 g, 68% yield). Spectral data are consistent with those previously reported.¹¹

¹⁰ Nervig, C. S.; Waller, P. J.; Kalyani, D. *Org. Lett.* **2012**, *14*, 4838.

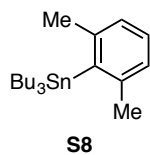
¹¹ Kuroda, J.-i.; Inamoto, K.; Hiroya, K.; Doi, T. *Eur. J. Org. Chem.* **2009**, 2251.

iii. Synthesis of Aryl Tributylstannane Precursors to **18**, **20**, **21**, **23**, and **24**

General Procedure: Aryl tributylstannanes were prepared according to a modified literature procedure:⁵ To an oven-dried 100 mL Schlenck flask equipped with a stirbar and a condenser under a N₂ atmosphere, was added THF and magnesium turnings (1.60 equiv). The magnesium turnings were pre-activated by crushing with a mortar and pestle in a N₂-filled glovebox. To the stirred mixture was added 1,2-dibromoethane (~30 drops) followed by the aryl bromide (1.00 equiv), added dropwise over ~5 minutes. The mixture slowly turned dark brown and the stirred mixture was heated to reflux overnight. The reaction mixture was cooled to room temperature and was transferred by cannula into a dried 100 mL Schlenk flask equipped with a stirbar and condenser under a N₂ atmosphere. To the stirred mixture was added Bu₃SnCl (1.20 equiv) dropwise over ~5 minutes. The stirred mixture was heated to reflux for 4 h and then cooled to room temperature. Aqueous 1.0 M NaOH (~3 x the volume of THF) was added and the mixture was stirred for ~1 h and then transferred to a separatory funnel. The aqueous layer was extracted with Et₂O [3 x (3 x the volume of THF)], and the organic extracts were combined, washed with brine, dried over MgSO₄, and filtered. The solvent was removed by rotary evaporation, and the crude residue was purified by flash column chromatography on silica gel.

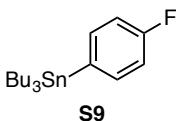


Tributyl(4-ethylphenyl)stannane (S7, precursor to **18):** Aryl stannane **S7** was prepared according to the general procedure using 1-bromo-4-ethylbenzene (2.8 mL, 20.0 mmol, 1.0 equiv), Mg turnings (790 mg, 32.0 mmol, 1.6 equiv), and Bu₃SnCl (6.7 mL, 24.0 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography on silica gel (*R_f* = 0.3 in 100% hexanes) to yield **S7** as a colorless oil (4.64 g, 59% yield); ¹H NMR (500 MHz, CDCl₃, δ): 7.40 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.59–1.53 (m, 6H), 1.38–1.31 (m, 6H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.07–1.03 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H); ¹³C{¹H} NMR (126 MHz, CDCl₃, δ): 144.1, 138.4, 136.7, 127.8, 29.3, 29.0, 27.6, 15.6, 13.8, 9.7; HRMS (ESI/Q-TOF) *m/z*: [M – Bu]⁺ Calcd for C₁₆H₂₇Sn 339.1129; Found 339.1108.

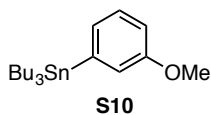


Tributyl(2,6-dimethylphenyl)stannane (S8, precursor to **20):** Aryl stannane **S8** was prepared according to the general procedure using 2-bromo-*m*-xylene (2.7 mL, 20.0 mmol, 1.0 equiv), Mg turnings (778 mg, 32.0 mmol, 1.6 equiv), and Bu₃SnCl (6.5 mL, 24.0 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography on silica gel (*R_f* = 0.89 in 100% hexanes) to yield **S8** as a colorless oil (4.66 g, 59% yield); ¹H NMR (500 MHz, CDCl₃, δ): 7.14–7.08 (m, 1H), 7.02–6.95 (m, 2H), 2.42 (s, 6H), 1.56–1.50 (m, 6H), 1.39–1.32 (m, 6H), 1.14–1.04 (m, 6H), 0.91 (t, *J* = 7.3 Hz, 9H); ¹³C{¹H} NMR (126 MHz, CDCl₃, δ): 145.3, 142.5, 128.3, 126.7, 29.3, 27.6, 25.9, 13.8, 12.8. Spectral data are consistent with those previously reported.¹²

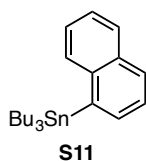
¹² Dughera, S. *Synthesis* **2006**, 7, 1117.



Tributyl(4-fluorophenyl)stannane (S9, precursor to 21): Aryl stannane **S9** was prepared according to the general procedure using 1-bromo-4-fluorobenzene (2.2 mL, 20.0 mmol, 1.0 equiv), Mg turnings (778 mg, 32.0 mmol, 1.6 equiv), and Bu₃SnCl (6.50 mL, 24.0 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography on silica gel (R_f = 0.8 in 100% hexanes) to yield **S9** as a colorless oil (6.65 g, 86% yield). Spectral data are consistent with those previously reported.¹³



Tributyl(3-methoxyphenyl)stannane (S10, precursor to 23): Aryl stannane **S10** was prepared according to the general procedure using 3-bromoanisole (2.5 mL, 20.0 mmol, 1.0 equiv), Mg turnings (778 mg, 32.0 mmol, 1.6 equiv), and Bu₃SnCl (6.5 mL, 24.0 mmol, 1.2 equiv). A portion of the crude residue (53% by mass) was purified by flash column chromatography on silica gel (R_f = 0.47 in 100% hexanes) to yield **S10** as a colorless oil (1.56 g, 37% yield based on the portion of the crude material purified by column chromatography). Spectral data are consistent with those previously reported.¹⁴



Tributyl(naphthalen-1-yl)stannane (S11, precursor to 24): Aryl stannane **S11** was prepared according to the general procedure using 1-bromonaphthalene (2.8 mL, 20.0 mmol, 1.0 equiv), Mg turnings (778 mg, 32.0 mmol, 1.6 equiv), and Bu₃SnCl (6.5 mL, 24.0 mmol, 1.2 equiv). The crude residue was purified by flash column chromatography on silica gel (R_f = 0.67 in 100% hexanes) to yield **S11** as a colorless oil (4.67 g, 56% yield). Spectral data are consistent with those previously reported.¹⁵

¹³ Ren, Y.; Dienes, Y.; Hettel, S.; Parvez, M.; Hoge, B.; Baumgartner, T. *Organometallics* **2009**, *28*, 734.

¹⁴ Lakshmi, B. V.; Wefelscheid, U. K.; Kazmaier, U. *Synlett* **2011**, 345.

¹⁵ Gu, Y.; Martín, R. *Angew. Chem. Int. Ed.* **2017**, *56*, 3187.

C. Reaction Optimization and Additive Screening (Expanded Tables 1, 2, and 3)

General Procedure. In a nitrogen atmosphere glovebox, the fluoride salt (KF, LiF, NaF, or CsF, 0.15 mmol, 3.0 equiv, if applicable), **1** (12.6 mg, 0.05 mmol, 1.0 equiv), PhSnBu₃ (18.4 mg, 0.05 mmol, 1.0 equiv), and any indicated additives were combined in a one-dram vial equipped with a stir bar. In a second vial was prepared a stock solution of Ni(cod)₂ and phosphine (0.01 M in Ni(cod)₂, 0.02 M in phosphine). The Ni/phosphine stock solution [250 μ L (0.0025 mmol, 5 mol% of Ni(cod)) and 0.005 mmol, 10 mol% of phosphine]] was added to the reaction vial. The vial was sealed with a PTFE-lined cap, removed from the glovebox, and stirred at the indicated temperature for 18 h. The reaction vial was cooled to room temperature, and undecane was added as a GC standard. The reaction mixture was diluted with Et₂O and shaken vigorously. An aliquot was removed, filtered through celite, and analyzed by GC. Table S1 corresponds to Tables 1, 2, and 3 in the manuscript, with additional entries not included in the manuscript.

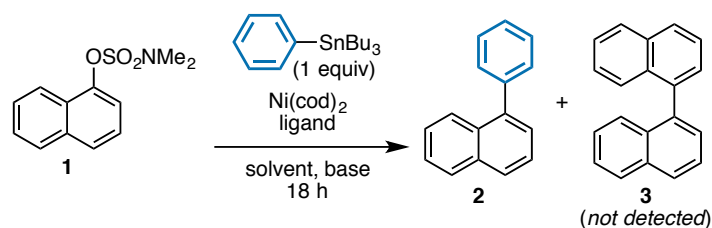


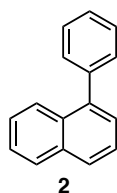
Table S1. Reaction optimization and additive screening.

entry	mol % of Ni(cod) ₂	Ligand (mol %)	Temp (°C)	Solvent	Base	Additive(s)	2 (% yield) ^a
1	5	PCy ₃ (10)	60	dioxane	KF (3 equiv)	--	27 ^b
2	5	PCy ₃ (10)	80	dioxane	KF (3 equiv)	--	60 ^b
3	5	PCy ₃ (10)	80	dioxane	KF (3 equiv)	LiCl (3 equiv)	n.d.
4	5	PBu ₃ (10)	80	dioxane	KF (3 equiv)	--	88 ^b
5	5	PPhEt ₂ (10)	80	dioxane	KF (3 equiv)	--	≥99 ^b
6	5	PPhEt ₂ (10)	80	toluene	KF (3 equiv)	--	49
7	none	PPhEt ₂ (10)	80	dioxane	KF (3 equiv)	--	n.d.
8	5	none	80	dioxane	KF (3 equiv)	--	n.d.
9	5	PPhEt ₂ (10)	80	dioxane	KF (3 equiv)	CuI (5 mol %)	n.d.
10	5	PPhEt ₂ (10)	80	dioxane	KF (2 equiv)	--	≥99
11	5	PPhEt ₂ (10)	80	dioxane	KF (1 equiv)	--	43
12	5	PPhMe ₂ (10)	80	dioxane	KF (3 equiv)	--	96 ^b
13	5	PPh ₂ Me (10)	80	dioxane	KF (3 equiv)	--	≥99 ^b
14	5	PPh ₃ (10)	80	dioxane	KF (3 equiv)	--	52 ^b
15	5	PPhEt ₂ (10)	80	dioxane	--	--	n.d.
16	5	PPhEt ₂ (10)	80	dioxane	KF (3 equiv)	LiCl (10 mol%)	13 ^b
17	5	PPhEt ₂ (10)	80	dioxane	KF (3 equiv)	12-crown-4 (20 mol%)	≥99 ^b
18	5	PPhEt ₂ (10)	80	dioxane	KF (3 equiv)	LiCl (10 mol%), 12-crown-4 (20 mol%)	13 ^b
19	5	PPhEt ₂ (10)	80	dioxane	KF (3 equiv)	NBu ₄ Cl (10 mol%)	10 ^b
20	5	PPhEt ₂ (10)	80	dioxane	KF (3 equiv)	KCl (10 mol%)	42 ^b
21	5	PPhEt ₂ (10)	80	dioxane	KF (3 equiv)	ZnCl ₂ (10 mol%)	n.d.
22	5	PPhEt ₂ (10)	80	dioxane	K ₃ PO ₄ (3 equiv)	--	6
23	5	PPhEt ₂ (10)	80	dioxane	LiF (3 equiv)	--	n.d.
24	5	PPhEt ₂ (10)	80	dioxane	NaF (3 equiv)	--	n.d.
25	5	PPhEt ₂ (10)	80	dioxane	CsF (3 equiv)	--	54 ^b

^aGC yield calibrated against undecane as an internal standard. Estimated error $\pm$ ~5%. n.d. = not detected. ^bAverage of two trials.

D. Cross-Coupling Reactions

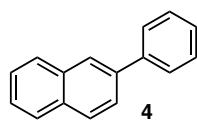
General Procedure. In a nitrogen atmosphere glovebox, KF (87.2 mg, 1.50 mmol, 3.00 equiv), C—O substrate (0.50 mmol, 1.00 equiv), and organostannane (0.50 mmol, 1.00 equiv) were combined in a one-dram vial equipped with a stir bar. In a second vial was prepared a stock solution of Ni(cod)₂ and phosphine in 1,4-dioxane. An aliquot of the Ni/phosphine stock solution was added to the reaction vial. The vial was sealed with a PTFE-lined cap, removed from the glovebox, and stirred at 80 °C for 18 h. The crude reaction mixture was concentrated onto silica gel by rotary evaporation, and the crude material was purified by flash column chromatography on silica gel that had been pre-treated with 1% Et₃N. For products that may be prone to oxidation or polymerization (**25–29**, **31–34**), BHT was added prior to initial concentration on silica gel, and again after purification by column chromatography prior to concentrating column fractions (for these products, percent yields are calculated after subtracting out the mass of BHT) .



1-Phenylnaphthalene (2): (*from aryl sulfamate 1*) Compound **2** was prepared according to the general procedure using tributylphenylstannane (183.6 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 1.00 mL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol%) and PPhMe₂ (0.05 mmol, 10 mol%) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **2** as a white solid (75.6 mg, 74% yield, R_f = 0.42 in 100% hexanes). Spectral data are consistent with those previously reported.¹⁶

(*from aryl tosylate 14*) Compound **2** was prepared according to the general procedure using tributylphenylstannane (183.6 mg, 0.50 mmol, 1.00 equiv), **14** (149.2 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhEt₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **2** as a white solid (88.5 mg, 87% yield).

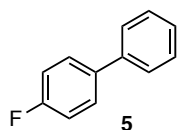
(*from aryl mesylate 17*) Compound **2** was prepared according to the general procedure using tributylphenylstannane (163.2 μL, 0.50 mmol, 1.00 equiv), **17** (111.1 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μL of a solution of Ni(cod)₂ (0.05 mmol, 10 mol %) and PBu₃ (0.10 mmol, 20 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **2** as a white solid (94.5 mg, 93% yield).



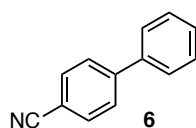
2-Phenylnaphthalene (4): Compound **4** was prepared according to the general procedure using tributylphenylstannane (183.6 mg, 0.50 mmol, 1.00 equiv), naphthalen-2-yl dimethylsulfamate (**S1**, 125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhEt₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N)

¹⁶ Zhang, Z.; Wang, Z. *J. Org. Chem.* **2006**, *71*, 7485.

afforded product **4** as a white solid (83.7 mg, 82% yield, R_f = 0.48 in 100% hexanes). Spectral data are consistent with those previously reported.¹⁷

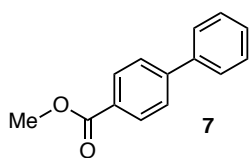


4-Fluoro-1,1'-biphenyl (5): Compound **5** was prepared according to the general procedure using tributylphenylstannane (163.2 μ L, 0.50 mmol, 1.00 equiv), 4-fluorophenyl dimethylsulfamate (**S2**, 109.6 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 1.00 mL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhEt₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **5** as a white powder (74.7 mg, 87% yield, R_f = 0.66 in 100% hexanes). Spectral data are consistent with those previously reported.¹⁸



[1,1'-Biphenyl]-4-carbonitrile (6): (*from aryl sulfamate S3*) Compound **6** was prepared according to the general procedure using tributylphenylstannane (163.2 μ L, 0.50 mmol, 1.00 equiv), 4-cyanophenyl dimethylsulfamate (**S3**, 113.1 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv) and 1.00 mL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhEt₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (89% hexanes, 10% EtOAc, 1% Et₃N) afforded product **6** as a white crystalline solid (73.6 mg, 82% yield, R_f = 0.51 in 90% hexanes, 10% EtOAc). Spectral data are consistent with those previously reported.¹⁹

(*from aryl tosylate 16*) Compound **6** was prepared according to the general procedure using tributylphenylstannane (183.6 mg, 0.50 mmol, 1.00 equiv), **16** (136.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μ L of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhMe₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **6** as a white crystalline solid (66.3 mg, 74% yield).



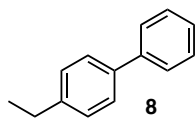
Methyl [1,1'-biphenyl]-4-carboxylate (7): Compound **7** was prepared according to the general procedure using tributylphenylstannane (163.2 μ L, 0.50 mmol, 1.00 equiv), methyl 4-((N,N-dimethylsulfamoyl)oxy)benzoate (**S4**, 129.6 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 1.00 mL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhMe₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (98% hexanes, 1% EtOAc, 1% Et₃N) afforded product **7** as a white solid (62.5 mg, 59% yield, R_f = 0.15 in 99% hexanes, 1% EtOAc). Spectral data are consistent with those previously reported.²⁰

¹⁷ Cho, C.-H.; Yun, H.-S.; Park, K. *J. Org. Chem.* **2003**, 68, 3017.

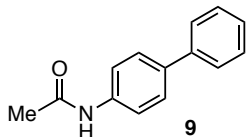
¹⁸ Watson, D. A.; Su, M.; Teverovskiy, G.; Zhang, Y.; García-Fortanet, J.; Kinzel, T.; Buchwald, S. L. *Science* **2009**, 325, 1661.

¹⁹ Grossman, O.; Gelman, D. *Org. Lett.* **2006**, 8, 1189.

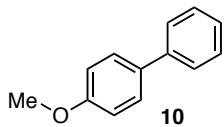
²⁰ Ackermann, L.; Gschrei, C. J.; Althammer, A.; Riederer, M. *Chem. Commun.* **2006**, 1419.



4-Ethyl-1,1'-biphenyl (8): Compound **8** was prepared according to the general procedure using tributylphenylstannane (163.2 μ L, 0.50 mmol, 1.00 equiv), 4-ethylphenyl dimethylsulfamate (114.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μ L of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhEt₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **8** as a yellow solid (68.0 mg, 75% yield, R_f = 0.69 in 100% hexanes). Spectral data are consistent with those previously reported.²¹



N-([1,1'-biphenyl]-4-yl)acetamide (9): Compound **9** was prepared according to the general procedure using tributylphenylstannane (163.2 μ L, 0.50 mmol, 1.00 equiv), 4-acetamidophenyl dimethylsulfamate (**S5**, 129.2 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μ L of a solution of Ni(cod)₂ (0.05 mmol, 10 mol %) and PBu₃ (0.10 mmol, 20 mol %) in 1,4-dioxane. Purification by flash column chromatography (40% hexanes, 59% EtOAc, 1% Et₃N) afforded product **9** as a white powder (70.0 mg, 66% yield, R_f = 0.50 in 40% hexanes, 60% EtOAc). ¹H NMR (500 MHz, CDCl₃, δ): 7.59–7.55 (m, 6H), 7.44–7.41 (m, 2H), 7.34–7.31 (m, 1H), 2.21 (s, 3H). The NH signal apparently overlaps with the residual solvent signal based on broadening of the base of the CHCl₃ signal at 7.26. Spectral data are consistent with those previously reported.²²

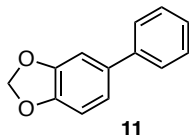


4-Methoxy-1,1'-biphenyl (10): (*from aryl sulfamate*) Compound **10** was prepared according to the general procedure using tributylphenylstannane (163.2 μ L, 0.50 mmol, 1.00 equiv), 4-methoxyphenyl dimethylsulfamate (115.6 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 1.00 mL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PBu₃ (10.1 mg, 0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (79% hexanes, 20% benzene, 1% Et₃N) afforded product **10** as a white powder (72.9 mg, 85% yield, R_f = 0.42 in 80% hexanes, 20% benzene). Spectral data are consistent with those previously reported.²²

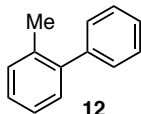
(*from aryl tosylate 15*) Compound **10** was prepared according to the general procedure using tributylphenylstannane (183.6 mg, 0.50 mmol, 1.00 equiv), **15** (139.4 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μ L of a solution of Ni(cod)₂ (0.05 mmol, 10 mol %) and PBu₃ (0.10 mmol, 20 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **10** as a white powder (70.1 mg, 76% yield).

²¹ Tsubouchi, A.; Muramatsu, D.; Takeda, T. *Angew. Chem. Int. Ed.* **2013** *52*, 12719.

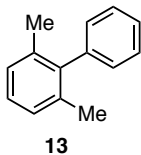
²² Zhou, W.-J.; Wang, K.-H.; Wang, J.-X. *Adv. Synth. Catal.* **2009**, *351*, 1378.



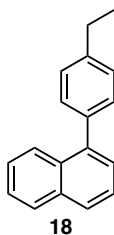
5-Phenylbenzo[d][1,3]dioxole (11): Compound **11** was prepared according to the general procedure using tributylphenylstannane (163.2 μ L, 0.50 mmol, 1.00 equiv), benzo[d][1,3]dioxol-5-yl dimethylsulfamate (**S6**, 122.6 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μ L of a solution of Ni(cod)₂ (0.05 mmol, 10 mol %) and PBu₃ (0.10 mmol, 20 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **11** as a brown oil (89.5 mg, 89% yield, R_f = 0.50 in 100% hexanes). Spectral data are consistent with those previously reported.²³



2-Methyl-1,1'-biphenyl (12): Compound **12** was prepared according to the general procedure using tributylphenylstannane (163.2 μ L, 0.50 mmol, 1.00 equiv), 2-methylphenyl dimethylsulfamate (107.6 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μ L of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhEt₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **12** as a colorless oil (66.3 mg, 79% yield, R_f = 0.57 in 100% hexanes). Spectral data are consistent with those previously reported.²⁴



2,6-Dimethyl-1,1'-biphenyl (13): Compound **13** was prepared according to the general procedure using tributylphenylstannane (163.2 μ L, 0.50 mmol, 1.00 equiv), 2,6-dimethylphenyl dimethylsulfamate (114.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μ L of a solution of Ni(cod)₂ (0.05 mmol, 10 mol %) and PPhEt₂ (0.10 mmol, 20 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **13** as a colorless oil (66.8 mg, 73% yield, R_f = 0.74 in 100% hexanes). Spectral data are consistent with those previously reported.²⁵



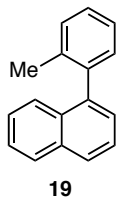
1-(4-ethylphenyl)naphthalene (18): Compound **18** was prepared according to the general procedure using tributyl(4-ethylphenyl)stannane (**S7**, 197.6 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 1.50 mL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhEt₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (79% hexanes, 20% EtOAc, 1% Et₃N) afforded product **18** as a light yellow oil (108.2 mg, 93% yield, R_f = 0.51 in 80% hexanes, 20% EtOAc). Spectral data are consistent with those previously reported.²⁶

²³ Scheuermann, G. M.; Rumi, L.; Steurer, P.; Bannwarth, W.; Mülhaupt, R. *J. Am. Chem. Soc.* **2009**, *131*, 8262.

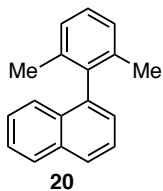
²⁴ Zim, D.; Lando, V. R.; Dupont, J.; Monteiro, A. L. *Org. Lett.* **2001**, *3*, 3049.

²⁵ Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9950.

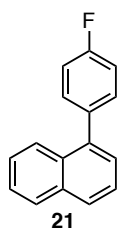
²⁶ Sabounchei, S. J.; Panahimehr, M.; Ahmadi, M.; Nasri, Z.; Khavasi, H. R. *J. Organomet. Chem.* **2013**, *723*, 207.



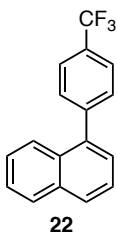
1-(o-Tolyl)naphthalene (19): Compound **19** was prepared according to the general procedure using tributyl(2-methylphenyl)stannane (190.6 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 1.00 mL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPh₂Me (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **19** as a white solid (99.5 mg, 91% yield, R_f = 0.55 in 100% hexanes). Spectral data are consistent with those previously reported.²⁷



1-(2,6-Dimethylphenyl)naphthalene (20): Compound **20** was prepared according to the general procedure using tributyl(2,6-dimethylphenyl)stannane (**S8**, 197.6 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 1.00 mL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPh₂Me (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (79% hexanes, 20% benzene, 1% Et₃N) afforded product **20** as a white solid (112.8 mg, 97% yield, R_f = 0.53 in 80% hexanes, 20% benzene). Spectral data are consistent with those previously reported.²⁸



1-(4-Fluorophenyl)naphthalene (21): Compound **21** was prepared according to the general procedure using tributyl(4-fluorophenyl)stannane (**S9**, 192.6 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhEt₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **21** as a pale yellow solid (85.9 mg, 77% yield, R_f = 0.54 in 100% hexanes). Spectral data are consistent with those previously reported.²⁹



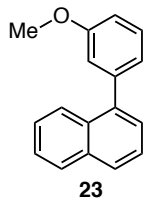
1-(4-(Trifluoromethyl)phenyl)naphthalene (22): Compound **22** was prepared according to the general procedure using tributyl(4-(trifluoromethyl)phenyl)stannane (217.6 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 1.00 mL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhMe₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (99% hexanes, 1% Et₃N) afforded product **22** as a white powder (109.5 mg, 80% yield, R_f = 0.53 in 100% hexanes). Spectral data are consistent with those previously reported.³⁰

²⁷ Wolf, C.; Xu, H. *J. Org. Chem.* **2008**, 73, 162.

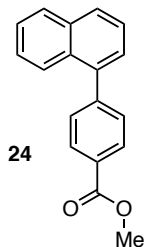
²⁸ Lipshutz, B. H.; Siegmann, K.; Garcia, E.; Kayser, F. *J. Am. Chem. Soc.* **1993**, 115, 9276.

²⁹ Quasdorf, K. W.; Antoft-Finch, A.; Liu, P.; Silberstein, A. L.; Komaromi, A.; Blackburn, T.; Ramgren, S. D.; Houk, K. N.; Snieckus, V.; Garg, N. K. *J. Am. Chem. Soc.* **2011**, 133, 6352.

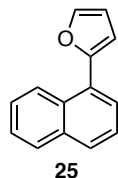
³⁰ Shi, S.; Meng, G.; Szostak, M. *Angew. Chem. Int. Ed.* **2016**, 55, 6959.



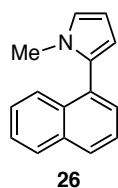
1-(3-Methoxyphenyl)naphthalene (23): Compound **23** was prepared according to the general procedure using tributyl(3-methoxyphenyl)stannane (**S10**, 198.6 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 1.50 mL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPh₂Me (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (89% hexanes, 10% benzene, 1% Et₃N) afforded product **23** as a colorless oil (70.3 mg, 64% yield, R_f = 0.34 in 90% hexanes, 10% benzene). Spectral data are consistent with those previously reported.³¹



Methyl 4-(naphthalen-1-yl)benzoate (24): Compound **24** was prepared according to the general procedure using tributyl(naphthalen-1-yl)stannane (**S11**, 208.6 mg, 0.50 mmol, 1.00 equiv), **1** (129.6 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhEt₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. Purification by flash column chromatography (79% hexanes, 20% EtOAc, 1% Et₃N) afforded product **24** as a white solid (98.1 mg, 75% yield, R_f = 0.66 in 80% hexanes, 20% EtOAc). Spectral data are consistent with those previously reported.⁷



2-(Naphthalen-1-yl)furan (25): Compound **25** was prepared according to the general procedure using 2-(tributylstannyl)furan (178.6 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhEt₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. BHT was added prior to concentration onto silica gel to inhibit product decomposition. Purification by flash column chromatography (99% hexanes, 1% Et₃N) followed by addition of BHT (~0.4 mol %) afforded product **25** as a yellow oil (80.1 mg, 82% yield, R_f = 0.57 in 100% hexanes). Spectral data are consistent with those previously reported.³²

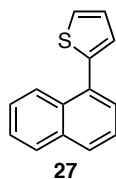


1-Methyl-2-(naphthalen-1-yl)-1H-pyrrole (26): Compound **26** was prepared according to the general procedure using 1-methyl-2-(tributylstannyl)pyrrole (185.1 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μL of a solution of Ni(cod)₂ (0.05 mmol, 10 mol %) and PPhEt₂ (0.10 mmol, 20 mol %) in 1,4-dioxane. BHT was added prior to concentration onto silica gel to inhibit product decomposition. Purification by flash column chromatography (99% hexanes, 1% Et₃N) followed by addition of BHT (~0.3 mol %) afforded product **26** as a colorless oil (78.8 mg, 76% yield, R_f = 0.44 in 100% hexanes). Spectral data are consistent with those previously reported.³³

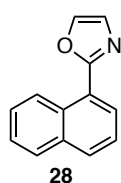
³¹ Cella, R.; Cunha, R. L. O. R.; Reis, A. E. S.; Pimenta, D. C.; Klitzke, C. F.; Stefani, H. A. *J. Org. Chem.* **2006**, *71*, 244.

³² Denmark, S. E.; Baird, J. D. *Org. Lett.* **2006**, *8*, 793.

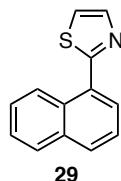
³³ Liu, Y.-X.; Xue, D.; Wang, J.-D.; Zhao, C.-J.; Zou, Q.-Z.; Wang, C.; Xiao, J. *Synlett* **2013**, *24*, 507.



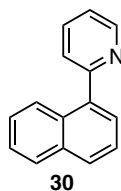
2-(Naphthalen-1-yl)thiophene (27): Compound **27** was prepared according to the general procedure using 2-(tributylstannyl)thiophene (186.6 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 1.00 mL of a stock solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhEt₂ (0.05 mmol, 10 mol %) in 1,4-dioxane. BHT was added prior to concentration onto silica gel to inhibit product decomposition. Purification by flash column chromatography (99% hexanes, 1% Et₃N) followed by addition of BHT (~0.8 mol%) afforded product **27** as a light yellow oil (100.8 mg, 95% yield, R_f = 0.56 in 99% hexanes). Spectral data are consistent with those previously reported.³²



2-(Naphthalen-1-yl)oxazole (28): Compound **28** was prepared according to the general procedure using 2-tributylstannyloxazole (179.1 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 1.00 mL of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhMe₂ (0.05 mmol, 10 mol %) in 1,4-dioxane (1.00 mL). BHT was added prior to concentration onto silica gel to inhibit product decomposition. Purification by flash column chromatography (94% hexanes, 5% EtOAc, 1% Et₃N) followed by addition of BHT (~0.3 mol%) afforded product **28** as a light yellow oil (83.8 mg, 86% yield, R_f = 0.37 in 95% hexanes, 5% EtOAc). Spectral data are consistent with those previously reported.³⁴



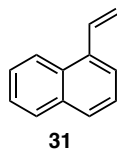
2-(Naphthalen-1-yl)thiazole (29): Compound **29** was prepared according to the general procedure using 2-tributylstannylthiazole (187.1 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μL of a solution of Ni(cod)₂ (0.05 mmol, 10 mol %) and PPhMe₂ (0.10 mmol, 20 mol %) in 1,4-dioxane. BHT was added prior to concentration onto silica gel to inhibit product decomposition. Purification by flash column chromatography (94% hexanes, 5% EtOAc, 1% Et₃N) followed by addition of BHT (~0.8 mol%) afforded product **29** as a light yellow oil (86.1 mg, 81% yield, R_f = 0.33 in 95% hexanes, 5% EtOAc). Spectral data are consistent with those previously reported.³⁴



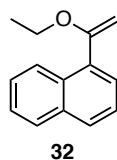
2-(Naphthalen-1-yl)pyridine (30): Compound **30** was prepared according to the general procedure using 2-tributylstannylpyridine (184.1 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μL of a solution of Ni(cod)₂ (0.05 mmol, 10 mol %) and PPhMe₂ (0.10 mmol, 20 mol %) in 1,4-dioxane. Purification by flash column chromatography (89% hexanes, 10% EtOAc, 1% Et₃N) afforded product **30** as a pale red oil (70.4 mg, 69% yield, R_f = 0.31 in 90% hexanes, 10% EtOAc); ¹H NMR (500 MHz, C₆D₆, δ): 8.66 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 8.39–8.37 (m, 1H), 7.69–7.68 (m, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.59 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.31–7.26 (m, 3H), 7.20 (ddd, *J* = 7.8, 1.1, 1.1 Hz, 1H), 7.14 (ddd, *J* = 7.7, 7.7, 1.8 Hz, 1H), 6.72 (ddd, *J* = 7.5, 4.8, 1.3 Hz, 1H); ¹³C{¹H} NMR (126 MHz, C₆D₆, δ): 159.9, 149.9,

³⁴ Zhu, F.; Tao, J.-L.; Wang, Z.-X. *Org. Lett.* **2015**, *17*, 4926.

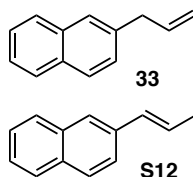
139.4, 135.9, 134.6, 131.9, 129.1, 128.6, 128.0, 126.54, 126.53, 126.1, 125.5, 125.0, 121.8. Spectral data are consistent with those previously reported.³⁵



1-Vinylnaphthalene (31): Compound **31** was prepared according to the general procedure using tributyl(vinyl)stannane (158.6 mg, 0.50 mmol, 1.00 equiv), **1** (125.8 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μ L of a solution of Ni(cod)₂ (0.05 mmol, 10 mol %) and PPhMe₂ (0.10 mmol, 20 mol %) in 1,4-dioxane. BHT was added prior to concentration onto silica gel to inhibit product decomposition. Purification by flash column chromatography (99% hexanes, 1% Et₃N) followed by addition of BHT (~2.6 mol%) afforded product **31** as a colorless oil (46.6 mg, 58% yield, *R*_f = 0.68 in 100% hexanes). Spectral data are consistent with those previously reported.³⁶



1-(1-Ethoxyvinyl)naphthalene (32): Compound **32** was prepared according to the general procedure using 1-ethoxytributyl(vinyl)tin (180.6 mg, 0.50 mmol, 1.00 equiv), **1** (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 1.00 mL of a solution of Ni(cod)₂ (0.05 mmol, 10 mol %) and PPhEt₂ (0.10 mmol, 20 mol %) in 1,4-dioxane. BHT was added prior to concentration onto silica gel to inhibit product decomposition. Purification by flash column chromatography (99% hexanes, 1% Et₃N) followed by addition of BHT (~0.2 mol%) afforded product **32** as a light yellow oil (85.1 mg, 86% yield, *R*_f = 0.47 in 100% hexanes). ¹H NMR (500 MHz, CDCl₃, δ): 8.18–8.16 (m, 1H), 7.85–7.82 (m, 2H), 7.54 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.52–7.46 (m, 2H), 7.44 (dd, *J* = 8.2, 7.1 Hz, 1H), 4.51 (d, *J* = 2.0 Hz, 1H), 4.40 (d, *J* = 2.0 Hz, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃, δ): 161.4, 136.1, 133.8, 131.4, 129.0, 128.2, 126.8, 126.2, 126.0, 125.9, 125.3, 87.1, 63.7, 14.7; HRMS (ESI/Q-TOF) *m/z*: [M + H]⁺ Calcd for C₁₄H₁₅O 199.1117; Found 199.1092.



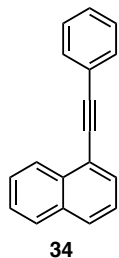
2-Allylnaphthalene (33): Compound **33** was prepared according to the general procedure using allyltributylstannane (165.6 mg, 0.50 mmol, 1.00 equiv), naphthalen-2-yl dimethylsulfamate (**S1**, 125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μ L of a solution of Ni(cod)₂ (0.025 mmol, 5 mol %) and PPhMe₂ (0.50 mmol, 5 mol %) in 1,4-dioxane. BHT was added prior to concentration onto silica gel to inhibit product decomposition. Purification by flash column chromatography (99% hexanes, 1% Et₃N) followed by addition of BHT (~0.5 mol%) afforded a clear oil comprising a ~9:1 mixture of **33** : **S12** (64.4 mg, 76% yield, *R*_f = 0.60 in 100% hexanes). Spectral data are consistent with those previously reported.^{37,38}

³⁵ Núñez, A.; Sánchez, A.; Burgos, C.; Alvarez-Builla, J. *Tetrahedron* **2004**, *60*, 6217.

³⁶ Bajracharya, G. B.; Pahadi, N. K.; Gridnev, I. D.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 6204.

³⁷ Seomoon, D.; Lee, P. H. *J. Org. Chem.* **2008**, *73*, 1165.

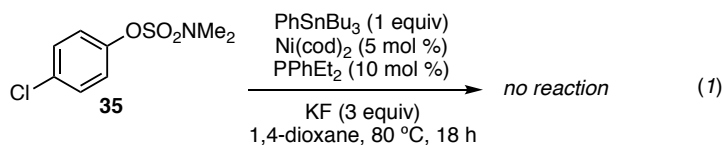
³⁸ Dong, D.-J.; Li, Y.; Wang, J.-Q.; Tian, S.-K. *Chem. Commun.* **2011**, *47*, 2158.



1-(Phenylethynyl)naphthalene (34): Compound **34** was prepared according to the general procedure using tributyl(phenylethynyl)stannane (175 μ L, 0.50 mmol, 1.00 equiv), **1** dimethylsulfamate (125.7 mg, 0.50 mmol, 1.00 equiv), KF (87.2 mg, 1.50 mmol, 3.00 equiv), and 670 μ L of a solution of Ni(cod)₂ (0.05 mmol, 10 mol %) and PPhMe₂ (0.10 mmol, 20 mol %) in 1,4-dioxane. BHT was added prior to concentration onto silica gel to inhibit product decomposition. Purification by flash column chromatography (99% hexanes, 1% Et₃N) followed by addition of BHT (~1.0 mol%) afforded product **34** as a light yellow oil (74.1 mg, 64% yield, *R*_f = 0.42 in 100% hexanes. ¹H NMR (500 MHz, CDCl₃, δ): 8.46 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.63–7.59 (m, 1H), 7.57–7.54 (m, 1H), 7.47 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.43–7.36 (m, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃, δ): 133.44, 133.38, 131.8, 130.5, 128.9, 128.6, 128.53, 128.46, 126.9, 126.6, 126.4, 125.4, 123.6, 121.1, 94.5, 87.7. Spectral data are consistent with those previously reported.³⁹

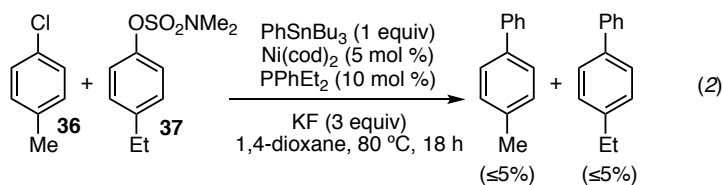
E. Mechanistic Experiments

i. Procedures for Equations 1 and 2



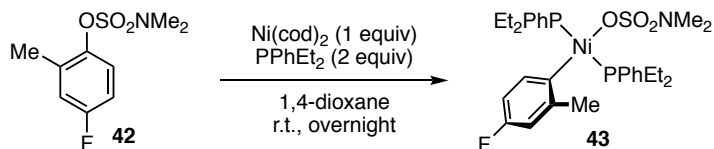
Procedure for Equation 1. In a nitrogen atmosphere glovebox, KF (8.7 mg, 0.15 mmol, 3.00 equiv), **35** (10.4 mg, 0.05 mmol, 1.00 equiv), and PhSnBu₃ (18.4 mg, 0.05 mmol, 1.00 equiv) were combined in a one-dram vial equipped with a stir bar. In a second vial was prepared a stock solution of Ni(cod)₂ and PPhEt₂ (0.01 *M* in Ni(cod)₂, 0.02 *M* in PPhEt₂) in 1,4-dioxane. The Ni/phosphine stock solution [250 μ L (0.0025 mmol, 5 mol% of Ni(cod) and 0.005 mmol, 10 mol% of PPhEt₂) was added to the first vial. The reaction vial was sealed with a PTFE-lined cap, removed from the glovebox, and stirred at 80 $^\circ$ C for 18 h. The reaction vial was cooled to room temperature, and undecane was added as a GC standard. The reaction mixture was diluted with Et₂O and shaken vigorously. An aliquot was removed, filtered through celite, and analyzed by GC.

³⁹ Thakur, K. G.; Sekar, G. *Synthesis* **2009**, 2785.

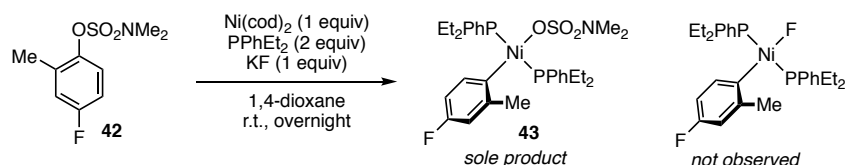


Procedure for Equation 2. In a nitrogen atmosphere glovebox, KF (8.7 mg, 0.15 mmol, 3.00 equiv), **36** (5.9 μ L mg, 0.05 mmol, 1.00 equiv), **37** (11.5 mg, 0.05 mmol, 1.00 equiv), and PhSnBu₃ (16.3 μ L, 0.05 mmol, 1.00 equiv) were combined in a one-dram vial equipped with a stir bar. In a second vial was prepared a stock solution of Ni(cod)₂ and PPhEt₂ (0.01 M in Ni(cod)₂, 0.02 M in PPhEt₂) in 1,4-dioxane. The Ni/phosphine stock solution [250 μ L (0.0025 mmol, 5 mol% of Ni(cod) and 0.005 mmol, 10 mol% of PPhEt₂) was added to the first vial. The vial was sealed with a PTFE-lined cap, removed from the glovebox, and stirred at 80 °C for 18 h. The reaction vial was cooled to room temperature, and undecane was added as a GC standard. The reaction mixture was diluted with Et₂O and shaken vigorously. An aliquot was removed, filtered through celite, and analyzed by GC. About 5% or less of each of the possible cross-coupled products were detected, and otherwise only unreacted starting materials were observed.

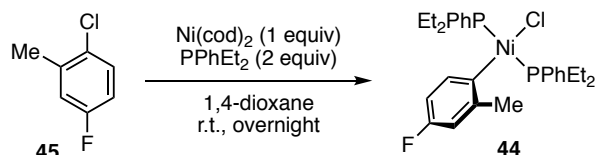
ii. Synthesis, Isolation, and Characterization of Oxidative Addition Complexes **43** and **44**



Complex 43. In a nitrogen atmosphere glovebox, Ni(cod)₂ (137.5 mg 0.50 mmol, 1.00 equiv), PPhEt₂ (138.2 mg 1.00 mmol, 2.00 equiv), **42** (116.6 mg, 0.50 mmol, 1.00 equiv), and 1,4-dioxane (2.50 mL) were combined in a one dram vial equipped with a magnetic stir bar, sealed with a PTFE-lined cap, and allowed to stir at room temperature overnight. The crude reaction mixture was concentrated under vacuum to provide a dark orange residue. In the glovebox, the crude residue was washed with degassed hexanes (6 x 4 mL). The remaining residue was dried under vacuum to yield product **43** as a yellow powder (180 mg, 67%). X-ray quality crystals were grown from THF/pentane at -25 °C. ¹H NMR (500 MHz, C₆D₆, δ): 7.29–7.26 (m, 4H), 7.02–7.00 (m, 6H), 6.46 (td, ⁴J_{HP} = 8.7 Hz, ⁴J_{HF} = 2.7 Hz, 1H), 6.34–6.28 (m, 2H), 2.70 (s, 6H), 2.63 (s, 3H), 2.15–2.08 (m, 2H), 1.79–1.74 (m, 4H), 1.55–1.49 (m, 2H), 0.98 (app quint, *J* = 8.0 Hz, 6H), 0.81 (app quint, *J* = 7.6 Hz, 6H); ¹³C{¹H} NMR (126 MHz, C₆D₆, δ): 163.1 (dt, ¹J_{CF} = 239.0 Hz, ⁵J_{CP} = 2.7 Hz), 146.0 (dt, ³J_{CF} = 5.4 Hz, ³J_{CP} = 3.0 Hz), 137.0 (dt, ³J_{CF} = 5.7 Hz, ³J_{CP} = 4.0 Hz), 134.2 (td, ²J_{CP} = 35.4 Hz, ⁴J_{CF} = 1.8 Hz), 132.7 (t, *J*_{CP} = 4.4 Hz), 132.5 (t, *J*_{CP} = 18.5 Hz), 130.2, 115.4 (dt, ²J_{CF} = 18.9 Hz, ⁴J_{CP} = 3.0 Hz), 111.6 (dt, ²J_{CF} = 19.1 Hz, ⁴J_{CP} = 2.8 Hz), 40.7, 26.4, 14.3 (t, ¹J_{CP} = 11.8 Hz), 13.6 (t, ¹J_{CP} = 11.6 Hz), 8.7, 8.2 (two aromatic ¹³C signals are coincidentally overlapping); ³¹P{¹H} NMR (203 MHz, C₆D₆, δ): 8.9; ¹⁹F NMR (C₆D₆, δ): -124.6. Structure was verified by X-ray diffraction (see p. S29).

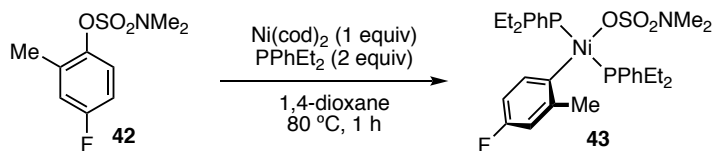


Complex 43: Synthesis in the Presence of KF. In an unsuccessful attempt to isolate a nickel-fluoride species, substrate **42** was reacted with Ni(cod)_2 and PPhEt_2 in the presence of KF . In a nitrogen atmosphere glovebox, Ni(cod)_2 (137.5 mg 0.50 mmol, 1.00 equiv), PPhEt_2 (138.2 mg 1.00 mmol, 2.00 equiv), **42** (116.6 mg, 0.50 mmol, 1.00 equiv), KF (29.0 mg, 0.50 mmol, 1.00 equiv), and 1,4-dioxane (2.50 mL) were combined in a one dram vial equipped with a magnetic stir bar, sealed with a PTFE-lined cap, and allowed to stir at room temperature overnight. The crude reaction mixture was concentrated under vacuum to provide a dark orange residue. In the glovebox, the crude residue was washed with degassed hexanes (6 x 4 mL). The remaining residue was dried under vacuum to yield product **43** as a yellow powder (155.6 mg, 50%). Spectra were consistent with compound **43** as described above.

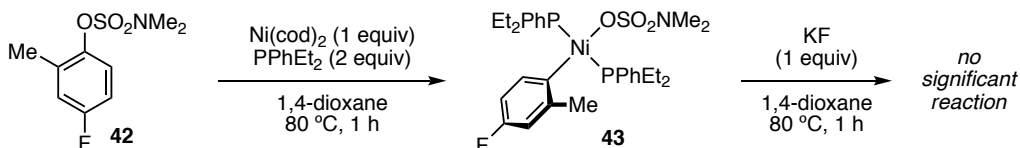


Complex 44. In a nitrogen atmosphere glovebox, Ni(cod)_2 (137.5 mg 0.50 mmol, 1.00 equiv), PPhEt_2 (138.2 mg 1.00 mmol, 2.00 equiv), **45** (60.9 μL , 0.50 mmol, 1.00 equiv), and 1,4-dioxane (2.50 mL) were combined in a one dram vial equipped with a magnetic stir bar, sealed with a PTFE-lined cap, and allowed to stir at room temperature overnight. The crude reaction mixture was filtered through celite and the celite was washed with 1,4-dioxane (2 mL). The filtrate was concentrated under vacuum to provide an air-stable burnt orange residue. Dry MeOH (3 mL) was added to the residue and the mixture was sonicated for 15 minutes, resulting in formation of a yellow precipitate. The precipitate was collected by filtration and washed with cold hexanes (3 x 2 mL). The collected precipitate was dried under vacuum to yield product **44** as a yellow powder (103.2 mg, 39%). X-ray quality crystals were grown from THF/pentane at 20 $^{\circ}\text{C}$. ^1H NMR (500 MHz, C_6D_6 , δ): 7.43 (app s, 4H), 7.05 (app s, 6H), 6.79–6.76 (m, 1H), 6.63–6.57 (m, 2H), 2.62 (s, 3H), 2.11–2.08 (m, 2H), 1.66–1.62 (m, 2H), 1.38–1.34 (m, 2H), 1.30–1.25 (m, 2H), 0.92 (app quint, $J = 7.9$ Hz, 6H), 0.72 (app quint, $J = 7.4$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , δ): 161.9 (dt, $^1J_{\text{CF}} = 238.6$ Hz, $^5J_{\text{CP}} = 2.8$ Hz), 144.3 (dt, $^3J_{\text{CF}} = 4.9$ Hz, $^3J_{\text{CP}} = 2.6$ Hz), 143.0 (td, $^2J_{\text{CP}} = 34.3$ Hz, $^4J_{\text{CF}} = 2.0$ Hz), 136.3 (dt, $^3J_{\text{CF}} = 5.1$ Hz, $^3J_{\text{CP}} = 4.9$ Hz), 132.3 (t, $J_{\text{CP}} = 17.6$ Hz), 131.8 (t, $J_{\text{CP}} = 4.2$ Hz), 129.1, 114.5 (dt, $^2J_{\text{CF}} = 18.5$ Hz, $^4J_{\text{CP}} = 2.8$ Hz), 111.0 (dt, $^2J_{\text{CF}} = 18.6$ Hz, $^4J_{\text{CP}} = 2.3$ Hz), 26.1 (d, $^4J_{\text{CF}} = 1.6$ Hz), 14.1 (t, $^1J_{\text{CP}} = 13.0$ Hz), 13.8 (t, $^1J_{\text{CP}} = 13.0$ Hz), 8.0, 7.5 (two aromatic ^{13}C signals are coincidentally overlapping); $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, C_6D_6 , δ): 11.9; ^{19}F NMR (C_6D_6 , δ): -124.8; Anal. Calcd for $\text{C}_{27}\text{H}_{36}\text{ClF}\text{NiP}_2$: C, 60.54; H, 6.77. Found: C, 60.25; H, 6.95. Structure was verified by X-ray diffraction (see p. S29).

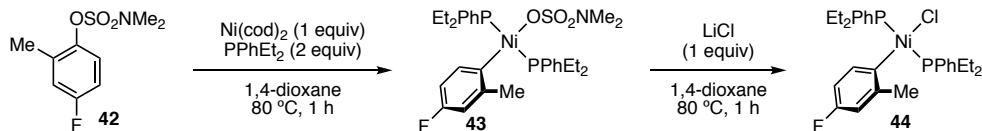
iii. NMR Studies on the Reaction of **43** with KF and LiCl



Demonstration that **43** is formed from **42** after 1 h at 80 °C in dioxane. In a nitrogen atmosphere glovebox, Ni(cod)₂ (5.5 mg 0.02 mmol, 1.00 equiv), PPhEt₂ (6.6 mg 0.04 mmol 2.00 equiv), **42** (4.7 mg, 0.02 mmol, 1.00 equiv), and 1,4-dioxane (700 μL) were combined in a one dram vial equipped with a magnetic stir bar and sealed with a PTFE-lined cap. The vial was removed from the glovebox and stirred at 80 °C for one hour, then transferred back into the glovebox, opened, and placed inside a drying chamber. The drying chamber was sealed, removed from the glovebox, and connected to a vacuum pump. The crude reaction mixture was concentrated under vacuum to provide a yellow-orange residue. The vacuum chamber was sealed (while under vacuum) and brought back into the glovebox. In the glovebox, the crude residue was taken up in C₆D₆ (1.0 mL) and filtered through celite. The filtrate was added to an NMR tube equipped with an external Ph₃PO standard (as a solution in C₆D₆ contained within a capillary tube). The spectral data (Figure S1B on p. S22) are consistent with those of the previously isolated sulfamate compound **43** (Figure S1A).



Reaction of **43** with KF. In a nitrogen atmosphere glovebox, Ni(cod)₂ (5.5 mg 0.02 mmol, 1.00 equiv), PPhEt₂ (6.6 mg 0.04 mmol, 2.00 equiv), **42** (4.7 mg, 0.02 mmol, 1.00 equiv), and 1,4-dioxane (700 μL) were combined in a one dram vial equipped with a magnetic stir bar and sealed with a PTFE-lined cap. The vial was removed from the glovebox and stirred at 80 °C for one hour, then transferred back into the glovebox and KF (1.2 mg, 0.02 mmol, 1.00 equiv) was added. The vial was again sealed, removed from the glovebox, and stirred at 80 °C for another hour, then transferred back into the glovebox, opened, and placed inside a drying chamber. The drying chamber was sealed, removed from the glovebox, and connected to a vacuum pump. The crude reaction mixture was concentrated under vacuum to provide a yellow-orange residue. The vacuum chamber was sealed (while under vacuum) and brought back into the glovebox. In the glovebox, the crude residue was taken up in C₆D₆ (1.0 mL) and filtered through celite. The filtrate was added to an NMR tube equipped with an external Ph₃PO standard (as a solution in C₆D₆ contained within a capillary tube). The spectral data (Figure S1C on p. S22) are consistent with those of the previously isolated sulfamate compound **43** (Figure S1A), indicating that no significant reaction with KF takes place under these conditions.



Reaction of **43 with LiCl.** In a nitrogen atmosphere glovebox, Ni(cod)_2 (5.5 mg 0.02 mmol, 1.00 equiv), PPhEt_2 (6.6 mg 0.04 mmol, 2.00 equiv), **42** (4.7 mg, 0.02 mmol, 1.00 equiv), and 1,4-dioxane (700 μL) were combined in a one dram vial equipped with a magnetic stir bar and sealed with a PTFE-lined cap. The vial was removed from the glovebox and stirred at 80 °C for one hour, then transferred back into the glovebox and LiCl (0.8 mg, 0.02 mmol, 1.00 equiv) was added. The vial was again sealed, removed from the glovebox, and stirred at 80 °C for another hour, then transferred back into the glovebox, opened, and placed inside a drying chamber. The drying chamber was sealed, removed from the glovebox, and connected to a vacuum pump. The crude reaction mixture was concentrated under vacuum to provide a yellow-orange residue. The vacuum chamber was sealed (while under vacuum) and brought back into the glovebox. In the glovebox, the crude residue was taken up in C_6D_6 (1.0 mL) and filtered through celite. The filtrate was added to an NMR tube equipped with an external Ph_3PO standard (as a solution in C_6D_6 contained within a capillary tube). The spectral data (Figure S1D on p. S22) are consistent with those of the previously isolated nickel(II) chloride compound **44** (Figure S1E), indicating that **43** reacts with LiCl to form **44** by anion exchange.

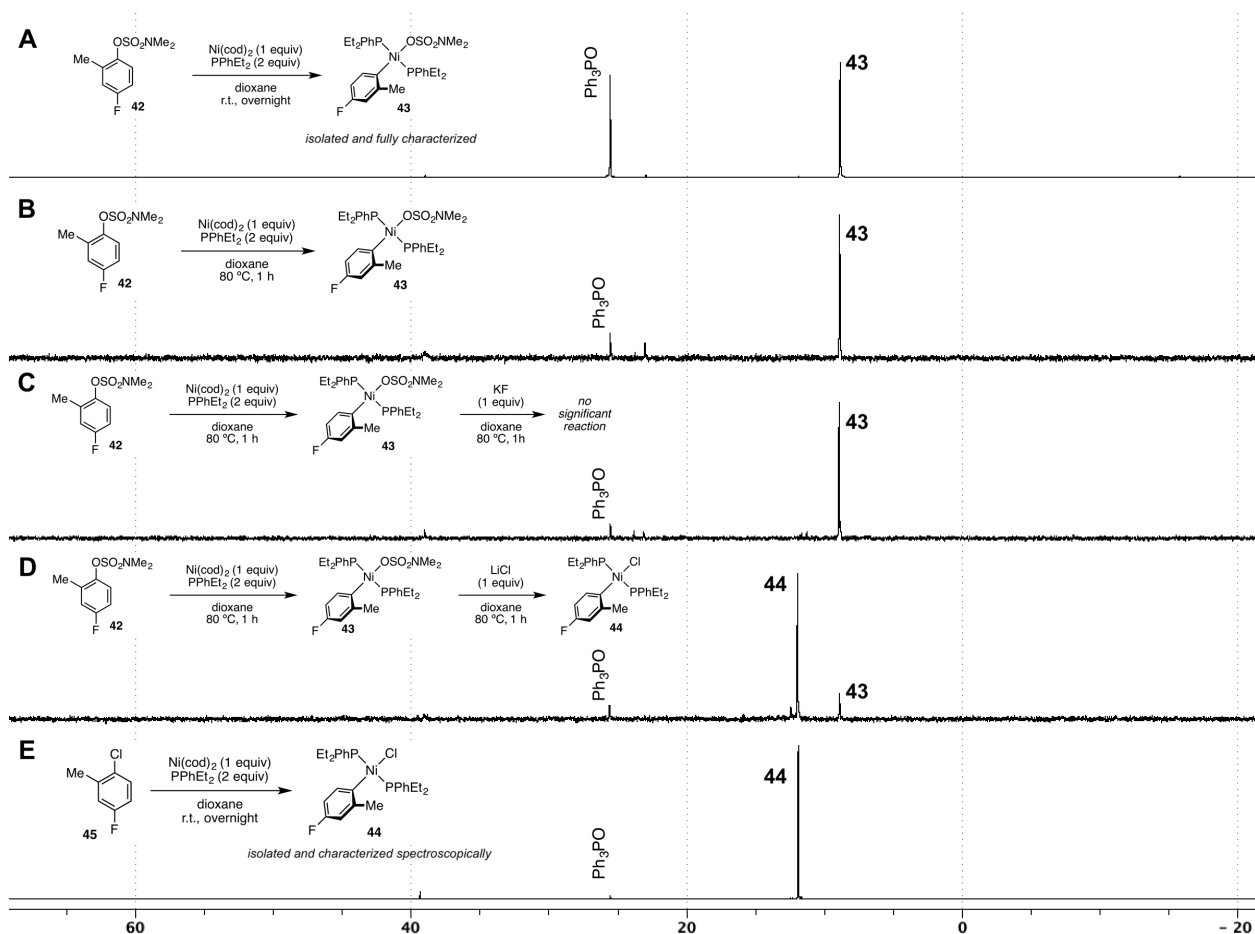
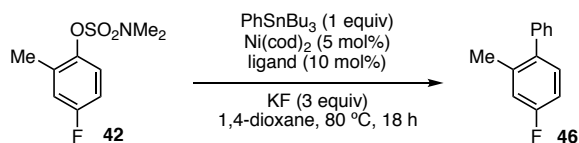


Figure S1. Comparison of ^{31}P NMR spectra of oxidative addition complexes. No other signals are detected outside of the window shown. Free phosphine (PPhEt_2) appears at about -15.8 (a trace amount of free phosphine can be seen in (A), but is not detected in the other spectra). Ph_3PO was added as an internal (A) or external chemical shift standard (B, C, D, E); the molar equivalents of Ph_3PO was not standardized across spectra.

iv. Evaluating the Catalytic Competence of **42** and PMe_3

Substrate **42** and phosphine ligand PMe_3 were employed as model compounds for the stoichiometric and computational studies, respectively. To confirm the relevance of these models to catalytic conditions, **42** and PMe_3 were evaluated under catalytic cross-coupling conditions.



General Procedure. In a nitrogen atmosphere glovebox, KF (8.7 mg, 0.15 mmol, 3.0 equiv), **42** (11.7 mg, 0.05 mmol, 1.0 equiv), and PhSnBu_3 (18.4 mg, 0.05 mmol, 1.0 equiv) were combined in a one-dram vial equipped with a stir bar. In a second vial was prepared a stock solution of Ni(cod)_2 and phosphine in 1,4-dioxane (0.01 M in Ni(cod)_2 , 0.02 M in phosphine). The Ni/phosphine stock solution [250 μL (0.0025 mmol, 5 mol% of Ni(cod) and 0.005 mmol, 10 mol% of phosphine)] was added to the reaction vial. The vial was sealed with a PTFE-lined cap, removed from the glovebox, and stirred at 80 $^\circ\text{C}$ for 18 h. The reaction vial was cooled to room temperature, and undecane was added as a GC standard. The reaction mixture was diluted with Et_2O and shaken vigorously. An aliquot was removed, filtered through celite, and analyzed by GC.

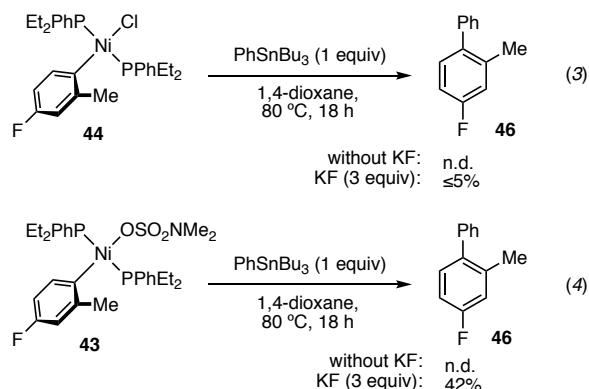
Table S2. Results of using **42** and PMe_3 under catalytic cross coupling conditions.

entry	Ligand	46 (% yield) ^a
1	PPhEt_2	≥ 99
2	PMe_3	25

^aGC yield calibrated against undecane as an internal standard. Average of two trials.

Discussion. Using a typical ligand for the Ni-catalyzed Stille coupling (PPhEt_2), substrate **42** gives quantitative conversion to cross-coupled product **46**. This result demonstrates that **42** is a competent substrate for catalysis. About 25% yield of **46** is obtained with PMe_3 , demonstrating that this small phosphine is a competent ligand for nickel under catalytic cross coupling conditions, albeit less effective than ligands such as PPhEt_2 .

v. Procedures for Equations 3 and 4



General Procedure. In a nitrogen atmosphere glovebox, KF (2.2 mg, 0.0375 mmol, 3.0 equiv), **43** (7.8 mg, 0.0125 mmol, 1.0 equiv) or **44** (6.7 mg, 0.0125 mmol, 1.0 equiv), PhSnBu_3 (4.6 mg, 0.0125 mmol, 1.0 equiv), and 1,4-dioxane (250 μL) were combined in a one-dram vial equipped with a stir bar. The reaction vial was sealed with a PTFE-lined cap, removed from the glovebox, and stirred at 80°C for 18 h. The reaction vial was cooled to room temperature, and undecane was added as a GC standard. The reaction mixture was diluted with Et_2O and shaken vigorously. An aliquot was removed, filtered through celite, and analyzed by GC. Yields are GC yields calibrated against undecane as an internal standard (n.d. = not detected).

Discussion. When complex **44** is heated with PhSnBu_3 and KF in 1,4-dioxane, only trace yield of the cross-coupled product **46** is observed (eq 3). This result is consistent with the hypothesis that the Ni-catalyzed Stille coupling is inhibited by chloride sources due to formation of a Ni(II)–chloride intermediate (such as **44**) that is slow to undergo transmetalation with organostannanes. In contrast, Ni(II)-sulfamate complex **43** provides ~42% yield of **46** under the same conditions using KF (eq 4). Notably, no cross coupling product is observed with either complex in the absence of KF, which supports the hypothesis that KF is necessary for the transmetallation step.

II. Computational Details

A. General Methods

Calculations were performed with Gaussian 09 (see reference in the next section). An ultrafine integration grid and the keyword 5d were used for all calculations. Geometry optimizations of stationary points were carried out in the gas phase with the Mo6L⁴⁰ functional with the LANL2DZ⁴¹ pseudopotential for Ni and Sn, the 6-31+G(d) basis set for O, F, K, and Cl, and the 6-31G(d) basis set for all other atoms. Frequency analyses were carried out at the same level to evaluate the zero-point vibrational energy and thermal corrections at 298 K. The nature of the stationary points was determined in each case according to the appropriate number of negative eigenvalues of the Hessian matrix. Forward and reverse intrinsic reaction coordinate (IRC) calculations were carried out on representative optimized transition structures to ensure that the TSs indeed connect the appropriate reactants and products.^{42–44} Notably, the potential energy surface is quite flat near the transition states for transmetallation, so most IRC calculations terminated early. Multiple conformations were considered for all structures when applicable, as well as configurational isomers of the complexes. In all cases, the *trans* complexes (with Ph *trans* to X, where X ≠ PMe₃) are significantly lower energy than the *cis* complexes (with Ph *cis* to PMe₃). The lowest energy conformations/configurations are reported. Single point energy calculations were performed on the gas-phase optimized geometries using the Mo6L functional with the SDD^{45,46} pseudopotential for Ni and Sn and the 6-311++G(2d,p) basis set for all other atoms. Bulk solvent effects in 1,4-dioxane were considered implicitly in the single point energy calculations through the CPCM continuum solvation model.⁴⁷ Images of optimized structures were generated with CYLview.⁴⁸

⁴⁰ Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101–194118.

⁴¹ Hay, P.J.; Wadt, W.R. *J. Chem. Phys.* **1985**, *82*, 299–310.

⁴² Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154–2161.

⁴³ Gonzalez, C.; Schlegel, H.B. *J. Phys. Chem.* **1990**, *94*, 5523–5527.

⁴⁴ Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363–368.

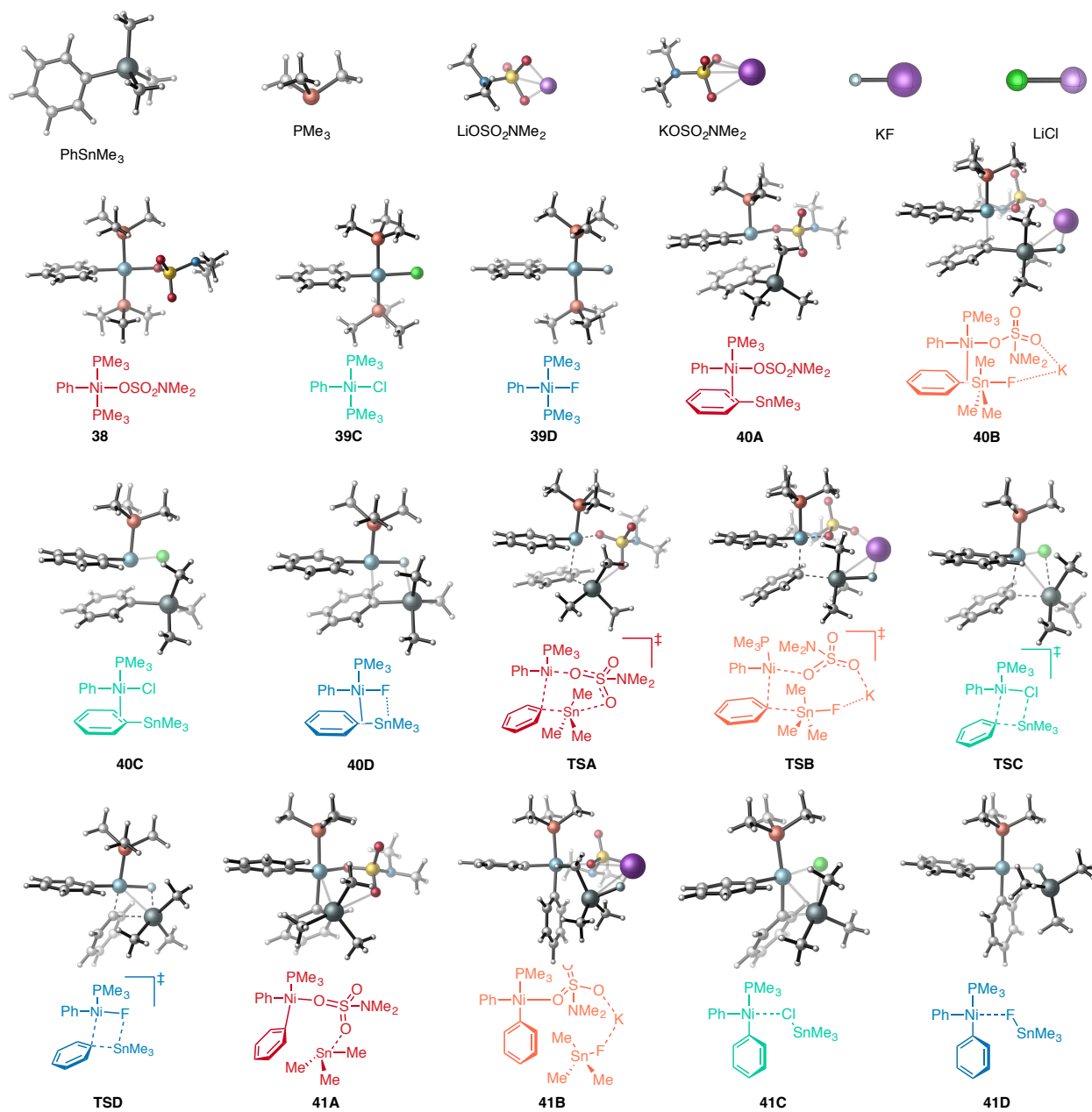
⁴⁵ Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866–872.

⁴⁶ Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H. Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123–141.

⁴⁷ Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669–681.

⁴⁸ CYLview, 1.0b; Legault CY, Université de Sherbrooke, 2009 (<http://www.cylview.org>)

B. Graphical Guide to Numbered Compounds



C. Energies, Entropies, and Lowest Frequencies of Minimum Energy Structures**Table S3.** Energies, Entropies, and Lowest Frequencies of Minimum Energy Structures^a

Structure	E _{elec} (Hartree)	E _{elec} + ZPE (Hartree)	H (Hartree)	S (cal mol ⁻¹ K ⁻¹)	G ^b (Hartree)	Lowest freq. (cm ⁻¹)	# of imag freq.
PhSnMe₃	-354.796223	-354.597565	-354.582613	122.1	-354.640650	22.2	0
PMe₃	-461.118031	-461.004584	-460.996950	77.7	-461.033891	177.2	0
LiOSO₂NMe₂	-766.120786	-766.021721	-766.012132	89.6	-766.054721	75.3	0
KOSO₂NMe₂	-1358.503420	-1358.406352	-1358.395691	98.6	-1358.442554	53.3	0
KF	-699.858880	-699.857943	-699.854340	54.3	-699.880123	411.2	0
LiCl	-467.849208	-467.847802	-467.844347	50.9	-467.868529	617.1	0
38	-2083.499890	-2083.080254	-2083.048892	194.6	-2083.141350	12.3	0
39C	-1785.239697	-1784.917462	-1784.892992	163.8	-1784.970798	24.2	0
39D	-1424.866893	-1424.544609	-1424.520067	165.0	-1424.598476	31.1	0
40A	-1977.147957	-1976.643118	-1976.604833	227.1	-1976.712725	21.9	0
40B	-2677.039145	-2676.532788	-2676.491084	241.9	-2676.606008	24.5	0
40C	-1678.887033	-1678.479988	-1678.448427	198.6	-1678.542783	14.0	0
40D	-1318.524969	-1318.117733	-1318.086484	196.0	-1318.179588	16.8	0
TSA	-1977.141716	-1976.636676	-1976.599395	219.7	-1976.703790	-42.3	1
TSB	-2677.038604	-2676.532389	-2676.491478	237.5	-2676.604323	-32.0	1
TSC	-1678.884716	-1678.477900	-1678.447086	193.1	-1678.538844	-33.1	1
TSD	-1318.519477	-1318.112177	-1318.081675	191.8	-1318.172789	-16.6	1
41A	-1977.144387	-1976.638726	-1976.600822	223.7	-1976.707097	30.3	0
41B	-2677.054323	-2676.547636	-2676.505941	243.1	-2676.621426	28.5	0
41C	-1678.887227	-1678.479824	-1678.448344	196.4	-1678.541649	29.7	0
41D	-1318.520299	-1318.112890	-1318.081565	198.6	-1318.175909	24.3	0

^aEnergy values calculated at the CPCM(1,4-dioxane)-Mo6L/6-311++G(2d,p)/SDD(Ni,Sn)//Mo6L/6-31+G(d)(O,F,K,Cl)/6-31G(d)(C,H,N,P,S)/LANL2DZ(Ni,Sn) level, referred to as (CPCM)/Mo6L/BS2//Mo6L/BS1. 1 Hartree = 627.51 kcal mol⁻¹. Thermal corrections at 298.15 K. ^bSolvent-corrected free energy given by $G[(CPCM)/Mo6L/BS2] = E_{elec}[(CPCM)/Mo6L/BS2] + G_{corr}[Mo6L/BS1]$, where G_{corr} is the thermal correction to Gibbs free energy obtained in the gas phase.

III. X-Ray Crystallographic Details for Compounds **43** and **44**

CCDC Deposition Numbers: 1881432 (**43**) and 1898148 (**44**)

X-ray diffraction data for **43** and **44** were collected at 100 K on a Bruker D8 Venture using MoK α -radiation ($\lambda=0.71073$ Å). Data have been corrected for absorption using SADABS⁴⁹ area detector absorption correction program. Using Olex2,⁵⁰ the structure was solved with the SHELXT⁵¹ structure solution program using Direct Methods and refined with the SHELXL⁵² refinement package using least squares minimization. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the investigated complex were located from difference Fourier maps but finally their positions were placed in geometrically calculated positions and refined using a riding model. Isotropic thermal parameters of the placed hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Calculations and refinement of structures were carried out using APEX3,⁵³ SHELXTL,⁵⁴ and Olex2 software.

Table S4. Crystal data and structure refinement for **43**.

Identification code	MSU_SN10(1-JR-172)
Empirical formula	C ₂₉ H ₄₂ FNNiO ₃ P ₂ S
Formula weight	624.34
Temperature/K	100
Crystal system	monoclinic
Space group	P2 ₁ /m
a/Å	8.6752(3)
b/Å	12.5702(4)
c/Å	14.4059(5)
α /°	90
β /°	101.7950(10)
γ /°	90
Volume/Å ³	1537.78(9)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.348
μ/mm^{-1}	0.839
F(000)	660.0
Crystal size/mm ³	0.21 × 0.16 × 0.03
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/°	5.778 to 55.106
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 15, -18 ≤ l ≤ 18
Reflections collected	42439
Independent reflections	3706 [R _{int} = 0.0268, R _{sigma} = 0.0127]
Data/restraints/parameters	3706/0/194
Goodness-of-fit on F ²	1.070
Final R indexes [I > 2 σ (I)]	R ₁ = 0.0238, wR ₂ = 0.0593
Final R indexes [all data]	R ₁ = 0.0275, wR ₂ = 0.0613
Largest diff. peak/hole / e Å ⁻³	0.43/-0.28

⁴⁹ Sheldrick, G. M. (1996). SADABS: Area Detector Absorption Correction; University of Göttingen, Germany.

⁵⁰ Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., *J. Appl. Cryst.* **2009**, *42*, 339-341.

⁵¹ Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3-8.

⁵² Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3-8.

⁵³ Bruker (2016). APEX3. Bruker AXS Inc., Madison, Wisconsin, USA.

⁵⁴ Sheldrick, G.M. *Acta Cryst.* **2008**, *A64*, 112-122.

Table S5. Crystal data and structure refinement for **44**.

Identification code	MSU_SN11(2-JR-16)
Empirical formula	C ₂₇ H ₃₆ ClFNiP ₂
Formula weight	535.66
Temperature/K	100
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	11.8371(9)
b/Å	14.1571(10)
c/Å	16.2044(12)
α /°	90
β /°	99.776(3)
γ /°	90
Volume/Å ³	2676.1(3)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.330
μ/mm^{-1}	0.964
F(000)	1128.0
Crystal size/mm ³	0.26 × 0.14 × 0.08
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	5.858 to 61.18
Index ranges	-16 ≤ h ≤ 16, -20 ≤ k ≤ 20, -23 ≤ l ≤ 23
Reflections collected	72735
Independent reflections	8200 [R_{int} = 0.0440, R_{sigma} = 0.0284]
Data/restraints/parameters	8200/0/294
Goodness-of-fit on F ²	1.040
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0304, wR_2 = 0.0658
Final R indexes [all data]	R_1 = 0.0460, wR_2 = 0.0708
Largest diff. peak/hole / e Å ⁻³	0.48/-0.30

Table S6. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **43**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Ni1	6992.0(2)	7500	7336.5(2)	10.43(7)
S1	8820.3(5)	7500	9436.8(3)	13.78(9)
P1	6986.7(3)	5748.2(2)	7187.4(2)	11.41(8)
F1	881.0(15)	7500	4413.0(9)	35.6(3)
O1	8811.7(14)	7500	8393.3(8)	14.0(2)
O2	8173.9(11)	6529.0(7)	9732.5(6)	20.9(2)
N1	10703.1(18)	7500	9963.8(10)	17.0(3)
C1	5120(2)	7500	6380.0(12)	13.2(3)
C2	3670(2)	7500	6678.4(13)	16.5(3)
C3	2255(2)	7500	6007.8(15)	22.1(4)
C4	2282(2)	7500	5056.8(14)	22.5(4)
C5	3663(2)	7500	4727.0(13)	19.4(4)
C6	5072(2)	7500	5397.6(12)	14.7(3)
C7	3585(2)	7500	7712.6(14)	22.9(4)
C8	5319.6(14)	5063.3(10)	7503.7(9)	15.0(2)
C9	4110.7(17)	4607.3(13)	6840.4(10)	26.6(3)
C10	2889.7(19)	4070.0(16)	7133.6(12)	37.6(4)
C11	2877.7(17)	3979.0(14)	8089.2(11)	31.3(3)

~Table S6 continued on the next page~

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C12	4059.0(17)	4442.0(12)	8752.4(10)	26.1(3)
C13	5266.9(16)	4988.4(11)	8465.5(9)	21.7(3)
C14	8666.4(14)	5061.9(10)	7920.6(9)	15.5(2)
C15	8664.6(16)	3855.2(10)	7782.0(9)	20.4(3)
C16	7023.9(15)	5282.5(10)	5989.9(8)	15.5(2)
C17	8511.5(16)	5642.0(13)	5662.8(10)	25.3(3)
C18	11554.6(17)	8469.2(11)	9796.6(10)	23.3(3)

Table S7. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **44**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U(eq)</i>
Ni1	2644.3(2)	2435.2(2)	4065.6(2)	11.13(5)
Cl1	2812.7(3)	1133.5(2)	3323.6(2)	16.25(7)
P1	1226.7(3)	1805.4(2)	4598.5(2)	12.33(7)
P2	4357.0(3)	2947.3(2)	3950.4(2)	12.16(7)
F1	1658.8(8)	5916.1(6)	5992.0(6)	26.4(2)
C1	2423.9(11)	3562.7(9)	4659.6(8)	12.7(2)
C2	1661.6(11)	4261.9(9)	4272.8(8)	13.7(2)
C3	1420.7(11)	5055.9(10)	4726.2(9)	16.2(3)
C4	1922.1(12)	5141.8(10)	5555.2(9)	16.7(3)
C5	2674.4(11)	4483.0(10)	5960.4(9)	16.6(3)
C6	2927.2(11)	3699.0(9)	5501.4(8)	14.6(3)
C7	1054.2(12)	4164.5(11)	3378.5(9)	19.7(3)
C8	1977.6(11)	1069.9(9)	5441.1(8)	13.9(2)
C9	2397.2(12)	182.2(10)	5264.3(9)	18.1(3)
C10	3052.0(13)	-344.9(11)	5890.4(10)	22.5(3)
C11	3315.8(13)	8.3(11)	6699.5(10)	24.1(3)
C12	2918.3(13)	889.9(12)	6882.8(9)	24.3(3)
C13	2247.0(13)	1416.9(11)	6257.7(9)	20.0(3)
C14	247.5(12)	1003.4(10)	3940.1(9)	18.8(3)
C15	-486.5(14)	1527.8(13)	3216.7(10)	29.4(4)
C16	269.5(12)	2549.0(10)	5096.8(9)	17.3(3)
C17	-628.9(13)	2032.8(11)	5503.6(11)	26.5(3)
C18	5273.2(11)	2661.8(10)	4940.7(8)	14.9(3)
C19	5197.1(13)	1757.9(11)	5272.6(9)	21.8(3)
C20	5869.5(14)	1509.1(13)	6033.0(10)	30.2(4)
C21	6606.5(14)	2168.4(14)	6471.4(10)	31.6(4)
C22	6683.6(13)	3064.7(13)	6157.7(9)	27.0(3)
C23	6029.2(12)	3313.8(11)	5391.0(9)	20.3(3)
C24	5070.3(12)	2357.8(10)	3169.3(9)	17.7(3)
C25	6301.3(13)	2675.0(11)	3162.4(10)	23.8(3)
C26	4605.0(12)	4199.6(10)	3784.8(9)	18.4(3)
C27	4091.3(15)	4529.8(12)	2904.3(11)	30.8(4)

Table S8. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **43**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni1	13.26(11)	8.88(11)	8.81(10)	0	1.46(8)	0

~Table S8 continued on the next page~

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S1	17.2(2)	14.4(2)	9.69(18)	0	2.59(15)	0
P1	14.07(15)	9.17(15)	10.92(14)	0.02(10)	2.41(11)	-0.43(11)
F1	22.7(6)	40.5(8)	35.6(7)	0	-13.1(5)	0
O1	16.4(6)	15.0(6)	9.5(5)	0	0.1(4)	0
O2	26.4(5)	20.0(5)	17.3(4)	2.1(4)	6.8(4)	-4.7(4)
N1	18.8(7)	18.0(8)	12.2(7)	0	-1.6(6)	0
C1	16.0(8)	8.6(7)	14.3(8)	0	1.8(6)	0
C2	19.2(9)	10.8(8)	19.6(8)	0	4.3(7)	0
C3	16.1(9)	17.5(9)	32.2(10)	0	3.5(8)	0
C4	19.6(9)	15.9(9)	26.2(10)	0	-9.0(7)	0
C5	28.4(10)	11.1(8)	15.4(8)	0	-3.2(7)	0
C6	19.5(8)	9.8(8)	14.2(8)	0	2.2(7)	0
C7	24.1(10)	24.8(10)	22.1(9)	0	10.4(8)	0
C8	16.0(6)	11.5(6)	17.9(6)	2.4(4)	4.6(5)	0.2(4)
C9	24.8(7)	34.5(8)	19.4(6)	2.6(6)	1.7(5)	-10.5(6)
C10	26.7(8)	53.0(11)	30.4(8)	3.7(7)	-0.3(6)	-20.8(7)
C11	23.1(7)	36.8(9)	35.3(8)	9.9(7)	9.2(6)	-8.7(6)
C12	27.2(7)	31.1(8)	22.3(7)	6.0(6)	10.6(6)	-2.5(6)
C13	23.2(7)	23.8(7)	18.8(6)	-0.8(5)	5.7(5)	-4.6(5)
C14	16.7(6)	13.3(6)	15.4(5)	1.5(4)	0.8(4)	1.7(5)
C15	23.7(7)	13.0(6)	23.6(6)	1.3(5)	2.9(5)	3.6(5)
C16	19.9(6)	13.9(6)	12.6(5)	-2.4(4)	3.3(4)	1.0(5)
C17	22.7(7)	36.3(8)	18.7(6)	0.1(6)	7.9(5)	2.4(6)
C18	22.7(7)	23.9(7)	21.4(6)	-2.7(5)	0.3(5)	-5.9(5)

Table S9. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **44**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni1	11.25(8)	11.00(8)	11.05(8)	-0.68(6)	1.68(6)	0.48(6)
Cl1	17.87(15)	14.78(15)	16.68(15)	-5.35(12)	4.58(12)	-2.14(11)
P1	11.66(15)	11.96(15)	13.46(16)	-0.96(12)	2.38(12)	-0.02(12)
P2	12.27(15)	11.48(15)	12.68(15)	1.77(12)	2.04(12)	0.97(12)
F1	30.6(5)	23.1(4)	24.5(5)	-11.9(4)	1.3(4)	7.8(4)
C1	11.7(5)	12.5(6)	14.5(6)	-0.5(5)	3.8(5)	-0.6(5)
C2	13.5(6)	14.3(6)	13.4(6)	0.3(5)	2.4(5)	-0.1(5)
C3	15.0(6)	15.0(6)	18.2(7)	0.0(5)	2.1(5)	2.6(5)
C4	17.6(6)	14.4(6)	18.8(7)	-6.3(5)	4.8(5)	0.1(5)
C5	15.5(6)	20.3(7)	13.8(6)	-3.1(5)	1.3(5)	-2.8(5)
C6	11.7(6)	15.7(6)	16.0(6)	1.1(5)	1.1(5)	0.6(5)
C7	21.7(7)	22.1(7)	14.5(6)	-1.0(5)	0.5(5)	5.7(5)
C8	13.1(6)	14.9(6)	14.4(6)	1.9(5)	4.1(5)	0.0(5)
C9	21.5(7)	15.9(6)	17.2(6)	-0.6(5)	4.4(5)	0.7(5)
C10	26.3(7)	17.1(7)	24.7(7)	3.1(6)	6.1(6)	6.3(6)
C11	24.5(7)	27.5(8)	20.3(7)	7.9(6)	3.8(6)	7.6(6)
C12	27.3(8)	29.8(8)	15.5(7)	0.8(6)	3.2(6)	6.6(6)
C13	23.5(7)	20.3(7)	16.6(7)	-1.5(6)	4.2(5)	5.6(6)
C14	15.1(6)	20.4(7)	20.4(7)	-5.5(6)	2.2(5)	-4.4(5)
C15	21.6(7)	36.2(9)	26.8(8)	-6.0(7)	-6.3(6)	0.1(7)
C16	15.4(6)	15.1(6)	22.2(7)	-0.8(5)	5.7(5)	2.4(5)
C17	22.5(7)	23.9(8)	37.1(9)	-2.4(7)	16.4(7)	-0.6(6)
C18	11.7(6)	19.1(6)	14.4(6)	1.4(5)	3.4(5)	3.4(5)

~Table S9 continued on the next page~

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C19	19.3(7)	24.0(7)	21.7(7)	6.8(6)	2.6(5)	0.7(6)
C20	25.6(8)	37.4(9)	27.4(8)	17.6(7)	4.0(6)	4.1(7)
C21	20.0(7)	57.4(12)	16.9(7)	11.9(7)	1.5(6)	4.5(7)
C22	19.9(7)	44.6(10)	15.9(7)	-4.2(7)	1.3(6)	-0.9(7)
C23	17.9(7)	24.5(7)	18.5(7)	-2.0(6)	3.4(5)	0.6(5)
C24	18.4(6)	19.7(7)	16.1(6)	0.2(5)	6.4(5)	2.0(5)
C25	21.7(7)	25.2(8)	27.6(8)	2.9(6)	12.7(6)	0.2(6)
C26	16.9(6)	13.1(6)	25.6(7)	4.0(5)	4.5(5)	-0.9(5)
C27	29.8(8)	24.0(8)	36.4(9)	15.9(7)	-0.3(7)	0.8(6)

Table S10. Bond Lengths for **43**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	P1 ¹	2.2124(3)	C1	C6	1.407(2)
Ni1	P1	2.2124(3)	C2	C3	1.399(3)
Ni1	O1	1.9563(12)	C2	C7	1.507(2)
Ni1	C1	1.9027(17)	C3	C4	1.375(3)
S1	O1	1.5018(12)	C4	C5	1.376(3)
S1	O2 ¹	1.4434(9)	C5	C6	1.394(2)
S1	O2	1.4434(9)	C8	C9	1.3899(18)
S1	N1	1.6545(16)	C8	C13	1.3987(17)
P1	C8	1.8193(13)	C9	C10	1.393(2)
P1	C14	1.8314(12)	C10	C11	1.384(2)
P1	C16	1.8283(12)	C11	C12	1.379(2)
F1	C4	1.370(2)	C12	C13	1.3848(19)
N1	C18 ¹	1.4700(16)	C14	C15	1.5298(18)
N1	C18	1.4699(16)	C16	C17	1.5298(18)
C1	C2	1.411(2)			

¹+X,3/2-Y,+Z**Table S11.** Bond Lengths for **44**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	Cl1	2.2277(4)	C5	C6	1.3965(19)
Ni1	P1	2.2020(4)	C8	C9	1.3988(19)
Ni1	P2	2.1907(4)	C8	C13	1.3966(19)
Ni1	C1	1.9047(13)	C9	C10	1.386(2)
P1	C8	1.8239(14)	C10	C11	1.388(2)
P1	C14	1.8306(14)	C11	C12	1.384(2)
P1	C16	1.8316(14)	C12	C13	1.393(2)
P2	C18	1.8230(14)	C14	C15	1.528(2)
P2	C24	1.8370(14)	C16	C17	1.529(2)
P2	C26	1.8243(14)	C18	C19	1.397(2)
F1	C4	1.3692(15)	C18	C23	1.401(2)
C1	C2	1.4124(18)	C19	C20	1.394(2)
C1	C6	1.4061(18)	C20	C21	1.388(3)
C2	C3	1.3985(19)	C21	C22	1.376(3)
C2	C7	1.5107(18)	C22	C23	1.393(2)
C3	C4	1.3787(19)	C24	C25	1.527(2)
C4	C5	1.3768(19)	C26	C27	1.526(2)

Table S12. Bond Angles for **43**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Ni1	P1 ¹	168.902(18)	C2	C1	Ni1	117.49(13)
O1	Ni1	P1 ¹	93.491(10)	C6	C1	Ni1	125.04(13)
O1	Ni1	P1	93.491(10)	C6	C1	C2	117.47(16)
C1	Ni1	P1 ¹	86.856(10)	C1	C2	C7	121.90(16)
C1	Ni1	P1	86.856(10)	C3	C2	C1	120.09(17)
C1	Ni1	O1	175.53(6)	C3	C2	C7	118.01(17)
O1	S1	N1	105.17(7)	C4	C3	C2	119.78(18)
O2	S1	O1	111.88(4)	F1	C4	C3	118.74(18)
O2 ¹	S1	O1	111.88(4)	F1	C4	C5	118.74(18)
O2	S1	O2 ¹	115.48(8)	C3	C4	C5	122.52(17)
O2	S1	N1	105.74(5)	C4	C5	C6	117.54(17)
O2 ¹	S1	N1	105.74(5)	C5	C6	C1	122.59(17)
C8	P1	Ni1	115.64(4)	C9	C8	P1	123.34(10)
C8	P1	C14	102.25(6)	C9	C8	C13	118.71(12)
C8	P1	C16	104.66(6)	C13	C8	P1	117.94(10)
C14	P1	Ni1	115.29(4)	C8	C9	C10	120.35(13)
C16	P1	Ni1	114.22(4)	C11	C10	C9	120.18(14)
C16	P1	C14	103.17(6)	C12	C11	C10	119.92(14)
S1	O1	Ni1	128.10(8)	C11	C12	C13	120.21(13)
C18 ¹	N1	S1	114.01(8)	C12	C13	C8	120.59(13)
C18	N1	S1	114.01(8)	C15	C14	P1	114.35(9)
C18	N1	C18 ¹	111.96(15)	C17	C16	P1	112.01(9)

¹+X₃/2-Y₂+Z**Table S13.** Bond Angles for **44**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Ni1	Cl1	91.190(14)	F1	C4	C3	118.43(12)
P2	Ni1	Cl1	93.375(14)	F1	C4	C5	118.78(12)
P2	Ni1	P1	160.959(15)	C5	C4	C3	122.79(13)
C1	Ni1	Cl1	176.86(4)	C4	C5	C6	117.65(12)
C1	Ni1	P1	87.83(4)	C5	C6	C1	122.14(12)
C1	Ni1	P2	88.50(4)	C9	C8	P1	120.30(10)
C8	P1	Ni1	102.58(4)	C13	C8	P1	120.81(10)
C8	P1	C14	105.19(7)	C13	C8	C9	118.57(12)
C8	P1	C16	104.92(6)	C10	C9	C8	120.52(13)
C14	P1	Ni1	118.15(5)	C9	C10	C11	120.37(14)
C14	P1	C16	103.62(7)	C12	C11	C10	119.83(14)
C16	P1	Ni1	120.65(5)	C11	C12	C13	119.97(14)
C18	P2	Ni1	105.81(4)	C12	C13	C8	120.72(13)
C18	P2	C24	103.38(6)	C15	C14	P1	111.53(11)
C18	P2	C26	104.98(7)	C17	C16	P1	116.29(10)
C24	P2	Ni1	116.66(5)	C19	C18	P2	118.32(11)
C26	P2	Ni1	120.57(5)	C19	C18	C23	118.70(13)
C26	P2	C24	103.64(7)	C23	C18	P2	122.97(11)
C2	C1	Ni1	119.67(10)	C20	C19	C18	120.48(15)
C6	C1	Ni1	122.24(10)	C21	C20	C19	119.84(16)
C6	C1	C2	117.90(12)	C22	C21	C20	120.43(14)
C1	C2	C7	121.73(12)	C21	C22	C23	120.08(15)
C3	C2	C1	120.14(12)	C22	C23	C18	120.45(15)
C3	C2	C7	118.10(12)	C25	C24	P2	114.98(10)
C4	C3	C2	119.36(12)	C27	C26	P2	112.75(11)

Table S14. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for **43**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)	
H3	1277	7500	6209		27
H5	3657	7500	4067		23
H6	6037	7500	5183		18
H7A	3291	8211	7895		34
H7B	4615	7306	8095		34
H7C	2794	6983	7820		34
H9	4117	4662	6184		32
H10	2063	3765	6676		45
H11	2057	3598	8288		38
H12	4044	4386	9408		31
H13	6067	5315	8926		26
H14A	9649	5356	7775		19
H14B	8674	5215	8596		19
H15A	8960	3690	7177		31
H15B	7609	3575	7779		31
H15C	9423	3528	8302		31
H16A	6969	4496	5976		19
H16B	6087	5559	5544		19
H17A	8487	5376	5021		38
H17B	9441	5360	6096		38
H17C	8559	6421	5662		38
H18A	11655	8493	9132		35
H18B	12605	8466	10208		35
H18C	10971	9096	9939		35

Table S15. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for **44**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)	
H3	916	5532	4465		19
H5	3010	4559	6532		20
H6	3456	3243	5767		18
H7A	1327	4655	3034		30
H7B	226	4235	3358		30
H7C	1215	3541	3164		30
H9	2232	-61	4711		22
H10	3322	-951	5765		27
H11	3768	-354	7126		29
H12	3103	1136	7435		29
H13	1969	2019	6388		24
H14A	697	507	3713		23
H14B	-258	692	4286		23
H15A	11	1814	2860		44
H15B	-928	2023	3440		44
H15C	-1013	1082	2885		44
H16A	745	2937	5531		21
H16B	-134	2987	4669		21
H17A	-1179	1719	5070		40
H17B	-1033	2488	5804		40
H17C	-250	1560	5898		40
H19	4683	1309	4978		26
H20	5823	890	6251		36

~Table S15 continued on the next page~

~Table S15 continued from the previous page~

H21	7061	2000	6991	38
H22	7184	3514	6464	32
H23	6096	3930	5172	24
H24A	5071	1669	3273	21
H24B	4614	2471	2607	21
H25A	6646	2271	2782	36
H25B	6746	2625	3729	36
H25C	6302	3332	2972	36
H26A	4267	4573	4198	22
H26B	5441	4321	3883	22
H27A	3271	4380	2791	46
H27B	4477	4208	2495	46
H27C	4196	5214	2862	46

Table S16. Atomic Occupancy for **43**.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
H7A	0.5	H7B	0.5	H7C	0.5

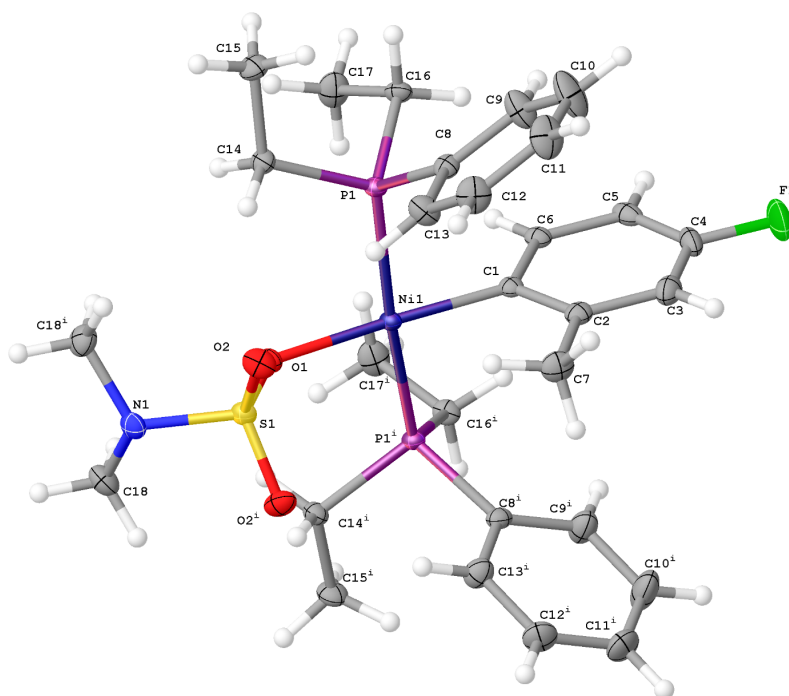


Figure S2. X-ray crystal structure of **43**. All thermal ellipsoids drawn at the 50% probability level.

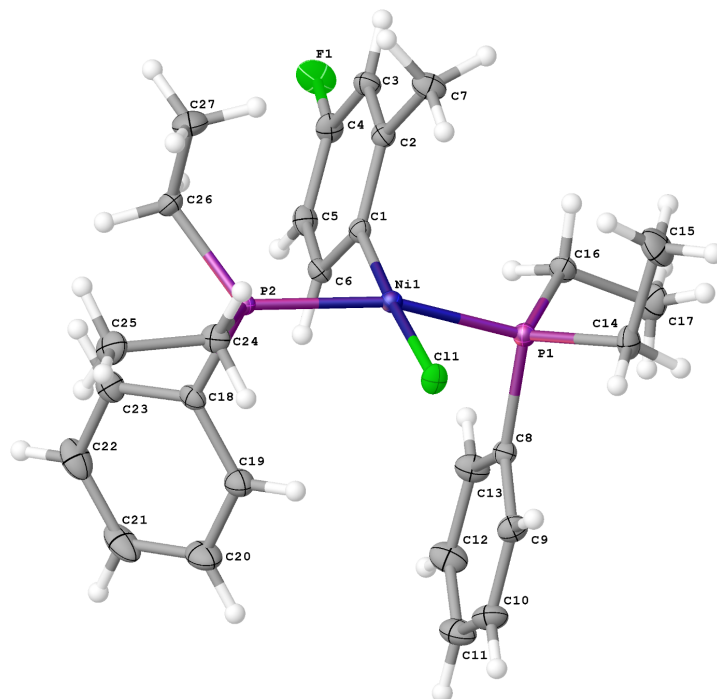


Figure S3. X-ray crystal structure of **44**. All thermal ellipsoids drawn at the 50% probability level.

IV. Cartesian Coordinates of Minimum Energy Calculated Structures

PhSnMe₃

```

Charge: 0      Multiplicity: 1
C   -3.182838  1.192883  -0.000016
C   -1.788903  1.197802  0.000012
C   -1.054321  0.003699  0.000026
C   -1.773715  -1.200778  0.000017
C   -3.166572  -1.215356  -0.000006
C   -3.874192  -0.015519  -0.000034
H   -3.731030  2.134377  -0.000027
H   -1.268328  2.157651  0.000048
H   -1.241820  -2.155408  0.000052
H   -3.702129  -2.164073  -0.000003
H   -4.963150  -0.023002  -0.000067
Sn  1.096325  0.007373  -0.000001
C   1.793844  -1.028327  -1.745947
H   2.883300  -1.139755  -1.735924
H   1.356727  -2.031447  -1.802792
H   1.517883  -0.494356  -2.660961
C   1.747964  2.049938  0.000399
H   1.382117  2.581501  0.885648
H   2.840633  2.119787  -0.000021
H   1.381445  2.582081  -0.884226
C   1.793797  -1.029013  1.745550
H   2.883340  -1.139610  1.736029
H   1.516939  -0.495871  2.660780
H   1.357414  -2.032507  1.801518

```

PMe₃

```

Charge: 0      Multiplicity: 1
P   -0.000047  0.000042  -0.614852
C   0.999757  1.270620  0.282371
H   2.055695  1.185644  0.002824
H   0.668415  2.276987  0.003434
H   0.922159  1.171362  1.373796
C   -1.600369  0.230384  0.282373
H   -2.055298  1.187006  0.002610
H   -2.305886  -0.560211  0.003873
H   -1.475460  0.213229  1.373780
C   0.600658  -1.501044  0.282324
H   -0.000105  -2.373392  0.002217
H   1.638211  -1.716527  0.004096
H   0.552699  -1.384485  1.373737

```

LiOSO₂NMe₂

```

Charge: 0      Multiplicity: 1
O   -0.898493  0.118483  1.347220
S   -0.560741  -0.272640  -0.081614
O   -1.343027  0.703011  -0.922543
O   -0.705252  -1.684755  -0.386275
N   1.059232  0.103924  -0.387445
C   1.391424  1.497480  -0.134318
H   2.404505  1.678631  -0.508857
H   0.705172  2.143377  -0.688316
H   1.366011  1.756216  0.939103
C   1.984954  -0.821070  0.260020
H   1.694466  -1.846831  0.027156
H   2.984497  -0.635937  -0.147519
H   2.019855  -0.690597  1.354932
Li  -2.100455  1.359175  0.660002

```

KOSO₂NMe₂

```

Charge: 0      Multiplicity: 1
O   0.205969  -0.000002  1.336318
K   2.706989  0.000024  0.129665
S   -0.121943  -0.000037  -0.123103
O   0.384380  -1.235254  -0.775092

```

```

O   0.384480  1.235111  -0.775158
N   -1.800280  0.000026  -0.352666
C   -2.425088  -1.211323  0.165183
H   -3.468931  -1.221950  -0.168610
H   -1.915129  -2.085084  -0.246528
H   -2.405069  -1.262801  1.267300
C   -2.424993  1.211439  0.165143
H   -1.914963  2.085147  -0.246595
H   -3.468834  1.222139  -0.168654
H   -2.404972  1.262951  1.267258

```

KF

```

Charge: 0      Multiplicity: 1
K   0.000000  0.000000  0.721969
F   0.000000  0.000000  -1.524157

```

LiCl

```

Charge: 0      Multiplicity: 1
Cl  0.000000  0.000000  0.308238
Li  0.000000  0.000000  -1.746685

```

38

```

Charge: 0      Multiplicity: 1
Ni  0.384013  -0.002097  0.383291
C   2.222614  0.083189  -0.040756
C   2.620005  0.060012  -1.385967
C   3.223253  0.134088  0.940544
C   3.971049  0.076404  -1.737733
H   1.863242  0.029452  -2.173464
C   4.573573  0.152990  0.590583
H   2.947871  0.155239  1.997166
C   4.953170  0.120567  -0.750413
H   4.255879  0.054848  -2.789708
H   5.334068  0.190463  1.370831
H   6.006998  0.132165  -1.023473
P   0.541446  -2.235256  0.295086
P   0.343038  2.235786  0.361945
C   1.636036  3.097474  1.328170
H   2.626737  2.812922  0.959269
H   1.523403  4.185587  1.250285
H   1.575590  2.815153  2.384672
C   -1.198070  2.992996  0.979003
H   -1.385039  2.668250  2.007166
H   -1.132943  4.087771  0.951264
H   -2.038534  2.658090  0.364619
C   0.556030  2.945905  -1.303104
H   1.530377  2.646395  -1.703843
H   -0.229916  2.555726  -1.955689
H   0.502449  4.041105  -1.277119
C   0.444343  -2.870729  -1.411990
H   0.512080  -3.965502  -1.430566
H   -0.506713  -2.557143  -1.854145
H   1.269343  -2.455688  -2.001187
C   -0.775403  -3.137768  1.179137
H   -1.739682  -2.861897  0.742274
H   -0.630975  -4.222222  1.099438
H   -0.779520  -2.853139  2.236217
C   2.077658  -3.007955  0.917622
H   2.934697  -2.651425  0.336964
H   2.248624  -2.736922  1.964728
H   2.021036  -4.100499  0.840814
O   -1.568675  -0.093059  0.808049
S   -2.385626  -0.115617  -0.476350
O   -1.972312  0.929341  -1.425440
O   -2.490347  -1.478788  -1.030602
N   -3.909973  0.384279  0.111040

```

C	-4.862982	0.563784	-0.980918
H	-5.765810	1.026501	-0.567052
H	-4.436481	1.233479	-1.731191
H	-5.144094	-0.388063	-1.463136
C	-4.424502	-0.527887	1.127648
H	-3.684933	-0.641016	1.924171
H	-5.332846	-0.085105	1.551377
H	-4.674664	-1.522180	0.719005

39C

Charge: 0		Multiplicity: 1	
Ni	-0.000326	0.565200	-0.093088
C	0.000753	-1.329553	-0.054691
C	0.001191	-2.109778	-1.218817
C	0.001156	-1.994915	1.180643
C	0.001993	-3.503531	-1.152399
H	0.000898	-1.625364	-2.197782
C	0.001968	-3.389266	1.250149
H	0.000836	-1.417965	2.109227
C	0.002377	-4.149775	0.082360
H	0.002318	-4.089133	-2.072210
H	0.002271	-3.883379	2.222143
H	0.003003	-5.237284	0.134249
P	-2.218763	0.565143	-0.041069
P	2.218105	0.567605	-0.041073
C	2.798985	1.149340	1.589574
H	2.466520	0.456702	2.370310
H	3.892471	1.228210	1.629657
H	2.352191	2.129128	1.787016
C	3.021694	1.719631	-1.207115
H	2.577699	2.711414	-1.078287
H	4.104219	1.770428	-1.037218
H	2.840587	1.397317	-2.237484
C	3.145077	-0.988042	-0.285750
H	2.814796	-1.737302	0.441526
H	2.939303	-1.392691	-1.282155
H	4.225121	-0.830302	-0.180066
C	-3.144036	-0.991513	-0.285777
H	-4.224251	-0.834958	-0.180080
H	-2.937832	-1.395909	-1.282195
H	-2.812930	-1.740431	0.441476
C	-3.023618	1.716319	-1.207077
H	-2.842176	1.394223	-2.237456
H	-4.106195	1.765939	-1.037164
H	-2.580692	2.708581	-1.078234
C	-2.800274	1.146197	1.589595
H	-2.467022	0.453918	2.370313
H	-2.354578	2.126482	1.787047
H	-3.893848	1.223839	1.629692
Cl	-0.001606	2.844178	0.066593

39D

Charge: 0		Multiplicity: 1	
Ni	-0.000060	-0.645324	-0.087505
C	0.000109	1.246318	-0.059079
C	0.000234	2.020791	-1.228858
C	0.000121	1.929264	1.168060
C	0.000366	3.415007	-1.177253
H	0.000231	1.528409	-2.204224
C	0.000255	3.324049	1.225353
H	0.000022	1.362535	2.103391
C	0.000381	4.073990	0.050877
H	0.000462	3.991702	-2.102951
H	0.000262	3.827546	2.192805
H	0.000487	5.162139	0.092301
P	2.198576	-0.755785	-0.024384
P	-2.198715	-0.755421	-0.024450
C	-2.723228	-1.349393	1.621174
H	-2.463867	-0.609974	2.386422

H	-3.802800	-1.540341	1.666474
H	-2.179938	-2.274447	1.838344
C	-2.867623	-2.026816	-1.147539
H	-2.278834	-2.937399	-1.000769
H	-3.928703	-2.228583	-0.955596
H	-2.750660	-1.709592	-2.188632
C	-3.248777	0.710555	-0.311299
H	-2.961635	1.508547	0.382173
H	-3.085909	1.090733	-1.325204
H	-4.313866	0.483706	-0.182078
C	3.248888	0.709983	-0.311396
H	4.313934	0.482979	-0.182095
H	3.086128	1.090044	-1.325362
H	2.961843	1.508118	0.381951
C	2.867326	-2.027452	-1.147257
H	2.750494	-1.710342	-2.188399
H	3.928357	-2.229389	-0.955215
H	2.278356	-2.937905	-1.000412
C	2.722930	-1.349592	1.621351
H	2.463634	-0.610026	2.386479
H	2.179506	-2.274542	1.838635
H	3.802473	-1.540682	1.666730
F	-0.000235	-2.528475	0.003675

40A

Charge: 0		Multiplicity: 1	
C	-0.627831	0.268035	2.854923
C	-1.942113	0.585895	3.194248
C	-0.377699	-0.672288	1.840466
H	-2.148330	1.300195	3.990039
C	-2.990957	-0.016421	2.505018
H	0.638991	-1.025458	1.694413
C	-1.429504	-1.255549	1.101357
C	-2.736222	-0.906027	1.459570
H	-4.020063	0.230836	2.764503
H	0.211206	0.693119	3.405994
Ni	0.168661	1.132945	0.469819
H	-3.582798	-1.323508	0.911285
C	-1.563414	1.720385	0.014891
C	-2.262280	1.195051	-1.079069
C	-2.205398	2.671522	0.818092
C	-3.583526	1.568986	-1.330521
H	-1.785393	0.463628	-1.734028
C	-3.524440	3.048730	0.566499
H	-1.676275	3.118938	1.661254
C	-4.219431	2.495604	-0.507059
H	-4.116236	1.131016	-2.174811
H	-4.009441	3.718721	1.211397
H	-5.247860	2.792266	-0.706436
P	0.835188	2.669766	-0.926645
C	0.858356	2.116594	-2.662417
H	-0.150226	1.820221	-2.970113
H	1.205092	2.927853	-3.314652
H	1.530431	1.257967	-2.755590
C	-0.094549	4.241337	-1.019344
H	0.429254	4.941626	-1.681431
H	-1.103503	4.066309	-1.403747
H	-0.187317	4.695896	-0.028023
C	2.541342	3.234547	-0.615815
H	3.223995	2.396095	-0.776593
H	2.796051	4.055817	-1.297022
H	2.642493	3.579311	0.417855
O	2.045009	0.660463	0.987320
S	2.739868	-0.381556	0.120857
O	2.092673	-1.699990	0.173063
Sn	-1.032956	-2.565679	-0.581182
C	-0.024865	-1.458987	-2.119093
H	0.875333	-1.983904	-2.453104
H	-0.673151	-1.268279	-2.983053
H	0.312434	-0.496472	-1.712204

C	-3.000203	-3.082008	-1.286946
H	-2.953439	-3.729280	-2.169577
H	-3.586259	-3.607534	-0.524454
H	-3.558115	-2.180876	-1.571220
C	0.046152	-4.300442	0.044867
H	-0.518041	-4.880454	0.782493
H	0.262432	-4.954181	-0.806920
H	0.998168	-3.995530	0.488772
O	3.002887	0.142801	-1.235104
N	4.208426	-0.567370	0.962463
C	5.005941	-1.660338	0.414438
H	5.850932	-1.830067	1.090618
H	4.400749	-2.568313	0.374379
H	5.399373	-1.439872	-0.592809
C	4.965811	0.675400	1.035435
H	5.824930	0.509297	1.694642
H	5.338985	1.007882	0.050521
H	4.340619	1.458866	1.471002

40B

Charge: 0		Multiplicity: 1	
C	-1.396989	-0.730456	3.003282
C	-2.345291	-1.741461	2.968472
C	-0.407769	-0.666862	2.009398
H	-3.109145	-1.804542	3.742954
C	-2.316327	-2.686673	1.935959
H	0.390531	0.071201	2.114014
C	-0.365585	-1.578309	0.927516
C	-1.364413	-2.583107	0.935242
H	-3.057260	-3.485866	1.912550
H	-1.407756	0.000232	3.813449
Ni	-0.870789	0.321592	-0.197891
H	-1.387991	-3.312999	0.120891
C	-2.685437	-0.178676	-0.237661
C	-3.182318	-1.173053	-1.088462
C	-3.566796	0.447125	0.648796
C	-4.522564	-1.547890	-1.037495
H	-2.512282	-1.676325	-1.788334
C	-4.912115	0.070926	0.700866
H	-3.205564	1.226189	1.323842
C	-5.393433	-0.925977	-0.142040
H	-4.888818	-2.333516	-1.698341
H	-5.582740	0.564169	1.404518
H	-6.441851	-1.217183	-0.104758
P	-1.485474	1.818775	-1.701532
C	-0.169679	2.364783	-2.846208
H	0.183018	1.506470	-3.427817
H	-0.565240	3.119916	-3.536828
H	0.660470	2.796575	-2.283477
C	-2.802665	1.368845	-2.887976
H	-2.909404	2.164964	-3.635058
H	-2.553071	0.434470	-3.401560
H	-3.757191	1.225012	-2.374054
C	-2.134449	3.367025	-0.984386
H	-1.345815	3.856202	-0.405488
H	-2.477485	4.047599	-1.773499
H	-2.980164	3.133648	-0.327887
O	1.062404	1.076164	-0.081369
S	1.591799	2.380962	0.479955
O	0.981811	3.558236	-0.157762
O	3.067490	2.346790	0.486823
Sn	1.561206	-2.039991	-0.287118
C	2.768978	-1.277414	1.354487
H	3.820755	-1.564232	1.228473
H	2.693267	-0.193261	1.509597
H	2.408516	-1.740558	2.281016
C	0.843494	-1.211996	-2.161296
H	1.250666	-1.804035	-2.989402
H	-0.255723	-1.224326	-2.216415
H	1.162797	-0.171339	-2.298586

C	1.408804	-4.173438	-0.264410
H	0.642592	-4.530049	-0.962817
H	2.366194	-4.608761	-0.568034
H	1.150754	-4.550243	0.731650
F	3.412194	-2.005081	-1.341471
K	3.990275	0.351752	-0.969546
N	1.138338	2.356345	2.127452
C	1.969936	3.228605	2.954082
H	1.836098	4.297697	2.716731
H	1.682871	3.064477	3.998229
H	3.019885	2.960510	2.829052
C	-0.280232	2.662875	2.283380
H	-0.566197	2.444244	3.318404
H	-0.512472	3.716509	2.056328
H	-0.875004	2.014435	1.622829

40C

Charge: 0		Multiplicity: 1	
C	-0.246735	3.378471	0.566133
C	-0.686615	3.150384	1.874392
C	0.558515	2.446069	-0.065636
H	-1.331134	3.877817	2.366056
C	-0.297854	1.999096	2.540453
H	0.878062	2.643283	-1.090763
C	0.973201	1.253543	0.574959
C	0.530984	1.062015	1.905464
H	-0.620845	1.821867	3.565721
H	-0.551975	4.281864	0.039655
Ni	-0.574590	-0.505716	0.421393
H	0.884739	0.202717	2.472975
Sn	2.525741	0.095711	-0.446503
C	1.672397	-1.267218	-1.875838
H	1.760544	-2.296736	-1.515165
H	0.602374	-1.053570	-2.003165
H	2.157768	-1.180196	-2.855101
C	3.953990	-0.736625	0.906042
H	4.959251	-0.341095	0.724160
H	3.669386	-0.511155	1.938620
H	3.972886	-1.826018	0.808418
C	3.480974	1.635773	-1.622851
H	3.738105	2.510586	-1.014824
H	4.407111	1.262550	-2.075583
H	2.836661	1.978202	-2.441467
C	-1.910779	0.632322	-0.270836
C	-1.901811	1.047422	-1.608093
C	-2.923640	1.109128	0.568527
C	-2.853242	1.949382	-2.082658
H	-1.129142	0.681314	-2.289001
C	-3.878168	2.012362	0.094814
H	-2.965192	0.787771	1.611224
C	-3.845040	2.435675	-1.231395
H	-2.820266	2.274121	-3.122803
H	-4.653175	2.382016	0.766687
H	-4.591921	3.135326	-1.603140
P	-1.887180	-2.159304	-0.108940
C	-2.525523	-2.937494	1.412675
H	-3.136227	-2.218322	1.968518
H	-3.138017	-3.817975	1.182080
H	-1.677370	-3.229774	2.039024
C	-3.394545	-1.900387	-1.107130
H	-3.927945	-2.849232	-1.242159
H	-4.056460	-1.175720	-0.623405
H	-3.130412	-1.495731	-2.089222
C	-1.071597	-3.528756	-0.997722
H	-0.189484	-3.846759	-0.435316
H	-1.763573	-4.371291	-1.119710
H	-0.746854	-3.192251	-1.987637
Cl	0.874424	-2.065676	1.335163

40D

Charge: 0	Multiplicity: 1	
C 0.496558	3.356115	-0.146483
C 0.929248	3.283605	-1.475209
C -0.385732	2.408884	0.347025
H 1.627848	4.025691	-1.859545
C 0.472911	2.264714	-2.297472
H -0.711504	2.483830	1.386748
C -0.870158	1.347701	-0.452661
C -0.412088	1.301243	-1.793210
H 0.799004	2.210809	-3.335843
H 0.863198	4.152404	0.500155
Ni 0.468323	-0.458179	-0.470675
H -0.801092	0.530470	-2.458859
Sn -2.479771	0.062239	0.317720
C -1.731335	-1.360733	1.754032
H -1.553869	-2.330914	1.277705
H -0.774912	-1.000866	2.158977
H -2.415300	-1.496600	2.600071
C -3.924637	-0.571554	-1.121347
H -4.938524	-0.247739	-0.863583
H -3.668606	-0.162004	-2.104481
H -3.906868	-1.661510	-1.213464
C -3.476905	1.519017	1.595973
H -3.717385	2.442966	1.056342
H -4.417172	1.114882	1.991549
H -2.858422	1.794801	2.459580
C 2.011275	0.369887	0.230079
C 2.107228	0.622241	1.605396
C 3.035654	0.840341	-0.600302
C 3.166556	1.363561	2.128716
H 1.327204	0.261205	2.280625
C 4.098438	1.580973	-0.079759
H 2.999041	0.644108	-1.673536
C 4.164800	1.848636	1.285462
H 3.209945	1.565170	3.199103
H 4.878667	1.949353	-0.746219
H 4.993966	2.425365	1.692264
P 1.484334	-2.338006	-0.185535
C 0.518108	-3.737188	-0.839656
H 0.335726	-3.589866	-1.907542
H 1.040807	-4.688209	-0.679451
H -0.460392	-3.762526	-0.353039
C 3.124020	-2.542292	-0.963046
H 3.510176	-3.555307	-0.797422
H 3.056086	-2.363681	-2.040956
H 3.824752	-1.814549	-0.542444
C 1.803566	-2.805800	1.549779
H 0.861405	-2.827481	2.107658
H 2.274709	-3.794507	1.608353
H 2.461987	-2.065129	2.015019
F -1.110558	-1.332124	-1.116196

TSA

Charge: 0	Multiplicity: 1	
C -0.273311	-0.825490	3.446114
C -1.625063	-0.847629	3.763946
C 0.144877	-1.109403	2.141401
H -1.951818	-0.641851	4.782681
C -2.564259	-1.146383	2.773645
H 1.209790	-1.150620	1.931399
C -0.779086	-1.369893	1.108216
C -2.146329	-1.388414	1.474266
H -3.626224	-1.169517	3.015509
H 0.469277	-0.610332	4.212999
Ni -0.204068	0.894826	0.375340
H -2.903226	-1.577602	0.711489
C -2.027740	1.130333	-0.037406
C -2.593458	0.737159	-1.254460
C -2.867925	1.648023	0.956991

C -3.974217	0.819126	-1.457191
H -1.963437	0.339248	-2.051899
C -4.243833	1.730449	0.755004
H -2.448990	1.963461	1.914874
C -4.802429	1.314730	-0.454062
H -4.399659	0.490561	-2.405444
H -4.884358	2.120695	1.546025
H -5.877255	1.382216	-0.613323
P 0.047744	2.837121	-0.577278
C 0.230209	2.726754	-2.387367
H -0.652144	2.250076	-2.827242
H 0.345288	3.728949	-2.818751
H 1.115866	2.126788	-2.620443
C -1.256078	4.100928	-0.372355
H -0.928528	5.047393	-0.819289
H -2.182669	3.774995	-0.853614
H -1.469961	4.265815	0.688327
C 1.557558	3.719190	-0.058167
H 2.429426	3.140421	-0.375078
H 1.586960	4.714725	-0.518066
H 1.583791	3.821596	1.030665
O 1.726594	0.921055	0.907590
S 2.662251	0.195907	-0.042052
O 2.290727	-1.218931	-0.217227
Sn -0.285692	-2.287099	-0.829020
C 0.290583	-0.981723	-2.432536
H 1.271989	-1.276990	-2.816661
H -0.442106	-1.002411	-3.248547
H 0.394937	0.050889	-2.080544
C -2.213820	-3.074223	-1.405067
H -2.130265	-3.644233	-2.338311
H -2.631354	-3.744634	-0.644858
H -2.942274	-2.271906	-1.578200
C 1.053718	-3.920601	-0.499149
H 0.540423	-4.886646	-0.550981
H 1.854486	-3.905342	-1.245330
H 1.524254	-3.823749	0.484087
O 2.873638	0.963335	-1.284908
N 4.096641	0.160603	0.874279
C 5.126962	-0.644975	0.224074
H 5.958475	-0.756540	0.928330
H 4.725265	-1.634510	-0.004184
H 5.508910	-0.183570	-0.702535
C 4.576428	1.499719	1.195580
H 5.423920	1.398095	1.882178
H 4.911255	2.059487	0.304795
H 3.785428	2.059591	1.700962

TSB

Charge: 0	Multiplicity: 1	
C -1.291968	-0.866939	3.149956
C -2.263640	-1.859004	3.097070
C -0.406885	-0.704856	2.078082
H -2.948569	-1.999274	3.932987
C -2.355606	-2.686184	1.972900
H 0.399530	0.025213	2.169794
C -0.500616	-1.479071	0.899301
C -1.508720	-2.473978	0.896539
H -3.109909	-3.471919	1.936052
H -1.208515	-0.231924	4.033086
Ni -0.827991	0.344408	-0.248373
H -1.635506	-3.096827	0.006978
C -2.659238	-0.095332	-0.279471
C -3.221917	-1.002126	-1.185050
C -3.485464	0.486178	0.687325
C -4.574166	-1.329522	-1.117179
H -2.595565	-1.475679	-1.944136
C -4.841845	0.157650	0.755926
H -3.070811	1.189603	1.412945
C -5.390428	-0.749643	-0.145831

H	-4.992259	-2.045865	-1.824528
H	-5.468972	0.615519	1.521066
H	-6.447565	-1.004773	-0.093737
P	-1.402063	1.972266	-1.638116
C	-0.094111	2.513033	-2.796010
H	0.192083	1.671907	-3.436740
H	-0.465038	3.327364	-3.430805
H	0.776424	2.864860	-2.238373
C	-2.773980	1.653806	-2.806128
H	-2.867850	2.497122	-3.501358
H	-2.584018	0.741620	-3.381503
H	-3.718032	1.520631	-2.270187
C	-1.957652	3.515276	-0.832361
H	-1.129920	3.946452	-0.262140
H	-2.299510	4.243597	-1.578208
H	-2.789068	2.888979	-0.155001
O	1.140640	1.025645	-0.074662
S	1.721688	2.289817	0.527182
O	1.183710	3.510399	-0.092952
O	3.194175	2.182368	0.560853
Sn	1.420098	-2.064524	-0.371632
C	2.649144	-1.451726	1.311891
H	3.680744	-1.800528	1.175731
H	2.639246	-0.372402	1.509136
H	2.251177	-1.931377	2.213875
C	0.765298	-1.162482	-2.230895
H	1.184464	-1.740229	-3.063296
H	-0.331328	-1.152909	-2.315595
H	1.108724	-0.124788	-2.325566
C	1.086016	-4.176005	-0.387326
H	0.269185	-4.449983	-1.064956
H	1.993254	-4.682905	-0.731950
H	0.830491	-4.550539	0.610003
F	3.269629	-2.126774	-1.394860
K	4.000011	0.184937	-0.955276
N	1.236826	2.250342	2.165045
C	2.083097	3.076637	3.023142
H	1.990069	4.154120	2.804912
H	1.771601	2.902643	4.058711
H	3.125378	2.774820	2.911135
C	-0.172837	2.604378	2.301832
H	-0.491890	2.358049	3.320964
H	-0.359375	3.674013	2.109820
H	-0.775620	2.004047	1.604211

TSC

Charge: 0	Multiplicity: 1		
C	-0.658375	-3.479937	1.007812
C	-0.678265	-3.316759	2.395443
C	-0.824026	-2.379826	0.181912
H	-0.532841	-4.177684	3.046844
C	-0.892647	-2.057183	2.942004
H	-0.764488	-2.522733	-0.897045
C	-1.033985	-1.081687	0.702634
C	-1.087427	-0.954728	2.106350
H	-0.921614	-1.927067	4.022882
H	-0.493787	-4.465674	0.575308
Ni	0.512541	0.450365	0.402919
H	-1.283187	0.020671	2.547552
Sn	-2.127843	0.306611	-0.707066
C	-1.101184	1.763631	-1.925302
H	-1.090478	2.728880	-1.409763
H	-0.061776	1.472490	-2.120631
H	-1.610749	1.866634	-2.891823
C	-3.767305	1.132990	0.382640
H	-4.729298	0.834801	-0.048330
H	-3.732605	0.798685	1.424125
H	-3.697802	2.224671	0.386592
C	-2.814942	-1.158826	-2.133504
H	-3.293573	-2.015471	-1.646688

H	-3.542607	-0.709849	-2.820171
H	-1.986059	-1.539419	-2.742734
C	1.602781	-0.860184	-0.413555
C	1.601328	-1.079534	-1.795248
C	2.397755	-1.681901	0.394068
C	2.355877	-2.112929	-2.354314
H	0.995452	-0.450235	-2.452280
C	3.153485	-2.712951	-0.163867
H	2.408674	-1.537221	1.476758
C	3.134982	-2.932140	-1.540622
H	2.334248	-2.276268	-3.431929
H	3.757904	-3.350754	0.481403
H	3.726452	-3.735507	-1.976601
P	2.206119	1.821969	0.222976
C	2.850699	2.213942	1.884858
H	3.222189	1.301832	2.363761
H	3.667071	2.945100	1.835030
H	2.033228	2.614452	2.492193
C	3.704712	1.346356	-0.706135
H	4.455703	2.144077	-0.656175
H	4.128730	0.421121	-0.304055
H	3.451089	1.159355	-1.754656
C	1.816572	3.457114	-0.488805
H	0.972843	3.892791	0.053431
H	2.686648	4.122124	-0.424179
H	1.532033	3.349915	-1.540471
Cl	-0.661316	2.171018	1.428258

TSD

Charge: 0	Multiplicity: 1		
C	-1.896994	3.433495	-0.086635
C	-2.610890	3.423663	-1.285658
C	-1.054824	2.373542	0.232724
H	-3.267001	4.255541	-1.538828
C	-2.479838	2.345071	-2.155540
H	-0.486234	2.409711	1.162481
C	-0.916998	1.260609	-0.617430
C	-1.649672	1.274593	-1.821233
H	-3.033298	2.330414	-3.094406
H	-1.990567	4.278375	0.595346
Ni	0.466662	-0.117948	-0.576661
H	-1.584798	0.421199	-2.495326
Sn	-1.742749	-0.967833	0.687036
C	-1.163021	-2.968073	1.226991
H	-1.434725	-3.675266	0.436793
H	-0.075985	-3.023156	1.367225
H	-1.629342	-3.288266	2.166189
C	-3.715061	-0.774299	-0.089725
H	-4.438970	-1.362452	0.485724
H	-4.024494	0.276221	-0.063158
H	-3.739708	-1.112621	-1.129965
C	-1.578328	0.172975	2.524658
H	-2.266244	1.024814	2.495149
H	-1.835746	-0.467120	3.377951
H	-0.566703	0.562474	2.677556
F	-0.874863	-1.413015	-1.234435
C	1.680729	1.068010	0.227609
C	2.032277	0.946426	1.578003
C	2.270284	2.094487	-0.521641
C	2.943380	1.827423	2.165212
H	1.597596	0.149748	2.186144
C	3.188635	2.967426	0.061333
H	1.996315	2.229704	-1.569034
C	3.526526	2.839876	1.407803
H	3.197612	1.717871	3.219610
H	3.632700	3.762022	-0.538406
H	4.237079	3.527392	1.863582
P	2.127051	-1.631762	-0.779690
C	3.531164	-1.042466	-1.792492
H	3.960013	-0.149467	-1.324692

H	4.310324	-1.807979	-1.890324
H	3.184535	-0.762879	-2.792857
C	1.631449	-3.188745	-1.595984
H	2.483855	-3.864573	-1.735486
H	0.865921	-3.688466	-0.994385
H	1.180470	-2.966389	-2.567597
C	2.978949	-2.208083	0.732705
H	3.427393	-1.352020	1.247417
H	2.266521	-2.679891	1.417987
H	3.765807	-2.932768	0.491106

41A

Charge: 0		Multiplicity: 1	
C	0.784596	-2.821269	2.740293
C	-0.435228	-3.192007	3.303254
C	0.821817	-1.980302	1.633642
H	-0.460709	-3.850832	4.170352
C	-1.621764	-2.733229	2.737301
H	1.785263	-1.725644	1.202941
C	-0.363046	-1.464616	1.059282
C	-1.581173	-1.894542	1.627594
H	-2.581732	-3.034153	3.154875
H	1.716509	-3.194256	3.162682
Ni	-0.242787	0.580687	0.496739
H	-2.521000	-1.565757	1.188803
C	-2.104572	0.864461	0.217768
C	-2.672087	1.157821	-1.029695
C	-2.945752	0.898545	1.341257
C	-4.033990	1.440067	-1.157435
H	-2.052505	1.153316	-1.926901
C	-4.304753	1.183403	1.217181
H	-2.536331	0.690443	2.330924
C	-4.856111	1.455087	-0.034309
H	-4.450038	1.648544	-2.142891
H	-4.936213	1.194725	2.105518
H	-5.917146	1.678383	-0.131219
P	-0.119522	2.816310	0.304891
C	-0.003308	3.435261	-1.407580
H	-0.883018	3.126987	-1.981823
H	0.053560	4.530868	-1.411958
H	0.897233	3.023424	-1.874060
C	-1.493926	3.805354	0.995732
H	-1.260443	4.874446	0.923211
H	-2.421463	3.601674	0.452128
H	-1.659076	3.550201	2.047425
C	1.343311	3.556577	1.106743
H	2.240629	3.229829	0.574931
H	1.275886	4.651067	1.078442
H	1.415905	3.224903	2.146843
O	1.728564	0.631093	0.914019
S	2.620872	0.401913	-0.289767
O	2.298772	-0.857980	-0.982743
Sn	-0.482607	-1.644506	-1.264277
C	0.009083	-0.154850	-2.736050
H	0.909782	-0.480897	-3.264901
H	-0.813594	-0.019039	-3.448133
H	0.245886	0.809984	-2.274241
C	-2.549115	-2.217949	-1.479358
H	-2.814199	-2.269929	-2.542835
H	-2.710901	-3.211036	-1.043788
H	-3.240624	-1.515802	-1.002759
C	0.651409	-3.443266	-1.480282
H	0.287955	-4.197052	-0.772373
H	0.552594	-3.850403	-2.493316
H	1.708752	-3.252008	-1.281847
O	2.705045	1.599696	-1.147732
N	4.121008	0.115436	0.465122
C	5.142029	-0.264345	-0.507997
H	6.029902	-0.587085	0.046453
H	4.779765	-1.101851	-1.108234

H	5.425209	0.566589	-1.176134
C	4.548271	1.242676	1.286469
H	5.451160	0.940991	1.828499
H	4.781552	2.142154	0.690123
H	3.768454	1.480230	2.014237

41B

Charge: 0		Multiplicity: 1	
C	0.829175	-1.478680	3.464010
C	1.400862	-2.703473	3.117624
C	0.097621	-0.745302	2.530544
H	1.976451	-3.272797	3.845970
C	1.207289	-3.193434	1.829818
H	-0.287905	0.228809	2.830722
C	-0.122664	-1.208233	1.220099
C	0.443326	-2.462980	0.909811
H	1.628733	-4.157099	1.539540
H	0.966930	-1.083956	4.471617
Ni	-1.128623	-0.141508	-0.031618
H	0.230810	-2.927255	-0.057984
C	-2.410372	-1.511661	0.079299
C	-2.382196	-2.665525	-0.715837
C	-3.515052	-1.337981	0.927608
C	-3.423151	-3.593137	-0.690069
H	-1.541247	-2.842198	-1.391901
C	-4.559679	-2.262522	0.956632
H	-3.567131	-0.464809	1.582524
C	-4.521362	-3.393916	0.144033
H	-3.376830	-4.475640	-1.329013
H	-5.406416	-2.099338	1.624082
H	-5.335238	-4.116917	0.166225
P	-2.428847	0.868124	-1.630029
C	-1.627348	1.941452	-2.885610
H	-0.878413	1.361962	-3.438714
H	-2.362494	2.326768	-3.603486
H	-1.141792	2.785101	-2.387308
C	-3.336431	-0.294668	-2.719257
H	-3.880633	0.248607	-3.501924
H	-2.638770	-0.994677	-3.192962
H	-4.045728	-0.886591	-2.132269
C	-3.800643	1.918773	-1.022542
H	-3.386094	2.795909	-0.516776
H	-4.450834	2.247896	-1.842902
H	-4.401814	1.344727	-0.307511
O	0.245264	1.495589	-0.007323
S	-0.026661	2.888005	0.523980
O	-1.108061	3.571508	-0.203685
O	1.251854	3.631328	0.605160
Sn	2.615916	-1.125378	-0.643227
C	2.979412	-0.010035	1.131748
H	3.989457	0.416313	1.071623
H	2.235045	0.776052	1.294700
H	2.935406	-0.669412	2.003934
C	1.040857	-0.897958	-2.065540
H	1.458484	-1.084532	-3.063412
H	0.205861	-1.583872	-1.886290
H	0.632487	0.118835	-2.034829
C	3.607530	-3.002573	-0.753429
H	2.913729	-3.798497	-1.043186
H	4.409486	-2.956624	-1.497885
H	4.045303	-3.271841	0.212836
F	3.789398	0.086704	-1.705818
K	2.771282	2.358798	-1.108682
N	-0.510624	2.660238	2.144265
C	-0.355120	3.873385	2.944264
H	-1.040875	4.680333	2.634012
H	-0.575312	3.611081	3.984753
H	0.674006	4.229249	2.877813
C	-1.876344	2.147391	2.217491
H	-2.066697	1.821527	3.246490

H	-2.626896	2.902361	1.929701
H	-1.977466	1.271584	1.555324

41C

Charge: 0	Multiplicity: 1
C	-2.176837
C	-2.726113
C	-1.470609
H	-3.274326
C	-2.581441
H	-1.038405
C	-1.286415
C	-1.885526
H	-3.016497
H	-2.294213
Ni	0.521118
H	-1.795788
Sn	-1.607459
C	-0.199355
H	0.756353
H	-0.604377
H	-0.012852
C	-3.305338
H	-4.067279
H	-2.999030
H	-3.751159
C	-2.174433
H	-3.003122
H	-2.487689
H	-1.335641
Cl	-0.160164
C	1.270785
C	1.712317
C	1.388007
C	2.246814
H	1.614274
C	1.913066
H	1.065701
C	2.347253
H	2.578434
H	1.985639
H	2.760968
P	2.583040
C	3.148850
H	3.175090
H	4.149607
H	2.436858
C	2.786076
H	3.805910
H	2.595734
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C	3.952299
H	3.760990
H	4.902214
H	4.031214

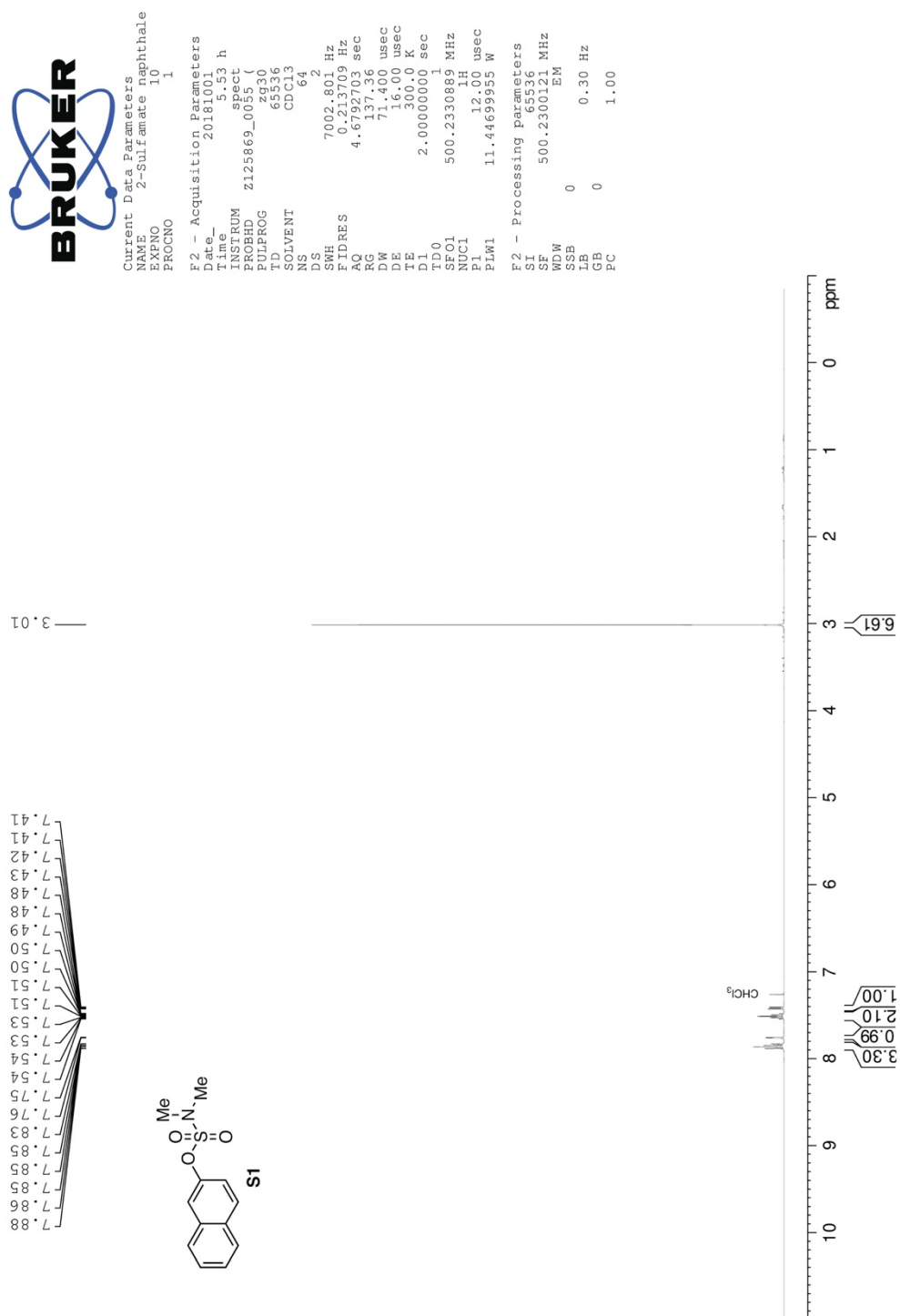
41D

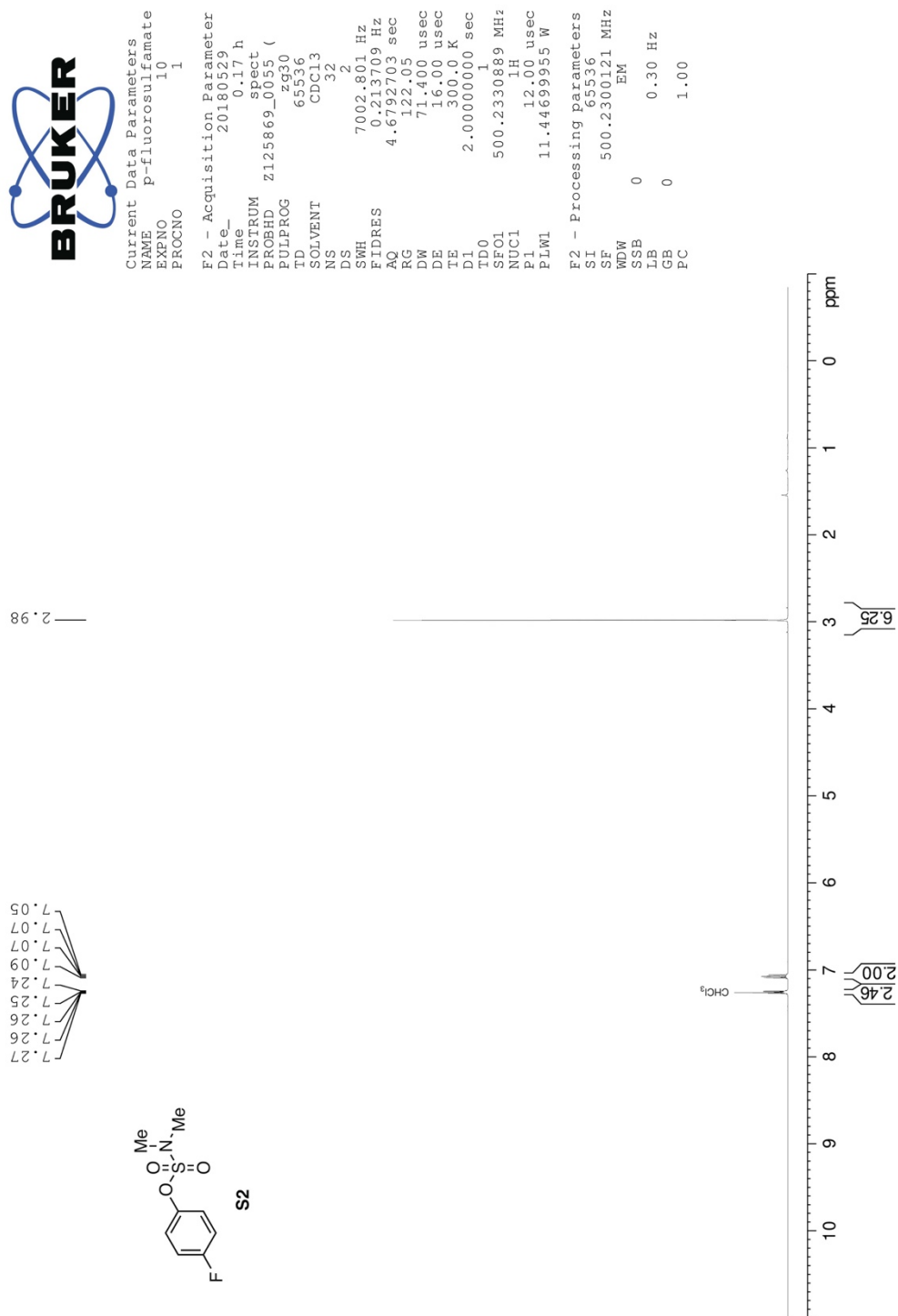
Charge: 0	Multiplicity: 1
C	-0.922136
C	-1.544036
C	-0.235100
H	-2.068461
C	-1.482068
H	0.284967
C	-0.176718
C	-0.814037
H	-1.960799
H	-0.957366
Ni	0.634312

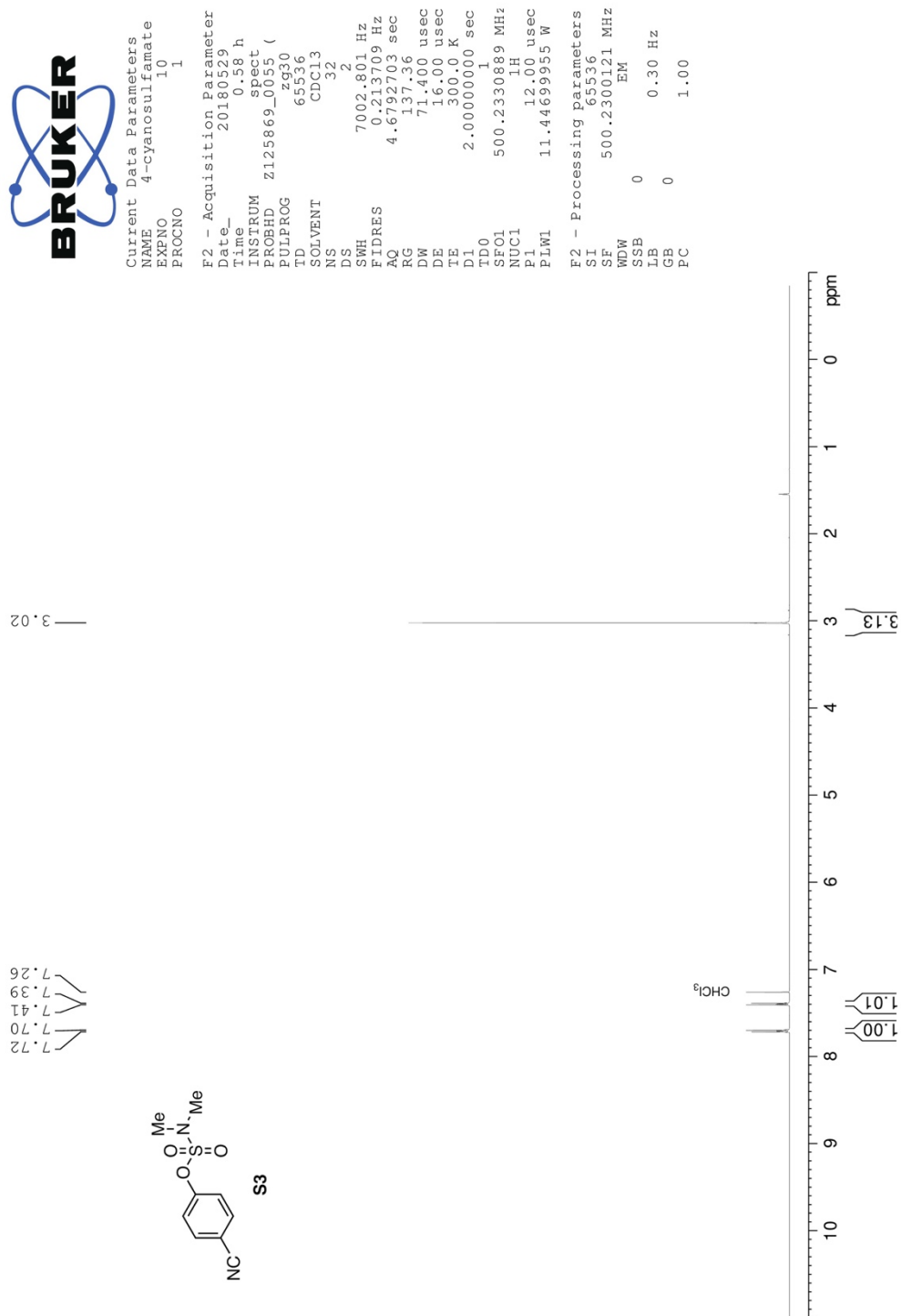
H	-0.800079
Sn	-2.409913
C	-3.494365
H	-4.329733
H	-3.905055
H	-2.845049
C	-3.596766
H	-4.561961
H	-3.081410
H	-3.782586
C	-1.184910
H	-0.825082
H	-1.724495
H	-0.308902
F	-1.182132
C	2.214568
C	2.456909
C	3.238150
C	3.687477
H	1.677338
C	4.470007
H	3.072541
C	4.702710
H	3.853724
H	5.250954
H	5.663549
P	1.654900
C	2.725594
H	3.483753
H	3.231108
H	2.134489
C	0.593487
H	1.179851
H	0.027586
H	-0.129754
C	2.823347
H	3.615766
H	2.310495
H	3.272530

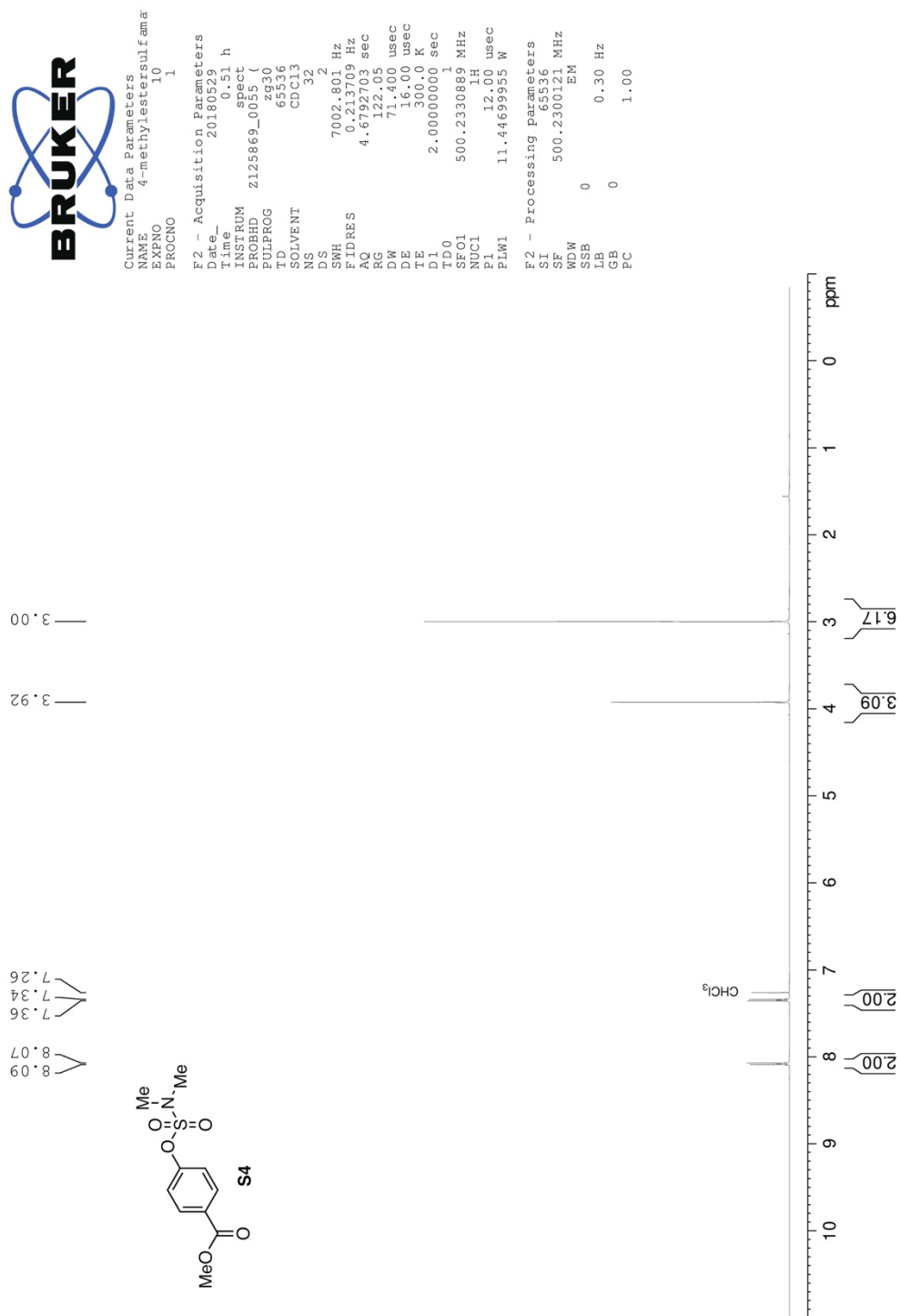
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0.454081
-0.909277
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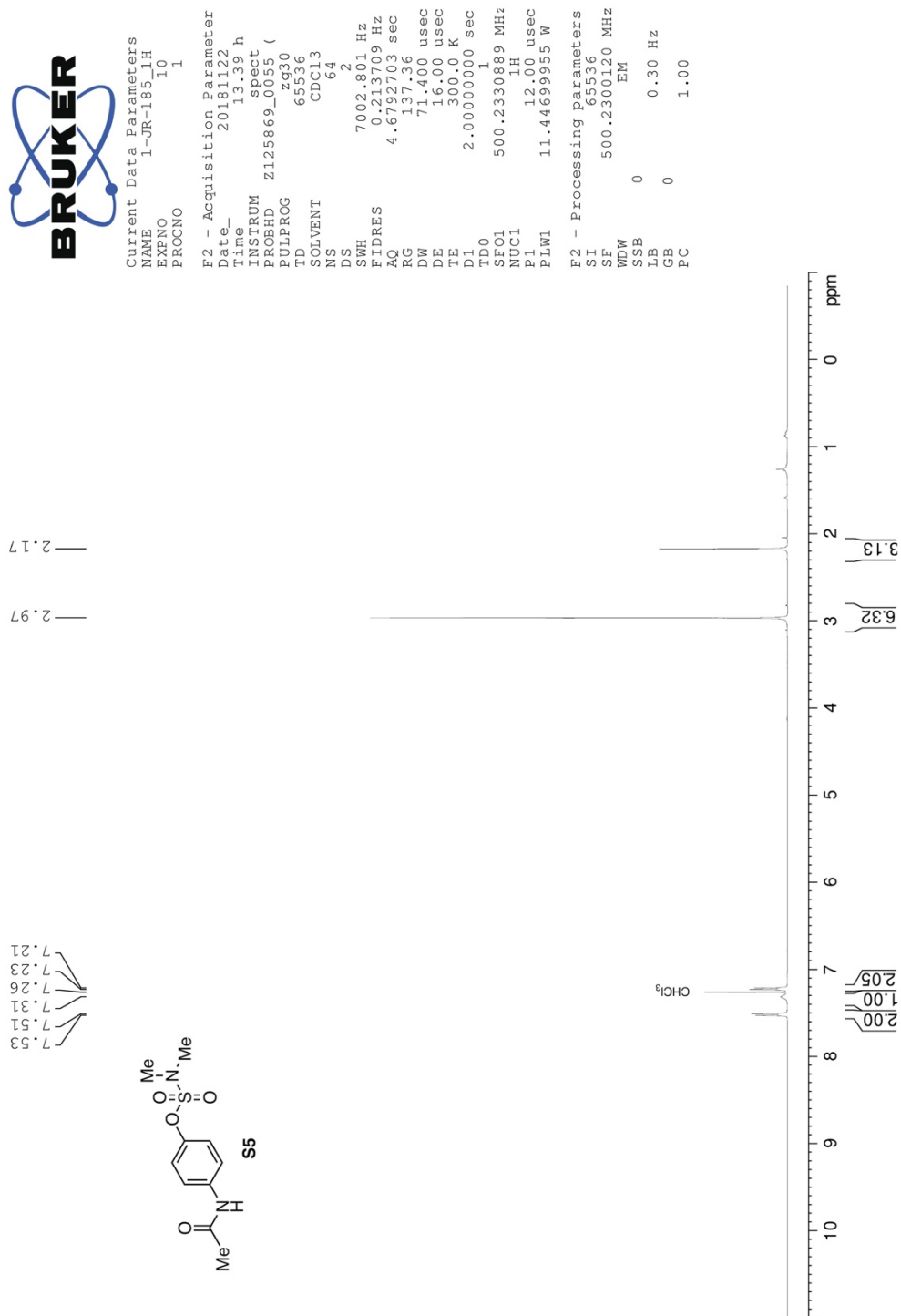
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2.367509
3.087991
2.053142
-1.033149
0.147312
1.523257
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0.679078









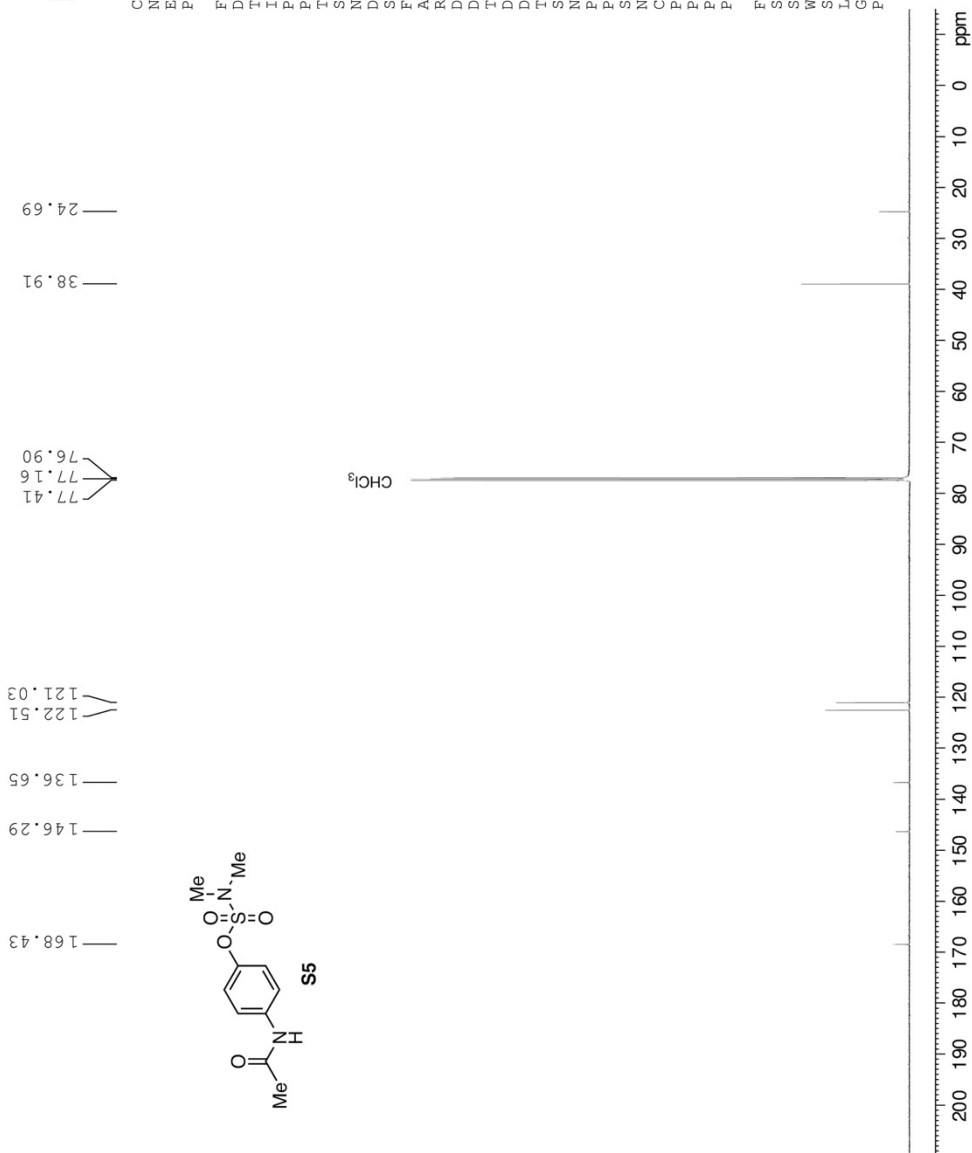


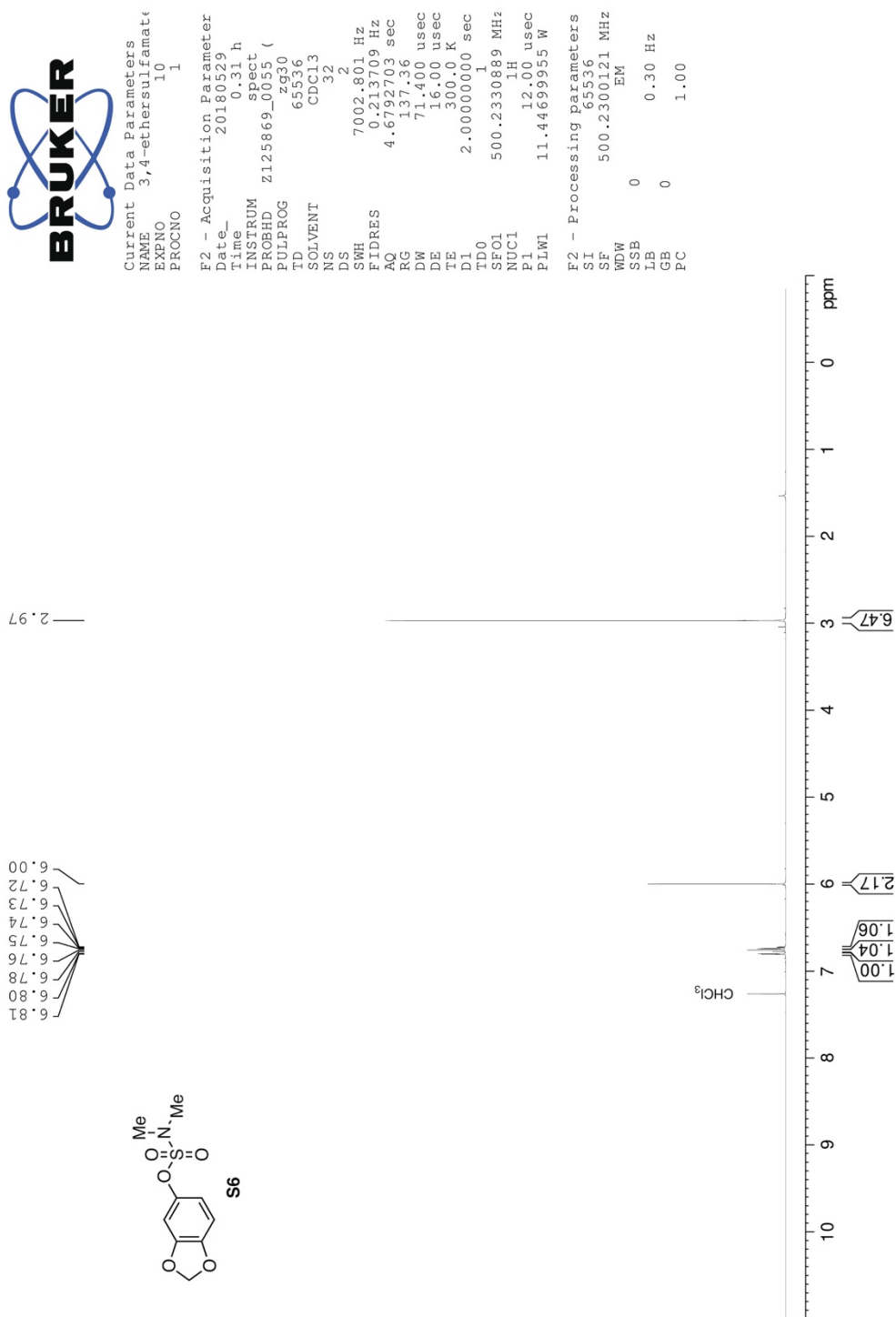


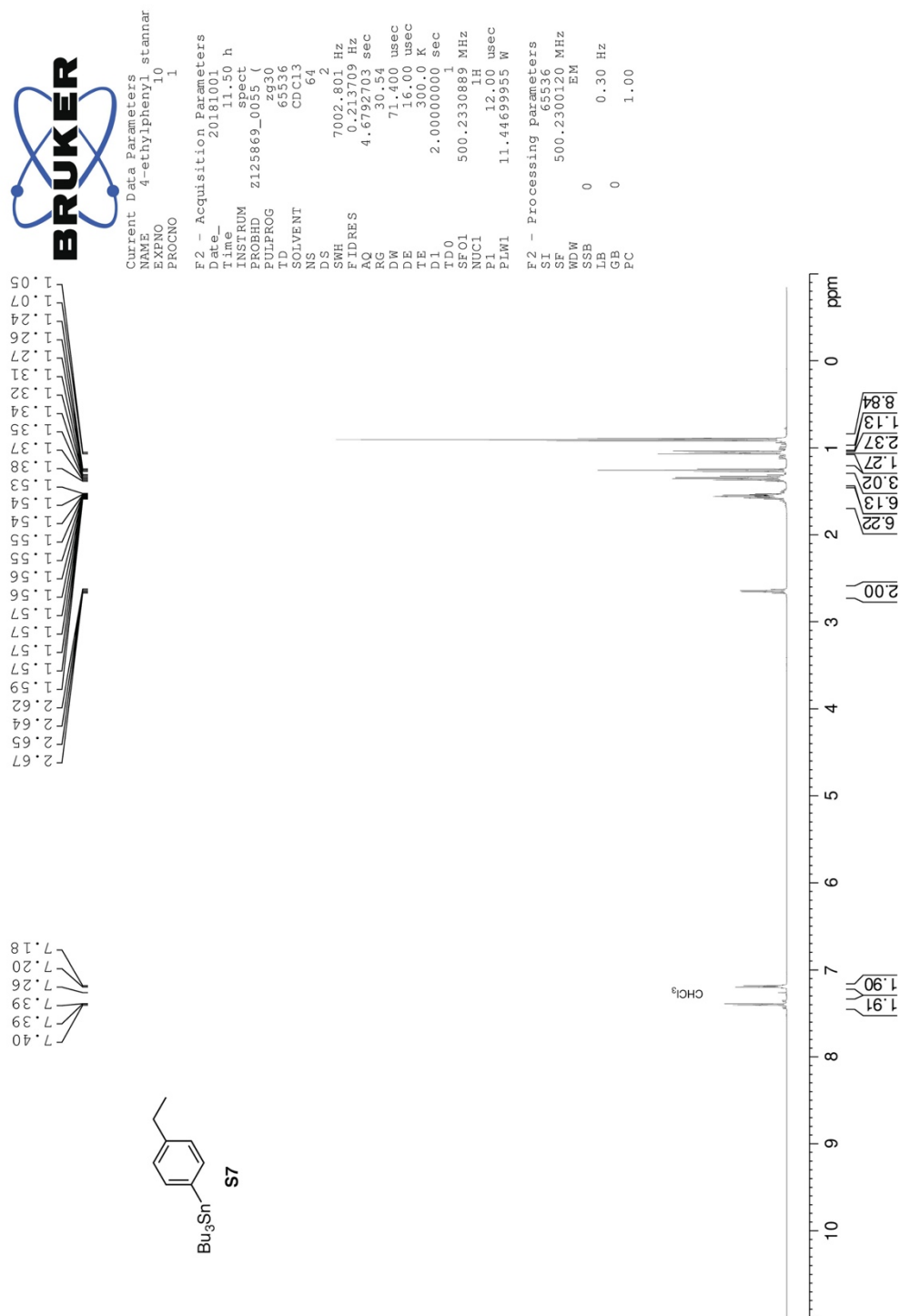
Current Data Parameters
 NAME 1-JR-185_13C
 EXPNO 10
 PROCNO 1

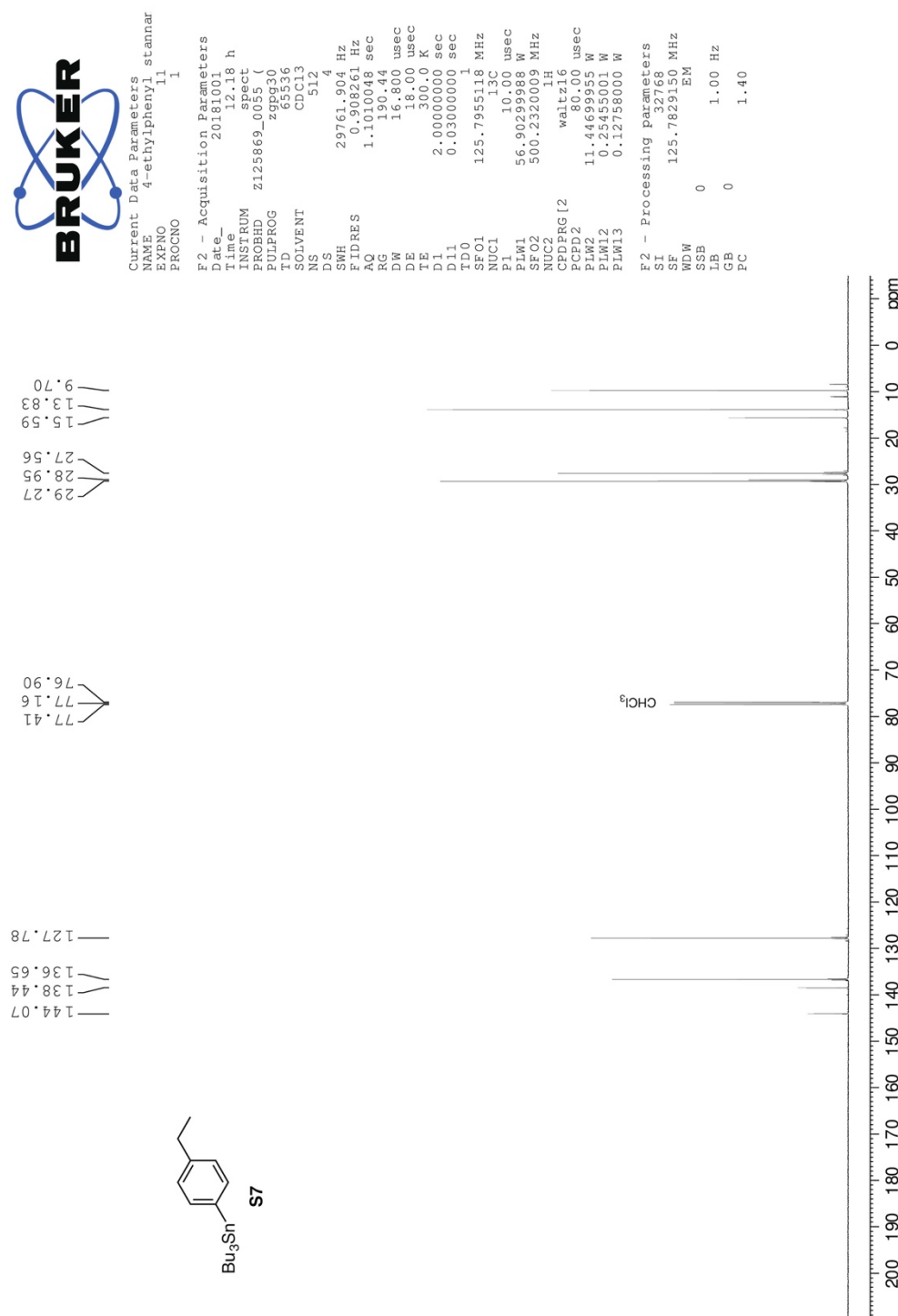
F2 - Acquisition Parameter
 Date_ 20181122
 Time 14.34 h
 INSTRUM spect
 PROBD 2125869_0055 (zpg30)
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.908261 Hz
 AQ 1.1010048 sec
 RG 190.44
 DW 16.800 usec
 DE 18.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1
 SFO1 125.7955118 MHz
 NUC1 13C
 P1 10.00 usec
 PLW1 56.90299988 W
 SFO2 500.2320009 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 11.44639955 W
 PLW12 0.25455001 W
 PLW13 0.12758000 W

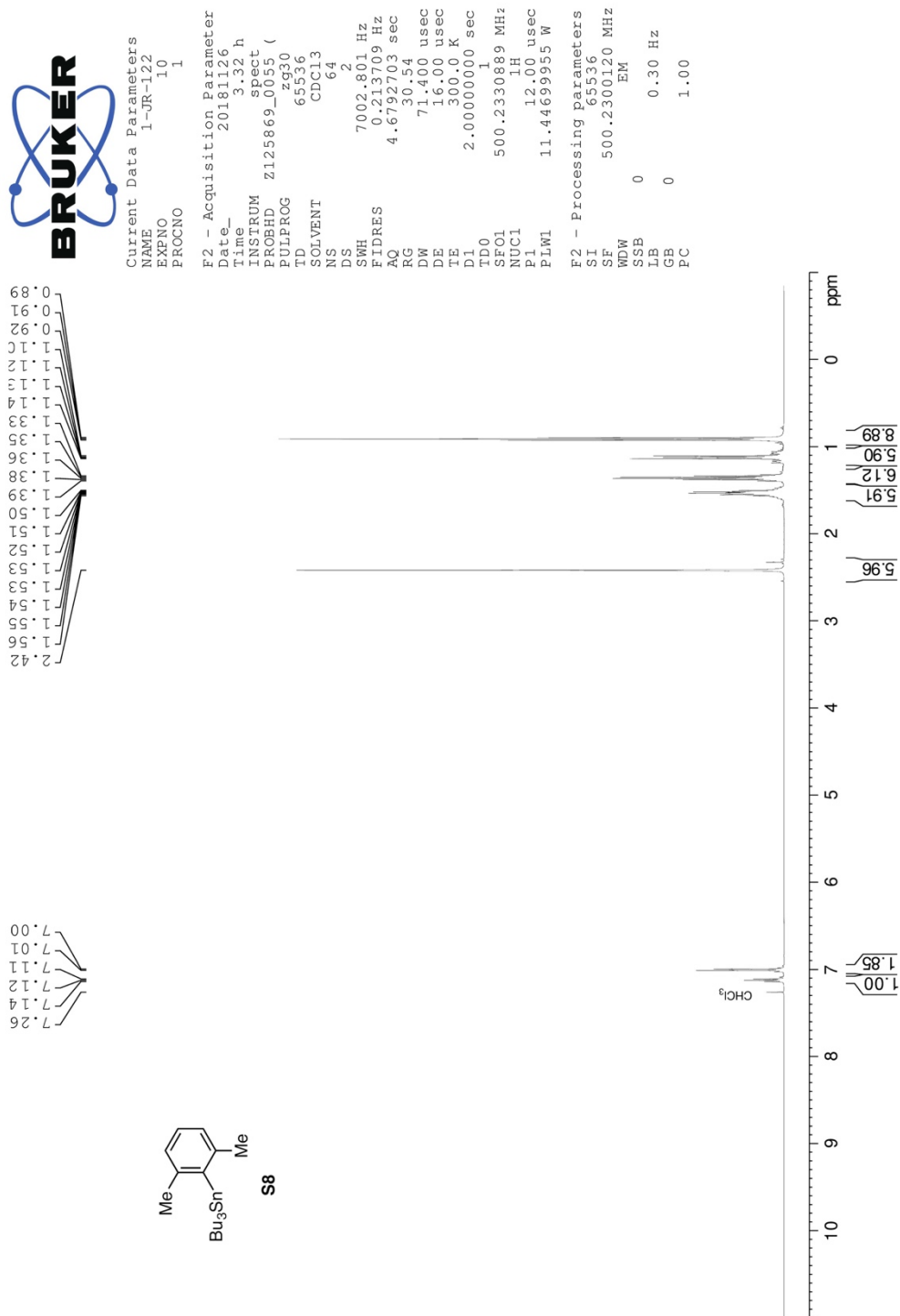
F2 - Processing parameters
 SI 32768
 SF 125.7829160 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

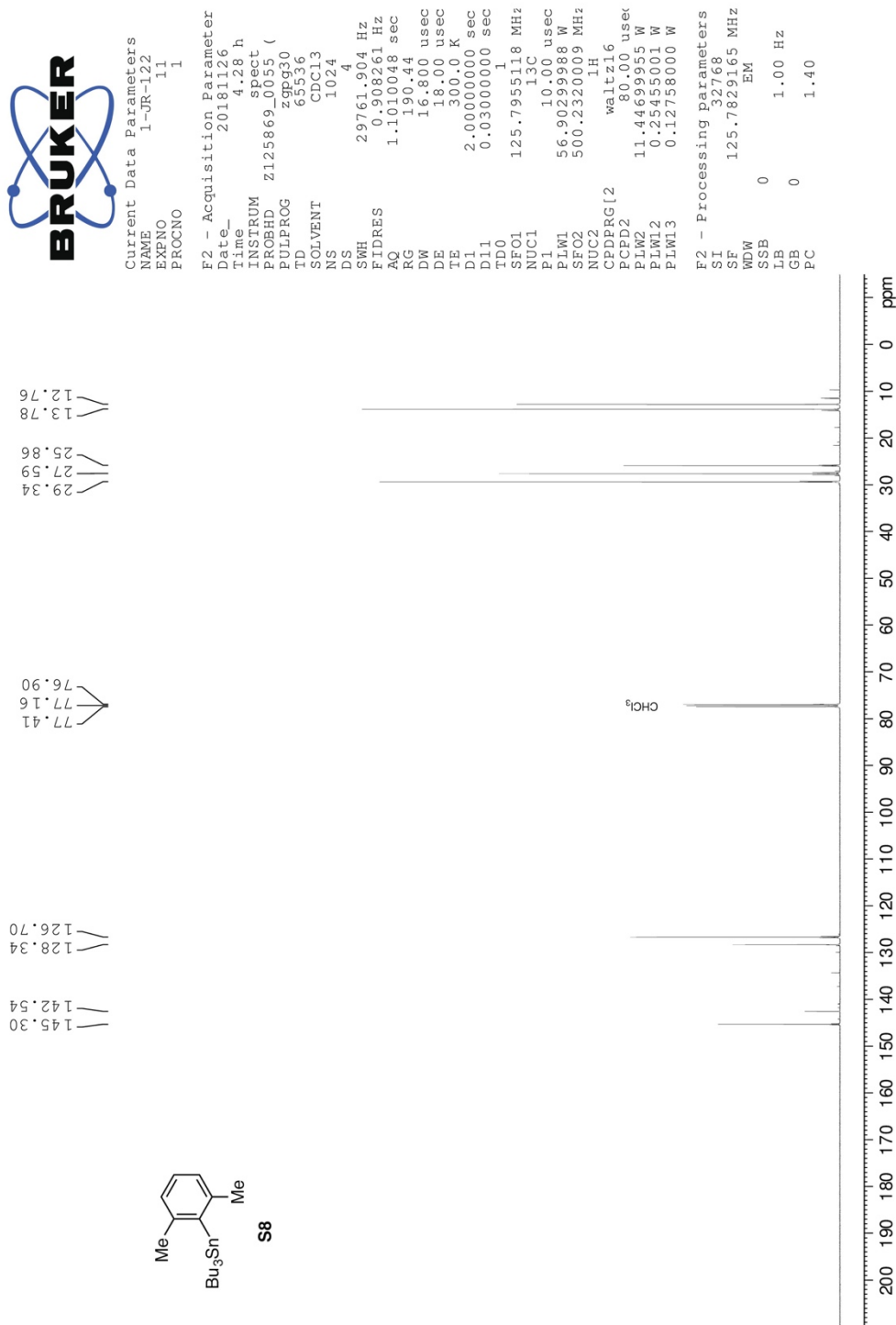


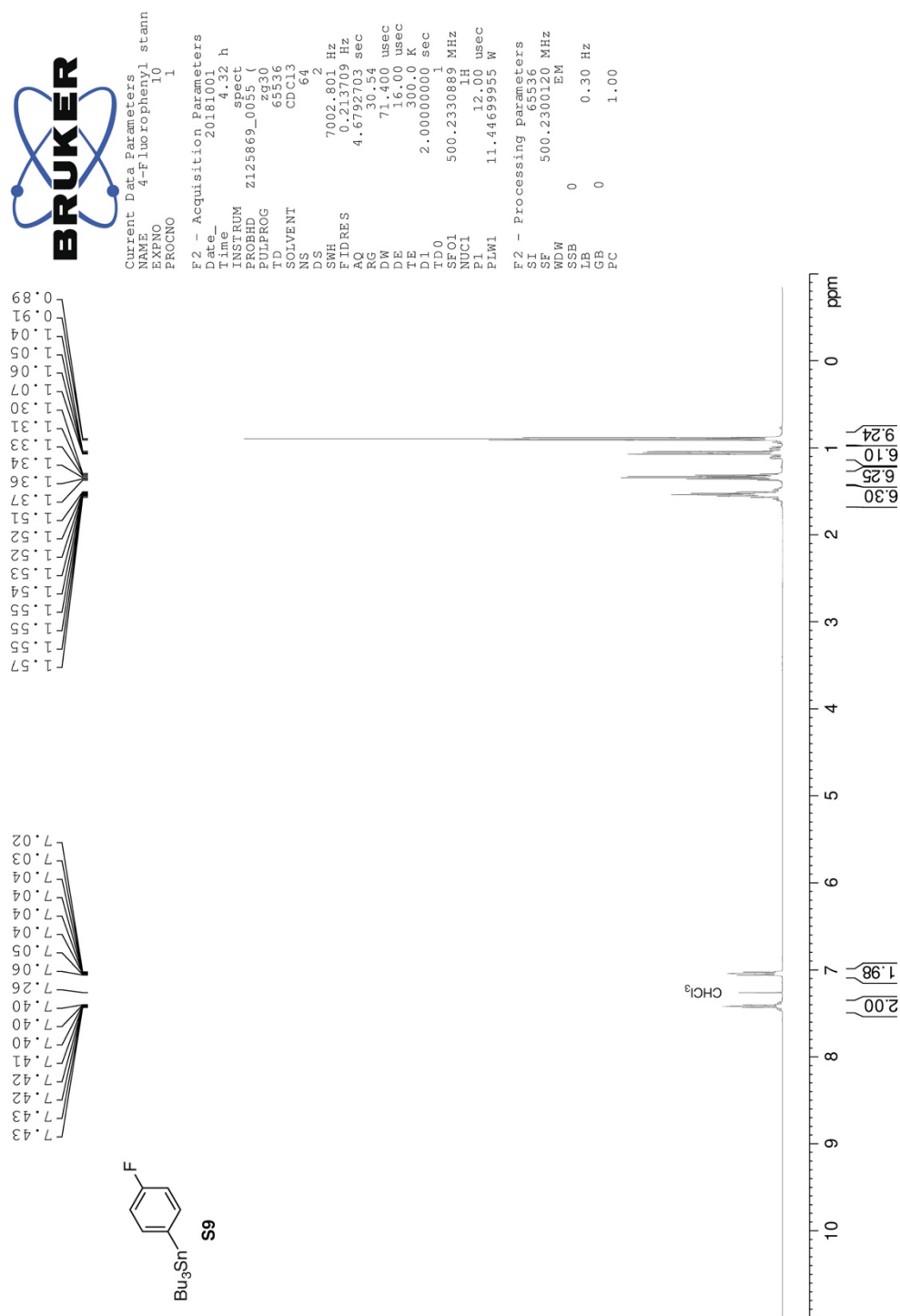






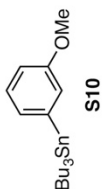


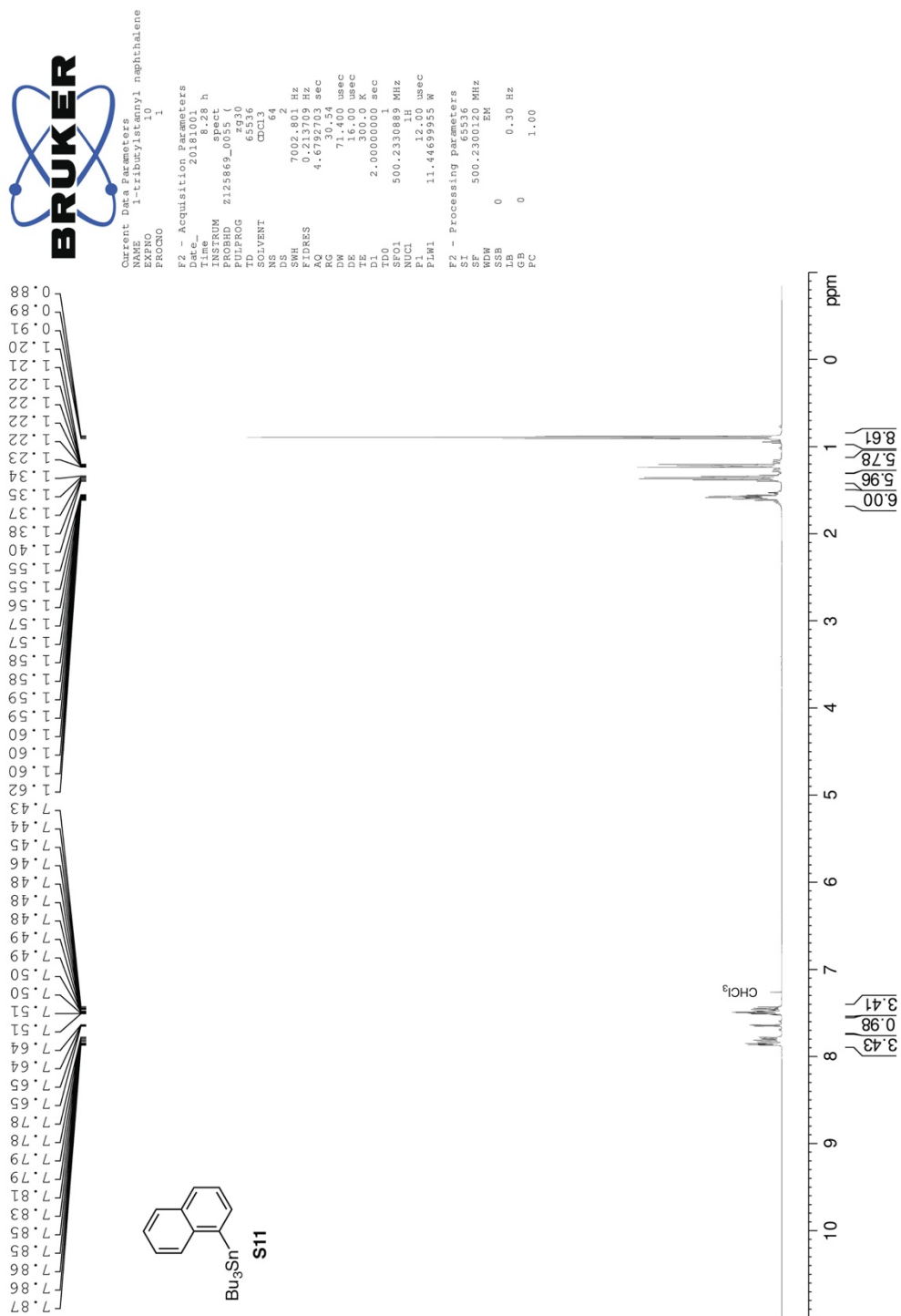


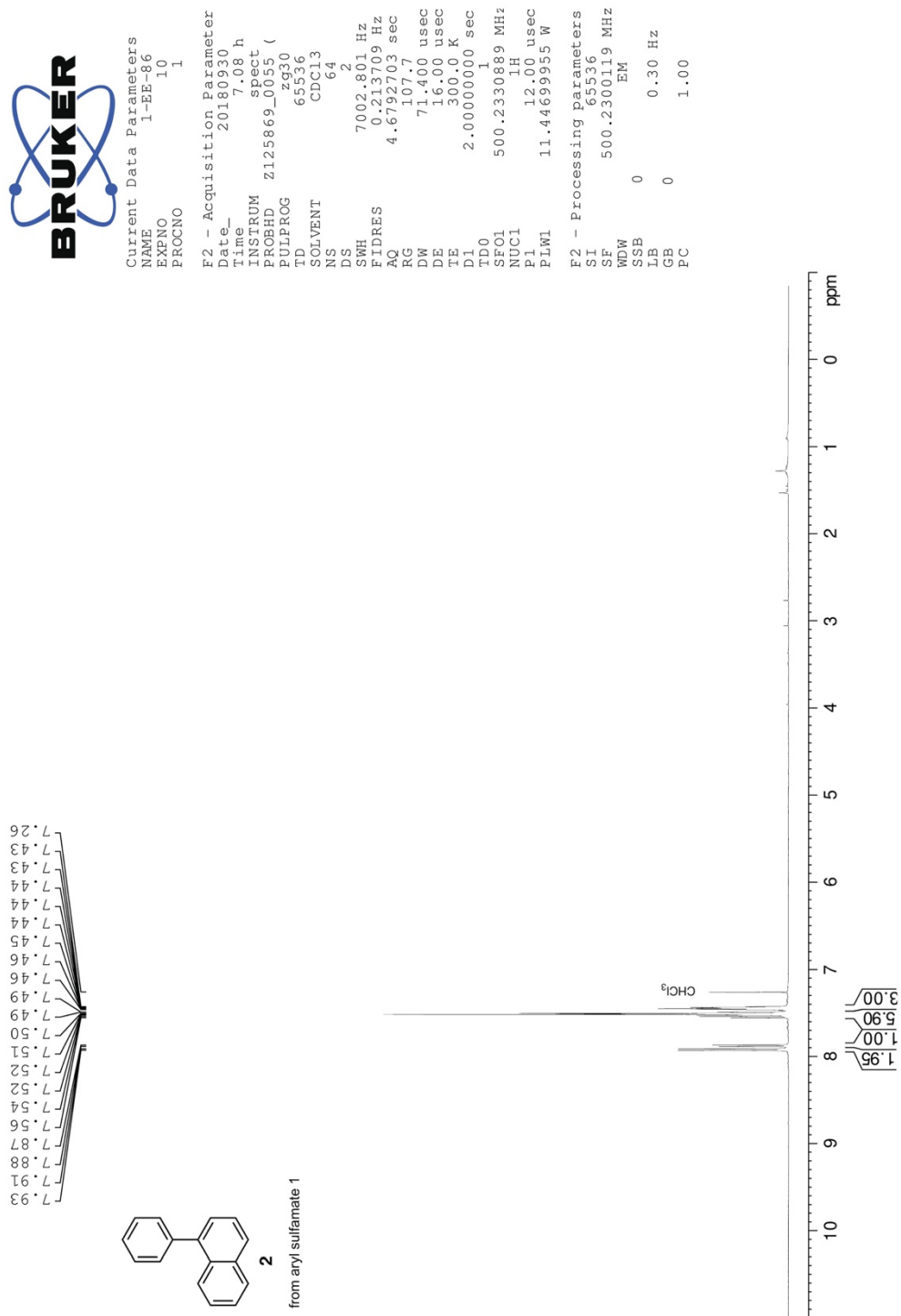


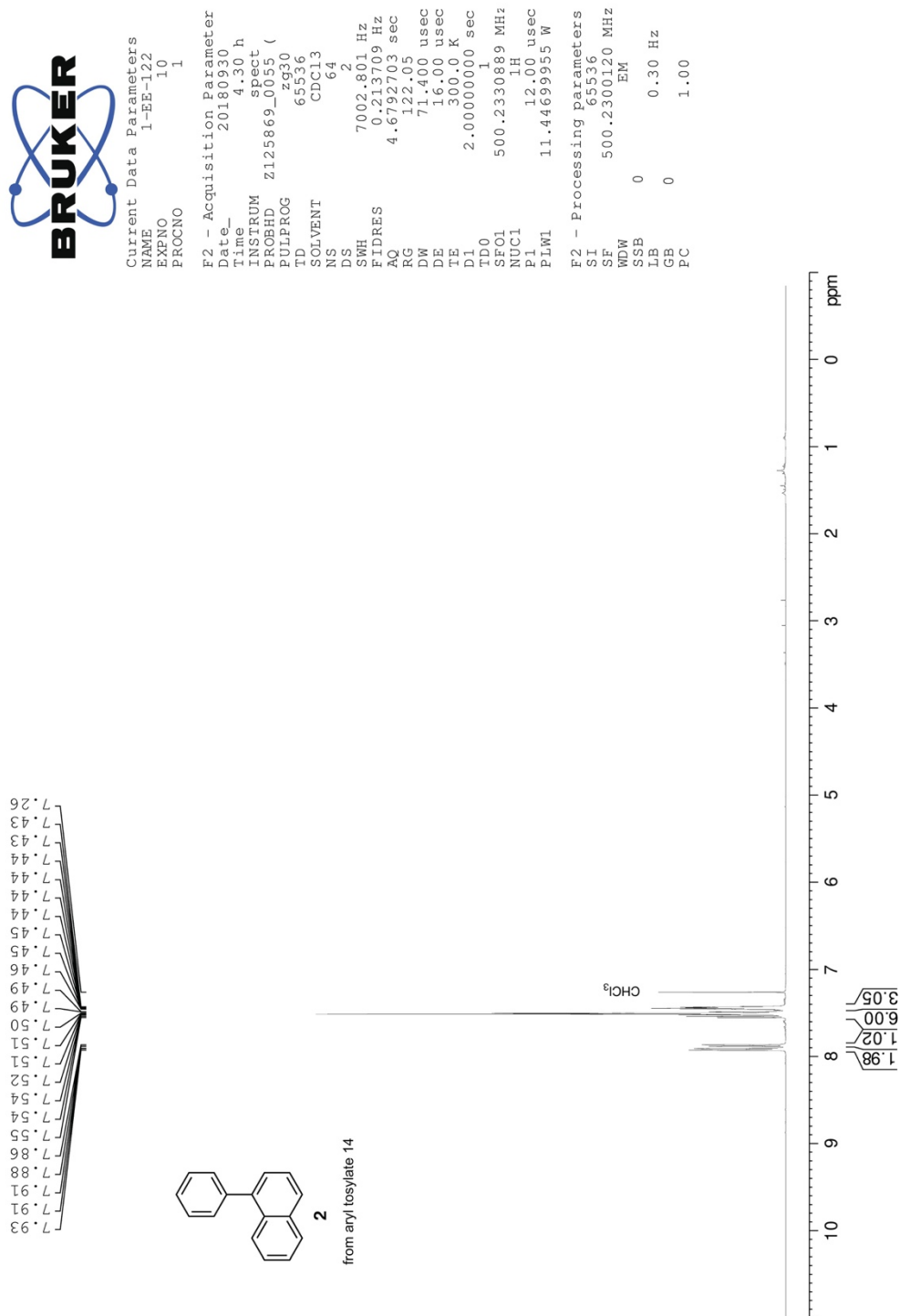


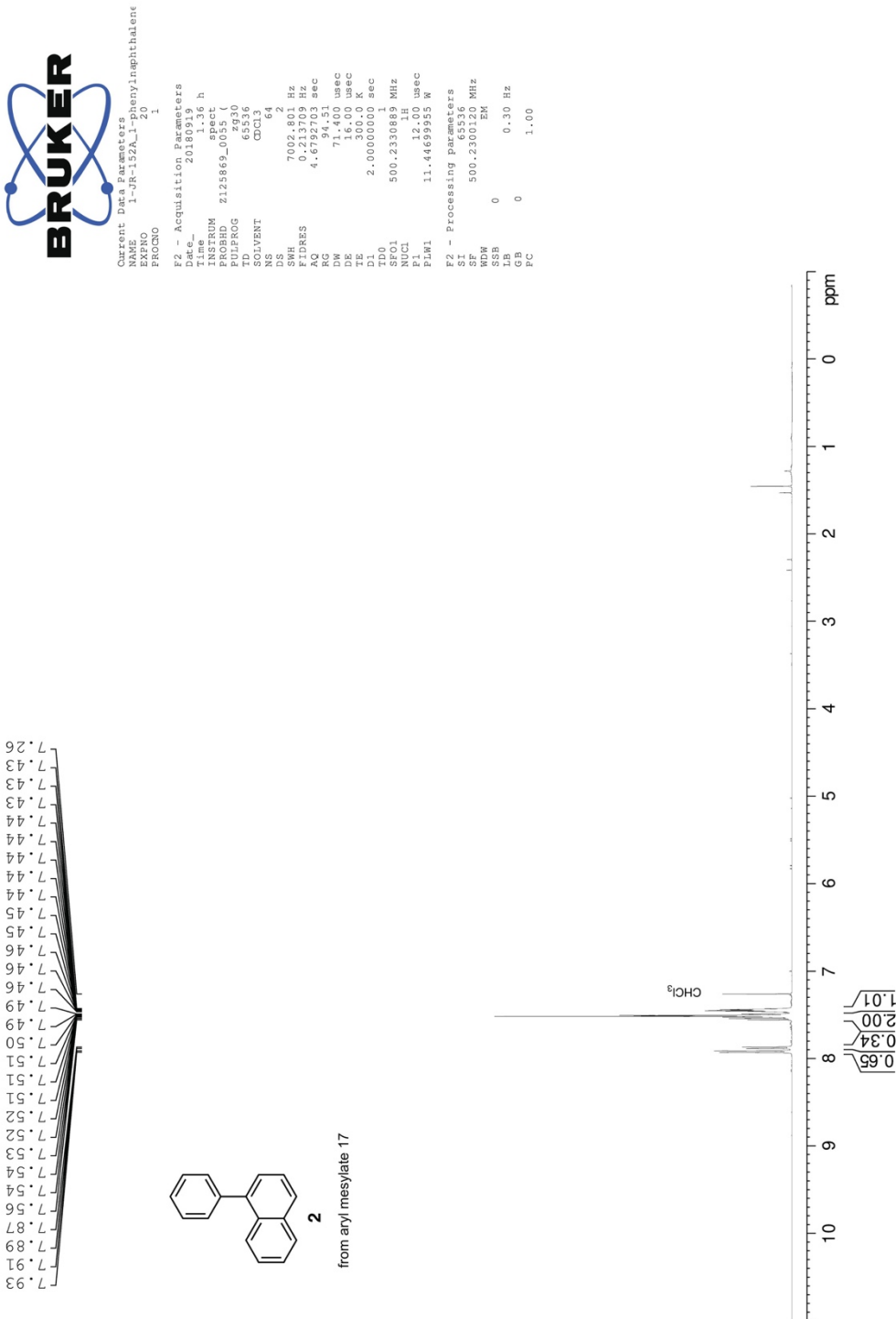
Current Data Parameters	
NAME	3-methoxyphenyl stannane
EXPO	10
PROCN	1
PF2 - Acquisition Parameters	
Date_	20181001
Time	9.48 h
INSTRUM	spect
NUMPROC	215869_0303 (
FILEPROG	42L20
TD	65336
SOLVENT	CDCl3
DS	64
NS	2
FSWHZ	7002.801 Hz
SF	0.213709 Hz
REDRES	4.6792703 sec
RG	30.54
DW	71.400 usec
DE	300.0 usec
TE	300.0 usec
DELTA	2.000000000 sec
TD0	1
FSF01	500.2330889 MHz
NUC1	1H
PLP1	12.00 usec
PLPW1	11.44699955 W
22 - Processing parameters	
SI	500.120 MHz
WDW	500.230889
SSB	EM
GB	0
LE	0.30 Hz
PC	1.00

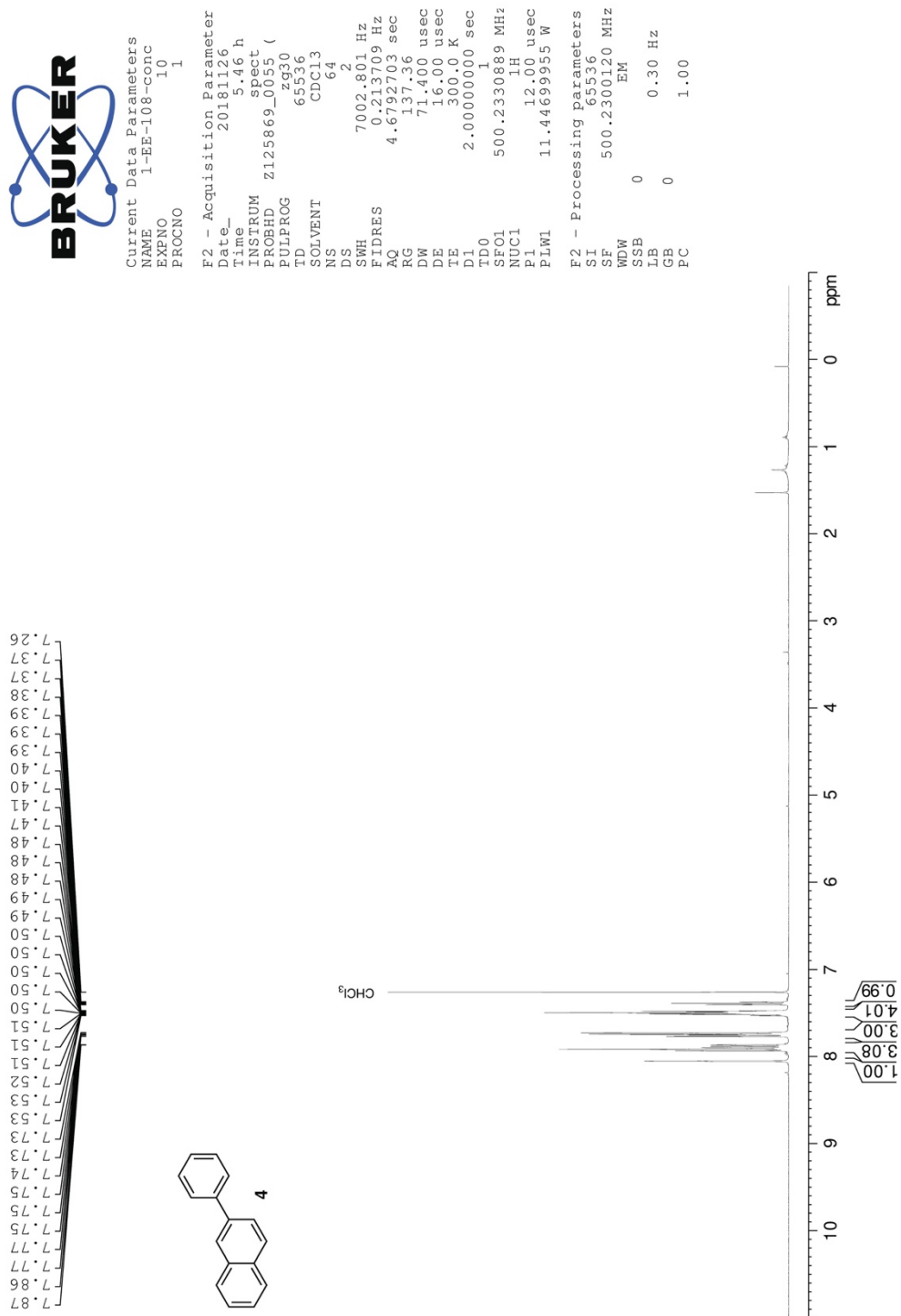


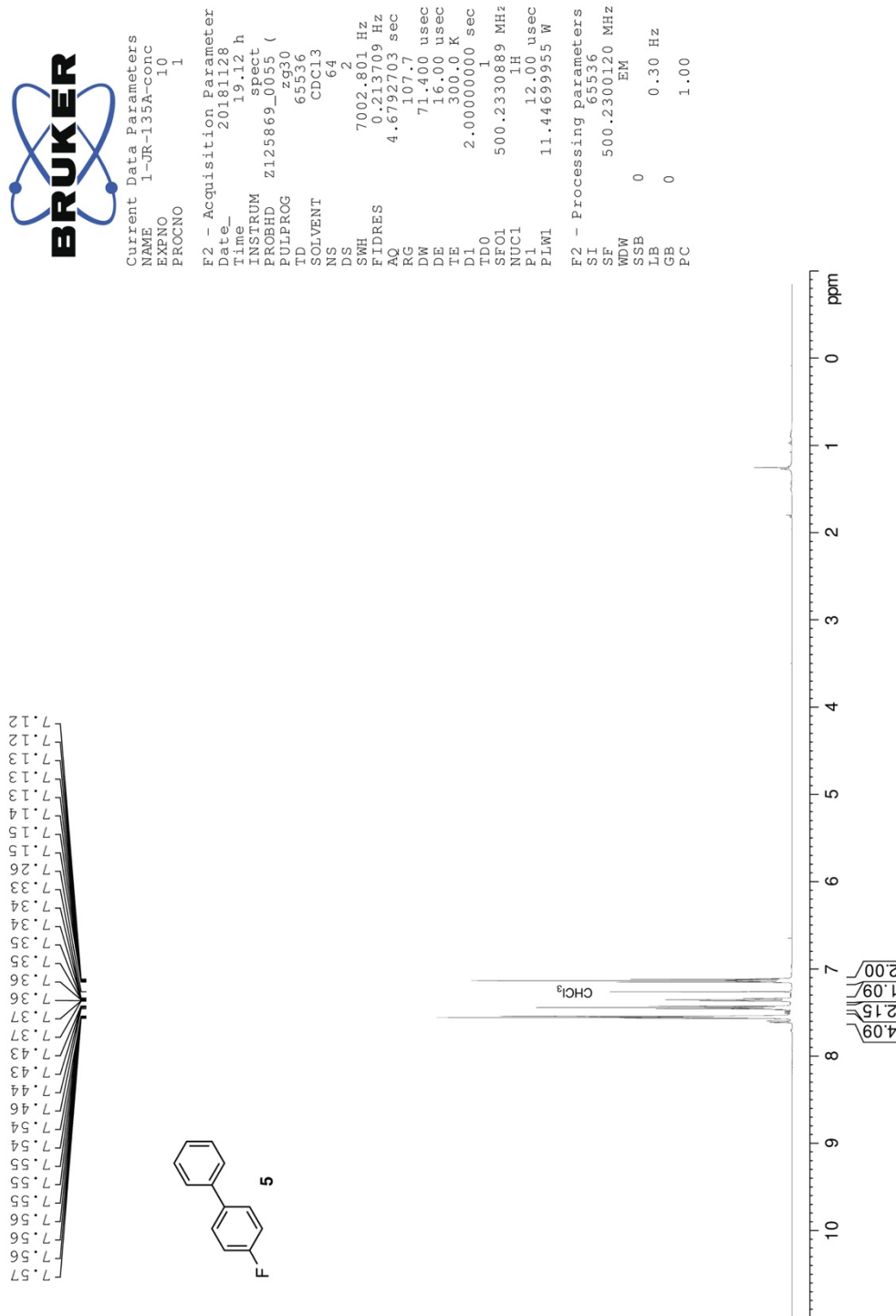












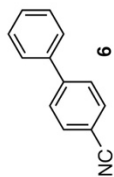


Current Data Parameters
 NAME 1-JR-118-conc
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameter
 Date_ 20181126
 Time 2.25 h
 INSTRUM spect
 PROBHD zg30
 PULPROG zg30
 TD 65536
 SOLVENT CDCl₃
 NS 64
 DS 2
 SWH 7002.801 Hz
 FIDRES 0.213709 Hz
 AQ 4.6792703 sec
 RG 137.36
 DW 71.400 usec
 DE 16.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 TD0 1
 SFO1 500.2330889 MHz
 NUC1 ¹H
 P1 12.00 usec
 PLW1 11.44699955 W

F2 - Processing parameters
 SI 65536
 SF 500.2300120 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

7.74
7.73
7.72
7.70
7.70
7.69
7.68
7.60
7.60
7.59
7.59
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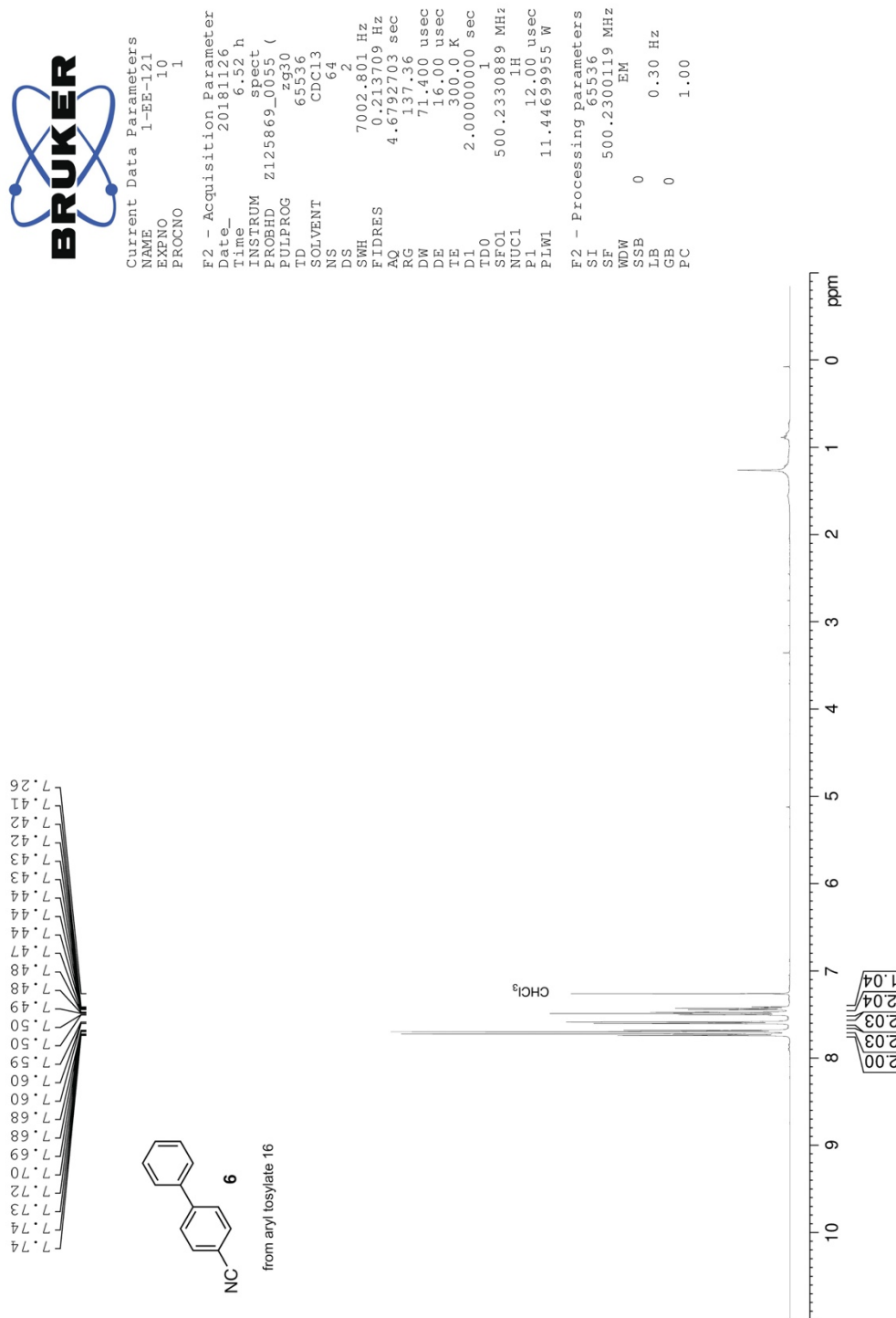


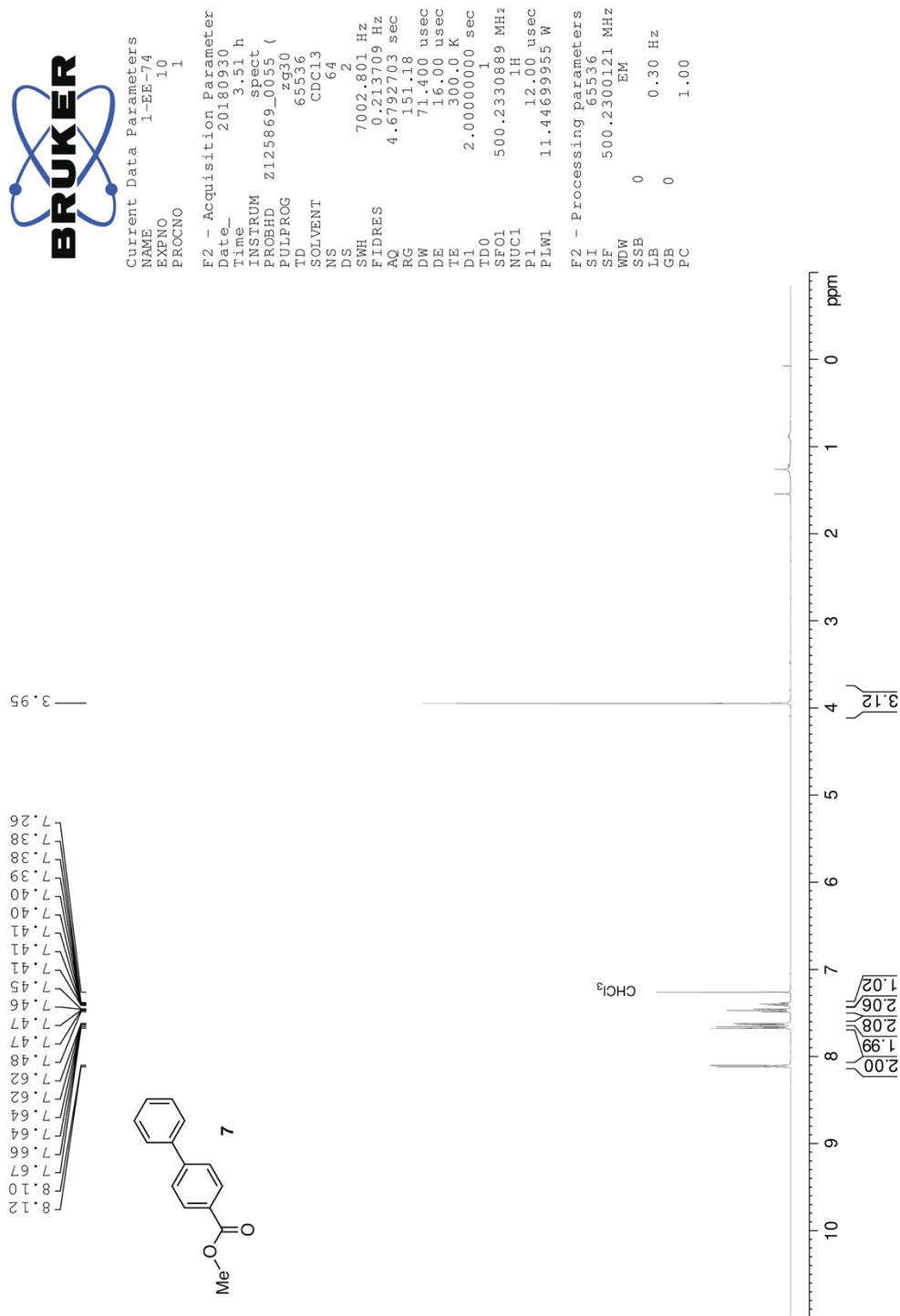
from aryl sulfamate S3

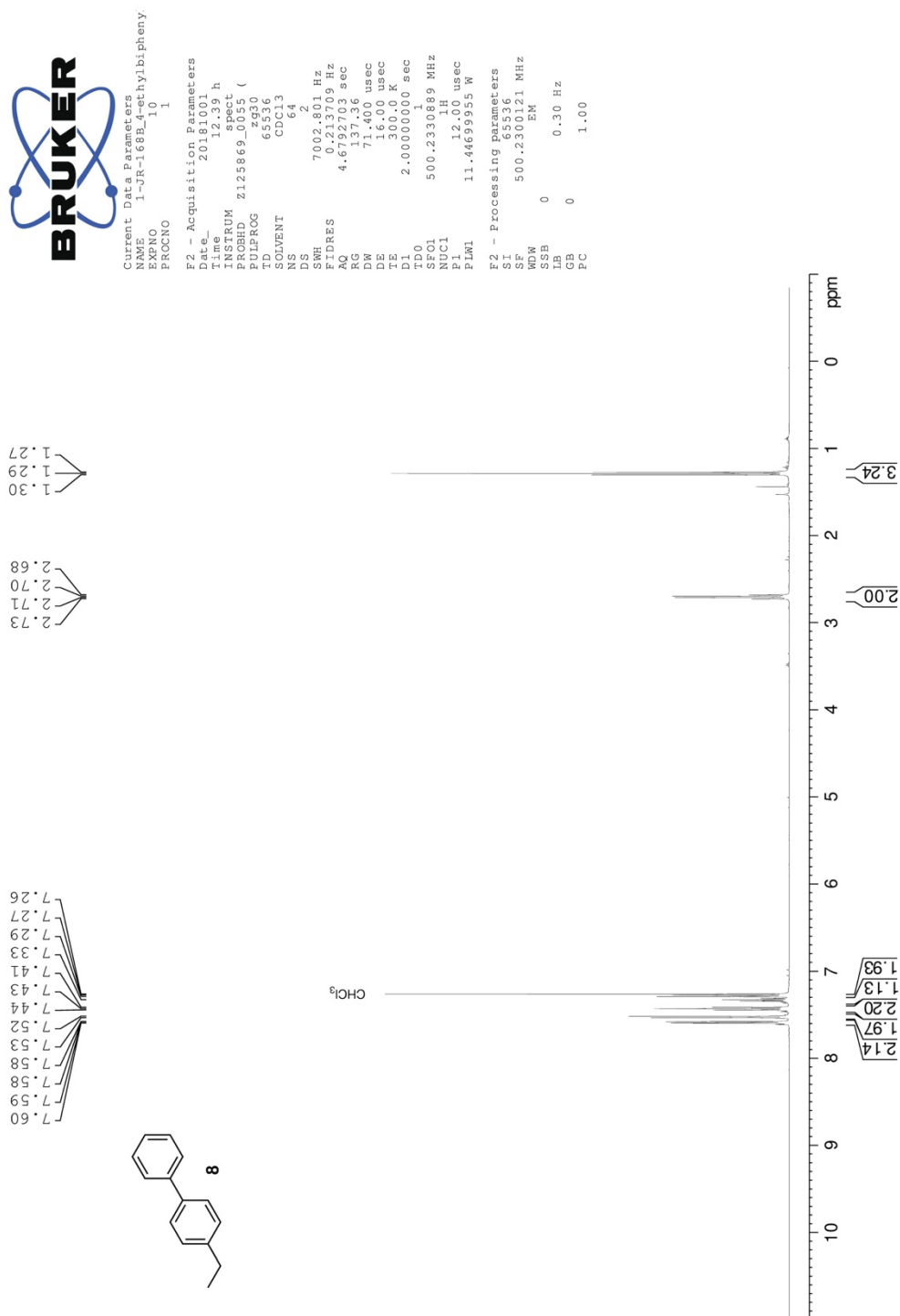
CHCl₃

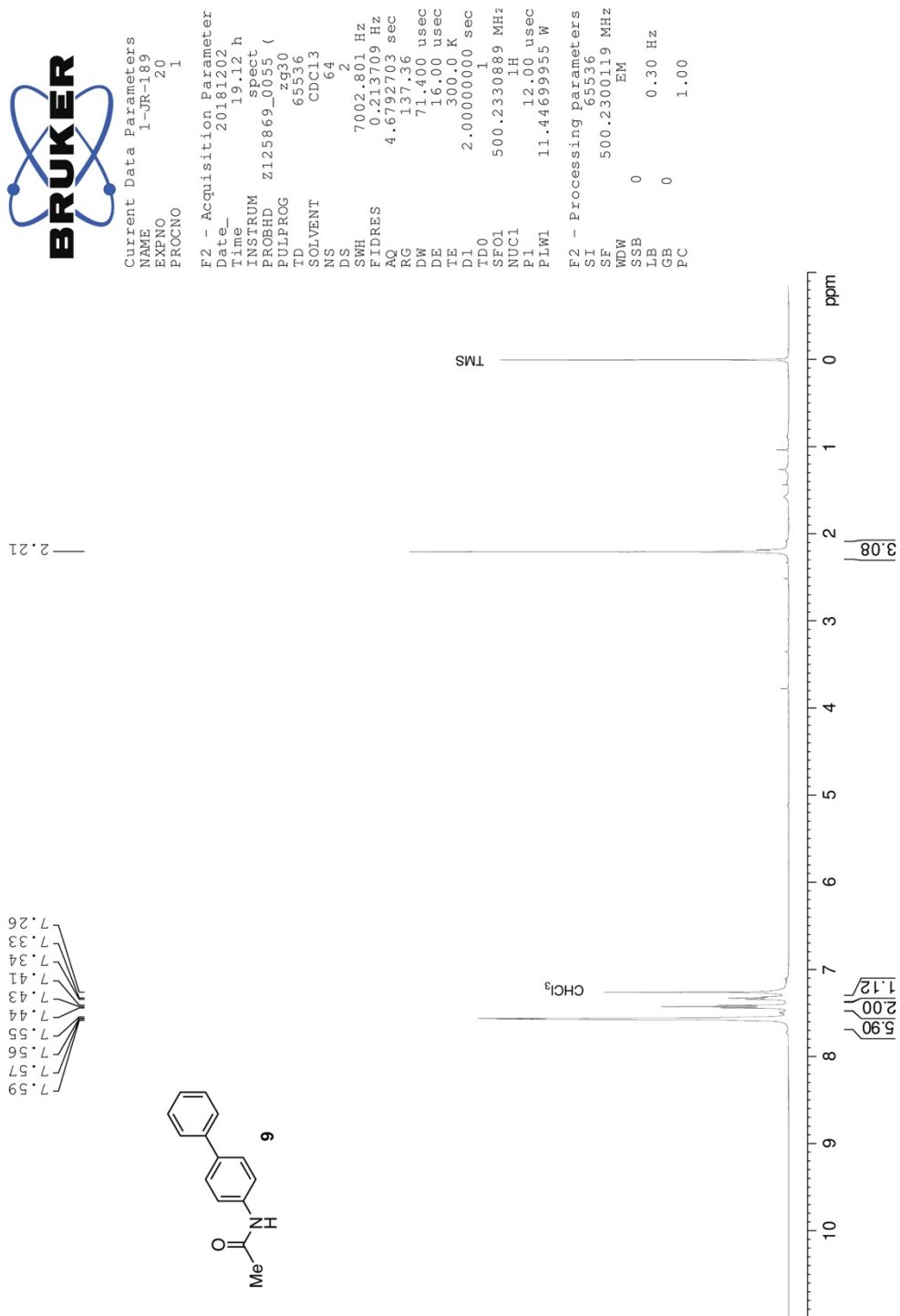
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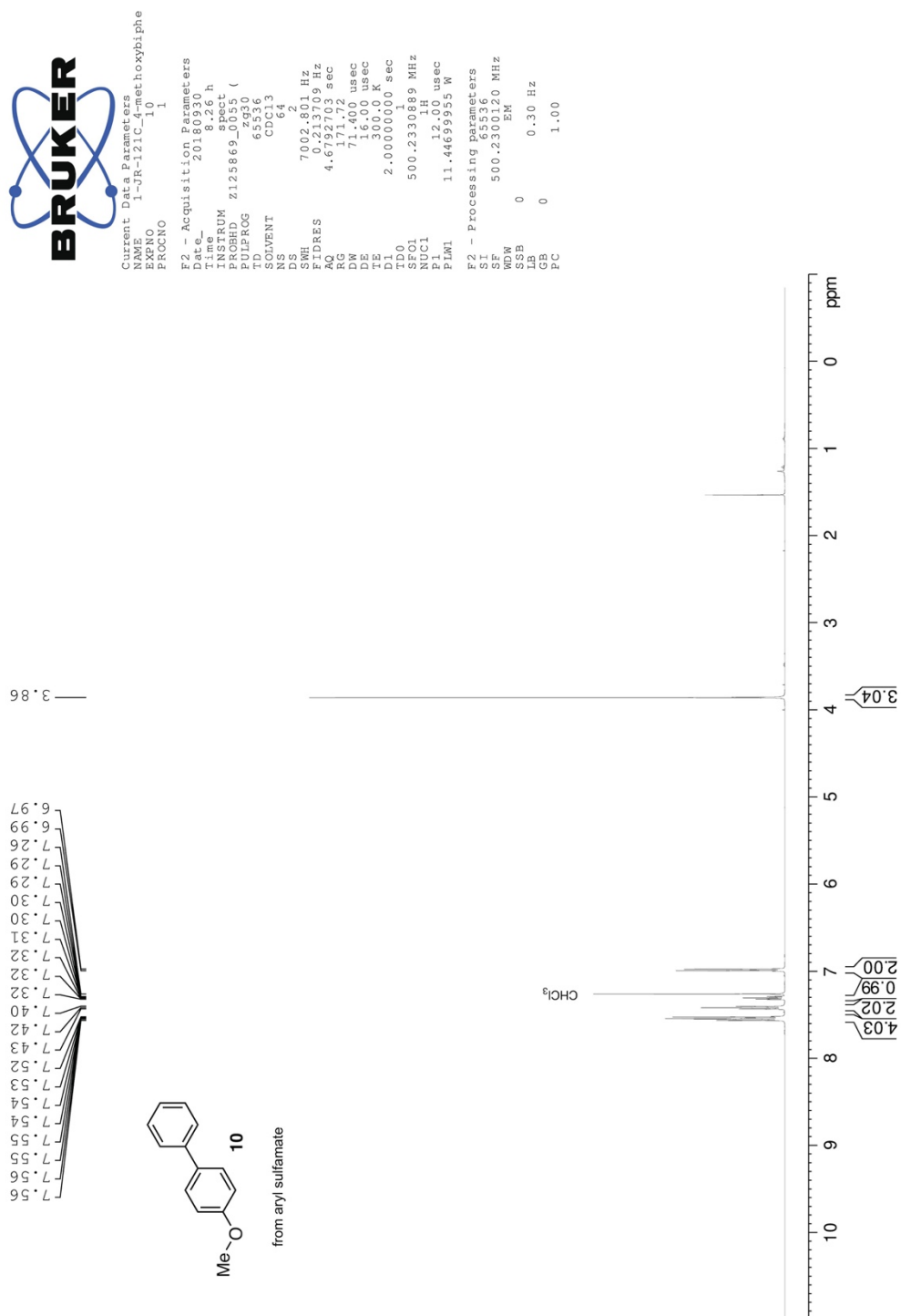
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2.02
2.00
2.01
1.00

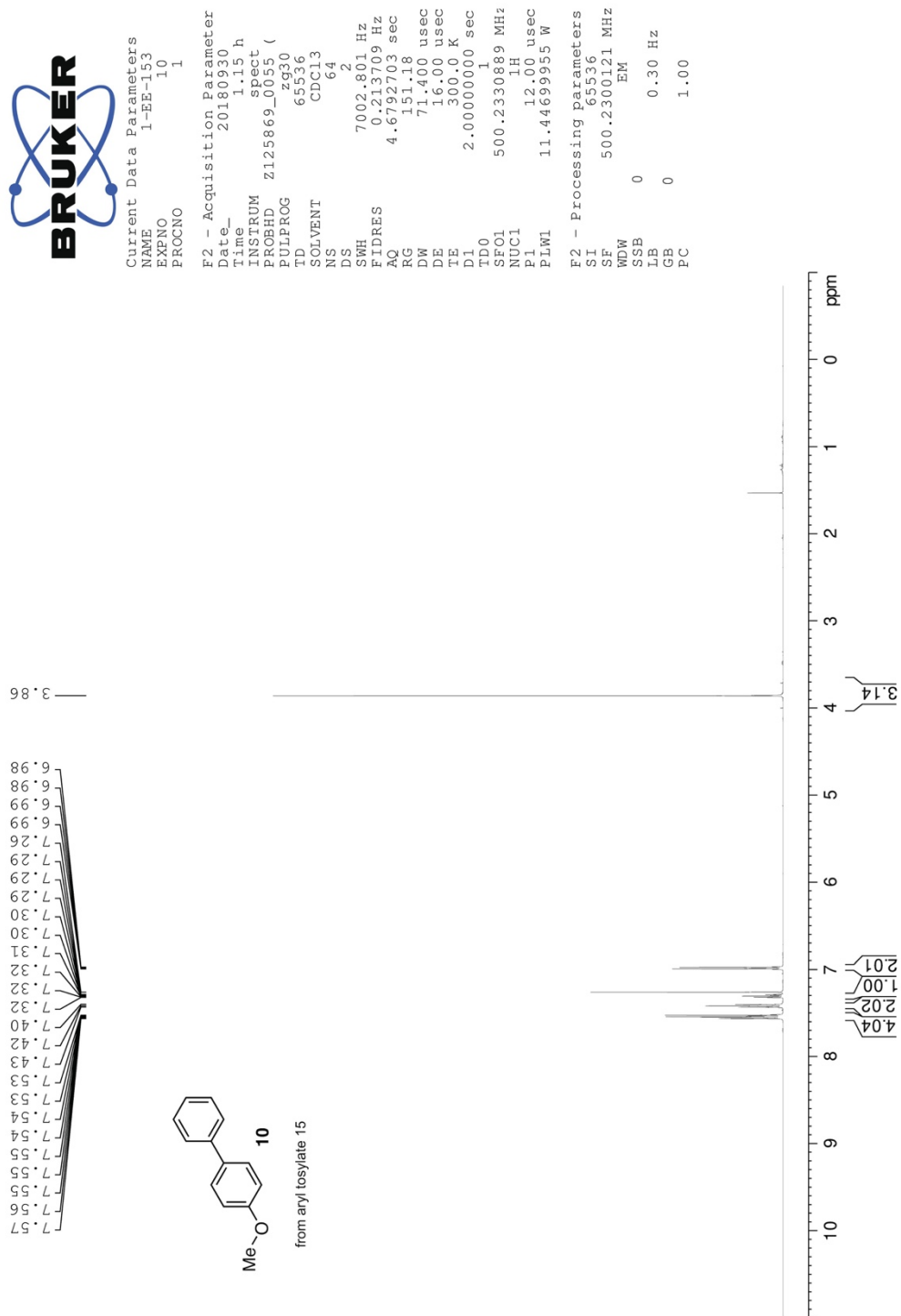


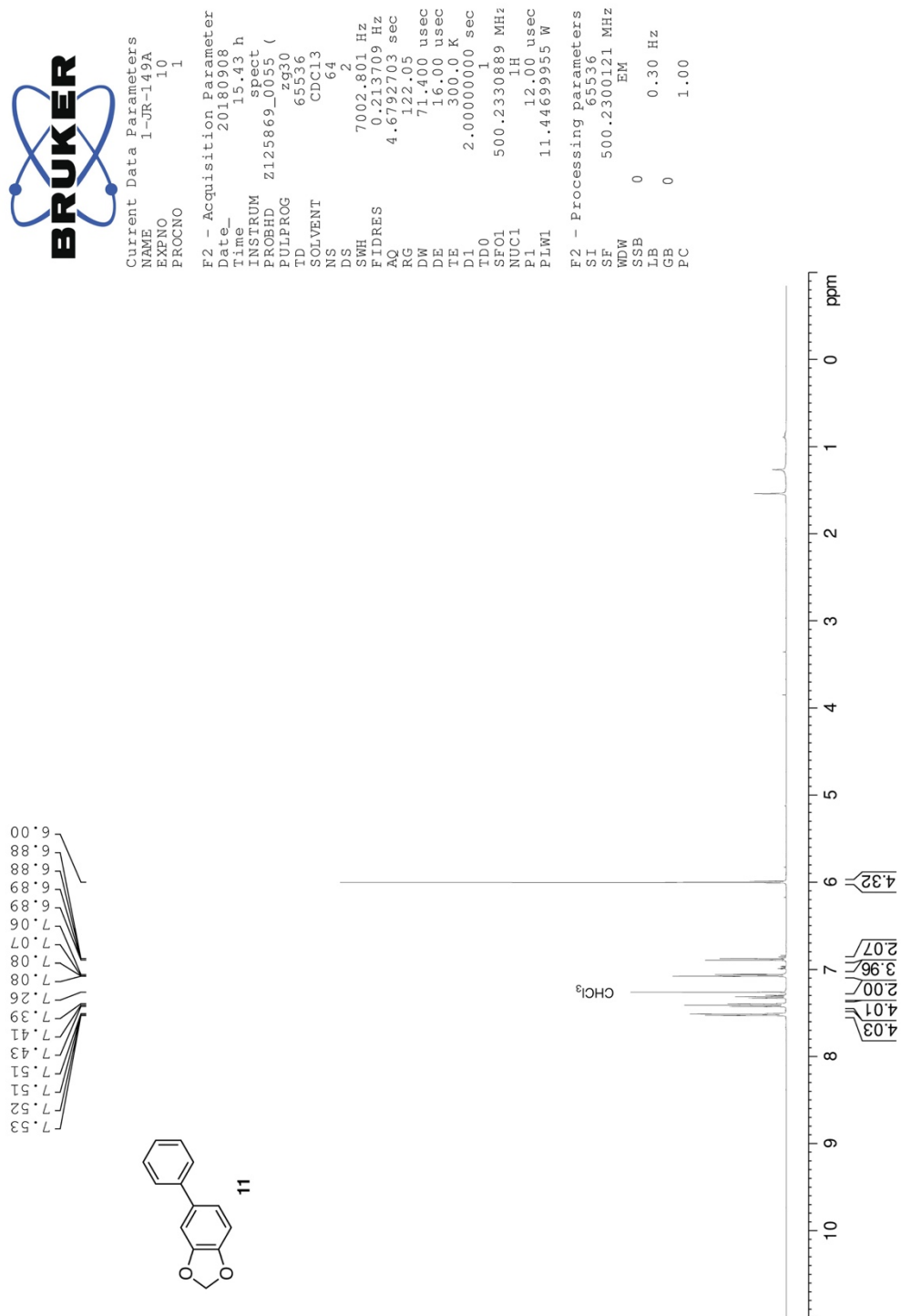


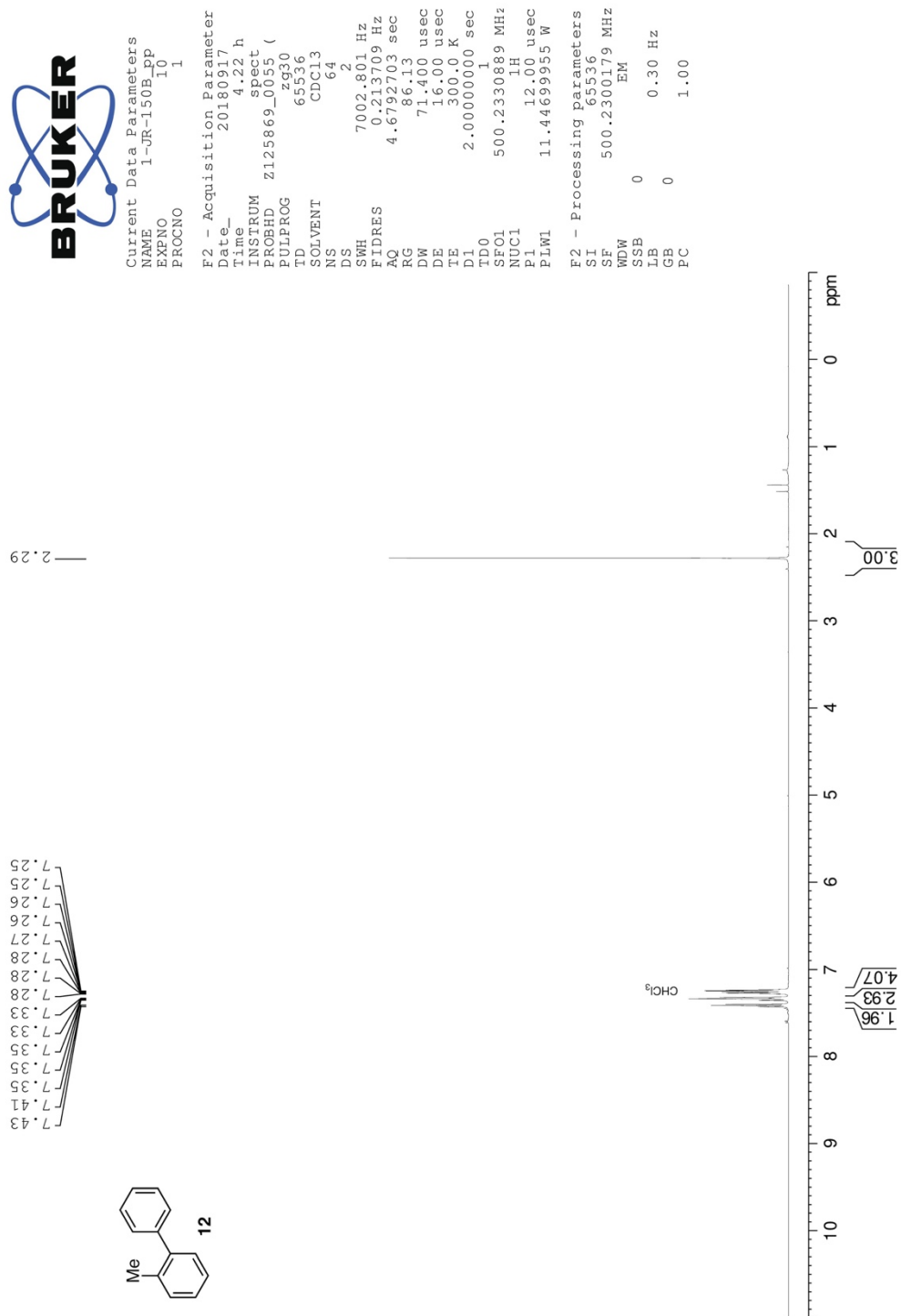


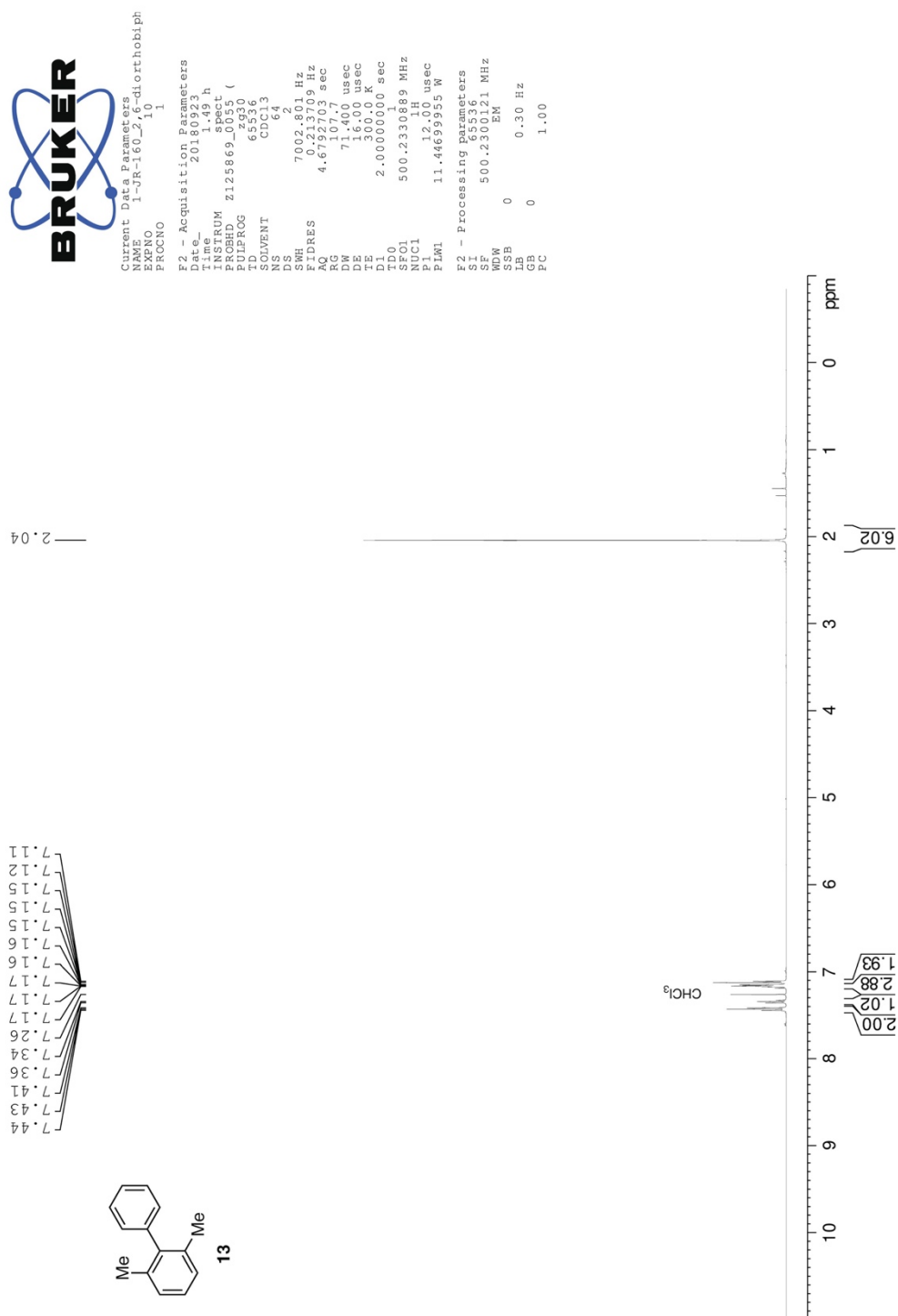


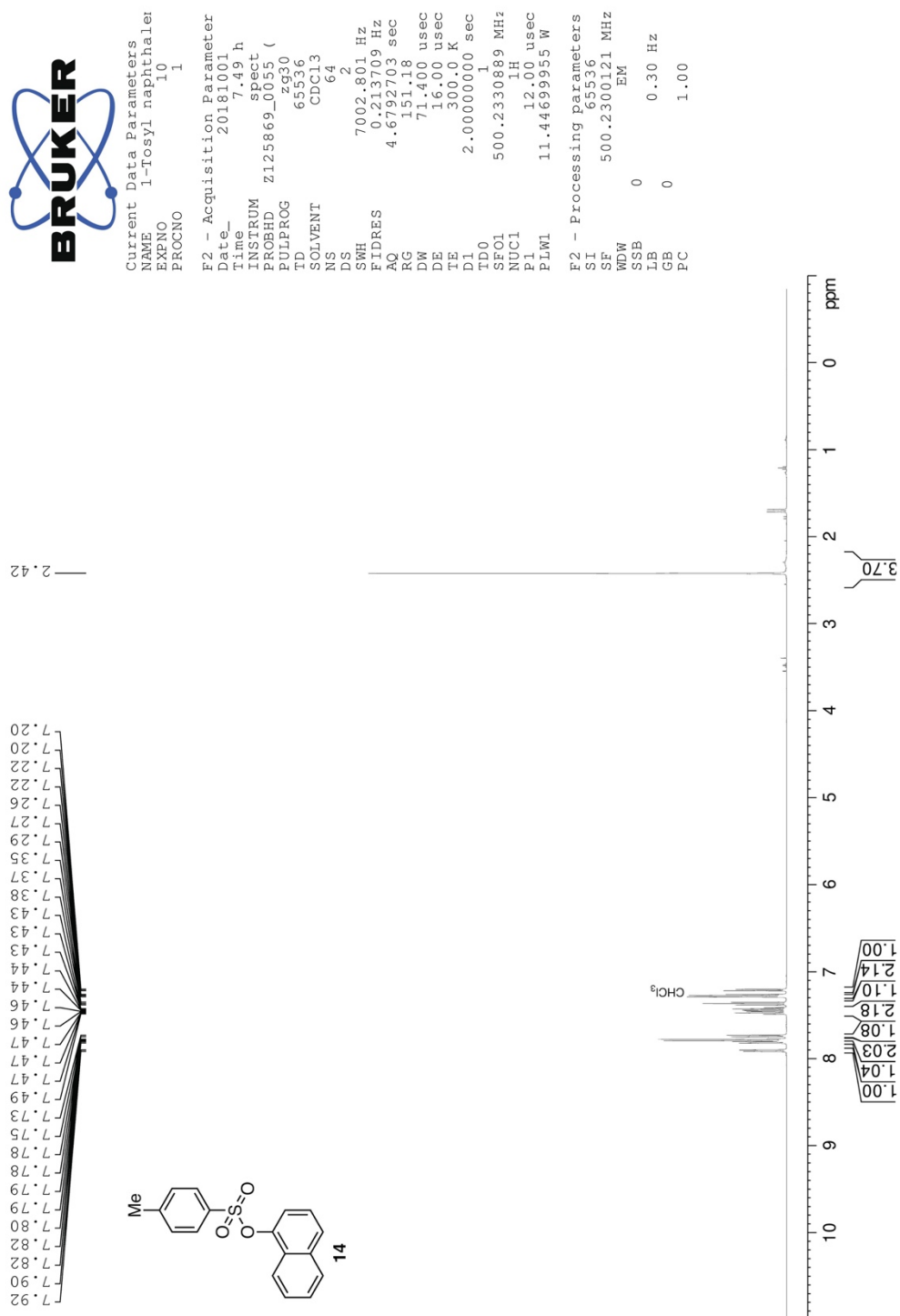


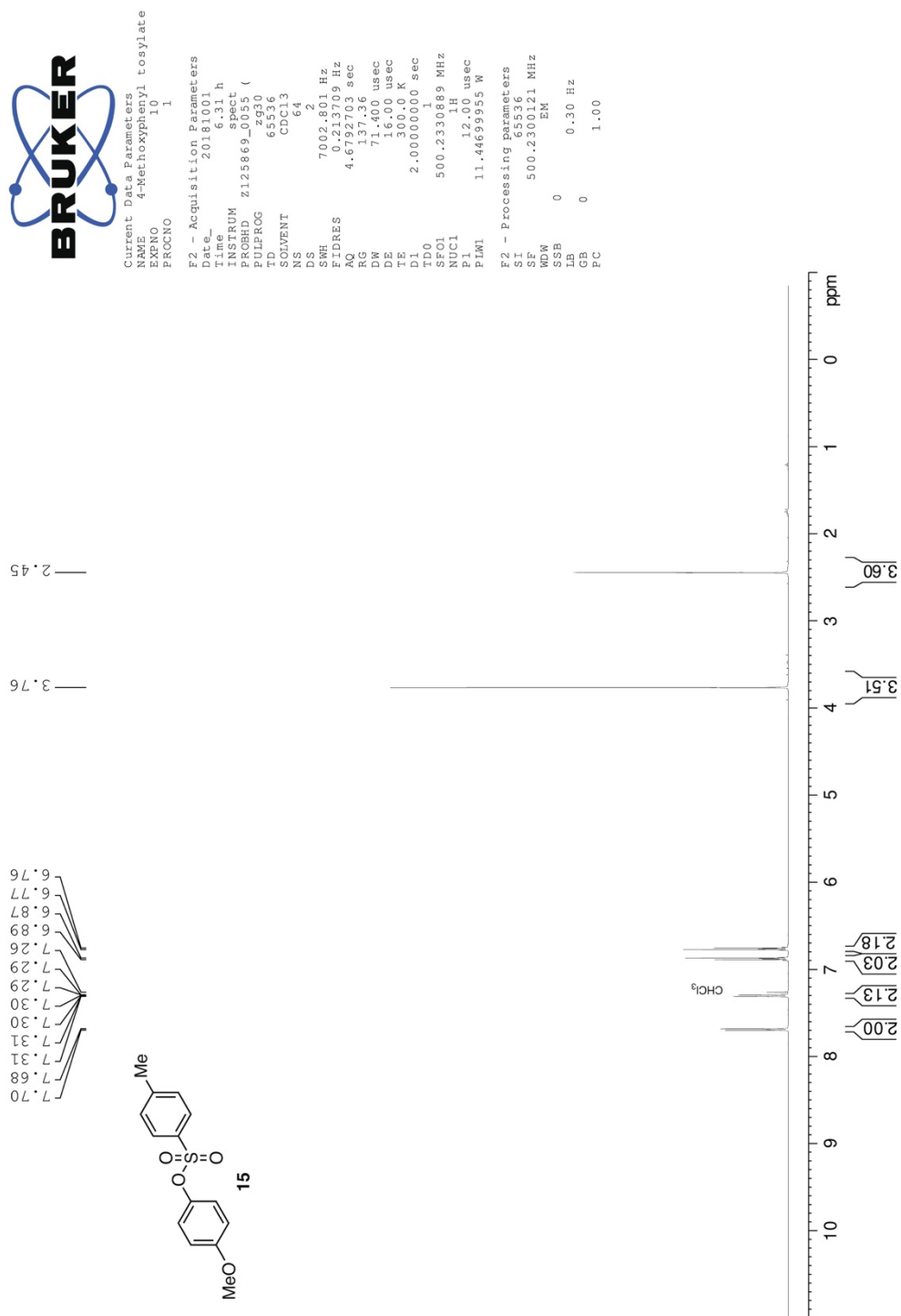


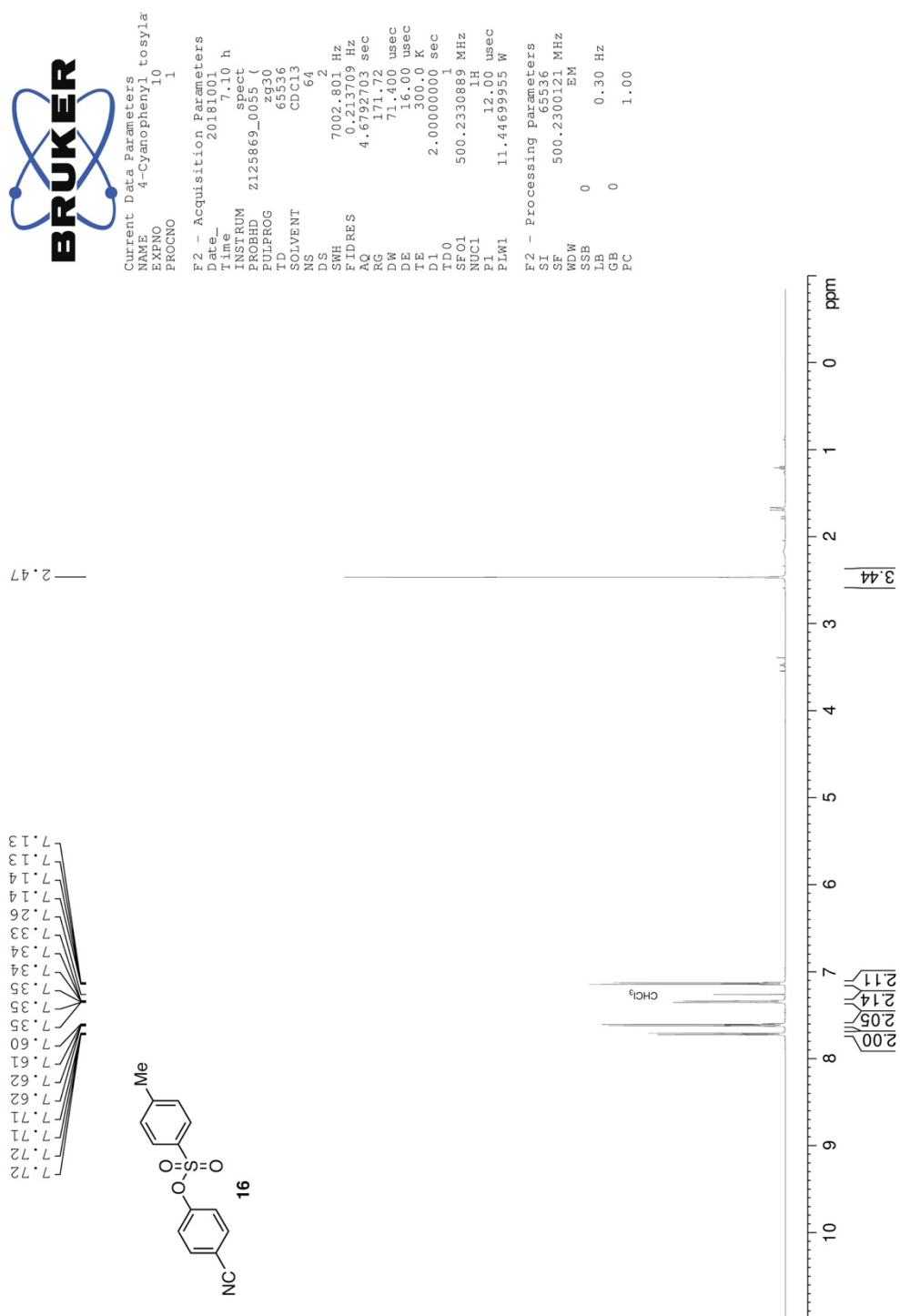


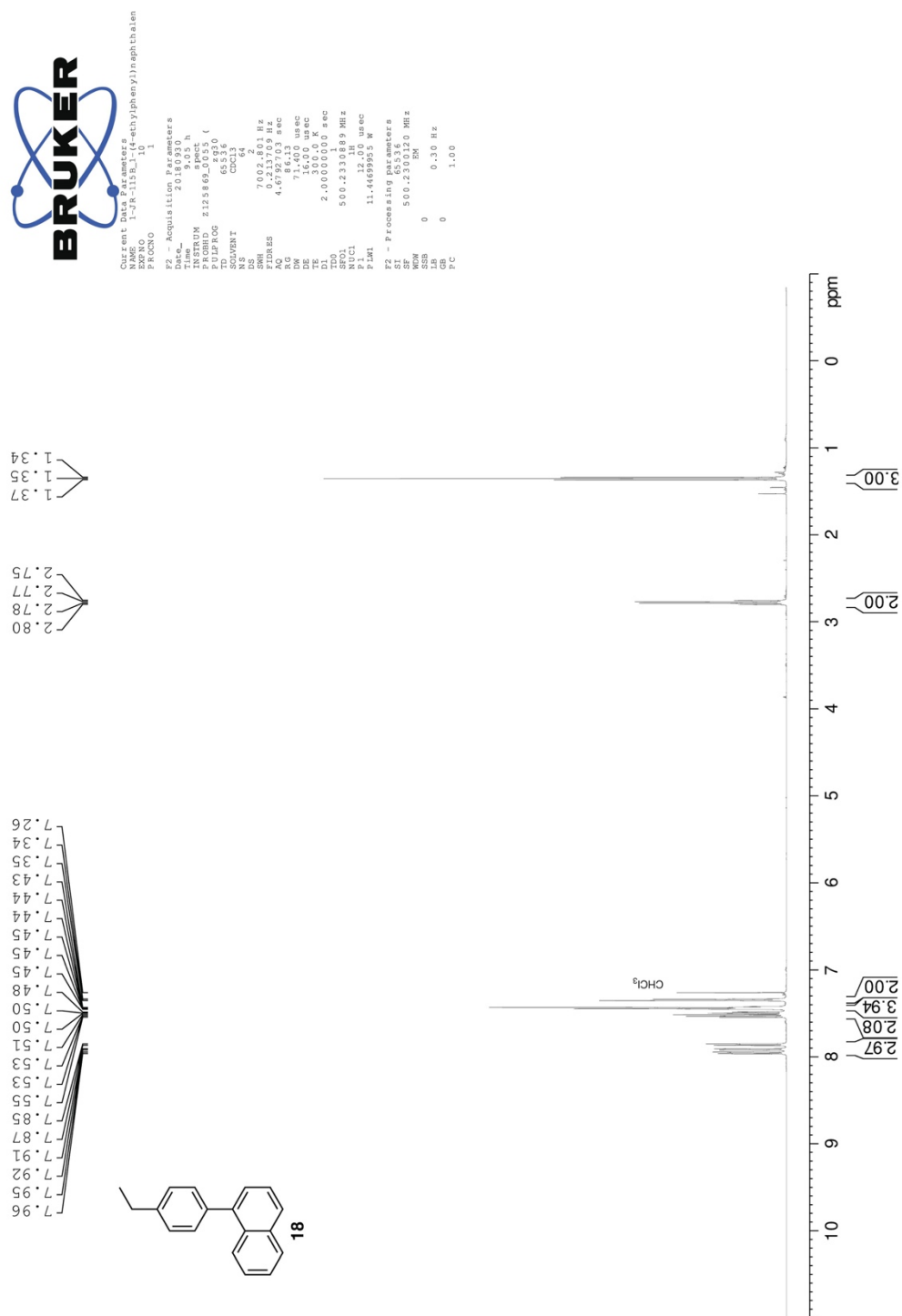


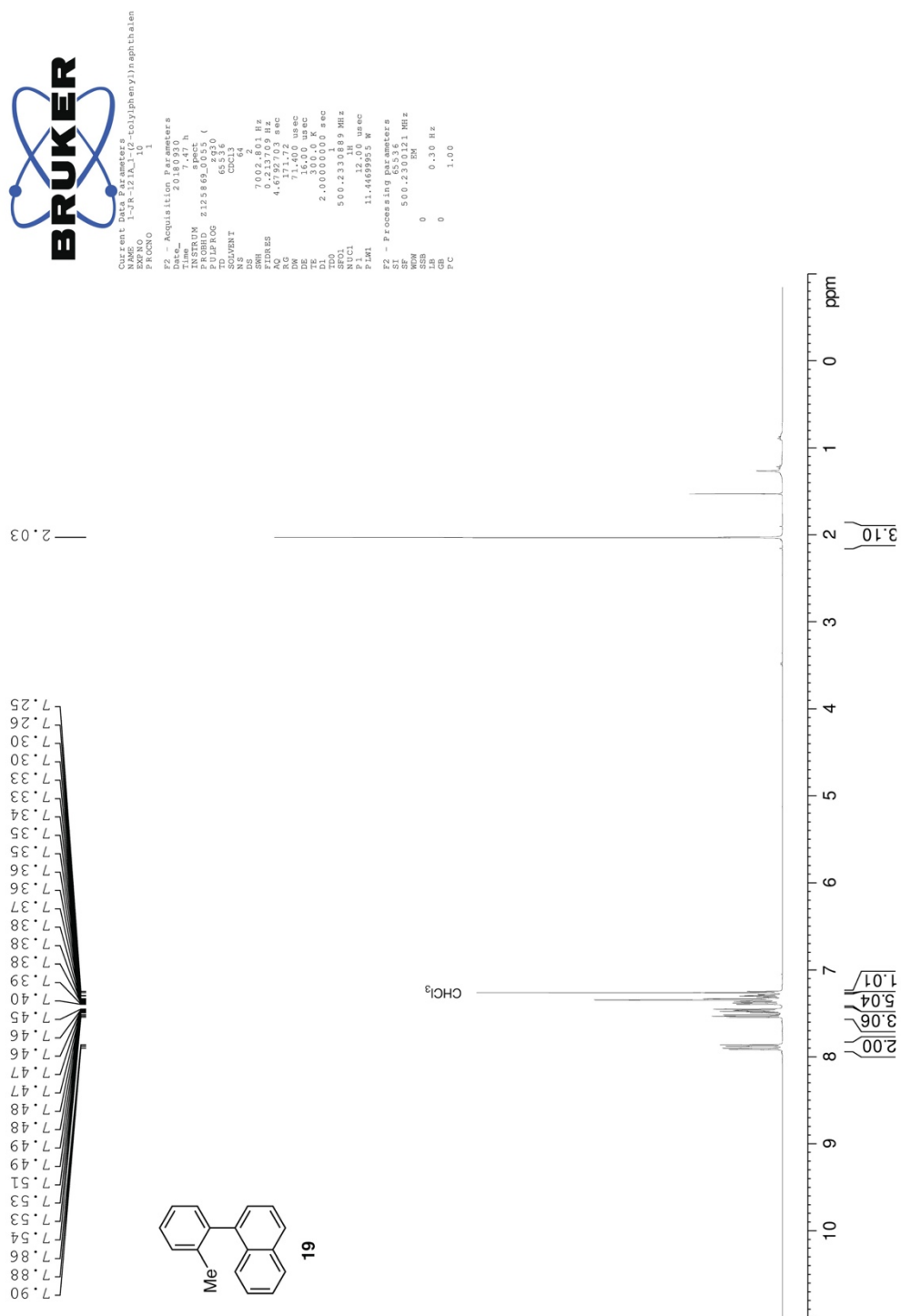


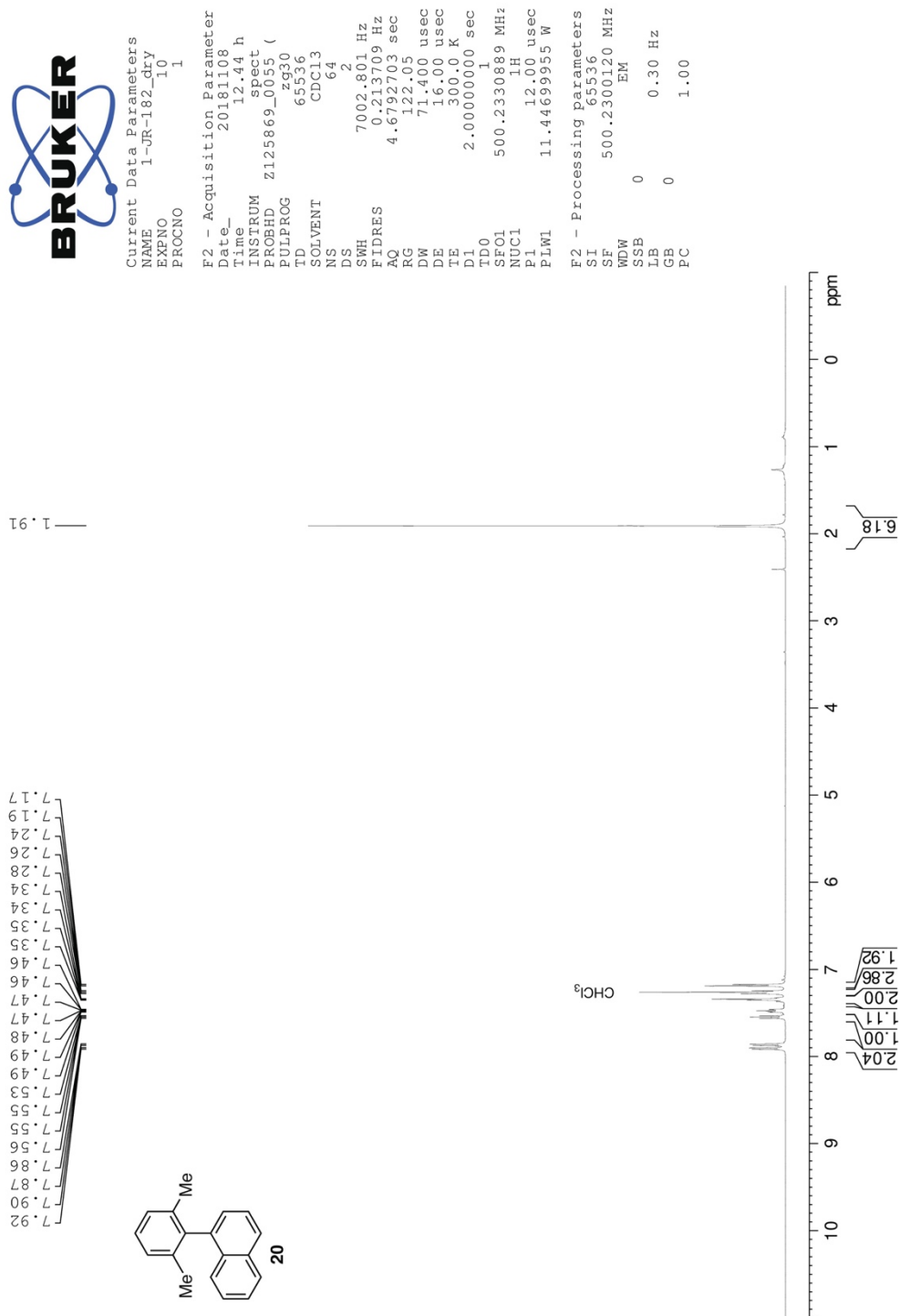


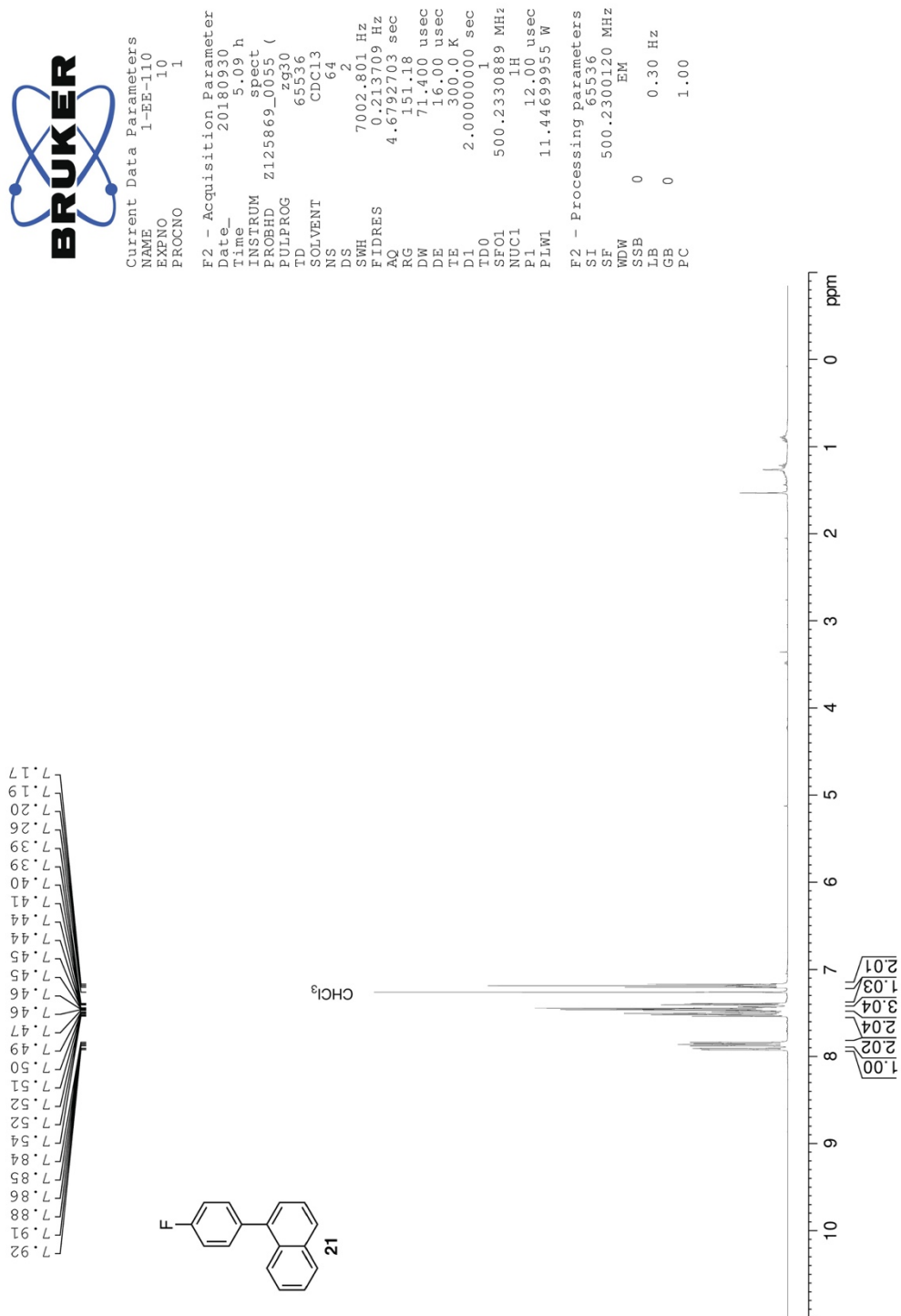


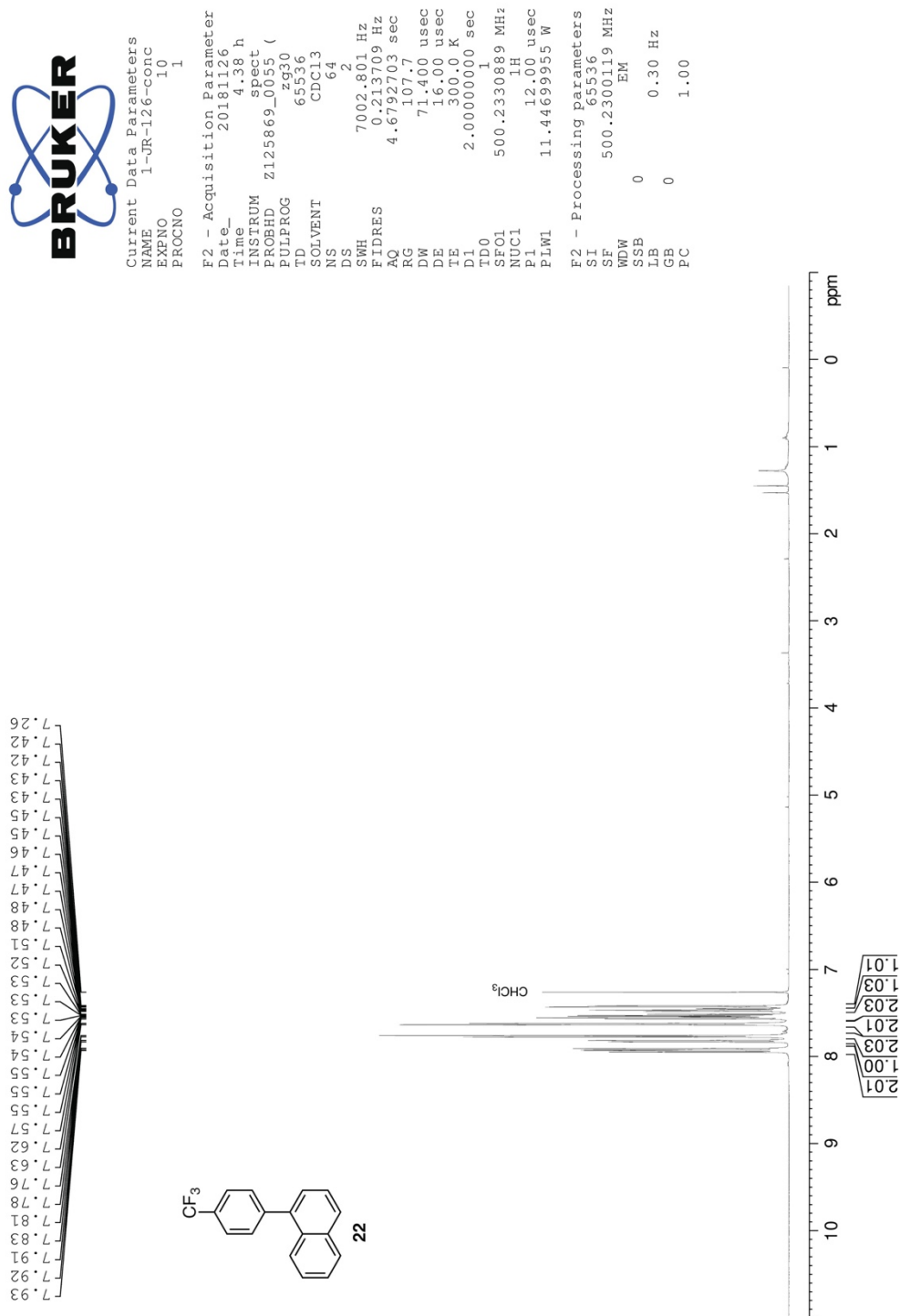


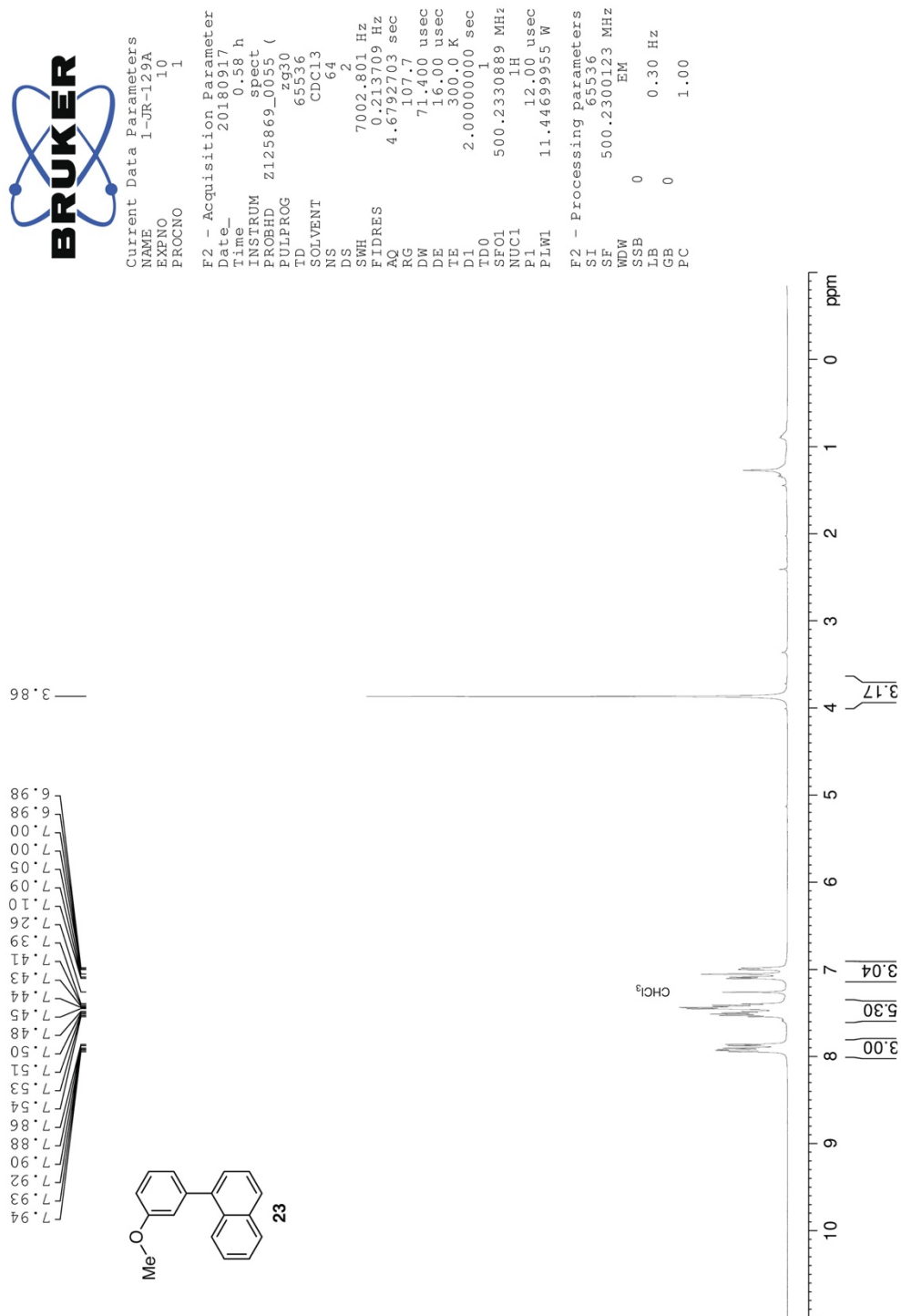


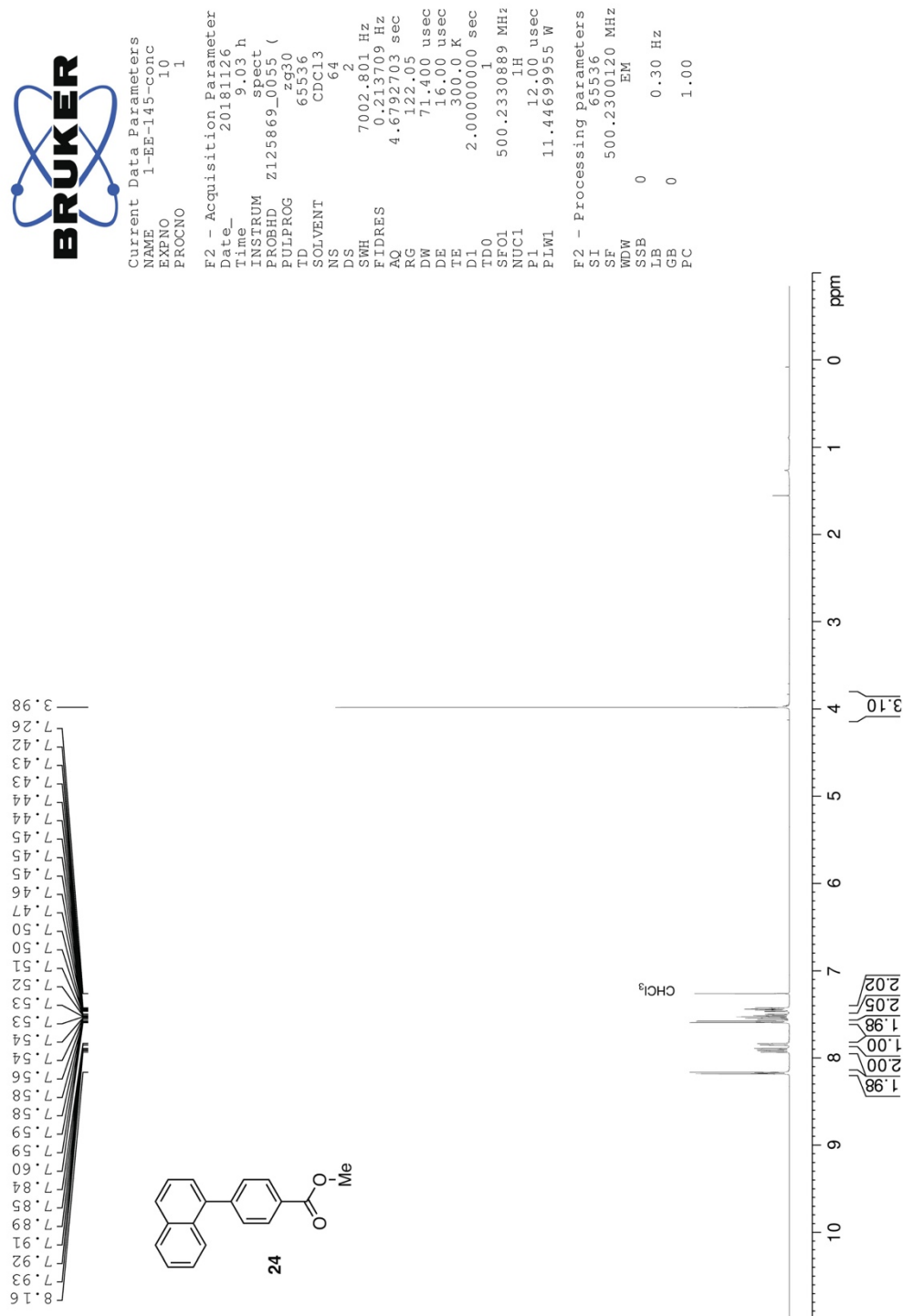












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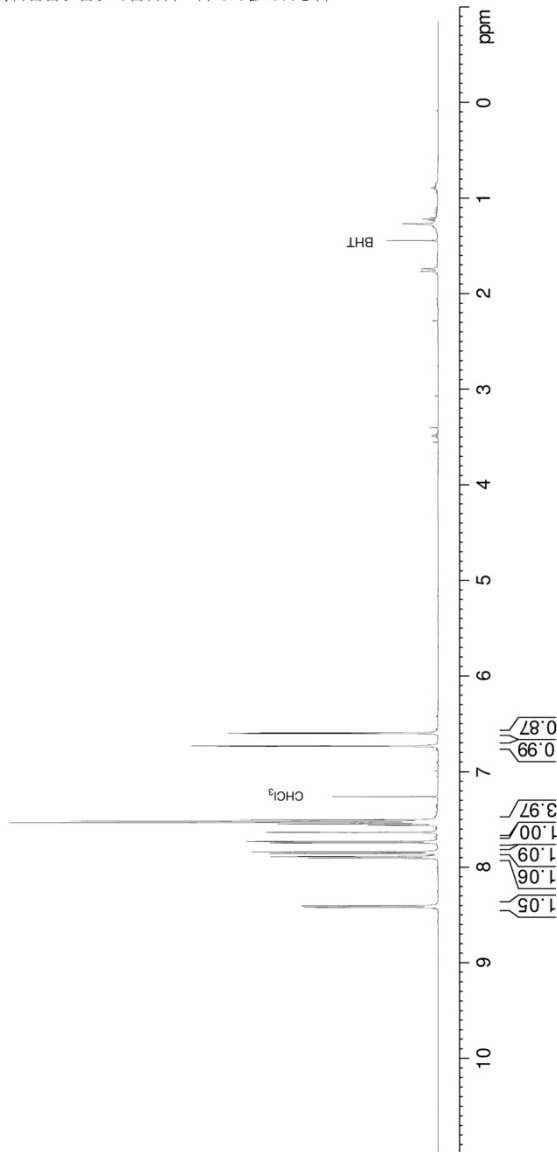
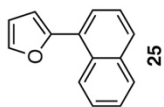
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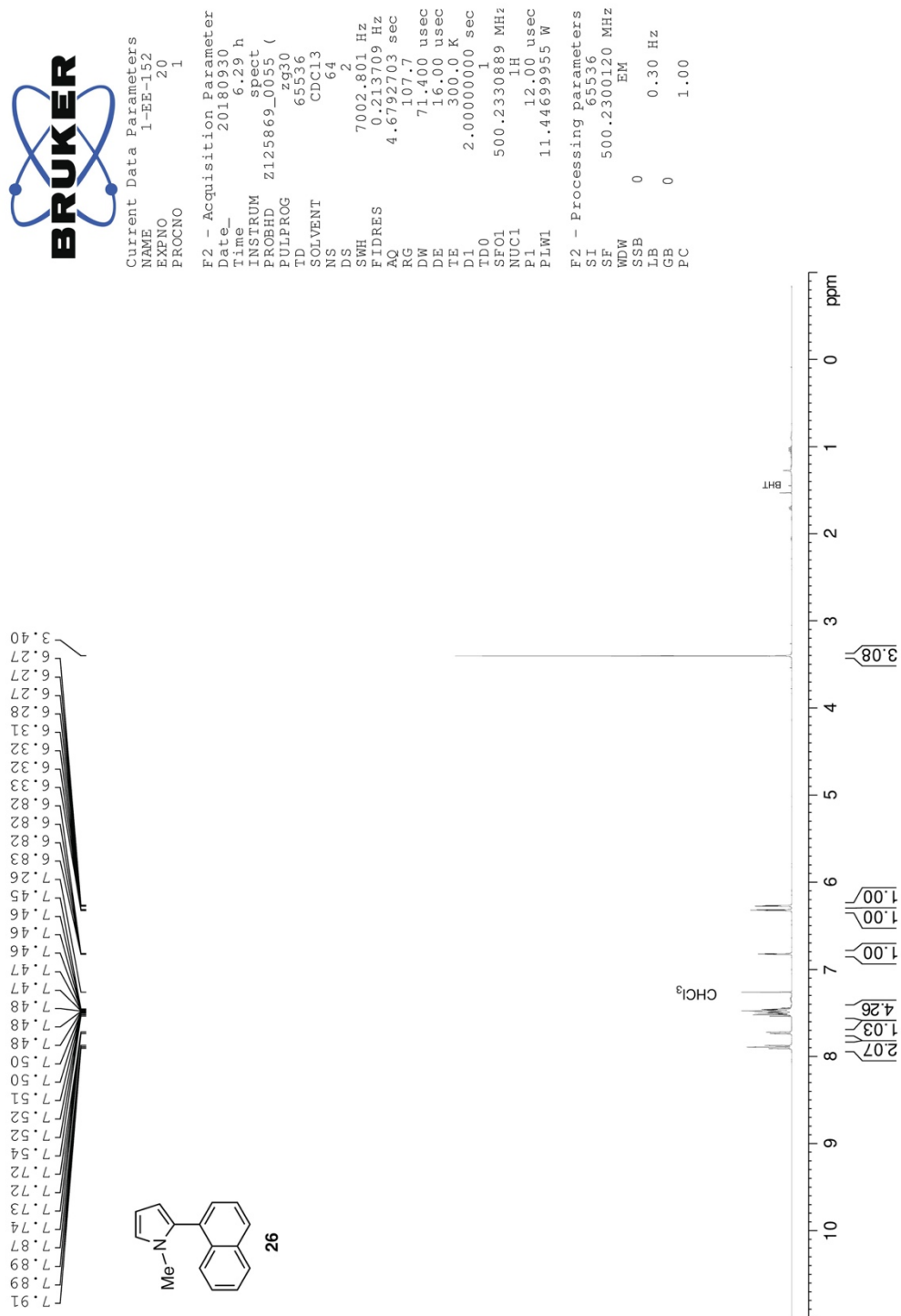
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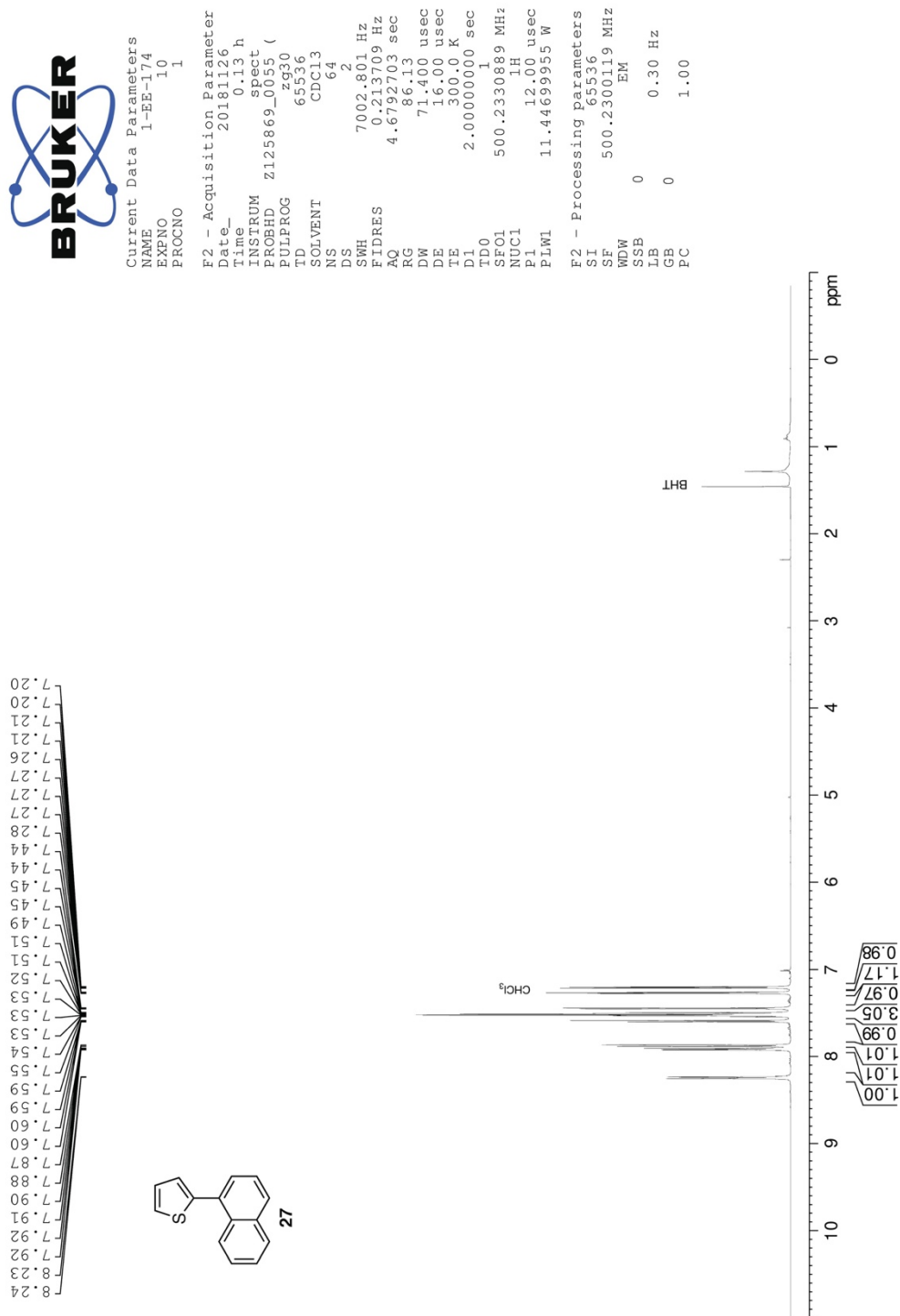
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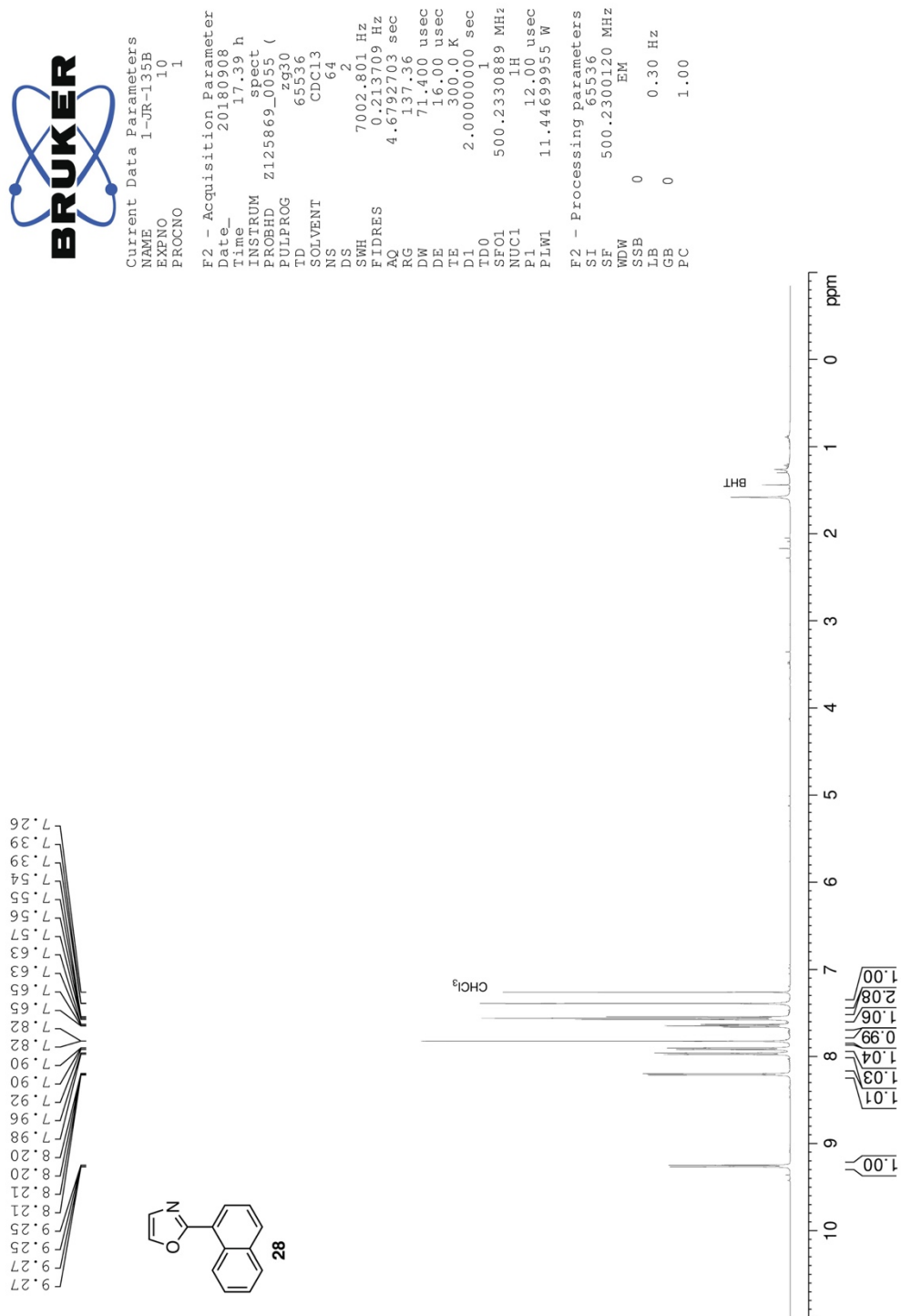
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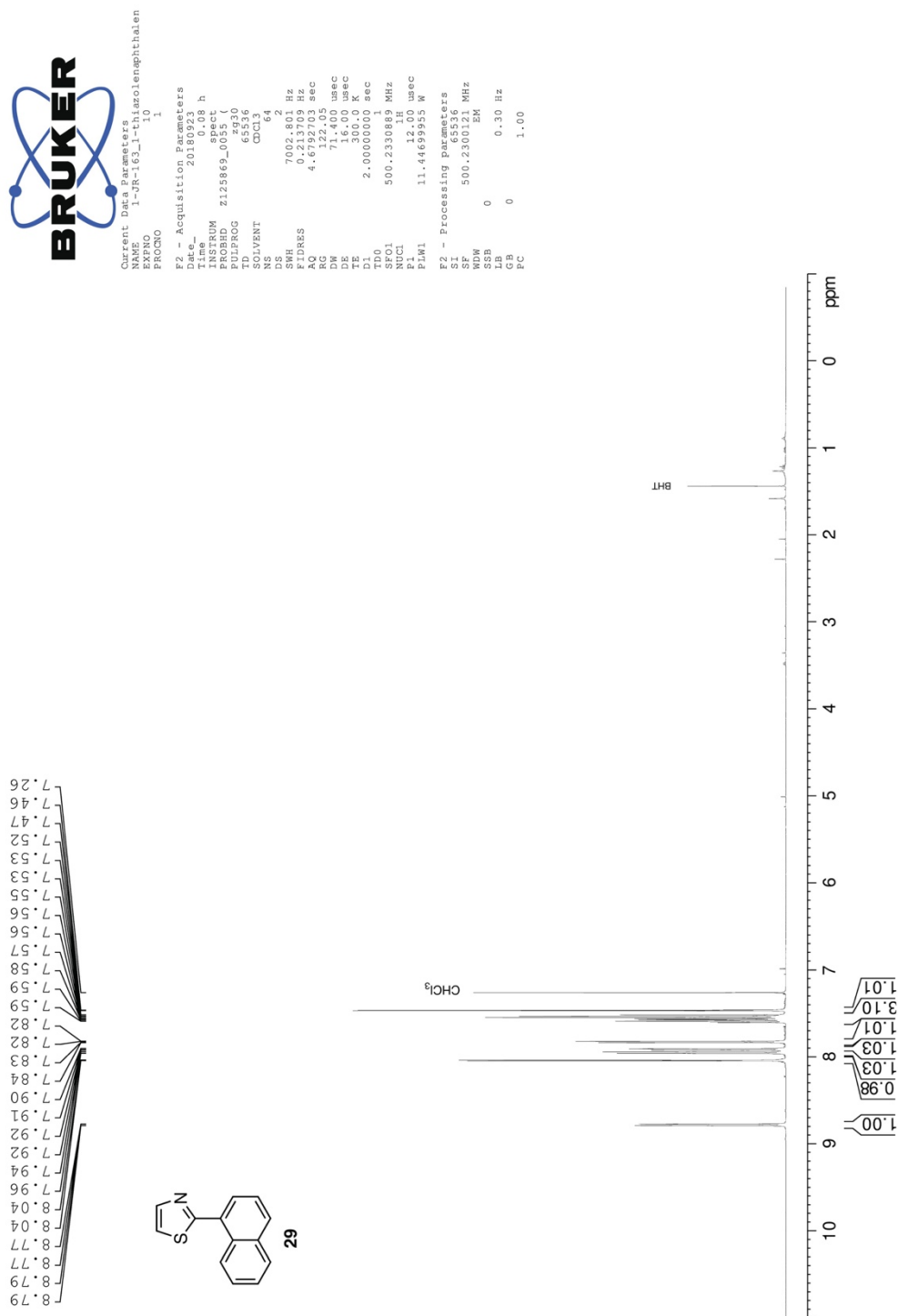
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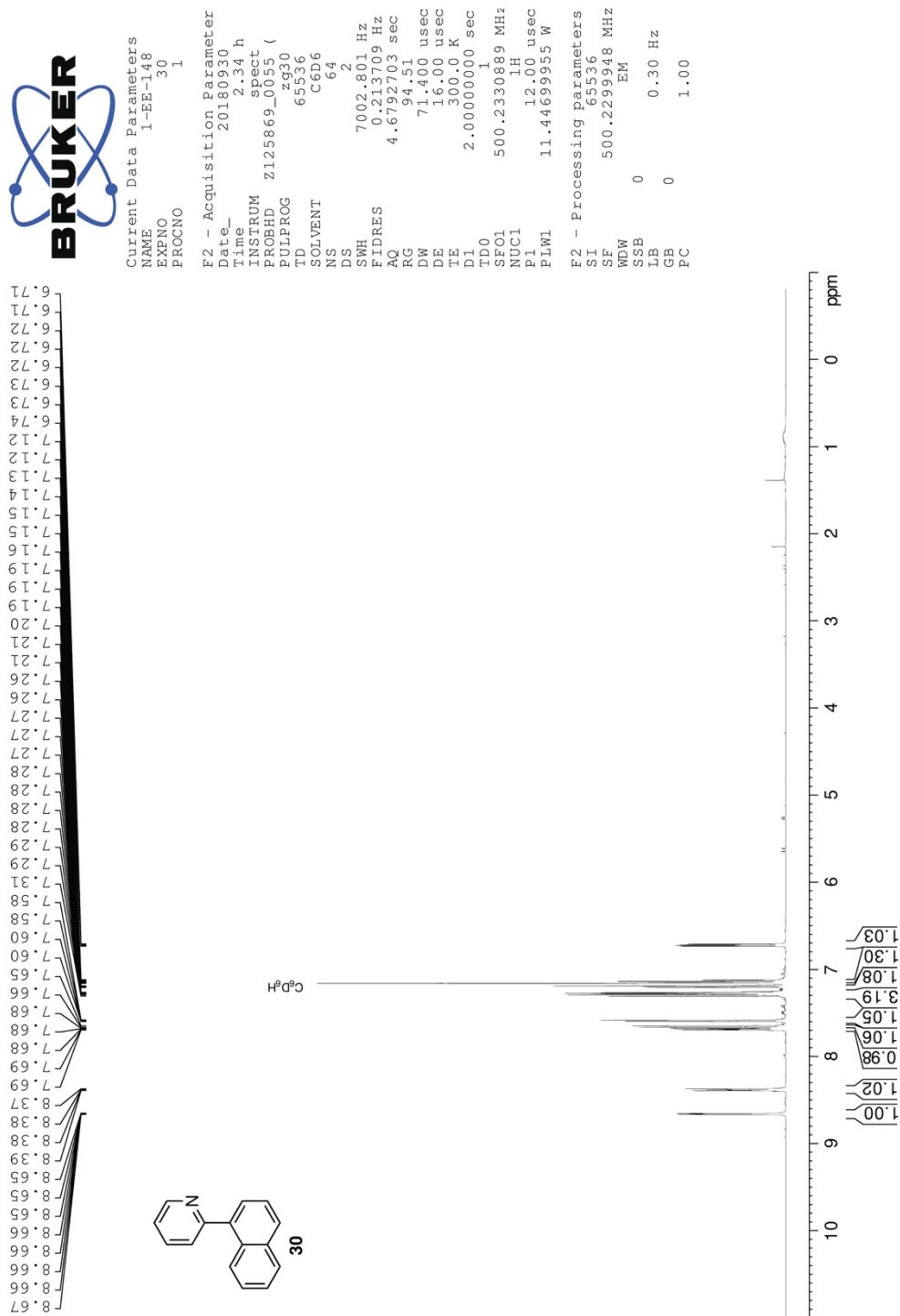


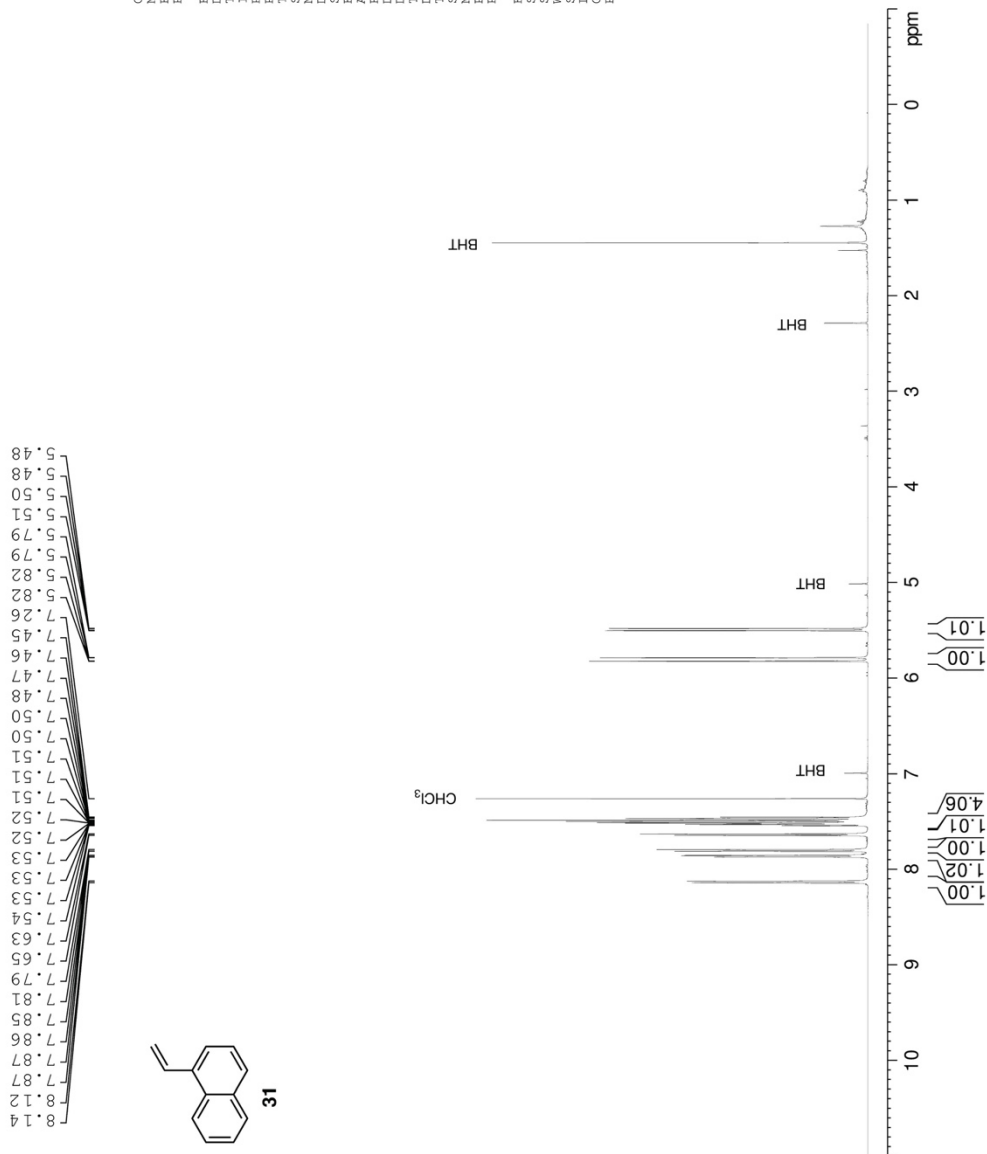


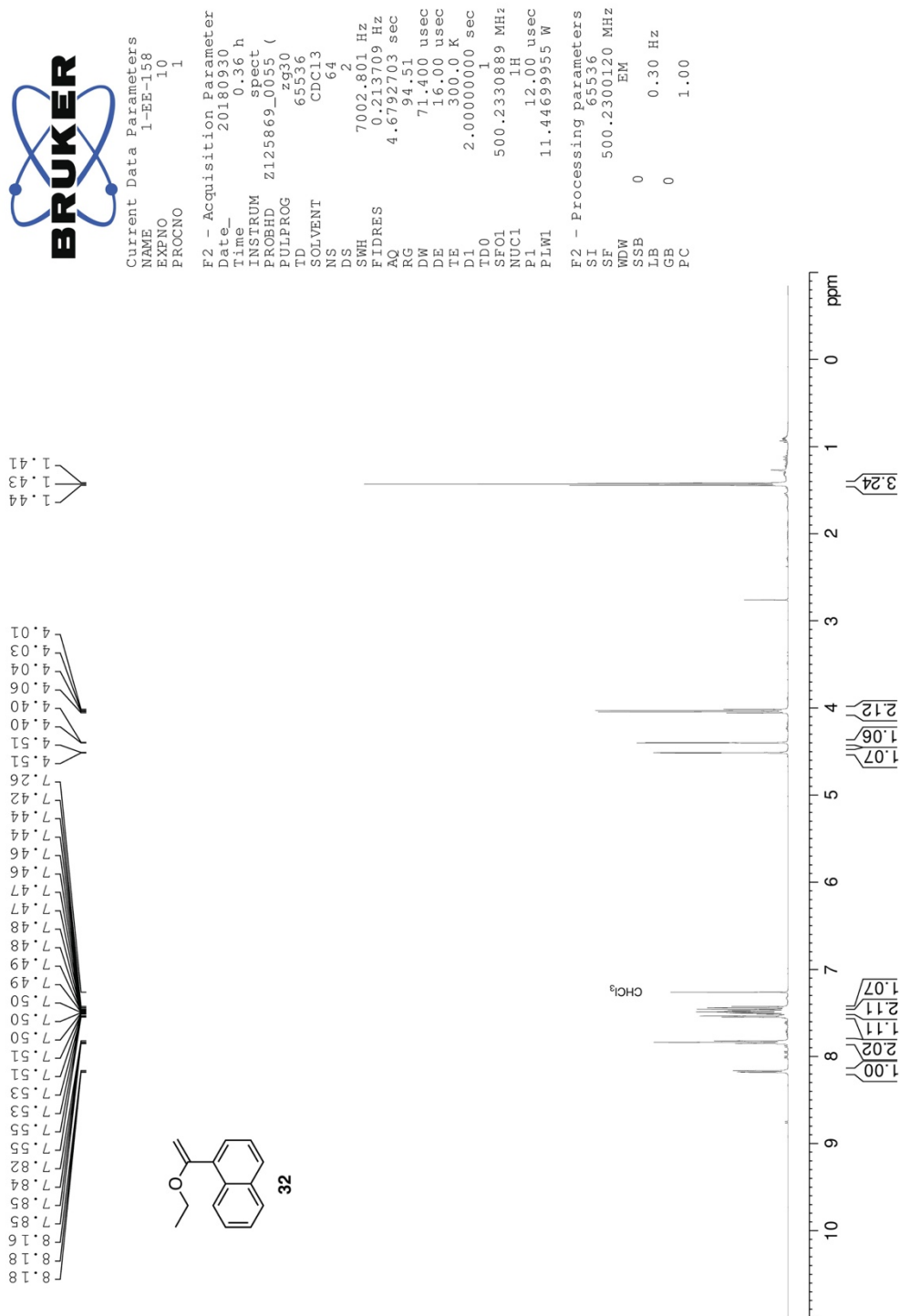


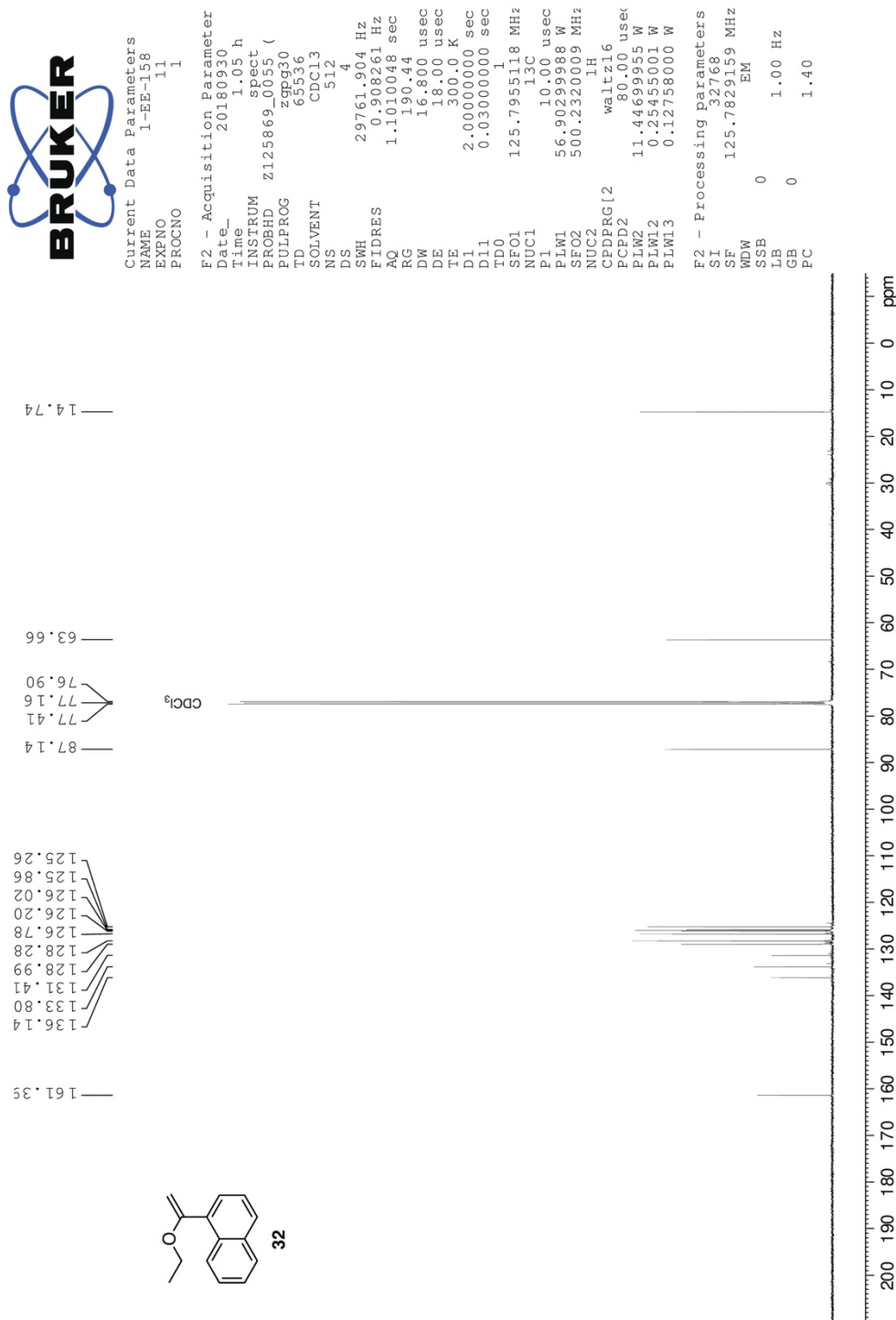


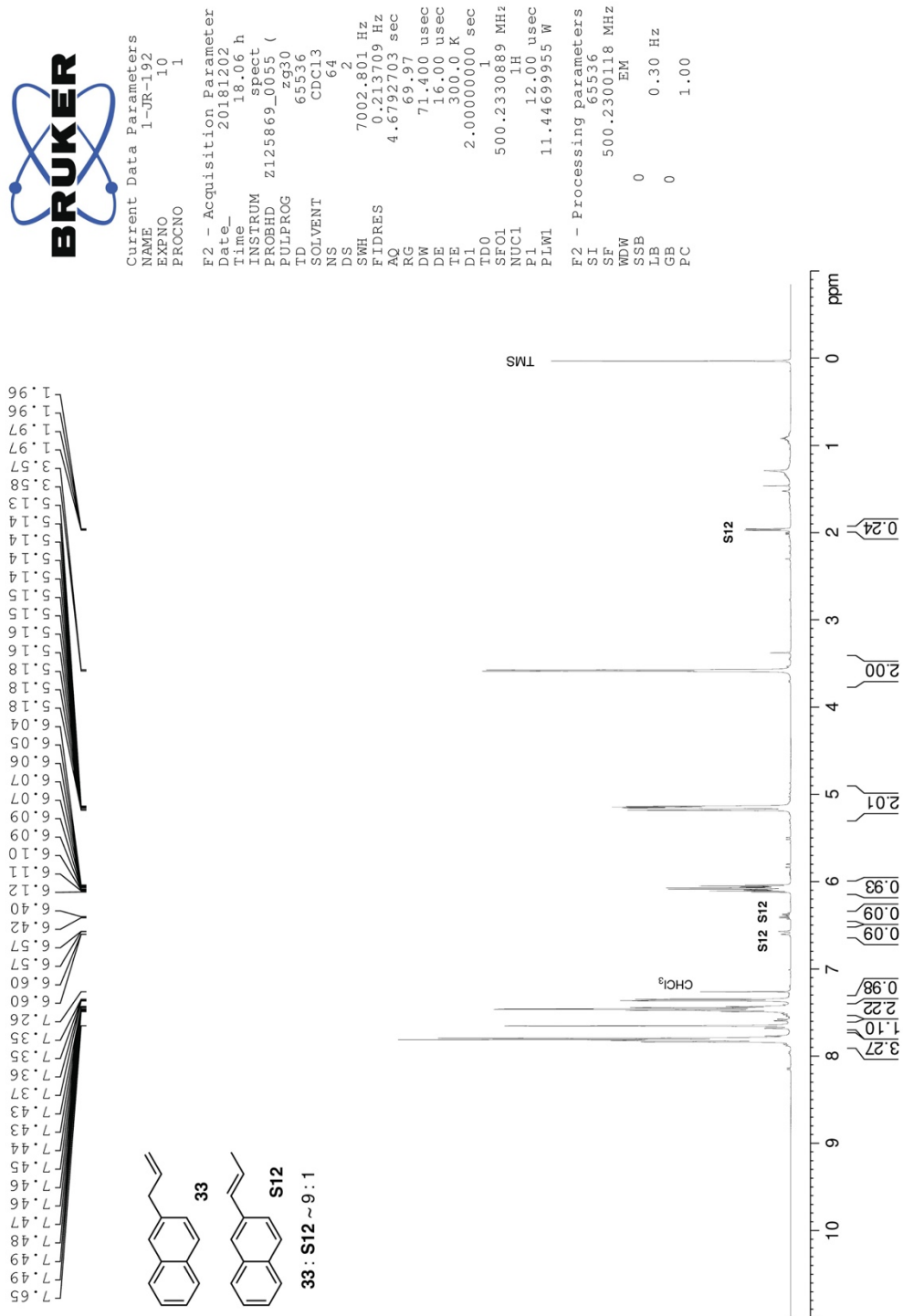


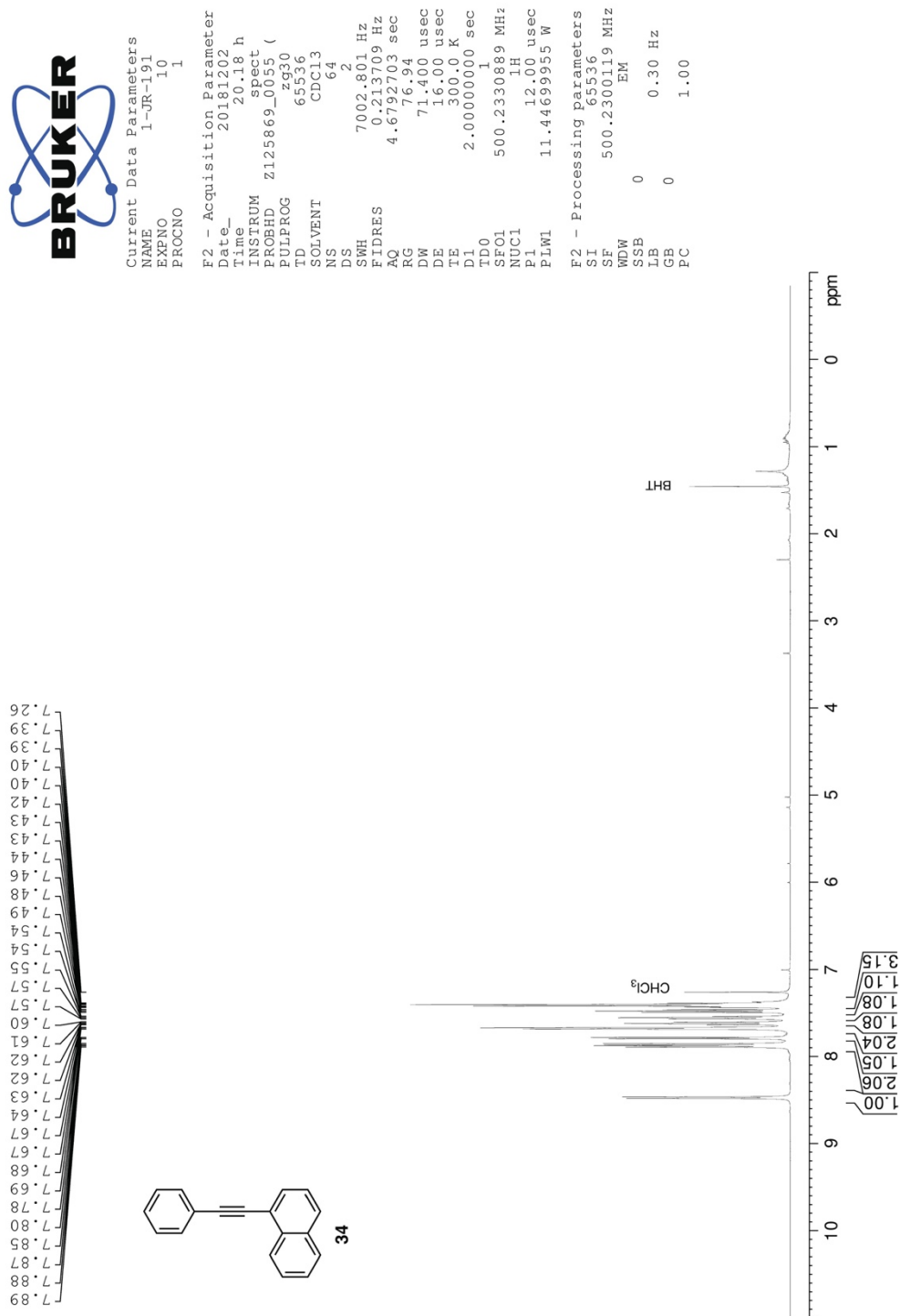


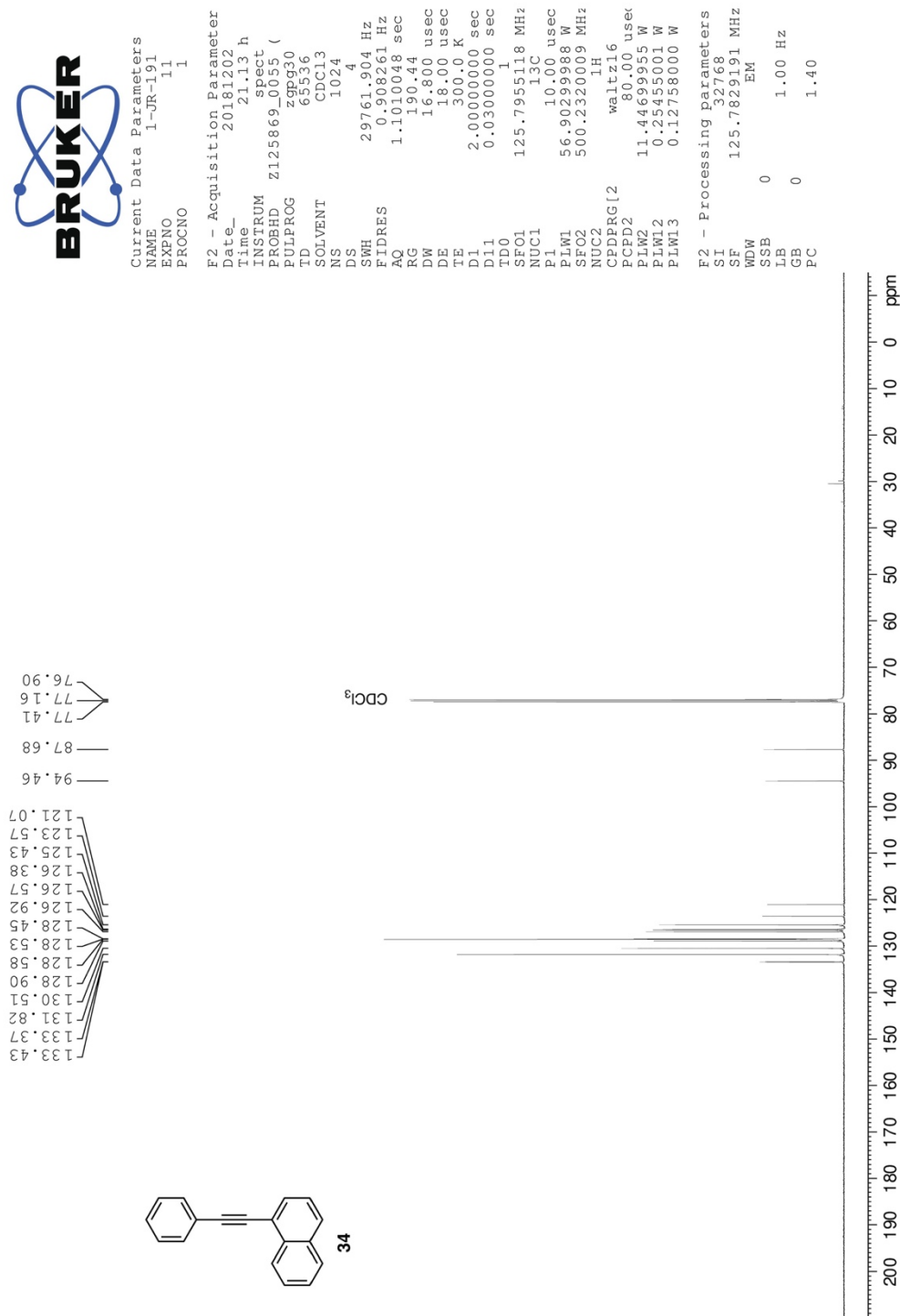




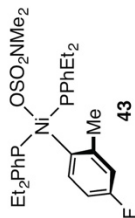
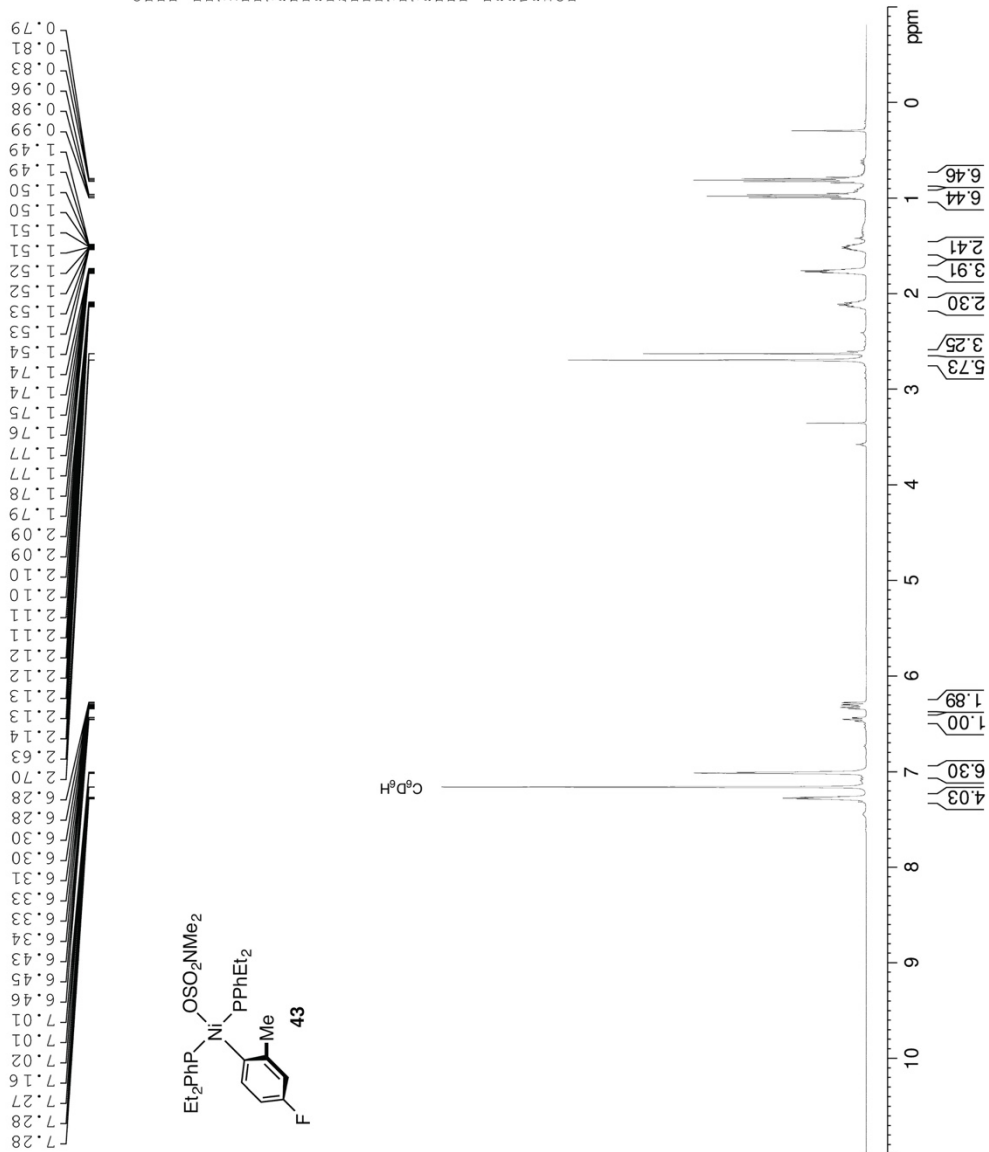


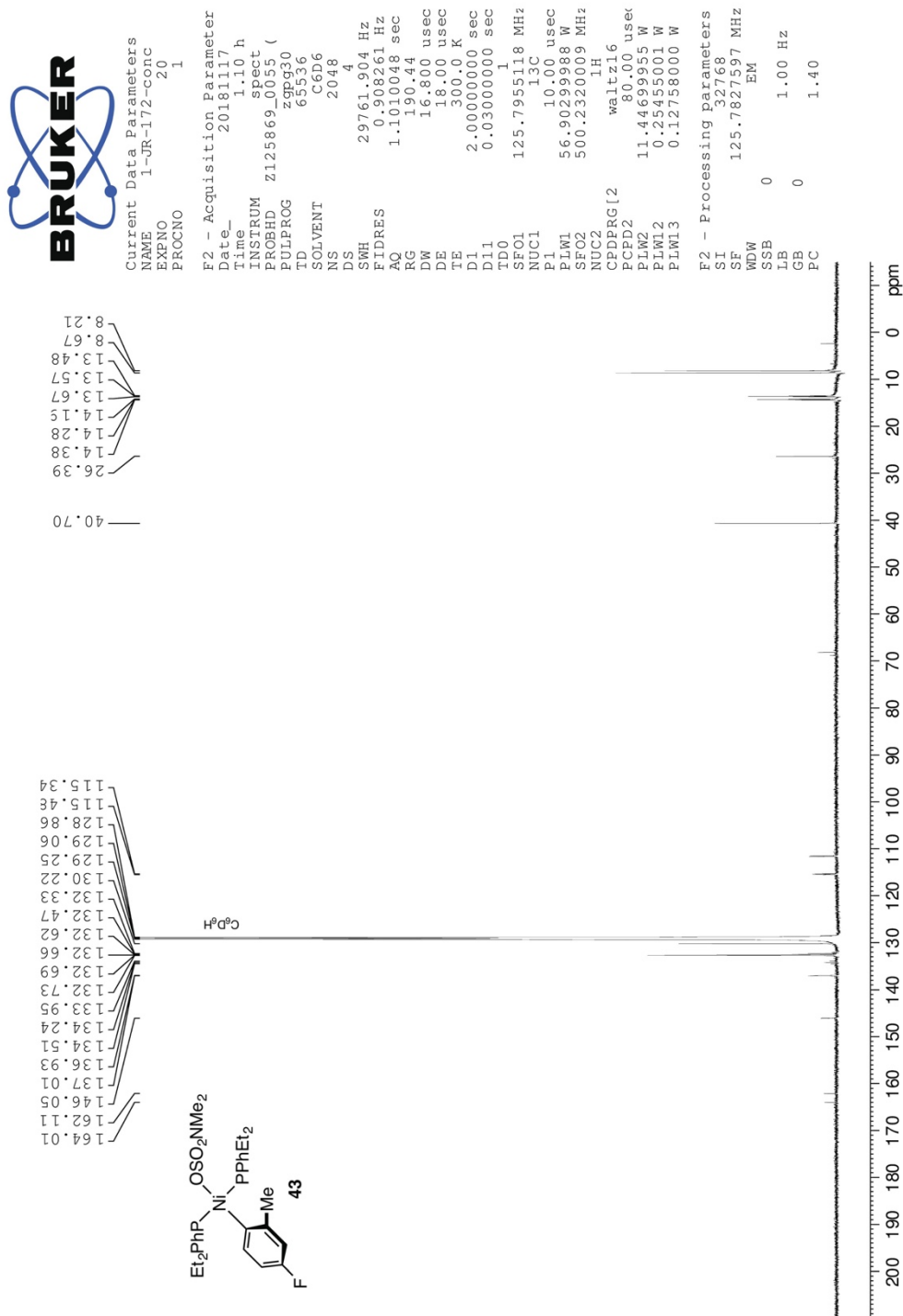


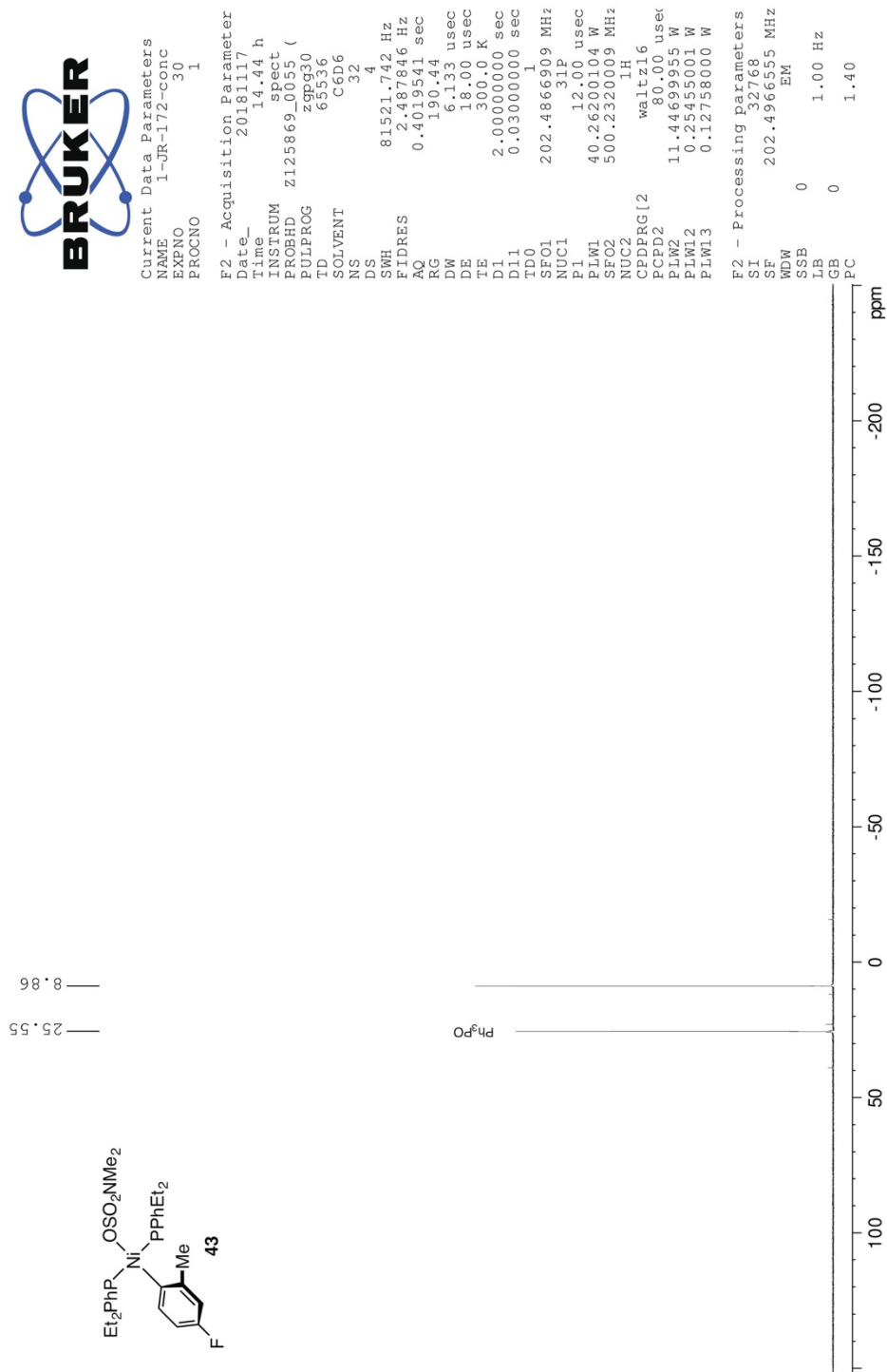


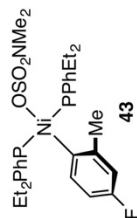


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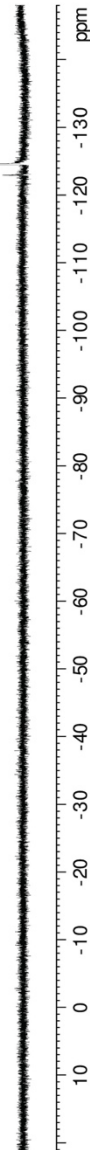


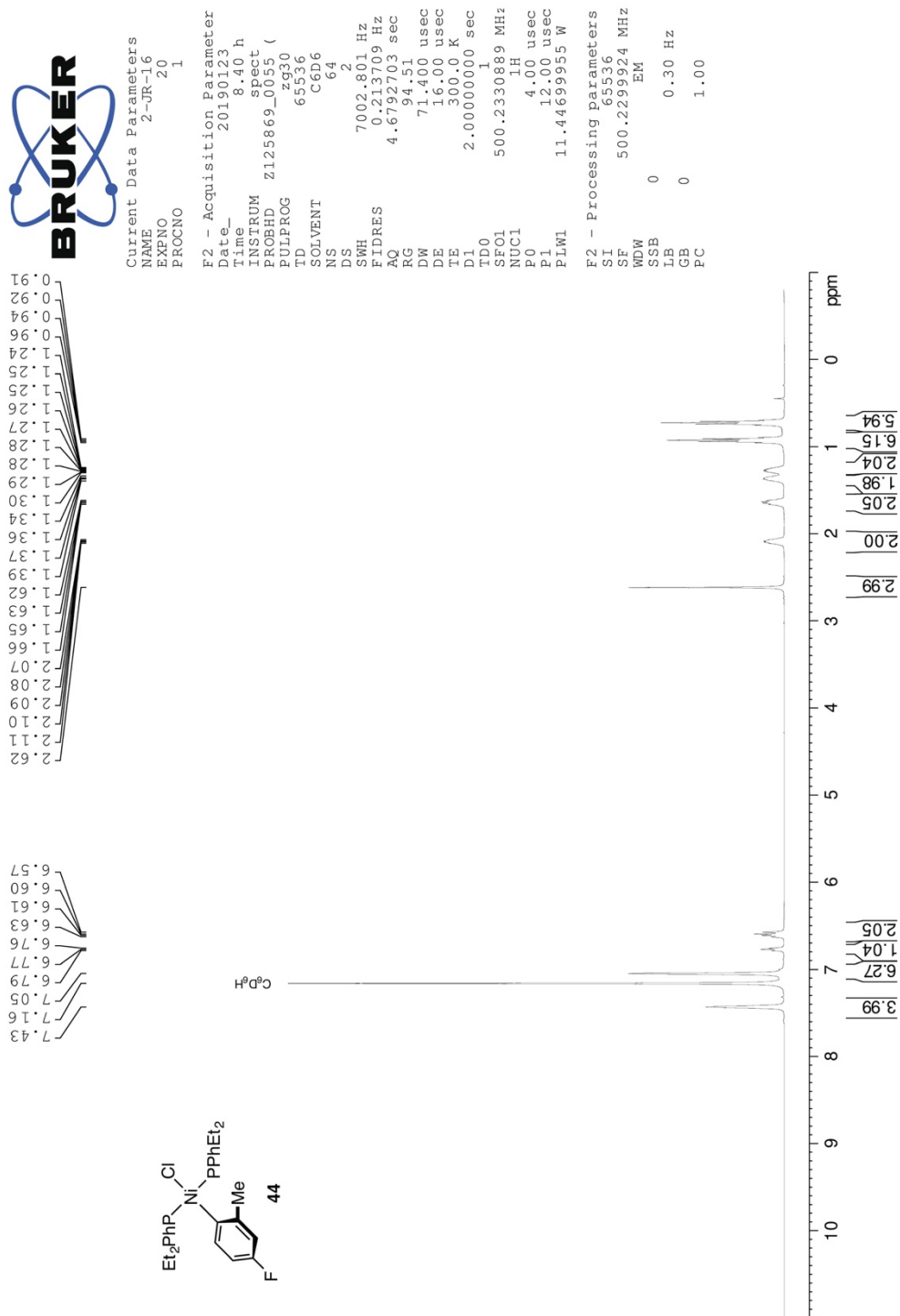


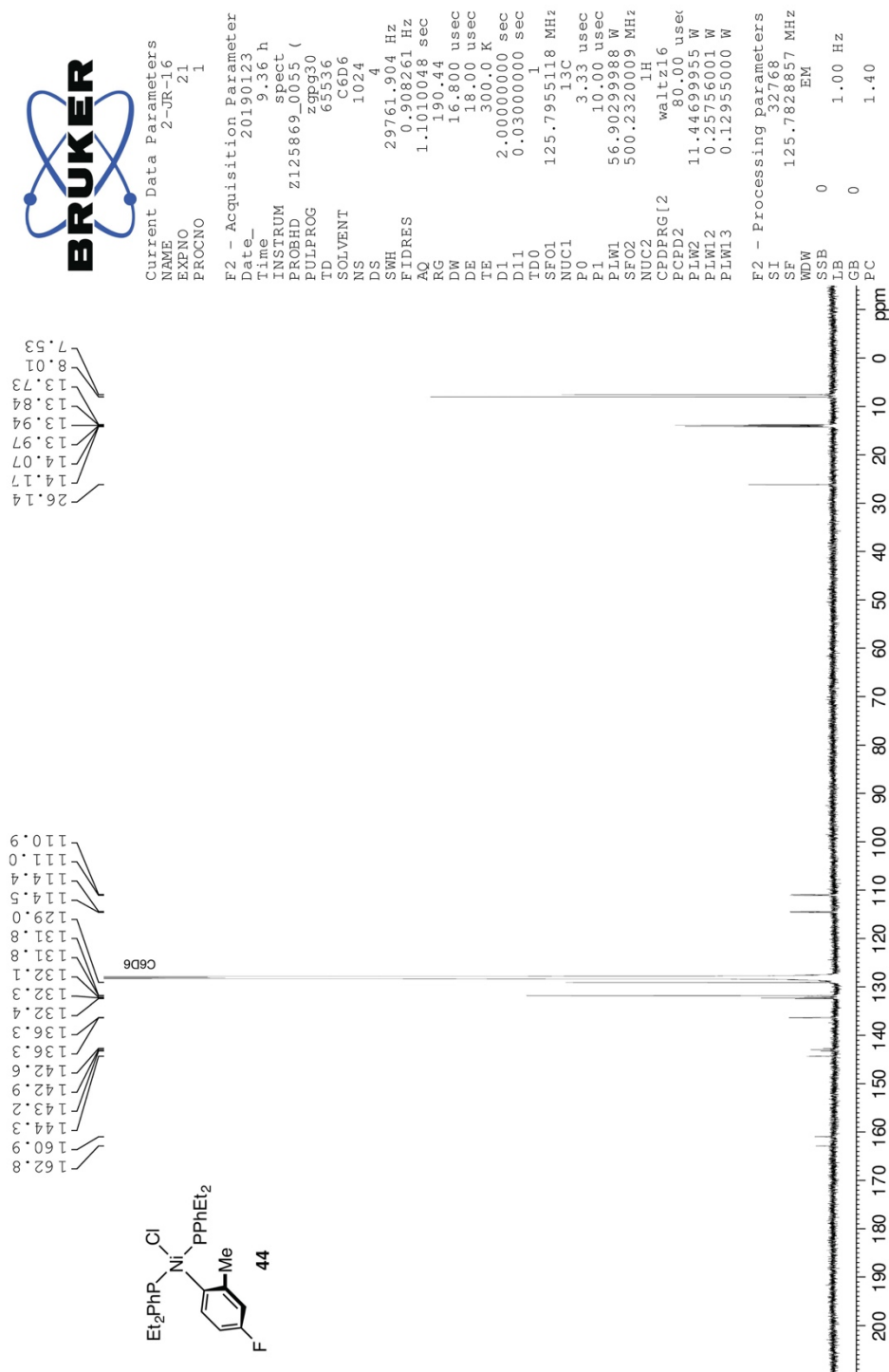




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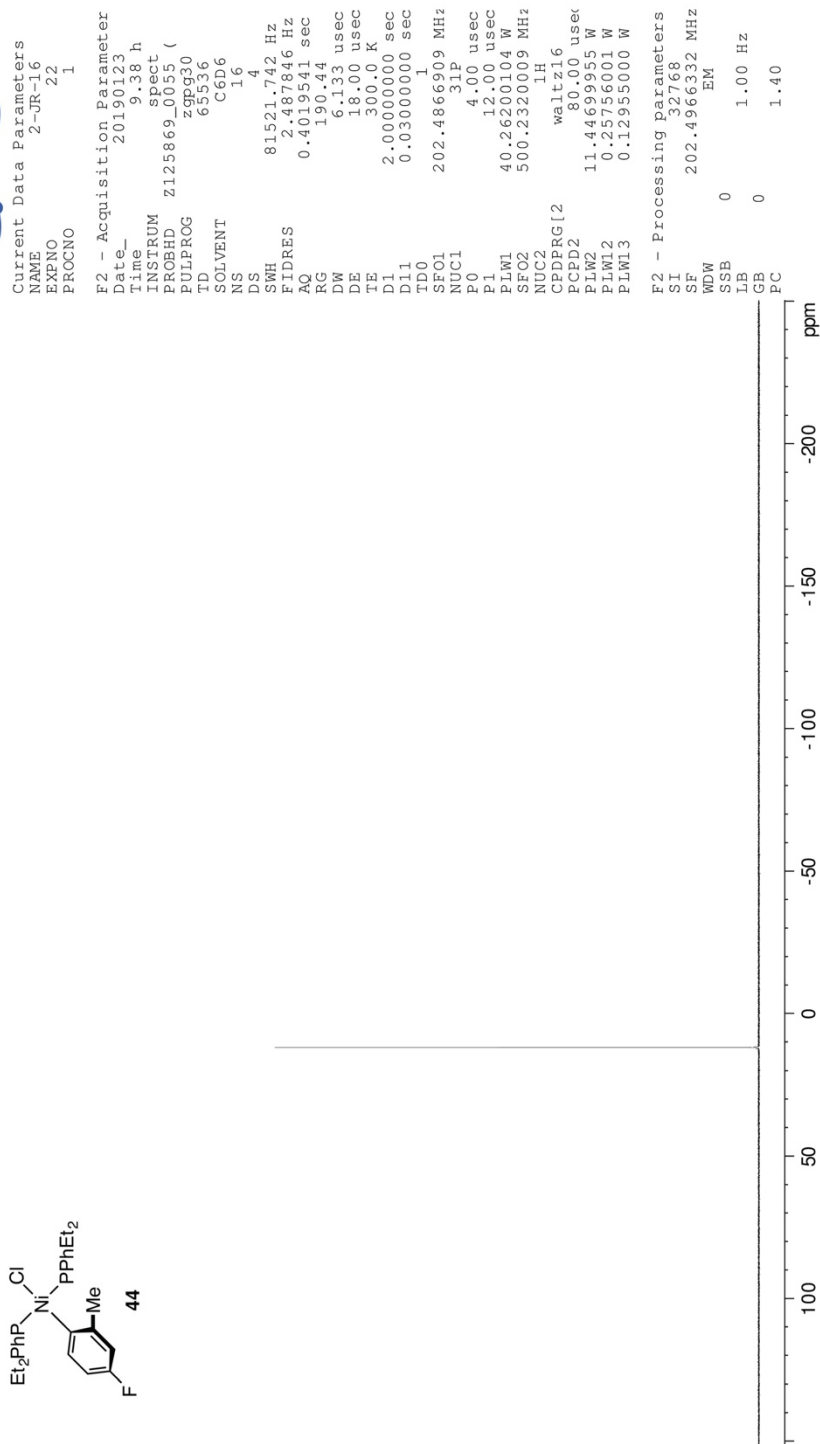
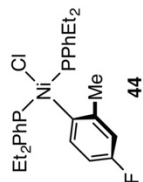








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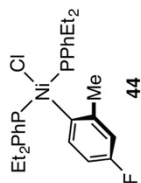
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ppm

APPENDIX B

CHAPTER THREE SUPPLEMENTAL

Supporting Information

for

Small Phosphine Ligands Enable Selective Oxidative Addition of Ar—O over Ar—Cl Bonds at Nickel(o)

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I. Experimental Details

A. General Materials and Methods

NMR spectra were recorded at 298 K on a Bruker Ascend Avance III HD 500 MHz (500.233 MHz for ^1H , 125.795 MHz for ^{13}C , or 202.487 MHz for ^{31}P), a Bruker DPX Avance I 300 MHz (121.511 MHz for ^{31}P or 282.425 MHz for ^{19}F), or a Bruker Avance III 600 MHz (600.130 MHz for ^1H or 150.903 MHz for ^{13}C) spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference [^1H : CHCl_3 (7.26 ppm), $\text{CD}_3(\text{CO})\text{CHD}_2$ (2.05 ppm) or $\text{C}_6\text{D}_5\text{H}$ (7.16 ppm); ^{13}C : CDCl_3 (77.16 ppm) or C_6D_6 (128.06 ppm)].¹ ^{31}P NMR chemical shifts are reported in ppm relative to phosphoric acid, with Ph_3PO used as an internal reference (24.95 ppm in C_6D_6). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), quintet (quint), multiplet (m), and broad resonance (br). GC data were collected using a Shimadzu GC-2010 Plus with a flame ionization detector equipped with a SH-Rxi-5ms capillary column (15 m x 0.25 mm ID x 0.25 μm df). HRMS data were collected on a Bruker Impact II (Q-TOF), a Waters GCT Premier HR-TOF, a Bruker MicroTOF, or a Bruker MicroTOF II.

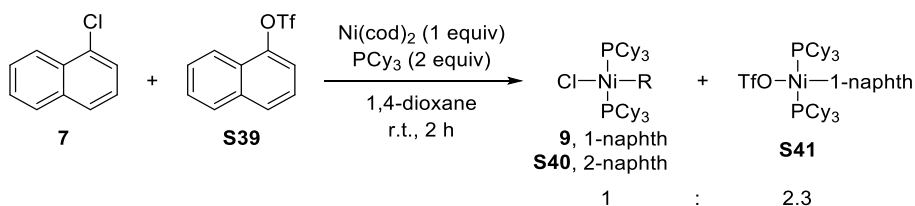
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chloride were made according to a literature procedure.⁸ Authentic samples of oxidative addition adducts **9** and **10** were made according to a literature procedure.⁹ An authentic sample of $\text{Ni}(\text{PMe}_3)_4$ was made according to a literature procedure.¹⁰ Flash column chromatography was performed on SiliCycle silica gel 60 (40-63 μm particle size) and thin layer chromatography was performed on SiliCycle TLC plates pre-coated with extra hard silica gel 60 F₂₅₄.

B. Stoichiometric Oxidative Addition Studies.

1. Intermolecular Competition Studies

General Procedure. In a nitrogen-atmosphere glovebox, a stock solution containing $\text{Ni}(\text{cod})_2$ and phosphine in a 1:2 ratio was prepared in 1,4-dioxane in a one-dram vial equipped with a magnetic stir bar (0.02 M with respect to $\text{Ni}(\text{cod})_2$). The solution was stirred until all solids were dissolved (typically about 10 min). To a second one-dram vial equipped with a stir bar was added 1-naphthyl chloride (85% purity; the balance is 2-naphthyl chloride, 2.7 μL , 0.02 mmol, 1.0 equiv) and/or phenolic electrophile (0.02 mmol, 1.0 equiv) and 1 mL of the Ni/phosphine stock solution (0.02 mmol, 1.0 equiv of Ni and 0.04 mmol, 2.0 equiv of PR_3). The vial was then sealed with a PTFE-lined cap and stirred at room temperature for 2 h. 500 μL of the reaction mixture was then transferred to an NMR tube, along with a capillary tube insert containing a solution of PPh_3O in C_6D_6 (0.1 M), and the sample was analyzed by ^{31}P NMR. To obtain the spectrum of nickel(0)/phosphine in the absence of substrate, an aliquot (500 μL) of the $\text{Ni}(\text{cod})_2$ /phosphine stock solution (after stirring for 2 hours) was transferred to an NMR tube, along with a capillary tube insert containing a solution of PPh_3O in C_6D_6 (0.1 M), and the sample was analyzed by ^{31}P NMR. When appropriate, the location of a ^{31}P NMR signal for $\text{Ni}(\text{II})(2\text{-naphthyl})(\text{Cl})$ resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was confirmed by the separate reaction of a $\text{Ni}(\text{cod})_2$ /phosphine solution with authentic 2-chloronaphthalene.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Triflate with PCy₃. The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl triflate (5.5 mg), and a Ni(cod)₂/PCy₃ stock solution. Reactions were analyzed by ³¹P{¹H} NMR (203 or 122 MHz, 1,4-dioxane). The signal at 46.0 ppm is assigned to a Ni(o)/PCy₃ adduct (Figure S1, spectrum A). The signal at 9.9 ppm corresponds to free PCy₃. The signals at 11.9 and 10.5 ppm are assigned to oxidative addition adducts **9** and **S41**, respectively (spectra B-D). Product **S40** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at 12.9 ppm in spectrum B. In the competition experiment (spectrum D), only a very small amount of **S40** was detected, and it was integrated together with **9** to obtain a ratio of oxidative addition of C—Cl to C—O of 1 : 2.3.

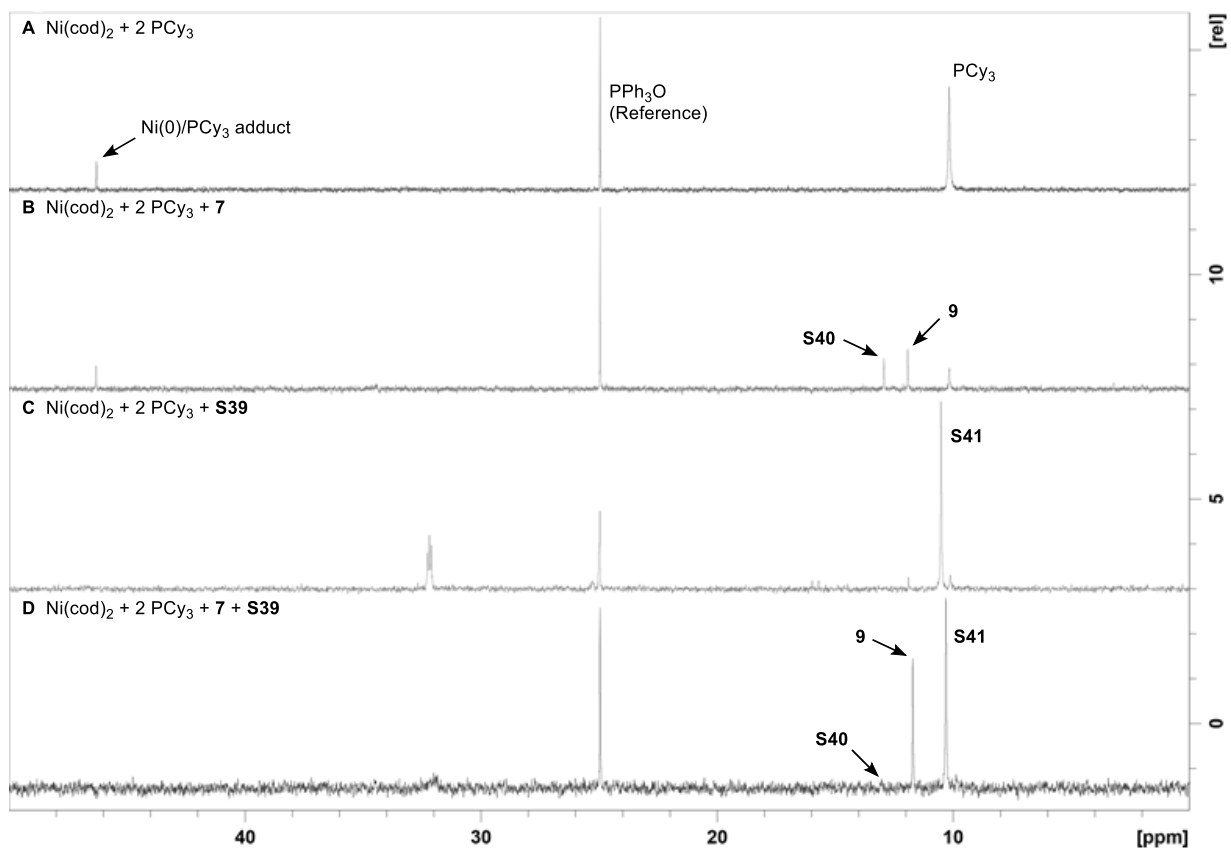
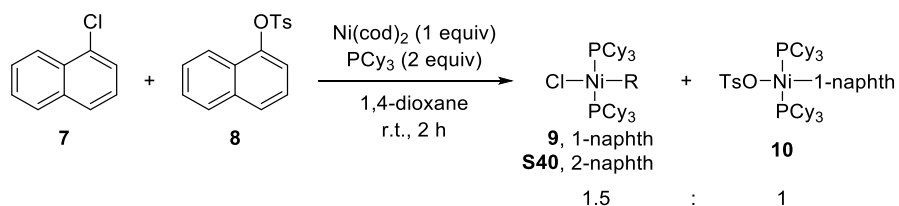


Figure S1. ³¹P NMR studies on oxidative addition at Ni/PCy₃ using 1-chloronaphthalene and 1-naphthyl triflate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Tosylate with PCy_3 . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a $\text{Ni(cod)}_2/\text{PCy}_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 46.0 ppm is assigned to a $\text{Ni(0)}/\text{PCy}_3$ adduct (Figure S2, spectrum A). The signal at 9.9 ppm corresponds to free PCy_3 . The signals at 11.9 and 10.9 ppm are assigned to oxidative addition adducts **9** and **10**, respectively (spectra B-D). Product **S40** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at 12.9 ppm in spectrum B. In the competition experiment (spectrum D), only a very small amount of **S40** was detected, and it was integrated together with **9** to obtain a ratio of oxidative addition of C—Cl to C—O of 1.5 : 1.

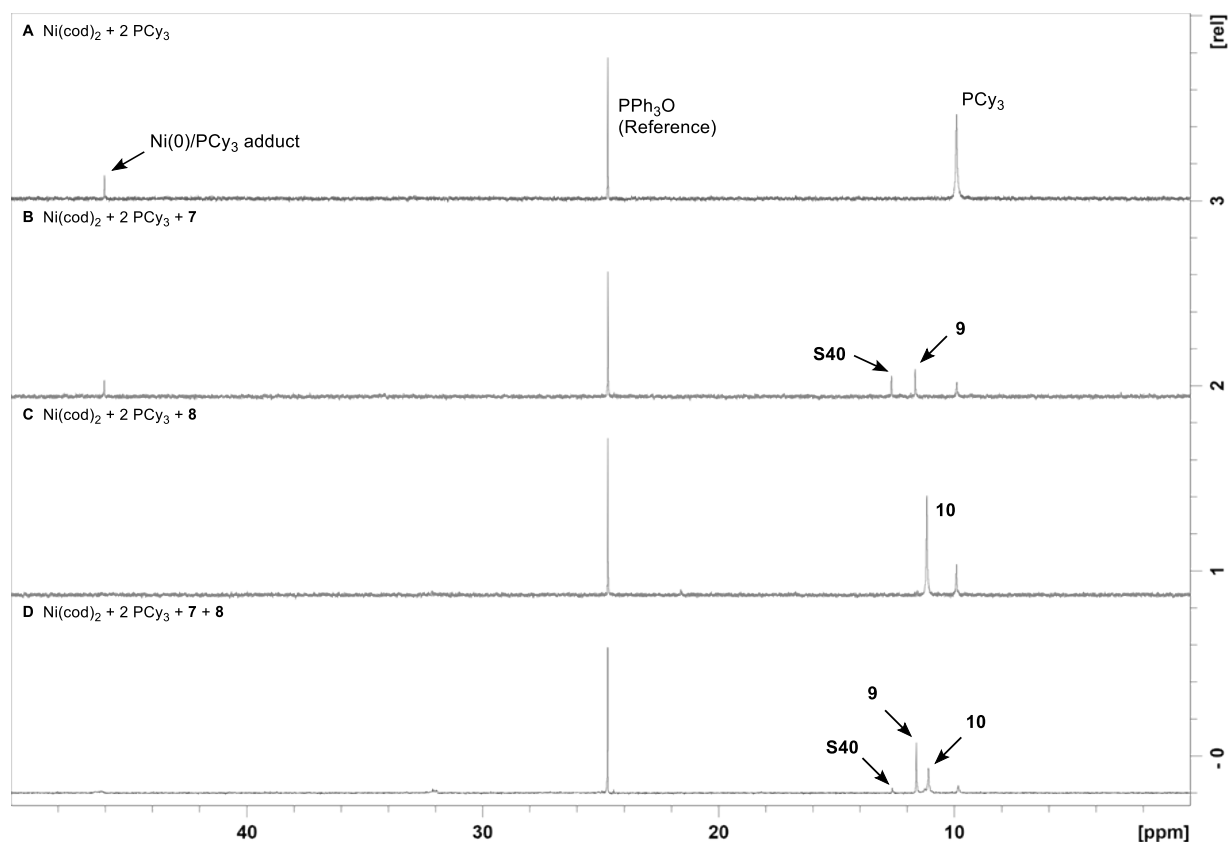
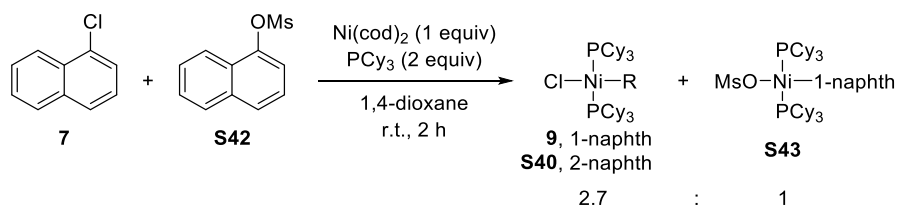


Figure S2. ^{31}P NMR studies on oxidative addition at Ni/PCy_3 using 1-chloronaphthalene and 1-naphthyl tosylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Mesylate with PCy₃. The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl mesylate (4.5 mg), and a Ni(cod)₂/PCy₃ stock solution. Reactions were analyzed by ³¹P{¹H} NMR (203 or 122 MHz, 1,4-dioxane). The signal at 46.0 ppm is assigned to a Ni(o)/PCy₃ adduct (Figure S3, spectrum A). The signal at 9.9 ppm corresponds to free PCy₃. The signals at 11.9 and 10.1 ppm are assigned to oxidative addition adducts **9** and **S43**, respectively (spectra B-D). Product **S40** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at 12.9 ppm in spectrum B. In the competition experiment (spectrum D), only a very small amount of **S40** was detected, and it was integrated together with **9** to obtain a ratio of oxidative addition of C–Cl to C–O of about 2.7 : 1 (some error is likely introduced into this ratio because the signal for **S43** partially overlaps with that of free PCy₃, making it difficult to accurately integrate the signal for **S43**).

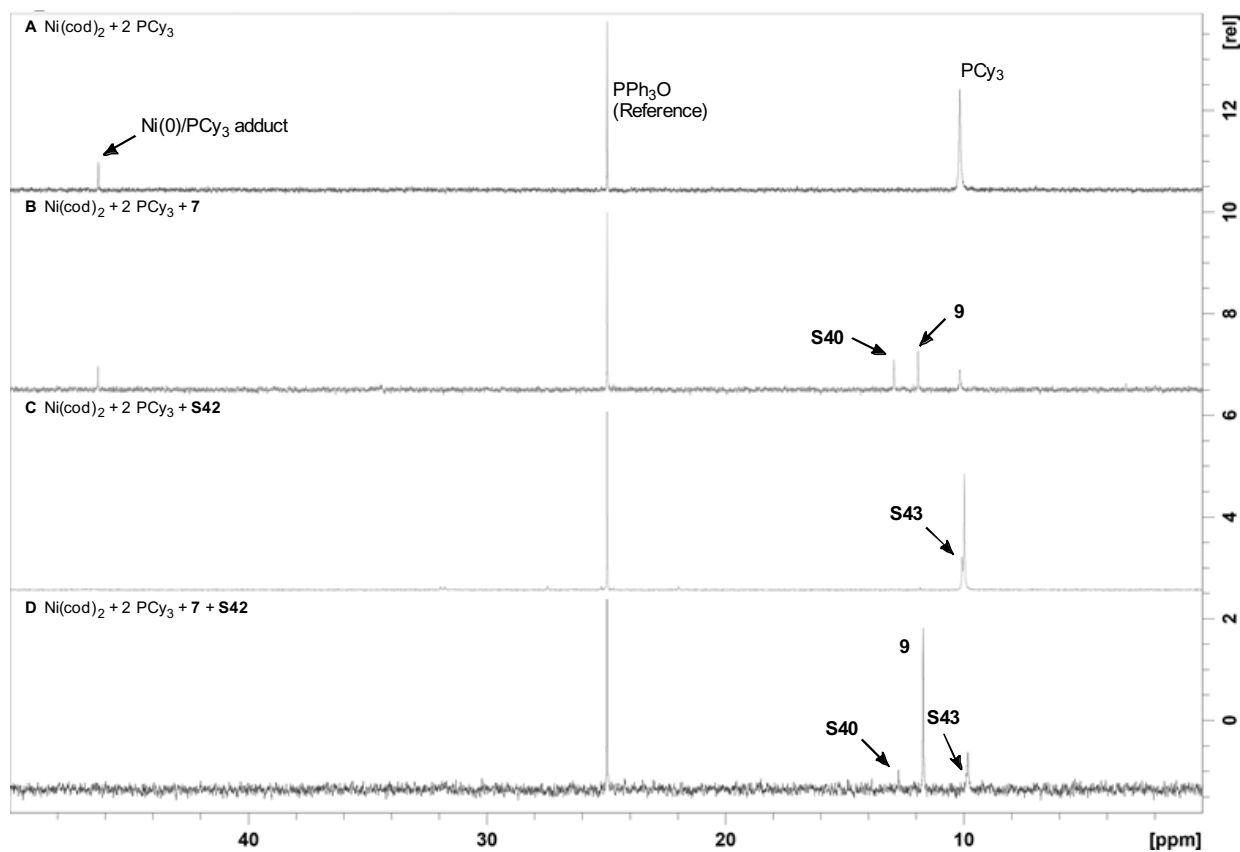
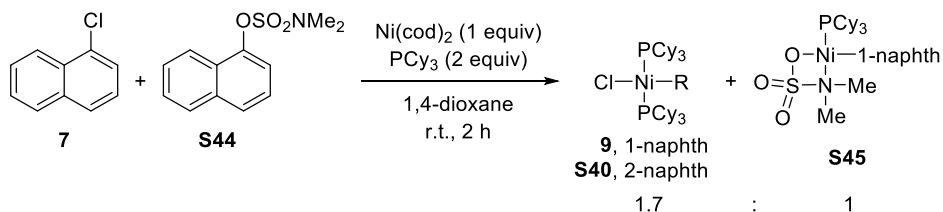


Figure S3. ³¹P NMR studies on oxidative addition at Ni/PCy₃ using 1-chloronaphthalene and 1-naphthyl mesylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Dimethylsulfamate with PCy₃.

The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl dimethylsulfamate (5.0 mg), and a Ni(cod)₂/PCy₃ stock solution. Reactions were analyzed by ³¹P{¹H} NMR (203 or 122 MHz, 1,4-dioxane). The signal at 46.0 ppm is assigned to a Ni(o)/PCy₃ adduct (Figure S4, spectrum A). The signal at 9.9 ppm corresponds to free PCy₃. The signals at 11.9 and 33.4 ppm are assigned to oxidative addition adducts **9** and **S45**, respectively (spectra B-D). The structural assignment of **S45** was made by analogy to a previously reported closely related complex resulting from oxidative addition of an aryl sulfamate at Ni(cod)₂/PCy₃.¹¹ Product **S40** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at 12.9 ppm in spectrum B. In the competition experiment (spectrum D), a small amount of **S40** was detected, and it was integrated together with **9** to obtain a ratio of oxidative addition of C—Cl to C—O of 1.7 : 1.

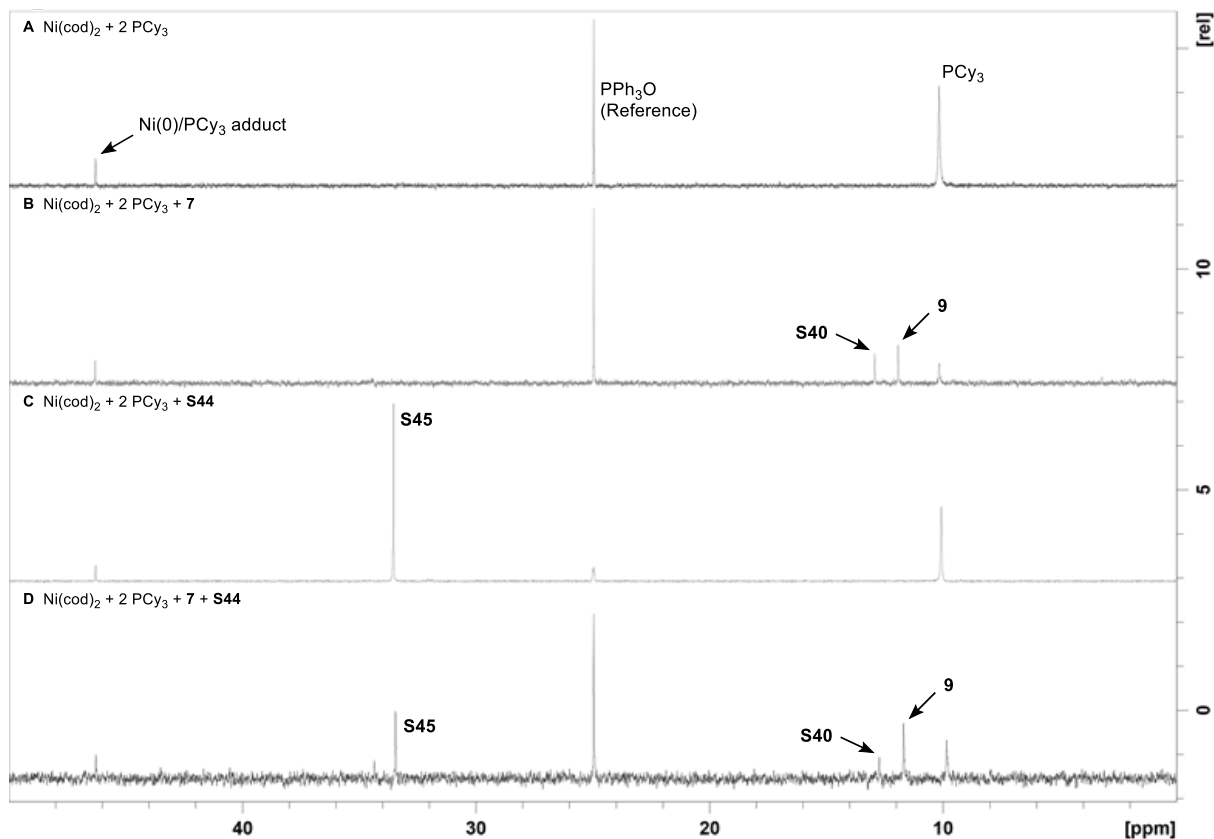
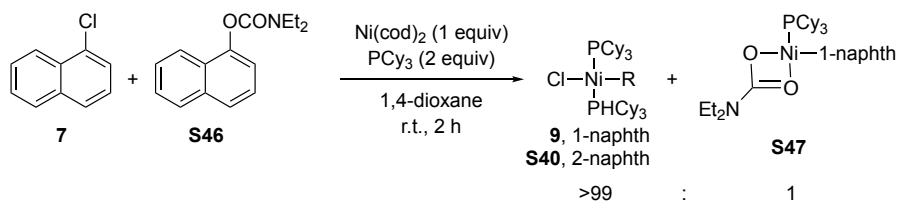


Figure S4. ³¹P NMR studies on oxidative addition at Ni/PCy₃ using 1-chloronaphthalene and 1-naphthyl dimethylsulfamate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Diethylcarbamate with PCy₃.

The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl diethylcarbamate (4.9 mg), and a Ni(cod)₂/PCy₃ stock solution. Reactions were analyzed by ³¹P{¹H} NMR (203 or 122 MHz, 1,4-dioxane). The signal at 46.0 ppm is assigned to a Ni(O)/PCy₃ adduct (Figure S5, spectrum A). The signal at 9.9 ppm corresponds to free PCy₃. The signal at 11.9 is assigned to oxidative addition adduct **9** (spectrum B). Product **S40** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at 12.9 ppm in spectrum B. A new signal at 21.9 ppm was observed in the non-competition experiment with **S46** (spectrum C) that is tentatively assigned to **S47**. However, this signal was not detected in the competition experiment (spectrum D); instead, only products **9** and **S40** were observed, leading to an estimated ratio of oxidative addition of C—Cl to C—O of >99 : 1.

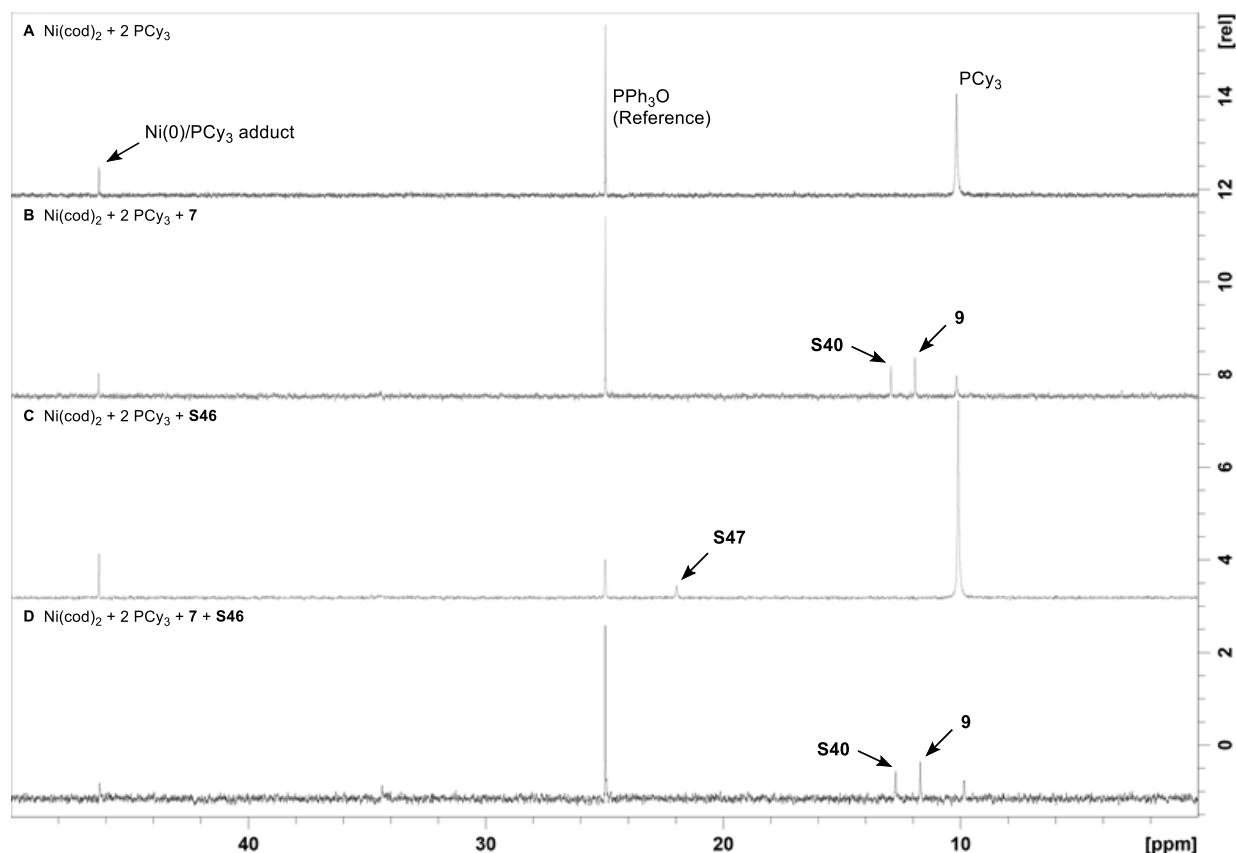
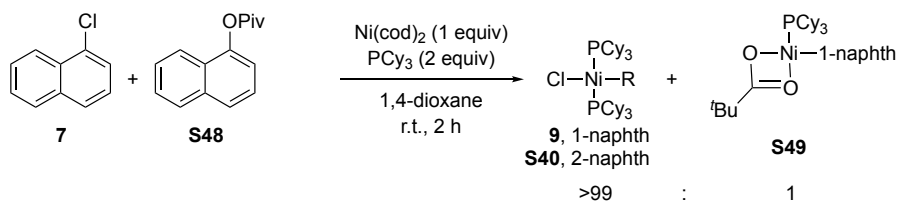


Figure S5. ³¹P NMR studies on oxidative addition at Ni/PCy₃ using 1-chloronaphthalene and 1-naphthyl diethylcarbamate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Pivalate with PCy_3 . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl pivalate (4.6 mg), and a $\text{Ni}(\text{cod})_2/\text{PCy}_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 46.0 ppm is assigned to a $\text{Ni}(\text{o})/\text{PCy}_3$ adduct (Figure S6, spectrum A). The signal at 9.9 ppm corresponds to free PCy_3 . The signal at 11.9 is assigned to oxidative addition adduct **9** (spectrum B). Product **S40** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at 12.9 ppm in spectrum B. A new signal at 22.2 ppm was observed in the non-competition experiment with **S48** (spectrum C) that is tentatively assigned to **S49**. However, this signal was not detected in the competition experiment (spectrum D); instead, only products **9** and **S40** were observed, leading to an estimated ratio of oxidative addition of C—Cl to C—O of >99 : 1.

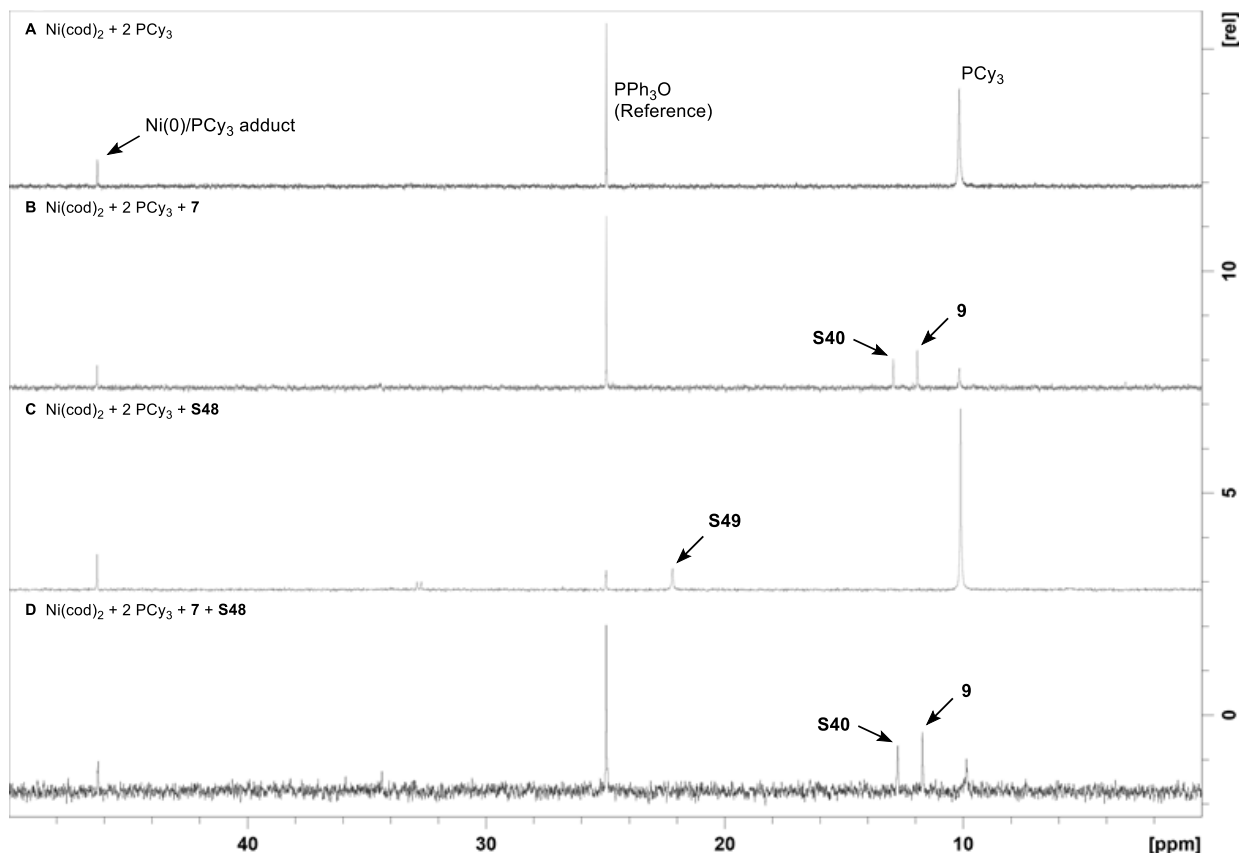
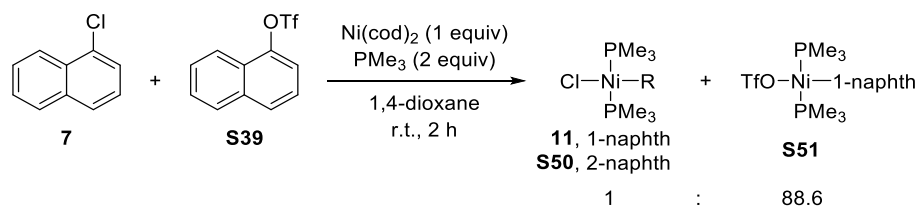


Figure S6. ^{31}P NMR studies on oxidative addition at Ni/PCy_3 using 1-chloronaphthalene and 1-naphthyl pivalate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Triflate with PMe_3 . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl triflate (5.5 mg), and a $\text{Ni(cod)}_2/\text{PMe}_3$ stock solution. Reactions were analyzed by $^3\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at -20.8 ppm corresponds to $\text{Ni(PMe}_3)_4$ (Figure S7, spectrum A). The signal at -8.4 ppm is assigned to another unidentified $\text{Ni(o)}/\text{PMe}_3$ adduct. No free PMe_3 is detected at -61.9 ppm (outside the window shown in Figure S7) in any of the spectra. The signals at -12.8 and -16.2 ppm are assigned to oxidative addition adducts **11** and **S51**, respectively (spectra B-D). A small amount of product **S50** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at -14.2 ppm in spectrum B. In the competition experiment (spectrum D), none of **S50** could be detected. The ratio of oxidative addition of C—Cl to C—O in spectrum D is 1 : 88.6.

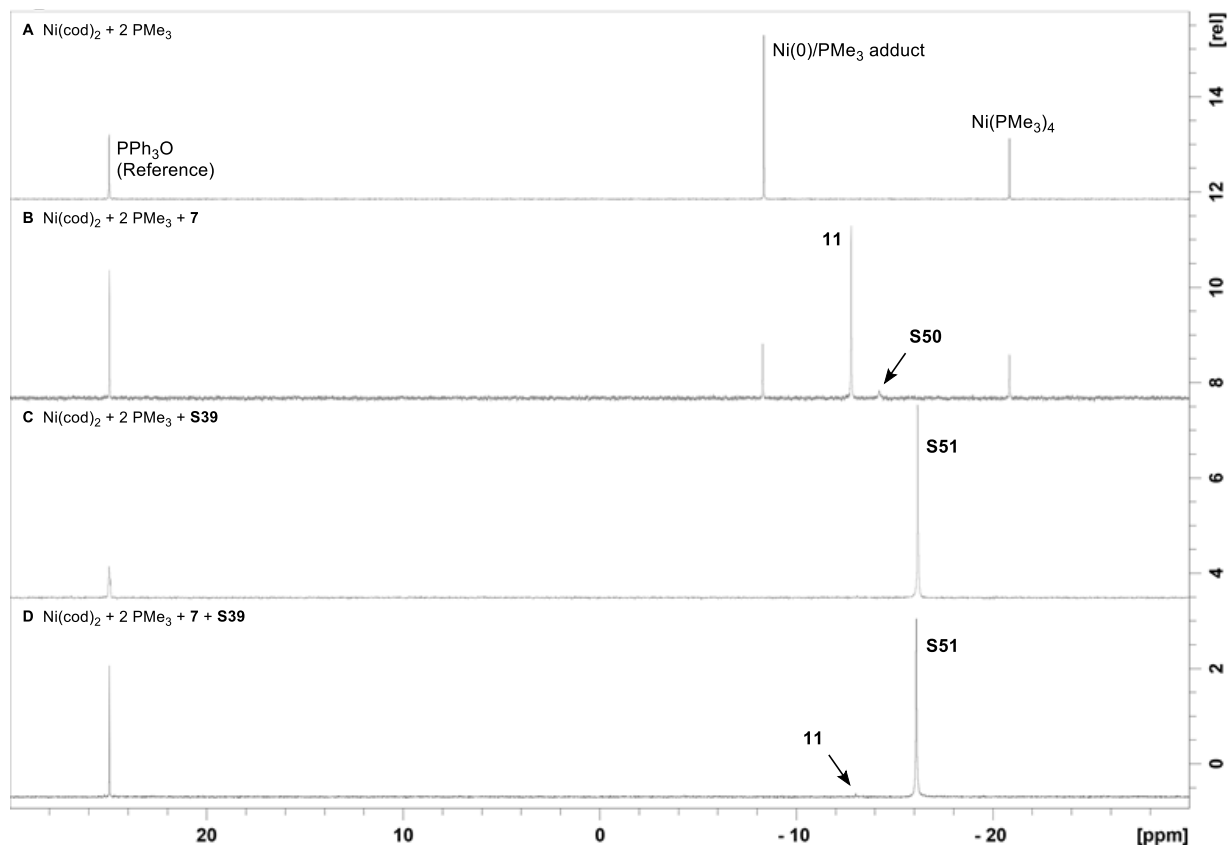
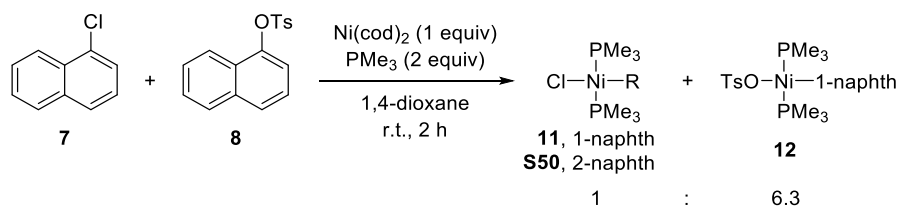


Figure S7. ^{31}P NMR studies on oxidative addition at Ni/PMe_3 using 1-chloronaphthalene and 1-naphthyl triflate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Tosylate with PMe_3 . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a $\text{Ni}(\text{cod})_2/\text{PMe}_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at -20.8 ppm corresponds to $\text{Ni}(\text{PMe}_3)_4$ (Figure S8, spectrum A). The signal at -8.4 ppm is assigned to another unidentified $\text{Ni}(\text{o})/\text{PMe}_3$ adduct. No free PMe_3 is detected at -61.9 ppm (outside the window shown in Figure S8) in any of the spectra. The signals at -12.8 and -15.6 ppm are assigned to oxidative addition adducts **11** and **12**, respectively (spectra B-D). A small amount of product **S50** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at -14.2 ppm in spectrum B. In the competition experiment (spectrum D), none of **S50** could be detected. The ratio of oxidative addition of C—Cl to C—O in spectrum D is 1 : 6.3.

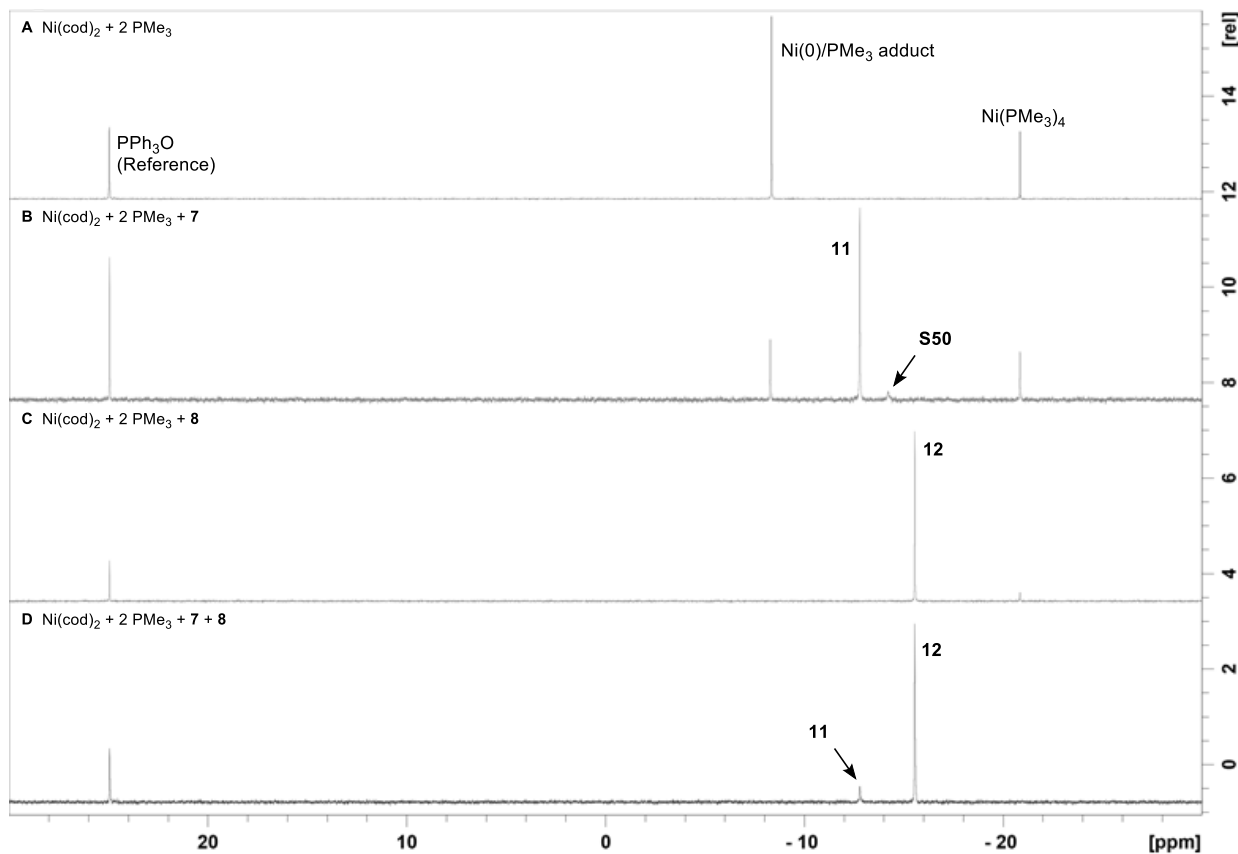
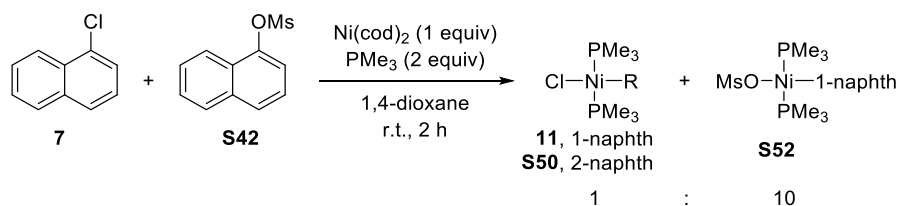


Figure S8. ^{31}P NMR studies on oxidative addition at Ni/PMe_3 using 1-chloronaphthalene and 1-naphthyl tosylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Mesylate with PMe_3 . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl mesylate (4.5 mg), and a $\text{Ni(cod)}_2/\text{PMe}_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at -20.8 ppm corresponds to $\text{Ni(PMe}_3)_4$ (Figure S9, spectrum A). The signal at -8.4 ppm is assigned to another unidentified $\text{Ni(o)}/\text{PMe}_3$ adduct. No free PMe_3 is detected at -61.9 ppm (outside the window shown in Figure S9) in any of the spectra. The signals at -12.8 and -15.4 ppm are assigned to oxidative addition adducts **11** and **S52**, respectively (spectra B-D). A small amount of product **S50** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at -14.2 ppm in spectrum B. In the competition experiment (spectrum D), none of **S50** could be detected. The ratio of oxidative addition of C—Cl to C—O in spectrum D is 1 : 10.

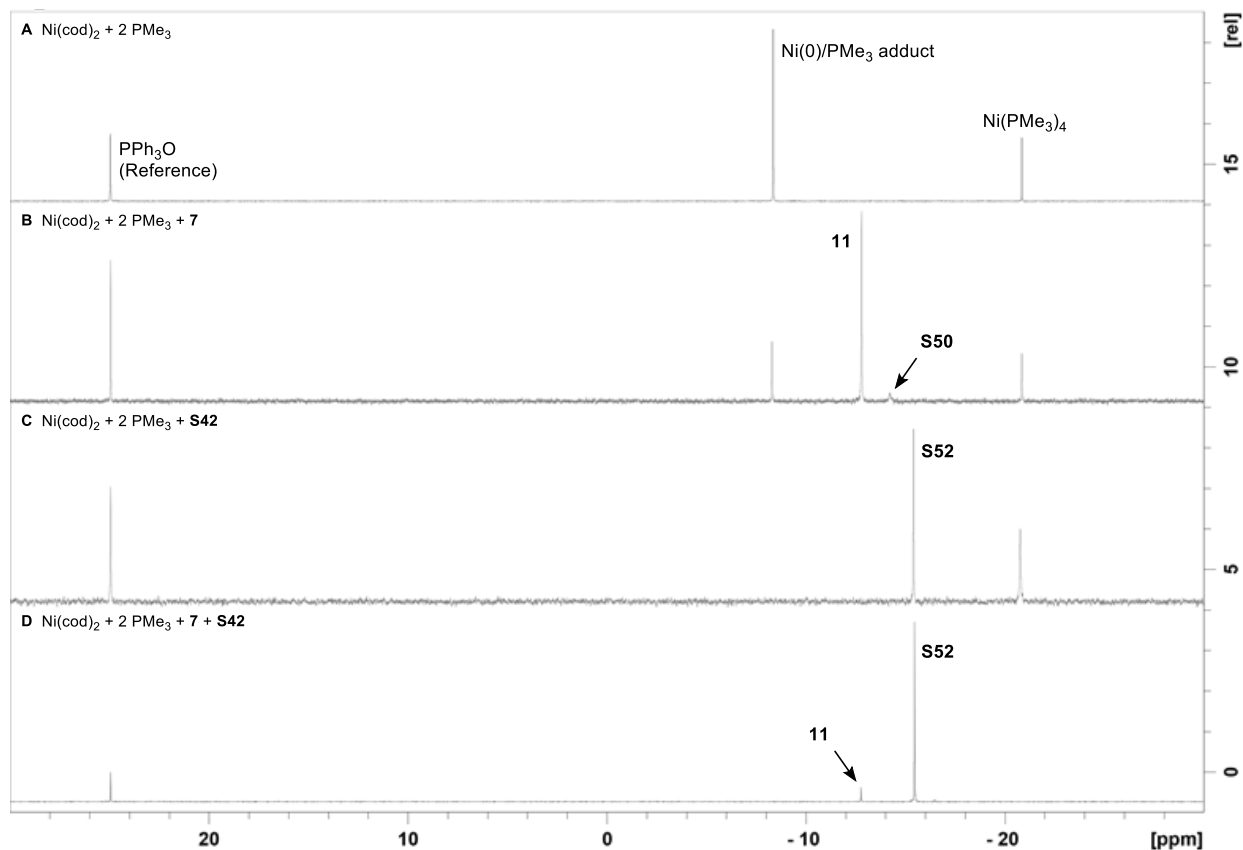
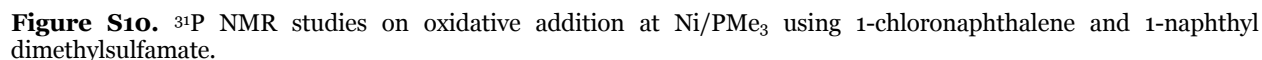
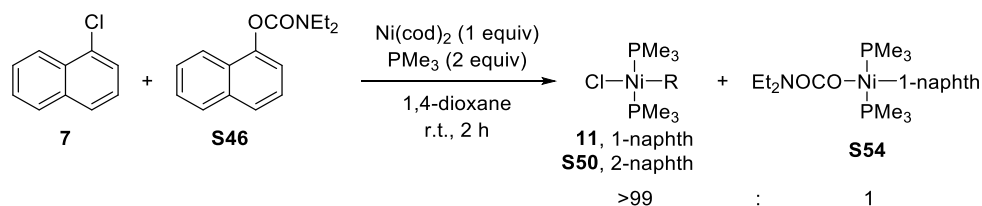


Figure S9. ^{31}P NMR studies on oxidative addition at Ni/PMe_3 using 1-chloronaphthalene and 1-naphthyl mesylate.

The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl dimethylsulfamate (5.0 mg), and a Ni(cod)₂/PMe₃ stock solution. Reactions were analyzed by ³¹P{¹H} NMR (203 or 122 MHz, 1,4-dioxane). The signal at -20.8 ppm corresponds to Ni(PMe₃)₄ (Figure S10, spectrum A). The signal at -8.4 ppm is assigned to another unidentified Ni(o)/PMe₃ adduct. No free PMe₃ is detected at -61.9 ppm (outside the window shown in Figure S10) in any of the spectra. The signals at -12.8 and -15.8 ppm are assigned to oxidative addition adducts **11** and **S53**, respectively (spectra B-D). A small amount of product **S50** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at -14.2 ppm in spectrum B. In the competition experiment (spectrum D), none of **S50** could be detected. The ratio of oxidative addition of C—Cl to C—O in spectrum D is 1 : 4.6.





Competition Between 1-Chloronaphthalene and 1-Naphthyl Diethylcarbamate with PMe_3 .

The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl diethylcarbamate (4.9 mg), and a $\text{Ni(cod)}_2/\text{PMe}_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at -20.8 ppm corresponds to $\text{Ni(PMe}_3)_4$ (Figure S11, spectrum A). The signal at -8.4 ppm is assigned to another unidentified $\text{Ni(o)}/\text{PMe}_3$ adduct. No free PMe_3 is detected at -61.9 ppm (outside the window shown in Figure S11) in any of the spectra. The signal at -12.8 ppm is assigned to oxidative addition adduct **11** (spectra B and D). A small amount of product **S50** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at -14.2 ppm in spectra B and D. No evidence for oxidative addition cleaving the C— OCONEt_2 bond was detected in either spectrum C or D. In the competition experiment (spectrum D), only products **11** and **S50** were observed, leading to an estimated ratio of oxidative addition of C—Cl to C—O of >99 : 1.

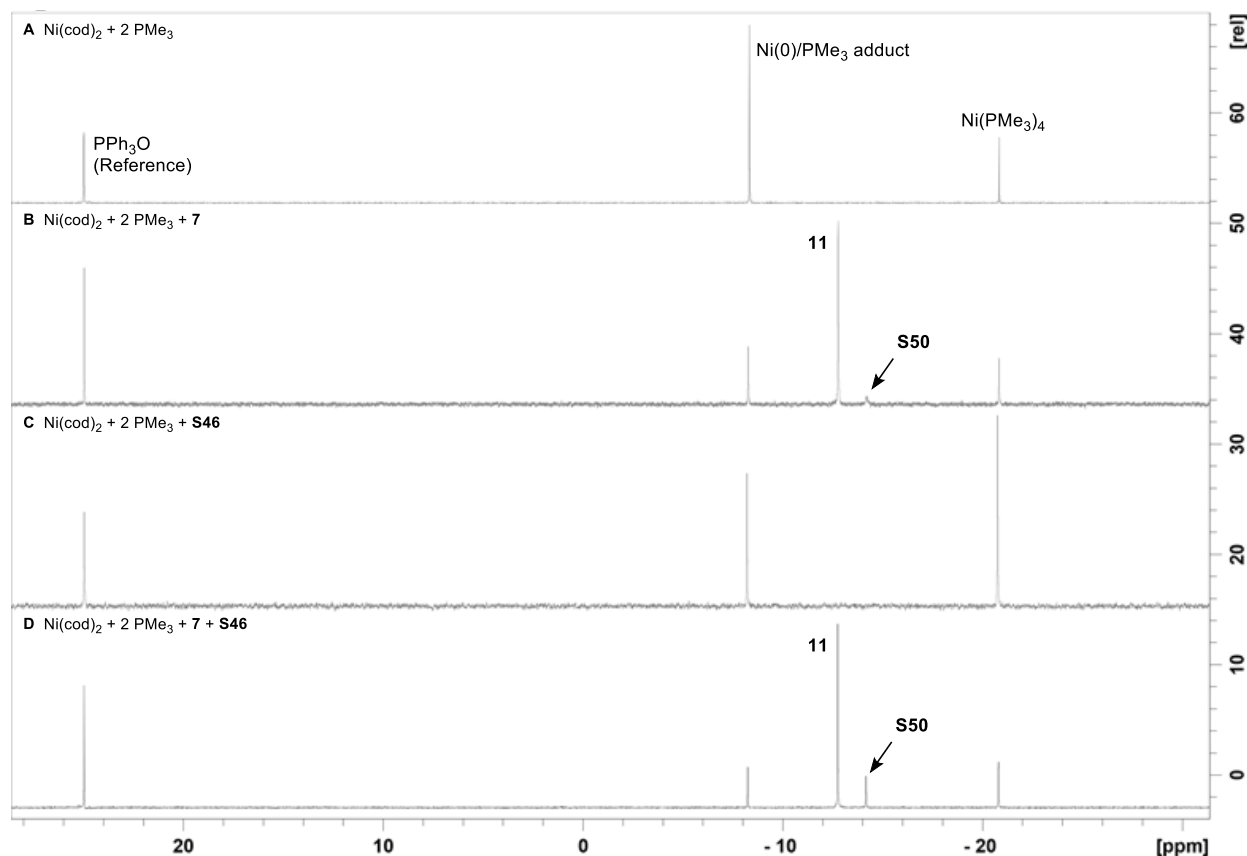
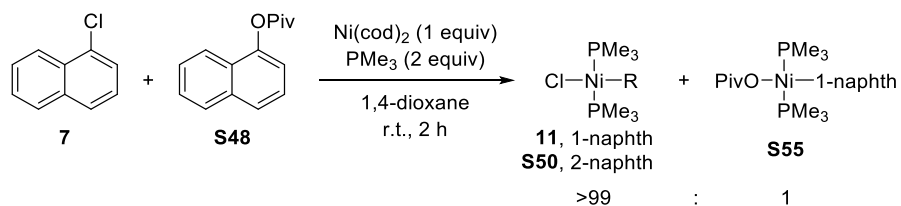


Figure S11. ^{31}P NMR studies on oxidative addition at Ni/PMe_3 using 1-chloronaphthalene and 1-naphthyl diethylcarbamate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Pivalate with PMe_3 . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl pivalate (4.6 mg), and a $\text{Ni(cod)}_2/\text{PMe}_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at -20.8 ppm corresponds to $\text{Ni(PMe}_3)_4$ (Figure S12, spectrum A). The signal at -8.4 ppm is assigned to another unidentified $\text{Ni(o)}/\text{PMe}_3$ adduct. No free PMe_3 is detected at -61.9 ppm (outside the window shown in Figure S12) in any of the spectra. The signal at -12.8 ppm is assigned to oxidative addition adduct **11** (spectra B and D). A small amount of product **S50** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at -14.2 ppm in spectra B and D. No evidence for oxidative addition cleaving the C—OPiv bond to make **S55** was detected in either spectrum C or D. In the competition experiment (spectrum D), only products **11** and **S50** were observed, leading to an estimated ratio of oxidative addition of C—Cl to C—O of >99 : 1.

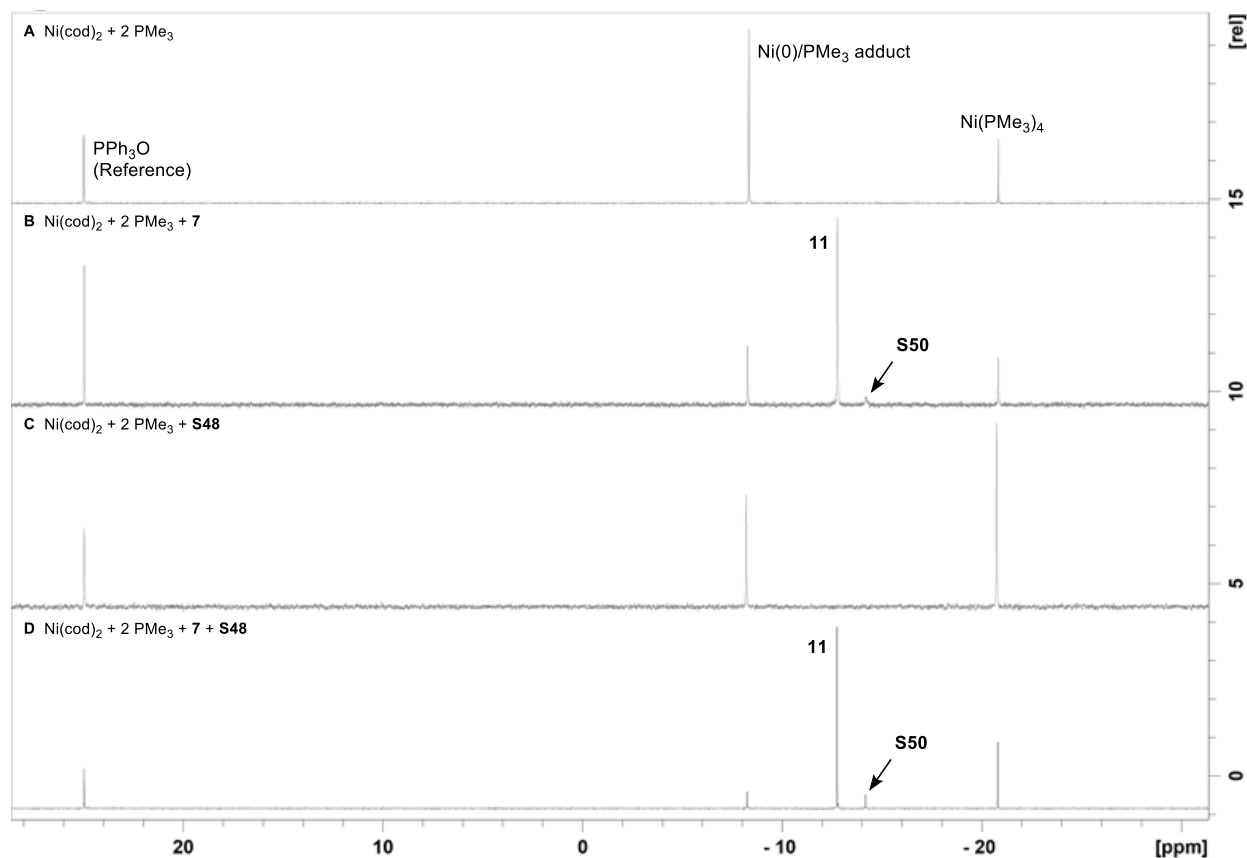
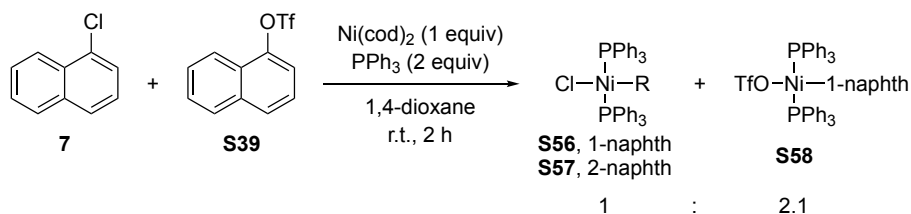


Figure S12. ^{31}P NMR studies on oxidative addition at Ni/PMe_3 using 1-chloronaphthalene and 1-naphthyl pivalate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Triflate with PPh_3 . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl triflate (5.5 mg), and a $\text{Ni(cod)}_2/\text{PPh}_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 39.8 ppm is assigned to a Ni(0)/PPh_3 adduct (Figure S13, spectrum A). No free PPh_3 is detected at -5.4 ppm (outside the window shown in Figure S13) in any of the spectra. The signals at 22.1 and 18.0 ppm are assigned to oxidative addition adducts **S56** and **S58**, respectively (spectra B-D). The signal for product **S57**, resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene), overlaps with that of **S56**. The ratio of oxidative addition of C—Cl to C—O in spectrum D is 1 : 2.1.

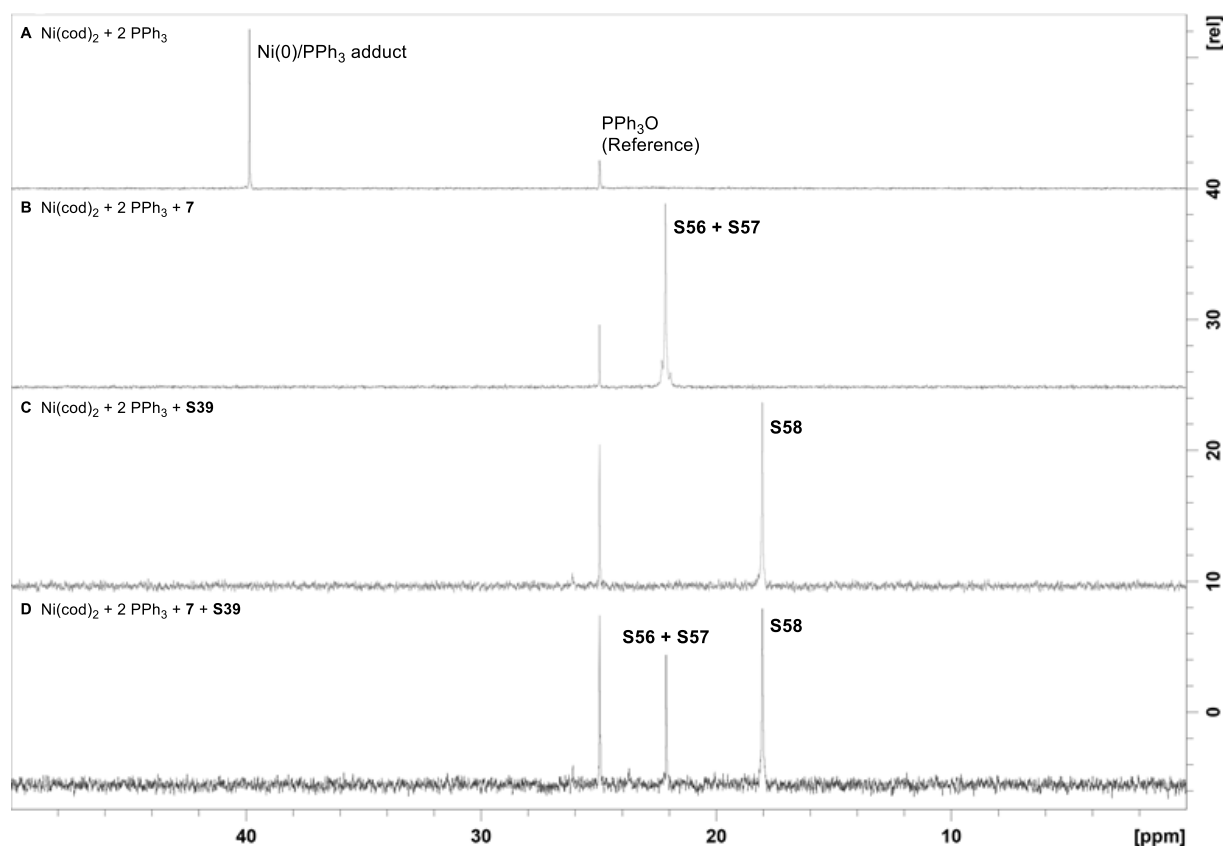
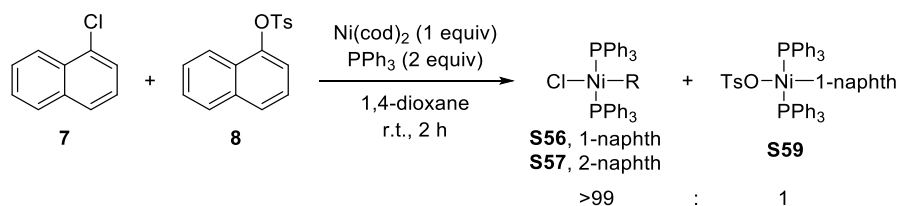


Figure S13. ^{31}P NMR studies on oxidative addition at Ni/PPh_3 using 1-chloronaphthalene and 1-naphthyl triflate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Tosylate with PPh₃. The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a Ni(cod)₂/PPh₃ stock solution. Reactions were analyzed by ³¹P{¹H} NMR (203 or 122 MHz, 1,4-dioxane). The signal at 39.8 ppm is assigned to a Ni(0)/PPh₃ adduct (Figure S14, spectrum A). No free PPh₃ is detected at -5.4 ppm (outside the window shown in Figure S14) in any of the spectra. The signals at 22.1 and 17.7 ppm are assigned to oxidative addition adducts **S56** and **S59**, respectively (spectra B-D), although very little reaction appears to have occurred in spectrum C. The signal for product **S57**, resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene), overlaps with that of **S56**. In the competition experiment (spectrum D), only product **S56** (with overlapping **S57**) was observed, leading to an estimated ratio of oxidative addition of C—Cl to C—O of >99 : 1.

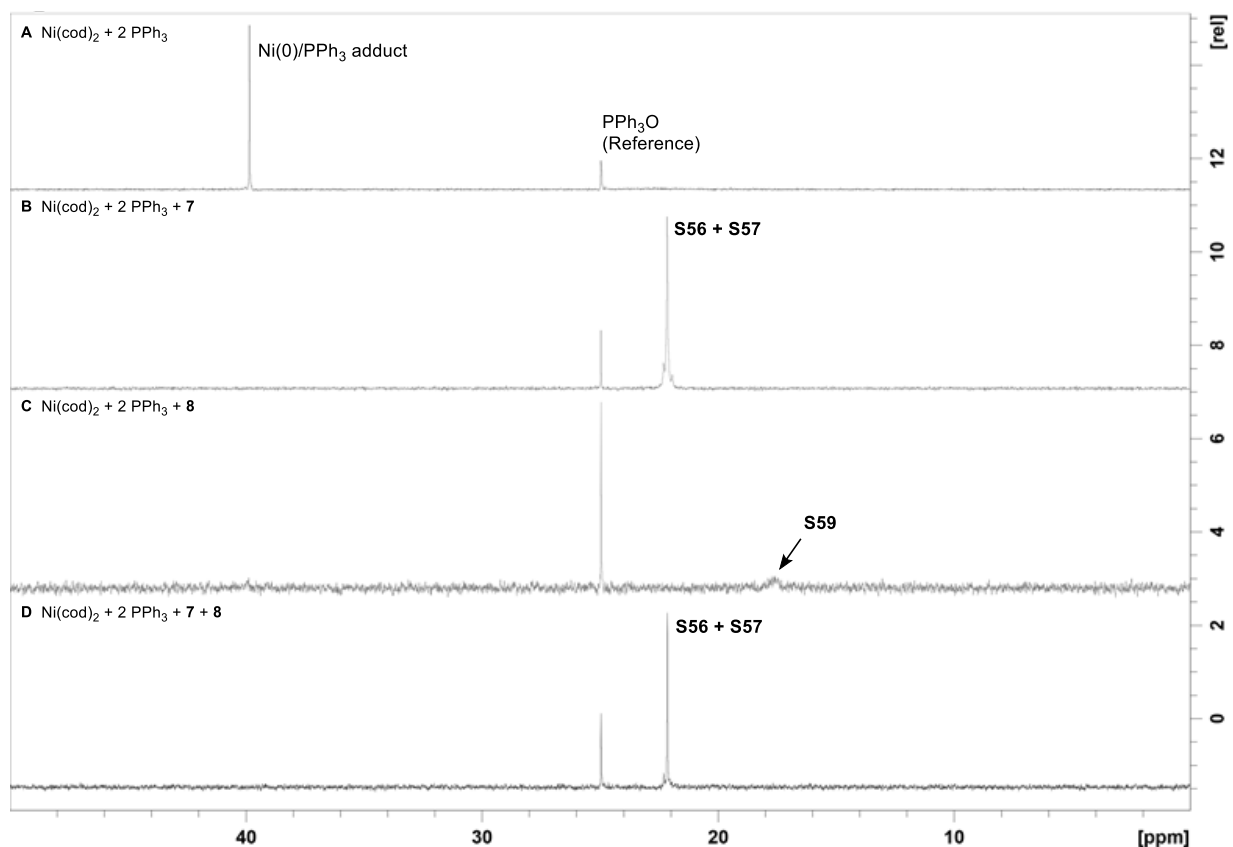
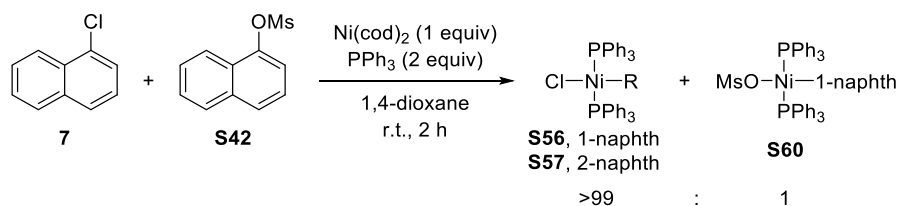


Figure S14. ³¹P NMR studies on oxidative addition at Ni/PPh₃ using 1-chloronaphthalene and 1-naphthyl tosylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Mesylate with PPh_3 . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl mesylate (4.5 mg), and a $\text{Ni(cod)}_2/\text{PPh}_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 39.8 ppm is assigned to a $\text{Ni(0)}/\text{PPh}_3$ adduct (Figure S15, spectrum A). No free PPh_3 is detected at -5.4 ppm (outside the window shown in Figure S15) in any of the spectra. The signal at 22.1 ppm is assigned to oxidative addition adduct **S56** (spectra B and D). The signal for product **S57**, resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene), overlaps with that of **S56**. No evidence for oxidative addition cleaving the C—OMs bond to make **S60** was detected in either spectrum C or D. In the competition experiment (spectrum D), only product **S56** (with overlapping **S57**) was observed, leading to an estimated ratio of oxidative addition of C—Cl to C—O of >99 : 1.

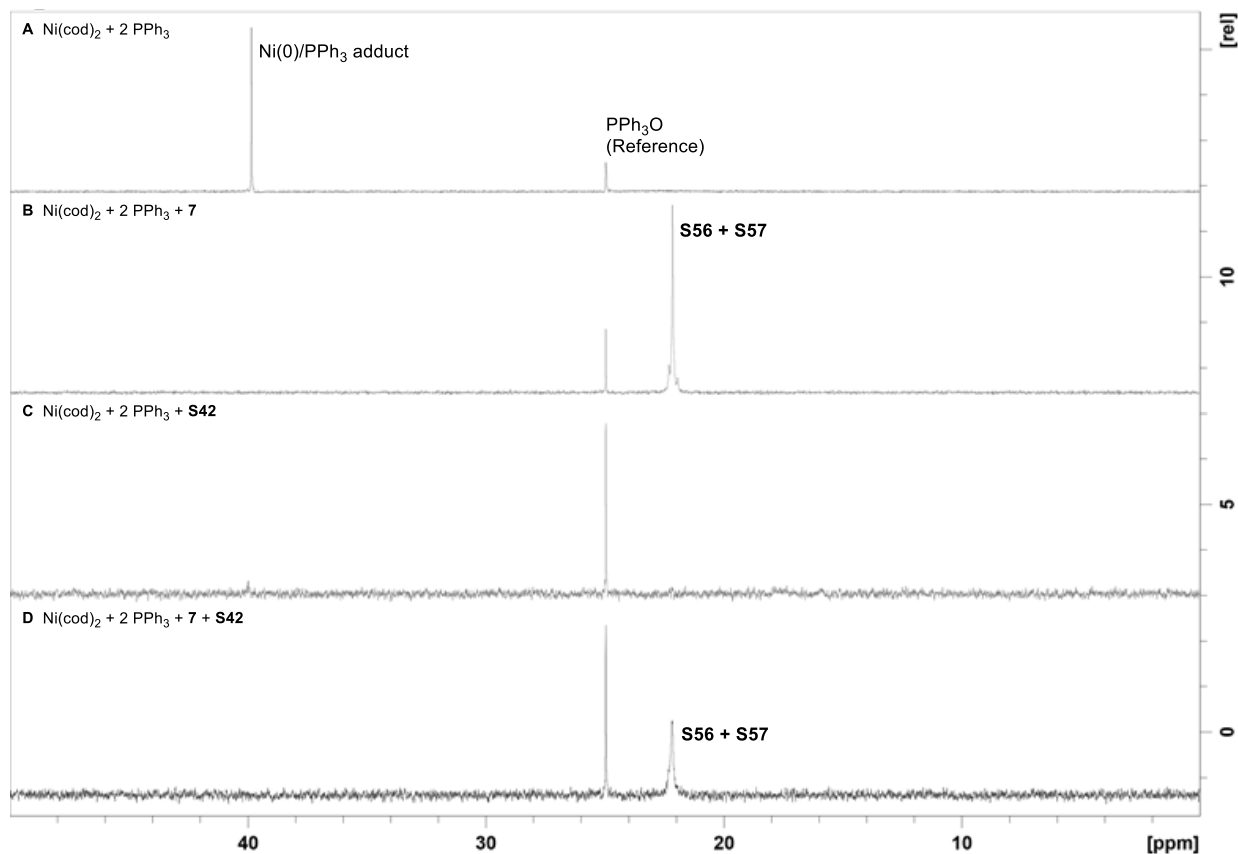
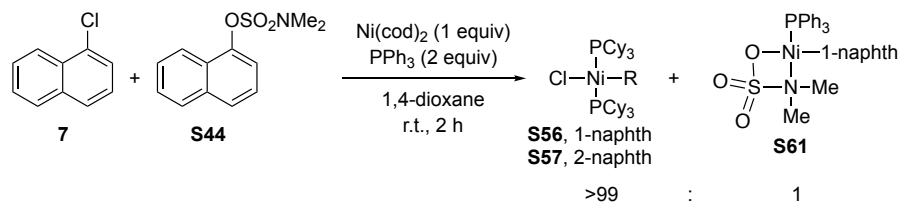


Figure S15. ^{31}P NMR studies on oxidative addition at Ni/PPh_3 using 1-chloronaphthalene and 1-naphthyl mesylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Dimethylsulfamate with PPh₃.

The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl dimethylsulfamate (5.0 mg), and a Ni(cod)₂/PPh₃ stock solution. Reactions were analyzed by ³¹P{¹H} NMR (203 or 122 MHz, 1,4-dioxane). The signal at 39.8 ppm is assigned to a Ni(O)/PPh₃ adduct (Figure S16, spectrum A). No free PPh₃ is detected at -5.4 ppm (outside the window shown in Figure S16) in any of the spectra. The signals at 22.1 and 30.4 ppm are assigned to oxidative addition adducts **S56** and **S61**, respectively (spectra B-D). However, the speciation of the C—O oxidative addition adduct (i.e., the structure of **S61**) is uncertain based on the splitting pattern of its ³¹P signal. The signal for product **S57**, resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene), overlaps with that of **S56**. The ratio of oxidative addition of C—Cl to C—O in spectrum D is >99 : 1.

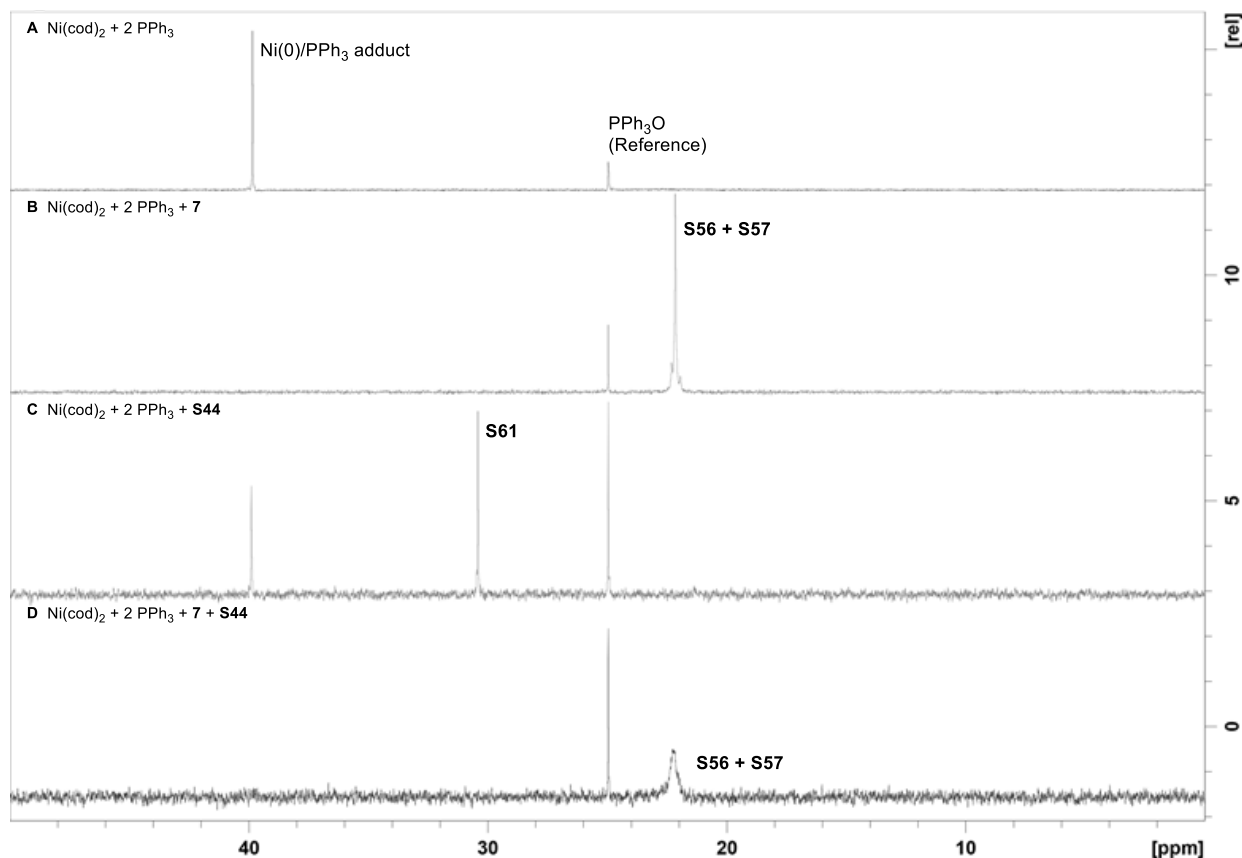
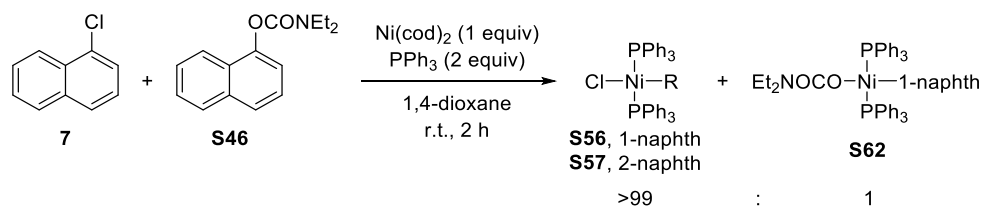


Figure S16. ³¹P NMR studies on oxidative addition at Ni/PPh₃ using 1-chloronaphthalene and 1-naphthyl dimethylsulfamate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Diethylcarbamate with PPh_3 .

The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl diethylcarbamate (4.9 mg), and a $\text{Ni(cod)}_2/\text{PPh}_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 39.8 ppm is assigned to a $\text{Ni(o)}/\text{PPh}_3$ adduct (Figure S17, spectrum A). No free PPh_3 is detected at -5.4 ppm (outside the window shown in Figure S17) in any of the spectra. The signal at 22.1 ppm is assigned to oxidative addition adduct **S56** (spectra B and D). The signal for product **S57**, resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene), overlaps with that of **S56**. No evidence for oxidative addition cleaving the C— OCONEt_2 bond to make **S62** (nor its mono- PPh_3 analogue with carbamate bound in a κ^2 -fashion) was detected in either spectrum C or D. In the competition experiment (spectrum D), only product **S56** (with overlapping **S57**) was observed, leading to an estimated ratio of oxidative addition of C—Cl to C—O of >99 : 1.

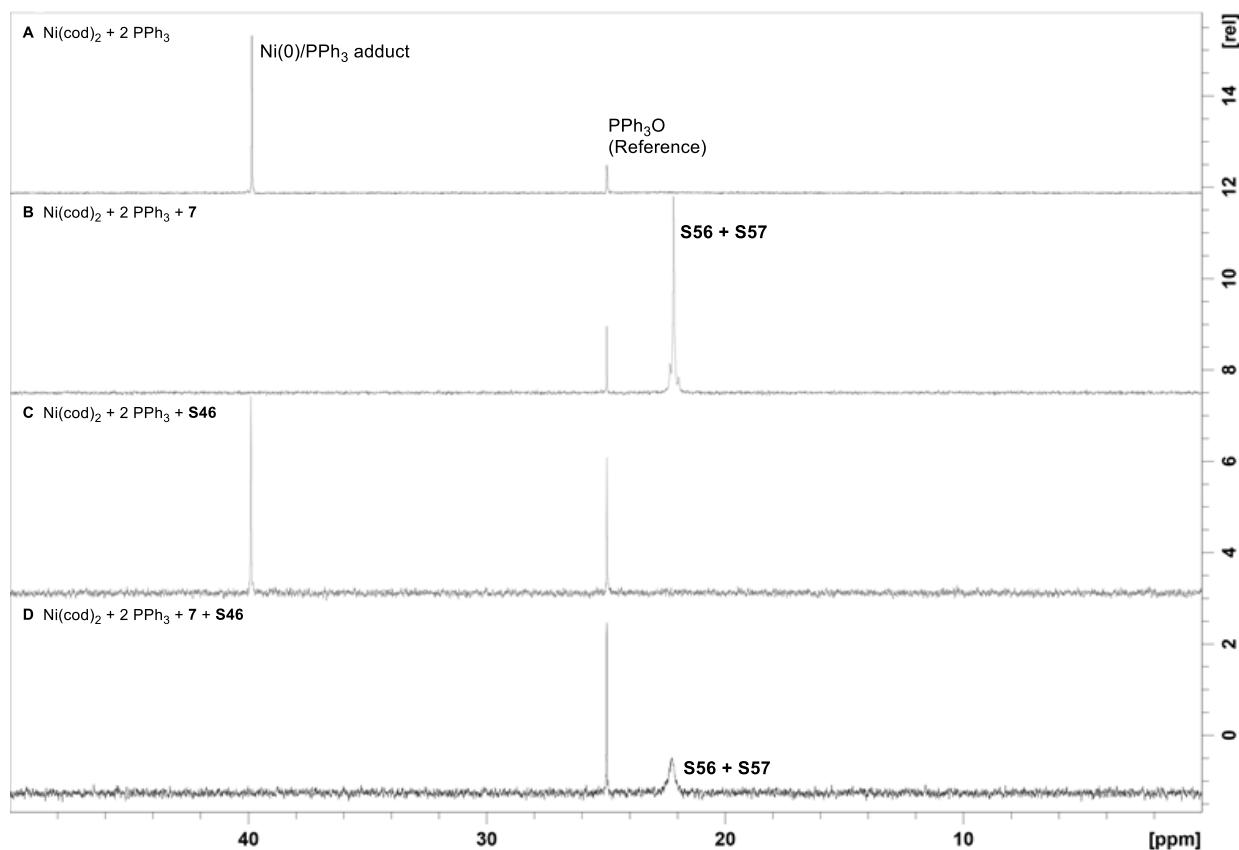
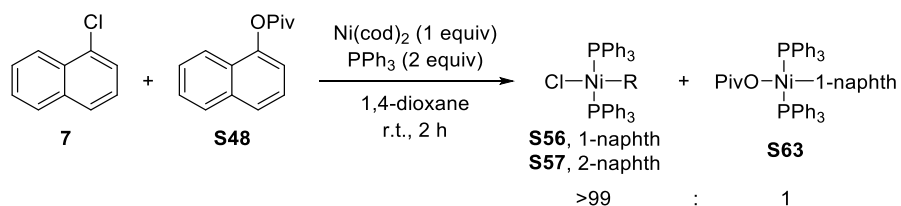


Figure S17. ^{31}P NMR studies on oxidative addition at Ni/PPh_3 using 1-chloronaphthalene and 1-naphthyl diethylcarbamate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Pivalate with PPh_3 . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl pivalate (4.6 mg), and a $\text{Ni(cod)}_2/\text{PPh}_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 39.8 ppm is assigned to a Ni(0)/PPh_3 adduct (Figure S18, spectrum A). No free PPh_3 is detected at -5.4 ppm (outside the window shown in Figure S18) in any of the spectra. The signal at 22.1 ppm is assigned to oxidative addition adduct **S56** (spectra B and D). The signal for product **S57**, resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene), overlaps with that of **S56**. No evidence for oxidative addition cleaving the C—OPiv bond to make **S63** (nor its mono- PPh_3 analogue with carbamate bound in a κ^2 -fashion) was detected in either spectrum C or D. In the competition experiment (spectrum D), only product **S56** (with overlapping **S57**) was observed, leading to an estimated ratio of oxidative addition of C—Cl to C—O of >99 : 1.

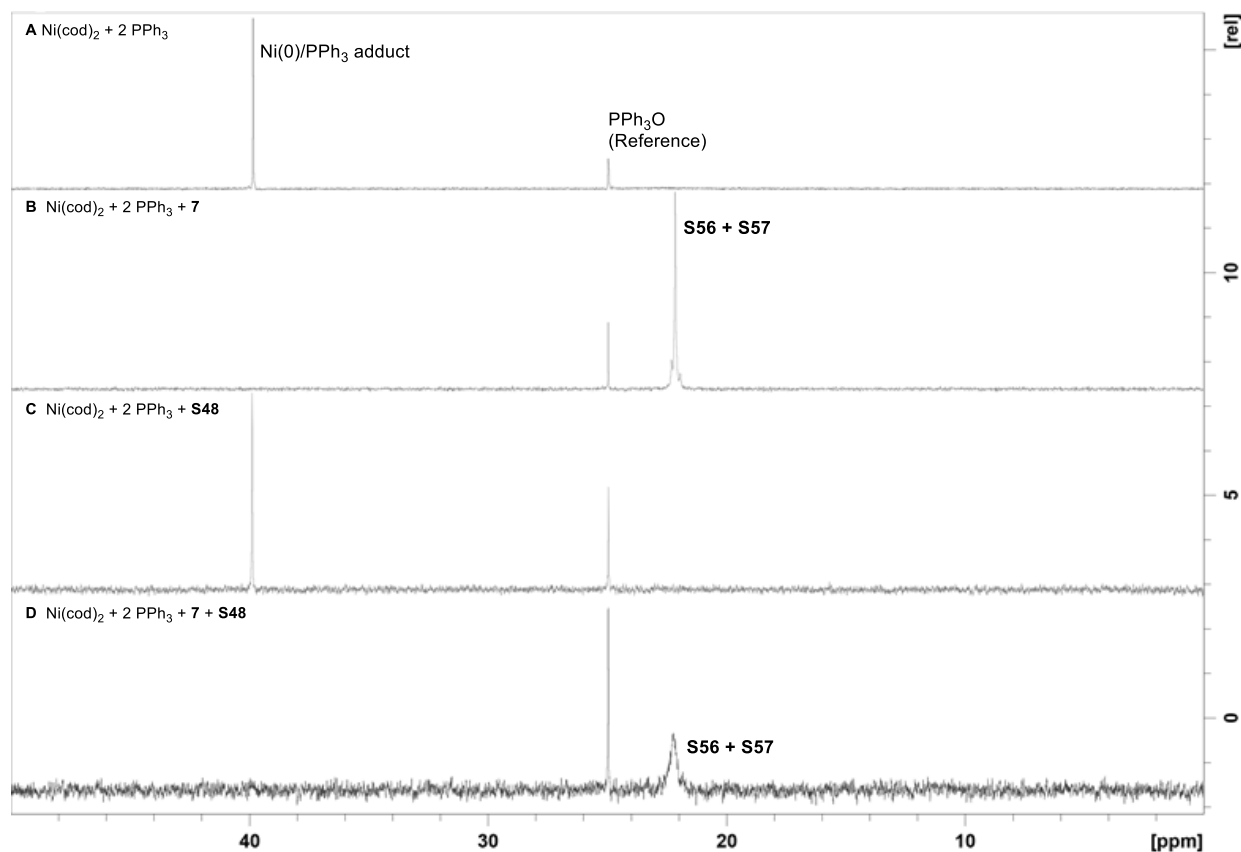
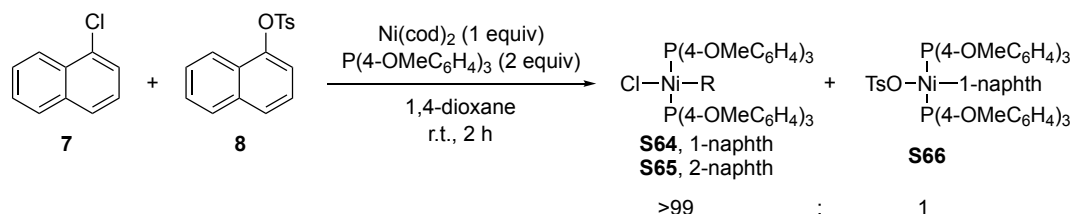


Figure S18. ^{31}P NMR studies on oxidative addition at Ni/PPh_3 using 1-chloronaphthalene and 1-naphthyl pivalate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Tosylate with $P(4\text{-MeOC}_6\text{H}_4)_3$.

The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a $\text{Ni(cod)}_2/\text{P}(4\text{-MeOC}_6\text{H}_4)_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 36.2 ppm is assigned to a $\text{Ni(0)}/\text{P}(4\text{-MeOC}_6\text{H}_4)_3$ adduct (Figure S19, spectrum A). No free $\text{P}(4\text{-MeOPh})_3$ is detected at -10.3 ppm (outside the window shown in Figure S19) in any of the spectra. The signals at 18.6 and 14.4 ppm are assigned to oxidative addition adducts **S64** and **S66**, respectively (spectra B-D). The signal for product **S65**, resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene), overlaps with that of **S64**. In the competition experiment (spectrum D), only products **S64** (with overlapping **S65**) were observed, leading to an estimated ratio of oxidative addition of C—Cl to C—O of >99 : 1.

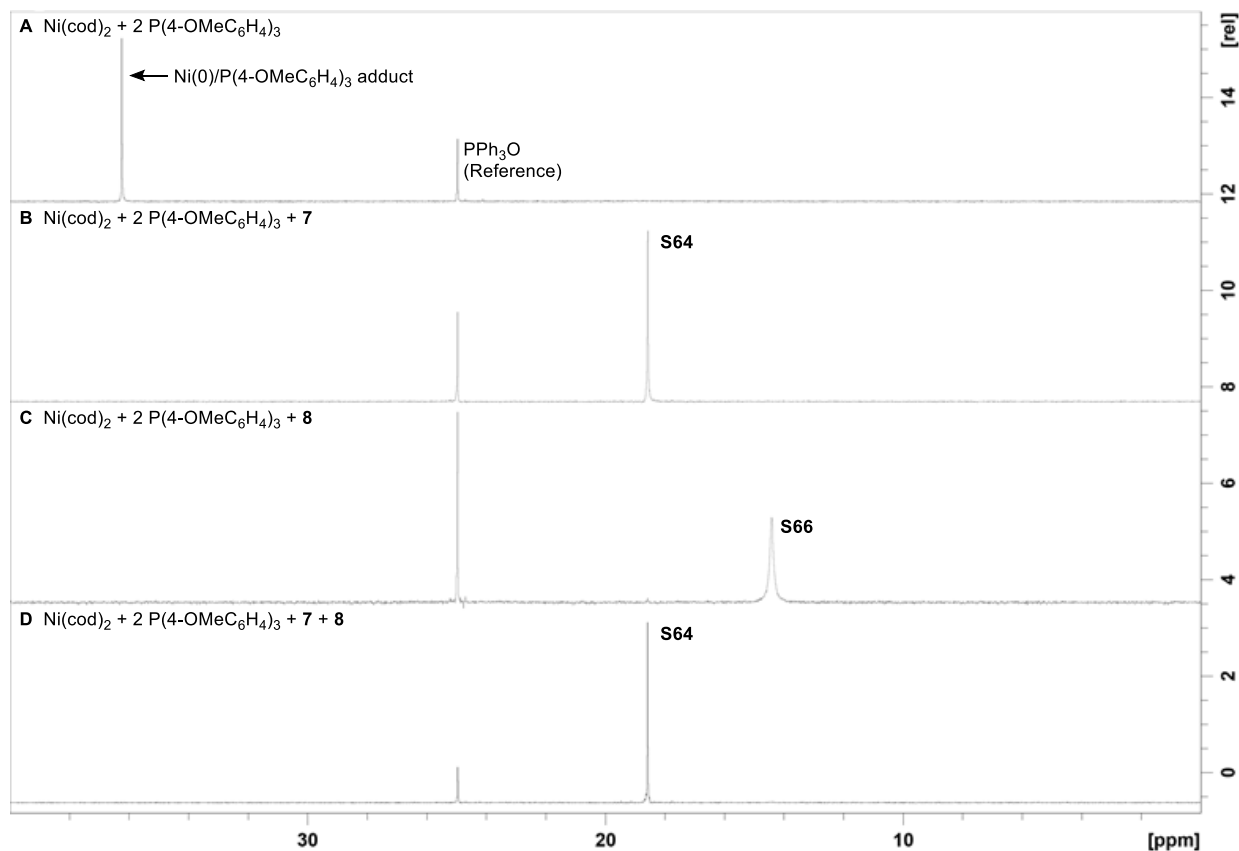
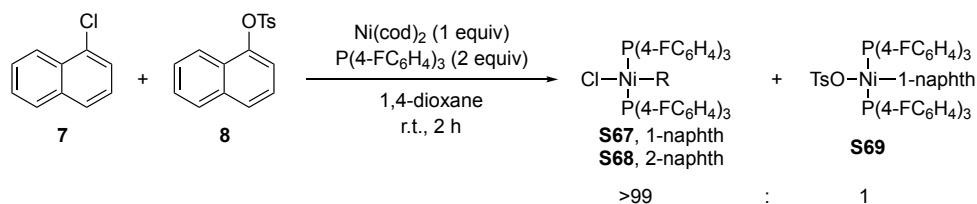


Figure S19. ^{31}P NMR studies on oxidative addition at $\text{Ni}/\text{P}(4\text{-MeOC}_6\text{H}_4)_3$ using 1-chloronaphthalene and 1-naphthyl tosylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Tosylate with $P(4\text{-FC}_6\text{H}_4)_3$. The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a $\text{Ni(cod)}_2/\text{P}(4\text{-FC}_6\text{H}_4)_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 37.5 ppm is assigned to a $\text{Ni(0)}/\text{P}(4\text{-FC}_6\text{H}_4)_3$ adduct (Figure S20, spectrum A). No free $\text{P}(4\text{-FC}_6\text{H}_4)_3$ is detected at -8.8 ppm (outside the window shown in Figure S20) in any of the spectra. The signals at 20.0 and 15.7 ppm are assigned to oxidative addition adducts **S67** and **S69**, respectively (spectra B-D). Product **S68** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at 19.8 ppm in spectrum B. In the competition experiment (spectrum D), only products **S67** and **S68** were observed, leading to an estimated ratio of oxidative addition of C—Cl to C—O of >99 : 1.

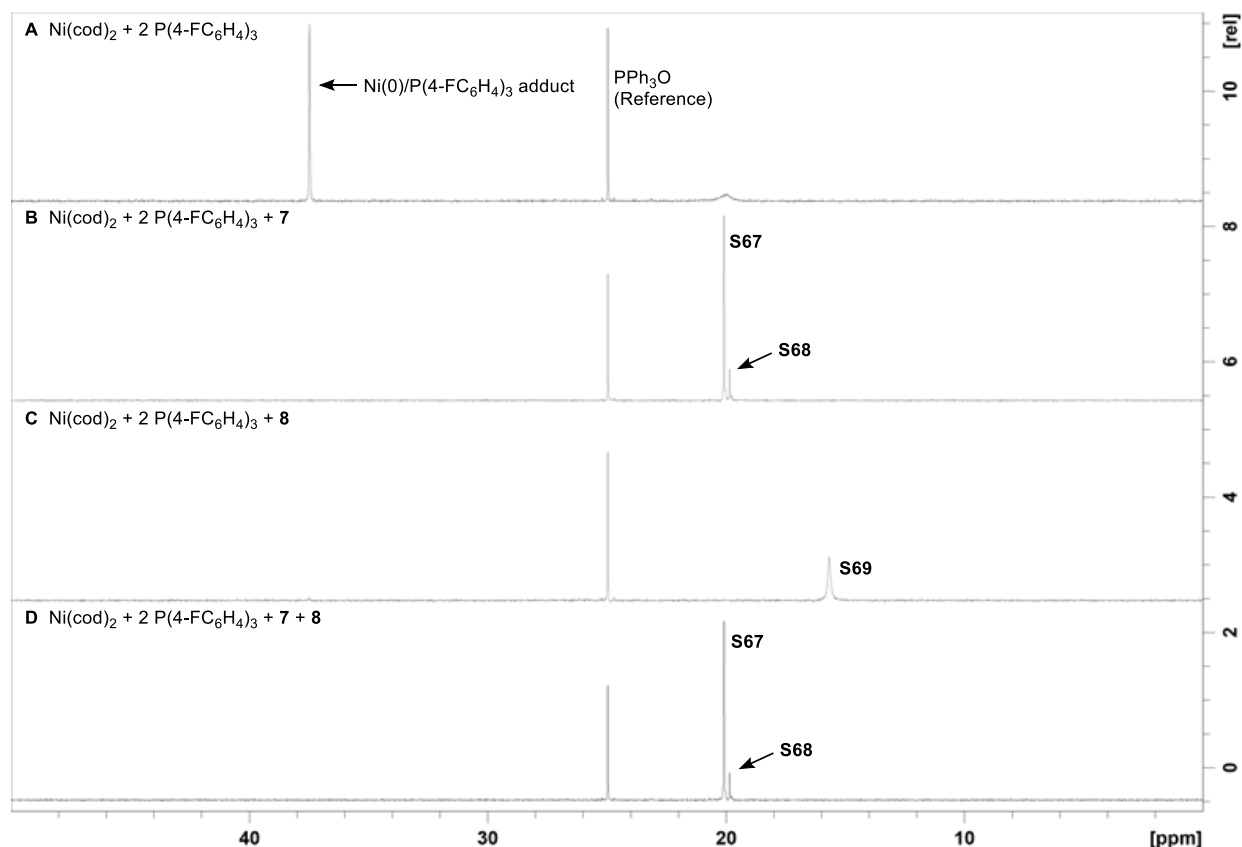
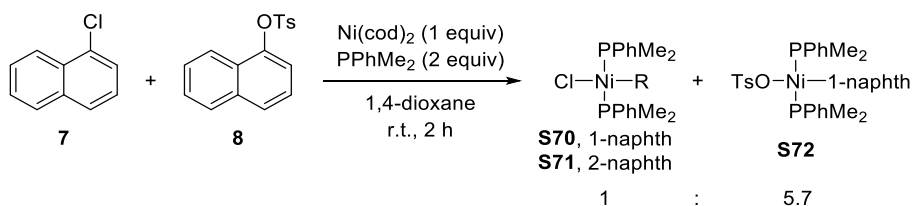


Figure S20. ^{31}P NMR studies on oxidative addition at $\text{Ni}/\text{P}(4\text{-FC}_6\text{H}_4)_3$ using 1-chloronaphthalene and 1-naphthyl tosylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Tosylate with PPhMe_2 . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a $\text{Ni}(\text{cod})_2/\text{PPhMe}_2$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signals at 4.1 and -8.9 ppm are assigned to $\text{Ni}(\text{o})/\text{PPhMe}_2$ adducts (Figure S21, spectrum A). No free PPhMe_2 is detected at -45.7 ppm (outside the window shown in Figure S21) in any of the spectra. The signals at -5.3 and -6.7 ppm are assigned to oxidative addition adducts **S70** and **S72**, respectively (spectra B-D). A small amount of product **S71** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at -5.3 ppm in spectrum B. None of **S71** was detected in the competition experiment (spectrum D). The ratio of oxidative addition of C—Cl to C—O in spectrum D is 1 : 5.7.

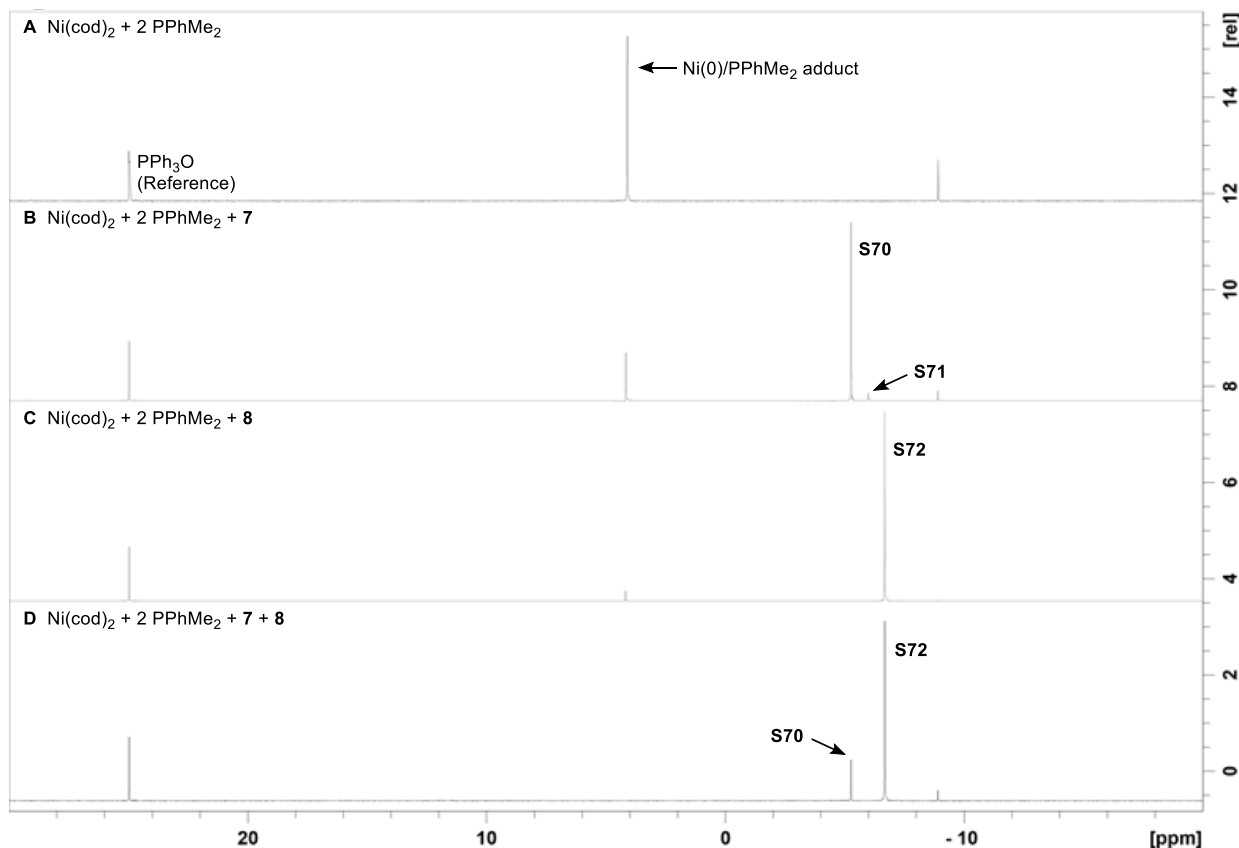
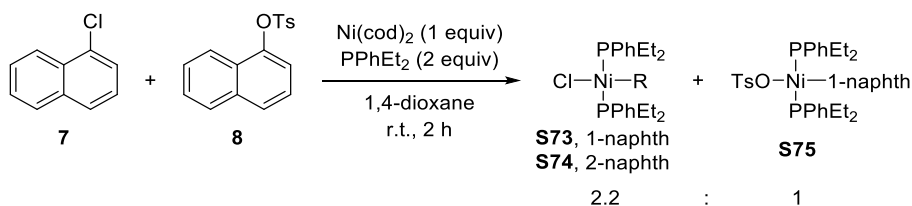


Figure S21. ^{31}P NMR studies on oxidative addition at Ni/PPhMe_2 using 1-chloronaphthalene and 1-naphthyl tosylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Tosylate with PPhEt_2 . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a $\text{Ni}(\text{cod})_2/\text{PPhEt}_2$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 23.6 ppm is assigned to a $\text{Ni}(\text{o})/\text{PPhEt}_2$ adduct (Figure S22, spectrum A). No free PPhEt_2 is detected at -16.2 ppm (outside the window shown in Figure S22) in any of the spectra. The signals at 12.4 and 10.4 ppm are assigned to oxidative addition adducts **S73** and **S75**, respectively (spectra B-D). A small amount of product **S74** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at 12.0 ppm in spectrum B. In the competition experiment (spectrum D), a small amount of **S74** was detected, and it was integrated together with **S73** to obtain a ratio of oxidative addition of C—Cl to C—O of 2.2 : 1.

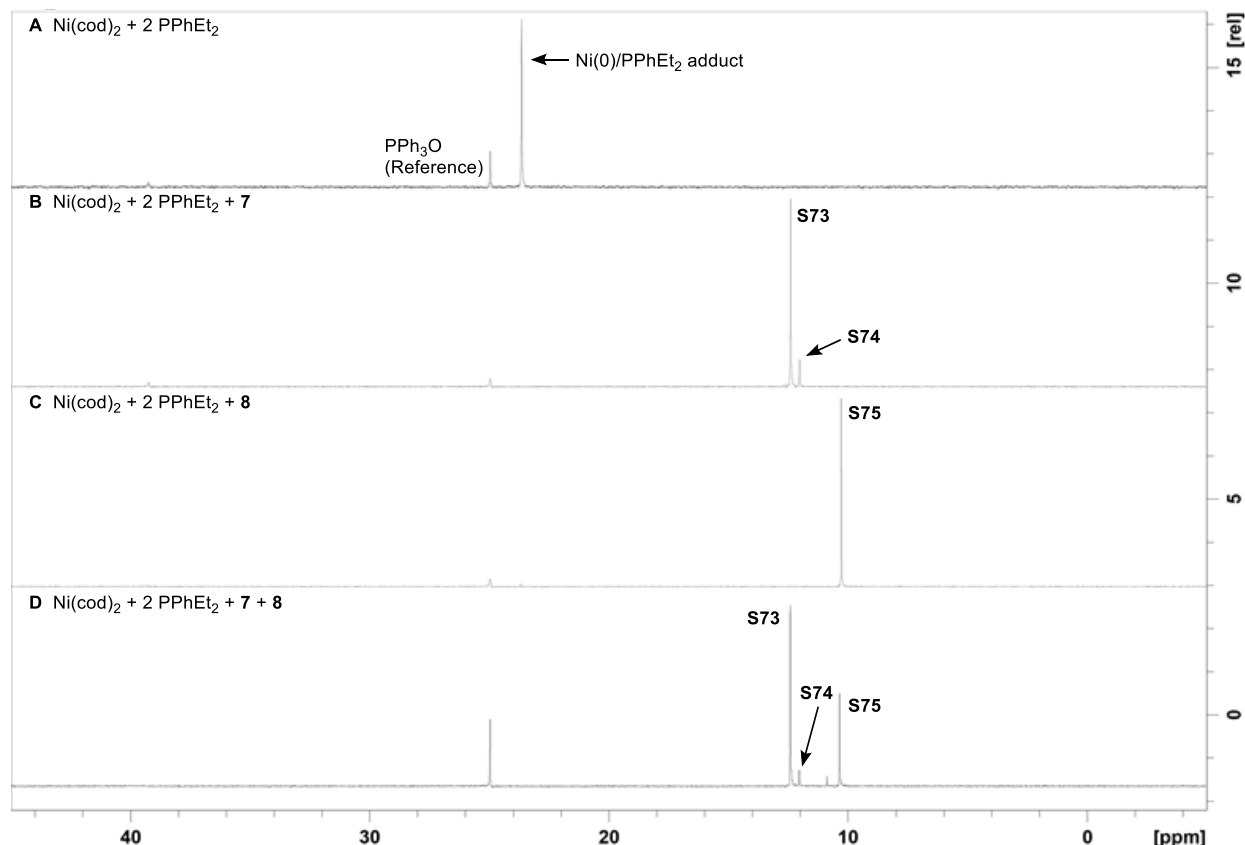
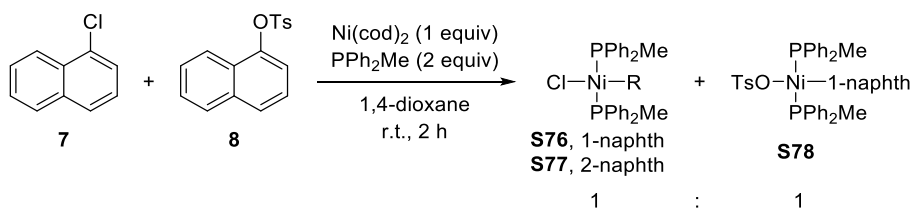


Figure S22. ^{31}P NMR studies on oxidative addition at Ni/PPhEt_2 using 1-chloronaphthalene and 1-naphthyl tosylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Tosylate with PPh_2Me . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a $\text{Ni(cod)}_2/\text{PPh}_2\text{Me}$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 21.0 ppm is assigned to a $\text{Ni(o)}/\text{PPh}_2\text{Me}$ adduct (Figure S23, spectrum A). No free PPh_2Me is detected at -26.8 ppm (outside the window shown in Figure S23) in any of the spectra. The signals at 8.9 and 5.3 ppm are assigned to oxidative addition adducts **S76** and **S78**, respectively (spectra B-D). A small amount of product **S77** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at 8.0 ppm in spectrum B. In the competition experiment (spectrum D), a small amount of **S77** was detected, and it was integrated together with **S76** to obtain a ratio of oxidative addition of C—Cl to C—O of 1 : 1.

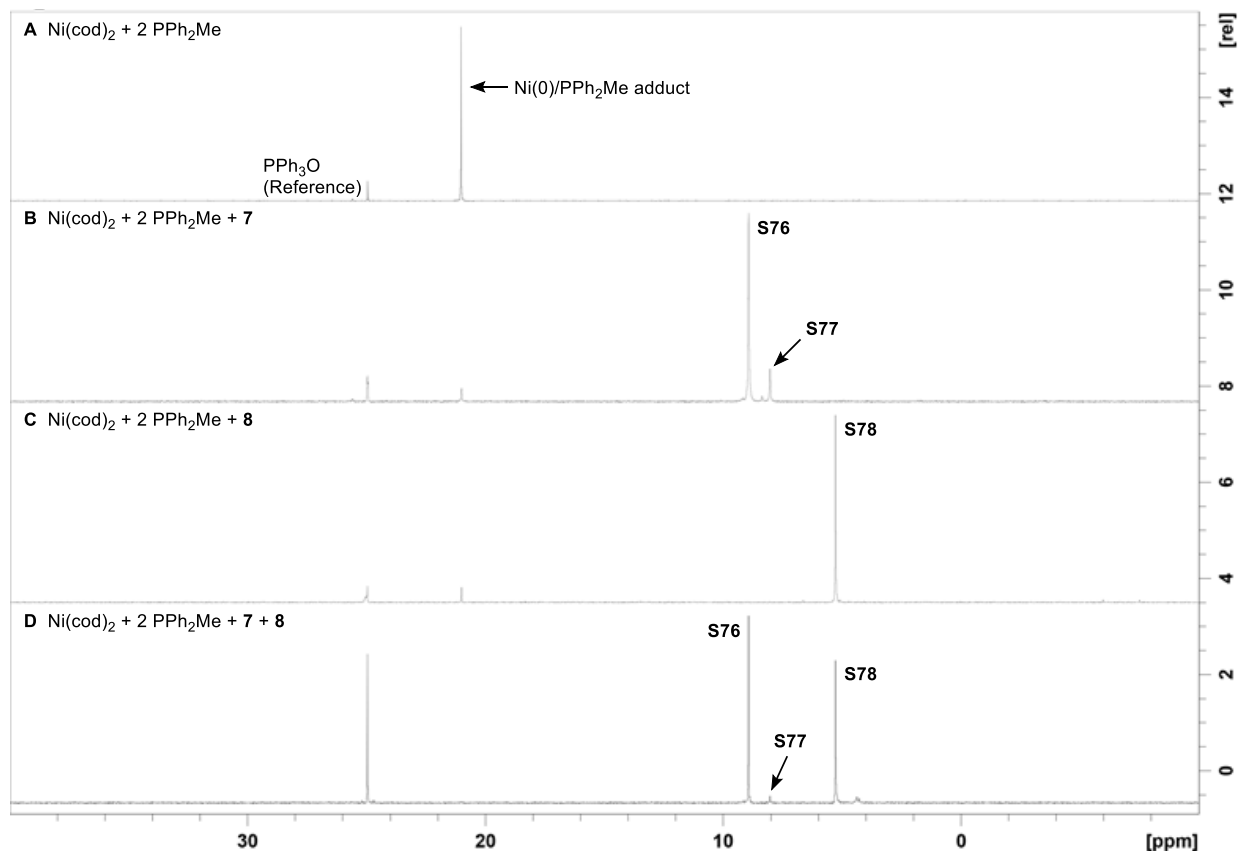
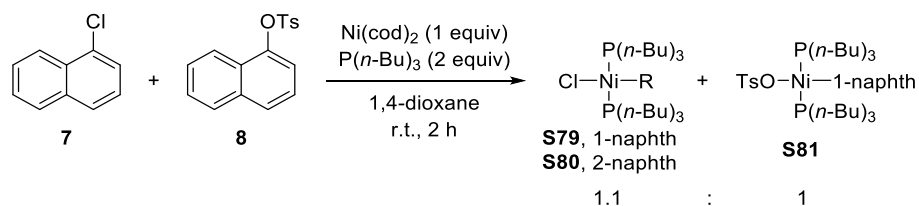


Figure S23. ^{31}P NMR studies on oxidative addition at $\text{Ni}/\text{PPh}_2\text{Me}$ using 1-chloronaphthalene and 1-naphthyl tosylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Tosylate with $\text{P}(n\text{-Bu})_3$. The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a $\text{Ni(cod)}_2/\text{P}(n\text{-Bu})_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 11.8 ppm is assigned to a $\text{Ni(0)}/\text{P}(n\text{-Bu})_3$ adduct (Figure S24, spectrum A). No free $\text{P}(n\text{-Bu})_3$ is detected at -32.0 ppm (outside the window shown in Figure S24) in any of the spectra. The signals at 4.4 and 1.5 ppm are assigned to oxidative addition adducts **S79** and **S81**, respectively (spectra B-D). A small amount of product **S80** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at 3.9 ppm in spectrum B. In the competition experiment (spectrum D), a small amount of **S80** was detected, and it was integrated together with **S79** to obtain a ratio of oxidative addition of C—Cl to C—O of 1.1 : 1.

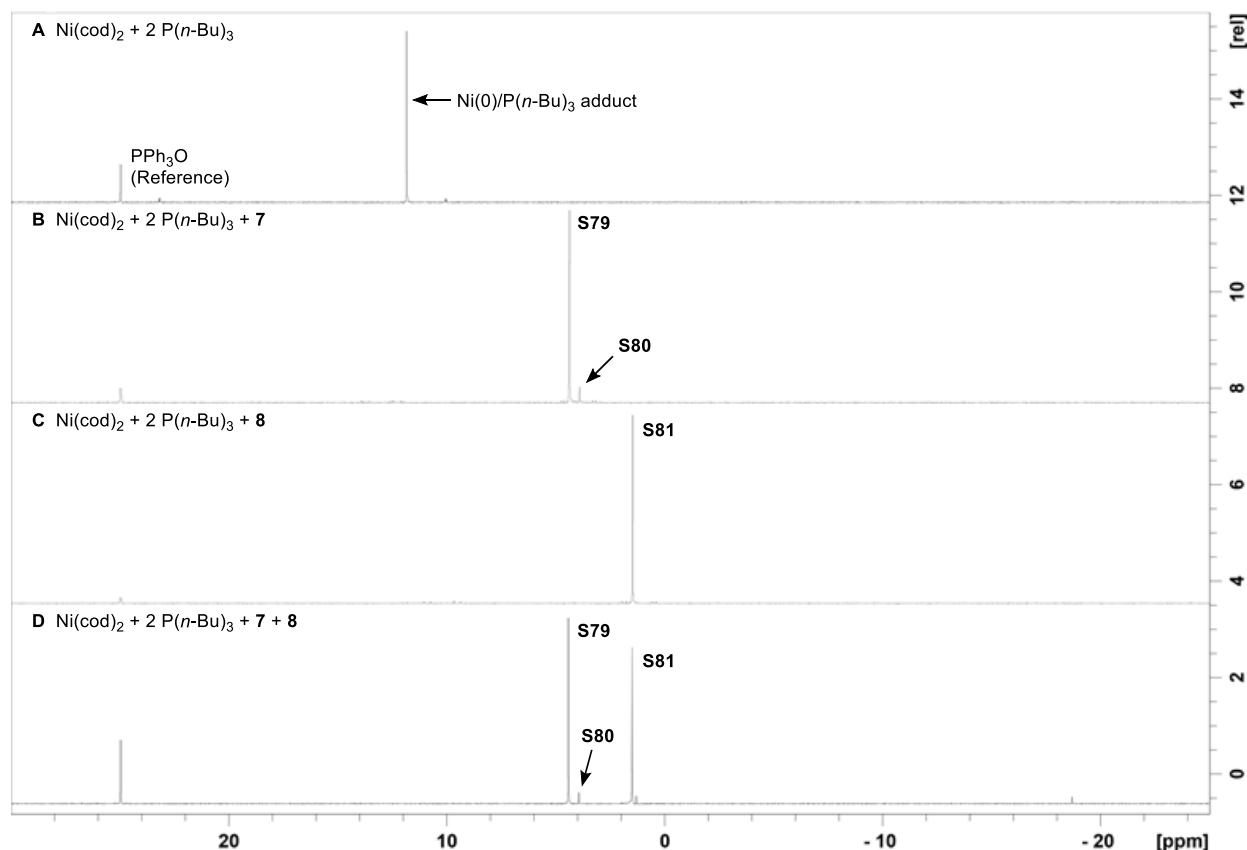
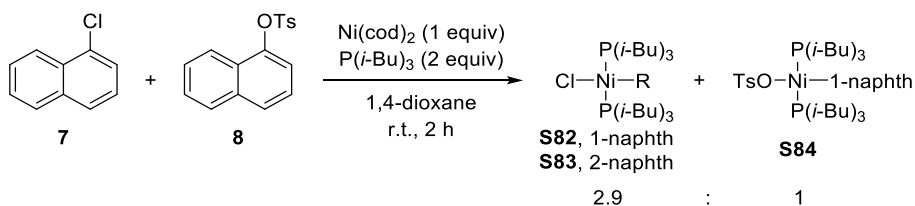


Figure S24. ^{31}P NMR studies on oxidative addition at $\text{Ni}/\text{P}(n\text{-Bu})_3$ using 1-chloronaphthalene and 1-naphthyl tosylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Tosylate with $\text{P}(i\text{-Bu})_3$. The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a $\text{Ni(cod)}_2/\text{P}(i\text{-Bu})_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 9.1 ppm is assigned to a $\text{Ni(o)}/\text{P}(i\text{-Bu})_3$ adduct (Figure S25, spectrum A). The signal at -44.7 ppm corresponds to free $\text{P}(i\text{-Bu})_3$. The signals at 4.8 and 0.8 ppm are assigned to oxidative addition adducts **S82** and **S84**, respectively (spectra B-D). A small amount of product **S83** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at 3.0 ppm in spectrum B. In the competition experiment (spectrum D), a small amount of **S83** was detected, and it was integrated together with **S82** to obtain a ratio of oxidative addition of C—Cl to C—O of 2.9 : 1.

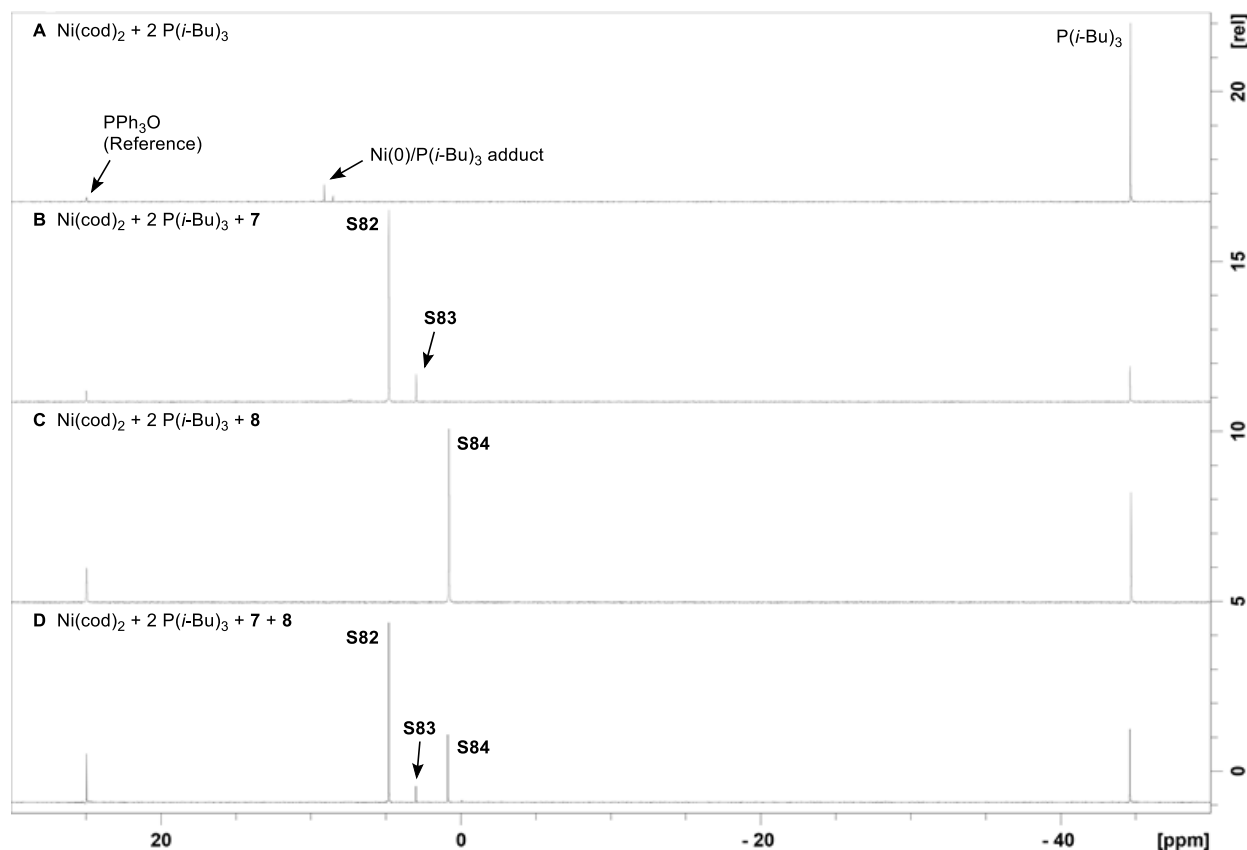
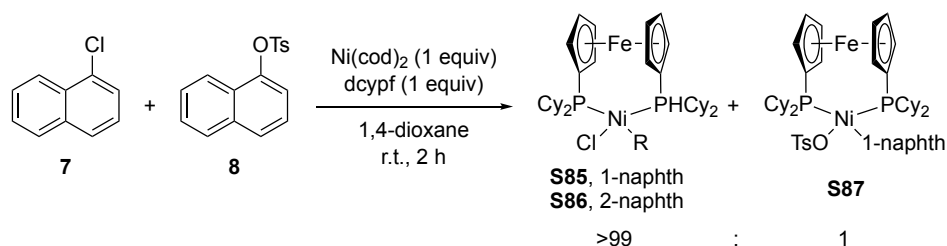


Figure S25. ^{31}P NMR studies on oxidative addition at $\text{Ni}/\text{P}(i\text{-Bu})_3$ using 1-chloronaphthalene and 1-naphthyl tosylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Tosylate with dcypf. The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg). A $\text{Ni(cod)}_2/\text{dcypf}$ stock solution was prepared with a 1:1 molar ratio of Ni(cod)_2 to dcypf (corresponding to a 1:2 ratio of Ni to P atoms). Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). No $\text{Ni(o)}/\text{dcypf}$ adduct could be detected in the acquisition window from +190 to -110.0 ppm (Figure S26, spectrum A). No free dcypf is detected at -9.3 ppm in any of the spectra. The signals at -4.8 and -8.1 ppm are assigned to oxidative addition adducts **S85** and **S87**, respectively (spectra B-D). A trace amount of product **S86** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at -8.7 ppm in spectrum B. In the competition experiment (spectrum D), only product **S85** was observed, leading to an estimated ratio of oxidative addition of C—Cl to C—O of $>99 : 1$.

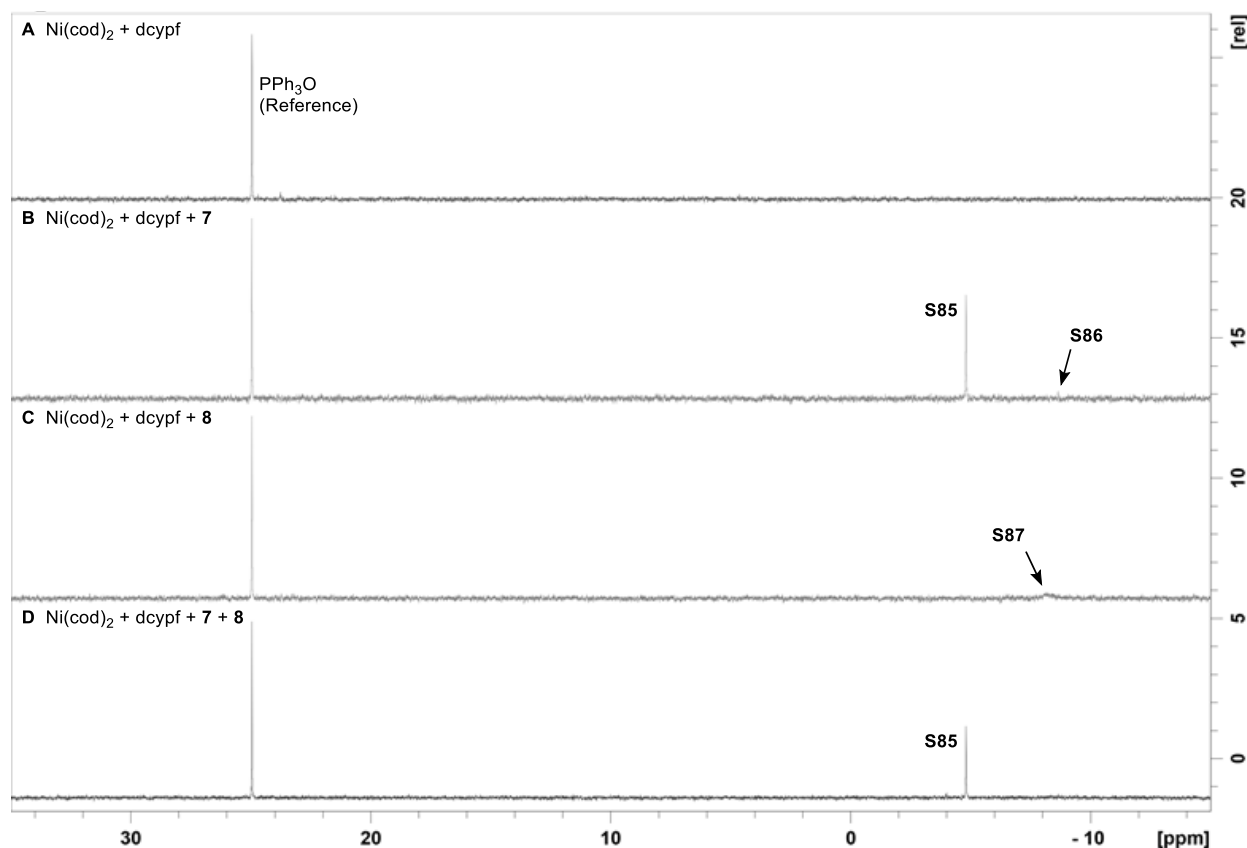
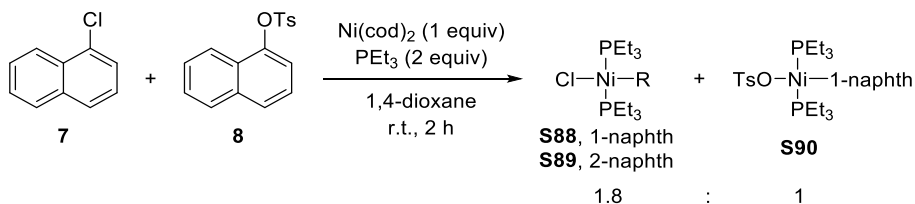


Figure S26. ^{31}P NMR studies on oxidative addition at Ni/dcypf using 1-chloronaphthalene and 1-naphthyl tosylate.



Competition Between 1-Chloronaphthalene and 1-Naphthyl Tosylate with PEt_3 . The studies were carried out according to the general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a $\text{Ni(cod)}_2/\text{PEt}_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). The signal at 18.5 ppm is assigned to a $\text{Ni(0)}/\text{PEt}_3$ adduct (Figure S27, spectrum A). No free PEt_3 is detected at -19.5 ppm (outside the window shown in Figure S27) in any of the spectra. The signals at 11.5 and 8.6 ppm are assigned to oxidative addition adducts **S88** and **S90**, respectively (spectra B-D). A small amount of product **S89** resulting from oxidative addition of 2-chloronaphthalene (contaminant in 1-chloronaphthalene) was detected at 11.6 ppm in spectrum B. In the competition experiment (spectrum D), a small amount of **S89** was detected, and it was integrated together with **S88** to obtain a ratio of oxidative addition of C—Cl to C—O of 1.8 : 1.

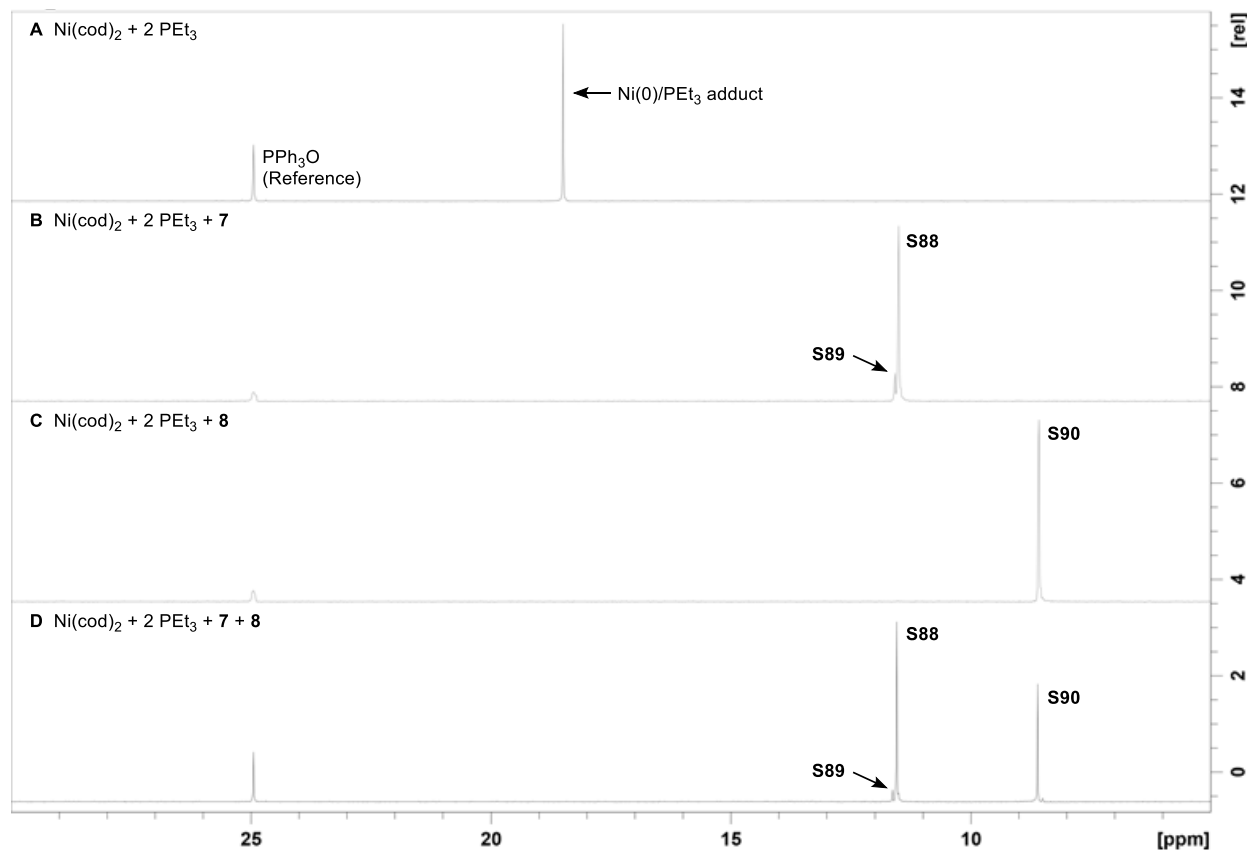
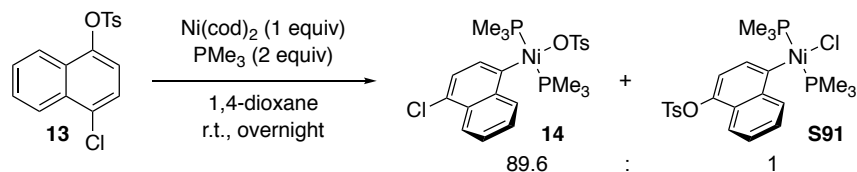


Figure S27. ^{31}P NMR studies on oxidative addition at Ni/PEt_3 using 1-chloronaphthalene and 1-naphthyl tosylate.

2. Intramolecular Competition: Synthesis, Isolation, and Characterization of **14**.



Synthesis, Isolation, and Characterization. In a nitrogen-atmosphere glovebox, Ni(cod)₂ (275.1 mg, 1.0 mmol, 1.0 equiv), PMe₃ (152.2 mg, 2.0 mmol, 2.0 equiv), and 1,4-dioxane (5 mL) were combined in a 20 mL glass vial equipped with a magnetic stir bar. The mixture was stirred for 10 minutes, substrate **13** (332.8 mg, 1.0 mmol, 1.0 equiv) was added, the vial was sealed with a Teflon-lined cap, and the reaction mixture was stirred overnight at room temperature. The vial cap was then loosened and the vial was transferred into a glass vacuum chamber. The chamber was sealed, removed from the glovebox, and connected to a Schlenk line. The reaction mixture was concentrated under high vacuum to yield a yellow solid. While under vacuum, the vacuum chamber was sealed, transferred back into the glovebox, and then opened. Hexanes (5 mL) was added to the reaction vial, and the vial was sealed and removed from the glovebox. The hexanes mixture was sonicated for 15 minutes to provide a uniform suspension. The vial was again transferred into the glovebox and the yellow precipitate was collected on a fritted glass filter, washed with hexanes (6 x 1 mL), and transferred to a 1 dram vial. The loosely-capped vial was placed inside a glass vacuum chamber, and the chamber was sealed, removed from the glovebox, and connected to a Schlenk line. Volatiles were removed under high vacuum to yield **14** (476.9 mg, 80% yield) as a fine yellow powder isolated as an adduct with dioxane (Ni:dioxane = 1 : 0.5). ¹H NMR (500 MHz, C₆D₆, δ): 9.75 (d, *J* = 8.1 Hz, 1H), 8.28 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 2H), 7.38 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.30 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 2H), 3.35 (s, 4H, ½ molecule of 1,4-dioxane), 1.96 (s, 3H), 0.68 (t, *J* = 3.8 Hz, 18H); ¹³C{¹H} NMR (151 MHz, C₆D₆, δ): 150.3 (t, *J*_{CP} = 37.4 Hz), 142.9, 140.6, 140.2, 133.5, 132.5 (t, *J*_{CP} = 4.9), 130.4 (br), 129.0, 127.2 (br), 126.9, 126.7, 125.5, 125.3, 124.8 (br), 67.2 (1,4-dioxane), 21.1, 12.4 (t, *J*_{CP} = 13.7 Hz); ³¹P{¹H} NMR (203 MHz, C₆D₆, δ): -17.4. HRMS (ESI/Q-TOF) *m/z*: [M - OTs - 1,4-dioxane]⁺ Calcd for C₁₆H₂₄ClNiP₂ 371.0390; Found 371.0378. X-ray quality crystals were grown from toluene/pentane at -25 °C. Structure was verified by X-ray diffraction (see p. S59 for details). The X-ray structure does not indicate dioxane in the crystal lattice, suggesting that it was displaced during the recrystallization procedure. Some toluene was detected in the crystal lattice by XRD. To further evaluate the presence of solvents in the crystals, a larger portion of **14** (synthesized in a separate experiment) was purified by recrystallization from toluene/pentane. After rinsing the crystals with pentane, crushing with a glass stir rod, and thoroughly drying the crystals under high vacuum, a ¹H NMR spectrum of **14** dissolved in C₆D₆ indicated that most of the 1,4-dioxane was removed through this recrystallization process (**14** : dioxane = 1 : 0.04). A significant amount of toluene was detected by ¹H NMR (**14** : toluene = 1 : 0.8), consistent with observation of this solvent in the crystal lattice by XRD.

³¹P NMR Analysis of Crude Reaction Mixture. A crude NMR was obtained after setting up an identical reaction as described above. The reaction was stopped after 2 hours, and an aliquot of the crude reaction mixture was transferred to an NMR tube, along with a capillary tube insert containing a solution of PPh₃O in C₆D₆ (0.1 M). The sample was analyzed by ³¹P{¹H} NMR. Figure S28 compares the crude reaction mixture (spectrum D) to the NMR spectrum for a Ni(cod)₂/PMe₃ mixture (spectrum A) and to similar oxidative addition adducts for reaction of a naphthyl chloride and tosylate. In spectrum A, the signal at -20.8 corresponds to (PMe₃)₄Ni, and the signal at -8.4 ppm is assigned to another unidentified Ni(o)/PMe₃ adduct. Reaction of the Ni(cod)₂/PMe₃ mixture with 1-chloronaphthalene **7** results in a signal at -12.8 ppm and a much smaller signal at -14.2 ppm (spectrum B). The former is assigned to the oxidative addition adduct **11**, while the latter is assigned to the adduct **S50** resulting from oxidative addition of 2-chloronaphthalene (a contaminant in commercial 1-chloronaphthalene). In the intramolecular competition using **13**, a very small signal is observed at -13.0 ppm, which is assigned to minor product **S91** on the basis of its similar chemical shift to **11** (spectrum D). Reaction of the Ni(cod)₂/PMe₃ mixture with 1-naphthyl tosylate **8** results in a signal at -15.4 ppm assigned to oxidative addition adduct **12** (spectrum C). In the intramolecular competition using **13**, the major product signal is observed at -15.7 ppm, which is assigned to product **14** on the basis of its similar chemical shift to **12** (spectrum D). The identity of **14** was further confirmed after isolation and characterization, as described above. In spectrum D, the ratio of **14** to putative **S91** is 89.6 : 1. Although this reaction was only run for 2 hours (compared to overnight for isolation), it appears that the reaction was essentially complete at 2 hours based on the absence of any detectable Ni(o)/PMe₃ adducts.

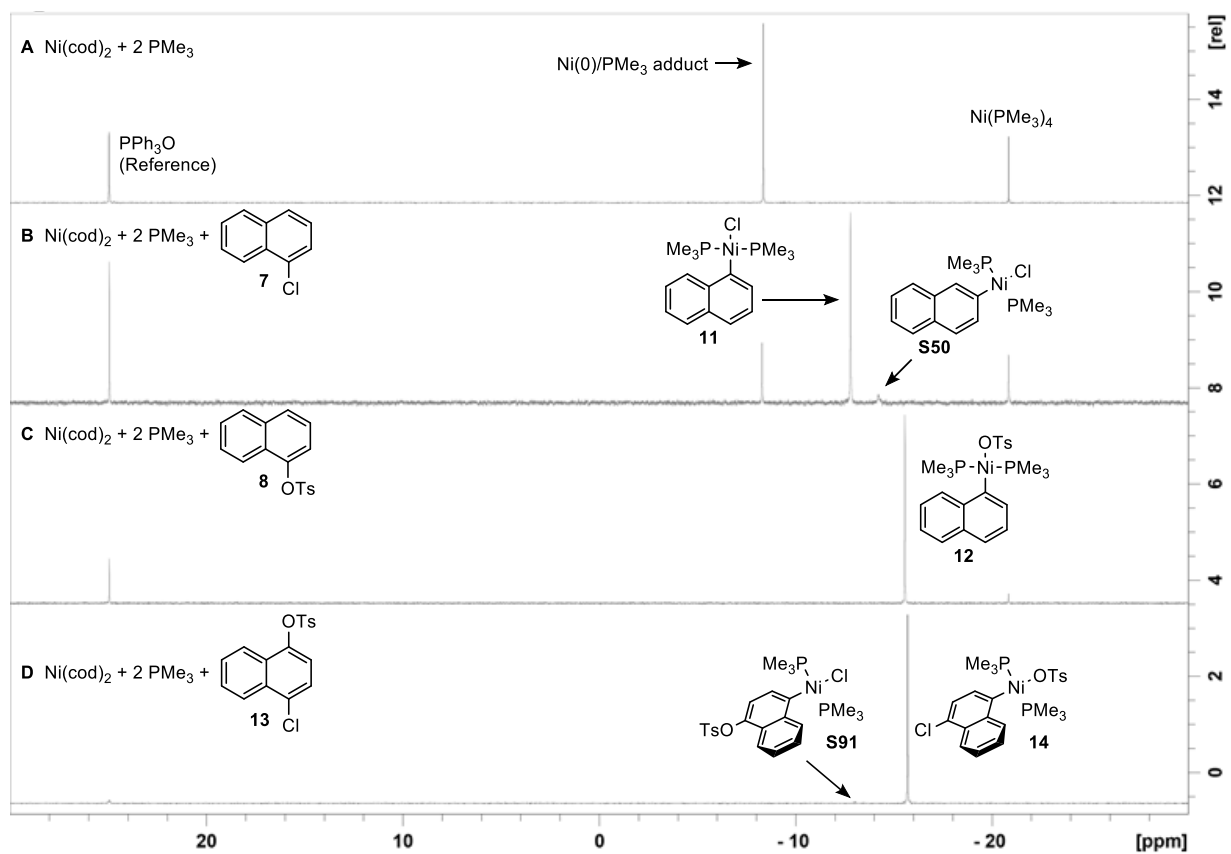


Figure S28. ^{31}P NMR studies on oxidative addition at Ni/PMe_3 using (B) 1-chloronaphthalene, (C) 1-naphthyl tosylate, and (D) 4-chloro-1-naphthyl tosylate.

3. Irreversibility of Oxidative Addition.

The following studies were performed to gather insight into the reversibility (or lack thereof) of oxidative addition of either Ar—Cl or Ar—OTs under the stoichiometric reaction conditions. As described below, the results show no evidence for reversibility. This conclusion is in agreement with DFT studies (see section II), where the calculated barrier for reductive elimination at $(\text{PR}_3)_2\text{Ni}^{\text{II}}(\text{X})\text{Ar}$ ($\text{X} = \text{Cl}$ or OTs) to give $(\text{PR}_3)_2\text{Ni}^0 + \text{ArX}$ ($\sim 30\text{--}40$ kcal/mol) is much larger than the barrier for oxidative addition ($\sim 9\text{--}16$ kcal/mol). Because oxidative addition is reversible, the distribution of oxidative addition products in the stoichiometric studies reflect the relative rates of oxidative addition (assuming no further decomposition of products).

Irreversibility Studies using PCy_3 . The studies were carried out according to a modified general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a $\text{Ni}(\text{cod})_2/\text{PCy}_3$ stock solution. Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane). Reaction of $\text{Ni}(\text{cod})_2/\text{PCy}_3$ with **7** provides the chloride oxidative addition adducts **9** and **S40** (resulting from oxidative addition of 2-chloronaphthalene, a contaminant in 1-chloronaphthalene) after 4 or 2 hours (Figure S29, A-B). When, after 2 hours, an equivalent of **8** is added and the reaction is allowed to stir for an additional 2 hours, no change is detected in the NMR spectrum (Figure S29C).

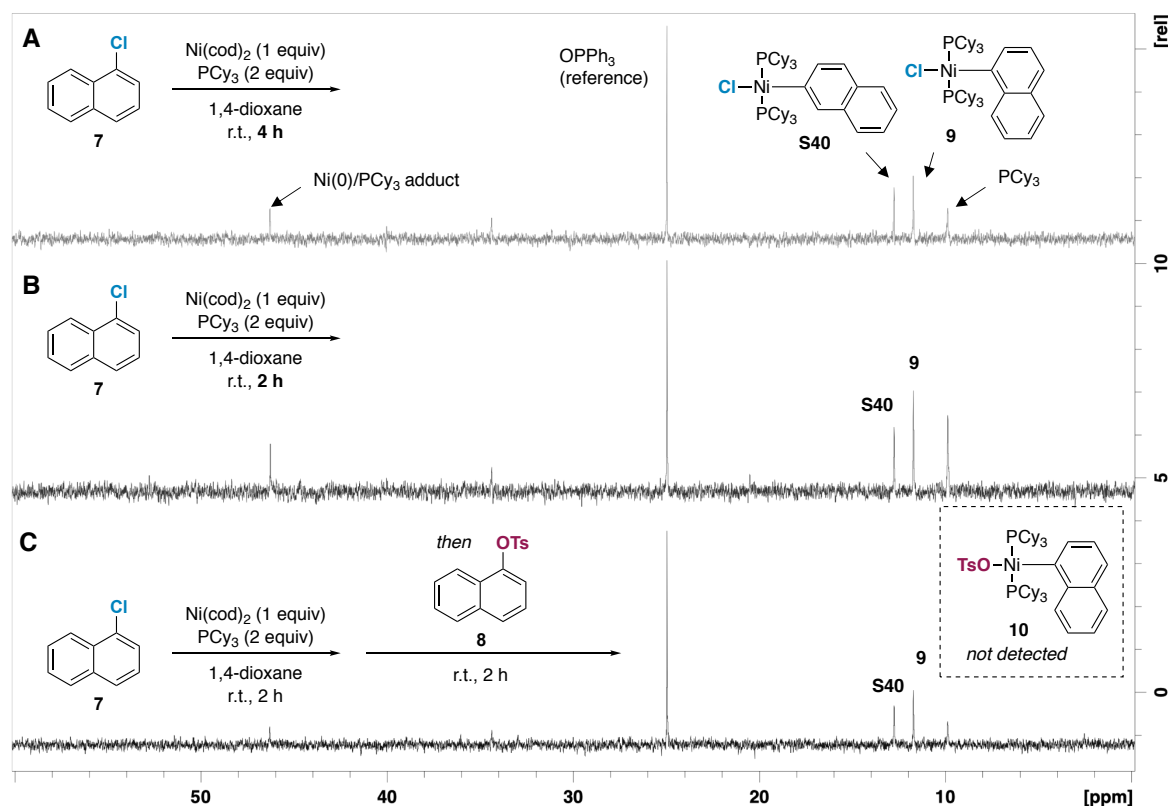


Figure S29. ^{31}P NMR studies on oxidative addition at Ni/PCy_3 using (A) 1-chloronaphthalene for 4 hours, (B) 1-chloronaphthalene for 2 hours, (C) 1-chloronaphthalene for 2 hours followed by 1-naphthyl tosylate for 2 hours.

Irreversibility Studies using PMe_3 . Studies were carried out according to a modified general procedure using 1-chloronaphthalene, 1-naphthyl tosylate (5.0 mg), and a $\text{Ni}(\text{cod})_2/\text{PMe}_3$ stock solution containing a 1:1.9 ratio of $\text{Ni}:\text{PMe}_3$. (Note: the amount of PPh_3O reference was not standardized across the reactions shown in Figures S30-S31.) Reactions were analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR (203 or 122 MHz, 1,4-dioxane).

Reaction of $\text{Ni}(\text{cod})_2/\text{PMe}_3$ with a mixture of **7** and **8** for 2 h provides primarily product **12** as well as a small amount of **11** (Figure S30A). Reaction of $\text{Ni}(\text{cod})_2/\text{PMe}_3$ with **7** alone provides the chloride oxidative addition adducts **11** and **S50** (resulting from oxidative addition of 2-chloronaphthalene, a contaminant in 1-chloronaphthalene) after 1 hour (Figure S30B). A large amount of unreacted $\text{Ni}(\text{o})/\text{PMe}_3$ adducts remains at this time. If an equivalent of **8** is then added and the reaction is stirred for 1 hour, the unreacted $\text{Ni}(\text{o})/\text{PMe}_3$ adducts disappear and a new signal appears for **12**; however, there is no apparent change in the signal for **11** (Figure S30C).

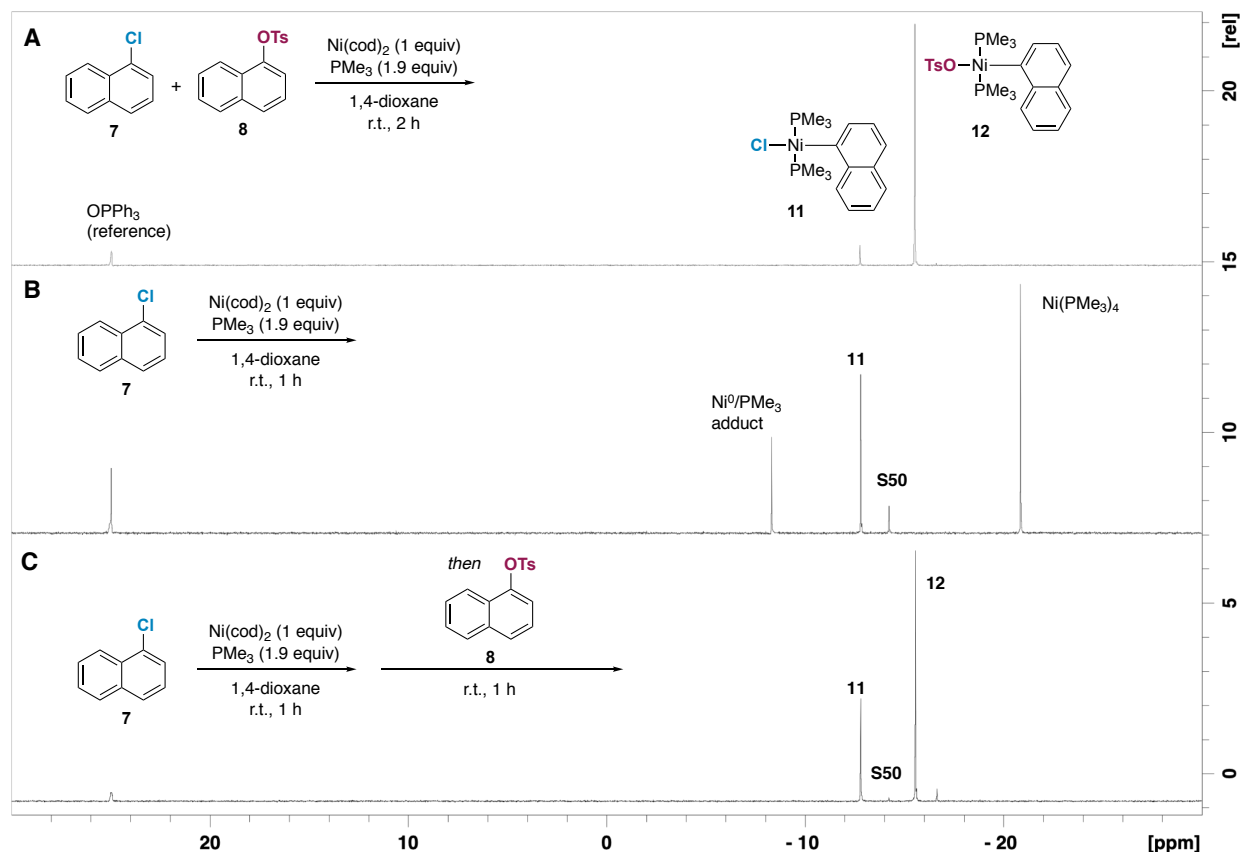


Figure S30. ^{31}P NMR studies on oxidative addition at Ni/PMe_3 using (A) 1-chloronaphthalene and 1-naphthyl tosylate for 2 hours, (B) 1-chloronaphthalene for 1 hour, and (C) 1-chloronaphthalene for 1 hour followed by 1-naphthyl tosylate for 1 hour.

Reaction of $\text{Ni(cod)}_2/\text{PMe}_3$ with **8** alone provides the tosylate oxidative addition adducts **12** after 1 hour (Figure S31B). When an equivalent of **7** is then added and the reaction is stirred for 1 hour further, a trace amount of the chloride adduct **11** appears; this signal is nearly undetectable and likely results from reaction of a trace amount of Ni(0) that remained before addition of **7** (Figure S31C).

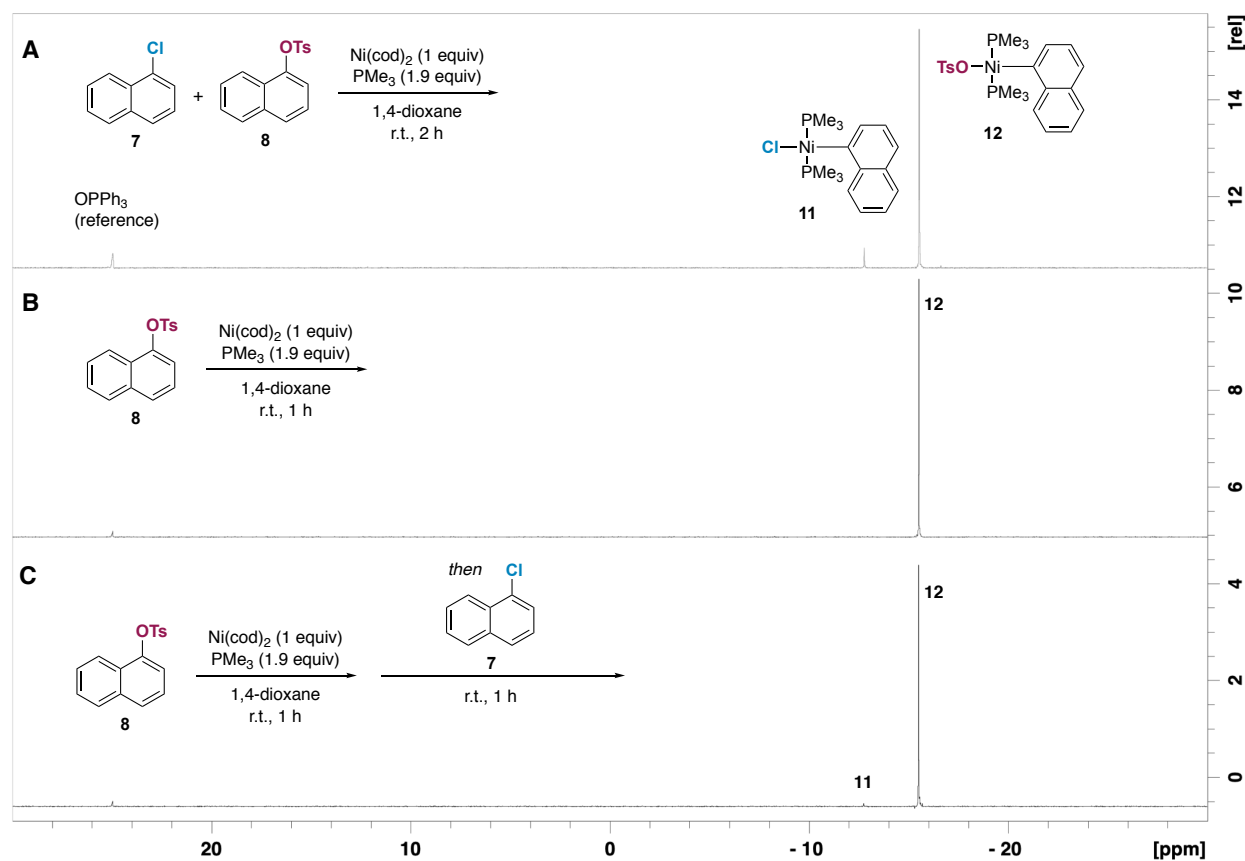
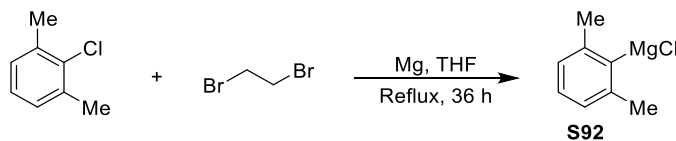


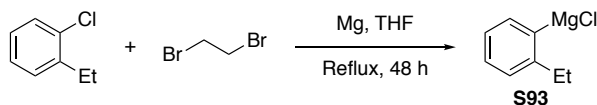
Figure S31. ^{31}P NMR studies on oxidative addition at Ni/PMe_3 using (A) 1-chloronaphthalene and 1-naphthyl tosylate for 2 hours, (B) 1-naphthyl tosylate for 1 hour, and (C) 1-naphthyl tosylate for 1 hour followed by 1-chloronaphthalene for 1 hour.

C. Synthesis of Reagents

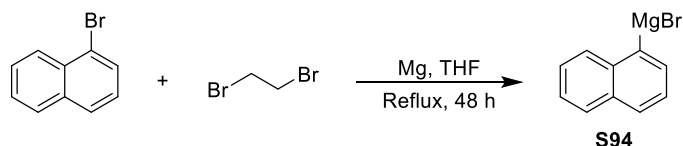
1. Aryl Grignard Reagents for use in Ni(II) Precatalyst Synthesis



2,6-Dimethylphenylmagnesium chloride (S92). Grignard **S92** was prepared according to a modified literature procedure.¹² To an oven-dried 25 mL Schlenk flask equipped with a stir bar, under nitrogen, was added magnesium turnings that had been activated by crushing with a mortar and pestle (155.6 mg, 6.4 mmol, 1.6 equiv). The flask containing the Mg was heated at 100 °C while flushing with nitrogen for 1 hour before cooling to room temperature. Once cool, dry degassed THF (8 mL) was added and the mixture was stirred while adding degassed 1,2-dibromoethane (~10 drops). 2,6-Dimethylphenyl chloride was then added dropwise over ~2 minutes (530.0 uL, 4.0 mmol, 1.0 equiv). The mixture darkened slightly and was stirred while heating to reflux for 36 hours. The resulting Grignard reagent **S92** as a solution in THF was used without purification for the synthesis of the corresponding Ni complex.

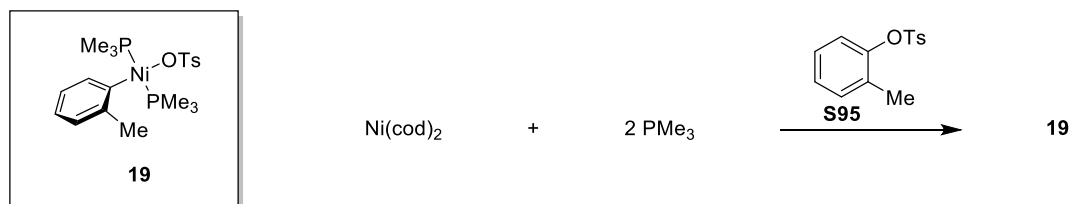


2-Ethylphenylmagnesium chloride (S93). Grignard **S93** was prepared according to a modified literature procedure.¹² To an oven-dried 25 mL Schlenk flask equipped with a stir bar, under nitrogen, was added magnesium turnings (233.4 mg, 9.6 mmol, 1.6 equiv) that had been activated by crushing with a mortar and pestle. This flask was heated at 100 °C while flushing with nitrogen for 1 hour before cooling to room temperature. Once cool, dry degassed THF (12 mL) was added and the mixture was stirred while adding degassed 1,2-dibromoethane (~15 drops). 2-Ethylphenyl chloride (811.2 uL, 6.0 mmol, 1.0 equiv) was then added dropwise over ~2 minutes. The mixture darkened slightly and was stirred while heating to reflux for 48 hours. The resulting Grignard reagent **S93** as a solution in THF was used without purification for the synthesis of the corresponding Ni complex.



1-Naphthylmagnesium bromide (S94). Grignard **S94** was prepared according to a modified literature procedure.¹² To an oven-dried 25 mL Schlenk flask equipped with a stir bar, under nitrogen, was added magnesium turnings (155.6 mg, 6.4 mmol, 1.6 equiv) that had been activated by crushing with a mortar and pestle. This flask was heated at 100 °C while flushing with nitrogen for 1 hour before cooling to room temperature. Once cool, dry degassed THF (8 mL) was added and the mixture was stirred while adding degassed 1,2-dibromoethane (~10 drops). 1-Naphthyl bromide (559.6 uL, 4.0 mmol, 1.0 equiv) was then added dropwise over ~2 minutes. The mixture darkened slightly and was stirred while heating to reflux for 48 hours. The resulting Grignard reagent **S94** as a solution in THF was used without purification for the synthesis of the corresponding Ni complex.

2. Nickel(II) Precatalysts

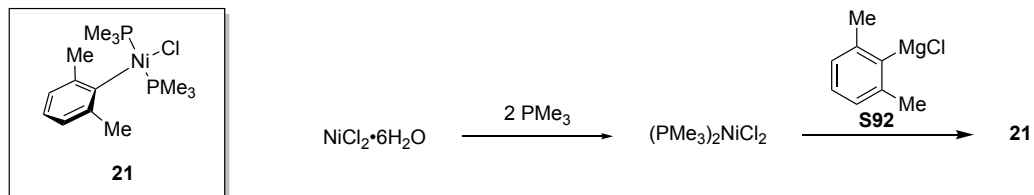


Trans-bis(trimethylphosphine)(2-methylphenyl)nickel(II) tosylate (19). In a nitrogen-atmosphere glovebox, Ni(cod)₂ (275.1 mg, 1.0 mmol, 1.0 equiv), PMe₃ (152.2 mg, 2.0 mmol, 2.0 equiv), and dioxane (5 mL) were combined in a 20 mL glass vial equipped with a magnetic stir bar. The mixture was stirred for 10 minutes, **S95** (262.3 mg, 1.0 mmol, 1.0 equiv) was added, the vial was sealed with a Teflon-lined cap, and the reaction mixture was stirred overnight at room temperature. The vial cap was loosened, and the vial was transferred into a glass vacuum chamber. The chamber was sealed, removed from the glovebox, and connected to a Schlenk line. The reaction mixture was concentrated under high vacuum to yield a yellow solid. The vacuum chamber was sealed under vacuum, transferred back into the glovebox, and opened. Hexanes (5 mL) was added to the reaction vial, and the vial was sealed and removed from the glovebox. The hexanes mixture was sonicated for 15 minutes to provide a uniform suspension. The vial was again transferred into the glovebox and the yellow precipitate was collected on a fritted glass filter, washed with hexanes (6 x 1 mL), and transferred to a 1 dram vial. The loosely-capped vial was placed inside a glass vacuum chamber, and the chamber was sealed, removed from the glovebox, and connected to a Schlenk line. Volatiles were removed under high vacuum to yield **19** (387.2 mg, 82% yield) as a fine yellow powder. ¹H NMR (500 MHz, C₆D₅CD₃, δ): 7.92 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 6.9 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.77–6.67 (multiple overlapping signals, 3H), 2.92 (s, 3H), 2.01 (s, 3H), 0.84 (t, *J* = 3.5 Hz, 18H); ¹³C{¹H}

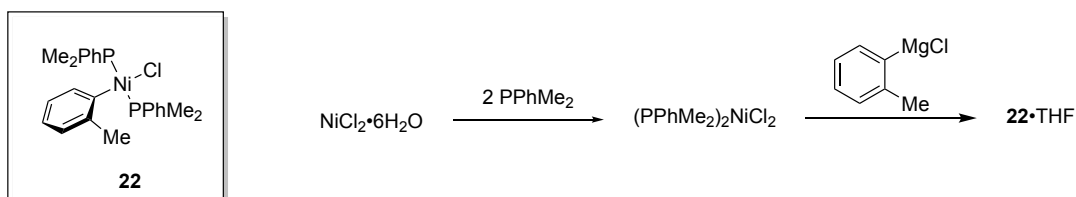
NMR (151 MHz, C₆D₆, δ): 147.6 (t, $J_{\text{CP}} = 35.8$ Hz), 143.3 (br), 142.2 (t, $J_{\text{CP}} = 3.6$ Hz), 139.9, 135.2 (t, $J_{\text{CP}} = 4.5$ Hz), 129.0, 127.6 (t, $J_{\text{CP}} = 7.1$ Hz), 126.8, 124.2 (t, $J_{\text{CP}} = 6.6$ Hz), 122.5 (t, $J_{\text{CP}} = 4.9$ Hz), 26.4, 21.1, 12.4 (t, $J_{\text{CP}} = 13.6$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, C₆D₆, δ): -17.5; HRMS (ESI/Q-TOF) m/z : [M - OTs]⁺ Calcd for C₁₃H₂₅NiP₂ 301.0779; Found 301.0757.



***Trans*-bis(trimethylphosphine)(2-methylphenyl)nickel(II) chloride (**20**).** Complex **20** was prepared by analogy to a literature procedure.¹³ In a nitrogen-atmosphere glovebox, (PMe₃)₂NiCl₂⁷ (563.5 mg, 2.0 mmol, 1.0 equiv) and THF (34 mL) were combined in an oven-dried 100 mL Schlenk flask equipped with a stir bar. The flask was sealed with a septum and removed from the glovebox. After all solids were completely dissolved, the flask was cooled in an ice bath for ~5 minutes. *o*-Tolyl magnesium chloride (1.4 mL of a ~1.4 M solution in THF, 2.0 mmol, 1.0 equiv) was added dropwise via cannula while stirring vigorously, resulting in a color change from dark red to brownish-yellow. The reaction was stirred at 0 °C under nitrogen for 1 hour before warming to room temperature. After this time, anhydrous MeOH (2 mL) was added under nitrogen to quench any remaining Grignard. The solvent was then removed under reduced pressure on a Schlenk line, and the flask was back-filled with nitrogen. A minimal amount of anhydrous degassed MeOH (5 mL) was added to the flask, which was then sonicated to obtain a uniform suspension (~10 minutes) before cooling to -25 °C in the glovebox freezer overnight. The precipitate was collected on a fritted glass filter by vacuum filtration in the glovebox, washed with degassed hexane (2 x 2 mL), and dried under high vacuum to yield **20** as a yellow powder (627.9 mg, 93% yield). ^1H NMR (600 MHz, C₆D₆, δ): 7.33 (d, $J = 7.2$ Hz, 1H), 6.89–6.86 (multiple signals, 2H), 6.83 (m, 1H), 2.73 (s, 3H), 0.81 (t, $J = 3.8$ Hz, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C₆D₆, δ): 156.2 (t, $J_{\text{CP}} = 34.9$ Hz), 142.4 (t, $J_{\text{CP}} = 3.7$ Hz), 135.0 (t, $J_{\text{CP}} = 4.5$ Hz), 127.6 (t, $J_{\text{CP}} = 3.3$ Hz), 124.3 (t, $J_{\text{CP}} = 3.0$ Hz), 122.1 (t, $J_{\text{CP}} = 2.5$ Hz), 26.5, 13.0 (t, $J_{\text{CP}} = 13.9$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz, C₆D₆, δ): -14.3; HRMS (ESI/Q-TOF) m/z : [M - Cl]⁺ Calcd for C₁₃H₂₅NiP₂ 301.0779; Found 301.0760.

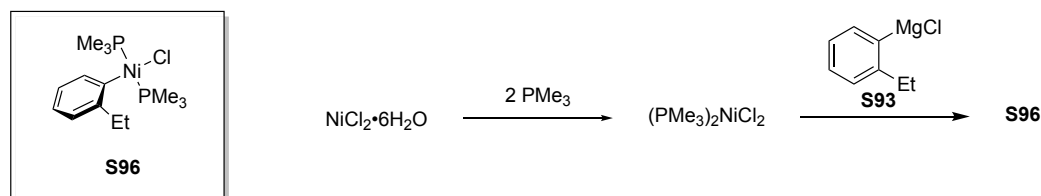


***Trans*-bis(trimethylphosphine)(2,6-dimethylphenyl)nickel(II) chloride (**21**).** Complex **21** was prepared by analogy to a literature procedure.¹³ In a nitrogen-atmosphere glovebox, (PMe₃)₂NiCl₂⁷ (563.5 mg, 2.0 mmol, 1.0 equiv) and THF (34 mL) were combined in an oven-dried 100 mL Schlenk flask equipped with a stir bar. The flask was sealed with a septum and removed from the glovebox. After all solids were completely dissolved, the flask was cooled in an ice bath for ~5 minutes. **S92** (4 mL of a ~0.5 M solution in THF, 2.0 mmol, 1.0 equiv) was added dropwise via cannula while stirring vigorously, resulting in a color change from dark red to brownish-yellow. The reaction was stirred at 0 °C under nitrogen for 45 min before warming to room temperature. After this time, anhydrous MeOH (2 mL) was added under nitrogen to quench any remaining Grignard. The solvent was then removed under reduced pressure on a Schlenk line, and the flask was back-filled with nitrogen. A minimal amount of anhydrous degassed MeOH (8 mL) was added to the flask, which was then sonicated to obtain a uniform suspension (~15 minutes) before cooling to -25 °C in the glovebox freezer overnight. The precipitate was collected on a fritted glass filter by vacuum filtration, washed with hexane (2 x 2 mL), and dried under high vacuum to yield **21** as a yellow powder (274.1 mg, 39% yield). ¹H NMR (500 MHz, C₆D₆, δ): 6.85 (m, 1H), 6.78–6.75 (multiple signals, 2H), 2.79 (s, 6H), 0.81 (t, *J* = 3.6 Hz, 18H); ¹³C{¹H} NMR (151 MHz, C₆D₆, δ): 156.2 (t, *J*_{CP} = 34.2 Hz), 141.3 (t, *J*_{CP} = 7.4 Hz), 124.9 (t, *J*_{CP} = 3.2 Hz), 122.9 (br), 26.1, 13.8 (t, *J*_{CP} = 13.8 Hz); ³¹P{¹H} NMR (203 MHz, C₆D₆, δ): -14.2; HRMS (ESI/Q-TOF) *m/z*: [M - Cl]⁺ Calcd for C₁₄H₂₈NiP₂ 315.0936; Found 315.0923. A minor impurity detected in the NMR spectra is believed to correspond to the nickel bromide analogue of **21** (Br source = dibromoethane from synthesis of the Grignard). Evidence for this assignment was obtained by synthesizing complex **21** from the magnesium bromide Grignard (prepared from xylyl bromide instead of chloride). The impurity in the original spectra was detected as the major product in the NMR spectra of the nickel complex prepared by this route.



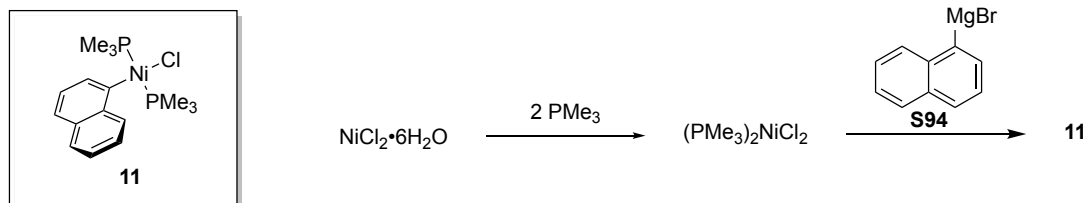
***Trans*-bis(dimethylphenylphosphine)(2-methylphenyl)nickel(II) chloride (**22**).** Complex **22** was prepared by analogy to a literature procedure.¹³ In a nitrogen-atmosphere glovebox, (PPhMe₂)₂NiCl₂⁷ (811.8 mg, 2.0 mmol, 1.0 equiv) and THF (34 mL) were combined in an oven-dried 100 mL Schlenk flask equipped with a stir bar. The flask was sealed with a septum and removed from the glovebox. After all solids were completely dissolved, the flask was cooled in an ice bath for ~5 minutes. *o*-Tolyl magnesium chloride

(1.4 mL of a ~1.4 M solution in THF, 2.0 mmol, 1.0 equiv) was added dropwise via cannula while stirring vigorously, resulting in a color change from dark red to dark yellow. The reaction was stirred at 0 °C under nitrogen for 1 hour before warming to room temperature. After this time, anhydrous MeOH (2 mL) was added under nitrogen to quench any remaining Grignard. The solvent was then removed under reduced pressure on a Schlenk line, and the flask was back-filled with nitrogen. A minimal amount of anhydrous degassed MeOH (5 mL) was added to the flask, which was then sonicated to obtain a uniform suspension (~10 minutes) before cooling to -25 °C in the glovebox freezer overnight. The precipitate was collected on a fritted glass filter by vacuum filtration, washed with hexane (2 x 2 mL), and dried under high vacuum to yield the mono-THF adduct of **22** as a yellow powder (579.2 mg, 54% yield). ^1H NMR (600 MHz, C_6D_6 , δ): 7.63–7.60 (multiple signals, 4H), 7.08–7.05 (multiple signals, 6H), 6.91 (d, J = 7.5 Hz, 1H), 6.79–6.75 (multiple signals, 2H), 6.71 (ddd, J = 7.9, 7.9, 2.3 Hz, 1H), 3.59 (br, 4H, THF), 2.61 (s, 3H), 1.44–1.40 (m, 4H, THF), 1.21 (t, J = 3.7 Hz, 6H), 0.84 (t, J = 3.6 Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , δ): 153.6 (t, J_{CP} = 34.7 Hz), 143.2 (t, J_{CP} = 3.6 Hz), 136.0 (t, J_{CP} = 4.5 Hz), 135.7 (t, J_{CP} = 18.9 Hz), 131.5 (t, J_{CP} = 5.2 Hz), 129.3, 128.3, 127.6 (t, J_{CP} = 3.2 Hz), 124.0 (t, J_{CP} = 2.0 Hz), 122.4 (t, J_{CP} = 5.0 Hz), 67.9 (THF), 26.2, 25.8 (THF), 12.9 (t, J_{CP} = 14.2 Hz), 11.3 (t, J_{CP} = 15.3 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, C_6D_6 , δ): -7.4; HRMS (ESI/Q-TOF) m/z : $[\text{M} - \text{Cl} - \text{THF}]^+$ Calcd for $\text{C}_{23}\text{H}_{29}\text{NiP}_2$ 425.1092; Found 425.1071.

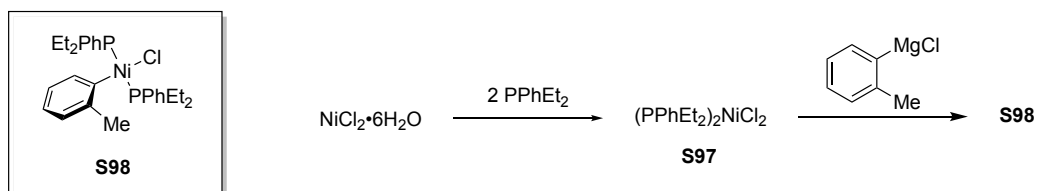


Trans-bis(trimethylphosphine)(2-ethylphenyl)nickel(II) chloride (S96). Complex **S96** was prepared by analogy to a literature procedure.⁸ In a nitrogen-atmosphere glovebox, $(\text{PMe}_3)_2\text{NiCl}_2$ (563.5 mg, 2.0 mmol, 1.0 equiv) and THF (34 mL) were combined in an oven-dried 100 mL Schlenk flask equipped with a stir bar. The flask was sealed with a septum and removed from the glovebox. After all solids were completely dissolved, the flask was cooled in an ice bath for ~5 minutes. **S93** (8 mL of a ~0.5 M solution in THF, 4 mmol, 1.0 equiv) was added dropwise via cannula while stirring vigorously, resulting in a color change from dark red to brownish-yellow. The reaction was stirred at 0 °C under nitrogen for 1 hour before warming to room temperature. After this time, anhydrous MeOH (2 mL) was added under nitrogen to quench any remaining Grignard. The solvent was then removed under reduced pressure on a Schlenk line, and the flask was back-filled with nitrogen. A minimal amount of anhydrous degassed MeOH (5 mL) was added to the flask, which was then sonicated to obtain a uniform suspension (~15 minutes) before cooling to -25 °C in the glovebox freezer overnight. The precipitate was collected on a fritted glass filter by vacuum filtration, washed with hexane (2 x 2 mL), and dried under high vacuum to yield **S96** as a yellow powder (389.8 mg, 55% yield). ^1H NMR (500 MHz, C_6D_6 , δ): 7.35–7.29 (m, 1H), 6.93–6.88 (multiple signals, 3H), 3.29 (q, J = 7.5 Hz, 2H), 1.35 (t, J = 7.5 Hz, 3H), 0.82 (t, J = 3.5 Hz, 18H), $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , δ): 155.8 (t, J_{CP} = 34.5 Hz), 147.9 (br), 134.8 (br), 125.4 (br), 124.6 (br), 122.3 (br), 33.3, 14.8, 13.0 (t, J_{CP} = 13.8

Hz); $^3\text{P}\{^1\text{H}\}$ NMR (203 MHz, C_6D_6 , δ): -14.3; HRMS (ESI/Q-TOF) m/z : $[\text{M} - \text{Cl}]^+$ Calcd for $\text{C}_{14}\text{H}_{27}\text{NiP}_2$ 315.0936; Found 315.0916. A minor impurity detected in the NMR spectra is believed to correspond to the nickel bromide analogue of **S96** (Br source = dibromoethane from synthesis of the Grignard). Evidence for this assignment was obtained by synthesizing complex **S96** from the magnesium bromide Grignard (prepared from 2-bromo-1-ethylbenzene). The impurity in the original spectra was detected as the major product in the NMR spectra of the nickel complex prepared by this route.

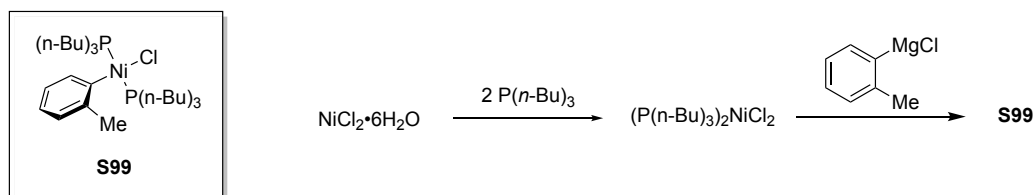


Trans-bis(trimethylphosphine)(1-naphthyl)nickel(II) chloride (11). Complex **11** was prepared by analogy to a literature procedure.⁸ In a nitrogen-atmosphere glovebox, $\text{P}(\text{Me}_3)_2\text{NiCl}_2$ (140.9 mg, 0.5 mmol, 1.0 equiv) and THF (8.5 mL) were combined in an oven-dried 25 mL Schlenk flask equipped with a stir bar. The flask was sealed with a septum and removed from the glovebox. After all solids were completely dissolved, the flask was cooled in an ice bath for ~5 minutes. **S94** (1 mL of a ~0.5 M solution in THF, 0.5 mmol, 1.0 equiv) was added dropwise via cannula while stirring vigorously, resulting in a color change from dark red to brownish-yellow. The reaction was stirred at 0 °C under nitrogen for 1 hour before warming to room temperature. After this time, anhydrous MeOH (1 mL) was added under nitrogen to quench any remaining Grignard. The solvent was then removed under reduced pressure on a Schlenk line, and the flask was back-filled with nitrogen. A minimal amount of anhydrous degassed MeOH (3 mL) was added to the flask, which was then sonicated to obtain a uniform suspension (~10 minutes) before cooling to -25 °C in the glovebox freezer overnight. The precipitate was collected on a fritted glass filter by vacuum filtration, washed with hexane (2 x 2 mL), and dried under high vacuum to yield **11** as a yellow powder (177 mg, 95% yield). ^1H NMR (600 MHz, C_6D_6 , δ): 9.25 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.46 (d, J = 7.0 Hz, 1H), 7.37 (dd, J = 7.5, 7.0 Hz, 1H), 7.32 (d, J = 7.9 Hz, 1H), 7.29 (dd, J = 7.5, 7.0 Hz, 1H), 7.12 (dd, J = 8.1, 8.0 Hz, 1H), 0.74 (t, J = 3.8 Hz, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , δ): 141.0 (br), 134.1 (br), 132.3, 132.1 (t, J_{CP} = 5.3 Hz), 129.0, 126.1, 125.4, 125.1 (t, J_{CP} = 3.2 Hz), 124.3, 121.9 (t, J_{CP} = 5.3), 13.8 (t, J_{CP} = 14.4 Hz); $^3\text{P}\{^1\text{H}\}$ NMR (122 MHz, C_6D_6 , δ): -14.0; HRMS (ESI/Q-TOF) m/z : $[\text{M} - \text{Cl}]^+$ Calcd for $\text{C}_{16}\text{H}_{25}\text{NiP}_2$ 337.0779; Found 337.0761.

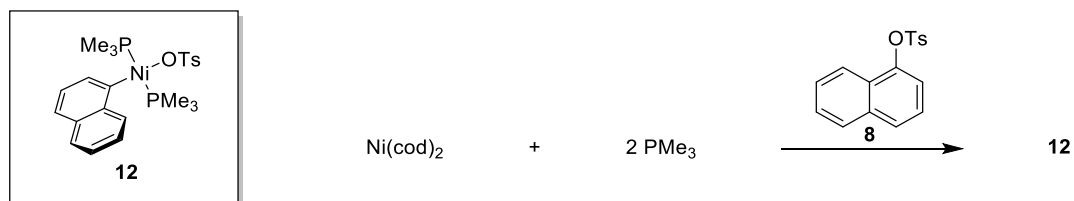


Bis(diethylphenylphosphine)nickel(II) chloride (S97). The $(\text{PPhEt}_2)_2\text{NiCl}_2$ intermediate was prepared by analogy to a literature procedure.⁷ $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (475.4 mg, 2.0 mmol, 1.0 equiv) and EtOH (8 mL) were combined in an oven-dried 25 mL round bottom flask equipped with a stir bar. The flask was sealed with a rubber septum and the reaction mixture was sparged with nitrogen for ~15 minutes while cooling in an ice bath. A solution of PPhEt_2 (767 μL , 4.4 mmol, 2.2 equiv) in THF (4.4 mL) was added dropwise through the septum via cannula under N_2 , during which time the mixture became cloudy and a dark red precipitate was formed. A reflux condenser was attached and the reaction was heated to reflux (~80 °C) while stirring for 1 hour. The reaction was allowed to cool to room temperature and then cooled further to -20 °C for 30 minutes. Under air, the precipitate was collected on a fritted glass filter via vacuum filtration and washed with cold EtOH (2 x 5 mL). The red solid was dissolved in diethyl ether (10 mL), filtered a second time through a fritted glass filter via vacuum filtration to remove any remaining $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and dried under reduced pressure. The resulting red crystals were transferred to a 20 mL vial and dried under high vacuum to yield **S97** as dark red crystals (812.1 mg, 88% yield). ^1H NMR (600 MHz, C_6D_6 , δ): 7.73 (br, 4H), 7.14 (br, 4H), 7.02 (br, 2H), 2.33 (br, 4H), 2.17 (br, 4H), 1.07 (br, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{C}_6\text{D}_5\text{CD}_3$, δ): 133.5, 133.4, 130.3, 128.6, 15.6 (br), 9.1 (the phosphorus signal is not detected, likely due to line broadening); HRMS (ESI/Q-TOF) m/z : $[\text{M} - \text{Cl}]^+$ Calcd for $\text{C}_{20}\text{H}_{30}\text{ClNiP}_2$ 425.0859; Found 425.0832.

Trans-bis(diethylphenylphosphine)(2-methylphenyl)nickel(II) chloride (S98). Complex **S98** was prepared by analogy to a literature procedure.¹³ In a nitrogen-atmosphere glovebox, $(\text{PPhEt}_2)_2\text{NiCl}_2 \cdot \text{THF}$ (462.0 mg, 1.0 mmol, 1.0 equiv) and THF (3.2 mL) were combined in an oven-dried 25 mL Schlenk flask equipped with a stir bar. The flask was sealed with a septum and removed from the glovebox. After all solids were completely dissolved, the flask was cooled in an ice bath for ~5 minutes. *o*-Tolyl magnesium chloride (700 μL of a ~1.4 M solution in THF, 1.0 mmol, 1.0 equiv) was added dropwise via cannula while stirring vigorously, resulting in a color change from a dark red to a brownish-yellow. The reaction was stirred at 0 °C under nitrogen for 45 minutes before warming to room temperature. After this time anhydrous MeOH (1 mL) was added under nitrogen to quench any remaining Grignard. The solvent was then removed under reduced pressure on a Schlenk line, and the flask was back-filled with nitrogen. A minimal amount of anhydrous degassed MeOH (2.6 mL) was added to the flask which was sonicated to obtain an even suspension (~10 minutes) before cooling to -25 °C in the glovebox freezer overnight. The precipitate was collected on a fritted glass filter by vacuum filtration, washed with hexane (2 x 2 mL), and dried under high vacuum to yield **S98** as a yellow powder (425.7 mg, 88% yield). ^1H NMR (600 MHz, C_6D_6 , δ): 7.53 (br, 4H), 7.06 (multiple signals, 7H), 6.83 (br, 2H), 6.78 (br, 1H), 2.78 (s, 3H), 2.16 (br, 2H), 1.66 (q, $J = 7.0$ Hz, 2H), 1.40 (br, 2H), 1.28 (br, 2H), 0.94 (multiple signals, 6H), 0.73 (multiple signals, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , δ): 151.7 (t, $J_{\text{CP}} = 33.6$ Hz), 143.3 (t, $J_{\text{CP}} = 2.5$ Hz), 136.8 (t, $J_{\text{CP}} = 3.9$ Hz), 132.5 (t, $J_{\text{CP}} = 17.4$ Hz), 132.0 (t, $J_{\text{CP}} = 4.3$ Hz), 129.0, 128.3, 127.5 (t, $J_{\text{CP}} = 4.8$ Hz), 123.9 (br), 122.5 (br), 26.6, 14.1 (t, $J_{\text{CP}} = 12.8$ Hz), 13.9 (t, $J_{\text{CP}} = 13.1$ Hz), 8.0, 7.5; $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, C_6D_6 , δ): 13.4; HRMS (ESI/Q-TOF) m/z : $[\text{M} - \text{Cl}]^+$ Calcd for $\text{C}_{27}\text{H}_{37}\text{NiP}_2$ 481.1718; Found 481.1701.



Trans-bis(trimethylphosphine)(2-methylphenyl)nickel(II) chloride (S99). Complex **S99** was prepared by analogy to a literature procedure.¹³ In a nitrogen-atmosphere glovebox, $(P(n\text{-Bu})_3)_2\text{NiCl}_2$ (422 mg, 0.79 mmol, 1.0 equiv) and THF (8.5 mL) were combined in an oven-dried 25 mL Schlenk flask equipped with a stir bar. The flask was sealed with a septum and removed from the glovebox. After all solids were completely dissolved, the flask was cooled in an ice bath for ~5 minutes. *o*-Tolyl magnesium chloride (600 μL of a ~1.4 M solution in THF, 0.79 mmol, 1.0 equiv) was added dropwise via cannula while stirring vigorously, resulting in a color change from dark red to yellowish-brown. The reaction was stirred at 0 °C under nitrogen for 1 hour before warming to room temperature. After this time, anhydrous MeOH (1 mL) was added under nitrogen to quench any remaining Grignard. The solvent was then removed under reduced pressure on a Schlenk line, and the flask was back-filled with nitrogen. A minimal amount of anhydrous degassed MeOH (3.4 mL) was added to the flask, which was then sonicated to obtain two separate liquid layers (~10 minutes) before cooling to -25 °C in the glovebox freezer overnight. The top layer (MeOH) was removed with a Pasteur pipette and discarded. The remaining liquid residue was mixed with a small portion of cold hexane, and allowed to separate into two liquid layers. The top layer (hexane) was removed and discarded, and the remaining liquid residue was transferred to a 20 mL vial and dried under high vacuum to yield **S99** as a yellow-brown, sticky syrup (431 mg, 92% yield). ^1H NMR (600 MHz, C_6D_6 , δ): 7.55 (d, $J = 7.1$ Hz, 1H), 6.90–6.87 (multiple signals, 2H), 6.84–6.82 (m, 1H), 3.02 (s, 3H), 1.59 (br, 12H), 1.50–1.42 (m, 12H), 1.30 (app sextet, $J = 7.2$ Hz, 12H), 0.89 (t, $J = 7.2$ Hz, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , δ): 154.2 (t, $J_{\text{CP}} = 33.2$ Hz), 142.7 (t, $J_{\text{CP}} = 2.7$ Hz), 136.8 (t, $J_{\text{CP}} = 3.6$ Hz), 127.3 (br), 123.9 (br), 122.0 (br), 27.4, 26.8, 25.0 (t, $J_{\text{CP}} = 6.1$ Hz), 22.6 (t, $J_{\text{CP}} = 11.9$ Hz), 13.9; $^3\text{P}\{^1\text{H}\}$ NMR (203 MHz, C_6D_6 , δ): 5.6; HRMS (ESI/Q-TOF) m/z : $[\text{M} - \text{Cl}]^+$ Calcd for $\text{C}_{31}\text{H}_{61}\text{NiP}_2$ 553.3596; Found 553.3593.

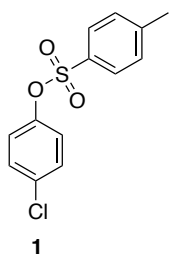


Trans-bis(trimethylphosphine)(1-naphthyl)nickel(II) tosylate (12). In a glovebox, $\text{Ni}(\text{cod})_2$ (275.1 mg, 1.0 mmol, 1.0 equiv), PMe_3 (152.2 mg, 2.0 mmol, 2.0 equiv), and dioxane (5 mL) were combined in a 20 mL glass vial equipped with a magnetic stir bar. The mixture was stirred for 10 minutes, **8** (298.4 mg, 1.0 mmol, 1.0 equiv) was added, the vial was sealed with a Teflon-lined cap, and the reaction mixture was stirred overnight at room temperature. The vial cap was loosened, and the vial was transferred into a

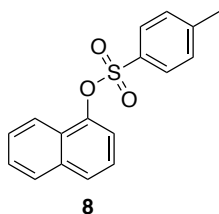
glass vacuum chamber. The chamber was sealed, removed from the glovebox, and connected to a Schlenk line. The reaction mixture was concentrated under high vacuum to yield a yellow solid. The vacuum chamber was sealed under vacuum, transferred back into the glovebox, and opened. Hexanes (5 mL) was added to the reaction vial, and the vial was sealed and removed from the glovebox. The hexanes mixture was sonicated for 15 minutes to provide a uniform suspension. The vial was again transferred into the glovebox and the yellow precipitate was collected on a fritted glass filter, washed with hexanes (6 x 1 mL), and transferred to a 1 dram vial. The loosely-capped vial was placed inside a glass vacuum chamber, and the chamber was sealed, removed from the glovebox, and connected to a Schlenk line. Volatiles were removed under high vacuum to yield **12** (484.7 mg, 95% yield) as a fine yellow powder. ^1H NMR (600 MHz, C_6D_6 , δ): 9.67 (d, $J = 8.2$ Hz, 1H), 8.09 (d, $J = 8.0$ Hz, 2H), 7.54 (d, $J = 8.2$ Hz, 1H), 7.42 (dd, $J = 8.2$, 7.5 Hz, 1H), 7.33 (d, $J = 7.0$ Hz, 1H), 7.27 (dd, $J = 8.2$, 7.0 Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.01 (dd, $J = 8.0$, 7.5 Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 2H), 1.97 (s, 3H), 0.73 (t, $J = 3.8$ Hz, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , δ): 150.7 (t, $J_{\text{CP}} = 36.8$ Hz), 143.1, 140.1, 139.9 (t, $J_{\text{CP}} = 2.6$ Hz), 133.6 (t, $J_{\text{CP}} = 3.0$ Hz), 133.1, 132.8 (t, $J_{\text{CP}} = 5.2$ Hz), 129.0, 128.8, 126.7, 125.6, 124.7, 124.6 (t, $J_{\text{CP}} = 3.4$ Hz), 122.3 (t, $J_{\text{CP}} = 2.6$ Hz), 21.1, 12.5 (t, $J_{\text{CP}} = 13.7$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, C_6D_6 , δ): -17.1; HRMS (ESI/Q-TOF) m/z : $[\text{M} - \text{OTs}]^+$ Calcd for $\text{C}_{16}\text{H}_{25}\text{NiP}_2$ 337.0779; Found 337.0761.

3. Aryl Tosylates

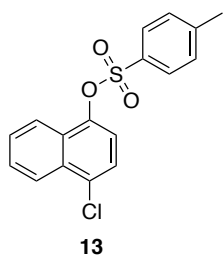
General Procedure. Aryl tosylates were prepared according to a modified literature procedure.¹⁴ Substituted phenol (1 equiv) and TsCl (1.8 equiv) were combined in a 100 mL round bottom flask with pyridine and stirred under nitrogen at 45 °C overnight. The reaction mixture was allowed to cool to room temperature, H₂O (5 mL) was added, and the mixture was stirred at room temperature for 1 h. The reaction mixture was then diluted with 25 mL benzene and 10 mL H₂O and transferred to a separatory funnel. The aqueous and organic layers were separated, and the organic layer was extracted with 10% aqueous HCl (2 x 25 mL), saturated aqueous NaHCO₃ (1 x 25 mL), and brine (1 x 25 mL). The organic layer was dried over MgSO₄, filtered, concentrated, and purified by recrystallization.



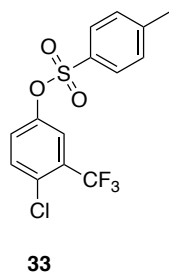
4-Chlorophenyl 4-methylbenzenesulfonate (1). Aryl tosylate **1** was prepared according to the general procedure using 4-chlorophenol (2.00 g, 15.6 mmol, 1.00 equiv), TsCl (5.05 g, 26.5 mmol, 1.7 equiv), and pyridine (20.0 mL). The crude solid was recrystallized from hexanes providing **1** as a white crystalline solid (4.26 g, 97% yield). Spectral data are consistent with those previously reported.¹⁵



Naphthalen-1-yl 4-methylbenzenesulfonate (8). Aryl tosylate **8** was prepared according to the general procedure using 1-naphthol (2.25 g, 15.6 mmol, 1.00 equiv), TsCl (5.05 g, 26.5 mmol, 1.7 equiv), and pyridine (20.0 mL). The crude solid was recrystallized from hexanes providing **8** as a pale tan solid (3.68 g, 79% yield). Spectral data are consistent with those previously reported.¹⁵

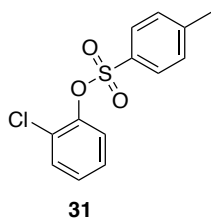


4-Chloronaphthalen-1-yl 4-methylbenzenesulfonate (13). Aryl tosylate **13** was prepared according to the general procedure using 4-chloronaphthol (2.79 g, 15.6 mmol, 1.00 equiv), TsCl (5.05 g, 26.5 mmol, 1.7 equiv), and pyridine (20.0 mL). The crude solid was recrystallized from 95:5 pentane: EtOAc providing **13** as a pale tan solid (4.03 g, 78% yield). Spectral data are consistent with those previously reported.¹⁶

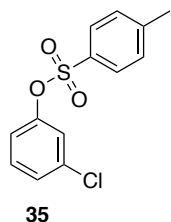


4-Chloro-3-(trifluoromethyl)phenyl 4-methylbenzenesulfonate (33). Aryl tosylate **33** was prepared according to the general procedure using 4-chloro-3-trifluoromethylphenol (1.00 g, 5.0 mmol, 1.00 equiv), TsCl (1.62 g, 8.5 mmol, 1.7 equiv), and pyridine (7.0 mL). The crude solid was recrystallized from 95:5 pentane:EtOAc providing **33** as a white crystalline solid (1.12 g, 64% yield). ¹H NMR (600 MHz, C₆D₆, δ): 7.47 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 2.8 Hz, 1H), 6.71 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.63 (d, *J* = 8.7 1H), 6.55 (d, *J* = 8.2 Hz, 2H), 1.74 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃, δ): 147.9, 146.4, 132.9, 131.8, 130.8 (q, *J*_{CF} = 2.0 Hz), 130.2, 129.7 (q, *J*_{CF} = 32.2 Hz), 128.7, 127.1, 122.2 (q, *J*_{CF} = 5.5), 122.0 (q, *J*_{CF}

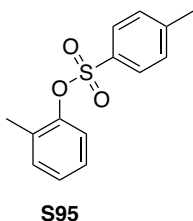
= 274.2 Hz), 21.9; ^{19}F NMR (282 MHz, C_6D_6 , δ): -62.9. HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{10}\text{ClF}_3\text{O}_3\text{SNa}$ 372.9883; Found 372.9868.



2-Chlorophenyl 4-methylbenzenesulfonate (31). Aryl tosylate **31** was prepared according to the general procedure using 2-chlorophenol (2.00 g, 15.6 mmol, 1.00 equiv), TsCl (5.05 g, 26.5 mmol, 1.7 equiv), and pyridine (20.0 mL). The crude solid was recrystallized from hexanes providing **31** as a white solid (2.42 g, 55% yield). Spectral data are consistent with those previously reported.¹⁷

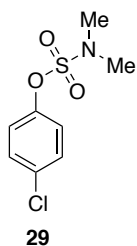


3-Chlorophenyl 4-methylbenzenesulfonate (35). Aryl tosylate **35** was prepared according to the general procedure using 3-chlorophenol (2.00 g, 15.6 mmol, 1.00 equiv), TsCl (5.05 g, 26.5 mmol, 1.7 equiv), and pyridine (20.0 mL). The crude solid was recrystallized from hexanes providing **35** as a pale pink solid (3.65 g, 83% yield). Spectral data are consistent with those previously reported.¹⁵



o-Tolyl 4-methylbenzenesulfonate (S95). Aryl tosylate **S95** was prepared according to the general procedure using 2-methylphenol (2.00 g, 18.4 mmol, 1.0 equiv), TsCl (6.2 g, 32.0 mmol, 1.7 equiv), and pyridine (20 mL). The crude solid was recrystallized from 2:1 hexanes:EtOAc providing **S95** as a white crystalline solid (2.73 g, 57% yield). Spectral data are consistent with those previously reported.¹⁸

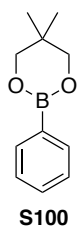
4. Aryl Sulfamate 29



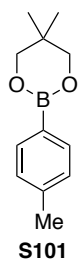
4-Chlorophenyl dimethylsulfamate (29). Aryl sulfamate **29** was prepared according to a modified literature procedure.¹⁹ NaH (440 mg of a 60% dispersion in oil, 11.00 mmol, 1.23 equiv) was cooled to 0 °C in a pear-shaped flask. A solution of 4-chlorophenol (1.15 g, 8.97 mmol, 1.00 equiv) in DME was added dropwise by cannula to the NaH. The resulting homogeneous solution was warmed to rt for 10 min and then cooled to 0 °C. A solution of N,N-dimethylsulfamoyl chloride (1.55 g, 10.76 mmol, 1.20 equiv) in DME was added dropwise by cannula to the reaction vessel (total volume of DME = 30 mL). The reaction was warmed to rt, stirred overnight, and then quenched with several drops of H₂O. DME was removed by rotary evaporation, and the solid residue was then dissolved in Et₂O (50 mL) and H₂O (15 mL) and transferred to a separatory funnel. The layers were separated, and the organic layer was washed with 1 M KOH (15 mL), then H₂O (15 mL). The combined aqueous layers were then extracted with Et₂O (3 x 20 mL), washed with brine (15 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (95% hexanes, 5% EtOAc, *R_f* = 0.52 in 95% hexanes/5%EtOAc) to afford product **29** as a white crystalline solid (1.75, 83% yield). Spectral data are consistent with those previously reported.²⁰

5. Boronic Esters

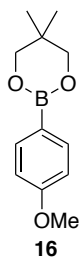
General Procedure. Aryl boronic esters were prepared according to a modified literature procedure.²¹ Aryl boronic acid (1 equiv), neopentyl glycol (1.2 equiv), MgSO₄ (0.83 equiv) and THF were added to a 250 mL round bottom flask and refluxed at 70 °C for 1 hour. The reaction mixture was allowed to cool to room temperature, then stirred at room temperature for 18 hours. The MgSO₄ was removed by filtration and the reaction mixture was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel or by taking up the residue in a nonpolar solvent and filtering through a silica plug or by recrystallization.



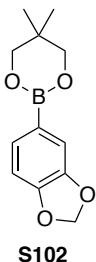
Phenylboronic acid neopentylglycol ester (S100). Boronic ester **S100** was prepared according to the general procedure using phenylboronic acid (1.22 g, 10 mmol, 1.0 equiv), neopentyl glycol (1.25 g, 12 mmol, 1.2 equiv), MgSO₄ (1.00 g, 8.3 mmol, 0.83 equiv), and THF (50 mL). The crude solid was recrystallized from 95:5 hexanes:EtOAc to provide **S100** as a white solid (1.50 g, 79% yield). Spectral data are consistent with those previously reported.²²



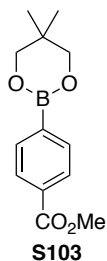
4-Methylphenylboronic acid neopentyl glycol ester (S101). Boronic ester **S101** was prepared according to the general procedure using 4-methylphenylboronic acid (1.36 g, 10 mmol, 1.0 equiv), neopentyl glycol (1.25 g, 12 mmol, 1.2 equiv), MgSO₄ (1.00 g, 8.3 mmol, 0.83 equiv), and THF (50 mL). The crude solid was purified by flash column chromatography on silica gel (*R_f* = 0.32 in 95% hexanes/5% EtOAc) to provide **S101** as a white solid (1.93 g, 95% yield). Spectral data are consistent with those previously reported.²³



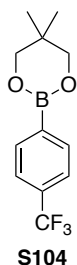
4-Methoxyphenylboronic acid neopentyl glycol ester (16). Boronic ester **16** was prepared according to the general procedure using 4-methoxyphenylboronic acid (2.28 g, 15 mmol, 1.0 equiv), neopentyl glycol (1.87 g, 18 mmol, 1.2 equiv), MgSO_4 (1.50 g, 12.5 mmol, 0.83 equiv), and THF (75 mL). The crude solid was purified by flash column chromatography on silica gel ($R_f = 0.44$ in 95% hexanes/5% EtOAc) to provide **16** as a white solid (3.09 g, 94% yield). Spectral data are consistent with those previously reported.²²



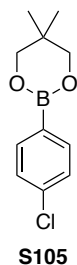
Benzo[d][1,3]dioxol-5-ylboronic acid neopentyl glycol ester (S102). Boronic ester **S102** was prepared according to the general procedure using benzo[d][1,3]dioxol-5-ylboronic acid (497.8 mg, 3 mmol, 1.0 equiv), neopentyl glycol (374.9 mg, 3.6 mmol, 1.2 equiv), MgSO_4 (299.7 mg, 2.50 mmol, 0.83 equiv), and THF (15 mL). The crude solid was purified by flash column chromatography on silica gel ($R_f = 0.25$ in 100% hexanes) to provide **S102** as a white solid (501.0 mg, 72% yield). Spectral data are consistent with those previously reported.²²



[4-(Methoxycarbonyl)phenyl]boronic acid neopentyl glycol ester (S103). Boronic ester **S103** was prepared according to the general procedure using [4-(methoxycarbonyl)phenyl]boronic acid (3.60 g, 20 mmol, 1.0 equiv), neopentyl glycol (2.50 g, 24 mmol, 1.2 equiv), MgSO_4 (2.00 g, 16.6 mmol, 0.83 equiv), and THF (100 mL). The crude solid was recrystallized from 95:5 hexanes:EtOAc to provide **S103** as a white solid (4.37 g, 88% yield). Spectral data are consistent with those previously reported.²⁴



4-Trifluoromethylphenylboronic acid neopentyl glycol ester (S104). Boronic ester **S104** was prepared according to the general procedure using 4-trifluoromethylphenylboronic acid (949.6 mg, 5 mmol, 1.0 equiv), neopentyl glycol (624.9 mg, 6 mmol, 1.2 equiv), MgSO_4 (752.3 mg, 6.25 mmol, 0.83 equiv), and THF (25 mL). The crude solid was recrystallized from 95:5 pentane:EtOAc to provide **S104** as a white crystalline solid (1.12 g, 87% yield). Spectral data are consistent with those previously reported.²²

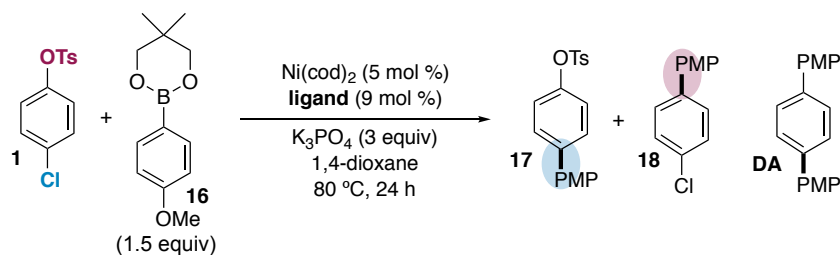


4-Chlorophenylboronic acid neopentyl glycol ester (S105). Boronic ester **S105** was prepared according to the general procedure using 4-chlorophenylboronic acid (2.27 g, 15.0 mmol, 1.0 equiv), neopentyl glycol (1.87 g, 18.0 mmol, 1.2 equiv), MgSO_4 (1.5 g, 12.5 mmol, 0.83 equiv), and THF (25 mL). The crude solid was purified by flash column chromatography on silica gel ($R_f = 0.37$ in 95% hexanes/5% EtOAc) to provide **S105** as a white solid (2.17 g, 64% yield). Spectral data are consistent with those previously reported.²⁵

D. Catalytic Reaction Optimization and Screening of Other Conditions

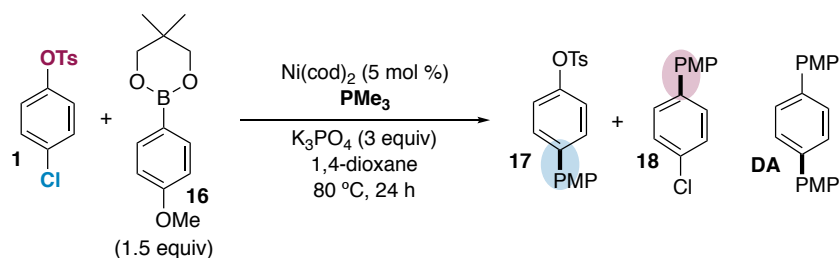
General Procedure. Chloroaryl tosylate (0.1 mmol, 1.0 equiv) and boronic ester (1.5 equiv) were combined in a 1-dram vial equipped with a stir bar. The vial was transferred into a nitrogen-atmosphere glovebox where K_3PO_4 (0.3 mmol, 3.00 equiv) was added. A solution of Ni(II) precatalyst or $Ni(cod)_2$ and phosphine ligand in 1,4-dioxane was prepared (14.3 mM with respect to nickel). 350 μ L of the nickel stock solution was added to the reaction vial (0.005 mmol of nickel, 5 mol %). The vial was sealed with a cap equipped with a PTFE-lined septum and removed from the glovebox. Within 60 s, a degassed solution of water in 1,4-dioxane (50 μ L of a 1.0 M solution, 0.5 equiv of H_2O) was added through the septum cap, and the puncture hole in the septum was immediately sealed with electrical tape. The reactions were stirred at 80 °C for 24 h unless otherwise indicated. Undecane (10.5 μ L, 0.5 equiv) was then added as an internal GC standard and the vial was diluted to the top with toluene and mixed well. An aliquot of the reaction mixture was filtered through celite and analyzed by GC.

Table S1. Screen of ligands with $Ni(cod)_2$.^a



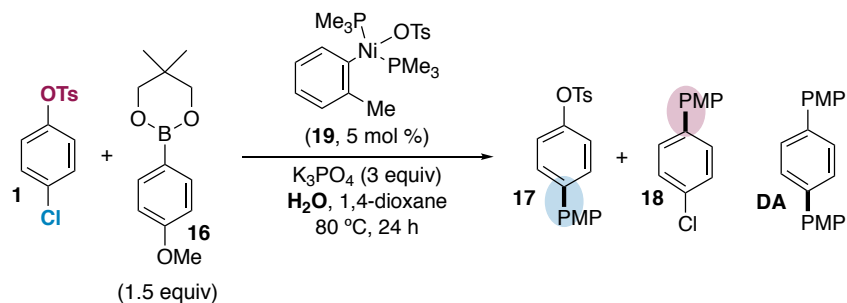
entry	ligand	1 ^b	17 (%) ^b	18 (%) ^b	DA (%) ^c	selectivity ^d
1	PMe_3	12	6	62	8	1 : 10
2	$PPhMe_2$	3	6	69	12	1 : 11
3	$PPhEt_2$	12	14	40	11	1 : 3
4	$PPhCy_2$	54	11	5	9	2 : 1
5	PPh_2Me	5	32	17	10	2 : 1
6	PCy_3	49	4	4	6	1 : 1
7	PPh_3	58	18	1	3	18 : 1
8	dmpe	36	1	15	9	1 : 15
9	dcypf	61	1	2	6	1 : 2

^aPMP = *p*-methoxyphenyl. dmpe = 1,2-bis(dimethylphosphino)ethane. dcypf = 1,2-bis(dicyclohexylphosphino)ferrocene. ^bCalibrated GC yield. ^c**DA** = diarylation; approximate yield assumes that the GC response factor of **DA** is identical to that of **17**, which has the same number of C–H bonds. ^dRatio of **17**:**18**.

Table S2. Screen of PMe_3 loading with $\text{Ni}(\text{cod})_2$.^a

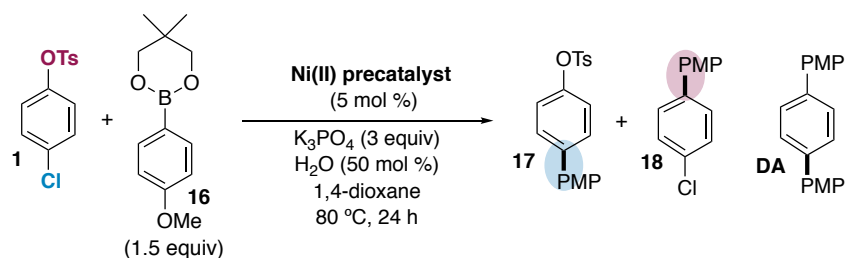
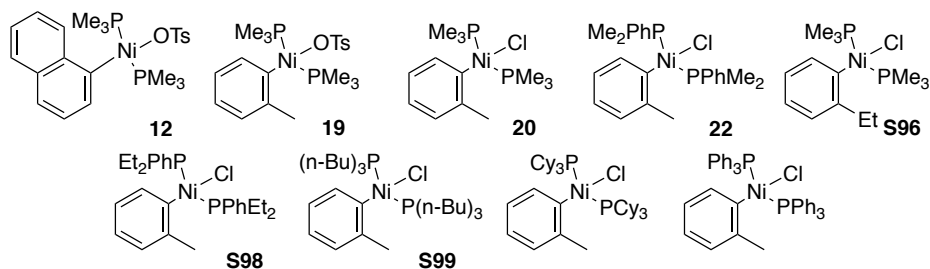
entry	PMe_3 (mol %)	1 ^b	17 (%) ^b	18 (%) ^b	DA (%) ^c	selectivity ^d
1	5	85	1	10	3	1 : 10
2	6	27	7	39	6	1 : 6
3	7	11	4	54	5	1 : 14
4	8	11	6	54	6	1 : 9
5	9	12	6	62	8	1 : 10
6	10	9	4	59	5	1 : 15
7	11	31	3	50	7	1 : 17
8	12	3	4	55	11	1 : 14
9	15	14	10	38	6	1 : 4

^a PMP = *p*-methoxyphenyl. Average of two runs. ^bCalibrated GC yield. ^c**DA** = diarylation; approximate yield assumes that the GC response factor of **DA** is identical to that of **17**, which has the same number of C–H bonds. ^dRatio of **17**:**18**.

Table S3. Screen of H_2O loading with $\text{Ni}(\text{II})$ precatalyst **19**.^a

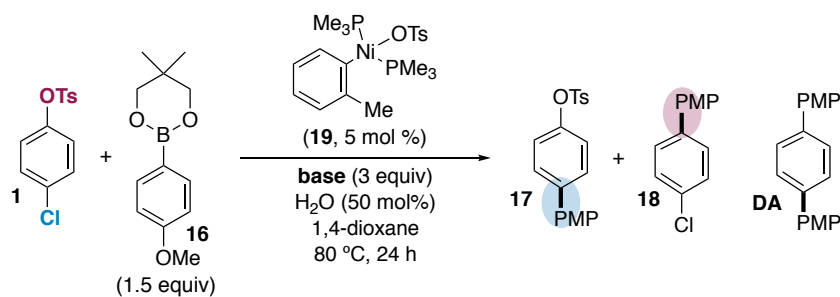
entry	H_2O (mol %)	1 ^b	17 (%) ^b	18 (%) ^b	DA (%) ^c	selectivity ^d
1	0	37	3	60	4	1 : 20
2	10	32	3	67	6	1 : 23
3	20	36	3	66	4	1 : 22
4	30	22	3	75	6	1 : 25
5	40	11	3	82	9	1 : 27
6	50	5	2	88	8	1 : 44
7	100	1	2	89	12	1 : 45

^a PMP = *p*-methoxyphenyl. Average of two runs. ^bCalibrated GC yield. ^c**DA** = diarylation; approximate yield assumes that the GC response factor of **DA** is identical to that of **17**, which has the same number of C–H bonds. ^dRatio of **17**:**18**.

Table S4. Screen of Ni(II) precatalysts.^a**Precatalysts:**

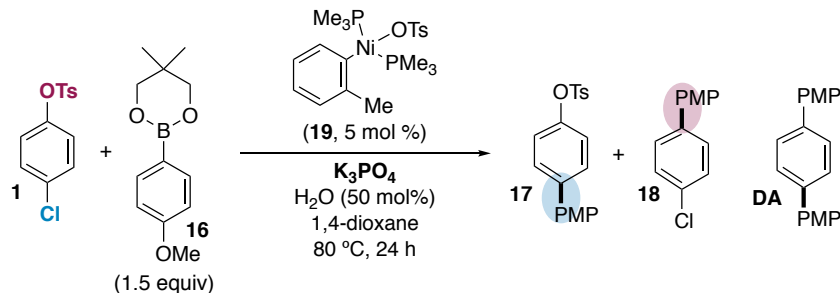
entry	precatalyst	1 ^b	17 (%) ^b	18 (%) ^b	DA (%) ^c	selectivity ^d
1	12	6	1	90	9	1 : 90
2	19	5	2	88	8	1 : 44
3	20	1	2	83	9	1 : 42
4 ^e	22	9	5	73	7	1 : 15
5 ^f	S96	6	3	88	6	1 : 29
6 ^f	S98	8	9	49	8	1 : 5
7 ^f	S99	23	9	50	7	1 : 5
8	(<i>o</i> -tol)Ni(PCy ₃) ₂ Cl	43	6	8	7	1 : 1
9	(<i>o</i> -tol)Ni(PPh ₃) ₂ Cl	59	14	12	6	1 : 1

^aPMP = *p*-methoxyphenyl. Average of 2 runs. ^bCalibrated GC yield. ^c**DA** = diarylation; approximate yield assumes that the GC response factor of **DA** is identical to that of **17**, which has the same number of C—H bonds. ^dRatio of **17**:**18**. ^eWith 4 mol % of the mono-THF adduct of precatalyst **22**. ^f1.2 equiv of **16**, 6 equiv of K₃PO₄, and 18 hours.

Table S5. Base screen with precatalyst **19**.^a

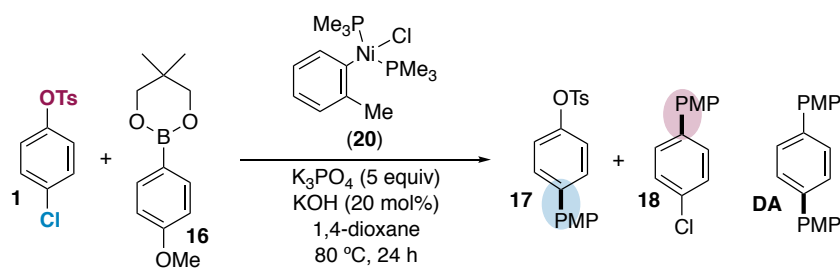
entry	base	17 (%) ^b	18 (%) ^b	DA (%) ^c	selectivity ^d
1	K ₂ CO ₃	2	70	5	1 : 35
2	KF	3	51	5	1 : 17
3	Na ₂ CO ₃	2	39	3	1 : 20
4	CsF	1	17	2	1 : 17
5	KOtBu	1	17	2	1 : 17
6	N(<i>i</i> -Pr) ₂ Et	1	4	0	1 : 4

^aPMP = *p*-methoxyphenyl. ^bCalibrated GC yield. ^c**DA** = diarylation; approximate yield assumes that the GC response factor of **DA** is identical to that of **17**, which has the same number of C–H bonds. ^dRatio of **17**:**18**.

Table S6. Base equivalents screen with precatalyst **19**.^a

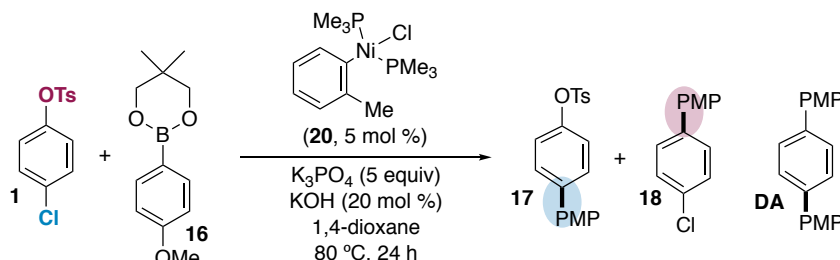
entry	K ₃ PO ₄ (equiv)	1 ^b	17 (%) ^b	18 (%) ^b	DA (%) ^c	selectivity ^d
1	3	5	2	88	8	1 : 44
2	4	0	1	80	8	1 : 80
3	5	0	1	78	8	1 : 78
4	6	0	1	70	7	1 : 70
5	7	0	1	73	10	1 : 73

^aPMP = *p*-methoxyphenyl. Average of two runs. ^bCalibrated GC yield. ^c**DA** = diarylation; approximate yield assumes that the GC response factor of **DA** is identical to that of **17**, which has the same number of C–H bonds. ^dRatio of **17**:**18**.

Table S7. Screen of precatalyst loading with **20**.^a


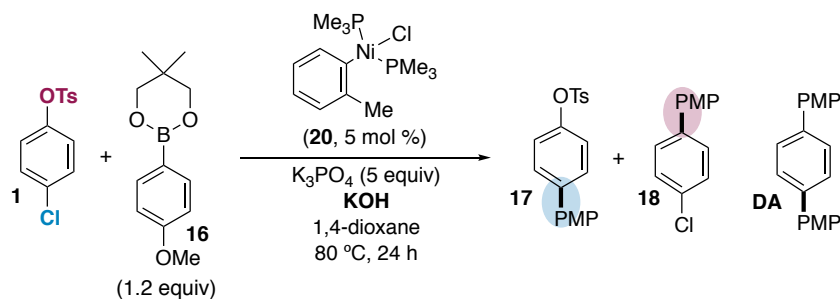
entry	20 (mol %)	1 ^b	17 (%) ^b	18 (%) ^b	DA (%) ^c	selectivity ^d
1	1	48	2	45	4	1 : 23
2	2	38	2	52	4	1 : 23
3	3	23	2	67	4	1 : 34
4	4	16	2	78	3	1 : 39
5	5	10	3	83	4	1 : 28
6	6	16	2	77	3	1 : 39
7	7	24	2	71	4	1 : 36
8	8	20	2	74	4	1 : 37
9	9	11	3	68	5	1 : 23
10	10	19	2	74	5	1 : 37

^aPMP = *p*-methoxyphenyl. Reaction concentration in 1,4-dioxane = 0.33 *M* instead of 0.25 *M*. ^bCalibrated GC yield. ^cDA = diarylation; approximate yield assumes that the GC response factor of **DA** is identical to that of **17**, which has the same number of C–H bonds. ^dRatio of **17**:**18**.

Table S8. Screen of boronic ester equivalents with precatalyst **20**.^a


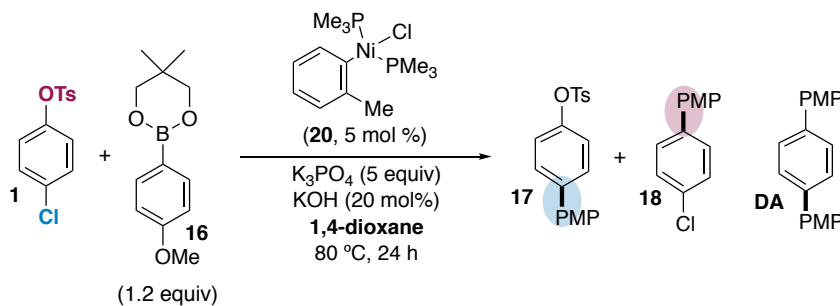
entry	16 (equiv)	1 ^b	17 (%) ^b	18 (%) ^b	DA (%) ^c	selectivity ^d
1	1	32	2	65	3	1 : 33
2	1.1	23	3	74	3	1 : 25
3	1.2	18	2	78	3	1 : 39
4	1.3	22	2	75	3	1 : 38
5	1.4	21	2	75	4	1 : 38
6	1.5	22	2	74	3	1 : 37

^aPMP = *p*-methoxyphenyl. Average of two runs. Reaction concentration in 1,4-dioxane = 0.33 *M* instead of 0.25 *M*. ^bCalibrated GC yield. ^cDA = diarylation; approximate yield assumes that the GC response factor of **DA** is identical to that of **17**, which has the same number of C–H bonds. ^dRatio of **17**:**18**.

Table S9. Screen of KOH equivalents with precatalyst **20**.^a

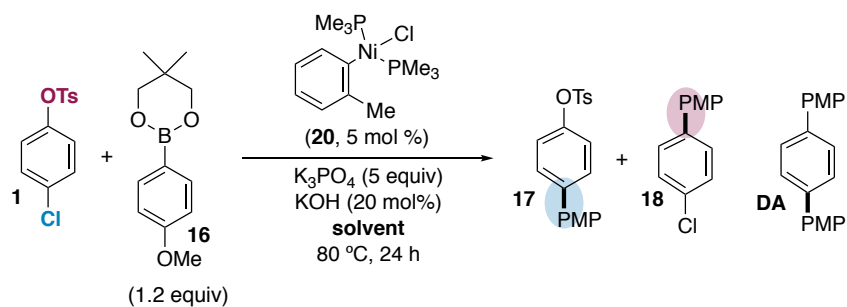
entry	KOH (mol %)	1 ^b	17 (%) ^b	18 (%) ^b	DA (%) ^c	selectivity ^d
1	5	33	2	61	3	1 : 31
2	10	30	2	66	4	1 : 33
3	15	22	2	68	4	1 : 34
4	20	15	2	80	3	1 : 40
5	50	27	2	55	4	1 : 28
6	100	14	3	73	6	1 : 24
7	200	9	1	39	4	1 : 39
8	300	0	2	26	2	1 : 13

^aPMP = *p*-methoxyphenyl. Reaction concentration in 1,4-dioxane = 0.33 M instead of 0.25 M. ^bCalibrated GC yield. ^cDA = diarylation; approximate yield assumes that the GC response factor of **DA** is identical to that of **17**, which has the same number of C—H bonds. ^dRatio of **17**:**18**.

Table S10. Screen of reaction concentration with precatalyst **20**.^a

entry	conc. (M)	1 ^b	17 (%) ^b	18 (%) ^b	DA (%) ^c	selectivity ^d
1	0.25	11	3	89	4	1 : 30
2	0.33	14	2	83	5	1 : 42
3	0.40	19	2	72	4	1 : 36
4	0.50	16	2	34	0	1 : 17

^aPMP = *p*-methoxyphenyl. ^bCalibrated GC yield. ^cDA = diarylation; approximate yield assumes that the GC response factor of **DA** is identical to that of **17**, which has the same number of C—H bonds. ^dRatio of **17**:**18**.

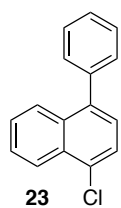
Table S11. Solvent screen with precatalyst **20**.^a

entry	solvent	1 ^b	17 (%) ^b	18 (%) ^b	DA (%) ^c	selectivity ^d
1	THF	46	2	52	2	1 : 26
2	2-methyl THF	16	3	71	5	1 : 24
3	toluene	23	2	68	4	1 : 34
4	xylenes	56	3	32	6	1 : 11

^aPMP = *p*-methoxyphenyl. Average of two runs. ^bCalibrated GC yield. ^cDA = diarylation; approximate yield assumes that the GC response factor of **DA** is identical to that of **17**, which has the same number of C–H bonds. ^dRatio of **17**:**18**.

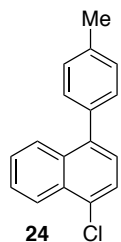
E. Cross-Coupling Reactions

General Procedure. Chloroaryl tosylate, sulfamate, or triflate (0.5 mmol, 1.0 equiv) and boronic ester (1.2–1.5 equiv) were combined in a 1-dram vial. The vial was transferred into a nitrogen-atmosphere glovebox where K₃PO₄ (3.0 mmol, 6.00 equiv) was added. *Note: while the original optimization reactions used 3 equiv of K₃PO₄, we found that slightly higher yields were obtained in these larger scale reactions when using 6 equiv of K₃PO₄.* A solution of Ni(II) precatalyst in 1,4-dioxane was prepared (17.6 mM with respect to nickel). 1.42 mL of the nickel stock solution was added to the reaction vial (0.025 mmol of nickel, 5 mol %). The vial was sealed with a cap equipped with a PTFE-lined septum and removed from the glovebox. Within 60 s, a degassed solution of water in 1,4-dioxane (100 μL of a 2.5 M solution, 0.5 equiv of H₂O) was added through the septum cap, and the puncture hole in the septum was sealed with tape. The reactions were stirred at 80 °C for 30 h unless otherwise indicated. The reaction mixture was diluted with toluene and filtered through celite. The reaction mixture was concentrated under vacuum and the major product was purified by flash column chromatography.

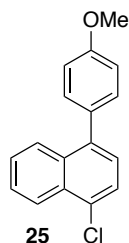


4-Chloro-1-phenylnaphthalene (23). Compound **23** was prepared according to the general procedure using phenylboronic acid neopentylglycol ester (**S100**, 142.5 mg, 0.75 mmol, 1.5 equiv), 4-chloronaphthyl tosylate (**13**, 166.4 mg, 0.50 mmol, 1.00 equiv), K₃PO₄ (636.8 mg, 3.0 mmol, 6.00 equiv), H₂O (100 μL of a 2.5 M solution in 1,4-dioxane, 0.5 equiv of H₂O), and (PMe₃)₂Ni(OTs)(*o*-tol) (**19**, 1.42 mL of a 17.6 mM solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 °C for 30 h. Purification by flash column chromatography (*R*_f = 0.73 in 99% hexanes, 1% CH₂Cl₂) followed by recrystallization from 100% pentane afforded product **23** as a white solid (86.0 mg, 72% yield). ¹H NMR (500 MHz, CDCl₃, δ): 8.37 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.64–7.61 (multiple signals, 2H), 7.52–7.44 (multiple signals, 6H), 7.34 (d, *J* = 7.6 Hz, 1H); ¹³C{¹H} NMR

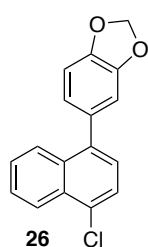
(126 MHz, CDCl₃, δ): 140.2, 139.8, 133.0, 131.5, 131.1, 130.2, 128.5, 127.7, 127.0, 126.9, 126.8, 125.9, 124.9 (two signals are coincidentally overlapping); HRMS (ESI/Q-TOF) m/z : [M]⁺ Calcd for C₁₆H₁₁Cl 238.0549; Found 238.0552.



4-Chloro-1-(4-methylphenyl)naphthalene (24). Compound **24** was prepared according to the general procedure using 4-methylphenylboronic acid neopentyl glycol ester (**S101**, 153.1 mg, 0.75 mmol, 1.5 equiv), 4-chloronaphthyl tosylate (**13**, 166.4 mg, 0.50 mmol, 1.00 equiv), K₃PO₄ (636.8 mg, 3.0 mmol, 6.00 equiv), H₂O (100 μ L of a 2.5 *M* solution in 1,4-dioxane, 0.5 equiv of H₂O), and (PMe₃)₂Ni(OTs)(*o*-tol) (**19**, 1.42 mL of a 17.6 *mM* solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 °C for 30 h. Purification by flash column chromatography (R_f = 0.36 in 98% hexanes, 2% CH₂Cl₂) afforded product **24** as a white solid (77.3 mg, 61% yield). ¹H NMR (500 MHz, CDCl₃, δ): 8.35 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.62-7.60 (multiple signals, 2H), 7.48 (app t, J = 7.5 Hz, 1H), 7.36-7.30 (multiple signals, 5H), 2.45 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃, δ): 139.9, 137.5, 137.2, 133.0, 131.3, 131.1, 130.1, 129.2, 127.0, 126.9, 126.8, 125.9, 124.9, 21.4 (two signals are coincidentally overlapping); HRMS (TOF MS EI⁺) m/z : [M]⁺ Calcd for C₁₇H₁₃Cl 252.0706; Found 252.0716.

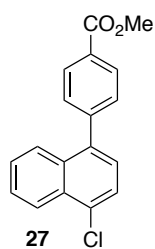


4-Chloro-1-(4-methoxyphenyl)naphthalene (25). Compound **25** was prepared according to the general procedure using 4-methoxyphenylboronic acid neopentyl glycol ester (**16**, 165.1 mg, 0.75 mmol, 1.5 equiv), 4-chloronaphthyl tosylate (**13**, 166.4 mg, 0.50 mmol, 1.00 equiv), K₃PO₄ (636.8 mg, 3.0 mmol, 6.00 equiv), H₂O (100 μ L of a 2.5 *M* solution in 1,4-dioxane, 0.5 equiv of H₂O), and (PMe₃)₂Ni(OTs)(*o*-tol) (**19**, 1.42 mL of a 17.6 *mM* solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 °C for 24 h. Purification by flash column chromatography (R_f = 0.36 in 98% hexanes, 2% CH₂Cl₂) followed by recrystallization from 9:1 pentane:EtOAc afforded product **25** as a white solid (105.21 mg, 78% yield). ¹H NMR (500 MHz, CDCl₃, δ): 8.35 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.62-7.57 (multiple signals, 2H), 7.50-7.48 (m, 1H), 7.39 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 7.6 Hz, 1H), 7.04 (d, J = 8.5 Hz, 2H), 3.90 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃, δ): 159.3, 139.5, 133.2, 132.5, 131.3, 131.2, 131.1, 127.0, 126.9, 126.85, 126.8, 125.9, 124.9, 114.0, 55.6; HRMS (ESI/Q-TOF) m/z : [M + H]⁺ Calcd for C₁₇H₁₄ClO 269.0728; Found 269.0730.

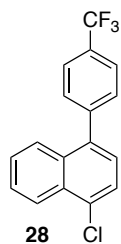


4-Chloro-1-(1,3-Benzodioxole)naphthalene (26). Compound **26** was prepared according to the general procedure using benzo[d][1,3]dioxol-5-ylboronic acid neopentyl glycol ester (**S102**, 175.6 mg, 0.75 mmol, 1.5 equiv), 4-chloronaphthyl tosylate (**13**, 166.4 mg, 0.50 mmol, 1.00 equiv), K₃PO₄ (636.8 mg, 3.0 mmol, 6.00 equiv), H₂O (100 μ L of a 2.5 *M* solution in 1,4-dioxane, 0.5 equiv of H₂O), and (PMe₃)₂Ni(OTs)(*o*-tol) (**19**, 1.42 mL of a 17.6 *mM* solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 °C for 30 h. Purification by flash column chromatography (R_f = 0.50 in 98% hexanes, 2% CH₂Cl₂) followed by

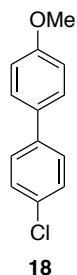
washing with cold pentane afforded product **26** as a white solid (106.0 mg, 75% yield). ^1H NMR (500 MHz, CDCl_3 , δ): 8.35 (d, $J = 8.5$ Hz, 1H), 7.94 (d, $J = 8.5$ Hz, 1H), 7.62–7.60 (multiple signals, 2H), 7.50 (m, 1H), 7.31 (d, $J = 7.6$ Hz, 1H), 6.94–6.93 (multiple signals, 3H), 6.05 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , δ): 147.8, 147.3, 139.4, 134.0, 133.1, 131.4, 131.1, 127.0, 126.9, 126.88, 126.7, 125.8, 124.9, 123.7, 110.8, 108.5, 101.4; HRMS (ESI/Q-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{17}\text{H}_{11}\text{ClO}_2$ 282.0442; Found 282.0448.



4-Chloro-1-(4-(methoxycarbonyl)phenyl)naphthalene (27). Compound **27** was prepared according to the general procedure using [4-(methoxycarbonyl)phenyl]boronic acid neopentyl glycol ester (**S103**, 193.5 mg, 0.75 mmol, 1.5 equiv), 4-chloronaphthyl tosylate (**13**, 166.4 mg, 0.50 mmol, 1.00 equiv), K_3PO_4 (636.8 mg, 3.0 mmol, 6.00 equiv), H_2O (100 μL of a 2.5 M solution in 1,4-dioxane, 0.5 equiv of H_2O), and $(\text{PMe}_3)_2\text{Ni}(\text{OTs})(o\text{-tol})$ (**19**, 1.42 mL of a 17.6 mM solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 $^\circ\text{C}$ for 20 h. Purification by flash column chromatography ($R_f = 0.31$ in 90% hexanes, 10% CH_2Cl_2) afforded product **27** as a white solid (92.0 mg, 62% yield). ^1H NMR (500 MHz, CDCl_3 , δ): 8.38 (d, $J = 8.5$ Hz, 1H), 8.2 (d, $J = 8.1$ Hz, 2H), 7.83 (d, $J = 8.5$ Hz, 1H), 7.63 (app t, $J = 7.6$ Hz, 2H), 7.55–7.49 (multiple signals, 3H), 7.34 (d, $J = 7.6$ Hz, 1H), 3.98 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , δ): 167.0, 144.9, 138.7, 132.6, 132.3, 131.1, 130.3, 129.8, 129.5, 127.3, 127.2, 126.9, 126.4, 125.8, 125.0, 52.4; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{14}\text{ClO}_2$ 297.0677; Found 297.0669



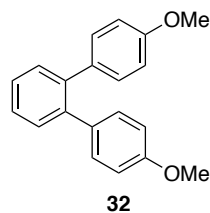
4-Chloro-1-(4-(trifluoromethyl)phenyl)naphthalene (28). Compound **28** was prepared according to the general procedure using 4-trifluoromethylphenyl boronic acid neopentyl glycol ester (**S104**, 193.5 mg, 0.75 mmol, 1.5 equiv), 4-chloronaphthyl tosylate (**13**, 166.4 mg, 0.50 mmol, 1.00 equiv), K_3PO_4 (636.8 mg, 3.0 mmol, 6.00 equiv), H_2O (100 μL of a 2.5 M solution in 1,4-dioxane, 0.5 equiv of H_2O), and $(\text{PMe}_3)_2\text{Ni}(\text{OTs})(o\text{-tol})$ (**19**, 1.42 mL of a 17.6 mM solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 $^\circ\text{C}$ for 30 h. Purification by flash column chromatography ($R_f = 0.57$ in 99% hexanes, 1% CH_2Cl_2) followed by recrystallization from 100% pentane afforded product **28** as a white solid (98.0 mg, 64% yield). ^1H NMR (500 MHz, CDCl_3 , δ): 8.38 (d, $J = 8.5$ Hz, 1H), 7.81 (d, $J = 8.5$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 2H), 7.67–7.63 (multiple signals, 2H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.52 (app t, $J = 8.2$ Hz, 1H), 7.33 (d, $J = 7.6$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , δ): 143.8, 138.2, 132.6, 132.4, 131.1, 130.6, 130.0 (q, $J_{\text{CF}} = 32.6$), 127.3, 127.0, 126.2, 126.0 (q, $J_{\text{CF}} = 209.2$ Hz), 125.8, 125.5 (q, $J_{\text{CF}} = 4.0$ Hz), 125.0, 123.5; ^{19}F (300 MHz, C_6D_6 , δ): -61.9. HRMS (TOF MS EI+) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{17}\text{H}_{10}\text{ClF}_3$ 306.0423; Found 306.0411.



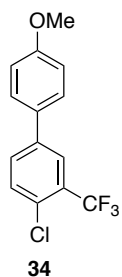
4-Chloro-4'-methoxybiphenyl (18). *From aryl tosylate 1.* Compound **18** was prepared according to the general procedure using 4-methoxyphenyl boronic acid neopentyl glycol ester (**16**, 165.1 mg, 0.75 mmol, 1.5 equiv), 4-chlorophenyl tosylate (**1**, 141.4 mg, 0.50 mmol, 1.00 equiv), K_3PO_4 (636.8 mg, 3.0 mmol, 6.00 equiv), H_2O (100 μL of a 2.5 *M* solution in 1,4-dioxane, 0.5 equiv of H_2O), and $(PMe_3)_2Ni(OTs)(1\text{-naphthyl})$ (**12**, 1.42 mL of a 17.6 *mM* solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 °C for 30 h. Purification by flash column chromatography (R_f = 0.46 in 98% hexanes, 2% CH_2Cl_2) followed by recrystallization from 95:5 pentane:EtOAc afforded product **18** as a white solid (79.0 mg, 72% yield). Spectral data are consistent with those previously reported.²⁶

From aryl sulfamate 29. Compound **18** was prepared according to the general procedure using 4-methoxyphenyl boronic acid neopentyl glycol ester (**16**, 132.1 mg, 0.60 mmol, 1.2 equiv), 4-chlorophenyl diethylsulfamate (**29**, 117.8 mg, 0.50 mmol, 1.00 equiv), K_3PO_4 (636.8 mg, 3.0 mmol, 6.00 equiv), H_2O (100 μL of a 2.5 *M* solution in 1,4-dioxane, 0.5 equiv of H_2O), and $(PMe_3)_2Ni(OTs)(1\text{-naphthyl})$ (**12**, 1.42 mL of a 17.6 *mM* solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 °C for 30 h. Purification by flash column chromatography (R_f = 0.46 in 98% hexanes, 2% CH_2Cl_2) followed by recrystallization from 95:5 pentane:EtOAc afforded product **18** as a white solid (42.5 mg, 39% yield). Spectral data are consistent with those previously reported.²⁶

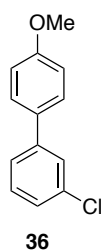
From aryl triflate 30. Compound **18** was prepared according to the general procedure using 4-methoxyphenyl boronic acid neopentyl glycol ester (**16**, 165.1 mg, 0.75 mmol, 1.5 equiv), 4-chlorophenyl triflate (**30**, 130.3 mg, 0.50 mmol, 1.00 equiv), K_3PO_4 (636.8 mg, 3.0 mmol, 6.00 equiv), H_2O (100 μL of a 2.5 *M* solution in 1,4-dioxane, 0.5 equiv of H_2O), and $(PMe_3)_2Ni(OTs)(1\text{-naphthyl})$ (**12**, 1.42 mL of a 17.6 *mM* solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 °C for 30 h. Purification by flash column chromatography (R_f = 0.46 in 98% hexanes, 2% CH_2Cl_2) followed by recrystallization from 95:5 pentane:EtOAc afforded product **18** as a white solid (52.3 mg, 48% yield). Spectral data are consistent with those previously reported.²⁶



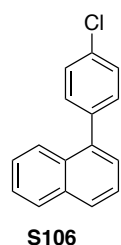
4,4''-Dimethoxy-1,1':2',1''-terphenyl (32). Compound **32** was prepared according to the general procedure using 4-methoxyphenylboronic acid neopentyl glycol ester (**16**, 165.1 mg, 0.75 mmol, 1.5 equiv), 2-chlorophenyl tosylate (**31**, 141.4 mg, 0.50 mmol, 1.00 equiv), K_3PO_4 (636.8 mg, 3.0 mmol, 6.00 equiv), H_2O (100 μL of a 2.5 *M* solution in 1,4-dioxane, 0.5 equiv of H_2O), and $(PMe_3)_2Ni(OTs)(1\text{-naphthyl})$ (**12**, 1.42 mL of a 17.6 *mM* solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 °C for 30 h. Purification by flash column chromatography (R_f = 0.29 in 98% hexanes, 2% CH_2Cl_2) afforded product **32** as a white solid (50.5 mg, 35% yield). Spectral data are consistent with those previously reported.²⁷



4-Chloro-3-trifluoromethyl-4'-methoxybiphenyl (34). Compound **34** was prepared according to the general procedure using 4-methoxyphenylboronic acid neopentyl glycol ester (**16**, 132.1 mg, 0.60 mmol, 1.2 equiv), 4-chloro-3-trifluoromethylphenyl tosylate (**33**, 175.4 mg, 0.50 mmol, 1.00 equiv), K_3PO_4 (636.8 mg, 3.0 mmol, 6.00 equiv), H_2O (100 μL of a 2.5 *M* solution in 1,4-dioxane, 0.5 equiv of H_2O), and $(PMe_3)_2Ni(OTs)(1\text{-naphthyl})$ (**12**, 1.42 mL of a 17.6 *mM* solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 °C for 30 h. Purification by flash column chromatography (R_f = 0.43 in 98% hexanes, 2% CH_2Cl_2) followed by washing with cold pentane afforded product **34** as a white solid (50.1 mg, 35% yield). Spectral data are consistent with those previously reported.²



3-Chloro-4'-methoxybiphenyl (36). Compound **36** was prepared according to the general procedure using 4-methoxyphenylboronic acid neopentyl glycol ester (**16**, 165.1 mg, 0.75 mmol, 1.5 equiv), 3-chlorophenyl tosylate (**35**, 141.4 mg, 0.50 mmol, 1.00 equiv), K_3PO_4 (636.8 mg, 3.0 mmol, 6.00 equiv), H_2O (100 μL of a 2.5 *M* solution in 1,4-dioxane, 0.5 equiv of H_2O), and $(PMe_3)_2Ni(Cl)(o\text{-tol})$ (**20**, 1.42 mL of a 17.6 *mM* solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 °C for 36 h. Purification by flash column chromatography (R_f = 0.36 in 98% hexanes, 2% CH_2Cl_2) afforded product **36** as a white solid (73.0 mg, 67% yield). Spectral data are consistent with those previously reported.²⁶

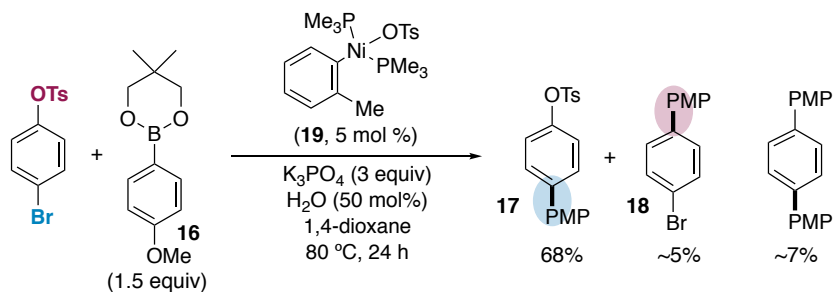


1-(4-Chlorophenyl)naphthalene (S106). Compound **S106** was prepared according to the general procedure using 4-chlorophenylboronic acid neopentyl glycol ester (**S105**, 168.4 mg, 0.75 mmol, 1.5 equiv), naphthyl tosylate (**8**, 149.2 mg, 0.50 mmol, 1.00 equiv), K_3PO_4 (636.8 mg, 3.0 mmol, 6.00 equiv), H_2O (100 μL of a 2.5 *M* solution in 1,4-dioxane, 0.5 equiv of H_2O), and $(PMe_3)_2Ni(OTs)(o\text{-tol})$ (**19**, 1.42 mL of a 17.6 *mM* solution in 1,4-dioxane, 0.025 mmol, 5 mol %). The reaction was stirred at 80 °C for 24 h. Purification by flash column chromatography (R_f = 0.37 in 98% hexanes, 2% CH_2Cl_2) followed by recrystallization from 100% pentane afforded product **S106** as a colorless crystalline solid (84.0 mg, 71% yield). Spectral data are consistent with those previously reported.²⁸

Cross Coupling Results Using Bromophenyl Tosylate

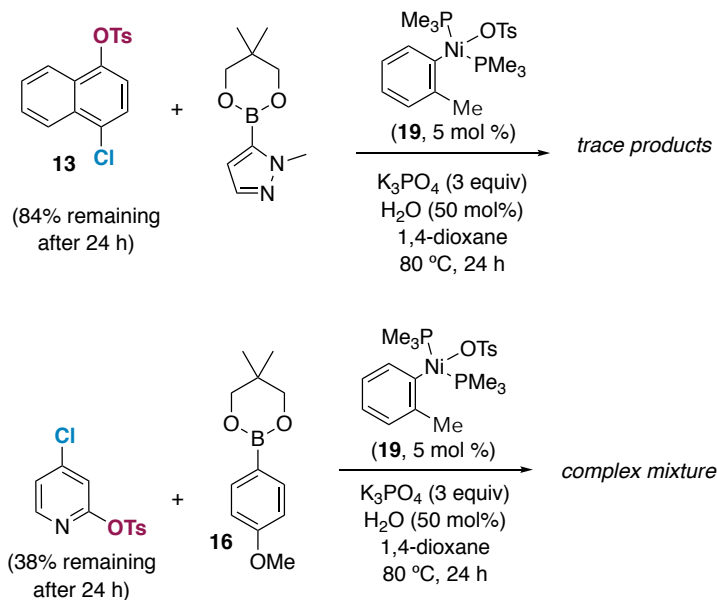
A modified version of the general procedure was followed using 4-methoxyphenylboronic acid neopentyl glycol ester (**16**, 33.0 mg, 0.15 mmol, 1.5 equiv), 4-bromophenyl tosylate (32.7 mg, 0.50 mmol, 1.00 equiv), K_3PO_4 (63.7 mg, 0.3 mmol, 3.00 equiv), H_2O (50 μL of a 1.0 *M* solution in 1,4-dioxane, 0.5 equiv of H_2O), and $(PMe_3)_2Ni(OTs)(o\text{-tol})$ (**19**, 350 μL of a 14.3 *mM* solution in 1,4-dioxane, 0.005 mmol, 5 mol %). The reaction was stirred at 80 °C for 24 h and analyzed by GC. The yield of **17** is a GC yield calibrated against

undecane as an internal standard. The results show that reaction at bromide is strongly favored over tosylate.



Attempted Cross Coupling with Heteroaromatic Coupling Partners

Efforts to cross-couple using a heteroarylboronic ester or a chloropyridyl tosylate substrate were unsuccessful. In the former case, primarily starting material was left after 24 h. In the latter case, much of the starting material was consumed to provide a complex mixture of products according to GC analysis, suggestive of substrate decomposition.



F. X-Ray Crystallographic Details for Compound **14**

X-ray diffraction data for **14** were collected at 100 K on a Bruker D8 Venture using MoK α -radiation ($\lambda=0.71073$ Å). Data have been corrected for absorption using SADABS²⁹ area detector absorption correction program. Using Olex2,³⁰ the structure was solved with the SHELXT³¹ structure solution program using Direct Methods and refined with the SHELXL³² refinement package using least squares minimization. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the investigated complex were located from difference Fourier maps but finally their positions were placed in geometrically calculated positions and refined using a riding model. Isotropic thermal parameters of the placed hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Calculations and refinement of structures were carried out using APEX3,³³ SHELXTL,³⁴ and Olex2 software.

Table S12. Crystal data and structure refinement for **14**.

Identification code	MSU_SN12 (2-JR-80)
Empirical formula	C _{26.5} H ₃₅ ClNiO ₃ P ₂ S
Formula weight	589.70
Temperature/K	100
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	10.9661(6)
b/Å	20.2493(11)
c/Å	12.9096(7)
α /°	90
β /°	102.242(2)
γ /°	90
Volume/Å ³	2801.5(3)
Z	4
ρ_{calc} /cm ³	1.398
μ /mm ⁻¹	1.003
F(000)	1236.0
Crystal size/mm ³	0.41 × 0.28 × 0.23
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/°	5.158 to 58.452
Index ranges	-12 ≤ h ≤ 15, -27 ≤ k ≤ 27, -17 ≤ l ≤ 17
Reflections collected	54495
Independent reflections	7571 [R _{int} = 0.0330, R _{sigma} = 0.0209]
Data/restraints/parameters	7571/45/327
Goodness-of-fit on F ²	1.039
Final R indexes [I > 2 σ (I)]	R ₁ = 0.0534, wR ₂ = 0.1298
Final R indexes [all data]	R ₁ = 0.0709, wR ₂ = 0.1453
Largest diff. peak/hole / e Å ⁻³	2.11/-1.27

Table S13. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **14**. U_{eq} is defined as $1/3$ of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>Y</i>	<i>z</i>	<i>U</i> (eq)
Ni1	3507.8(3)	3903.3(2)	4832.1(3)	27.31(11)
Cl1	-2117.4(9)	3475.3(7)	2185.5(8)	67.4(3)
S1	5403.9(7)	3483.2(3)	6669.7(6)	32.62(17)
P1	3975.4(7)	3147.2(3)	3737.6(7)	31.86(18)
P2	2898.8(8)	4732.2(3)	5717.1(6)	31.53(18)
O1	5213(2)	3912.6(9)	5705.2(16)	29.6(4)
O2	5391(2)	2788.4(10)	6406.5(19)	43.9(6)
O3	4571(2)	3669.2(11)	7352.8(18)	40.1(5)
C1	1852(3)	3829.3(13)	4066(2)	31.8(6)
C2	1369(3)	4162.5(16)	3138(3)	41.4(7)
C3	143(4)	4052.0(19)	2566(3)	49.7(9)
C4	-611(3)	3605.1(19)	2920(3)	45.7(8)
C5	-198(3)	3248.0(15)	3868(3)	35.0(6)
C6	-958(3)	2775.8(17)	4273(3)	43.0(8)
C7	-522(3)	2448.2(16)	5181(3)	42.1(8)
C8	696(3)	2559.7(14)	5759(3)	36.9(7)
C9	1453(3)	3004.9(13)	5397(2)	31.9(6)
C10	1045(3)	3367.0(13)	4446(2)	30.8(6)
C11	6934(3)	3678.6(14)	7350(2)	31.2(6)
C12	7126(3)	4103.9(19)	8207(3)	51.2(9)
C13	8326(4)	4246(2)	8751(3)	53.7(10)
C14	9353(3)	3967.1(15)	8460(3)	36.6(6)
C15	9157(3)	3550.1(15)	7588(2)	36.9(7)
C16	7969(3)	3402.9(15)	7042(2)	36.3(7)
C17	10651(3)	4102.0(19)	9083(3)	46.3(8)
C18	3155(3)	2367.5(15)	3709(4)	51.1(10)
C19	3668(3)	3390.0(18)	2349(3)	45.4(8)
C20	5607(3)	2909.7(15)	3979(3)	37.0(7)
C21	1995(4)	5373.7(14)	4918(3)	43.8(8)
C22	1931(3)	4510.7(14)	6648(3)	38.9(7)
C23	4162(3)	5202.0(14)	6514(3)	41.8(8)
C24	5274(13)	4428(5)	10039(9)	62(2)
C25	6146(13)	4912(5)	10441(9)	74(4)
C26	5845(13)	5575(5)	10270(10)	80(3)
C27	4671(12)	5755(5)	9699(10)	62(2)
C28	3798(12)	5272(6)	9297(10)	73(3)
C29	4100(12)	4608(5)	9468(10)	80(3)
C30	5535(12)	3717(5)	10161(9)	91(4)

Table S14. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **14**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni1	35.4(2)	16.13(16)	37.6(2)	-6.08(12)	23.89(16)	-5.06(12)
Cl1	41.5(5)	105.8(9)	53.2(5)	-18.6(6)	5.9(4)	25.1(5)
S1	45.9(4)	22.8(3)	35.5(4)	0.0(3)	22.9(3)	-9.6(3)

~Table S14 continued on the next page~

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P1	30.5(4)	23.3(3)	47.9(4)	-15.7(3)	22.3(3)	-7.5(3)
P2	47.4(4)	15.4(3)	41.5(4)	-4.6(3)	31.1(3)	-4.7(3)
O1	40.4(11)	21.8(9)	32.4(10)	-2.1(7)	21.0(9)	-7.8(8)
O2	66.9(16)	21.5(10)	47.5(13)	1.1(9)	21.8(12)	-12.6(10)
O3	46.0(12)	41.4(12)	40.9(12)	2.9(10)	26.8(10)	-9.8(10)
C1	40.1(15)	21.7(12)	40.3(15)	-4.7(10)	23.7(13)	1.6(10)
C2	53.0(19)	33.8(15)	45.3(18)	3.9(13)	27.9(15)	11.3(14)
C3	61(2)	52(2)	38.7(17)	-0.5(15)	16.5(16)	29.5(18)
C4	38.2(17)	56(2)	47.2(18)	-11.9(16)	18.1(14)	14.2(15)
C5	32.0(14)	36.0(15)	40.9(16)	-13.5(12)	16.5(12)	5.3(11)
C6	25.2(14)	47.4(18)	62(2)	-25.9(16)	21.7(14)	-4.4(12)
C7	43.2(17)	33.8(15)	59(2)	-14.0(14)	31.9(16)	-10.4(13)
C8	43.3(16)	26.1(13)	48.6(17)	-7.1(12)	26.1(14)	-4.7(12)
C9	35.4(14)	22.2(12)	43.7(16)	-5.5(11)	20.6(13)	-2.5(10)
C10	30.8(13)	24.4(12)	42.2(15)	-9.6(11)	18.9(12)	1.0(10)
C11	43.8(16)	24.2(12)	31.7(13)	2.8(10)	21.8(12)	-3.1(11)
C12	47.2(19)	53(2)	63(2)	-29.5(18)	34.0(18)	-10.9(16)
C13	53(2)	52(2)	64(2)	-30.3(18)	29.0(18)	-14.1(17)
C14	45.6(17)	31.6(14)	36.1(15)	5.4(12)	16.6(13)	-1.0(12)
C15	45.9(17)	36.5(15)	31.1(14)	7.3(12)	14.4(13)	15.4(13)
C16	52.7(18)	30.8(14)	27.8(13)	1.3(11)	13.9(13)	10.8(13)
C17	50(2)	44.7(18)	46.4(19)	2.6(15)	15.3(16)	-0.9(15)
C18	48.4(19)	25.8(14)	92(3)	-24.5(16)	45(2)	-13.4(13)
C19	43.3(18)	50.2(19)	46.2(18)	-21.0(15)	17.1(15)	-1.2(15)
C20	30.8(14)	33.8(14)	50.9(18)	-15.3(13)	18.9(13)	-2.5(11)
C21	63(2)	22.4(13)	56(2)	-0.2(13)	35.1(17)	6.3(13)
C22	54.8(19)	24.4(13)	49.7(18)	-4.5(12)	38.7(16)	-3.8(12)
C23	61(2)	23.4(13)	50.0(18)	-14.1(12)	32.7(16)	-12.9(13)
C24	66(3)	65(5)	50(6)	5(4)	4(4)	5(4)
C25	92(7)	60(6)	55(6)	-19(5)	-17(6)	-2(5)
C26	58(3)	74(6)	99(7)	-31(5)	-1(4)	0(4)
C27	66(3)	65(5)	50(6)	5(4)	4(4)	5(4)
C28	40(4)	83(7)	93(10)	-19(6)	11(5)	6(4)
C29	58(3)	74(6)	99(7)	-31(5)	-1(4)	0(4)
C30	119(9)	43(4)	87(7)	5(5)	-31(7)	-26(5)

Table S15. Bond Lengths for **14**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	P1	2.2159(7)	C5	C6	1.438(5)
Ni1	P2	2.2118(7)	C5	C10	1.429(4)
Ni1	O1	1.968(2)	C6	C7	1.343(5)
Ni1	C1	1.881(3)	C7	C8	1.404(5)
Cl1	C4	1.741(4)	C8	C9	1.373(4)
S1	O1	1.497(2)	C9	C10	1.419(4)
S1	O2	1.447(2)	C11	C12	1.382(4)
S1	O3	1.448(2)	C11	C16	1.396(4)
S1	C11	1.766(3)	C12	C13	1.383(5)
P1	C18	1.814(3)	C13	C14	1.381(5)

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P1	C19	1.820(4)	C14	C15	1.386(4)
P1	C20	1.814(3)	C14	C17	1.505(5)
P2	C21	1.817(4)	C15	C16	1.377(5)
P2	C22	1.820(3)	C24	C25	1.3900
P2	C23	1.811(3)	C24	C29	1.3900
C1	C2	1.379(5)	C24	C30	1.471(13)
C1	C10	1.443(4)	C25	C26	1.3900
C2	C3	1.408(5)	C26	C27	1.3900
C3	C4	1.368(6)	C27	C28	1.3900
C4	C5	1.411(5)	C28	C29	1.3900

Table S16. Bond Angles for **14**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P2	Ni1	P1	171.76(4)	C3	C4	C5	121.6(3)
O1	Ni1	P1	92.96(6)	C5	C4	Cl1	119.2(3)
O1	Ni1	P2	92.93(6)	C4	C5	C6	123.5(3)
C1	Ni1	P1	86.44(8)	C4	C5	C10	117.5(3)
C1	Ni1	P2	88.18(8)	C10	C5	C6	119.0(3)
C1	Ni1	O1	174.98(10)	C7	C6	C5	121.3(3)
O1	S1	C11	103.56(12)	C6	C7	C8	120.4(3)
O2	S1	O1	112.15(13)	C9	C8	C7	120.1(3)
O2	S1	O3	114.84(14)	C8	C9	C10	122.1(3)
O2	S1	C11	107.20(15)	C5	C10	C1	121.2(3)
O3	S1	O1	111.14(13)	C9	C10	C1	121.7(3)
O3	S1	C11	107.11(14)	C9	C10	C5	117.1(3)
C18	P1	Ni1	115.69(11)	C12	C11	S1	120.4(2)
C18	P1	C19	103.17(19)	C12	C11	C16	118.8(3)
C18	P1	C20	103.85(16)	C16	C11	S1	120.8(2)
C19	P1	Ni1	114.95(11)	C11	C12	C13	120.2(3)
C20	P1	Ni1	115.24(10)	C14	C13	C12	121.3(3)
C20	P1	C19	102.18(16)	C13	C14	C15	118.3(3)
C21	P2	Ni1	115.94(11)	C13	C14	C17	121.0(3)
C21	P2	C22	103.12(16)	C15	C14	C17	120.7(3)
C22	P2	Ni1	115.87(10)	C16	C15	C14	120.9(3)
C23	P2	Ni1	114.45(11)	C15	C16	C11	120.4(3)
C23	P2	C21	101.92(16)	C25	C24	C29	120.0
C23	P2	C22	103.71(16)	C25	C24	C30	123.2(7)
S1	O1	Ni1	114.79(11)	C29	C24	C30	116.8(7)
C2	C1	Ni1	124.6(2)	C26	C25	C24	120.0
C2	C1	C10	117.5(3)	C25	C26	C27	120.0
C10	C1	Ni1	117.8(2)	C28	C27	C26	120.0
C1	C2	C3	121.7(3)	C27	C28	C29	120.0
C4	C3	C2	120.5(3)	C28	C29	C24	120.0
C3	C4	Cl1	119.3(3)				

Table S17. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for **14**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H2	1876.9	4474.85	2877.97	50
H3	-163.36	4289.65	1929.25	60
H6	-1784.65	2693.93	3890.92	52
H7	-1042.51	2138.93	5433.14	50
H8	997.11	2326.77	6400.81	44
H9	2276.63	3072.84	5796.76	38
H12	6433.08	4299.28	8423.64	61
H13	8445.53	4540.52	9336.03	64
H15	9853.35	3363.23	7364.9	44
H16	7851.82	3112	6452.07	44
H17A	11161.85	3703.38	9098.71	69
H17B	10615.65	4228.31	9808.52	69
H17C	11022.47	4462.17	8746.84	69
H18A	3458.8	2059.81	3235.07	77
H18B	2258.53	2440.44	3451.87	77
H18C	3304.85	2181.02	4425.64	77
H19A	3937.97	3037.1	1929.39	68
H19B	4128.29	3795.69	2273.37	68
H19C	2771.99	3467.92	2097.77	68
H20A	5839.61	2691.42	4670.72	56
H20B	6123.54	3304.02	3974.96	56
H20C	5737.86	2605.21	3423.04	56
H21A	2480.53	5559.76	4432.17	66
H21B	1798.65	5723.1	5382.03	66
H21C	1218.5	5184.39	4508.93	66
H22A	1167.73	4294.55	6266.5	58
H22B	1712.22	4910.38	6996.5	58
H22C	2392.49	4208.02	7183.22	58
H23A	4671.95	4911	7040.59	63
H23B	3817.49	5559.12	6877.31	63
H23C	4680.59	5390.24	6056.45	63
H25	6948.68	4788.87	10831.37	89
H26	6441.04	5905.87	10544.6	96
H27	4464.68	6208.95	9582.15	74
H28	2995.95	5395.02	8906.48	87
H29	3503.57	4278.01	9193.25	96
H30A	6433.58	3641.03	10247.64	136
H30B	5087.65	3482.53	9529.26	136
H30C	5257.26	3552.17	10786.58	136

Table S18. Atomic Occupancy for **14**.

Atom	<i>Occupancy</i>	Atom	<i>Occupancy</i>	Atom	<i>Occupancy</i>
C24	0.5	C25	0.5	H25	0.5
C26	0.5	H26	0.5	C27	0.5
H27	0.5	C28	0.5	H28	0.5
C29	0.5	H29	0.5	C30	0.5
H30A	0.5	H30B	0.5	H30C	0.5

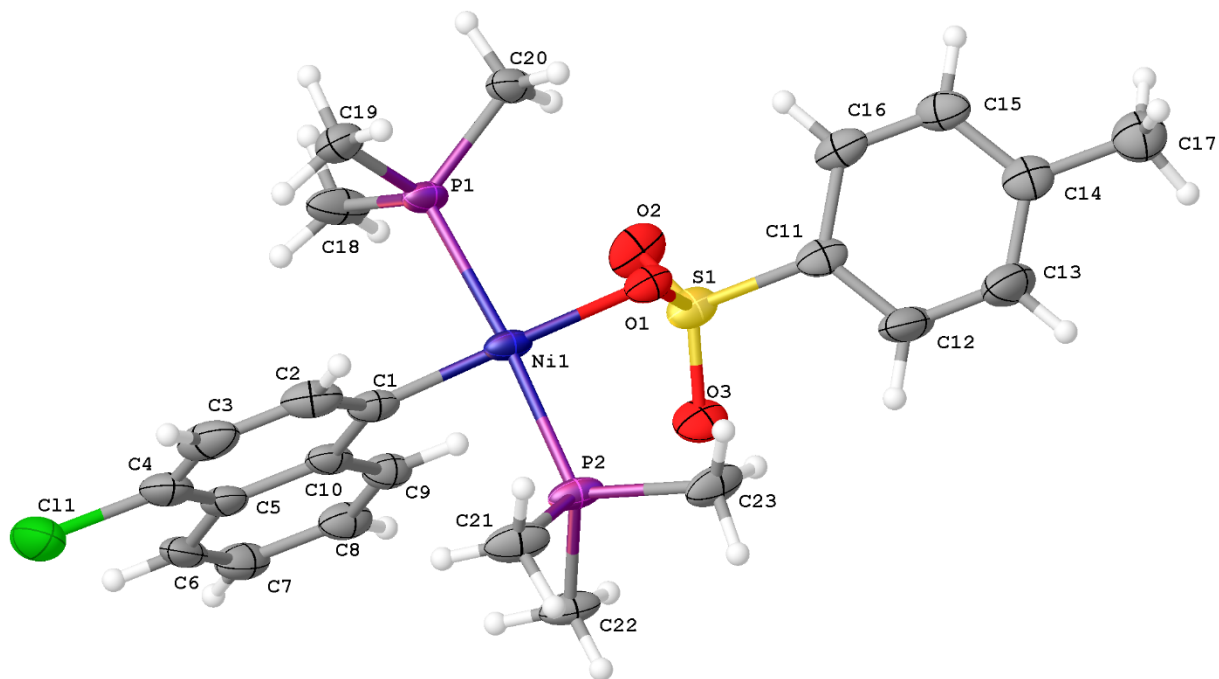


Figure S32. X-ray crystal structure of **14**. All thermal ellipsoids drawn at the 50% probability level.

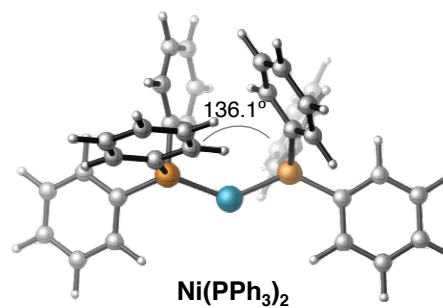
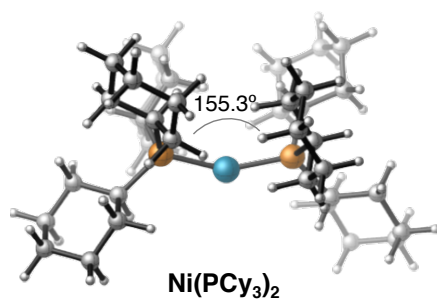
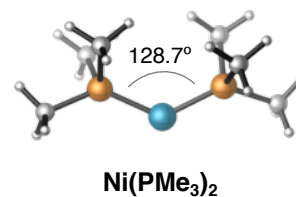
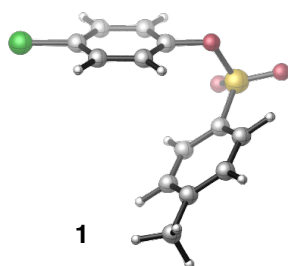
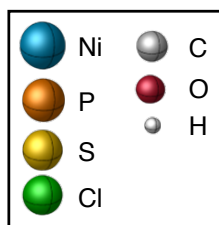
II. Computational Details

A. General Comments

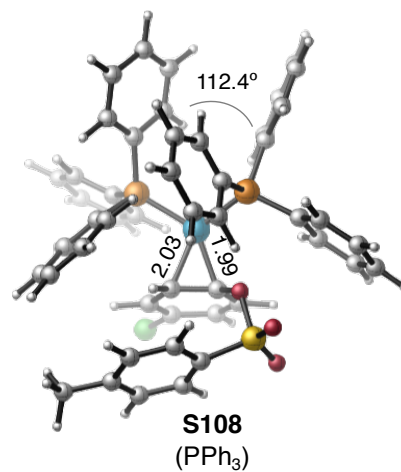
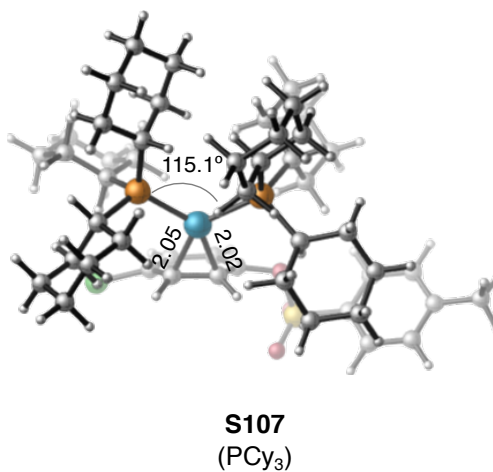
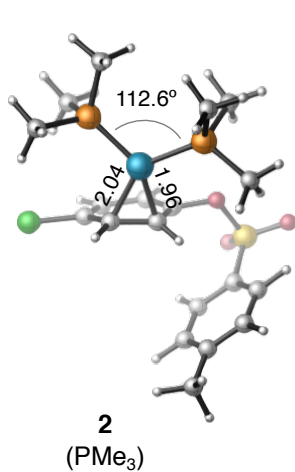
Calculations were performed with Gaussian 16.³⁵ An ultrafine integration grid and the keyword 5d were used for all calculations. Unless otherwise specified in Section E, geometry optimizations of stationary points were carried out in the gas phase with the MN15L³⁶ functional with BS1 (BS1 = the LANL2DZ³⁷ pseudopotential for Ni, the 6-31+G(d) basis set for O and Cl, and the 6-31G(d) basis set for all other atoms). Frequency analyses were carried out at the same level to evaluate the zero-point vibrational energy and thermal corrections at 298.15 K. Gibbs free energy values are reported after applying Cramer and Truhlar's anharmonic correction to frequencies that are less than 100 cm⁻¹.³⁸ The nature of the stationary points was determined in each case according to the appropriate number of negative eigenvalues of the Hessian matrix. Forward and reverse intrinsic reaction coordinate (IRC) calculations were carried out on the optimized transition structures to ensure that the TSs indeed connect the appropriate reactants and products.³⁹ Multiple conformations were considered for all structures, and the lowest energy conformations are reported. A major conformational consideration is the orientation of the tosylate group (in particular, rotation around the C—OTs and CO—S bonds). Multiple conformations of this group were evaluated for each stationary point. It is also worth noting that the lowest-energy π -complexes are not necessarily directly connected to the oxidative addition transition structures on the potential energy surfaces (i.e., in some cases the IRC calculations lead to different higher-energy π complexes than the lowest-energy structures reported). This factor is unimportant to the overall energetics, assuming that the barrier to interconverting π -complexes is low (e.g., by nickel ring-walking or by tosylate rotation). An initial input geometry for PCy₃ was obtained from the crystal structure of Ni(PCy₃)(C₂H₄)₂.⁴⁰ Unless otherwise specified in Section E, single point energy calculations were performed on the gas-phase optimized geometries using the MN15L functional with BS2 (BS2 = the SDD⁴¹ pseudopotential for Ni and the 6-311++G(2d,p) basis set for all other atoms). Bulk solvent effects in 1,4-dioxane were considered implicitly in the single point energy calculations through the CPCM continuum solvation model.⁴² Images of optimized structures were generated with CYLview.⁴³

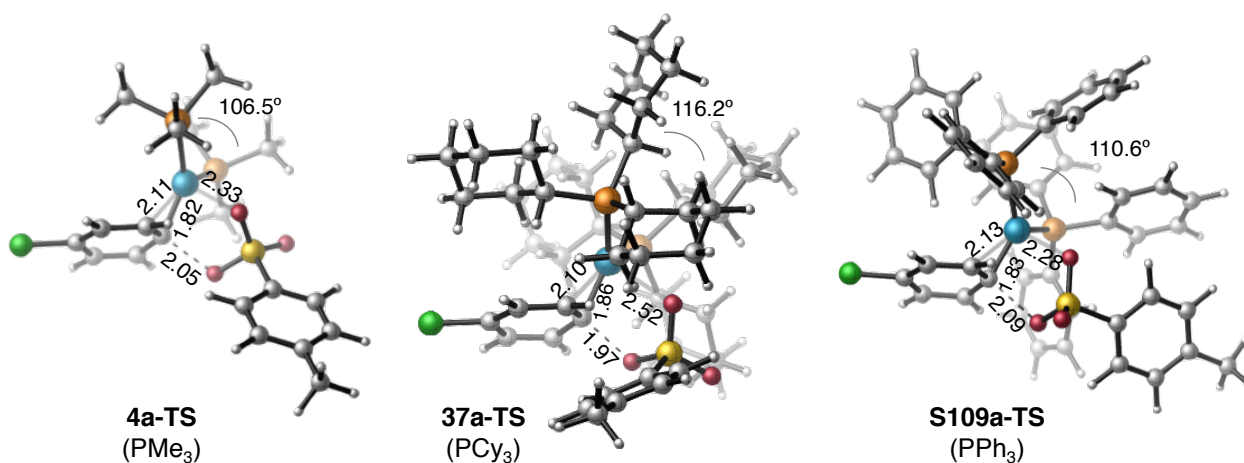
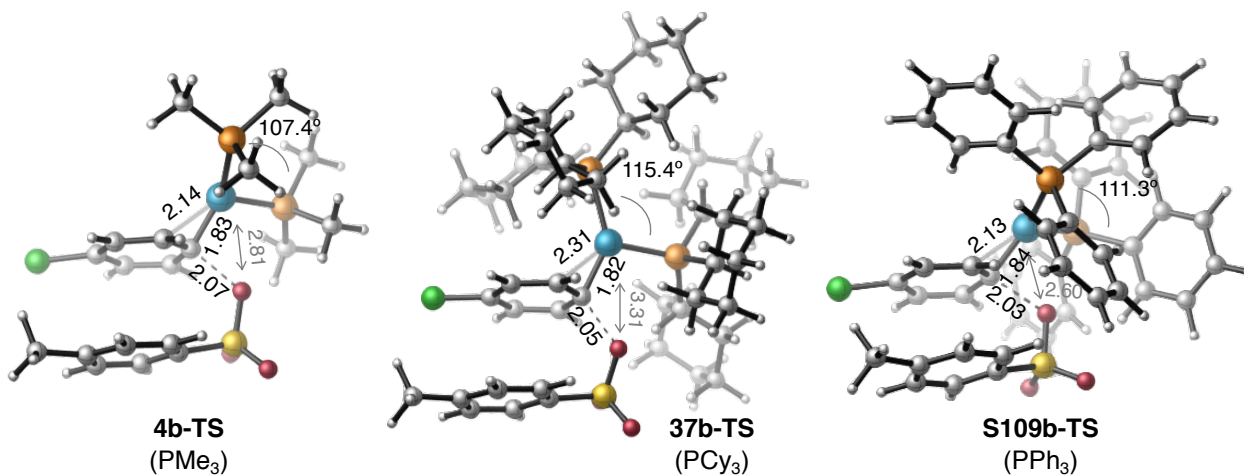
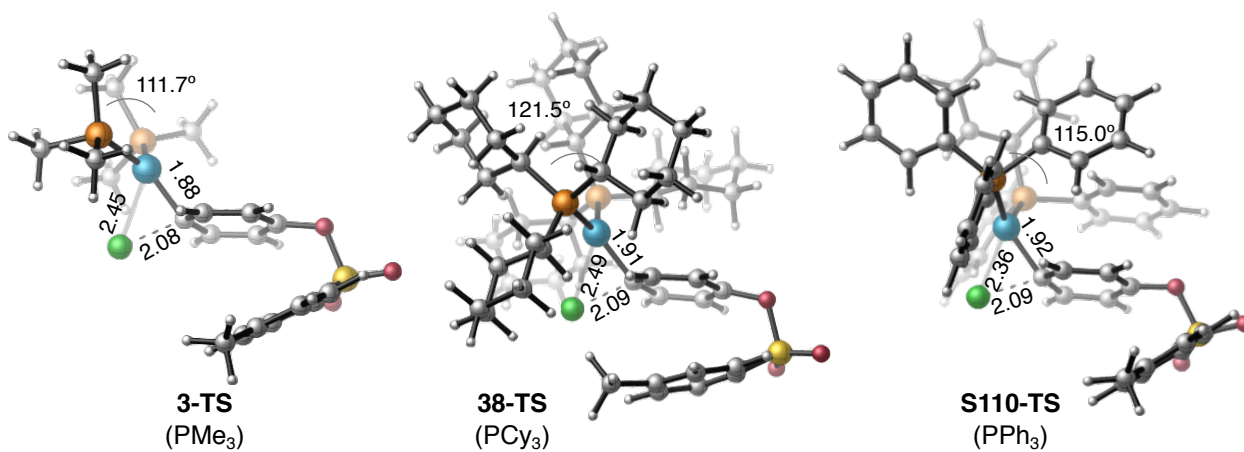
B. Graphical Guide to Numbered Compounds Including Relevant Geometry Parameters

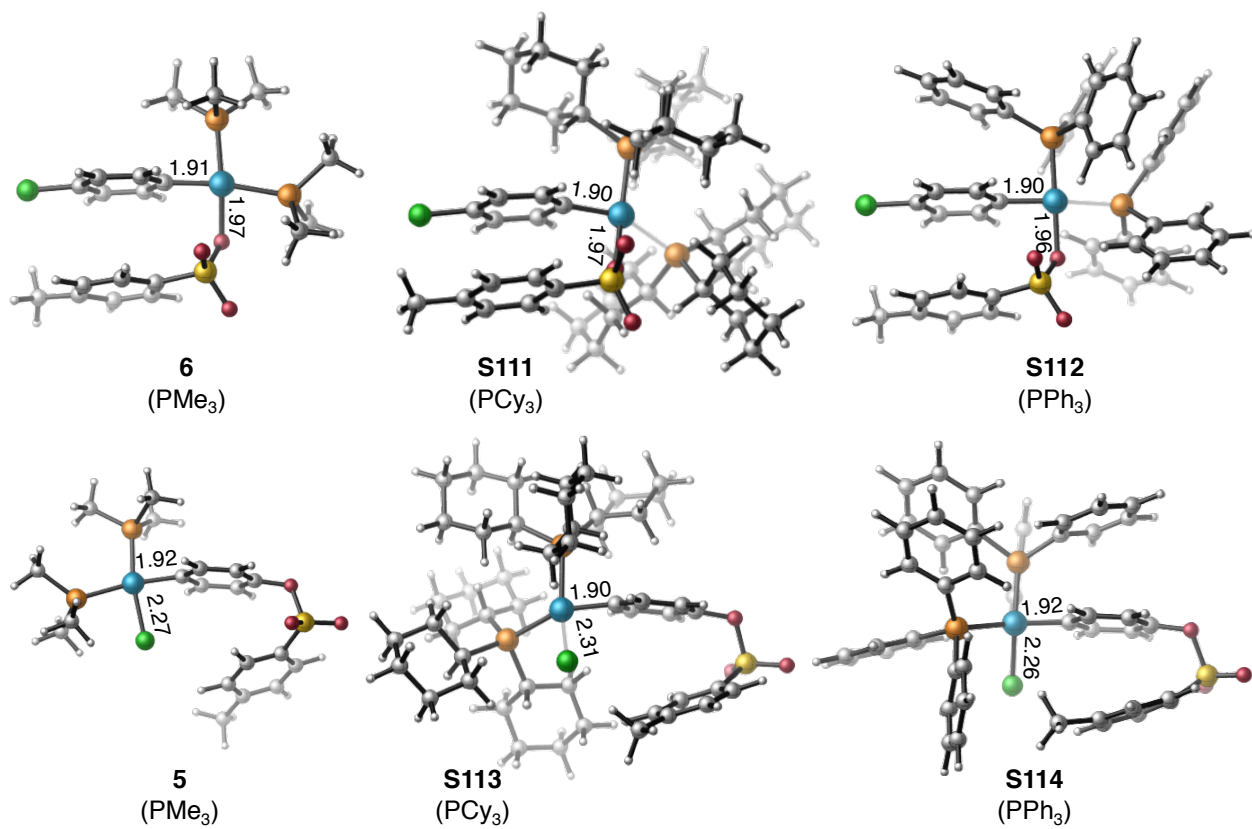
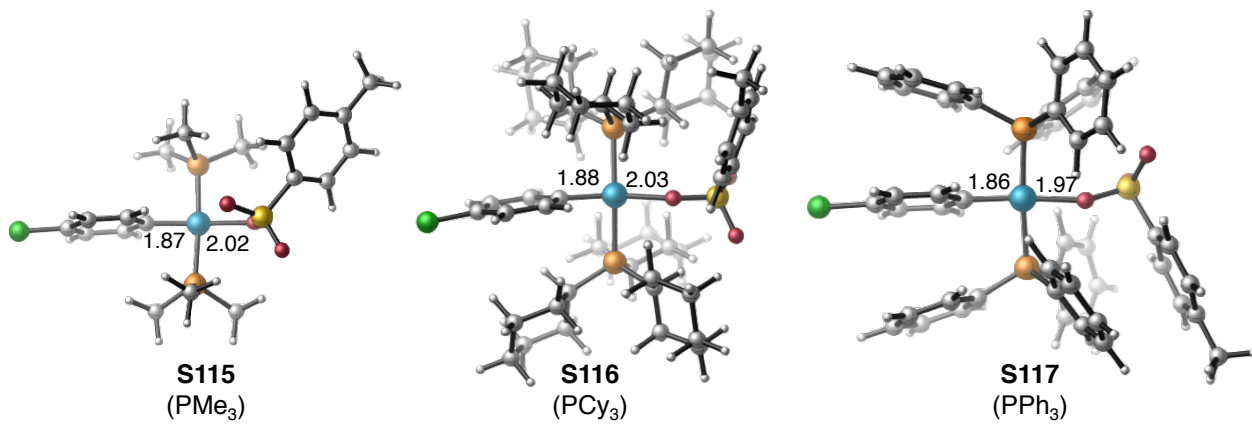
Substrate and Catalysts:

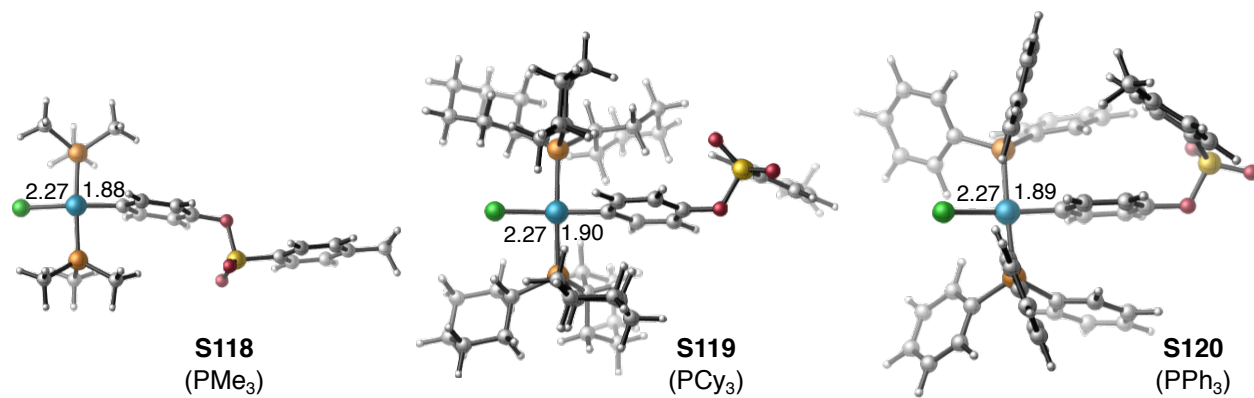


Substrate-Ni(o) π Complexes:



5-Centered Tosylate Oxidative Addition Transition Structures:Dissociation Tosylate Oxidative Addition Transition Structures:Chloride Oxidative Addition Transition Structures:

Post-Oxidative Addition cis-Ni(II) Complexes:Post-Oxidative Addition trans-Ni(II) Complexes:



C. Free Energy Diagrams

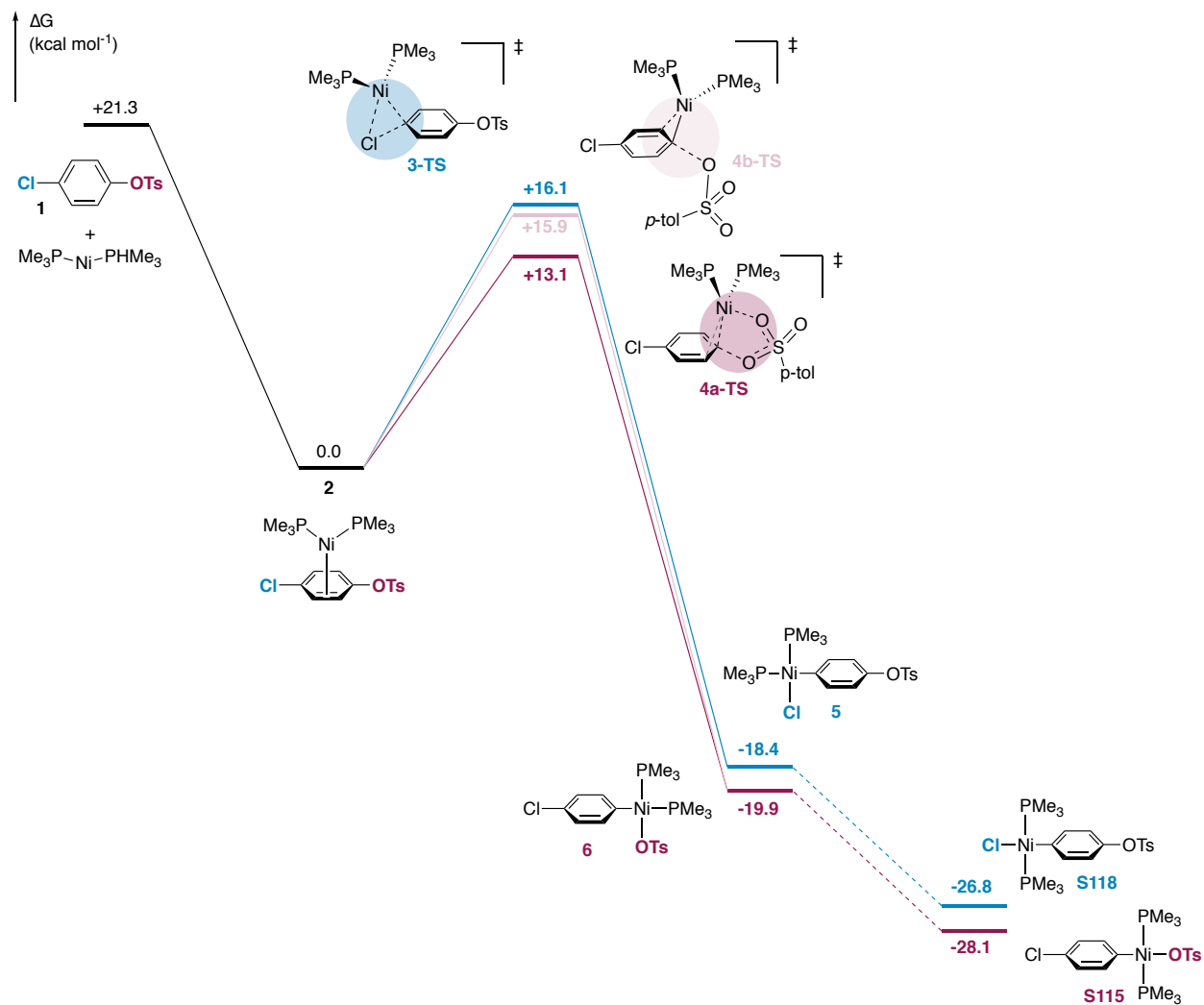


Figure S33. Free energy diagram for oxidative addition at Ni(PMe₃)₂.

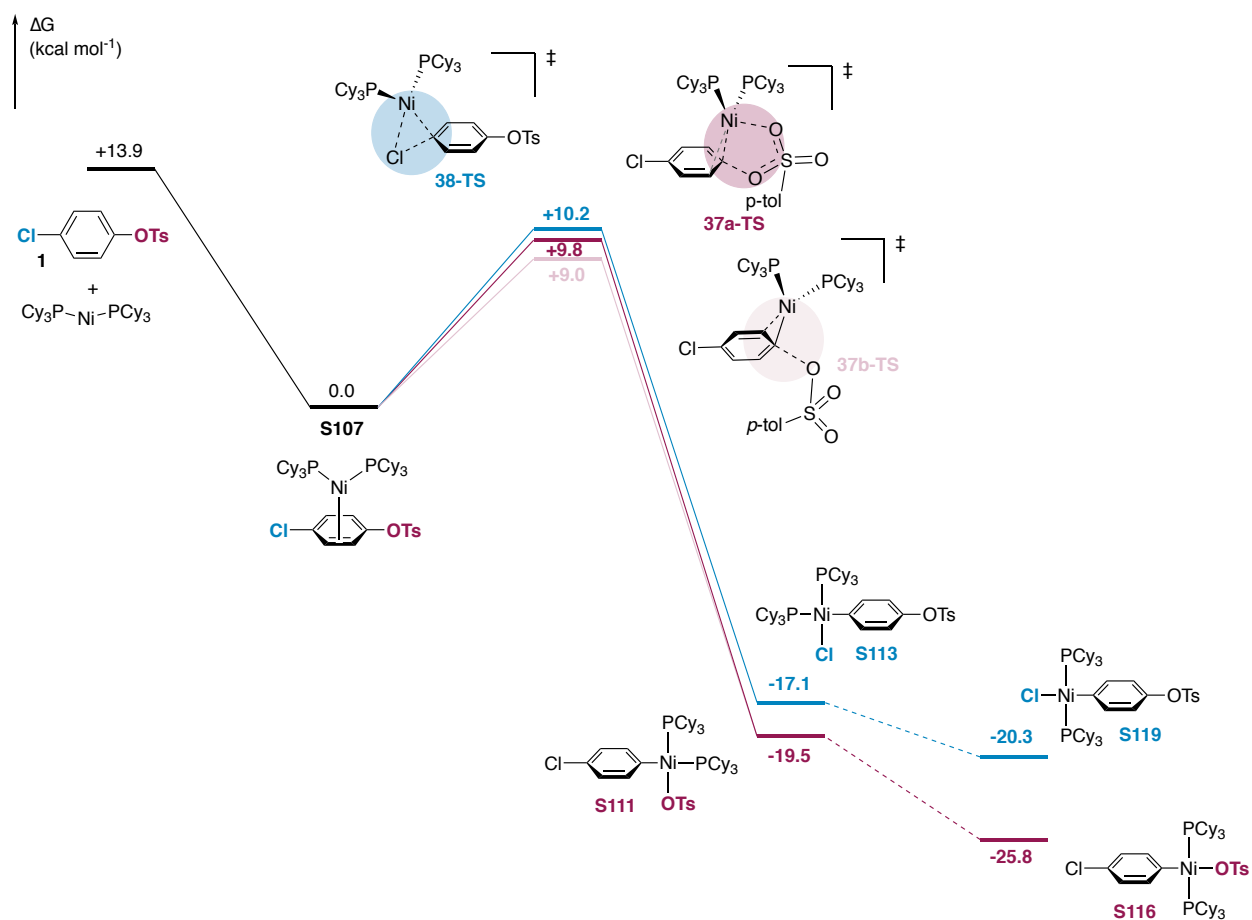


Figure S34. Free energy diagram for oxidative addition at $\text{Ni}(\text{PCy}_3)_2$.

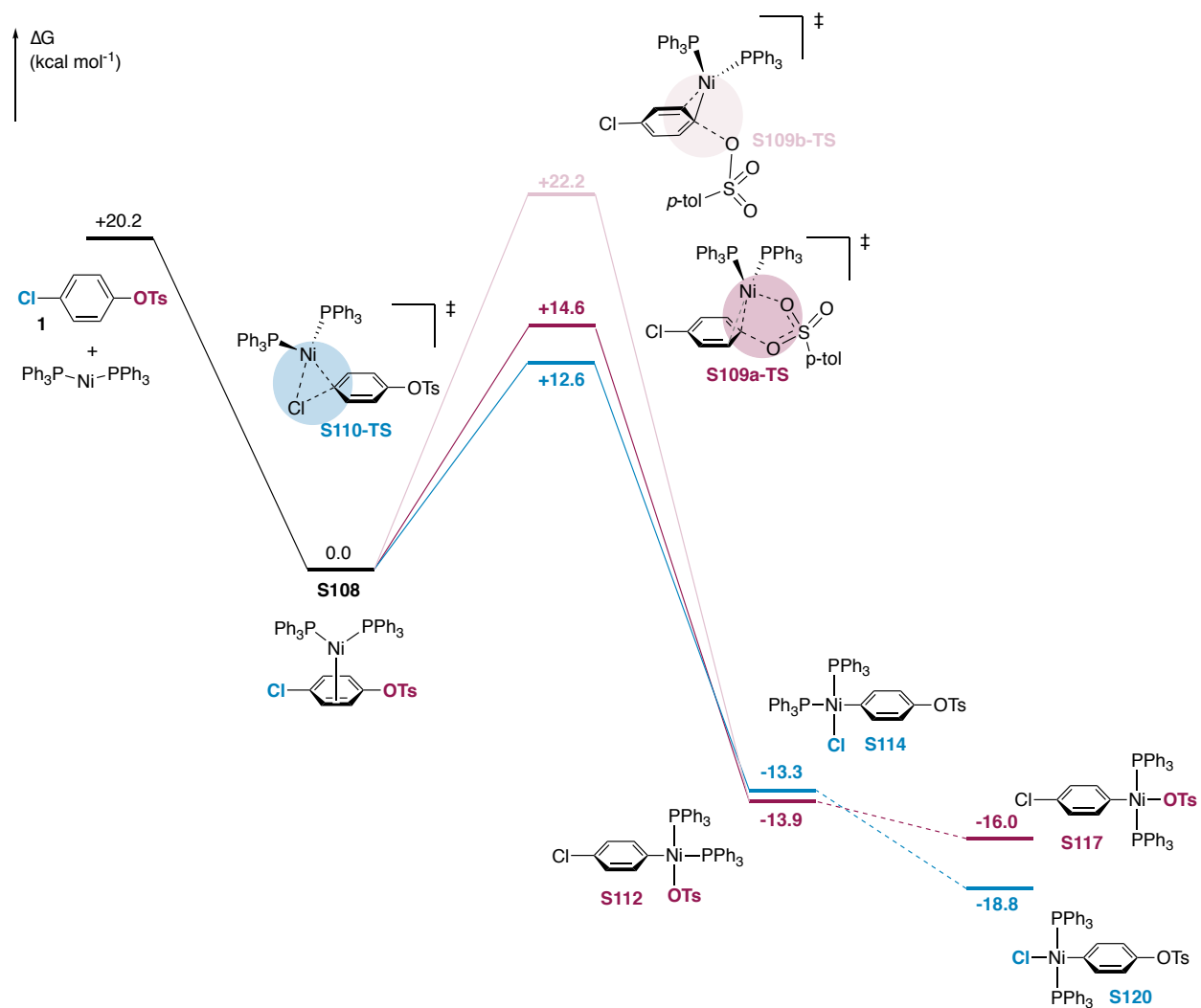


Figure S35. Free energy diagram for oxidative addition at $\text{Ni}(\text{PPh}_3)_2$.

D. Table of Energies, Entropies, and Lowest Frequencies of Minimum Energy Structures**Table S19.** Energies, Entropies, and Lowest Frequencies of Minimum Energy Structures^a

Structure	E _{elec} (Hartree)	E _{elec} + ZPE (Hartree)	H (Hartree)	S (cal mol ⁻¹ K ⁻¹)	G ^b (Hartree)	G _{corrected} ^c (Hartree)	Lowest freq. (cm ⁻¹)	# of imag freq.
1	-1585.576471	-1585.362155	-1585.345004	134.8	-1585.409060	-1585.404237	14.1	0
Ni(PMe₃)₂	-1091.987595	-1091.758554	-1091.741331	127.7	-1091.801997	-1091.799893	33.0	0
Ni(PCy₃)₂	-2263.383871	-2262.412095	-2262.370156	237.0	-2262.482747	-2262.476721	18.6	0
Ni(PPh₃)₂	-2241.844806	-2241.294515	-2241.258731	220.7	-2241.363608	-2241.354081	19.1	0
2	-2677.623691	-2677.179426	-2677.144871	211.5	-2677.245346	-2677.238070	19.9	0
S107	-3849.013512	-3847.824263	-3847.765651	309.1	-3847.912499	-3847.903053	21.4	0
S108	-3827.482432	-3826.716526	-3826.663978	291.8	-3826.802617	-3826.790462	19.7	0
4a-TS	-2677.600439	-2677.158602	-2677.123940	215.3	-2677.226213	-2677.217213	-154.5	1
37a-TS	-3848.996278	-3847.808990	-3847.750445	309.1	-3847.897307	-3847.887452	-210.3	1
S109a-TS	-3827.457161	-3826.692745	-3826.639886	296.7	-3826.780834	-3826.767163	-93.8	1
4b-TS	-2677.596845	-2677.154215	-2677.119959	208.3	-2677.218944	-2677.212684	-179.1	1
37b-TS	-3848.995622	-3847.809596	-3847.750277	318.8	-3847.901743	-3847.888691	-132.7	1
S109b-TS	-3827.444945	-3826.680874	-3826.628041	294.8	-3826.768123	-3826.755151	-190.3	1
3-TS	-2677.596066	-2677.153759	-2677.119019	215.8	-2677.221575	-2677.212475	-217.3	1
38-TS	-3848.995262	-3847.808036	-3847.749289	310.9	-3847.896993	-3847.886834	-196.4	1
S110-TS	-3827.460239	-3826.695856	-3826.642878	299.4	-3826.785117	-3826.770371	-203.7	1
6	-2677.657199	-2677.211581	-2677.177399	207.4	-2677.275921	-2677.269719	20.8	0
S111	-3849.044511	-3847.854905	-3847.795816	312.4	-3847.944255	-3847.934050	22.2	0
S112	-3827.504121	-3826.738169	-3826.685321	293.3	-3826.824664	-3826.812649	16.0	0
5	-2677.655934	-2677.209397	-2677.175029	213.0	-2677.276253	-2677.267375	14.4	0
S113	-3849.041451	-3847.851538	-3847.792524	313.0	-3847.941238	-3847.930350	18.3	0
S114	-3827.504724	-3826.737538	-3826.685084	288.5	-3826.822147	-3826.811724	18.0	0
S115	-2677.668825	-2677.223827	-2677.189032	213.4	-2677.290440	-2677.282845	18.3	0
S116	-3849.054150	-3847.865016	-3847.805686	314.7	-3847.955220	-3847.944214	14.1	0
S117	-3827.506564	-3826.741161	-3826.688088	295.0	-3826.828234	-3826.815908	16.9	0
S118	-2677.667477	-2677.222169	-2677.187262	219.7	-2677.291663	-2677.280769	7.2	0
S119	-3849.047741	-3847.857116	-3847.798018	319.8	-3847.949963	-3847.935370	11.2	0
S120	-3827.512977	-3826.746109	-3826.693118	297.6	-3826.834516	-3826.820467	14.5	0

^aEnergy values calculated at the CPCM(1,4-dioxane)-MN15L/BS2//MN15L/BS1 level, where BS2 = 6-311++G(2d,p)/SDD(Ni) and BS1 = 6-31+G(d)(O,Cl)/6-31G(d)(C,H,S,P)/LANL2DZ(Ni). 1 Hartree = 627.51 kcal mol⁻¹. Thermal corrections at 298.15 K. ^bSolvent-corrected free energy given by G[(CPCM)/MN15L/BS2] = E_{elec}[(CPCM)/MN15L/BS2] + G_{corr}[MN15L/BS1], where G_{corr} is the thermal correction to Gibbs free energy obtained in the gas phase. ^cSolvent-corrected free energy given by G[(CPCM)/MN15L/BS2] = E_{elec}[(CPCM)/MN15L/BS2] + G_{corr}^{*}[MN15L/BS1], where G_{corr}^{*} is the thermal correction to Gibbs free energy obtained in the gas phase after applying Cramer and Truhlar's anharmonic correction.³⁸

E. Evaluation of Other DFT Methods

Figure S36 illustrates the difference between energy barriers for reaction at tosylate vs. chloride ($\Delta\Delta G^\ddagger_{\text{OTs-Cl}}$) using a variety of DFT methods. A negative value of $\Delta\Delta G^\ddagger$ means that reaction at tosylate is calculated to be more facile than reaction at chloride. Values were calculated based on lowest-energy transition structures for reaction at each site. The x-axis is labeled with the DFT method, where the second term represents the functional used for gas-phase optimization with BS1 and the first term is the functional used to obtain a single-point energy in implicit 1,4-dioxane (CPCM) with BS2. For example, the left-most entry, MN15L//MN15L represents the method used to obtain the numbers reported in the manuscript.

The black and red arrows near the top of the graph illustrate the calculated trend in $\Delta\Delta G^\ddagger$ going from PMe_3 to PCy_3 to PPh_3 . All the black arrows correspond to methods that predict the following trend for preference of reaction at tosylate: $\text{PMe}_3 > \text{PCy}_3 > \text{PPh}_3$. The red arrows represent exceptions to the trend. Most methods follow this trend. Also, the majority of methods predict that PMe_3 should favor reaction at tosylate (negative $\Delta\Delta G^\ddagger$), and most methods predict that PPh_3 should favor reaction at chloride (positive $\Delta\Delta G^\ddagger$).

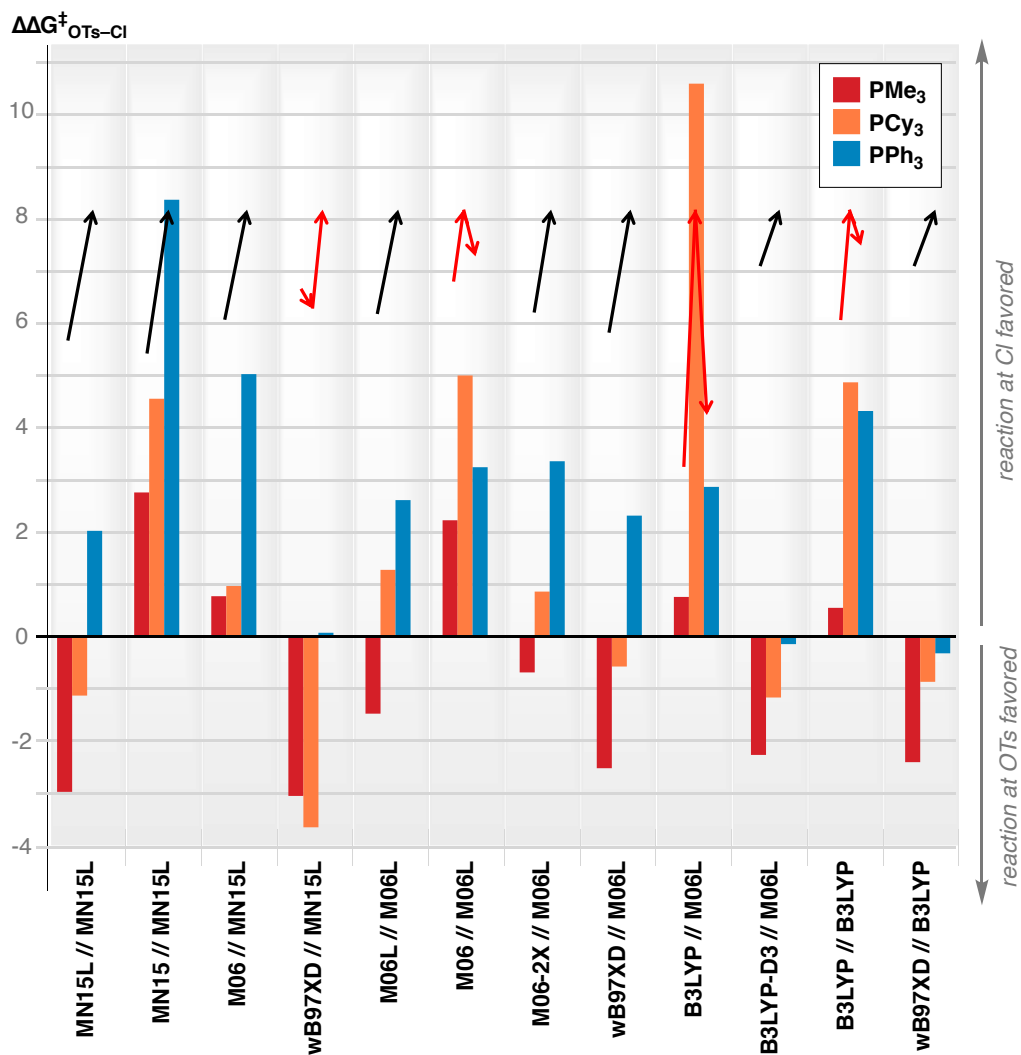


Figure S36. Comparison of preference for oxidative addition at tosylate vs. chloride with various DFT methods.

F. Distortion-Interaction Analysis

Table S20 is an expanded version of Table 5 in the manuscript, and includes a distortion-interaction analysis of the transition structures using PPh_3 .

Table S20. Expanded Table 5: Distortion-Interaction Analysis of Transition Structures.

	TS	ΔE_{dist}			$\Delta\Delta E_{\text{dist}}$	ΔE_{int}	$\Delta\Delta E_{\text{int}}$	$\Delta E^\ddagger$	$\Delta\Delta E^\ddagger$
		cat.	subst.	total					
PMe_3	4a-TS	5.2	57.4	62.6	45.0	-48.0	-47.7	14.6	-2.7
	4b-TS	2.9	53.5	56.4		-39.6		16.8	
	3-TS	1.3	16.3	17.6	38.8	-0.3	-39.3	17.3	-0.5
PCy_3	37a-TS	1.3	47.4	48.7	41.9	-37.9	-42.6	10.8	-0.7
	37b-TS	2.6	52.8	55.4		-44.2		11.2	
	38-TS	-3.9	10.7	6.8	48.6	4.7	-48.9	11.5	-0.3
PPh_3	S109a-TS	1.9	68.5	70.4	60.6	-54.5	-58.6	15.9	2.0
	S109b-TS	6.9	50.5	57.4		-33.9		23.5	
	S110-TS	-4.3	14.1	9.8	47.6	4.1	-38.0	13.9	9.6

Table S21 illustrates an alternate approach to distortion-interaction analysis that normalizes for differences in the earliness/lateness of transition structures. Transition structures involving C—O cleavage were analyzed at a C---O distance of 2.06 ± 0.01 Å, and those involving C—Cl cleavage were analyzed at a C---Cl distance of 2.085 ± 0.005 Å. For transition structures whose geometries fall outside of these ranges, analysis was instead performed at an appropriate point along each intrinsic reaction coordinate near to the transition state. As in Table S20, activation energies were measured from the preceding minimum-energy pi complex.

Table S21. Distortion-Interaction Analysis Based on Structures Normalized for Earliness/Lateness.

	TS	ΔE_{dist}			$\Delta\Delta E_{\text{dist}}$	ΔE_{int}	$\Delta\Delta E_{\text{int}}$	$\Delta E^\ddagger$	$\Delta\Delta E^\ddagger$
		cat.	subst.	total					
PMe_3	4a-TS	5.2	57.4	62.6	45.0	-48.0	-47.7	14.6	-2.7
	4b-TS	2.9	53.5	56.4		-39.6		16.8	
	3-TS	1.3	16.3	17.6	38.8	-0.3	-39.3	17.3	-0.5
PCy_3	37a-TS*	1.3	52.7	54.0	47.2	-44.0	-48.7	10.0	-1.5
	37b-TS	2.6	52.8	55.4		-44.2		11.2	
	38-TS	-3.9	10.7	6.8	48.6	4.7	-48.9	11.5	-0.3
PPh_3	S109a-TS*	1.7	61.0	62.7	53.0	-46.2	-50.4	16.5	2.6
	S109b-TS*	7.0	53.0	60.0		-36.9		23.1	
	S110-TS	-4.3	14.1	9.8	50.3	4.1	-41.1	13.9	9.2

*A nearby point on the IRC was analyzed instead of the actual transition structure.

The distortion-interaction analysis using PMe_3 and PCy_3 was also conducted using other functionals. We selected a few functionals (MN15, Mo6L, ωB97XD , and B3LYP) for further analysis because these functionals provide a range of predictions (including incorrect predictions) about the Cl vs. OTs selectivity. Each of these functionals was used to calculate energy values [using BS2 in dioxane(CPCM)] of the structures or fragments of structures that had been optimized at the MN15L/BS1 level of theory. The results are summarized in Tables S22-S25. Statements from the manuscript have been extracted and reproduced below. The first set of statements holds true with all of the additional functionals, indicating that the distortion-interaction analysis conclusions are independent of DFT methods. The second set of statements do not hold true with all the functionals; these are the statements that relate to overall Cl vs. OTs predictions and represent failures of these functionals as illustrated previously in Figure S36.

Statements from the manuscript that are functional-independent:

- With both PCy_3 and PMe_3 , reaction at tosylate involves greater distortion energy than reaction at chloride.
- In fact, the catalyst distortion energy is actually slightly negative (favorable) during insertion of $\text{Ni}(\text{PCy}_3)_2$ into C—Cl (**38-TS**).
- If reaction at tosylate is desired, the dissociation mechanism with $\text{Ni}(\text{PCy}_3)_2$ (**37b-TS**) has a larger distortion disadvantage than either 5-centered mechanism **37a-TS** or **4a-TS**.
- However, this bending also leads to a large interaction energy advantage for [**37b-TS**] the dissociation mechanism ($\Delta\Delta E_{\text{int}}$).
- The 5-centered mechanism with PCy_3 (**37a-TS**) has a much smaller distortion disadvantage than either **37b-TS** or **4a-TS**.
- However, **37a-TS** also has less of an interaction energy advantage than the corresponding transition structure using PMe_3 .

Statements from the manuscript that are functional-dependent:

Note: these statements are valid using functionals that predict selectivity consistent with experiment, and are incorrect for functionals that are inconsistent with experiment.

- The effects of $\Delta\Delta E_{\text{dist}}$ and $\Delta\Delta E_{\text{int}}$ nearly cancel each other out for **37b-TS**, and this dissociation mechanism for reaction at tosylate using PCy_3 is only slightly lower-energy than reaction at chloride.
- As a result, the effects of $\Delta\Delta E_{\text{dist}}$ and $\Delta\Delta E_{\text{int}}$ again nearly cancel out and **37a-TS** has a similar energy barrier as that for reaction at chloride (**38-TS**).
- ...a value of $\Delta\Delta E_{\text{int}}$ for **4a-TS** that outweighs the influence of distortion energy ($\Delta\Delta E_{\text{dist}}$) and makes reaction at tosylate more facile than reaction at chloride.

Table S22. Distortion-Interaction Analysis of Transition Structures using **MN15**.

TS	cat ΔE dist	sub ΔE dist	total ΔE dist	$\Delta\Delta E$ dist	ΔE_{int}	$\Delta\Delta E_{int}$	$\Delta E^\ddagger$	$\Delta\Delta E^\ddagger$
4a-TS	4.6	60.7	65.3	47.2	-44.8	-44.4	20.5	2.8
4b-TS	2.5	59.3	61.8	43.7	-39.1	-38.7	22.7	5.1
3-TS	0.9	17.2	18.1		-0.5		17.7	
37a-TS	1.2	51.5	52.7	42.6	-34.0	-37.9	18.7	4.6
37b-TS	1.6	59.3	60.9	50.8	-41.4	-45.3	19.5	5.4
38-TS	-3.3	13.5	10.2		3.9		14.1	

Table S23. Distortion-Interaction Analysis of Transition Structures using **Mo6**.

TS	cat ΔE dist	sub ΔE dist	total ΔE dist	$\Delta\Delta E$ dist	ΔE_{int}	$\Delta\Delta E_{int}$	$\Delta E^\ddagger$	$\Delta\Delta E^\ddagger$
4a-TS	5.1	58.8	63.9	47.2	-46.3	-46.2	17.5	1.0
4b-TS	3.1	58.1	61.3	44.6	-40.7	-40.5	20.5	4.0
3-TS	1.2	15.4	16.7		-0.2		16.5	
37a-TS	2.2	50.5	52.6	43.3	-34.6	-40.8	18.1	2.6
37b-TS	2.4	58.0	60.4	51.1	-44.9	-51.1	15.5	0.0
38-TS	-3.9	13.2	9.3		6.2		15.5	

Table S24. Distortion-Interaction Analysis of Transition Structures using **ω B97XD**.

TS	cat ΔE dist	sub ΔE dist	total ΔE dist	$\Delta\Delta E$ dist	ΔE_{int}	$\Delta\Delta E_{int}$	$\Delta E^\ddagger$	$\Delta\Delta E^\ddagger$
4a-TS	5.2	61.3	66.5	48.5	-50.7	-51.4	15.9	-2.9
4b-TS	3.4	60.3	63.6	45.6	-46.5	-47.2	17.1	-1.6
3-TS	1.6	16.4	18.1		0.7		18.8	
37a-TS	1.4	51.8	53.2	43.6	-39.1	-45.2	14.0	-1.6
37b-TS	2.0	60.1	62.2	52.6	-50.7	-56.8	11.4	-4.2
38-TS	-4.3	13.9	9.6		6.1		15.6	

Table S25. Distortion-Interaction Analysis of Transition Structures using **B3LYP**.

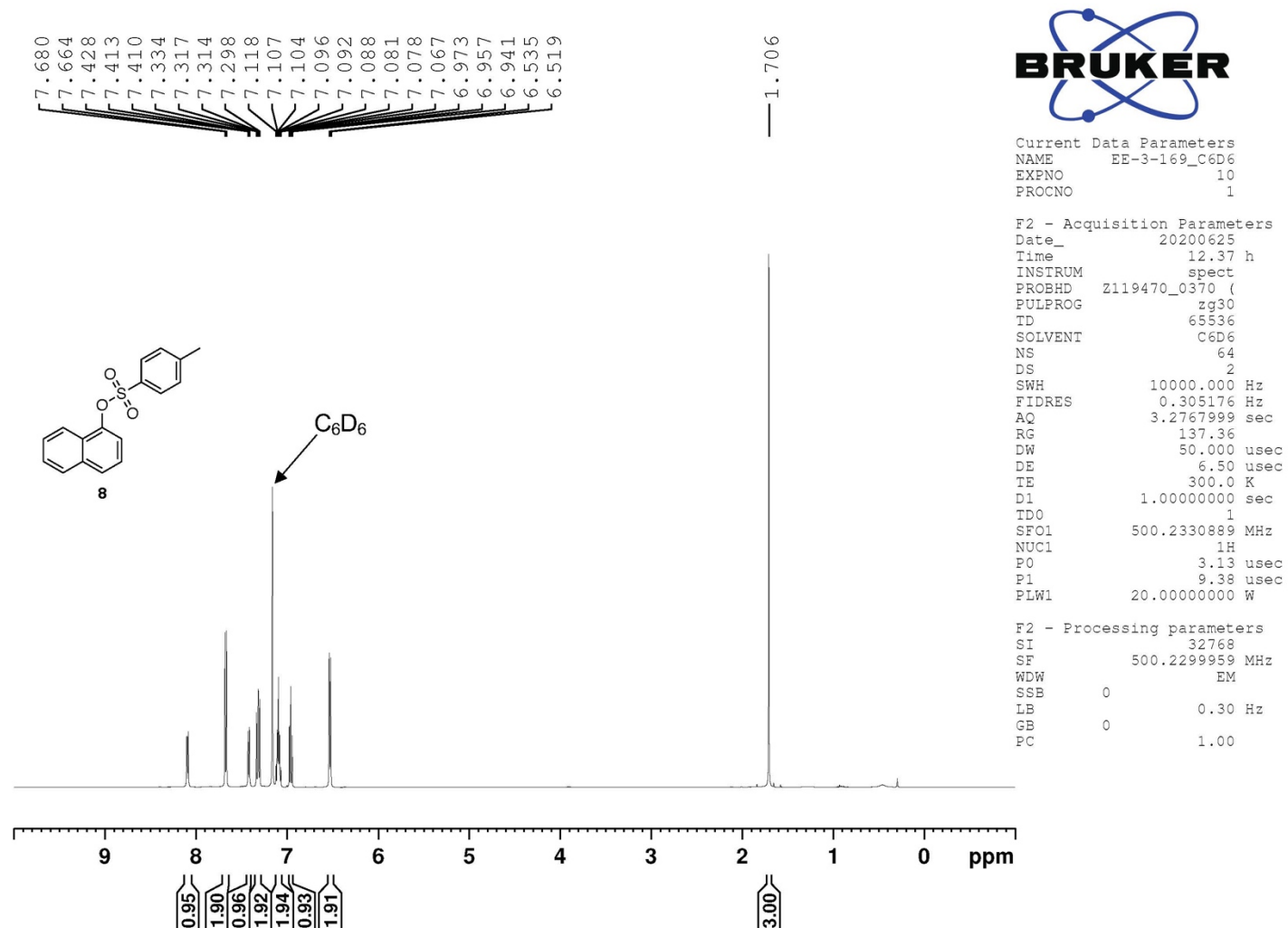
TS	cat ΔE dist	sub ΔE dist	total ΔE dist	$\Delta\Delta E$ dist	ΔE_{int}	$\Delta\Delta E_{int}$	$\Delta E^\ddagger$	$\Delta\Delta E^\ddagger$
4a-TS	6.1	52.5	58.6	42.4	-50.5	-45.1	8.1	-2.7
4b-TS	4.4	59.2	63.6	47.4	-48.6	-43.1	15.1	4.3
3-TS	1.9	14.3	16.2		-5.4		10.8	
37a-TS	1.7	49.5	51.2	37.7	-37.6	-34.7	13.6	3.0
37b-TS	2.6	61.8	64.4	50.9	-56.7	-53.8	7.7	-2.9
38-TS	-5.1	18.6	13.5		-2.9		10.6	

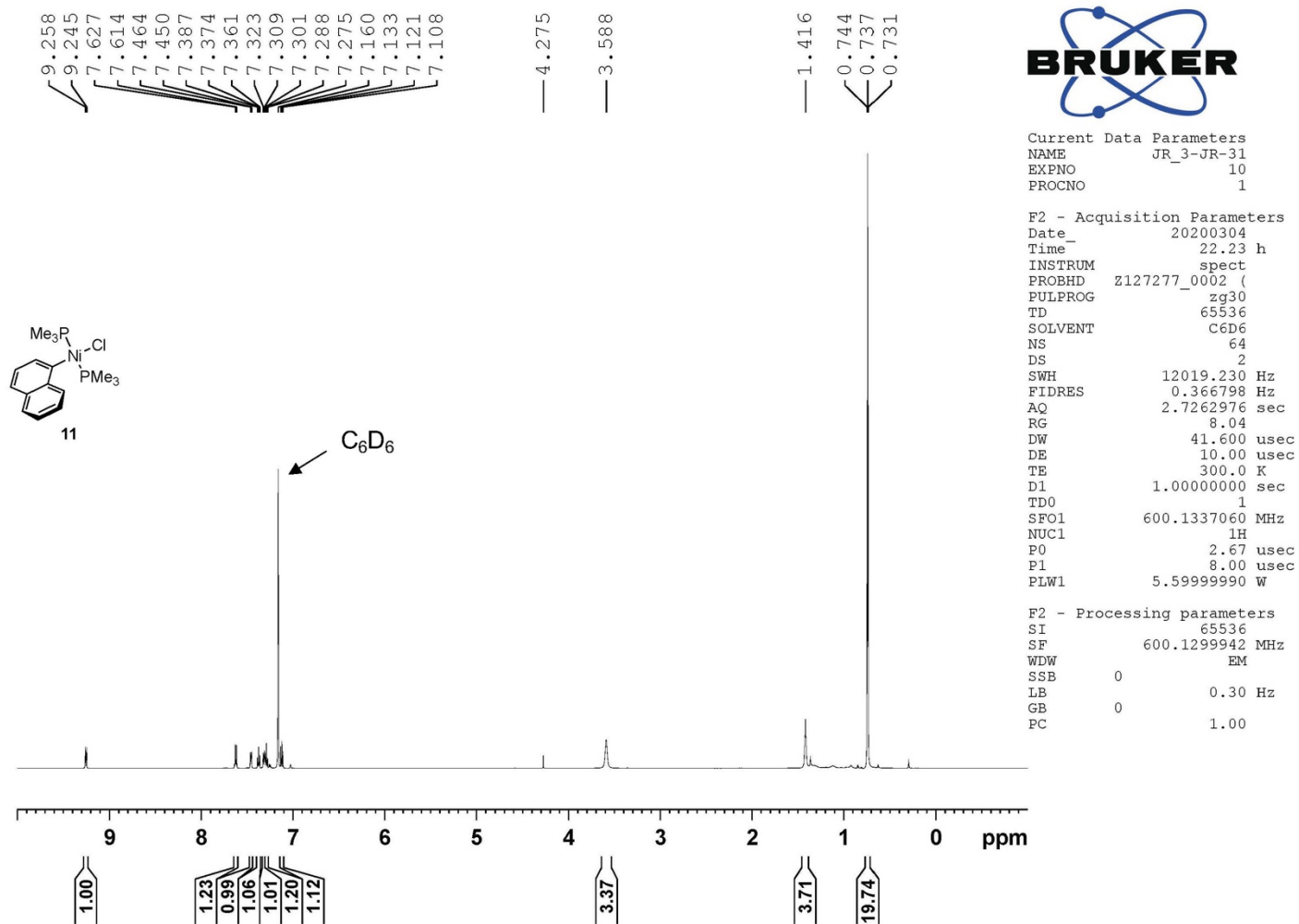
III. References

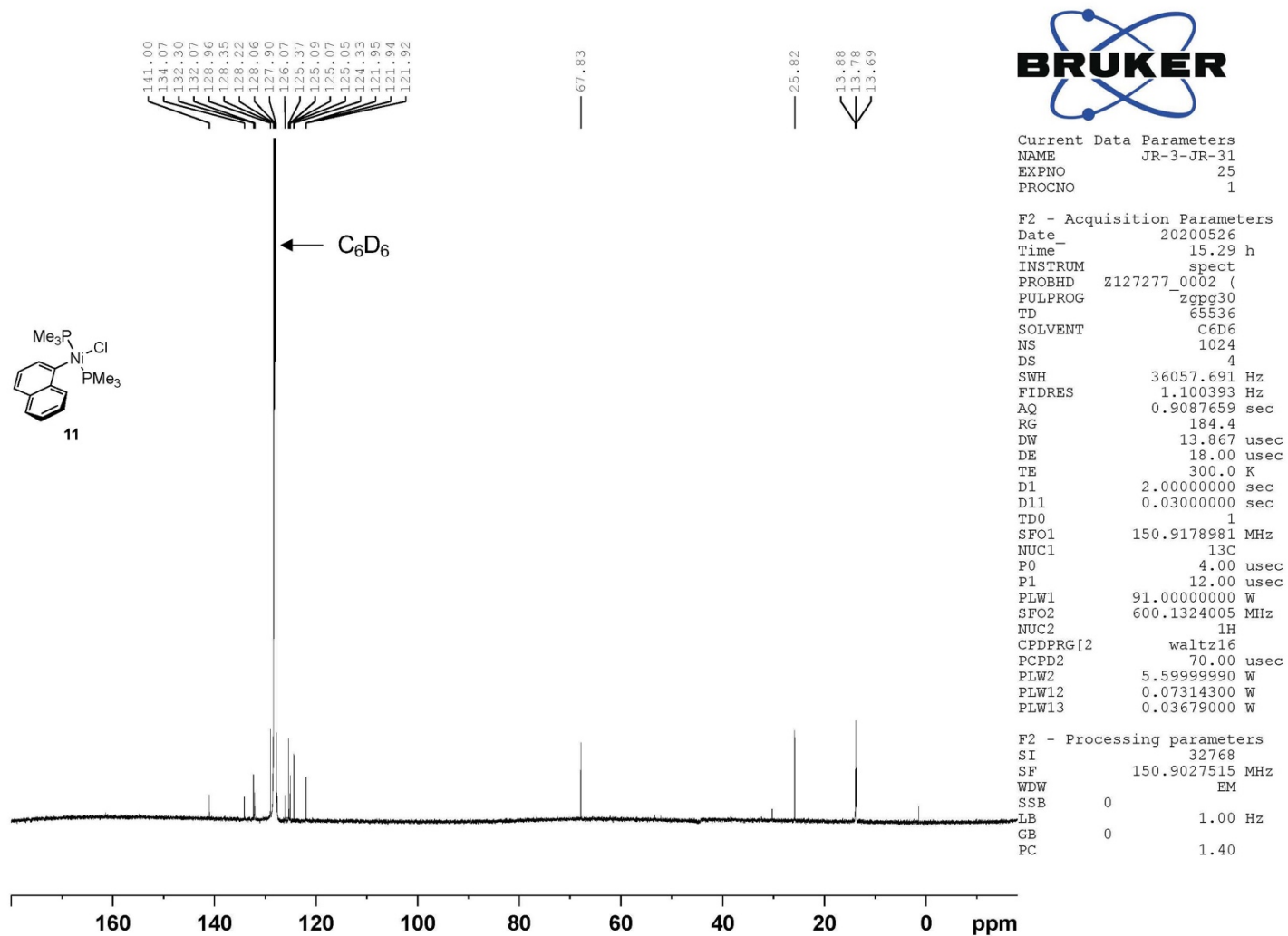
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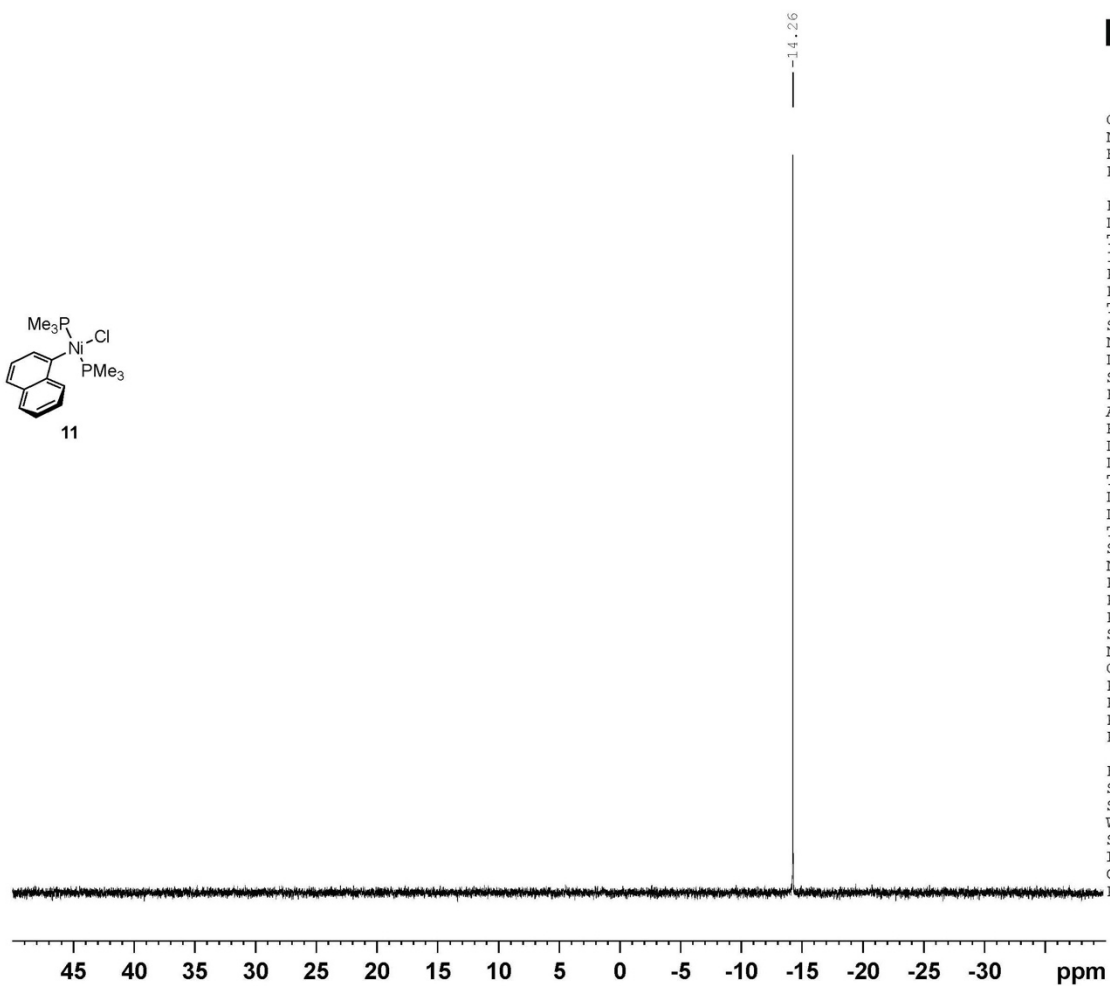
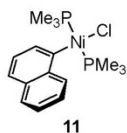
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IV. Spectral Data









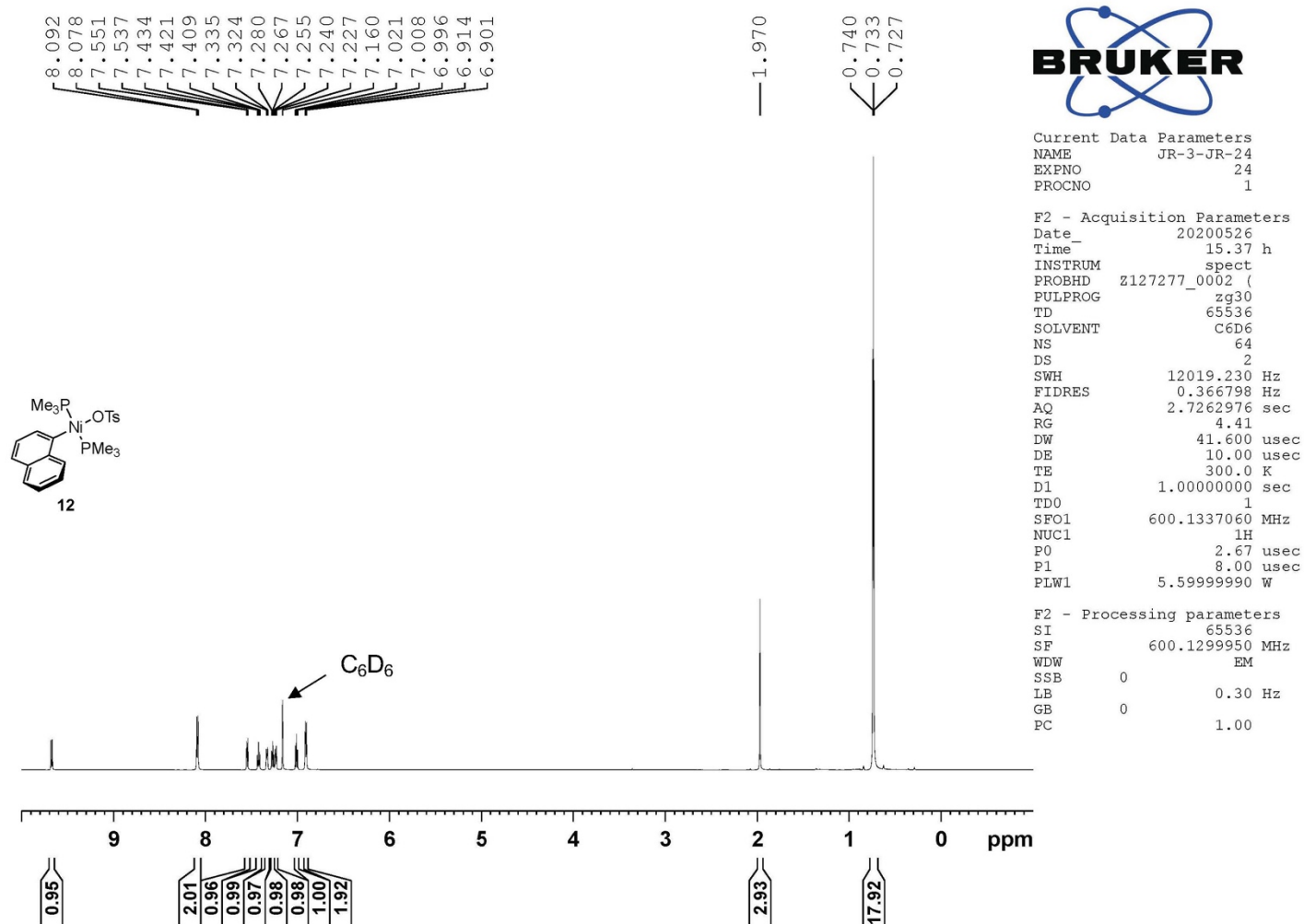
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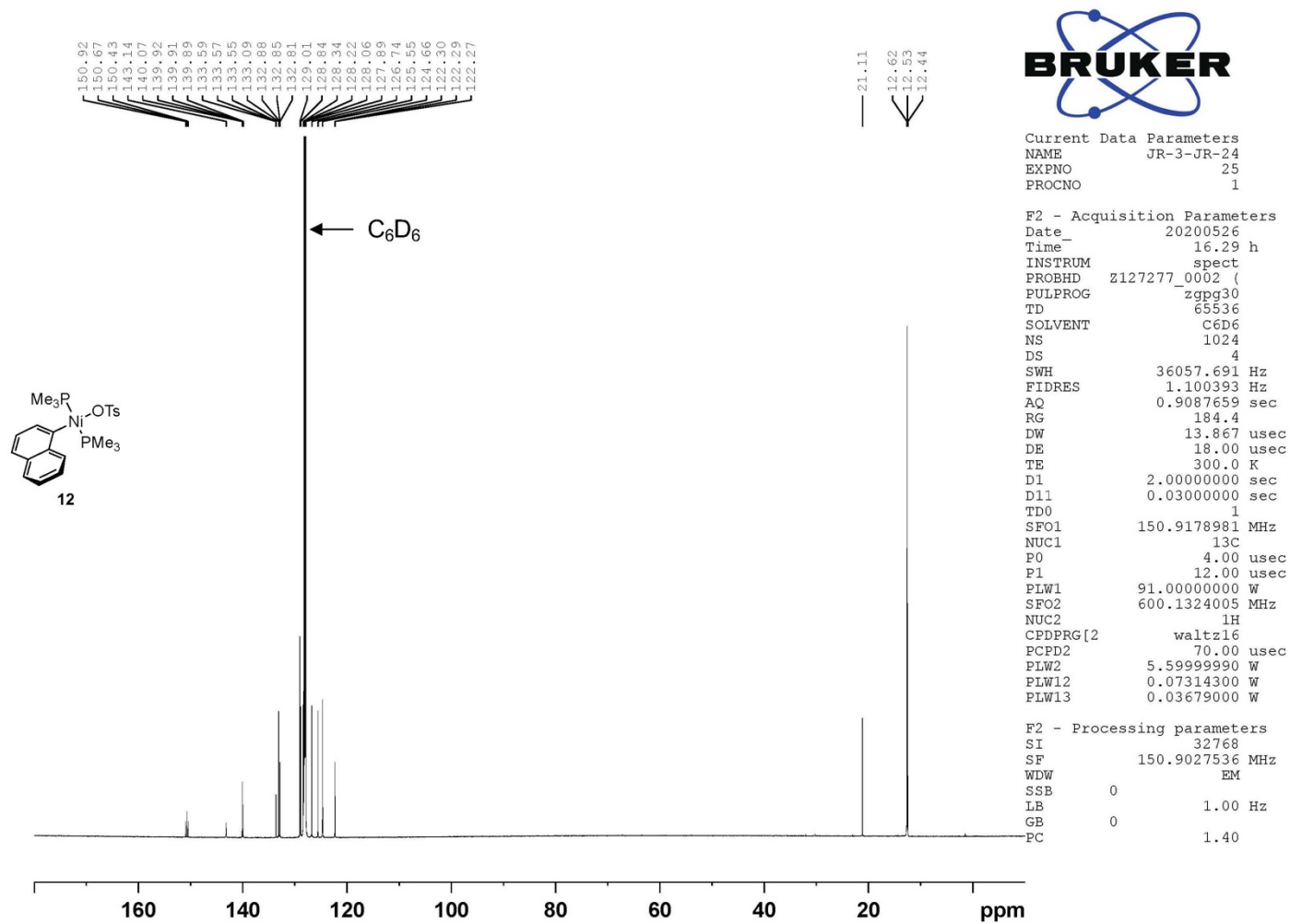


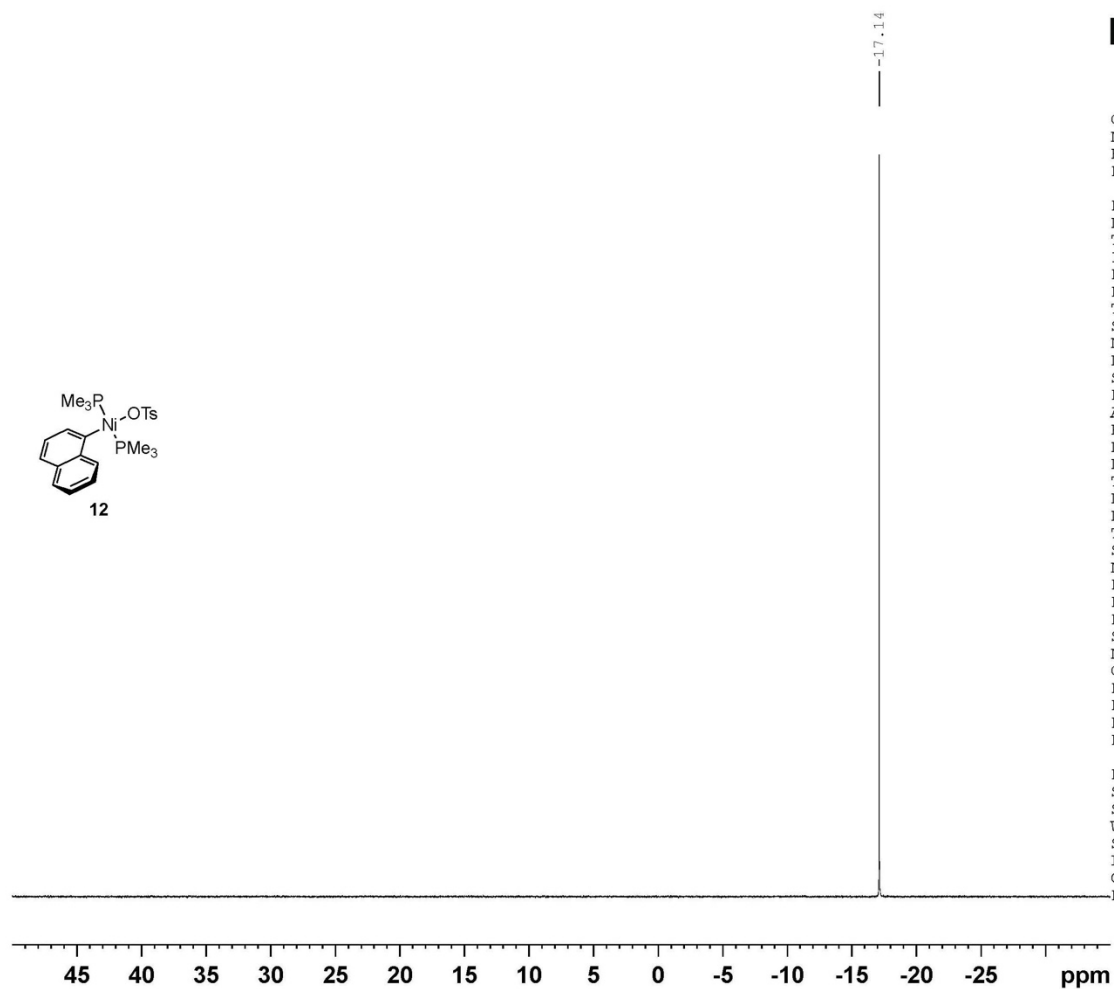
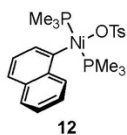
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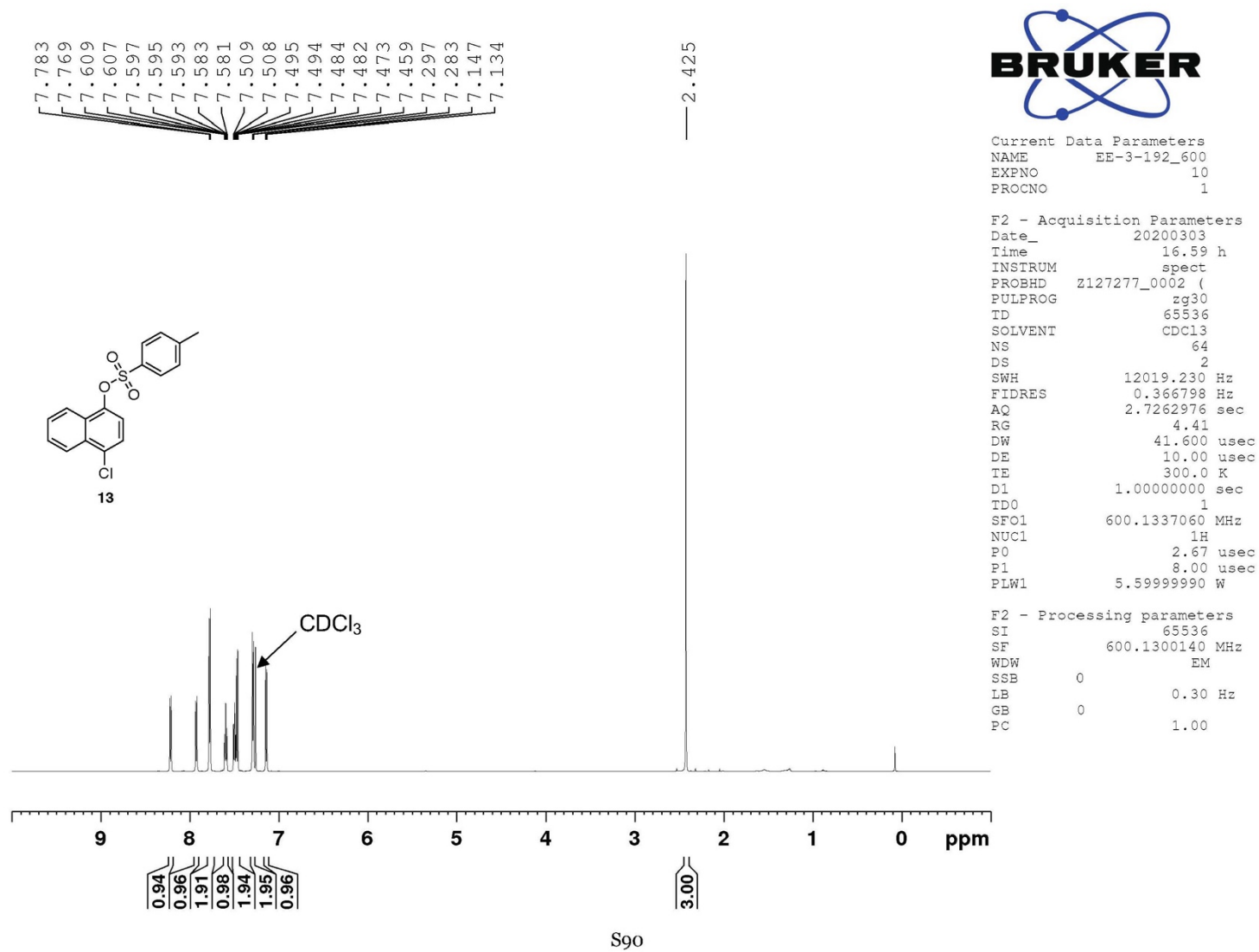


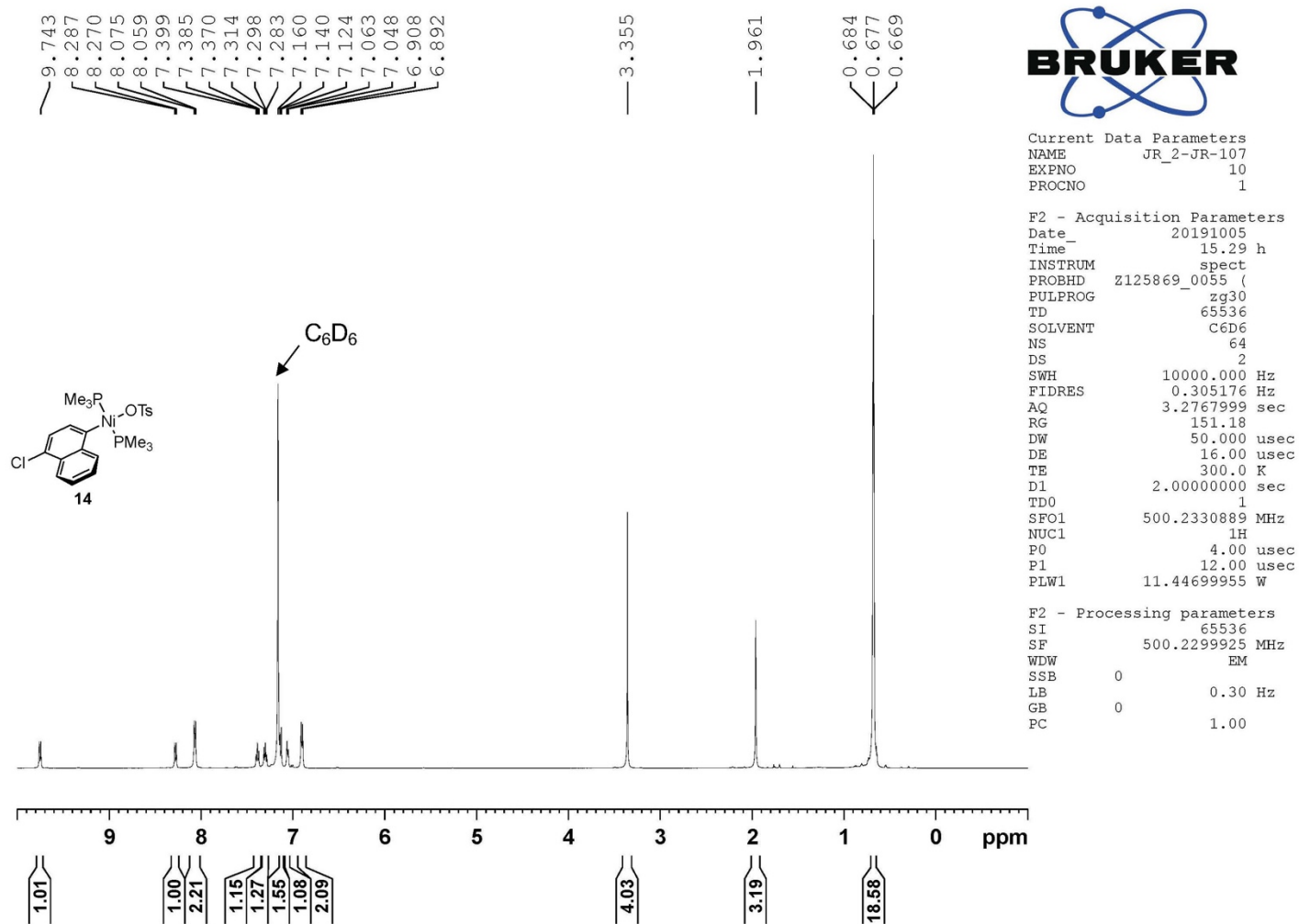


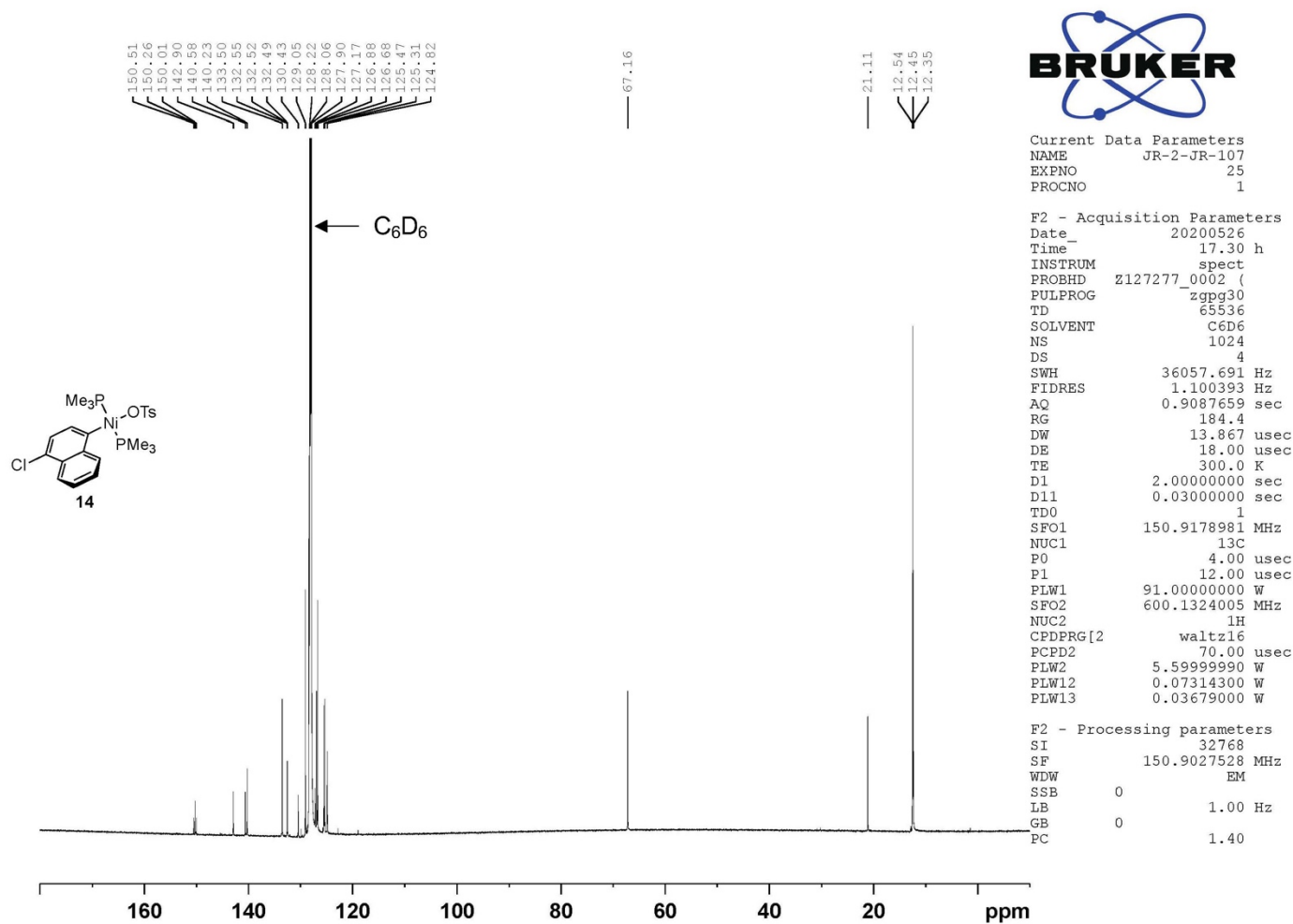
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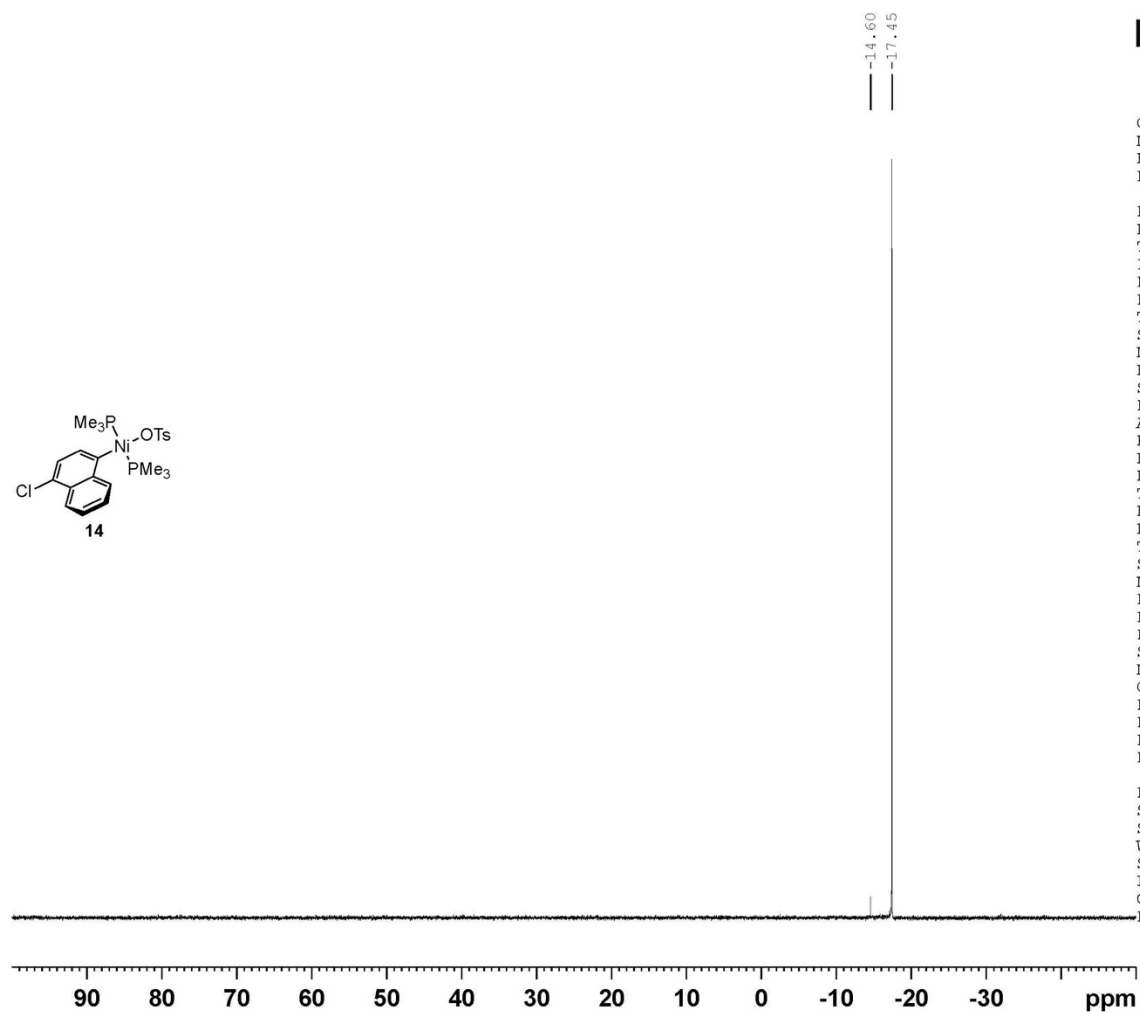
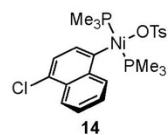
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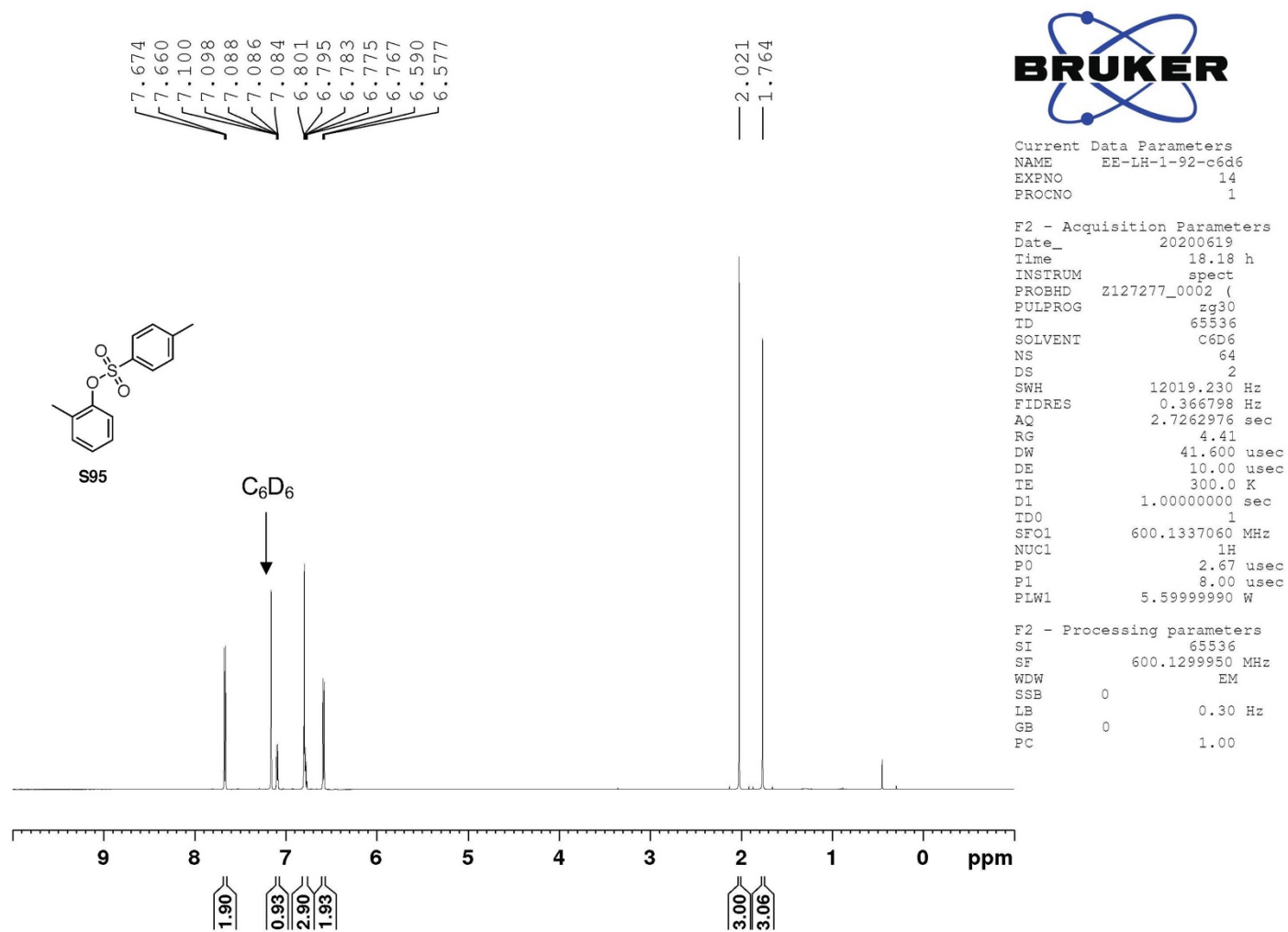


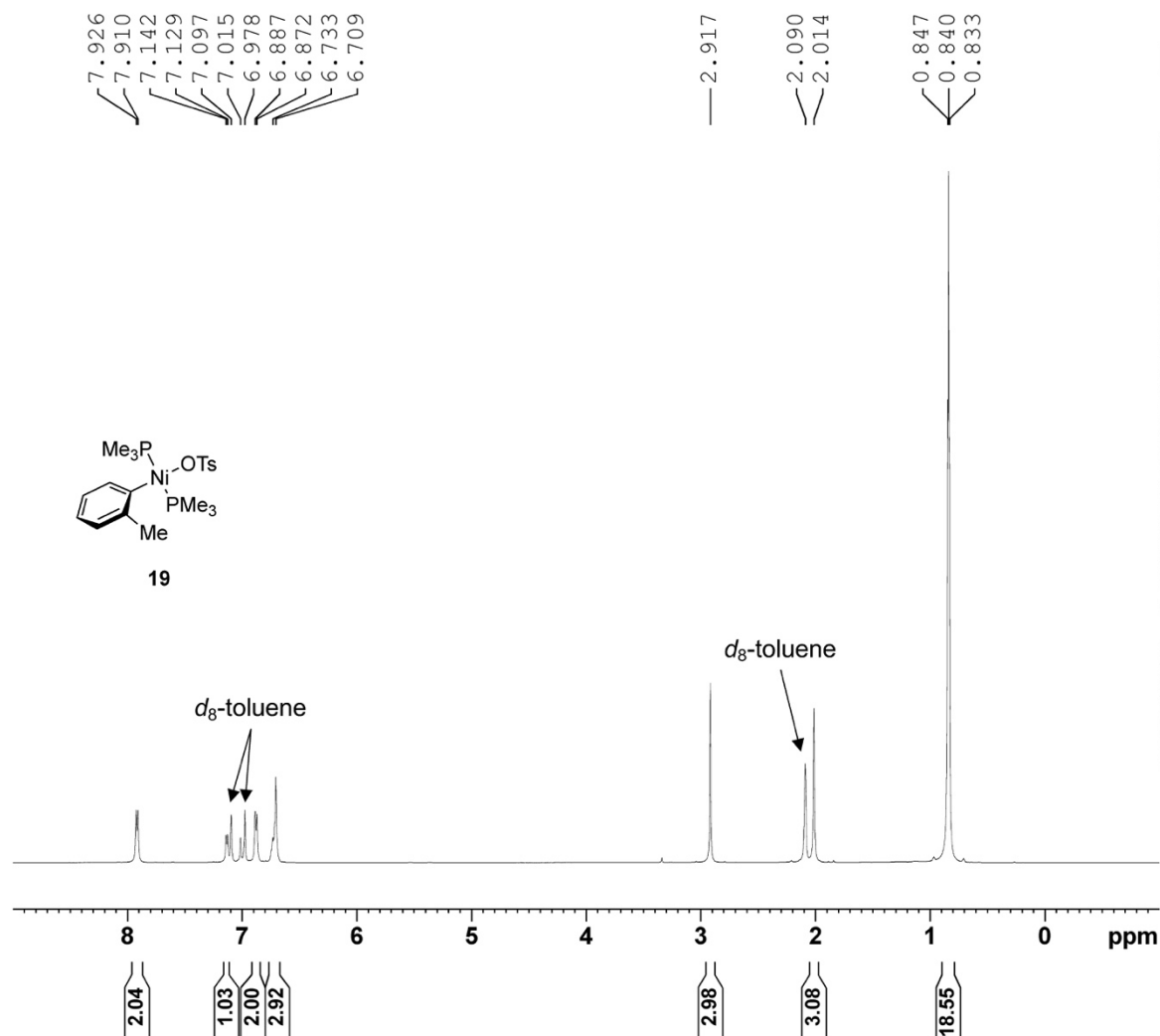


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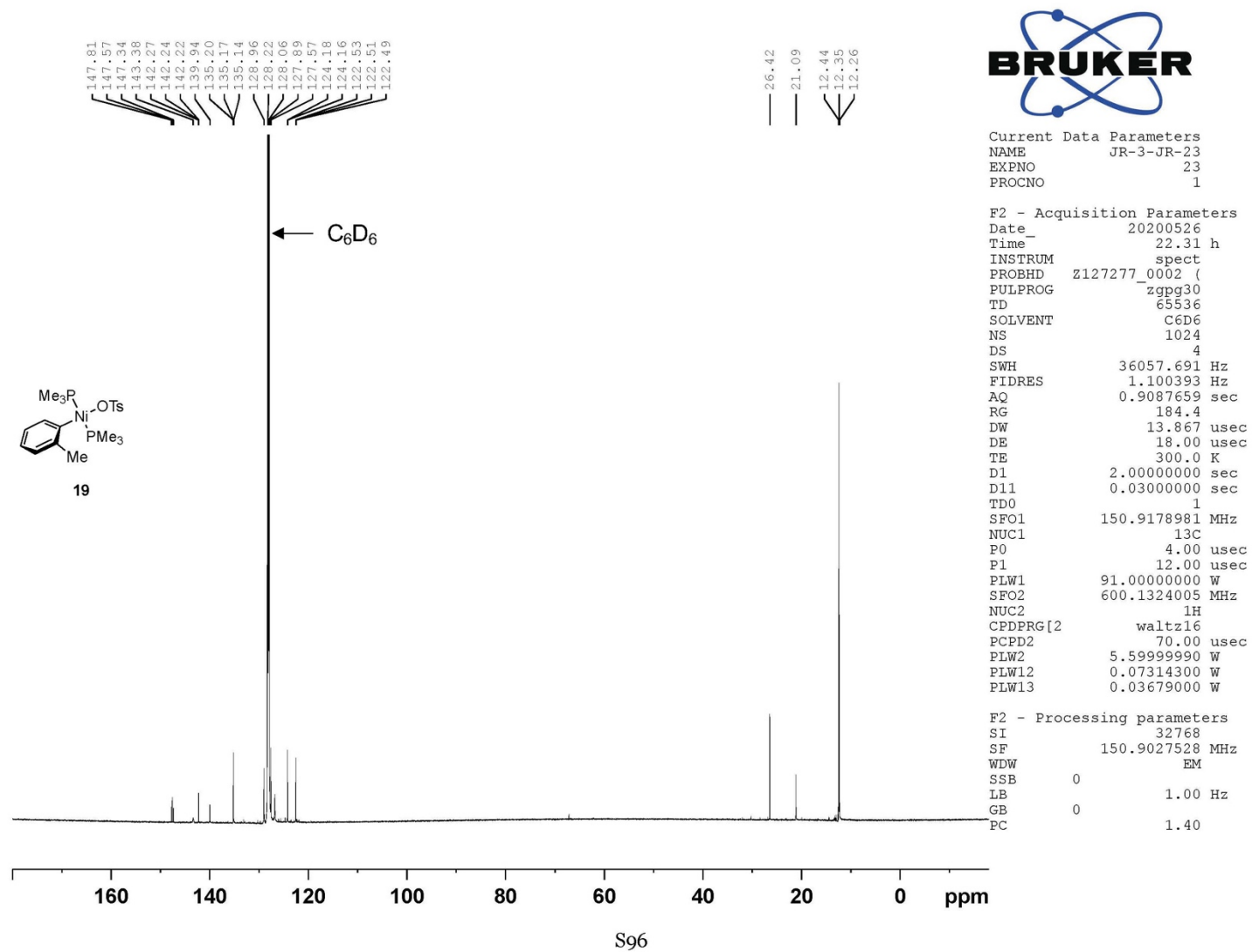


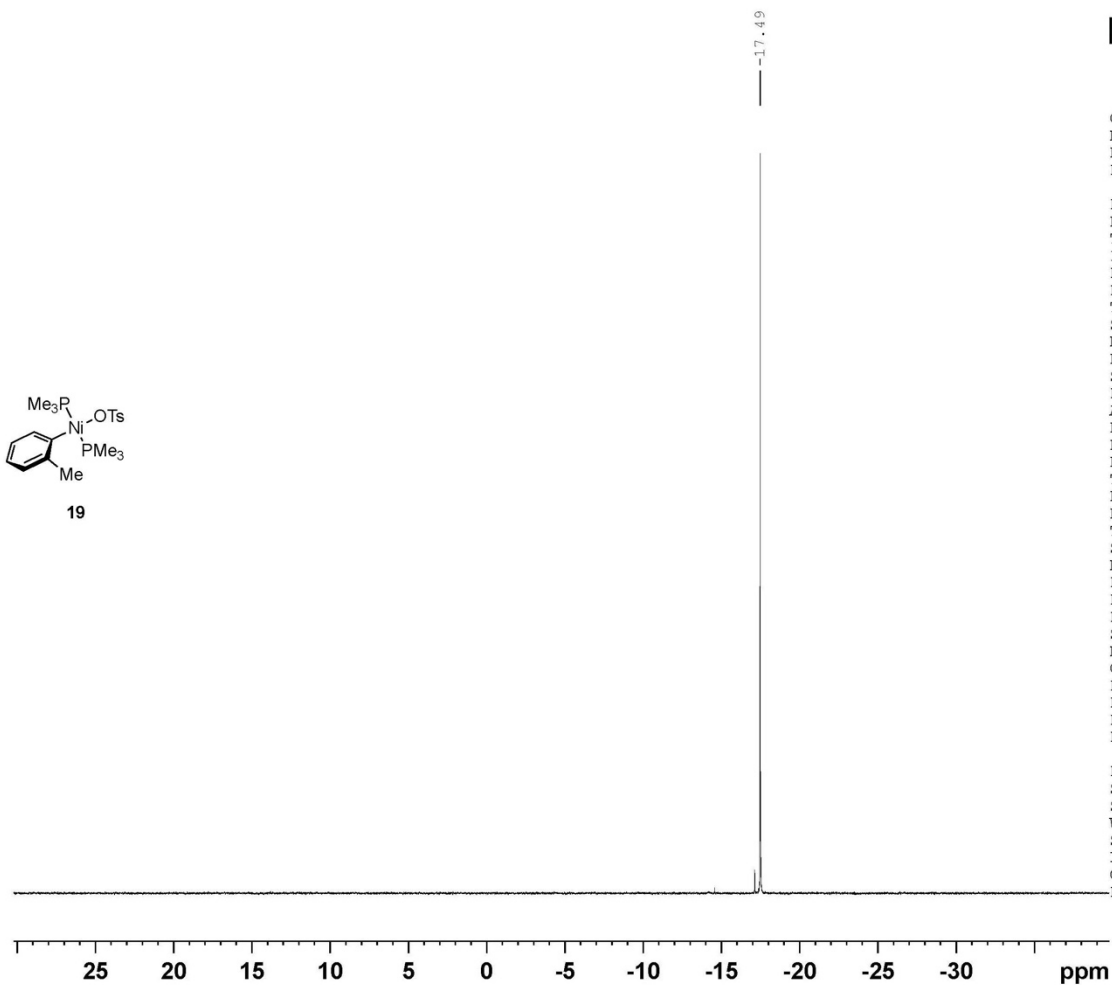
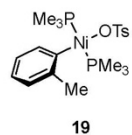


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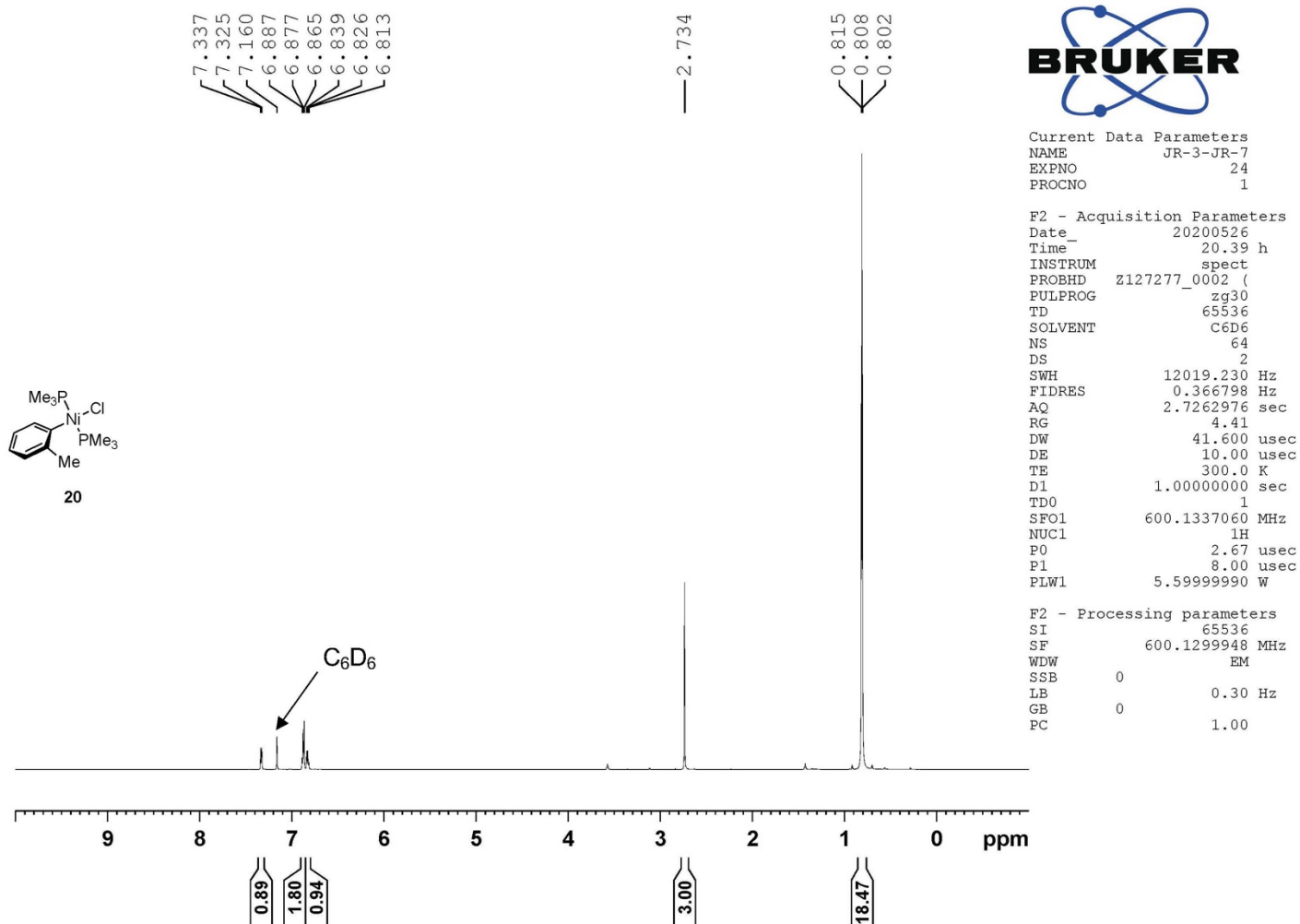
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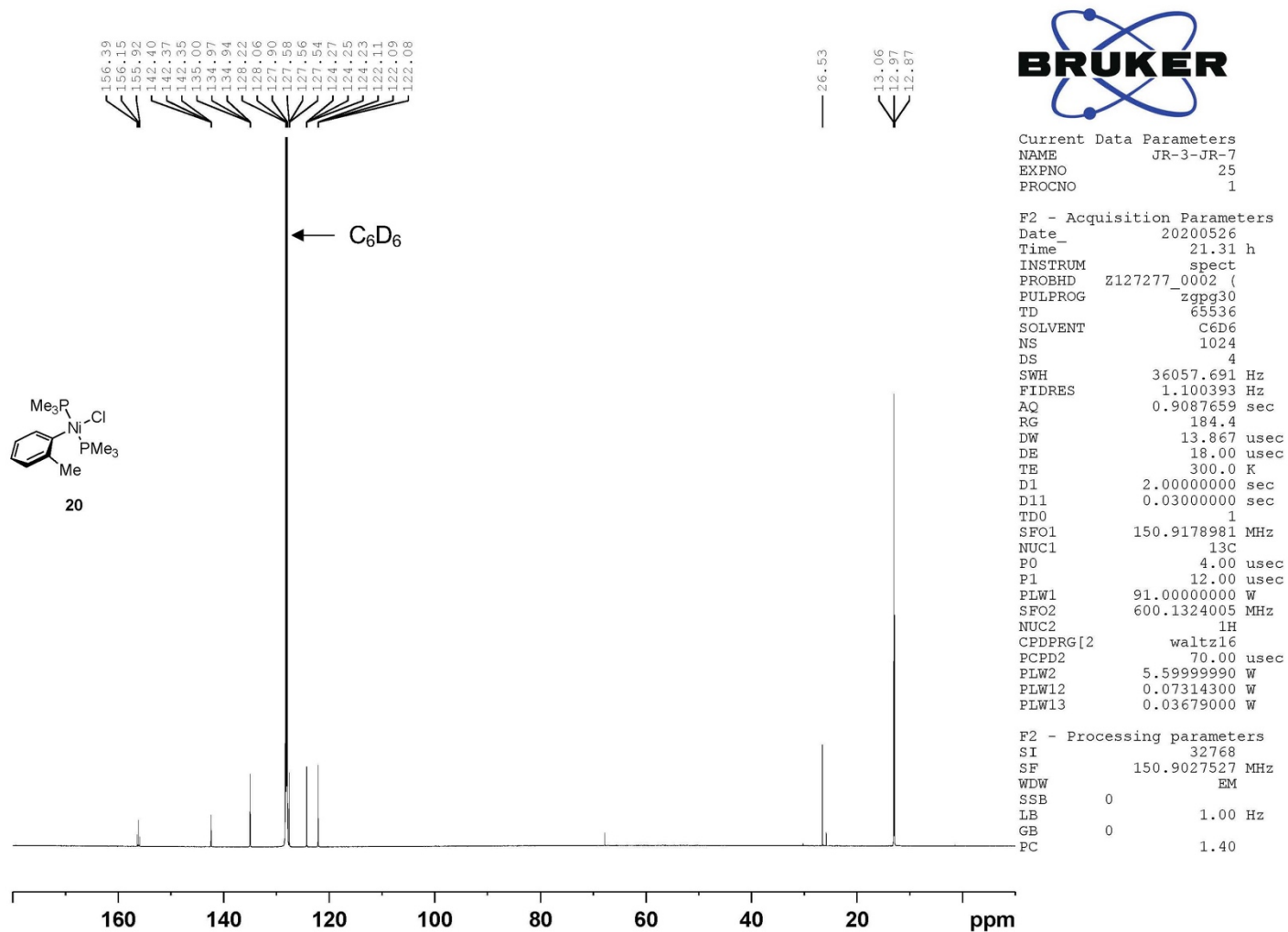


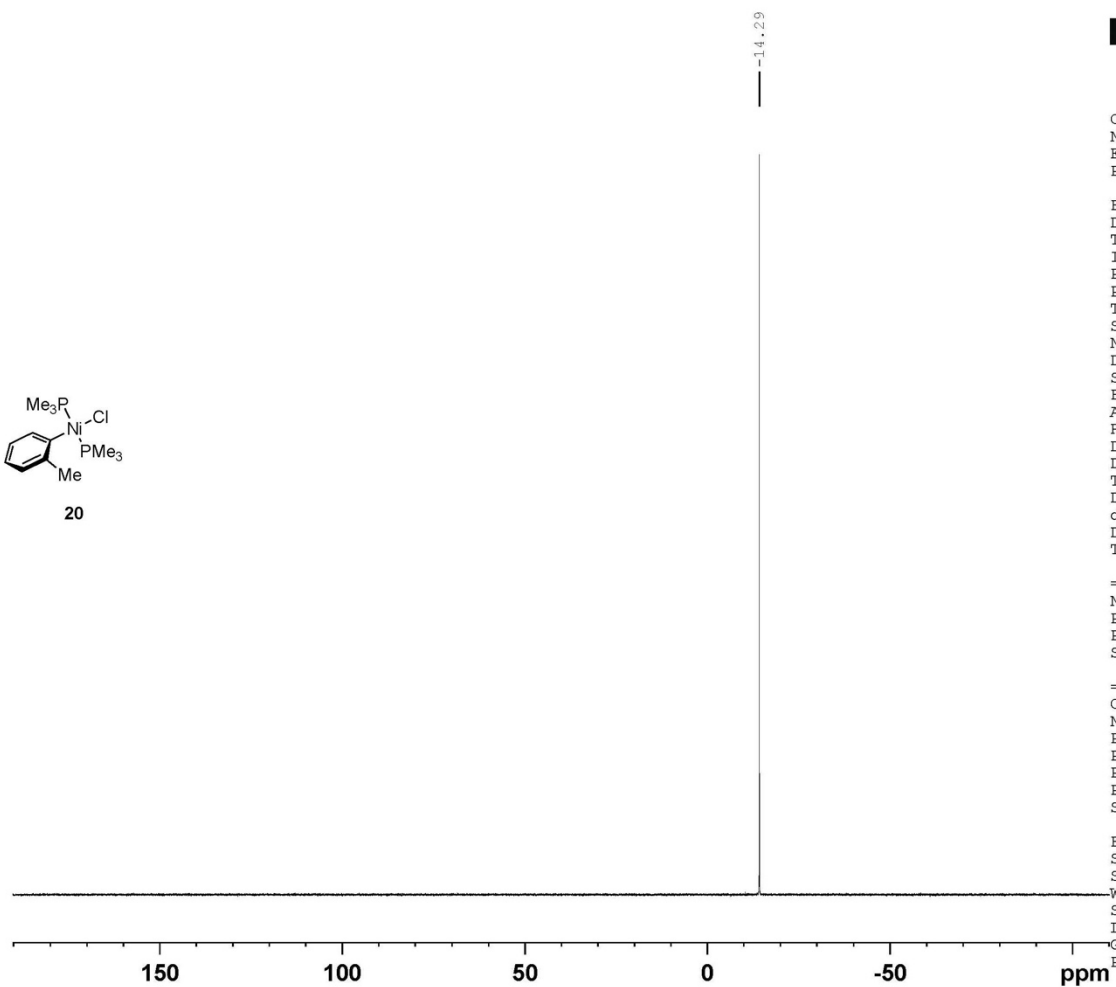
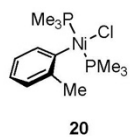
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 RG 190.44
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 DE 6.50 usec
 TE 300.0 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1
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 P0 3.33 usec
 P1 10.00 usec
 PLW1 40.20000076 W
 SFO2 500.2320009 MHz
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S100



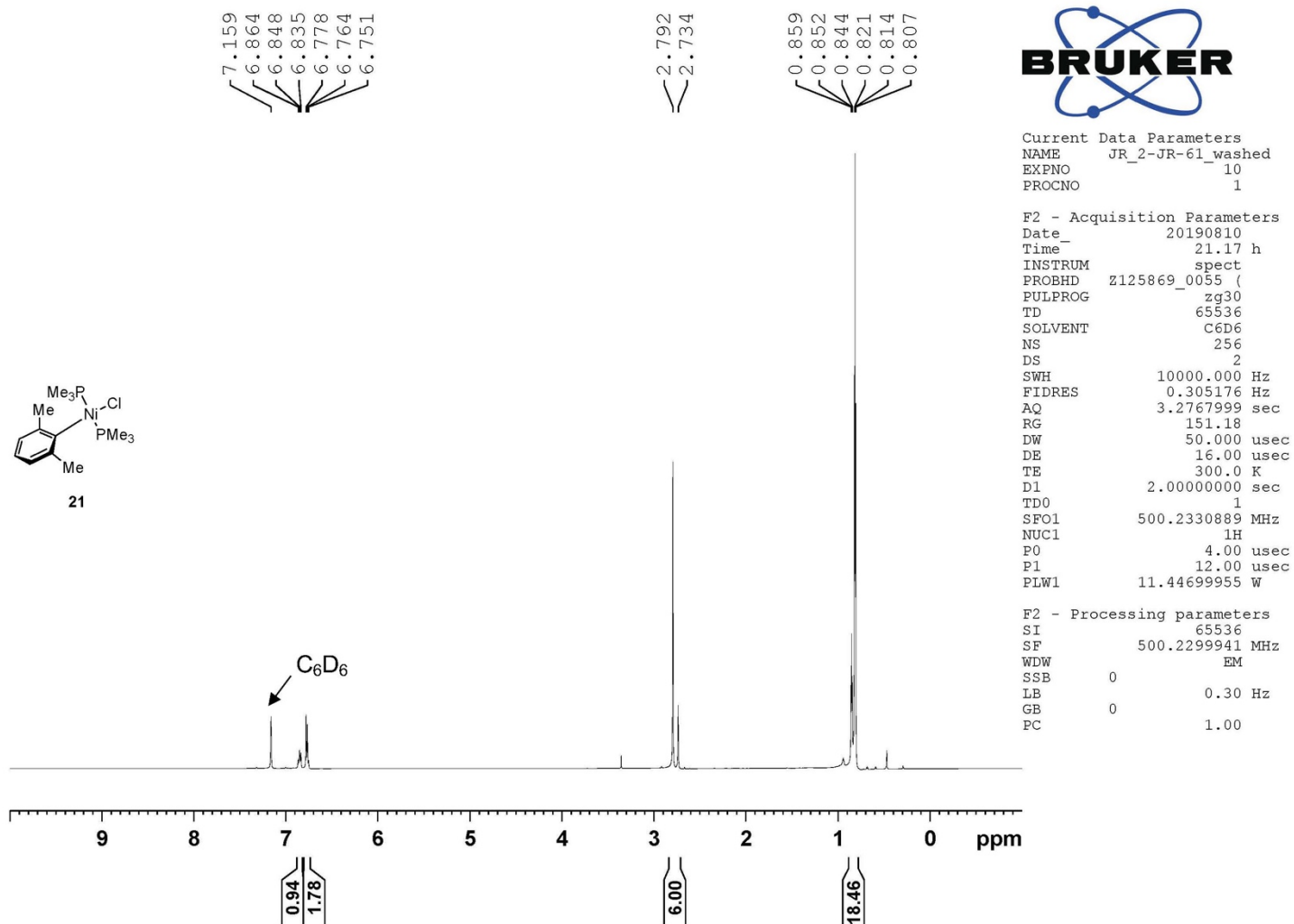
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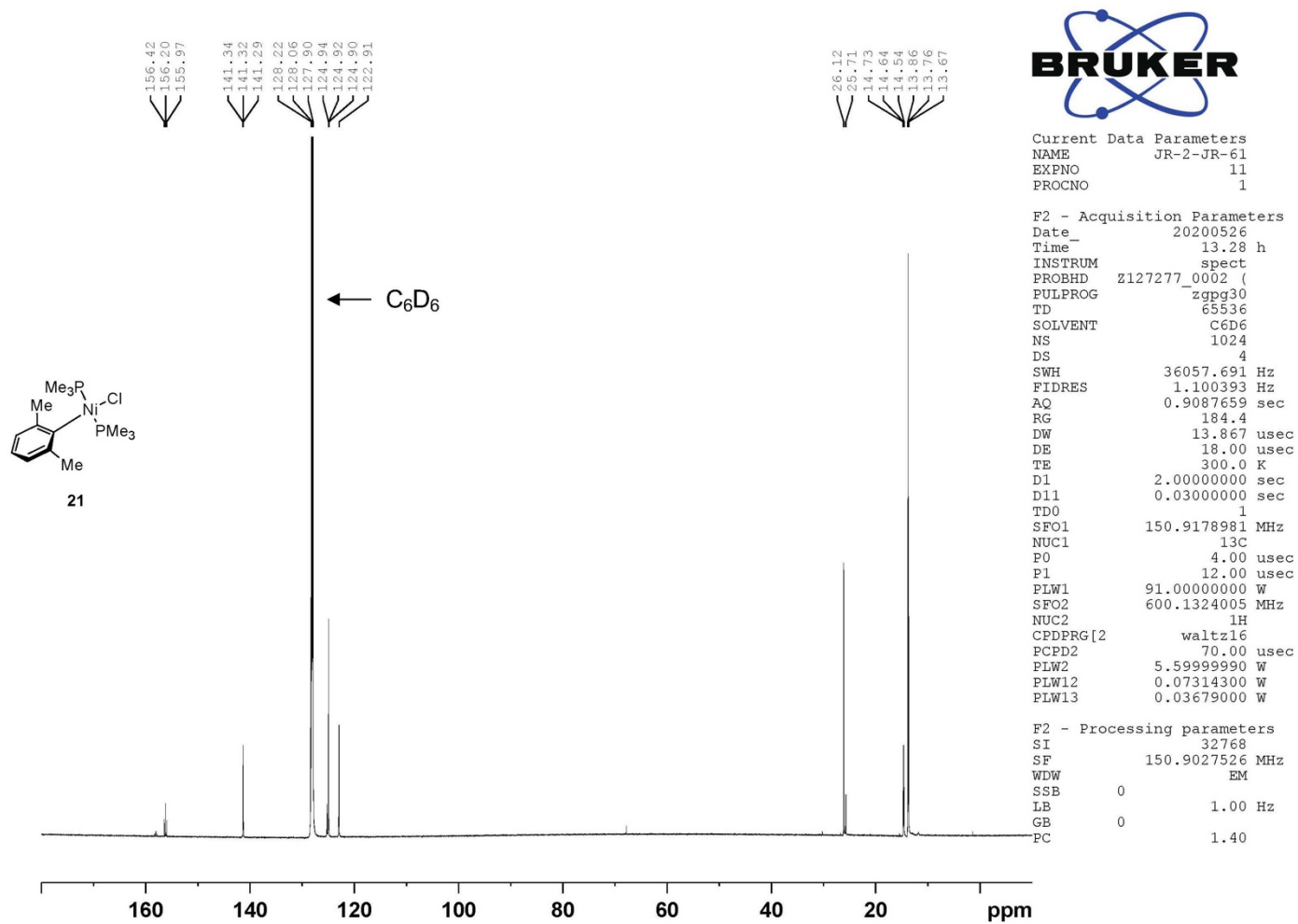
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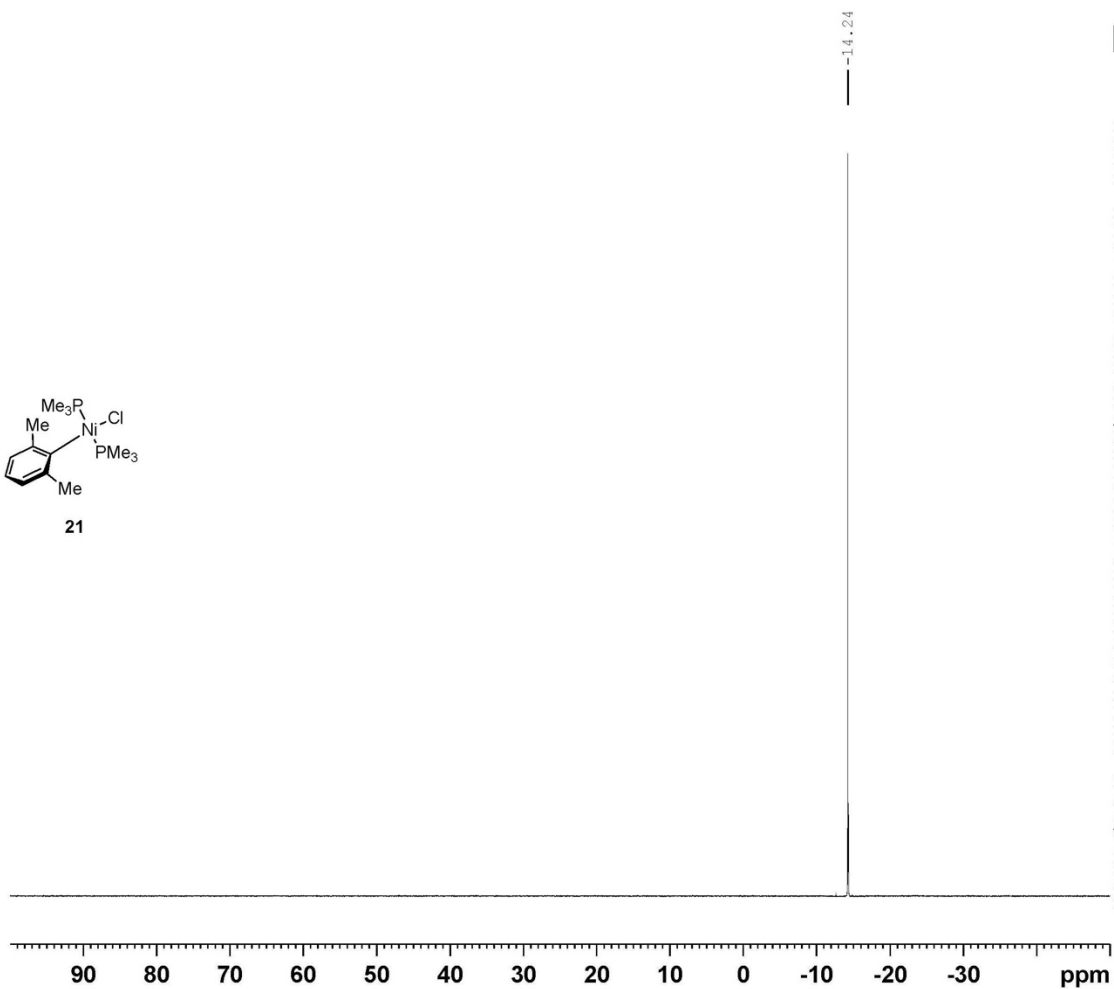
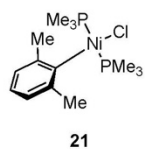
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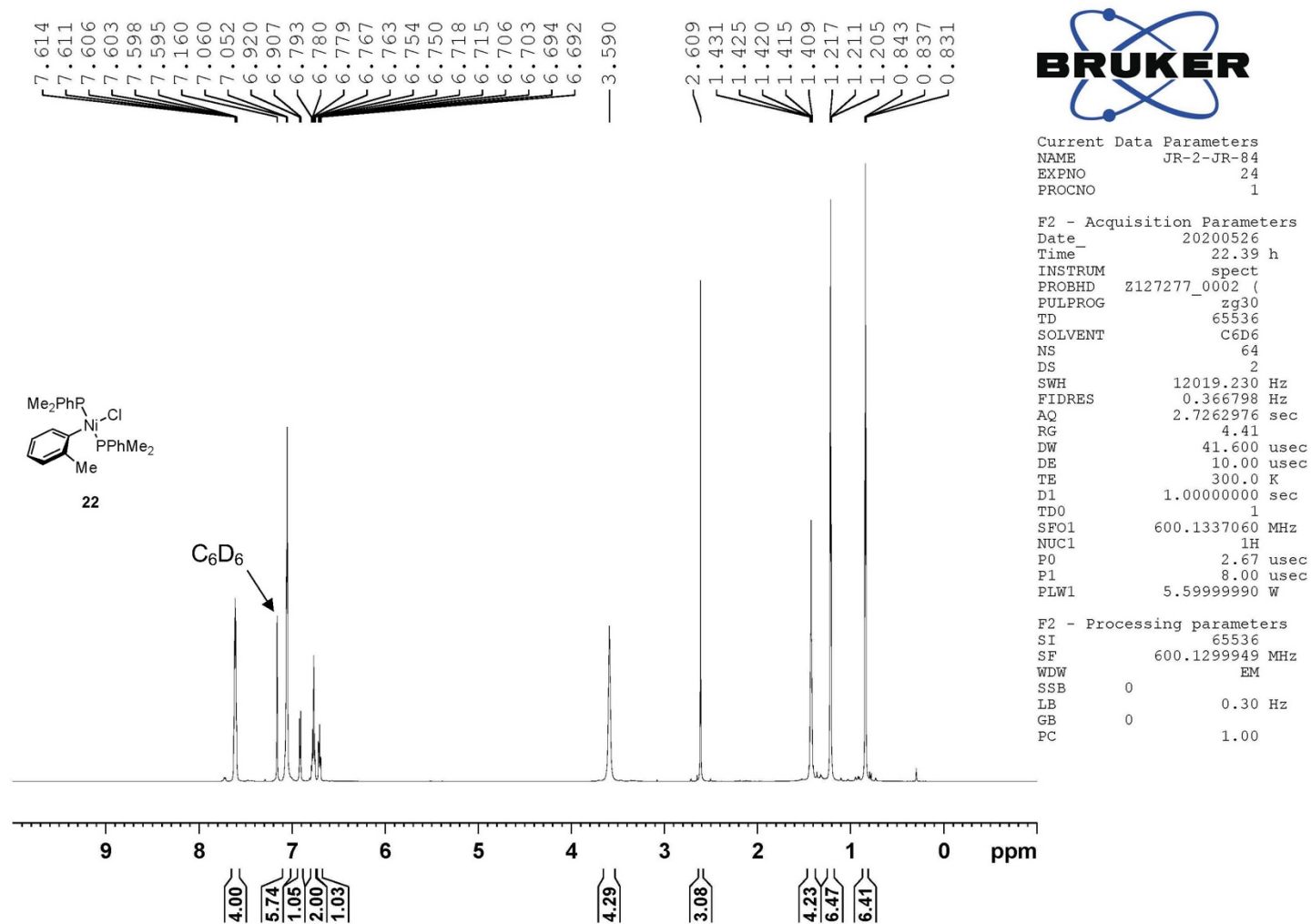


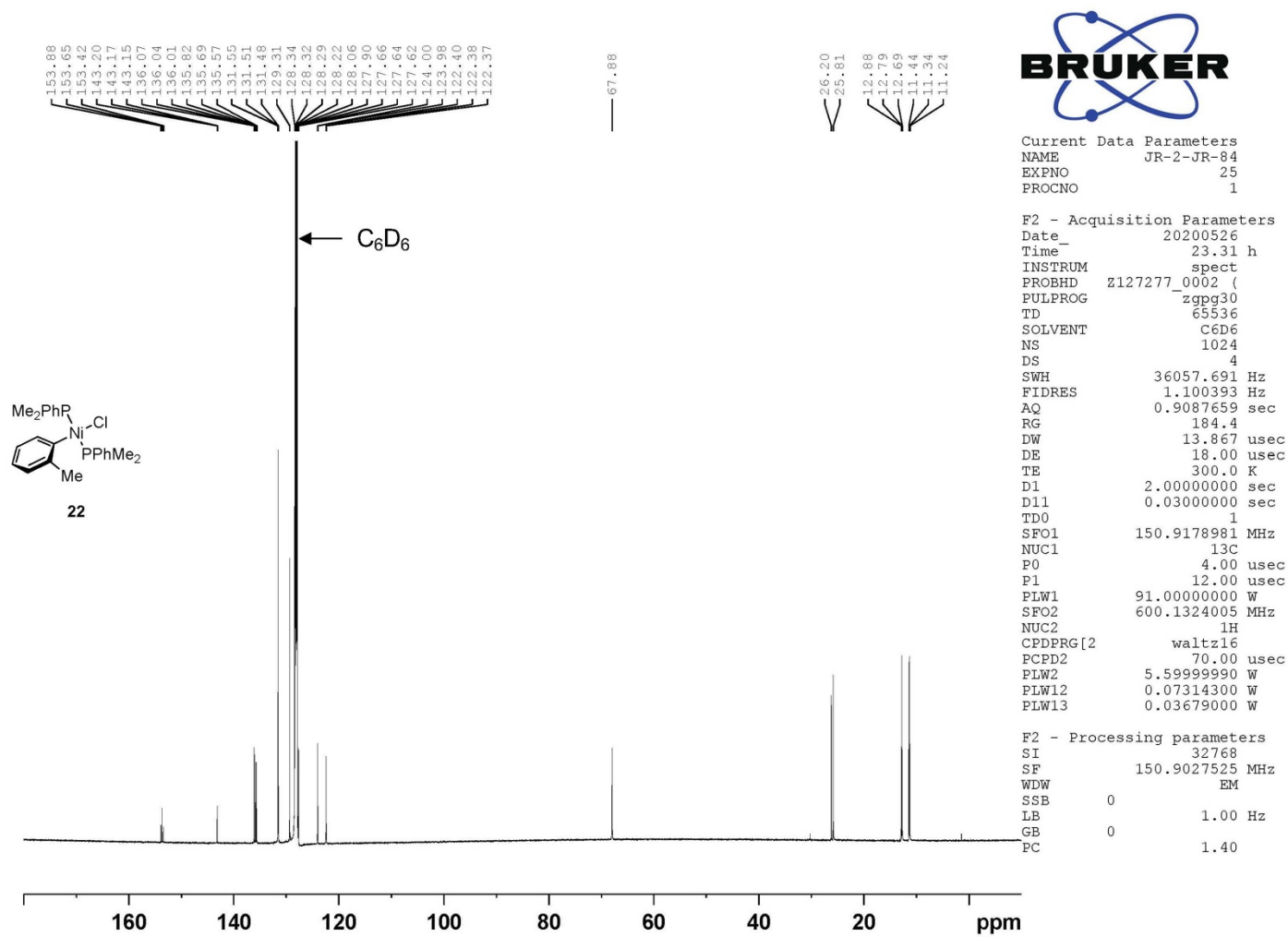


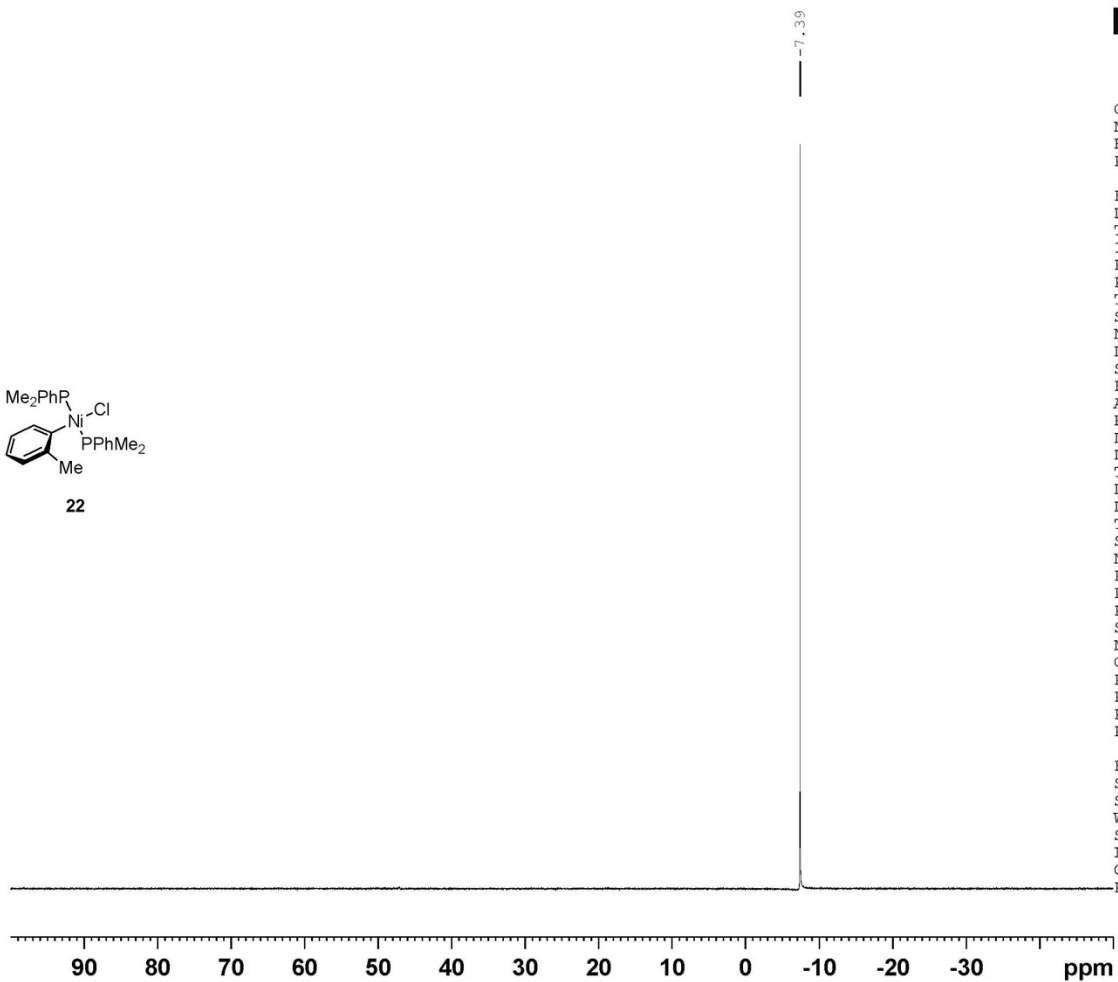
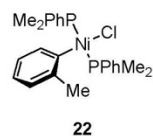
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 Time 17.36 h
 INSTRUM spect
 PROBHD Z125869_0055 (
 PULPROG zgpg30
 TD 65536
 SOLVENT C6D6
 NS 16
 DS 4
 SWH 81521.742 Hz
 FIDRES 2.487846 Hz
 AQ 0.4019541 sec
 RG 190.44
 DW 6.133 usec
 DE 18.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1
 SFO1 202.4866909 MHz
 NUC1 31P
 P0 4.00 usec
 P1 12.00 usec
 PLW1 40.26200104 W
 SFO2 500.2320009 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 11.44699955 W
 PLW12 0.25756001 W
 PLW13 0.12955000 W

F2 - Processing parameters
 SI 32768
 SF 202.4968157 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40







S106

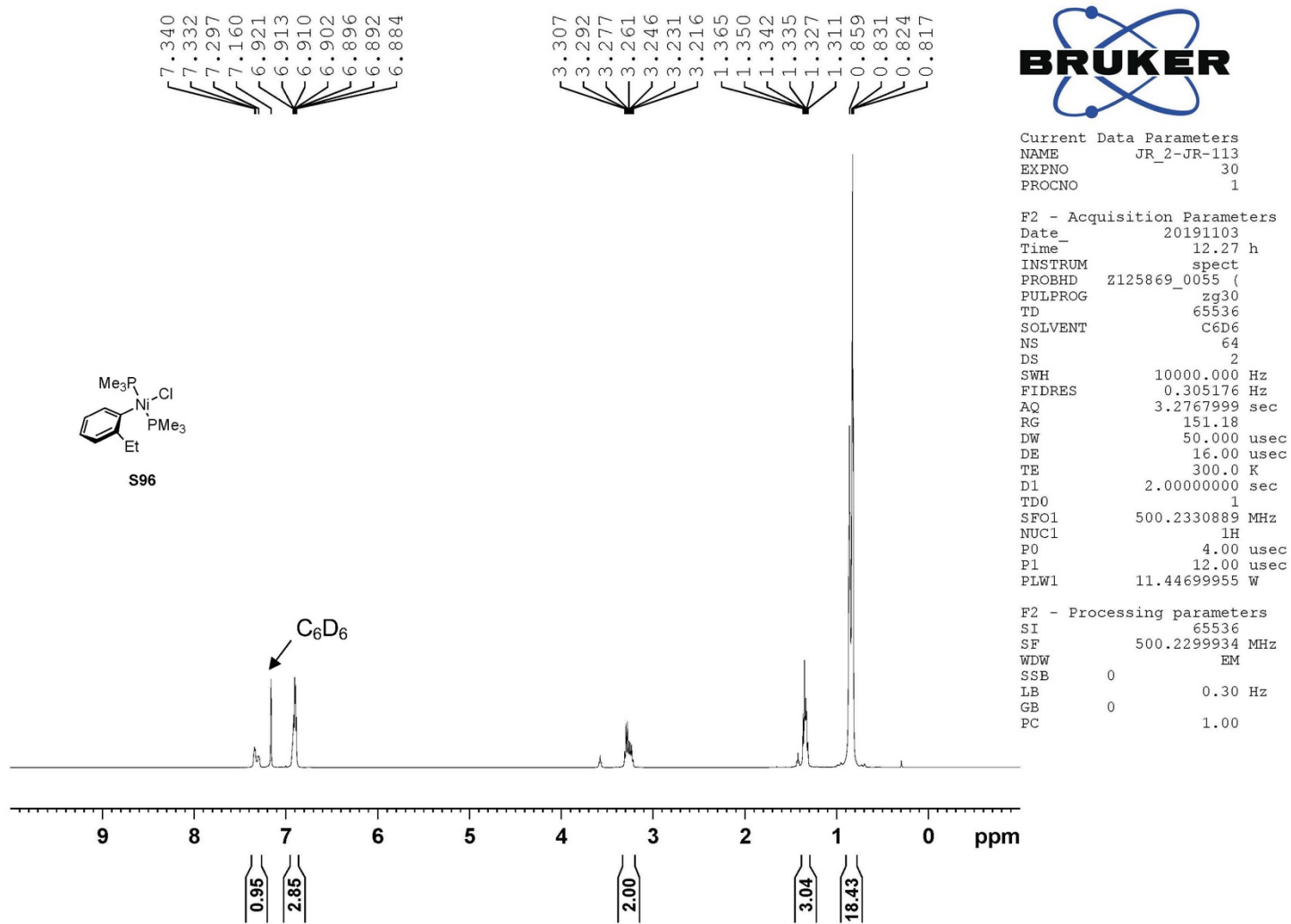


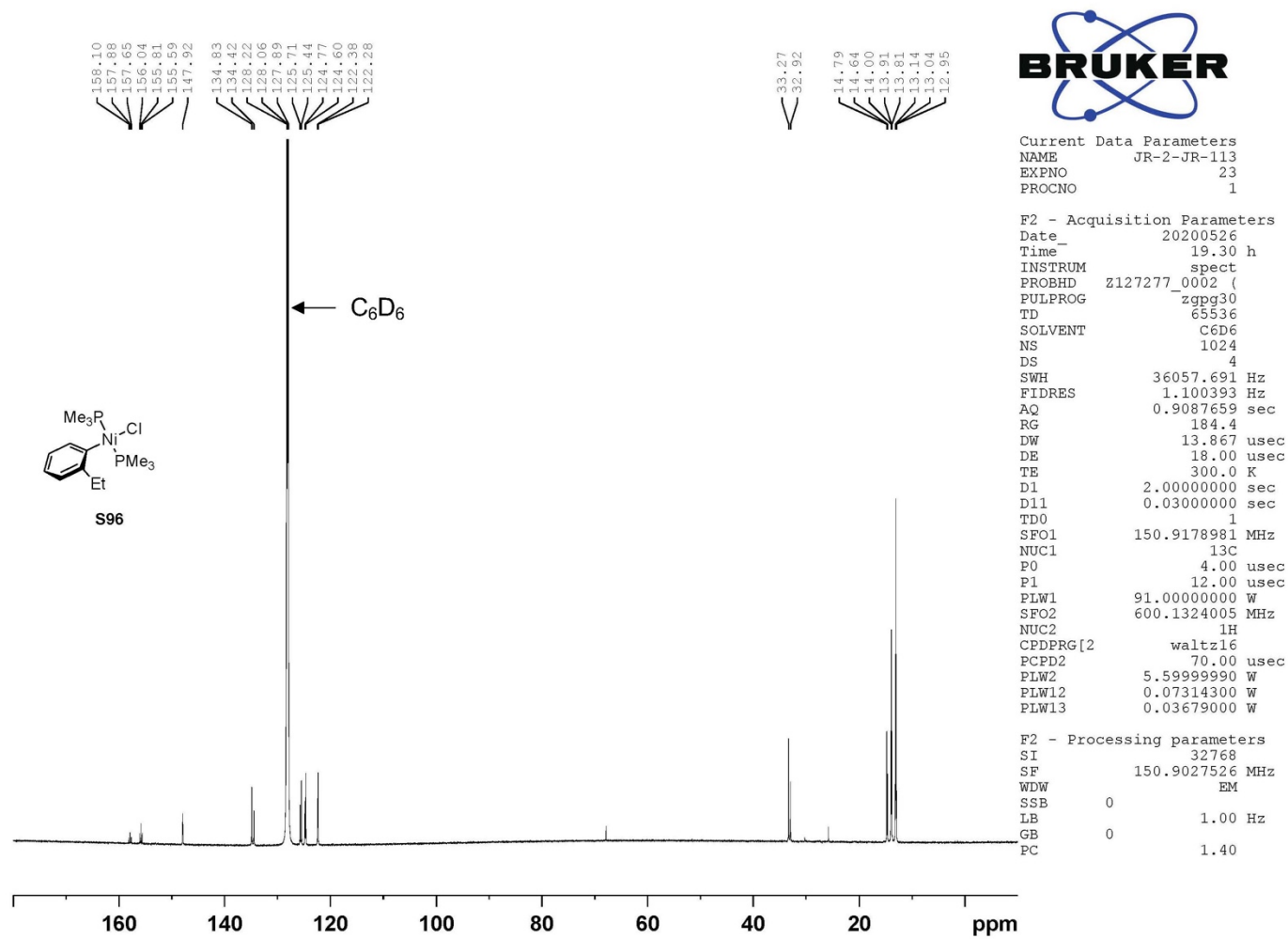
Current Data Parameters
 NAME JR_2-JR-84
 EXPNO 21
 PROCNO 1

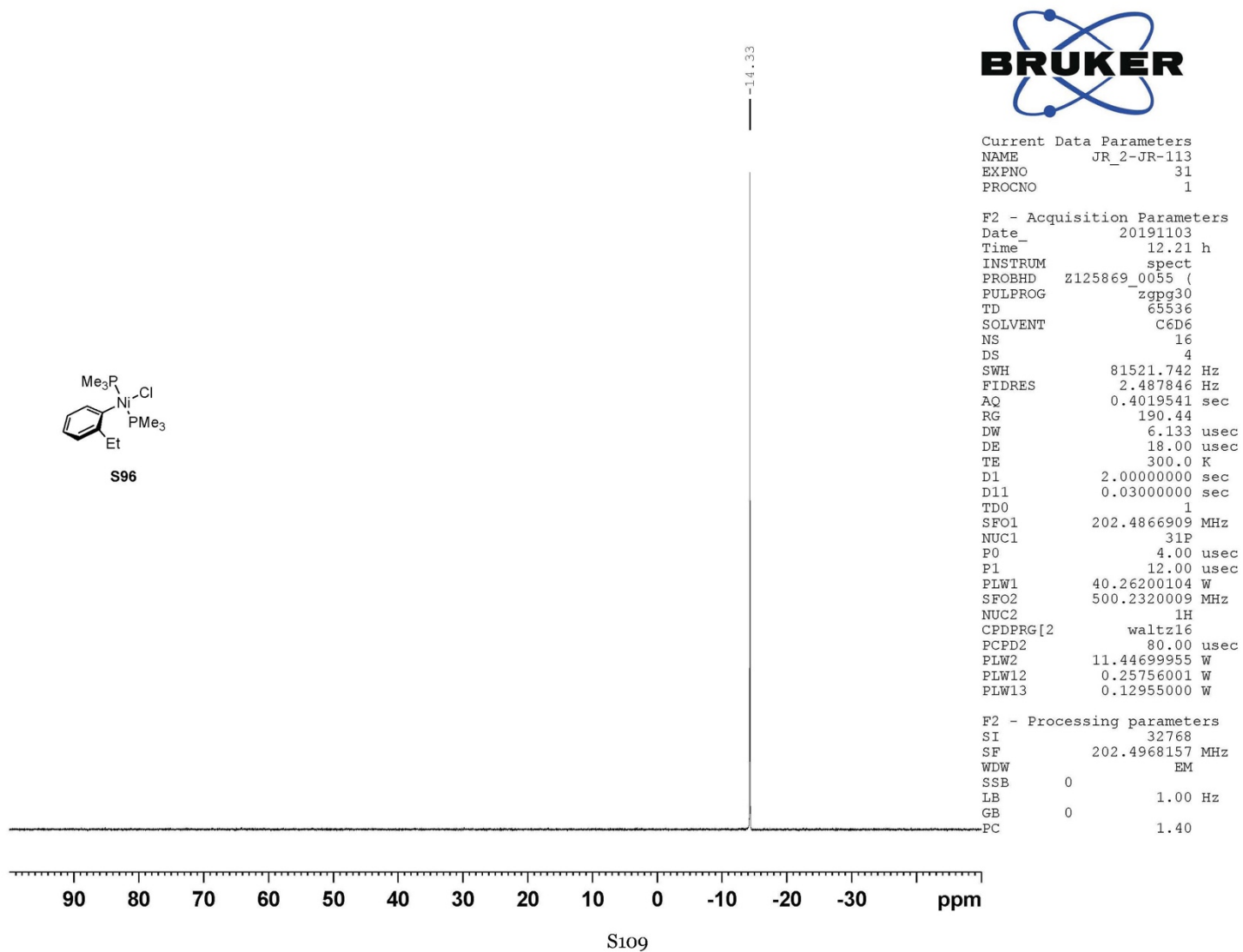
F2 - Acquisition Parameters
 Date_ 20191106
 Time 17.48 h
 INSTRUM spect
 PROBHD Z125869_0055 (
 PULPROG zgpg30
 TD 65536
 SOLVENT C6D6
 NS 16
 DS 4
 SWH 81521.742 Hz
 FIDRES 2.487846 Hz
 AQ 0.4019541 sec
 RG 190.44
 DW 6.133 usec
 DE 18.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1
 SFO1 202.4866909 MHz
 NUC1 31P
 P0 4.00 usec
 P1 12.00 usec
 PLW1 40.26200104 W
 SFO2 500.2320009 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 11.44699955 W
 PLW12 0.25756001 W
 PLW13 0.12955000 W

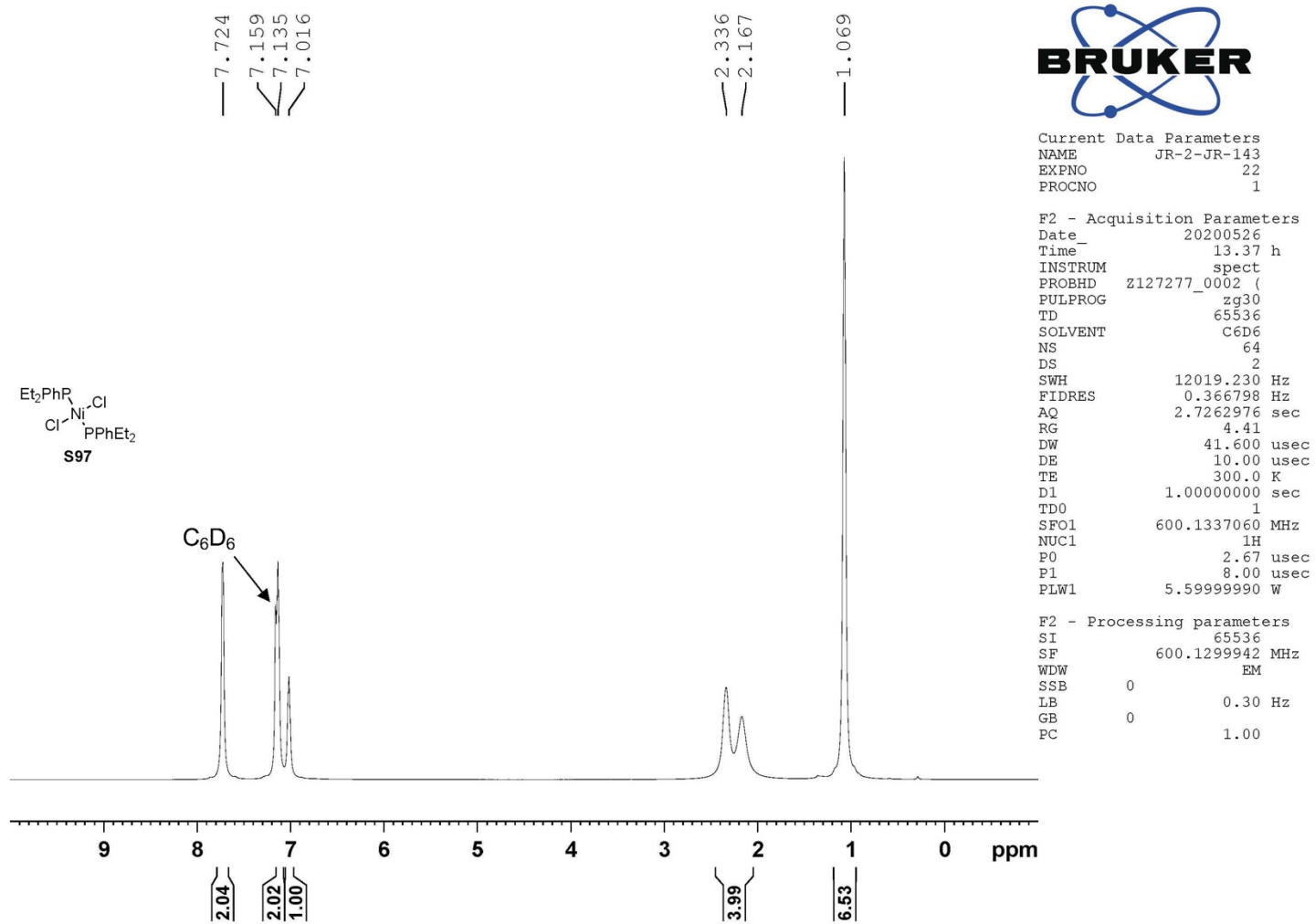
F2 - Processing parameters
 SI 32768
 SF 202.4968157 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

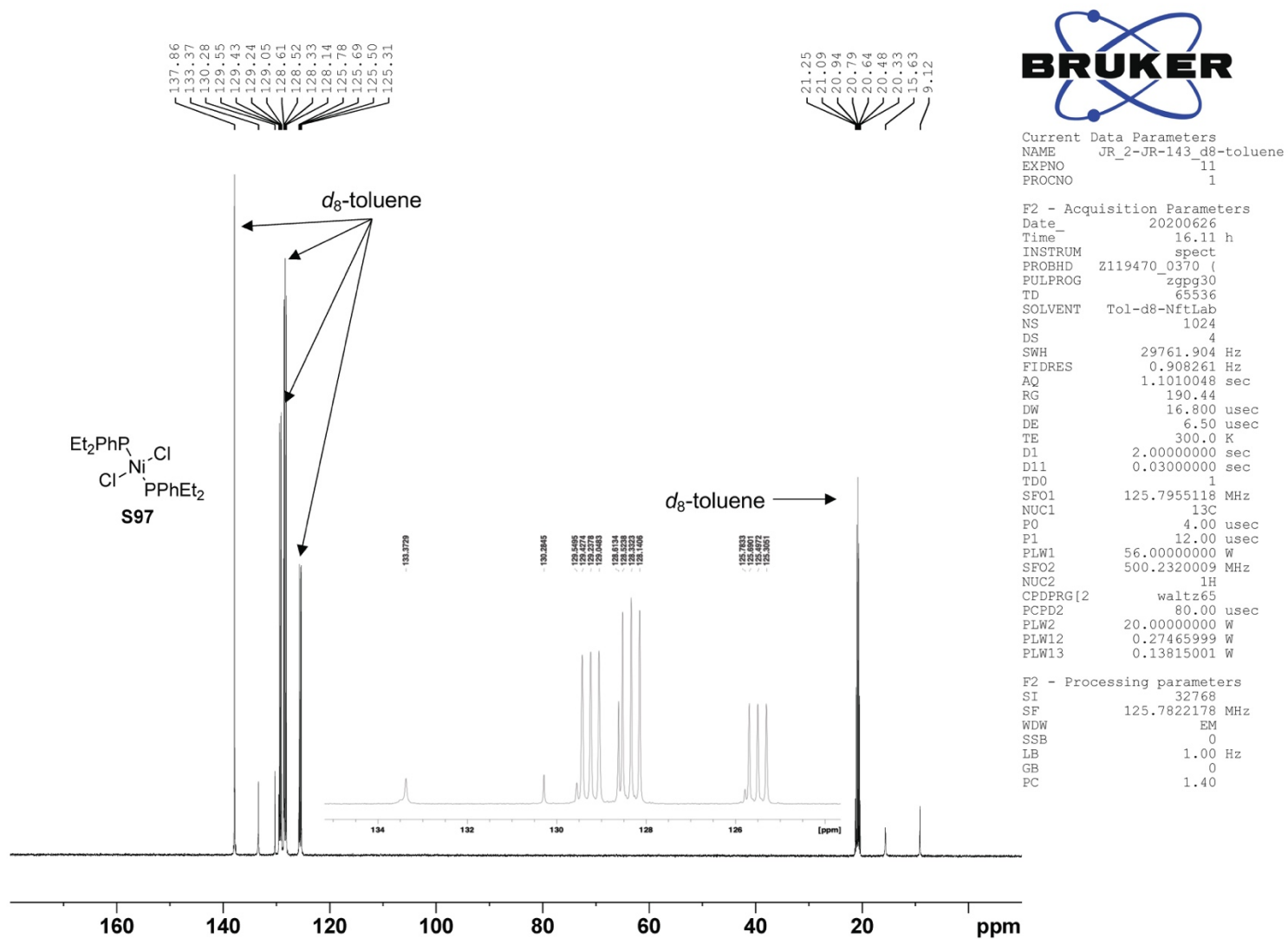
300

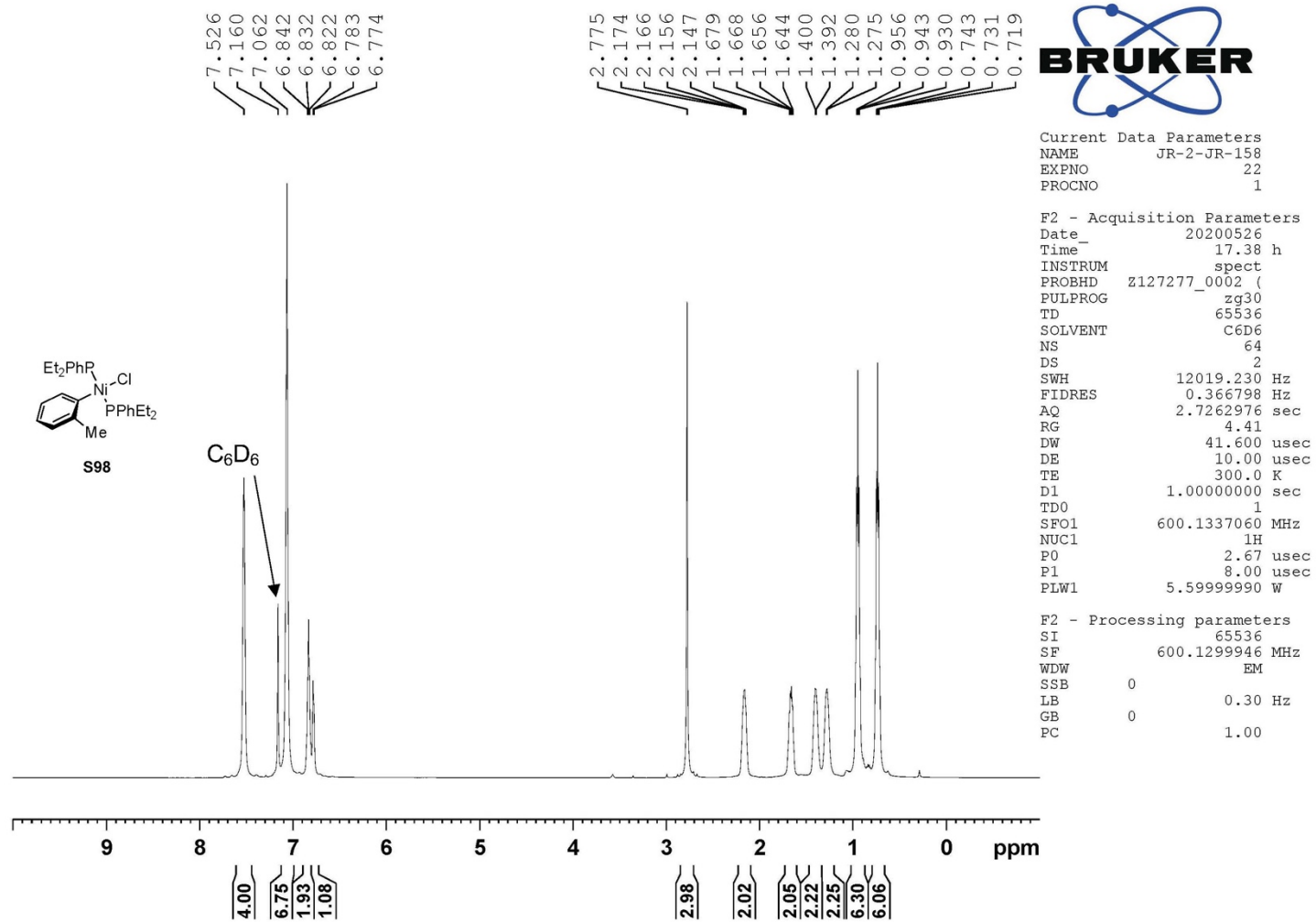


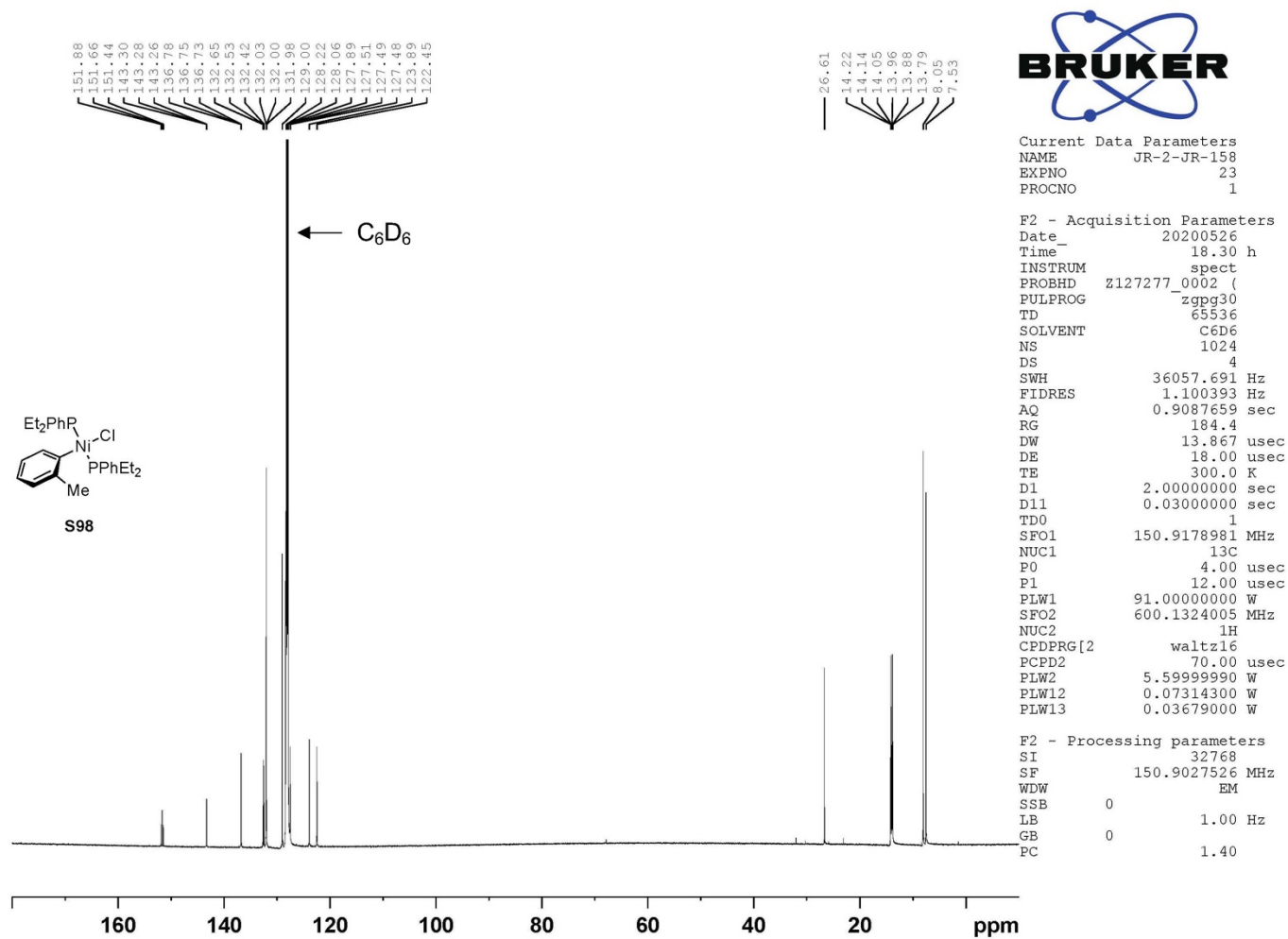


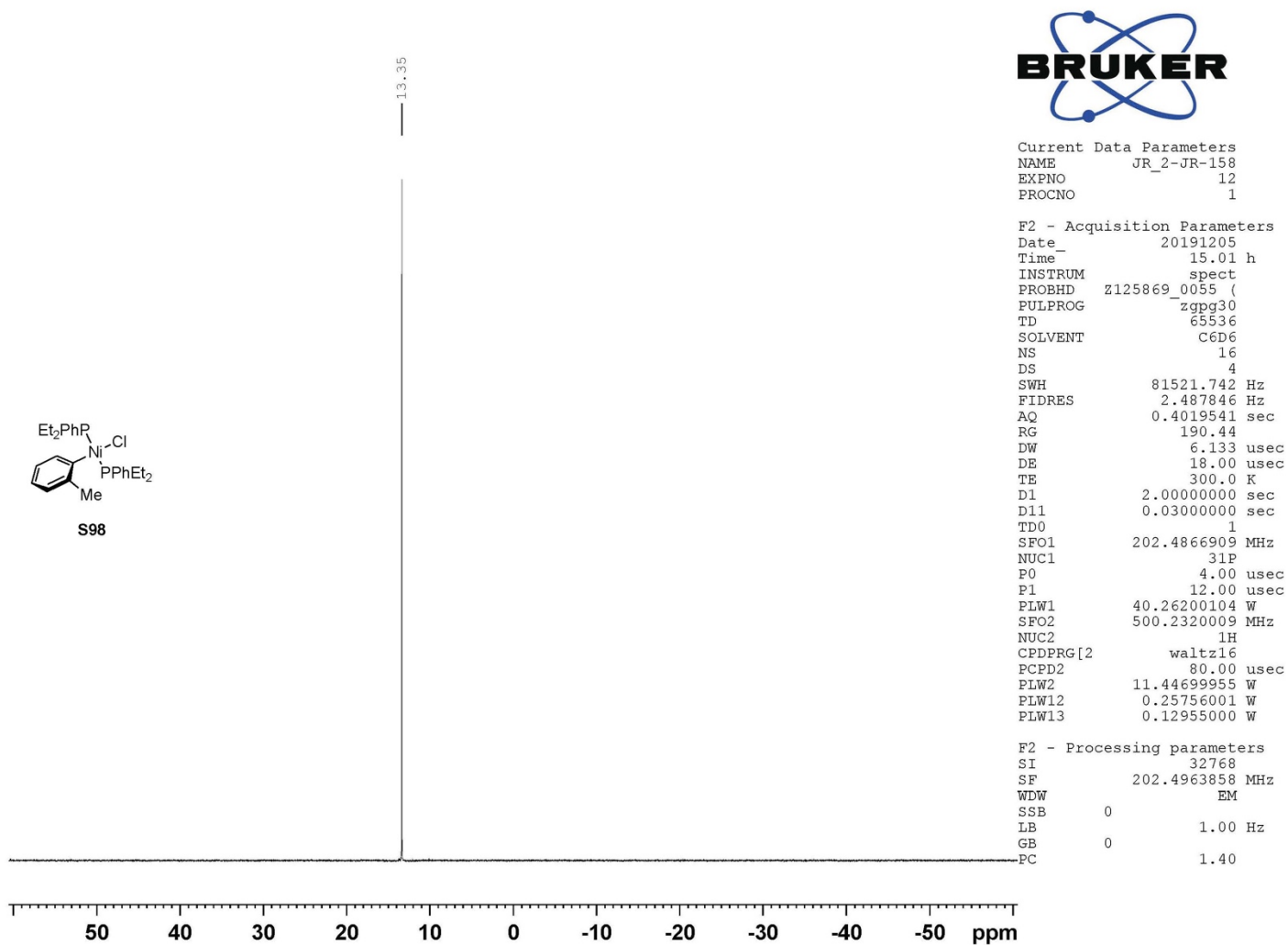


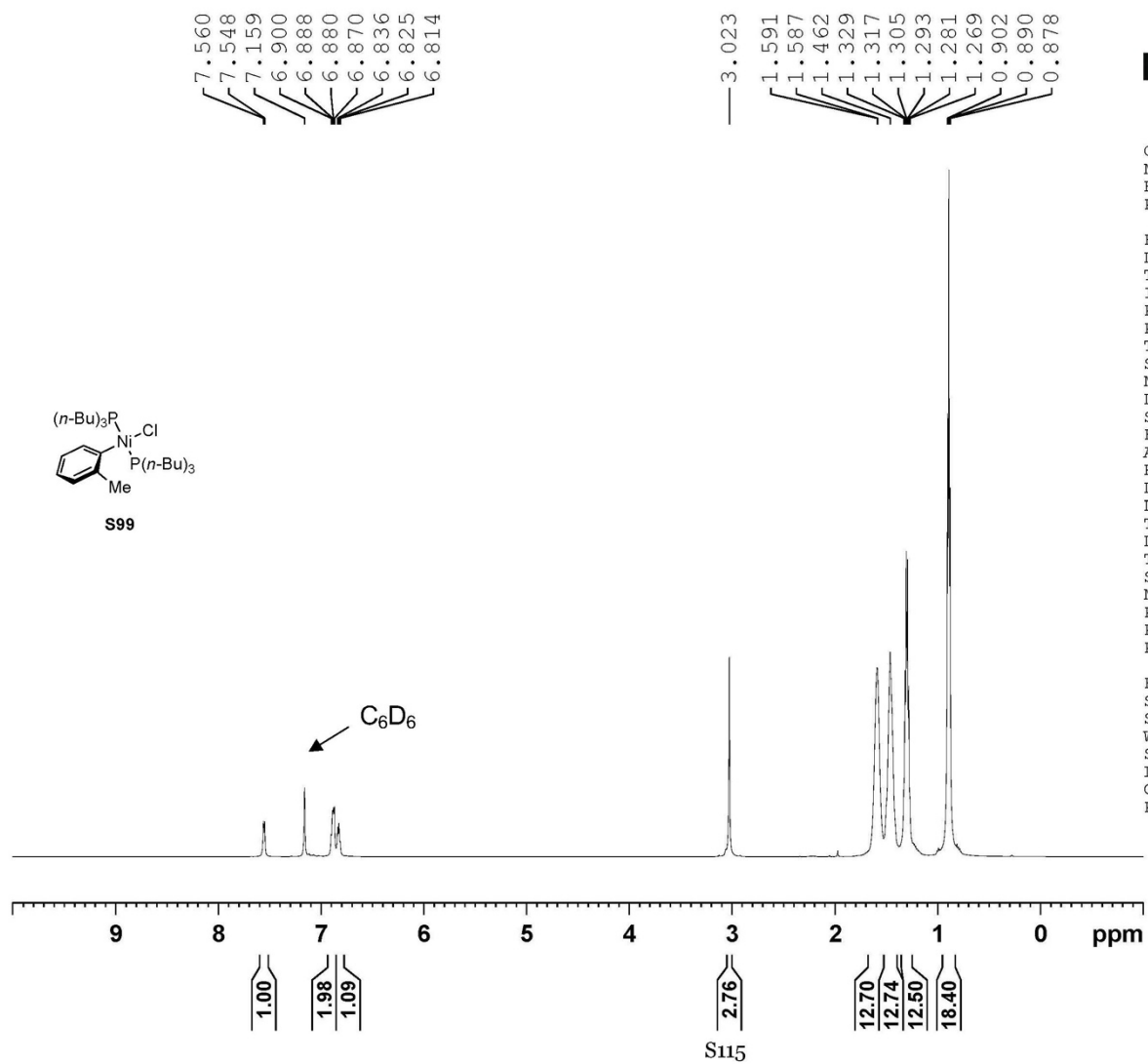








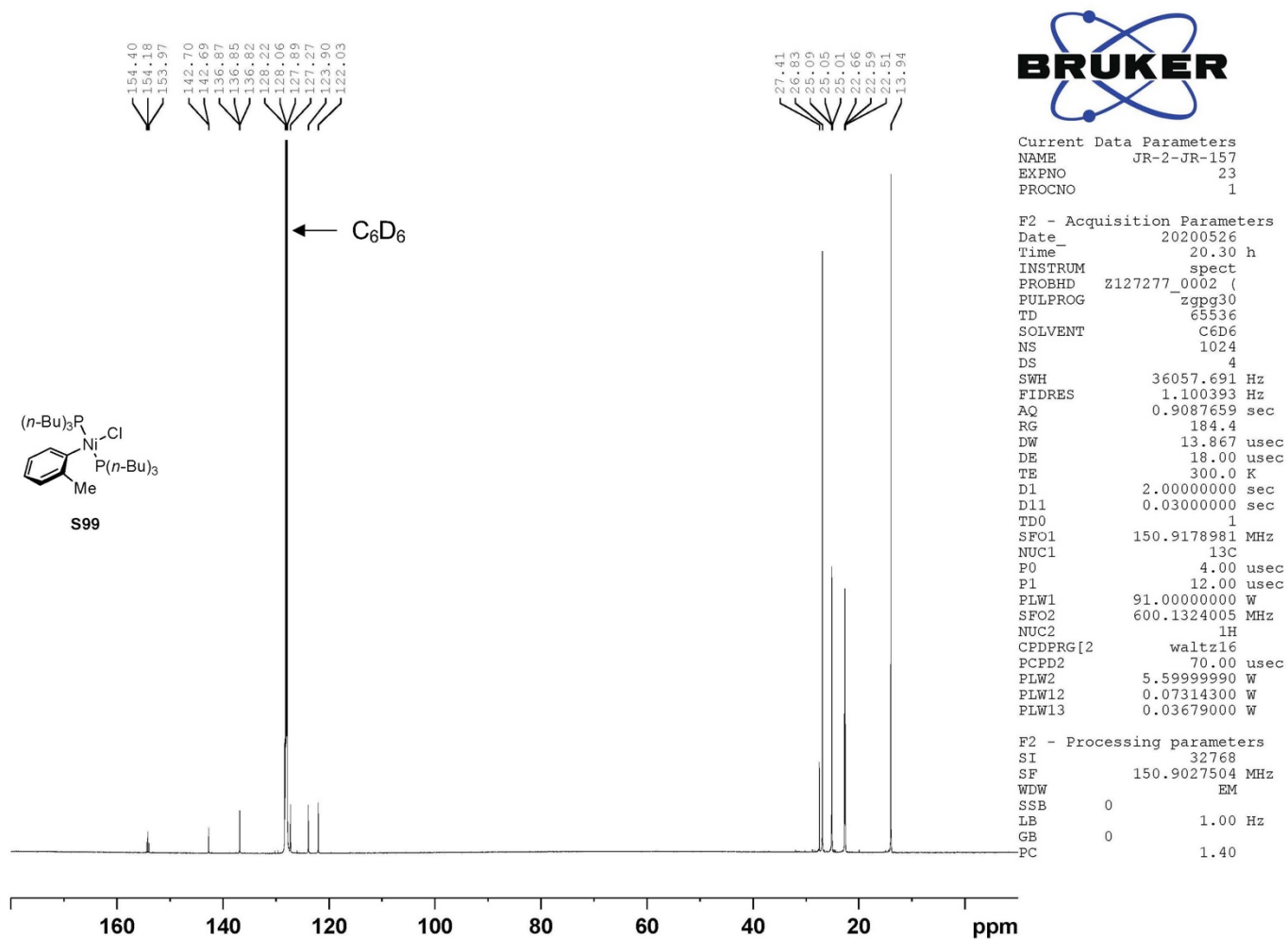


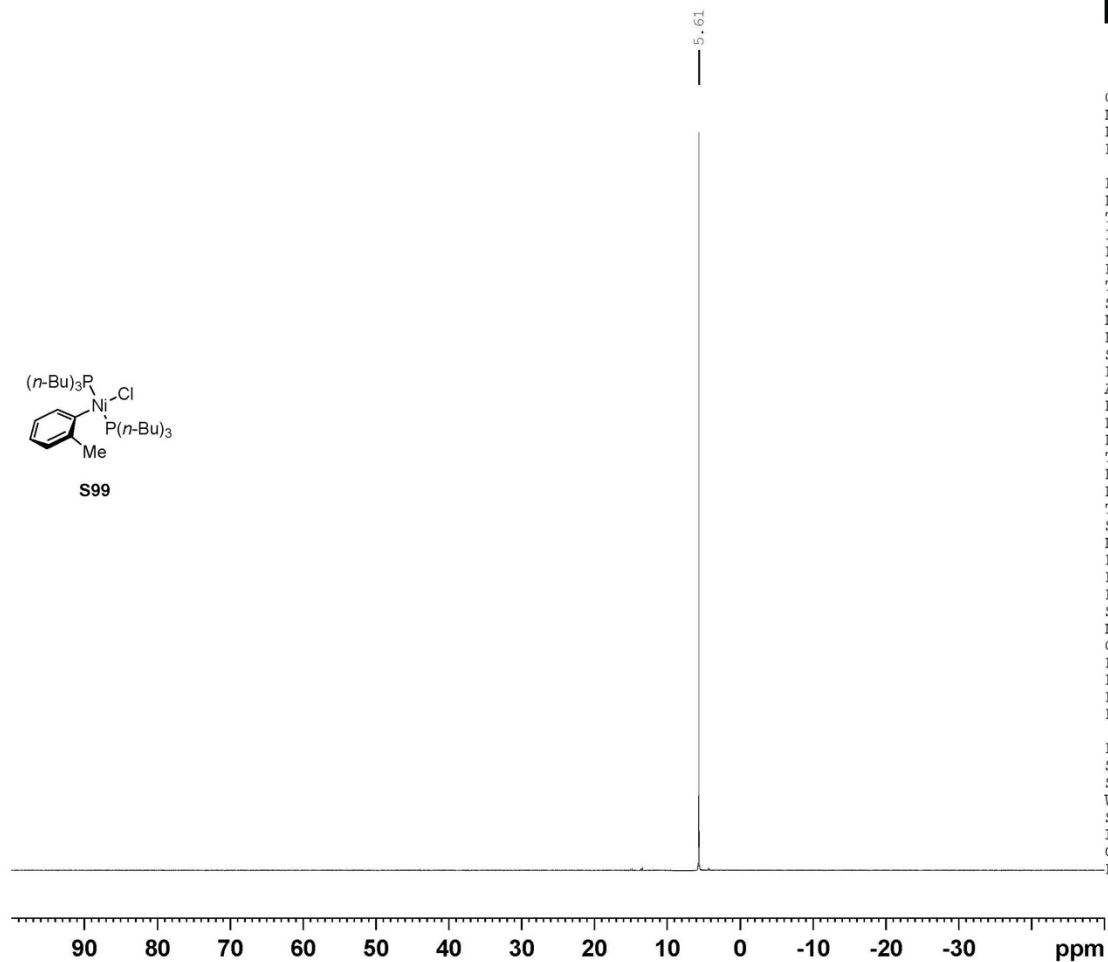
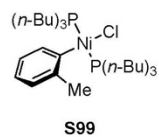


Current Data Parameters
 NAME JR-2-JR-157
 EXPNO 22
 PROCNO 1

F2 - Acquisition Parameters
 Date 20200526
 Time 19.38 h
 INSTRUM spect
 PROBHD Z127277_0002 (
 PULPROG zg30
 TD 65536
 SOLVENT C6D6
 NS 64
 DS 2
 SWH 12019.230 Hz
 FIDRES 0.366798 Hz
 AQ 2.7262976 sec
 RG 4.41
 DW 41.600 usec
 DE 10.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1
 SFO1 600.1337060 MHz
 NUC1 1H
 P0 2.67 usec
 P1 8.00 usec
 PLW1 5.59999990 W

F2 - Processing parameters
 SI 65536
 SF 600.1299950 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

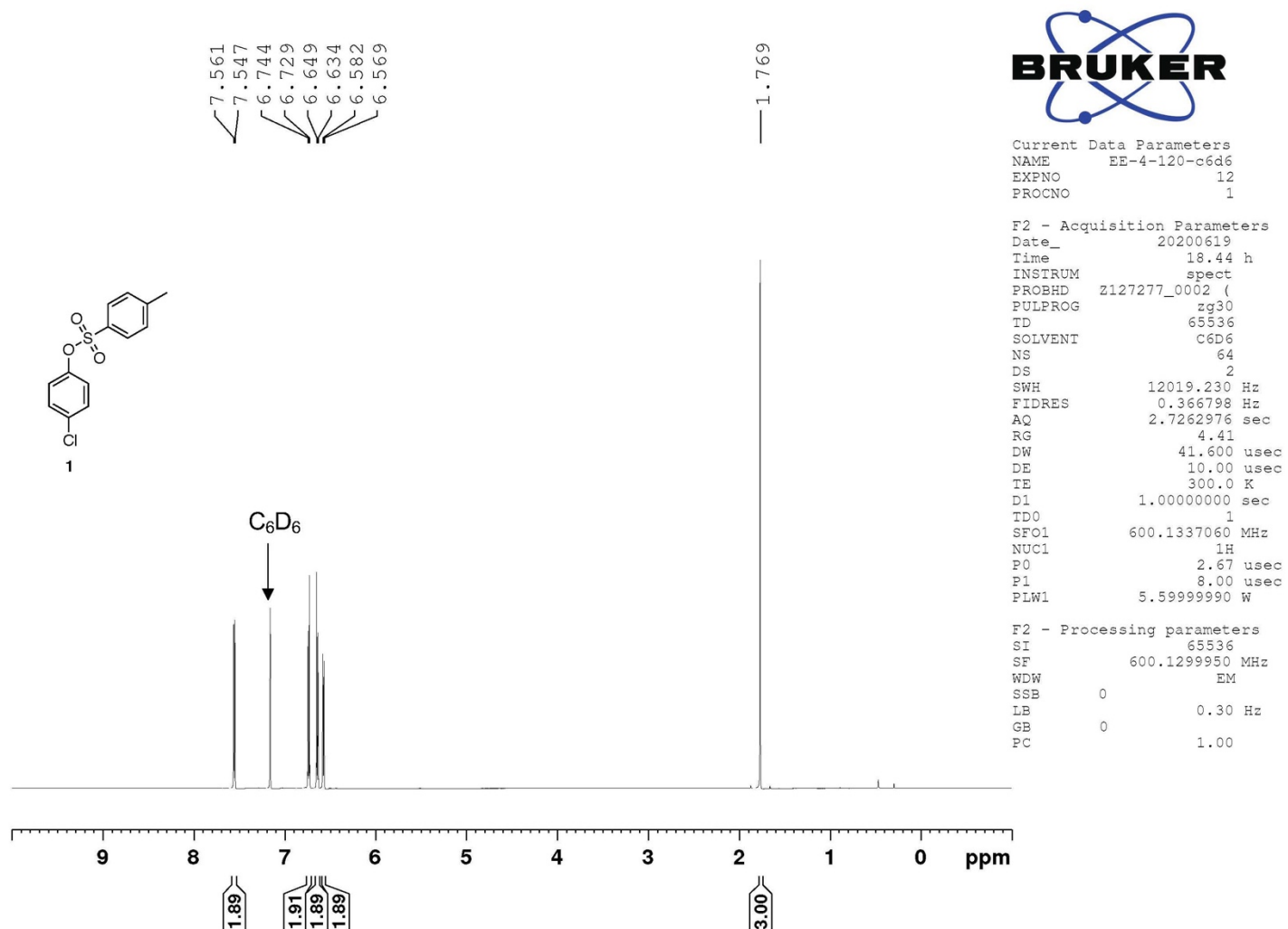


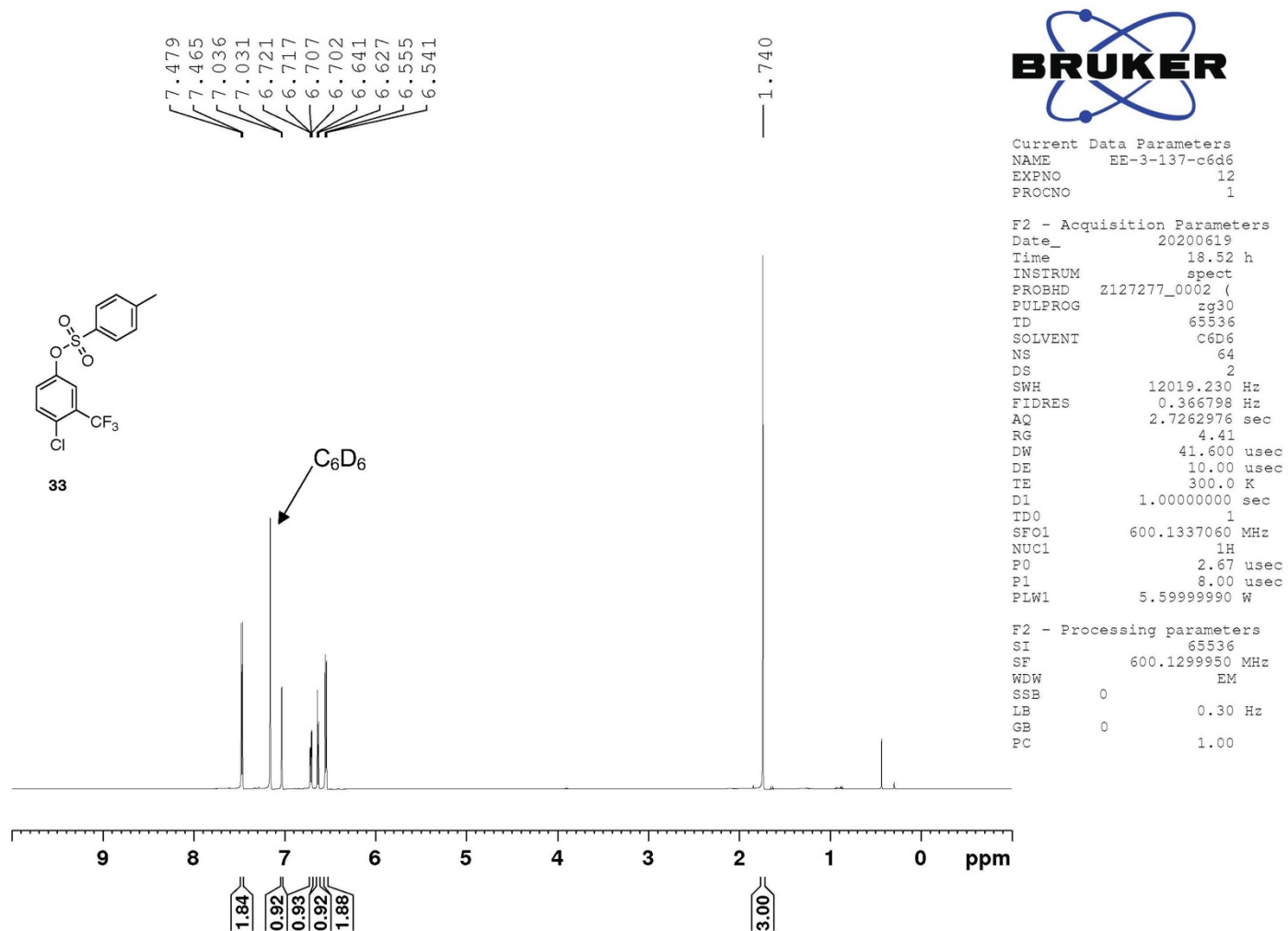


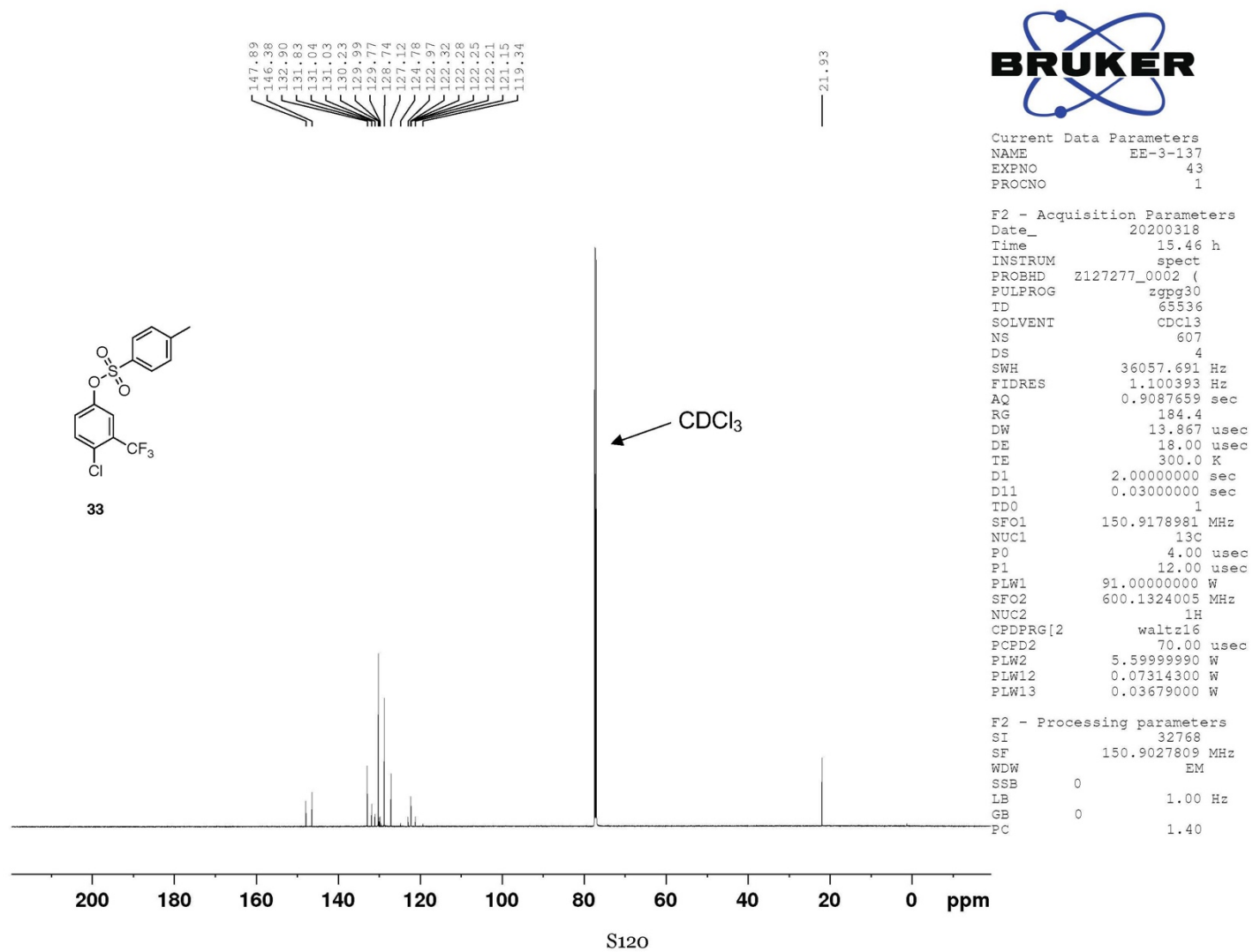
Current Data Parameters
 NAME JR_2-JR-157
 EXPNO 12
 PROCNO 1

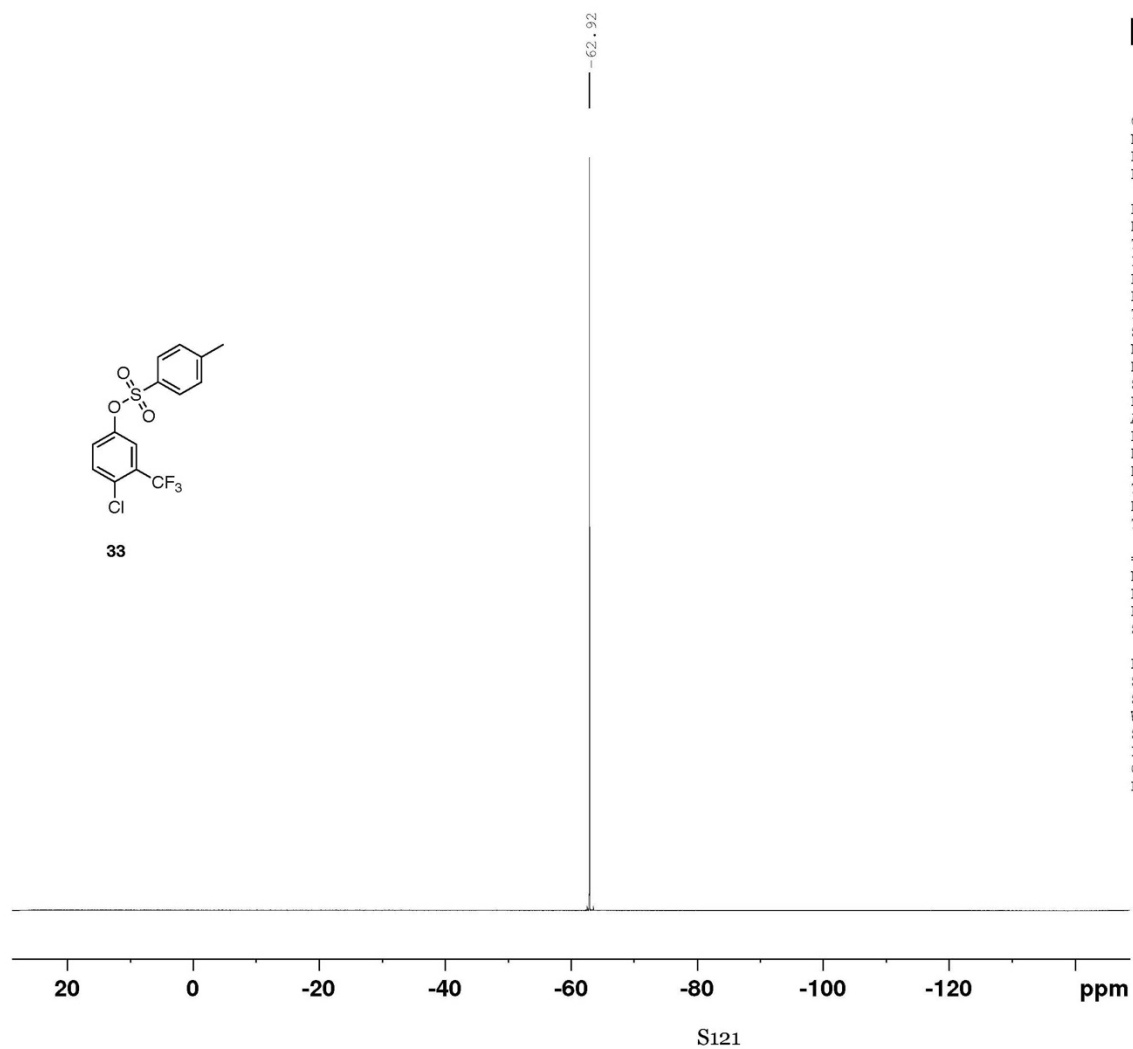
F2 - Acquisition Parameters
 Date_ 20191205
 Time_ 13.53 h
 INSTRUM spect
 PROBHD Z125869 0055 (
 PULPROG zgpg30
 TD 65536
 SOLVENT C6D6
 NS 16
 DS 4
 SWH 81521.742 Hz
 FIDRES 2.487846 Hz
 AQ 0.4019541 sec
 RG 190.44
 DW 6.133 usec
 DE 18.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1
 SFO1 202.4866909 MHz
 NUC1 31P
 P0 4.00 usec
 P1 12.00 usec
 PLW1 40.26200104 W
 SFO2 500.2320009 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 11.44699955 W
 PLW12 0.25756001 W
 PLW13 0.12955000 W

F2 - Processing parameters
 SI 32768
 SF 202.4964281 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40







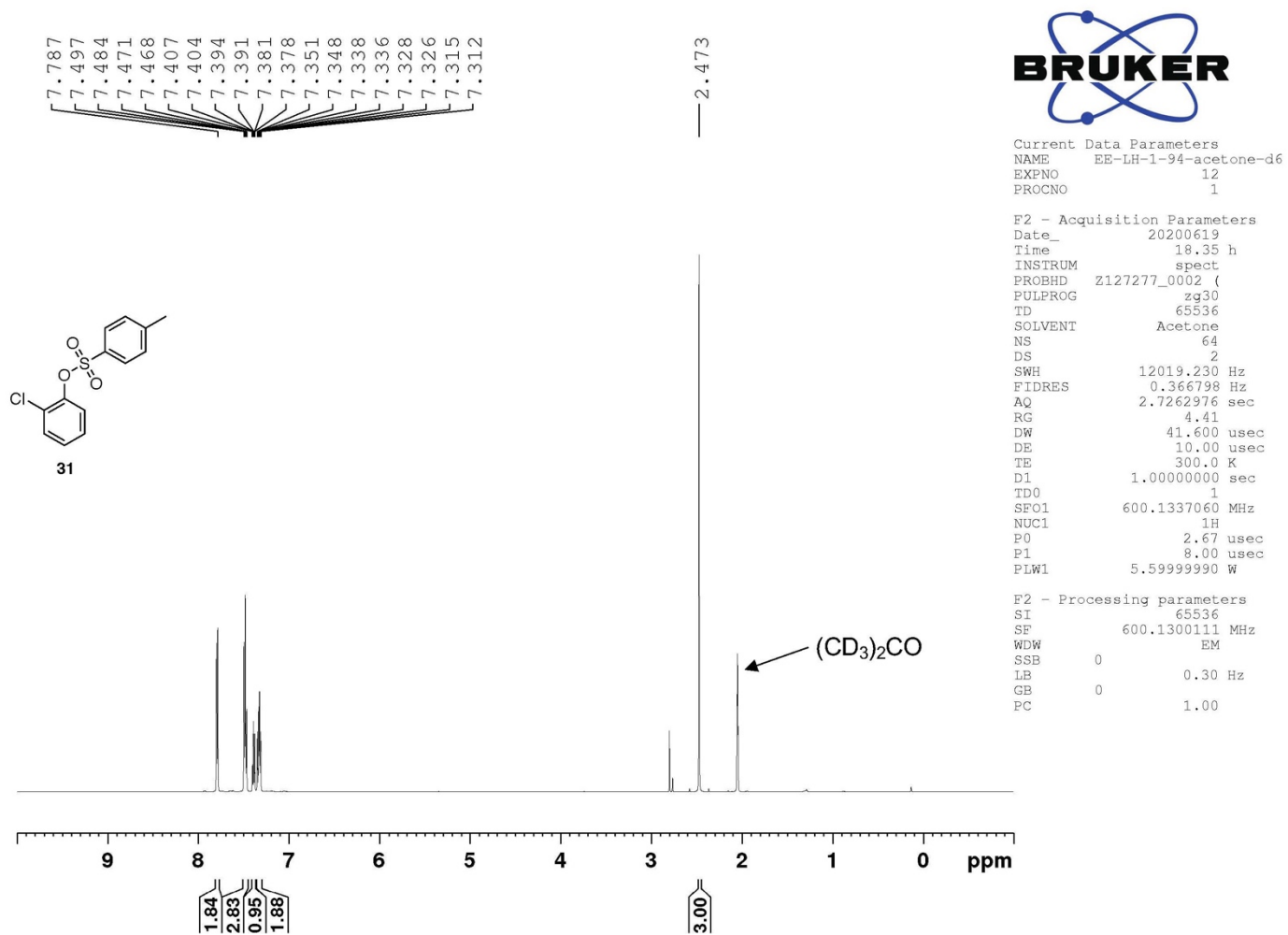


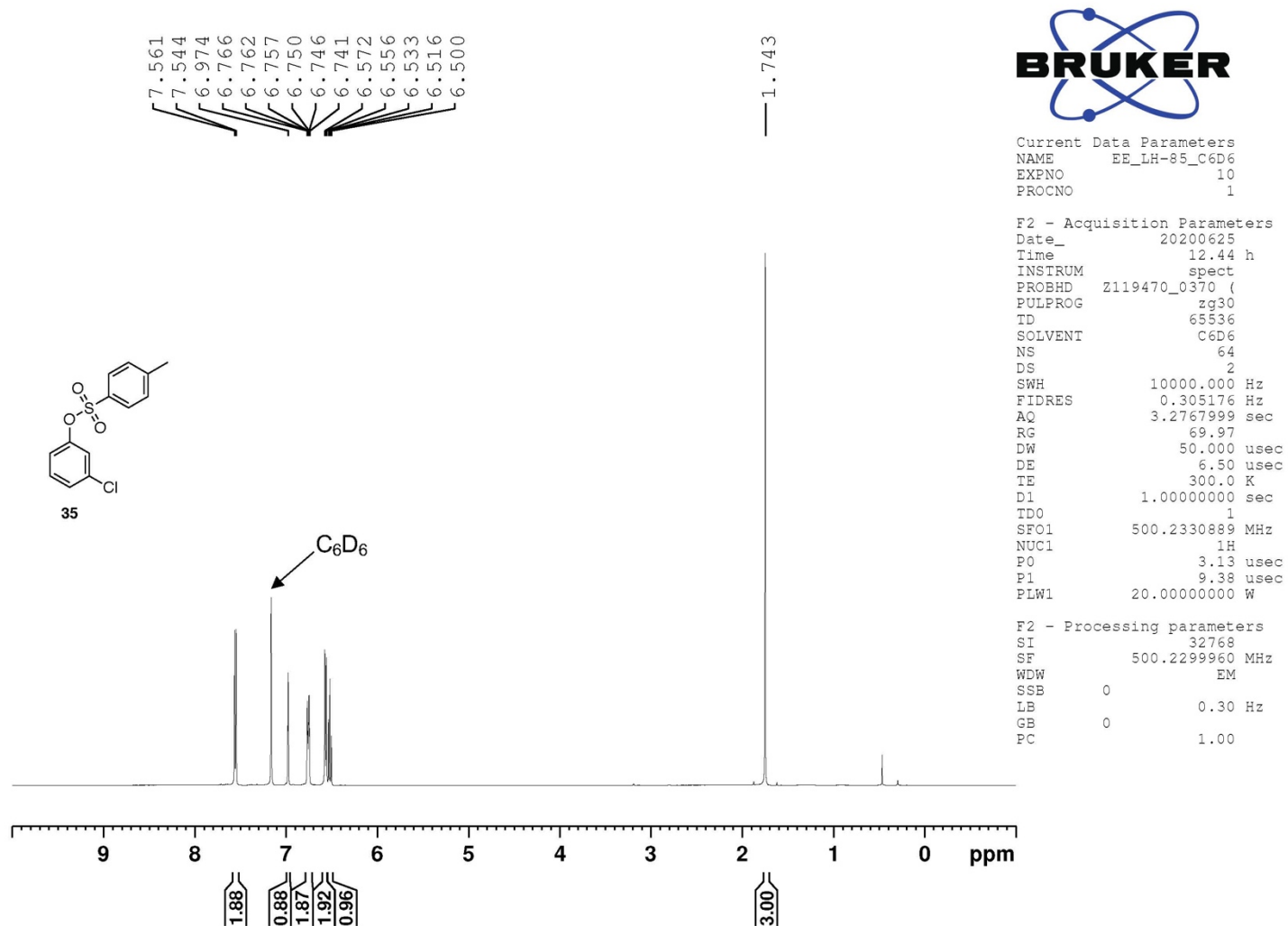
Current Data Parameters
NAME EE-3-137_19F
EXPNO 2
PROCNO 2

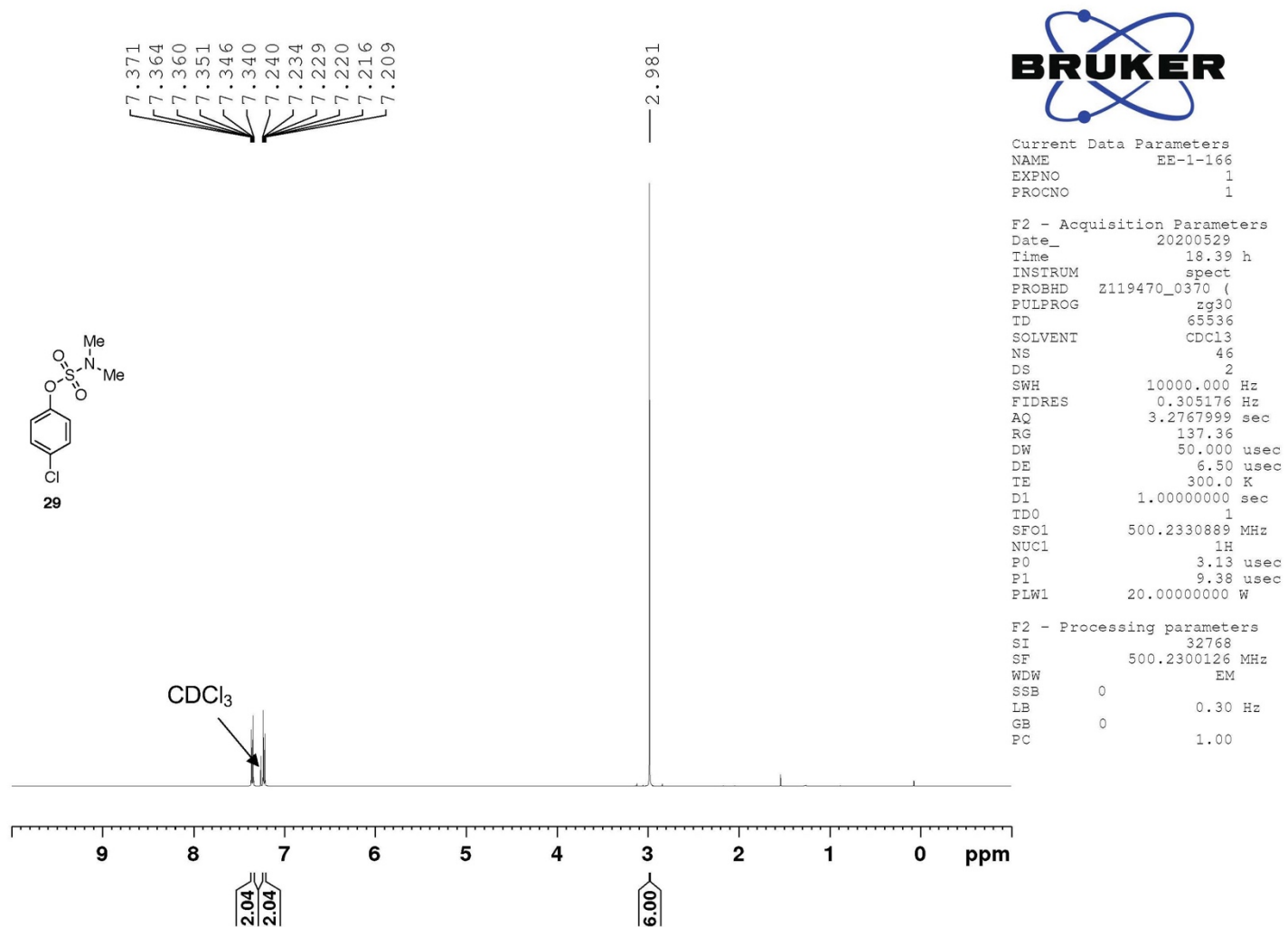
F2 - Acquisition Parameters
Date_ 20200619
Time 11.51
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgfglqn
TD 32768
SOLVENT C6D6
NS 128
DS 0
SWH 50125.313 Hz
FIDRES 1.529703 Hz
AQ 0.3268608 sec
RG 1448.2
DW 9.975 usec
DE 6.00 usec
TE 683.2 K
D1 1.50000000 sec
TD0 1

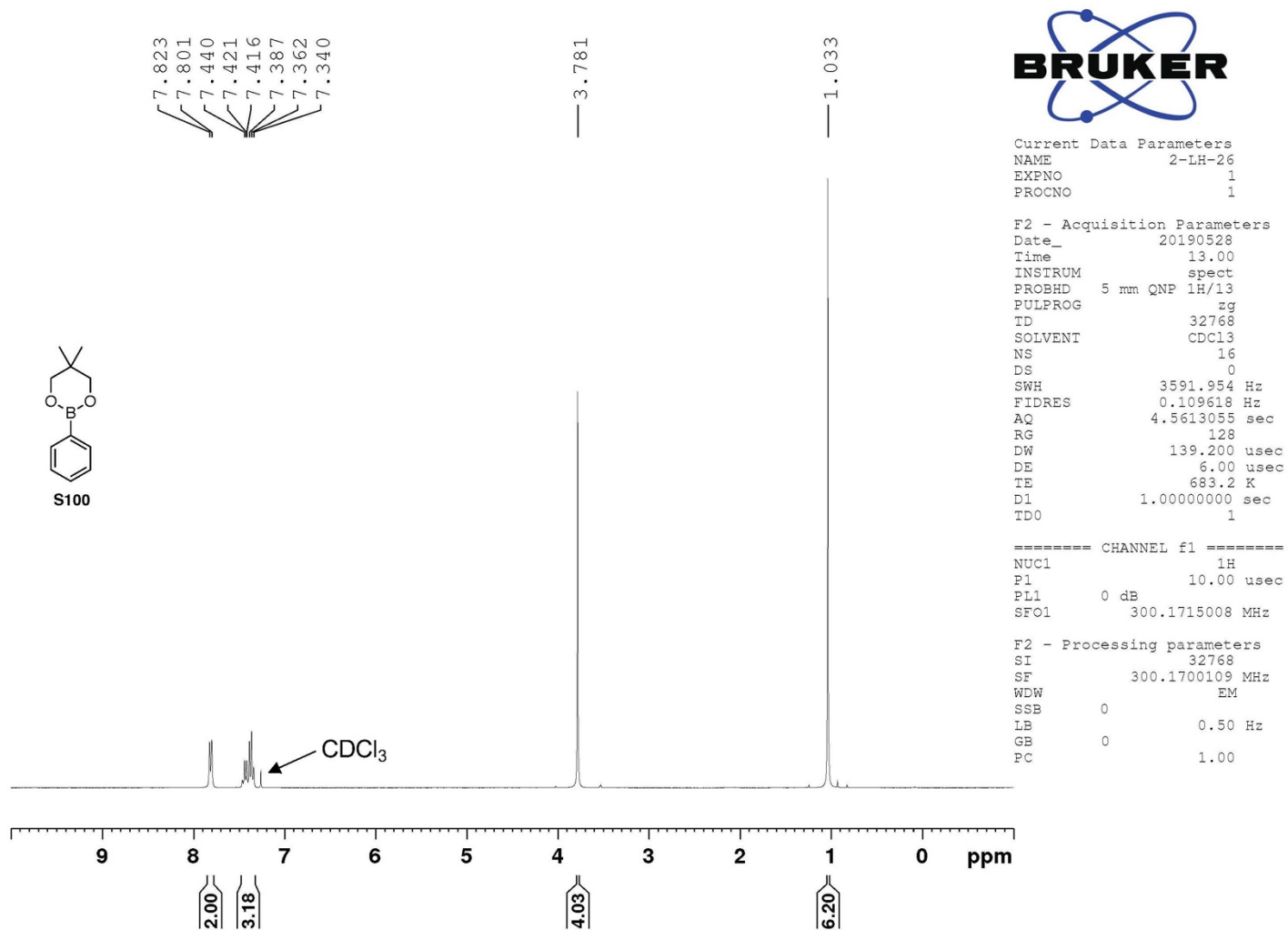
===== CHANNEL f1 =====
NUC1 19F
P1 9.00 usec
PL1 0 dB
SFO1 282.4250465 MHz

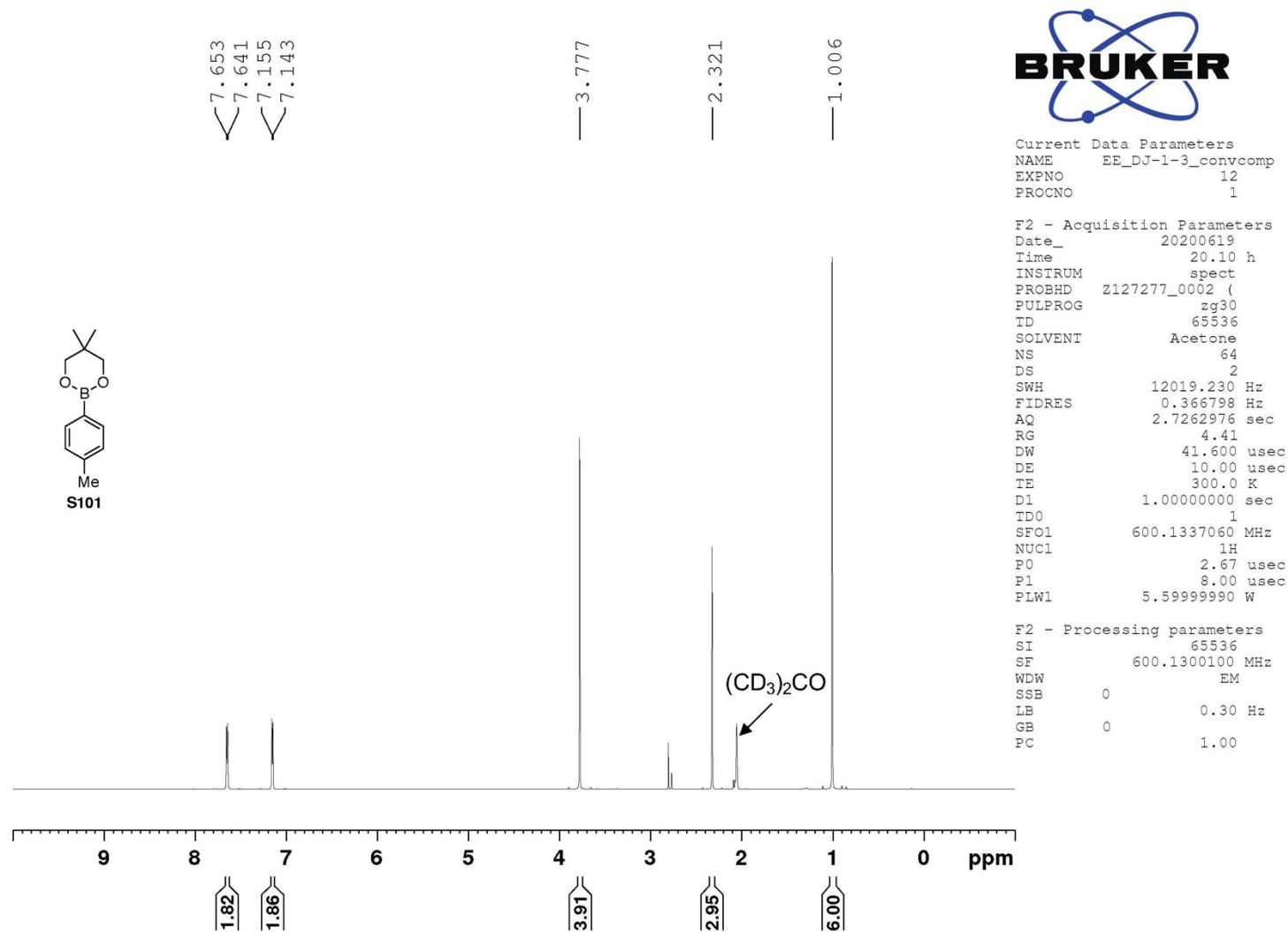
F2 - Processing parameters
SI 65536
SF 282.4419930 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

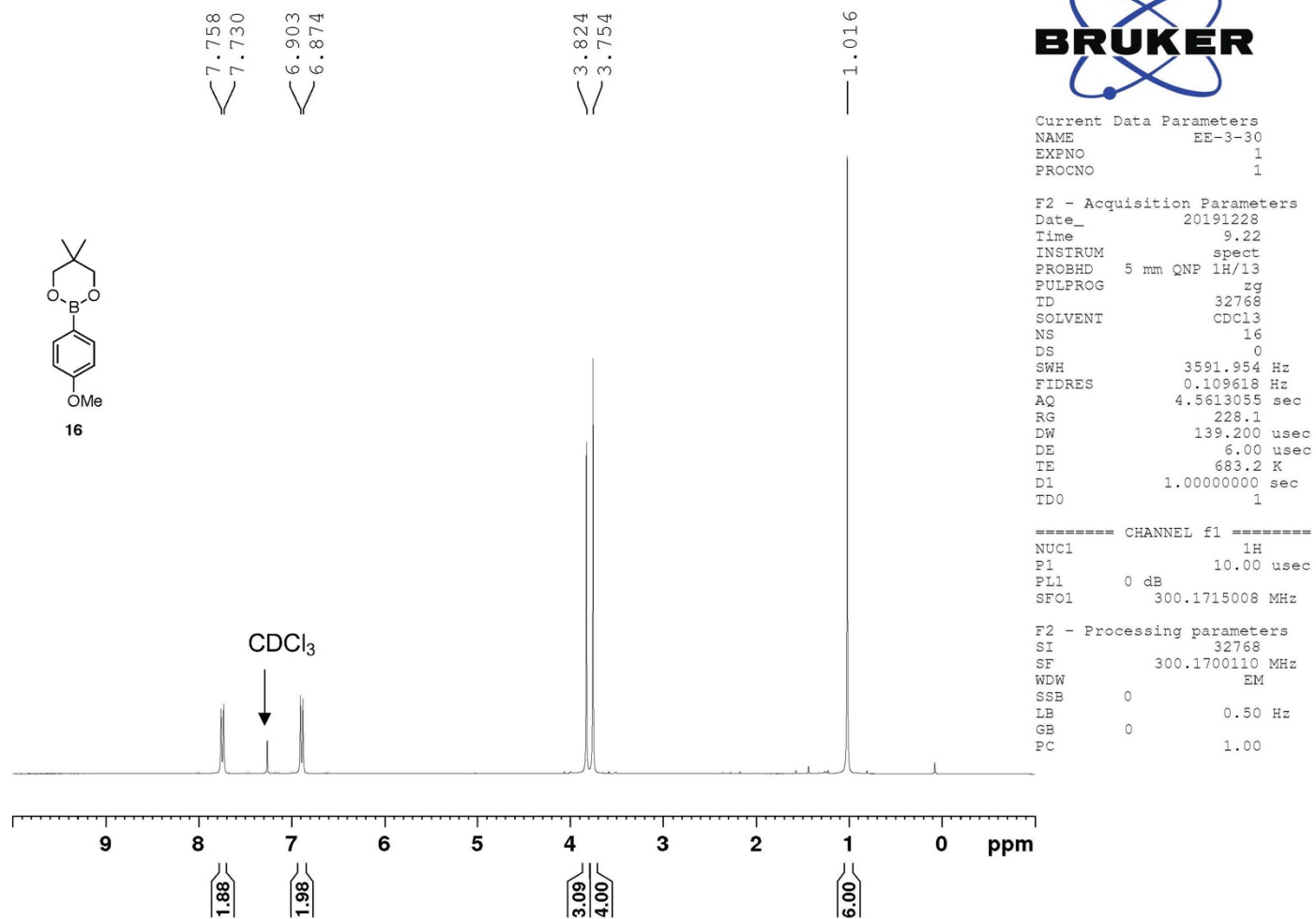


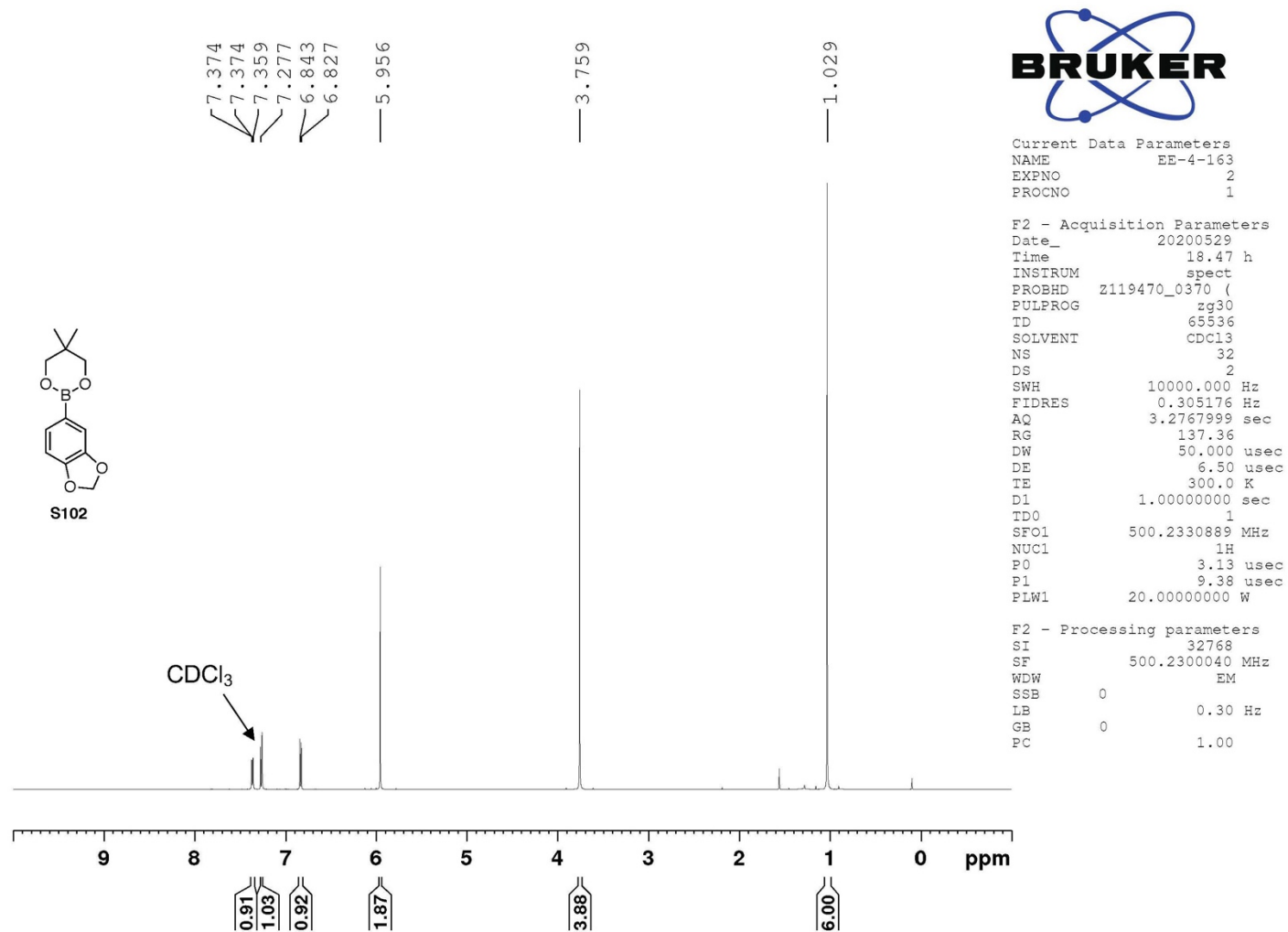


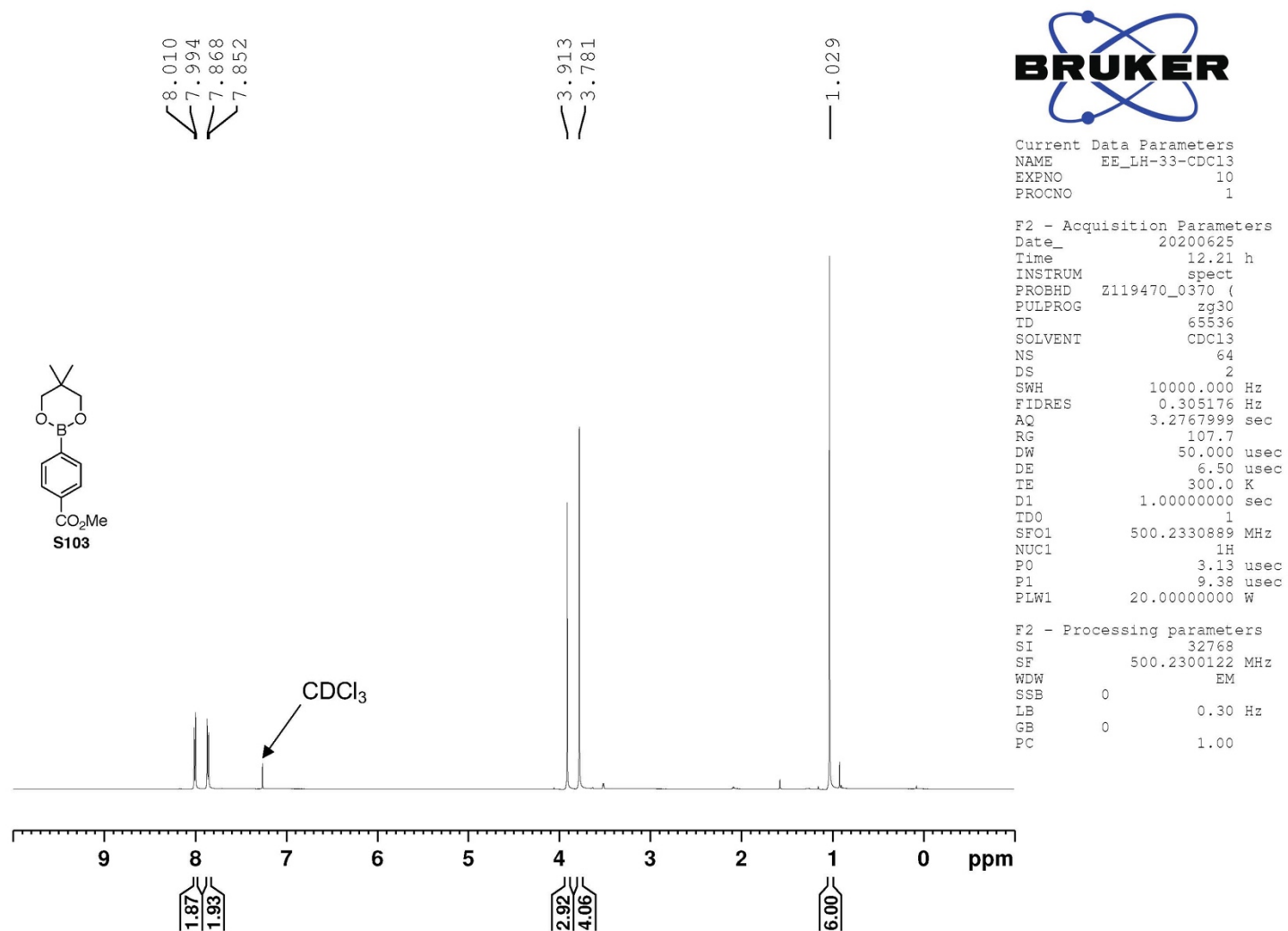


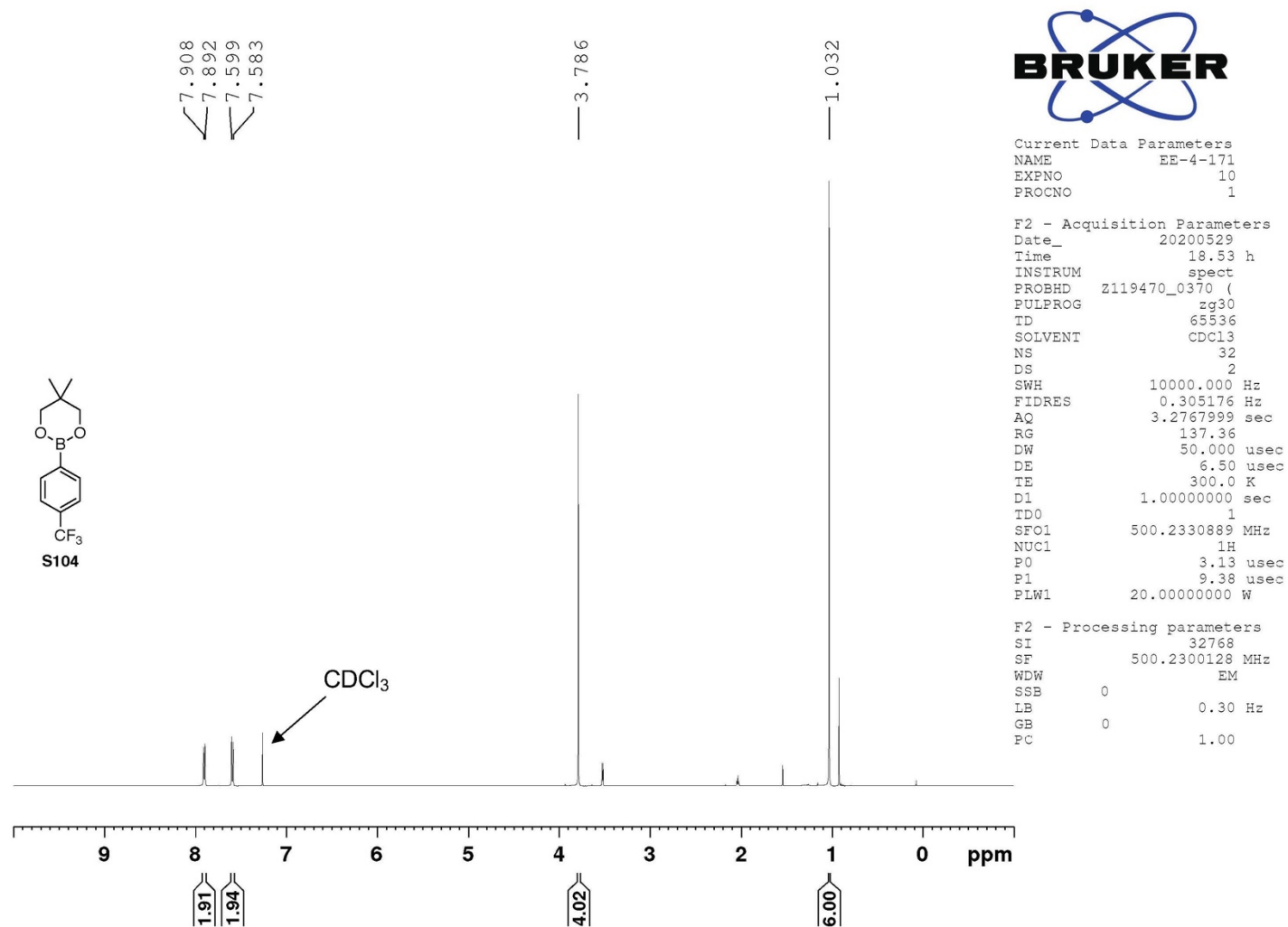


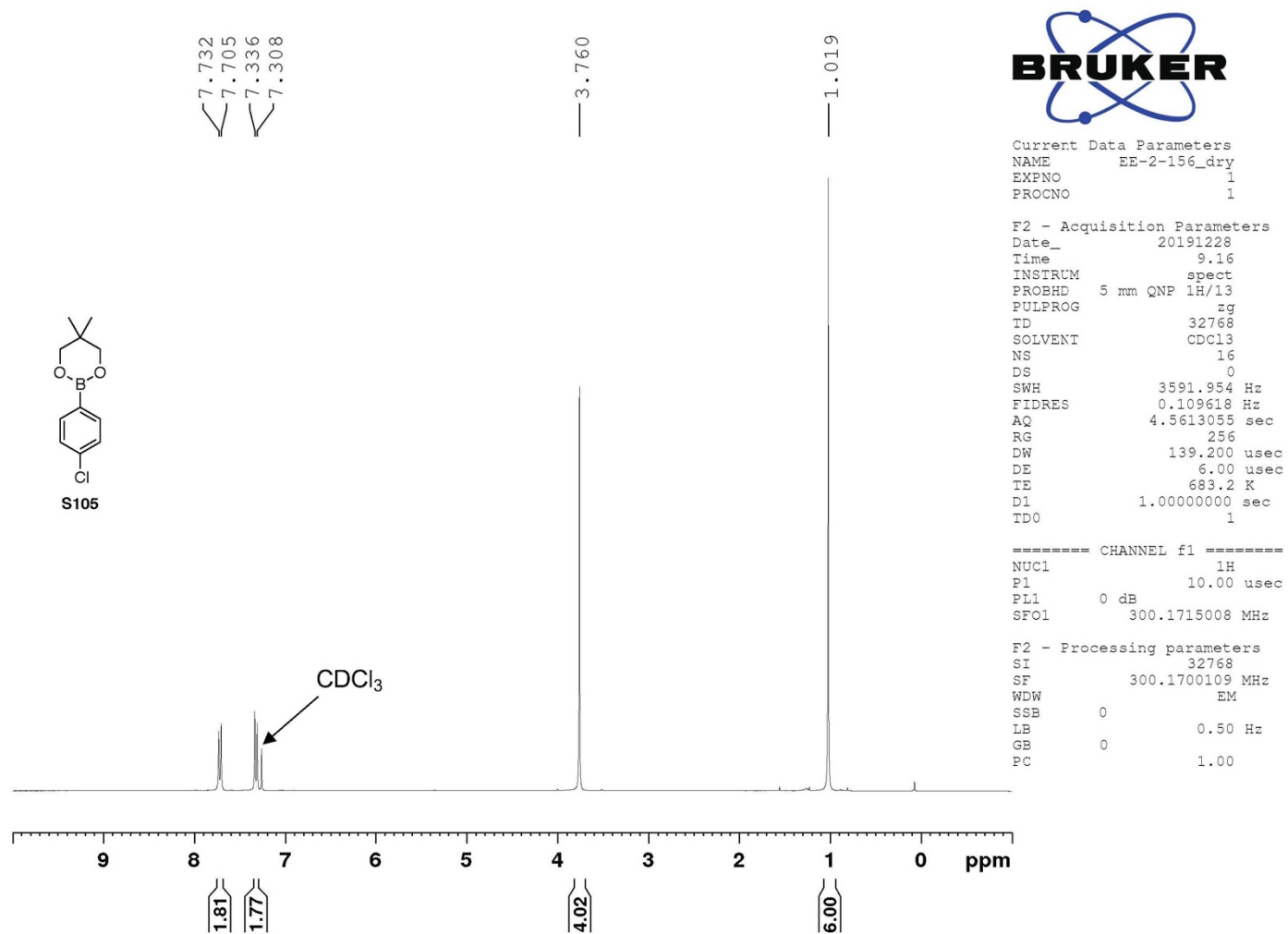


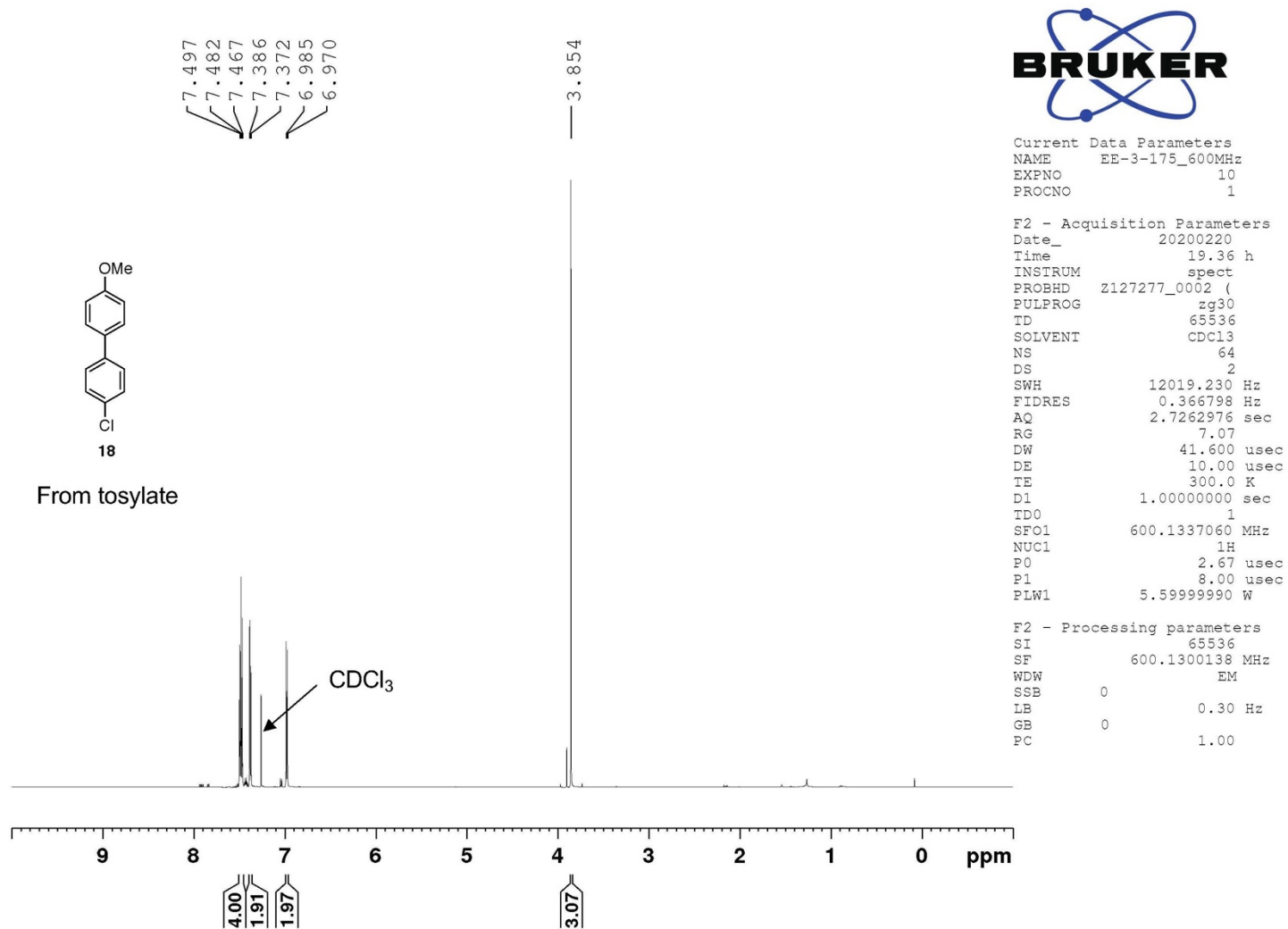


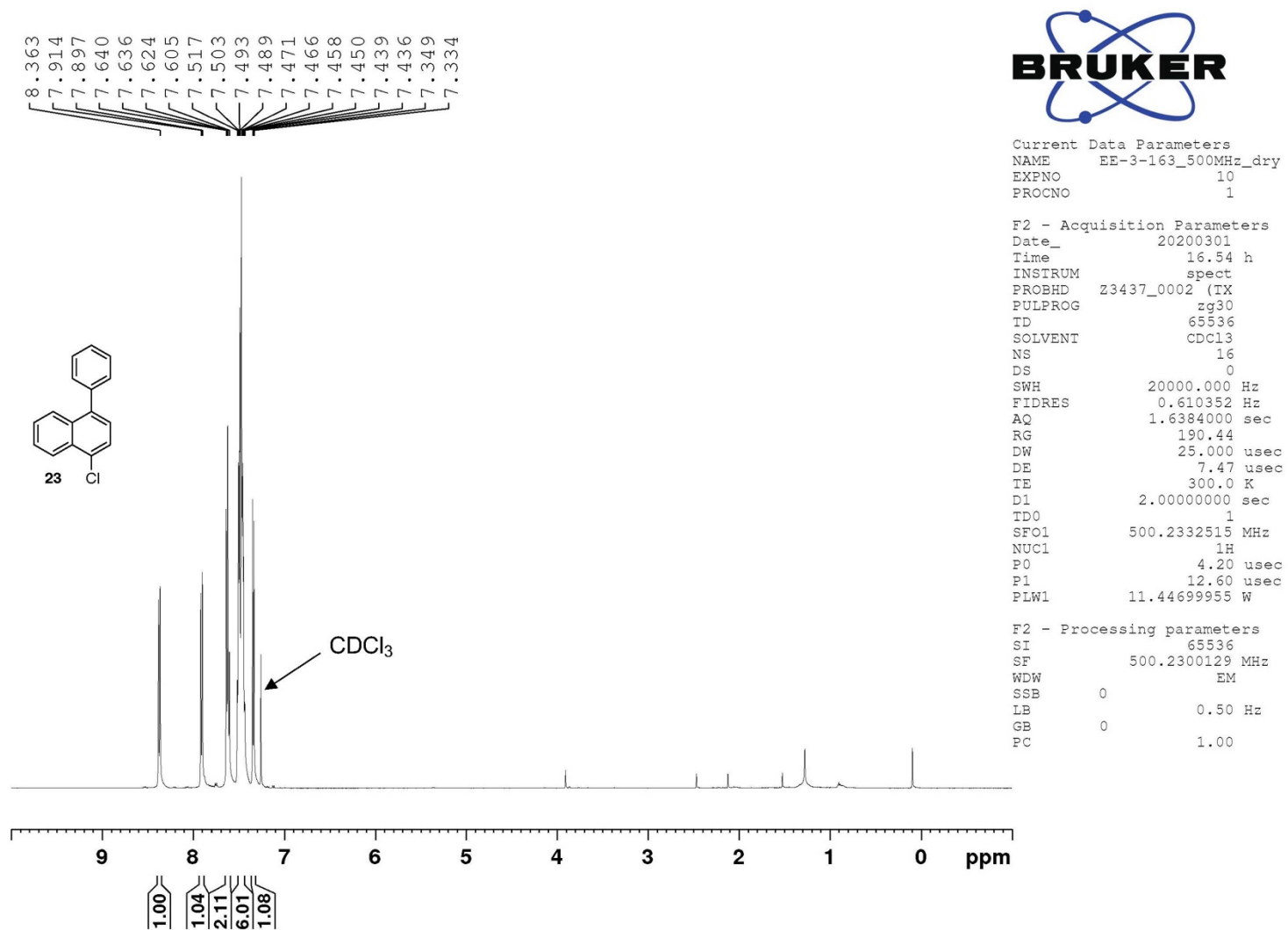


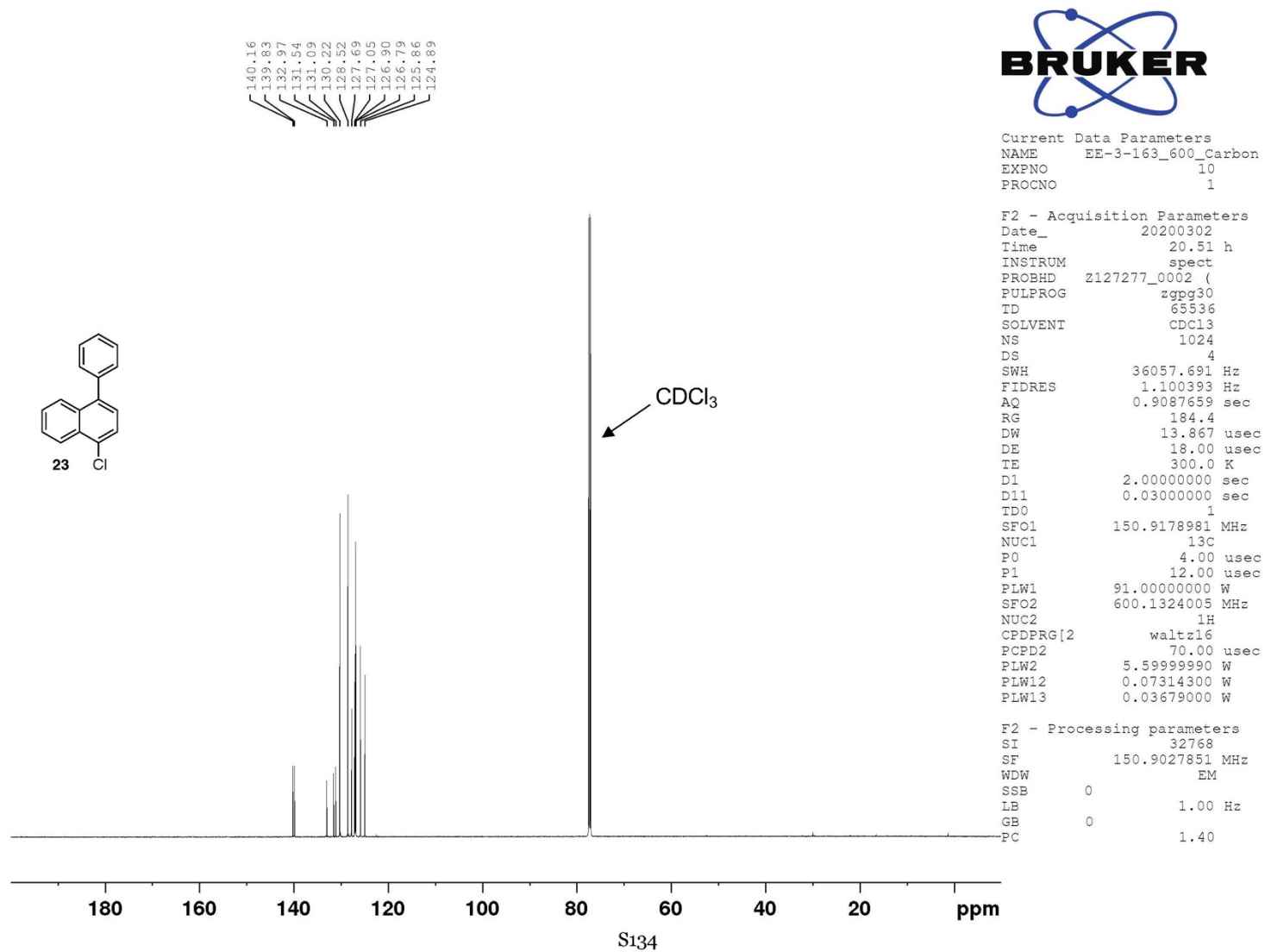


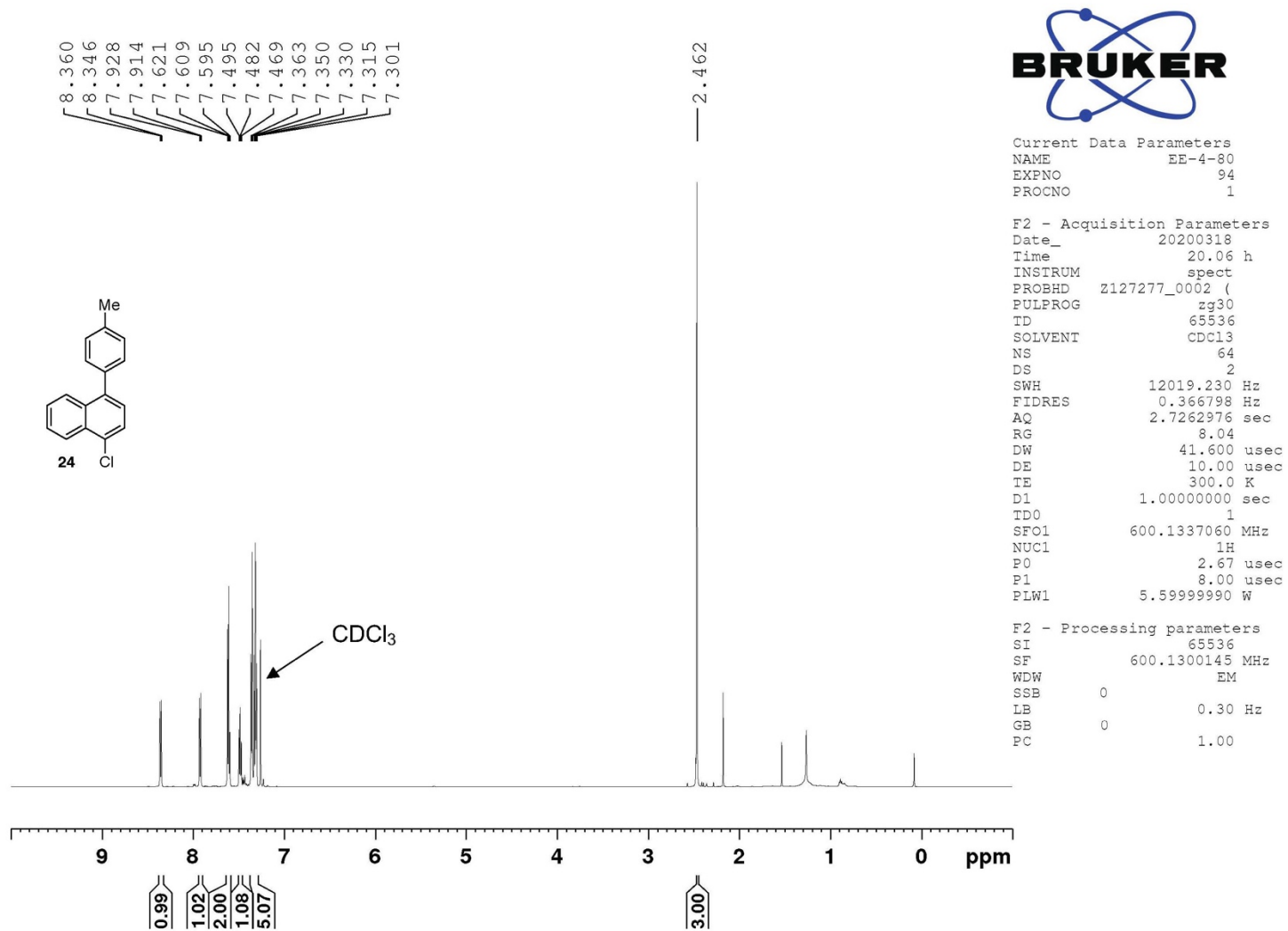


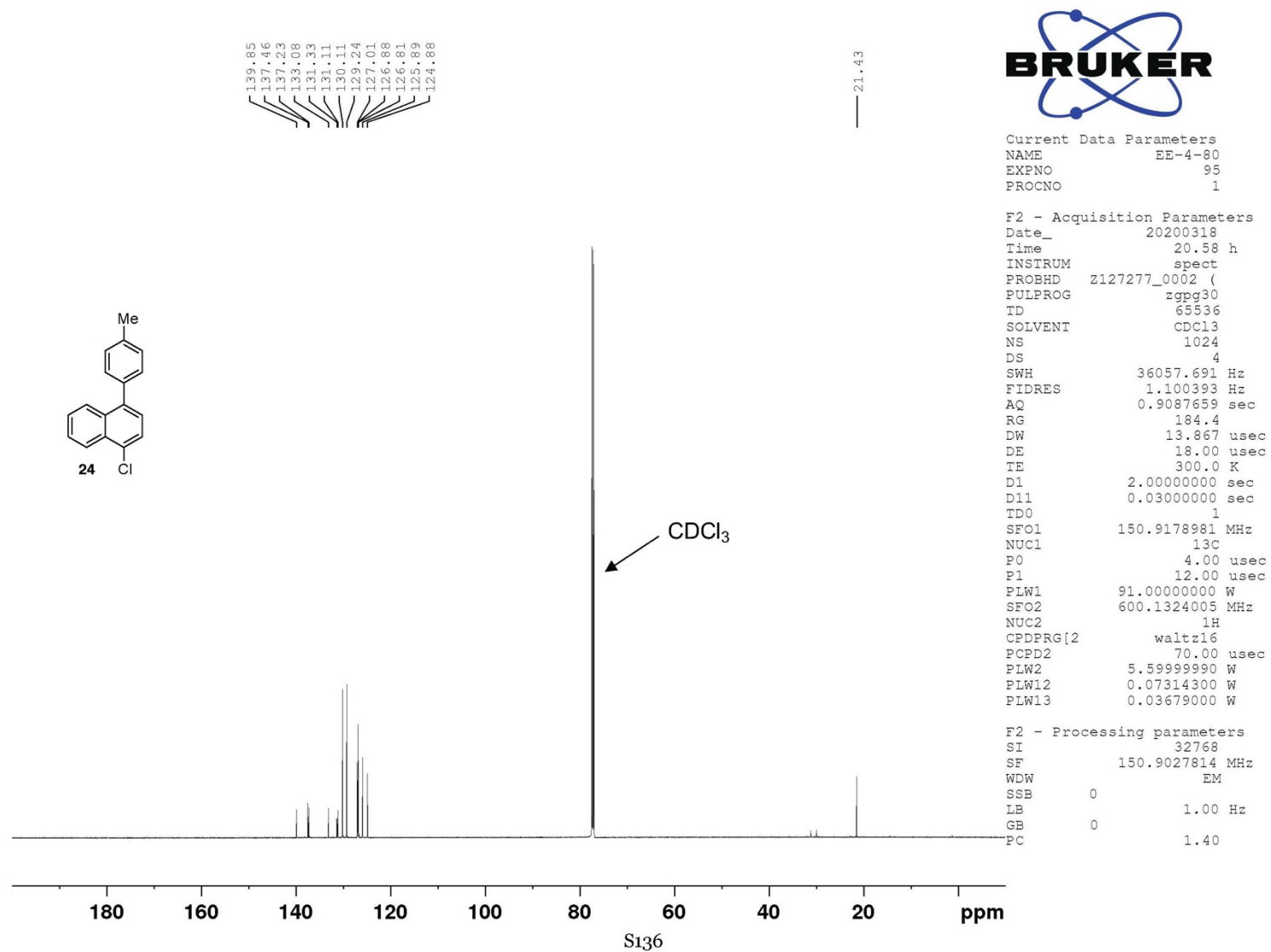


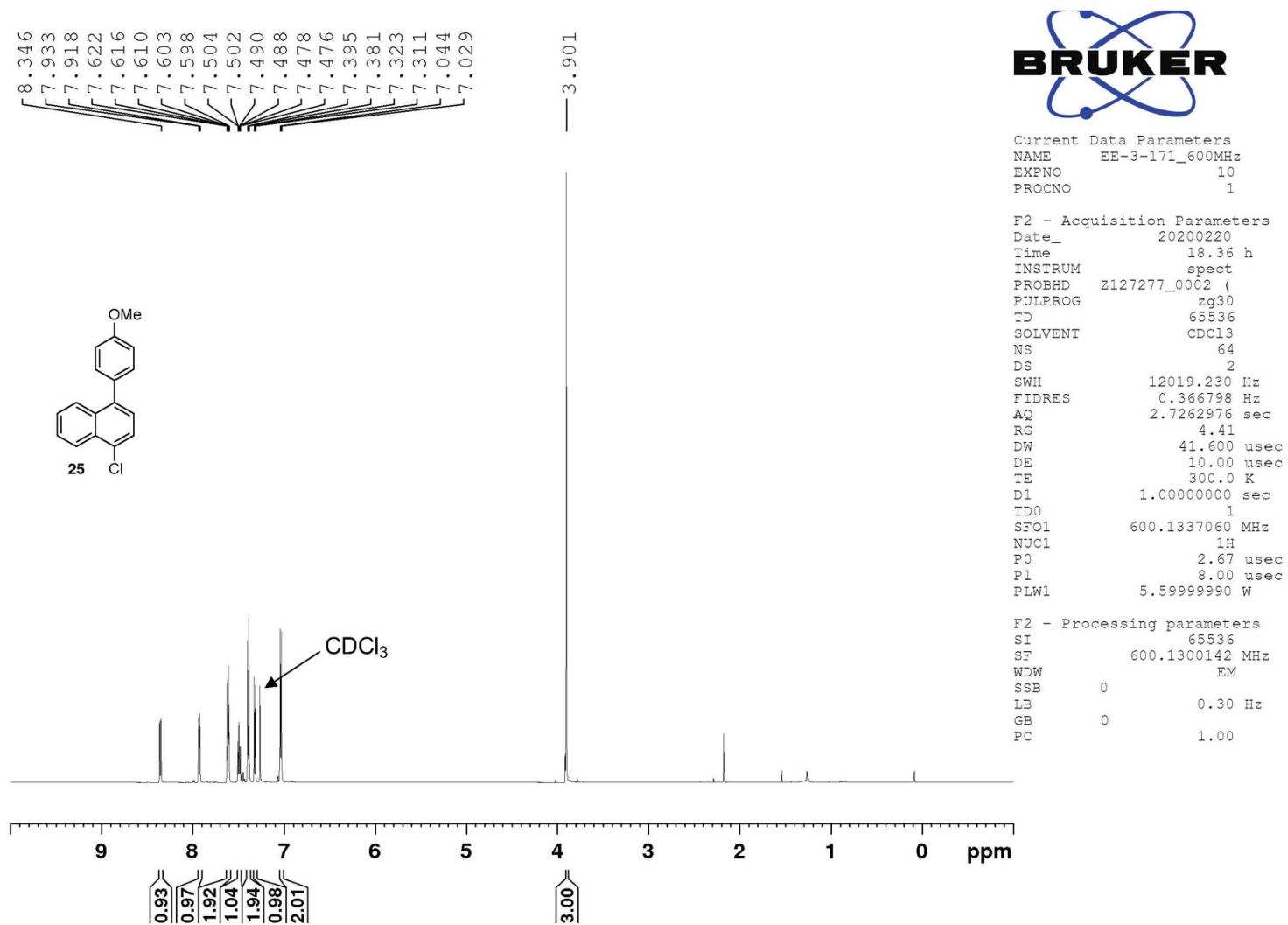


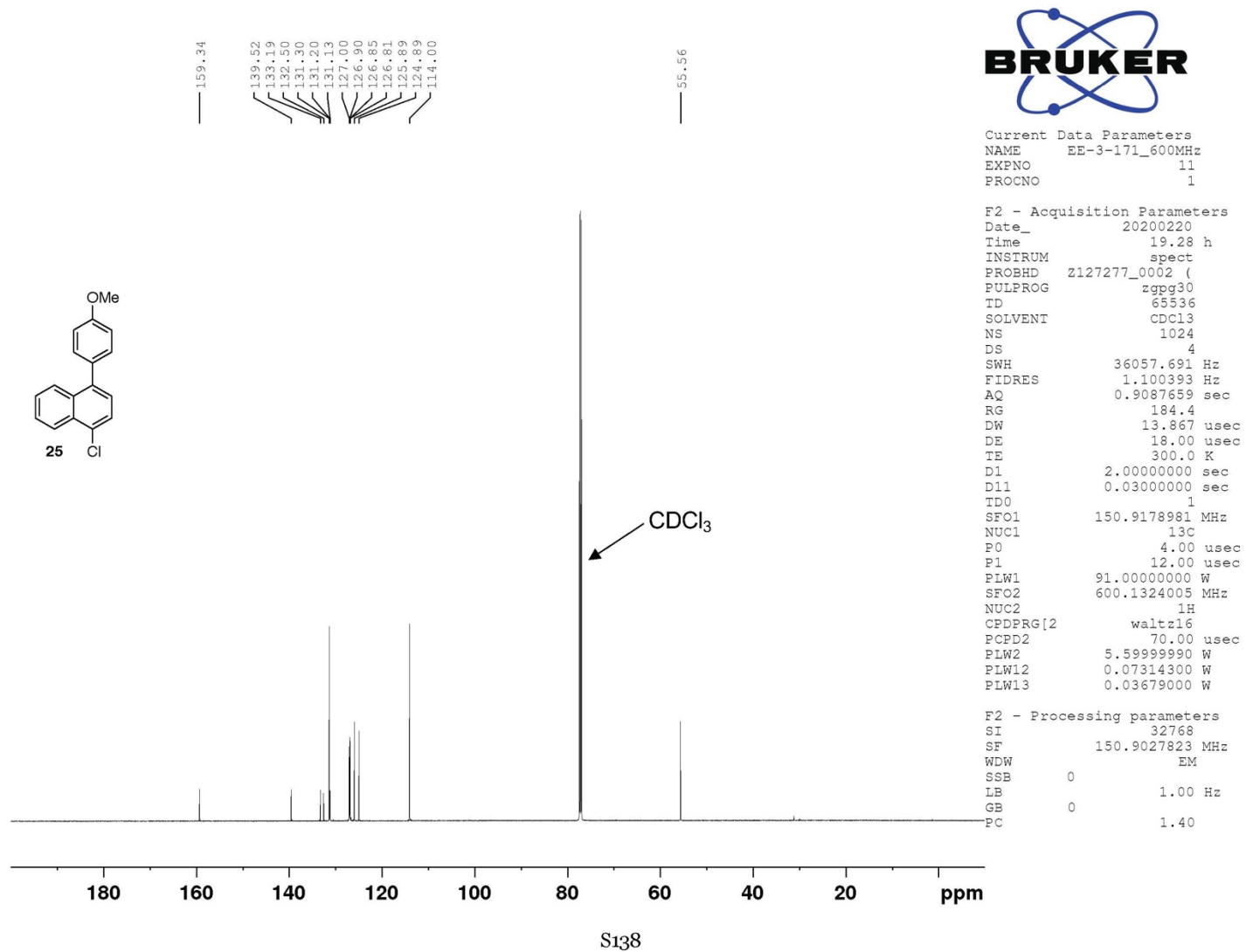


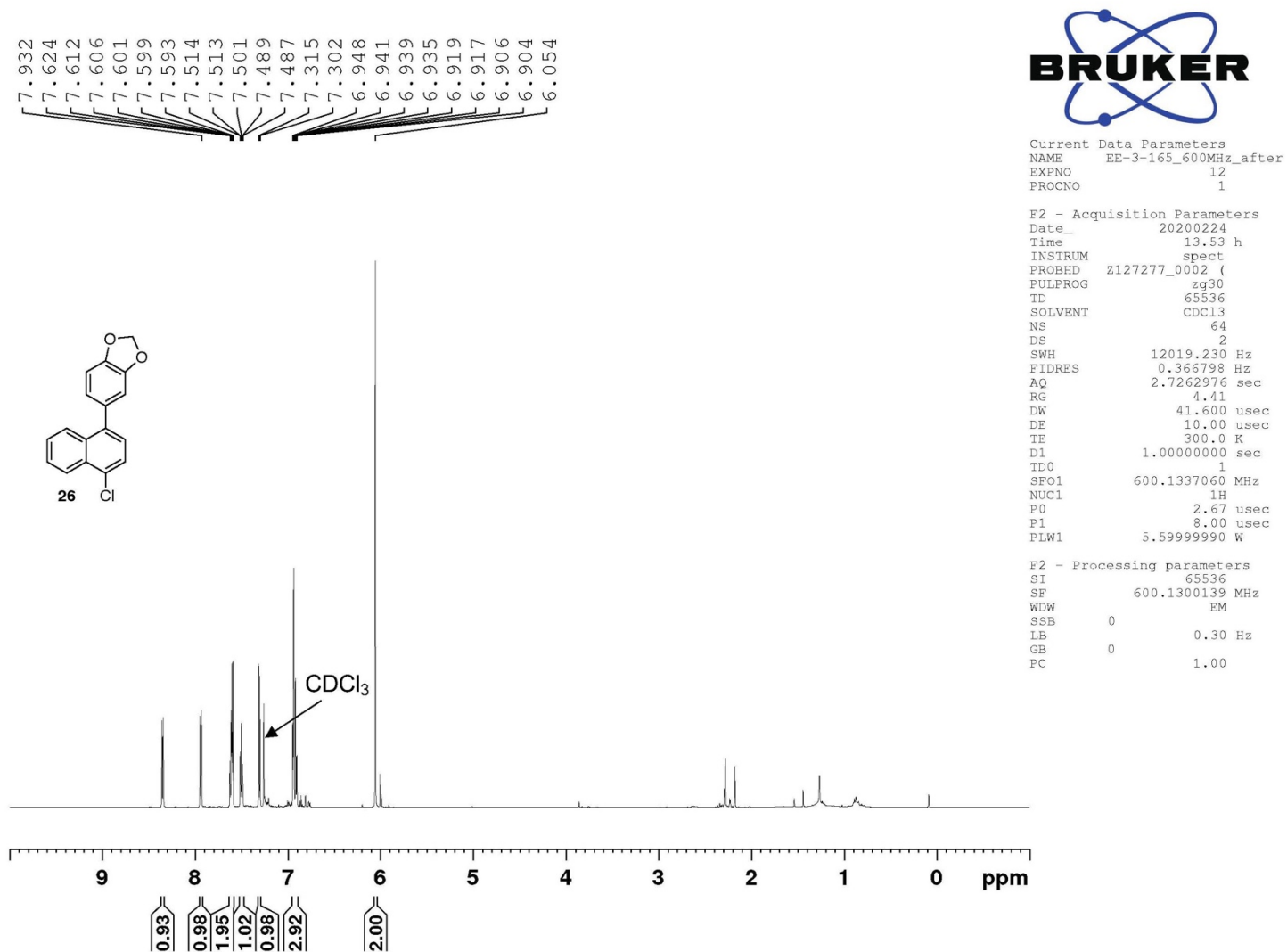


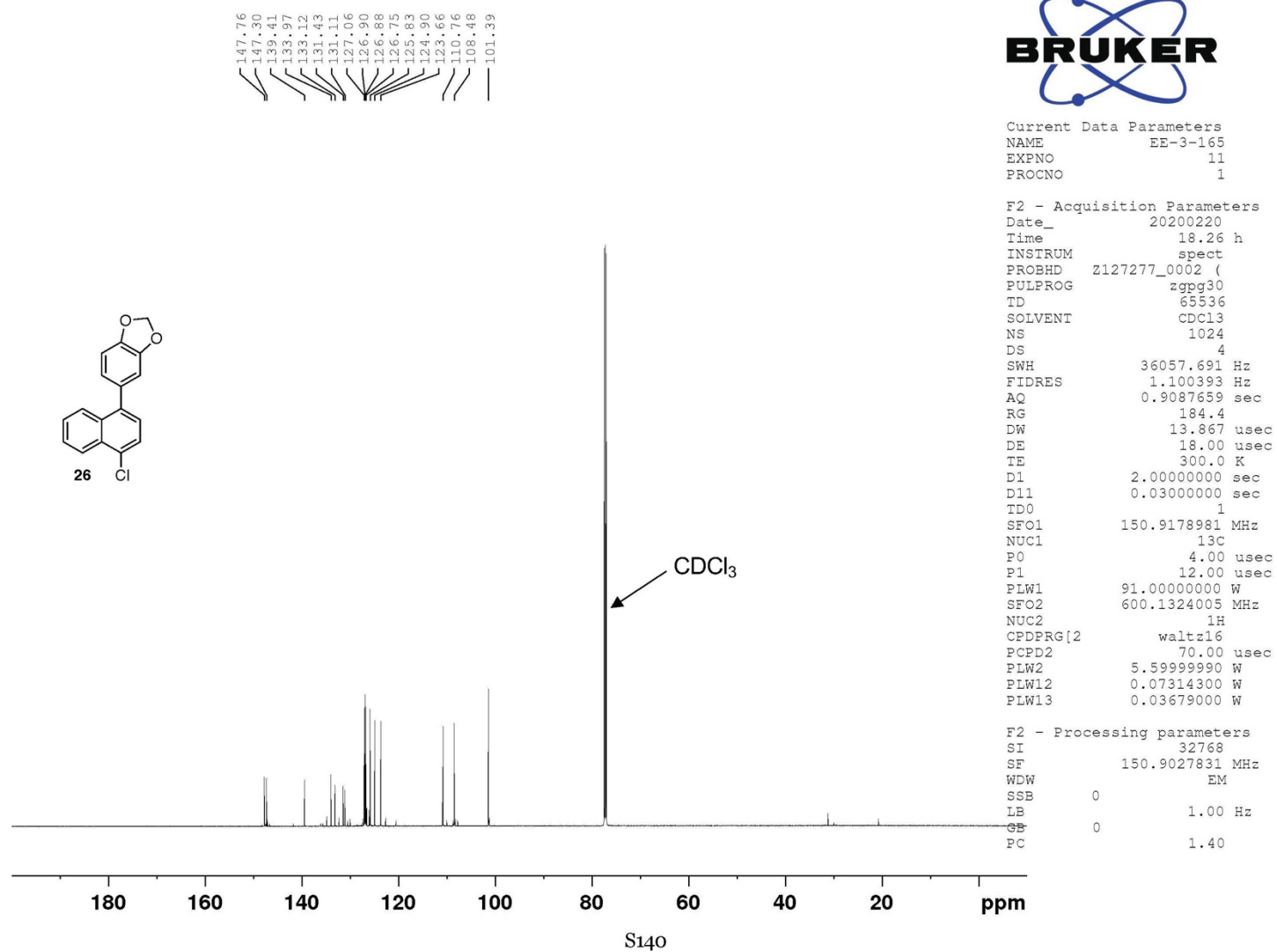


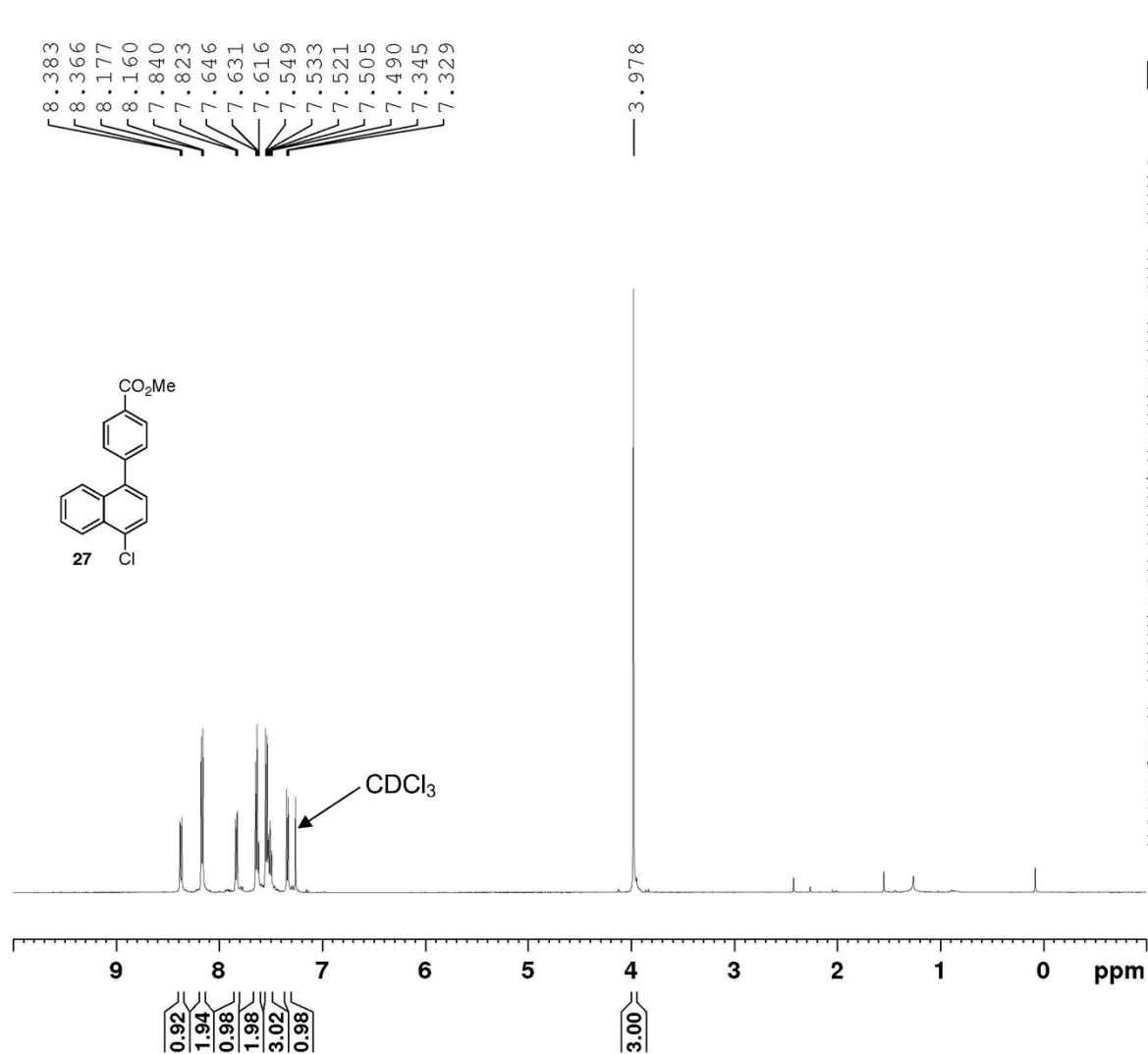








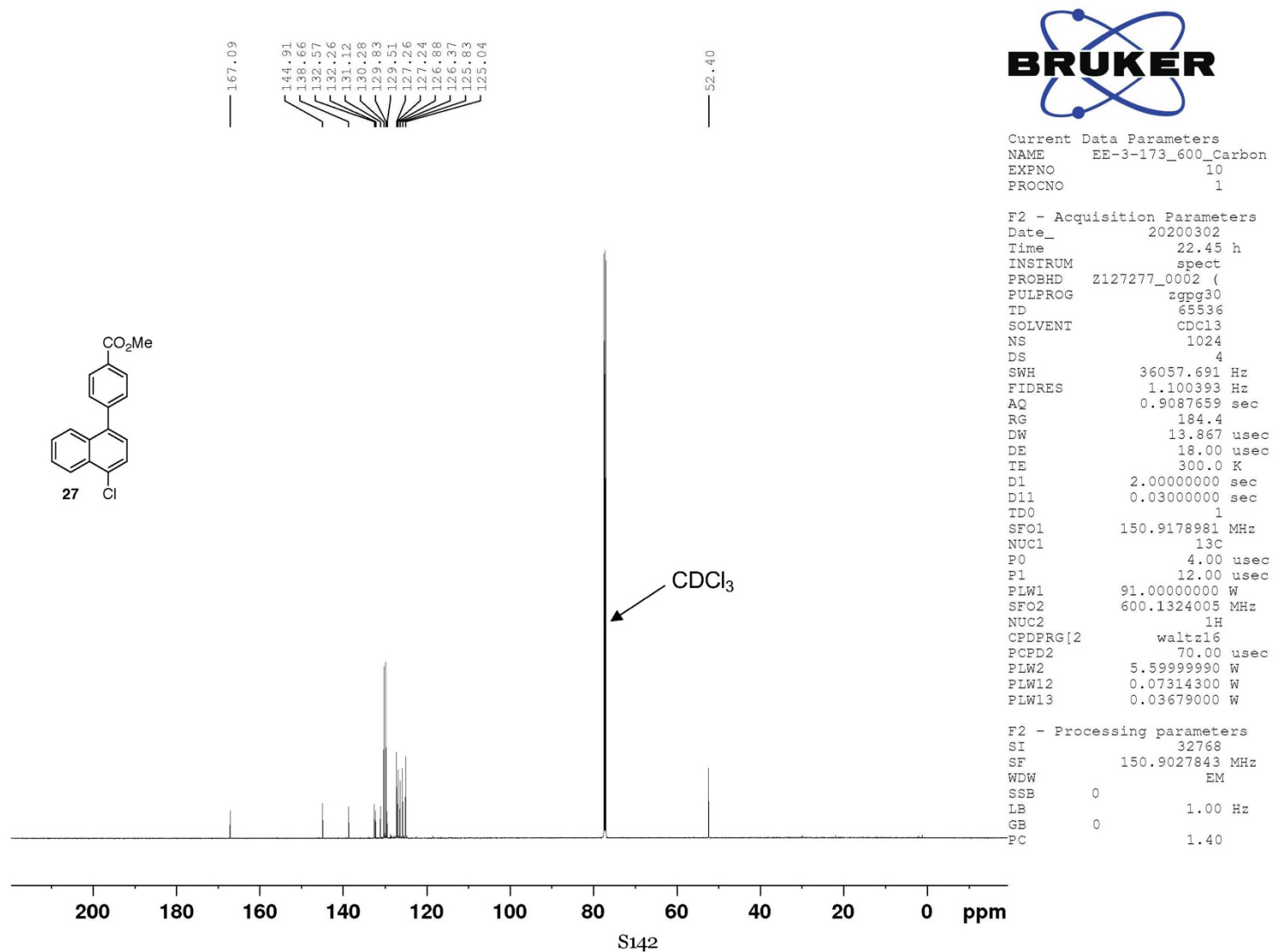


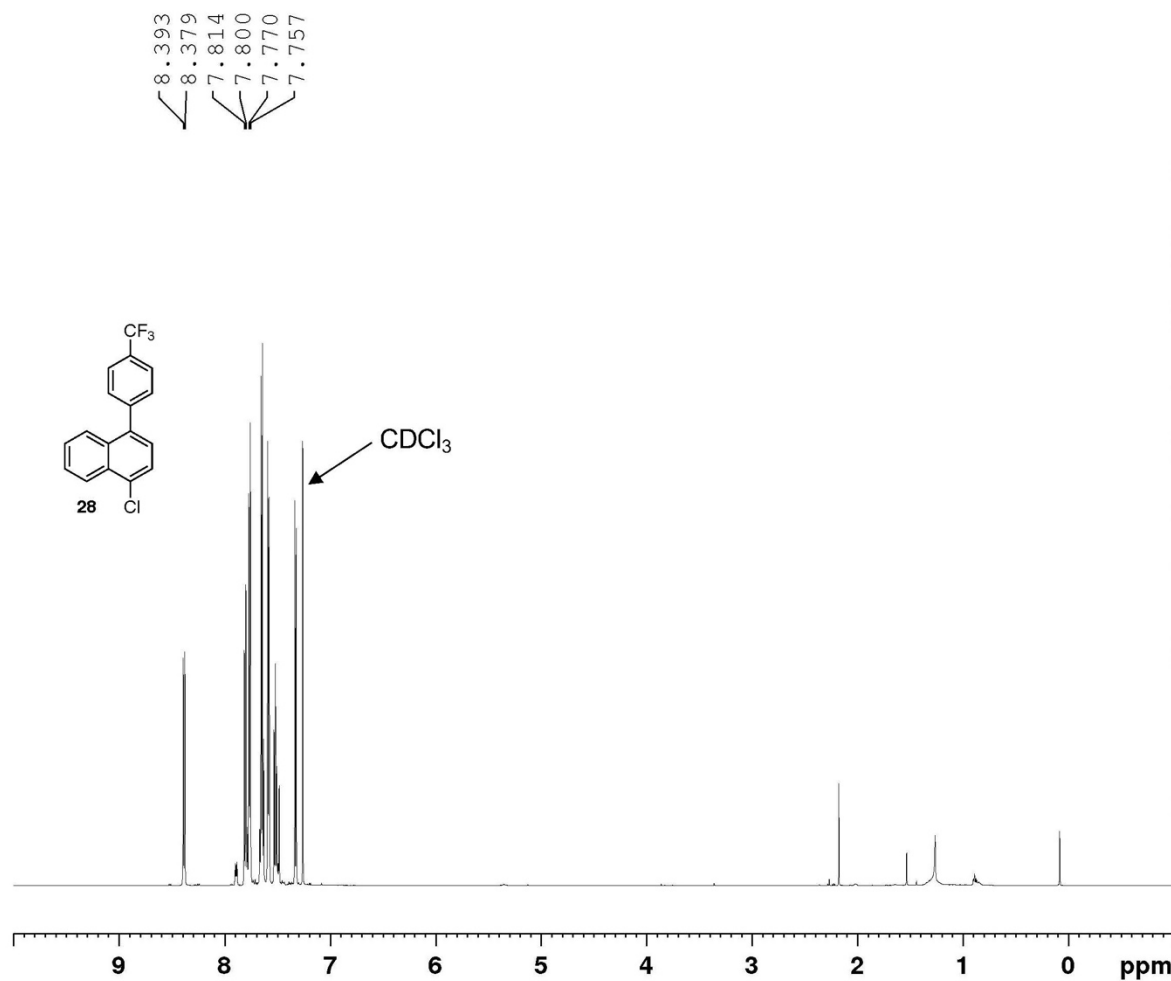


Current Data Parameters
 NAME EE-3-173_500MHz
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20200229
 Time 12.10 h
 INSTRUM spect
 PROBHD Z3437_0002 (TX)
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 20000.000 Hz
 FIDRES 0.610352 Hz
 AQ 1.6384000 sec
 RG 190.44
 DW 25.000 usec
 DE 7.47 usec
 TE 300.0 K
 D1 2.00000000 sec
 TD0 1
 SFO1 500.2332515 MHz
 NUC1 1H
 P0 4.20 usec
 P1 12.60 usec
 PLW1 11.44699955 W

F2 - Processing parameters
 SI 65536
 SF 500.2300125 MHz
 WDW EM
 SSB 0
 LB 0.50 Hz
 GB 0
 PC 1.00

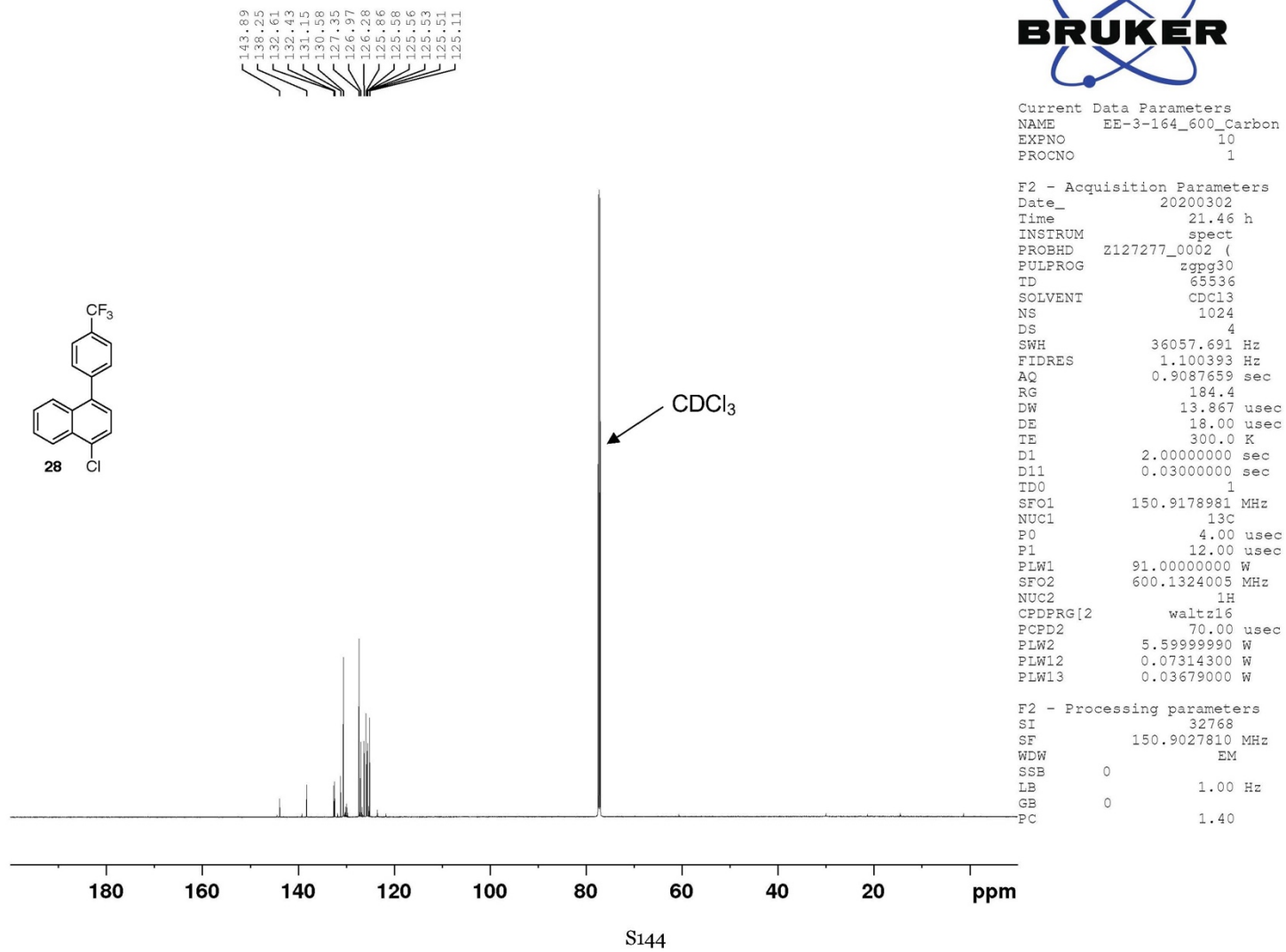


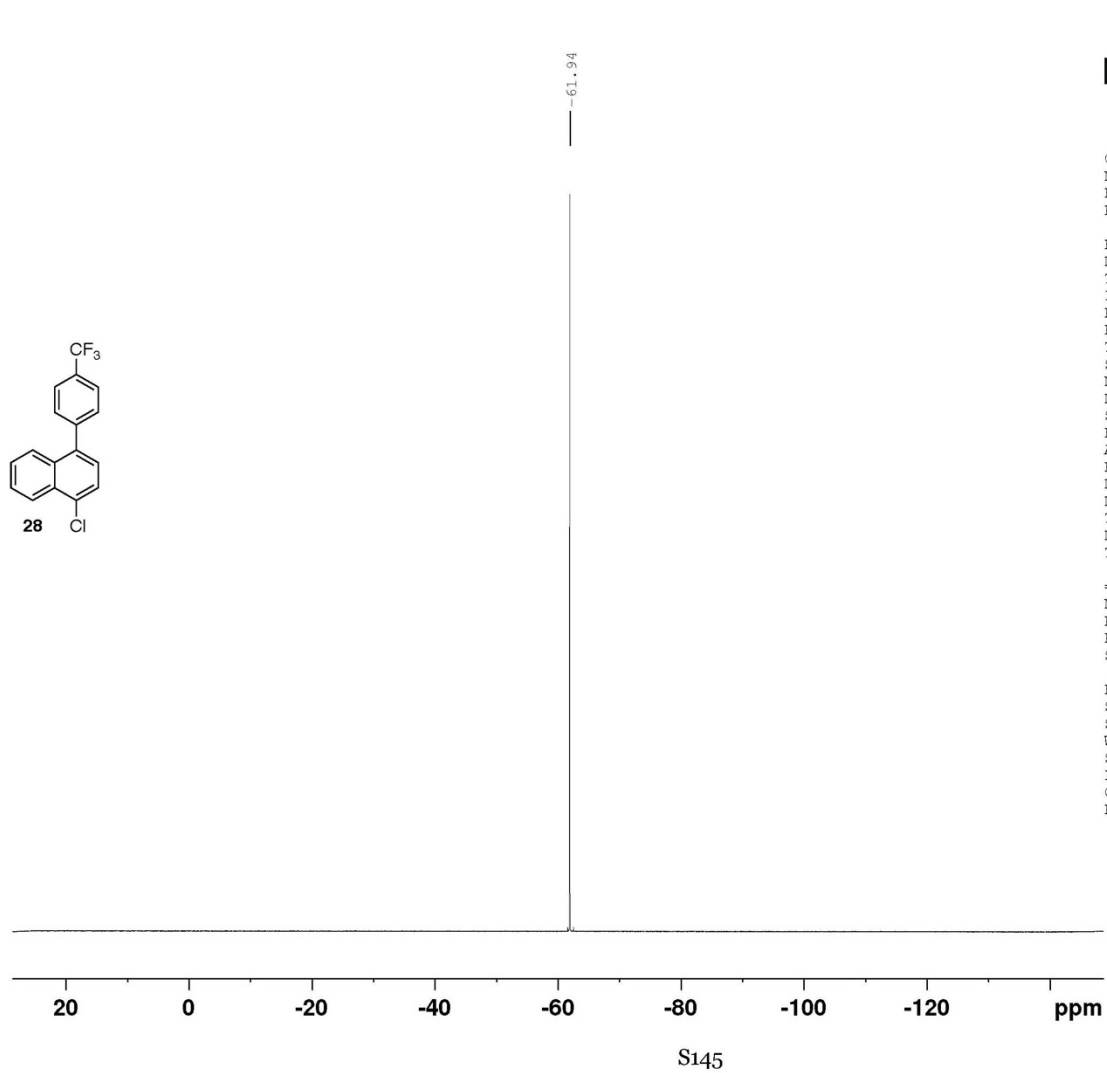


Current Data Parameters
 NAME EE-3-164_600MHz
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20200220
 Time 16.32 h
 INSTRUM spect
 PROBHD Z127277_0002 (
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 64
 DS 2
 SWH 12019.230 Hz
 FIDRES 0.366798 Hz
 AQ 2.7262976 sec
 RG 7.07
 DW 41.600 usec
 DE 10.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1
 SFO1 600.1337060 MHz
 NUC1 1H
 P0 2.67 usec
 P1 8.00 usec
 PLW1 5.59999990 W

F2 - Processing parameters
 SI 65536
 SF 600.1300140 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



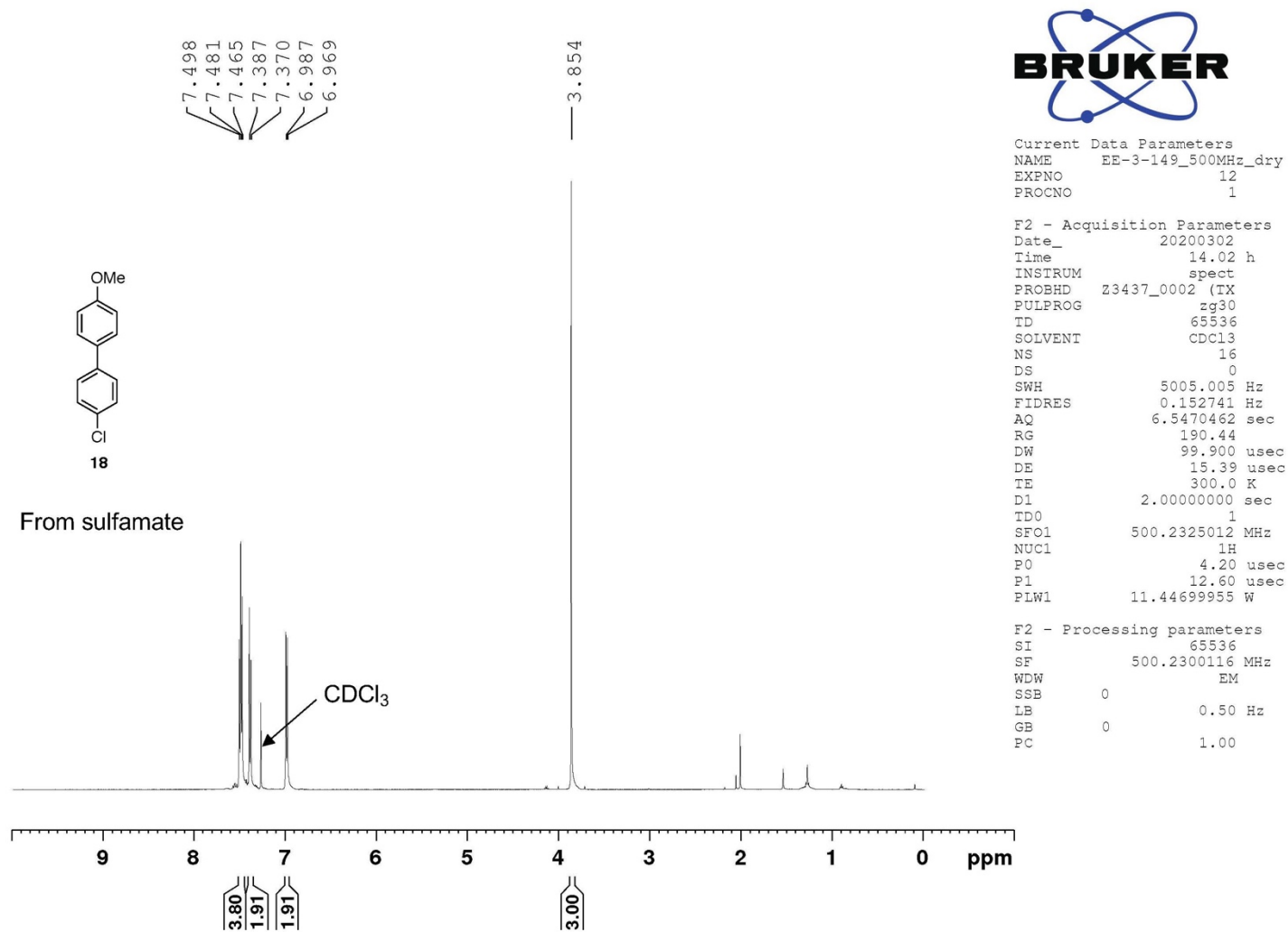


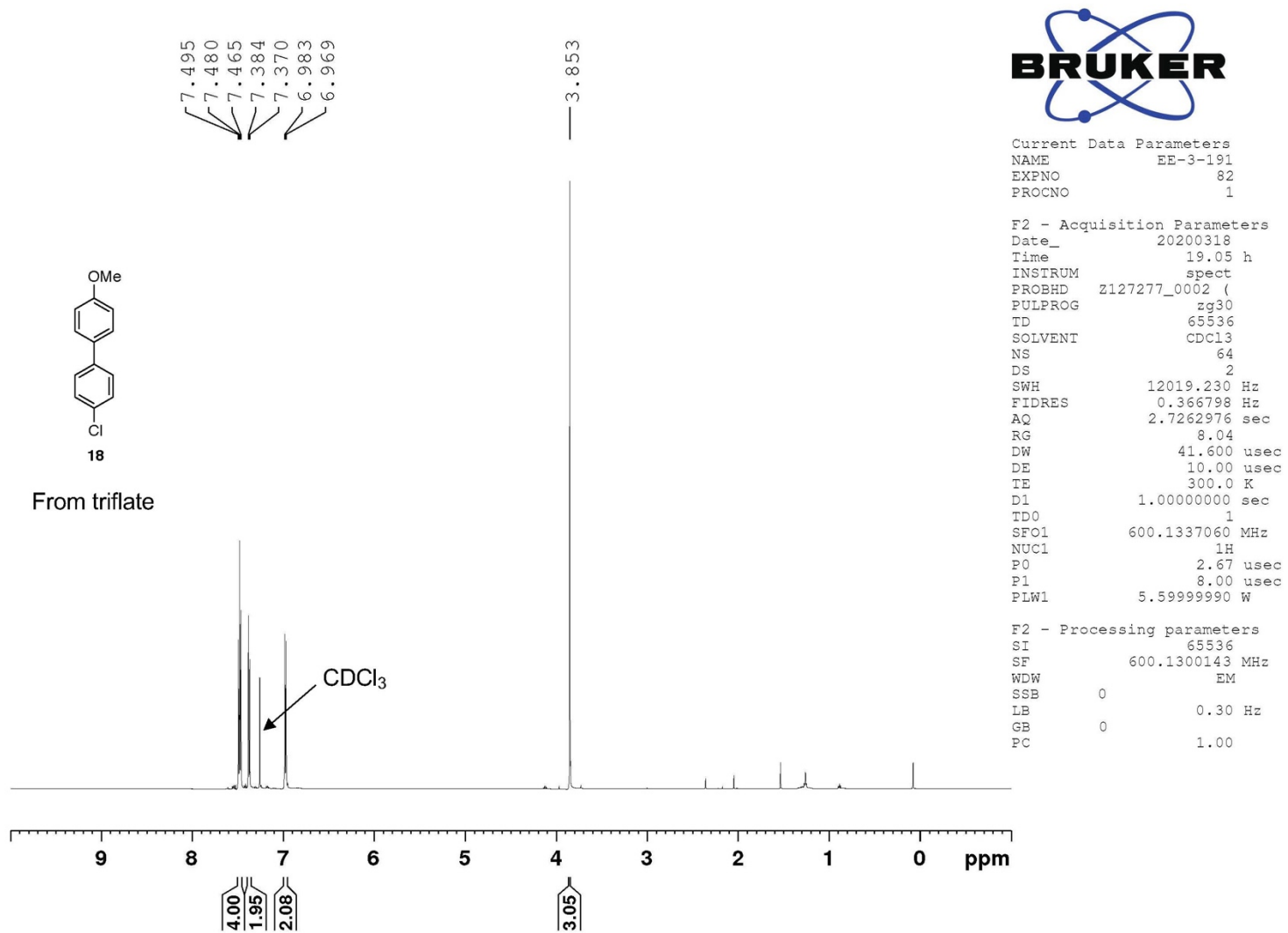
Current Data Parameters
 NAME EE-3-164_19F
 EXPNO 2
 PROCNO 2

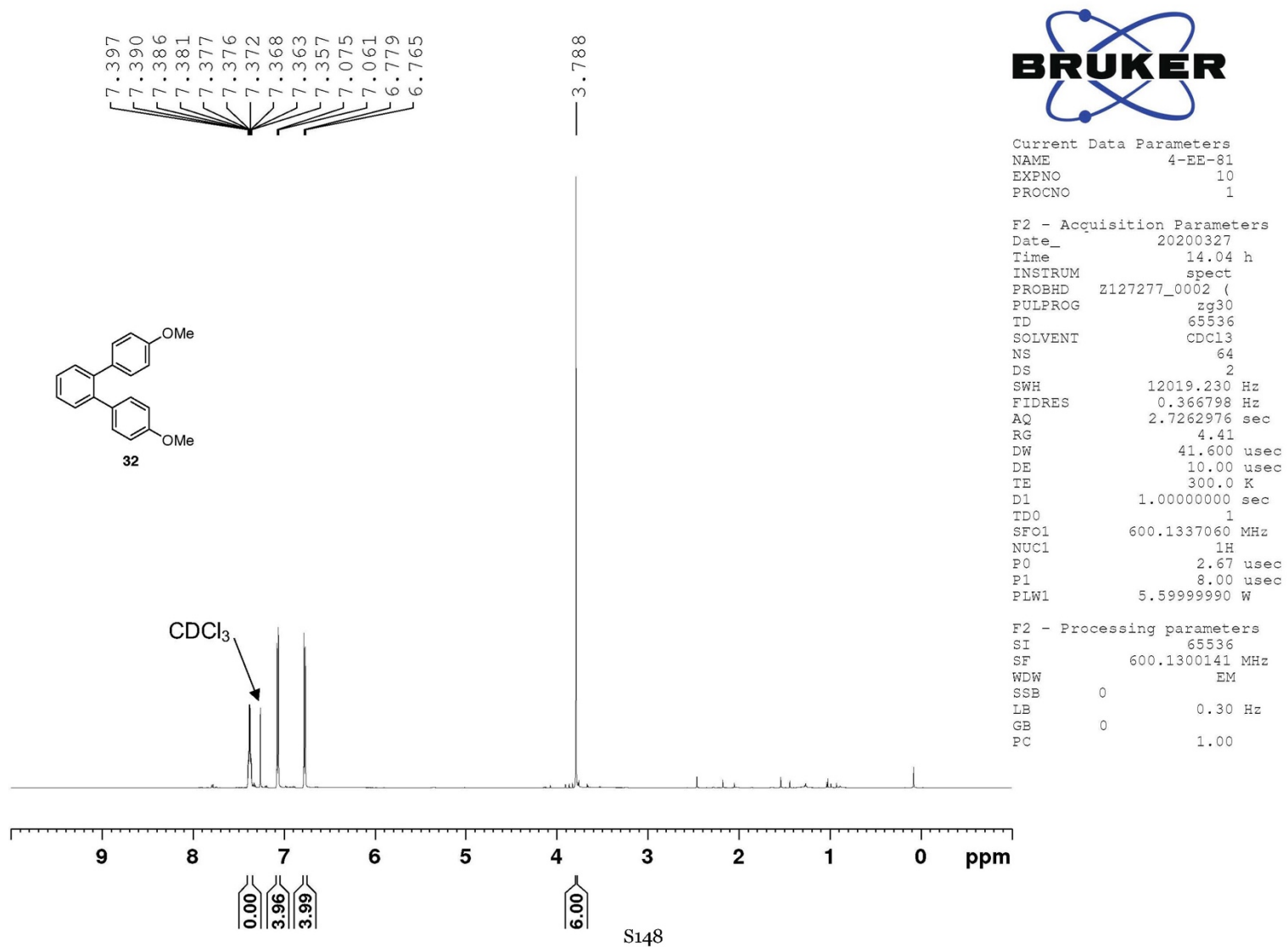
F2 - Acquisition Parameters
 Date_ 20200619
 Time 11.46
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zgpg30
 TD 32768
 SOLVENT C6D6
 NS 128
 DS 0
 SWH 50125.313 Hz
 FIDRES 1.529703 Hz
 AQ 0.3268608 sec
 RG 1824.6
 DW 9.975 usec
 DE 6.00 usec
 TE 683.2 K
 D1 1.50000000 sec
 TDO 1

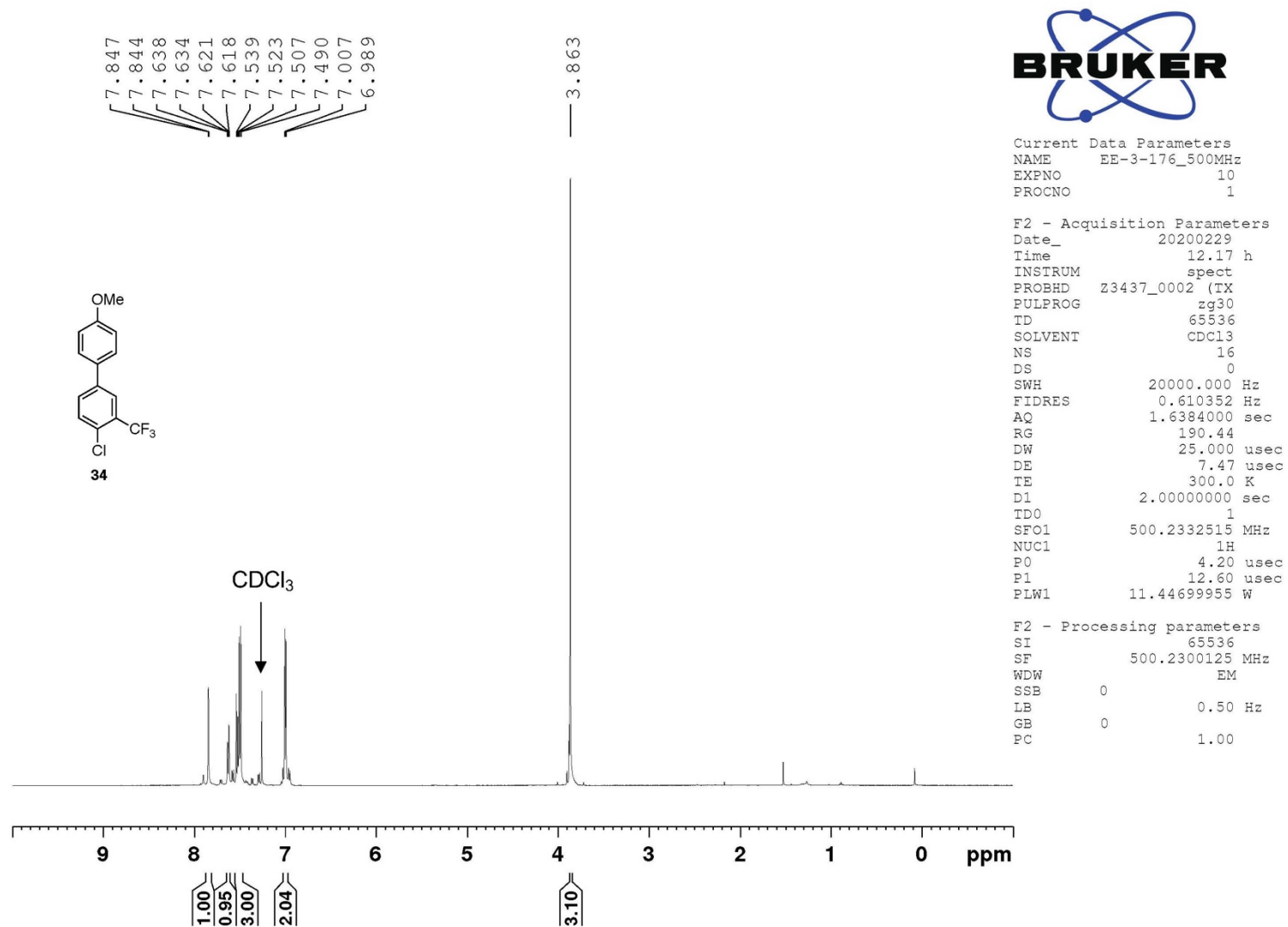
===== CHANNEL f1 =====
 NUC1 19F
 P1 9.00 usec
 PL1 0 dB
 SFO1 282.4250465 MHz

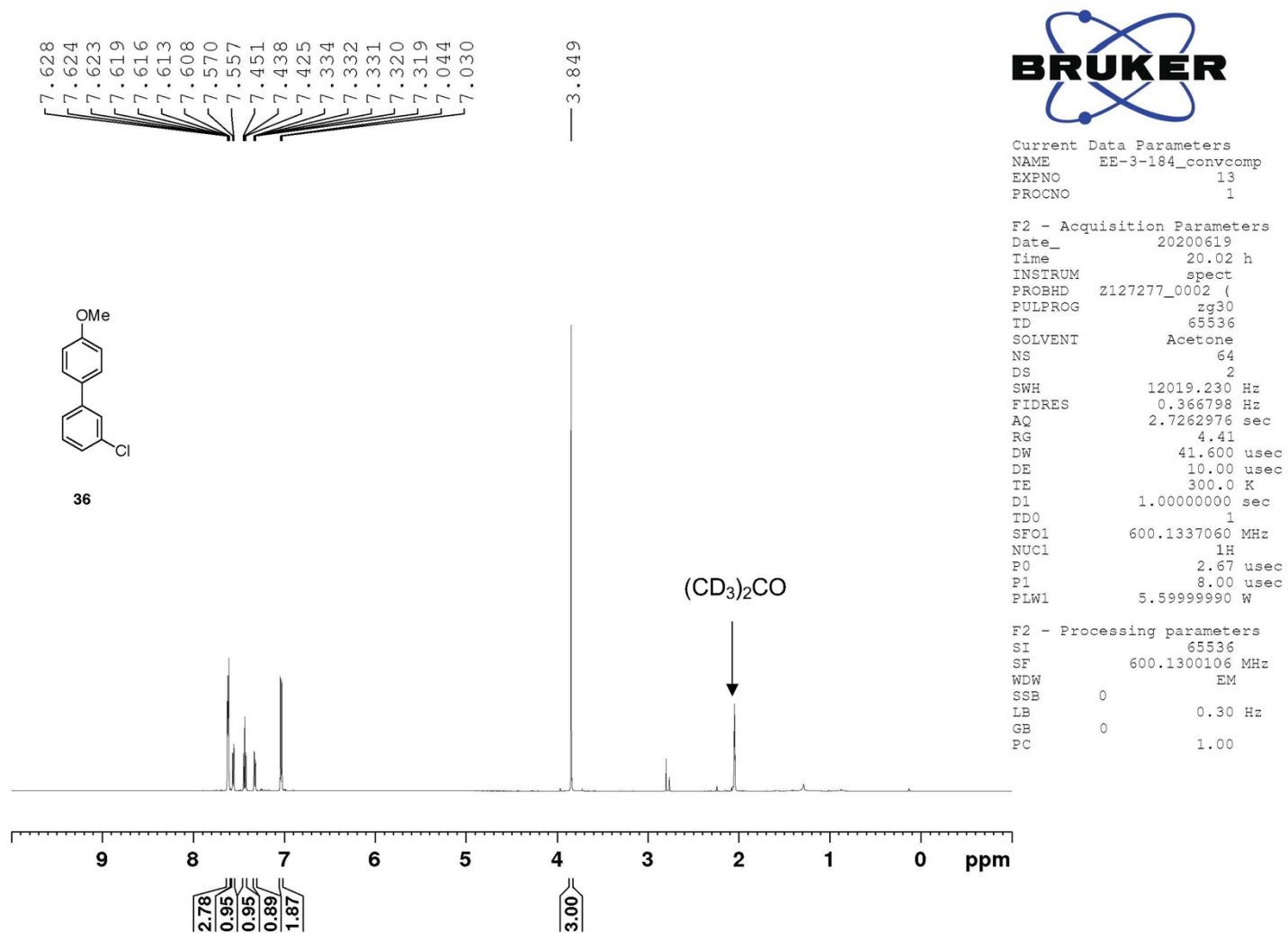
F2 - Processing parameters
 SI 65536
 SF 282.4419930 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

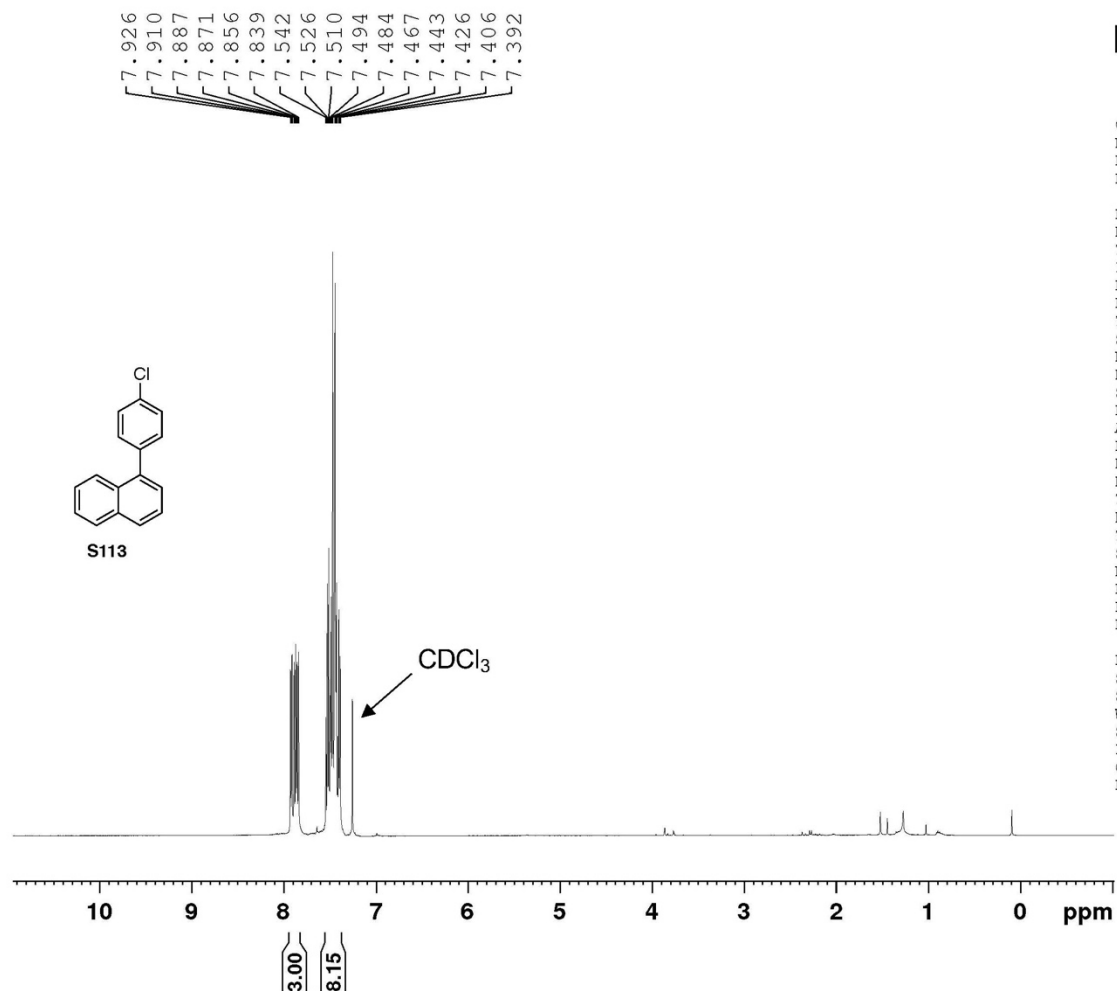












Current Data Parameters
 NAME EE-3-185_500MHz
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20200229
 Time 12.23 h
 INSTRUM spect
 PROBHD Z3437_0002 (TX)
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 20000.000 Hz
 FIDRES 0.610352 Hz
 AQ 1.6384000 sec
 RG 190.44
 DW 25.000 usec
 DE 7.47 usec
 TE 300.0 K
 D1 2.00000000 sec
 TD0 1
 SFO1 500.2332515 MHz
 NUC1 1H
 P0 4.20 usec
 P1 12.60 usec
 PLW1 11.44699955 W

F2 - Processing parameters
 SI 65536
 SF 500.2300125 MHz
 WDW EM
 SSB 0
 LB 0.50 Hz
 GB 0
 PC 1.00