# Functionalization of λ$^5$-Phosphinines *via* Metalation Strategies – A New Route towards Fluorescent 3D-Aromatics.

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# SUPPORTING INFORMATION

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# GENERAL INFORMATION

All reactions were carried out under dry argon or nitrogen atmosphere with anhydrous solvents in flame-dried glassware, unless otherwise stated. Syringes, which were used to transfer anhydrous solvents or reagents, were purged with argon or nitrogen three times prior to use. THF (stabilized) was purchased in 99.5 % purity from Acros Organics. Lithium amylate and diethylzinc (both as solution in heptanes) were obtained from Sigma-Aldrich. Titration of Grignard reagents was performed with benzoic acid in THF at 0 °C, using 4-phenylazodiphenylamine as indicator. Zinc–species were titrated against iodine in THF at 0 °C.

**Chromatographic purifications** were performed using silica gel ($SiO_2$, 0.040-0.063 mm, 230-400 mesh ASTM) from Merck. The spots were visualized under UV (254 nm) or by staining the TLC plate with $KMnO_4$ solution ($K_2CO_3$, 10 g – $KMnO_4$, 1.5 g – $H_2O$, 150 mL – NaOH 10% in $H_2O$, 1.25 mL). Yields refer to isolated yields of compounds estimated to be >95% pure as determined by $^1$H-NMR.

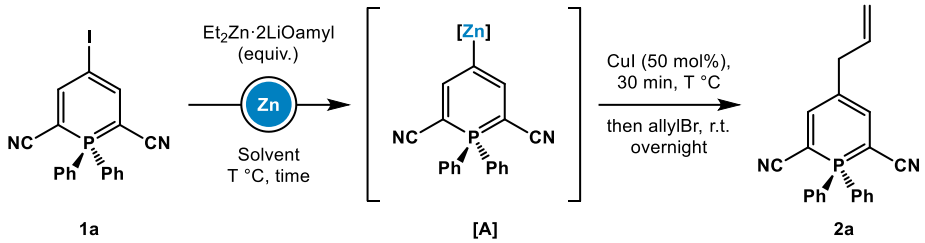
The **$^{13}$C, $^{31}$P and $^1$H-NMR** spectra were recorded on Bruker DRX 500, ARX 300 and AC 300 spectrometer. Chemical shifts are reported as δ values in ppm relative to the residual solvent peak ($^1$H-NMR, $^{13}$C-NMR) in deuterated chloroform ($CDCl_3$: δ 7.26 ppm for $^1$H-NMR and δ 77.16 ppm for $^{13}$C-NMR) or deuterated MeOD (MeOD-$d_4$: δ 3.31 ppm for $^1$H-NMR and δ 49.00 ppm for $^{13}$C-NMR). Abbreviations for signal coupling are as follows: s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintuplet), m (multiplet) and br (broad).

**High resolution mass spectra (HRMS)** were recorded on a Bruker Impact II (ESI) or GC Orbitrap Exploris (Thermo Fisher, EI/CI). Reagents, whose preparation is not described were obtained from commercial sources.

**Fluorescence spectra and absolute emission quantum yields** were measured with a *FLS1000* spectrometer from *Edinburgh Instruments* equipped with a cooled photomultiplier detector PMT-980. A xenon arc lamp Xe2 (450 W) was used for excitation. Absolute luminescence quantum yields $\Phi$ were determined using an integration sphere from *Edinburgh Instruments*. Relative uncertainty of $\Phi$ is estimated to be ± 10%.

# OPTIMIZATION TABLES

## X/Zn exchange




1a [A] 2a

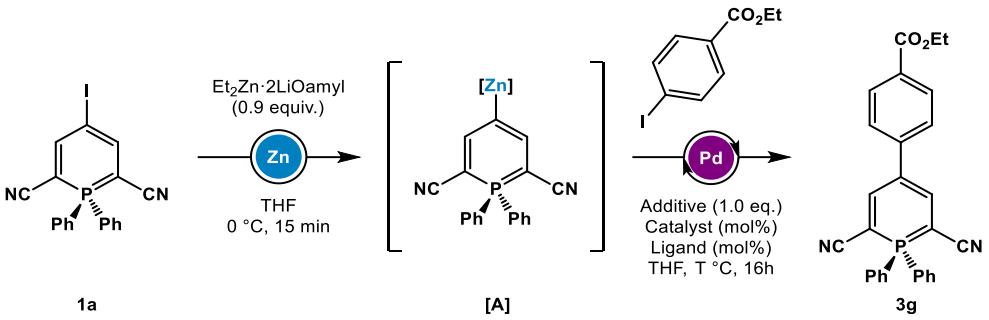
| Entry | Equiv. [Zn] | Solvent | T °C | Time | Metalation | Yield[a] |
|---|---|---|---|---|---|---|
| **1** | 0.9 | Toluene | rt | 17 h | Partial | - |
| **2** | 0.9 | Toluene/THF (1:1) | rt | 5 min | Complete | 16% |
| **3** | 0.9 | THF | rt | 5 min | Complete | 56% |
| **4** | 0.7 | THF | rt | 1 h | Partial | Traces |
| **5** | 0.9 | THF | 0 °C | 5 min | Complete | 44%[b] |
| **6** | 0.9 | THF | 0 °C | 5 min | Complete | 71% |
| **7** | 0.9 | THF | -20 °C | 5 min | Complete | 47% |
| **8** | 0.9 | THF | -40 °C | 1 h | Partial | Traces |
| **9** | 0.9 | THF | -78 °C | 1 h | Partial | - |

[a] isolated yields; [b] 2 h of reaction time

Observations:

Using 0.9 equivalent of the exchange reagent seemed essential for achieving complete metalation of the iodo-phosphinine **1a** (**Entry 3**). Changing the solvent did not improve the yield (**Entries 1 and 2**); however, a decrease in temperature generally reduced the level of degradation in the reaction mixture. Metalation at 0 °C for 5 minutes resulted in the desired allylated product **2a** with the highest yield of 71% (**Entry 6**).

## Negishi coupling



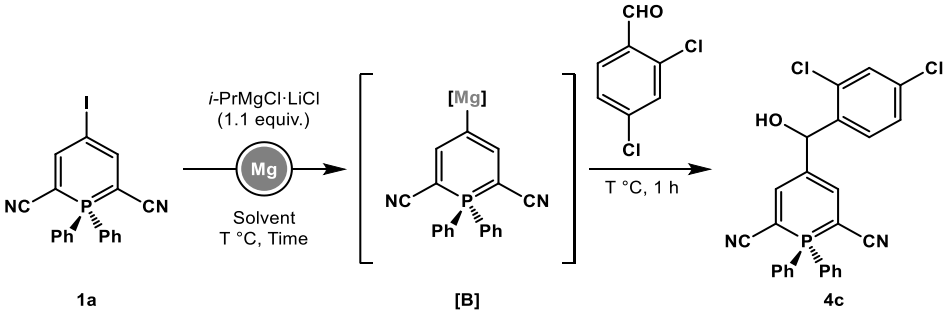

| Entry | Additive | Catalyst | mol% | Ligand | mol% | T °C | Yield[a] |
|---|---|---|---|---|---|---|---|
| **1** | - | $Pd(dba)_2$ | 3 | P(*o*-furyl)$_3$ | 6 | 0 °C | 23% |
| **2** | - | $Pd(dba)_2$ | 3 | SPhos | 6 | 0 °C | 20% |
| **3** | - | $Pd(dba)_2$ | 3 | RuPhos | 6 | 0 °C | 23% |
| **4** | - | Pd-PEPPSI-*i*Pent | 3 | - | | 0 °C | - |
| **5** | - | $Pd(OAc)_2$ | 3 | DavePhos | 6 | 0 °C | Traces |
| **6** | - | $Pd_2(dba)_3$ | 3 | SPhos | 6 | 0 °C | Traces |
| **7** | - | $Pd(dba)_2$ | 5 | P(*o*-furyl)$_3$ | 8 | 0 °C | 28% |
| **8** | $Bu_4NBr$ | $Pd(dba)_2$ | 5 | P(*o*-furyl)$_3$ | 8 | r.t. | 19% |
| **9** | $ZnCl_2$ | $Pd(dppf)Cl_2$ | 5 | - | | r.t. | 19% |
| **10** | $ZnCl_2$ | $Pd(dba)_2$ | 5 | P(*o*-furyl)$_3$ | 8 | 0 °C | 31% |
| **11** | $ZnCl_2$ | $Pd(dba)_2$ | 5 | P(*o*-furyl)$_3$ | 8 | r.t. | 50% |

[a] isolated yields

Observations:

After screening several palladium catalysts and ligands, $Pd(dba)_2$ and P(o-furyl)$_3$ appeared to be the optimal combination for the Negishi coupling of iodo-phosphinines (**Entries 1–7**). To reduce degradation of the zinc intermediate, the coupling was initially carried out at 0 °C, but this did not result in high yields. However, the addition of zinc chloride and raising the temperature to room temperature led to the desired functionalized phosphinine **3g** with 50% yield (**Entry 11**).

## X/Mg exchange




| Entry | Solvent | T °C | Time | Metalation | Yield[a] |
|---|---|---|---|---|---|
| **1** | THF | 0 °C | 15 min | Complete | Traces |
| **2** | THF | -20 °C | 1 h | Partial | - |
| **3** | THF | -40 °C | 2 h | Partial | - |
| **4** | THF | -10 °C | 15 min | Complete | 38% |
| **5** | $Et_2O$ | -10 °C | 1 h | - | - |
| **6** | Dioxane | r.t. | 1 h | Partial | - |

[a] isolated yields

Observations:

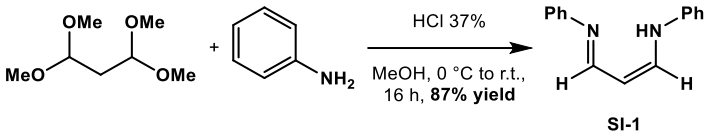
The desired alcohol **4c** was obtained in 38% yield when the metalation was performed at -10 °C (**Entry 4**). Higher temperatures resulted in degradation of the mixture, while lower temperatures or solvent changes did not lead to any conversion of the iodo-phosphinine **1a**.

These metalation conditions (**Entry 4**) were used with others electrophilic quenches, such as $CO_2$, which resulted in the desired product **4b** with 72% yield. Therefore, these optimized conditions were used for all the iodine/magnesium exchanges.

# EXPERIMENTAL DATA OF PRODUCTS

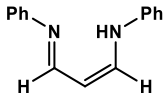
## Preparation of $\lambda^5$-Phosphinines

### (*1E,3E*)-$N_1$,$N_3$-Diphenylpropane-1,3-diimine (SI-1)




SI-1

According to previously reported procedure,[1,2] conc. HCl (6 mL, 31 mmol, 1.0 equiv.) was added to a solution of 1,1,3,3-tetramethoxypropane (5.1 mL, 31 mmol, 1.0 equiv.) and aniline (5.6 mL, 62 mmol, 2.0 equiv.) in 75 mL dry methanol at 0 °C. After stirring the mixture for 16 h at r.t., the mixture was concentrated *in vacuo*. The crude dialdimine was recrystallized from methanol to give the desired product **SI-1** as yellow solid (5.9 g, 27 mmol, 87% yield).



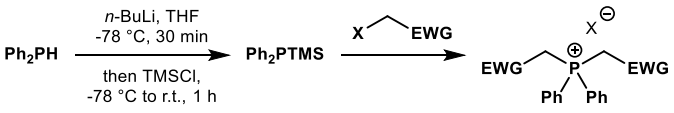

**$^1$H NMR (500 MHz, MeOD)** δ 8.72 (d, *J* = 11.6 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 4H), 7.39 (d, *J* = 8.1 Hz, 4H), 7.27 (t, *J* = 7.5 Hz, 2H), 6.28 (t, *J* = 11.6 Hz, 1H).

**$^{13}$C NMR (126 MHz, MeOD)** δ 159.7, 139.8, 131.1, 127.7, 118.8, 99.4, 49.5, 49.3, 49.2, 49.0, 48.8, 48.7, 48.5.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{15}H_{14}N_2H^+$: 223.1230 found: 223.1232.

Spectral characteristics are similar with previously reported data.[1,2]

### General Procedure A for Phosphonium Salt Synthesis



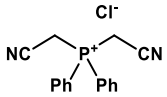

SI-2 SI-3

According to previously reported procedure,[3,4] a flamed-dried flask purged with argon was charged with diphenylphosphine (3.7 mL, 22 mmol, 1.0 equiv.) and 50 mL of dry THF. The resulting colorless solution was cooled to -78 °C and *n*-BuLi (16.4 mL, 33 mmol, 1.5 equiv., 2.5 M) was then added dropwise, the resulting orange mixture was stirred for 30 min at -78 °C. Finally, TMSCl (4.22 mL, 33 mmol, 1.5 equiv.) was added dropwise and the crude colorless mixture was allowed to stir at r.t. for 1 h. Pentane (20 mL) was then added to complete precipitation of LiCl and the reaction crude filtered through a pad of Celite (under argon). 2x10 mL of pentane were added to wash the pad and the solvents

were removed under vacuo using the Schlenk line. The obtained diphenyl(TMS)phosphane **SI-2** was not isolated and was engaged directly in the next step.

An excess of the electrophile (110 mmol, 5.0 equiv.) was added to diphenyl(TMS)phosphane **SI-2** (22 mmol, 1.0 equiv.) under argon and the mixture was stirred at the corresponding temperature. The precipitate was then filtered using $CHCl_3$ and washed with $Et_2O$. Finally, the white phosphonium salt **SI-3** was dried under vacuum for 2 h at 70 °C.

**Bis(cyanomethyl)diphenylphosphonium chloride (SI-3a)**




Phosphonium salt **SI-3a** was synthesized according to general procedure **A**, with chloroacetonitrile (6.98 mL, 110 mmol, 5.0 equiv.). Reaction mixture was stirred for two days at 60 °C to afford the white salt (3.5 g, 11.5 mmol, 52% yield over 2 steps).

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.13 (dd, *J* = 13.6, 7.8 Hz, 4H), 8.01 – 7.88 (m, 2H), 7.81 (td, *J* = 7.7, 3.9 Hz, 4H), 6.10 (d, *J* = 17.1 Hz, 4H).

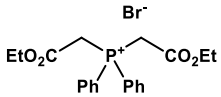
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 137.1 (d, *J* = 3.4 Hz), 134.2 (d, J = 10.6 Hz), 131.0 (d, *J* = 13.5 Hz), 112.9 (d, *J* = 86.4 Hz), 110.6 (d, *J* = 9.5 Hz), 15.6 (d, *J* = 55.6 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 24.7.

**HRMS (ESI)** m/z: $[M]^+$ calcd for $C_{16}H_{14}N_2P^+$: 265.0889 found: 265.0891.

Spectral characteristics are similar with previously reported data.[2]

**Bis(2-ethoxy-2-oxoethyl)diphenylphosphonium bromide (SI-3b)**




Phosphonium salt **SI-3b** was synthesized according to general procedure **A**, with ethyl 2-bromoacetate (12.2 mL, 110 mmol, 5.0 equiv.). Reaction mixture was stirred for two hours at r.t. to afford the white salt (4.4 g, 10.1 mmol, 46% yield over 2 steps).

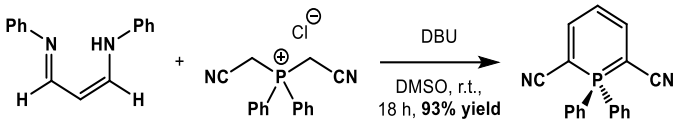
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.02 (dd, *J* = 13.7, 7.1 Hz, 4H), 7.78 – 7.70 (m, 2H), 7.62 (td, *J* = 7.8, 3.6 Hz, 4H), 5.15 (d, *J* = 13.9 Hz, 4H), 4.00 (q, *J* = 7.1 Hz, 4H), 1.03 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 164.7 (d, *J* = 3.4 Hz), 135.1 (d, *J* = 3.1 Hz), 133.8 (d, *J* = 10.8 Hz), 130.0 (d, *J* = 13.4 Hz), 116.8 (d, *J* = 88.5 Hz), 62.9, 31.6 (d, *J* = 58.1 Hz), 13.8.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 20.4.

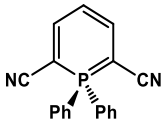
**HRMS (ESI)** m/z: $[M]^+$ calcd for $C_{20}H_{24}O_4P^+$: 359.1407 found: 359.1404.

**1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (SI-4)**




SI-1 SI-3a SI-4

According to previously reported procedure,[2] bis(cyanomethyl)diphenylphosphonium chloride **SI-3a** (3.3 g, 11.0 mmol, 1.0 equiv.) and dialdimine **SI-1** (2.9 g, 13.2 mmol, 1.2 equiv.) were dissolved in DMSO (55 mL). After DBU (3.28 mL, 22.0 mmol, 2.0 equiv.) was added, the mixture was stirred for 18 h at r.t. The reaction mixture was added 1M HCl aq. and stirred for 15 min, and extracted three times with EtOAc. The combined organic layer was washed with brine, dried by $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified by a column chromatography on silica gel (Pentane/Acetone 80:20) to give DCNP **SI-4** as a yellow solid (3.0 g, 10.2 mmol, 93% yield).




**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.72 – 7.60 (m, 10H), 7.43 (dd, *J* = 27.6, 8.4 Hz, 2H), 5.46 (td, *J* = 8.4, 2.3 Hz, 1H).

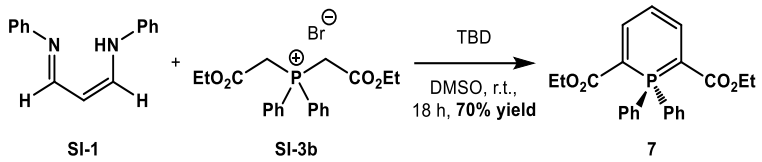
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 146.8 (d, *J* = 2.4 Hz), 133.7 (d, *J* = 3.0 Hz), 132.6 (d, *J* = 11.5 Hz), 129.8 (d, *J* = 13.4 Hz), 126.1 (d, *J* = 92.8 Hz), 119.1 (d, *J* = 12.1 Hz), 103.0 (d, *J* = 12.8 Hz), 57.8 (d, *J* = 109.2 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 11.9.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{19}H_{12}N_2PH^+$: 301.0889 found: 301.0889.

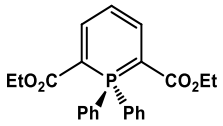
Spectral characteristics are similar with previously reported data.[2]

**Diethyl 1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (7)**




SI-1 SI-3b 7

According to an adaptation of previous reported procedure,[5] bis(2-ethoxy-2-oxoethyl)diphenylphosphonium bromide **SI-3b** (4.4 g, 10.0 mmol, 1.0 equiv.) and dialdimine **SI-1** (2.7 g, 12.0 mmol, 1.2 equiv.) were dissolved in DMSO (20 mL). After TBD (2.8 g, 20.0 mmol, 2.0 equiv.) was added, the mixture was stirred for 18 h at r.t. The reaction mixture was added 1M HCl aq. and stirred for 15 min, and extracted three times with EtOAc. The combined organic layer was washed with brine, dried by $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified by a column chromatography on silica gel (Pentane/Acetone 90:10) to give $DCO_2EtP$ **7** as an orange solid (2.8 g, 7.0 mmol, 70% yield).



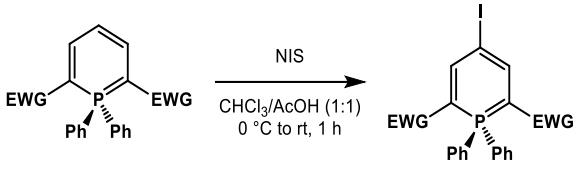

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.01 (dd, *J* = 28.7, 8.3 Hz, 2H), 7.90 – 7.74 (m, 4H), 7.58 – 7.43 (m, 6H), 5.45 (td, *J* = 8.4, 2.2 Hz, 1H), 3.99 (q, *J* = 7.1 Hz, 4H), 1.01 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 167.0 (d, *J* = 12.2 Hz), 146.3 (d, *J* = 4.2 Hz), 133.6 (d, *J* = 11.4 Hz), 131.3 (d, *J* = 3.1 Hz), 128.1 (d, *J* = 96.0 Hz), 128.0 (d, *J* = 13.3 Hz), 100.9 (d, *J* = 12.9 Hz), 82.1 (d, *J* = 101.7 Hz), 59.9, 14.3.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 6.4.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{23}H_{23}O_4PH^+$: 395.1407 found: 395.1408.

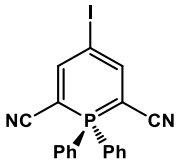
**General Procedure B for Iodination of Phosphinines**




**SI-4**, 7 **1a**, **1b**

According to previously reported procedure,[6] the corresponding phosphinine (10 mmol, 1.0 equiv.) was dissolved in $CHCl_3$ and AcOH (0.1 M, 1:1 ratio) and *N*-iodosuccinimide (20 mmol, 2.0 equiv.) was added at 0 °C by portion. The solution was then stirred at 0 °C for 15 min, at r.t. for 1 h and was then quenched with water, washed with sat. aq. $Na_2S_2O_3$ and extracted 3 times with DCM. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by silica gel column to give the corresponding iodo-phosphinine.

**4-iodo-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (1a)**




I-DCNP **1a** was synthesized according to general procedure **B** and the crude product was quickly purified with 100% DCM to afford the pure dark orange solid (4.0 g, 9.4 mmol, 94% yield).

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.82 – 7.60 (m, 12H).

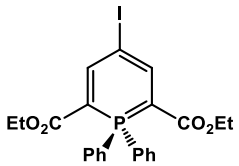
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 153.2 (d, *J* = 2.1 Hz), 134.2 (d, *J* = 3.1 Hz), 132.7 (d, *J* = 11.5 Hz), 130.0 (d, *J* = 13.7 Hz), 125.1 (d, *J* = 93.8 Hz), 117.6 (d, *J* = 11.8 Hz), 61.7 (d, *J* = 109.4 Hz), 55.3 (d, *J* = 11.1 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 8.7.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{19}H_{12}IN_2PH^+$: 426.9856 found: 426.9856.

Spectral characteristics are similar with previously reported data.[6]

**Diethyl 4-iodo-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (1b)**




I-DCO$_2$EtP **1b** was synthesized according to general procedure **B** and the crude product was quickly purified with 100% DCM to afford the pure brown solid (4.9 g, 9.5 mmol, 95% yield).

**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.23 (d, *J* = 27.6 Hz, 2H), 7.89 – 7.67 (m, 4H), 7.57 – 7.40 (m, 6H), 3.99 (q, *J* = 7.2 Hz, 4H), 1.03 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 165.8 (d, *J* = 11.8 Hz), 153.1 (d, *J* = 3.9 Hz), 133.7 (d, *J* = 11.4 Hz), 131.7 (d, *J* = 3.2 Hz), 128.2 (d, *J* = 13.6 Hz), 127.1 (d, *J* = 97.2 Hz), 85.7 (d, *J* = 102.9 Hz), 60.3, 56.5 (d, *J* = 11.6 Hz), 14.3.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 3.2.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{23}H_{22}IO_4PH^+$: 521.0379 found: 521.0379.

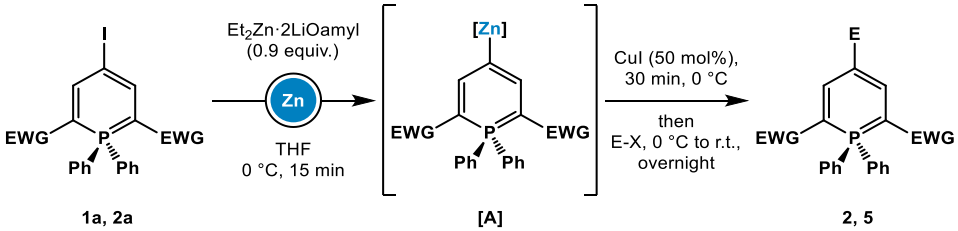
# I/Zn Exchange

### Preparation of $Et_2Zn{\cdot}2LiOamyl$

The exchange reagent $Et_2Zn{\cdot}2LiOamyl$ was prepared according to reported literature.[ref] A multiple times flame-dried Schlenk-flask equipped with stirring bar was charged with lithium *tert*-amylate in heptanes (20 mmol, 2.0 equiv.). A carefully titrated solution of $Et_2Zn$ in heptanes (10 mmol, 1.0 equiv.) was added dropwise at r.t. and the reaction mixture was allowed to stir for 2 h at r.t. Iodometric titration of the exchange reagent gave concentrations ranging from 0.56 to 0.58 M, corresponding to yields of 93 to 97% of $Et_2Zn{\cdot}2LiOamyl$.

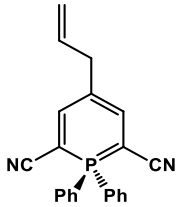
## Allylation, Acylation and Other Functionalizations

### General Procedure C for Allylation and Acylation of Iodinated Phosphinines




A flame-dried Schlenk flask was charged with the respective iodo-phosphinine (0.20 mmol, 1.0 equiv.) and dry THF (1 mL) was added. $Et_2Zn{\cdot}2LiOamyl$ (0.18 mmol, 0.9 equiv.) was added dropwise at 0 °C, and the reaction mixture was allowed to stir at this temperature for 15 min. Solid copper(I) iodide (0.1 mmol, 50 mol%) was added in one portion to the mixture, and the solution was allowed to stir for 30 min at 0 °C. The respective electrophile (0.4 mmol, 2.0 equiv. or as specified) was added to the mixture and the Schlenk flask was sealed and the mixture stirred overnight at r.t. Then, sat. aq. $NH_4Cl$ (2 mL) was added, followed by water (5 mL) and the mixture was transferred to a separatory funnel. The aqueous fraction was extracted with EtOAc (3 × 10 mL), the combined organic phases were washed with brine (20 mL) and dried over anhydrous $MgSO_4$. Filtration, concentration *in vacuo*, and purification by flash column chromatography ($SiO_2$) furnished the desired functionalized phosphinines.

**4-Allyl-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2a)**




According to general procedure **C**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using allylbromide (35 μL, 0.40 mmol, 2.0 equiv.). The crude product was purified with a mixture pentane/acetone (90:10) to afford the pure dark orange oil **2a** (48 mg, 0.14 mmol, 71% yield).

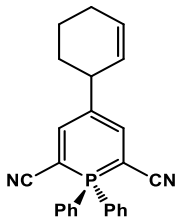
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.75 – 7.56 (m, 10H), 7.29 (d, *J* = 27.2 Hz, 2H), 5.87 – 5.73 (m, 1H), 5.12 – 4.95 (m, 2H), 2.95 (d, *J* = 6.5 Hz, 2H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 147.1 (d, *J* = 2.5 Hz), 137.2, 133.6 (d, *J* = 3.1 Hz), 132.5 (d, *J* = 11.5 Hz), 129.7 (d, *J* = 13.3 Hz), 126.1 (d, *J* = 92.8 Hz), 119.3 (d, *J* = 12.3 Hz), 116.3, 113.2 (d, *J* = 10.0 Hz), 57.0 (d, *J* = 110.1 Hz), 39.2.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 10.6.

**HRMS (EI)** m/z: [M] calcd for $C_{22}H_{17}N_2P$: 340.1124 found: 340.1124.

**4-(Cyclohex-2-en-1-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2b)**




According to general procedure **C**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 3-bromocyclohex-1-ene (46 μL, 0.40 mmol, 2.0 equiv.). The crude product was purified with a mixture pentane/acetone (90:10) to afford the pure orange oil **2b** (60 mg, 0.16 mmol, 79% yield).

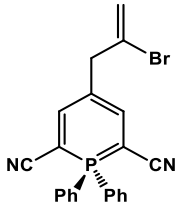
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.72 – 7.57 (m, 10H), 7.32 (d, *J* = 27.5 Hz, 2H), 5.95 – 5.82 (m, 1H), 5.49 (dd, *J* = 10.1, 2.7 Hz, 1H), 2.99 – 2.90 (m, 1H), 2.02 (s, 1H), 1.91 – 1.82 (m, 1H), 1.70 – 1.59 (m, 1H), 1.59 – 1.51 (m, 1H), 1.41 – 1.31 (m, 1H), 1.29 – 1.24 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 146.5 (d, *J* = 2.4 Hz), 133.5 (d, *J* = 3.0 Hz), 132.4 (d, *J* = 11.4 Hz), 129.7, 129.6 (d, *J* = 13.4 Hz), 129.3, 126.3 (d, *J* = 92.5 Hz), 120.1 (d, *J* = 8.9 Hz), 56.6 (d, *J* = 110.5 Hz), 40.8, 32.5, 24.9, 20.6.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 11.0.

**HRMS (EI)** m/z: [M] calcd for $C_{25}H_{21}N_2P$: 380.1437 found: 380.1428.

**4-(2-Bromoallyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2c)**




According to general procedure **C**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 2,3-dibromoprop-1-ene (39 µL, 0.40 mmol, 2.0 equiv.). The crude product was purified with a mixture pentane/acetone (95:5 to 90:10) to afford the pure orange/brown oil **2c** (51 mg, 0.12 mmol, 61% yield).

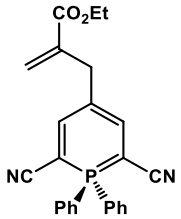
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.75 – 7.60 (m, 10H), 7.31 (d, *J* = 27.1 Hz, 2H), 5.59 (d, *J* = 2.0 Hz, 1H), 5.46 (d, *J* = 1.9 Hz, 1H), 3.26 (s, 2H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 147.5 (d, *J* = 2.5 Hz), 133.8 (d, *J* = 3.2 Hz), 133.6, 132.6 (d, *J* = 11.5 Hz), 129.8 (d, *J* = 13.4 Hz), 125.7 (d, *J* = 92.9 Hz), 119.0 (d, *J* = 12.3 Hz), 117.8, 110.9 (d, *J* = 10.3 Hz), 57.8 (d, *J* = 109.8 Hz), 46.9.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 10.5.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{22}H_{16}BrN_2PH^+$: 419.0307 found: 419.0225.

**Ethyl 2-((2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)methyl)acrylate (2d)**




According to general procedure **C**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using ethyl 2-(bromomethyl)acrylate (55 µL, 0.40 mmol, 2.0 equiv.). The crude product was purified with a mixture pentane/acetone (80:20) to afford the pure orange solid **2d** (48 mg, 0.12 mmol, 59% yield).

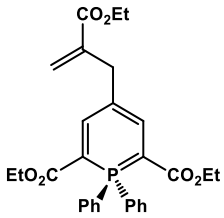
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.74 – 7.58 (m, 10H), 7.32 (d, *J* = 27.3 Hz, 2H), 6.18 (s, 1H), 5.49 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.17 (s, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 166.6, 147.5 (d, *J* = 2.4 Hz), 140.2, 133.6 (d, *J* = 3.2 Hz), 132.5 (d, *J* = 11.5 Hz), 129.7 (d, *J* = 13.4 Hz), 126.0 (d, *J* = 92.9 Hz), 125.8, 119.2 (d, *J* = 12.0 Hz), 112.1 (d, *J* = 10.2 Hz), 60.9, 57.2 (d, *J* = 109.8 Hz), 37.6, 14.3.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 10.3.

**HRMS (EI)** m/z: [M] calcd for $C_{25}H_{21}N_2O_2P$: 412.1335 found: 412.1324.

**diethyl 4-(2-(ethoxycarbonyl)allyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate** (**5a)**




According to general procedure **C**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.), using ethyl 2-(bromomethyl)acrylate (55 µL, 0.40 mmol, 2.0 equiv.). The crude product was purified with a mixture pentane/acetone (95:5 to 90:10) to afford the pure orange oil **5a** (80 mg, 0.16 mmol, 79% yield).

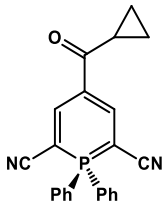
**$^1$H NMR (500 MHz, CDCl$_3$)** δ 7.87 (d, *J* = 28.3 Hz, 2H), 7.81 – 7.71 (m, 4H), 7.53 – 7.42 (m, 6H), 6.18 (d, *J* = 1.6 Hz, 1H), 5.48 (d, *J* = 1.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.97 (q, *J* = 7.1 Hz, 4H), 3.27 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 167.4, 167.0 (d, *J* = 11.9 Hz), 147.4 (d, *J* = 4.4 Hz), 141.5, 133.5 (d, *J* = 11.4 Hz), 131.3 (d, *J* = 3.2 Hz), 128.0 (d, *J* = 13.3 Hz), 128.0 (d, *J* = 96.3 Hz), 125.3, 109.5 (d, *J* = 10.7 Hz), 81.7 (d, *J* = 102.5 Hz), 60.8, 59.9, 37.7, 14.3, 14.3.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 4.8.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{29}H_{31}O_6PH^+$: 507.1931 found: 507.1929.

**4-(Cyclopropanecarbonyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2e)**




According to general procedure **C**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using cyclopropanecarbonyl chloride (36 µL, 0.40 mmol, 2.0 equiv.). The crude product was purified with a mixture pentane/acetone (80:20) to afford the pure yellow oil **2e** (25 mg, 0.07 mmol, 34% yield).

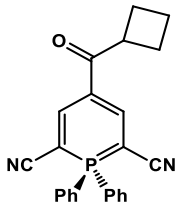
**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.41 (d, *J* = 28.1 Hz, 2H), 7.83 – 7.60 (m, 10H), 2.29 – 2.21 (m, 1H), 1.16 – 1.09 (m, 2H), 1.01 – 0.91 (m, 2H).

**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 194.1, 148.9 (d, *J* = 2.2 Hz), 134.5 (d, *J* = 3.1 Hz), 132.8 (d, *J* = 11.5 Hz), 130.1 (d, *J* = 13.6 Hz), 123.8 (d, *J* = 93.7 Hz), 117.7 (d, *J* = 12.8 Hz), 116.0 (d, *J* = 8.2 Hz), 62.6 (d, *J* = 108.3 Hz), 15.4, 10.8.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 9.1.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{23}H_{17}N_2OPH^+$: 369.1151 found: 369.1151.

**4-(Cyclobutanecarbonyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2f)**



According to general procedure **C**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using cyclobutanecarbonyl chloride (46 µL, 0.40 mmol, 2.0 equiv.). The crude product was purified with a mixture pentane/acetone (95:5 to 90:10) to afford the pure yellow oil **2f** (19 mg, 0.05 mmol, 25% yield).

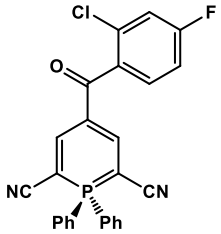
**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.23 (d, *J* = 28.2 Hz, 2H), 7.82 – 7.60 (m, 10H), 3.65 (p, *J* = 8.5 Hz, 1H), 2.47 – 2.28 (m, 2H), 2.27 – 2.13 (m, 2H), 2.10 – 1.97 (m, 1H), 1.93 – 1.81 (m, 1H).

**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 195.2, 149.0 (d, *J* = 2.2 Hz), 134.5 (d, *J* = 3.0 Hz), 134.0 (d, *J* = 3.0 Hz), 132.8 (d, *J* = 11.5 Hz), 132.7 (d, *J* = 13.7 Hz), 130.1 (d, *J* = 13.5 Hz), 129.9, 129.8, 123.7 (d, *J* = 93.7 Hz), 117.6 (d, *J* = 12.9 Hz), 113.6 (d, *J* = 8.2 Hz), 62.6 (d, *J* = 108.0 Hz), 40.7, 25.3, 18.3.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 9.1.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{24}H_{19}N_2OPH^+$: 383.1308 found: 383.1309.

**4-(2-Chloro-4-fluorobenzoyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2g)**



According to general procedure **C**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 2-chloro-4-fluorobenzoyl chloride (53 µL, 0.40 mmol, 2.0 equiv.). The crude product was purified with a mixture pentane/acetone (95:5 to 90:10) to afford the pure yellow solid **2g** (41 mg, 0.09 mmol, 45% yield).

**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.10 (d, J = 28.1 Hz, 2H), 7.81 – 7.66 (m, 10H), 7.29 (dd, J = 8.5, 5.9 Hz, 1H), 7.20 (dd, J = 8.5, 2.4 Hz, 1H), 7.08 (td, J = 8.3, 2.4 Hz, 1H).

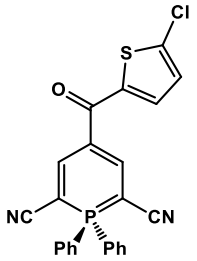
**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 188.5, 163.1 (d, *J* = 253.4 Hz), 150.6, 134.8 (d, *J* = 3.2 Hz), 134.4 (d, *J* = 3.8 Hz), 132.9 (d, *J* = 11.5 Hz), 132.4 (d, *J* = 10.3 Hz), 130.4 (d, *J* = 9.1 Hz), 130.2 (d, *J* = 13.5 Hz), 123.0 (d, *J* = 93.9 Hz), 117.9 (d, *J* = 25.1 Hz), 117.8 (d, *J* = 24.8 Hz), 117.0 (d, *J* = 9.3 Hz), 114.8 (d, *J* = 21.1 Hz), 114.7 (d, *J* = 21.4 Hz), 114.6 (d, *J* = 8.6 Hz), 64.4 (d, *J* = 115.9 Hz).

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 8.8.

**$^{19}$F NMR (471 MHz, CDCl$_3$)** δ -108.1.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{26}H_{15}ClFN_2OPH^+$: 457.0641 found: 457.0641.

**4-(5-Chlorothiophene-2-carbonyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2h)**




According to general procedure **C**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 5-chlorothiophene-2-carbonyl chloride (48 µL, 0.40 mmol, 2.0 equiv.). The crude product was purified with a mixture pentane/acetone (95:5 to 80:20) to afford the pure yellow oil (39 mg, 0.09 mmol, 44% yield).

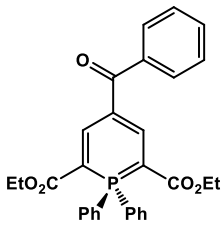
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.31 (d, *J* = 28.1 Hz, 2H), 7.82 – 7.61 (m, 10H), 7.30 (d, *J* = 4.0 Hz, 1H), 6.96 (d, *J* = 4.0 Hz, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 181.3, 150.1 (d, *J* = 1.9 Hz), 141.4, 138.3, 134.7 (d, *J* = 3.0 Hz), 132.9 (d, *J* = 11.7 Hz), 131.7, 130.2 (d, *J* = 13.5 Hz), 127.1, 123.4 (d, *J* = 93.8 Hz), 117.3 (d, *J* = 12.6 Hz), 114.3 (d, *J* = 9.1 Hz), 63.5 (d, *J* = 107.3 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.1.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{24}H_{14}ClN_2OPSH^+$: 445.0326 found: 445.0329.

**diethyl 4-benzoyl-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate** (**5b)**




According to general procedure **C**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.), using benzoyl chloride (45 µL, 0.40 mmol, 2.0 equiv.). The crude product was purified with a mixture pentane/EtOAc (4:1) to afford the pure red solid **5b** (35 mg, 0.07 mmol, 35% yield).

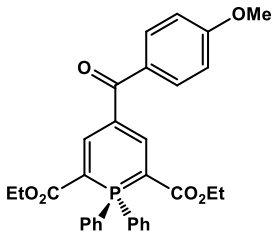
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.81 (d, *J* = 29.2 Hz, 2H), 7.81 (dd, *J* = 13.9, 7.8 Hz, 4H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.61 – 7.37 (m, 9H), 4.02 (q, *J* = 7.1 Hz, 4H), 1.04 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 193.2, 166.1 (d, *J* = 12.8 Hz), 149.8 (d, *J* = 3.7 Hz), 139.6, 133.7 (d, *J* = 11.4 Hz), 132.1 (d, *J* = 3.2 Hz), 130.8, 129.0, 128.4 (d, *J* = 13.5 Hz), 128.2, 125.9 (d, *J* = 97.0 Hz), 112.8 (d, *J* = 9.5 Hz), 87.1 (d, *J* = 100.9 Hz), 60.6, 14.2.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 4.7.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{30}H_{27}O_5PH^+$: 499.1669 found: 499.1674.

**diethyl 4-(4-methoxybenzoyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate** (**5c**)




According to general procedure **C**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.), using 4-methoxybenzoyl chloride (68 mg, 0.40 mmol, 2.0 equiv.). The crude product was purified with a mixture pentane/acetone (3:2) to afford the pure yellow oil **5c** (31 mg, 0.06 mmol, 30% yield).

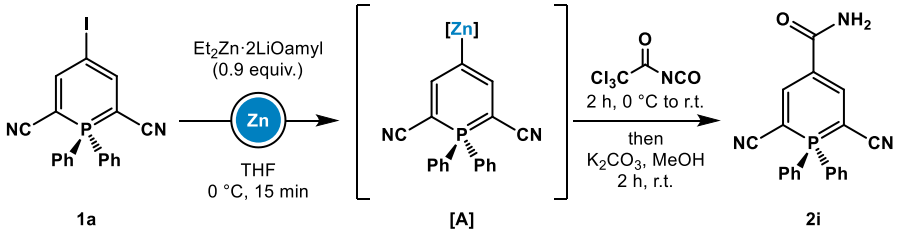
**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.79 (d, *J* = 29.4 Hz, 2H), 7.85 – 7.76 (m, 4H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.60 – 7.44 (m, 6H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.02 (q, *J* = 7.1 Hz, 4H), 3.87 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 192.4, 166.2 (d, *J* = 12.7 Hz), 162.0, 149.8, 133.7 (d, *J* = 11.5 Hz), 132.1 (d, *J* = 3.2 Hz), 131.9, 131.4, 128.4 (d, *J* = 13.5 Hz), 126.1 (d, *J* = 96.8 Hz), 113.5, 113.0 (d, *J* = 9.6 Hz), 86.7 (d, *J* = 100.6 Hz), 60.6, 55.5, 14.3.

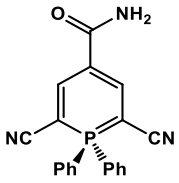
**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 4.3.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{31}H_{29}O_6PH^+$: 529.1775 found: 529.1775.

**2,6-Dicyano-1,1-diphenyl-1λ$^5$-phosphinine-4-carboxamide (2i)**




According to an adaptation of previous reported procedure,[7] a flame-dried Schlenk flask was charged with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.) and dry THF (1 mL) was added. Et$_2$Zn·2LiOamyl (0.18 mmol, 0.9 equiv.) was added dropwise at 0 °C, and the reaction mixture was allowed to stir at this temperature for 15 min. 2,2,2-Trichloroacetyl isocyanate (26 µL, 0.22 mmol, 1.1 equiv.) was then added to the mixture at 0 °C and stirred for 2 h allowing to warm up to r.t. After addition of $K_2CO_3$ (42 mg, 0.30 mmol, 1.5 equiv.) and MeOH (0.5 mL), the reaction mixture was stirred for two additional hours. Then, sat. aq. $NH_4Cl$ (2 mL) was added, followed by water (5 mL) and the mixture was transferred to a separatory funnel. The aqueous fraction was extracted with EtOAc (3 × 10 mL), the combined organic phases were washed with brine (20 mL) and dried over anhydrous $MgSO_4$. Filtration, concentration *in vacuo*, and purification by flash column chromatography ($SiO_2$, DCM/MeOH 98:2) furnished the desired pure orange oil **2i** (33 mg, 0.10 mmol, 49% yield).



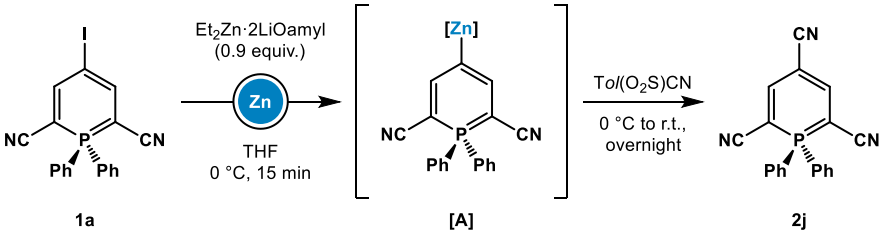
**$^{1}$H NMR (500 MHz, $CDCl_3$)** δ 7.8 – 7.6 (m, 10H), 7.3 (d, *J* = 27.2 Hz, 2H), 5.9 – 5.7 (m, 1H), 5.1 – 4.9 (m, 2H), 2.9 (d, *J* = 6.5 Hz, 2H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 170.2, 147.5, 134.5 (d, *J* = 3.3 Hz), 132.8 (d, *J* = 11.6 Hz), 130.1 (d, *J* = 13.5 Hz), 124.1 (d, *J* = 93.9 Hz), 61.5 (d, *J* = 108.0 Hz).

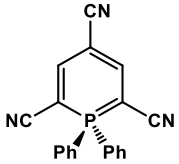
**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.5.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{20}H_{14}N_3OPH^+$: 344.0947 found: 344.0962.

**1,1-Diphenyl-1λ$^5$-phosphinine-2,4,6-tricarbonitrile (2j)**




A flame-dried Schlenk flask was charged with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.) and dry THF (1 mL) was added. $Et_2Zn·2LiOamyl$ (0.18 mmol, 0.9 equiv.) was added dropwise at 0 °C, and the reaction mixture was allowed to stir at this temperature for 15 min. *p*-Toluenesulfonyl cyanide (72 mg, 0.4 mmol, 2.0 equiv.) was added to the mixture and the Schlenk flask was sealed and the mixture stirred overnight at r.t. Then, sat. aq. $NH_4Cl$ (2 mL) was added, followed by water (5 mL) and the mixture was transferred to a separatory funnel. The aqueous fraction was extracted with EtOAc (3 × 10 mL), the combined organic phases were washed with brine (20 mL) and dried over anhydrous $MgSO_4$. Filtration, concentration *in vacuo*, and purification by flash column chromatography ($SiO_2$, pentane/acetone 80:20 to 70:30) furnished the desired pure yellow oil **2j** (40 mg, 0.12 mmol, 62% yield).



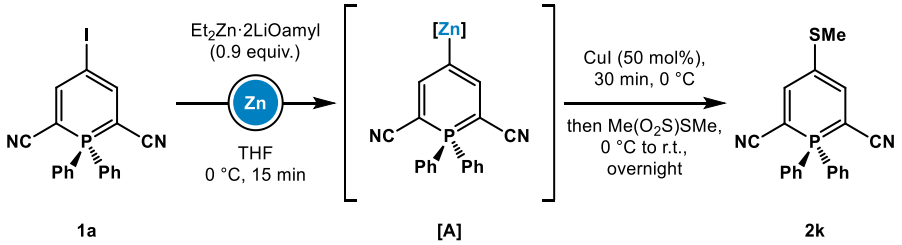
**$^{1}$H NMR (500 MHz, $CDCl_3$)** δ 7.83 – 7.76 (m, 2H), 7.75 – 7.63 (m, 10H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 150.1 (d, *J* = 1.9 Hz), 134.9 (d, *J* = 3.1 Hz), 132.9 (d, *J* = 11.6 Hz), 130.3 (d, *J* = 13.6 Hz), 123.1 (d, *J* = 94.4 Hz), 116.3 (d, *J* = 11.5 Hz), 86.9 (d, *J* = 13.0 Hz), 64.2 (d, *J* = 106.2 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 8.8.

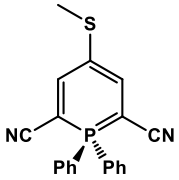
**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{20}H_{12}N_3PH^+$: 326.0842 found: 326.0863.

**4-(Methylthio)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2k)**




1a [A] 2k

A flame-dried Schlenk flask was charged with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.) and dry THF (1 mL) was added. $Et_2Zn{\cdot}2LiOamyl$ (0.18 mmol, 0.9 equiv.) was added dropwise at 0 °C, and the reaction mixture was allowed to stir at this temperature for 15 min. Solid copper(I) iodide (0.1 mmol, 50 mol%) was added in one portion to the mixture, and the solution was allowed to stir for 30 min at 0 °C. *S*-Methyl methanesulfonothioate (38 μL, 0.4 mmol, 2.0 equiv.) was added to the mixture and the Schlenk flask was sealed and the mixture stirred overnight at r.t. Then, sat. aq. $NH_4Cl$ (2 mL) was added, followed by water (5 mL) and the mixture was transferred to a separatory funnel. The aqueous fraction was extracted with EtOAc (3 × 10 mL), the combined organic phases were washed with brine (20 mL) and dried over anhydrous $MgSO_4$. Filtration, concentration *in vacuo*, and purification by flash column chromatography ($SiO_2$, pentane/acetone 90:10 to 80:20) furnished the desired pure orange solid **2k** (17 mg, 0.05 mmol, 25% yield).




**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.72 – 7.61 (m, 12H), 2.27 (s, 3H).

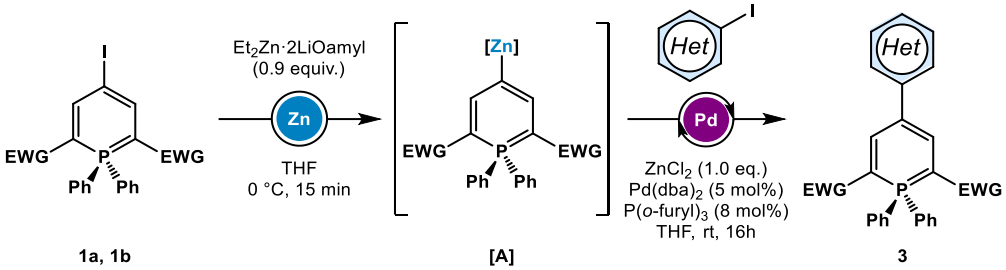
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 153.2 (d, *J* = 2.4 Hz), 134.0 (d, *J* = 3.2 Hz), 132.7 (d, *J* = 11.5 Hz), 129.9 (d, *J* = 13.4 Hz), 125.2 (d, *J* = 93.4 Hz), 118.2 (d, *J* = 12.1 Hz), 107.4 (d, *J* = 10.6 Hz), 60.2 (d, *J* = 109.1 Hz), 22.4.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 8.7.

**HRMS (EI)** m/z: [M] calcd for $C_{20}H_{15}N_2PS$: 346.0688 found: 346.0685.

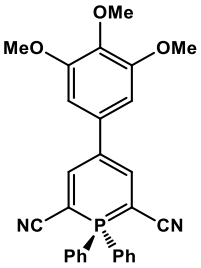
## NEGISHI COUPLING

**General Procedure D for Negishi Coupling of Iodinated Phosphinines**




A flame-dried Schlenk flask was charged with the respective iodo-phosphinine (0.20 mmol, 1.0 equiv.) and dry THF (1 mL) was added. $Et_2Zn{\cdot}2LiOamyl$ (0.18 mmol, 0.9 equiv.) was added dropwise at 0 °C, and the reaction mixture was allowed to stir at this temperature for 15 min. $ZnCl_2$ (0.2 mL, 0.20 mmol, 1.0 equiv., in solution in 1M THF), $Pd(dba)_2$ (6 mg, 0.01 mmol, 5 mol%), P(*o*-furyl)$_3$ (4 mg, 0.016 mmol, 8 mol%) and the coupling partner (0.18 mmol, 0.9 equiv.) were added in one portion to the mixture, and the solution was allowed to warm up and stir overnight at r.t. Then, sat. aq. $NH_4Cl$ (2 mL) was added, followed by water (5 mL) and the mixture was transferred to a separatory funnel. The aqueous fraction was extracted with EtOAc (3 × 10 mL), the combined organic phases were washed with brine (20 mL) and dried over anhydrous $MgSO_4$. Filtration, concentration *in vacuo*, and purification by flash column chromatography ($SiO_2$) furnished the desired functionalized phosphinines.

**1,1-diphenyl-4-(3,4,5-trimethoxyphenyl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (3a)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 5-iodo-1,2,3-trimethoxybenzene (53 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (80:20) to afford the pure red solid **3a** (55 mg, 0.12 mmol, 66% yield).

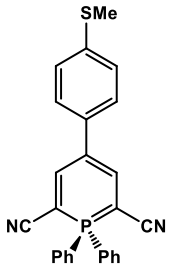
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.80 – 7.60 (m, 12H), 6.45 (s, 2H), 3.88 (s, 6H), 3.84 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 153.6, 146.0 (d, *J* = 2.3 Hz), 136.9, 135.8, 133.9 (d, *J* = 3.2 Hz), 132.6 (d, *J* = 11.6 Hz), 129.8 (d, *J* = 13.4 Hz), 125.5 (d, *J* = 93.0 Hz), 119.0 (d, *J* = 12.3 Hz), 117.0 (d, *J* = 10.0 Hz), 102.5, 61.0, 58.8 (d, *J* = 109.0 Hz), 56.3.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.8.

**HRMS (EI)** m/z: [M] calcd for $C_{28}H_{23}N_2O_3P$: 466.1441 found: 466.1439.

**4-(4-(methylthio)phenyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3b)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using (4-iodophenyl)(methyl)sulfane (45 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (95:5) to afford the pure orange solid **3b** (25 mg, 0.06 mmol, 33% yield).

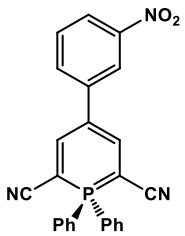
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.82 – 7.59 (m, 12H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 2.49 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 145.8 (d, *J* = 2.3 Hz), 133.9 (d, *J* = 3.2 Hz), 132.7 (d, *J* = 11.4 Hz), 129.9 (d, *J* = 13.4 Hz), 127.5, 125.5 (d, *J* = 93.0 Hz), 125.4, 119.0 (d, *J* = 12.2 Hz), 116.3 (d, *J* = 10.0 Hz), 59.1 (d, *J* = 109.1 Hz), 16.3.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.6.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{26}H_{19}N_2PSH^+$: 423.1079 found: 423.1079.

**4-(3-nitrophenyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3c)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 1-iodo-3-nitrobenzene (44 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10) to afford the pure red solid **3c** (65 mg, 0.15 mmol, 87% yield).

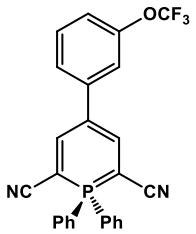
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.15 (t, *J* = 2.1 Hz, 1H), 8.05 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.80 (d, *J* = 27.3 Hz, 2H), 7.77 – 7.70 (m, 6H), 7.67 (td, *J* = 7.8, 3.8 Hz, 4H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 148.9, 146.0 (d, *J* = 2.4 Hz), 141.4, 134.1 (d, *J* = 3.2 Hz), 132.7 (d, *J* = 11.5 Hz), 130.3 (d, *J* = 86.7 Hz), 129.9 (d, *J* = 13.4 Hz), 124.9 (d, *J* = 93.4 Hz), 120.8, 119.6, 118.4 (d, *J* = 11.9 Hz), 114.2 (d, *J* = 10.1 Hz), 60.4 (d, *J* = 108.5 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.4.

**HRMS (EI)** m/z: [M] calcd for $C_{25}H_{16}N_3O_2P$: 421.0975 found: 421.0975.

**1,1-diphenyl-4-(3-(trifluoromethoxy)phenyl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (3d)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 1-iodo-3-(trifluoromethoxy)benzene (28 μL, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10) to afford the pure orange solid **3d** (60 mg, 0.13 mmol, 73% yield).

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.78 – 7.63 (m, 12H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.13 (s, 1H), 7.08 (d, *J* = 8.2 Hz, 1H).

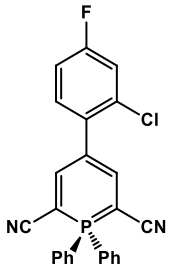
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 149.9, 146.0 (d, *J* = 2.3 Hz), 141.8, 134.0 (d, *J* = 3.2 Hz), 132.6 (d, *J* = 11.6 Hz), 130.3, 129.9 (d, *J* = 13.4 Hz), 125.2 (d, *J* = 93.4 Hz), 123.2, 118.4, 117.5, 115.2 (d, *J* = 9.9 Hz), 59.7 (d, *J* = 108.8 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.6.

**$^{19}$F NMR (471 MHz, $CDCl_3$)** δ -57.6.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{26}H_{16}F_3N_2OPH^+$: 461.1025 found: 461.1028.

**4-(2-chloro-4-fluorophenyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3e)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 3-chloro-4-fluoroiodobenzene (23 μL, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10) to afford the pure orange solid **3e** (27 mg, 0.06 mmol, 32% yield).

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.81 – 7.55 (m, 12H), 7.30 (d, *J* = 6.7 Hz, 1H), 7.11 (d, *J* = 6.8 Hz, 2H).

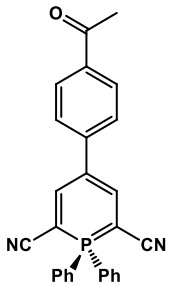
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 156.9 (d, *J* = 248.1 Hz), 145.8 (d, *J* = 2.3 Hz), 137.2 (d, *J* = 3.9 Hz), 134.0 (d, *J* = 3.1 Hz), 132.6 (d, *J* = 11.6 Hz), 129.9 (d, *J* = 13.4 Hz), 127.3, 125.2 (d, *J* = 93.2 Hz), 124.7 (d, *J* = 6.9 Hz), 121.4 (d, *J* = 18.0 Hz), 118.7 (d, *J* = 12.0 Hz), 117.0 (d, *J* = 21.0 Hz), 114.7 (d, *J* = 10.2 Hz), 59.6 (d, *J* = 108.8 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.5.

**$^{19}$F NMR (471 MHz, $CDCl_3$)** δ -119.3.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{25}H_{15}ClFN_2PH^+$: 429.0718 found: 429.0720.

**4-(4-acetylphenyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3f)**



According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 4'-iodoacetophenone (44 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 80:20) to afford the pure orange solid **3f** (49 mg, 0.12 mmol, 65% yield).

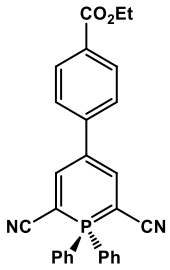
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 27.4 Hz, 2H), 7.77 – 7.59 (m, 10H), 7.37 (d, *J* = 8.3 Hz, 2H), 2.59 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 197.4, 146.1 (d, *J* = 2.4 Hz), 144.1, 134.7, 134.1 (d, *J* = 3.2 Hz), 132.6 (d, *J* = 11.7 Hz), 129.9 (d, *J* = 13.5 Hz), 129.3, 125.0 (d, *J* = 93.3 Hz), 124.5, 118.6 (d, *J* = 12.2 Hz), 115.2 (d, *J* = 10.0 Hz), 60.3 (d, *J* = 108.6 Hz), 26.6.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.3.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{27}H_{19}N_2OPH^+$: 419.1308 found: 419.1308.

**ethyl 4-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)benzoate (3g)**



According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using ethyl 4-iodobenzoate (30 μL, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 80:20) to afford the pure yellow solid **3g** (40 mg, 0.09 mmol, 50% yield).

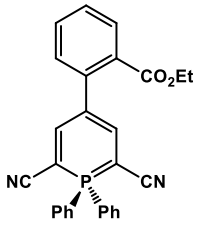
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.82 (d, *J* = 27.5 Hz, 2H), 7.78 – 7.70 (m, 6H), 7.69 – 7.61 (m, 4H), 7.35 (d, *J* = 8.5 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 166.5, 146.2 (d, *J* = 2.3 Hz), 143.9, 134.1 (d, *J* = 3.1 Hz), 132.7 (d, *J* = 11.5 Hz), 130.4, 129.9 (d, *J* = 13.4 Hz), 128.1, 125.2 (d, *J* = 93.2 Hz), 124.4, 118.7 (d, *J* = 12.0 Hz), 115.5 (d, *J* = 10.0 Hz), 61.0, 60.1 (d, *J* = 108.7 Hz), 14.5.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.4.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{28}H_{21}N_2O_2PH^+$: 449.1413 found: 449.1424.

**ethyl 2-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)benzoate (3h)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using ethyl 2-iodobenzoate (30 μL, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 80:20) to afford the pure yellow solid **3h** (49 mg, 0.11 mmol, 61% yield).

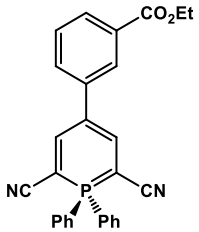
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.79 – 7.61 (m, 10H), 7.46 (d, *J* = 27.3 Hz, 2H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 (td, *J* = 7.6, 1.3 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 168.3, 147.3 (d, *J* = 2.3 Hz), 140.8, 133.8 (d, *J* = 3.0 Hz), 132.6 (d, *J* = 11.5 Hz), 131.7, 130.7, 130.2, 130.0, 129.8 (d, *J* = 13.4 Hz), 126.9, 125.6 (d, *J* = 93.0 Hz), 118.9 (d, *J* = 12.0 Hz), 116.3 (d, *J* = 10.7 Hz), 61.3, 58.1 (d, *J* = 109.6 Hz), 14.3.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.5.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{28}H_{21}N_2O_2PH^+$: 449.1413 found: 449.1414.

**ethyl 3-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)benzoate** (**3i)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using ethyl 2-iodobenzoate (30 μL, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 80:20) to afford the pure orange solid **3i** (31 mg, 0.07 mmol, 39% yield).

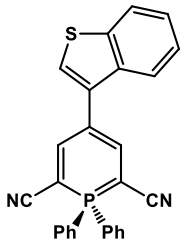
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.96 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.83 – 7.70 (m, 8H), 7.69 – 7.63 (m, 4H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 166.5, 146.1 (d, *J* = 2.3 Hz), 140.0, 134.0 (d, *J* = 3.2 Hz), 132.7 (d, *J* = 11.5 Hz), 131.2, 129.9 (d, *J* = 13.4 Hz), 129.1 (d, *J* = 12.3 Hz), 127.3, 126.0, 125.3 (d, *J* = 93.3 Hz), 118.8 (d, *J* = 12.2 Hz), 115.8 (d, *J* = 10.0 Hz), 61.3, 59.5 (d, *J* = 109.1 Hz), 14.5.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.6.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{28}H_{21}N_2O_2PH^+$: 449.1413 found: 449.1411.

**4-(benzo[*b*]thiophen-3-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile** (**3j)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 3-iodobenzo[*b*]thiophene (25 µL, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 80:20) to afford the pure yellow solid **3j** (49 mg, 0.11 mmol, 64% yield).

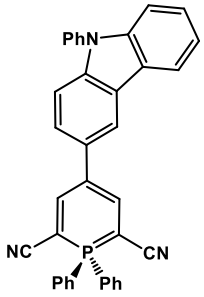
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.84 – 7.64 (m, 13H), 7.39 (p, *J* = 7.1 Hz, 2H), 7.18 (s, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 147.3 (d, *J* = 2.3 Hz), 140.6, 137.8, 136.1, 133.9 (d, *J* = 3.1 Hz), 132.6 (d, *J* = 11.5 Hz), 129.9 (d, *J* = 13.4 Hz), 125.6 (d, *J* = 93.1 Hz), 124.5 (d, *J* = 20.5 Hz), 123.2, 122.4, 121.7, 118.8 (d, *J* = 11.9 Hz), 111.2 (d, *J* = 11.0 Hz), 58.7 (d, *J* = 108.9 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 10.0.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{27}H_{17}N_2PSH^+$: 433.0923 found: 433.0924.

**1,1-diphenyl-4-(9-phenyl-9*H*-carbazol-3-yl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (3k)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 3-iodo-*N*-phenylcarbazole (66 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 80:20) to afford the pure red solid **3k** (85 mg, 0.16 mmol, 88% yield).

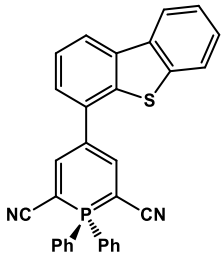
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 1.9 Hz, 1H), 7.87 (d, *J* = 27.6 Hz, 2H), 7.78 (dd, *J* = 13.6, 7.2 Hz, 4H), 7.74 – 7.65 (m, 6H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 3.7 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.35 – 7.28 (m, 2H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 146.4 (d, *J* = 2.2 Hz), 141.5, 139.8, 137.7, 133.8 (d, *J* = 3.0 Hz), 132.7 (d, *J* = 11.5 Hz), 132.3, 130.1, 129.8 (d, *J* = 13.4 Hz), 127.6, 127.1, 126.4, 125.9 (d, *J* = 93.0 Hz), 123.8, 123.7 (d, *J* = 87.3 Hz), 120.5, 120.2, 119.4 (d, *J* = 12.2 Hz), 117.9 (d, *J* = 10.0 Hz), 116.9, 110.1 (d, *J* = 22.4 Hz), 58.6 (d, *J* = 109.3 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 10.0.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{37}H_{24}N_3PH^+$: 542.1781 found: 542.1783.

**4-(dibenzo[*b,d*]thiophen-4-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3l)**



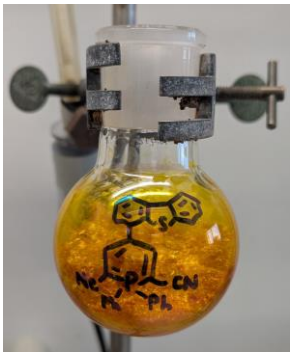

According to general procedure **D**, made on a bigger scale: with I-DCNP **1a** (472 mg, 1.1 mmol, 1.0 equiv.) in 10 mL of THF, using $Et_2Zn.2Oamyl$ (2.36 mL, 0.99 mmol, 0.9 equiv., 0.423M) for the exchange, followed by the addition of $ZnCl_2$ (1.1 mL, 1.1 mmol, 1.0 equiv., 1M in THF), $Pd(dba)_2$ (32 mg, 0.06 mmol, 5mol%), $P(o\text{-furyl})_3$ (20 mg, 0.09 mmol, 8mol%), and using 4-iododibenzo[*b,d*]thiophene (307 mg, 0.99 mmol, 0.9 equiv.) as coupling partner. The crude product was purified with a mixture pentane/acetone (95:5 to 70:30) to afford the pure orange solid **3l** (400 mg, 0.83 mmol, 84% yield).

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.15 (dd, *J* = 6.0, 3.2 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.93 – 7.84 (m, 3H), 7.83 – 7.77 (m, 4H), 7.76 – 7.64 (m, 6H), 7.52 – 7.44 (m, 3H), 7.27 (d, *J* = 7.5 Hz, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 147.0 (d, *J* = 2.2 Hz), 139.3, 138.3, 136.4, 136.0, 135.4, 134.0 (d, *J* = 3.1 Hz), 132.7 (d, *J* = 11.5 Hz), 129.9 (d, *J* = 13.4 Hz), 127.1, 125.4 (d, *J* = 17.0 Hz), 125.4 (d, *J* = 93.2 Hz), 124.7, 122.8, 122.0, 120.1, 118.8 (d, *J* = 12.3 Hz), 115.9 (d, *J* = 10.8 Hz), 69.6, 59.0 (d, *J* = 108.9 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.8.

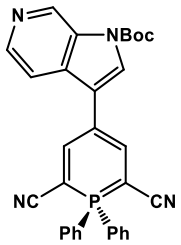
**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{31}H_{19}N_2PSH^+$: 483.1079 found: 483.1079.



Scale-up reaction:

1.1 mmol of I-DCNP **1a** – pure **3l**: 400 mg, 0.83 mmol, 84% yield

***tert*-butyl 3-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)-1*H*-pyrrolo[2,3-*c*]pyridine-1-carboxylate (3m)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using *tert*-butyl 3-iodo-1*H*-pyrrolo[2,3-*c*]pyridine-1-carboxylate (62 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 80:20) to afford the pure orange/red oil **3m** (64 mg, 0.12 mmol, 70% yield).

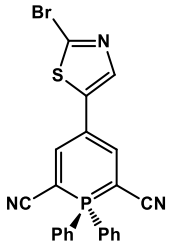
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 9.43 (s, 1H), 8.45 (d, *J* = 5.4 Hz, 1H), 7.82 – 7.65 (m, 12H), 7.61 (s, 1H), 7.52 (d, *J* = 5.2 Hz, 1H), 1.70 (s, 9H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 148.9, 146.5 (d, *J* = 2.3 Hz), 142.3, 137.9, 134.2, 134.0 (d, *J* = 3.0 Hz), 132.6 (d, *J* = 11.6 Hz), 129.9 (d, *J* = 13.6 Hz), 125.4 (d, *J* = 93.2 Hz), 124.2, 120.0, 118.7 (d, *J* = 11.9 Hz), 113.9, 107.7 (d, *J* = 11.3 Hz), 85.2, 59.4 (d, *J* = 108.6 Hz), 28.3.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.9.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{31}H_{25}N_4O_2PH^+$: 517.1788 found: 517.1796.

**4-(2-bromothiazol-5-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3n)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 2-bromo-5-iodothiazole (52 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 80:20) to afford the pure red oil **3n** (51 mg, 0.11 mmol, 61% yield).

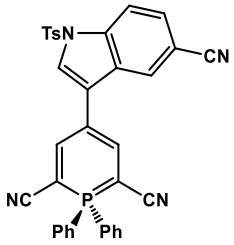
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.84 – 7.65 (m, 10H), 7.61 (d, *J* = 27.0 Hz, 2H), 7.35 (s, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 145.8 (d, *J* = 2.3 Hz), 142.6, 135.5, 134.3 (d, *J* = 3.2 Hz), 132.7 (d, *J* = 11.5 Hz), 131.9, 130.0 (d, *J* = 13.7 Hz), 124.6 (d, *J* = 93.6 Hz), 118.0 (d, *J* = 11.9 Hz), 106.2 (d, *J* = 11.2 Hz), 60.7 (d, *J* = 107.8 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.6.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{22}H_{13}BrN_3PSH^+$: 461.9824 found: 461.9825.

**4-(5-cyano-1-tosyl-1*H*-indol-3-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3o)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 3-iodo-1-tosyl-1*H*-indole-5-carbonitrile (76 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (80:20 to 60:40) to afford the pure orange solid **3o** (80 mg, 0.13 mmol, 75% yield).

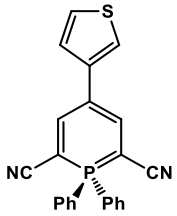
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 8.6 Hz, 1H), 7.87 (s, 1H), 7.82 – 7.72 (m, 8H), 7.71 – 7.66 (m, 4H), 7.66 – 7.52 (m, 4H), 7.28 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 146.6 (d, *J* = 2.3 Hz), 146.0, 136.9, 134.7, 134.2 (d, *J* = 3.3 Hz), 132.7 (d, *J* = 11.6 Hz), 130.4, 130.0 (d, *J* = 13.4 Hz), 129.5, 128.1, 127.0, 125.2 (d, *J* = 93.4 Hz), 125.0, 123.3, 122.6, 119.3, 118.4 (d, *J* = 11.8 Hz), 114.9, 107.3, 106.6 (d, *J* = 11.0 Hz), 59.9 (d, *J* = 108.3 Hz), 21.8.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.9.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{35}H_{23}N_4O_2PSH^+$: 595.1352 found: 595.1356.

**1,1-diphenyl-4-(thiophen-3-yl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (3p)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 3-iodothiophene (18 μL, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 80:20) to afford the pure red solid **3p** (30 mg, 0.07 mmol, 44% yield).

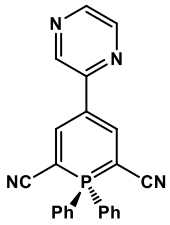
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.76 – 7.62 (m, 12H), 7.33 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.08 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.05 – 7.00 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 145.4 (d, *J* = 2.3 Hz), 140.8, 133.9 (d, *J* = 3.2 Hz), 132.6 (d, *J* = 11.6 Hz), 129.8 (d, *J* = 13.4 Hz), 126.7, 125.8, 125.0, 119.0 (d, *J* = 11.1 Hz), 116.4, 112.5 (d, *J* = 10.4 Hz), 58.7 (d, *J* = 109.2 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.8.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{23}H_{15}N_2PSH^+$: 383.0740 found: 383.0744.

**1,1-diphenyl-4-(pyrazin-2-yl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (3q)**



According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using iodopyrazine (20 μL, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 80:20) to afford the pure orange solid **3q** (15 mg, 0.04 mmol, 22% yield).

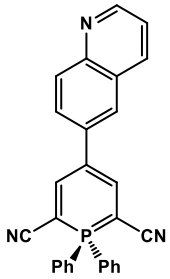
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.70 (s, 1H), 8.42 (s, 1H), 8.33 (d, *J* = 27.8 Hz, 2H), 8.33 (s, 1H), 7.79 – 7.70 (m, 6H), 7.70 – 7.61 (m, 4H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 151.0, 146.0 (d, *J* = 2.1 Hz), 143.6, 141.2, 139.1, 134.3 (d, *J* = 3.2 Hz), 132.8 (d, *J* = 11.5 Hz), 130.0 (d, *J* = 13.5 Hz), 124.6 (d, *J* = 93.5 Hz), 118.3 (d, *J* = 12.1 Hz), 112.1 (d, *J* = 9.9 Hz), 61.4 (d, *J* = 108.2 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.5.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{23}H_{15}N_4PH^+$: 379.1107 found: 379.1112.

**1,1-diphenyl-4-(quinolin-6-yl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (3r)**



According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 6-iodoquinoline (46 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 70:30) to afford the pure orange solid **3r** (63 mg, 0.15 mmol, 83% yield).

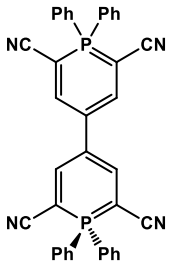
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.85 (d, *J* = 4.6 Hz, 1H), 8.13 – 8.07 (m, 2H), 7.89 (d, *J* = 27.4 Hz, 2H), 7.78 – 7.72 (m, 4H), 7.70 (dd, *J* = 7.3, 2.1 Hz, 2H), 7.68 – 7.63 (m, 6H), 7.38 (dd, *J* = 8.3, 4.2 Hz, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 149.9, 146.2 (d, *J* = 2.3 Hz), 137.8, 135.9, 134.0, 132.6 (d, *J* = 11.5 Hz), 130.0, 129.8 (d, *J* = 13.4 Hz), 127.5, 126.1, 125.2 (d, *J* = 93.1 Hz), 122.4, 121.7, 121.7, 118.8 (d, *J* = 12.1 Hz), 115.7 (d, *J* = 9.8 Hz), 59.8 (d, *J* = 108.9 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.5.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{28}H_{18}N_3PH^+$: 428.1311 found: 428.1324.

**1,1,1',1'-tetraphenyl-1λ$^5$,1'λ$^5$-[4,4'-biphosphinine]-2,2',6,6'-tetracarbonitrile (3s)**



According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using I-DCNP **1a** (76 mg, 0.18 mmol, 0.9 equiv.) as coupling partner. The crude product was purified with a mixture pentane/acetone (90:10 to 70:30) to afford the pure dark red solid **3s** (55 mg, 0.09 mmol, 51% yield).

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.74 – 7.60 (m, 20H), 7.39 (d, *J* = 27.1 Hz, 4H).

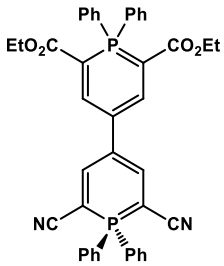
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 144.9 (d, *J* = 2.4 Hz), 133.9 (d, *J* = 3.0 Hz), 132.5 (d, *J* = 11.5 Hz), 129.8 (d, *J* = 13.3 Hz), 125.5 (d, *J* = 93.0 Hz), 118.8 (d, *J* = 12.0 Hz), 116.1 (d, *J* = 10.3 Hz), 111.2 (d, *J* = 9.4 Hz), 58.3 (d, *J* = 109.2 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.5.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{38}H_{24}N_4P_2H^+$: 599.1549 found: 599.1546.

Spectral characteristics are similar with previously reported data.[8]

**diethyl 2',6'-dicyano-1,1,1',1'-tetraphenyl-1λ$^5$,1'λ$^5$-[4,4'-biphosphinine]-2,6-dicarboxylate (3t)**



According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using I-DCO$_2$EtP **1b** (94 mg, 0.18 mmol, 0.9 equiv.) as coupling partner. The crude product was purified with a mixture pentane/acetone (90:10 to 70:30) to afford the pure dark red solid **3t** (44 mg, 0.06 mmol, 35% yield).

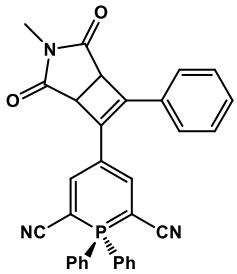
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 28.1 Hz, 2H), 7.83 – 7.61 (m, 16H), 7.56 (d, *J* = 27.5 Hz, 2H), 7.52 – 7.46 (m, 4H), 4.02 (q, *J* = 7.0 Hz, 4H), 1.03 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 166.8 (d, *J* = 11.8 Hz), 145.0 (d, *J* = 2.3 Hz), 144.0 (d, *J* = 4.3 Hz), 133.6 (d, *J* = 3.0 Hz), 133.5 (d, *J* = 11.4 Hz), 132.6 (d, *J* = 11.5 Hz), 131.4 (d, *J* = 3.3 Hz), 129.7 (d, *J* = 13.4 Hz), 128.1 (d, *J* = 13.3 Hz), 127.5 (d, *J* = 96.7 Hz), 126.0 (d, *J* = 92.6 Hz), 119.4 (d, *J* = 12.1 Hz), 118.1 (d, *J* = 10.0 Hz), 113.4 (d, *J* = 10.4 Hz), 82.7 (d, *J* = 102.2 Hz), 60.2, 57.5 (d, *J* = 109.7 Hz), 14.3.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.7, 4.2.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{42}H_{34}N_2O_4P_2H^+$: 693.2067 found: 693.2069.

**4-(3-methyl-2,4-dioxo-7-phenyl-3-azabicyclo[3.2.0]hept-6-en-6-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile** (**3u)**



According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 6-iodo-3-methyl-7-phenyl-3-azabicyclo[3.2.0]hept-6-ene-2,4-dione (61 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 70:30) to afford the pure red solid **3u** (40 mg, 0.08 mmol, 43% yield).

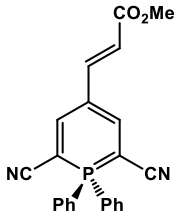
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 27.5 Hz, 2H), 7.80 – 7.63 (m, 10H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 3.98 (d, *J* = 3.6 Hz, 1H), 3.91 (d, *J* = 3.6 Hz, 1H), 2.96 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 175.2 (d, *J* = 16.7 Hz), 145.8 (d, *J* = 2.1 Hz), 137.5, 134.3 (d, *J* = 3.2 Hz), 133.3, 132.7 (d, *J* = 11.5 Hz), 132.3, 130.0 (d, *J* = 13.4 Hz), 129.0, 128.6, 126.5, 124.4 (d, *J* = 93.4 Hz), 118.0 (d, *J* = 12.2 Hz), 109.6 (d, *J* = 11.1 Hz), 60.6 (d, *J* = 107.4 Hz), 44.7 (d, *J* = 25.5 Hz), 24.9.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 8.6.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{32}H_{22}N_3OPH^+$: 512.1522 found: 512.1515.

**methyl (*E*)-3-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)acrylate (3v)**



According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using methyl (*E*)-3-iodoacrylate (36 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (80:20) to afford the pure orange oil (51 mg, 0.13 mmol, 79% yield).

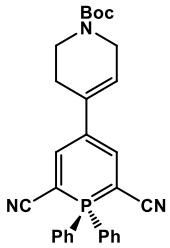
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.77 – 7.62 (m, 12H), 7.27 (d, *J* = 15.8 Hz, 1H), 5.87 (d, *J* = 15.7 Hz, 1H), 3.74 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 167.9, 147.5 (d, *J* = 2.3 Hz), 144.0, 134.4 (d, *J* = 3.0 Hz), 132.7 (d, *J* = 11.5 Hz), 130.0 (d, *J* = 13.6 Hz), 124.0 (d, *J* = 93.5 Hz), 117.7 (d, *J* = 12.1 Hz), 110.8 (d, *J* = 10.7 Hz), 109.2, 62.0 (d, *J* = 107.7 Hz), 51.5.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.6.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{23}H_{17}N_4O_2PH^+$: 385.1100 found: 385.1104.

***tert*-butyl 4-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)-3,6-dihydropyridine-1(*2H*)-carboxylate (3w)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using *tert*-butyl 4-bromo-3,6-dihydropyridine-1(*2H*)-carboxylate (32 μL, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 80:20) to afford the pure orange oil (15 mg, 0.04 mmol, 19% yield).

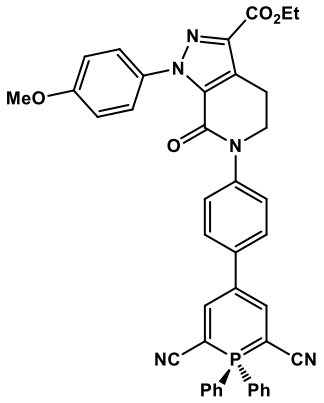
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.78 – 7.61 (m, 10H), 7.54 (d, *J* = 27.6 Hz, 2H), 5.60 (s, 1H), 3.98 (q, *J* = 2.8 Hz, 2H), 3.56 (t, *J* = 5.6 Hz, 2H), 2.39 – 2.22 (m, 2H), 1.48 (s, 9H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 154.9, 146.8 (d, *J* = 2.4 Hz), 144.1 (d, *J* = 2.3 Hz), 133.9 (d, *J* = 3.2 Hz), 132.6 (d, *J* = 11.5 Hz), 129.8 (d, *J* = 13.4 Hz), 125.5 (d, *J* = 93.0 Hz), 119.1 (d, *J* = 12.0 Hz), 116.7 (d, *J* = 9.5 Hz), 116.4, 79.9, 58.3 (d, *J* = 109.3 Hz), 43.6, 40.1, 28.6, 27.3.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 10.1.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{29}H_{28}N_3O_2PH^+$: 482.1992 found: 482.1994.

**ethyl 6-(4-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)phenyl)-1-(4-methoxyphenyl)-7-oxo-4,5,6,7-tetrahydro-1*H*-pyrazolo[3,4-*c*]pyridine-3-carboxylate** (**3x)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using ethyl 6-(4-iodophenyl)-1-(4-methoxyphenyl)-7-oxo-4,5,6,7-tetrahydro-1*H*-pyrazolo[3,4-*c*]pyridine-3-carboxylate (93 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 70:30) to afford the pure orange solid **3x** (27 mg, 0.04 mmol, 22% yield).

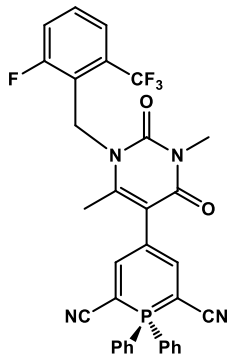
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.80 – 7.62 (m, 12H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 4.12 (t, *J* = 6.7 Hz, 2H), 3.80 (s, 3H), 3.33 (t, *J* = 6.7 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 162.2, 159.9, 157.2, 145.8 (d, *J* = 2.3 Hz), 139.9, 139.0, 137.9, 133.8 (d, *J* = 3.2 Hz), 133.1, 132.6 (d, *J* = 11.6 Hz), 129.8 (d, *J* = 13.6 Hz), 127.5, 127.0, 126.9, 125.8, 125.4 (d, *J* = 92.9 Hz), 125.3, 118.8 (d, *J* = 12.1 Hz), 116.0 (d, *J* = 10.0 Hz), 113.6, 61.2, 59.2 (d, *J* = 108.8 Hz), 55.5, 51.1, 30.9, 21.6, 14.4.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.5.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{41}H_{32}N_5O_4PH^+$: 690.2265 found: 690.2266.

**4-(1-(2-fluoro-6-(trifluoromethyl)benzyl)-3,6-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3y)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 1-(2-fluoro-6-(trifluoromethyl)benzyl)-5-iodo-3,6-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (80 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 80:20) to afford the pure yellow/orange oil **3y** (27 mg, 0.04 mmol, 26% yield).

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.80 – 7.62 (m, 10H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.45 (q, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 27.5 Hz, 2H), 7.29 – 7.24 (m, 1H), 5.47 (s, 2H), 3.40 (s, 3H), 2.20 (s, 3H).

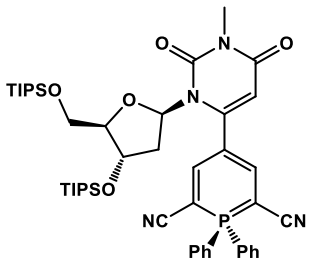
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 162.9, 161.4 (d, *J* = 249.0 Hz), 150.3 (d, *J* = 395.3 Hz), 149.4 (d, *J* = 2.3 Hz), 133.9, 132.6 (d, *J* = 60.2 Hz), 129.9 (d, *J* = 13.4 Hz), 129.6 (d, *J* = 9.6 Hz), 122.8, 122.2 (d, *J* = 11.9 Hz), 118.7 (d, *J* = 12.0 Hz), 113.2, 108.2 (d, *J* = 11.1 Hz), 69.6, 58.5 (d, *J* = 109.1 Hz), 43.0, 28.7, 18.3.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.3.

**$^{19}$F NMR (471 MHz, $CDCl_3$)** δ -59.7, -116.9.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{33}H_{23}F_4N_4O_2PH^+$: 615.1568 found: 615.1568.

**4-(1-methyl-2,6-dioxo-3-((2*R*,4*S*,5*R*)-4-((triisopropylsilyl)oxy)-5-(((triisopropylsilyl)oxy)methyl)tetrahydrofuran-2-yl)-1,2,3,6-tetrahydropyrimidin-4-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3z)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 6-iodo-3-methyl-1-(4-((triisopropylsilyl)oxy)-5-(((triisopropylsilyl)oxy)methyl)tetrahydrofuran-2-yl)pyrimidine-2,4(1*H*,3*H*)-dione (123 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 70:30) to afford the yellow oil **3z** (75 mg, 0.09 mmol, 49% yield).

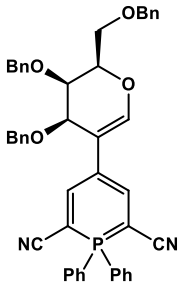
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.72 – 7.66 (m, 6H), 7.65 – 7.59 (m, 4H), 7.52 (d, *J* = 27.7 Hz, 2H), 7.51 (s, 1H), 6.38 (dd, *J* = 9.0, 5.1 Hz, 1H), 4.60 (d, *J* = 5.3 Hz, 1H), 4.05 (d, *J* = 2.5 Hz, 1H), 3.91 (dd, *J* = 11.3, 2.5 Hz, 1H), 3.85 (dd, *J* = 11.4, 2.5 Hz, 1H), 3.36 (s, 3H), 2.38 (dd, *J* = 12.8, 5.2 Hz, 1H), 2.07 – 1.97 (m, 1H), 1.10 – 0.90 (m, 42H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 162.7, 150.5, 147.7 (d, *J* = 2.1 Hz), 133.8 (d, *J* = 3.0 Hz), 132.9, 132.6 (d, *J* = 11.5 Hz), 129.7 (d, *J* = 13.4 Hz), 125.7 (d, *J* = 93.1 Hz), 118.6 (d, *J* = 11.9 Hz), 113.7, 108.3 (d, *J* = 11.0 Hz), 88.7, 86.1, 73.1, 63.7, 58.6 (d, *J* = 108.7 Hz), 53.9, 42.2, 28.2, 18.0, 12.1, 11.8.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.2.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{47}H_{65}N_4O_5PSi_2H^+$: 853.4303 found: 853.4311.

**4-((2*R*,3*R*,4*R*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-3,4-dihydro-2*H*-pyran-5-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3aa)**




According to general procedure **D**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using (2*R*,3*S*,4*S*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-5-iodo-3,4-dihydro-2*H*-pyran (93 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10 to 70:30) to afford the pure orange solid **3aa** (40 mg, 0.06 mmol, 31% yield).

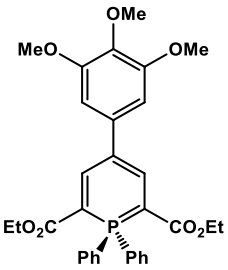
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.80 – 7.58 (m, 10H), 7.42 – 7.30 (m, 12H), 7.29 – 7.19 (m, 5H), 6.28 (s, 1H), 4.82 (dd, *J* = 15.3, 11.8 Hz, 2H), 4.72 (d, *J* = 11.7 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.53 (t, *J* = 11.2 Hz, 2H), 4.43 – 4.34 (m, 1H), 4.23 (d, *J* = 3.7 Hz, 1H), 4.09 – 4.04 (m, 1H), 3.93 (dd, *J* = 10.8, 7.8 Hz, 1H), 3.81 (dd, *J* = 10.7, 3.8 Hz, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 146.6 (d, *J* = 2.1 Hz), 140.8, 133.7 (d, *J* = 3.2 Hz), 132.5 (d, *J* = 11.5 Hz), 129.7 (d, *J* = 13.4 Hz), 128.6, 128.6, 128.5, 128.1, 128.1, 128.0, 128.0, 127.9, 125.9 (d, *J* = 92.7 Hz), 119.1 (d, *J* = 12.0 Hz), 113.4, 112.3 (d, *J* = 10.5 Hz), 75.3, 73.5, 73.4, 73.2, 73.1, 72.3, 67.9, 57.6 (d, *J* = 109.4 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.8.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{46}H_{39}N_2O_4PH^+$: 715.2378 found: 715.2370.

**diethyl 1,1-diphenyl-4-(3,4,5-trimethoxyphenyl)-1λ$^5$-phosphinine-2,6-dicarboxylate** (**5d)**




According to general procedure **D**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.), using 5-iodo-1,2,3-trimethoxybenzene (53 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10) to afford the pure orange solid **5d** (84 mg, 0.15 mmol, 75% yield).

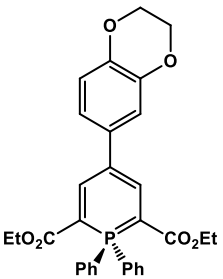
**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.32 (d, *J* = 28.4 Hz, 2H), 7.81 (ddd, *J* = 13.9, 7.8, 1.9 Hz, 4H), 7.58 – 7.46 (m, 6H), 6.63 (s, 2H), 4.02 (q, *J* = 7.1 Hz, 4H), 3.92 (s, 6H), 3.85 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 167.0 (d, *J* = 11.8 Hz), 153.4, 145.4 (d, *J* = 4.2 Hz), 137.9, 136.3, 133.6 (d, *J* = 11.4 Hz), 131.5 (d, *J* = 3.2 Hz), 128.1 (d, *J* = 13.5 Hz), 127.3, 114.5 (d, *J* = 10.4 Hz), 102.8, 83.1 (d, *J* = 101.8 Hz), 61.1, 60.1, 56.3, 53.9, 14.3.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 4.5.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{32}H_{33}O_7PH^+$: 561.2037 found: 561.2040.

**diethyl 4-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (5e)**




According to general procedure **D**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.), using 6-iodo-2,3-dihydrobenzo[*b*][1,4]dioxine (47 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (4:1) to afford the pure red oil **5e** (37 mg, 0.07 mmol, 39% yield).

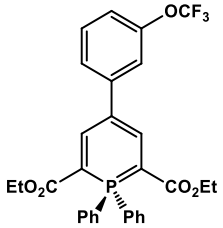
**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.30 (d, *J* = 28.5 Hz, 2H), 7.81 (ddd, *J* = 13.8, 7.4, 1.7 Hz, 4H), 7.55 – 7.44 (m, 6H), 6.97 (d, *J* = 2.2 Hz, 1H), 6.93 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 4.30 – 4.22 (m, 4H), 4.02 (q, *J* = 7.1 Hz, 4H), 1.03 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 167.0 (d, *J* = 12.0 Hz), 145.1 (d, *J* = 4.1 Hz), 143.6, 141.6, 135.5, 133.6 (d, *J* = 11.3 Hz), 131.4 (d, *J* = 3.2 Hz), 128.1 (d, *J* = 13.3 Hz), 127.2, 117.9 (d, *J* = 120.7 Hz), 113.9, 113.7 (d, *J* = 10.4 Hz), 83.0 (d, *J* = 102.4 Hz), 64.6, 64.5, 60.1, 53.9, 29.4, 14.3.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 4.3.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{31}H_{29}O_6PH^+$: 529.1775 found: 529.1771.

**diethyl 1,1-diphenyl-4-(3-(trifluoromethoxy)phenyl)-1λ$^5$-phosphinine-2,6-dicarboxylate** (**5f)**




According to general procedure **D**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.), using 1-iodo-3-(trifluoromethoxy)benzene (52 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture DCM/pentane (3:2) to afford the pure orange oil **5f** (51 mg, 0.09 mmol, 52% yield).

**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.37 (d, *J* = 28.2 Hz, 2H), 7.82 (ddd, *J* = 14.0, 7.7, 1.8 Hz, 4H), 7.60 – 7.48 (m, 6H), 7.44 – 7.32 (m, 2H), 7.30 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 4H), 1.04 (t, *J* = 7.1 Hz, 6H).

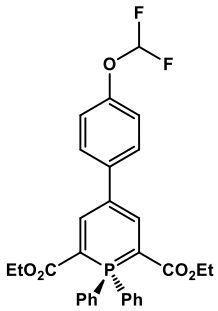
**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 166.9 (d, *J* = 11.8 Hz), 149.9 (d, *J* = 2.0 Hz), 145.3 (d, *J* = 4.1 Hz), 143.8, 133.6 (d, *J* = 11.4 Hz), 131.6 (d, *J* = 3.3 Hz), 129.9, 129.1, 128.5, 128.2 (d, *J* = 13.4 Hz), 127.7, 127.0, 125.6, 123.3, 121.7, 119.7, 117.4 (d, *J* = 30.0 Hz), 112.6 (d, *J* = 10.4 Hz), 83.9 (d, *J* = 101.9 Hz), 60.3, 14.3.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 4.3.

**$^{19}$F NMR (471 MHz, CDCl$_3$)** δ -57.5.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{30}H_{26}F_3O_5PH^+$: 555.1543found: 555.1551.

**diethyl 4-(4-(difluoromethoxy)phenyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (5g)**




According to general procedure **D**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.), using 1-(difluoromethoxy)-4-iodobenzene (26 μL, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture DCM/pentane (4:1) to afford the pure orange oil **5g** (21 mg, 0.04 mmol, 24% yield).

**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.33 (d, *J* = 28.3 Hz, 2H), 7.89 – 7.77 (m, 4H), 7.56 – 7.48 (m, 6H), 7.45 – 7.38 (m, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.51 (t, *J* = 74.3 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 4H), 1.03 (t, *J* = 7.1 Hz, 6H).

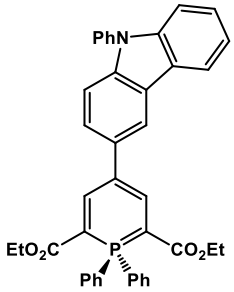
**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 167.0 (d, *J* = 11.9 Hz), 149.1, 145.3 (d, *J* = 4.1 Hz), 143.5, 139.2, 133.6 (d, *J* = 11.4 Hz), 131.5 (d, *J* = 3.3 Hz), 130.7, 128.8 (d, *J* = 72.3 Hz), 128.2 (d, *J* = 13.5 Hz), 127.5 (d, *J* = 96.7 Hz), 126.3, 125.6, 120.0, 116.3 (t, *J* = 259.2 Hz), 113.1 (d, *J* = 10.3 Hz), 83.5 (d, *J* = 102.2 Hz), 60.2, 14.3.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 4.2.

**$^{19}$F NMR (471 MHz, CDCl$_3$)** δ -80.3.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{30}H_{27}F_2O_5PH^+$: 537.1637 found: 537.1639.

**diethyl 1,1-diphenyl-4-(9-phenyl-9H-carbazol-3-yl)-1λ$^5$-phosphinine-2,6-dicarboxylate (5h)**




According to general procedure **D**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.), using 3-iodo-9-phenyl-9*H*-carbazole (66 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (90:10) to afford the pure orange solid **5h** (55 mg, 0.09 mmol, 49% yield).

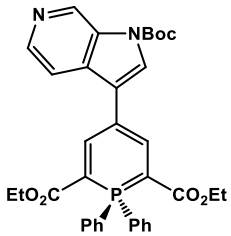
**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.49 (d, *J* = 28.4 Hz, 2H), 8.24 – 8.16 (m, 2H), 7.92 – 7.84 (m, 4H), 7.67 – 7.58 (m, 4H), 7.56 – 7.50 (m, 7H), 7.48 – 7.39 (m, 4H), 7.34 – 7.27 (m, 1H), 4.07 (q, *J* = 7.1 Hz, 4H), 1.05 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 167.2 (d, *J* = 11.9 Hz), 145.8 (d, *J* = 4.2 Hz), 141.4, 139.4, 138.0, 134.3, 133.7 (d, *J* = 11.4 Hz), 131.4 (d, *J* = 3.1 Hz), 130.0, 128.2, 128.1 (d, *J* = 13.3 Hz), 127.5, 127.4, 127.1, 126.0, 124.3, 123.8 (d, *J* = 29.3 Hz), 120.5, 119.9, 116.9, 115.3 (d, *J* = 10.4 Hz), 109.9, 83.0 (d, *J* = 102.1 Hz), 60.1, 14.4.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 4.4.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{41}H_{34}NO_4PH^+$: 635.2220 found: 635.2224.

**diethyl 4-(1-(*tert*-butoxycarbonyl)-1*H*-pyrrolo[2,3-*c*]pyridin-3-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (5i)**




According to general procedure **D**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.), using *tert*-butyl 3-iodo-1*H*-pyrrolo[2,3-*c*]pyridine-1-carboxylate (62 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/ethyl acetate (3:2) to afford the pure orange solid **5i** (72 mg, 0.12 mmol, 59% yield).

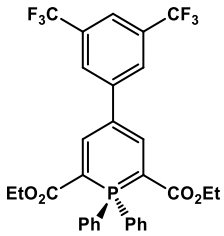
**$^1$H NMR (500 MHz, CDCl$_3$)** δ 9.44 (s, 1H), 8.44 (d, *J* = 5.5 Hz, 1H), 8.33 (d, *J* = 28.4 Hz, 2H), 7.88 – 7.79 (m, 4H), 7.74 – 7.68 (m, 2H), 7.57 – 7.47 (m, 6H), 4.03 (q, *J* = 7.1 Hz, 4H), 1.71 (s, 9H), 1.02 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 166.8 (d, *J* = 11.8 Hz), 149.1, 145.9 (d, *J* = 4.2 Hz), 141.7, 137.3, 135.3, 133.6 (d, *J* = 11.4 Hz), 131.6 (d, *J* = 3.1 Hz), 128.2 (d, *J* = 13.4 Hz), 127.5 (d, *J* = 96.7 Hz), 123.9, 122.0, 114.8, 105.1 (d, *J* = 11.4 Hz), 84.9, 83.5 (d, *J* = 101.5 Hz), 60.2, 28.3, 14.3.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 4.5.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{35}H_{35}N_2O_6PH^+$: 611.2306 found: 611.2308.

**Diethyl 4-(3,5-bis(trifluoromethyl)phenyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate** (**5j)**



According to general procedure **D**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.), using 1-iodo-3,5-bis(trifluoromethyl)benzene (61 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture DCM/pentane (3:2) to afford the pure orange solid **5j** (63 mg, 0.10 mmol, 58% yield).

**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.37 (d, *J* = 28.0 Hz, 2H), 7.84 (s, 2H), 7.84 – 7.76 (m, 4H), 7.65 (s, 1H), 7.58 – 7.43 (m, 6H), 4.05 (q, *J* = 7.2 Hz, 4H), 1.03 (t, *J* = 7.1 Hz, 6H).

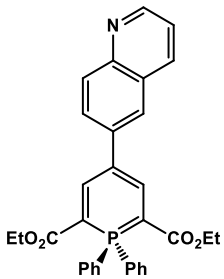
**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 166.7 (d, *J* = 11.5 Hz), 145.3 (d, *J* = 4.2 Hz), 143.7, 133.6 (d, *J* = 11.4 Hz), 132.1, 131.8 (d, *J* = 3.4 Hz), 128.3 (d, *J* = 13.4 Hz), 127.2 (d, *J* = 97.0 Hz), 124.8, 123.7 (d, *J* = 272.8 Hz), 118.4, 111.3 (d, *J* = 10.5 Hz), 84.9 (d, *J* = 101.4 Hz), 60.5, 14.3.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 4.3.

**$^{19}$F NMR (471 MHz, CDCl$_3$)** δ -62.2.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{31}H_{25}F_6O_4PH^+$: 607.1467 found: 607.1468.

**diethyl 1,1-diphenyl-4-(quinolin-6-yl)-1λ$^5$-phosphinine-2,6-dicarboxylate** (**5k)**



According to general procedure **D**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.), using 6-iodoquinoline (45 mg, 0.18 mmol, 0.9 equiv.). The crude product was purified with a mixture pentane/acetone (4:1) to afford the pure orange solid **5k** (67 mg, 0.13 mmol, 72% yield).

**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.82 (d, *J* = 2.4 Hz, 1H), 8.53 (d, *J* = 28.4 Hz, 2H), 8.13 (d, *J* = 22.6, 8.6 Hz, 2H), 7.91 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.88 – 7.80 (m, 5H), 7.57 – 7.48 (m, 6H), 7.38 (dd, *J* = 8.3, 4.3 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 4H), 1.04 (t, *J* = 7.1 Hz, 6H).

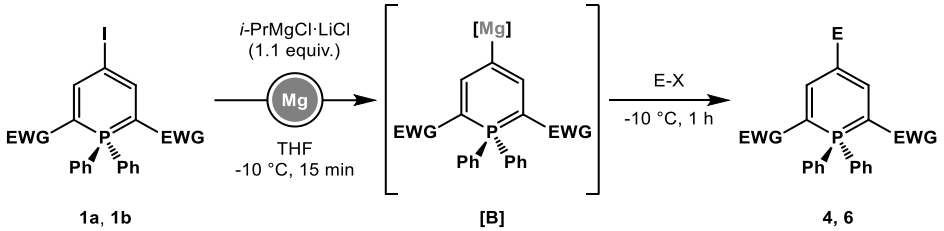
**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 166.9 (d, *J* = 11.7 Hz), 149.0, 146.5, 145.6 (d, *J* = 4.2 Hz), 139.8, 136.1, 133.6 (d, *J* = 11.4 Hz), 131.6 (d, *J* = 3.2 Hz), 129.4, 128.9, 128.3, 128.2 (d, *J* = 13.4 Hz), 127.4 (d, *J* = 96.7 Hz), 121.7, 121.4, 113.0 (d, *J* = 10.3 Hz), 84.1 (d, *J* = 101.8 Hz), 60.3, 14.3.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 4.5.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{32}H_{28}NO_4PH^+$: 522.1829 found: 522.1836

# I/Mg Exchange

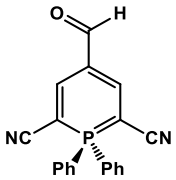
### General Procedure E for Functionalization of Iodinated Phosphinines *via* I/Mg Exchange




**1a**, **1b** **[B]** **4**, **6**

A flame-dried Schlenk flask was charged with the respective iodo-phosphinine (0.20 mmol, 1.0 equiv.) and dry THF (1 mL) was added. *i*-PrMgCl·LiCl (0.22 mmol, 1.1 equiv.) was added dropwise at -10 °C, and the reaction mixture was allowed to stir at this temperature for 15 min. The corresponding electrophile (0.50 mmol, 2.5 equiv. or other corresponding equivalent) was added to the mixture, and the solution was stirred for 1 h at -10 °C. Then, sat. aq. $NH_4Cl$ (2 mL) was added, followed by water (5 mL) and the mixture was transferred to a separatory funnel. The aqueous fraction was extracted with EtOAc (3 × 10 mL), the combined organic phases were washed with brine (20 mL) and dried over anhydrous $MgSO_4$. Filtration, concentration *in vacuo*, and purification by flash column chromatography ($SiO_2$) furnished the desired functionalized phosphinines.

### 4-formyl-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (4a)




According to general procedure **E**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using *N*,*N*-dimethylformamide (39 μL, 0.50 mmol, 2.5 equiv.). The crude product was purified with a mixture pentane/acetone (80:20) to afford the pure yellow oil **4a** (29 mg, 0.09 mmol, 45% yield).

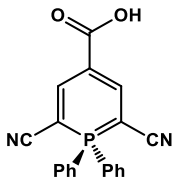
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 9.25 (s, 1H), 8.09 (d, *J* = 27.1 Hz, 2H), 7.80 – 7.65 (m, 10H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 186.1, 149.9, 134.8 (d, *J* = 3.2 Hz), 132.8 (d, *J* = 11.5 Hz), 130.2 (d, *J* = 13.7 Hz), 123.0 (d, *J* = 93.6 Hz), 116.8 (d, *J* = 12.9 Hz), 115.7 (d, *J* = 8.7 Hz), 53.7 (d, *J* = 44.9 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 11.4.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{20}H_{13}N_2OPH^+$: 329.0838 found: 329.0838.

**2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinine -4-carboxylic acid (4b)**



According to general procedure **E**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.). Carbon dioxide was used as an electrophile and was bubbling into the mixture for 15 min before keeping the mixture in a $CO_2$ atmosphere for 1 h. The crude product was purified with a mixture DCM/MeOH (98:2) to afford the pure yellow solid **4b** (50 mg, 0.16 mmol, 72% yield).

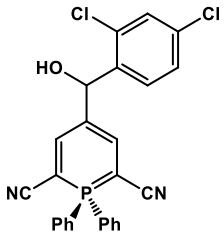
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.35 (d, *J* = 28.3 Hz, 2H), 7.90 – 7.58 (m, 10H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 169.6, 150.1, 134.5 (d, *J* = 3.1 Hz), 132.8 (d, *J* = 11.6 Hz), 130.1 (d, *J* = 13.6 Hz), 123.5 (d, *J* = 93.7 Hz), 117.3 (d, *J* = 12.5 Hz), 104.9 (d, *J* = 10.4 Hz), 63.0 (d, *J* = 107.7 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.2.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{20}H_{13}N_2O_2PH^+$: 345.0787 found: 345.0789.

**4-((2,4-dichlorophenyl)(hydroxy)methyl)-1,1-diphenyl-1λ$^5$-phosphinine -2,6-dicarbonitrile (4c)**



According to general procedure **E**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 2,4-dichlorobenzaldehyde (88 mg, 0.50 mmol, 2.5 equiv.). The crude product was purified with a mixture pentane/acetone (85:15) to afford the pure yellow oil **4c** (36 mg, 0.08 mmol, 38% yield).

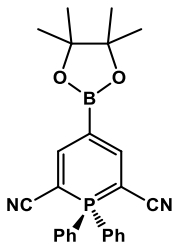
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.81 – 7.52 (m, 11H), 7.41 (d, *J* = 27.4 Hz, 2H), 7.35 (d, *J* = 2.1 Hz, 1H), 7.32 (dd, *J* = 8.4, 2.2 Hz, 1H), 5.60 (s, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 146.8 (d, *J* = 2.4 Hz), 138.9, 134.0, 133.9 (d, *J* = 3.1 Hz), 132.7, 132.6 (d, *J* = 11.5 Hz), 129.8 (d, *J* = 13.4 Hz), 129.7, 128.1, 127.6, 125.5 (d, *J* = 93.0 Hz), 118.8 (d, *J* = 12.5 Hz), 116.2 (d, *J* = 9.3 Hz), 72.3, 58.3 (d, *J* = 109.6 Hz).

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 10.9.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{26}H_{17}Cl_2N_2OPH^+$: 475.0528 found: 475.0377.

**1,1-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (4d)**



According to general procedure **E**, with I-DCNP **1a** (85 mg, 0.20 mmol, 1.0 equiv.), using 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.10 mL, 0.50 mmol, 2.5 equiv.). The crude product was purified with a mixture pentane/acetone (85:15) to afford the pure yellow oil **4d** (20 mg, 0.05 mmol, 24% yield).

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 28.4 Hz, 2H), 7.73 – 7.65 (m, 6H), 7.65 – 7.58 (m, 4H), 1.27 (s, 12H).

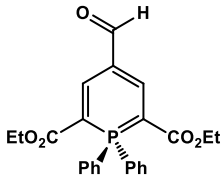
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 153.8 (d, *J* = 2.6 Hz), 133.9 (d, *J* = 3.2 Hz), 132.7 (d, *J* = 11.4 Hz), 129.8 (d, *J* = 13.4 Hz), 125.3 (d, *J* = 92.9 Hz), 118.5 (d, *J* = 12.9 Hz), 83.8, 60.6 (d, *J* = 108.6 Hz), 24.9.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 9.3.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{25}H_{24}BN_2O_2PH^+$: 427.1741 found: 427.1748.

Spectral characteristics are similar with previously reported data.[9]

**diethyl 4-formyl-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (6a)**



According to general procedure **E**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.), using *N*,*N*-dimethylformamide (39 μL, 0.50 mmol, 2.5 equiv.). The crude product was purified with a mixture pentane/acetone (80:20) to afford the pure yellow/orange oil **6a** (19 mg, 0.04 mmol, 23% yield).

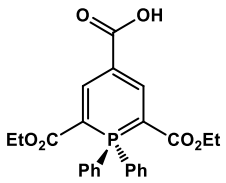
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 9.37 (s, 1H), 8.61 (s, 2H), 7.88 – 7.70 (m, 4H), 7.63 – 7.44 (m, 6H), 4.05 (q, *J* = 7.1 Hz, 4H), 1.09 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 188.2, 165.8 (d, *J* = 13.0 Hz), 133.7 (d, *J* = 11.4 Hz), 132.3 (d, *J* = 3.1 Hz), 128.5 (d, *J* = 13.7 Hz), 125.5 (d, *J* = 97.0 Hz), 114.1 (d, *J* = 9.7 Hz), 60.8, 14.3.

**$^{31}$P NMR (202 MHz, $CDCl_3$)** δ 6.4.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{24}H_{23}O_5PH^+$: 423.1356 found: 423.1362.

**2,6-bis(ethoxycarbonyl)-1,1-diphenyl-1λ$^5$-phosphinine-4-carboxylic acid (6b)**




According to general procedure **E**, with I-DCO$_2$EtP **1b** (104 mg, 0.20 mmol, 1.0 equiv.). Carbon dioxide was used as an electrophile and was bubbling into the mixture for 15 min before keeping the mixture in a $CO_2$ atmosphere for 1 h. The crude product was purified with a mixture pentane/acetone (80:20) to afford the pure yellow/orange solid **6b** (20 mg, 0.04 mmol, 23% yield).

**$^1$H NMR (500 MHz, CDCl$_3$)** δ 8.88 (d, *J* = 29.3 Hz, 2H), 7.86 – 7.73 (m, 4H), 7.59 – 7.46 (m, 6H), 4.05 (q, *J* = 7.1 Hz, 4H), 1.10 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR (126 MHz, CDCl$_3$)** δ 171.6, 166.1 (d, *J* = 12.9 Hz), 148.7 (d, *J* = 3.6 Hz), 133.7 (d, *J* = 11.5 Hz), 132.0 (d, *J* = 3.2 Hz), 128.4 (d, *J* = 13.6 Hz), 125.9 (d, *J* = 97.5 Hz), 102.4 (d, *J* = 10.6 Hz), 86.9 (d, *J* = 101.6 Hz), 60.6, 14.3.

**$^{31}$P NMR (202 MHz, CDCl$_3$)** δ 4.1.

**HRMS (ESI)** m/z: $[H]^+$ calcd for $C_{24}H_{23}O_6PH^+$: 439.1305 found: 439.1314.

# REFERENCES


(1) Brun, M. A.; Tan, K.-T.; Nakata, E.; Hinner, M. J.; Johnsson, K. *J. Am. Chem. Soc.* **2009**, *131* (16), 5873–5884.

(2) Hashimoto, N.; Umano, R.; Ochi, Y.; Shimahara, K.; Nakamura, J.; Mori, S.; Ohta, H.; Watanabe, Y.; Hayashi, M. *J. Am. Chem. Soc.* **2018**, *140* (6), 2046–2049.

(3) Ramírez-López, P.; Ros, A.; Estepa, B.; Fernández, R.; Fiser, B.; Gómez-Bengoa, E.; Lassaletta, J. M. *ACS Catal.* **2016**, *6* (6), 3955–3964.

(4) Tunney, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52* (5), 748–753.

(5) Sugiyama, R.; Okada, R.; Noda, T.; Meguro, N.; Yoshida, N.; Hoshi, K.; Ohta, H.; Hayashi, M.; Sasabe, H.; Kido, J. *Chem. – Eur. J.* **2024**, *30* (21), e202304328.

(6) Ledos, N.; Sangchai, T.; Knysh, I.; Bousquet, M. H. E.; Manzhi, P.; Cordier, M.; Tondelier, D.; Geffroy, B.; Jacquemin, D.; Bouit, P.-A.; Hissler, M. *Org. Lett.* **2022**, *24* (37), 6869–6873.

(7) Schade, M. A.; Manolikakes, G.; Knochel, P. *Org. Lett.* **2010**, *12* (16), 3648–3650.

(8) Sangchai, T.; Ledos, N.; Vacher, A.; Cordier, M.; Le Guennic, B.; Hissler, M.; Jacquemin, D.; Bouit, P.-A. *Chem. – Eur. J.* **2023**, *29* (41), e202301165.

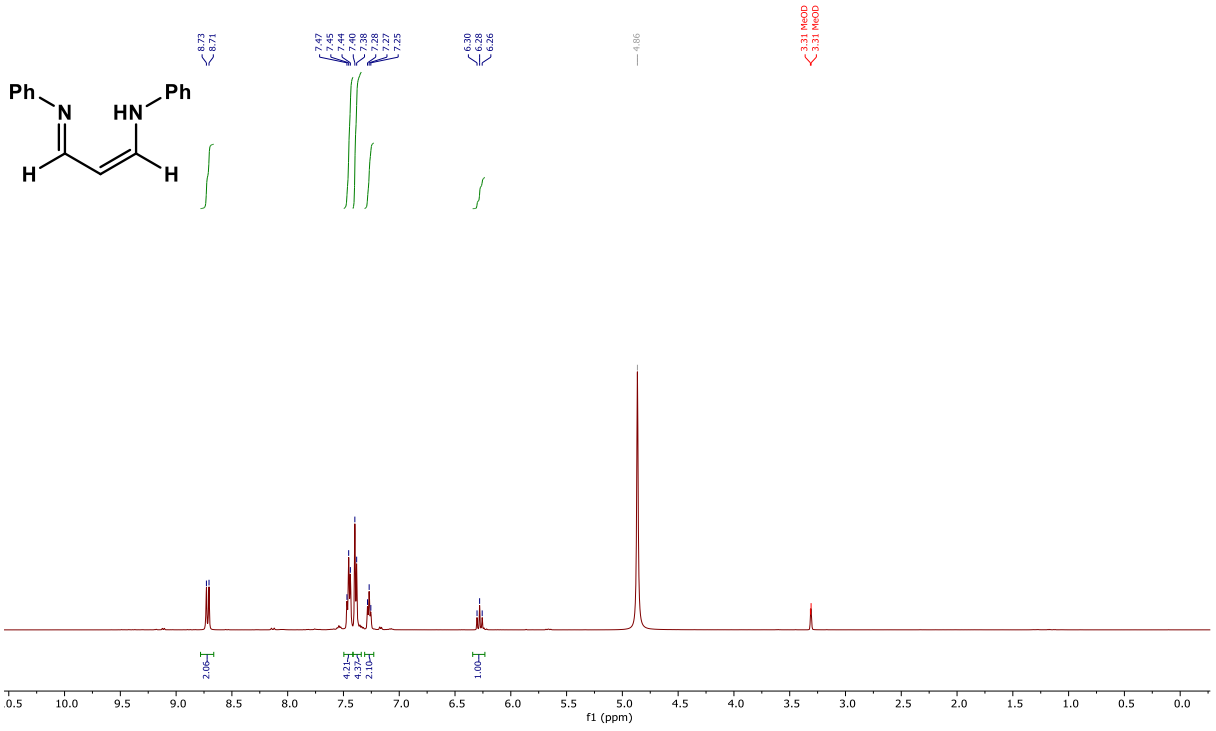
(9) Hayashi, M.; Yano, M.; Trang, D. T. H.; Ikeda, R.; Ohta, H. *Eur. J. Org. Chem.* **2025**.

# NMR SPECTRA

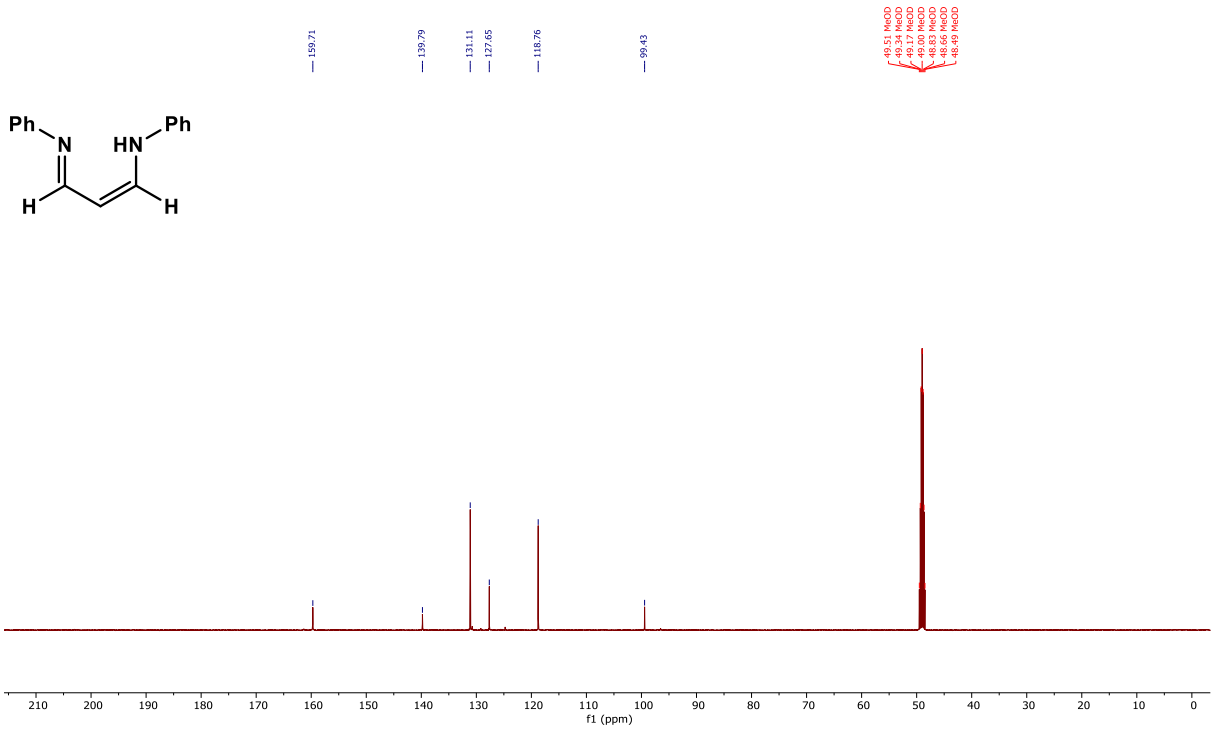
## Preparation of $\lambda^5$-Phosphinines

### (*1E*,*3E*)-$N_1$,$N_3$-Diphenylpropane-1,3-diimine (SI-1)

$^1$H NMR (500 MHz)

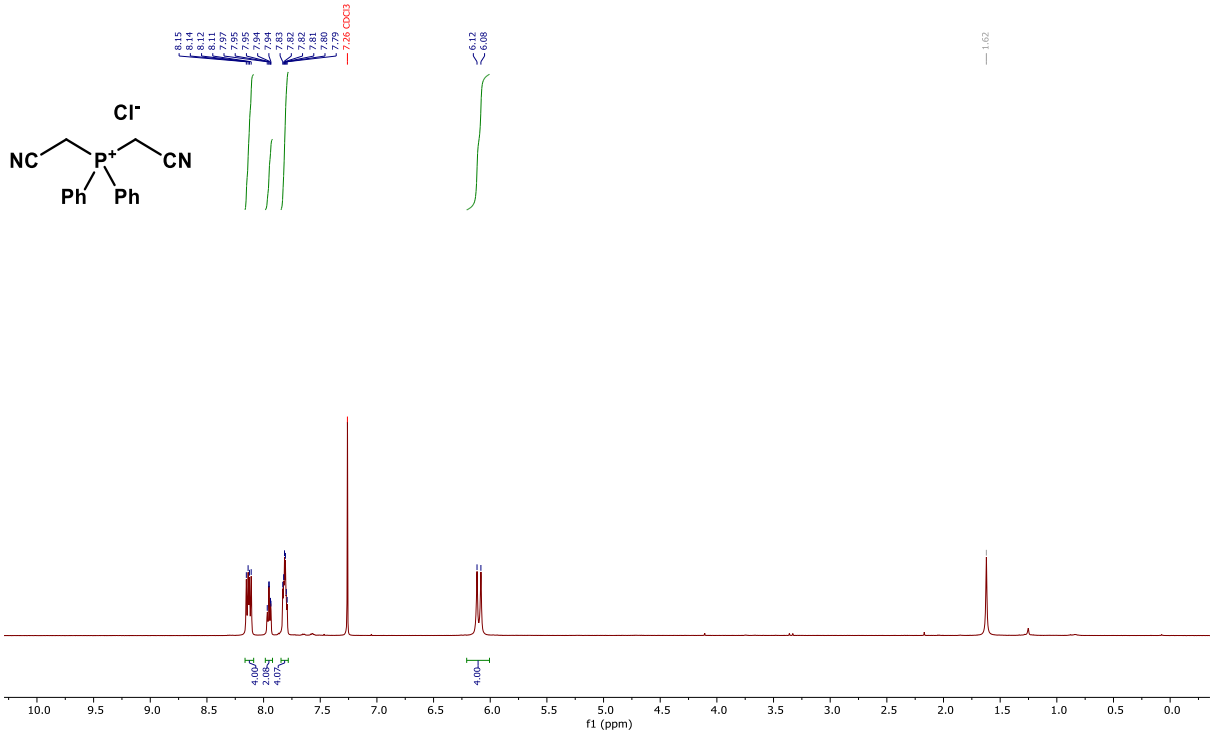



$^{13}$C NMR (126 MHz)

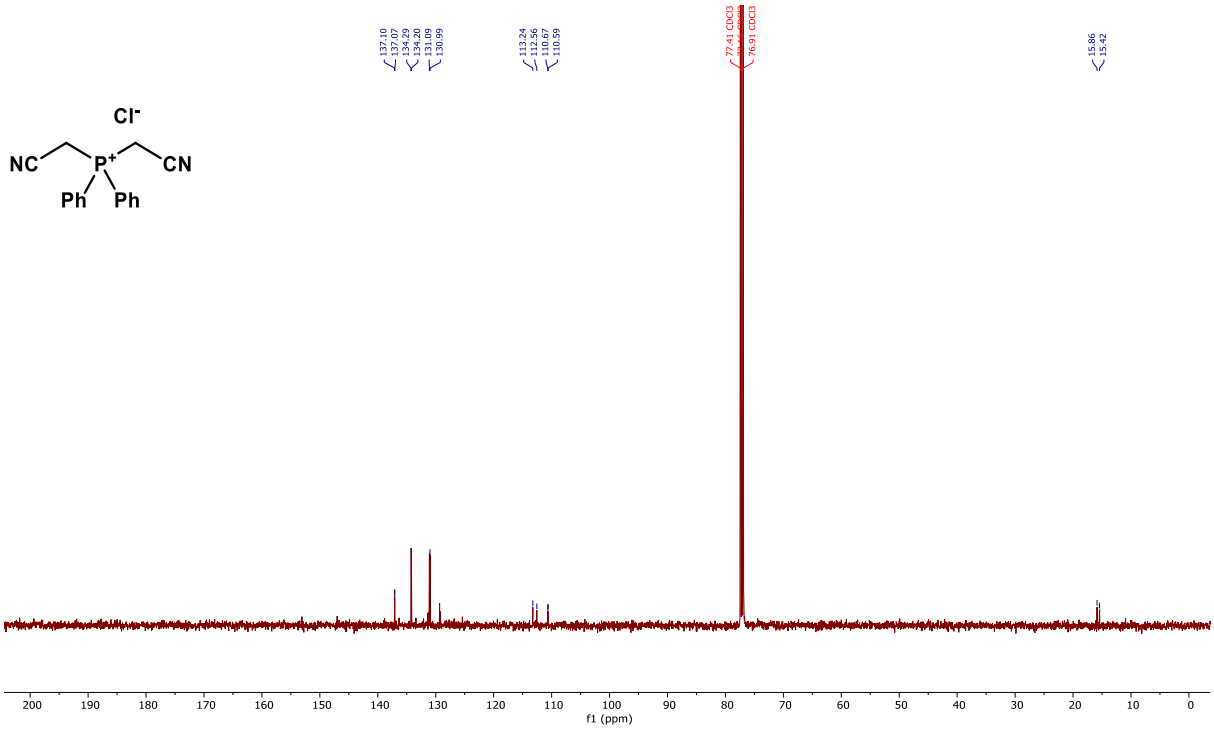


**Bis(cyanomethyl)diphenylphosphonium chloride (SI-3a)**

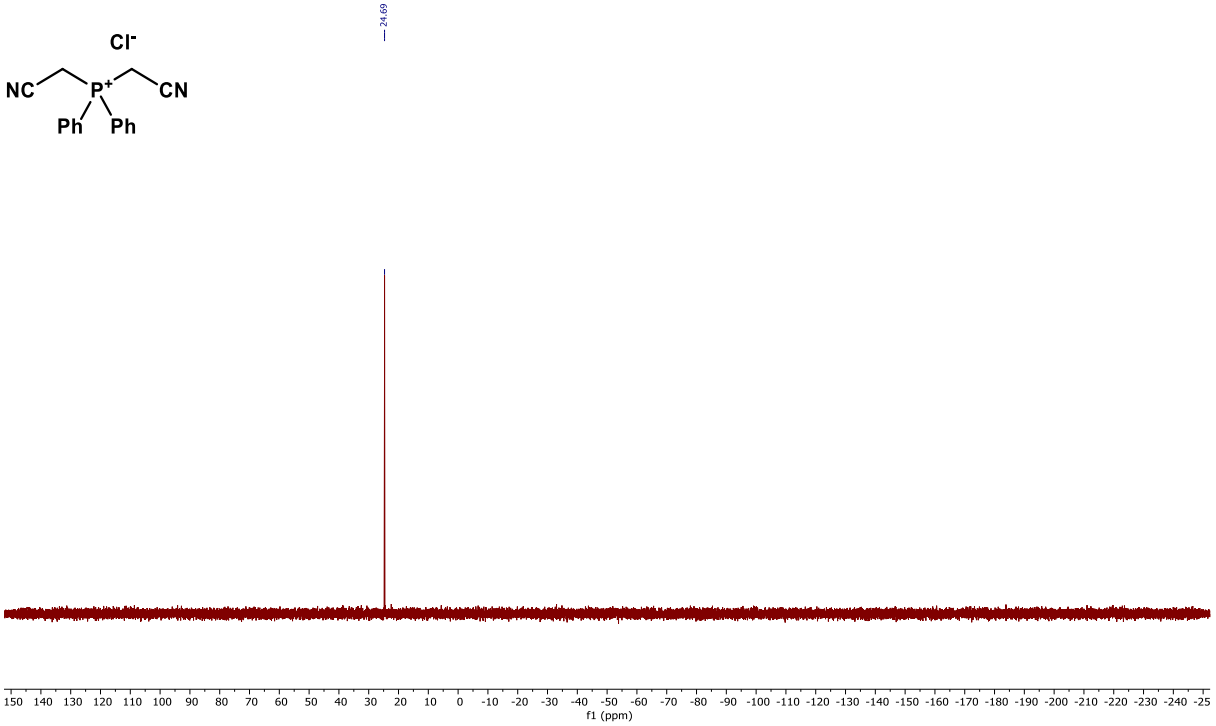
$^{1}$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

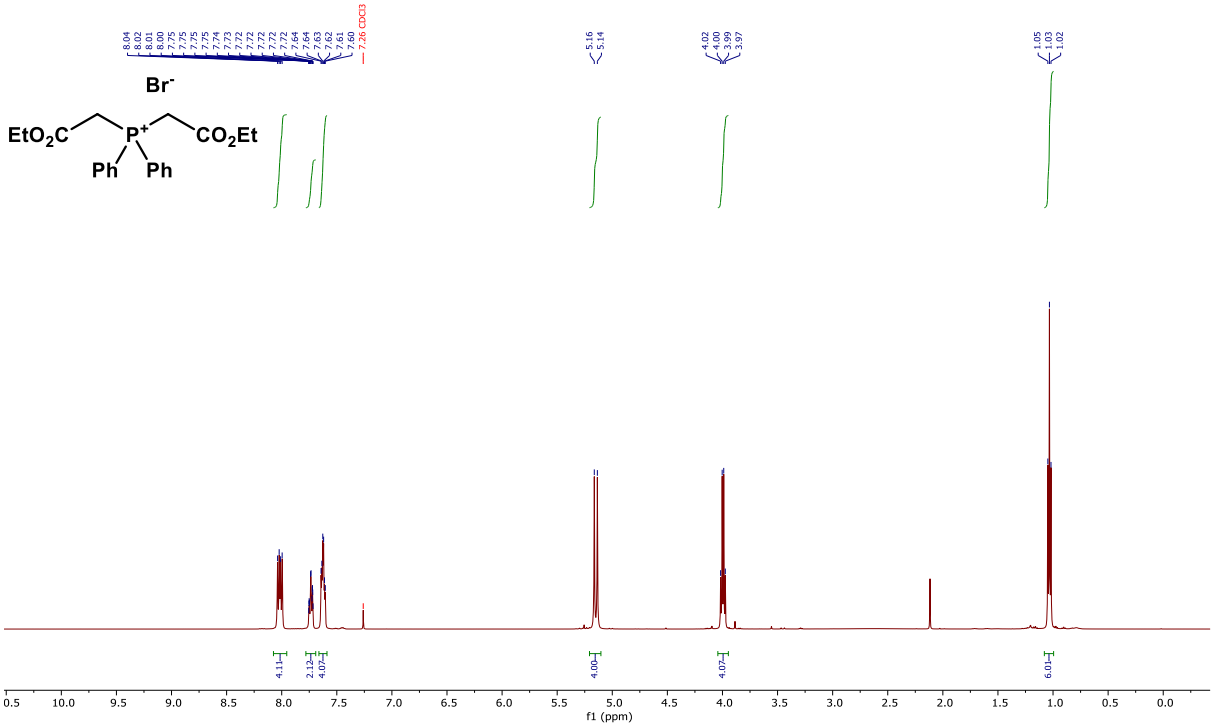


$^{31}$P NMR (202 MHz)

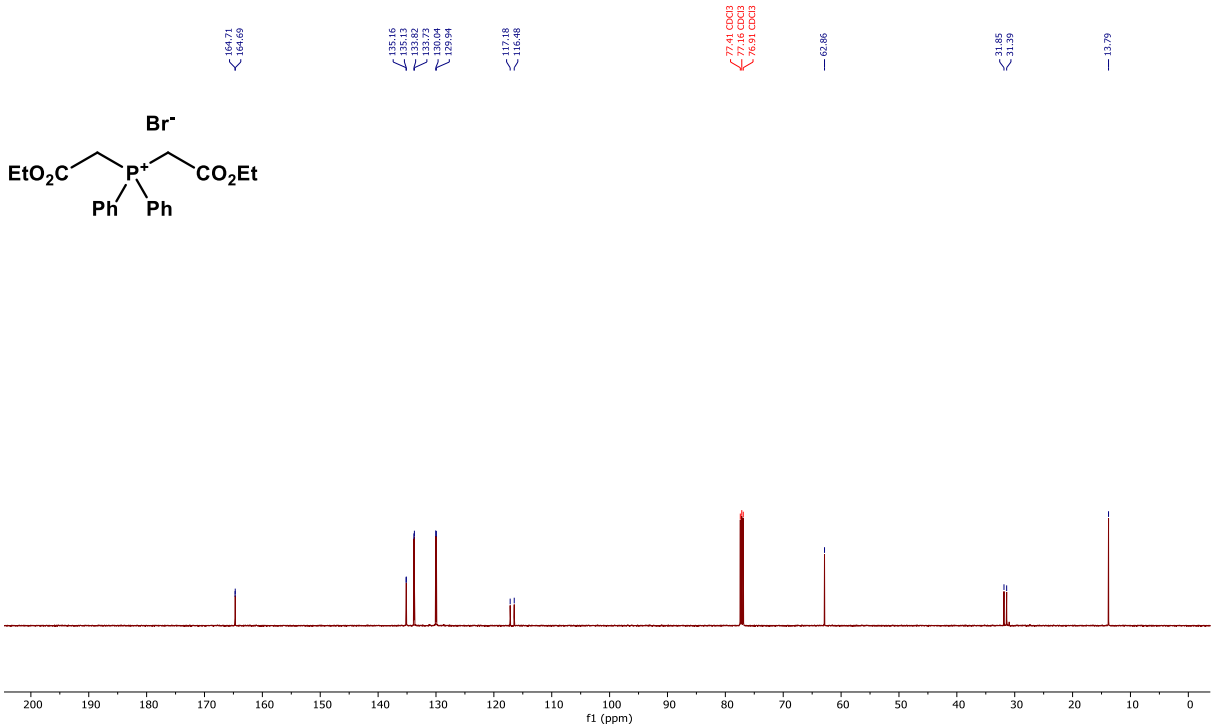


**Bis(2-ethoxy-2-oxoethyl)diphenylphosphonium bromide (SI-3b)**

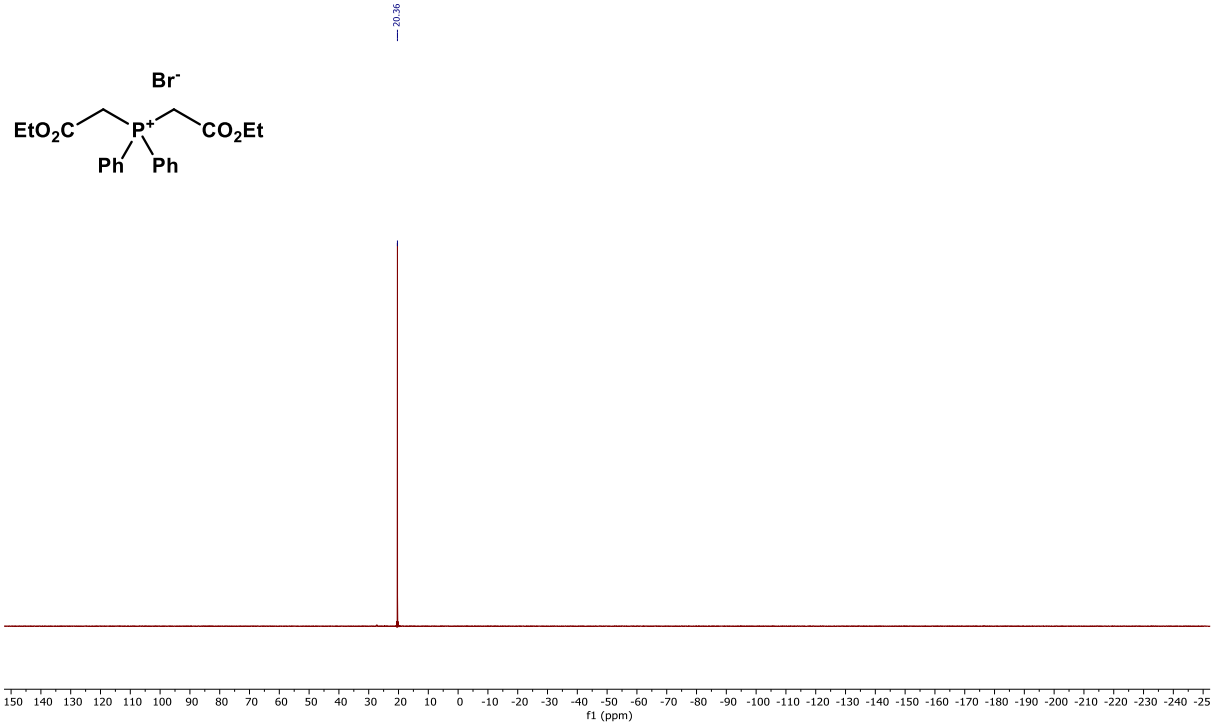
$^{1}$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

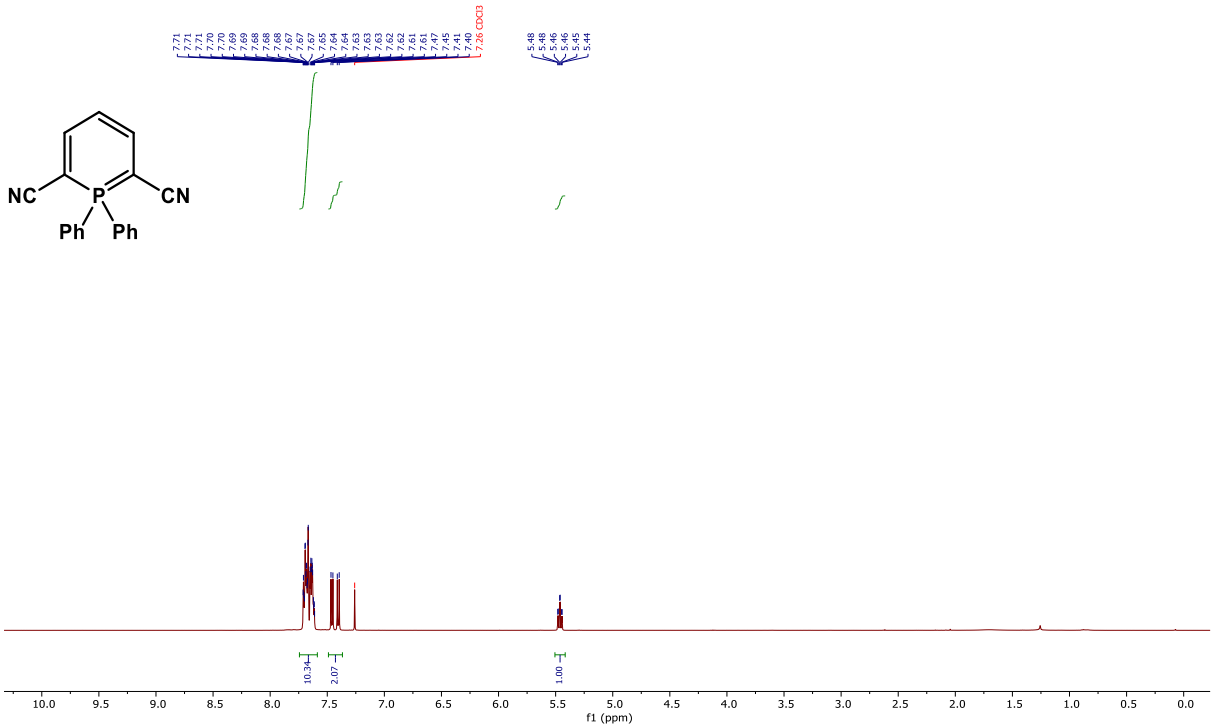


$^{31}$P NMR (202 MHz)

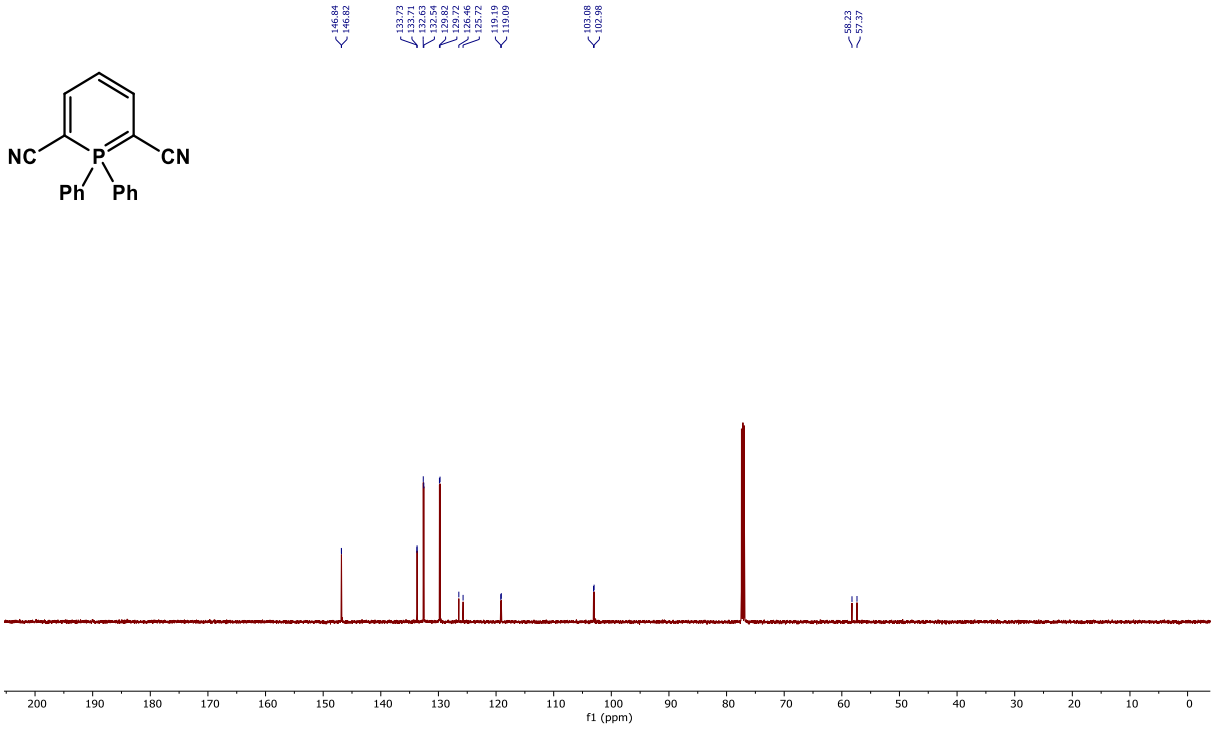


**1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (SI-4)**

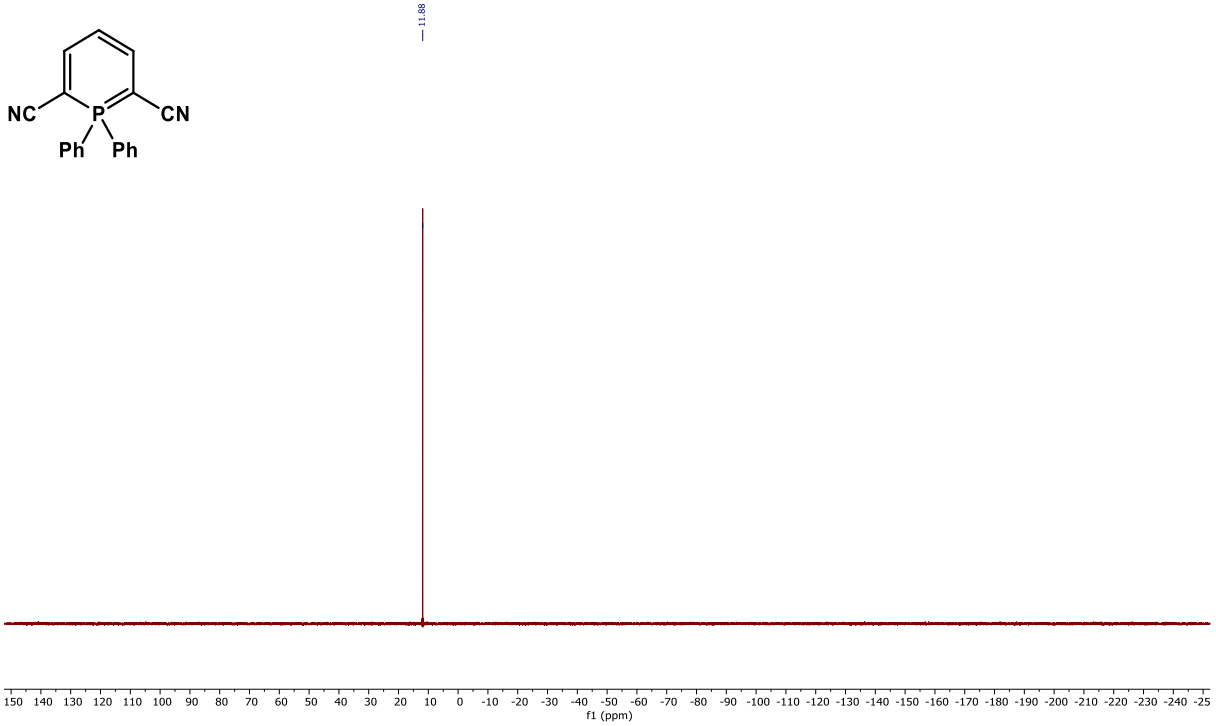
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

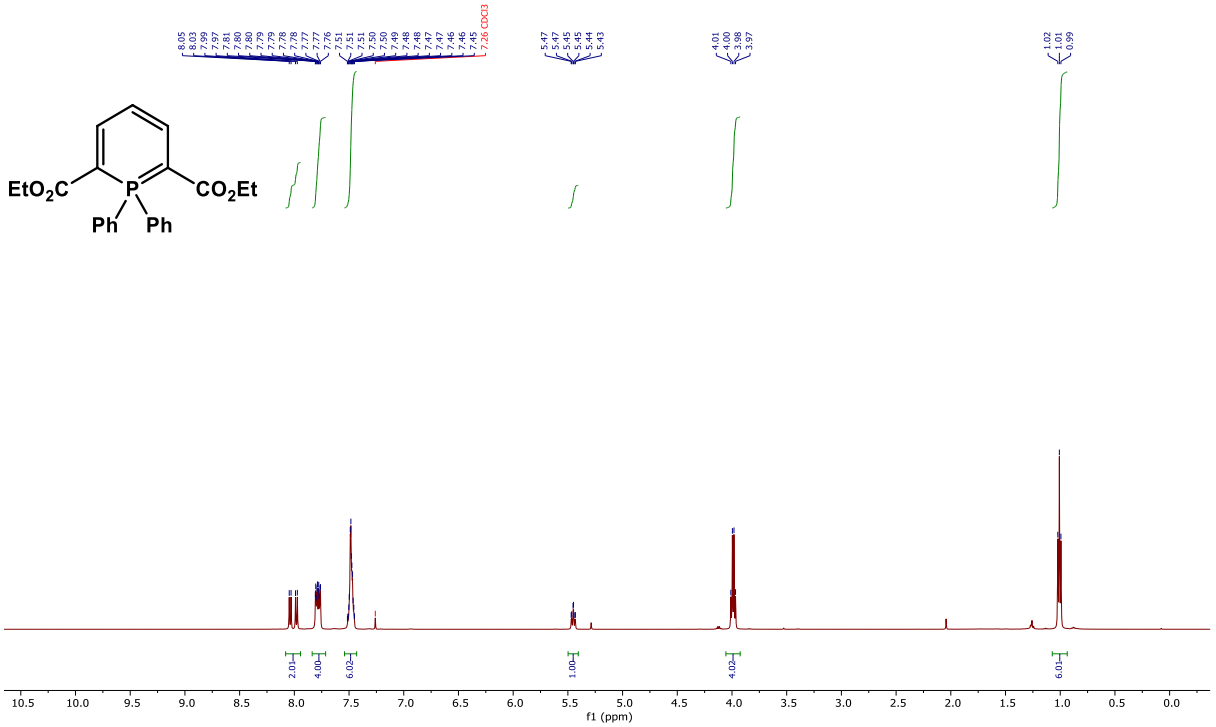


$^{31}$P NMR (202 MHz)

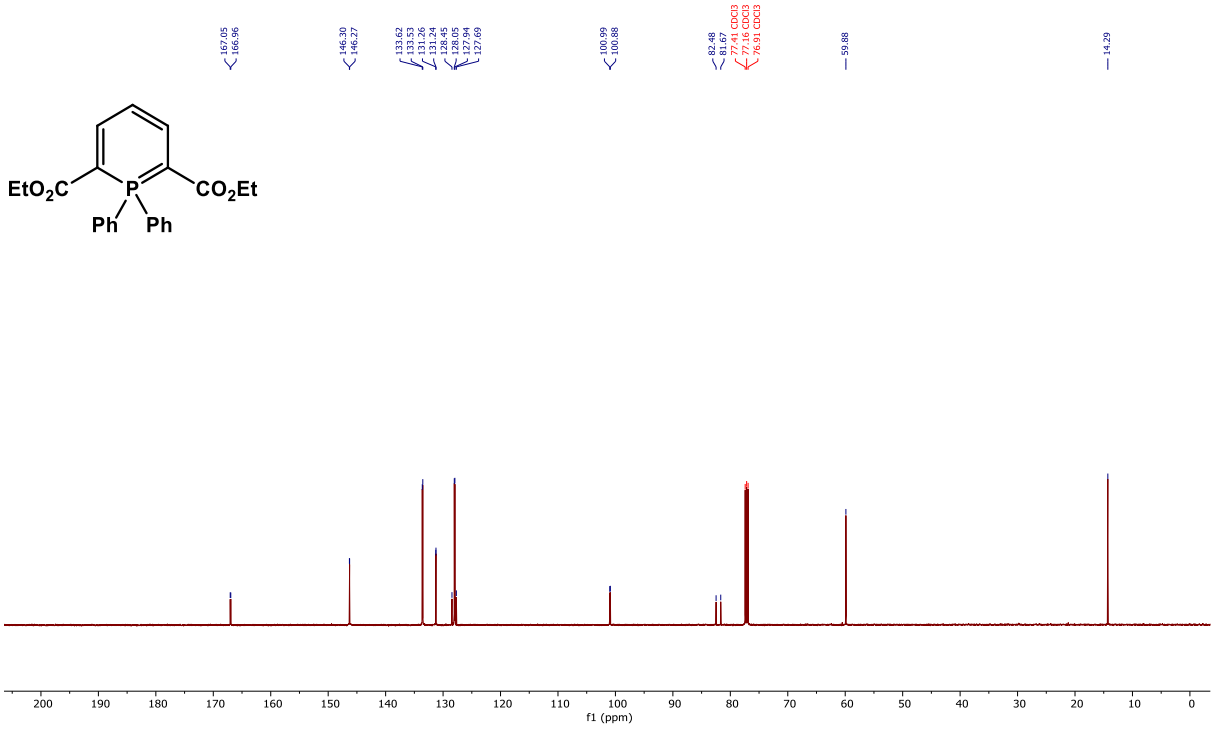


**Diethyl 1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (7)**

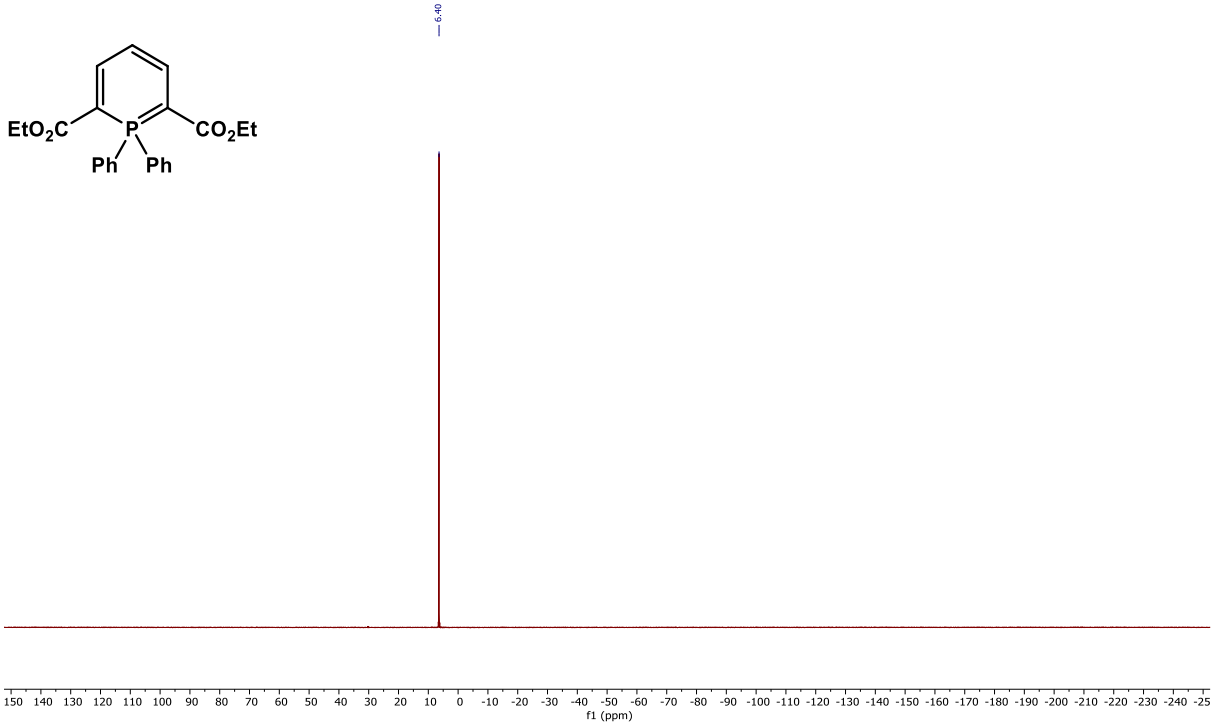
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

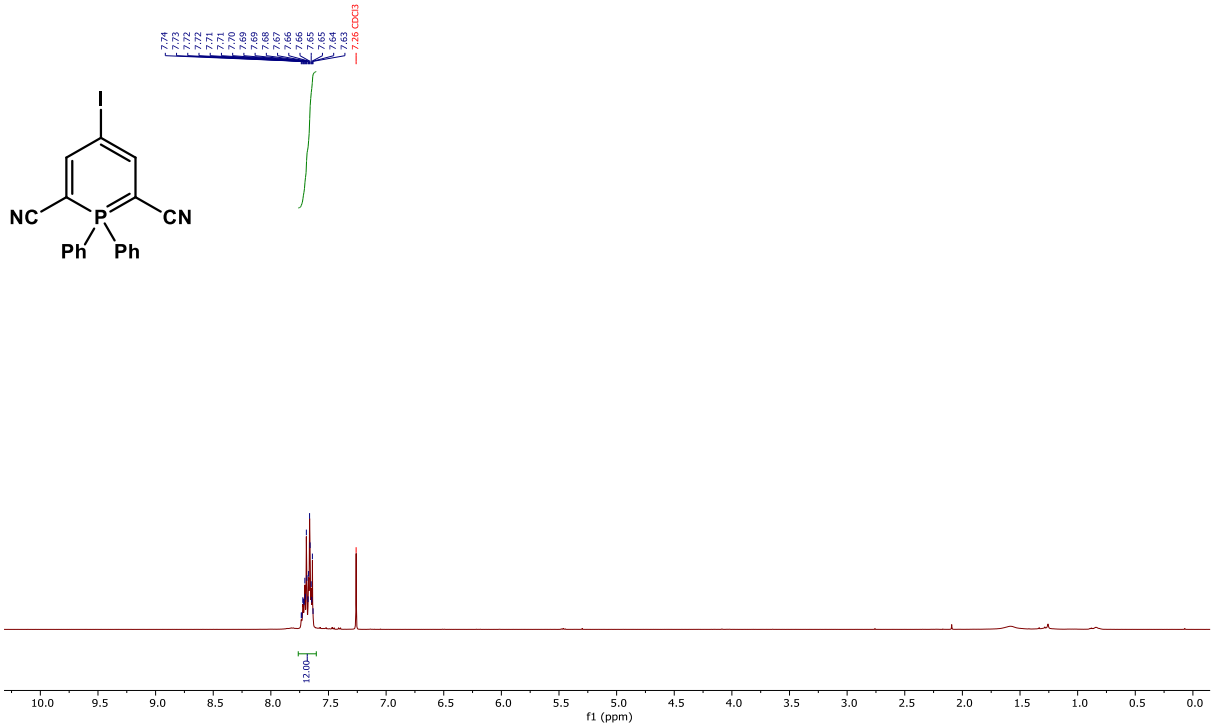


$^{31}$P NMR (202 MHz)

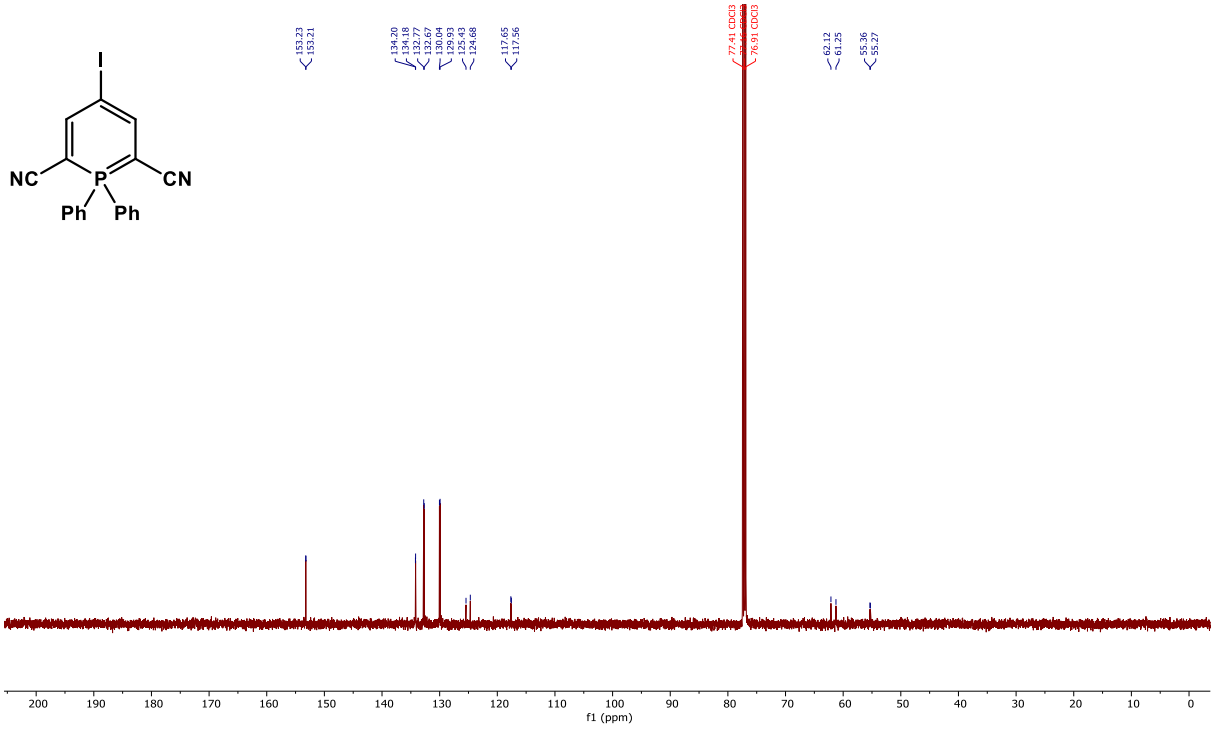


**4-iodo-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (1a)**

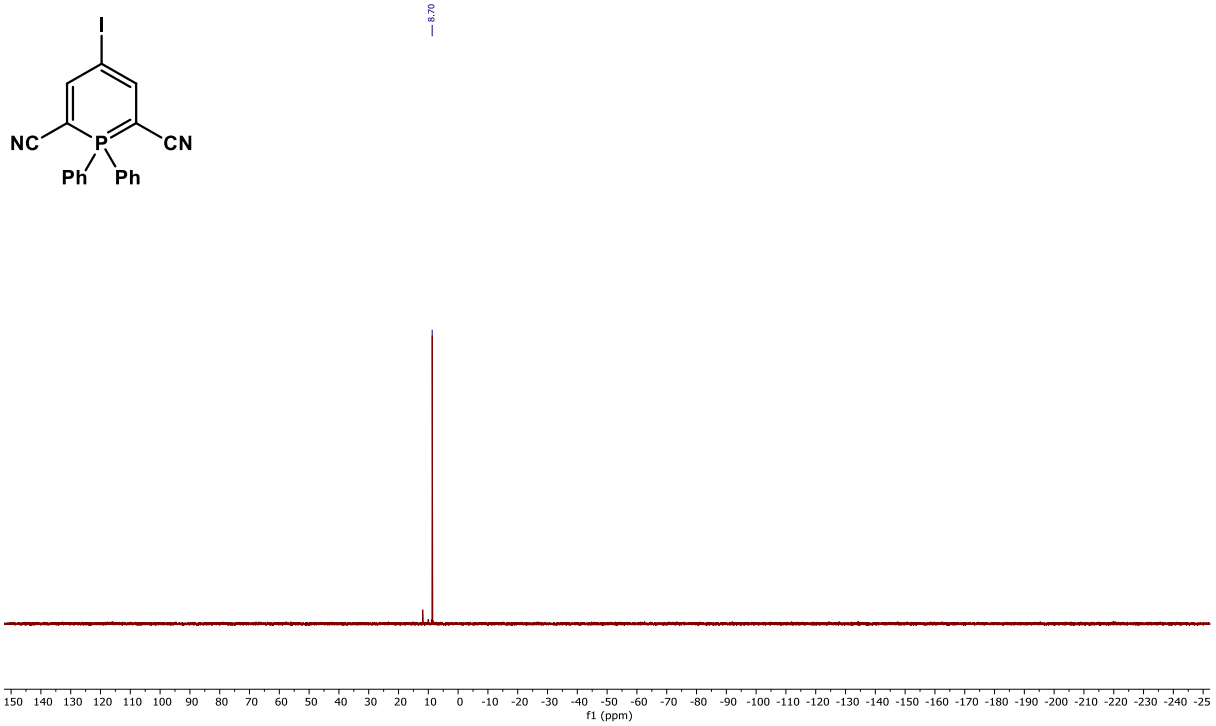
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

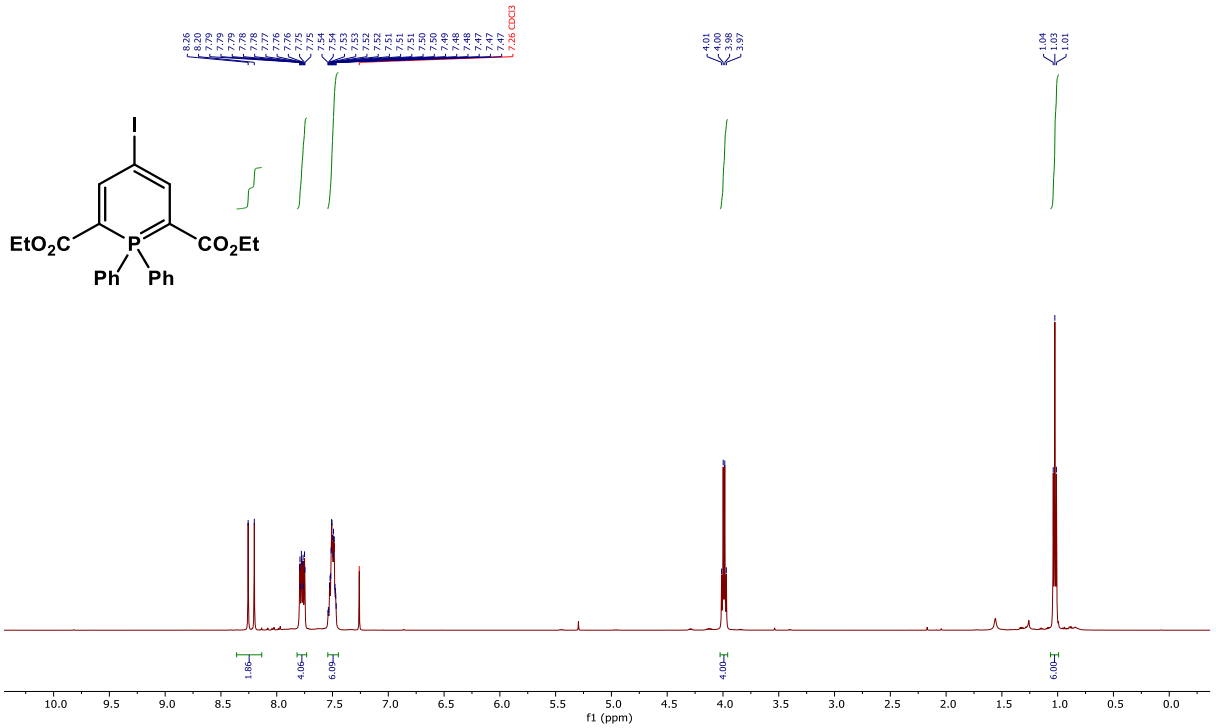


$^{31}$P NMR (202 MHz)

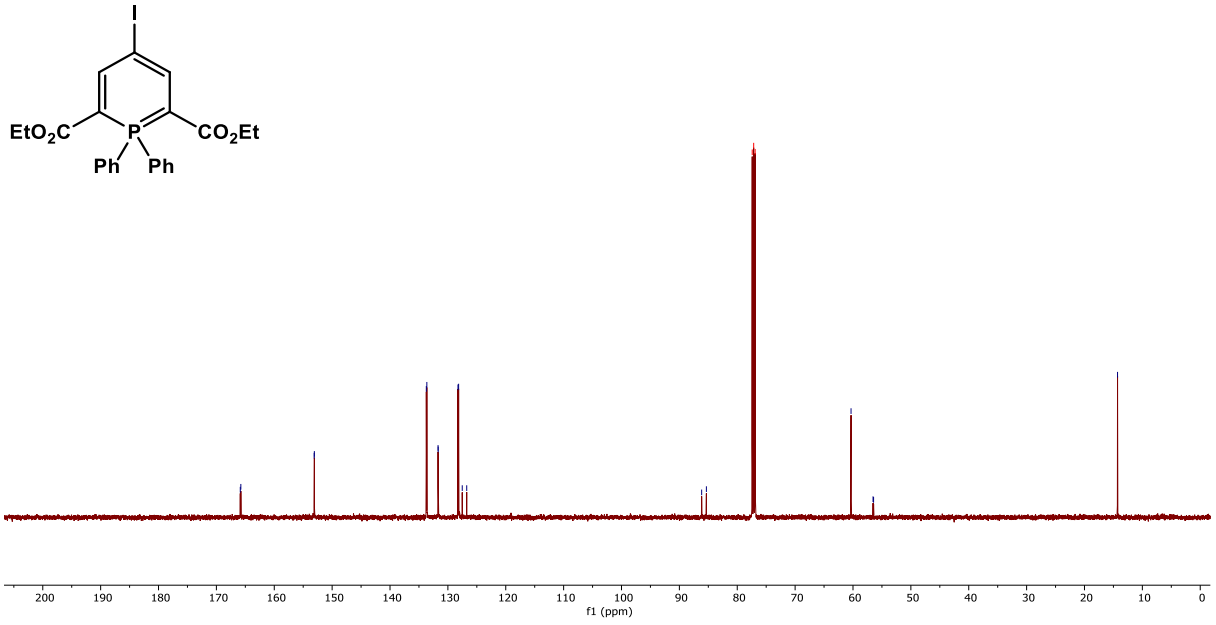


**Diethyl 4-iodo-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (1b)**

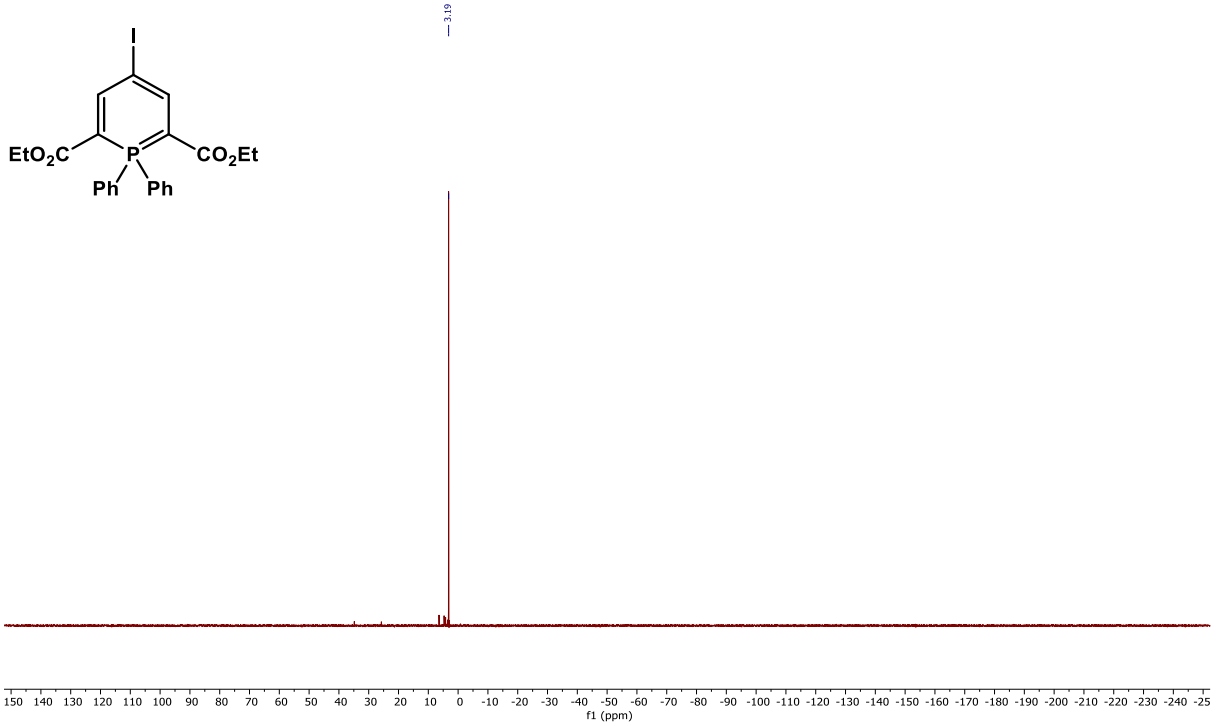
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)



$^{31}$P NMR (202 MHz)

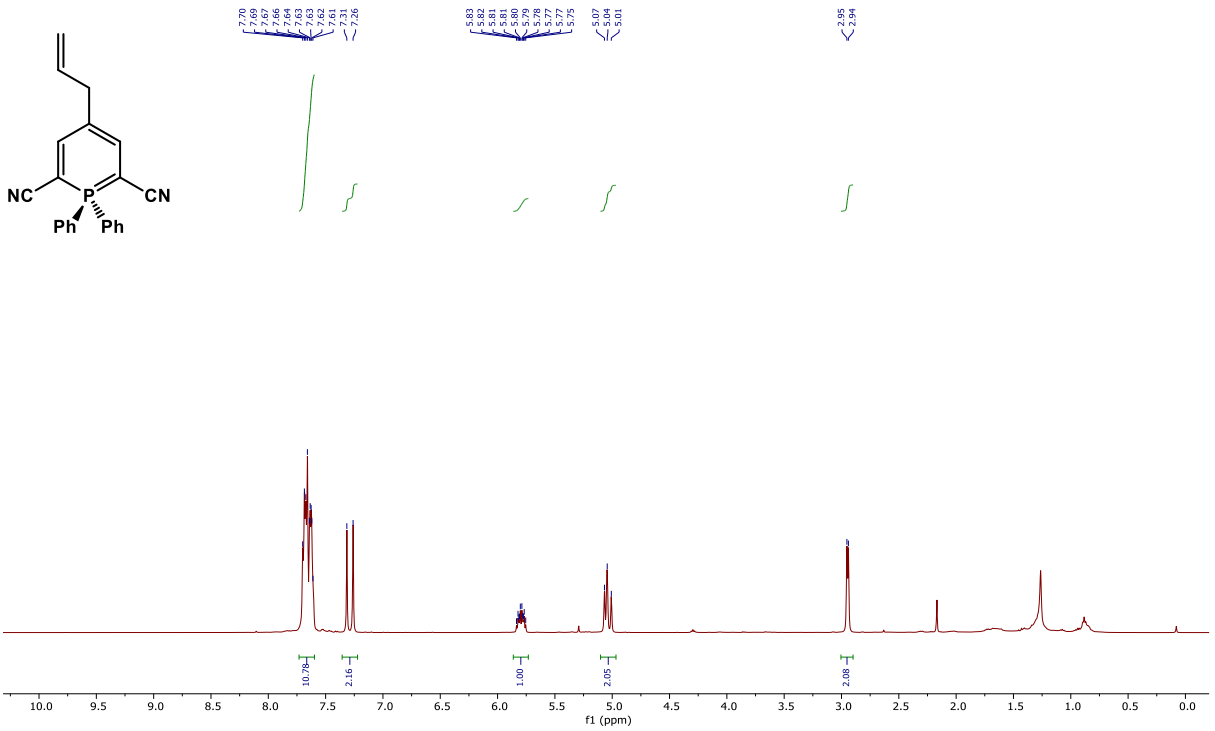


# I/Zn Exchange

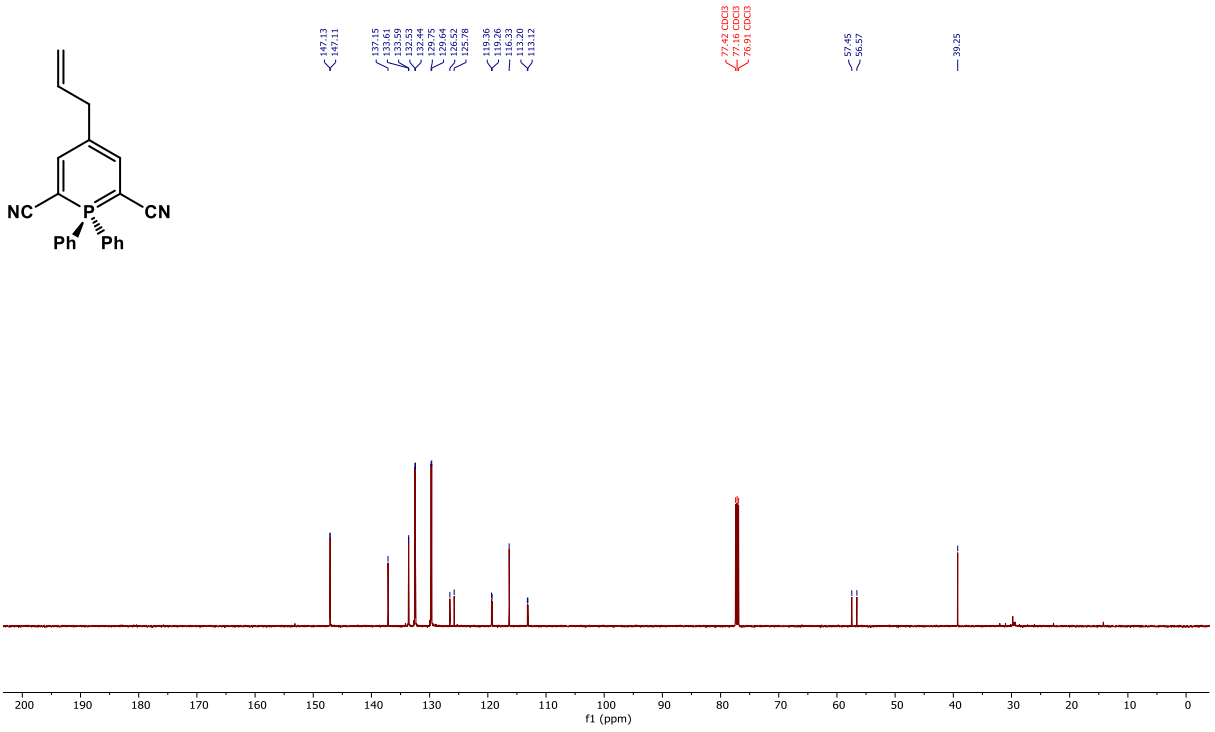
## ALLYLATION, ACYLATION AND OTHER FUNCTIONALIZATIONS

### 4-Allyl-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2a)

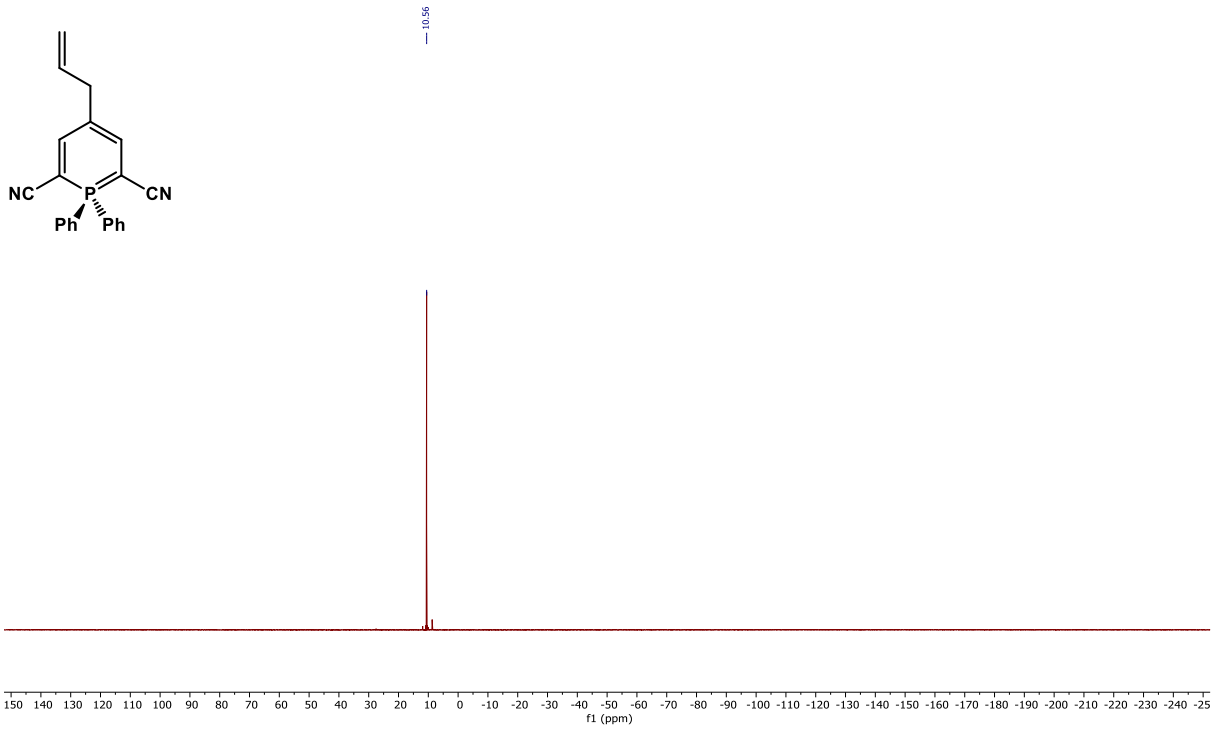
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

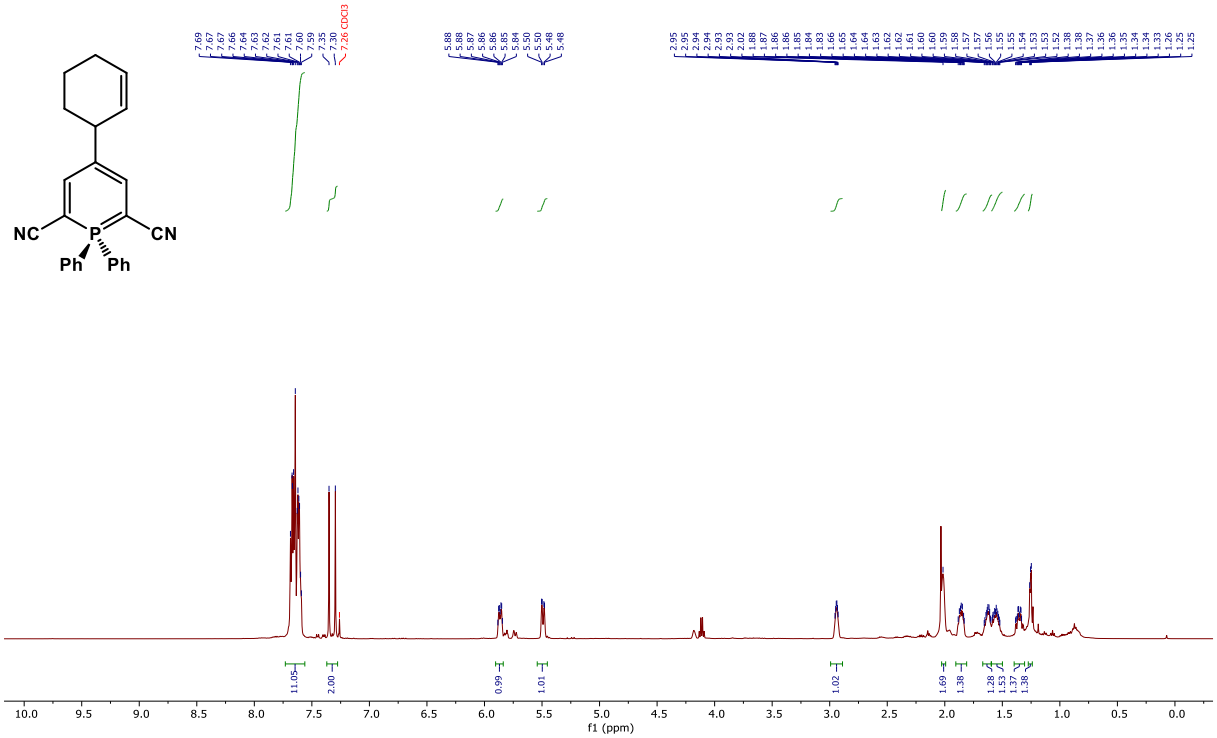



$^{31}$P NMR (202 MHz)

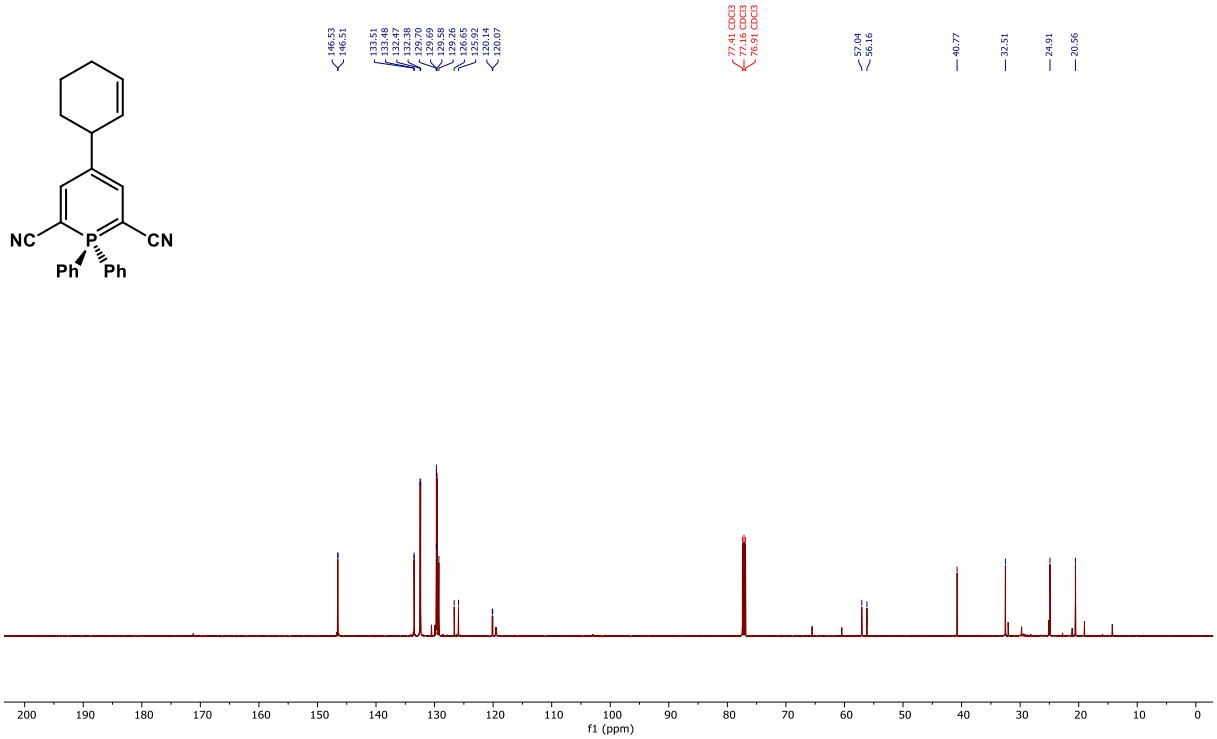

10.56
NC
P
CN
Ph
Ph
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25
f1 (ppm)

## 4-(Cyclohex-2-en-1-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2b)

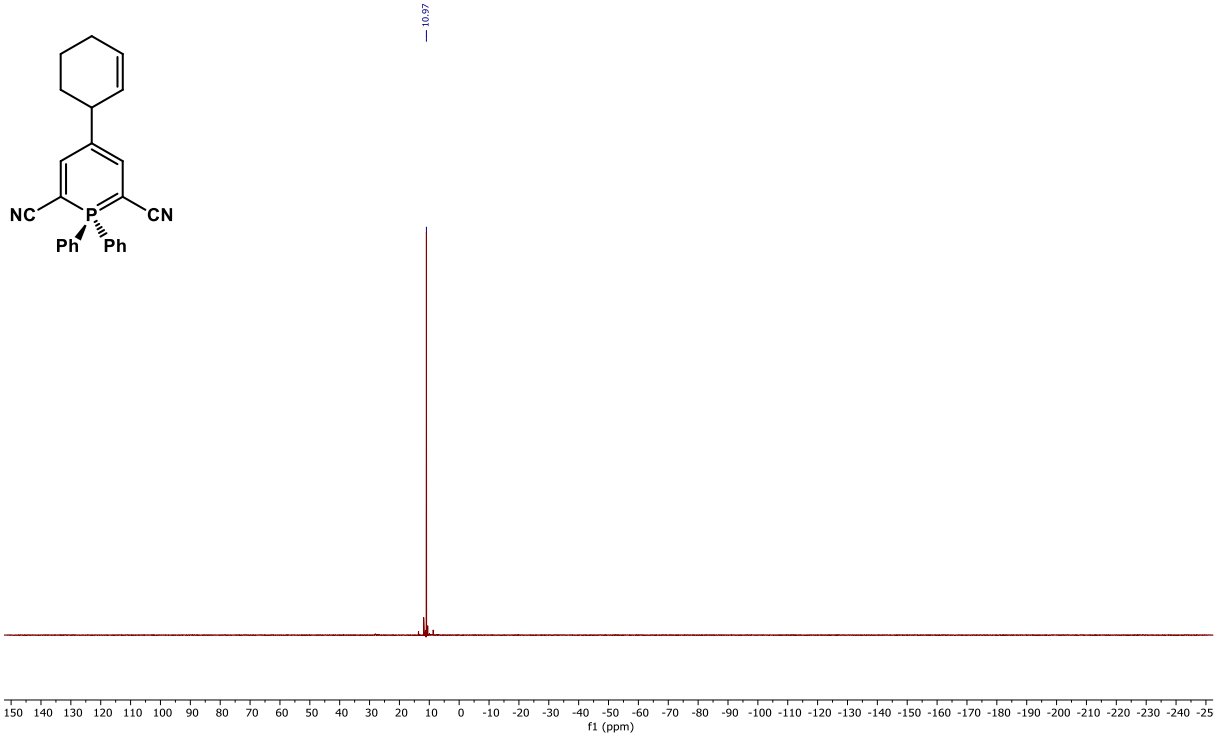
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

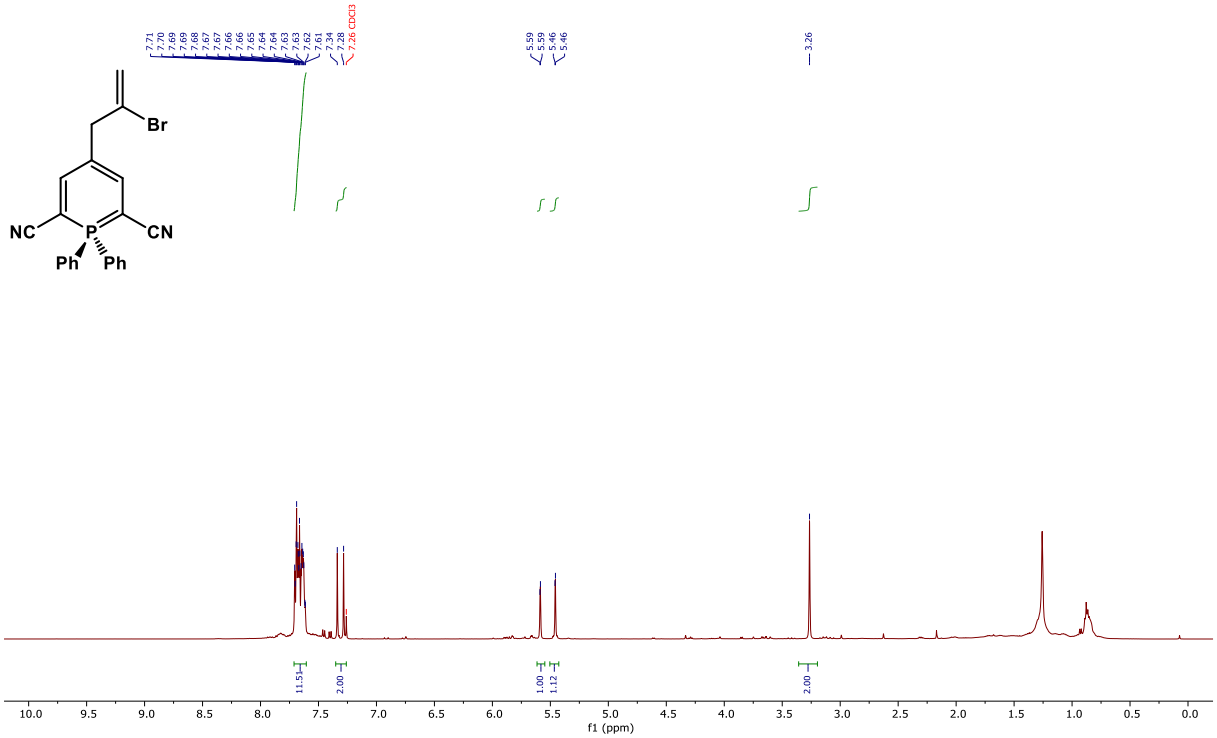


$^{31}$P NMR (202 MHz)

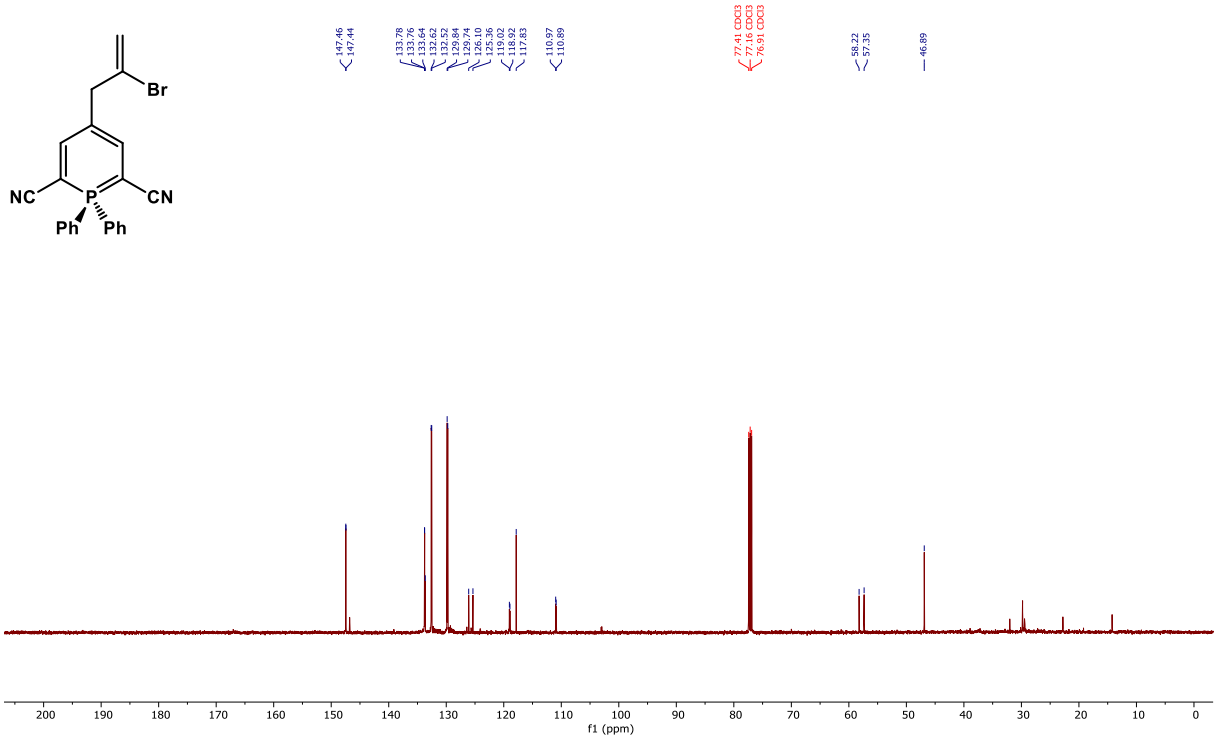


**4-(2-Bromoallyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2c)**

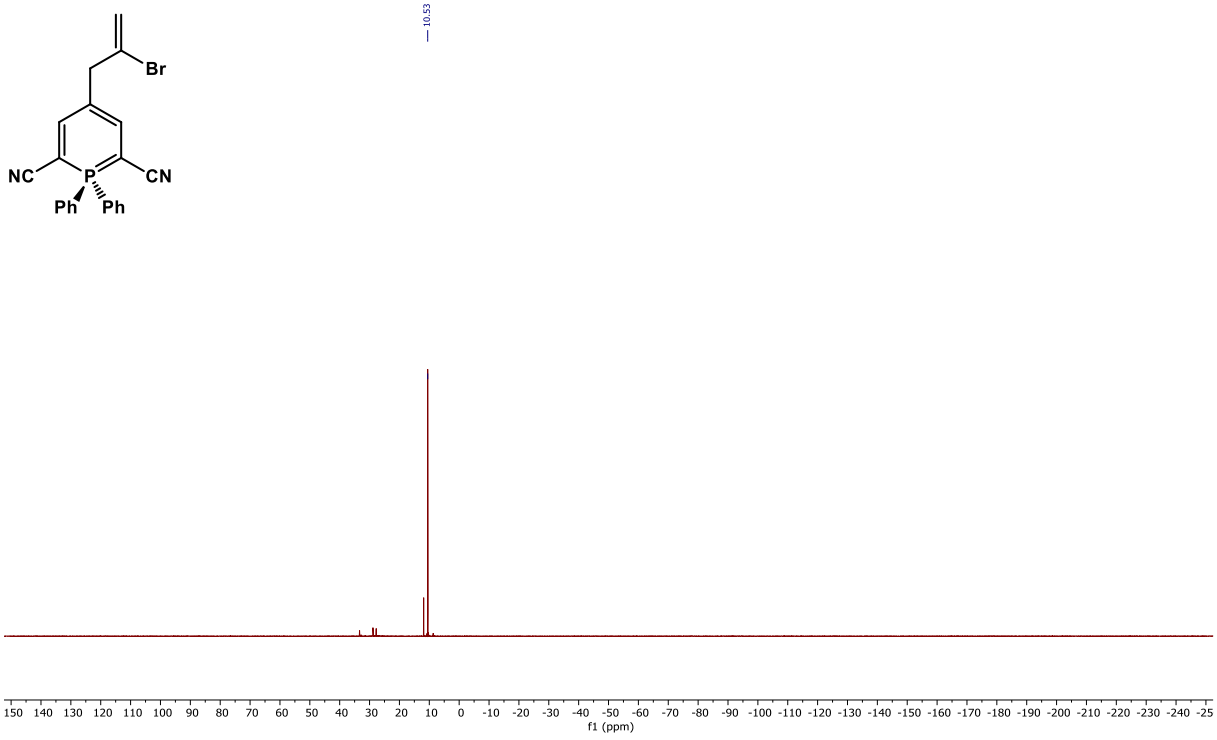
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

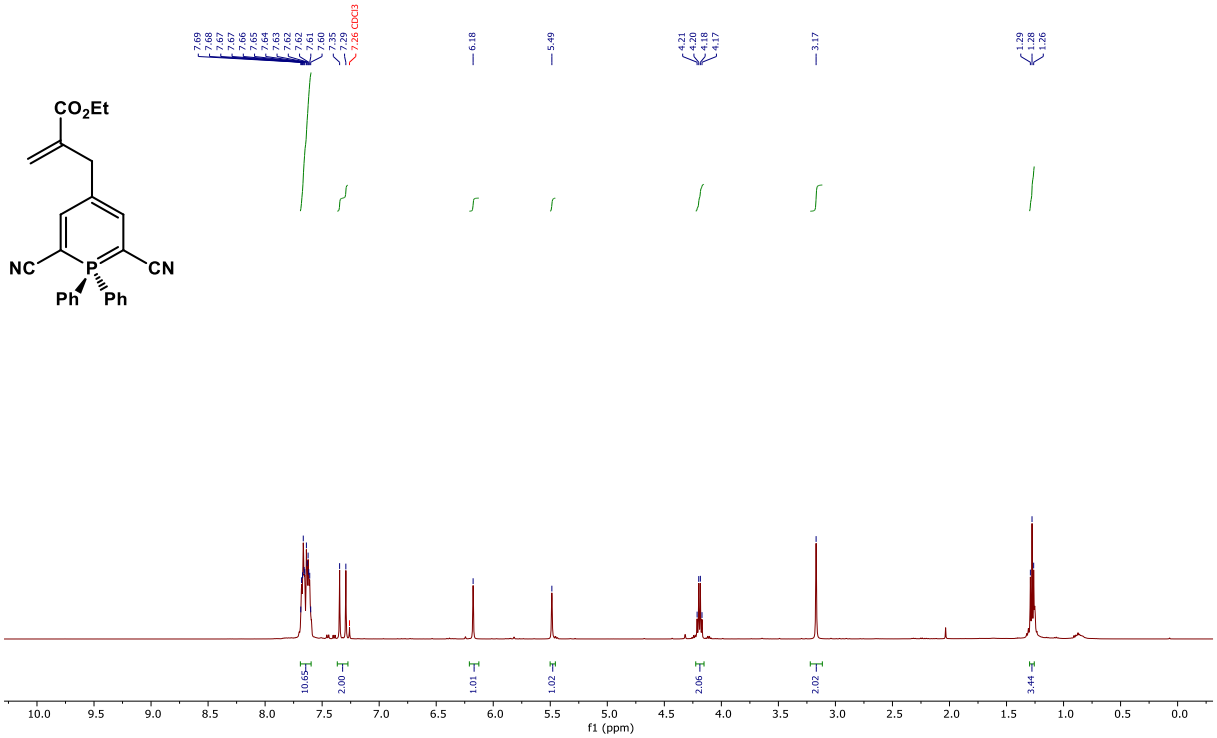


$^{31}$P NMR (202 MHz)

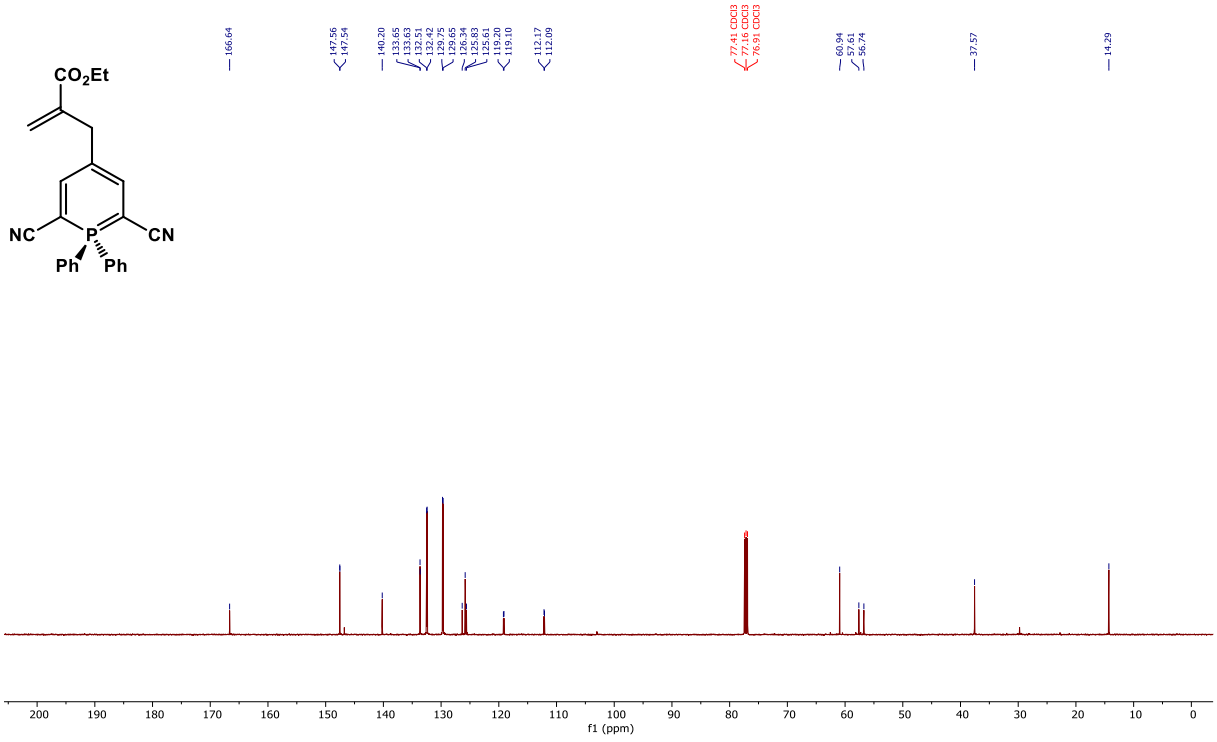


**Ethyl 2-((2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)methyl)acrylate (2d)**

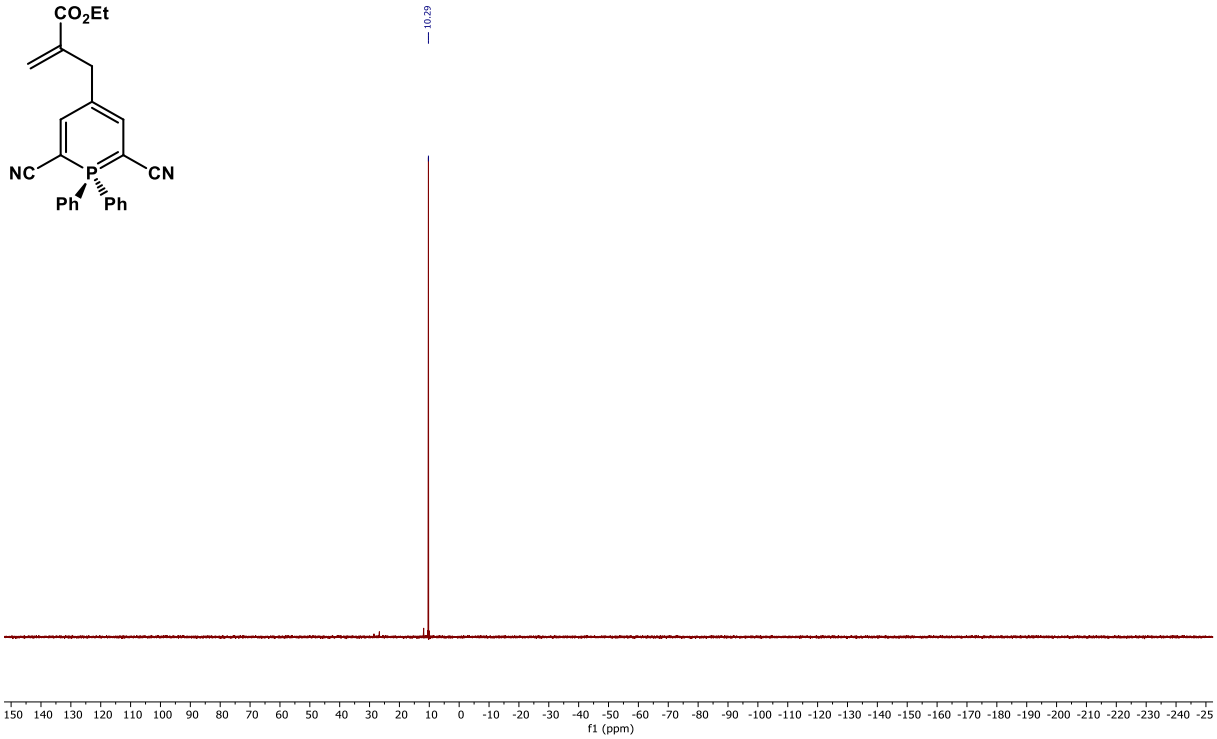
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

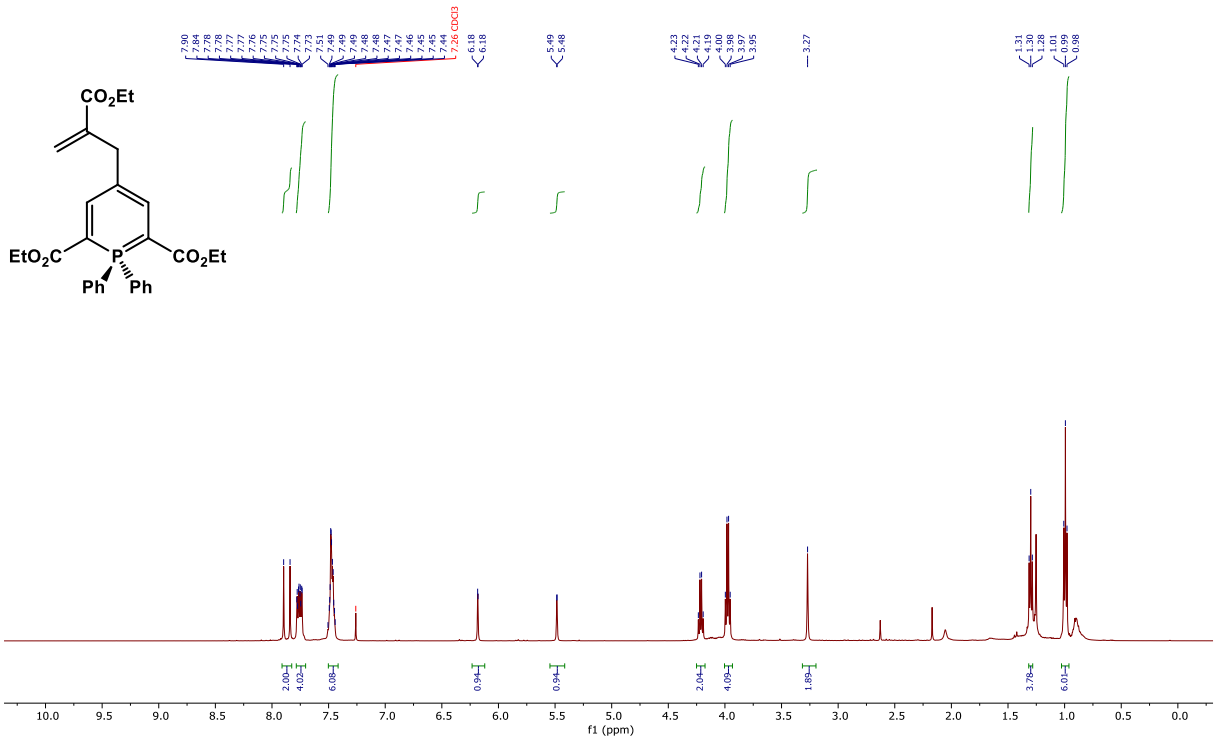


$^{31}$P NMR (202 MHz)

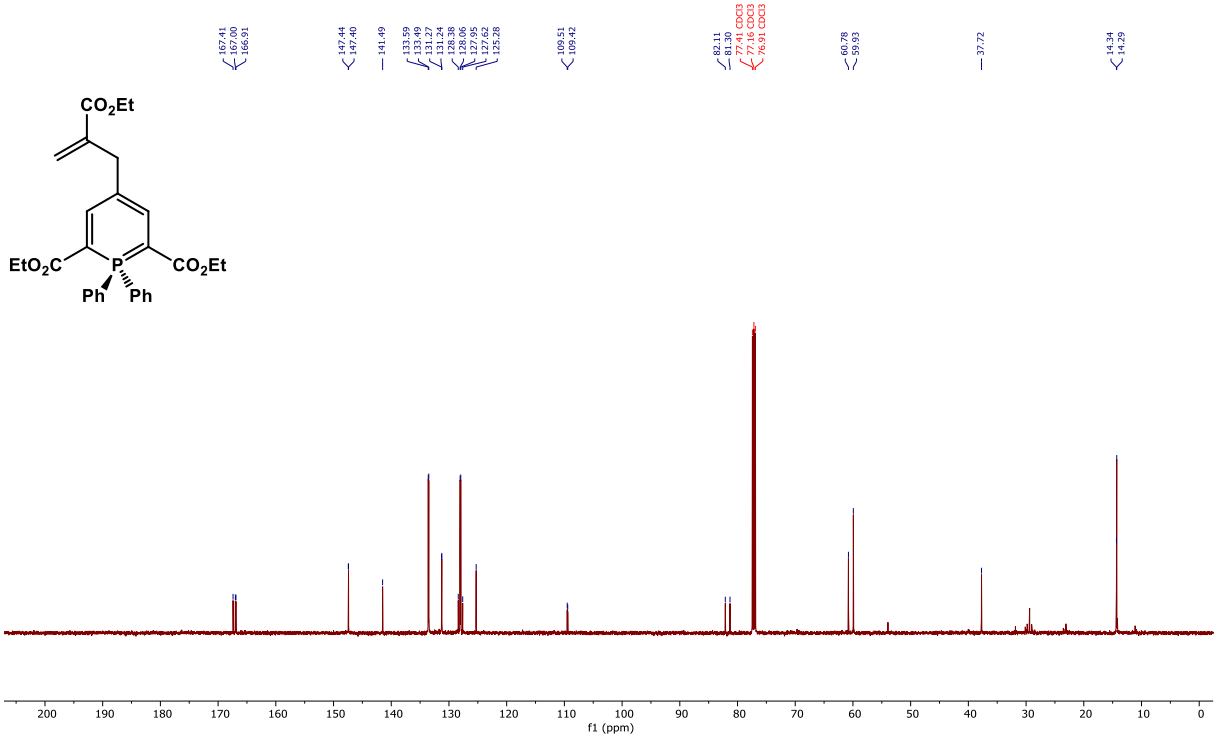


**diethyl 4-(2-(ethoxycarbonyl)allyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (5a)**

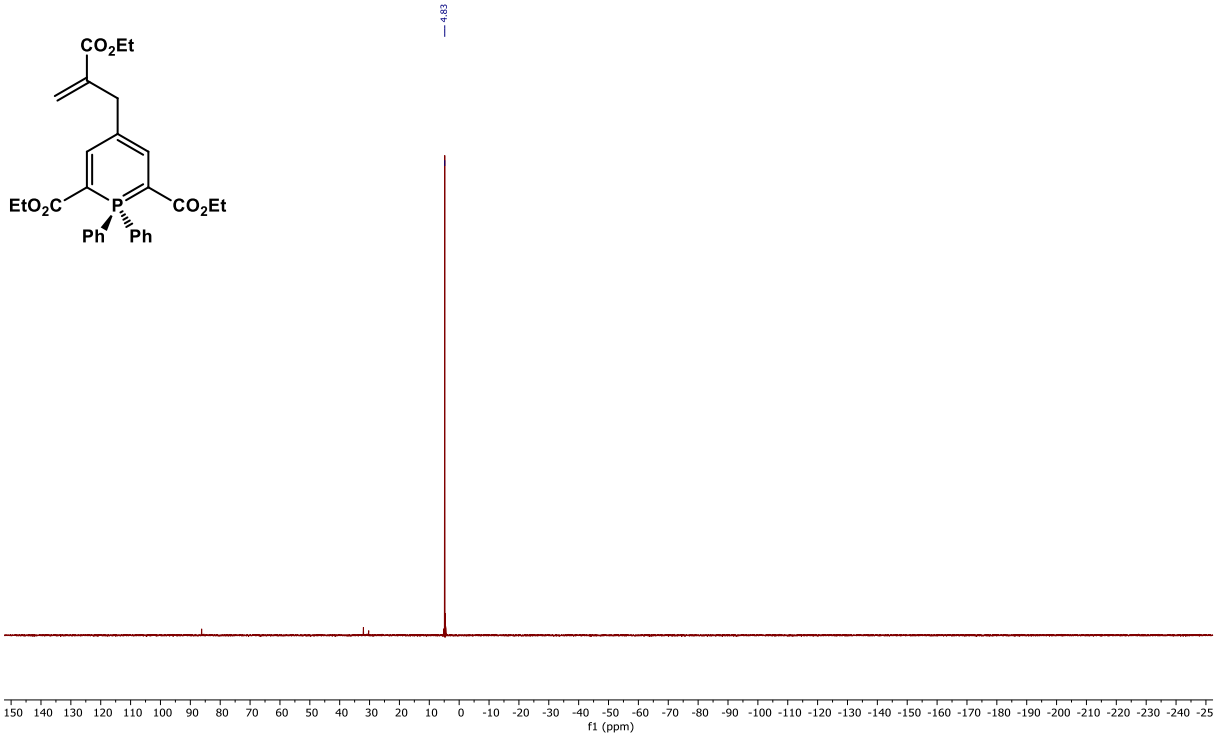
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

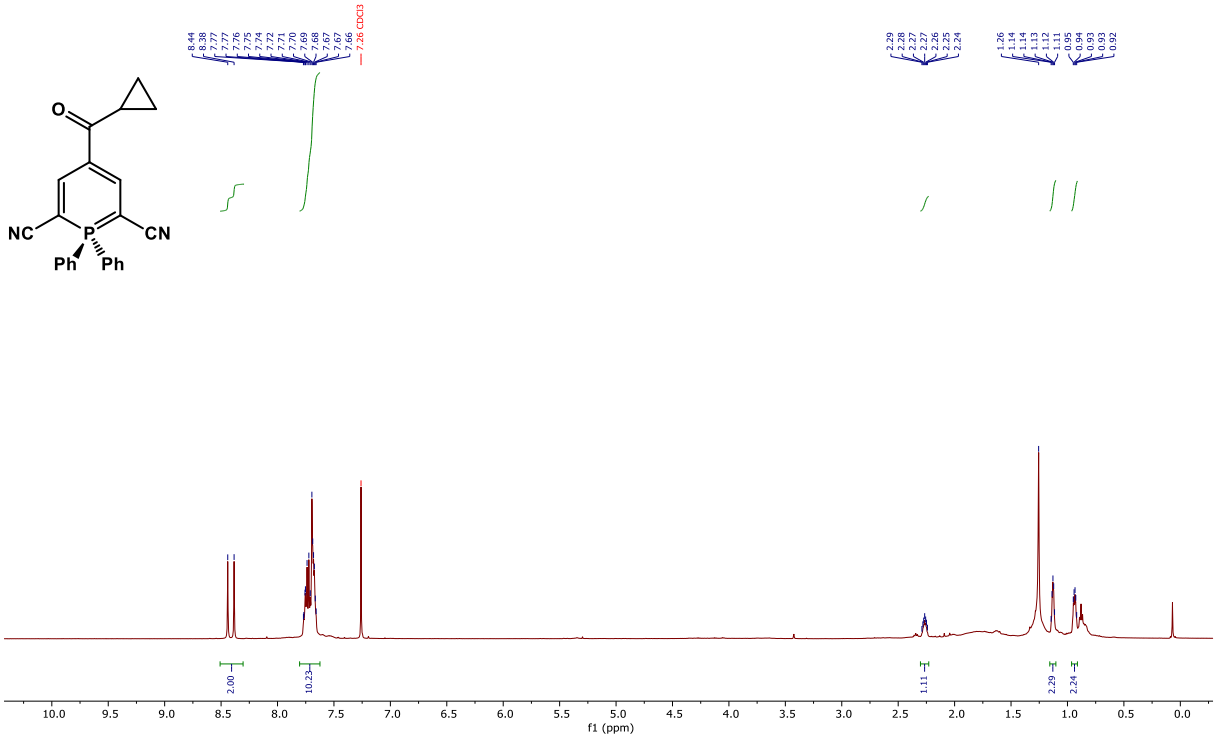


$^{31}$P NMR (202 MHz)

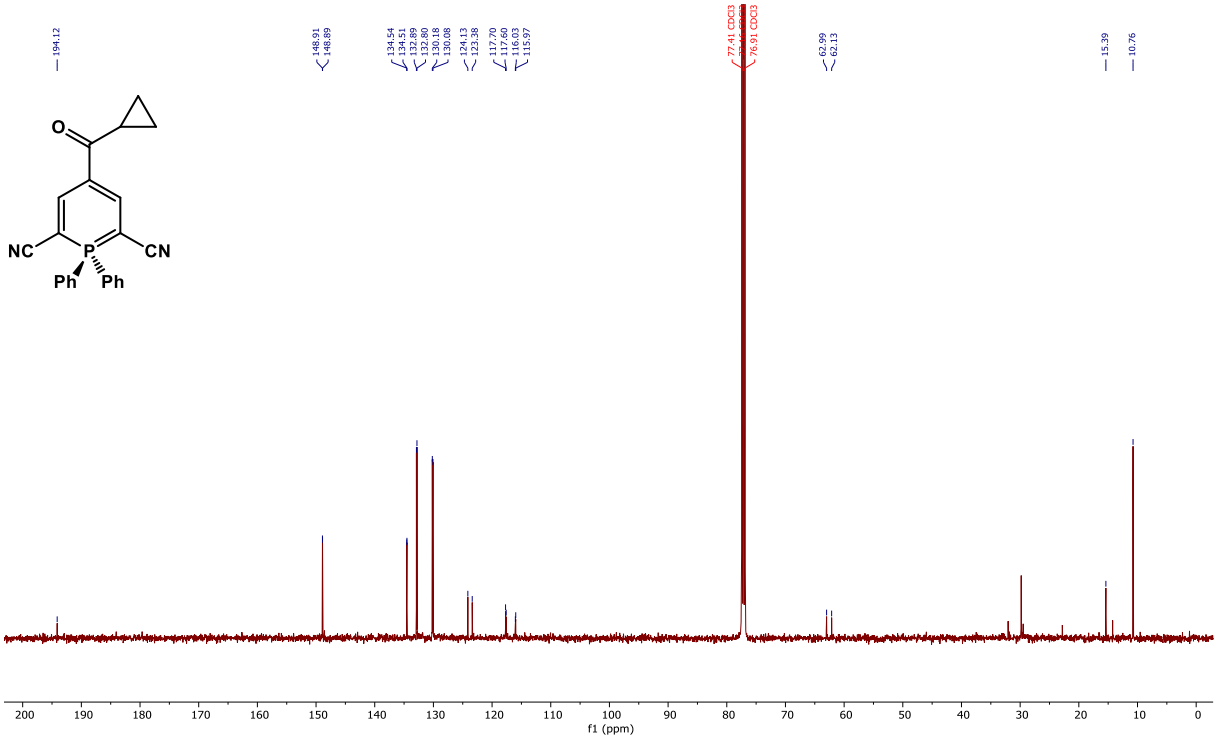


**4-(Cyclopropanecarbonyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2e)**

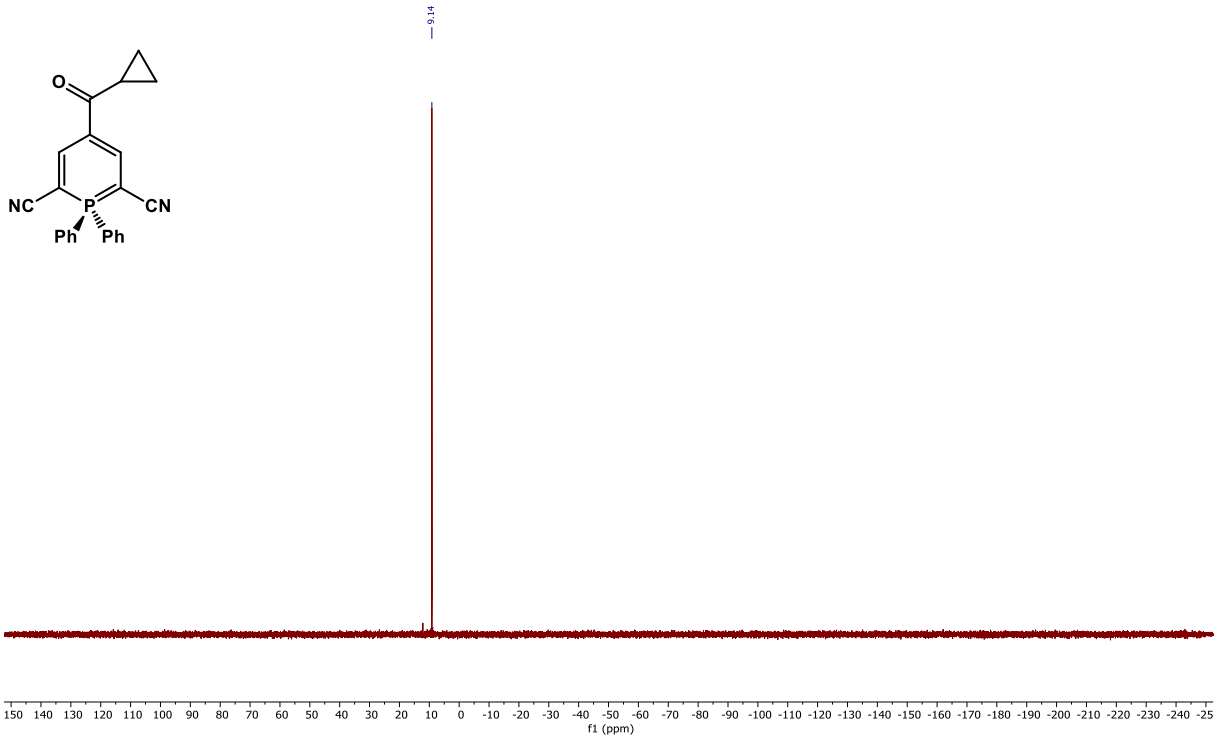
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

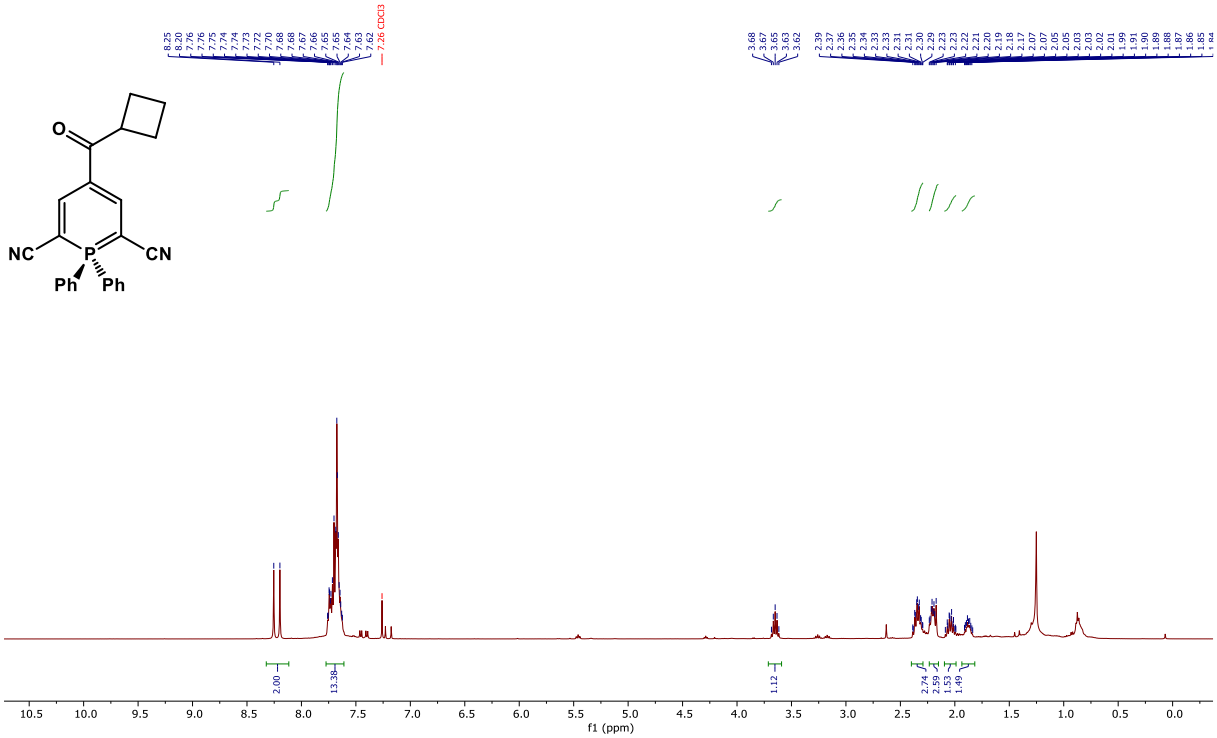


$^{31}$P NMR (202 MHz)

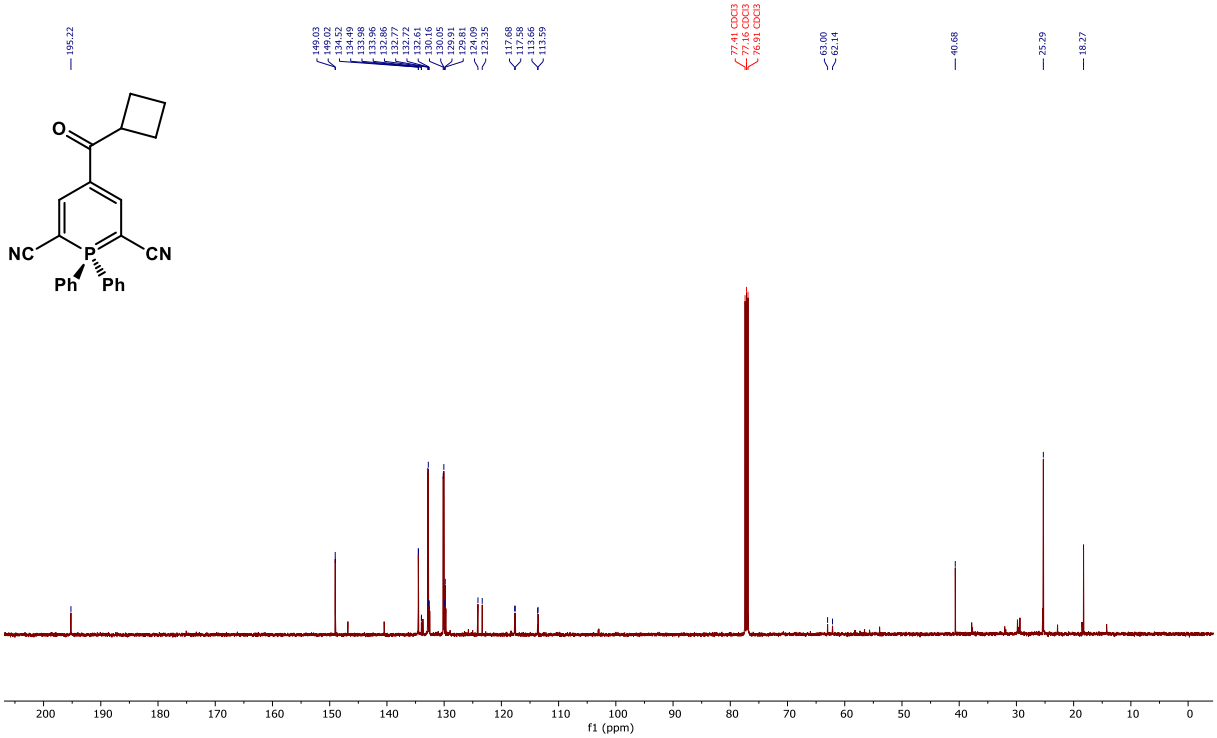


## 4-(Cyclobutanecarbonyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2f)

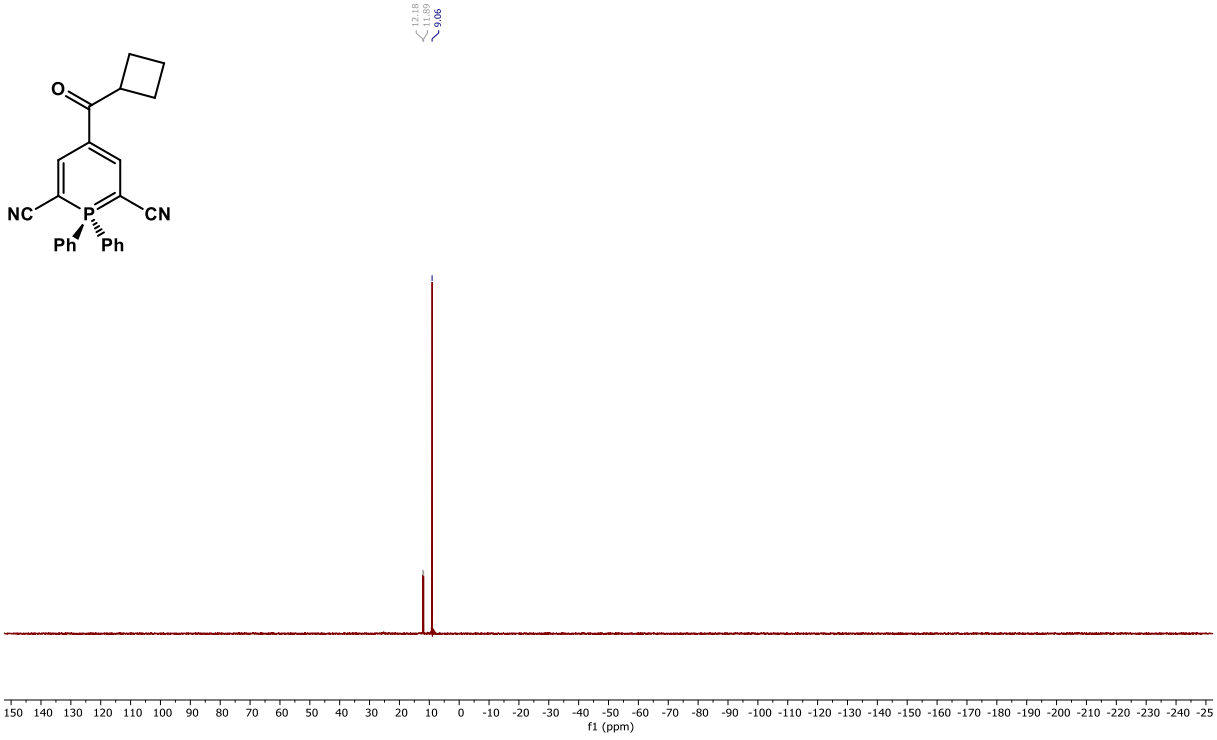
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

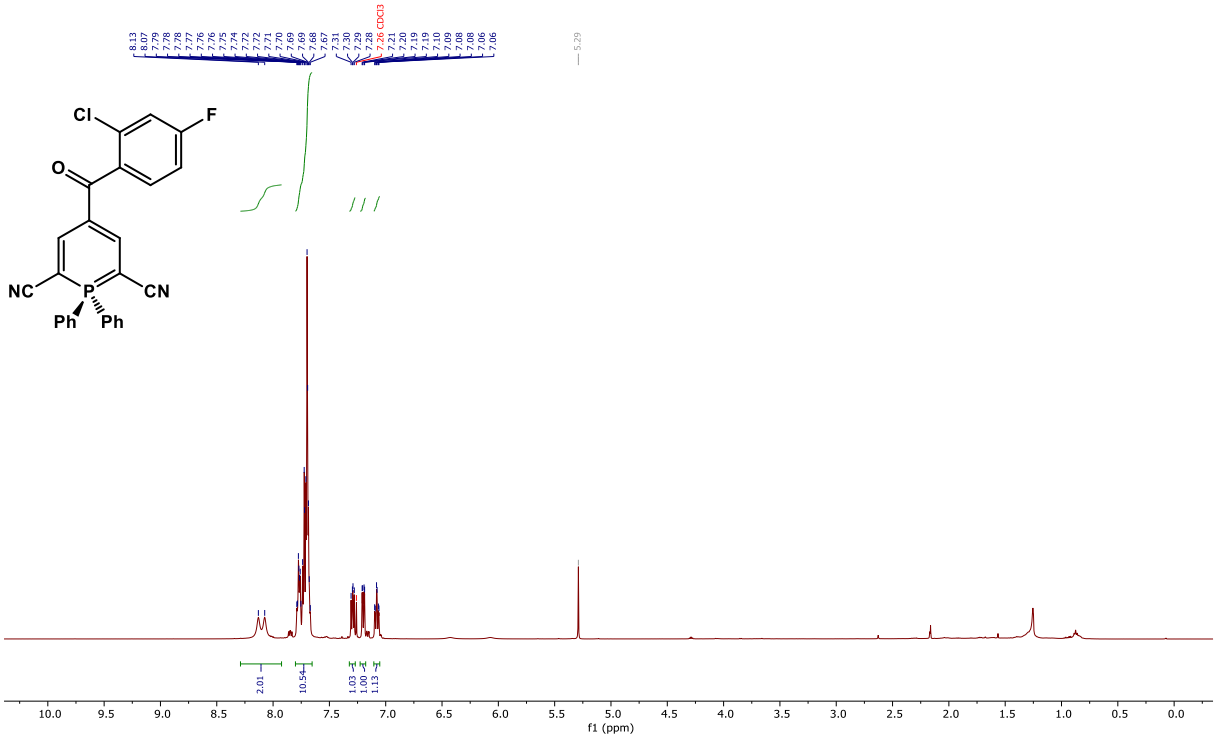


$^{31}$P NMR (202 MHz)

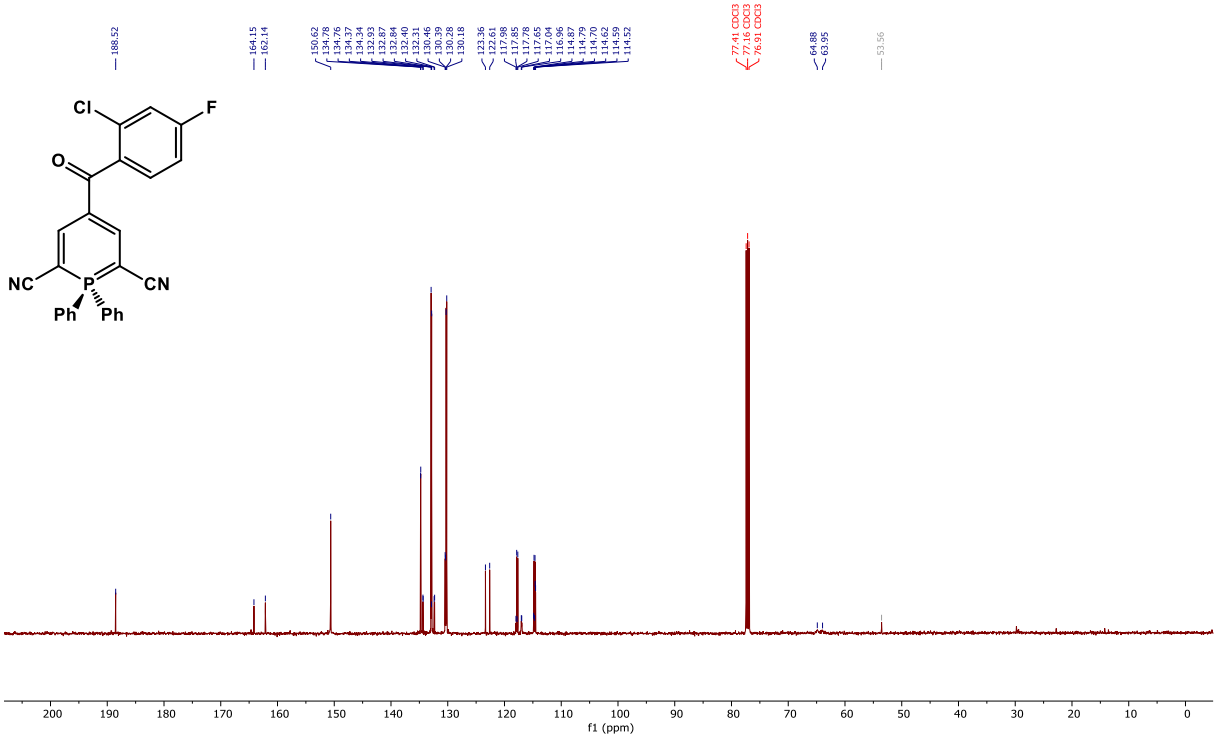


**4-(2-Chloro-4-fluorobenzoyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2g)**

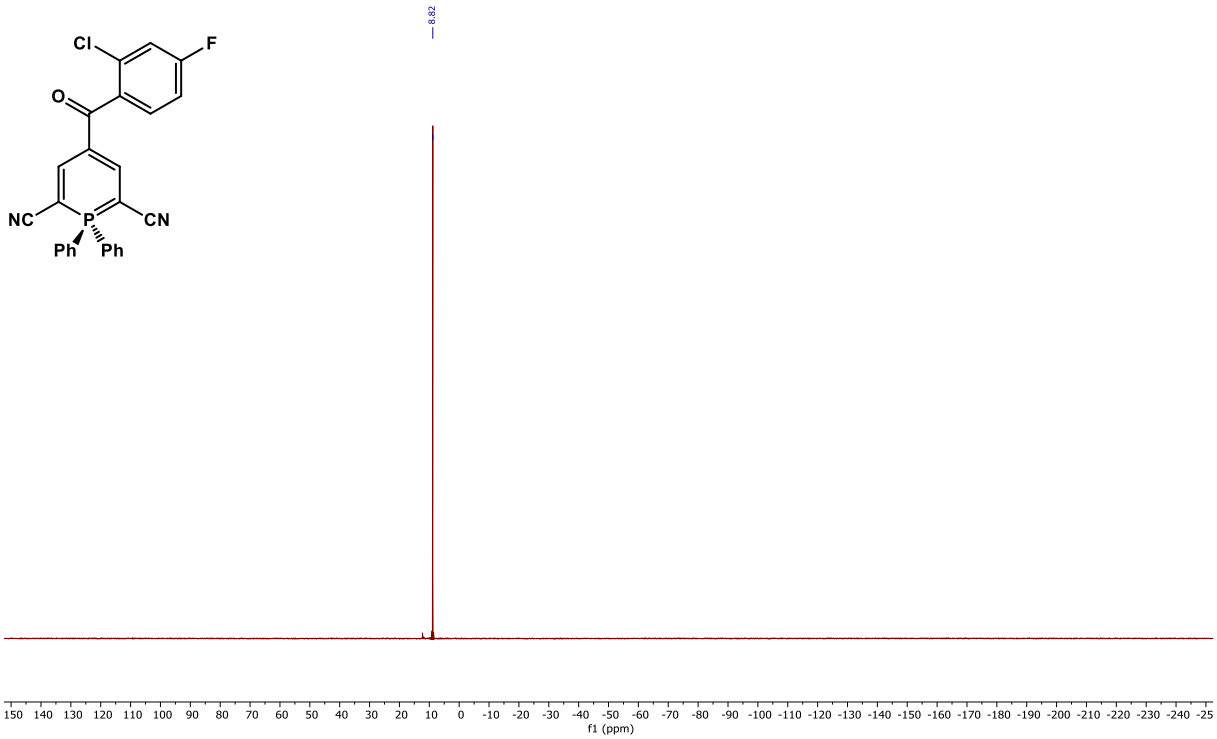
$^1$H NMR (500 MHz)



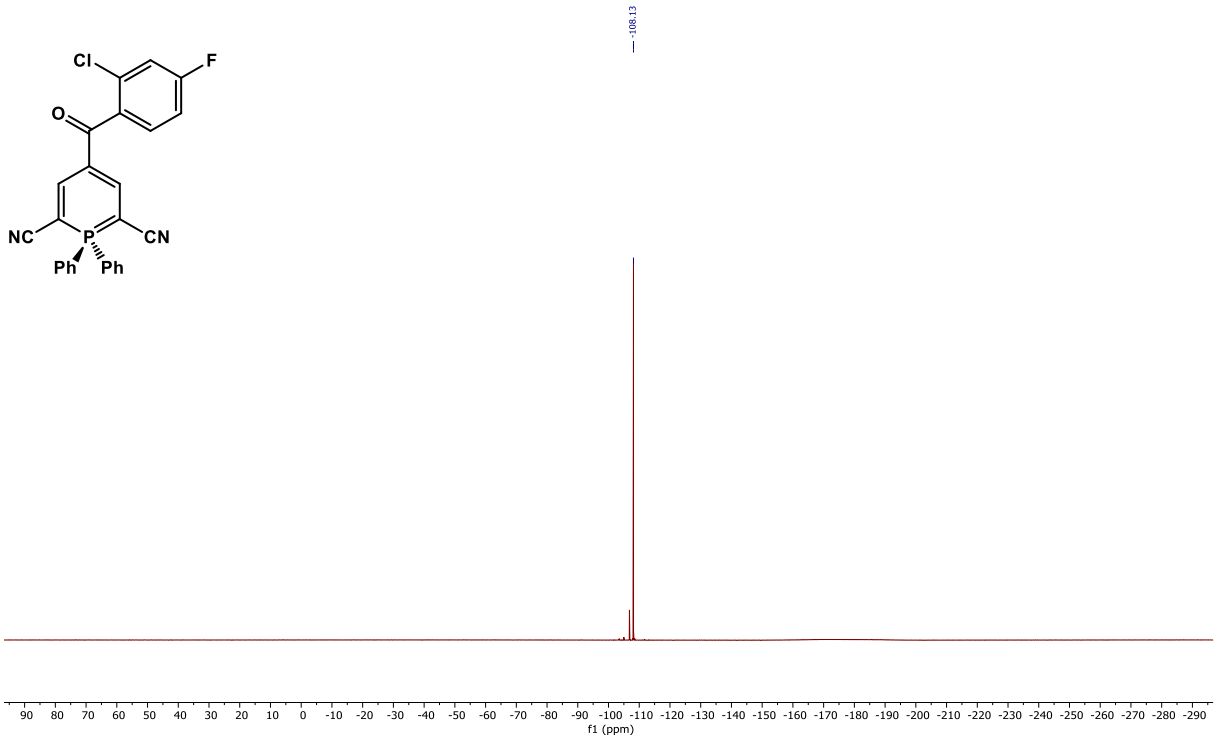

$^{13}$C NMR (126 MHz)



$^{31}$P NMR (202 MHz)

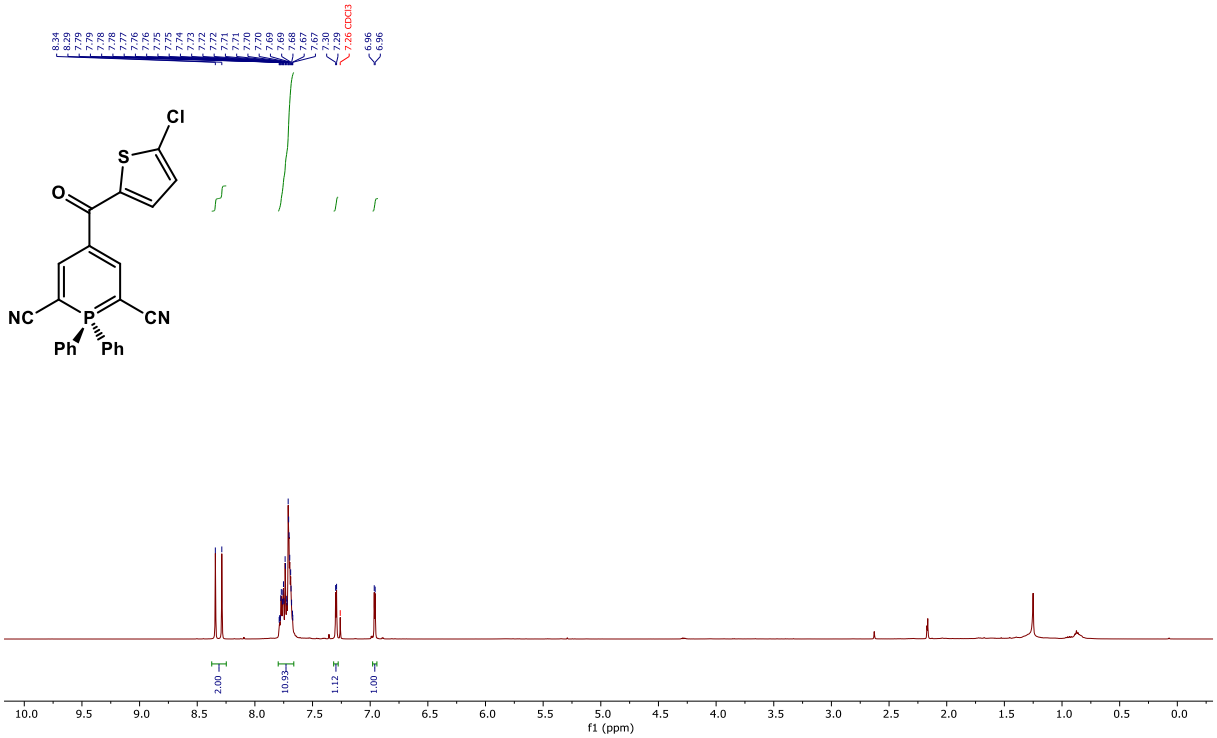



$^{19}$F NMR (471 MHz)

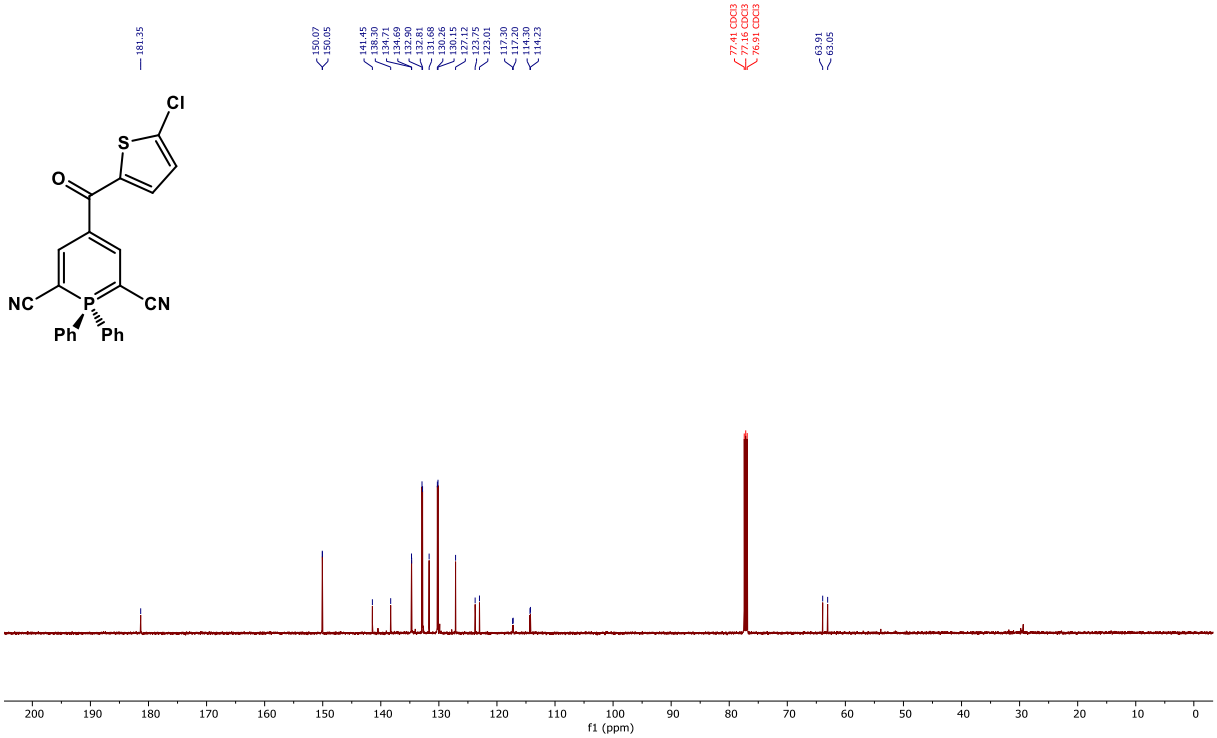


**4-(5-Chlorothiophene-2-carbonyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2h)**

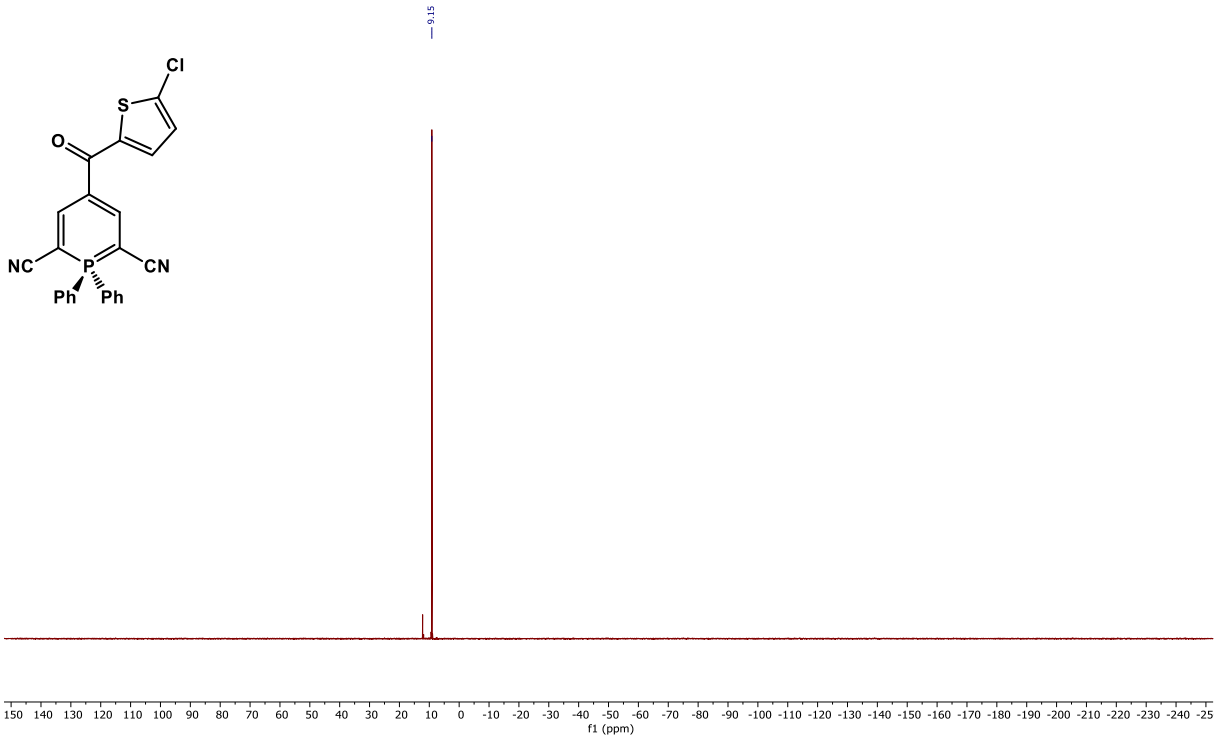
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

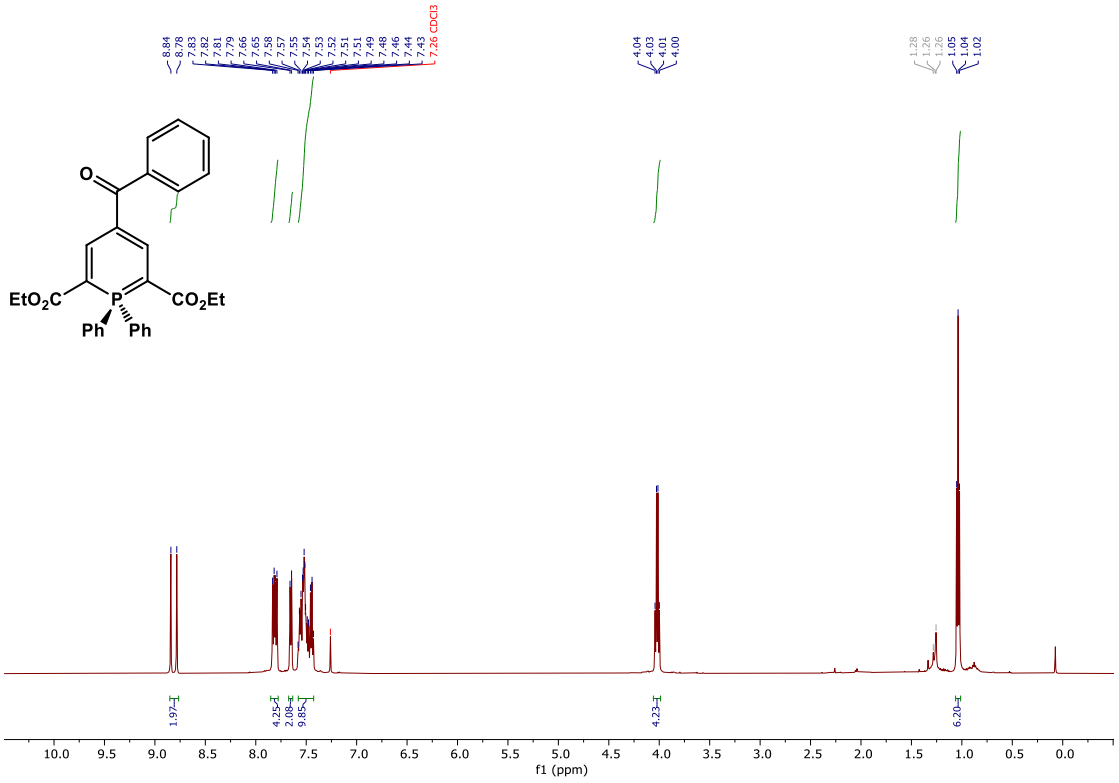


$^{31}$P NMR (202 MHz)

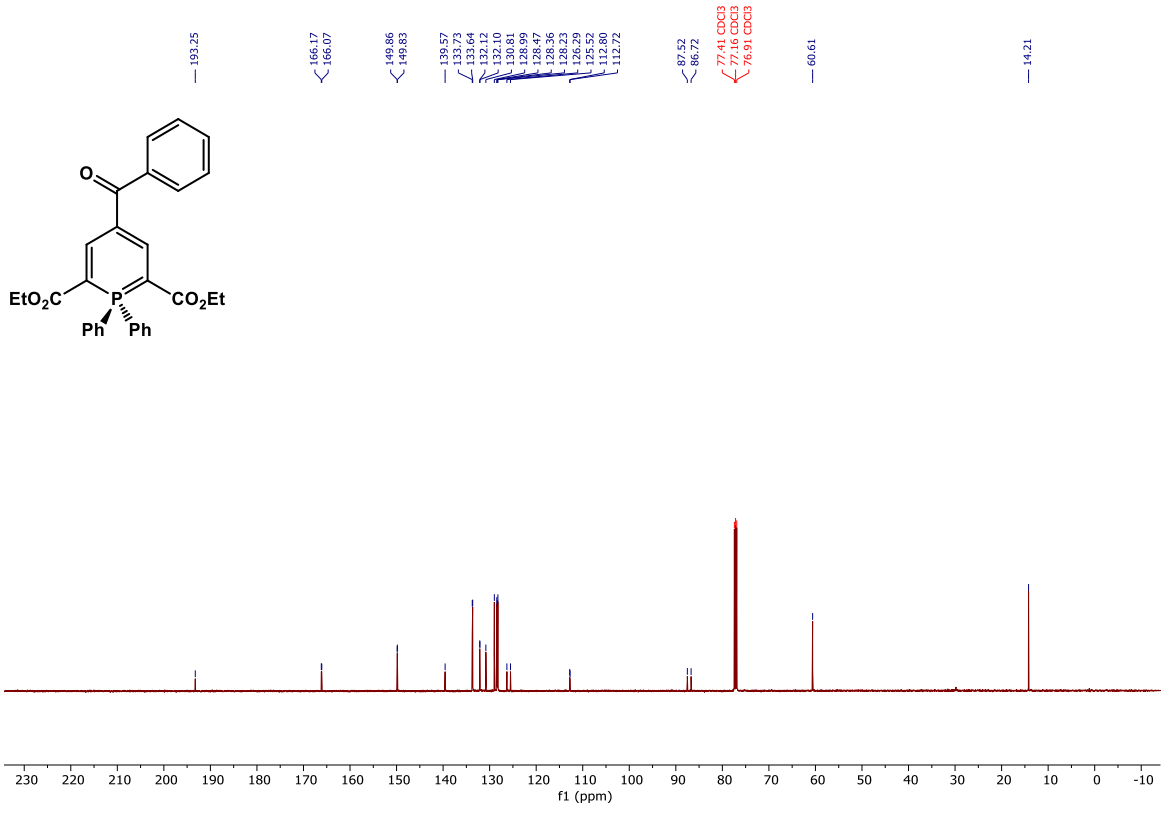


**diethyl 4-benzoyl-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (5b)**

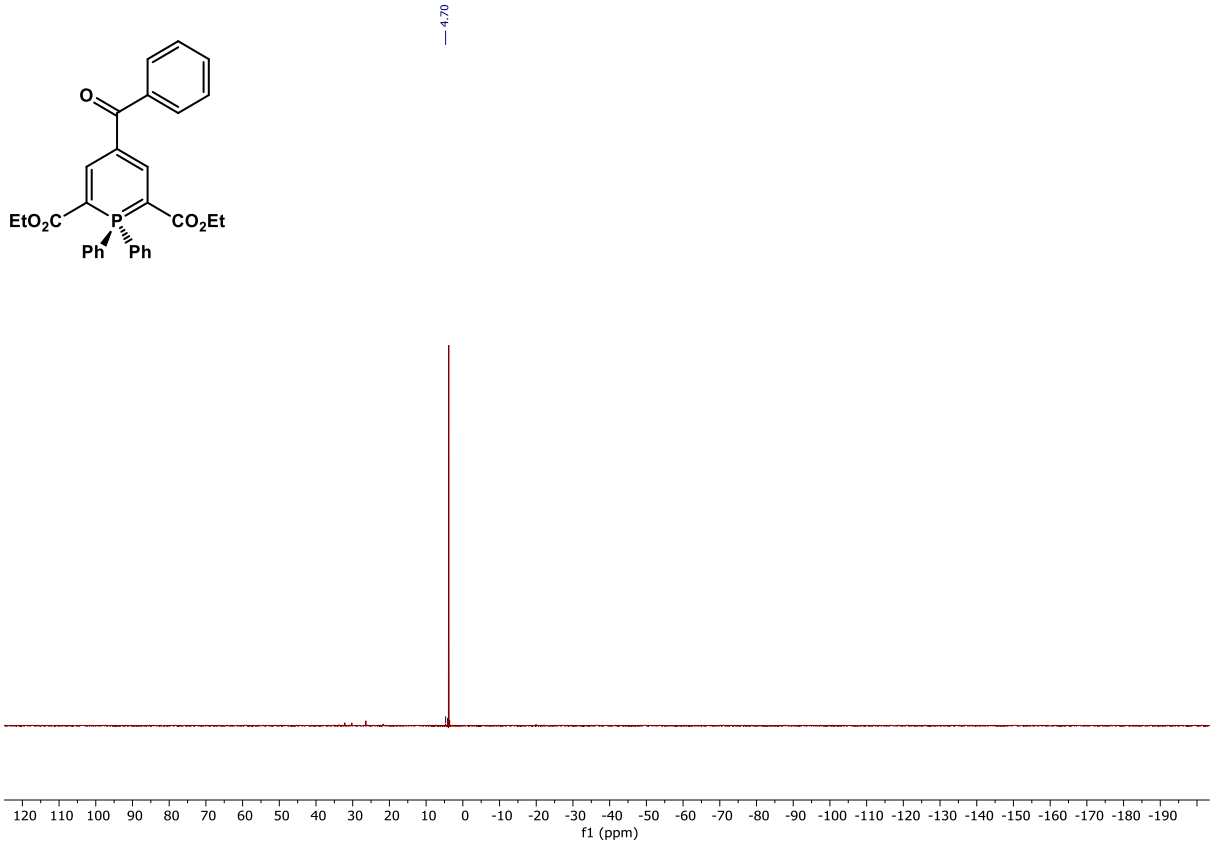
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

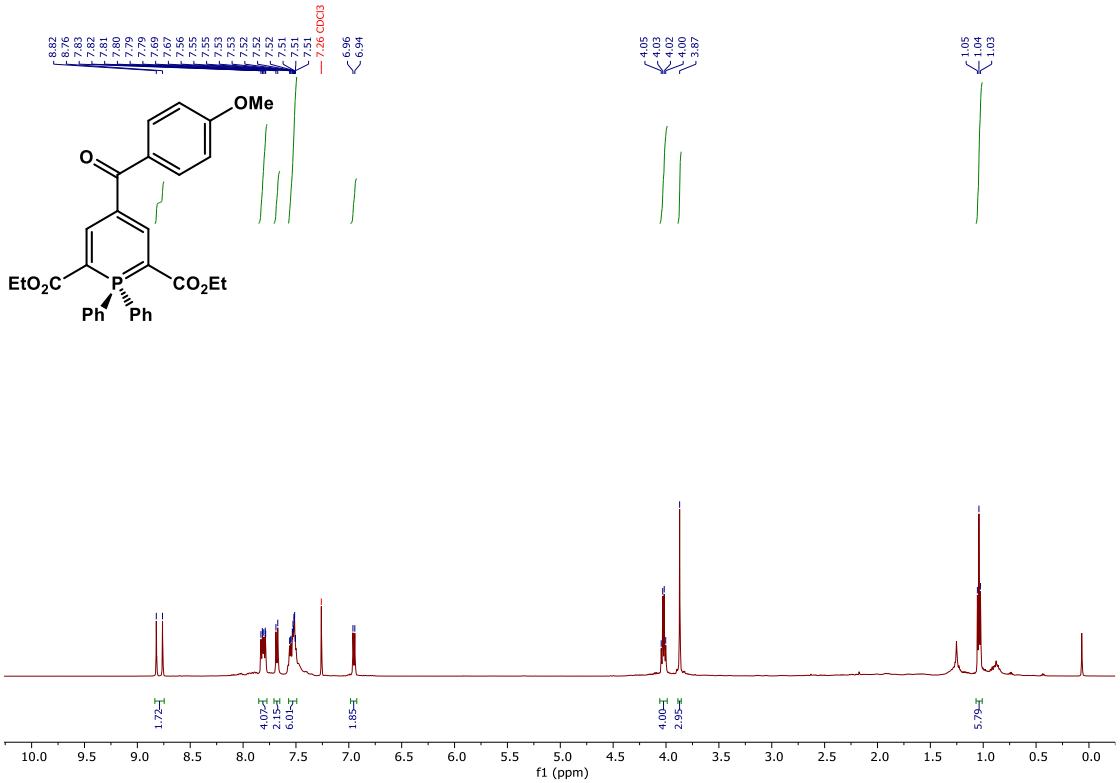


$^{31}$P NMR (202 MHz)

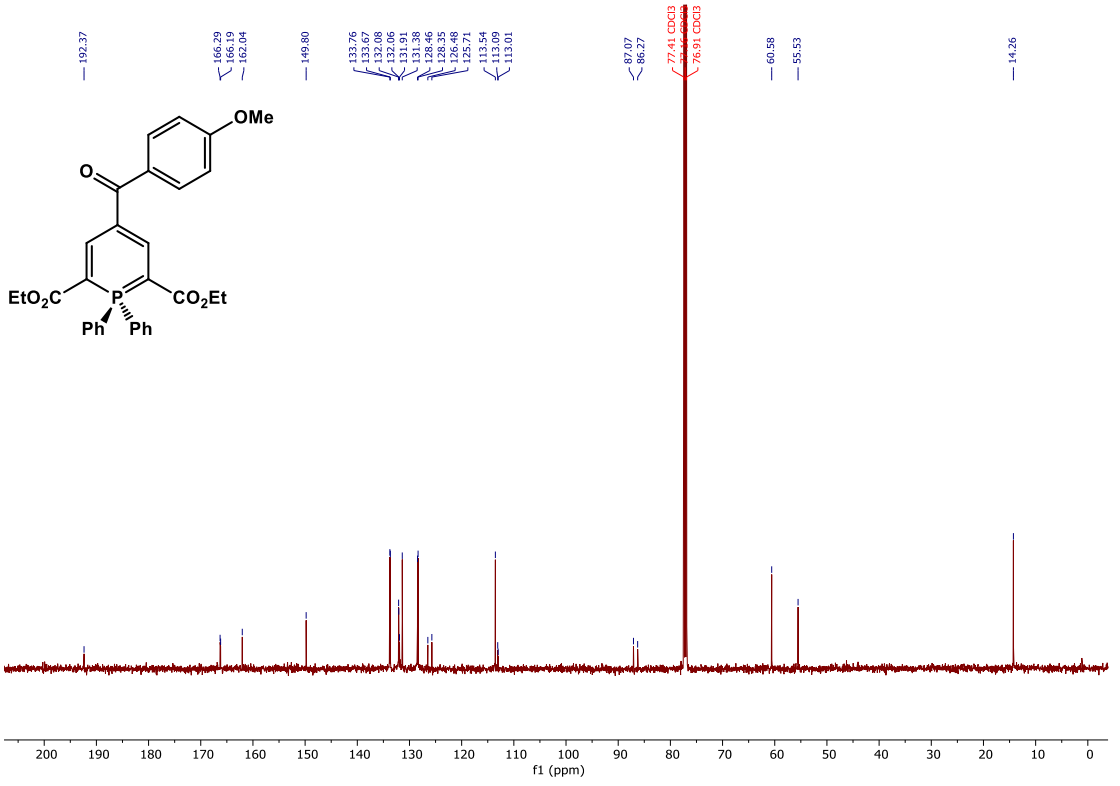


**diethyl 4-(4-methoxybenzoyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (5c)**

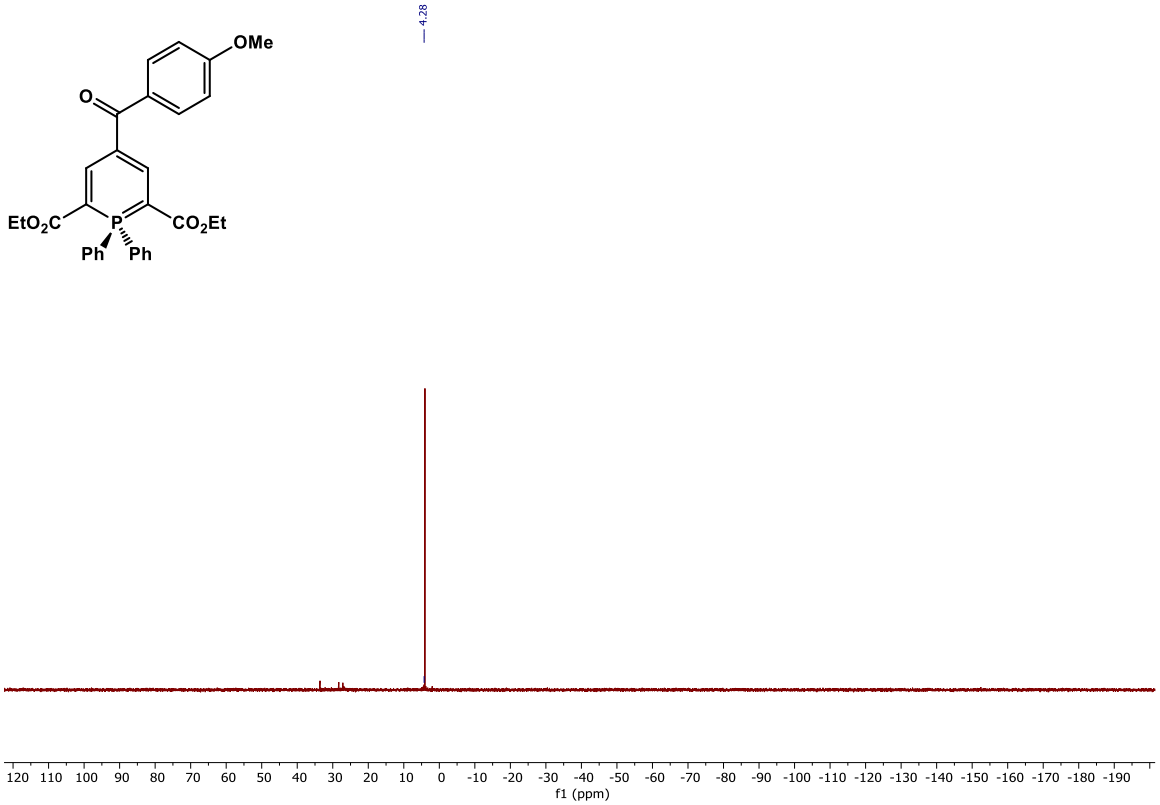
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

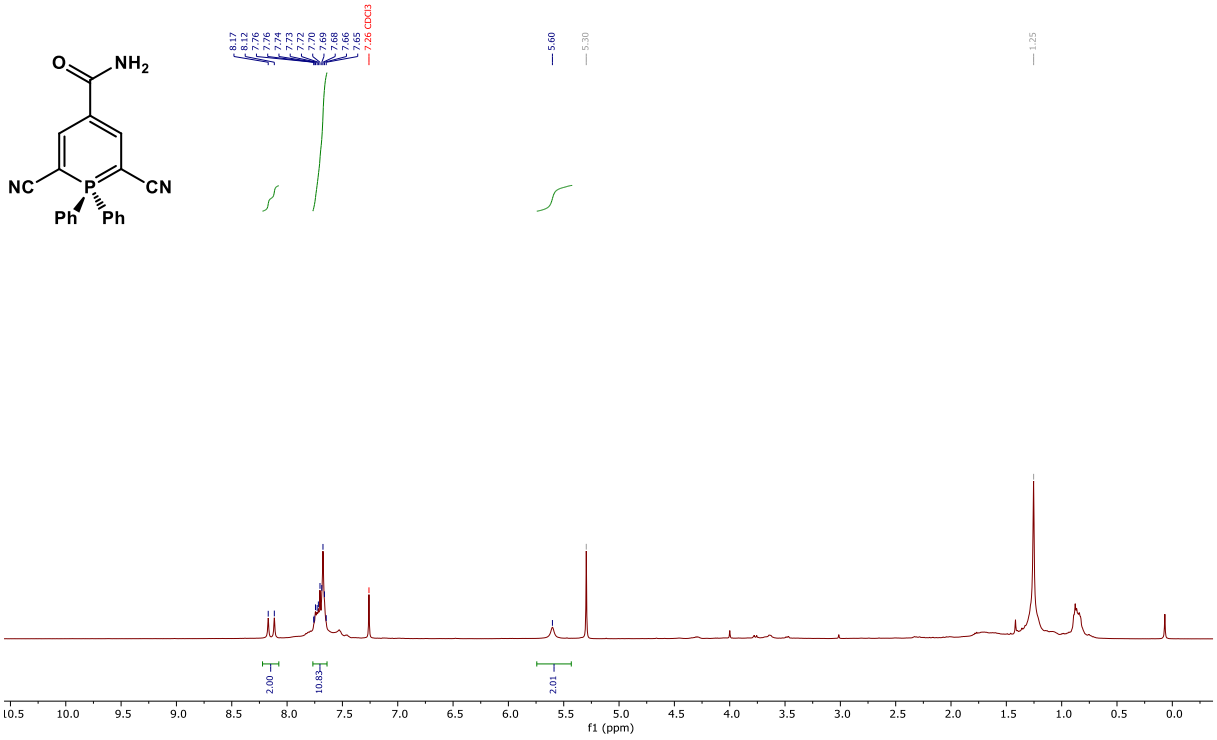


$^{31}$P NMR (202 MHz)

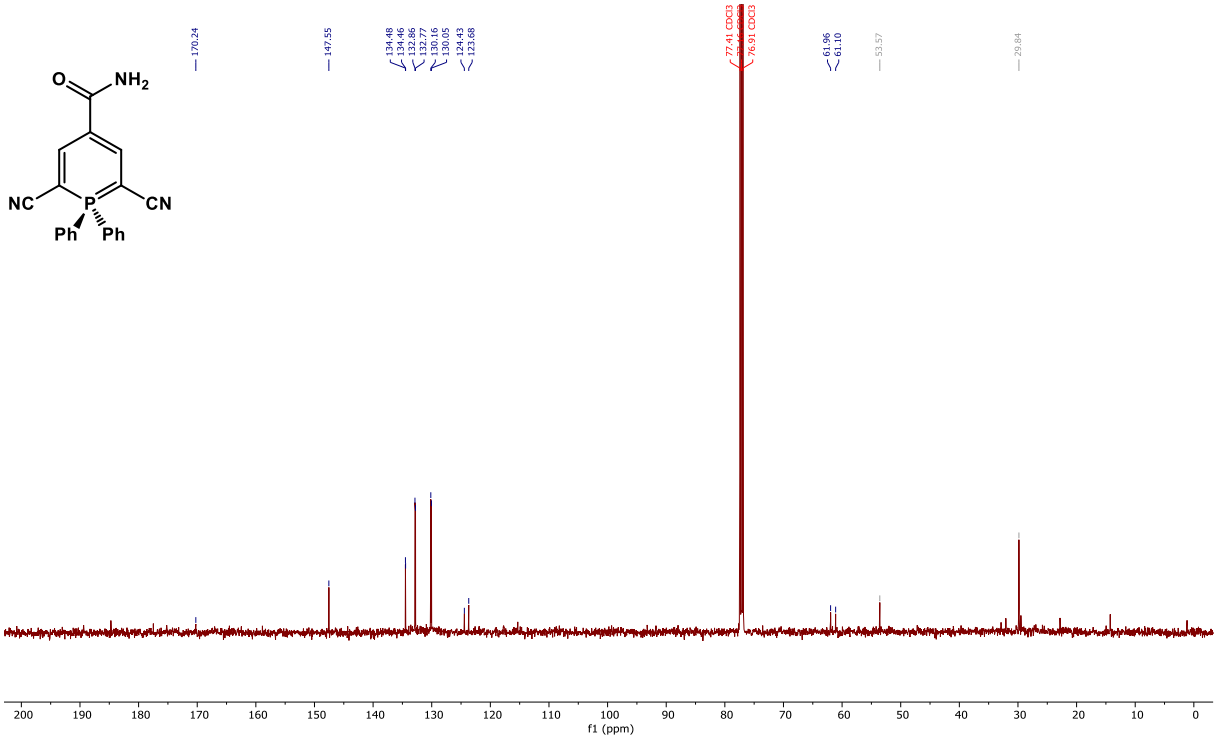


## 2,6-Dicyano-1,1-diphenyl-1λ$^5$-phosphinine-4-carboxamide (2i)

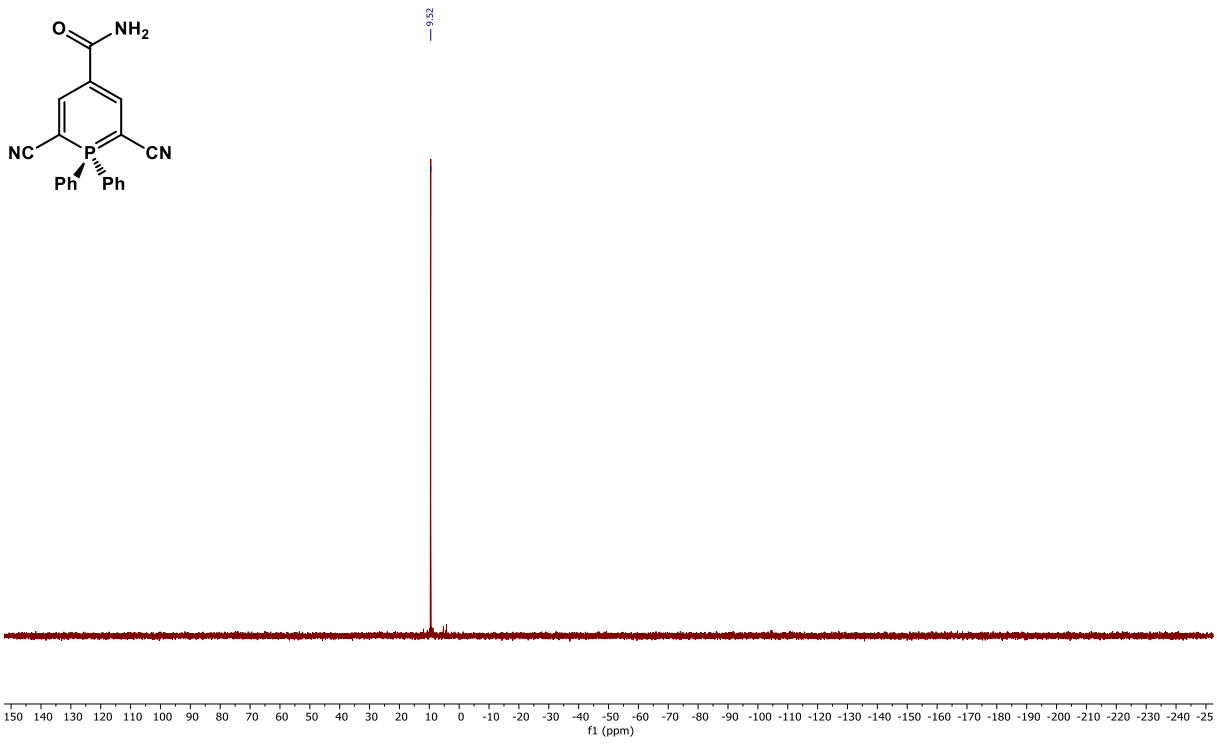
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

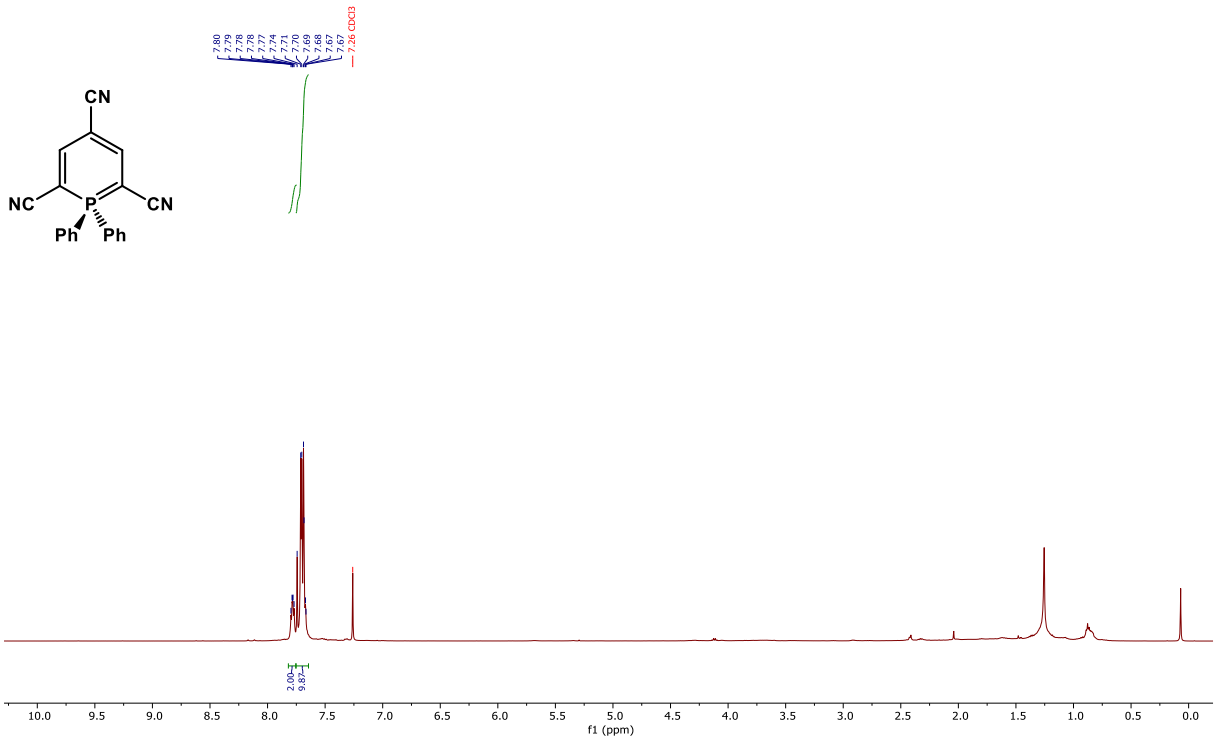


$^{31}$P NMR (202 MHz)

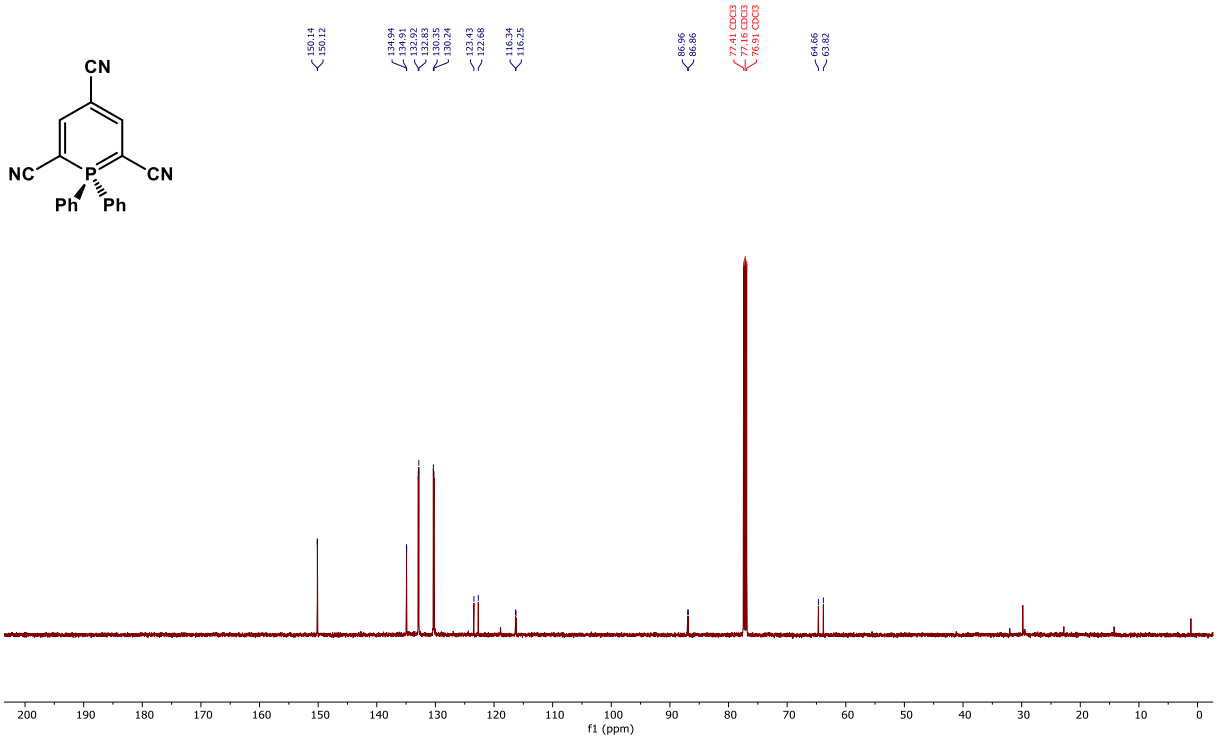


## 1,1-Diphenyl-1λ$^5$-phosphinine-2,4,6-tricarbonitrile (2j)

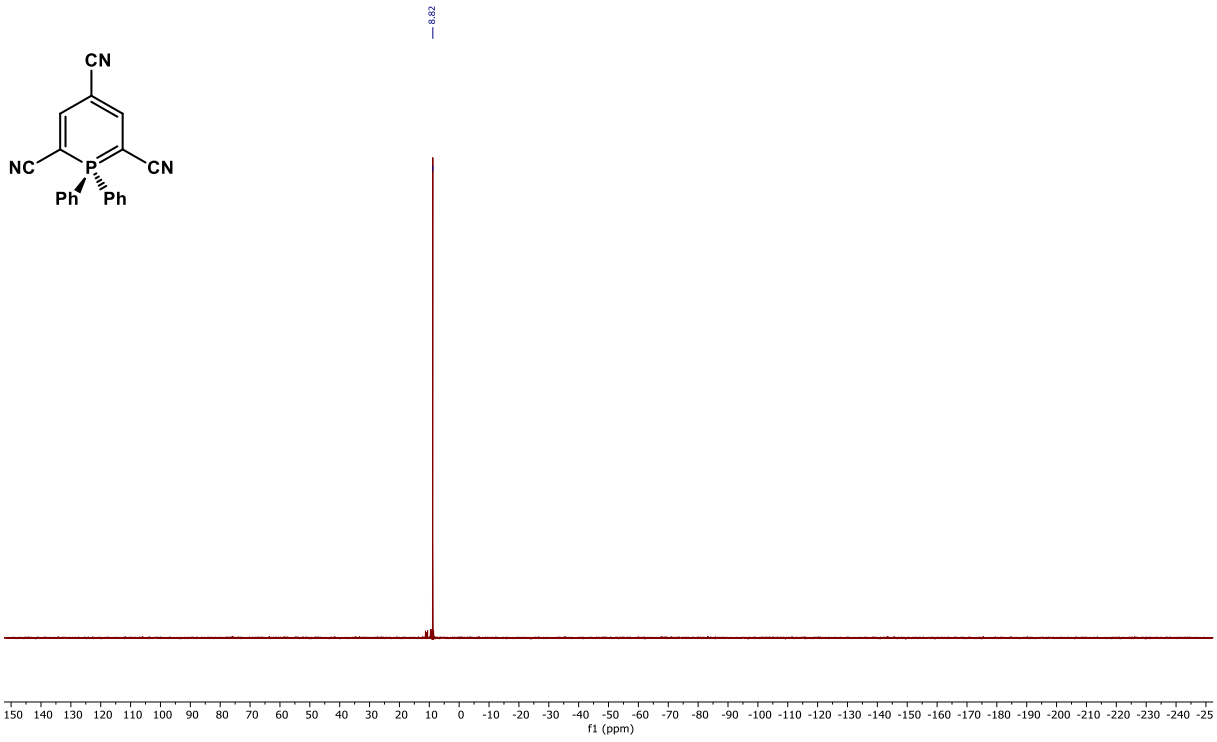
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

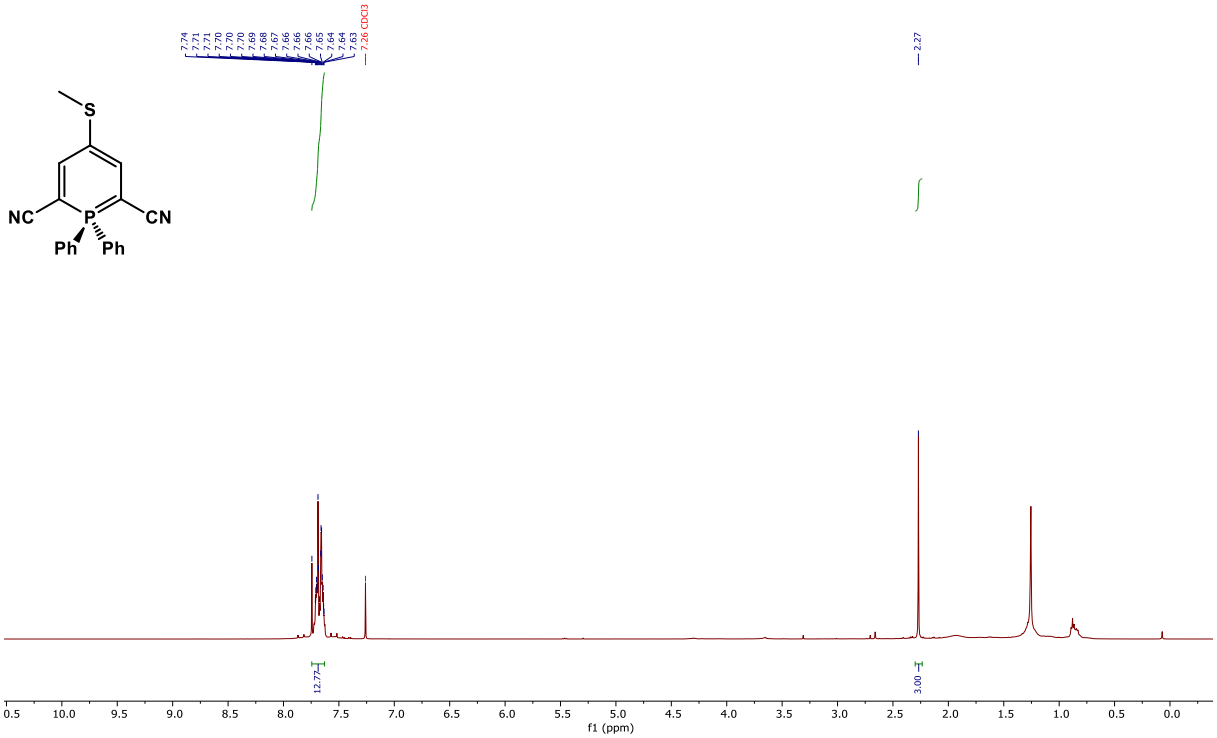


$^{31}$P NMR (202 MHz)

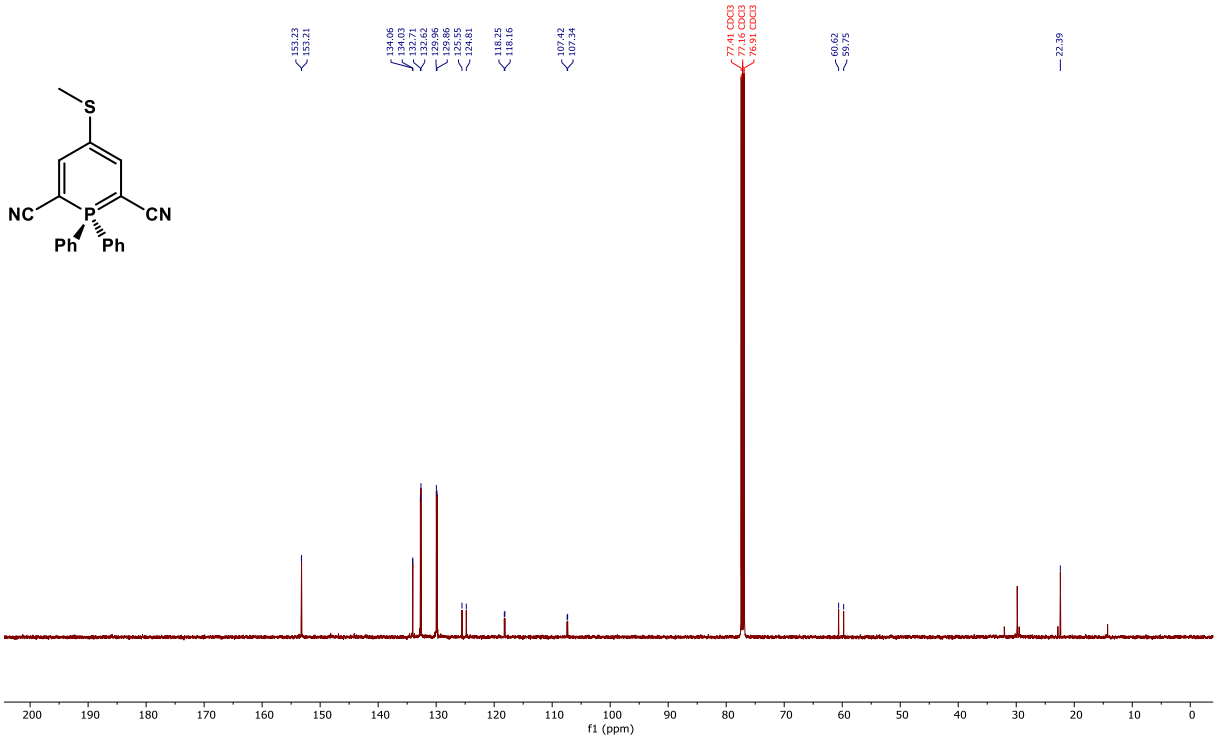


**4-(Methylthio)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (2k)**

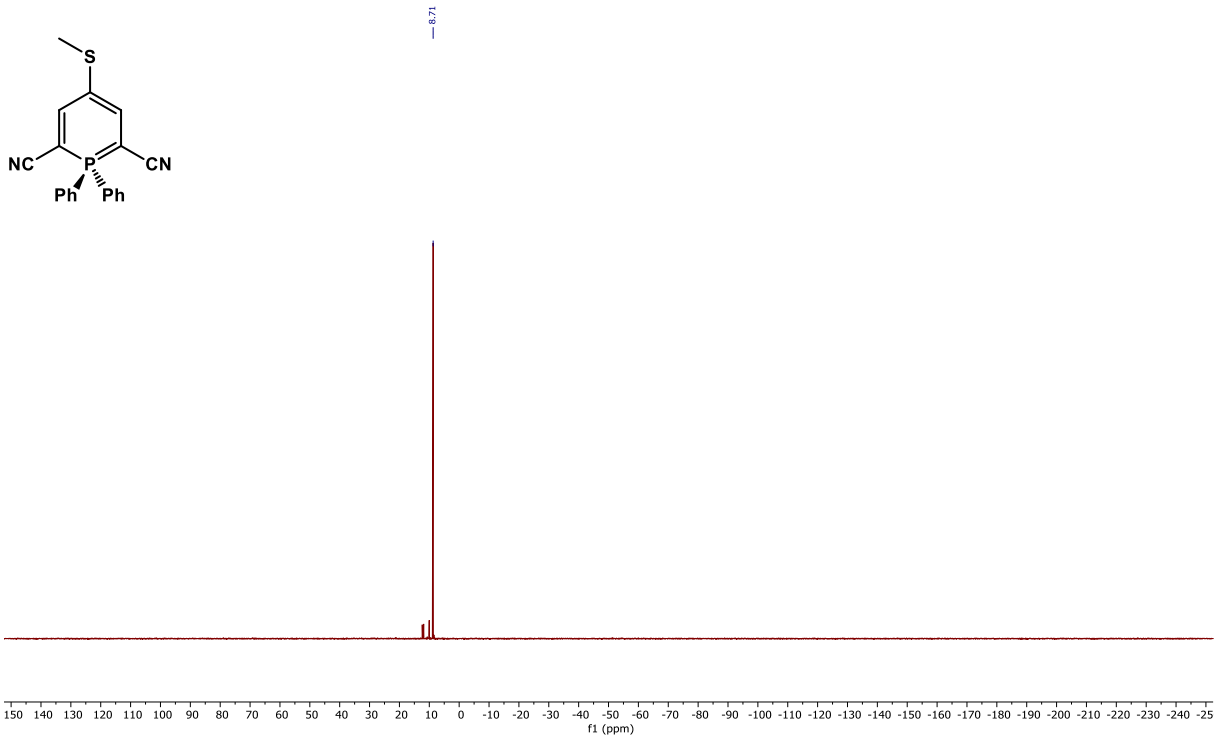
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)



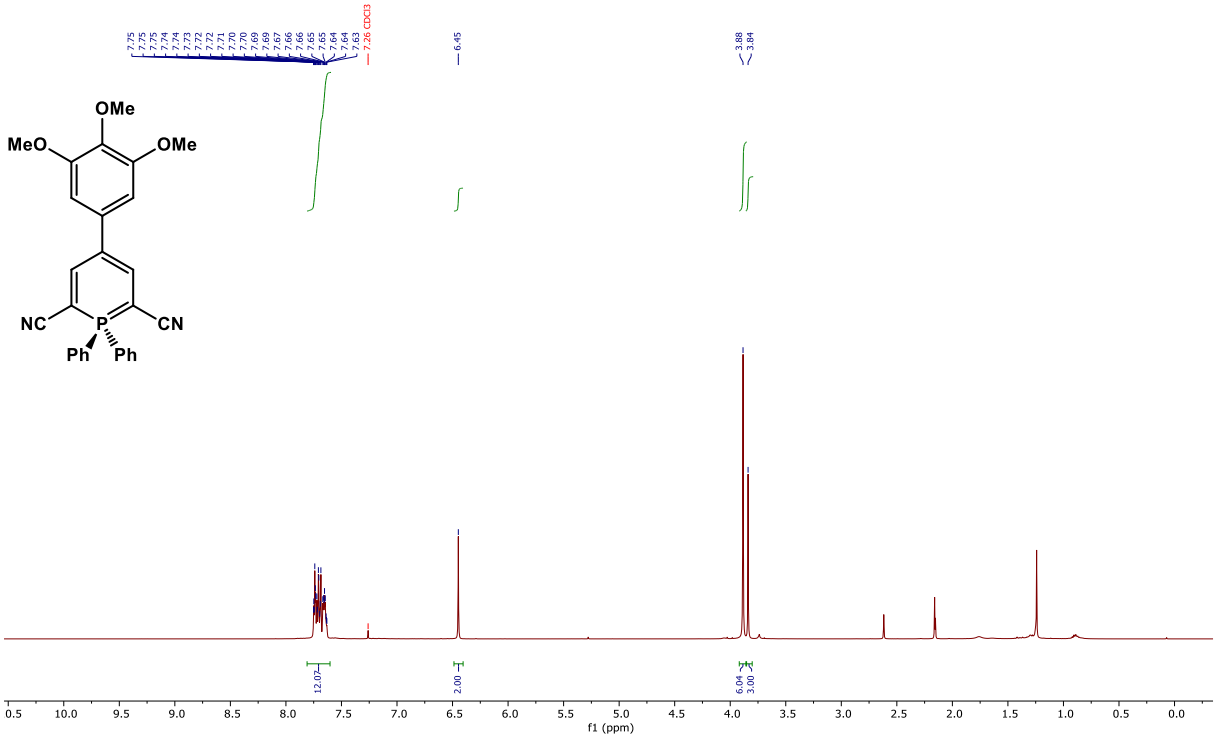
$^{31}$P NMR (202 MHz)



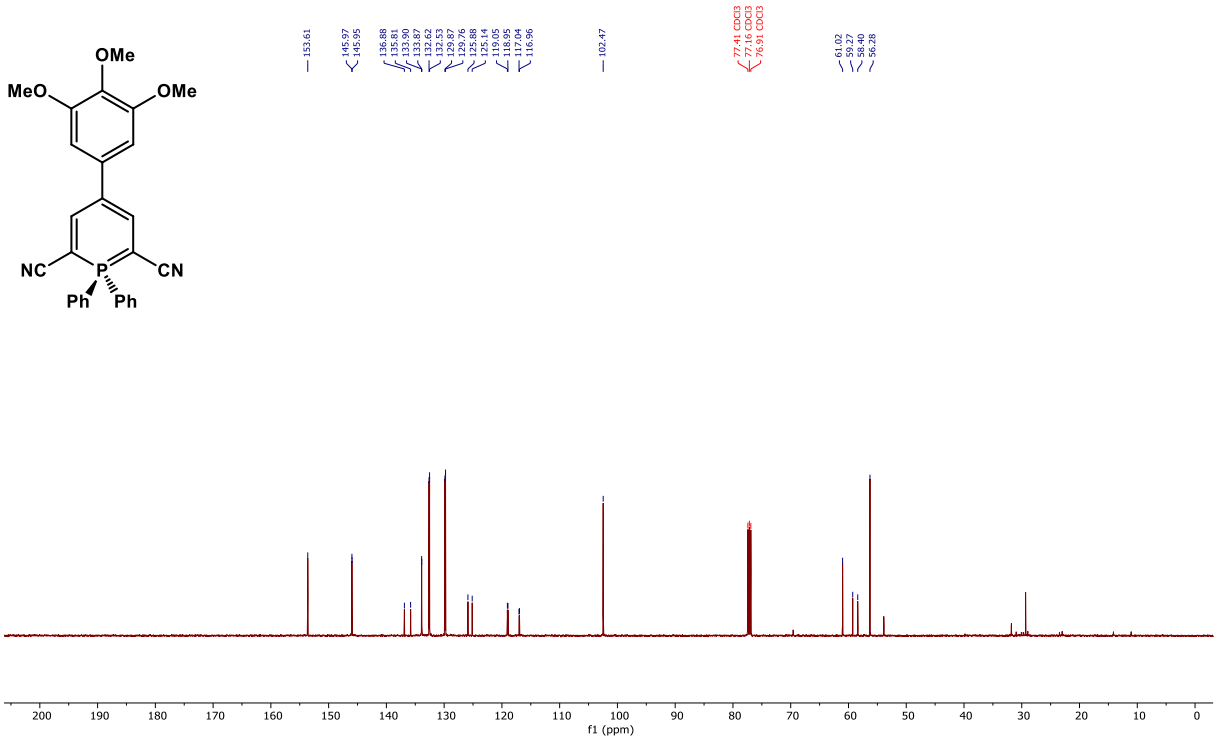
## NEGISHI COUPLING

### 1,1-diphenyl-4-(3,4,5-trimethoxyphenyl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (3a)

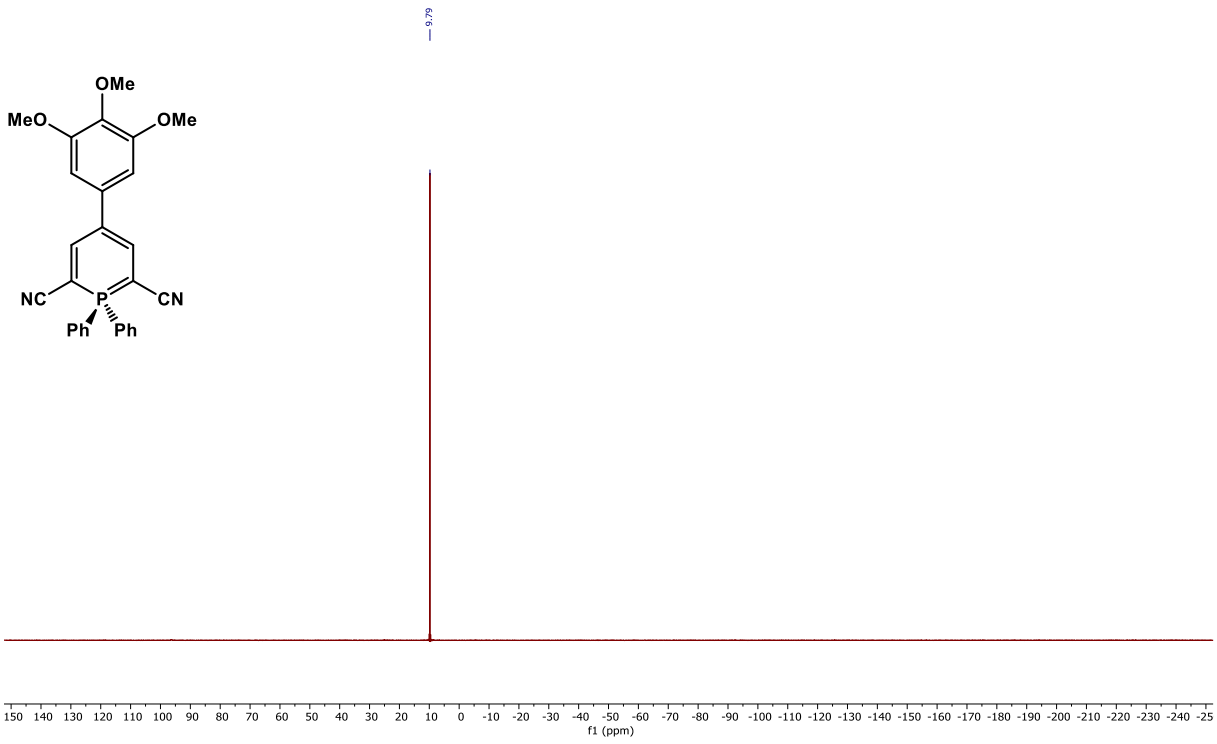
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

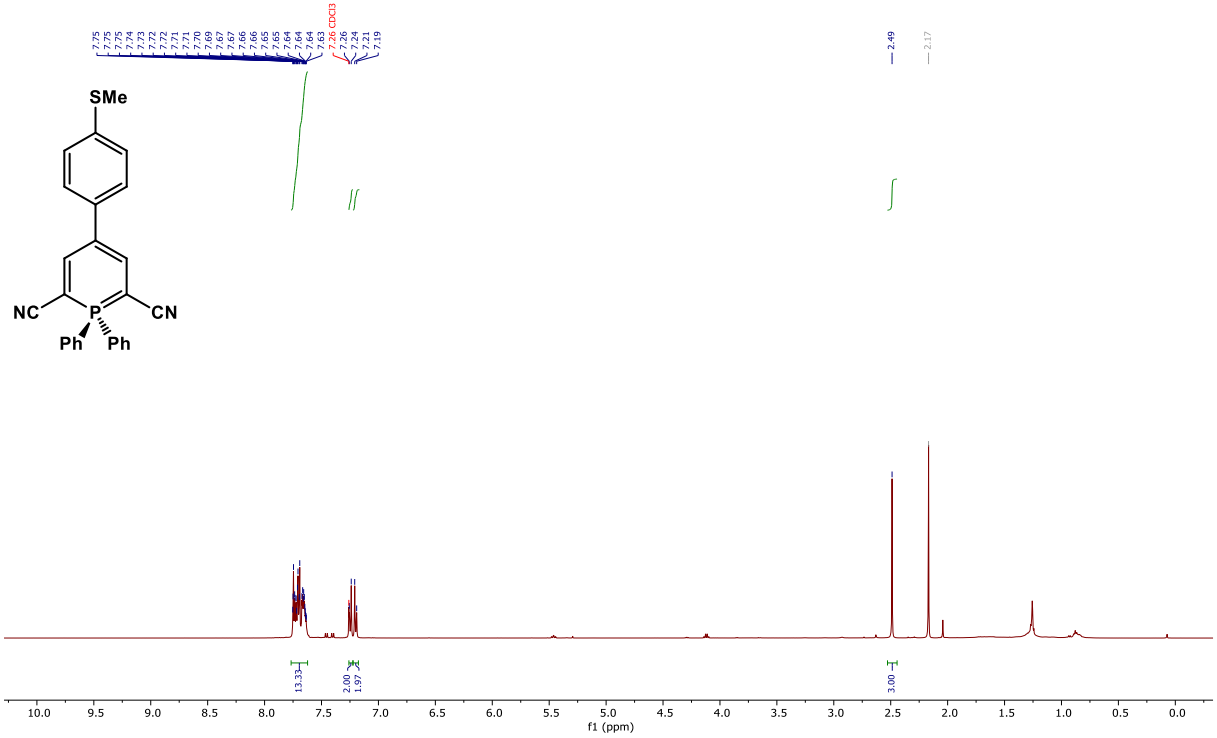


$^{31}$P NMR (202 MHz)

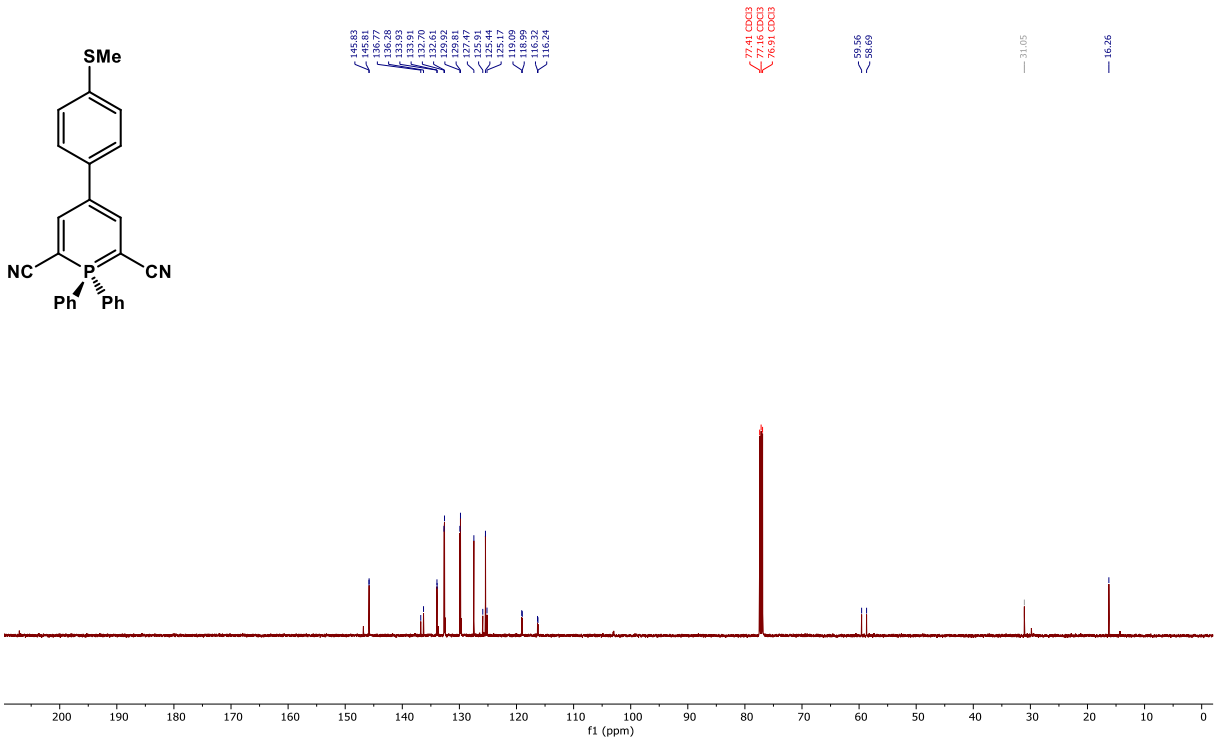


## 4-(4-(methylthio)phenyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3b)

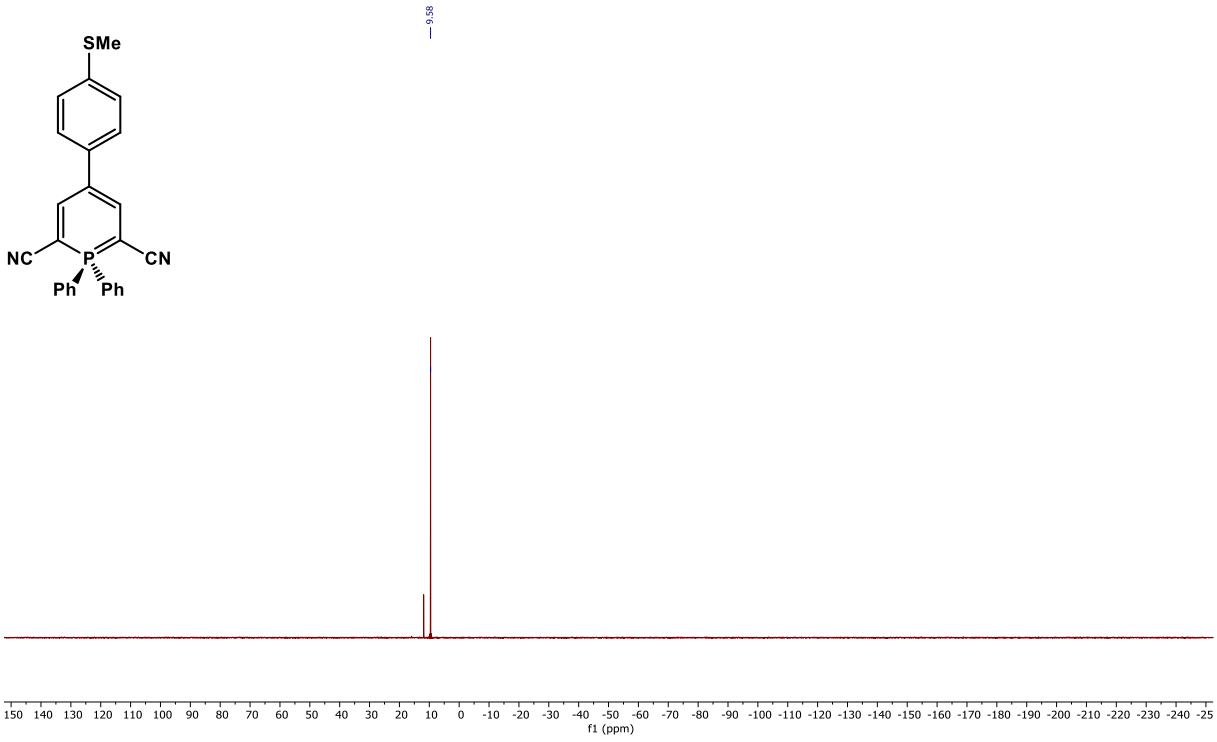
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

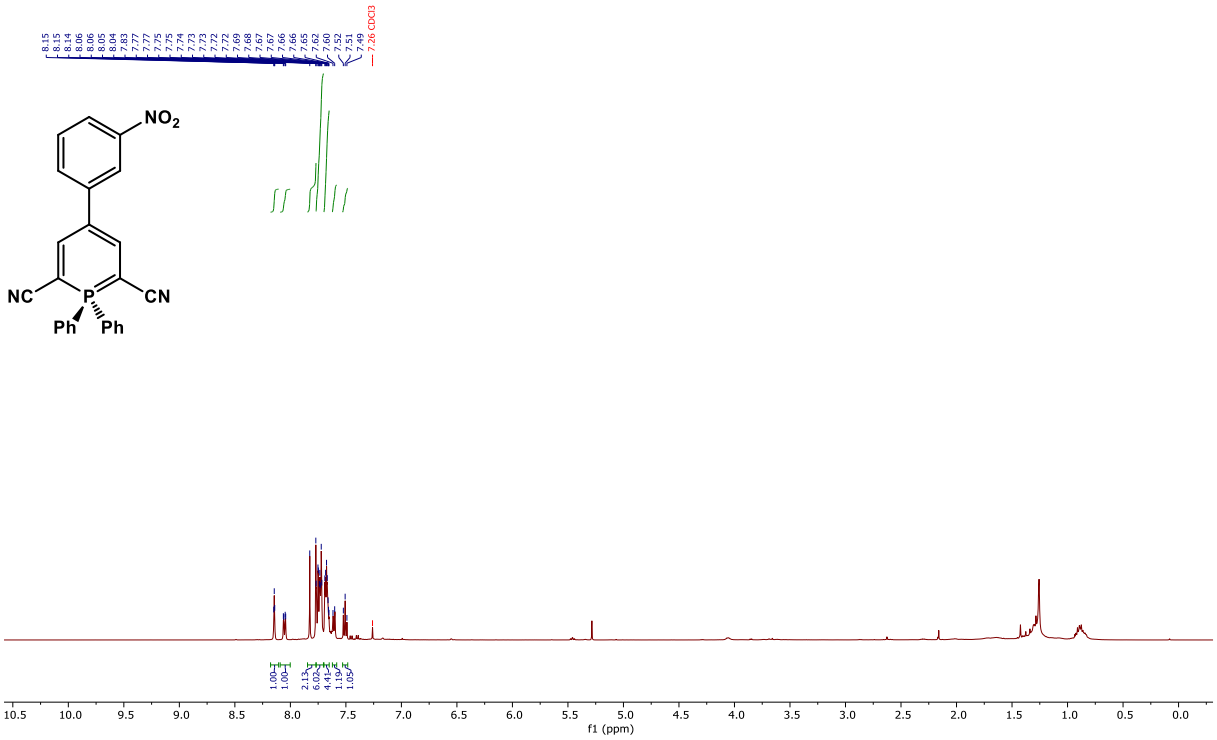


$^{31}$P NMR (202 MHz)

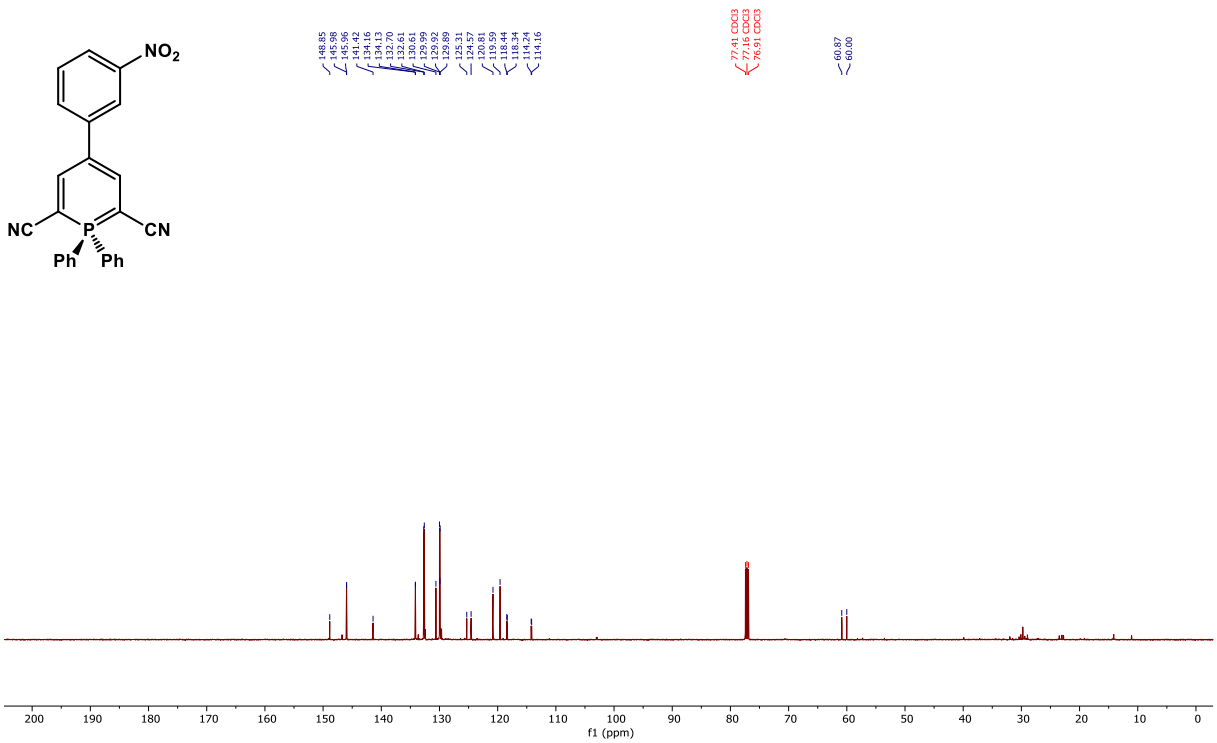


**4-(3-nitrophenyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3c)**

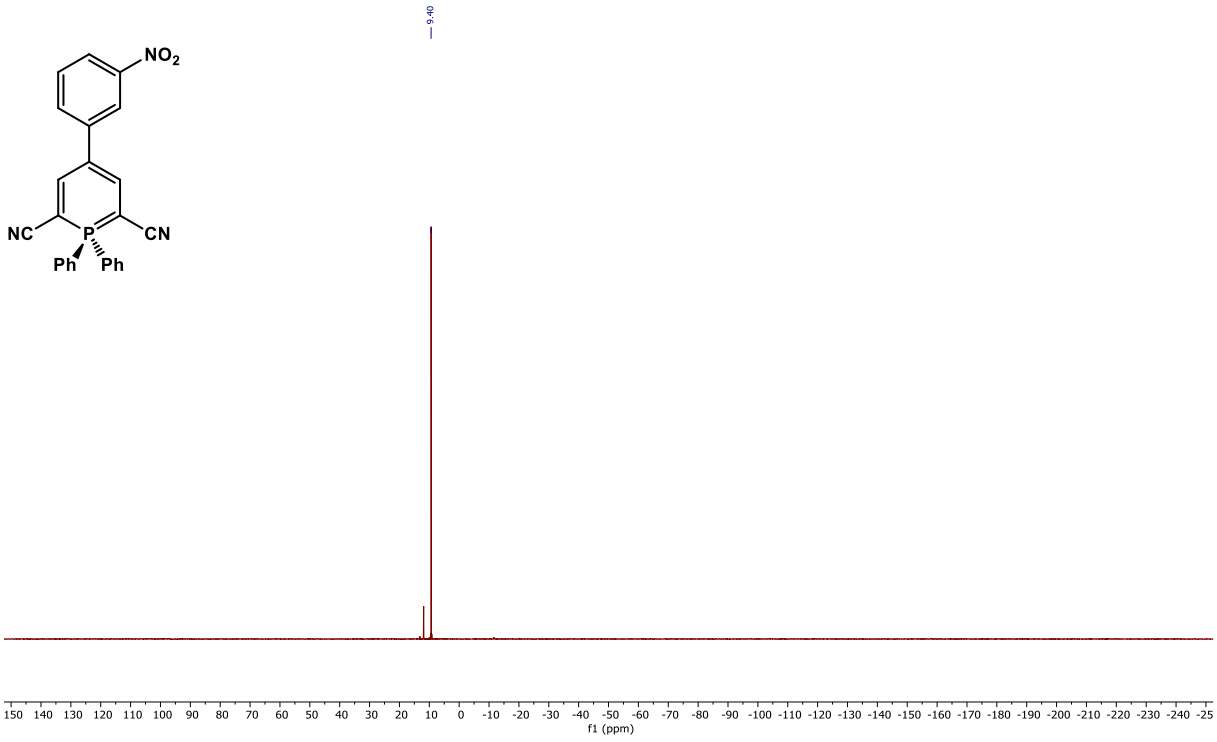
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

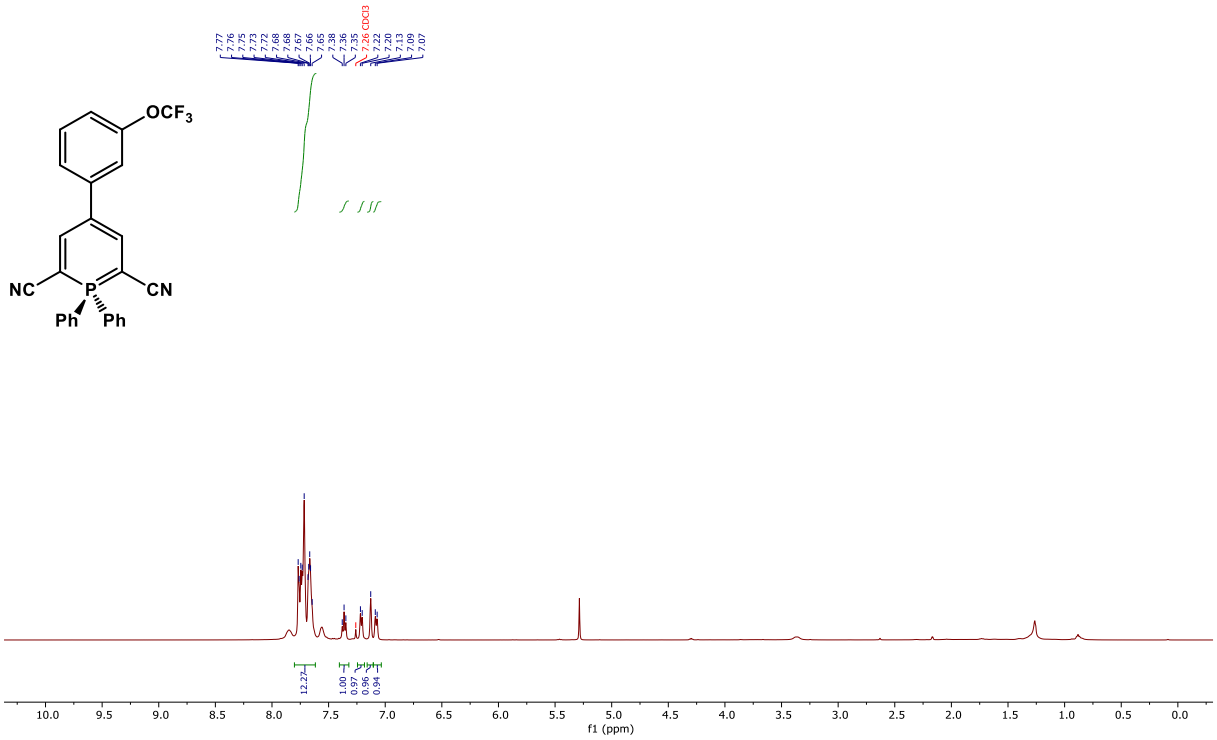


$^{31}$P NMR (202 MHz)

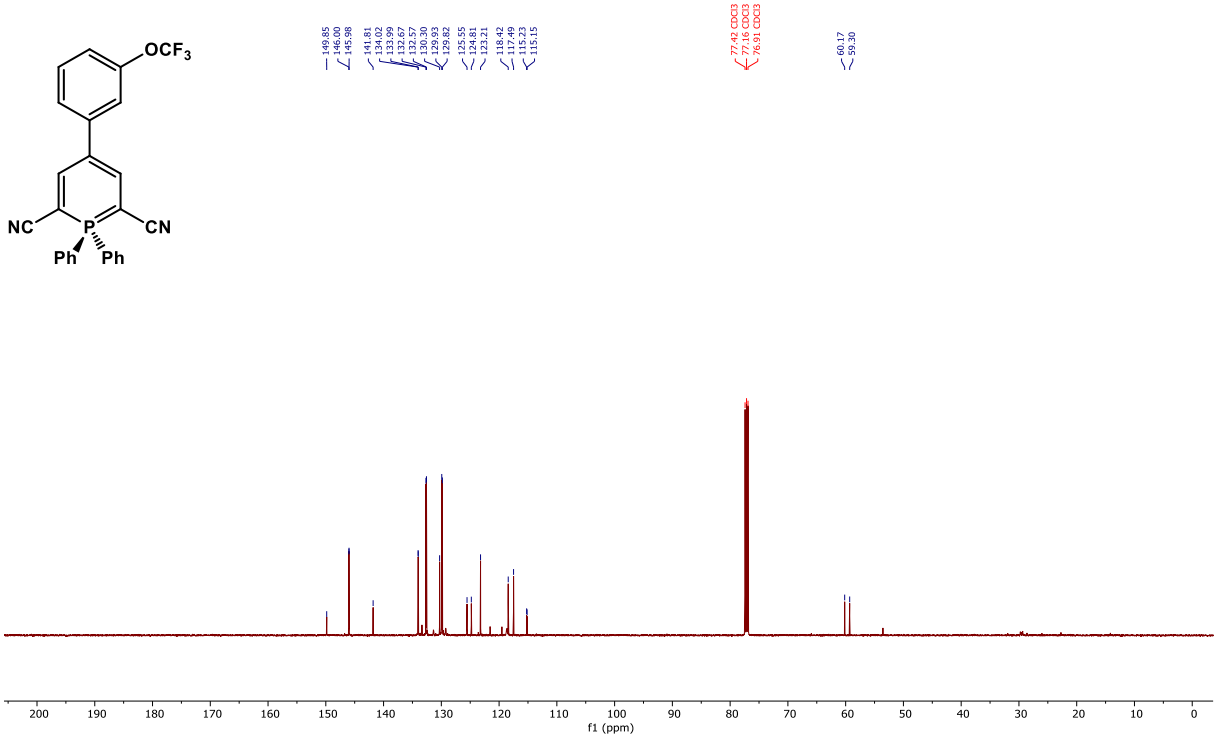


**1,1-diphenyl-4-(3-(trifluoromethoxy)phenyl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (3d)**

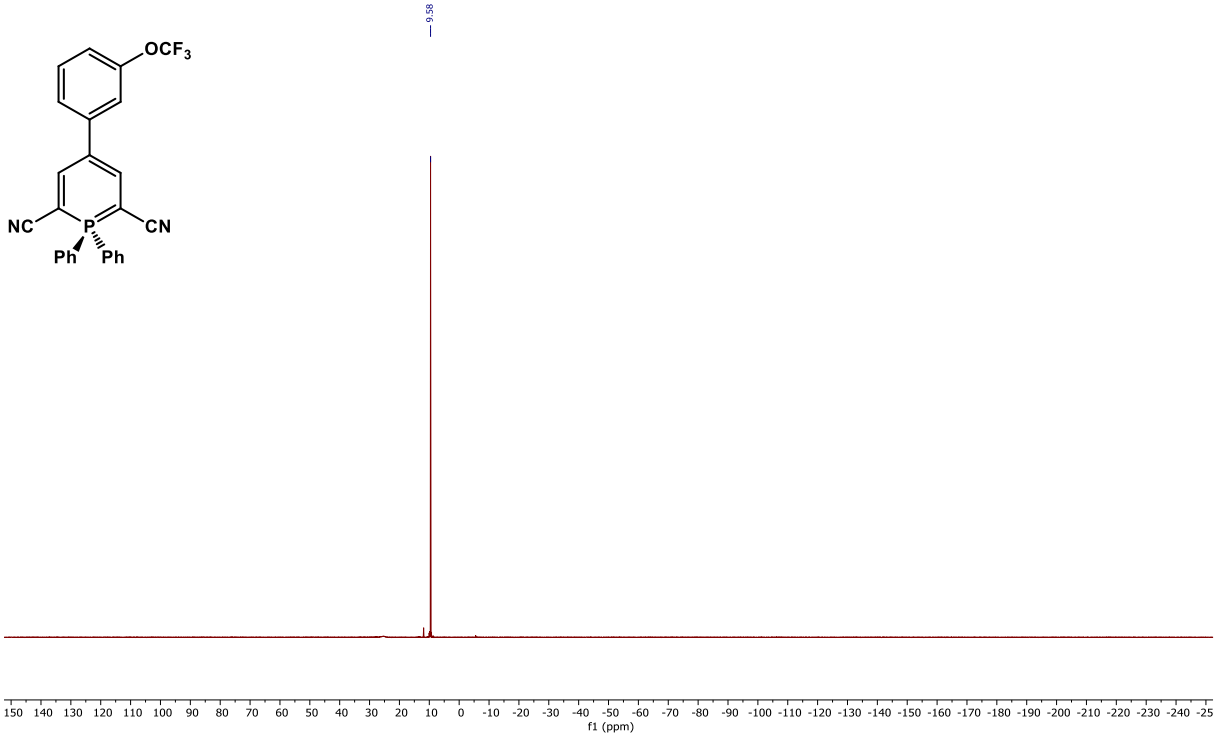
$^1$H NMR (500 MHz)



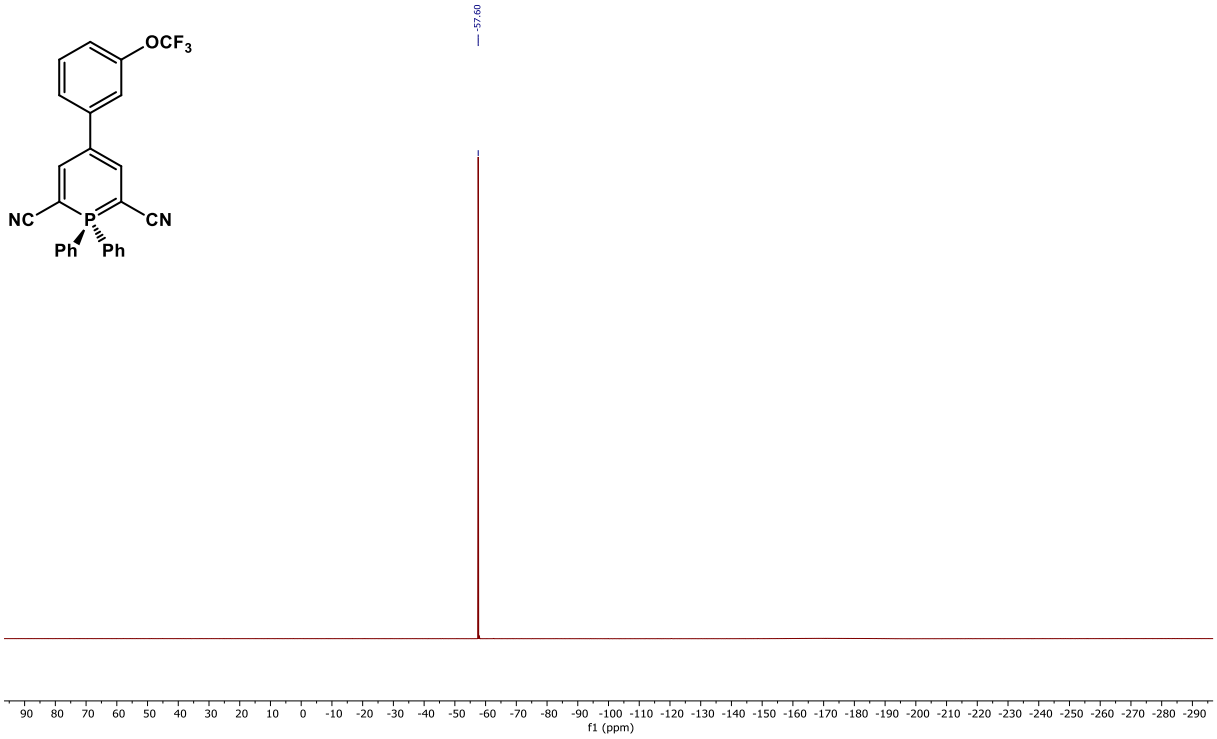

$^{13}$C NMR (126 MHz)



$^{31}$P NMR (202 MHz)

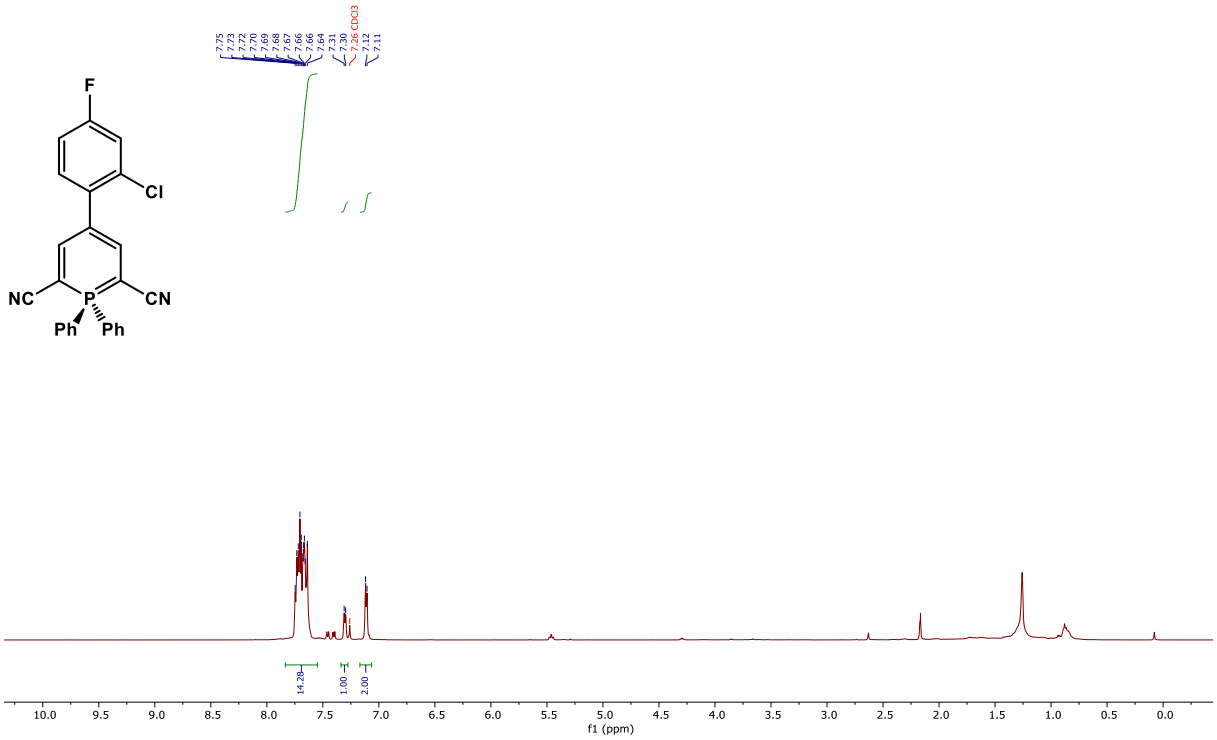



$^{19}$F NMR (471 MHz)

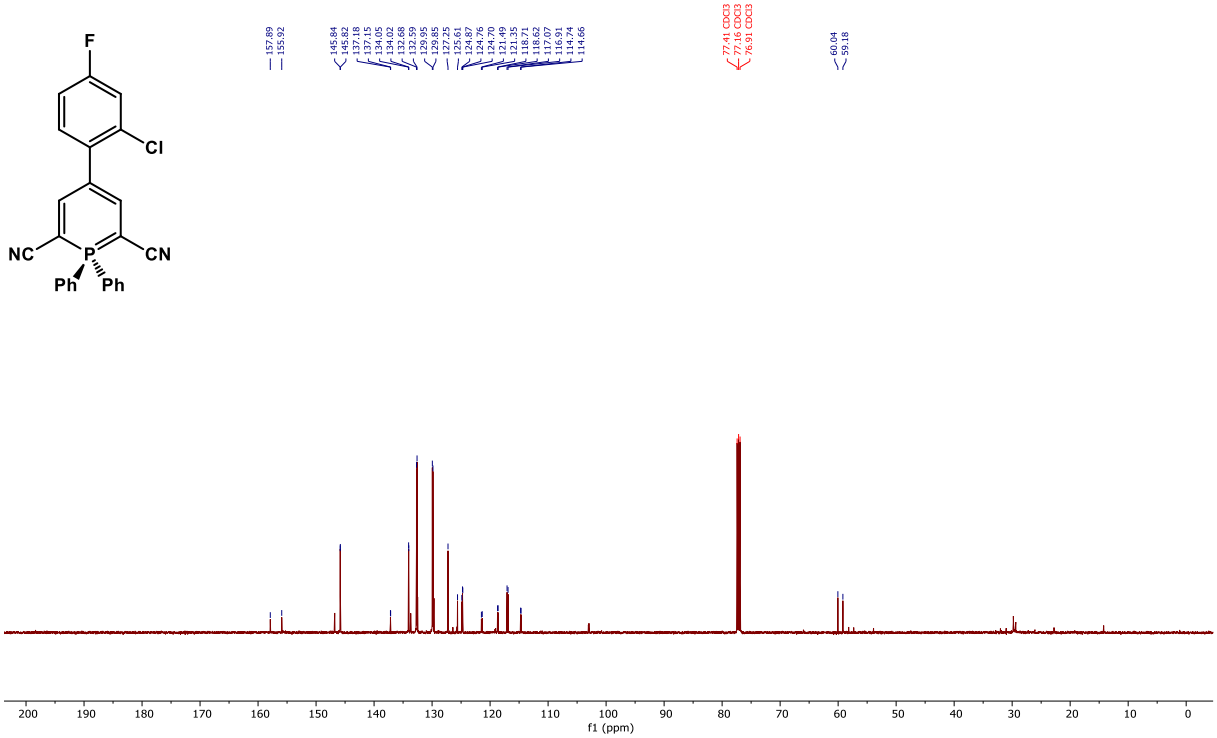


**4-(2-chloro-4-fluorophenyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3e)**

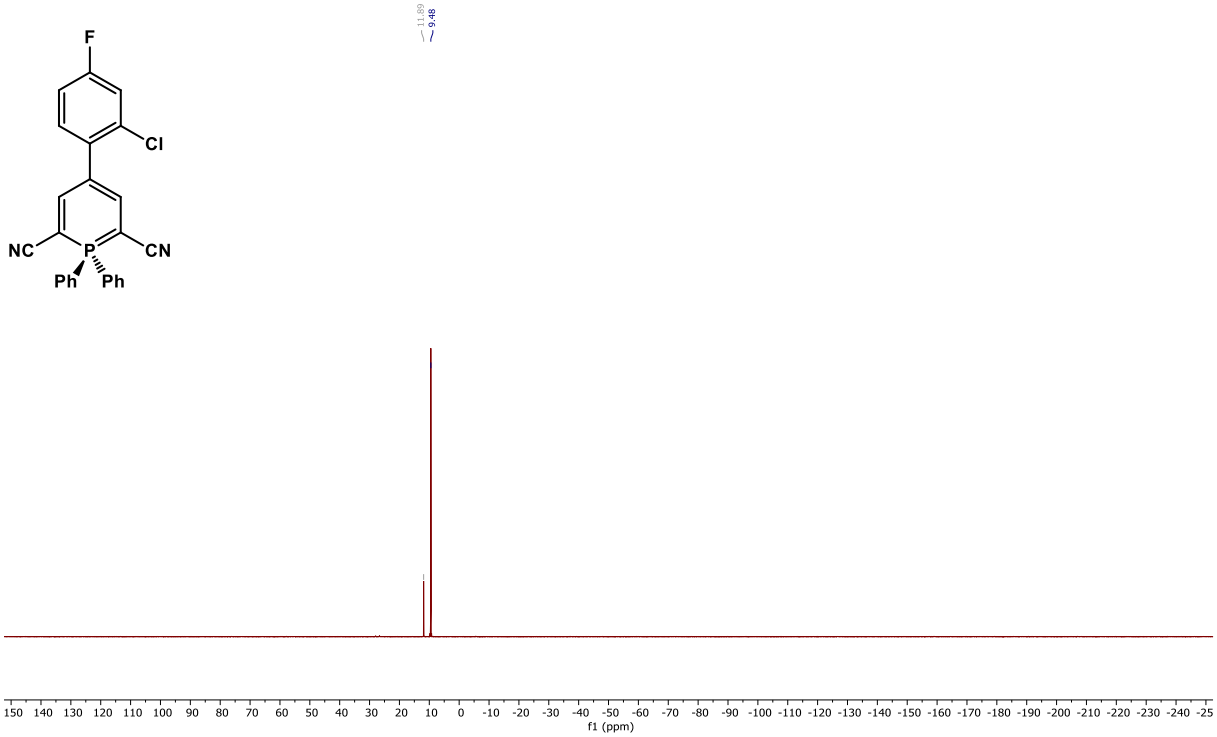
$^1$H NMR (500 MHz)



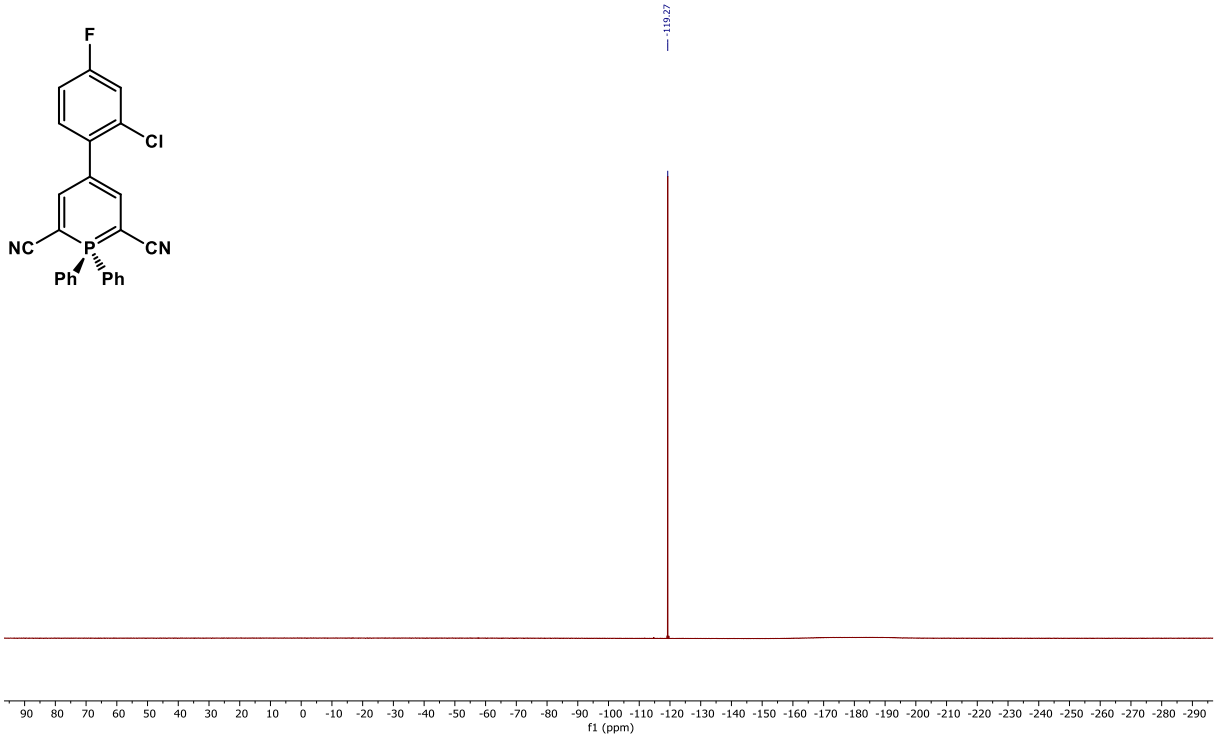

$^{13}$C NMR (126 MHz)



$^{31}$P NMR (202 MHz)

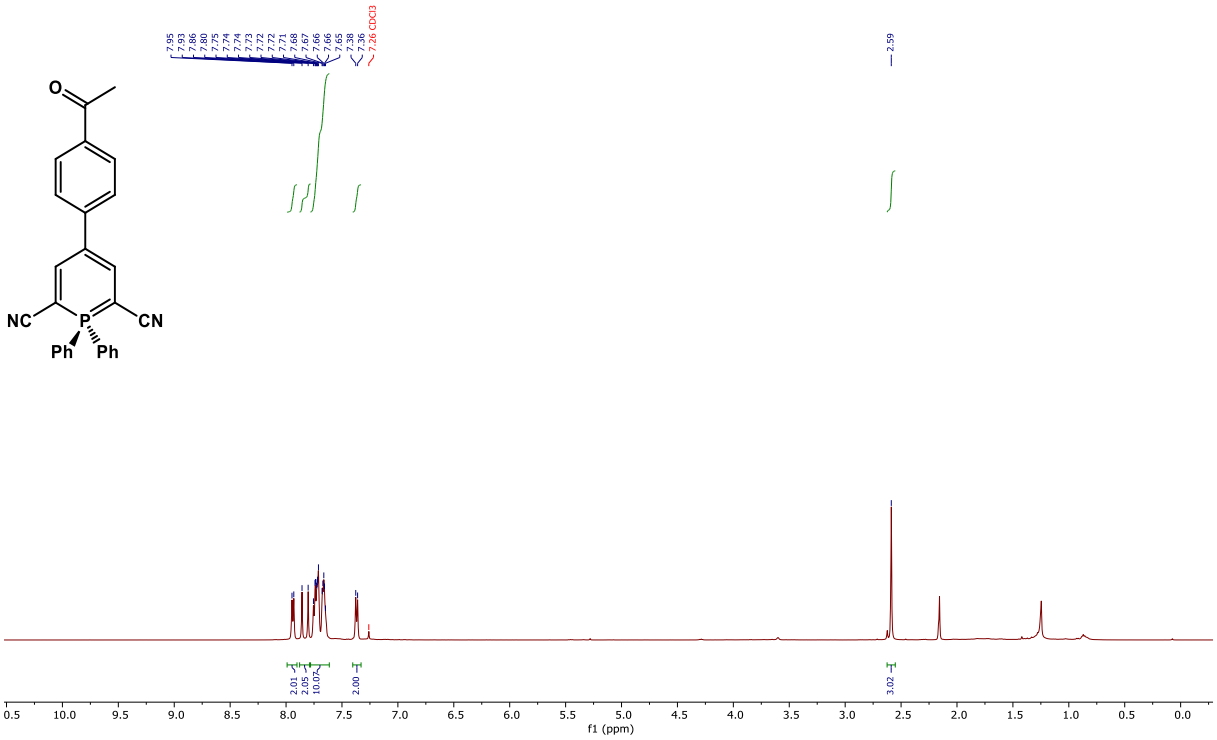



$^{19}$F NMR (471 MHz)

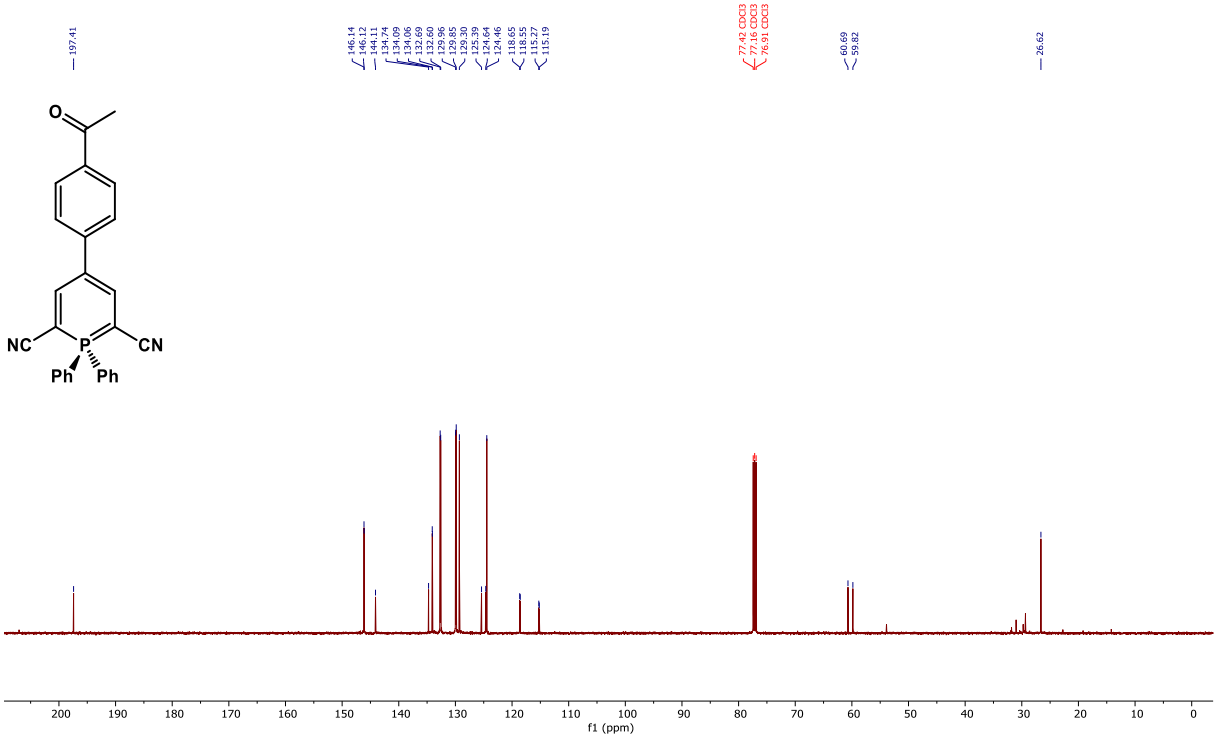


**4-(4-acetylphenyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3f)**

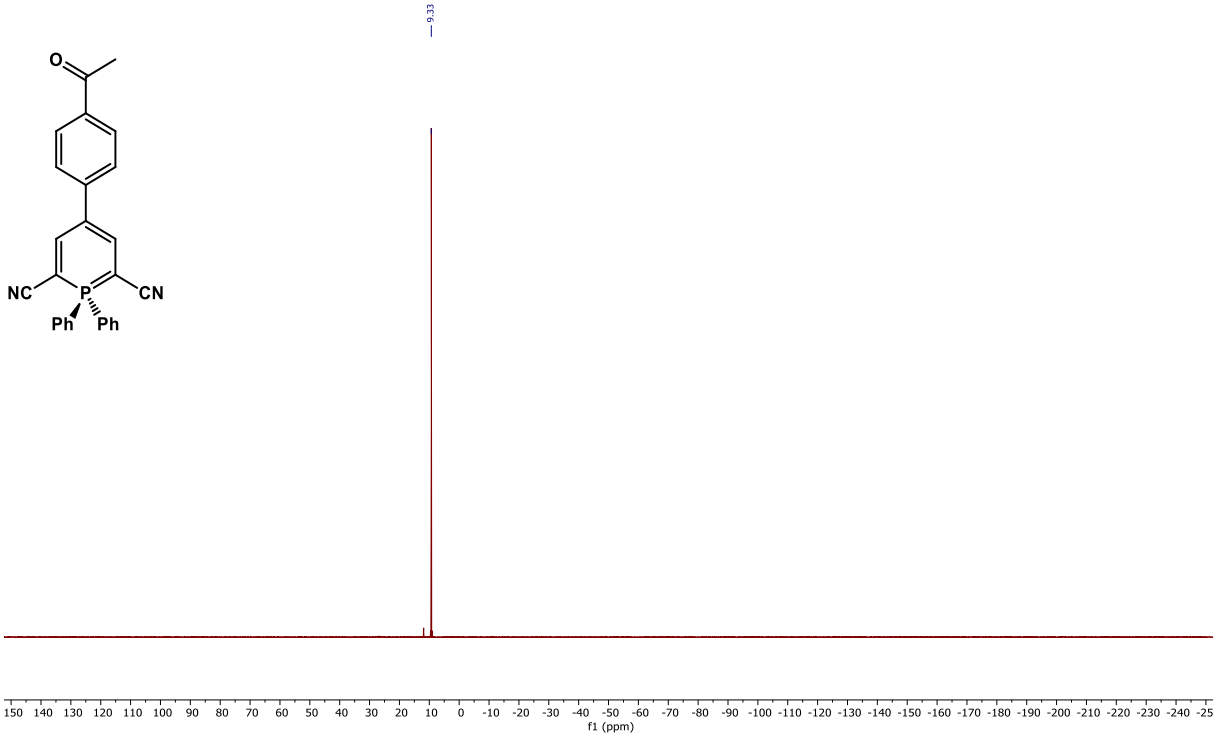
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

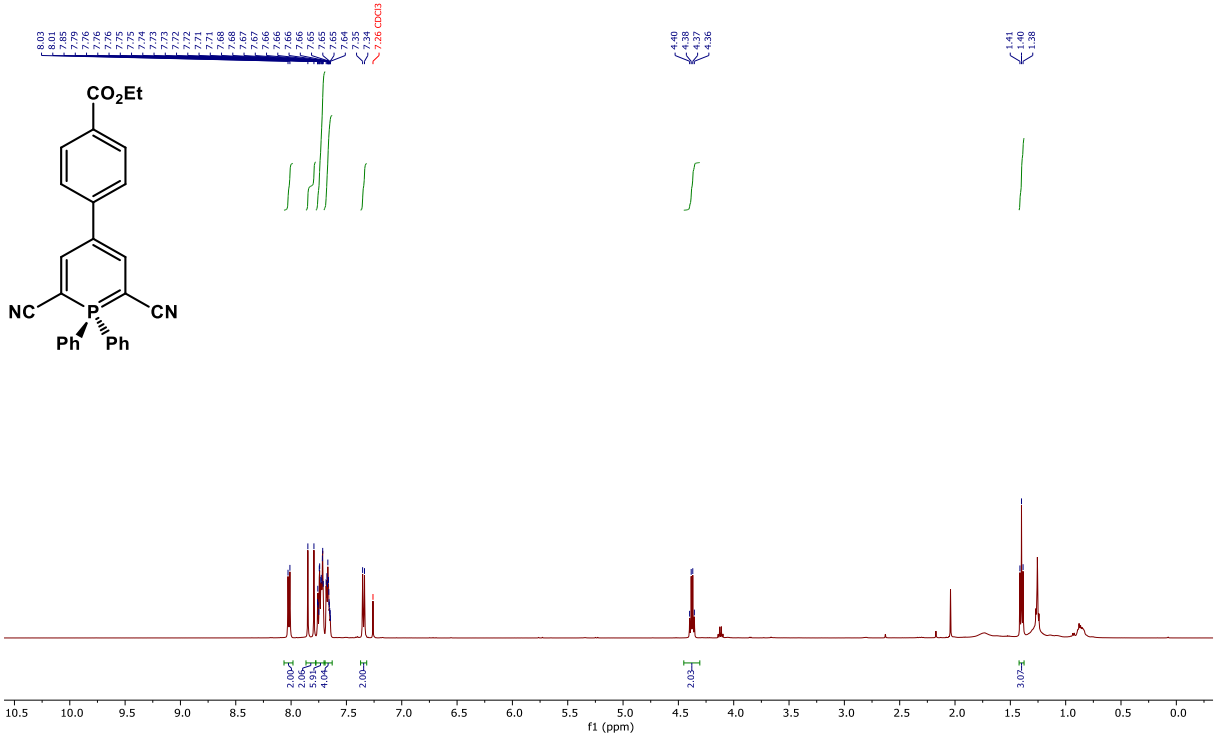


$^{31}$P NMR (202 MHz)

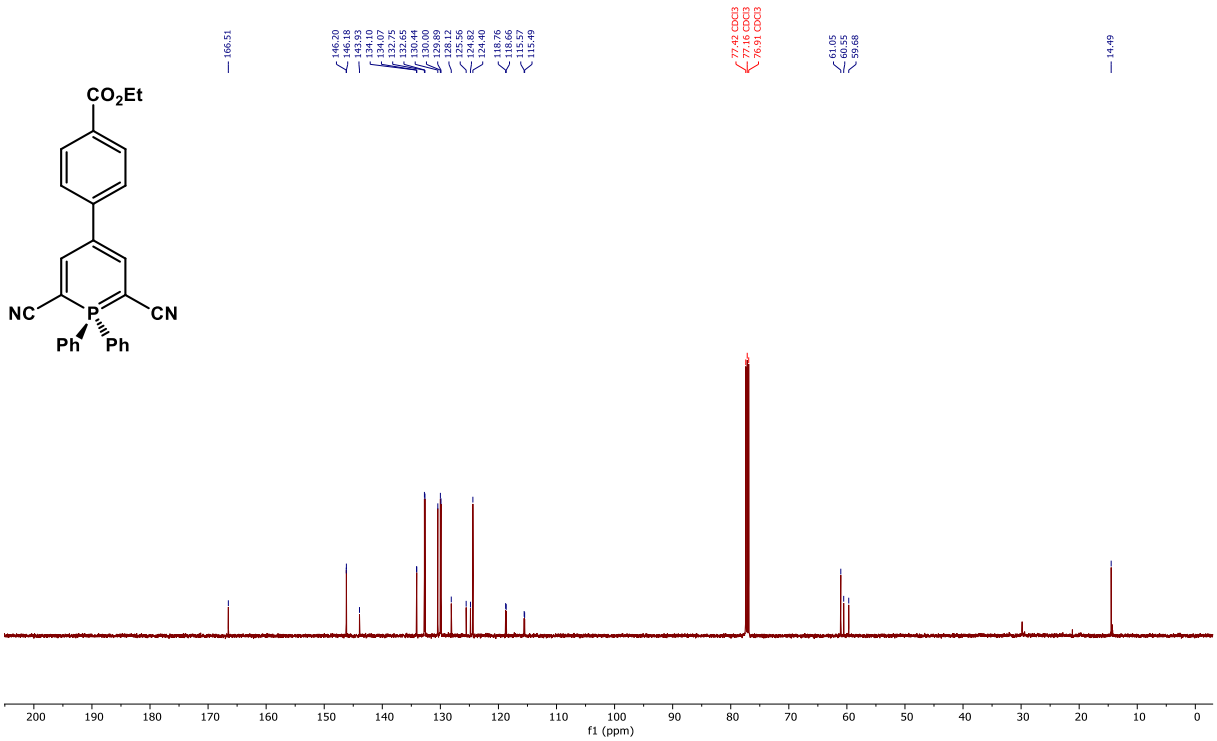


**ethyl 4-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)benzoate (3g)**

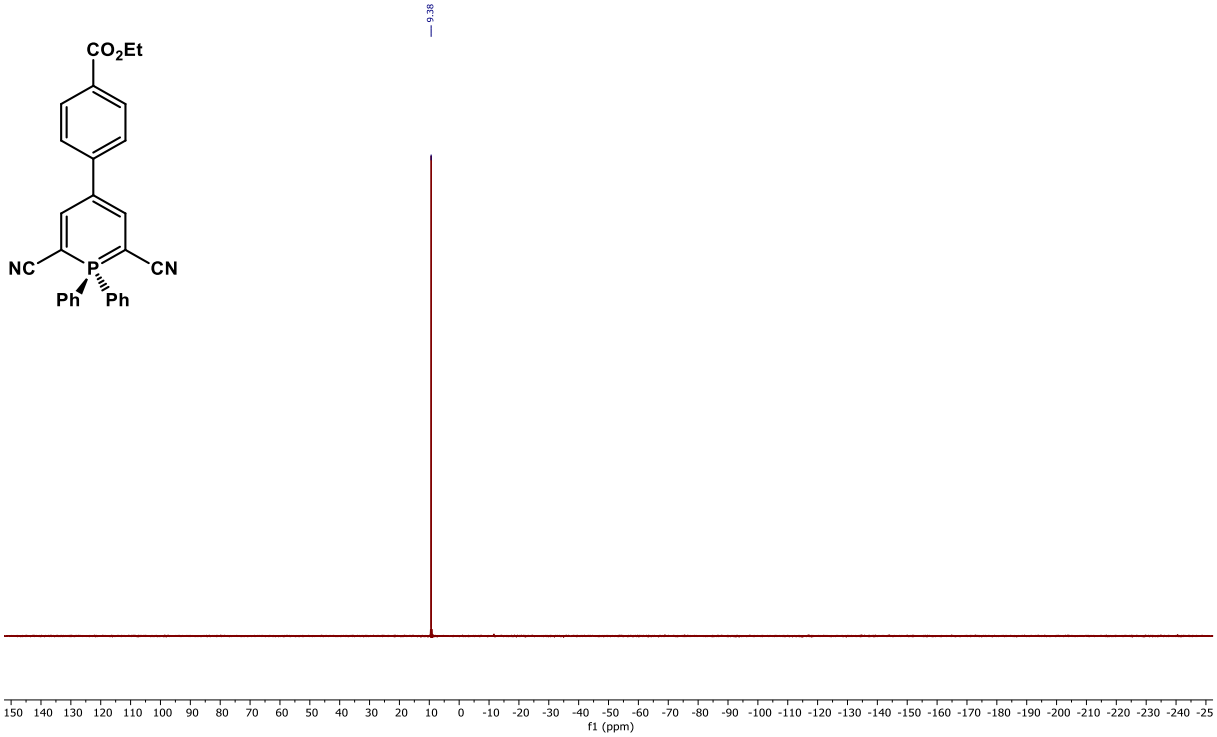
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

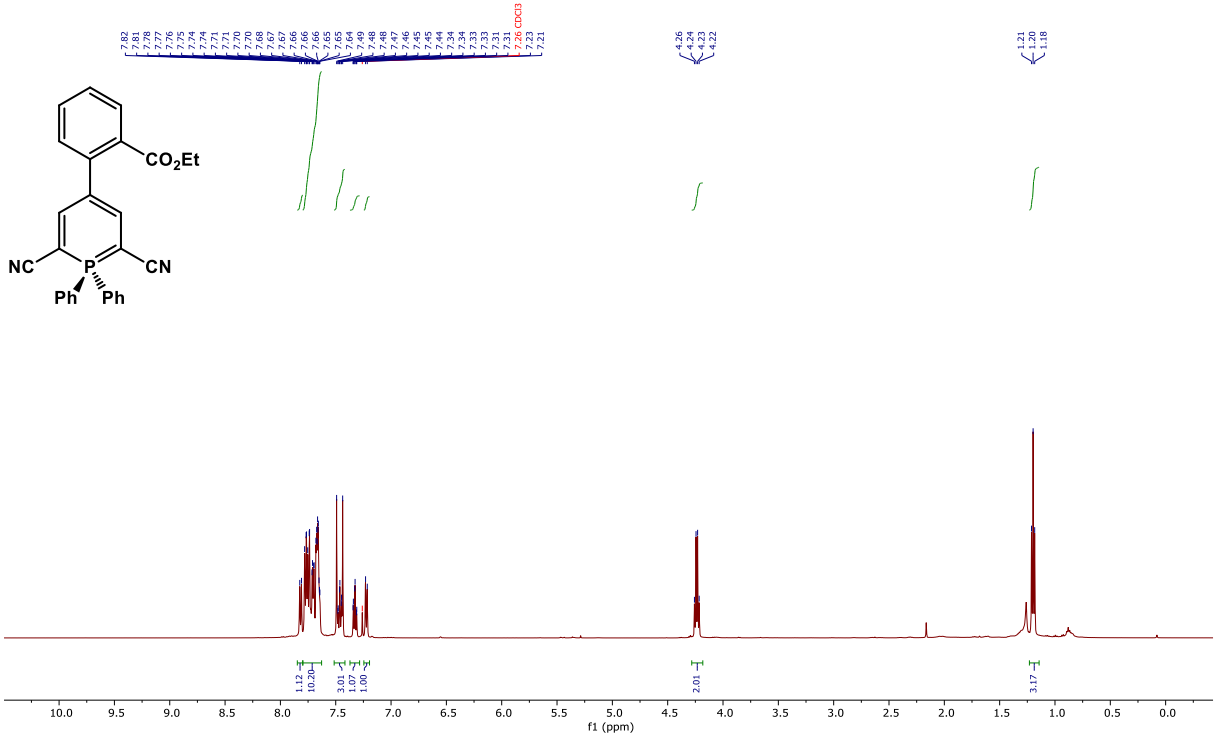


$^{31}$P NMR (202 MHz)

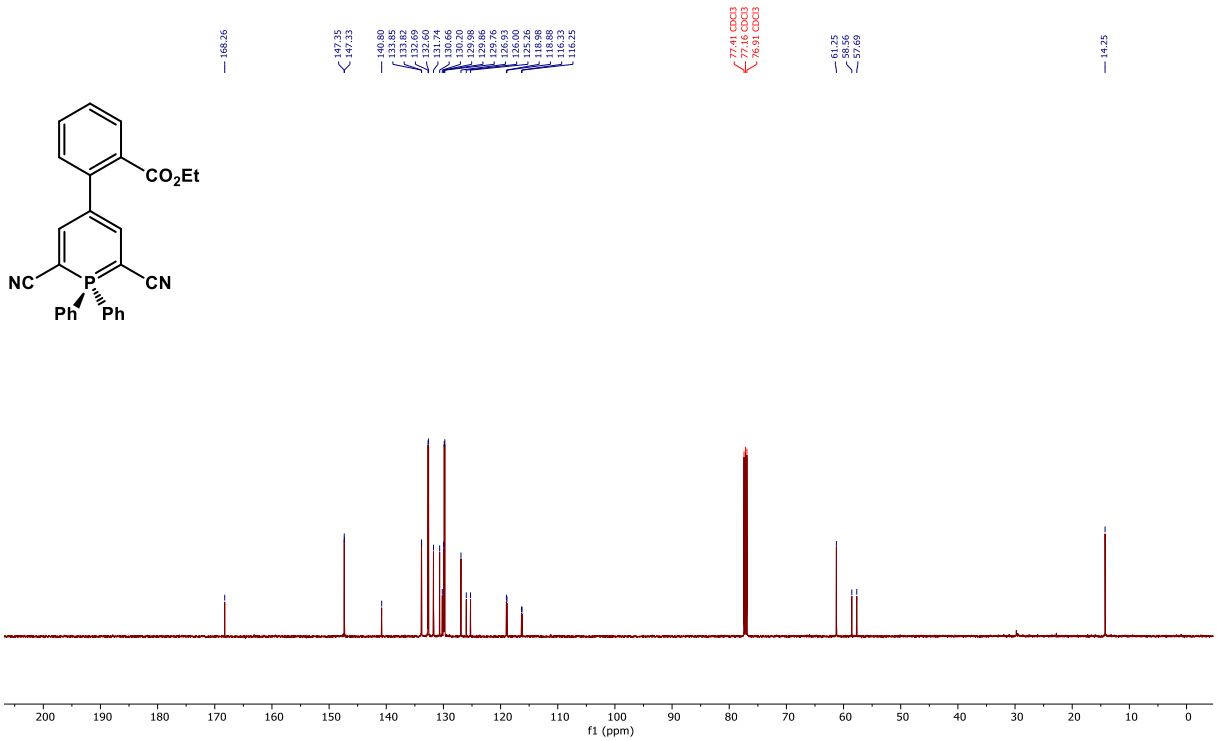


**ethyl 2-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)benzoate (3h)**

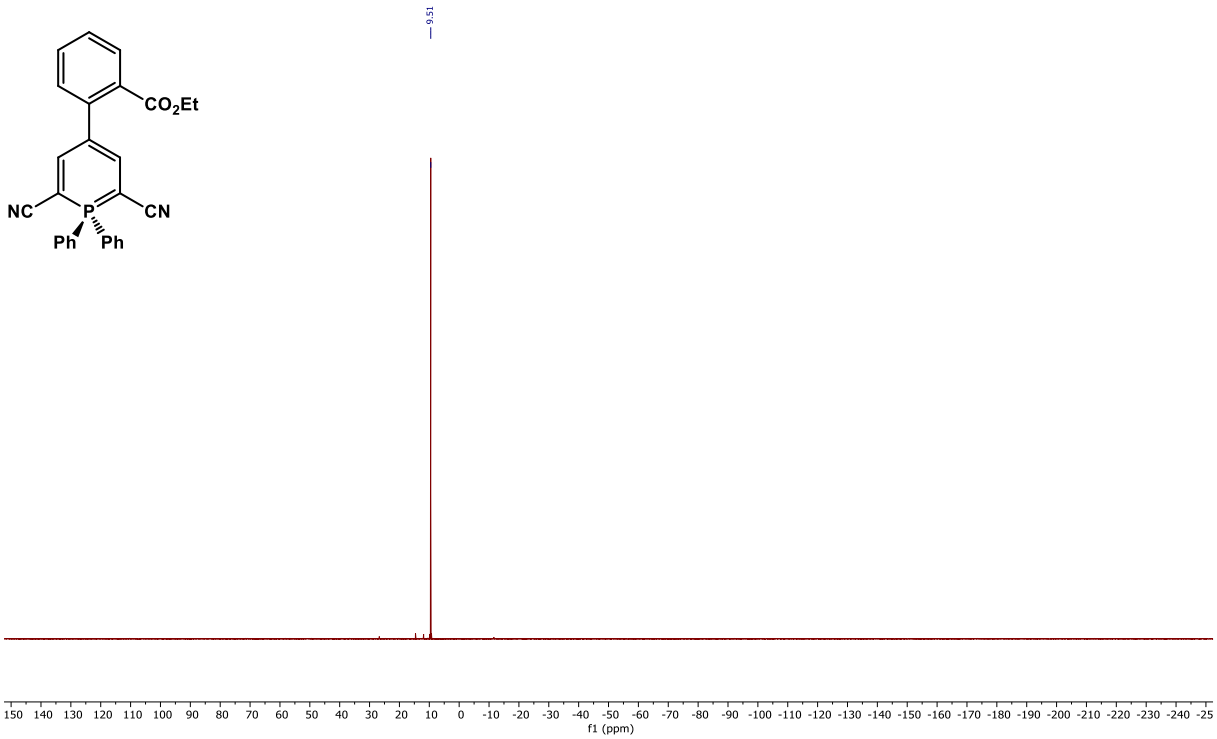
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

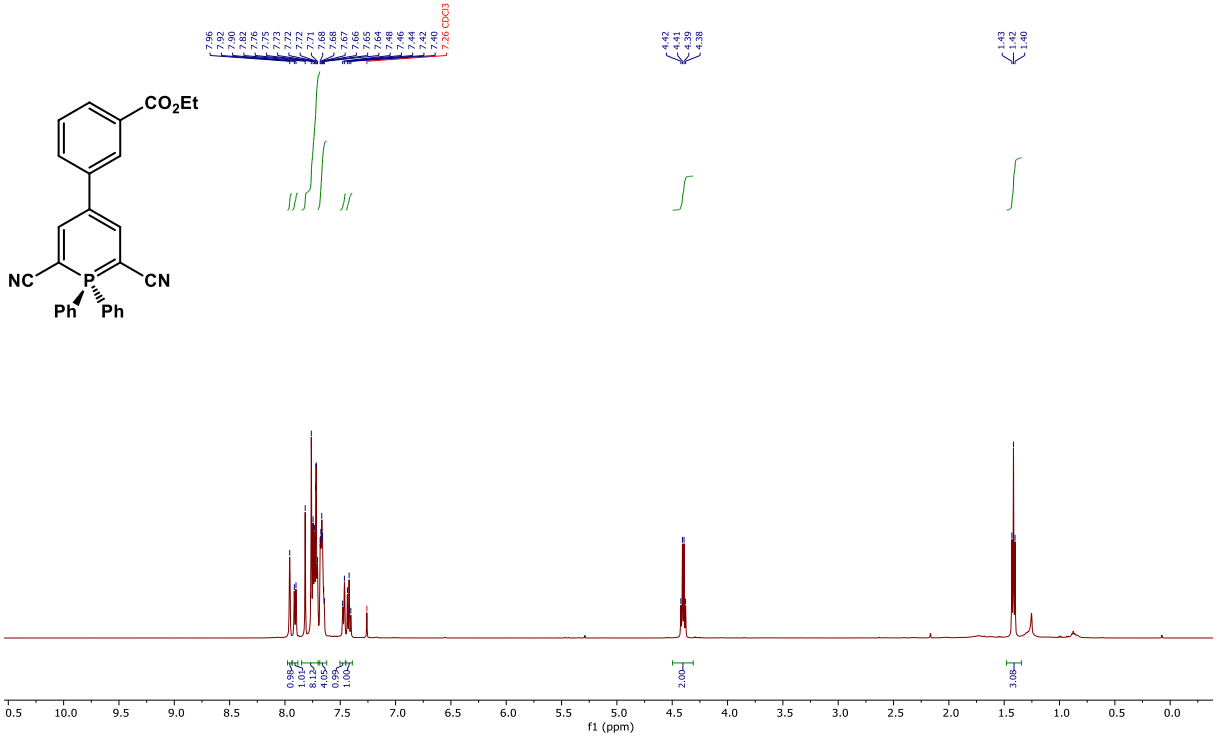


$^{31}$P NMR (202 MHz)

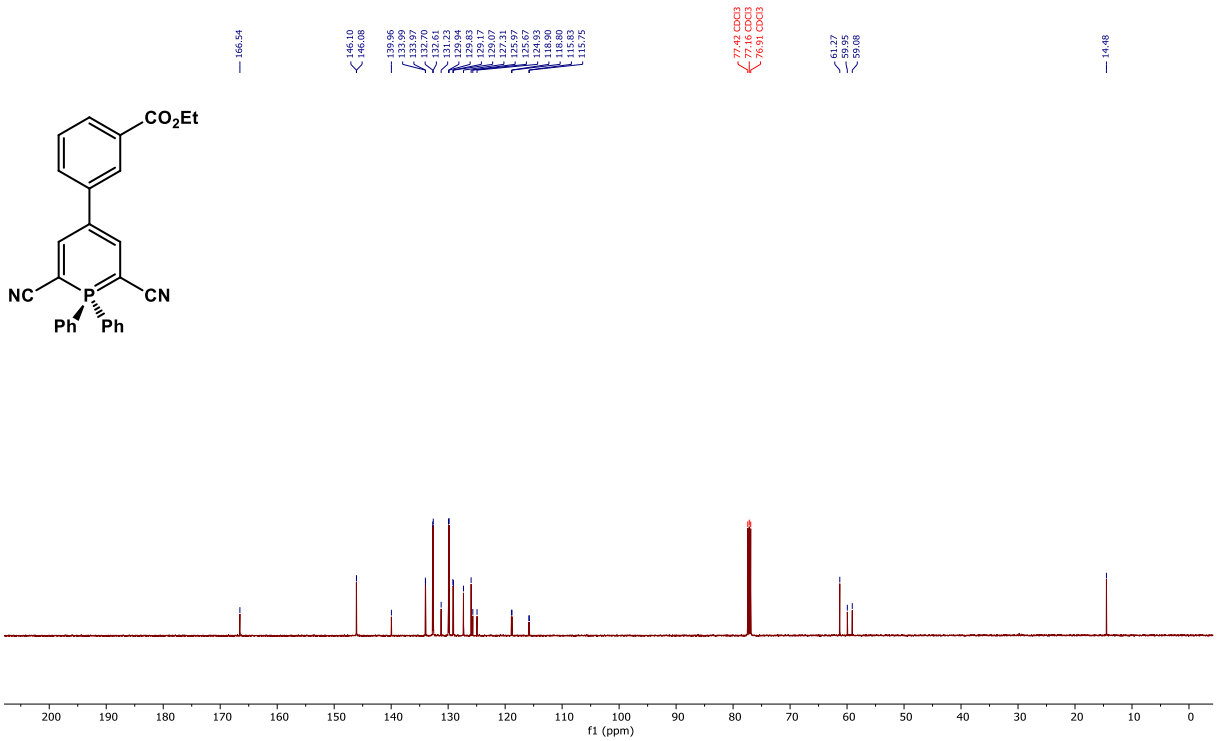


**ethyl 3-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)benzoate (3i)**

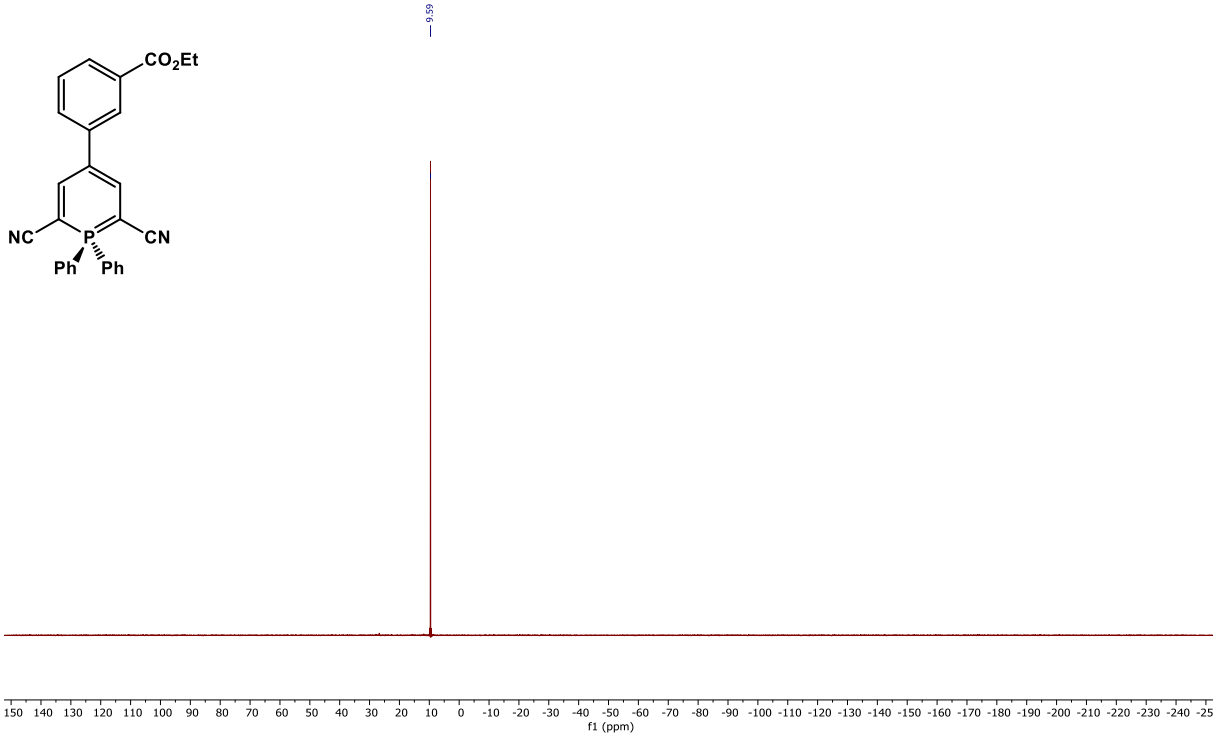
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

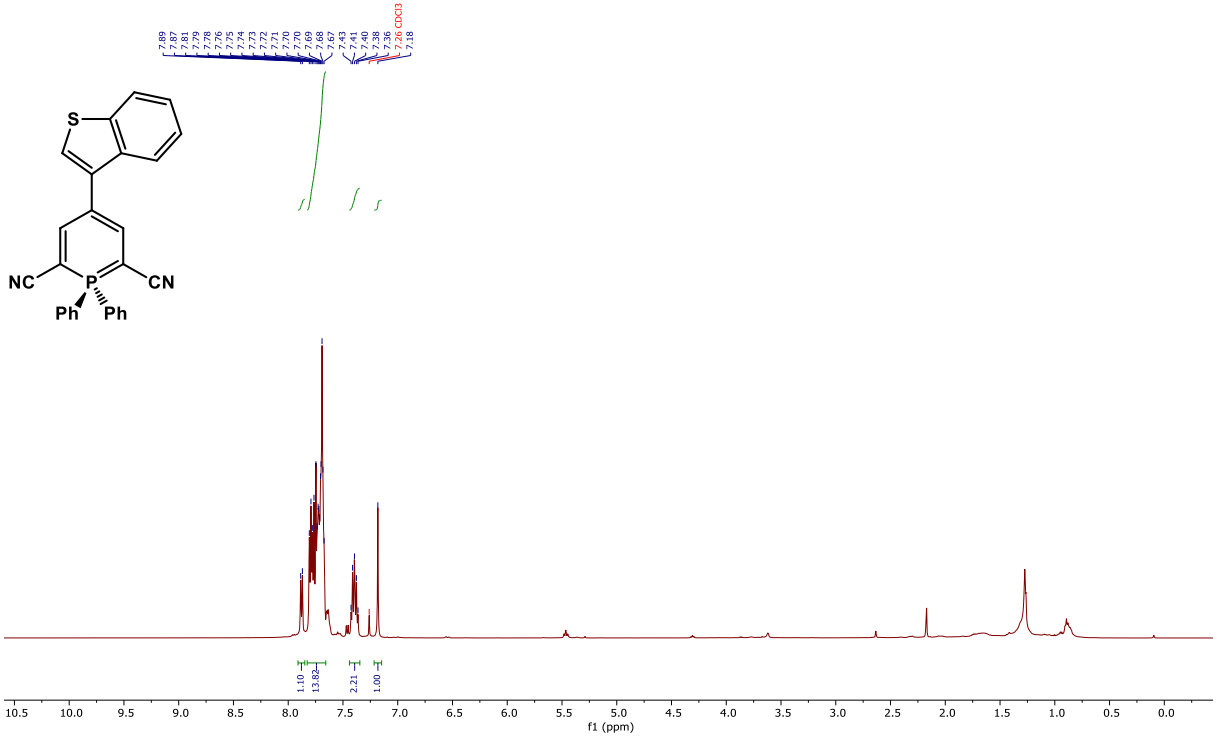


$^{31}$P NMR (202 MHz)

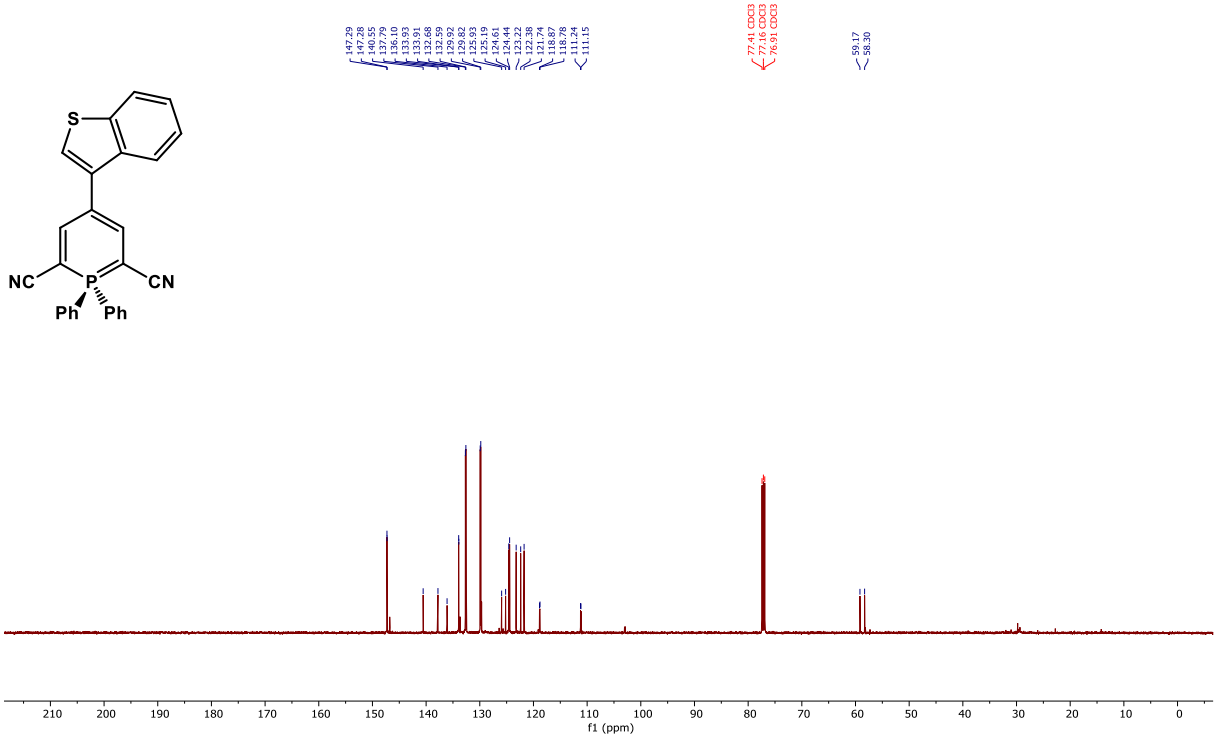


**4-(benzo[*b*]thiophen-3-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3j)**

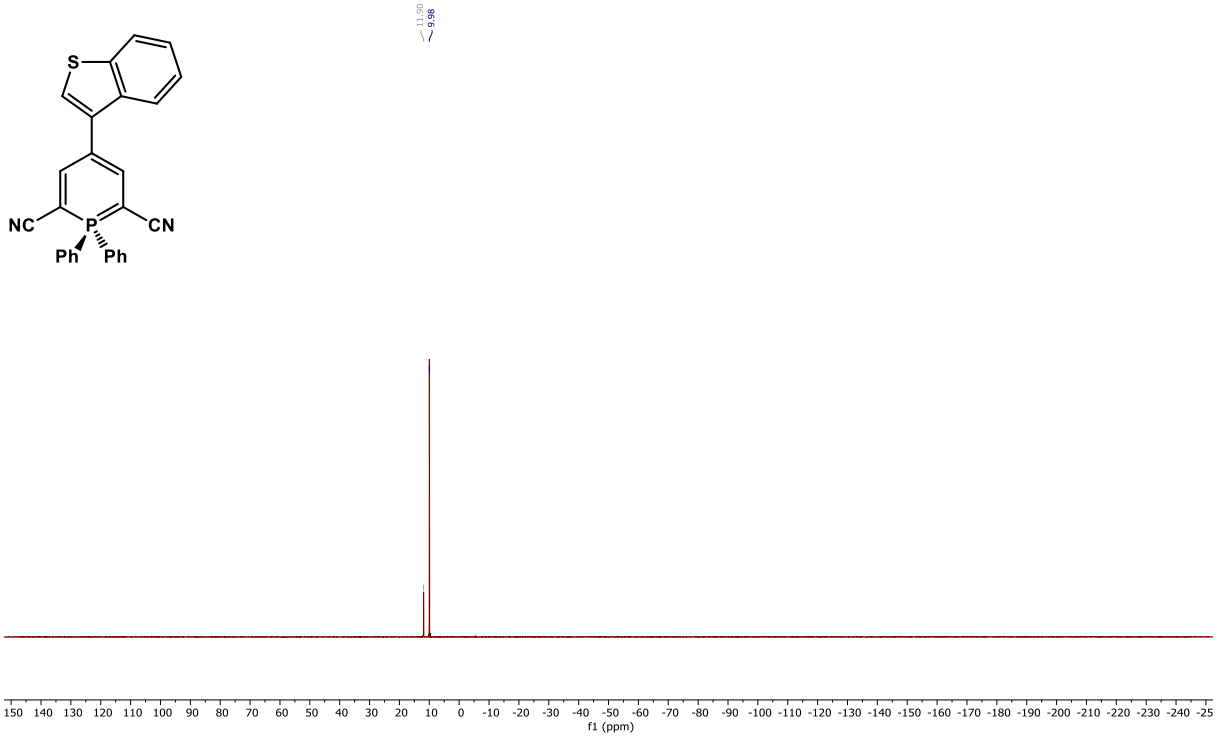
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

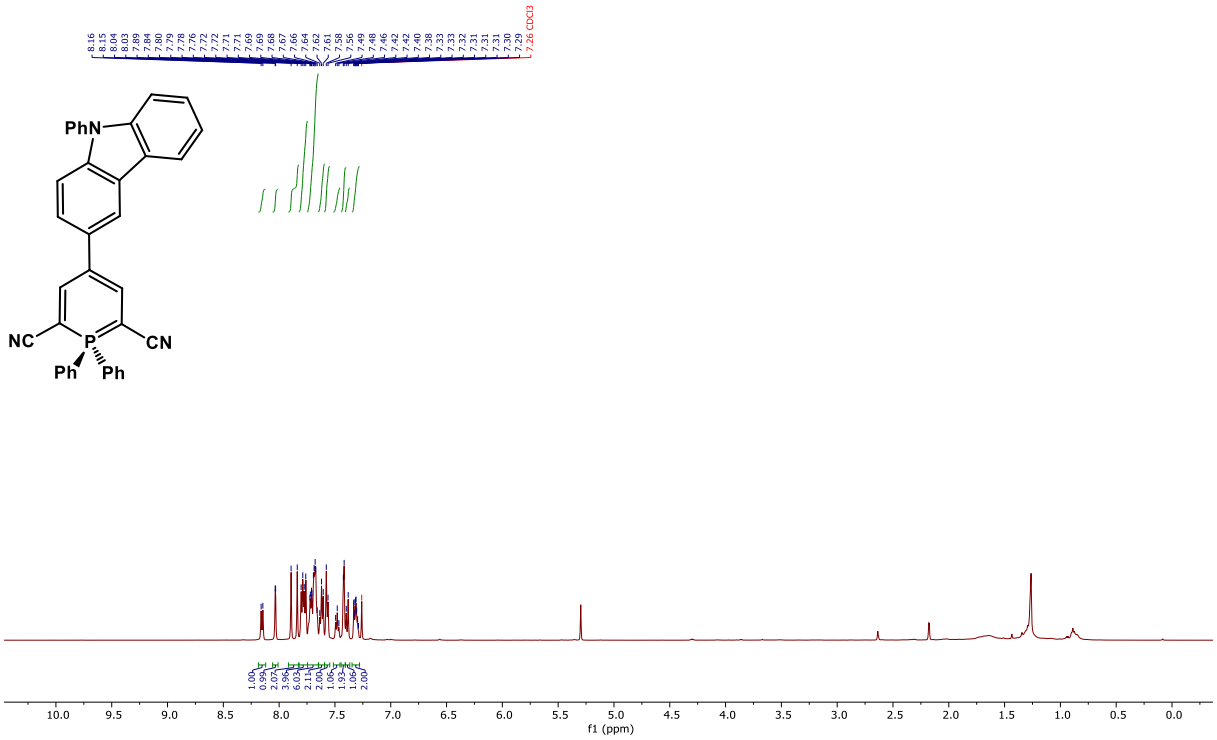


$^{31}$P NMR (202 MHz)

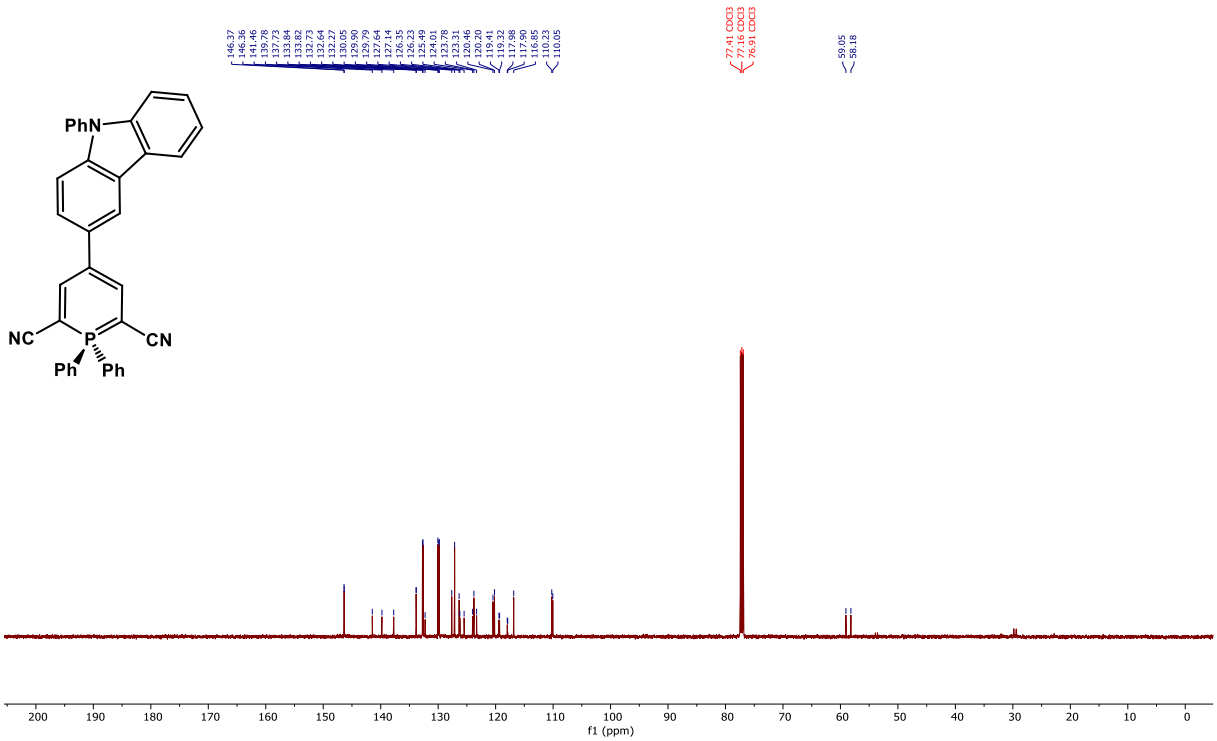


**1,1-diphenyl-4-(9-phenyl-9*H*-carbazol-3-yl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (3k)**

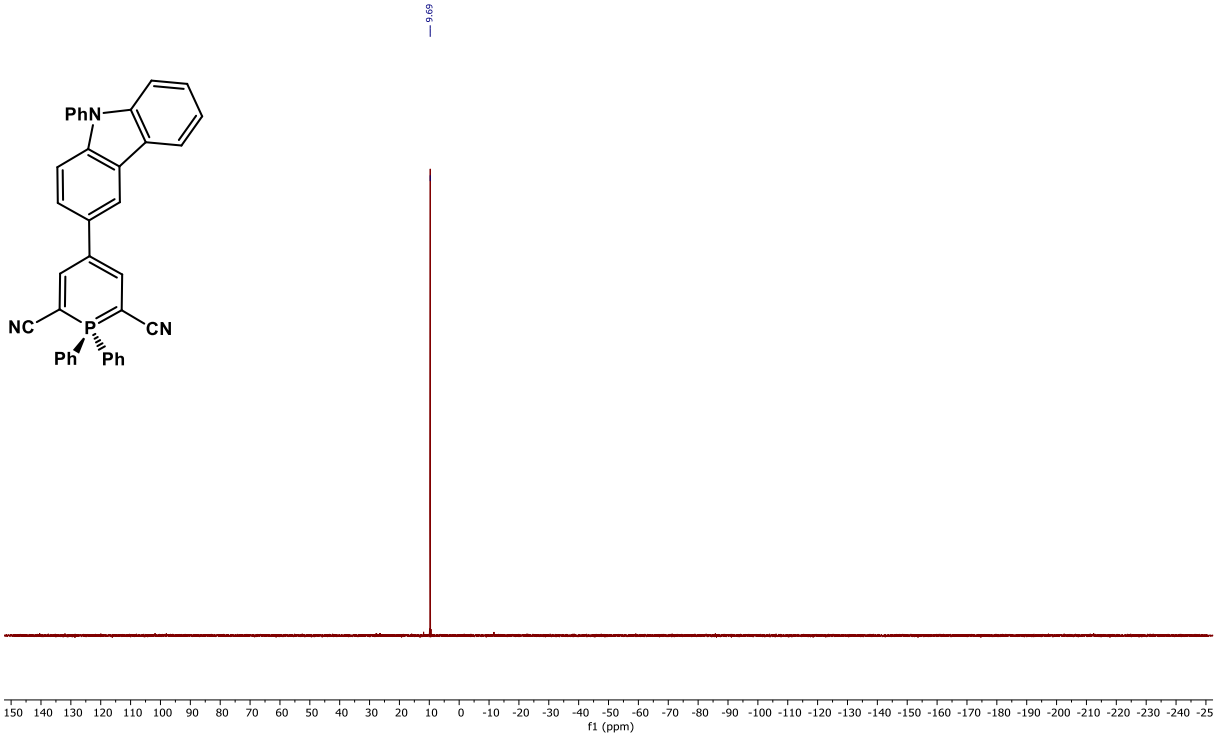
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

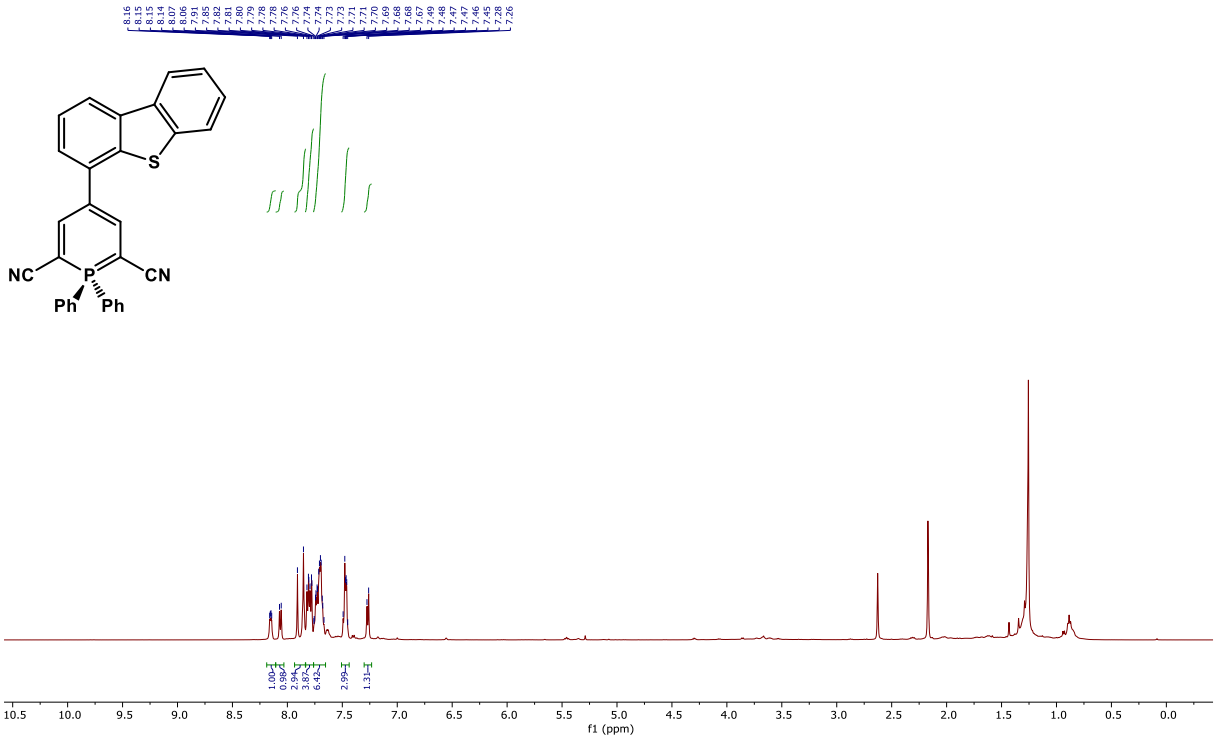


$^{31}$P NMR (202 MHz)

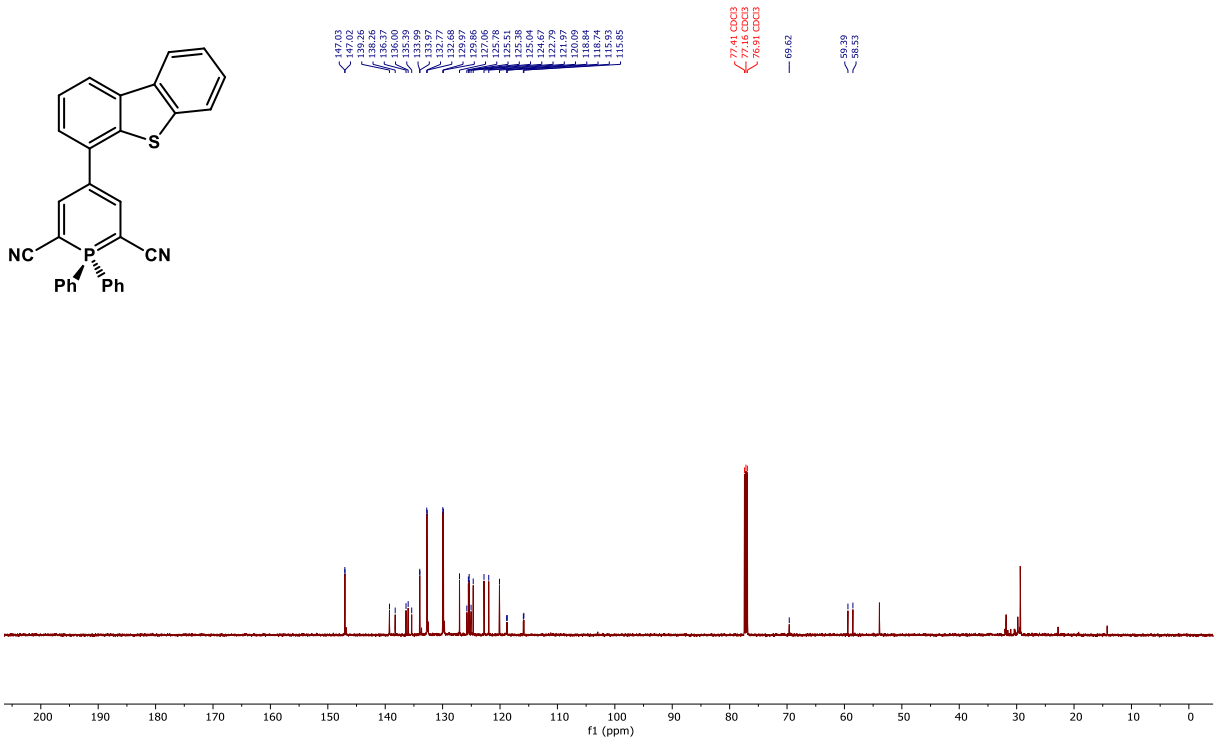


**4-(dibenzo[*b*,*d*]thiophen-4-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3l)**

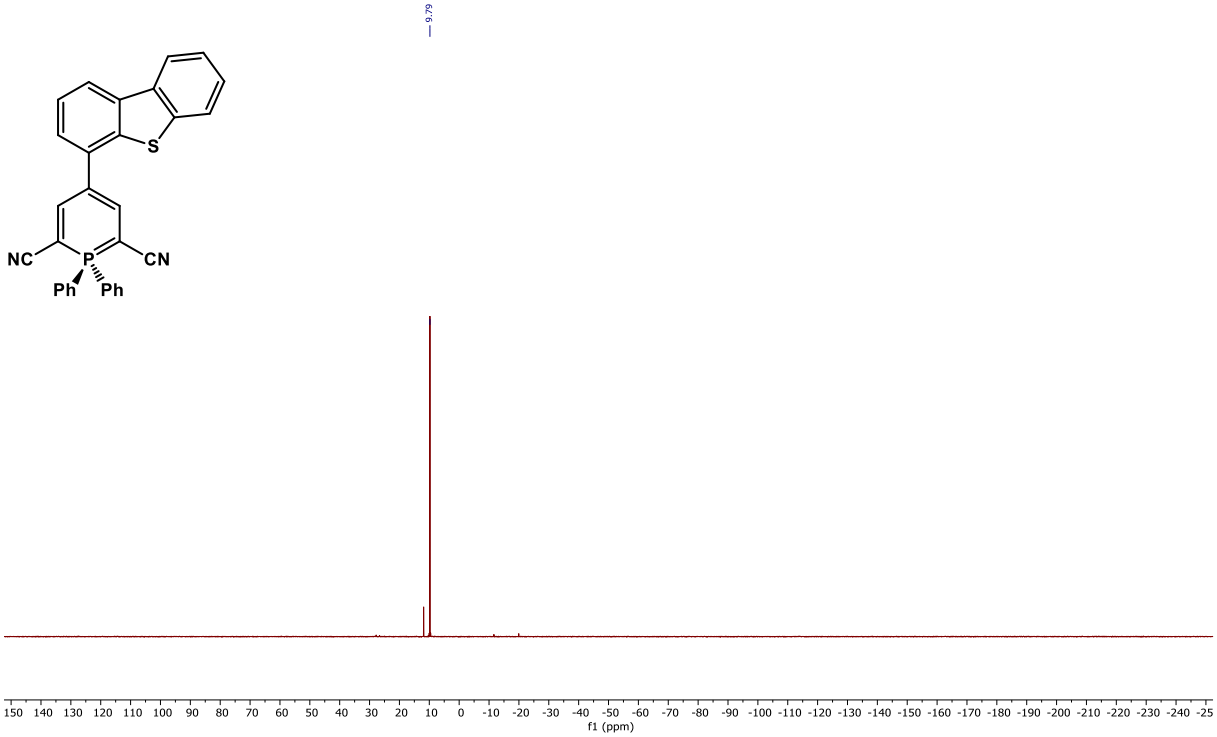
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

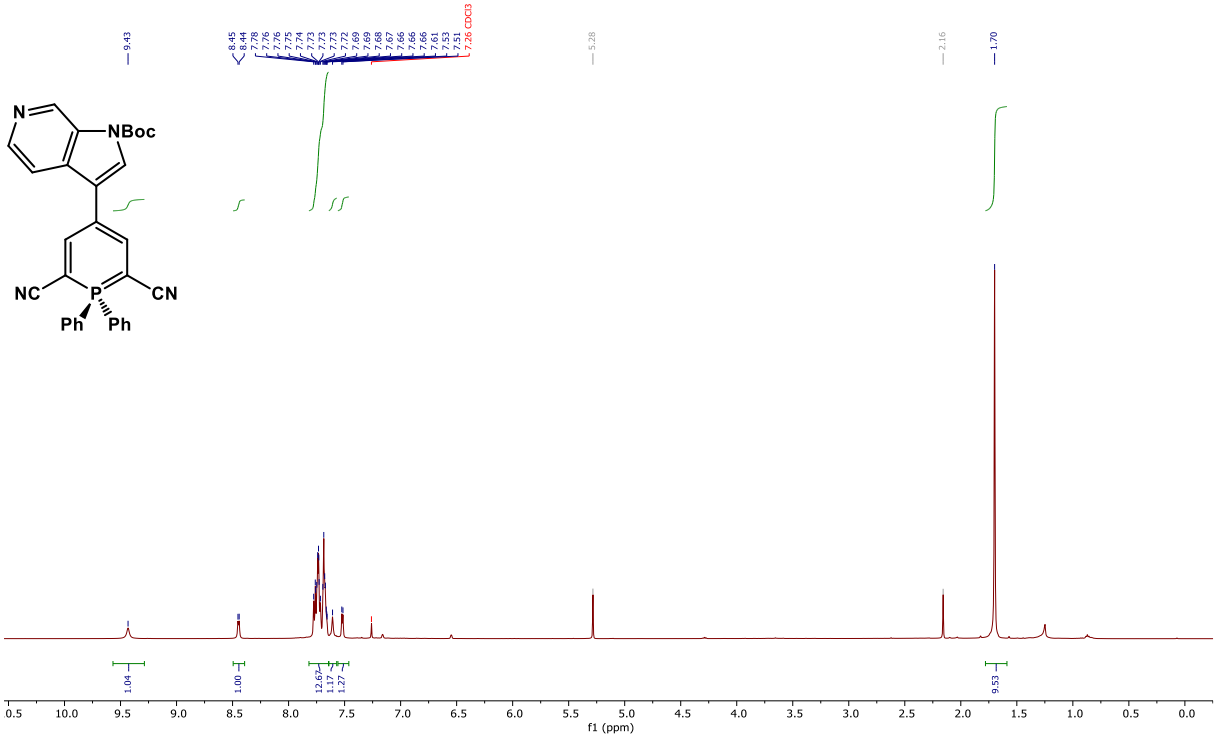


$^{31}$P NMR (202 MHz)

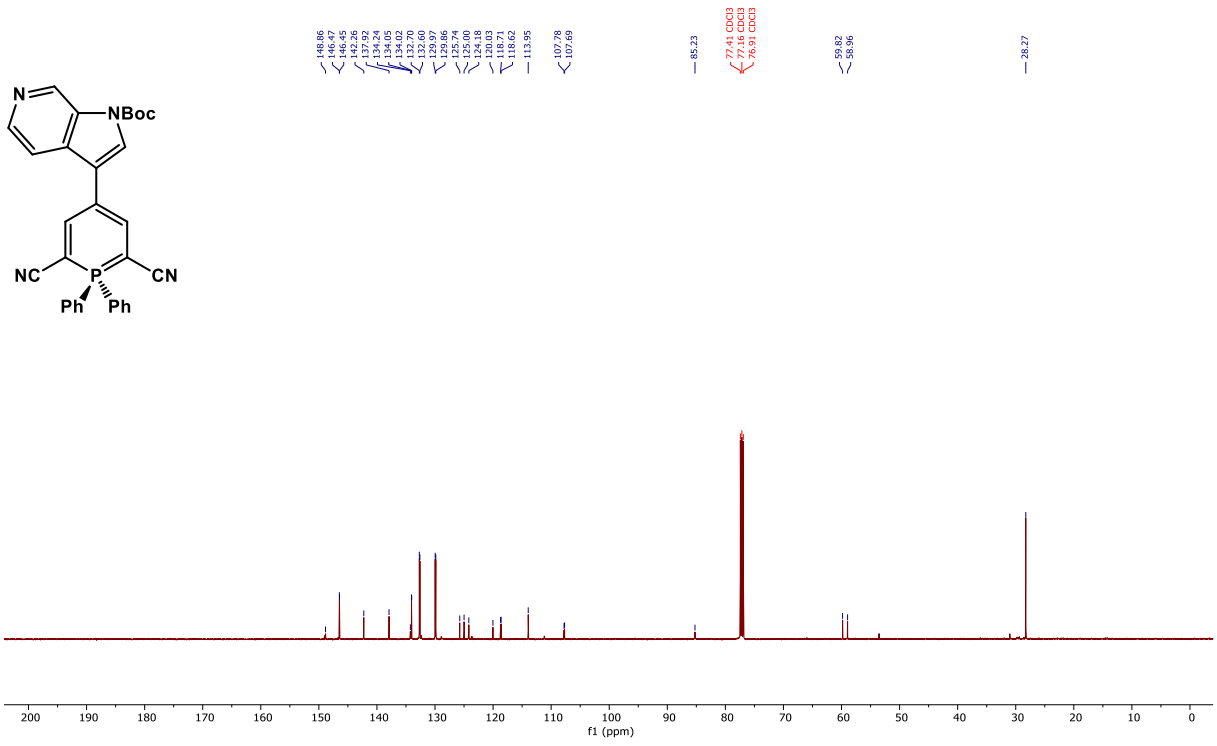


***tert*-butyl 3-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)-1*H*-pyrrolo[2,3-*c*]pyridine-1-carboxylate (3m)**

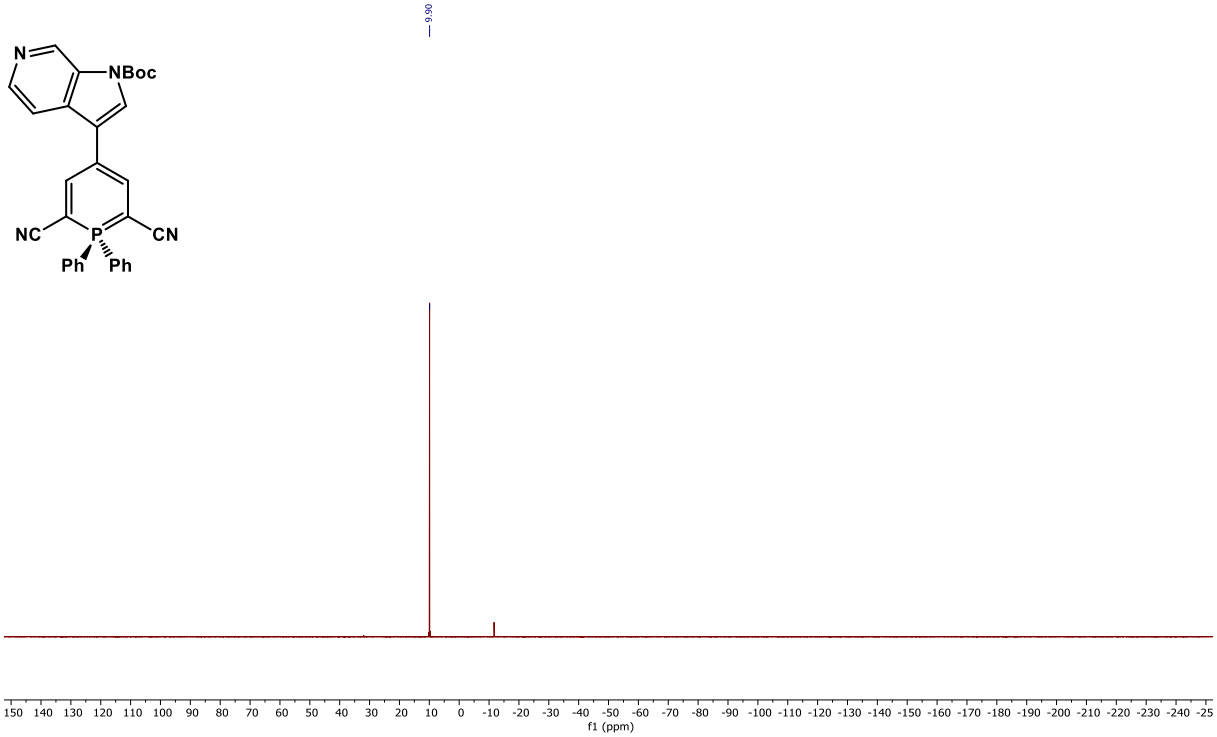
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

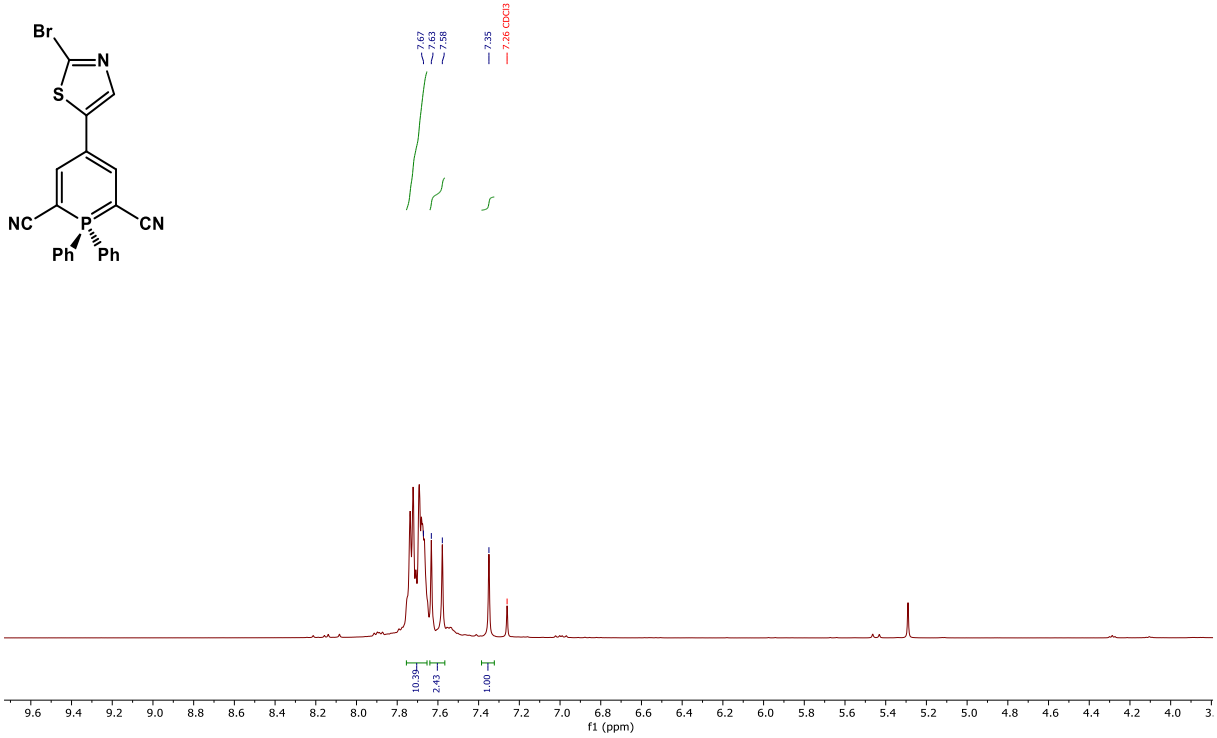


$^{31}$P NMR (202 MHz)

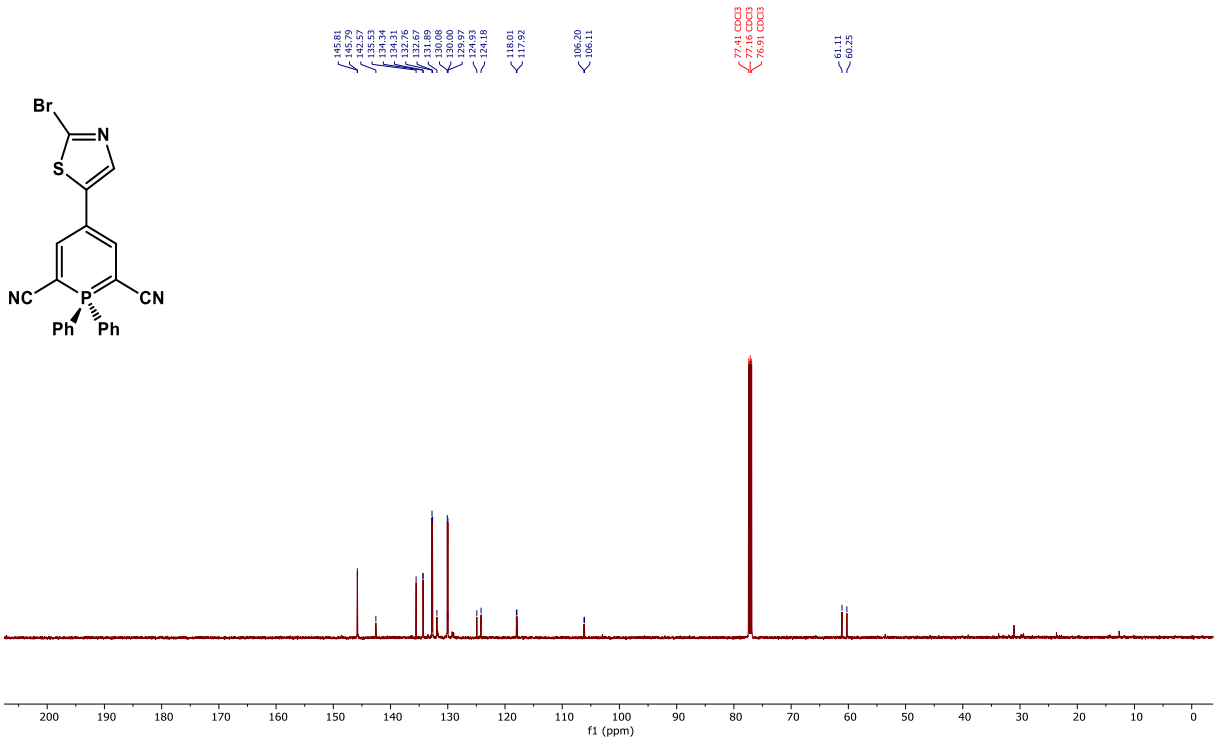


**4-(2-bromothiazol-5-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3n)**

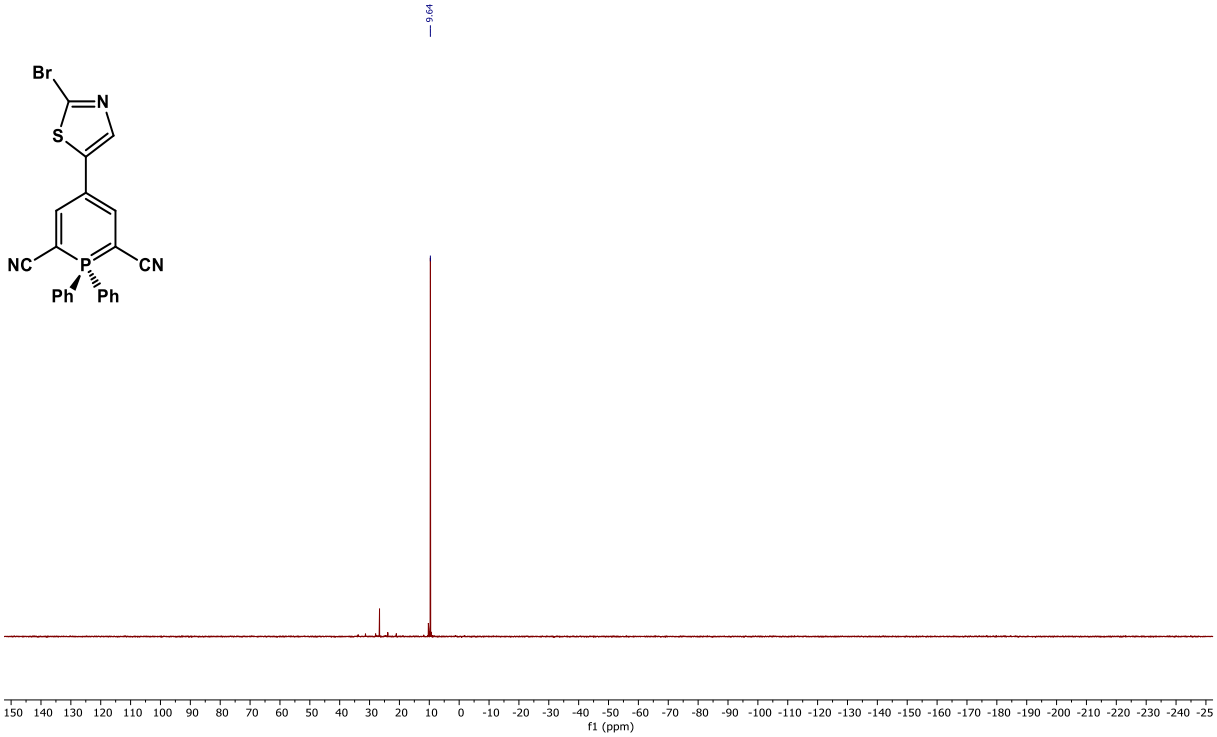
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

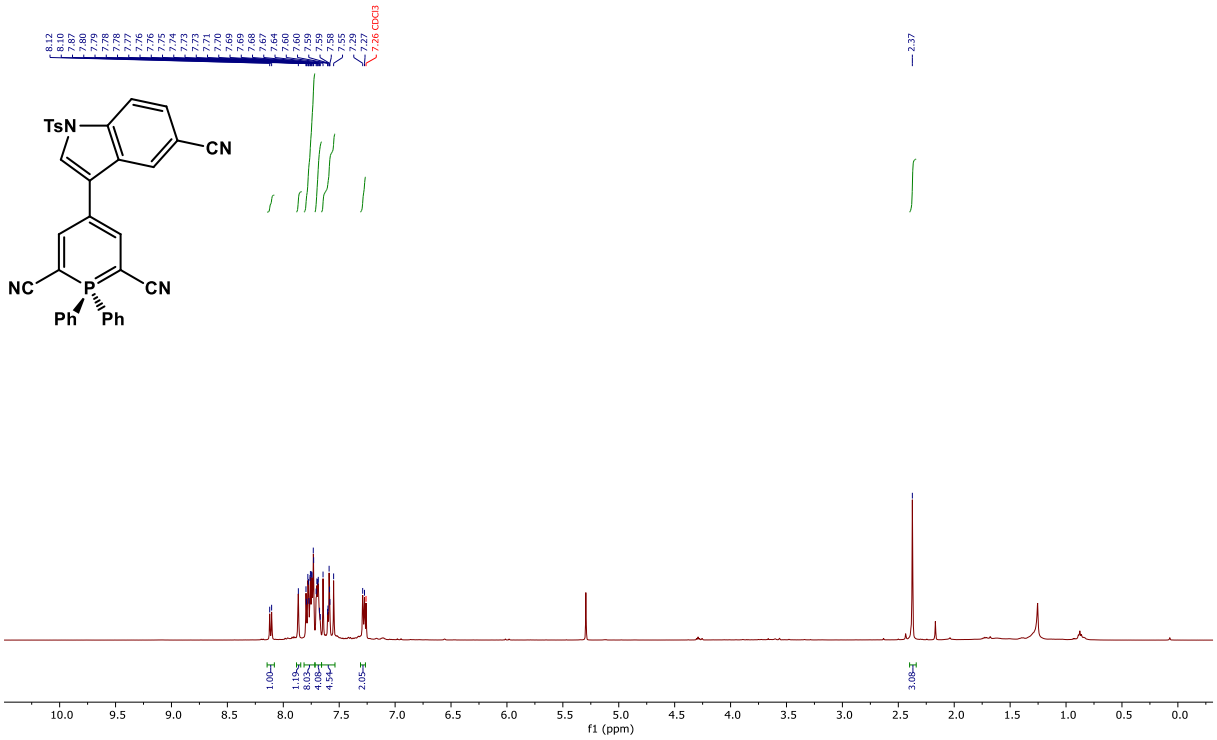


$^{31}$P NMR (202 MHz)

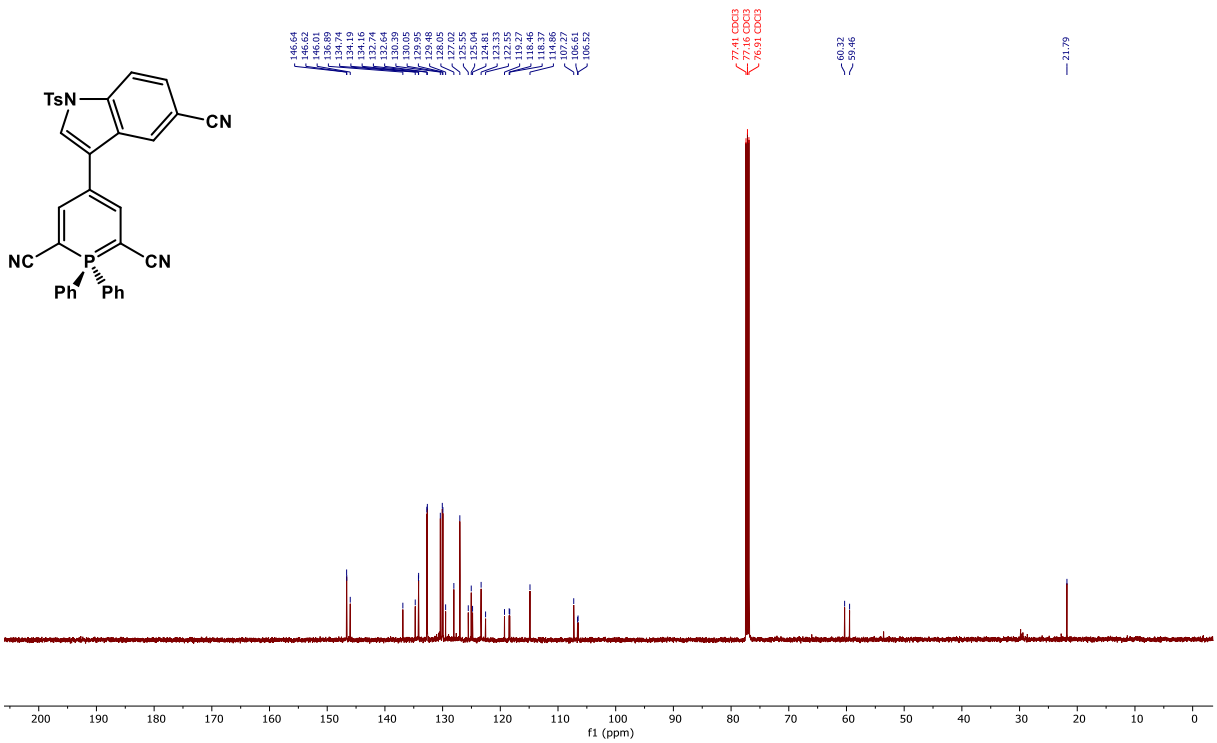


**4-(5-cyano-1-tosyl-1*H*-indol-3-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3o)**

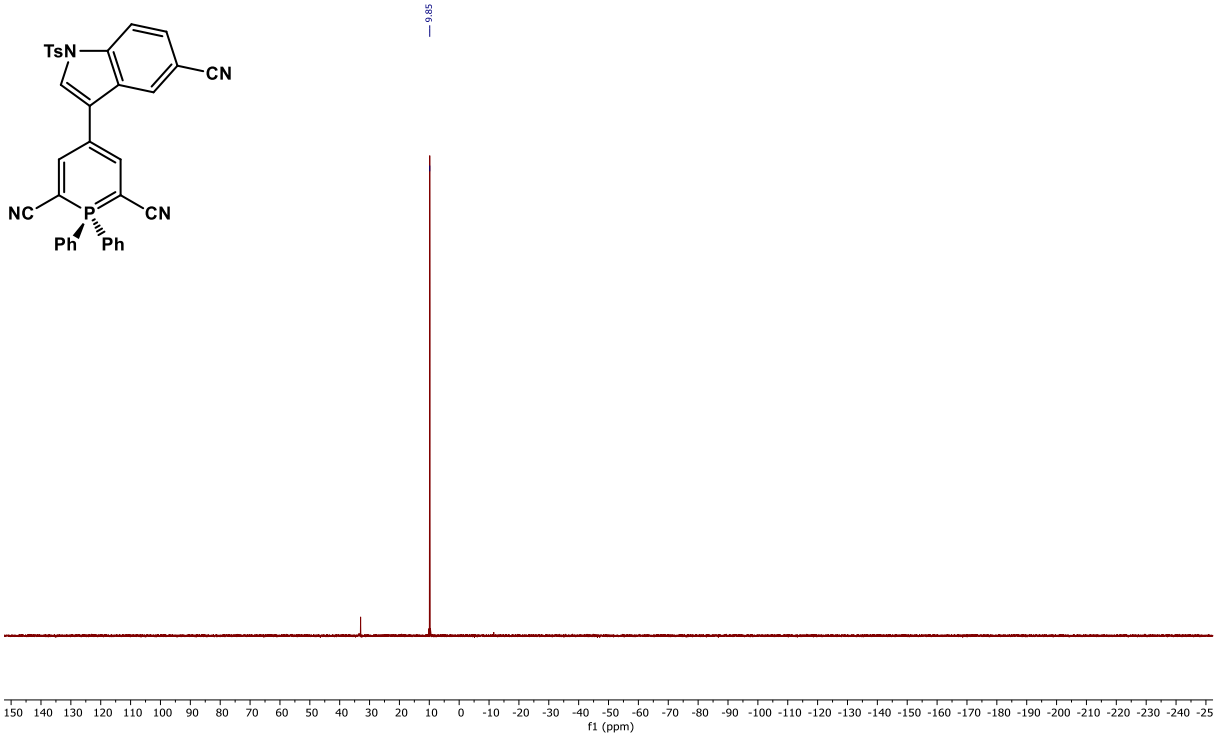
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

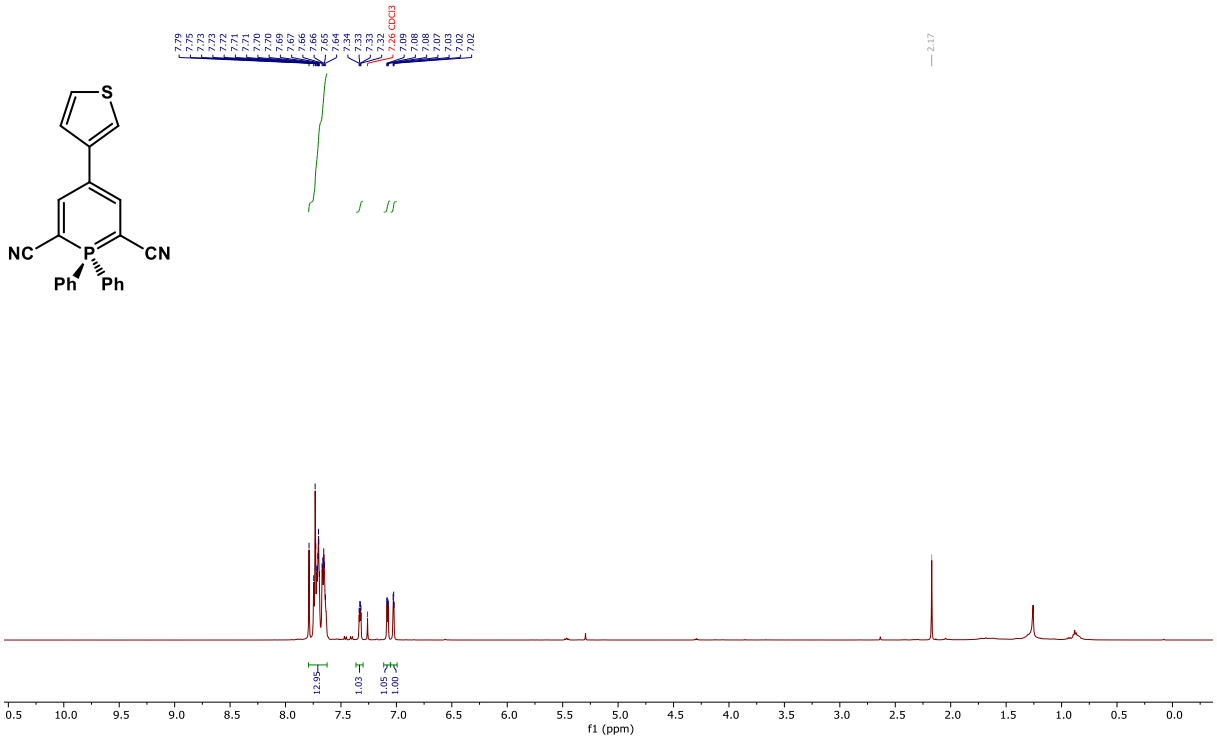


$^{31}$P NMR (202 MHz)

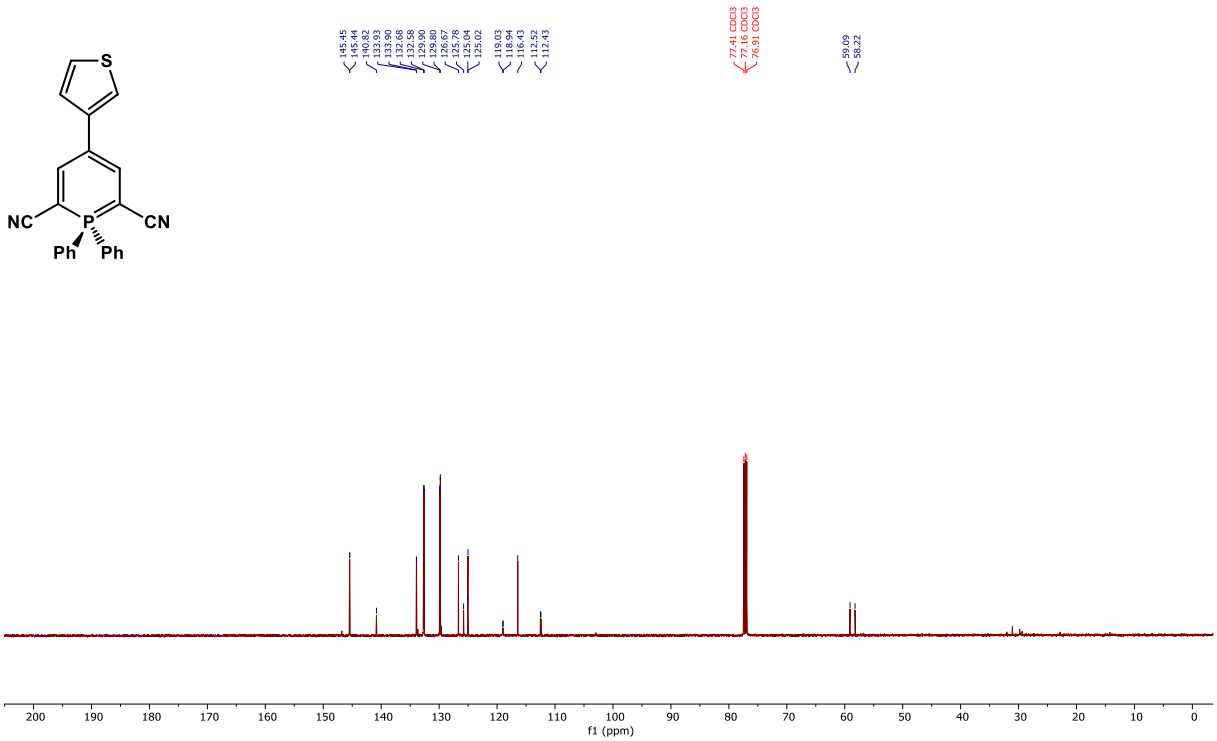


## 1,1-diphenyl-4-(thiophen-3-yl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (3p)

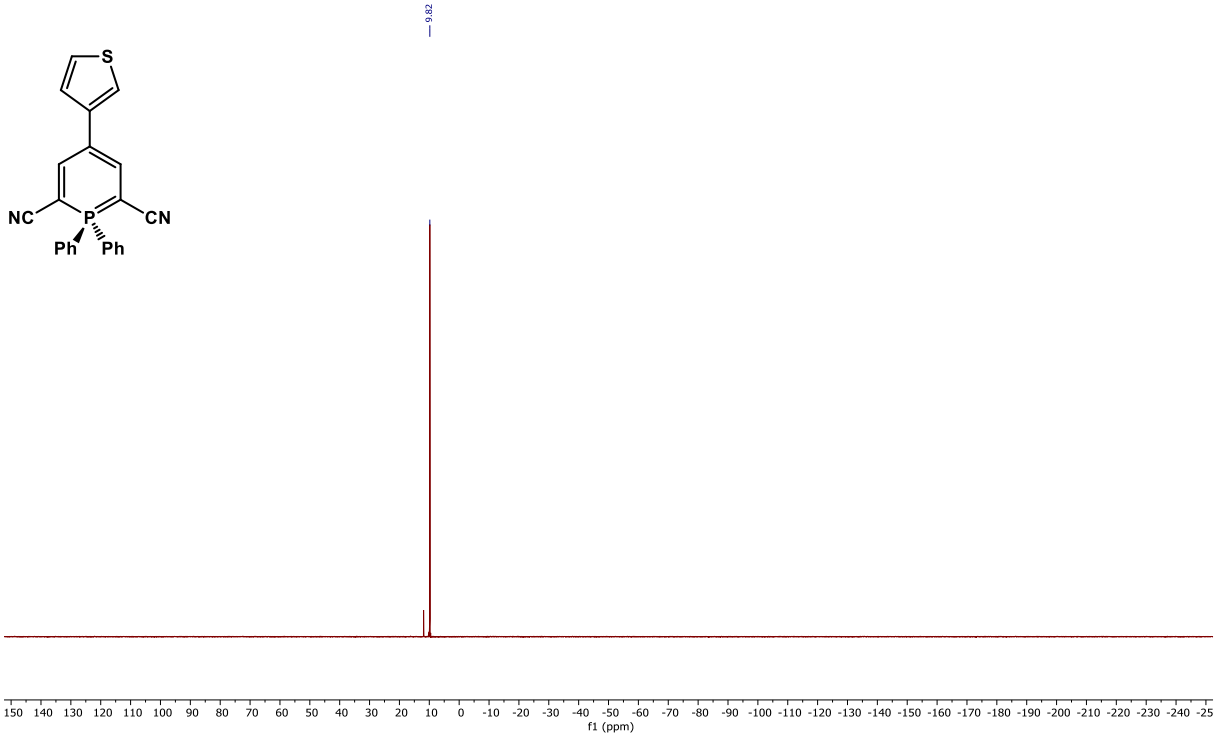
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

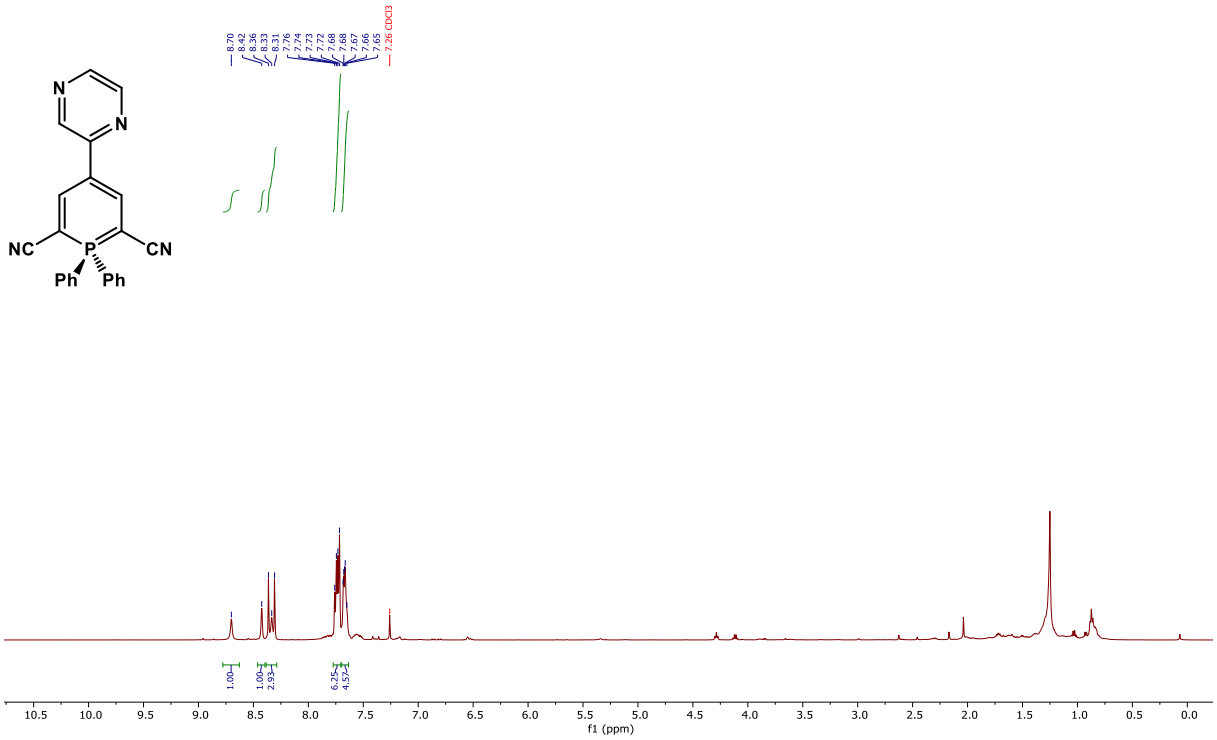


$^{31}$P NMR (202 MHz)

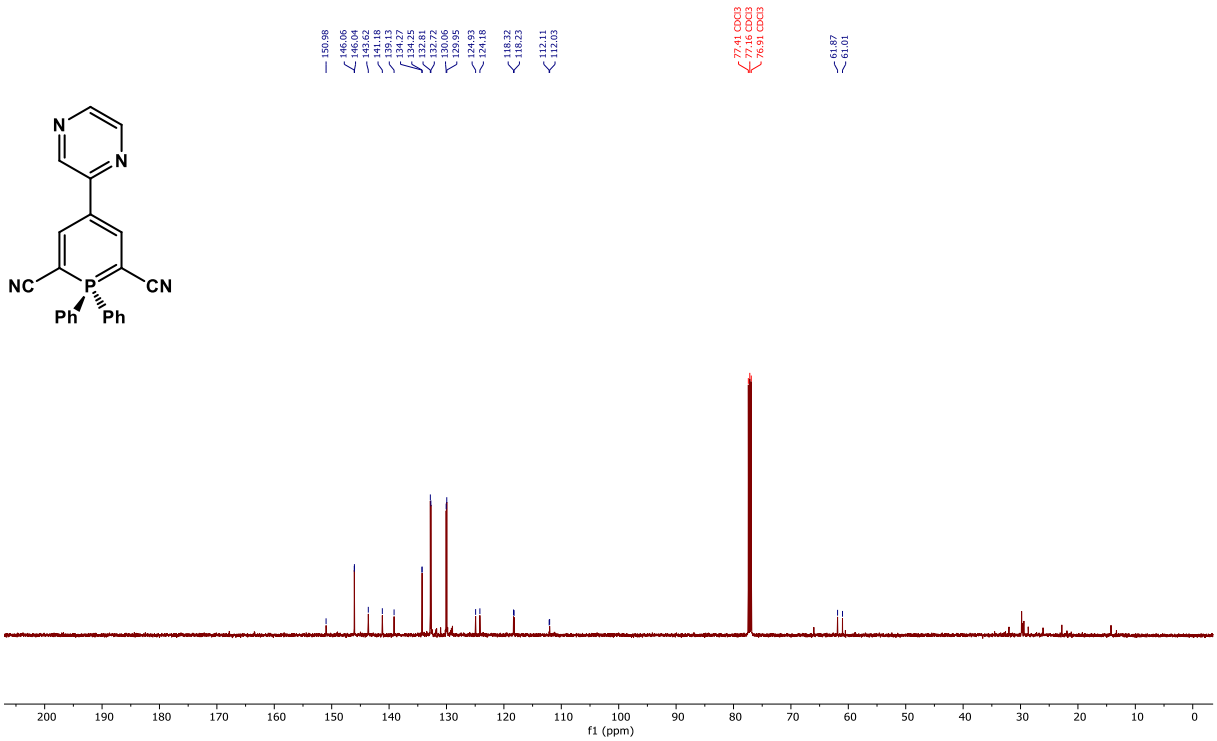


**1,1-diphenyl-4-(pyrazin-2-yl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (3q)**

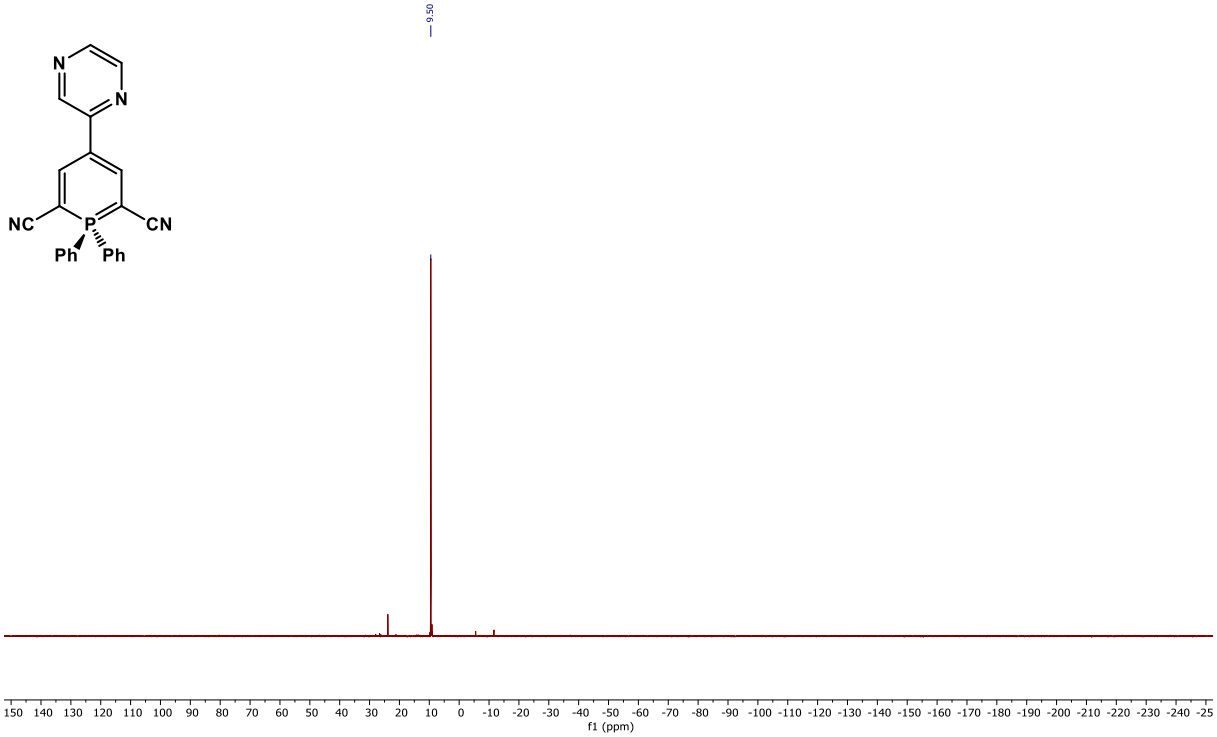
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

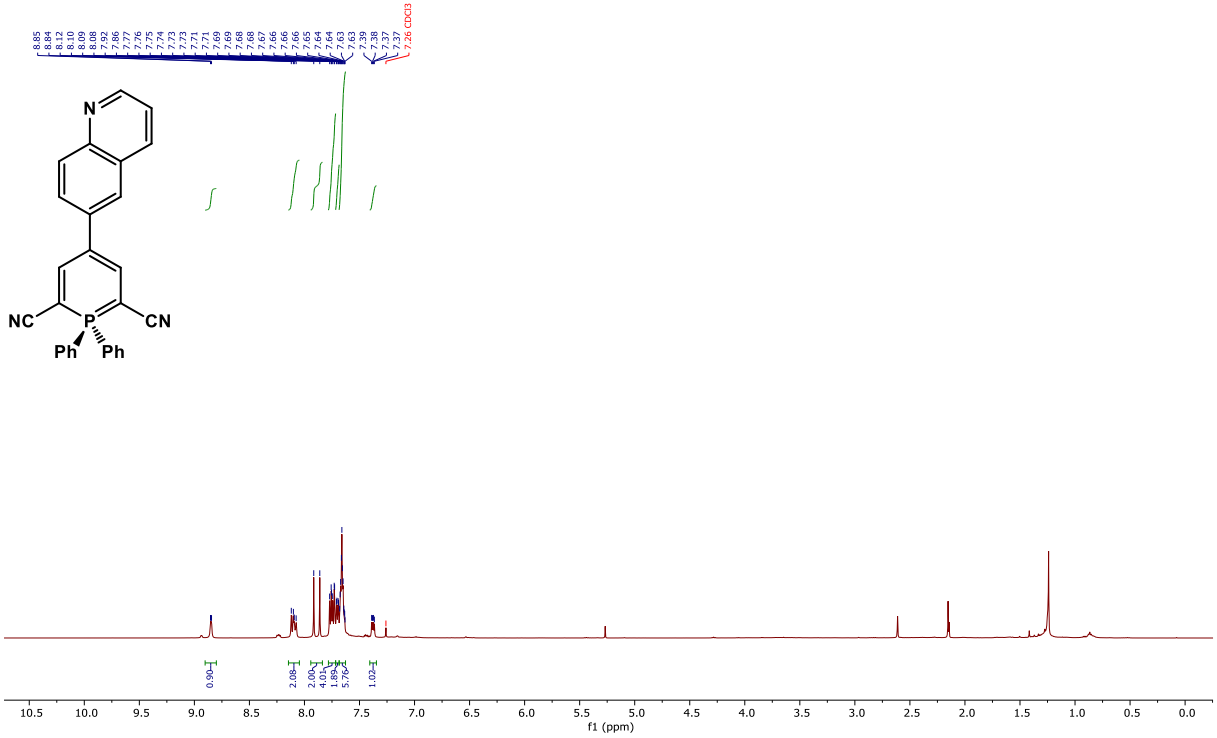


$^{31}$P NMR (202 MHz)

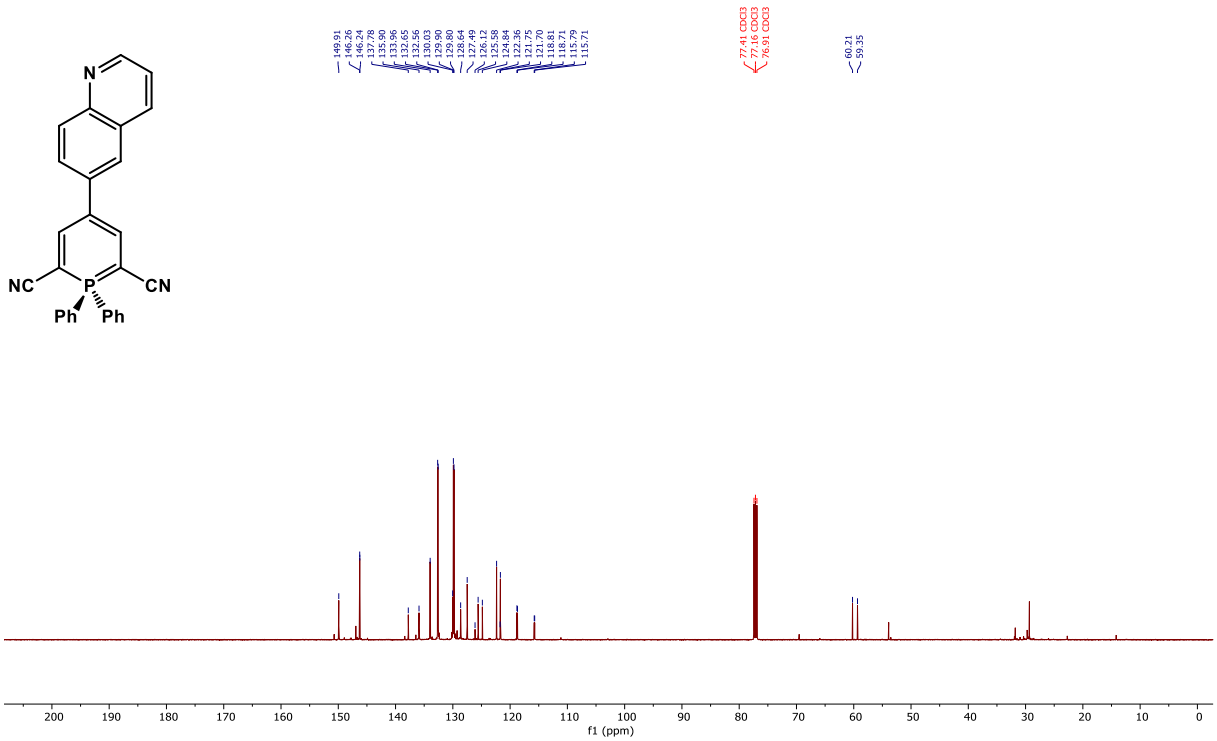


**1,1-diphenyl-4-(quinolin-6-yl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (3r)**

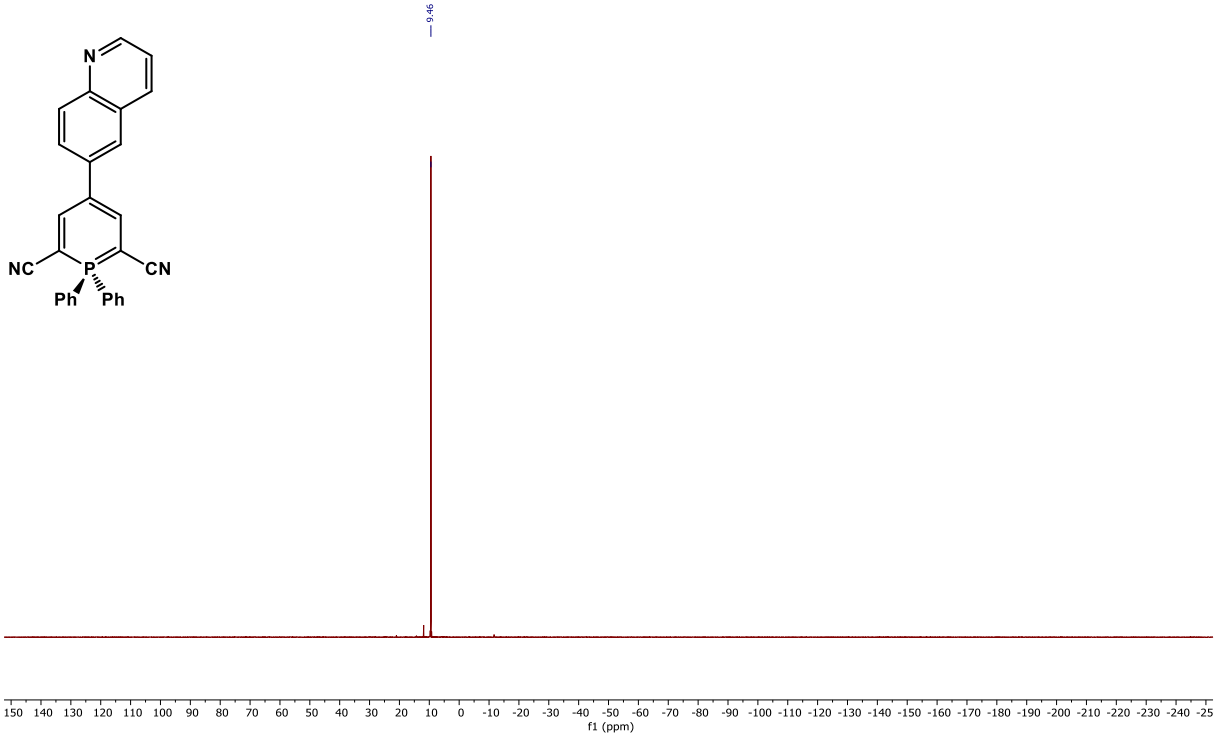
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

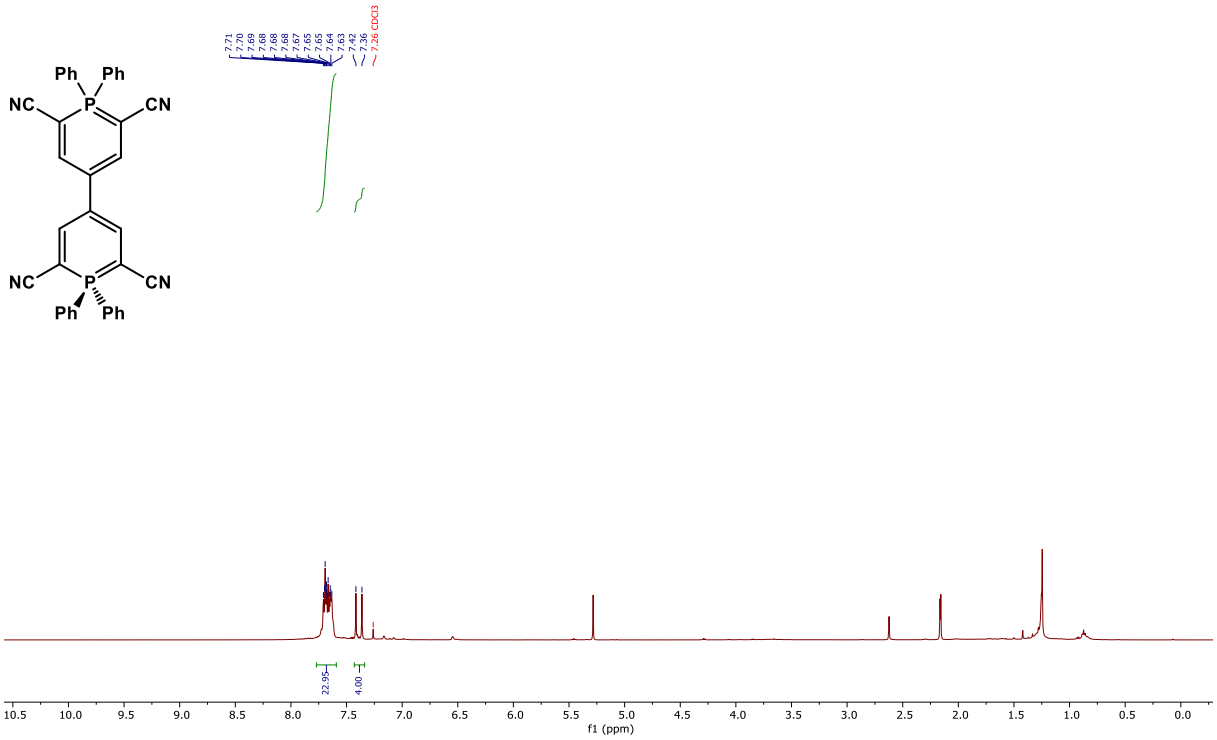


$^{31}$P NMR (202 MHz)

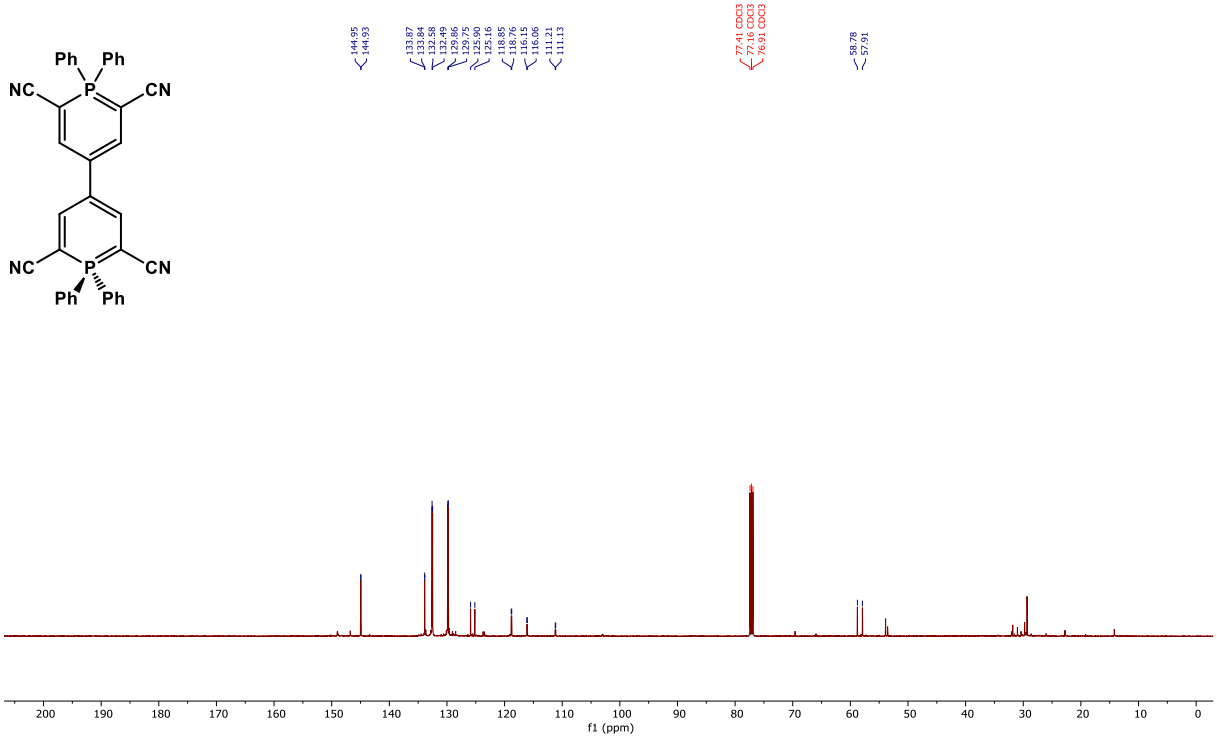


**1,1,1',1'-tetraphenyl-1λ⁵,1'λ⁵-[4,4'-biphosphinine]-2,2',6,6'-tetracarbonitrile (3s)**

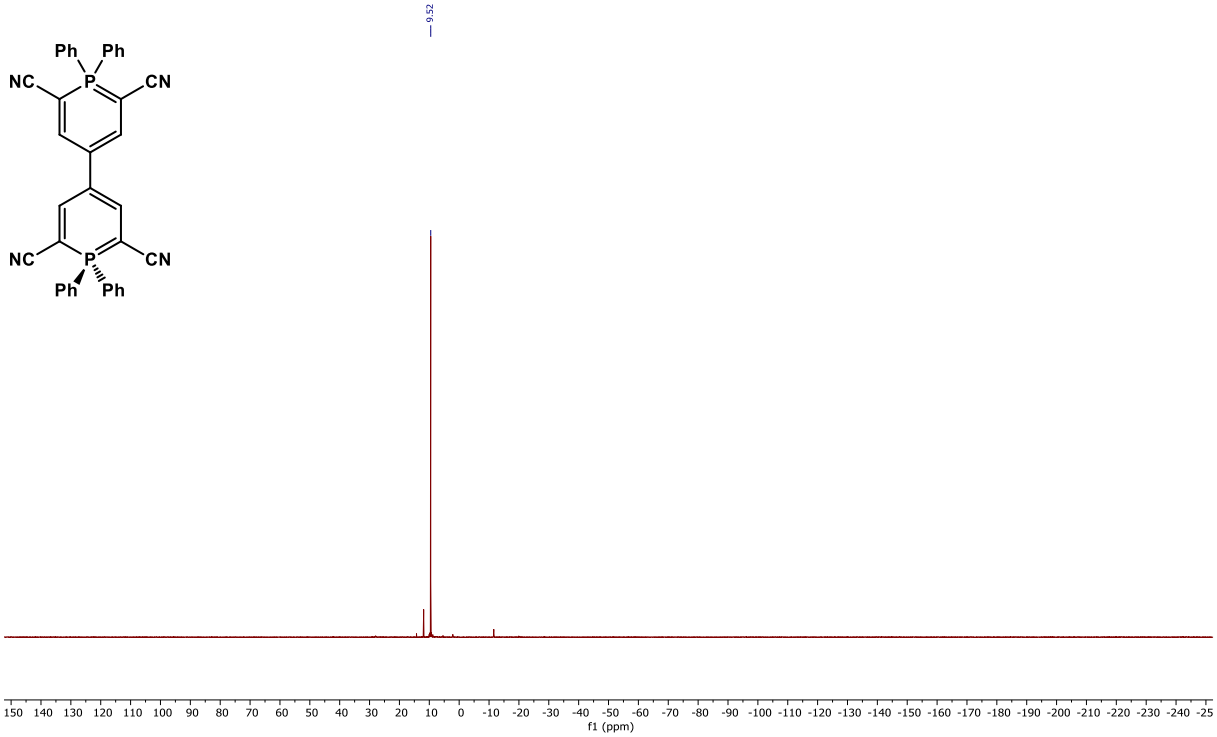
$^{1}$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

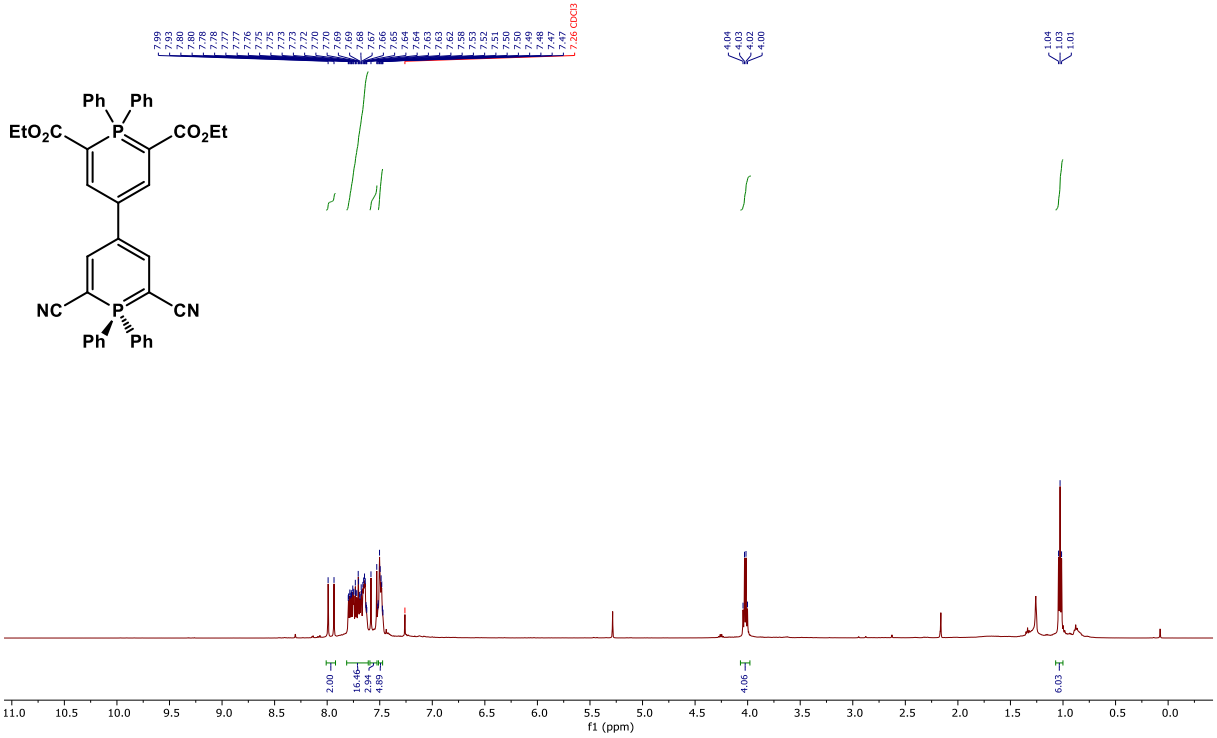


$^{31}$P NMR (202 MHz)

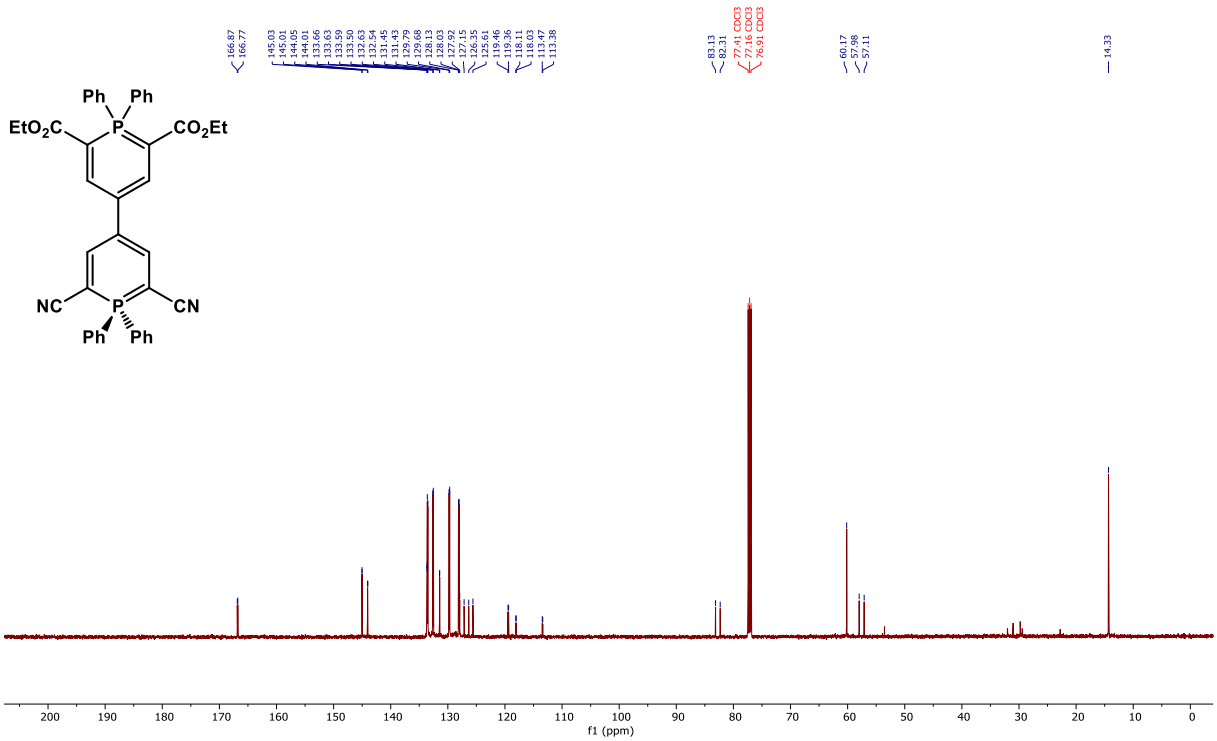


**diethyl 2',6'-dicyano-1,1,1',1'-tetraphenyl-1λ$^5$,1'λ$^5$-[4,4'-biphosphinine]-2,6-dicarboxylate (3t)**

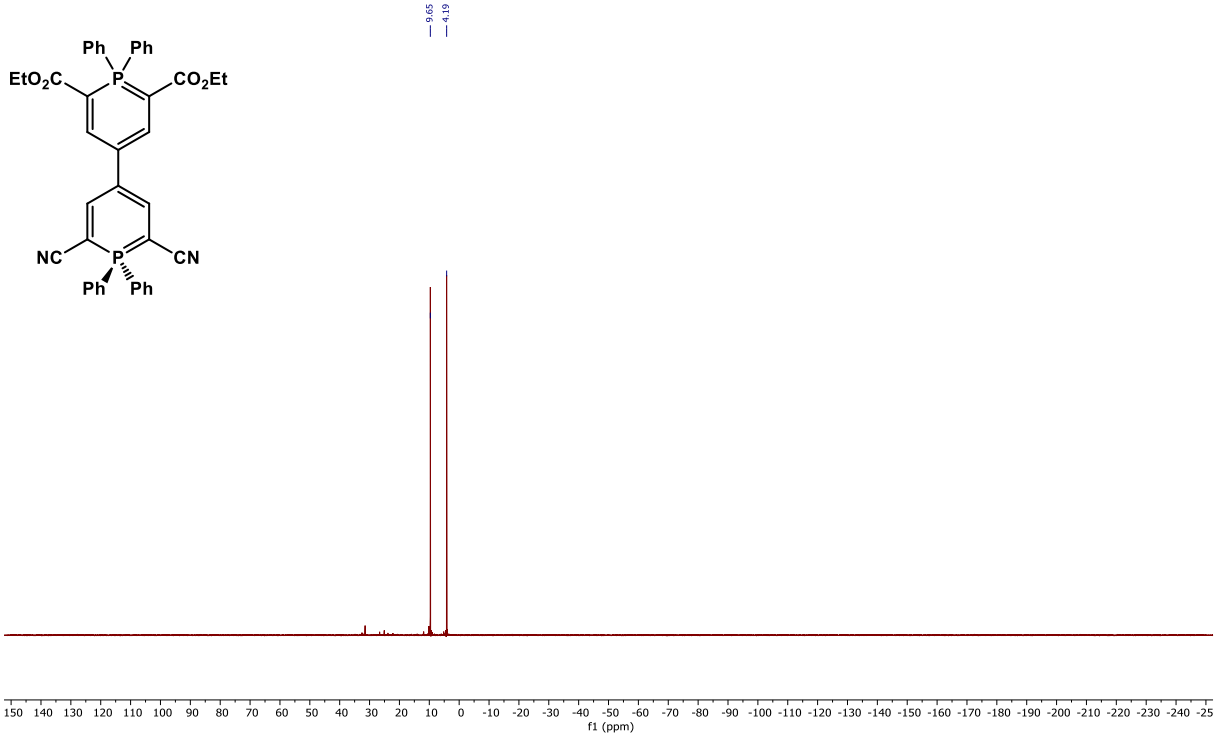
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

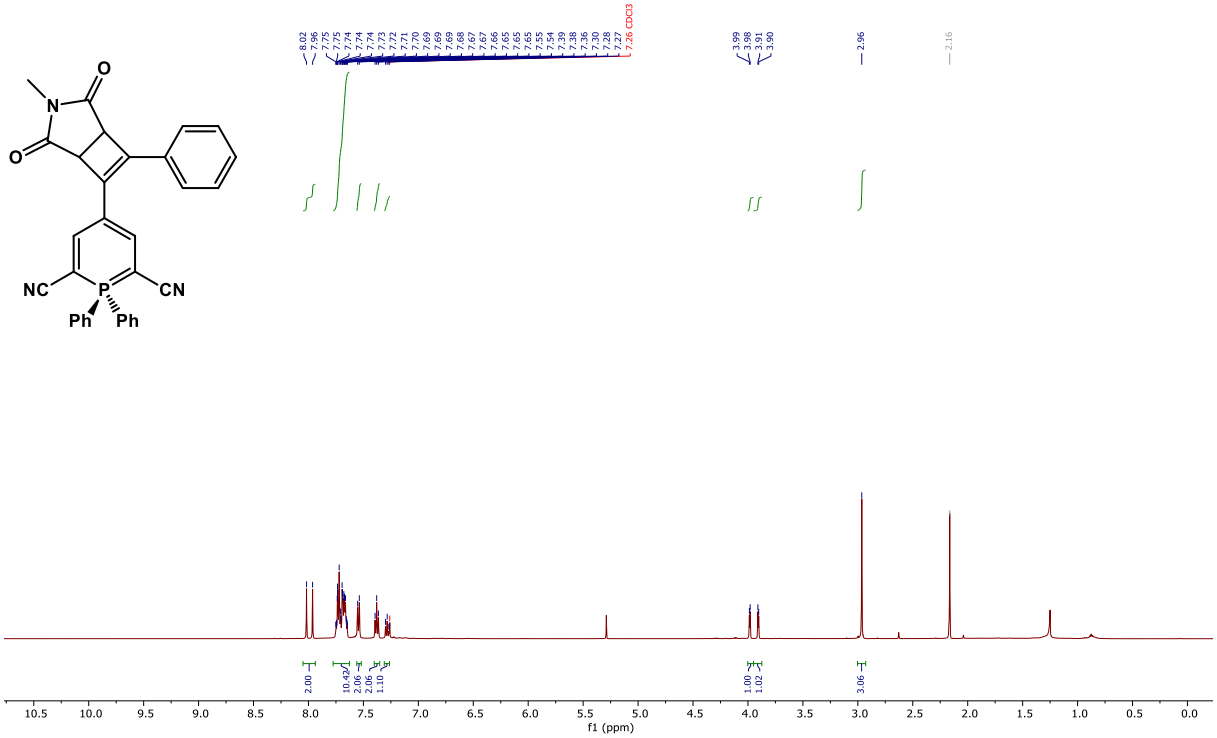


$^{31}$P NMR (202 MHz)

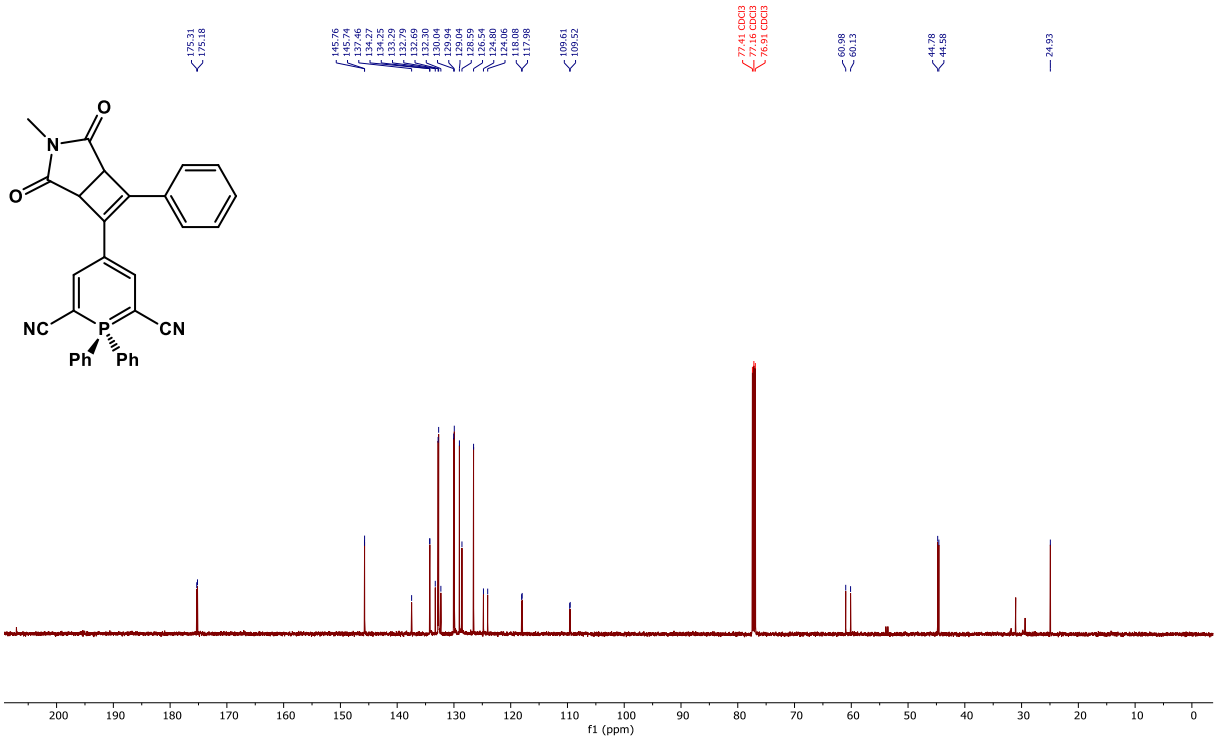


**4-(3-methyl-2,4-dioxo-7-phenyl-3-azabicyclo[3.2.0]hept-6-en-6-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3u)**

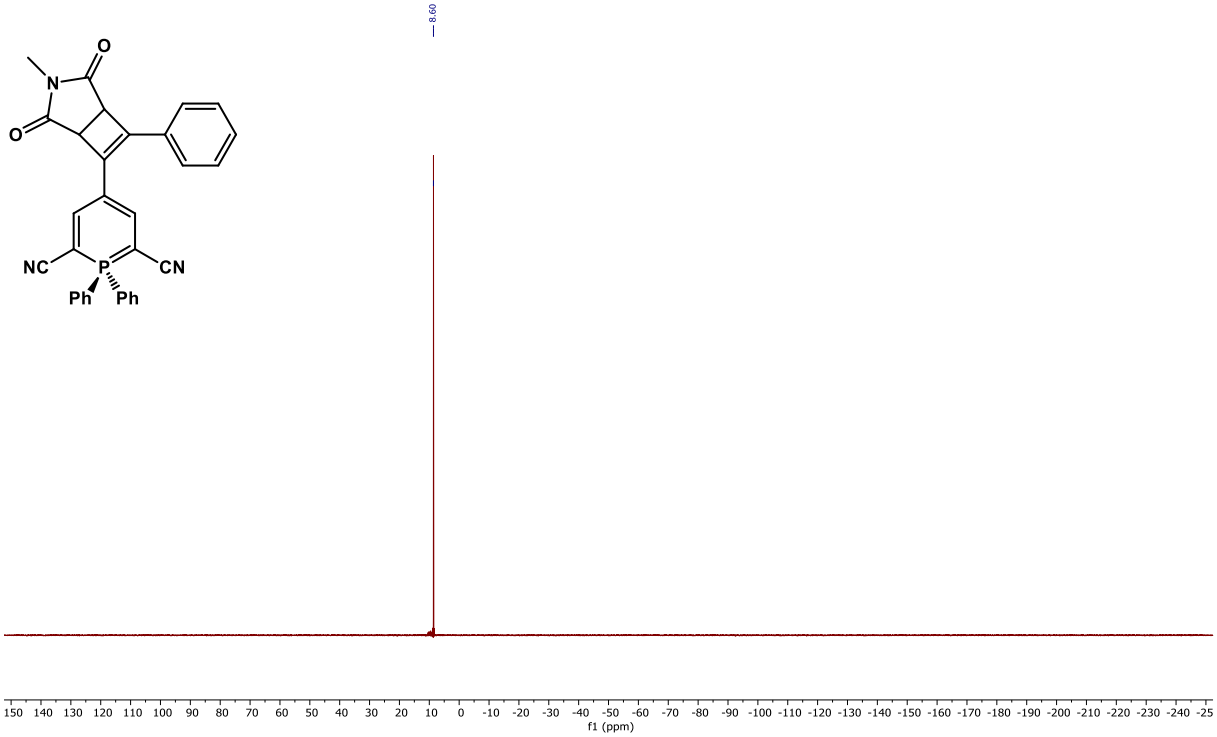
$^1$H NMR (500 MHz)



$^{13}$C NMR (126 MHz)

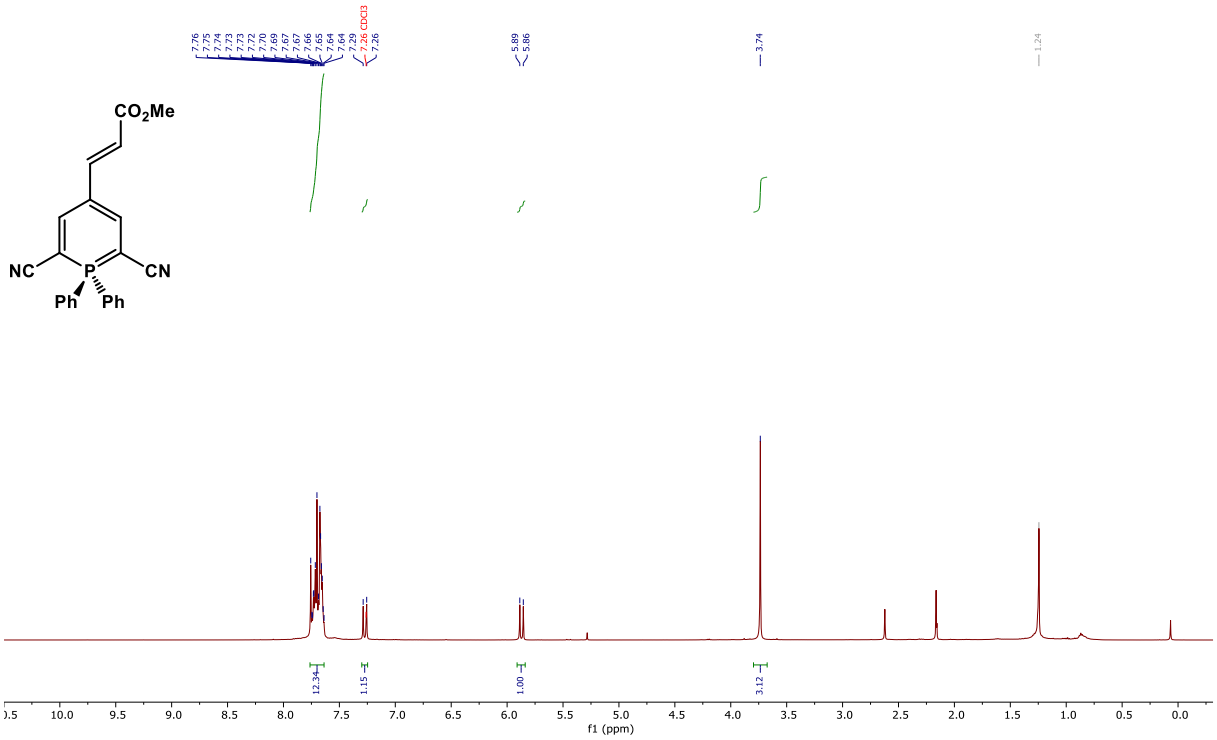


$^{31}$P NMR (202 MHz)

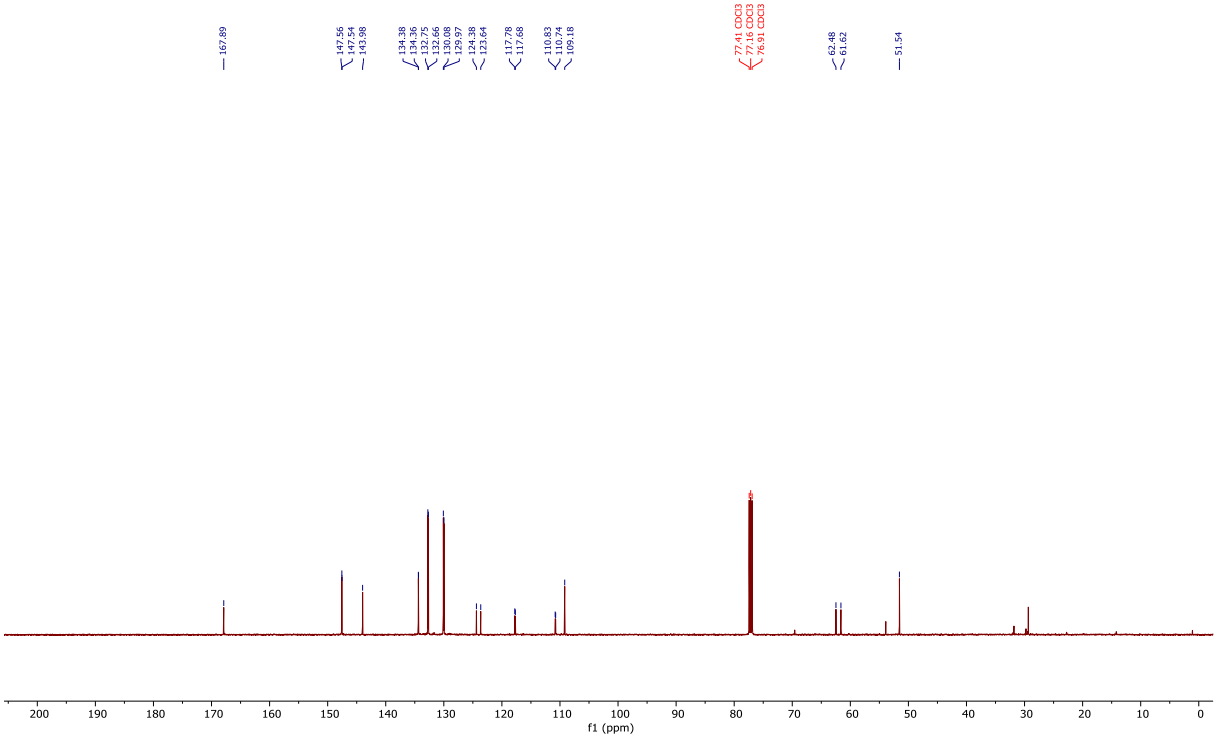


**methyl (*E*)-3-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)acrylate (3v)**

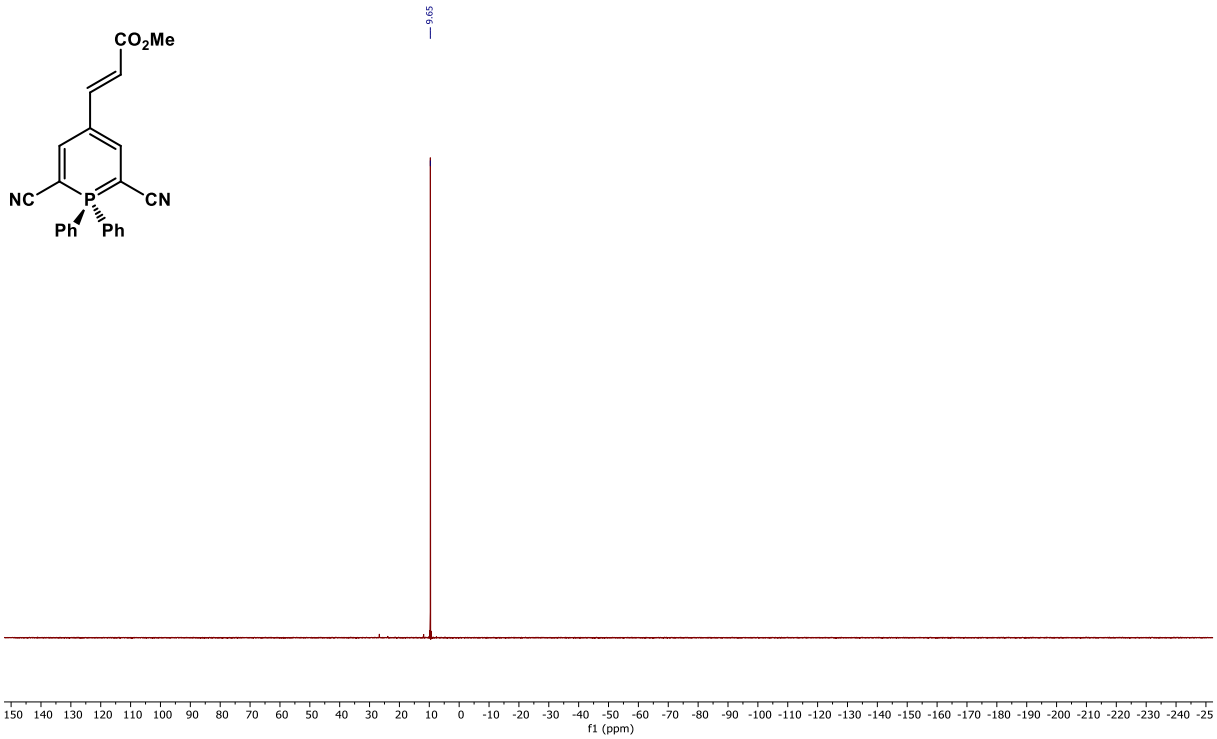
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

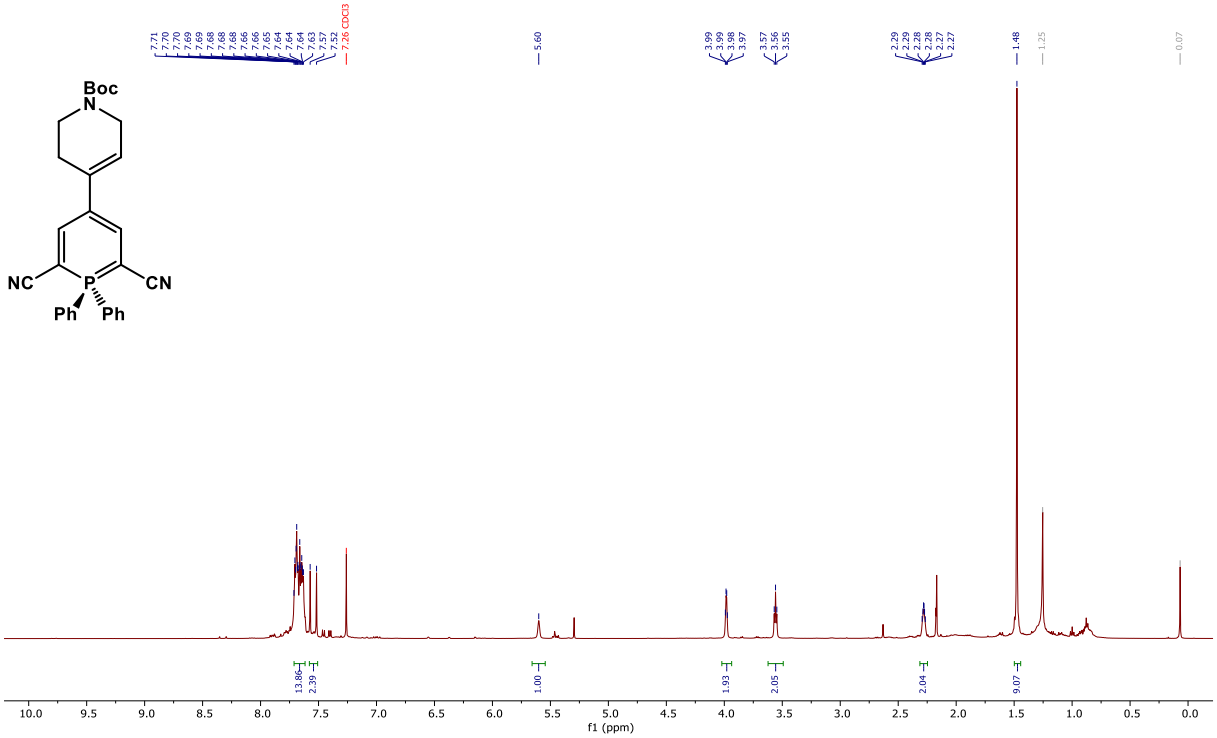


$^{31}$P NMR (202 MHz)

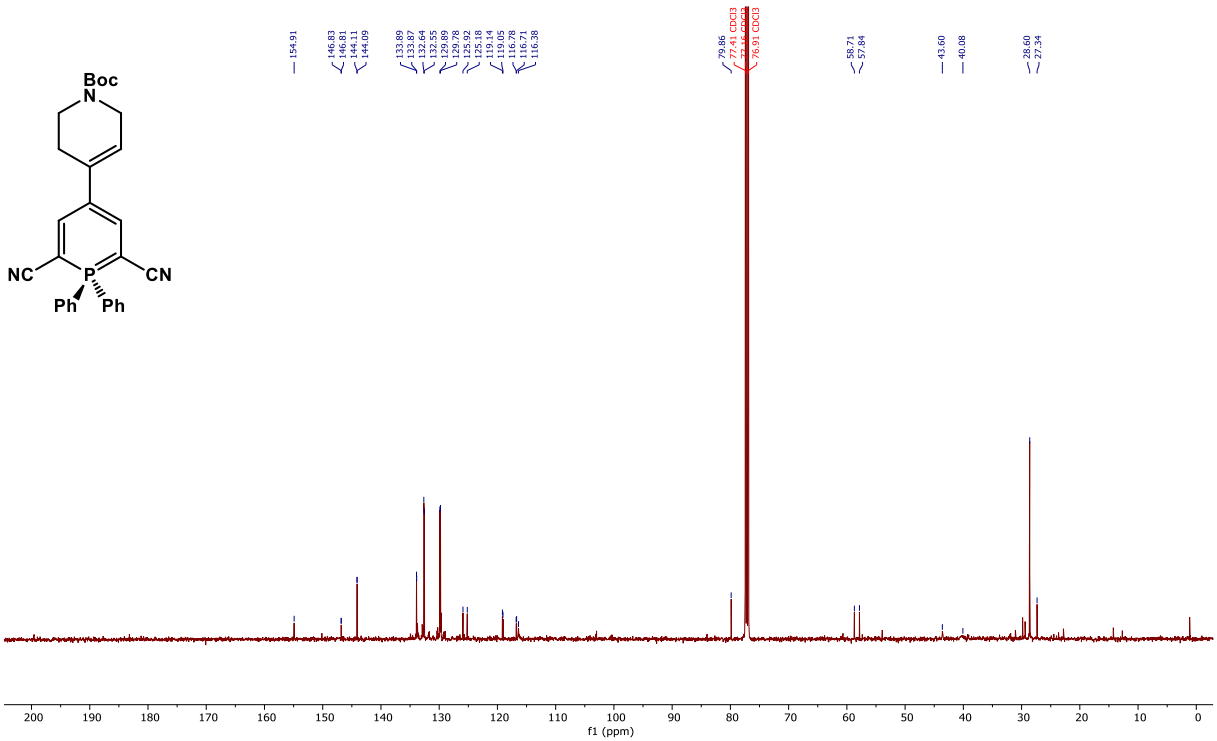


***tert*-butyl 4-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)-3,6-dihydropyridine-1(*2H*)-carboxylate (3w)**

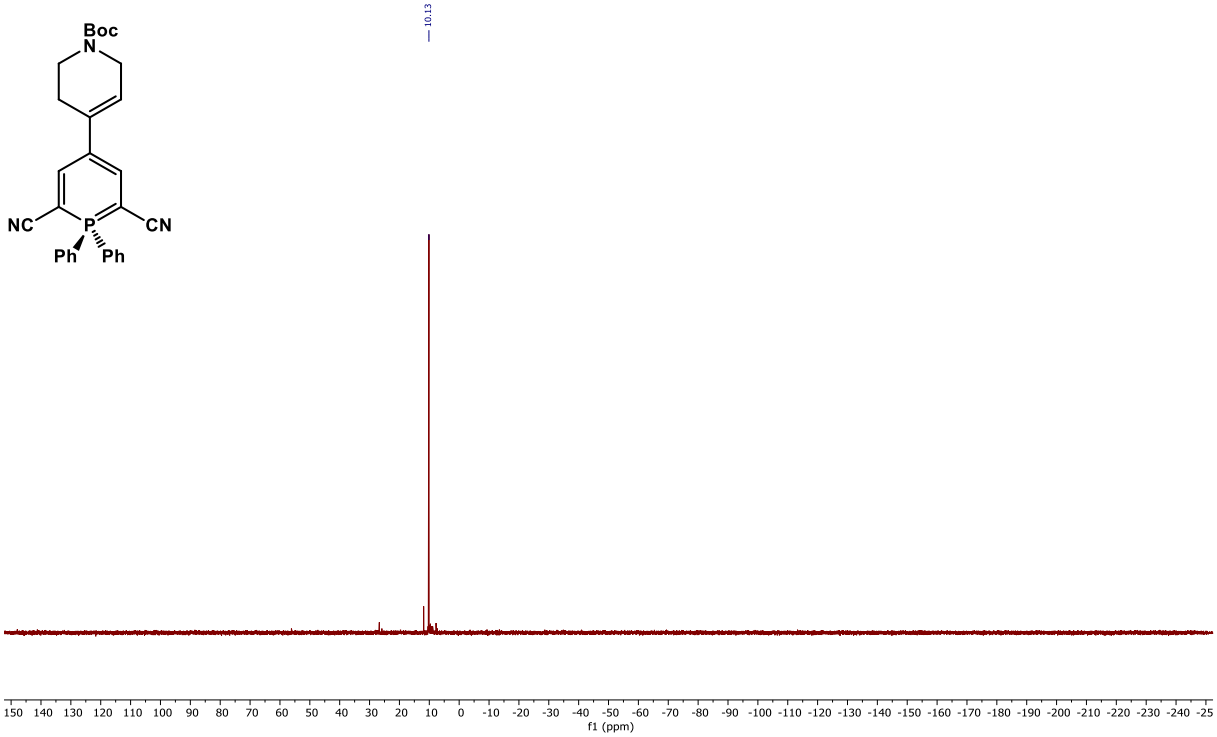
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

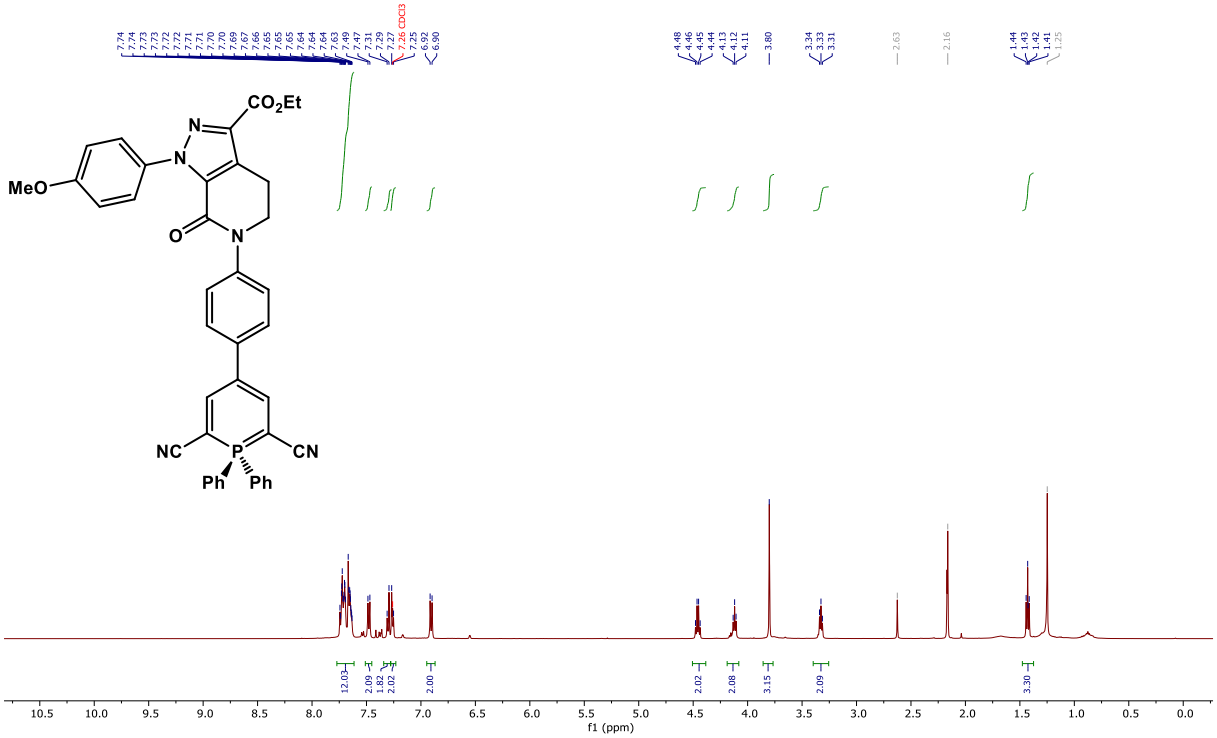


$^{31}$P NMR (202 MHz)

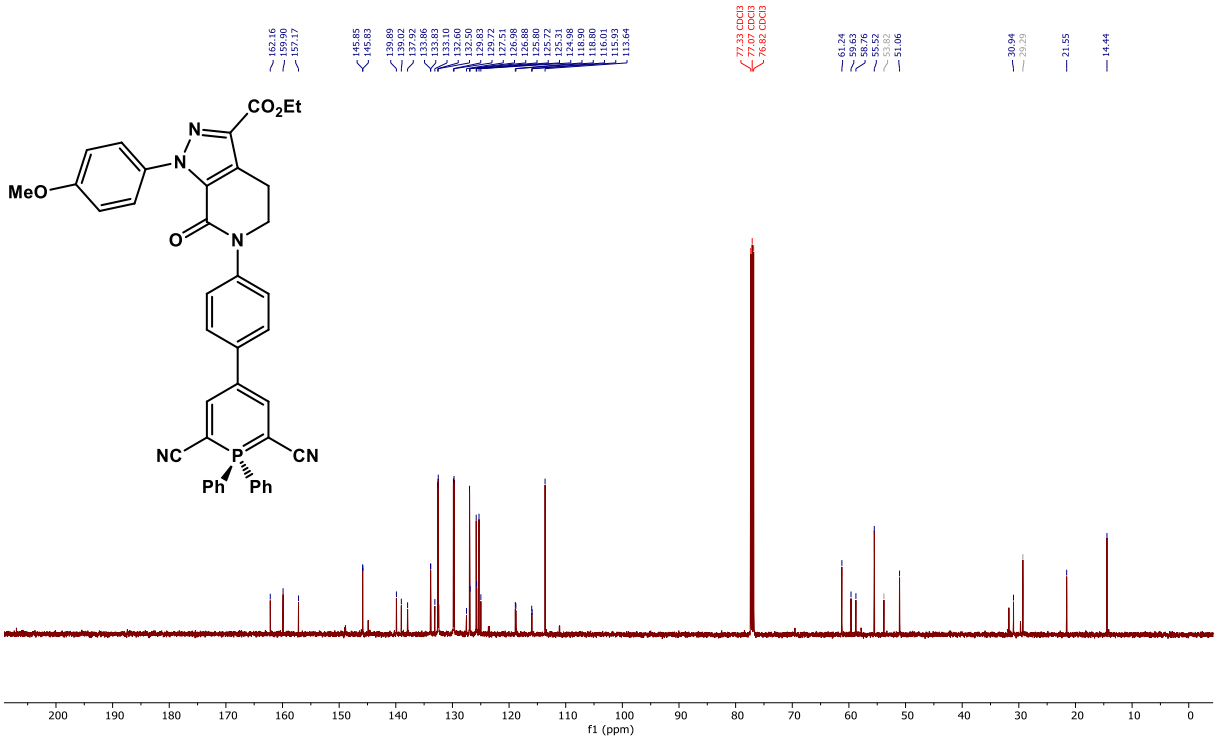


**ethyl 6-(4-(2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinin-4-yl)phenyl)-1-(4-methoxyphenyl)-7-oxo-4,5,6,7-tetrahydro-1*H*-pyrazolo[3,4-*c*]pyridine-3-carboxylate (3x)**

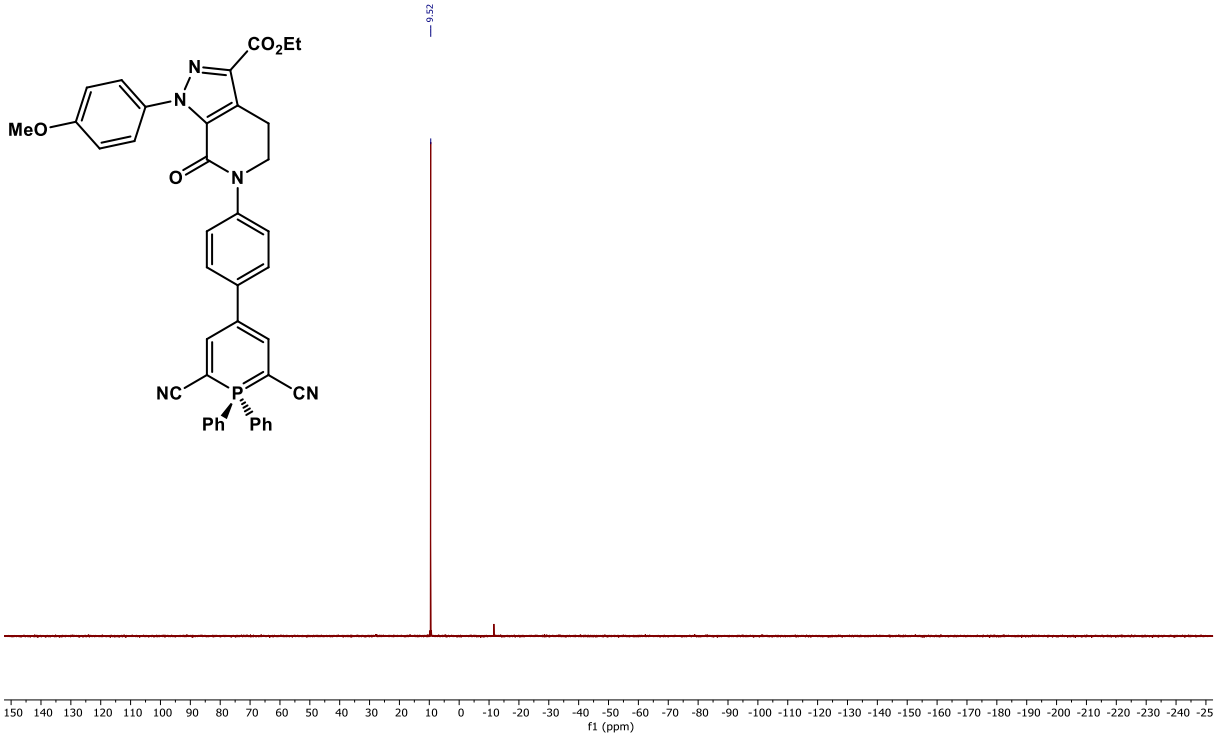
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

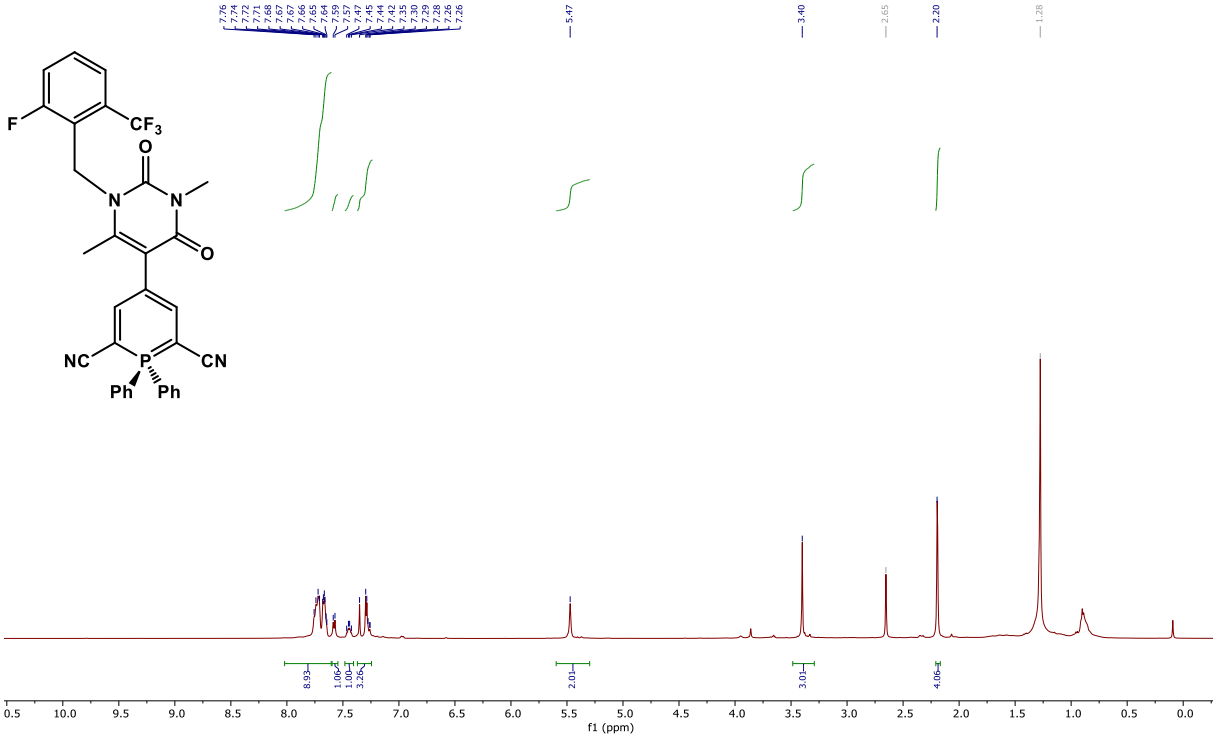


$^{31}$P NMR (202 MHz)

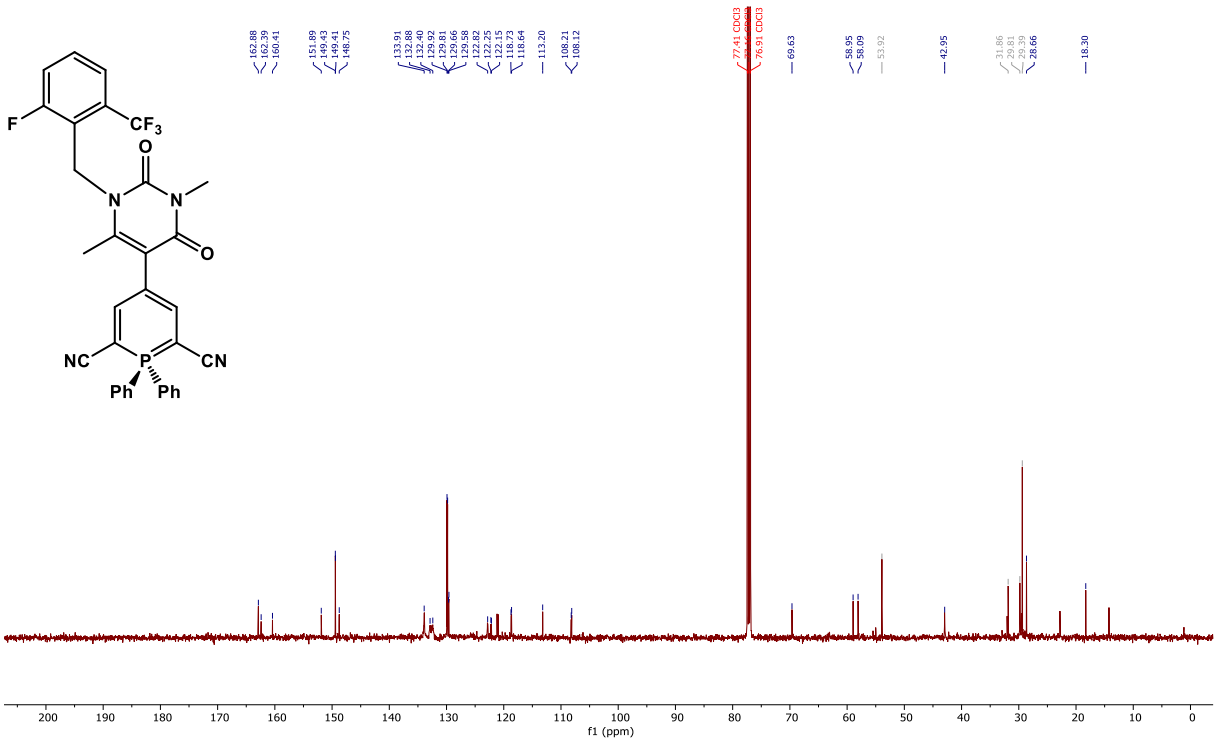


**4-(1-(2-fluoro-6-(trifluoromethyl)benzyl)-3,6-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3y)**

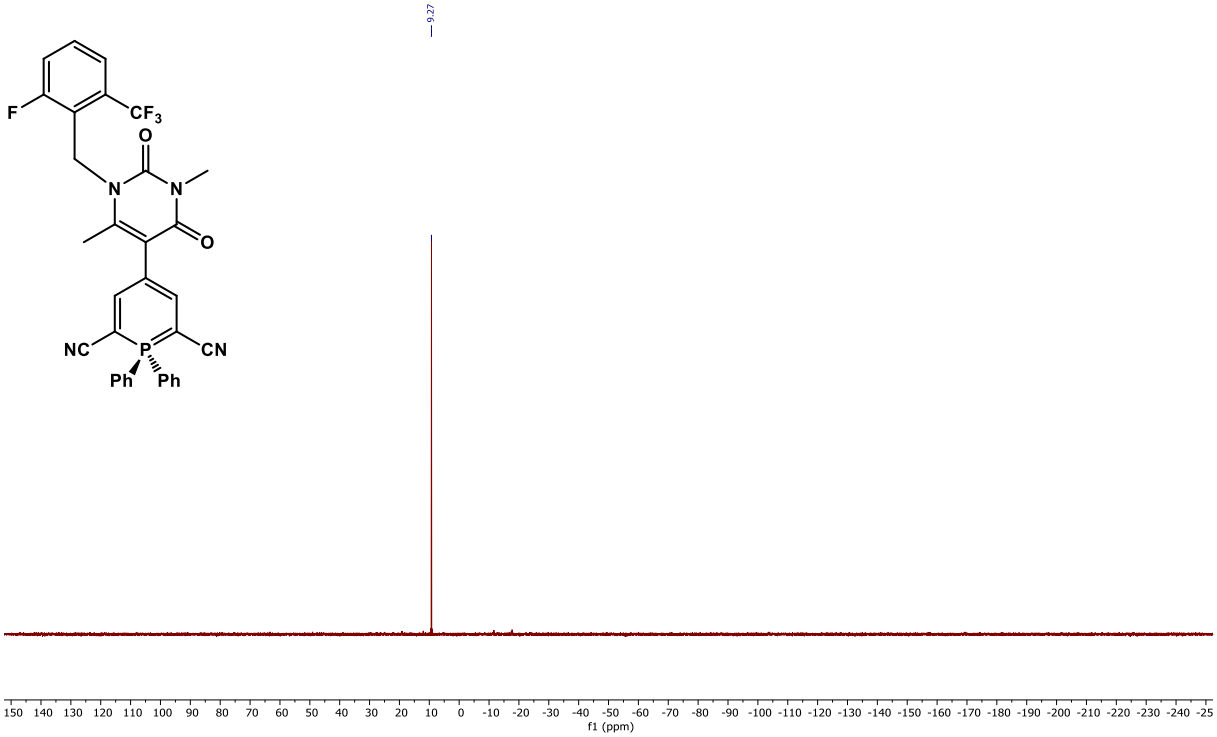
$^1$H NMR (500 MHz)



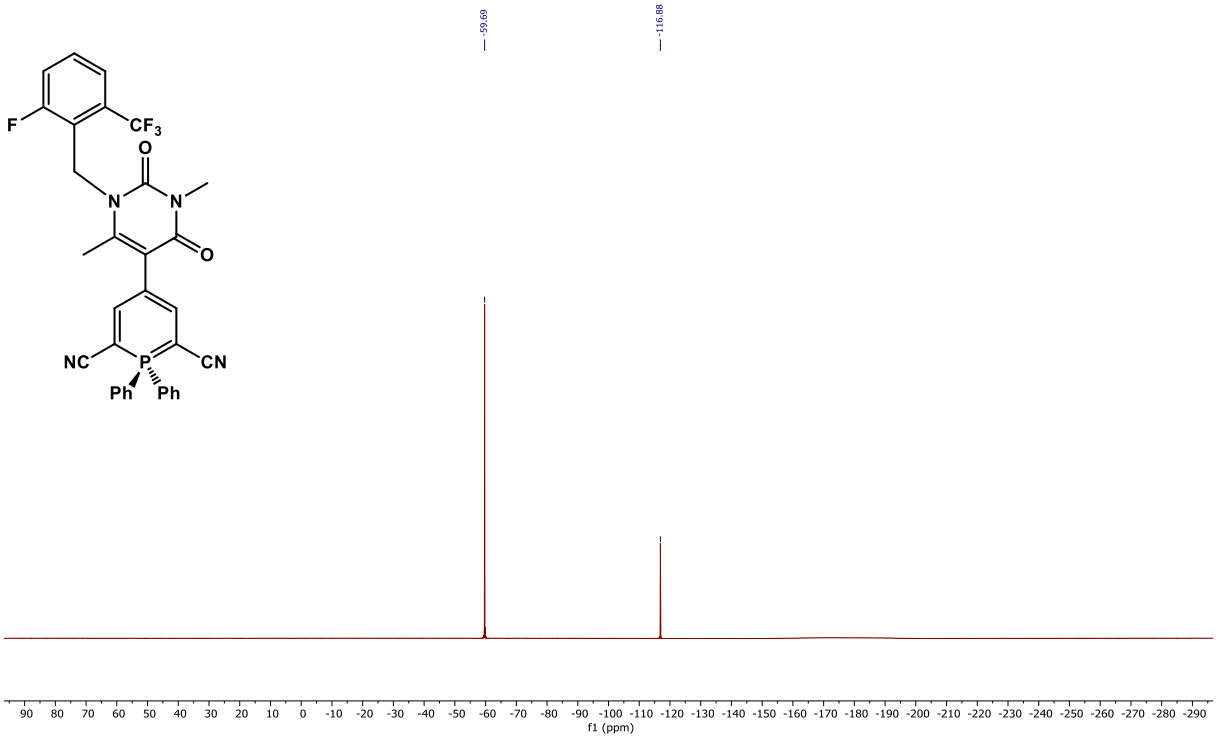

$^{13}$C NMR (126 MHz)



$^{31}$P NMR (202 MHz)

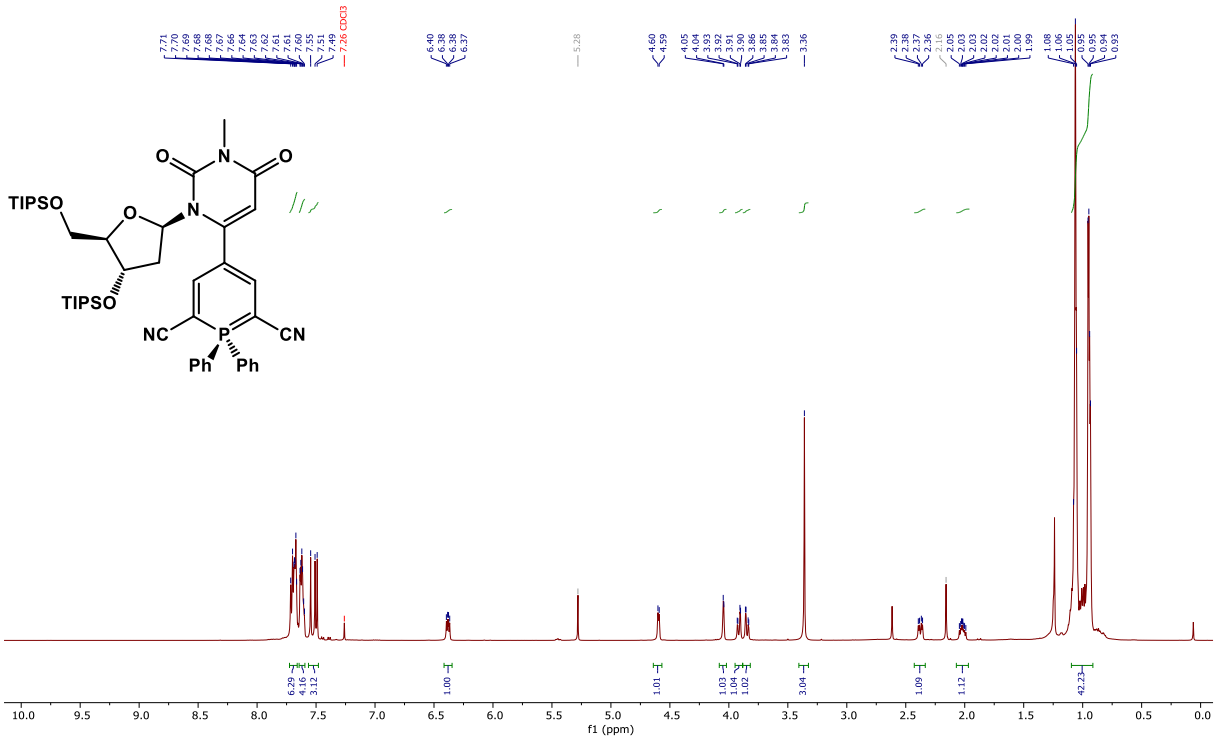



$^{19}$F NMR (471 MHz)

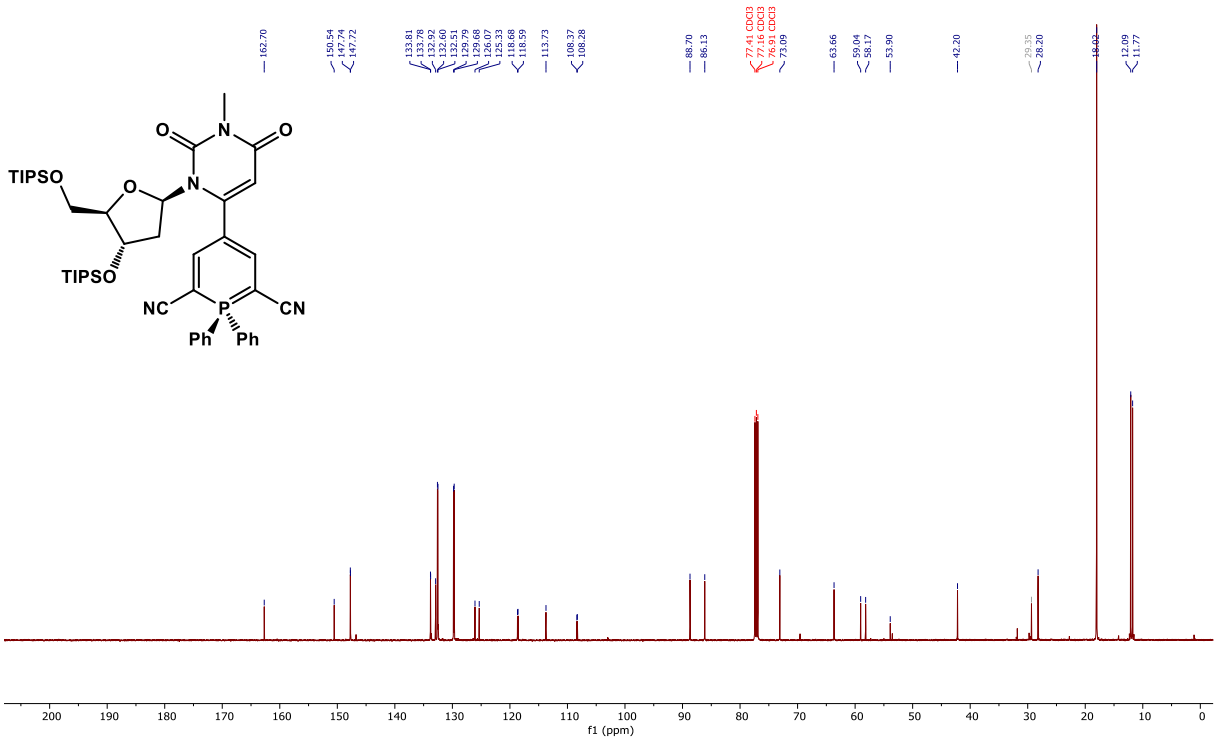


**4-(1-methyl-2,6-dioxo-3-((2*R*,4*S*,5*R*)-4-((triisopropylsilyl)oxy)-5-(((triisopropylsilyl)oxy)methyl)tetrahydrofuran-2-yl)-1,2,3,6-tetrahydropyrimidin-4-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3z)**

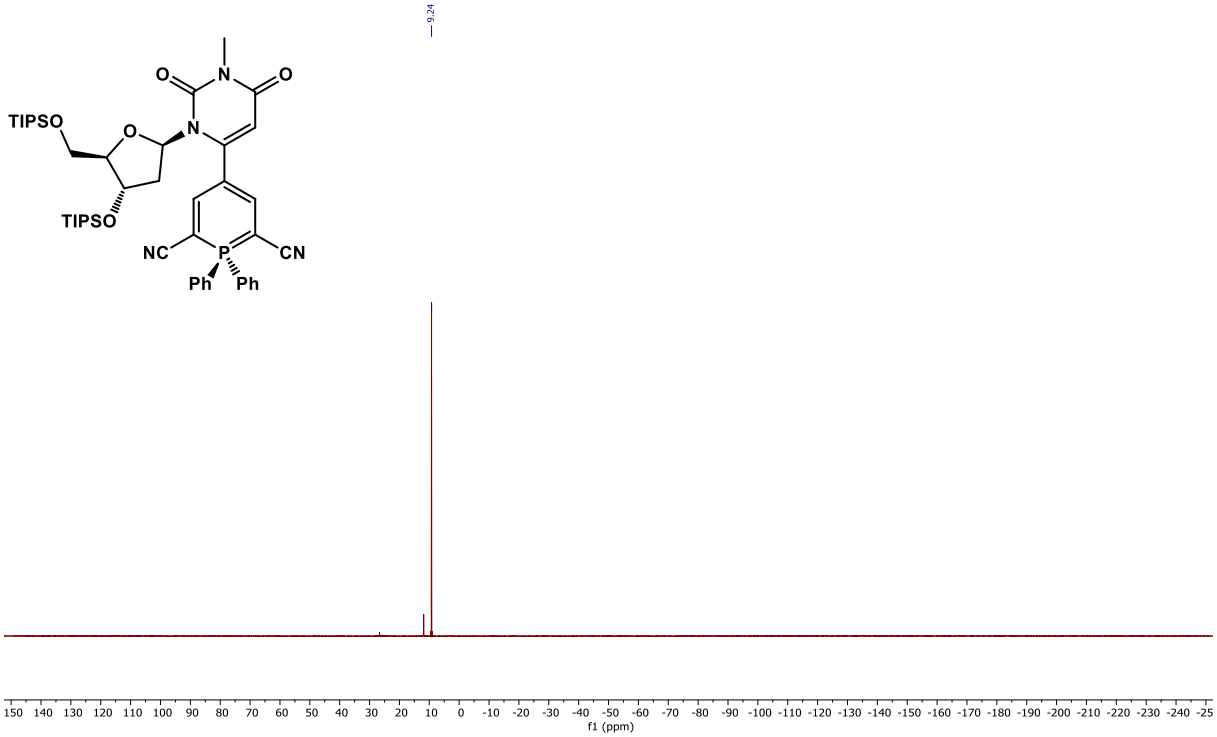
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

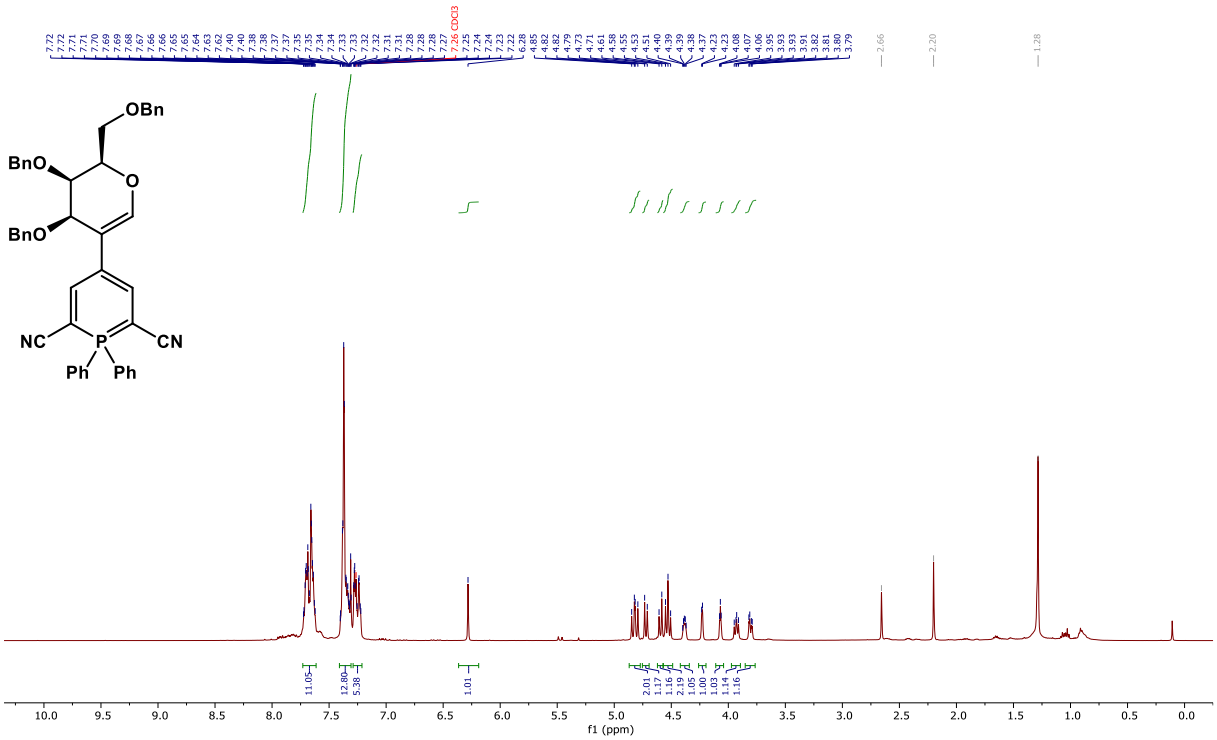


$^{31}$P NMR (202 MHz)

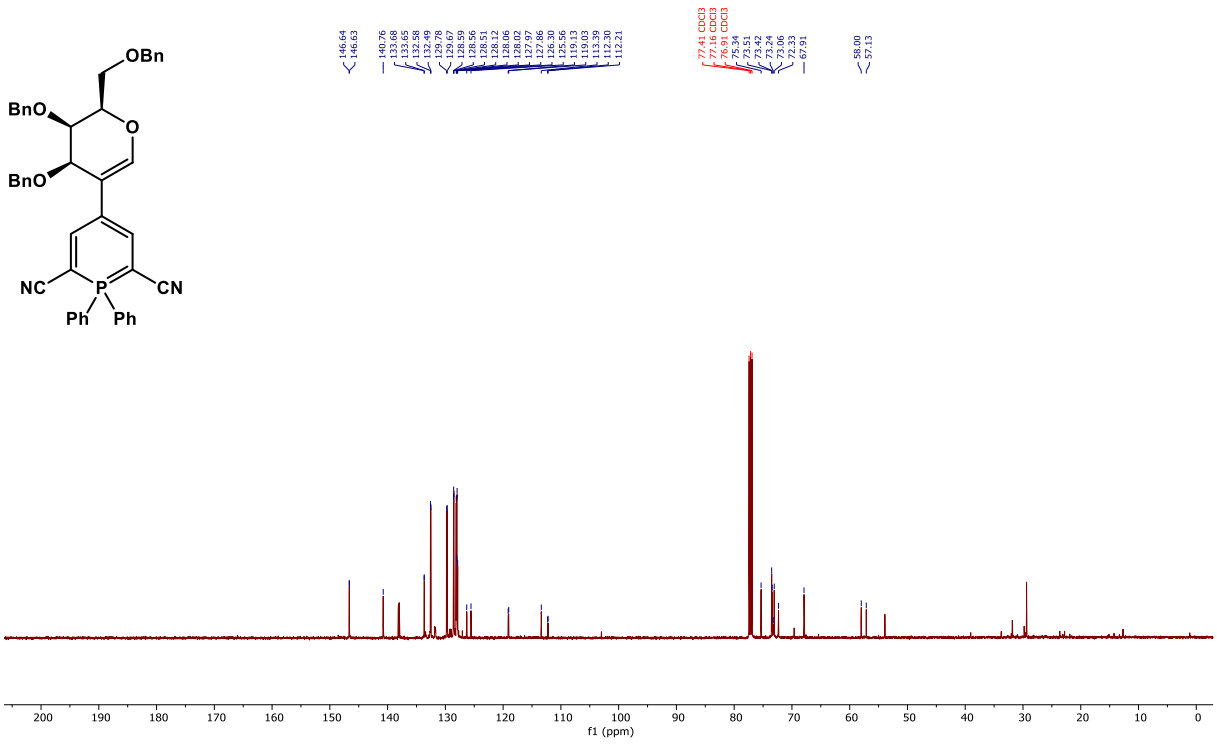


**4-((2*R*,3*R*,4*R*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-3,4-dihydro-2*H*-pyran-5-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (3aa)**

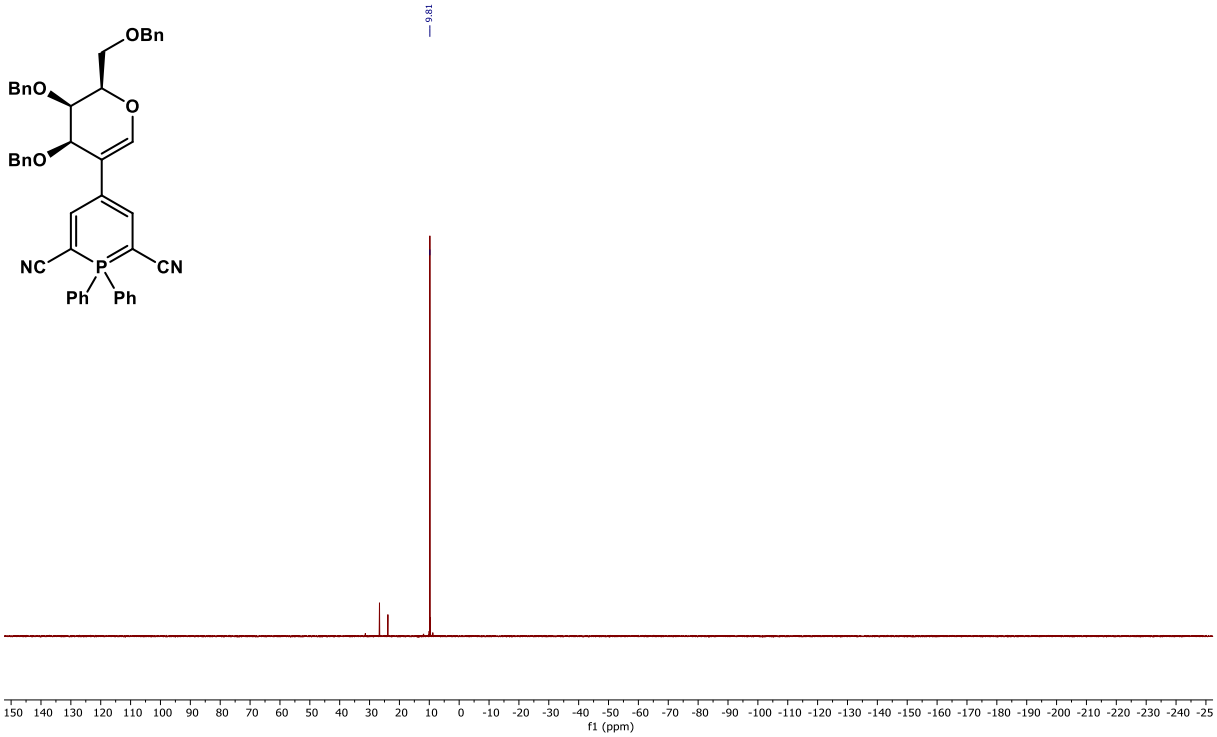
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

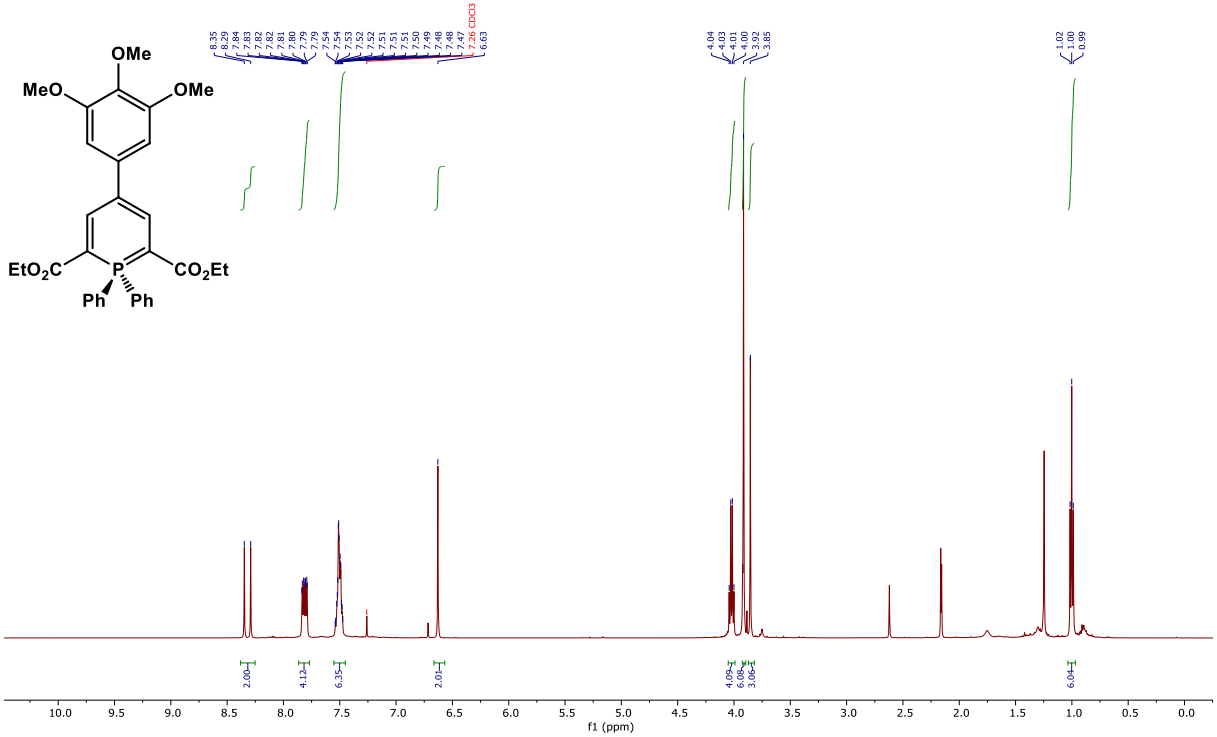


$^{31}$P NMR (202 MHz)

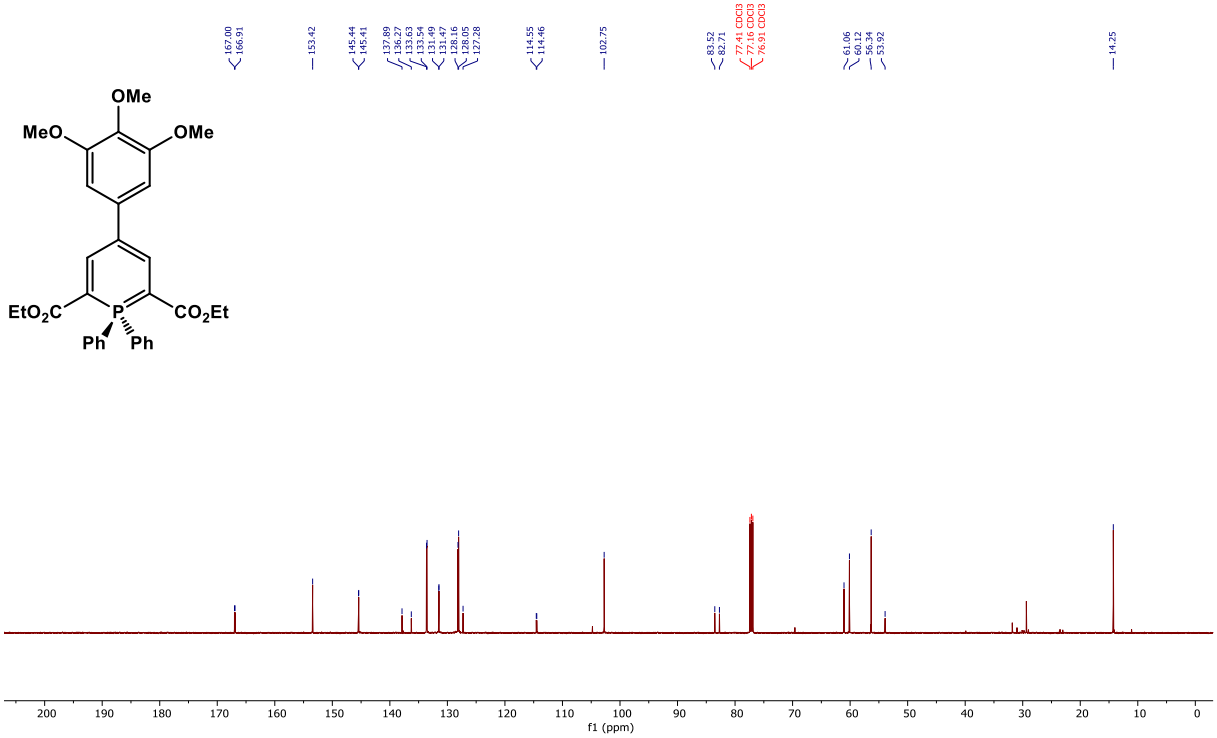


**diethyl 1,1-diphenyl-4-(3,4,5-trimethoxyphenyl)-1λ$^5$-phosphinine-2,6-dicarboxylate (5d)**

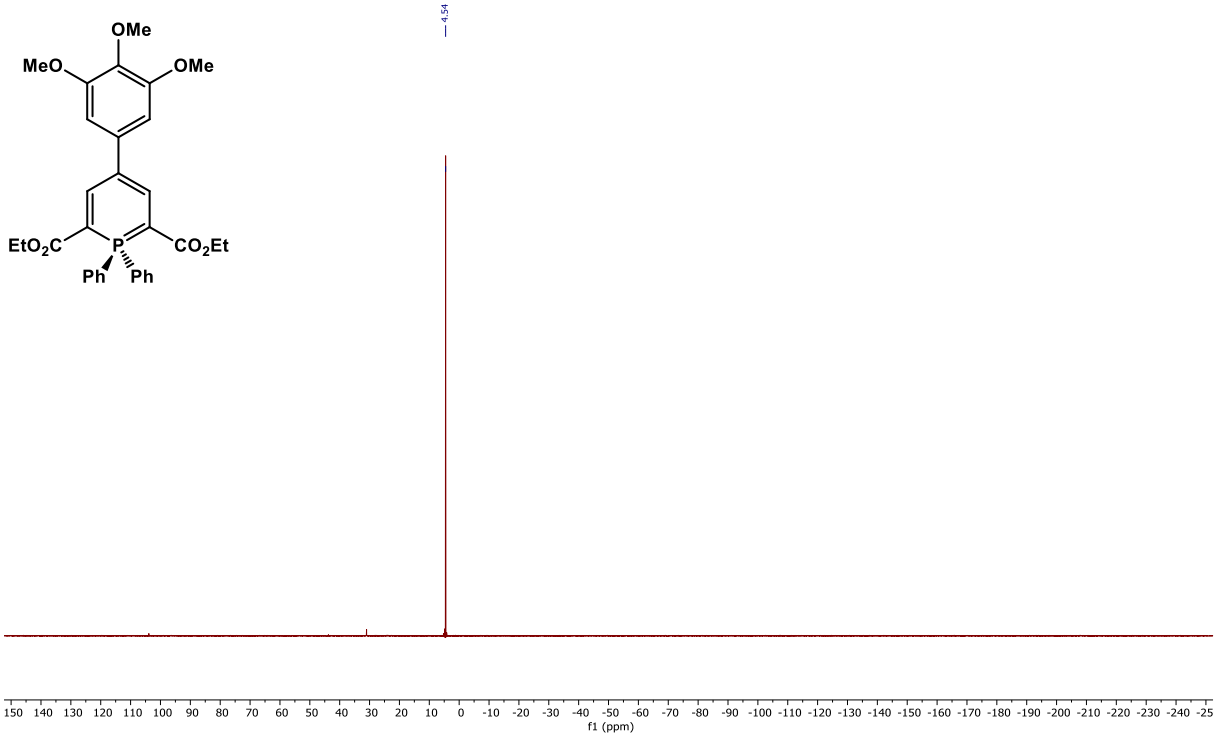
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

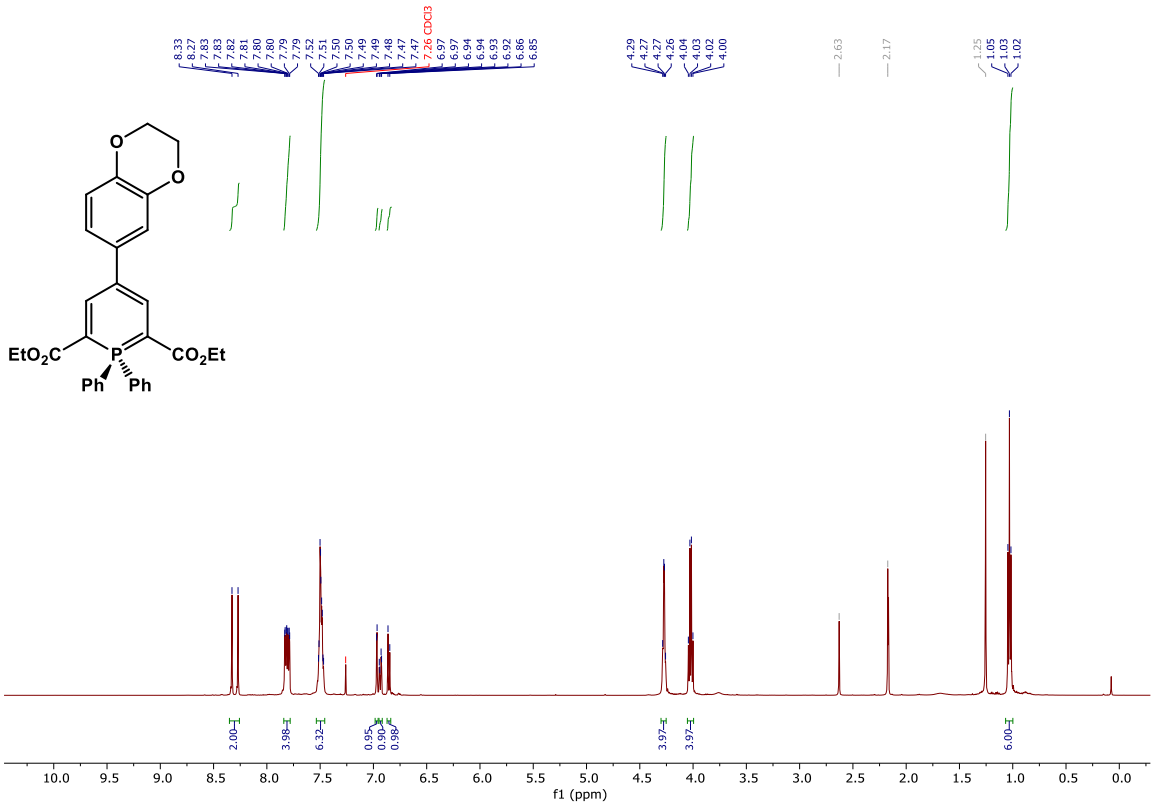


$^{31}$P NMR (202 MHz)

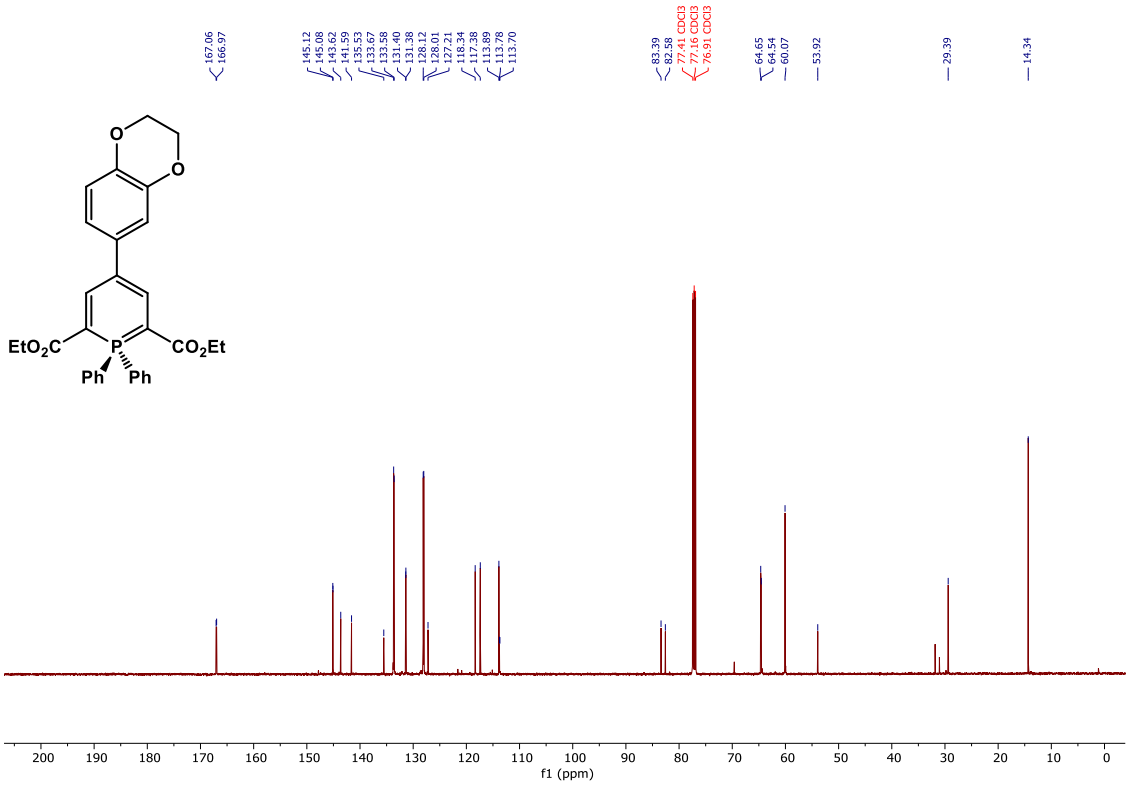


**diethyl 4-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (5e)**

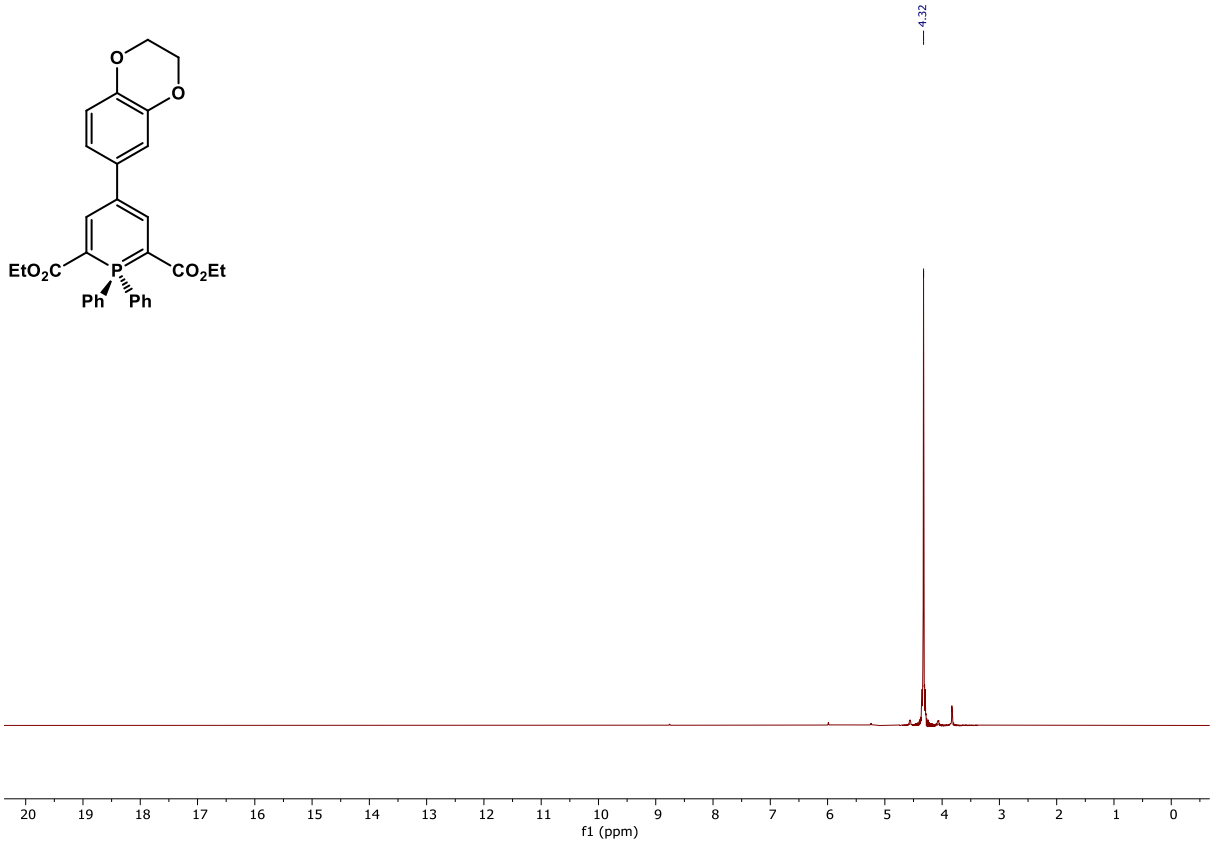
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

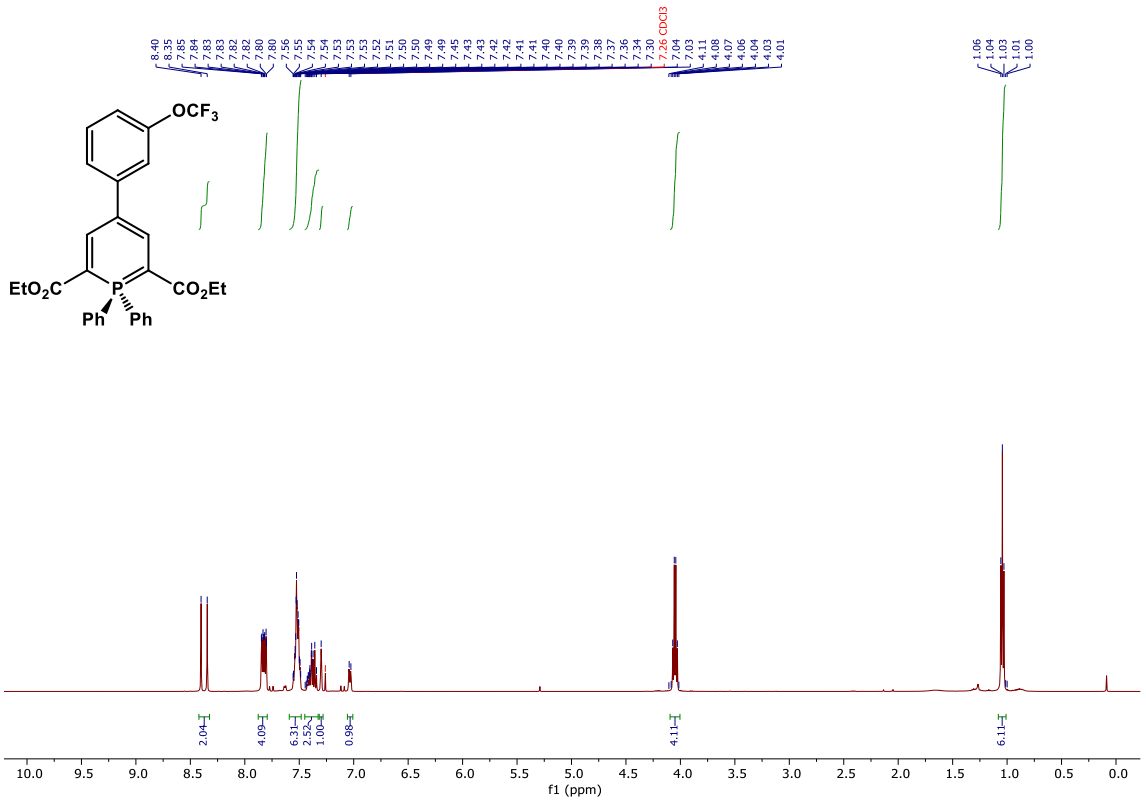


$^{31}$P NMR (202 MHz)

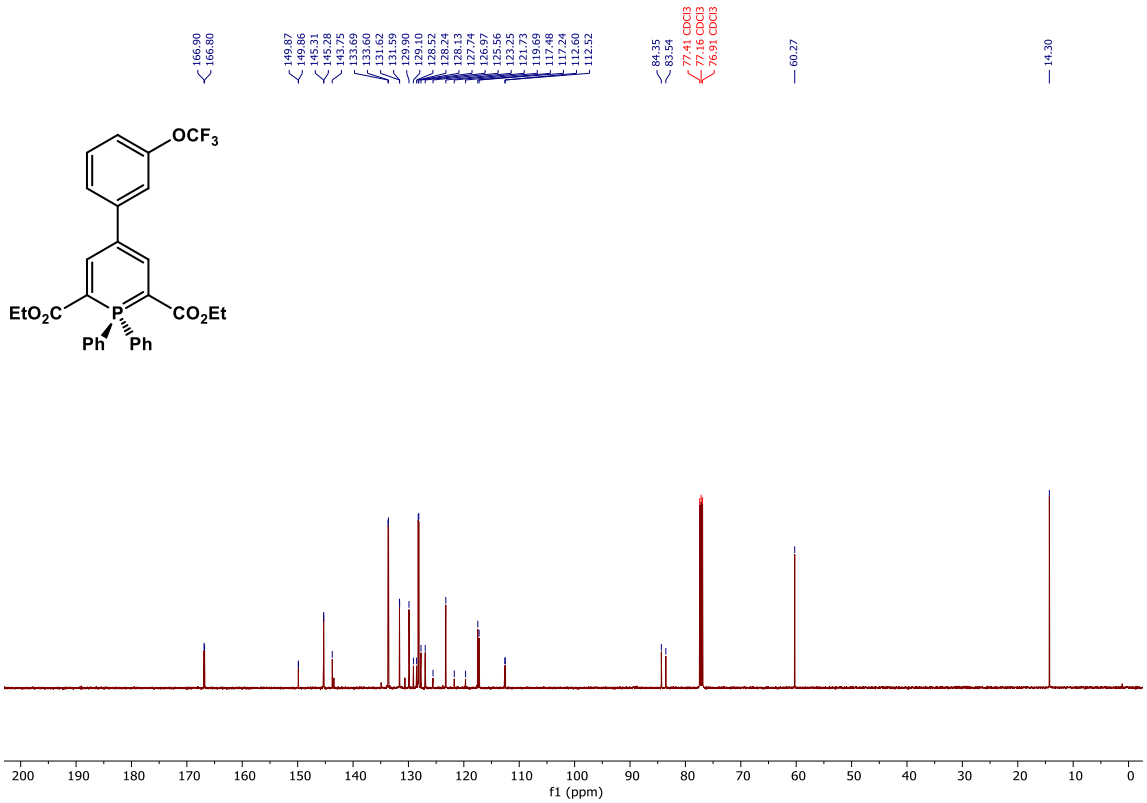


**diethyl 1,1-diphenyl-4-(3-(trifluoromethoxy)phenyl)-1λ$^5$-phosphinine-2,6-dicarboxylate (5f)**

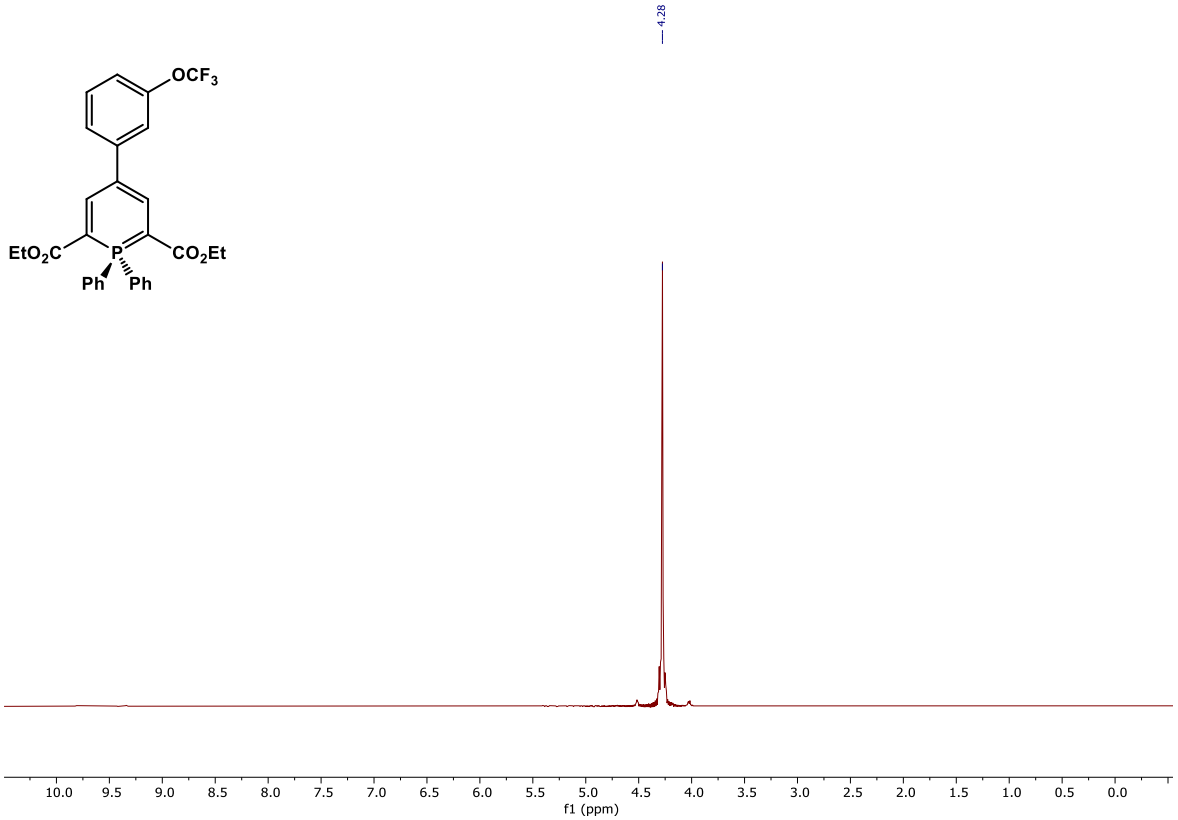
$^1$H NMR (500 MHz)



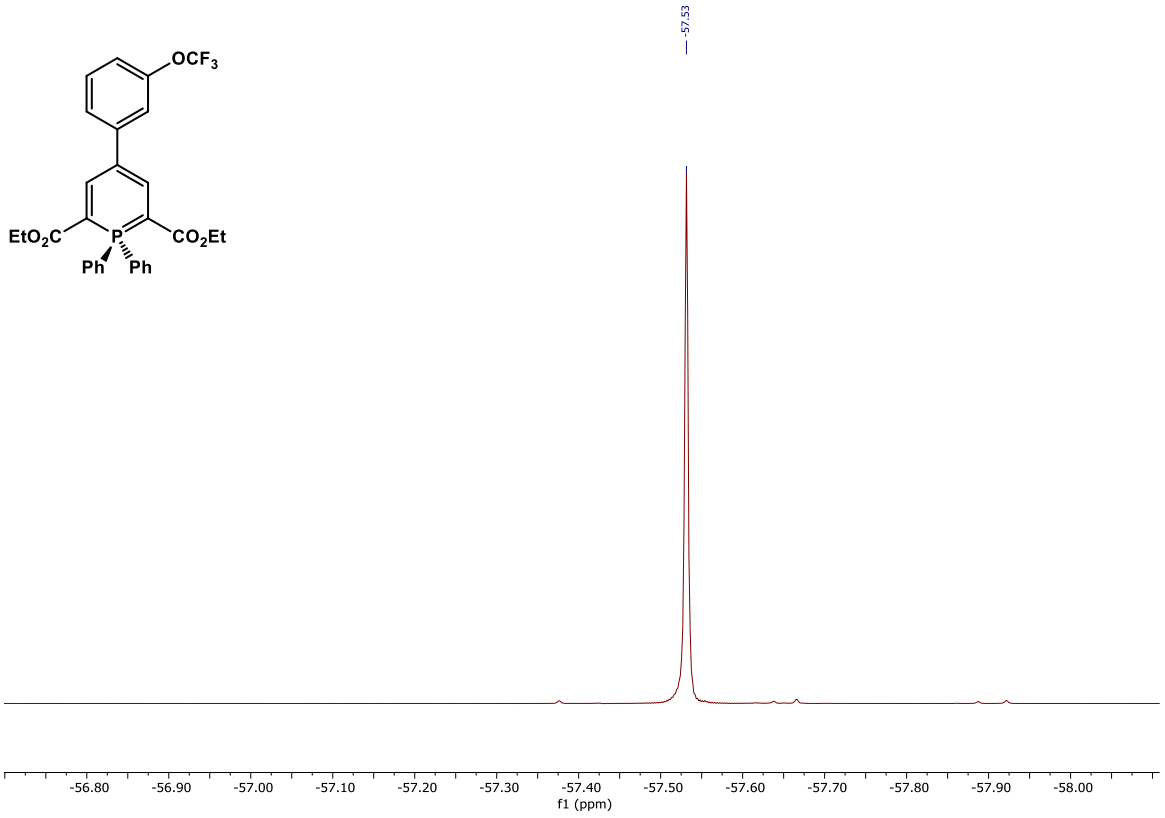

$^{13}$C NMR (126 MHz)



$^{31}$P NMR (202 MHz)

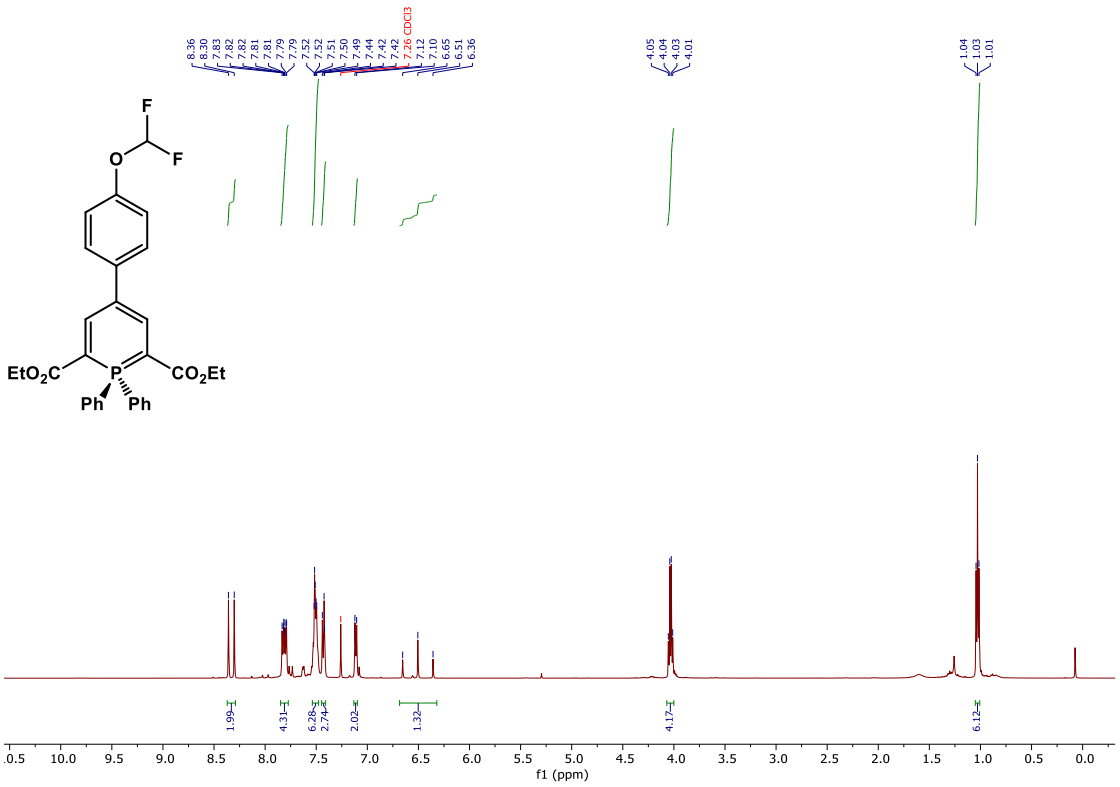



$^{19}$F NMR (471 MHz)

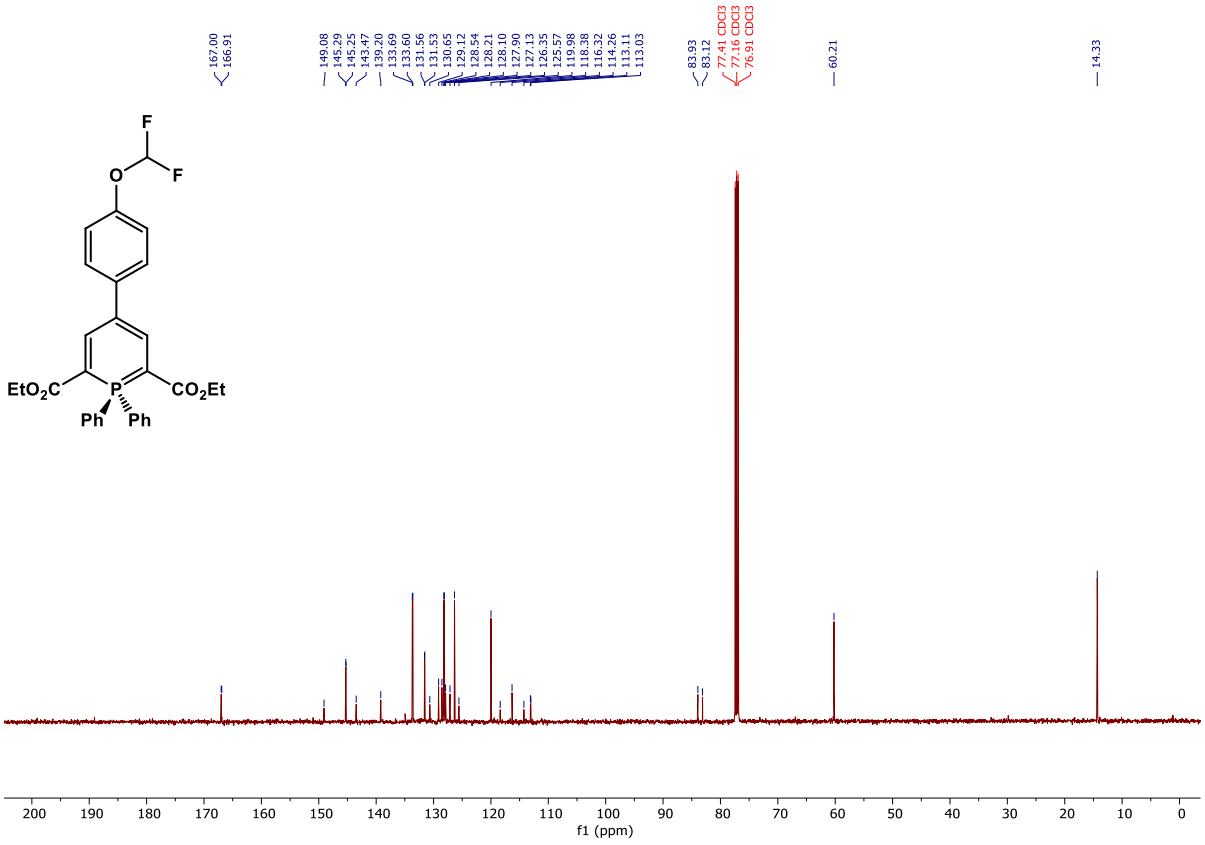


**diethyl 4-(4-(difluoromethoxy)phenyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (5g)**

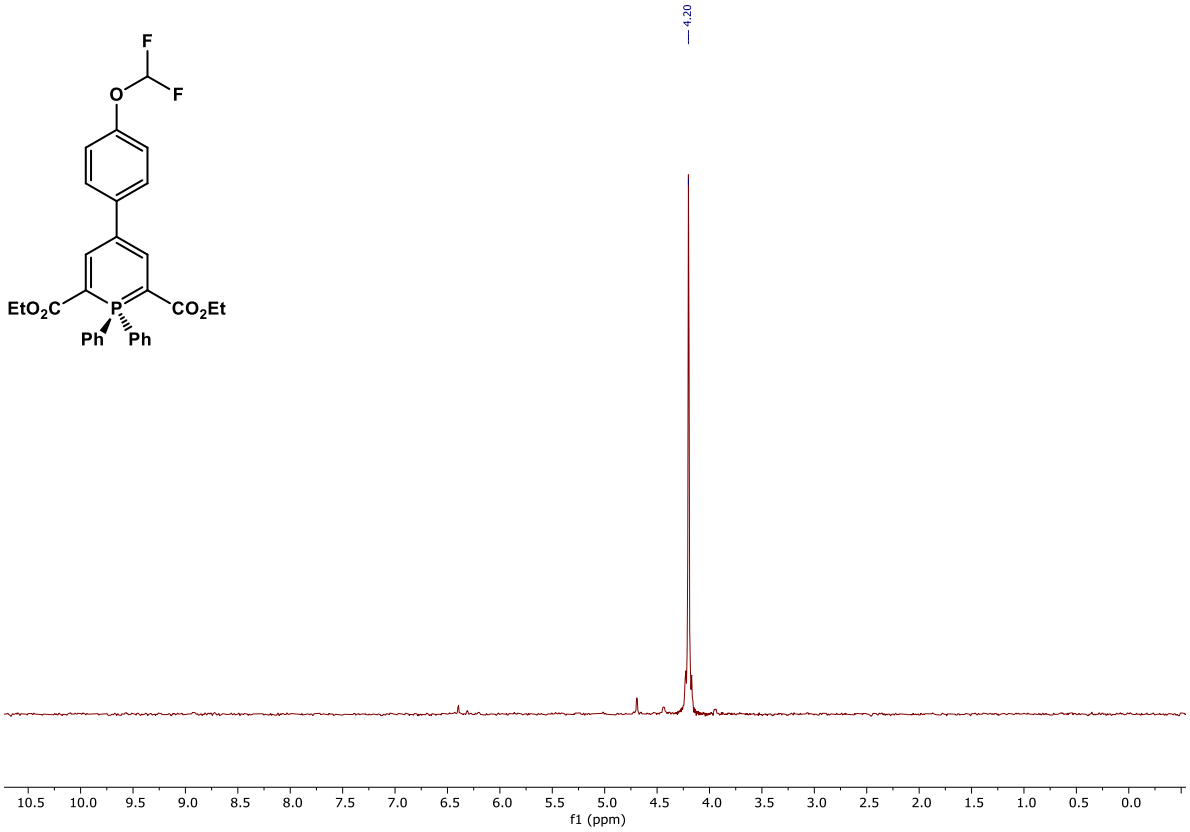
$^1$H NMR (500 MHz)



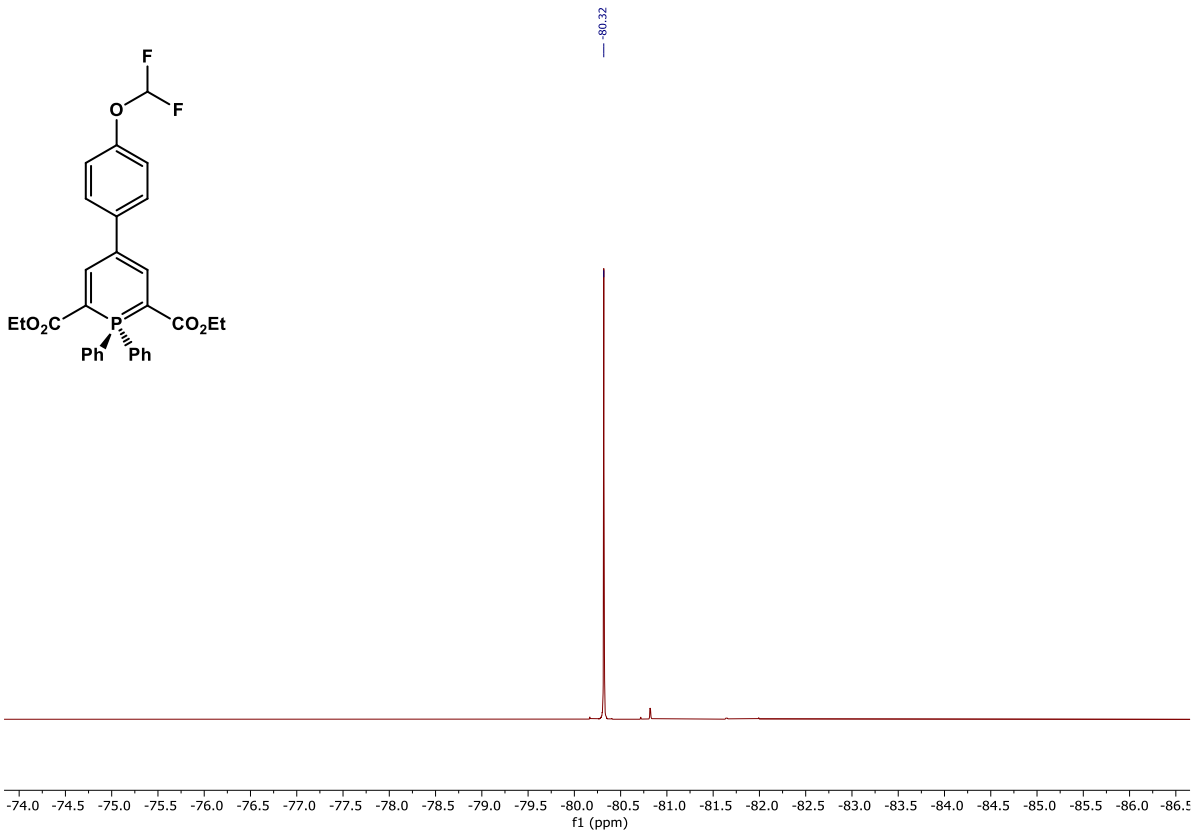

$^{13}$C NMR (126 MHz)



$^{31}$P NMR (202 MHz)

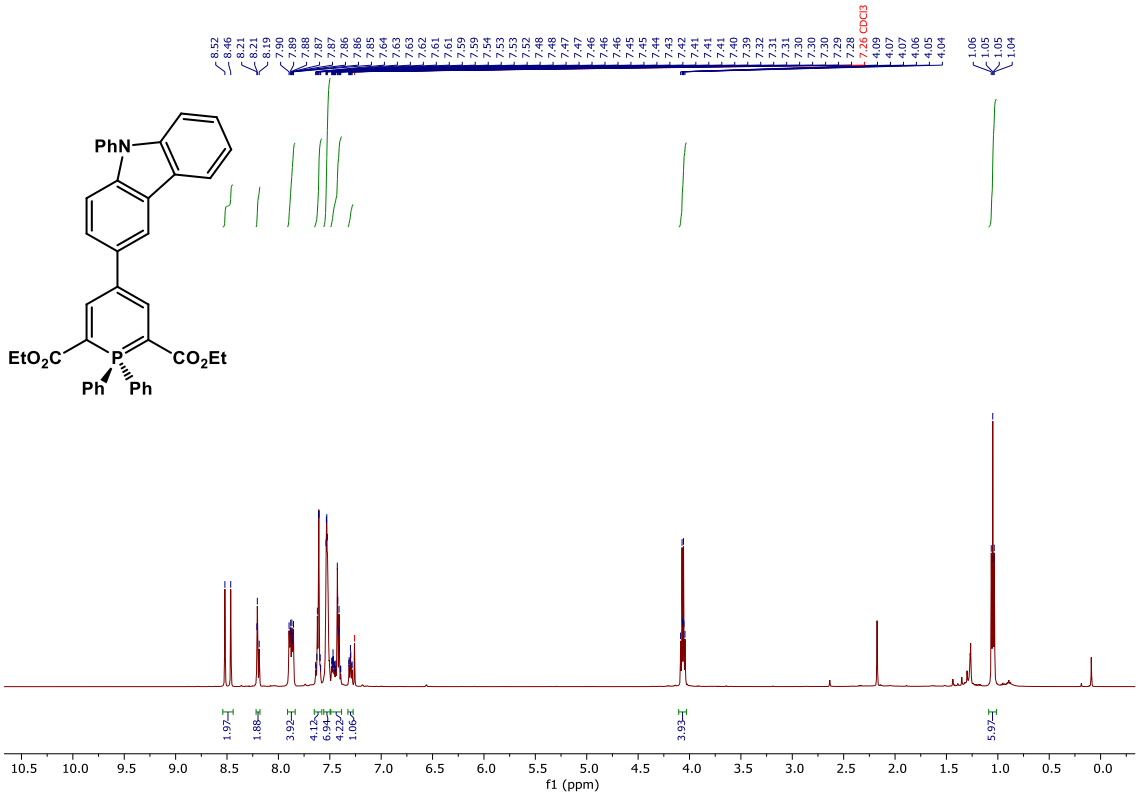



$^{19}$F NMR (471 MHz)

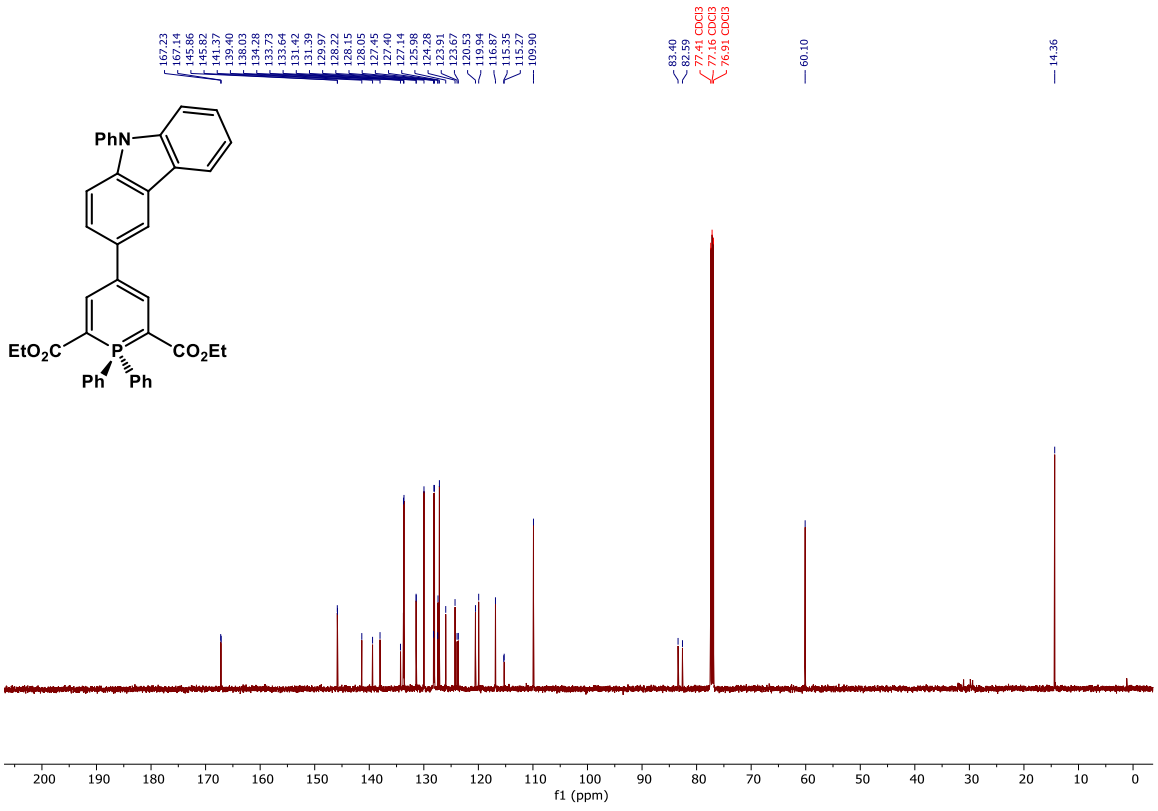


**diethyl 1,1-diphenyl-4-(9-phenyl-9H-carbazol-3-yl)-1λ$^5$-phosphinine-2,6-dicarboxylate (5h)**

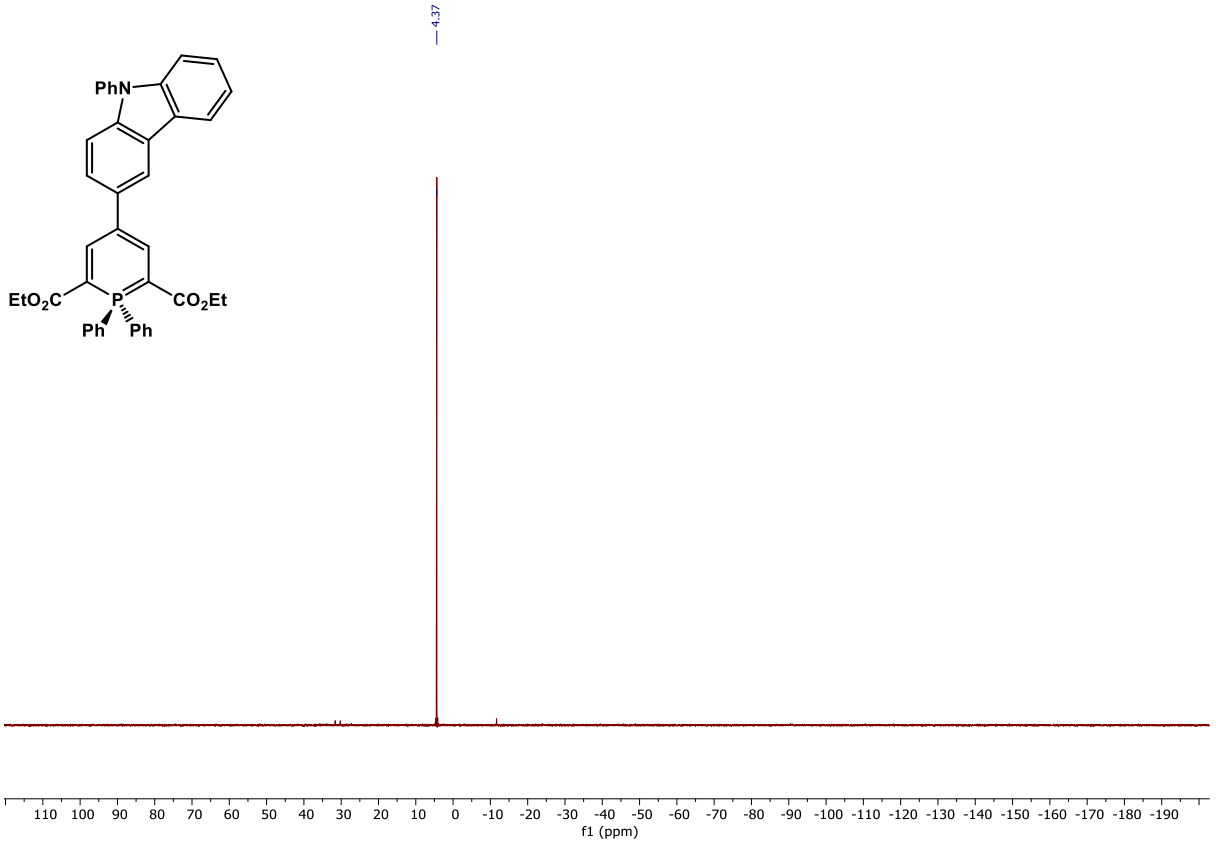
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

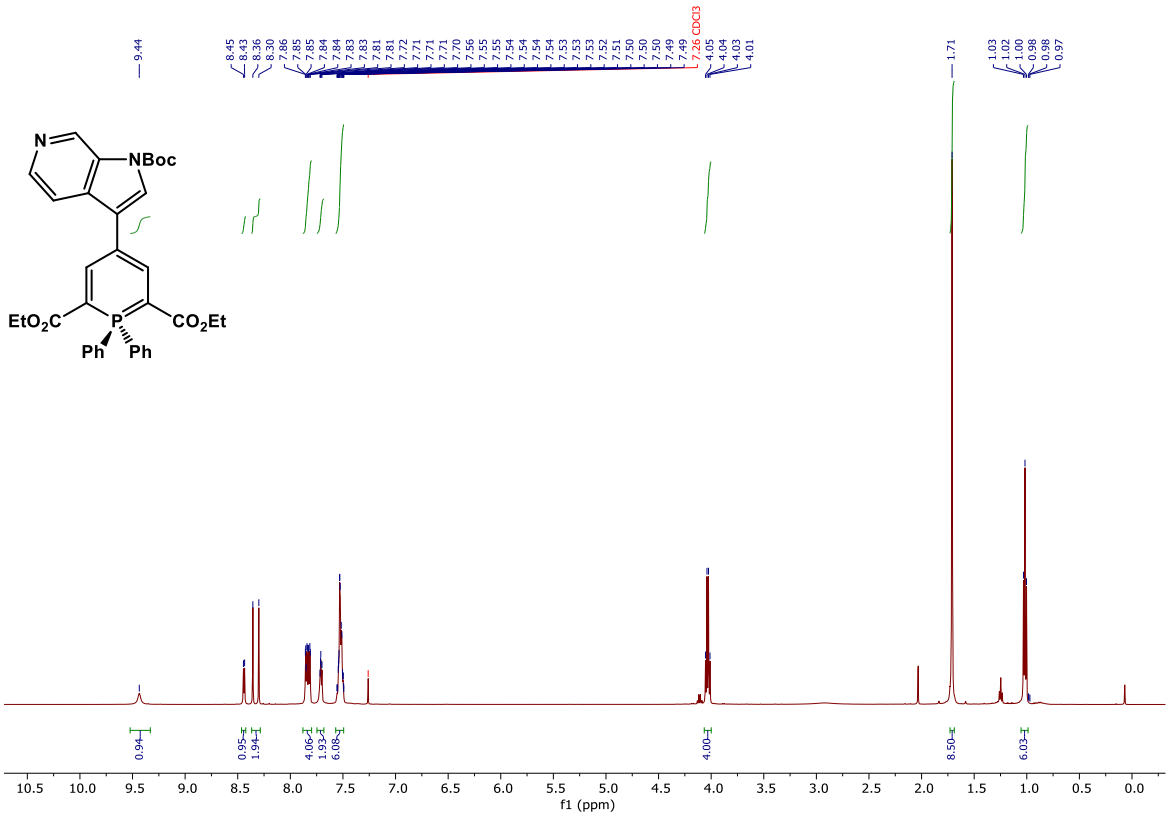


$^{31}$P NMR (202 MHz)

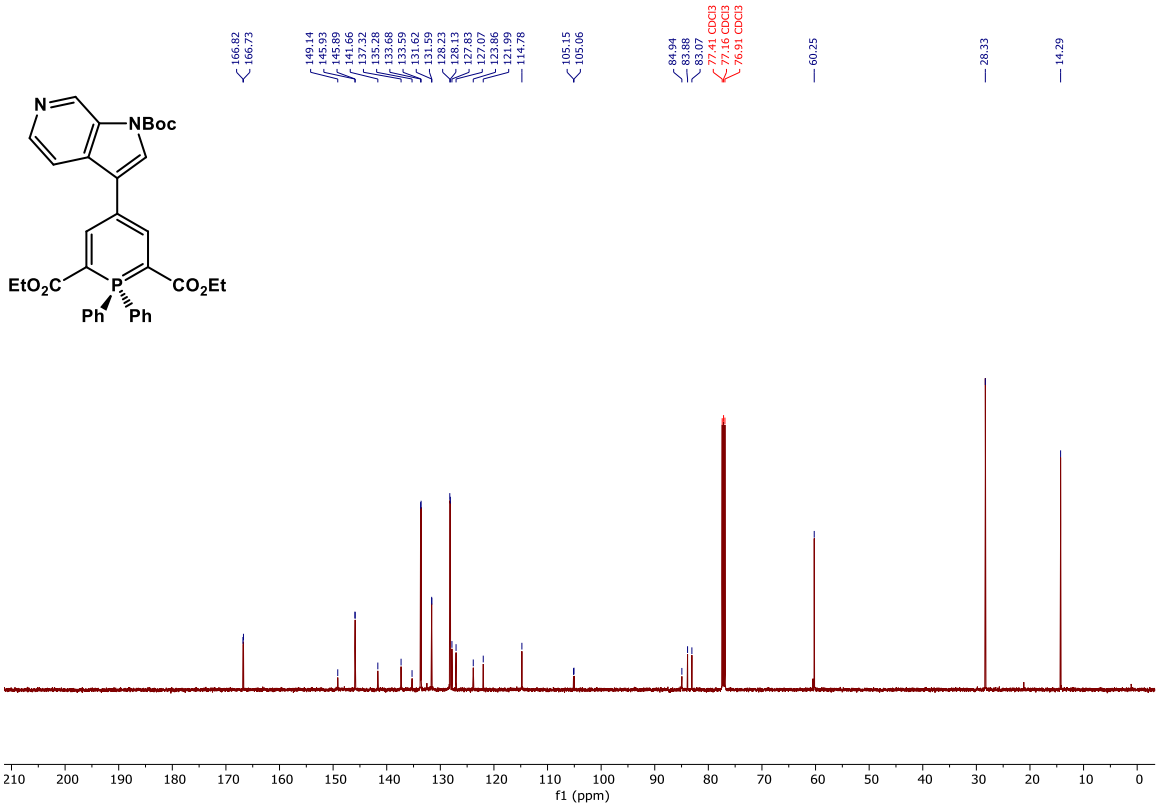


**diethyl 4-(1-(*tert*-butoxycarbonyl)-1*H*-pyrrolo[2,3-*c*]pyridin-3-yl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (5i)**

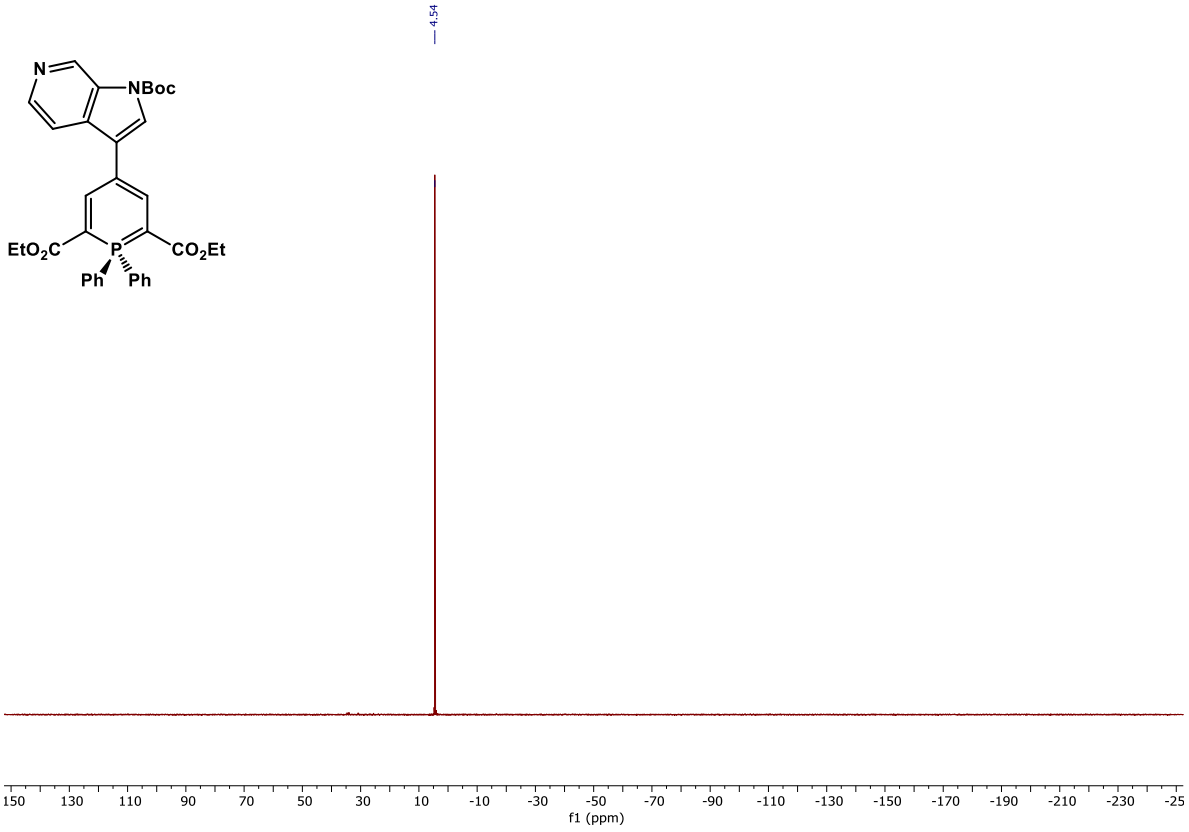
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

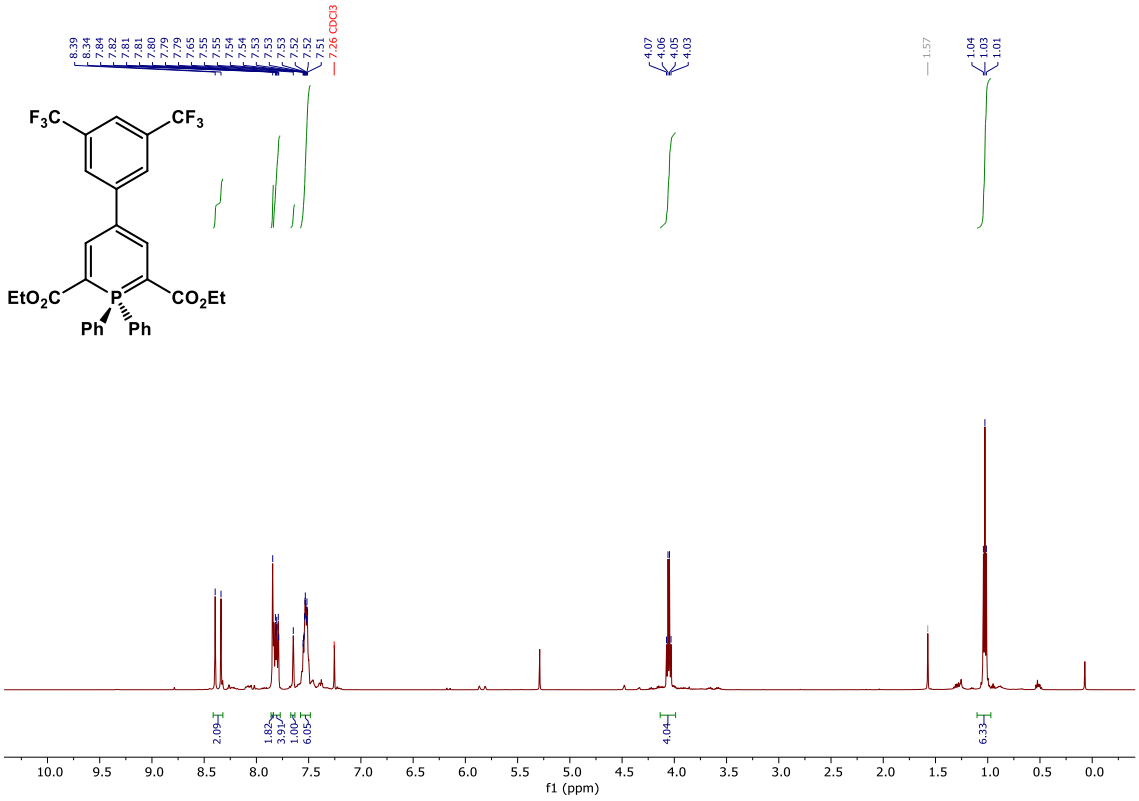


$^{31}$P NMR (202 MHz)

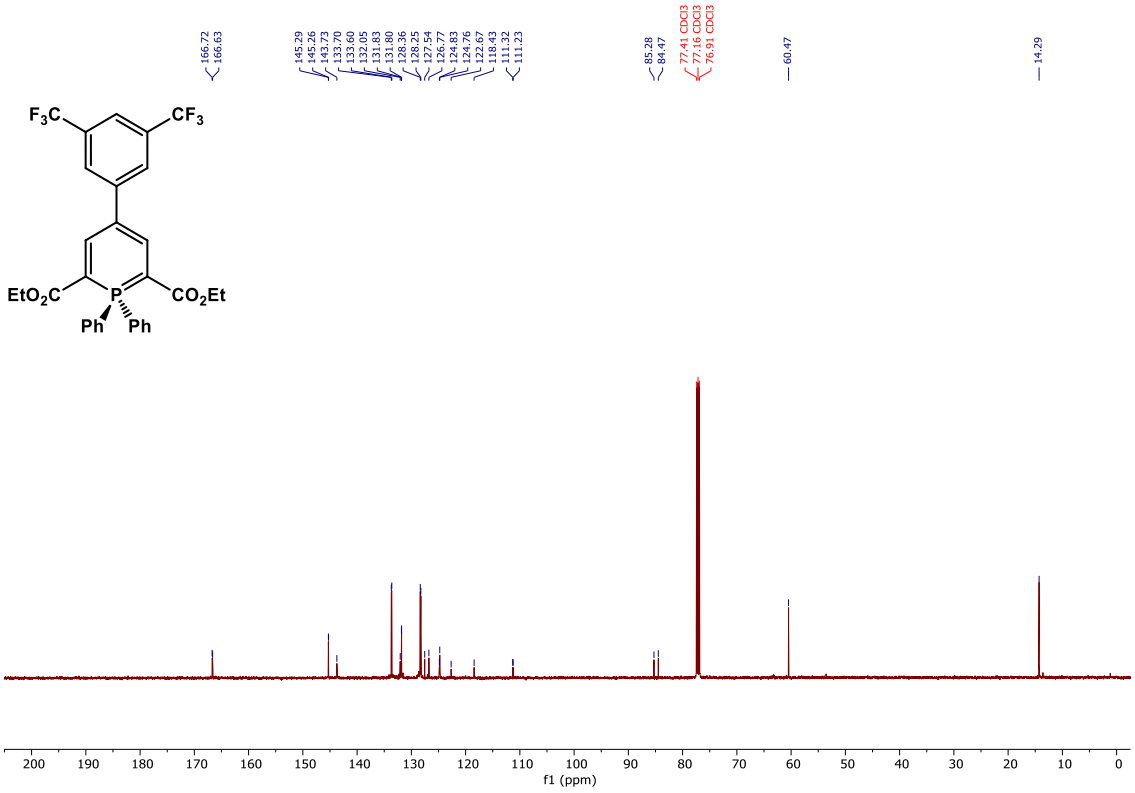


**diethyl 4-(3,5-bis(trifluoromethyl)phenyl)-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (5j)**

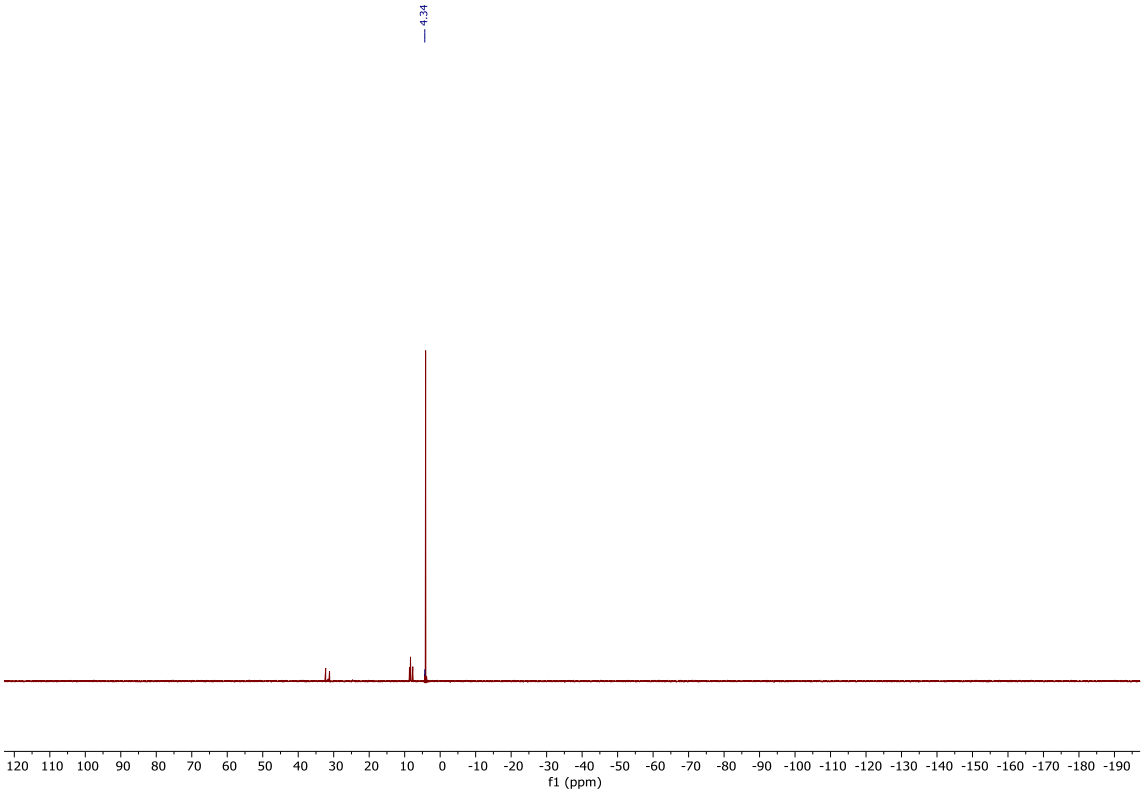
$^1$H NMR (500 MHz)



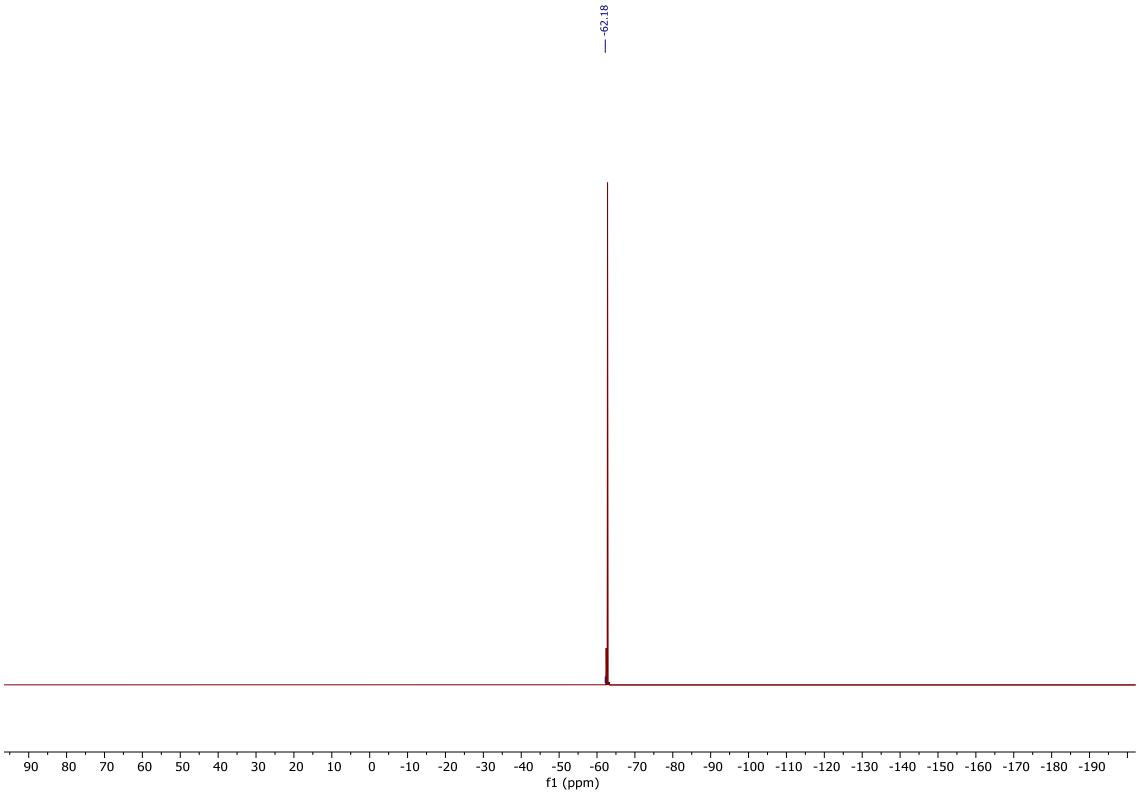

$^{13}$C NMR (126 MHz)



$^{31}$P NMR (202 MHz)

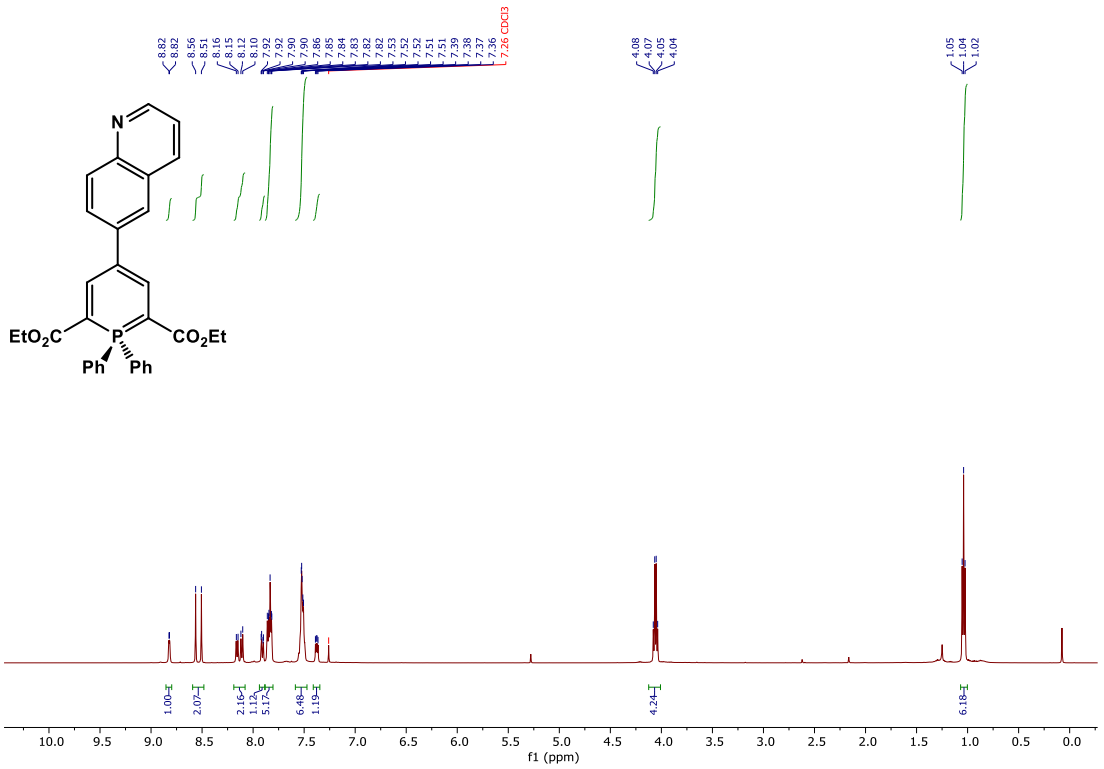



$^{19}$F NMR (471 MHz)

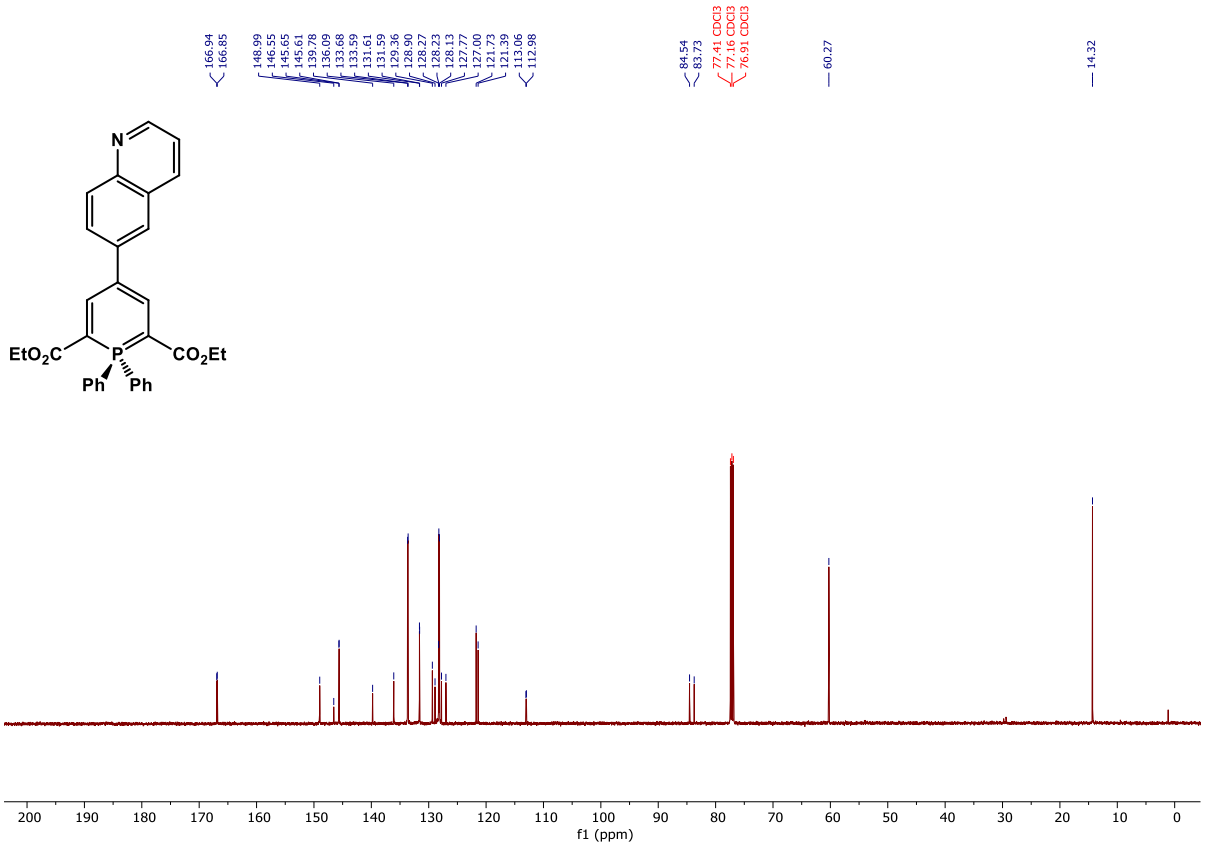


**diethyl 1,1-diphenyl-4-(quinolin-6-yl)-1λ$^5$-phosphinine-2,6-dicarboxylate (5k)**

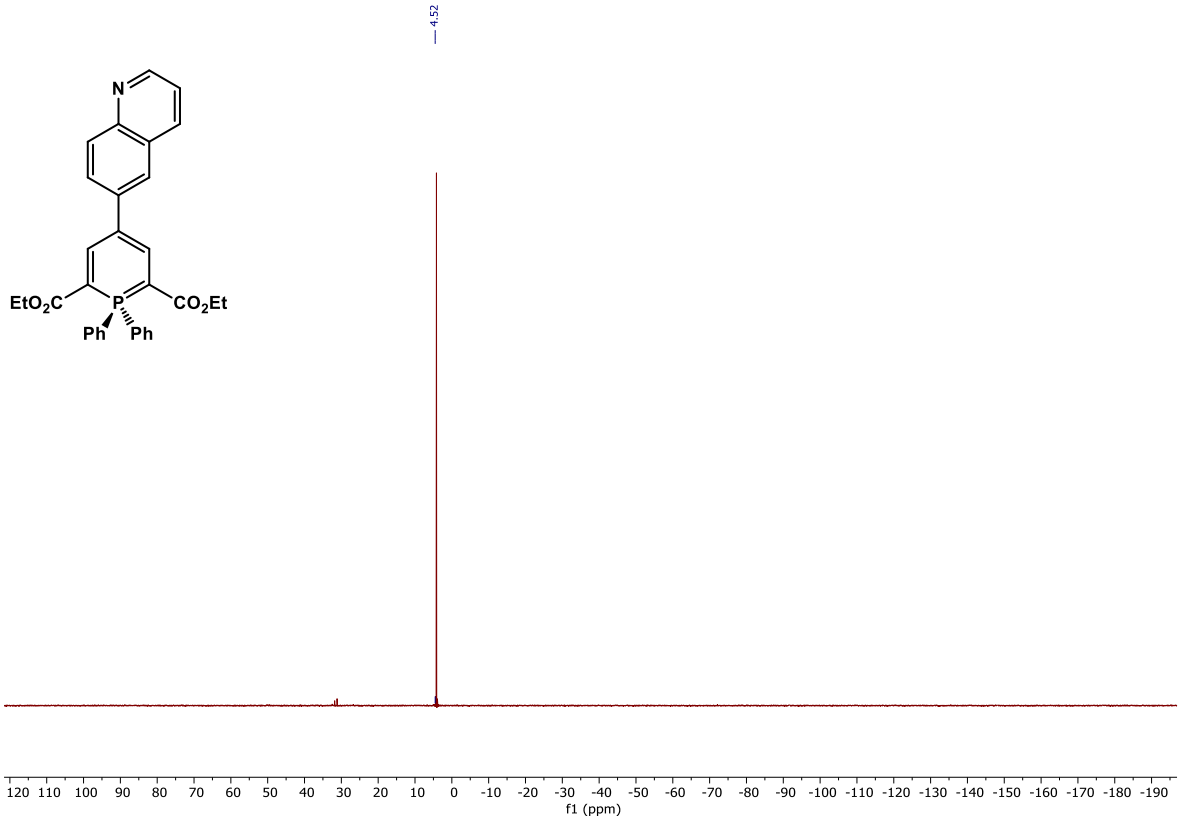
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)



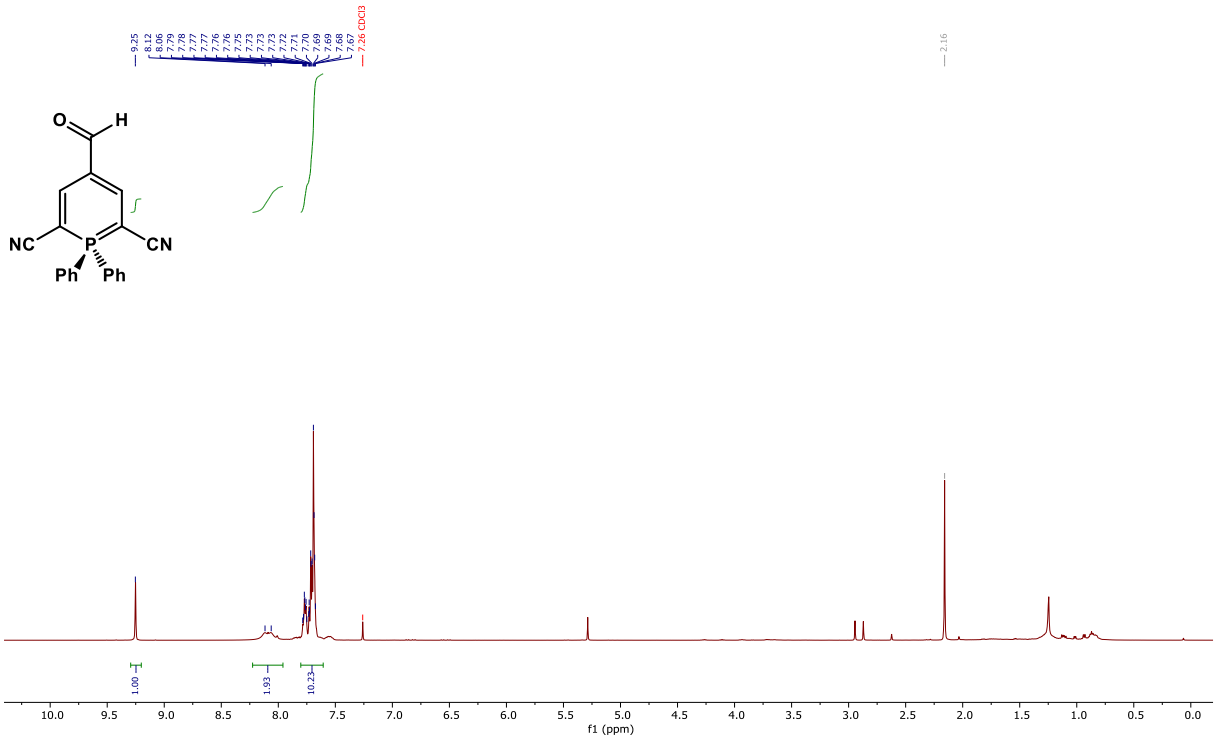
$^{31}$P NMR (202 MHz)



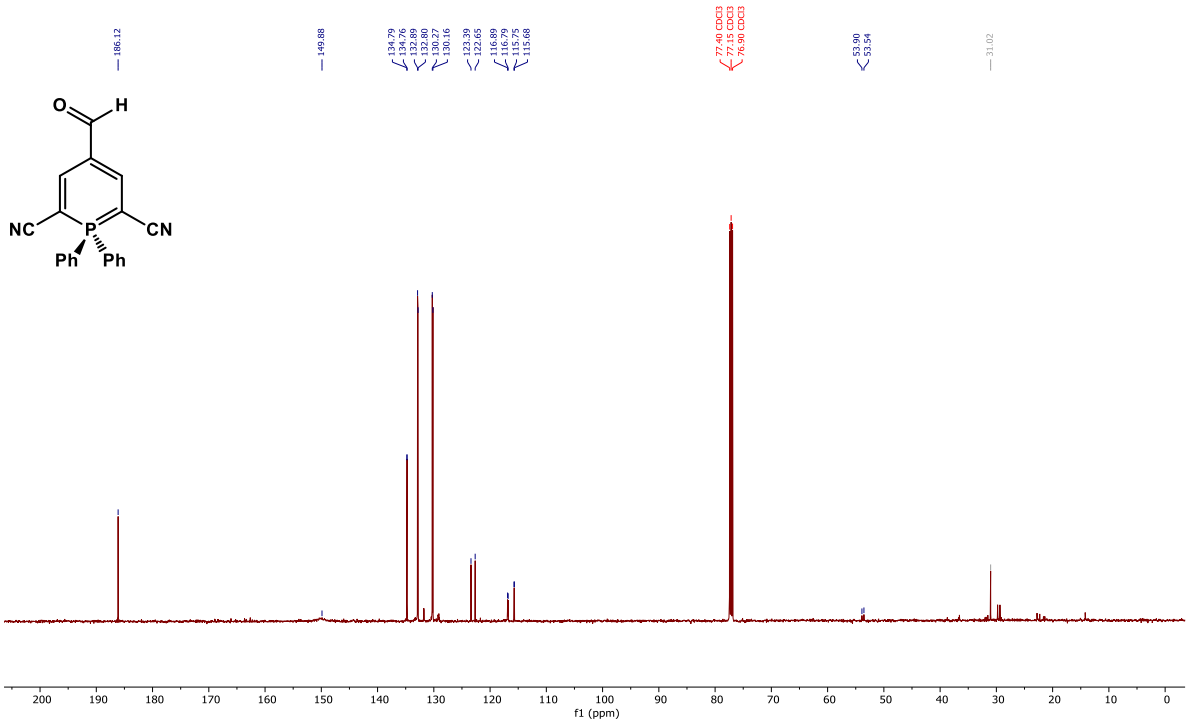
# I/Mg Exchange

## 4-formyl-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarbonitrile (4a)

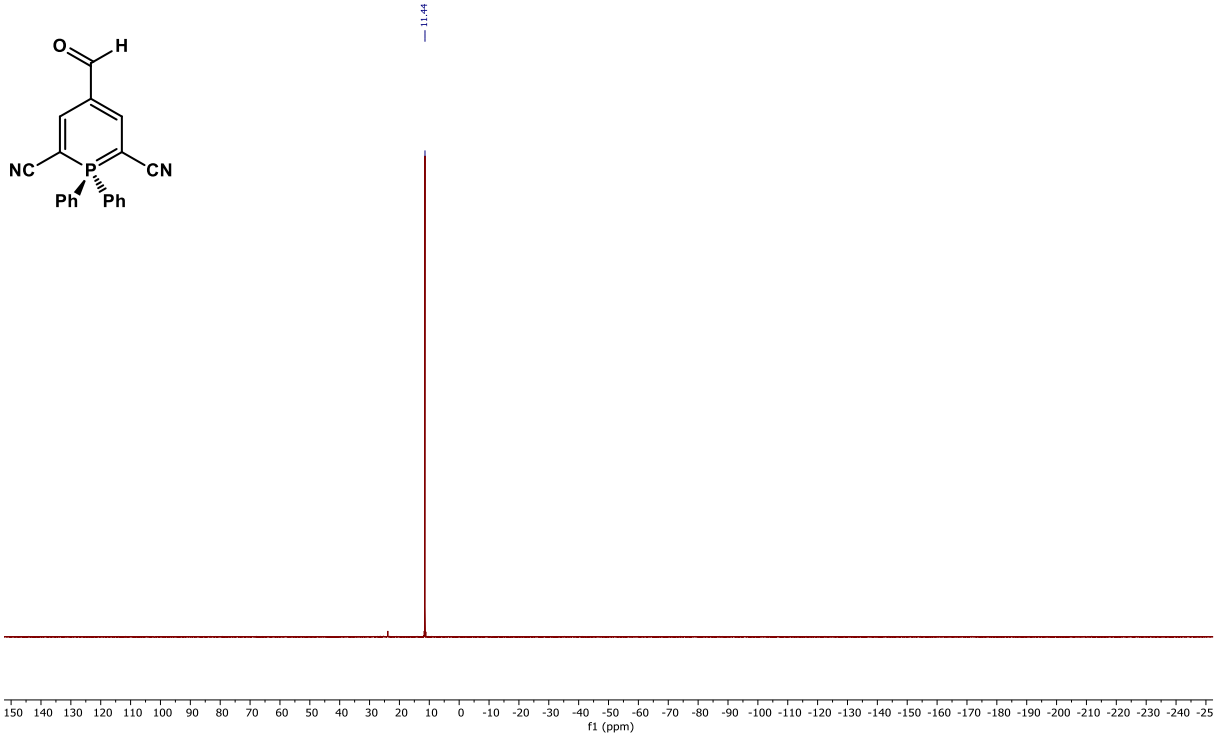
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

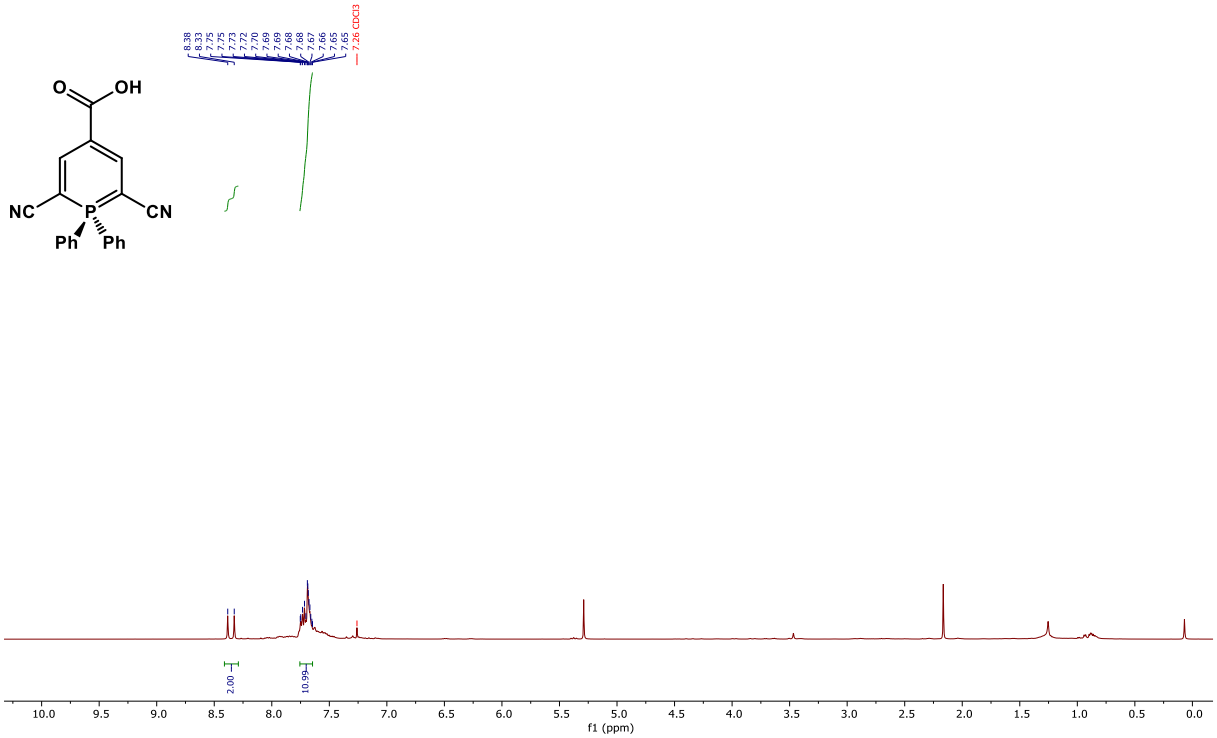


$^{31}$P NMR (202 MHz)

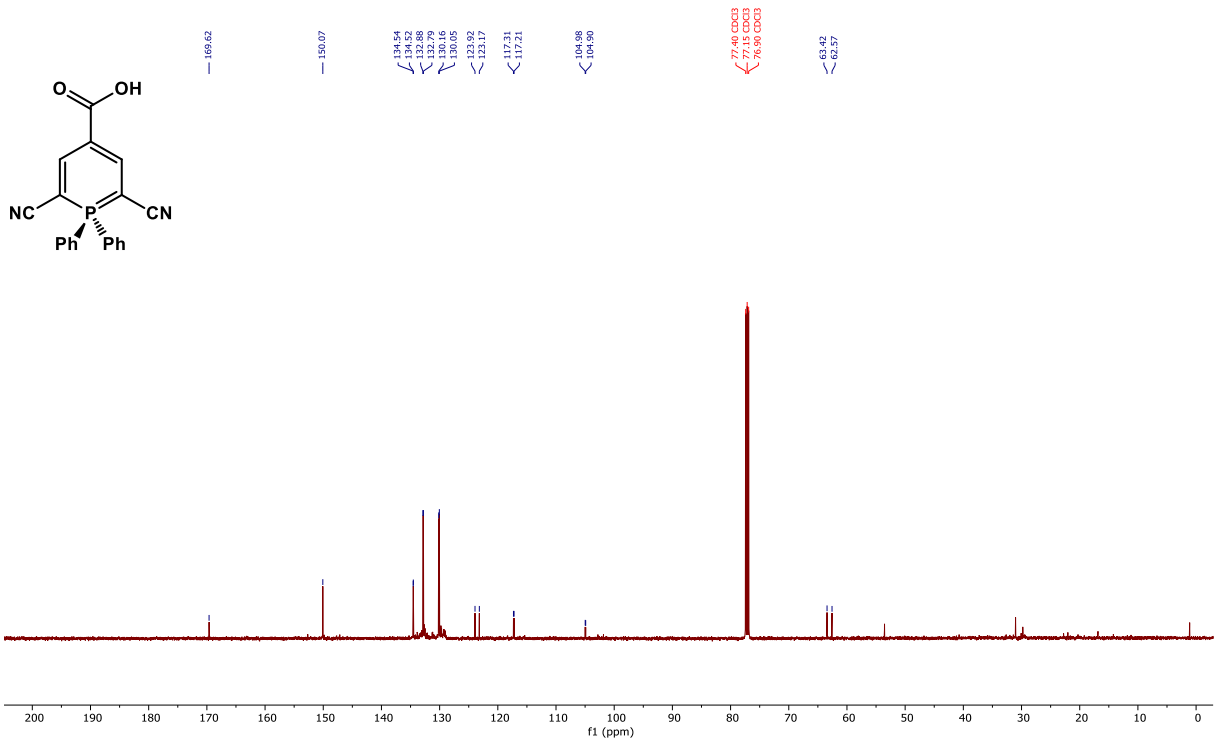


## 2,6-dicyano-1,1-diphenyl-1λ$^5$-phosphinine -4-carboxylic acid (4b)

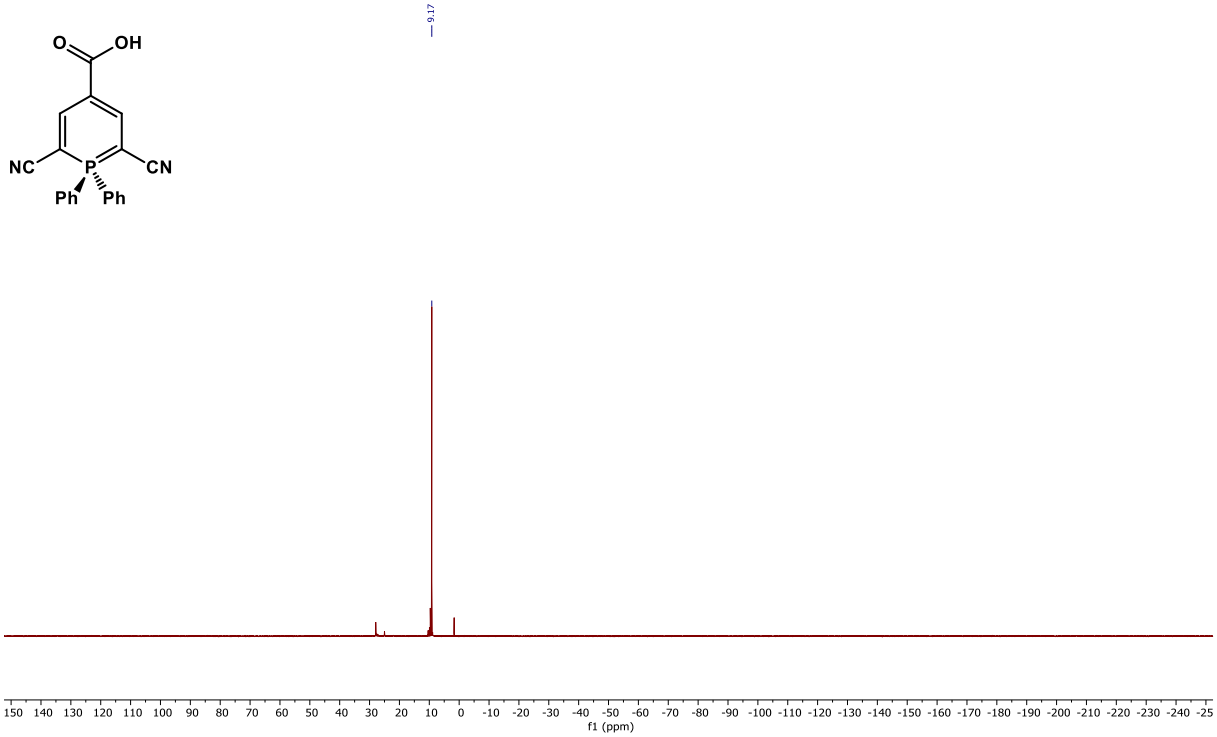
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

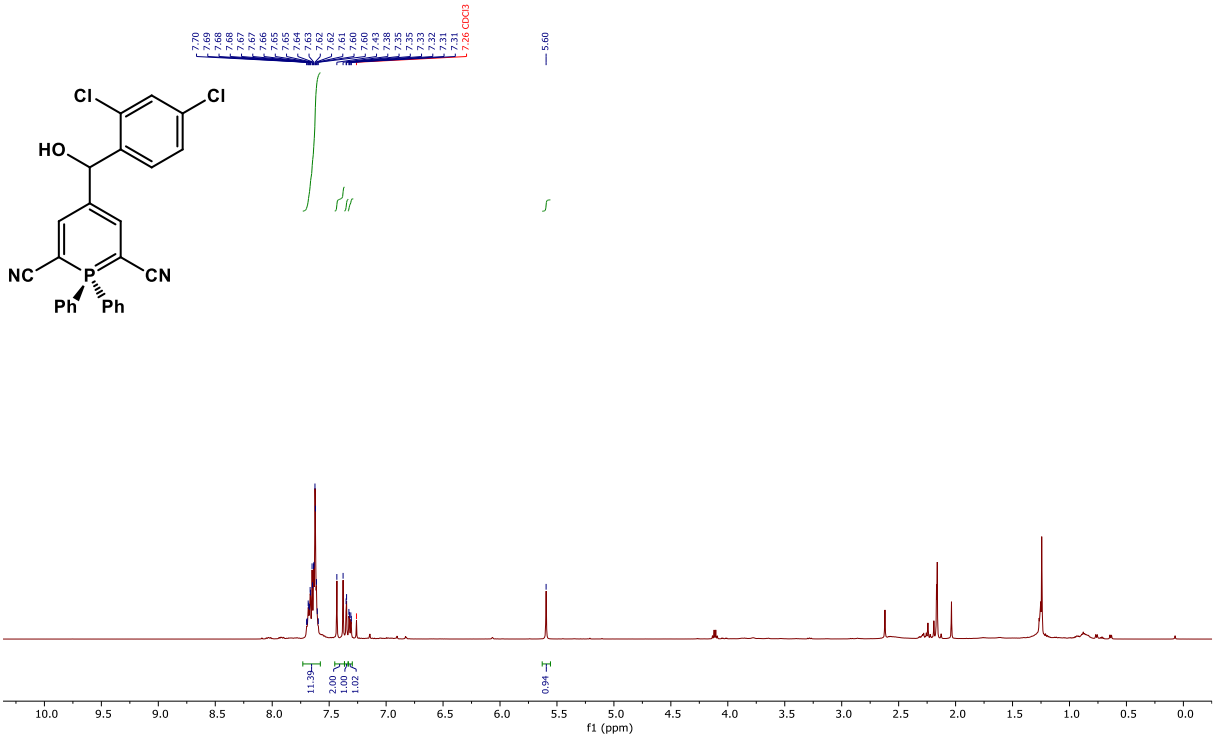


$^{31}$P NMR (202 MHz)

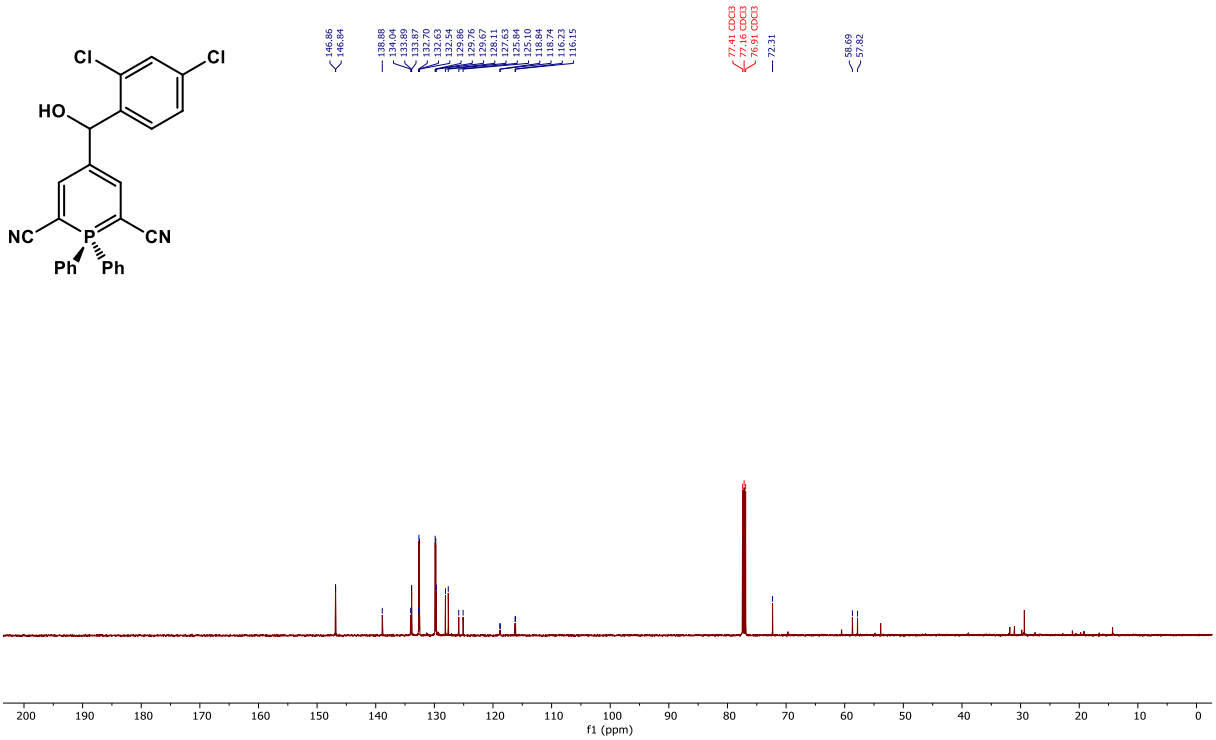


**4-((2,4-dichlorophenyl)(hydroxy)methyl)-1,1-diphenyl-1λ$^5$-phosphinine -2,6-dicarbonitrile (4c)**

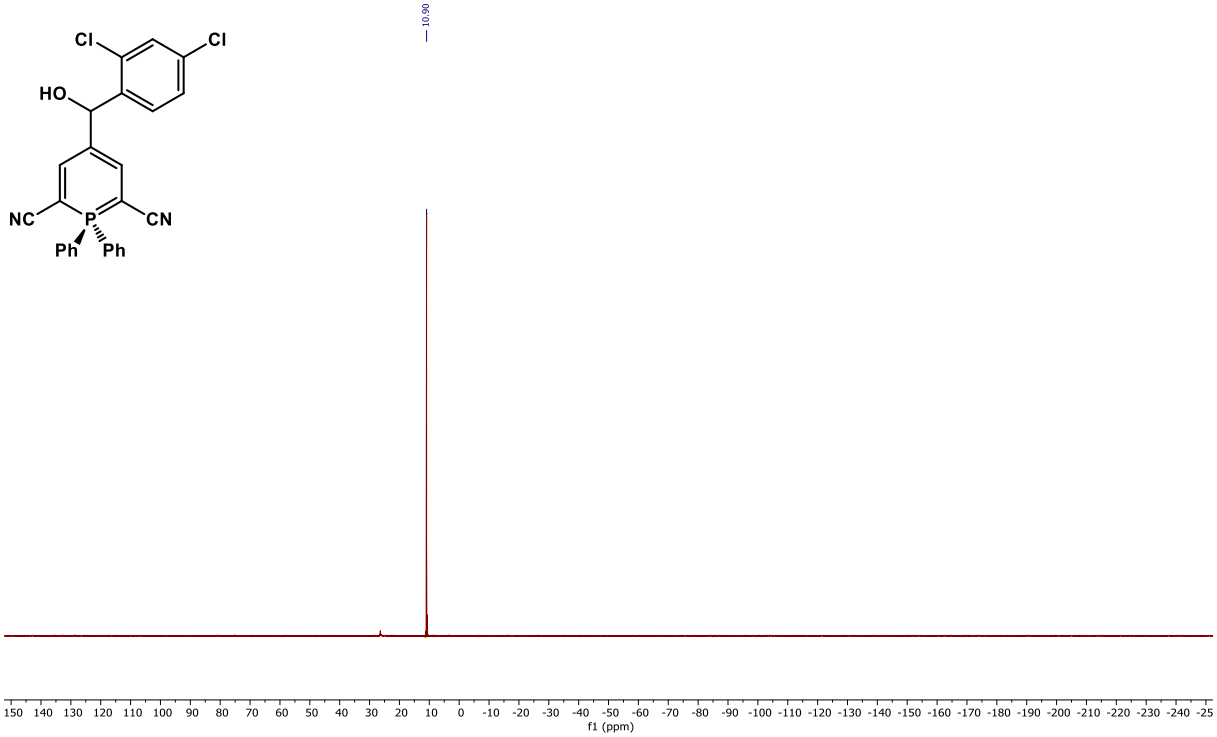
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

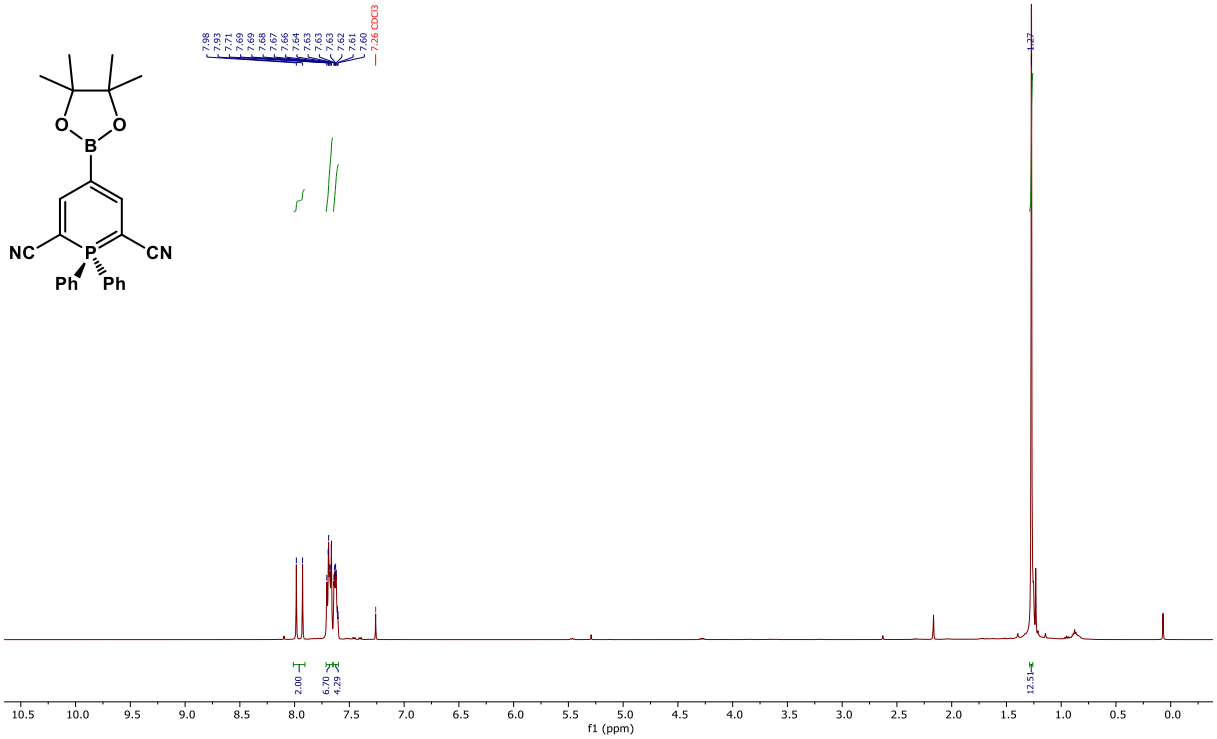


$^{31}$P NMR (202 MHz)

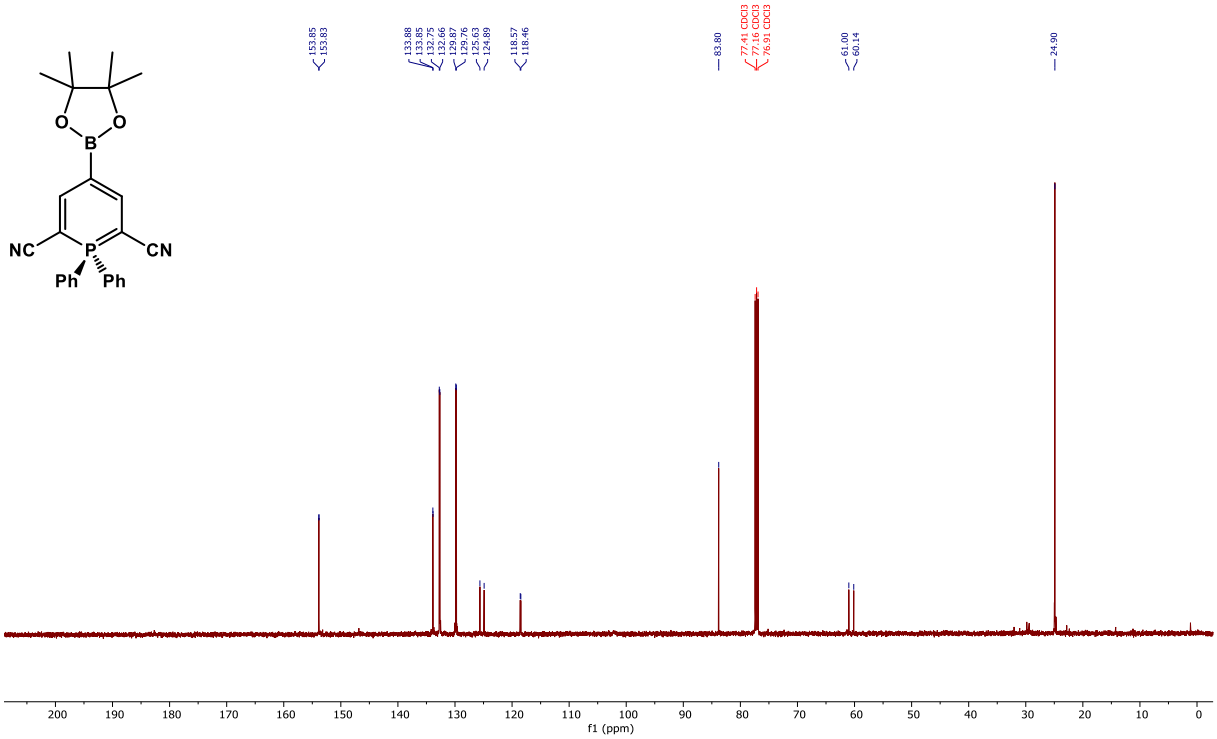


**1,1-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1λ$^5$-phosphinine-2,6-dicarbonitrile (4d)**

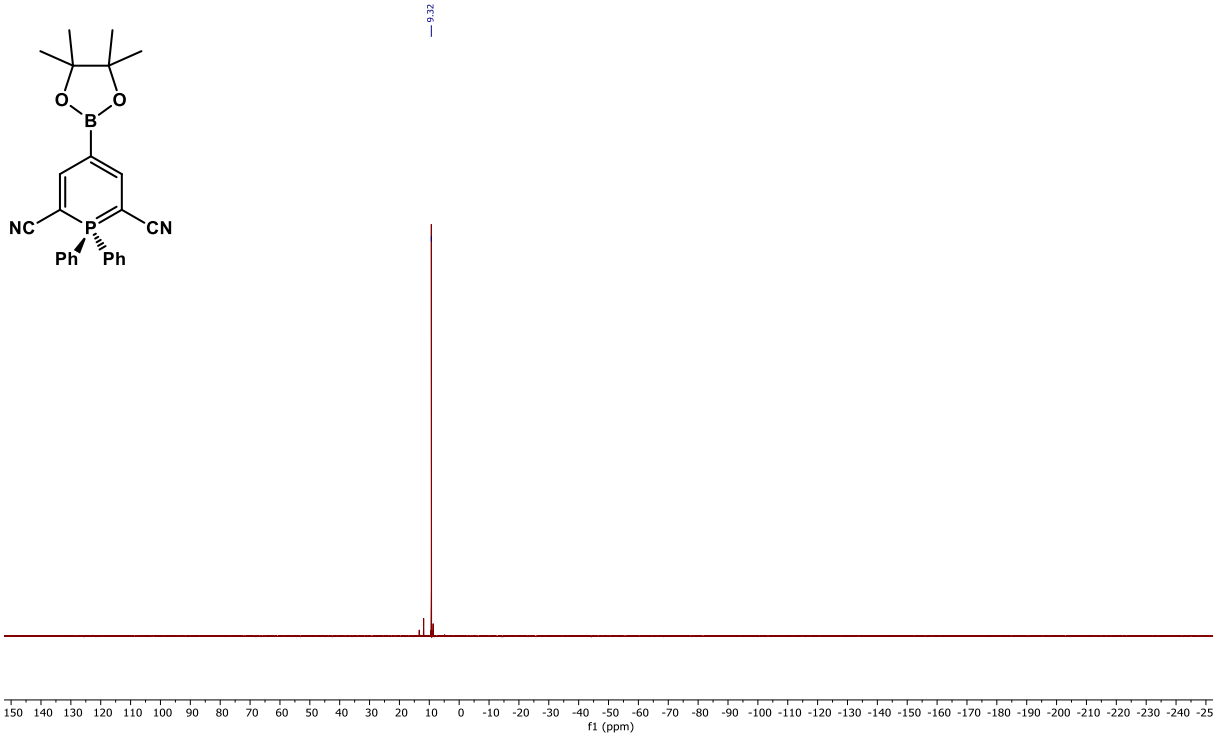
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

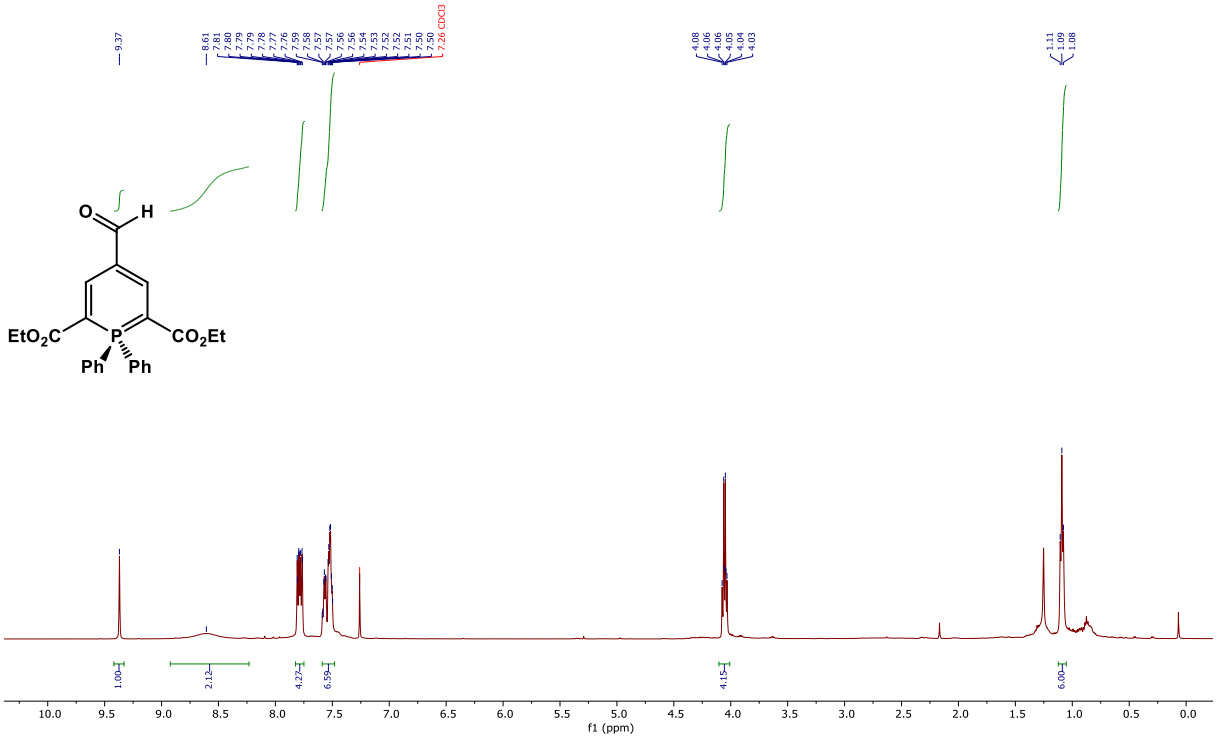


$^{31}$P NMR (202 MHz)

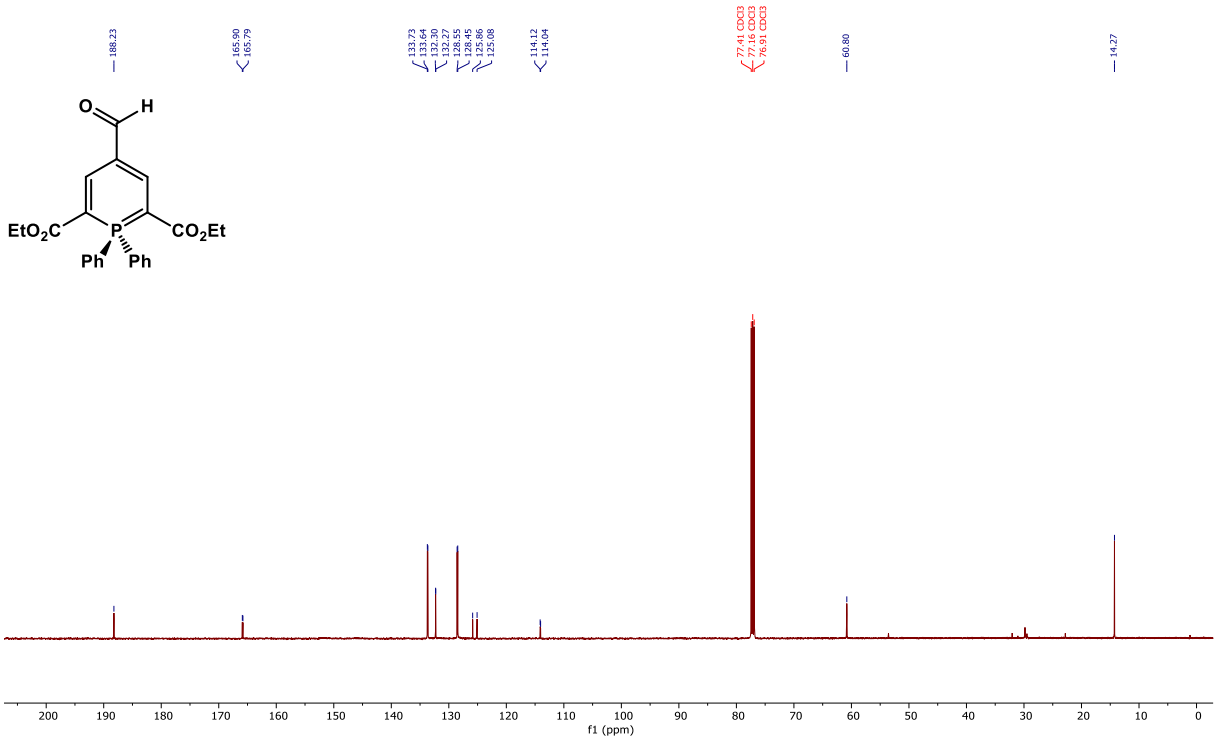


**diethyl 4-formyl-1,1-diphenyl-1λ$^5$-phosphinine-2,6-dicarboxylate (6a)**

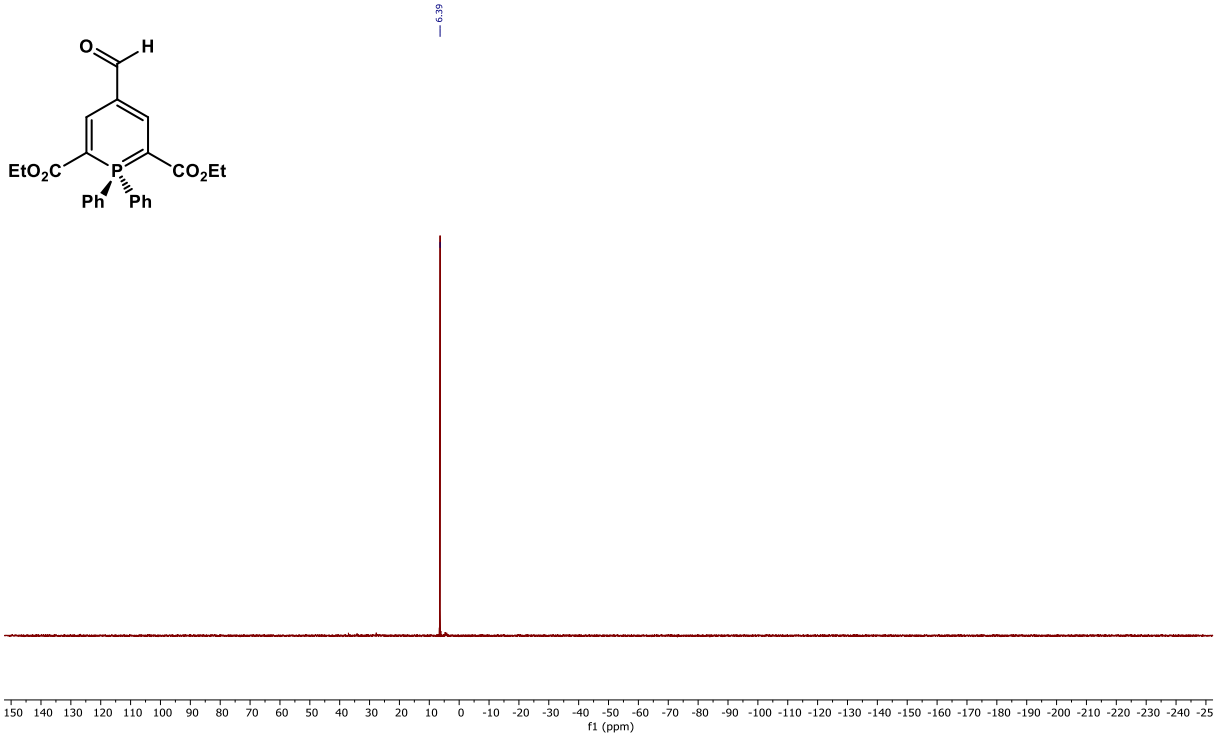
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

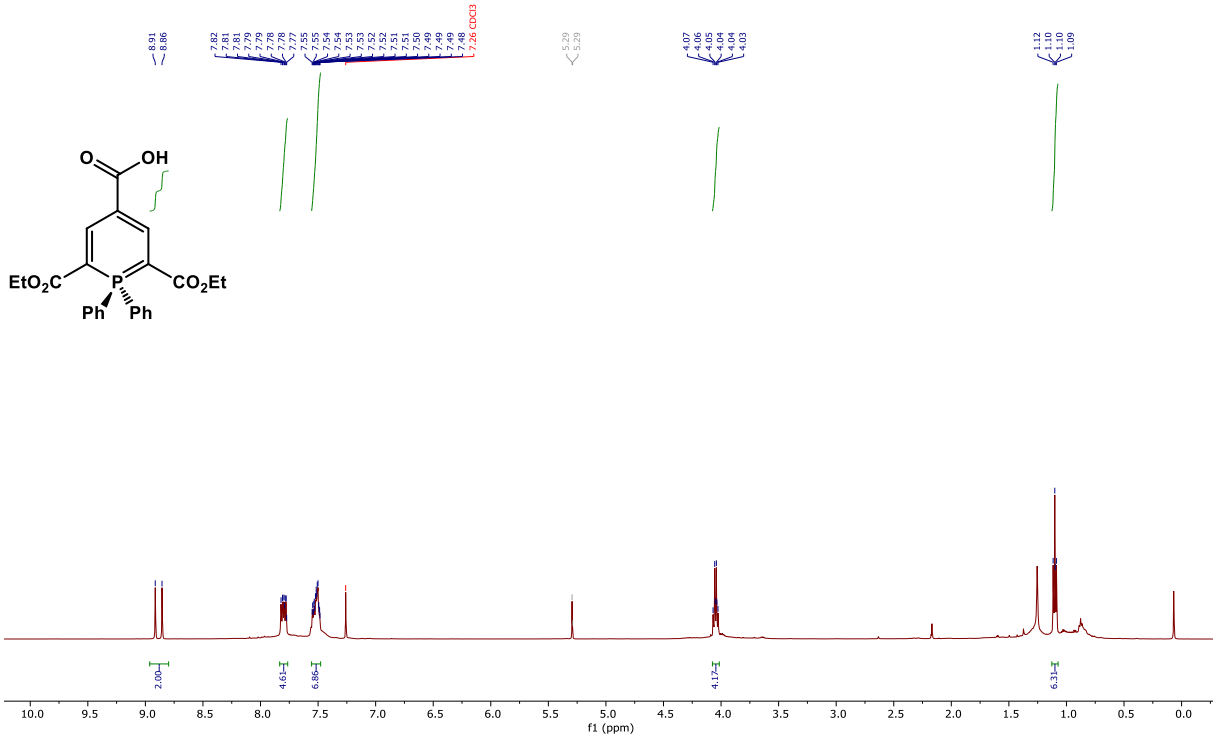


$^{31}$P NMR (202 MHz)

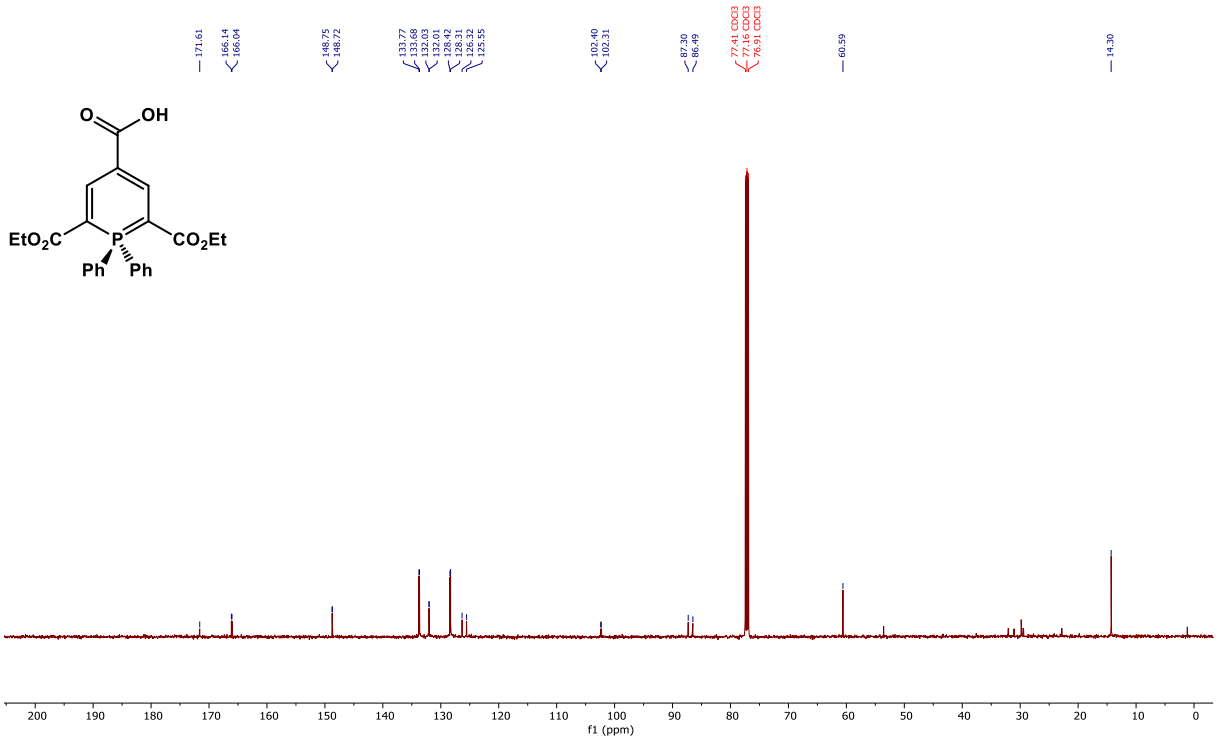


## 2,6-bis(ethoxycarbonyl)-1,1-diphenyl-1λ$^5$-phosphinine-4-carboxylic acid (6b)

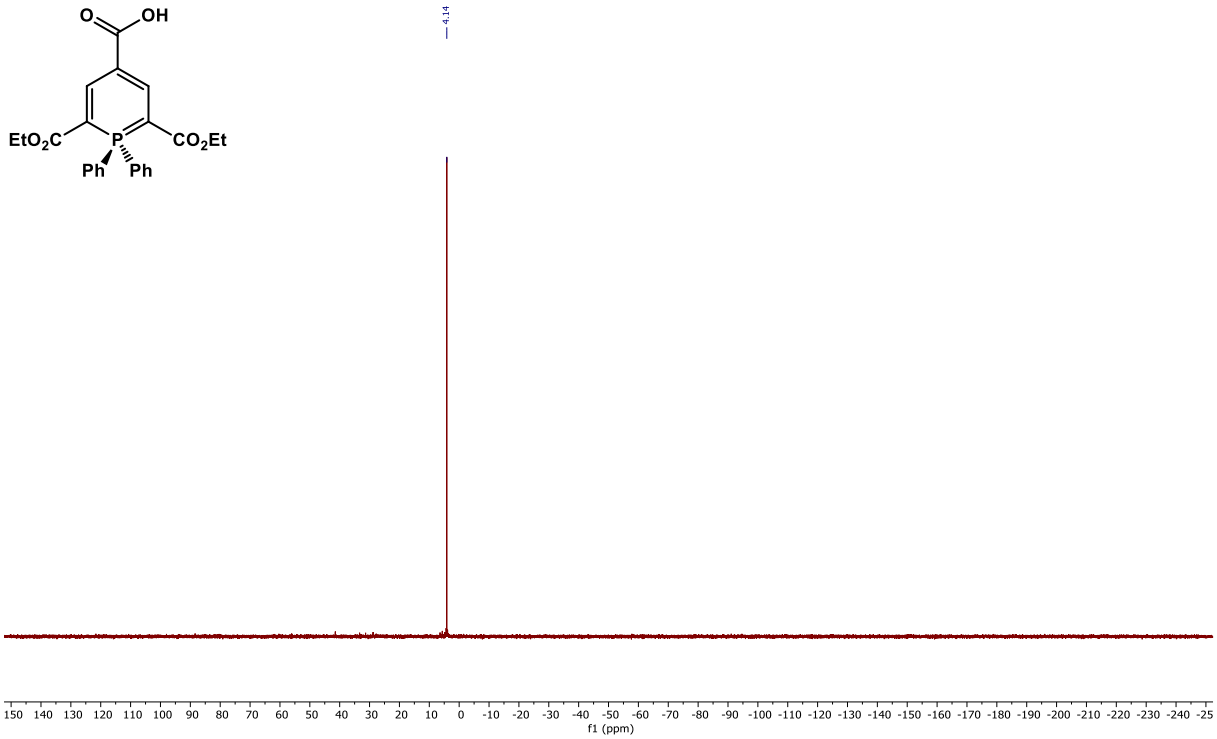
$^1$H NMR (500 MHz)




$^{13}$C NMR (126 MHz)

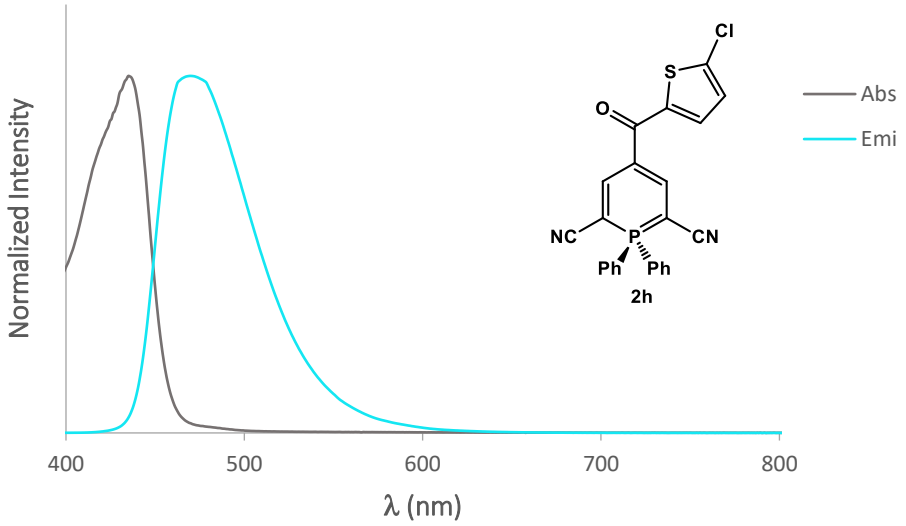


$^{31}$P NMR (202 MHz)

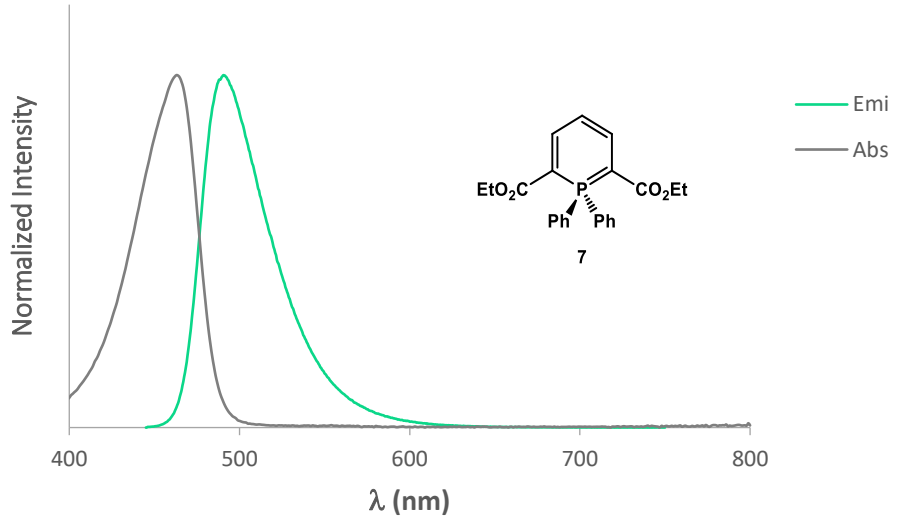


# ABSORPTION AND EMISSION SPECTRA OF *PARA*-SUBSTITUTED $\lambda^5$-PHOSPHININES

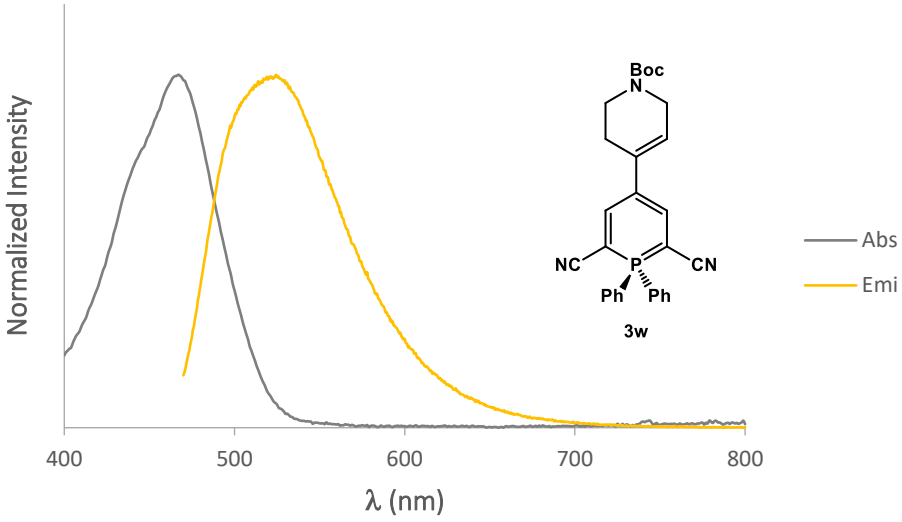
Absorption and emission spectra of compound **2h**



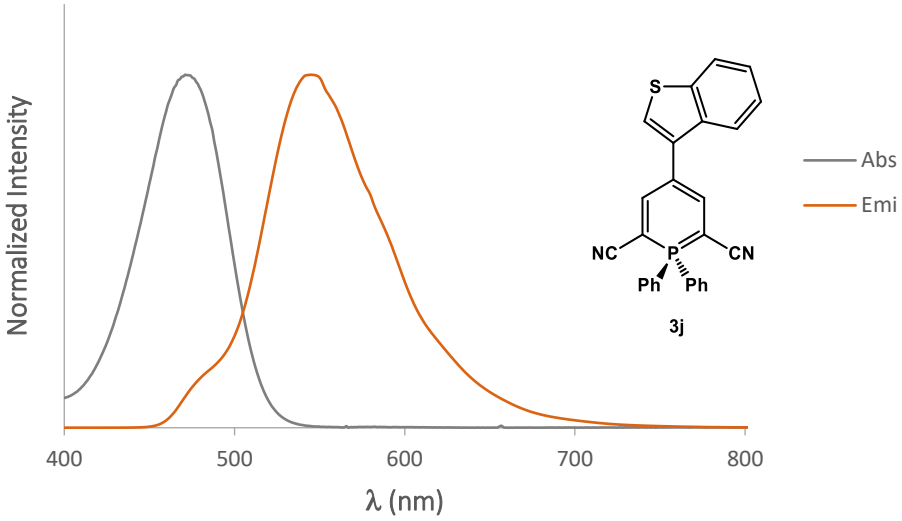

Absorption and emission spectra of compound **7**



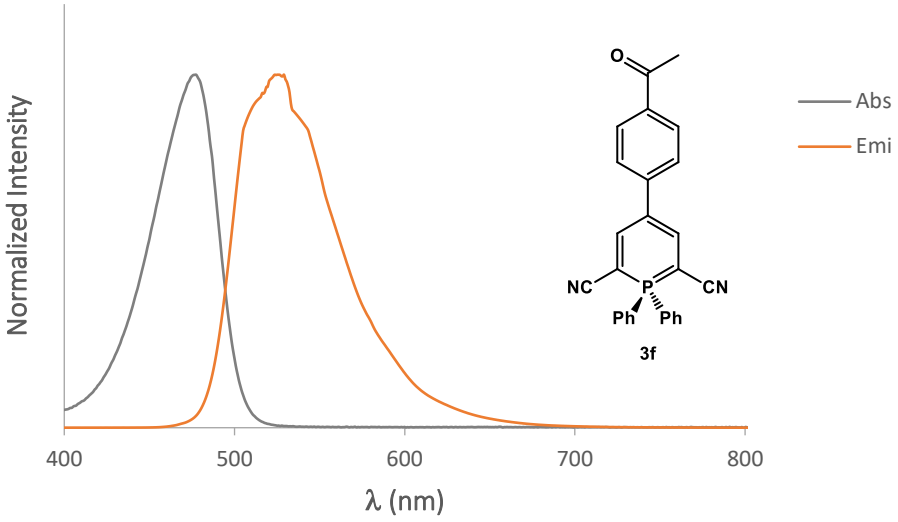
Absorption and emission spectra of compound **3w**



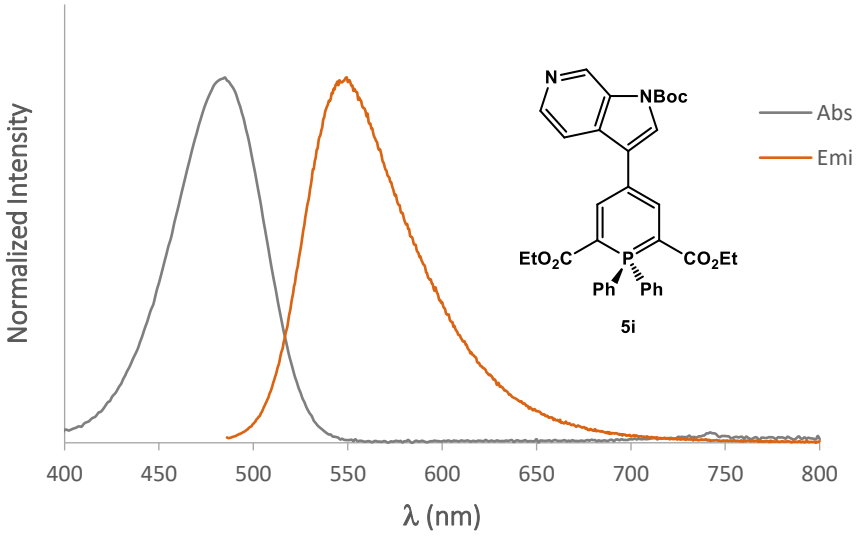

Absorption and emission spectra of compound **3j**



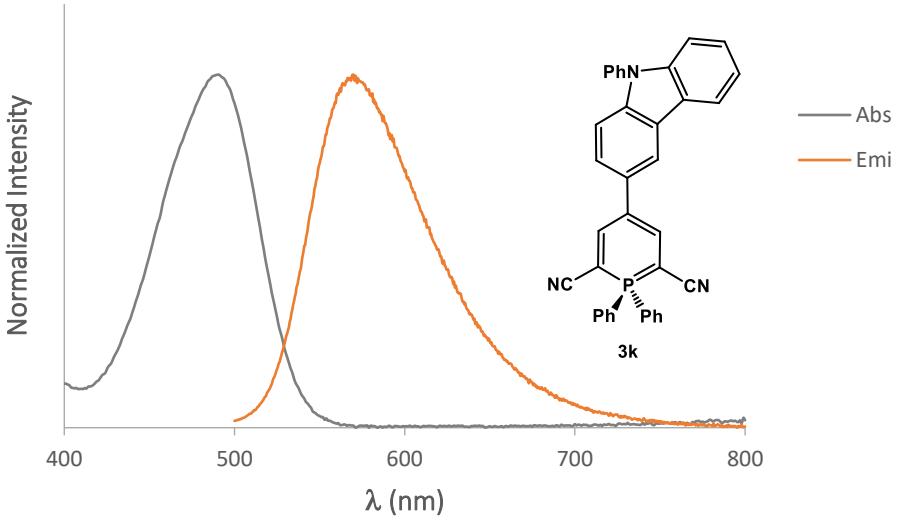
Absorption and emission spectra of compound **3f**



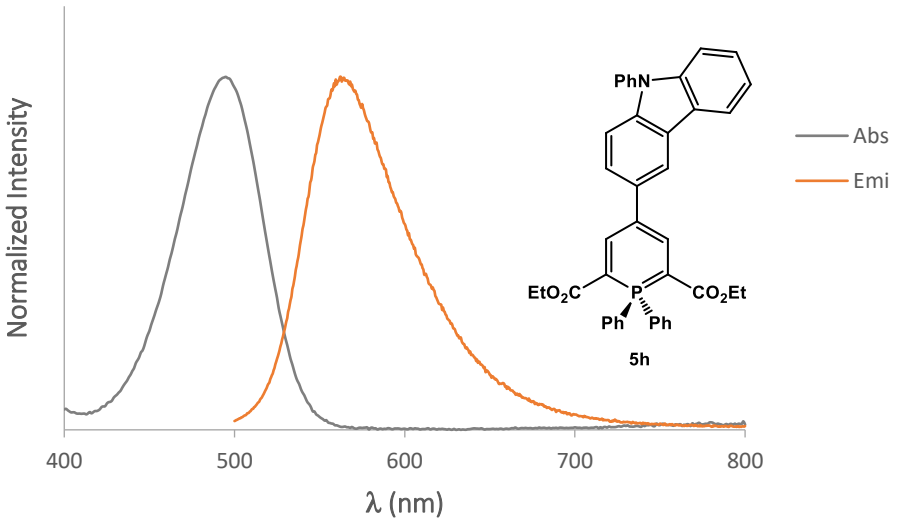

Absorption and emission spectra of compound **5i**



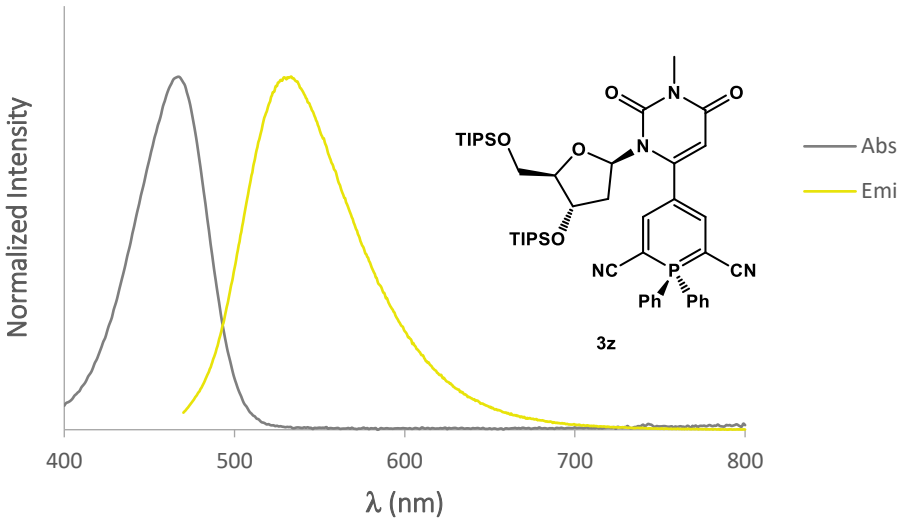
Emission spectra of compound **3k**



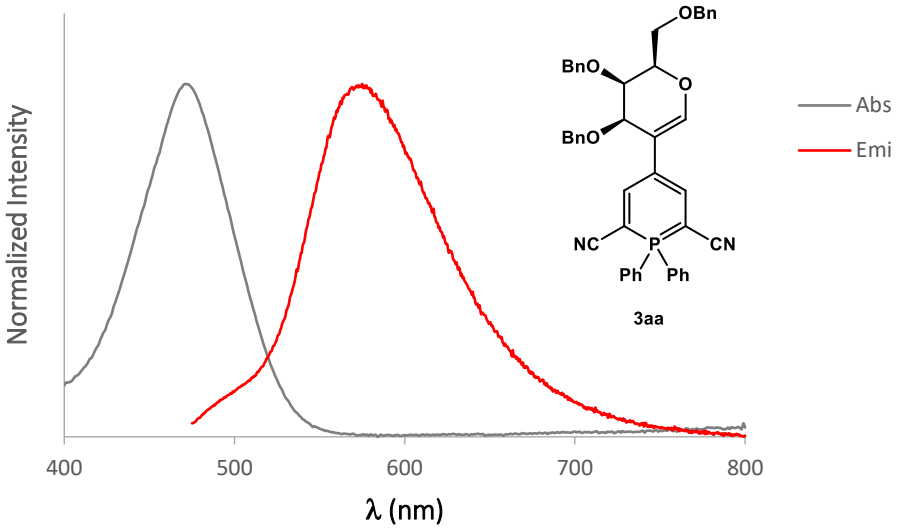

Absorption and emission spectra of compound **5h**



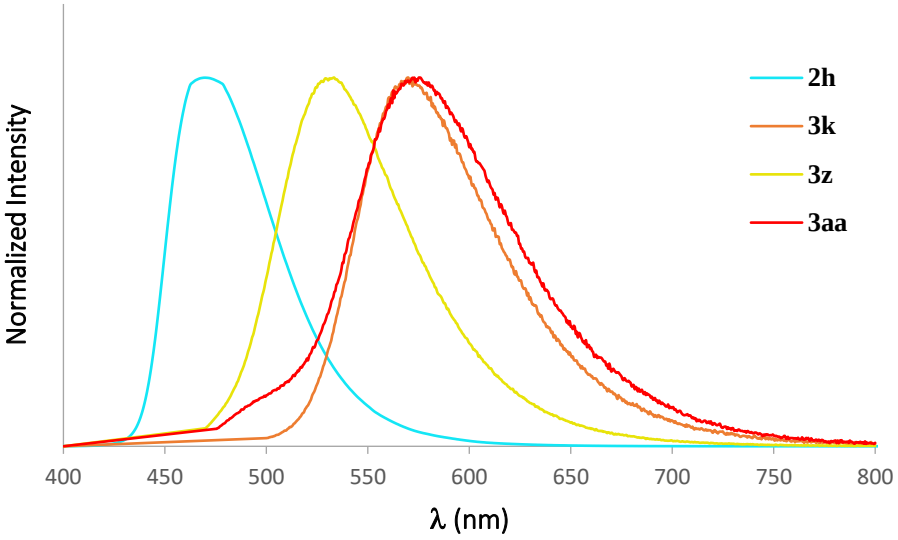
Absorption and emission spectra of compound **3z**

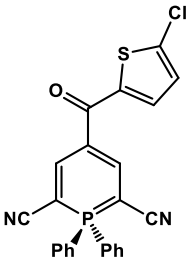



Absorption and emission spectra of compound **3aa**

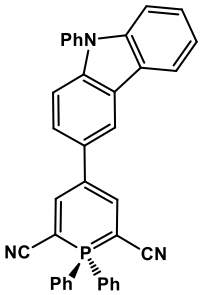


Emission spectra of compound **2h**, **3k**, **3z** and **3aa**

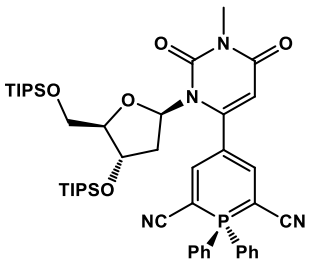


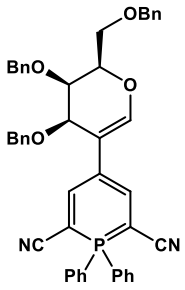

2h




3k




3z

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