# Synthesis of Ni(dppe)$_2$ and Nickel (I) Catalysts and their Ability to Catalyzed Cross-Coupling

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# Abstract

Nickel catalysts play a growing role in effecting a variety of cross-coupling reactions in which carbon-carbon bonds are formed. Nickel compounds have several advantages over more frequently used palladium analogues, including the ability to activate aliphatic electrophiles and to avoid β-hydrogen elimination by alkyl-metal intermediates. Both Ni(II) and Ni(0) precursors are commonly utilized, with the latter oxidation state often believed to function as the catalytically active species. In recent years, however, a number of Ni(I) compounds have also been reported to behave as apparent catalysts and, since Ni(0) and Ni(I) compounds may be readily interconvertible, it is not always clear which oxidation state forms the actual catalyst in any particular cross-coupling reaction. Ni(0) was synthesised using a zinc reduction and analyzed by NMR spectroscopy. Ni(I) was produced using comproportionation reaction and analyzed with elemental analysis. This thesis describes an investigation in which we compare Ni(0), Ni(I) and Ni(II) complexes containing phosphine and halide ($Cl^-$, $Br^-$, $I^-$) ligands , in this case 1,2-bis(diphenylphosphino)ethane (dppe) for their abilities to effect e.g. Buchwald-Hartwig Amination, Heck-Mizoroki and Suzuki-Miyaura reactions with different types of substrates.

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# List of Symbols and Abbreviations

| | |
|---|---|
| Å | Ångström |
| acac | acetylacetonate |
| Ar | aryl group |
| br | broad |
| $^{t}$Bu | tert-butyl group |
| °C | degrees Celsius |
| $C_6D_6$ | deuterated benzene |
| COD | 1,5-Cyclooctadiene |
| $\delta$ | chemical shift |
| d | Doublet |
| DCM | dichloromethane |
| DFT | density functional theory |
| DMF | Dimethylformamide |
| DPB | 1,3-diphenylbut-1-ene |
| dmso | dimethyl sulfoxide |
| dppe | 1,2-bis(diphenylphosphino)ethane |
| dppf | 1,1’-bis(diphenylphosphino)ferrocene |
| dppp | 1,3-bis(diphenylphosphino)propane |
| EPR | electron paramagnetic resonance |
| equiv | Equivalent |
| Et | Ethyl |

| | |
|---|---|
| EWG | electron withdrawing group |
| g | Grams |
| GC | gas chromatography |
| h | Hour |
| $^1H$ NMR | proton NMR |
| HMBC | heteronuclear multiple bond correlation |
| *J* | coupling constant |
| m | Multiplet |
| Me | methyl group |
| MeCN | Acetonitrile |
| mg | Milligram |
| MHz | Megahertz |
| min | Minutes |
| mL | Millilitres |
| mmol | Millimoles |
| mol | Moles |
| $NiBr_2$ | nickel(II) bromide |
| $NiCl_2.6H_2O$ | hexahydrate nickel(II) chloride |
| $NiI_2$ | nickel(II) iodide |
| NMR | nuclear magnetic resonance |
| NR | no reaction |
| OAc | Acetate |
| OTf | Triflate |

| | |
|---|---|
| $^{31}$P NMR | phosphorus NMR |
| Ph | phenyl group |
| R | alkyl group |
| s | Singlet |
| t | Triplet |
| THF | Tetrahydrofuran |
| TPPTS | tris(3-sulfophenyl)phosphine trisodium salt |

# Chapter 1

# Introduction

## 1.1 Cross-Coupling Reactions

### 1.1.1 Background

Carbon-carbon bond formation reactions catalyzed by various transition metals play an important role in organic chemistry. Cross-coupling reactions have found their way into several industries such as pharmaceuticals, natural products, and liquid crystals.[1, 2] The general reaction involves an organic electrophile (R-X) and a main group metal-based nucleophile (m-R’) in the presence of a transition metal catalyst (M) which form carbon-carbon and carbon-heteroatom R’-R bonds (Figure 1).[1, 2]

$$\text{R-X} + \text{m-R'} \xrightarrow{\text{M}} \text{R'-R} + \text{m-X}$$

R’ = alkenyl, aryl, alkyl; X = I, Br, Cl, OTf; M = Ni, Pd;
m =Mg (Kumada-Tamao-Corriu), Sn (Migita-Kosugi-Stille), B (Suzuki-Miyaura), etc

Figure 1. General cross-coupling reaction for C-C bond formation

### 1.1.2 Catalytic Cycle

The generally accepted catalytic cycle for cross-coupling reactions begins with the oxidative addition of R-X to the metal center, followed by transmetalation to produce diorganometal intermediates. The finally step is reductive elimination to regenerate the catalyst and form carbon-carbon bonds (Figure 2).[1] The general mechanistic pathway depends on the main group organometallic nucleophile and the transition metal catalyst used in the cross-coupling.

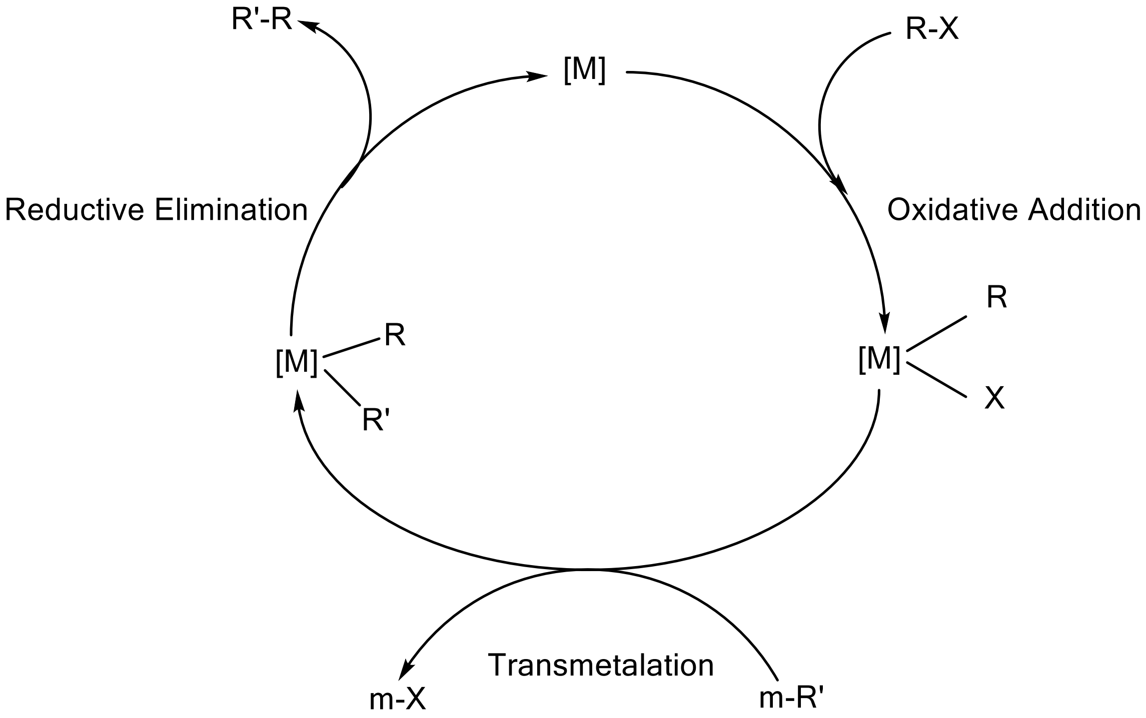


Figure 2. A general catalytic cycle

Most commonly used for cross coupling reactions catalyzed by Pd(0) compounds are believed to be type $PdL_2$ species (L = phosphine ligand) and are involved in catalytic cycles similar to the general mechanism.[2] The mechanism begins with the oxidative addition of RX to the catalytically active $PdL_2$, converting Pd(0) to a Pd(II) $PdRXL_2$ species via a two-electron process. Followed by transmetalation of metal-based nucleophiles m-nuc (m = Mg, Si, Sn, Zn, etc.; nuc or R'= alkyl, aryl, amide, alkoxy, etc.) to give $PdR(nuc)L_2$, facilitated by base. Finally, the reductive elimination of R-nuc forms the cross-coupling product and regenerates the catalyst ($PdL_2$) (Figure 3).

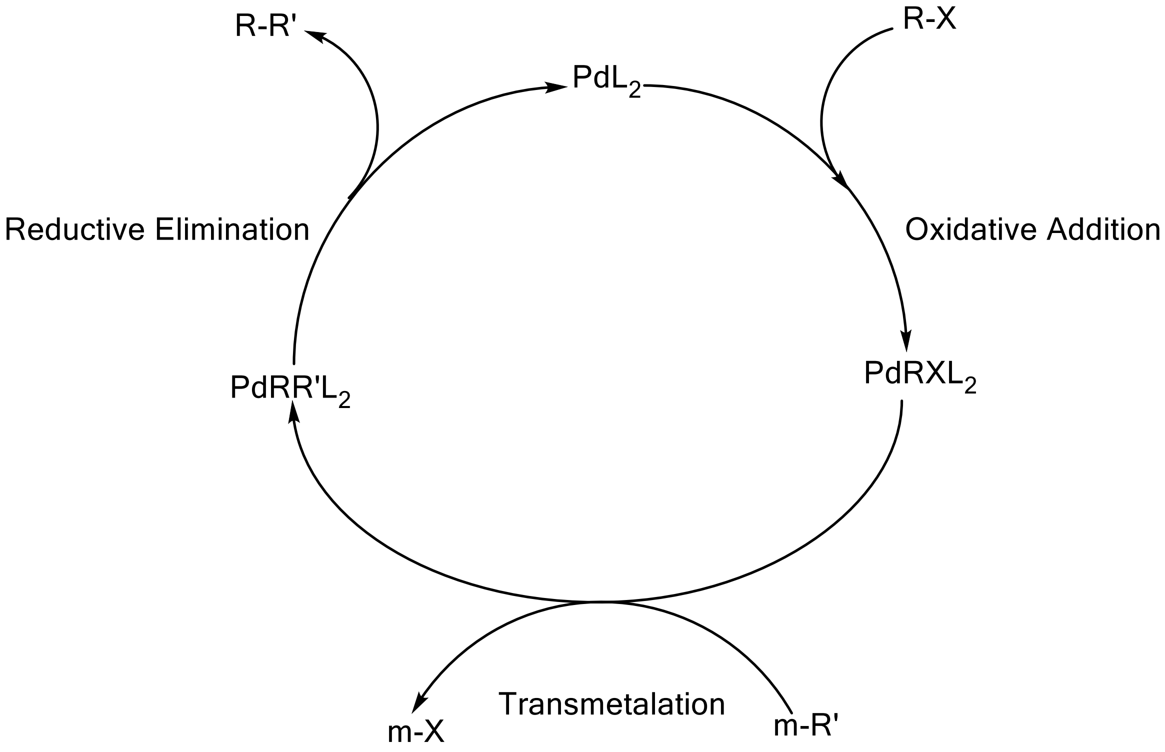


Figure 3. Conventional mechanism for palladium-catalyzed cross-coupling via two-electron transfer

### 1.1.3 Nickel-Catalyzed Cross-Coupling Reactions

Palladium and nickel complexes containing phosphine ligands are the most widely used catalytic precursors for cross-coupling reactions. Although many studies focusing on the development of Pd-based catalysts, some of the nickel-based catalytic systems have also been investigated. Nickel catalysts have important advantages over palladium, such as being cheaper and more environmentally friendly.[3]

The oxidative addition of alkyl halides using palladium as a catalyst is often either quite slow or do not occurs. When alkyl-palladium species are formed, they undergo a facile β-hydrogen elimination reaction that obstruct the reaction process.[4] β-Hydrogen elimination reactions are more difficult for nickel-based catalysts compared to palladium and therefore do not compete with reductive elimination steps that yield the products. Most palladium-catalyzed reactions follow the two-electron process mechanism (Figure 3). On the other hand, nickel has accessible Ni(0)/Ni(II) and Ni(I)/Ni(III) oxidation states that introduce a different reactivity mode and a radical mechanism.[4]

The catalytic cycles based on Ni(0)/Ni(II) are widespread in cross-coupling reactions and the reaction mechanism of Ni(0) species similar to that of Pd(0), as shown in Figure 3.[4] Ni(I) complexes are synthesized via comproportionation reactions between Ni(0) and Ni(II) complexes and are thus directly involved in the catalytic cycles of cross-coupling reactions. The Ni(I)-based mechanism undergoes a one-electron process in contrast to the Ni(0)/Ni(II) mechanism.

The proposed mechanism of the Ni(I)-based single electron catalytic cycle (Figure 4) consists of three main steps. Transmetalation with m-R’ produces $L_n$Ni-R’, followed by oxidative addition of R-X to $L_n$Ni-R’ to form NiXRR’$L_n$ via a radical pathway.[5,6] This pathway begins with the abstraction of a halogen atom from R-X by $L_n$Ni-R' to give the Ni(II) species, NiR'X$L_n$, plus an organic radical R•, followed by a combination of NiR’X$L_n$ and R•. The final step of this mechanism is the reductive elimination, producing the coupling product R’-R and regenerating the catalyst, $L_n$Ni-X.[5, 6]

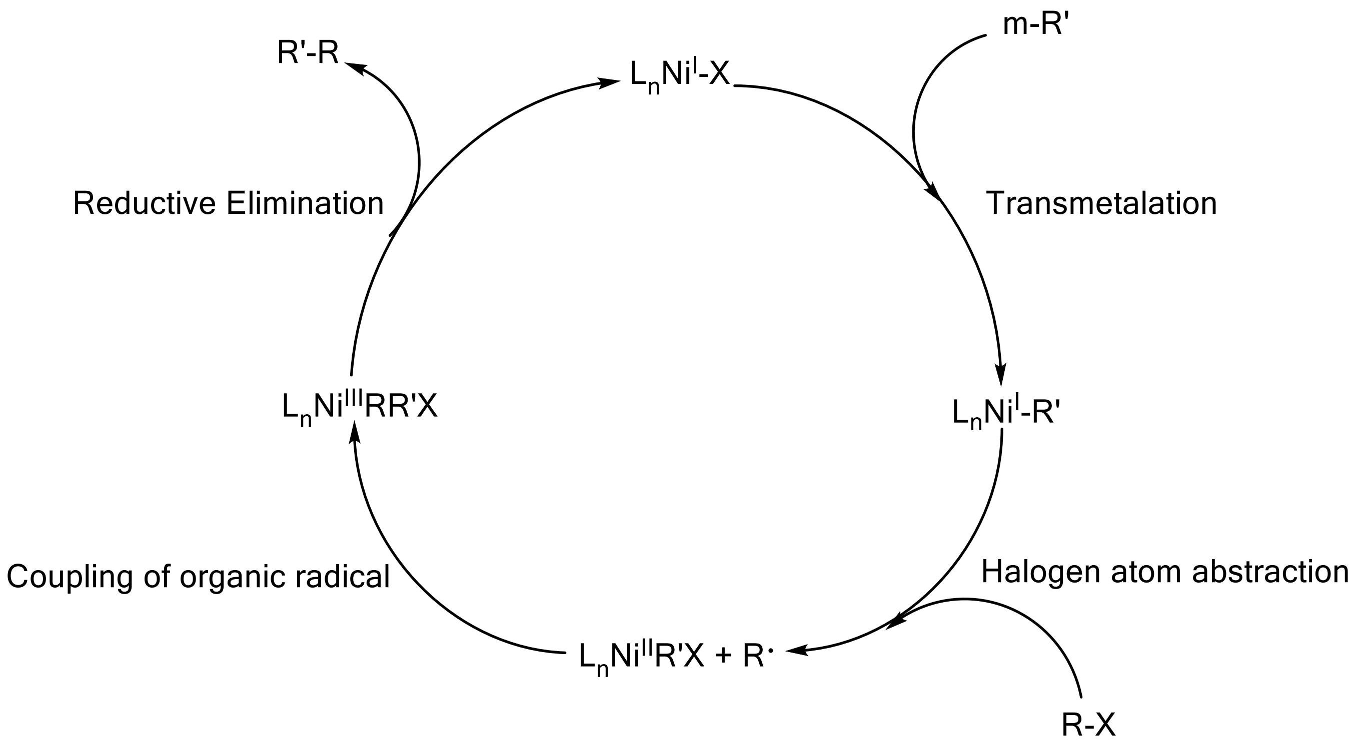


Figure 4. The proposed mechanism of Ni(I)-based, single electron catalytic cycle

### 1.1.4 Development of Nickel-Catalyzed Containing Phosphine Ligands in Cross-Coupling

Pioneering work on cross-coupling reactions of nickel-phosphine complexes with organic halides was reported in 1972 by Kumada et al., using Grignard reagents (Figure 5).[7]

$$\text{R-X} + \text{R'-MgX'} \xrightarrow[\text{Solvent}]{\text{Catalyst}} \text{R-R'} + \text{MgXX'}$$

Catalyst: $NiX_2L_2$ ($L_2$ = diphosphine), solvent: ether, RX: organic halide

Figure 5. Coupling of Grignard reagents with organic halides catalyzed by nickel complexes

The reaction was performed by adding a Grignard reagent to different organic halides in the presence of $NiCl_2$(dppe) as a catalyst. A possible mechanism for the formation of the desired product was also proposed. It was shown that the catalytic activity is strongly dependent on the electronic nature of the ligand and follows this order: $[NiCl_2(dppp)] > [NiCl_2(dppe)] > [NiCl_2(dmpe)] \approx [NiCl_2(PPh_3)_2] >> [NiCl_2(PEt_3)_2] \approx [NiCl_2(PPh_2Me)_2]$.[7] In the same year, Corriu published his work on the coupling of trans-β-bromostyrene with phenylmagnesium bromide using $Ni(acac)_2$ as a catalyst.[8] There are different kinds of cross-coupling reactions which utilize organometallic compounds other than the Kumad coupling, such as Suzuki coupling, Heck coupling, etc.

### 1.1.5 Suzuki- Miyaura Reactions

The Suzuki–Miyaura cross-coupling is a transition metal-catalyzed cross-coupling reaction between an organoboron compound and an organic halide (Figure 6).[9]

$$R^1\text{-}BY_2 + R^2\text{-}X \xrightarrow[\text{Base}]{\text{Catalyst/ Ligand}} R^1\text{-}R^2$$

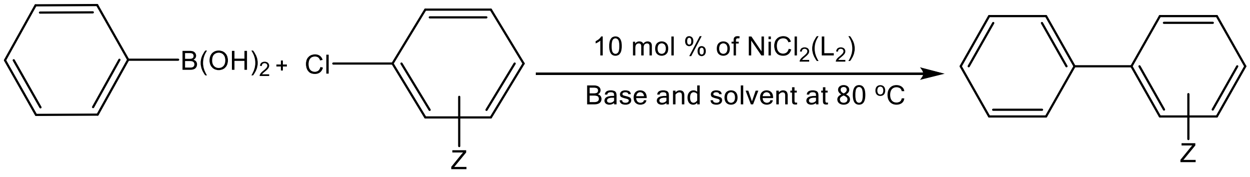
$R^1$= alkyl, alkenyl, allyl, aryl; $R^2$= alkenyl, aryl, alkyl; $Y_2$=OH, OR, R; X= Cl, Br, I, OTf

Figure 6. The general reaction for the Suzuki coupling

It has various applications in industries such as pharmaceuticals, agriculture and natural products. Suzuki coupling has many advantages such as the reactants are readily available, low toxicity, and stability towards air and water. [9,10] The organoboron compounds are also inexpensive, environmentally benign and easy to prepare in various ways.[9, 10]

The reaction mechanism follows a Ni(0)/Ni(II) pathway, which begins with the oxidative addition of organic halides to give a Ni(II) species. The next step is transmetalation of the Ni(II) intermediate, followed by reductive elimination to produce the coupled products and regenerate the Ni(0) catalyst.[9]

In previous years, researchers focused on Suzuki–Miyaura cross-coupling using palladium-based catalysts. However, many reactions are nowadays carried out using nickel as well as palladium-based catalysts. The first use of a nickel-based catalyst for Suzuki–Miyaura coupling was reported in 1996 by Miyaura and co-workers.[11] Their report described the use of [$NiCl_2(L_2)$]/BuLi catalyst systems with aryl chlorides and aryl boronic acids in the presence of $K_3PO_4$ as a base (Figure 7).



Z**=** 4-CN, 4-$COCH_3$, 4-NHAc, 3- or 4-$CH_3$, etc.

Figure 7. Nickel catalyst with aryl chlorides and aryl boronic acids

$NiCl_2L_2$ ($L_2$=dppf, dppe, dppp, dppb, $PPh_3$) was prepared in situ using BuLi as a reducing agent. The coupling was carried out using various conditions at 80°C.

In 1999, Genet worked on the cross-coupling of aryl chlorides using a water-soluble nickel catalyst. The reaction was done in situ using $NiCl_2$dppe, TPPTS and zinc (Figure 8).[12]

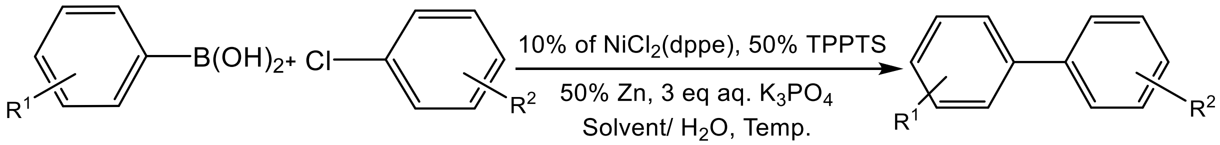


Figure 8. Water-soluble nickel catalyst from $NiCl_2$dppe and TPPTS

In 2004, Percec et al. described the use of $NiCl_2(L_2)/L_2$ ($L_2$=dppf, dppe, $PCy_3$, dppb, $PPh_3$) as a catalyst for the coupling of different aryl halides (Figure 9).[13] These studies demonstrated that the Suzuki–Miyaura coupling using nickel-based catalysts was highly sensitive to the reaction conditions, and any slight change in these conditions such as different nickel–phosphine complexes, ligands, organic halides, solvents, and bases significantly influenced the reaction outcome.

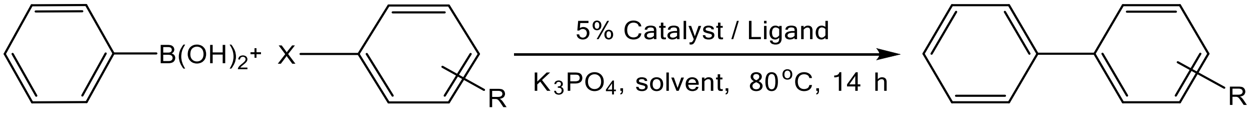
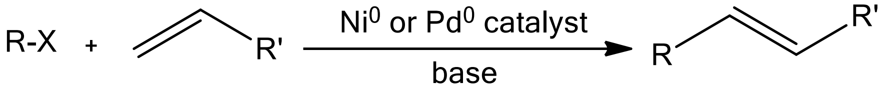


Figure 9. $NiCl_2$(dppe) catalyzed cross-coupling of aryl halides with arylboronic acids

High yields were obtained when $NiCl_2$dppe/$PPh_3$ was used. In general, using aryl chlorides, bromides, and iodides in dioxane and toluene with $K_3PO_4$ as a base gives good yields.

### 1.1.6 Mizoroki–Heck Reactions

The Heck cross-coupling reaction is a transition metal-catalyzed cross-coupling reaction between an organohalide and an alkene in presence of base producing a substituted alkene (Figure 10).[14]



R = alkenyl, aryl, allyl, alkynyl; R' = alkyl, alkenyl, aryl, $CO_2R$, OR

X = I, Br, Cl, OTf

Figure 10. The Mizoroki-Heck reactions

The traditional reaction mechanism with a $Pd(0)L_2$ species as catalyst ($L_2$= phosphine ligands) starts with organohalide oxidative addition, followed by alkene coordination due to the dissociation of the phosphine ligands or the halide anion. The vacant coordination site is therefore occupied by the alkene substrate, followed by migratory insertion of the olefin at the aryl-Pd or alkenyl-Pd bond.[14] The β-hydride elimination gives the coupling product, and base-mediated reductive elimination regenerates the palladium(0) catalyst by removing HX from the complex (Figure 11).[14]

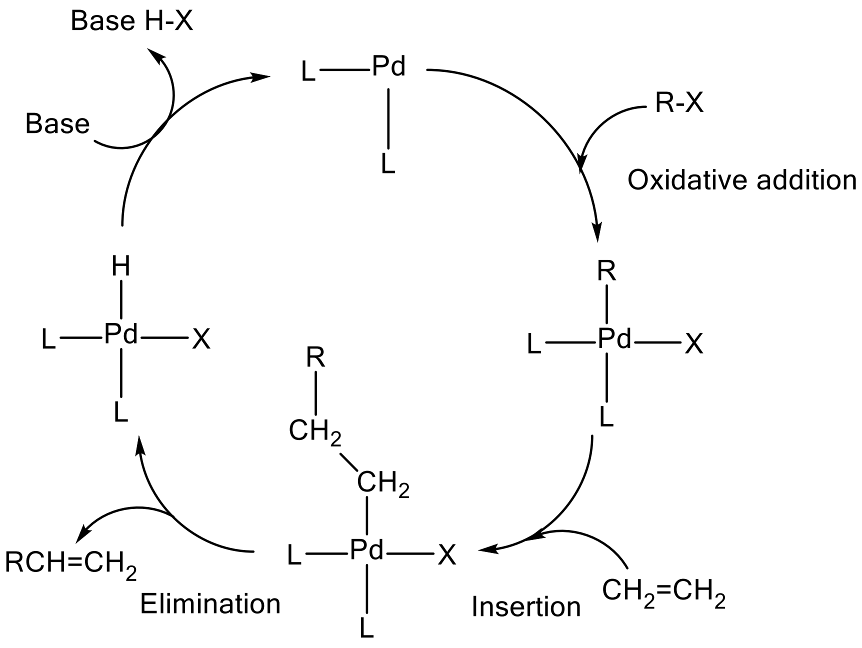


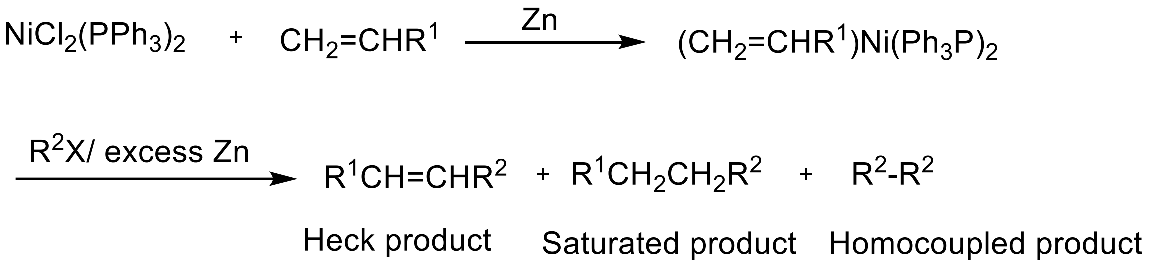
Figure 11. The traditional catalytic cycle for the Mizoroki-Heck reactions

Researchers recently began showing interest in transition metals other than Pd, such as Cu and Ni, for the Heck reactions. Compared to palladium, nickel is inexpensive and may show some bright prospects.

The reaction mechanism for nickel catalysts is similar to that for palladium.[14] However, compared to palladium, the nickel catalytic cycle exhibits both advantages and disadvantages.[14] Both the oxidative addition and insertion steps in the nickel catalytic cycle are faster than in the case of palladium. However, the β-hydrogen elimination step is more difficult for the Ni than for the Pd. The final step of the mechanism, namely HX elimination that regenerates the catalyst, is more difficult with Ni than with the Pd catalyst, which shows that the mechanism cannot regenerate the Ni(0) species effectively by HX elimination using a base similar to the one used for the Pd system.[14]

Researchers found that the Ni-catalyzed reaction required the use of a reducing agent to effect the catalytic cycle.[15]

The Ni-catalyzed Heck reaction was developed in 1986 by using $NiCl_2(PPh_3)_2$ in the presence of zinc dust as a reducing agent and changing the reaction conditions to make a comparison (Figure 12).[15]



$R^1$= EWG, $R^2$= aryl, X=Br, I, Cl

Figure 12. Nickel complex in the presence of zinc as a reductant in Heck reaction

The reaction gave the Heck product (*trans*-isomer) as well as saturated and homocoupled by-products; thus the yields were generally poor.

In 1988, Lebedev et al. studied the $NiCl_2(PPh_3)_2$/ zinc**/** pyridine/ bromobenzene catalytic system (Table 1).[16] They found that the addition of pyridine gave a high yield of stilbene and decreased DPB.

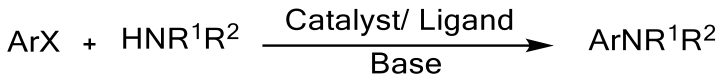
Table 1**.** Heck reactions of aryl bromides with nickel catalyst/ pyridine in the presence of zinc

| Entry | Styrene[a] | Zinc[a] | Pyridine[a] | Catalyst[b] | Stilbene[c] | DPB[c] |
|---|---|---|---|---|---|---|
| 1 | 4 | 1 | 4 | 5 | 92 | 25 |
| 3 | 4 | 1 | 8 | 5 | 90 | 9 |

a= mmol, b= mol.%, c=%yield

### 1.1.7 Buchwald-Hartwig Amination Reactions

The Buchwald-Hartwig amination is a cross-coupling reaction forming a carbon-nitrogen bond. This reaction is a transition metal-catalyzed cross-coupling reaction between an aryl halide and an amine in the presence of a strong base (Figure 13).[17]



$R^1$= alkyl, aryl, H; $R^2$= alkyl, aryl; X= Br, I, Cl, OTf

Figure 13. Buchwald-Hartwig amination reactions

The reaction mechanism starts with the oxidative addition of the aryl halide, followed by coordination of the amine then deprotonation by a strong base to form the amide. Finally, reductive elimination produces the aryl amine product and regenerates the catalyst.[17, 18]

Most of the amination studies were done using $Ni(COD)_2$ as catalyst with various excess ligands such as dppf, dppe, dppp, etc. under various conditions to obtain good yields. However, no research was done on using $NiCl_2$dppe or $Ni(dppe)_2$ for the amination reaction.[19,20]

## 1.2 Ligand

### 1.2.1 1, 2-Bis (diphenylphosphino) ethane= dppe

1,2-Bis(diphenylphosphino)ethane is a colorless crystalline compound which is often used as a ligand in organometallic chemistry. Its $^1H$ NMR spectrum is shown in Figure A1, and its $^{31}P$ NMR spectrum exhibits a resonance at –11.63 ppm (Figure A2).

1,2-Bis(diphenylphosphino)ethane can be prepared by following the procedure of Hewertson and Watson which was performed in liquid ammonia.[21] The first step of the dppe synthesis is the reaction of sodium and triphenylphosphine ($P(C_6H_5)_3$) in liquid ammonia to give $NaPPh_2$ (Figure 14). [21]

$$Ph_3P + 2\ Na \longrightarrow NaPPh_2 + NaPh$$

Figure 14. The first step of dppe preparation

The mixture has a deep orange colour due to sodium diphenylphosphide. The second step is adding dichloroethane to react with sodium diphenylphosphide to produce the product (dppe) in good yield (82%) (Figure 15).

$$2\ NaPPh_2 + C_2H_5Cl_2 \longrightarrow Ph_2PCH_2CH_2PPh_2 + 2\ NaCl$$

Figure 15. The final step of dppe preparation

## 1.3 Research Objectives

Palladium catalysts dominate the cross-coupling reactions, but researchers have switched their attention to nickel catalysts due to their lower cost and the high abundance of nickel complexes. There are a number of publications focused on Ni(0) and Ni(II) catalysts for cross-coupling reactions. On the other hand, there are few reported attempts of using Ni(I) as a catalytic species. We used the potentially important dppe ligand in our research. Although the chemistry of nickel complexes containing phosphorus ligands has been studied, there is little data on nickel complexes with dppe.

The objectives of this thesis are to synthesize and characterize nickel compounds (Ni(II), Ni(0), Ni(I)) containing different halides and investigate their abilities to catalyze different cross-coupling reactions, e.g., Suzuki-Miyaura, Mizoroki-Heck and Buchwald-Hartwig.

# Chapter 2

# Experimental Section

## 2.1.1 General Procedures

All syntheses were carried out under a dry, deoxygenated argon atmosphere using standard Schlenk line techniques. Glassware was cleaned well and dried in an oven overnight. Air sensitive chemicals were kept in tightly closed vials and handled under a nitrogen atmosphere in an LCBT-1 Bench Top Glovebox. Solvents were purchased from EMD Chemicals Inc. and dried by storage over activated 3Å molecular sieves under an argon atmosphere for at least 24 h. NMR spectra were obtained using Bruker AV400, AV500 and AV600 spectrometers. $^{1}$H NMR data are referenced to TMS at δ 0 ppm via the residual protons signals of the deuterated solvents and $^{31}$P NMR spectra were referenced to external 85% $H_3PO_4$. GC analyses were recorded on a Varian 3900 GC equipped with a CP-8400 autosampler, a CP-1177 injector, an FID detector and a Varian WCOT Fused Silica column (CP-Sil 8CB, 25 m x 0.32 mm ID, DF = 0.52). EPR spectra were run in the solid state at 77 K by Dr. Bruce Hill of the Department of Biochemistry, Queen’s University. Elemental analyses were conducted by Canadian Microanalytical Service Ltd., Delta, BC.

## 2.1.2 Chemical Supplies

1,2-Bis(diphenylphosphino)ethane (dppe; NMR spectra in Figures A1, A2), zinc dust and $NiBr_2$ were purchased from Strem Chemicals, $NiI_2$ from Sigma Aldrich, and $NiCl_2.6H_2O$ from Sigma-Aldrich and Fisher Scientific. All other chemicals were purchased from Sigma-Aldrich. Deuterated solvents were purchased from Cambridge Isotope Laboratories.

### 2.3 Synthesis of $NiX_2$dppe (X = Cl, Br, I)

#### 2.3.1 Synthesis of $NiCl_2$dppe[22]

$$NiCl_2.6H_2O + \text{dppe} \xrightarrow{\text{methanol/ 2-propanol}} NiCl_2\text{dppe}$$

Figure 16. Preparation of $NiCl_2$dppe

A solution of 0.96 g $NiCl_2.6H_2O$ (4.02 mmol) in 90 mL of warm 2:1 2-propanol:methanol was added to a hot solution of 1.51 g dppe (3.78 mmol) in 150 mL of 2-propanol, giving 1.82 g of an orange precipitate which was filtered, washed with ethyl ether and dried under reduced pressure (yield 91.5%). The orange powder was recrystallized from hot $CH_2Cl_2$. $^1$H NMR ($CD_2Cl_2$, 500 MHz): δ 2.19 (m, 4H, $CH_2$), 7.56 (m, 8H, Ph), 7.66 (m, 4H, Ph), 8.02 (m, 8H, Ph). $^{31}$P NMR ($CD_2Cl_2$): δ 57.53 (Figures A3, A4).

#### 2.3.2 Synthesis of $NiBr_2$dppe[22]

$$NiBr_2 + \text{dppe} \xrightarrow[\text{reflux, 2h}]{\text{methanol/ toluene}} NiBr_2\text{dppe}$$

Figure 17. Preparation of $NiBr_2$dppe

A mixture of 1.57 g $NiBr_2$ (7.15 mmol) in 150 mL warm methanol was added to a solution of 1.91 g dppe (4.81 mmol) in 20 mL hot toluene to give a red precipitate. The mixture was refluxed for 2 h and the red product was filtered and dried in vacuum. Yield was 2.4 g (81%). $^1$H NMR ($CD_2Cl_2$, 400 MHz): δ 2.15 (m, 4H, $CH_2$), 7.57 (m, 8H, Ph), 7.63 (m, 4H, Ph), 8.02 (m, 8H, Ph). $^{31}$P NMR ($CD_2Cl_2$): δ 67.11 (Figures A5, A6).

### 2.3.3 Synthesis of $NiI_2$dppe[22]

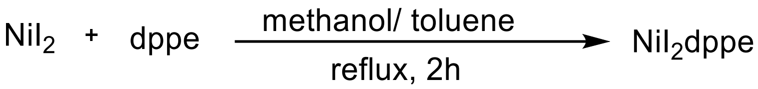


Figure 18. Preparation of $NiI_2$dppe

This compound was synthesized according to similar procedure as $NiBr_2$dppe but using 2.29 g $NiI_2$ (7.15 mmol) in 150 mL warm methanol. The mixture was added to a hot solution of 1.91 g dppe (4.81 mmol) in 20 mL toluene to give a purple precipitate. The reaction mixture was refluxed for 2 h and the purple powder was collected and dried in vacuum. Yield was 2.72 g (79%). $^1H$ NMR ($CD_2Cl_2$, 400 MHz): δ 2.01 (m, 4H, $CH_2$), 7.46 (m, 12H, Ph), 7.86 (m, 8H, Ph). $^{31}P$ NMR ($CD_2Cl_2$): δ 77.56 (Figures A7, A8).

## 2.4 Synthesis of $Ni(dppe)_2$ Utilizing $NiX_2$dppe as Starting Materials

### 2.4.1 Synthesis of $Ni(dppe)_2$ Utilizing $NiCl_2$dppe as Starting Material

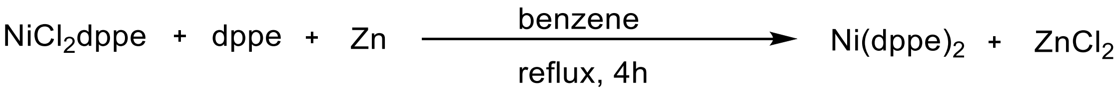
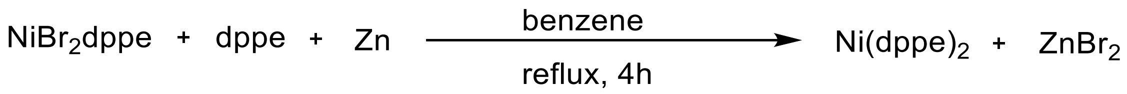


Figure 19. Preparation of $Ni(dppe)_2$ utilizing $NiCl_2$dppe as starting material

Under argon, a mixture of 1.0 g zinc (15.3 mmol), 1.5 g $NiCl_2$dppe (2.8 mmol) and 1.13 g dppe (2.8 mmol) in 80 mL dry benzene was refluxed for 4 h. The reaction mixture was filtered to give a colourless precipitate, mixed with zinc, and a yellow solution. The benzene solvent was removed under vacuum to give 0.89 g of yellow $Ni(dppe)_2$ (yield 37%). Yellow $Ni(dppe)_2$ is air-sensitive, turning white when exposed to air, and it was therefore stored in the glove box. $^1H$ NMR (toluene-$d_8$, 600 MHz): δ 2.09 (br s, 11H, $CH_2$, toluene), 6.93 (br m, 27H, Ph, toluene), 7.43 (br s, 18H, Ph, toluene). $^{31}P$ NMR (toluene-$d_8$, 600 MHz): δ 44.30 (Figures A9, A10).

The $^1H$ and $^{31}P$ NMR spectra of the colorless precipitate in dmso-$d_6$ are shown in Figures A11 and A12 respectively, and will be discussed in the Results and Discussion section. Synthesis of Ni(dppe)$_2$ was also attempted without added dppe, but no colour change of the reaction mixture was observed and only NiCl$_2$dppe was isolated.

### 2.4.2 Synthesis of Ni(dppe)$_2$ Utilizing NiBr$_2$dppe as Starting Material

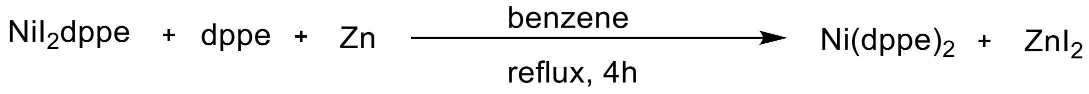


$$\mathrm{NiBr_2dppe} + \mathrm{dppe} + \mathrm{Zn} \xrightarrow[\text{reflux, 4h}]{\text{benzene}} \mathrm{Ni(dppe)_2} + \mathrm{ZnBr_2}$$

Figure 20. Preparation of Ni(dppe)$_2$ utilizing NiBr$_2$dppe as starting material

Under argon, a mixture of 1.0 g zinc (15.3 mmol), 1.5 g NiBr$_2$dppe (2.43 mmol) and 0.96 g dppe (2.43 mmol) in 80 mL dry benzene was refluxed for 4 h. The reaction mixture was filtered, giving a colourless precipitate mixed with zinc and a yellow solution of Ni(dppe)$_2$. The benzene solvent was removed under vacuum, giving 0.89 g of yellow Ni(dppe)$_2$. Yield (37%). $^1H$ NMR (toluene-$d_8$, 400 MHz): δ 2.13 (br s, 11H, CH$_2$, toluene), 6.96 (br, 27H, Ph, toluene), 7.46 (br, 18H, Ph, toluene). $^{31}P$ NMR (toluene-$d_8$): δ 45.46 (Figure A13, A14).

### 2.4.3 Synthesis of Ni(dppe)$_2$ Utilizing NiI$_2$dppe as Starting Material



$$\mathrm{NiI_2dppe} + \mathrm{dppe} + \mathrm{Zn} \xrightarrow[\text{reflux, 4h}]{\text{benzene}} \mathrm{Ni(dppe)_2} + \mathrm{ZnI_2}$$

Figure 21. Preparation of Ni(dppe)$_2$ utilizing NiI$_2$dppe as starting material

Under argon, a freshly prepared mixture of 1.0 g zinc (15.3 mmol), 1.74 g NiI$_2$dppe (2.43 mmol) and 0.96 g dppe (2.43 mmol) in 80 mL dry benzene turned yellowish-green immediately; after 10 min., it turned purple. The mixture was refluxed for 4 h and then filtered to give a colourless precipitate mixed with zinc and a yellow solution of Ni(dppe)$_2$. The solvent was removed under vacuum to give 0.97 g of yellow product. Yield 40%. The $^1$H NMR spectrum (toluene-d$_8$, 400 MHz) exhibited the resonances of Ni(dppe)$_2$ (δ 2.12, 6.95, 7.16 and 7.45) in addition to several other unidentified peaks. The $^{31}$P NMR spectrum (toluene-d$_8$) exhibited a single resonance at δ 45.40 (Figures A15, A16).

## 2.5 Attempted Syntheses of Ni(I) Compounds via Comproportionation Reactions

### 2.5.1 Reaction of NiCl$_2$dppe and Ni(dppe)$_2$ (1:1)

$$\mathrm{NiCl_2dppe} + \mathrm{Ni(dppe)_2} \xrightarrow{\text{benzene}} [\mathrm{NiCl(dppe)_n}]_x$$

Figure 22. Reaction of NiCl$_2$dppe and Ni(dppe)$_2$ (1:1)

Under argon, a mixture of 0.32 g NiCl$_2$dppe (0.6 mmol) and 0.51 g Ni(dppe)$_2$ (0.6 mmol) in 50 mL dry benzene was refluxed for 24 h at room temperature. There was no colour change. Unreacted NiCl$_2$dppe was filtered off and identified by NMR spectroscopy (Figure A17, A18), and unreacted Ni(dppe)$_2$ was obtained on removing the solvent from the filtrate (Figures A19, A20).

### 2.5.2 Reaction of NiCl$_2$dppe and Ni(dppe)$_2$ (1:2)

Under argon, a mixture of 0.215 g NiCl$_2$dppe (0.409 mmol) and 0.70 g Ni(dppe)$_2$ (0.82 mmol) in 48 mL dry benzene was stirred at room temperature for 24 h to give pale yellow precipitate and a yellow solution. The pale yellow precipitate was filtered off, leaving unreacted Ni(dppe)$_2$ in solution (Figure A21, A22) and was washed with benzene and dried under vacuum for 3 h in a hot water bath. *Anal.* Calcd for NiCl(dppe), C 63.40, H, 4.91, Cl 7.20; for $NiCl(dppe)_2$, C, 70.10; H, 5.43; Cl, 4.00. Found: C, 68.74; H, 5.61; Cl, 2.16.

### 2.5.3 Reaction of $NiBr_2$dppe and $Ni(dppe)_2$ (1:1)

$$\mathrm{NiBr_2dppe} + \mathrm{Ni(dppe)_2} \xrightarrow{\text{benzene}} [\mathrm{NiBr(dppe)}_n]_x$$

Figure 23. Reaction of $NiBr_2$dppe and $Ni(dppe)_2$ (1:1)

Under argon, a mixture of 0.22 g $Ni(dppe)Br_2$ (0.35 mmol) and 0.30 g $Ni(dppe)_2$ (0.35 mmol) in 48 mL benzene was refluxed for 24 h at room temperature. There was no colour change, and the reaction mixture was filtered to give unreacted $Ni(dppe)Br_2$ (red precipitate) (Figure A23, A24) and $Ni(dppe)_2$ in solution (Figure A25, A26). The same procedure in THF gives a red precipitate (Figure A27, A28) and light red solid from the filtrate (Figure A29, A30).

### 2.5.4 Reaction of $NiI_2$dppe and $Ni(dppe)_2$ (1:1)

$$\mathrm{NiI_2dppe} + \mathrm{Ni(dppe)_2} \xrightarrow{\text{benzene}} [\mathrm{NiI(dppe)}_n]_x$$

Figure 24. Reaction of $NiI_2$dppe and $Ni(dppe)_2$ (1:1)

Under argon, a mixture 0.43 g $Ni(dppe)I_2$ (0.60 mmol) and 0.51 g $Ni(dppe)_2$ (0.60 mmol) in 50 mL benzene was refluxed for 24 h at room temperature. There was no colour change, and the reaction mixture was filtered to give unreacted $Ni(dppe)I_2$ (purple precipitate) (Figure A31, A32) and $Ni(dppe)_2$ in solution (Figure A33, A34).

## 2.6 Cross-Coupling Reactions

### 2.6.1 Buchwald-Hartwig Amination Reactions

#### 2.6.1.1 Utilizing 4-Bromoanisole

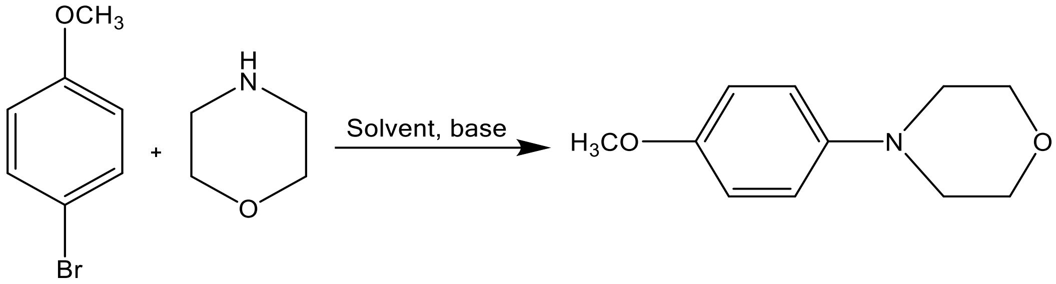


Figure 25. Amination reactions with 4-bromoanisole

A mixture of 0.17 g Ni(dppe)$_2$ (0.2 mmol), 0.37 g 4-bromoanisole (2 mmol), 0.21 g morpholine (2.4 mmol) and 0.27 g NaO$^t$Bu (2.8 mmol) in 6 mL dry dioxane in a test tube was stirred under argon at 75 $^oC$ for 24 h, with 0.1 mL aliquots being removed at specified intervals, diluted with ~10 mL dioxane and analysed by GC. A similar reaction was performed using dry toluene.

A mixture of 0.105 g NiCl$_2$dppe (0.2 mmol), 0.37 g 4-bromoanisole (2 mmol), 0.21 g morpholine (2.4 mmol) and 0.22 g LiO$^t$Bu (2.8 mmol) in 6 mL dry dioxane was stirred under argon at 85 $^oC$ for 24 h, with 0.1 mL aliquots being removed at specified intervals, diluted with ~10 mL dioxane and analysed by GC. The reaction was performed similarly using NiCl(dppe)$_2$ catalysts as well under the same conditions.

#### 2.6.1.2 Utilizing 2-Iodopropane

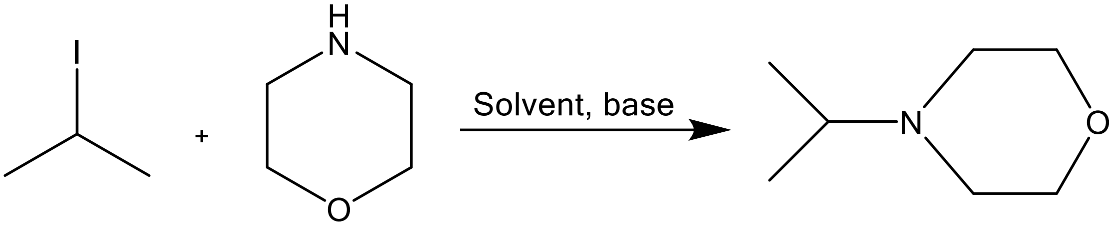


Figure 26. Amination reactions with 2-iodopropane

A mixture of 0.17 g Ni(dppe)$_2$ (0.2 mmol), 0.34 g 2-idopropane (2 mmol), 0.21 g morpholine (2.4 mmol) and 0.27 g NaO$^t$Bu (2.8 mmol) in 6 mL dry dioxane was stirred under argon at 85 $^o$C for 24 h, with 0.1 mL aliquots being removed at specified intervals, diluted with ~10 mL dioxane and analysed by GC.

#### 2.6.1.3 Utilizing 1-Iodobutane

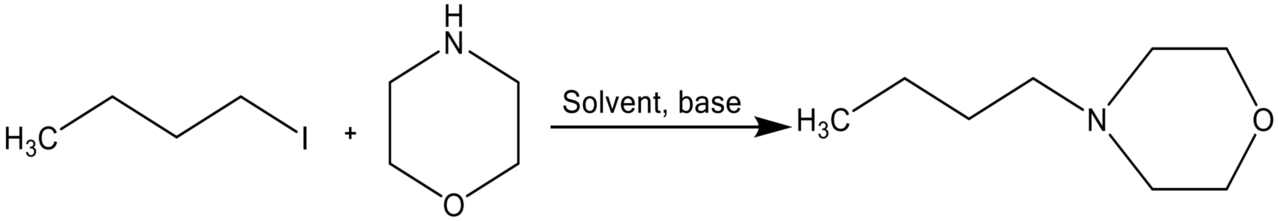


Figure 27. Amination reactions with 1-iodobutane

A mixture of 0.17 g Ni(dppe)$_2$ (0.2 mmol), 0.37 g iodobutane (2 mmol), 0.21 g morpholine (2.4 mmol) and 0.27 g NaO$^t$Bu (2.8 mmoles) in 6 mL dry toluene was stirred under argon at 85 °C for 24 h, with 0.1 mL aliquots being removed at specified intervals, diluted with ~10 mL toluene and analysed by GC.

A mixture of 0.105 g $NiCl_2$dppe (0.2 mmol), 0.37 g iodobutane (2 mmol), 0.21 g morpholine (2.4 mmol) and 0.27 g $LiO^tBu$ (2.8 mmol) in 6 mL non-dried dioxane was stirred under argon at 85 °C for 24 h, with 0.1 mL aliquots being removed at specified intervals, diluted with 10 mL dioxane and analysed by GC.

### 2.6.2 Heck-Mizoroki Reactions

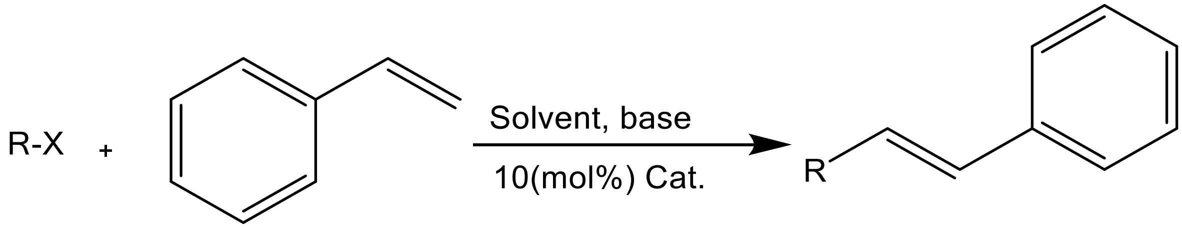


Figure 28. Heck reactions with bromobenzene

#### 2.6.2.1 Utilizing Bromobenzene

A mixture of 0.053 g $NiCl_2$dppe (0.1 mmol), 0.065 g zinc dust (1 mmol), 0.32 g pyridine (4 mmol), 0.42 g styrene (4 mmol), 0.16 g bromobenzene (1 mmol) in 3 mL dry acetonitrile was stirred under argon for 4 h at 65 °C, with 0.1 mL of aliquots being removed at specified intervals, diluted with ~10 mL acetonitrile and analysed by GC.

A mixture of 0.089 g $NiCl(dppe)_2$ (0.1 mmol) 0.32 g pyridine (4 mmol), 0.42 g styrene (4 mmol), 0.16 g bromobenzene (1 mmol) in 3 mL dry acetonitrile was stirred under argon at 65 °C for 4 h, with 0.1 mL aliquots being removed at specified intervals, diluted with ~10 mL acetonitrile and analysed by GC.

### 2.6.3 Suzuki- Miyaura Reactions

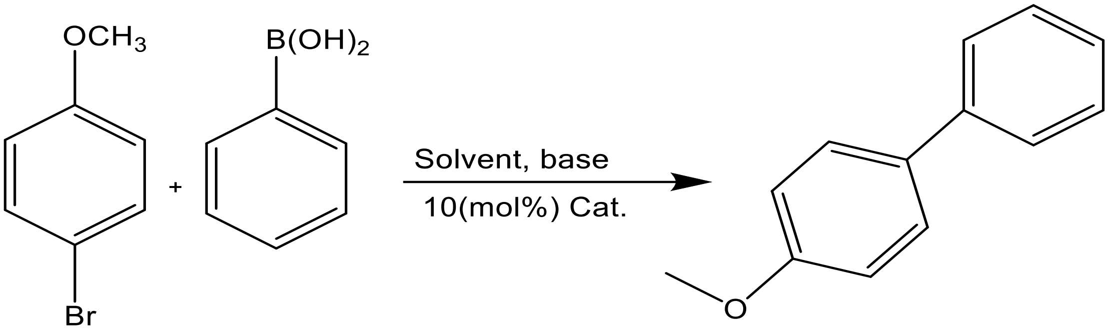


Figure 29. Suzuki reactions with 4-bromoanisole

A mixture of 0.086 g Ni(dppe)$_2$ (0.1 mmol), 0.12 g phenylboronic acid (1 mmol), 0.19 g 4-bromoanisole (1 mmol), 0.65 g $Cs_2CO_3$ (2 mmol) in 3 mL THF was stirred under argon at 56 $^oC$ for 22 h, with 0.1 mL aliquots being removed at specified intervals, diluted by ~10 mL of THF and analyzed by GC. The reaction was performed similarly using benzene and dioxane as solvent and different catalysts (NiCl(dppe)$_2$, NiCl$_2$dppe) as well under the same conditions.

# Chapter 3

# Results and Discussion

## 3.1 Syntheses and Properties of the Complexes NiX$_2$dppe (X = Cl, Br, I)

The three compounds NiX$_2$dppe were all prepared using literature methods,[22] and all were identified by their $^1$H and $^{31}$P NMR spectra (Figures A3-A8) which agree with literature data.[23,24] All assume square-planar structures and thus all are diamagnetic.

## 3.2 Synthesis and Properties of the Ni(0) Complex Ni(dppe)$_2$

### 3.2.1 Utilizing NiCl$_2$dppe as Starting Material

For the synthesis of Ni(dppe)$_2$, the reaction involved reduction of NiCl$_2$dppe to Ni(0) using zinc dust in the presence of one equivalent of dppe under argon. Several solvents were assessed (benzene, toluene, THF, dioxane), and the best solvent for the synthesis was found to be benzene. The reaction was done at room temperature over 24 h, but to generate Ni(0) faster we also performed it under reflux for 4 to 5 h. In most cases, a colourless precipitate mixed with zinc and a yellow solution formed and, after filtration, the benzene solvent was removed under vacuum to give Ni(dppe)$_2$ in 37% yield. Yellow Ni(dppe)$_2$ is air-sensitive, turning white when exposed to air, and it was therefore stored in the glove box. Synthesis of Ni(dppe)$_2$ was also attempted without added dppe but no colour change was observed and only NiCl$_2$dppe was isolated. The $^1$H and $^{31}$P NMR spectra (Figures A9, A10) were consistent with literature values.[25] Using an HMBC spectrum (Figure A35), the $^{31}$P resonance at δ 44.30 correlated to $^1$H resonances at δ 2.09, 6.93 and 7.43.

The $^1H$ and $^{31}P$ NMR spectra of the colorless precipitate in dmso-$d_6$ are shown in Figures A11 and A12, and an EPR spectrum at 77 K (solid state) shown in Figure A36.

### 3.2.2 Utilizing $NiBr_2$dppe as Starting Material

In the synthesis of Ni(dppe)$_2$, the reaction involved reduction of $NiBr_2$dppe to Ni(0) via zinc dust in benzene under reflux for 4 to 5 h. A colourless precipitate mixed with zinc and a yellow solution was formed. After filtration, the benzene solvent was removed under vacuum to give yellow Ni(dppe)$_2$ in 37% yield. The $^1H$ NMR spectrum (Figure A13) exhibited resonances at δ 2.13 (br s, $CH_2$, toluene), 6.9 (br, Ph, toluene), 7.46 (br, Ph, toluene). The $^{31}P$ NMR spectrum exhibited a sharp singlet at δ 45.63 (Figure A14).

### 3.2.3 Utilizing $NiI_2$dppe as Starting Material

The reduction of $NiI_2$dppe to Ni(0) with zinc dust in benzene involved refluxing for 4 to 5 h to give a colourless precipitate mixed with zinc and a yellow solution. After filtration, the benzene solvent was removed under vacuum to give yellow Ni(dppe)$_2$ in 40% yield. The $^1H$ NMR spectrum (Figure A15) exhibited broadened resonances of Ni(dppe)$_2$ at δ 2.12, 6.95, 7.16 and 7.45 in addition to several other unidentified peaks. The $^{31}P$ NMR spectrum of Ni(dppe)$_2$ exhibited a sharp singlet at δ 45.63 (Figure A16).

In conclusion, the best-starting material to produce Ni(dppe)$_2$ is $NiCl_2$dppe.

## 3.3 Attempted Syntheses of Ni(I) Compounds via Comproportionation Reactions

### 3.3.1 Comproportionation Reactions of $NiCl_2$dppe and Ni(dppe)$_2$

Comproportionation reaction as in Figure 22 (n=1, 2/x=1, 2) was attempted using $NiCl_2$dppe and Ni(dppe)$_2$ (1:1 molar ratio) in benzene. The reaction was carried out under reflux for 5 to 7 h, and at room temperature for two to three days. In all cases, unreacted $NiCl_2$dppe was filtered off and identified by NMR spectroscopy (Figure A17, A18), and unreacted Ni(dppe)$_2$ was obtained by removing the solvent from the filtrate (Figures A19, A20).

This reaction also was also attempted using NiCl$_2$dppe and Ni(dppe)$_2$ (1:2) ratio in benzene at room temperature for 24 h. This time the reaction mixture resulted in a pale yellow precipitate and a solution of unreacted Ni(dppe)$_2$ (Figure A21, A22). The pale yellow precipitate was filtered, washed with benzene and dried under vacuum for 3 h in a hot water bath, and was characterized using elemental analysis because the low solubility and the paramagnetic shifts of Ni(I) compounds are difficult to identify in NMR spectra. Although the crude material could not be recrystallized, the analytical data correspond most closely to the formula NiCl(dppe)$_2$.

The zinc reduction of NiCl$_2$dppe, as we discussed above, gave a pale yellow precipitate mixed with zinc and a solution of Ni(dppe)$_2$. The reaction ran for 5 to 7 h, and also overnight, but the pale yellow precipitate did not disappear and the amount of Ni(dppe)$_2$ remained the same. We assumed that the pale yellow precipitate might contain a Ni(I) complex, so we used the technique of electron paramagnetic resonance (EPR) spectroscopy to obtain useful information (Figure A36). As can be seen, a very complex spectrum was observed, suggesting the possibility of there being more than one Ni(I) species present.

A marker shows the position of $g = 2.00$, determined following the following formula:

$$g = 0.714484\ (\text{frequency (MHz)}/\text{Field strength (gauss)})$$

The pale precipitate might contain Ni(I) according to the $g = 2.1 – 2.2$, which agrees with the literature data.[26]

Similar reactions involving $NiBr_2$dppe and $NiI_2$dppe appeared not to work because no colour changes were observed and because starting materials were identified by $^1H$ and $^{31}P$ NMR spectroscopy (Figures A23 – A34).

## 3.4 Cross-Coupling Reactions

### 3.4.1 Buchwald-Hartwig Amination Reactions

The catalytic activities of $NiCl_2$dppe, $Ni(dppe)_2$ and Ni(I) were assessed for the Buchwald-Hartwig amination reactions involving various organic halides with morpholine. Different substrate, parameters, bases, temperature and solvents were used. In no cases was catalysis observed (Table 2).

Table 2. Nickel-Catalyzed Amination of aryl and alkyl halides

| Entry | Organic Halide | Catalyst | Temp. | Base | Solvent | Yield[a] |
|---|---|---|---|---|---|---|
| 1 | 4-MeO-$C_6H_4$ Br | $Ni(dppe)_2$ | 75°C | NaO$^t$Bu | Dioxane | NR |
| 2 | 4-MeO-$C_6H_4$ Br | $Ni(dppe)_2$ | 75°C | NaO$^t$Bu | Toluene | NR |
| 3 | 4-MeO-$C_6H_4$ Br | $NiCl(dppe)_2$ | 75°C | NaO$^t$Bu | Dioxane | NR |
| 4 | 4-MeO-$C_6H_4$ Br | $NiCl_2$dppe | 90°C | LiO$^t$Bu | Dioxane | NR |
| 5 | $(CH_3)_2CHI$ | $Ni(dppe)_2$ | 85°C | NaO$^t$Bu | Dioxane | NR |
| 6 | $CH_3(CH_2)_3I$ | $Ni(dppe)_2$ | 85°C | LiO$^t$Bu | Toluene | 95-100% |
| 7 | $CH_3(CH_2)_3I$ | $Ni(dppe)_2$ | 85°C | LiO$^t$Bu | Dioxane | 95-100% |
| 8 | $CH_3(CH_2)_3I$ | $Ni(dppe)_2$ [b] | 85°C | LiOtBu | Dioxane[c] | 95-100% |
| 9 | $CH_3(CH_2)_3I$ | $NiCl_2$dppe | 85°C | LiOtBu | Dioxane[c] | 95-100% |
| 10 | $CH_3(CH_2)_3I$ | No cat. | 85°C | LiOtBu | Dioxane | 95-100% |

a=based on GC,b=with access dppe 5%, c=dry and wet solvent

Using different catalysts (Ni(II), Ni(0) and Ni(I)) and parameters, the catalytic runs were unsuccessful with 4-bromoanisole. Unfortunately, when the catalytic run was performed with alkyl halide such as 1-iodobutane as shown in entry 6-9 (Table 2), the reaction goes in controlled run as alkyl halide goes through $SN_2$ reactions. We performed the reaction under the same conditions (entry 6-9) with an absent of catalysts in entry 10 (control experiment).

### 3.4.2 Heck- Mizoroki Coupling Reactions

Heck reactions were attempted using Ni(0) and Ni(I) catalysts under the same conditions (base, solvent and temperature) as shown in Table 3.

Table 3. Heck reactions of bromobenzene using $Ni(dppe)_2$ and Ni(I) as catalyst

| Entry | Organic Halide | Catalyst | Temp. | Base | Solvent | Yield[a] |
|---|---|---|---|---|---|---|
| **1** | $C_6H_5Br$ | $Ni(dppe)_2$ | 65°C | Pyridine | Acetonitrile | 97% |
| **2** | $C_6H_5Br$ | $NiCl_2dppe$[b] | 65°C | Pyridine | Acetonitrile | 97% |
| **3** | $C_6H_5Br$ | Ni(I)[c] | 65°C | Pyridine | Acetonitrile | NR |
| **4** | $C_6H_5Br$ | No cat. | 65°C | Pyridine | Acetonitrile | NR |

a= based on GC, b= zinc addition, c= $NiCl(dppe)_2$

The product, *trans*-stilbene, was obtained with the Ni(0) catalytic system based on GC. The reaction was performed using bromobenzene and $NiCl_2dppe$ in presence of zinc and pyridine in acetonitrile. The reaction also was attempted using Ni(I) but it didn't give a product which supports the traditional two electron transfer process mechanism as shown in Figure 11.

### 3.4.3 Suzuki-Miyaura Reactions

Bromoanisole and phenylboronic acid were used as reactants in Suzuki coupling. Different solvents were used (dioxane, benzene, THF) and catalytic runs were performed with Ni(I), Ni(II) and Ni(0) complexes but unfortunately none gave significant product (Table 4).

Table 4. Nickel-Catalyzed Suzuki coupling of 4-bromoanisole

| **Entry** | **Organic Halide** | **Catalyst** | **Temp.** | **Base** | **Solvent** | **Yield[a]** |
|---|---|---|---|---|---|---|
| 1 | 4-MeO-$C_6H_4$ Br | Ni(dppe)$_2$ | 60$^o$C | $Cs_2CO_3$ | Benzene | NR |
| 2 | 4-MeO-$C_6H_4$ Br | Ni(I)[b] | 60$^o$C | $Cs_2CO_3$ | Benzene | NR |
| 3 | 4-MeO-$C_6H_4$ Br | Ni(dppe)$_2$ | 60$^o$C | $Cs_2CO_3$ | Dioxane | NR |
| 4 | 4-MeO-$C_6H_4$ Br | Ni(I)[b] | 60$^o$C | $Cs_2CO_3$ | Dioxane | NR |
| 5 | 4-MeO-$C_6H_4$ Br | $NiCl_2$dppe | 60$^o$C | $Cs_2CO_3$ | Dioxane | NR |
| 6 | 4-MeO-$C_6H_4$ Br | Ni(dppe)$_2$ | 56$^o$C | $Cs_2CO_3$ | THF | NR |
| 7 | 4-MeO-$C_6H_4$ Br | Ni(I)[b] | 56$^o$C | $Cs_2CO_3$ | THF | NR |
| 8 | 4-MeO-$C_6H_4$ Br | $NiCl_2$dppe | 56$^o$C | $Cs_2CO_3$ | THF | NR |

a=based on GC, b=NiCl(dppe)$_2$

# Chapter 4

## Conclusions and Future work

### 4.1 Conclusions

Ni(0) was generated using zinc reduction of $NiX_2$dppe to $Ni(dppe)_2$. Different solvents and temperatures were used and the products were analyzed using NMR spectroscopy. Nickel(I) species of unknown structures were synthesized using comproportionation reactions, again using different solvents and temperatures. Due to low solubility of the Ni(I) products, they could not be purified and elemental analyses did nothing to aid in characterization. Neither Ni(II) nor Ni(0) compounds were found to be the catalytic active species for Suzuki coupling or Buchwald-Hartwig amination reactions. Comparison was made between Ni(0) and Ni(I) for Heck-Mizoroki coupling reactions, which conclude that the Ni(II) compound was effective with the catalytic system involving zinc, pyridine and acetonitrile, indicating that Ni(0) may be the active species in Heck-Mizoroki coupling. Ni(I) was not active in various cross-coupling reactions such as Buchwald-Hartwig amination and Suzuki and Heck reactions.

### 4.2 Future Work

Further research on Ni(I) could be done by exploring the catalytic activity of Ni(I) in various cross-coupling reactions. Once the conditions are optimized, comparison can be made between Ni(I) and Ni(0) and further insight into the mechanism could be obtained. The use of zinc to generate Ni(0) and Ni(I) compounds with other ligands could be investigated.

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# Appendix A

## NMR and EPR Spectra

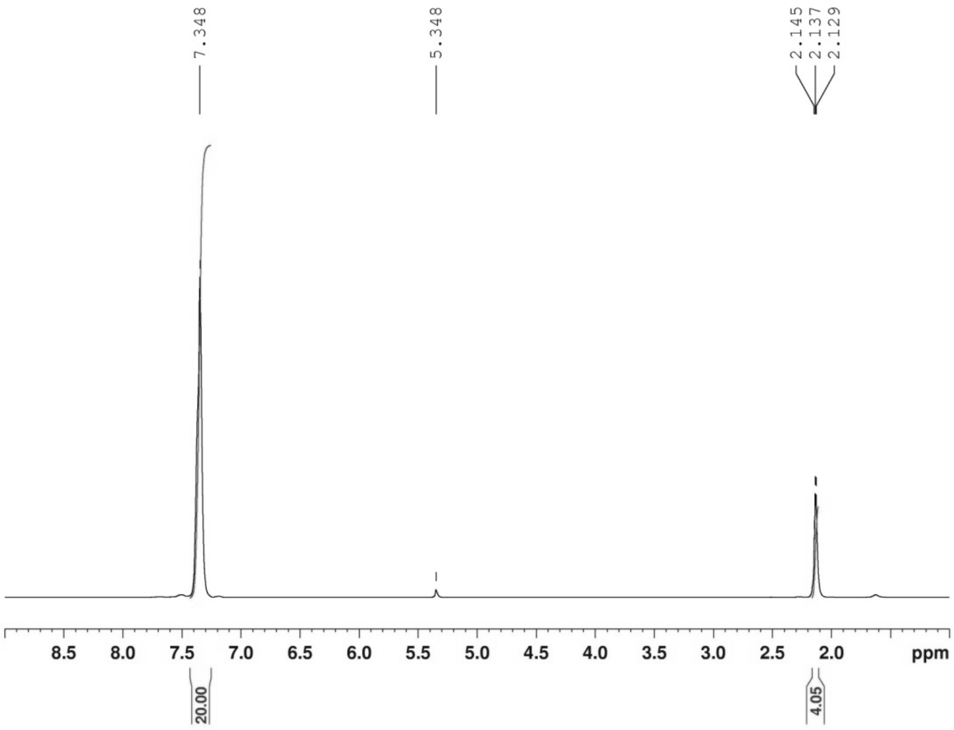

Figure A1: $^1$H NMR spectrum of dppe in $CD_2Cl_2$ (AV400)

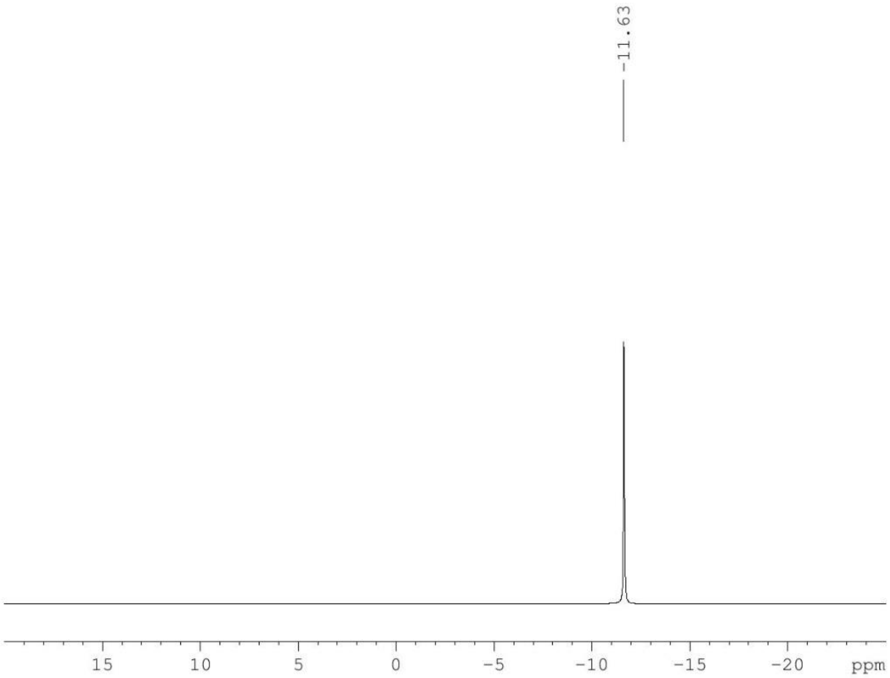

Figure A2: $^{31}$P NMR spectrum of dppe in $CD_2Cl_2$ (AV400)

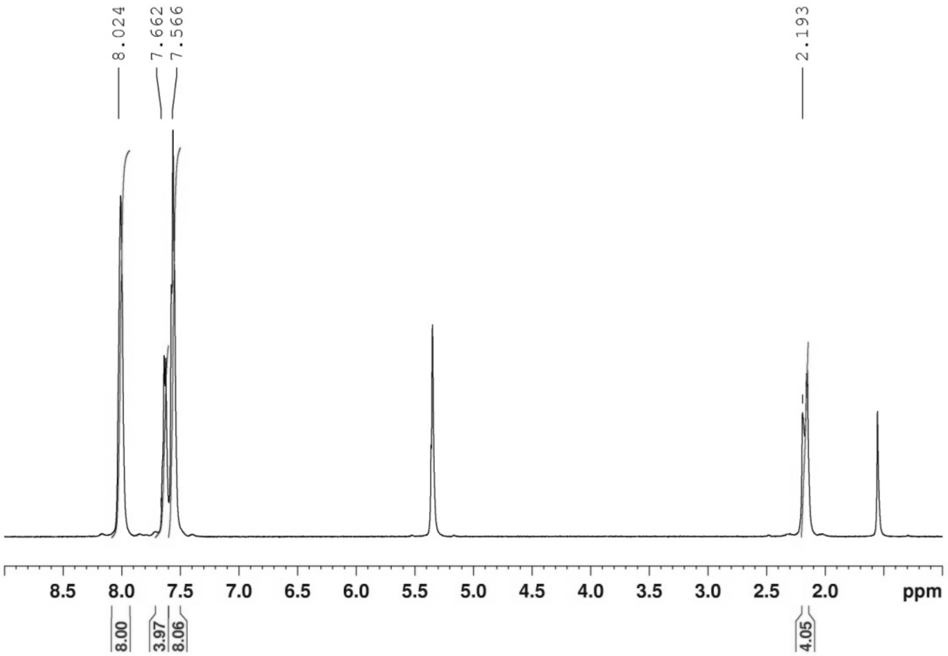

Figure A3: $^1$H NMR spectrum of $NiCl_2$dppe in $CD_2Cl_2$ (AV500)

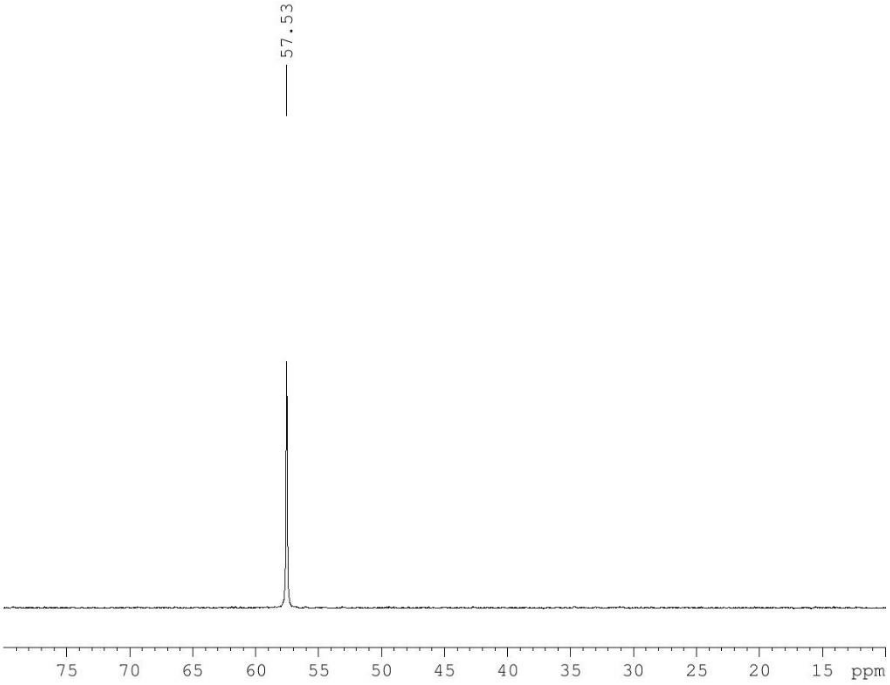

Figure A4: $^{31}$P NMR spectrum of $NiCl_2$dppe in $CD_2Cl_2$ (AV500)

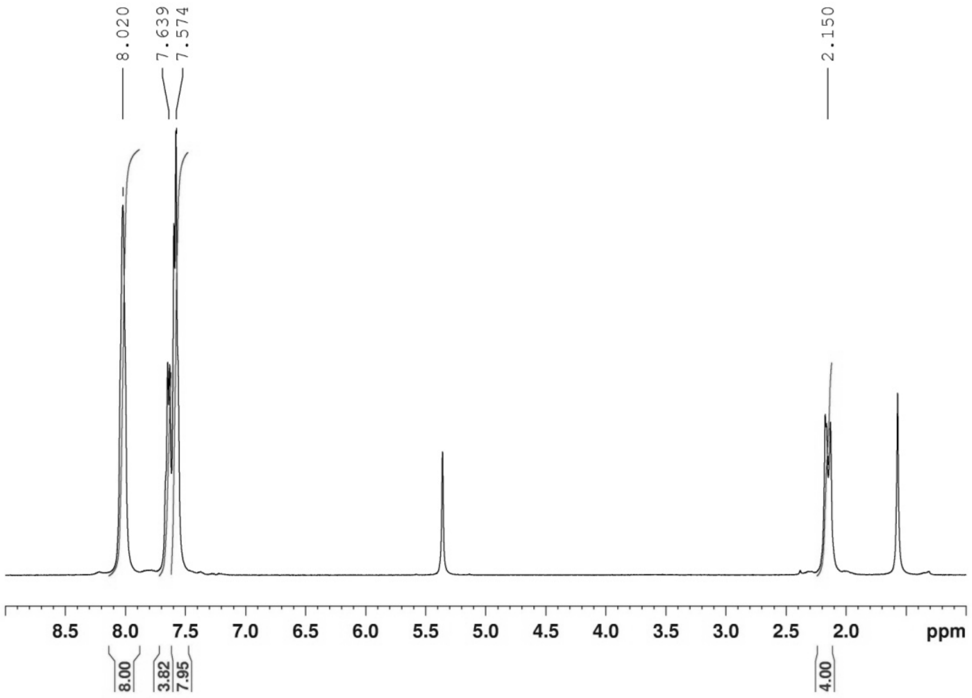

Figure A5: $^1$H NMR spectrum of $NiBr_2$dppe in $CD_2Cl_2$ (AV400)

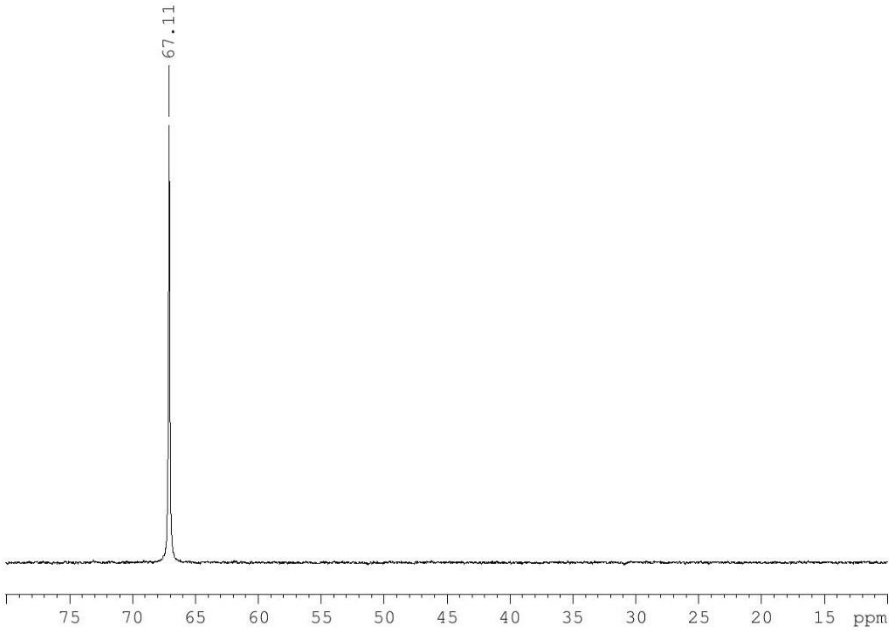

Figure A6: $^{31}$P NMR spectrum of $NiBr_2dppe$ in $CD_2Cl_2$ (AV400)

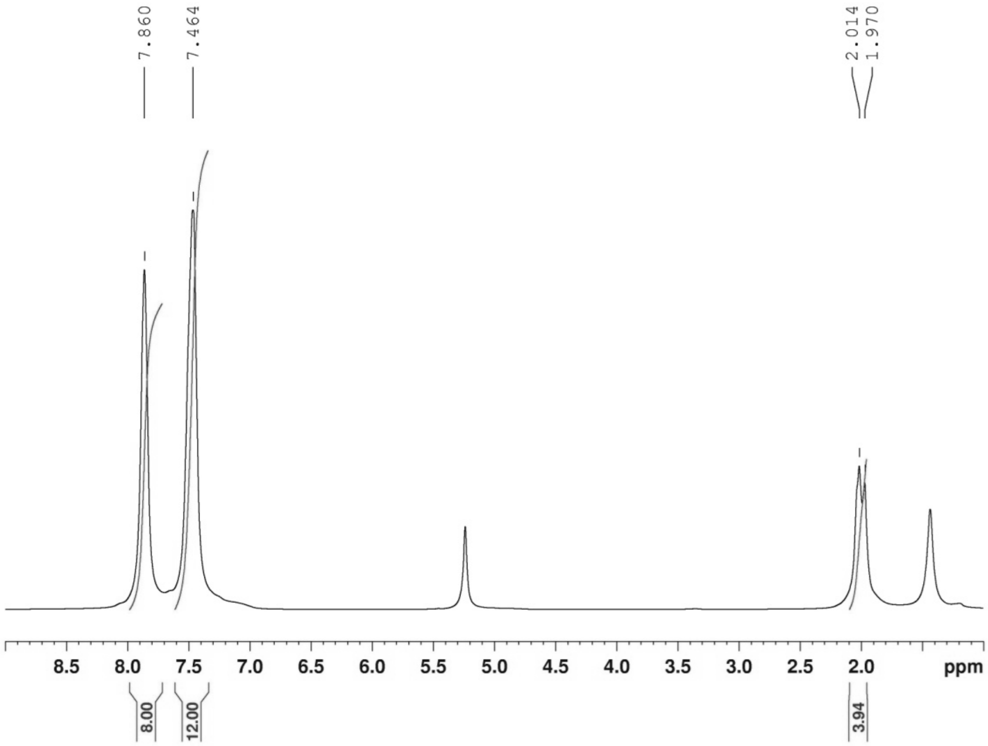

Figure A7: $^1$H NMR spectrum of $NiI_2$dppe in $CD_2Cl_2$ (AV400)

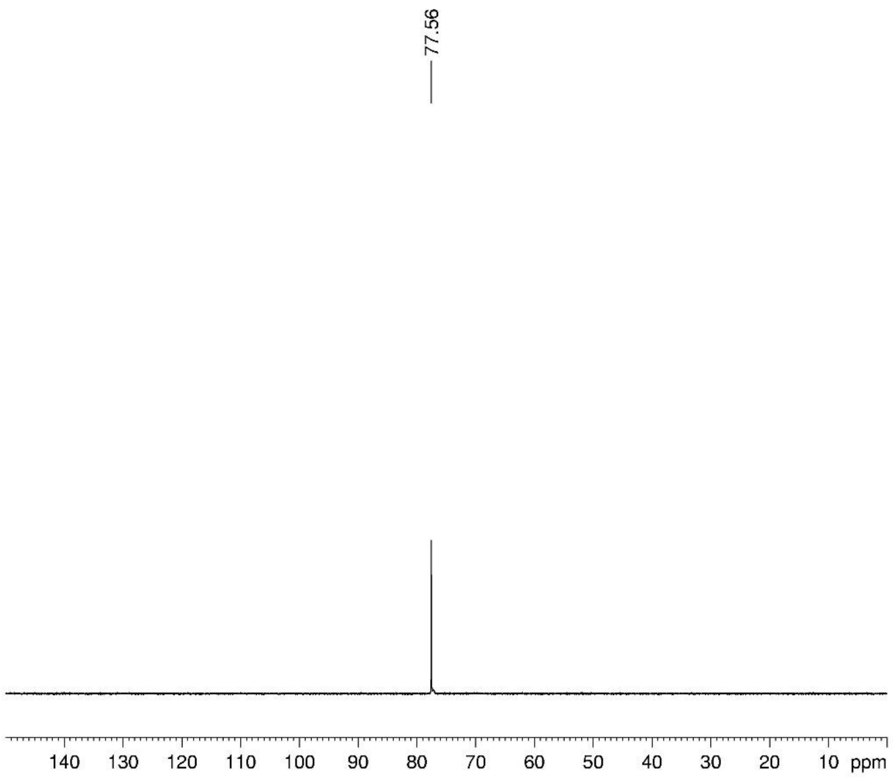

Figure A8: $^{31}$P NMR spectrum of $NiI_2$dppe in $CD_2Cl_2$ (AV400)

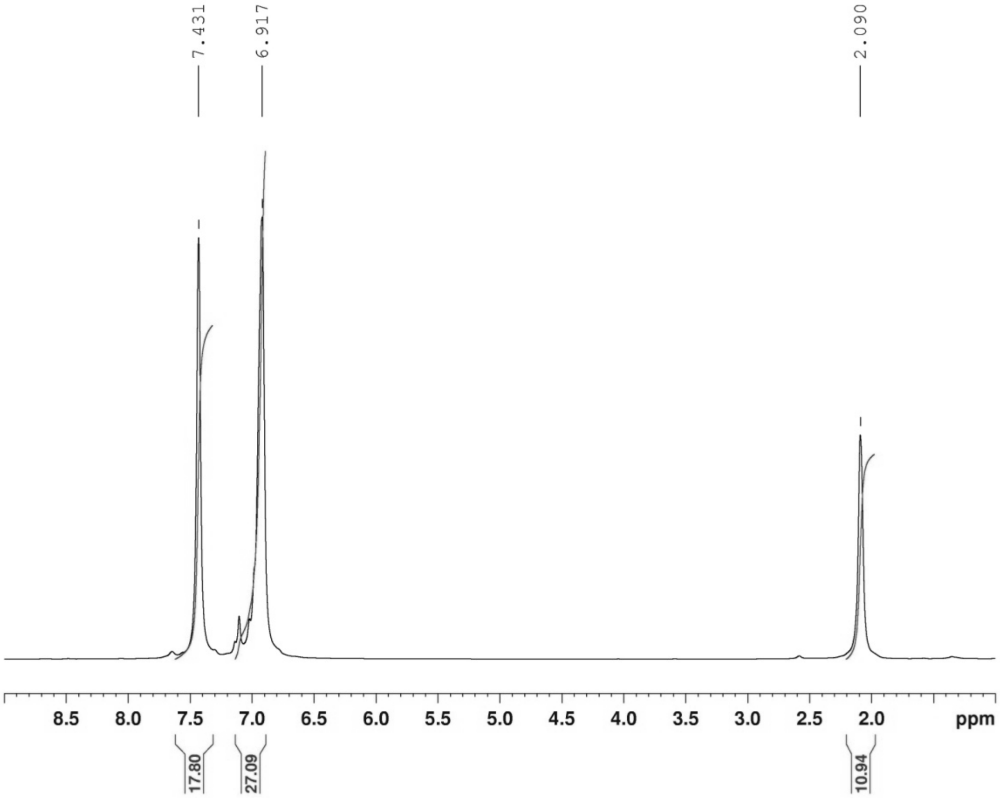

Figure A9: $^1$H NMR spectrum of Ni(dppe)$_2$ utilizing NiCl$_2$dppe as starting material in toluene-d$_8$ (AV600)

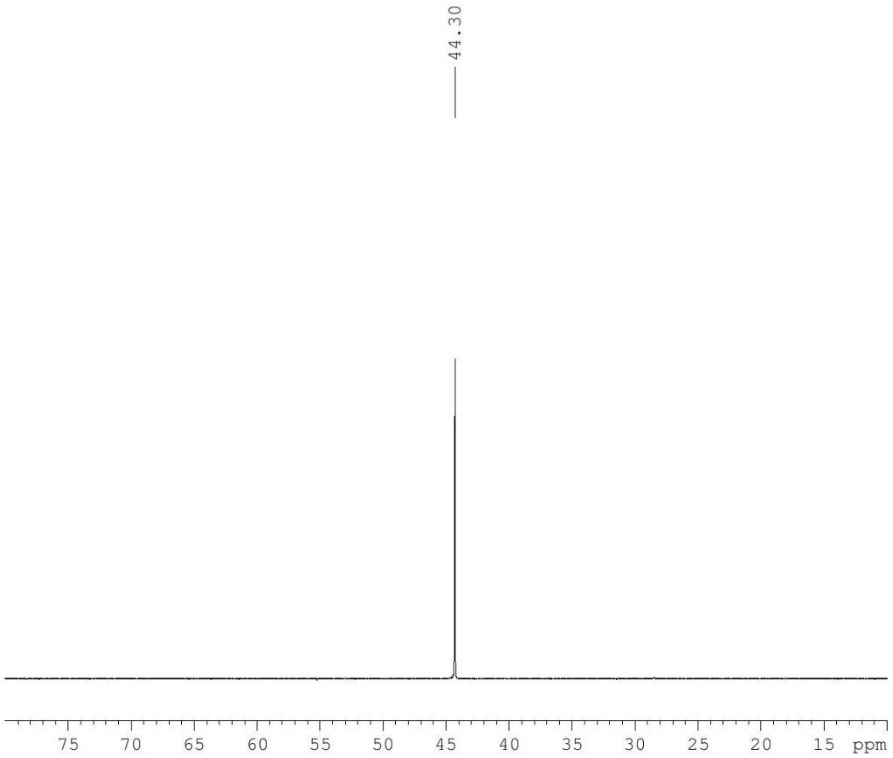

Figure A10: $^{31}P$ NMR spectrum of $Ni(dppe)_2$ utilizing $NiCl_2dppe$ as starting material in toluene-$d_8$ (AV600)

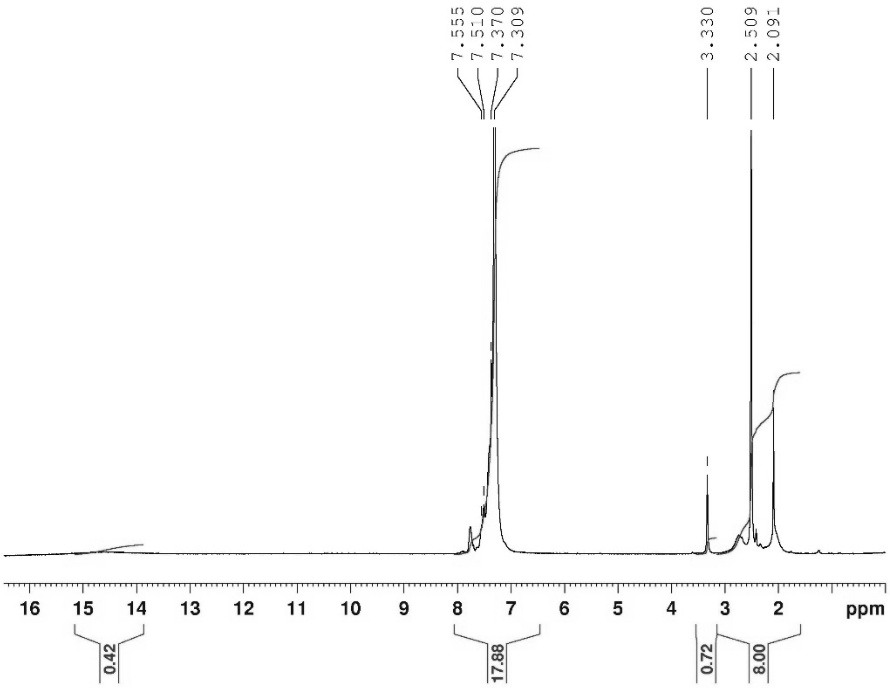

Figure A11: $^1$H NMR spectrum of the colourless precipitate from synthesis of Ni(dppe)$_2$ utilizing NiCl$_2$dppe as starting material in dmso-d$_6$ (AV400)

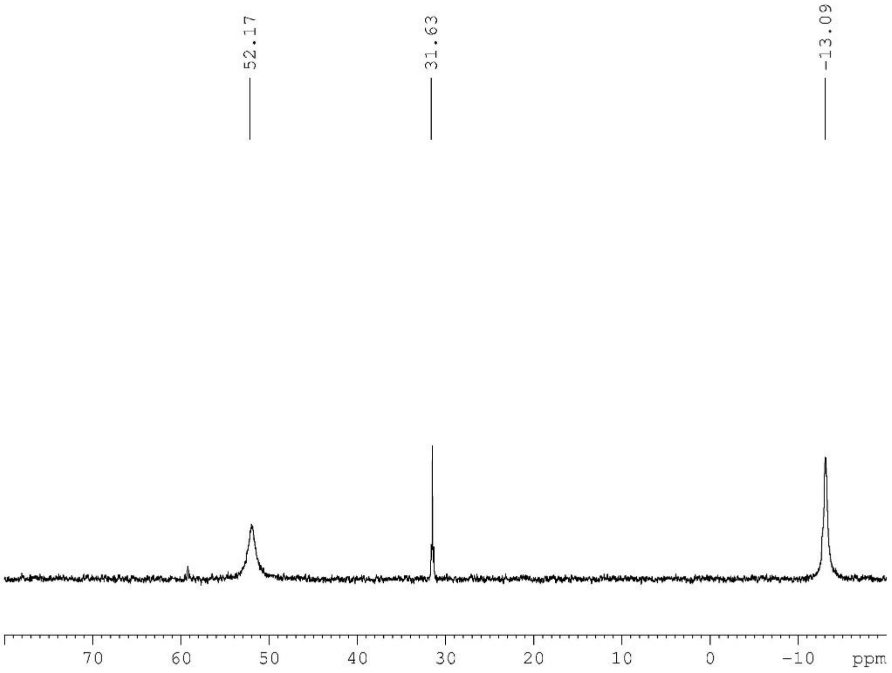

Figure A12: $^{31}$P NMR spectrum of the colourless precipitate from synthesis of Ni(dppe)$_2$ utilizing NiCl$_2$dppe as starting material in dmso-d$_6$ (AV400)

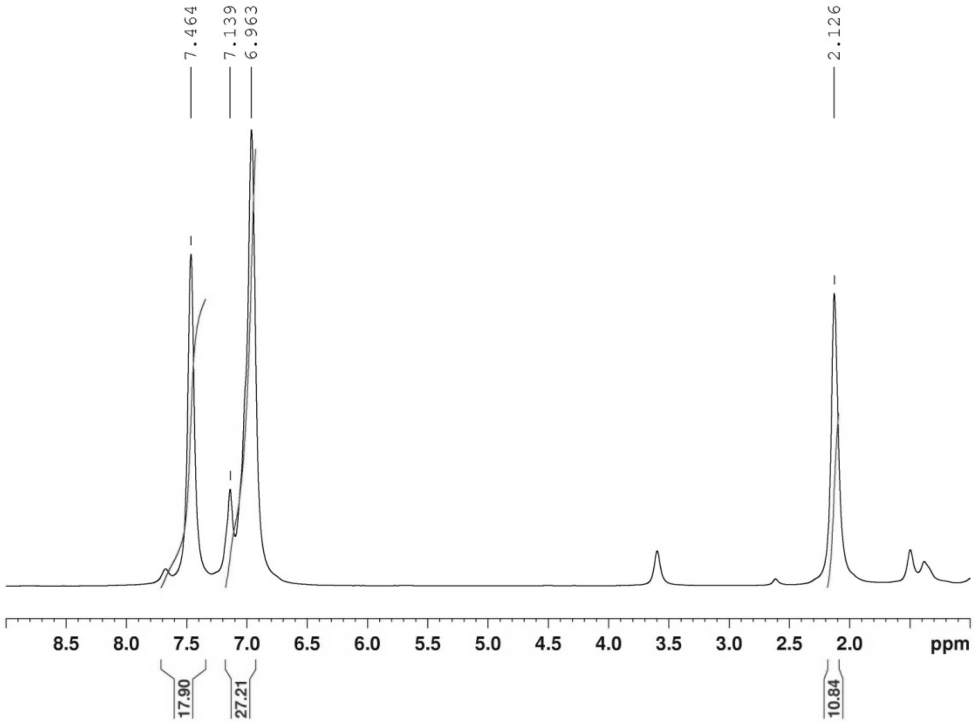

Figure A13: $^1$H NMR spectrum of Ni(dppe)$_2$ utilizing NiBr$_2$dppe as starting material in toluene-d$_8$ (AV400)

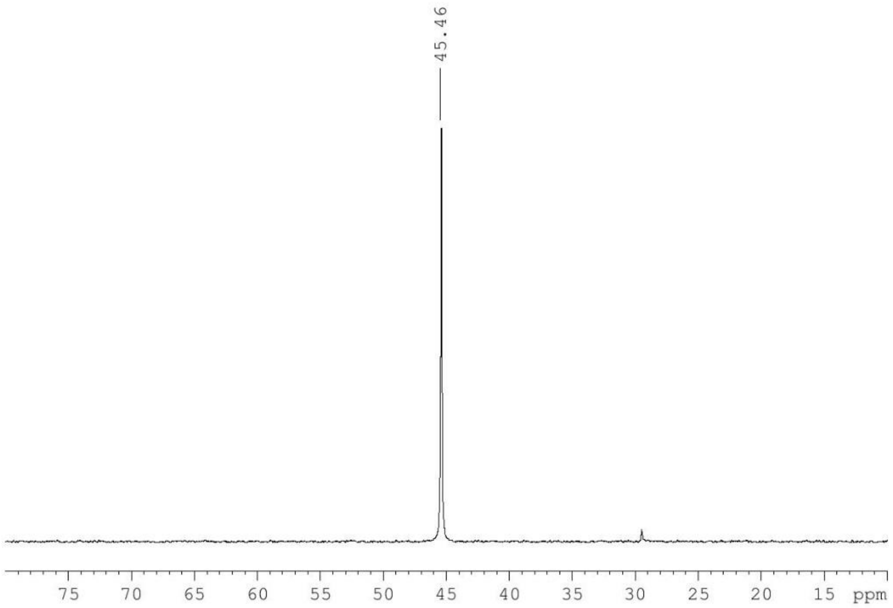

Figure A14: $^{31}P$ NMR spectrum of Ni(dppe)$_2$ utilizing NiBr$_2$dppe as starting material in toluene-d$_8$ (AV400)

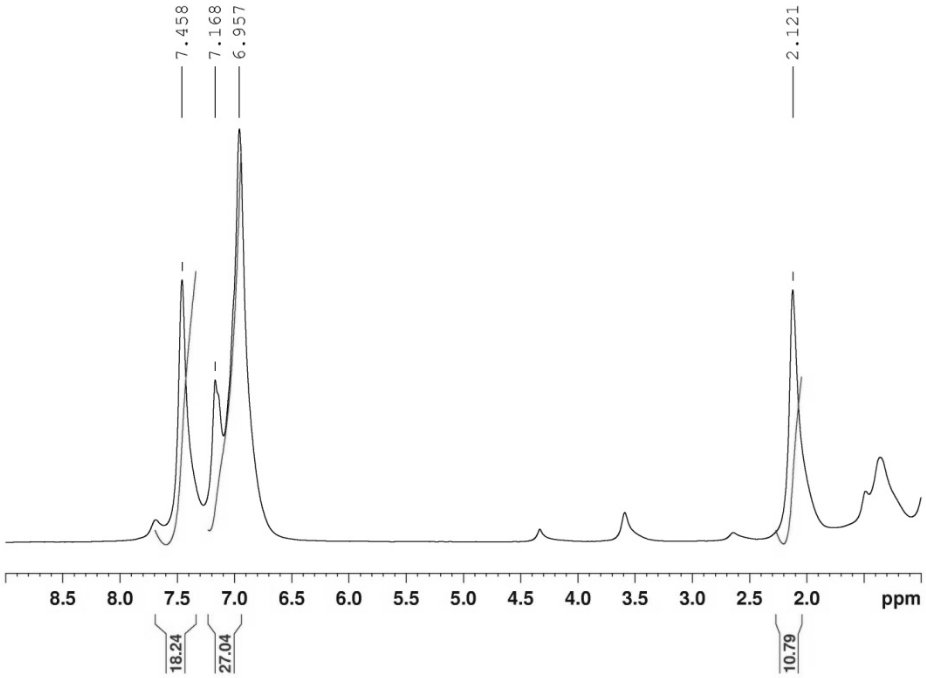

Figure A15: $^1$H NMR spectrum of Ni(dppe)$_2$ utilizing NiI$_2$dppe as starting material in toluene-d$_8$ (AV400)

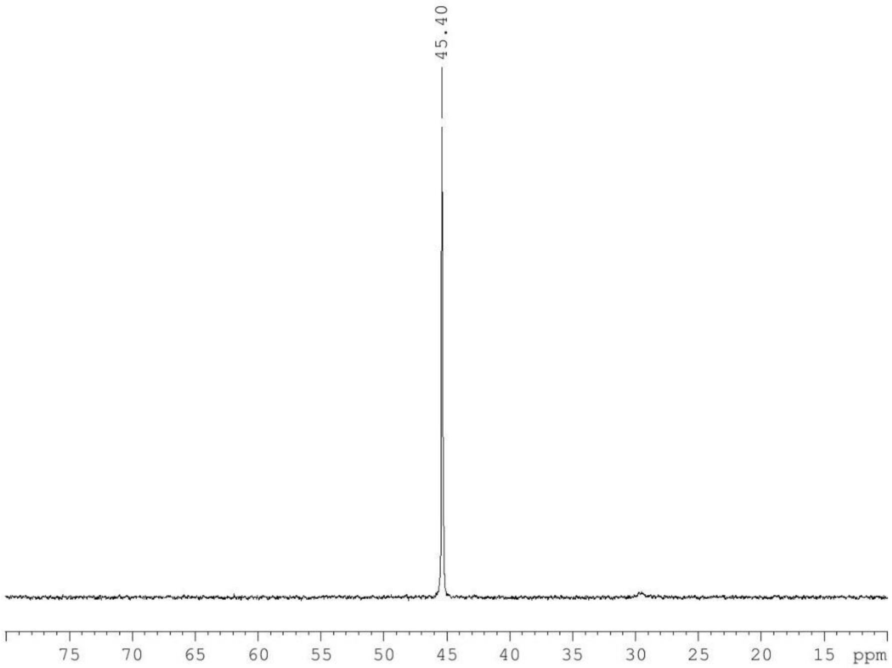

Figure A16: $^{31}$P NMR spectrum of Ni(dppe)$_2$ utilizing NiI$_2$dppe as starting material in toluene-d$_8$ (AV400)

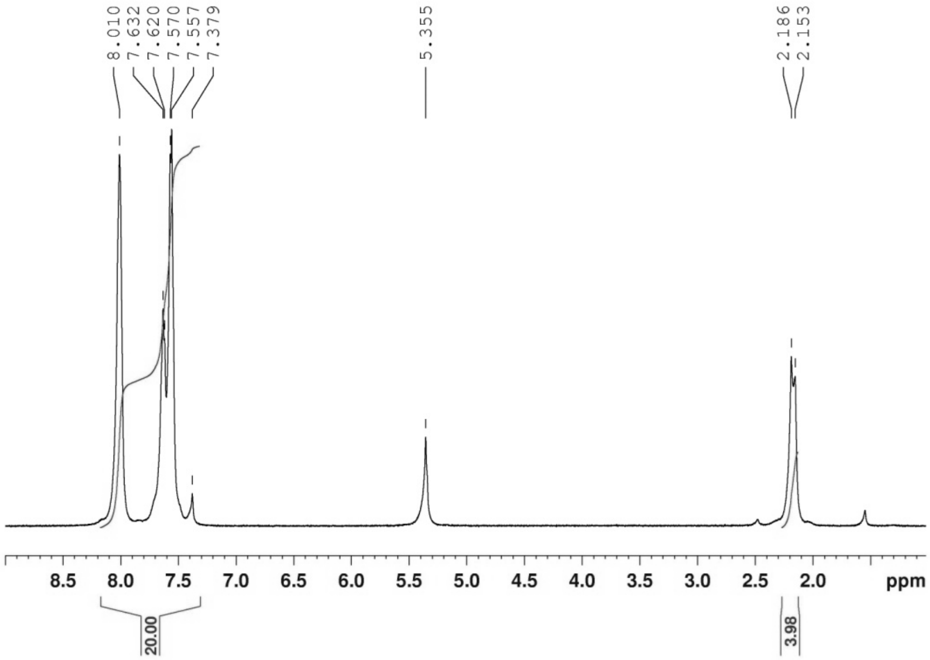

Figure A17: $^1$H NMR spectrum of unreacted $NiCl_2$dppe from reaction of $NiCl_2$dppe and $Ni(dppe)_2$ (1:1) in $CD_2Cl_2$ (AV500)

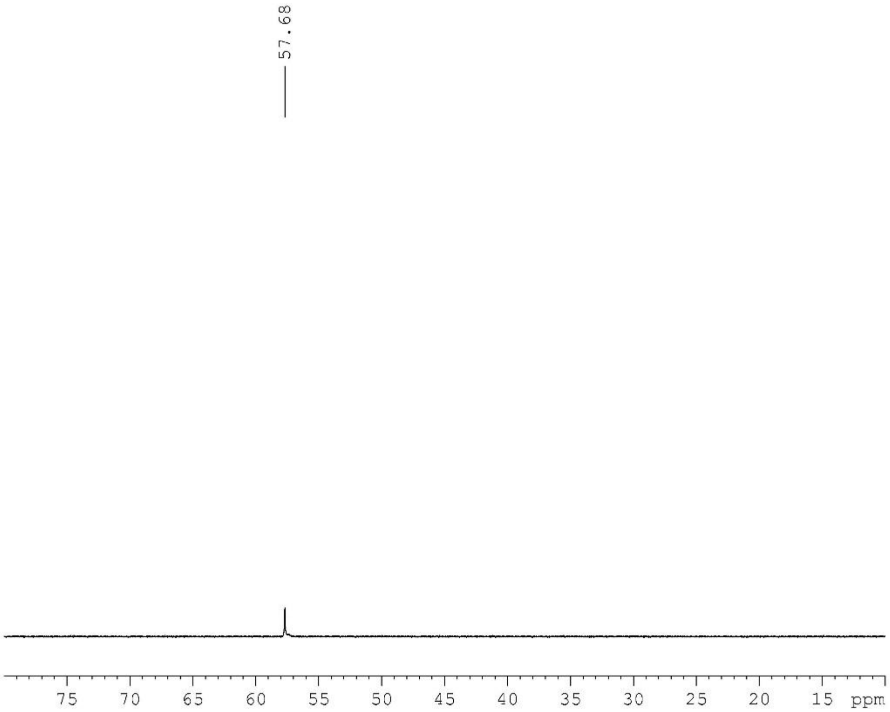

Figure A18: $^{31}$P NMR spectrum of unreacted $NiCl_2$dppe from reaction of $NiCl_2$dppe and $Ni(dppe)_2$ (1:1) in $CD_2Cl_2$ (AV500)

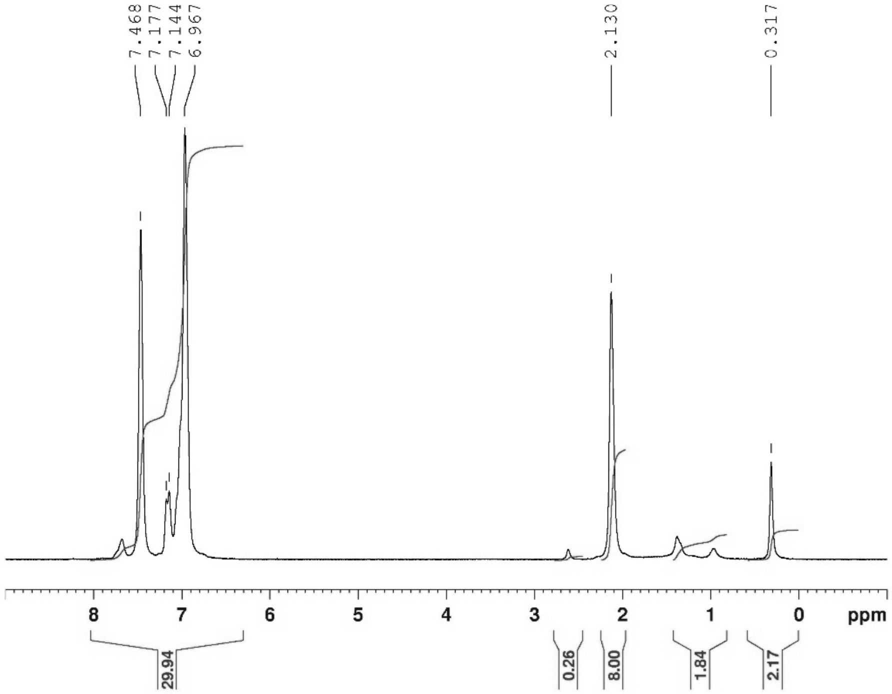

Figure A19: $^1$H NMR spectrum of unreacted Ni(dppe)$_2$ from reaction of NiCl$_2$dppe and Ni(dppe)$_2$ (1:1) in toluene-d$_8$ (AV500)

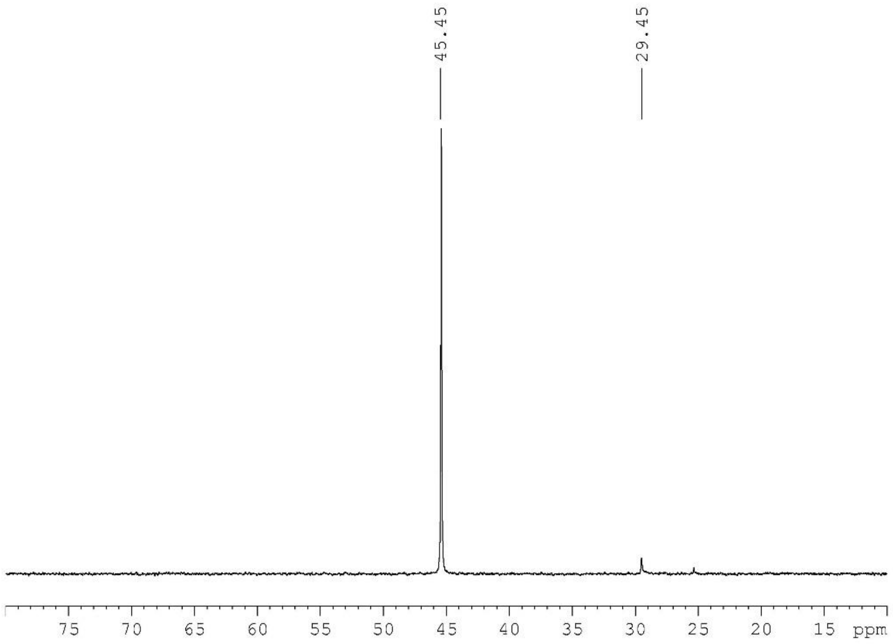

Figure A20: $^{31}$P NMR spectrum of unreacted Ni(dppe)$_2$ from reaction of NiCl$_2$dppe and Ni(dppe)$_2$ (1:1) in toluene-d$_8$ (AV500)

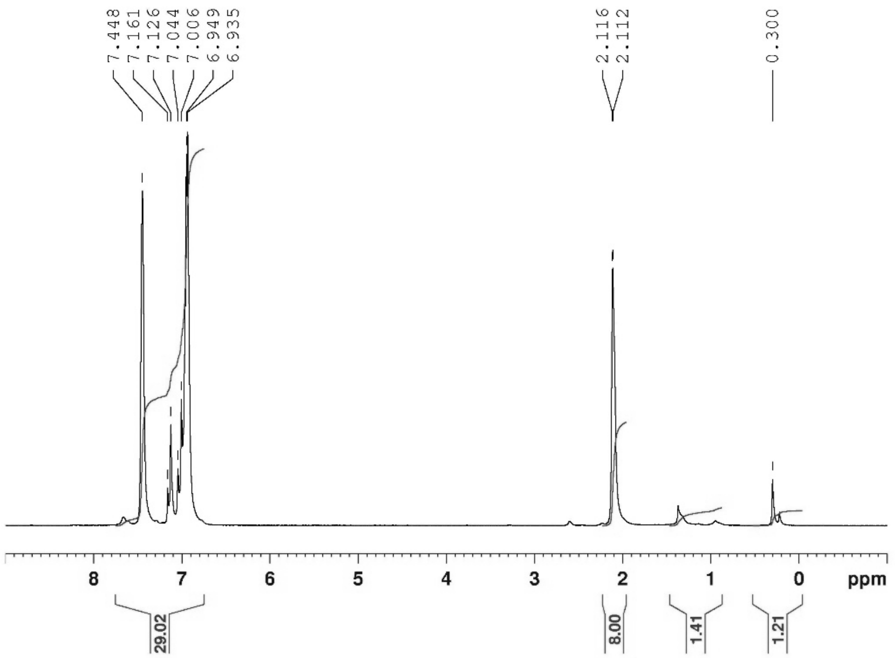

Figure A21: $^1$H NMR spectrum of unreacted Ni(dppe)$_2$ from reaction of NiCl$_2$dppe and Ni(dppe)$_2$ (1:2) in toluene-d$_8$ (AV400)

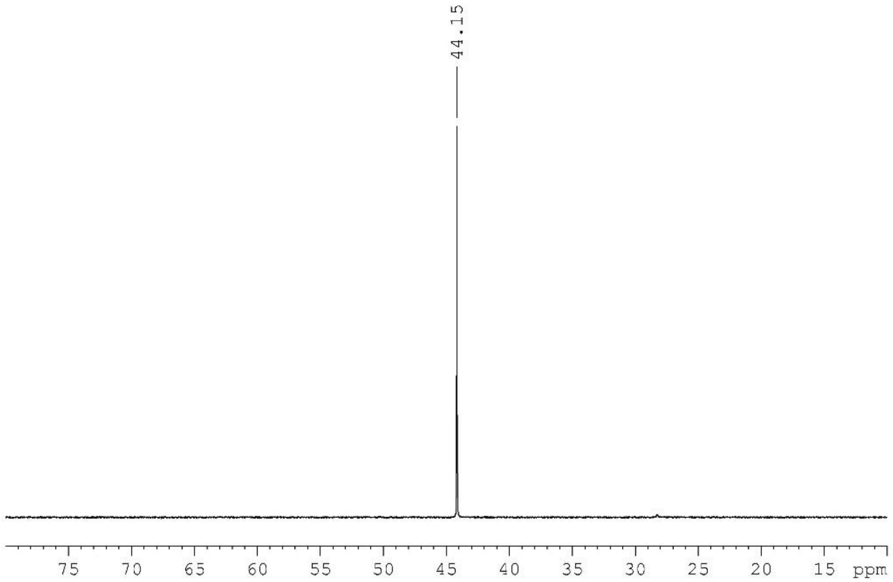

Figure A22: $^{31}P$ NMR spectrum of unreacted $Ni(dppe)_2$ from reaction of $NiCl_2dppe$ and $Ni(dppe)_2$ (1:2) in toluene-$d_8$ (AV400)

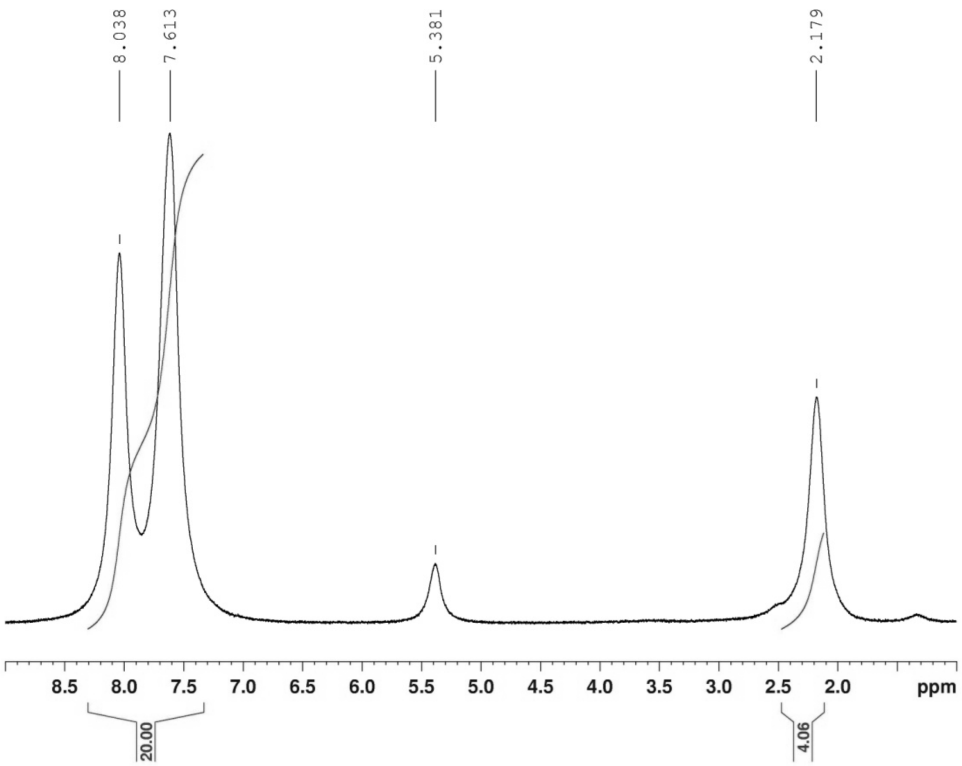

Figure A23: $^{1}$H NMR spectrum of unreacted $NiBr_2$dppe from reaction of $NiBr_2$dppe and $Ni(dppe)_2$ (1:1) in $CD_2Cl_2$ (AV400)

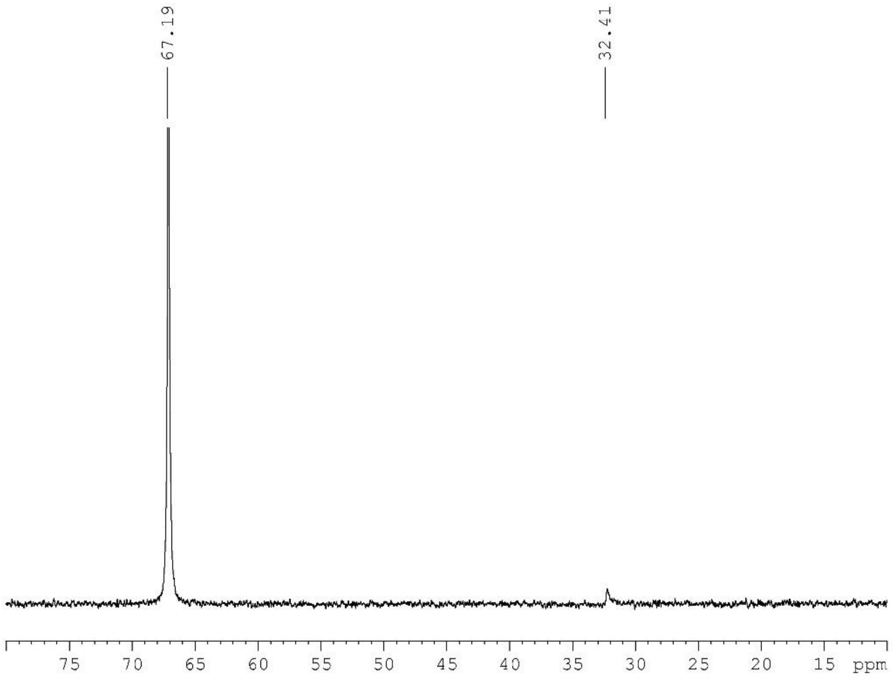

Figure A24: ${}^{31}$P NMR spectrum of unreacted NiBr$_2$dppe from reaction of NiBr$_2$dppe and Ni(dppe)$_2$ (1:1) in CD$_2$Cl$_2$ (AV400)

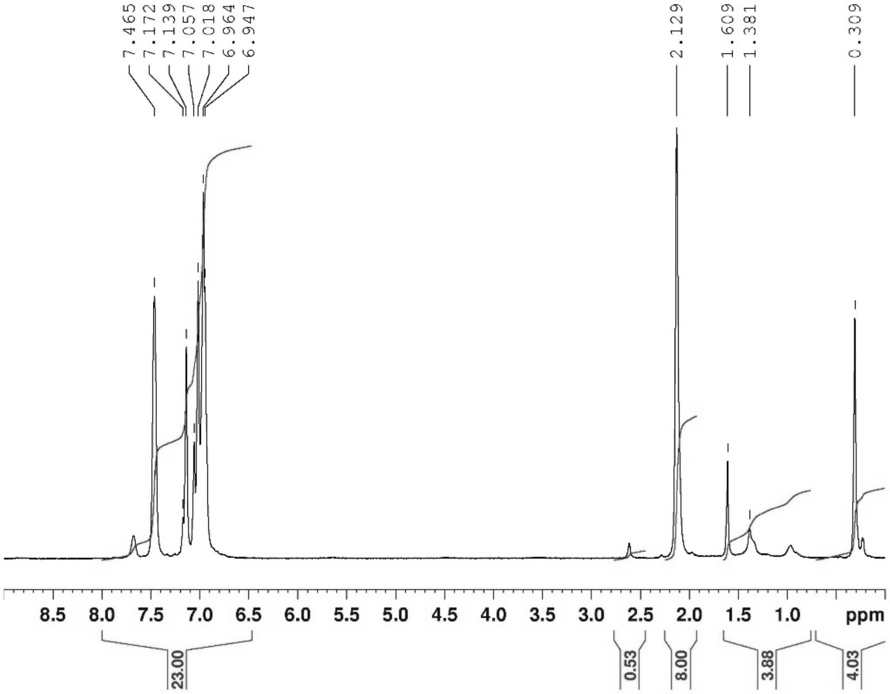

Figure A25: $^1$H NMR spectrum of unreacted Ni(dppe)$_2$ from reaction of NiBr$_2$dppe and Ni(dppe)$_2$ (1:1) in toluene-d$_8$ (AV400)

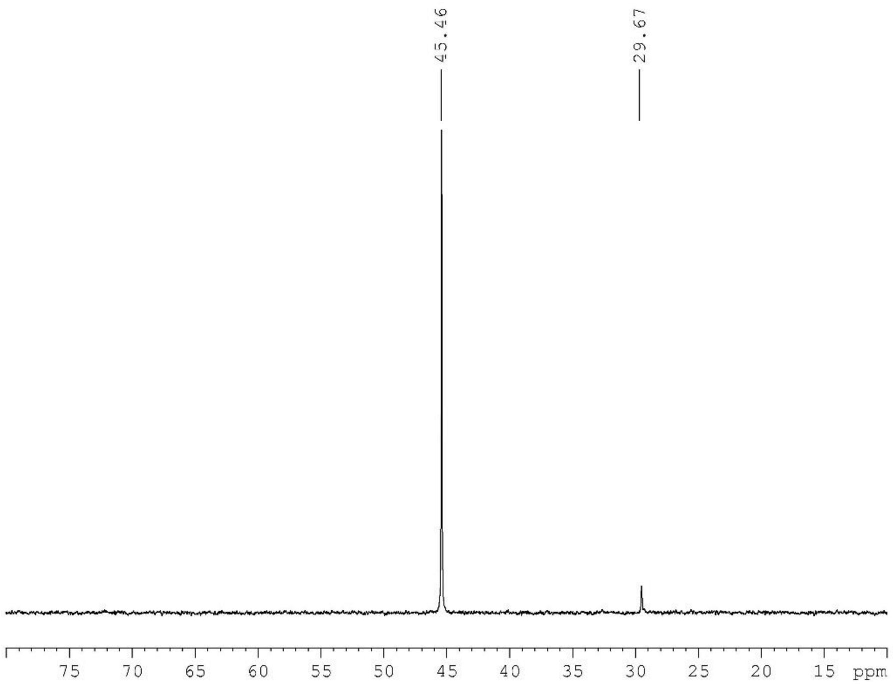

Figure A26: $^{31}$P NMR spectrum of unreacted Ni(dppe)$_2$ from reaction of NiBr$_2$dppe and Ni(dppe)$_2$ (1:1) in toluene-d$_8$ (AV400)

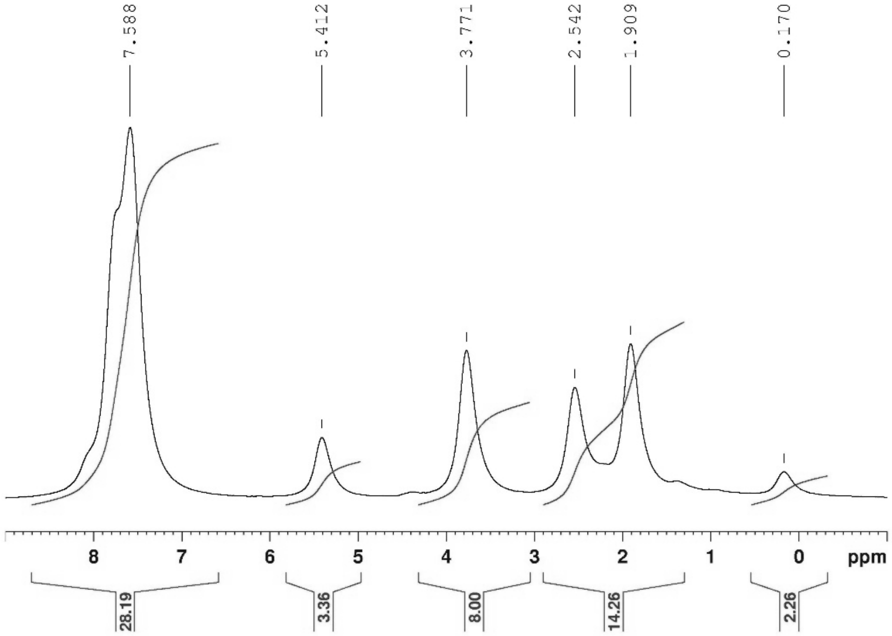

Figure A27: $^1$H NMR spectrum of red precipitate from reaction of $NiBr_2$dppe and Ni(dppe)$_2$ (1:1) in $CD_2Cl_2$ (AV400)

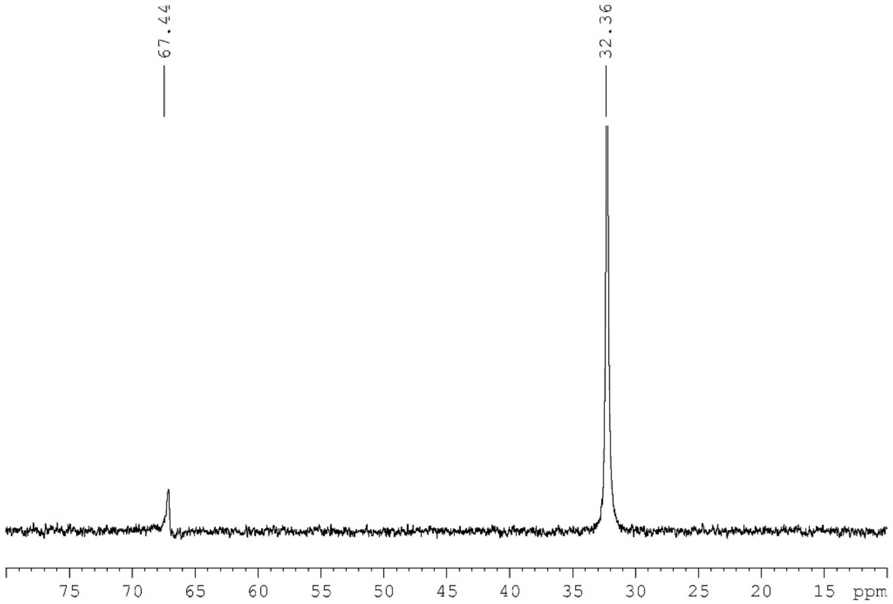

Figure A28: $^{31}$P NMR spectrum of red precipitate from reaction of $NiBr_2$dppe and $Ni(dppe)_2$ (1:1) in $CD_2Cl_2$ (AV400)

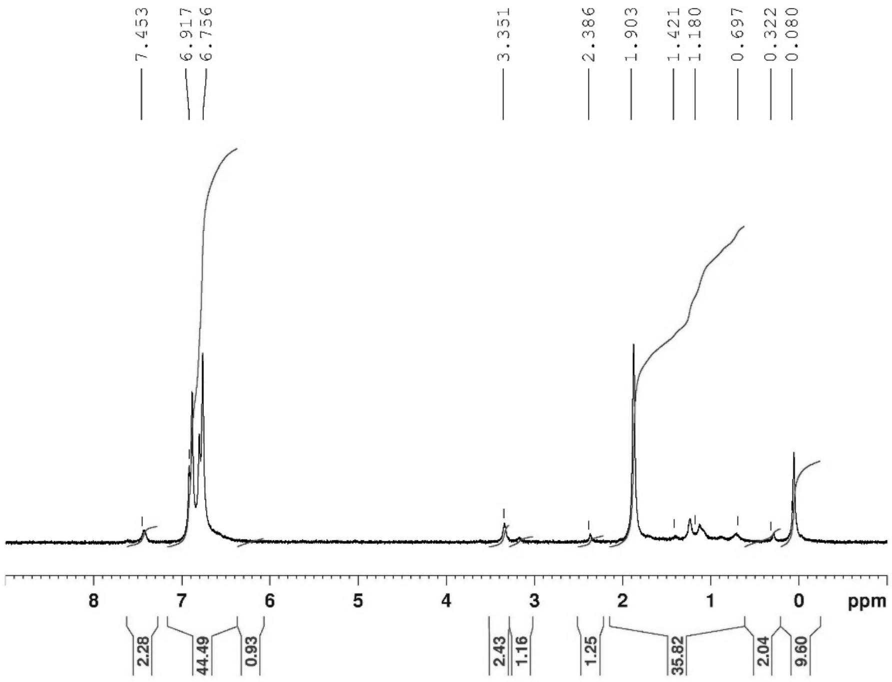

Figure A29: $^1$H NMR spectrum of light red precipitate from reaction of $NiBr_2$dppe and $Ni(dppe)_2$ (1:1) in toluene-$d_8$ (AV400)

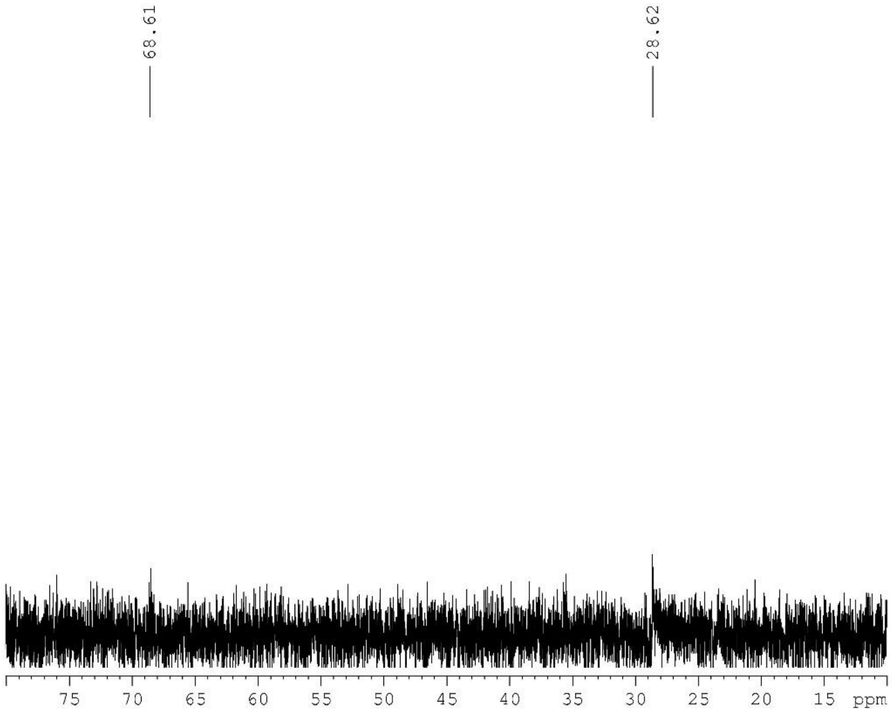

Figure A30: $^{31}$P NMR spectrum of light red precipitate from reaction of $NiBr_2$dppe and $Ni(dppe)_2$ (1:1) in toluene-$d_8$ (AV400)

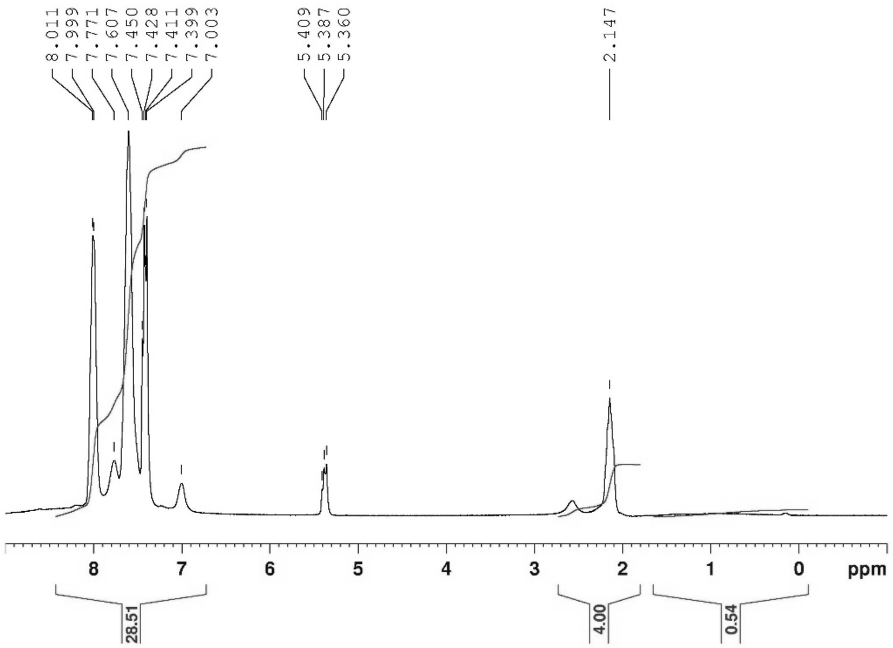

Figure A31: $^1$H NMR spectrum of unreacted $NiI_2$dppe from reaction of $NiI_2$dppe and $Ni(dppe)_2$ (1:1) in $CD_2Cl_2$ (AV400)

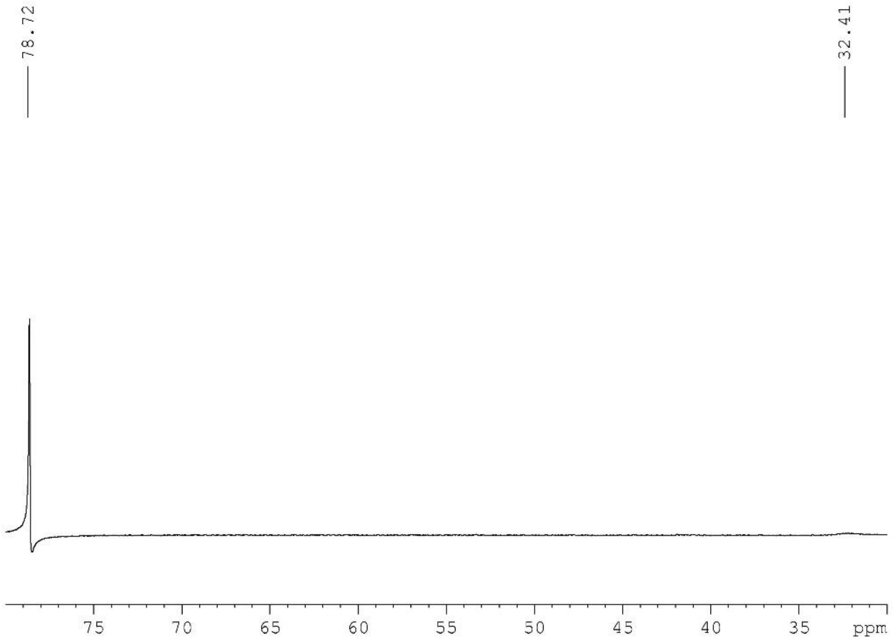

Figure A32: $^{31}$P NMR spectrum of unreacted $NiI_2$dppe from reaction of $NiI_2$dppe and $Ni(dppe)_2$ (1:1) in $CD_2Cl_2$ (AV400)

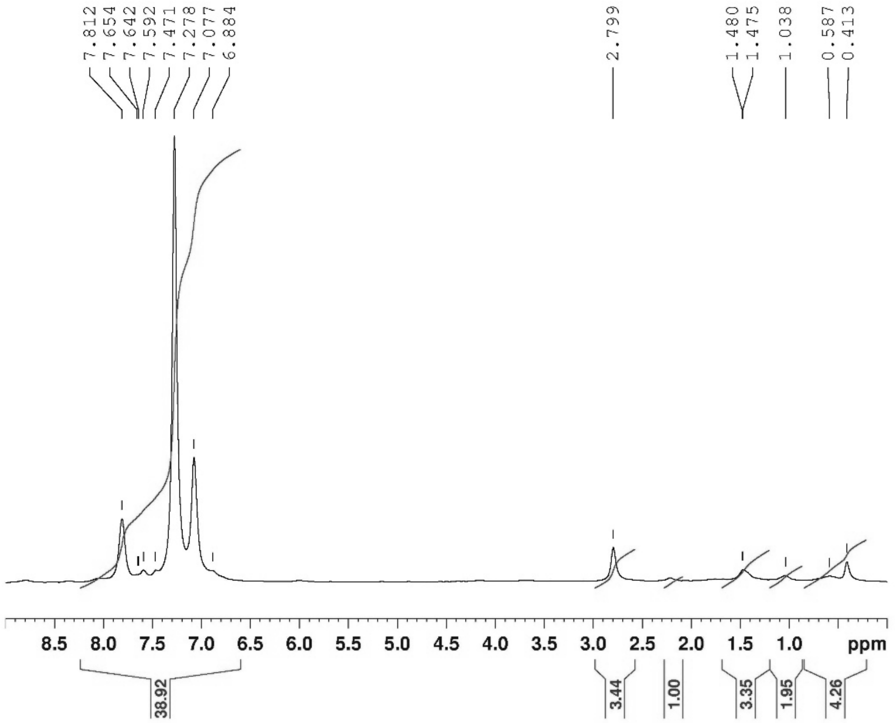

Figure A33: $^1$H NMR spectrum of the yellow powder from reaction of $NiI_2$dppe and $Ni(dppe)_2$ (1:1) in $C_6D_6$ (AV400)

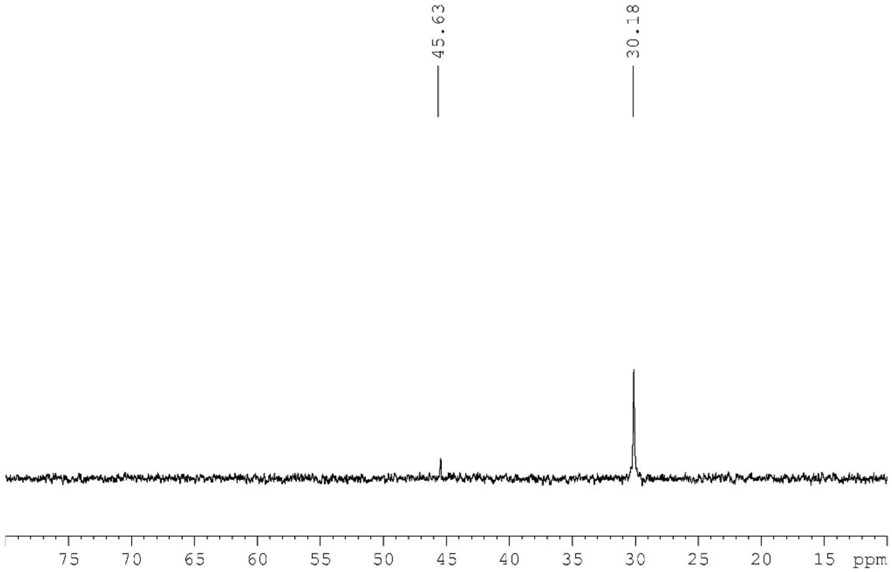

Figure A34: $^{31}P$ NMR spectrum of the yellow powder from reaction of $NiI_2dppe$ and $Ni(dppe)_2$ (1:1) in $C_6D_6$ (AV400)

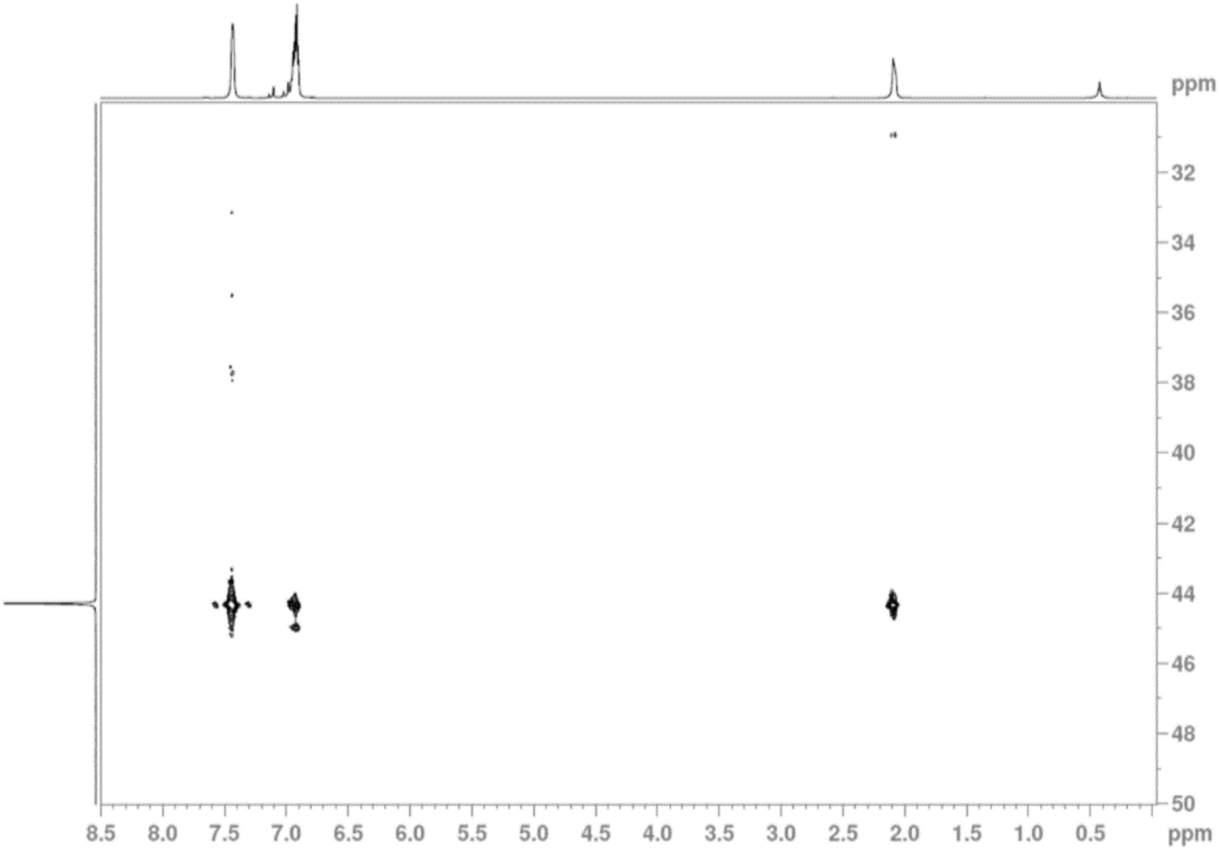

Figure A35: HMBC spectrum of Ni(0) species, Ni(dppe)$_2$ utilizing NiCl$_2$dppe as starting material, performed with Bruker AV600 in deuterated toluene .

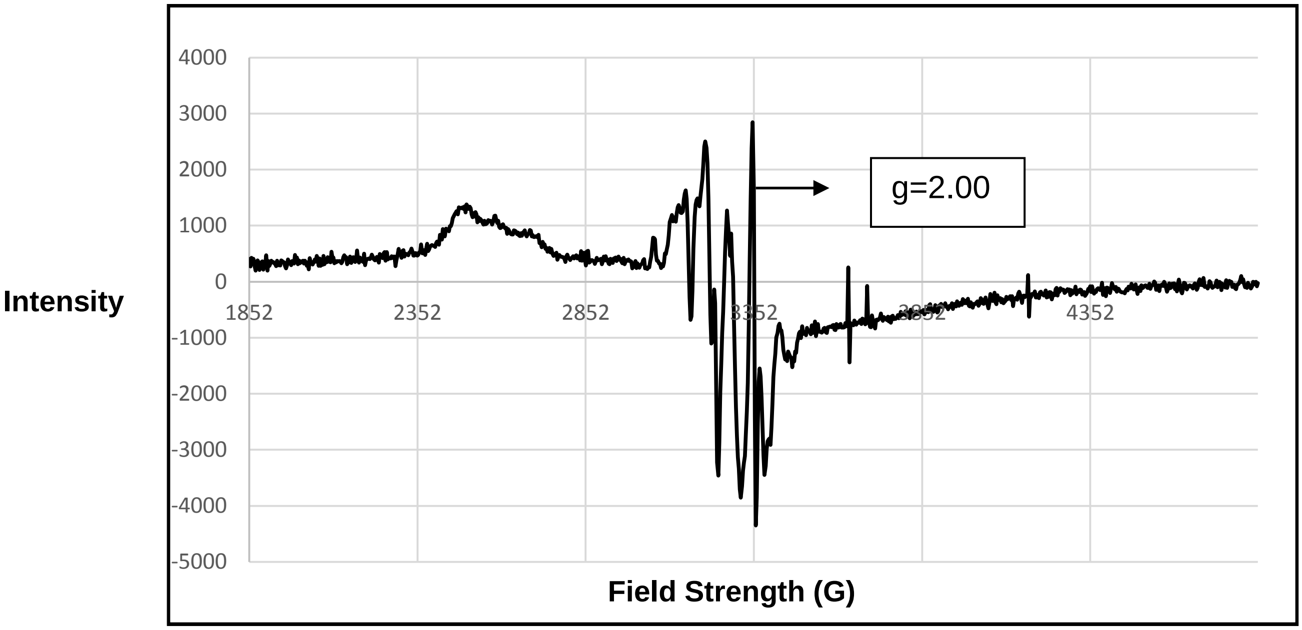

Figure A36: EPR spectrum of the white precipitate from synthesis of Ni(0) utilizing $NiCl_2dppe$ as starting material; toluene solution at 77 K.