# Hydrophosphination using [GeCl{N(SiMe$_3$)$_2$}$_3$] as a pre-catalyst

Authors

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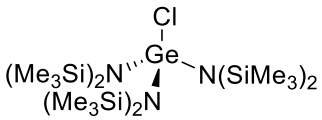
## Contents

## 1. General Considerations

Reagents were obtained from commercial sources (Sigma Aldrich, Fischer, ACROS) and dried/distilled before use. Pentane, diethyl ether, tetrahydrofuran, toluene and acetonitrile were dried over sodium/benzophenone and distilled before use. Dichloromethane was dried over calcium hydride and distilled before use. NMR data was collected at 300, 400 or 500 MHz on Bruker or Agilent instruments in $C_6D_6$/$CDCl_3$/$CD_3CN$ at 298 K and referenced to residual protic solvent. All manipulations were carried out under an inert atmosphere using standard Schlenk and glovebox techniques, unless otherwise stated. All catalytic reactions were undertaken in Teflon-sealed J-Young NMR tubes under an atmosphere of argon. Crystal structures were obtained from either a Rigaku Oxford Diffraction Xcalibur (MoKα (λ = 0.71073)) or Supernova (CuKα (λ = 1.54184)) diffractometer.

## 2. Catalyst Synthesis and Spectroscopic Data

**1**



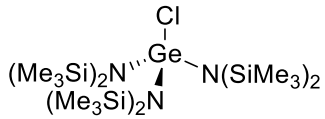

$NaN(SiMe_3)_2$ (3.3 g, 18 mmol) was added to $GeCl_4$ (0.386 g, 1.8 mmol) in THF (20 mL). The solution was then refluxed for 96h after which the solvent was removed in *vacuo*. The solid residue was extracted with pentane (3 x 10 mL) and the extract concentrated before being stored at -35 °C in the glovebox, yielding **1** as colorless crystals (0.663 g, 63%).

$^1H$ NMR (300 MHz, 298 K, $C_6D_6$): δ 0.25 (s, 54H, N(Si*Me*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $C_6D_6$): δ 6.9 (N(Si*Me*$_3$)$_2$). IR (solid): ν 2947, 2094, 1602, 1438, 1249, 1181, 1058, 932, 880, 816 $cm^{-1}$. Melting Point: 141-143 °C.

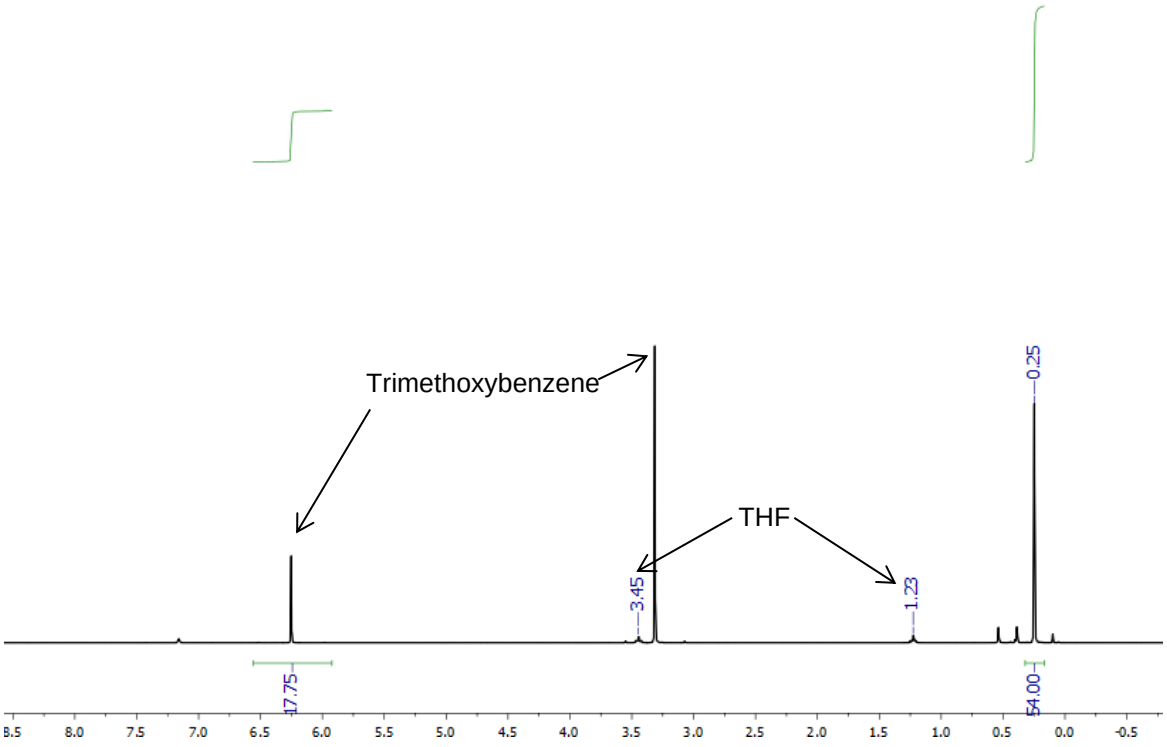
Peaks corresponding to THF are also present in both $^1H$ and $^{13}C$ NMR (see below). As mentioned in the main text, $[Ge(N(SiMe_3)_2)_4(THF)_2]$ was proposed as the product of the same reaction undertaken by Thomas and co-workers.[1] DOSY analysis was performed on a sample of **1** in order to see if the THF present was coordinated to Ge, similar to that proposed by Thomas. The DOSY spectrum below clearly shows that **1** and the THF molecules diffuse at different speeds in solution, indicating that the THF is not in fact coordinating in this case. This is further evidenced by the crystal structure of **1**.

NMR Spectra:

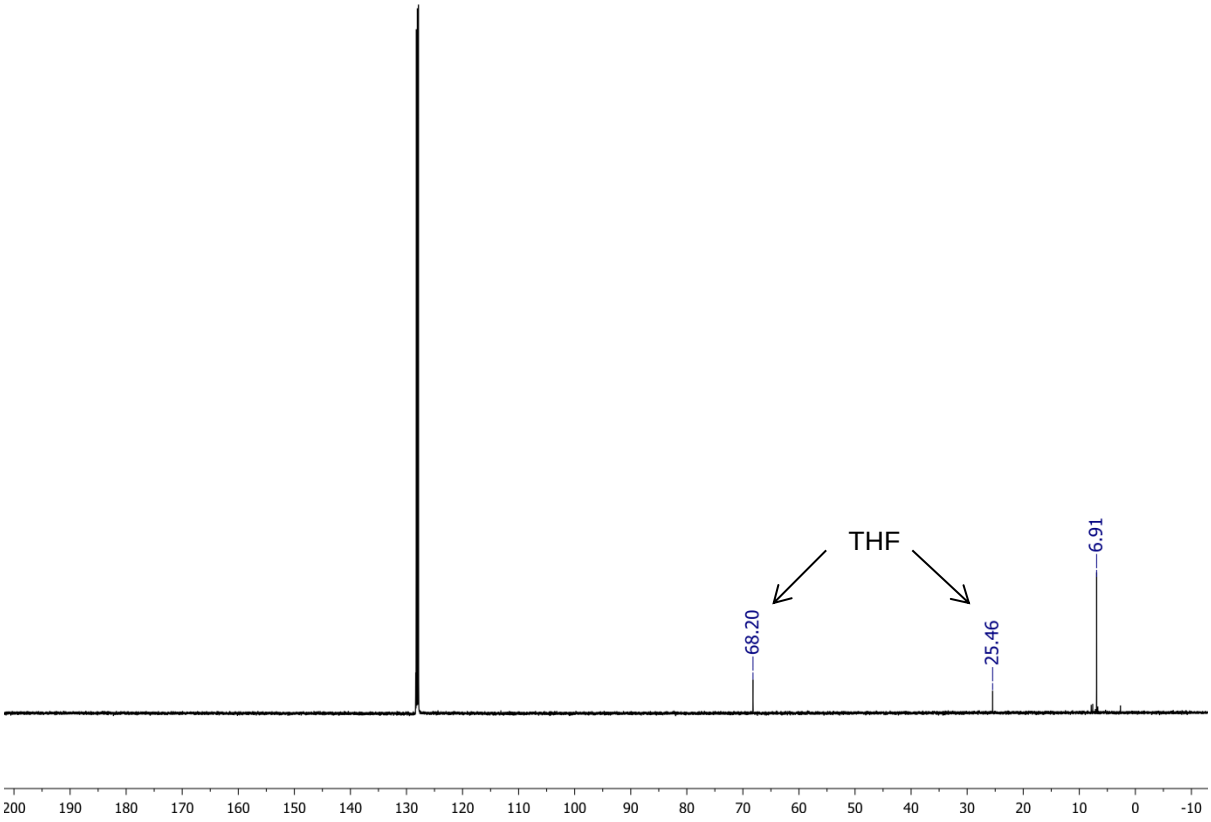
**1**



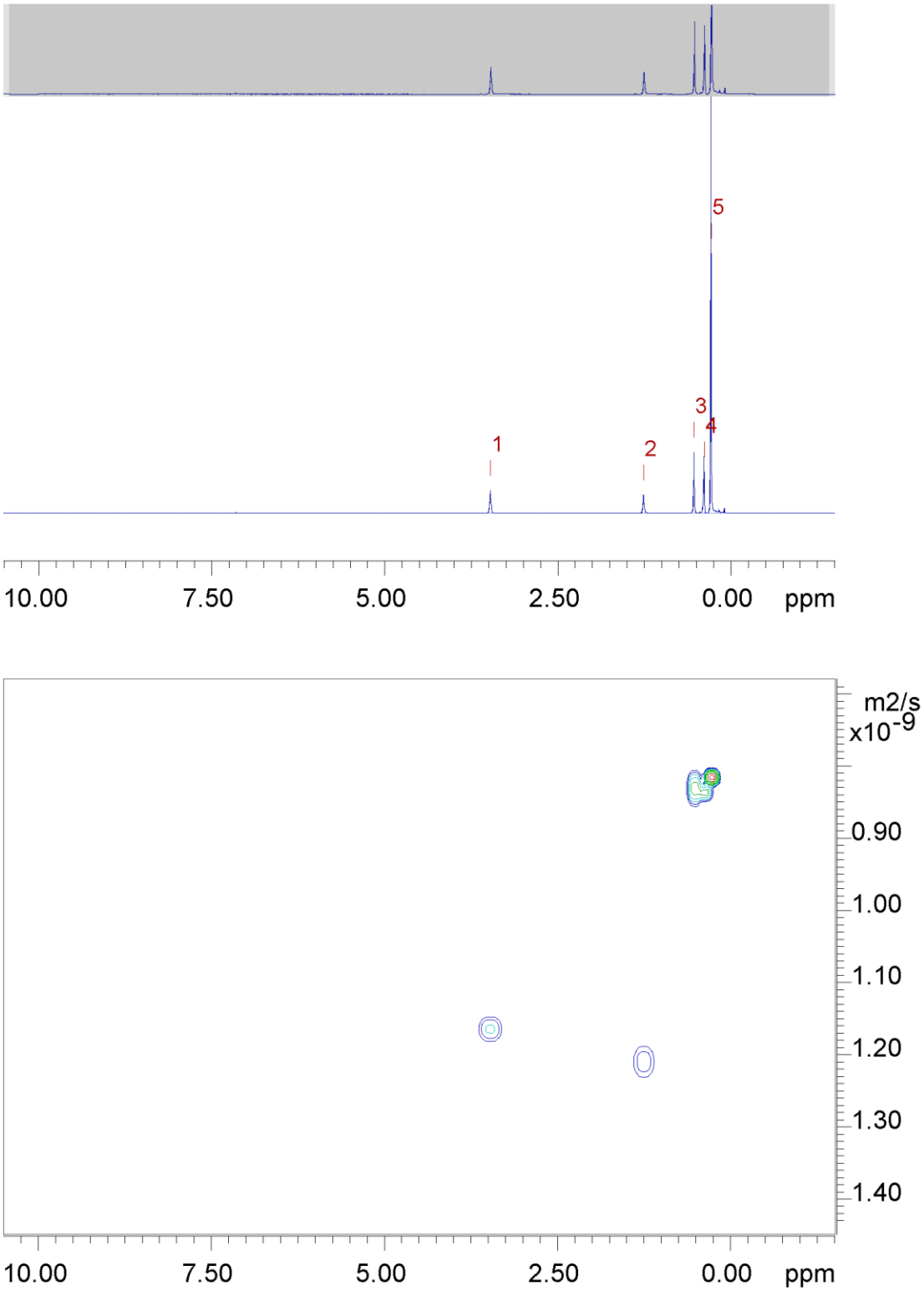

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



$^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, $C_6D_6$):



$^{1}$H DOSY (500 MHz, 298 K, $C_6D_6$):

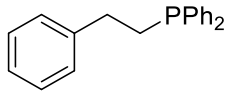


## 3. General Method for the Hydrophosphination of Styrenes with 1

**1** (14.7 mg, 5 mol%) was added to a J-Young NMR tube along with a measured amount of trimethoxybenzene internal standard. $C_6D_6$ (0.6 mL) was added before the addition of styrene (0.6 mmol) then $Ph_2PH$ (87 μL, 0.5 mmol). After the reagents were mixed, the reaction was left at RT for 18 h. Spectroscopic yield was determined by integration of product alkyl $CH_2$ signal against the trimethoxybenzene internal standard in the $^1H$ NMR spectrum. In the cases of **2r** and **2s**, spectroscopic yield was determined by integration of product signal against a $P(OEt)_3$ capillary in the inverse-gated $^{31}P\{^1H\}$ NMR.

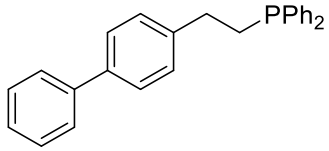
## 4. Spectroscopic Data for Hydrophosphination Products

**2a**



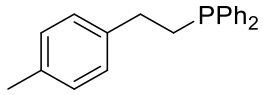

Not isolated. Spectroscopic Yield: 94%. $^1H$ NMR (300 MHz, 298K, $C_6D_6$): δ 7.46-7.40 (m, 4H), 7.16-7.04 (m, 8H), 6.99 (d, 2H, $^3J_{H-H}$ = 7.9 Hz), 2.75-2.64 (m, 2H), 2.30-2.20 (m, 2H). $^{31}P$ NMR (121.5 MHz, 298 K, $C_6D_6$): δ -16.1 (s). The values are in accordance to the literature.[2]

**2b**



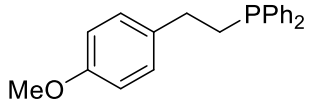

Not isolated. Spectroscopic Yield: 98%. $^1H$ NMR (300 MHz, 298K, $C_6D_6$): δ 7.55-7.40 (m, 8H), 7.29-7.00 (m, 11H), 2.81-2.67 (m, 2H), 2.35-2.24 (m, 2H). $^{31}P$ NMR (121.5 MHz, 298 K, $C_6D_6$): δ -15.1 (s). The values are in accordance to the literature.[2]

**2c**



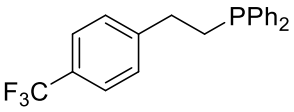

Not isolated. Spectroscopic Yield: 94%[a]. $^1H$ NMR (300 MHz, 298K, $C_6D_6$): δ 7.48-7.42 (m, 4H), 7.26-6.95 (m, 10 H), 2.76-2.69 (m, 2H), 2.33-2.28 (m, 2H), 2.17 (s, 3H). $^{31}P$ NMR (121.5 MHz, 298 K, $C_6D_6$): δ -16.1 (s). The values are in accordance to the literature.[2]

**2d**



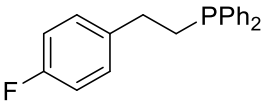

Not isolated. Spectroscopic Yield: 56%.[a] $^1H$ NMR (300 MHz, 298K, $C_6D_6$): δ 7.49-7.44 (m, 4H), 7.24 (d, 2H, $^3J_{H-H}$ = 8.7 Hz), 7.17-7.09 (m, 6H), 6.96 (d, 2H, $^3J_{H-H}$ = 8.7 Hz), 3.39 (s, 3H) 2.74-2.68 (m, 2H), 2.33-2.28 (m, 2H). $^{31}P$ NMR (121.5 MHz, 298 K, $C_6D_6$): δ -16.3 (s). The values are in accordance to the literature.[2]

**2e**



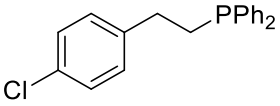

Not isolated. Spectroscopic Yield: 83%.[a] .$^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.46-7.31 (m, 6H), 7.19-7.01 (m, 6H), 6.80 (d, 2H, $^{3}J_{H-H}$ = 7.9 Hz), 2.61-2.53 (m, 2H), 2.17-2.11 (m, 2H). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ -16.2 (s). The values are in accordance to the literature.[2]

**2f**



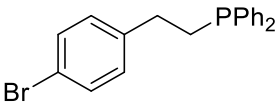

Not isolated. Spectroscopic Yield: 76%.[a] $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.46-7.37 (m, 4H), 7.15-6.97 (m, 6H), 6.83-6.69 (m, 4H), 2.62-2.51 (m, 2H), 2.20-2.11 (m, 2H). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ -15.5 (s). The values are in accordance to the literature.[3]

**2g**



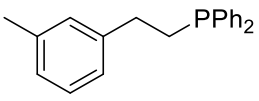

Not isolated. Spectroscopic Yield: 94%. $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.46-7.38 (m, 4H), 7.18-7.05 (m, 8H) 6.68 (d, 2H, $^{3}J_{H-H}$ = 8.4 Hz), 2.57-2.50 (m, 2H), 2.17-2.11 (m, 2H). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ -16.3 (s). The values are in accordance to the literature.[2]

**2h**



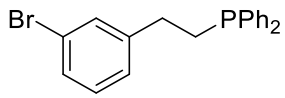

Not isolated. Spectroscopic Yield: 51%. z$^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.48-7.33 (m, 6H), 7.26-7.20 (m, 4H) 6.86 (d, 2H, $^{3}J_{H-H}$ = 8.3 Hz), 6.60 (d, 2H, $^{3}J_{H-H}$ = 8.3 Hz), 2.56-2.44 (m, 2H), 2.16-2.06 (m, 2H). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ -15.4 (s). The values are in accordance to the literature.[2]

**2i**



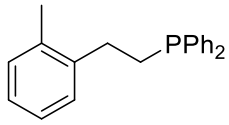

Not isolated. Spectroscopic Yield: 92%. $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.48-7.42 (m, 4H), 7.16-7.07 (m, 6H), 6.93 (d, 1H, $^{3}J_{H-H}$ = 7.7 Hz), 6.90-6.84 (m, 3H), 2.76-2.69 (m, 2H), 2.33-2.27 (m, 2H), 2.16 (s, 3H). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ -15.9 (s). The values are in accordance to the literature.[2]

**2j**



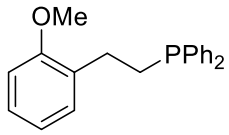

Not isolated. Spectroscopic Yield: 82%. $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.47-7.34 (m, 4H), 7.16-7.09 (m, 6H), 7.02-6.96 (m, 1H) 6.8-6.71 (m, 3H), 2.56-2.44 (m, 2H), 2.15-2.07 (m, 2H). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ -16.1 (s). The values are in accordance to the literature.[2]

**2k**



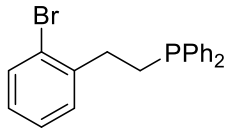

Not isolated. Spectroscopic Yield: 92%. $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.48-7.38 (m, 4H), 7.15-6.95 (m, 10H), 2.74-2.64 (m, 2H), 2.24-2.16 (m, 2H), 1.98 (s, 3H). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ -14.8 (s). The values are in accordance to the literature.[4]

**2l**



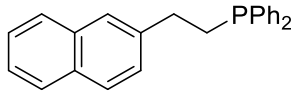

Not isolated. Spectroscopic Yield: 89%. $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.53-7.44 (m, 4H), 7.15-7.05 (m, 7H), 7.02 (dd, 1H, J = 7.6 Hz, 1.8 Hz), 6.85 (apt. td, 1H, J = 7.6 Hz, 1.2 Hz), 6.55 (dd, 1H, J = 8.3 Hz, 1.1 Hz), 3.29 (s, 3H), 2.99-2.89 (m, 2H), 2.45-2.36 (m, 2H). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ -14.8 (s). The values are in accordance to the literature.[2]

**2m**



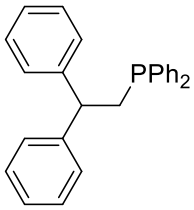

Not isolated. Spectroscopic Yield: 84%. $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.49-7.42 (m, 4H), 7.25 (dd, 1H, J = 7.8 Hz, 1.8 Hz), 7.16-7.07 (m, 6H), 6.92-6.85 (m, 2H), 6.72-6.67 (m, 1H), 2.90-2.80 (m, 2H), 2.33-2.24 (m, 2H). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ -15.7 (s). The values are in accordance to the literature.[4]

**2n**



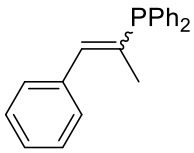

Not isolated. Spectroscopic Yield: 90%. $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.66-7.53 (m, 4H), 7.49-7.43 (m, 4H), 7.31-7.20 (m, 3H), 7.14-6.05 (m, 6H), 2.87-2.80 (m, 2H), 2.36-2.30 (m, 2H). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ -15.8 (s). The values are in accordance to the literature.[3]

**2o**



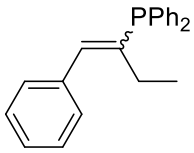

Not isolated. Spectroscopic Yield: 70%.[a] $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.43-6.99 (m, 20H), 4.04 (app. q, 1H, J = 8.0 Hz), 2.81 (d, 2H, $^{3}J_{H-H}$ = 7.9 Hz). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ -20.0 (s). The values are in accordance to the literature.[3]

**2p**



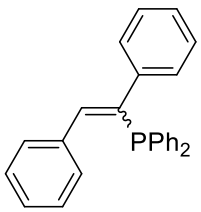

Not isolated. Spectroscopic Yield: 84%.[b] *E*:*Z* = 3.9:1. $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.58-6.93 (m, 16H, Ar), 2.01 (dd, 3H, J = 8.8 Hz, 1.5 Hz, *Z*-product -$CH_3$) 1.78 (dd, 3H, J = 2.8, 1.6 Hz, *E*-product –$CH_3$). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ 9.5 (m, *Z*-product), -12.3 (d, J = 25.9 Hz, *E*-product). The values are in accordance to the literature.[5]

**2q**



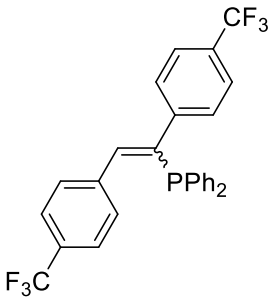

Not isolated. Spectroscopic Yield: 99%.[a] *E*:*Z* = 1:1. $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.60-7.42 (m, 8H, *Z*+*E*-product Ar), 7.31 (d, 1H, J = 26.6 Hz, *E*-product C*H*), 7.17-7.08 (m, 7H), 6.66 (d, 1H, J = 9.9 Hz, *Z*-product CH), 2.60-2.47 (m, 2H, *E*-product –$CH_2$), 2.20-2.07 (m, 2H, *Z*-product –$CH_2$), 1.15 (t, 3H, J = 7.5 Hz, *Z*-product –$CH_3$), 0.87 (t, 3H, J = 7.3 Hz, *E*-product-$CH_3$). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ 2.2 (m, *E*-product), -10.5 (d, J = 26.6 Hz, *Z*-product). FTIR (solid): v 3053, 2965, 2929, 2872, 1585, 1478, 1433, 1374, 1307, 1179, 1092, 1068, 1026, 909, 742, 695. HRMS (ESI): $[M+H]^+$ 317.1461 (calcd.), 317.1459 (obs.).

**2r**




Not isolated. Spectroscopic Yield: 81%.[c] *E*:*Z* = 1.3:1. $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.64-6.73 (m, 21H). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ 8.8 (s, *E*-product), -7.1 (s, *Z*-product). The values are in accordance to the literature.[5]

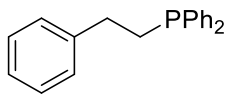
**2s**



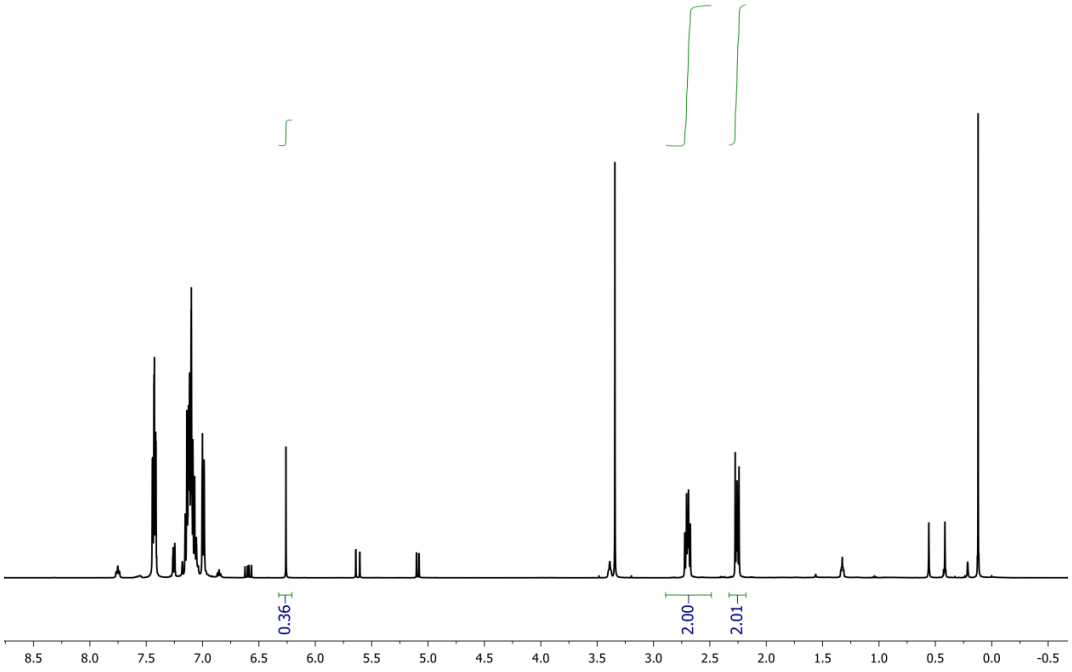

Not isolated. Spectroscopic Yield: 41%.[b] *E*:*Z* = 2:1. $^{1}$H NMR (300 MHz, 298K, $C_6D_6$): δ 7.49 – 6.55 (m, 19H). $^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$): δ 1.52 (s, *Z*-product), -9.2 (s, *E*-product). $^{19}$F NMR (470.6 MHz, 298K, $C_6D_6$) -62.7 (s). FTIR (solid): 3055, 1614, 1480, 1435, 1407, 1319, 1167, 1119, 1106, 1065, 840, 830, 741, 694. HRMS (ESI): $[M+H]^+$ 501.1213 (calcd.), 501.1205 (obs.).

## 5. Crude NMR Spectra for Hydrophosphination Products

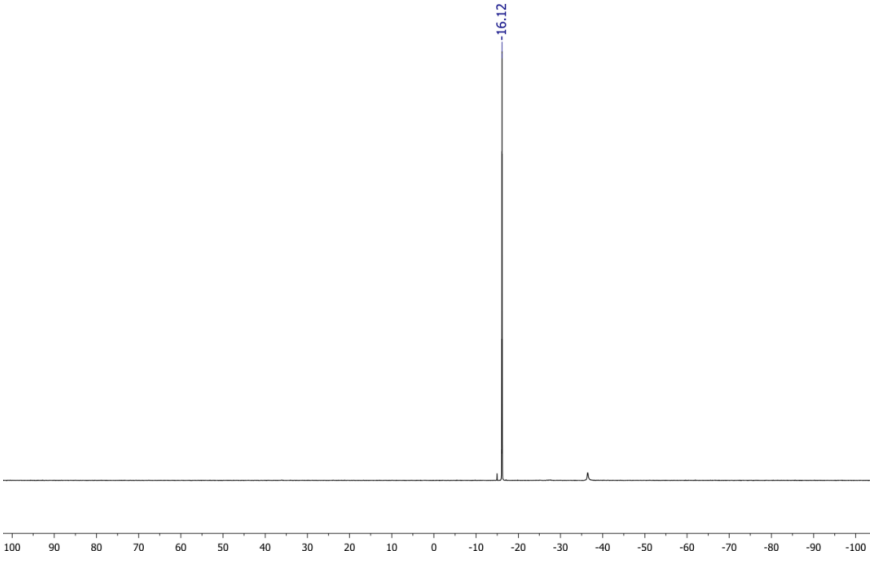
### 2a




$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):




$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



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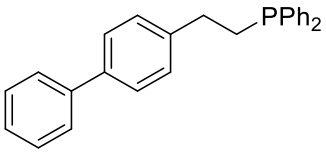
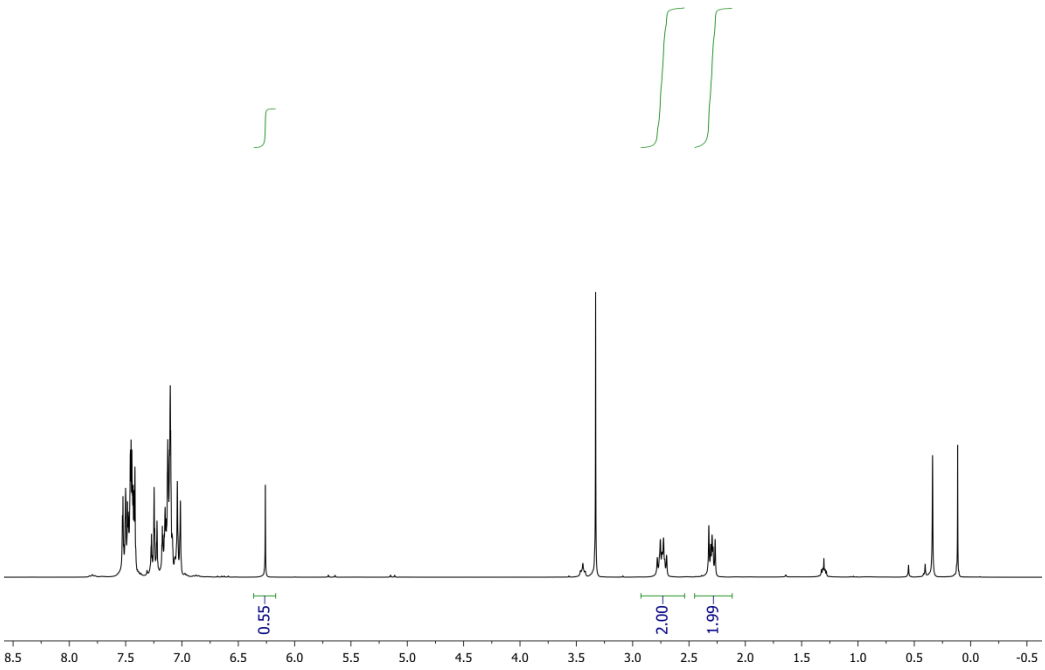
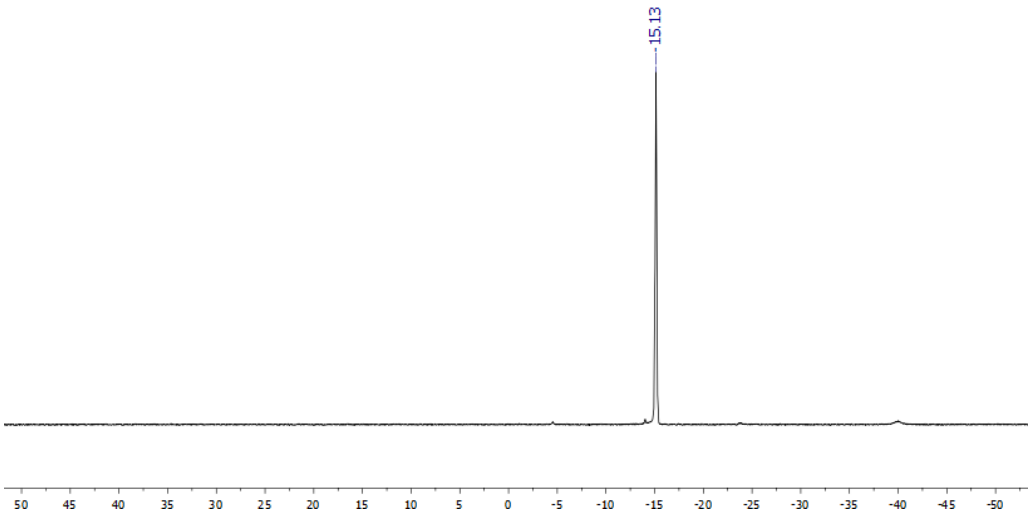


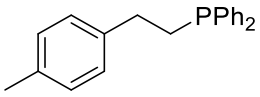

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



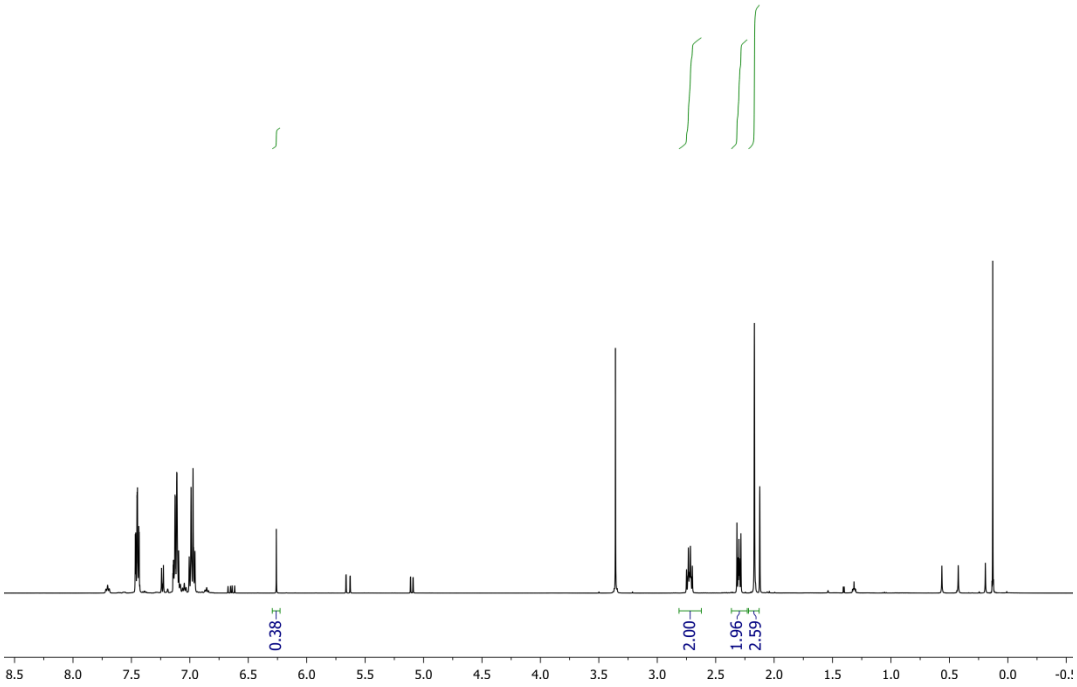

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



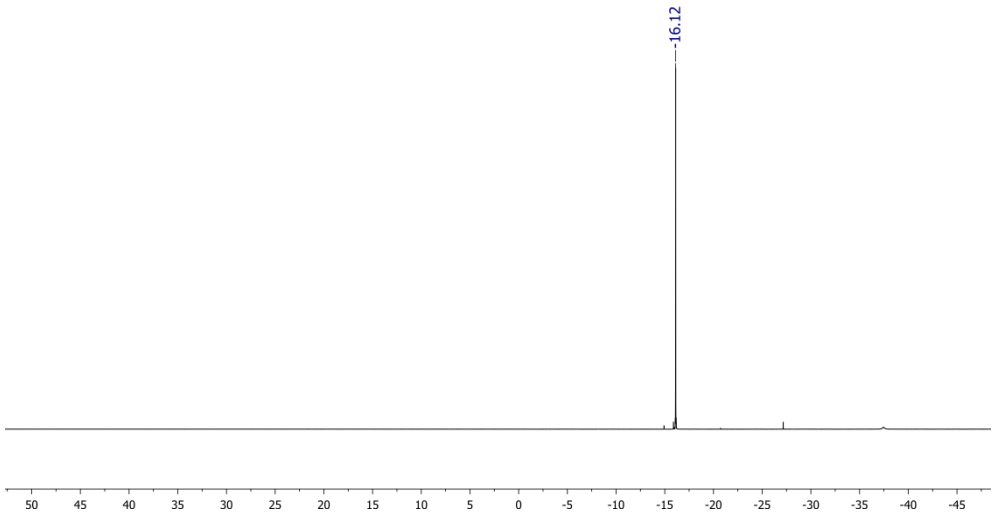
**2c**



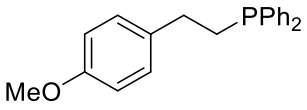

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



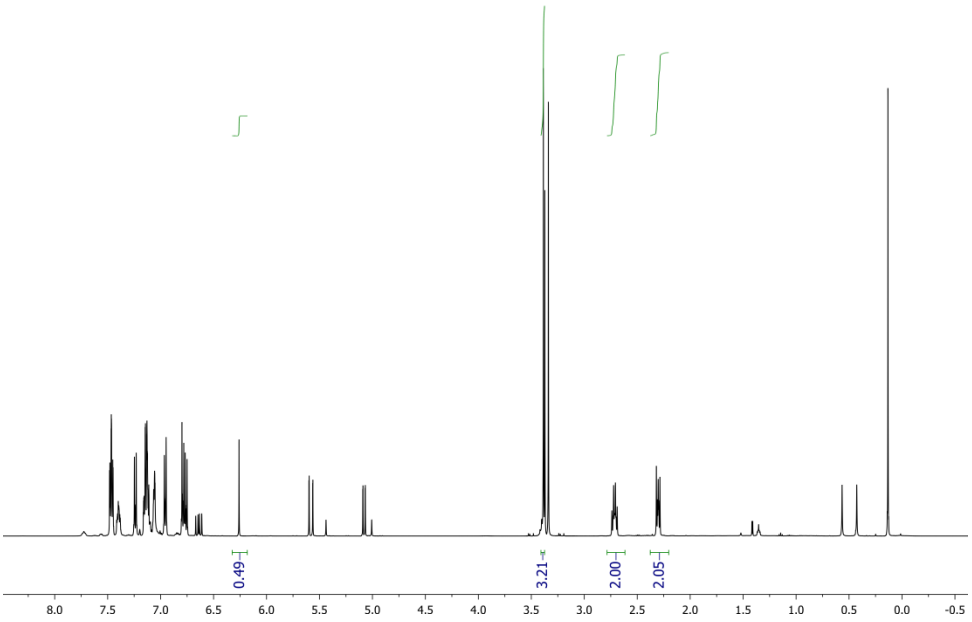

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



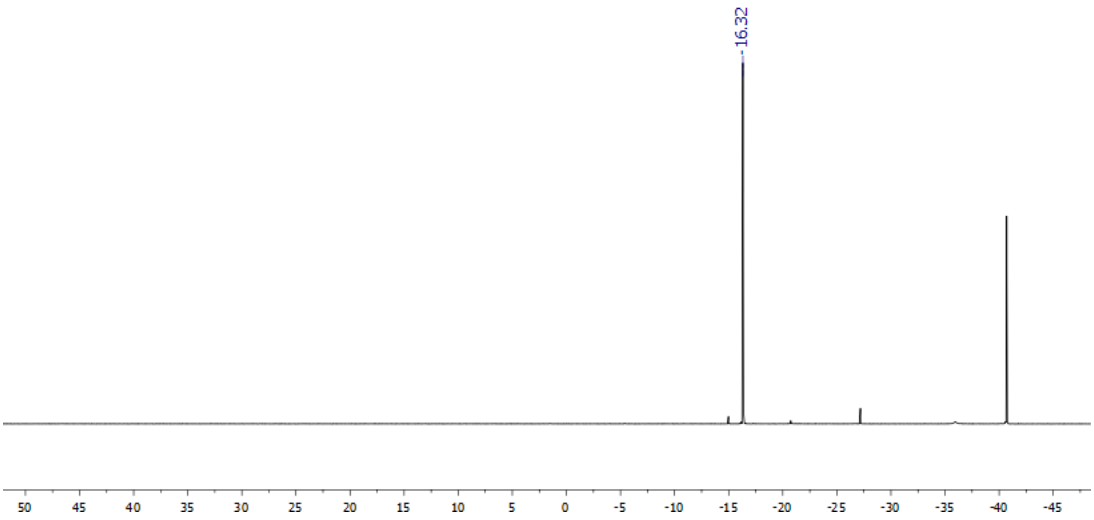
**2d**



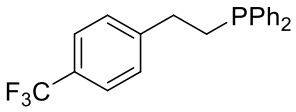

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



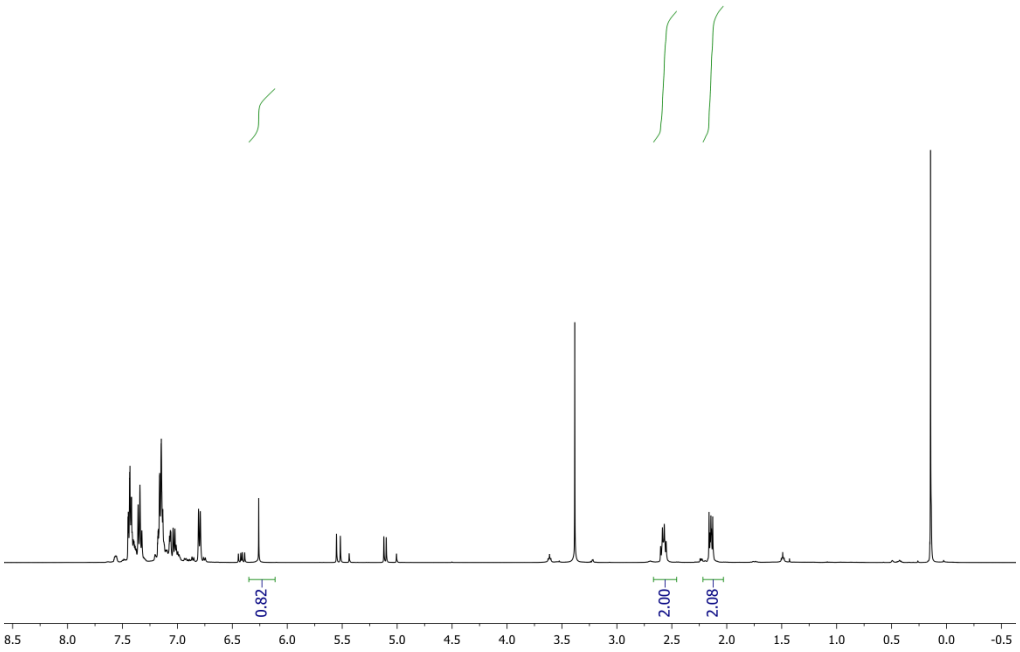

$^{31}$P NMR (121.5MHz, 298 K, $C_6D_6$):



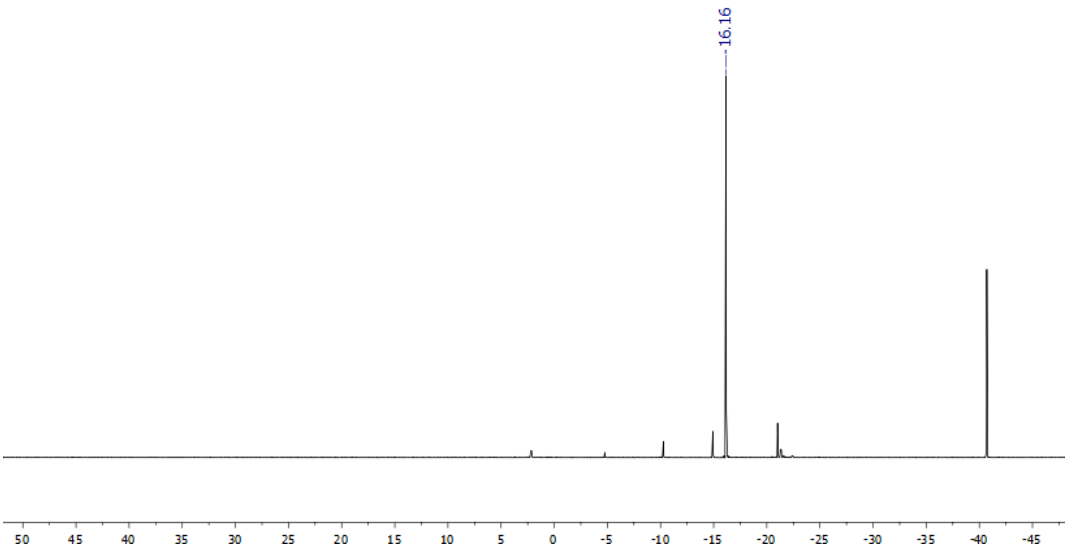
**2e**



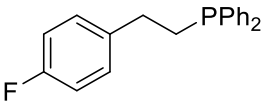

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



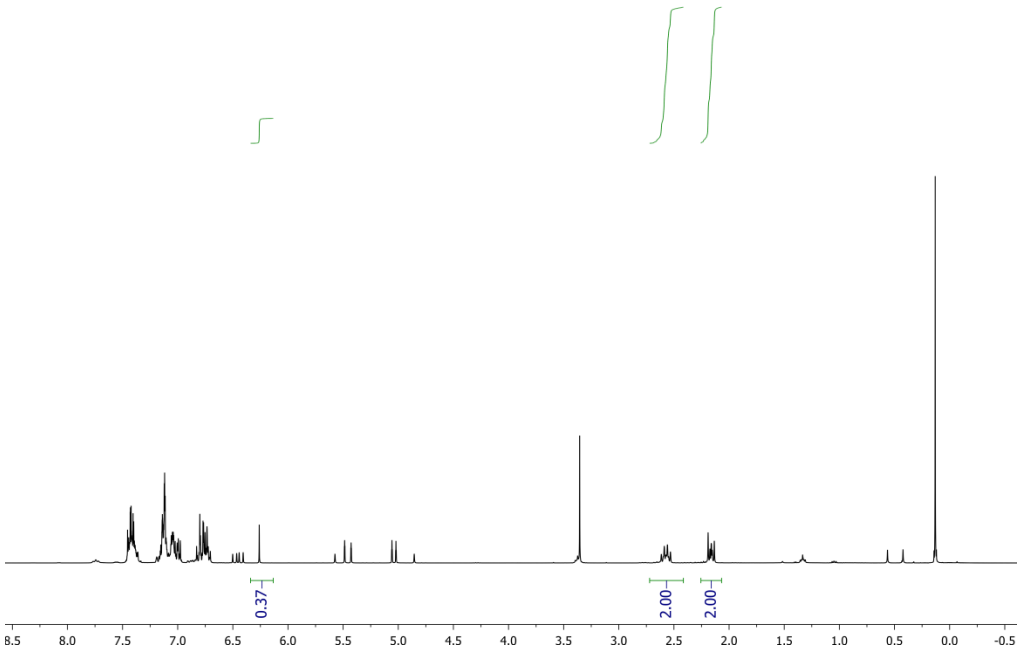

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



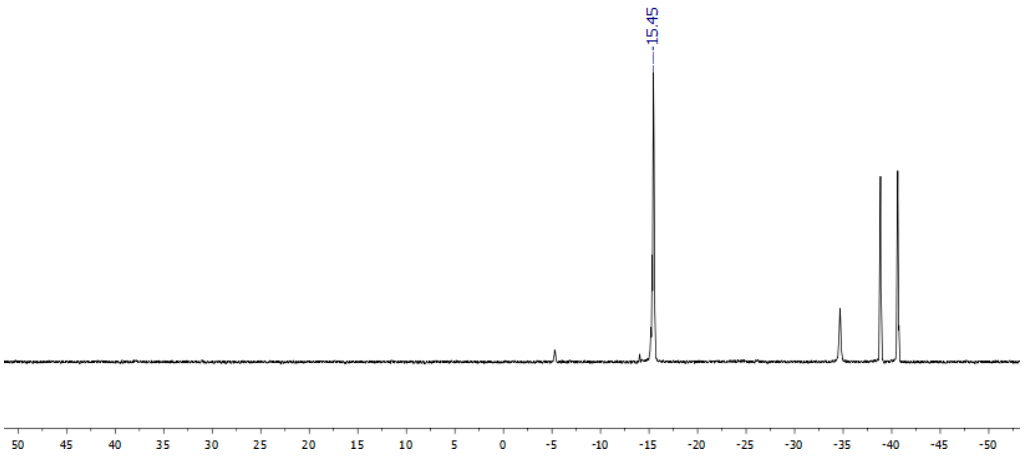
**2f**



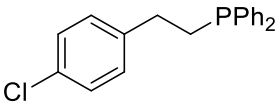

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



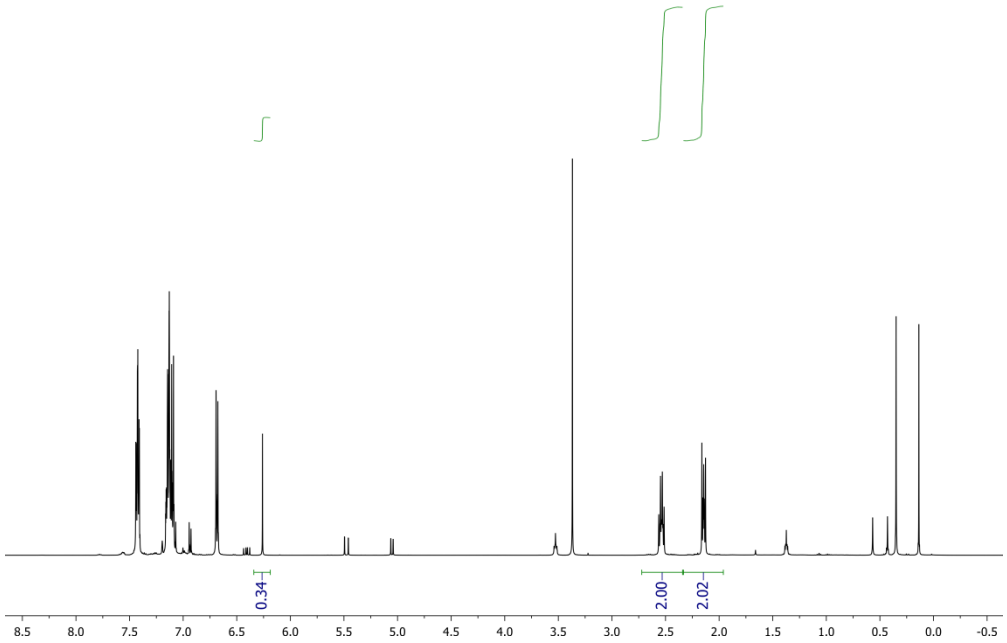

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



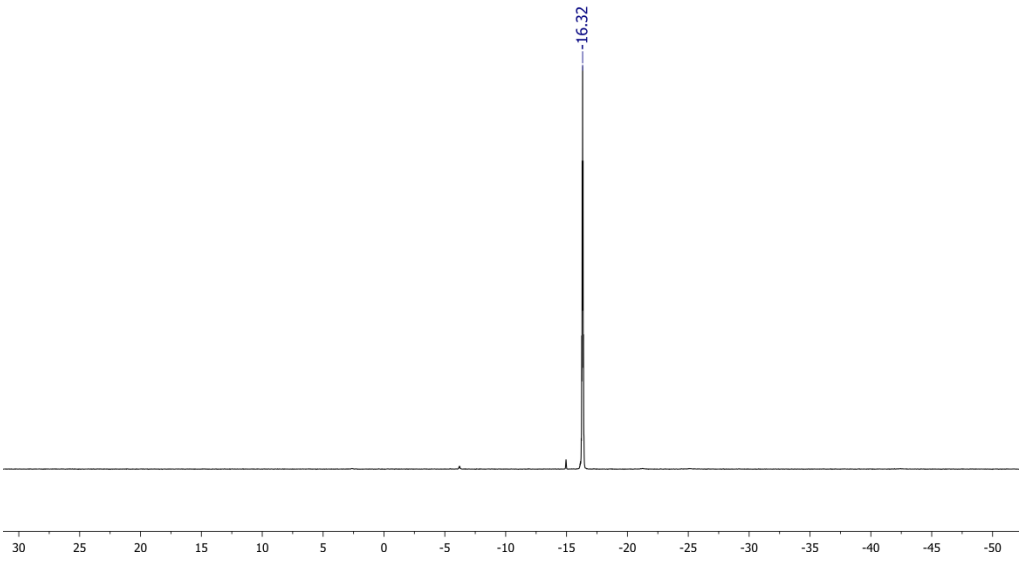
**2g**



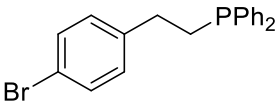

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



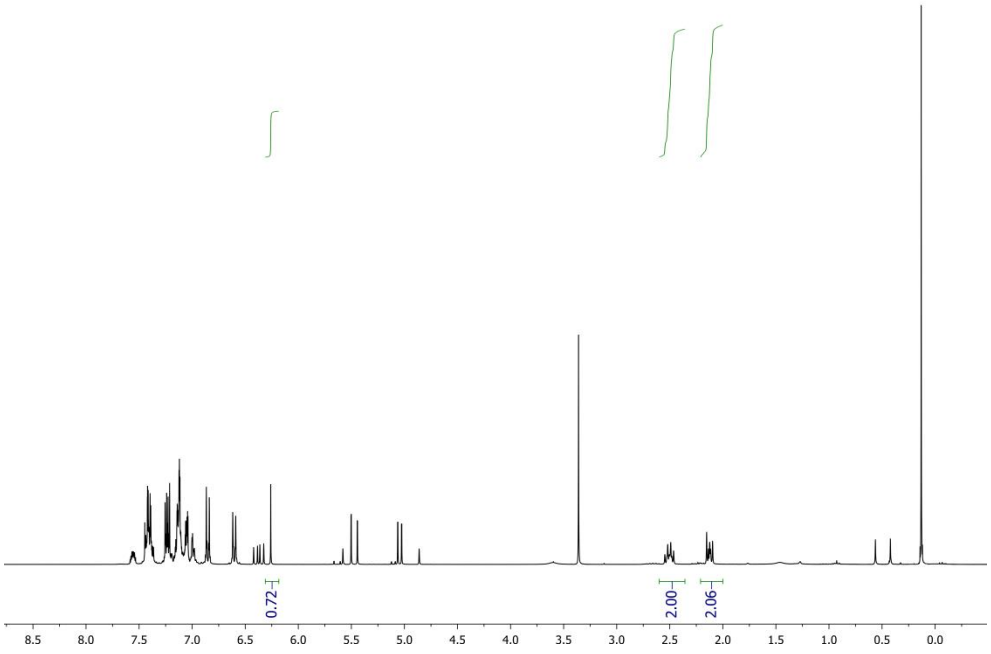

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



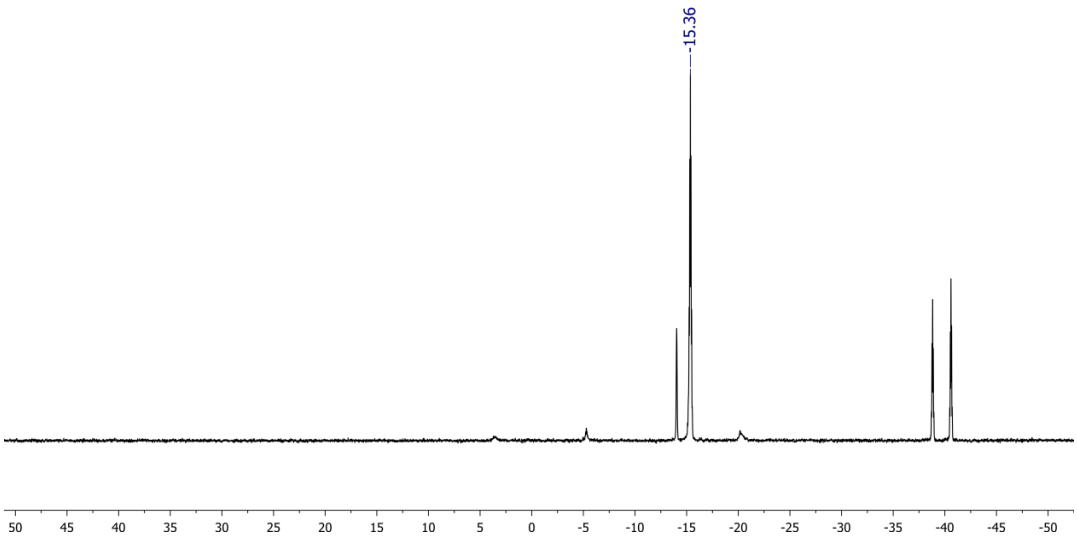
**2h**



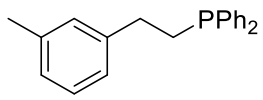

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



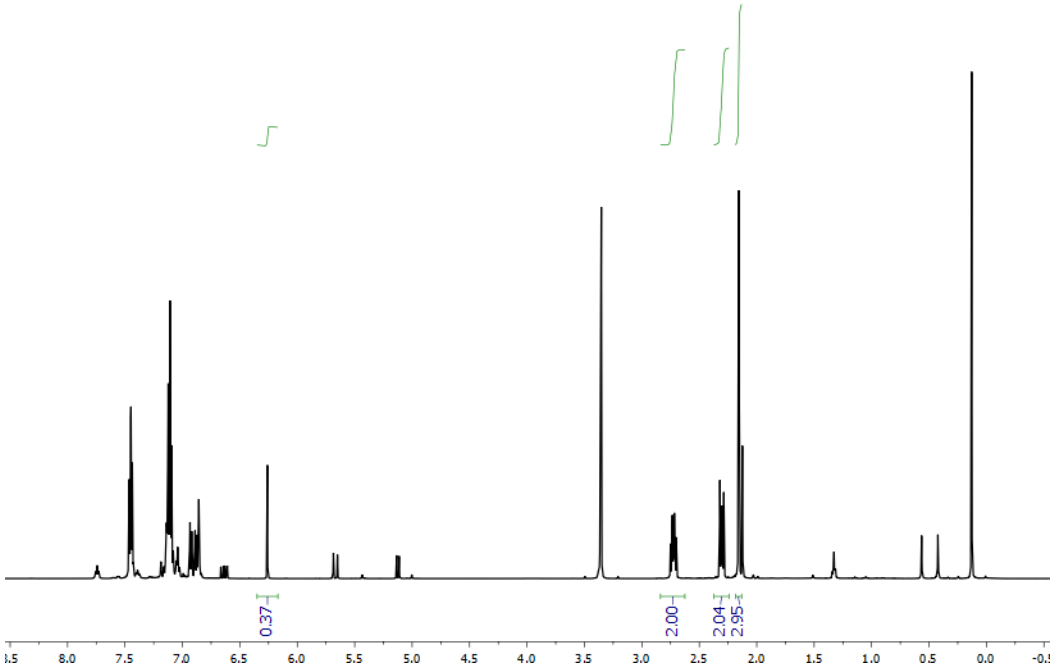

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



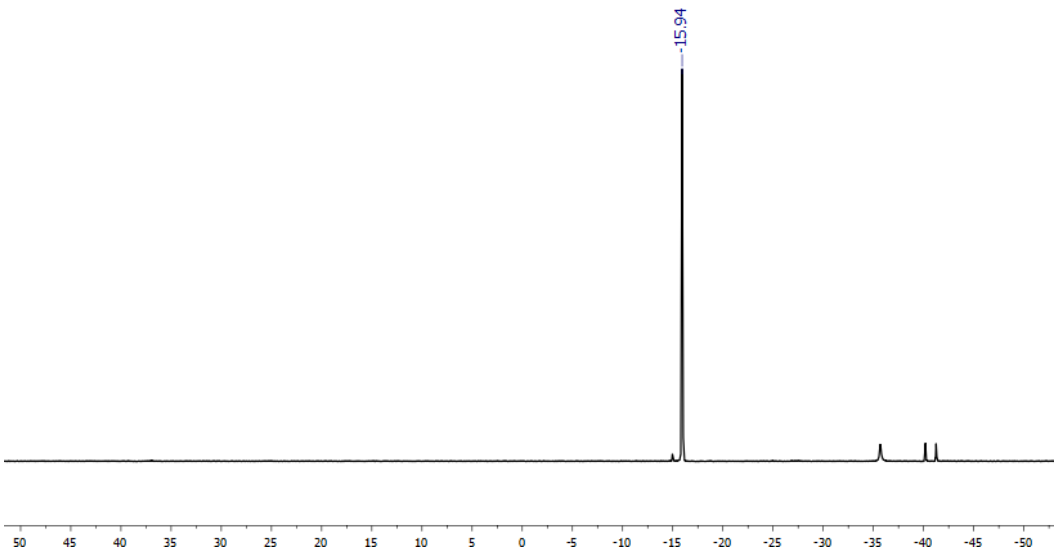
**2i**



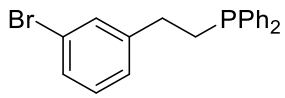

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



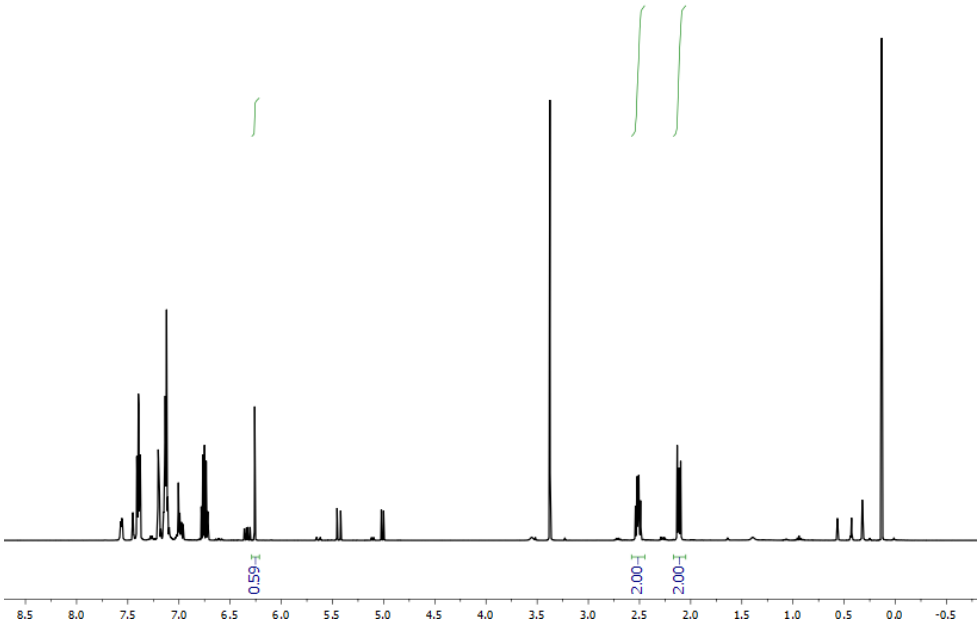

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$:



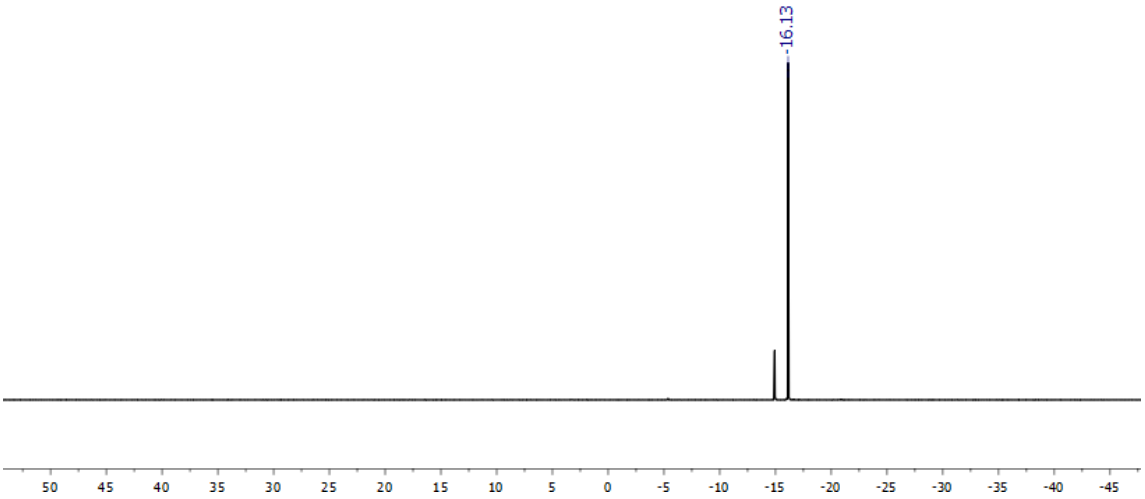
**2j**



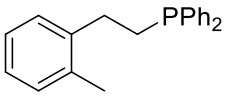

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



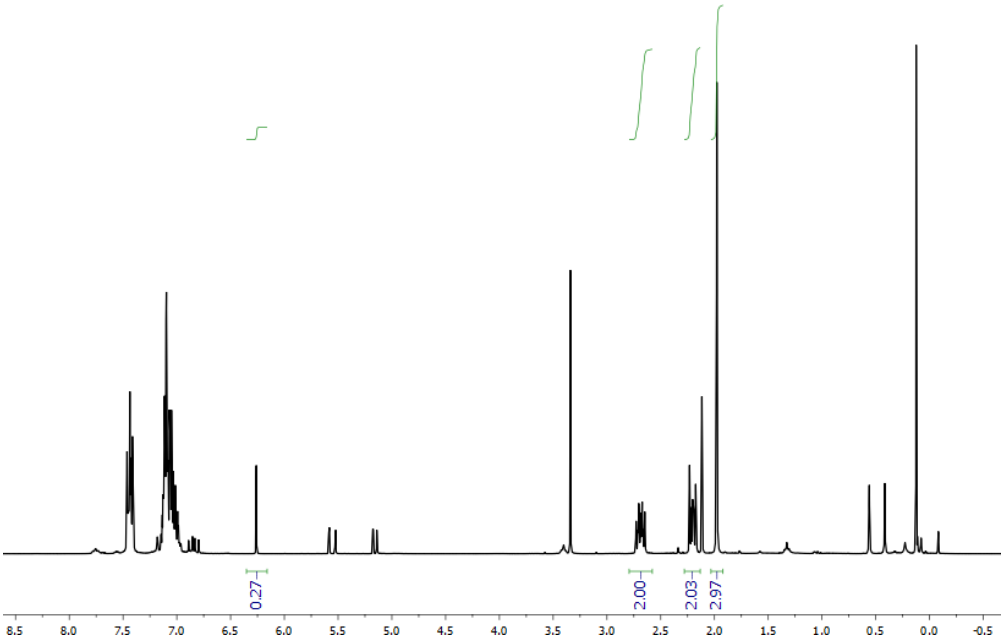

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



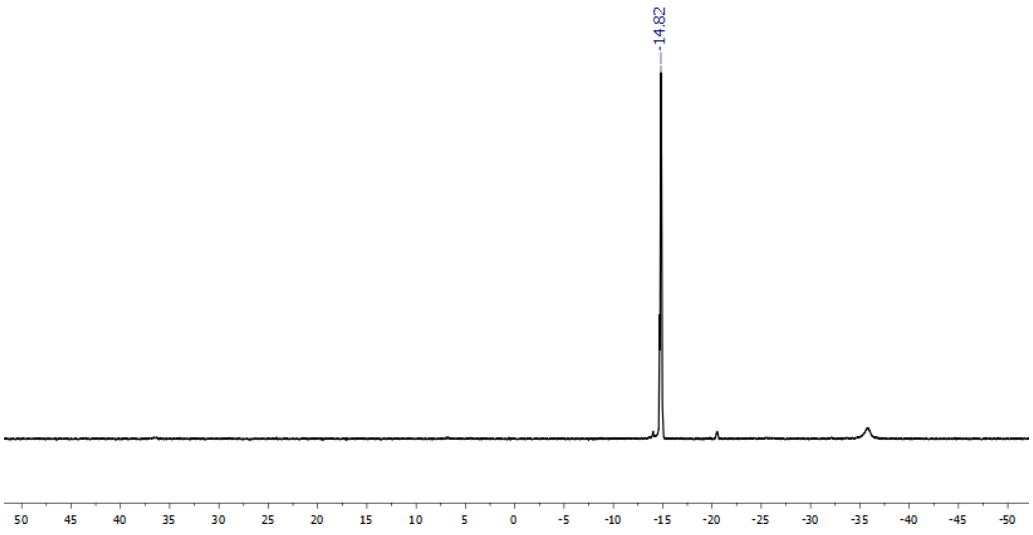
**2k**




$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):




$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



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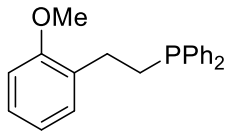
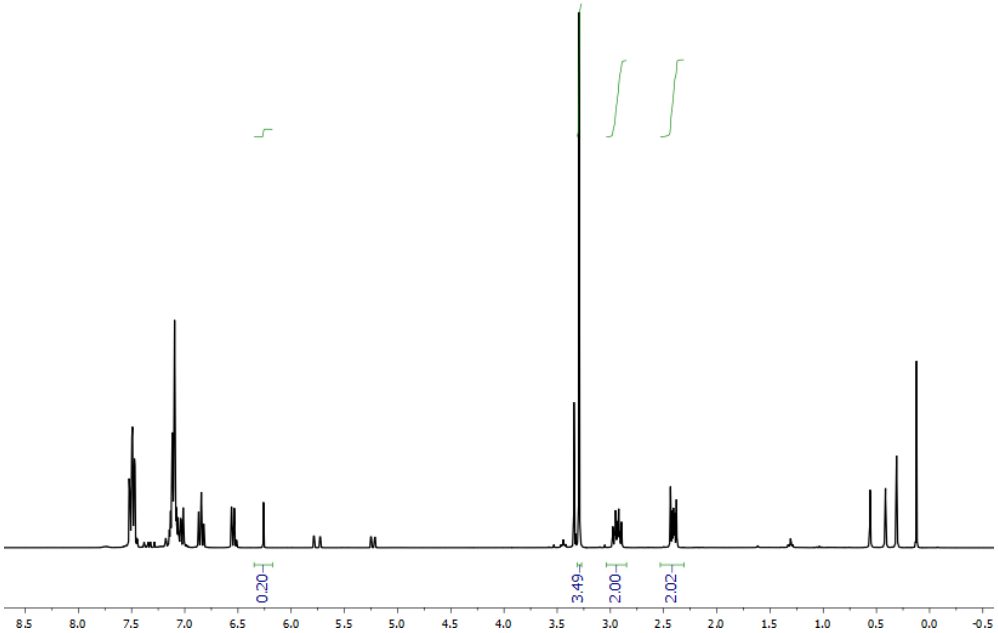
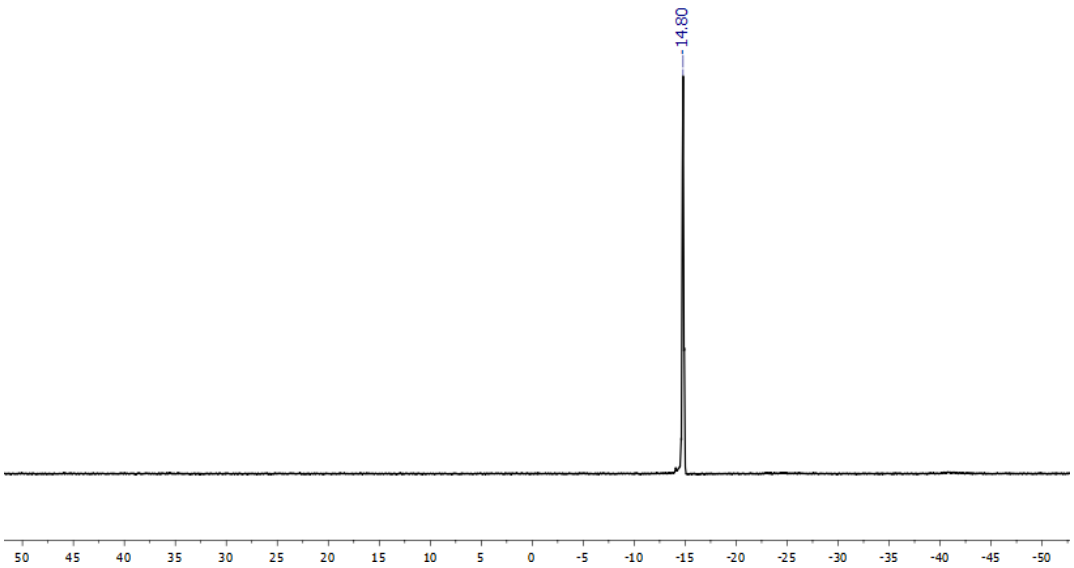


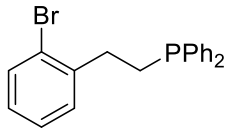

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



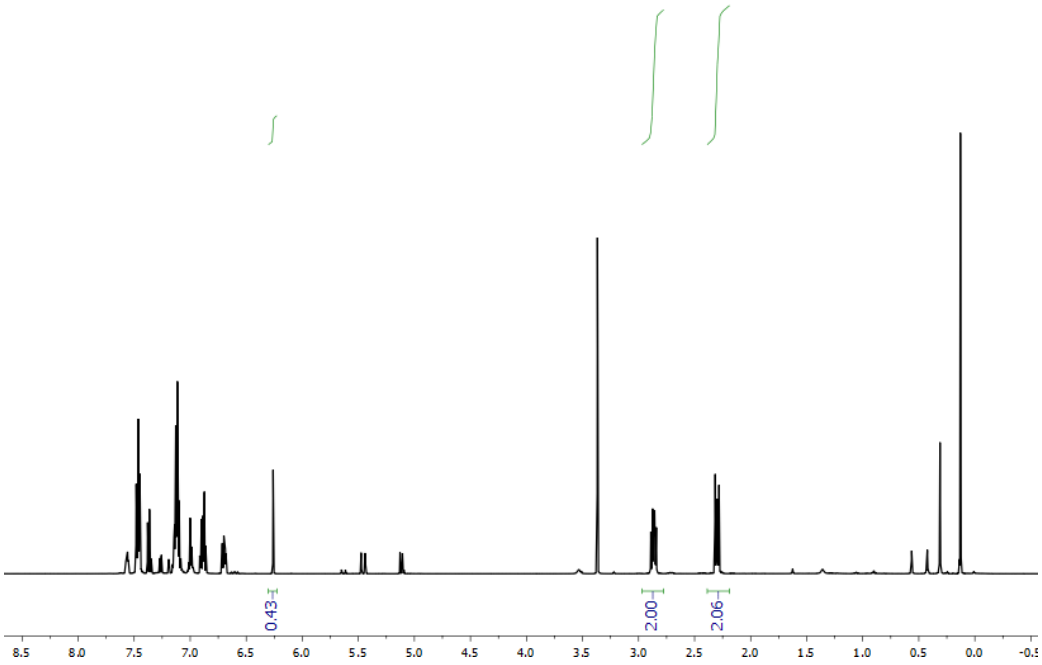

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



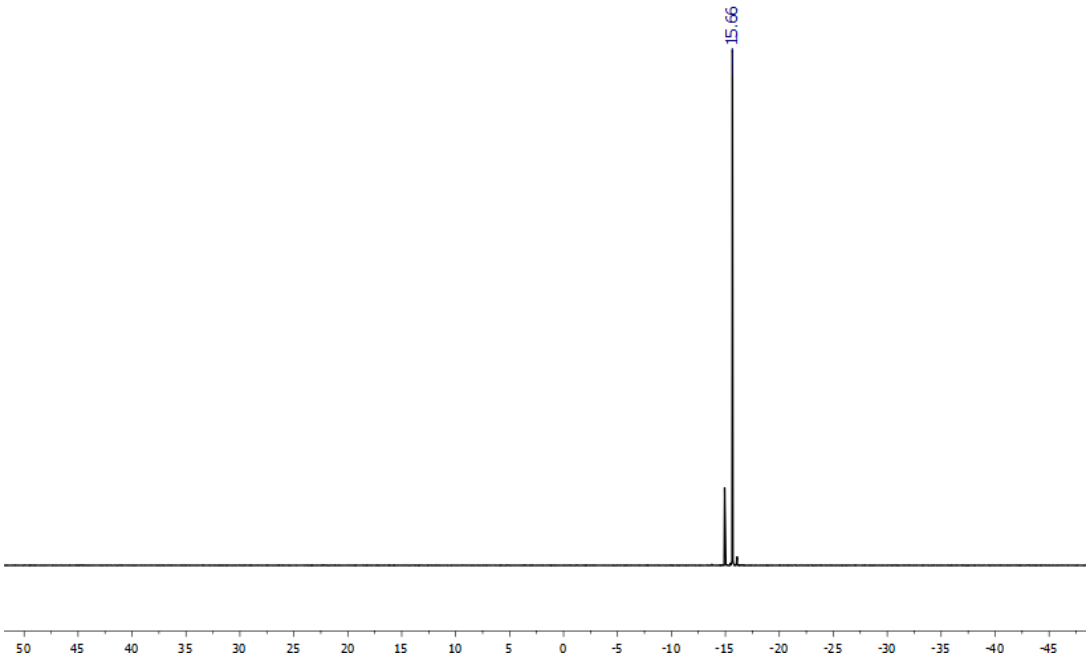
**2m**



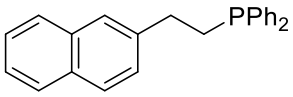

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



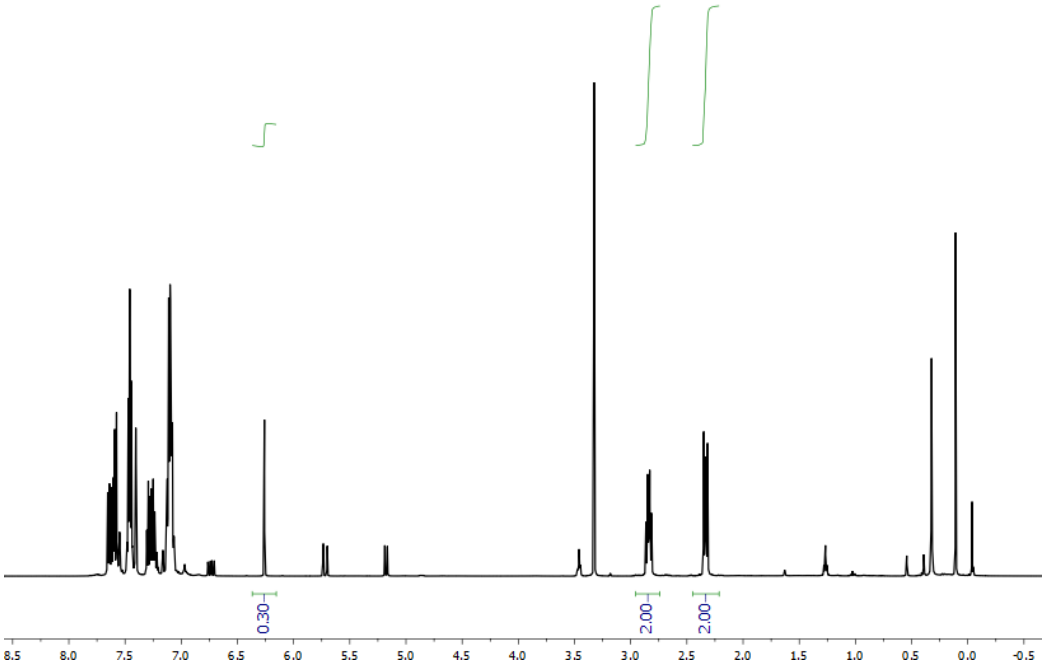

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



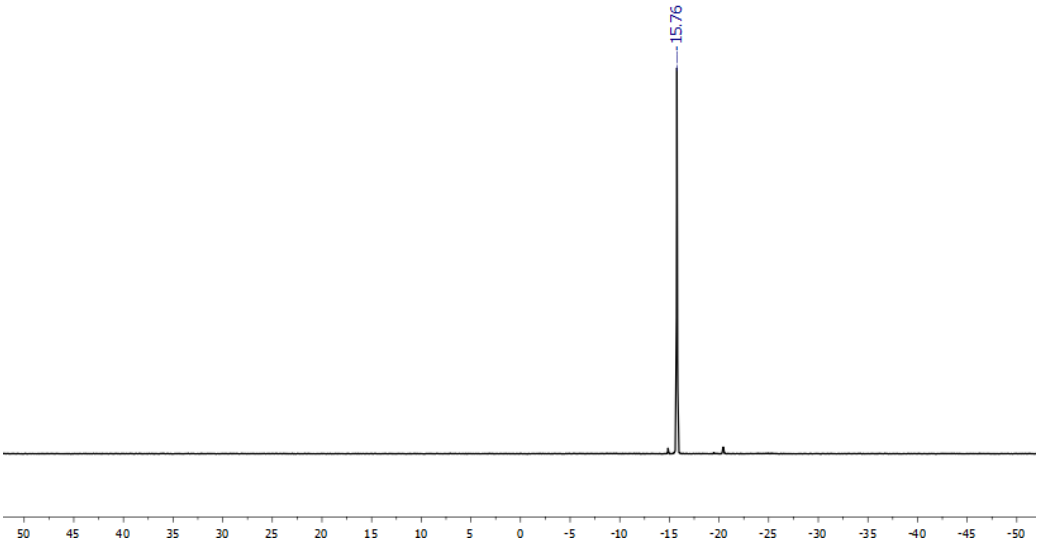
**2n**



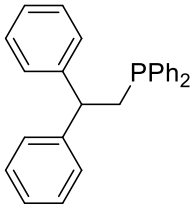

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



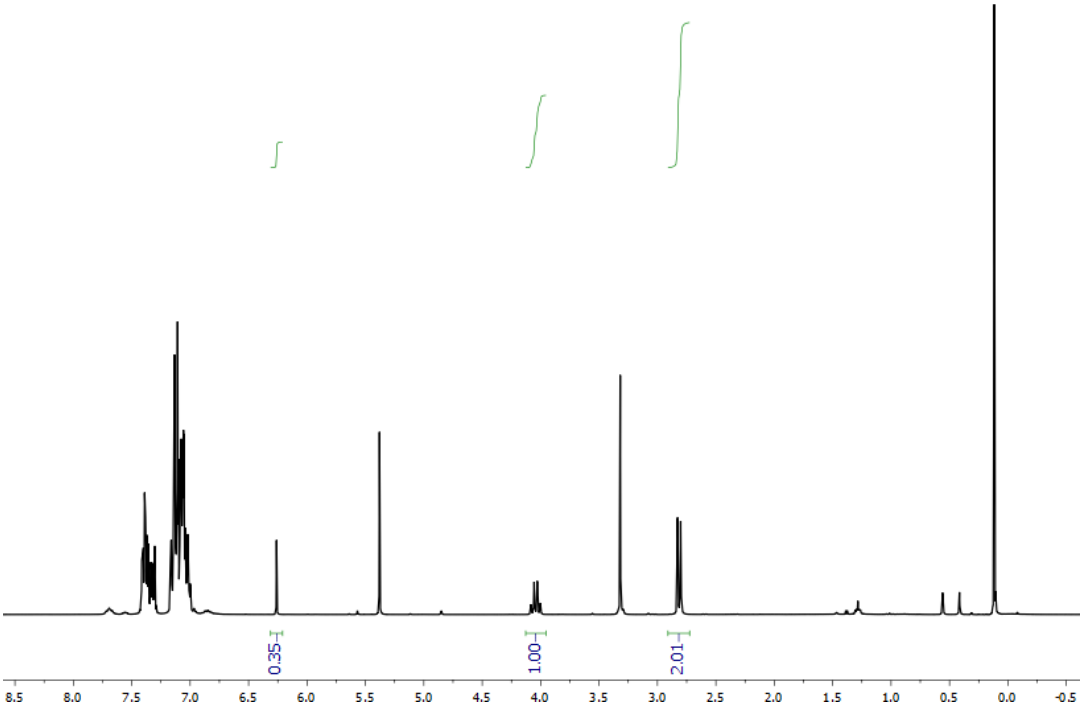

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



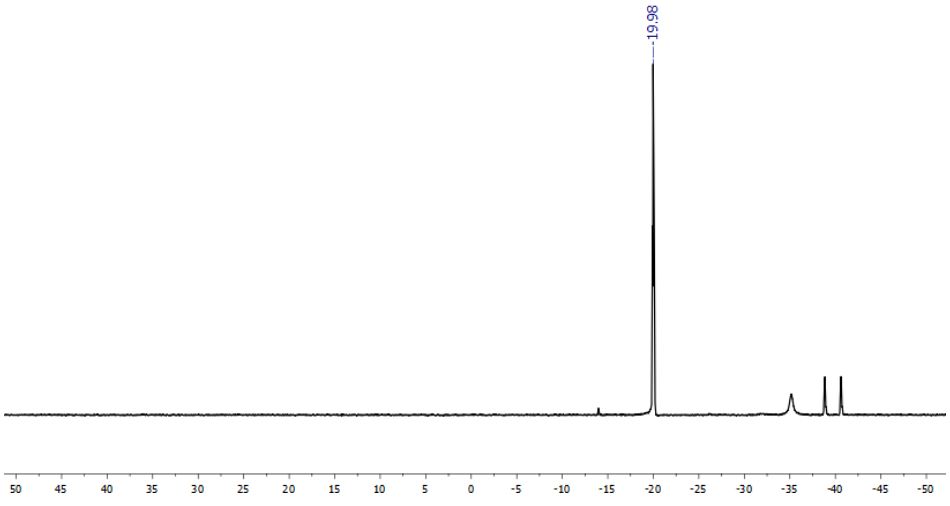
**2o**



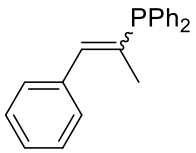

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



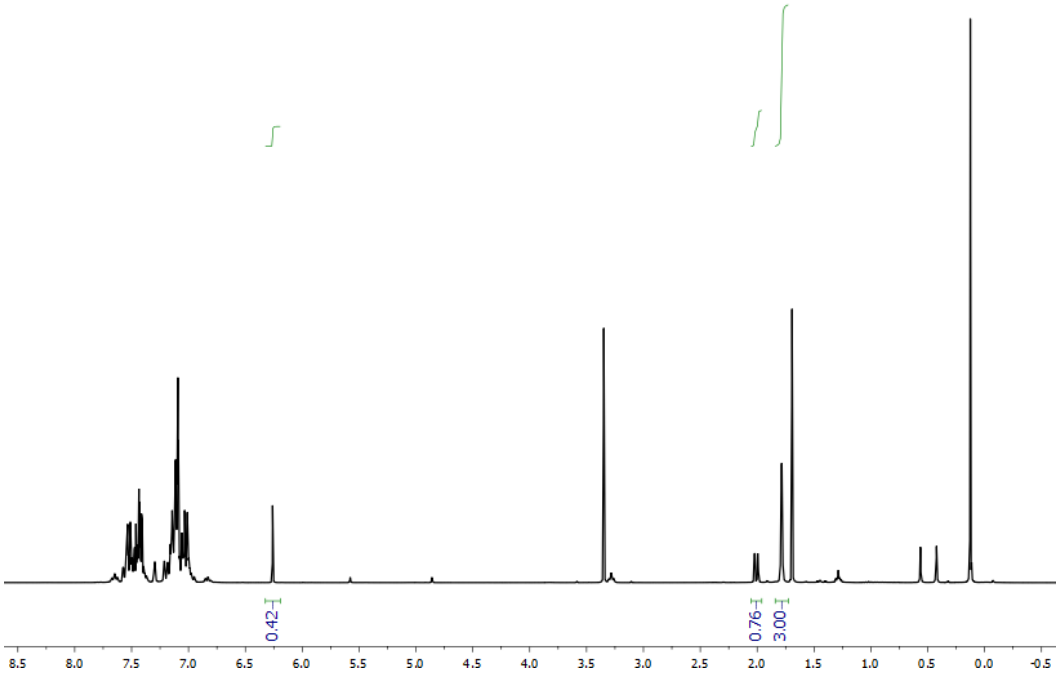

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



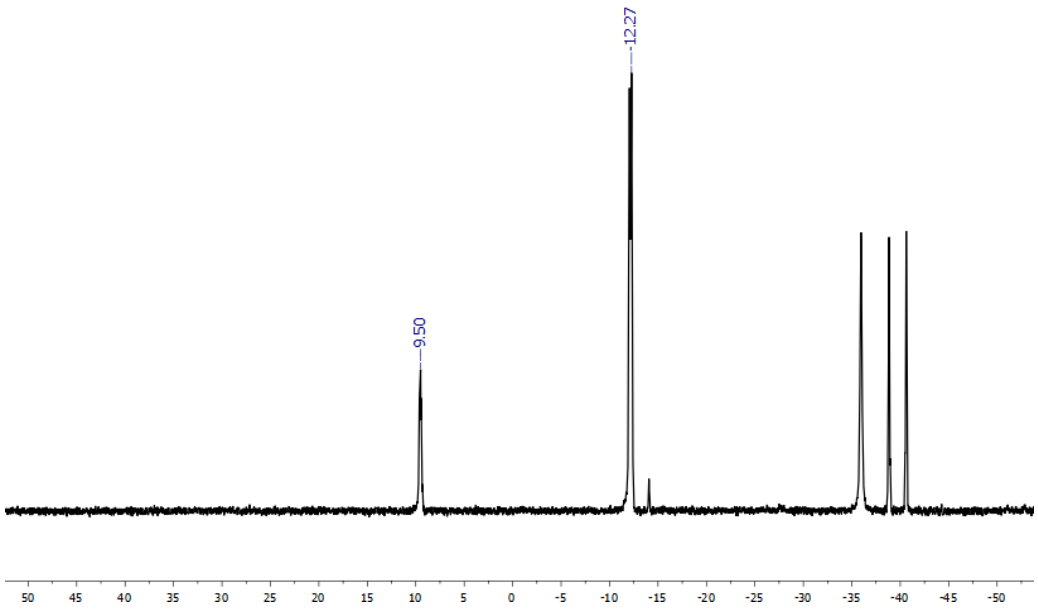
**2p**



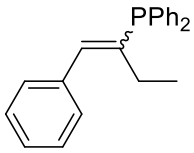

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



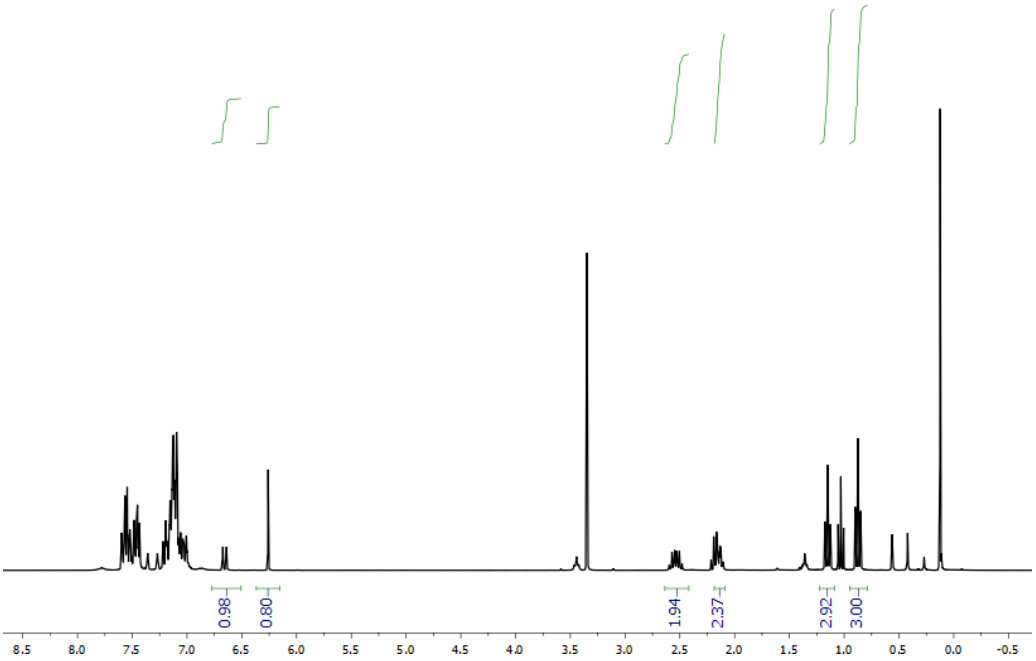

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



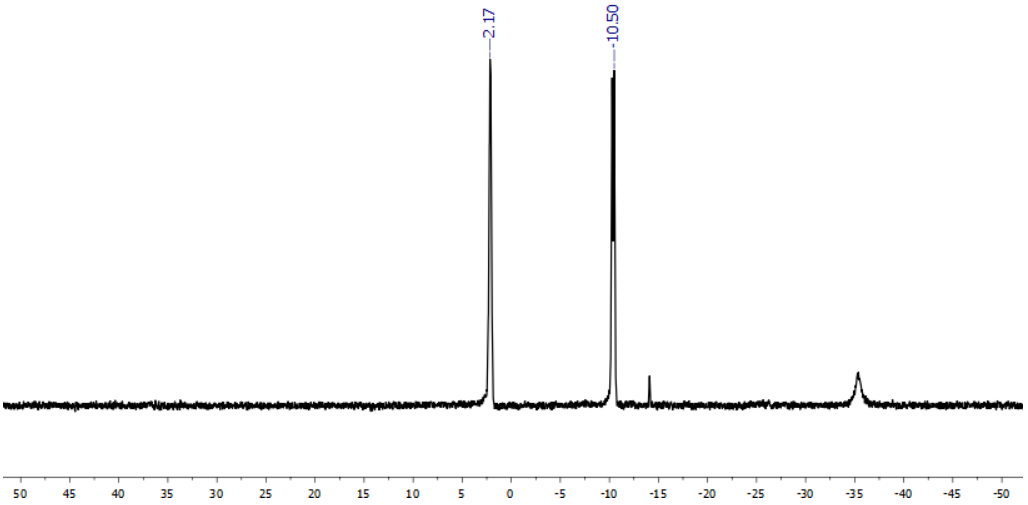
**2q**



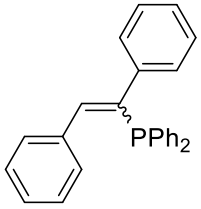

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



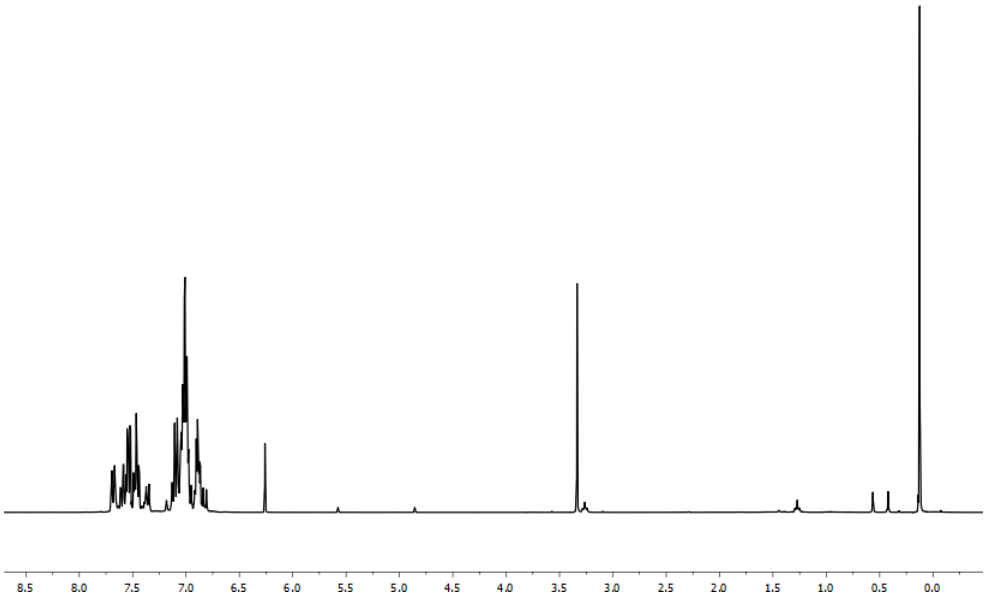

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



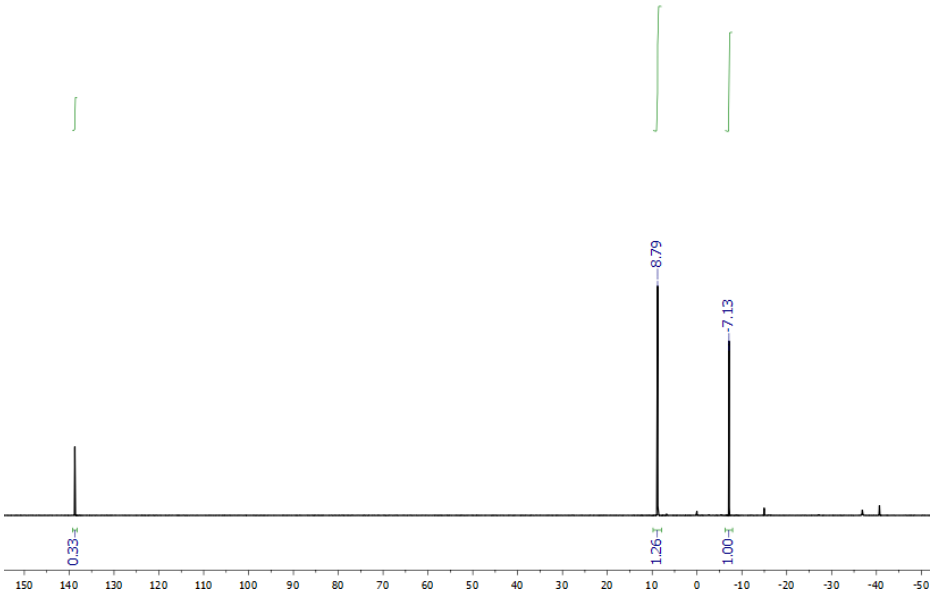
**2r**



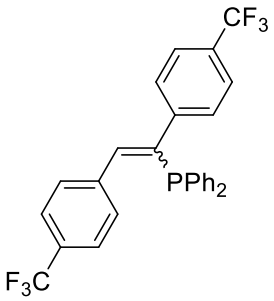

$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):



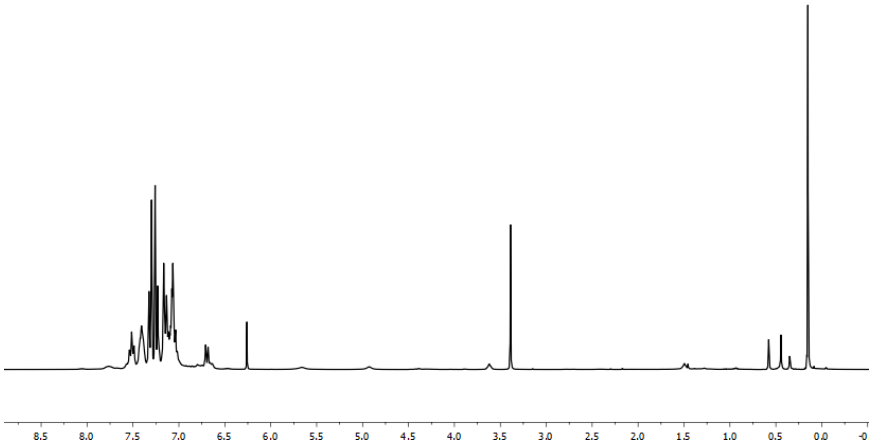

$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



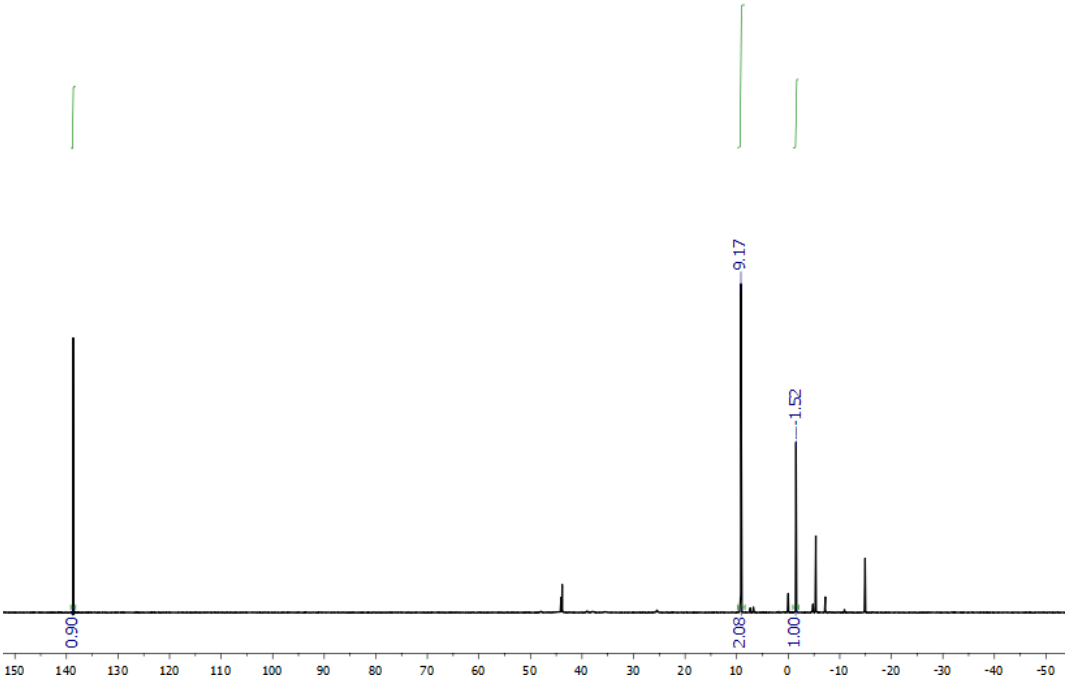
**2s**




$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):

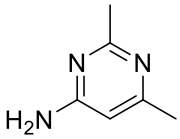



$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



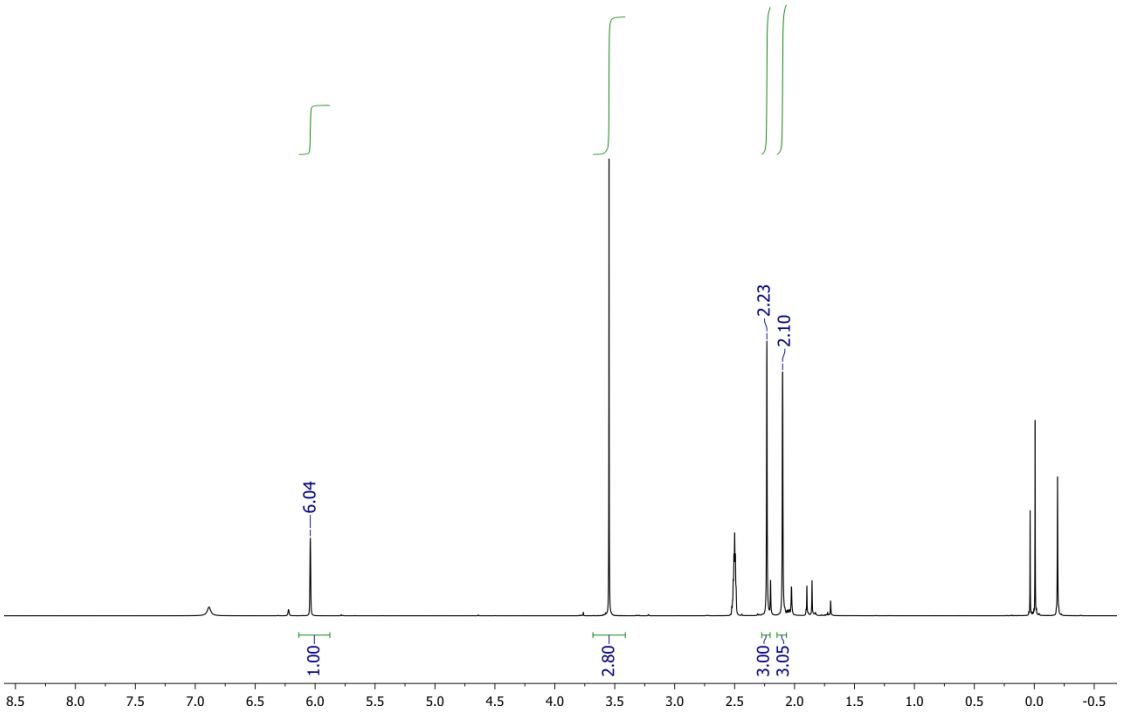
## 6. Procedure for Acetonitrile Trimerization and Spectroscopic Data

**1** (60 mg, 5 mol%) was added to a J-Young NMR tube along with acetonitrile (0.6 mL). After the reagents were mixed, the reaction was heated to 70 °C for 24 h. The reaction was allowed to cool before remaining acetonitrile was removed in vacuo. The resulting solid was re-dissolved in $\delta_6$-DMSO and a known amount of 1,4-dioxane was added as an internal standard. TON was determined by integration of product Ar-H signal against the internal standard in the $^1$H NMR spectrum.




Not isolated. TON: 7. $^1$H NMR (300 MHz, 298K, $C_6D_6$): δ 6.04 (s, 1H, Ar-H), 2.23 (s, 3H), 2.81 (s, 3H). The values are in accordance to the literature.[6]

$^1$H NMR (300 MHz, 298K, $CDCl_3$):



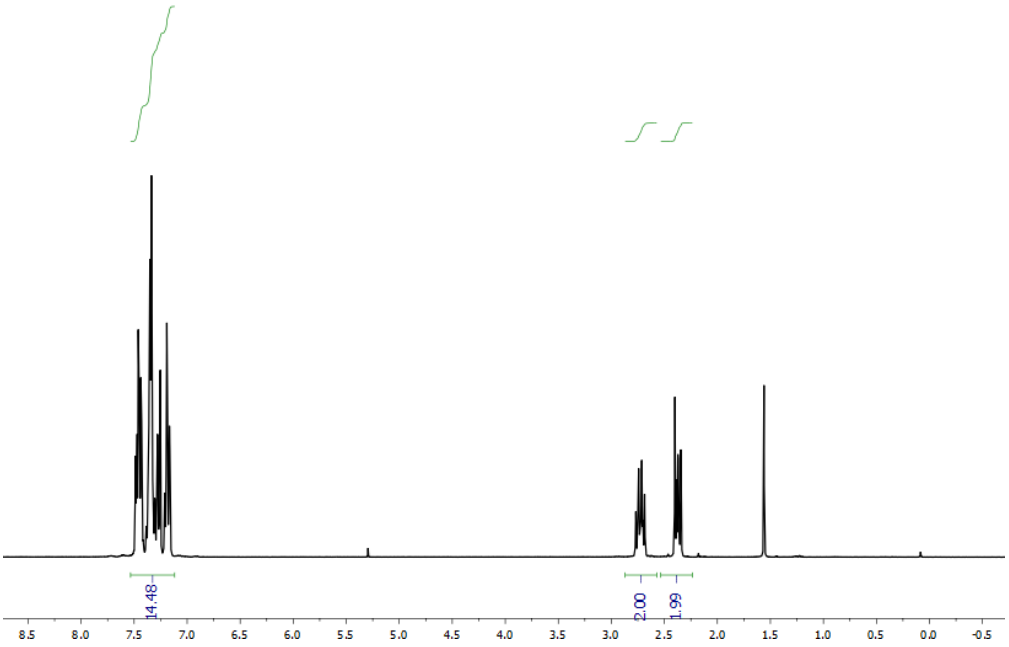
## 7. Scale-up and Iterative Addition Reactions

Procedure for scale-up reaction:

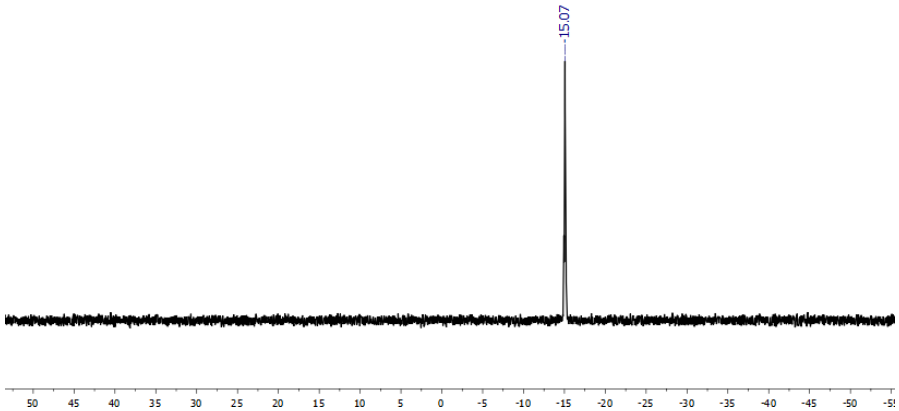
**1** (73.5 mg, 0.125 mmol, 2.5 mol%) was added to a J-Young's Schlenk flask along with $C_6D_6$ (3 mL). Styrene (705 μL, 6 mmol) was added before addition of diphenylphosphine (870 μL, 5 mmol). The resulting yellow solution was stirred at room temperature for 24 h, before approximate conversion was measured by $^{31}P\{^1H\}$ NMR (94%). The volatiles were then removed in vacuo, before the product was exposed to air and isolated via column chromatography (silica, pentane flush, subsequent elution with dichloromethane) to give **2a** as a colorless oil (0.96 g, 66%).

NMR spectra of isolated product:

$^1H$ NMR (300 MHz, 298K, $CDCl_3$):



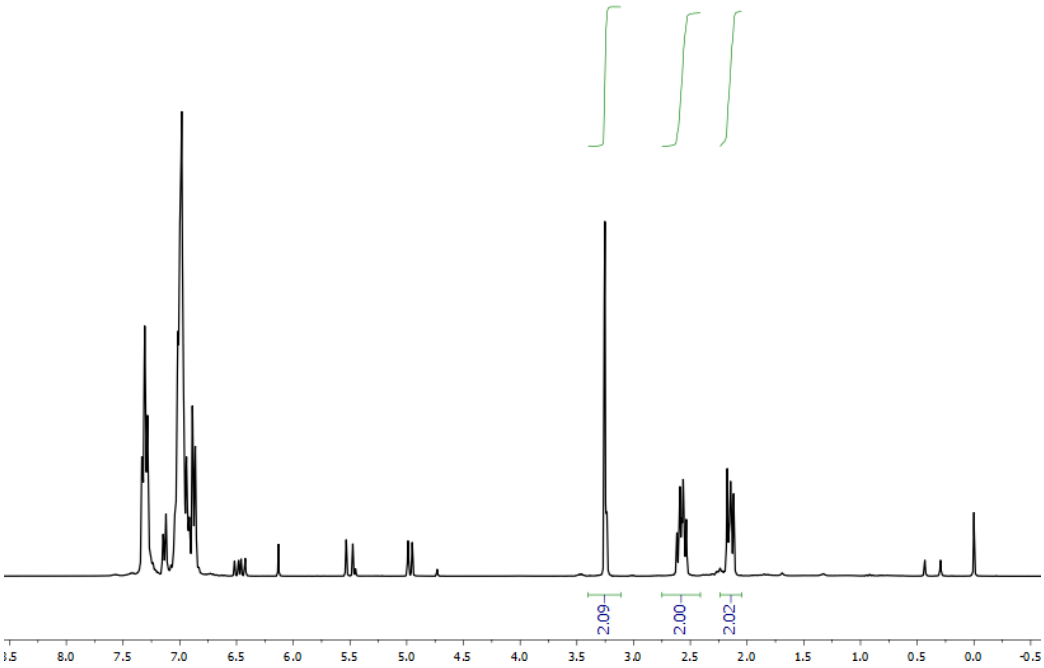

$^{31}P$ NMR (121.5 MHz, 298 K, $CDCl_3$):



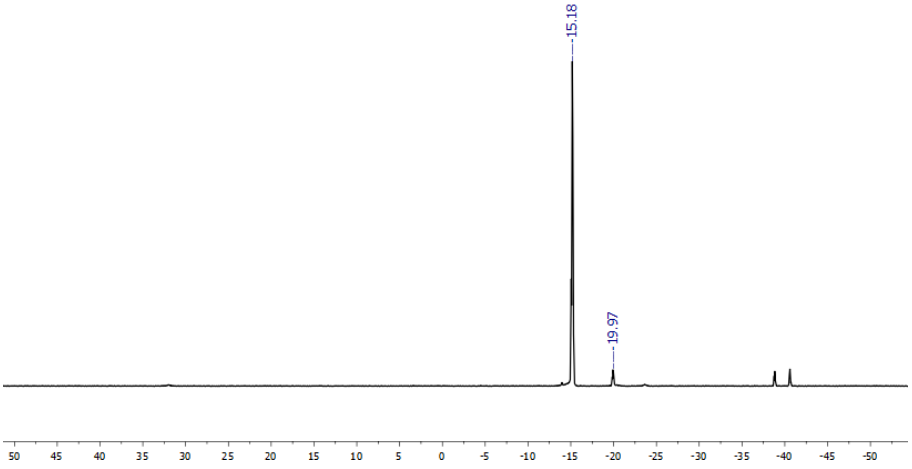
Procedure for iterative addition experiment:

A hydrophosphination reaction with diphenylphosphine and styrene was set up under the general reaction procedure in a J-Young's Schlenk flask. The reaction was monitored by 31P NMR, with additional styrene and diphenylphosphine added each time the reaction had gone to completion. In total, 6 additions (3 mmol diphenylphosphine) were completed over a time period of 10 days. Spectroscopic yield was measured by adding a known amount of 1,2-dioxane internal standard before integrating against the product $CH_2$ signal in the $^1H$ NMR (87%).

$^1H$ NMR (300 MHz, 298 K, $C_6D_6$):




$^{31}P$ NMR (121.5 MHz, 298 K, $C_6D_6$):



## 8. Stoichiometric Reactions

Separate stoichiometric reactions were undertaken between **1** and styrene and **1** and diphenylphosphine to investigate if a potential intermediate species could be observed.

Reaction of **1** and 1 eq. styrene:

Styrene (28.8 µL, 0.25 mmol) was added to a $C_6D_6$ solution of **1** (0.145 g, 0.25 mmol). No change was observed in the $^1H$ NMR for either species after 18 h at RT or after a further 18 h at 50 °C.

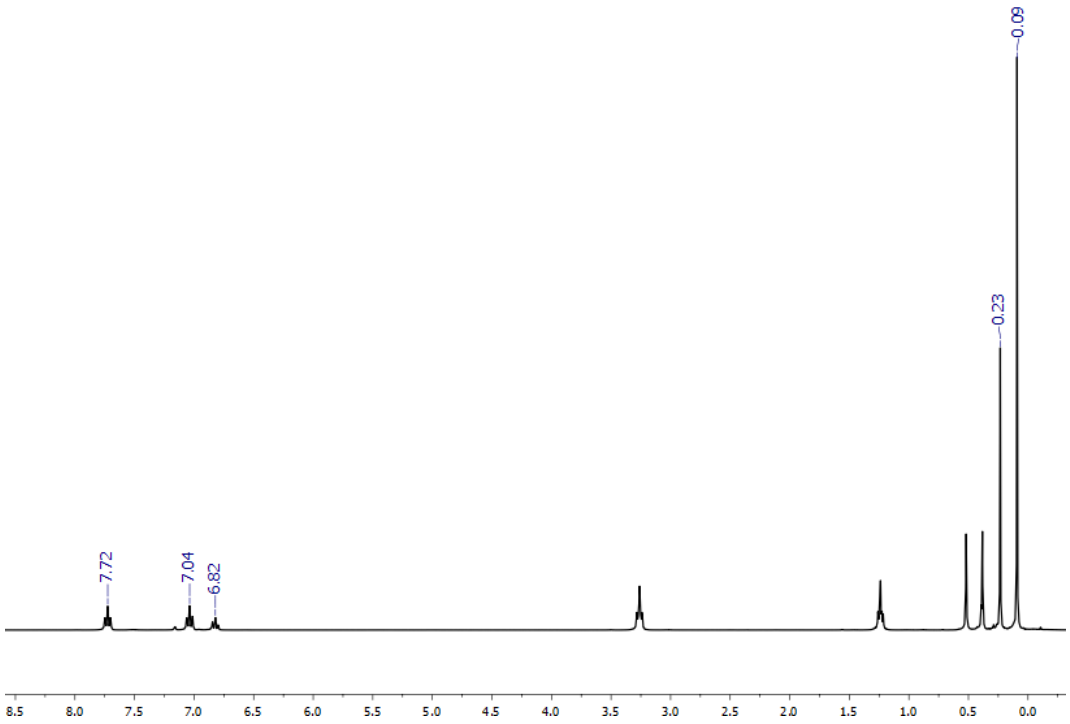
Reaction of **1** and 1/3 eq. $Ph_2PH$:

$HPPh_2$ (43.5/130.5 µL, 0.25/0.75 mmol) was added to a $C_6D_6$ solution of **1** (0.145 g, 0.25 mmol) to yield a bright yellow solution in an instant reaction.

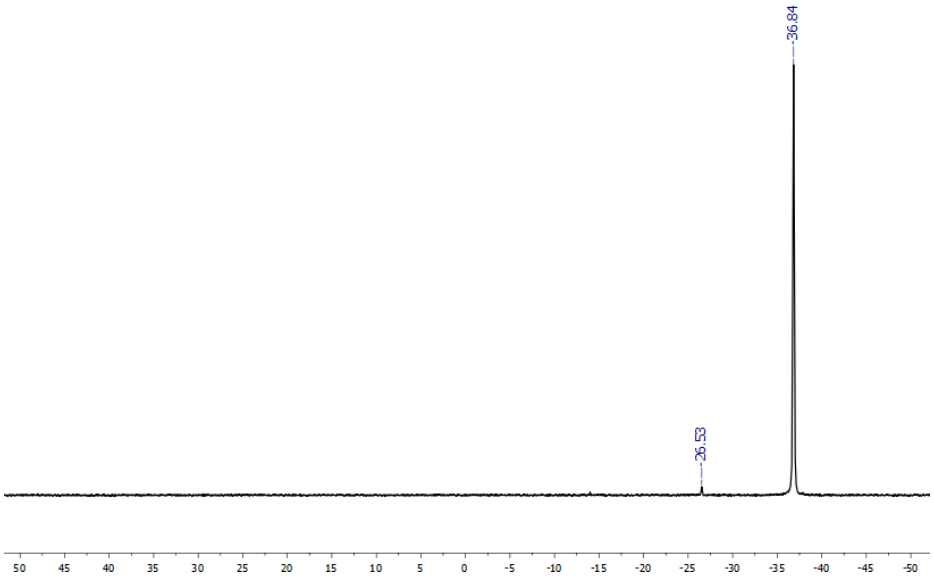
<u>Reaction with 1 eq. $Ph_2PH$:</u>

Complete conversion to a singlet at -36.8 ppm in the $^{31}P$ NMR (signal at -26.5 ppm also observed at low intensity). Loss of P-H signal in $^1H$ NMR as well as shifted phosphine-aryl signals to 6.82, 7.04 and 7.72 ppm. Catalyst $SiMe_3$ signals are split to two signals at 0.23 and 0.09 ppm:

$^1H$ NMR (300 MHz, 298 K, $C_6D_6$):



$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):

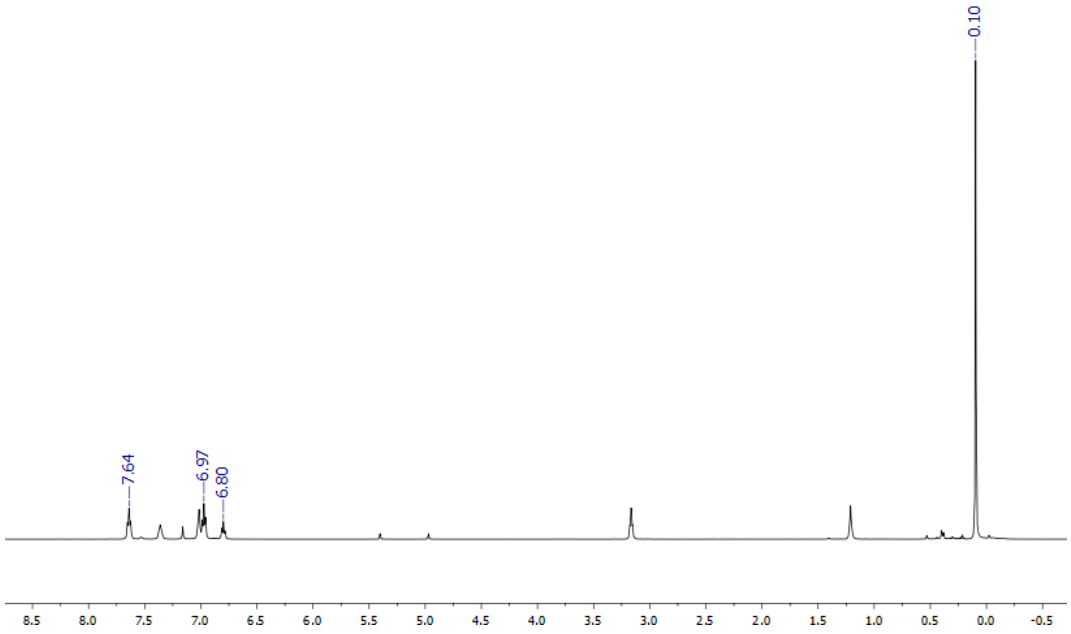



Reaction with 3 eq. $Ph_2PH$:

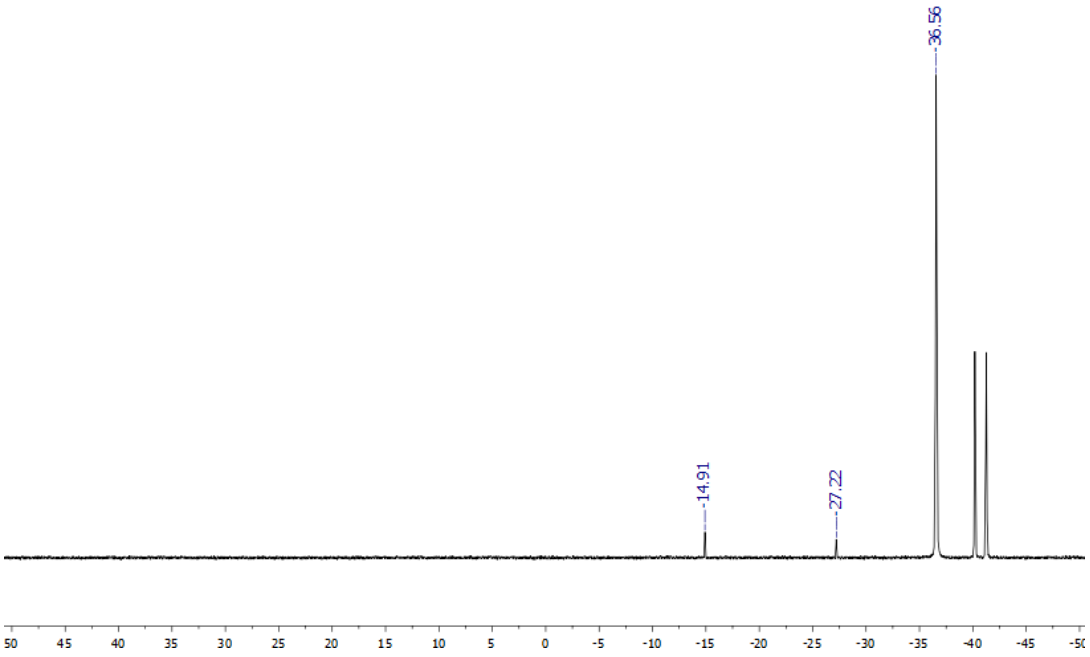
Conversion to a singlet at -36.6 ppm in the $^{31}$P NMR. Free diphenylphosphine also visible as well as low intensity singlets at -27.2 and 14.9 ppm. Catalyst $SiMe_3$ signals fully converted to singlet at 0.10 ppm in the 1H NMR, whilst some free phosphine P-H and P-aryl signals are observed as well as the shifted phosphine aryl signals at 6.80, 6.97 and 7.64 ppm.

A $^1$H DOSY spectrum was also obtained for this reaction. Here, the $SiMe_3$ signals show a larger diffusion coefficient in comparison to the $SiMe_3$ signals in the DOSY spectrum of **1**. Additionally the phenyl protons of the diphenylphosphine moiety show a smaller diffusion coefficient. Both indicate the formation of a [Ge]-$PPh_2$ species and release of $HN(SiMe_3)_2$.

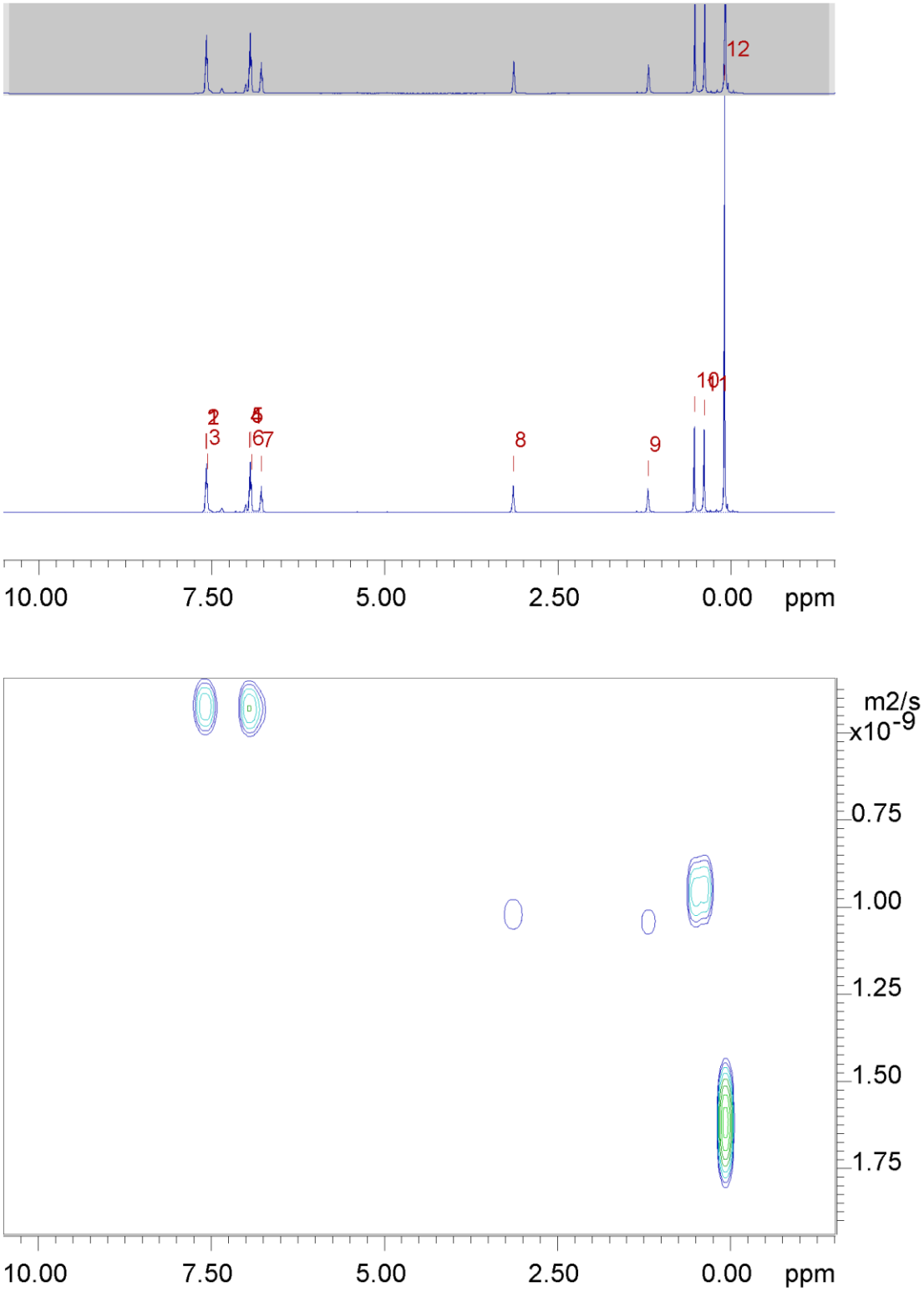
$^{1}$H NMR (300 MHz, 298 K, $C_6D_6$):




$^{31}$P NMR (121.5 MHz, 298 K, $C_6D_6$):



$^{1}$H DOSY (500 MHz, 298 K, $C_6D_6$):



Attempts were made to crystalize the products from the reaction of **1** + 3 eq.diphenylphosphine in both toluene and THF at – 30 °C. Whilst in both cases crystals were obtained, upon screening the structures were found to match that of **1**. Although by NMR complete conversion to a new species was observed, it is possible that the free HMDS in solution can exchange with the Ge-bound –$PPh_2$. If **1** is more stable in the solid state than the phosphide complex, then this exchange may occur and lead to selective crystallization of **1** over any Ge-phosphido species.

## 9. Radical Clock Studies

A range of radical clocks were used to probe for radicals. Rather than monitor rates of reaction in the presence of the radical traps we opted, in the first instance, to probe for the presence of the products of radical ring opening/ring closure, along with change in yield of the product.

Procedure for radical trap experiments:

A hydrophosphination reaction was set up following the general procedure (pg. S6). Shortly after the diphenylphosphine was added, the trap reagent was then added (5-100 mol%) and the reaction shaken and left at r.t. Spectroscopic yield was measured after 18 h.

The initial radical clocks tested were chloro(methyl)cyclopropane, 6-bromo-1-hexene and 1-bromo-2-(3-buten-1-yl)benzene, which would give 1-butene, methylcyclopentane and 1-methyl-2,3-dihydro-1H-indene respectively if radicals were present. At 5 mol% loading of radical trap none of these products were observed and there is only a small drop-off in conversion to the hydrophosphination product **2a** in the presence of chloro(methyl)cyclopropane and 6-bromo-1-hexene. This drop-off in yield is spectroscopically attributed to the formation of the product of nucleophilic attack of $Ph_2PH$ (giving (cyclopropylmethyl)diphenylphosphine and hex-5-en-1-yldiphenylphosphane).

At loadings of >5 mol% there is again no radical ring opening or ring closure observed when the reaction is undertaken in the presence of the radical clocks. However, a more significant drop-off in yield of **2a** is observed with all radical clocks. We rationalize this as being due to **1** being deactivated (in the form $GeX_n(HMDS)_{4-n}$) as a consequence of the nucleophilic substitution reaction with the trap, as evidenced by a color change in the solution (yellow to colorless), and therefore preventing or greatly reducing the catalytic turnover.

In order to fully ensure our hypothesis that the observed reduction in conversion derives from the nucleophilic substitution side reaction with the radical traps used above rather than any radical activity, 2-bromoethylbenzene was tested as a trap for the reaction. 2-bromoethylbenzene should not react with radical species, however will readily undergo nucleophilic substitution. At 10/100 mol% loadings of 2-bromoethylbenzene, a significant drop-off in conversion to **2a** is observed in both cases, implying that nucleophilic substitution leading to catalyst deactivation had occurred. This was confirmed in a stoichiometric reaction with **1**, $HPPh_2$ and 2-bromoethylbenzene, yielding **2a** as the sole product of a nucleophilic substitution reaction.

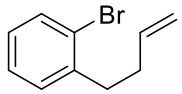
An additional radical trap was also synthesized, 1-bromo-2-(3-buten-1-yl)benzene. In this case, the aryl-bromide would not be susceptible to a substitution reaction, and the trap would ring close to form 1-methylindane in the presence of radicals.[7] The hydrophosphination reaction showed no significant reduction in conversion when 100 mol% of the trap was added and no ring-closed product was observed, further evidencing against the involvement of radicals in the reaction. A summary of results with radical traps is displayed below in Table S1

**Table S1.** Results of radical clock studies

| Radical clock | Color change | Conversion to 2a (%) |
|---|---|---|
| chloro(methyl)cyclopropane (5 mol%) | None | 89 |
| chloro(methyl)cyclopropane (10 mol%) | Loss of yellow | 10 |
| chloro(methyl)cyclopropane (50 mol%) | Loss of yellow | 7 |
| chloro(methyl)cyclopropane (100 mol%) | Loss of yellow | 7 |
| 6-bromo-1-hexene (5 mol%) | None | 9 |
| 6-bromo-1-hexene (10 mol%) | None | 41 |
| 6-bromo-1-hexene (100 mol%) | Loss of yellow | 9 |
| 2-bromoethylbenzene (5 mol%) | None | 94 |
| 2-bromoethylbenzene (10 mol%) | Loss of yellow | 12 |
| 1-bromo-2-(3-buten-1-yl)benzene (100 mol%) | None | 83%* |

* Slight reduction in conversion attributed to a higher than usual conversion of dehydrocoupled product $Ph_4P_2$, observed by $^{31}P$ NMR. It is possible that the alkene group of 1-bromo-2-(3-buten-1-yl)benzene is able to accept hydrogen gas, making this side reaction more competitive in this case.

**Synthesis of 1-bromo-2-(3-buten-1-yl)benzene:**

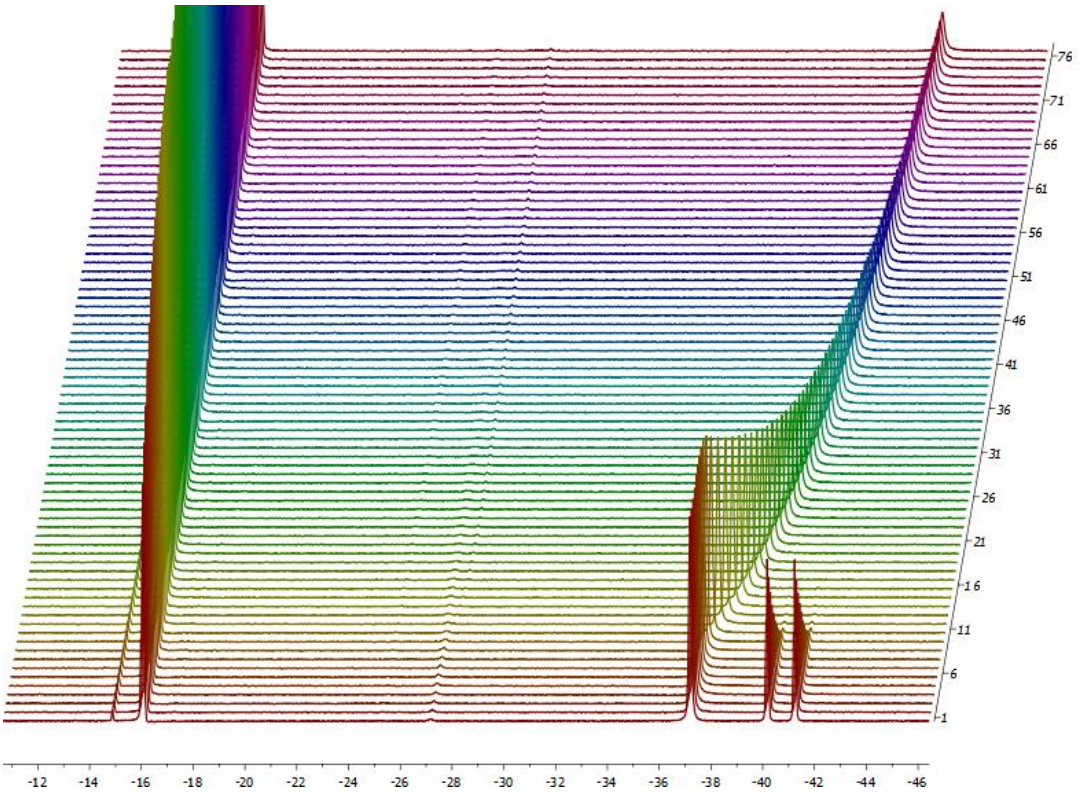



In an adaptation of a literature procedure,[8] magnesium (0.55 mg, 22.5 mmol) was flame-dried under vacuum in a reflux condenser-fitted Schlenk flask. THF (10mL) was added alongside a crystal of iodine, and the solution was stirred until the brown color dissipated. A THF (10 mL) solution of allyl bromide was then added (1.3 mL, 15 mmol) slowly, causing self-initiation of the Grignard reaction. The reaction was allowed to cool to room temperature and stirred for 4 h. The Grignard reagent was then filtered via cannula into a THF (6 mL) solution of 2-bromobenzyl bromide (2.50 g, 10 mmol) held at 0 °C. The reaction was then heated to reflux for 2 h, before being cooled to room temperature. The reaction was again cooled in an ice bath before the addition of saturated $NH_4Cl$ solution (15 mL) and subsequent extraction with diethyl ether (3 x 20 mL). The organic layers were combined and dried over $MgSO_4$, before filtration and removal of solvents in vacuo. The crude product was then purified by column chromatography (silica, hexane) to give 1-bromo-2-(3-buten-1-yl)benzene as a colorless liquid.

$^1H$ NMR (300 MHz, 298 K, $CDCl_3$): δ 7.56-7.51 (m, 1H, Ar), 7.25-7.20 (m, 2H, Ar), 7.10-7.03 (m, 1H, Ar), 5.96-5.82 (m, 1H, *H*C=$CH_2$), 5.12-4.98 (m, 2H, HC=C*H*$_2$), 2.88-2.79 (m, 2H, Ar-C*H*$_2$), 2.43-2.33 (m, 2H, C*H*$_2$-CH=$CH_2$). The values are in accordance to the literature.[8]

## 10. $^{31}$P NMR Reaction Monitoring Studies

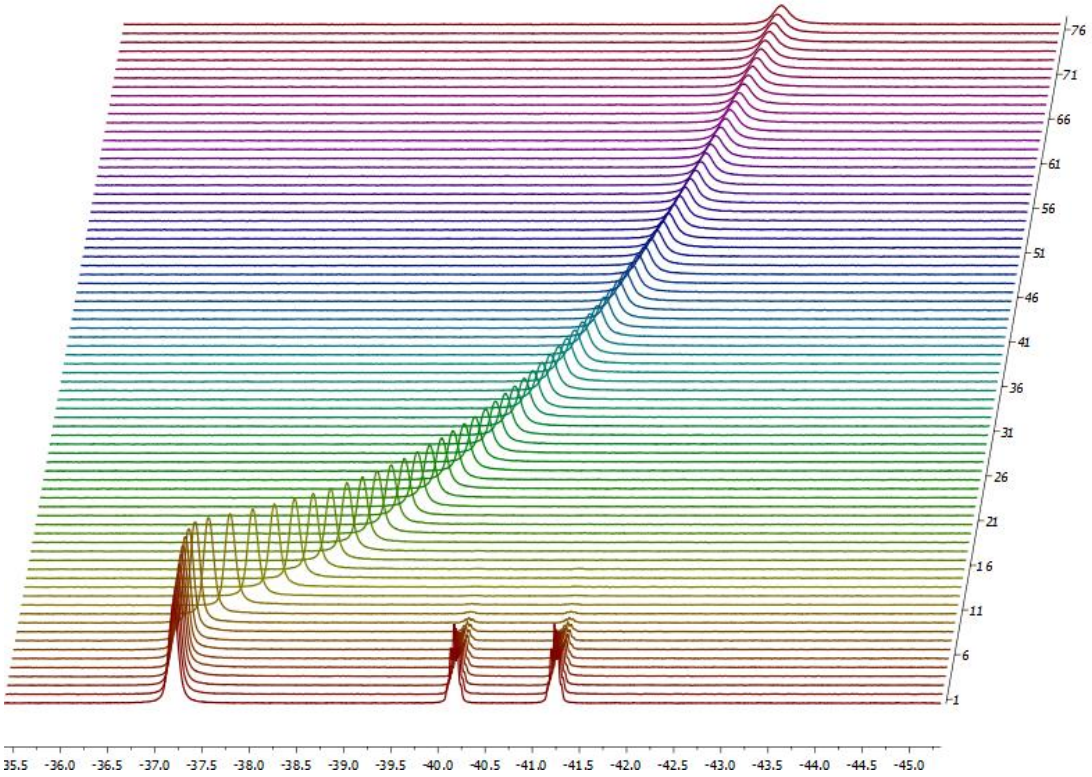
In order to investigate if a catalytic intermediate could be observed by $^{31}$P NMR during the course of the hydrophosphination reaction, a reaction was undertaken following the standard hydrophosphination procedure, with the exception of 15 mol% loading of **1**. The reaction was then monitored overnight, with a $^{31}$P NMR spectrum of the reaction obtained in ten minute intervals for 12 h. The stacked spectra are shown below:

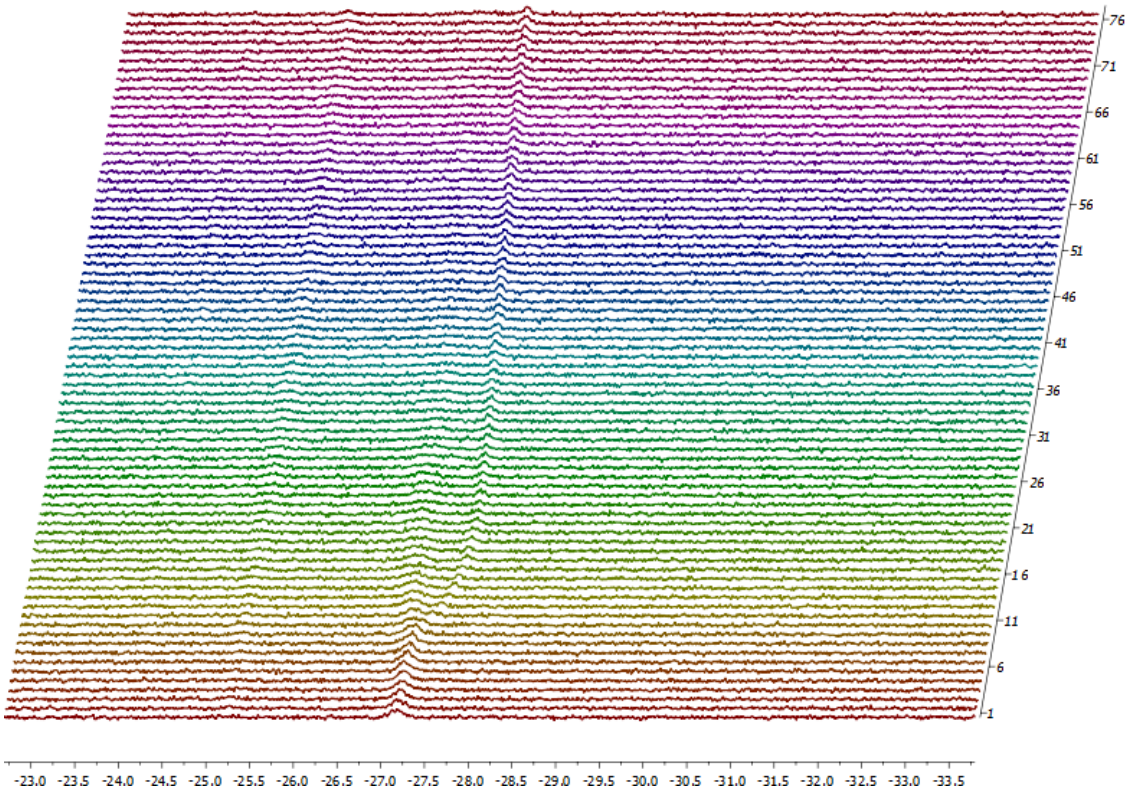



Observed are the signals for the hydrophosphination product (-16 ppm), diphenylphosphine (d, -40,5 ppm) and an intermediate species (-37 ppm). The diphenylphosphine signal decreases in intensity as the signal at -37 ppm increases in intensity until all diphenylphosphine has reacted, at which point the intermediate species slowly decreases to yield the hydrophosphination product. At the point where the concentration of the species corresponding to the signal at -37 ppm is highest it integrates to approximately 40% of the total $^{31}$P signal, hence we tentatively assign this to a [Ge]-$(PPh_2)_3$ species as this percentage could only be reached by a Ge species if 3 phosphine molecules are bound to each Ge centre. As all diphenylphosphine is depleted at this point, we propose that protonolysis occurs via the free HMDS in solution for the remainder of the reaction.

The presence of a singlet at -27 ppm was also observed, albeit at very low intensity. Interestingly, both this signal and the signal at -37 ppm show an upfield shift once the diphenylphosphine has completely reacted, as seen below.

Upfield Shift in $^{31}P$ NMR signals over time:



## 11. Procedure for Kinetic Analysis

Reactions were set up as per the general hydrophosphination procedure above with styrene and $Ph_2PH$. $^1H$ NMR spectra were then recorded over a period of 14 hours, with 10 minute intervals. The data was processed and analysed using VTNA.[9]

Separate reactions were undertaken with each of the following deviations from standard procedure:

2.5 mol% **1**

3.75 mol% **1**

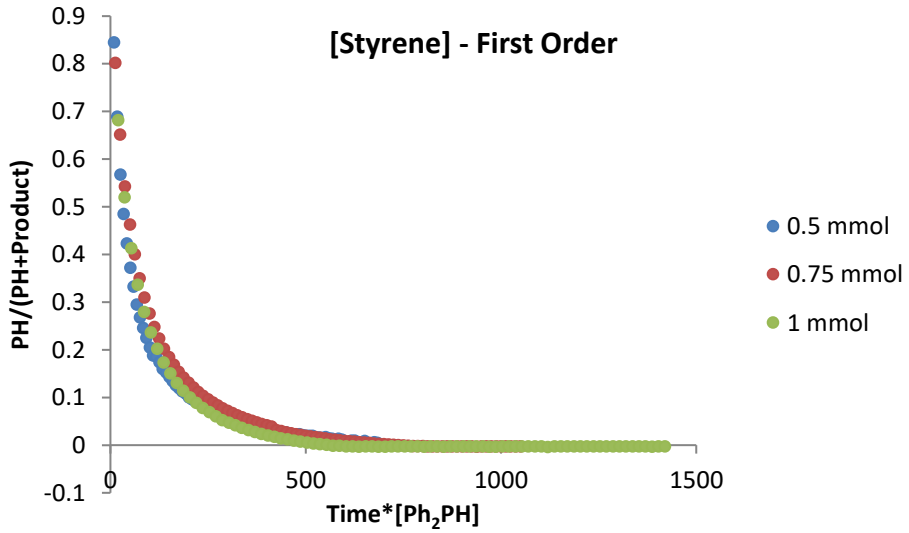
0.75 mmol $Ph_2PH$

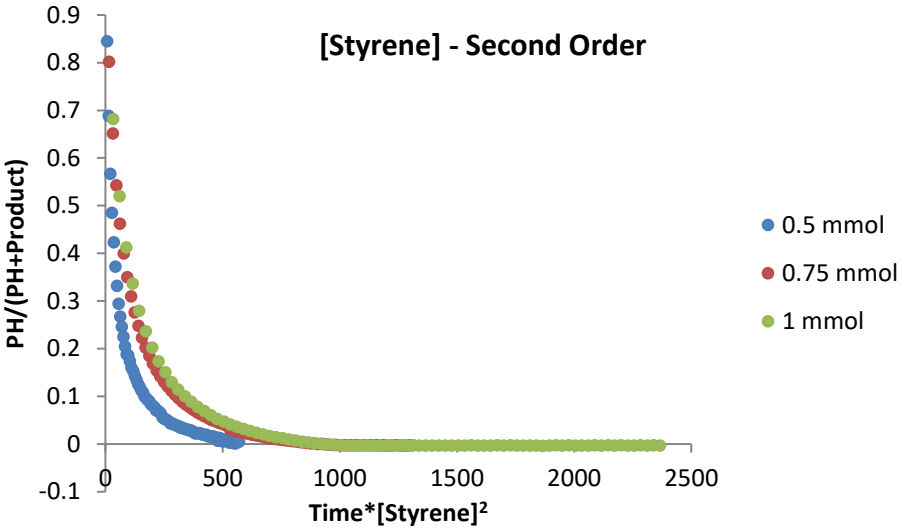
1 mmol $Ph_2PH$

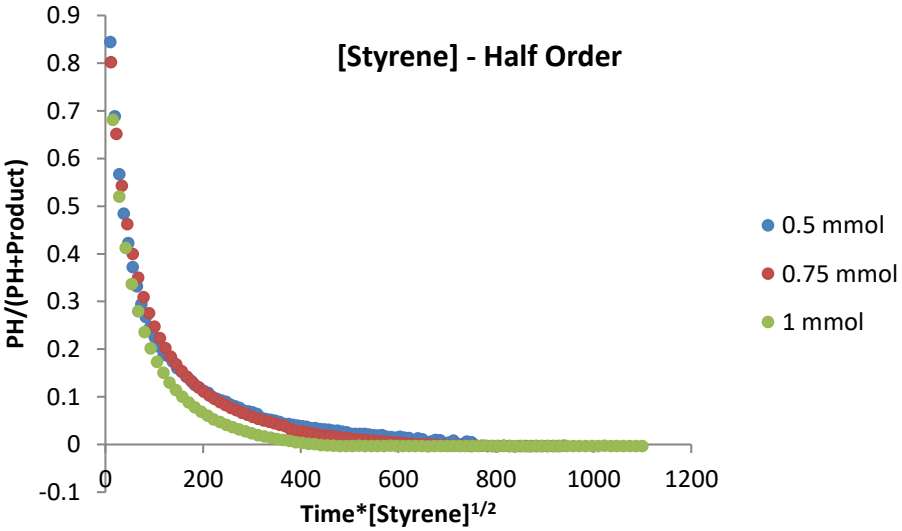
0.75 mmol Styrene

1 mmol Styrene

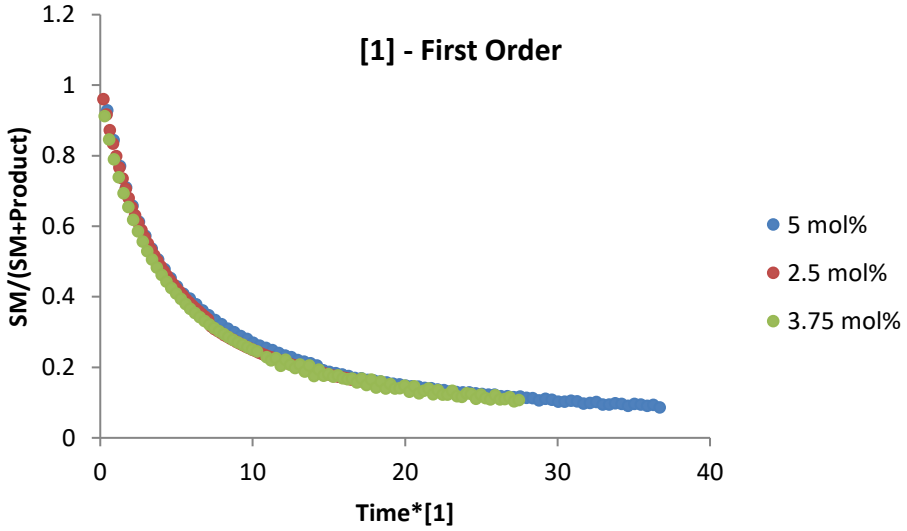
VTNA graphs for order in styrene:

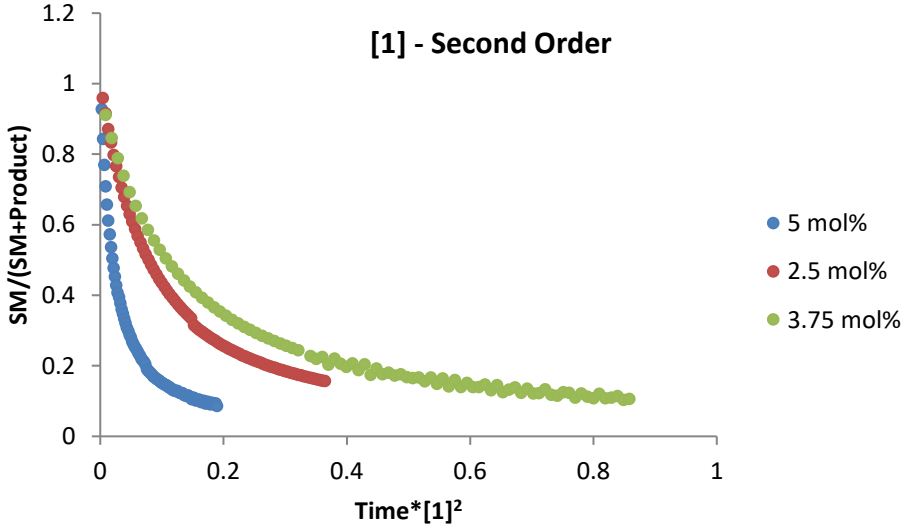


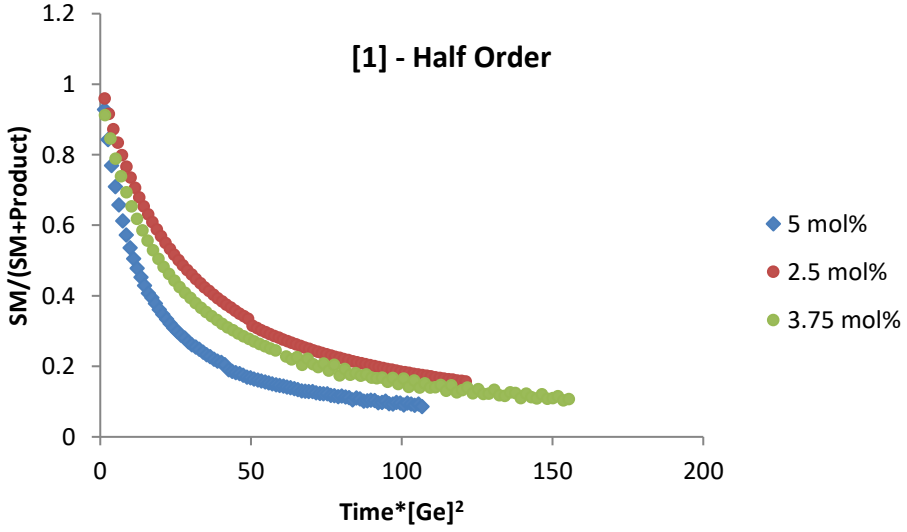

[Styrene] - Second Order
PH/(PH+Product)
Time*[Styrene]²
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
500
1000
1500
2000
2500
0.5 mmol
0.75 mmol
1 mmol


[Styrene] - Half Order
PH/(PH+Product)
Time*[Styrene]¹/²
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
200
400
600
800
1000
1200
0.5 mmol
0.75 mmol
1 mmol

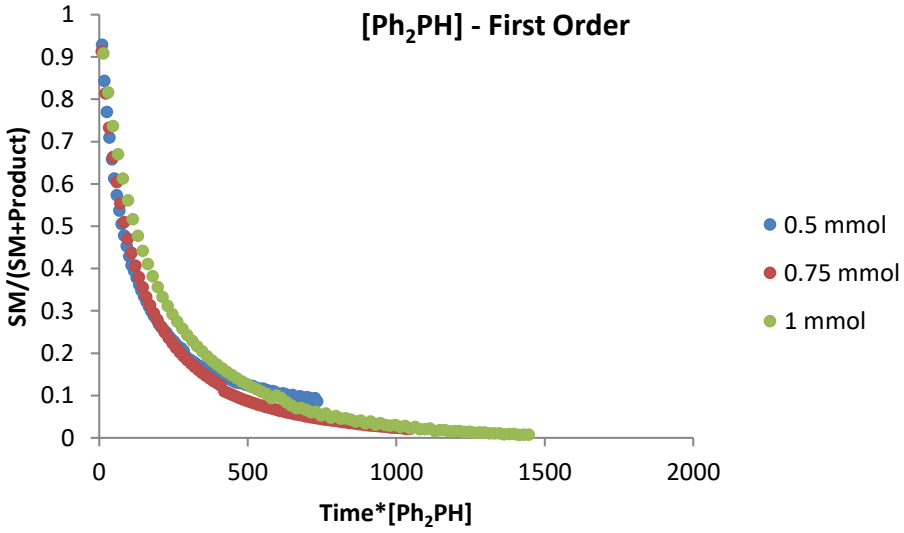
VTNA graphs for order in **1**:

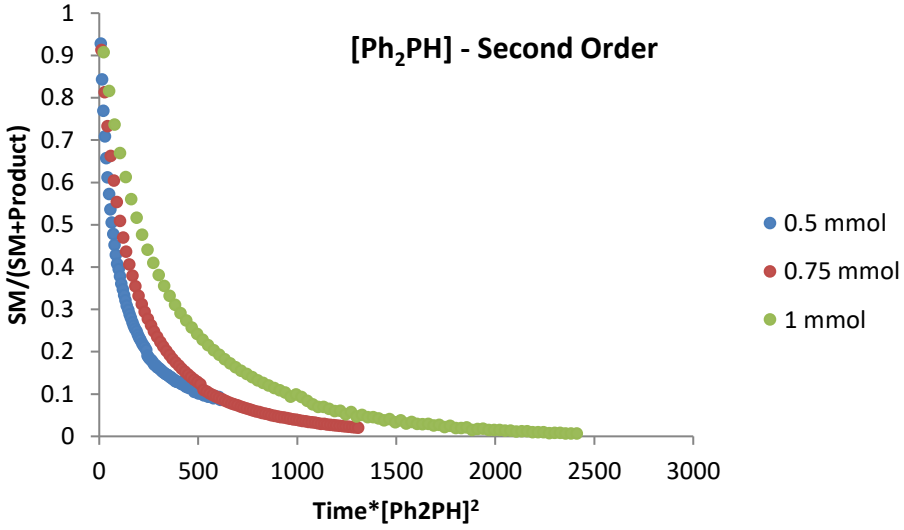


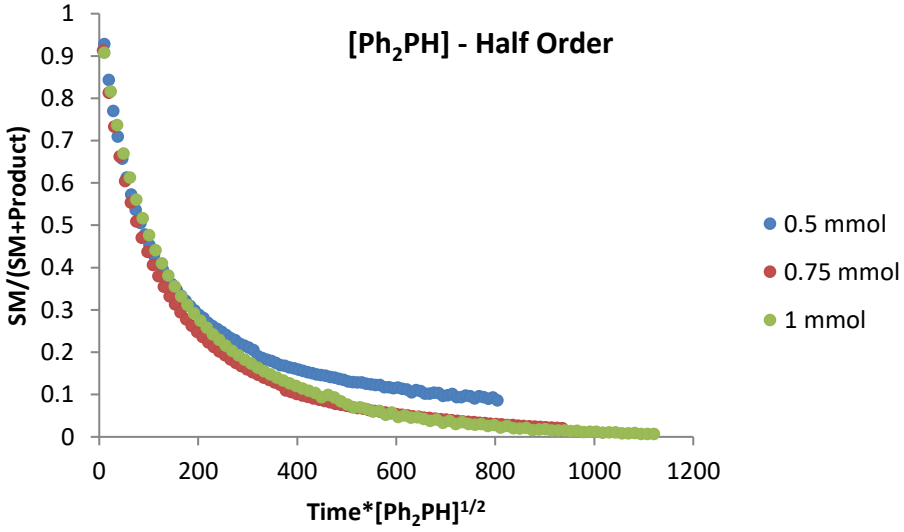



VTNA graphs for order in diphenylphosphine:

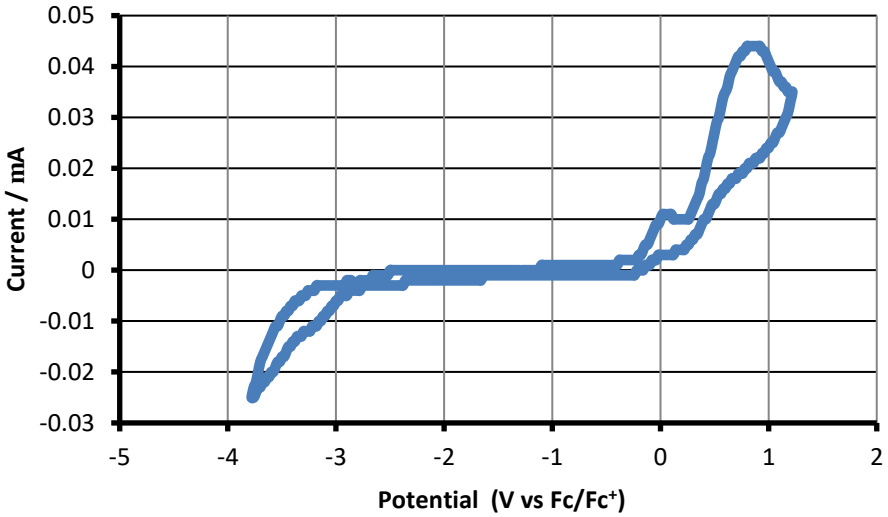


## 12. Cyclic Voltammetry Studies

Cyclic voltammery experiments were performed under an argon atmosphere using standard Schlenk techniques and a custom built three-necked Schlenk flask. To 25 mL of dry THF was added 1 (47 mg, 5 mm) and tetrabutylammonium hexafluorophosphate (1.16 g, 1 M). A standard three electrode setup was used (glassy carbon working electrode, platinum counter electrode and platinum wire pseudo-reference electrode). Voltammogram was referenced to $Fc/Fc^{+}$ oxidation potential by addition of 1 mg Ferrocene to the solution. Oxidation of THF solvent is observed, but there are no redox events at Ge, confirming that Ge remains as Ge(IV) during catalysis.



## 13. References


1. J. Guo, P. Haquette, J. Martin, K. Salim and C. M. Thomas, *Angew. Chem. Int. Ed.*, 2013, **52**, 13584-13587.
2. K. J. Gallagher and R. L. Webster, *Chem. Commun.*, 2014, **50**, 12109-12111.
3. J. Yuan, H. Hu and C. Cui, *Chem. Eur. J.*, 2016, **22**, 5778-5785.
4. Y. Zhang, L. Qu, Y. Wang, D. Yuan, Y. Yao and Q. Shen, *Inorg. Chem.*, 2018, **57**, 139-149.
5. H. Hu and C. Cui, *Organometallics*, 2012, **31**, 1208-1211.
6. A. U. Buranov and T. C. Morrill, *Tetrahedron Lett.*, 2003, **44**, 6301-6304.
7. M. Newcomb, Radical Kinetics and Clocks, *Encyclopedia of Radicals in Chemistry, Biology and Materials*, 2012.
8. D. A. Leigh, R. G. Pritchard and A. J. Stephens, *Nat, Chem,*, 2014, **6**, 978-982.
9. J. Bures, *Angew. Chem. Int. Ed.*, 2016, **55**, 2028-2031.