Supporting Information

Silver-promoted Cascade Radical Cyclization of γ, δ-Unsaturated Oxime Esters with P(O)H Compounds: Synthesis of Phosphorylated Pyrrolines

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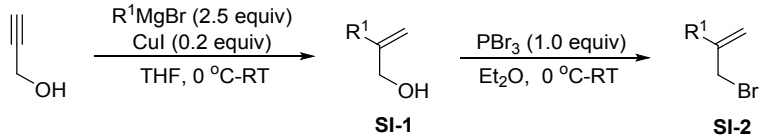
General Information:

The ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR were recorded with Bruker 400 MHz spectrometer instruments in $CDCl_3$. The chemical shifts (δ) of ^{1}H NMR and ^{13}C NMR were measured in ppm, referenced to residual ^{1}H and ^{13}C signals of nondeuterated $CDCl_3$ (δ = 7.26 and 77.00), as internal standards. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200–300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF 254 plates and visualized by UV-light (254 nm). HRMS were recorded on VG ZAB-HS mass spectrometer with ESI resource.

Preparation and Characterization of Starting Materials:

General Procedure 1:

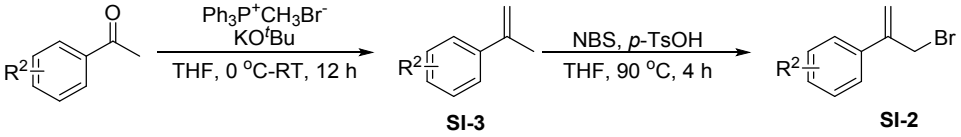


Step 1: To a stirred solution of propargyl alcohol (1.0 equiv) in anhydrous THF (1.5 mL/mol) under N_2, was added CuI (0.2 equiv). The resulting suspension was cooled to 0 °C. R^1MgBr (2.5 equiv) in anhydrous THF, which was freshly prepared from Mg and R^1Br, was added via cannula, at such a rate as to maintain the temperature below 0 °C. The reaction was allowed to warm slowly to room temperature overnight. The reaction was again cooled to 0 °C, and then was treated with H_2O to give a light green suspension. Then it was treated with EtOAc. After treatment with 1 M hydrochloric acid, a green gelatinous precipitate was formed, which was thoroughly extracted with EtOAc. The combined organic layers were dried with Na_2SO_4. After removing the solvent, the residue was purified by column chromatography to give **SI-1**. (*Angew. Chem. Int. Ed*. **2015**, *54*, 3092)

Step 2: To a solution of the appropriate alcohol (1.0 equiv) in anhydrous Et_2O at 0 °C was added PBr_3 (1.0 equiv). The solution was warmed to room temperature and stirred

for 7 hours. The reaction was cooled to 0 °C and water was added. The organic portion was isolated, washed with brine, dried and concentrated in vacuum to afford **SI-2**, which was used in the next step without further purification. (*Angew. Chem. Int. Ed*. **2015**, *54*, 3092)

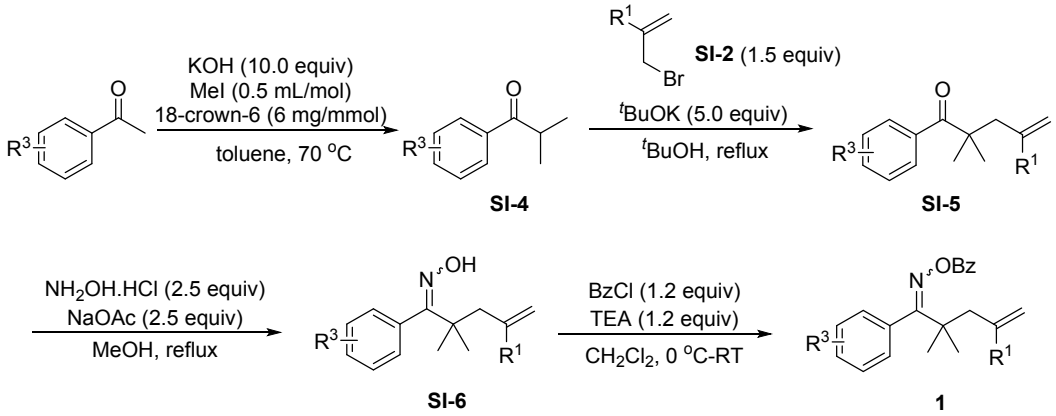
General Procedure 2:



Step 1: A solution of methyl triphenylphosphonium bromide (1.2 equiv) in anhydrous THF (1.5 mL/mol) was cooled to 0 °C under argon, followed by addition of ^{t}BuOK (1.2 equiv). The reaction mixture was stirred at 0 °C for 1 h, and then a solution of substituted acetophenone (1.0 equiv) in anhydrous THF (0.5 mL/mol) was added dropwise. The resulting mixture was warmed gradually to room temperature and kept stirring for 12 h. The resultant reaction solution was filtered over Celite, and the filtrate was concentrated under reduced pressure to yield a residue which was further purified over silica gel flash column chromatography to afford the product.

Step 2: To a solution of **SI-3** (1.0 equiv) in anhydrous THF (1.5 mL/mol) was added *N*-bromosuccinimide (1.1 equiv) and *p*-TsOH (0.1 equiv).The reaction mixture was heated to 90 °C and kept stirring for 4 h. Then the reaction solution was cooled to room temperature, concentrated under reduced pressure, and purified by silica gel flash column chromatography to afford the **SI-2**.

General Procedure 3:



Step 1: To a stirred suspension of KOH (10.0 equiv) in toluene (1.0 mL/mol)

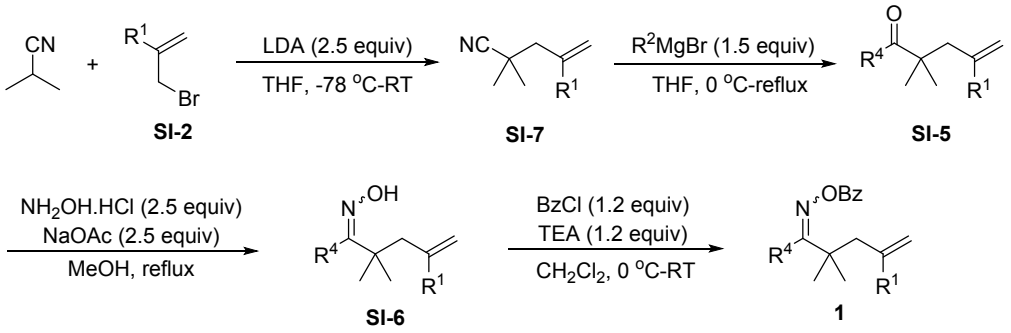
containing of substituted acetophenone (1.0 equiv) and 18-crown-6 (6.0 mg/mmol) was added CH_3I (0.5 mL/mol) dropwise. The mixture was stirred at 70 °C for 24 h. After cooling to room temperature, separation of the solid phase by filtration and evaporation of the toluene. The remainder was purified by column chromatography on silica gel to afford corresponding products **SI-4**. (*Org. Lett*. **2017**, *19*, 5940)

Step 2: To a solution of **SI-4** (1.0 equiv) in anhydrous ^{t}BuOH (3.0 mL/mmol) was added ^{t}BuOK (5.0 equiv) and the mixture was stirred at room temperature for 5 minutes. Then, **SI-2** (1.5 equiv) was added via syringe and the mixture was heated at 90 °C for 16 hours. The mixture was cooled to room temperature and H_2O was added. The mixture was extracted with EtOAc. The organic extracts were combined, washed with brine, dried with Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatography to give **SI-5**. (*Angew. Chem. Int. Ed*. **2015**, *54*, 3092)

Step 3: $NH_2OH{\cdot}HCl$ (2.5 equiv) and NaOAc (2.5 equiv) were added to a solution of **SI-5** (1.0 equiv) in MeOH (4.0 mL/mmol) in a round-bottomed flask which was fitted with a reflux condenser. The mixture was heated at 80 °C until consumption of starting material was observed by TLC. After cooling to room temperature, the mixture was diluted with EtOAc, washed with brine, dried with Na_2SO_4 and concentrated in vacuum to give **SI-6**, which was used for the next step without further purification. (*Angew. Chem. Int. Ed*. **2015**, *54*, 3092)

Step 4: To a solution of **SI-6** (1.0 equiv) in anhydrous DCM (4.0 mL/mmol) at 0 °C was added Et_3N (1.2 equiv) followed by BzCl (1.2 equiv) dropwise via syringe. The mixture was then warmed to room temperature and stirred until the reaction was complete as observed by TLC. MeOH (1.0 mL/mmol) was then added and the mixture stirred for further 10 minutes. The mixture was diluted with DCM, washed with brine, dried with Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatograph to afford **1a**, **1c**, **1d**, **1e**, **1g**, **1h**, **1r-1t**. (*Angew. Chem. Int. Ed*. **2015**, *54*, 3092)

General Procedure 4:

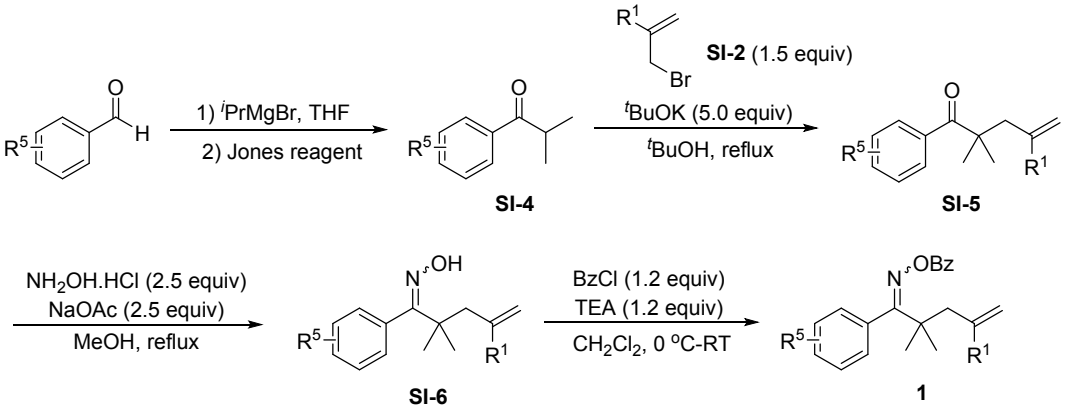


Step 1: To a flame-dried round-bottomed flask equipped with a stirring bar was added diisopropylamine (2.5 equiv) and ^{n}BuLi (2.5 equiv) in THF, and the reaction mixture was stirred at 0 °C for 30 minutes. Then nitriles (1.0 equiv) was slowly added at -78 °C. After stirring for 1 h, **SI-2** (1.2 equiv) was added dropwise and the reaction mixture was allowed to warm up to room temperature while stirring overnight. The reaction was quenched with saturated aqueous NH_4Cl solution. Organic materials were then extracted three times with EtOAc. The organic phase was washed with water and brine, and dried with Na_2SO_4. After filtration, the solvent was evaporated to give a crude mixture, which was purified by flash column chromatography to afford **SI-7**. (*ACS Catal*. **2016**, *6*, 5571)

Step 2: To a flame-dried round-bottomed flask equipped with a stirring bar was added **SI-7** (1.0 equiv). It was solubilized in anhydrous THF. The solution was cooled to 0 °C and R^2MgBr (1.5 equiv) was slowly added to the reaction flask. Then, the mixture was stirred overnight in a sealed tube at 60 °C. After cooling down to 0 °C, reaction was quenched with 3 N HCl (aq.) and warmed up for 4 h to finish the hydrolysis. The crude mixture was then extracted with EtOAc, washed with brine, dried with Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography to give **SI-5**. (*ACS Catal*. **2016**, *6*, 5571)

The remaining procedures follow the **General Procedure 3:** step 3 and step 4 to afford **1b**, **1f**, **1j**.

General Procedure 5:

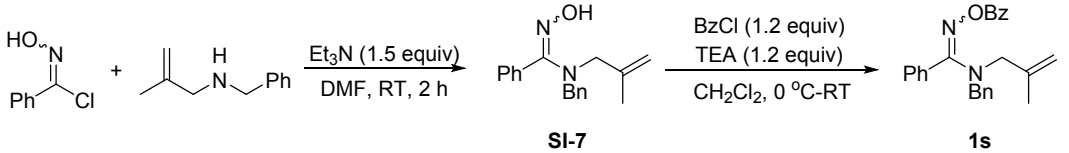


Step 1: 1) To a magnetically stirred aldehyde (1.0 equiv), was added isopropylmagnesium bromide (1.5 equiv), which was prepared from magnesium (1.5 equiv) and isopropyl bromide (1.5 equiv). The reaction mixture was stirred at room temperature for 36 h. Then, it was poured into saturated aqueous NH_4Cl solution and the aqueous layer was extracted with EtOAc. The combined organic layers were dried with Na_2SO_4 and concentrated in *vacuo*. The crude secondary alcohol was purified by column chromatography on silica using petroleum ether/ethyl acetate as eluent.

Step 1: 2) A solution of secondary alcohol (1.0 equiv) in ^{t}BuOMe was stirred at 0 ^{o}C while Jones reagent (4.0 equiv) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred overnight. The ^{t}BuOMe layer was then separated from the aqueous layer, which was extracted with EtOAc for 3 times. The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in *vacuo*. The crude ketone product **SI-4** was directly used in the next step without further purification.

The remaining procedures follow the **General Procedure 3:** step 2, step 3 and step 4 to afford **1i** and **1k**.

General Procedure 6:

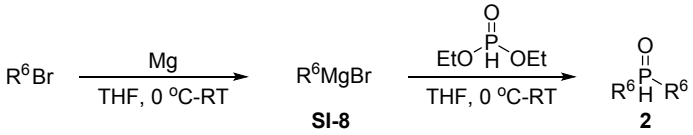


Step 1: To a round bottom flask were charged *N*-Allylbenzylamine (1.0 equiv), triethylamine (1.5 equiv) and DMF (1.5 mL/mmol). *N*-hydroxybenzimidoyl chloride

(1.2 equiv) in DMF (0.5 mL/mmol) was added dropwise to the mixture while stirring. After the addition was complete, the mixture was stirred at room temperature for 2 h. The reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated. The resulting residue was purified by flash column chromatography using petroleum (petroleum ether/ethyl acetate = 25:1) as eluent to afford **SI-7** as a yellow oil.

The remaining procedure follows the **General Procedure 3:** step 4 to afford **1u.**

General Procedure 7:



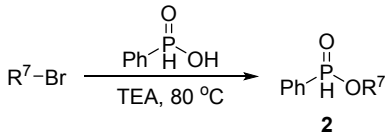
Step 1: SI-8 was prepared from aryl bromides or alkyl bromides (3.5 equiv) and magnesium (3.5 equiv). $HP(O)(OEt)_2$ (1.0 equiv) was added dropwise to a solution of **SI-8** at 0 °C. The mixture was aged for 15 minutes at 0 °C, then stirred at ambient temperature for two hours.

Step 2: (R^6 = aryl) After that cooled again to 0 °C, and 75 mL NH_4Cl aqueous was added slowly. The mixture was extracted with diethyl ether. Washed the organic phase with $NaHCO_3$ aqueous and brine, then dried with Na_2SO_4. After the solvent was completely removed under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the **2i**, **2j** and **2l**.

Step 2: (R^6 = alkyl) After that cooled again to 0 °C, 0.1 N HCl was then added dropwise over 20 minutes, then ^{t}BuOMe was added, and the mixture agitated well for 5 minutes. The upper organic phase was decanted from the gel and saved. To the remaining gel was added CH_2Cl_2, and the mixture agitated well for 5 minutes. The resultant mixture was then filtered through a Celite pad, washing the pad with CH_2Cl_2. The filtrate phases were separated, and the organic phase combined with the first organic phase, dried ($MgSO_4$), and the solvents removed in vacuum. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate

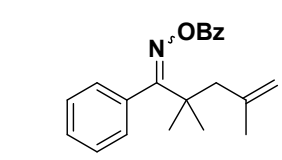
as eluent to give the **2n** and **2o**.

General Procedure 8:

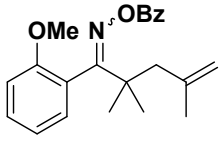


2

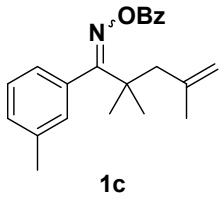
To the phenyl-H-phosphinic acid (1.0 equiv) was added R^7-Br (1.2 equiv) and TEA (1.1 equiv), and the mixture was closed and heated at 80 °C for 3 h. The residue was purified by column chromatograph to afford **2p**, **2q**, **2r** and **2s**.



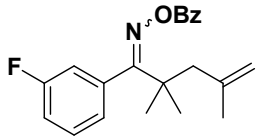
1a



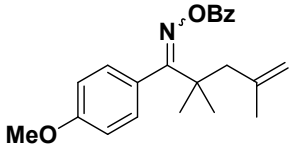
1b



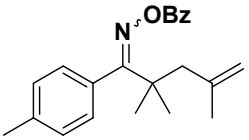
1c



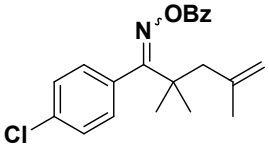
1d



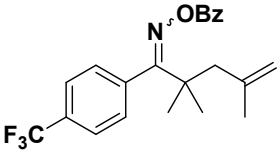
1e



1f



1g



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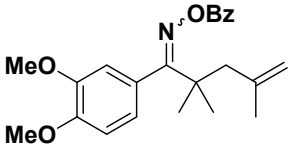
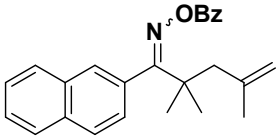


1i



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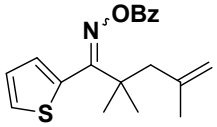

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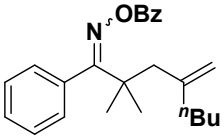

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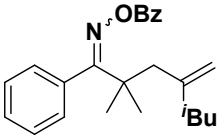

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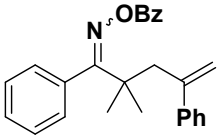
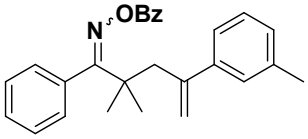
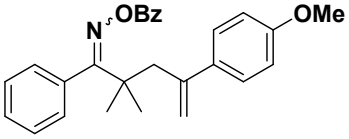


1n



1o



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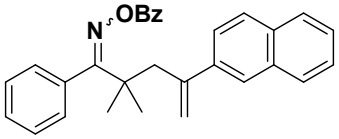

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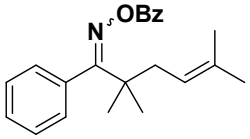
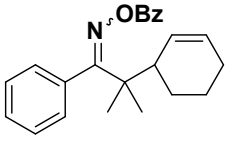
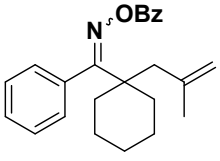


1r



1s



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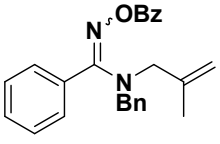
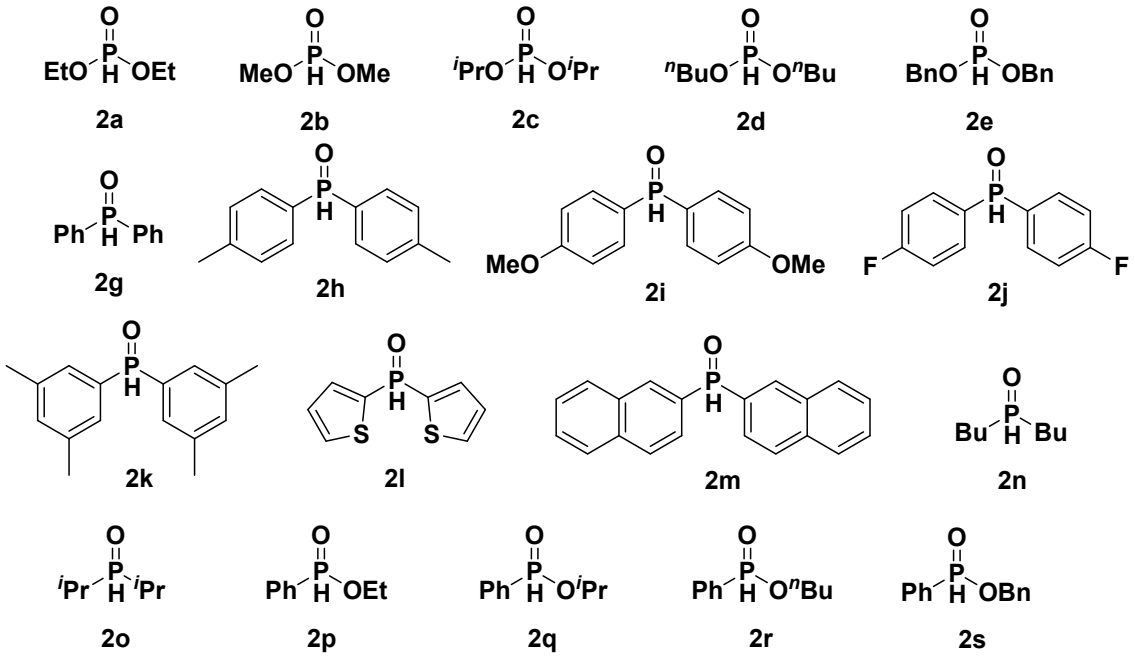


1u



1a, **1c**, **1d**, **1e**, **1g**, **1h**, **1r-1t** were synthesized by **General Procedure 3**

1l and **1m** were synthesized by **General Procedure 1** and **General Procedure 3**

1b, **1f**, **1j** were synthesized by **General Procedure 4**

1i and **1k** was synthesized by **General Procedure 5**

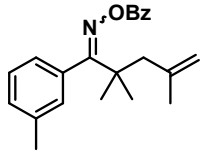
1n-1q were synthesized by **General Procedure 2** and **General Procedure 3**

1u was synthesized by **General Procedure 6**

2a-2h, 2k, 2m are commercial available

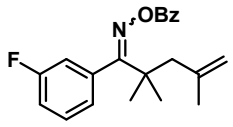
2i, 2j, 2l, 2n and **2o** were synthesized by **General Procedure 7**

2p-2s were synthesized by **General Procedure 8**



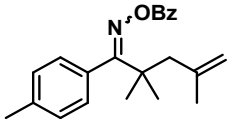
2,2,4-trimethyl-1-(m-tolyl)pent-4-en-1-one O-benzoyl oxime **(1c)** was synthesized by **General Procedure 3**. *^{1}H and ^{13}C NMR data listed is for the major isomer.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.42 – 7.35 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.16 (m, 3H), 6.95 – 6.91 (m, 2H), 4.93 – 4.91 (m, 1H), 4.83 – 4.81 (m, 1H), 2.37 (s, 2H), 2.34 (s, 3H), 1.79 (s, 3H), 1.28 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.92, 163.33, 141.94, 137.33, 133.06, 132.64, 129.06, 128.74, 128.01, 127.65, 126.92, 123.62, 114.90, 46.63, 41.19, 26.13, 25.11, 21.25. **HRMS (ESI)** Calcd for $C_{22}H_{25}NO_2$: [M+H$^+$] 336.1958, found 336.1960.



1-(3-fluorophenyl)-2,2,4-trimethylpent-4-en-1-one O-benzoyl oxime (**1d**) was synthesized by **General Procedure 3**. *^{1}H ,^{13}C and ^{19}F NMR data listed is for the major isomer.*

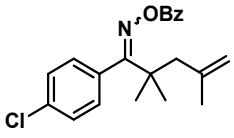
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.39 (m, 2H), 7.32 – 7.27 (m, 2H), 7.15 – 7.10 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.95 – 6.91 (m, 1H), 4.97 (s, 1H), 4.87 (s, 1H), 2.38 (s, 2H), 1.82 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.66 (d, *J* = 1.0 Hz), 163.39, 162.29 (d, *J* = 246.0 Hz), 141.97, 135.34 (d, *J* = 8.0 Hz), 133.01, 129.76 (d, *J* = 8.0 Hz), 129.30, 128.83, 128.31, 122.68 (d, *J* = 3.0 Hz), 115.38, 115.20, 114.07 (d, *J* = 23.0 Hz), 46.89, 41.49, 26.34, 25.32, 25.29. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.20 (s). **HRMS (ESI)** Calcd for $C_{21}H_{22}FNO_2$: [M+H$^+$] 340.1707, found 340.1711.



2,2,4-trimethyl-1-(p-tolyl)pent-4-en-1-one O-benzoyl oxime (**1f**) was synthesized by **General Procedure 4**. *^{1}H and ^{13}C NMR data listed is for the major isomer.*

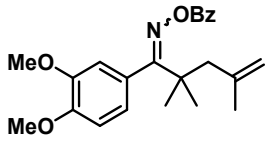
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.43 – 7.38 (m, 1H), 7.25 – 7.19 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.93 – 4.90 (m, 1H), 4.83 – 4.81 (m, 1H), 2.37 (s, 3H), 2.35 (s, 2H), 1.79 (s, 3H), 1.28 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.11, 163.48, 142.01, 137.78, 132.68, 130.33, 130.15, 129.14, 128.45, 128.07, 126.46, 114.87, 46.68, 41.32, 41.32, 26.16, 25.15, 21.10. **HRMS (ESI)** Calcd for $C_{22}H_{25}NO_2$:

[M+H$^+$] 336.1958, found 336.1960.



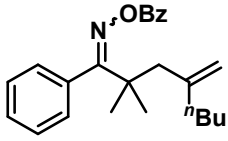
1-(4-chlorophenyl)-2,2,4-trimethylpent-4-en-1-one O-benzoyl oxime (**1g**) was synthesized by **General Procedure 3**. *^{1}H and ^{13}C NMR data listed is for the major isomer.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 1H), 7.53 – 7.48 (m, 2H), 7.44 – 7.40 (m, 2H), 7.31 – 7.26 (m, 2H), 7.14 – 7.11 (m, 2H), 4.96 (t, *J* = 1.6 Hz, 1H), 4.87 – 4.86 (m, 1H), 2.35 (s, 2H), 1.81 (s, 3H), 1.31 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.89, 162.18, 141.85, 134.37, 134.27, 132.91, 131.65, 130.38, 129.15, 128.23, 128.11, 115.06, 46.77, 41.40, 26.24, 25.17. HRMS (ESI) Calcd for $C_{21}H_{22}ClNO_2$: [M+H$^+$] 356.1412, found 356.1412.



1-(3,4-dimethoxyphenyl)-2,2,4-trimethylpent-4-en-1-one O-benzoyl oxime (**1i**) was synthesized by **General Procedure 5**. *^{1}H and ^{13}C NMR data listed is for the major isomer.*

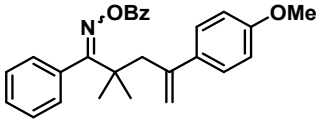
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.45 – 7.40 (m, 1H), 7.28 – 7.24 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.73 – 6.67 (m, 2H), 4.94 – 4.92 (m, 1H), 4.85 (s, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 2.34 (s, 2H), 1.79 (s, 3H), 1.30 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.63, 163.54, 148.59, 148.23, 142.11, 132.77, 129.13, 128.85, 128.16, 125.43, 119.20, 114.74, 110.35, 110.09, 55.78, 55.66, 46.82, 41.51, 26.32, 25.16. **HRMS (ESI)** Calcd for $C_{23}H_{27}NO_4$: [M+H$^+$] 382.2013, found 382.2014.



2,2-dimethyl-4-methylene-1-phenyloctan-1-one O-benzoyl oxime (**1l**) was synthesized by **General Procedure 1** and **3**. *^{1}H and ^{13}C NMR data listed is for the major isomer.*

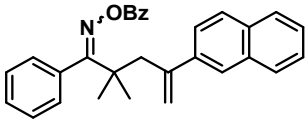
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.45 – 7.38 (m, 4H), 7.27 – 7.22 (m, 2H), 7.17 – 7.13 (m, 2H), 4.96 (s, 1H), 4.92 (s, 1H), 2.34 (s, 2H), 2.03 (t, *J* = 7.2 Hz, 2H), 1.43 – 1.37 (m, 2H), 1.31 (s, 6H), 1.26 (t, *J* = 6.8 Hz, 2H), 0.87 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.28, 163.54, 146.12, 133.38, 132.83, 129.27,

129.00, 128.20, 127.92, 126.66, 113.46, 44.92, 41.53, 38.17, 30.29, 26.19, 22.39, 13.96. **HRMS (ESI)** Calcd for $C_{24}H_{29}NO_2$: [M+H$^+$] 364.2271, found 364.2272.



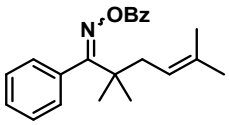
4-(4-methoxyphenyl)-2,2-dimethyl-1-phenylpent-4-en-1-one O-benzoyl oxime (**1p**) was synthesized by **General Procedure 2** and **3**. *^{1}H and ^{13}C NMR data listed is for the major isomer.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.44 – 7.37 (m, 4H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.07 – 7.04 (m, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 5.30 (s, 1H), 5.13 (s, 1H), 3.73 (s, 3H), 2.93 (s, 2H), 1.15 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.09, 163.52, 158.83, 144.83, 135.49, 133.33, 132.84, 129.23, 128.93, 128.19, 128.14, 127.91, 127.63, 126.57, 116.60, 113.45, 55.11 (d, *J* = 5.0 Hz), 44.35, 41.84, 26.14 (d, *J* = 2.0 Hz). **HRMS (ESI)** Calcd for $C_{27}H_{27}NO_3$: [M+H$^+$] 414.2064, found 414.2068.



2,2-dimethyl-4-(naphthalen-2-yl)-1-phenylpent-4-en-1-one O-benzoyl oxime (**1q**) was synthesized by **General Procedure 2** and **3**. *^{1}H and ^{13}C NMR data listed is for the major isomer.*

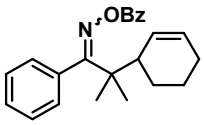
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 4H), 7.55 – 7.50 (m, 3H), 7.42 – 7.37 (m, 6H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.08 – 7.05 (m, 2H), 5.51 (s, 1H), 5.33 (s, 1H), 3.09 (s, 2H), 1.17 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.04, 163.59, 145.48, 140.48, 133.35, 133.25, 132.84, 132.63, 129.29, 128.20, 128.05, 127.95, 127.78, 127.43, 126.65, 126.04, 125.70, 125.16, 125.13, 118.64, 44.34, 42.01, 26.22. **HRMS (ESI)** Calcd for $C_{30}H_{27}NO_2$: [M+H$^+$] 434.2115, found 434.2118.



2,2,5-trimethyl-1-phenylhex-4-en-1-one O-benzoyl oxime (**1r**) was synthesized by **General Procedure 3**. *^{1}H and ^{13}C NMR data listed is for the major isomer.*

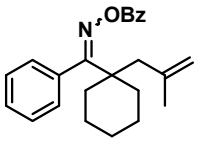
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H), 7.46 – 7.39 (m, 4H), 7.29 – 7.24 (m, 2H), 7.14 – 7.11 (m, 2H), 5.29 (t, *J* = 6.8 Hz, 1H), 2.27 (d, *J* = 7.2 Hz, 2H), 1.76

(s, 3H), 1.60 (s, 3H), 1.29 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.94, 163.57, 134.20, 133.49, 132.78, 129.29, 129.14, 128.19, 128.11, 127.91, 126.68, 119.79 (d, *J* = 4.0 Hz), 42.02, 38.19, 25.99, 25.57, 18.12. **HRMS (ESI)** Calcd for $C_{22}H_{25}NO_2$: [M+H$^+$] 336.1958, found 336.1962.



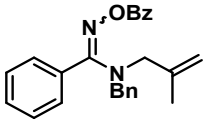
2-(cyclohex-2-en-1-yl)-2-methyl-1-phenylpropan-1-one O-benzoyl oxime (**1s**) was synthesized by **General Procedure 3**. *^{1}H and ^{13}C NMR data listed is for the major isomer.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.46 – 7.38 (m, 4H), 7.29 – 7.24 (m, 2H), 7.15 – 7.12 (m, 2H), 5.86 – 5.74 (m, 2H), 2.47 (s, 1H), 1.99 (s, 2H), 1.86 – 1.78 (m, 2H), 1.51 – 1.40 (m, 2H), 1.28 (s, 3H), 1.24 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.03, 163.60, 133.45, 132.82, 129.44, 129.28, 129.07, 128.21, 128.15, 127.96, 127.76, 126.75, 44.57, 40.82, 25.17, 23.83, 23.54, 22.48, 21.21. **HRMS (ESI)** Calcd for $C_{23}H_{25}NO_2$: [M+H$^+$] 348.1958, found 348.1960.



(1-(2-methylallyl)cyclohexyl)(phenyl)methanone O-benzoyl oxime (**1t**) was synthesized by **General Procedure 3**. *^{1}H and ^{13}C NMR data listed is for the major isomer.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.46 – 7.38 (m, 4H), 7.29 – 7.21 (m, 4H), 4.97 (s, 1H), 4.95 (s, 1H), 2.38 (s, 2H), 2.04 – 2.00 (m, 2H), 1.84 (s, 3H), 1.70 – 1.65 (m, 3H), 1.59 – 1.53 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.43, 163.60, 141.90, 133.27, 132.82, 129.31, 129.09, 128.25, 128.22, 127.91, 126.82, 114.92, 45.14, 34.25, 31.91, 29.35, 25.95, 25.47, 22.68, 22.46. **HRMS (ESI)** Calcd for $C_{24}H_{27}NO_2$: [M+H$^+$] 362.2115, found 362.2116.

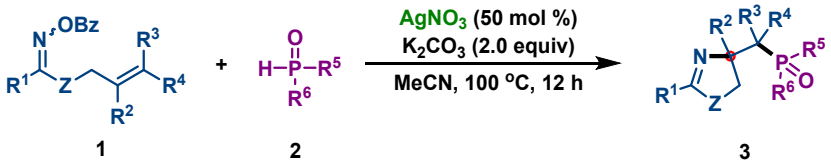


N'-(benzoyloxy)-N-benzyl-N-(2-methylallyl)benzimidamide (**1u**) was synthesized by **General Procedure 6**. *^{1}H and ^{13}C NMR data listed is for the major isomer.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.49 – 7.36 (m, 10H), 7.33 – 7.27 (m, 3H), 4.98 (s, 1H), 4.92 (s, 1H), 4.57 (s, 2H), 3.72 (s, 2H), 1.70 (s, 3H). **^{13}C NMR**

(100 MHz, $CDCl_3$) δ 167.33, 164.52, 140.52, 137.25, 132.33, 131.56, 129.76, 129.38, 129.05, 128.52, 128.46, 128.07, 127.66, 127.32, 112.88, 52.56, 50.11, 20.22. **HRMS (ESI)** Calcd for $C_{25}H_{24}N_2O_2$: $[M+H^+]$ 385.1911, found 385.1913.

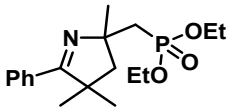
Synthesis and Characterization of Phosphorylated Pyrrolines:



1 2 3

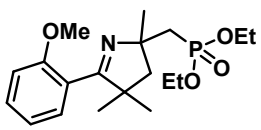
In a 25.0 mL sealed tube, **1** (0.2 mmol, 1.0 equiv), **2** (0.2 or 0.4 mmol, 1.0 or 2.0 equiv), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv) were added to a solution of $AgNO_3$ (17.0 mg, 0.1 mmol, 0.5 equiv) in MeCN (3.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction was allowed to stir at 100 °C for 12 h. Afterward, the resulting mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired pure products **3** listed in Scheme 2 and Scheme 3.

***Diethyl((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate* (3aa)**



Yield: 96%, 64.8 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.38 – 7.29 (m, 3H), 4.16 – 4.00 (m, 4H), 2.40 (d, *J* = 13.6 Hz, 1H), 2.34 (dd, *J* = 18.4, 15.2 Hz, 1H), 2.04 (dd, *J* = 18.4, 15.2 Hz, 1H), 1.92 (d, *J* = 13.6 Hz, 1H), 1.48 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H), 1.32 – 1.25 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.18 (d, *J* = 1.0 Hz), 134.78, 129.21, 128.03, 127.94, 69.49, 61.29 (d, *J* = 6.0 Hz), 61.23 (d, *J* = 5.0 Hz), 51.98, 51.92, 39.21 (d, *J* = 136.0 Hz), 29.70 (d, *J* = 4.0 Hz), 28.77 (d, *J* = 2.0 Hz), 28.38 (d, *J* = 2.0 Hz), 16.34 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.25 (s). **HRMS (ESI)** Calcd for $C_{18}H_{28}NO_3P$: [M+H$^+$] 338.1880, found 338.1887.

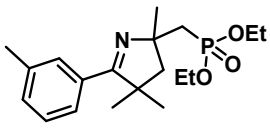
***Diethyl((5-(2-methoxyphenyl)-2,4,4-trimethyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate* (3ba)**



Yield: 93%, 68.2 mg; appearance: brown oil; R_f: 0.2 (petroleum

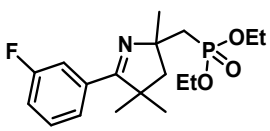
ether/ethyl acetate = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 1H), 7.08 – 7.05 (m, 1H), 6.92 – 6.85 (m, 2H), 4.15 – 4.03 (m, 4H), 3.73 (s, 3H), 2.36 (dd, *J* = 18.4, 15.2 Hz, 1H), 2.35 (d, *J* = 13.2 Hz, 1H), 2.04 (dd, *J* = 18.0, 15.2 Hz, 1H), 1.89 (d, *J* = 13.6 Hz, 1H), 1.49 (s, 3H), 1.33 – 1.26 (m, 6H), 1.14 (s, 3H), 1.14 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.44, 156.96, 129.38, 129.29, 124.83, 119.80, 110.91, 70.81, 61.28, 61.31 (d, *J* = 6.0 Hz), 61.20 (d, *J* = 6.0 Hz), 55.33 (d, *J* = 4.0 Hz), 53.61, 49.67, 39.16 (d, *J* = 136.0 Hz), 29.59 (d, *J* = 3.0 Hz), 27.80 (d, *J* = 2.0 Hz), 27.69 (d, *J* = 2.0 Hz), 16.33 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.46 (s). **HRMS (ESI)** Calcd for $C_{19}H_{30}NO_4P$: [M+H$^+$] 368.1985, found 368.1990.

***Diethyl((2,4,4-trimethyl-5-(m-tolyl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate* (3ca)**



Yield: 90%, 63.1 mg; appearance: green oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.43 – 7.40 (m, 1H), 7.25 – 7.15 (m, 2H), 4.15 – 4.02 (m, 4H), 2.40 (d, *J* = 13.6 Hz, 1H), 2.35 (dd, *J* = 18.4, 15.2 Hz, 1H), 2.34 (s, 3H), 2.04 (dd, *J* = 18.0, 15.2 Hz, 1H), 1.92 (d, *J* = 13.2 Hz, 1H), 1.49 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H), 1.33 – 1.27 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.41, 137.74, 134.74, 130.00, 128.77, 127.85, 124.79, 69.44, 61.30 (d, *J* = 4.0 Hz), 61.24 (d, *J* = 5.0 Hz), 51.94, 39.21 (d, *J* = 136.0 Hz), 29.68 (d, *J* = 4.0 Hz), 28.83 (d, *J* = 2.0 Hz), 28.45 (d, *J* = 1.0 Hz), 21.35 (d, *J* = 3.0 Hz), 16.36 (d, *J* = 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.29 (s). **HRMS (ESI)** Calcd for $C_{19}H_{30}NO_3P$: [M+H$^+$] 352.2036, found 352.2041.

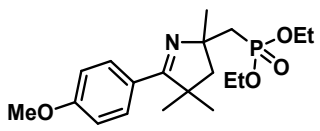
***Diethyl((5-(3-fluorophenyl)-2,4,4-trimethyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate* (3da)**



Yield: 96%, 68.0 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 7.34 – 7.27 (m, 1H), 7.09 – 7.03 (m, 1H), 4.15 – 4.01 (m, 4H), 2.41 (d, *J* = 13.2 Hz, 1H), 2.32 (dd, *J* = 18.4, 15.2 Hz, 1H), 2.04 (dd, *J* = 18.4, 15.2 Hz, 1H), 1.92 (d, *J* = 13.2 Hz, 1H), 1.47 (s, 3H), 1.37 (s,

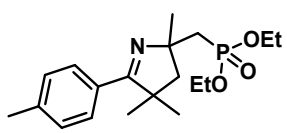
3H), 1.34 (s, 3H), 1.32 – 1.26 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.03, 162.42 (d, *J* = 244.0 Hz), 136.94 (d, *J* = 7.0 Hz), 129.63 (d, *J* = 8.0 Hz), 123.65 (d, *J* = 3.0 Hz), 116.22 (d, *J* = 22.0 Hz), 115.14 (d, *J* = 22.0 Hz), 69.66, 61.34 (d, *J* = 6.0 Hz), 61.28 (d, *J* = 6.0 Hz), 52.00, 51.89, 39.14 (d, *J* = 136.0 Hz), 29.74 (d, *J* = 4.0 Hz), 28.74 (d, *J* = 2.0 Hz), 28.27 (d, *J* = 2.0 Hz), 16.35 (d, *J* = 6.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.91 (s). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.01 (s). **HRMS (ESI)** Calcd for $C_{18}H_{27}FNO_3P$: [M+H$^+$] 356.1785, found 356.1784.

Diethyl((5-(4-methoxyphenyl)-2,4,4-trimethyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate **(3ea)**



Yield: 95%, 69.7 mg; appearance: green oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.14 – 4.01 (m, 4H), 3.79 (s, 3H), 2.38 (d, *J* = 13.6 Hz, 1H), 2.33 (dd, *J* = 18.4, 15.6 Hz, 1H), 2.02 (dd, *J* = 18.0, 15.2 Hz, 1H), 1.92 (d, *J* = 13.6 Hz, 1H), 1.46 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H), 1.31 – 1.25 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.06 (d, *J* = 1.0 Hz), 160.54, 129.60, 126.96, 113.41, 69.01, 61.28 (d, *J* = 3.0 Hz), 61.22 (d, *J* = 3.0 Hz), 52.17 (d, *J* = 5.0 Hz), 52.46 (d, *J* = 2.0 Hz), 51.57, 39.27 (d, *J* = 135.0 Hz), 29.71 (d, *J* = 4.0 Hz), 28.94 (d, *J* = 2.0 Hz), 28.58 (d, *J* = 2.0 Hz), 16.34 (d, *J* = 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.38 (s). **HRMS (ESI)** Calcd for $C_{19}H_{30}NO_4P$: [M+H$^+$] 368.1985, found 368.1991.

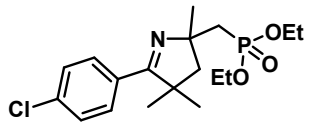
Diethyl((2,4,4-trimethyl-5-(p-tolyl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate **(3fa)**



Yield: 75%, 52.7 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.15 – 4.02 (m, 4H), 2.40 (d, *J* = 13.2 Hz, 1H), 2.35 (dd, *J* = 18.4, 15.6 Hz, 1H), 2.35 (s, 3H), 2.04 (dd, *J* = 18.4, 15.6 Hz, 1H), 1.92 (d, *J* = 13.2 Hz, 1H), 1.48 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H), 1.33 – 1.27 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.88,

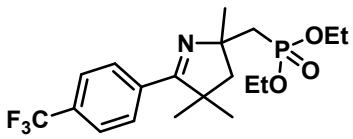
139.34, 131.80, 128.77, 127.99, 69.31, 61.32 (d, *J* = 4.0 Hz), 61.25 (d, *J* = 4.0 Hz), 52.23, 51.80, 39.28 (d, *J* = 135.0 Hz), 29.72 (d, *J* = 4.0 Hz), 28.89 (d, *J* = 1.0 Hz), 28.53 (d, *J* = 1.0 Hz), 21.24 (d, *J* = 4.0 Hz), 16.38 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.37 (s). **HRMS (ESI)** Calcd for $C_{19}H_{30}NO_3P$: [M+H$^+$] 352.2036, found 352.2045.

Diethyl((5-(4-chlorophenyl)-2,4,4-trimethyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate **(3ga)**



Yield: 85%, 63.2 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.33 – 7.29 (m, 2H), 4.14 – 4.02 (m, 4H), 2.40 (d, *J* = 13.6 Hz, 1H), 2.31 (dd, *J* = 18.8, 15.6 Hz, 1H), 2.03 (dd, *J* = 18.4, 15.6 Hz, 1H), 1.92 (d, *J* = 13.6 Hz, 1H), 1.47 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H), 1.32 – 1.26 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.03, 135.44, 133.12, 129.40, 128.30, 69.58, 61.33 (d, *J* = 6.0 Hz), 61.27 (d, *J* = 6.0 Hz), 52.05, 51.81, 39.15 (d, *J* = 136.0 Hz), 29.75 (d, *J* = 6.0 Hz), 28.76, 28.31 (d, *J* = 1.0 Hz), 16.36 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.05 (s). **HRMS (ESI)** Calcd for $C_{18}H_{27}ClNO_3P$: [M+H$^+$] 372.1490, found 372.1492.

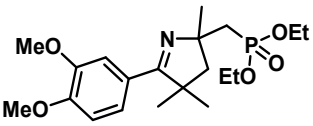
Diethyl((2,4,4-trimethyl-5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate **(3ha)**



Yield: 91%, 73.7 mg; appearance: brown oil; Rf: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 4.13 – 4.00 (m, 4H), 2.42 (d, *J* = 13.6 Hz, 1H), 2.30 (dd, *J* = 18.4, 15.2 Hz, 1H), 2.04 (dd, *J* = 18.0, 15.2 Hz, 1H), 1.92 (d, *J* = 13.6 Hz, 1H), 1.46 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H), 1.31 – 1.23 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.12, 138.38, 131.09 (q, *J* = 33.0 Hz), 128.32, 124.95 (q, *J* = 3.0 Hz), 123.89 (q, *J* = 271.0 Hz), 69.96, 61.31 (d, *J* = 6.0 Hz), 61.22 (d, *J* = 6.0 Hz), 51.97, 51.79, 39.09 (d, *J* = 137.0 Hz), 29.75 (d, *J* = 6.0 Hz), 28.60 (d, *J* = 2.0 Hz), 28.10 (d, *J* = 3.0 Hz), 16.29 (d,

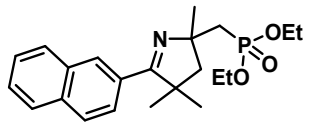
J = 4.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.84 (s). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.84 (s). **HRMS (ESI)** Calcd for $C_{19}H_{27}F_3NO_3P$: [M+H$^+$] 406.1753, found 406.1758.

***Diethyl((5-(3,4-dimethoxyphenyl)-2,4,4-trimethyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate* (3ia)**



Yield: 93%, 73.8 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.26 – 7.22 (m, 1H), 6.80 – 6.76 (m, 1H), 4.10 – 4.00 (m, 4H), 3.87 – 3.83 (m, 6H), 2.38 – 2.27 (m, 2H), 2.05 – 1.95 (m, 1H), 1.89 (d, *J* = 13.6 Hz, 1H), 1.45 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H), 1.30 – 1.23 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.90, 150.18, 148.52, 127.17, 120.82, 111.51, 110.14, 68.95, 61.22 (d, *J* = 5.0 Hz), 61.15 (d, *J* = 4.0 Hz), 55.78 (d, *J* = 5.0 Hz), 55.73 (d, *J* = 5.0 Hz), 52.58 (d, *J* = 2.0 Hz), 51.52, 39.24 (d, *J* = 136.0 Hz), 29.63 (d, *J* = 5.0 Hz), 29.01 (d, *J* = 1.0 Hz), 28.67, 16.30 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.32 (s). **HRMS (ESI)** Calcd for $C_{20}H_{32}NO_5P$: [M+H$^+$] 398.2091, found 398.2100.

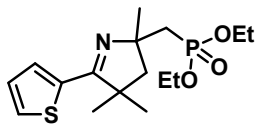
***Diethyl((2,4,4-trimethyl-5-(naphthalen-2-yl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate* (3ja)**



Yield: 79%, 61.2 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.152 (s, 1H), 7.88 – 7.81 (m, 4H), 7.52 – 7.46 (m, 2H), 4.18 – 4.05 (m, 4H), 2.48 (d, *J* = 13.2 Hz, 1H), 2.41 (dd, *J* = 18.4, 15.2 Hz, 1H), 2.12 (dd, *J* = 18.4, 15.6 Hz, 1H), 2.00 (d, *J* = 13.6 Hz, 1H), 1.55 (s, 3H), 1.49 (s, 3H), 1.46 (s, 3H), 1.35 – 1.29 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.00, 133.66, 132.80, 132.12, 128.56, 127.74, 127.66, 127.57, 126.70, 126.20, 125.75, 69.61, 61.38 (d, *J* = 4.0 Hz), 61.32 (d, *J* = 5.0 Hz), 52.34, 52.05, 39.30 (d, *J* = 136.0 Hz), 29.83 (d, *J* = 5.0 Hz), 29.05 (d, *J* = 0.8 Hz), 28.65 (d, *J* = 0.8 Hz), 16.41 (d, *J* = 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.26 (s). **HRMS (ESI)** Calcd for $C_{22}H_{30}NO_3P$: [M+H$^+$]

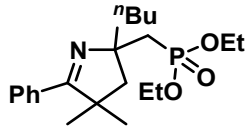
388.2036, found 388.2034.

Diethyl((2,4,4-trimethyl-5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate **(3ka)**



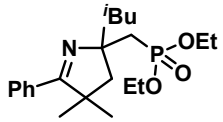
Yield: 55%, 37.9 mg; appearance: brown oil; Rf: 0.3 (petroleum ether/ethyl acetate = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 1H), 7.37 – 7.34 (m, 1H), 7.04 (dd, *J* = 5.2, 4.0 Hz, 1H), 4.16 – 4.02 (m, 4H), 2.43 (d, *J* = 13.2 Hz, 1H), 2.34 (dd, *J* = 18.4, 15.6 Hz, 1H), 2.06 (dd, *J* = 18.0, 15.2 Hz, 1H), 1.94 (d, *J* = 13.6 Hz, 1H), 1.47 (s, 6H), 1.46 (s, 3H), 1.33 – 1.27 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.77, 138.08, 128.33, 127.99, 127.32, 70.06, 61.39 (d, *J* = 7.0 Hz), 61.31 (d, *J* = 6.0 Hz), 52.46(d, *J* = 2.0 Hz), 51.52, 39.21 (d, *J* = 136.0 Hz), 29.96 (d, *J* = 6.0 Hz), 28.81 (d, *J* = 22.0 Hz), 16.40 (d, *J* = 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.09 (s). **HRMS (ESI)** Calcd for $C_{16}H_{26}NO_3PS$: [M+H$^+$] 344.1444, found 344.1450.

Diethyl((2-butyl-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate **(3la)**



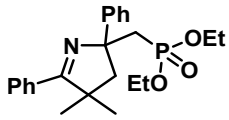
Yield: 88%, 66.7 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.35 – 7.30 (m, 3H), 4.12 – 4.01 (m, 4H), 2.38 (d, *J* = 13.6 Hz, 1H), 2.34 (dd, *J* = 18.8, 15.6 Hz, 1H), 2.02 (dd, *J* = 18.4, 15.6 Hz, 1H), 1.92 (d, *J* = 13.6 Hz, 1H), 1.83 – 1.70 (m, 2H), 1.39 (s, 3H), 1.32 – 1.24 (m, 13H), 0.89 (t, *J* = 2.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.45, 135.01, 129.09, 127.99, 127.98, 72.48, 61.27 (d, *J* = 6.0 Hz), 61.14 (d, *J* = 7.0 Hz), 51.66, 49.26, 41.91 (d, *J* = 7.0 Hz), 37.28 (d, *J* = 137.0 Hz), 28.73 (d, *J* = 1.0 Hz), 28.43 (d, *J* = 2.0 Hz), 26.61, 23.12, 16.33 (d, *J* = 6.0 Hz), 14.02. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.50 (s). **HRMS (ESI)** Calcd for $C_{21}H_{34}NO_3P$: [M+H$^+$] 380.2349, found 380.2358.

Diethyl((2-isobutyl-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate **(3ma)**



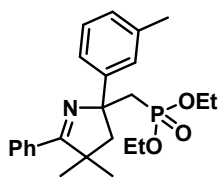
Yield: 75%, 56.9 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.36 – 7.30 (m, 3H), 4.14 – 4.01 (m, 4H), 2.44 (d, *J* = 13.6 Hz, 1H), 2.36 (dd, *J* = 18.4, 15.2 Hz, 1H), 2.06 (dd, *J* = 18.8, 15.2 Hz, 1H), 1.92 (d, *J* = 13.6 Hz, 1H), 1.86 – 1.66 (m, 3H), 1.43 (s, 3H), 1.33 (s, 3H), 1.32 – 1.25 (m, 6H), 1.00 (d, *J* = 6.4 Hz, 3H), 0.96 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.72, 134.97, 129.14, 128.04, 72.92 (d, *J* = 1.0 Hz), 61.33 (d, *J* = 6.0 Hz), 61.19 (d, *J* = 6.0 Hz), 51.38, 50.90 (d, *J* = 6.0 Hz), 50.36, 37.38 (d, *J* = 136.0 Hz), 28.74 (d, *J* = 1.0 Hz), 28.43 (d, *J* = 2.0 Hz), 25.05, 24.78, 24.57, 16.37 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.52 (s). **HRMS (ESI)** Calcd for $C_{21}H_{34}NO_3P$: [M+H$^+$] 380.2349, found 380.2358.

***Diethyl((4,4-dimethyl-2,5-diphenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate* (3na)**



Yield: 90%, 71.9 mg; appearance: brown oil; R_f: 0.3 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.56 – 7.53 (m, 2H), 7.40 – 7.36 (m, 3H), 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 1H), 4.06 – 3.90 (m, 2H), 3.88 – 3.80 (m, 2H), 2.83 (d, *J* = 13.2 Hz, 1H), 2.66 – 2.44 (m, 3H), 1.43 (s, 3H), 1.23 – 1.18 (m, 3H), 1.14 – 1.10 (m, 3H), 1.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.46, 147.99 (d, *J* = 9.0 Hz), 134.76, 129.38, 128.14, 128.05, 127.98, 126.43, 125.98, 73.94 (d, *J* = 2.0 Hz), 61.35 (d, *J* = 7.0 Hz), 61.01 (d, *J* = 6.0 Hz), 52.20 (d, *J* = 3.0 Hz), 51.50, 41.19 (d, *J* = 136.0 Hz), 27.43 (d, *J* = 1.0 Hz), 27.02 (d, *J* = 2.0 Hz), 16.29 (d, *J* = 2.0 Hz), 16.23 (d, *J* = 2.0 Hz), 16.17 (d, *J* = 2.0 Hz), 16.10 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.64 (s). **HRMS (ESI)** Calcd for $C_{23}H_{30}NO_3P$: [M+H$^+$] 400.2036, found 400.2044.

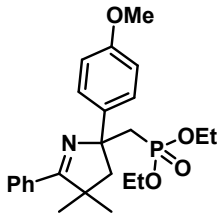
***Diethyl((4,4-dimethyl-5-phenyl-2-(m-tolyl)-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate* (3oa)**



Yield: 89%, 73.6 mg; appearance: brown oil; R_f: 0.3 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 –

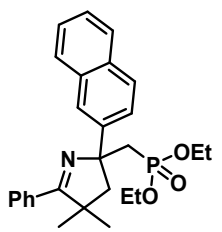
7.76 (m, 2H), 7.40 – 7.31 (m, 5H), 7.21 – 7.16 (m, 1H), 7.03 – 7.00 (m, 1H), 4.07 – 3.90 (m, 2H), 3.90 – 3.82 (m, 2H), 2.85 (d, *J* = 13.2 Hz, 1H), 2.64 – 2.45 (m, 3H), 2.33 (s, 3H), 1.42 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.49, 148.13 (d, *J* = 10.0 Hz), 137.48, 134.89, 129.34, 128.17, 128.06, 127.88, 127.15, 126.62, 122.99, 73.96 (d, *J* = 3.0 Hz), 61.36 (d, *J* = 7.0 Hz), 61.00 (d, *J* = 7.0 Hz), 52.08 (d, *J* = 2.0 Hz), 51.51, 41.20 (d, *J* = 136.0 Hz), 27.39 (d, *J* = 1.0 Hz), 27.13 (d, *J* = 2.0 Hz), 21.54 (d, *J* = 4.0 Hz), 16.29 (d, *J* = 5.0 Hz), 16.17 (d, *J* = 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.76 (s). **HRMS (ESI)** Calcd for $C_{24}H_{32}NO_3P$: [M+H$^+$] 414.2193, found 414.2192.

Diethyl((2-(4-methoxyphenyl)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate **(3pa)**



Yield: 86%, 73.7 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 2H), 7.49 – 7.44 (m, 2H), 7.40 – 7.34 (m, 3H), 6.86 – 6.81 (m, 2H), 4.04 – 3.90 (m, 2H), 3.89 – 3.80 (m, 2H), 3.77 (s, 3H), 2.78 (d, *J* = 13.2 Hz, 1H), 2.59 (dd, *J* = 18.4, 15.6 Hz, 1H), 2.51 (d, *J* = 13.2 Hz, 1H), 2.45 (dd, *J* = 18.0, 15.6 Hz, 1H), 1.41 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 1.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.29, 158.08, 140.03, 134.80, 129.37, 128.11, 128.07, 127.12, 113.26, 73.55 (d, *J* = 2.0 Hz), 61.32 (d, *J* = 7.0 Hz), 60.57 (d, *J* = 6.0 Hz), 55.16 (d, *J* = 5.0 Hz), 52.18 (d, *J* = 2.0 Hz), 51.54, 41.34 (d, *J* = 135.0 Hz), 27.46 (d, *J* = 2.0 Hz), 26.96 (d, *J* = 3.0 Hz), 16.29 (d, *J* = 6.0 Hz), 16.18 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.80 (s). **HRMS (ESI)** Calcd for $C_{24}H_{32}NO_4P$: [M+H$^+$] 430.2142, found 430.2142.

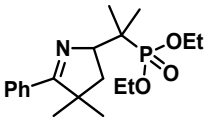
Diethyl((4,4-dimethyl-2-(naphthalen-2-yl)-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate **(3qa)**



Yield: 74%, 66.5 mg; appearance: brown oil; R_f: 0.3 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.83 – 7.78 (m, 5H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.40 (m,

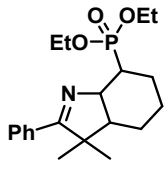
5H), 4.07 – 3.92 (m, 2H), 3.87 – 3.79 (m, 2H), 2.93 (d, *J* = 13.2 Hz, 1H), 2.71 (dd, *J* = 18.0, 15.6 Hz, 1H), 2.65 (d, *J* = 13.2 Hz, 1H), 2.58 (dd, *J* = 17.6, 15.6 Hz, 1H), 1.46 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.07 (s, 3H), 1.03(t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.92, 145.41 (d, *J* = 9.0 Hz), 134.82, 133.07, 132.19, 129.45, 128.19, 128.14, 128.12, 127.74, 127.35, 125.87, 125.59, 124.77, 124.20, 74.13 (d, *J* = 2.0 Hz), 61.44 (d, *J* = 6.0 Hz), 61.05 (d, *J* = 7.0 Hz), 52.10 (d, *J* = 3.0 Hz), 51.63, 41.10 (d, *J* = 136.0 Hz), 27.40 (d, *J* = 2.0 Hz), 27.14 (d, *J* = 3.0 Hz), 16.26 (d, *J* = 4.0 Hz), 16.04 (d, *J* = 4.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.64 (s). **HRMS (ESI)** Calcd for $C_{27}H_{32}NO_3P$: [M+H$^+$] 450.2193, found 450.2196.

Diethyl(2-(4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)propan-2-yl)phosphonate **(3ra)**



Yield: 70%, 49.0 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 3H), 7.24 – 7.20 (m, 2H), 4.21 – 4.09 (m, 4H), 2.22 – 2.11 (m, 1H), 1.92 – 1.83 (m, 1H), 1.80 – 1.73 (m, 1H), 1.55 (s, 3H), 1.38 – 1.33 (m, 9H), 1.23 (s, 3H), 1.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.71, 140.73 (d, *J* = 2.0 Hz), 127.87, 127.63, 127.54, 61.57 (d, *J* = 7.0 Hz), 61.50 (d, *J* = 7.0 Hz), 56.29, 39.44 (d, *J* = 138.0 Hz), 35.71 (d, *J* = 12.0 Hz), 34.80 (d, *J* = 5.0 Hz), 31.56, 28.44 (d, *J* = 2.0 Hz), 26.50 (d, *J* = 2.0 Hz), 25.01. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.31 (s). **HRMS (ESI)** Calcd for $C_{19}H_{30}NO_3P$: [M+H$^+$] 352.2036, found 352.2034.

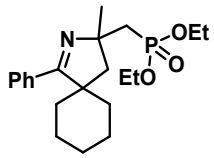
Diethyl (3,3-dimethyl-2-phenyl-3a,4,5,6,7,7a-hexahydro-3H-indol-7-yl)phosphonate **(3sa)**



Yield: 62%, 45.0 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (d, *J* = 6.0 Hz, 2H), 7.38 – 7.35 (m, 3H), 4.37 – 4.32 (m, 1H), 4.20 – 4.12 (m, 4H), 2.72 – 2.64 (m, 1H), 2.14 – 2.09 (m, 1H), 1.95 – 1.88 (m, 2H), 1.69 – 1.59 (m, 3H), 1.51 (s, 1H), 1.37 – 1.32 (m, 9H), 1.19 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.71 (d, *J* = 2.0 Hz), 135.36, 129.40, 128.12, 127.53, 64.81 (d, *J* = 3.0 Hz), 61.68

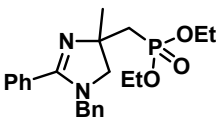
(d, *J* = 6.0 Hz), 61.53 (d, *J* = 7.0 Hz), 53.47, 48.56 (d, *J* = 2.0 Hz), 36.01 (d, *J* = 139.0 Hz), 24.18 (d, *J* = 1.0 Hz), 23.35, 21.66 (d, *J* = 4.0 Hz), 21.13 (d, *J* = 2.0 Hz), 20.47 (d, *J* = 4.0 Hz), 16.48 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.04 (s). **HRMS (ESI)** Calcd for $C_{20}H_{30}NO_3P$: [M+H$^+$] 364.2036, found 364.2033.

Diethyl((3-methyl-1-phenyl-2-azaspiro[4.5]dec-1-en-3-yl)methyl)phosphonate **(3ta)**



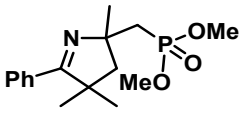
Yield: 91%, 68.6 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.37 – 7.33 (m, 3H), 4.15 – 4.04 (m, 4H), 2.40 (d, *J* = 14.0 Hz, 1H), 2.35 (dd, *J* = 18.4, 15.2 Hz, 1H), 2.05 (dd, *J* = 18.4, 15.2 Hz, 1H), 1.99 (d, *J* = 13.6 Hz, 1H), 1.72 – 1.55 (m, 7H), 1.49 (s, 3H), 1.42 – 1.37 (m, 1H), 1.35 – 1.28 (m, 6H), 1.24 (s, 1H), 1.15 – 1.05 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.31 (d, *J* = 1.0 Hz), 135.84, 128.71, 128.03, 127.93, 70.35, 61.39 (d, *J* = 7.0 Hz), 61.30 (d, *J* = 6.0 Hz), 58.05, 45.21 (d, *J* = 1.0 Hz), 39.42 (d, *J* = 136.0 Hz), 35.36 (d, *J* = 23.0 Hz), 30.53 (d, *J* = 5.0 Hz), 25.36, 23.05 (d, *J* = 11.0 Hz), 16.39 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.27 (s). **HRMS (ESI)** Calcd for $C_{21}H_{32}NO_3P$: [M+H$^+$] 378.2193, found 378.2188.

Diethyl((1-benzyl-4-methyl-2-phenyl-4,5-dihydro-1H-imidazol-4-yl)methyl)phosphonate **(3ua)**



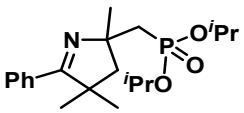
Yield: 60%, 48.0 mg; appearance: brown oil; R_f: 0.3 (ethyl acetate/methanol = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.41 – 7.31 (m, 5H), 7.29 – 7.20 (m, 3H), 4.40 (d, *J* = 15.6 Hz, 1H), 4.22 (d, *J* = 15.6 Hz, 1H), 4.12 – 4.00 (m, 4H), 3.65 (d, *J* = 10.4 Hz, 1H), 3.25 (d, *J* = 10.0 Hz, 1H), 2.26 (dd, *J* = 17.6, 15.2 Hz, 1H), 2.13 (dd, *J* = 17.6, 15.6 Hz, 1H), 1.45 (s, 3H), 1.30 – 1.24 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.47, 137.82, 131.01, 129.95, 128.64, 128.47, 128.26, 127.30, 127.12, 65.20 (d, *J* = 1.0 Hz), 61.41 (d, *J* = 6.0 Hz), 61.27 (d, *J* = 7.0 Hz), 61.14, 52.38, 37.85 (d, *J* = 134.0 Hz), 28.65 (d, *J* = 4.0 Hz), 16.35 (d, *J* = 7.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.87 (s). **HRMS (ESI)** Calcd for $C_{22}H_{29}N_2O_3P$: [M+H$^+$] 401.1989, found 401.1990.

***Dimethyl((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate* (3ab)**



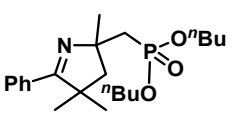
Yield: 89%, 54.9 mg; appearance: brown oil; R_f: 0.3 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.37 – 7.31 (m, 3H), 3.72 (dd, *J* = 10.8, 9.2 Hz, 6H), 2.37 (d, *J* = 13.2 Hz, 1H), 2.34 (dd, *J* = 18.4, 15.6 Hz, 1H), 2.08 (dd, *J* = 18.0, 15.2 Hz, 1H), 1.93 (d, *J* = 13.2 Hz, 1H), 1.48 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.47, 134.77, 129.26, 128.08, 127.94, 69.36, 51.98, 38.26 (d, *J* = 136.0 Hz), 29.82 (d, *J* = 6.0 Hz), 28.81 (d, *J* = 1.0 Hz), 28.35 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.96 (s). **HRMS (ESI)** Calcd for $C_{16}H_{24}NO_3P$: [M+H$^+$] 310.1567, found 310.1570.

***Diisopropyl((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate* (3ac)**



Yield: 92%, 67.2 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.36 – 7.30 (m, 3H), 4.76 – 4.64 (m, 2H), 2.42 (d, *J* = 13.6 Hz, 1H), 2.33 (dd, *J* = 18.4, 15.2 Hz, 1H), 1.97 (dd, *J* = 18.4, 15.2 Hz, 1H), 1.91 (d, *J* = 13.2 Hz, 1H), 1.49 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H), 1.32 – 1.27 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.92 (d, *J* = 2.0 Hz), 134.87, 129.18, 128.03, 127.97, 69.86 (d, *J* = 1.0 Hz), 69.79 (d, *J* = 2.0 Hz), 69.65, 51.98, 51.89, 40.78 (d, *J* = 137.0 Hz), 29.55 (d, *J* = 3.0 Hz), 28.74 (d, *J* = 2.0 Hz), 28.48 (d, *J* = 2.0 Hz), 24.05. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.29 (s). **HRMS (ESI)** Calcd for $C_{20}H_{32}NO_3P$: [M+H$^+$] 366.2193, found 366.2194.

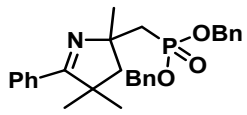
***Dibutyl((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate* (3ad)**



Yield: 91%, 71.6 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 –

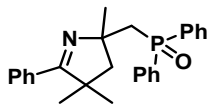
7.61 (m, 2H), 7.38 – 7.29 (m, 3H), 4.06 – 3.95 (m, 4H), 2.40 (d, *J* = 13.6 Hz, 1H), 2.11 (dd, *J* = 14.8, 10.4 Hz, 1H), 2.02 (dd, *J* = 15.2, 10.0 Hz, 1H), 1.96 (d, *J* = 13.2 Hz, 1H), 1.82 – 1.62 (m, 5H), 1.55 – 1.44 (m, 7H), 1.39 (s, 3H), 1.39 (s, 3H), 1.36 – 1.30 (m, 3H), 0.91 – 0.84 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.25, 134.61, 129.29, 128.05, 127.93, 70.70 (d, *J* = 5.0 Hz), 53.26 (d, *J* = 2.0 Hz), 51.69, 40.86 (d, *J* = 62.0 Hz), 30.90 (d, *J* = 5.0 Hz), 32.49 (d, *J* = 6.0 Hz), 30.08 (d, *J* = 18.0 Hz), 29.47 (d, *J* = 18.0 Hz), 28.92 (d, *J* = 2.0 Hz), 28.39 (d, *J* = 1.0 Hz), 24.27 (d, *J* = 2.0 Hz), 24.12 (d, *J* = 2.0 Hz), 24.06 (d, *J* = 3.0 Hz), 23.91 (d, *J* = 4.0 Hz), 13.54. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 47.12 (s). **HRMS (ESI)** Calcd for $C_{22}H_{36}NO_3P$: [M+H$^+$] 394.2506, found 394.2504.

***Dibenzyl((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphonate* (3ae)**



Yield: 50%, 46.1 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.39 – 7.30 (m, 13H), 5.09 – 4.93 (m, 4H), 2.42 (dd, *J* = 18.8, 15.6 Hz, 1H), 2.39 (d, *J* = 13.2 Hz, 1H), 2.15 (dd, *J* = 18.4, 15.6 Hz, 1H), 1.92 (d, *J* = 13.2 Hz, 1H), 1.51 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.40 (d, *J* = 1.0 Hz), 136.47 (d, *J* = 1.0 Hz), 136.41 (d, *J* = 1.0 Hz), 134.76, 129.28, 128.48, 128.22, 128.09, 128.02, 127.92, 127.86, 69.53, 66.99 (d, *J* = 6.0 Hz), 66.91 (d, *J* = 7.0 Hz), 52.19 (d, *J* = 2.0 Hz), 51.95, 39.72 (d, *J* = 136.0 Hz), 29.91 (d, *J* = 5.0 Hz), 28.78 (d, *J* = 2.0 Hz), 28.38 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.45 (s). **HRMS (ESI)** Calcd for $C_{28}H_{32}NO_3P$: [M+H$^+$] 462.2193, found 462.2191.

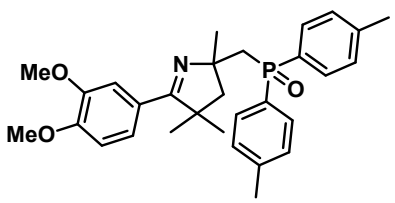
***Diphenyl((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphine oxide* (3ag)**



Yield: 97%, 77.8 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 –

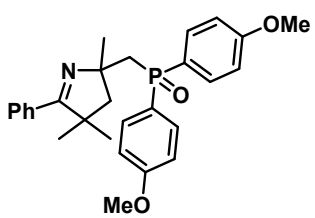
7.75 (m, 4H), 7.48 – 7.40 (m, 8H), 7.36 – 7.27 (m, 3H), 2.96 (dd, *J* = 14.8, 10.4 Hz, 1H), 2.69 (dd, *J* = 14.8, 10.8 Hz, 1H), 2.64 (d, *J* = 13.6 Hz, 1H), 1.97 (d, *J* = 13.6 Hz, 1H), 1.37 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.31, 134.99 (d, *J* = 98.0 Hz), 134.54, 134.92 (d, *J* = 98.0 Hz), 131.31 (d, *J* = 3.0 Hz), 131.23 (d, *J* = 3.0 Hz), 130.62 (d, *J* = 2.0 Hz), 130.53 (d, *J* = 2.0 Hz), 129.22, 128.51 (d, *J* = 11.0 Hz), 128.49 (d, *J* = 12.0 Hz), 127.96, 127.94, 71.01 (d, *J* = 3.0 Hz), 52.40, 51.97, 42.45 (d, *J* = 69.0 Hz), 30.68 (d, *J* = 7.0 Hz), 28.94 (d, *J* = 1.0 Hz), 28.32 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.11 (s). **HRMS (ESI)** Calcd for $C_{26}H_{28}NOP$: [M+H$^+$] 402.1981, found 402.1983.

((5-(3,4-dimethoxyphenyl)-2,4,4-trimethyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)di-p-tolylphosphine oxide **(3ih)**



Yield: 72%, 70.4 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.58 (m, 4H), 7.24 – 7.13 (m, 6H), 6.77 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 2.93 (dd, *J* = 14.8, 9.6 Hz, 1H), 2.62 – 2.54 (m, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 1.96 (d, *J* = 13.6 Hz, 1H), 1.38 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.95, 149.34 (d, *J* = 172.0 Hz), 141.58 (d, *J* = 2.0 Hz), 141.47 (d, *J* = 2.0 Hz), 132.40 (d, *J* = 42.0 Hz), 131.40 (d, *J* = 42.0 Hz), 130.64, 130.54, 130.45, 129.21 (d, *J* = 5.0 Hz), 129.09 (d, *J* = 5.0 Hz), 127.15, 120.97, 110.85 (d, *J* = 149.0 Hz), 70.54 (d, *J* = 2.0 Hz), 55.84 (d, *J* = 6.0 Hz), 55.79 (d, *J* = 5.0 Hz), 53.03, 51.65, 42.62 (d, *J* = 69.0 Hz), 30.48, 29.15 (d, *J* = 2.0 Hz), 28.70 (d, *J* = 2.0 Hz), 21.42 (d, *J* = 3.0 Hz), 21.39 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.72 (s). **HRMS (ESI)** Calcd for $C_{30}H_{36}NO_3P$: [M+H$^+$] 490.2506, found 490.2509.

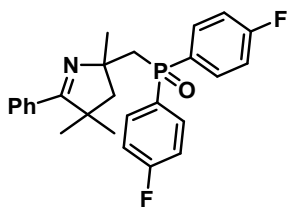
Bis(4-methoxyphenyl)((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphine oxide **(3ai)**



Yield: 63%, 58.1 mg; appearance: green oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:3). **^{1}H NMR** (400 MHz,

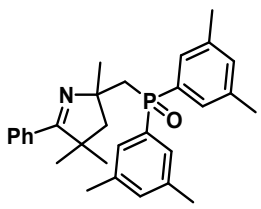
$CDCl_3$) δ 7.67 – 7.55 (m, 4H), 7.38 – 7.34 (m, 2H), 7.25 – 7.18 (m, 3H), 6.89 – 6.82 (m, 4H), 3.74 (s, 3H), 3.72 (s, 3H), 2.80 (dd, *J* = 15.2, 10.4 Hz, 1H), 2.57 (d, *J* = 13.6 Hz, 1H), 2.53 (dd, *J* = 14.8, 10.8 Hz, 1H), 1.87 (d, *J* = 13.6 Hz, 1H), 1.28 (s, 3H), 1.27 (s, 3H), 1.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.24, 161.93 (d, *J* = 3.0 Hz), 161.88 (d, *J* = 2.0 Hz), 134.58, 132.41 (d, *J* = 2.0 Hz), 132.31 (d, *J* = 2.0 Hz), 129.21, 127.97, 127.92, 126.77 (d, *J* = 17.0 Hz), 125.73 (d, *J* = 17.0 Hz), 114.07 (d, *J* = 3.0 Hz), 113.94 (d, *J* = 4.0 Hz), 71.01 (d, *J* = 3.0 Hz), 55.24 (d, *J* = 5.0 Hz), 52.15, 51.97, 42.74 (d, *J* = 71.0 Hz), 30.64 (d, *J* = 5.0 Hz), 28.92 (d, *J* = 1.0 Hz), 28.33 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.53 (s). **HRMS (ESI)** Calcd for $C_{28}H_{32}NO_3P$: [M+H$^+$] 462.2193, found 462.2201.

Bis(4-fluorophenyl)((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphine oxide **(3aj)**



Yield: 85%, 74.3 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 4H), 7.43 – 7.40 (m, 2H), 7.38 – 7.33 (m, 1H), 7.32 – 7.27 (m, 2H), 7.18 – 7.09 (m, 4H), 2.89 (dd, *J* = 15.2, 10.8 Hz, 1H), 2.69 (dd, *J* = 15.2, 10.8 Hz, 1H), 2.64 (d, *J* = 13.2 Hz, 1H), 1.97 (d, *J* = 13.2 Hz, 1H), 1.39 (s, 6H), 1.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.45, 165.95 (t, *J* = 3.0 Hz), 163.43 (t, *J* = 3.0 Hz), 134.21, 132.95 (dd, *J* = 13.0, 2.0 Hz), 132.95 (dd, *J* = 19.0, 13.0 Hz), 131.06 (dd, *J* = 9.0, 3.0 Hz), 130.05 (dd, *J* = 11.0, 4.0 Hz), 129.36, 127.93, 127.88, 116.00 (dd, *J* = 12.0, 7.0 Hz), 115.79 (dd, *J* = 13.0, 8.0 Hz), 70.88 (d, *J* = 3.0 Hz), 52.41, 51.90, 42.63 (d, *J* = 71.0 Hz), 30.84 (d, *J* = 5.0 Hz), 28.91 (d, *J* = 2.0 Hz), 28.23 (d, *J* = 2.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -107.37 (s), -107.51 (s). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.57 (s). **HRMS (ESI)** Calcd for $C_{26}H_{26}F_2NOP$: [M+H$^+$] 438.1793, found 438.1791.

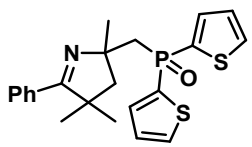
Bis(3,5-dimethylphenyl)((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphine oxide **(3ak)**



Yield: 97%, 88.7 mg; appearance: brown oil; R_f: 0.2

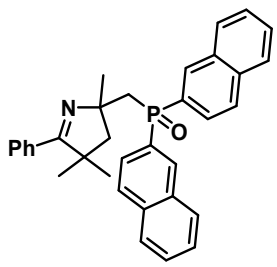
(petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 4H), 7.37 – 7.27 (m, 5H), 7.07 (d, *J* = 9.2 Hz, 2H), 2.96 (dd, *J* = 15.2, 10.0 Hz, 1H), 2.61 (d, *J* = 13.6 Hz, 1H), 2.60 (dd, *J* = 15.2, 11.2 Hz, 1H), 2.32 (s, 6H), 2.28 (s, 6H), 1.98 (d, *J* = 13.6 Hz, 1H), 1.36 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.11, 138.14 (d, *J* = 2.0 Hz), 138.02 (d, *J* = 2.0 Hz), 135.32 (d, *J* = 29.0 Hz), 134.35 (d, *J* = 28.0 Hz), 134.49, 134.21, 132.91 (d, *J* = 6.0 Hz), 129.20, 128.14, 128.05, 127.97, 127.92, 71.00 (d, *J* = 3.0 Hz), 55.48, 51.97, 42.74 (d, *J* = 69.0 Hz), 30.47 (d, *J* = 4.0 Hz), 28.93 (d, *J* = 1.0 Hz), 28.34 (d, *J* = 1.0 Hz), 21.23 (d, *J* = 3.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.36 (s). **HRMS (ESI)** Calcd for $C_{30}H_{36}NOP$: [M+H$^+$] 458.2607, found 458.2609.

Di(thiophen-2-yl)((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphine oxide **(3al)**



Yield: 86%, 71.0 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 3H), 7.57 (dd, *J* = 6.8, 3.2 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.15 (d, *J* = 13.6 Hz, 2H), 2.97 (dd, *J* = 14.8, 10.8 Hz, 1H), 2.73 (dd, *J* = 14.8, 12.0 Hz, 1H), 2.58 (d, *J* = 13.6 Hz, 1H), 1.99 (d, *J* = 13.6 Hz, 1H), 1.43 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.48, 136.65 (d, *J* = 14.0 Hz), 135.53 (d, *J* = 14.0 Hz), 135.04 (d, *J* = 7.0 Hz), 134.94 (d, *J* = 6.0 Hz), 134.44, 133.08 (d, *J* = 5.0 Hz), 132.93 (d, *J* = 5.0 Hz), 129.31, 128.26 (d, *J* = 6.0 Hz), 128.12 (d, *J* = 6.0 Hz), 128.00, 127.97, 70.98 (d, *J* = 3.0 Hz), 52.36 (d, *J* = 2.0 Hz), 52.00, 47.02 (d, *J* = 78.0 Hz), 30.31 (d, *J* = 6.0 Hz), 28.89 (d, *J* = 2.0 Hz), 28.34 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.42 (s). **HRMS (ESI)** Calcd for $C_{22}H_{24}NOPS_2$: [M+H$^+$] 414.1110, found 414.1111.

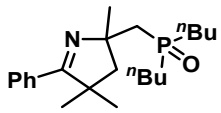
Di(naphthalen-2-yl)((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphine oxide **(3am)**



Yield: 92%, 92.1 mg; appearance: brown solid; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1); M.P.: 156-160 ºC. **^{1}H**

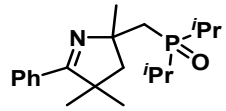
NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 13.2 Hz, 1H), 8.46 (d, *J* = 13.2 Hz, 1H), 7.94 – 7.77 (m, 8H), 7.55 – 7.47 (m, 4H), 7.32 – 7.29 (m, 2H), 7.25 – 7.22 (m, 1H), 7.12 – 7.07 (m, 2H), 3.16 (dd, *J* = 15.2, 10.4 Hz, 1H), 2.92 (dd, *J* = 15.2, 10.8 Hz, 1H), 2.76 (d, *J* = 13.2 Hz, 1H), 2.04 (d, *J* = 13.6 Hz, 1H), 1.45 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.25, 134.33 (d, *J* = 5.0 Hz), 134.30 (d, *J* = 5.0 Hz), 132.59 (d, *J* = 4.0 Hz), 132.47 (d, *J* = 3.0 Hz), 132.31 (d, *J* = 5.0 Hz), 132.23 (d, *J* = 5.0 Hz), 131.50 (d, *J* = 4.0 Hz), 129.09, 128.31 (d, *J* = 11.0 Hz), 128.30 (d, *J* = 95.0 Hz), 127.78 (d, *J* = 8.0 Hz), 127.64 (d, *J* = 5.0 Hz), 126.73 (d, *J* = 6.0 Hz), 125.68 (d, *J* = 10.0 Hz), 125.53 (d, *J* = 11.0 Hz), 71.04 (d, *J* = 3.0 Hz), 52.54, 51.87, 42.24 (d, *J* = 70.0 Hz), 30.82 (d, *J* = 4.0 Hz), 28.90 (d, *J* = 2.0 Hz), 28.27 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.44 (s). **HRMS (ESI)** Calcd for $C_{34}H_{32}NOP$: [M+H$^+$] 502.2294, found 502.2294.

***Dibutyl((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphine oxide* (3an)**



Yield: 96%, 69.3 mg; appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.37 – 7.30 (m, 3H), 2.47 (d, *J* = 13.2 Hz, 1H), 2.11 (dd, *J* = 14.8, 10.0 Hz, 1H), 2.02 (dd, *J* = 15.2, 10.0 Hz, 1H), 1.96 (d, *J* = 13.2 Hz, 1H), 1.82 – 1.63 (m, 5H), 1.55 – 1.45 (m, 7H), 1.39 (s, 3H), 1.39 (s, 3H), 1.36 – 1.30 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.25, 134.61, 129.29, 128.05, 127.93, 70.70 (d, *J* = 5.0 Hz), 53.26 (d, *J* = 2.0 Hz), 51.69, 40.86 (d, *J* = 62.0 Hz), 30.90 (d, *J* = 5.0 Hz), 30.09 (d, *J* = 18.0 Hz), 29.43 (d, *J* = 18.0 Hz), 28.92 (d, *J* = 2.0 Hz), 28.39 (d, *J* = 1.0 Hz), 24.27 (d, *J* = 2.0 Hz), 24.12 (d, *J* = 2.0 Hz), 24.06 (d, *J* = 3.0 Hz), 23.91 (d, *J* = 4.0 Hz), 13.54. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.42 (s). **HRMS (ESI)** Calcd for $C_{22}H_{36}NOP$: [M+H$^+$] 362.2607, found 362.2614.

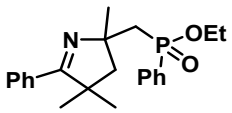
***Diisopropyl((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphine oxide* (3ao)**



Yield: 95%, 63.3 mg; appearance: brown oil; R_f: 0.2 (petroleum

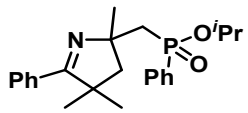
ether/ethyl acetate = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 2H), 7.36 – 7.30 (m, 3H), 2.42 (d, *J* = 13.6 Hz, 1H), 2.18 – 2.04 (m, 3H), 2.02 (d, *J* = 13.6 Hz, 1H), 1.94 (dd, *J* = 15.2, 8.8 Hz, 1H), 1.53 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H), 1.25 – 1.14 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.16, 134.91, 129.13, 128.04, 127.91, 70.82 (d, *J* = 3.0 Hz), 53.04 (d, *J* = 2.0 Hz), 51.83, 35.29 (d, *J* = 58.0 Hz), 30.97 (d, *J* = 3.0 Hz), 28.83 (d, *J* = 2.0 Hz), 28.52 (d, *J* = 2.0 Hz), 27.68 (d, *J* = 7.0 Hz), 27.04 (d, *J* = 8.0 Hz), 16.12. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 53.83 (s). **HRMS (ESI)** Calcd for $C_{22}H_{36}NOP$: [M+H$^+$] 334.2294, found 334.2298.

***Ethylphenyl((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphinate* (3ap)**



Yield: 80%, 59.1 mg (dr = 1:1); appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 4H), 7.57 – 7.41 (m, 10H), 7.35 – 7.24 (m, 6H), 4.07 – 3.98 (m, 2H), 3.78 – 3.70 (m, 2H), 2.63 – 2.47 (m, 4H), 2.30 (dd, *J* = 17.6, 15.6 Hz, 1H), 2.25 (dd, *J* = 17.2, 15.2 Hz, 1H), 1.96 (d, *J* = 13.6 Hz, 1H), 1.89 (d, *J* = 13.2 Hz, 1H), 1.53 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H), 1.27 – 1.20 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.99 (d, *J* = 10.0 Hz), 134.58 (d, *J* = 16.0 Hz), 133.09 (d, *J* = 19.0 Hz), 133.89 (d, *J* = 2.0 Hz), 131.87 (d, *J* = 19.0 Hz), 131.84 (d, *J* = 3.0 Hz), 131.59 (d, *J* = 10.0 Hz), 129.19 (d, *J* = 6.0 Hz), 128.47 (d, *J* = 12.0 Hz), 127.98, 127.96, 127.89, 70.03, 60.13 (d, *J* = 7.0 Hz), 60.06 (d, *J* = 6.0 Hz), 52.15 (d, *J* = 97.0 Hz), 43.31 (d, *J* = 24.0 Hz), 42.33 (d, *J* = 24.0 Hz), 30.57 (d, *J* = 7.0 Hz), 29.81, 28.91 (d, *J* = 2.0 Hz), 28.85 (d, *J* = 2.0 Hz), 28.43 (d, *J* = 2.0 Hz), 28.06 (d, *J* = 3.0 Hz), 16.40 (d, *J* = 2.0 Hz), 16.33 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 41.1 (s), 41.0 (s). **HRMS (ESI)** Calcd for $C_{22}H_{28}NO_2P$: [M+H$^+$] 370.1930, found 370.1930.

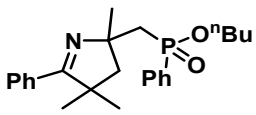
***Isopropylphenyl((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphinate* (3aq)**



Yield: 83%, 63.6 mg (dr = 1:1.4); appearance: brown oil; R_f:

0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 4.8H), 7.52 – 7.33 (m, 12H), 7.29 – 7.17 (m, 7.2H), 4.43 – 4.32 (m, 2.4H), 2.51 (dd, *J* = 18.0, 15.2 Hz, 1H), 2.48 – 2.44 (m, 2.4H), 2.42 (dd, *J* = 15.2, 11.2 Hz, 1H), 2.22 (dd, *J* = 17.6, 15.2 Hz, 1H), 2.16 (dd, *J* = 15.2, 10.4 Hz, 1.4H), 1.90 (d, *J* = 13.2 Hz, 1H), 1.82 (d, *J* = 13.2 Hz, 1.4H), 1.47 (s, 4.2H), 1.33 – 1.26 (m, 20.4H), 1.20 (s, 4.2H), 1.01 (d, *J* = 6.4 Hz, 7.2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.86 (d, *J* = 16.0 Hz), 134.57 (d, *J* = 15.0 Hz), 133.86 (d, *J* = 20.0 Hz), 132.64 (d, *J* = 19.0 Hz), 131.74 (d, *J* = 2.0 Hz), 131.68 (d, *J* = 3.0 Hz), 129.16 (d, *J* = 7.0 Hz), 128.33 (d, *J* = 12.0 Hz), 127.97, 127.95, 127.92, 127.85, 70.05, 69.25 (d, *J* = 3.0 Hz), 69.19 (d, *J* = 2.0 Hz), 69.13 (d, *J* = 3.0 Hz), 51.57 (d, *J* = 110.0 Hz), 51.81, 43.57 (d, *J* = 32.0 Hz), 42.49 (d, *J* = 33.0 Hz), 30.57 (d, *J* = 7.0 Hz), 29.65 (d, *J* = 13.0 Hz), 28.90 (d, *J* = 2.0 Hz), 28.83 (d, *J* = 2.0 Hz), 28.42 (d, *J* = 2.0 Hz), 28.04 (d, *J* = 2.0 Hz), 24.56 (d, *J*= 2.0 Hz), 23.80. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 39.6 (s), 39.5 (s).**HRMS (ESI)** Calcd for $C_{23}H_{30}NO_2P$: $[M+H^+]$ 384.2087, found 384.2086.

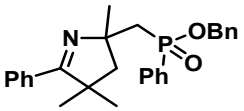
Butylphenyl((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphinate **(3ar)**



Yield: 70%, 55.5 mg (dr = 1:1); appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 4H), 7.57 – 7.42 (m, 10H), 7.35 – 7.24 (m, 6H), 4.02 – 3.92 (m, 2H), 3.68 – 3.59 (m, 2H), 2.60 (dd, *J* = 17.2, 15.2 Hz, 1H), 2.55 (dd, *J* = 17.2, 15.6 Hz, 1H), 2.52 – 2.47 (m, 2H), 2.30 (dd, *J* =17.6, 15.6 Hz, 1H), 2.25 (dd, *J* = 18.4, 15.2 Hz, 1H), 1.97 (d, *J* = 13.6 Hz, 1H), 1.90 (d, *J* = 13.6 Hz, 1H), 1.63 – 1.53 (m, 4H),1.53 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.33 – 1.28 (m, 4H), 1.27 (s, 3H), 0.89 – 0.82 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.01 (d, *J* = 14.0 Hz), 134.55 (d, *J* = 14.0 Hz), 132.98 (d, *J* = 21.0 Hz), 131.90 (d, *J* = 3.0 Hz), 131.84 (d, *J* = 2.0 Hz), 131.59 (d, *J* = 10.0 Hz), 129.21 (d, *J* = 6.0 Hz), 128.47 (d, *J* = 12.0 Hz), 127.98, 127.96, 127.89, 70.01, 63.86 (d, *J* = 7.0 Hz), 63.79 (d, *J* = 6.0 Hz), 52.16 (d, *J* = 97.0 Hz), 51.86, 43.28 (d, *J* = 23.0 Hz), 42.29 (d, *J* = 24.0 Hz), 32.46 (d, *J* = 7.0 Hz), 30.54 (d, *J* = 7.0 Hz), 29.73, 28.91 (d, *J* = 1.0 Hz),

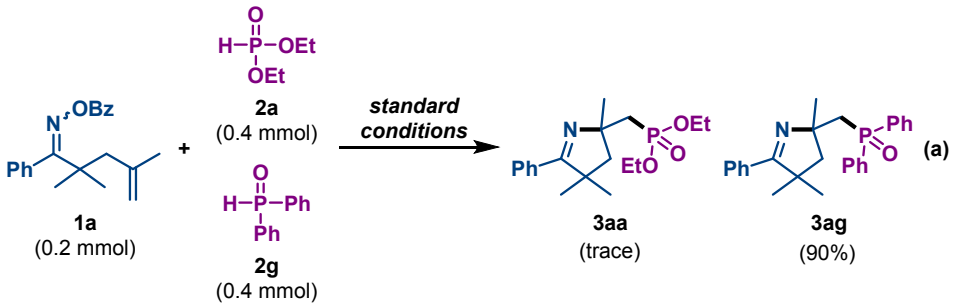
28.83 (d, *J* = 2.0 Hz), 28.47 (d, *J* = 3.0 Hz), 28.08 (d, *J* = 3.0 Hz), 18.75 (d, *J* = 2.0 Hz), 13.52. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 41.1 (s), 40.9 (s). **HRMS (ESI)** Calcd for $C_{24}H_{32}NO_2P$: [M+H$^+$] 398.2243, found 398.2244.

Benzylphenyl((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)phosphinate **(3as)**

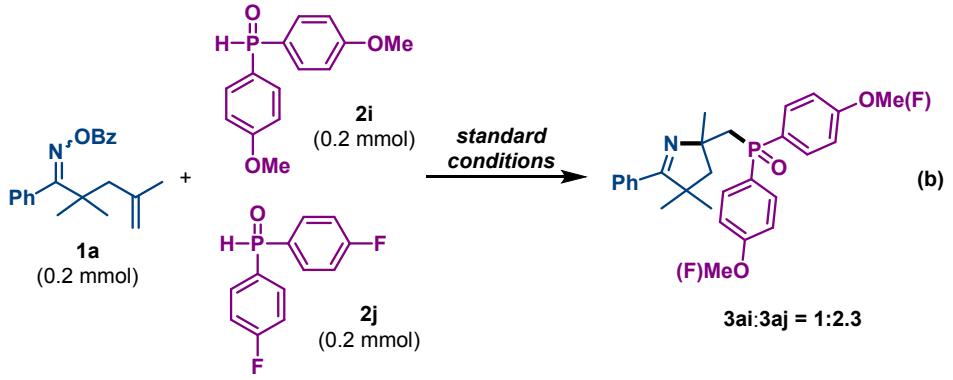


Yield: 53%, 45.7 mg (dr = 1: 0.25); appearance: brown oil; R_f: 0.2 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 2.5H), 7.54 – 7.43 (m, 6.5H), 7.37 – 7.26 (m, 9.75H), 5.04 (dd, *J* = 12.0, 6.8 Hz, 1.25H), 4.67 (dd, *J* = 11.6, 6.8 Hz, 1.25H), 2.65 (dd, *J* = 18.0, 15.2Hz, 0.25H), 2.54 (m, 2.25H), 2.39 (d, *J* = 15.6 Hz, 1H), 2.33 (d, *J* = 15.2 Hz, 0.25H), 1.97 (d, 13.6 Hz, 1H), 1.91 (d, *J* = 13.6 Hz, 0.25H), 1.54 (s, 0.75H), 1.39 – 1.37 (m, 6.75H), 1.33 (s, 3H), 1.29 (s, 0.75H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.02, 136.45 (d, *J* = 8.0 Hz), 134.59, 132.43 (d, *J* = 87.0 Hz), 132.05 (d, *J* = 2.0 Hz), 131.68 (d, *J* = 10.0 Hz), 129.23, 128.55 (d, *J* = 12.0 Hz), 128.38, 128.06, 127.99, 127.82, 127.81 (d, *J* = 21.0 Hz), 70.02, 65.55 (d, *J* = 6.0 Hz), 52.78 (d, *J* = 2.0 Hz), 51.87, 43.04 (d, *J* = 97.0 Hz), 29.86, 28.84 (d, *J* = 2.0 Hz), 28.43 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 42.3 (s), 42.1 (s). **HRMS (ESI)** Calcd for $C_{27}H_{30}NO_2P$: [M+H$^+$] 432.2087, found 432.2088.

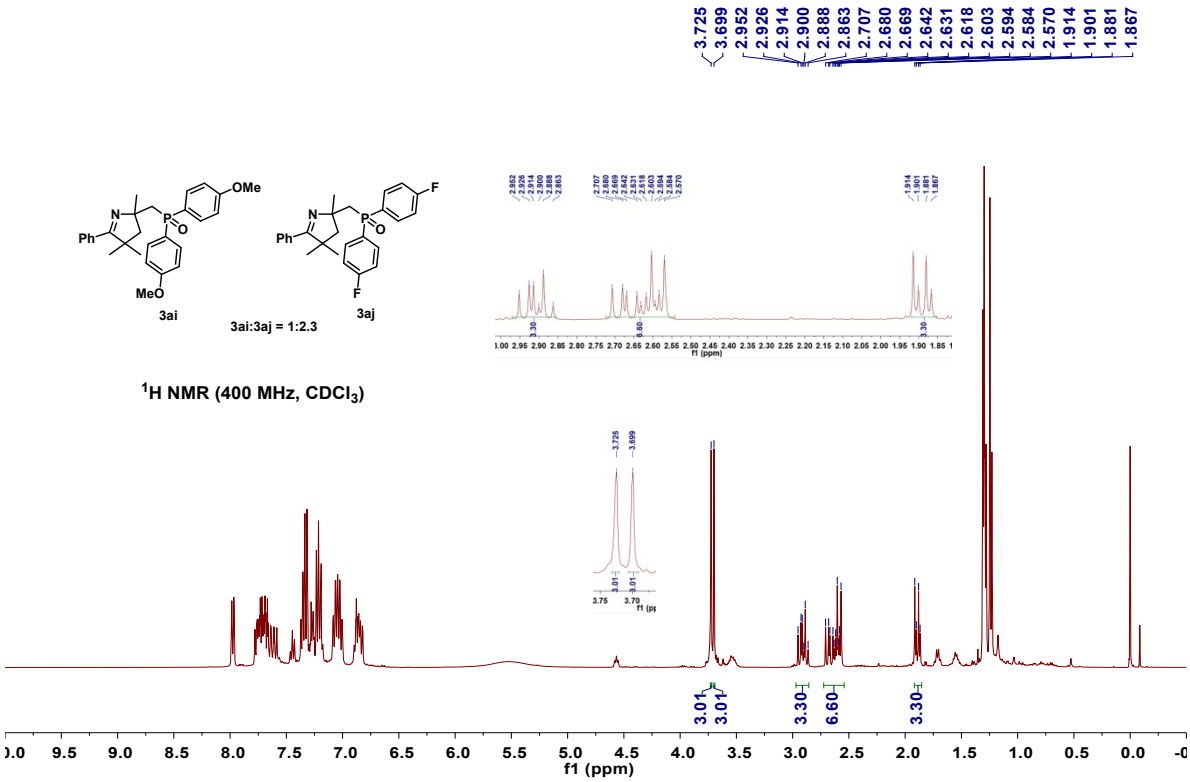
Control Experiments:

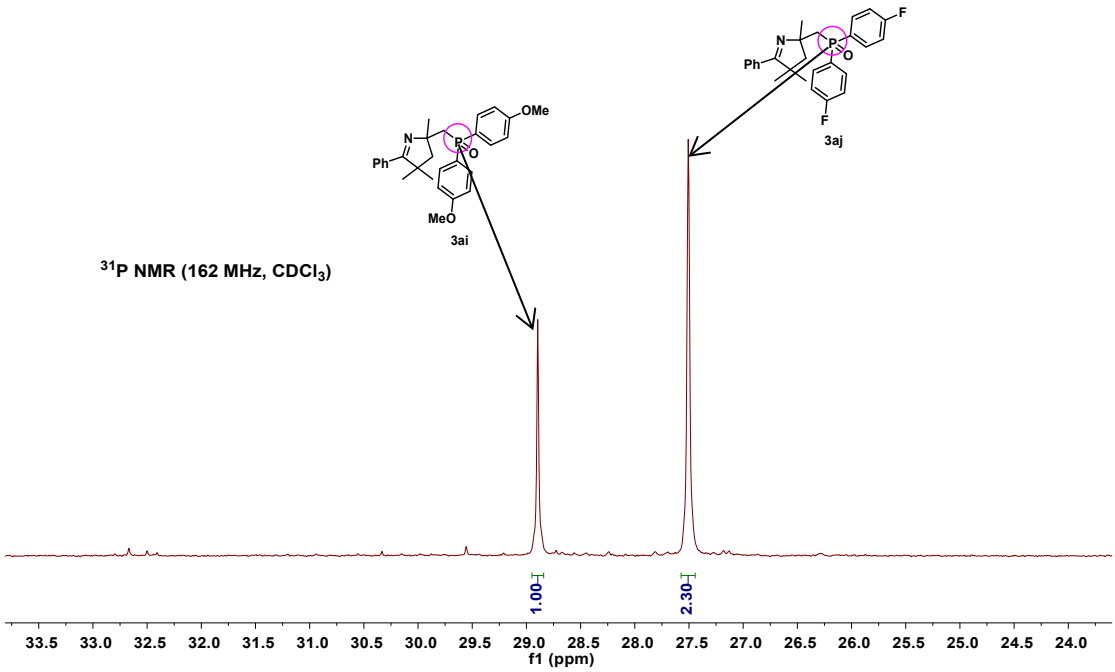


In a 25.0 mL sealed tube, **1a** (0.2 mmol, 64.3 mg, 1.0 equiv), **2a** (0.4 mmol, 55.2 mg, 2.0 equiv), **2g** (0.4 mmol, 80.9 mg, 2.0 equiv), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv) were added to a solution of $AgNO_3$ (17.0 mg, 0.1 mmol, 0.5 equiv) in MeCN (3.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction was allowed to stir at 100 °C for 12 h. Afterward, the resulting mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **3ag** in 90% yield.

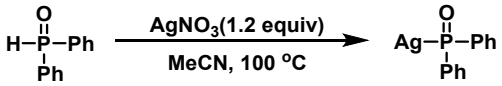


In a 25.0 mL sealed tube, **1a** (0.2 mmol, 64.3 mg, 1.0 equiv), **2i** (0.2 mmol, 52.4 mg, 1.0 equiv), **2j** (0.2 mmol, 47.6 mg, 1.0 equiv), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv) were added to a solution of $AgNO_3$ (17.0 mg, 0.1 mmol, 0.5 equiv) in MeCN (3.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction was allowed to stir at 100 °C for 12 h. Afterward, the resulting mixture was concentrated under reduced pressure. The residue was purified by short column chromatography on silica gel to afford the mixed products.

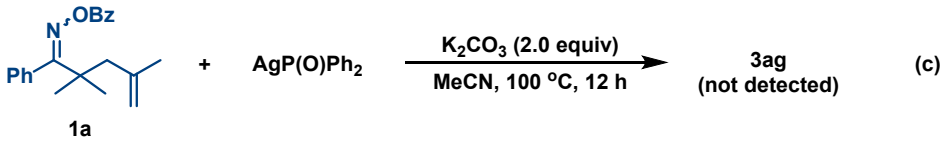

3.725
3.699
2.952
2.926
2.914
2.900
2.888
2.863
2.707
2.680
2.669
2.642
2.631
2.618
2.603
2.594
2.584
2.570
1.914
1.901
1.881
1.867
OMe
Ph
MeO
3ai
F
3aj
3ai:3aj = 1:2.3
^{1}H NMR (400 MHz, CDCl$_3$)
3.01
3.01
3.30
6.60
3.30
f1 (ppm)


F
Ph
3aj
OMe
MeO
3ai
^{31}P NMR (162 MHz, CDCl$_3$)
1.00
2.30
f1 (ppm)

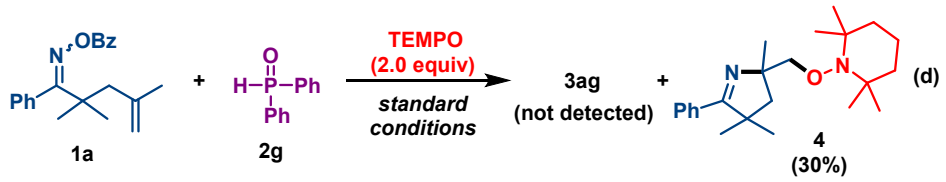
Synthesis of $AgP(O)Ph_2$:



In a 25.0 ml sealed tube, diphenylphosphine oxide (202 mg, 1.0 mmol) and $AgNO_3$ (203 mg, 1.2 mmol) were added. After 3 vacuum/N_2 cycles, CH_3CN (4 mL) was added. The reaction mixture was stirred at 100 °C overnight. The mixture was filtered and the filter cake was washed with water and then CH_3CN. The residue was dried under vacuum to afford $AgP(O)Ph_2$ as a white solid.

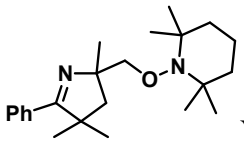


In a 25.0 mL sealed tube, **1a** (0.2 mmol, 64.3 mg, 1.0 equiv) and K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv) were added to a solution of $AgP(O)Ph_2$ (61.9 mg, 0.2 mmol, 1.0 equiv) in MeCN (3.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction was allowed to stir at 100 °C for 12 h. Thin-layer chromatography (TLC) analysis indicated that **3ag** was not detected.

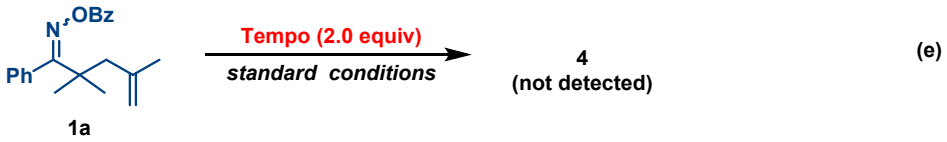


In a 25.0 mL sealed tube, **1a** (0.2 mmol, 64.3 mg, 1.0 equiv), **2g** (0.2 mmol, 52.4 mg, 1.0 equiv), TEMPO (0.4 mmol, 62.5 mg, 2.0 equiv), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv) were added to a solution of $AgNO_3$ (17.0 mg, 0.1 mmol, 0.5 equiv) in MeCN (3.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction was allowed to stir at 100 °C for 12 h. Afterward, the resulting mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **4** in 30% yield.

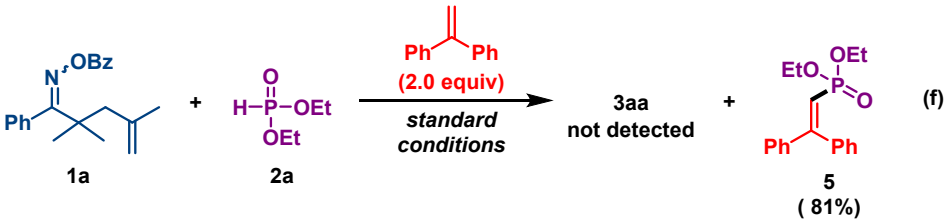
***2,2,6,6-tetramethyl-1-((2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methoxy)piperidine* (4)**



Yield: 30%, 21.4 mg; appearance: yellow oil; R_f: 0.4 (petroleum ether/ethyl acetate = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 2H), 7.36 – 7.33 (m, 3H), 3.91 (d, *J* = 8.4 Hz, 1H), 3.79 (d, *J* = 8.8 Hz, 1H), 2.35 (d, *J* = 12.8 Hz, 1H), 1.69 (d, *J* = 12.8 Hz, 1H), 1.51 – 1.43 (m, 9H), 1.34 (s, 3H), 1.32 (s, 3H), 1.24 (s, 3H), 1.20 (s, 3H), 1.13 (s, 3H), 1.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.01, 135.37, 128.97, 128.07, 128.01, 82.70, 72.54, 60.08, 51.93, 48.98, 39.78, 33.20 (d, *J* = 16.0 Hz), 29.61, 27.95, 26.71, 20.50 (d, *J* = 28.0 Hz), 17.07. **HRMS (ESI)** Calcd for $C_{23}H_{36}N_2O$: [M+H$^+$] 357.2900, found 357.2896.



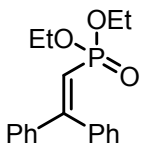
In a 25.0 mL sealed tube, **1a** (0.2 mmol, 64.3 mg, 1.0 equiv), Tempo (0.4 mmol, 62.5 mg, 2.0 equiv), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv) were added to a solution of $AgNO_3$ (17.0 mg, 0.1 mmol, 0.5 equiv) in MeCN (3.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction was allowed to stir at 100 °C for 12 h. Thin-layer chromatography (TLC) analysis indicated that **4** was not detected.



In a 25.0 mL sealed tube, **1a** (0.2 mmol, 64.3 mg, 1.0 equiv), **2a** (0.4 mmol, 52.2 mg, 1.0 equiv), ethene-1,1-diyldibenzene (0.4 mmol, 62.5 mg, 2.0 equiv), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv) were added to a solution of $AgNO_3$ (17.0 mg, 0.1

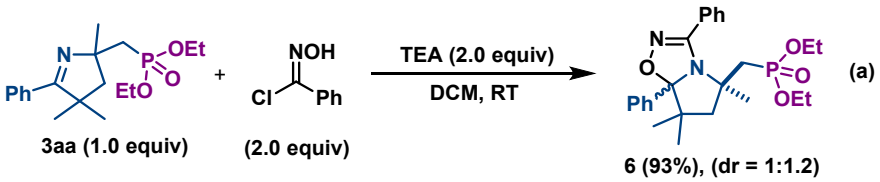
mmol, 0.5 equiv) in MeCN (3.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction was allowed to stir at 100 ^oC for 12 h. Afterward, the resulting mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **5** in 81% isolated yield.

***Diethyl (2,2-diphenylvinyl)phosphonate* (5)**



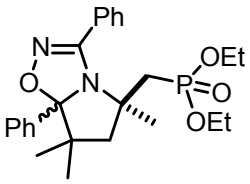
Yield: 81%, 51.3 mg; appearance: yellow oil; R_f: 0.3 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (s, 5H), 7.25 – 7.17 (m, 5H), 6.10 (d, *J* = 15.6 Hz, 1H), 3.86 – 3.69 (m, 4H), 1.04 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.96 (d, *J* = 6.0 Hz), 141.46 (d, *J* = 22.0 Hz), 138.86 (d, *J* = 8.0 Hz), 129.68 (d, *J* = 2.0 Hz), 129.29, 128.55, 128.18 (d, *J* = 11.0 Hz), 127.75, 114.78 (d, *J* = 192.0 Hz), 61.44 (d, *J* = 6.0 Hz), 16.10 (d, *J* = 2.0 Hz), 16.04 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.67 (s). Spectral data were in agreement with reported literature *(Eur. J. Org. Chem.* **2019**, 2138)

Transformations of Phosphorylated Pyrrolines:

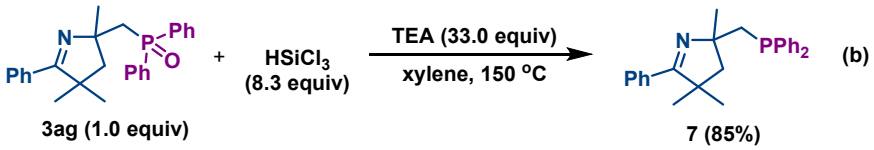


To a 25 mL round-bottom flask equipped with a magnetic stirring bar were added **3aa** (135.3 mg, 0.4 mmol, 1.0 equiv), *N*-hydroxybenzimidoyl chloride (124.5 mg, 0.8 mmol, 2.0 equiv), Et_3N (90.0 mg, 0.8 mmol, 2.0 equiv) and DCM (10 mL). The mixture was stirred at room temperature for 5 h. The solvent was removed in *vacuo*, and the crude product was purified by column chromatography using (petroleum ether/ethyl acetate = 5:1) as eluent to give the product **6** (170.5 mg, 93%) as a yellow oil.

***Diethyl((4-methyl-3,6a-diphenyl-3a,5,6,6a-tetrahydro-4H-cyclopenta[d]isoxazol-4-yl)methyl)phosphonate* (6)**

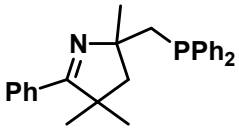


Yield: 93%, 170.5 mg (dr = 1:1.2); appearance: yellow oil; R_f: 0.2 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 4.4H), 7.65 – 7.61 (m, 4.4H), 7.31 – 7.28 (m, 6.6H), 7.25 – 7.15 (m, 6.6H), 4.05 – 3.78 (m, 8.4H), 2.75 – 2.65 (m, 1H), 2.62 (d, *J* = 13.2 Hz, 1H), 2.49 (d, *J* = 13.2 Hz, 1.2H), 2.35 (dd, *J* = 19.6, 15.6 Hz, 1H), 2.12 – 2.06 (m, 2.2H), 1.93 (dd, *J* =20.8, 14.4 Hz, 1.2H), 1.74 (s, 3.6H), 1.64 (dd, *J* =21.2, 14.4 Hz, 1.2H), 1.25 – 1.15 (m, 19.2H), 1.09 (t, *J* = 7.2 Hz, 3.6H), 0.76 (s, 3H), 0.76 (s, 3.6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.91 (d, *J* = 1.0 Hz), 159.86, 140.17, 130.62, 130.42, 129.03, 128.94, 128.77, 128.55, 127.95, 127.34, 127.31, 125.82, 125.80, 113.57, 113.40 (d, *J* = 2.0 Hz), 64.55, 64.51, 64.30, 64.28, 61.48, 61.46, 61.42, 61.39, 61.35, 54.28, 52.71, 43.72, 43.65, 41.31, 39.98, 39.36, 38.00, 30.52, 28.30, 28.28, 28.06, 24.62, 24.60, 24.45, 24.43, 16.20, 16.18. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.83 (s), 26.39 (s). **HRMS (ESI)** Calcd for $C_{26}H_{34}NO_4P$: $[M+H^+]$ 457.2251, found 457.2257.



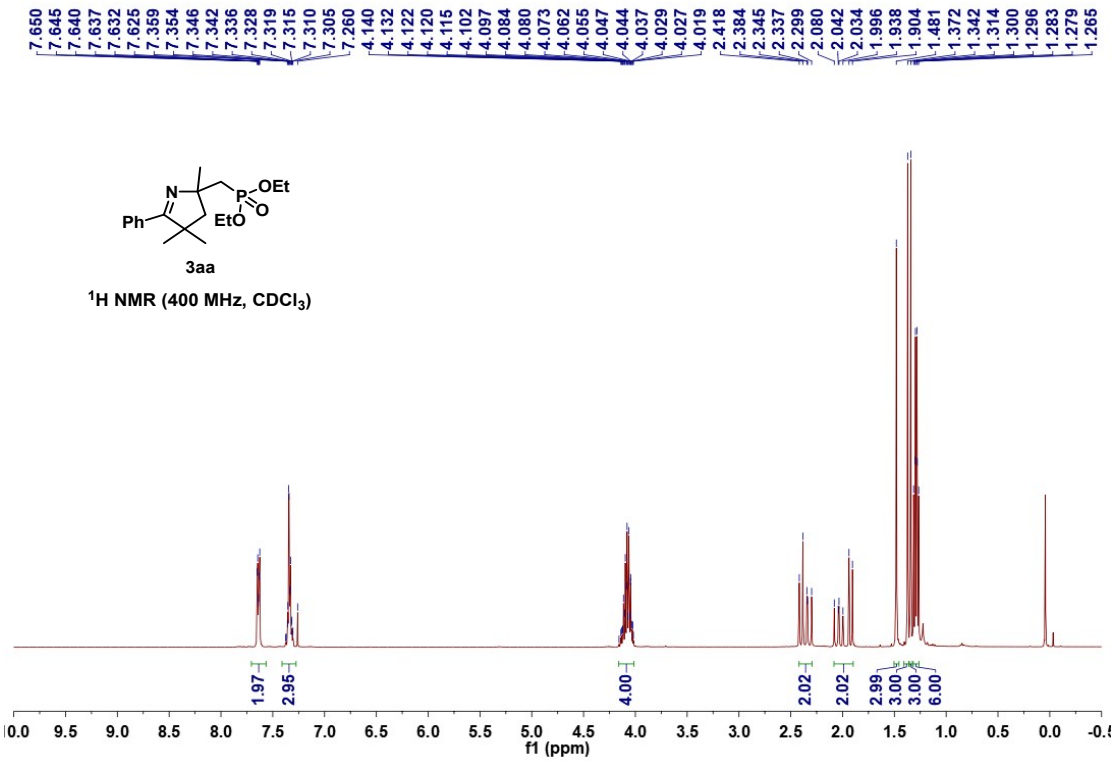
To a 25 mL sealed tube equipped with a magnetic stirring bar were added **3ag** (80.4 mg, 0.2 mmol, 1.0 equiv), trichlorosilane (216.7 mg, 1.66 mmol, 8.3 equiv), Et_3N (667.9 mg, 6.6 mmol, 33.0 equiv) and xylene (4 mL). The mixture was stirred at 150 °C for 48 h. The solvent was removed in *vacuo*, and the crude product was purified by column chromatography using (petroleum ether/ethyl acetate = 5:1) as eluent to give the product **7** (55.5 mg, 85%) as a yellow oil.

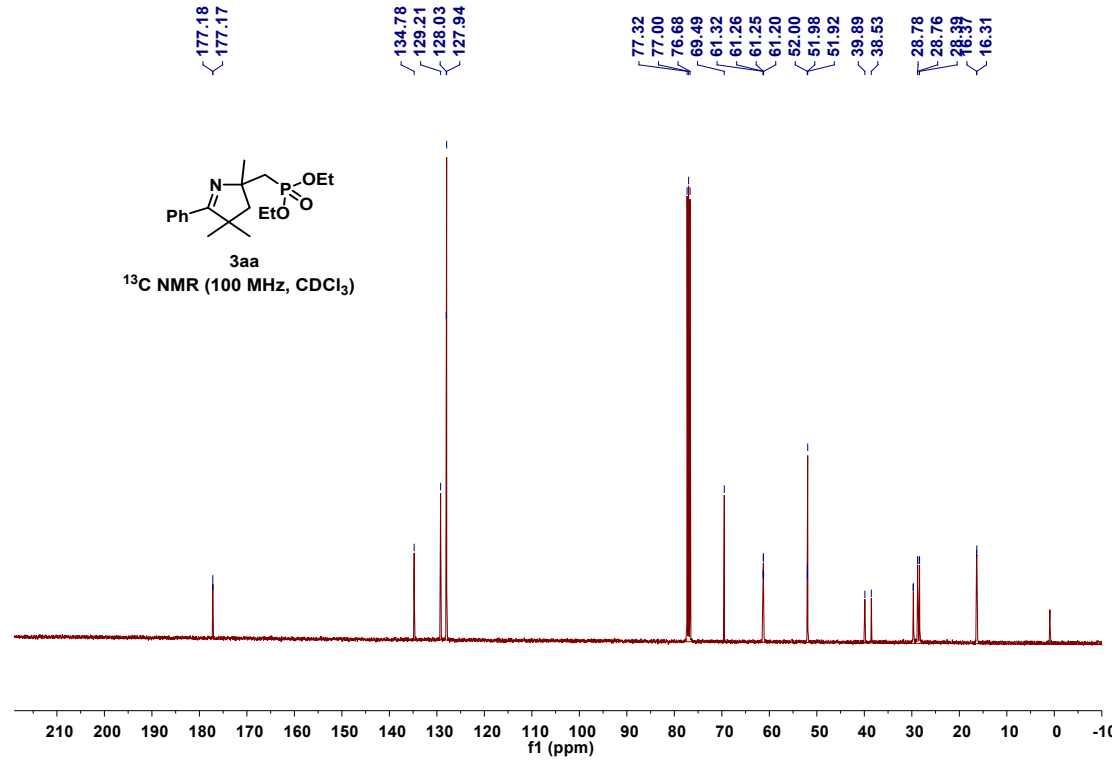
***2-((diphenylphosphanyl)methyl)-2,4,4-trimethyl-5-phenyl-3,4-dihydro-2H-pyrrole* (7)**

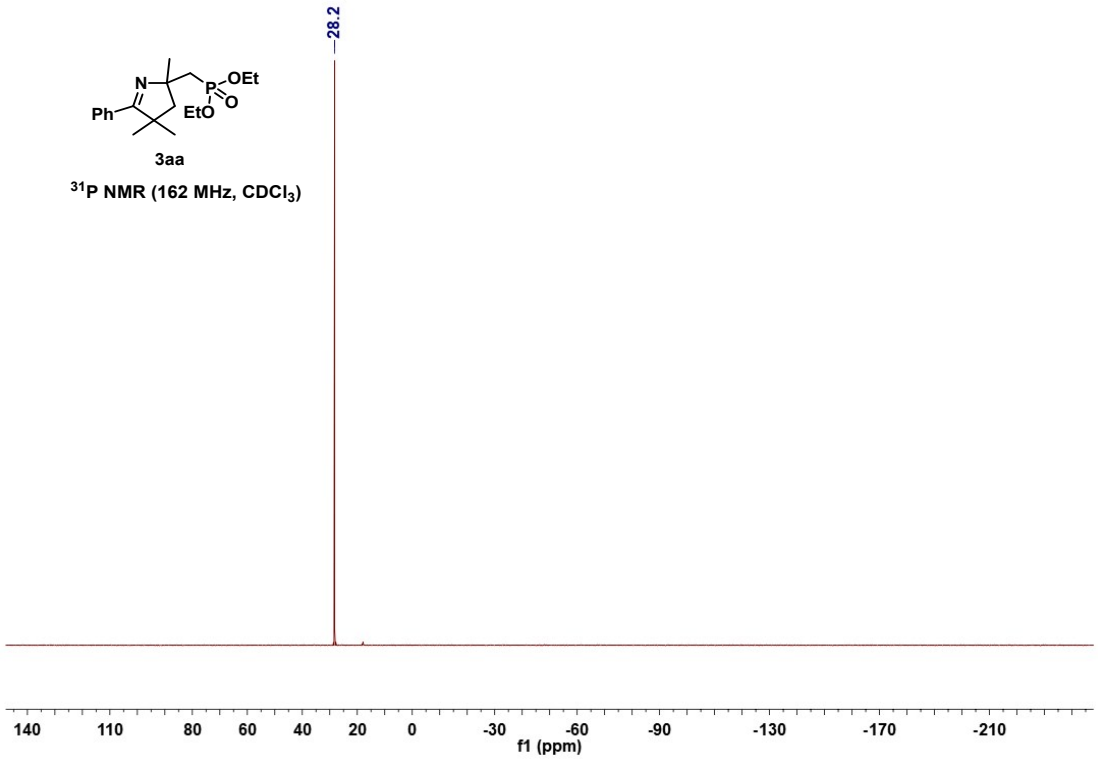


Yield: 85%, 65.5 mg; appearance: brown oil; R_f: 0.5 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 6H), 7.34 – 7.27 (m, 9H), 2.62 (dd, *J* = 14.0, 3.2 Hz, 1H), 2.58 (dd, *J* = 14.0, 3.6 Hz, 1H), 2.22 (d, *J* = 13.2 Hz, 1H), 1.87 (d, *J* = 13.2 Hz, 1H), 1.44 (s, 3H), 1.43 (s, 3H), 1.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.76, 139.95 (d, *J* = 2.0 Hz), 139.83 (d, *J* = 2.0 Hz), 134.86, 133.14 (d, *J* = 6.0 Hz) ,132.95 (d, *J* = 5.0 Hz), 129.09, 128.39, 128.33, 128.27, 128.22, 128.09, 127.95, 71.91 (d, *J* = 15.0 Hz), 53.11 (d, *J* = 8.0 Hz), 51.65, 44.22 (d, *J* = 15.0 Hz), 30.66 (d, *J* = 8.0 Hz), 29.26 (d, *J* = 1.0 Hz), 27.98. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -23.10 (s). **HRMS (ESI)** Calcd for $C_{26}H_{28}NP$: [M+H$^+$] 386.2032, found 386.2032.

NMR Spectra:

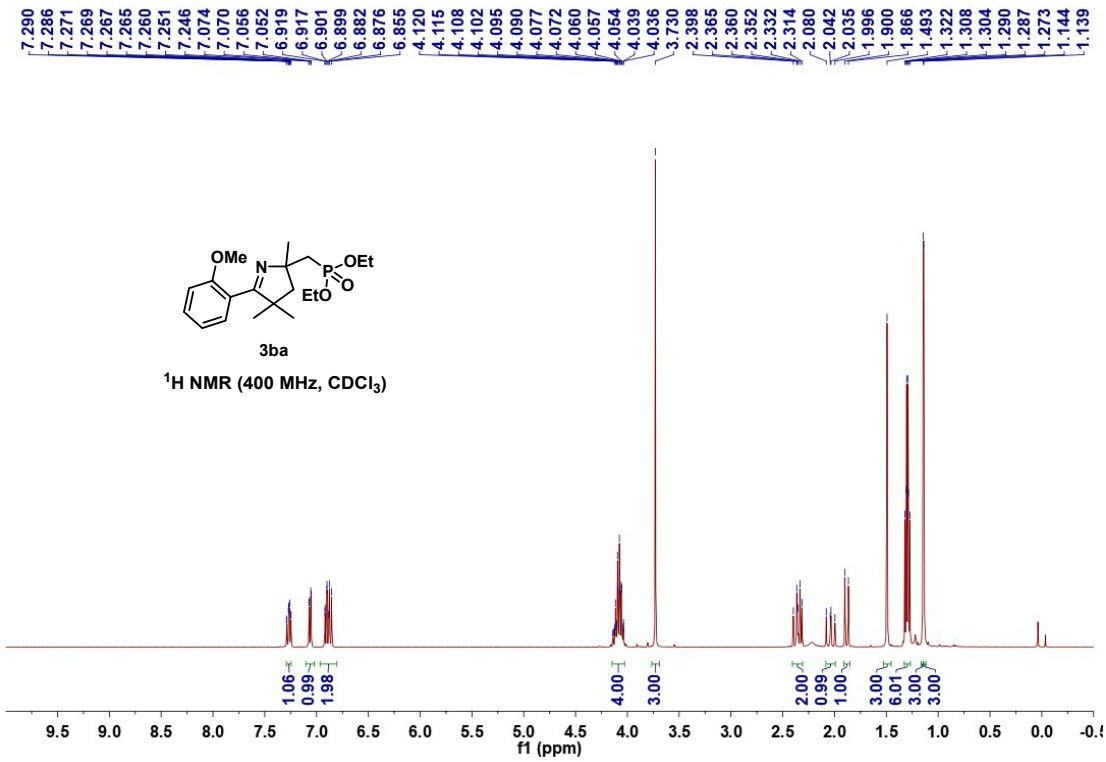

7.650 7.645 7.640 7.637 7.632 7.625 7.359 7.354 7.346 7.342 7.336 7.328 7.319 7.315 7.310 7.305 7.260 4.140 4.132 4.122 4.120 4.115 4.102 4.097 4.084 4.080 4.073 4.062 4.055 4.047 4.044 4.037 4.029 4.027 4.019 2.418 2.384 2.345 2.337 2.299 2.080 2.042 2.034 1.996 1.938 1.904 1.481 1.372 1.342 1.314 1.300 1.296 1.283 1.279 1.265
N
P
OEt
O
Ph
EtO
3aa
1H NMR (400 MHz, CDCl3)
1.97 2.95 4.00 2.02 2.02 2.99 3.00 3.00 6.00
f1 (ppm)


177.18 177.17 134.78 129.21 128.03 127.94 77.32 77.00 76.68 69.49 61.32 61.26 61.25 61.20 52.00 51.98 51.92 39.89 38.53 28.78 28.76 16.37 16.31
N
P
OEt
O
Ph
EtO
3aa
13C NMR (100 MHz, CDCl3)
f1 (ppm)



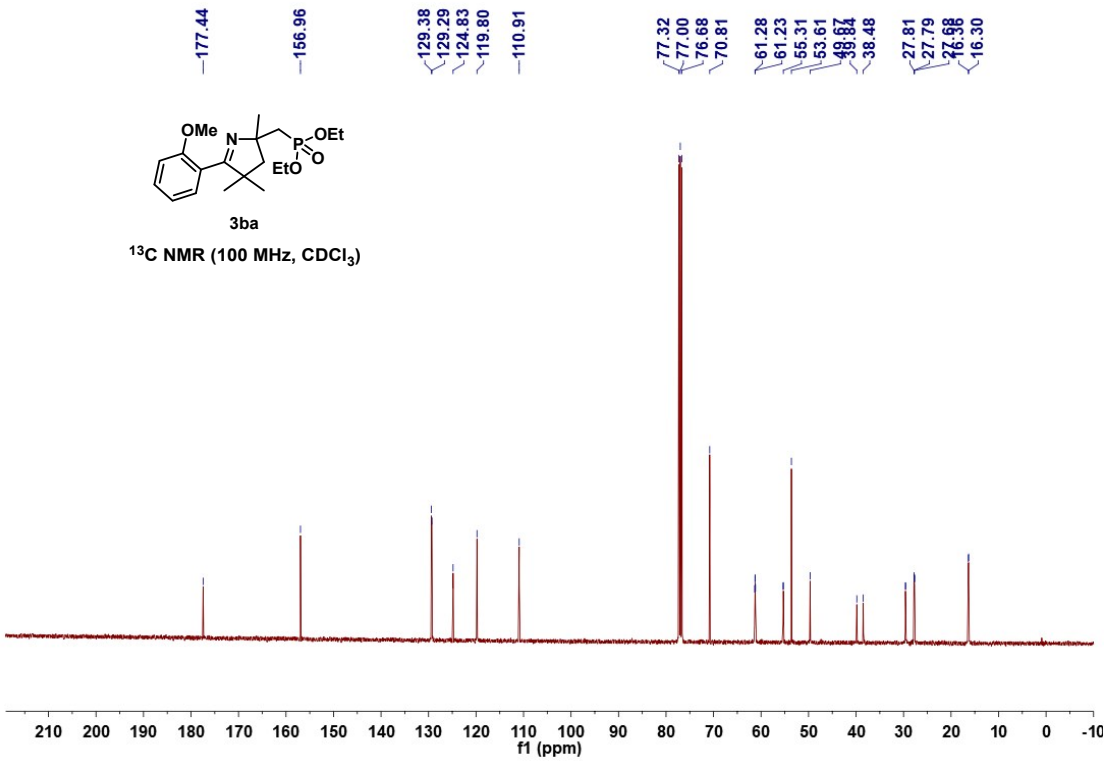
3aa

^{31}P NMR (162 MHz, $CDCl_3$)



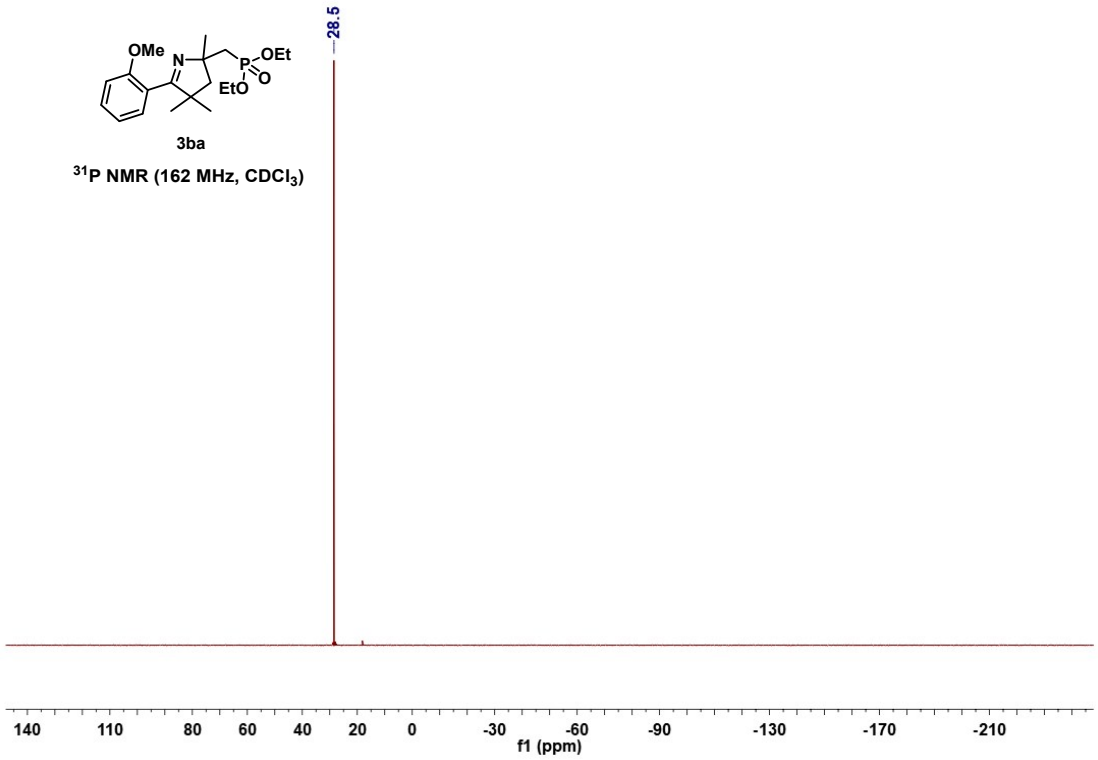
3ba

^{1}H NMR (400 MHz, $CDCl_3$)



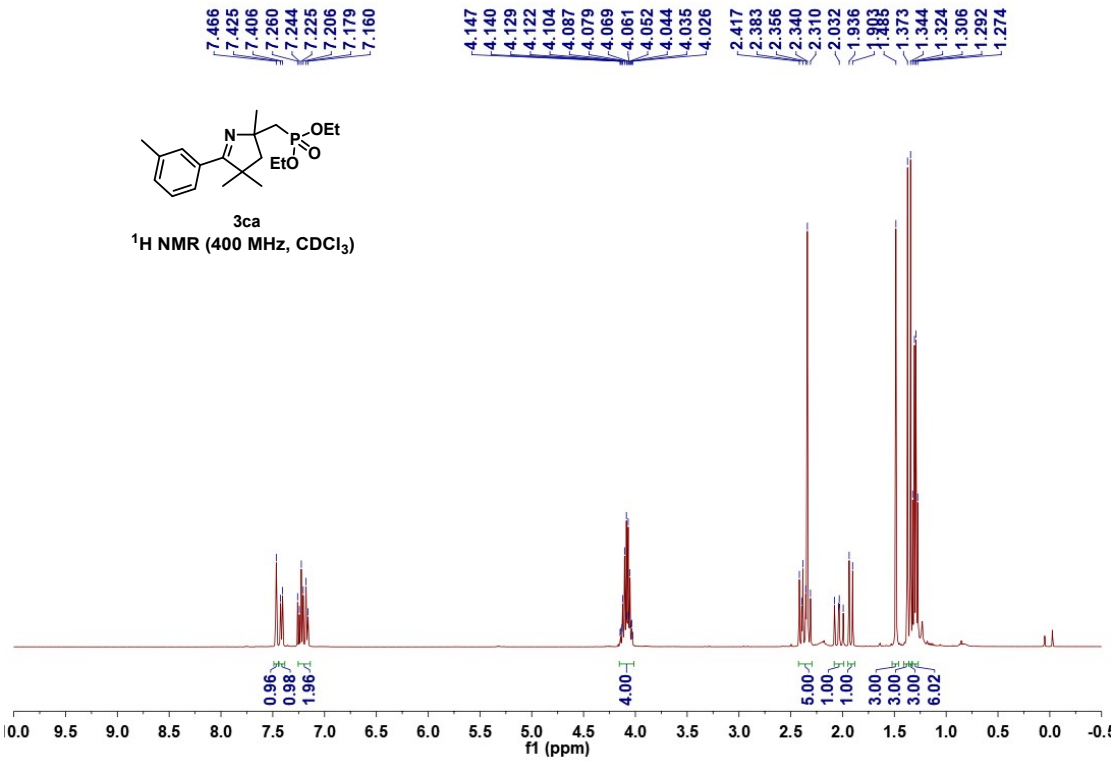
3ba

^{13}C NMR (100 MHz, $CDCl_3$)



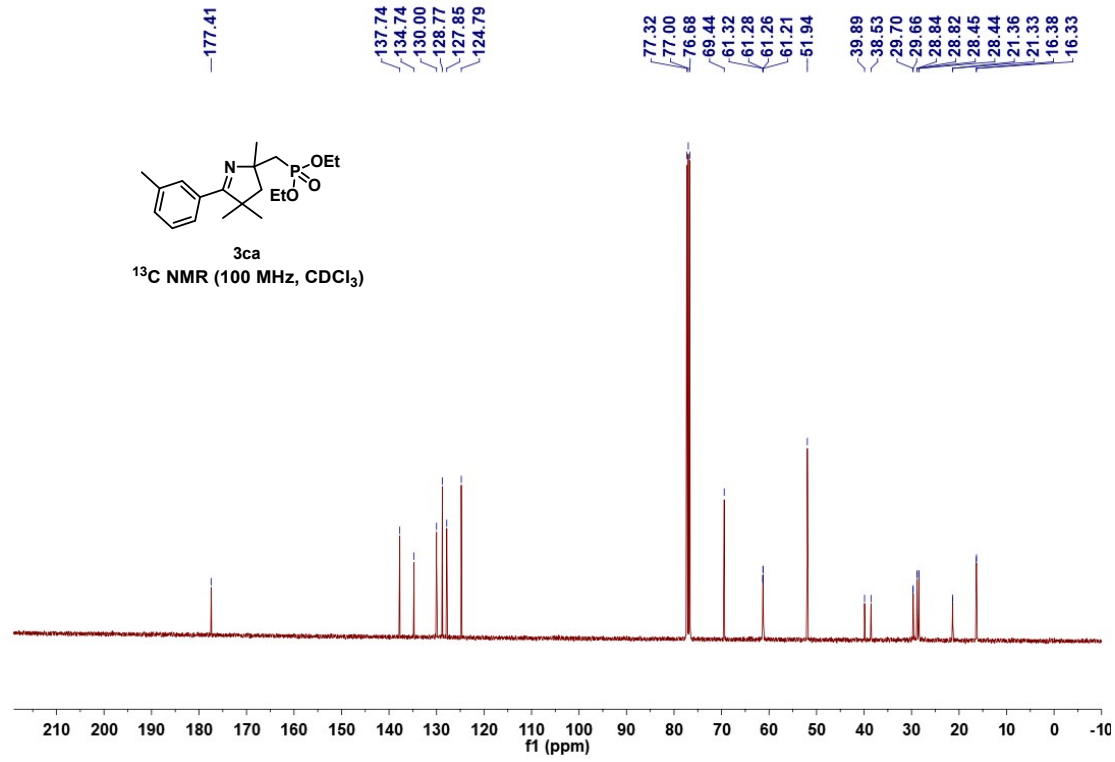
3ba

^{31}P NMR (162 MHz, $CDCl_3$)



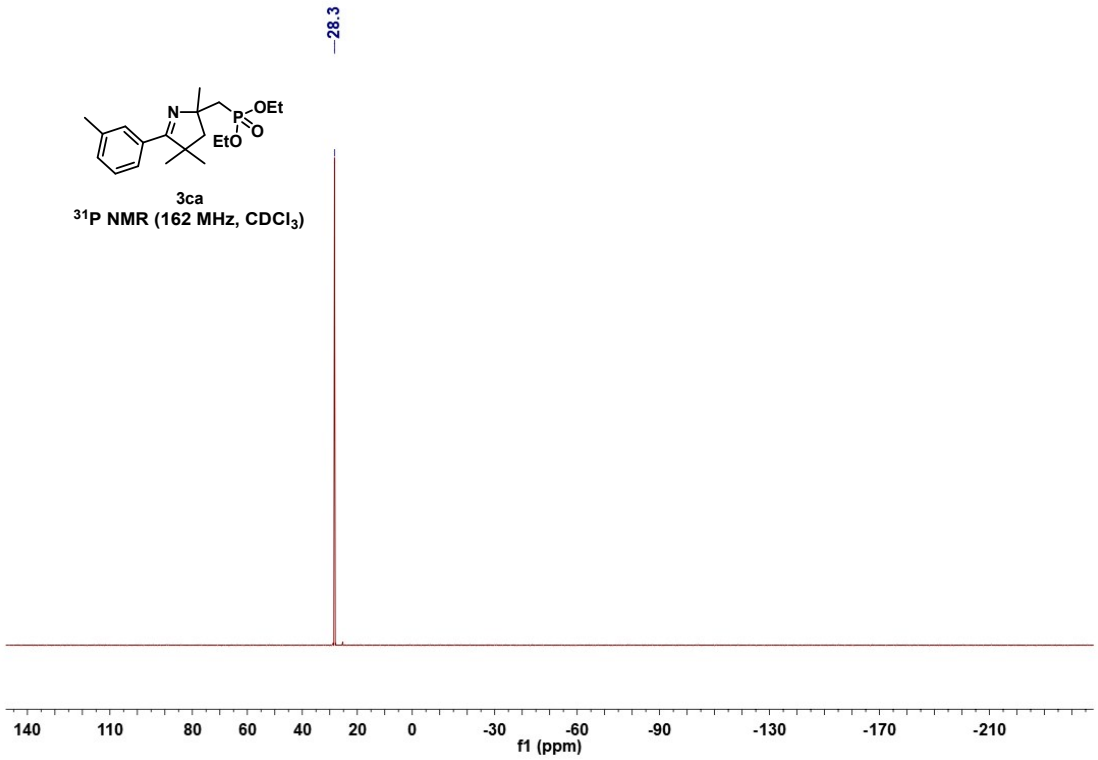
3ca

^{1}H NMR (400 MHz, $CDCl_3$)

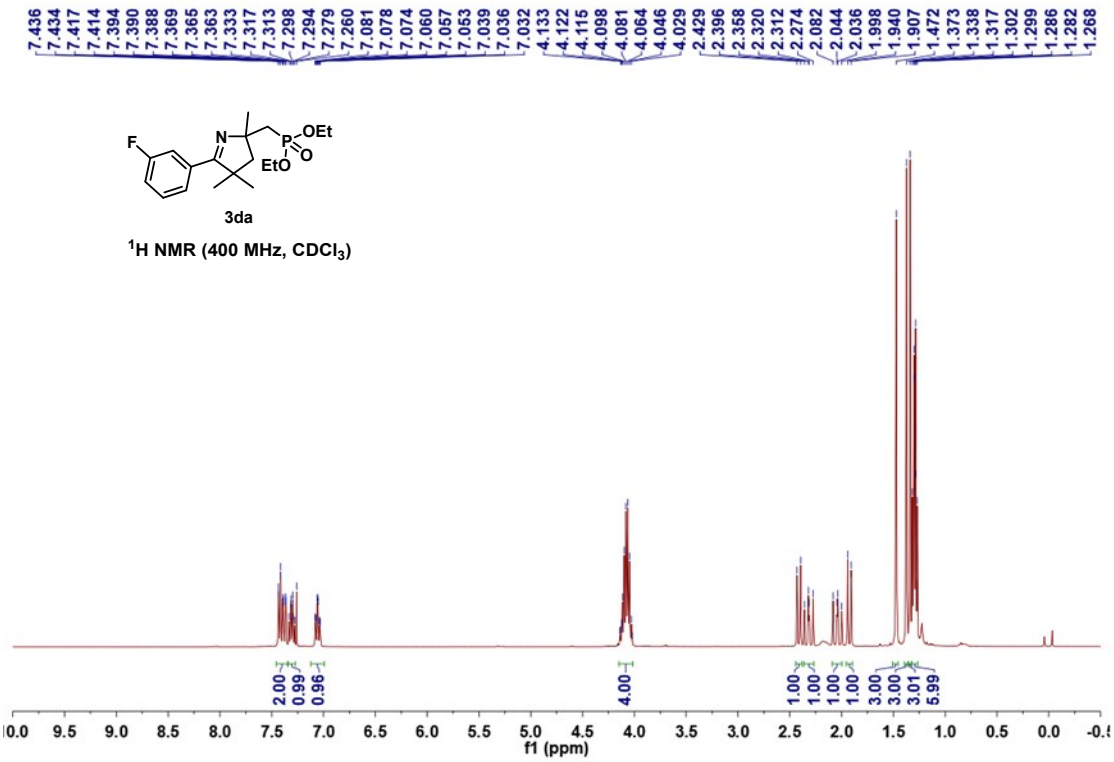


3ca

^{13}C NMR (100 MHz, $CDCl_3$)

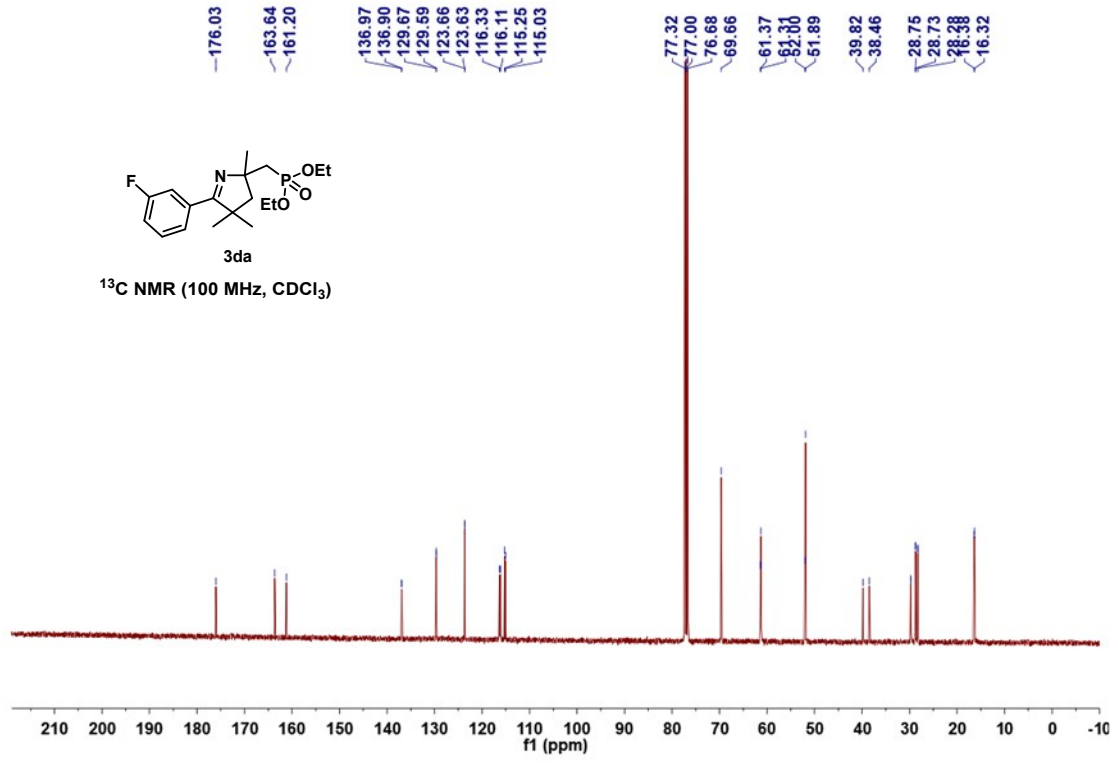


3ca
^{31}P NMR (162 MHz, $CDCl_3$)



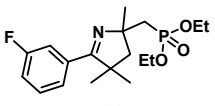
3da

^{1}H NMR (400 MHz, $CDCl_3$)



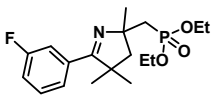
3da

^{13}C NMR (100 MHz, $CDCl_3$)



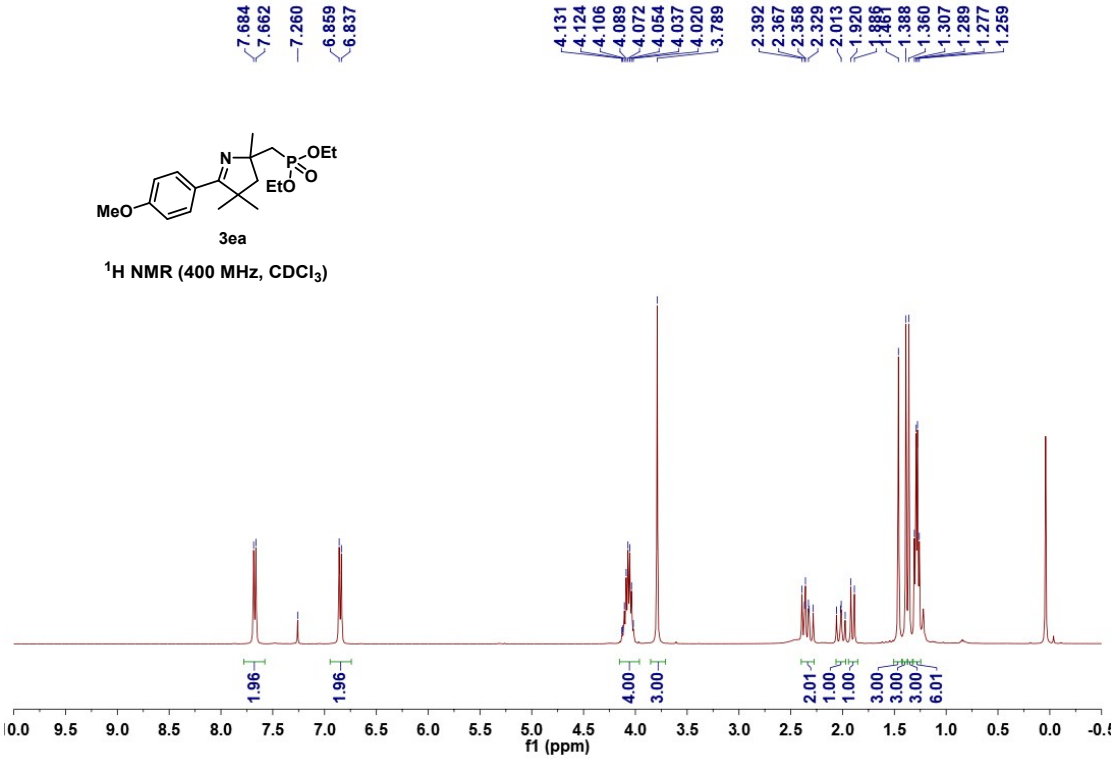
3da

^{19}F NMR (376 MHz, $CDCl_3$)



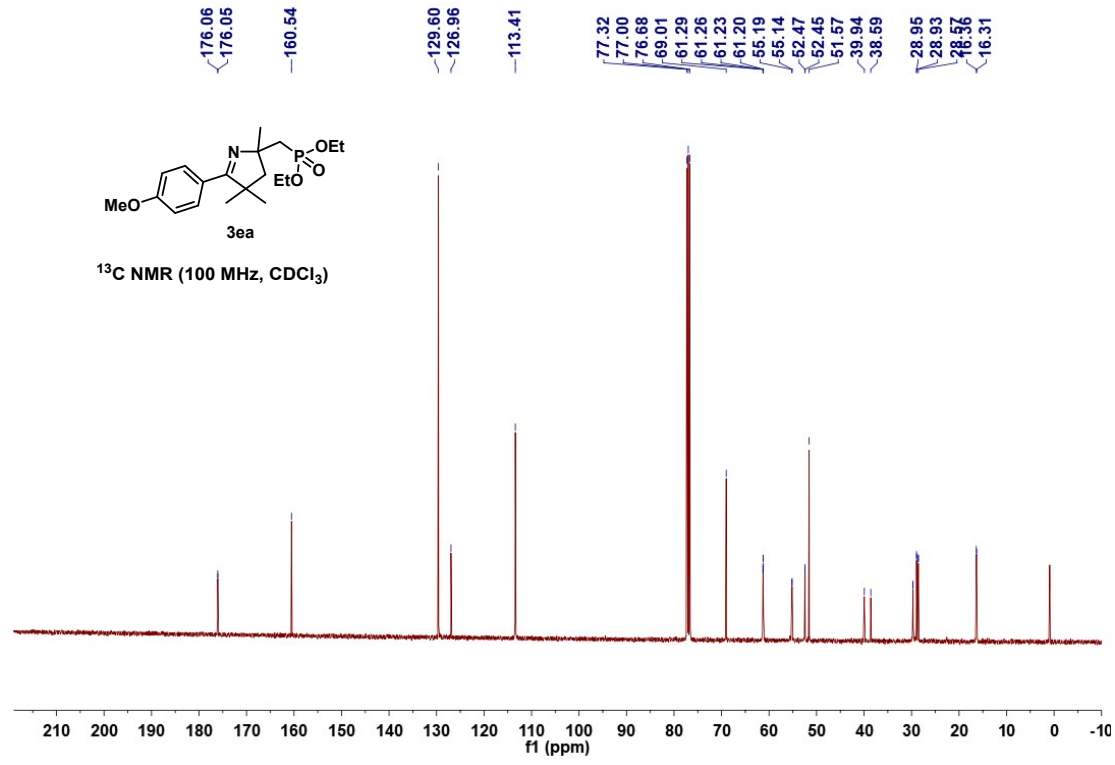
3da

^{31}P NMR (162 MHz, $CDCl_3$)



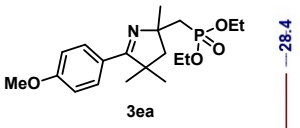
3ea

^{1}H NMR (400 MHz, $CDCl_3$)



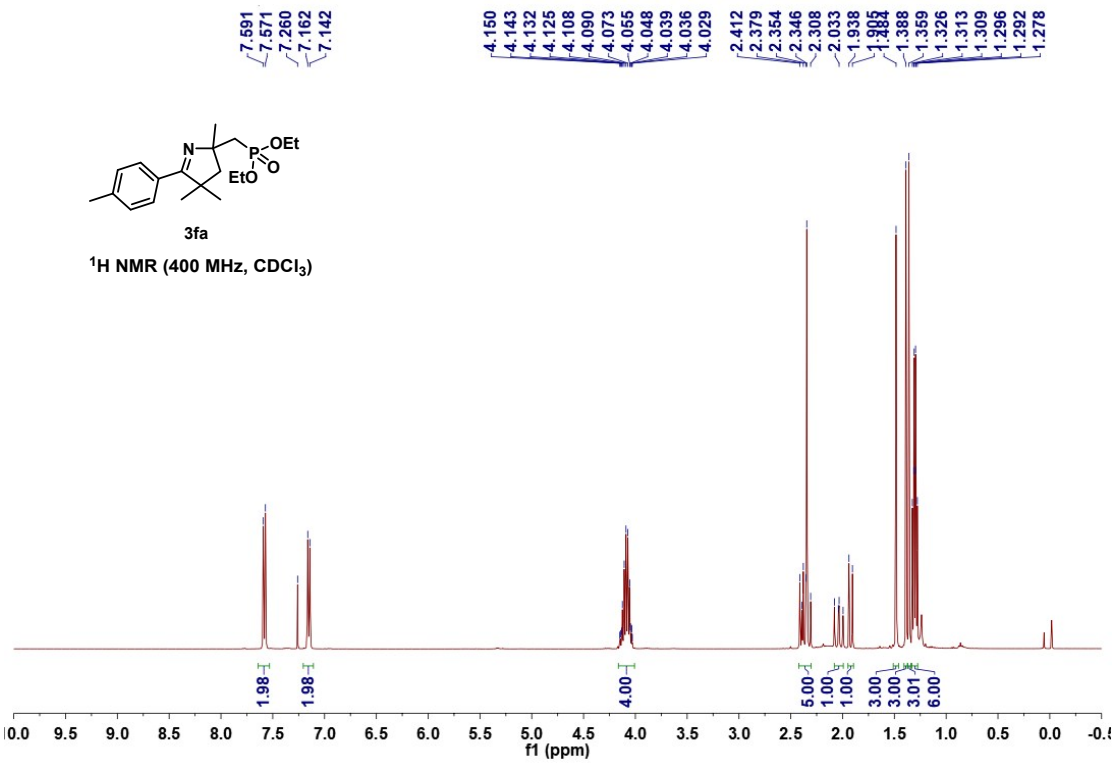
3ea

^{13}C NMR (100 MHz, $CDCl_3$)



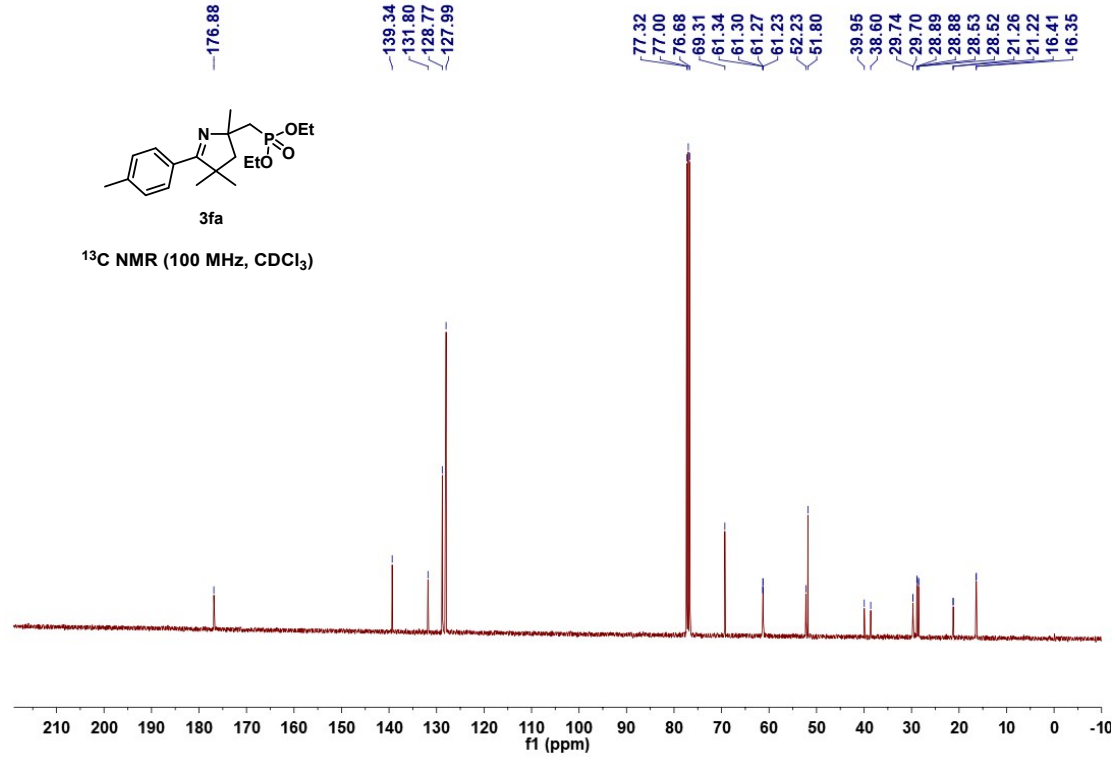
3ea

^{31}P NMR (162 MHz, $CDCl_3$)



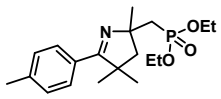
3fa

^{1}H NMR (400 MHz, $CDCl_3$)



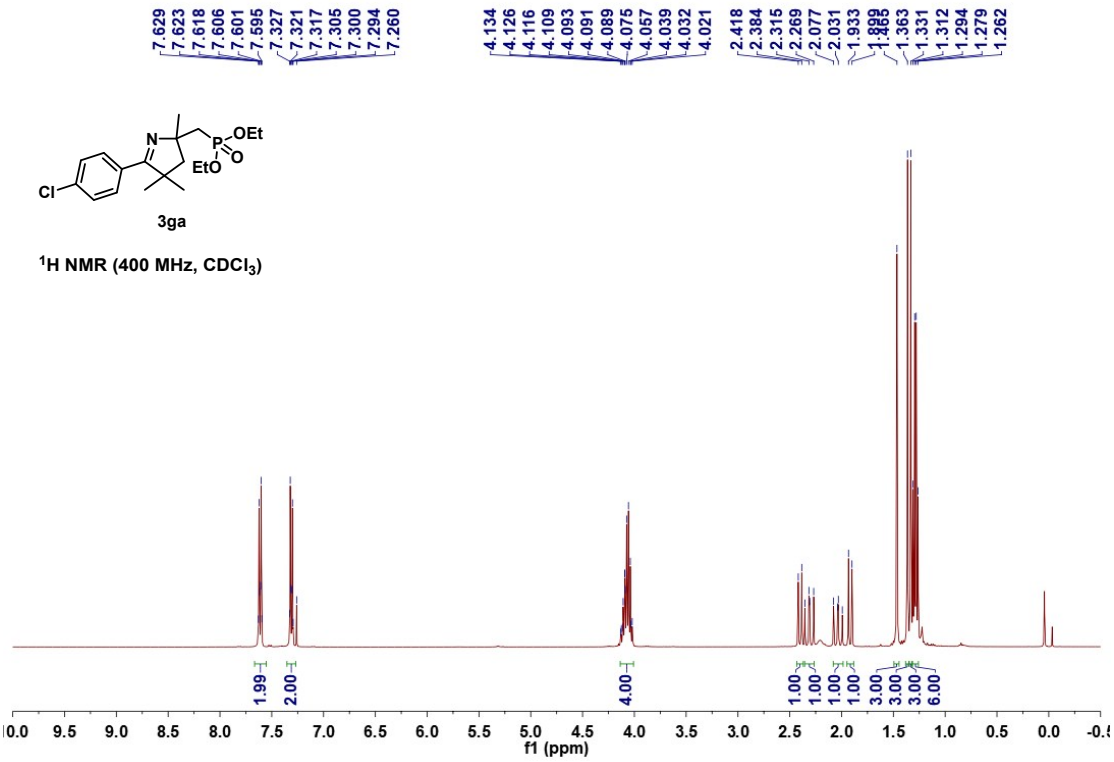
3fa

^{13}C NMR (100 MHz, $CDCl_3$)



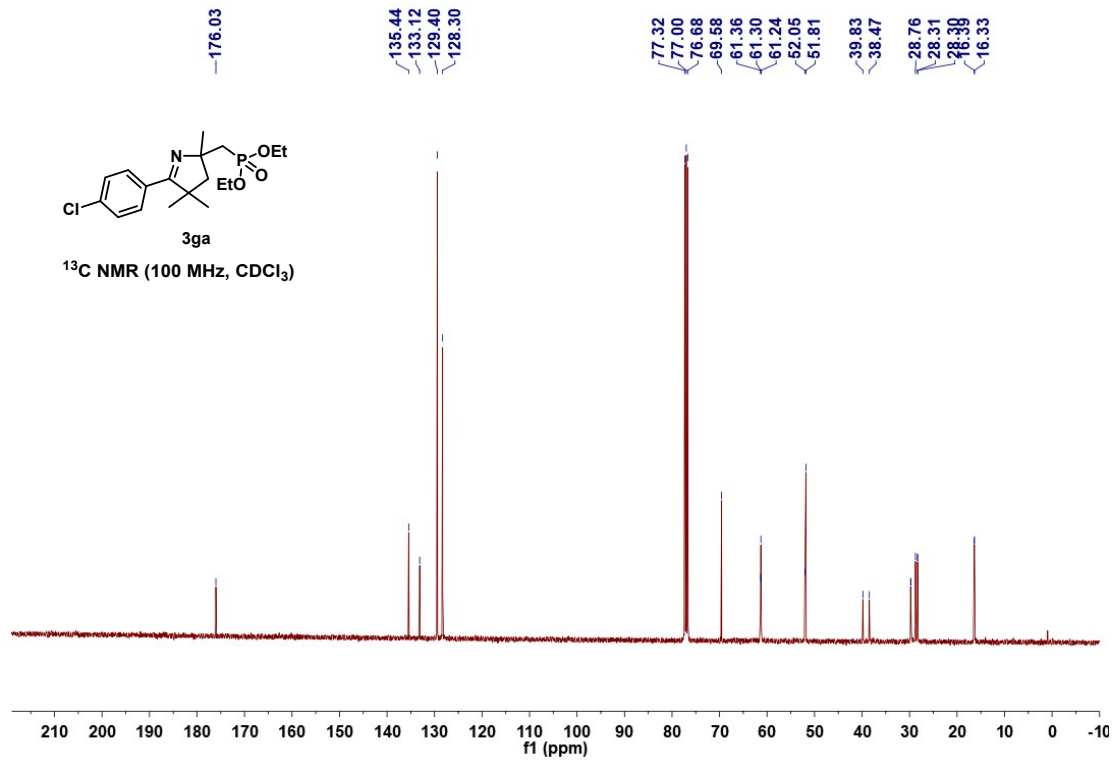
3fa

^{31}P NMR (162 MHz, $CDCl_3$)



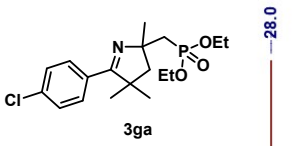
3ga

^{1}H NMR (400 MHz, $CDCl_3$)



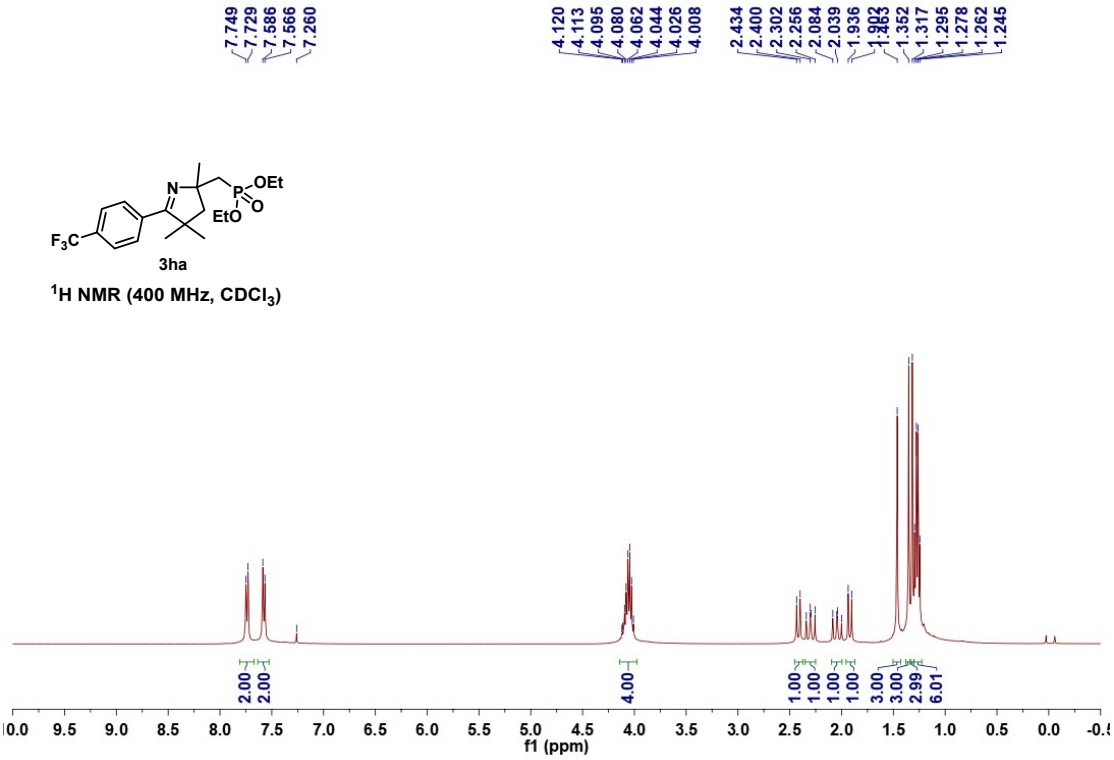
3ga

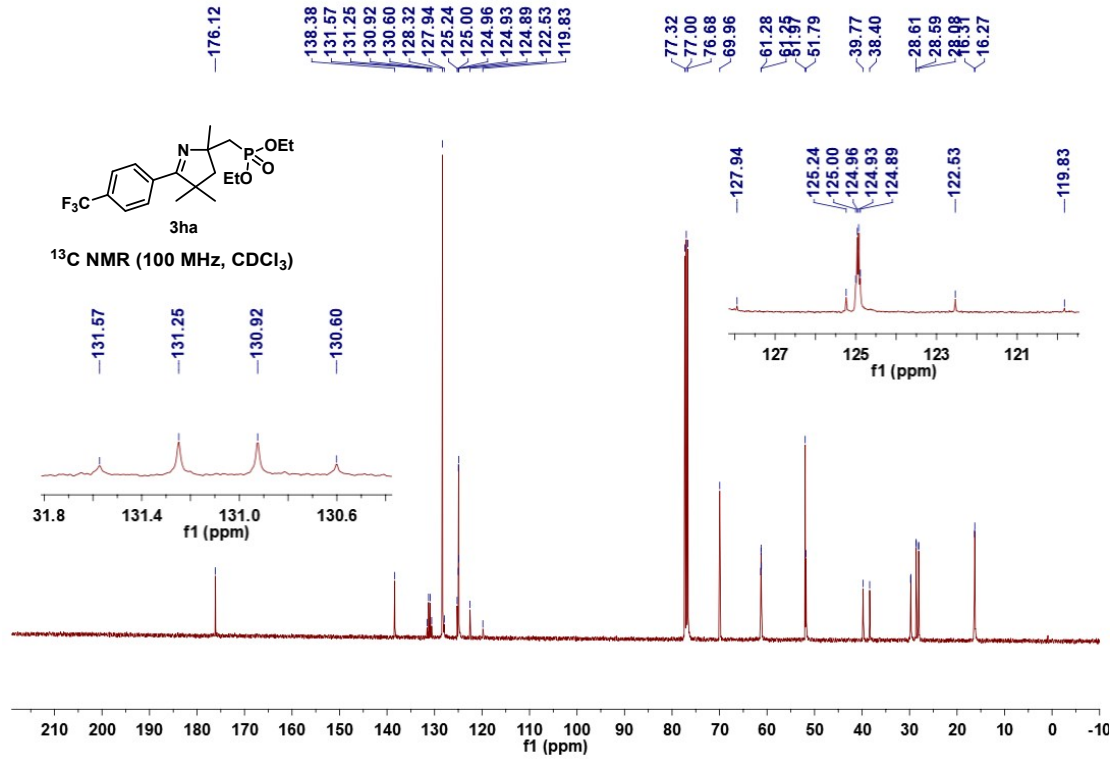
^{13}C NMR (100 MHz, $CDCl_3$)

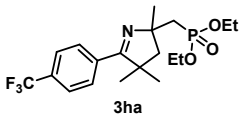


3ga

^{31}P NMR (162 MHz, $CDCl_3$)

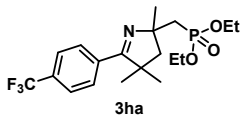

7.749
7.729
7.586
7.566
7.260
4.120
4.113
4.095
4.080
4.062
4.044
4.026
4.008
2.434
2.400
2.302
2.256
2.084
2.039
1.936
1.352
1.317
1.295
1.278
1.262
1.245
N
P
OEt
O
EtO
F3C
3ha
1H NMR (400 MHz, CDCl3)
2.00
2.00
4.00
1.00
1.00
1.00
3.00
3.00
2.99
6.01
f1 (ppm)


176.12
138.38
131.57
131.25
130.92
130.60
128.32
127.94
125.24
125.00
124.96
124.93
124.89
122.53
119.83
77.32
77.00
76.68
69.96
61.28
51.79
39.77
38.40
28.61
28.59
16.27
N
P
OEt
O
EtO
F3C
3ha
13C NMR (100 MHz, CDCl3)
131.57
131.25
130.92
130.60
31.8
131.4
131.0
130.6
f1 (ppm)
127.94
125.24
125.00
124.96
124.93
124.89
122.53
119.83
127
125
123
121
f1 (ppm)
f1 (ppm)



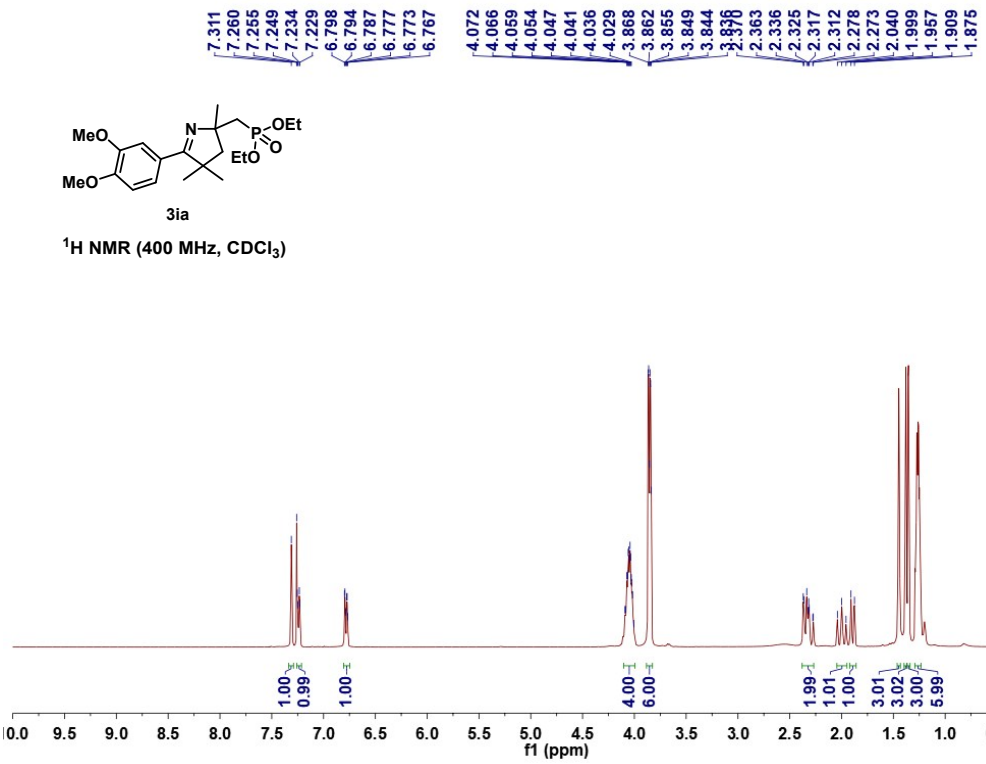
3ha

^{19}F NMR (376 MHz, $CDCl_3$)



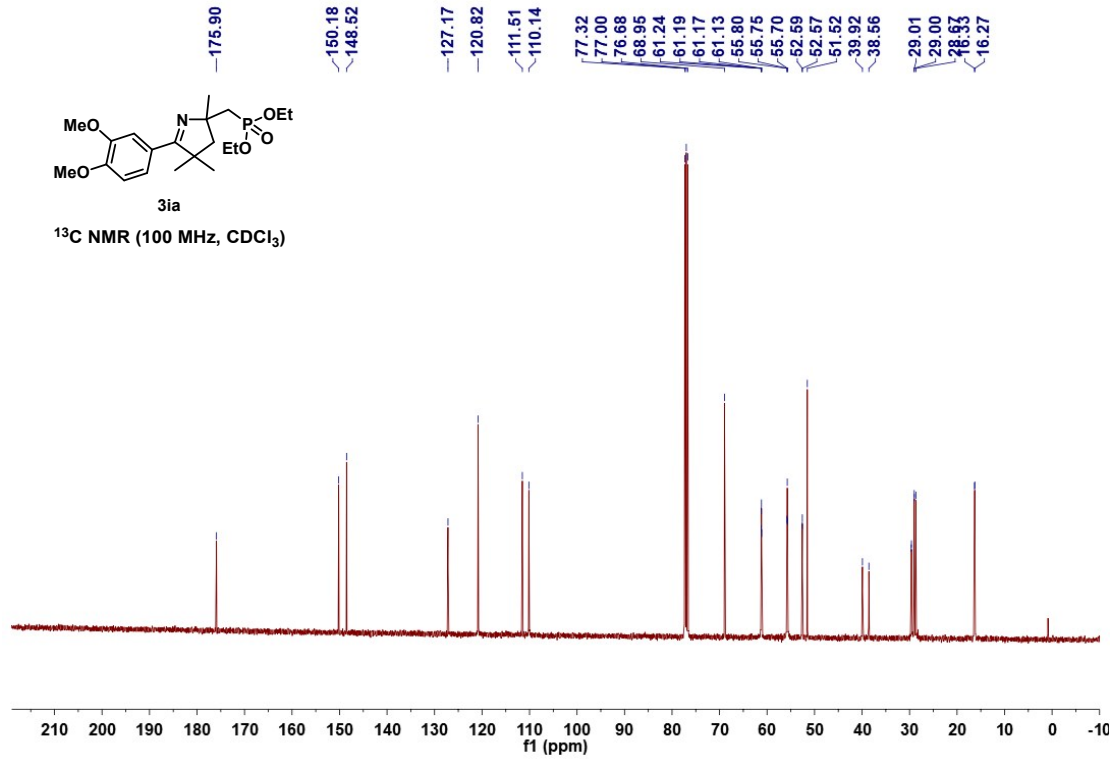
3ha

^{31}P NMR (162 MHz, $CDCl_3$)



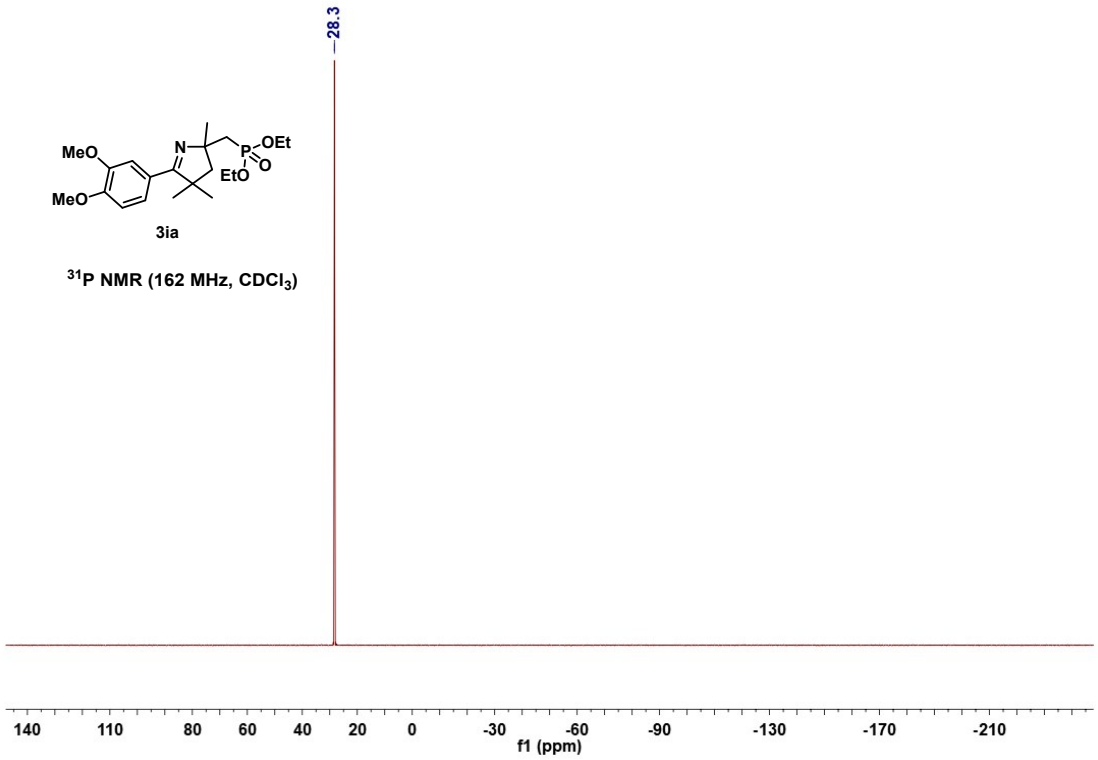
3ia

^{1}H NMR (400 MHz, $CDCl_3$)



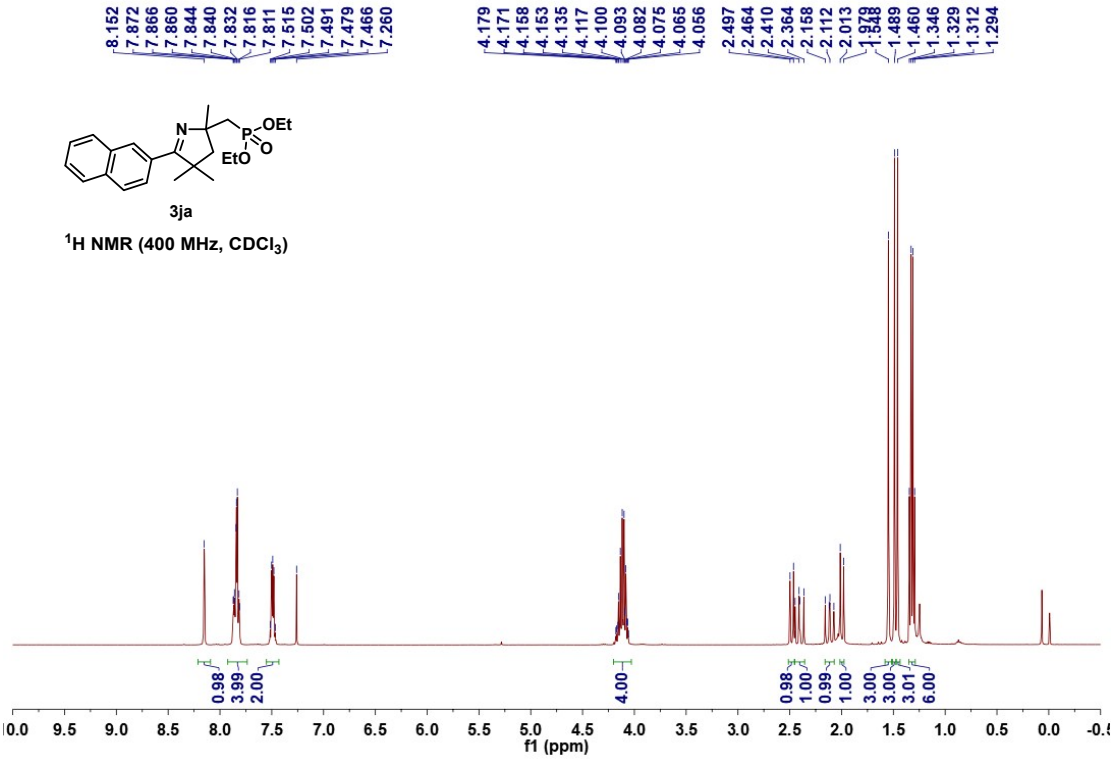
3ia

^{13}C NMR (100 MHz, $CDCl_3$)



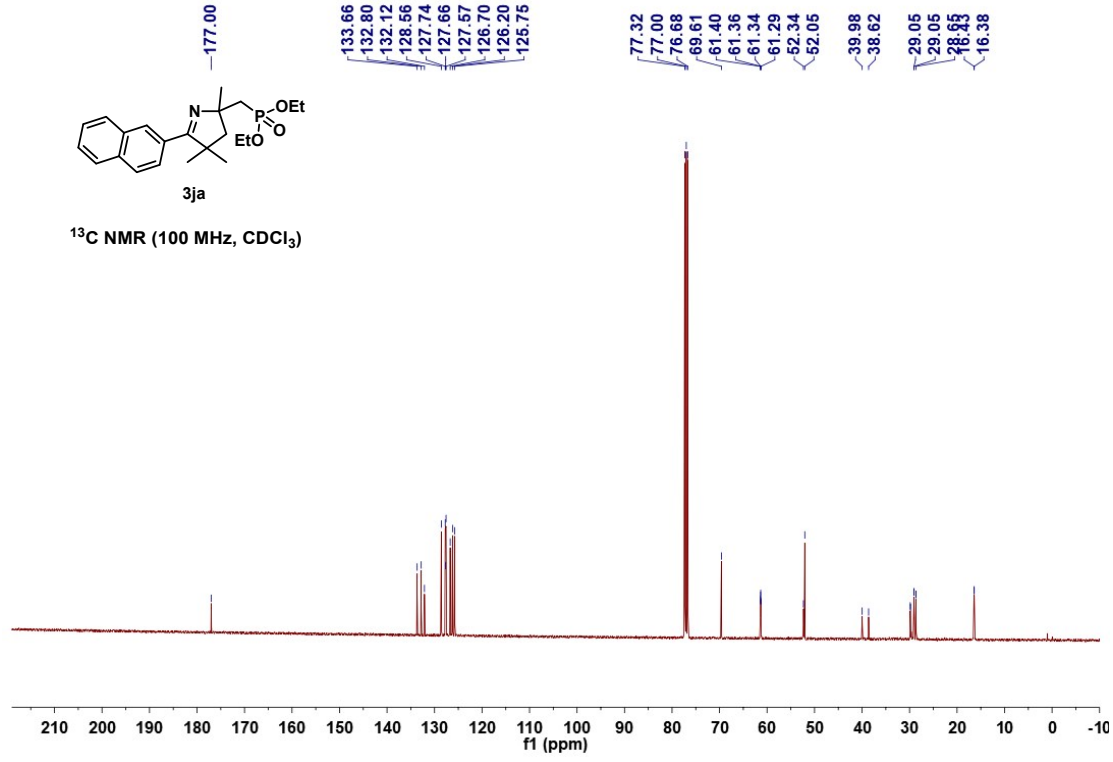
3ia

^{31}P NMR (162 MHz, $CDCl_3$)



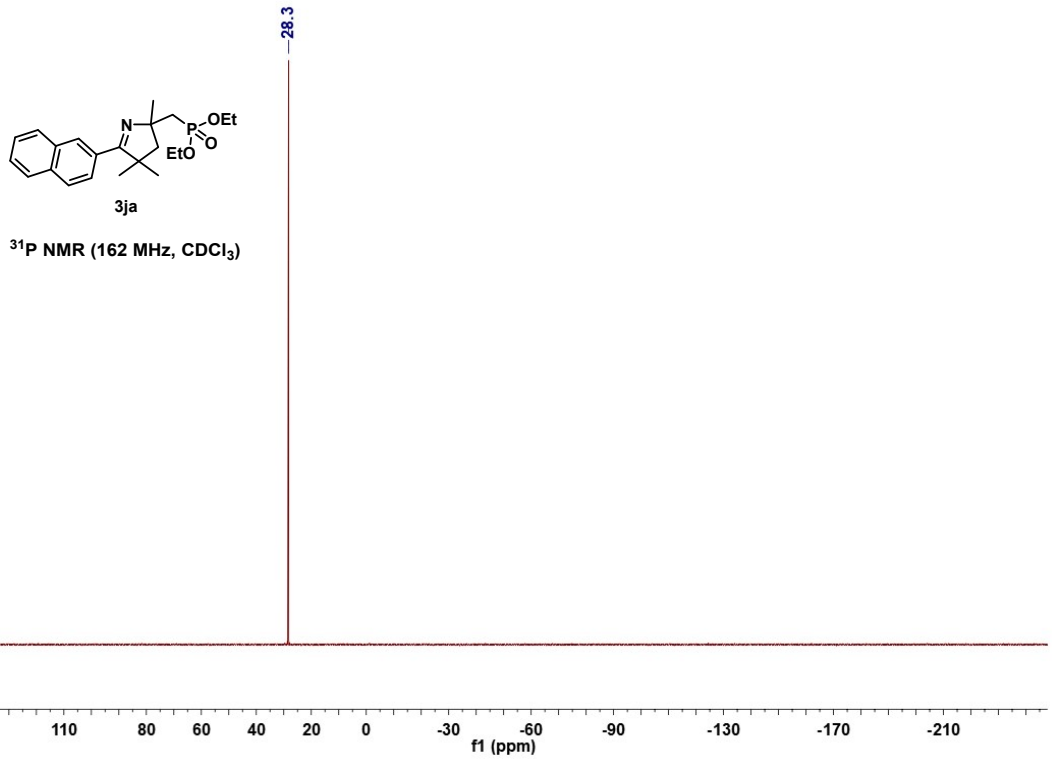
3ja

^{1}H NMR (400 MHz, $CDCl_3$)



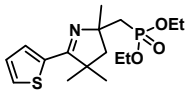
3ja

^{13}C NMR (100 MHz, $CDCl_3$)



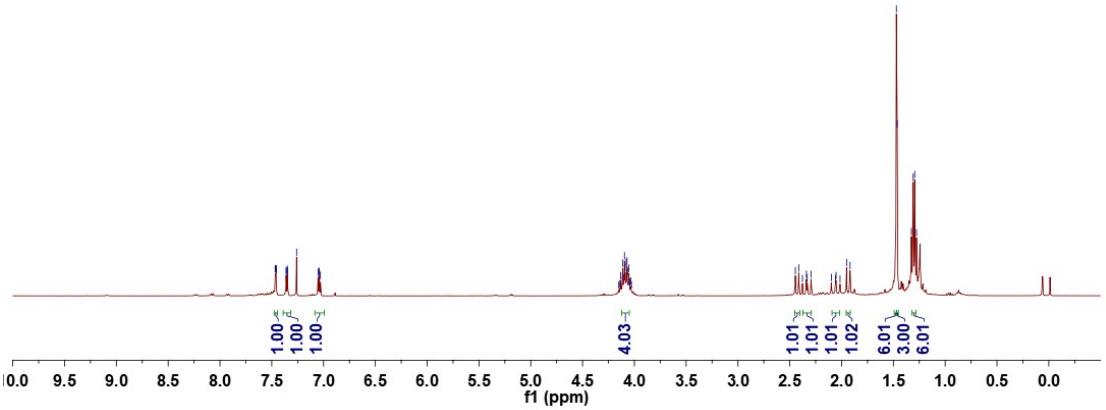
3ja

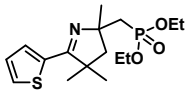
^{31}P NMR (162 MHz, $CDCl_3$)



3ka

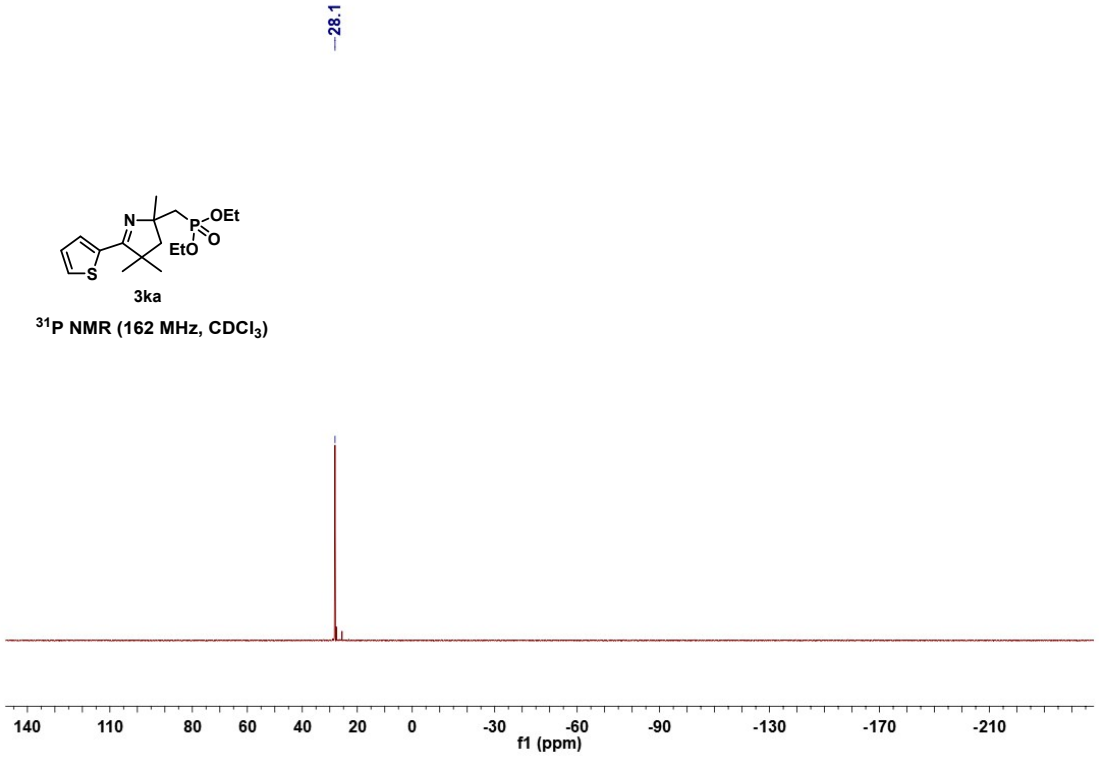
^{1}H NMR (400 MHz, $CDCl_3$)





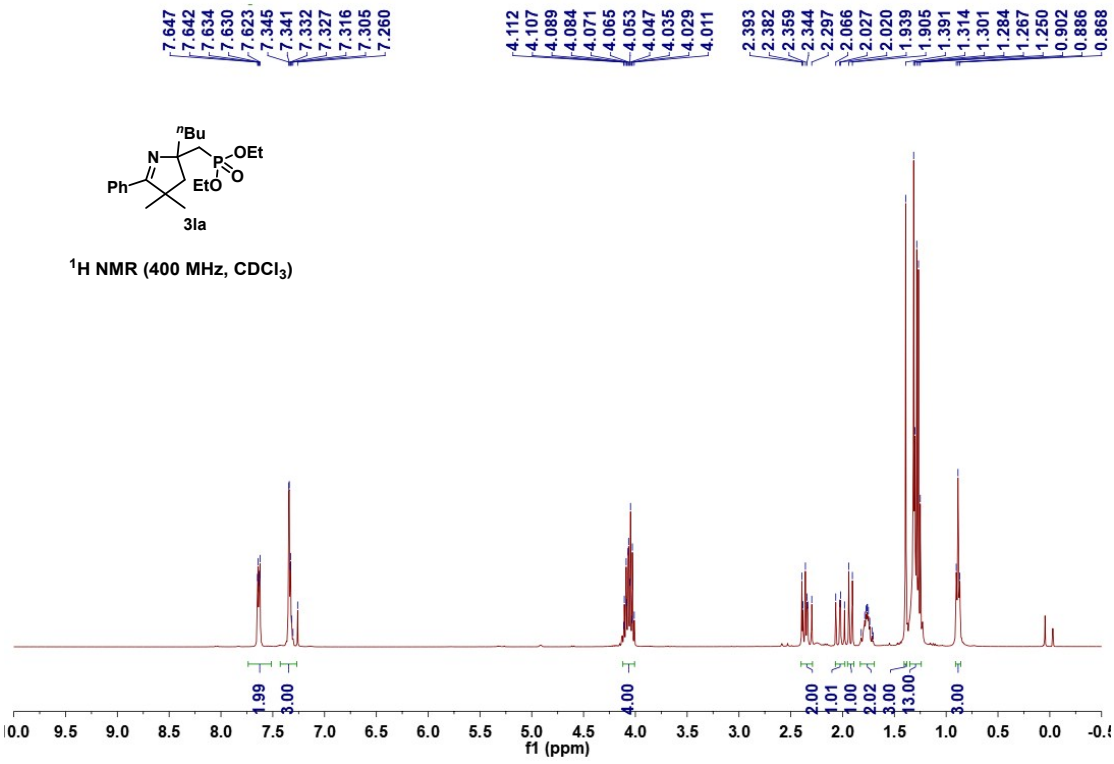
3ka

^{13}C NMR (100 MHz, $CDCl_3$)

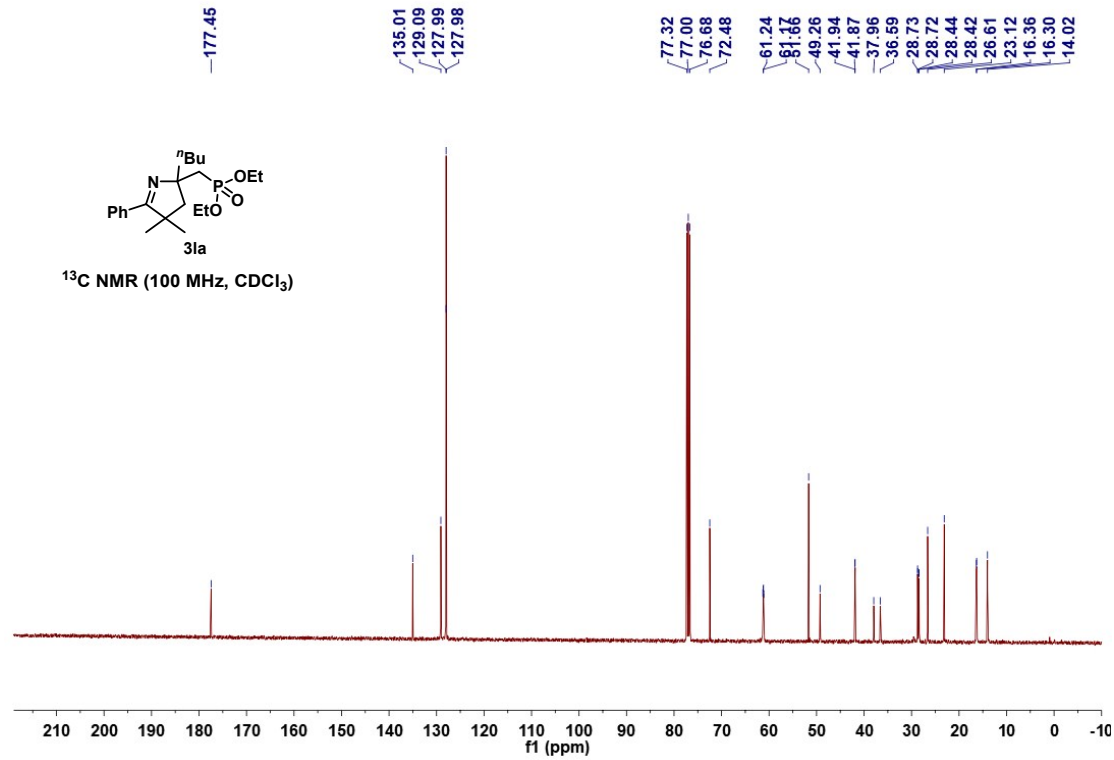


3ka

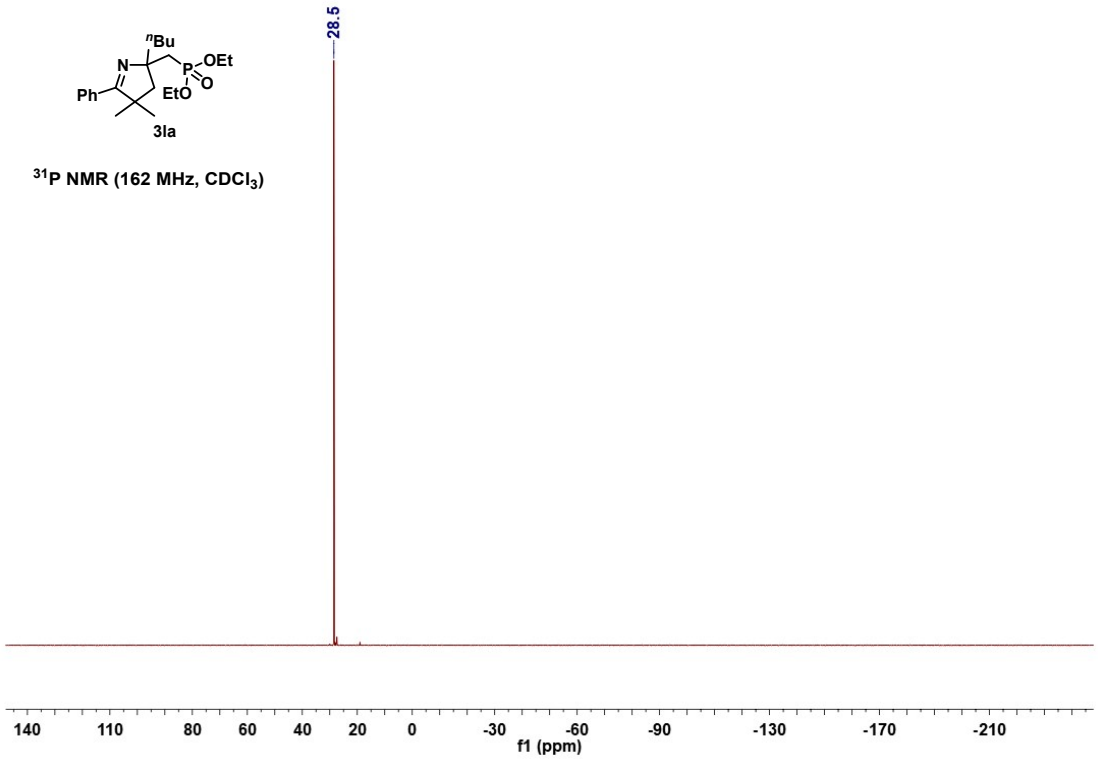
^{31}P NMR (162 MHz, $CDCl_3$)



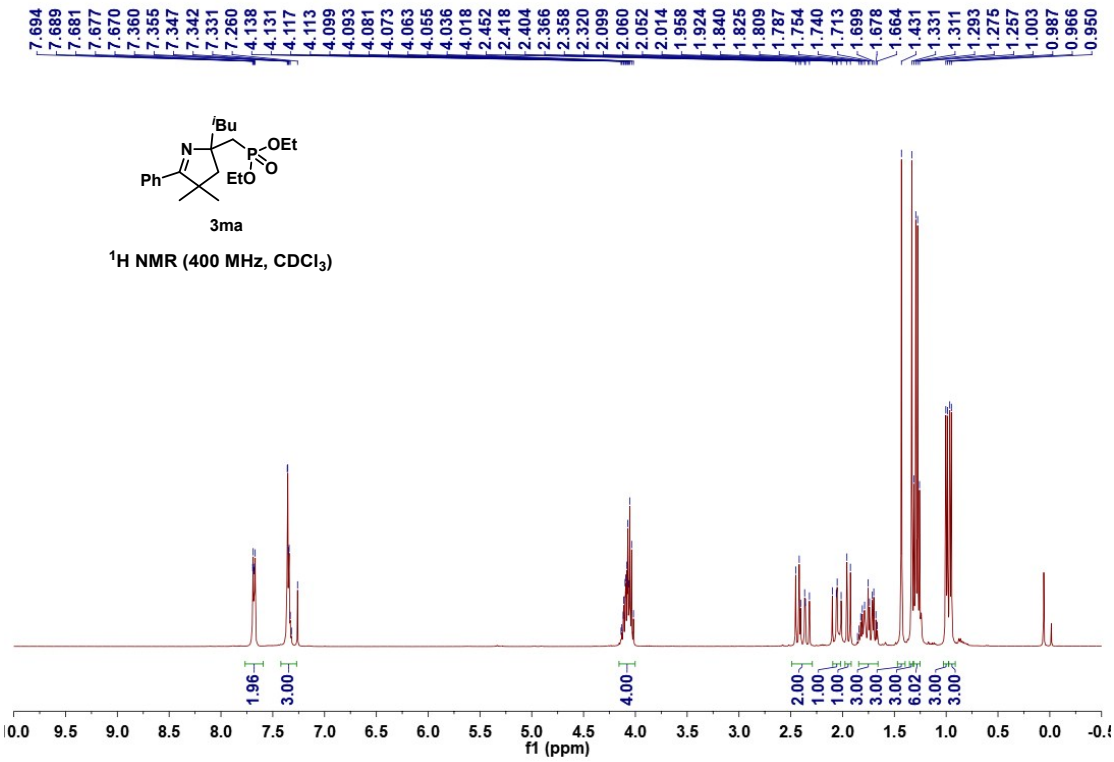
^{1}H NMR (400 MHz, $CDCl_3$)

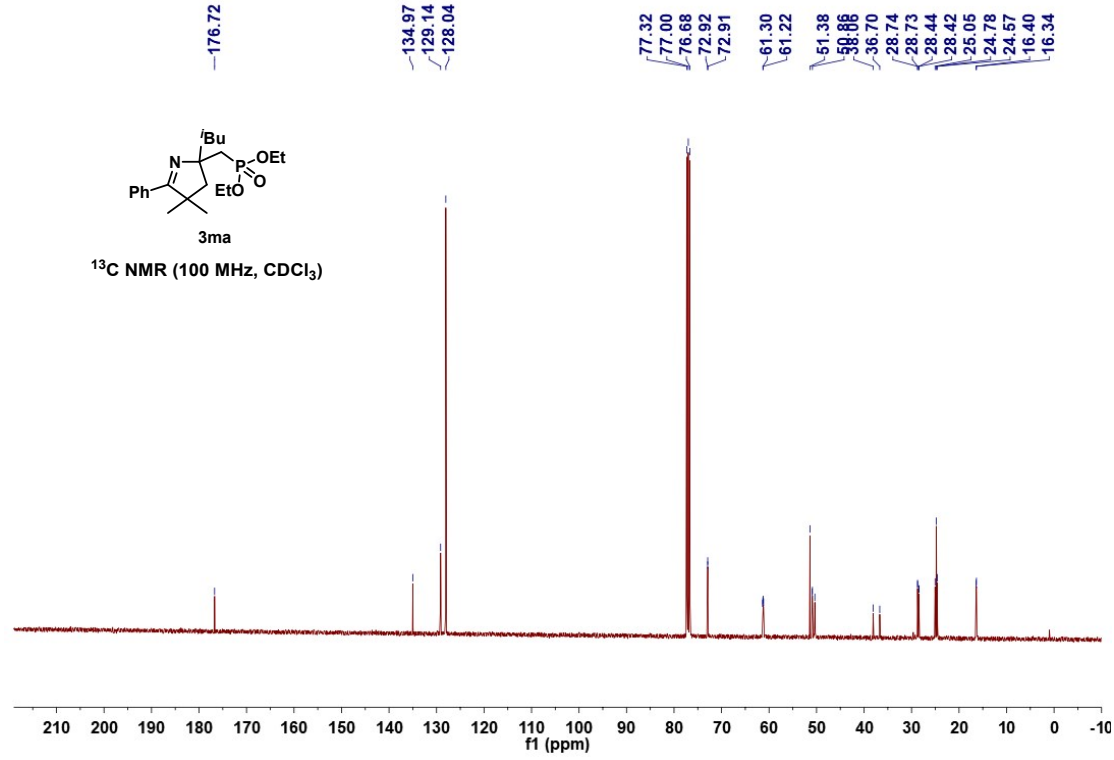


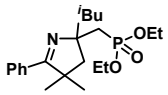
^{13}C NMR (100 MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)

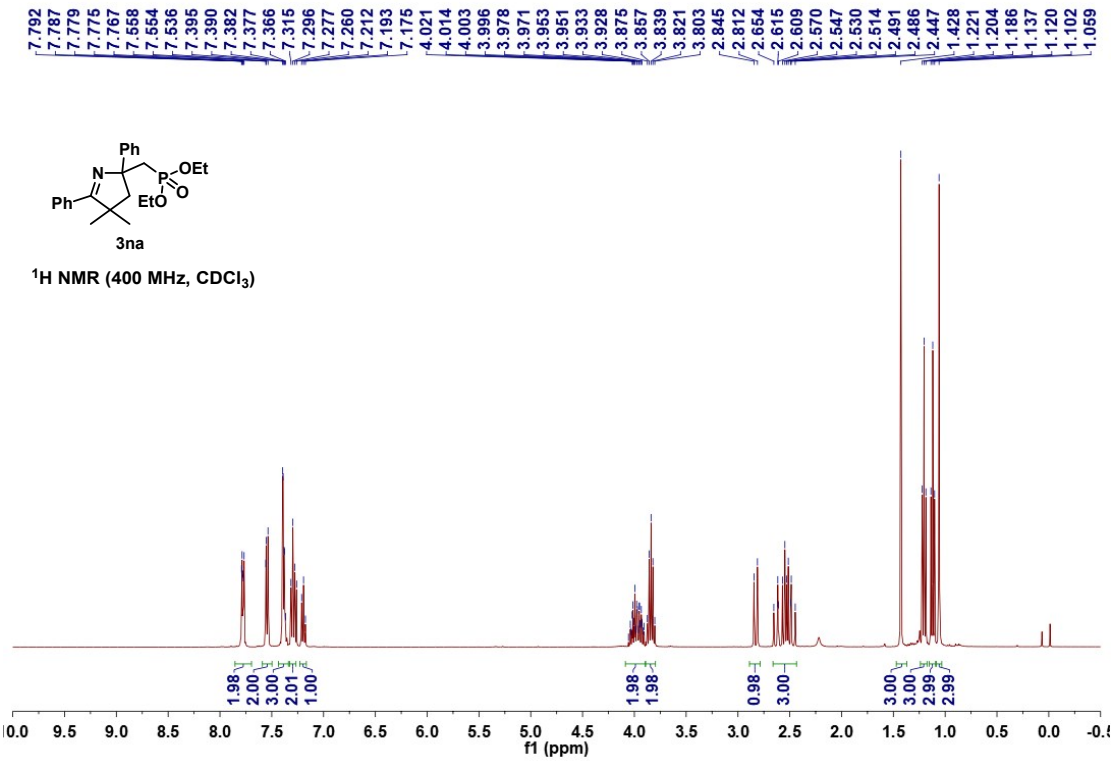

7.694
7.689
7.681
7.677
7.670
7.360
7.355
7.347
7.342
7.331
7.260
4.138
4.131
4.117
4.113
4.099
4.093
4.081
4.073
4.063
4.055
4.036
4.018
2.452
2.418
2.404
2.366
2.358
2.320
2.099
2.060
2.052
2.014
1.958
1.924
1.840
1.825
1.809
1.787
1.754
1.740
1.713
1.699
1.678
1.664
1.431
1.331
1.311
1.293
1.275
1.257
1.003
0.987
0.966
0.950
tBu
N
P
OEt
O
Ph
EtO
3ma
1H NMR (400 MHz, CDCl3)
1.96
3.00
4.00
2.00
1.00
1.00
3.00
3.00
3.00
6.02
3.00
3.00
f1 (ppm)

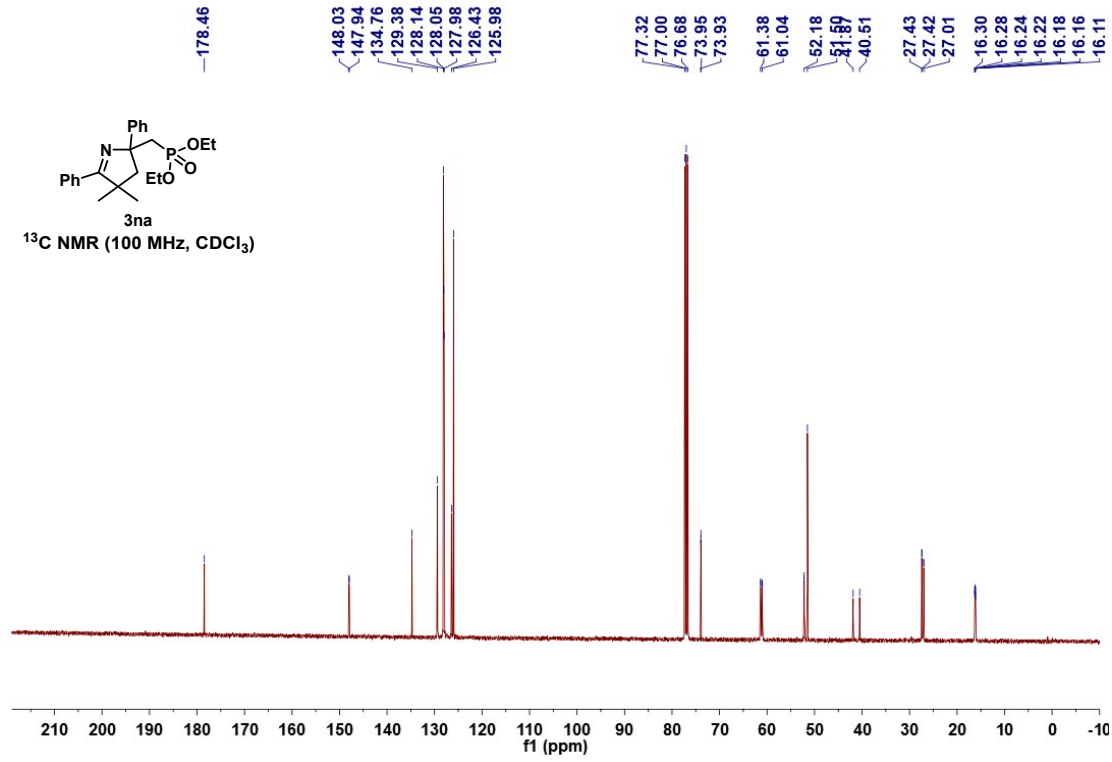

176.72
134.97
129.14
128.04
77.32
77.00
76.68
72.92
72.91
61.30
61.22
51.38
36.70
28.74
28.73
28.44
28.42
25.05
24.78
24.57
16.40
16.34
tBu
N
P
OEt
O
Ph
EtO
3ma
13C NMR (100 MHz, CDCl3)
f1 (ppm)

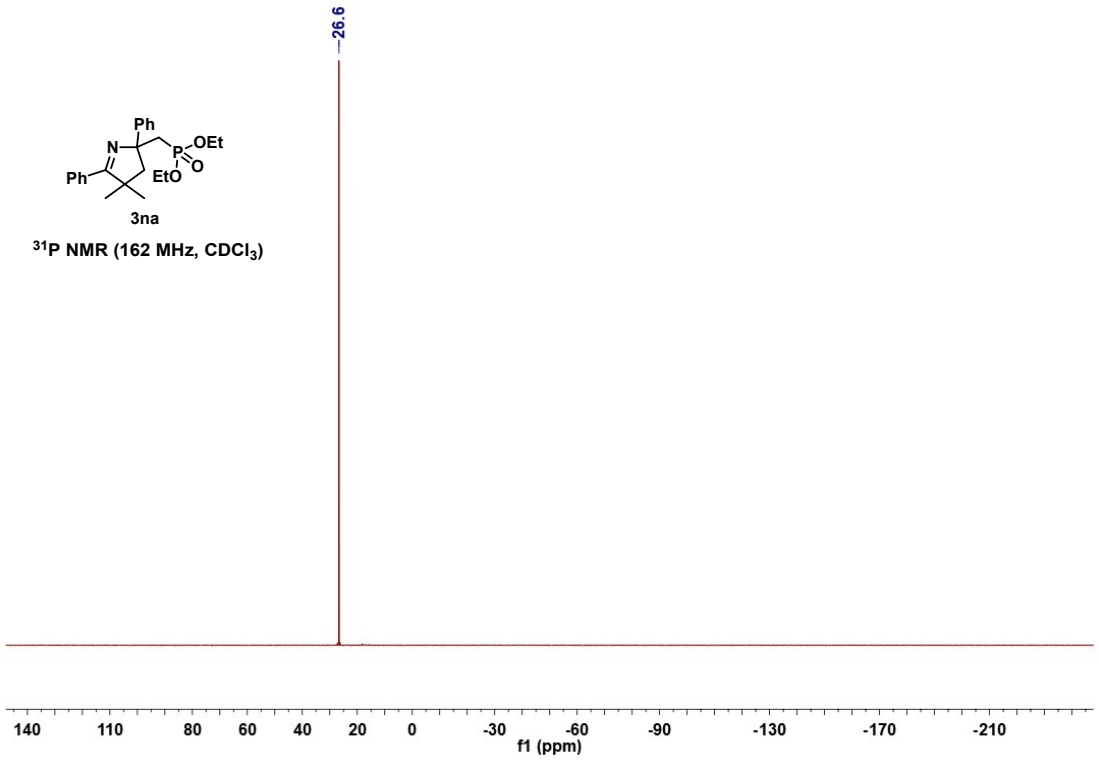


3ma

^{31}P NMR (162 MHz, $CDCl_3$)

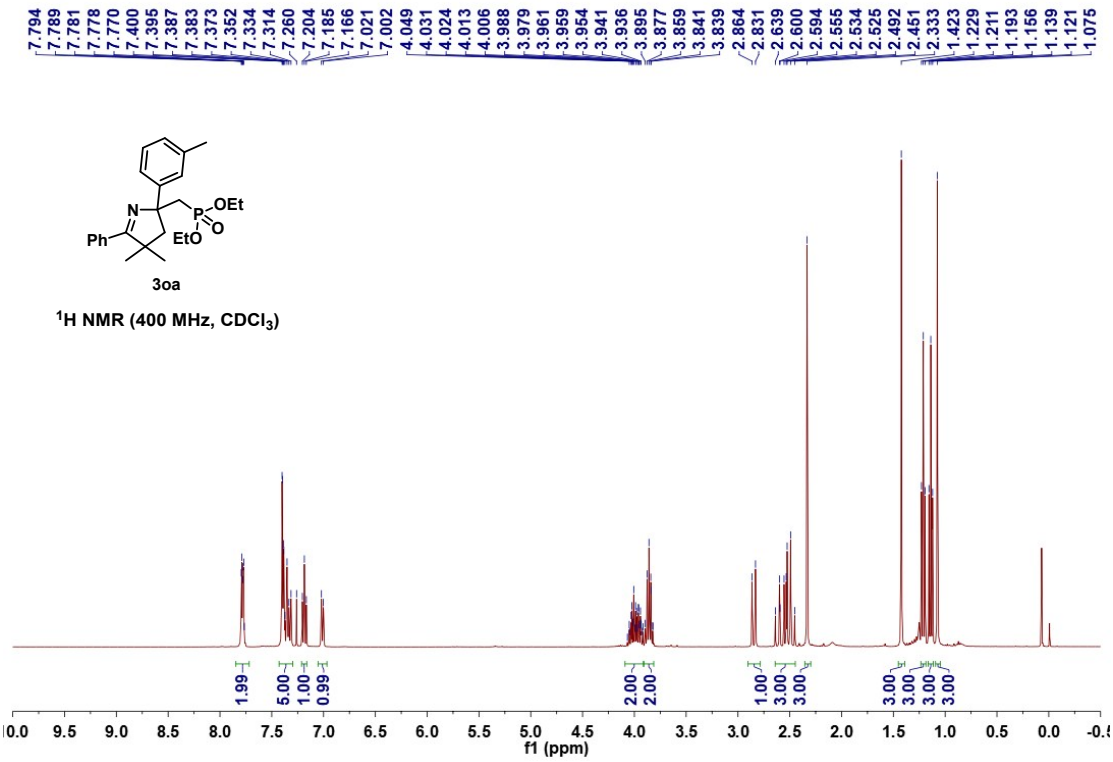

7.792
7.787
7.779
7.775
7.767
7.558
7.554
7.536
7.395
7.390
7.382
7.377
7.366
7.315
7.296
7.277
7.260
7.212
7.193
7.175
4.021
4.014
4.003
3.996
3.978
3.971
3.953
3.951
3.933
3.928
3.875
3.857
3.839
3.821
3.803
2.845
2.812
2.654
2.615
2.609
2.570
2.547
2.530
2.514
2.491
2.486
2.447
1.428
1.221
1.204
1.186
1.137
1.120
1.102
1.059
Ph
N
P
OEt
O
EtO
Ph
3na
1H NMR (400 MHz, CDCl3)
1.98
2.00
3.00
2.01
1.00
1.98
1.98
0.98
3.00
3.00
3.00
2.99
2.99
f1 (ppm)

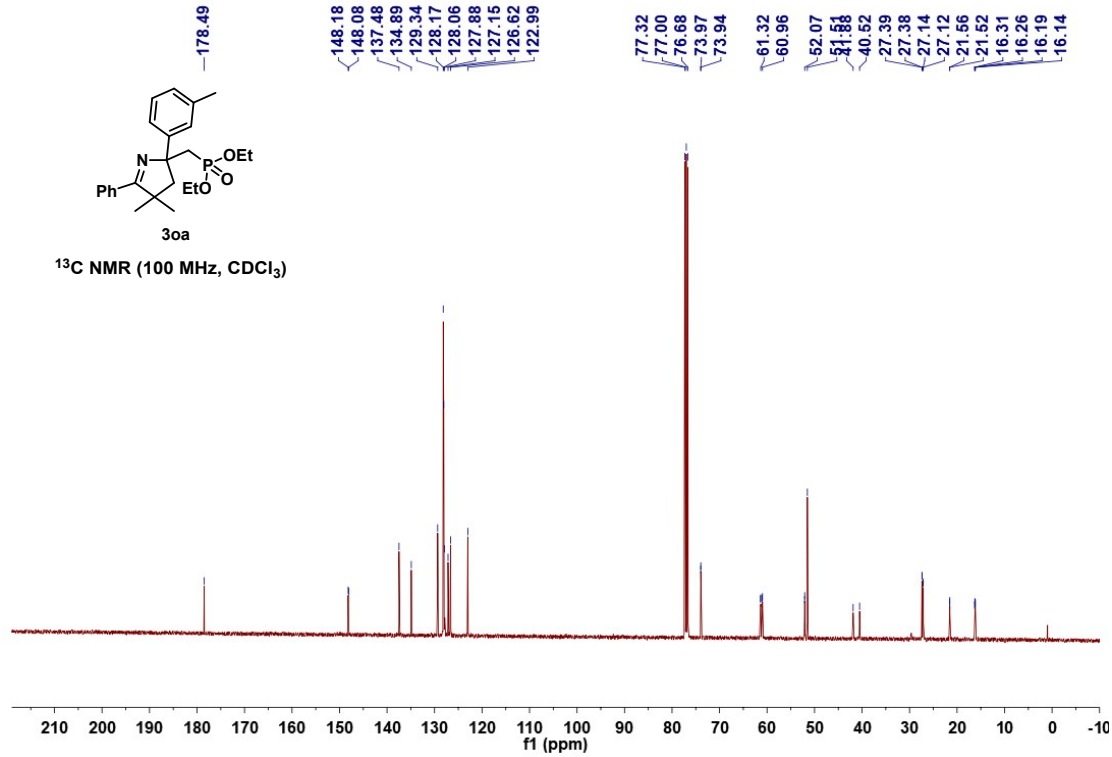

178.46
148.03
147.94
134.76
129.38
128.14
128.05
127.98
126.43
125.98
77.32
77.00
76.68
73.95
73.93
61.38
61.04
52.18
51.59
41.87
40.51
27.43
27.42
27.01
16.30
16.28
16.24
16.22
16.18
16.16
16.11
Ph
N
P
OEt
O
EtO
Ph
3na
13C NMR (100 MHz, CDCl3)
f1 (ppm)

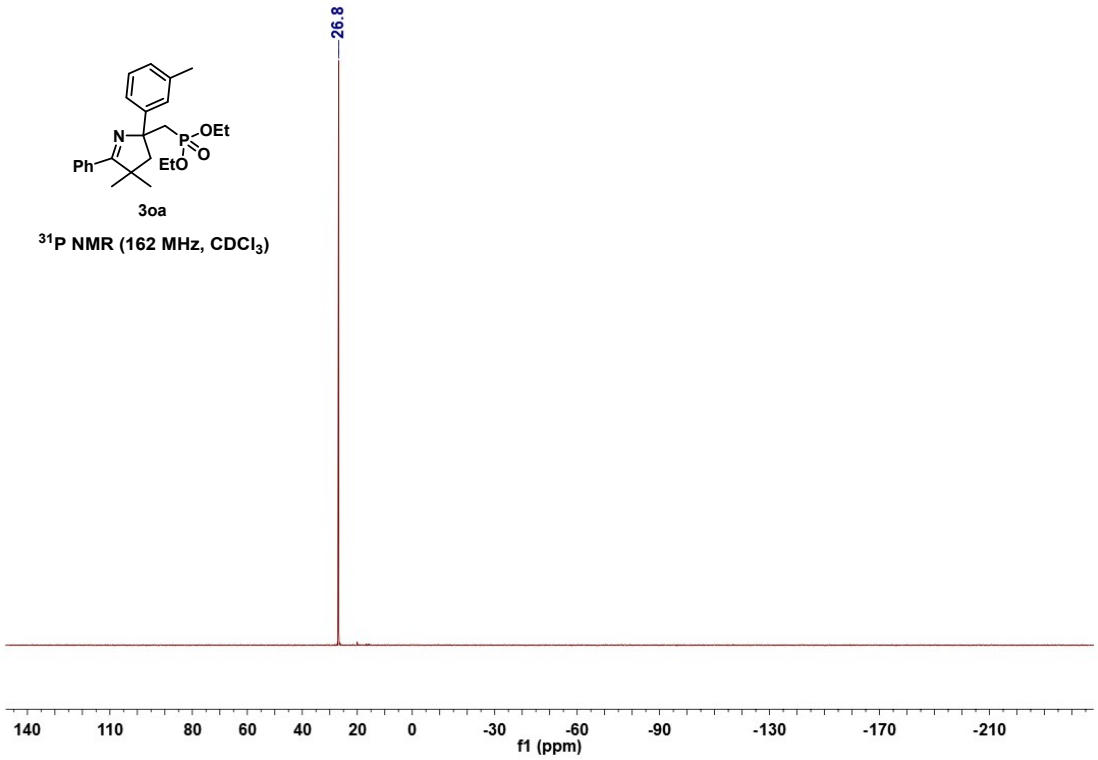


3na

^{31}P NMR (162 MHz, $CDCl_3$)

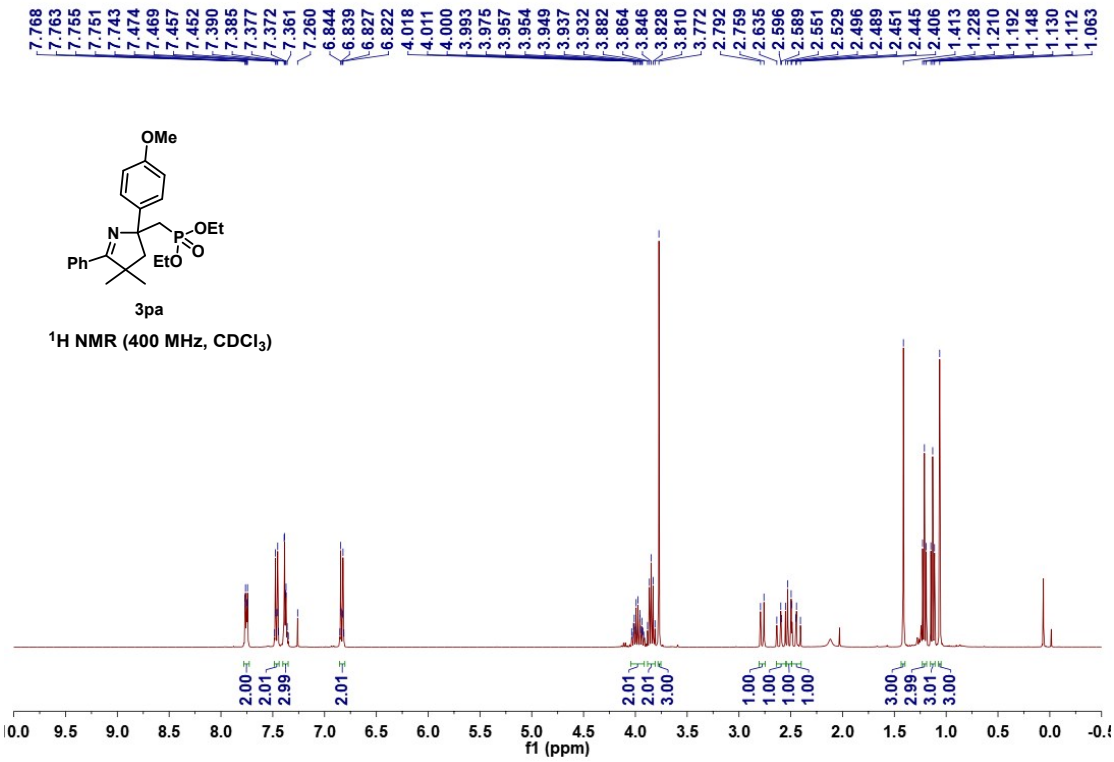

7.794
7.789
7.781
7.778
7.770
7.400
7.395
7.387
7.383
7.373
7.352
7.334
7.314
7.260
7.204
7.185
7.166
7.021
7.002
4.049
4.031
4.024
4.013
4.006
3.988
3.979
3.961
3.959
3.954
3.941
3.936
3.895
3.877
3.859
3.841
3.839
2.864
2.831
2.639
2.600
2.594
2.555
2.534
2.525
2.492
2.451
2.333
1.423
1.229
1.211
1.193
1.156
1.139
1.121
1.075
N
P
OEt
O
EtO
Ph
3oa
1H NMR (400 MHz, CDCl3)
1.99
5.00
1.00
0.99
2.00
2.00
1.00
3.00
3.00
3.00
3.00
3.00
3.00
f1 (ppm)

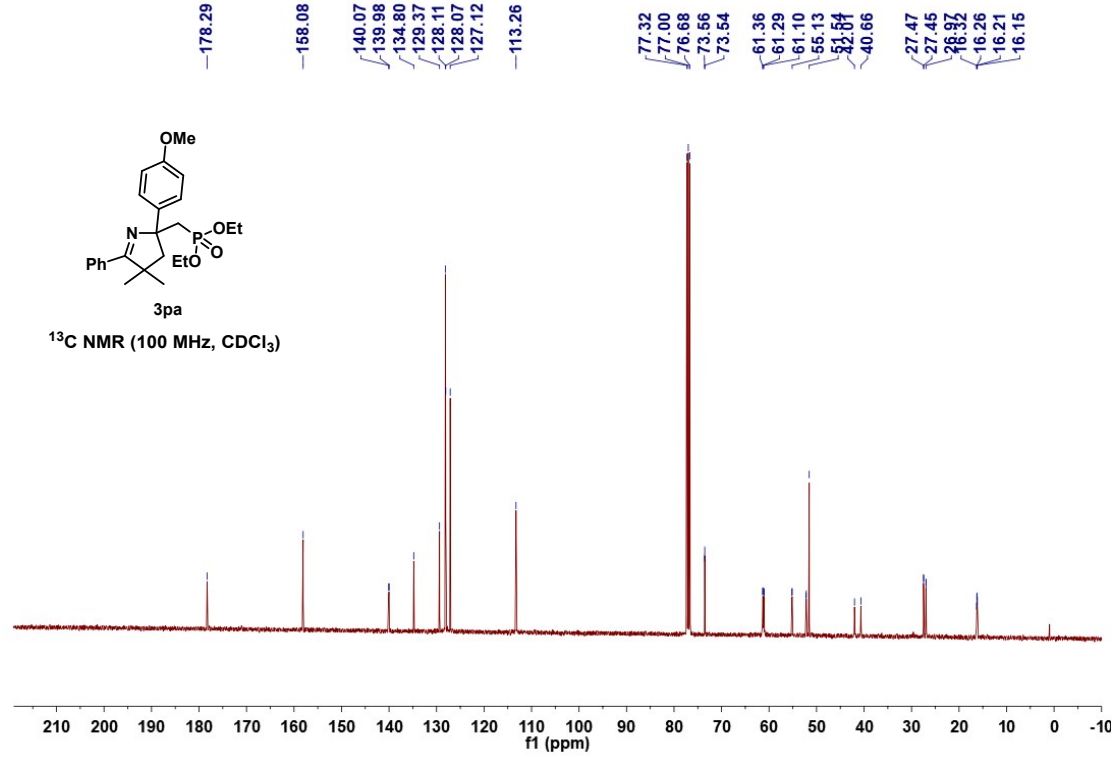

178.49
148.18
148.08
137.48
134.89
129.34
128.17
128.06
127.88
127.15
126.62
122.99
77.32
77.00
76.68
73.97
73.94
61.32
60.96
52.07
51.51
51.38
40.52
27.39
27.38
27.14
27.12
21.56
21.52
16.31
16.26
16.19
16.14
N
P
OEt
O
EtO
Ph
3oa
13C NMR (100 MHz, CDCl3)
f1 (ppm)

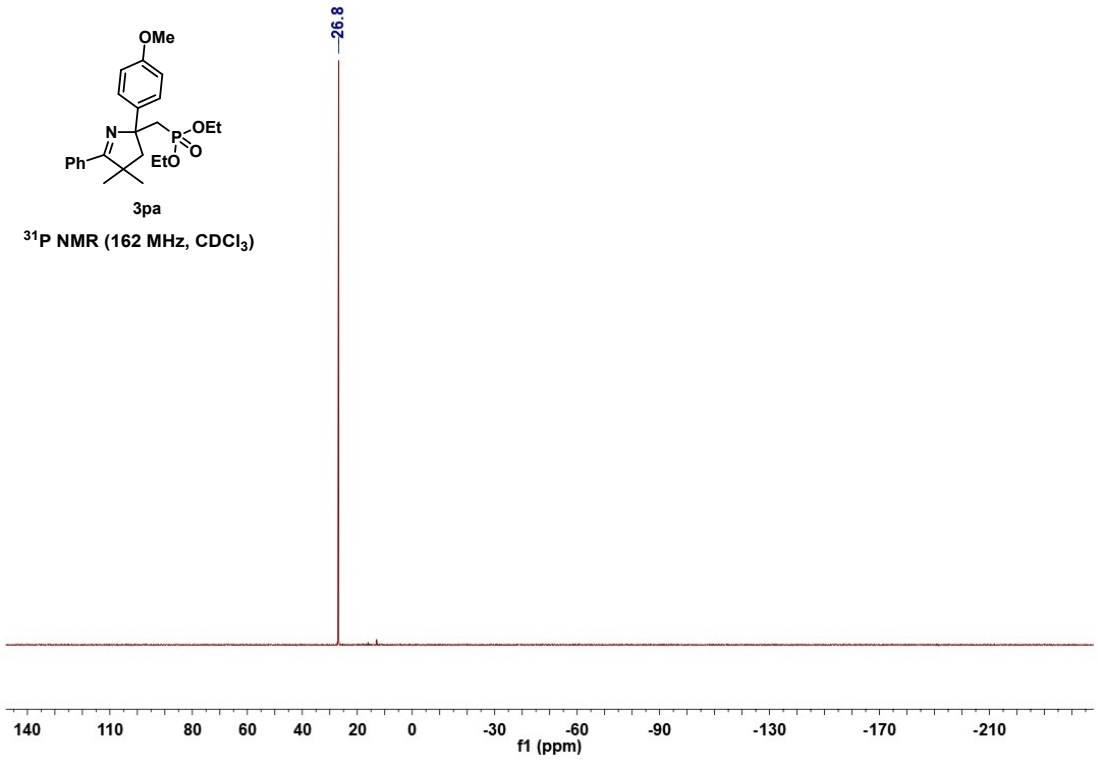


3oa

^{31}P NMR (162 MHz, $CDCl_3$)

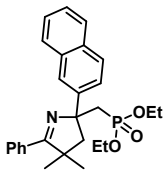

7.768
7.763
7.755
7.751
7.743
7.474
7.469
7.457
7.452
7.390
7.385
7.377
7.372
7.361
7.260
6.844
6.839
6.827
6.822
4.018
4.011
4.000
3.993
3.975
3.957
3.954
3.949
3.937
3.932
3.882
3.864
3.846
3.828
3.810
3.772
2.792
2.759
2.635
2.596
2.589
2.551
2.529
2.496
2.489
2.451
2.445
2.406
1.413
1.228
1.210
1.192
1.148
1.130
1.112
1.063
OMe
N
P
OEt
O
EtO
Ph
3pa
1H NMR (400 MHz, CDCl3)
2.00
2.01
2.99
2.01
2.01
2.01
3.00
1.00
1.00
1.00
1.00
3.00
2.99
3.01
3.00
f1 (ppm)


178.29
158.08
140.07
139.98
134.80
129.37
128.11
128.07
127.12
113.26
77.32
77.00
76.68
73.56
73.54
61.36
61.29
61.10
55.13
51.54
42.01
40.66
27.47
27.45
26.97
26.32
16.26
16.21
16.15
OMe
N
P
OEt
O
EtO
Ph
3pa
13C NMR (100 MHz, CDCl3)
f1 (ppm)



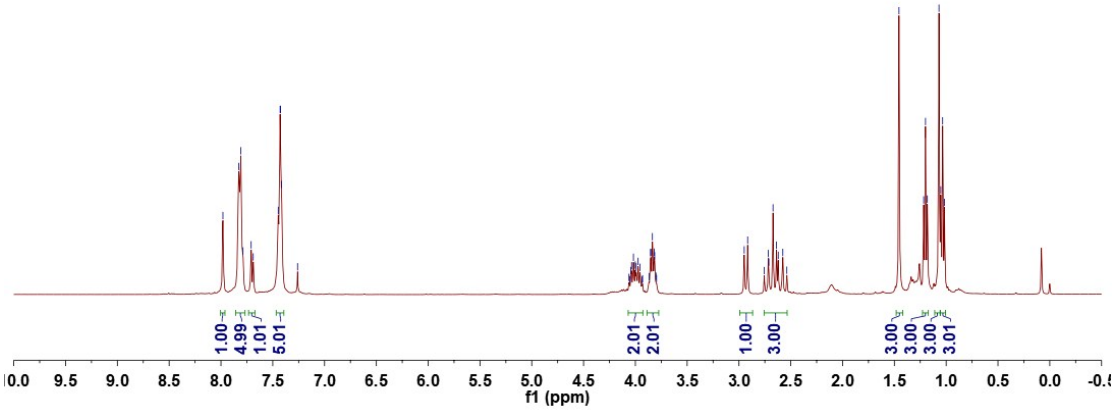
3pa

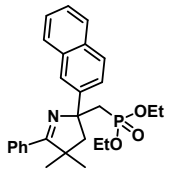
^{31}P NMR (162 MHz, $CDCl_3$)



3qa

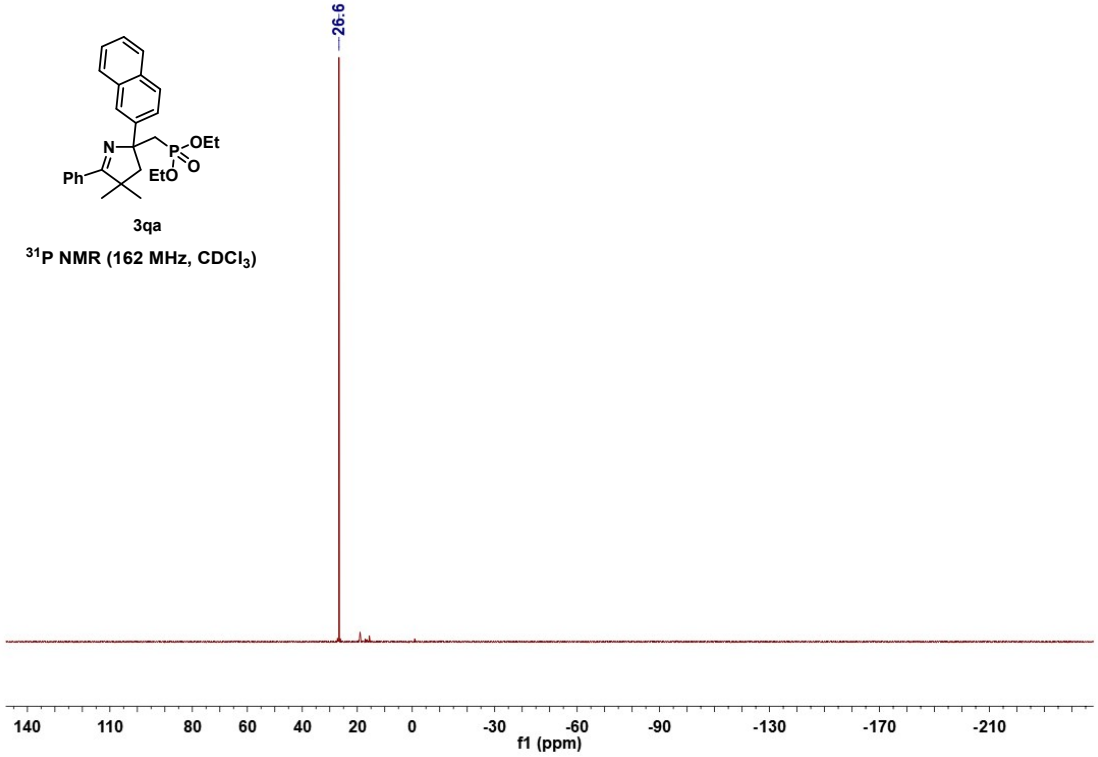
^{1}H NMR (400 MHz, $CDCl_3$)





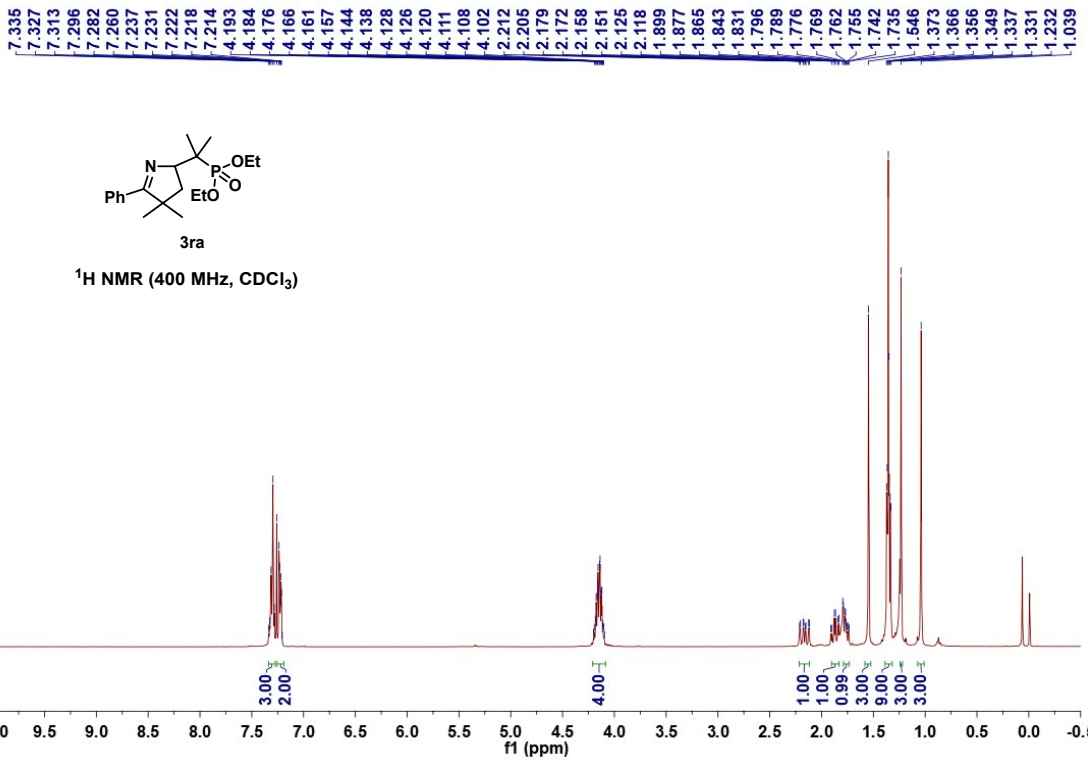
3qa

^{13}C NMR (100 MHz, $CDCl_3$)



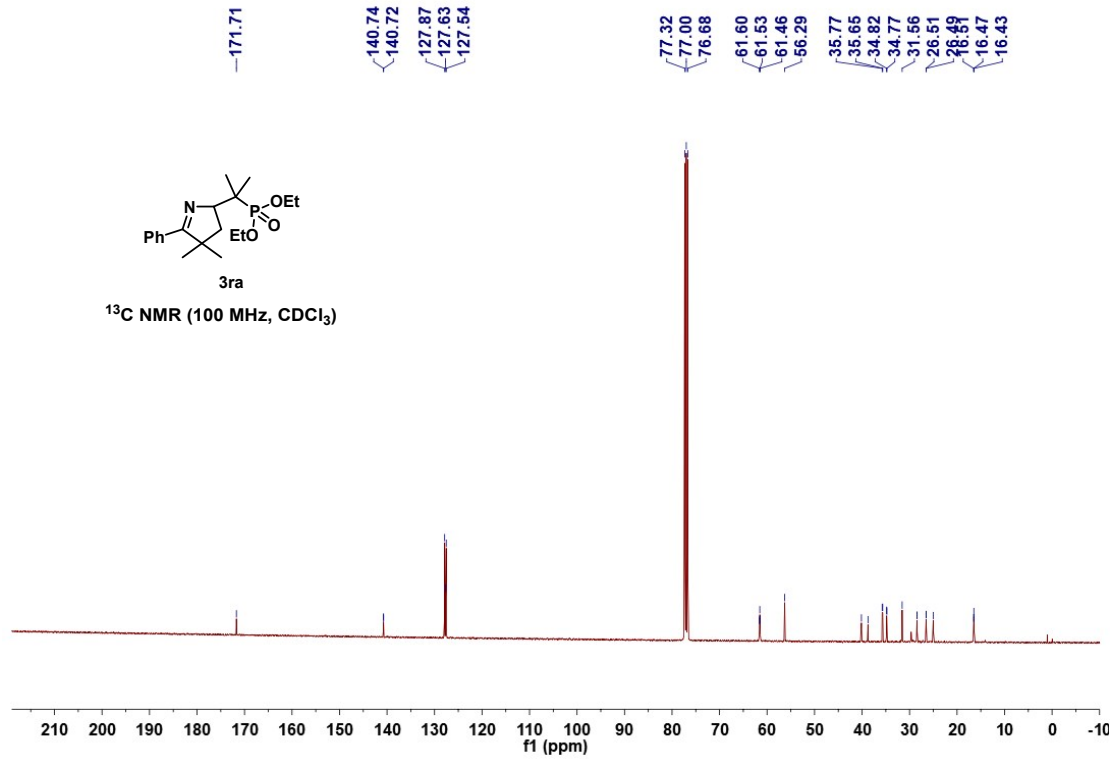
3qa

^{31}P NMR (162 MHz, $CDCl_3$)



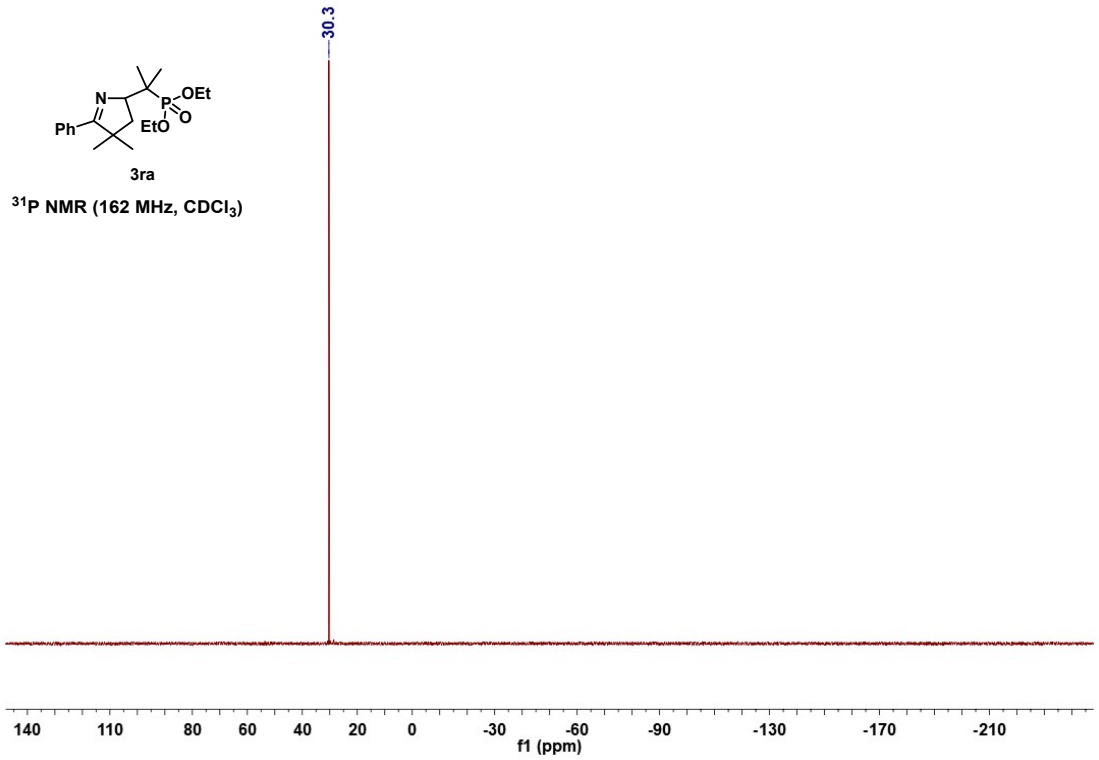
3ra

^{1}H NMR (400 MHz, $CDCl_3$)



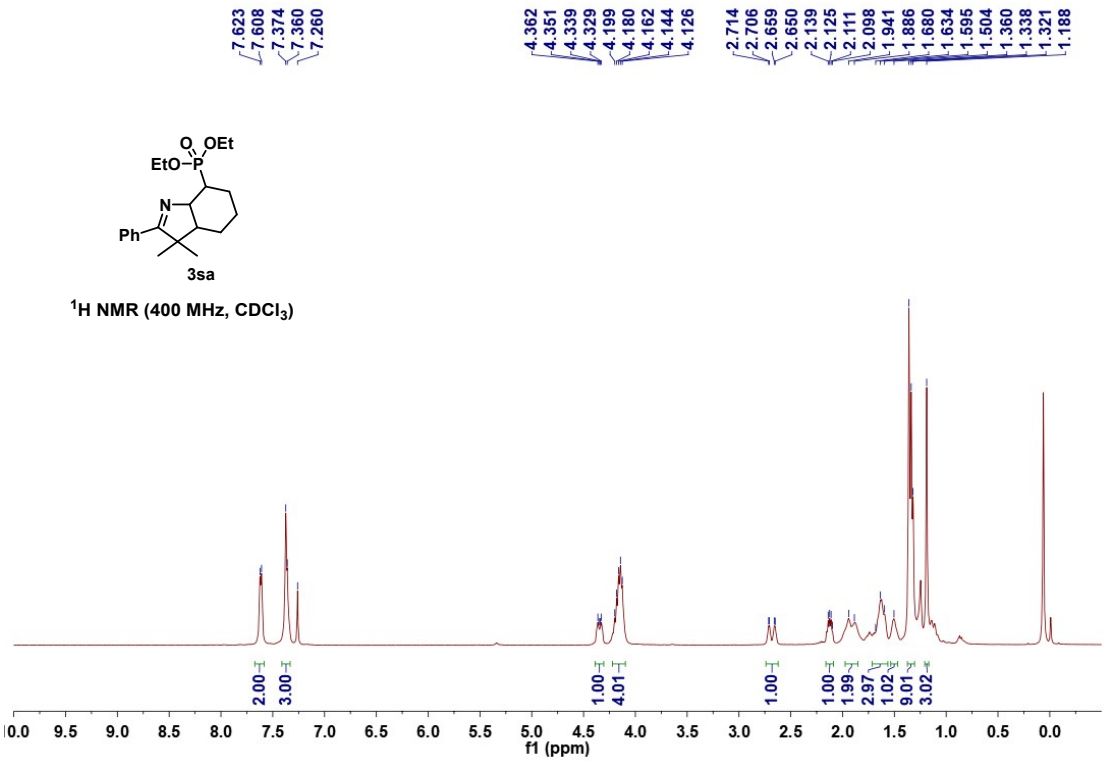
3ra

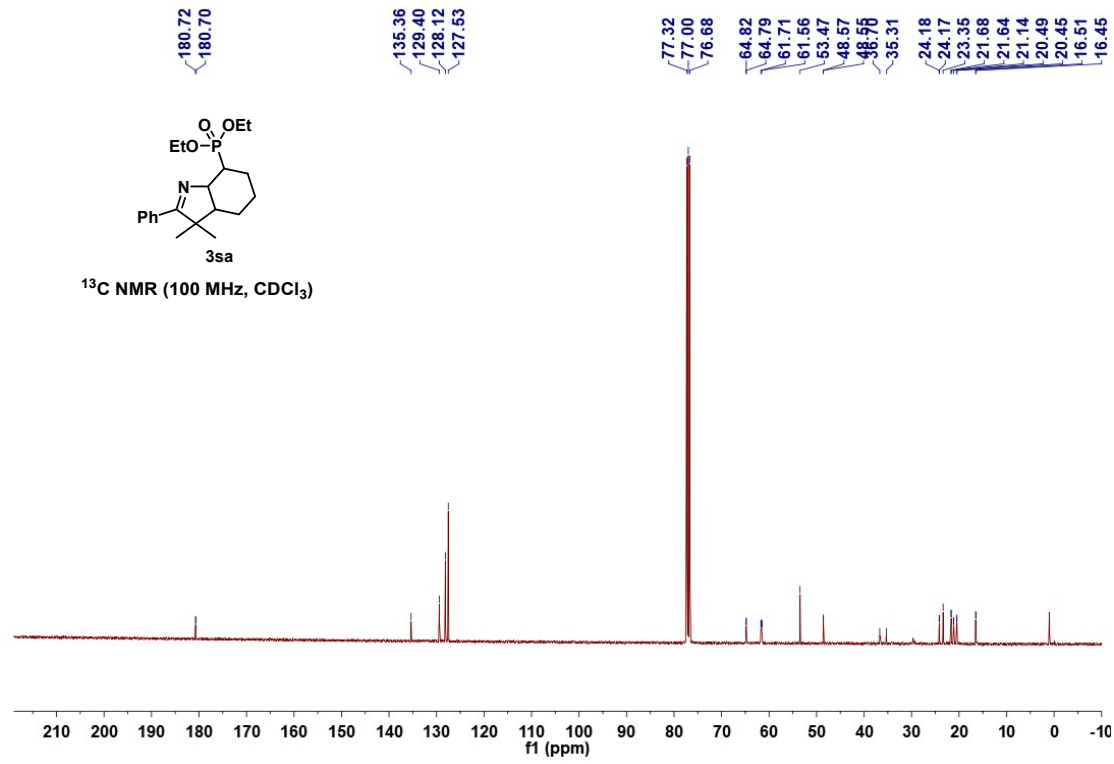
^{13}C NMR (100 MHz, $CDCl_3$)

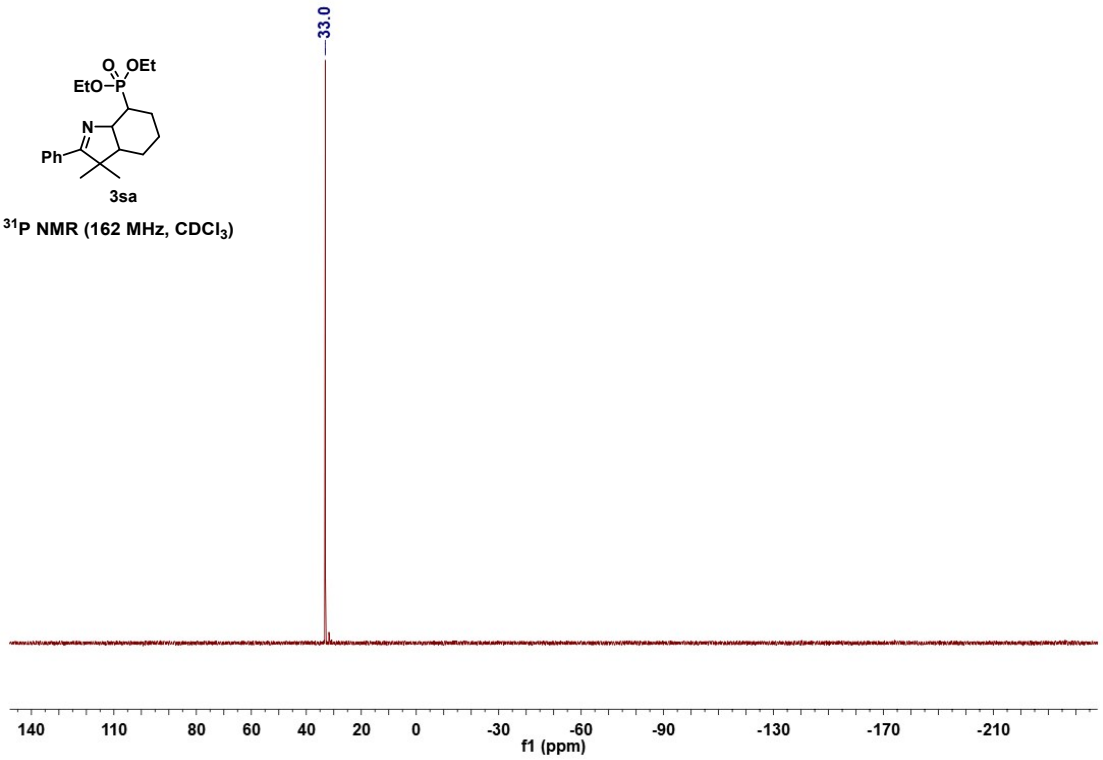


3ra

^{31}P NMR (162 MHz, $CDCl_3$)

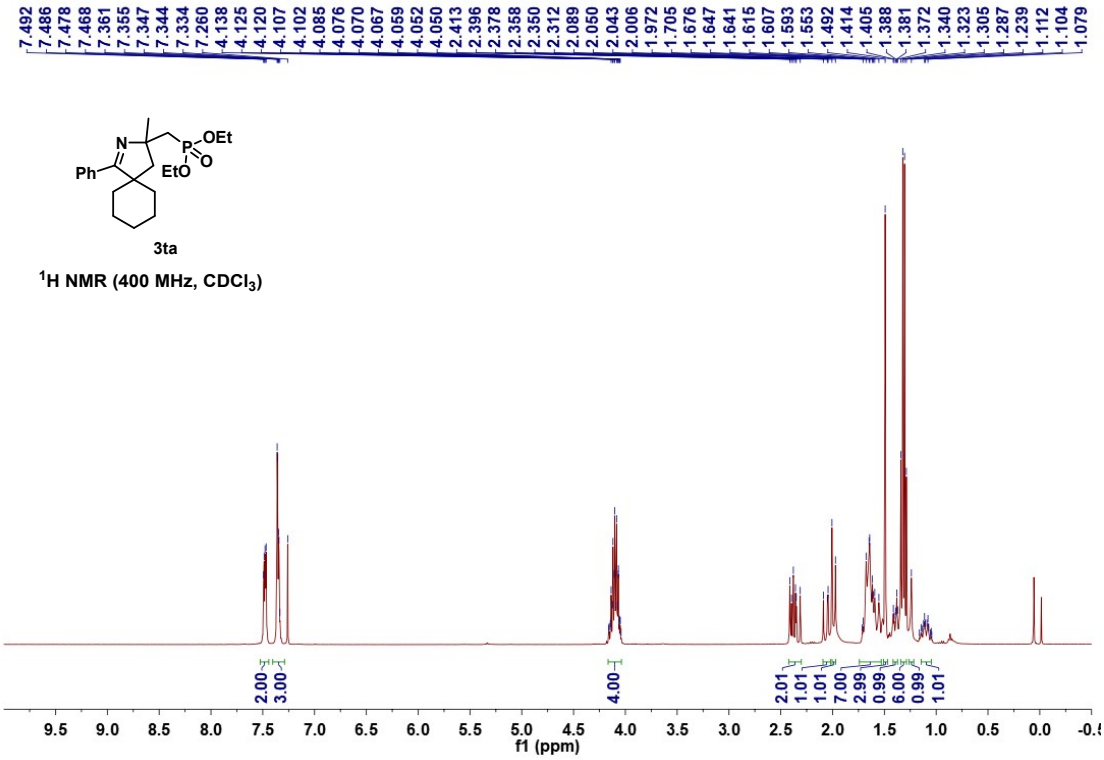

7.623
7.608
7.374
7.360
7.260
4.362
4.351
4.339
4.329
4.199
4.180
4.162
4.144
4.126
2.714
2.706
2.659
2.650
2.139
2.125
2.111
2.098
1.941
1.886
1.680
1.634
1.595
1.504
1.360
1.338
1.321
1.188
O
OEt
EtO
P
N
Ph
3sa
1H NMR (400 MHz, CDCl3)
2.00
3.00
1.00
4.01
1.00
1.00
1.99
2.97
1.02
9.01
3.02
f1 (ppm)


180.72
180.70
135.36
129.40
128.12
127.53
77.32
77.00
76.68
64.82
64.79
61.71
61.56
53.47
48.57
35.31
24.18
24.17
23.35
21.68
21.64
21.14
20.49
20.45
16.51
16.45
O
OEt
EtO
P
N
Ph
3sa
13C NMR (100 MHz, CDCl3)
f1 (ppm)



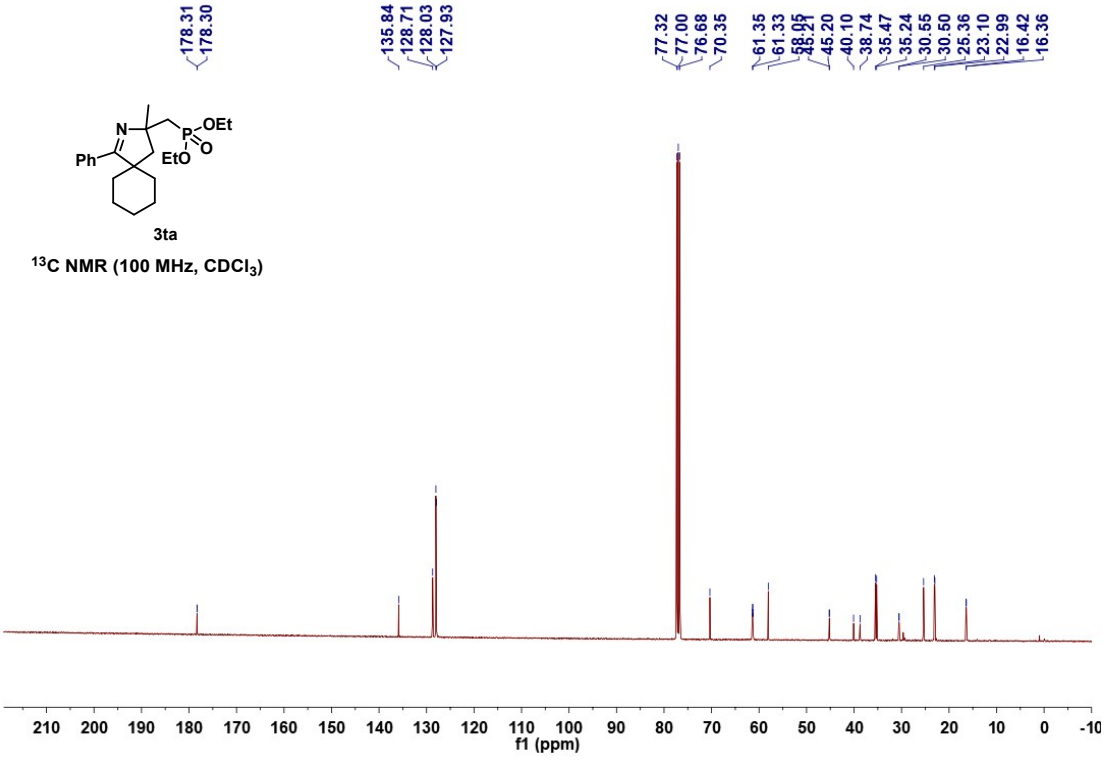
3sa

^{31}P NMR (162 MHz, $CDCl_3$)



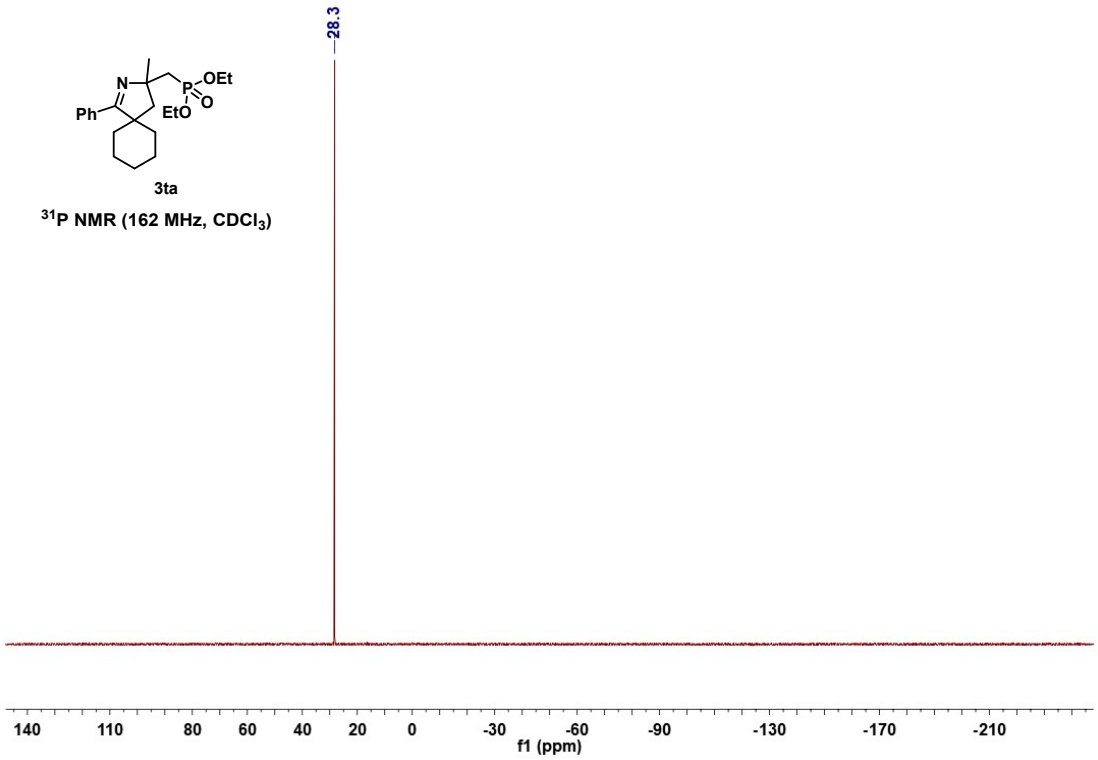
3ta

^{1}H NMR (400 MHz, $CDCl_3$)



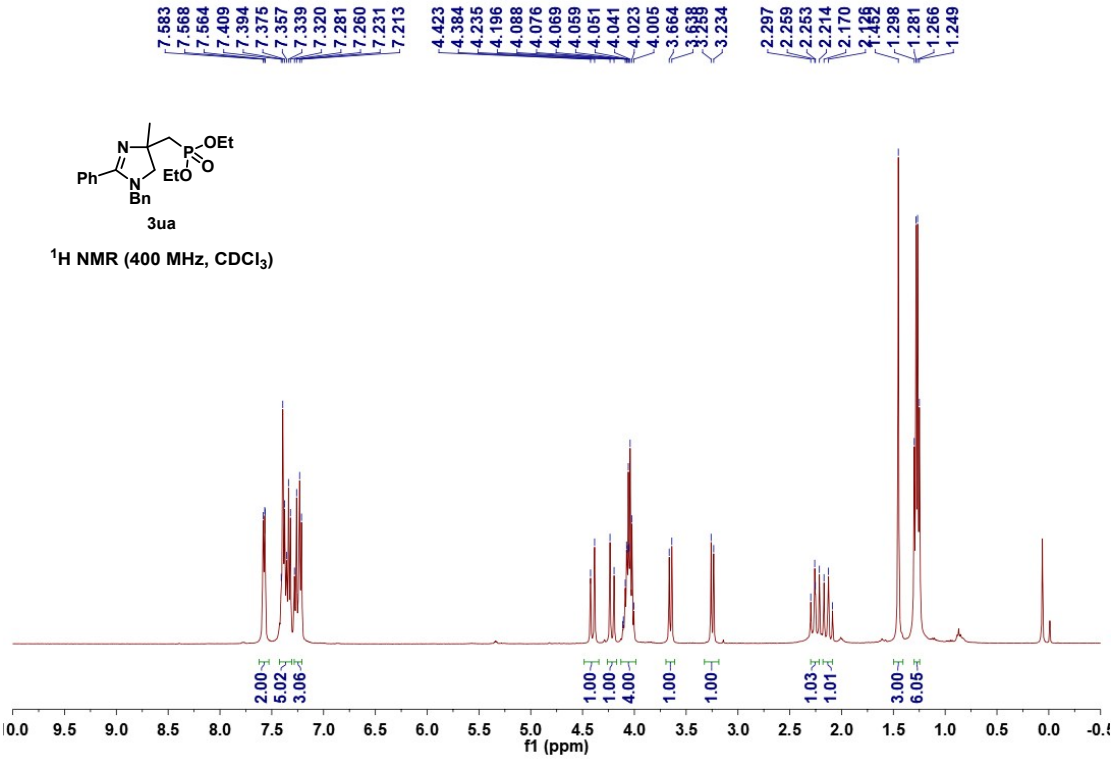
3ta

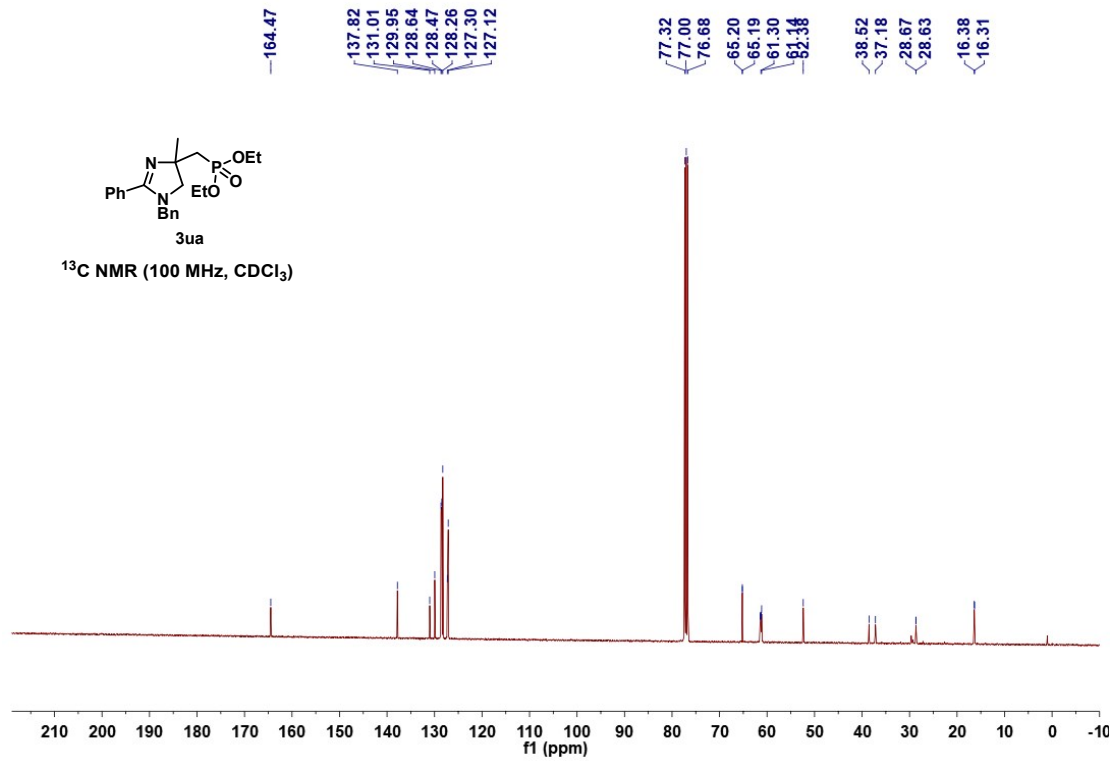
^{13}C NMR (100 MHz, $CDCl_3$)

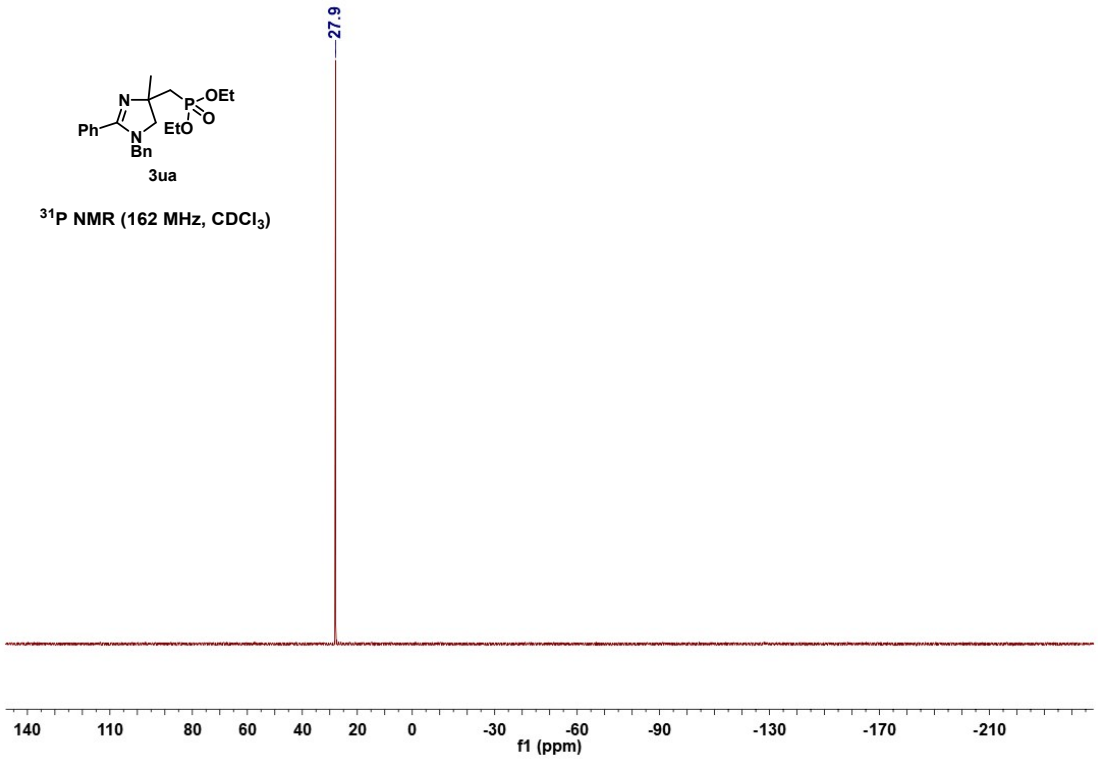


3ta

^{31}P NMR (162 MHz, $CDCl_3$)

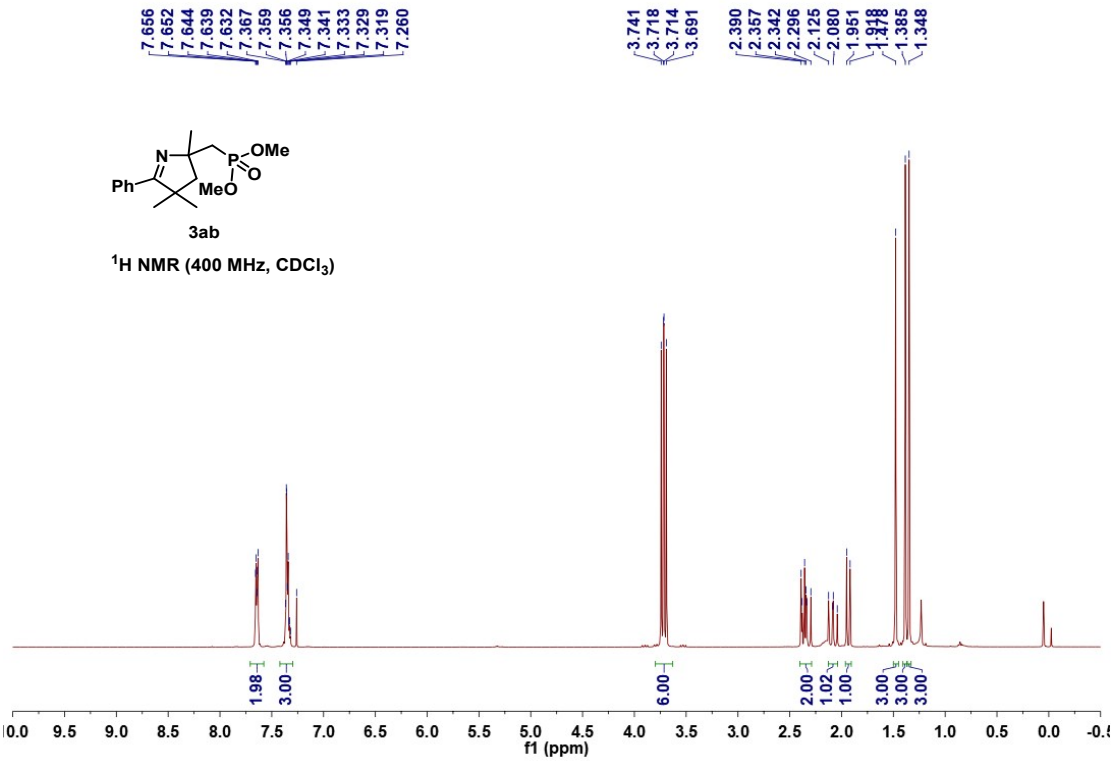

7.583
7.568
7.564
7.409
7.394
7.375
7.357
7.339
7.320
7.281
7.260
7.231
7.213
4.423
4.384
4.235
4.196
4.088
4.076
4.069
4.059
4.051
4.041
4.023
4.005
3.664
3.638
3.259
3.234
2.297
2.259
2.253
2.214
2.170
2.126
1.452
1.298
1.281
1.266
1.249
N
P
OEt
O
EtO
Ph
N
Bn
3ua
1H NMR (400 MHz, CDCl3)
2.00
5.02
3.06
1.00
1.00
4.00
1.00
1.00
1.03
1.01
3.00
6.05
f1 (ppm)


164.47
137.82
131.01
129.95
128.64
128.47
128.26
127.30
127.12
77.32
77.00
76.68
65.20
65.19
61.30
61.14
52.38
38.52
37.18
28.67
28.63
16.38
16.31
N
P
OEt
O
EtO
Ph
N
Bn
3ua
13C NMR (100 MHz, CDCl3)
f1 (ppm)



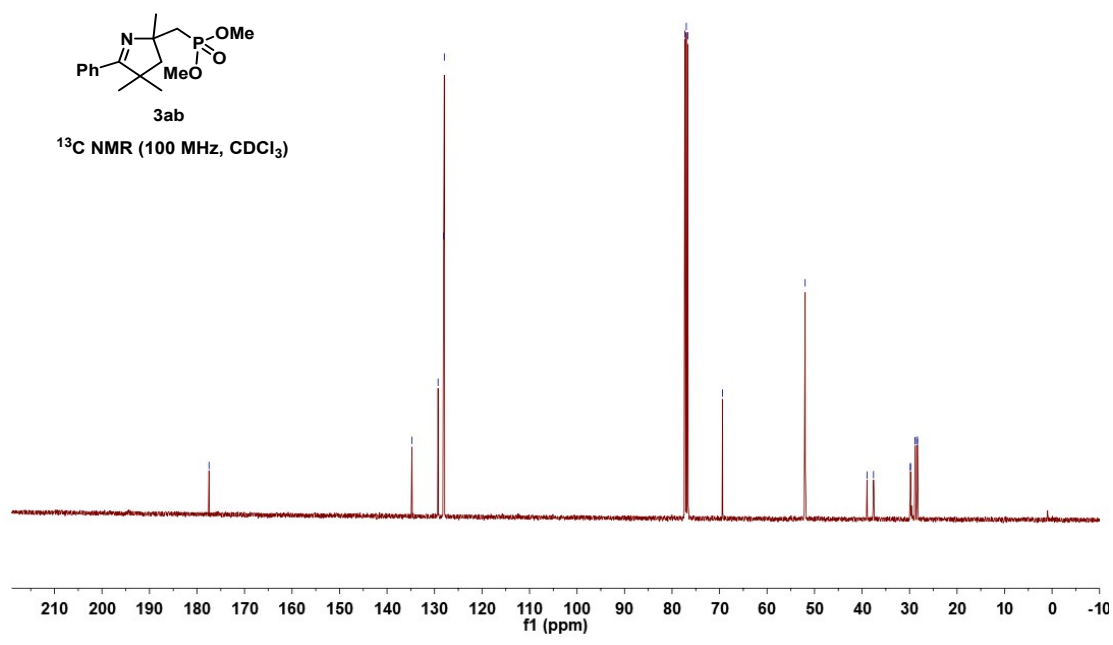
3ua

^{31}P NMR (162 MHz, $CDCl_3$)



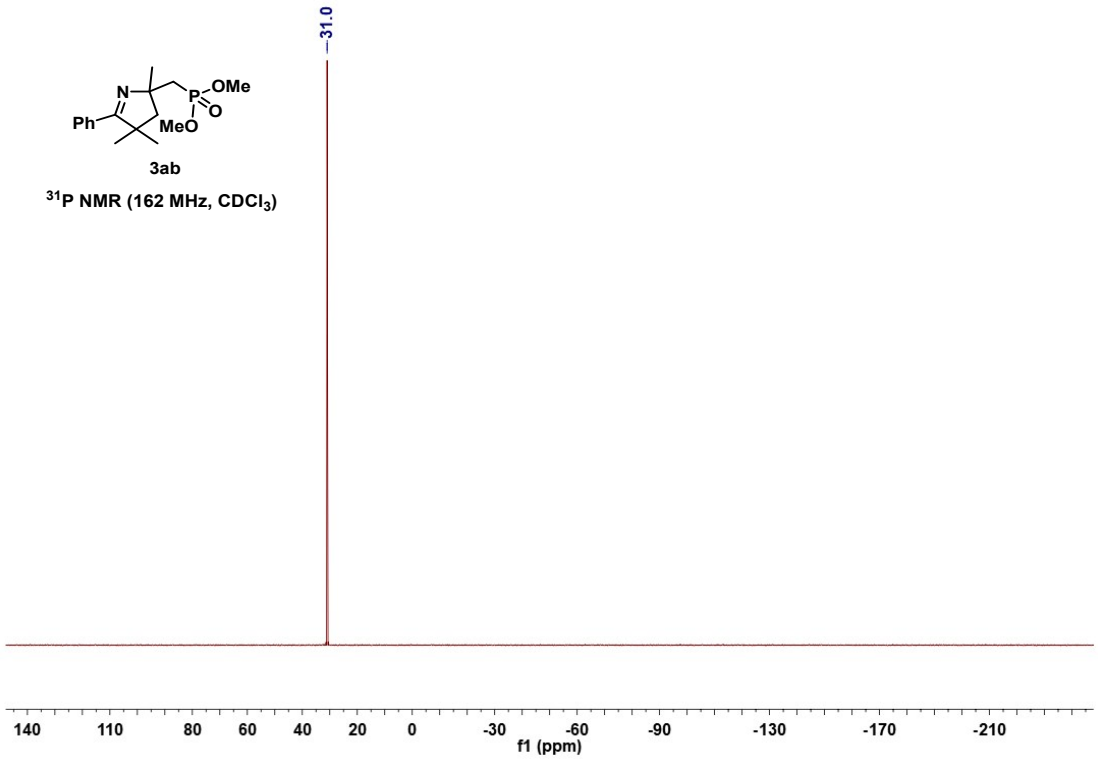
3ab

^{1}H NMR (400 MHz, $CDCl_3$)



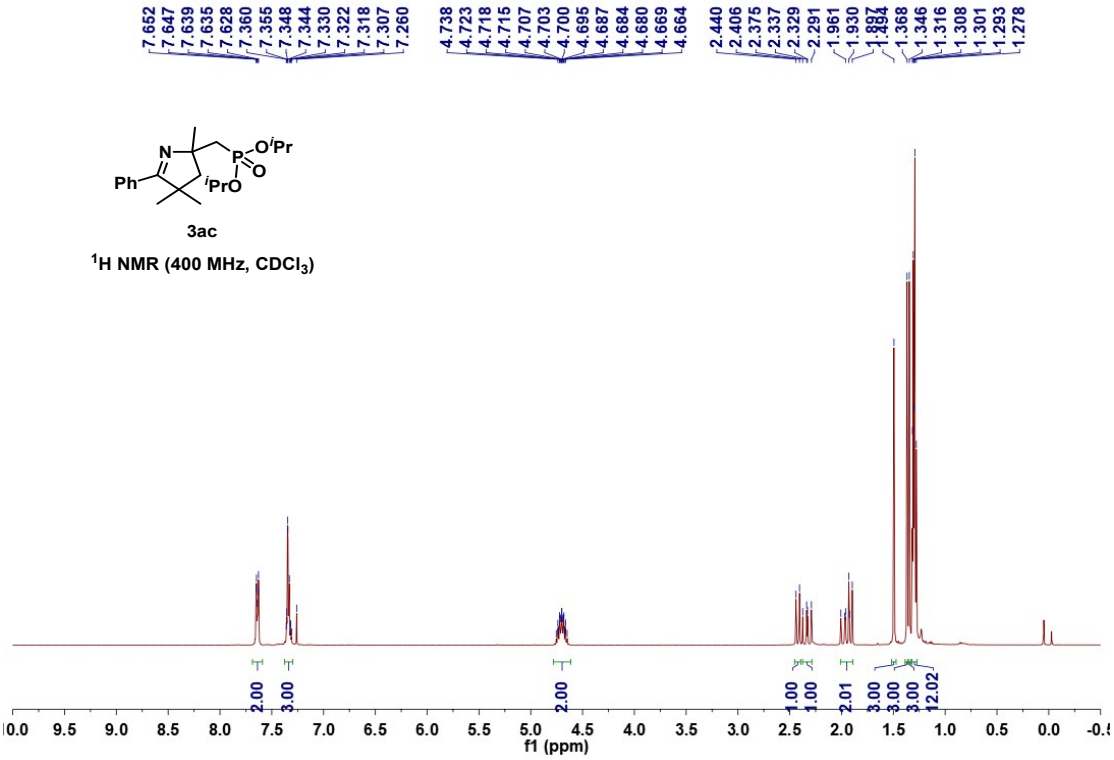
3ab

^{13}C NMR (100 MHz, $CDCl_3$)



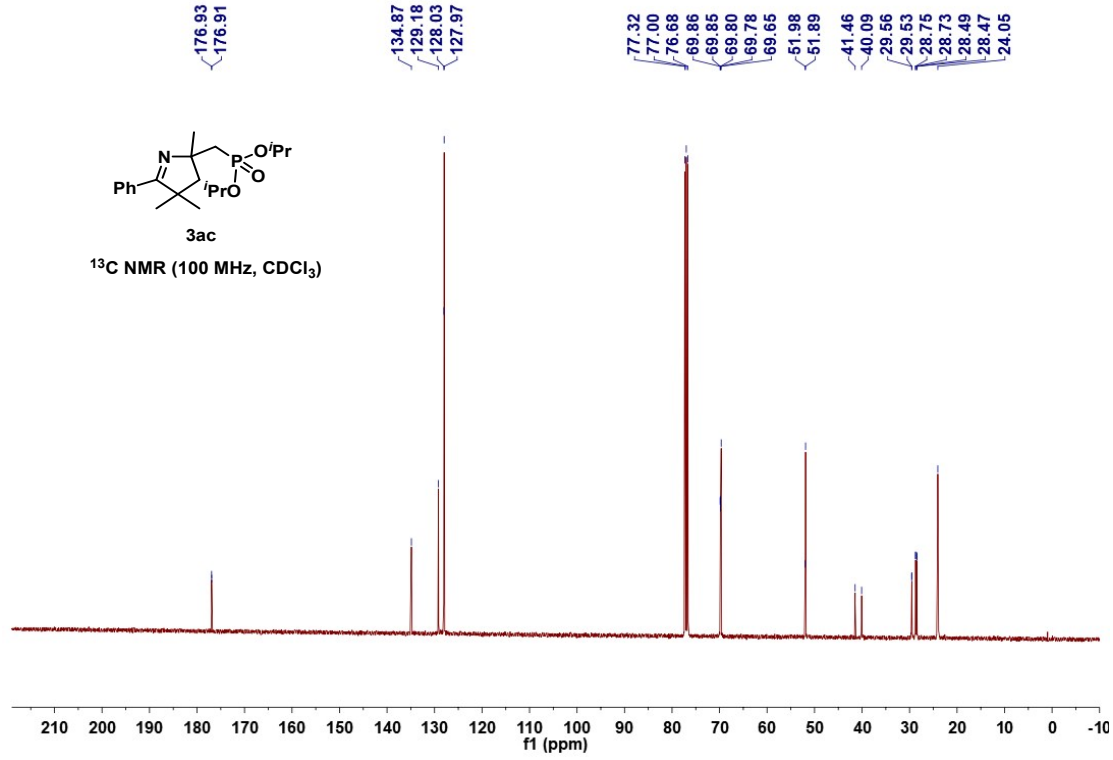
3ab

^{31}P NMR (162 MHz, $CDCl_3$)



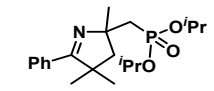
3ac

^{1}H NMR (400 MHz, $CDCl_3$)



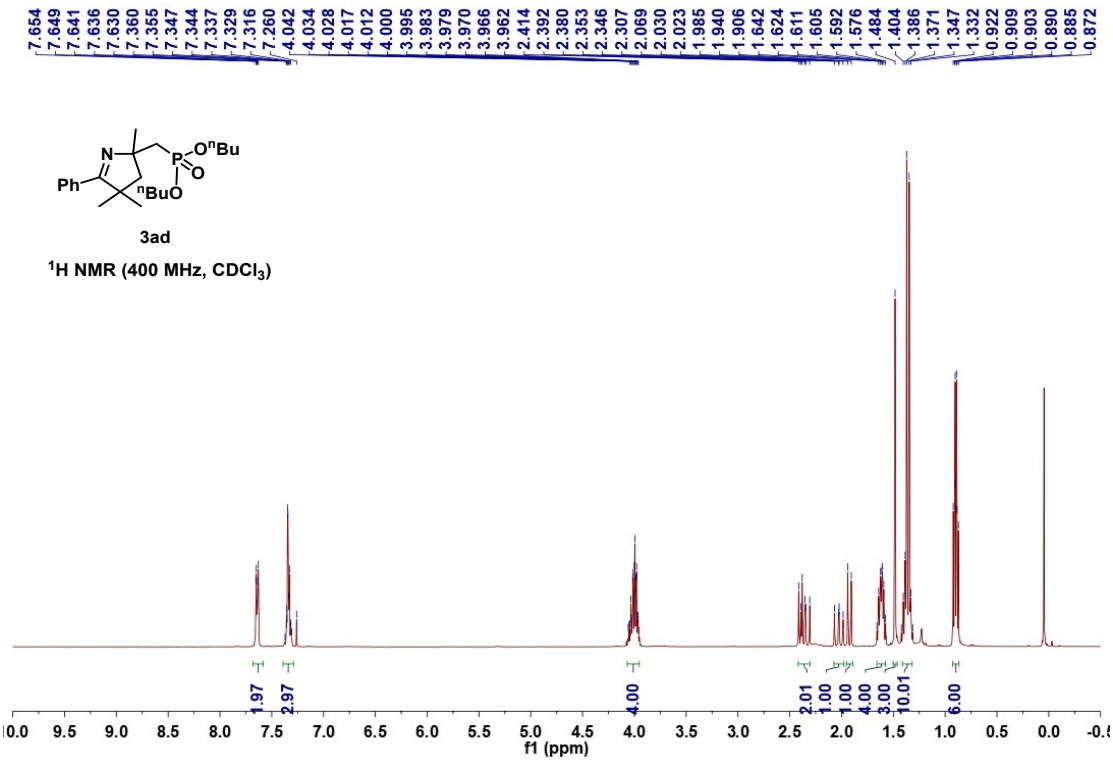
3ac

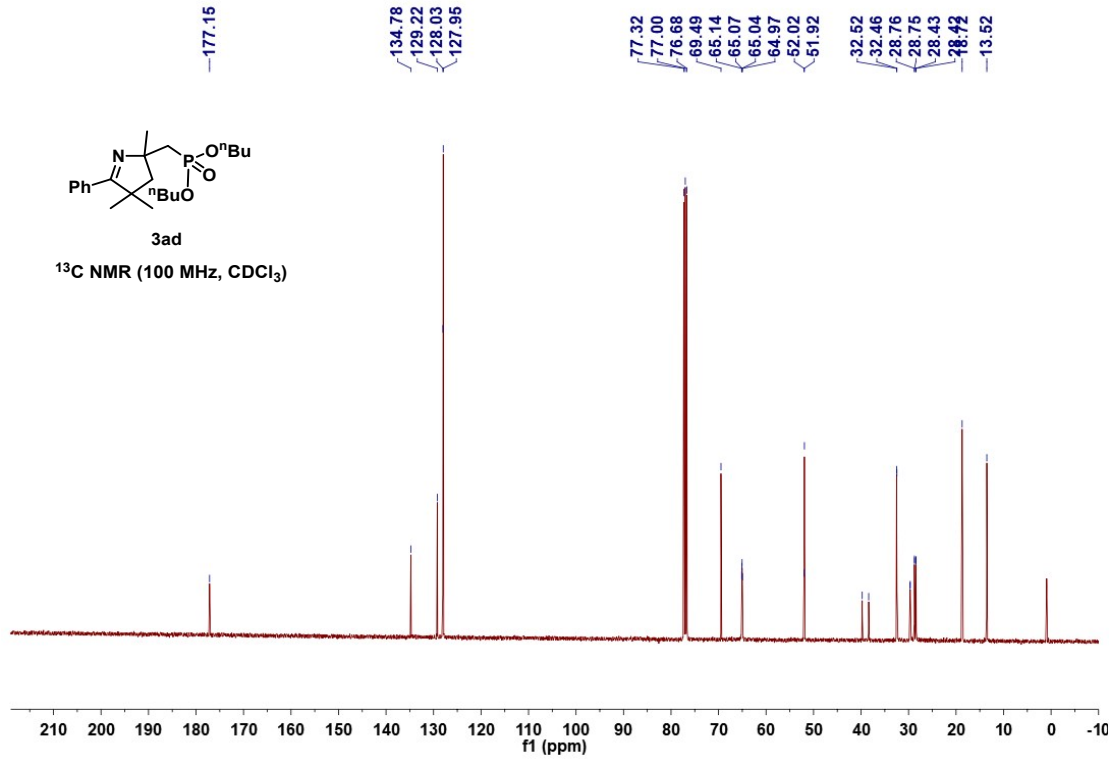
^{13}C NMR (100 MHz, $CDCl_3$)

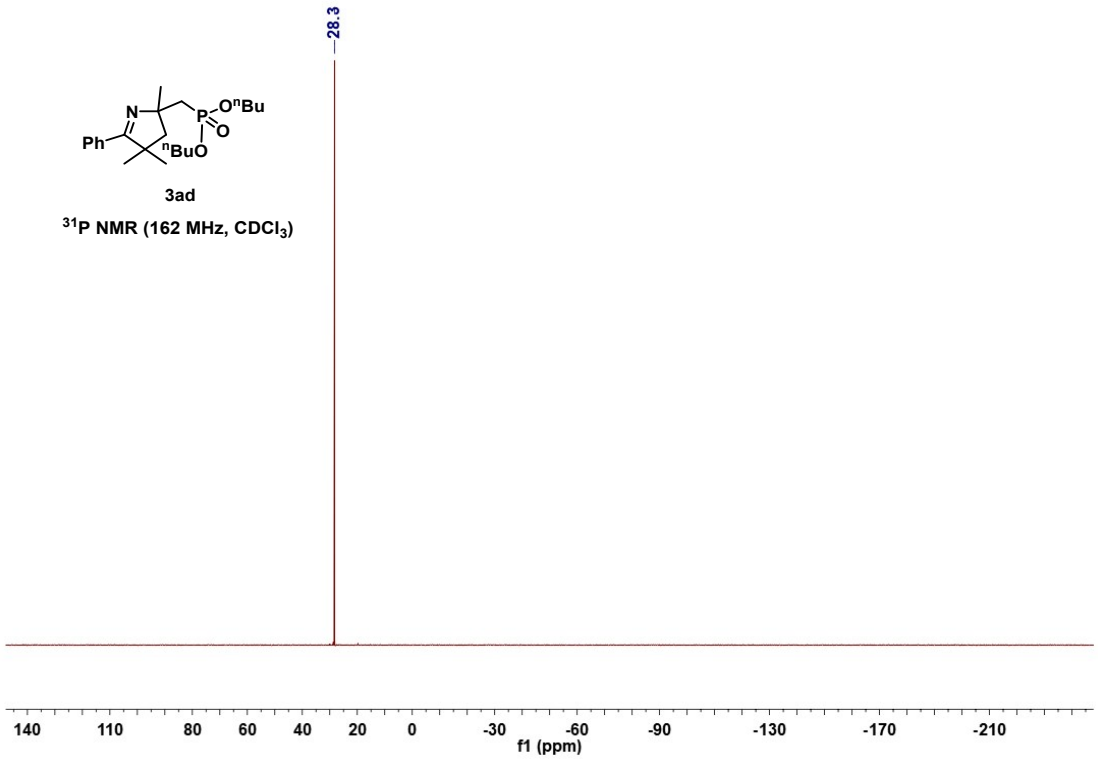


3ac

^{31}P NMR (162 MHz, $CDCl_3$)

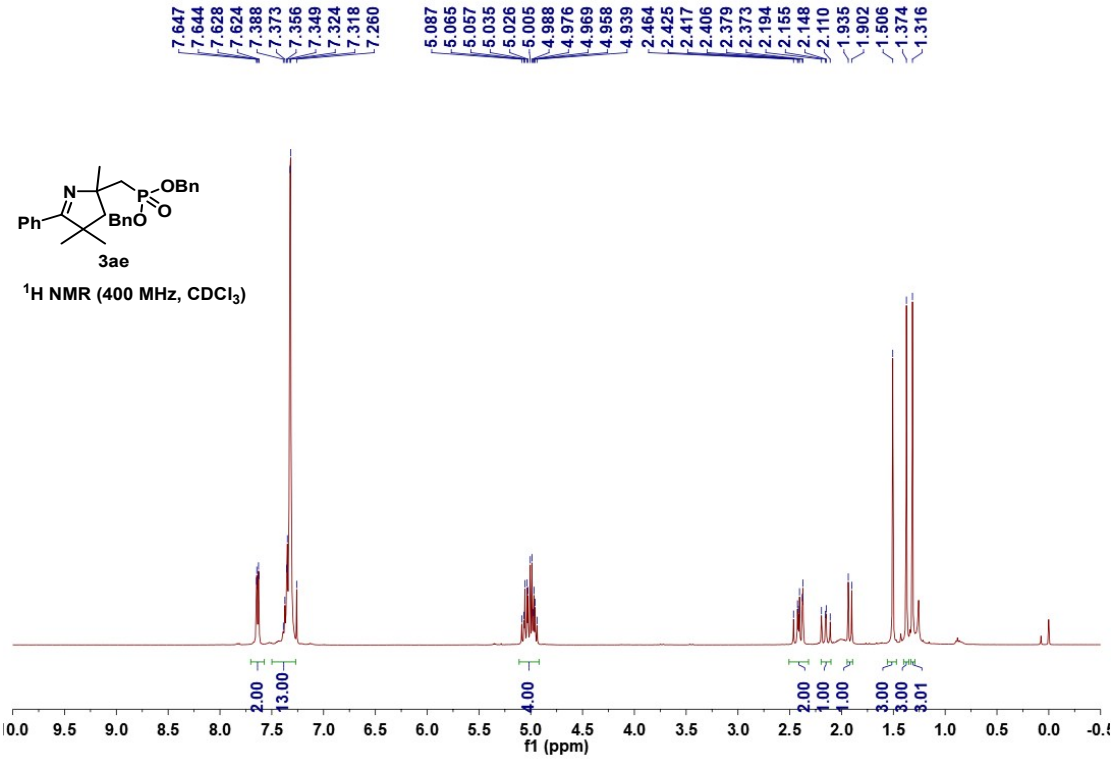

7.654
7.649
7.641
7.636
7.630
7.360
7.355
7.347
7.344
7.337
7.329
7.316
7.260
4.042
4.034
4.028
4.017
4.012
4.000
3.995
3.983
3.979
3.970
3.966
3.962
2.414
2.392
2.380
2.353
2.346
2.307
2.069
2.030
2.023
1.985
1.940
1.906
1.642
1.624
1.611
1.605
1.592
1.576
1.484
1.404
1.386
1.371
1.347
1.332
0.922
0.909
0.903
0.890
0.885
0.872
Ph
N
P
O
nBuO
OnBu
3ad
1H NMR (400 MHz, CDCl3)
1.97
2.97
4.00
2.01
1.00
1.00
4.00
3.00
10.01
6.00
f1 (ppm)


177.15
134.78
129.22
128.03
127.95
77.32
77.00
76.68
69.49
65.14
65.07
65.04
64.97
52.02
51.92
32.52
32.46
28.76
28.75
28.43
28.42
28.41
13.52
Ph
N
P
O
nBuO
OnBu
3ad
13C NMR (100 MHz, CDCl3)
f1 (ppm)

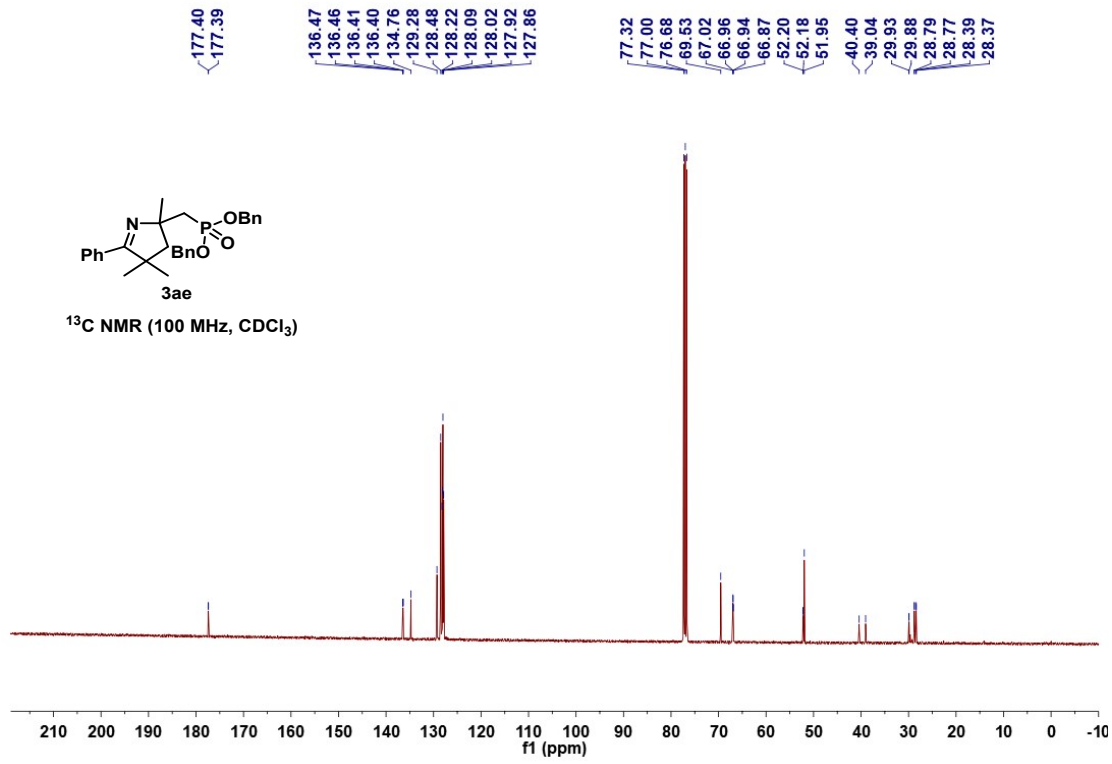


3ad

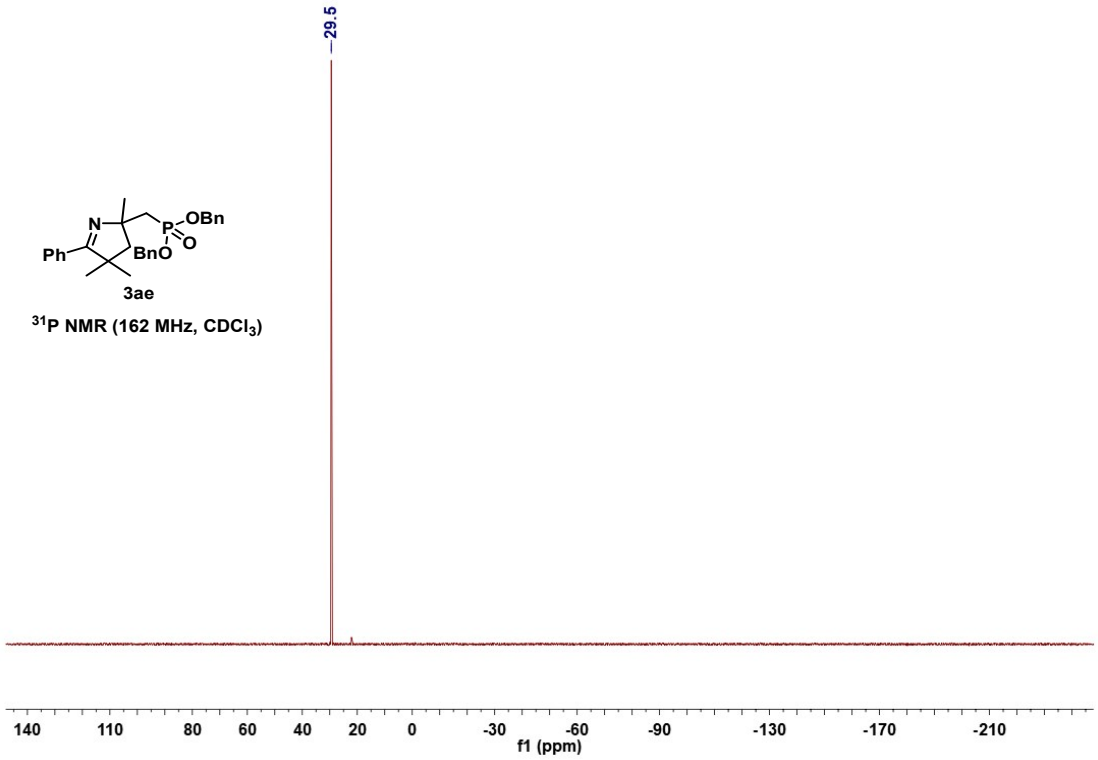
^{31}P NMR (162 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

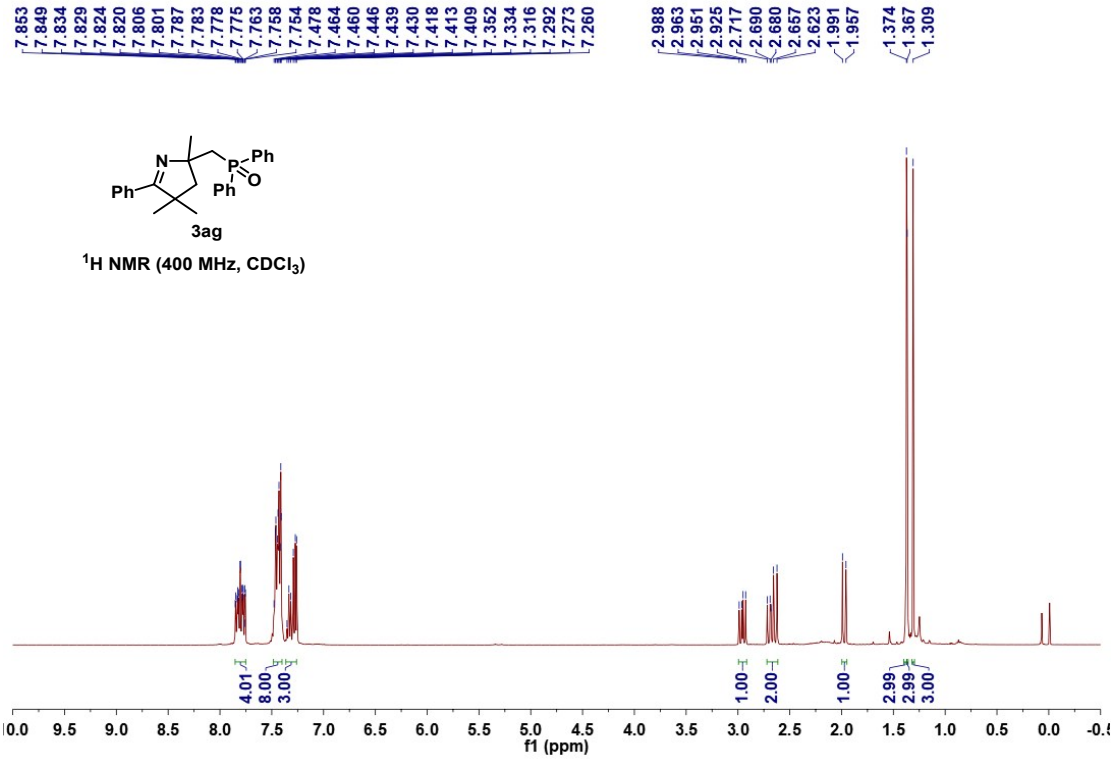


^{13}C NMR (100 MHz, $CDCl_3$)

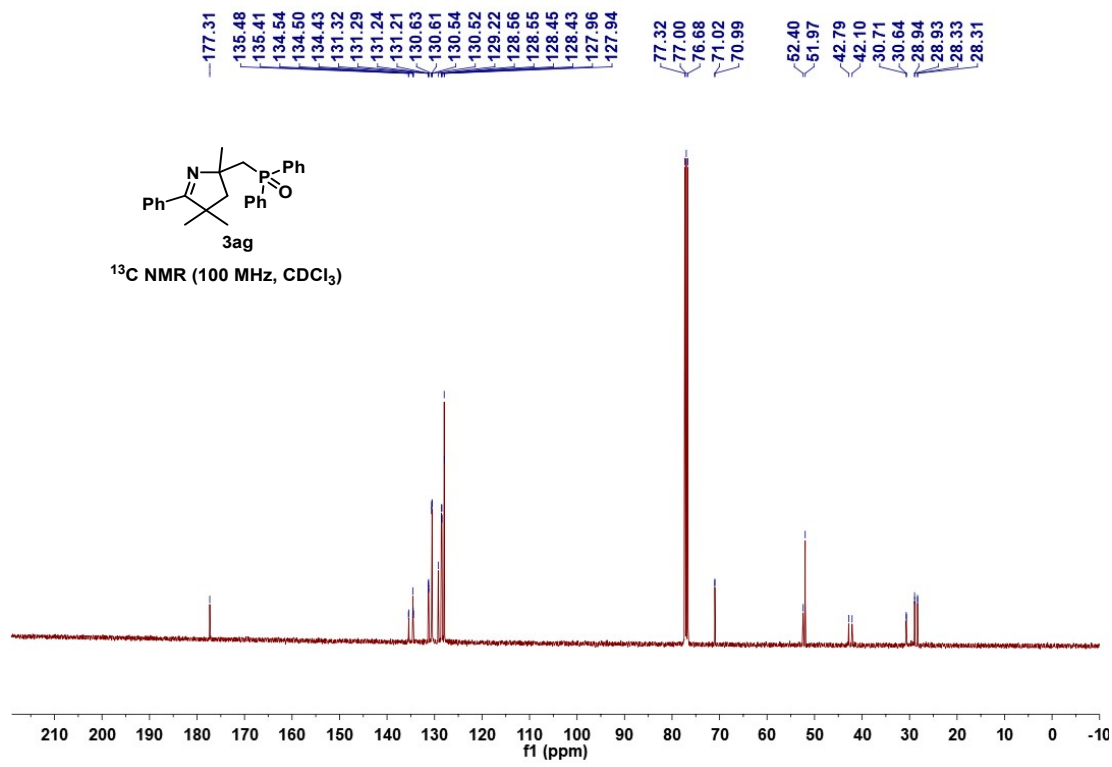


3ae

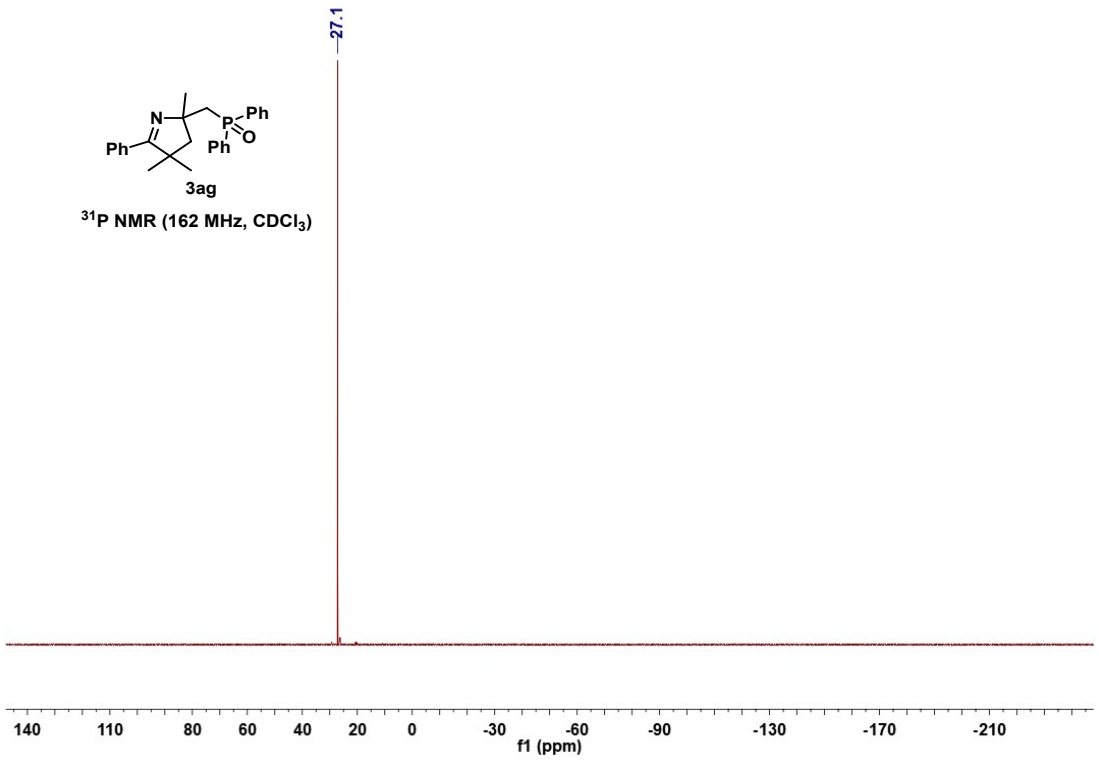
^{31}P NMR (162 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

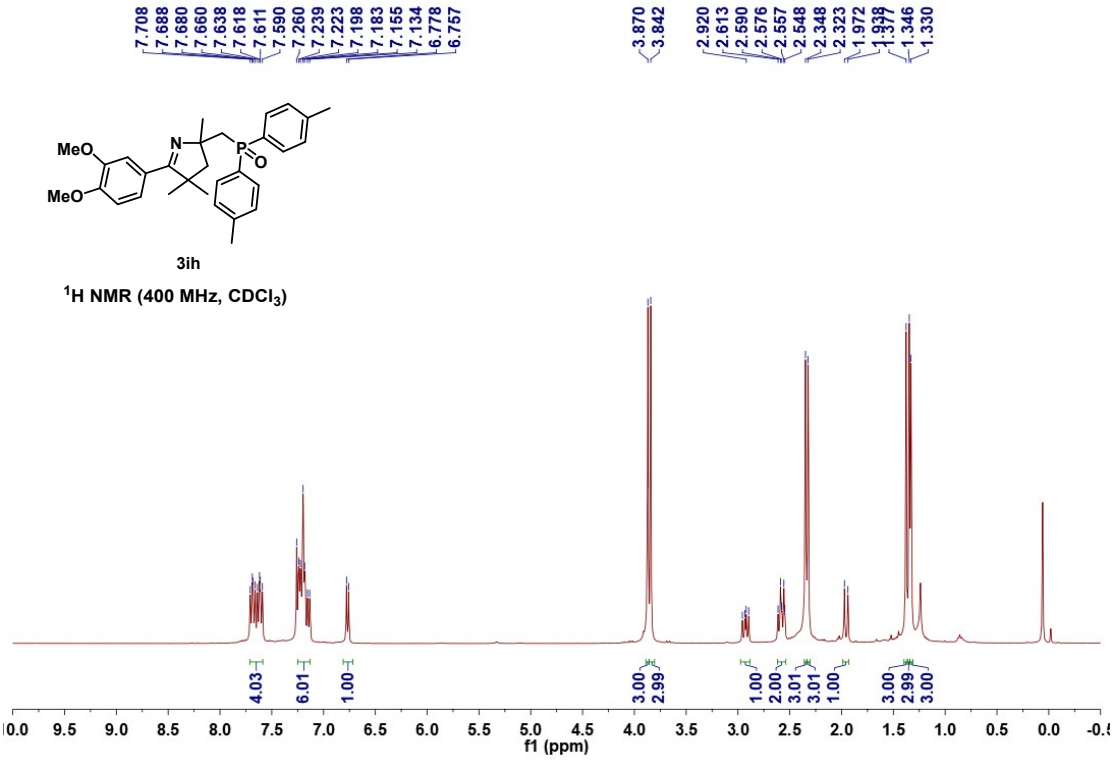


^{13}C NMR (100 MHz, $CDCl_3$)



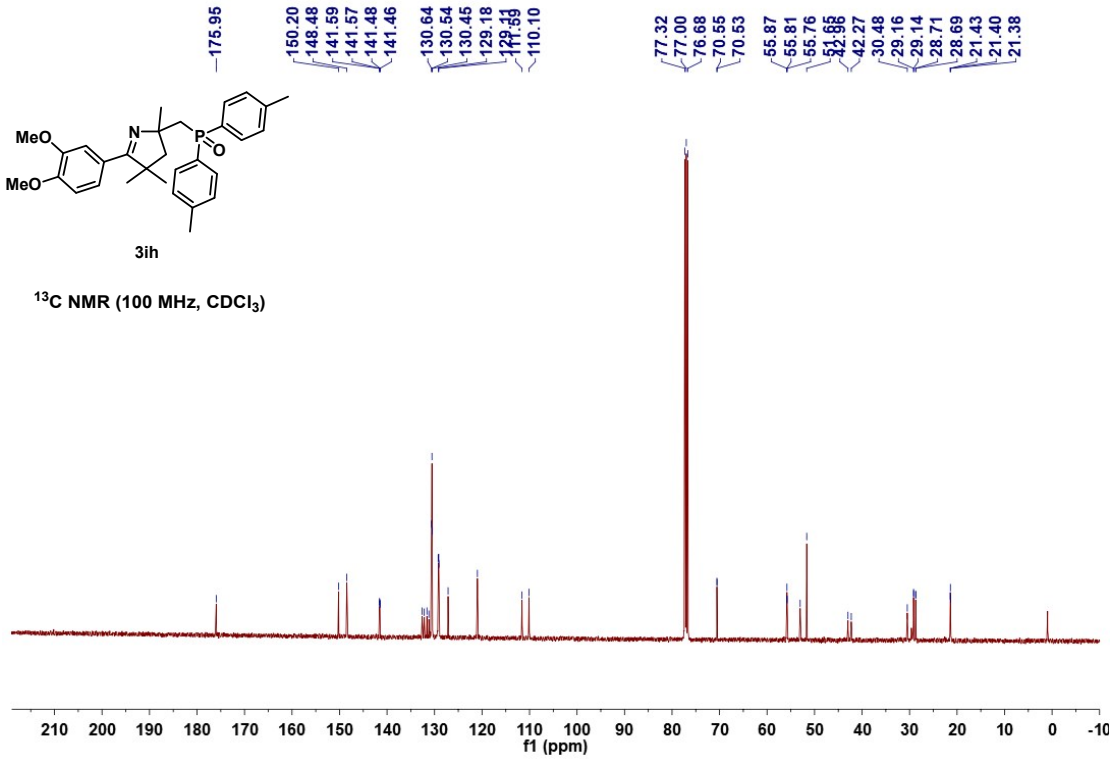
3ag

^{31}P NMR (162 MHz, $CDCl_3$)



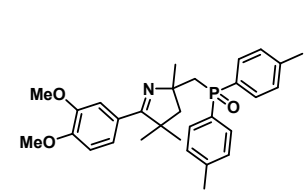
3ih

^{1}H NMR (400 MHz, $CDCl_3$)



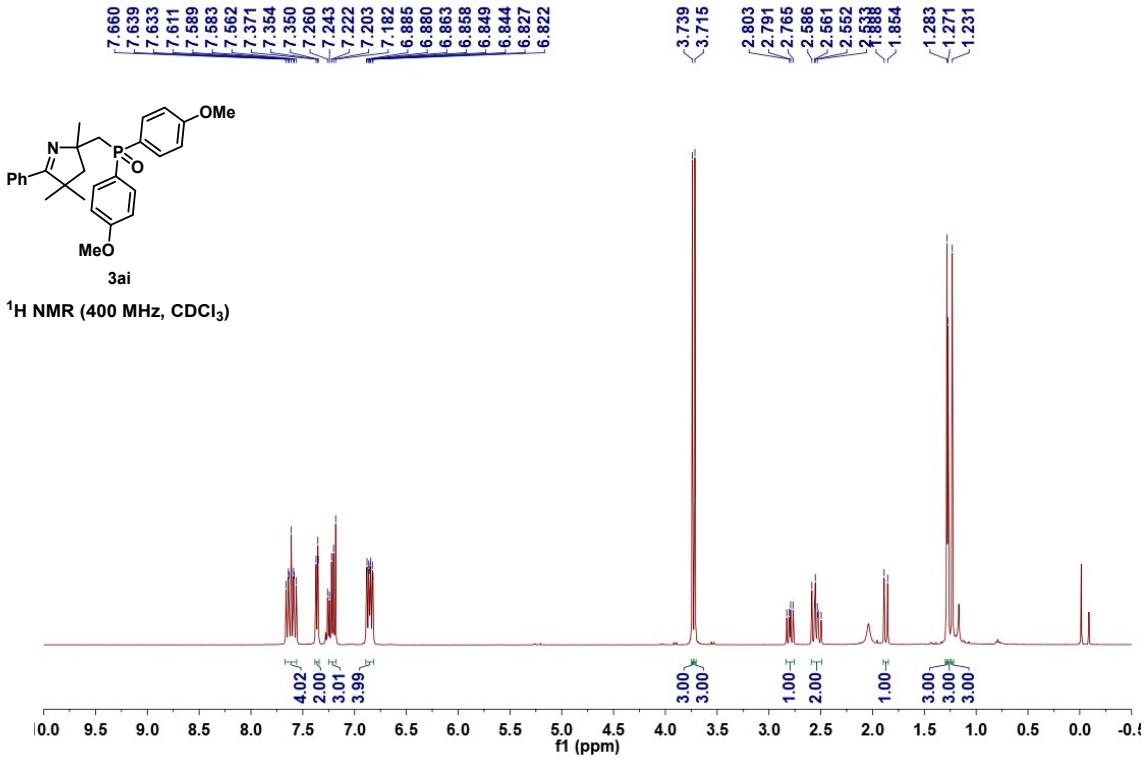
3ih

^{13}C NMR (100 MHz, $CDCl_3$)



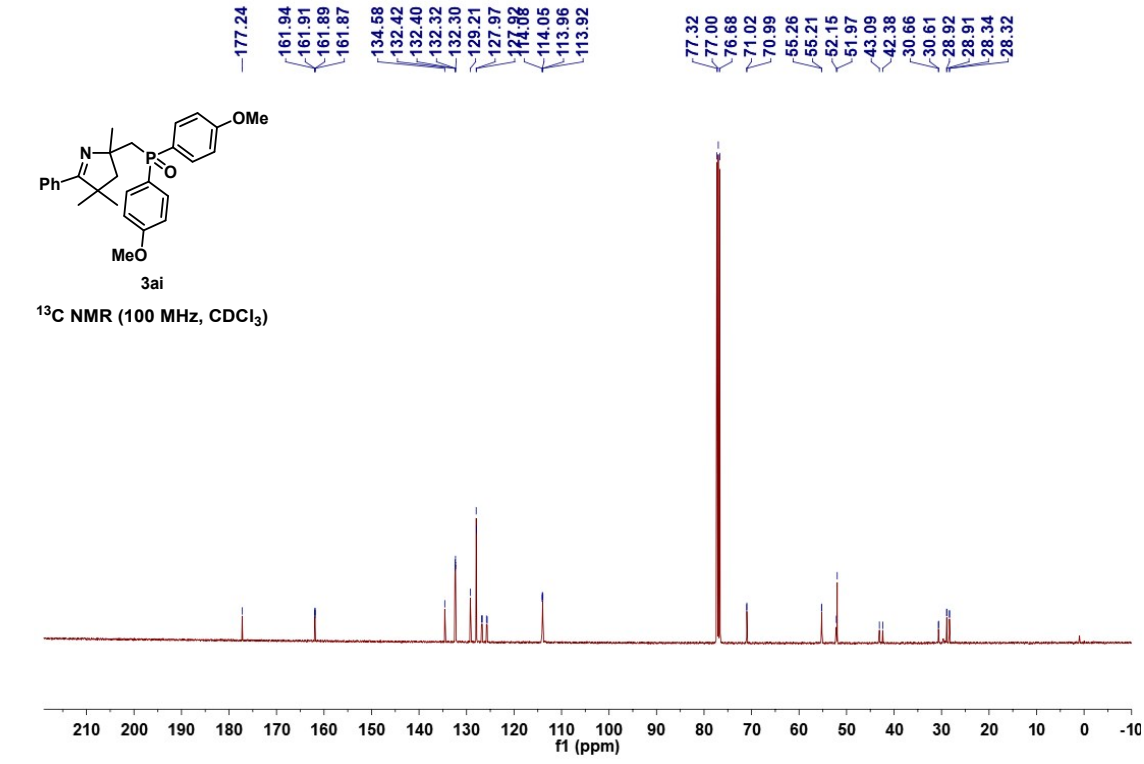
3ih

^{31}P NMR (162 MHz, $CDCl_3$)



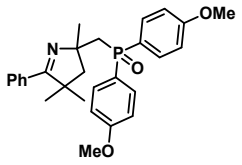
3ai

^{1}H NMR (400 MHz, $CDCl_3$)



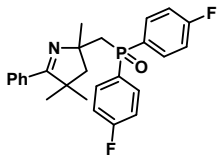
3ai

^{13}C NMR (100 MHz, $CDCl_3$)



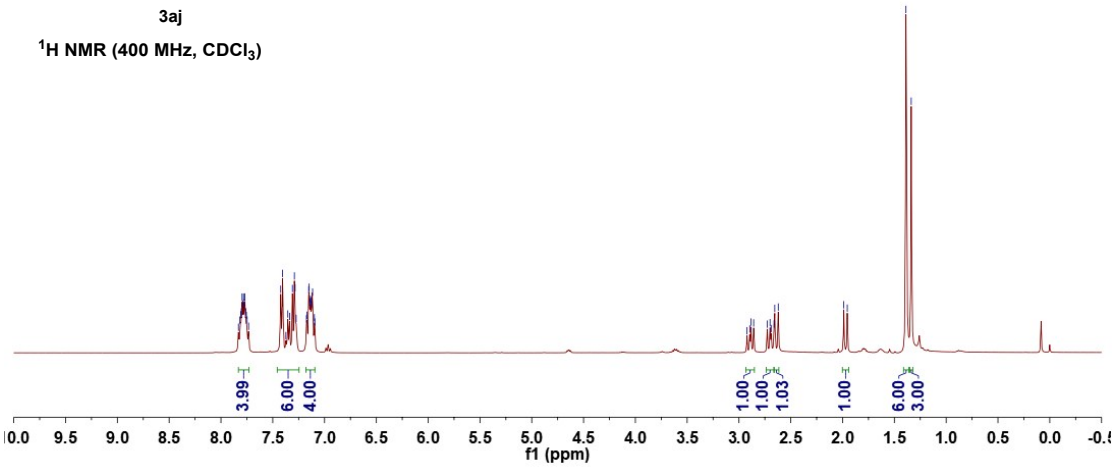
3ai

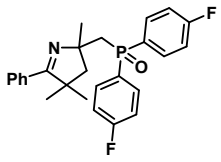
^{31}P NMR (162 MHz, $CDCl_3$)



3aj

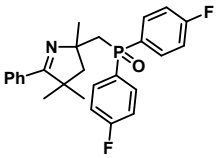
^{1}H NMR (400 MHz, $CDCl_3$)





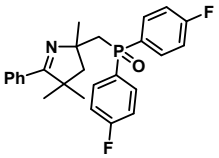
3aj

^{13}C NMR (100 MHz, $CDCl_3$)



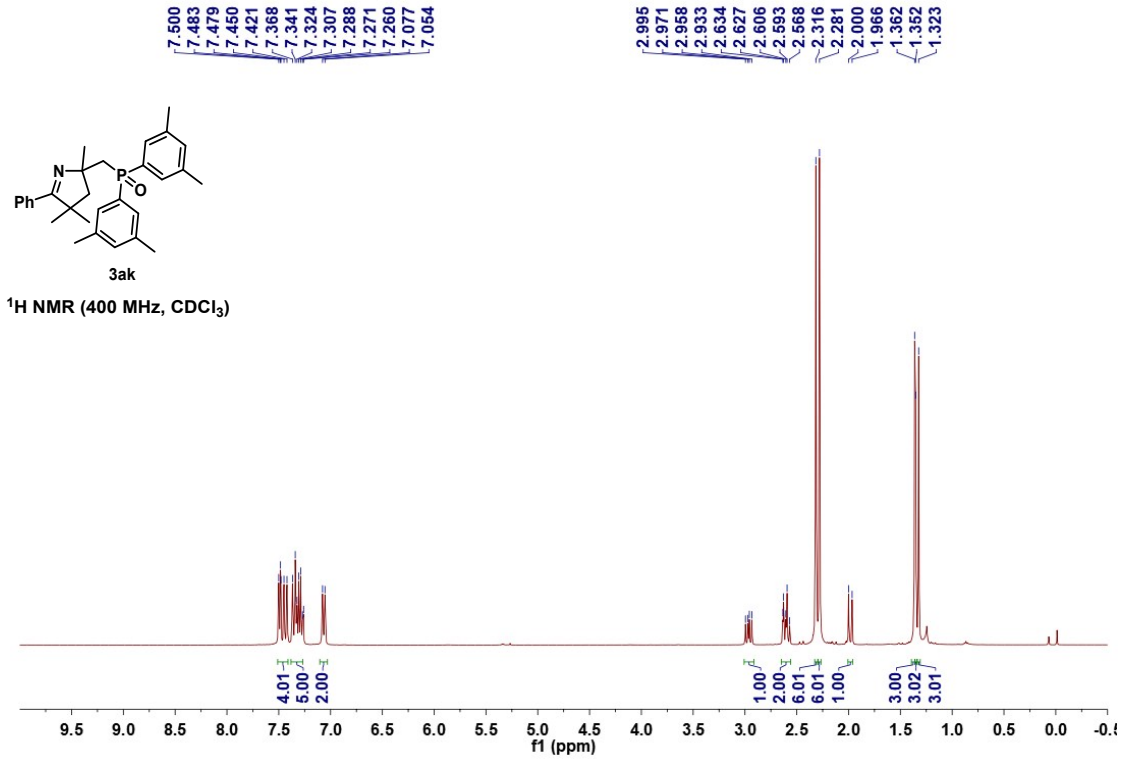
3aj

^{19}F NMR (376 MHz, $CDCl_3$)



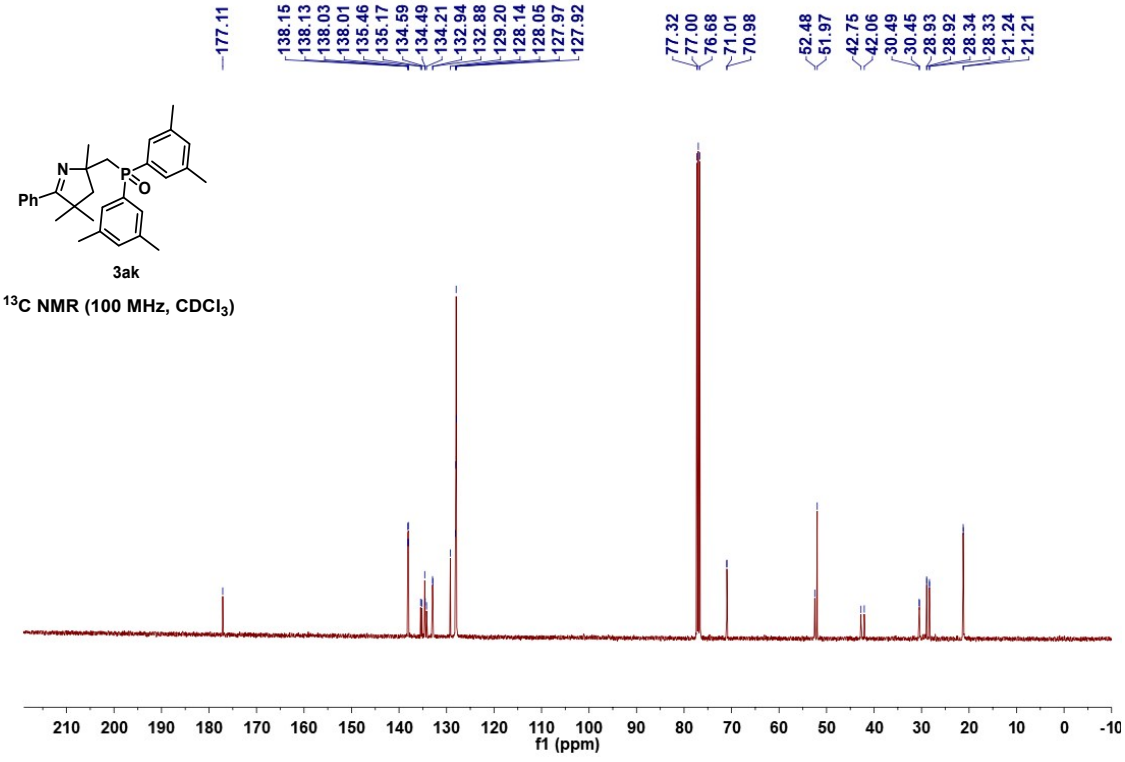
3aj

^{31}P NMR (162 MHz, $CDCl_3$)



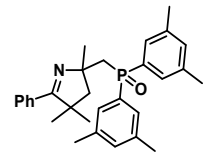
3ak

^{1}H NMR (400 MHz, $CDCl_3$)



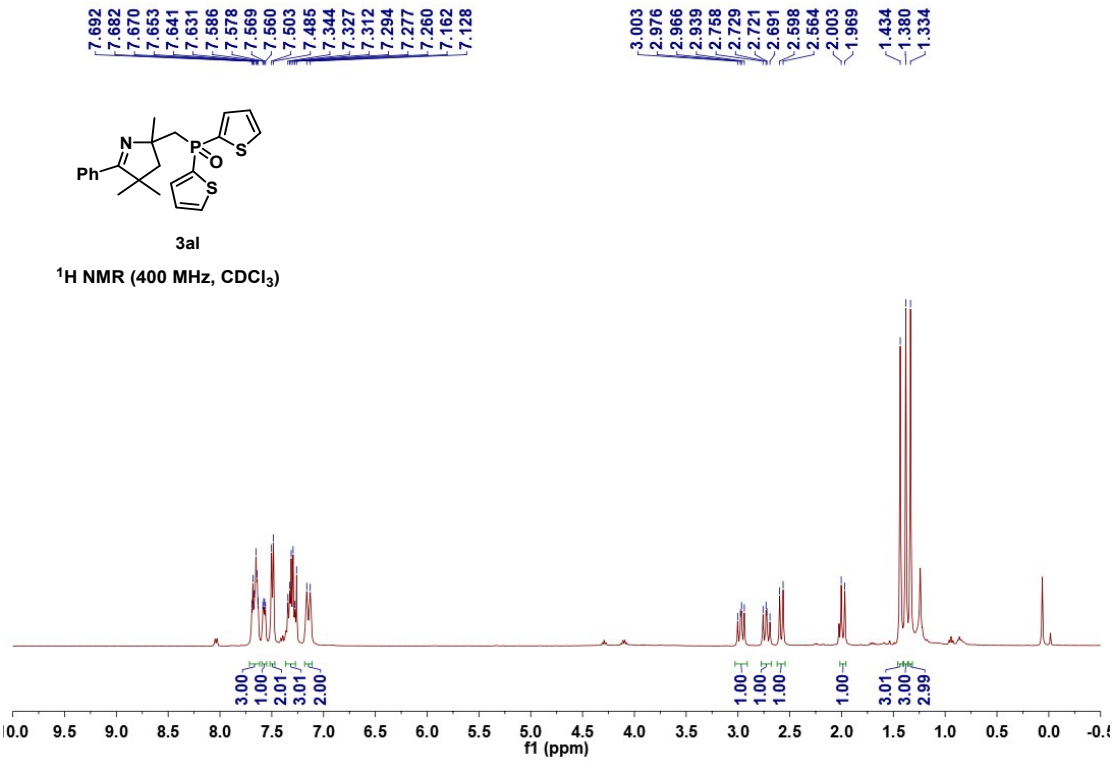
3ak

^{13}C NMR (100 MHz, $CDCl_3$)



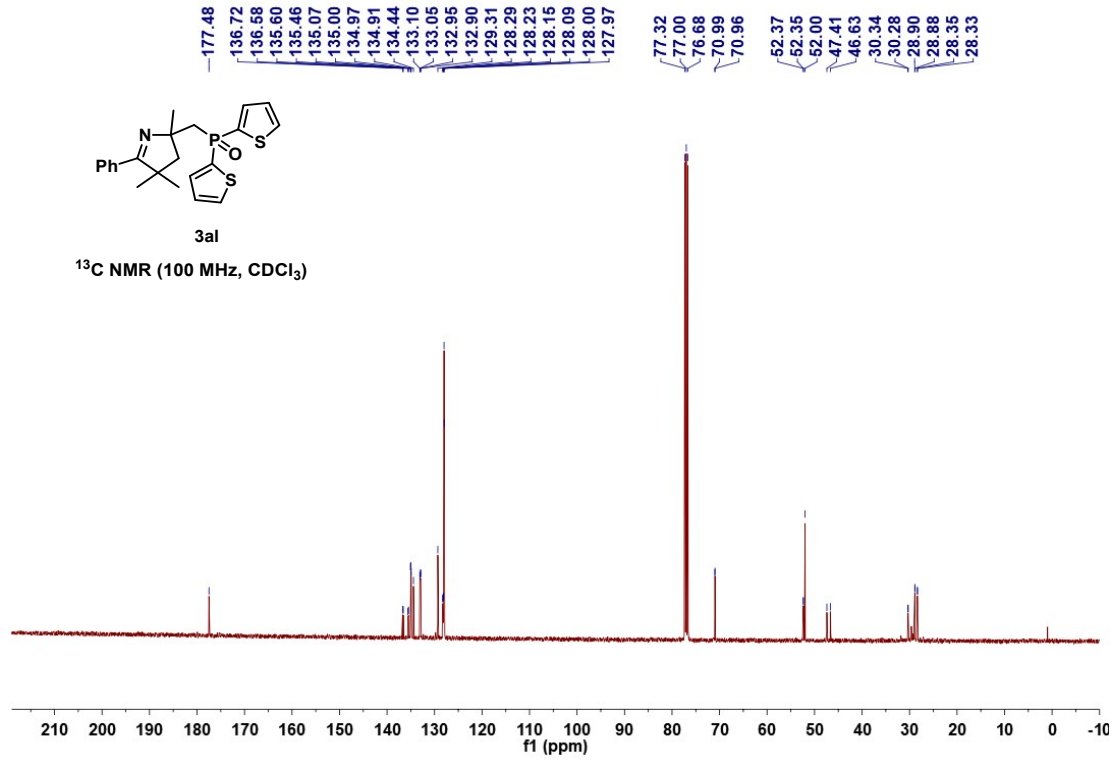
3ak

^{31}P NMR (162 MHz, $CDCl_3$)



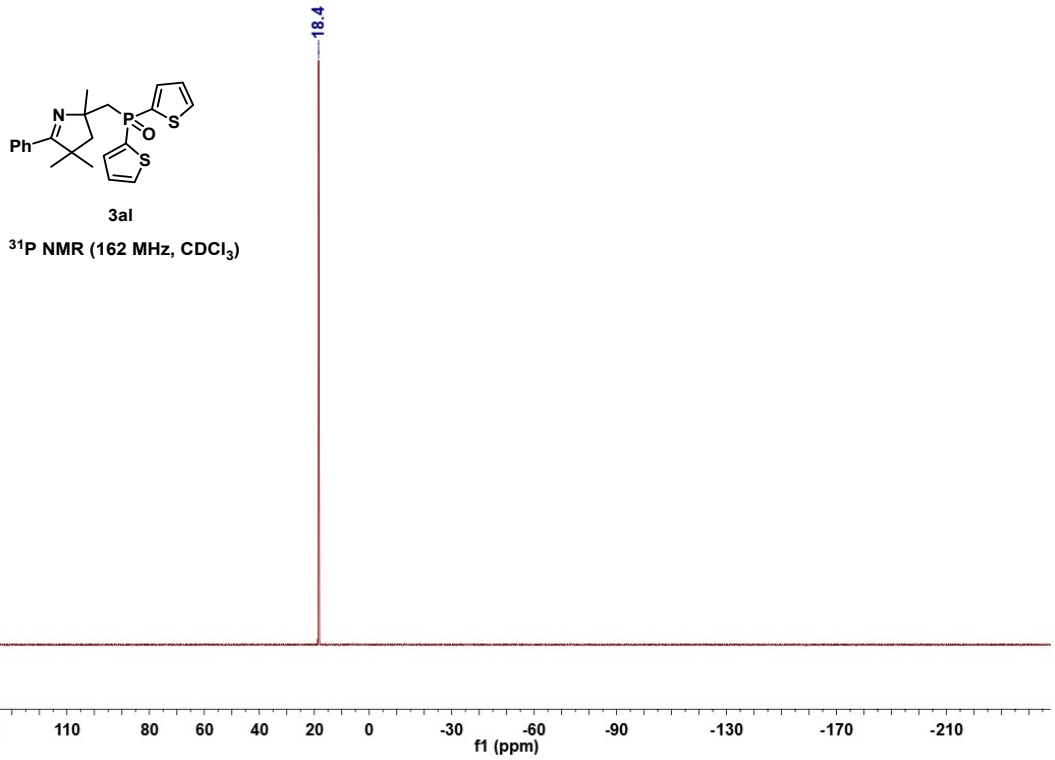
3al

^{1}H NMR (400 MHz, $CDCl_3$)



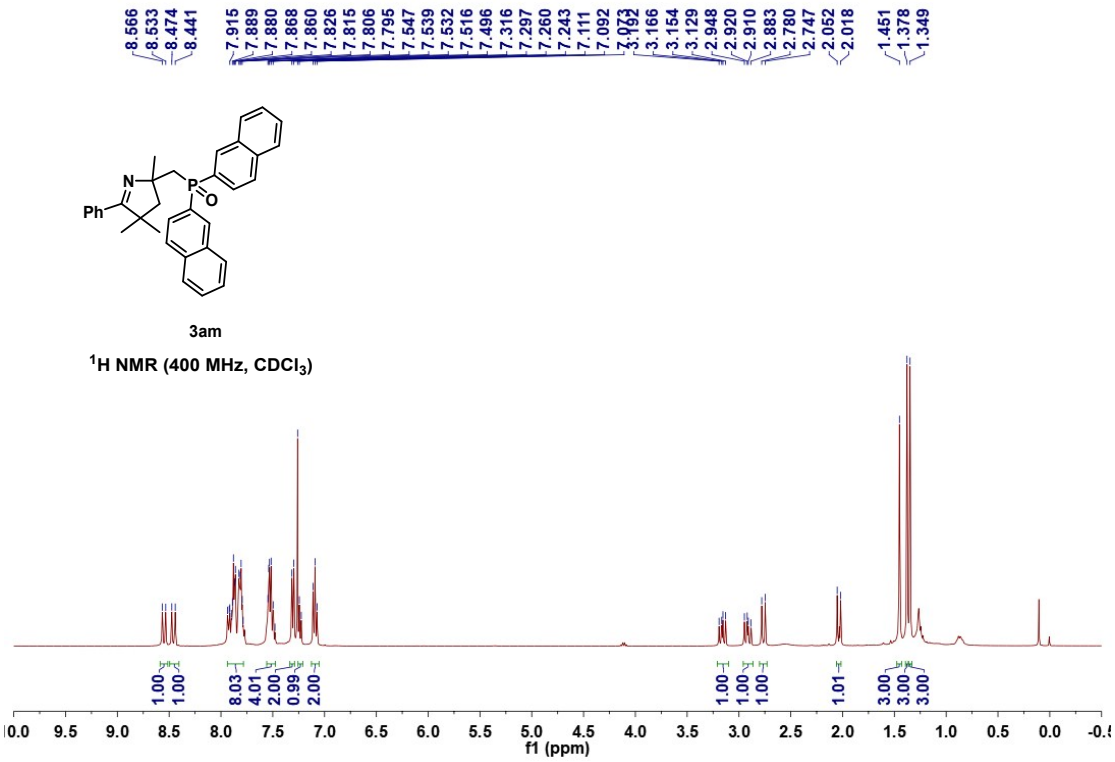
3al

^{13}C NMR (100 MHz, $CDCl_3$)



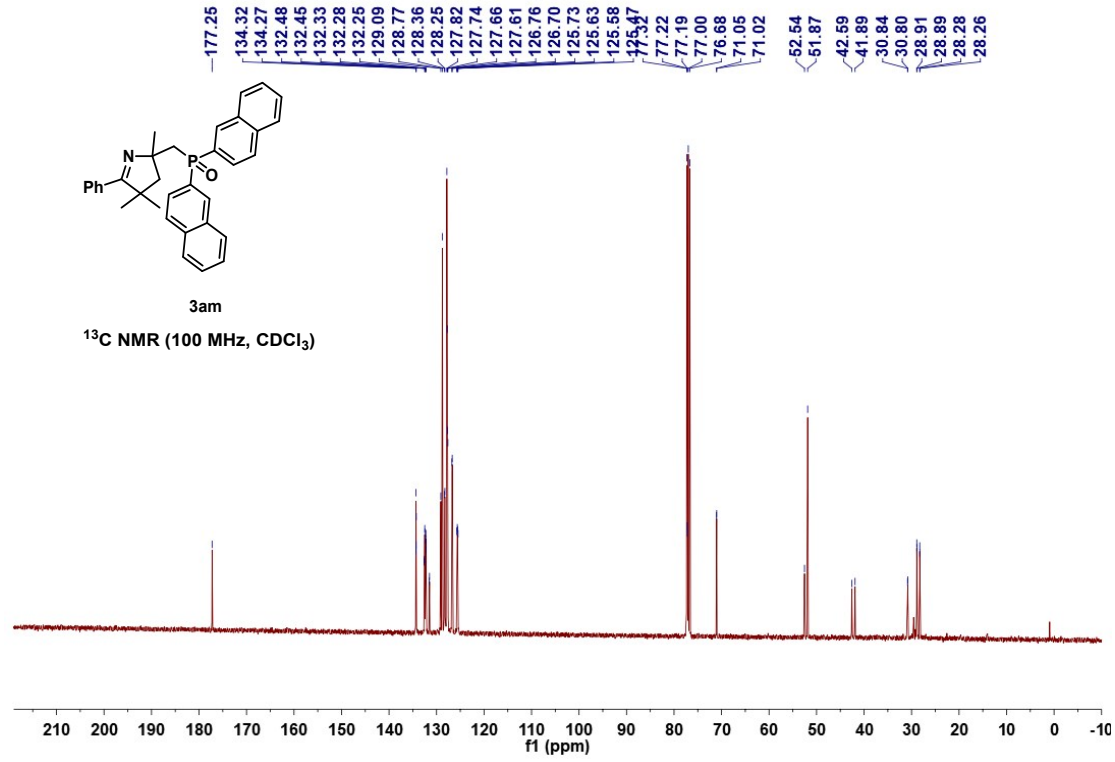
3al

^{31}P NMR (162 MHz, $CDCl_3$)



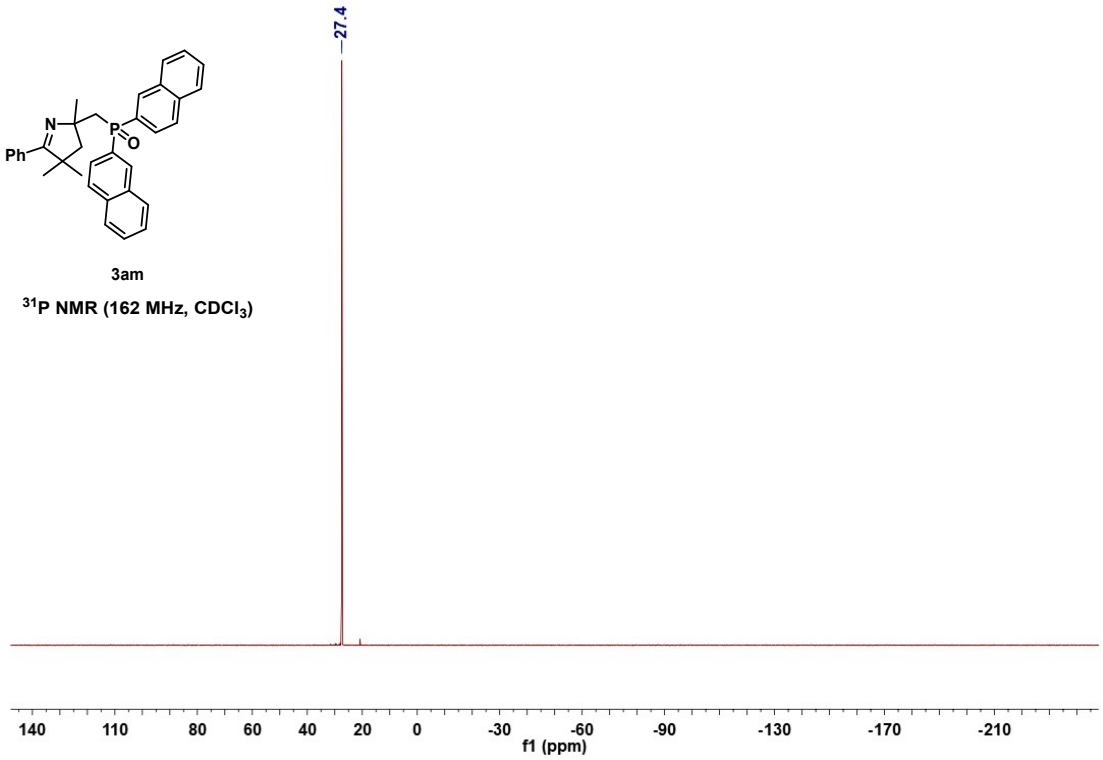
3am

^{1}H NMR (400 MHz, $CDCl_3$)



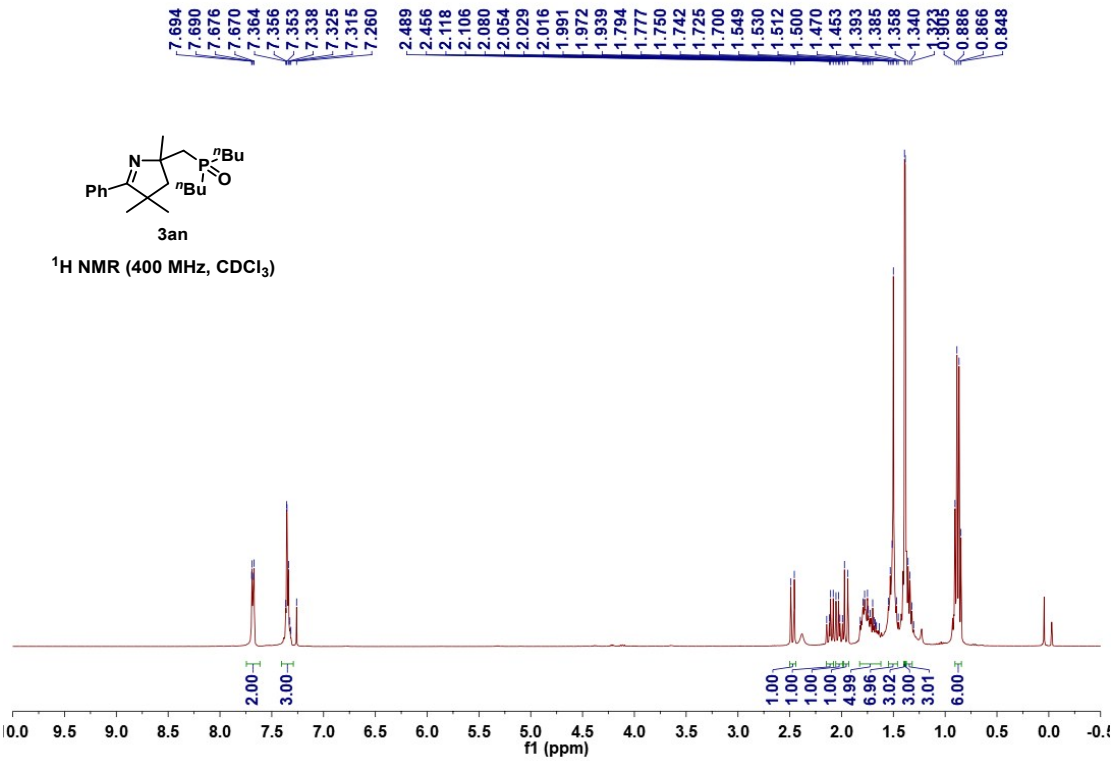
3am

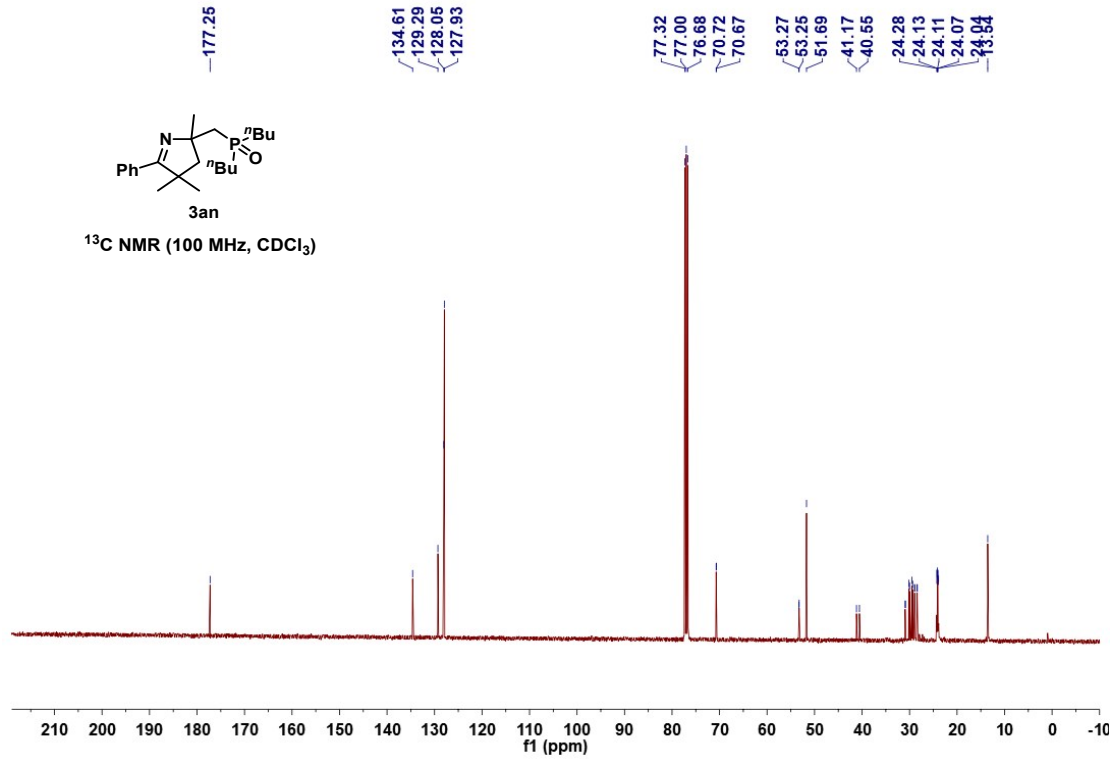
^{13}C NMR (100 MHz, $CDCl_3$)

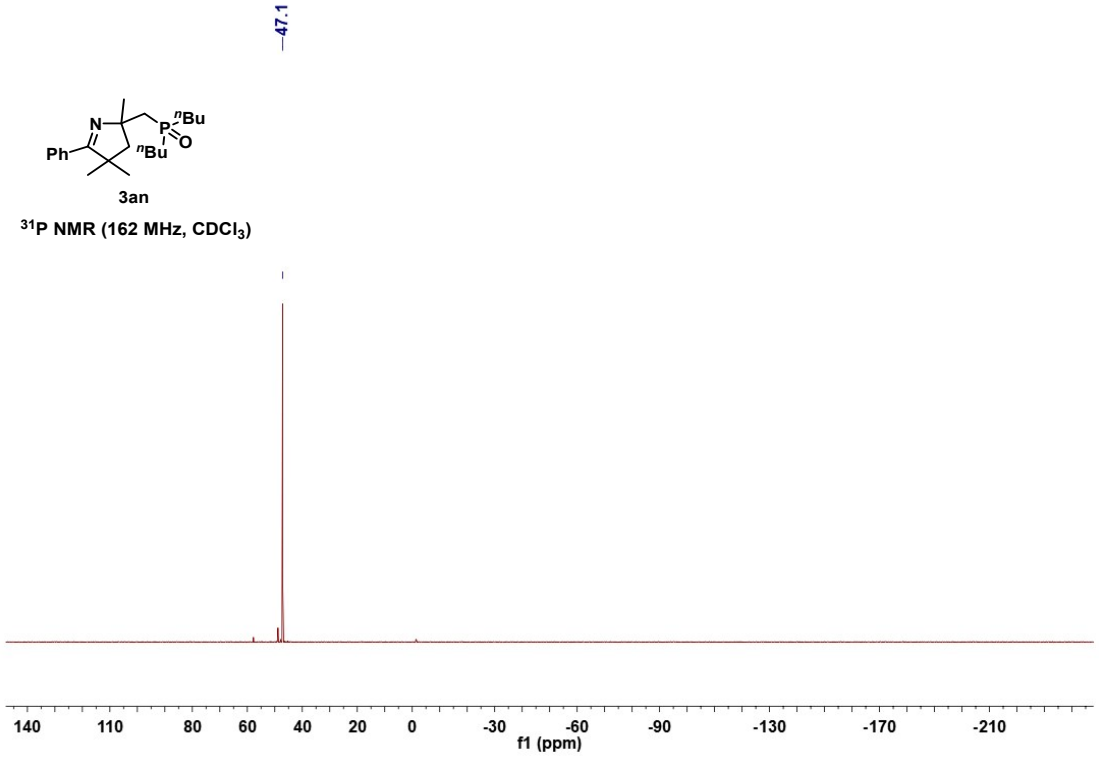


3am

^{31}P NMR (162 MHz, $CDCl_3$)

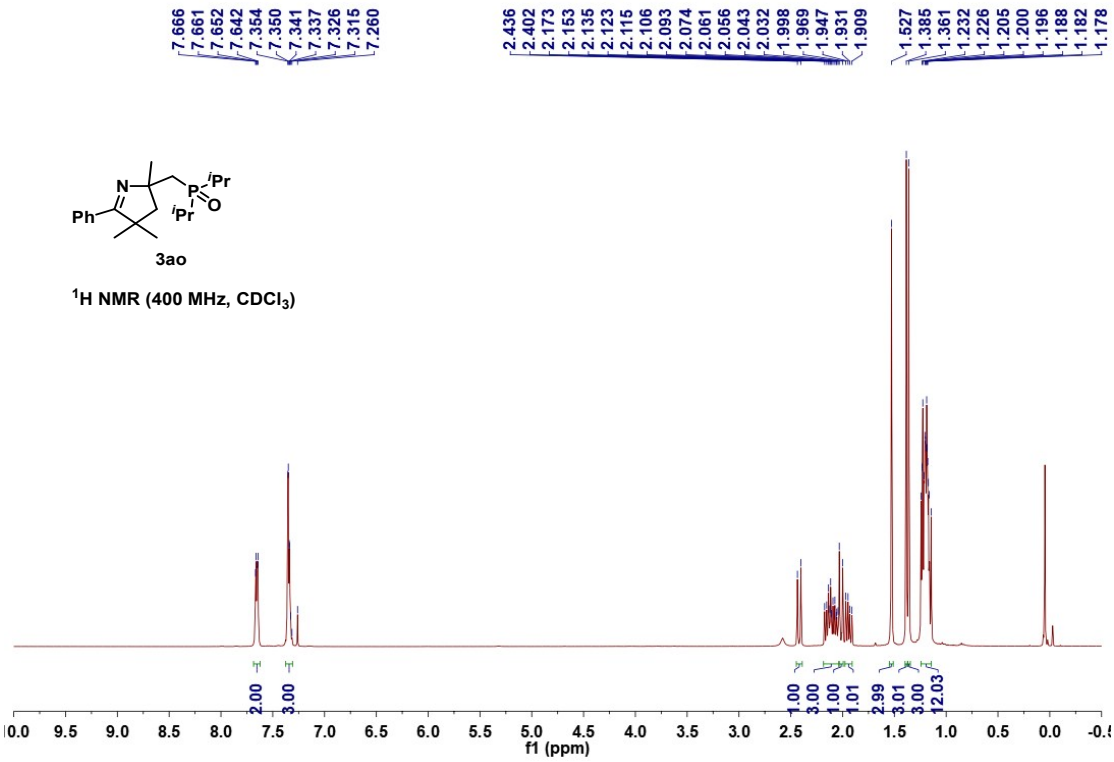

7.694
7.690
7.676
7.670
7.364
7.356
7.353
7.338
7.325
7.315
7.260
2.489
2.456
2.118
2.106
2.080
2.054
2.029
2.016
1.991
1.972
1.939
1.794
1.777
1.750
1.742
1.725
1.700
1.549
1.530
1.512
1.500
1.470
1.453
1.393
1.385
1.358
1.340
0.905
0.886
0.866
0.848
N
P
O
Ph
nBu
nBu
3an
1H NMR (400 MHz, CDCl3)
2.00
3.00
1.00
1.00
1.00
1.00
4.99
6.96
3.02
3.00
3.01
6.00
f1 (ppm)

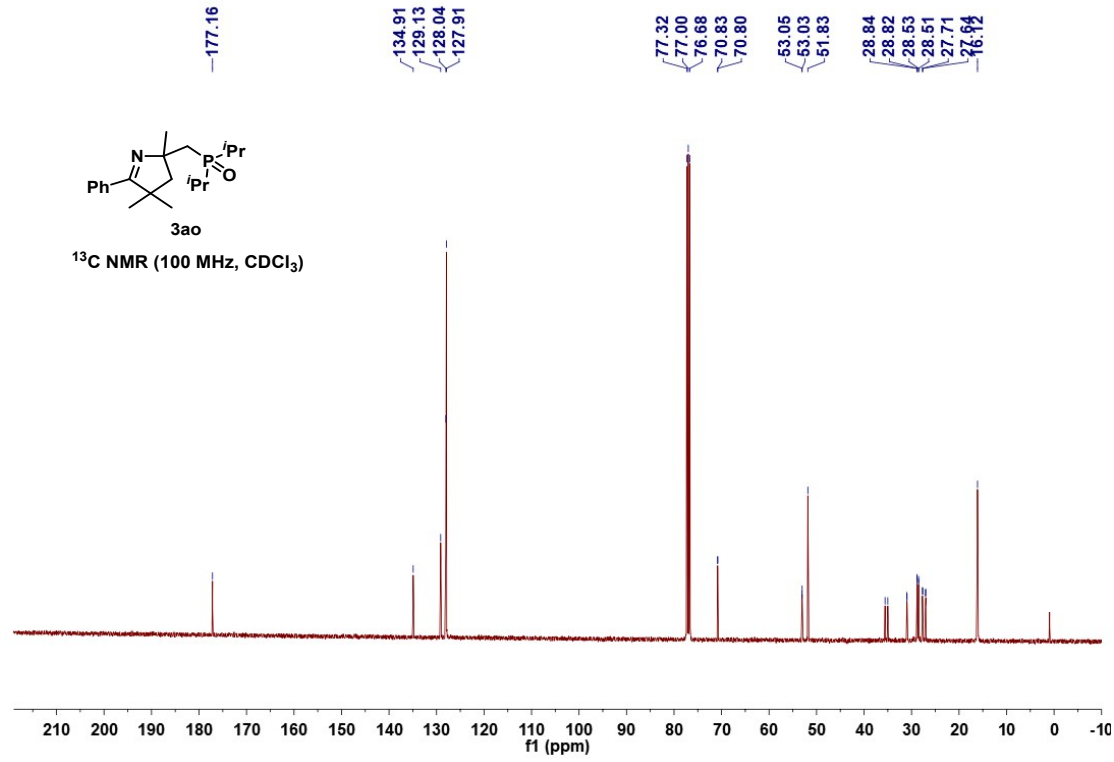

177.25
134.61
129.29
128.05
127.93
77.32
77.00
76.68
70.72
70.67
53.27
53.25
51.69
41.17
40.55
24.28
24.13
24.11
24.07
24.04
13.54
N
P
O
Ph
nBu
nBu
3an
13C NMR (100 MHz, CDCl3)
f1 (ppm)

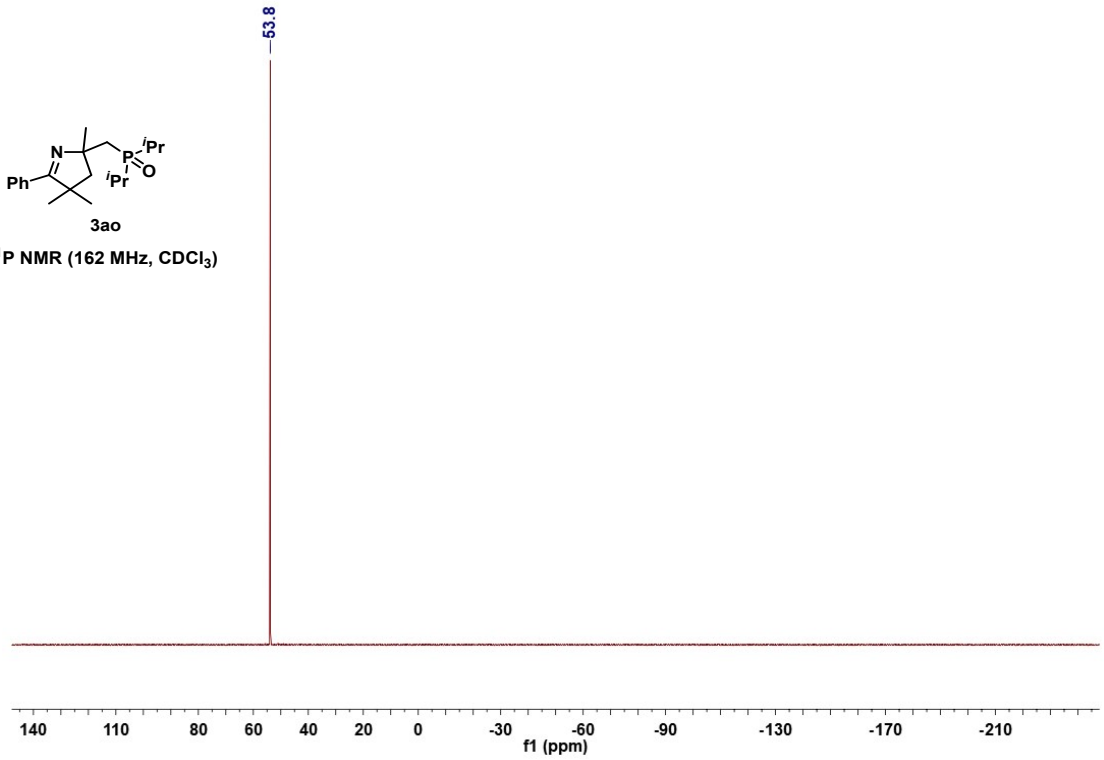


3an

^{31}P NMR (162 MHz, $CDCl_3$)

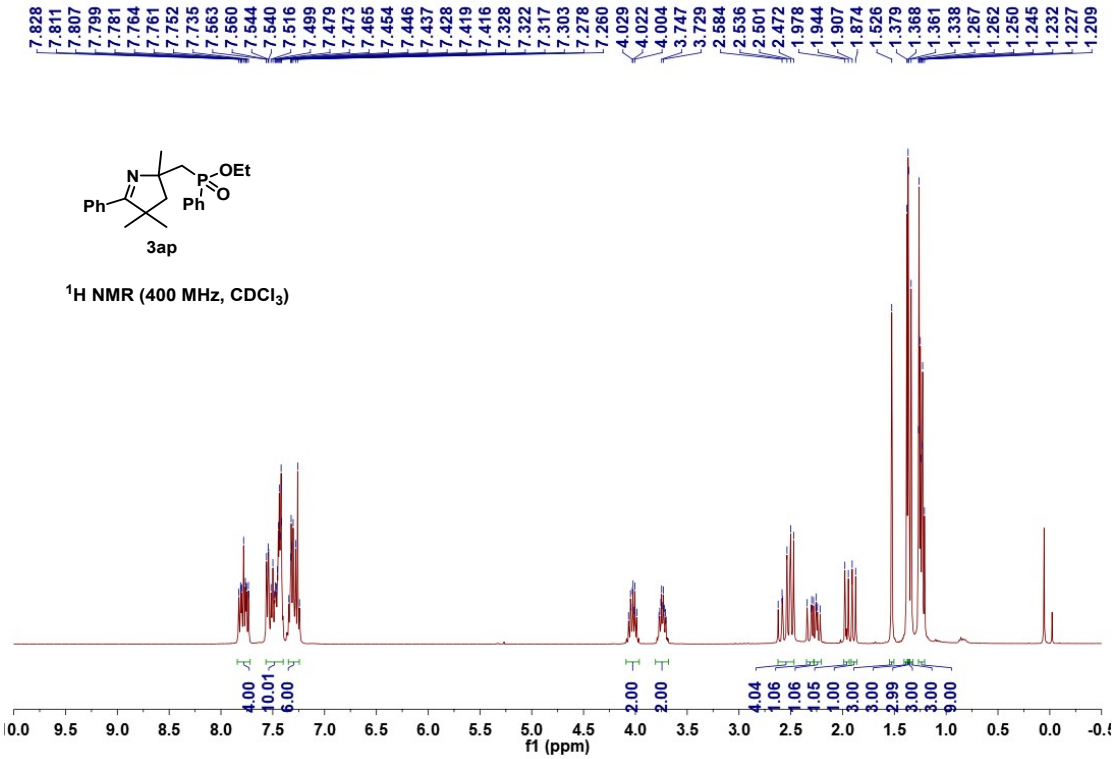

7.666
7.661
7.652
7.642
7.354
7.350
7.341
7.337
7.326
7.315
7.260
2.436
2.402
2.173
2.153
2.135
2.123
2.115
2.106
2.093
2.074
2.061
2.056
2.043
2.032
1.998
1.969
1.947
1.931
1.909
1.527
1.385
1.361
1.232
1.226
1.205
1.200
1.196
1.188
1.182
1.178
Ph
N
P
O
iPr
iPr
3ao
1H NMR (400 MHz, CDCl3)
2.00
3.00
1.00
3.00
1.00
1.01
2.99
3.01
3.00
12.03
f1 (ppm)

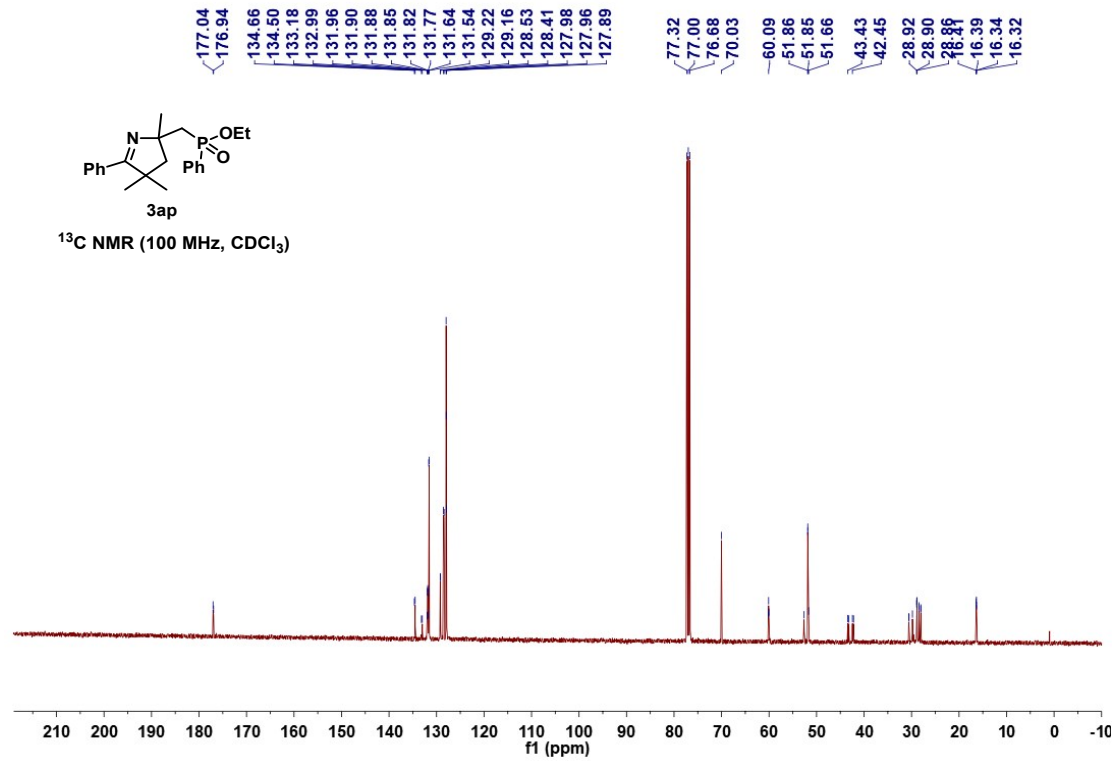

177.16
134.91
129.13
128.04
127.91
77.32
77.00
76.68
70.83
70.80
53.05
53.03
51.83
28.84
28.82
28.53
28.51
27.71
Ph
N
P
O
iPr
iPr
3ao
13C NMR (100 MHz, CDCl3)
f1 (ppm)

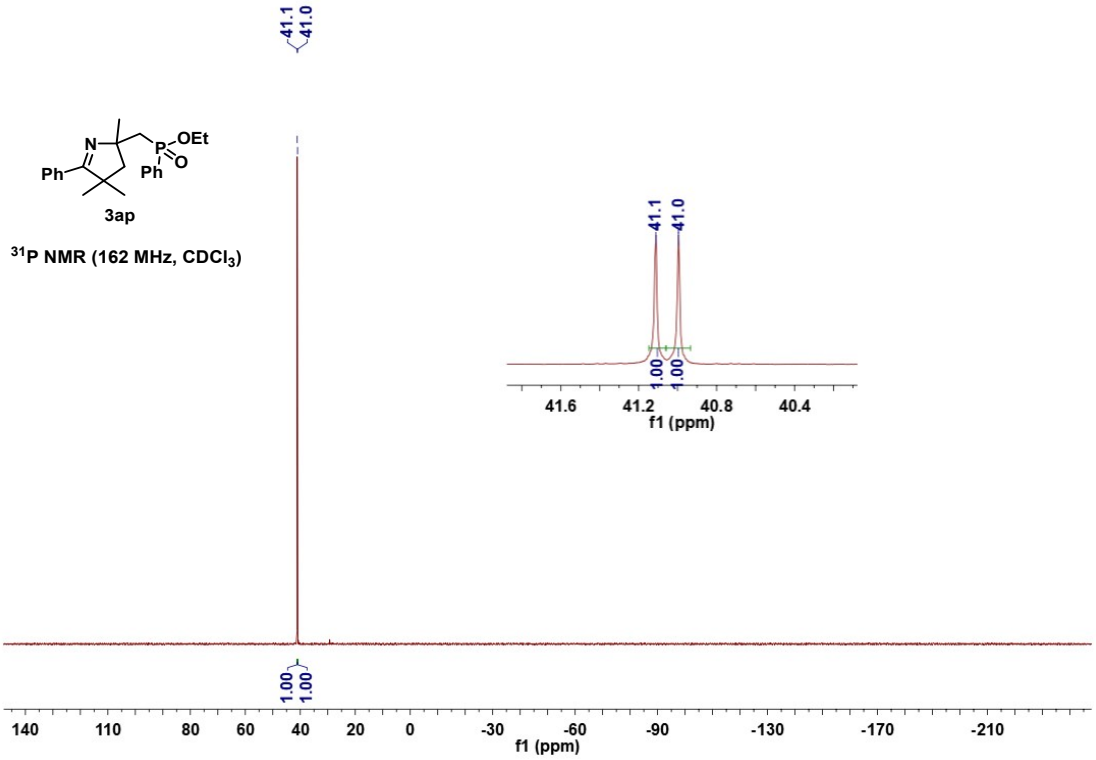


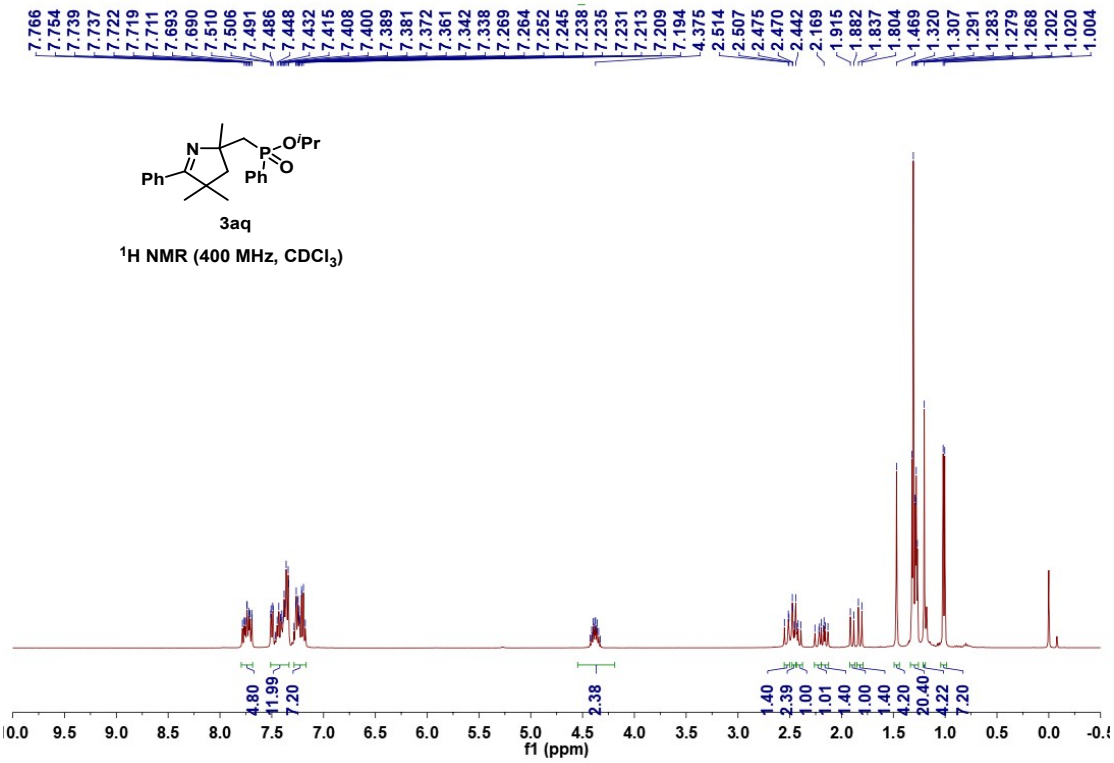
3ao

^{31}P NMR (162 MHz, $CDCl_3$)


7.828
7.811
7.807
7.799
7.781
7.764
7.761
7.752
7.735
7.563
7.560
7.544
7.540
7.516
7.499
7.479
7.473
7.465
7.454
7.446
7.437
7.428
7.419
7.416
7.328
7.322
7.317
7.303
7.278
7.260
4.029
4.022
4.004
3.747
3.729
2.584
2.536
2.501
2.472
1.978
1.944
1.907
1.874
1.526
1.379
1.368
1.361
1.338
1.267
1.262
1.250
1.245
1.232
1.227
1.209
N
P
OEt
O
Ph
Ph
3ap
1H NMR (400 MHz, CDCl3)
4.00
10.01
6.00
2.00
2.00
4.04
1.06
1.06
1.05
1.00
3.00
3.00
2.99
3.00
3.00
9.00
f1 (ppm)

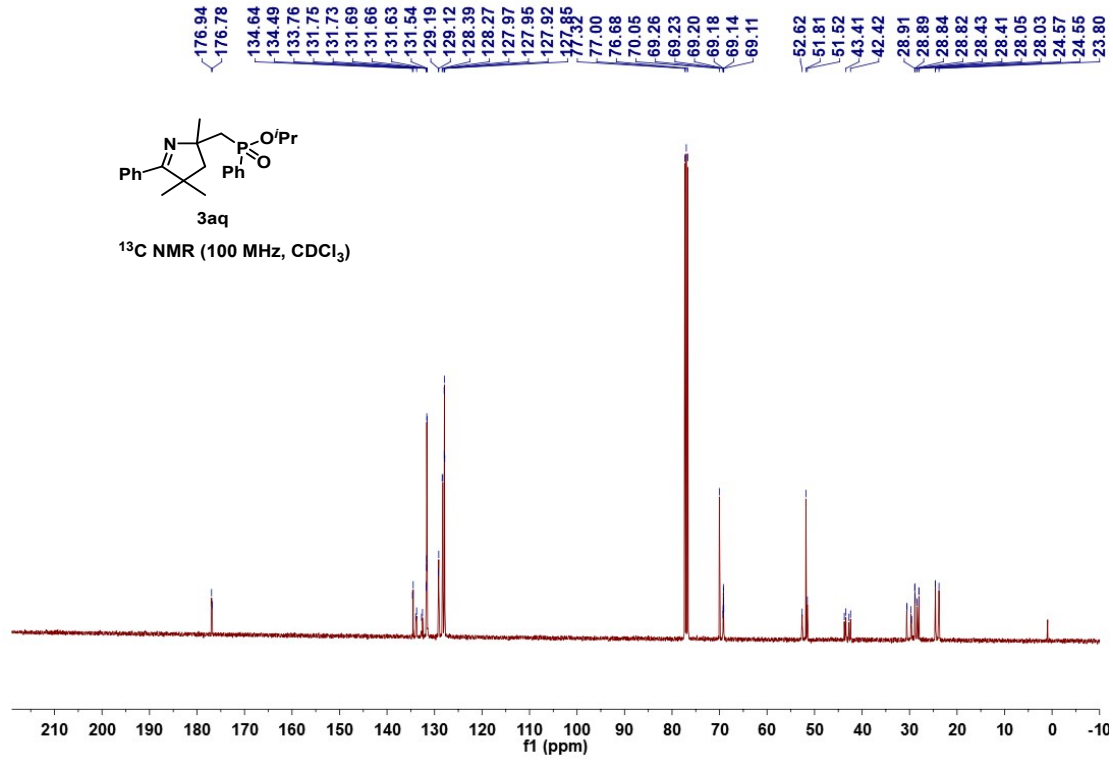

177.04
176.94
134.66
134.50
133.18
132.99
131.96
131.90
131.88
131.85
131.82
131.77
131.64
131.54
129.22
129.16
128.53
128.41
127.98
127.96
127.89
77.32
77.00
76.68
70.03
60.09
51.86
51.85
51.66
43.43
42.45
28.92
28.90
16.41
16.39
16.34
16.32
N
P
OEt
O
Ph
Ph
3ap
13C NMR (100 MHz, CDCl3)
f1 (ppm)


41.1
41.0
N
P
OEt
O
Ph
Ph
3ap
^{31}P NMR (162 MHz, CDCl$_3$)
41.1
41.0
1.00
1.00
41.6
41.2
40.8
40.4
f1 (ppm)
1.00
1.00
140
110
80
60
40
20
0
-30
-60
-90
-130
-170
-210
f1 (ppm)



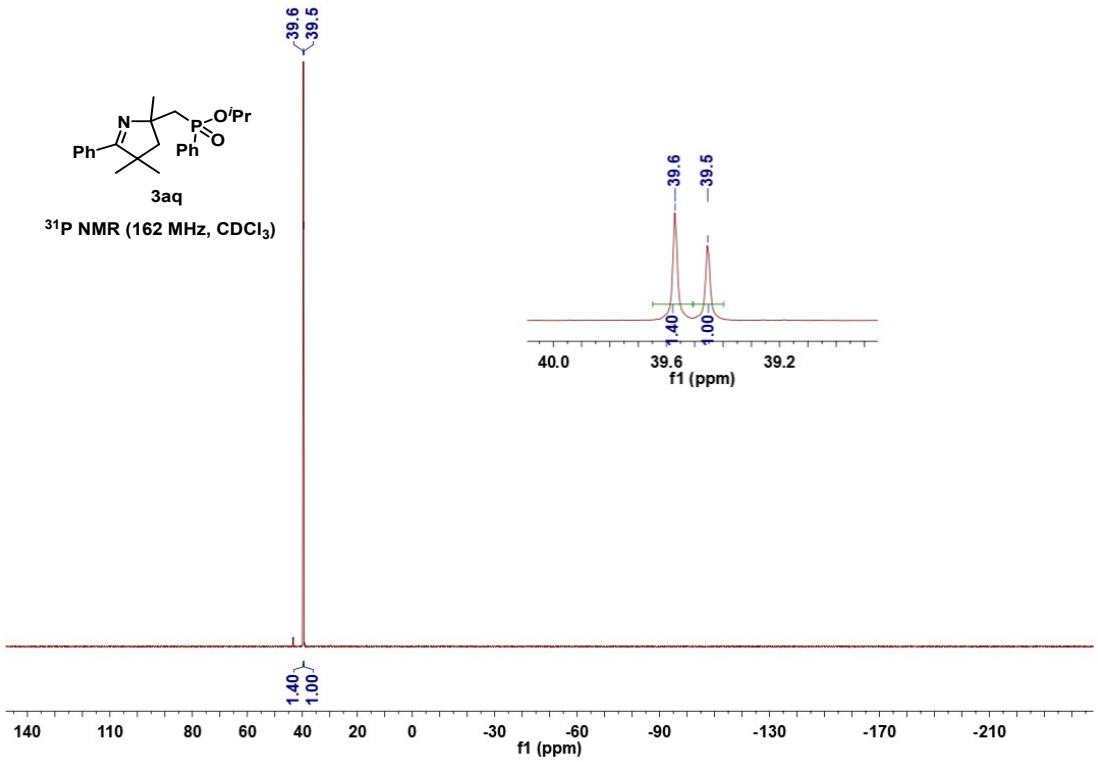
3aq

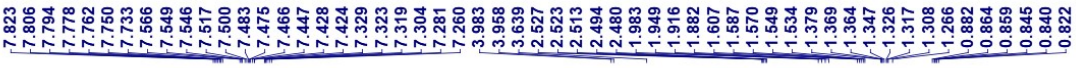
^{1}H NMR (400 MHz, $CDCl_3$)

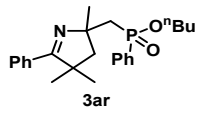


3aq

^{13}C NMR (100 MHz, $CDCl_3$)

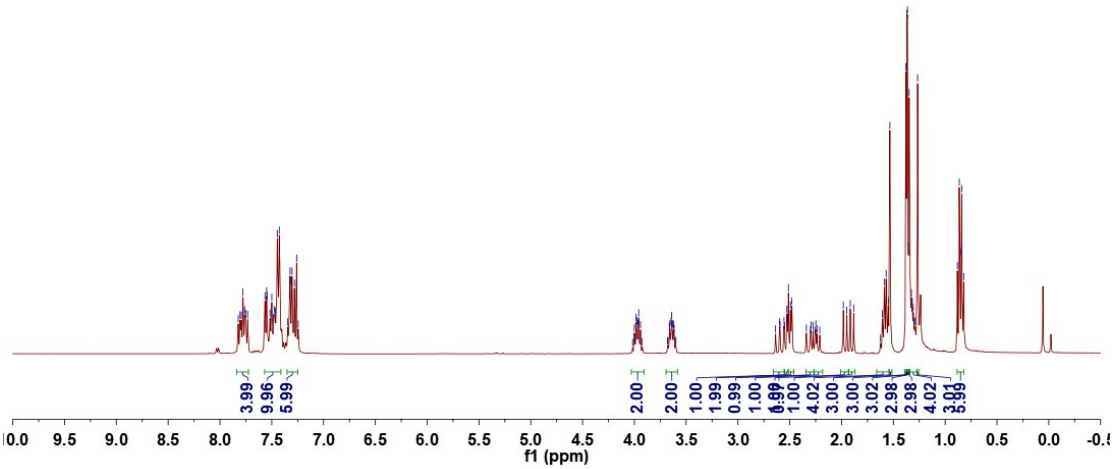

39.6
39.5
N
P
O
O^{i}Pr
Ph
Ph
3aq
^{31}P NMR (162 MHz, CDCl$_3$)
39.6
39.5
1.40
1.00
40.0
39.6
39.2
f1 (ppm)
1.40
1.00
140
110
80
60
40
20
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

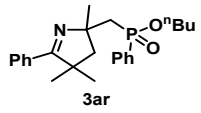




3ar

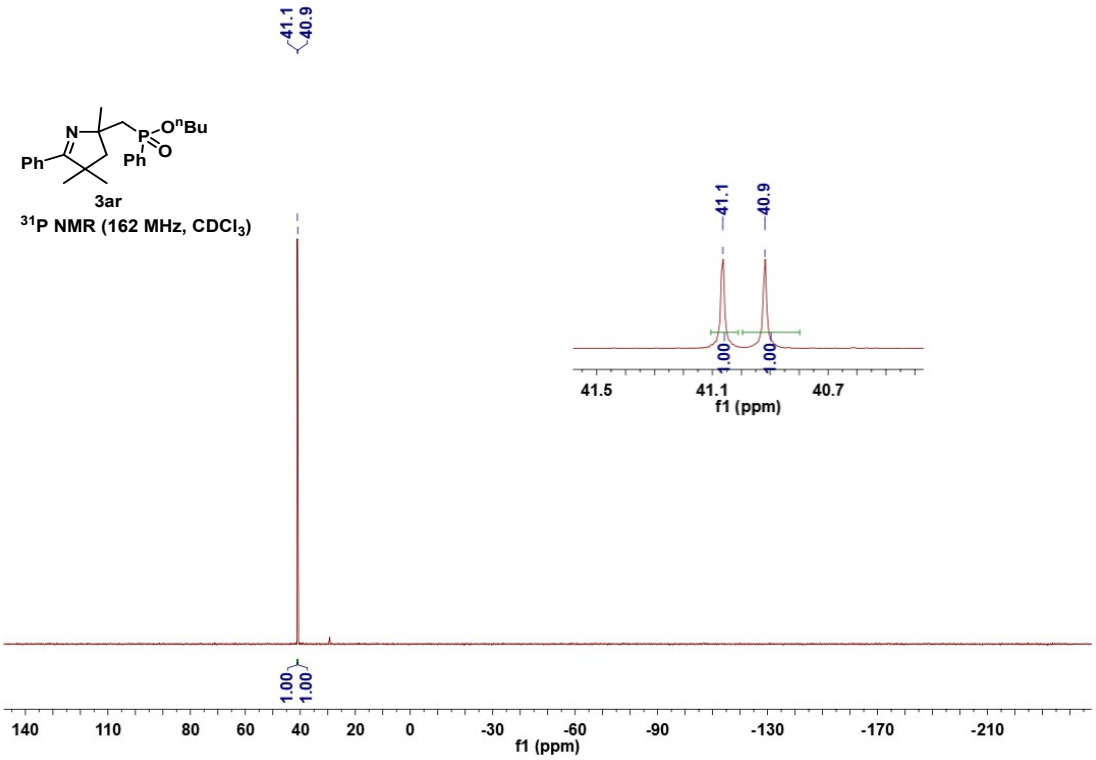
^{1}H NMR (400 MHz, $CDCl_3$)

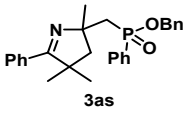




3ar

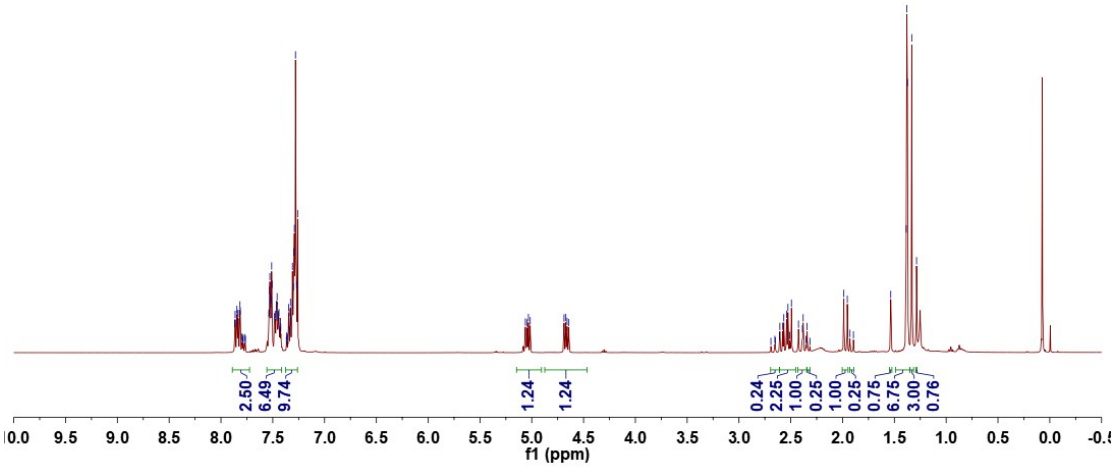
^{13}C NMR (100 MHz, $CDCl_3$)

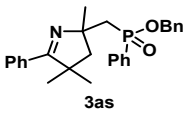

41.1
40.9
Ph
N
P
O
O^{n}Bu
Ph
3ar
^{31}P NMR (162 MHz, CDCl$_3$)
41.1
40.9
1.00
1.00
41.5
41.1
40.7
f1 (ppm)
1.00
1.00
140
110
80
60
40
20
0
-30
-60
-90
-130
-170
-210
f1 (ppm)



3as

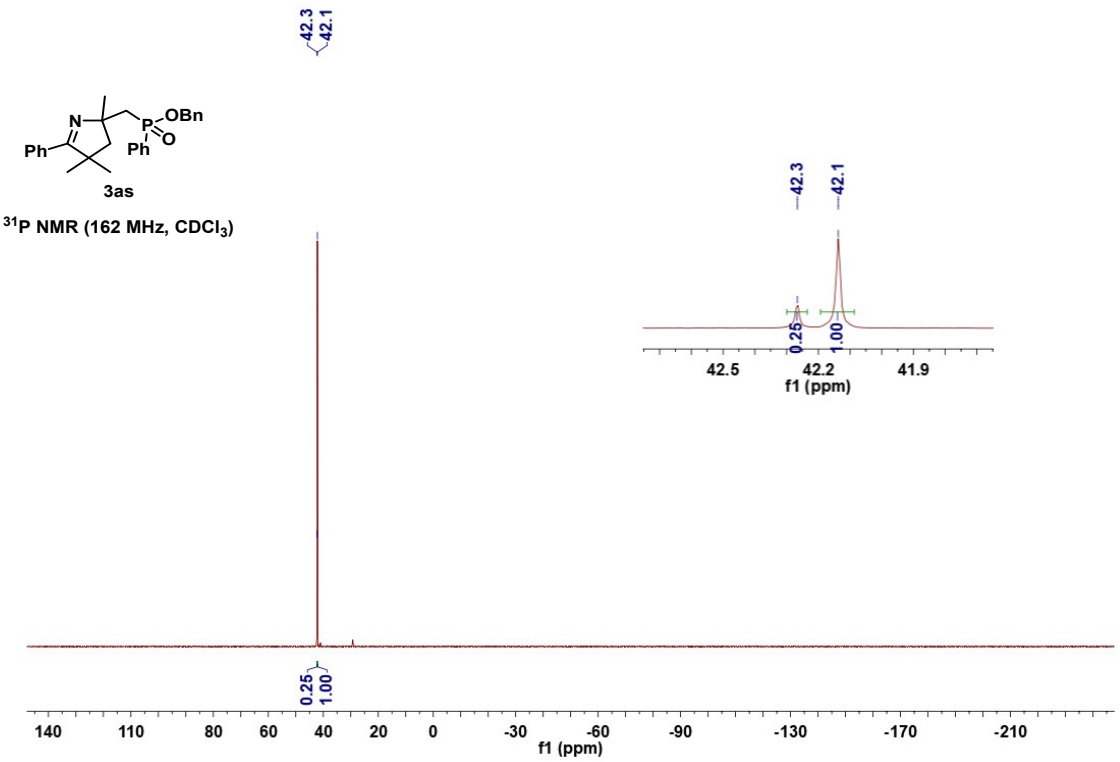
^{1}H NMR (400 MHz, $CDCl_3$)

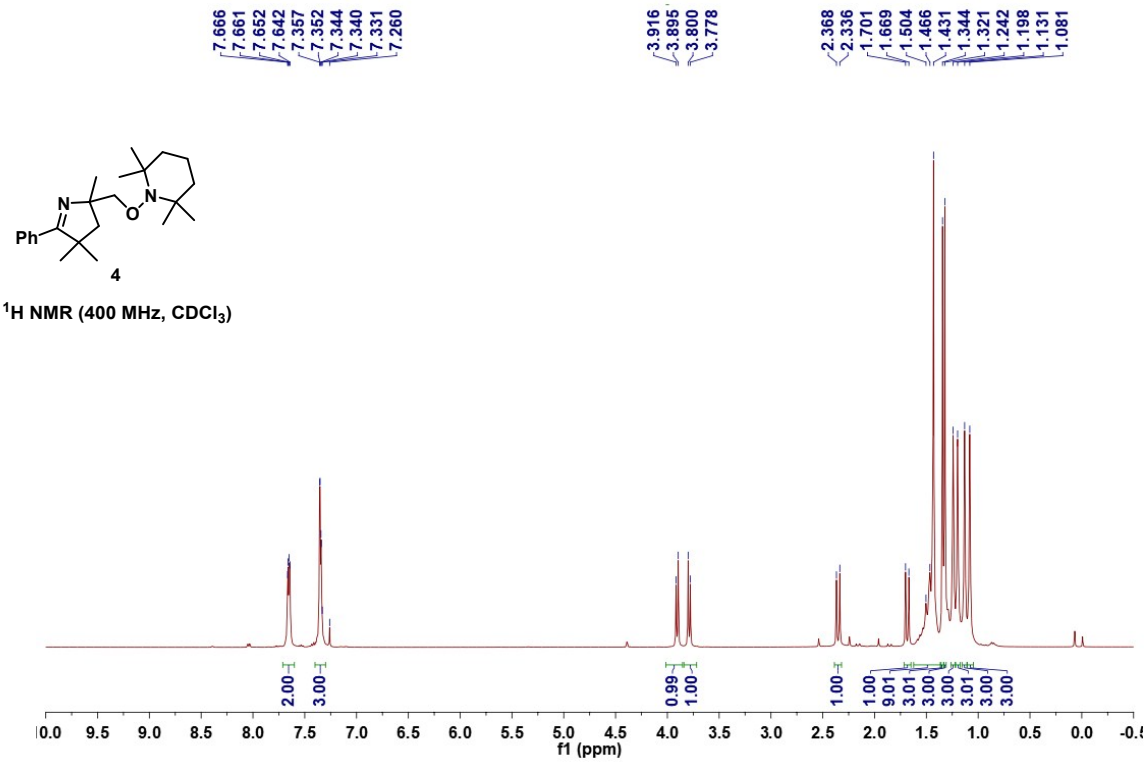




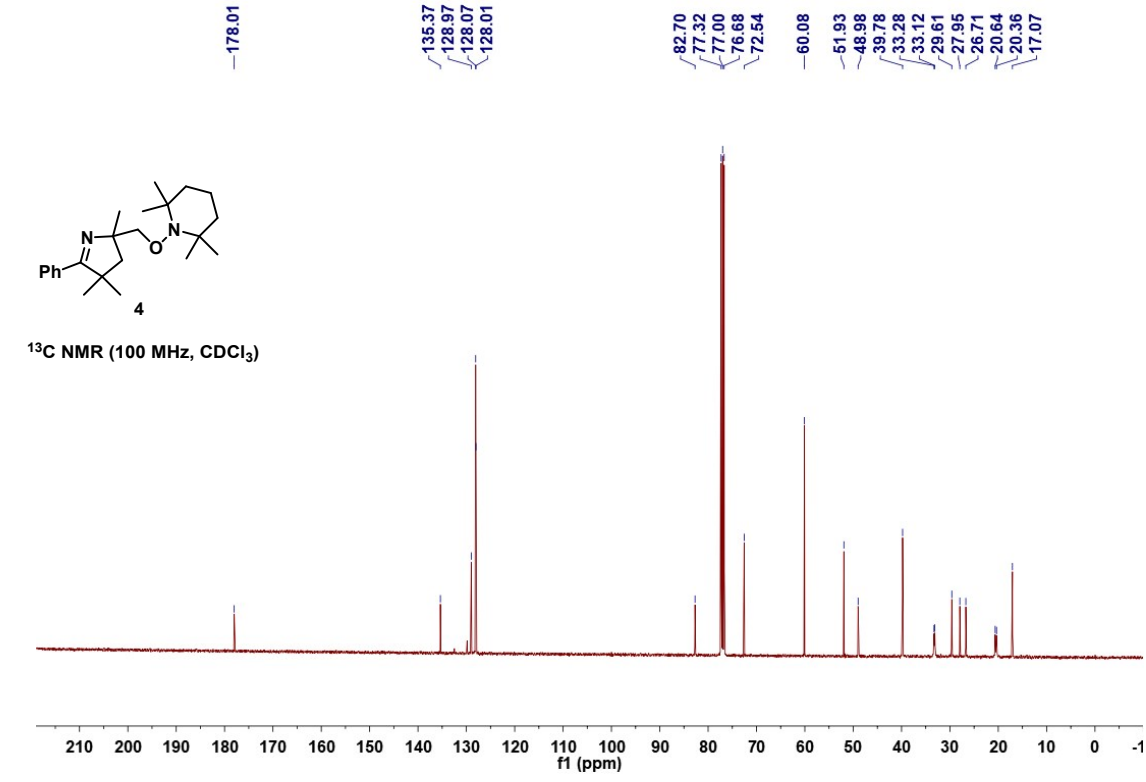
3as

^{13}C NMR (100 MHz, $CDCl_3$)

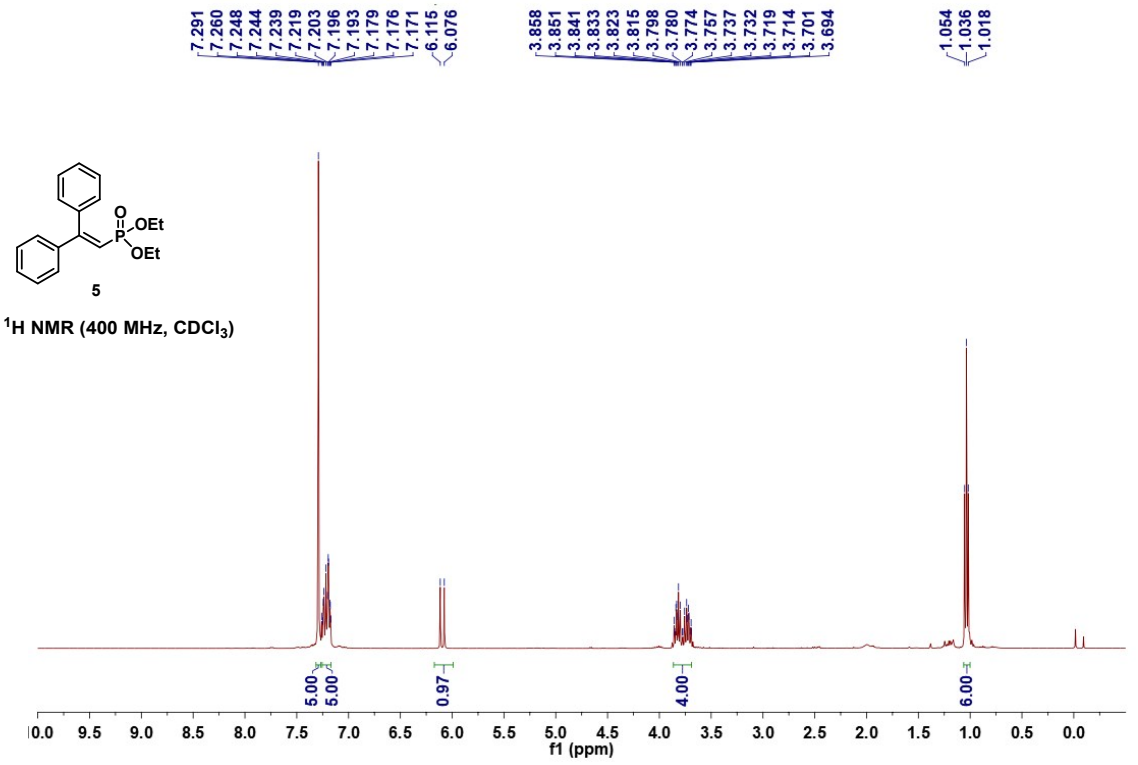

42.3
42.1
N
P
OBn
O
Ph
Ph
3as
31P NMR (162 MHz, CDCl3)
42.3
42.1
0.25
1.00
42.5
42.2
41.9
f1 (ppm)
0.25
1.00
140
110
80
60
40
20
0
-30
-60
-90
-130
-170
-210
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)

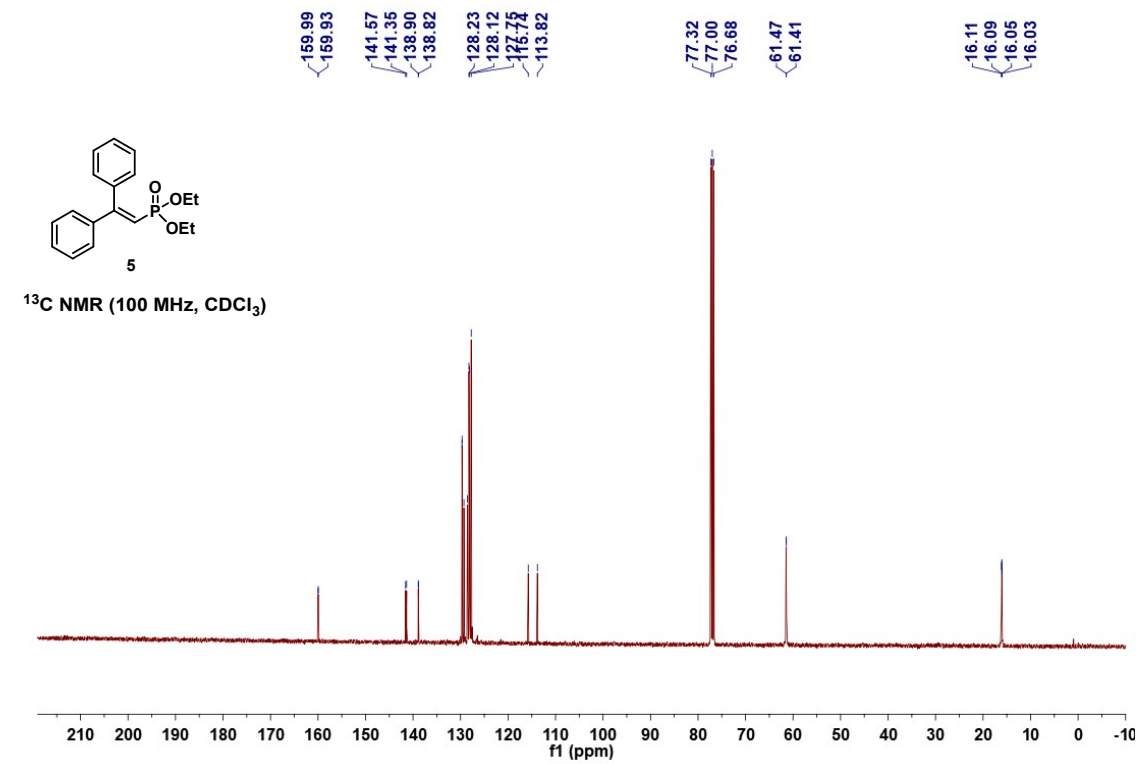


^{13}C NMR (100 MHz, $CDCl_3$)



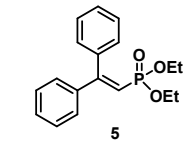
5

^{1}H NMR (400 MHz, $CDCl_3$)



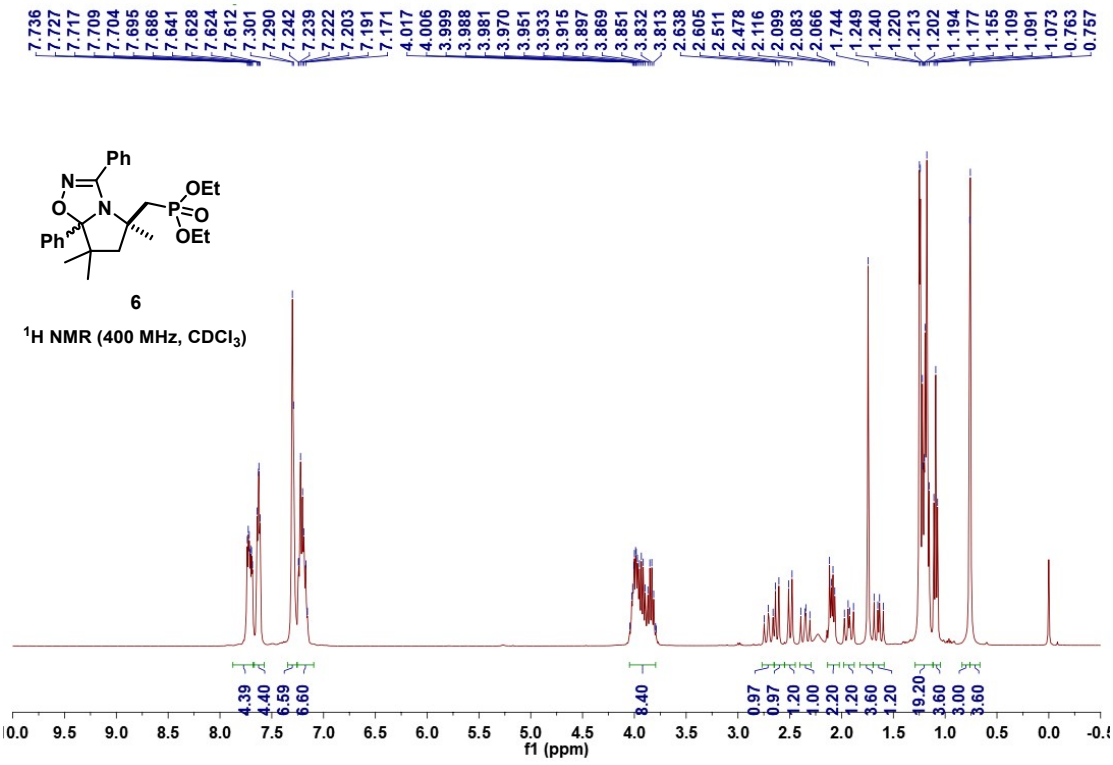
5

^{13}C NMR (100 MHz, $CDCl_3$)



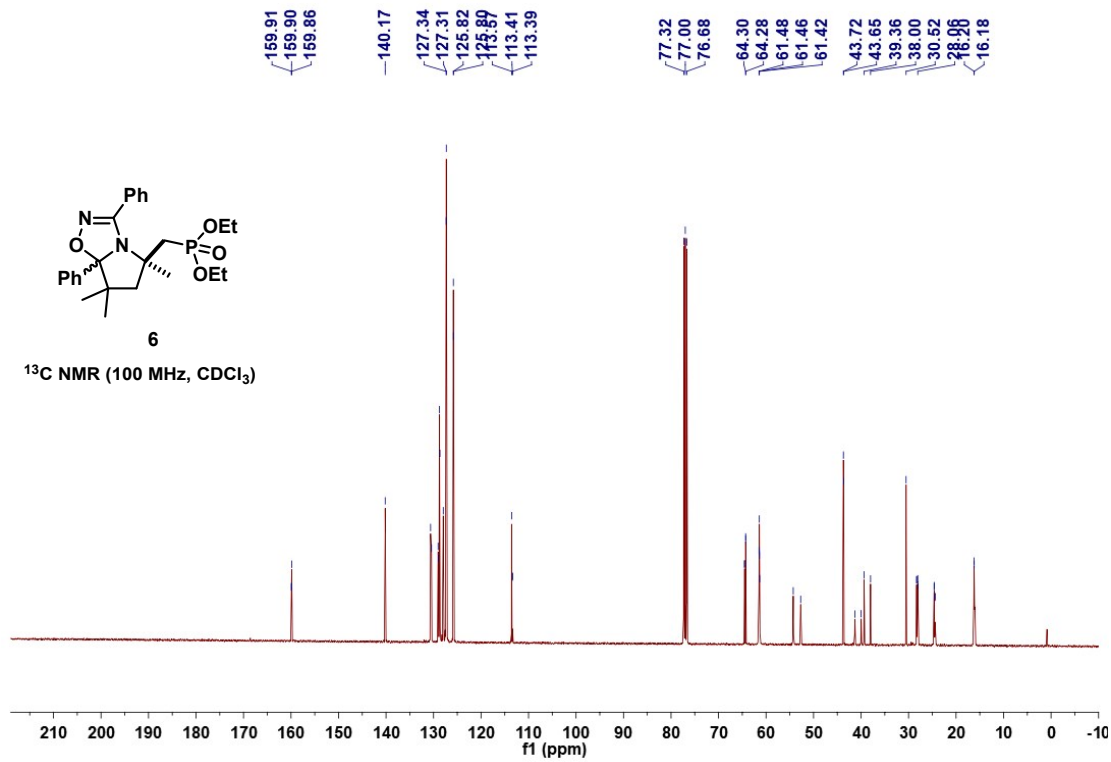
5

^{31}P NMR (162 MHz, $CDCl_3$)



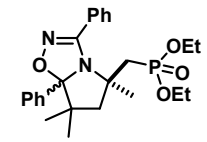
6

^{1}H NMR (400 MHz, $CDCl_3$)



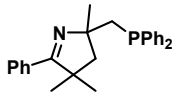
6

^{13}C NMR (100 MHz, $CDCl_3$)



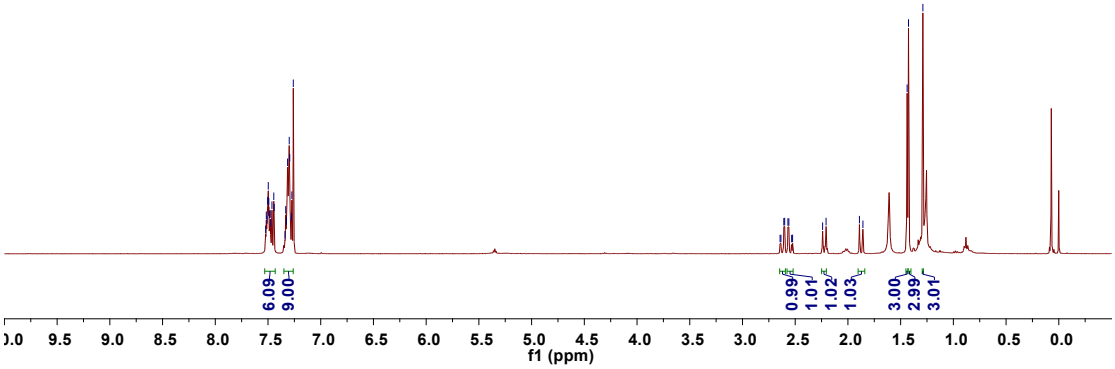
6

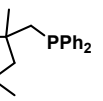
^{31}P NMR (162 MHz, $CDCl_3$)



7

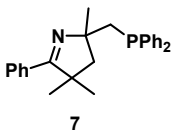
^{1}H NMR (400 MHz, $CDCl_3$)





7

^{13}C NMR (100 MHz, $CDCl_3$)



7

^{31}P NMR (162 MHz, $CDCl_3$)