Supporting Information for

P-Alkynyl Functionalized Benzazaphospholes as Transmetalating Agents

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1. Experimentals and NMR Spectra for New Compounds:

General Experimental Details. Unless otherwise specified, all reactions and manipulations were performed under a nitrogen atmosphere in a MBraun glovebox or using standard Schlenk techniques. All glassware was oven-dried overnight (at minimum) at 140 °C prior to use. Anhydrous solvents were purchased directly from chemical suppliers (Aldrich or Acros), pumped directly into the glove box, and stored over oven-activated 4 or 5 Å molecular sieves (Aldrich). 4N HCl in dioxane, TMS–I, BrMgCCPh, Na_2PdCl_4, P(*t*-Bu)$_2$Cy, P(*t*-Bu)Cy$_2$, PCy$_3$, CuI, and anhydrous NH(*i*-Pr)$_2$ were purchased from commercial suppliers. Benzazaphosphole **1** and Pd(II) complexes **C** and **D** were prepared by the published methods referenced in the manuscript. NMR spectra were obtained on either Varian spectrometers operating at 300, 400, or 500 MHz; all spectra are displayed in the Supporting Information. NMR chemical shifts are reported as ppm relative to tetramethylsilane and are referenced to the residual proton or ^{13}C signal of the solvent (^1H $CDCl_3$, 7.27 ppm; ^1H C_6D_6, 7.16 ppm; ^{13}C $CDCl_3$ 77.16 ppm; ^{13}C C_6D_6, 128.06 ppm).

IMPORTANT NOTE

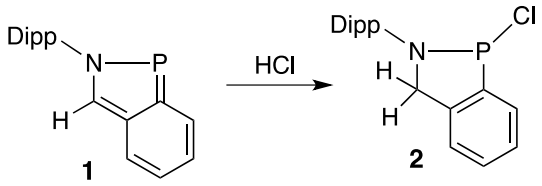
Some of the NMR spectra shown below feature an artifact with the following chemical shifts:

^1H NMR spectroscopy: 5 ppm

$^{13}C\{^1H\}$ NMR spectroscopy: 110 ppm

The artifact is most likely the result of intermittent problems with the spectrometer's reference generator board. Currently, due to budget problems at the University of Hawaii, repairs to address this problem have been delayed, and the COVID-19 outbreak has further complicated the situation.

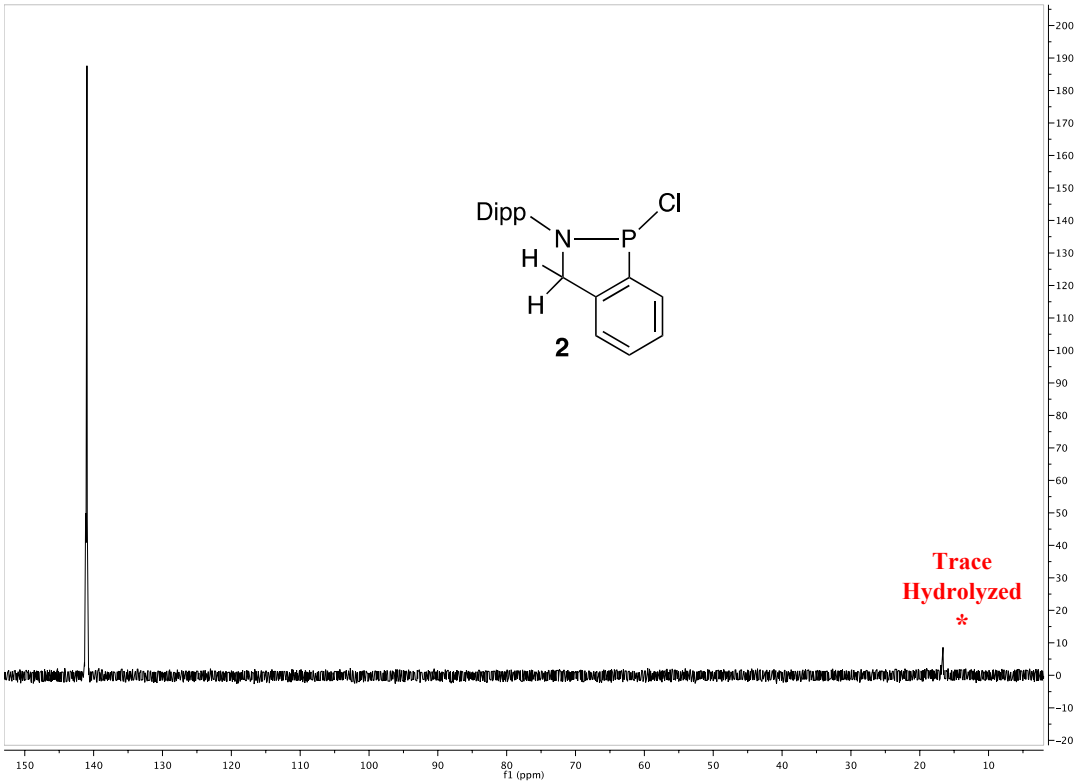
Synthesis of 2



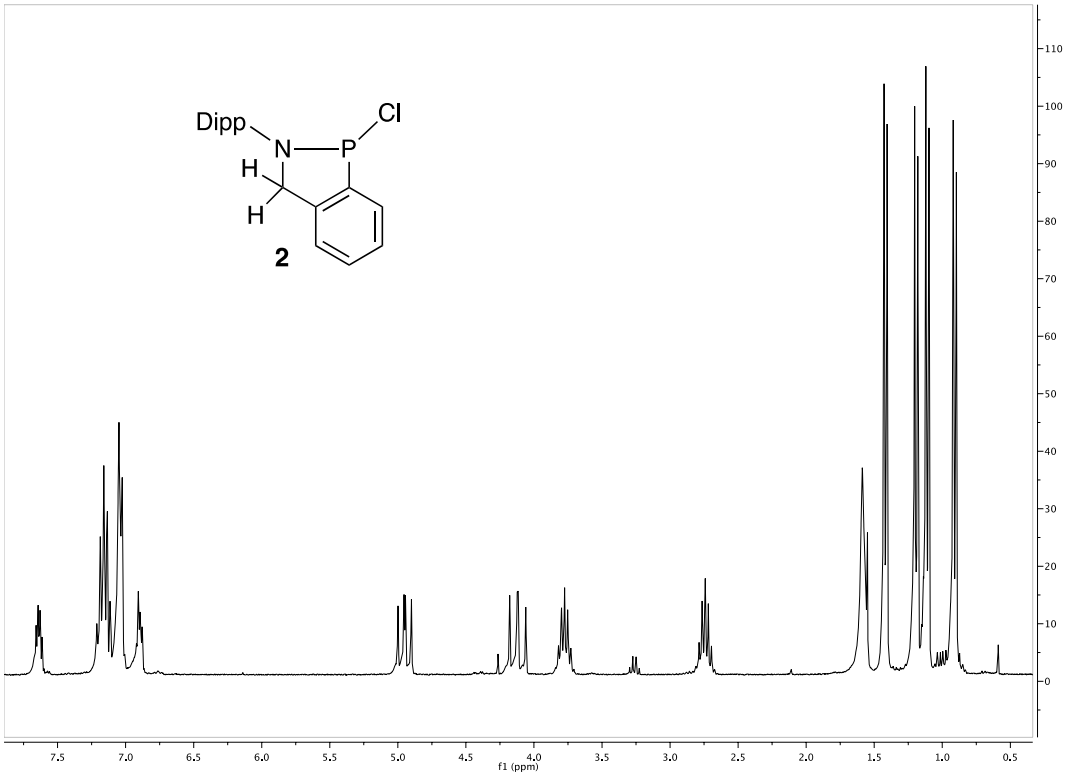
Compound **1** (100 mg, 0.339 mmol) was dissolved in 3 mL of toluene in a Schlenk bomb in the glovebox. The solution was taken out of the glovebox and 4N HCl in dioxane (169 μL, 0.678 mmol, 2 equiv.) was injected via syringe under positive N_2 pressure and stirred for 15 min. The reaction mixture was concentrated under vacuum, and the residual yellow solid was recrystallized from 10 mL of a 1:1 mixture of $CHCl_3$ and MeCN at –35 ºC to give a white solid **2** (70 mg, 0.211 mmol, 63%). Crystals suitable for X-ray diffraction were obtained from this recrystallization.

Anal. Calcd for $C_{19}H_{23}ClNP$: C, 68.77; H, 6.99; N, 4.22. Found: C, 68.67; H, 6.98; N, 4.08. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): **δ** 141.0. ^1H NMR (500 MHz, C_6D_6): **δ** 7.64 (m, 1H, Ar), 7.15 (m, 3H, Ar), 7.04 (m, 2H, Ar), 6.89 (m, 1H, Ar), 4.95 (dd, *J* = 18, 6 Hz, 1H, CH_2), 4.12 (dd, *J* = 18, 6 Hz, 1H, CH_2), 3.78 (sept, *J* = 6 Hz, 1H, CH), 2.74 (sept, *J* = 6 Hz, 1H, CH), 1.42 (d, *J* = 6 Hz, 3H, Me), 1.19 (d, *J* = 6 Hz, 3H, Me), 1.11 (d, *J* = 6 Hz, 3H, Me), 0.9 (d, *J* = 6 Hz, 3H, Me). ^{13}C NMR (125 MHz, C_6D_6): δ 149.1 (d, *J* = 4 Hz, Ar), 147.0 (d, *J* = 4 Hz Ar), 143.9 (Ar), 143.6 (d, *J* = 21 Hz, Ar) 136.8 (d, *J* = 13 Hz, Ar), 130.3 (Ar), 128.5 (Ar), 128.3 (d, *J* = 5 Hz, Ar), 128.1 (d, *J* = 7 Hz, Ar), 124.5 (Ar), 124.2 (Ar), 122.4 (Ar), 64.1 (d, *J* = 16 Hz, CH_2), 28.5 (CH), 28.4 (CH), 25.17 (Me), 25.13 (Me), 24.9 (d, *J* = 5 Hz, Me), 24.7 (Me).

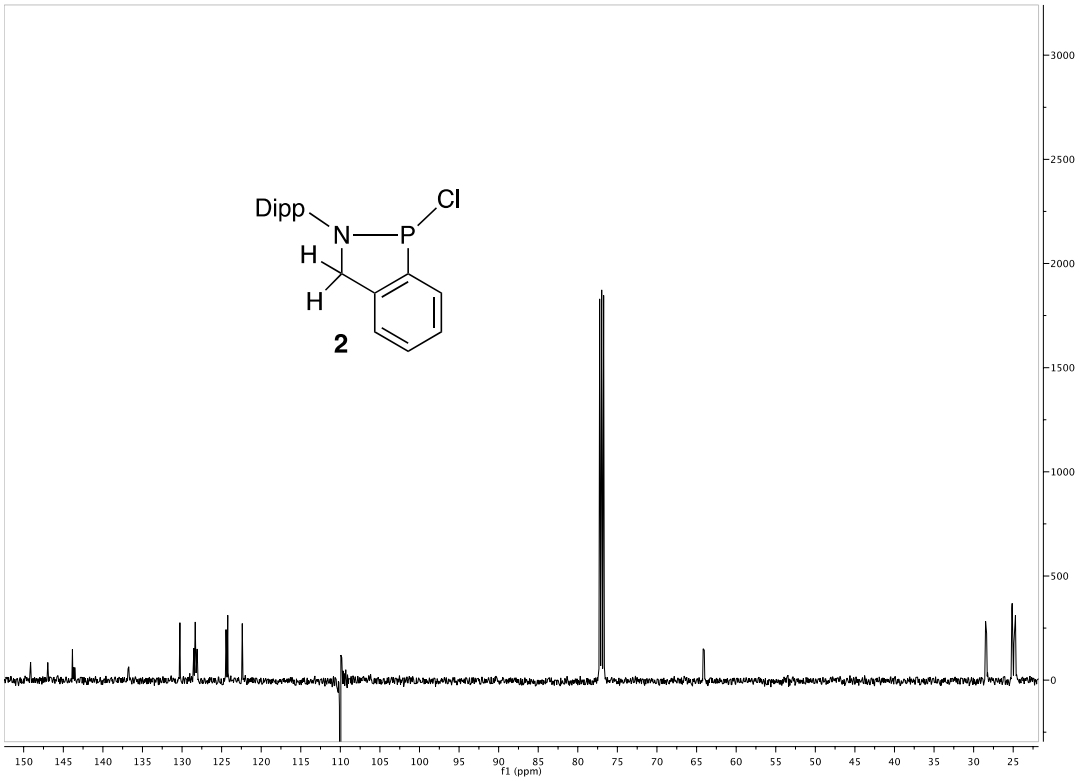
$^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6)



^{1}H NMR (500 MHz, C_6D_6)



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



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Date of report	8/10/2018 6:54:44PM
User ID	Administrator
Comments	PMA 343 [Cain / Miura-Akagi]

DATE & TIME	8/10/2018 6:53:53 PM	P_ID	EA LAB
SAMPLE ID	18410	USER ID	Administrator
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CARBON	68.665%
HYDROGEN	6.982%
NITROGEN	4.078%

Special Handling

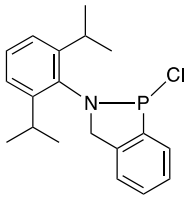
The sample was transferred under argon and was combusted in a tin capsule that was crimp-sealed with a die apparatus.

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

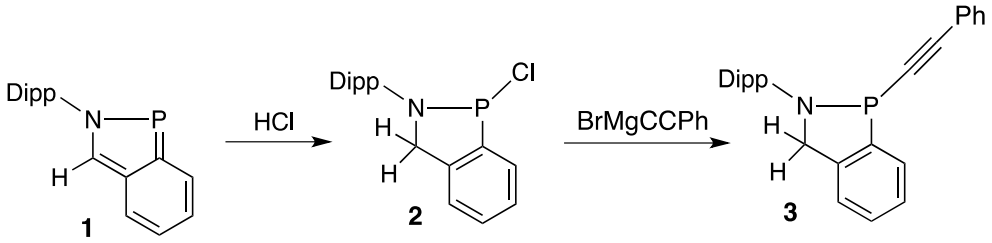
Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Air-sensitive samples were handled in a VAC Atmospheres glovebox.



Chemical Formula: $C_{19}H_{23}ClNP$
Exact Mass: 331.1257
Molecular Weight: 331.8238
Elemental Analysis: C, 68.77; H, 6.99; Cl, 10.68; N, 4.22; P, 9.33

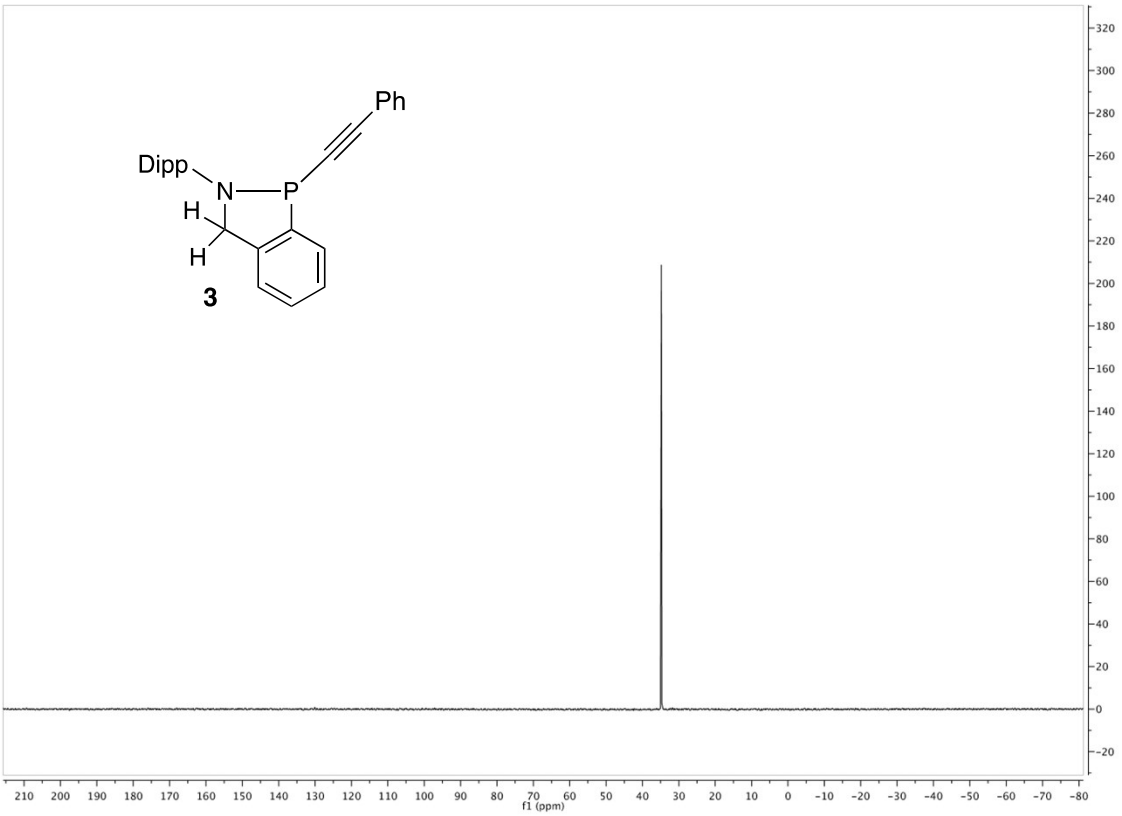
Synthesis of 3



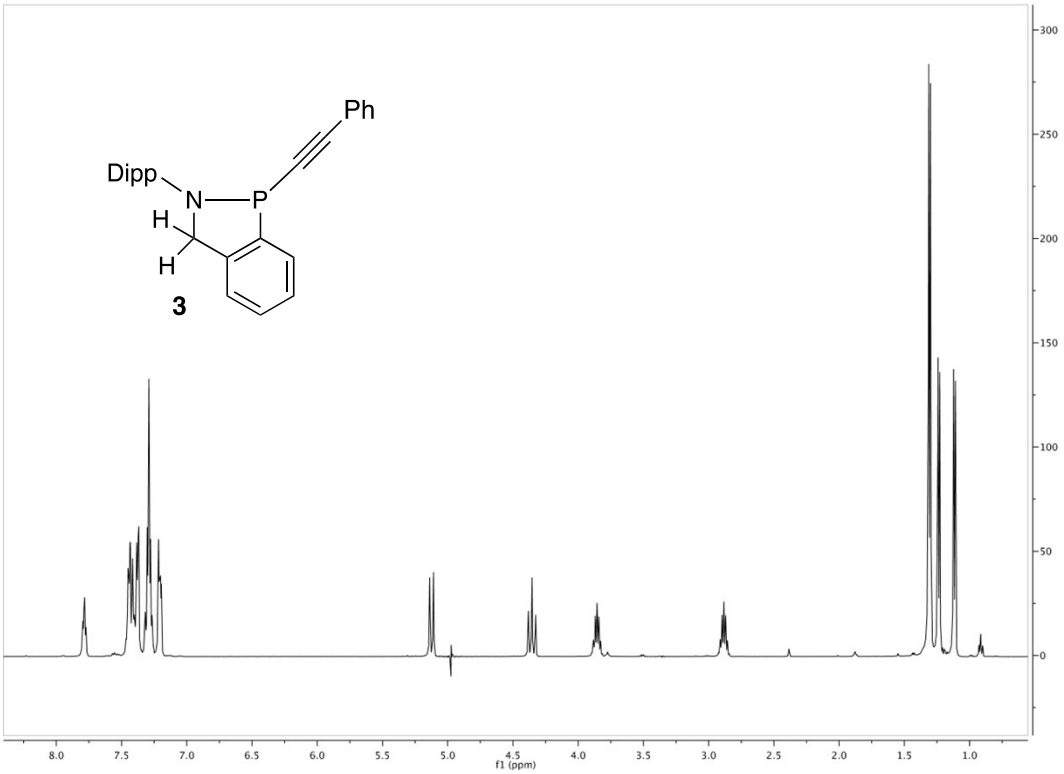
Compound **1** (3.69 g, 12.5 mmol) and a stir bar were loaded in a Schlenk bomb inside the glovebox and dissolved in 10 mL of toluene. The bomb was taken outside the glovebox and HCl (4 N in 1,4-dioxane, 6.25 mL, 25.0 mmol, 2.00 equiv.) was injected through a septum via syringe under positive N_2 pressure. The mixture was stirred at room temperature for 15 min. The bomb was brought back into the glovebox, and the reaction mixture was concentrated under vacuum. The residue was washed with 10 mL of pentane, re-concentrated, and then dissolved in 10 mL of THF. The bomb was taken back outside the glovebox and placed in an ice bath at 0 ˚C and BrMgCCPh (1.0M in THF, 25.0 mL, 25.0 mmol, 2.00 equiv.) was injected through a septum via syringe under positive N_2 pressure. The reaction mixture was warmed to room temperature overnight and then concentrated under vacuum on the Schlenk line. The residue was brought back inside the glovebox and extracted with pentane and filtered through Celite. The filtrate was concentrated to 50 mL and put in the freezer at -35 ˚C, resulting in the precipitation of the product as a white crystalline solid (3.07 g, 7.72 mmol, 62%). Redissolving a portion of the crystalline product in pentane, followed by subsequent cooling to -35 ˚C afforded X-ray quality crystals.

Anal. Calcd. for $C_{27}H_{28}NP$: C, 81.58; H, 7.10; N, 3.52. Found: C, 81.09; H, 6.97; N, 3.23. $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ 34.8. ^1H NMR (500 MHz, $CDCl_3$): δ 7.82-7.75 (m, 1H, Ar), 7.49-7.36 (m, 5H, Ar), 7.34-7.26 (m, 4H, Ar), 7.24-7.18 (m, 2H, Ar), 5.12 (d, J = 15 Hz, 1H, CH_2), 4.35 (dd, J =14, 14 Hz, 1H, CH_2), 3.86 (septet, J = 7 Hz, 1H, CH), 2.88 (septet, J = 7 Hz, 1H, CH), 1.31 (d, J = 7 Hz, 6H, Me), 1.24 (d, J = 7 Hz, 3H, Me), 1.12 (d, J = 7 Hz, 3H, Me). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 150.7 (Ar), 148.1 (Ar), 144.3 (Ar), 139.9 (d, J = 16 Hz, Ar), 139.7 (d, J = 10 Hz, Ar), 131.6 (Ar), 128.6 (d, J = 19 Hz, Ar), 128.2 (Ar), 127.9 (Ar), 127.6 (d, J = 7 Hz, Ar), 127.5 (Ar), 127.3 (Ar), 124.2 (Ar), 123.8 (Ar), 122.9 (Ar), 122.4 (Ar), 104.8 (d, J = 11 Hz, P-C≡C), 92.0 (d, J = 77 Hz, P-C≡C), 62.8 (d, J = 11 Hz, CH_2), 28.8 (CH), 28.4 (CH), 25.4 (Me), 25.1 (Me), 24.7 (Me), 24.6 (Me).

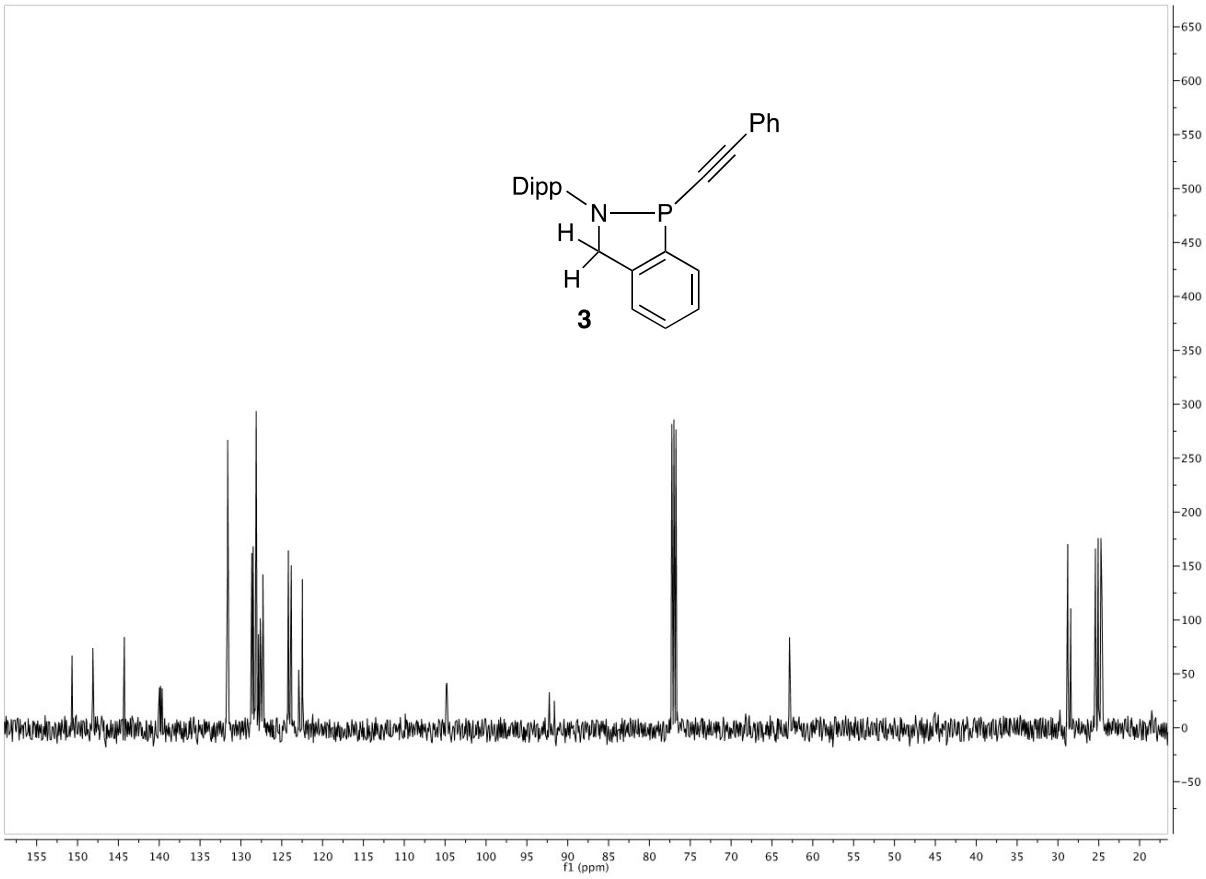
$^{31}P\{^{1}H\}$ NMR (160 MHz, C_6D_6)



^{1}H NMR (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



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Date of report	11/22/2019 6:36:27PM
User ID	Administrator
Comments	DYZ-47 [Cain / Zhou]

DATE & TIME	11/22/2019 4:29:22 PM	P_ID	EA LAB
SAMPLE ID	19630	USER ID	Administrator
WEIGHT (mg)	1.907	MODE	CHN

CARBON	81.093%
HYDROGEN	6.968%
NITROGEN	3.226%

Special Handling

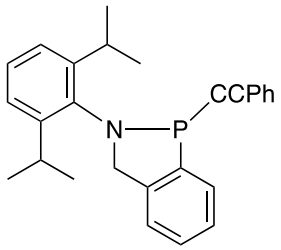
The sample was transferred under argon and was combusted in a tin capsule that was crimp-sealed with a die apparatus.

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

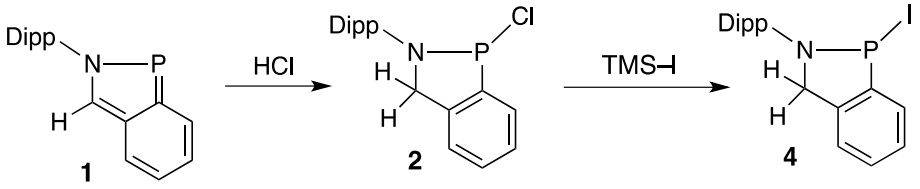
Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Air-sensitive samples were handled in a VAC Atmospheres glovebox.



Chemical Formula: $C_{27}H_{28}NP$
Exact Mass: 397.1959
Molecular Weight: 397.5018
Elemental Analysis: C, 81.58; H, 7.10; N, 3.52; P, 7.79

Synthesis of 4

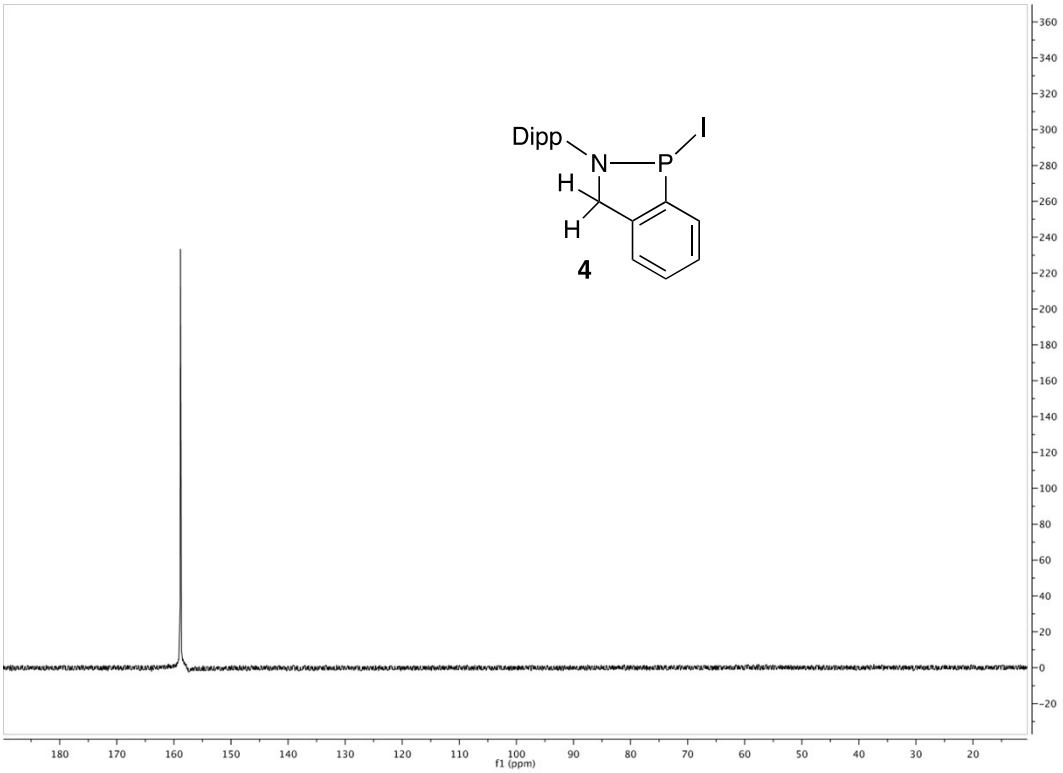


Compound **1** (0.250 g, 0.85 mmol) and a stir bar were loaded in a Schlenk bomb inside the glovebox and dissolved in 10 mL of toluene. The bomb was taken outside the glovebox and HCl (4 N in 1,4-dioxane, 0.425 mL, 1.7 mmol, 2.00 equiv.) was injected through a septum via syringe under positive N_2 pressure. The mixture was stirred at room temperature for 15 min. The bomb was brought back into the glovebox and the reaction mixture was concentrated under vacuum. The residue was then dissolved in 10 mL of DCM, TMS-I (0.186 g, 0.93 mmol, 1.1 equiv.) was added dropwise, and the reaction mixture was stirred overnight then concentrated. The crude solid was recrystallized from a 2:1 mixture of Et_2O/pentane at -35 ˚C, resulting in the precipitation of the product as a yellow crystalline solid (0.253 g, 0.60 mmol, 71%).

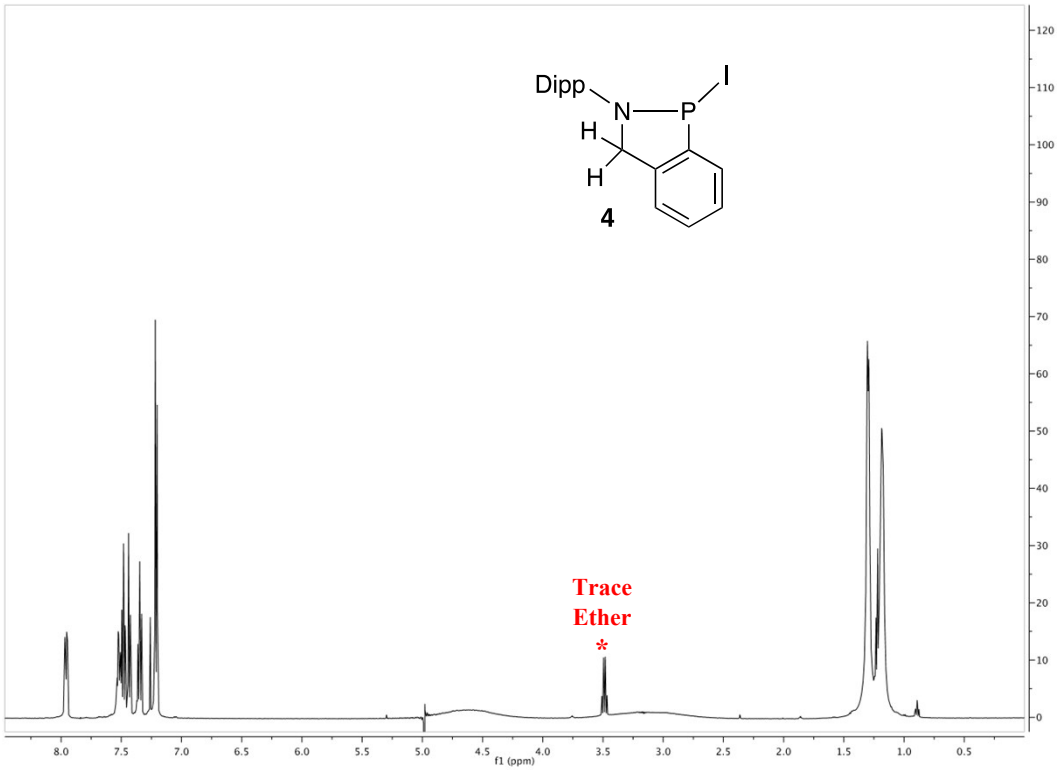
*Initially, we attempted to prepare **4** using KI instead of TMS–I, which never fully converted **2** to **4**. Attempted purification of the **4:2** mixture by recrystallization from pentane at -35 ˚C afforded X-ray quality crystals in which the halogen site was refined as 75% I and 25% Cl with fixed P-X distances.*

Anal. Calcd. for $C_{27}H_{28}NP$: C, 53.91; H, 5.48; N, 3.31. Found: C, 54.33; H, 5.56; N, 3.17. $^{31}P\{^1H\}$ NMR (160 MHz, C_7D_8): δ 158.8. ^1H NMR (500 MHz, $CDCl_3$): δ 7.96 (dd, J = 7, 3.5 Hz, 1H, Ar), 7.54-7.43 (m, 4H, Ar), 7.36-7.33 (m, 1H, Ar), 7.26-7.20 (m, 1H, Ar), 4.68 (br, 2H, CH_2), 3.14 (br, 2H, CH), 1.30 (d, J = 6 Hz, 6H, Me), 1.19 (d, J = 6 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 157.8 (Ar), 143.9 (Ar), 143.0 (d, J = 28 Hz, Ar), 136.4 (d, J = 12 Hz, Ar), 130.1 (Ar), 128.6 (Ar), 128.2 (Ar), 128.1 (d, J = 20 Hz, Ar), 124.7 (Ar), 122.3 (Ar), 65.2 (d, J = 17 Hz, CH_2), 28.5 (Me), 25.1 (overlapping CH and Me).

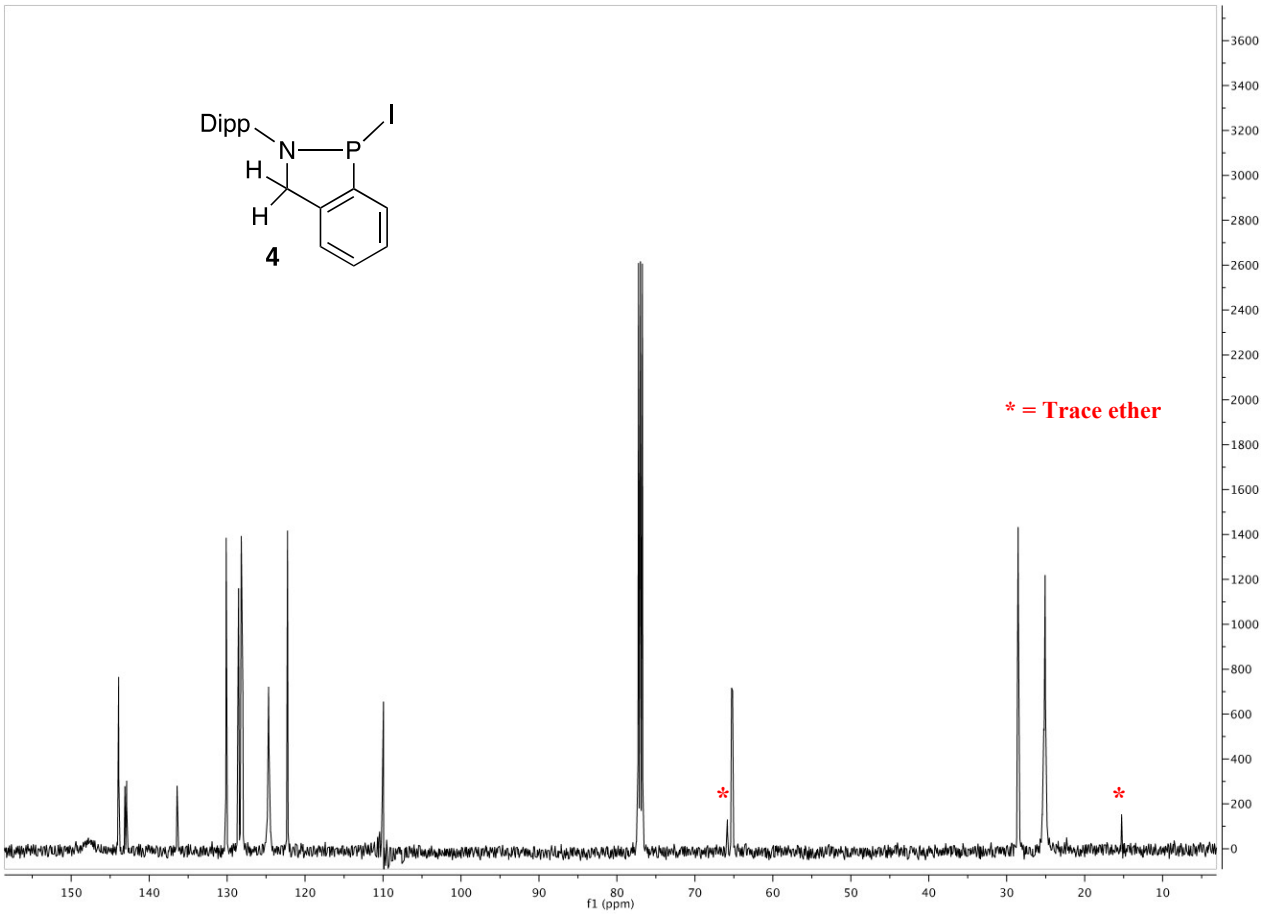
$^{31}P\{^{1}H\}$ NMR (160 MHz, C_7D_8)



^{1}H NMR (500 MHz, $CDCl_3$)



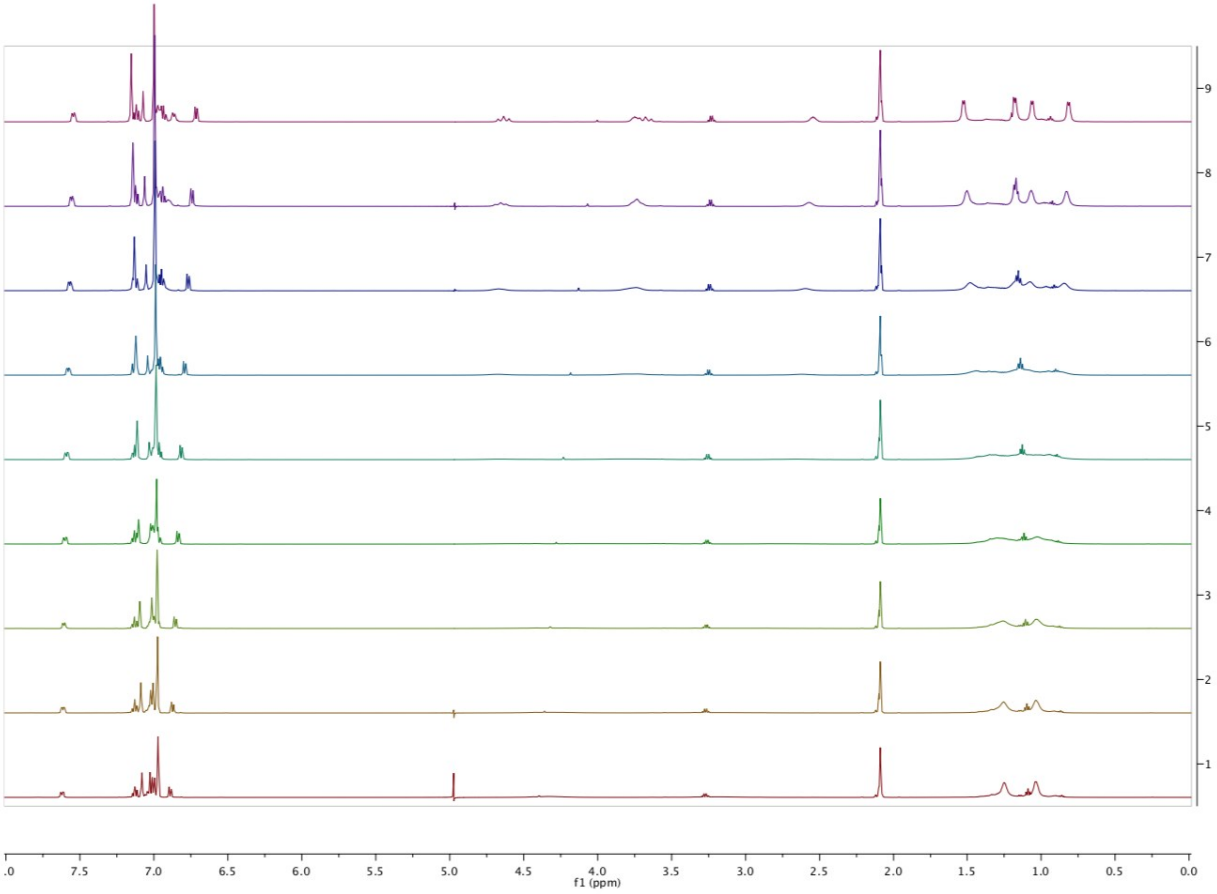
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



VT NMR spectroscopy

-60 °C (top) to +60 °C (bottom), 15 ° intervals

^{1}H NMR (500 MHz, C_7D_8)



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Date of report	3/20/2020 3:37:24PM
User ID	Administrator
Comments	DZ-56 [Cain / Zhou]

DATE & TIME	3/20/2020 2:32:45 PM	P_ID	EA LAB
SAMPLE ID	20095	USER ID	Administrator
WEIGHT (mg)	2.439	MODE	CHN

CARBON	54.327%
HYDROGEN	5.563%
NITROGEN	3.169%

Special Handling

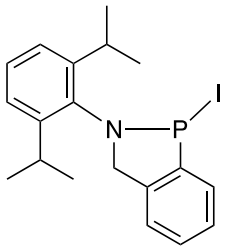
The sample was transferred under argon and was combusted in a tin capsule that was crimp-sealed with a die apparatus.

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

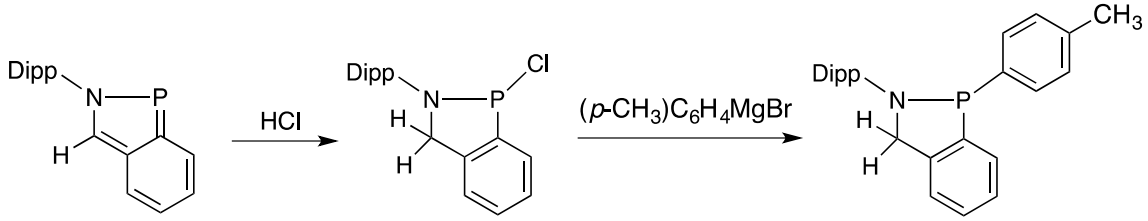
Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Air-sensitive samples were handled in a VAC Atmospheres glovebox.



Chemical Formula: $C_{19}H_{23}INP$
Exact Mass: 423.0613
Molecular Weight: 423.2782
Elemental Analysis: C, 53.91; H, 5.48; I, 29.98; N, 3.31; P, 7.32

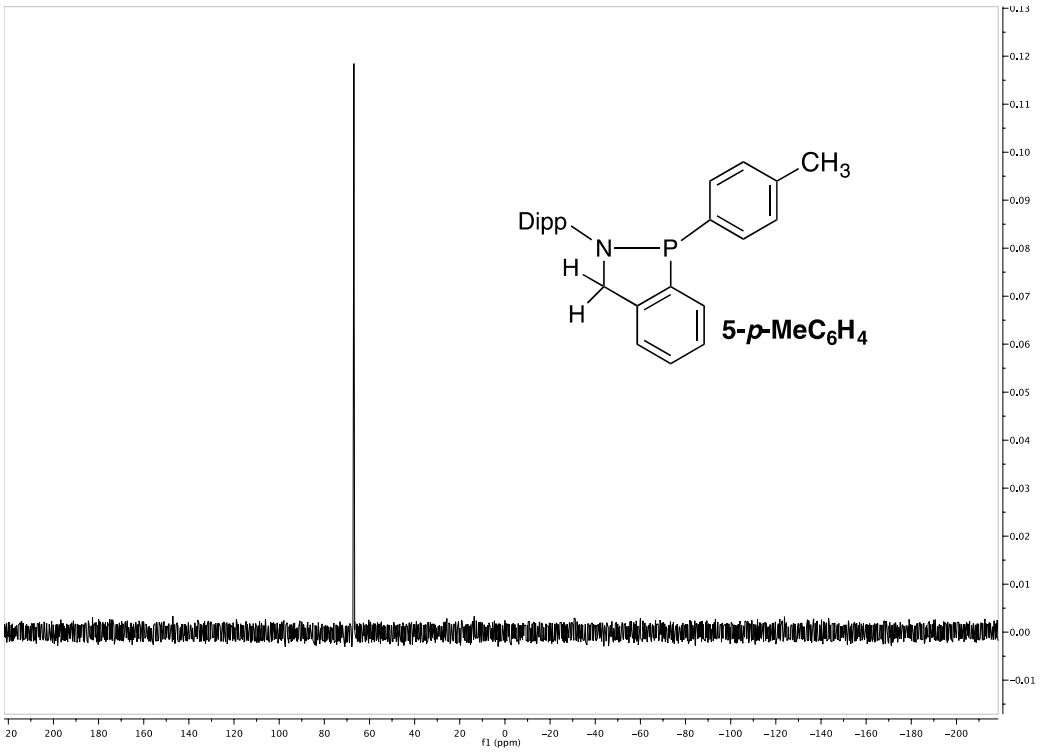
Synthesis of 5-*p*-MeC$_6$H$_4$.



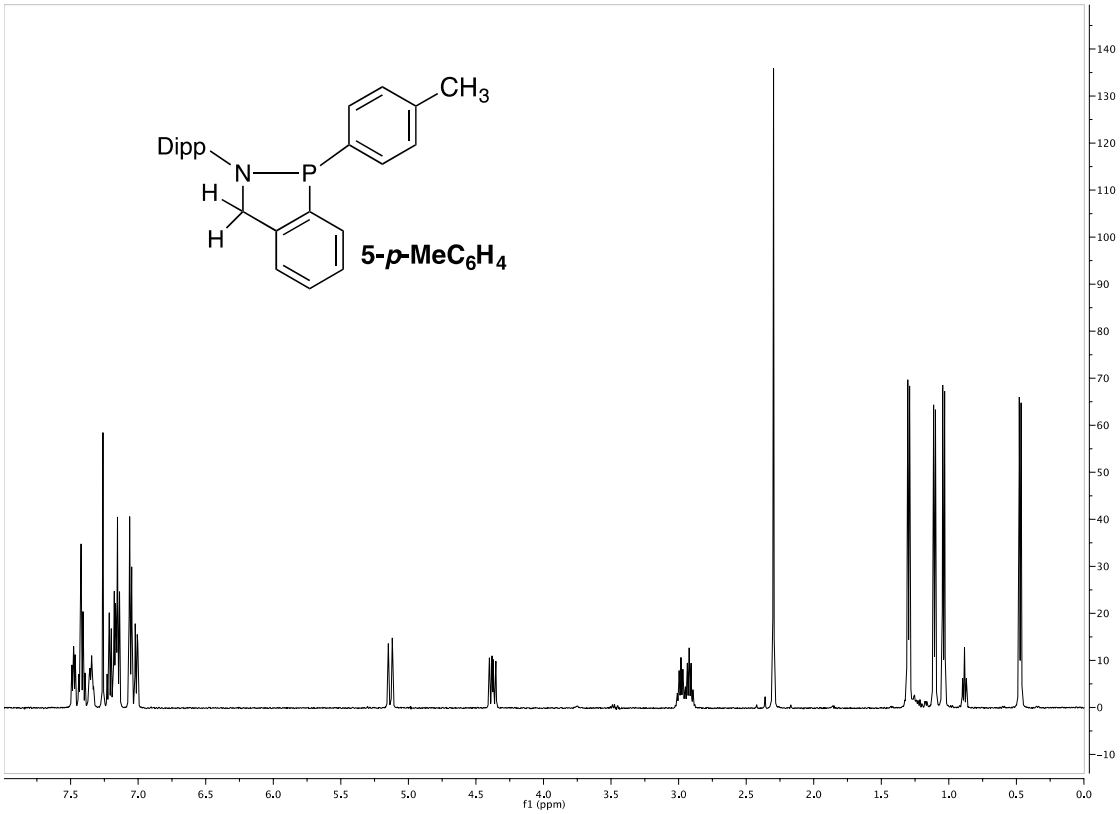
Compound **1** (200 mg, 0.677 mmol) and a stir bar were loaded in a Schlenk bomb inside the glovebox and dissolved in 4 mL of toluene. The bomb was taken outside of the glovebox and HCl (4 N in 1,4-dioxane, 340 μL, 1.35 mmol, 2.00 equiv) was injected through a septum via syringe under positive N_2 pressure. The mixture was stirred at room temperature for 15 min. The bomb was brought back into the glovebox, and the reaction mixture was concentrated under vacuum. The residue was washed with 5 mL of pentane, re-concentrated, and then dissolved in 5 mL of THF. The bomb was taken back outside the glovebox and placed in an ice bath at 0 ˚C and (*p*-Me)C$_6$H$_4$MgBr (1.0 M in THF, 1.35 mL, 1.35 mmol, 2.00 equiv) was injected through a septum via syringe under positive N_2 pressure. The reaction mixture was warmed to room temperature over the course of 30 min and then brought back inside the glovebox and concentrated under vacuum. The residue was suspended in 5 mL of pentane, filtered through a Celite plug, and then washed with an additional 5 mL of pentane. The filtrates were combined and concentrated to ~5 mL and put in the freezer at -35 ˚C, resulting in the precipitation of the product as a white crystalline solid (89 mg, 0.230 mmol, 34%). Dissolving 10 mg of this solid in 3 mL of acetonitrile, followed by subsequent cooling to -35 ˚C afforded X-ray quality crystals.

Anal. Calcd. for $C_{26}H_{30}NP$: C, 80.59; H, 7.80; N, 3.61. Found: C, 80.25; H, 7.78; N, 3.73. $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$): δ 66.9. ^1H NMR (500 MHz, $CDCl_3$): δ 7.49-7.33 (m, 4H, Ar), 7.23-7.14 (m, 4H, Ar), 7.06-7.00 (m, 3H, Ar), 5.13 (d, J = 15 Hz, 1H, CH_2), 4.38 (dd, J = 15, 10 Hz, 1H, CH_2), 2.98 (septet, J = 7 Hz, 1H, CH), 2.92 (septet, J = 7 Hz, 1H, CH), 2.30 (3H, Me), 1.30 (d, J = 7 Hz, 3H, Me), 1.10 (d, J = 7 Hz, 3H, Me), 1.04 (d, J = 7 Hz, 3H, Me), 0.47 (d, J = 7 Hz, 3H, Me). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 150.3 (Ar), 148.4 (Ar), 144.2 (Ar), 142.4 (Ar), 141.2 (d, J = 17 Hz, Ar), 140.7 (d, J = 40 Hz, Ar), 139.7 (Ar), 132.8 (d, J = 23 Hz), 128.8 (d, J = 7 Hz, Ar), 128.5 (d, J = 25 Hz, Ar), 128.2 (Ar), 127.4 (d, J = 8 Hz, Ar), 126.8 (Ar), 124.4 (Ar), 123.5 (Ar), 122.2 (Ar), 63.5 (d, J = 10 Hz, CH_2), 28.3 (d, J = 6 Hz, CH), 28.2 (CH), 25.0 (Me), 24.7 (Me), 24.6 (Me), 23.8 (Me), 21.4 (Me).

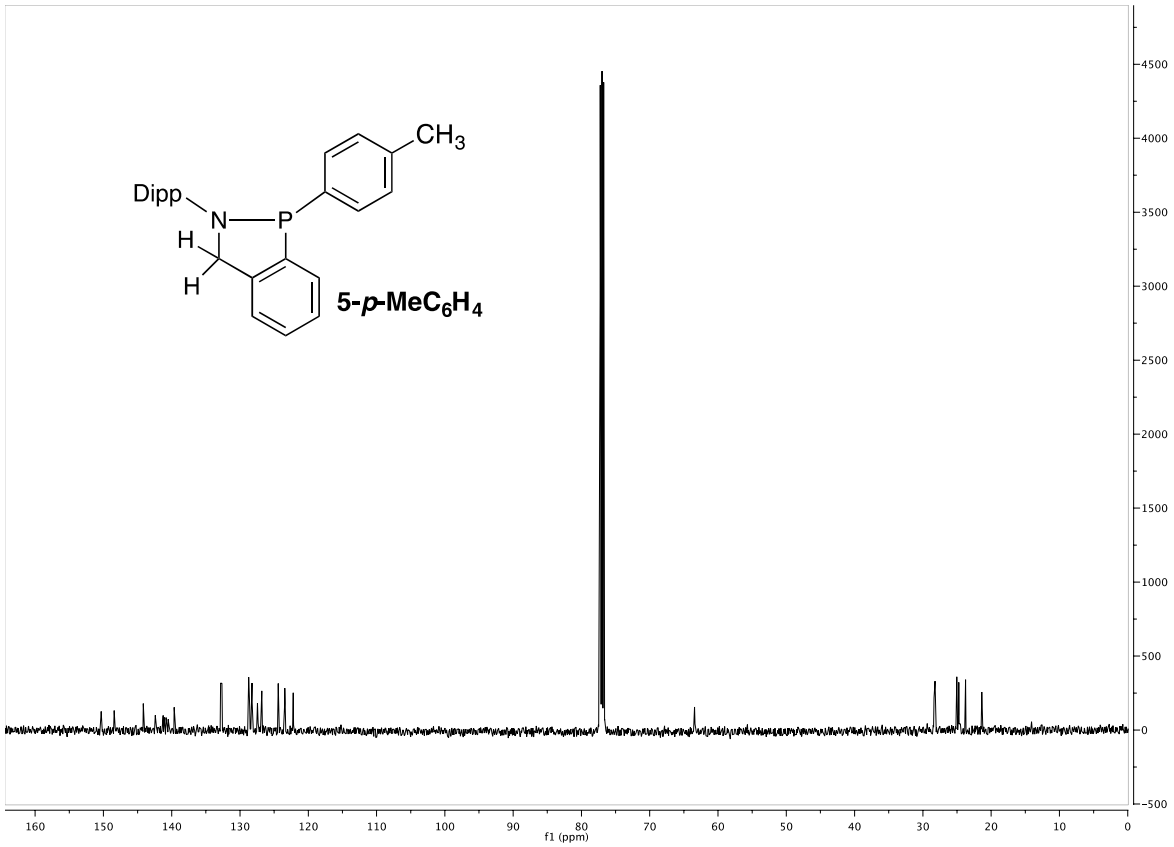
$^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



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Date of report	6/26/2020 1:33:08PM
User ID	Administrator
Comments	MC 4-49 [Cain]

DATE & TIME	6/26/2020 1:31:53 PM	P_ID	EA LAB
SAMPLE ID	20146	USER ID	Administrator
WEIGHT (mg)	2.474	MODE	CHN

CARBON	80.251%
HYDROGEN	7.780%
NITROGEN	3.728%

Special Handling

The sample was transferred under argon and was combusted in a tin capsule that was crimp-sealed with a die apparatus.

Acknowledgment

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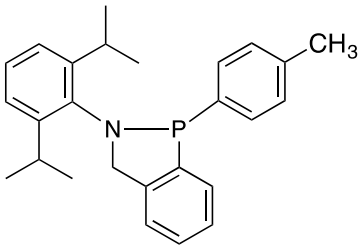
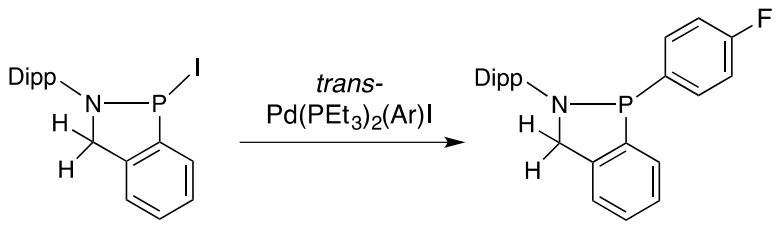
Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Air-sensitive samples were handled in a VAC Atmospheres glovebox.



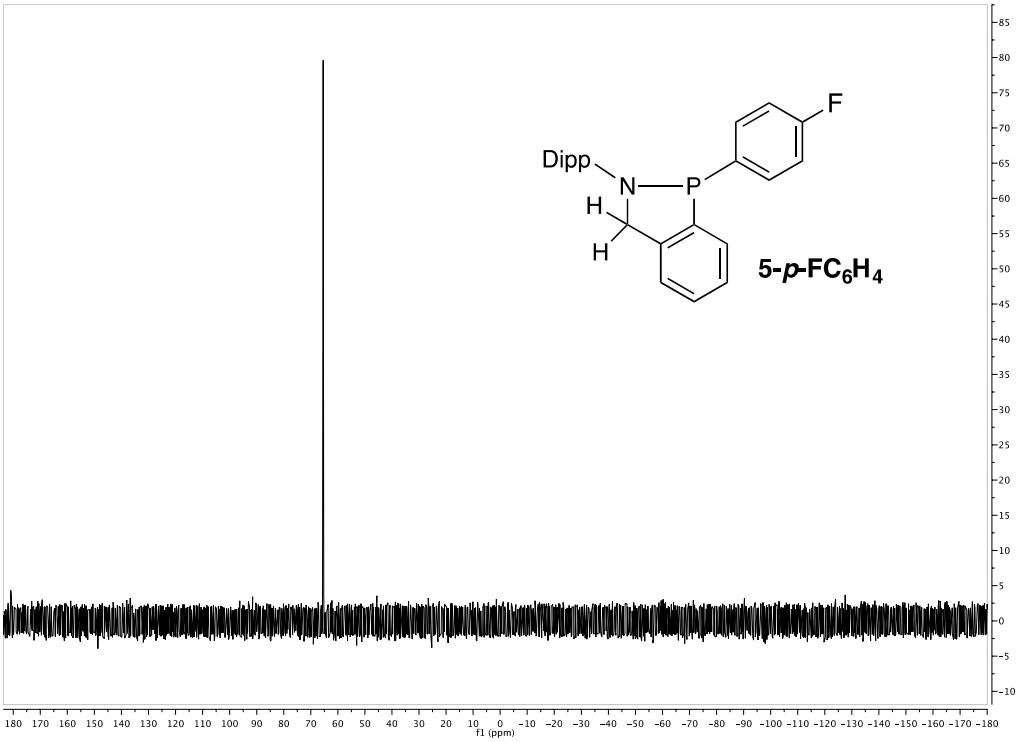
Chemical Formula: $C_{26}H_{30}NP$
Exact Mass: 387.2116
Molecular Weight: 387.5068
m/z: 387.2116 (100.0%), 388.2149 (28.1%), 389.2183 (2.7%), 389.2183 (1.1%)
Elemental Analysis: C, 80.59; H, 7.80; N, 3.61; P, 7.99

Generation of 5-*p*-FC_6H_4.

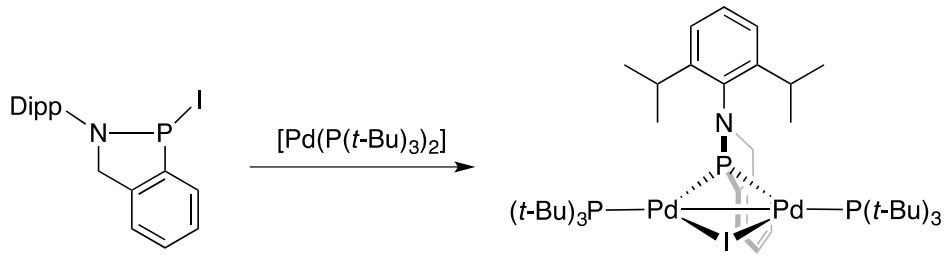


Compounds **4** (58 mg, 0.137 mmol) and **D** (78 mg, 0.137 mmol) were combined in a vial, dissolved in 5 mL of toluene, and transferred to a Schlenk bomb inside the glovebox. The bomb was taken outside the glovebox and placed in an oil bath at 120 ˚C. After 24 h, $^{31}P\{^{1}H\}$ NMR spectroscopy revealed the formation of **5-*p*-FC_6H_4** (65.6 ppm) and *trans*-$PdI_2(PEt_3)_2$ (8.0 ppm) as the major products accompanied by a trace amount of **1** (182.2 ppm) and presumably *trans*-$Pd(p\text{-}FC_6H_4)_2(PEt_3)_2$ (16.7 ppm). The reaction mixture was subsequently brought back inside the glovebox and concentrated under vacuum. The crude product mixture was recrystallized from CH_3CN, which removed **1** and *trans*-$Pd(p\text{-}FC_6H_4)_2(PEt_3)_2$. Dissolving the remaining two components of the precipitate in 1 mL of pentane followed by filtration through a silica plug, followed by further elution with 2-3 mL of pentane afforded a filtrate with only a single ^{31}P NMR (121 MHz, $CDCl_3$) signal (65.9 ppm). Concentration of the filtrate under vacuum afforded 7 mg of a slightly impure white solid by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. Diagnostic ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.12 (d, J = 15 Hz, 1H, CH_2), 4.38 (dd, J = 15, 15 Hz, 1H, CH_2), 2.95 (septet, J = 7 Hz, 1H, CH), 2.87 (septet, J = 7 Hz, 1H, CH).

$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)



Synthesis of 6-Pd_2-($P(t\text{-}Bu)_3)_2$.

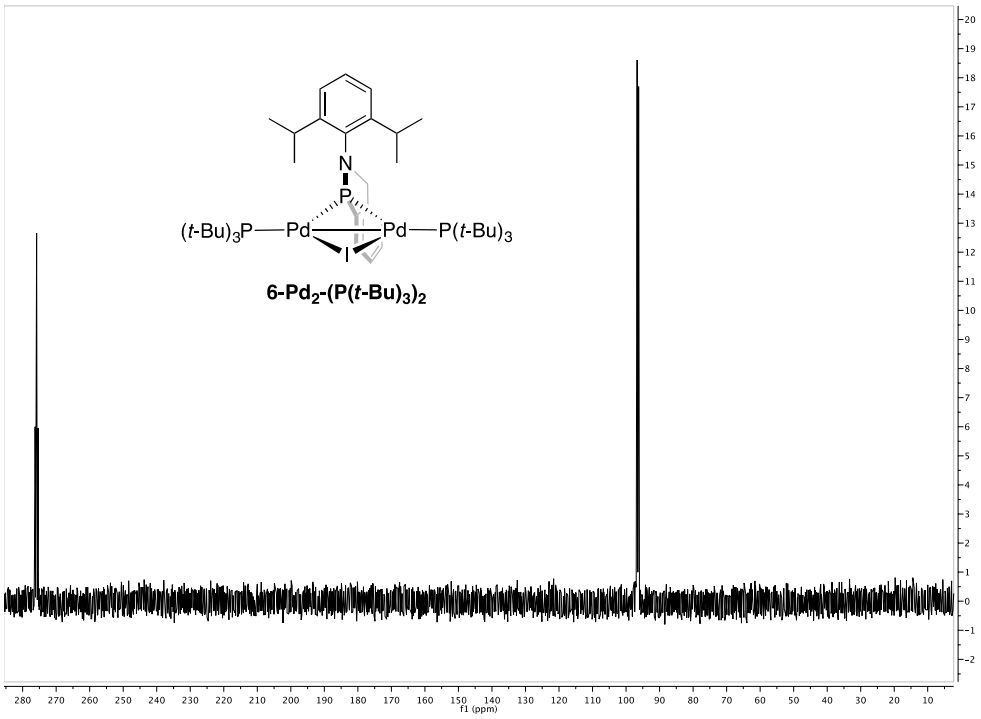


Synthesis of 6-Pd_2-($P(t\text{-}Bu)_3)_2$. 1:1 Stoichiometry. Compound **4** (50 mg, 0.118 mmol), [Pd($P(t\text{-}Bu)_3)_2$] (60 mg, 0.118 mmol), and a stir bar were combined in a vial and dissolved in 3 mL of toluene, resulting in a dark reaction mixture. After 24 h at room temperature, $^{31}P\{^1H\}$ NMR spectroscopy revealed that **4** had been consumed. The reaction mixture was subsequently concentrated under vacuum, and the dark residue was extracted with pentane (2 x 5 mL) and filtered through a Celite plug. The filtrate was concentrated under vacuum and re-dissolved in 2 mL of ether, followed by the addition of 4 mL of acetonitrile. The Et_2O/CH_3CN solution was then cooled to -35 °C, leading to the precipitation of dark crystals suitable for X-ray diffraction (< 10 mg).

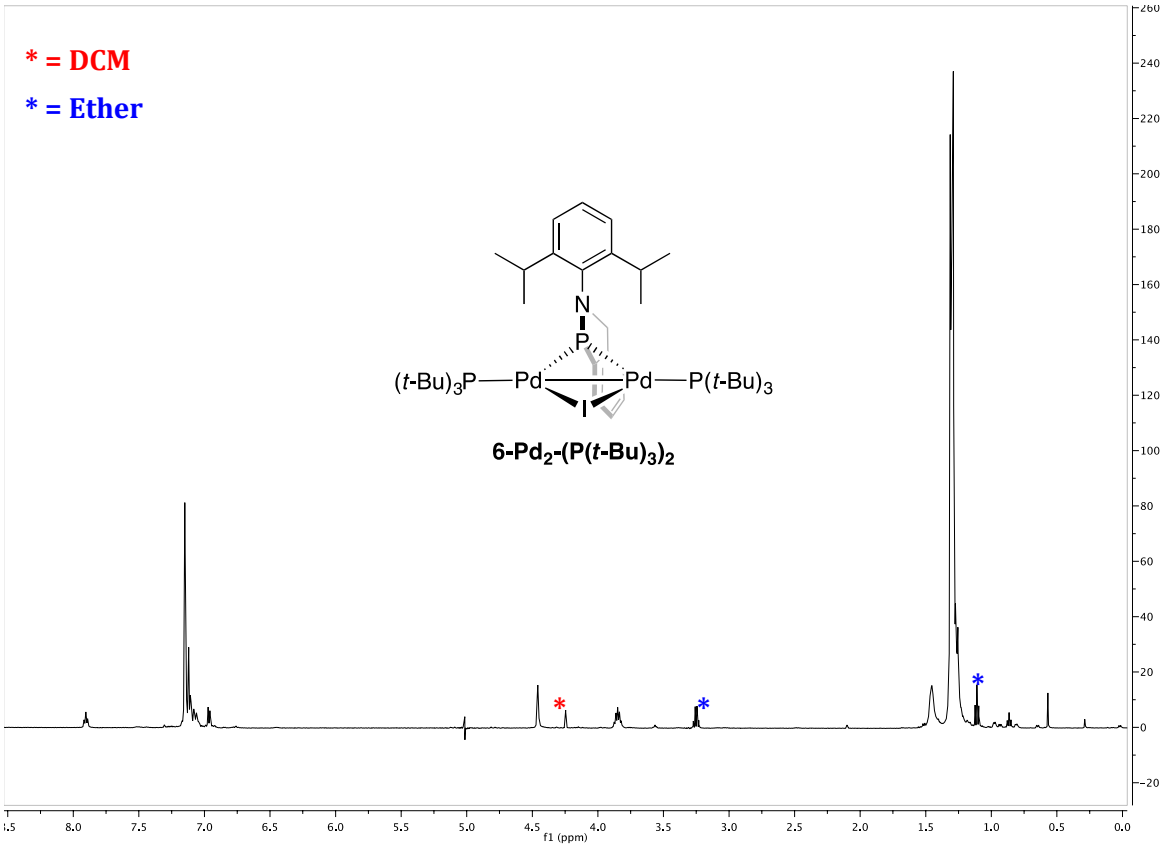
1:2 Stoichiometry. Compound **4** (31 mg, 0.0732 mmol), [Pd($P(t\text{-}Bu)_3)_2$] (75 mg, 0.147 mmol, 2 equiv), and a stir bar were combined in a vial and dissolved in 3 mL of toluene, resulting in a dark reaction mixture. After 24 h at room temperature, $^{31}P\{^1H\}$ NMR spectroscopy revealed that **4** had been consumed. The reaction mixture was concentrated under vacuum, pentane was added, and the mixture was re-concentrated. Extraction of the dark residue with additional pentane (3 x 5 mL) followed by filtration through a Celite plug afforded a dark filtrate that was concentrated under vacuum. The crude product mixture was dissolved in 2 mL of ether, 4 mL of acetonitrile was added, and the solution was cooled to -35 °C, resulting in the precipitation of dark crystalline solid. In order to remove an unidentified impurity (^{31}P NMR (C_6D_6): 84.7 ppm) that was not present in the 1:1 stoichiometric case, the crystalline solid was washed with cold pentane, affording analytically pure material (23 mg, 0.0220 mmol, 30%).

Anal. Calcd. for $C_{43}H_{77}INP_3Pd_2$: C, 49.62; H, 7.46; N, 1.35. Found: C, 49.60; H, 7.51; N, 1.32. $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ 275.8 (t, J = 73 Hz, PN), 96.5 (d, J = 73 Hz, $P(t\text{-}Bu)_3$). ^1H NMR (500 MHz, C_6D_6): δ 7.90 (t, J = 7 Hz, 1H, Ar), 7.14-7.06 (br m, 5H, overlapping Ar), 6.96 (d, J = 7 Hz, 1H, Ar), 4.46 (br, 2H, CH_2), 3.85 (septet, J = 7 Hz, 2H, CH), 1.45 (br, 6H, Me), 1.30 (br m, 60H, overlapping *t*-Bu and Me). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 147.1 (Ar), 146.4 (Ar), 140.4 (Ar), 139.7 (Ar), 129.2 (d, J = 24 Hz, Ar), 128.8 (Ar), 127.4 (d, J = 11 Hz, Ar), 126.8 (Ar), 125.3 (Ar), 122.3 (Ar), 63.9 (CH_2), 36.5 (quat), 32.8 (*t*-Bu), 29.0 (CH), 27.9 (Me), 25.6 (Me).

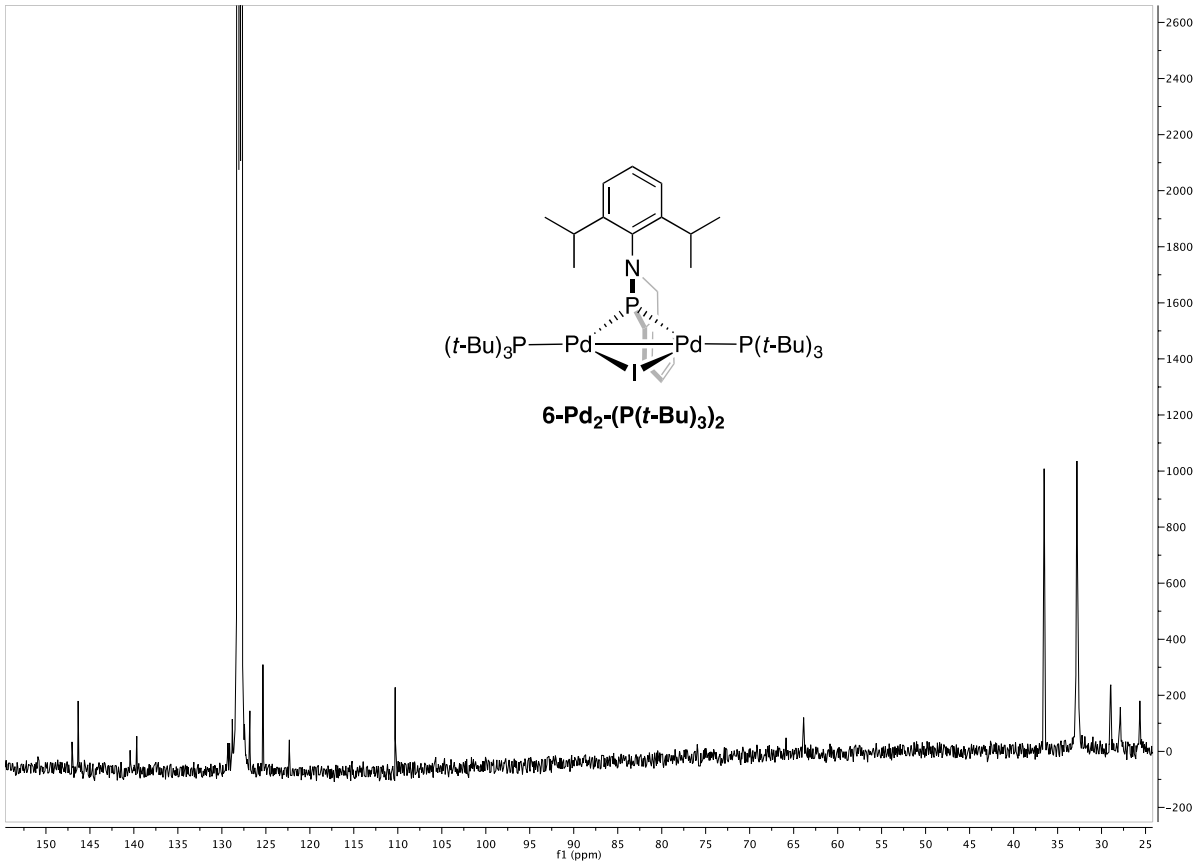
$^{31}P\{^{1}H\}$ NMR (160 MHz, C_6D_6)



^{1}H NMR (500 MHz, C_6D_6)



$^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6)



CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	10/9/2020 3:00:41PM
User ID	Administrator
Comments	MC 5-18 [Cain]

DATE & TIME	10/9/2020 10:26:18 AM	P_ID	EA LAB
SAMPLE ID	20307	USER ID	Administrator
WEIGHT (mg)	2.138	MODE	CHN

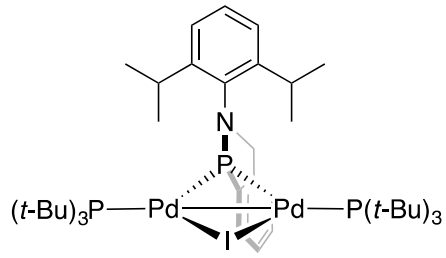
CARBON	49.599%
HYDROGEN	7.507%
NITROGEN	1.323%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

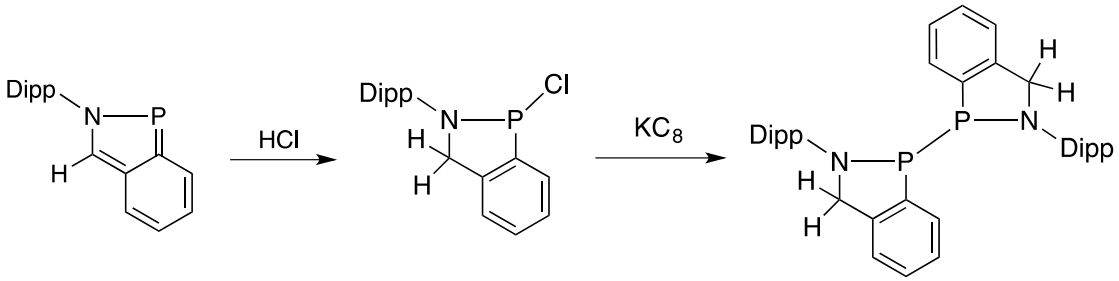
Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.



Chemical Formula: $C_{43}H_{77}INP_3Pd_2$
Exact Mass: 1039.2383
Molecular Weight: 1040.7618
Elemental Analysis: C, 49.62; H, 7.46; I, 12.19; N, 1.35; P, 8.93; Pd, 20.45

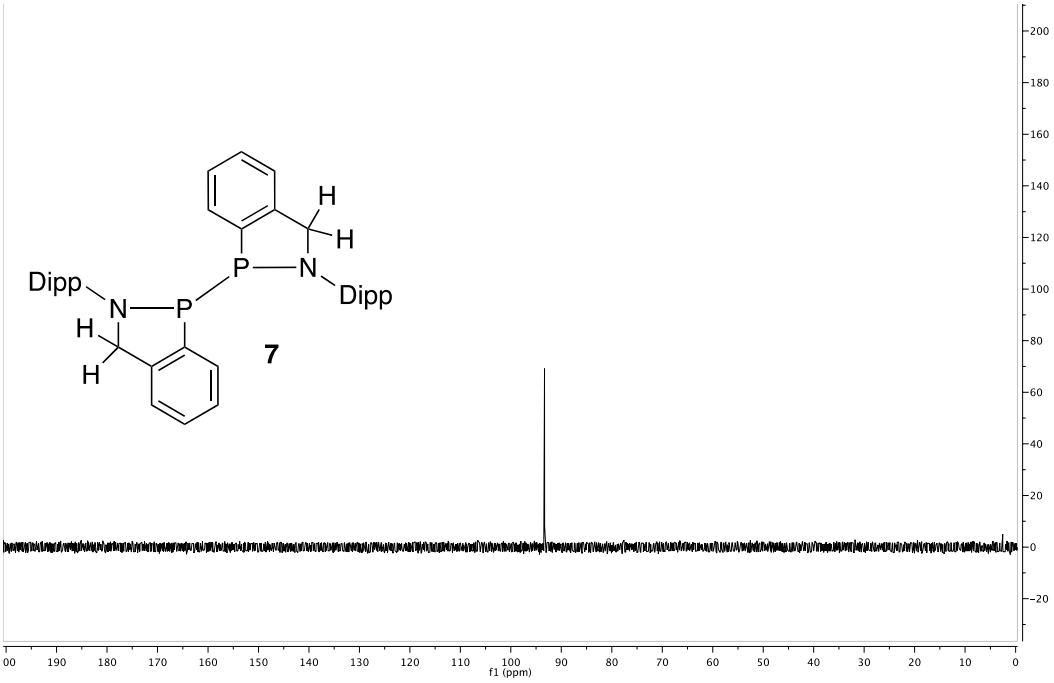
Synthesis of 7.



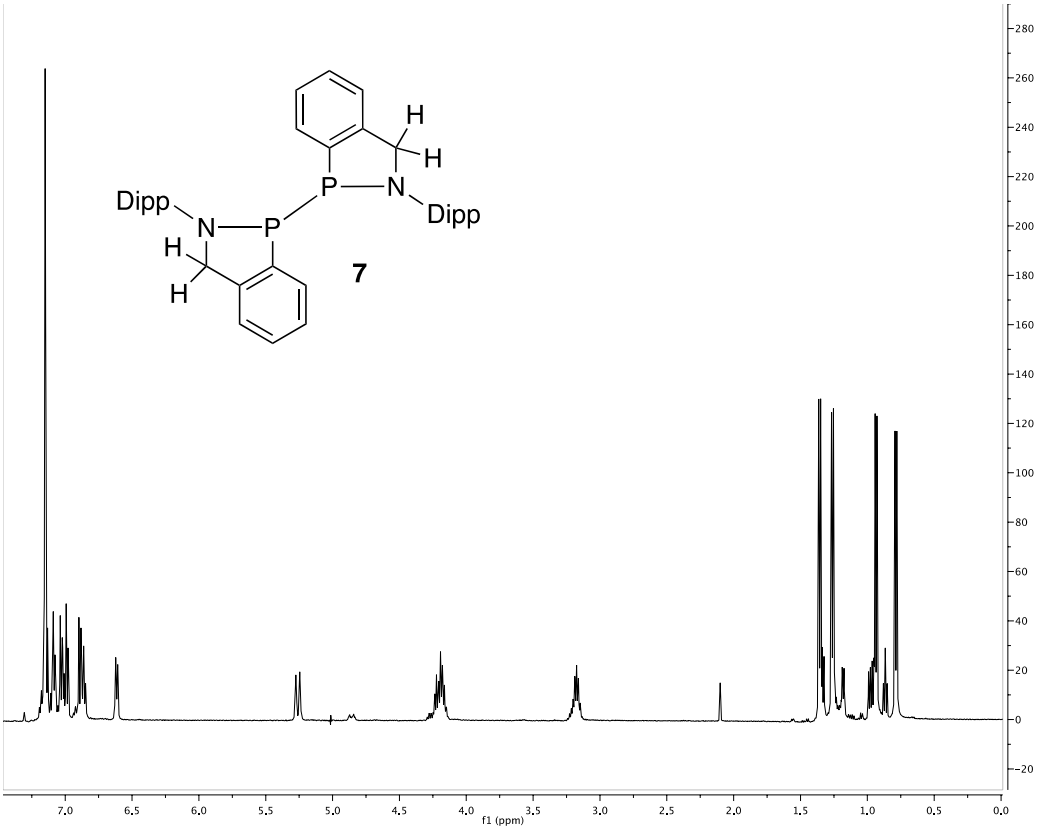
Compound **1** (200 mg, 0.68 mmol) and a stir bar were loaded in a Schlenk bomb inside the glovebox and dissolved in 5 mL of toluene. The bomb was taken outside the glovebox and HCl (4 N in 1,4-dioxane, 0.34 mL, 1.36 mmol, 2.00 equiv.) was injected through a septum via syringe under positive N_2 pressure. The reaction mixture was stirred at room temperature for 15 min. The bomb was then brought back into the glovebox, and the reaction mixture was concentrated under vacuum. The residue was washed with 10 mL of pentane, concentrated under vacuum, and then dissolved in 10 mL of THF. Solid KC_8 (0.100 g, 0.74 mmol, 1.1 equiv.) was added, and the reaction mixture was stirred overnight. The heterogeneous mixture was concentrated under vacuum, extracted with pentane, and filtered through a Celite plug. The filtrate was transferred to a 25 mL Schlenk bomb and concentrated again. Anhydrous octane (10 mL) was added to give a slurry and the Schlenk bomb was taken outside the glovebox. The slurry was heated at 70 ˚C until it became homogenous. The solution was then cooled to room temperature, resulting in the precipitation of white X-ray quality crystals (87 mg, 0.15 mmol, 43%).

Anal. Calcd. for $C_{38}H_{46}N_2P_2$: C, 77.00; H, 7.82; N, 4.73. Found: C, 76.96; H, 8.09; N, 4.44. $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$): δ 93.3. ^1H NMR (500 MHz, C_6D_6): δ 7.15-7.13 (m, 2H, Ar), 7.11-6.98 (m, 6H, Ar), 6.90-6.85 (m, 4H, Ar), 6.61 (d, J = 7.5 Hz, 2H, Ar), 5.26 (d, J = 15 Hz, 2H, CH_2), 4.24-4.15 (overlapping m, 4H, overlapping CH w/ diastereotopic CH_2), 3.18 (septet, J = 7 Hz, 2H, CH), 1.36 (d, J = 7 Hz, 6H, CH_3), 1.26 (d, J = 7 Hz, 6H, CH_3), 0.94 (d, J = 7 Hz, 6H, CH_3), 0.79 (d, J = 7 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 150.3 (Ar), 148.3 (Ar), 144.7 (Ar), 129.9 (t, J = 13 Hz, Ar), 127.4 (Ar), 126.5 (Ar), 124.8 (Ar), 124.1 (Ar), 121.2 (Ar), 64.6 (CH_2), 29.0 (CH), 28.8 (CH), 26.1 (Me), 25.2 (Me), 24.6 (Me), 23.3 (Me). Once isolated, diphosphine **7** routinely decomposed in solution. In $CDCl_3$, the decomposition was fast, but even in C_6D_6, slow decomposition was apparent as evidenced by the appearance of other diastereotopic-type CH_2 and *N*-Dipp methyl signals. The $^{13}C\{^1H\}$ NMR spectrum has fewer than the expected amount of Ar resonances likely due to overlap with the residual solvent signal.

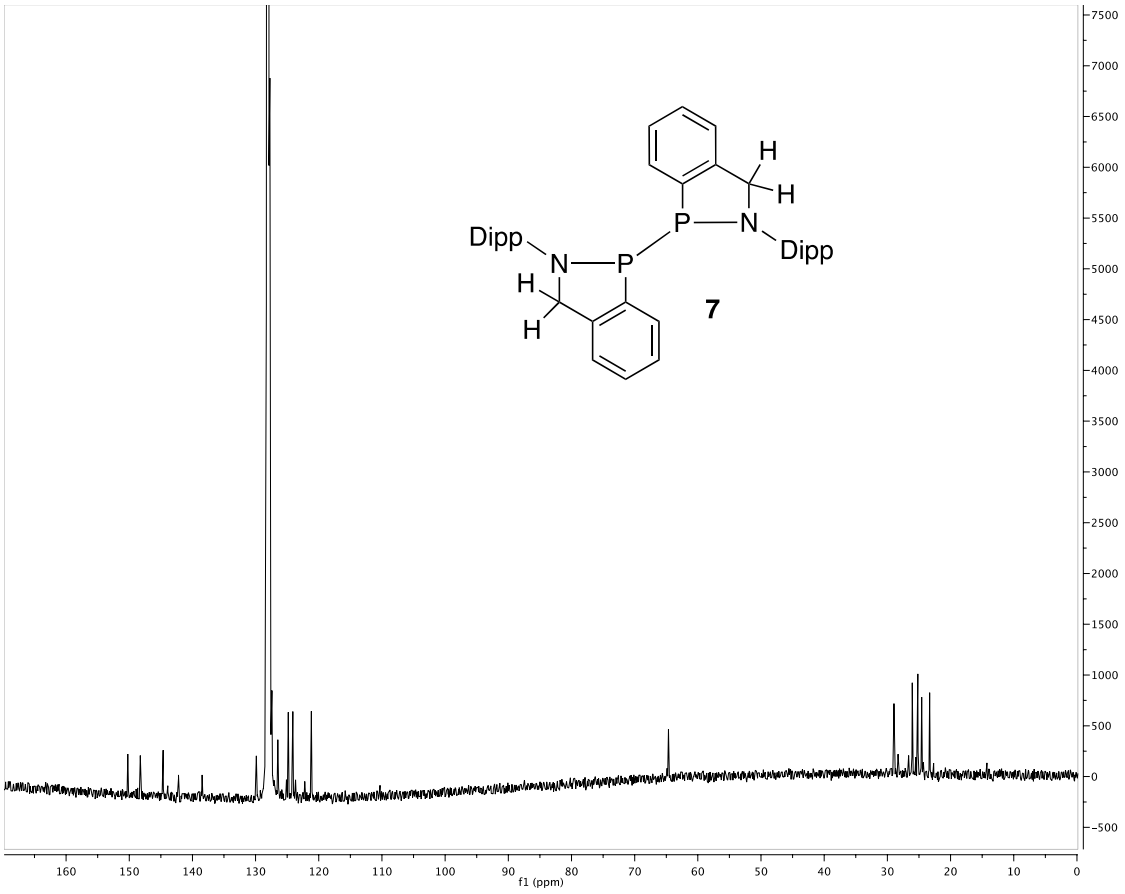
$^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, C_6D_6)



$^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6)



CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	9/11/2020 2:09:04PM
User ID	Administrator
Comments	DZ-78 [Cain / Zhou]

DATE & TIME	9/11/2020 2:01:59 PM	P_ID	EA LAB
SAMPLE ID	20264D	USER ID	Administrator
WEIGHT (mg)	2.100	MODE	CHN

CARBON	76.957%
HYDROGEN	8.088%
NITROGEN	4.436%

DATE & TIME	9/11/2020 1:56:54 PM	P_ID	EA LAB
SAMPLE ID	20264	USER ID	Administrator
WEIGHT (mg)	2.435	MODE	CHN

CARBON	76.696%
HYDROGEN	8.125%
NITROGEN	4.431%

Special Handling

The sample was transferred under argon and was combusted in a tin capsule that was crimp-sealed with a die apparatus.

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

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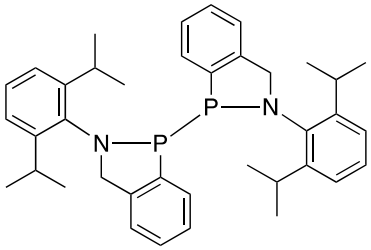
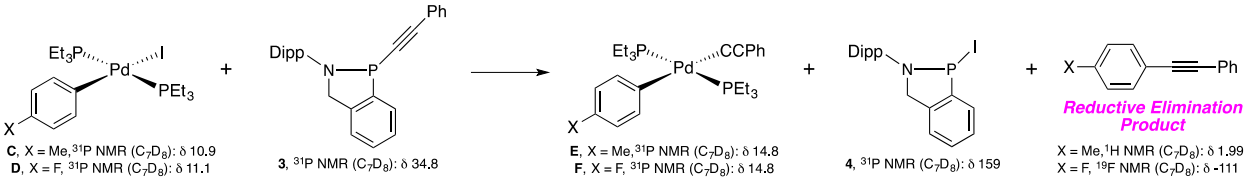


Chemical Formula: $C_{38}H_{46}N_2P_2$
Exact Mass: 592.3136
Molecular Weight: 592.7475
m/z: 592.3136 (100.0%), 593.3170 (41.1%), 594.3203 (8.2%)
Elemental Analysis: C, 77.00; H, 7.82; N, 4.73; P, 10.45

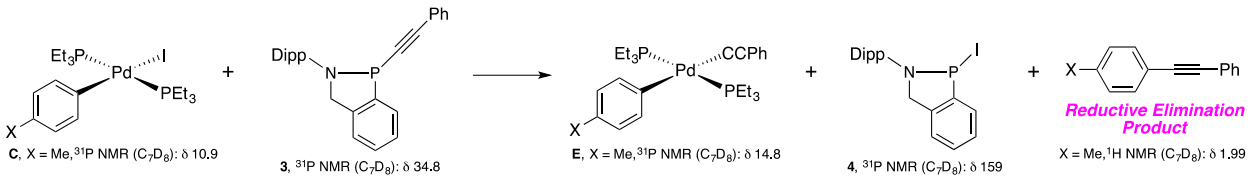
2. Stoichiometric and Catalytic Studies

Stoichiometric –CCPh Transfer



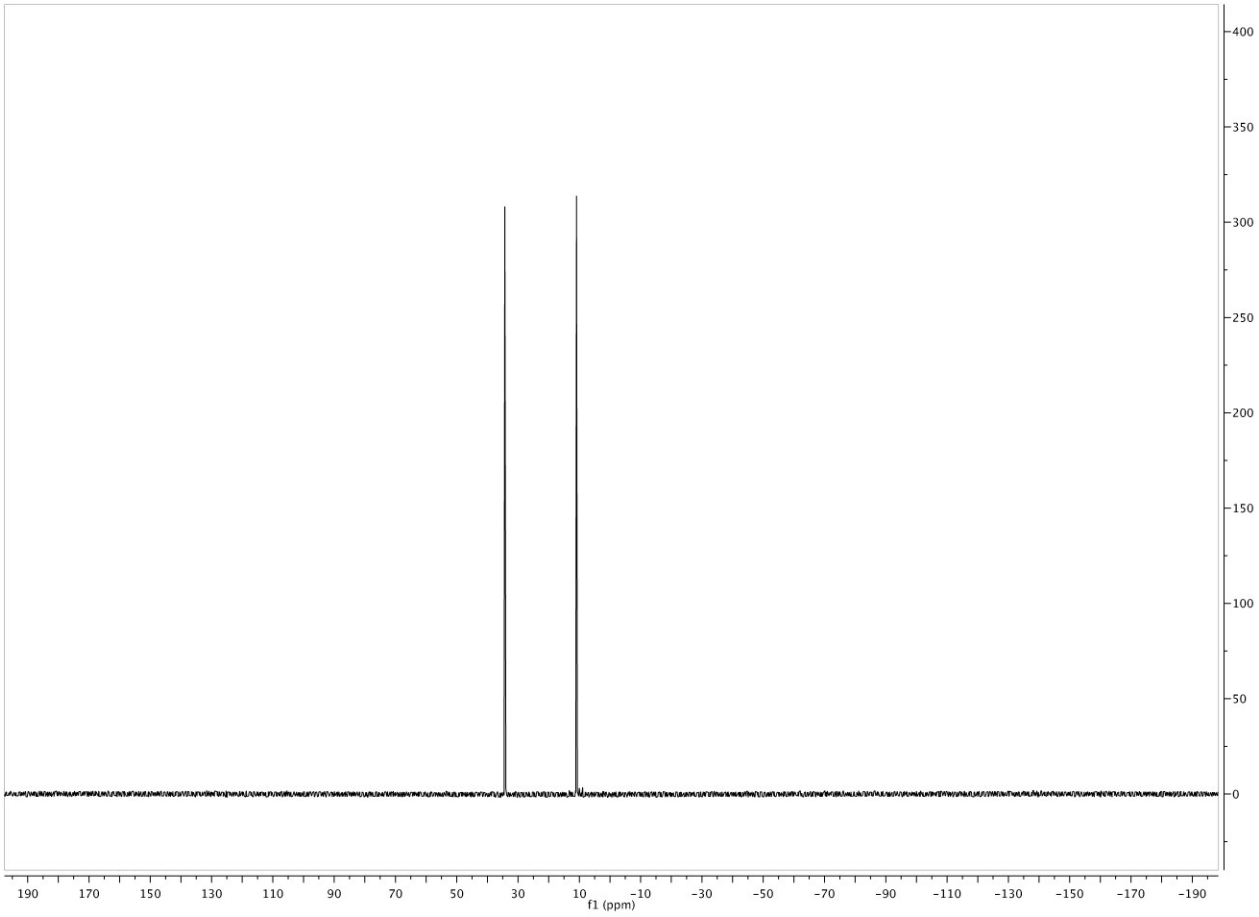
General Experimental Details: Alkynyl-functionalized benzazaphosphole **3** (25 mg, 0.063 mmol) was dissolved in approximately 1.5 ml of C_7D_8 and added to Pd complex **C** or **D** (35 mg, 0.063 mol). The reaction mixture was transferred to a J-Young tube and placed in an oil bath at 120 ˚C. The reaction was monitored by ^{1}H and $^{31}P\{H\}$ for **C** and $^{31}P\{H\}$ and ^{19}F NMR spectroscopy for **D** in 12 h intervals until >95% conversion was reached.

Stoichiometric Studies → C + 3 (^{31}P Tracking)



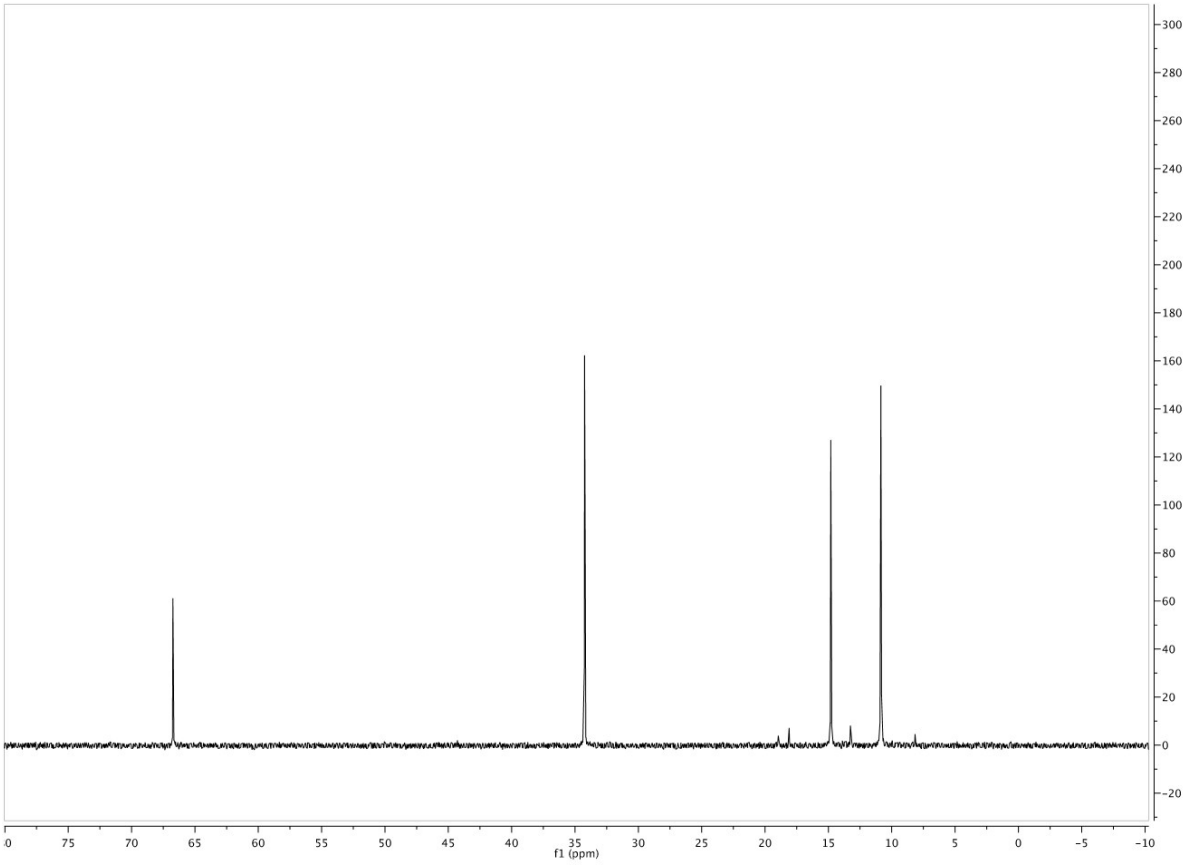
^{31}P{^{1}H} NMR (121 MHz, C_7D_8)

t = 0, no heat applied



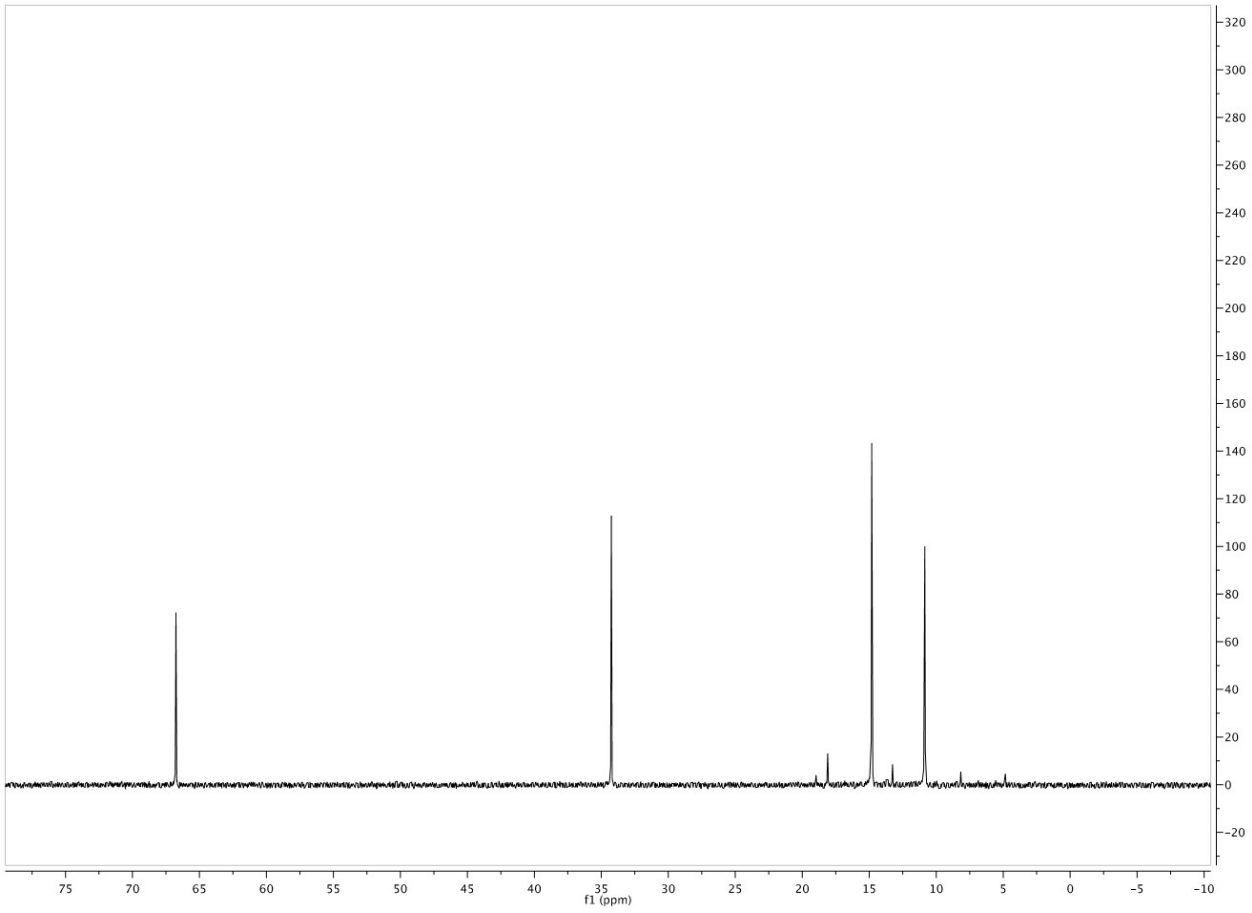
$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 12 h, 120 °C



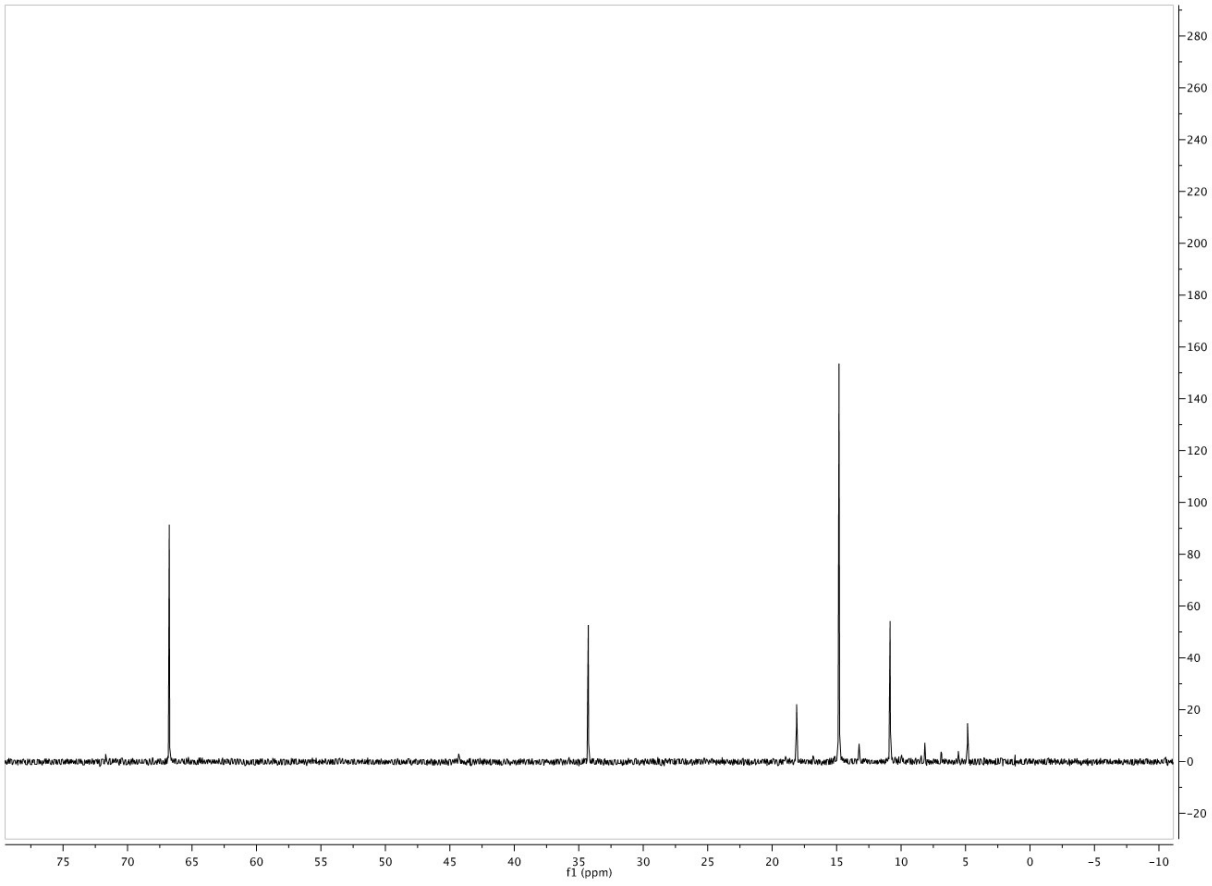
$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 24 h, 120 °C



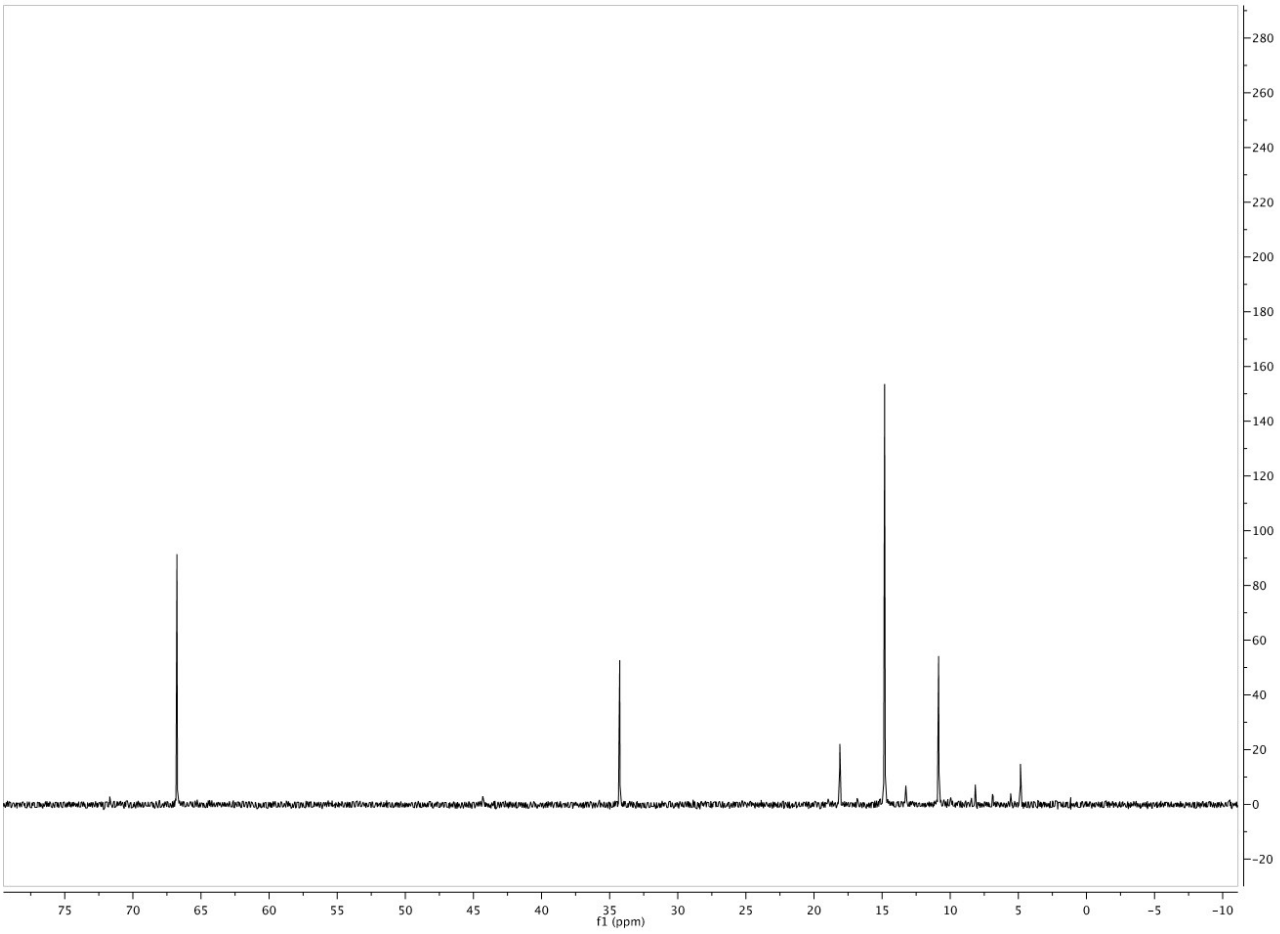
$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 36 h, 120 °C



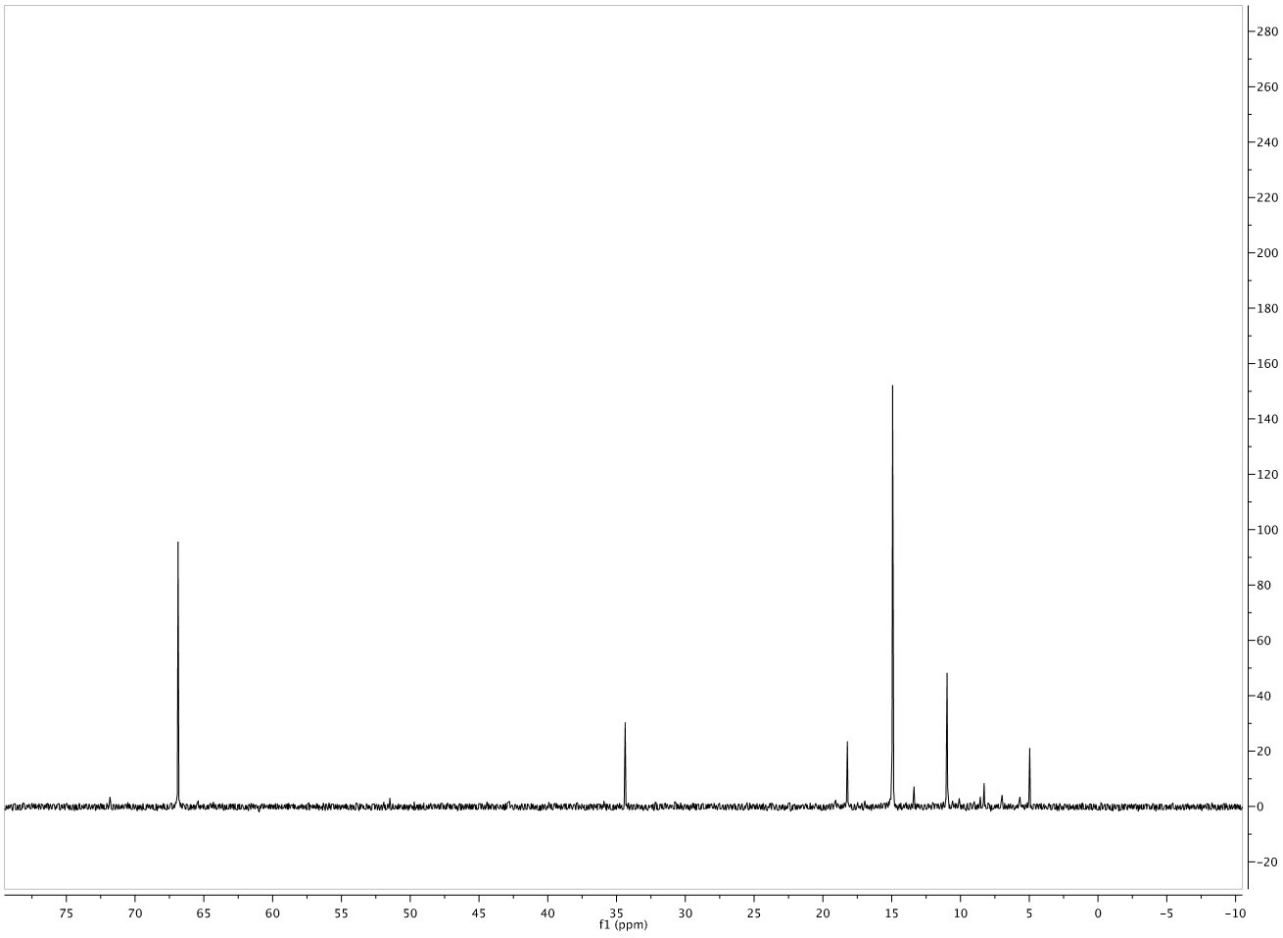
$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 48 h, 120 °C



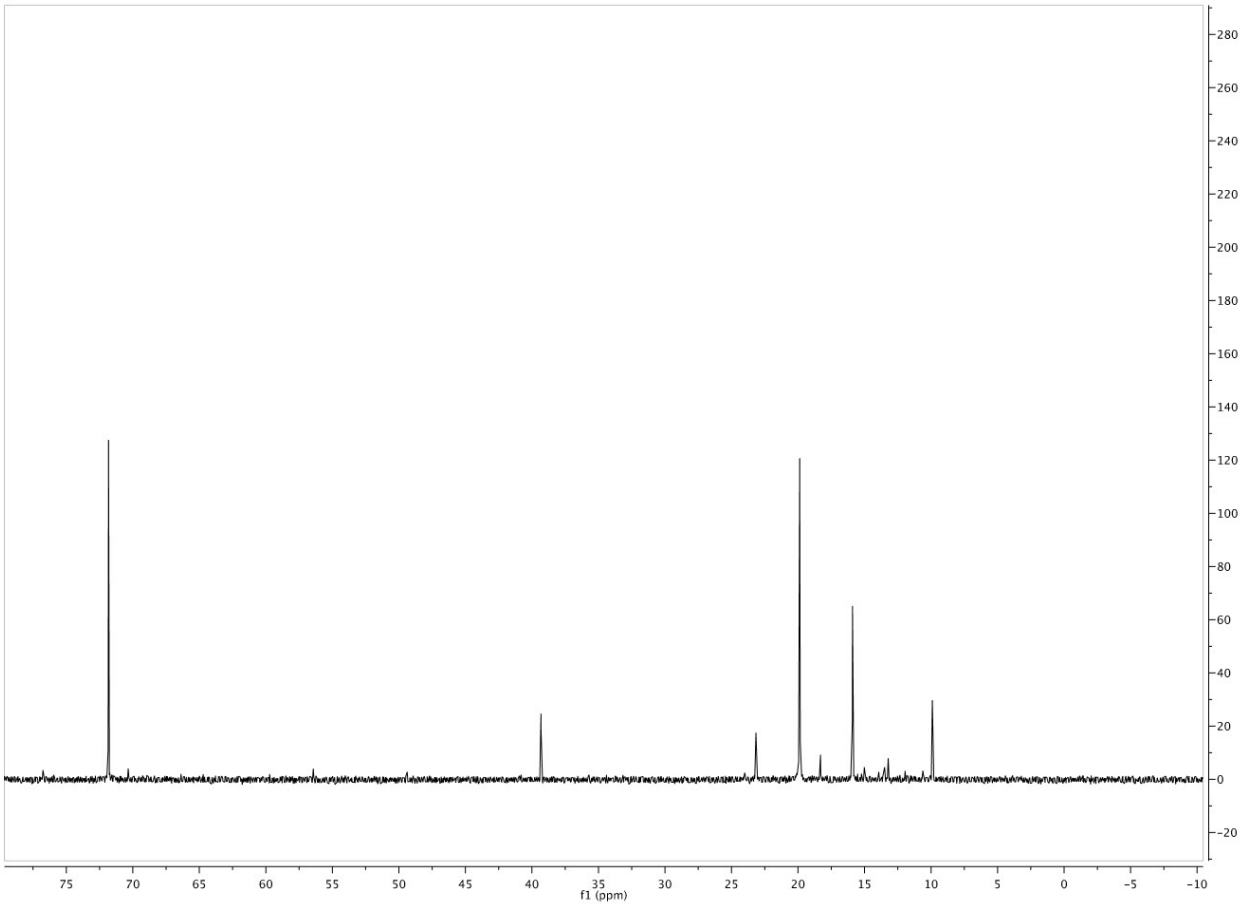
$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 60 h, 120 °C



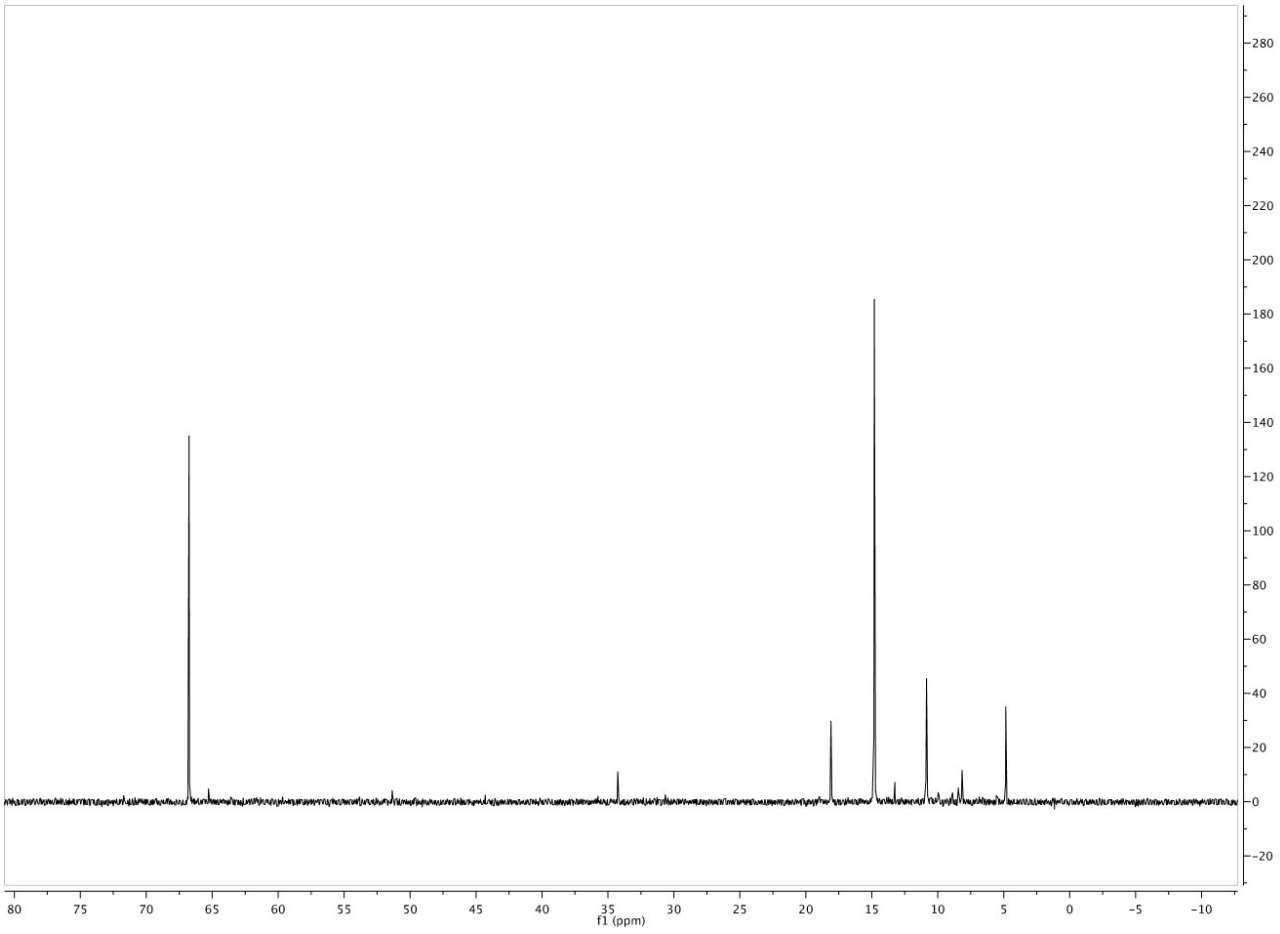
$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 72 h, 120 °C



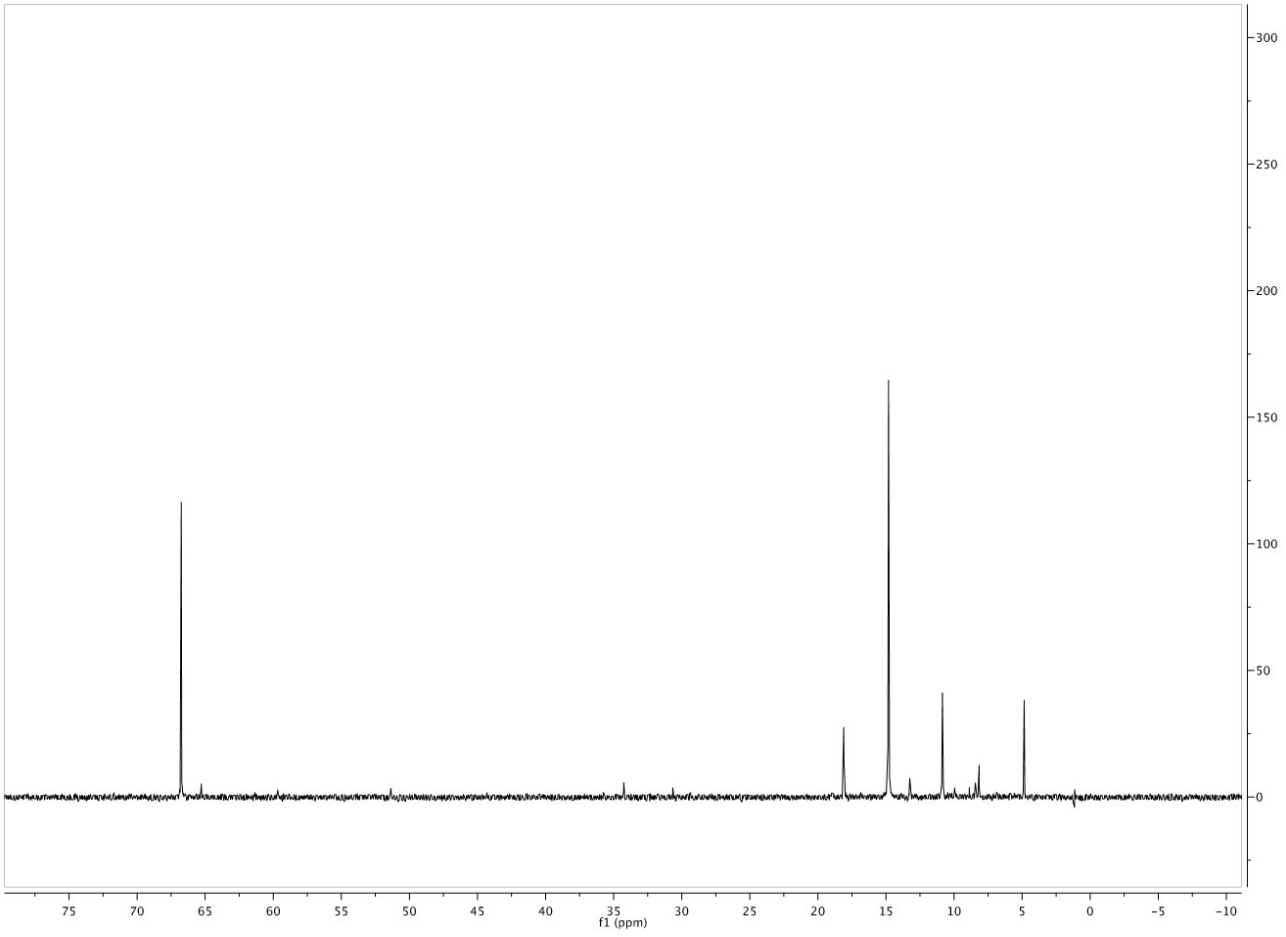
$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 84 h, 120 °C



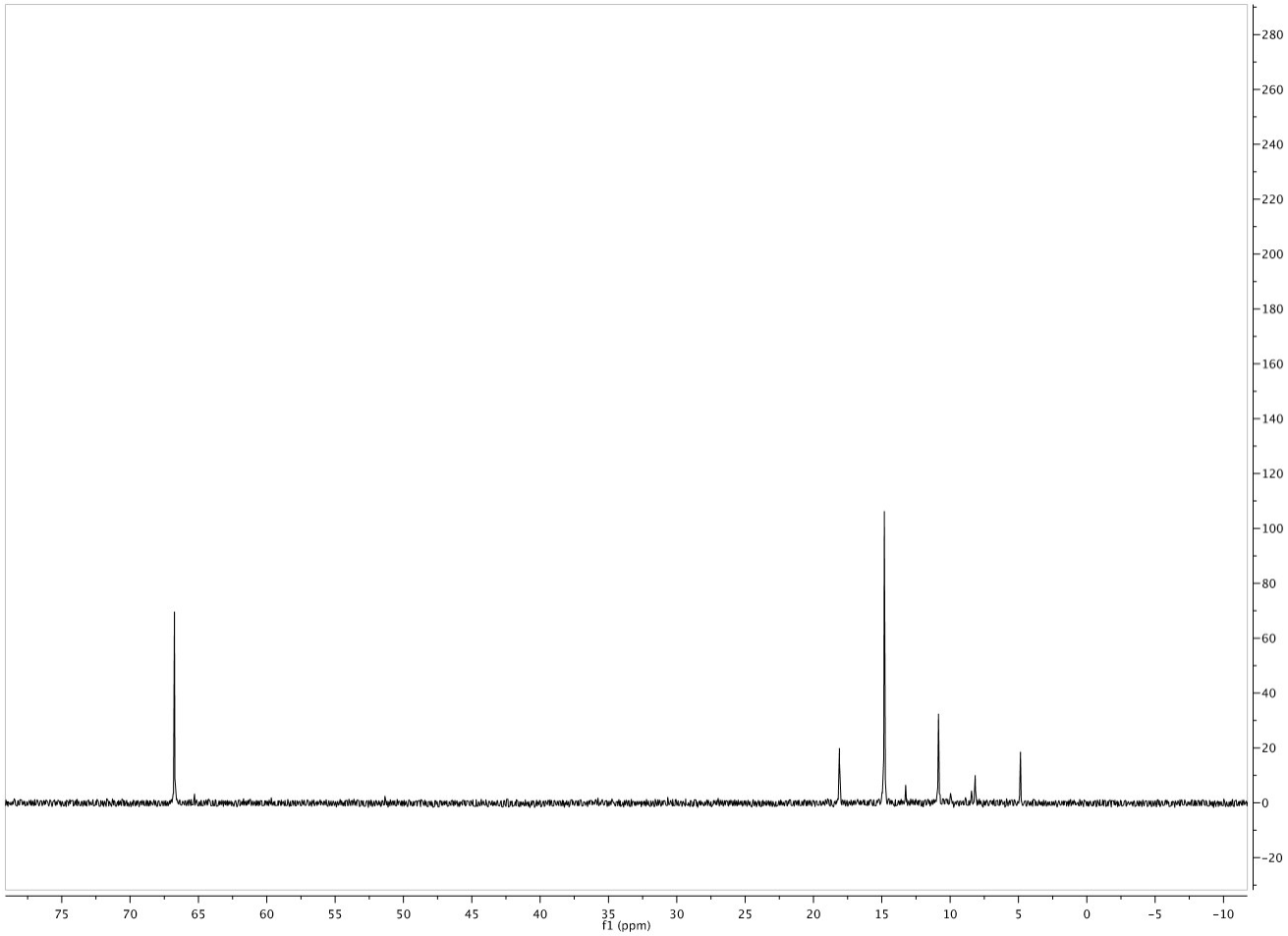
$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 96 h, 120 °C

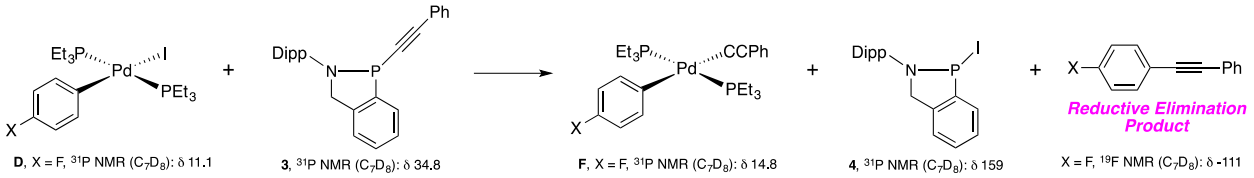


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 108 h, 120 °C



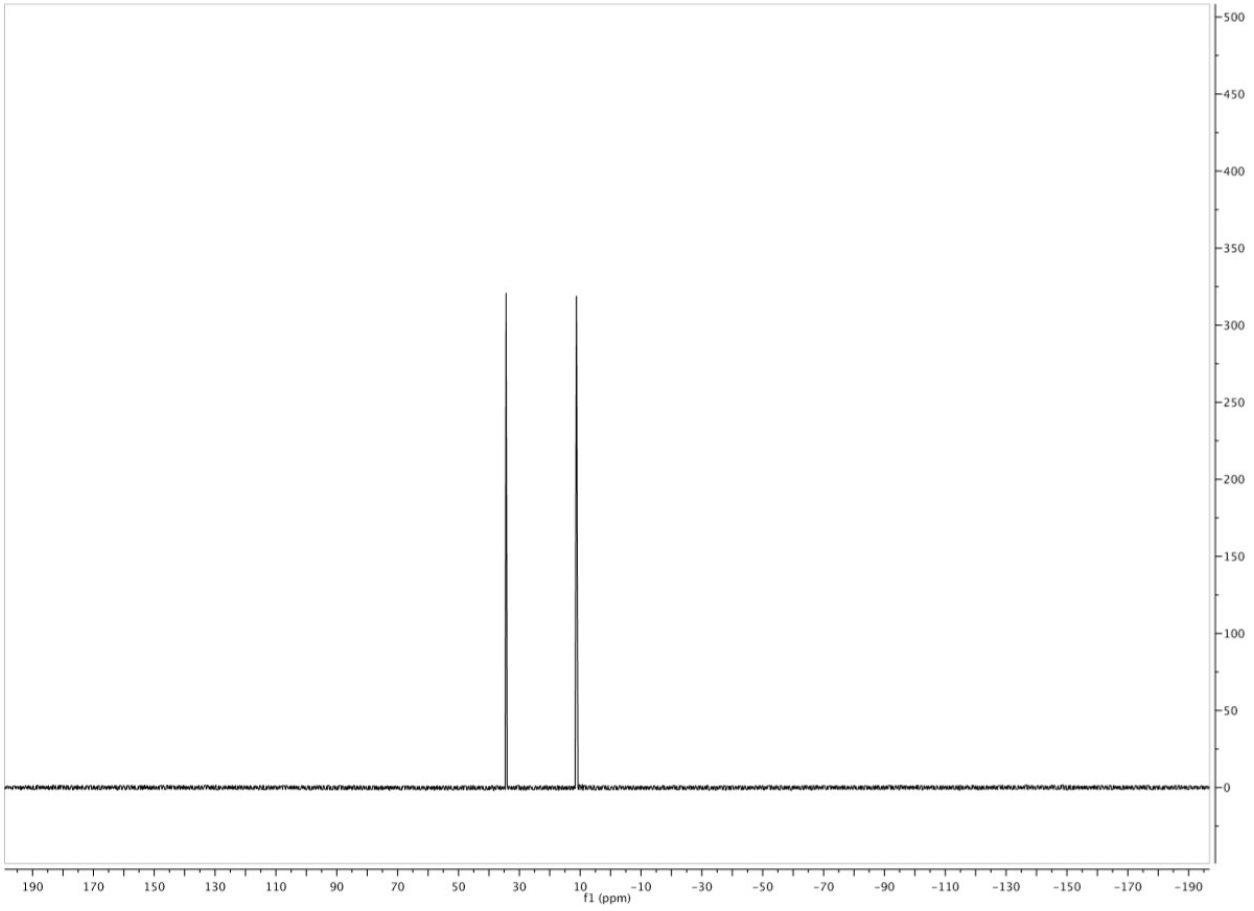
Stoichiometric Studies → D + 3 (^{31}P and ^{19}F Tracking)



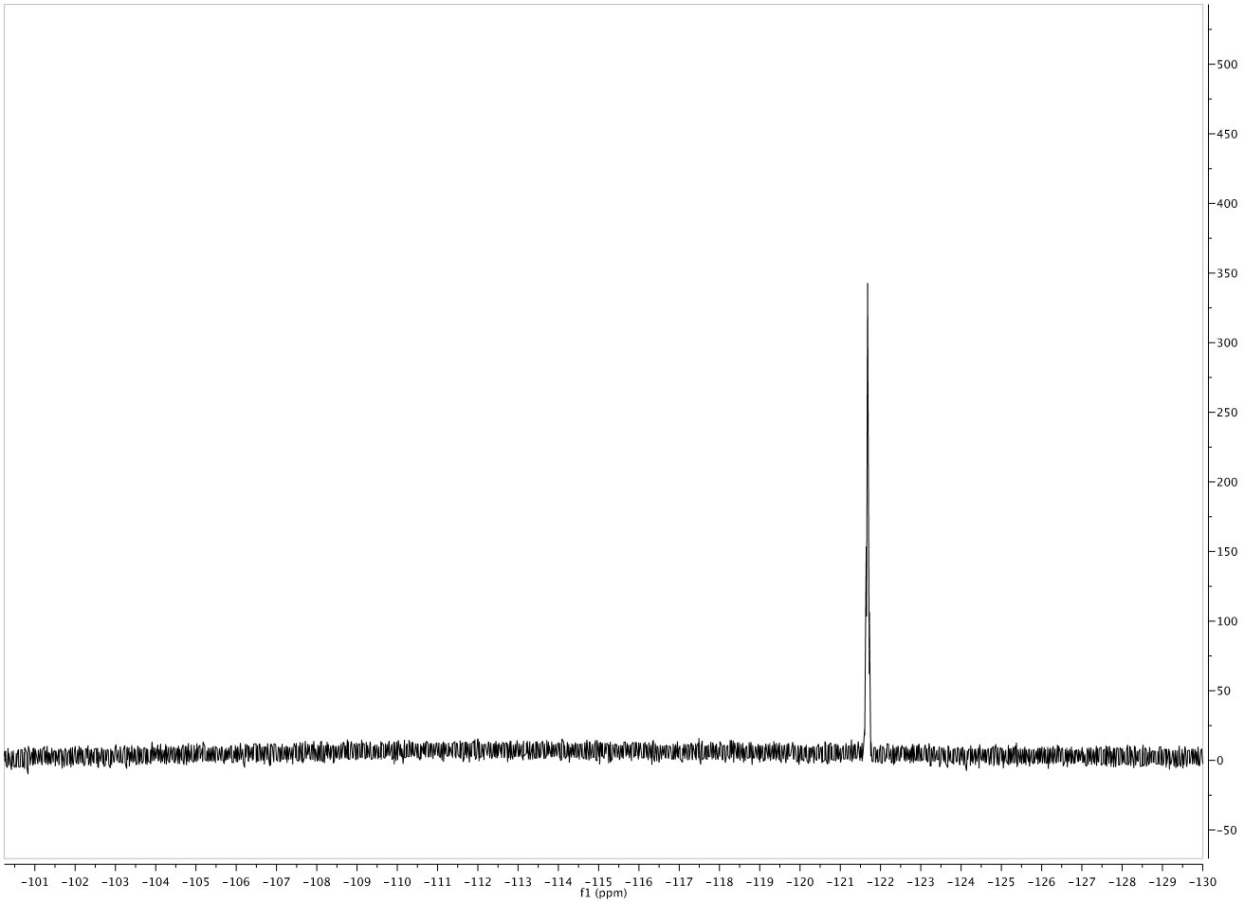
D, X = F, ^{31}P NMR (C_7D_8): δ 11.1 | **3**, ^{31}P NMR (C_7D_8): δ 34.8 | **F**, X = F, ^{31}P NMR (C_7D_8): δ 14.8 | **4**, ^{31}P NMR (C_7D_8): δ 159 | X = F, ^{19}F NMR (C_7D_8): δ -111

^{31}P{^{1}H} NMR (121 MHz, C_7D_8)

t = 0 h, no heat applied

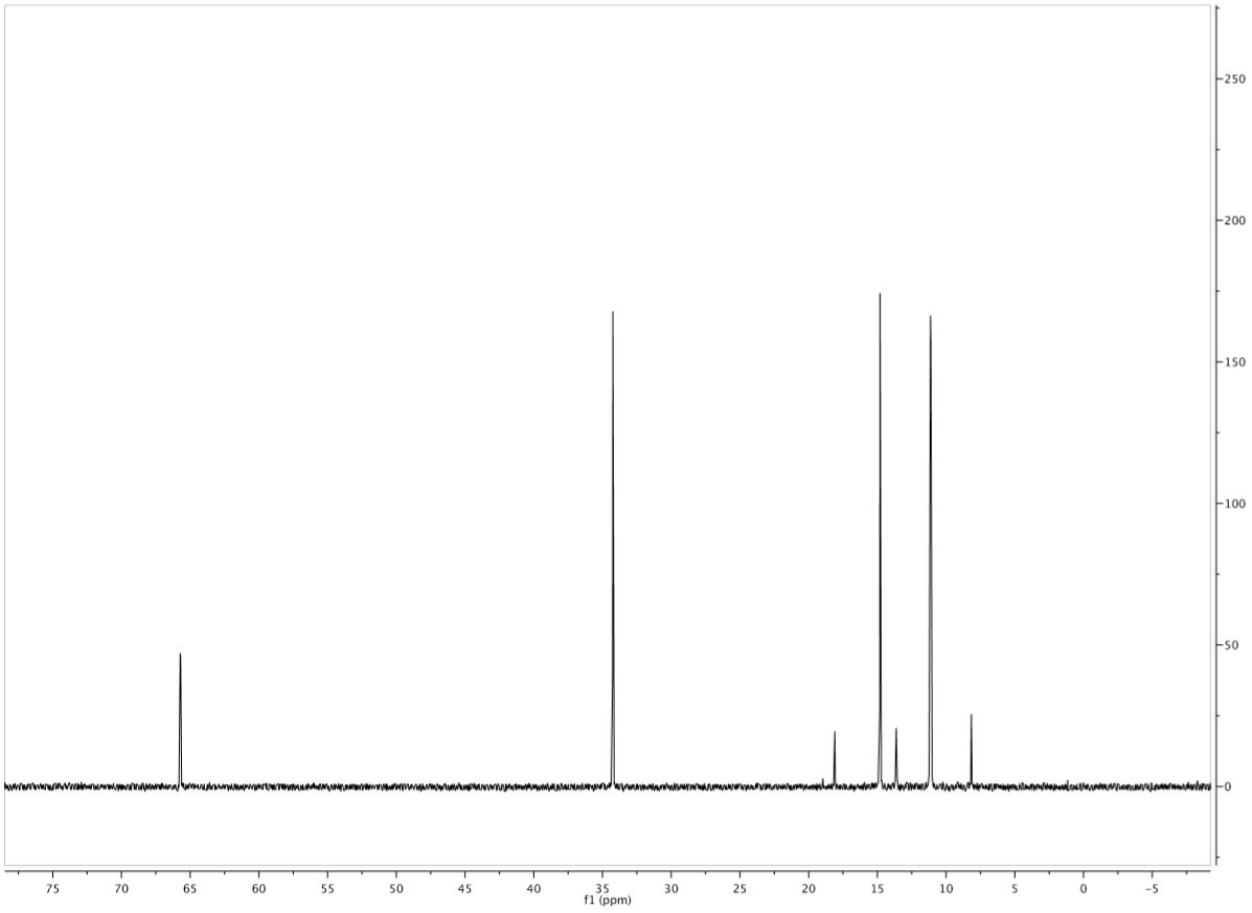


$^{19}F\{^{1}H\}$ NMR (282 MHz, C_7D_8)

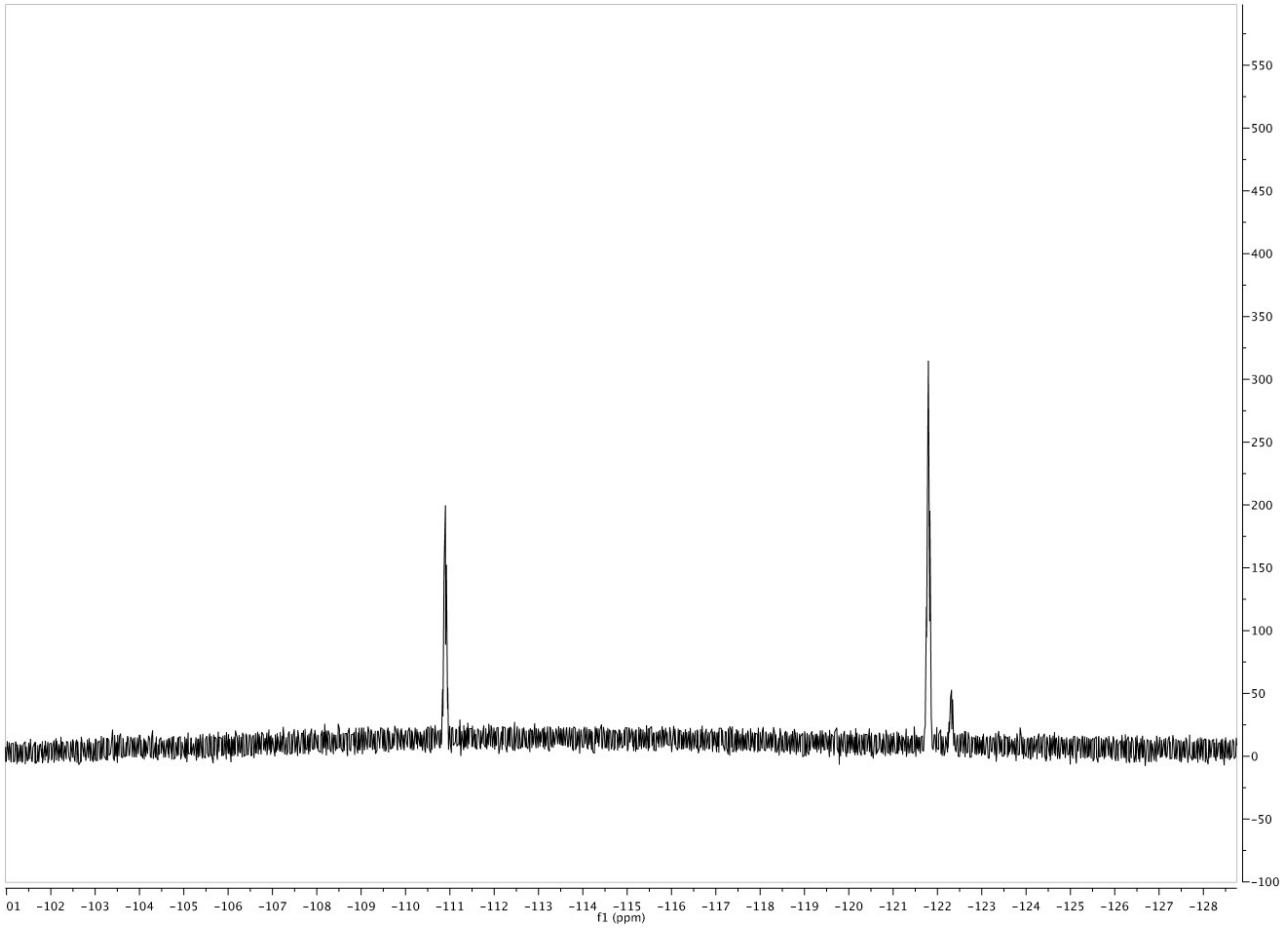


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 12 h, 120 °C

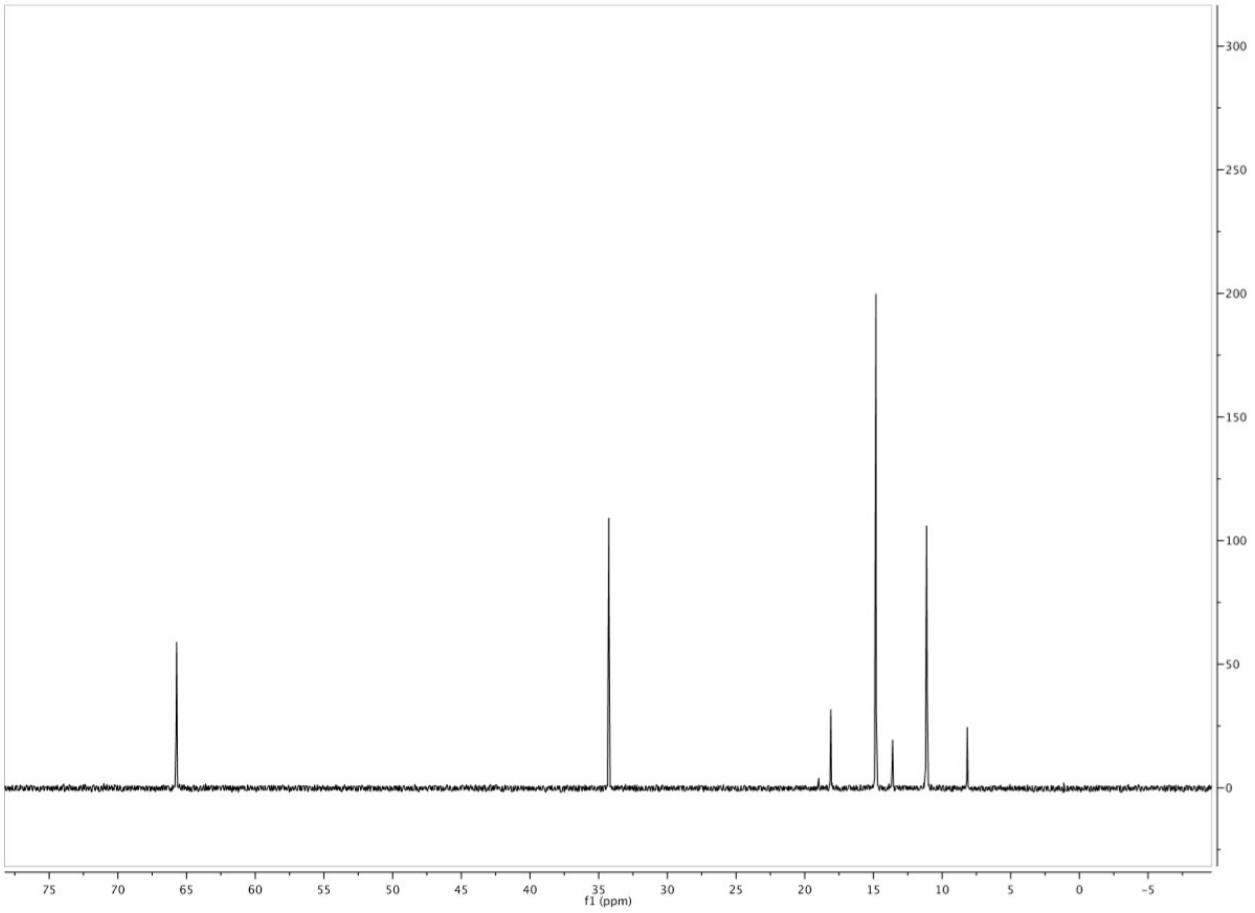


$^{19}F\{^{1}H\}$ NMR (282 MHz, C_7D_8)

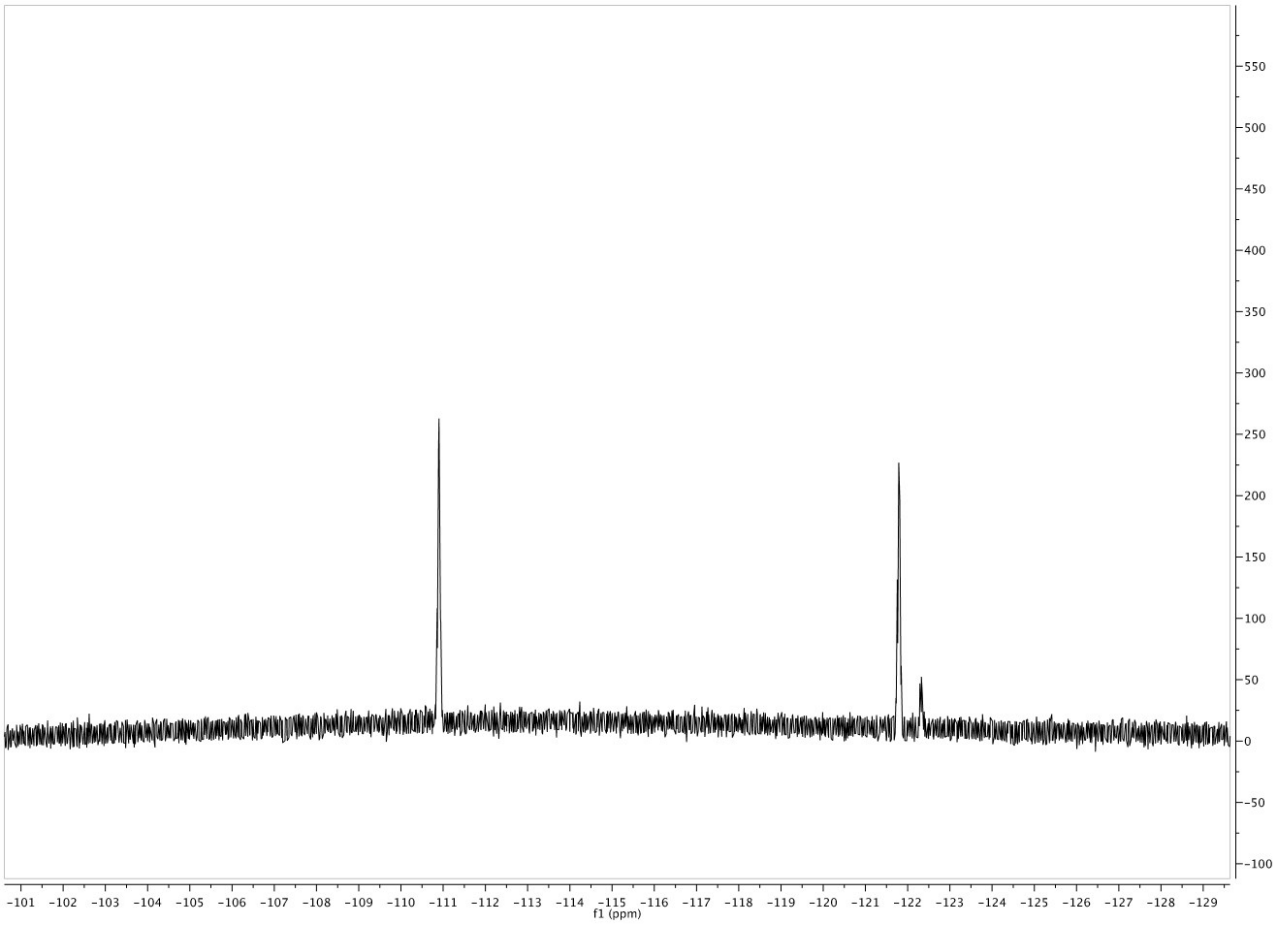


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 24 h, 120 °C

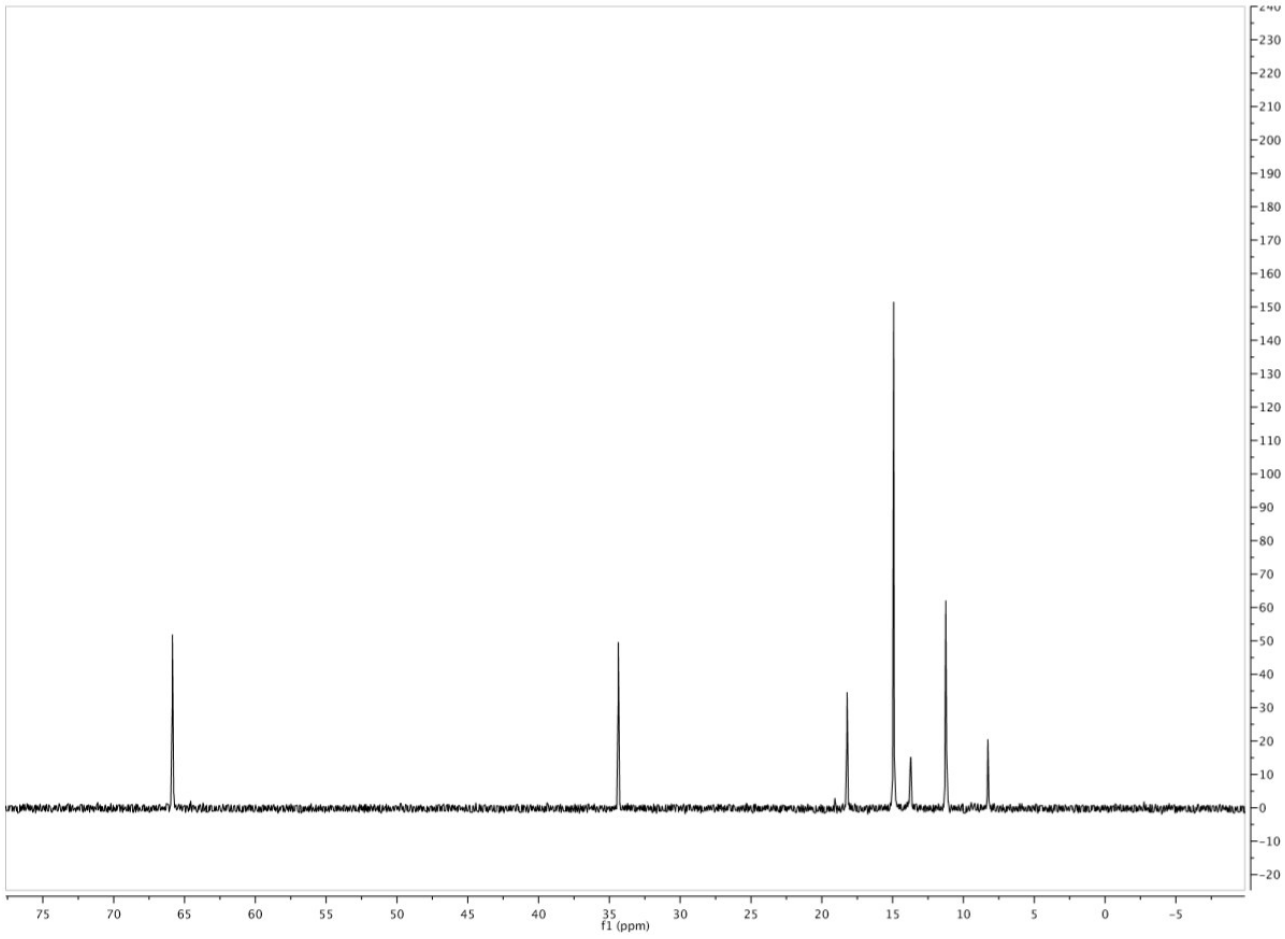


$^{19}F\{^{1}H\}$ NMR (282 MHz, C_7D_8)

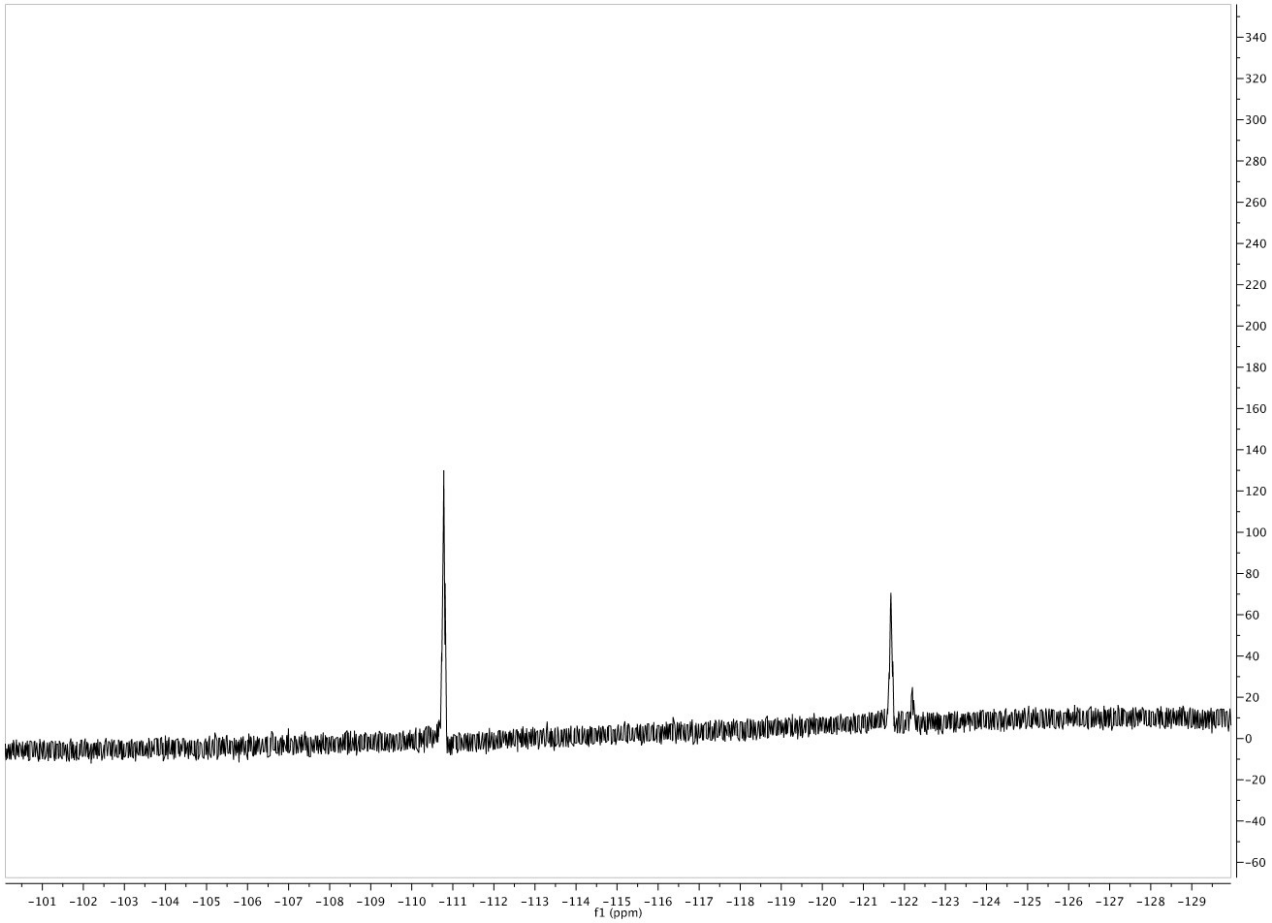


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 36 h, 120 °C

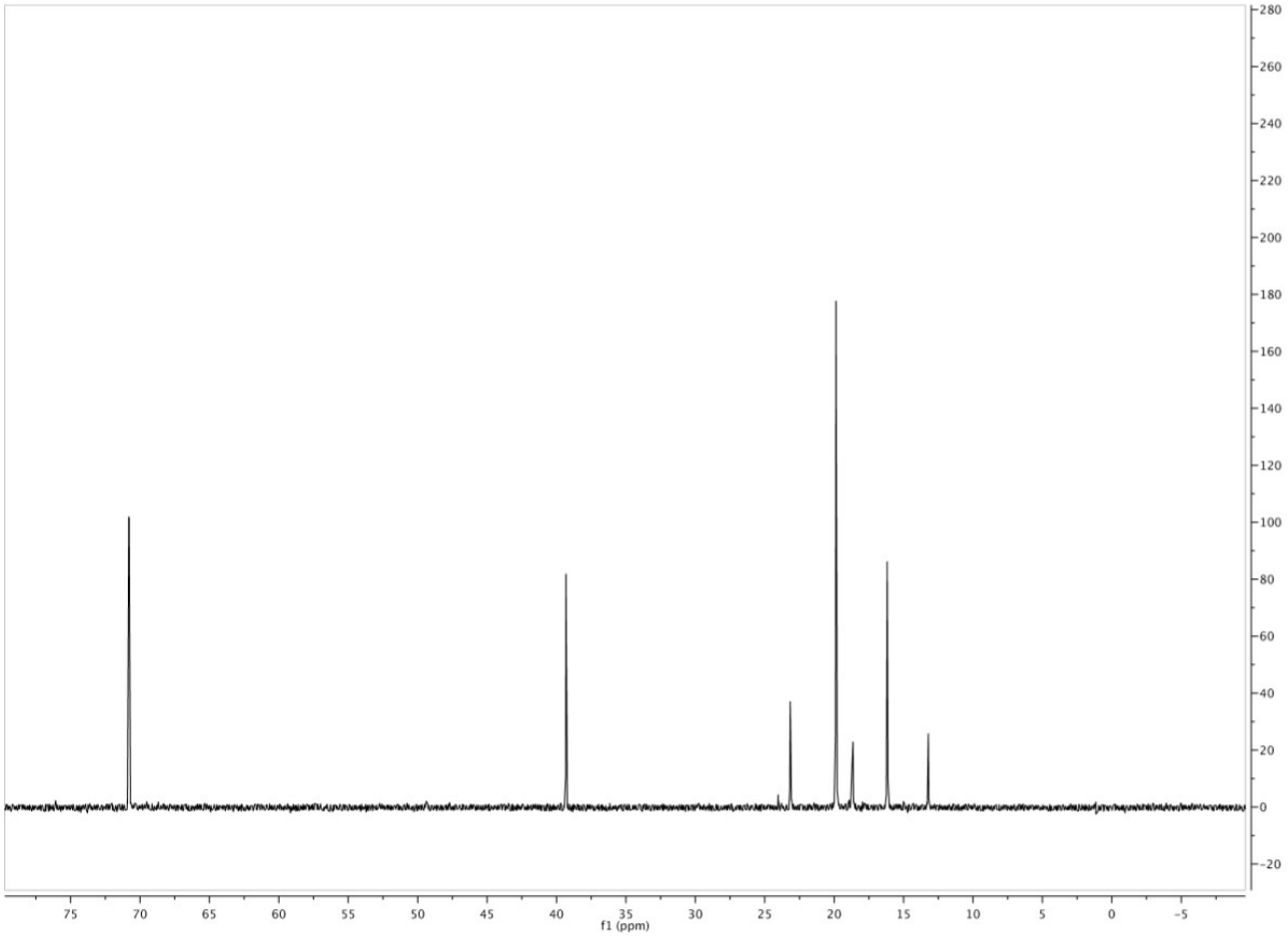


$^{19}F\{^{1}H\}$ NMR (282 MHz, C_7D_8)

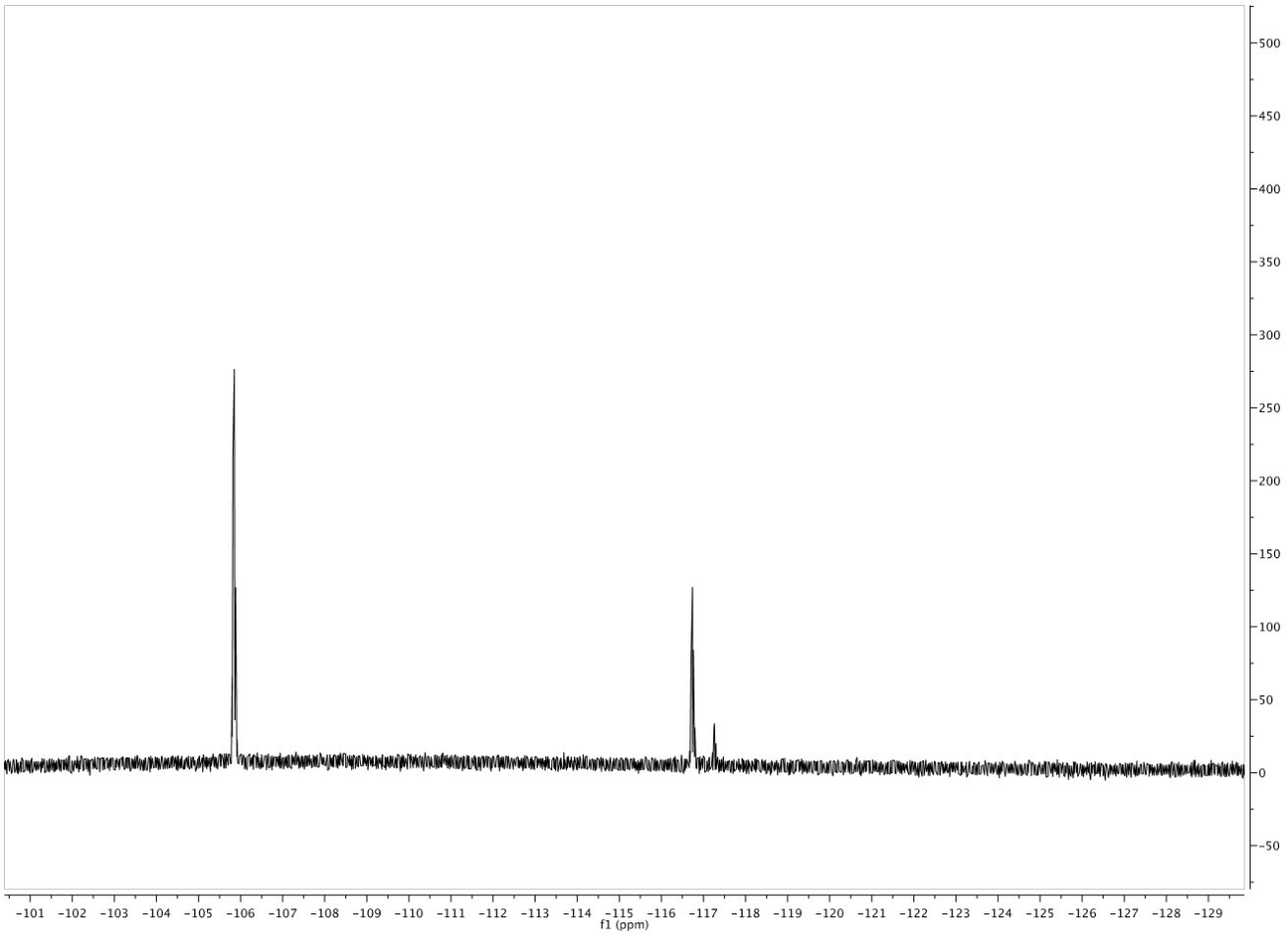


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 48 h, 120 °C

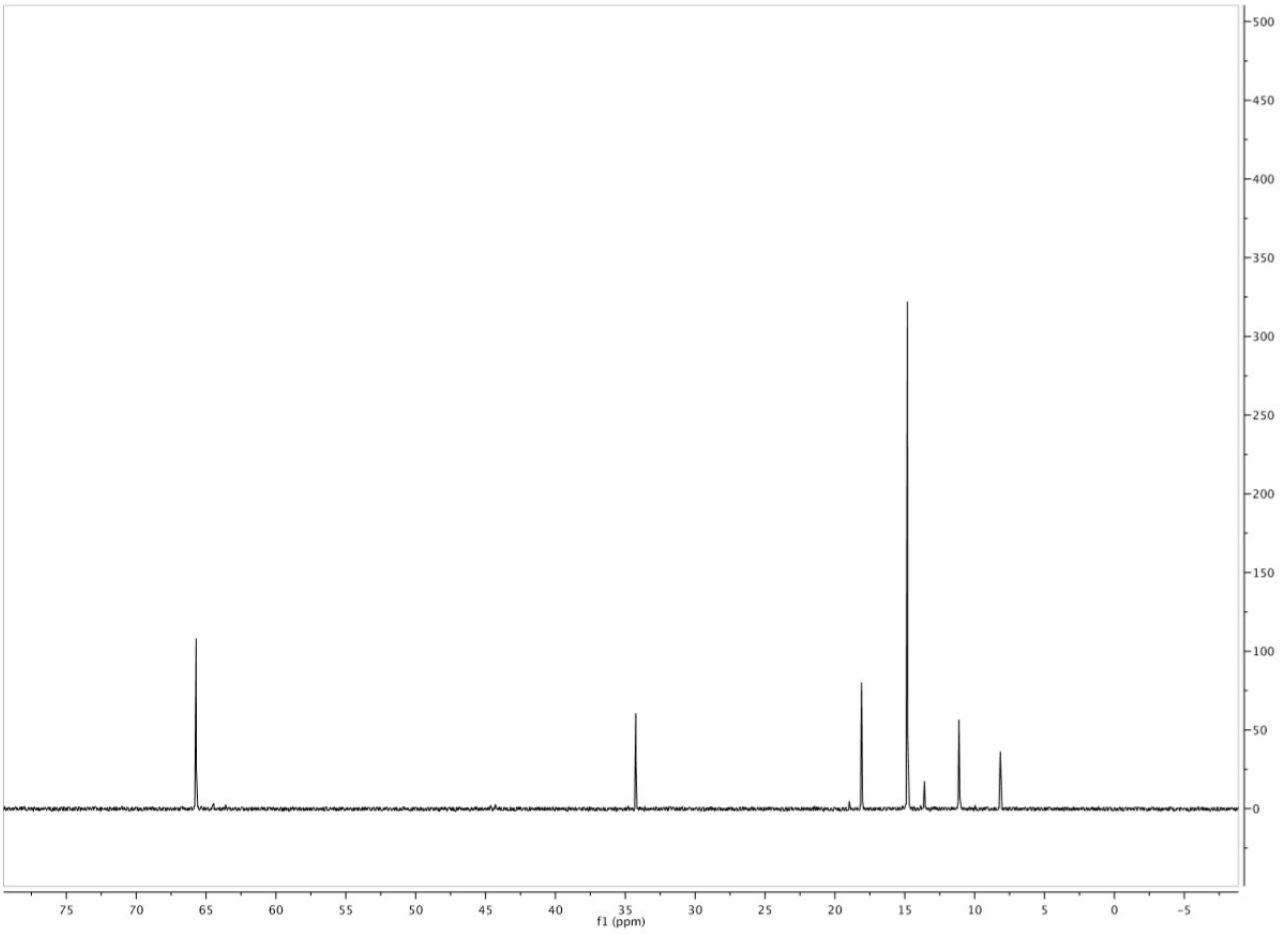


$^{19}F\{^{1}H\}$ NMR (282 MHz, C_7D_8)

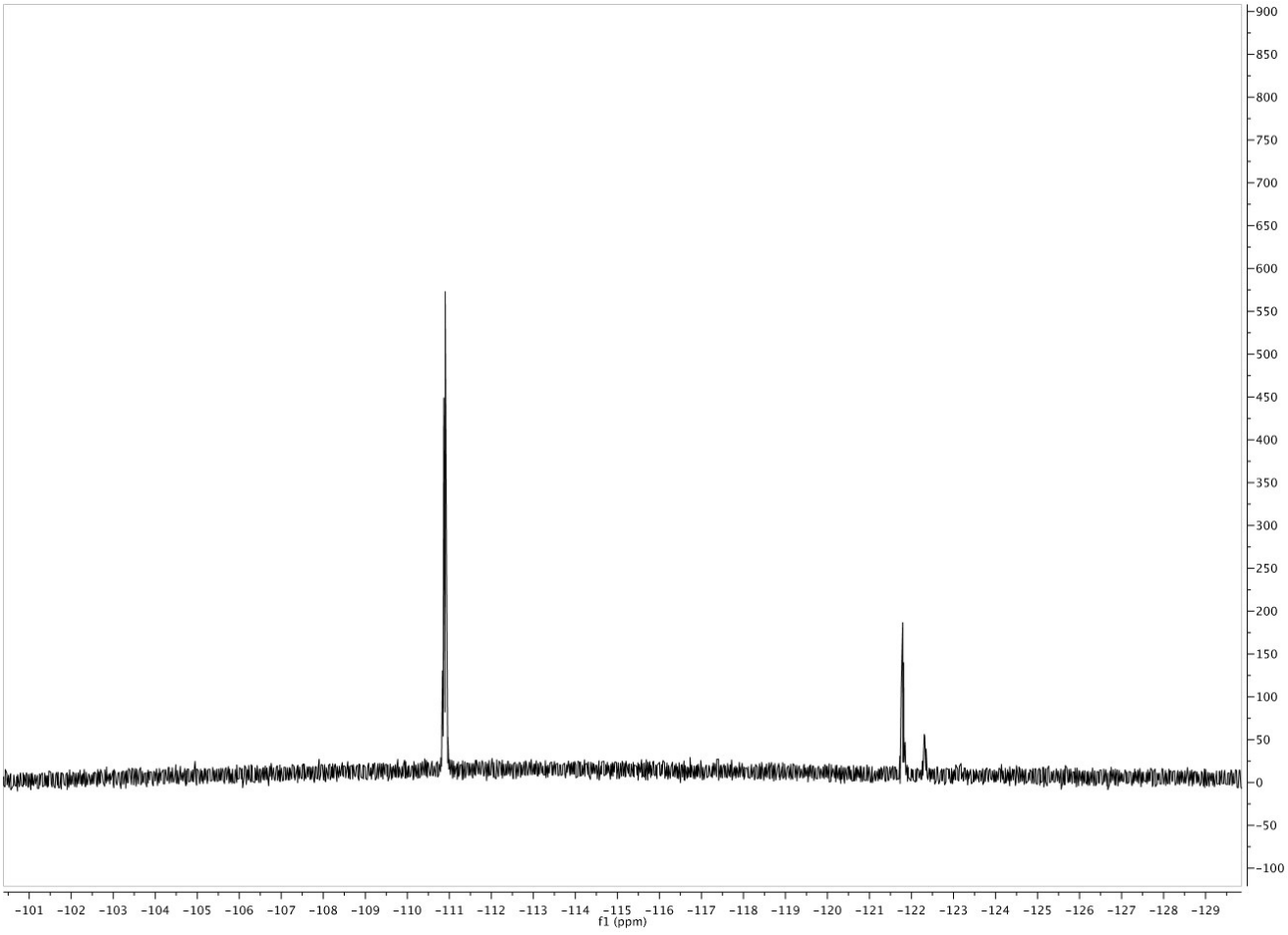


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 60 h, 120 °C

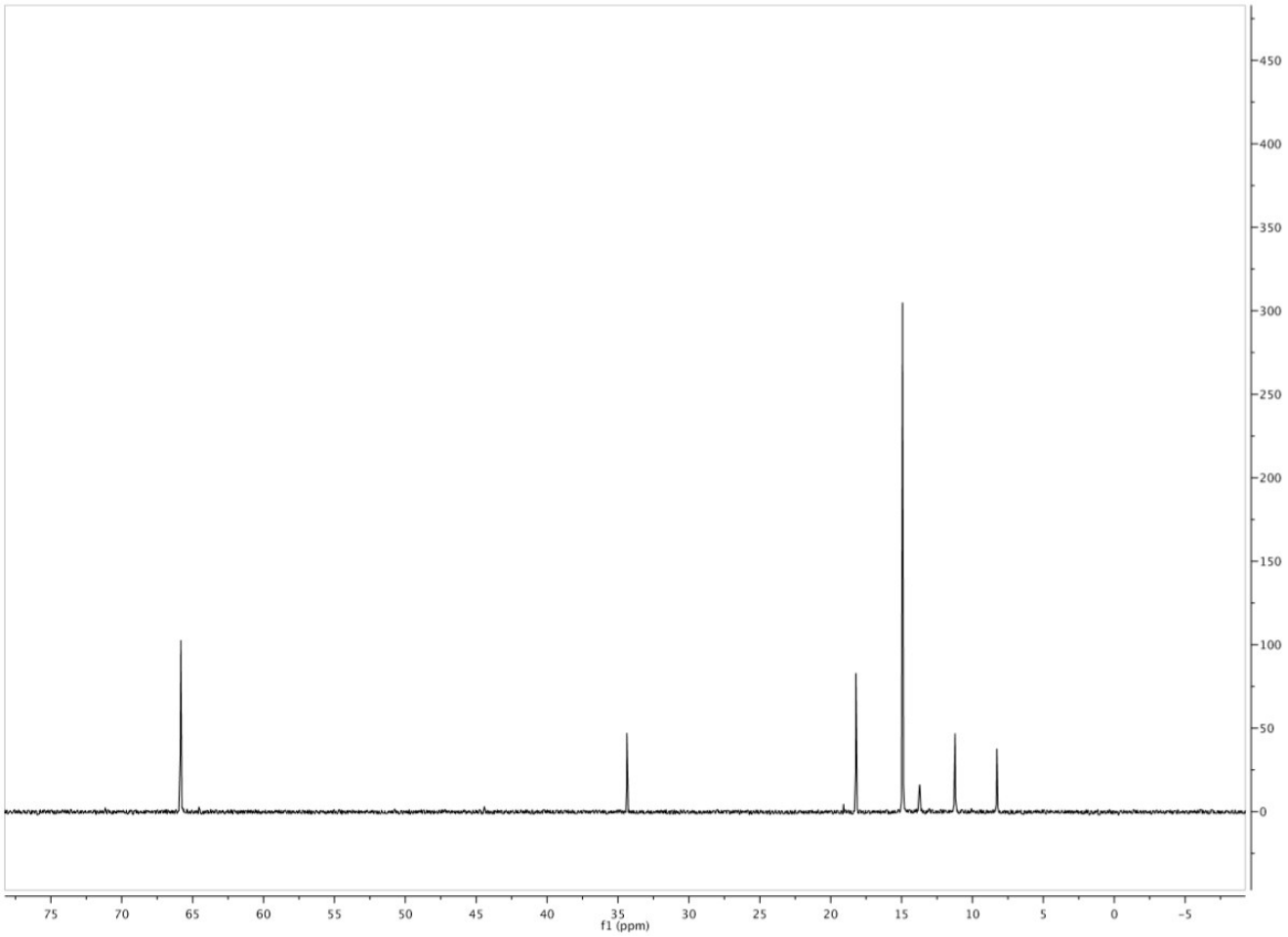


$^{19}F\{^{1}H\}$ NMR (282 MHz, C_7D_8)

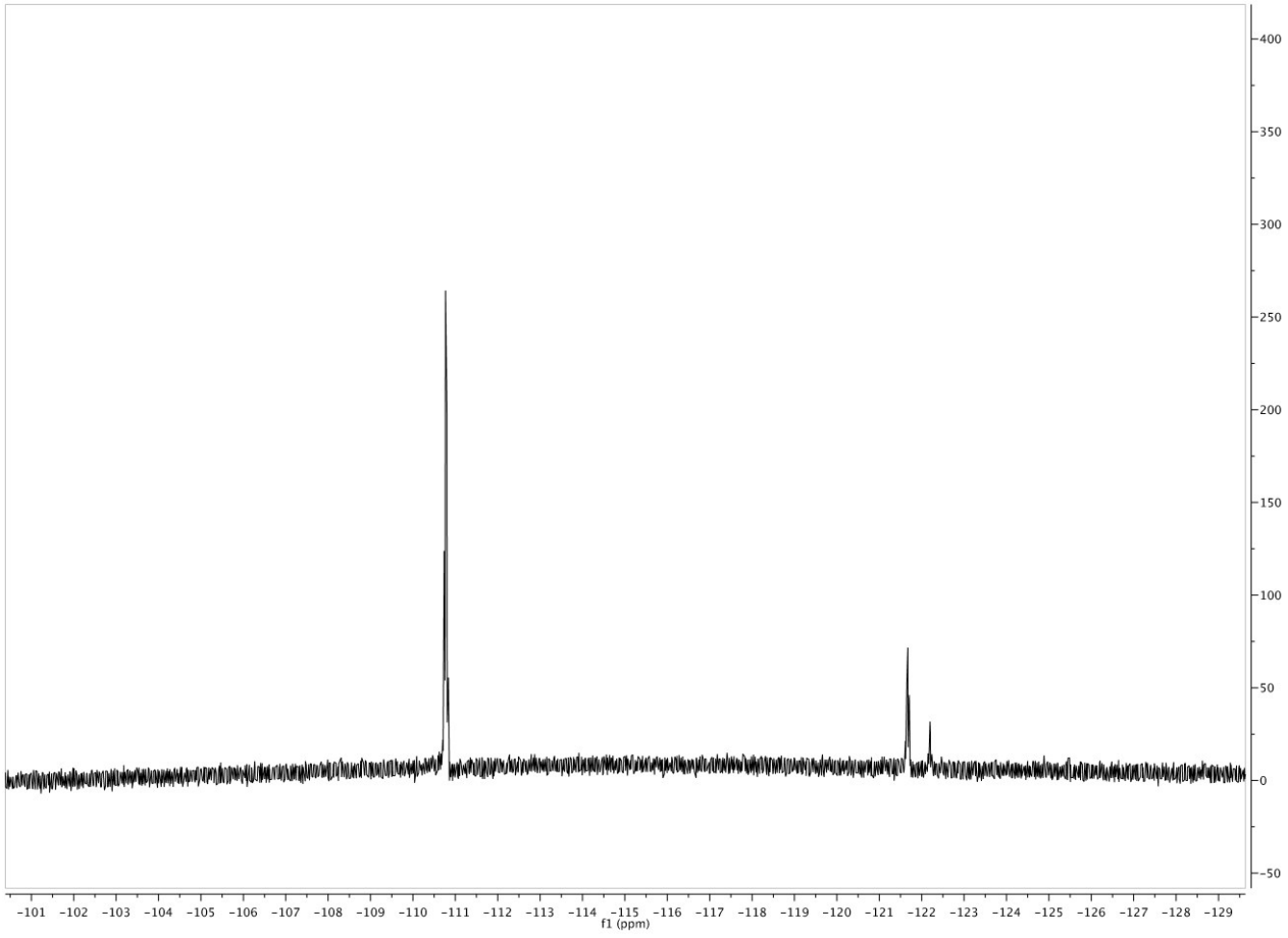


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 72 h, 120 °C

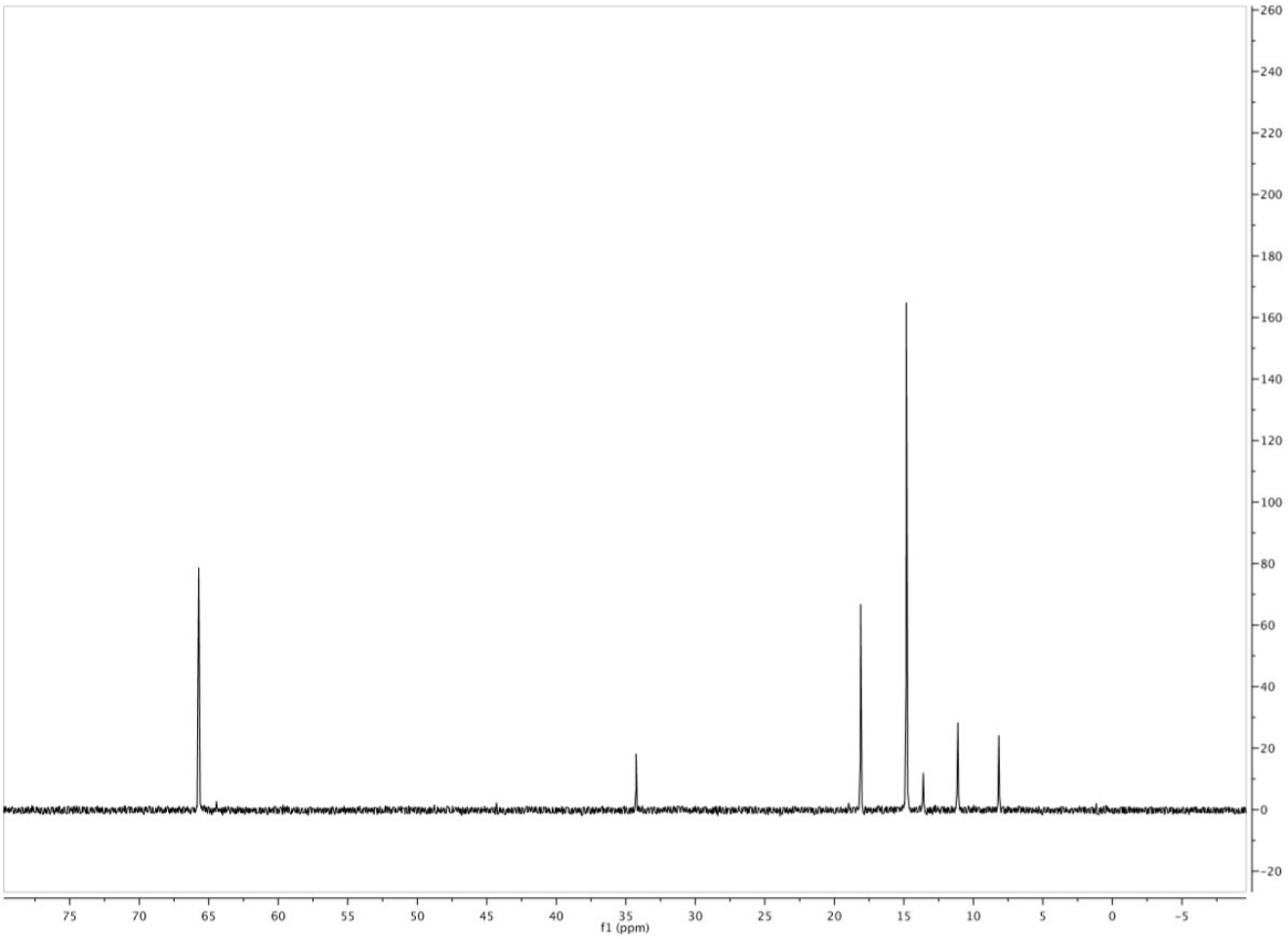


$^{19}F\{^{1}H\}$ NMR (282 MHz, C_7D_8)

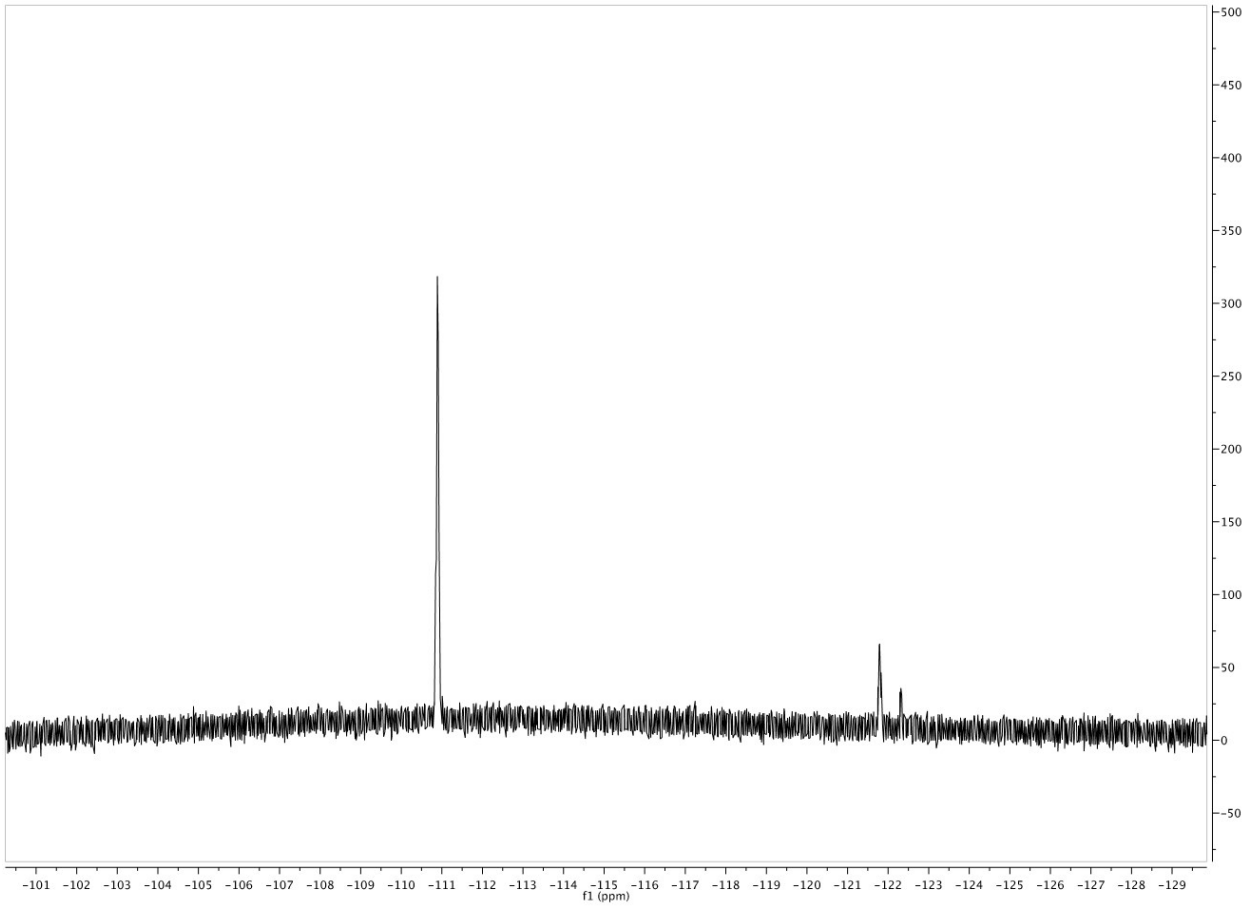


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 84 h, 120 °C

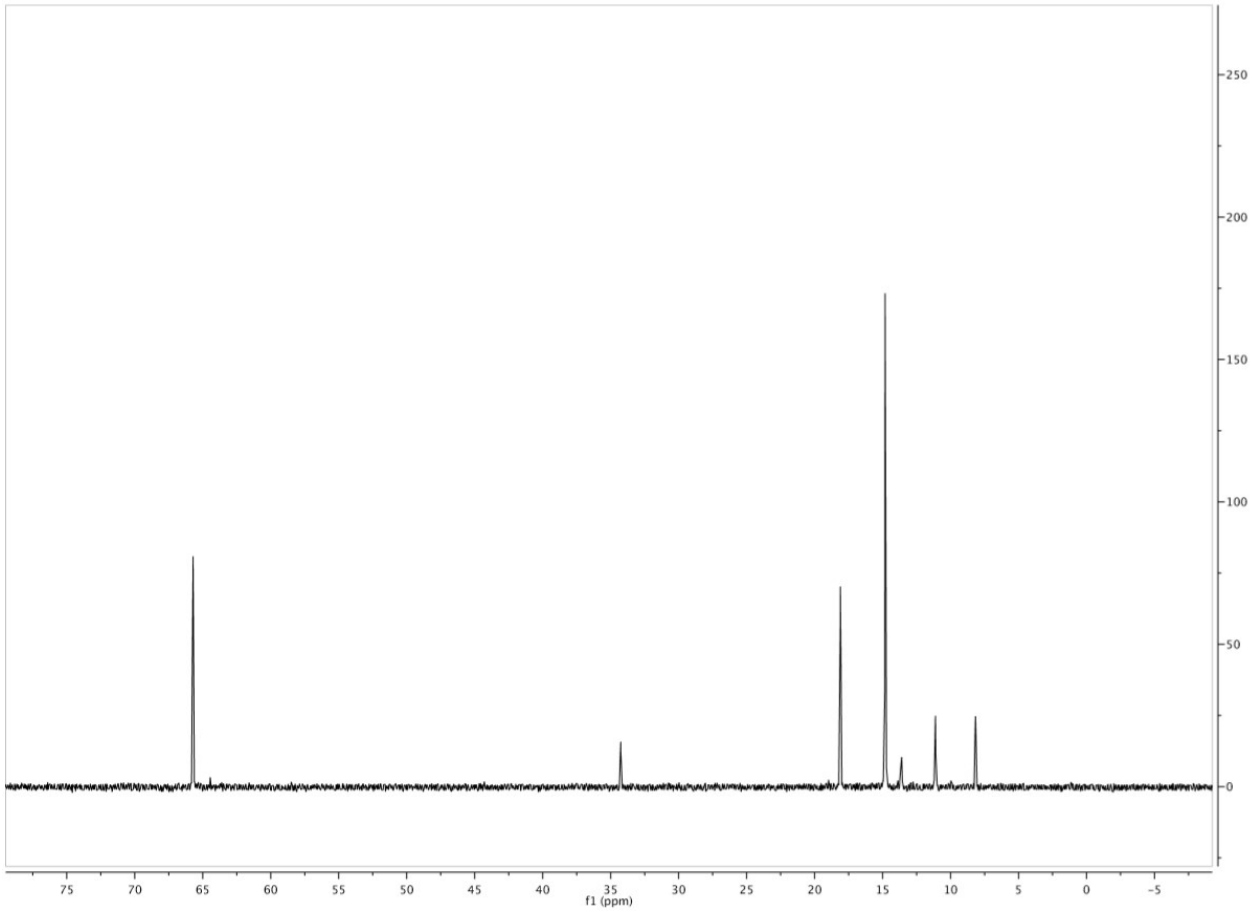


$^{19}F\{^{1}H\}$ NMR (282 MHz, C_7D_8)

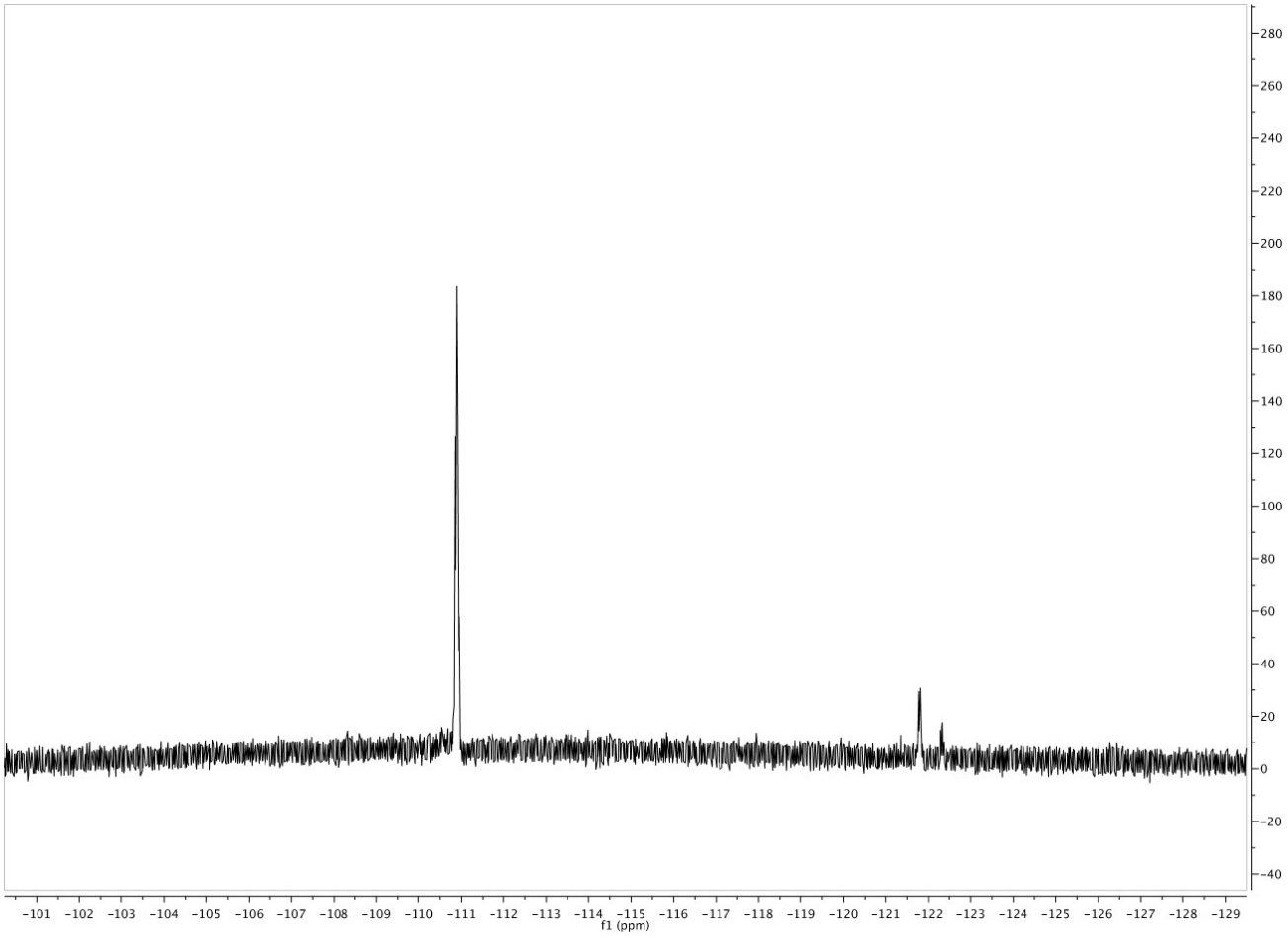


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 96 h, 120 °C

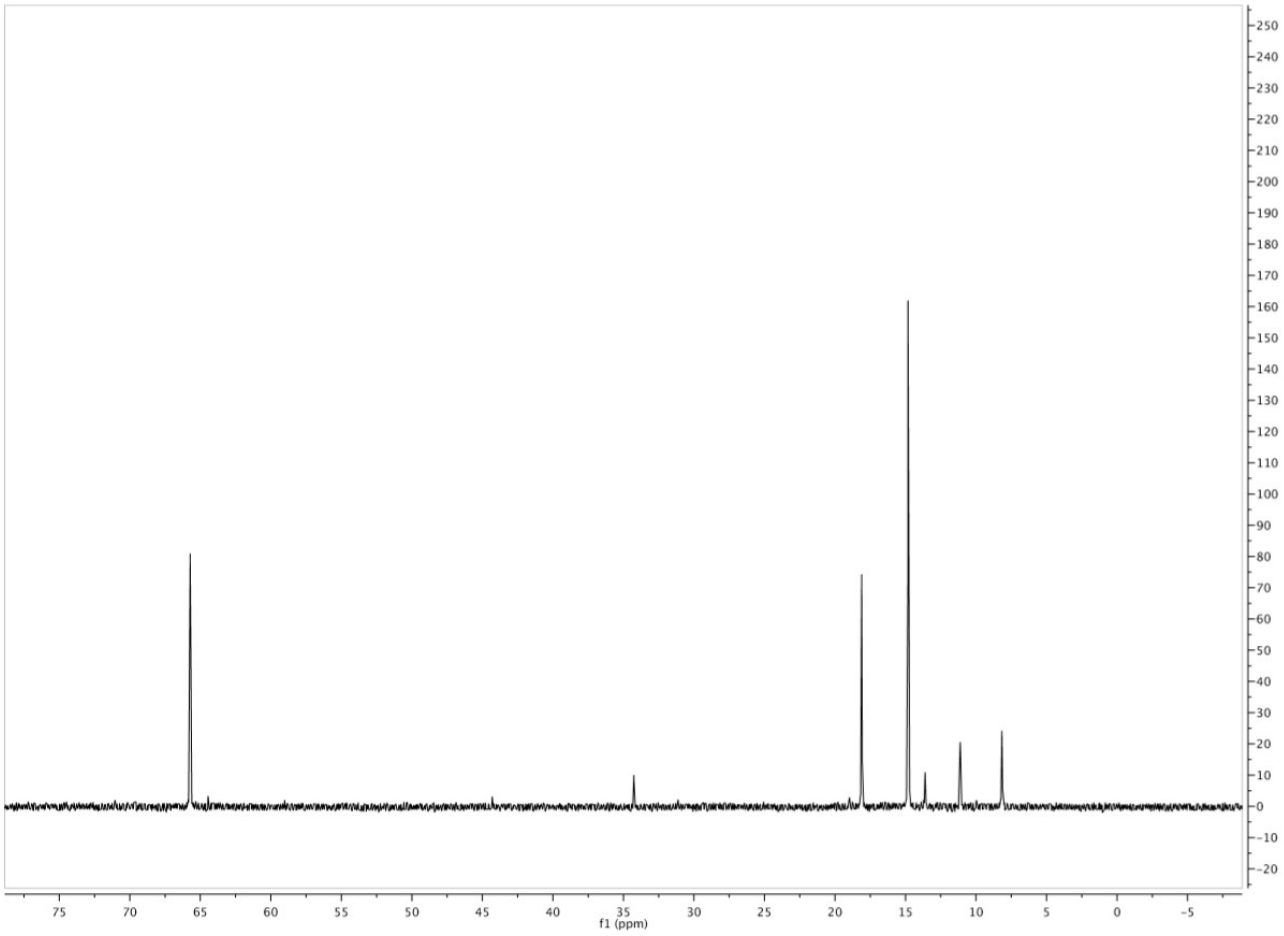


$^{19}F\{^{1}H\}$ NMR (282 MHz, C_7D_8)

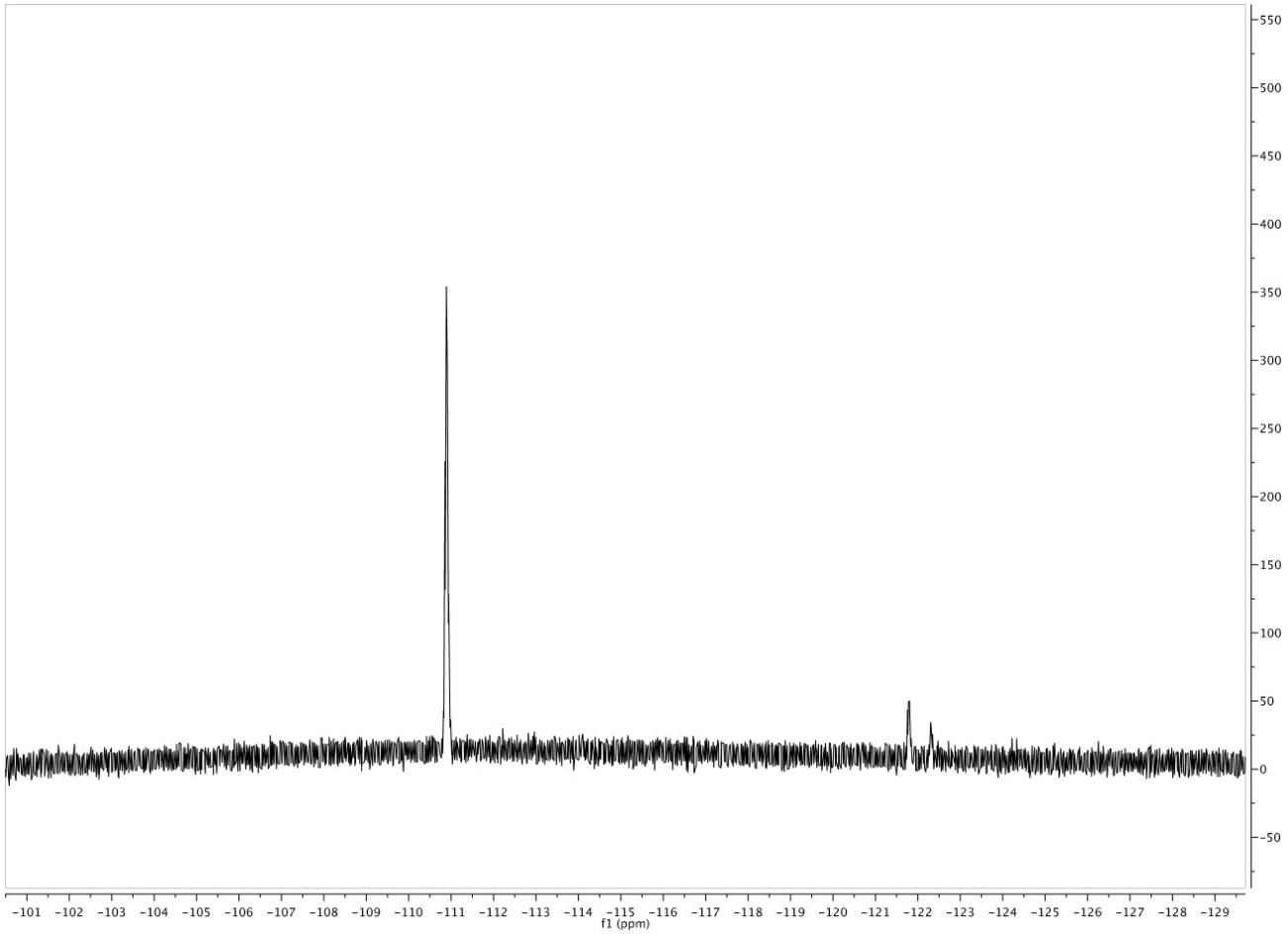


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 108 h, 120 °C

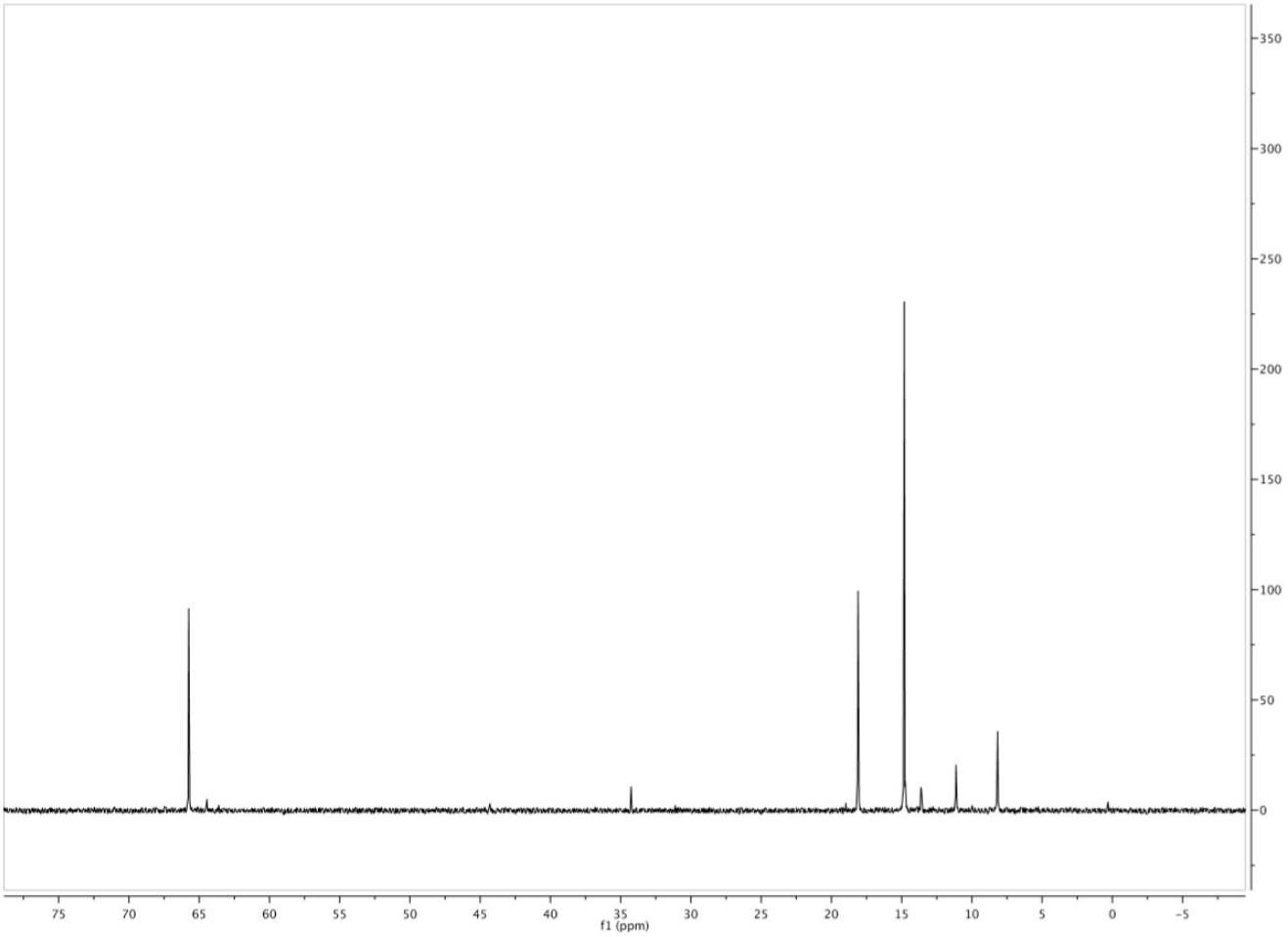


$^{19}F\{^{1}H\}$ NMR (282 MHz, C_7D_8)

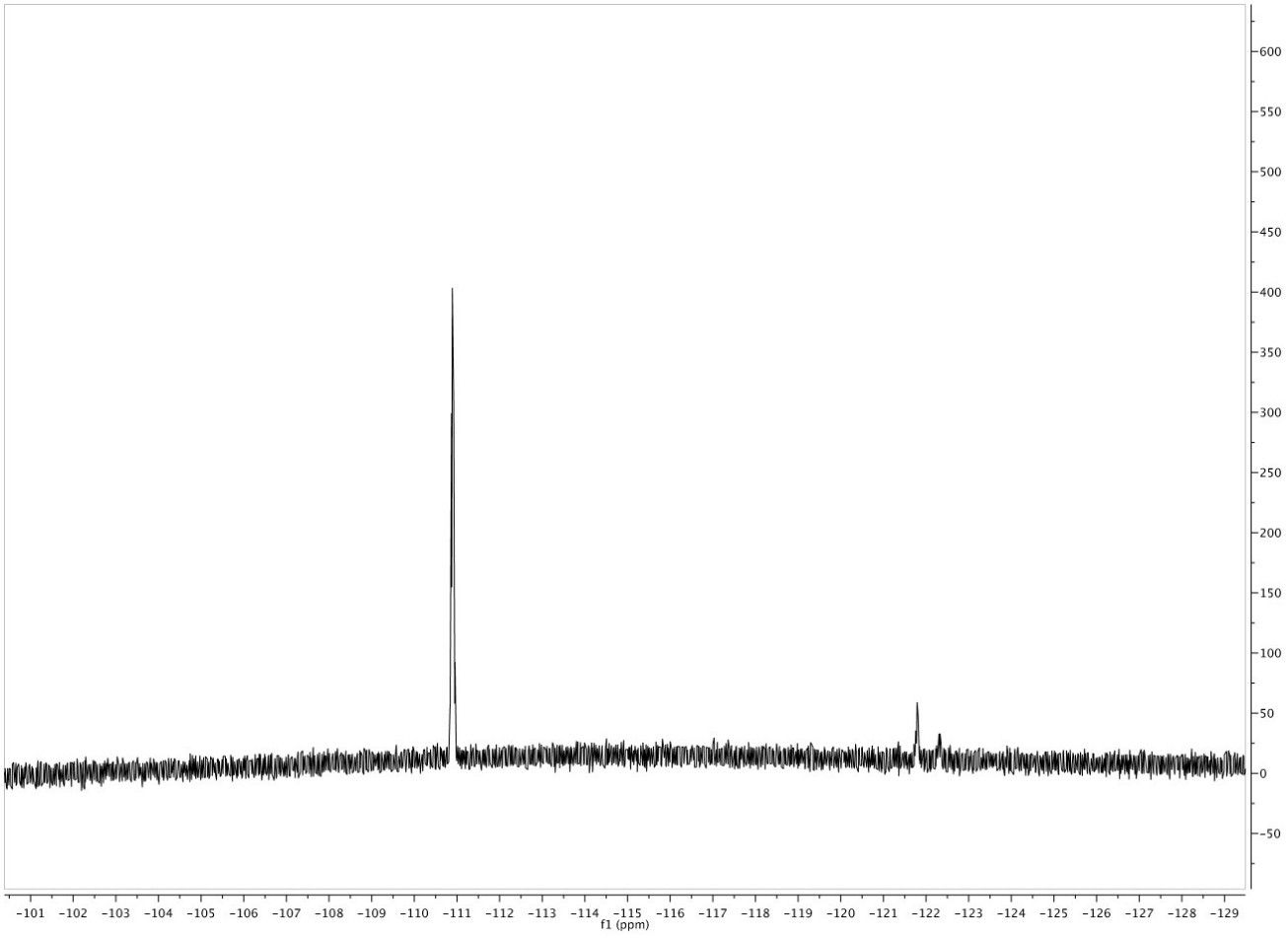


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

t = 120 h, 120 °C

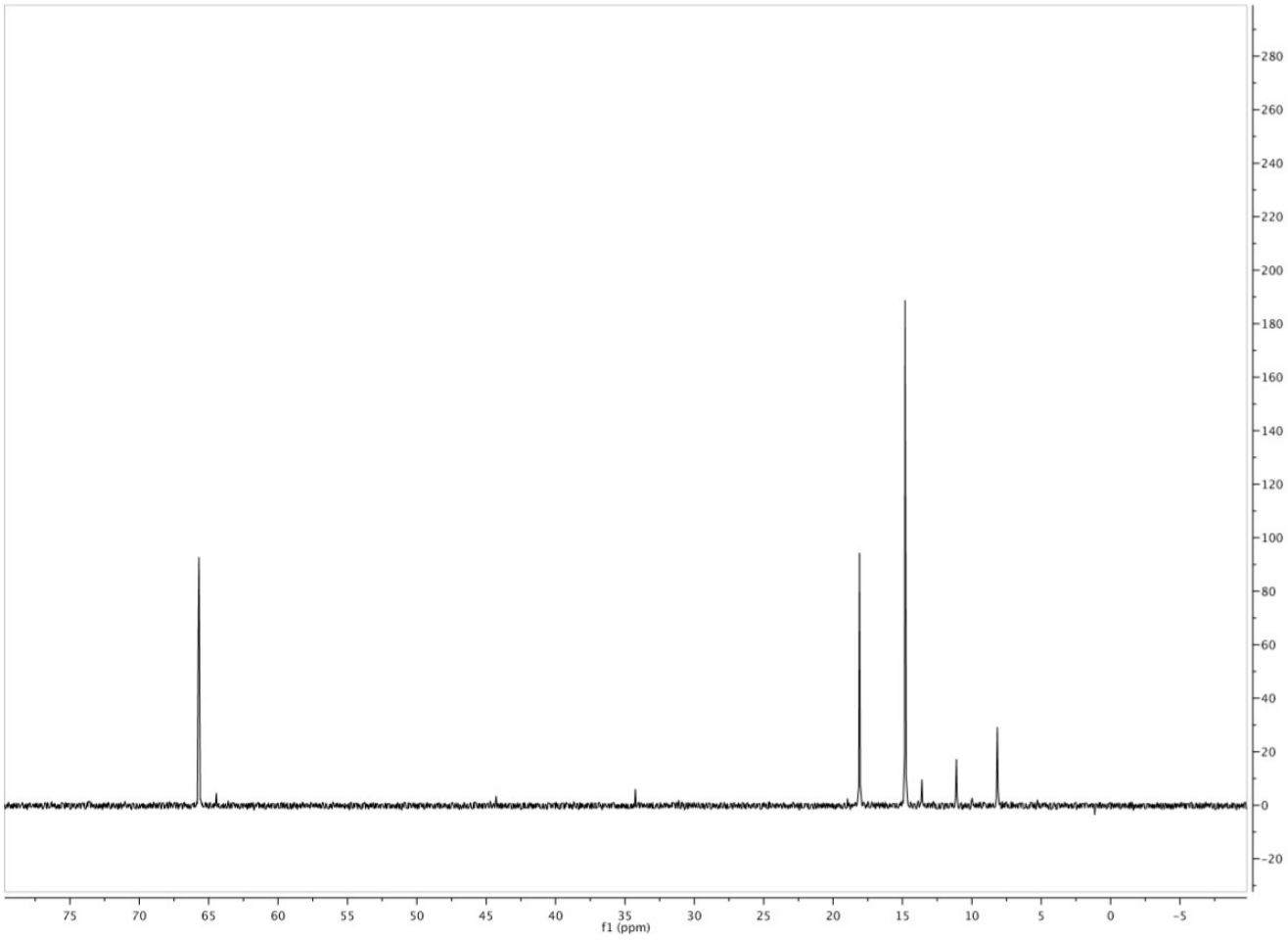


$^{19}F\{^{1}H\}$ NMR (282 MHz, C_7D_8)

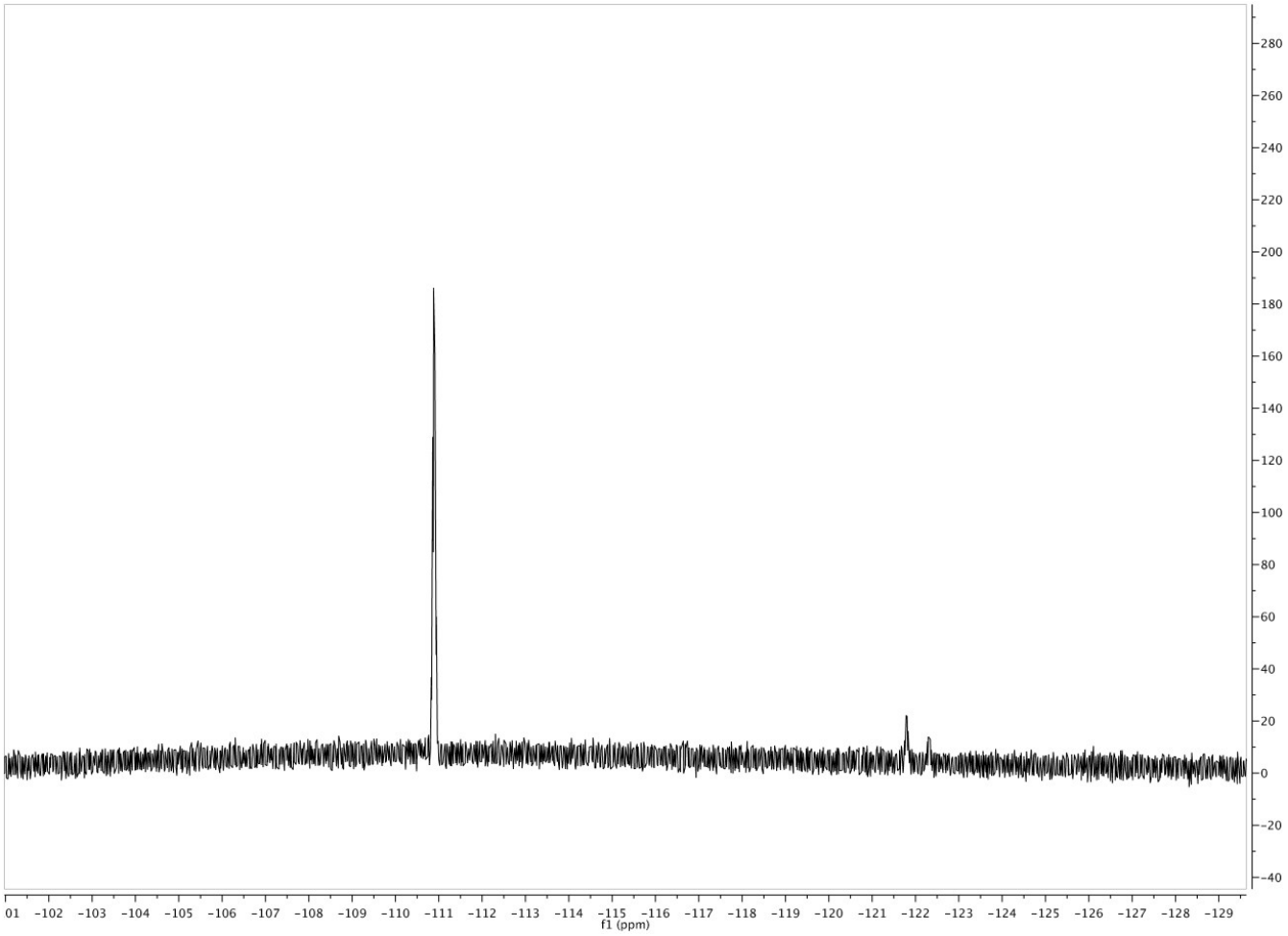


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8)

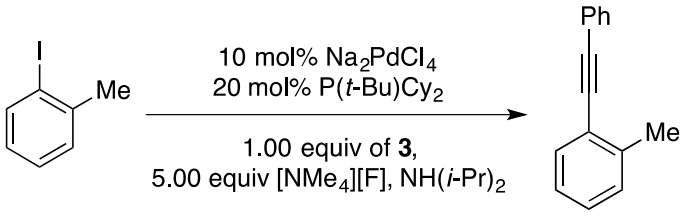
t = 132 h, 120 °C



$^{19}F\{^{1}H\}$ NMR (282 MHz, C_7D_8)



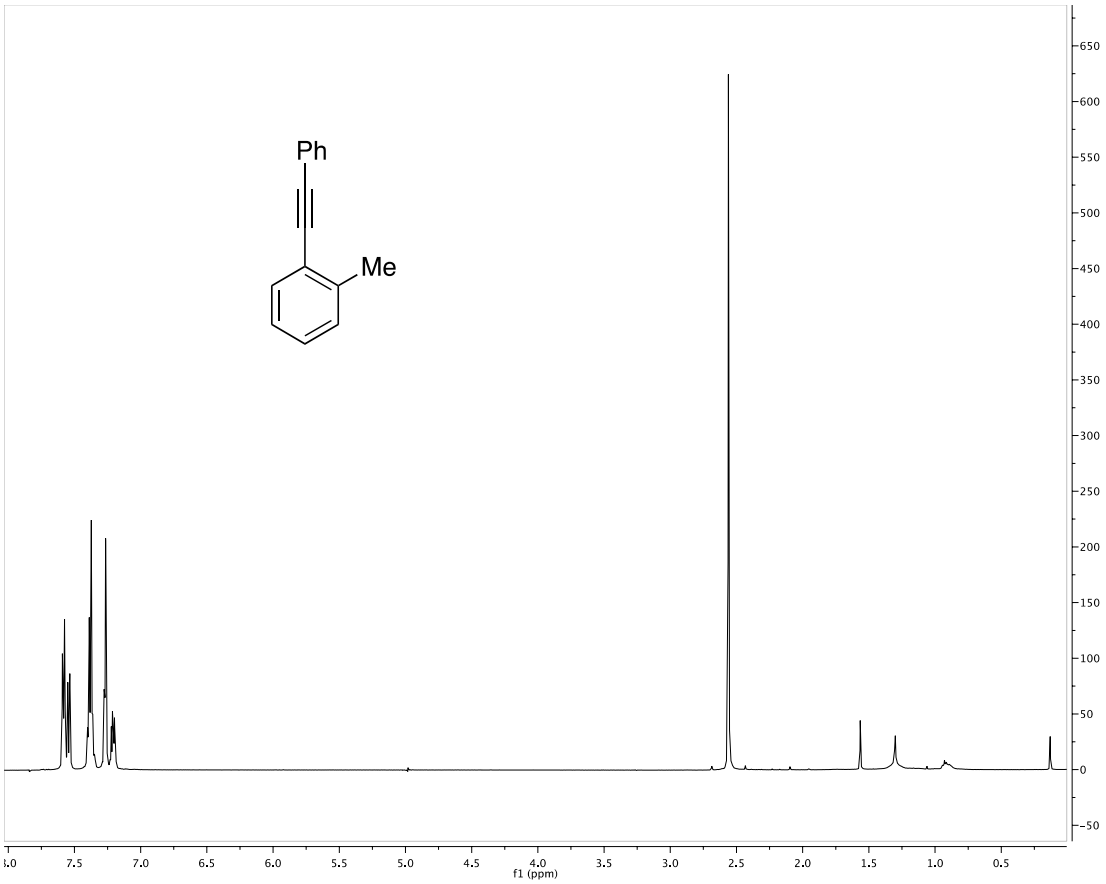
Catalytic Studies.



Na_2PdCl_4 (19 mg, 0.065 mmol, 10 mol%) and P(*t*-Bu)Cy_2 (32 mg, 0.126 mmol, 20 mol%) were loaded into a Schlenk bomb fitted with a screw-top Teflon cap and suspended in ~10 mL of NH(*i*-Pr)$_2$. The Schlenk bomb was sealed and brought outside of the glovebox, the Teflon cap was replaced with a rubber septum under positive N_2 pressure, and 1-iodo-2-methylbenzene was injected via syringe (80 μL, 0.628 mmol, 1 equiv). The rubber septum was removed under positive N_2 pressure, the Schlenk bomb was resealed, and the reaction mixture was placed in an oil bath at 80 °C for 20 min (for activation), affording a pale-yellow solution. The Schlenk bomb was brought back inside the glovebox and tetramethylammonium fluoride (TMAF) (293 mg, 3.15 mmol, 5 equiv) was added followed by [PN]–CCPh (**3**) (250 mg, 0.629 mmol, 1 equiv). The contents of the Schlenk bomb were brought back outside the glovebox and heated at 120 °C. Over the next 96 h, the reaction mixture grew increasingly orange, but its appearance was obscured by a large amount of grey precipitate. The reaction mixture was then concentrated under vacuum at 80 °C to remove the relatively high boiling amine solvent. The residual non-volatiles were extracted with 10 mL of pentane and filtered through a silica plug. The plug was washed with an additional 25 mL of pentane and the filtrate was concentrated under vacuum, affording a clear oil (33 mg, 0.172 mmol, 27%). The purity of Ph–C≡C–(*o*-Tol) was confirmed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (see below).

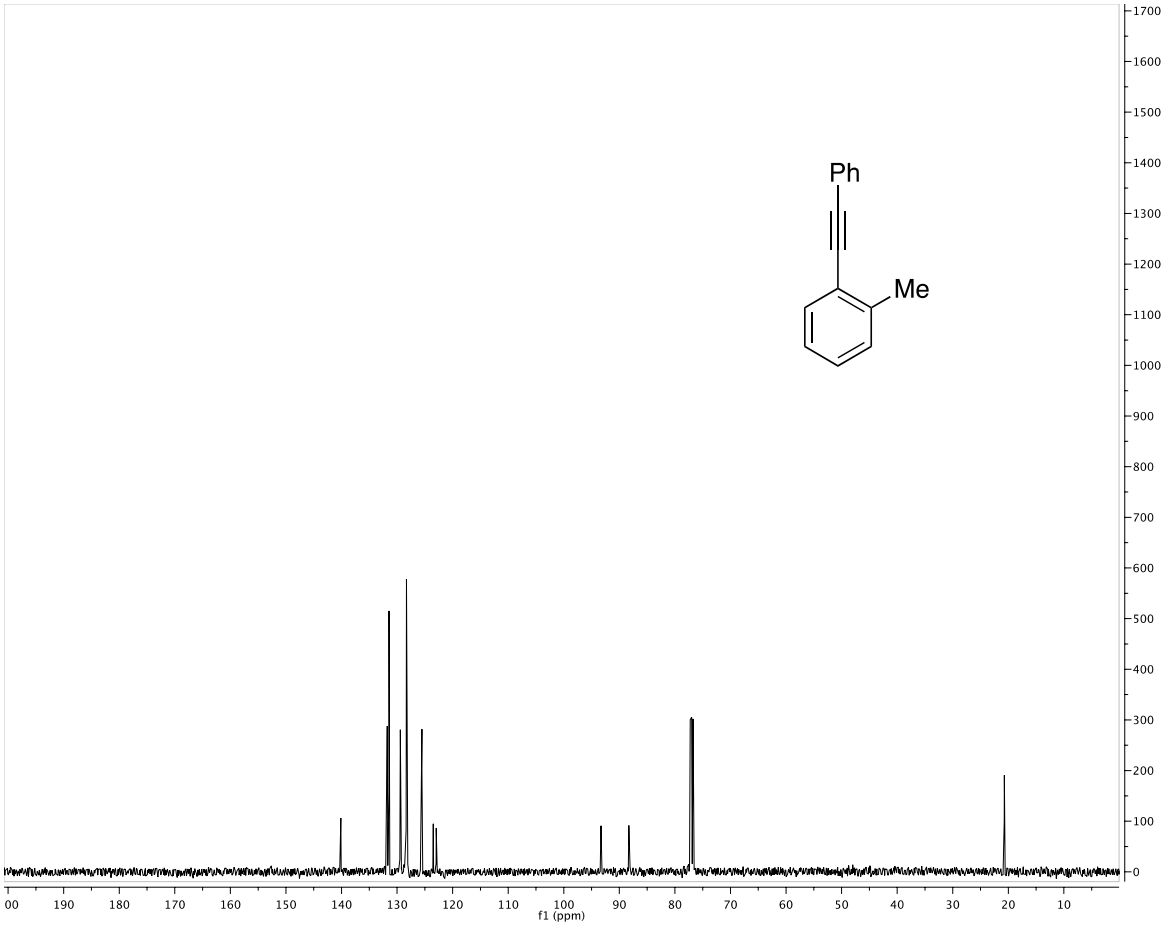
^{1}H NMR (500 MHz, $CDCl_3$)

($CDCl_3$ from benchtop containing water and residual grease)



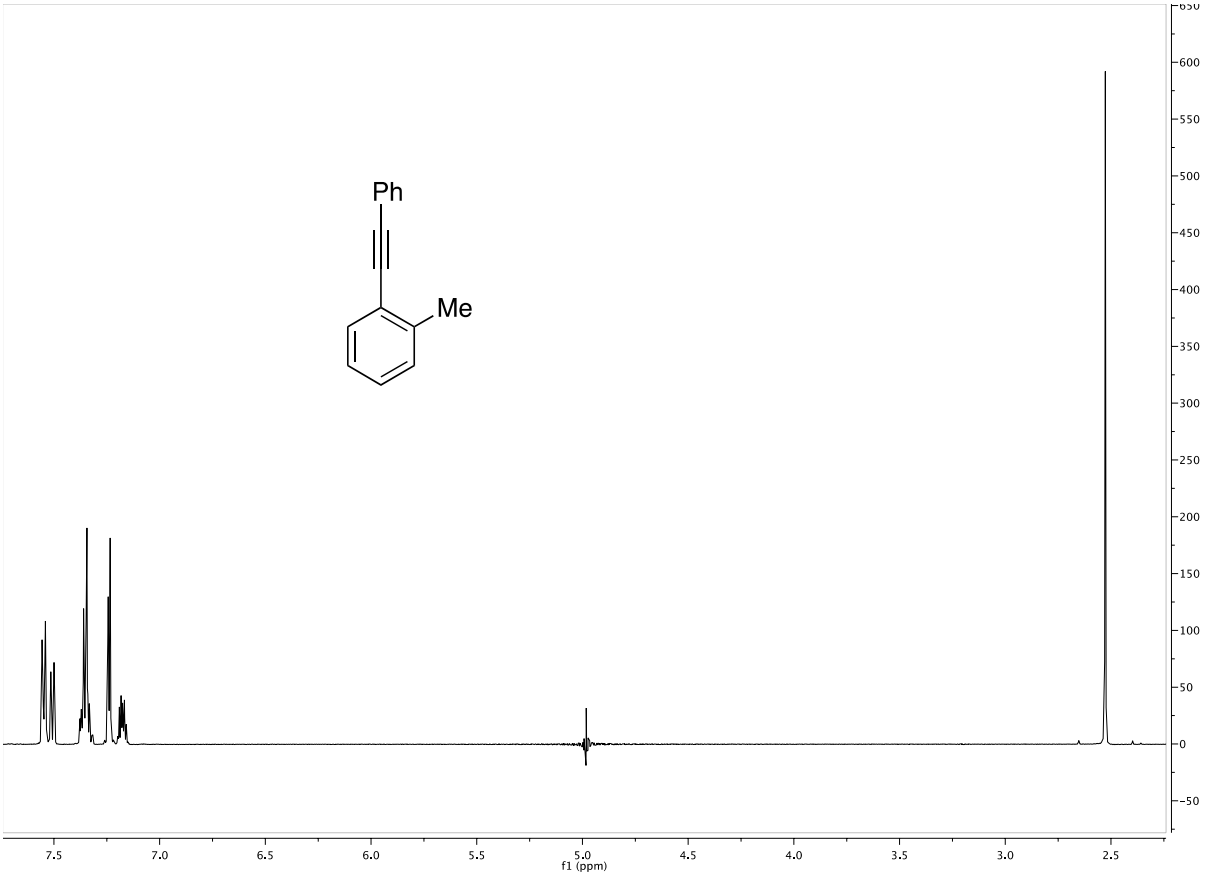
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

($CDCl_3$ from benchtop containing water and residual grease)

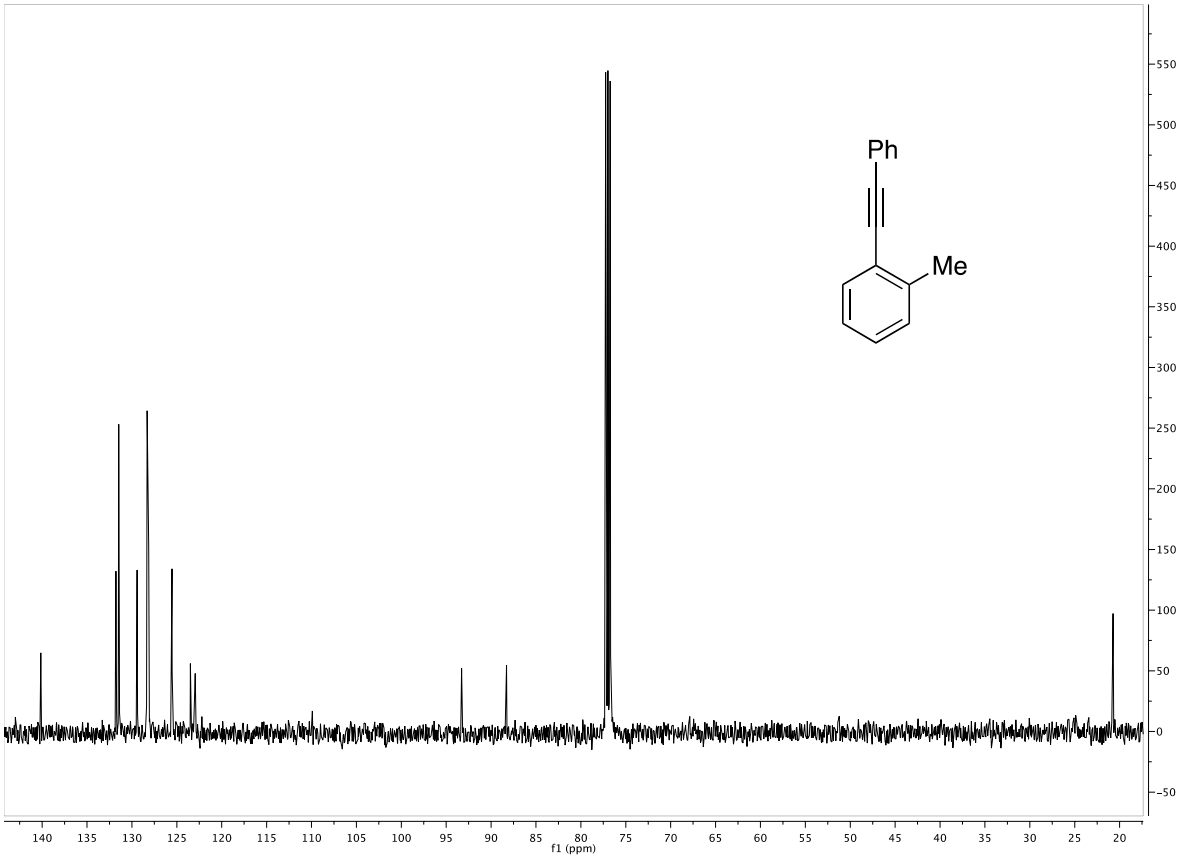


Pre-Revision Catalysis. In an earlier iteration, the catalysis was performed using CuI as the additive (instead of CsF or TMAF). After comments by the reviewers and subsequent experiments, the effect of / advantages associated with CuI became unclear. Under these conditions and using a workup similar to what is described above, the desired product (Ph–C≡C–(*o*-Tol)) was contaminated with diyne (Ph–C≡C–C≡C–Ph). Separation of these two components required reverse-phase HPLC using a Phenomenex Gemini C18 preparative column (250 x 21.2 mm, 5 μm; PDA detection, flowrate: 12 mL/min) with 75% (acetonitrile/water with 0.1% formic acid) isocratic condition, yielding pure fractions of the targeted product and diyne. The clean fractions are shown below.

^{1}H NMR (500 MHz, $CDCl_3$)

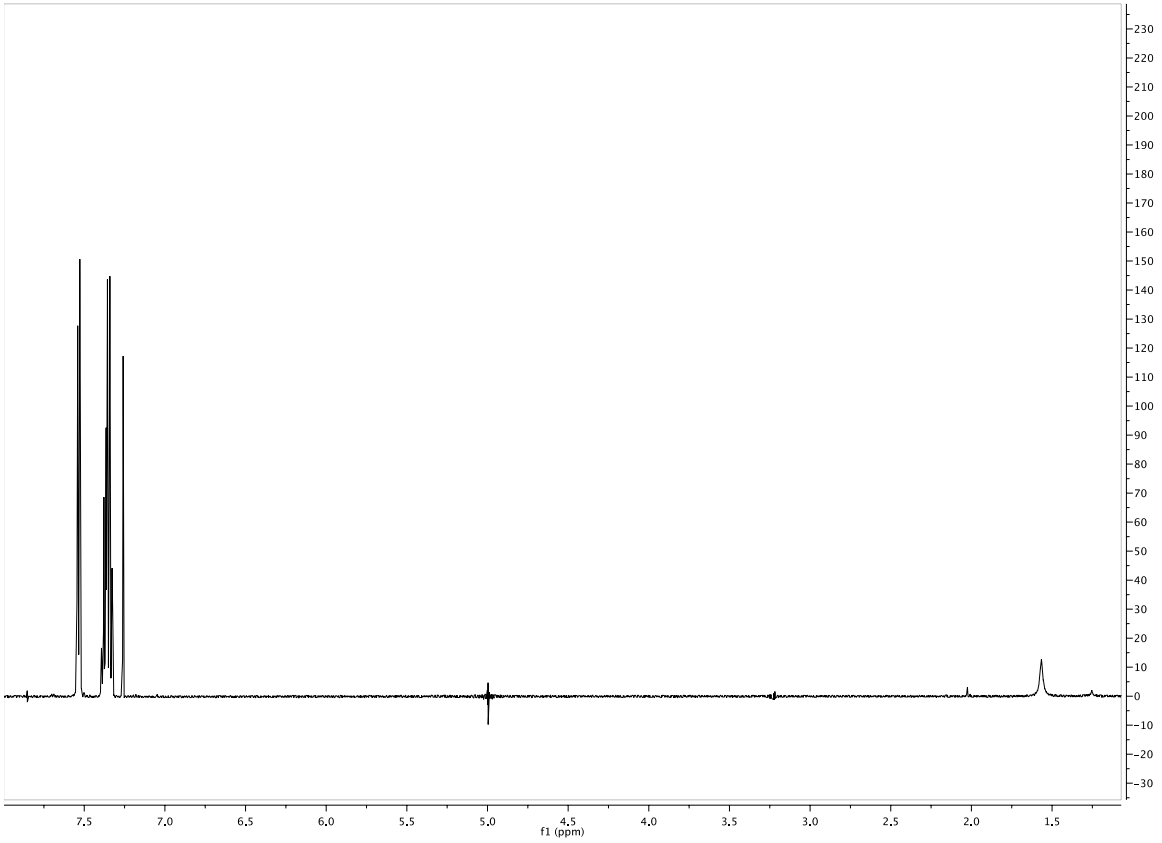


$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



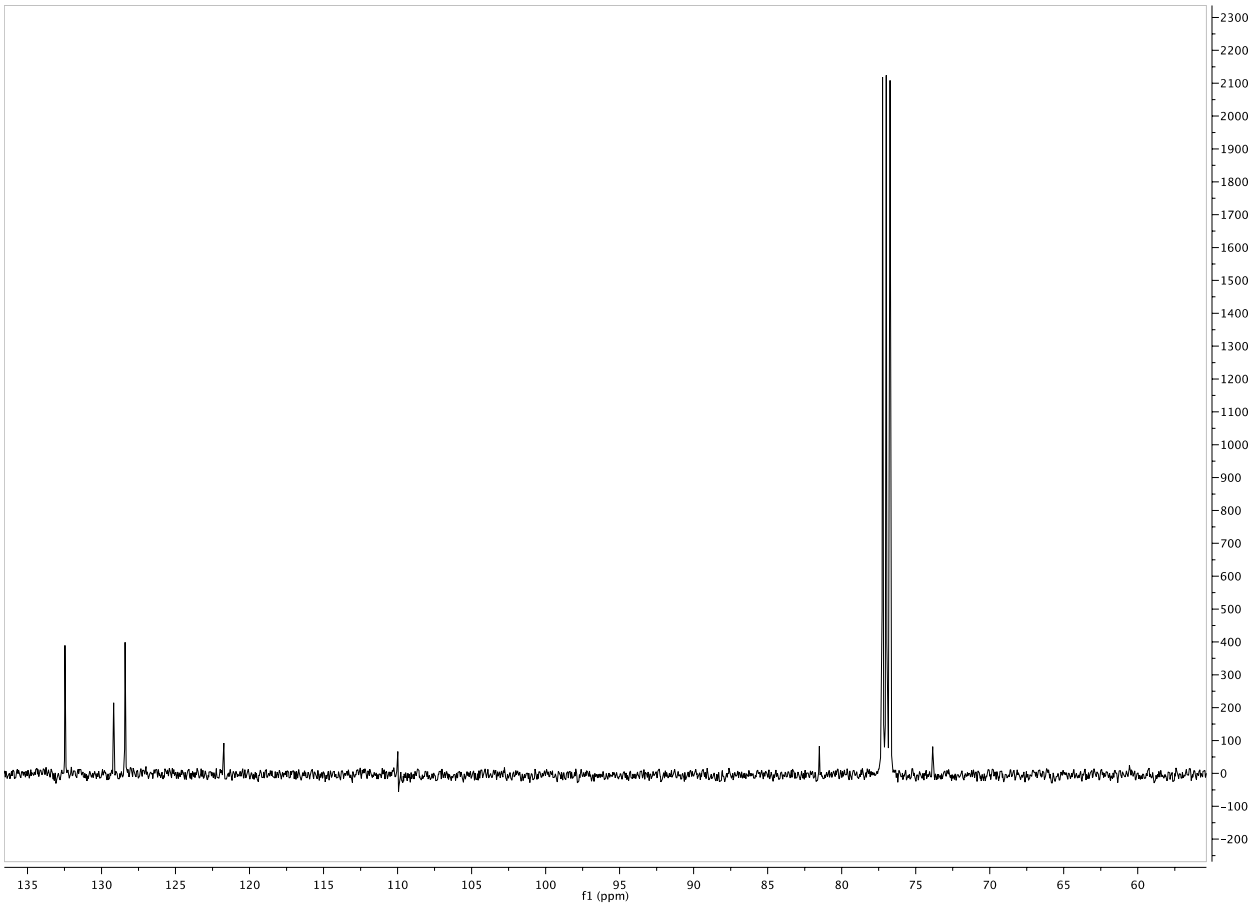
^{1}H NMR (500 MHz, $CDCl_3$)

Diyne Byproduct (Ph–C≡C–C≡C–Ph)

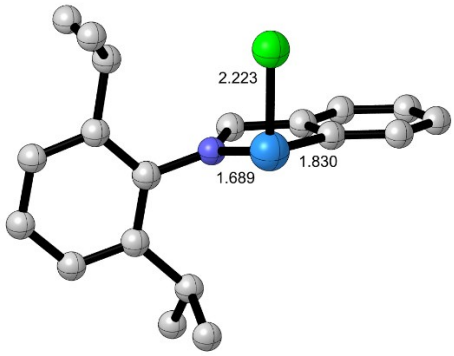
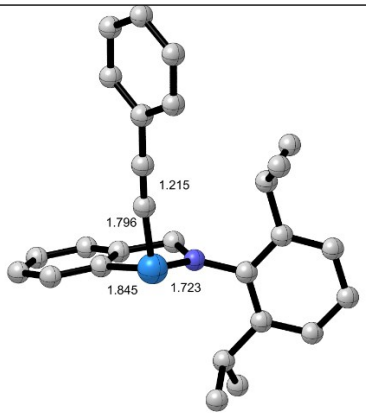
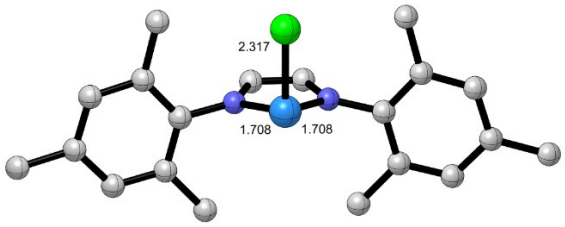
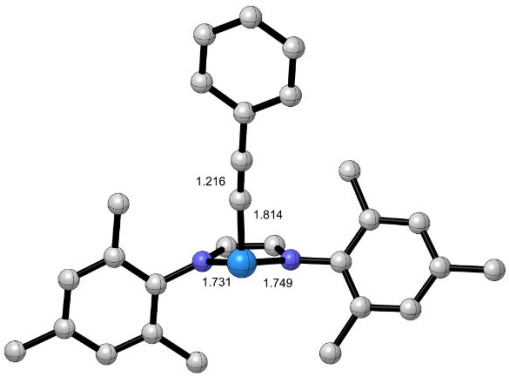


$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

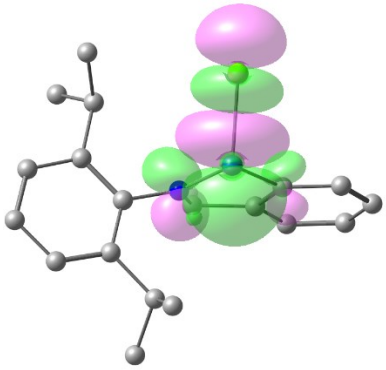
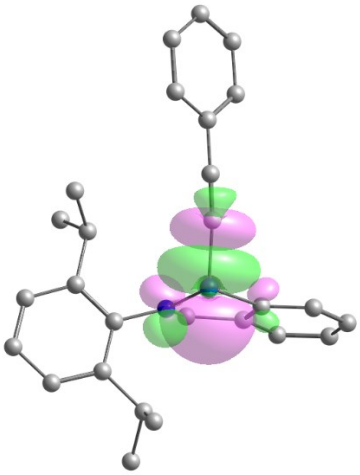
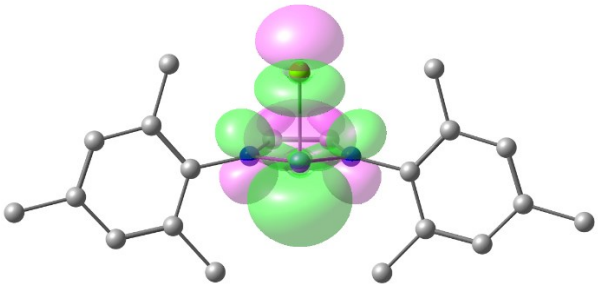
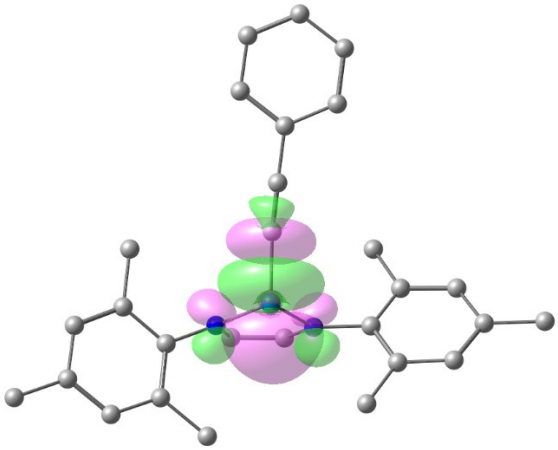
Diyne Byproduct (Ph–C≡C–C≡C–Ph)



3. DFT AND NBO RESULTS FOR AZAPHOSPHOLANES: Calculated Structures (B3LYP-D3/LACV3P)**

CAIN71	CAIN79
 NBO charges P +1.06 Cl -0.41 P-Cl is 45% ionic WBI 0.735	 NBO charges P +1.03 C -0.36 P-C is 31% ionic WBI 0.937
DIAZAPHOSPHOLANE-CHLORO	**DIAZAPHOSPHOLANE-ALKYNYL**
 NBO charges P +1.21 Cl -0.50 P-Cl is 50% ionic WBI 0.613	 NBO charges P +1.20 C -0.38 P-C is 31% ionic WBI 0.906

The P-Cl and P-CC bonds are shorter in each of your compounds due to lower occupancy of the P-Cl or P-C σ* orbital, as shown in the NLMOs below. This occupancy, which makes for a longer bond, comes from (mostly) delocalization of the adjacent N-lone pair(s) i.e. hyperconjugation. The stabilization in each case is quantified in kcal/mol below.

CAIN71	CAIN79
 P-Cl σ* occupancy 0.180e Delocalization energy of N_{lp} 21.8 kcal/mol	 P-C σ* occupancy 0.067e Delocalization energy of N_{lp} 8.1 kcal/mol
DIAZAPHOSPHOLANE-CHLORO	DIAZAPHOSPHOLANE-ALKYNYL
 P-Cl σ* occupancy 0.335e Delocalization energy of $2N_{lp}$ 43.4 kcal/mol	 P-C σ* occupancy 0.098e Delocalization energy of $2N_{lp}$ 14.5 kcal/mol

4. Electrochemistry Experimental Details including all Cyclic Voltammetry Plots

General Experimental Details:

All electrochemical measurements on **4** were conducted on a CHI 600E Electrochemical Analyzer with a three-electrode system. A glassy carbon working electrode, a silver wire as the quasi-reference electrode, and a platinum wire as the counter electrode were employed. All cyclic voltammograms were investigated under anhydrous conditions inside a nitrogen-filled glove box. All scans were performed in tetrahydrofuran (THF) with 0.1 M tetrabutylammonium tetrafluorophosphate $[Bu_4N][PF_6]$ as the supporting electrolyte. Ferrocene was used as an internal standard.

CV plots at varying scan rate are shown below. Also, an overlay plot is included.

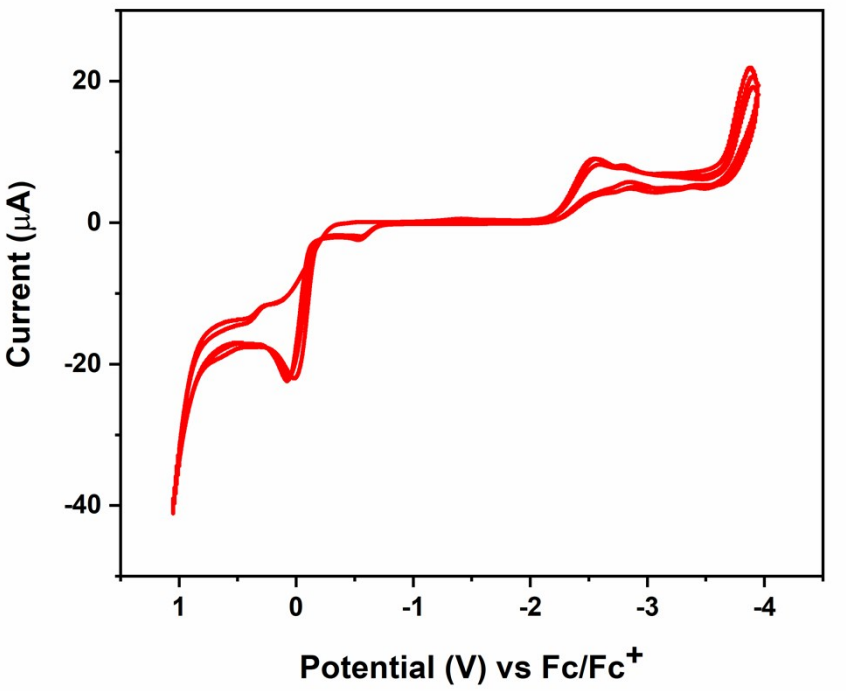


Figure 1: Cyclic Voltammogram at 25 mV scan rate.

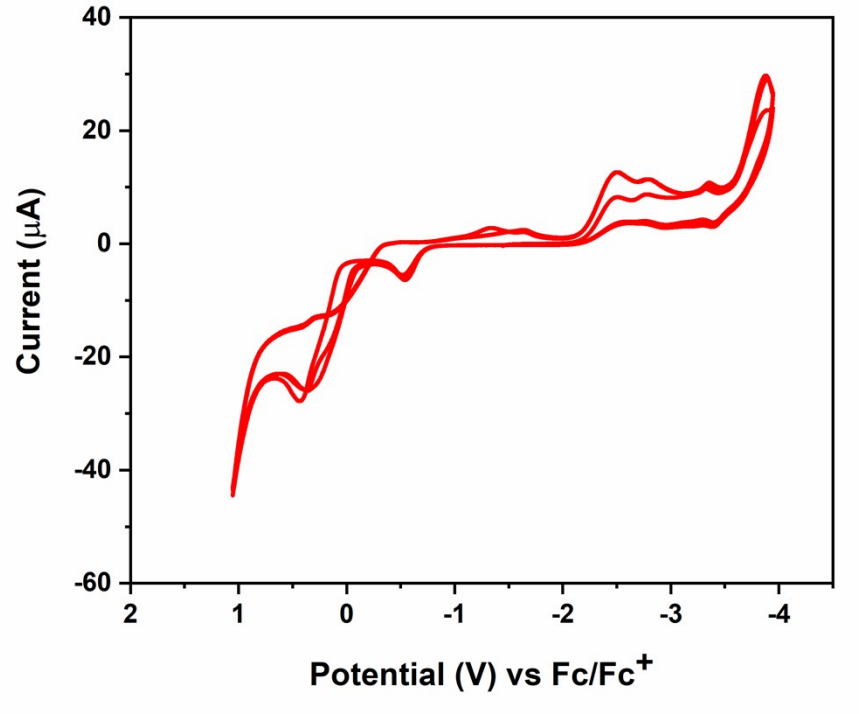


Figure 2: Cyclic Voltammogram at 50 mV scan rate.

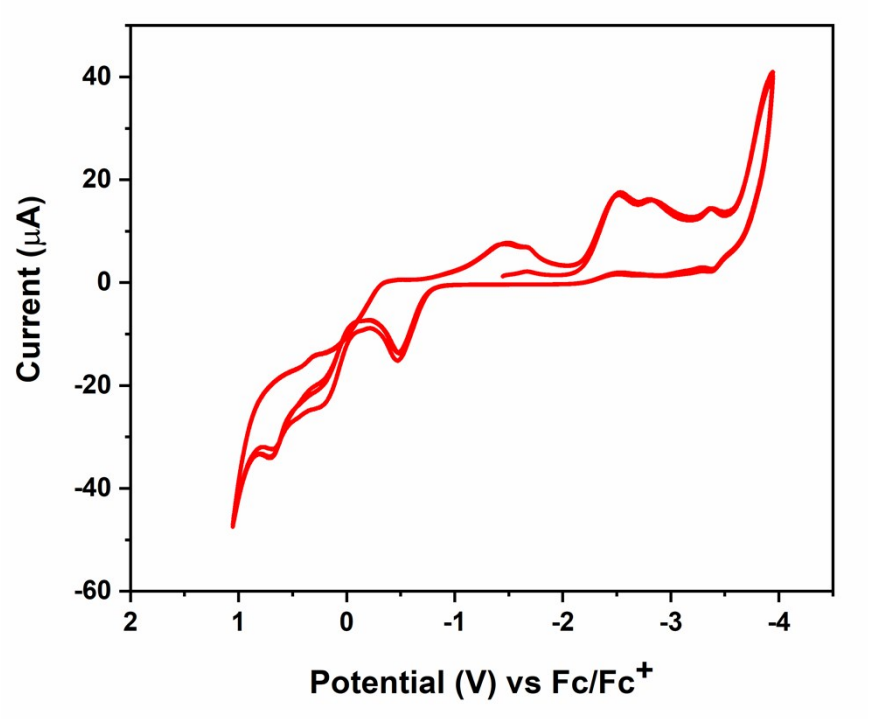


Figure 3: Cyclic Voltammogram at 100 mV scan rate.

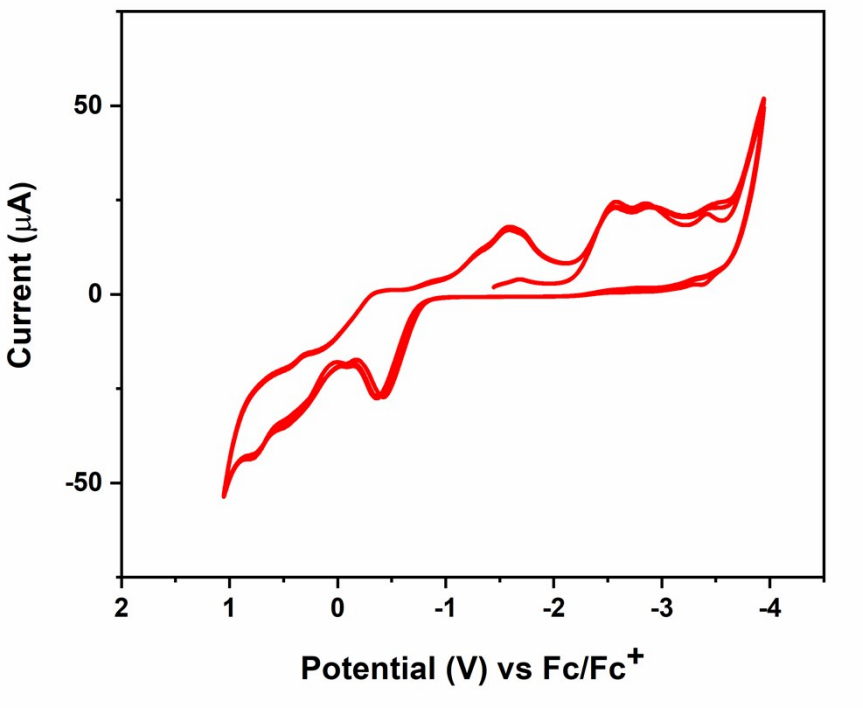


Figure 4: Cyclic Voltammogram at 200 mV scan rate.

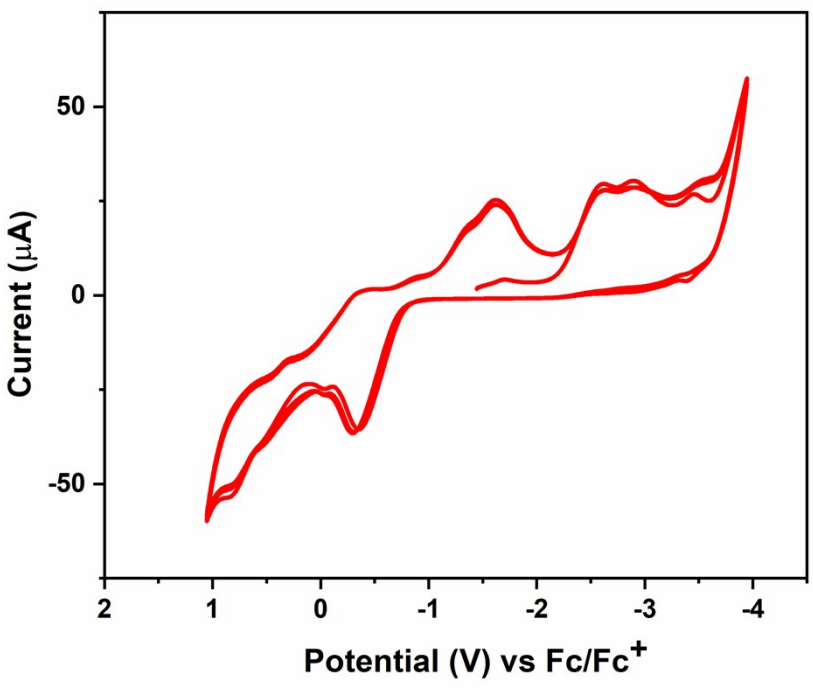


Figure 5: Cyclic Voltammogram at 300 mV scan rate.

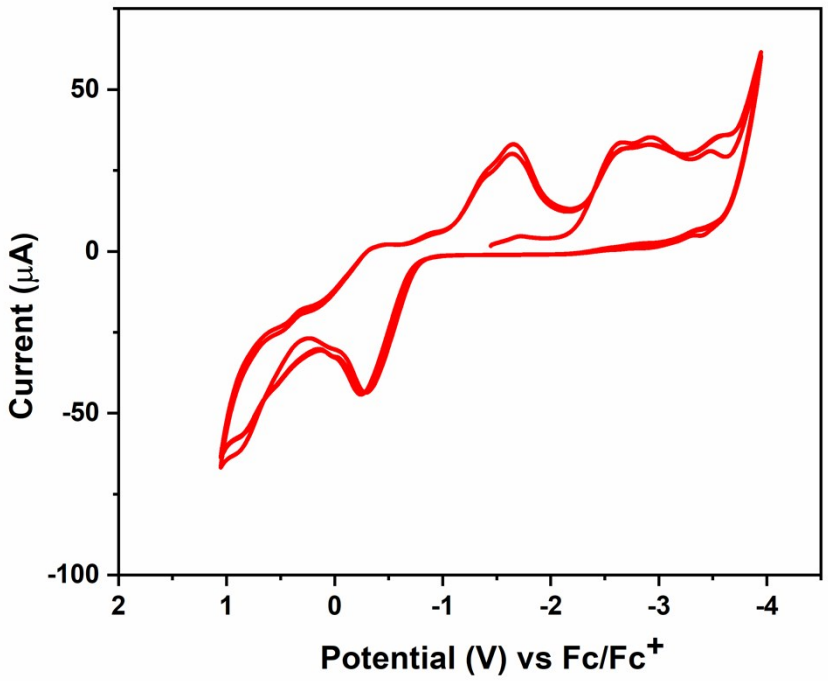


Figure 6: Cyclic Voltammogram at 400 mV scan rate.

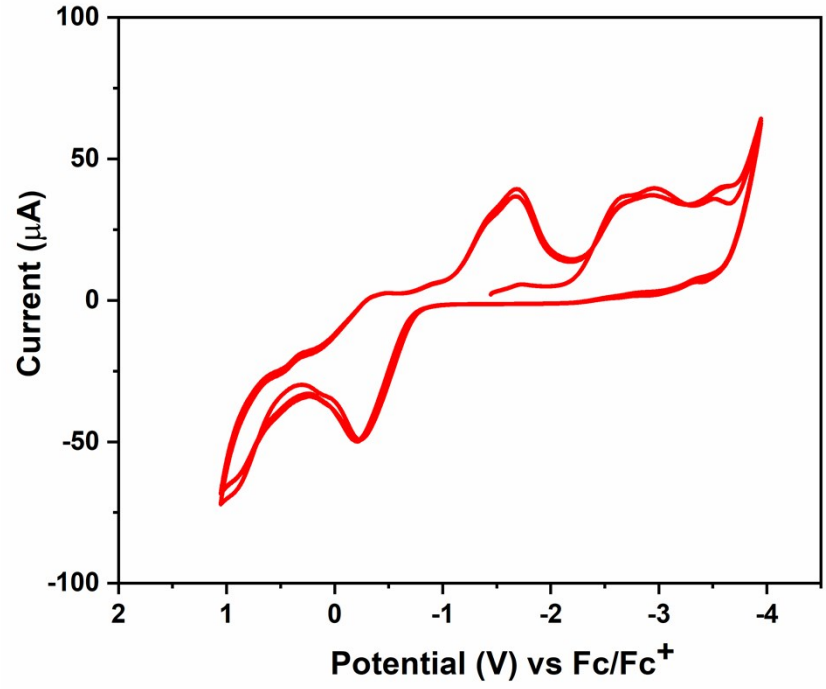


Figure 7: Cyclic Voltammogram at 500 mV scan rate.

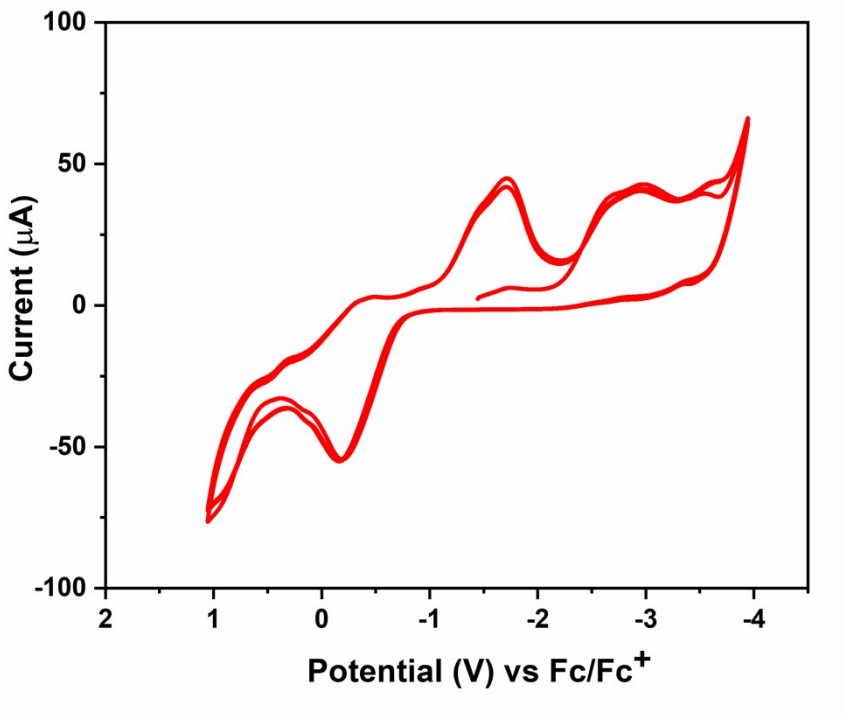


Figure 8: Cyclic Voltammogram at 600 mV scan rate.

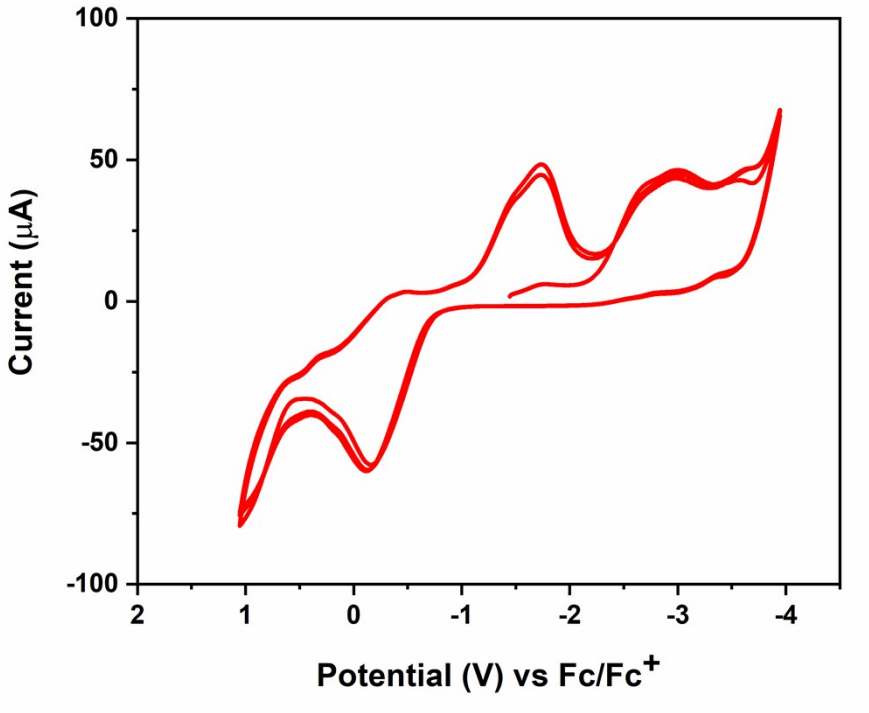


Figure 9: Cyclic Voltammogram at 700 mV scan rate.

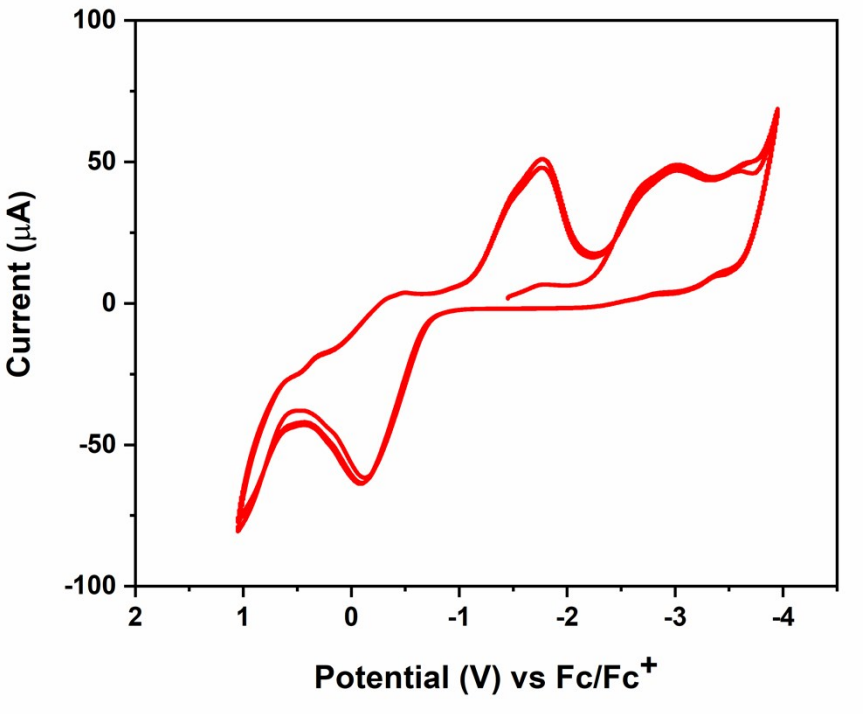


Figure 10: Cyclic Voltammogram at 800 mV scan rate.

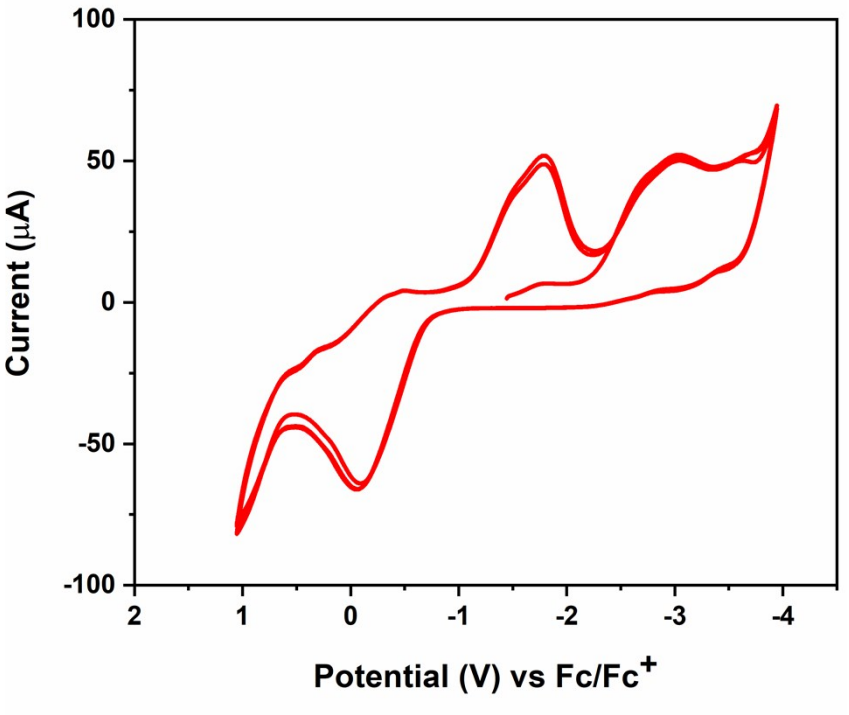


Figure 11: Cyclic Voltammogram at 900 mV scan rate.

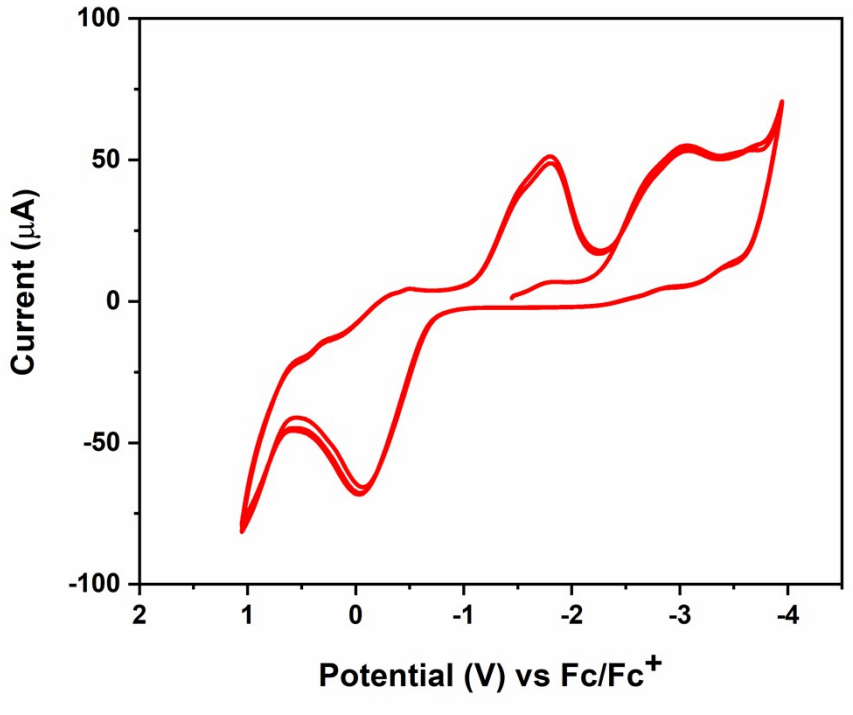


Figure 12: Cyclic Voltammogram at 1000 mV scan rate.

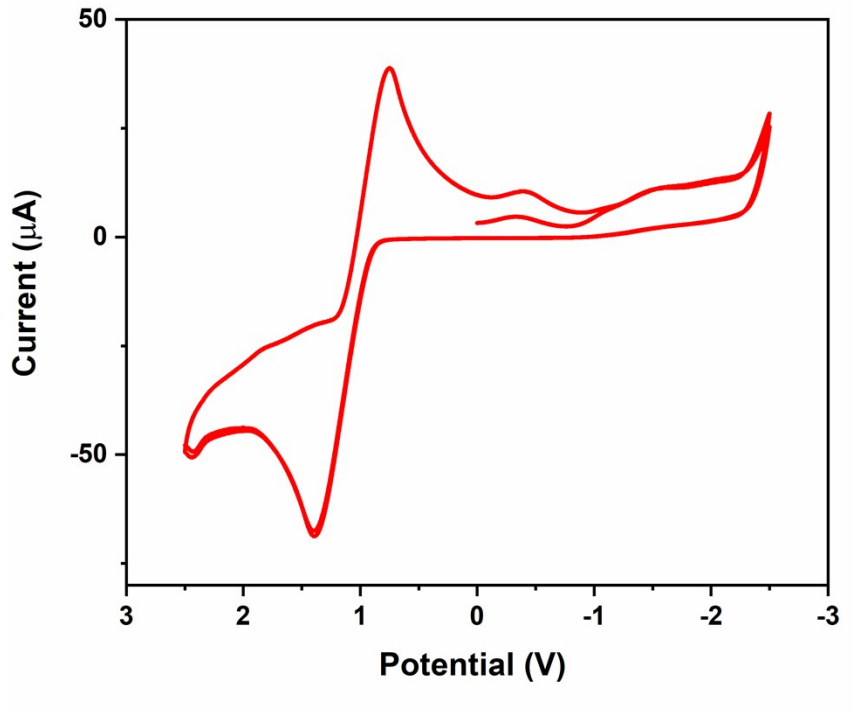


Figure 13: Cyclic Voltammogram + ferrocene at 100 mV scan rate.

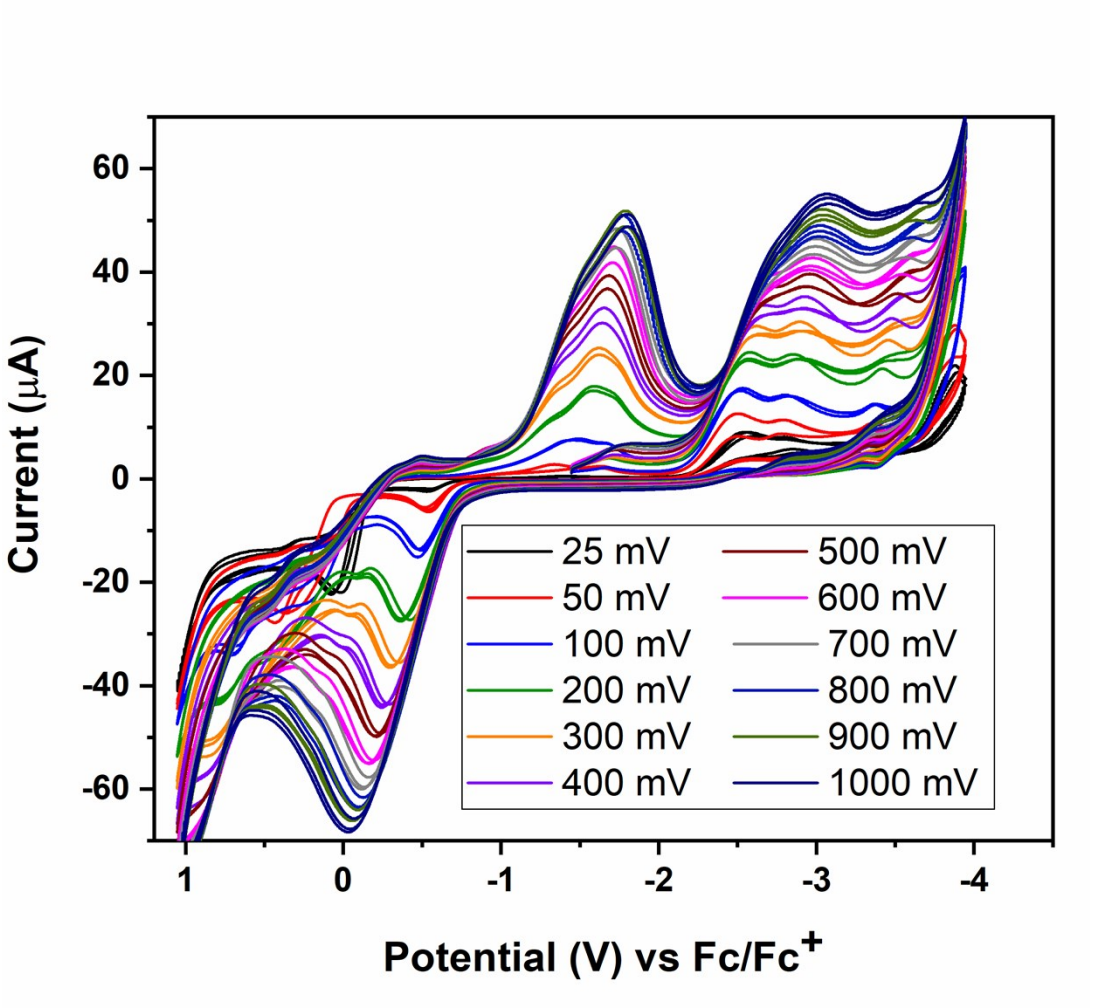


Figure 14: Overlay of Cyclic Voltammograms at varying scan rates

5. Experimental Details for Crystal Structure Refinement and Acquisition

Full crystallographic descriptions of the structure determinations are provided in the Supporting Information. Data for all three structures were collected at 100K using Bruker diffractometers with rotating-anode sources and micro-focus optics. Standard data collection procedures and data processing programs were employed. For **4**, the halogen site was refined as 75% I and 25% Cl with fixed P-X distances. For **3**, highly disordered pentane was treated as a diffuse contribution using the program SQUEEZE (found: 73e/unit cell; req: for two mol. pentane, 84 e/unit cell). For structures **5-*p*-MeC$_6$H$_4$**, **6-Pd$_2$-(P(*t*-Bu)$_3$)$_2$**, and **7(O)**, all three structures were determined using a Bruker Ultra, mini-rotating-anode diffractometer with a microfocus mirror colimnator. Details for each are provided in the SI tables. In all cases, standard methods were used throughout. OLEX2 (Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339-341) software was used for structure refinement and data processing. The structure of 92 revealed compositional disorder resulting in a 62/38 ratio of phosphine and phosphine oxide.

Table 1. Crystal data and structure refinement for cain71_0m_a (Compound **2**).

Identification code	PMA 343	
Empirical formula	C19 H23 Cl N P	
Formula weight	331.80	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.7432(6) Å	α= 90°.
	b = 10.4564(5) Å	β= 105.441(3)°.
	c = 15.0518(11) Å	γ = 90°.
Volume	1781.52(18) Å^3	
Z	4	
Density (calculated)	1.237 Mg/m^3	
Absorption coefficient	2.698 mm^{-1}	
F(000)	704	
Crystal size	0.33 x 0.29 x 0.27 mm^3	
Theta range for data collection	3.905 to 70.234°.	
Index ranges	-14<=h<=13, -12<=k<=12, -16<=l<=18	
Reflections collected	14613	
Independent reflections	3381 [R(int) = 0.0472]	
Completeness to theta = 67.679°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.6188	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3381 / 0 / 203	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1232	
R indices (all data)	R1 = 0.0497, wR2 = 0.1256	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.147 and -0.380 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for cain71_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	8604(1)	5650(1)	5393(1)	30(1)
P(1)	7040(1)	4785(1)	4499(1)	19(1)
N(1)	7347(1)	4540(2)	3492(1)	16(1)
C(1)	8014(2)	3370(2)	3387(1)	19(1)
C(2)	7938(2)	2531(2)	4191(1)	16(1)
C(3)	8304(2)	1261(2)	4324(1)	20(1)
C(4)	8119(2)	598(2)	5073(1)	23(1)
C(5)	7587(2)	1190(2)	5688(1)	25(1)
C(6)	7251(2)	2467(2)	5574(1)	22(1)
C(7)	7433(2)	3135(2)	4820(1)	17(1)
C(8)	6944(2)	5366(2)	2705(1)	15(1)
C(9)	7733(2)	6239(2)	2476(1)	17(1)
C(10)	7319(2)	6984(2)	1684(1)	20(1)
C(11)	6165(2)	6884(2)	1146(1)	22(1)
C(12)	5396(2)	6028(2)	1386(1)	20(1)
C(13)	5770(2)	5246(2)	2165(1)	17(1)
C(14)	8990(2)	6407(2)	3063(2)	21(1)
C(15)	9884(2)	6197(3)	2498(2)	33(1)
C(16)	9151(2)	7738(2)	3511(2)	35(1)
C(17)	4896(2)	4318(2)	2401(1)	20(1)
C(18)	3990(2)	5060(2)	2772(2)	27(1)
C(19)	4285(2)	3482(2)	1576(2)	26(1)

Table 3. Bond lengths [Å] and angles [°] for cain71_0m_a.

Cl(1)-P(1)	2.1649(8)
P(1)-N(1)	1.6681(16)
P(1)-C(7)	1.818(2)
N(1)-C(1)	1.485(3)
N(1)-C(8)	1.440(2)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(1)-C(2)	1.517(3)
C(2)-C(3)	1.394(3)
C(2)-C(7)	1.395(3)
C(3)-H(3)	0.9500
C(3)-C(4)	1.389(3)
C(4)-H(4)	0.9500
C(4)-C(5)	1.392(3)
C(5)-H(5)	0.9500
C(5)-C(6)	1.391(3)
C(6)-H(6)	0.9500
C(6)-C(7)	1.396(3)
C(8)-C(9)	1.408(3)
C(8)-C(13)	1.408(3)
C(9)-C(10)	1.399(3)
C(9)-C(14)	1.515(3)
C(10)-H(10)	0.9500
C(10)-C(11)	1.385(3)
C(11)-H(11)	0.9500
C(11)-C(12)	1.386(3)
C(12)-H(12)	0.9500
C(12)-C(13)	1.400(3)
C(13)-C(17)	1.521(3)
C(14)-H(14)	1.0000
C(14)-C(15)	1.533(3)
C(14)-C(16)	1.536(3)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800

C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17)	1.0000
C(17)-C(18)	1.538(3)
C(17)-C(19)	1.532(3)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800

N(1)-P(1)-Cl(1)	106.02(6)
N(1)-P(1)-C(7)	89.74(9)
C(7)-P(1)-Cl(1)	96.76(6)
C(1)-N(1)-P(1)	118.12(13)
C(8)-N(1)-P(1)	123.57(13)
C(8)-N(1)-C(1)	118.22(15)
N(1)-C(1)-H(1A)	110.9
N(1)-C(1)-H(1B)	110.9
N(1)-C(1)-C(2)	104.27(16)
H(1A)-C(1)-H(1B)	108.9
C(2)-C(1)-H(1A)	110.9
C(2)-C(1)-H(1B)	110.9
C(3)-C(2)-C(1)	125.74(18)
C(3)-C(2)-C(7)	120.29(18)
C(7)-C(2)-C(1)	113.96(18)
C(2)-C(3)-H(3)	120.6
C(4)-C(3)-C(2)	118.88(19)
C(4)-C(3)-H(3)	120.6
C(3)-C(4)-H(4)	119.6
C(3)-C(4)-C(5)	120.9(2)
C(5)-C(4)-H(4)	119.6
C(4)-C(5)-H(5)	119.8

C(6)-C(5)-C(4)	120.5(2)
C(6)-C(5)-H(5)	119.8
C(5)-C(6)-H(6)	120.6
C(5)-C(6)-C(7)	118.8(2)
C(7)-C(6)-H(6)	120.6
C(2)-C(7)-P(1)	111.88(15)
C(6)-C(7)-P(1)	127.46(16)
C(6)-C(7)-C(2)	120.64(19)
C(9)-C(8)-N(1)	119.77(17)
C(9)-C(8)-C(13)	121.60(18)
C(13)-C(8)-N(1)	118.60(17)
C(8)-C(9)-C(14)	122.36(18)
C(10)-C(9)-C(8)	117.87(18)
C(10)-C(9)-C(14)	119.76(18)
C(9)-C(10)-H(10)	119.3
C(11)-C(10)-C(9)	121.34(19)
C(11)-C(10)-H(10)	119.3
C(10)-C(11)-H(11)	120.0
C(10)-C(11)-C(12)	120.05(19)
C(12)-C(11)-H(11)	120.0
C(11)-C(12)-H(12)	119.5
C(11)-C(12)-C(13)	120.94(19)
C(13)-C(12)-H(12)	119.5
C(8)-C(13)-C(17)	122.63(18)
C(12)-C(13)-C(8)	118.19(18)
C(12)-C(13)-C(17)	119.17(18)
C(9)-C(14)-H(14)	108.2
C(9)-C(14)-C(15)	111.38(18)
C(9)-C(14)-C(16)	110.33(18)
C(15)-C(14)-H(14)	108.2
C(15)-C(14)-C(16)	110.5(2)
C(16)-C(14)-H(14)	108.2
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5

H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(13)-C(17)-H(17)	107.9
C(13)-C(17)-C(18)	109.74(17)
C(13)-C(17)-C(19)	111.97(17)
C(18)-C(17)-H(17)	107.9
C(19)-C(17)-H(17)	107.9
C(19)-C(17)-C(18)	111.24(17)
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cain71_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	35(1)	27(1)	25(1)	-8(1)	4(1)	-1(1)
P(1)	20(1)	21(1)	18(1)	0(1)	7(1)	4(1)
N(1)	17(1)	14(1)	15(1)	1(1)	4(1)	2(1)
C(1)	28(1)	12(1)	14(1)	2(1)	3(1)	0(1)
C(2)	16(1)	18(1)	15(1)	-1(1)	2(1)	-3(1)
C(3)	20(1)	17(1)	21(1)	-3(1)	4(1)	-2(1)
C(4)	25(1)	15(1)	23(1)	2(1)	-2(1)	-4(1)
C(5)	26(1)	27(1)	20(1)	6(1)	3(1)	-7(1)
C(6)	23(1)	26(1)	18(1)	0(1)	7(1)	-3(1)
C(7)	15(1)	19(1)	17(1)	-1(1)	2(1)	-2(1)
C(8)	17(1)	13(1)	14(1)	-1(1)	4(1)	2(1)
C(9)	19(1)	13(1)	20(1)	-3(1)	7(1)	0(1)
C(10)	24(1)	15(1)	24(1)	1(1)	11(1)	-2(1)
C(11)	29(1)	16(1)	21(1)	5(1)	6(1)	2(1)
C(12)	18(1)	18(1)	21(1)	2(1)	0(1)	1(1)
C(13)	18(1)	13(1)	20(1)	1(1)	6(1)	1(1)
C(14)	17(1)	21(1)	26(1)	-1(1)	7(1)	-3(1)
C(15)	21(1)	45(2)	36(1)	1(1)	12(1)	1(1)
C(16)	26(1)	29(1)	45(1)	-13(1)	2(1)	-9(1)
C(17)	17(1)	17(1)	25(1)	3(1)	4(1)	-1(1)
C(18)	22(1)	25(1)	36(1)	1(1)	11(1)	-1(1)
C(19)	22(1)	21(1)	32(1)	-1(1)	3(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cain71_0m_a.

	x	y	z	U(eq)
H(1A)	8846	3578	3418	23
H(1B)	7651	2942	2792	23
H(3)	8674	856	3909	24
H(4)	8358	-270	5167	27
H(5)	7452	717	6190	30
H(6)	6905	2878	6001	26
H(10)	7839	7571	1511	24
H(11)	5900	7402	613	27
H(12)	4603	5971	1017	24
H(14)	9142	5753	3566	25
H(15A)	9778	5339	2226	50
H(15B)	10688	6279	2901	50
H(15C)	9759	6838	2007	50
H(16A)	9035	8393	3029	52
H(16B)	9950	7811	3922	52
H(16C)	8570	7858	3865	52
H(17)	5346	3741	2902	24
H(18A)	4394	5486	3350	40
H(18B)	3398	4465	2885	40
H(18C)	3599	5702	2318	40
H(19A)	3807	4023	1085	39
H(19B)	3774	2858	1767	39
H(19C)	4883	3031	1348	39

Table 1. Crystal data and structure refinement for cain79_0m_a_sq (Compound **3**).

Identification code	DYZ9	
Empirical formula	C27 H28 N P	
Formula weight	397.47	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.4342(5) Å	α= 97.641(2)°.
	b = 10.7526(6) Å	β= 103.063(2)°.
	c = 14.1948(8) Å	γ = 90.538(2)°.
Volume	1241.83(12) $Å^3$	
Z	2	
Density (calculated)	1.063 Mg/m^3	
Absorption coefficient	0.122 mm^{-1}	
F(000)	424	
Crystal size	0.26 x 0.25 x 0.22 mm^3	
Theta range for data collection	1.487 to 28.357°.	
Index ranges	-11<=h<=11, -14<=k<=14, -18<=l<=18	
Reflections collected	15194	
Independent reflections	6203 [R(int) = 0.0942]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.777 and 0.706	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6203 / 0 / 266	
Goodness-of-fit on F^2	0.986	
Final R indices [I>2sigma(I)]	R1 = 0.0540, wR2 = 0.1434	
R indices (all data)	R1 = 0.0784, wR2 = 0.1567	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.673 and -0.434 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for cain79_0m_a_sq. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	6908(1)	5047(1)	7908(1)	18(1)
N(1)	8525(2)	4737(1)	7398(1)	17(1)
C(16)	10174(2)	5004(2)	7944(1)	17(1)
C(17)	11005(2)	6110(2)	7867(1)	19(1)
C(14)	6388(2)	3967(2)	6052(1)	19(1)
C(9)	5540(2)	4309(2)	6776(1)	18(1)
C(21)	10930(2)	4148(2)	8564(1)	21(1)
C(10)	3872(2)	4077(2)	6598(1)	22(1)
C(22)	10244(2)	7044(2)	7204(1)	21(1)
C(7)	6274(2)	7783(2)	7953(2)	25(1)
C(6)	6040(2)	9112(2)	8102(2)	28(1)
C(25)	10070(2)	2956(2)	8677(1)	26(1)
C(19)	13355(2)	5523(2)	9022(2)	30(1)
C(20)	12511(2)	4433(2)	9096(1)	28(1)
C(18)	12601(2)	6347(2)	8409(1)	24(1)
C(8)	6479(2)	6665(2)	7828(1)	22(1)
C(15)	8193(2)	4290(2)	6352(1)	22(1)
C(11)	3054(2)	3504(2)	5683(2)	26(1)
C(13)	5551(2)	3392(2)	5132(1)	25(1)
C(12)	3892(2)	3166(2)	4956(2)	27(1)
C(24)	10320(3)	8378(2)	7764(2)	30(1)
C(23)	11062(3)	7041(2)	6346(1)	29(1)
C(3)	5616(3)	11685(2)	8373(2)	48(1)
C(5)	6242(3)	9766(2)	9014(2)	49(1)
C(4)	6019(4)	11047(2)	9150(2)	55(1)
C(27)	9855(3)	2975(2)	9705(2)	51(1)
C(1)	5662(4)	9771(2)	7309(2)	65(1)
C(26)	11042(4)	1799(2)	8426(2)	70(1)
C(2)	5476(4)	11065(3)	7459(2)	74(1)

Table 3. Bond lengths [Å] and angles [°] for cain79_0m_a_sq.

P(1)-N(1)	1.6986(15)
P(1)-C(9)	1.8305(18)
P(1)-C(8)	1.7932(19)
N(1)-C(16)	1.437(2)
N(1)-C(15)	1.461(2)
C(16)-C(17)	1.404(2)
C(16)-C(21)	1.414(2)
C(17)-C(22)	1.516(2)
C(17)-C(18)	1.393(3)
C(14)-C(9)	1.393(3)
C(14)-C(15)	1.509(3)
C(14)-C(13)	1.395(3)
C(9)-C(10)	1.386(3)
C(21)-C(25)	1.511(3)
C(21)-C(20)	1.385(3)
C(10)-H(10)	0.9500
C(10)-C(11)	1.384(3)
C(22)-H(22)	1.0000
C(22)-C(24)	1.538(3)
C(22)-C(23)	1.528(3)
C(7)-C(6)	1.438(3)
C(7)-C(8)	1.212(3)
C(6)-C(5)	1.361(3)
C(6)-C(1)	1.389(3)
C(25)-H(25)	1.0000
C(25)-C(27)	1.509(3)
C(25)-C(26)	1.543(3)
C(19)-H(19)	0.9500
C(19)-C(20)	1.394(3)
C(19)-C(18)	1.383(3)
C(20)-H(20)	0.9500
C(18)-H(18)	0.9500
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900

C(11)-H(11)	0.9500
C(11)-C(12)	1.389(3)
C(13)-H(13)	0.9500
C(13)-C(12)	1.378(3)
C(12)-H(12)	0.9500
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(3)-H(3)	0.9500
C(3)-C(4)	1.356(4)
C(3)-C(2)	1.357(4)
C(5)-H(5)	0.9500
C(5)-C(4)	1.386(3)
C(4)-H(4)	0.9500
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(1)-H(1)	0.9500
C(1)-C(2)	1.395(3)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(2)-H(2)	0.9500

N(1)-P(1)-C(9)	89.64(8)
N(1)-P(1)-C(8)	106.70(8)
C(8)-P(1)-C(9)	99.89(8)
C(16)-N(1)-P(1)	121.93(11)
C(16)-N(1)-C(15)	120.02(14)
C(15)-N(1)-P(1)	117.82(12)
C(17)-C(16)-N(1)	119.93(15)
C(17)-C(16)-C(21)	120.99(16)
C(21)-C(16)-N(1)	119.08(16)

C(16)-C(17)-C(22)	122.57(16)
C(18)-C(17)-C(16)	118.68(16)
C(18)-C(17)-C(22)	118.74(17)
C(9)-C(14)-C(15)	114.70(16)
C(9)-C(14)-C(13)	119.80(17)
C(13)-C(14)-C(15)	125.48(17)
C(14)-C(9)-P(1)	111.26(14)
C(10)-C(9)-P(1)	127.91(15)
C(10)-C(9)-C(14)	120.84(17)
C(16)-C(21)-C(25)	122.58(16)
C(20)-C(21)-C(16)	118.10(17)
C(20)-C(21)-C(25)	119.31(16)
C(9)-C(10)-H(10)	120.5
C(11)-C(10)-C(9)	118.92(18)
C(11)-C(10)-H(10)	120.5
C(17)-C(22)-H(22)	108.0
C(17)-C(22)-C(24)	111.66(15)
C(17)-C(22)-C(23)	110.89(15)
C(24)-C(22)-H(22)	108.0
C(23)-C(22)-H(22)	108.0
C(23)-C(22)-C(24)	110.20(15)
C(8)-C(7)-C(6)	179.7(2)
C(5)-C(6)-C(7)	121.7(2)
C(5)-C(6)-C(1)	118.1(2)
C(1)-C(6)-C(7)	120.1(2)
C(21)-C(25)-H(25)	108.8
C(21)-C(25)-C(26)	110.62(19)
C(27)-C(25)-C(21)	111.40(16)
C(27)-C(25)-H(25)	108.8
C(27)-C(25)-C(26)	108.5(2)
C(26)-C(25)-H(25)	108.8
C(20)-C(19)-H(19)	120.2
C(18)-C(19)-H(19)	120.2
C(18)-C(19)-C(20)	119.52(18)
C(21)-C(20)-C(19)	121.60(18)
C(21)-C(20)-H(20)	119.2

C(19)-C(20)-H(20)	119.2
C(17)-C(18)-H(18)	119.4
C(19)-C(18)-C(17)	121.11(18)
C(19)-C(18)-H(18)	119.4
C(7)-C(8)-P(1)	168.38(18)
N(1)-C(15)-C(14)	105.40(15)
N(1)-C(15)-H(15A)	110.7
N(1)-C(15)-H(15B)	110.7
C(14)-C(15)-H(15A)	110.7
C(14)-C(15)-H(15B)	110.7
H(15A)-C(15)-H(15B)	108.8
C(10)-C(11)-H(11)	119.8
C(10)-C(11)-C(12)	120.49(18)
C(12)-C(11)-H(11)	119.8
C(14)-C(13)-H(13)	120.4
C(12)-C(13)-C(14)	119.17(18)
C(12)-C(13)-H(13)	120.4
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-C(11)	120.78(18)
C(13)-C(12)-H(12)	119.6
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(4)-C(3)-H(3)	120.3
C(4)-C(3)-C(2)	119.4(2)
C(2)-C(3)-H(3)	120.3
C(6)-C(5)-H(5)	119.4

C(6)-C(5)-C(4)	121.3(2)
C(4)-C(5)-H(5)	119.4
C(3)-C(4)-C(5)	120.5(2)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(6)-C(1)-H(1)	120.1
C(6)-C(1)-C(2)	119.9(3)
C(2)-C(1)-H(1)	120.1
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(3)-C(2)-C(1)	120.7(3)
C(3)-C(2)-H(2)	119.6
C(1)-C(2)-H(2)	119.6

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cain79_0m_a_sq. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	18(1)	17(1)	20(1)	1(1)	4(1)	1(1)
N(1)	14(1)	18(1)	17(1)	-1(1)	1(1)	0(1)
C(16)	15(1)	18(1)	16(1)	-1(1)	3(1)	1(1)
C(17)	18(1)	19(1)	18(1)	-1(1)	6(1)	1(1)
C(14)	20(1)	13(1)	23(1)	3(1)	3(1)	2(1)
C(9)	21(1)	11(1)	21(1)	3(1)	0(1)	1(1)
C(21)	20(1)	21(1)	19(1)	1(1)	2(1)	2(1)
C(10)	22(1)	16(1)	28(1)	4(1)	7(1)	2(1)
C(22)	21(1)	18(1)	23(1)	3(1)	6(1)	0(1)
C(7)	16(1)	23(1)	34(1)	1(1)	8(1)	-1(1)
C(6)	22(1)	17(1)	46(1)	2(1)	9(1)	1(1)
C(25)	31(1)	18(1)	26(1)	4(1)	0(1)	1(1)
C(19)	17(1)	39(1)	29(1)	4(1)	-2(1)	-4(1)
C(20)	24(1)	34(1)	24(1)	7(1)	-2(1)	4(1)
C(18)	20(1)	26(1)	24(1)	0(1)	6(1)	-4(1)
C(8)	18(1)	21(1)	26(1)	-1(1)	6(1)	0(1)
C(15)	21(1)	23(1)	20(1)	-1(1)	3(1)	-2(1)
C(11)	18(1)	19(1)	35(1)	3(1)	-1(1)	-3(1)
C(13)	30(1)	20(1)	22(1)	-2(1)	5(1)	0(1)
C(12)	28(1)	21(1)	26(1)	-2(1)	-4(1)	-3(1)
C(24)	34(1)	21(1)	35(1)	2(1)	10(1)	0(1)
C(23)	34(1)	30(1)	26(1)	6(1)	9(1)	-2(1)
C(3)	50(2)	18(1)	78(2)	1(1)	21(1)	9(1)
C(5)	72(2)	25(1)	47(2)	0(1)	14(1)	5(1)
C(4)	75(2)	28(1)	60(2)	-12(1)	23(2)	2(1)
C(27)	66(2)	53(2)	33(1)	2(1)	16(1)	-30(1)
C(1)	108(3)	30(1)	53(2)	4(1)	9(2)	26(2)
C(26)	86(2)	30(1)	100(3)	-6(2)	43(2)	7(1)
C(2)	121(3)	31(1)	69(2)	14(1)	16(2)	31(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cain79_0m_a_sq.

	x	y	z	U(eq)
H(10)	3300	4306	7095	26
H(22)	9072	6780	6934	25
H(25)	8971	2875	8219	31
H(19)	14442	5699	9390	35
H(20)	13032	3873	9521	33
H(18)	13180	7087	8356	28
H(15A)	8824	3541	6221	26
H(15B)	8483	4953	5991	26
H(11)	1910	3340	5551	31
H(13)	6118	3159	4632	30
H(12)	3314	2775	4332	32
H(24A)	9840	8361	8330	44
H(24B)	9711	8936	7333	44
H(24C)	11459	8686	7986	44
H(23A)	12208	7321	6592	44
H(23B)	10508	7612	5907	44
H(23C)	10995	6190	5990	44
H(3)	5432	12559	8468	58
H(5)	6541	9337	9567	58
H(4)	6150	11481	9793	66
H(27A)	10920	3112	10165	76
H(27B)	9360	2170	9767	76
H(27C)	9146	3655	9853	76
H(1)	5529	9342	6664	78
H(26A)	11204	1780	7762	105
H(26B)	10436	1033	8467	105
H(26C)	12103	1849	8890	105
H(2)	5250	11517	6915	89

Table 1. Crystal data and structure refinement for cain83_0m_a (Mixture of **4** and the Chloride).

Identification code	DYZ-24	
Empirical formula	C19 H23 Cl0.25 I0.75 N P	
Formula weight	400.40	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.4221(5) Å	α= 90°.
	b = 9.8317(8) Å	β= 101.724(3)°.
	c = 20.1049(12) Å	γ = 90°.
Volume	1823.6(2) $Å^3$	
Z	4	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	2.003 mm^{-1}	
F(000)	836	
Crystal color, size	Yellow, 0.25 x 0.24 x 0.22 mm^3	
Theta range for data collection	2.069 to 28.345°.	
Index ranges	-11<=h<=12, -13<=k<=11, -26<=l<=26	
Reflections collected	16478	
Independent reflections	4539 [R(int) = 0.0331]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6760	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4539 / 0 / 207	
Goodness-of-fit on F^2	1.156	
Final R indices [I>2sigma(I)]	R1 = 0.0282, wR2 = 0.0616	
R indices (all data)	R1 = 0.0344, wR2 = 0.0635	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.737 and -0.371 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for cain83_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	7724(1)	3940(1)	5006(1)	20(1)
Cl(1)	7701(7)	4151(5)	4899(3)	20(1)
P(1)	6370(1)	5413(1)	4005(1)	17(1)
N(1)	7468(2)	5664(2)	3464(1)	15(1)
C(1)	6860(2)	7061(2)	4385(1)	17(1)
C(2)	6252(3)	7727(2)	4875(1)	23(1)
C(3)	6743(3)	9030(2)	5074(1)	27(1)
C(4)	7820(3)	9647(2)	4802(1)	27(1)
C(5)	8436(3)	8970(2)	4323(1)	22(1)
C(6)	7936(2)	7681(2)	4112(1)	17(1)
C(7)	8439(2)	6849(2)	3578(1)	17(1)
C(8)	7474(2)	4820(2)	2879(1)	15(1)
C(9)	8603(2)	3881(2)	2885(1)	17(1)
C(10)	8576(3)	3100(2)	2304(1)	23(1)
C(11)	7466(3)	3214(2)	1742(1)	26(1)
C(12)	6357(3)	4135(2)	1747(1)	21(1)
C(13)	6347(2)	4973(2)	2307(1)	16(1)
C(14)	9810(2)	3664(2)	3500(1)	20(1)
C(15)	11283(3)	4012(3)	3341(1)	31(1)
C(16)	9805(3)	2201(2)	3758(1)	31(1)
C(17)	5111(2)	5968(2)	2280(1)	18(1)
C(18)	3738(3)	5195(3)	2354(1)	25(1)
C(19)	4823(3)	6822(2)	1629(1)	24(1)

Table 3. Bond lengths [Å] and angles [°] for cain83_0m_a.

I(1)-P(1)	2.5937(7)
Cl(1)-P(1)	2.329(5)
P(1)-N(1)	1.6657(17)
P(1)-C(1)	1.811(2)
N(1)-C(7)	1.470(3)
N(1)-C(8)	1.441(2)
C(1)-C(2)	1.398(3)
C(1)-C(6)	1.388(3)
C(2)-H(2)	0.9500
C(2)-C(3)	1.393(3)
C(3)-H(3)	0.9500
C(3)-C(4)	1.387(4)
C(4)-H(4)	0.9500
C(4)-C(5)	1.391(3)
C(5)-H(5)	0.9500
C(5)-C(6)	1.388(3)
C(6)-C(7)	1.501(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.407(3)
C(8)-C(13)	1.405(3)
C(9)-C(10)	1.393(3)
C(9)-C(14)	1.515(3)
C(10)-H(10)	0.9500
C(10)-C(11)	1.379(3)
C(11)-H(11)	0.9500
C(11)-C(12)	1.384(3)
C(12)-H(12)	0.9500
C(12)-C(13)	1.396(3)
C(13)-C(17)	1.514(3)
C(14)-H(14)	1.0000
C(14)-C(15)	1.525(3)
C(14)-C(16)	1.530(3)
C(15)-H(15A)	0.9800

C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17)	1.0000
C(17)-C(18)	1.533(3)
C(17)-C(19)	1.533(3)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800

N(1)-P(1)-I(1)	108.43(7)
N(1)-P(1)-Cl(1)	105.93(17)
N(1)-P(1)-C(1)	90.23(9)
C(1)-P(1)-I(1)	97.42(7)
C(1)-P(1)-Cl(1)	95.74(16)
C(7)-N(1)-P(1)	117.72(13)
C(8)-N(1)-P(1)	123.64(14)
C(8)-N(1)-C(7)	118.59(16)
C(2)-C(1)-P(1)	127.62(18)
C(6)-C(1)-P(1)	111.72(15)
C(6)-C(1)-C(2)	120.6(2)
C(1)-C(2)-H(2)	120.9
C(3)-C(2)-C(1)	118.2(2)
C(3)-C(2)-H(2)	120.9
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-C(2)	121.1(2)
C(4)-C(3)-H(3)	119.5
C(3)-C(4)-H(4)	119.8
C(3)-C(4)-C(5)	120.4(2)
C(5)-C(4)-H(4)	119.8
C(4)-C(5)-H(5)	120.5

C(6)-C(5)-C(4)	119.0(2)
C(6)-C(5)-H(5)	120.5
C(1)-C(6)-C(7)	113.95(18)
C(5)-C(6)-C(1)	120.7(2)
C(5)-C(6)-C(7)	125.3(2)
N(1)-C(7)-C(6)	105.45(16)
N(1)-C(7)-H(7A)	110.7
N(1)-C(7)-H(7B)	110.7
C(6)-C(7)-H(7A)	110.7
C(6)-C(7)-H(7B)	110.7
H(7A)-C(7)-H(7B)	108.8
C(9)-C(8)-N(1)	119.95(19)
C(13)-C(8)-N(1)	118.64(18)
C(13)-C(8)-C(9)	121.39(18)
C(8)-C(9)-C(14)	122.69(18)
C(10)-C(9)-C(8)	118.0(2)
C(10)-C(9)-C(14)	119.28(19)
C(9)-C(10)-H(10)	119.2
C(11)-C(10)-C(9)	121.5(2)
C(11)-C(10)-H(10)	119.2
C(10)-C(11)-H(11)	120.1
C(10)-C(11)-C(12)	119.7(2)
C(12)-C(11)-H(11)	120.1
C(11)-C(12)-H(12)	119.3
C(11)-C(12)-C(13)	121.3(2)
C(13)-C(12)-H(12)	119.3
C(8)-C(13)-C(17)	123.07(18)
C(12)-C(13)-C(8)	117.99(19)
C(12)-C(13)-C(17)	118.9(2)
C(9)-C(14)-H(14)	108.1
C(9)-C(14)-C(15)	111.21(19)
C(9)-C(14)-C(16)	110.8(2)
C(15)-C(14)-H(14)	108.1
C(15)-C(14)-C(16)	110.3(2)
C(16)-C(14)-H(14)	108.1
C(14)-C(15)-H(15A)	109.5

C(14)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(13)-C(17)-H(17)	108.0
C(13)-C(17)-C(18)	109.54(18)
C(13)-C(17)-C(19)	112.68(17)
C(18)-C(17)-H(17)	108.0
C(19)-C(17)-H(17)	108.0
C(19)-C(17)-C(18)	110.41(19)
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cain83_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	30(1)	17(1)	12(1)	4(1)	3(1)	-5(1)
Cl(1)	30(1)	17(1)	12(1)	4(1)	3(1)	-5(1)
P(1)	17(1)	20(1)	16(1)	-3(1)	6(1)	-4(1)
N(1)	16(1)	15(1)	13(1)	-1(1)	4(1)	-2(1)
C(1)	18(1)	17(1)	14(1)	-2(1)	-1(1)	1(1)
C(2)	22(1)	29(1)	17(1)	-2(1)	2(1)	5(1)
C(3)	31(1)	26(1)	21(1)	-7(1)	-2(1)	11(1)
C(4)	38(2)	16(1)	21(1)	-2(1)	-6(1)	4(1)
C(5)	29(1)	16(1)	19(1)	3(1)	-2(1)	-1(1)
C(6)	20(1)	15(1)	14(1)	2(1)	-2(1)	2(1)
C(7)	18(1)	16(1)	17(1)	1(1)	4(1)	-2(1)
C(8)	18(1)	14(1)	14(1)	0(1)	5(1)	-2(1)
C(9)	19(1)	16(1)	18(1)	2(1)	6(1)	-1(1)
C(10)	27(1)	21(1)	24(1)	-1(1)	11(1)	7(1)
C(11)	38(2)	23(1)	19(1)	-5(1)	10(1)	5(1)
C(12)	27(1)	21(1)	15(1)	0(1)	3(1)	0(1)
C(13)	18(1)	15(1)	16(1)	1(1)	5(1)	0(1)
C(14)	18(1)	19(1)	24(1)	2(1)	5(1)	2(1)
C(15)	21(1)	36(1)	37(1)	-3(1)	9(1)	0(1)
C(16)	29(1)	24(1)	36(1)	9(1)	-1(1)	3(1)
C(17)	19(1)	17(1)	17(1)	-1(1)	0(1)	2(1)
C(18)	21(1)	28(1)	26(1)	3(1)	4(1)	1(1)
C(19)	27(1)	22(1)	22(1)	5(1)	1(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cain83_0m_a.

	x	y	z	U(eq)
H(2)	5523	7302	5067	28
H(3)	6333	9504	5401	32
H(4)	8139	10536	4944	32
H(5)	9187	9384	4142	27
H(7A)	8367	7380	3154	20
H(7B)	9457	6558	3737	20
H(10)	9340	2474	2295	28
H(11)	7462	2663	1354	31
H(12)	5587	4199	1361	26
H(14)	9637	4286	3869	24
H(15A)	11490	3393	2991	46
H(15B)	12035	3915	3754	46
H(15C)	11272	4951	3177	46
H(16A)	10099	1582	3428	46
H(16B)	8827	1962	3816	46
H(16C)	10485	2121	4195	46
H(17)	5374	6601	2675	22
H(18A)	3485	4536	1983	38
H(18B)	2938	5840	2336	38
H(18C)	3914	4715	2790	38
H(19A)	5726	7260	1572	37
H(19B)	4097	7520	1660	37
H(19C)	4464	6232	1238	37

Table 1. Crystal data and structure refinement for cain89_0m_a (Compound **5-*p*-MeC$_6$H$_4$**).

Identification code	MC 4-49 F2	
Empirical formula	C26 H30 N P	
Formula weight	387.48	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.1766(2) Å	α= 90°.
	b = 20.7413(4) Å	β= 109.8390(10)°.
	c = 11.3263(2) Å	γ = 90°.
Volume	2248.82(7) Å^3	
Z	4	
Density (calculated)	1.144 Mg/m^3	
Absorption coefficient	1.140 mm^{-1}	
F(000)	832	
Crystal size	0.32 x 0.21 x 0.14 mm^3	
Theta range for data collection	4.263 to 68.474°.	
Index ranges	-12<=h<=11, -25<=k<=24, -13<=l<=11	
Reflections collected	12696	
Independent reflections	4100 [R(int) = 0.0221]	
Completeness to theta = 67.679°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6524	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4100 / 0 / 258	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0929	
R indices (all data)	R1 = 0.0377, wR2 = 0.0954	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.354 and -0.264 e.Å^{-3}	

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for cain89_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	5233(1)	6732(1)	5305(1)	16(1)
N(1)	4284(1)	6903(1)	6251(1)	16(1)
C(8)	6540(1)	6129(1)	6160(1)	17(1)
C(5)	6473(1)	8369(1)	7253(1)	21(1)
C(6)	5833(1)	7793(1)	6742(1)	18(1)
C(2)	7250(1)	7735(1)	5408(1)	21(1)
C(16)	1761(1)	6832(1)	5115(1)	20(1)
C(15)	2957(1)	6608(1)	6077(1)	17(1)
C(21)	1814(1)	7399(1)	4286(1)	22(1)
C(1)	6224(1)	7474(1)	5828(1)	17(1)
C(9)	7453(1)	6203(1)	7390(1)	22(1)
C(7)	4687(1)	7465(1)	7074(1)	19(1)
C(20)	2868(1)	6111(1)	6887(1)	21(1)
C(11)	8341(1)	5121(1)	7387(1)	25(1)
C(13)	6559(1)	5547(1)	5554(1)	22(1)
C(24)	4137(1)	5894(1)	7980(1)	23(1)
C(4)	7488(1)	8630(1)	6826(1)	24(1)
C(12)	7450(1)	5048(1)	6154(1)	26(1)
C(3)	7870(1)	8316(1)	5907(1)	24(1)
C(17)	491(1)	6525(1)	4946(1)	26(1)
C(10)	8331(1)	5706(1)	7990(1)	25(1)
C(19)	1571(2)	5823(1)	6684(1)	30(1)
C(26)	3885(2)	5949(1)	9231(1)	36(1)
C(22)	1476(2)	7194(1)	2920(1)	31(1)
C(23)	838(2)	7942(1)	4376(2)	38(1)
C(25)	4588(2)	5212(1)	7789(1)	31(1)
C(18)	395(2)	6023(1)	5716(1)	33(1)
C(14)	9290(2)	4581(1)	8064(2)	37(1)

Table 4. Bond lengths [Å] and angles [°] for cain89_0m_a.

P(1)-N(1)	1.7058(11)
P(1)-C(8)	1.8433(13)
P(1)-C(1)	1.8263(13)
N(1)-C(15)	1.4335(16)
N(1)-C(7)	1.4608(16)
C(8)-C(9)	1.3963(18)
C(8)-C(13)	1.3920(18)
C(5)-H(5)	0.9500
C(5)-C(6)	1.3907(18)
C(5)-C(4)	1.390(2)
C(6)-C(1)	1.3945(18)
C(6)-C(7)	1.5043(17)
C(2)-H(2)	0.9500
C(2)-C(1)	1.3946(18)
C(2)-C(3)	1.3875(19)
C(16)-C(15)	1.4084(18)
C(16)-C(21)	1.5180(18)
C(16)-C(17)	1.3940(19)
C(15)-C(20)	1.4038(18)
C(21)-H(21)	1.0000
C(21)-C(22)	1.5266(19)
C(21)-C(23)	1.527(2)
C(9)-H(9)	0.9500
C(9)-C(10)	1.3830(19)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(20)-C(24)	1.5220(18)
C(20)-C(19)	1.3962(19)
C(11)-C(12)	1.392(2)
C(11)-C(10)	1.393(2)
C(11)-C(14)	1.5076(19)
C(13)-H(13)	0.9500
C(13)-C(12)	1.391(2)
C(24)-H(24)	1.0000

C(24)-C(26)	1.528(2)
C(24)-C(25)	1.525(2)
C(4)-H(4)	0.9500
C(4)-C(3)	1.389(2)
C(12)-H(12)	0.9500
C(3)-H(3)	0.9500
C(17)-H(17)	0.9500
C(17)-C(18)	1.383(2)
C(10)-H(10)	0.9500
C(19)-H(19)	0.9500
C(19)-C(18)	1.384(2)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(18)-H(18)	0.9500
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800

N(1)-P(1)-C(8)	105.85(5)
N(1)-P(1)-C(1)	89.35(5)
C(1)-P(1)-C(8)	100.44(5)
C(15)-N(1)-P(1)	122.16(8)
C(15)-N(1)-C(7)	118.37(10)
C(7)-N(1)-P(1)	118.10(8)
C(9)-C(8)-P(1)	124.49(10)
C(13)-C(8)-P(1)	117.26(10)

C(13)-C(8)-C(9)	118.15(12)
C(6)-C(5)-H(5)	120.4
C(4)-C(5)-H(5)	120.4
C(4)-C(5)-C(6)	119.18(13)
C(5)-C(6)-C(1)	120.29(12)
C(5)-C(6)-C(7)	125.30(12)
C(1)-C(6)-C(7)	114.40(11)
C(1)-C(2)-H(2)	120.4
C(3)-C(2)-H(2)	120.4
C(3)-C(2)-C(1)	119.17(12)
C(15)-C(16)-C(21)	122.05(11)
C(17)-C(16)-C(15)	118.29(12)
C(17)-C(16)-C(21)	119.65(12)
C(16)-C(15)-N(1)	119.50(11)
C(20)-C(15)-N(1)	119.36(11)
C(20)-C(15)-C(16)	121.13(12)
C(16)-C(21)-H(21)	107.7
C(16)-C(21)-C(22)	111.56(11)
C(16)-C(21)-C(23)	111.68(11)
C(22)-C(21)-H(21)	107.7
C(22)-C(21)-C(23)	110.19(12)
C(23)-C(21)-H(21)	107.7
C(6)-C(1)-P(1)	111.97(9)
C(6)-C(1)-C(2)	120.31(12)
C(2)-C(1)-P(1)	127.71(10)
C(8)-C(9)-H(9)	119.7
C(10)-C(9)-C(8)	120.53(12)
C(10)-C(9)-H(9)	119.7
N(1)-C(7)-C(6)	105.89(10)
N(1)-C(7)-H(7A)	110.6
N(1)-C(7)-H(7B)	110.6
C(6)-C(7)-H(7A)	110.6
C(6)-C(7)-H(7B)	110.6
H(7A)-C(7)-H(7B)	108.7
C(15)-C(20)-C(24)	121.62(12)
C(19)-C(20)-C(15)	118.32(12)

C(19)-C(20)-C(24)	120.04(12)
C(12)-C(11)-C(10)	118.38(12)
C(12)-C(11)-C(14)	121.11(13)
C(10)-C(11)-C(14)	120.50(13)
C(8)-C(13)-H(13)	119.4
C(12)-C(13)-C(8)	121.29(12)
C(12)-C(13)-H(13)	119.4
C(20)-C(24)-H(24)	107.4
C(20)-C(24)-C(26)	111.66(12)
C(20)-C(24)-C(25)	111.87(12)
C(26)-C(24)-H(24)	107.4
C(25)-C(24)-H(24)	107.4
C(25)-C(24)-C(26)	110.74(12)
C(5)-C(4)-H(4)	119.7
C(3)-C(4)-C(5)	120.56(12)
C(3)-C(4)-H(4)	119.7
C(11)-C(12)-H(12)	119.8
C(13)-C(12)-C(11)	120.31(12)
C(13)-C(12)-H(12)	119.8
C(2)-C(3)-C(4)	120.48(12)
C(2)-C(3)-H(3)	119.8
C(4)-C(3)-H(3)	119.8
C(16)-C(17)-H(17)	119.4
C(18)-C(17)-C(16)	121.18(13)
C(18)-C(17)-H(17)	119.4
C(9)-C(10)-C(11)	121.31(13)
C(9)-C(10)-H(10)	119.3
C(11)-C(10)-H(10)	119.3
C(20)-C(19)-H(19)	119.4
C(18)-C(19)-C(20)	121.13(13)
C(18)-C(19)-H(19)	119.4
C(24)-C(26)-H(26A)	109.5
C(24)-C(26)-H(26B)	109.5
C(24)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26C)	109.5

H(26B)-C(26)-H(26C)	109.5
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(17)-C(18)-C(19)	119.89(13)
C(17)-C(18)-H(18)	120.1
C(19)-C(18)-H(18)	120.1
C(11)-C(14)-H(14A)	109.5
C(11)-C(14)-H(14B)	109.5
C(11)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cain89_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	14(1)	18(1)	14(1)	-1(1)	3(1)	-1(1)
N(1)	14(1)	17(1)	18(1)	-2(1)	4(1)	-2(1)
C(8)	15(1)	17(1)	21(1)	-1(1)	7(1)	-1(1)
C(5)	19(1)	19(1)	23(1)	-1(1)	4(1)	-1(1)
C(6)	15(1)	17(1)	18(1)	3(1)	2(1)	1(1)
C(2)	17(1)	25(1)	20(1)	3(1)	6(1)	2(1)
C(16)	17(1)	26(1)	16(1)	-2(1)	5(1)	-1(1)
C(15)	15(1)	20(1)	16(1)	-2(1)	5(1)	-2(1)
C(21)	17(1)	26(1)	21(1)	4(1)	4(1)	1(1)
C(1)	14(1)	17(1)	17(1)	3(1)	1(1)	1(1)
C(9)	23(1)	18(1)	24(1)	-4(1)	5(1)	1(1)
C(7)	18(1)	20(1)	18(1)	-3(1)	7(1)	-3(1)
C(20)	23(1)	22(1)	18(1)	-1(1)	6(1)	-4(1)
C(11)	22(1)	18(1)	36(1)	4(1)	13(1)	2(1)
C(13)	20(1)	22(1)	24(1)	-5(1)	8(1)	-3(1)
C(24)	26(1)	20(1)	20(1)	3(1)	4(1)	-2(1)
C(4)	20(1)	18(1)	31(1)	1(1)	3(1)	-4(1)
C(12)	28(1)	16(1)	36(1)	-5(1)	15(1)	-1(1)
C(3)	16(1)	25(1)	29(1)	7(1)	7(1)	-2(1)
C(17)	16(1)	41(1)	20(1)	1(1)	3(1)	-4(1)
C(10)	23(1)	24(1)	24(1)	1(1)	2(1)	2(1)
C(19)	30(1)	33(1)	25(1)	5(1)	9(1)	-12(1)
C(26)	41(1)	43(1)	20(1)	0(1)	5(1)	9(1)
C(22)	30(1)	40(1)	22(1)	4(1)	9(1)	-7(1)
C(23)	41(1)	40(1)	38(1)	15(1)	19(1)	18(1)
C(25)	36(1)	24(1)	33(1)	1(1)	11(1)	-1(1)
C(18)	23(1)	46(1)	28(1)	0(1)	8(1)	-16(1)
C(14)	34(1)	25(1)	50(1)	7(1)	12(1)	10(1)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cain89_0m_a.

	x	y	z	U(eq)
H(5)	6219	8583	7886	26
H(2)	7521	7518	4789	25
H(21)	2789	7572	4589	26
H(9)	7470	6598	7819	27
H(7A)	5027	7330	7966	22
H(7B)	3882	7759	6935	22
H(13)	5952	5489	4714	26
H(24)	4926	6190	8017	28
H(4)	7924	9025	7164	29
H(12)	7451	4657	5720	31
H(3)	8560	8501	5619	29
H(17)	-323	6664	4290	32
H(10)	8940	5764	8829	30
H(19)	1493	5483	7219	35
H(26A)	3615	6392	9344	54
H(26B)	4743	5836	9918	54
H(26C)	3135	5653	9235	54
H(22A)	2122	6853	2871	46
H(22B)	1574	7565	2421	46
H(22C)	515	7032	2591	46
H(23A)	-129	7788	4069	57
H(23B)	935	8308	3864	57
H(23C)	1083	8078	5253	57
H(25A)	3825	4910	7725	47
H(25B)	5412	5092	8504	47
H(25C)	4816	5195	7015	47
H(18)	-477	5816	5581	39
H(14A)	8850	4344	8580	56
H(14B)	10183	4760	8604	56
H(14C)	9453	4288	7450	56

Table 1. Crystal data and structure refinement for cain94_0m_a (Compound **6-Pd_2-($P(t\text{-}Bu)_3)_2$**).

Identification code	MC 5-17	
Empirical formula	C43 H77 I N P3 Pd2	
Formula weight	1040.66	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 13.6610(2) Å	α= 90°.
	b = 23.3921(3) Å	β= 106.8940(10)°.
	c = 15.1918(2) Å	γ = 90°.
Volume	4645.17(11) $Å^3$	
Z	4	
Density (calculated)	1.488 Mg/m^3	
Absorption coefficient	1.571 mm^{-1}	
F(000)	2128	
Crystal size	0.29 x 0.27 x 0.17 mm^3	
Theta range for data collection	1.649 to 28.312°.	
Index ranges	-16<=h<=18, -30<=k<=31, -18<=l<=20	
Reflections collected	38348	
Independent reflections	11515 [R(int) = 0.0594]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6555	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11515 / 0 / 472	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0712	
R indices (all data)	R1 = 0.0399, wR2 = 0.0769	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.831 and -0.510 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for cain94_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	7200(1)	5050(1)	8790(1)	14(1)
Pd(1)	6432(1)	6133(1)	8264(1)	10(1)
Pd(2)	7834(1)	5717(1)	7575(1)	9(1)
P(1)	6912(1)	6495(1)	7082(1)	10(1)
P(3)	9395(1)	5494(1)	7301(1)	11(1)
P(2)	5769(1)	6680(1)	9254(1)	13(1)
N(1)	6149(2)	6670(1)	6016(2)	12(1)
C(8)	5559(2)	6282(1)	5323(2)	13(1)
C(13)	5802(2)	6226(1)	4481(2)	14(1)
C(28)	5375(2)	7445(1)	8847(2)	17(1)
C(7)	6021(2)	7290(1)	5816(2)	16(1)
C(9)	4718(2)	5988(1)	5459(2)	14(1)
C(1)	7426(2)	7211(1)	7215(2)	12(1)
C(40)	9195(2)	4836(1)	6530(2)	14(1)
C(10)	4165(2)	5618(1)	4769(2)	18(1)
C(32)	9924(2)	6096(1)	6714(2)	13(1)
C(43)	8580(2)	5016(1)	5555(2)	19(1)
C(17)	6670(2)	6544(1)	4242(2)	17(1)
C(41)	10162(2)	4511(1)	6482(2)	21(1)
C(6)	6867(2)	7580(1)	6532(2)	14(1)
C(42)	8495(2)	4417(1)	6852(2)	19(1)
C(12)	5211(2)	5859(1)	3808(2)	17(1)
C(11)	4401(2)	5548(1)	3954(2)	18(1)
C(2)	8240(2)	7419(1)	7924(2)	15(1)
C(35)	9015(2)	6366(1)	5980(2)	18(1)
C(4)	7919(2)	8363(1)	7269(2)	21(1)
C(36)	10418(2)	5321(1)	8419(2)	18(1)
C(20)	6865(2)	6726(1)	10378(2)	20(1)
C(3)	8484(2)	7996(1)	7951(2)	20(1)
C(33)	10740(2)	5923(1)	6247(2)	19(1)
C(38)	11526(2)	5297(1)	8365(2)	22(1)

C(21)	7874(2)	6830(1)	10137(2)	25(1)
C(24)	4622(2)	6340(1)	9540(2)	22(1)
C(19)	6260(2)	7036(1)	3551(2)	22(1)
C(14)	4305(2)	6092(1)	6277(2)	15(1)
C(29)	6331(2)	7795(1)	8886(2)	21(1)
C(39)	10184(2)	4737(1)	8790(2)	21(1)
C(37)	10347(2)	5769(1)	9140(2)	23(1)
C(5)	7110(2)	8161(1)	6554(2)	19(1)
C(31)	4764(2)	7770(1)	9386(2)	24(1)
C(15)	4083(2)	5538(1)	6720(2)	22(1)
C(34)	10365(2)	6578(1)	7408(2)	21(1)
C(30)	4757(2)	7427(1)	7825(2)	23(1)
C(18)	7303(2)	6148(1)	3818(2)	21(1)
C(25)	4770(3)	5684(1)	9559(3)	27(1)
C(16)	3338(2)	6462(1)	5959(2)	22(1)
C(23)	6768(2)	7188(1)	11078(2)	26(1)
C(26)	4423(3)	6524(1)	10447(3)	31(1)
C(27)	3652(2)	6457(1)	8753(3)	31(1)
C(22)	7011(3)	6143(1)	10875(2)	29(1)

Table 3. Bond lengths [Å] and angles [°] for cain94_0m_a.

I(1)-Pd(1)	2.7678(2)
I(1)-Pd(2)	2.7441(2)
Pd(1)-Pd(2)	2.6215(3)
Pd(1)-P(1)	2.2491(7)
Pd(1)-P(2)	2.3494(7)
Pd(2)-P(1)	2.2157(6)
Pd(2)-P(3)	2.3467(7)
P(1)-N(1)	1.701(2)
P(1)-C(1)	1.804(2)
P(3)-C(40)	1.906(3)
P(3)-C(32)	1.915(3)
P(3)-C(36)	1.903(3)
P(2)-C(28)	1.919(3)
P(2)-C(20)	1.919(3)
P(2)-C(24)	1.916(3)
N(1)-C(8)	1.445(3)
N(1)-C(7)	1.483(3)
C(8)-C(13)	1.417(4)
C(8)-C(9)	1.405(4)
C(13)-C(17)	1.530(4)
C(13)-C(12)	1.398(4)
C(28)-C(29)	1.528(4)
C(28)-C(31)	1.531(4)
C(28)-C(30)	1.536(4)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(7)-C(6)	1.499(4)
C(9)-C(10)	1.399(4)
C(9)-C(14)	1.526(4)
C(1)-C(6)	1.394(4)
C(1)-C(2)	1.392(4)
C(40)-C(43)	1.534(4)
C(40)-C(41)	1.544(4)
C(40)-C(42)	1.545(4)

C(10)-H(10)	0.9500
C(10)-C(11)	1.377(4)
C(32)-C(35)	1.543(4)
C(32)-C(33)	1.539(4)
C(32)-C(34)	1.541(4)
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800
C(17)-H(17)	1.0000
C(17)-C(19)	1.547(4)
C(17)-C(18)	1.531(4)
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800
C(6)-C(5)	1.397(3)
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
C(12)-H(12)	0.9500
C(12)-C(11)	1.395(4)
C(11)-H(11)	0.9500
C(2)-H(2)	0.9500
C(2)-C(3)	1.387(3)
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(4)-H(4)	0.9500
C(4)-C(3)	1.393(4)
C(4)-C(5)	1.388(4)
C(36)-C(38)	1.540(4)
C(36)-C(39)	1.546(4)
C(36)-C(37)	1.539(4)
C(20)-C(21)	1.545(4)
C(20)-C(23)	1.547(4)
C(20)-C(22)	1.543(4)
C(3)-H(3)	0.9500

C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(24)-C(25)	1.549(4)
C(24)-C(26)	1.541(4)
C(24)-C(27)	1.530(5)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(14)-H(14)	1.0000
C(14)-C(15)	1.529(4)
C(14)-C(16)	1.536(4)
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(5)-H(5)	0.9500
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800

C(34)-H(34C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800

Pd(2)-I(1)-Pd(1)	56.795(6)
Pd(2)-Pd(1)-I(1)	61.146(6)
P(1)-Pd(1)-I(1)	113.708(17)
P(1)-Pd(1)-Pd(2)	53.457(17)
P(1)-Pd(1)-P(2)	124.20(2)
P(2)-Pd(1)-I(1)	119.846(19)
P(2)-Pd(1)-Pd(2)	156.989(19)
Pd(1)-Pd(2)-I(1)	62.059(7)
P(1)-Pd(2)-I(1)	115.765(19)
P(1)-Pd(2)-Pd(1)	54.638(18)

P(1)-Pd(2)-P(3)	125.40(2)
P(3)-Pd(2)-I(1)	118.288(17)
P(3)-Pd(2)-Pd(1)	163.728(19)
Pd(2)-P(1)-Pd(1)	71.90(2)
N(1)-P(1)-Pd(1)	127.58(8)
N(1)-P(1)-Pd(2)	130.52(8)
N(1)-P(1)-C(1)	89.72(11)
C(1)-P(1)-Pd(1)	117.04(9)
C(1)-P(1)-Pd(2)	124.05(9)
C(40)-P(3)-Pd(2)	108.24(8)
C(40)-P(3)-C(32)	108.26(12)
C(32)-P(3)-Pd(2)	113.81(8)
C(36)-P(3)-Pd(2)	111.02(9)
C(36)-P(3)-C(40)	108.29(12)
C(36)-P(3)-C(32)	107.06(12)
C(28)-P(2)-Pd(1)	115.20(9)
C(28)-P(2)-C(20)	107.93(13)
C(20)-P(2)-Pd(1)	104.70(9)
C(24)-P(2)-Pd(1)	114.37(9)
C(24)-P(2)-C(28)	106.78(12)
C(24)-P(2)-C(20)	107.45(14)
C(8)-N(1)-P(1)	126.95(16)
C(8)-N(1)-C(7)	117.2(2)
C(7)-N(1)-P(1)	115.65(17)
C(13)-C(8)-N(1)	119.2(2)
C(9)-C(8)-N(1)	120.5(2)
C(9)-C(8)-C(13)	120.2(2)
C(8)-C(13)-C(17)	124.8(2)
C(12)-C(13)-C(8)	118.6(2)
C(12)-C(13)-C(17)	116.6(2)
C(29)-C(28)-P(2)	109.29(19)
C(29)-C(28)-C(31)	107.8(2)
C(29)-C(28)-C(30)	105.4(2)
C(31)-C(28)-P(2)	115.8(2)
C(31)-C(28)-C(30)	109.2(2)
C(30)-C(28)-P(2)	108.75(18)

N(1)-C(7)-H(7A)	110.6
N(1)-C(7)-H(7B)	110.6
N(1)-C(7)-C(6)	105.9(2)
H(7A)-C(7)-H(7B)	108.7
C(6)-C(7)-H(7A)	110.6
C(6)-C(7)-H(7B)	110.6
C(8)-C(9)-C(14)	123.6(2)
C(10)-C(9)-C(8)	118.6(3)
C(10)-C(9)-C(14)	117.5(2)
C(6)-C(1)-P(1)	112.32(19)
C(2)-C(1)-P(1)	127.5(2)
C(2)-C(1)-C(6)	120.1(2)
C(43)-C(40)-P(3)	108.21(17)
C(43)-C(40)-C(41)	109.0(2)
C(43)-C(40)-C(42)	105.3(2)
C(41)-C(40)-P(3)	117.04(19)
C(41)-C(40)-C(42)	108.6(2)
C(42)-C(40)-P(3)	108.05(18)
C(9)-C(10)-H(10)	119.0
C(11)-C(10)-C(9)	122.0(3)
C(11)-C(10)-H(10)	119.0
C(35)-C(32)-P(3)	107.73(17)
C(33)-C(32)-P(3)	116.34(17)
C(33)-C(32)-C(35)	108.3(2)
C(33)-C(32)-C(34)	108.4(2)
C(34)-C(32)-P(3)	110.12(19)
C(34)-C(32)-C(35)	105.5(2)
C(40)-C(43)-H(43A)	109.5
C(40)-C(43)-H(43B)	109.5
C(40)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5
C(13)-C(17)-H(17)	108.4
C(13)-C(17)-C(19)	111.7(2)
C(13)-C(17)-C(18)	112.1(2)

C(19)-C(17)-H(17)	108.4
C(18)-C(17)-H(17)	108.4
C(18)-C(17)-C(19)	107.6(2)
C(40)-C(41)-H(41A)	109.5
C(40)-C(41)-H(41B)	109.5
C(40)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(1)-C(6)-C(7)	113.6(2)
C(1)-C(6)-C(5)	120.6(3)
C(5)-C(6)-C(7)	125.8(2)
C(40)-C(42)-H(42A)	109.5
C(40)-C(42)-H(42B)	109.5
C(40)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(13)-C(12)-H(12)	119.3
C(11)-C(12)-C(13)	121.4(3)
C(11)-C(12)-H(12)	119.3
C(10)-C(11)-C(12)	119.0(3)
C(10)-C(11)-H(11)	120.5
C(12)-C(11)-H(11)	120.5
C(1)-C(2)-H(2)	120.2
C(3)-C(2)-C(1)	119.6(3)
C(3)-C(2)-H(2)	120.2
C(32)-C(35)-H(35A)	109.5
C(32)-C(35)-H(35B)	109.5
C(32)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(3)-C(4)-H(4)	119.5
C(5)-C(4)-H(4)	119.5
C(5)-C(4)-C(3)	121.0(2)

C(38)-C(36)-P(3)	116.0(2)
C(38)-C(36)-C(39)	107.3(2)
C(39)-C(36)-P(3)	109.68(19)
C(37)-C(36)-P(3)	107.95(18)
C(37)-C(36)-C(38)	109.3(2)
C(37)-C(36)-C(39)	106.3(2)
C(21)-C(20)-P(2)	108.5(2)
C(21)-C(20)-C(23)	108.3(2)
C(23)-C(20)-P(2)	116.8(2)
C(22)-C(20)-P(2)	110.0(2)
C(22)-C(20)-C(21)	104.9(3)
C(22)-C(20)-C(23)	107.8(2)
C(2)-C(3)-C(4)	120.1(3)
C(2)-C(3)-H(3)	120.0
C(4)-C(3)-H(3)	120.0
C(32)-C(33)-H(33A)	109.5
C(32)-C(33)-H(33B)	109.5
C(32)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(36)-C(38)-H(38A)	109.5
C(36)-C(38)-H(38B)	109.5
C(36)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(25)-C(24)-P(2)	107.69(19)
C(26)-C(24)-P(2)	117.1(2)
C(26)-C(24)-C(25)	108.5(3)

C(27)-C(24)-P(2)	109.1(2)
C(27)-C(24)-C(25)	105.7(2)
C(27)-C(24)-C(26)	108.2(3)
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(9)-C(14)-H(14)	108.1
C(9)-C(14)-C(15)	113.0(2)
C(9)-C(14)-C(16)	108.7(2)
C(15)-C(14)-H(14)	108.1
C(15)-C(14)-C(16)	110.7(2)
C(16)-C(14)-H(14)	108.1
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(36)-C(39)-H(39A)	109.5
C(36)-C(39)-H(39B)	109.5
C(36)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(36)-C(37)-H(37A)	109.5
C(36)-C(37)-H(37B)	109.5
C(36)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(6)-C(5)-H(5)	120.7
C(4)-C(5)-C(6)	118.6(3)
C(4)-C(5)-H(5)	120.7

C(28)-C(31)-H(31A)	109.5
C(28)-C(31)-H(31B)	109.5
C(28)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(32)-C(34)-H(34A)	109.5
C(32)-C(34)-H(34B)	109.5
C(32)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(28)-C(30)-H(30A)	109.5
C(28)-C(30)-H(30B)	109.5
C(28)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(20)-C(23)-H(23A)	109.5
C(20)-C(23)-H(23B)	109.5
C(20)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(24)-C(26)-H(26A)	109.5
C(24)-C(26)-H(26B)	109.5
C(24)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(24)-C(27)-H(27A)	109.5
C(24)-C(27)-H(27B)	109.5
C(24)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(20)-C(22)-H(22A)	109.5
C(20)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cain94_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	17(1)	11(1)	14(1)	3(1)	7(1)	2(1)
Pd(1)	11(1)	9(1)	11(1)	0(1)	5(1)	0(1)
Pd(2)	9(1)	8(1)	10(1)	1(1)	4(1)	1(1)
P(1)	10(1)	10(1)	10(1)	0(1)	3(1)	1(1)
P(3)	10(1)	12(1)	11(1)	1(1)	4(1)	0(1)
P(2)	14(1)	11(1)	15(1)	-2(1)	7(1)	0(1)
N(1)	14(1)	9(1)	12(1)	1(1)	2(1)	0(1)
C(8)	14(1)	9(1)	13(1)	2(1)	-2(1)	3(1)
C(13)	13(1)	13(1)	14(1)	3(1)	0(1)	4(1)
C(28)	19(1)	12(1)	23(2)	-1(1)	8(1)	2(1)
C(7)	21(1)	10(1)	15(1)	3(1)	4(1)	2(1)
C(9)	13(1)	12(1)	15(1)	0(1)	1(1)	2(1)
C(1)	13(1)	10(1)	15(1)	0(1)	9(1)	1(1)
C(40)	16(1)	11(1)	20(2)	-2(1)	9(1)	1(1)
C(10)	13(1)	17(1)	21(2)	-1(1)	1(1)	0(1)
C(32)	13(1)	15(1)	14(1)	1(1)	6(1)	-1(1)
C(43)	19(1)	24(1)	16(2)	-7(1)	7(1)	-2(1)
C(17)	16(1)	20(1)	15(1)	2(1)	5(1)	0(1)
C(41)	24(1)	17(1)	25(2)	-4(1)	13(1)	4(1)
C(6)	16(1)	12(1)	16(1)	-1(1)	8(1)	-1(1)
C(42)	20(1)	14(1)	26(2)	-3(1)	10(1)	-2(1)
C(12)	18(1)	16(1)	15(1)	1(1)	2(1)	7(1)
C(11)	14(1)	16(1)	19(2)	-3(1)	-1(1)	1(1)
C(2)	13(1)	16(1)	17(1)	-1(1)	5(1)	0(1)
C(35)	18(1)	18(1)	20(2)	5(1)	9(1)	2(1)
C(4)	27(2)	12(1)	28(2)	-3(1)	15(1)	-6(1)
C(36)	15(1)	20(1)	16(2)	5(1)	1(1)	1(1)
C(20)	23(1)	25(1)	13(1)	-4(1)	6(1)	1(1)
C(3)	16(1)	18(1)	27(2)	-8(1)	7(1)	-8(1)
C(33)	18(1)	20(1)	22(2)	3(1)	11(1)	1(1)
C(38)	12(1)	32(2)	21(2)	10(1)	1(1)	1(1)

C(21)	16(1)	36(2)	21(2)	-7(1)	1(1)	2(1)
C(24)	24(2)	16(1)	34(2)	-5(1)	20(1)	-3(1)
C(19)	24(2)	26(1)	17(2)	9(1)	6(1)	-1(1)
C(14)	12(1)	14(1)	19(2)	-1(1)	4(1)	0(1)
C(29)	26(2)	15(1)	28(2)	-3(1)	15(1)	-5(1)
C(39)	17(1)	26(1)	19(2)	12(1)	5(1)	3(1)
C(37)	24(2)	31(2)	11(2)	-1(1)	2(1)	-1(1)
C(5)	26(2)	9(1)	25(2)	3(1)	11(1)	2(1)
C(31)	22(1)	16(1)	36(2)	-7(1)	14(1)	1(1)
C(15)	29(2)	15(1)	23(2)	-1(1)	10(1)	-1(1)
C(34)	24(2)	15(1)	24(2)	2(1)	7(1)	-5(1)
C(30)	25(2)	18(1)	24(2)	-1(1)	4(1)	6(1)
C(18)	18(1)	31(2)	16(2)	-2(1)	7(1)	0(1)
C(25)	32(2)	19(1)	40(2)	-2(1)	23(2)	-6(1)
C(16)	15(1)	23(1)	27(2)	0(1)	5(1)	4(1)
C(23)	30(2)	29(2)	19(2)	-10(1)	9(1)	-3(1)
C(26)	39(2)	26(2)	42(2)	-6(1)	33(2)	-4(1)
C(27)	20(2)	22(1)	54(2)	-10(2)	14(2)	-6(1)
C(22)	39(2)	30(2)	18(2)	2(1)	7(1)	7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cain94_0m_a.

	x	y	z	U(eq)
H(7A)	5346	7423	5853	19
H(7B)	6073	7373	5192	19
H(10)	3610	5408	4866	22
H(43A)	7978	5234	5582	29
H(43B)	8361	4674	5175	29
H(43C)	9009	5254	5285	29
H(17)	7132	6712	4820	20
H(41A)	10612	4772	6277	31
H(41B)	9964	4193	6047	31
H(41C)	10524	4362	7093	31
H(42A)	8868	4258	7452	29
H(42B)	8286	4106	6403	29
H(42C)	7887	4621	6903	29
H(12)	5364	5821	3240	20
H(11)	4018	5292	3497	21
H(2)	8626	7168	8387	18
H(35A)	8793	6109	5450	27
H(35B)	9226	6733	5782	27
H(35C)	8447	6429	6242	27
H(4)	8090	8757	7294	25
H(3)	9037	8141	8434	24
H(33A)	11307	5731	6695	28
H(33B)	10996	6266	6015	28
H(33C)	10437	5664	5734	28
H(38A)	11581	5000	7928	34
H(38B)	11990	5208	8974	34
H(38C)	11711	5668	8159	34
H(21A)	7961	6533	9710	38
H(21B)	8450	6816	10700	38
H(21C)	7852	7206	9847	38

H(19A)	5794	6879	2985	33
H(19B)	6834	7227	3409	33
H(19C)	5892	7312	3822	33
H(14)	4831	6311	6752	18
H(29A)	6701	7879	9528	32
H(29B)	6132	8153	8548	32
H(29C)	6775	7576	8606	32
H(39A)	9468	4728	8791	31
H(39B)	10630	4683	9418	31
H(39C)	10307	4431	8394	31
H(37A)	10524	6147	8952	34
H(37B)	10823	5669	9738	34
H(37C)	9647	5778	9189	34
H(5)	6729	8413	6089	23
H(31A)	4145	7554	9372	35
H(31B)	5184	7817	10025	35
H(31C)	4572	8147	9107	35
H(15A)	3636	5294	6248	33
H(15B)	3744	5629	7189	33
H(15C)	4727	5338	7006	33
H(34A)	9868	6679	7736	32
H(34B)	10506	6913	7079	32
H(34C)	11000	6447	7851	32
H(30A)	5156	7233	7473	35
H(30B)	4604	7819	7595	35
H(30C)	4115	7220	7756	35
H(18A)	7502	5807	4204	32
H(18B)	7919	6350	3780	32
H(18C)	6895	6034	3200	32
H(25A)	4843	5556	8967	41
H(25B)	4174	5497	9669	41
H(25C)	5386	5582	10052	41
H(16A)	3508	6828	5724	32
H(16B)	3066	6532	6479	32
H(16C)	2823	6263	5469	32
H(23A)	6765	7568	10805	39

H(23B)	7349	7157	11634	39
H(23C)	6130	7130	11236	39
H(26A)	4993	6399	10968	47
H(26B)	3786	6350	10490	47
H(26C)	4363	6942	10460	47
H(27A)	3472	6863	8753	47
H(27B)	3090	6223	8835	47
H(27C)	3774	6360	8166	47
H(22A)	6411	6059	11082	44
H(22B)	7623	6157	11407	44
H(22C)	7093	5844	10451	44

Table 1. Crystal data and structure refinement for cain92_0m_a (Compound **7(O)**).

Identification code	DZ-75	
Empirical formula	C38 H46 N2 O0.38 P2	
Formula weight	598.87	
Temperature	100.15 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.6914(5) Å	α= 95.100(2)°.
	b = 12.0731(5) Å	β= 94.213(2)°.
	c = 13.1054(6) Å	γ = 113.203(2)°.
Volume	1681.56(13) $Å^3$	
Z	2	
Density (calculated)	1.183 Mg/m^3	
Absorption coefficient	1.388 mm^{-1}	
F(000)	642	
Crystal size	0.31 x 0.29 x 0.28 mm^3	
Theta range for data collection	3.410 to 68.328°.	
Index ranges	-13<=h<=14, -14<=k<=14, -15<=l<=15	
Reflections collected	15973	
Independent reflections	6003 [R(int) = 0.0366]	
Completeness to theta = 67.679°	97.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6619	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6003 / 0 / 397	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0370, wR2 = 0.0948	
R indices (all data)	R1 = 0.0405, wR2 = 0.0976	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.433 and -0.278 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for cain92_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(2)	5330(1)	4447(1)	7084(1)	14(1)
P(1)	7050(1)	4647(1)	8150(1)	18(1)
N(2)	4139(1)	3509(1)	7681(1)	14(1)
N(1)	7981(1)	4261(1)	7385(1)	15(1)
C(27)	3274(1)	2355(1)	7154(1)	14(1)
C(25)	4248(1)	5443(1)	8379(1)	17(1)
C(28)	2443(1)	2296(1)	6292(1)	16(1)
C(8)	7943(1)	3055(1)	7213(1)	15(1)
C(20)	5094(1)	5766(1)	7649(1)	16(1)
C(10)	7350(1)	1154(1)	6121(1)	22(1)
C(21)	5591(1)	6951(1)	7405(1)	21(1)
C(9)	7360(1)	2320(1)	6268(1)	17(1)
C(13)	8506(1)	2630(1)	7987(1)	17(1)
C(6)	9002(1)	6414(1)	7563(1)	16(1)
C(1)	8060(1)	6243(1)	8201(1)	16(1)
C(7)	9002(1)	5259(1)	7030(1)	17(1)
C(14)	6766(1)	2763(1)	5413(1)	19(1)
C(32)	3286(1)	1290(1)	7504(1)	16(1)
C(22)	5230(2)	7811(1)	7894(1)	25(1)
C(5)	9847(2)	7586(1)	7468(1)	22(1)
C(29)	1695(1)	1156(1)	5749(1)	20(1)
C(26)	3767(1)	4117(1)	8537(1)	19(1)
C(2)	7987(1)	7240(1)	8781(1)	20(1)
C(30)	1745(1)	105(1)	6054(1)	22(1)
C(17)	9197(1)	3423(1)	8994(1)	20(1)
C(4)	9759(2)	8578(1)	8031(1)	24(1)
C(12)	8463(1)	1455(1)	7804(1)	22(1)
C(23)	4393(2)	7490(2)	8622(1)	27(1)
C(33)	2332(1)	3421(1)	5943(1)	19(1)
C(35)	972(1)	3309(2)	5862(1)	24(1)
C(31)	2521(1)	173(1)	6931(1)	19(1)

C(19)	8682(2)	2823(2)	9938(1)	28(1)
C(36)	4073(1)	1323(1)	8491(1)	20(1)
C(16)	5406(2)	1881(2)	5056(1)	27(1)
C(11)	7890(2)	722(1)	6880(1)	24(1)
C(24)	3903(2)	6310(1)	8877(1)	24(1)
C(15)	7537(2)	2981(2)	4496(1)	25(1)
C(3)	8842(2)	8400(1)	8691(1)	23(1)
C(37)	3222(2)	647(2)	9267(1)	34(1)
C(38)	5033(2)	792(2)	8277(1)	30(1)
C(18)	10604(1)	3739(2)	9031(1)	24(1)
C(34)	2866(2)	3689(2)	4916(1)	28(1)
O(1)	6733(2)	4146(2)	8989(2)	19(1)

Table 3. Bond lengths [Å] and angles [°] for cain92_0m_a.

P(2)-P(1)	2.2793(5)
P(2)-N(2)	1.7053(12)
P(2)-C(20)	1.8235(14)
P(1)-N(1)	1.6981(12)
P(1)-C(1)	1.8124(15)
P(1)-O(1)	1.310(2)
N(2)-C(27)	1.4340(18)
N(2)-C(26)	1.4702(18)
N(1)-C(8)	1.4363(18)
N(1)-C(7)	1.4631(18)
C(27)-C(28)	1.4123(19)
C(27)-C(32)	1.4085(19)
C(25)-C(20)	1.395(2)
C(25)-C(26)	1.513(2)
C(25)-C(24)	1.391(2)
C(28)-C(29)	1.398(2)
C(28)-C(33)	1.5203(19)
C(8)-C(9)	1.411(2)
C(8)-C(13)	1.410(2)
C(20)-C(21)	1.393(2)
C(10)-H(10)	0.9500
C(10)-C(9)	1.398(2)
C(10)-C(11)	1.386(2)
C(21)-H(21)	0.9500
C(21)-C(22)	1.390(2)
C(9)-C(14)	1.520(2)
C(13)-C(17)	1.523(2)
C(13)-C(12)	1.398(2)
C(6)-C(1)	1.393(2)
C(6)-C(7)	1.5036(19)
C(6)-C(5)	1.394(2)
C(1)-C(2)	1.401(2)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900

C(14)-H(14)	1.0000
C(14)-C(16)	1.533(2)
C(14)-C(15)	1.535(2)
C(32)-C(31)	1.397(2)
C(32)-C(36)	1.5185(19)
C(22)-H(22)	0.9500
C(22)-C(23)	1.387(2)
C(5)-H(5)	0.9500
C(5)-C(4)	1.392(2)
C(29)-H(29)	0.9500
C(29)-C(30)	1.385(2)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(2)-H(2)	0.9500
C(2)-C(3)	1.386(2)
C(30)-H(30)	0.9500
C(30)-C(31)	1.387(2)
C(17)-H(17)	1.0000
C(17)-C(19)	1.531(2)
C(17)-C(18)	1.531(2)
C(4)-H(4)	0.9500
C(4)-C(3)	1.390(2)
C(12)-H(12)	0.9500
C(12)-C(11)	1.387(2)
C(23)-H(23)	0.9500
C(23)-C(24)	1.393(2)
C(33)-H(33)	1.0000
C(33)-C(35)	1.536(2)
C(33)-C(34)	1.532(2)
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(31)-H(31)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800

C(36)-H(36)	1.0000
C(36)-C(37)	1.532(2)
C(36)-C(38)	1.527(2)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(11)-H(11)	0.9500
C(24)-H(24)	0.9500
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(3)-H(3)	0.9500
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800

N(2)-P(2)-P(1)	101.90(4)
N(2)-P(2)-C(20)	90.64(6)
C(20)-P(2)-P(1)	99.23(5)
N(1)-P(1)-P(2)	105.89(4)
N(1)-P(1)-C(1)	90.58(6)
C(1)-P(1)-P(2)	102.93(5)
O(1)-P(1)-P(2)	111.38(12)
O(1)-P(1)-N(1)	121.29(12)
O(1)-P(1)-C(1)	121.64(13)
C(27)-N(2)-P(2)	120.58(9)
C(27)-N(2)-C(26)	120.15(11)

C(26)-N(2)-P(2)	115.06(9)
C(8)-N(1)-P(1)	123.52(9)
C(8)-N(1)-C(7)	118.87(11)
C(7)-N(1)-P(1)	116.84(9)
C(28)-C(27)-N(2)	120.30(12)
C(32)-C(27)-N(2)	118.69(12)
C(32)-C(27)-C(28)	121.01(13)
C(20)-C(25)-C(26)	114.24(12)
C(24)-C(25)-C(20)	120.01(14)
C(24)-C(25)-C(26)	125.74(14)
C(27)-C(28)-C(33)	122.49(13)
C(29)-C(28)-C(27)	118.24(13)
C(29)-C(28)-C(33)	119.28(12)
C(9)-C(8)-N(1)	119.67(12)
C(13)-C(8)-N(1)	119.37(12)
C(13)-C(8)-C(9)	120.95(13)
C(25)-C(20)-P(2)	110.73(11)
C(21)-C(20)-P(2)	128.64(11)
C(21)-C(20)-C(25)	120.57(13)
C(9)-C(10)-H(10)	119.3
C(11)-C(10)-H(10)	119.3
C(11)-C(10)-C(9)	121.33(14)
C(20)-C(21)-H(21)	120.4
C(22)-C(21)-C(20)	119.30(14)
C(22)-C(21)-H(21)	120.4
C(8)-C(9)-C(14)	122.01(12)
C(10)-C(9)-C(8)	118.25(13)
C(10)-C(9)-C(14)	119.74(13)
C(8)-C(13)-C(17)	122.22(13)
C(12)-C(13)-C(8)	118.54(13)
C(12)-C(13)-C(17)	119.21(13)
C(1)-C(6)-C(7)	114.47(13)
C(1)-C(6)-C(5)	119.92(14)
C(5)-C(6)-C(7)	125.60(13)
C(6)-C(1)-P(1)	111.37(10)
C(6)-C(1)-C(2)	120.43(14)

C(2)-C(1)-P(1)	128.20(12)
N(1)-C(7)-C(6)	106.34(11)
N(1)-C(7)-H(7A)	110.5
N(1)-C(7)-H(7B)	110.5
C(6)-C(7)-H(7A)	110.5
C(6)-C(7)-H(7B)	110.5
H(7A)-C(7)-H(7B)	108.7
C(9)-C(14)-H(14)	107.8
C(9)-C(14)-C(16)	111.76(13)
C(9)-C(14)-C(15)	111.07(12)
C(16)-C(14)-H(14)	107.8
C(16)-C(14)-C(15)	110.42(12)
C(15)-C(14)-H(14)	107.8
C(27)-C(32)-C(36)	122.00(13)
C(31)-C(32)-C(27)	118.26(13)
C(31)-C(32)-C(36)	119.72(13)
C(21)-C(22)-H(22)	119.9
C(23)-C(22)-C(21)	120.10(15)
C(23)-C(22)-H(22)	119.9
C(6)-C(5)-H(5)	120.2
C(4)-C(5)-C(6)	119.57(14)
C(4)-C(5)-H(5)	120.2
C(28)-C(29)-H(29)	119.4
C(30)-C(29)-C(28)	121.20(13)
C(30)-C(29)-H(29)	119.4
N(2)-C(26)-C(25)	105.93(11)
N(2)-C(26)-H(26A)	110.6
N(2)-C(26)-H(26B)	110.6
C(25)-C(26)-H(26A)	110.6
C(25)-C(26)-H(26B)	110.6
H(26A)-C(26)-H(26B)	108.7
C(1)-C(2)-H(2)	120.4
C(3)-C(2)-C(1)	119.12(14)
C(3)-C(2)-H(2)	120.4
C(29)-C(30)-H(30)	120.1
C(29)-C(30)-C(31)	119.85(14)

C(31)-C(30)-H(30)	120.1
C(13)-C(17)-H(17)	107.9
C(13)-C(17)-C(19)	112.03(13)
C(13)-C(17)-C(18)	110.16(12)
C(19)-C(17)-H(17)	107.9
C(19)-C(17)-C(18)	110.84(12)
C(18)-C(17)-H(17)	107.9
C(5)-C(4)-H(4)	119.9
C(3)-C(4)-C(5)	120.28(14)
C(3)-C(4)-H(4)	119.9
C(13)-C(12)-H(12)	119.5
C(11)-C(12)-C(13)	121.08(14)
C(11)-C(12)-H(12)	119.5
C(22)-C(23)-H(23)	119.6
C(22)-C(23)-C(24)	120.90(14)
C(24)-C(23)-H(23)	119.6
C(28)-C(33)-H(33)	107.7
C(28)-C(33)-C(35)	111.77(12)
C(28)-C(33)-C(34)	111.16(12)
C(35)-C(33)-H(33)	107.7
C(34)-C(33)-H(33)	107.7
C(34)-C(33)-C(35)	110.50(12)
C(33)-C(35)-H(35A)	109.5
C(33)-C(35)-H(35B)	109.5
C(33)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(32)-C(31)-H(31)	119.4
C(30)-C(31)-C(32)	121.25(13)
C(30)-C(31)-H(31)	119.4
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5

H(19B)-C(19)-H(19C)	109.5
C(32)-C(36)-H(36)	108.1
C(32)-C(36)-C(37)	109.99(12)
C(32)-C(36)-C(38)	111.40(13)
C(37)-C(36)-H(36)	108.1
C(38)-C(36)-H(36)	108.1
C(38)-C(36)-C(37)	110.90(13)
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(10)-C(11)-C(12)	119.84(14)
C(10)-C(11)-H(11)	120.1
C(12)-C(11)-H(11)	120.1
C(25)-C(24)-C(23)	119.12(15)
C(25)-C(24)-H(24)	120.4
C(23)-C(24)-H(24)	120.4
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(2)-C(3)-C(4)	120.62(14)
C(2)-C(3)-H(3)	119.7
C(4)-C(3)-H(3)	119.7
C(36)-C(37)-H(37A)	109.5
C(36)-C(37)-H(37B)	109.5
C(36)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(36)-C(38)-H(38A)	109.5
C(36)-C(38)-H(38B)	109.5

C(36)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cain92_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(2)	12(1)	12(1)	20(1)	4(1)	4(1)	5(1)
P(1)	11(1)	16(1)	26(1)	-4(1)	1(1)	5(1)
N(2)	12(1)	13(1)	17(1)	1(1)	2(1)	4(1)
N(1)	12(1)	14(1)	19(1)	2(1)	2(1)	6(1)
C(27)	11(1)	14(1)	16(1)	2(1)	4(1)	4(1)
C(25)	14(1)	16(1)	20(1)	0(1)	-1(1)	5(1)
C(28)	14(1)	18(1)	16(1)	3(1)	4(1)	5(1)
C(8)	12(1)	15(1)	19(1)	3(1)	4(1)	6(1)
C(20)	11(1)	15(1)	21(1)	1(1)	-2(1)	6(1)
C(10)	21(1)	18(1)	24(1)	-1(1)	3(1)	6(1)
C(21)	18(1)	17(1)	28(1)	6(1)	3(1)	8(1)
C(9)	13(1)	17(1)	19(1)	1(1)	3(1)	4(1)
C(13)	12(1)	19(1)	21(1)	4(1)	3(1)	6(1)
C(6)	17(1)	17(1)	16(1)	3(1)	-2(1)	8(1)
C(1)	13(1)	17(1)	18(1)	0(1)	-4(1)	6(1)
C(7)	19(1)	16(1)	18(1)	5(1)	5(1)	7(1)
C(14)	20(1)	18(1)	19(1)	-1(1)	0(1)	8(1)
C(32)	14(1)	16(1)	18(1)	4(1)	5(1)	6(1)
C(22)	25(1)	15(1)	38(1)	4(1)	1(1)	9(1)
C(5)	22(1)	20(1)	23(1)	5(1)	4(1)	7(1)
C(29)	17(1)	22(1)	17(1)	1(1)	-1(1)	5(1)
C(26)	18(1)	17(1)	19(1)	1(1)	5(1)	6(1)
C(2)	16(1)	21(1)	23(1)	-3(1)	0(1)	7(1)
C(30)	21(1)	16(1)	22(1)	-3(1)	2(1)	2(1)
C(17)	19(1)	23(1)	20(1)	2(1)	0(1)	11(1)
C(4)	24(1)	16(1)	29(1)	3(1)	1(1)	4(1)
C(12)	22(1)	21(1)	27(1)	7(1)	4(1)	12(1)
C(23)	26(1)	19(1)	38(1)	-4(1)	4(1)	12(1)
C(33)	17(1)	19(1)	20(1)	4(1)	-1(1)	7(1)
C(35)	20(1)	26(1)	28(1)	5(1)	1(1)	12(1)
C(31)	21(1)	13(1)	23(1)	3(1)	5(1)	6(1)

C(19)	25(1)	36(1)	24(1)	5(1)	4(1)	13(1)
C(36)	19(1)	16(1)	22(1)	4(1)	-1(1)	7(1)
C(16)	22(1)	31(1)	26(1)	1(1)	-4(1)	8(1)
C(11)	26(1)	16(1)	33(1)	3(1)	6(1)	10(1)
C(24)	21(1)	22(1)	28(1)	-2(1)	6(1)	8(1)
C(15)	30(1)	25(1)	21(1)	3(1)	3(1)	11(1)
C(3)	23(1)	16(1)	27(1)	-4(1)	-3(1)	8(1)
C(37)	29(1)	46(1)	22(1)	12(1)	2(1)	8(1)
C(38)	26(1)	29(1)	41(1)	10(1)	0(1)	16(1)
C(18)	19(1)	30(1)	24(1)	3(1)	-2(1)	10(1)
C(34)	27(1)	33(1)	28(1)	15(1)	6(1)	14(1)
O(1)	21(2)	22(2)	15(1)	9(1)	7(1)	7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cain92_0m_a.

	x	y	z	U(eq)
H(10)	6965	648	5487	26
H(21)	6170	7169	6911	25
H(7A)	8863	5230	6272	21
H(7B)	9814	5205	7212	21
H(14)	6761	3558	5696	23
H(22)	5558	8620	7728	30
H(5)	10480	7708	7023	26
H(29)	1142	1100	5159	24
H(26A)	4143	4023	9208	23
H(26B)	2844	3767	8523	23
H(2)	7359	7121	9231	24
H(30)	1248	-660	5664	26
H(17)	9075	4199	9012	24
H(4)	10328	9379	7964	29
H(12)	8833	1154	8321	27
H(23)	4150	8083	8950	33
H(33)	2842	4127	6474	23
H(35A)	469	2679	5295	36
H(35B)	953	4088	5730	36
H(35C)	628	3088	6510	36
H(31)	2534	-554	7147	23
H(19A)	7775	2593	9882	42
H(19B)	9085	3396	10565	42
H(19C)	8856	2096	9971	42
H(36)	4537	2192	8798	24
H(16A)	5390	1114	4724	41
H(16B)	5025	2238	4564	41
H(16C)	4934	1727	5654	41
H(11)	7867	-75	6767	29
H(24)	3341	6100	9386	29

H(15A)	8399	3560	4733	38
H(15B)	7163	3311	3974	38
H(15C)	7543	2210	4196	38
H(3)	8802	9081	9084	27
H(37A)	2599	987	9377	51
H(37B)	3730	738	9924	51
H(37C)	2794	-217	8998	51
H(38A)	4599	-48	7943	45
H(38B)	5510	806	8928	45
H(38C)	5607	1277	7821	45
H(18A)	10750	2992	9017	37
H(18B)	11044	4280	9666	37
H(18C)	10920	4146	8433	37
H(34A)	3731	3751	4979	42
H(34B)	2854	4457	4741	42
H(34C)	2356	3030	4372	42