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**Synthesis of Novel PCP-Pincer Functionalized Metal Organic
Frameworks for Selective CO₂ Chemisorption**

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(Simon M. Humphrey)

(Richard A. Jones)

**Synthesis of Novel PCP-Pincer Functionalized Metal Organic
Framework for Selective CO₂ Chemisorption**

by

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Thesis

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Dedication

尊前慈母在，浪子不觉寒。

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Dr. Simon Humphrey, my advisor, for his guidance and his mentorship. He is always very supportive specially when I was having hard time!

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I must thank my friends from the neighboring labs who let me borrow chemicals.

Abstract

Synthesis of Novel PCP-Pincer Functionalized Metal Organic Framework for Selective CO₂ Chemisorption

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The University of Texas at Austin, 2016

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Herein, we report the synthesis of a novel tetra(carboxylated) PCP-pincer ligand as building block of Metal Organic Frameworks (MOFs). The pincer ligand is potentially appropriate for cyclometallating various of soft metals, such as Pd, and the resulting cyclometallated pincer ligand is geometrically rigid for synthesis of MOFs. A porous 3D MOF is formed by reacting the cyclometallogand and Co(II) ions via solvothermal synthesis method and studied by single crystal X-ray diffraction. The adsorption-desorption isotherm of the crystalline materials indicates CO₂ gas is preferentially able to access the pores over other gases like N₂ and CO. Furthermore, after the Pd-Cl groups inside the pores are modified to be Pd-Me, CO₂ gas can be inserted rapidly at 1 atm and room temperature. More interestingly, taking the advantage of adsorption property, CO insertion is unflavored in Pd-N₃ modified version. Detailed explorations are done via FT-IR and solid state MSA-NMR.

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Chapter 1: Introduction

1.1 Pincer Ligands

Pincer chemistry has been focused by chemists for over 30 years due to its applications particularly in metal-mediated catalysis.¹ Pincer ligand refers to a tridentate agent which developed along with different donor systems. Figure 1 shows the general components of a pincer ligand: the soft donors (E or E') coordinating and changing the electronic properties of the metal, Y controlling the length of the arm or chirality, and X being either anionic or neutral to vary the coordination number of metal. For example, PCP pincer ligand which will be discussed in detail offers coordination of phosphorus, sp^2 -carbon, and another phosphorus atom. With different identity of X, Y, and E, pincer ligands are widely used in catalysis with high activity and selectivity.

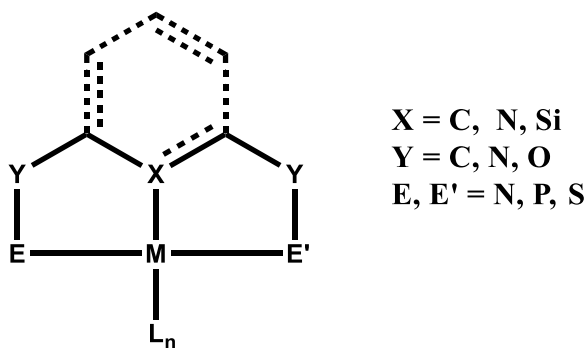


Figure 1: Composition of Pincer Ligands

1.1.1 Pincer Ligands and Their Conformations

η^3 - E, X, E' pincers can be classified as 4-coordinate, 5-coordinate, and 6-coordinate systems depending on L_n . One of the interesting features for pincer ligands is

the coplanarity of ligating atoms (E, X, E', M). If we categorize pincer ligands with different configurations, there are three types of bending modes found in pincer ligands: symmetric C_2 twisting, symmetric C_s "gull wing", and asymmetric bending (Figure 2).² The most common C_2 twisting mode, also known as meridional pincer, normally responds to the number of coordination sites of the metal. The more coordination sites on the metal, the twist distortion will increase in order to maximize the space for ligands. Geometrically, due to the decreasing bonding angle of C, N, and O atoms, the bridging arms of pincer reduce the C_2 twisting respectively. Notably, associative or oxidative addition of gas molecules to a 4-coordinate pincer system usually end up with the trans formation from C_2 twisting to C_s gull wing mode. The less common asymmetric bending happens when E and E' are two distinct atoms or being a transition state in the process of catalysis.

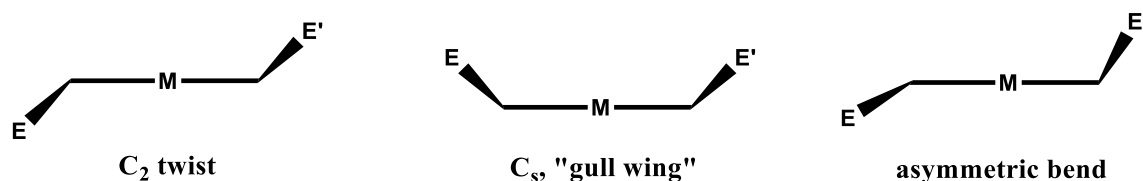
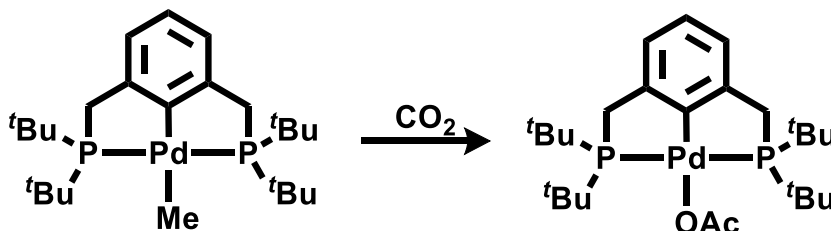


Figure 2: Types of Pincer Bending Conformations

1.1.2 PCP Pincers and CO_2 Activation

The first reported pincer complexes were benzylic $PC_{sp^2}P$ type complexes.³ Since then, a lot of efforts have been put in the field of activation of CO_2 using PCP pincer ligands because activation of inexpensive and inert CO_2 forming C-C bonds is very useful for chemical synthesis.⁴ An early investigation in 2005 by Wendt and co-workers displayed

the reactivity of PCP-Pd methyl complex toward CO₂ (Scheme 1).⁵ Based on this observation, Wendt further reported the catalytic conversion from ZnMe₂ to Zn(OAc)₂ with PCP-Pd complex.



Scheme 1: Synthesis of Carboxylated of PCP Pincer Ligand.

1.2 Metal Organic Frameworks (MOFs)

1.2.1 Fundamentals of MOFs

To achieve the activation or reaction of gas molecules typically involving the consideration of contact between gases and active species and naturally expecting high pressure. Meeting the requirement of green chemistry, metal organic frameworks (MOFs) could provide a platform to keep the gases in touch with active sites. MOFs are crystalline and porous materials consist of modifiable organic linkers and various inorganic metal clusters. Since 1990 more than 20,000 MOF structures were reported, and yet the enthusiasm to MOF chemistry did not degrade due to the potential applications of MOFs.⁶

Organic linker, also called building block in MOF chemistry, is the key to functionalize the framework and provide more application potentials than zeolite. Conventionally, building blocks have rigid structures, such as benzene ring and alkyne, to

limit the orientations when they coordinate to metal clusters and so accelerate the crystallization process. Additionally, carboxylate is another feature for MOF constructions.

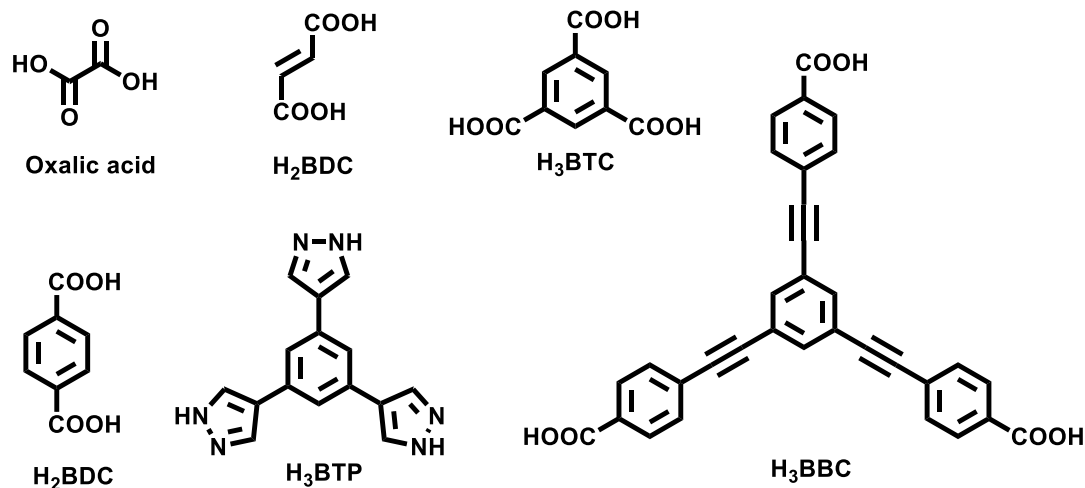


Figure 3: Some Common Building Blocks for MOF Synthesis.

1.2.2 *Pre-synthetic and Post-synthetic Modification of MOFs*

Many functionalization of MOFs can be done via designing and synthesizing building blocks, and all the efforts that put in before the formation of the frameworks are called pre-synthetic modifications. Nevertheless, some cases especially involving coordination of transition metals remain significant challenge due to the presence of carboxylate groups. Also, it is well explored that small changes of the organic linkers may cause problems in MOF synthesis. Alternatively, post-synthetic modifications are fantastic strategies, for instance, Cohen and co-workers demonstrated excellent follow up which the soft donor bipyridine post-synthetically coordinated to more earth-abundant Mn instead of Re yielding catalytic active MOF with turnover number of approximately 110 in 18 h.⁷

1.3 Phosphine Coordination Materials (PCMs)

Phosphine Coordination Materials (PCMs) are a branch of MOFs which specifically use phosphine ligands as organic linkers. Since 2009 the first PCM reported by Humphrey, the applications of PCMs such as catalysis, sensing, and small molecule sequestration have been proven via pre- or/and post-synthetic modifications of the phosphine sites.⁸ For instance, PCM-10 is a 3-dimensional framework produced by Ca(II) and tris(*p*-carboxylated)triphenylphosphine.⁹ Amazingly Humphrey and co-workers reported a wide range of post-synthetic methods to modify the free phosphine sites, and the PCM-10 after treated with (Me₂S)AuCl showed the catalytic ability of C-O coupling reactions of alkenes with phenols and carboxylic acids. Later, PCM-18 was published using BBCB (Figure 4) which is a pre-formed cyclometallated bisphosphine installed with *p*-carboxylic acid.¹⁰ This pre-synthetic metallation allows the active metal sites evenly layout in the framework and maximize the possibilities that the active sites contact with reagents, such as ethyldiazoacetate.

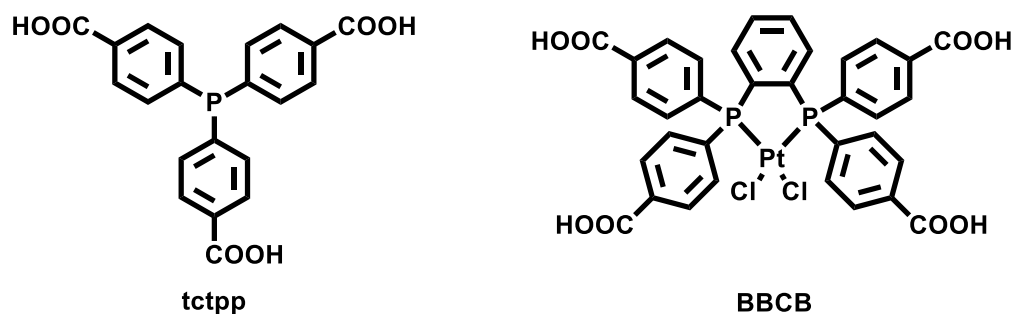


Figure 4: Some Common Building Blocks for MOF Synthesis.

1.3.1 Combination of Pincer Ligand and MOF

Phosphine Coordination Materials (PCMs) are a branch of MOFs which specifically use phosphine ligands as organic linkers. The applications of PCMs such as catalysis, sensing, and small molecule sequestration have been proven via pre- or/and post-synthetic modifications of the phosphine sites. There is few demonstration using PCP pincer ligands as building block. By utilizing pincer ligands in framework, we are expecting would do gas activation and taking the advantages of porous framework structures to enhance the contact possibilities between gas and active metal sites. More importantly, based on different frameworks gas adsorption properties, keeping the undesired gas outside of the materials and ultimately reach the goal of selective gas chemisorption.

1.3.2 Hard-Soft Acid-Base Theory (HSAB) and Chelating Effect

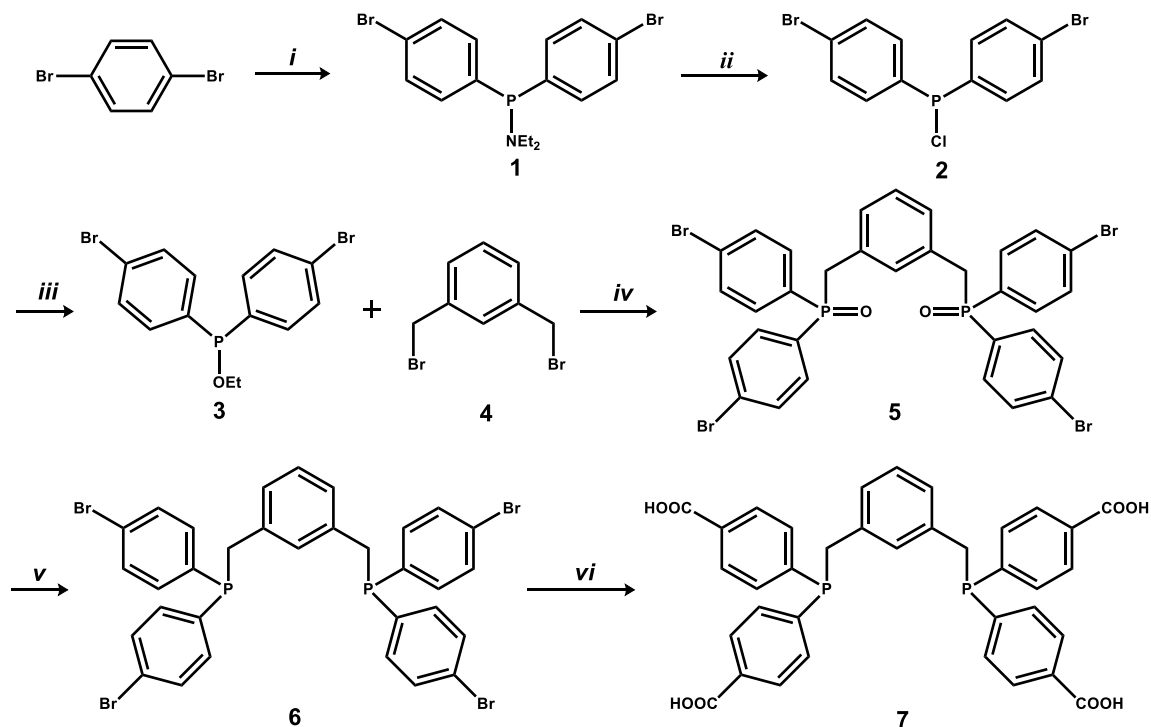
Although coordinating two distinct metals precisely and separately to phosphine and carboxylate acid is problematic, luckily this can be solved by Hard-Soft Acid-Base Theory (HSAB, also called Pearson acid base concept). In HSAB theory, hard acids prefer to coordinate with hard bases, and soft acids prefer to coordinate with soft bases. In the case of using pincer ligand as MOF building block, the soft donor phosphine would coordinate with soft acids like Pd^{2+} in the absence of water. The coordinated phosphines are air- and moisture stable, and the hard base carboxylates can coordinate to hard acids like Zn^{2+} , Co^{2+} and so on.

Unfortunately, PCMs formations need high temperature which may result in the leaching of transition metals and even worse forming nanoparticles in some cases. The pioneer work for PCM-18 by Humphrey and co-workers in 2013 showed the construction of framework were carried out at 50 °C, and no higher temperature examples succeeded either under hydrothermal conditions or solvothermal conditions.¹⁰ Comparing to monodentate (one coordinate bond) or bidentate carboxylate, pincer ligand has three coordinate bonds to enhancing affinity between ligand and metal.

Chapter 2: Result and Discussion

2.1 Carboxylated PCP Pincer Ligand

2.1.1. Ligand Synthesis

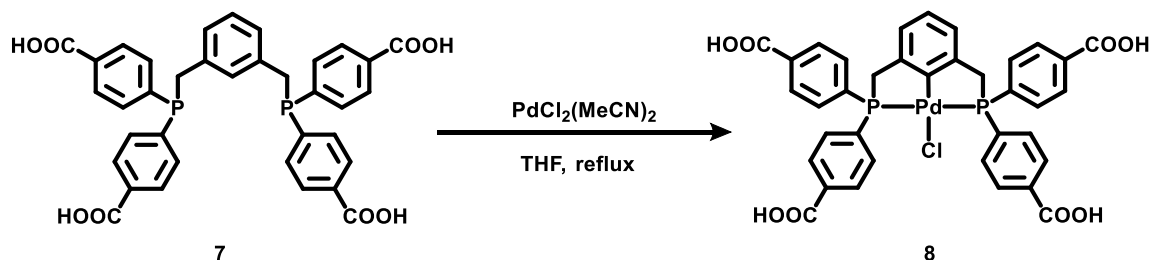


Scheme 2: Synthesis of Carboxylated of PCP Pincer Ligand. (i) 1 eq. n-BuLi, THF, $-78\text{ }^{\circ}\text{C}$, 1 h, then added 1/2 eq. $\text{PCl}_2(\text{NEt}_2)$, warmed to r.t.; (ii) reflux in excess PCl_3 ; (iii) 1 eq. NaOEt in EtOH with **1** in Et_2O , $-20\text{ }^{\circ}\text{C}$, 30 min; (iv) **2** and 0.42 eq. 1,3- $(\text{CH}_2\text{Br})\text{C}_6\text{H}_4$, *p*-xylene reflux, 18 h; (v) 15 eq. HSiCl_3 , toluene reflux, 18 h, NaHCO_3 quench; (vi) 5 eq. n-BuLi, THF, $-78\text{ }^{\circ}\text{C}$, 1 h, then added excess CO_2 , warmed to r.t., dissolution in degassed H_2O , acidification with 2.0 M HCl to pH 1.

Following Scheme 2, PCP pincer precursor was synthesized with 42% overall yield. We started from lithiating 1,2-dibromobenzene at $-78\text{ }^{\circ}\text{C}$ under N_2 protection for an hour; then the lithium salt intermediate reacted with diethylphosphoramidous dichloride to give bis(4-bromophenyl)*N,N*-diethylaminophosphor-amidite **1**. By refluxing compound **1** in phosphorus trichloride, desired bis(4-bromophenyl)chlorophosphine **2** was isolated by distilling off excess phosphorus trichloride and byproducts with 86% yield. After generating sodium ethoxide in situ with sodium metal and ethanol, an substitution of chloro group to ethoxy group was done by reacting compound **2** and sodium ethoxide at $-20\text{ }^{\circ}\text{C}$ under inert atmosphere to give ethyl bis(4-bromophenyl)phosphinite **3**, 90% yield. Subsequently, Arbuzov reaction was performed by refluxing 2.4 eq. of phosphinite **3** and 1,3-bis(bromomethyl)benzene in dry degassed *p*-xylene overnight. The crude product was crashed out with addition of excess of hexanes and filtered. Further purification using column chromatography gave white powder 1,3-bis[methyldi(4-bromophenyl)phosphine oxide]benzene **4** in 71% yield. Phosphine oxide **4** was reduced in presence of excess of trichlorosilane to give 1,3-bis[methyldi(4-bromophenyl)phosphine]benzene **5** in

quantitative yield. Carboxylation in last step was carried out with 81% yield, and the desired product 4,4',4'',4'''-((1,3-phenylenebis(methylene))bis(phosphinetriyl))-tetrabenzoic acid **6** was identified by NMR and HRMS.

2.1.2. Metallation and X-ray structure



Scheme 3: Metallation of Carboxylated of PCP Pincer Ligand

First successful attempt of metallation was reacting carboxylated PCP pincer ligand **7** with bis(acetonitrile)dichloropalladium(II) in dry and degassed THF. Theoretically, after $\text{Csp}^2\text{-H}$ was activated, a molecule of HCl should be eliminated; therefore, addition of base such as triethylamine will help the completion of reaction. Practically, the pincer ligands precipitated as soon as the base was added and hardly reacted due to the solubility. Luckily, HCl escaped slowly over three days to give desired cyclometallated product **8**.

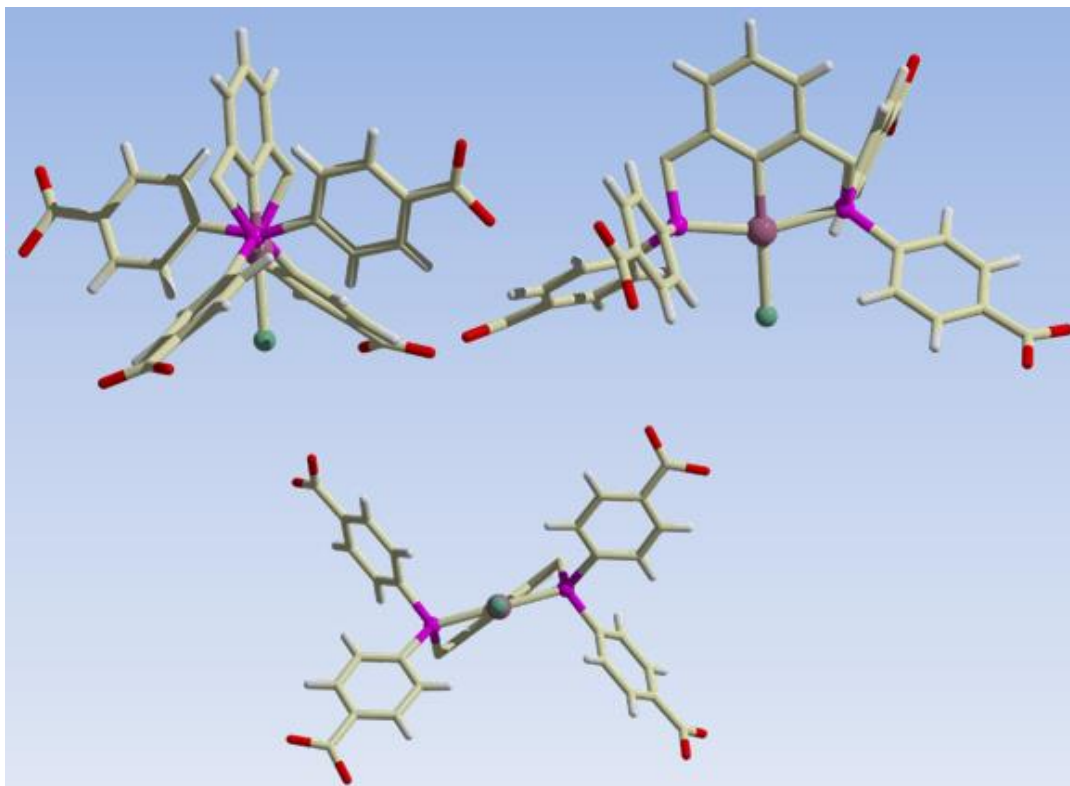


Figure 5: Synthesis of Carboxylated of PCP Pincer Ligand

After purified by column chromatography, we successfully obtained the single crystal structure of PCP-PdCl complex (Figure 5). Like most of the pincer complexes, the four atoms (two phosphines, carbanion, and palladium) are perfectly laying on the same plane. Two methylene groups twist to give so called C2 twist conformation which is common with most of d^8 4-coordinate pincer systems. Also, the tridentate structure offers two 5 member rings which stabilizes the metal thermodynamically benefiting the synthesis of PCM in later step.

2.2 PCM-36

2.2.1. Synthesis and Characterizations of PCM-36-Cl

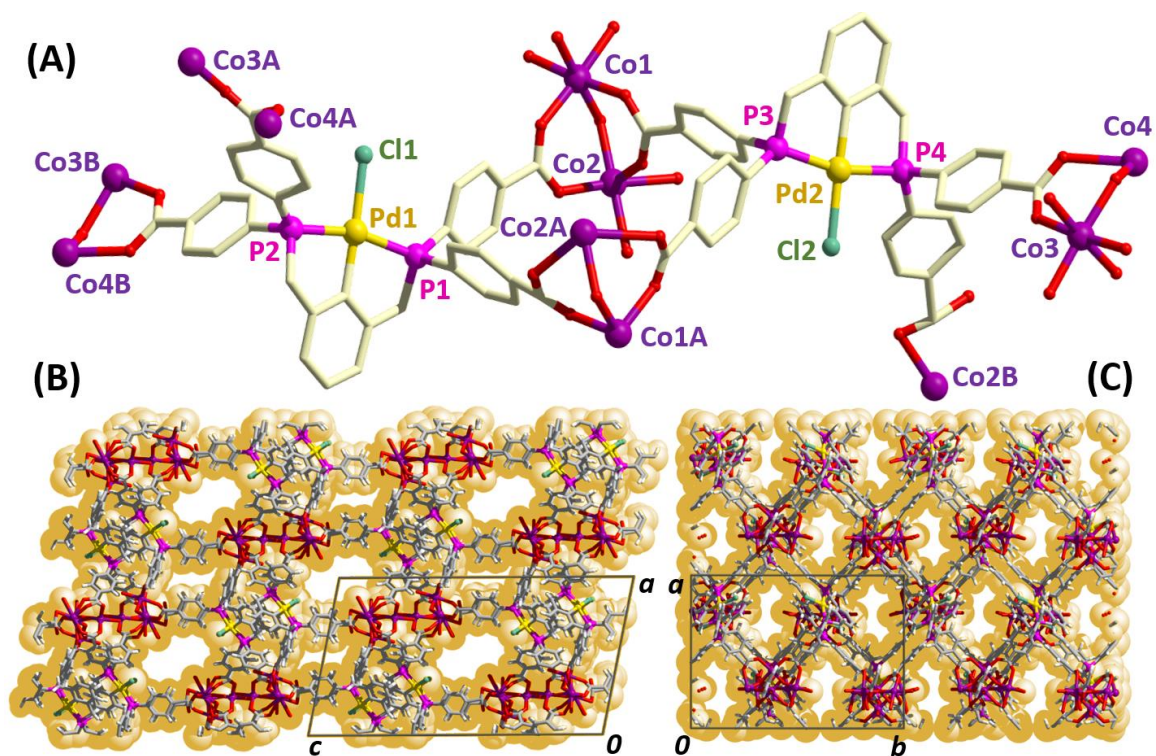
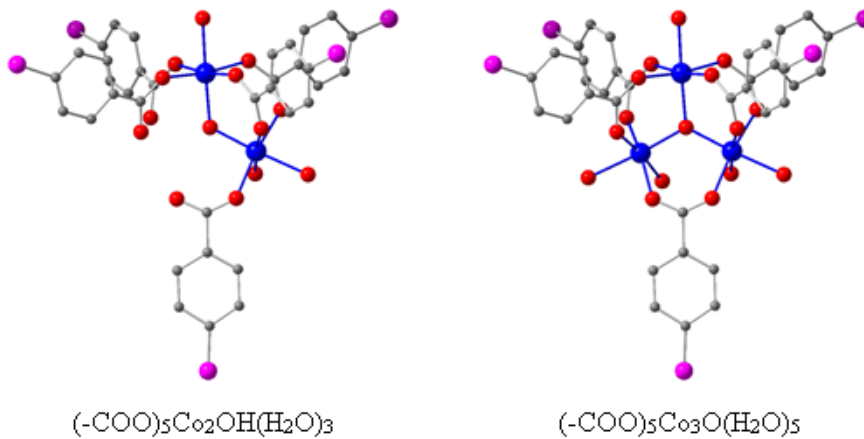


Figure 6. (A) The asymmetric unit of the PCM-36 polymer framework showing Co(II)-carboxylate connectivity (pore constituents are omitted for clarity). (B) Space-filling and superimposed ball-and-stick representation in the crystallographic ac-plane showing the largest oval shaped pores. (C) Alternative view in the ab-plane.

A mixture of 1:5 equivalences of PCP-PdCl complex to $\text{Co}(\text{BF}_4)_2$ in DMF, ethanol, and water (2:3:1) at 50 °C for two to three weeks will produce purple crystalline material named PCM-36-Cl. PCM-36-Cl has two distinct PCP pincer ligands in the asymmetric unit, and all carboxylate groups are connected to Co(II) ions. This 3-dimensional structure displays micropores in all three directions To discuss the metal cluster, it is somehow

confusing since there are two different types of inorganic nodes: a 5-connected $[\text{Co}_3(\mu^3\text{-OH})(\text{OH}_2)_5]^{5+}$ node; and a 3-connected $[\text{Co}_2(\mu^2\text{-OH})(\text{OH}_2)_6]^{3+}$ node, and both of nodes are disordered. (Figure 7) Half occupancies of each missing Co ion between $(-\text{COO})_5\text{CoOH}(\text{H}_2\text{O})_3$ and $(-\text{COO})_5\text{Co}_3\text{O}(\text{H}_2\text{O})_5$, and between $(-\text{COO})_3\text{Co}(\text{H}_2\text{O})_3$ and $(-\text{COO})_3\text{Co}_2\text{OH}(\text{H}_2\text{O})_6$. Considering charge balance by having protonated dimethylamine ions (from decomposition of dimethylformamide), the overall formula turns out to be $[\text{H}_2\text{N}(\text{CH}_3)_2]_3[\text{Co}_8(\text{OH})_3(\mathbf{8})_4(\text{OH}_2)_{17}] \cdot \text{solv}$. The presence of nitrogen is proven by elemental microanalysis of a bulk crystalline sample (observed{calculated}: C, 44.22 {44.15}; H, 3.04 {3.68}; N, 0.99 {1.03}; Cl, 3.24 {3.48} %).

(-COO)₅ node (A):



(-COO)₃ node (B):

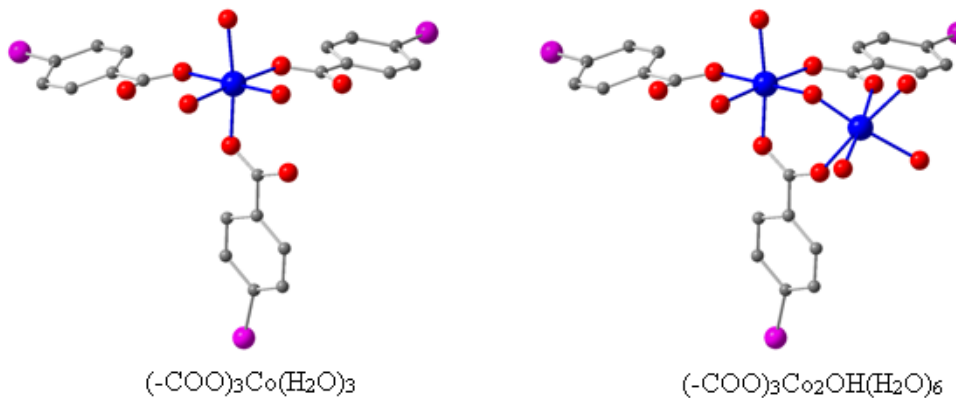


Figure 7: Coordination nodes in PCM-36

Thermogravimetric analysis (TGA) is important to reveal the thermal stability of materials. TGA using freshly as-synthesized PCM-36-Cl showed the material is stable under about 370 °C after uncoordinated solvent inside the pores was removed below 120 °C. Another valuable measurement is adsorption study using Brunauer–Emmett–Teller (BET) method. Figure 8 shows the bulk materials have relatively low surface area about 112 m²g⁻¹ using CO₂ gas. However, the adsorption and desorption experiments show that

CO and N₂ have even lower uptake which means CO₂ would most likely to access the pores of PCM-36 while CO and N₂ would not. Additionally, to ensure the bulk materials remain crystallinity after activation at 80 °C under vacuum and solvent exchange (PCM-36-Cl was set in pure MeOH or 1:1 MeOH/H₂O for a day once the fresh sample was actiated), Powder X-ray diffraction experiment (PXRD) were done comparing to the data simulated from single crystal. According to the PXRD data, PCM-36-Cl is not only stable after activation, but also stable after solvent exchanged.

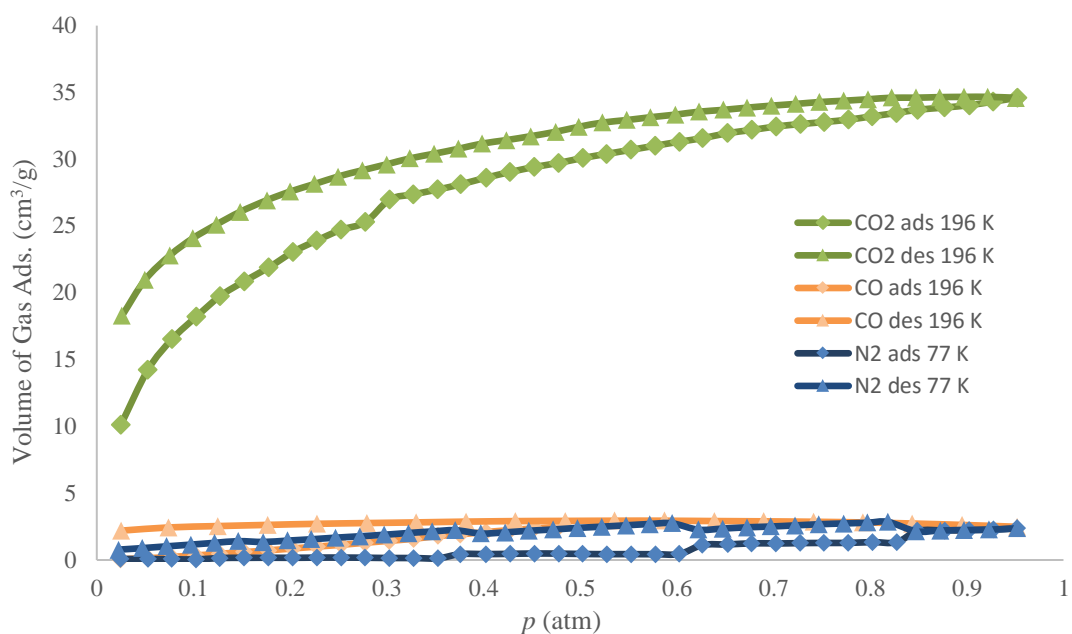


Figure 8. Adsorption and desorption isotherms for PCM-36-Cl.

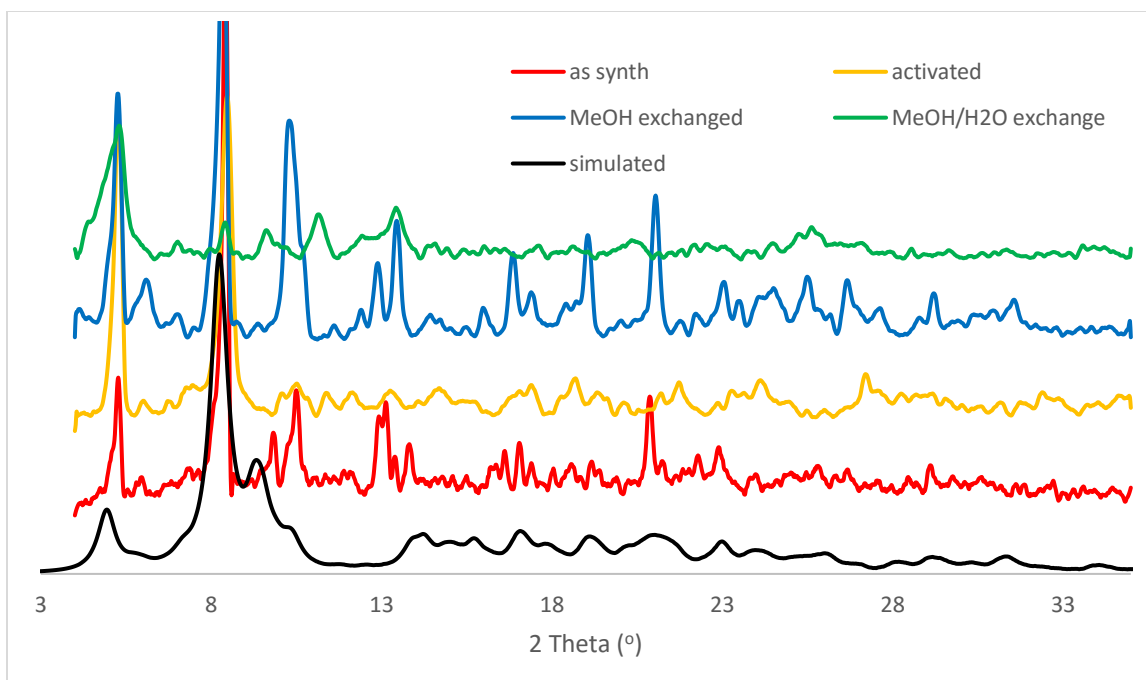
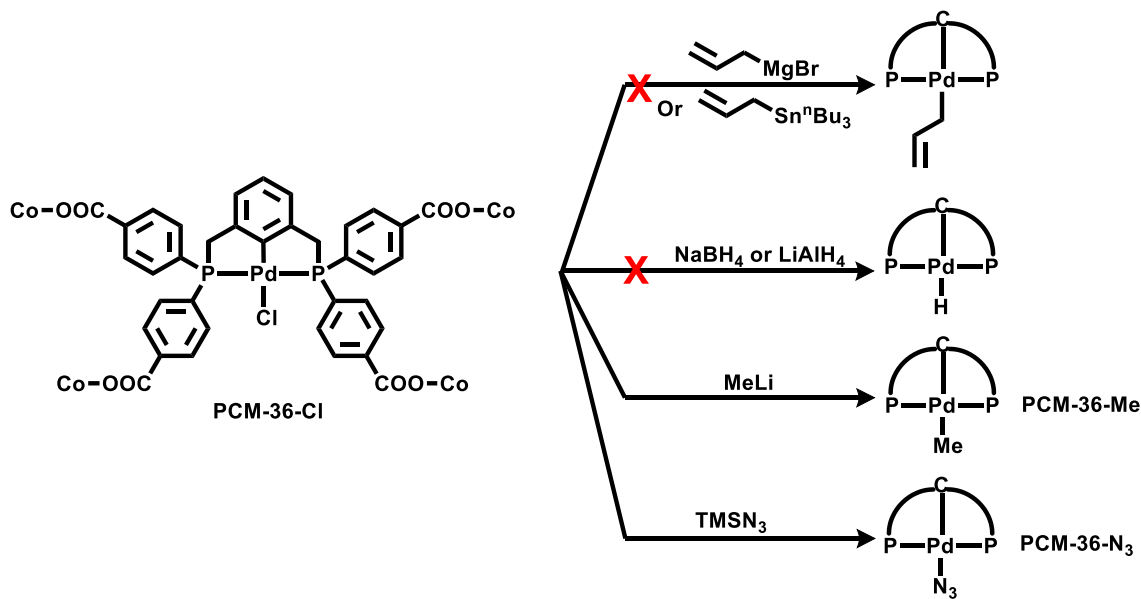


Figure 9. PXRD spectra for as-synthesized, activated, and solvent exchanged PCM-36-Cl versus simulated from single crystal data.

2.2.2. Post-synthetic Modified PCM-36 and Selective CO₂ Chemisorption

Several post-synthetic modifications to activate Pd-Cl bond were failed at the first place, such as reacting with allylmagnesium bromide, NaH, LiAlH₄ and so forth. It relates to the accessibility of the reagents, and what's more the materials should be tolerant the oxidation or reduction environments otherwise decomposition of the framework would happen. Accidentally, by screening all the routes to activate Pd-Cl bond, treating PCM-36-Cl with methyllithium and trimethylsilyl azide we were able to replace Pd-Cl bond to Pd-Me and Pd-N₃ respectively. Each activation took place in different conditions: 1) 10 eq. of methyllithium was added to PCM-36-Cl in dry THF at -30 °C. Swirl the vial every 15 min.

for 4 h, then washed the solids with THF three times and assigned as PCM-36-Me. 2) 15 eq of TMSN_3 was added dropwise to the vial at room temperature with intermittent swirling. Reaction took overnight and assigned as PCM-36- N_3 .

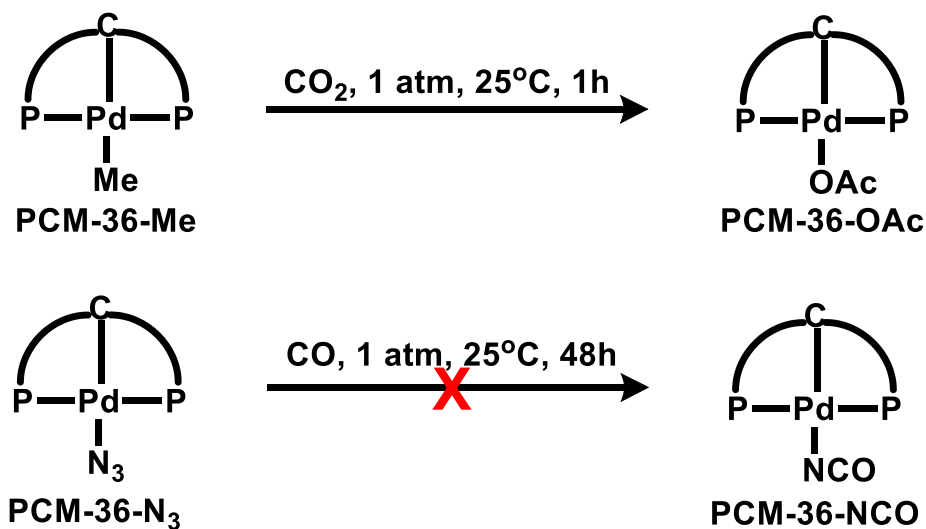


Scheme 4: Post-synthetic Modifications of PCM-36-Cl

Wendt and co-workers reported examples of CO_2 inserted into Pd-Me bond in PCP pincer in solution. When activated PCM-36-Me was exposed to dry CO_2 for 6 h at room temperature, first evidence was the new band around 1645 cm^{-1} observed in the FT-IR spectrum which was not observed from PCM-36-Me. It is also indicating that the Pd-O bond is shorter than the other, and it is called a *pseudo*-monodentate mode. By comparison, carbonyl stretch for LiOAc is centered around 1588 cm^{-1} which means reaction of residual methyl lithium and CO_2 is not responsible to the new band at 1645 cm^{-1} .¹¹ To verify this statement, we exposed the freshly prepared PCM-36-Me to 99.5% $^{13}\text{CO}_2$ and analyzed by

direct excitation ^{13}C -MAS-NMR. Although there are paramagnetic centers (high-spin Co(II), $S = 3/2$) in PCM-36, we fortunately observed a single broad peak at 167 ppm by increasing the scan number.

Another experiment was done using PCM-36- N_3 . According to the observation of Lee et. al, PCP-Pd- N_3 is able to reaction with CO gas to form NCO by Curtius Rearrangement releasing N_2 at 1 atm over 12 h quantitatively. In solid state the process can be simply monitored by FT-IR since the characteristic N_3 symmetric stretching *ca.* 2075 cm^{-1} and NCO *ca.* 2188 cm^{-1} . We then exposed PCM-36- N_3 under 1 atm CO atmosphere, no reaction was observed even after 48 h. Only increase pressure to 4 atm for 72 h, partial conversion from N_3 to NCO was detected. Recall the result from PCM-36 gas up take experiment of CO, a rational explanation is that CO gas is notable to access the pores of PCM-36, and it is only reacting Pd- N_3 on the surface of PCM-36.



Scheme 5: Post-synthetic Modifications of PCM-36-Cl

Chapter 3: Materials and Methods

3.1. General Procedures and Reagents

All ligand syntheses were performed under an N₂ atmosphere using standard Schlenk techniques. 1,4-dibromobenzene (Alfa Aesar; 98%), phosphorus trichloride (Sigma-Aldrich), n-butyllithium (1.6 M and 2.5 M solution in hexanes; Acros), sodium metal (Alfa Aesar; in mineral oil, ≥99%), 1,3-bis(bromomethyl)benzene (Combi-Blocks; ≥98%), trichlorosilane (Aldrich; 99%), Na₂SO₄ (Fisher, ≥99%) NaHCO₃ (Aldrich; ≥97%), bis(acetonitrile) dichloropalladium (Combi-Blocks; ≥98%), methyllithium (3 M solution in ether; Acros), Co(BF₄)₂ (Alfa Aesar; ≥96%) and trimethylsilyl azide (Alfa Aesar) were used as received. *p*-xylene was distilled prior to use by refluxing over sodium metal. Other organic solvents (tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), ethanol, diethyl ether and toluene) were obtained from Fisher Scientific and dried/degassed using a Solvent Purification System (Innovative Technology, Inc.), degassed using freeze-thaw cycles and stored over molecular sieves prior to use. Bench solvents including hexanes, acetone, and all aqueous solutions were purged with N₂ for 30 min prior to use. Solution ¹H-NMR, ¹³C-NMR and ³¹P-NMR were collected in-house using a Varian Unity 400 MHz spectrometer; FT-IR spectra and Far-IR spectra were obtained directly from solid samples using a Nicolet iS*50 spectrophotometer fitted with

an attenuated total reflectance apparatus; thermogravimetric analyses (TGA) were collected using a TA Instruments Q50 system.

Solid-State MAS-NMR. $^{13}\text{C}\{^1\text{H}\}$ MAS-NMR spectra were obtained with a Bruker Avance-400 spectrometer (400 MHz for protons) equipped with a standard 2.5-mm MAS probe head. A standard 4 mm zirconium oxide rotor was used at a spinning rate of 5.5 kHz. Standard one-pulse (direct nuclear excitation) and/or CP pulse sequences were applied in these experiments at the contact times were adjusted for the ^{13}C nucleus.

Single Crystal X-Ray Diffraction (SCXRD). Crystals were mounted on thin glass fibers using perfluoropolyether oil, which was frozen in situ by a nitrogen gas Cryostream flow. Data was collected at 100 K. Structures were solved using direct methods, with full-matrix least squares refinement. All data was collected using $\text{CuK}\alpha$ radiation (1.7902 Å) on an Agilent Super Nova diffractometer equipped with an AtlasS2 CCD, and Oxford 700 low-temperature attachment.

Powder X-ray diffraction (PXRD). Phase purity of the PCM-36 materials before and after activation were confirmed by analysis of powdered crystalline samples that were sealed inside borosilcate capillary tubes and spun in situ to prevent preferential orientation of the crystallites. Spectra were recorded on a Rigaku R-Axis Spider diffractometer with an image plate detector, using $\text{CoK}\alpha$ radiation (1.7902 Å). Reflection data was collected in the range $3.0\text{--}40.0^\circ$ 2θ using multiple scans, which were subsequently averaged. The PXRD spectra were then compared directly to their corresponding simulated patterns that were generated using the SimPowPatt function in PLATON using the single crystal model for the hkl reflection data obtained from the single crystal experiment.

3.2. Ligand and PCM Synthesis and Characterizations

Bis(4-bromophenyl)N,N-Diethylaminophosphoramidite (1).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 0.87$ (t, $J = 7.04$ Hz, 6 H), 2.91-3.04 (m, 4 H), 7.16-7.21 (m, 4 H), 7.37-7.44 (m, 4 H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 13.4$ (d, $J = 2.99$ Hz), 43.2 (d, $J = 15.71$ Hz), 121.9 (d, $J = 1.50$ Hz), 130.3 (d, $J = 5.98$ Hz), 132.4 (d, $J = 1.00$ Hz), 137.90 (d, $J = 16.46$ Hz); $^{31}\text{P-NMR}$ (161.8 MHz, CDCl_3): $\delta = 58.9$.

Bis(4-bromophenyl)chlorophosphine (2).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.37$ -7.44 (m, 2 H) 7.54 (dd, $J = 8.22, 0.98$ Hz, 2 H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 132.0$ (d, $J = 7.48$ Hz) 133.2 (d, $J = 1.00$ Hz) 137.4 (d, $J = 1.00$ Hz); $^{31}\text{P-NMR}$ (161.8 MHz, CDCl_3): $\delta = 77.8$.

Ethyl Bis(4-bromophenyl)phosphinite (3).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 1.29$ (t, $J = 7.04$ Hz, 3 H), 3.83-3.96 (m, 2 H), 7.26-7.34 (m, 4 H), 7.49 (d, $J=1.00$ Hz, 4 H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 17.1$ (d, $J=8.39$ Hz), 66.1 (d, $J = 21.00$ Hz), 124.0 (s), 131.6 (d, $J = 9.00$ Hz), 131.8 (s), 140.9 (d, $J = 19.07$ Hz); $^{31}\text{P-NMR}$ (161.8 MHz, CDCl_3): $\delta = 107.6$.

1,3-bis{methyldi(4-bromophenyl)phosphine oxide}benzene (5).

M.p. = 215-217 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 3.60-3.70 (m, 4 H), 7.07 (d, J = 7.83 Hz, 2 H), 7.36 (t, J = 7.73 Hz, 1 H), 7.42-7.57 (m, 16 H); ³¹P-NMR (161.8 MHz, CDCl₃): δ = 28.7.

1,3-bis{methyl(4-bromophenyl)phosphine}benzene (6).

M.p. = 61-64 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 3.07-3.27 (m, 4 H), 6.70 (d, J = 9.00 Hz, 3 H), 6.83-6.98 (m, 1 H), 7.09 (t, J = 6.75 Hz, 8 H), 7.30-7.46 (m, 8H); ¹³C-NMR (101 MHz, CDCl₃): δ = 35.7 (d, J = 16.79 Hz), 123.6 (s), 127.2 (dd, J = 6.87, 3.05 Hz), 128.1-128.6 (m), 129.0 (s), 130.2 (t, J = 7.25 Hz), 131.6 (d, J = 6.87 Hz), 134.3 (d, J = 19.08 Hz), 136.8 (d, J = 17.55 Hz); ³¹P-NMR (161.8 MHz, CDCl₃): δ = -12.1.

4,4',4'',4'''-((1,3-phenylenebis(methylene))bis(phosphinetriyl))tetrabenzoic acid (7).

M.p. = 165-169 °C. ¹H-NMR (400 MHz, DMSO-d₆): δ = 3.43-3.60 (m, 4 H), 6.78 (d, J = 7.04 Hz, 2 H), 6.92 (t, J = 7.43 Hz, 2 H), 7.19-7.56 (m, 10 H), 7.72-7.93 (m, 6 H), 12.99 (br. s., 4 H); ¹³C-NMR (101 MHz, DMSO-d₆): δ = 27.1 (s), 129.0 (d, J = 6.87 Hz), 129.4 (d, J = 6.87 Hz), 129.6 (d, J = 6.87 Hz), 131.1 (s), 131.5 (s), 132.7 (d, J = 17.55 Hz), 133.2 (d, J = 19.07 Hz), 133.5 (d, J = 19.84 Hz), 143.7 (d, J = 19.07 Hz); ³¹P-NMR (161.8 MHz, DMSO-d₆): δ = -9.8. HRMS (ESI, m/z): for C₃₆H₂₈O₈P₂ calculated 649.1199; found 649.1187.

PdCl{C₆H₃-2,6-[CH₂P(C₆H₅-4-COOH)₂]₂} (8).

$^1\text{H-NMR}$ (400 MHz, DMSO- d_6): δ = 4.24 (br. s., 4 H), 7.03 (d, J = 7.28 Hz, 1 H), 7.13 (d, J = 7.50 Hz, 2 H), 7.92-8.10 (m, 16 H); $^{13}\text{C-NMR}$ (101 MHz, DMSO- d_6): δ = 63.2 (s), 123.8-124.4 (m), 126.4-127.0 (m), 129.9 (t, J = 4.96 Hz), 133.2-134.1 (m), 136.8 (s), 147.7-148.3 (m), 159.2 (s), 167.2 (s); $^{31}\text{P-NMR}$ (161.8 MHz, DMSO- d_6): δ = 34.5. HRMS (ESI, m/z): for $\text{C}_{36}\text{H}_{27}\text{ClO}_8\text{P}_2\text{Pd}$ calculated 788.9847; found 788.9842.

PCM-36-Cl

The metalloligand 5 (15 mg, 19 μmol), trimethylamine (1.5 equiv.) and $\text{Co}(\text{BF}_4)_2$ (5 equiv.) were dissolved in 6.0 cm^3 of a DMF:EtOH:H $_2$ O mixture (2:3:1 v/v/v). The solution was heated in a 20 cm^3 scintillation vial at 50 $^\circ\text{C}$ for 14 d in a graphite thermal bath. The resulting purple crystalline material was isolated by decantation and washed with fresh solvent. Average yield: 3 mg. FT-IR (solid/ cm^{-1}): ν_{max} = 3044 (br), 1651 (s), 1582 (s), 1532 (m), 1381 (m), 1185 (m), 1095 (s), 1016 (s), 958 (s), 837 (s), 770 (s), 718 (s), 696 (s), 632 (s), 584 (s), 529 (s), 487 (m), 380 (br), 270 (m), 165 (m), 154 (s), 145 (m).

PCM-36-Me.

PCM-36-Cl (15 mg per reaction) was vacuum-activated to remove residual solvent (80 $^\circ\text{C}$, overnight) in a 10 cm^3 vial screw-cap vial within a vacuum chamber. Then, under N_2 protection, a solution of MeLi (3.0 M, 10 equiv.) dissolved in dry diethyl ether was added dropwise to the vial in a dry ice bath at -30 $^\circ\text{C}$ over 15 mins with intermittent swirling. The solids were then allowed to stand in the closed vial at -30 $^\circ\text{C}$ for a further 4 h with

occasional agitation. The product was then isolated by decanting away the solution and washing with dry THF over several cycles, allowing to stand in-between cycles. FT-IR (solid/cm⁻¹): ν_{\max} = 3675.94 (s), 2926 (br, m), 1594.90 (m), 1538.11 (s), 1494.85 (s), 1382.76 (s), 1251.47 (m), 1096.97 (s), 1057.85 (s), 1016.36 (s), 955.97 (s), 827.63 (s), 772.44 (s), 718.06 (m), 481.48 (br), 409.81 (br), 386.33 (br), 246.85 (m), 202.84 (m), 168.08 (m), 150.82 (m).

PCM-36-N₃.

Similarly, vacuum activated PCM-36-Cl samples (15mg) were placed in 10 cm³ vials under N₂ protection. TMSN₃ (15 equiv.) was added dropwise to the vial at room temperature, with intermittent swirling. The solids were allowed to stand in the closed vial overnight with intermittent agitation. The product was then isolated by decanting away the solution and washing with dry THF over several cycles, allowing to stand in-between cycles. FT-IR (solid/cm⁻¹): ν_{\max} = 2931.23 (br, m), 2075.68 (s), 1713.66 (s), 1650.89 (s), 1592.43 (s), 1538.37 (s), 1495.11 (s), 1382.10 (s), 1251.13 (s), 1183.37 (s), 1095.19 (s), 1056.84 (s), 1016.36 (s), 957.35 (s), 837.95 (s), 770.64 (s), 719.12 (s), 695.57 (s), 631.79 (s), 587.03 (s), 480.42 (br), 382.70 (br), 176.63 (m), 150.61 (s), 140.78 (s).

3.3. Other Supporting Informations

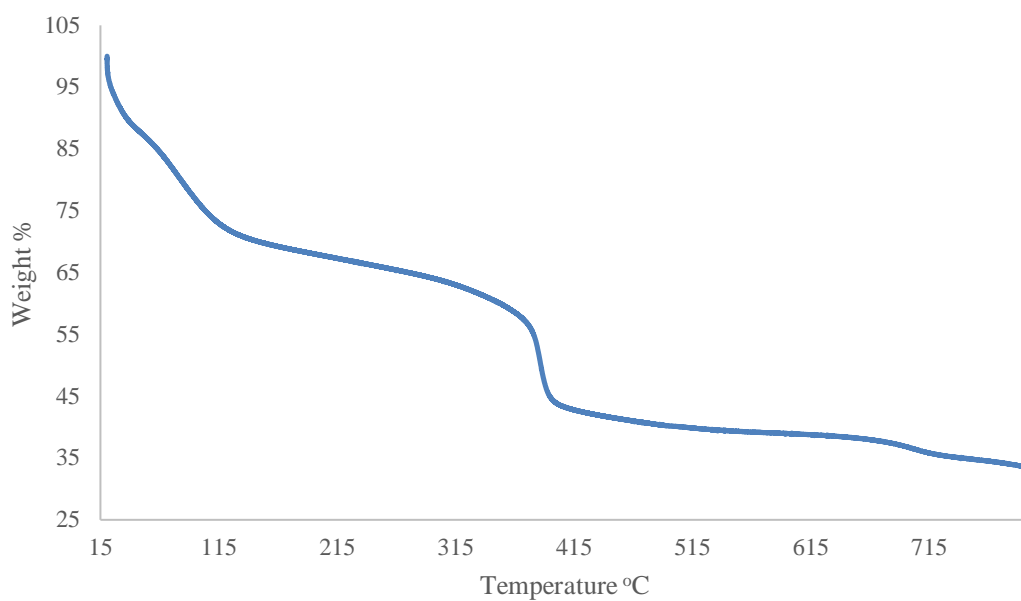


Figure 10: TGA for PCM-36-Cl.

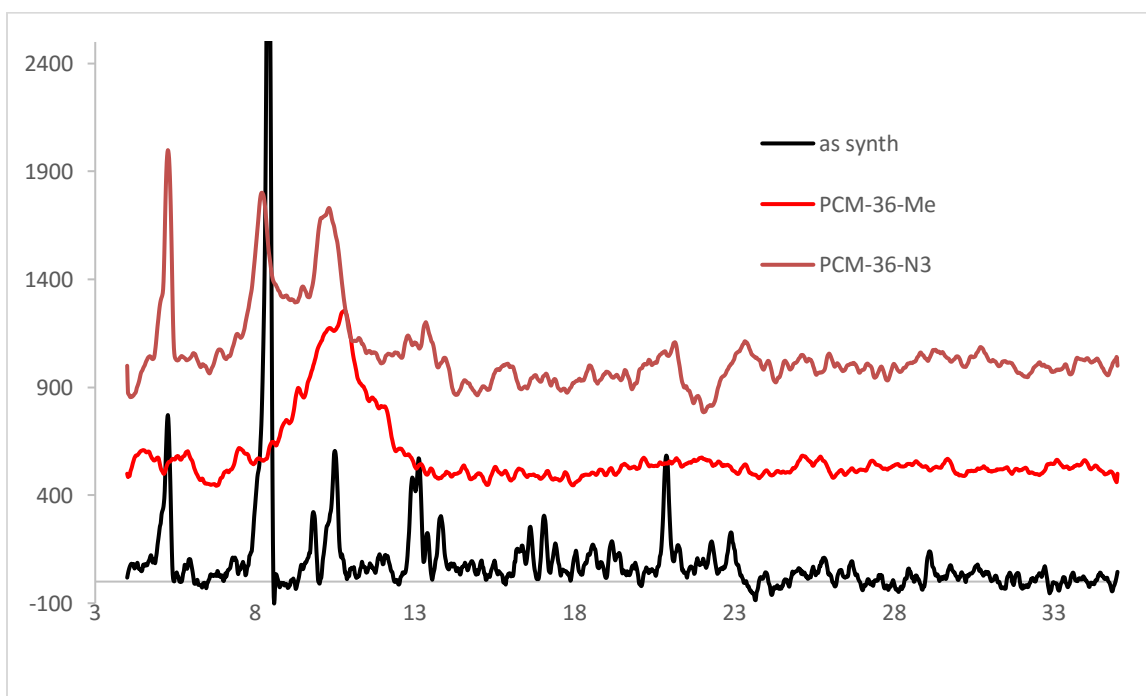


Figure 11: PXRD spectra for as-synthesized PCM-36-Cl, PCM-36-Me, and PCM-36-N₃.

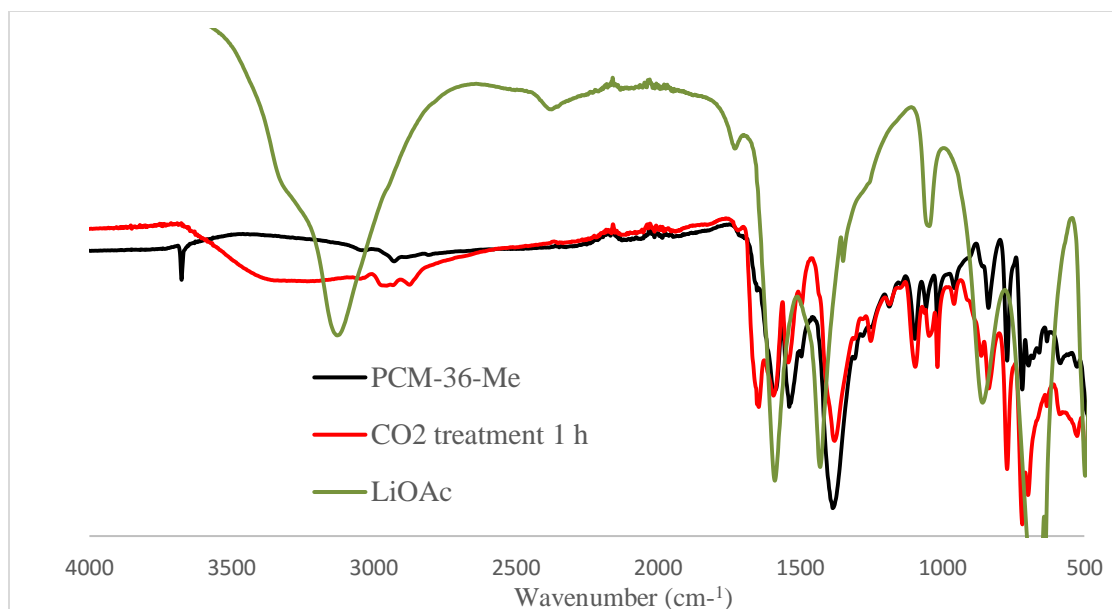


Figure 12: FT-IR spectral comparisons for PCM-36-Me, and after treatment with 1 atm CO₂ for 6 h.

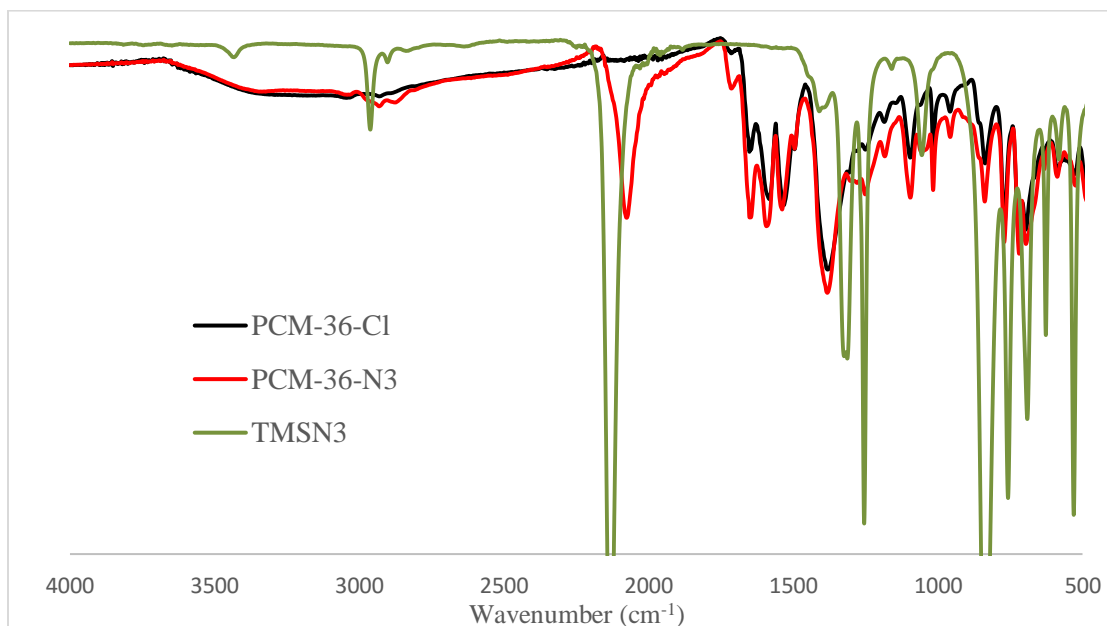


Figure 13: FT-IR spectral comparisons for PCM-36-Cl and PCM-36-N₃.

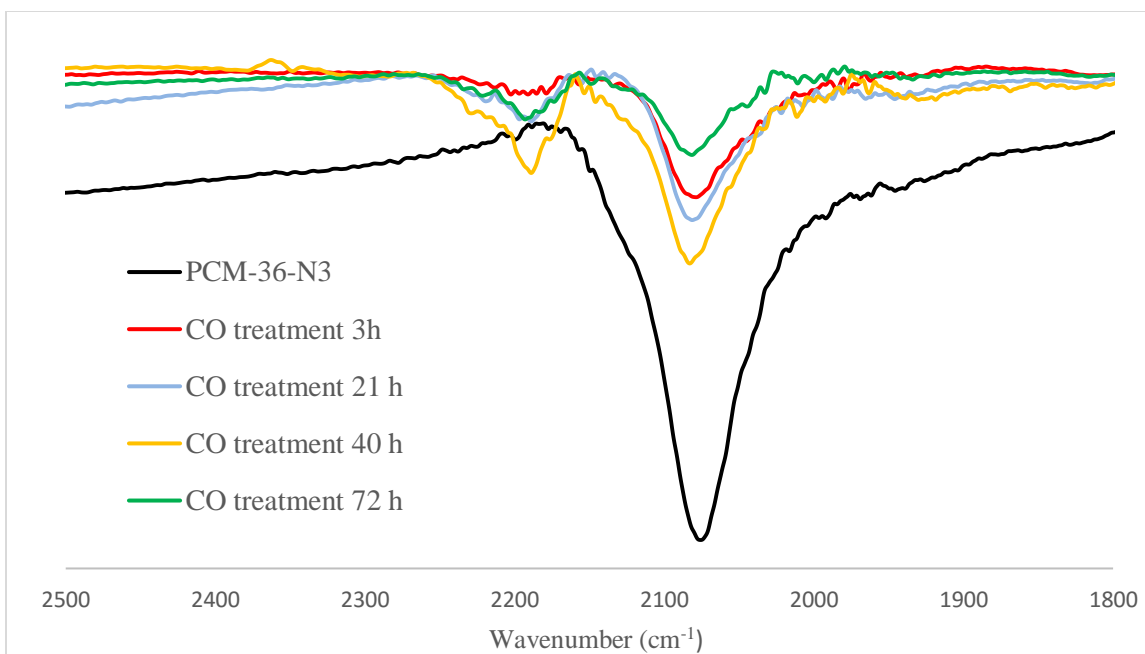


Figure 14: FT-IR spectral comparisons for PCM-36-N₃, and after treatment with 3 atm CO.

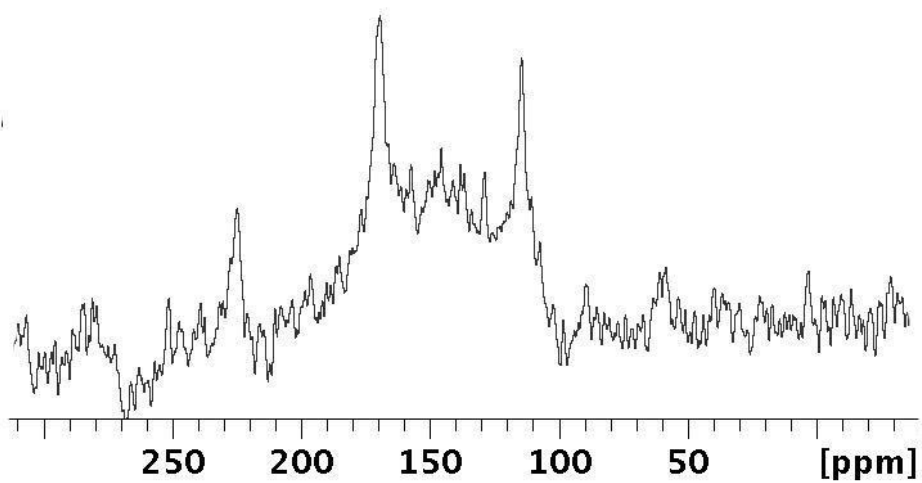
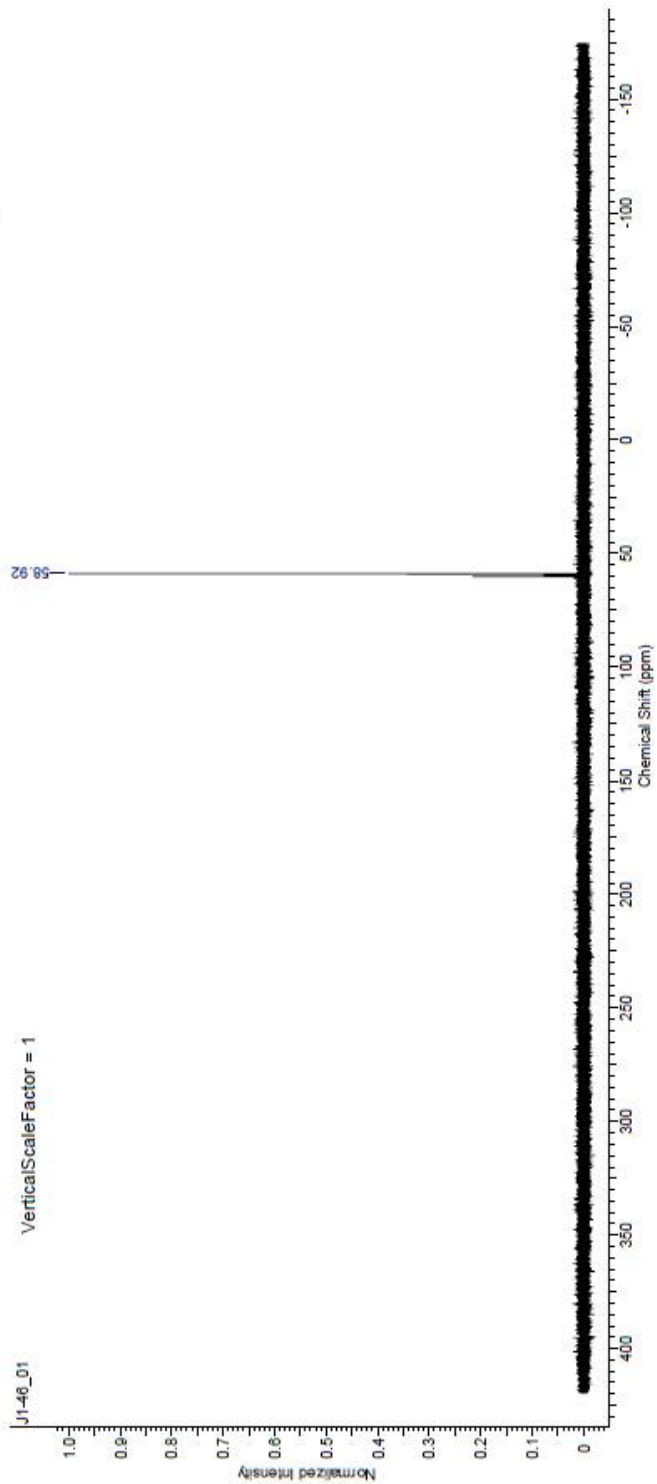
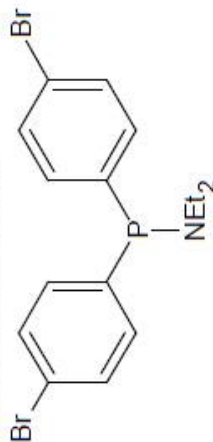


Figure 15: ¹³C{¹H}CP/MAS-NMR spectrum for PCM-36-Me after treatment of 1 atm ¹³CO₂ for 6 h.

Bis(4-bromophenyl)N,N-Diethylaminophosphoramidite (**1**) :

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Acquisition Time (sec)	1.8000	Date	Mar 1 2014	Date Stamp	Mar 1 2014
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				Temperature (degree C)	AMBIENT TEMPERATURE

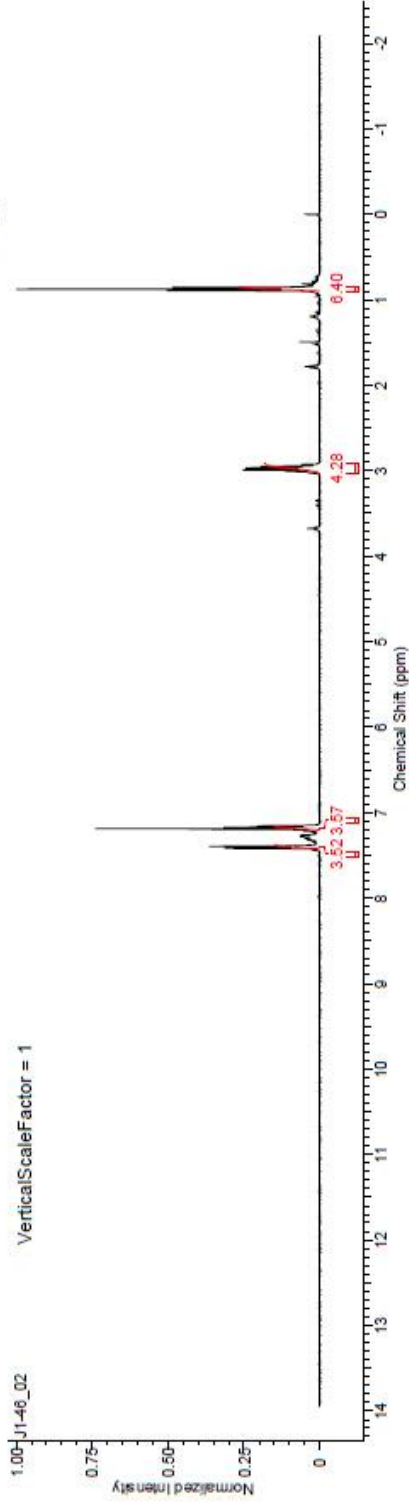
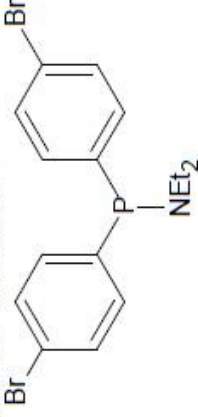


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Formula C₁₄H₁₀Br₂NP FW 415.1026

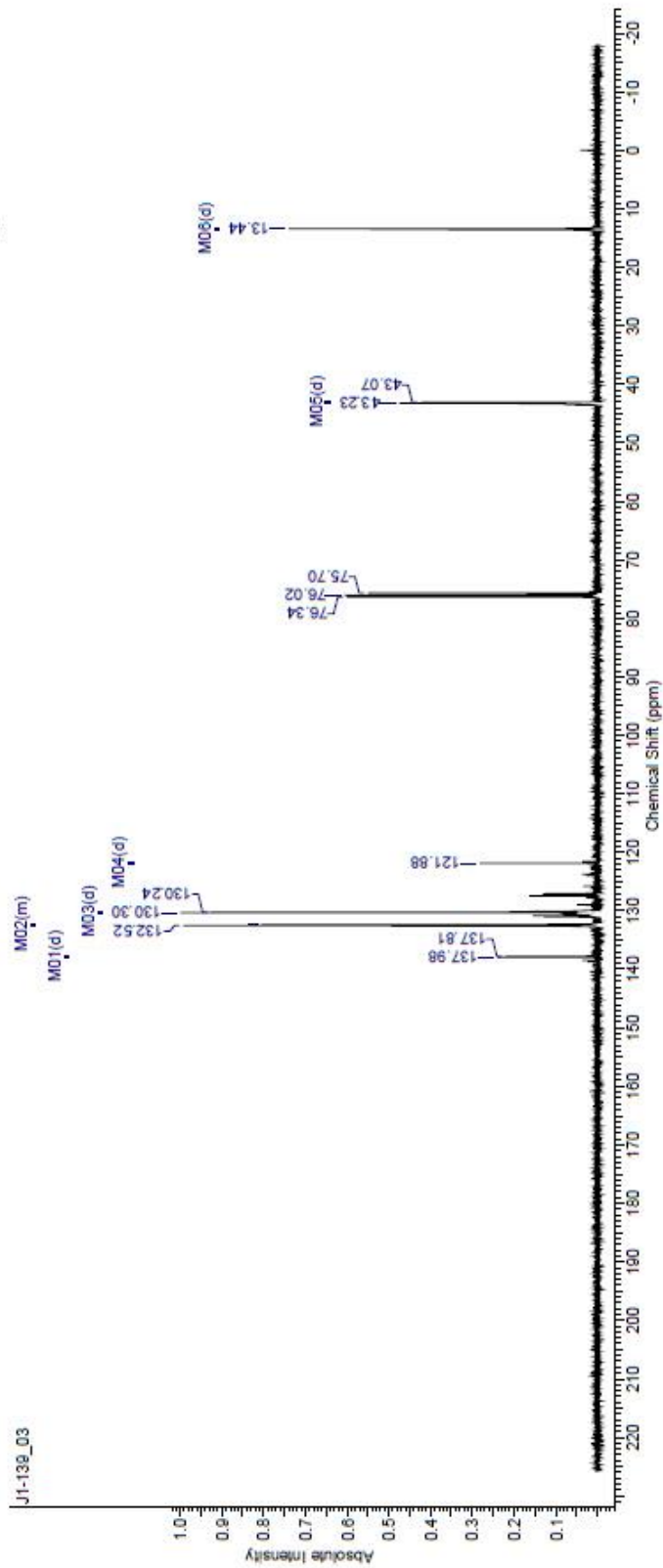
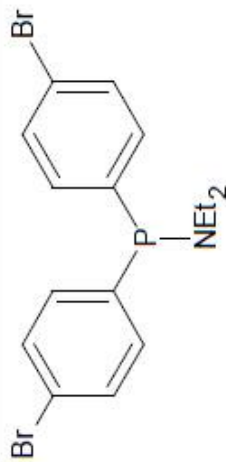
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Pulse Sequence	s2pul	Receiver Gain	60.00	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	2370.9810	Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	AMBIENT TEMPERATURE

¹H NMR (400 MHz, CHLOROFORM-d) δ ppm 0.87 (t, $J=7.04$ Hz, 6 H) 2.91 - 3.04 (m, 4 H) 7.16 - 7.21 (m, 4 H) 7.37 - 7.44 (m, 4 H)



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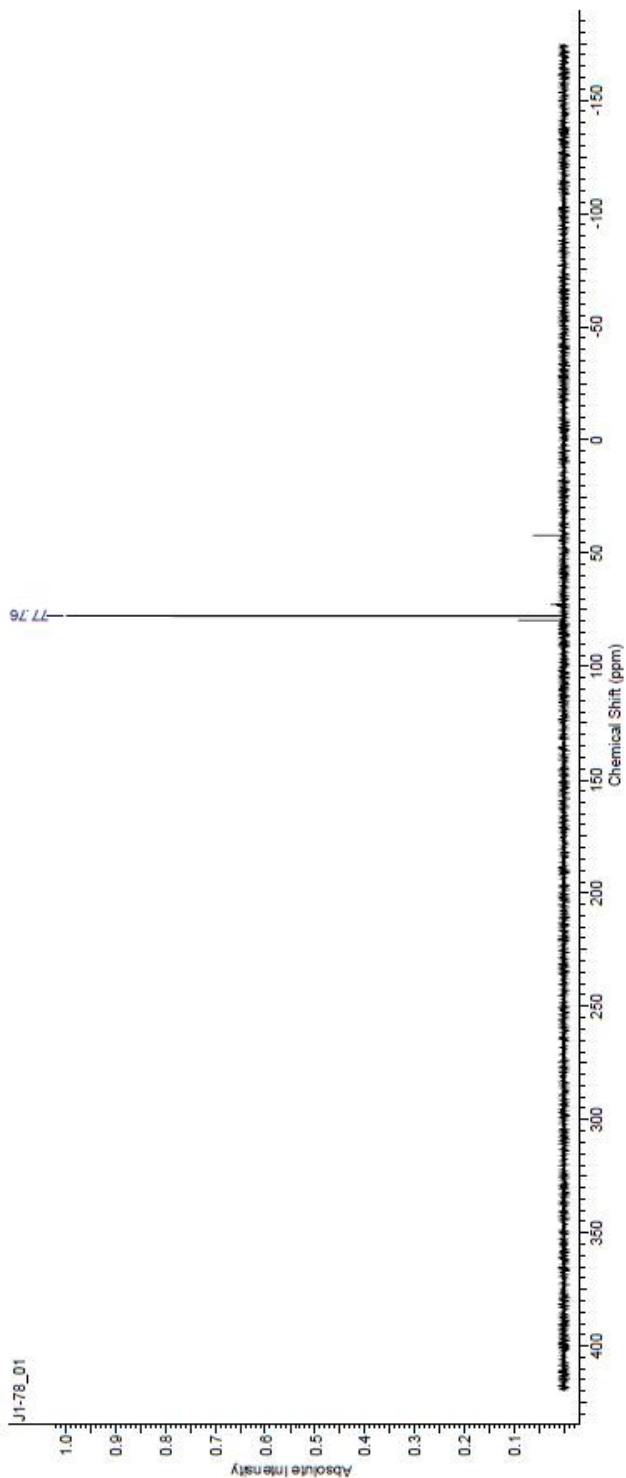
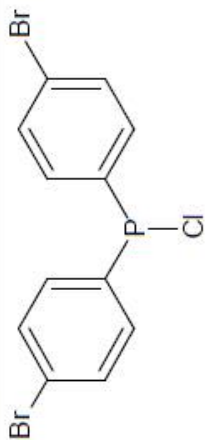
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		Solvent	CHLOROFORM-d
		Temperature (degree C)	AMBIENT TEMPERATURE
		Frequency (MHz)	100.54
		Points Count	32768
		Spectrum Offset (Hz)	10444.7910



Bis(4-bromophenyl)chlorophosphine (2) :

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Formula	C ₁₀ H ₈ Br ₂ ClP	FW	378.4267		
Acquisition Time (sec)	1.6000	Date	Apr 15 2014		
File Name	C:\Users\Smallorange\Documents\Academy\PH.D - Chemistry\PhD Research\NMR data\J1-78_01.fid.fid	Research/NMR data\J1-78_01.fid.fid	Frequency (MHz)	161.86	
Nucleus	31P	Number of Transients	64	Original Points Count	153650
Pulse Sequence	szpul	Receiver Gain	40.00	Solvent	CHLOROFORM-d
Spectrum Type	STANDARD	Sweep Width (Hz)	96153.80	Temperature (degree C)	AMBIENT TEMPERATURE
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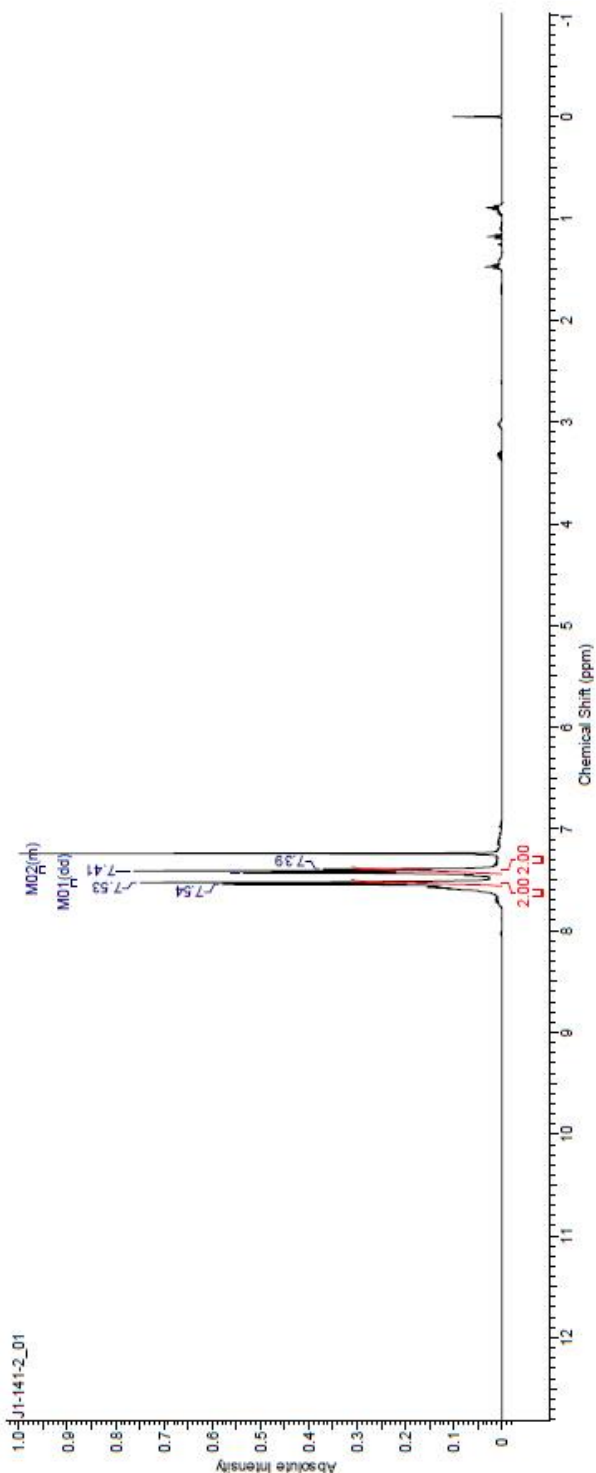
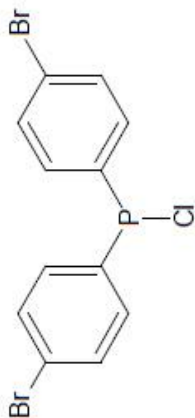


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Formula C₁₂H₈Br₂ClP FW 378.4267

Acquisition Time (sec)	4.0000	Date	Sep 25 2014	Date Stamp	Sep 25 2014
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Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	AMBIENT TEMPERATURE

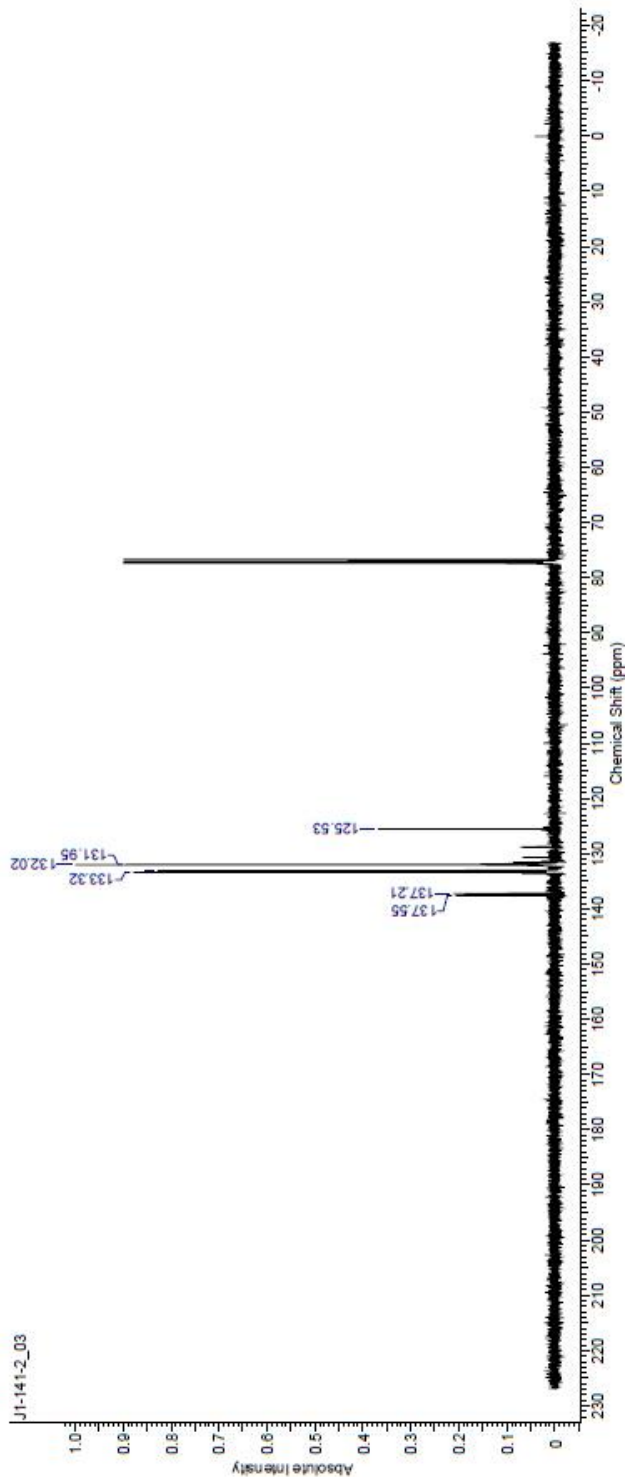
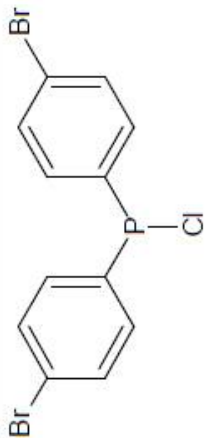
¹H NMR (400 MHz, CHLOROFORM-d) δ ppm 7.37 - 7.44 (m, 2 H) 7.54 (dd, $J=8.22, 0.98$ Hz, 2 H)



This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Formula	C H Br Cl P	FW	378.4267
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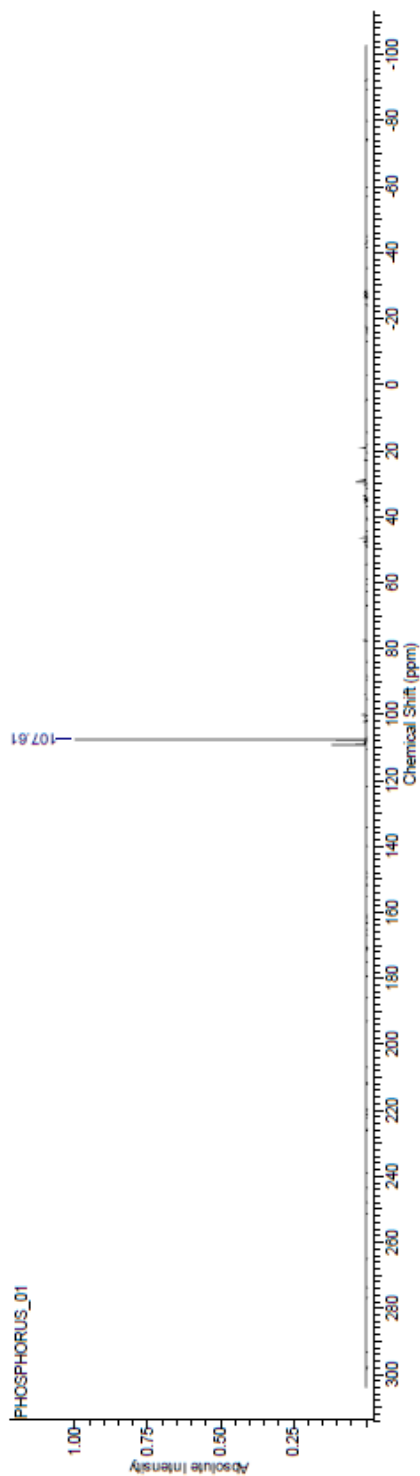
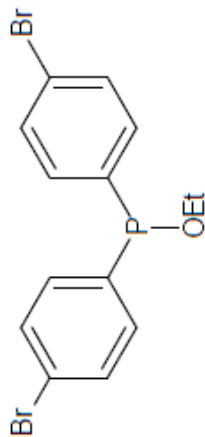
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Pulse Sequence	52pul	Receiver Gain	30.00	Temperature (degree C)	AMBIENT TEMPERATURE		
Spectrum Type	STANDARD	Sweep Width (Hz)	24509.80				



Ethyl Bis(4-bromophenyl)phosphinite (3) :

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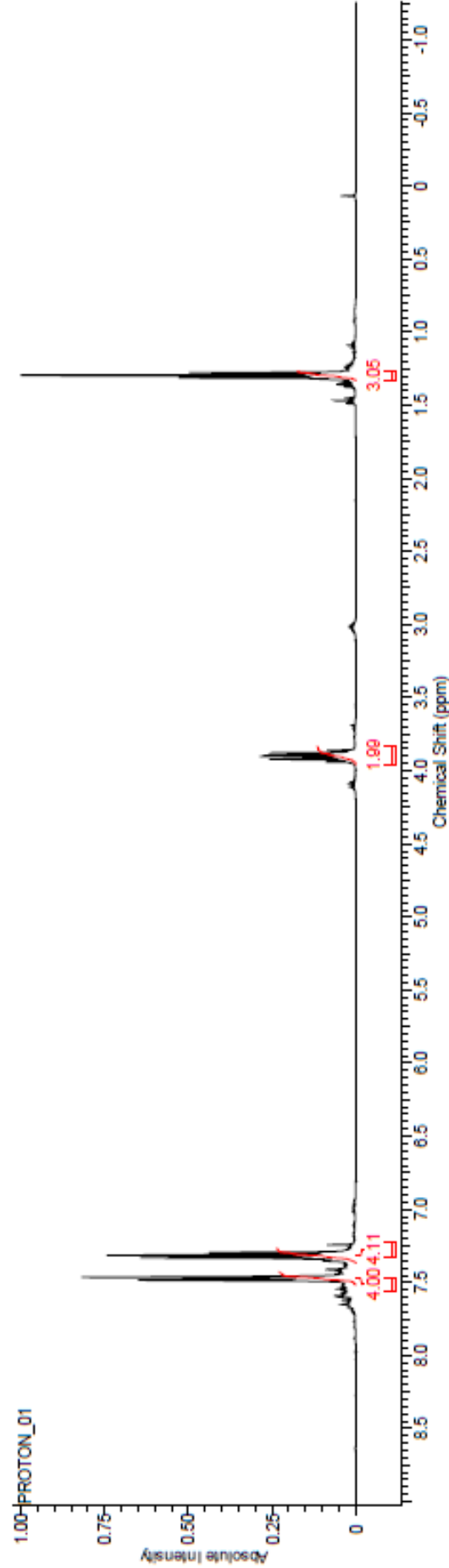
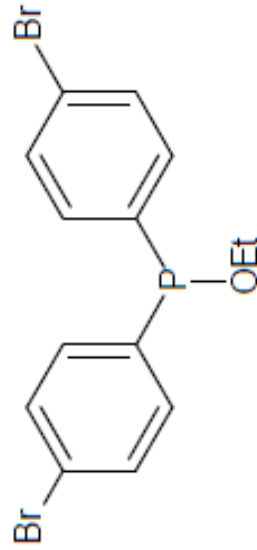
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Sweep Width (Hz)	65789.48					
Original Points Count	65536					
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Temperature (degree C)	25.000					



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Formula C₁₄H₁₀Br₂OP
FW 388.0642

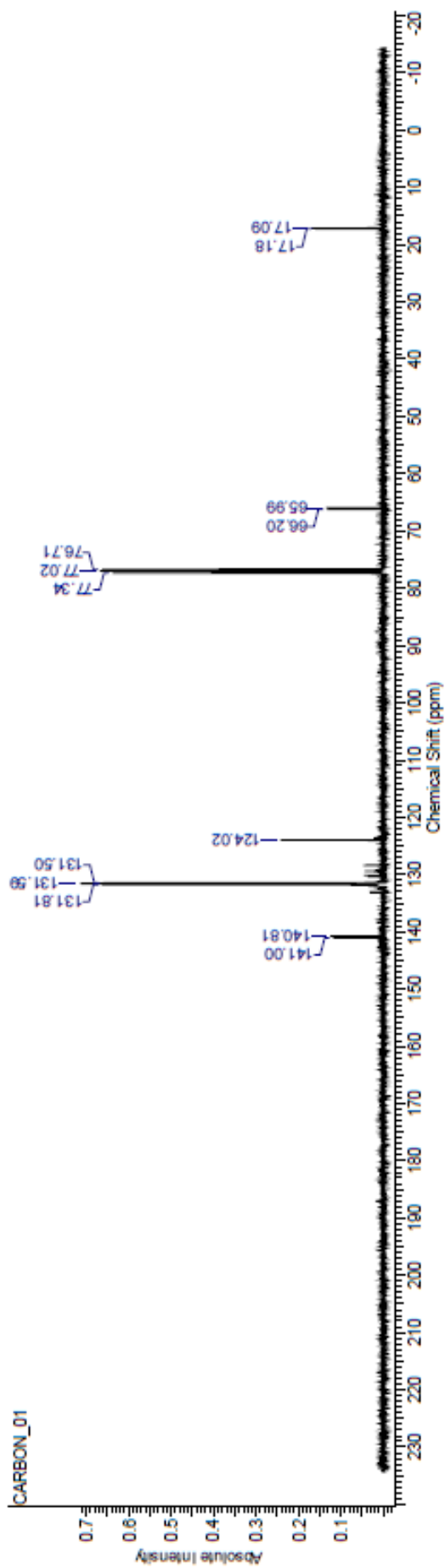
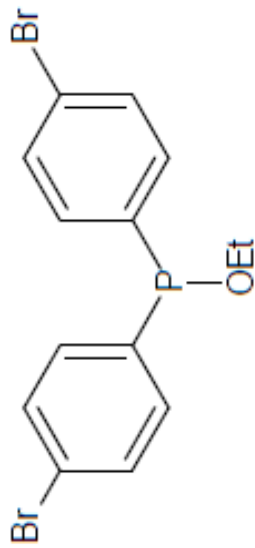
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This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Formula C₁₄H₉Br₂OP
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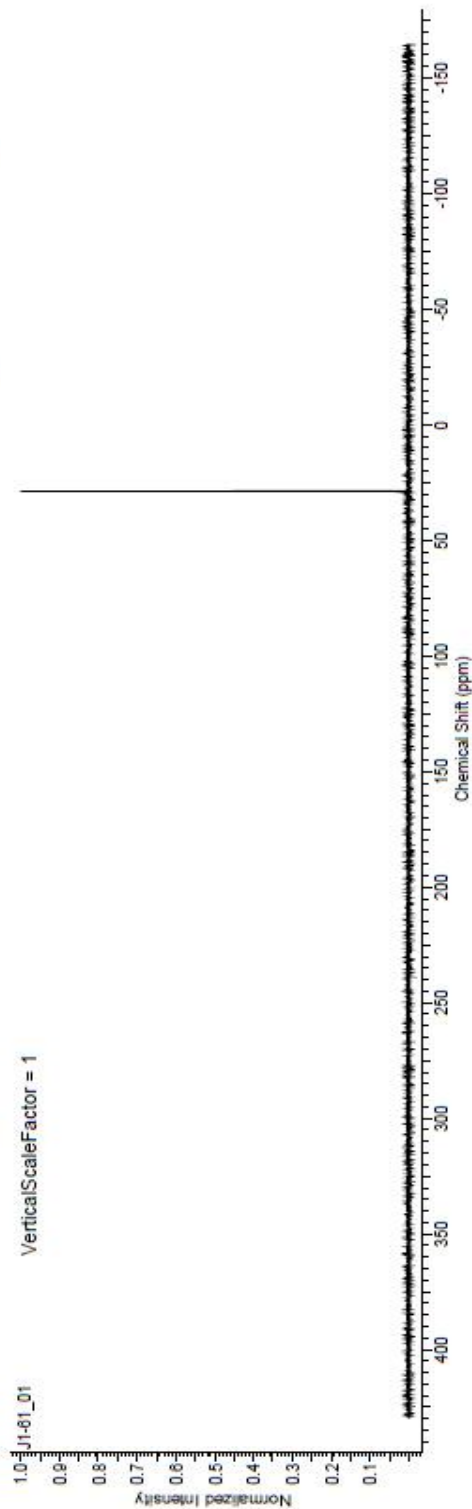
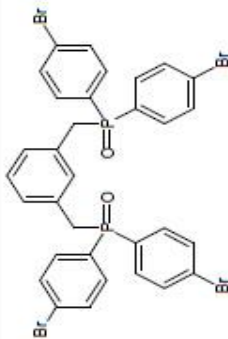
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1,3-bis[methyldi(4-bromophenyl)phosphine oxide]benzene (4) :

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Receiver Gain	40.00	Temperature (degree C)	AMBIENT TEMPERATURE
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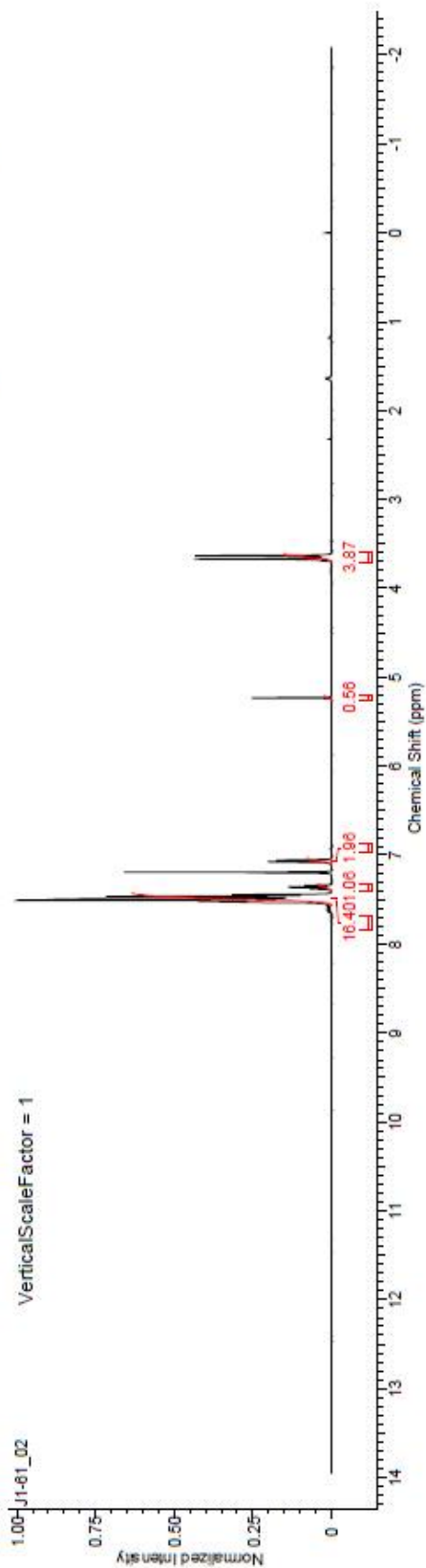
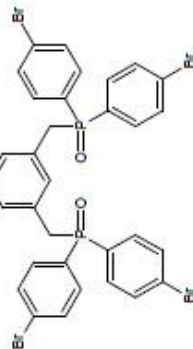
No.	(ppm)	(Hz)	Height
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This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Formula C₁₄H₈Br₄O₂ FW 822.0863

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Pulse Sequence	s2pul	Receiver Gain	60.00	Solvent	CHLOROFORM-d		
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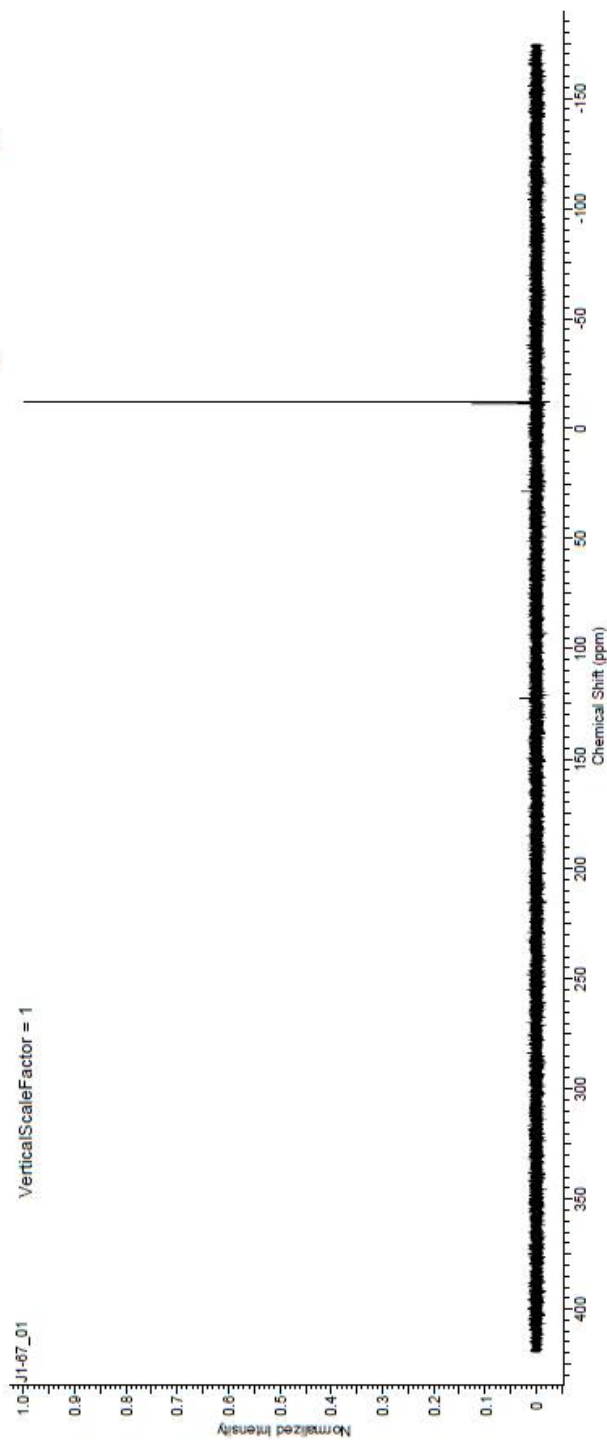
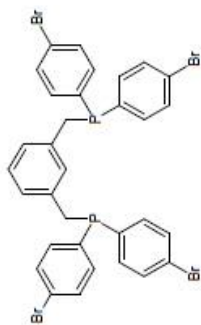
¹H NMR (400 MHz, CHLOROFORM-d) δ ppm 3.60 - 3.70 (m, 4 H) 7.07 (d, $J=7.83$ Hz, 2 H) 7.36 (t, $J=7.73$ Hz, 1 H) 7.42 - 7.57 (m, 16 H)



1,3-bis[methyldi(4-bromophenyl)phosphine]benzene (**5**) :

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Formula	C ₁₄ H ₁₀ Br ₄ P ₂	FW	790.0965
Acquisition Time (sec)	1.6000	Date	Apr. 1. 2014
File Name	C:\Users\Smallorange\Documents\Academy\PH.D - Chemistry\PhD Research\NMR data\J1-67_01.fid.tif	Date Stamp	Apr. 1. 2014
Nucleus	31P	Original Points Count	153850
Pulse Sequence	s2pul	Receiver Gain	40.00
Spectrum Type	STANDARD	Solvent	CHLOROFORM-d
		Temperature (degree C)	AMBIENT TEMPERATURE
		Frequency (MHz)	161.86
		Points Count	262144
		Spectrum Offset (Hz)	19825.8457

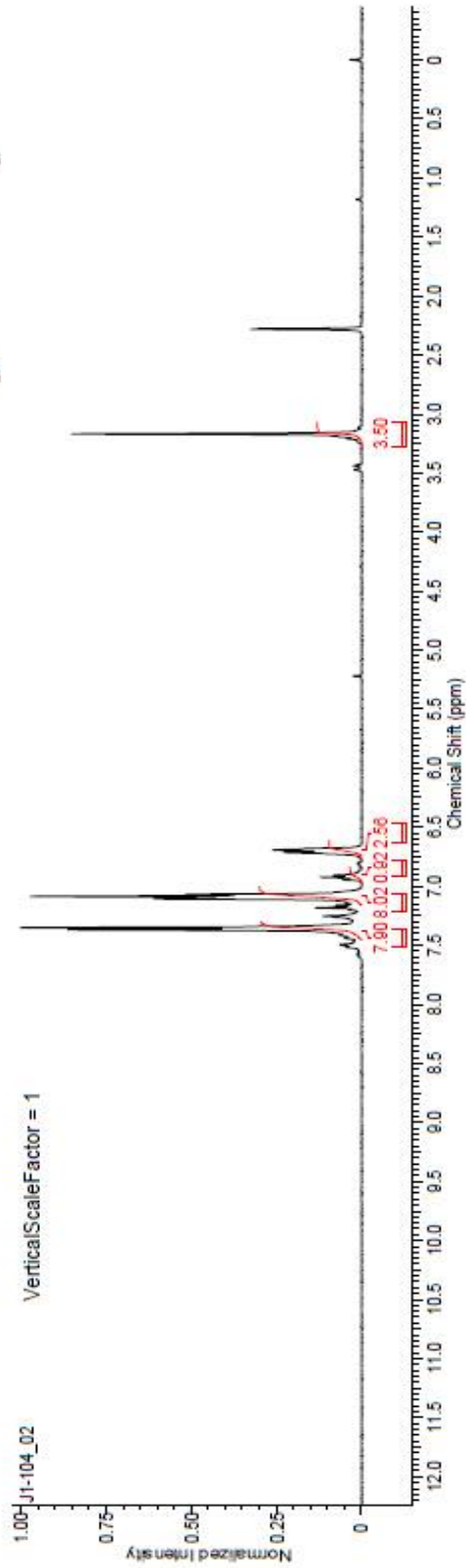
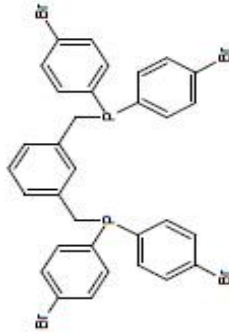


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Formula C₁₂H₈Br₄P₂ FW 790.0965

Acquisition Time (sec)	4.0000	Date	Jun 19 2014	Date Stamp	Jun 19 2014	Frequency (MHz)	398.81
File Name	C:\Users\Smallorange\Documents\Academy\PH.D - Chemistry\PH.D Research\NMR data\J1-104_02.fid\fid					Points Count	32788
Nucleus	1H	Number of Transients	8	Original Points Count	25841	Spectrum Offset (Hz)	2387.6553
Pulse Sequence	s2pul	Receiver Gain	58.00	Solvent	CHLOROFORM-d	Temperature (degree C)	AMBIENT TEMPERATURE
Spectrum Type	STANDARD	Sweep Width (Hz)	6410.26	Temperature (degree C)	AMBIENT TEMPERATURE		

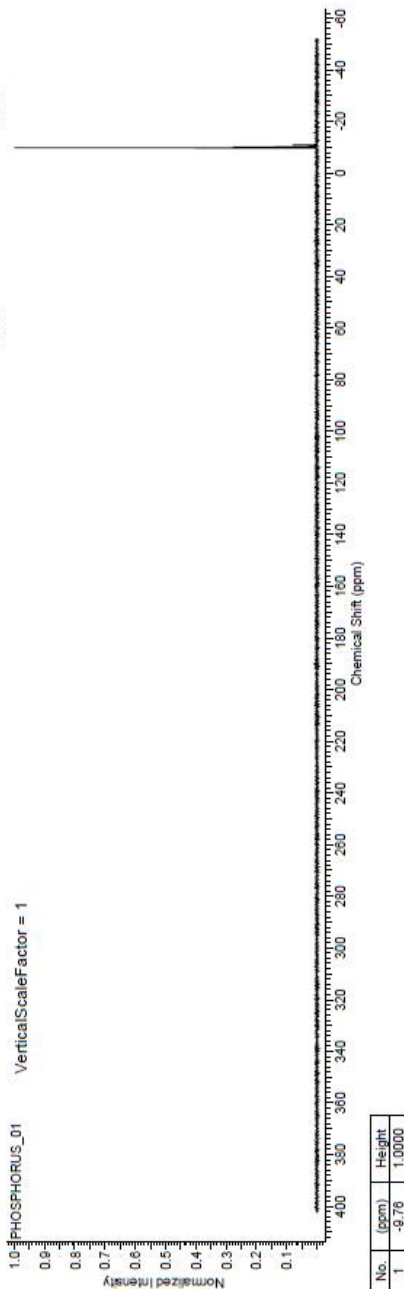
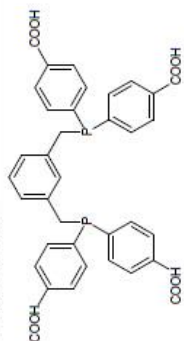
¹H NMR (400 MHz, CHLOROFORM-d) δ ppm 3.07 - 3.27 (m, 4 H) 6.70 (d, J=9.00 Hz, 3 H) 6.83 - 6.98 (m, 1 H) 7.09 (t, J=6.75 Hz, 8 H) 7.30 - 7.46 (m, 8 H)



4,4',4'',4'''-((1,3-phenylenebis(methylene))bis(phosphinetriyl))tetrabenzoic acid (**6**) :

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Formula	C ₄₀ H ₂₀ O ₈ P ₄	FW	650.5502
Acquisition Time (sec)	0.8913	Date	Aug 28, 2014
File Name	C:\Users\Smallorange\Documents\Academy\PH.D - Chemistry\PhD Research\NMR data\J1-131_20140828_02\PHOSPHORUS_01.fid\fid	Date Stamp	Aug 28, 2014
Frequency (MHz)	161.86	Nucleus	³¹ P
Points Count	65536	Number of Transients	64
Spectrum Offset (Hz)	28352.8516	Receiver Gain	50.00
		Solvent	DMSO-d6
		Temperature (degree C)	26.000
		Sweep Width (Hz)	73529.41
		Spectrum Type	STANDARD

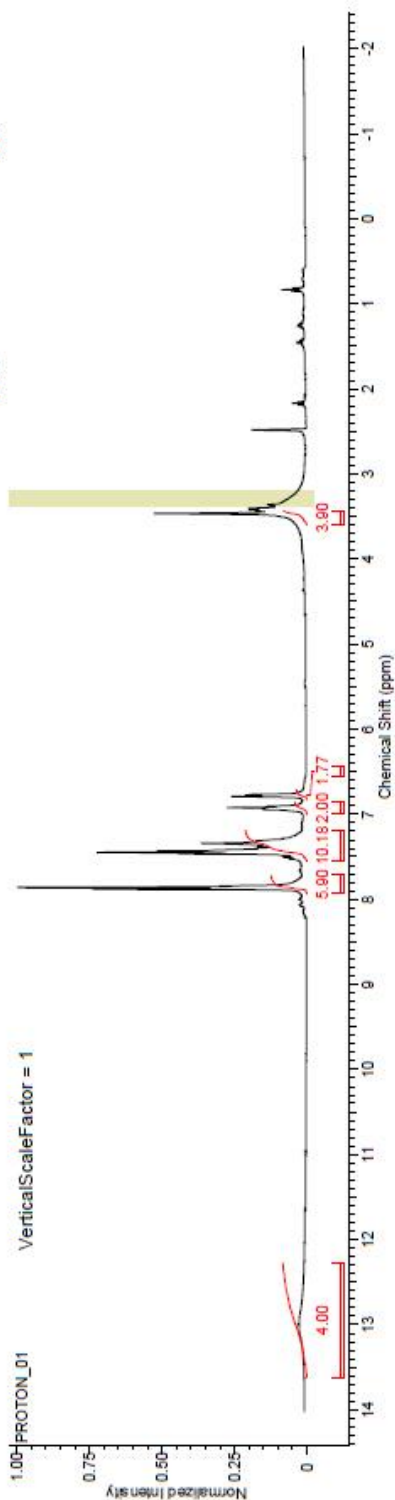
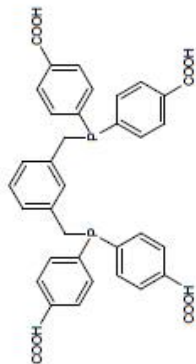


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Formula C₁₄H₁₀O₆P₂ FW 660.5602

Acquisition Time (sec)	Date	Date Stamp
2.5559	J1-131	Aug 28 2014
File Name	C:\Users\Smaiorana\Documents\Academy\PHD - Chemistry\PHD Research\NMR data\J1-131_20140828_02\PROTON_01.fid.tif	
Frequency (MHz)	Nucleus	Original Points Count
369.78	¹ H	16384
Points Count	Pulse Sequence	Solvent
16384	s2oul	DMSO-d6
Spectrum Offset (Hz)	Spectrum Type	Temperature (degree C)
2398.6201	STANDARD	26.000

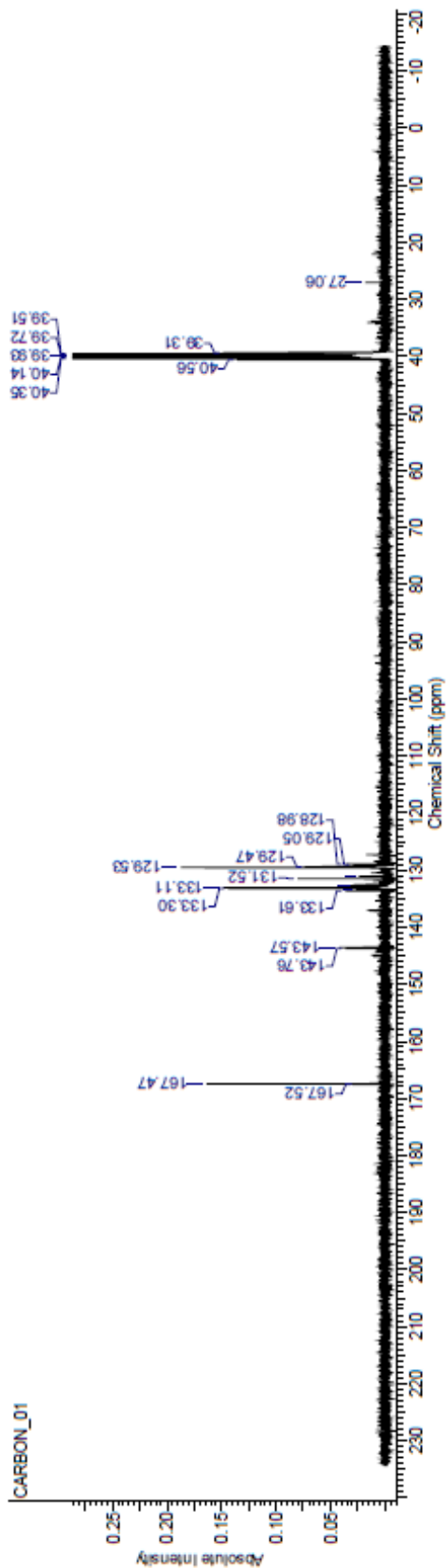
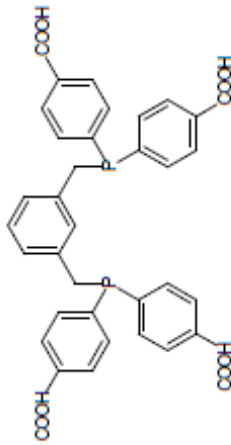
¹H NMR (400 MHz, DMSO-*d*₆) δ ppm 3.43 - 3.60 (m, 4 H) 6.78 (d, *J*=7.04 Hz, 2 H) 6.92 (t, *J*=7.43 Hz, 2 H) 7.19 - 7.56 (m, 10 H) 7.72 - 7.93 (m, 6 H) 12.99 (br. s., 4 H)



This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Formula C₂₄H₁₆O₆P
FW 660.6602

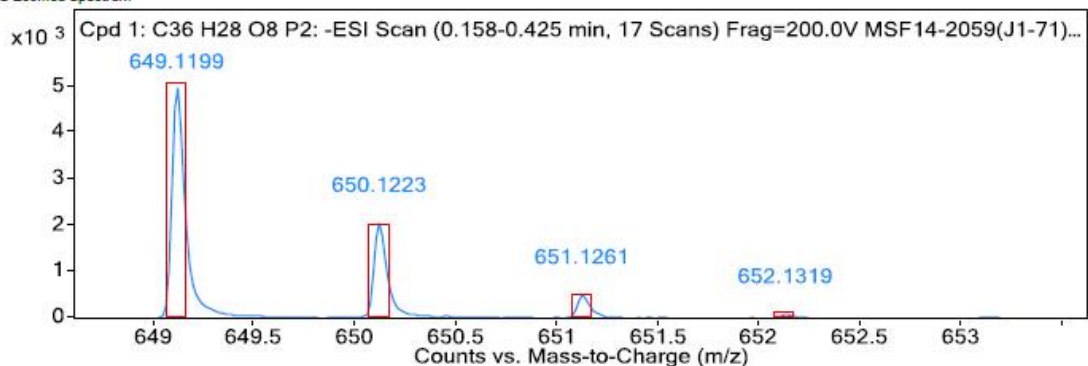
Acquisition Time (sec)	1.3107	Date	Aug 28 2014	Date Stamp	Aug 28 2014
File Name	C:\Users\Smallorange\Documents\Academy\PH.D - Chemistry\PhD Research\Data\NMR data\J1-131-C-1 20140828_01\CARBON_01.fid.tif				
Frequency (MHz)	100.63	Nucleus	13C	Number of Transients	512
Points Count	32768	Pulse Sequence	s2pul	Receiver Gain	30.00
Spectrum Offset (Hz)	11057.5391	Spectrum Type	STANDARD	Sweep Width (Hz)	25000.00
				Solvent	DMSO-d6
				Temperature (degree C)	26.000



Target Compound Screening Report

Data File	MSF14-2059(J1-71)_hrESIneg1.d	Sample Name	2059	Comment	J1-71
Position	P1-C7	Instrument Name	Instrument 1	User Name	
Acq Method	neg.m	Acquired Time	4/9/2014 1:04:47 PM	DA Method	Ian.m

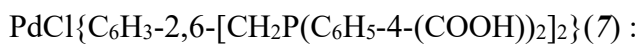
MS Zoomed Spectrum



MS Spectrum Peak List

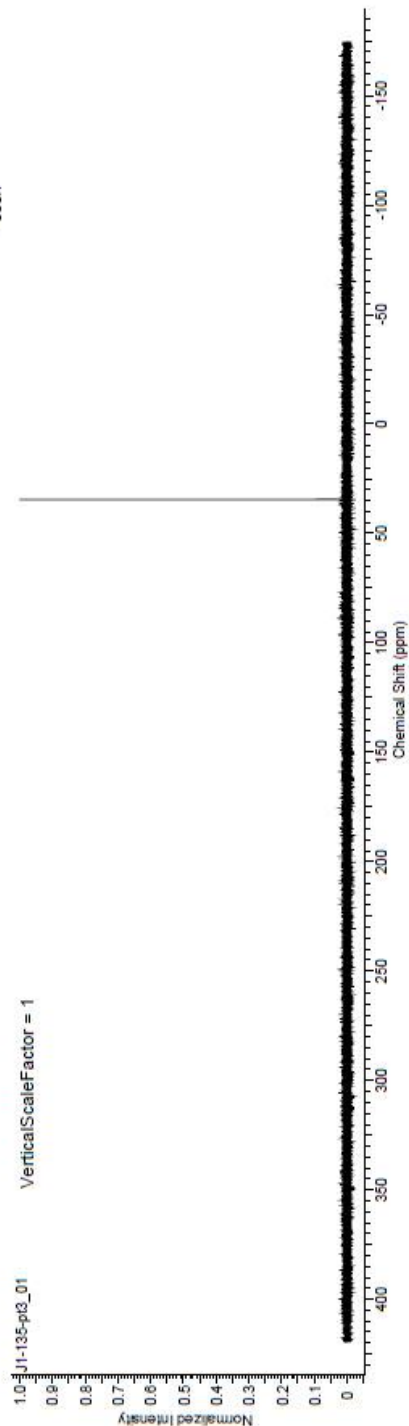
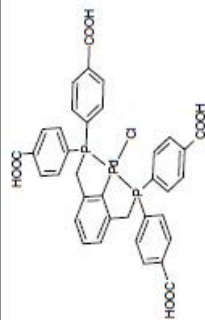
Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
605.13040			5485.2			
649.11990	649.11870	1	4984.27	C ₃₆ H ₂₈ O ₈ P ₂	(M-H) ⁻	-1.89
650.12230	650.12200	1	2054.14	C ₃₆ H ₂₈ O ₈ P ₂	(M-H) ⁻	-0.39
651.12610	651.12500	1	495.66	C ₃₆ H ₂₈ O ₈ P ₂	(M-H) ⁻	-1.65
652.13190	652.12780	1	78.96	C ₃₆ H ₂₈ O ₈ P ₂	(M-H) ⁻	-6.27

--- End Of Report ---



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Formula C ₄ H ₄ O ₄ P ₂ Pd		FW 791.4151	
Acquisition Time (sec)	1.6000	Date	Sep. 3.2014
File Name	C:\Users\Smallorange\Documents\Academy\PH.D. - Chemistry\PhD Research\NMR data\J1-135-p13_01.fid.fid	Date Stamp	Sep. 3.2014
Nucleus	31P	Original Points Count	153850
Pulse Sequence	s2nul	Receiver Gain	40.00
Spectrum Type	STANDARD	Sweep Width (Hz)	96133.80
		Temperature (degree C)	AMBIENT TEMPERATURE
		Solvent	DMSO-d6
		Points Count	262144
		Frequency (MHz)	161.86
		Spectrum Offset (Hz)	19825.9883



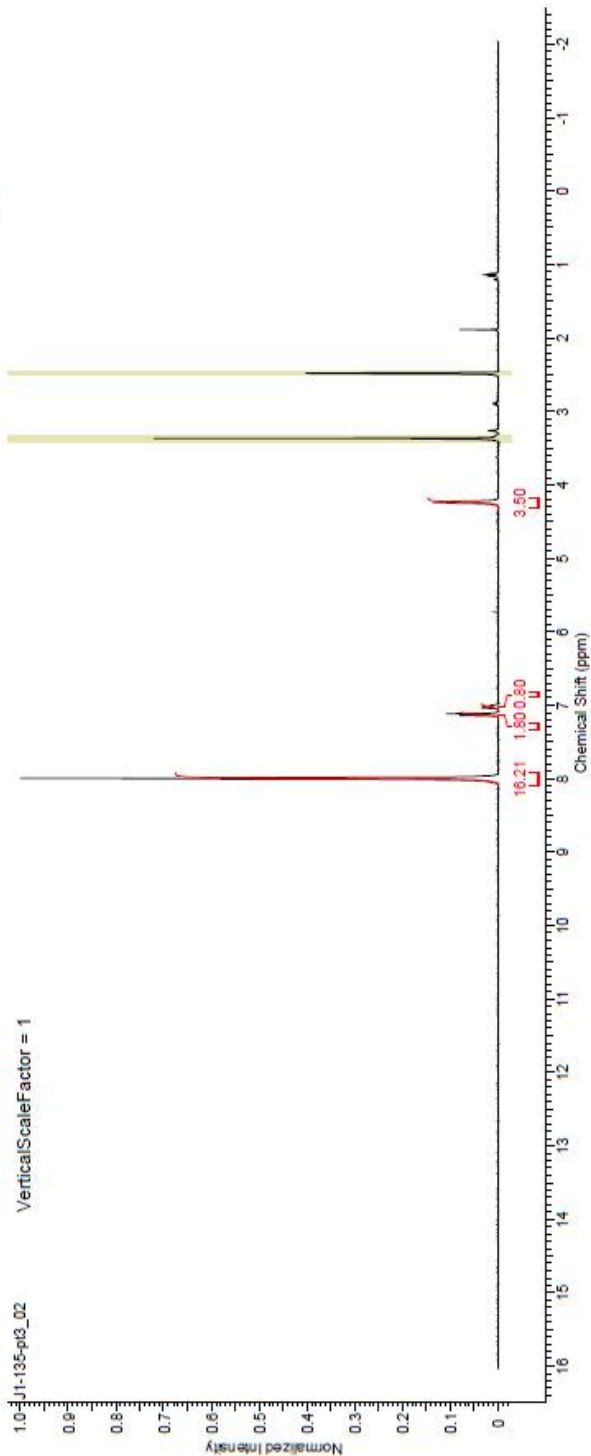
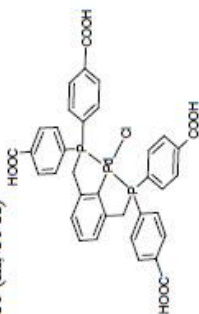
No.	(ppm)	Height
1	34.54	1.0000

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

Formula C₂₄H₁₆O₄PPd
FW 781.4151

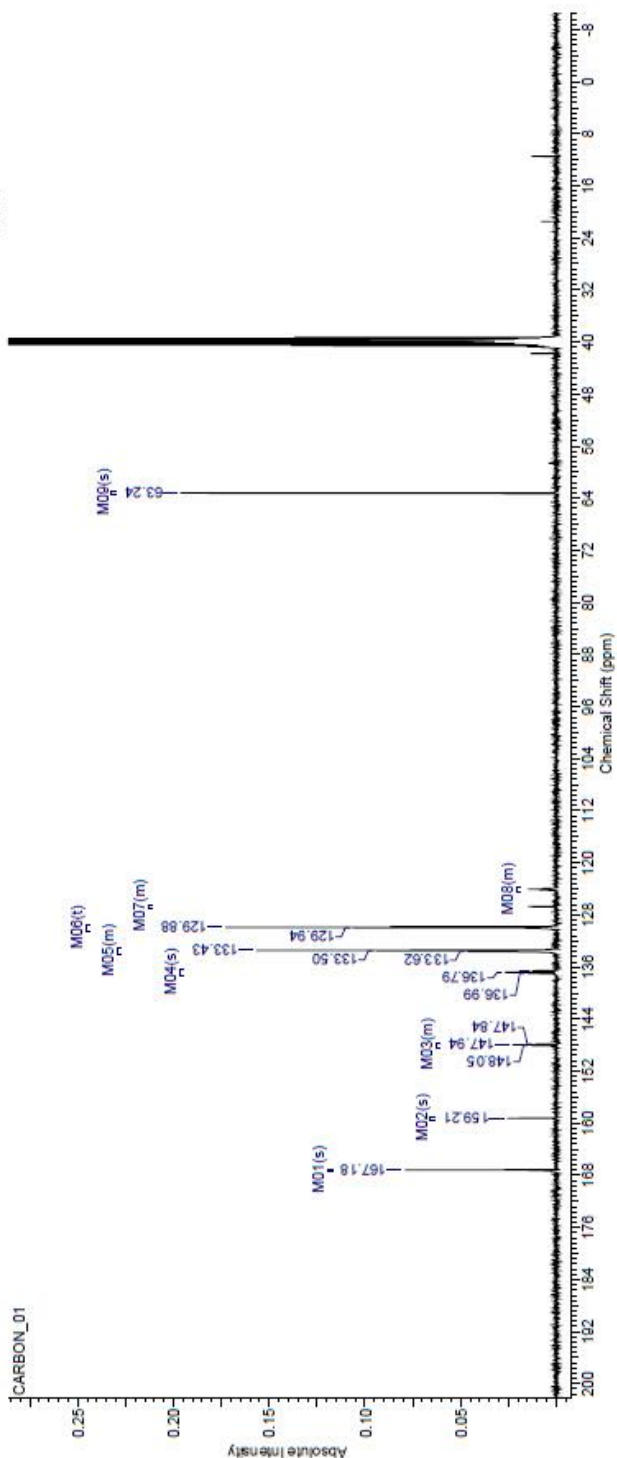
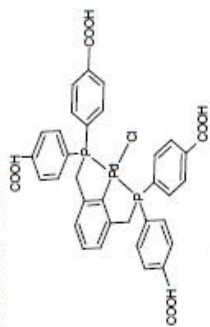
Acquisition Time (sec)	4.0000	Date	Sep. 3.2014	Date Stamp	Sep. 3.2014	Frequency (MHz)	398.81
File Name	C:\Users\Smallorange\Documents\Academy\PhD - Chemistry\PhD_Research\NMR_data\J1-135-pd3_02.fid.tif	Number of Transients	8	Original Points Count	28802	Points Count	32768
Nucleus	¹ H	Receiver Gain	56.00	Solvent	DMSO-d6	Spectrum Offset (Hz)	2788.8641
Pulse Sequence	s2pul	Sweep Width (Hz)	7225.43	Temperature (degree C)	AMBIENT TEMPERATURE		
Spectrum Type	STANDARD						

¹H NMR (400 MHz, DMSO-d₆) δ ppm 4.24 (br. s., 4 H) 7.03 (d, J=7.28 Hz, 1 H) 7.13 (d, J=7.50 Hz, 2 H) 7.92 - 8.10 (m, 16 H)



This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

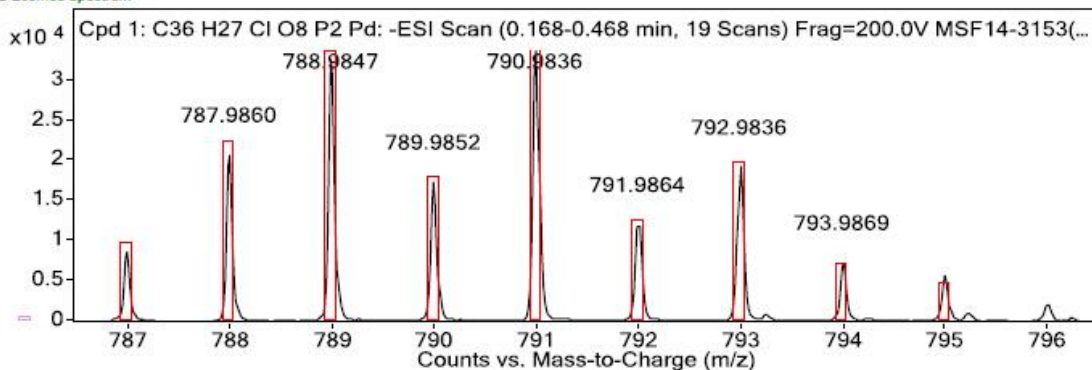
Formula C ₂₄ H ₁₆ O ₆ Pd		FW 781.4152	
Acquisition Time (sec)	1.3107	Comment	J1-135-p3-13C
File Name	C:\Users\Smallorange\Documents\Academy\PH.D - Chemistry\PhD Research\NMR\data\J1-135-p3-13C_20140903_01\CARBON_01.fid.fid	Date	Sep 3 2014
Frequency (MHz)	100.63	Number of Transients	16000
Points Count	32768	Receiver Gain	30.00
Spectrum Offset (Hz)	11057.6391	Sweep Width (Hz)	25000.00
		Solvent	DMSO-d6
		Temperature (degree C)	20.000
		Original Points Count	32768



Target Compound Screening Report

Data File	MSF14-3153(J1-106)_hrESI.neg2.d	Sample Name	3153(J1-106)
Position	P1-B5	Instrument Name	Instrument 1
Acq Method	neg.m	Acquired Time	7/1/2014 4:17:44 PM
		Comment	3153(J1-106)
		User Name	Ian.m
		DA Method	Ian.m

MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
160.84960			49737.64			
786.98400	786.98380	1	8784.97	C36H27ClO8P2Pd	(M-H)-	-0.26
787.98600	787.98520	1	20843.94	C36H27ClO8P2Pd	(M-H)-	-1.06
788.98470	788.98420	1	33159.8	C36H27ClO8P2Pd	(M-H)-	-0.66
789.98520	789.98530	1	17437.17	C36H27ClO8P2Pd	(M-H)-	0.16
790.98360	790.98350	1	34005.84	C36H27ClO8P2Pd	(M-H)-	-0.11
791.98640	791.98650	1	12151.14	C36H27ClO8P2Pd	(M-H)-	0.04
792.98360	792.98400	1	19301.45	C36H27ClO8P2Pd	(M-H)-	0.53
793.98690	793.98680	1	7404.25	C36H27ClO8P2Pd	(M-H)-	-0.02
794.98430	794.98450	1	5660.11	C36H27ClO8P2Pd	(M-H)-	0.29

--- End Of Report ---

Reference

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