Supporting Information

Catalyst-Free Synthesis of Phosphinochalcogenoic Anhydrides *via* Oxygen–Chalcogen Exchange with Elemental Sulfur or Selenium

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Contents

1. General information

1.1 General remarks

Unless specifically noted, all reactions were performed in flame-dried glass apparatus under N_2 atmosphere with freshly distilled anhydrous solvents. Commercially available reagents and solvents were purchased from Energy chemical, Tansoole, or Bide Pharmatech Ltd., and used without further purification. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Flash column chromatography was performed using 200-300 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates were used. ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz),$^{31}P\{^{1}H\}$ (162 MHz), $^{19}F\{^{1}H\}$ (376 MHz) were recorded on a 400 MHz Bruker spectrometer in $CDCl_3$. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CHCl_3$ (δ= 7.26 for ^{1}H NMR and δ = 77.16 for ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. The electron ionization method was used for HRMS measurements, and the mass analyzer type used for the HRMS measurement is Q Exactive Orbitrap.

1.2 Representative important organophosphorus compounds

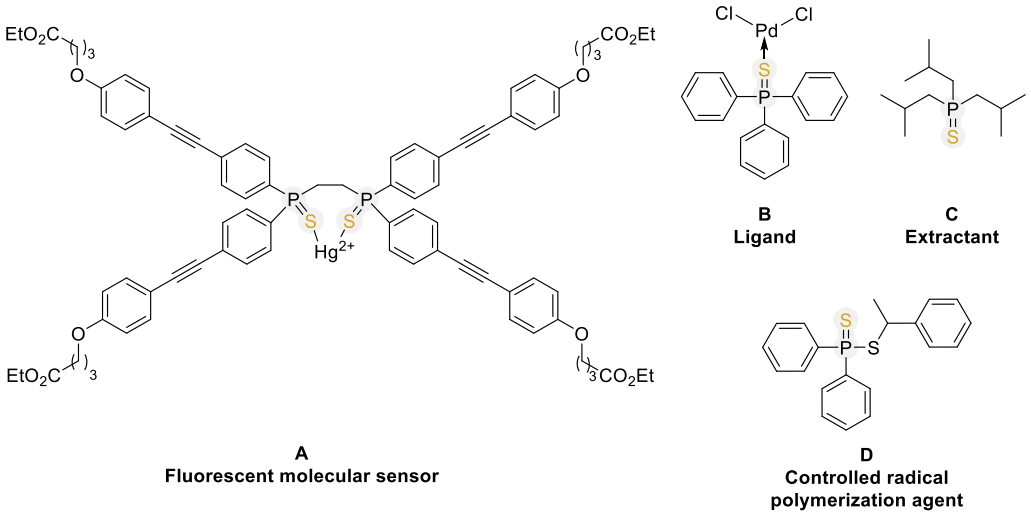
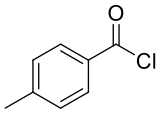


Figure S1. Representative important organophosphorus compounds featuring P=S bonds

2. Starting materials

All reagents—including acyl chlorides, acid anhydrides, sulfur powder, and selenium powder—were commercially sourced and used without further purification. The *H*-phosphine oxides were either obtained commercially or prepared according to previously reported procedures.[1-3]

2.1 Compound list for acyl chlorides and acid anhydrides (1)



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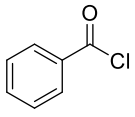

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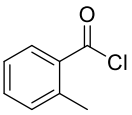

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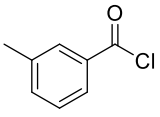

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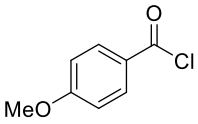

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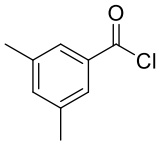

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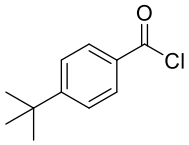

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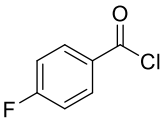

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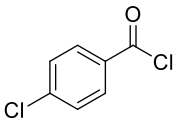

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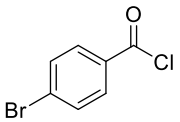

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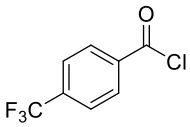

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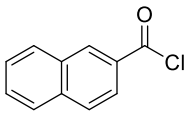

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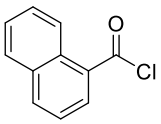

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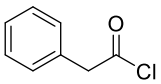

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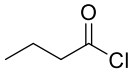

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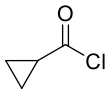

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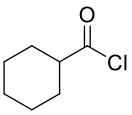

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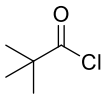

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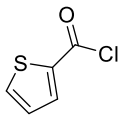

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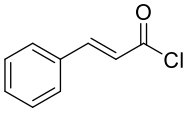

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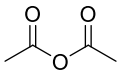

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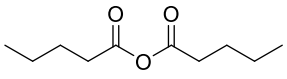

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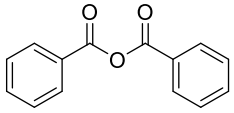

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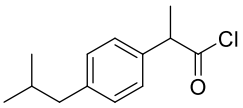
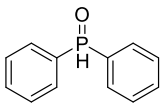


1y

2.1 Compound list for P(O)-H compounds (2)



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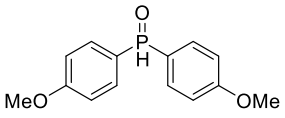

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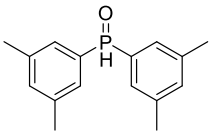

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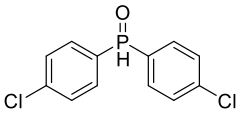

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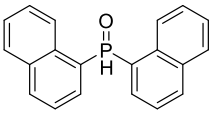

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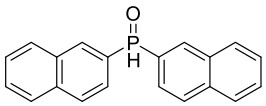

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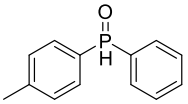

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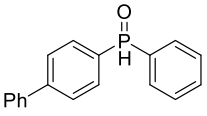

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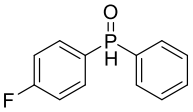

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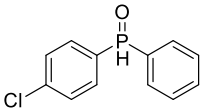

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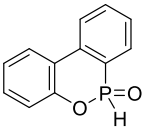

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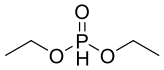

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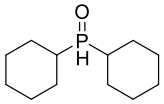
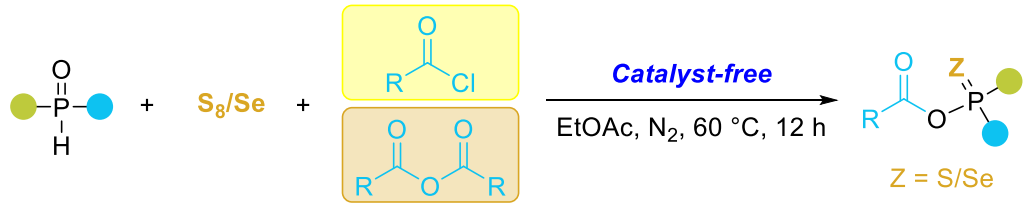


2m

3. General procedures

3.1 General procedure for the synthesis of compounds 3-5



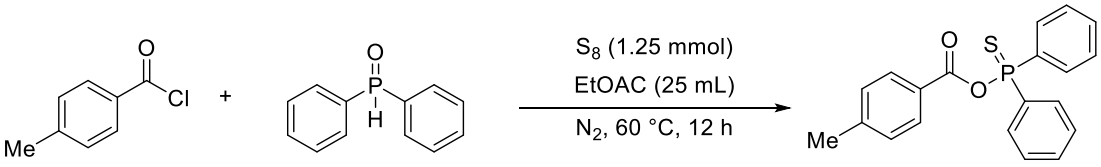
2
0.2 mmol

1
0.2 mmol

3-5

A Schlenk tube equipped with a magnetic stir bar was evacuated and refilled with nitrogen three times. Under a nitrogen atmosphere, P(O)H compound (**2**, 0.2 mmol, 1.0 equiv.), sulfur powder (M.W. = 256 g/mol, 12.8 mg, 0.05 mmol, 0.25 equiv. (*per* molecule)) or selenium powder (31.6 mg, 0.4 mmol, 2.0 equiv.), and acyl chlorides or acid anhydrides (**1**, 0.2 mmol, 1.0 equiv.) were sequentially added to the reaction vessel. (Note: 0.25 equiv. of S_8 provides 2.0 equiv. of atomic sulfur.) Finally, ethyl acetate (1 mL) was introduced. The reaction mixture was stirred at 60 °C for 12 hours using an IKA magnetic stirrer equipped with a nine-well aluminum heating block. After complete consumption of the starting material, the mixture was quenched with water (3.0 mL) and extracted three times with ethyl acetate (10 mL each time). The combined organic layers were washed with saturated sodium chloride solution (10 mL) and dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the resulting residue was purified by flash column chromatography using petroleum ether/ethyl acetate (20:1-3:1, v/v) as the eluent to afford the pure products **3-5**.

3.2 Gram-scale synthesis of 3a and 3j



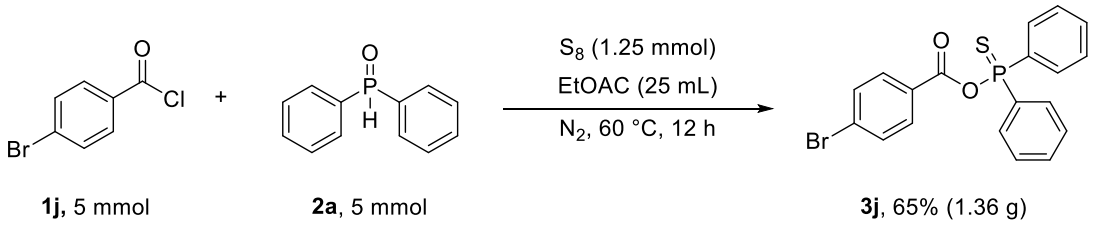
1a, 5 mmol

2a, 5 mmol

3a, 62% (1.10 g)

In a 100 mL reaction flask equipped with a magnetic stir bar, the reaction flask

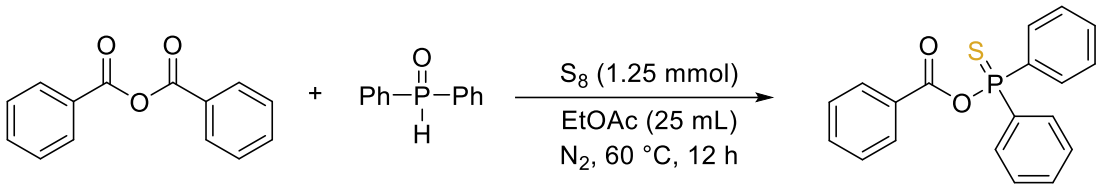
was vacuumed with a pump and backfilled with nitrogen for three cycles. Subsequently, in the nitrogen atmosphere, diphenylphosphine oxide (**2a**, 5 mmol, 1.01 g), 4-methylbenzoyl chloride (**1a**, 5 mmol, 773.0 mg), S_8 (1.25 mmol, 320 mg) and 25 mL ethyl acetate were added. The reaction mixture was vigorously stirred in an oil bath at 60 °C for 12 hours. Upon reaction completion (monitored by TLC), the reaction mixture was concentrated under vacuum. The residue was sequentially washed with brine and extracted three times with ethyl acetate. The combined mixture was concentrated using a rotary vacuum evaporator and separated on a flash silica gel column with a petroleum ether/ethyl acetate eluent (v:v = 20:1) to yield **3a** (1.10 g, 62% yield).



1j, 5 mmol **2a**, 5 mmol **3j**, 65% (1.36 g)

In a 100 mL reaction flask equipped with a magnetic stir bar, the reaction flask was vacuumed with a pump and backfilled with nitrogen for three cycles. Subsequently, in the nitrogen atmosphere, diphenylphosphine oxide (**2a**, 5 mmol, 1.01 g), 4-bromobenzoyl chloride (**1j**, 5 mmol, 1.09 g), S_8 (1.25 mmol, 320 mg) and 25 mL EtOAc were added. The reaction mixture was vigorously stirred in an oil bath at 60 °C for 12 hours. Upon reaction completion (monitored by TLC), the reaction mixture was concentrated under vacuum. The residue was sequentially washed with brine and extracted three times with ethyl acetate. The combined mixture was concentrated using a rotary vacuum evaporator and separated on a flash silica gel column with a petroleum ether/ethyl acetate eluent (v:v = 20:1) to yield **3j** (1.36 g, 65% yield).

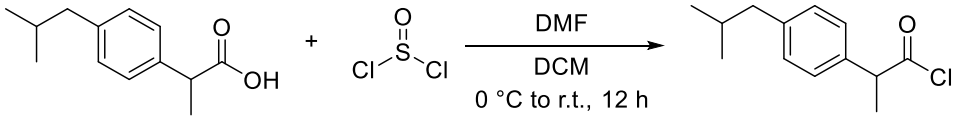
3.3 Gram-scale synthesis of 3b



1v, 5 mmol **2a**, 5 mmol **3b,** 75% (1.26 g)

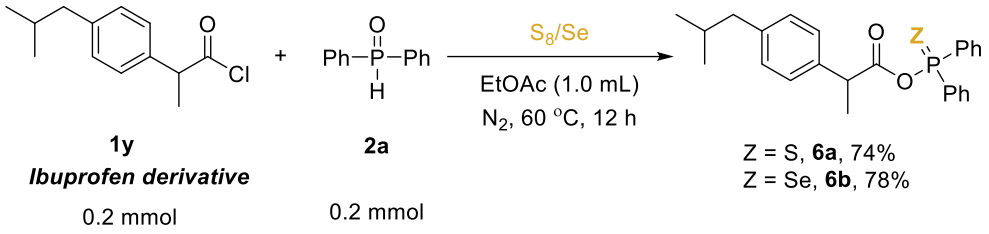
In a 100 mL reaction flask equipped with a magnetic stir bar, the reaction flask was vacuumed with a pump and backfilled with nitrogen for three cycles. Subsequently, in the nitrogen atmosphere, diphenylphosphine oxide (**2a**, 5 mmol, 1.01 g), benzoic anhydride (**1v**, 5 mmol, 1.13 g), sulfur (1.25 mmol, 320 mg) and 25 mL EtOAc were added. The reaction mixture was vigorously stirred in an oil bath at 60 °C for 12 hours. Upon reaction completion (monitored by TLC), the reaction mixture was concentrated under vacuum. The residue was sequentially washed with brine and extracted three times with ethyl acetate. The combined mixture was concentrated using a rotary vacuum evaporator and separated on a flash silica gel column with a petroleum ether/ethyl acetate eluent (v:v = 20:1) to yield **3b** (1.26 g, 75% yield).

3.4 Synthesis of *ibuprofen* derivatives 6a and 6b



Ibuprofen **1y** ***Ibuprofen derivative***

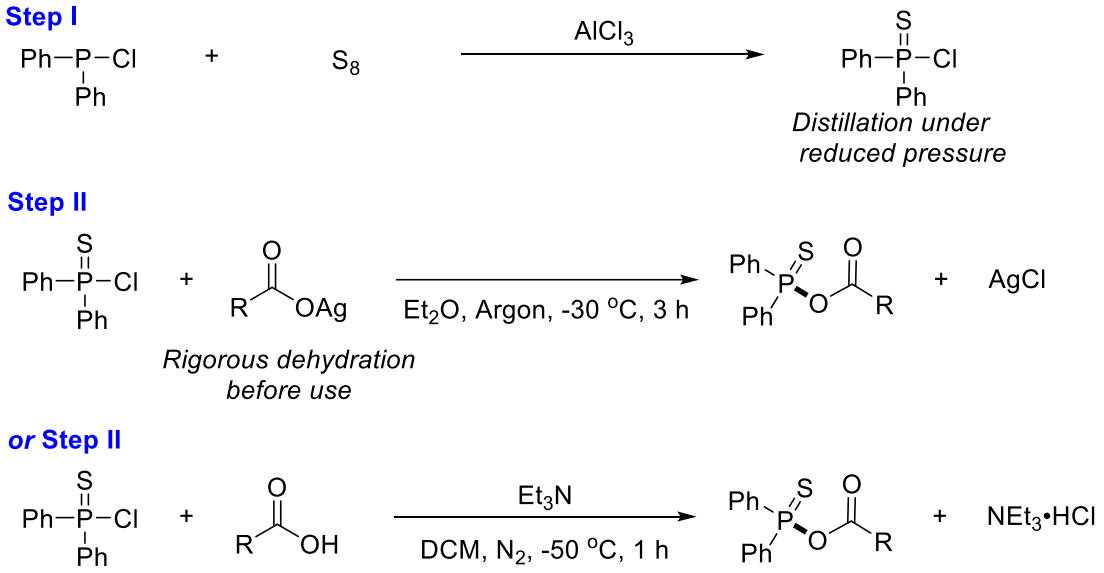
Ibuprofen (49.5 mg, 0.24 mmol, 1.0 equiv.) was dissolved in anhydrous dichloromethane (DCM, 2 mL). The resulting colorless solution was cooled to 0 °C, and one drop of DMF was added as a catalyst. Thionyl chloride (34.5 mg, 0.29 mmol, 1.2 equiv.) was then added dropwise to the mixture. After complete addition, the reaction mixture was allowed to warm slowly to room temperature and stirred for an additional 12 h. Volatile components were subsequently removed under reduced pressure, and the residue was reserved for later use.



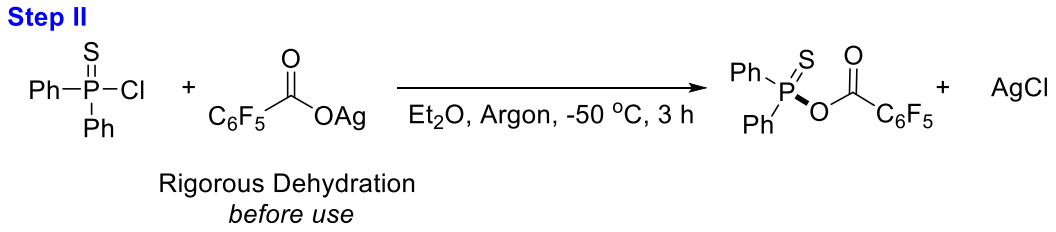
A Schlenk tube equipped with a magnetic stir bar was evacuated and refilled with nitrogen three times. Under a nitrogen atmosphere, P(O)H compound (**2a**, 0.2 mmol), S_8 (12.8 mg, 0.05 mmol) or selenium powder (31.6 mg, 0.4 mmol), and 2-(4-isobutylphenyl)propanoyl chloride (**1y**, 0.2 mmol) were sequentially added to the reaction vessel. Finally, ethyl acetate (1 mL) was introduced. The reaction mixture was stirred at 60 °C for 12 hours using an IKA magnetic stirrer equipped with a nine-well aluminum heating block. After complete consumption of the starting material, the mixture was quenched with water (3.0 mL) and extracted three times with ethyl acetate (10 mL each time). The combined organic layers were washed with saturated sodium chloride solution (10 mL) and dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the resulting residue was purified by flash column chromatography using petroleum ether/ethyl acetate (20:1, v/v) as the eluent to afford the pure products **6a** and **6b**.

4. Comparison between the conventional Sartori method and this work

(A) *Z. Naturforsch.*, 1984, *39b*, 284-289



(B) *J. Fluorine Chem.*, 1985, *27*, 193-201



Scheme S1. Prior work reported by the Sartori group (A: *Z. Naturforsch. B*, **1984**, *39B*, 284; B: *J. Fluorine Chem.*, **1985**, *27*, 193-201)

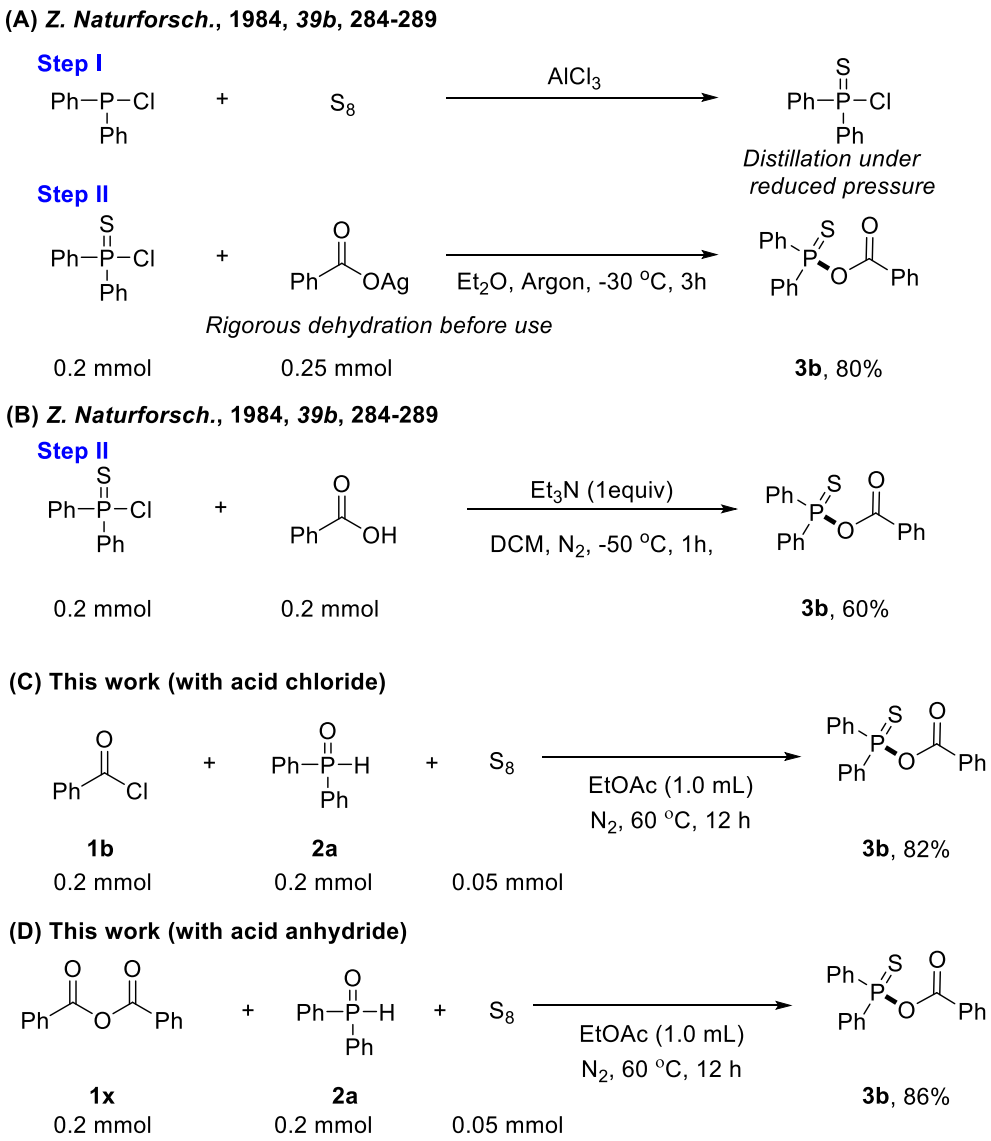
Table S1. Comparison between the Conventional Sartori Method and This Work

Comparison Dimension	**Sartori's Method A (Scheme S1A**, *Z. Naturforsch. B*, **1984**, *39B*, 284)[4]	**Sartori's Method B (Scheme S1B,** *J. Fluorine Chem.*, **1985**, *27*, 193-201)[5]	**This Work: Catalyst-Free Three-Component Coupling**	**Green Advantage Highlighted**
Key Steps & Process	● Synthesis of $Ph_2P(S)Cl$: Requires handling of corrosive PCl_3/S_8 or similar; isolation with reduced pressure distillation. ● Coupling: Reaction with carboxylate (Ag salt) or carboxylic acid (with Et_3N).	*same as left*	● One-pot, three-component coupling of $R_2P(O)H$, elemental chalcogen (S_8/Se), and acylating agents.	● **Avoids the step-wise synthesis**, isolation, and handling of sensitive P(S)Cl intermediates. ● **Reduces purification steps and associated waste.**
Key Reagents	● $Ph_2P(S)Cl$ (sensitive, moisture-sensitive, pre-synthesis) ● Stoichiometric Ag salts (expensive, heavy metal) or Stoichiometric Et_3N (base, requires removal)	*same as left*	● **Elemental S_8 or Se** (bench-stable, low-cost); ● Acyl chlorides/ anhydrides and *H*-Phosphine Oxides (commercially available or easily prepared).	● **Benign & Atom-Economic Reagents**: Replaces stoichiometric heavy metal (Ag) with benign elements. ● **Avoids specialized, toxic thionation reagents** (*e.g.*, Lawesson's and P_4S_{10}).
Chalcogen Source	● Pre-installed in P(S)Cl reagent (requires prior S incorporation)	*same as left*	● Elemental S_8 or Se directly used, without pre-activation.	● **Simpler & Greener Sourcing**: Employs the most atom-economical and fundamental form of sulfur/selenium.

Typical Conditions	● Requires anhydrous conditions, inert atmosphere for P(S)Cl; ● Highly hazardous solvent (Et_2O) or hazardous solvent DCM;[6] ● Sub-zero temperatures.	*same as left*	● Requires N_2 atmosphere, 60 °C in EtOAc.	● **Comparable Operational Simplicity**: Both require controlled conditions, but our method avoids the most sensitive intermediate (P(S)Cl)
Waste Profile	● Stoichiometric inorganic waste (AgCl) or ammonium salts (from $Et_3N{\cdot}HCl$).	*same as left*	● Main by-products: HCl and/or H_2O. ● Co-products from possible anhydride intermediate are benign or recyclable in the cycle.	● **Reduced & Less Hazardous Waste**: Avoids heavy metal waste (AgCl). Primary waste is simple inorganic acid/water, easier to treat. |
Overall Green Assessment	A reliable, classic method but involves multi-step synthesis, stoichiometric metal/base, and generation of heavy metal waste.	*same as left*	A concise, one-pot protocol that uses benign elements as chalcogen sources, avoids metals, and minimizes stoichiometric by-products.	● **Provides a potential cleaner and more atom-efficient pathway** to the same $(Ar)_2P(S)OCOR$ scaffold, ● **aligning with multiple Green Chemistry Principles** (Prevention, Atom Economy, Less Hazardous Synthesis).

5. Calculation of green metrics

5.1. Synthesis of compound 3b: literature method *vs*. this work.



Scheme S2. Synthesis of compound **3b**: literature method[4] *vs*. this work.

5.2. Calculations

Table S2. Material statement

Entry	Substrate 1	Substrate 2	Substrate 3	Additive	Yield	Product
Ag salt method[4]	$Ph_2P(S)Cl$, 0.2 mmol, MW 252.70, 50.5 mg	PhCOOAg, 0.25 mmol, MW 228.98, 57.2 mg	-	-	80%	**3b**, 0.16 mmol, MW 338.36, 54.1 mg
PhCOOH mehod[4]	$Ph_2P(S)Cl$, 0.2 mmol, MW 252.70, 50.5 mg	PhCOOH, 0.2 mmol, MW 122.12, 24.4 mg	-	Et_3N, 0.2 mmol, MW 101.19, 20.2 mg	60%	**3b**, 0.12 mmol, MW 338.36, 40.6 mg
This work (with acid chloride)	PhCOCl, 0.2 mmol, MW 140.57, 28.1 mg	$Ph_2P(O)H$, 0.2 mmol, MW 202.19, 40.4 mg	S_8, 0.05 mmol, MW 256, 12.8 mg	-	82%	**3b**, 0.164 mmol, MW 338.36, 55.5 mg
This work (with acid anhydride)	$(PhCO)_2O$, 0.2 mmol, MW 226.23, 45.2 mg	$Ph_2P(O)H$, 0.2 mmol, MW 202.19, 40.4 mg	S_8, 0.05 mmol, MW 256, 12.8 mg	-	86%	**3b**, 0.172 mmol, MW 338.36, 58.2 mg

Environmental fact, *E*-factor

◆ ***E-factor (reagents only) = [m (staring materials)-m (product)]/m (product)***

E1 = (50.5 + 57.2 – 54.1)/54.1 = 0.99

E2 = (50.5 + 24.4 + 20.2 – 40.6)/40.6 = 1.34

E3 = (28.1 + 40.4 + 12.8 – 55.5)/55.5 = 0.46

E4 = (45.2 + 40.4 + 12.8 – 58.2)/58.2 = 0.69

◆ ***E-factor (operational) = total mass of waste/mass of product***

*E1*** = {[*m* ($Ph_2P(S)Cl$, Et_2O solution, 2 mL) + *m* (PhCOOAg, Et_2O solution, 4 mL) + *m* (precipitator, PE, 4 mL)] – [*m* (product) + *m* (recovered Et_2O ~95%) + *m* (recovered PE ~95%)

= (0.0505 + 0.0572 + 0.71*6 + 0.65*4) - (0.0541 + 0.71*6*0.95 + 0.65*4*0.95)/ 0.0541

= (6.9677 -6.5711)/ 0.0541

= 7.33

**Since the original literature (Sartori method[4]) does not provide the specific data required to estimate the first step, this calculation excludes the waste generated therein. If that step were included, the reported AE value would be higher.

E3 = {[*m* (**1b**) + *m* (**2a**) + *m* (**S8**) + *m* (solvent EtOAc, 1 mL) + *m* (extration EtOAc) + *m* (NaCl aq) +*m* (anhydrous Na_2SO_4) +*m* (silica gel) + *m* (eluent: PE:EA = 20:1, 105 mL)] - [*m* (product) + *m* (recovered solvent EtOAc ~95%) + *m* (recovered extration EtOAc ~95%) + *m* (recovered NaCl aq ~90%) + *m* (recovered eluent ~95%)]}/*m* (product)

= {[0.0281 + 0.0404 + 0.0128 + 0.902*1 + 0.902*30 + 10*36% + 0.5 + 3 + (0.65*100 + 0.902*5)] – [0.0555 + 0.902*1*0.95+ 0.902*30*0.95 + 10*36%*0.90 + (0.65*100*0.95 + 0.902*5*0.95)]}/ 0.0555

= (104.6533 – 95.8939) / 0.0555

= 211.88

Atom economy, AE

AE = MW (product)/MW (staring materials) × 100%

AE1 = 338.36/(252.70 + 228.98) = 70%**

AE2 = 338.36/(252.70 + 122.12+101.19) = 71%**

AE3 = 338.36/(140.57 + 202.19+1/8*256) = 90%

AE4 = 338.36/(226.23 + 202.19+1/8*256) = 73%

** This AE calculation for the Sartori method[4] starts from $Ph_2P(S)Cl$. The overall AE, if including the synthesis of this reagent, would be lower.

Reaction mass efficiency, **RME**

RME = m (product)/total mass of reactants × 100%

RME1 = 54.1/(50.5 + 57.2) = 50%

RME2 = 40.6/(50.5 + 24.4)= 54%

RME3 = 55.5/(28.1 + 40.4 + 12.8) = 68%

RME4 =58.2/(45.2 + 40.4 + 12.8) = 59%

Optimum efficiency, **OE**

OE = RME/AE × 100%

OE*1* = 50%/70% = 71%

OE2 = 54%/71% = 76%

OE3 = 68%/90% = 76%

OE4 = 59%/93% = 63%

To determine the ***E*-factor (reagents only)**, we mainly assumed the reaction profile considering that the solvent could be recovered and the least amounts of waste/by-products produced. The eluent, petroleum ether and ethyl acetate was recovered and reused for the column chromatography; the amount of water used in the work-up procedure is not accounted. To determine the ***E*-factor (operational)**, we assumed a 95%

recovery rate for all reaction solvents, precipitation solvents, and column chromatography eluents, and a 90% recovery rate for saturated NaCl solution. Water used in the work-up procedure was not accounted for.

Notably, in evaluating the green chemistry metrics of our method, we aimed to ensure a fair and reproducible comparison with the literature procedures. For the silver carboxylate route reported by Sartori *et al.*,[4] the literature specifies that PhCOOAg was employed in a 10–40% excess; a value of 25% excess was adopted for this calculation. The reported yield for product **3b** in this route ranges from 70% to 90%, and the midpoint value of 80% was used. For the alternative carboxylic acid/Et_3N route,[4] the yield of **3b** is documented between 40% and 80%, and a value of 60% was taken in our assessment.

5.3. Discussion

The direct comparison of operational *E*-factors initially appears unfavorable to the present method. However, this result merits contextualization, as it reflects a fundamental difference in purification strategy rather than a disparity in the intrinsic greenness of the chemical transformations themselves.

The literature method benefits from purification by precipitation—a inherently low-solvent and highly efficient process. This is feasible because the products described in that work possess physical properties conducive to such isolation (*e.g.*, high crystallinity, low solubility in common organic solvents) and were typically prepared on a 2 mmol scale. In contrast, the present study aims to demonstrate a broad substrate scope and to ensure high purity for full characterization—a standard expectation in modern synthetic methodology. To meet this requirement, flash column chromatography was employed for all products. While this technique is essential for ensuring generality and analytical rigor, it is notably solvent-intensive and substantially inflates the operational *E*-factor.

It is important to recognize that the principal green merits of this approach arise

from the bond-forming event itself, independent of the laboratory-scale purification protocol. To support this, we draw attention to the reagents-only *E*-factor (0.46). This metric isolates the efficiency of the chemical reaction, demonstrating that our transformation generates significantly less inherent waste than the Sartori methods (0.99 and 1.34) at the bond-forming stage. This high atom economy and low reagent waste are direct consequences of our catalyst-free, additive-free design and the use of benign elemental chalcogens.

In a future industrial or process-scale setting, where continuous chromatography or crystallization optimization could be pursued, the operational *E*-factor of our method could be drastically reduced. Accordingly, both the reagents-only and operational *E*-factors are now presented in **Table 6** (manuscript), with clear labels and defined system boundaries, and a detailed breakdown of the calculations is provided in the Supporting Information. We hope this transparent and contextualized presentation allows readers to appreciate the genuine green merits of our chemistry while acknowledging the practical realities of laboratory-scale purification.

6. Bioactivity investigation

Cell Culture

HepG2 and LX2 cells were cultured in DMEM medium supplemented with 10% fetal bovine serum (FBS) and 1% penicillin-streptomycin. The cells were maintained at 37 °C in a humidified incubator with 5% CO_2.

Cell Proliferation Assay of HepG2 Cells

HepG2 cells were seeded at a density of 2×10^4 cells/mL, with 100 μL of cell suspension added to each well of a 96-well plate. After 24 hours of incubation, 10 μM of the compound was introduced, followed by an additional 24-hour culture period. After compounds treatment, 10 μL of CCK-8 reagent (Beyotime, China, C0039) was added to each well. The plate was then incubated at 37°C for 1 hour. Absorbance values at 450 nm and 650 nm were measured. Relative HepG2 cell viability was calculated by subtracting the OD_{650} value from the OD_{450} value, and then normalizing the data to the control group.

Cell Toxicity Test of LX2 Cells

Cell viability was determined by crystal violet staining. Briefly, LX2 cells were seeded at a density of 2×10^5 cells/mL. After 24 hours of incubation, 10 μM of the compound was added into media, and then incubated for 24 hours. Next, the media was removed, and then 4% paraformaldehyde was added to fix the cells for 5 min. Cells were stained with 100 μL 0.05% crystal violet for 15 min and washed with water 2 times. 100 μL of ethanol was added to each well, and the plate was incubated for 15 min at room temperature. Absorbance at 590 nm was measured. The LX2 cell viability was normalized the data to the control group. The therapeutic index (TI) was calculated by dividing the viability of LX2 cells by the viability of HepG2 cells.

Table S3. Cell viability data

No	HepG2 viability at 10 μM (%)[a]	LX2 viability at 10 μM (%)[b]	TI[c]
3f	93.77 ± 6.24	114.13 ± 24.65	1.22 ± 0.34
3g	97.36 ± 6.28	123.82 ± 24.72	1.27 ± 0.34
3m	90.99 ± 12.52	137.62 ± 13.75	1.51 ± 0.36
3p	87.43 ± 1.85	127.05 ± 18.42	1.45 ± 0.24
4g	87.21 ± 0.86	102.20 ± 18.48	1.17 ± 0.22

[a]The HepG2 cells were treated with 10 μM of the compounds for 24 h. Subsequently, CCK8 was added and the cells were incubated for 30 min. The absorbance values at OD450 - OD650 were measured and then normalized to those of the control group for calculation of cell viability. [b]The LX2 cells were treated with 10 μM of the compound for 24 h. Subsequently, 0.05% crystal violet solution was added, and the cells were incubated for 10 min. The absorbance values at 590 nm were measured and then normalized to those of the control group for calculation of cell viability. [c]The therapeutic index (TI) was calculated by dividing the viability of LX2 cells treated with 10 μM of the compound by that of HepG2 cells treated with the same concentration (10 μM).

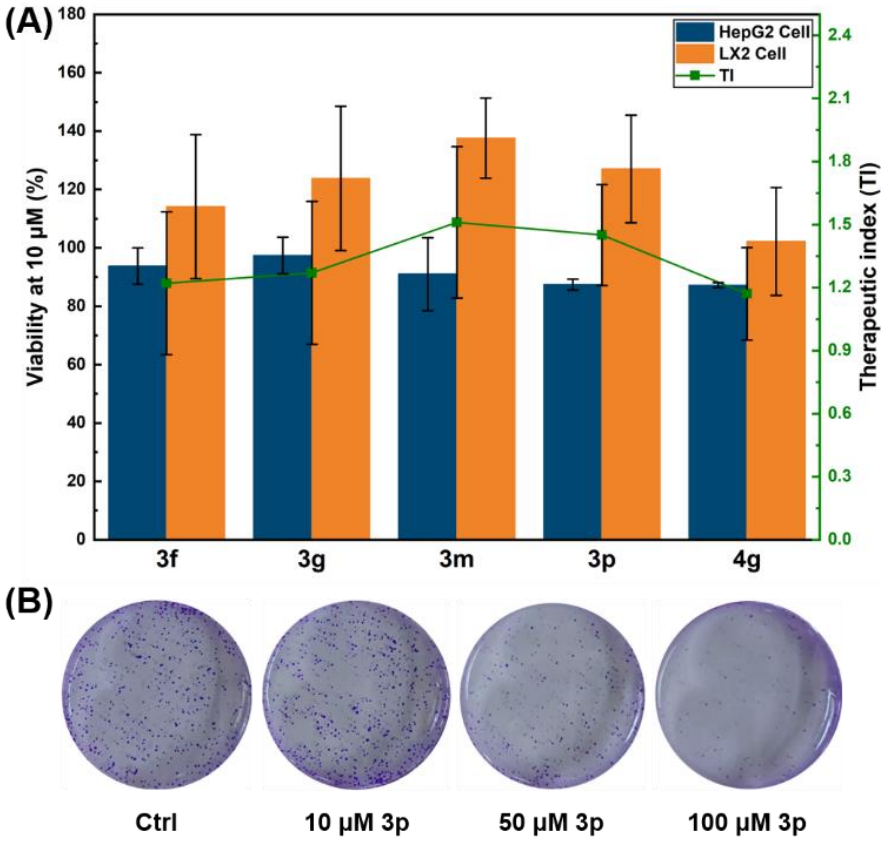


Figure S2. Bioactivity investigation of selected compounds.

7. X-ray information for compound 5f

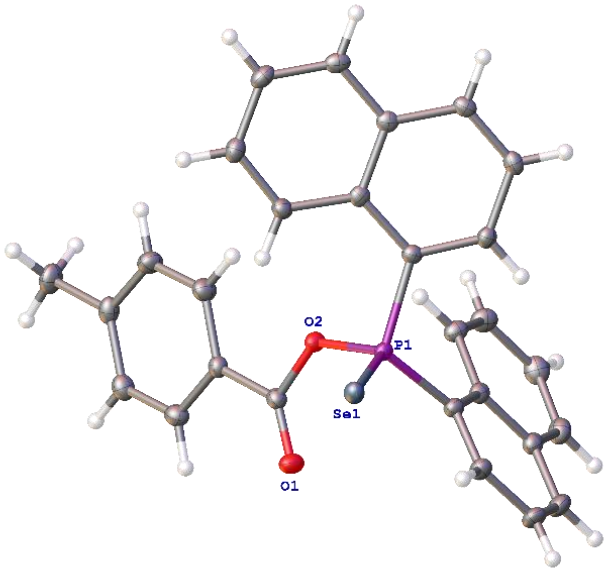


Figure S3. X-ray information for compound **5f** (CCDC: 2497078)

Table S4 Crystal data and structure refinement for compound 5f.

Identification code	**5f**
Empirical formula	$C_{28}H_{21}O_2PSe$
Formula weight	499.38
Temperature/K	120.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.20299(15)
b/Å	13.2426(2)
c/Å	16.7176(3)
α/°	90
β/°	91.5224(14)
γ/°	90
Volume/Å^3	2258.00(6)
Z	4
ρ_{calc}g/cm^3	1.469
μ/mm^{-1}	3.103

F(000)	1016.0
Crystal size/mm^3	0.15 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.52 to 145.882
Index ranges	-11 ≤ h ≤ 12, -15 ≤ k ≤ 16, -20 ≤ l ≤ 19
Reflections collected	17321
Independent reflections	4341 [R_{int} = 0.0317, R_{sigma} = 0.0315]
Data/restraints/parameters	4341/0/290
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0303, wR_2 = 0.0708
Final R indexes [all data]	R_1 = 0.0387, wR_2 = 0.0738
Largest diff. peak/hole / e Å^{-3}	0.36/-0.45

Crystal structure determination of compound 5f

Crystal Data for $C_{28}H_{21}O_2PSe$ (*M* = 499.38 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 10.20299(15) Å, *b* = 13.2426(2) Å, *c* = 16.7176(3) Å, *β* = 91.5224(14), *V* = 2258.00(6) Å^3, *Z* = 4, *T* = 120.00(10) K, μ(Cu Kα) = 3.103 mm^{-1}, *Dcalc* = 1.469 g/cm^3, 17321 reflections measured (8.52° ≤ 2Θ ≤ 145.882°), 4341 unique (R_{int} = 0.0317, R_{sigma} = 0.0315) which were used in all calculations. The final R_1 was 0.0303 (I > 2σ(I)) and wR_2 was 0.0738 (all data).

Refinement model description

Table S5 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 44166_SE. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Se1	5897.7(2)	3937.2(2)	4486.4(2)	21.37(8)
P1	6548.5(5)	4940.1(4)	3621.8(3)	16.99(12)
O1	3843.4(15)	5659.7(12)	3082.5(10)	27.3(4)
O2	5853.6(14)	6061.8(11)	3597.7(9)	20.2(3)
C1	4331(2)	7385.0(17)	3425.8(13)	20.0(5)
C2	5263(2)	8046.0(18)	3757.1(14)	26.2(5)
C3	4989(2)	9069.3(18)	3806.4(15)	27.1(5)
C4	3799(2)	9461.7(17)	3526.7(14)	24.0(5)
C5	2873(2)	8794.6(18)	3194.3(14)	25.5(5)
C6	3130(2)	7768.8(18)	3147.4(14)	24.1(5)
C7	4586(2)	6285.5(17)	3344.3(13)	20.0(5)
C8	6371(2)	4461.9(16)	2605.1(13)	19.5(5)
C9	5865(2)	3503.7(17)	2519.4(14)	22.6(5)
C10	5657(2)	3059.5(18)	1765.1(14)	26.0(5)
C11	5929(2)	3592.0(18)	1091.8(15)	26.7(5)
C12	6437(2)	4588.6(17)	1141.2(13)	21.6(5)
C13	6726(2)	5131.2(19)	437.4(14)	26.7(5)
C14	7257(2)	6076.3(19)	480.5(15)	28.6(5)
C15	7495(2)	6526.4(18)	1234.8(14)	26.7(5)
C16	7209(2)	6033.3(17)	1927.3(14)	22.2(5)
C17	6675(2)	5040.9(16)	1906.5(13)	19.6(5)
C18	3536(3)	10584.5(18)	3577.0(16)	31.5(6)
C19	8211(2)	5360.1(16)	3819.7(12)	16.8(4)
C20	9185(2)	5012.2(16)	3334.0(13)	18.4(4)
C21	10518(2)	5250.3(17)	3498.4(13)	20.1(5)
C22	10853(2)	5828.4(16)	4148.3(13)	19.2(4)
C23	9884(2)	6198.5(15)	4668.1(13)	17.9(4)
C24	8538(2)	5964.9(15)	4511.5(12)	17.0(4)
C25	7605(2)	6334.6(16)	5057.3(13)	20.3(5)
C26	7989(2)	6916.4(17)	5702.5(13)	23.3(5)

Table S5 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 44166_SE. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C27	9311(2)	7153.2(17)	5848.2(13)	22.7(5)
C28	10242(2)	6795.1(16)	5343.0(13)	20.8(5)

Table S6 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 44166_SE. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Se1	21.49(13)	19.21(13)	23.62(13)	-1.64(10)	4.67(9)	-1.0(1)
P1	16.7(3)	14.0(3)	20.3(3)	-2.6(2)	-0.3(2)	0.4(2)
O1	21.7(8)	21.6(8)	38.2(10)	-5.8(7)	-5.6(7)	-0.2(7)
O2	17.6(7)	16.1(7)	26.8(8)	-3.3(6)	-3.5(6)	3.6(6)
C1	19.6(11)	19.2(11)	21.1(11)	-0.5(9)	1.3(9)	2.6(9)
C2	21.9(12)	22.8(12)	33.7(13)	-0.9(10)	-2.7(10)	3.1(10)
C3	26.3(12)	20.6(12)	34.4(13)	-2.7(10)	-1.4(10)	-2.2(10)
C4	29.6(12)	19.0(11)	23.8(12)	2.6(9)	6.7(10)	3.7(10)
C5	24.6(12)	24.6(12)	27.4(12)	3.6(10)	1.9(10)	5.6(10)
C6	21.1(11)	25.1(12)	25.9(12)	1.2(10)	-1.8(9)	-0.6(10)
C7	17.8(11)	21.3(12)	20.8(11)	-0.6(9)	0.1(9)	2.0(9)
C8	18.4(11)	16.7(11)	23.4(12)	-3.1(9)	-1.4(9)	0.4(9)
C9	24.1(12)	18.0(11)	25.8(12)	-2.3(9)	0.7(9)	-1.2(9)
C10	27.0(12)	18.0(11)	32.9(13)	-7.6(10)	-1.2(10)	-3.5(10)
C11	29.3(13)	23.4(12)	27.1(13)	-8.8(10)	-3.4(10)	0.0(10)
C12	20.8(11)	20.4(11)	23.4(12)	-2.4(9)	-1.4(9)	3.3(9)
C13	29.4(13)	29.4(13)	21.2(12)	-1.4(10)	-0.9(10)	5.1(10)
C14	31.4(13)	28.3(13)	26.0(12)	7.6(11)	1.3(10)	5.9(11)
C15	29.1(13)	19.4(12)	31.3(13)	4.2(10)	-3.1(10)	-0.8(10)
C16	24.7(11)	18.1(11)	23.5(11)	0.1(9)	-4.7(9)	0.9(9)
C17	18.4(11)	17.5(11)	22.7(11)	-1.2(9)	-2.3(9)	3.9(9)
C18	39.7(15)	19.4(12)	35.7(14)	-0.6(11)	5.6(12)	6.6(11)
C19	16.9(10)	14.2(10)	19.4(11)	2.1(8)	-0.6(8)	0.4(8)
C20	21.0(11)	14.5(10)	19.8(11)	0.3(9)	0.7(8)	1.8(9)

Table S6 Anisotropic Displacement Parameters ($Å^2×10^3$) for 44166_SE. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C21	19.6(11)	19.7(11)	21.2(11)	5.3(9)	4.4(9)	3.1(9)
C22	16.9(10)	17.5(11)	23.0(11)	5.9(9)	-0.8(8)	-0.4(9)
C23	20.8(11)	13.7(10)	19.0(11)	5.2(8)	-0.8(8)	0.5(9)
C24	20.1(11)	12.2(10)	18.8(10)	3.7(8)	0.0(8)	1.2(8)
C25	17.4(11)	19.0(11)	24.4(12)	-0.4(9)	-0.1(9)	1.6(9)
C26	28.7(12)	19.6(11)	21.7(11)	-1.1(9)	1.7(9)	4.5(10)
C27	30.9(12)	17.1(11)	19.8(11)	-1.4(9)	-4.3(9)	0.3(9)
C28	23.8(11)	14.9(10)	23.5(11)	5.2(9)	-5.3(9)	-2.2(9)

Table S7 Bond Lengths for compound 5f.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Se1	P1	2.0844(6)	C11	C12	1.419(3)
P1	O2	1.6461(15)	C12	C13	1.416(3)
P1	C8	1.818(2)	C12	C17	1.428(3)
P1	C19	1.807(2)	C13	C14	1.365(3)
O1	C7	1.198(3)	C14	C15	1.410(3)
O2	C7	1.382(3)	C15	C16	1.367(3)
C1	C2	1.396(3)	C16	C17	1.423(3)
C1	C6	1.395(3)	C19	C20	1.379(3)
C1	C7	1.486(3)	C19	C24	1.439(3)
C2	C3	1.387(3)	C20	C21	1.415(3)
C3	C4	1.390(3)	C21	C22	1.365(3)
C4	C5	1.398(3)	C22	C23	1.421(3)
C4	C18	1.514(3)	C23	C24	1.425(3)
C5	C6	1.386(3)	C23	C28	1.417(3)
C8	C9	1.376(3)	C24	C25	1.423(3)
C8	C17	1.438(3)	C25	C26	1.374(3)
C9	C10	1.403(3)	C26	C27	1.400(3)
C10	C11	1.363(3)	C27	C28	1.372(3)

Table S8 Bond Angles for compound 5f.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	P1	Se1	116.55(6)	C11	C12	C17	119.7(2)
O2	P1	C8	105.02(9)	C13	C12	C11	120.5(2)
O2	P1	C19	97.37(9)	C13	C12	C17	119.8(2)
C8	P1	Se1	113.62(7)	C14	C13	C12	120.8(2)
C19	P1	Se1	112.58(7)	C13	C14	C15	119.6(2)
C19	P1	C8	110.36(10)	C16	C15	C14	121.3(2)
C7	O2	P1	126.85(14)	C15	C16	C17	120.7(2)
C2	C1	C7	122.1(2)	C12	C17	C8	118.0(2)
C6	C1	C2	119.1(2)	C16	C17	C8	124.3(2)
C6	C1	C7	118.7(2)	C16	C17	C12	117.7(2)
C3	C2	C1	120.0(2)	C20	C19	P1	118.49(16)
C2	C3	C4	121.4(2)	C20	C19	C24	120.27(19)
C3	C4	C5	118.2(2)	C24	C19	P1	120.98(16)
C3	C4	C18	120.2(2)	C19	C20	C21	121.0(2)
C5	C4	C18	121.6(2)	C22	C21	C20	119.9(2)
C6	C5	C4	121.0(2)	C21	C22	C23	121.1(2)
C5	C6	C1	120.3(2)	C22	C23	C24	119.71(19)
O1	C7	O2	122.8(2)	C28	C23	C22	120.7(2)
O1	C7	C1	126.9(2)	C28	C23	C24	119.60(19)
O2	C7	C1	110.26(18)	C23	C24	C19	118.04(19)
C9	C8	P1	116.50(17)	C25	C24	C19	124.2(2)
C9	C8	C17	119.7(2)	C25	C24	C23	117.72(19)
C17	C8	P1	123.72(16)	C26	C25	C24	121.0(2)
C8	C9	C10	121.9(2)	C25	C26	C27	121.0(2)
C11	C10	C9	119.7(2)	C28	C27	C26	119.7(2)
C10	C11	C12	121.0(2)	C27	C28	C23	121.0(2)

Table S9 Torsion Angles for compound 5f.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Se1	P1	O2	C7	-71.10(18)	C10	C11	C12	C13	179.5(2)
Se1	P1	C8	C9	-1.3(2)	C10	C11	C12	C17	0.4(3)
Se1	P1	C8	C17	175.97(16)	C11	C12	C13	C14	-177.7(2)

Table S9 Torsion Angles for compound 5f.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Se1	P1	C19	C20	108.69(16)	C11	C12	C17	C8	-0.7(3)
Se1	P1	C19	C24	-65.43(18)	C11	C12	C17	C16	178.8(2)
P1	O2	C7	O1	-2.4(3)	C12	C13	C14	C15	-1.3(4)
P1	O2	C7	C1	179.27(14)	C13	C12	C17	C8	-179.8(2)
P1	C8	C9	C10	178.71(18)	C13	C12	C17	C16	-0.3(3)
P1	C8	C17	C12	-177.33(16)	C13	C14	C15	C16	0.2(4)
P1	C8	C17	C16	3.2(3)	C14	C15	C16	C17	0.8(4)
P1	C19	C20	C21	-174.91(16)	C15	C16	C17	C8	178.7(2)
P1	C19	C24	C23	174.80(15)	C15	C16	C17	C12	-0.8(3)
P1	C19	C24	C25	-4.3(3)	C17	C8	C9	C10	1.3(3)
O2	P1	C8	C9	-129.84(17)	C17	C12	C13	C14	1.3(3)
O2	P1	C8	C17	47.5(2)	C18	C4	C5	C6	179.6(2)
O2	P1	C19	C20	-128.49(17)	C19	P1	O2	C7	169.07(17)
O2	P1	C19	C24	57.39(18)	C19	P1	C8	C9	126.20(18)
C1	C2	C3	C4	-0.4(4)	C19	P1	C8	C17	-56.5(2)
C2	C1	C6	C5	0.5(3)	C19	C20	C21	C22	0.3(3)
C2	C1	C7	O1	178.6(2)	C19	C24	C25	C26	-179.4(2)
C2	C1	C7	O2	-3.1(3)	C20	C19	C24	C23	0.8(3)
C2	C3	C4	C5	0.3(4)	C20	C19	C24	C25	-178.3(2)
C2	C3	C4	C18	-179.1(2)	C20	C21	C22	C23	0.1(3)
C3	C4	C5	C6	0.3(4)	C21	C22	C23	C24	0.0(3)
C4	C5	C6	C1	-0.7(4)	C21	C22	C23	C28	179.77(19)
C6	C1	C2	C3	0.0(3)	C22	C23	C24	C19	-0.4(3)
C6	C1	C7	O1	-2.7(4)	C22	C23	C24	C25	178.75(19)
C6	C1	C7	O2	175.61(19)	C22	C23	C28	C27	-179.9(2)
C7	C1	C2	C3	178.8(2)	C23	C24	C25	C26	1.5(3)
C7	C1	C6	C5	-178.3(2)	C24	C19	C20	C21	-0.7(3)
C8	P1	O2	C7	55.61(19)	C24	C23	C28	C27	-0.1(3)
C8	P1	C19	C20	-19.4(2)	C24	C25	C26	C27	-0.8(3)
C8	P1	C19	C24	166.46(16)	C25	C26	C27	C28	-0.4(3)
C8	C9	C10	C11	-1.6(4)	C26	C27	C28	C23	0.8(3)
C9	C8	C17	C12	-0.1(3)	C28	C23	C24	C19	179.81(19)
C9	C8	C17	C16	-179.6(2)	C28	C23	C24	C25	-1.0(3)

Table S9 Torsion Angles for compound 5f.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C9	C10	C11	C12	0.8(4)					

Table S10 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for compound 5f.

Atom	*x*	*y*	*z*	U(eq)
H2	6085.1	7794.81	3948.86	31
H3	5627.59	9511.65	4036.27	33
H5	2054.96	9048.05	2997.62	31
H6	2485.8	7325.19	2924.88	29
H9	5650.05	3132.61	2984.31	27
H10	5327.05	2390.04	1723.56	31
H11	5776.35	3291.57	581.79	32
H13	6549.04	4833.49	-71.04	32
H14	7464.14	6428.73	5.3	34
H15	7862.21	7185.23	1262.47	32
H16	7368.44	6356.83	2427.65	27
H18A	3610.77	10802.68	4136.57	47
H18B	2650.36	10727.83	3366.33	47
H18C	4177.81	10950.05	3260.86	47
H20	8958.44	4606.75	2882.45	22
H21	11177.72	5008.18	3157.03	24
H22	11749.16	5985.87	4254.71	23
H25	6703.09	6176.91	4974.48	24
H26	7346.98	7161.79	6055.17	28
H27	9562.93	7559.67	6294.69	27
H28	11139.32	6949.47	5447.06	25

Experimental

Single crystals of $C_{28}H_{21}O_2PSe$ (compound **5f**) were prepared by dissolving the compound in *n*-hexane and ethyl acetate, followed by saturation and precipitation at low temperature in a refrigerator. A suitable crystal was selected and measured on a

ROD, Synergy Custom system, HyPix-Arc 150 diffractometer. The crystal was kept at 120.00(10) K during data collection.

8. X-ray information for compound 7

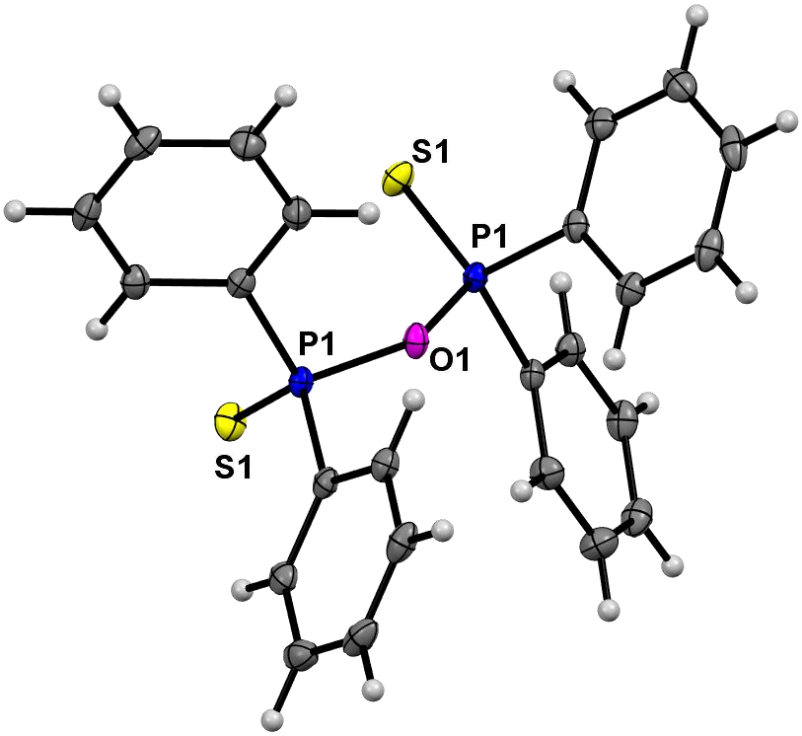


Figure S4. X-ray information for compound **7** (CCDC: 2483557)

Table S11 Crystal data and structure refinement for compound 7.

Identification code	**7**
Empirical formula	$C_{24}H_{20}OP_2S_2$
Formula weight	450.46
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	15.2303(11)
b/Å	9.0769(5)
c/Å	17.0558(13)
α/°	90
β/°	113.675(9)
γ/°	90
Volume/Å^3	2159.4(3)
Z	4
ρ_{calc}g/cm^3	1.386

μ/mm^{-1}	0.408
F(000)	936.0
Crystal size/mm^3	0.16 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.216 to 52.738
Index ranges	-18 ≤ h ≤ 18, -9 ≤ k ≤ 11, -21 ≤ l ≤ 16
Reflections collected	8844
Independent reflections	2193 [R_{int} = 0.0498, R_{sigma} = 0.0403]
Data/restraints/parameters	2193/0/132
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0317, wR_2 = 0.0861
Final R indexes [all data]	R_1 = 0.0346, wR_2 = 0.0883
Largest diff. peak/hole / e Å^{-3}	0.39/-0.38

Table S12 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for compound 7. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
P1	4963.7(3)	1643.4(4)	6608.0(2)	13.08(13)
S1	4288.6(3)	-192.8(4)	6236.4(3)	20.17(14)
O1	5000	2336.9(16)	7500	16.1(3)
C1	6207.1(11)	1608.2(16)	6767.6(10)	14.1(3)
C8	4815.3(11)	4616.4(17)	6163.4(11)	17.7(3)
C7	4441.5(11)	3198.0(17)	5915.7(10)	15.0(3)
C12	3684.7(11)	2984.1(18)	5125.7(11)	18.4(3)
C6	6894.8(12)	2485.4(18)	7386.3(11)	19.7(3)
C2	6469.8(11)	771.4(17)	6208.7(10)	17.8(3)
C3	7407.2(12)	811.6(18)	6267.9(11)	20.3(3)
C9	4421.2(12)	5803.7(18)	5620.6(12)	21.9(4)
C4	8083.4(12)	1687.4(18)	6881.4(12)	21.6(4)
C11	3294.0(12)	4183(2)	4586.9(11)	23.1(4)
C10	3662.5(12)	5589.0(19)	4838.1(12)	23.6(4)
C5	7830.4(12)	2519.1(19)	7441.0(11)	23.4(4)

Table S13 Anisotropic Displacement Parameters ($Å^2×10^3$) for compound 7. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P1	15.4(2)	11.3(2)	14.9(2)	-0.51(13)	8.53(17)	-0.50(13)
S1	22.5(2)	13.6(2)	26.1(3)	-3.35(15)	11.50(19)	-4.34(14)
O1	22.4(8)	13.3(7)	17.3(8)	0	12.9(7)	0
C1	16.0(7)	12.8(7)	15.7(7)	2.9(5)	8.6(6)	0.9(5)
C8	18.3(8)	16.8(8)	20.8(8)	-0.5(6)	10.9(7)	0.7(6)
C7	16.0(7)	16.1(8)	16.9(7)	1.2(6)	10.9(6)	1.9(5)
C12	16.5(7)	22.5(8)	19.3(8)	-1.6(6)	10.4(6)	0.1(6)
C6	20.2(8)	21.1(8)	19.4(8)	-3.5(6)	9.6(7)	0.5(6)
C2	21.4(8)	14.7(8)	19.0(8)	-0.4(6)	9.9(7)	-0.4(6)
C3	24.5(8)	17.5(8)	25.1(9)	1.5(6)	16.4(7)	4.5(6)
C9	25.6(9)	16.2(8)	32.3(9)	3.3(7)	20.3(8)	2.9(6)
C4	18.2(8)	20.5(9)	29.5(9)	5.2(6)	13.3(7)	3.5(6)
C11	18.8(8)	32.6(10)	18.9(8)	4.2(7)	8.6(7)	5.3(7)
C10	25.7(9)	25.2(9)	27.7(9)	12.2(7)	18.8(8)	10.9(7)
C5	19.1(8)	24.2(9)	26.0(9)	-3.4(7)	8.3(7)	-3.2(6)

Table S14 Bond Lengths for compound 7.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	S1	1.9270(5)	C7	C12	1.391(2)
P1	O1	1.6268(7)	C12	C11	1.394(2)
P1	C1	1.8020(16)	C6	C5	1.391(2)
P1	C7	1.8066(16)	C2	C3	1.391(2)
C1	C6	1.399(2)	C3	C4	1.386(3)
C1	C2	1.397(2)	C9	C10	1.384(3)
C8	C7	1.402(2)	C4	C5	1.387(2)
C8	C9	1.390(2)	C11	C10	1.391(3)

Table S15 Bond Angles for compound 7.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	P1	S1	117.10(5)	C12	C7	P1	120.01(12)
O1	P1	C1	103.09(5)	C12	C7	C8	119.89(15)
O1	P1	C7	98.61(7)	C7	C12	C11	119.87(15)
C1	P1	S1	115.08(5)	C5	C6	C1	119.99(15)

Table S15 Bond Angles for compound 7.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	P1	C7	105.83(7)	C3	C2	C1	120.21(15)
C7	P1	S1	115.08(6)	C4	C3	C2	119.98(15)
P1	O1	P1[1]	134.47(10)	C10	C9	C8	120.20(16)
C6	C1	P1	121.80(12)	C3	C4	C5	120.26(15)
C2	C1	P1	118.56(12)	C10	C11	C12	120.04(16)
C2	C1	C6	119.42(14)	C9	C10	C11	120.24(15)
C9	C8	C7	119.77(15)	C4	C5	C6	120.14(16)
C8	C7	P1	120.08(12)				

[1]1-X,+Y,3/2-Z

Table S16 Torsion Angles for compound 7.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
P1	C1	C6	C5	-174.59(13)	C1	C2	C3	C4	-0.2(2)
P1	C1	C2	C3	174.77(12)	C8	C7	C12	C11	-0.7(2)
P1	C7	C12	C11	-178.93(12)	C8	C9	C10	C11	-0.5(2)
S1	P1	O1	P1[1]	32.97(2)	C7	P1	O1	P1[1]	156.97(5)
S1	P1	C1	C6	-148.46(12)	C7	P1	C1	C6	83.29(14)
S1	P1	C1	C2	36.91(14)	C7	P1	C1	C2	-91.34(13)
S1	P1	C7	C8	173.72(11)	C7	C8	C9	C10	0.0(2)
S1	P1	C7	C12	-8.04(14)	C7	C12	C11	C10	0.2(2)
O1	P1	C1	C6	-19.76(15)	C12	C11	C10	C9	0.4(2)
O1	P1	C1	C2	165.61(12)	C6	C1	C2	C3	0.0(2)
O1	P1	C7	C8	48.29(13)	C2	C1	C6	C5	0.0(2)
O1	P1	C7	C12	-133.46(12)	C2	C3	C4	C5	0.4(3)
C1	P1	O1	P1[1]	-94.47(5)	C3	C4	C5	C6	-0.4(3)
C1	P1	C7	C8	-58.03(14)	C9	C8	C7	P1	178.83(12)
C1	P1	C7	C12	120.21(13)	C9	C8	C7	C12	0.6(2)
C1	C6	C5	C4	0.2(3)					

[1]1-X,+Y,3/2-Z

Table S17 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for compound 7.

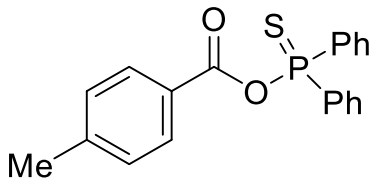
Atom	*x*	*y*	*z*	U(eq)
H8	5336.03	4765.22	6700.3	21

Table S17 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for compound 7.

Atom	*x*	*y*	*z*	U(eq)
H12	3434.66	2022.95	4953.62	22
H6	6722.62	3058.09	7769	24
H2	6006.69	173.23	5786.81	21
H3	7584.22	239	5888.18	24
H9	4673.36	6765.38	5787.17	26
H4	8722.51	1718.1	6918.78	26
H11	2775.75	4039.02	4047.86	28
H10	3392.47	6405.01	4471.31	28
H5	8297.42	3112.98	7862.41	28

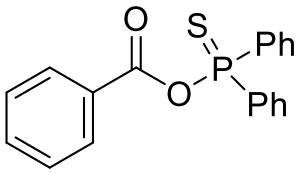
9. Analytical data for the compounds

4-Methylbenzoic diphenylphosphinothioic anhydride (3a)



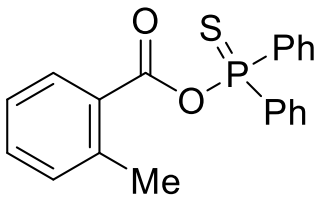
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3a** (56.0 mg, 0.159 mmol, 80%) as a white solid. mp: 103.7-105.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.77 (m, 6H), 7.42 – 7.31 (m, 6H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, *J* = 8.0 Hz), 145.5, 133,3 (d, *J* = 109.0 Hz), 132.2, (d, *J* = 3.1 Hz), 131.1 (d, *J* = 11.9 Hz), 130.6, 129.5, 128.6 (d, *J* = 14.0 Hz), 126.2 (d, *J* = 3.5 Hz), 21.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}O_2PS$ 353.0760; Found 353.0762.

Benzoic diphenylphosphinothioic anhydride (3b)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3b** (55.3 mg, 0.164 mmol, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.96 (m, 6H), 7.66 – 7.46 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (d, *J* = 8.0 Hz), 134.5, 133.3 (d, *J* = 109.5 Hz), 132.4 (d, *J* = 3.1 Hz), 131.3 (d, *J* = 11.9 Hz), 130.7, 129.1 (d, *J* = 3.3 Hz), 128.8 (d, *J* = 3.6 Hz), 128.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}O_2PS$ 339.0603; Found 339.0601.

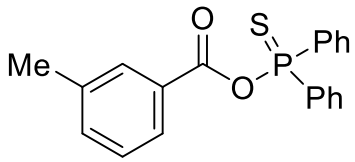
2-Methylbenzoic diphenylphosphinothioic anhydride (3c)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3c** (51.6 mg, 0.146 mmol, 73%) as a colorless oil.

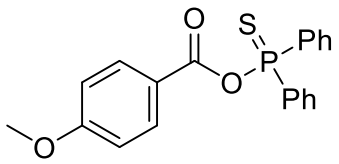
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.92 (m, 5H), 7.59 – 7.41 (m, 7H), 7.31 – 7.25 (m, 2H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (d, *J* = 7.9 Hz), 142.7, 134.1, 132.99 (d, *J* = 133.0 Hz), 132.97, 132.3 (d, *J* = 0.6 Hz), 131.6, 131.2 (d, *J* = 11.9 Hz), 128.7 (d, *J* = 13.9 Hz), 127.8 (d, *J* = 3.1 Hz), 126.2, 22.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 77.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}O_2PS$ 353.0760; Found 353.0764.

3-Methylbenzoic diphenylphosphinothioic anhydride (3d)



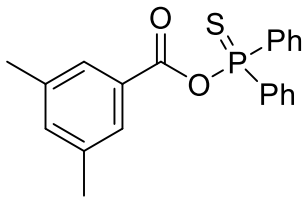
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3d** (53.8 mg, 0.153 mmol, 76%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 14.2, 7.0 Hz, 4H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.58 – 7.43 (m, 7H), 7.37 (t, *J* = 7.5 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (d, *J* = 8.1 Hz), 138.7, 135.3, 133.4 (d, *J* = 111.1 Hz), 132.3 (d, *J* = 3.1 Hz), 131.2 (d, *J* = 11.9 Hz), 131.1, 129.0 (d, *J* = 3.3 Hz), 128.7 (d, *J* = 14.14 Hz), 128.2 (d, *J* = 9.4 Hz), 21.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}O_2PS$ 353.0760; Found 353.0765.

4-Methoxybenzoic diphenylphosphinothioic anhydride (3e)



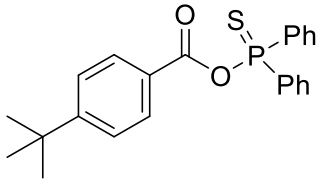
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3e** (60.0 mg, 0.163 mmol, 81%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 6H), 7.54 – 7.49 (m, 5H), 6.95 (d, *J* = 8.9 Hz, 3H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 161.6 (d, *J* = 7.7 Hz), 134.1, 133.0, 132.3 (d, *J* = 3.1 Hz), 131.3 (d, *J* = 11.9 Hz), 130.9 (d, *J* = 49.8 Hz), 128.7 (d, *J* = 13.9 Hz), 121.4 (d, *J* = 3.5 Hz), 114.2 (d, *J* = 12.1 Hz), 55.7 (d, *J* = 4.7 Hz), 29.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 77.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}O_3PS$ 369.0709; Found 369.0706.

3,5-Dimethylbenzoic diphenylphosphinothioic anhydride (3f)



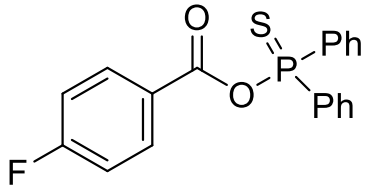
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3f** (55.8 mg, 0.152 mmol, 76%) as a white solid. mp: 136.6-138.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 4H), 7.59 (s, 2H), 7.52 – 7.37 (m, 6H), 7.18 (s, 1H), 2.28 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 8.1 Hz), 136.2, 133.4 (d, *J* = 110.1 Hz), 132.4 (d, *J* = 3.1 Hz), 131.3 (d, *J* = 11.9 Hz), 129.0 (d, *J* = 3.3 Hz), 128.7 (d, *J* = 13.9 Hz), 128.4, 21.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}O_2PS$ 367.0916; Found 367.0919.

4-(Tert-butyl)benzoic diphenylphosphinothioic anhydride (3g)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3g** (55.0 mg, 0.140 mmol, 70%) as a white solid. mp: 125.8-127.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 6H), 7.52 (m, *J* = 18.1, 10.6, 4.6 Hz, 8H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (d, *J* = 8.0 Hz), 158.5, 133.5 (d, *J* = 110.7 Hz), 132.4 (d, *J* = 3.1 Hz), 131.3 (d, *J* = 11.9 Hz), 130.6, 128.7 (d, *J* = 13.9 Hz), 126.3 (d, *J* = 3.6 Hz), 125.9, 35.4, 31.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 77.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{24}O_2PS$ 395.1229; Found 395.1226.

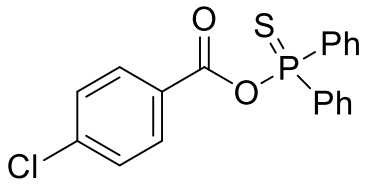
4-Fluorobenzoic diphenylphosphinothioic anhydride (3h)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3h** (55.6 mg, 0.156 mmol, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.7, 5.4 Hz, 2H), 8.04 – 7.96 (m, 4H), 7.59 – 7.49 (m, 6H), 7.15 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ166.7 (d,

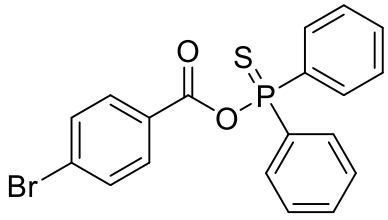
J = 256.8 Hz), 161.0 (d, *J* = 7.9 Hz), 133.7, 133.4 (d, *J* = 9.7 Hz), 132.6, 132.5 (d, *J* = 3.1 Hz), 131.3 (d, *J* = 12.0 Hz), 131.0 (d, *J* = 9.5 Hz), 128.8 (d, *J* = 14.0 Hz), 125.4 (dd, *J* = 6.3 Hz, *J* = 3.1 Hz), 116.2 (d, *J* = 22.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 79.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.50 HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}FO_2PS$ 357.0509; Found 357.0506.

4-Chlorobenzoic diphenylphosphinothioic anhydride (3i)



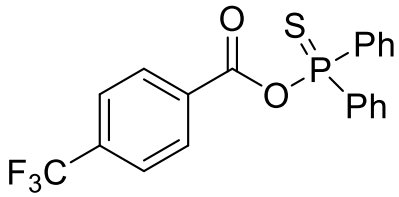
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3i** (58.3 mg, 0.156 mmol, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 6H), 7.61 – 7.49 (m, 6H), 7.47 – 7.43 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, *J* = 8.0 Hz), 141.2, 133.7, 132.5 (d, *J* = 3.2 Hz), 132.0, 131.3 (d, *J* = 12.0 Hz), 129.3, 128.8 (d, *J* = 14.0 Hz), 127.6 (d, *J* = 3.4 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ 79.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H15ClO_2PS$ 373.0213; Found 373.0217.

4-Bromobenzoic diphenylphosphinothioic anhydride(3j)



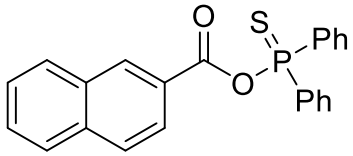
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3j** (63.4 mg, 0.152 mmol, 76%) as a white solid. mp: 108.7-109.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 4H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.56 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.52 (dd, *J* = 7.7, 3.8 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, *J* = 7.9 Hz), 133.2 (d, *J* = 110.2 Hz), 132.6 (d, *J* = 3.1 Hz), 132.3, 132.1, 131.4, 131.3, 130.0, 129.6, 128.8 (d, *J* = 14.0 Hz), 128.1 (d, *J* = 3.4 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ 79.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}BrO_2PS$ 416.9708; Found 416.9705.

4-(Trifluoromethyl)benzoic diphenylphosphinothioic anhydride (3k)



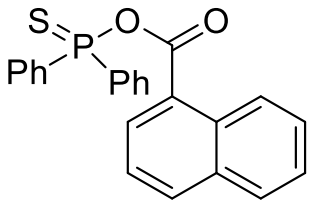
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3k** (65.1 mg, 0.160 mmol, 80%) as a white solid. mp: 110.9-112.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 21.0, 8.2 Hz, 2H), 8.03 – 7.87 (m, 4H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.61 – 7.50 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9 (d, *J* = 7.8 Hz), 135.7 (d, *J* = 32.9 Hz), 132.9 (d, *J* = 110.4 Hz), 132.7 (d, *J* = 3.1 Hz), 132.4, 131.34 (d, *J* = 12.0 Hz), 131.1, 130.7, 128.9 (d, *J* = 14.0 Hz), 125.9 (d, *J* = 11.2 Hz), 126.0 (d, *J* = 3.7 Hz), 123.5 (d, *J* = 274.0 Hz), 29.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 80.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}F_3O_2PS$ 407.0477; Found 407.0480.

2-Naphthoic diphenylphosphinothioic anhydride (3l)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3l** (52.6 mg, 0.135 mmol, 68%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.12 – 8.01 (m, 5H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.91 (dd, *J* = 8.4, 3.5 Hz, 2H), 7.68 – 7.62 (m, 1H), 7.61 – 7.49 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 8.0 Hz), 136.2, 133.9, 132.9 (d, *J* = 5.9 Hz), 132.5 (d, *J* = 3.1 Hz), 132.4, 131.4 (d, *J* = 11.9 Hz), 129.5 (d, *J* = 48.4 Hz), 128.9, 128.8, 128.7, 127.6 (d, *J* = 82.7 Hz), 126.3 (d, *J* = 3.3 Hz), 125.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}O_2PS$ 389.0760; Found 389.0764.

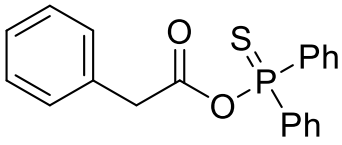
1-Naphthoic diphenylphosphinothioic anhydride (3m)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3m** (54.2 mg, 0.140 mmol, 70%) as a white solid.

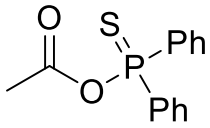
mp: 95.4-96.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 8.7, 1.3 Hz, 1H), 8.41 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.14 – 8.00 (m, 5H), 7.90 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.62 – 7.48 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 7.9 Hz), 135.6, 134.0 (d, *J* = 11.6 Hz), 133.0, 132.4 (d, *J* = 2.8 Hz), 131.9, 131.3 (d, *J* = 11.9 Hz), 128.808 (d, *J* = 14.0 Hz), 128.803 (d, *J* = 5.6 Hz), 126.3 (d, *J* = 101.2 Hz), 124.8 (d, *J* = 3.2 Hz), 124.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}O_2PS$ 389.0760; Found 389.0765.

2-Phenylacetic diphenylphosphinothioic anhydride (3n)



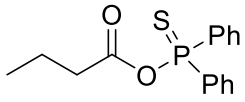
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3n** (53.8 mg, 0.153 mmol, 76%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 14.2, 7.9 Hz, 4H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.32 – 7.24 (m, 7H), 7.19 – 7.16 (m, 2H), 3.71 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3 (d, *J* = 9.3 Hz), 133.6, 132.5 (d, *J* = 5.0 Hz), 132.3 (d, *J* = 3.1 Hz), 131.1 (d, *J* = 12.0 Hz), 129.1 (d, *J* = 97.0 Hz), 128.7 (d, *J* = 40.4 Hz), 127.7, 43.0 (d, *J* = 2.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 77.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}O_2PS$ 353.0760; Found 353.0763.

Acetic diphenylphosphinothioic anhydride (3o)



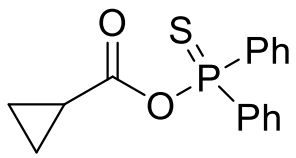
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3o** (31.6 mg, 0.114 mmol, 57%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 4H), 7.55 – 7.45 (m, 6H), 2.27 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 133.1 (d, *J* = 110.1 Hz), 132.3 (d, *J* = 3.1 Hz), 131.2 (d, *J* = 11.9 Hz), 128.5 (d, *J* = 27.5 HZ), 128.4, 23.0 (d, *J* = 2.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 77.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}O_2PS$ 277.0447; Found 277.0445.

Butyric diphenylphosphinothioic anhydride (3p)



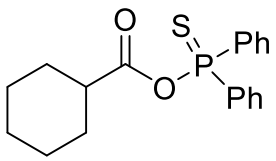
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3p** (39.7 mg, 0.130 mmol, 65%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.85 (m, 4H), 7.55 – 7.44 (m, 6H), 2.51 (t, *J* = 7.3 Hz, 2H), 1.70 (q, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7 (d, *J* = 9.2 Hz), 133.4 (d, *J* = 109.8 Hz), 132.3 (d, *J* = 3.1 Hz), 131.2 (d, *J* = 11.9 Hz), 128.7 (d, *J* = 13.9 Hz), 37.9 (d, *J* = 2.4 Hz), 18.1, 13.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 76.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}O_2PS$ 305.0760; Found 305.0763.

Cyclopropanecarboxylic diphenylphosphinothioic anhydride (3q)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3q** (25.4 mg, 0.084 mmol, 42%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.85 (m, 4H), 7.55 – 7.44 (m, 6H), 1.82 – 1.75 (m, 1H), 1.15 (m, *J* = 4.2, 3.8 Hz, 2H), 1.01 (m, *J* = 7.8, 4.6, 4.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0 (d, *J* = 8.3 Hz), 133.4 (d, *J* = 110.1 Hz), 132.3 (d, *J* = 3.1 Hz), 131.2 (d, *J* = 11.9 Hz), 128.7 (d, *J* = 13.9 Hz), 14.6 (d, *J* = 4.0 Hz), 10.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 76.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}O_2PS$ 303.0603; Found 303.0601.

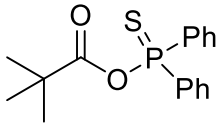
Cyclohexanecarboxylic diphenylphosphinothioic anhydride (3r)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3r** (43.2 mg, 0.125 mmol, 63%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 4H), 7.54 – 7.43 (m, 6H), 2.58 – 2.43 (m, 1H), 2.05 – 1.97 (m, 2H), 1.77 (dd, *J* = 12.9, 3.7 Hz, 2H), 1.64 (dd, *J* = 11.3, 4.0 Hz, 1H), 1.55 – 1.45 (m, 2H), 1.35 – 1.20 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9 (d, *J* = 9.4 Hz), 133.4 (d, *J* = 109.8 Hz), 132.2 (d, *J* = 3.1

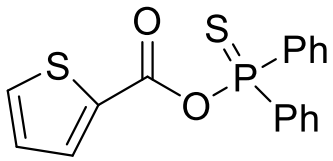
Hz), 131.1 (d, J = 11.9 Hz), 128.6 (d, J = 13.9 Hz), 44.3 (d, J = 2.2 Hz), 28.5, 25.6, 25.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 76.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}O_2PS$ 345.1073; Found 345.1076.

Diphenylphosphinothioic pivalic anhydride (3s)



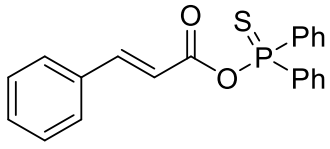
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3s** (43.5 mg, 0.137 mmol, 68%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 4H), 7.56 – 7.44 (m, 6H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4 (d, J = 9.7 Hz), 133.6 (d, J = 110.0 Hz), 132.3 (d, J = 3.1 Hz), 131.1 (d, J = 11.8 Hz), 128.7 (d, J = 13.9 Hz), 40.4 (d, J = 2.2 Hz), 26.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 76.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}O_2PS$ 319.0916; Found 319.0912.

Diphenylphosphinothioic thiophene-2-carboxylic anhydride (3t)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3t** (46.8 mg, 0.136 mmol, 68%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.90 (m, 4H), 7.77 (dd, J = 8.0, 4.2 Hz, 3H), 7.70 – 7.48 (m, 2H), 7.27 – 7.14 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 142.0, 135.7, 135.5 (d, J = 107.8 Hz), 134.0, 132.5 (d, J = 3.2 Hz), 131.3 (d, J = 12.0 Hz), 128.8, 128.7, 128.4.^{31}P NMR (162 MHz, $CDCl_3$) δ 78.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}O_2PS_2$ 345.0167; Found 345.0169.

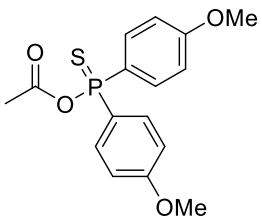
(E)-Cinnamic diphenylphosphinothioic anhydride (3u)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3u** (52.5 mg, 0.144 mmol, 72%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$)

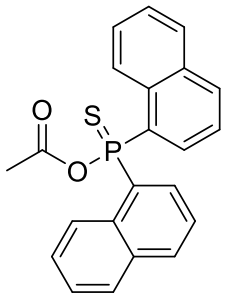
δ 7.97 (m, *J* = 14.2, 8.3, 1.5 Hz, 4H), 7.77 (d, *J* = 15.9 Hz, 1H), 7.58 – 7.47 (m, 8H), 7.41 (d, *J* = 7.4 Hz, 3H), 6.51 (dd, *J* = 15.9, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 148.8,133.8, 133.5 (d, *J* = 110.4 Hz), 132.4 (d, *J* = 3.2 Hz), 131.42, 131.38, 131.3, 129.2, 128.8, 128.7 (d, *J* = 4.2 Hz), 117.2 (d, *J* = 4.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 77.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}O_2PS$ 365.0760; Found 365.0763.

Acetic bis(4-methoxyphenyl)phosphinothioic anhydride(3v)



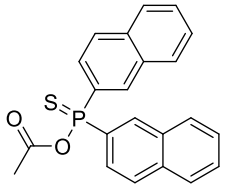
According to the general procedure and work-up, purification by flash column·chromatography using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3v** (59.1 mg, 0.176 mmol, 88%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 13.5, 8.9 Hz, 4H), 6.95 (dd, *J* = 8.9, 2.9 Hz, 4H), 3.84 (s, 6H), 2.23 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (d, *J* = 8.6 Hz), 162.7 (d, *J* = 3.1 Hz), 133.3, 133.1, 124.6 (d, *J* = 117.6 Hz), 114.0 (d, *J* = 15.3 Hz), 55.5, 23.0 (d, *J* = 2.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 77.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}O_4PS$ 337.0658; Found 337.0654.

Acetic di(naphthalen-1-yl)phosphinothioic anhydride (3w)



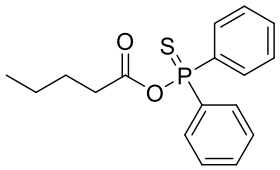
According to the general procedure and work-up, purification by flash column·chromatography using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3w** (63.9 mg, 0.170 mmol, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.5 Hz, 2H), 8.31 (dd, *J* = 19.5, 7.1 Hz, 2H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.59 – 7.42 (m, 6H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (d, *J* = 8.9 Hz), 134.6, 134.5, 134.2 (d, *J* = 3.3 Hz), 134.1 (d, *J* = 10.3 Hz), 131.6 (d, *J* = 9.1 Hz), 129.5, 129.5, 128.8 (d, *J* = 106.2 Hz), 127.5, 126.5, 126.2 (d, *J* = 5.6 Hz), 124.9 (d, *J* = 17.0 Hz), 22.9 (d, *J* = 2.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.1. $[M+H]^+$ Calcd for $C_{22}H_{18}O_2PS$ 377.0760; Found 377.0764.

Aceticdi(naphthalen-2-yl)phosphinothioic anhydride (3x)



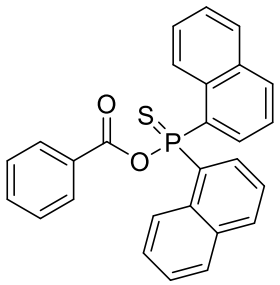
According to the general procedure and work-up, purification by flash column·chromatography using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3x** (60.2 mg, 0.160 mmol, 80%) as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 16.8 Hz, 2H), 7.98 – 7.83 (m, 8H), 7.62 – 7.54 (m, 4H), 2.34 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1 (d, *J* = 8.6 Hz), 134.9 (d, *J* = 2.7 Hz), 133.7 (d, *J* = 12.6 Hz), 132.4 (d, *J* = 15.8 Hz), 130.3 (d, *J* = 110.8 Hz), 129.4, 128.7, 128.6, 127.9, 127.3, 125.8 (d, *J* = 11.8 Hz), 23.2 (d, *J* = 2.7 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ 77.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}O_2PS$ 377.0760; Found 377.0763.

Pentanoic diphenylphosphinothioic anhydride (3y)



According to the general procedure and work-up, purification by flash column·chromatography using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3y** (52.9 mg, 0.166 mmol, 83%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.83 (m, 4H), 7.49 (m, *J* = 18.6, 10.9, 4.6 Hz, 6H), 2.53 (t, *J* = 7.4 Hz, 2H), 1.71 – 1.59 (m, 2H), 1.36 (q, *J* = 7.5 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8 (d, *J* = 9.1 Hz), 133.3 (d, *J* = 109.9 Hz), 132.3 (d, *J* = 3.1 Hz), 131.2, 131.1, 128.7, 128.5, 35.7 (d, *J* = 2.4 Hz), 26.5, 22.1, 13.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 76.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}O_2PS$ 319.0916; Found 319.0914.

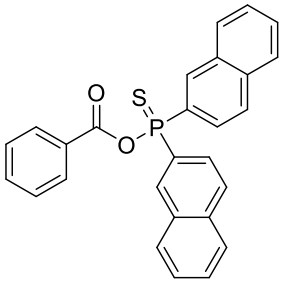
Benzoic di(naphthalen-1-yl)phosphinothioic anhydride (3z)



According to the general procedure and work-up, purification by flash column·chromatography using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3z** (72.8 mg, 0.166 mmol, 83%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.6 Hz, 2H), 8.32 (dd, *J* = 19.9, 7.3 Hz, 2H), 8.09 (d, *J* = 8.3 Hz, 2H), 7.97 (dd, *J* = 18.6, 8.0 Hz, 4H), 7.61 – 7.47 (m, 5H), 7.44 – 7.38 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, *J* = 8.2 Hz), 134.7 (d, *J* = 15.4 Hz),

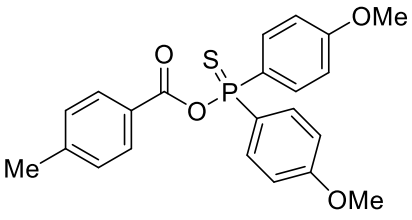
134.3 (d, *J* = 12.5 Hz), 134.1, 134.0, 131.7 (d, *J* = 8.5 Hz), 130.6, 129.5 (d, *J* = 1.7 Hz), 129.0 (d, *J* = 3.3 Hz), 128.7, 128.6 (d, *J* = 106.7 Hz), 127.5, 126.5, 126.4 (d, *J* = 5.5 Hz), 124.9 (d, *J* = 17.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 80.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{20}O_2PS$ 439.0916; Found 439.0913.

Benzoic di(naphthalen-2-yl)phosphinothioic anhydride (3aa)



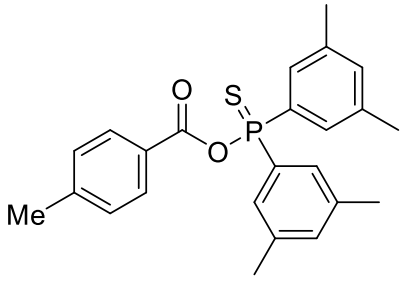
According to the general procedure and work-up, purification by flash column·chromatography using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **3aa** (74.5 mg, 0.170 mmol, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 17.2 Hz, 2H), 8.12 (d, *J* = 7.3 Hz, 2H), 8.03 – 7.92 (m, 6H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.62 (m, *J* = 15.6, 7.0 Hz, 5H), 7.50 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 7.8 Hz), 135.0 (d, *J* = 2.8 Hz), 134.6, 134.1 (d, *J* = 13.6 Hz), 132.4 (d, *J* = 16.0 Hz), 130.8, 130.5 (d, *J* = 98.3 Hz), 129.2 (d, *J* = 53.3 Hz), 128.8, 128.79, 128.7, 127.6 (d, *J* = 60.5 Hz), 125.8 (d, *J* = 11.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 79.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{20}O_2PS$ 439.0916; Found 439.0912.

Bis(4-methoxyphenyl)phosphinothioic 4-methylbenzoic anhydride (4a)



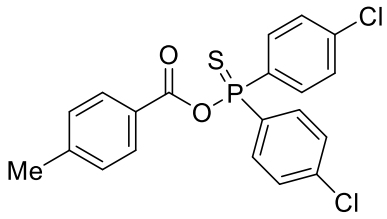
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **4a** (66.8 mg, 0.162 mmol, 81%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.77 (m, 6H), 7.20 – 7.14 (m, 2H), 6.94 – 6.87 (m, 4H), 3.76 (s, 6H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, *J* = 3.1 Hz), 162.1 (d, *J* = 8.1 Hz), 145.4, 133.3 (d, *J* = 13.5 Hz), 130.7, 129.5, 126.6 (d, *J* = 3.4 Hz), 124.9 (d, *J* = 118.3 Hz), 114.2 (d, *J* = 15.2 Hz), 55.5, 21.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{22}O_4PS$ 413.0971; Found 413.0974.

Bis(3,5-dimethylphenyl)phosphinothioic 4-methylbenzoic anhydride (4b)



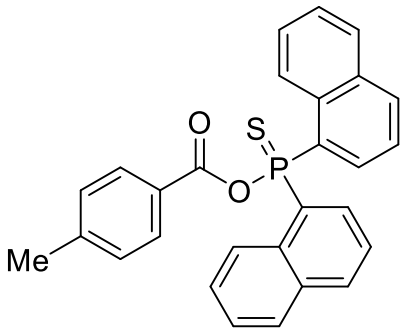
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **4b** (59.4 mg, 0.145 mmol, 73%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 14.5 Hz, 4H), 7.29 (dd, *J* = 8.3, 3.0 Hz, 3H), 7.16 (s, 1H), 2.43 (s, 3H), 2.36 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (d, *J* = 8.1 Hz), 145.4, 138.4 (d, *J* = 14.6 Hz), 134.2 (d, *J* = 3.1 Hz), 133.4 (d, *J* = 108.0 Hz), 130.8, 129.6, 128.8 (d, *J* = 11.8 Hz), 126.7 (d, *J* = 3.4 Hz), 22.0, 21.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 79.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{26}O_2PS$ 409.1386; Found 409.1383.

Bis(4-chlorophenyl)phosphinothioic 4-methylbenzoic anhydride (4c)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **4c** (63.8 mg, 0.151 mmol, 76%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.21 (m, 12H), 2.44 (d, *J* = 3.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.1, 146.0, 145.7, 145.6, 139.3 (d, *J* = 3.7 Hz), 134.7, 132.8, 132.9 (d, *J* = 13.0 Hz), 131.7 (d, *J* = 113.8 Hz), 130.8, 129.76, 129.7, 129.2 (d, *J* = 14.8 Hz), 128.7, 128.4, 127.1, 125.9, 21.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 75.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}Cl_2O_2PS$ 420.9980; Found 420.9983.

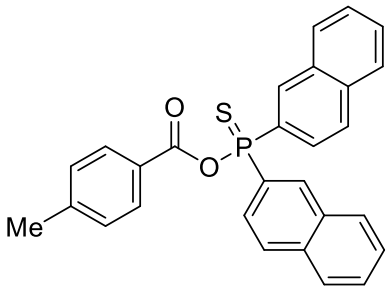
4-Methylbenzoic di(naphthalen-1-yl)phosphinothioic anhydride (4d)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **4d** (69.3 mg, 0.153 mmol, 77%) as a white solid. mp: 188.6-190.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.6 Hz, 2H), 8.30 (dd, *J* = 19.8,

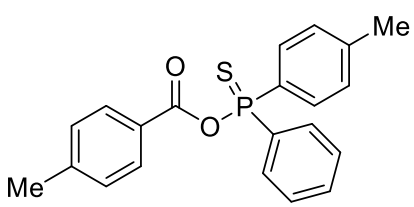
7.1 Hz, 2H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.91 (dd, *J* = 26.9, 8.2 Hz, 4H), 7.57 – 7.48 (m, 4H), 7.44 – 7.39 (m, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, *J* = 8.1 Hz), 145.4, 134.6 (d, *J* = 15.6 Hz), 134.2, 134.1 (d, *J* = 3.4 Hz), 131.8 (d, *J* = 8.5 Hz), 130.8, 129.5, 129.5 (d, *J* = 1.5 Hz), 128.8 (d, *J* = 107.1 Hz), 127.5, 126.5 (d, *J* = 4.0 Hz), 126.3 (d, *J* = 3.4 Hz), 124.9 (d, *J* = 17.2 Hz), 21.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 79.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{22}O_2PS$ 453.1073; Found 453.1070.

4-Methylbenzoic di(naphthalen-2-yl)phosphinothioic anhydride (4e)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **4e** (71.2 mg, 0.157 mmol, 79%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 16.8 Hz, 2H), 8.04 – 7.83 (m, 10H), 7.62 – 7.54 (m, 4H), 7.27 (dd, *J* = 12.0, 4.6 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (d, *J* = 8.0 Hz), 145.7, 134.9 (d, *J* = 2.6 Hz), 133.8 (d, *J* = 12.9 Hz), 132.5 (d, *J* = 15.9 Hz), 130.5 (d, *J* = 111.6 Hz), 130.9, 129.7, 129.4, 128.8, 128.7 (d, *J* = 4.0 Hz), 127.6 (d, *J* = 68.7 Hz), 126.4 (d, *J* = 3.1 Hz), 125.8 (d, *J* = 11.4 Hz), 22.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{22}O_2PS$ 453.1073; Found 453.1075.

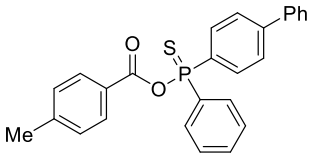
4-Methylbenzoic phenyl(p-tolyl)phosphinothioic anhydride (4f)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **4f** (58.9 mg, 0.161 mmol, 80%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.78 (m, 6H), 7.48 – 7.39 (m, 3H), 7.24 – 7.18 (m, 4H), 2.35 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 7.9 Hz), 145.5, 143.1 (d, *J* = 2.9 Hz), 133.8 (d, *J* = 111.4 Hz), 132.3 (d, *J* = 3.0

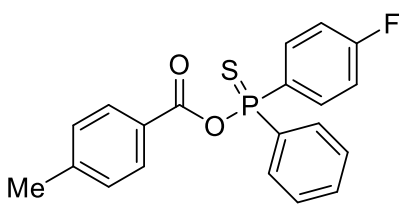
Hz), 131.3 (d, *J* = 33,3 Hz), 131.3 (d, *J* = 9.0 Hz), 130.8, 129.6, 129.4, 128.7 (d, *J* = 13.9 Hz), 126.4 (d, *J* = 3.4 Hz), 22.0, 21.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}O_2PS$ 367.0916; Found 367.0919.

[1,1'-biphenyl]-4-yl(phenyl)phosphinothioic 4-methylbenzoic anhydride (4g)



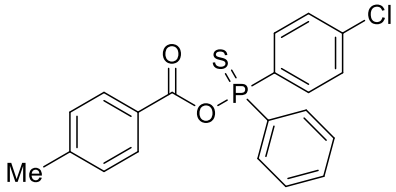
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **4g** (62.2 mg, 0.145 mmol, 73%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.88 (m, 6H), 7.63 – 7.60 (m, 2H), 7.53 – 7.27 (m, 8H), 7.21 – 7.15 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 8.0 Hz), 145.6, 145.1 (d, *J* = 3.1 Hz), 139.8, 133.50 (d, *J* = 110.2 Hz), 132.51, 132.4 (d, *J* = 3.0 Hz), 131.8 (d, *J* = 12.2 Hz), 131.3 (d, *J* = 11.9 Hz), 130.8, 129.8 (d, *J* = 103.0 Hz), 129.6, 129.1, 128.8 (d, *J* = 14.0 Hz), 128.4, 127.5, 127.4 (d, *J* = 5.2 Hz), 126.4 (d, *J* = 3.4 Hz), 22.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 77.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}O_2PS$ 429.1073; Found 429.1076.

(4-Fluorophenyl)(phenyl)phosphinothioic 4-methylbenzoic anhydride (4h)



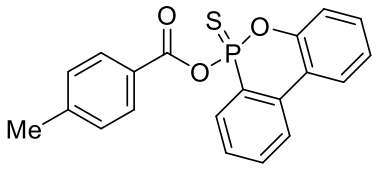
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **4h** (58.0 mg, 0.157 mmol, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.84 (m, 6H), 7.52 – 7.39 (m, 3H), 7.22 – 7.17 (m, 2H), 7.13 – 7.06 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (d, *J* = 259.1 Hz), 161.9 (d, *J* = 7.9 Hz), 145.7, 134.03 (d, *J* = 23.2 Hz), 134.02 (d, *J* = 4.7 Hz), 133.3 (d, *J* = 112.7 Hz), 132.5 (d, *J* = 3.1 Hz), 131.2 (d, *J* = 11.9 Hz), 130.7, 130.0 (d, *J* = 3.4 Hz), 129.6, 128.8 (d, *J* = 14.0 Hz), 126.2 (d, *J* = 3.4 Hz), 116.1 (d, *J* = 36.4 Hz), 116.1 (d, *J* = 6.3 Hz), 22.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 76.7 (d, *J* = 1.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.15, -106.16. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}FO_2PS$ 371.0665; Found 371.0662.

(4-Chlorophenyl)(phenyl)phosphinothioic 4-methylbenzoic anhydride (4i)



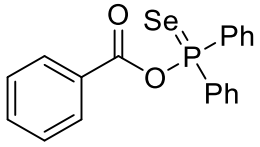
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **4i** (57.2 mg, 0.148 mmol, 74%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 6H), 7.51 – 7.37 (m, 5H), 7.21 – 7.18 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (d, *J* = 7.8 Hz), 145.8, 139.1 (d, *J* = 3.7 Hz), 133.6, 132.8, 132.7, 132.6 (d, *J* = 3.0 Hz), 132.0 (d, *J* = 101.4 Hz) 131.2 (d, *J* = 11.9 Hz), 130.8, 129.7, 129.1, 129.0 (d, *J* = 2.0 Hz), 128.8, 126.1 (d, *J* = 3.6 Hz), 22.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 76.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}ClO_2PS$ 387.0370; Found 387.0374.

6-Sulfidodibenzo[c,e][1,2]oxaphosphinin-6-yl 4-methylbenzoate (4j)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **4j** (59.4 mg, 0.162 mmol, 81%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 17.8, 7.7 Hz, 1H), 7.96 – 7.90 (m, 2H), 7.76 – 7.71 (m, 1H), 7.66 – 7.55 (m, 3H), 7.46 – 7.37 (m, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, *J* = 7.7 Hz), 150.1 (d, *J* = 12.7 Hz), 145.6, 134.7 (d, *J* = 5.4 Hz), 134.0 (d, *J* = 2.7 Hz), 133.2 (d, *J* = 15.9 Hz), 130.8, 130.7, 129.4, 128.6 (d, *J* = 17.2 Hz), 126.7, 125.5 (d, *J* = 4.5 Hz), 125.4 (d, *J* = 1.2 Hz), 125.3, 123.9 (d, *J* = 10.7 Hz), 122.8 (d, *J* = 12.4 Hz), 120.3 (d, *J* = 6.6 Hz), 100.1, 21.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 69.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}O_3PS$ 367.0552; Found 367.0556.

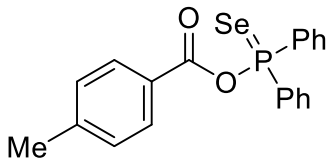
Benzoic diphenylphosphinoselenoic anhydride (5a)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **5a** (58.3 mg, 0.151

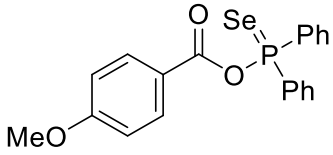
mmol, 76%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.96 (m, 6H), δ 7.75 – 7.61 (m, 1H). 7.57 – 7.45 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (d, J = 7.9 Hz), 134.5, 133.3 (d, J = 97.5 Hz), 132.4 (d, J = 3.2 Hz), 131.3 (d, J = 12.3 Hz), 130.5, 128.9 (d, J = 3.1 Hz), 128.8 (d, J = 8.7 Hz), 128.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 79.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}O_2PSe$ 387.0048; Found 387.0044.

4-Methylbenzoic diphenylphosphinoselenoic anhydride (5b)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **5b** (64.7 mg, 0.162 mmol, 81%) as a white solid. mp: 123.3-124.1 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.85 (m, 6H), 7.48 – 7.35 (m, 6H), 7.21 – 7.15 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, J = 7.8 Hz), 145.6, 133.5 (d, J = 98.0 Hz), 132.4 (d, J = 3.1 Hz), 131.4 (d, J = 12.2 Hz), 130.7, 129.6, 128.7 (d, J = 13.9 Hz), 126.3 (d, J = 3.2 Hz), 21.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}O_2PSe$ 401.0204; Found 401.0207.

4-Methoxybenzoic diphenylphosphinoselenoic anhydride (5c)

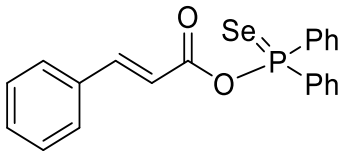


According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **5c** (65.0 mg, 0.157 mmol, 78%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 6H), 7.56 – 7.47 (m, 6H), 6.94 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 161.7 (d, J = 7.9 Hz), 133.7 (d, J = 97.6 Hz), 133.0, 132.4 (d, J = 3.1 Hz), 131.5 (d, J = 12.2 Hz), 128.7 (d, J = 13.8 Hz), 121.3 (d, J = 3.4 Hz), 114.2, 55.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}O_3PSe$ 417.0153; Found 417.0157.

4-Fluorobenzoic diphenylphosphinoselenoic anhydride (5d)

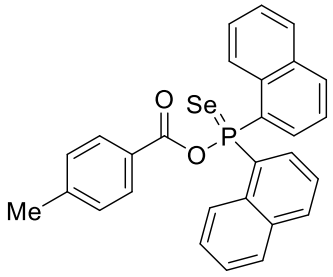
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **5d** (65.3 mg, 0.162 mmol, 81%) as a red oli. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 7.93 (m, 6H), 7.52 (m, *J* = 10.6, 8.7, 7.9, 4.2 Hz, 6H), 7.19 – 7.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6 (d, *J* = 257.5 Hz), 161.1 (d, *J* = 7.7 Hz), 133.3 (d, *J* = 97.0 Hz), 133.4 (d, *J* = 9.7 Hz), 132.5 (d, *J* = 3.1 Hz), 131.4 (d, *J* = 12.3 Hz), 128.7 (d, *J* = 13.9 Hz), 125.3, 116.2 (d, *J* = 22.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 79.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}FO_2PSe$ 404.9953; Found 404.9956.

(E)-Cinnamic diphenylphosphinoselenoic anhydride (5e)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **5e** (58.9 mg, 0.143 mmol, 72%) as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 4H), 7.77 (d, *J* = 15.9 Hz, 1H), 7.52 (m, *J* = 11.5, 7.0, 2.8 Hz, 8H), 7.41 (d, *J* = 7.3 Hz, 3H), 6.50 (dd, *J* = 15.9, 1.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 7.8 Hz), 148.9, 131.7, 133.6 (d, *J* = 97.8 Hz) 131.5, 131.4, 129.2, 128.7 (d, *J* = 4.0 Hz), 128.6, 117.1 (d, *J* = 3.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}O_2PSe$ 413.0204; Found 413.0201.

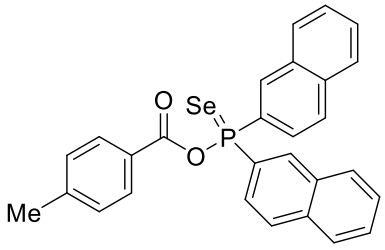
4-Methylbenzoic di(naphthalen-1-yl)phosphinoselenoic anhydride (5f)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **5f** (73.2 mg, 0.147 mmol, 73%) as a white solid. mp: 180.6-182.3 °C ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.5 Hz, 2H), 8.33 (dd, *J* = 20.3, 6.9 Hz, 2H), 8.08 (d,

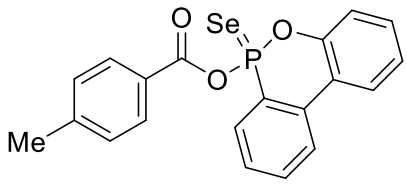
J = 8.2 Hz, 2H), 7.91 (dd, *J* = 27.4, 8.2 Hz, 4H), 7.58 – 7.48 (m, 4H), 7.45 – 7.38 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, *J* = 7.8 Hz), 145.5, 135.1 (d, *J* = 17.0 Hz), 134.3, 134.2 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 7.8 Hz), 130.7, 129.55, 129.45 (d, *J* = 1.4 Hz), 128.5 (d, *J* = 93.9 Hz), 127.4, 126.6, 126.5 (d, *J* = 5.5 Hz), 126.3 (d, *J* = 3.1 Hz), 124.9 (d, *J* = 17.4 Hz), 21.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{22}O_2PSe$ 501.0517; Found 501.0515.

4-Methylbenzoic di(naphthalen-2-yl)phosphinoselenoic anhydride (5g)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **5g** (76.7 mg, 0.154 mmol, 77%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 17.2 Hz, 2H), 7.93 – 7.78 (m, 10H), 7.54 – 7.46 (m, 4H), 7.21 – 7.17 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 7.9 Hz), 145.7, 134.9 (d, *J* = 2.5 Hz), 134.0 (d, *J* = 13.5 Hz), 132.4 (d, *J* = 15.9 Hz), 130.8, 130.6 (d, *J* = 98.7 Hz), 129.5 (d, *J* = 20.8 Hz), 128.7 (d, *J* = 15.2 Hz), 127.6 (d, *J* = 62.9 Hz), 126.4 (d, *J* = 3.0 Hz), 125.8 (d, *J* = 11.6 Hz), 22.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 79.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{22}O_2PSe$ 501.0517; Found 501.0513.

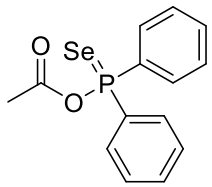
6-Selenidodibenzo[c,e][1,2]oxaphosphinin-6-yl 4-methylbenzoate (5h)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **5h** (69.5 mg, 0.168 mmol, 84%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.25 (m, 1H), 7.84 (dd, *J* = 7.6, 6.4 Hz, 2H), 7.67 – 7.62 (m, 1H), 7.57 – 7.48 (m, 3H), 7.37 – 7.29 (m, 2H), 7.23 – 7.17 (m, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, *J* = 8.1 Hz), 145.7, 134.1 (d, *J* = 2.8 Hz), 133.9 (d, *J* = 18.3 Hz), 133.6 (d, *J* = 4.6 Hz),

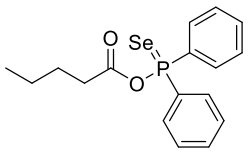
130.8 (d, *J* = 9.5 Hz), 129.4, 128.5 (d, *J* = 17.5 Hz), 125.5 (d, *J* = 4.1 Hz), 125.4 (d, *J* = 2.2 Hz), 123.8 (d, *J* = 10.0 Hz), 122.6 (d, *J* = 12.4 Hz), 120.3 (d, *J* = 6.4 Hz), 21.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 73.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}O_3PSe$ 414.9997; Found 414.9999.

Acetic diphenylphosphinoselenoic anhydride (5i)



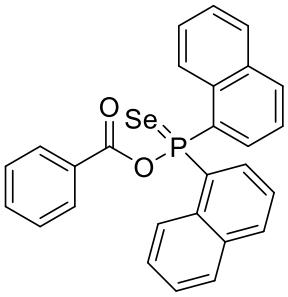
According to the general procedure and work-up, purification by flash column·chromatography using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **5i** (51.7 mg, 0.160 mmol, 80%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 14.4, 7.5 Hz, 4H), 7.58 – 7.40 (m, 6H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (d, *J* = 8.6 Hz), 133.3 (d, *J* = 97.3 Hz), 132.4 (d, *J* = 3.1 Hz), 131.4 (d, *J* = 12.2 Hz), 128.7, 128.6, 23.1 (d, *J* = 2.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 77.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}O_2PSe$ 324.9891; Found 324.9895.

Pentanoic diphenylphosphinoselenoic anhydride (5j)



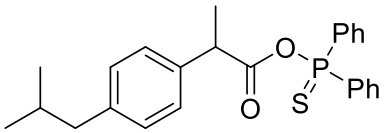
According to the general procedure and work-up, purification by flash column·chromatography using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **5j** (62.8 mg, 0.172 mmol, 86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 4H), 7.53 – 7.44 (m, 6H), 2.53 (m, *J* = 7.5, 0.9 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.41 – 1.31 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9 (d, *J* = 9.1 Hz), 133.4 (d, *J* = 97.1 Hz), 132.4 (d, *J* = 3.3 Hz), 131.4, 131.2, 128.6, 128.5, 35.79 (d, *J* = 2.2 Hz), 26.4, 22.1, 13.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 77.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}O_2PSe$ 367.0361; Found 367.0364.

Benzoic di(naphthalen-1-yl)phosphinoselenoic anhydride (5k)



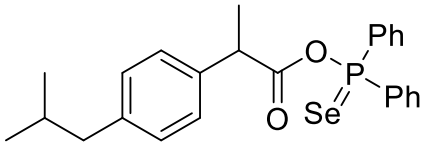
According to the general procedure and work-up, purification by flash column·chromatography using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **5k** (79.6 mg, 0.164 mmol, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.6 Hz, 2H), 8.34 (dd, *J* = 20.5, 7.3 Hz, 2H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.97 (dd, *J* = 17.4, 7.8 Hz, 4H), 7.60 – 7.55 (m, 5H), 7.41 (q, *J* = 8.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, *J* = 7.9 Hz), 135.1 (d, *J* = 16.5 Hz), 134.4, 134.3, 131.5 (d, *J* = 7.9 Hz), 130.7, 130.3, 129.5 (d, *J* = 1.7 Hz), 129.0 (d, *J* = 3.2 Hz), 128.8, 128.3 (d, *J* = 68.9 Hz), 127.5, 126.6, 126.4 (d, *J* = 5.5 Hz), 124.9 (d, *J* = 17.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 79.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{20}O_2PSe$ 487.0361; Found 487.0364.

2-(4-Isobutylphenyl)propanoic diphenylphosphinothioic anhydride (6a)



According to the general procedure and work-up, purification by flash column·chromatography using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **6a** (62.5 mg, 0.148 mmol, 74%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (m, *J* = 14.0, 8.4, 1.4 Hz, 2H), 7.60 – 7.54 (m, 2H), 7.53 – 7.40 (m, 3H), 7.35 (m, *J* = 17.9, 11.4, 7.6, 3.8 Hz, 4H), 7.17 (s, 3H), 3.86 (d, *J* = 7.1 Hz, 1H), 2.51 (d, *J* = 7.2 Hz, 2H), 1.89 (m, *J* = 13.5, 6.8 Hz, 1H), 1.50 (d, *J* = 7.1 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2 (d, *J* = 9.8 Hz), 141.3, 136.3, 133.7 (d, *J* = 44.1 Hz), 132.1 (d, *J* = 2.9 Hz), 131.0 (d, *J* = 25.7 Hz), 130.9 (d, *J* = 2.0 Hz), 129.6, 128.7 (d, *J* = 14.5 Hz), 128.4 (d, *J* = 2.1 Hz), 128.4 (d, *J* = 25.8 Hz), 127.6, 46.7 (d, *J* = 2.5 Hz), 45.1, 30.4, 22.4, 17.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 76.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{28}O_2PS$ 423.1542; Found 423.1546.

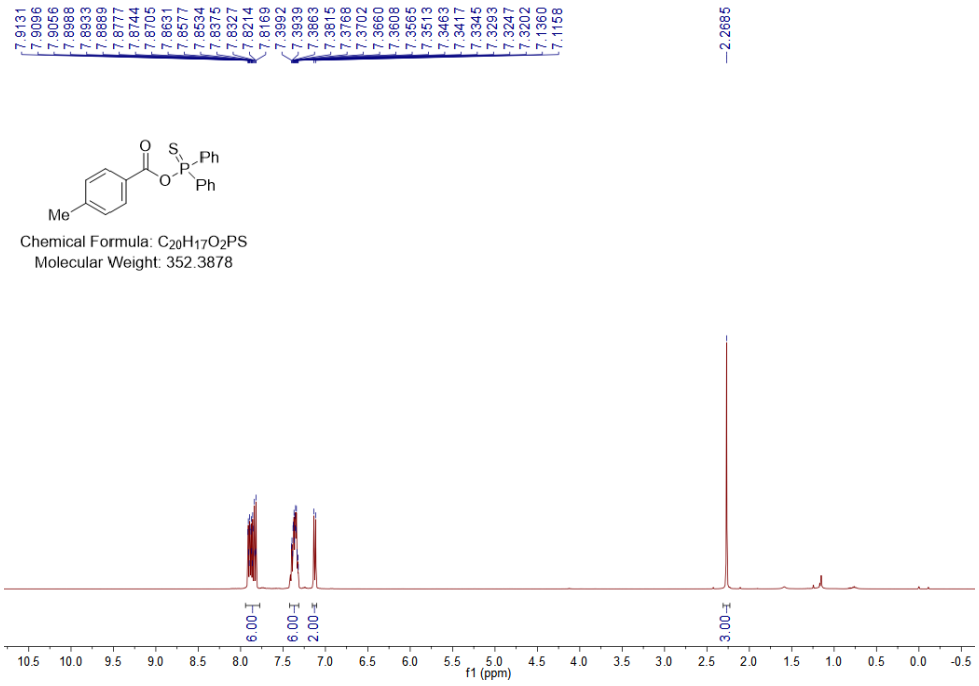
2-(4-Isobutylphenyl)propanoic diphenylphosphinoselenoic anhydride (6b)



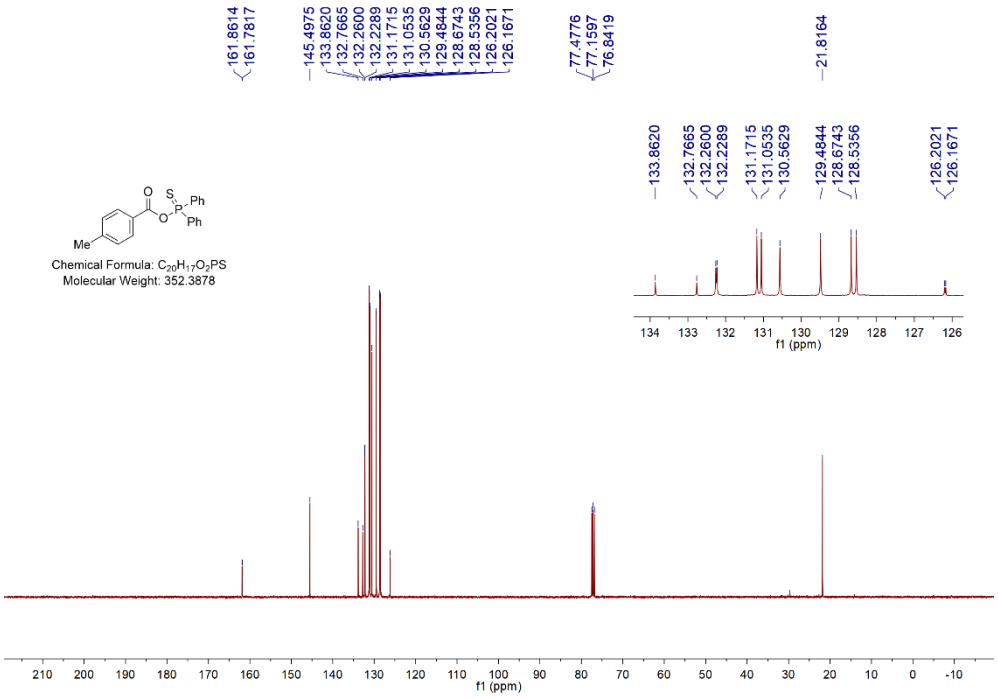
According to the general procedure and work-up, purification by flash column·chromatography using petroleum·ether/ethyl acetate as eluent (v:v = 20:1) gave product **6b** (73.2 mg, 0.156 mmol, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H), 7.61 – 7.55 (m, 2H), 7.53 – 7.40 (m, 3H), 7.39 – 7.33 (m, 4H), 7.17 (s, 3H), 3.91 – 3.85 (m, 1H), 2.51 (d, *J* = 7.2 Hz, 2H), 1.94 – 1.87 (m, 1H), 1.50 (d, *J* = 7.1 Hz, 3H), 0.93 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3 (d, *J* = 9.4 Hz), 141.4, 136.3, 133.8 (d, *J* = 48.4 Hz), 132.9 (d, *J* = 41.8 Hz), 132.3, 132.25 (d, *J* = 6.9 Hz), 131.3 (d, *J* = 12.5 Hz), 131.1 (d, *J* = 12.1 Hz), 128.7 (d, *J* = 199.4 Hz), 128.4 (d, *J* = 2.3 Hz), 128.43 (d, *J* = 25.4 Hz), 46.9 (d, *J* = 2.3 Hz), 45.1, 30.4, 22.5, 17.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 77.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{28}O_2PSe$ 471.0987; Found 471.0984.

10. Copies of ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra of isolated compounds

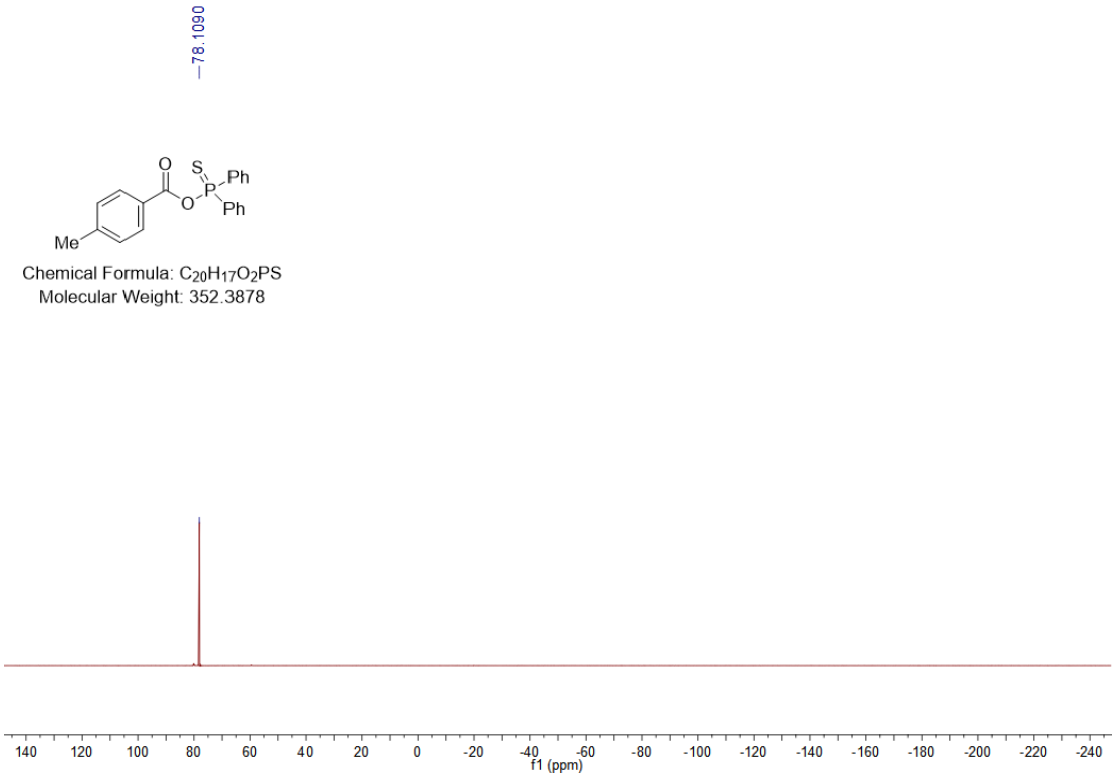
4-Methylbenzoic diphenylphosphinothioic anhydride (3a)



^{1}H NMR spectrum of 3a, 400 MHz, $CDCl_3$

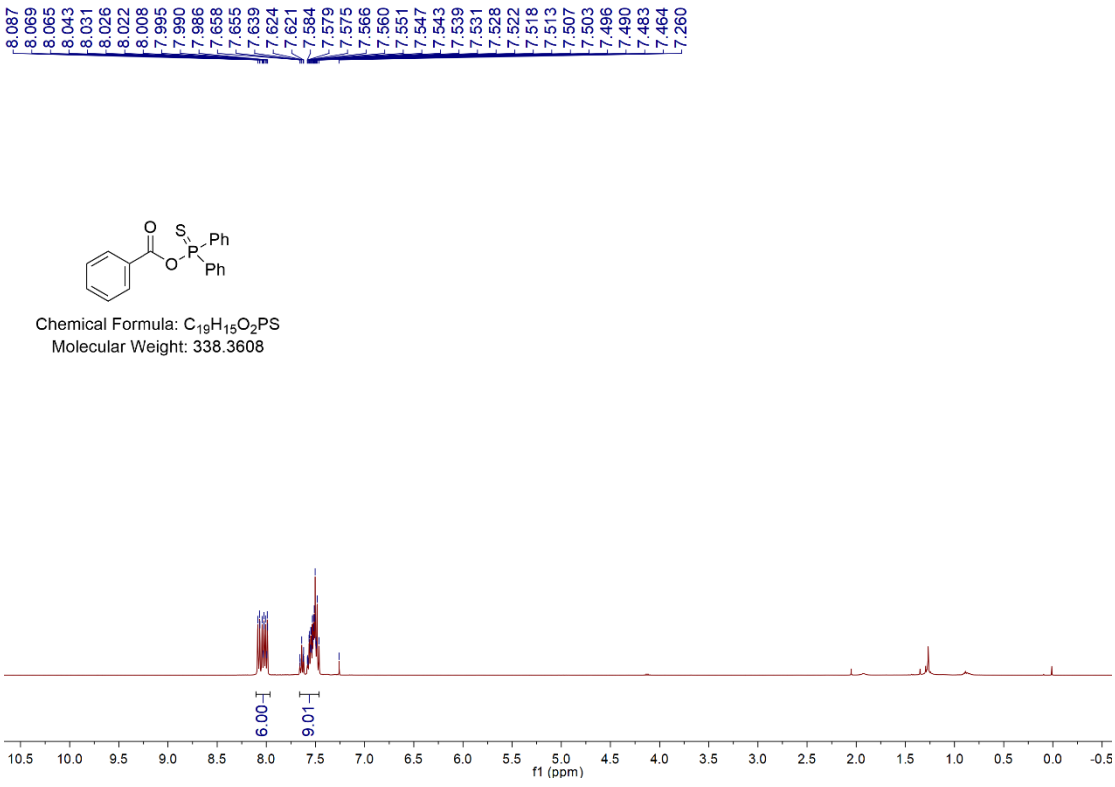


^{13}C NMR spectrum of 3a, 100 MHz, $CDCl_3$

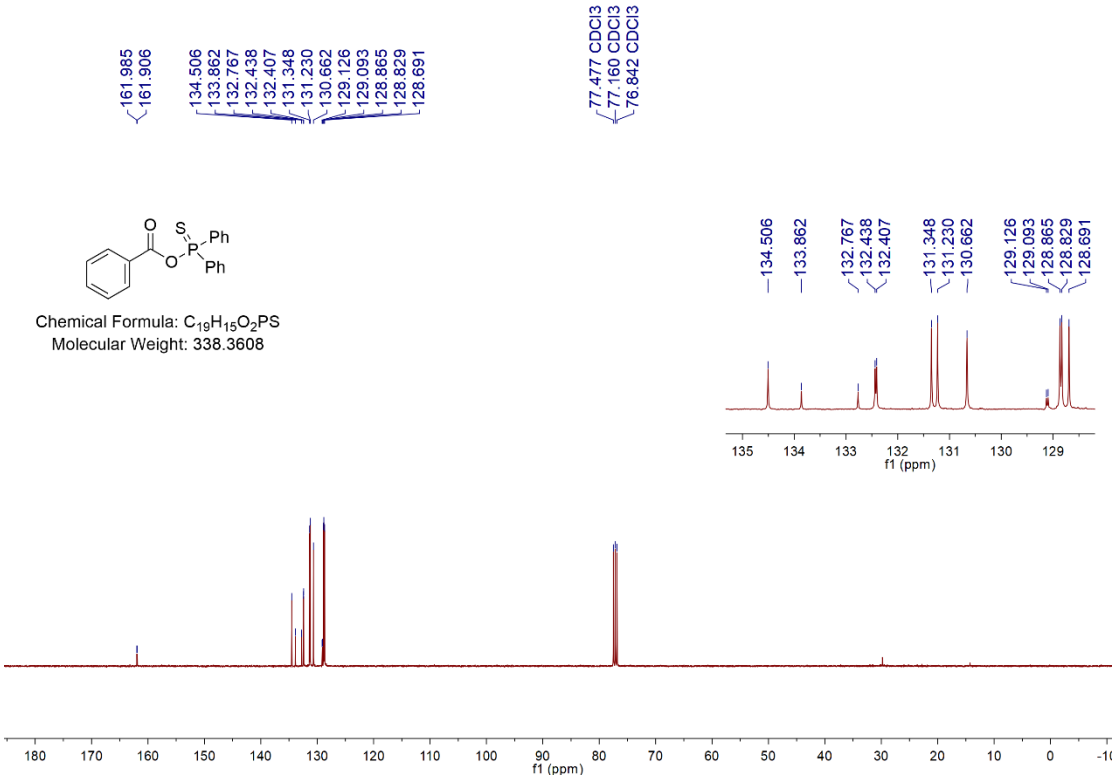


^{31}P NMR spectrum of 3a, 162 MHz, $CDCl_3$

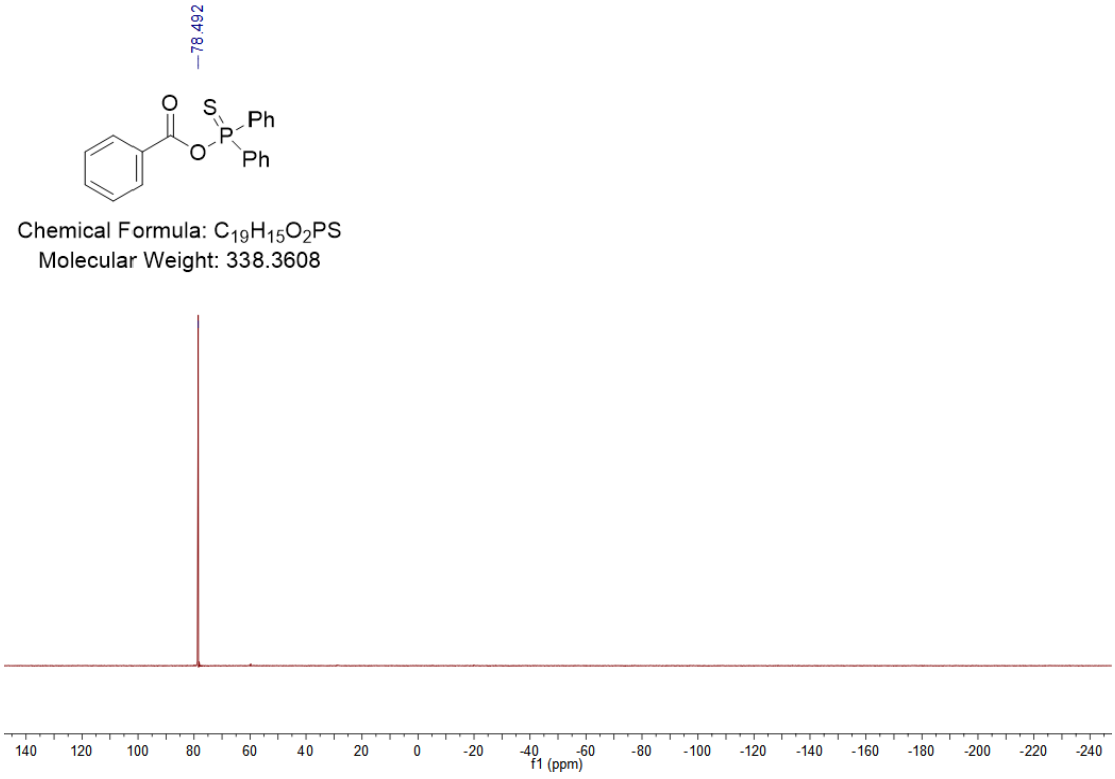
Benzoic diphenylphosphinothioic anhydride (3b)



^{1}H NMR spectrum of 3b, 400 MHz, $CDCl_3$

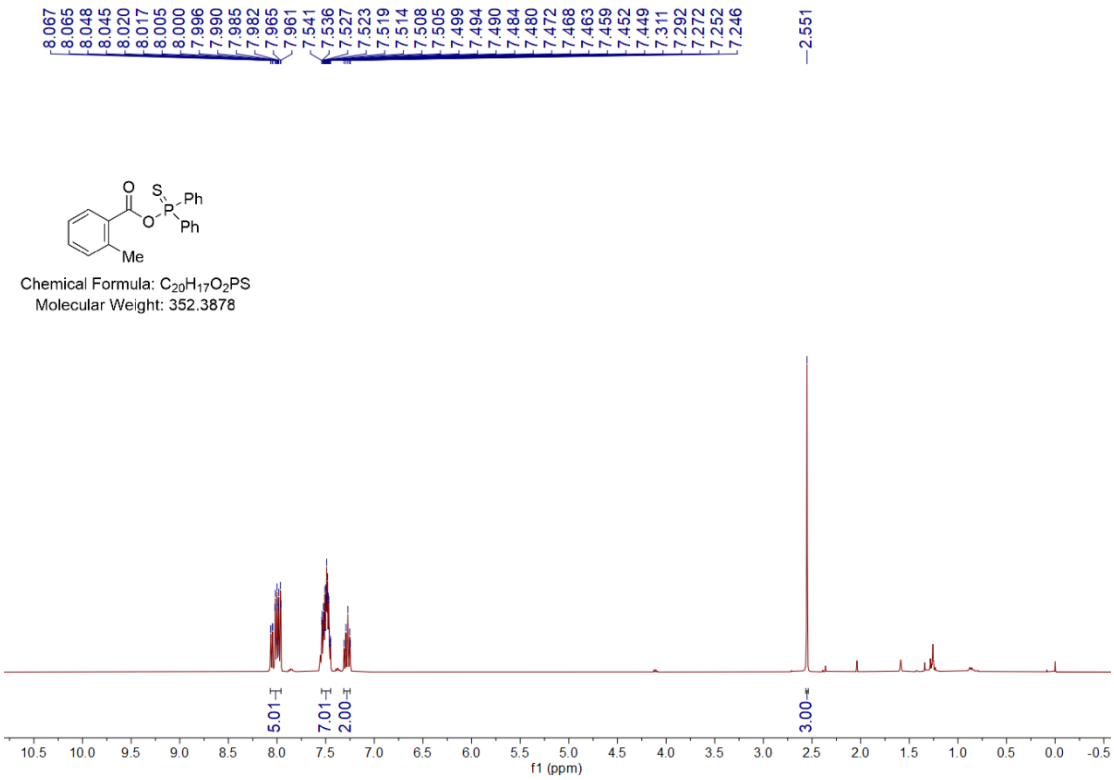


^{13}C NMR spectrum of 3b, 100 MHz, $CDCl_3$

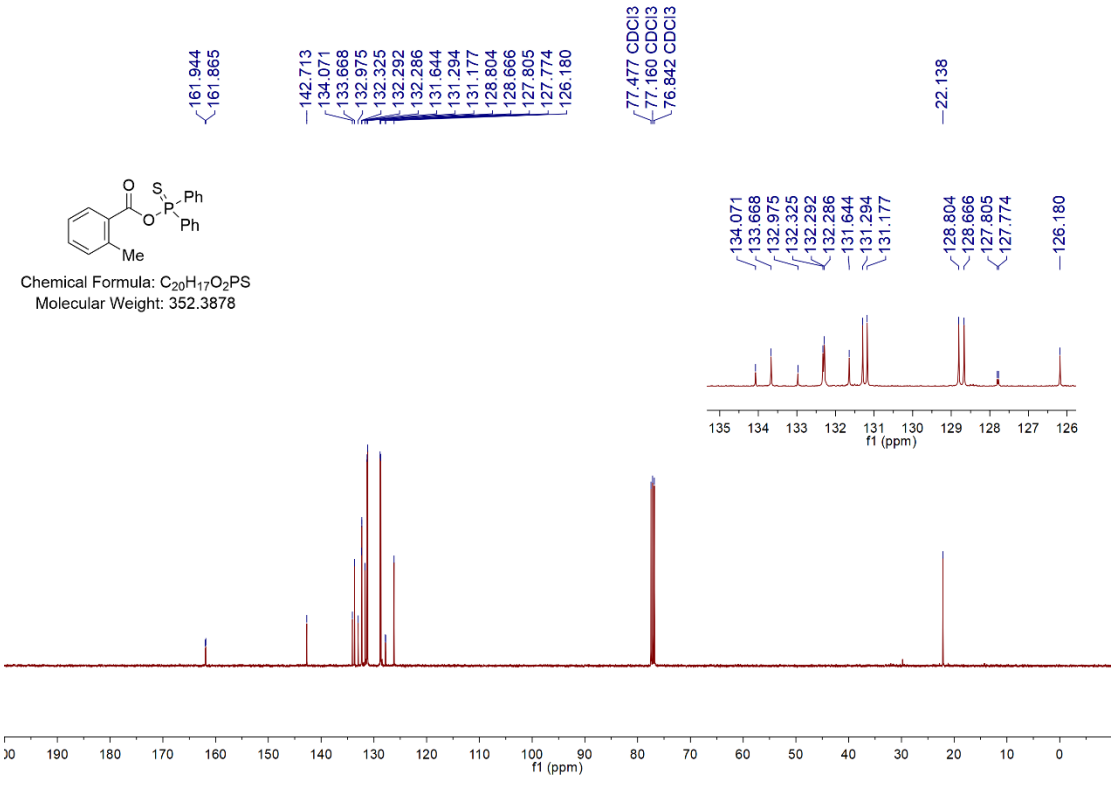


^{31}P NMR spectrum of 3b, 162 MHz, $CDCl_3$

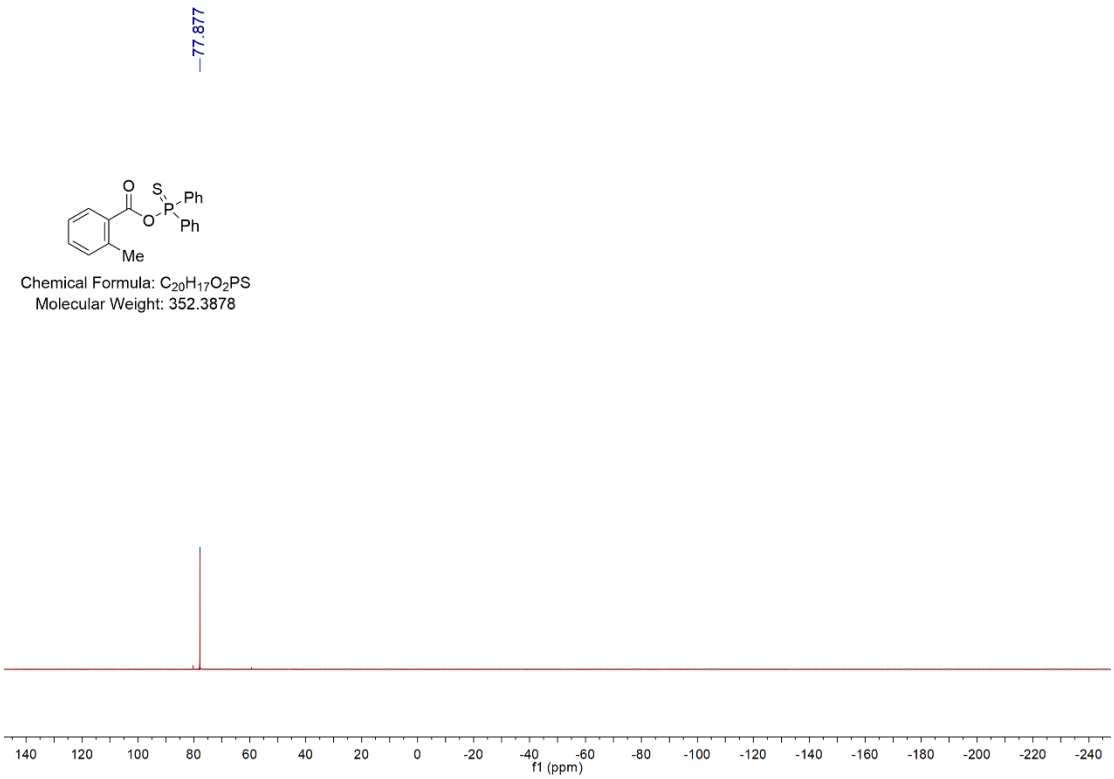
2-Methylbenzoic diphenylphosphinothioic anhydride (3c)



^{1}H NMR spectrum of 3c, 400 MHz, $CDCl_3$

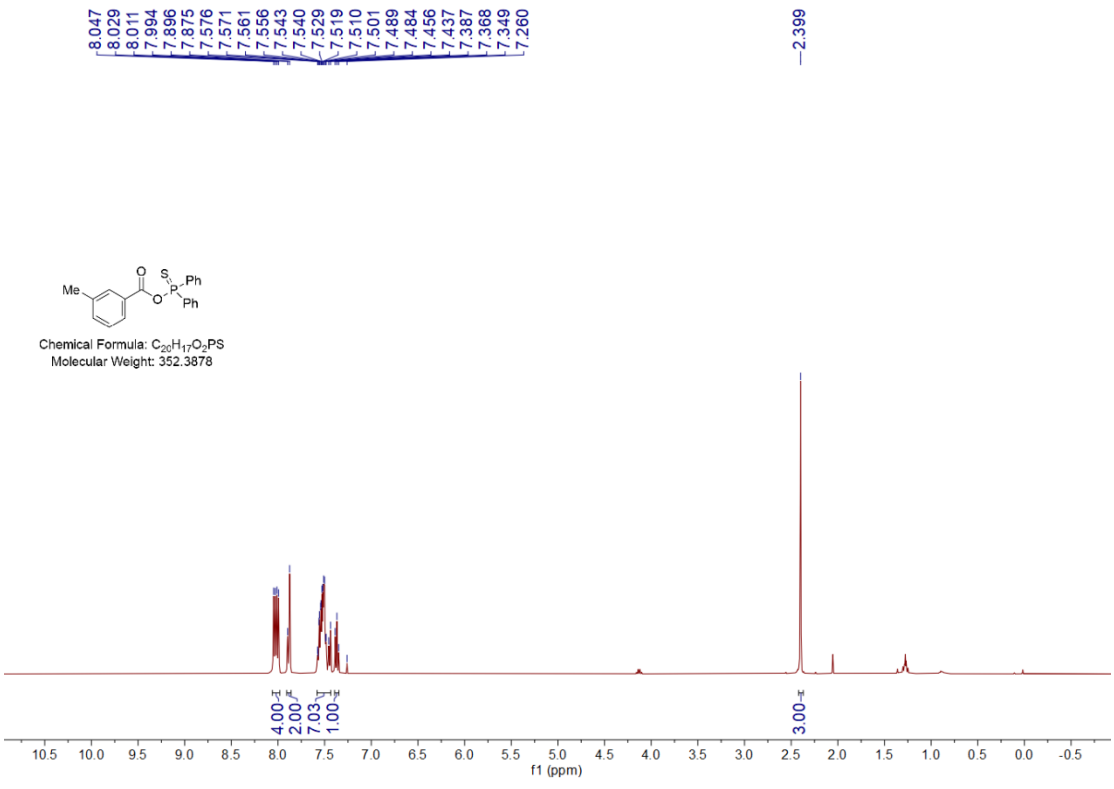


^{13}C NMR spectrum of 3c, 100 MHz, $CDCl_3$

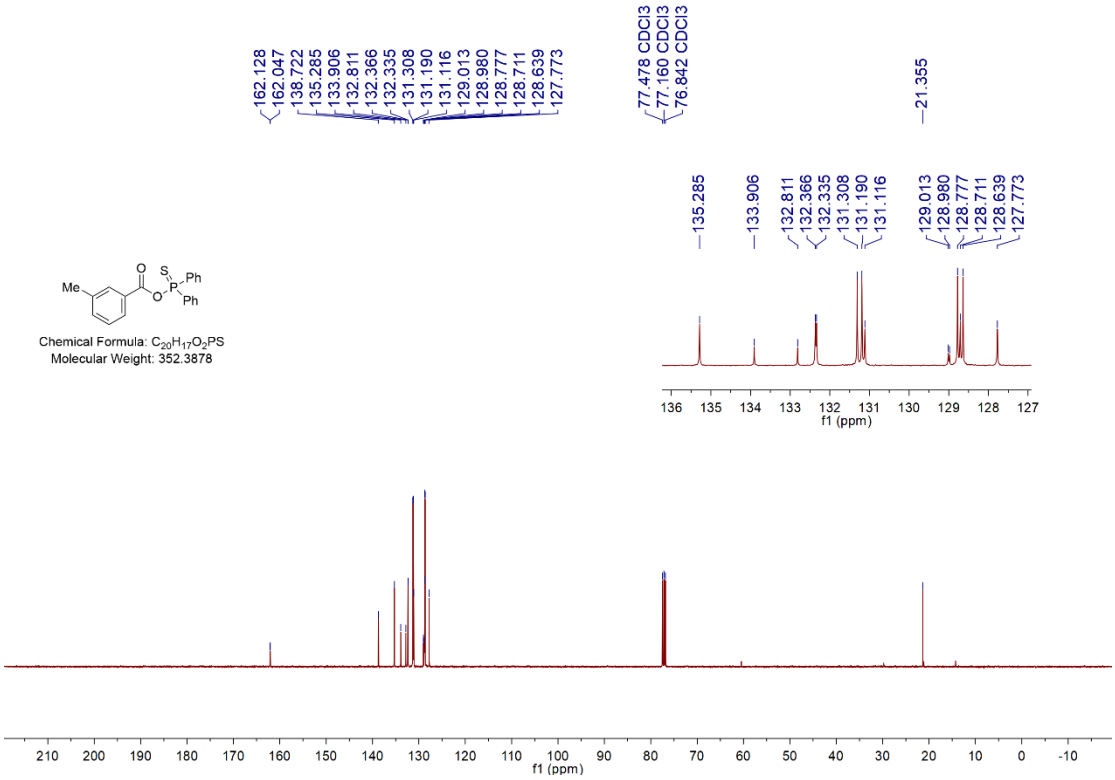


^{31}P NMR spectrum of 3c, 162 MHz, $CDCl_3$

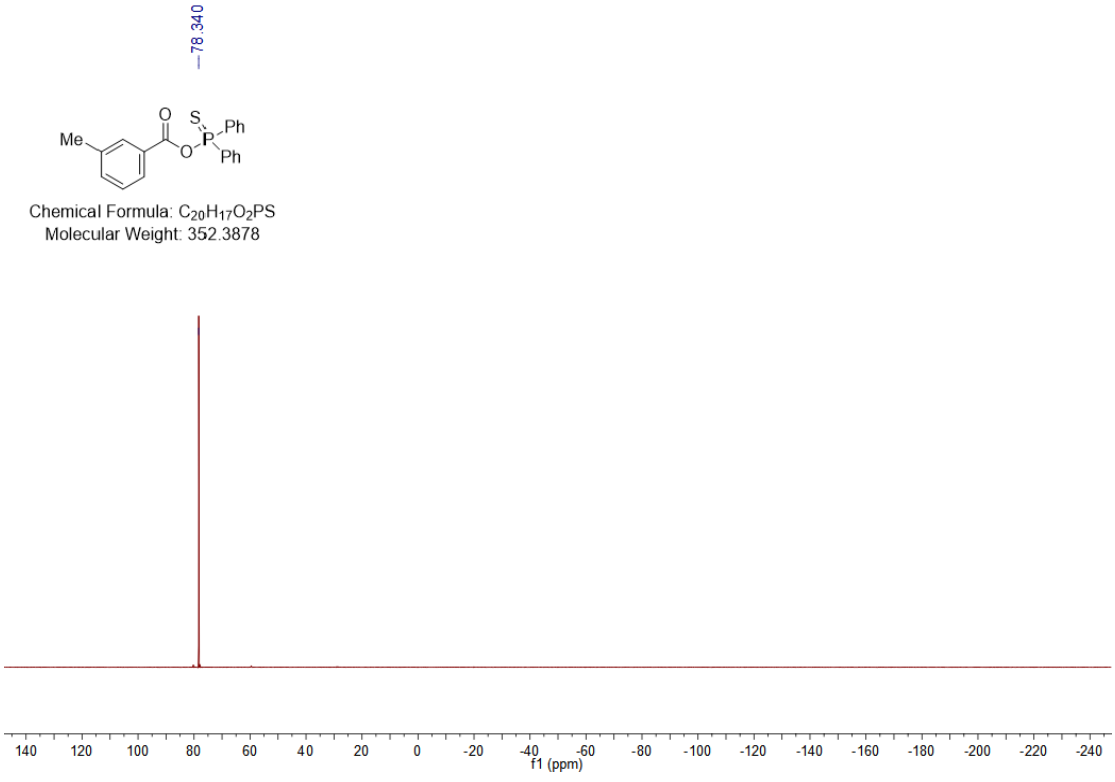
3-Methylbenzoic diphenylphosphinothioic anhydride (3d)



^{1}H NMR spectrum of 3d, 400 MHz, $CDCl_3$

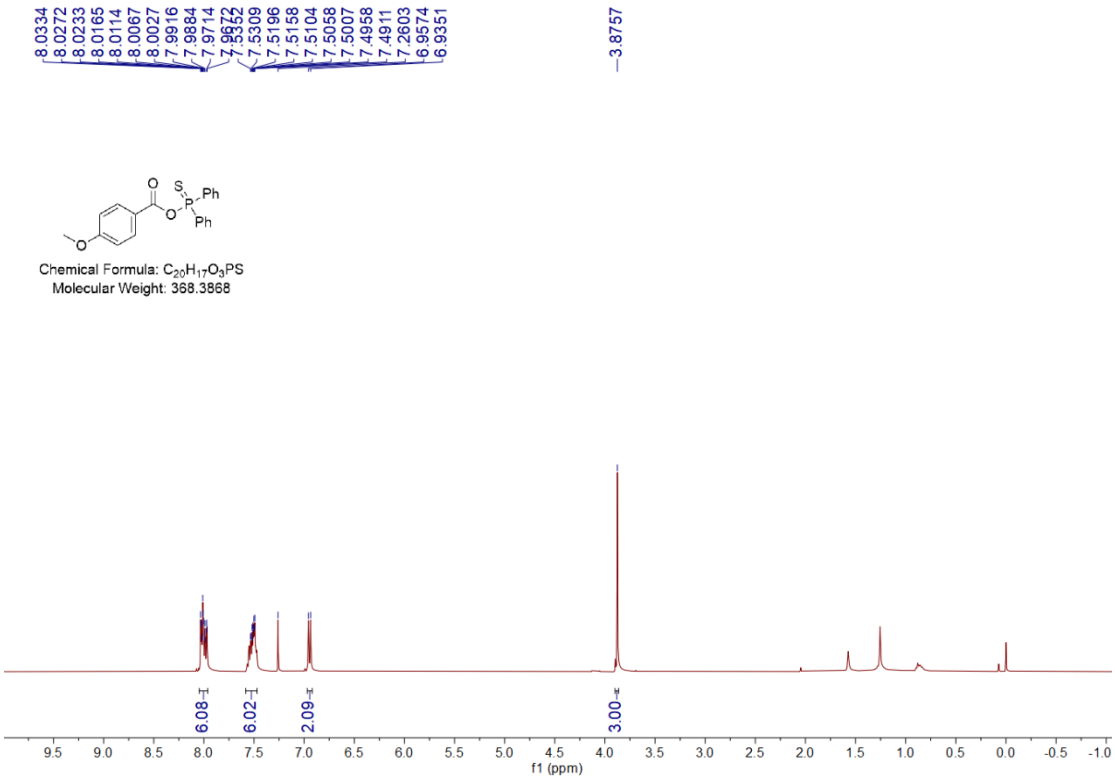


^{13}C NMR spectrum of 3d, 100 MHz, $CDCl_3$

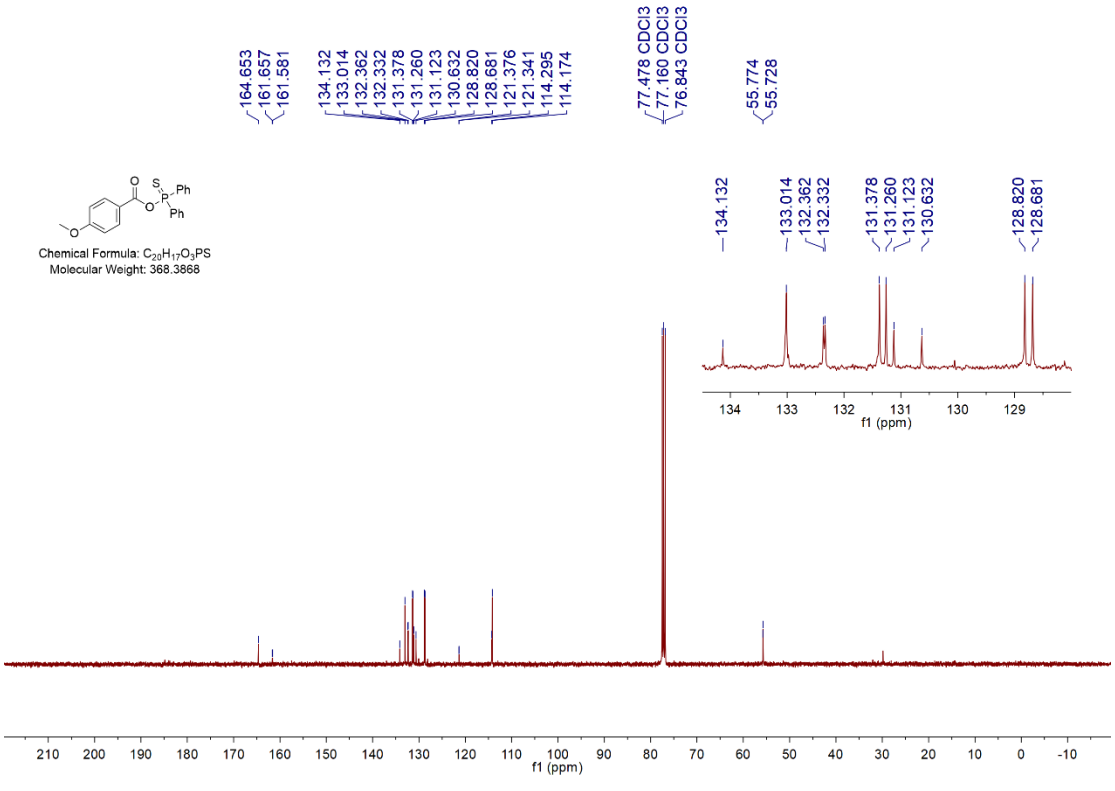


^{31}P NMR spectrum of 3d, 162 MHz, $CDCl_3$

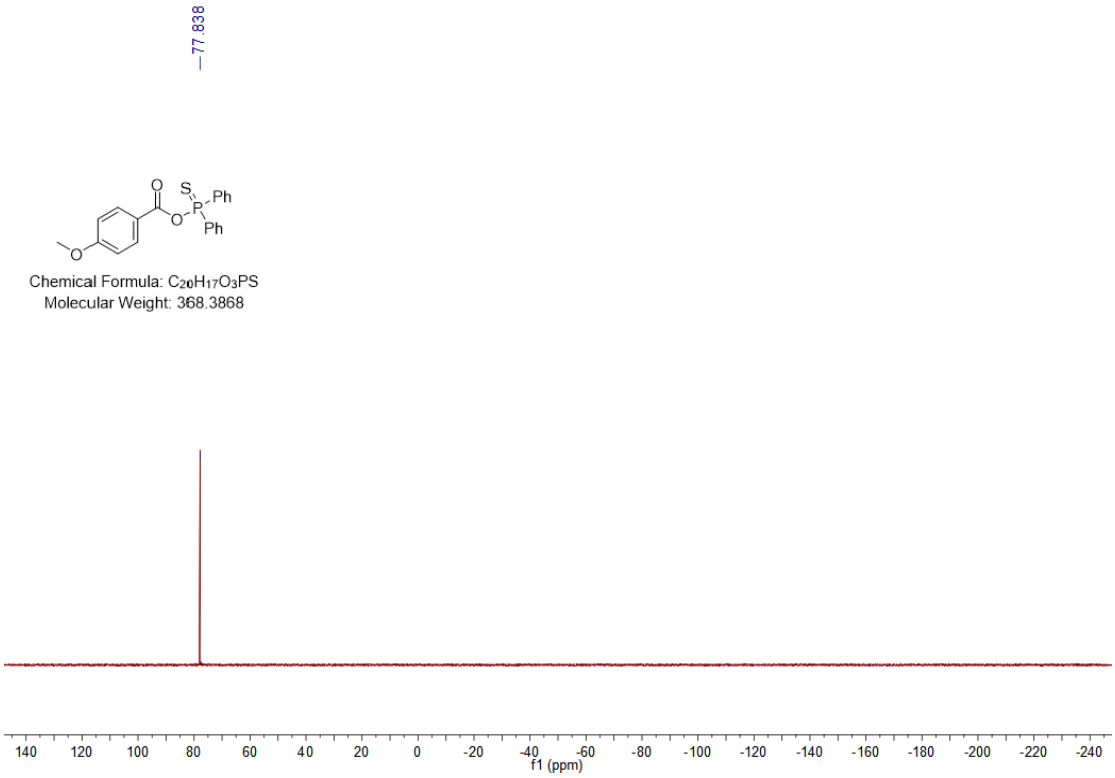
4-Methoxybenzoic diphenylphosphinothioic anhydride (3e)



^{1}H NMR spectrum of 3e, 400 MHz, $CDCl_3$

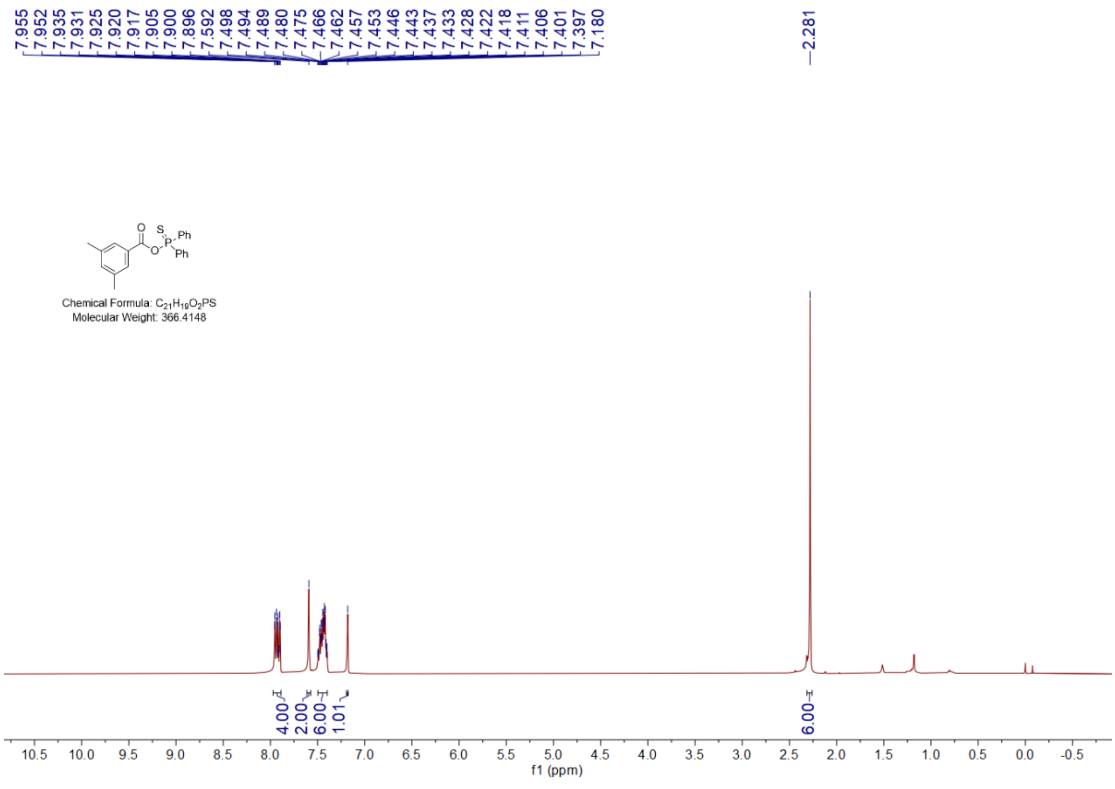


^{13}C NMR spectrum of 3e, 100 MHz, $CDCl_3$

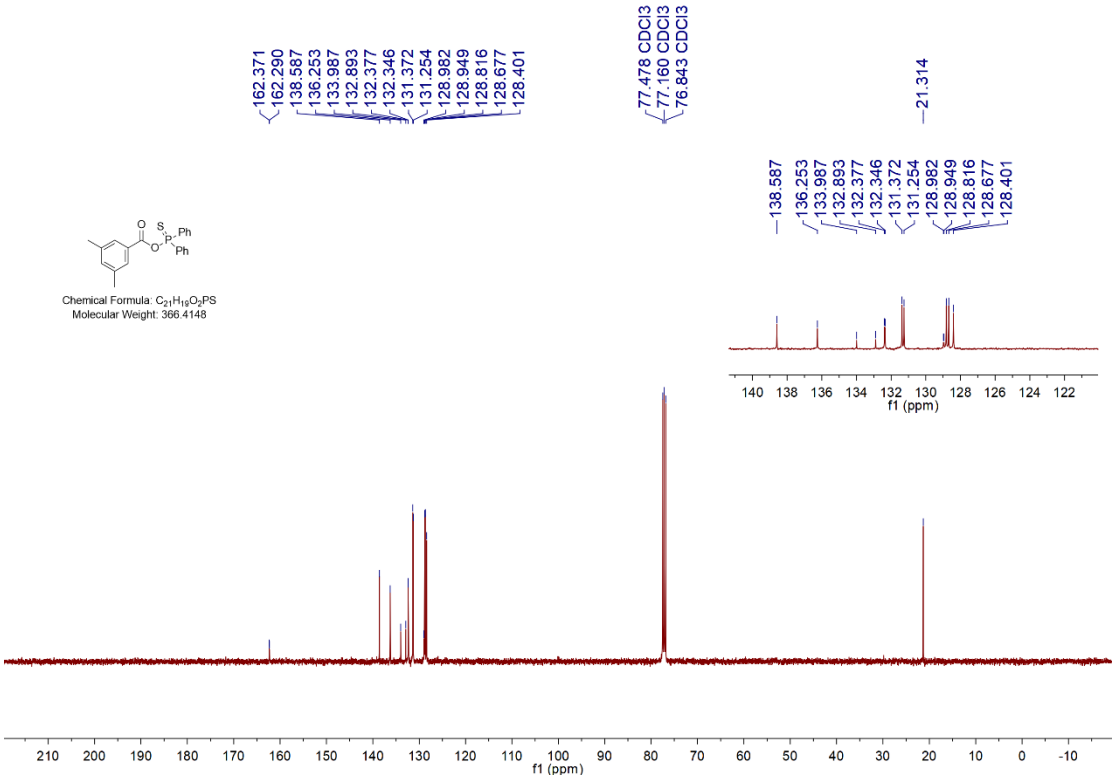


^{31}P NMR spectrum of 3e, 162 MHz, $CDCl_3$

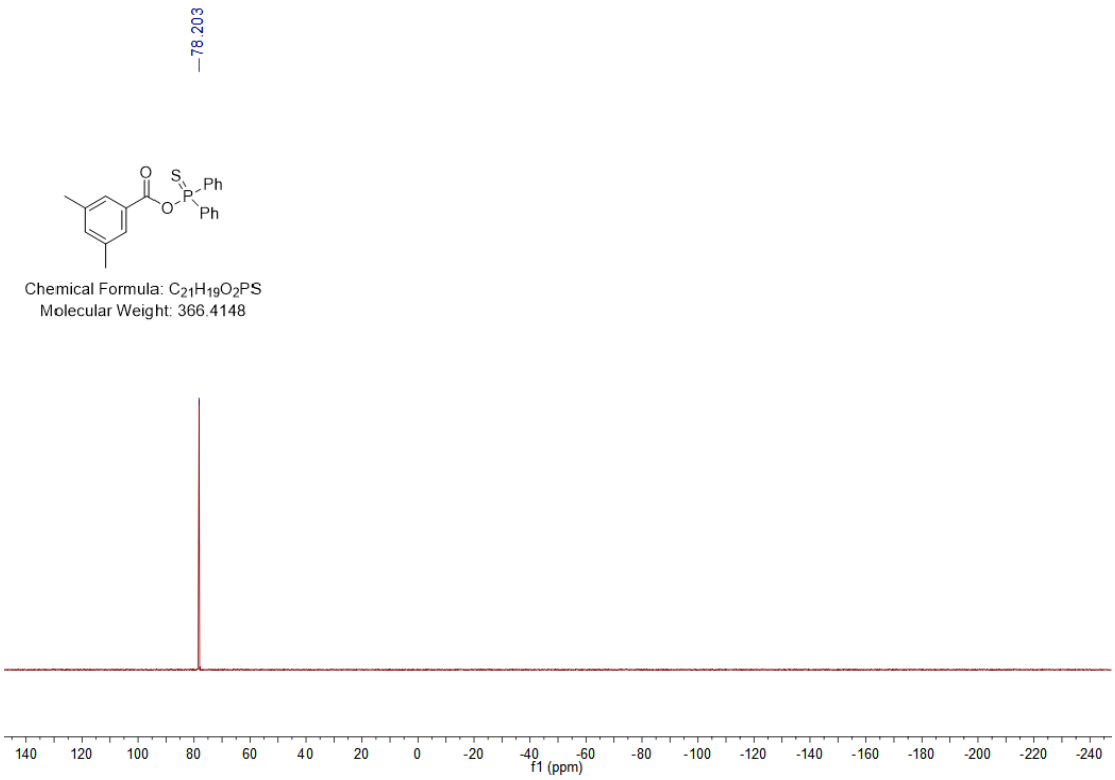
3,5-Dimethylbenzoic diphenylphosphinothioic anhydride (3f)



^{1}H NMR spectrum of 3f, 400 MHz, $CDCl_3$

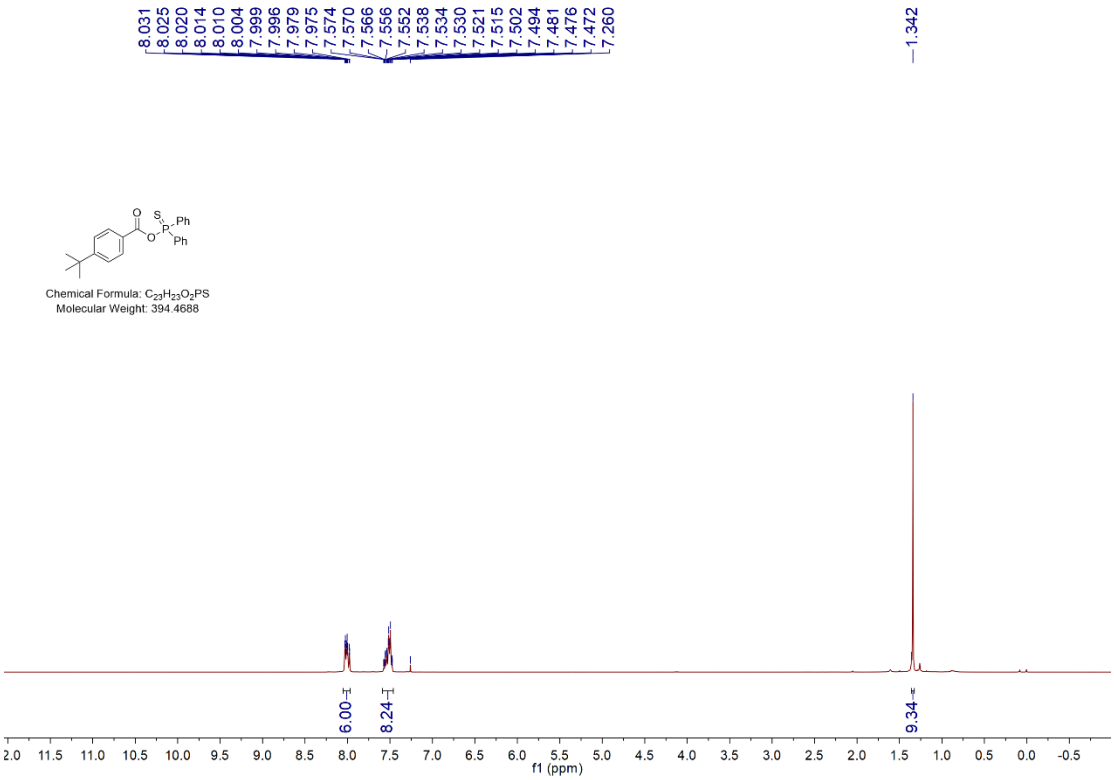


^{13}C NMR spectrum of 3f, 100 MHz, $CDCl_3$

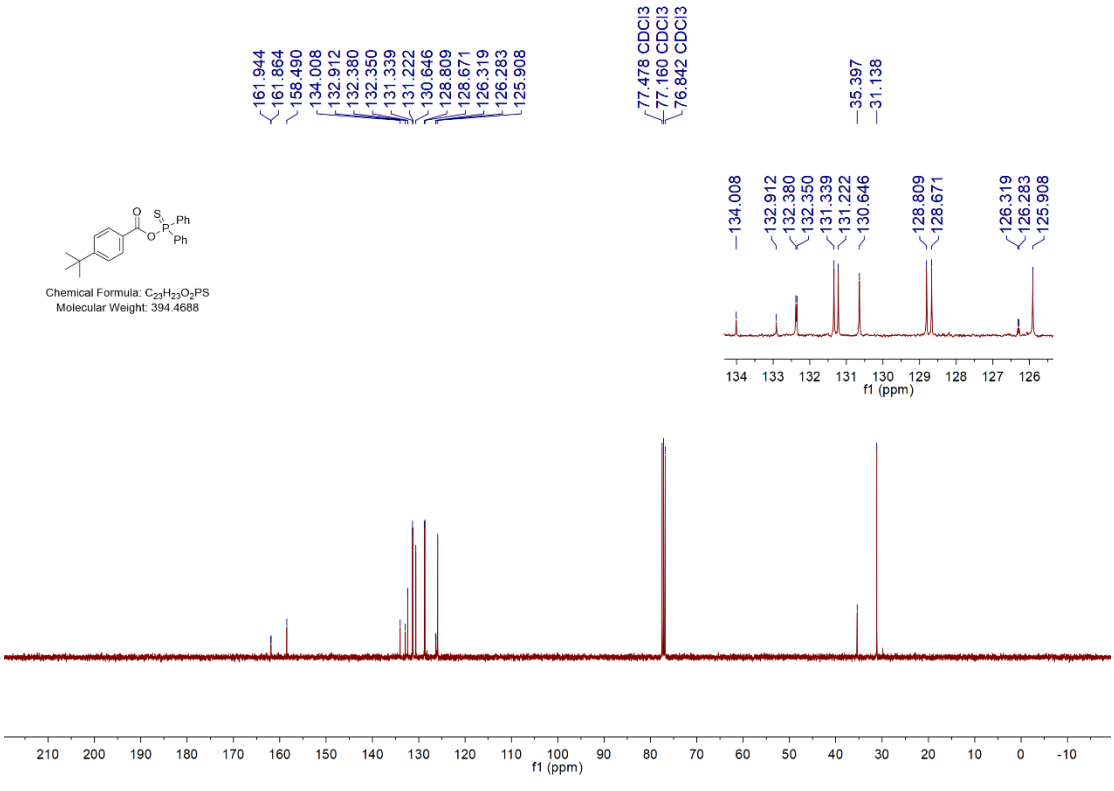


^{31}P NMR spectrum of 3f, 162 MHz, $CDCl_3$

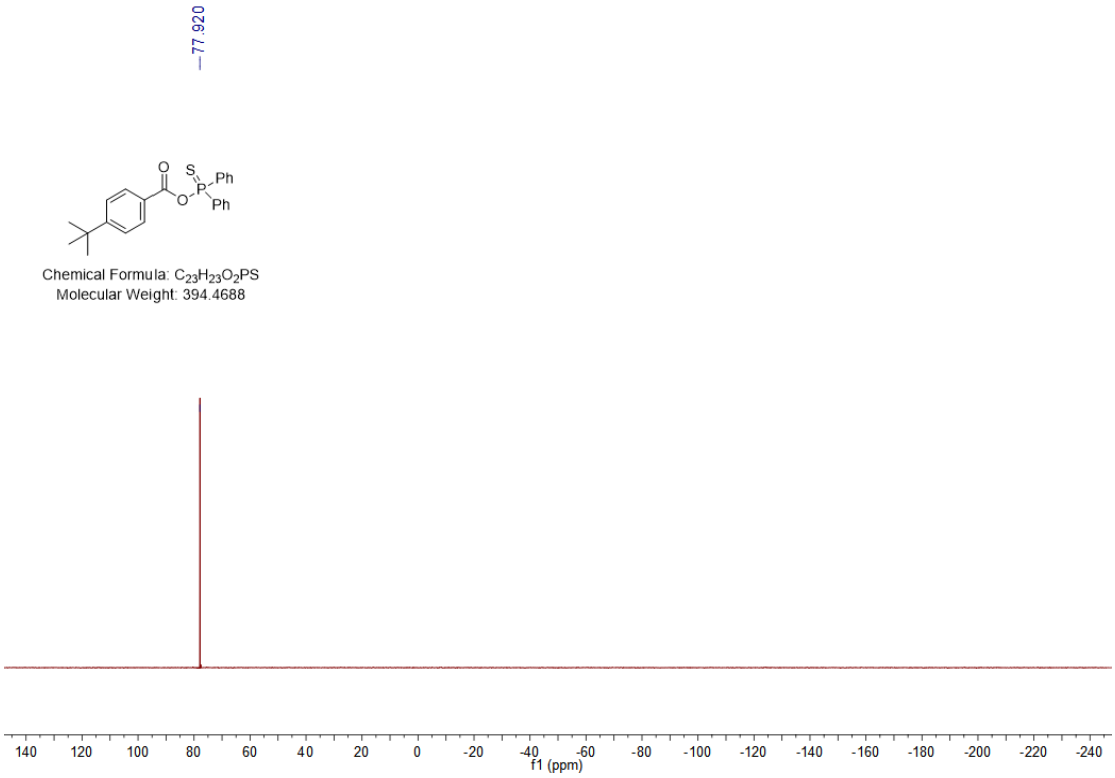
4-(Tert-butyl)benzoic diphenylphosphinothioic anhydride (3g)



^{1}H NMR spectrum of 3g, 400 MHz, $CDCl_3$

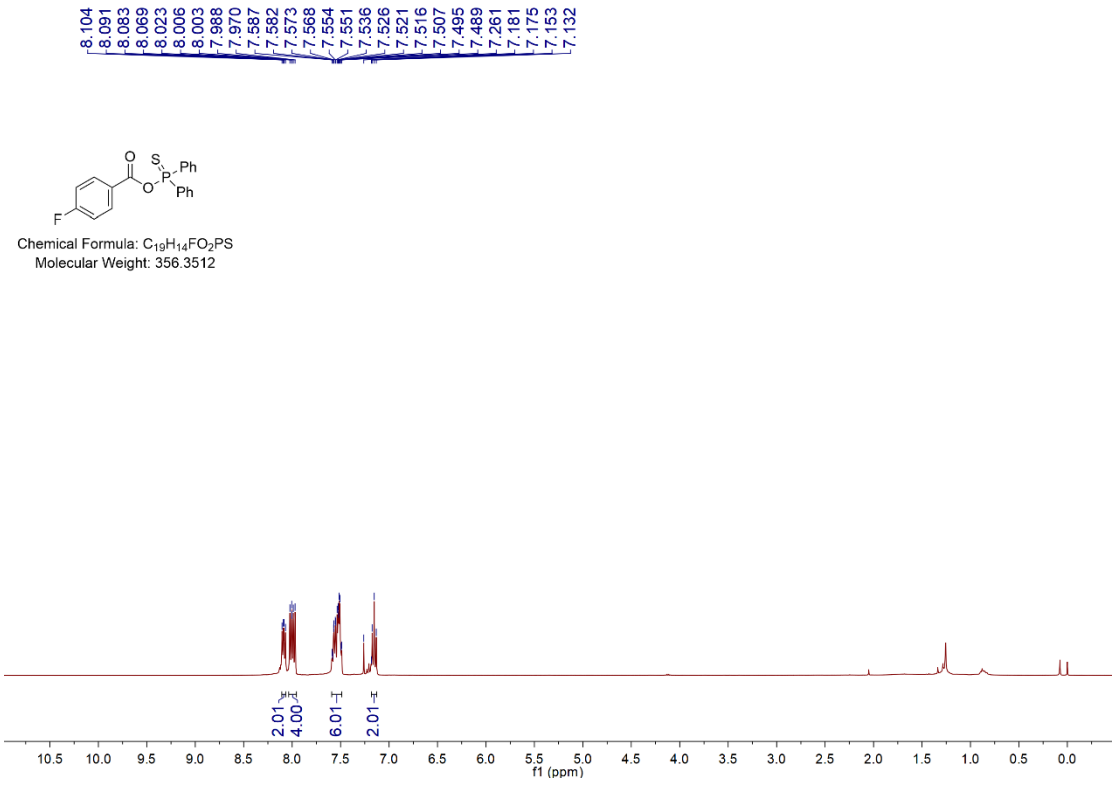


^{13}C NMR spectrum of 3g, 100 MHz, $CDCl_3$

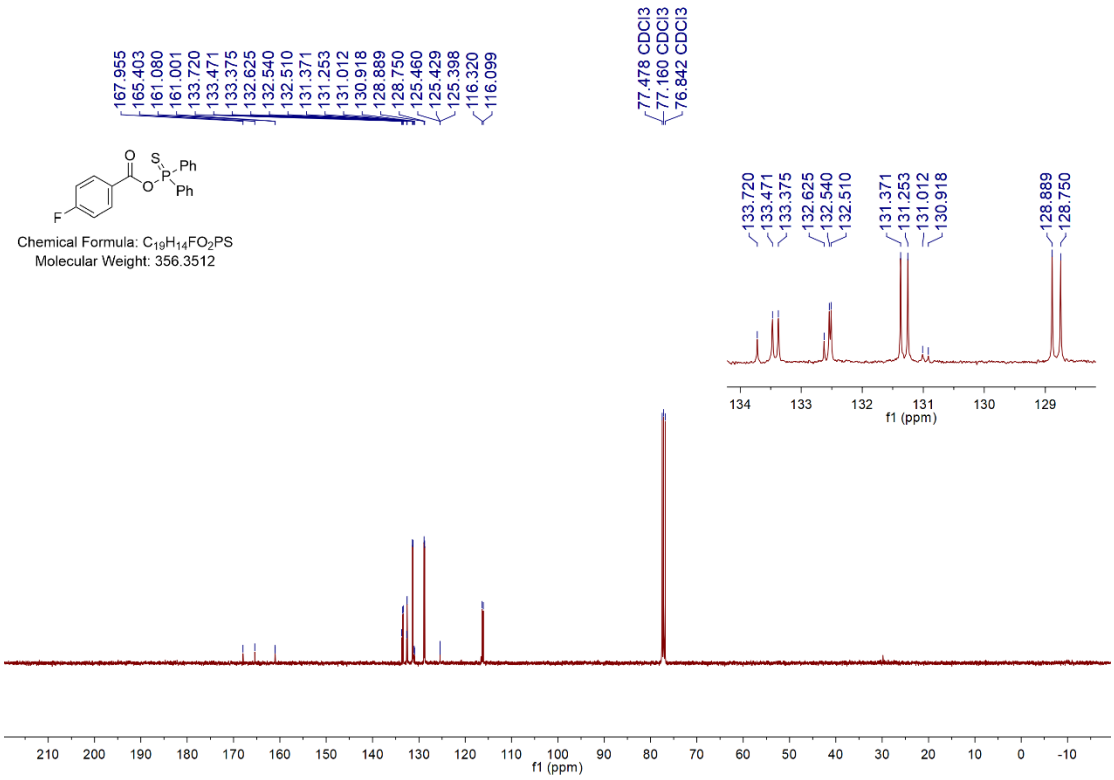


^{31}P NMR spectrum of 3g, 162 MHz, $CDCl_3$

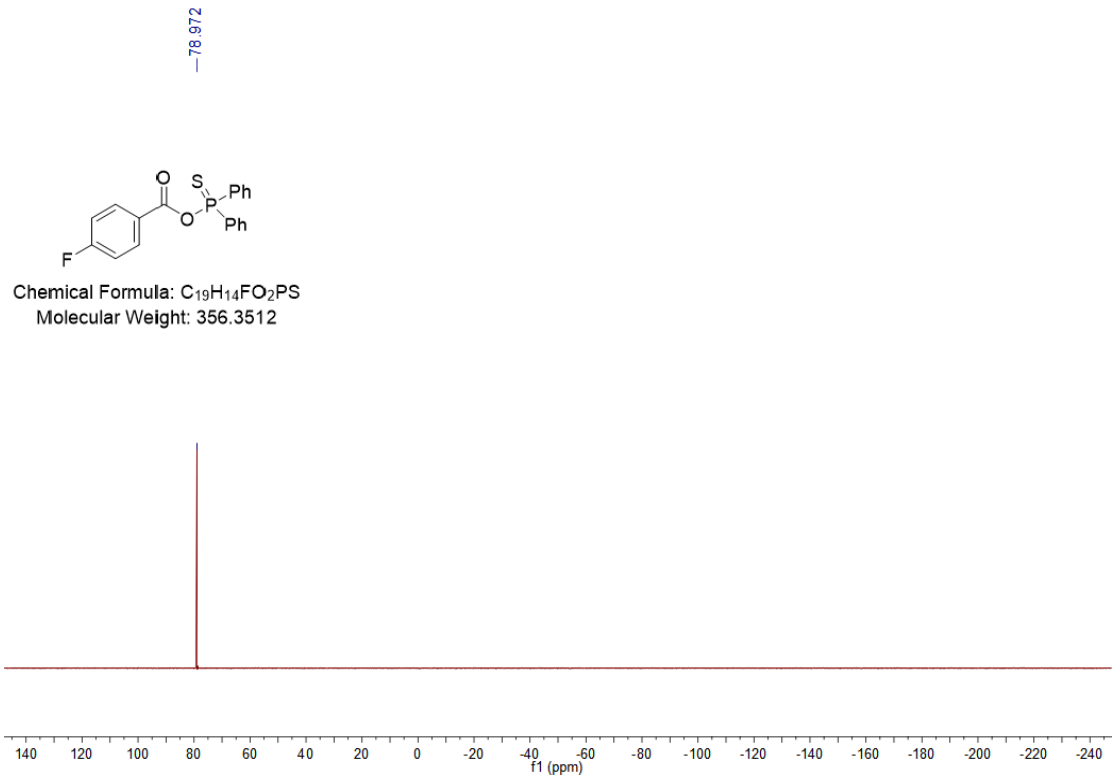
4-Fluorobenzoic diphenylphosphinothioic anhydride (3h)



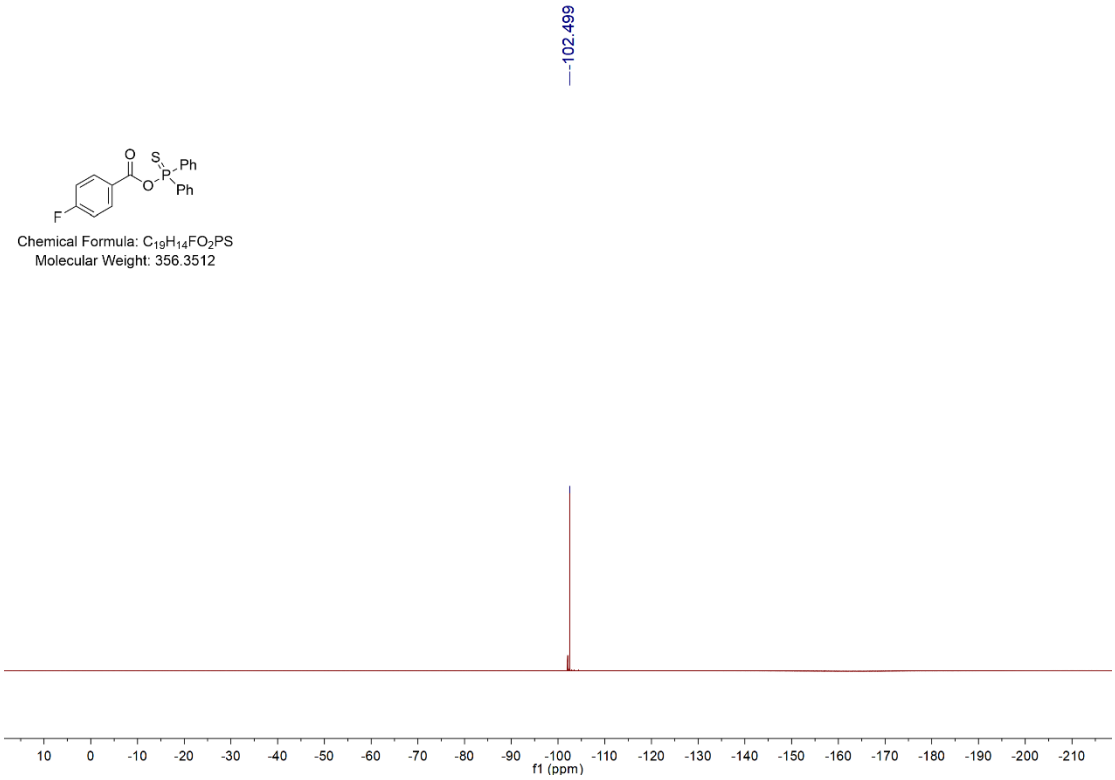
^{1}H NMR spectrum of 3h, 400 MHz, $CDCl_3$



^{13}C NMR spectrum of 3h, 100 MHz, $CDCl_3$

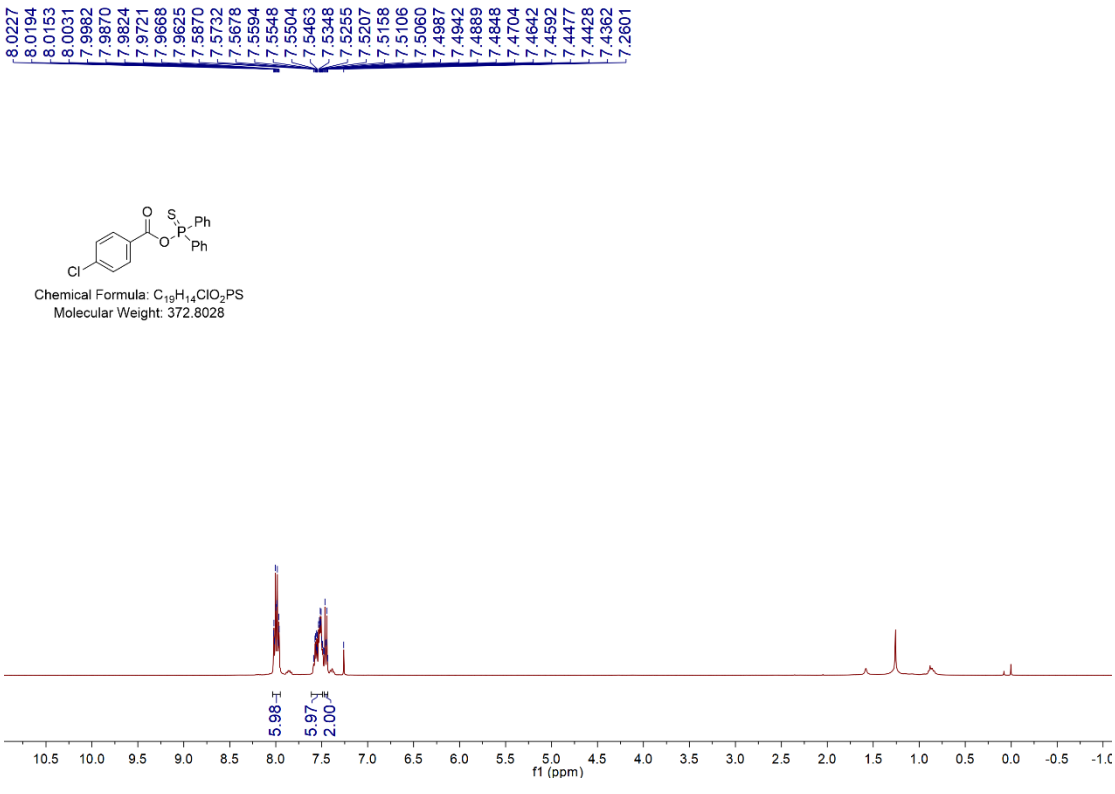


^{31}P NMR spectrum of 3h, 162 MHz, $CDCl_3$

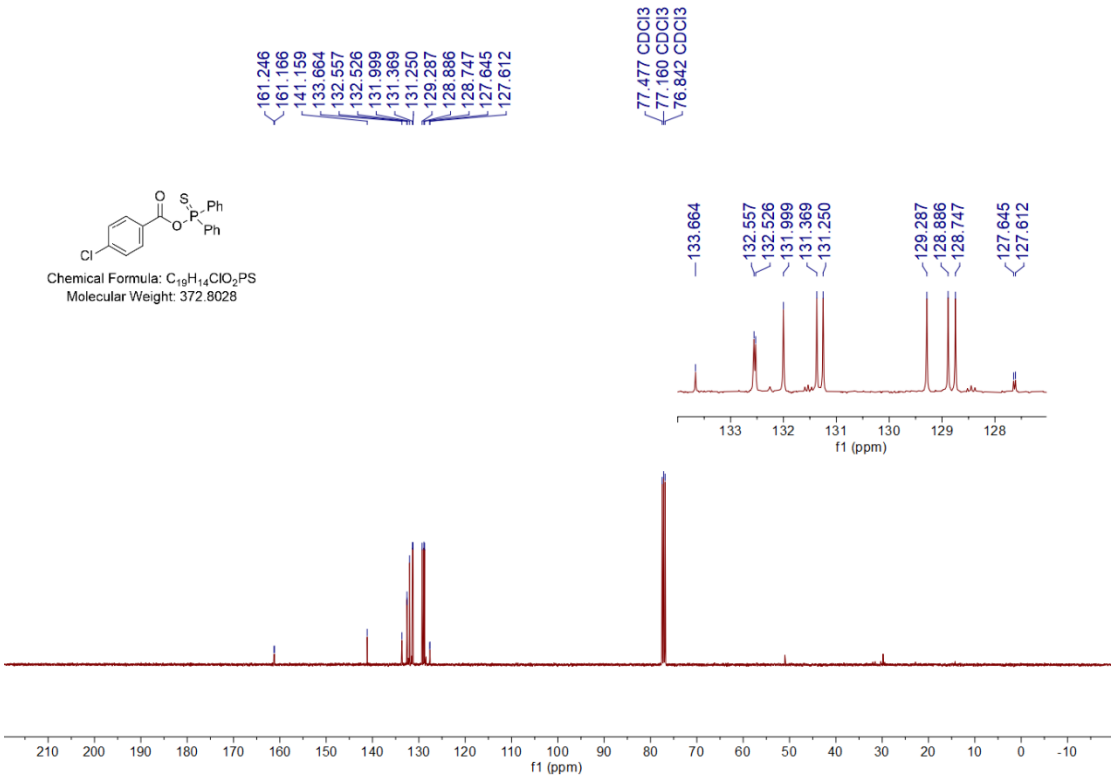


^{19}F NMR spectrum of 3h, 376 MHz, $CDCl_3$

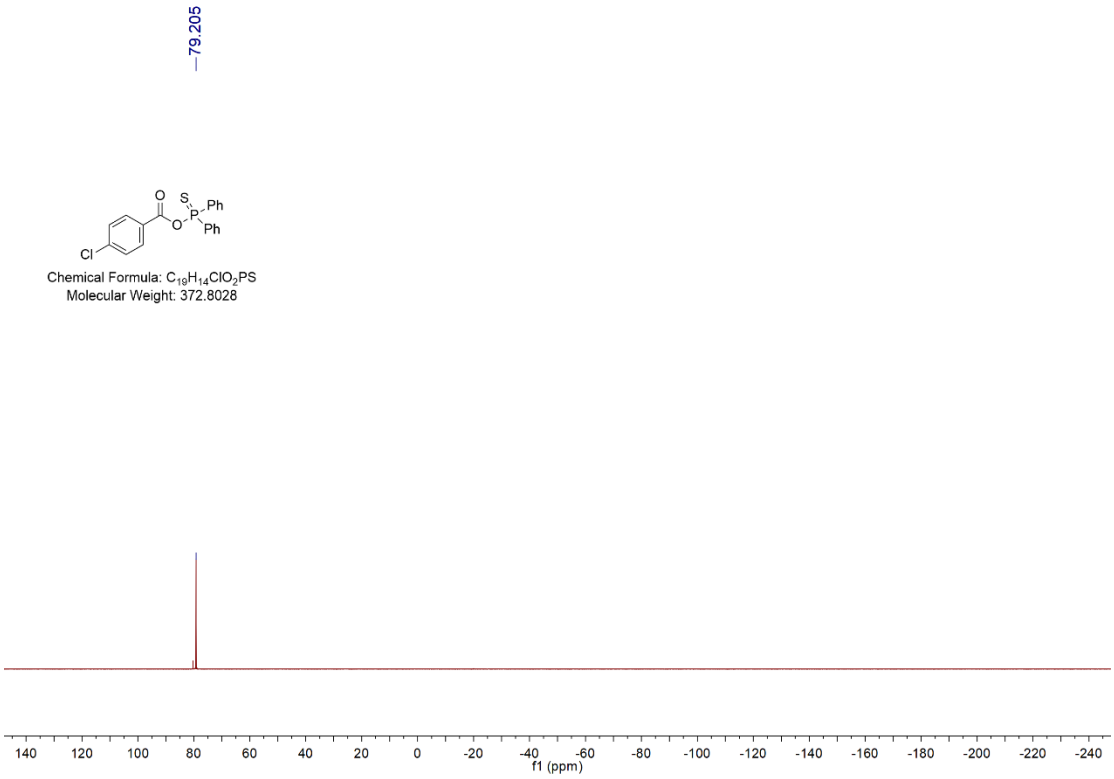
4-Chlorobenzoic diphenylphosphinothioic anhydride (3i)



^{1}H NMR spectrum of 3i, 400 MHz, $CDCl_3$

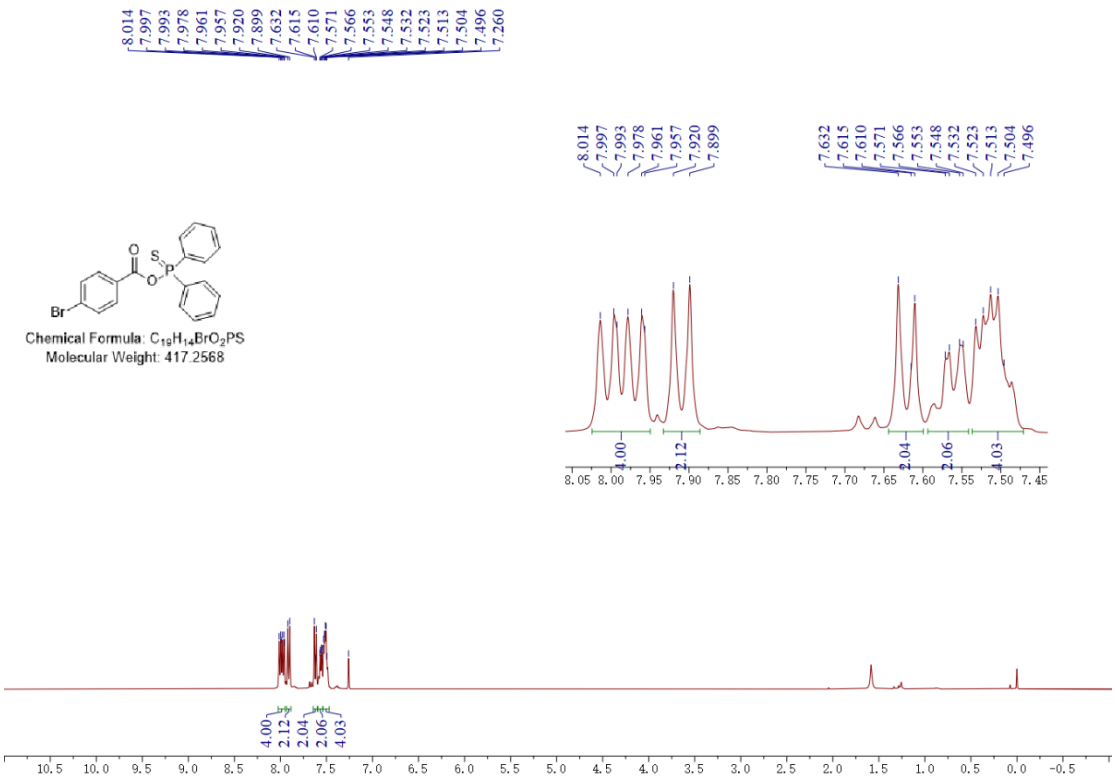


^{13}C NMR spectrum of 3i, 100 MHz, $CDCl_3$

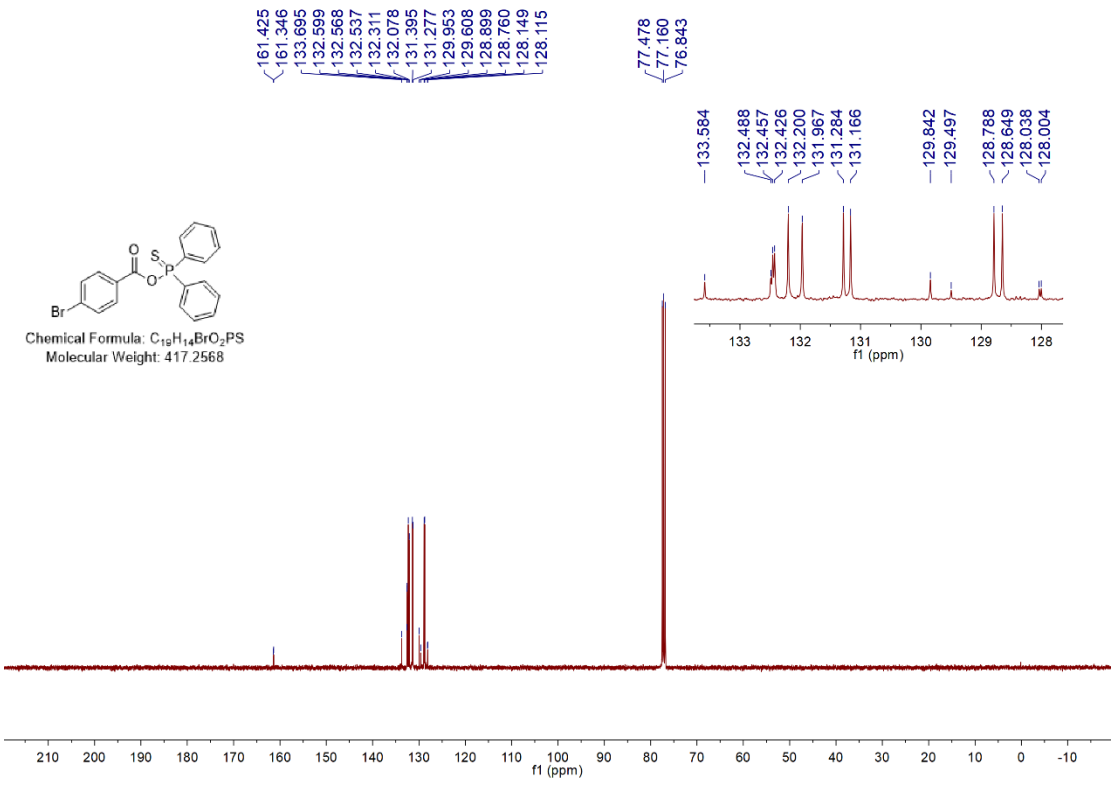


^{31}P NMR spectrum of 3i, 162 MHz, $CDCl_3$

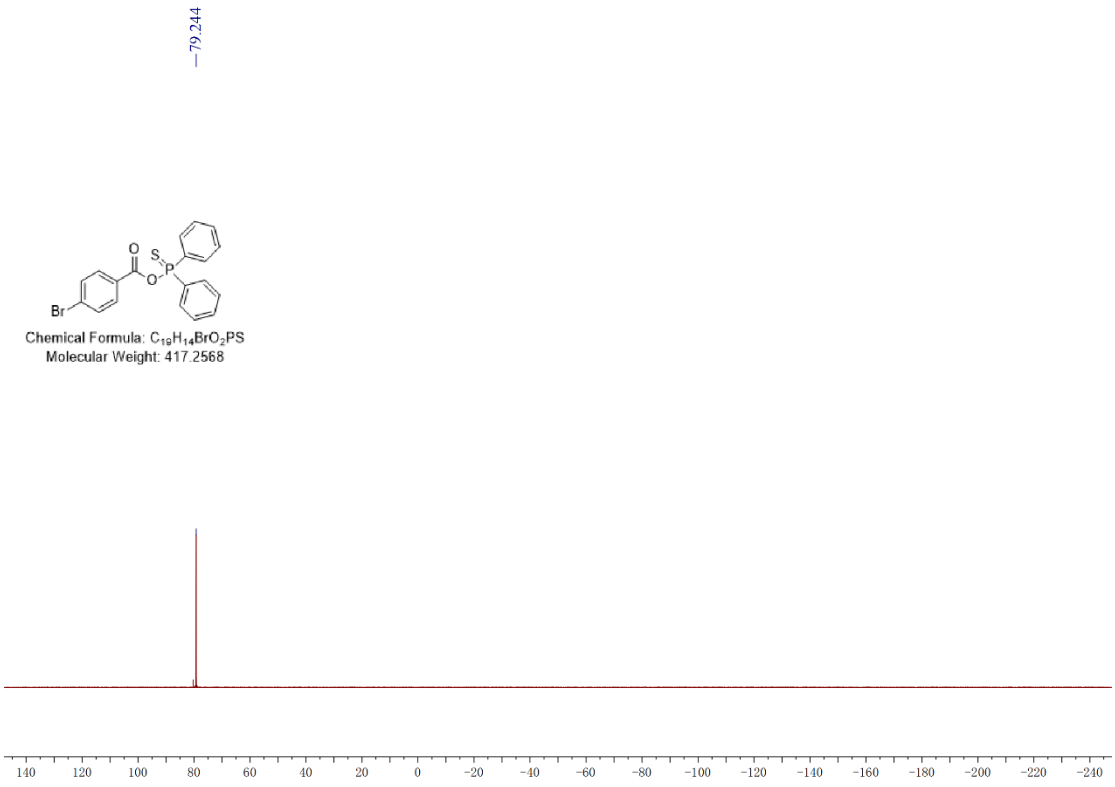
4-Bromobenzoic diphenylphosphinothioic anhydride (3j)



^{1}H NMR spectrum of 3j, 400 MHz, $CDCl_3$

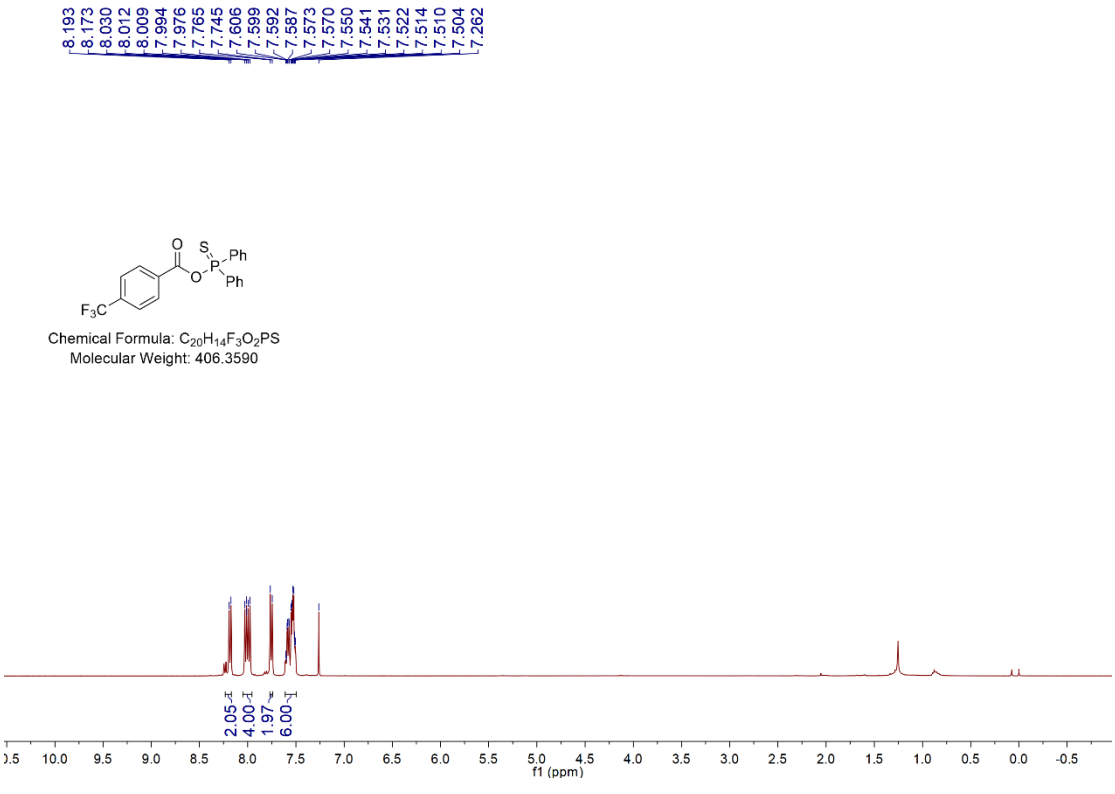


^{13}C NMR spectrum of 3j, 100 MHz, $CDCl_3$

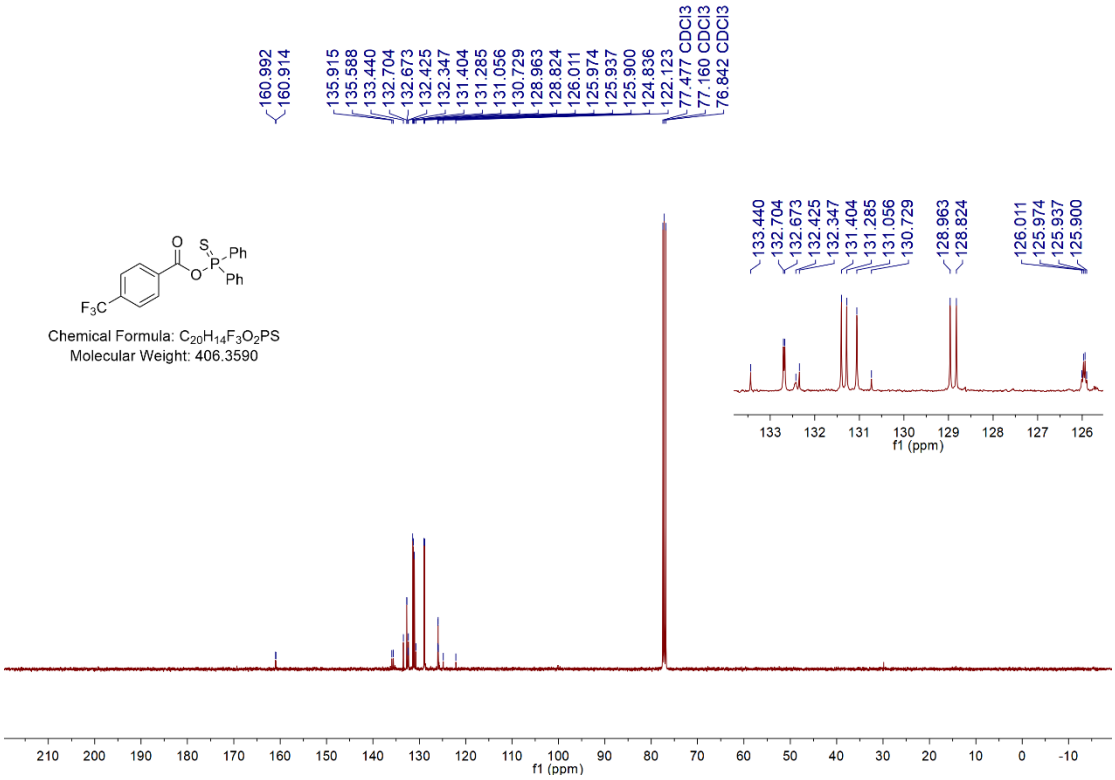


^{31}P NMR spectrum of 3j, 162 MHz, $CDCl_3$

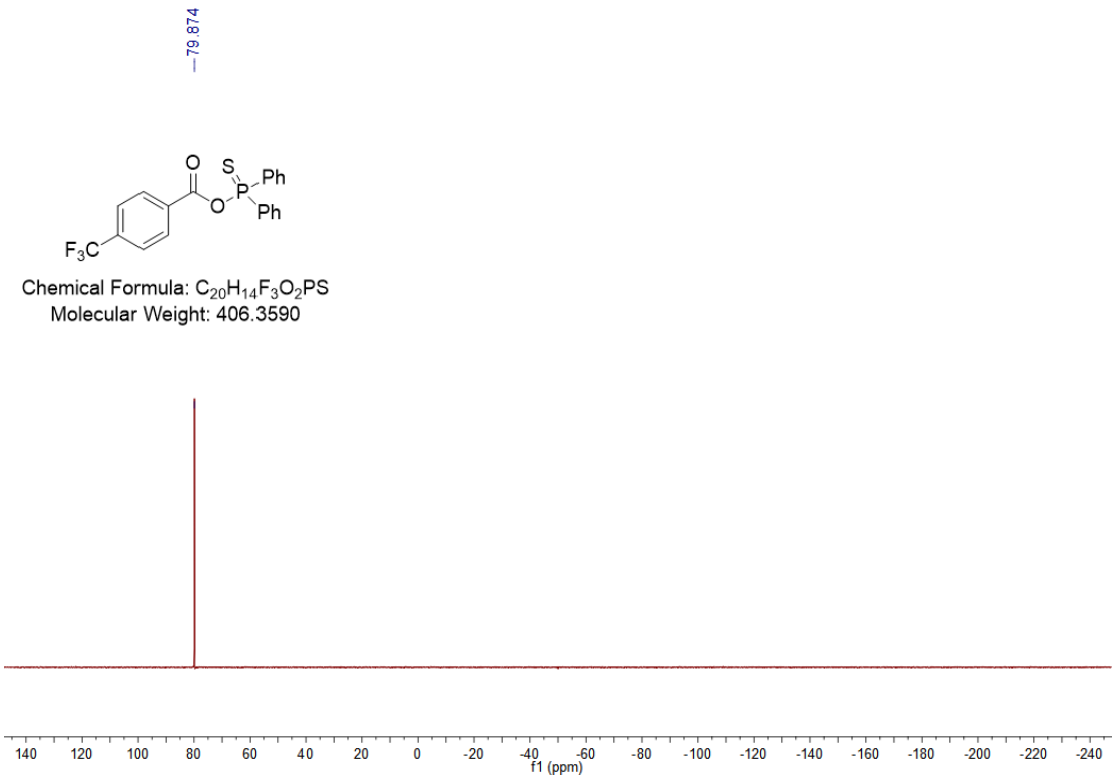
4-(Trifluoromethyl)benzoic diphenylphosphinothioic anhydride (3k)



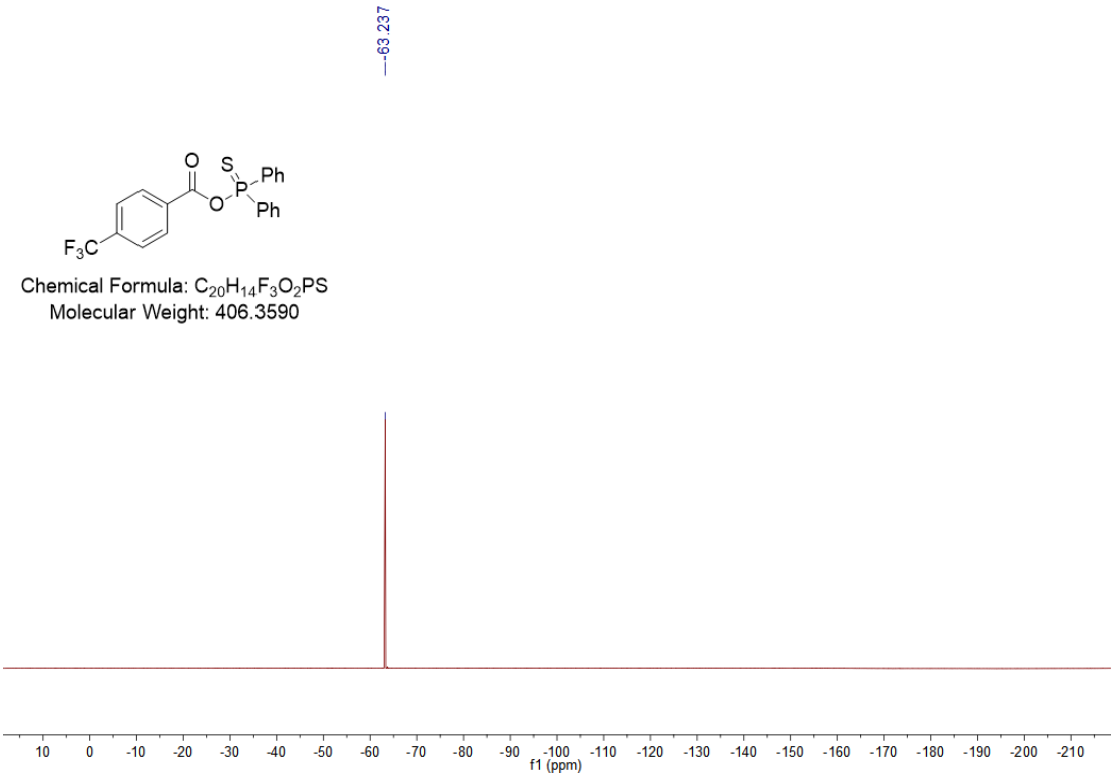
^{1}H NMR spectrum of 3k, 400 MHz, $CDCl_3$



^{13}C NMR spectrum of 3k, 100 MHz, $CDCl_3$

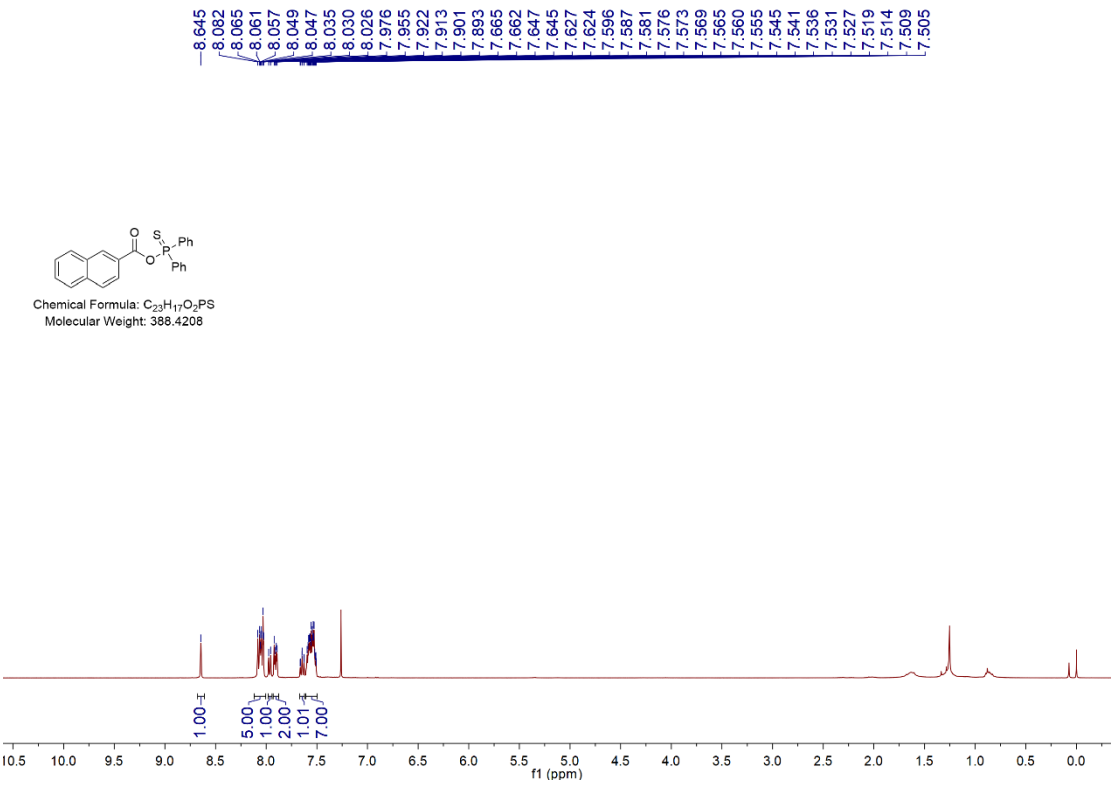


^{31}P NMR spectrum of 3k, 162 MHz, $CDCl_3$

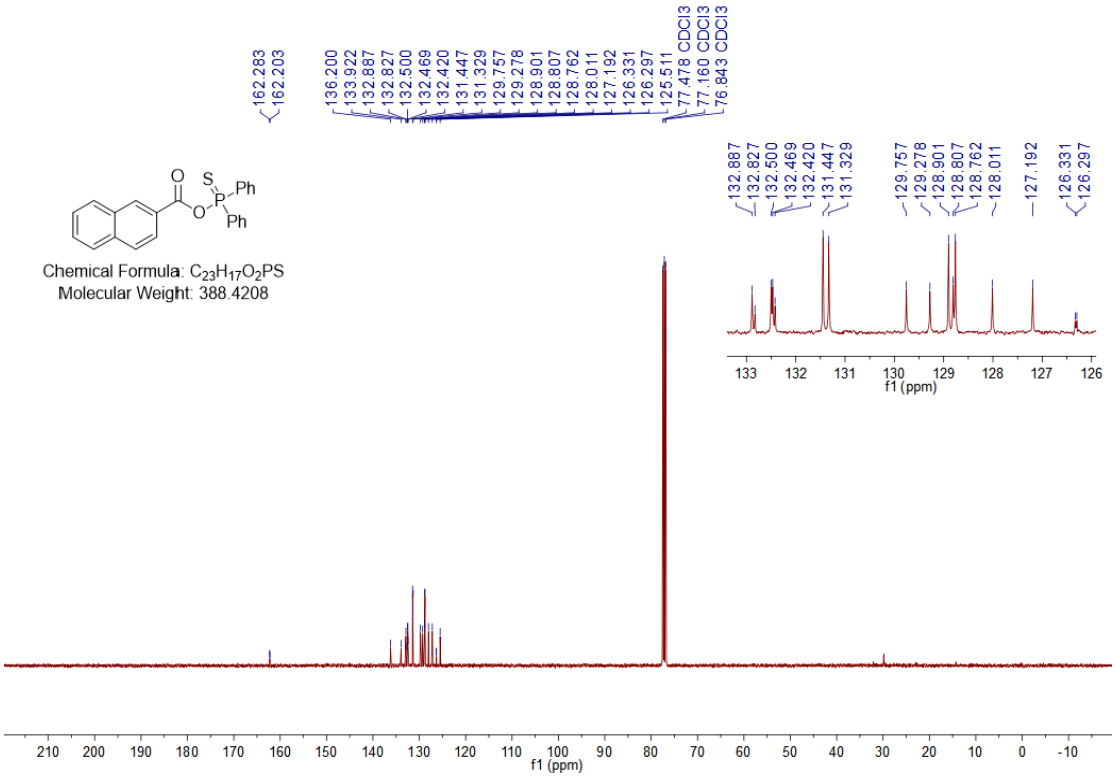


^{19}F NMR spectrum of 3k, 376 MHz, $CDCl_3$

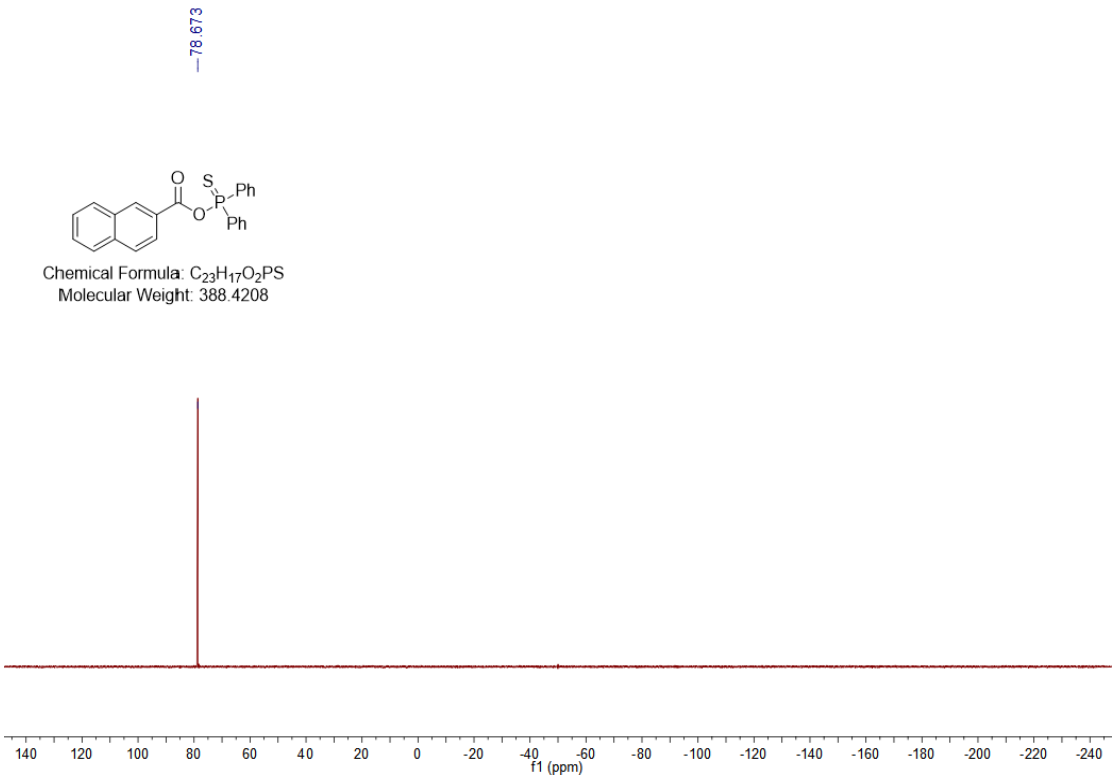
2-Naphthoic diphenylphosphinothioic anhydride (3l)



^{1}H NMR spectrum of 3l, 400 MHz, $CDCl_3$

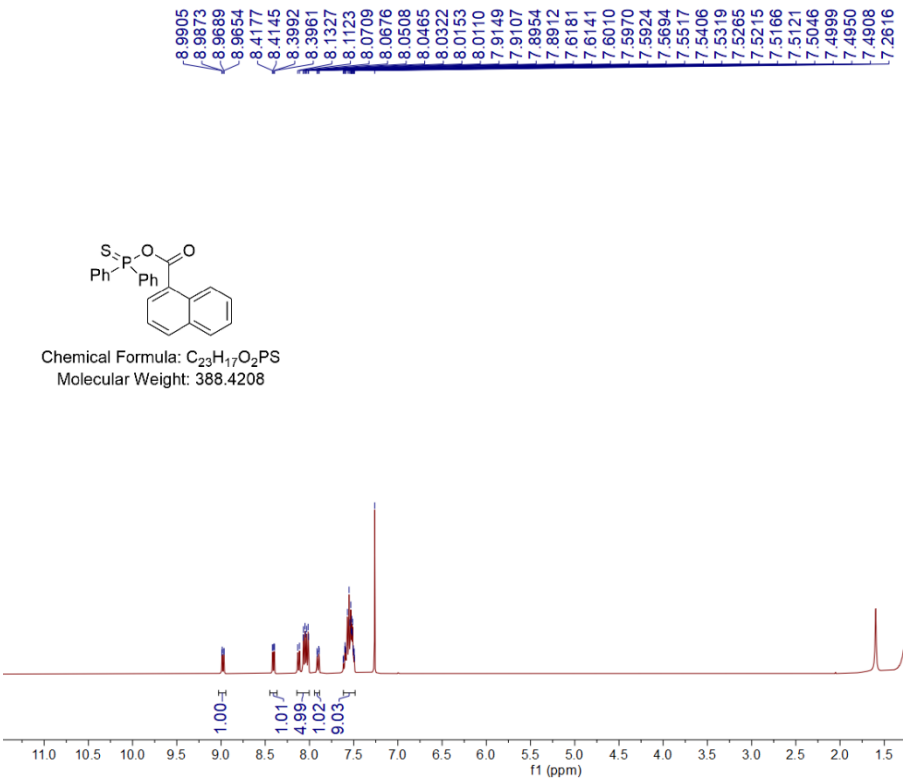


^{13}C NMR spectrum of 3l, 100 MHz, $CDCl_3$

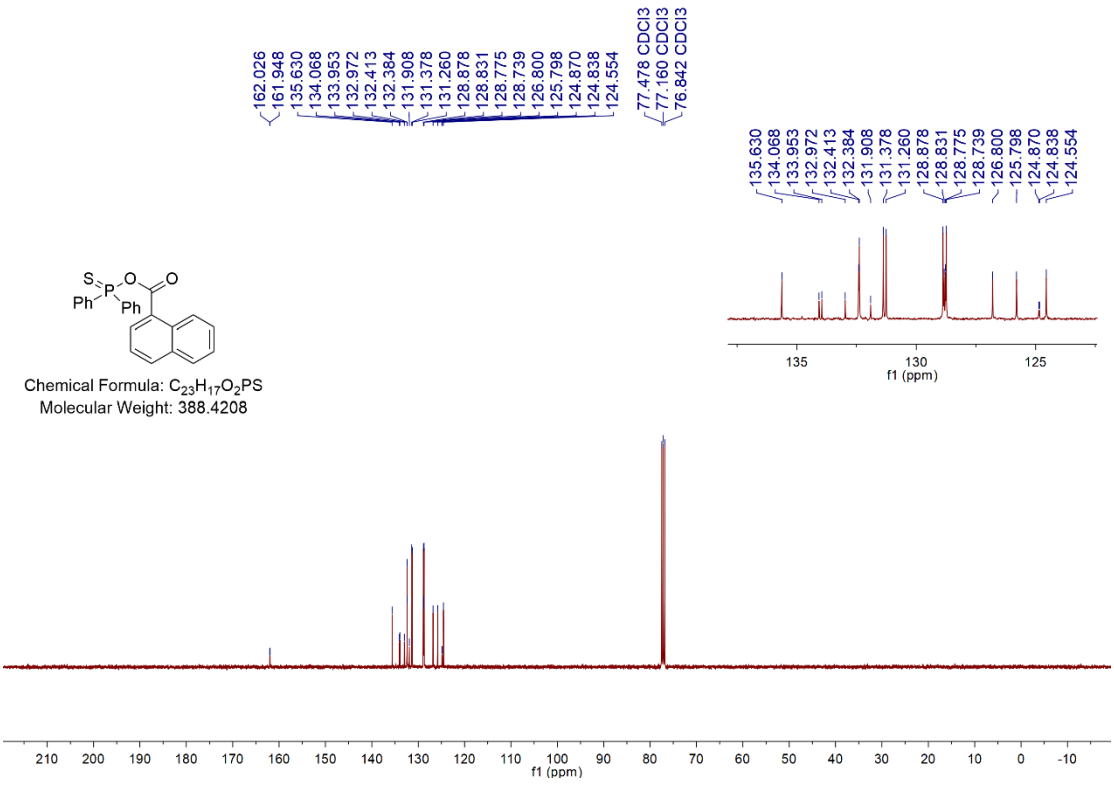


^{31}P NMR spectrum of 3l, 162 MHz, $CDCl_3$

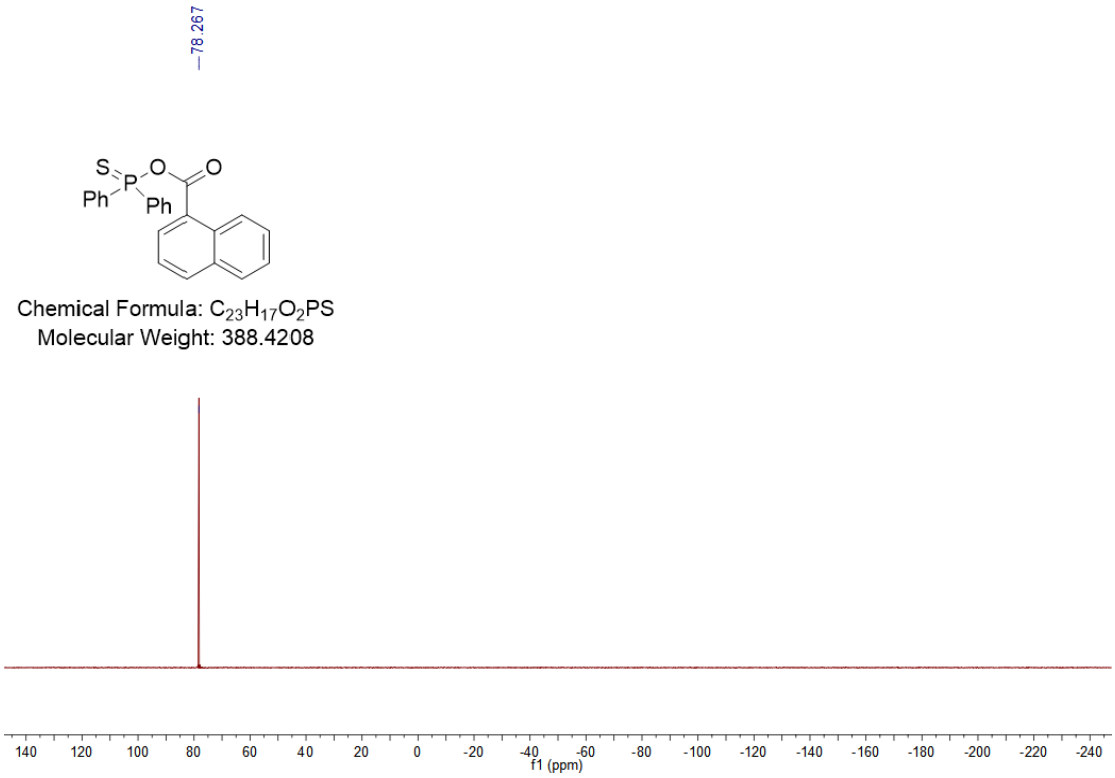
1-Naphthoic diphenylphosphinothioic anhydride (3m)



^{1}H NMR spectrum of 3m, 400 MHz, $CDCl_3$

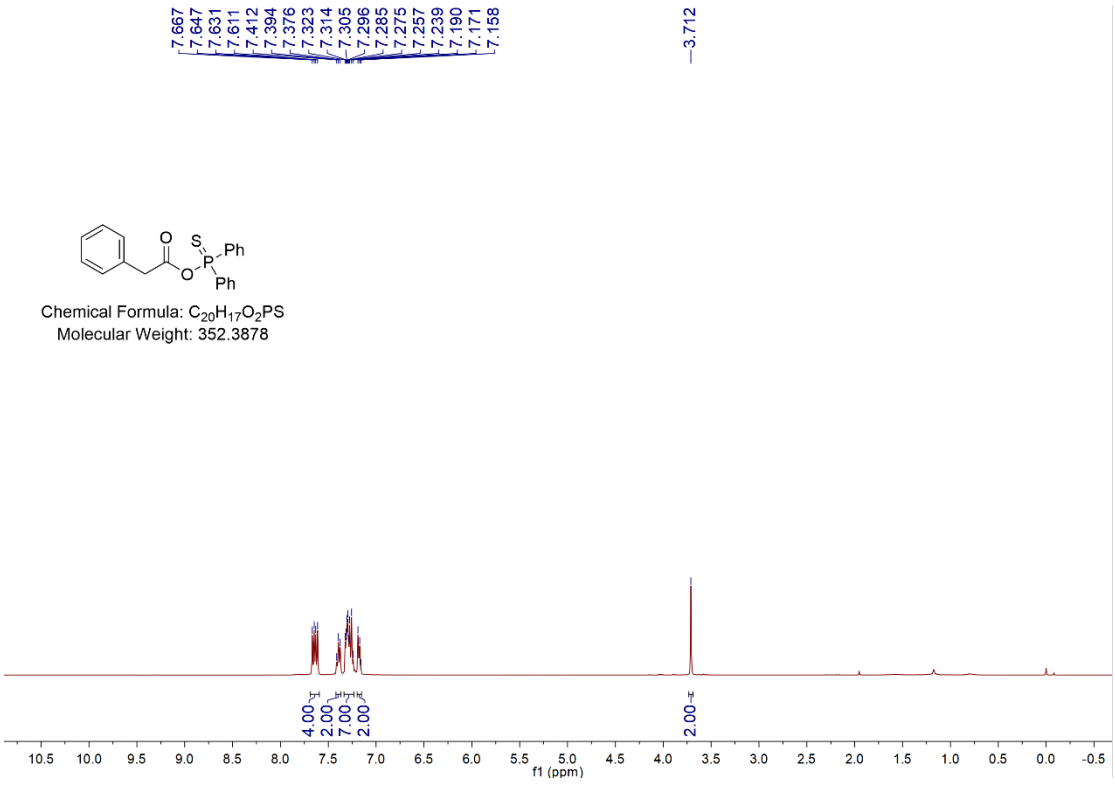


^{13}C NMR spectrum of 3m, 100 MHz, $CDCl_3$

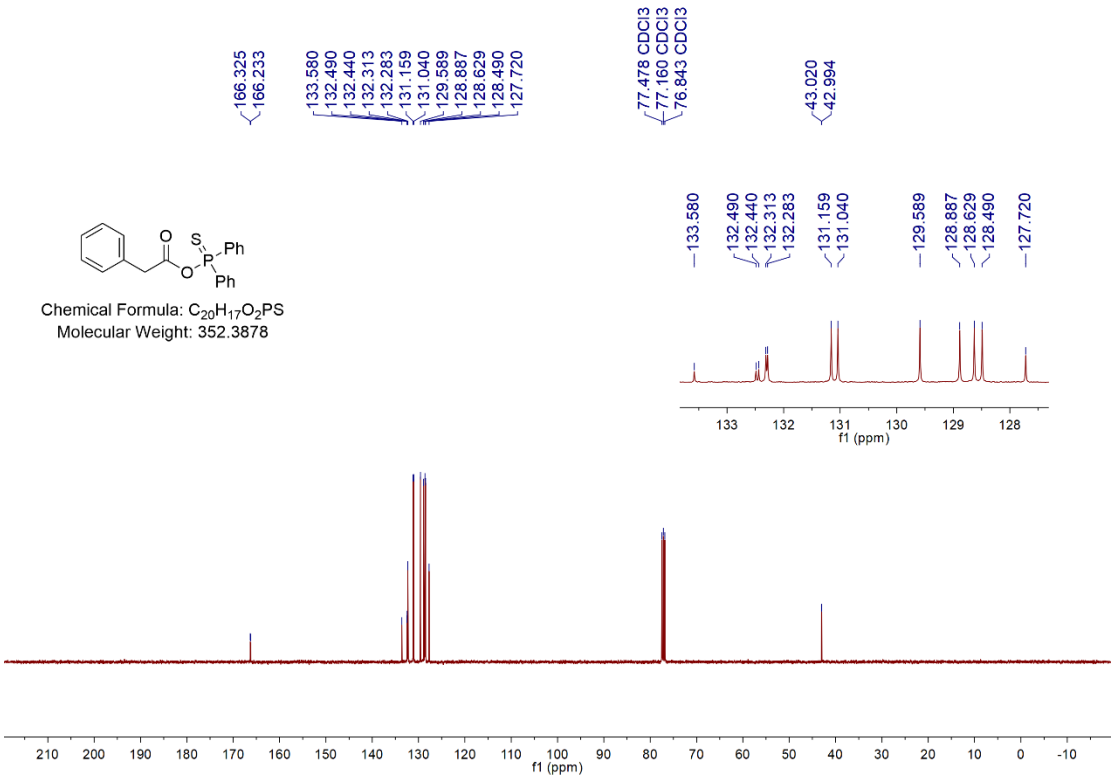


^{31}P NMR spectrum of 3m, 162 MHz, $CDCl_3$

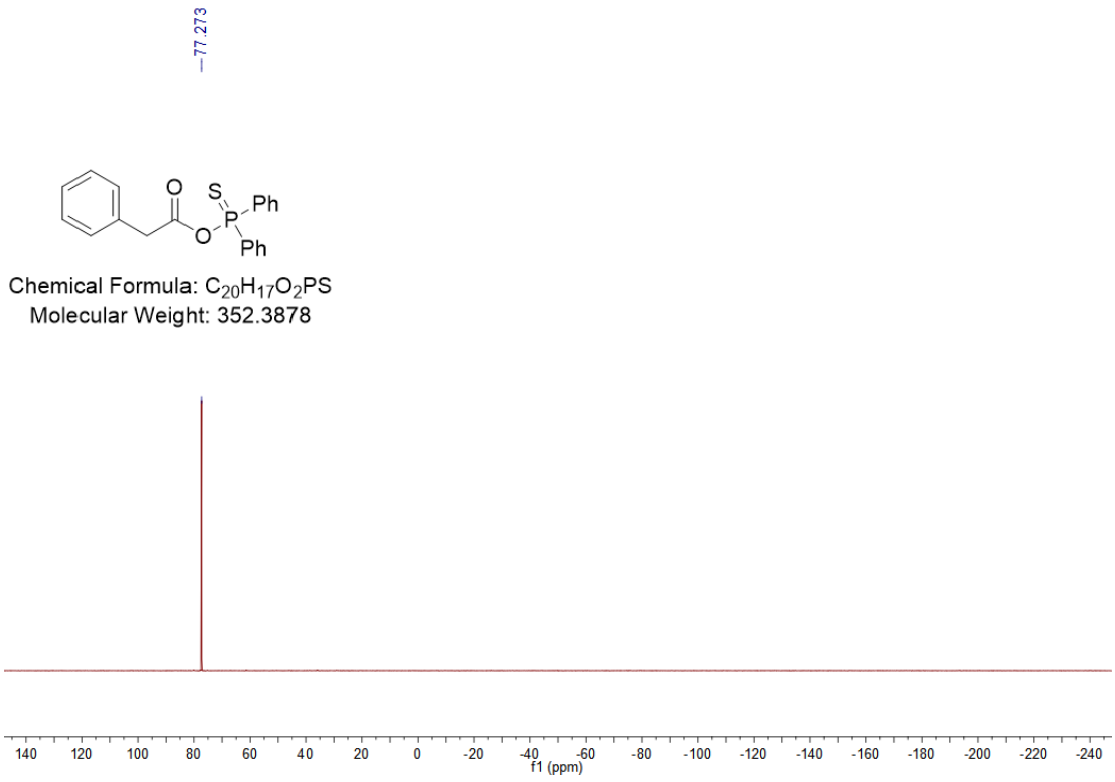
2-Phenylacetic diphenylphosphinothioic anhydride (3n)



^{1}H NMR spectrum of 3n, 400 MHz, $CDCl_3$

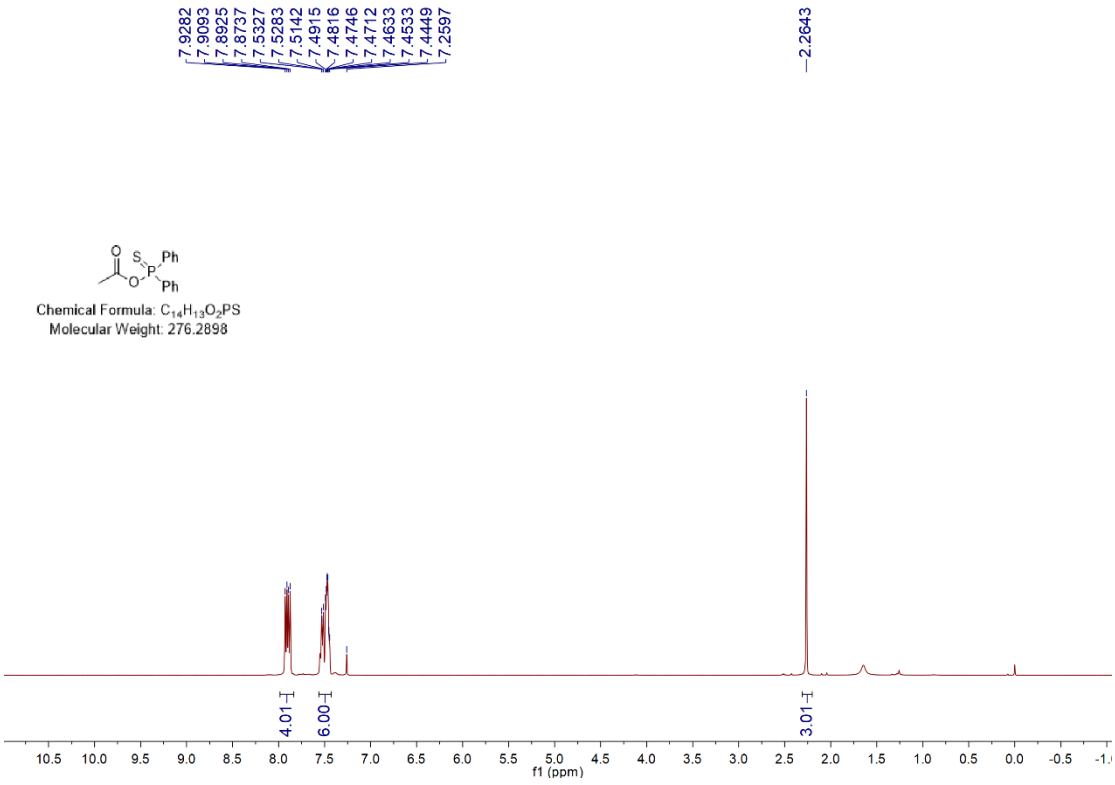


^{13}C NMR spectrum of 3n, 100 MHz, $CDCl_3$

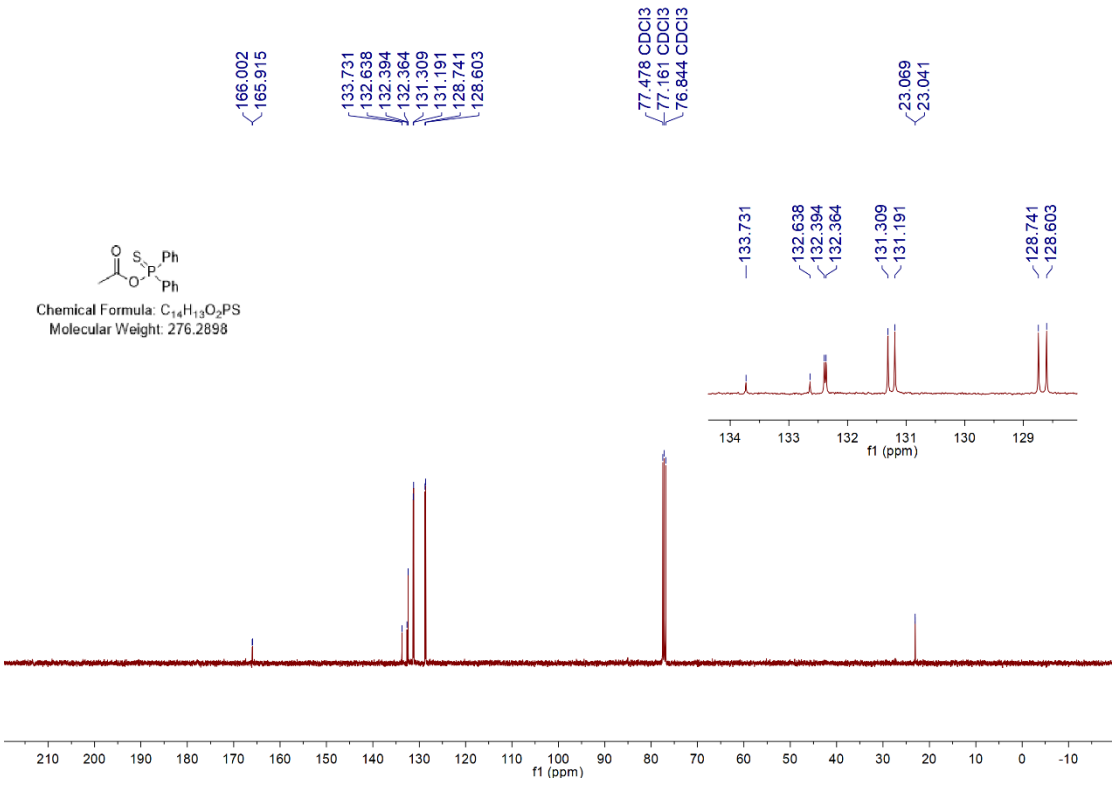


^{31}P NMR spectrum of 3n, 162 MHz, $CDCl_3$

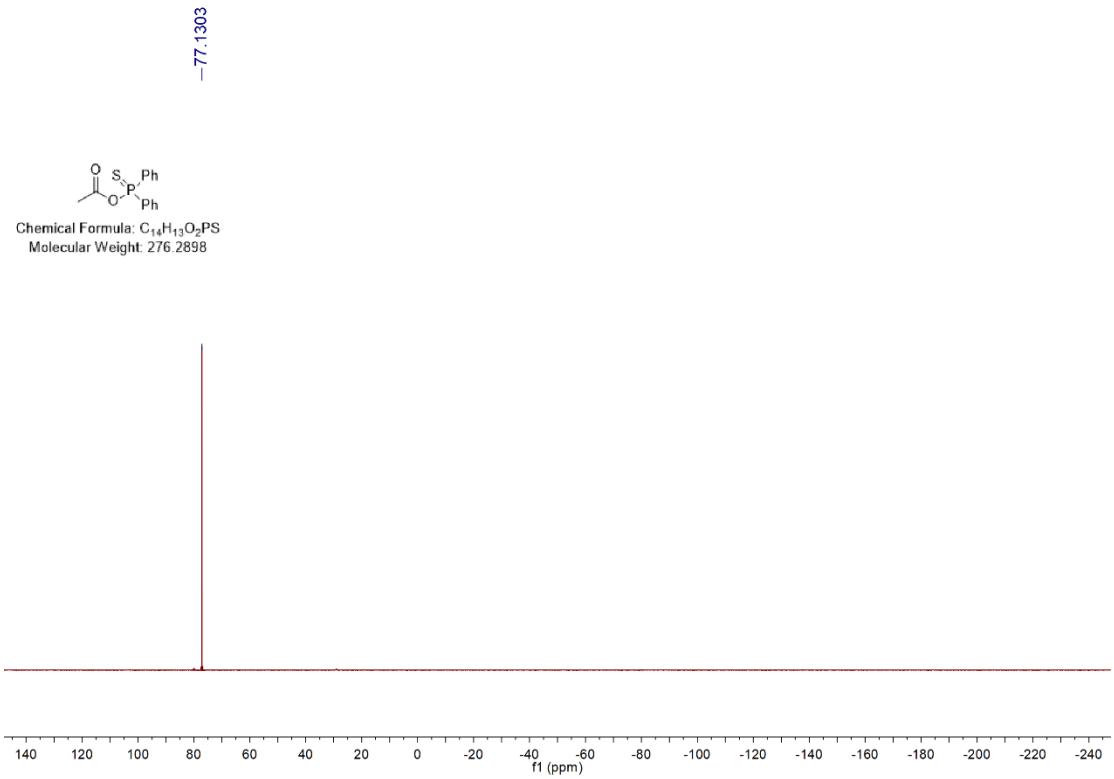
Acetic diphenylphosphinothioic anhydride (3o)



^{1}H NMR spectrum of 3o, 400 MHz, $CDCl_3$

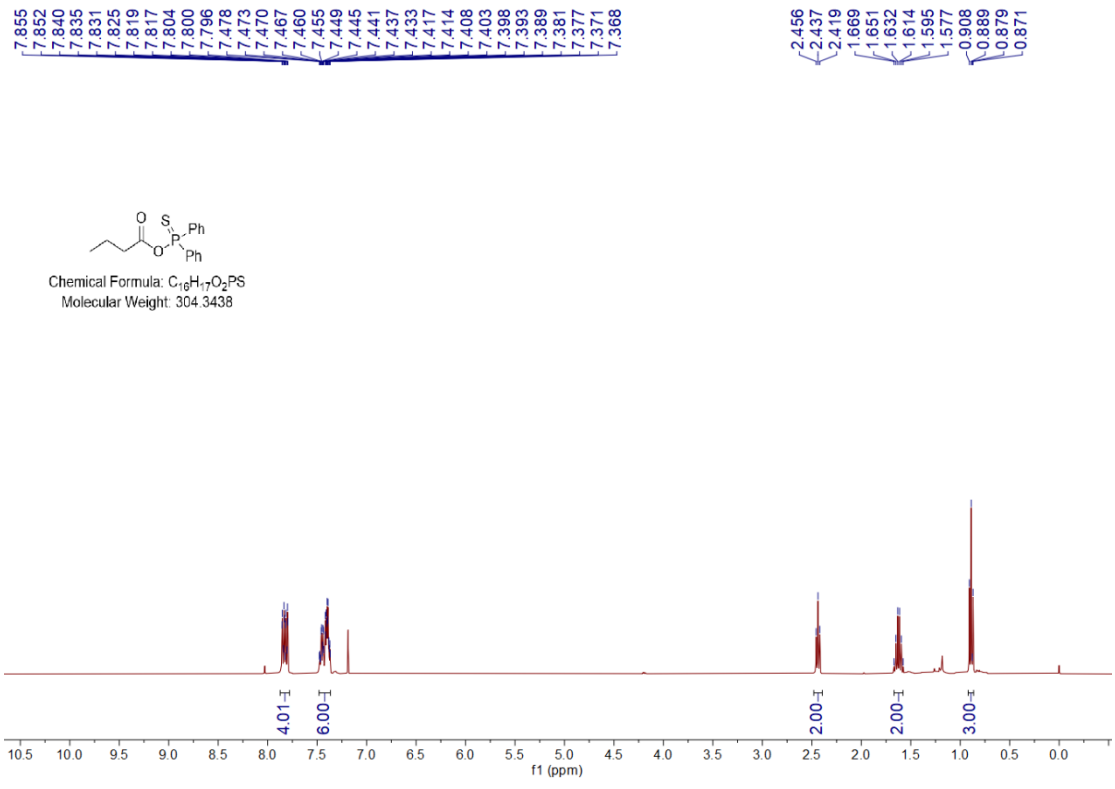


^{13}C NMR spectrum of 3o, 100 MHz, $CDCl_3$

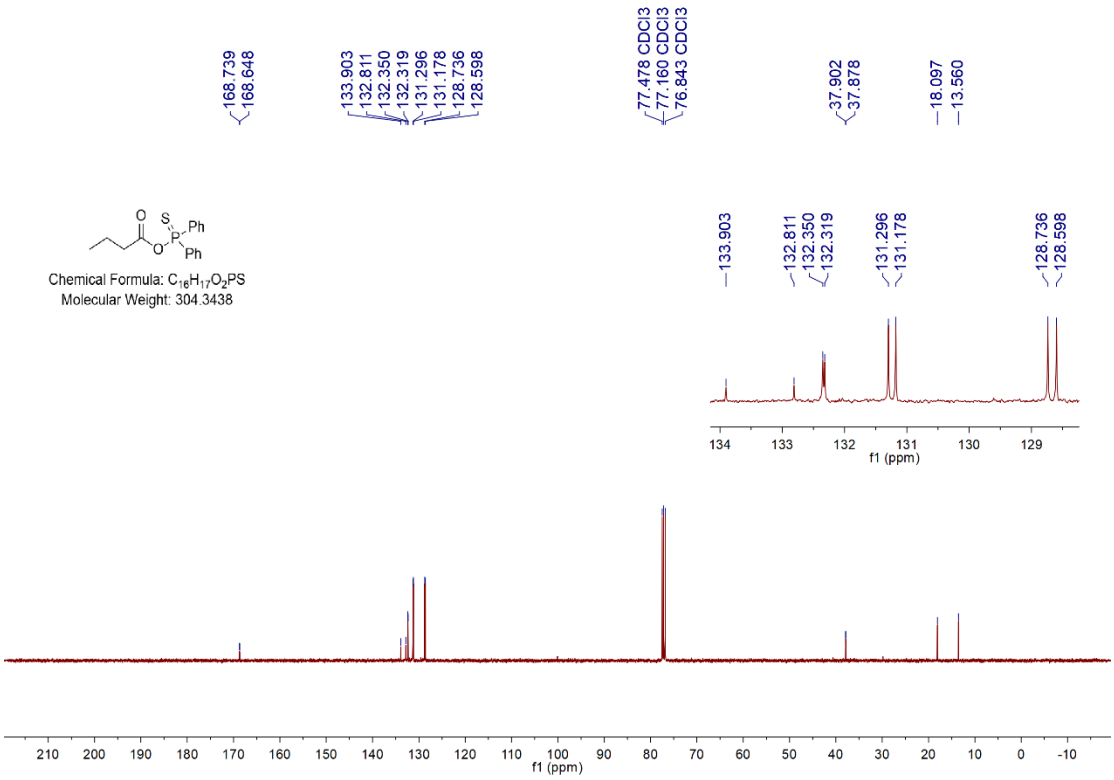


^{31}P NMR spectrum of 3o, 162 MHz, $CDCl_3$

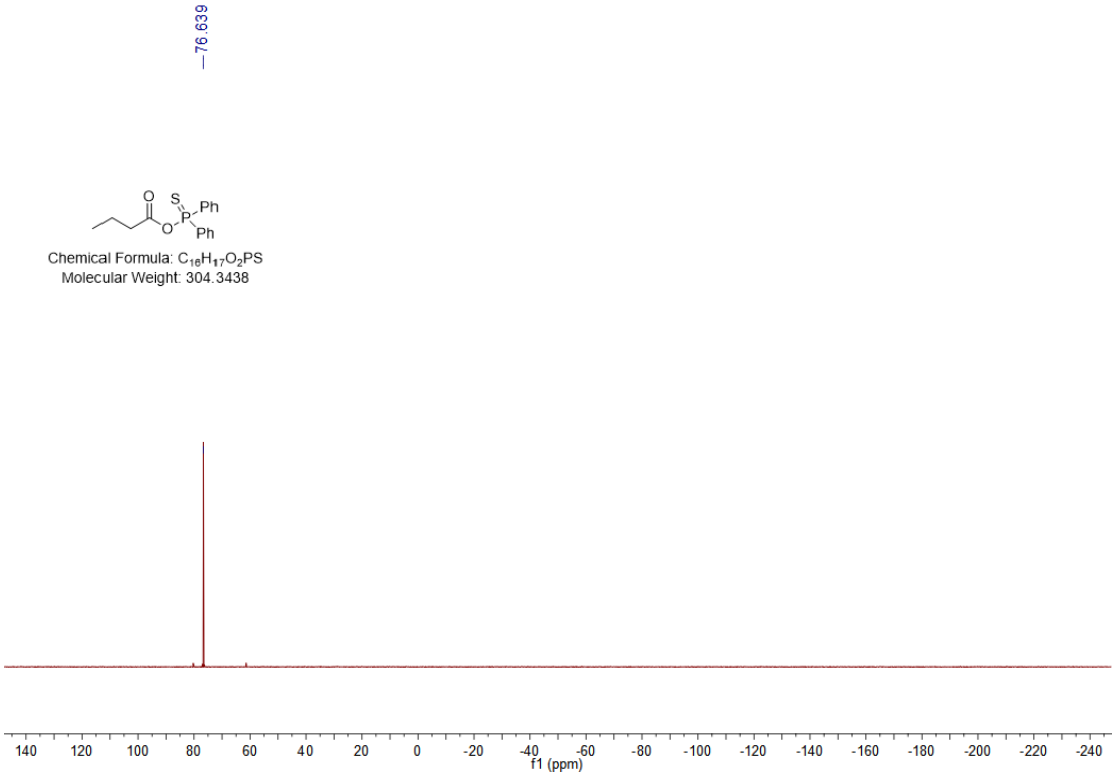
Butyric diphenylphosphinothioic anhydride (3p)



^{1}H NMR spectrum of 3p, 400 MHz, $CDCl_3$

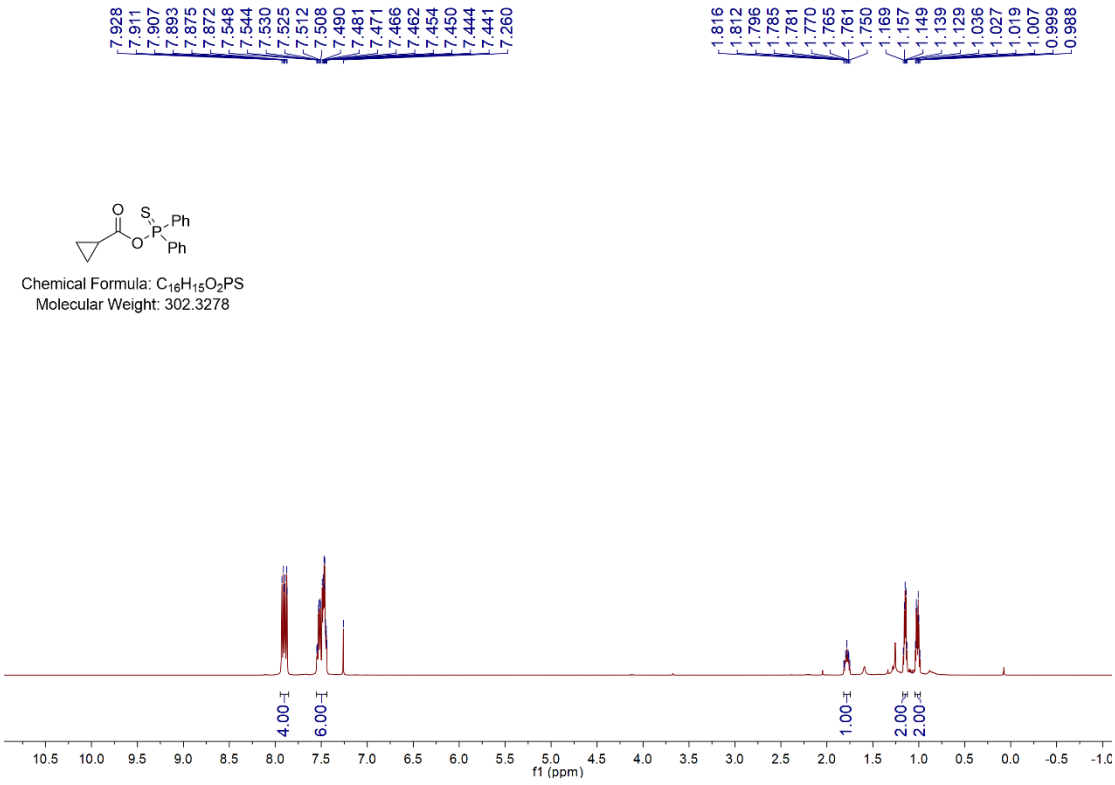


^{13}C NMR spectrum of 3p, 100 MHz, $CDCl_3$

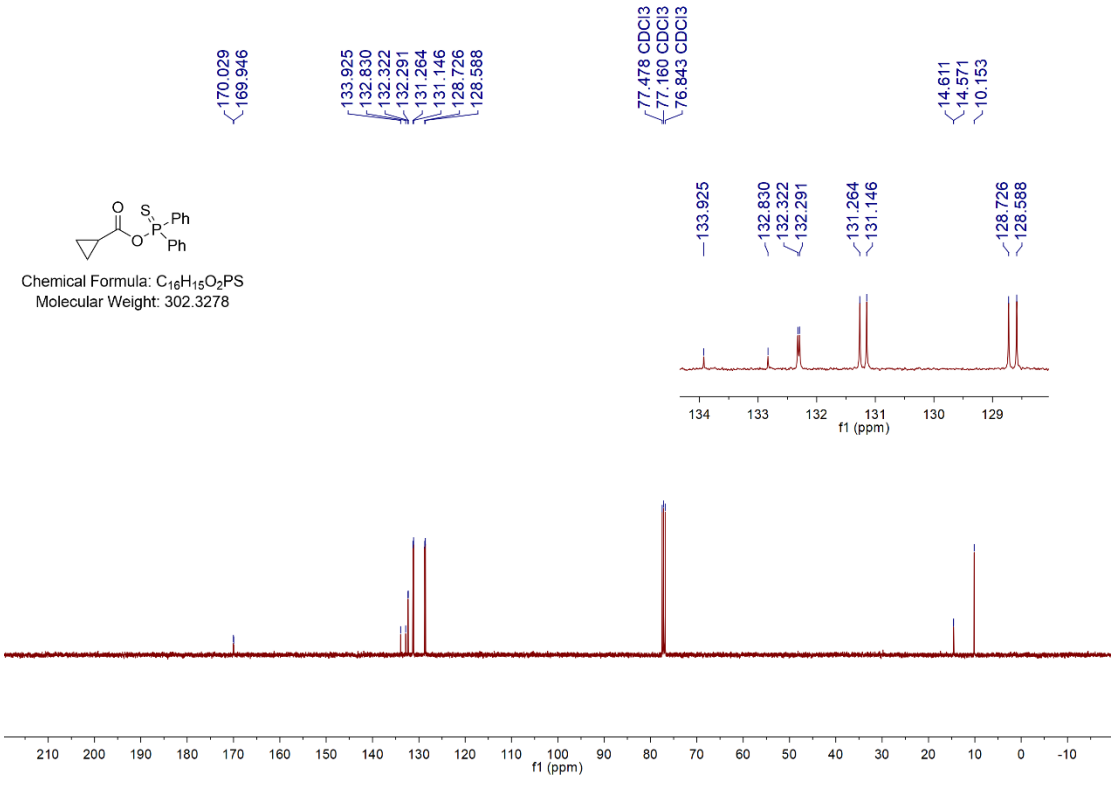


^{31}P NMR spectrum of 3p, 162 MHz, $CDCl_3$

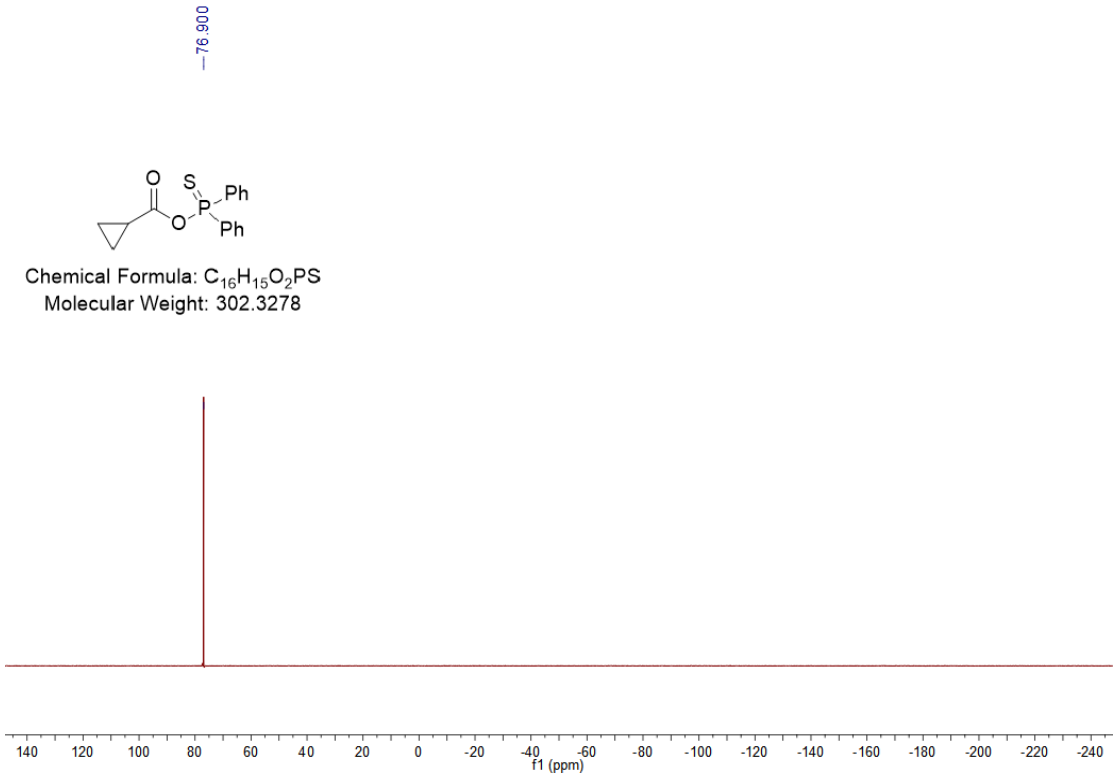
Cyclopropanecarboxylic diphenylphosphinothioic anhydride (3q)



^{1}H NMR spectrum of 3q, 400 MHz, $CDCl_3$

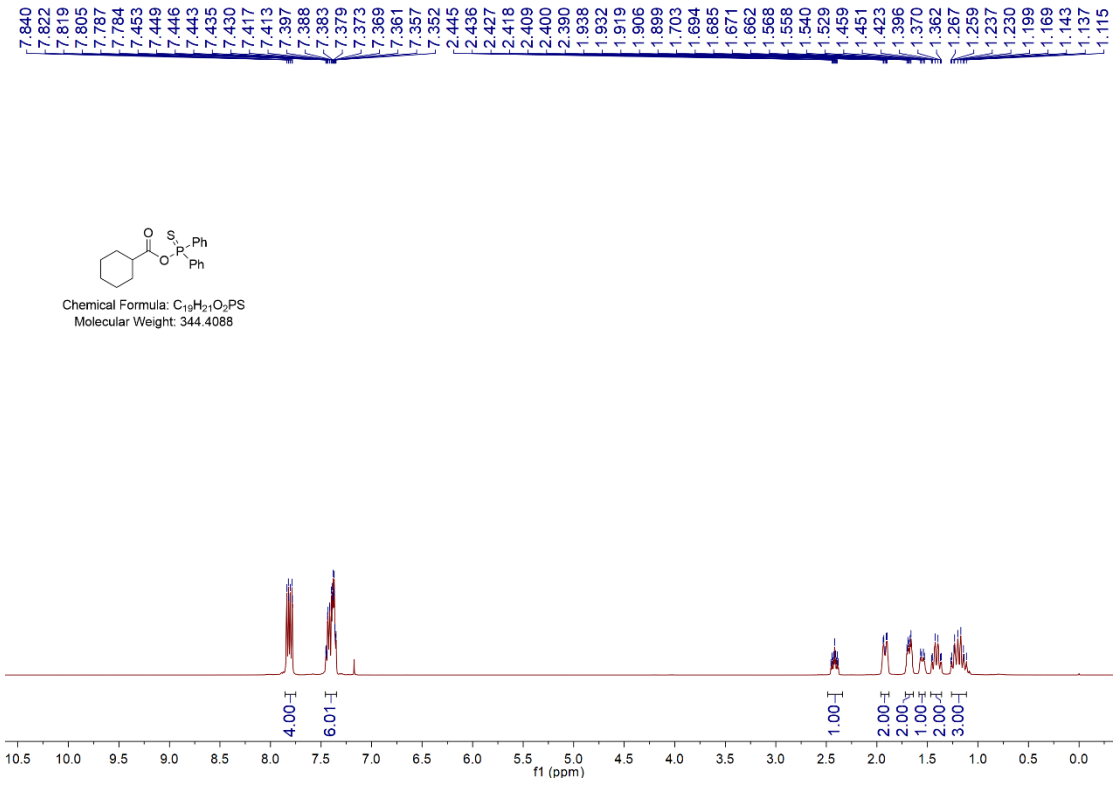


^{13}C NMR spectrum of 3q, 100 MHz, $CDCl_3$

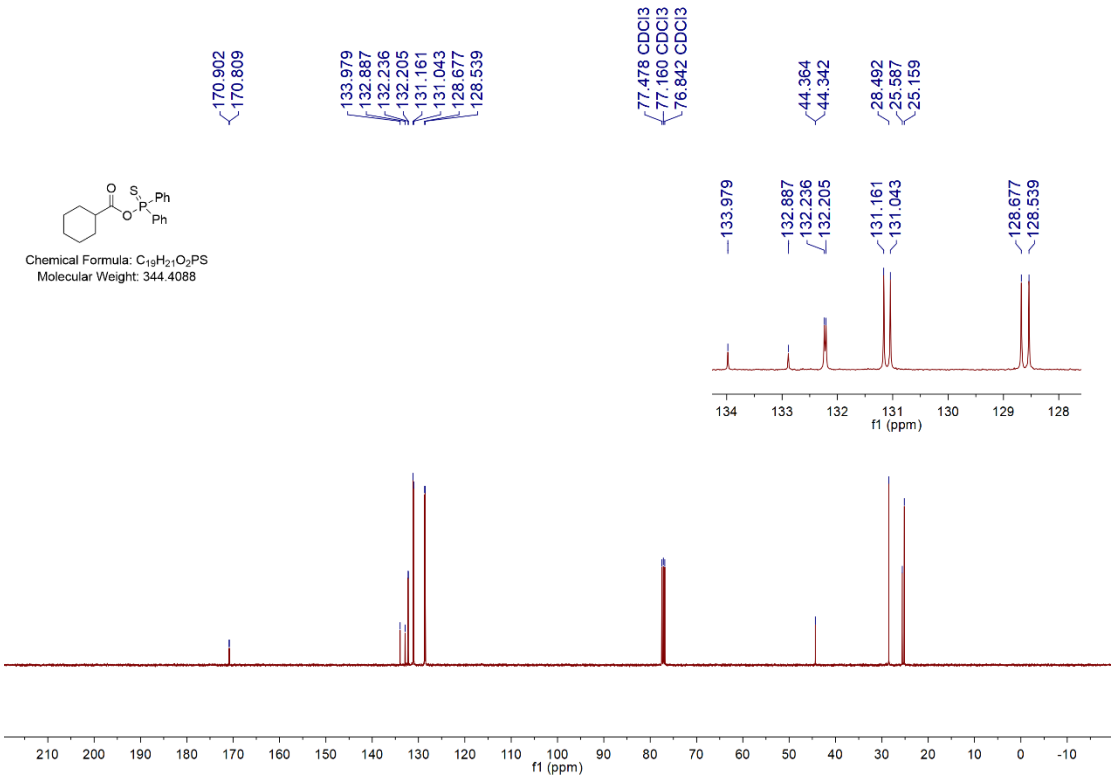


^{31}P NMR spectrum of 3q, 162 MHz, $CDCl_3$

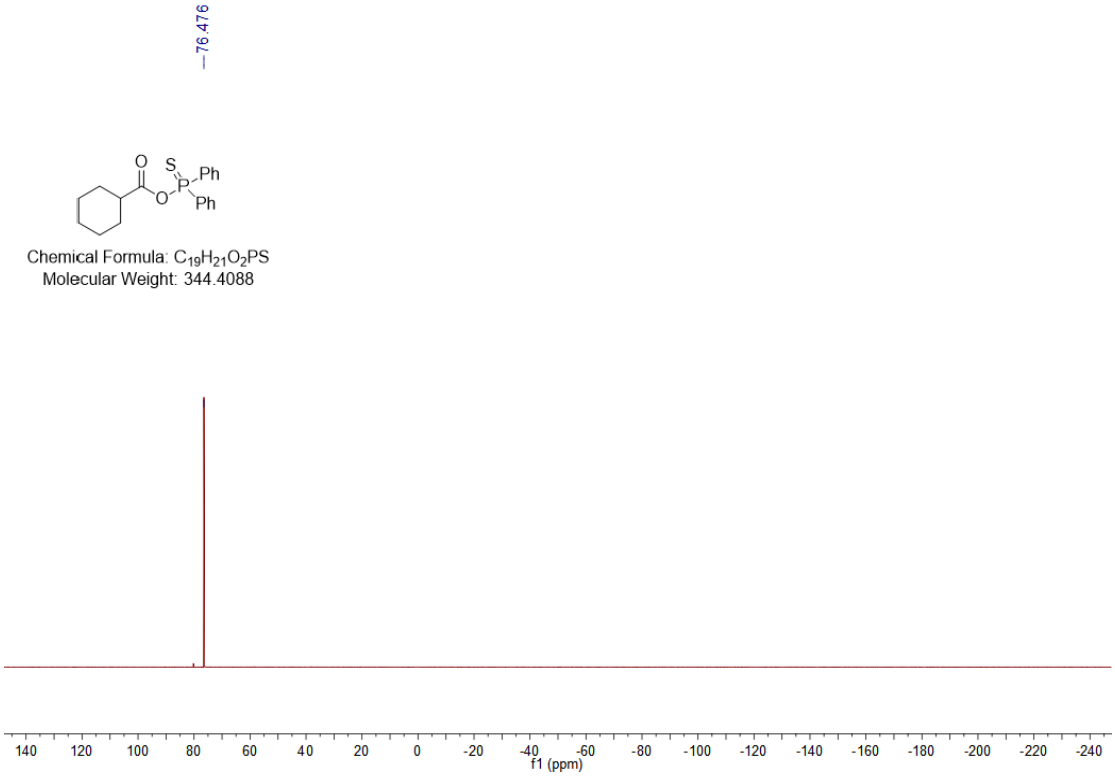
Cyclohexanecarboxylic diphenylphosphinothioic anhydride (3r)



^{1}H NMR spectrum of 3r, 400 MHz, $CDCl_3$

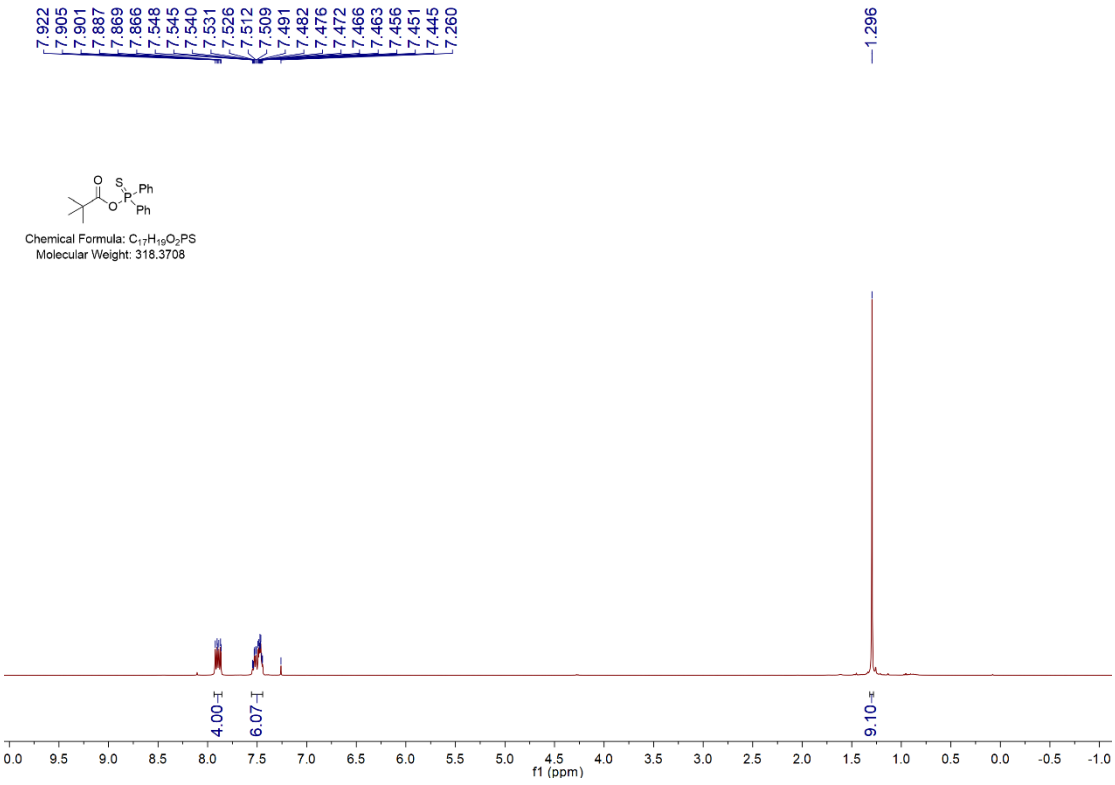


^{13}C NMR spectrum of 3r, 100 MHz, $CDCl_3$

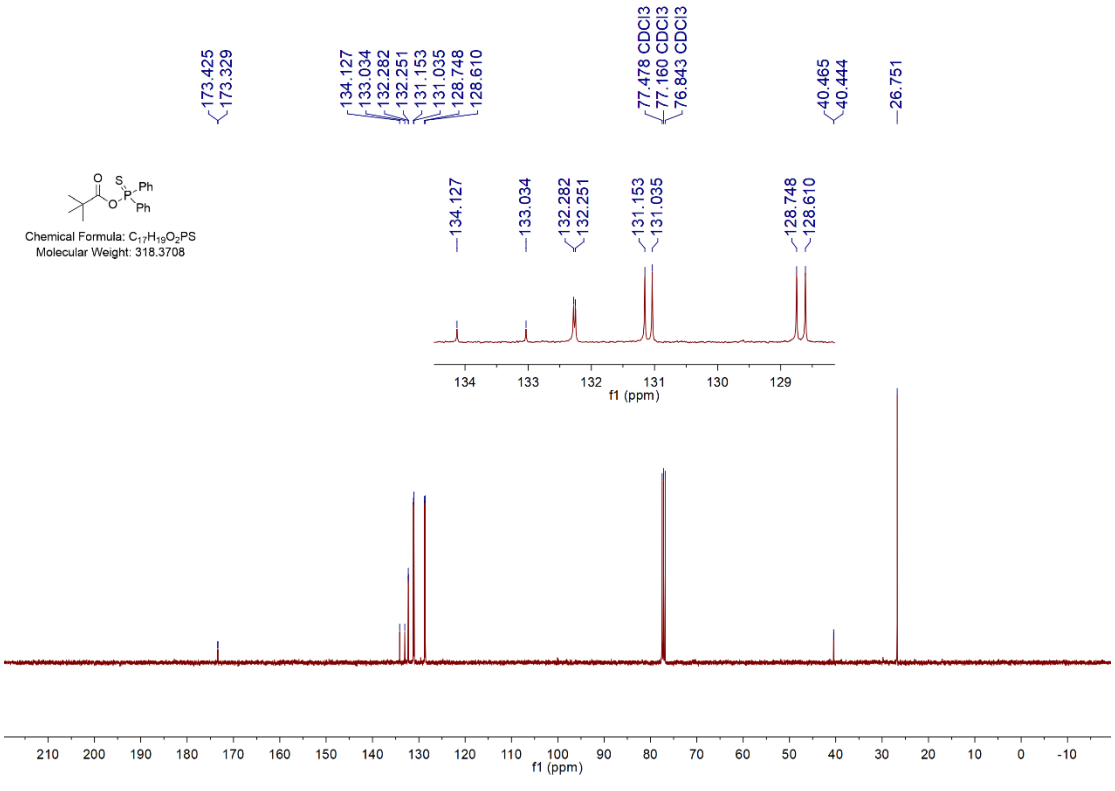


^{31}P NMR spectrum of 3r, 162 MHz, $CDCl_3$

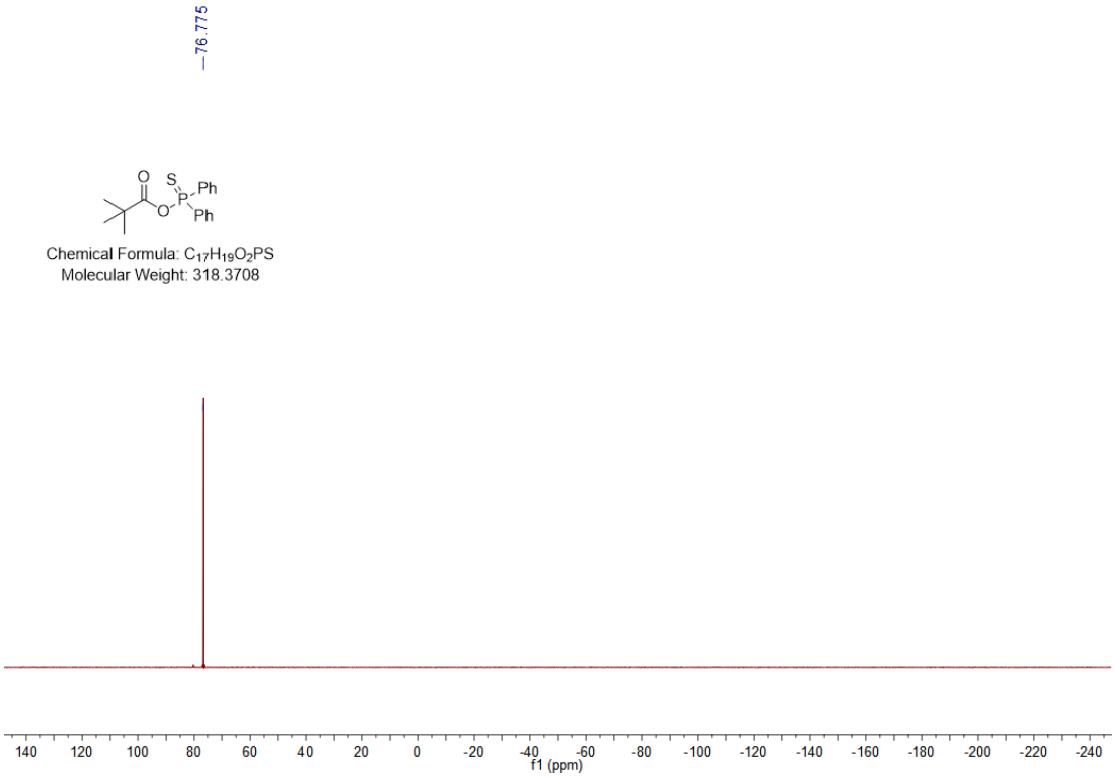
Diphenylphosphinothioic pivalic anhydride (3s)



^{1}H NMR spectrum of 3s, 400 MHz, $CDCl_3$

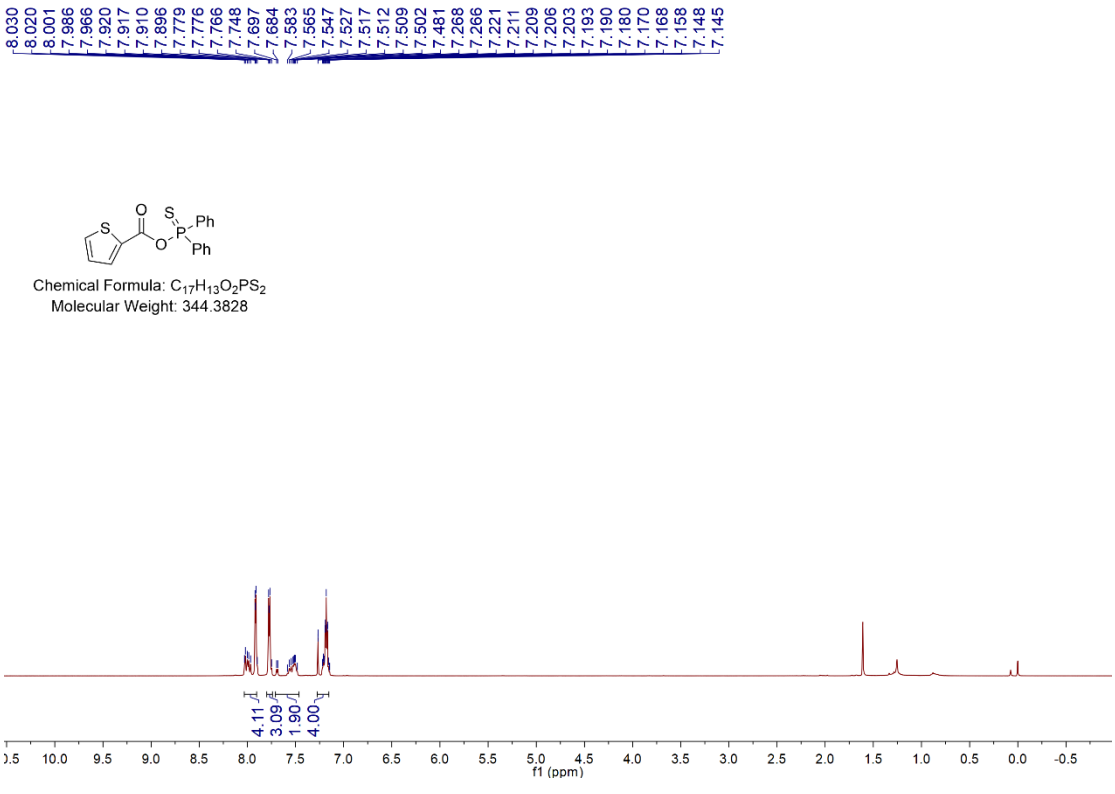


^{13}C NMR spectrum of 3s, 100 MHz, $CDCl_3$

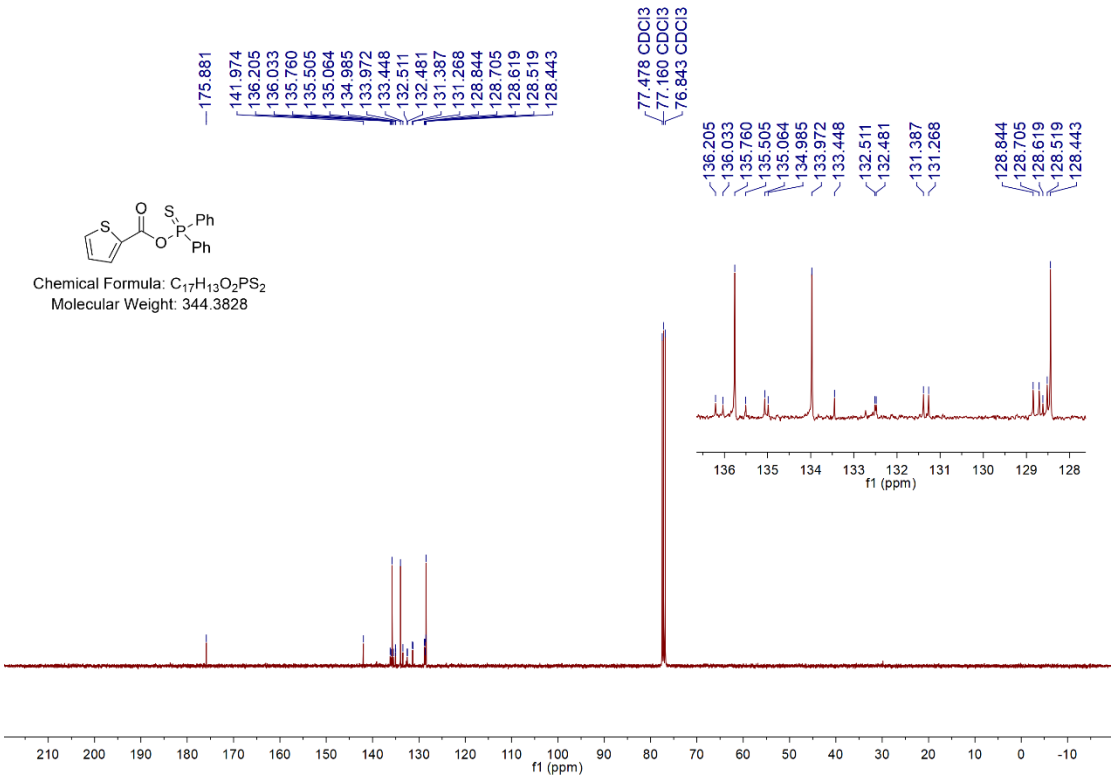


^{31}P NMR spectrum of 3s, 162 MHz, $CDCl_3$

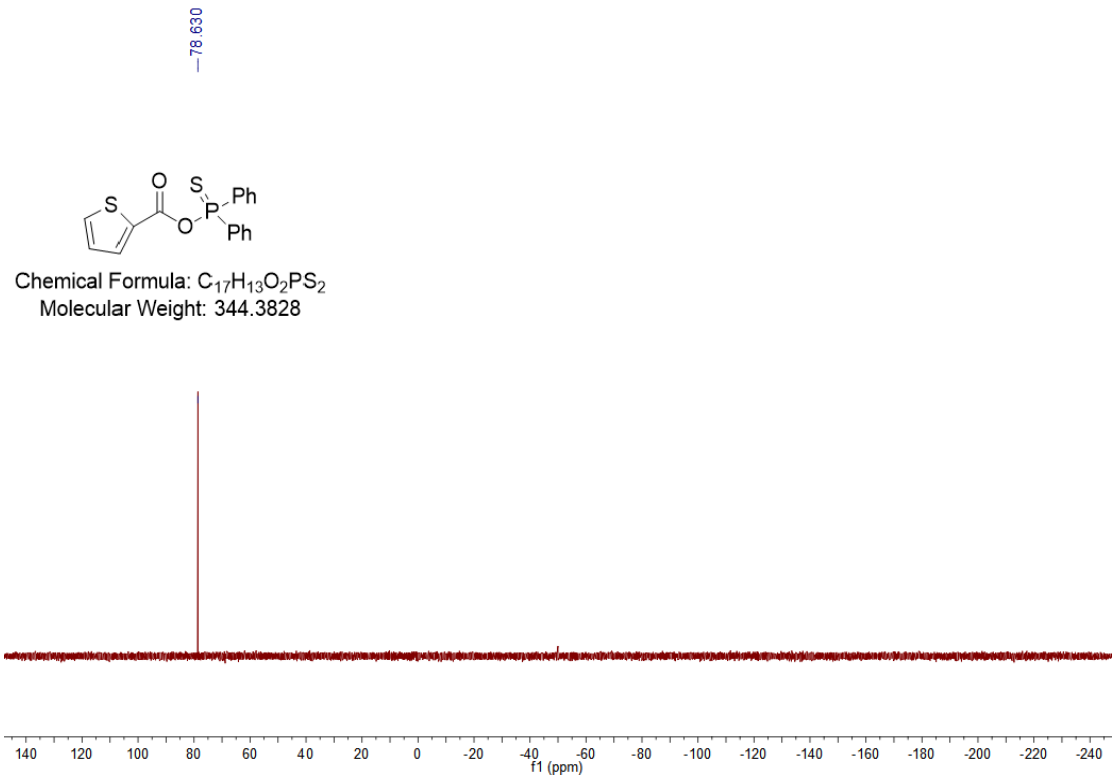
Diphenylphosphinothioic thiophene-2-carboxylic anhydride (3t)



^{1}H NMR spectrum of 3t, 400 MHz, $CDCl_3$

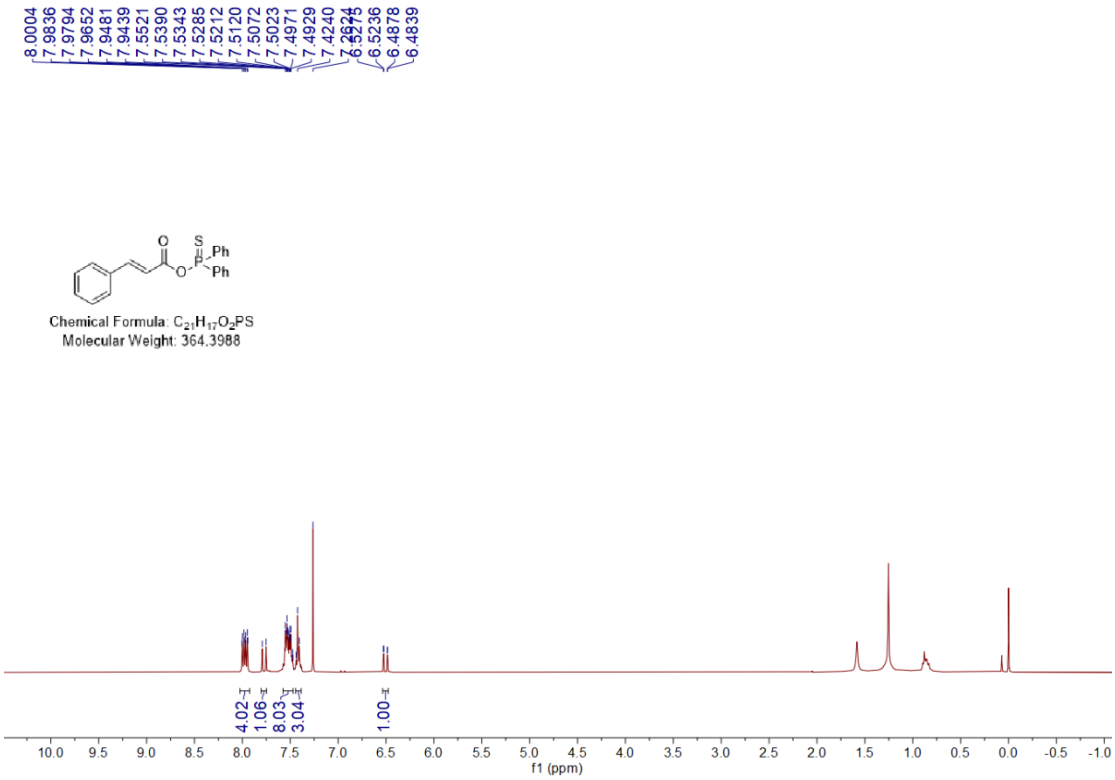


^{13}C NMR spectrum of 3t, 100 MHz, $CDCl_3$

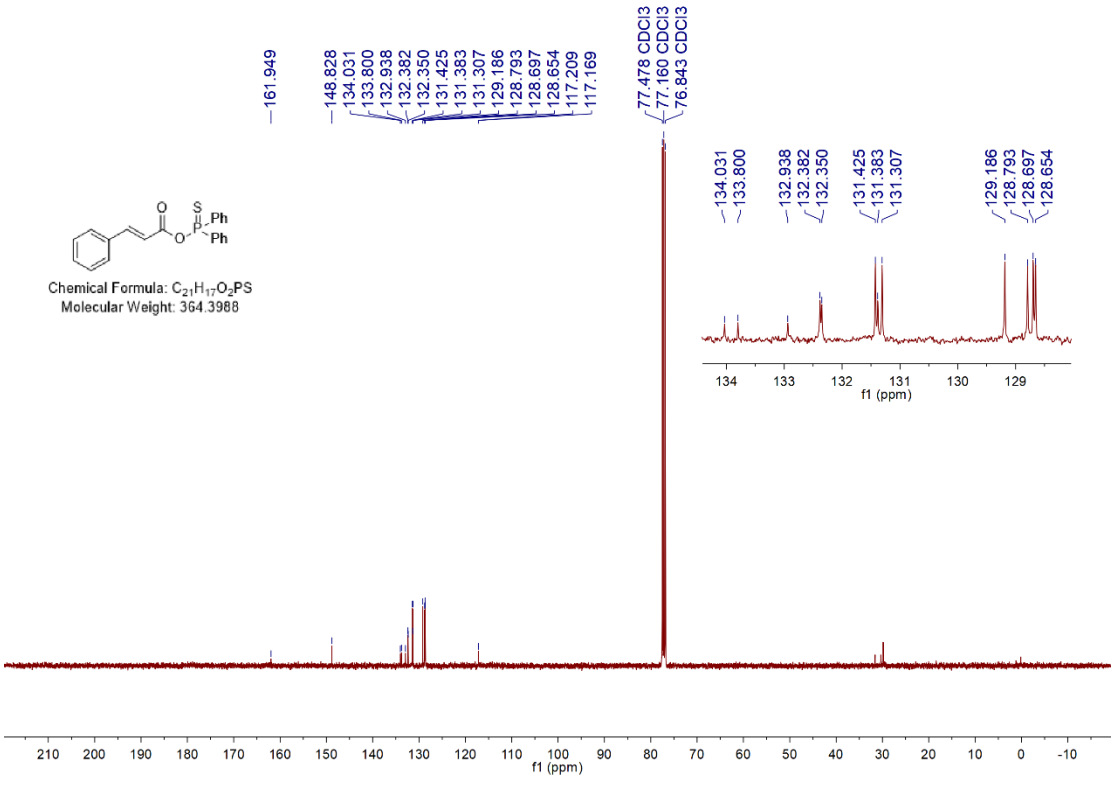


^{31}P NMR spectrum of 3t, 162 MHz, $CDCl_3$

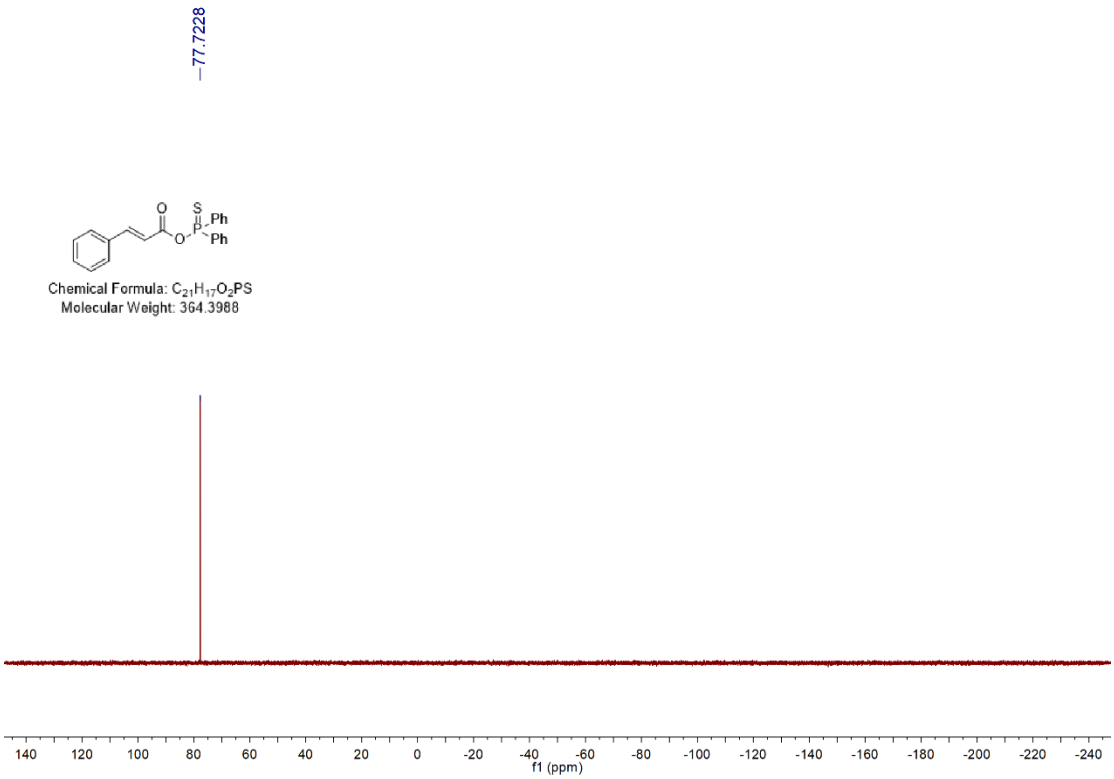
(E)-Cinnamic diphenylphosphinothioic anhydride (3u)



^{1}H NMR spectrum of 3u, 400 MHz, $CDCl_3$

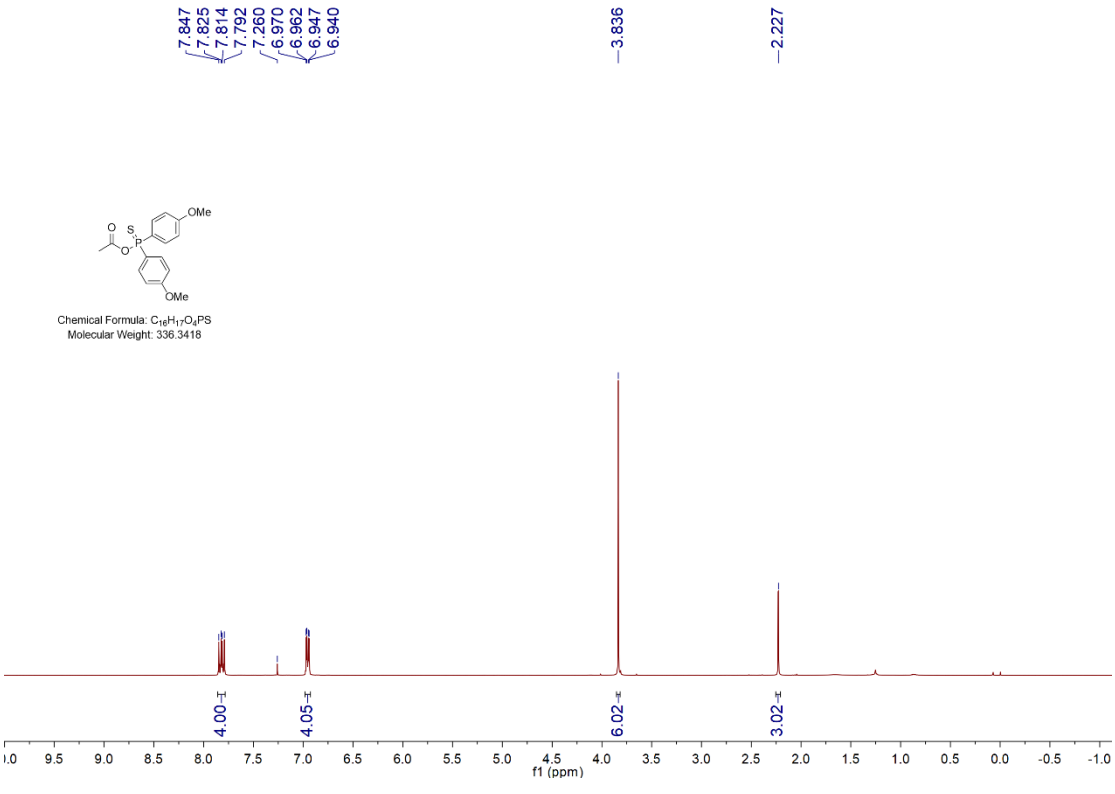


^{13}C NMR spectrum of 3u, 100 MHz, $CDCl_3$

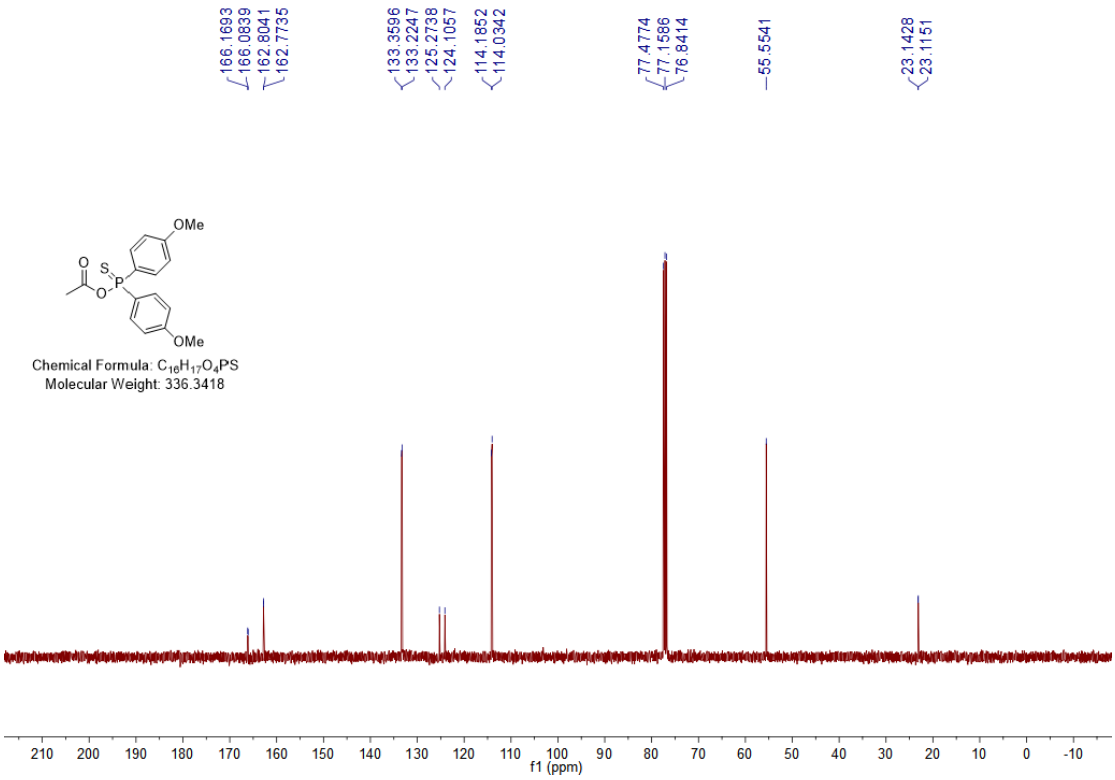


^{31}P NMR spectrum of 3u, 162 MHz, $CDCl_3$

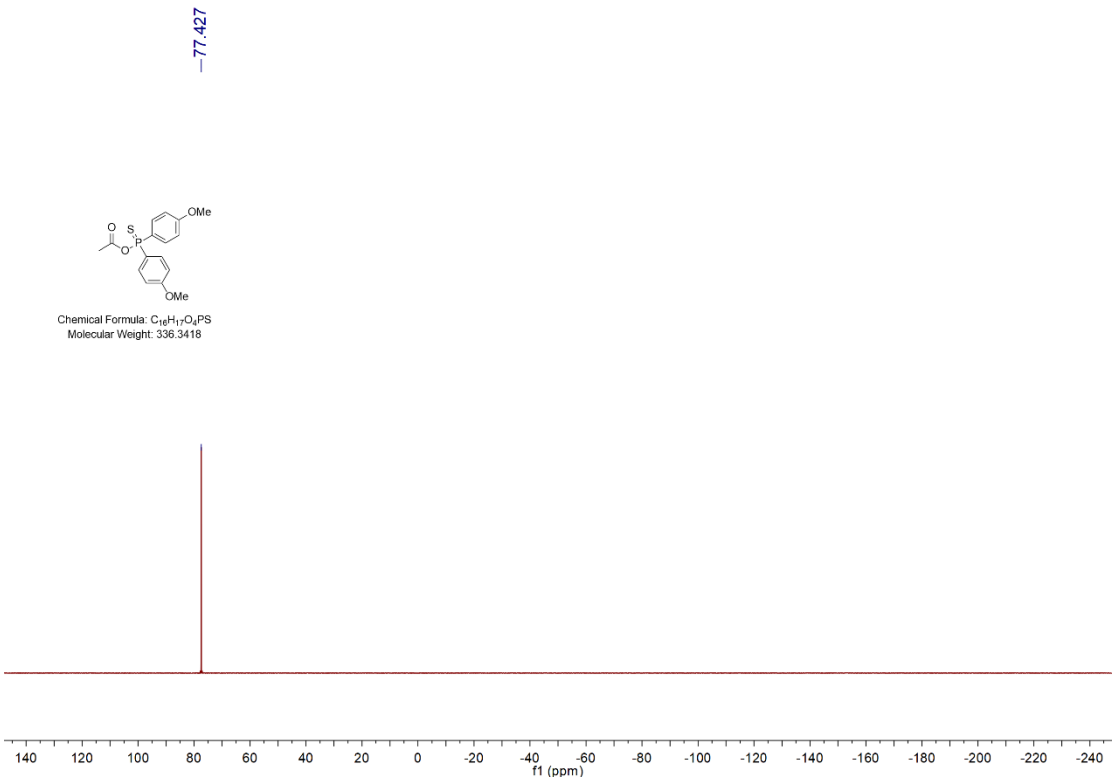
Acetic bis(4-methoxyphenyl)phosphinothioic anhydride (3v)



^{1}H NMR spectrum of 3v, 400 MHz, $CDCl_3$

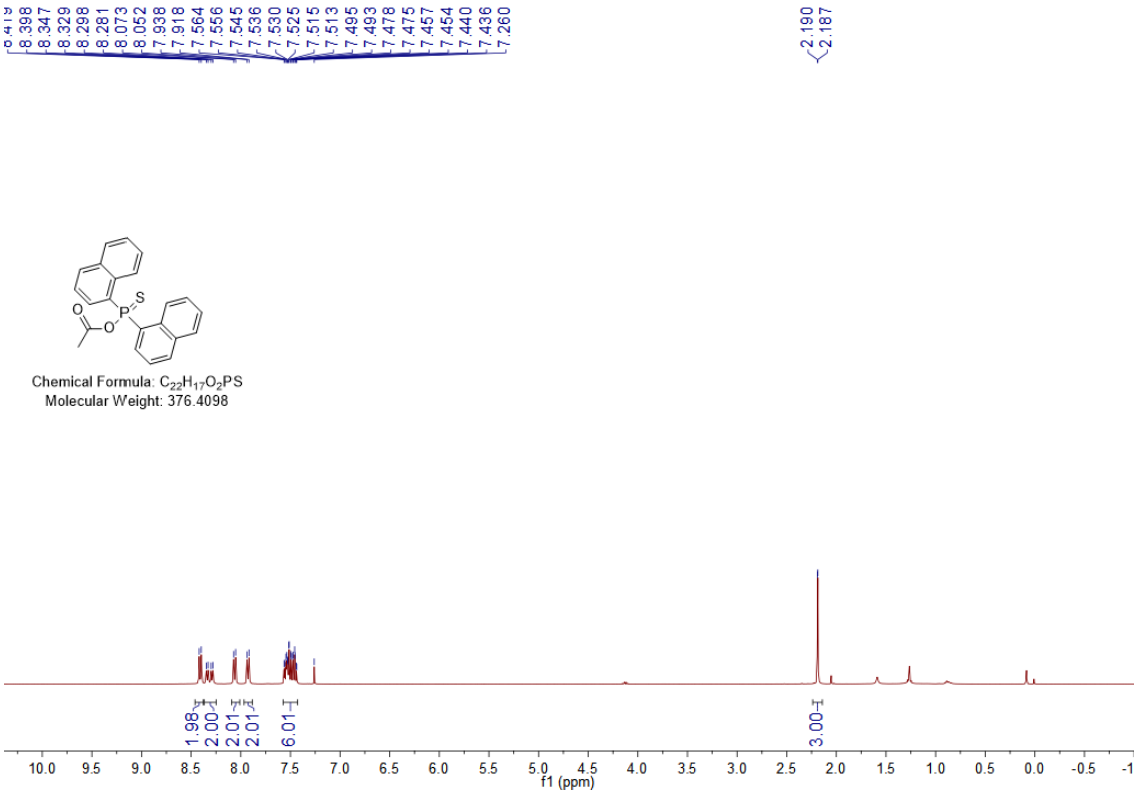


^{13}C NMR spectrum of 3v, 100 MHz, $CDCl_3$

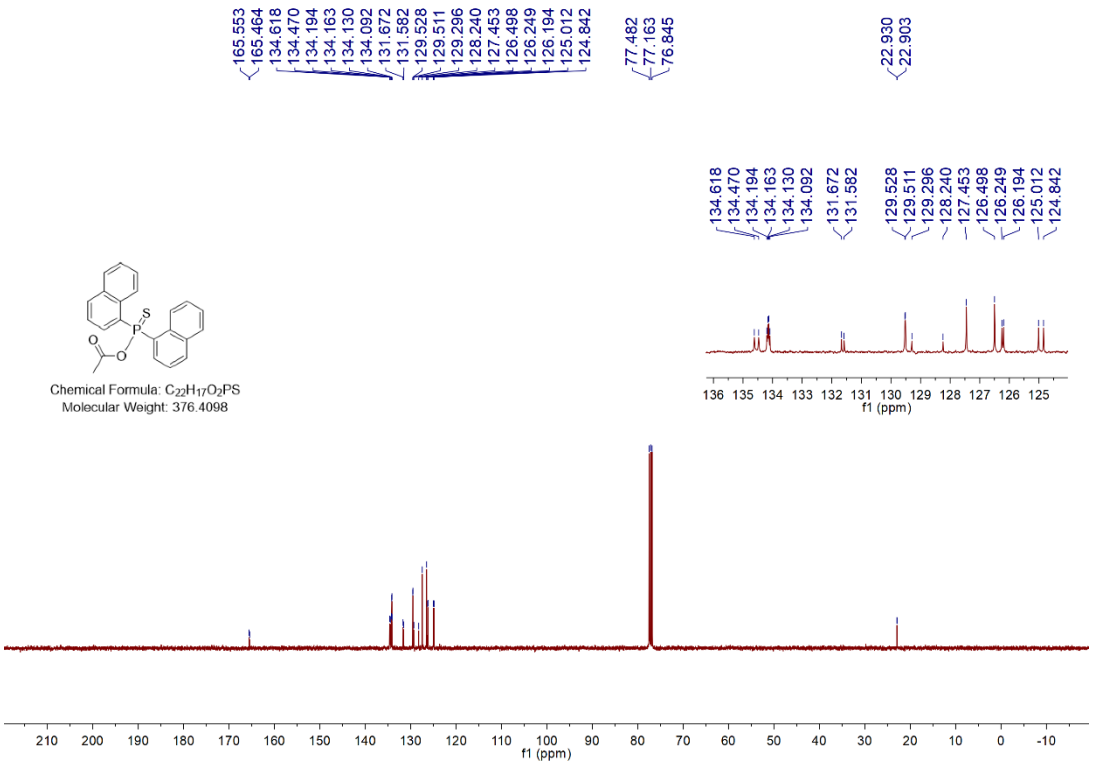


^{31}P NMR spectrum of 3v, 162 MHz, $CDCl_3$

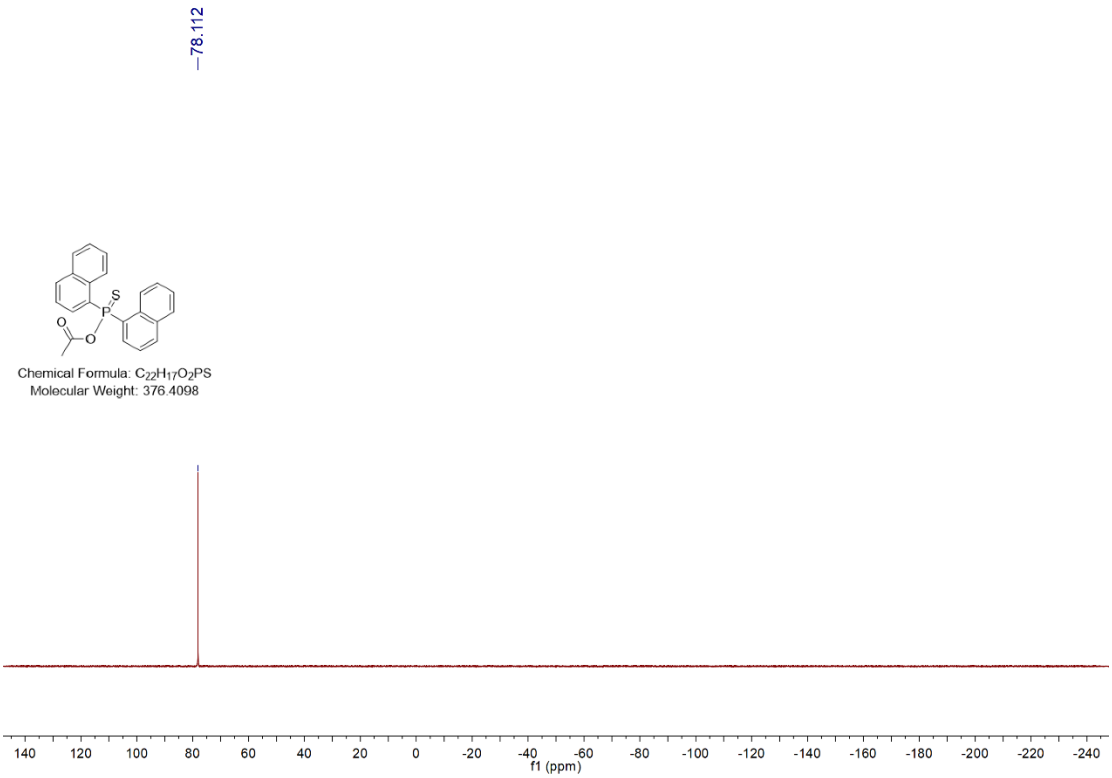
Acetic di(naphthalen-1-yl)phosphinothioic anhydride (3w)



^{1}H NMR spectrum of 3w, 400 MHz, $CDCl_3$

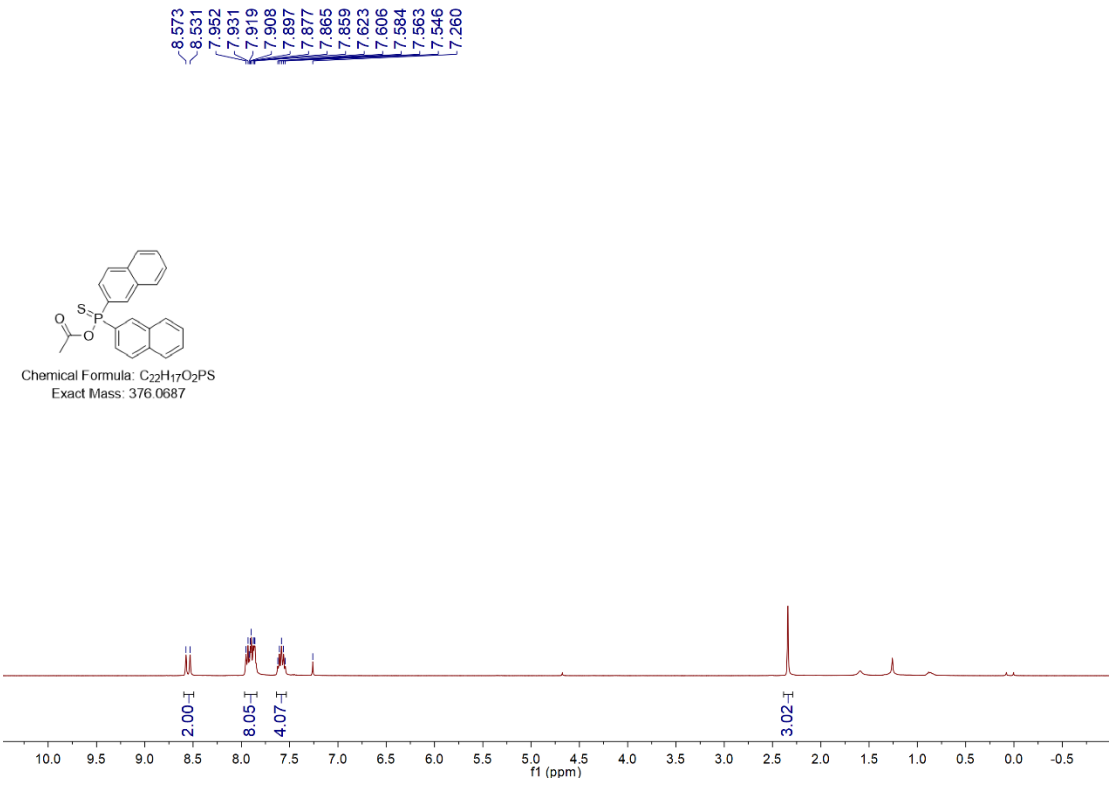


^{13}C NMR spectrum of 3w, 100 MHz, $CDCl_3$

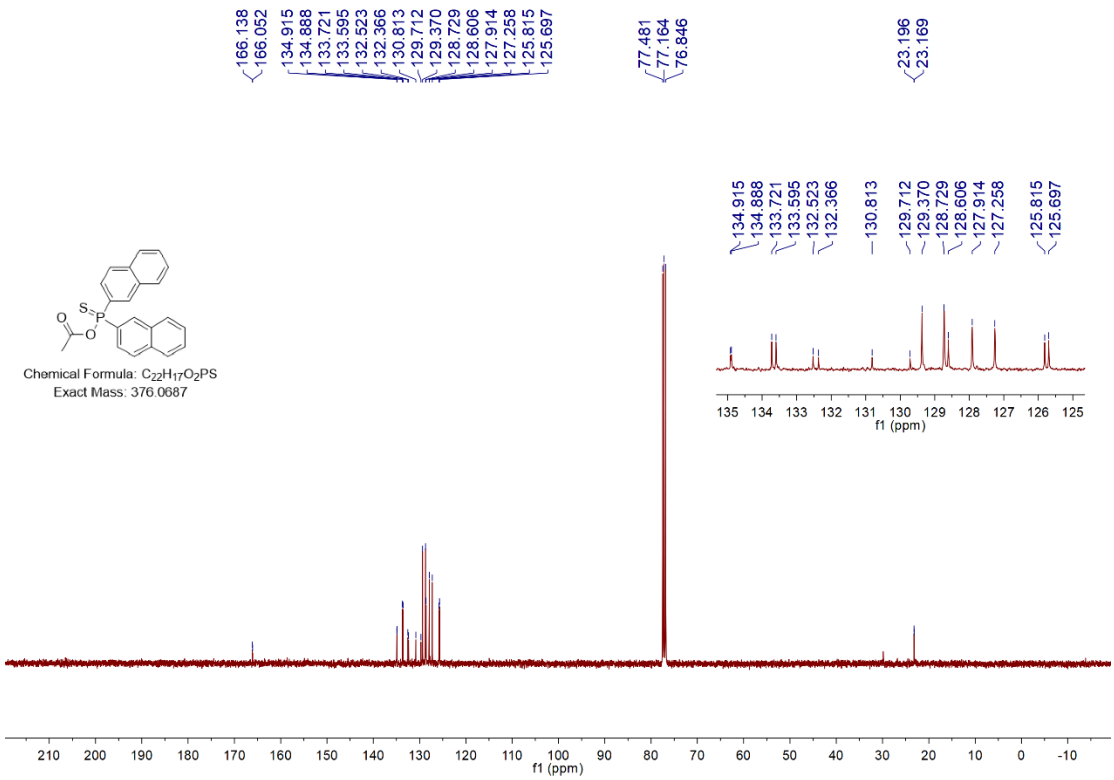


^{31}P NMR spectrum of 3w, 162 MHz, $CDCl_3$

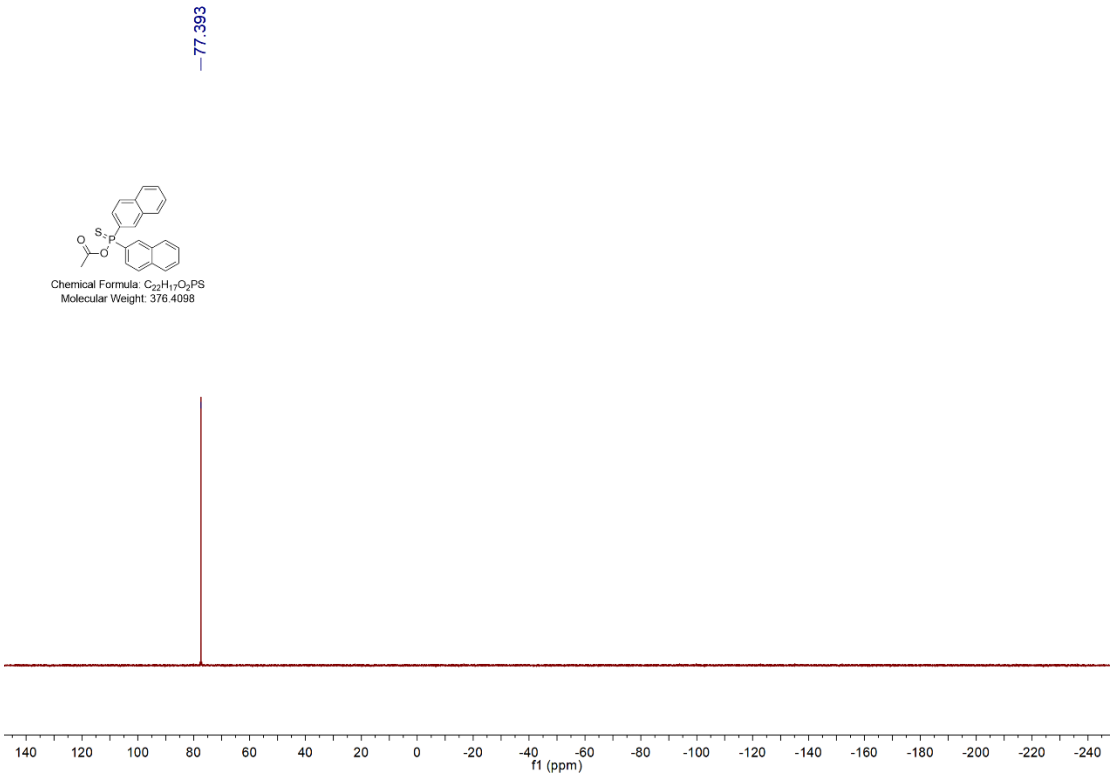
Acetic di(naphthalen-2-yl)phosphinothioic anhydride (3x)



^{1}H NMR spectrum of 3x, 400 MHz, $CDCl_3$

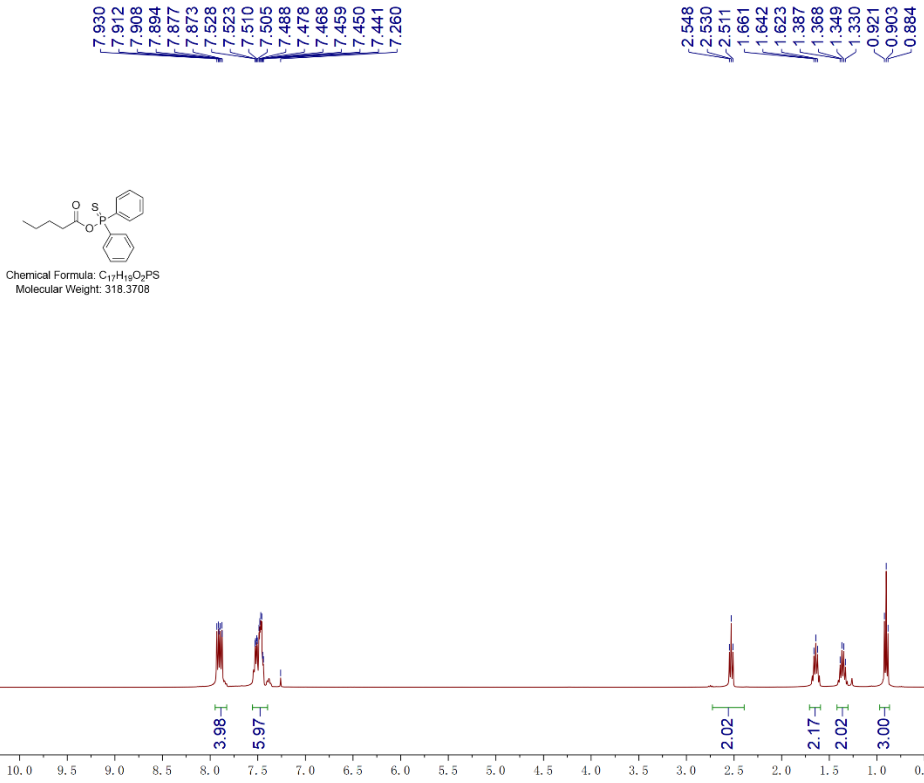


^{13}C NMR spectrum of 3x, 100 MHz, $CDCl_3$

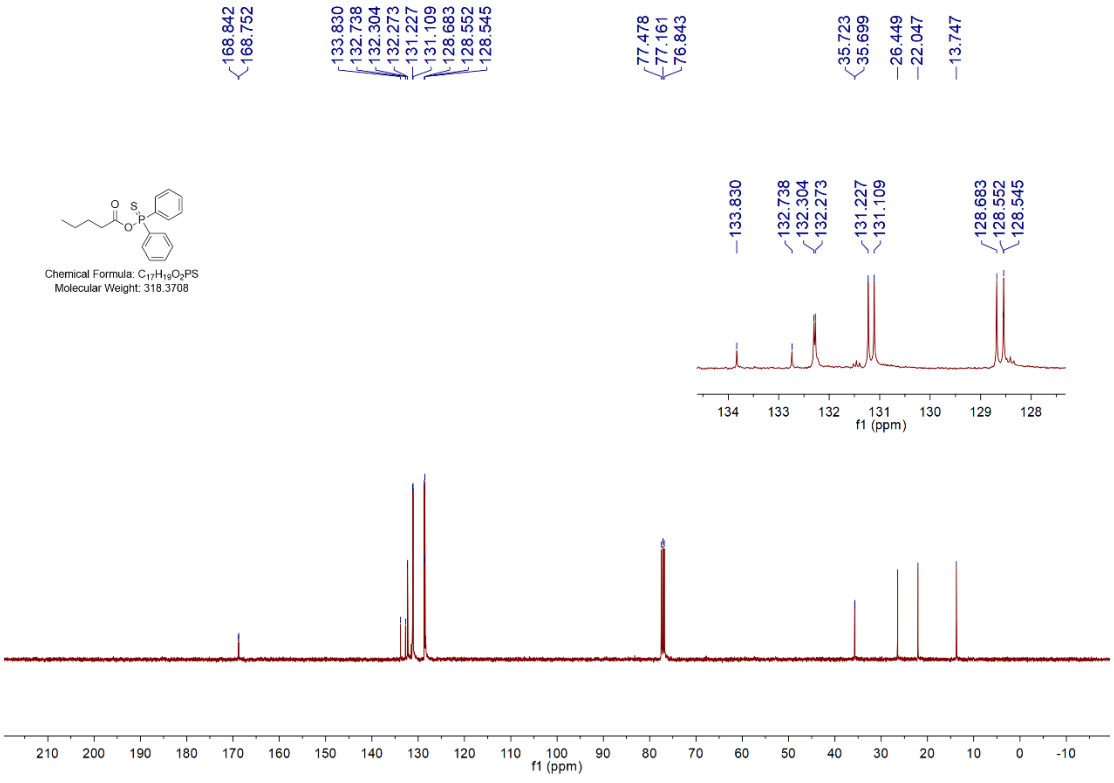


^{31}P NMR spectrum of 3x, 162 MHz, $CDCl_3$

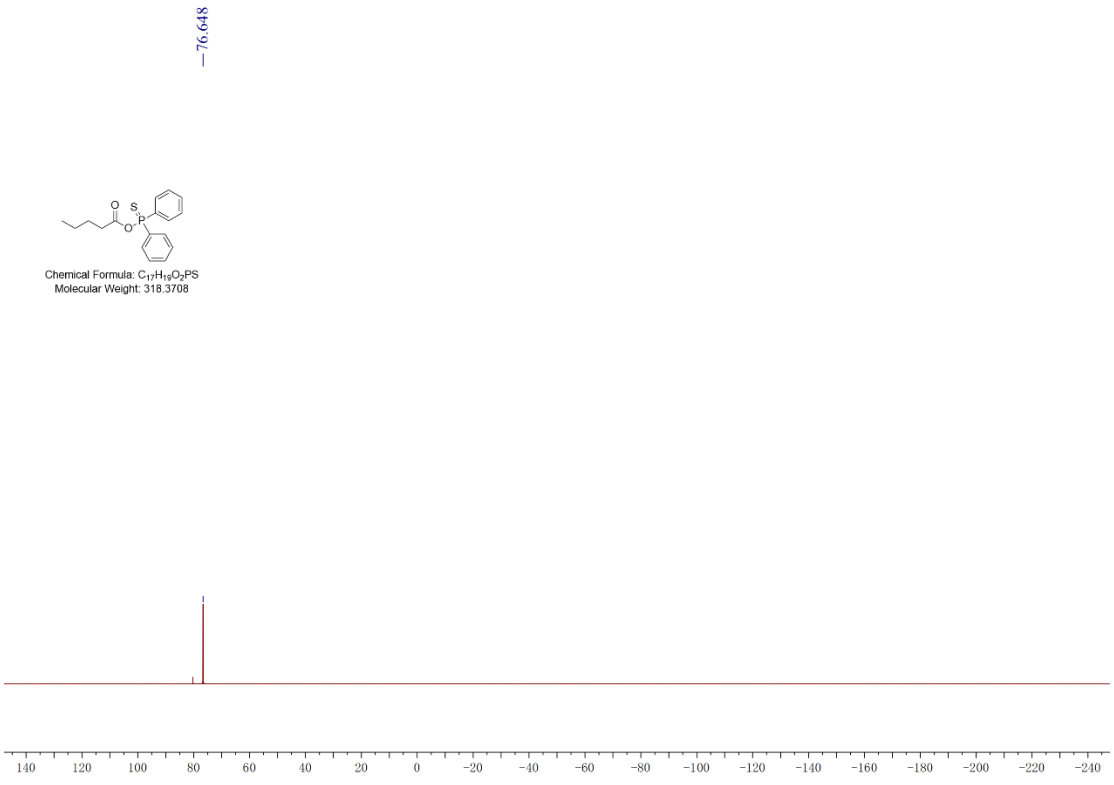
Pentanoic diphenylphosphinothioic anhydride (3y)



^{1}H NMR spectrum of 3y, 400 MHz, $CDCl_3$

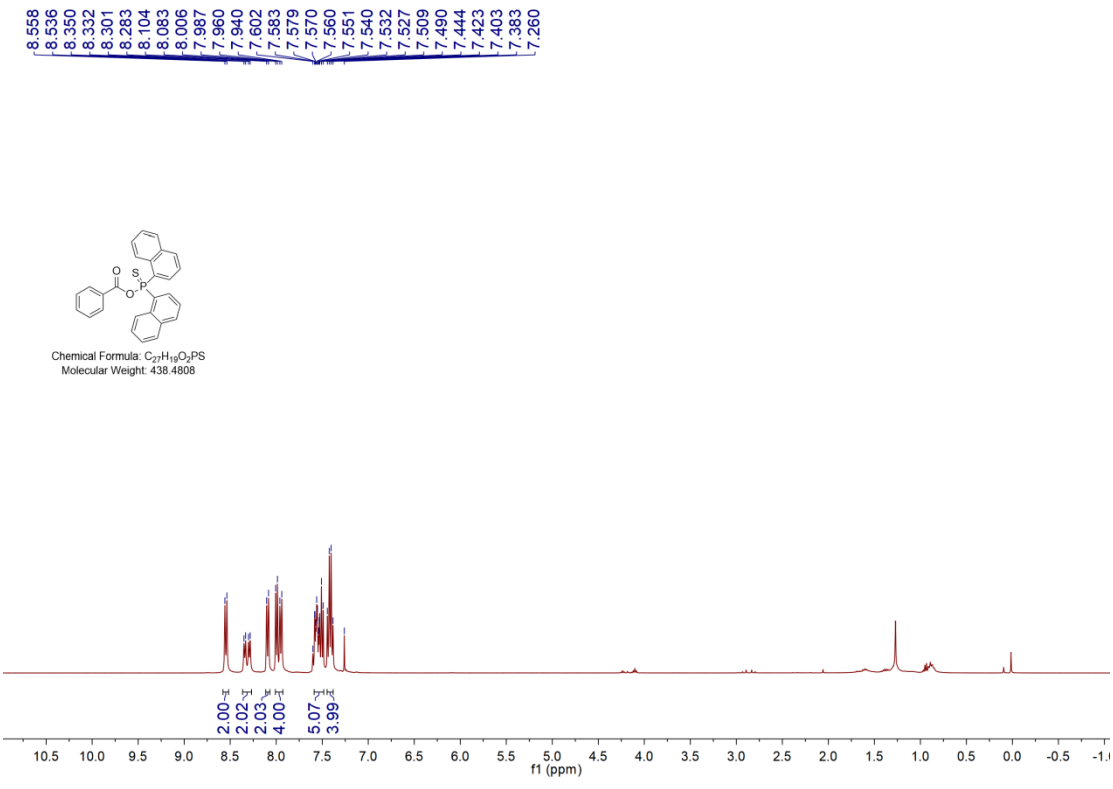


^{13}C NMR spectrum of 3y, 100 MHz, $CDCl_3$

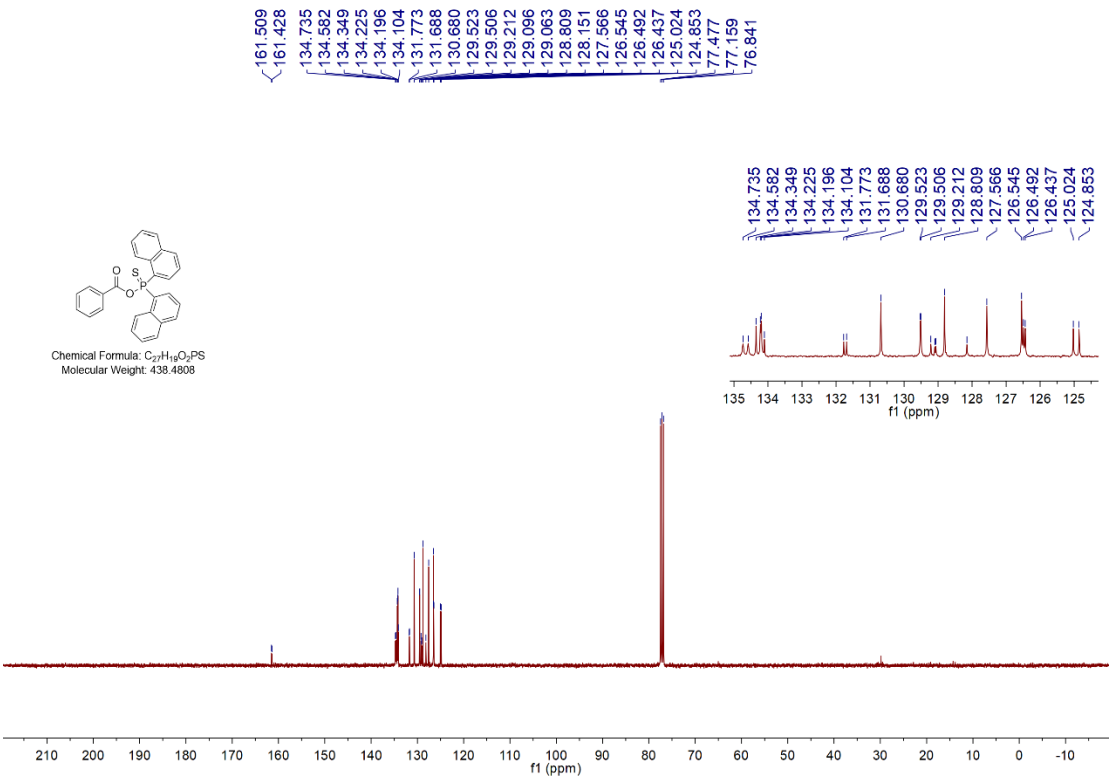


^{31}P NMR spectrum of 3y, 162 MHz, $CDCl_3$

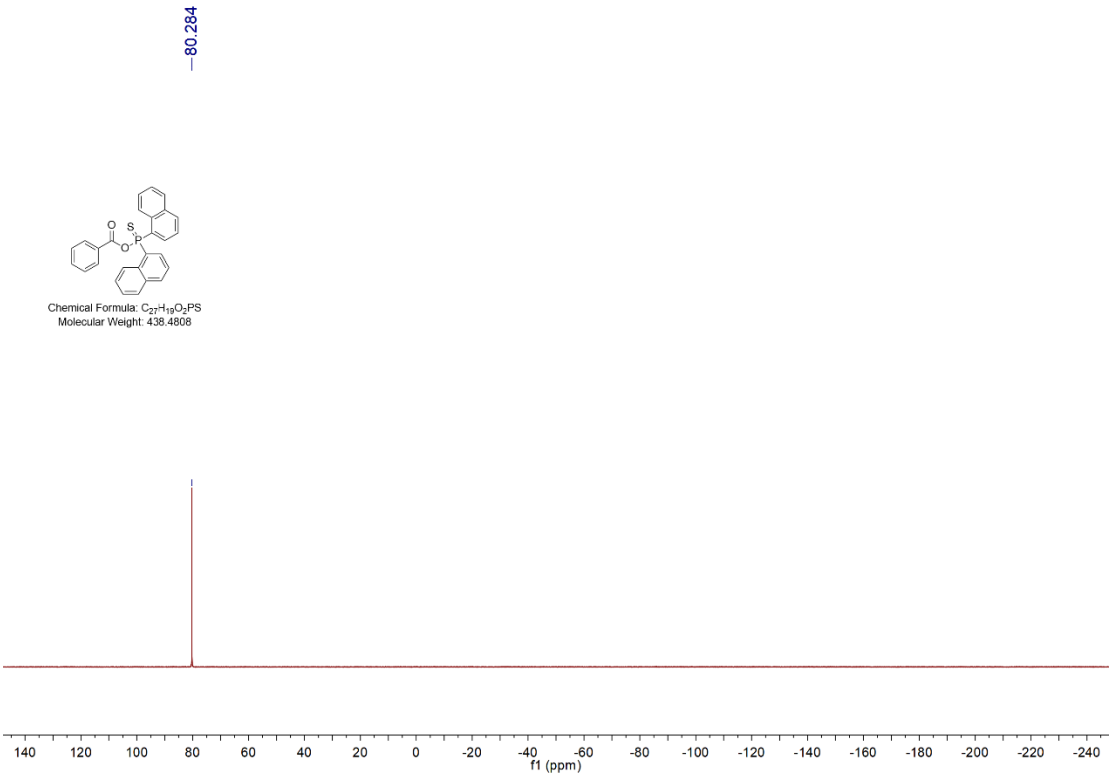
Benzoic di(naphthalen-1-yl)phosphinothioic anhydride (3z)



^{1}H NMR spectrum of 3z, 400 MHz, $CDCl_3$

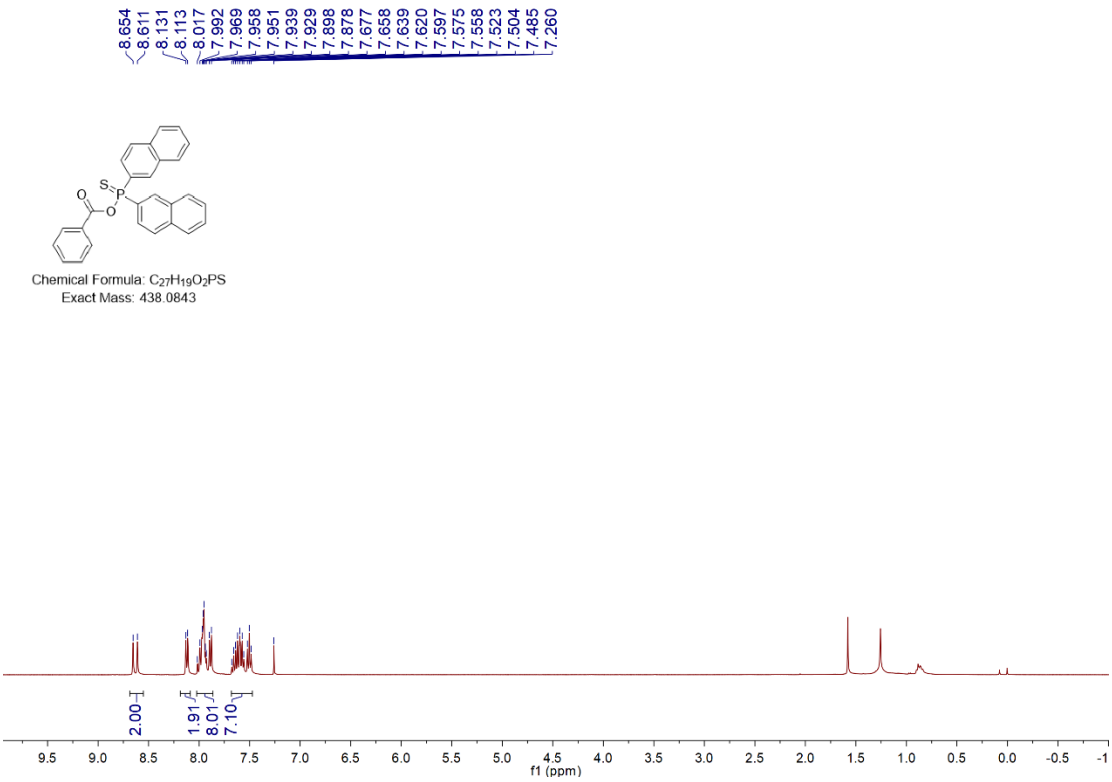


^{13}C NMR spectrum of 3z, 100 MHz, $CDCl_3$

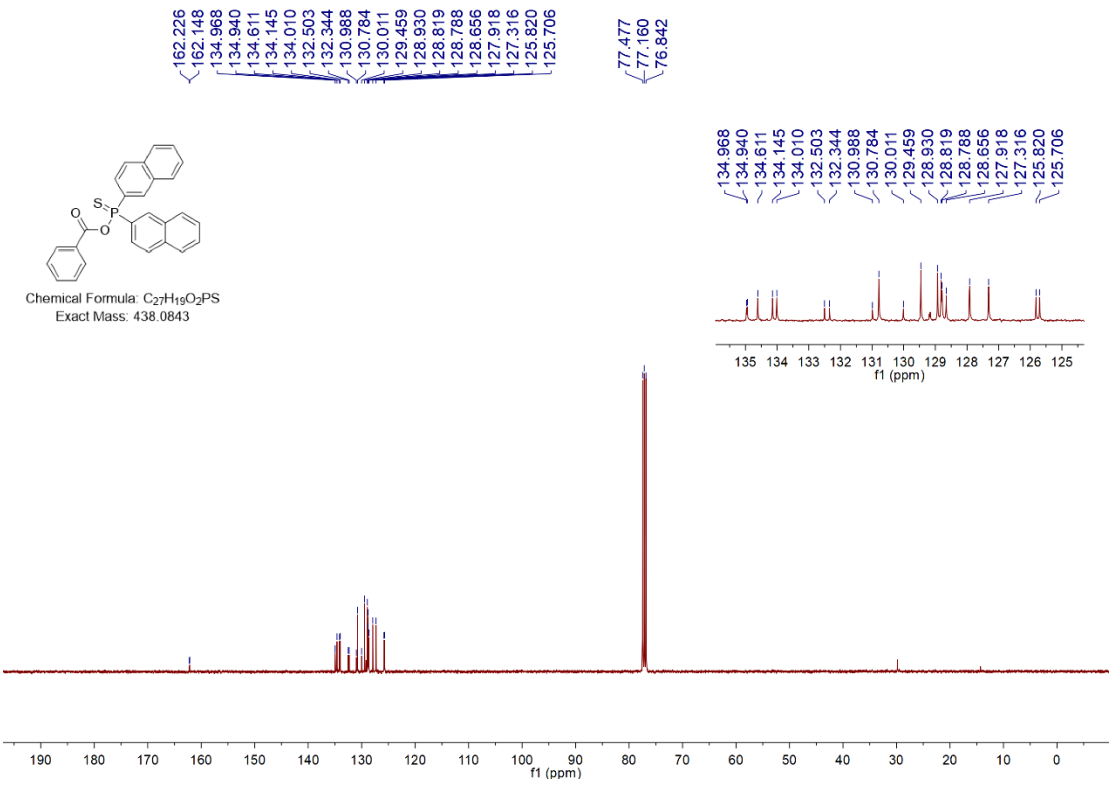


^{31}P NMR spectrum of 3z, 162 MHz, $CDCl_3$

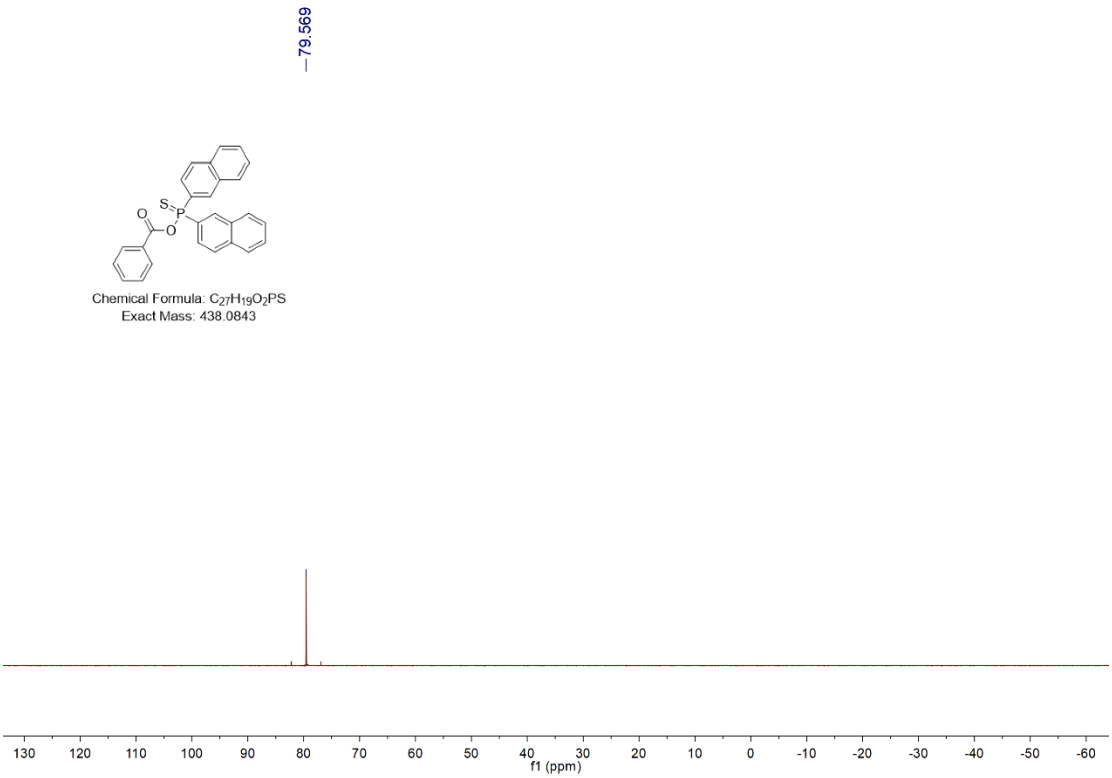
Benzoic di(naphthalen-2-yl)phosphinothioic anhydride (3aa)



^{1}H NMR spectrum of 3aa, 400 MHz, $CDCl_3$

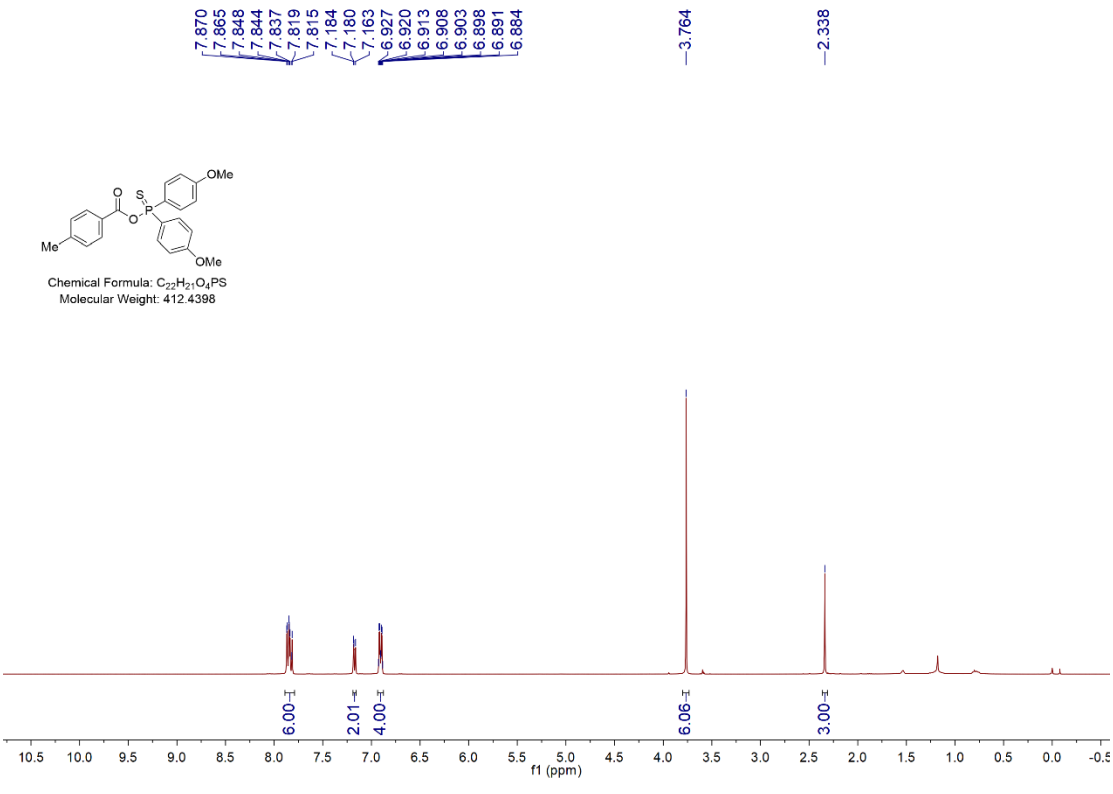


^{13}C NMR spectrum of 3aa, 100 MHz, $CDCl_3$

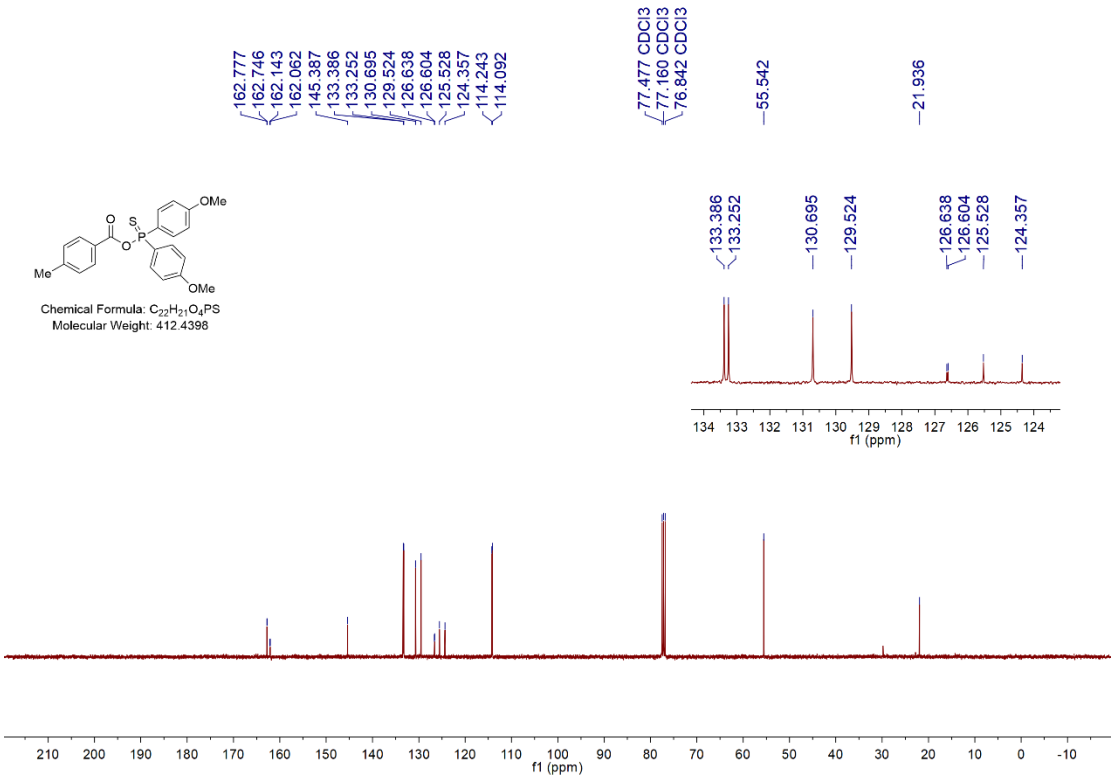


^{31}P NMR spectrum of 3aa, 162 MHz, $CDCl_3$

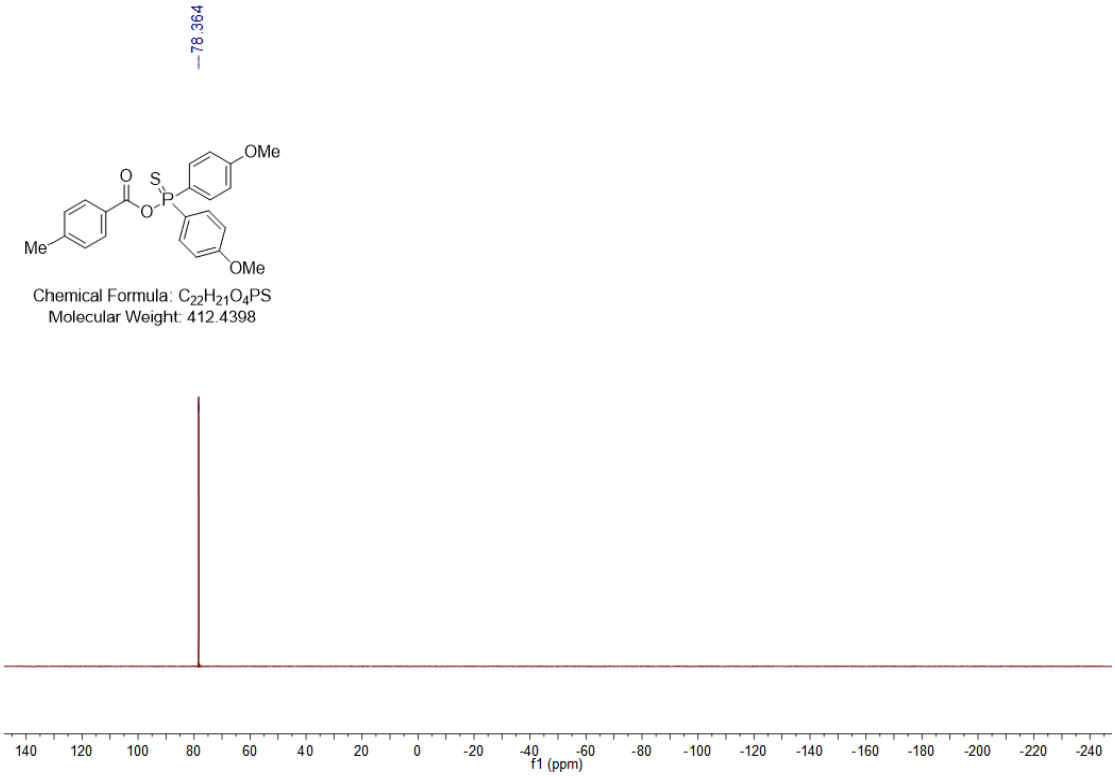
Bis(4-methoxyphenyl)phosphinothioic 4-methylbenzoic anhydride (4a)



^{1}H NMR spectrum of 4a, 400 MHz, $CDCl_3$

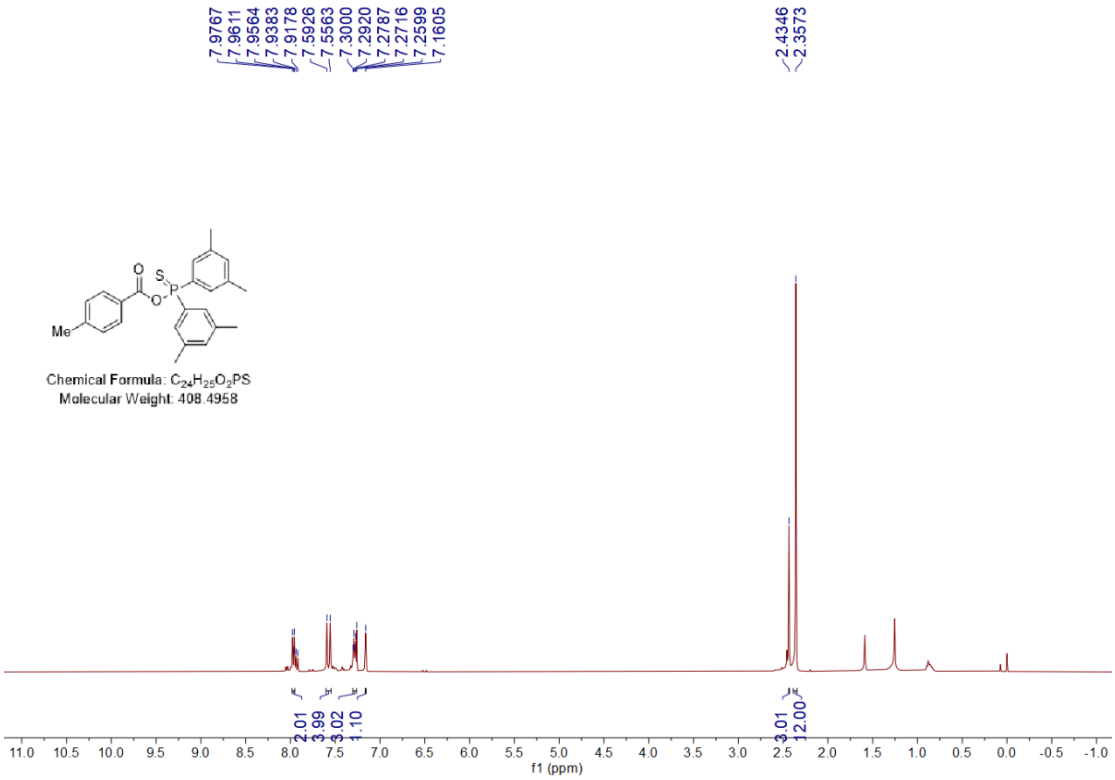


^{13}C NMR spectrum of 4a, 100 MHz, $CDCl_3$

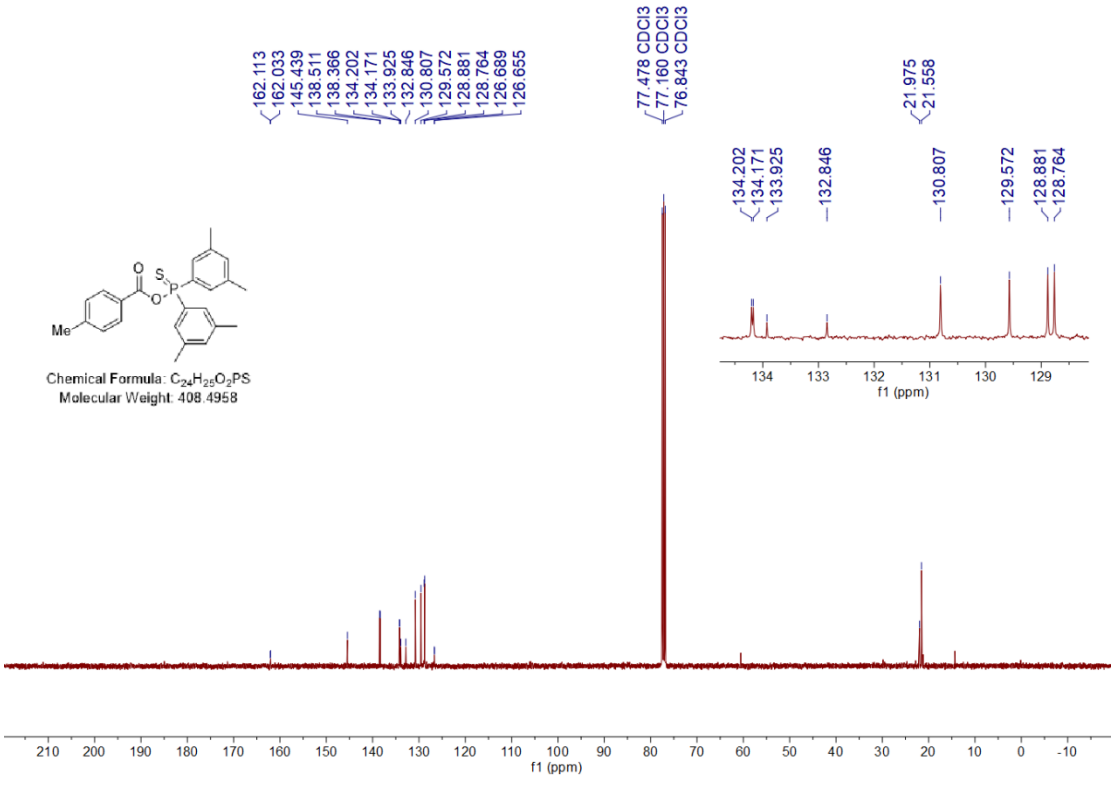


^{31}P NMR spectrum of 4a, 162 MHz, $CDCl_3$

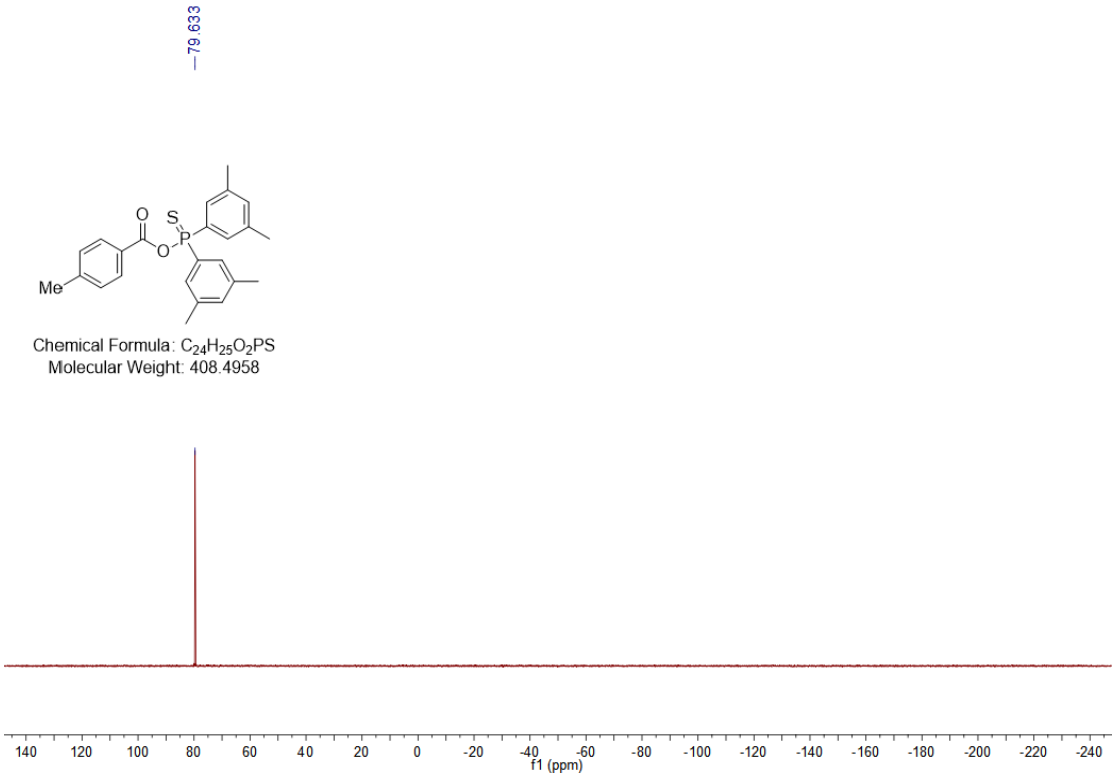
Bis(3,5-dimethylphenyl)phosphinothioic 4-methylbenzoic anhydride (4b)



^{1}H NMR spectrum of 4b, 400 MHz, $CDCl_3$

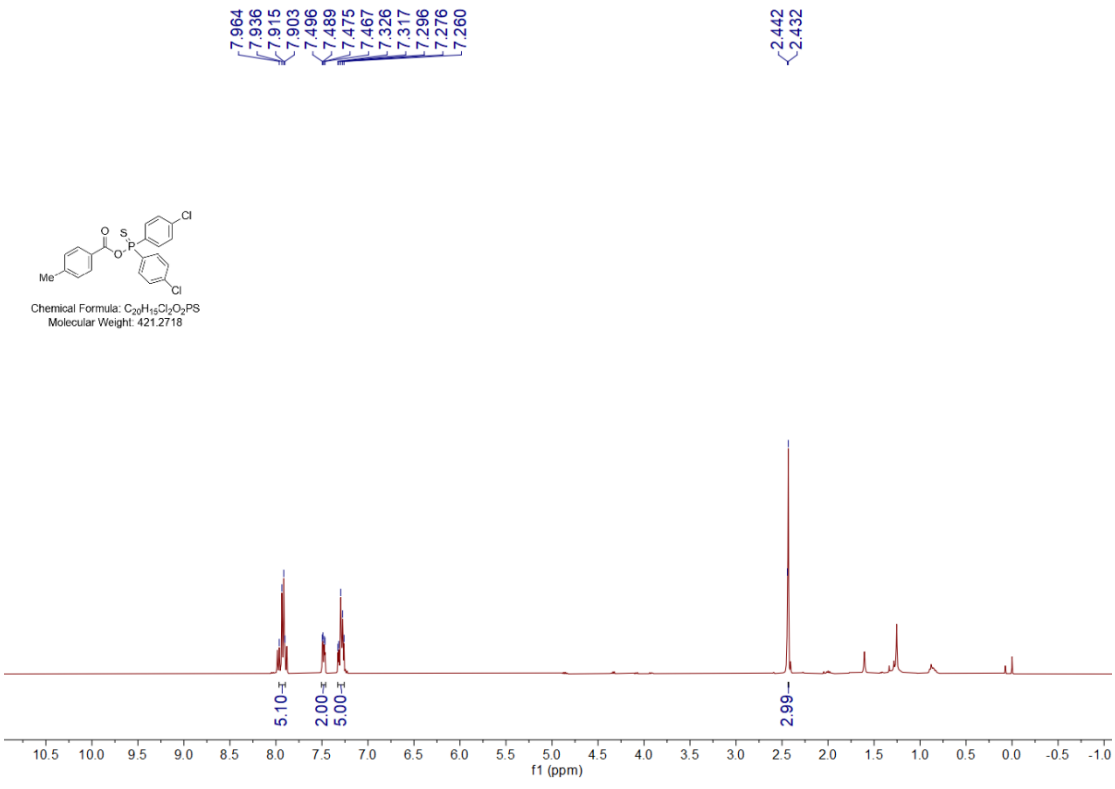


^{13}C NMR spectrum of 4b, 100 MHz, $CDCl_3$

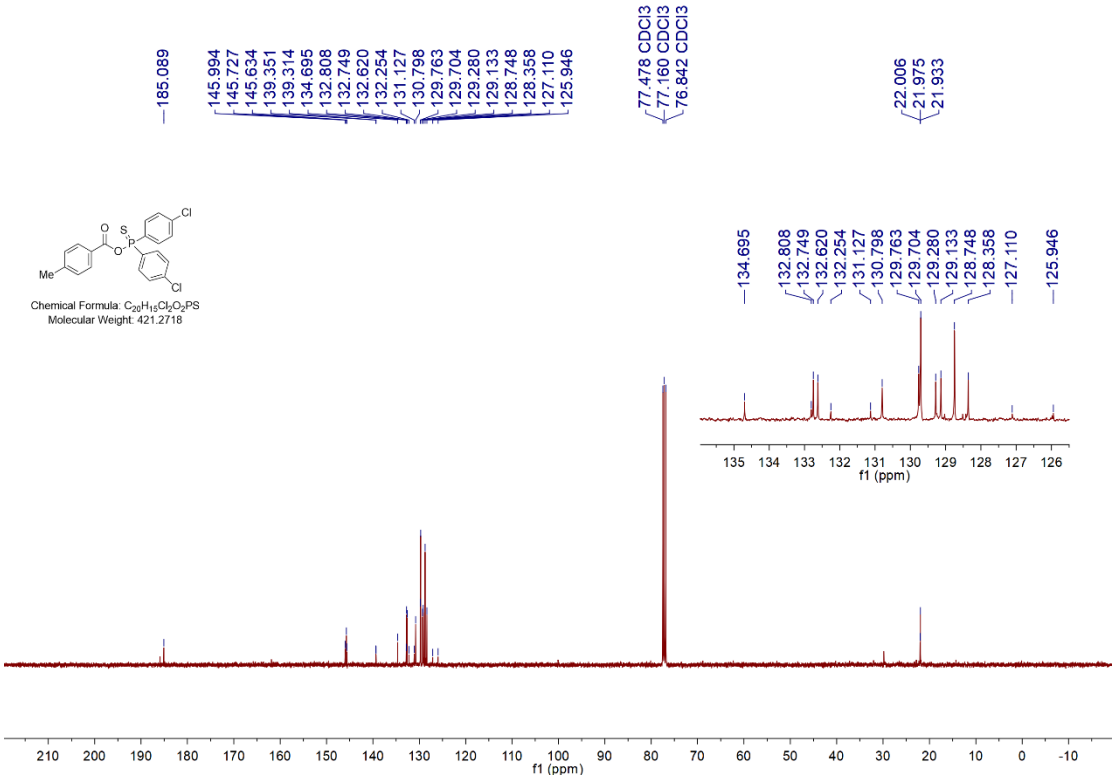


^{31}P NMR spectrum of 4b, 162 MHz, $CDCl_3$

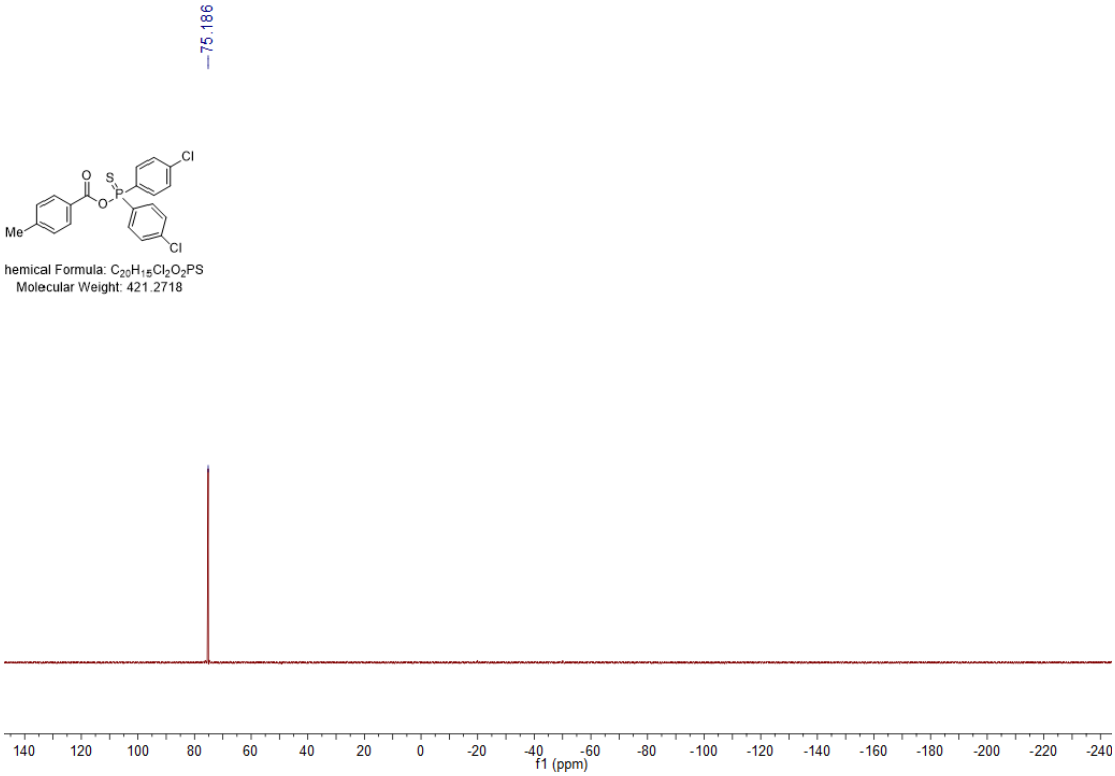
Bis(4-chlorophenyl)phosphinothioic 4-methylbenzoic anhydride (4c)



^{1}H NMR spectrum of 4c, 400 MHz, $CDCl_3$

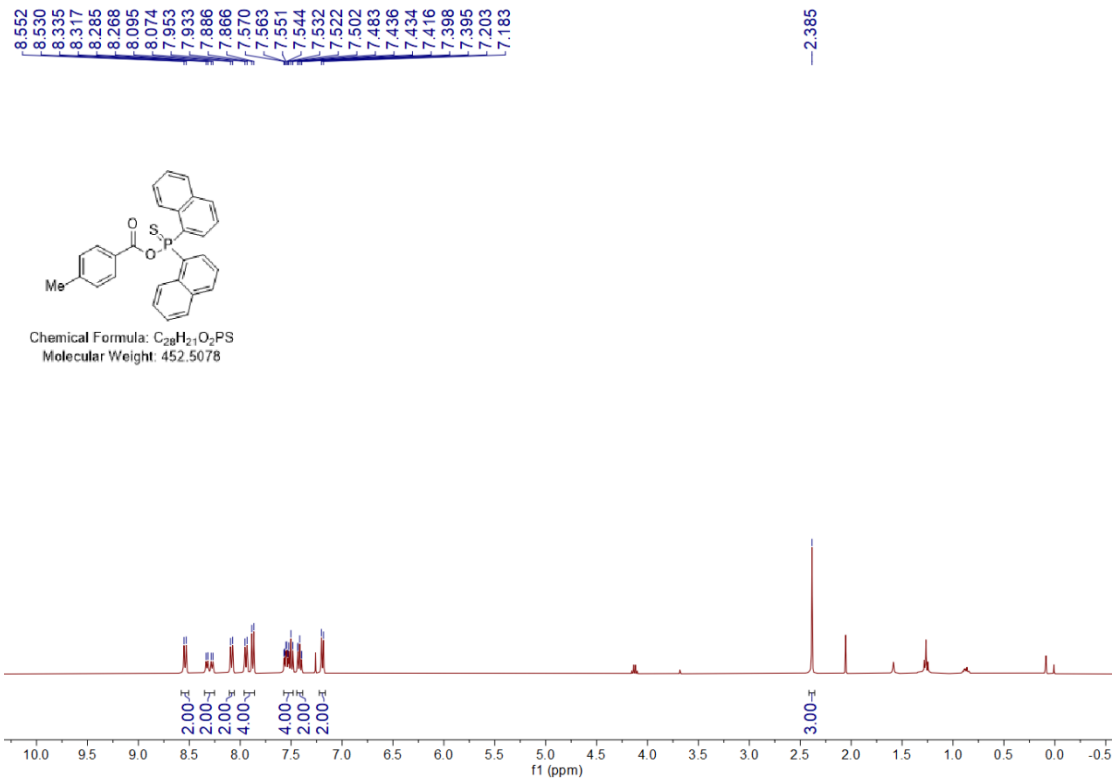


^{13}C NMR spectrum of 4c, 100 MHz, $CDCl_3$

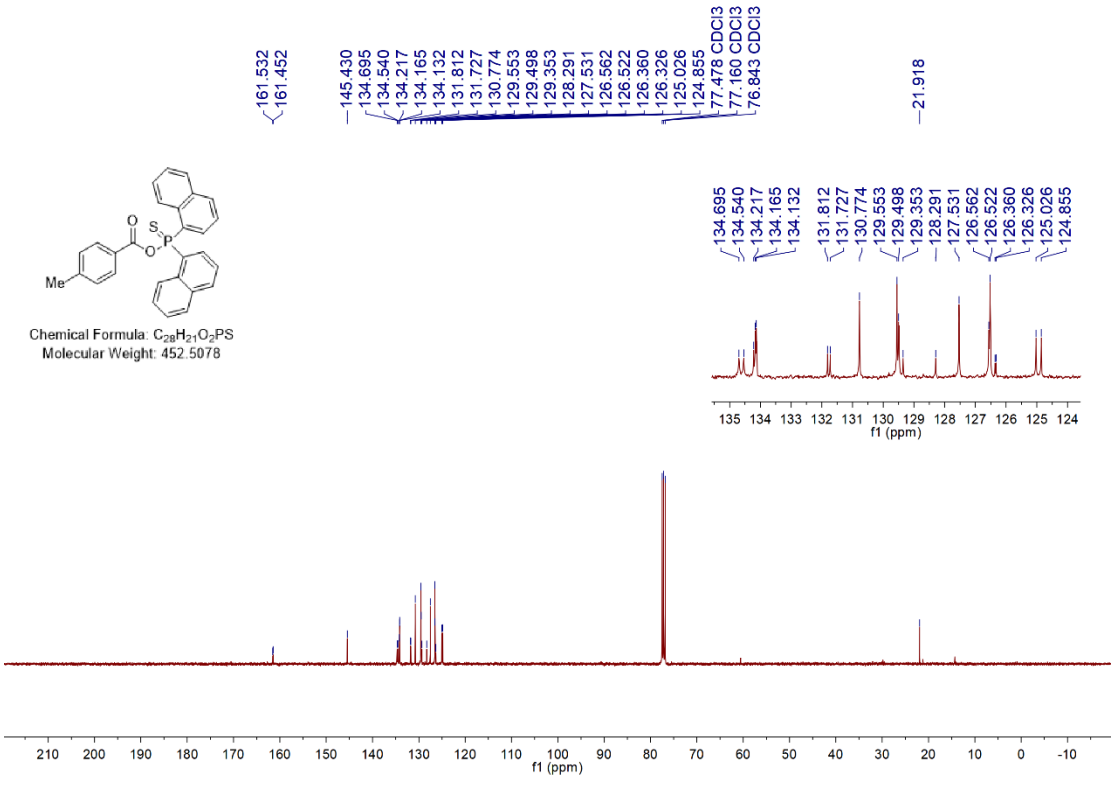


^{31}P NMR spectrum of 4c, 162 MHz, $CDCl_3$

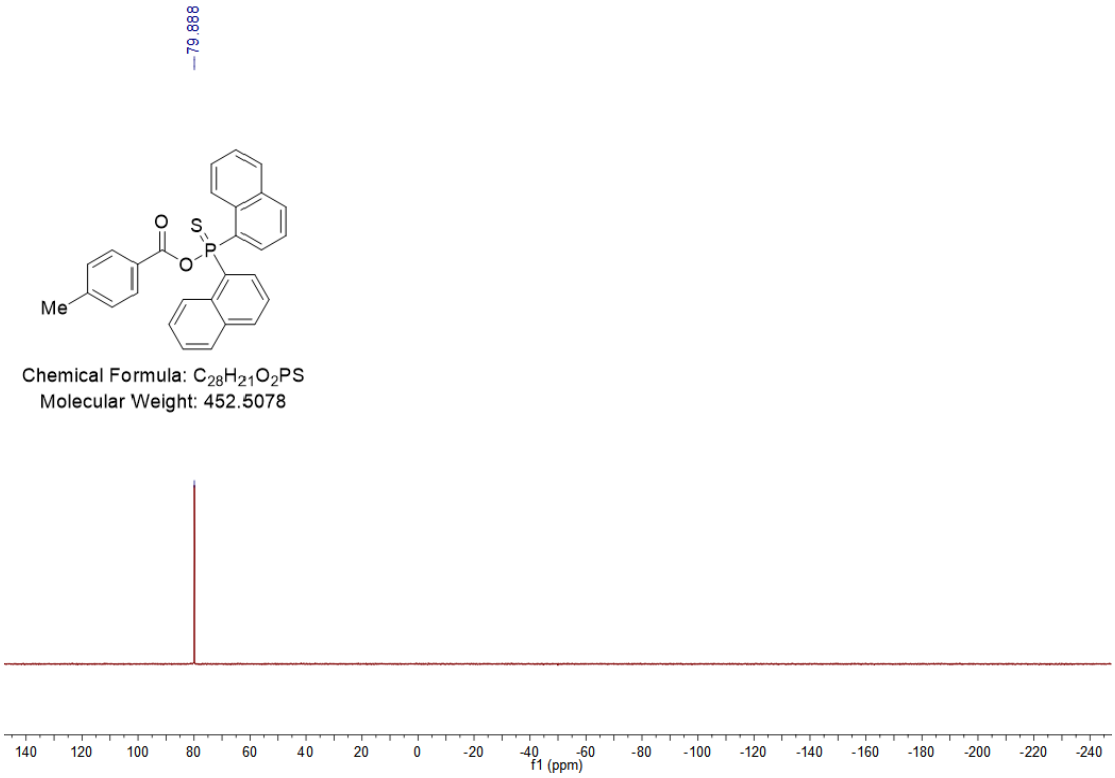
4-Methylbenzoic di(naphthalen-1-yl)phosphinothioic anhydride (4d)



^{1}H NMR spectrum of 4d, 400 MHz, $CDCl_3$

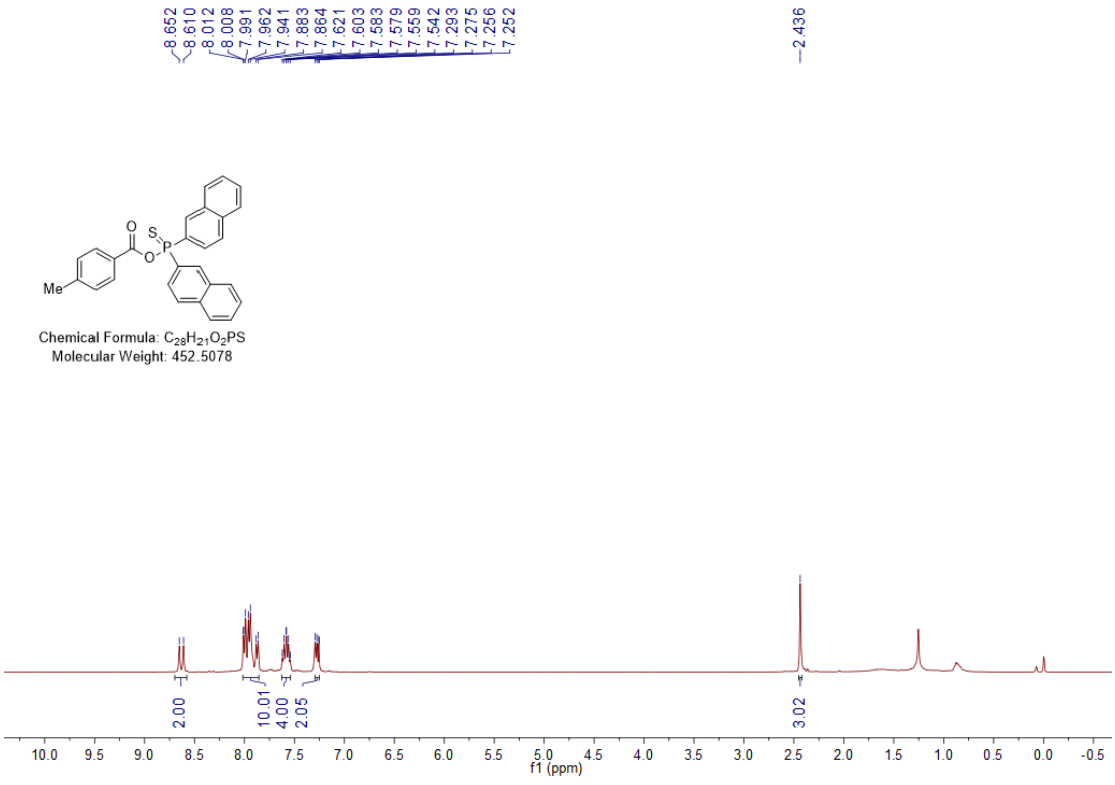


^{13}C NMR spectrum of 4d, 100 MHz, $CDCl_3$

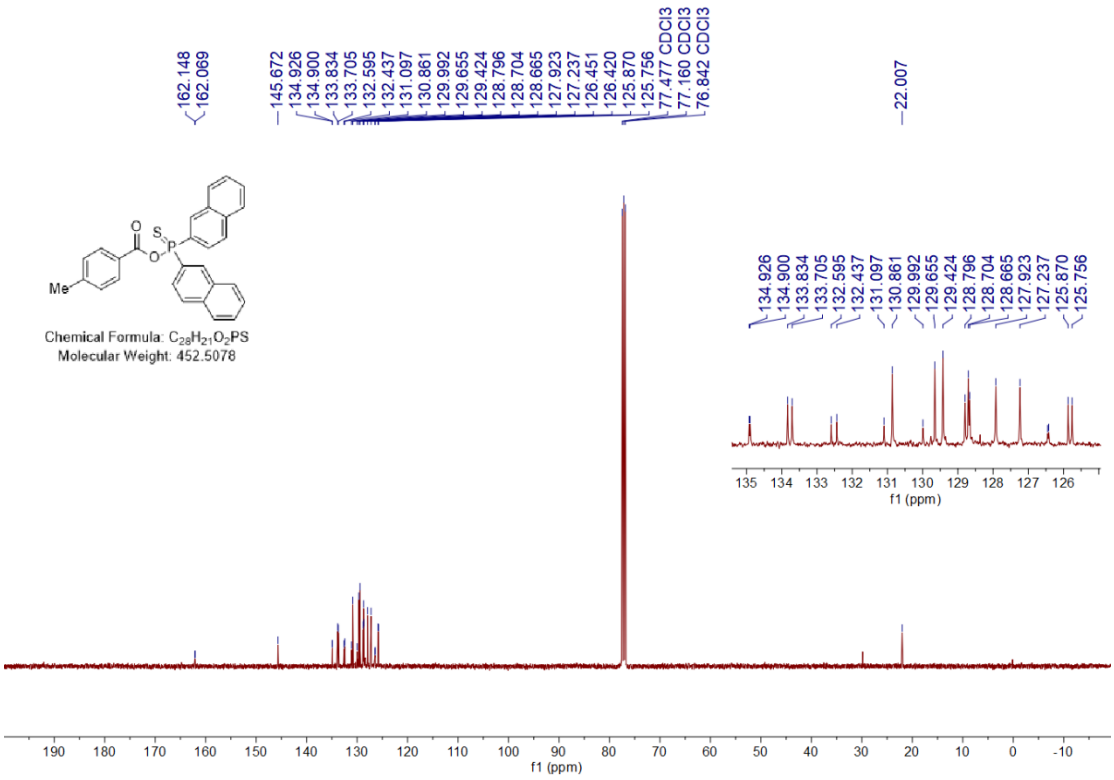


^{31}P NMR spectrum of 4d, 162 MHz, $CDCl_3$

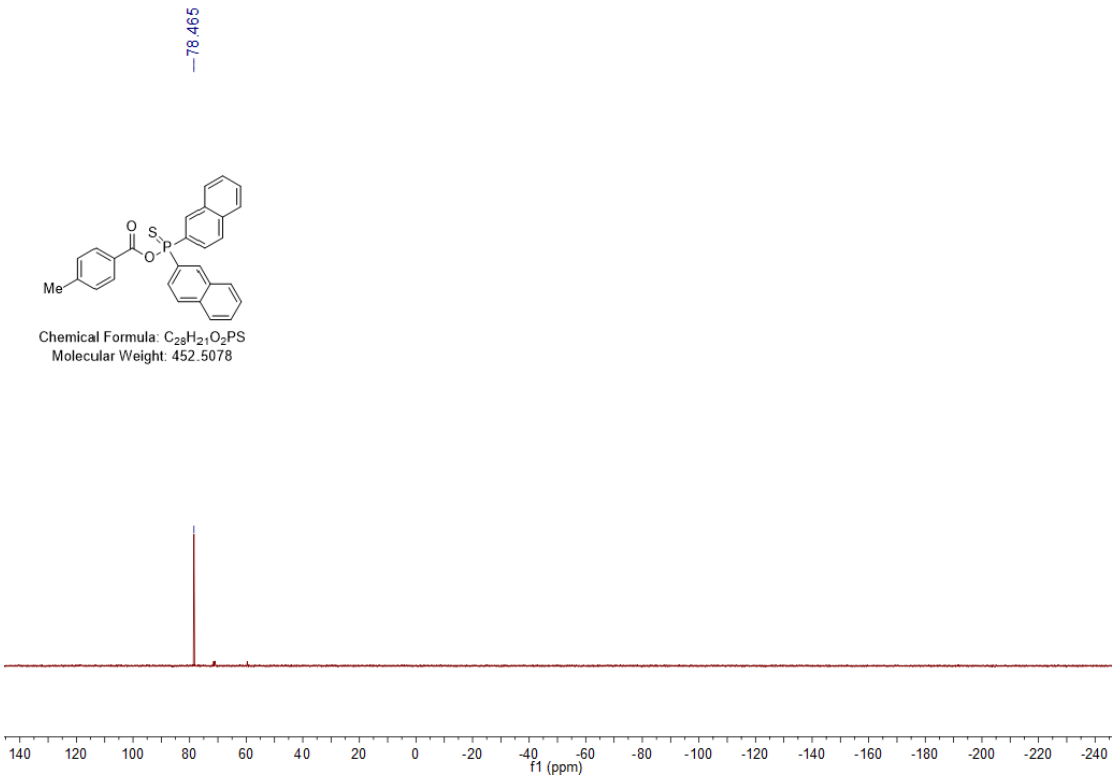
4-Methylbenzoic di(naphthalen-2-yl)phosphinothioic anhydride (4e)



^{1}H NMR spectrum of 4e, 400 MHz, $CDCl_3$

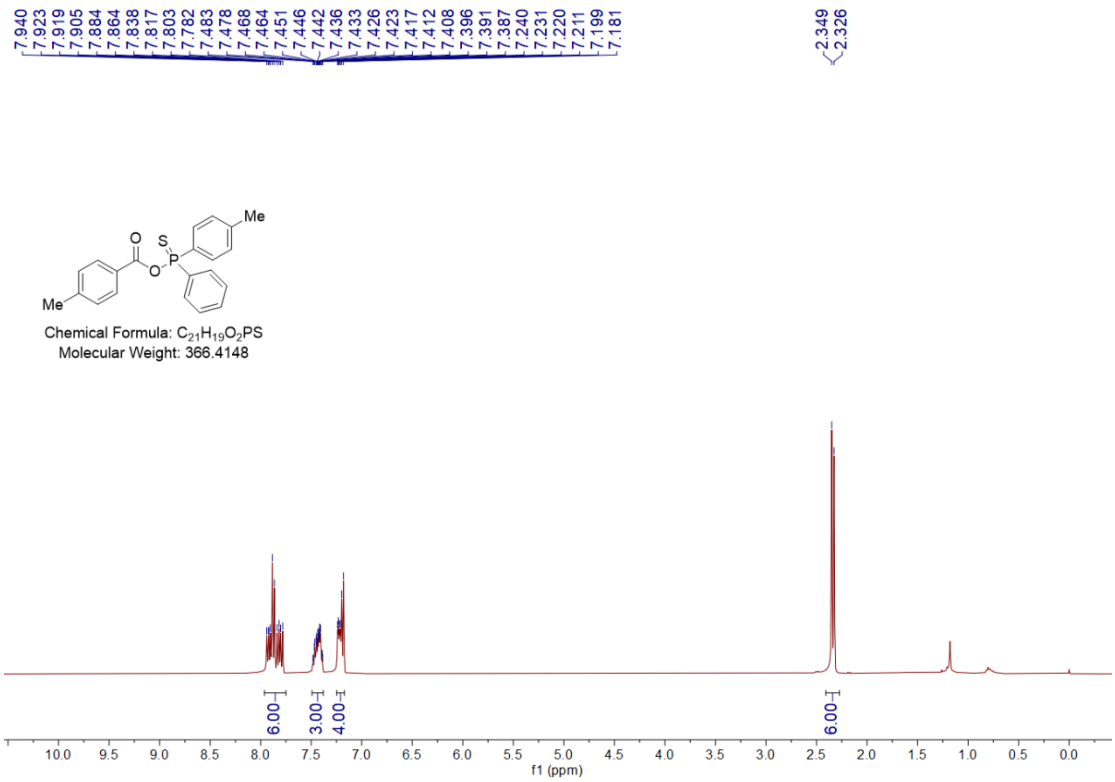


^{13}C NMR spectrum of 4e, 100 MHz, $CDCl_3$

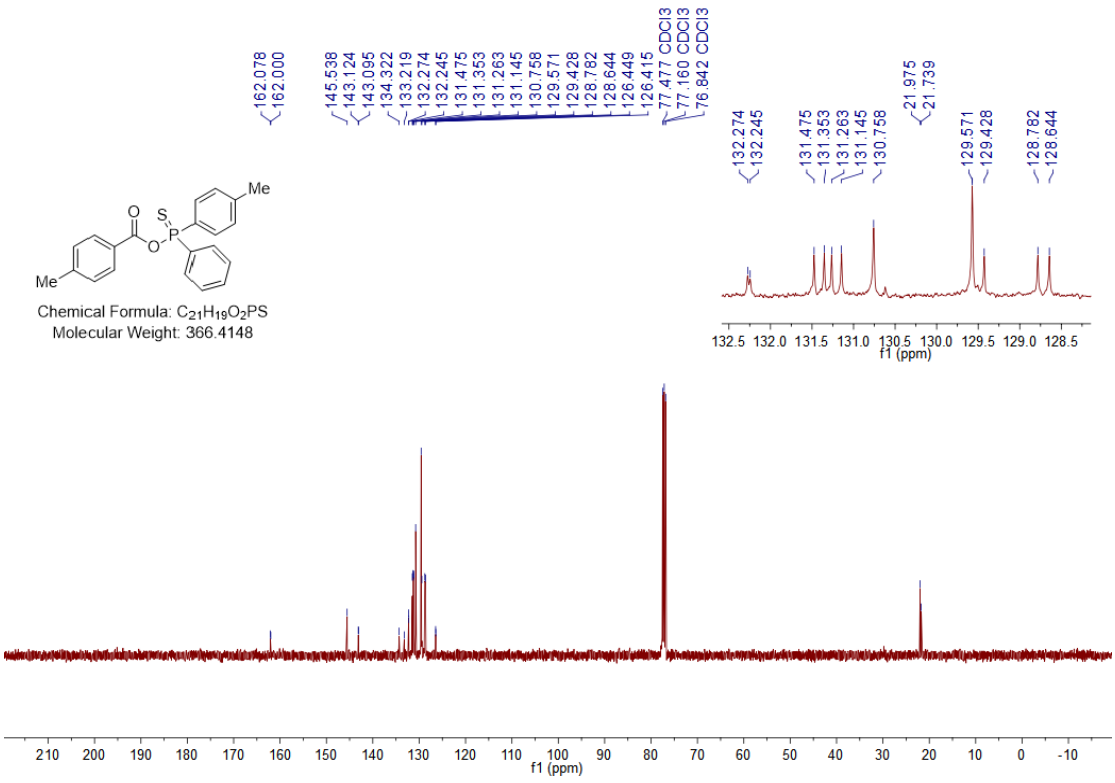


^{31}P NMR spectrum of 4e, 162 MHz, $CDCl_3$

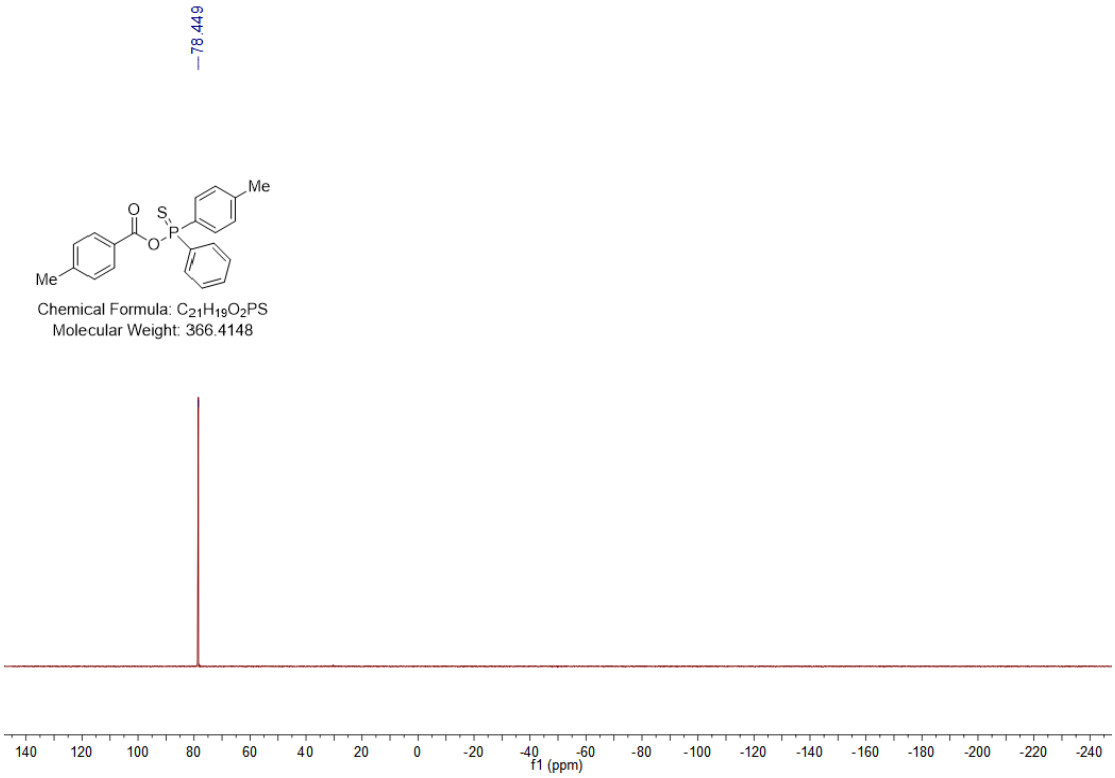
4-Methylbenzoic phenyl(p-tolyl)phosphinothioic anhydride (4f)



^{1}H NMR spectrum of 4f, 400 MHz, $CDCl_3$

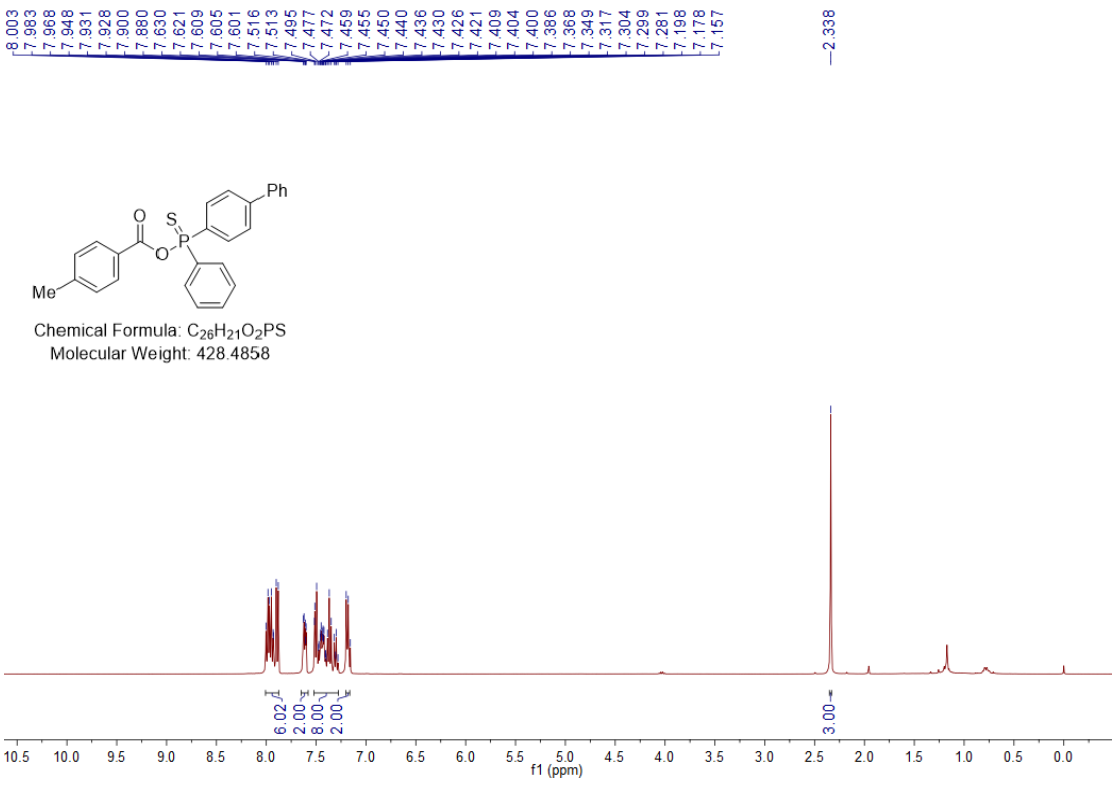


^{13}C NMR spectrum of 4f, 100 MHz, $CDCl_3$

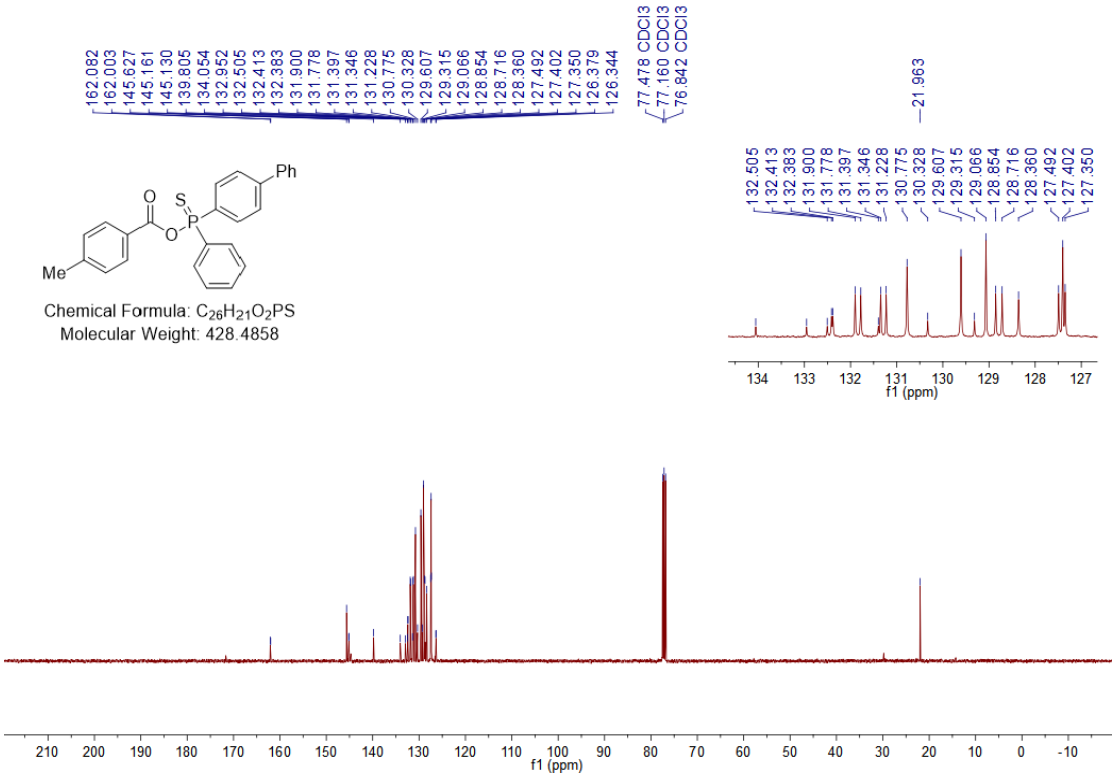


^{31}P NMR spectrum of 4f, 162 MHz, $CDCl_3$

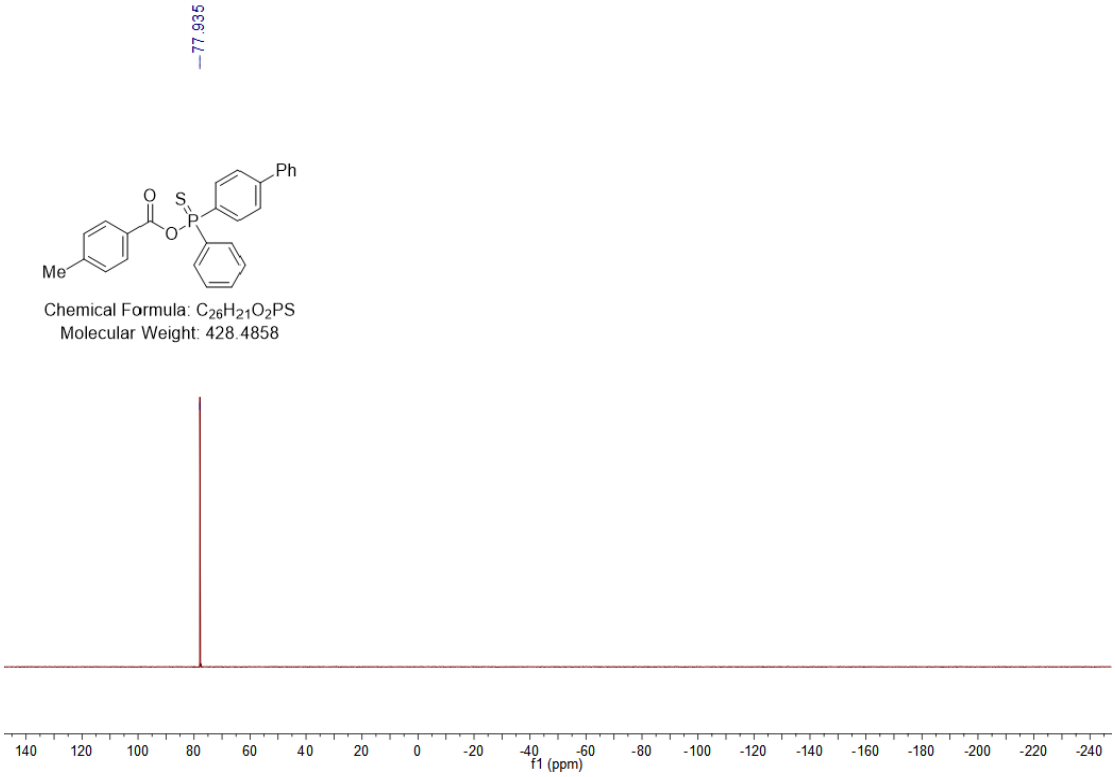
[1,1'-biphenyl]-4-yl(phenyl)phosphinothioic 4-methylbenzoic anhydride (4g)



^{1}H NMR spectrum of 4g, 400 MHz, $CDCl_3$

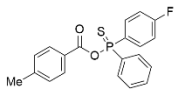


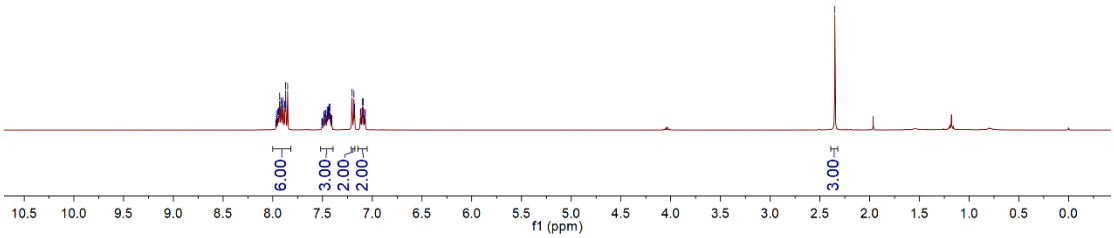
^{13}C NMR spectrum of 4g, 100 MHz, $CDCl_3$



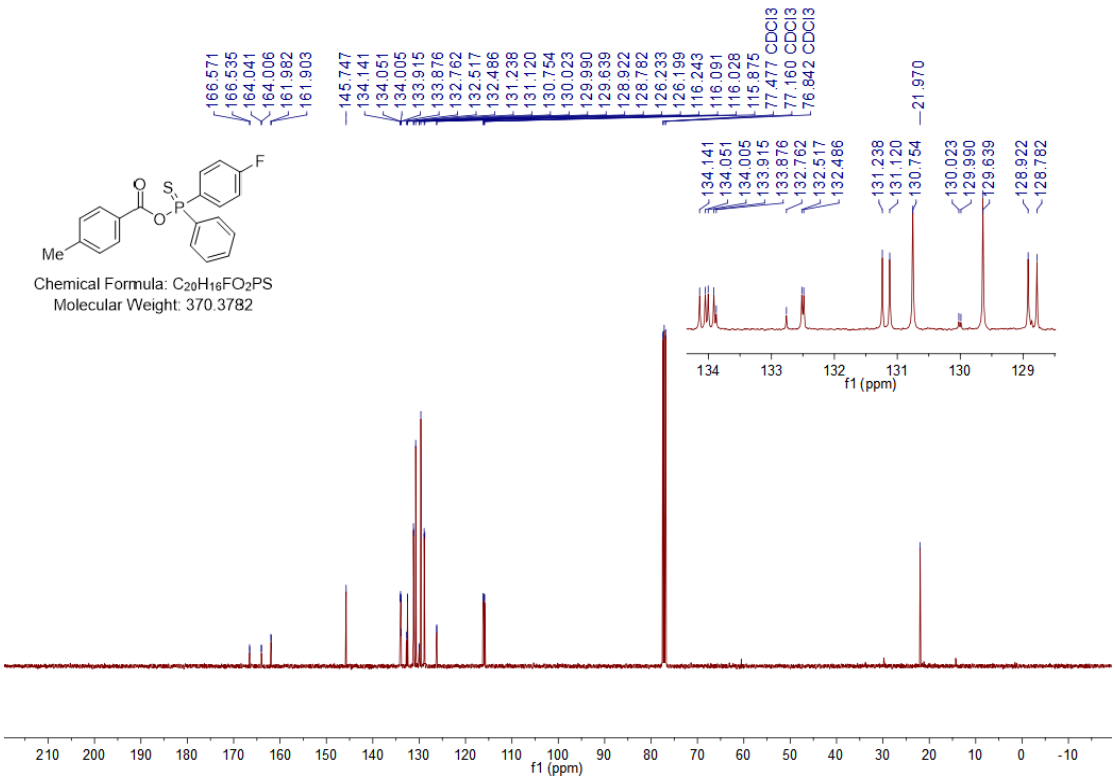
^{31}P NMR spectrum of 4g, 162 MHz, $CDCl_3$

(4-Fluorophenyl)(phenyl)phosphinothioic 4-methylbenzoic anhydride (4h)

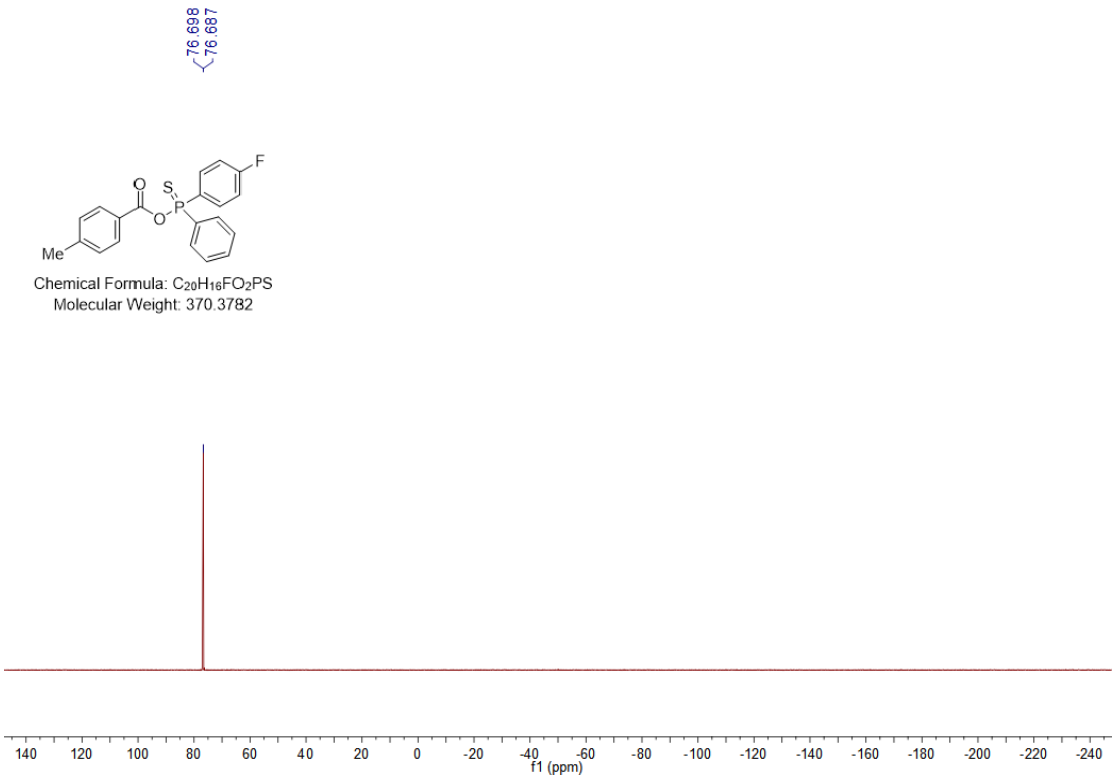




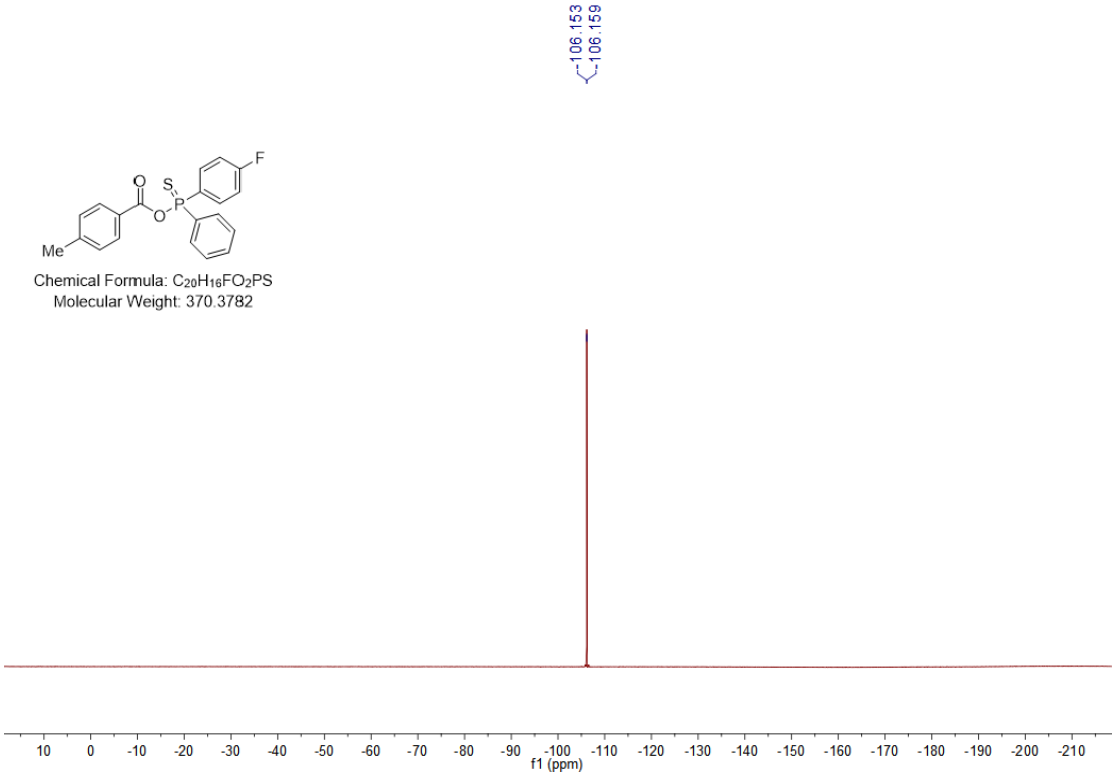
^{1}H NMR spectrum of 4h, 400 MHz, $CDCl_3$



^{13}C NMR spectrum of 4h, 100 MHz, $CDCl_3$

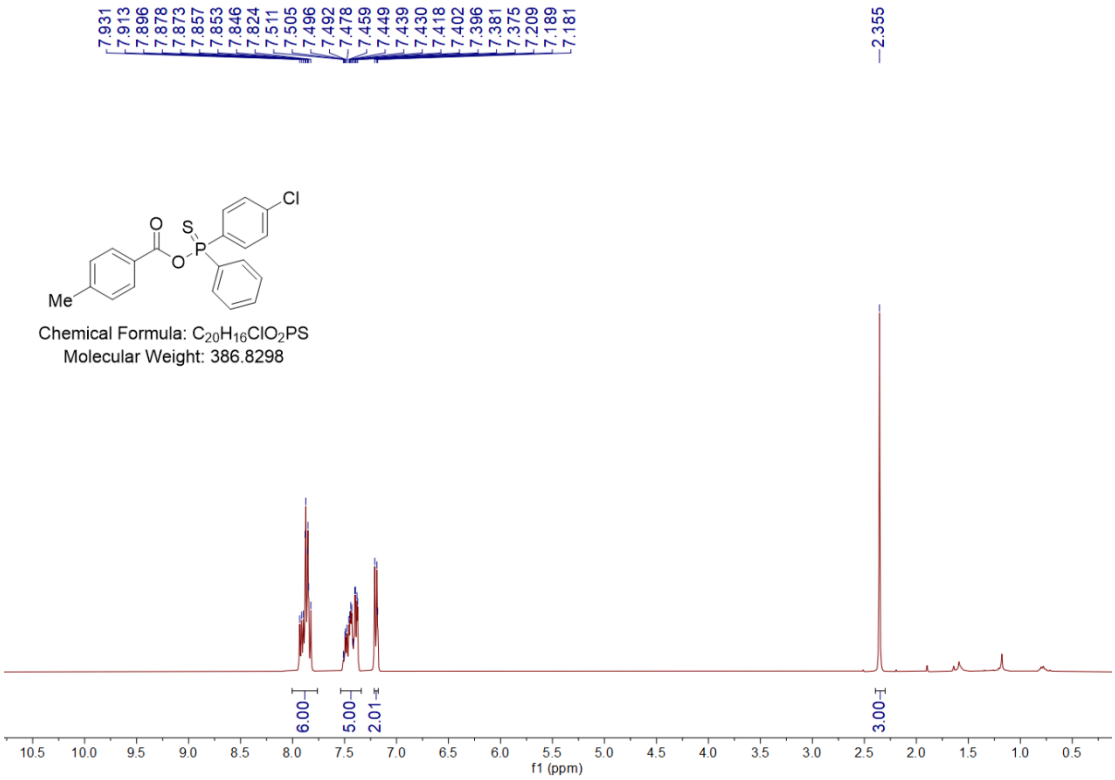


^{31}P NMR spectrum of 4h, 162 MHz, $CDCl_3$

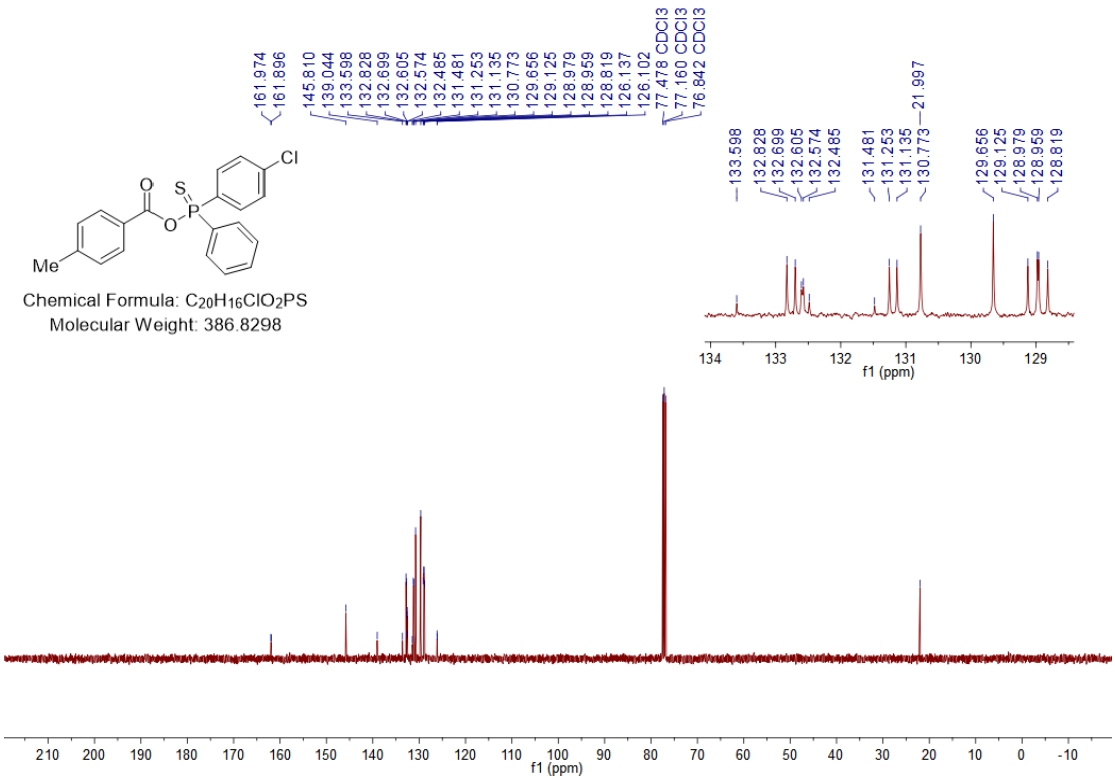


^{19}F NMR spectrum of 4h, 376 MHz, $CDCl_3$

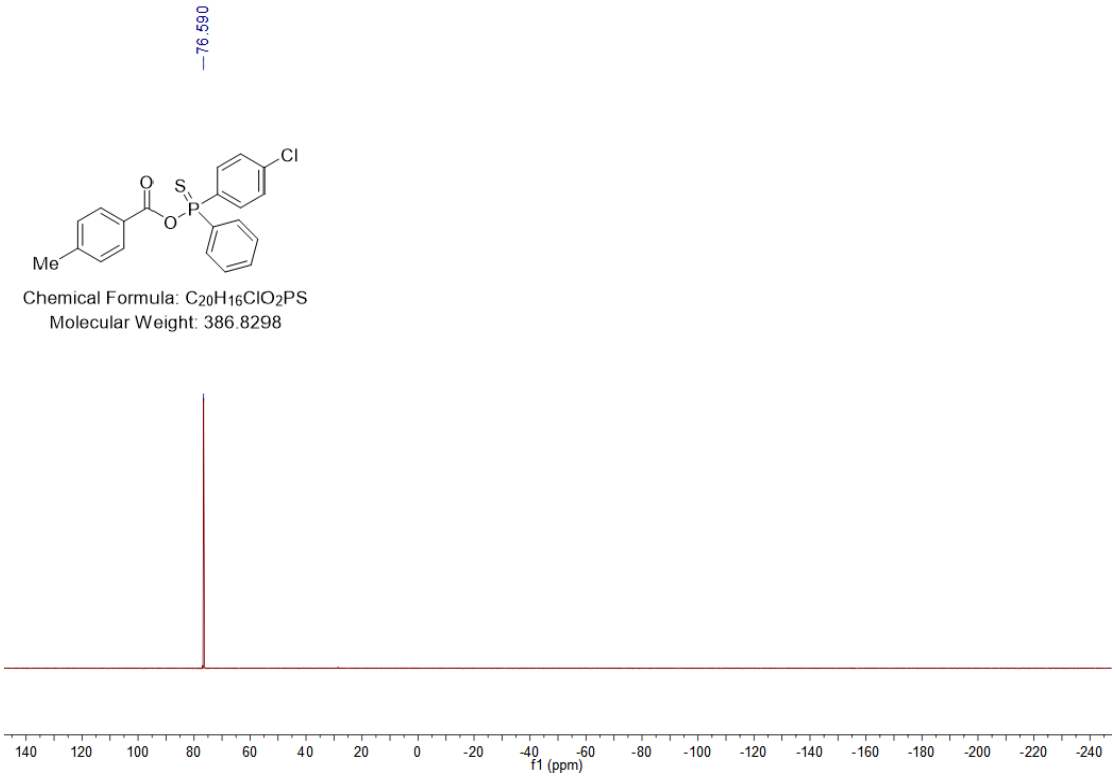
(4-Chlorophenyl)(phenyl)phosphinothioic 4-methylbenzoic anhydride (4i)



^{1}H NMR spectrum of 4i, 400 MHz, $CDCl_3$

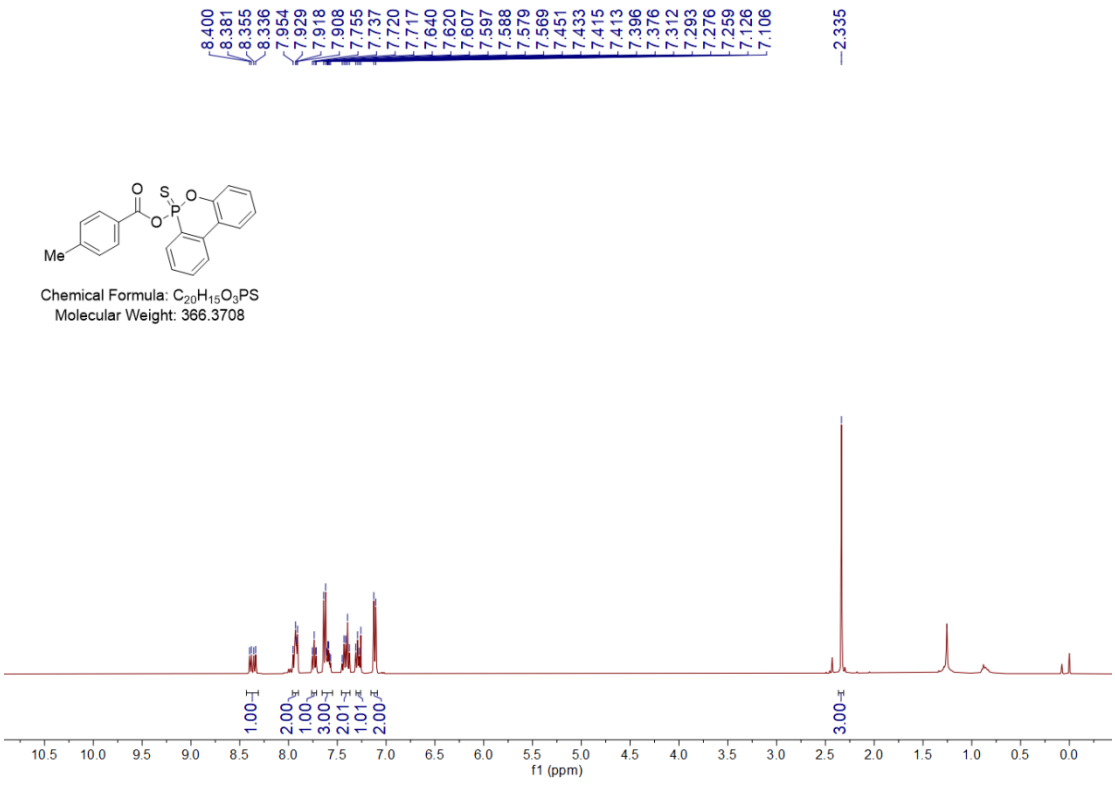


^{13}C NMR spectrum of 4i, 100 MHz, $CDCl_3$

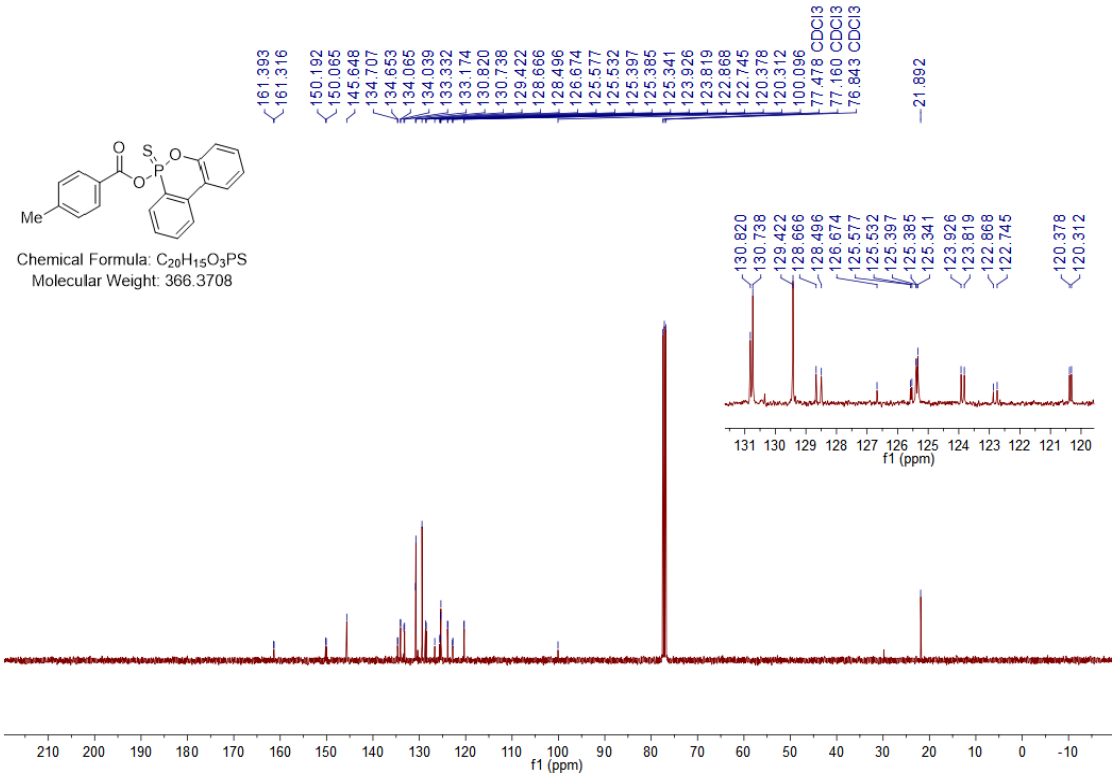


^{31}P NMR spectrum of 4i, 162 MHz, $CDCl_3$

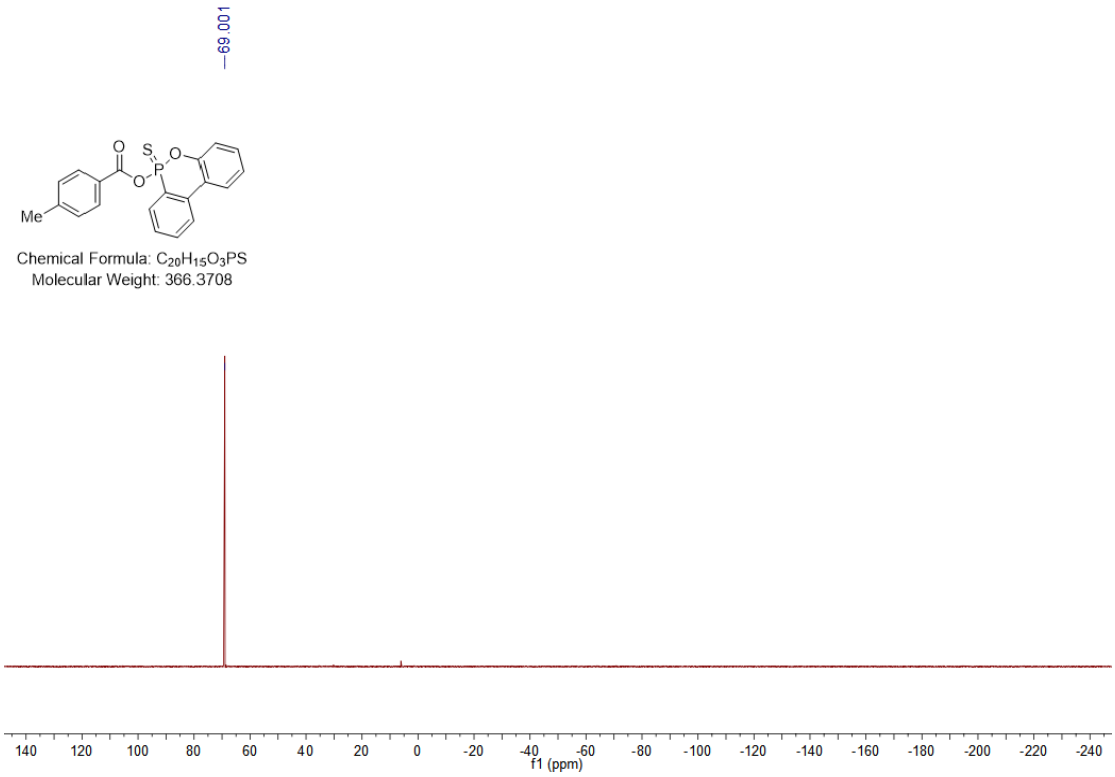
6-Sulfidodibenzo[c,e][1,2]oxaphosphinin-6-yl 4-methylbenzoate (4j)



^{1}H NMR spectrum of 4j, 400 MHz, $CDCl_3$

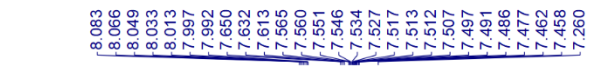


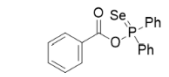
^{13}C NMR spectrum of 4j, 100 MHz, $CDCl_3$



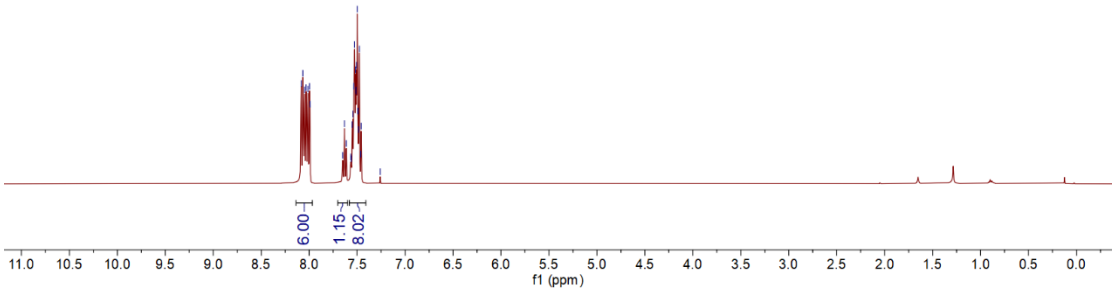
^{31}P NMR spectrum of 4j, 162 MHz, $CDCl_3$

Benzoic diphenylphosphinoselenoic anhydride (5a)

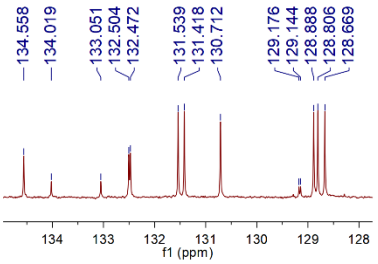


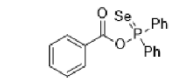


Chemical Formula: $C_{19}H_{15}O_2PSe$
Molecular Weight: 385.2726

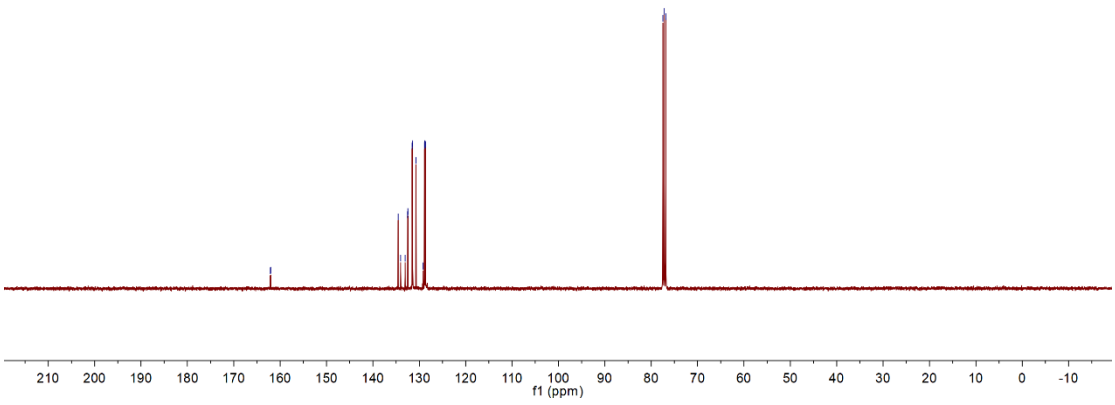


^{1}H NMR spectrum of 5a, 400 MHz, $CDCl_3$

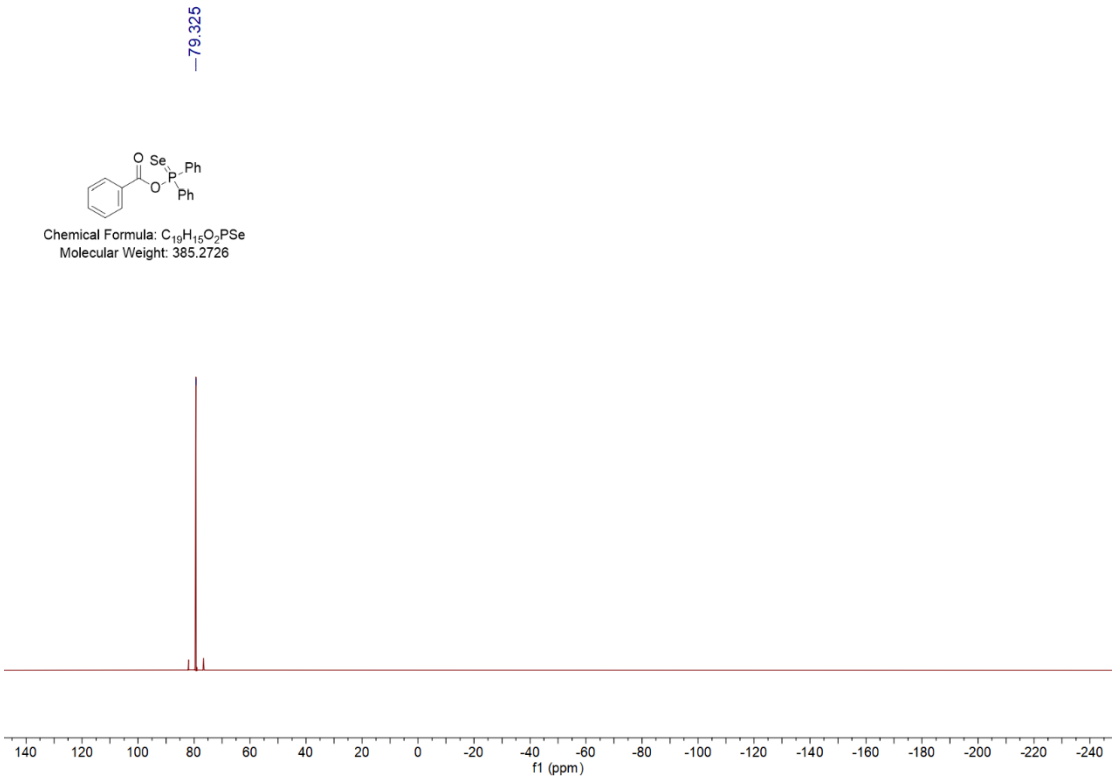




Chemical Formula: $C_{19}H_{15}O_2PSe$
Molecular Weight: 385.2718

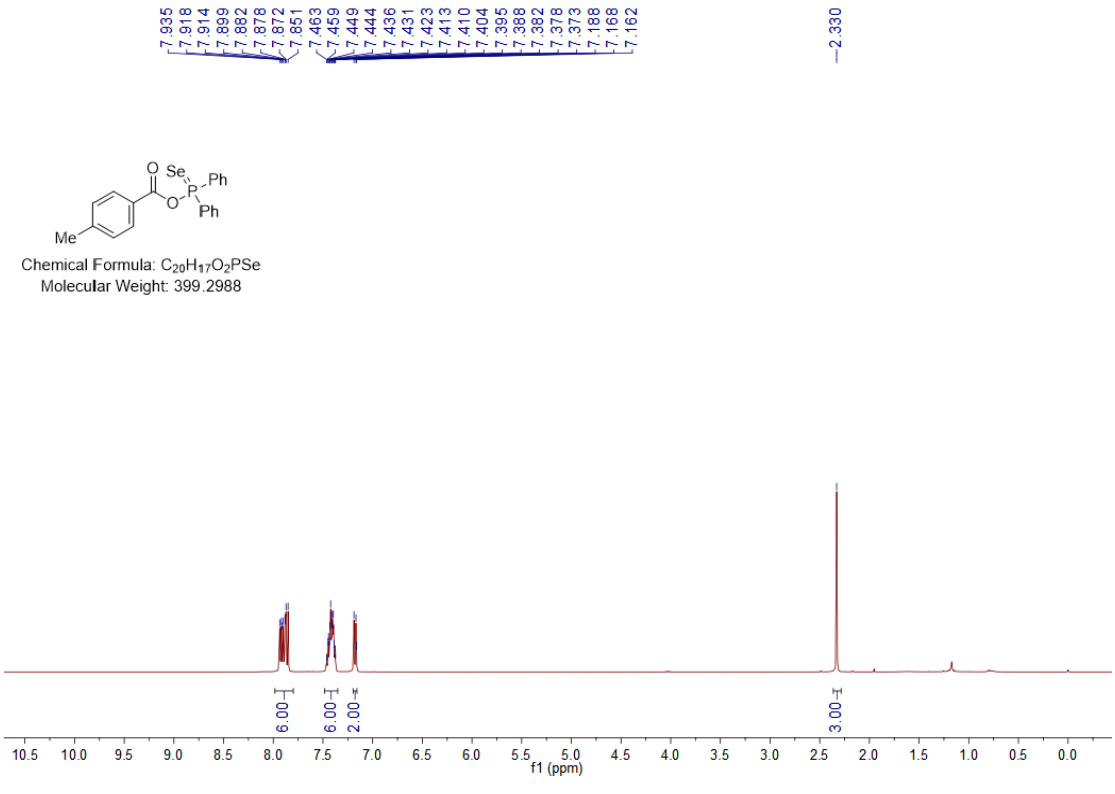


^{13}C NMR spectrum of 5a, 100 MHz, $CDCl_3$

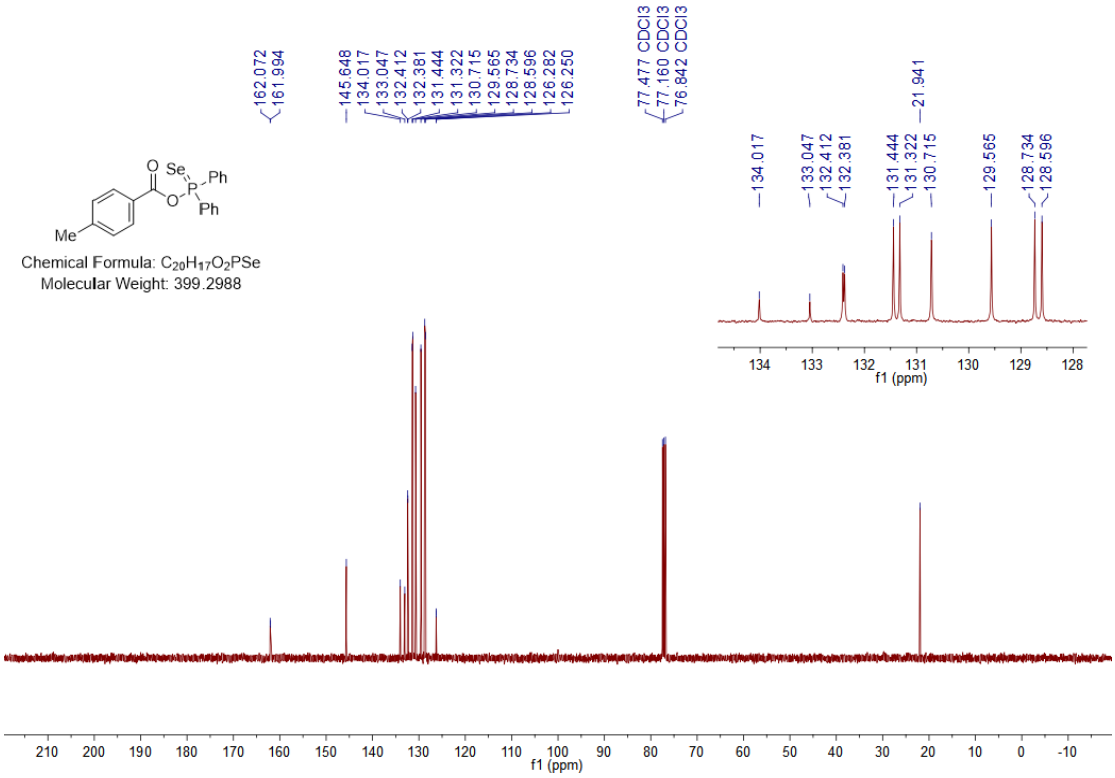


^{31}P NMR spectrum of 5a, 162 MHz, $CDCl_3$

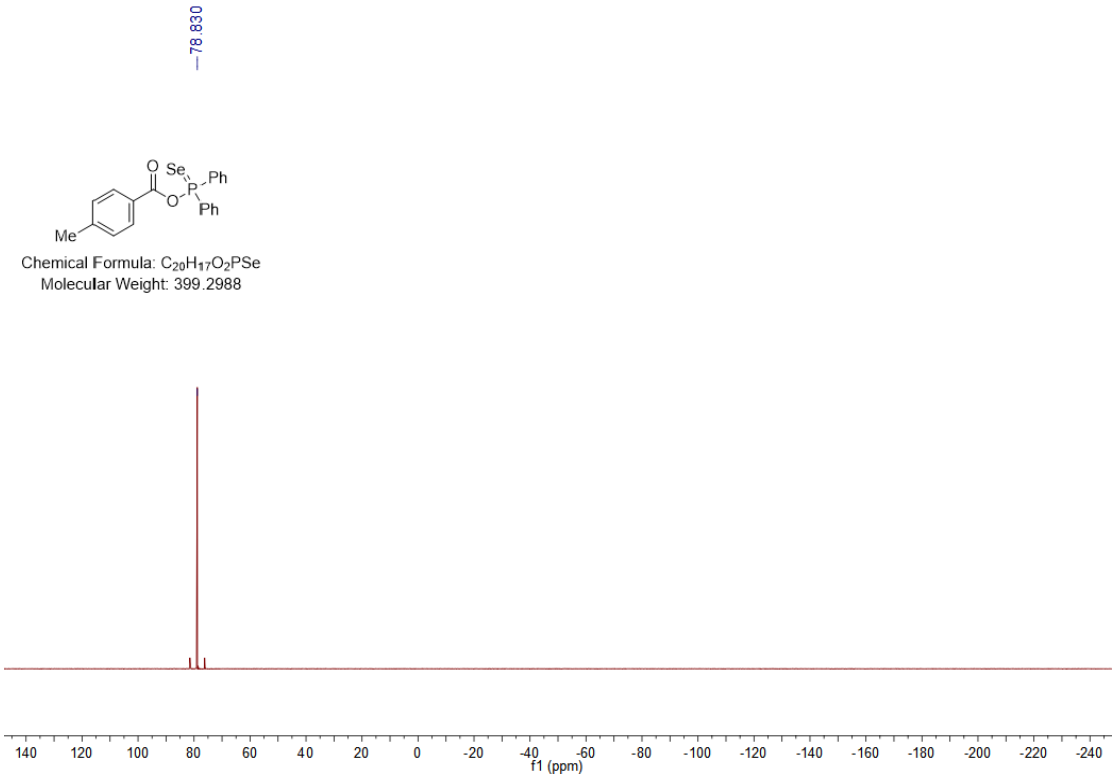
4-Methylbenzoic diphenylphosphinoselenoic anhydride (5b)



^{1}H NMR spectrum of 5b, 400 MHz, $CDCl_3$

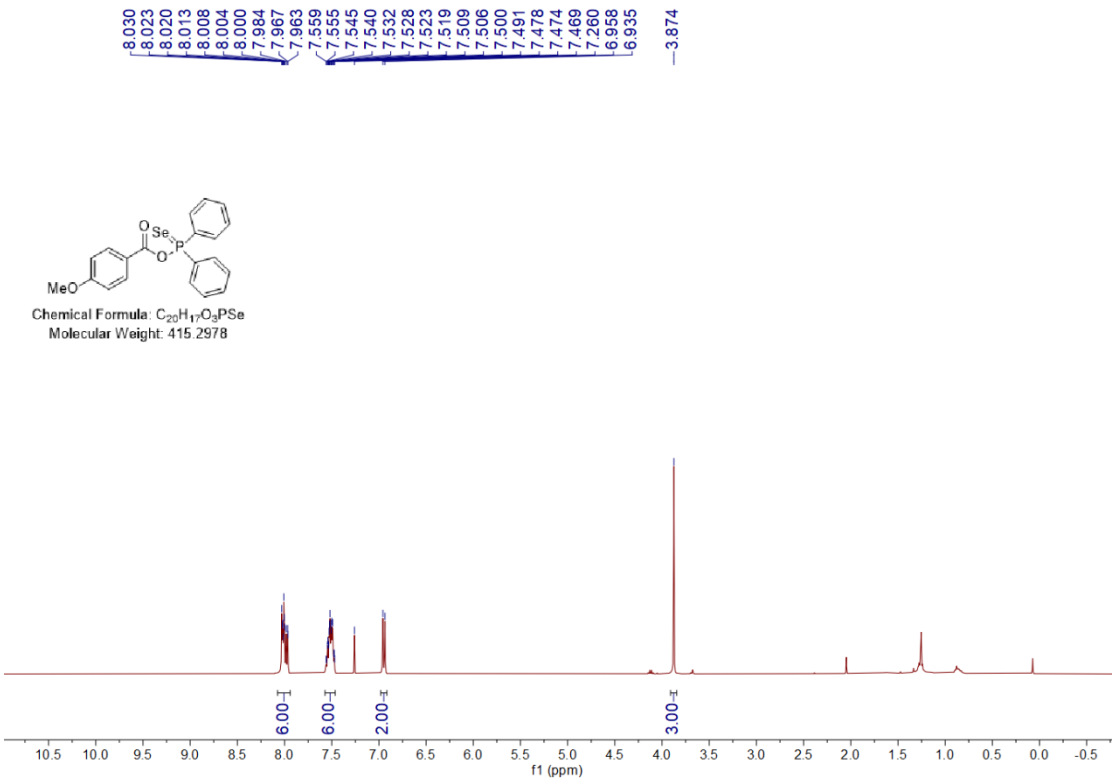


^{13}C NMR spectrum of 5b, 100 MHz, $CDCl_3$

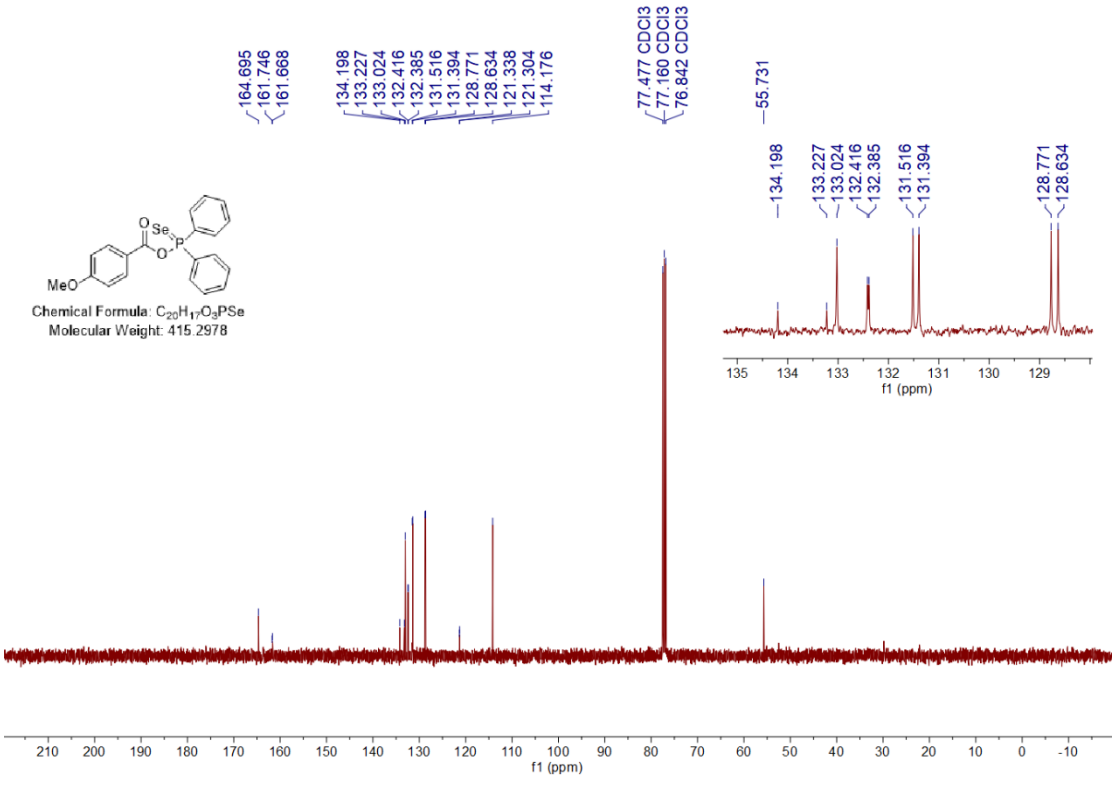


^{31}P NMR spectrum of 5b, 162 MHz, $CDCl_3$

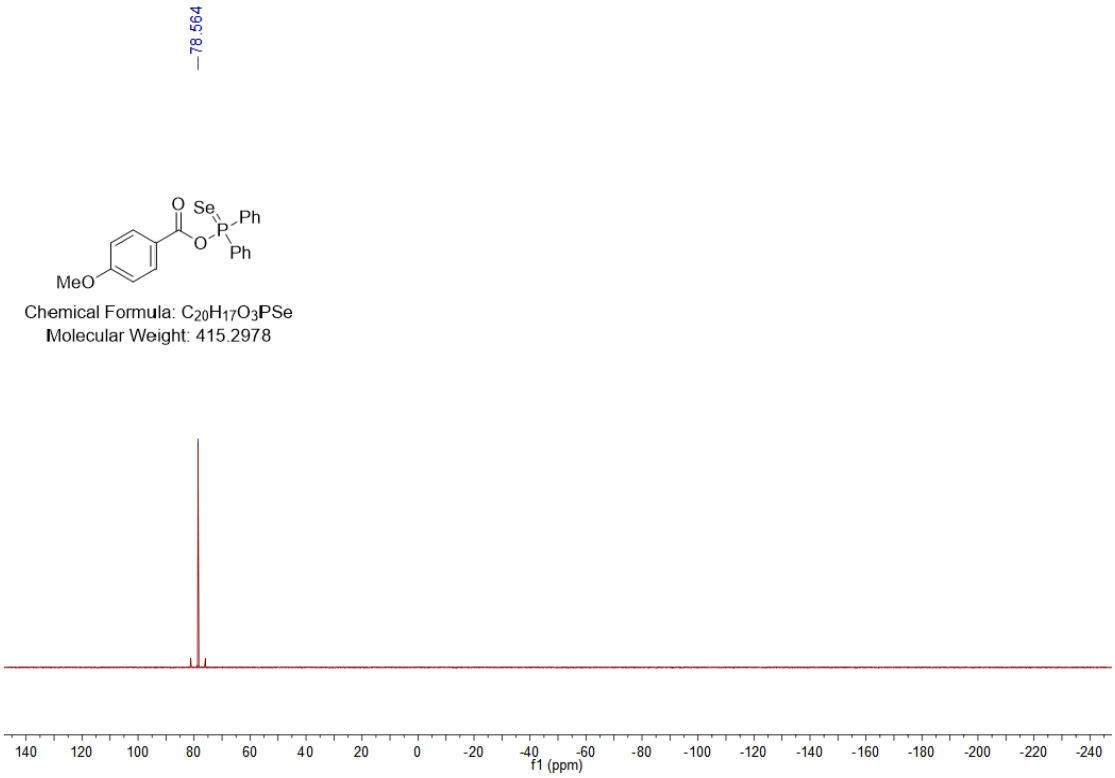
4-Methoxybenzoic diphenylphosphinoselenoic anhydride (5c)



^{1}H NMR spectrum of 5c, 400 MHz, $CDCl_3$

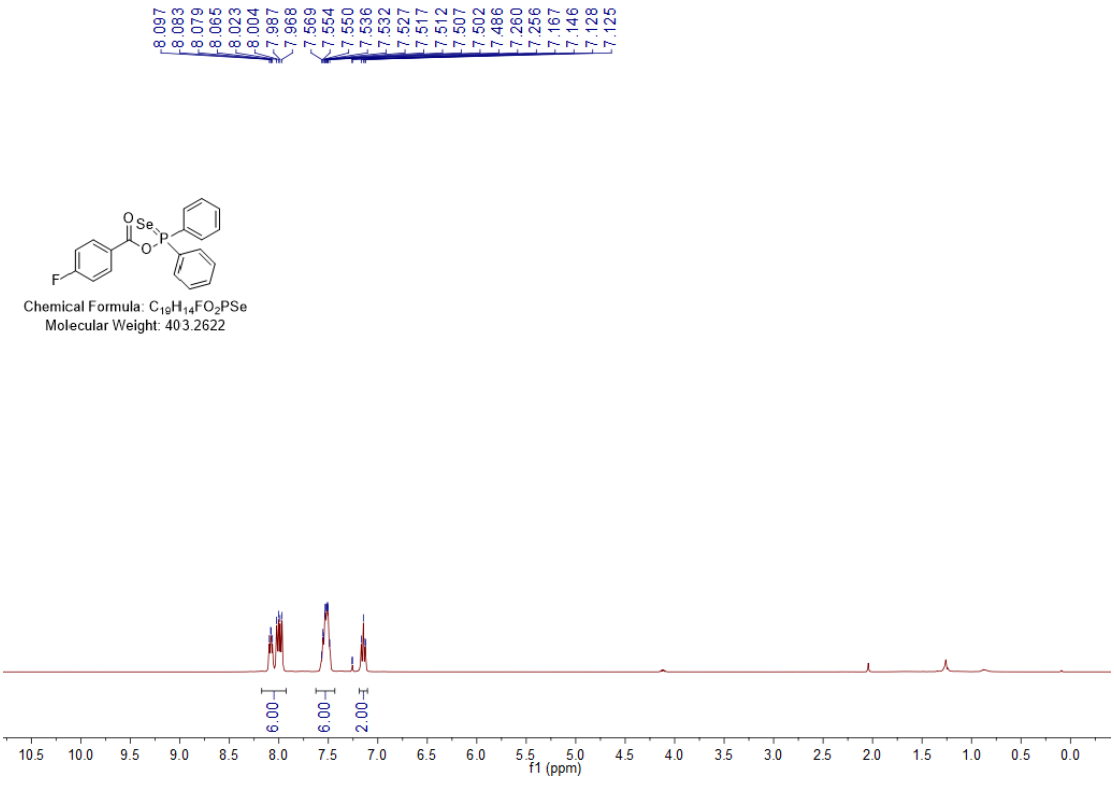


^{13}C NMR spectrum of 5c, 100 MHz, $CDCl_3$

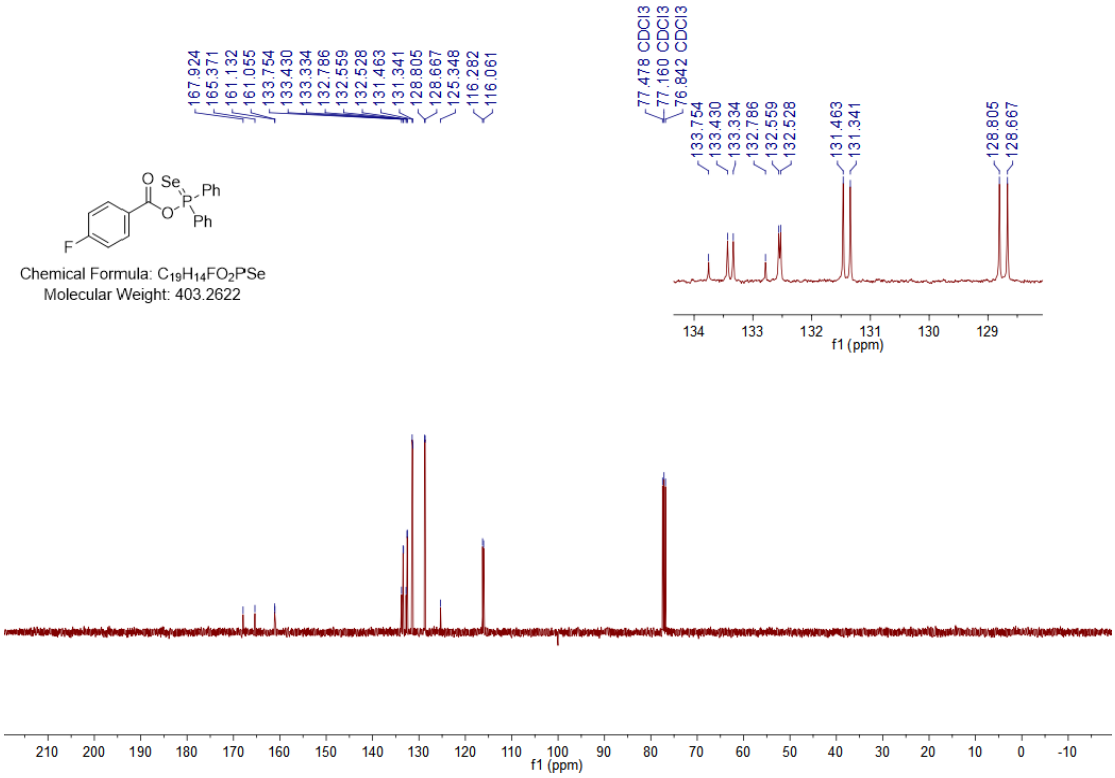


^{31}P NMR spectrum of 5c, 162 MHz, $CDCl_3$

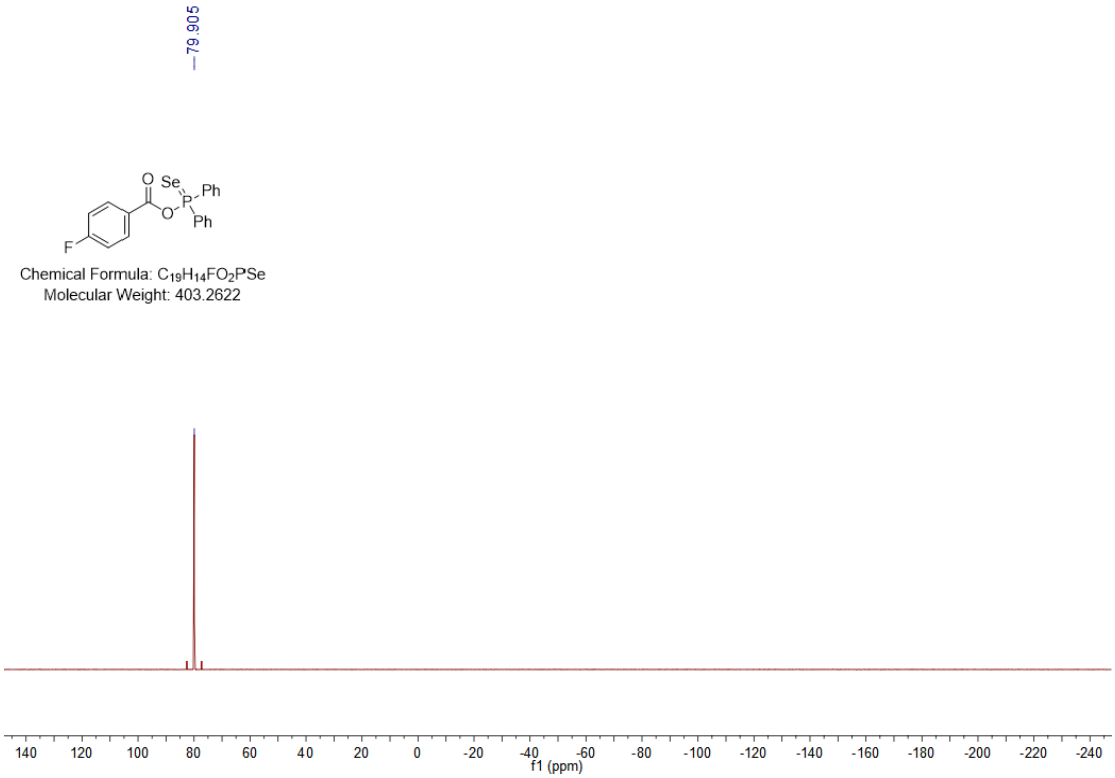
4-Fluorobenzoic diphenylphosphinoselenoic anhydride (5d)



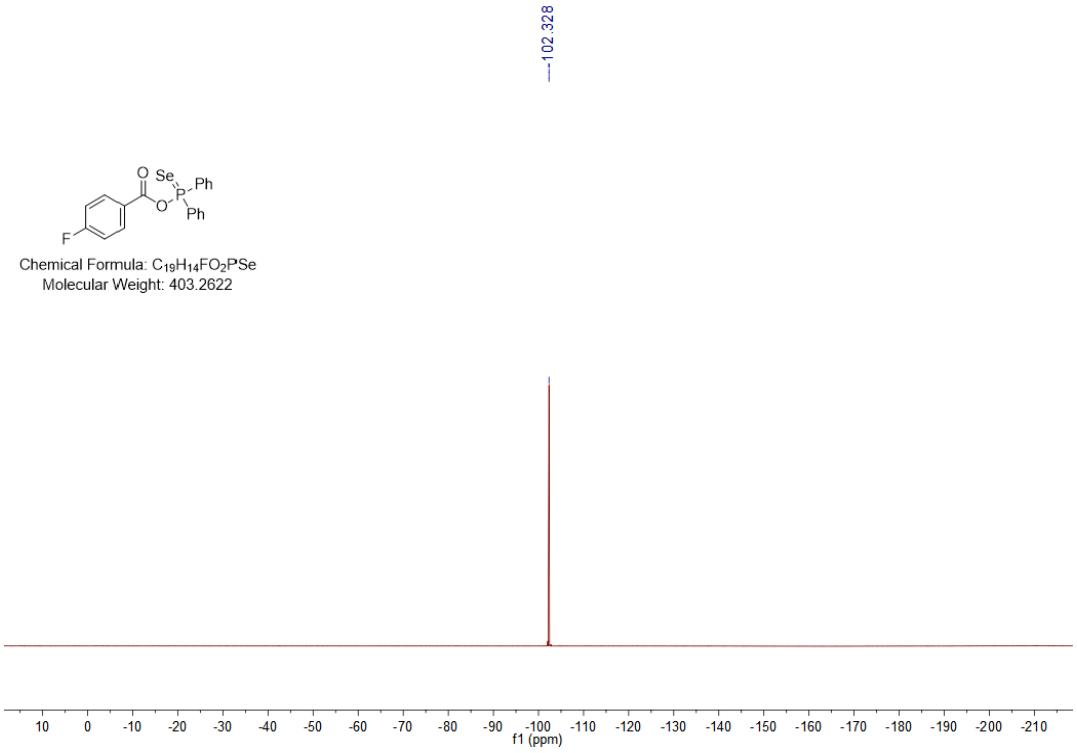
^{1}H NMR spectrum of 5d, 400 MHz, $CDCl_3$



^{13}C NMR spectrum of 5d, 100 MHz, $CDCl_3$

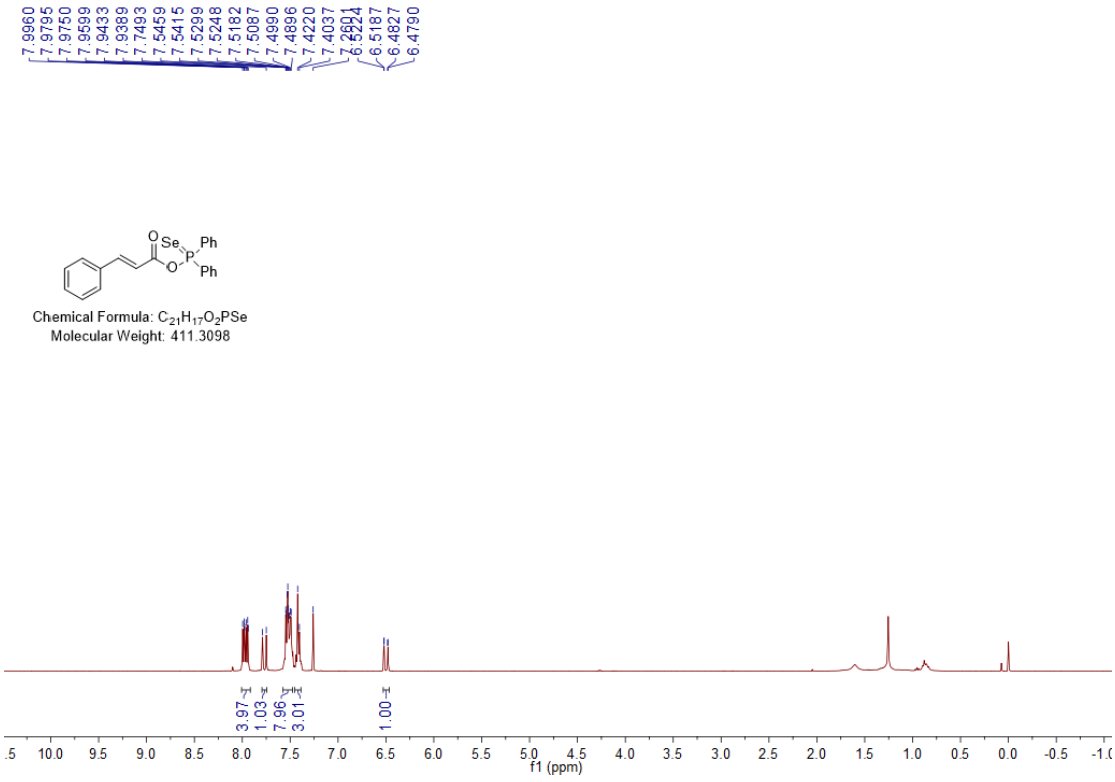


^{31}P NMR spectrum of 5d, 162 MHz, $CDCl_3$

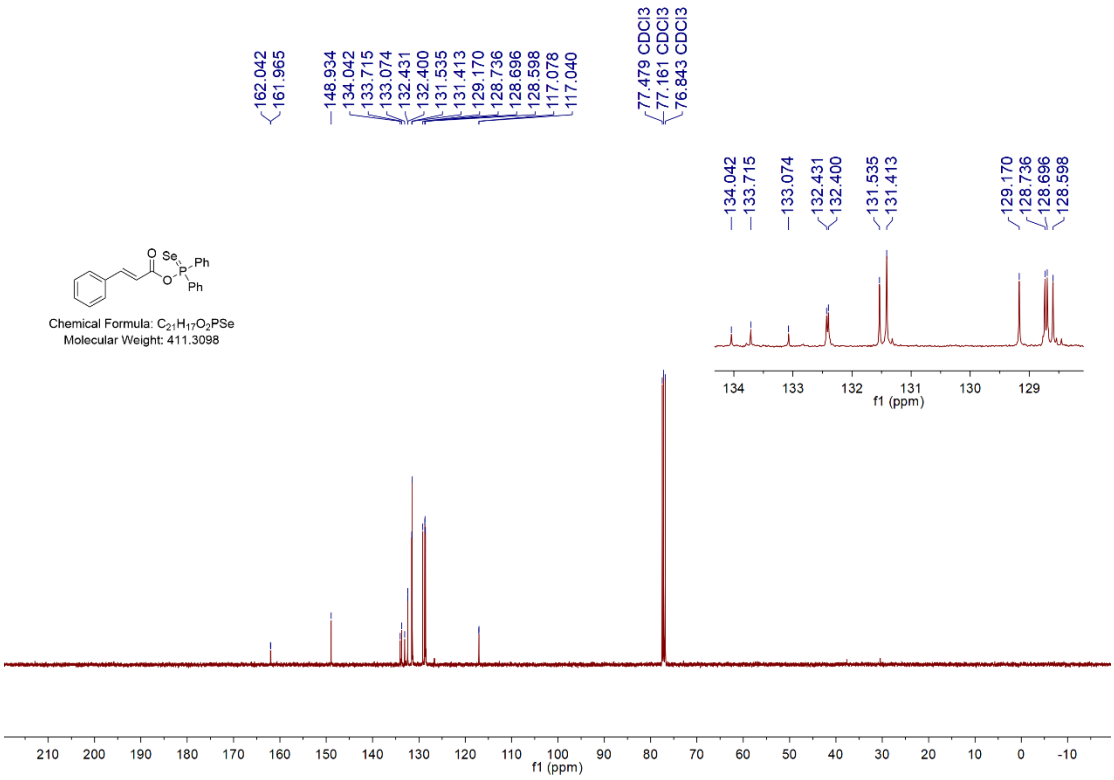


^{19}F NMR spectrum of 5d, 376 MHz, $CDCl_3$

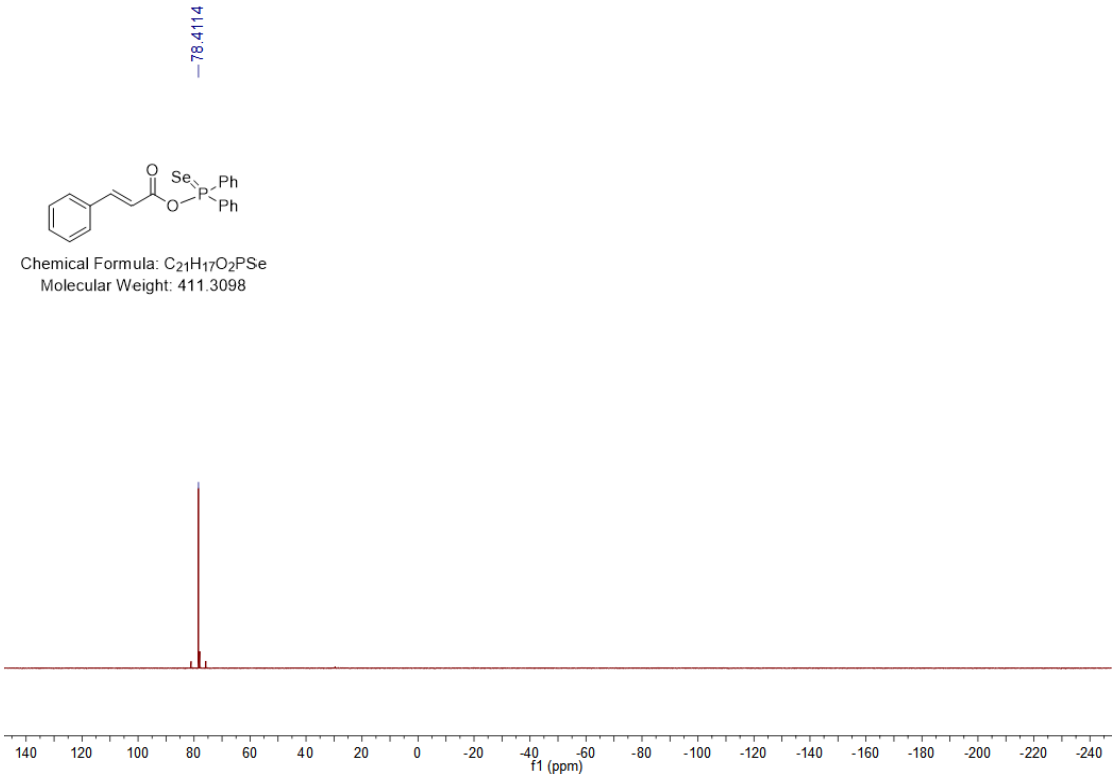
(E)-Cinnamic diphenylphosphinoselenoic anhydride (5e)



^{1}H NMR spectrum of 5e, 400 MHz, $CDCl_3$

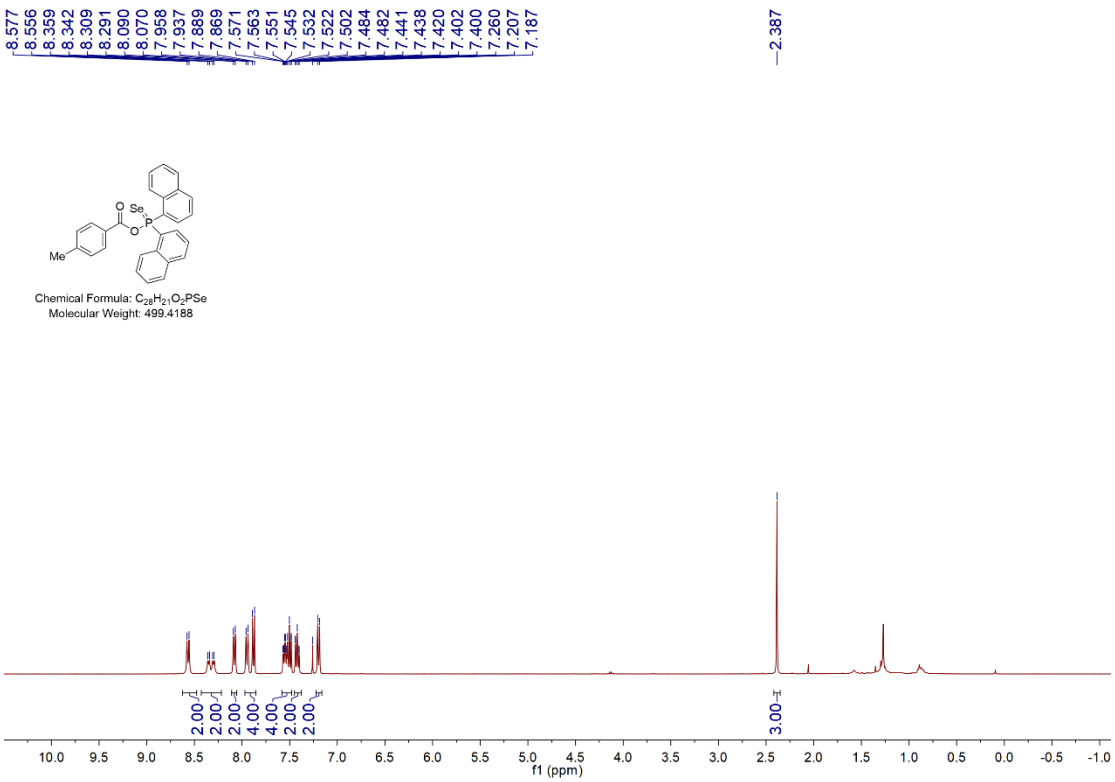


^{13}C NMR spectrum of 5e, 100 MHz, $CDCl_3$

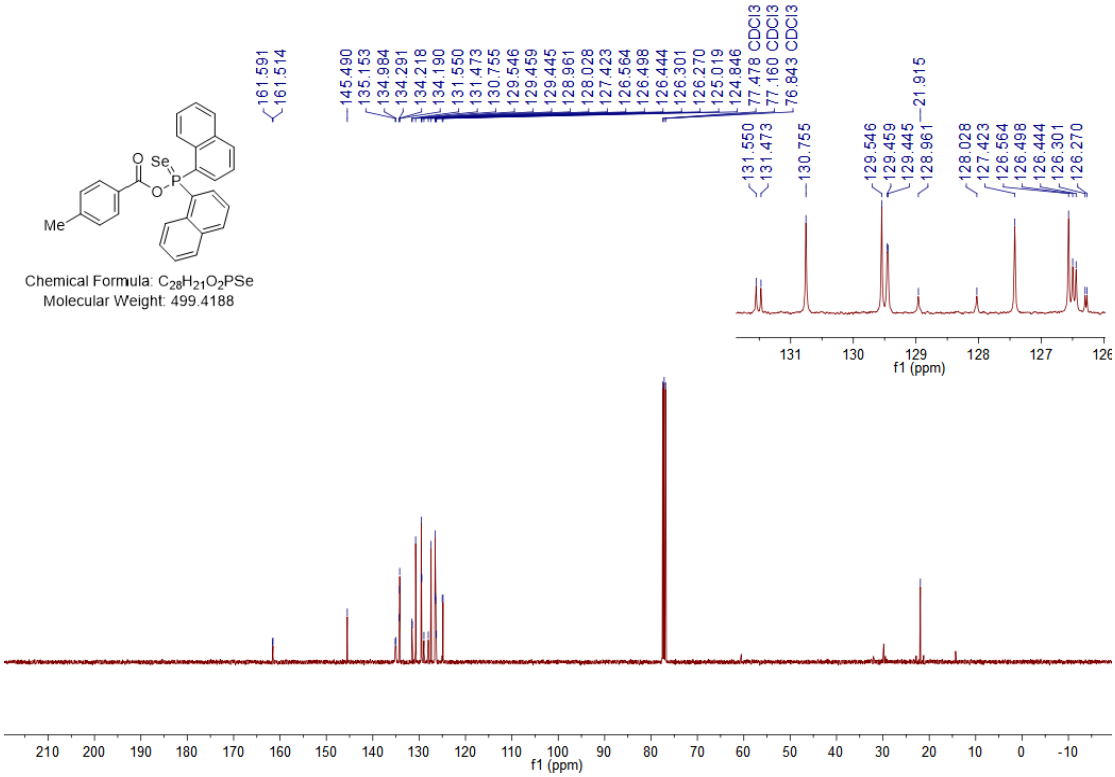


^{31}P NMR spectrum of 5e, 162 MHz, $CDCl_3$

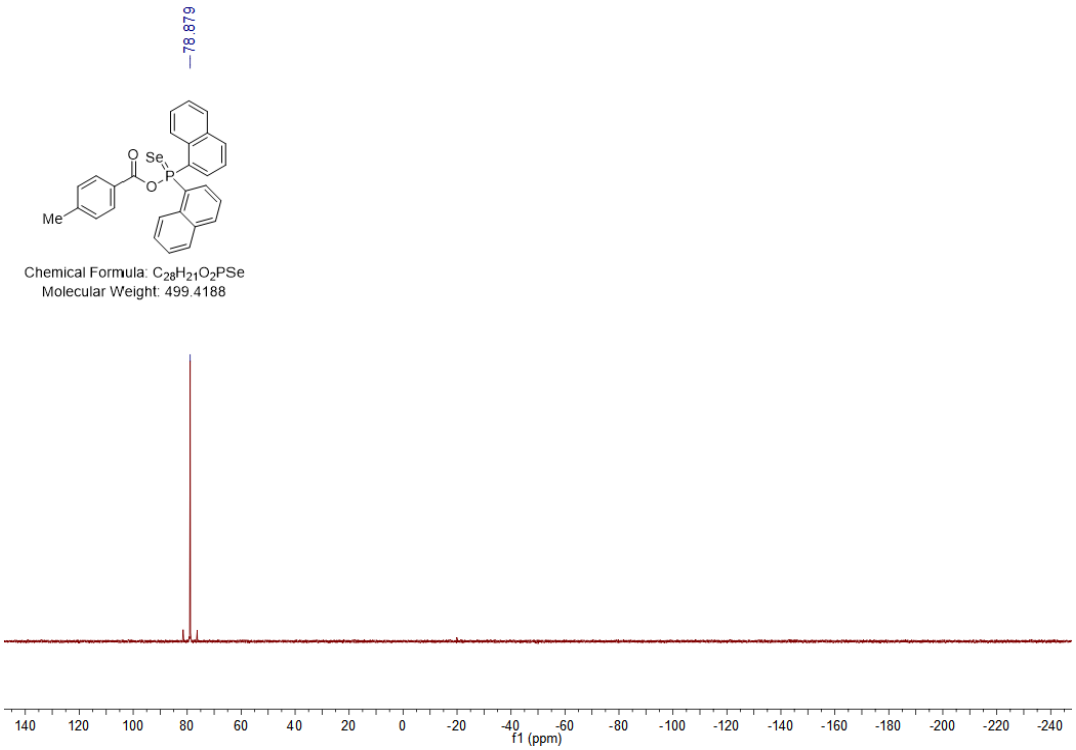
4-Methylbenzoic di(naphthalen-1-yl)phosphinoselenoic anhydride (5f)



^{1}H NMR spectrum of 5f, 400 MHz, $CDCl_3$

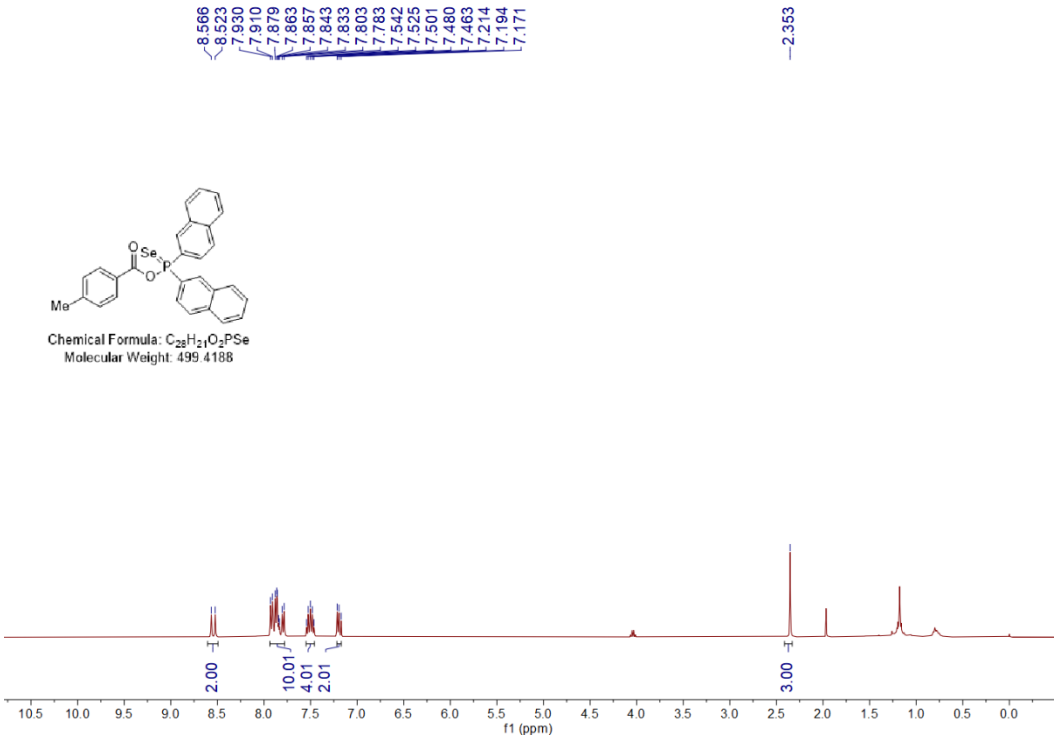


^{13}C NMR spectrum of 5f, 100 MHz, $CDCl_3$

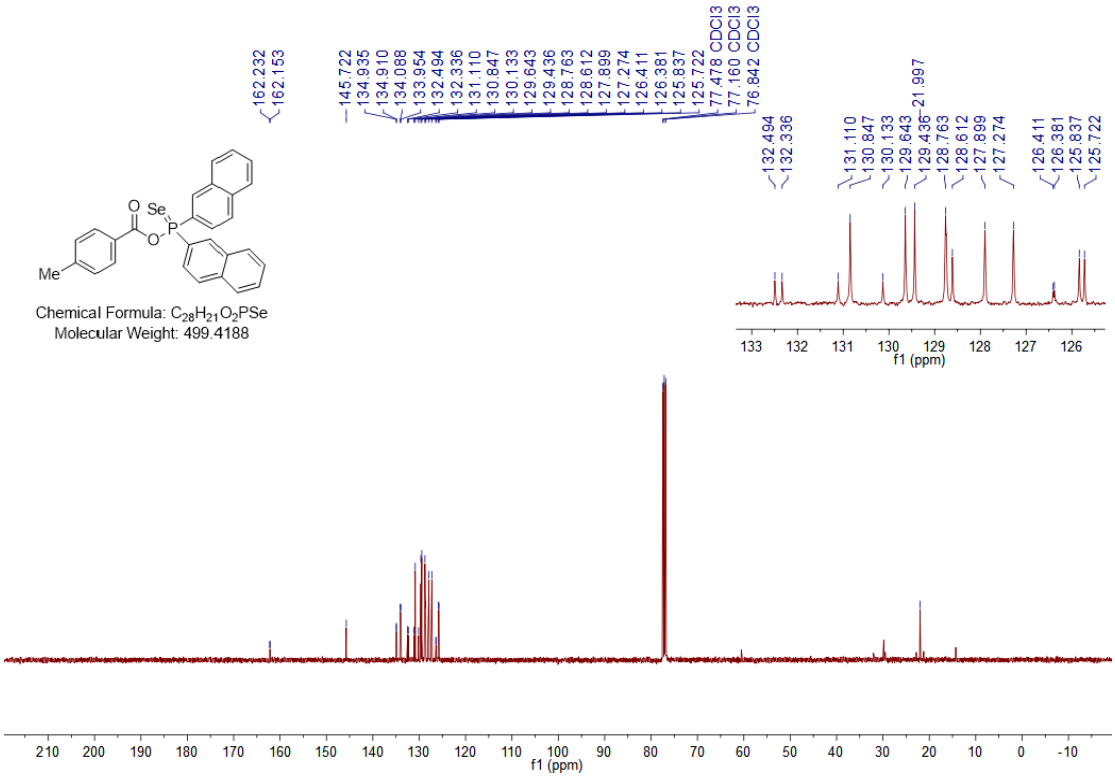


^{31}P NMR spectrum of 5f, 162 MHz, $CDCl_3$

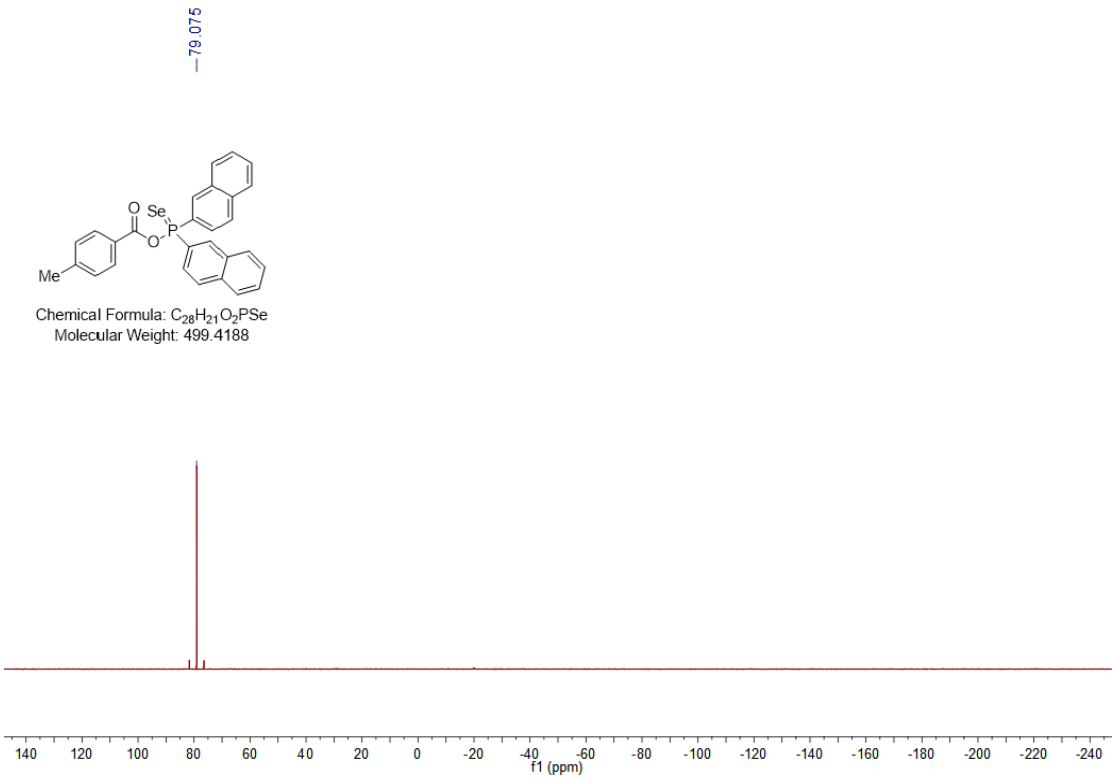
4-Methylbenzoic di(naphthalen-2-yl)phosphinoselenoic anhydride (5g)



^{1}H NMR spectrum of 5g, 400 MHz, $CDCl_3$

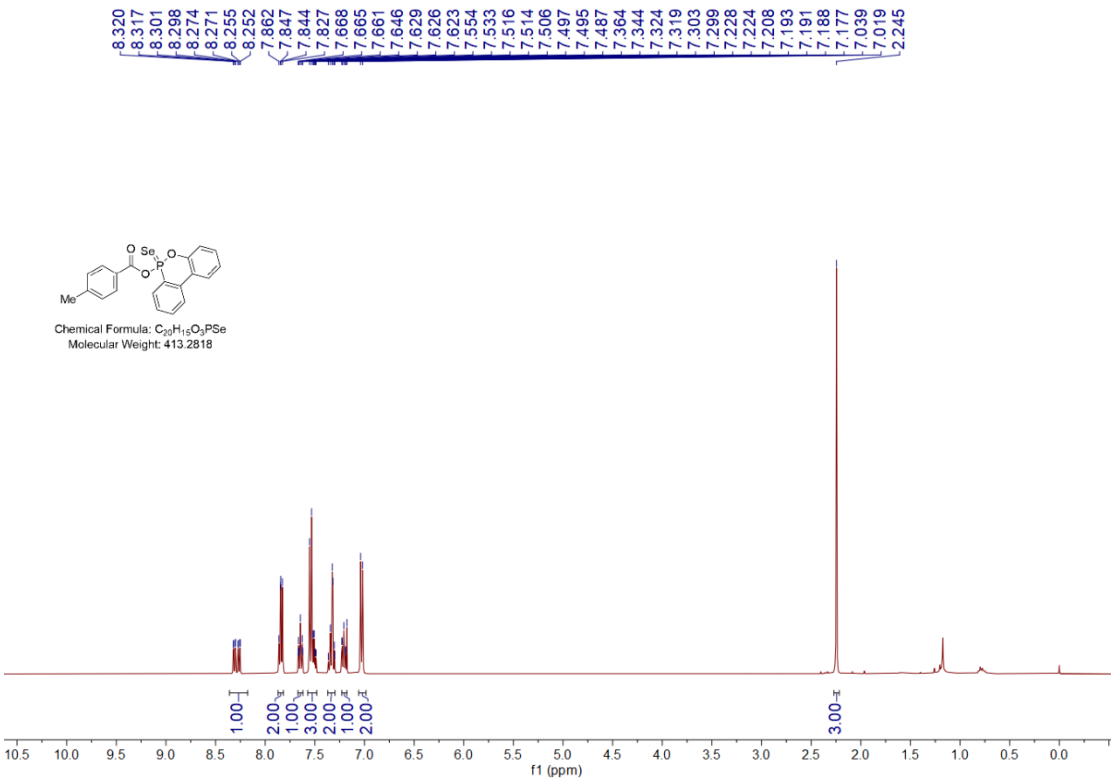


^{13}C NMR spectrum of 5g, 100 MHz, $CDCl_3$

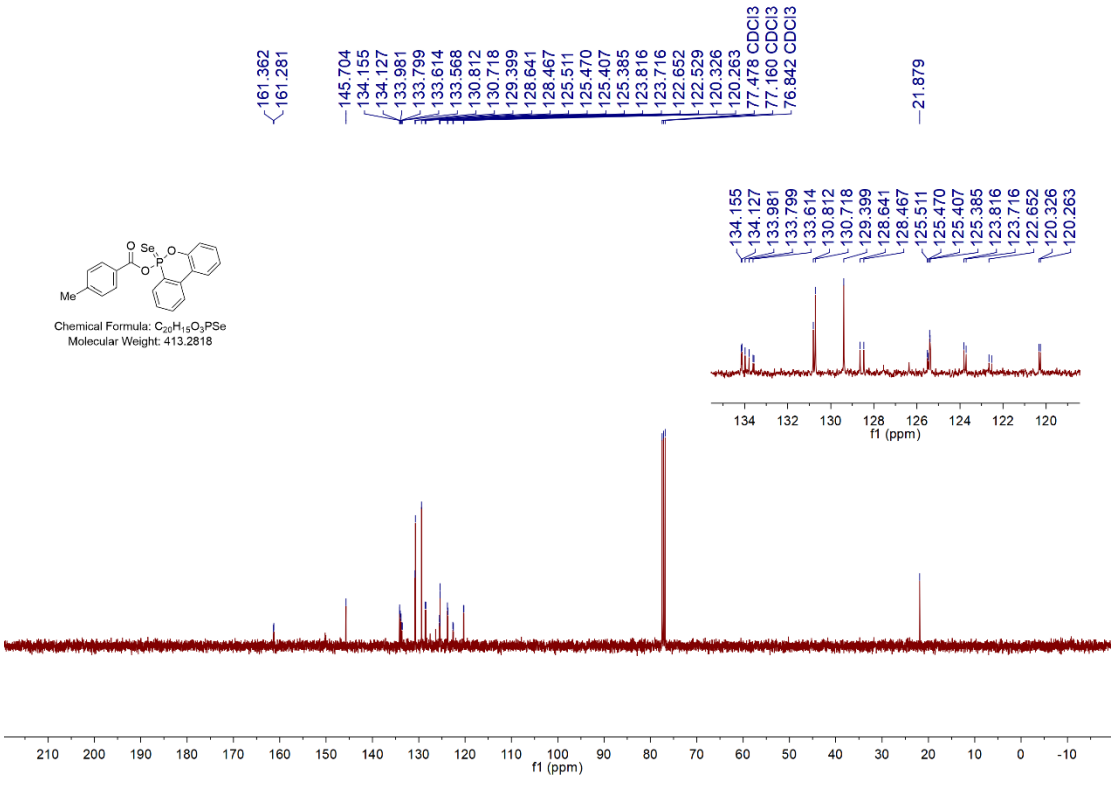


^{31}P NMR spectrum of 5g, 162 MHz, $CDCl_3$

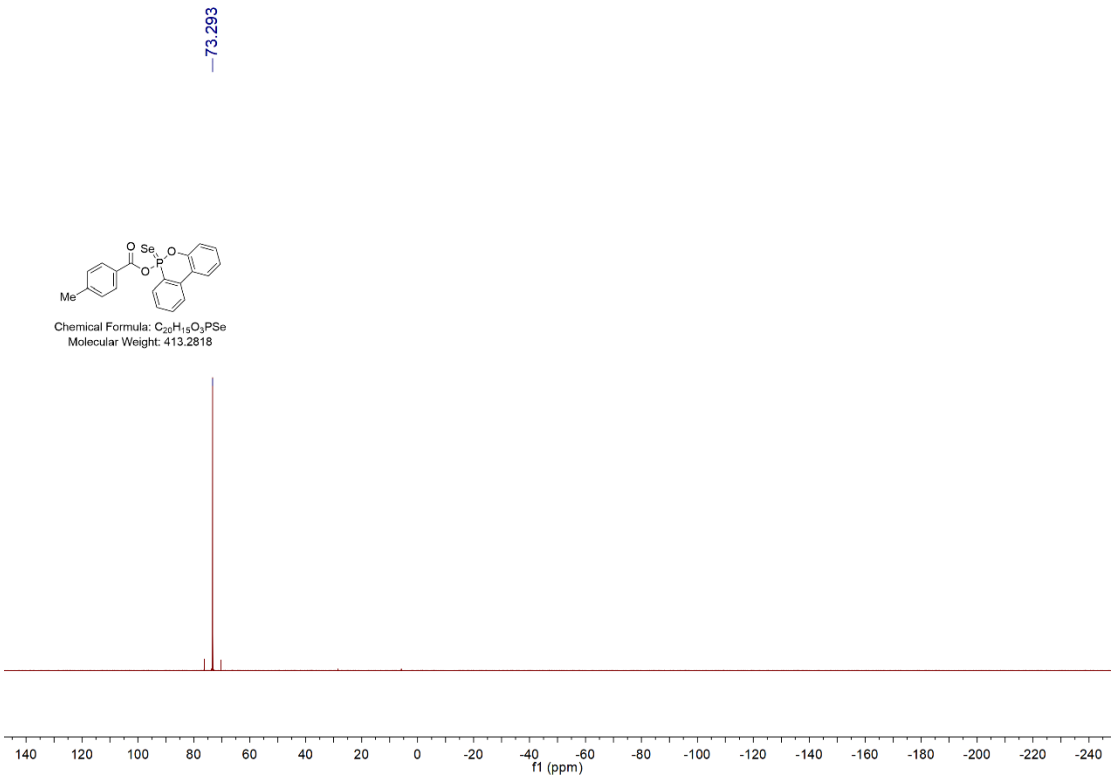
6-Selenidodibenzo[c,e][1,2]oxaphosphinin-6-yl 4-methylbenzoate (5h)



^{1}H NMR spectrum of 5h, 400 MHz, $CDCl_3$

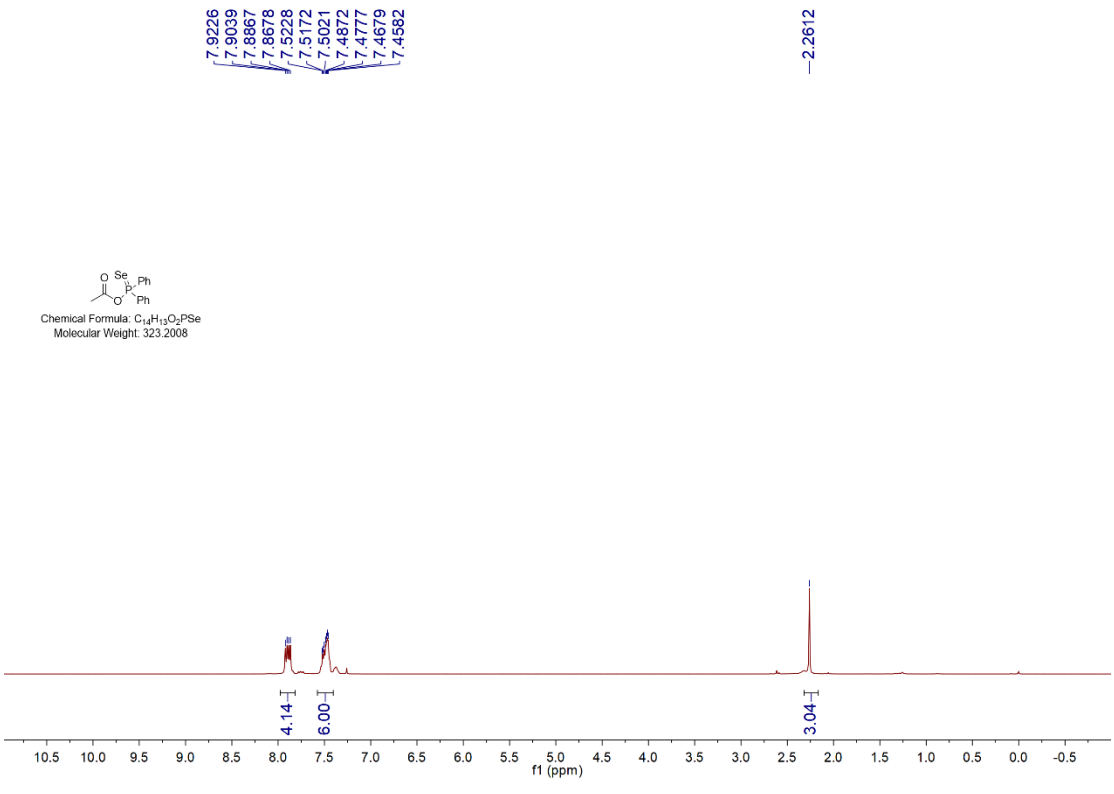


^{13}C NMR spectrum of 5h, 100 MHz, $CDCl_3$

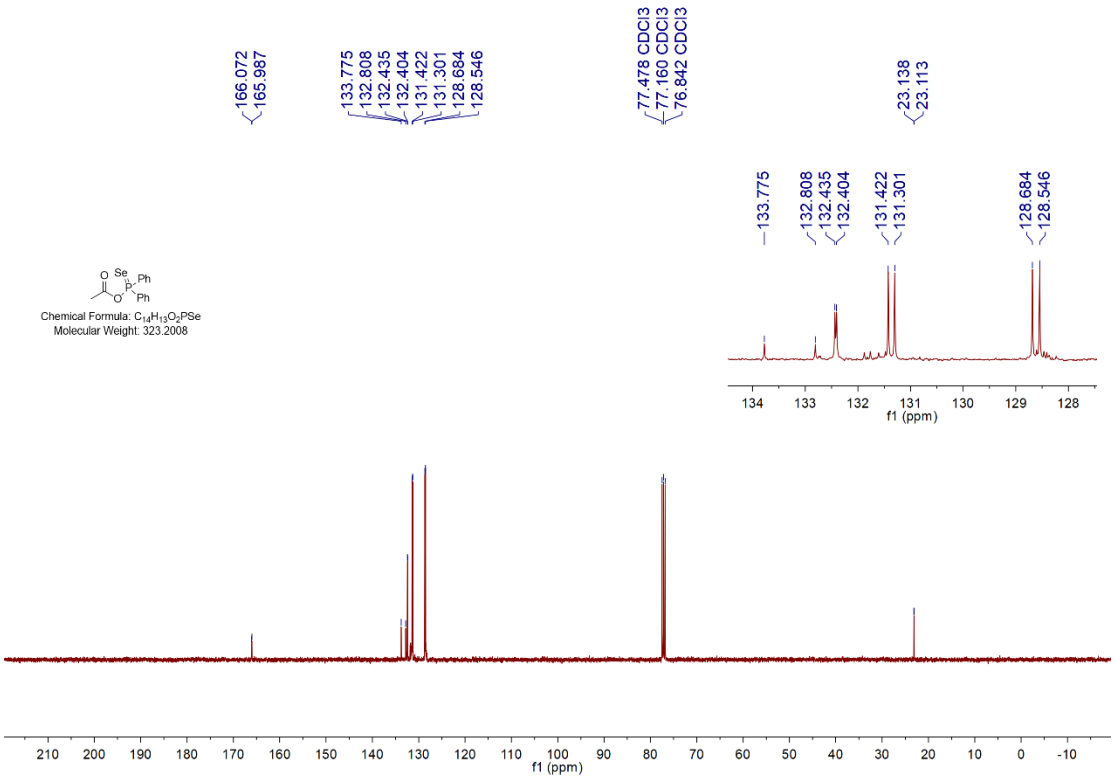


^{31}P NMR spectrum of 5h, 162 MHz, $CDCl_3$

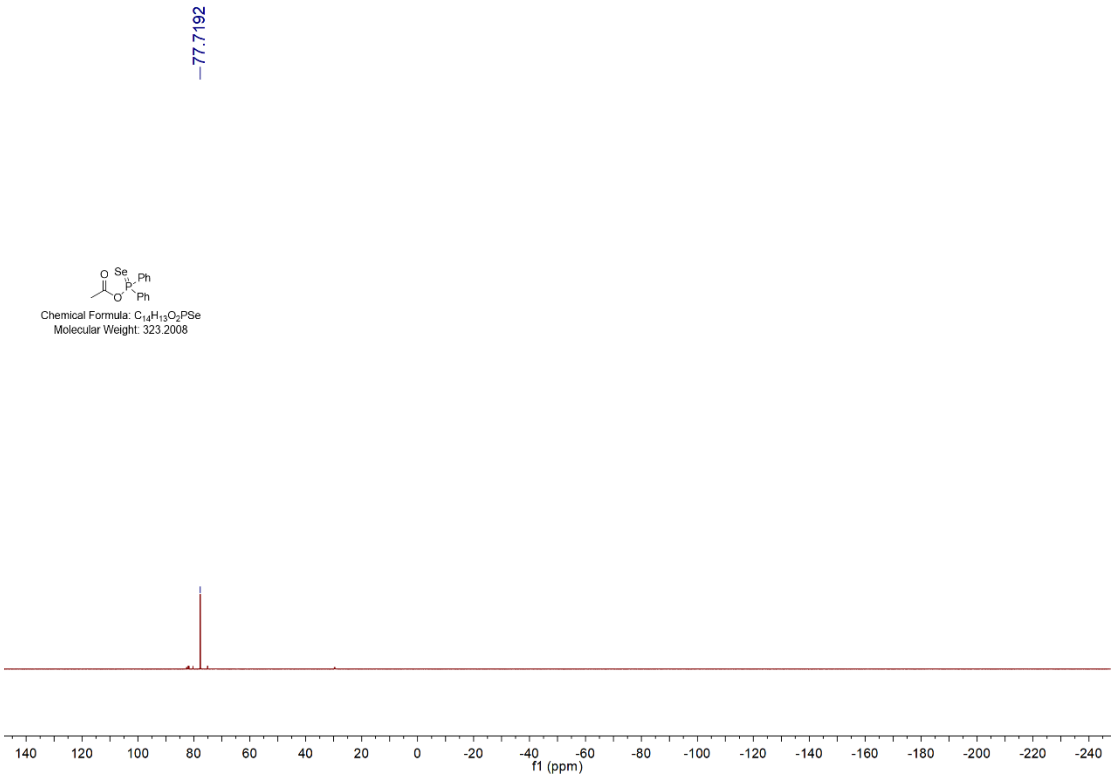
Acetic diphenylphosphinoselenoic anhydride (5i)



^{1}H NMR spectrum of 5i, 400 MHz, $CDCl_3$

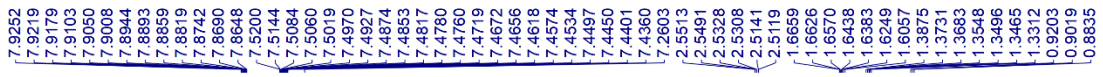


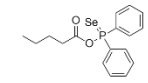
^{13}C NMR spectrum of 5i, 100 MHz, $CDCl_3$

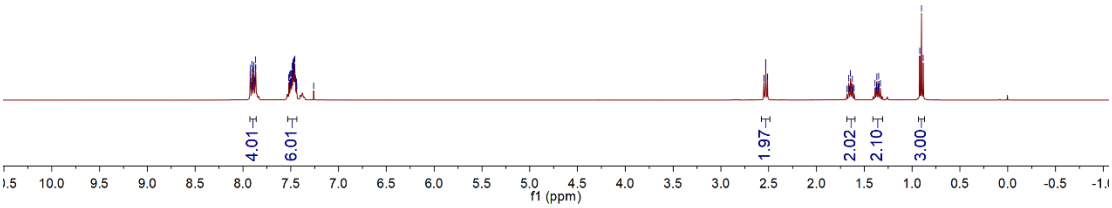


^{31}P NMR spectrum of 5i, 162 MHz, $CDCl_3$

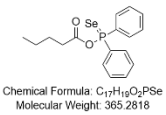
Pentanoic diphenylphosphinoselenoic anhydride (5j)

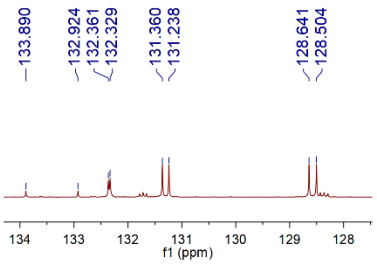


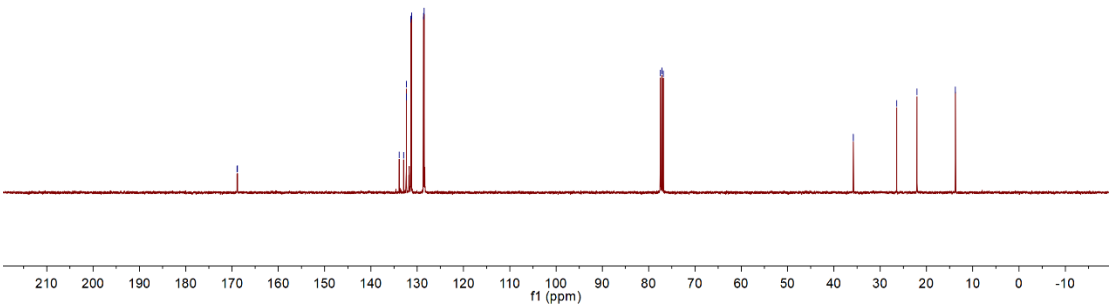




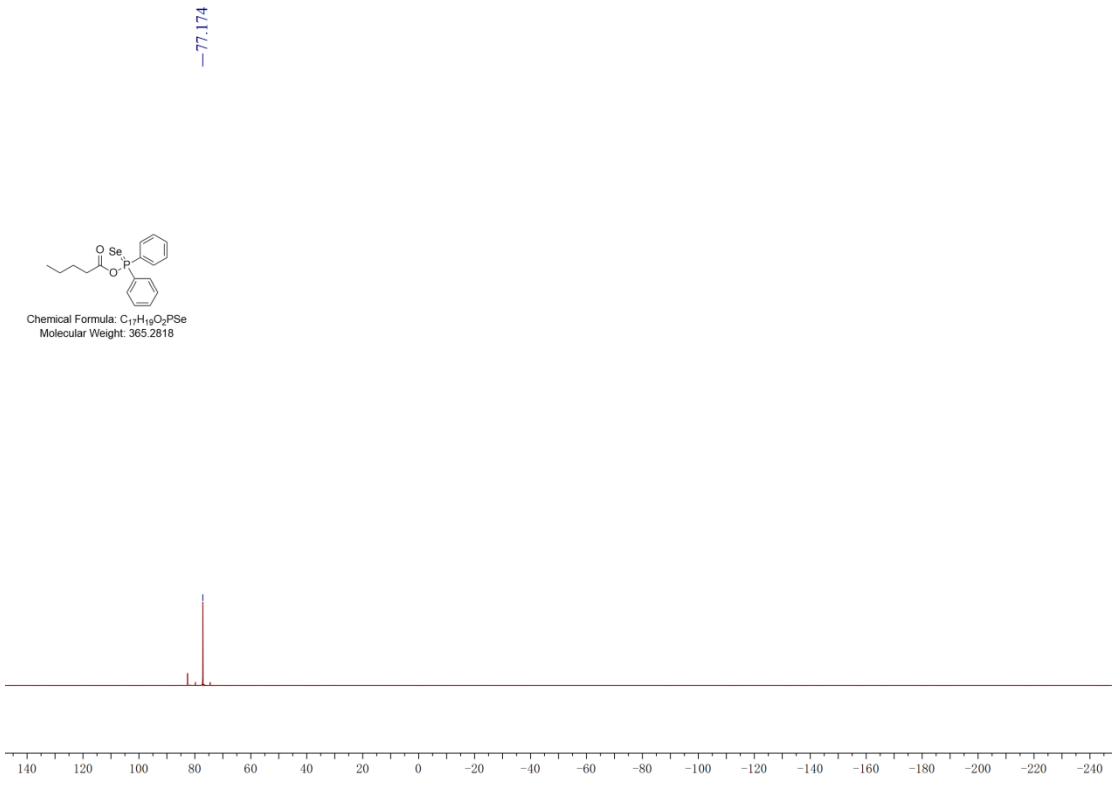
^{1}H NMR spectrum of 5j, 400 MHz, $CDCl_3$





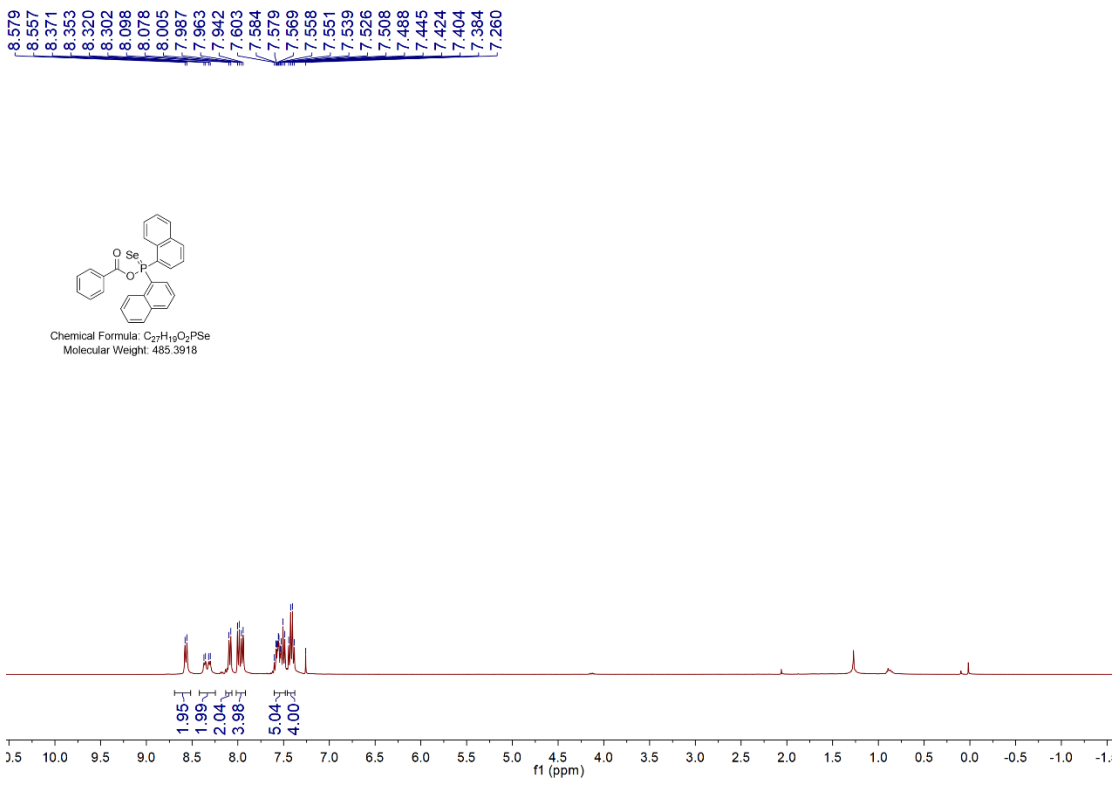


^{13}C NMR spectrum of 5j, 100 MHz, $CDCl_3$

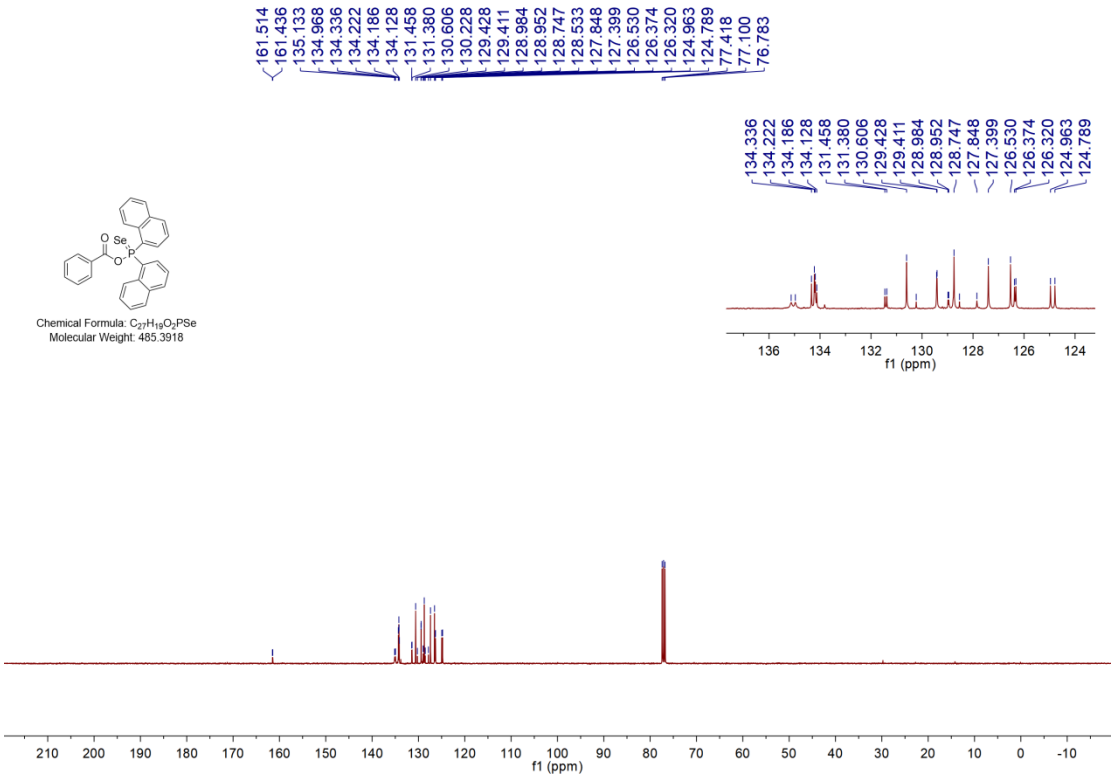


^{31}P NMR spectrum of 5j, 162 MHz, $CDCl_3$

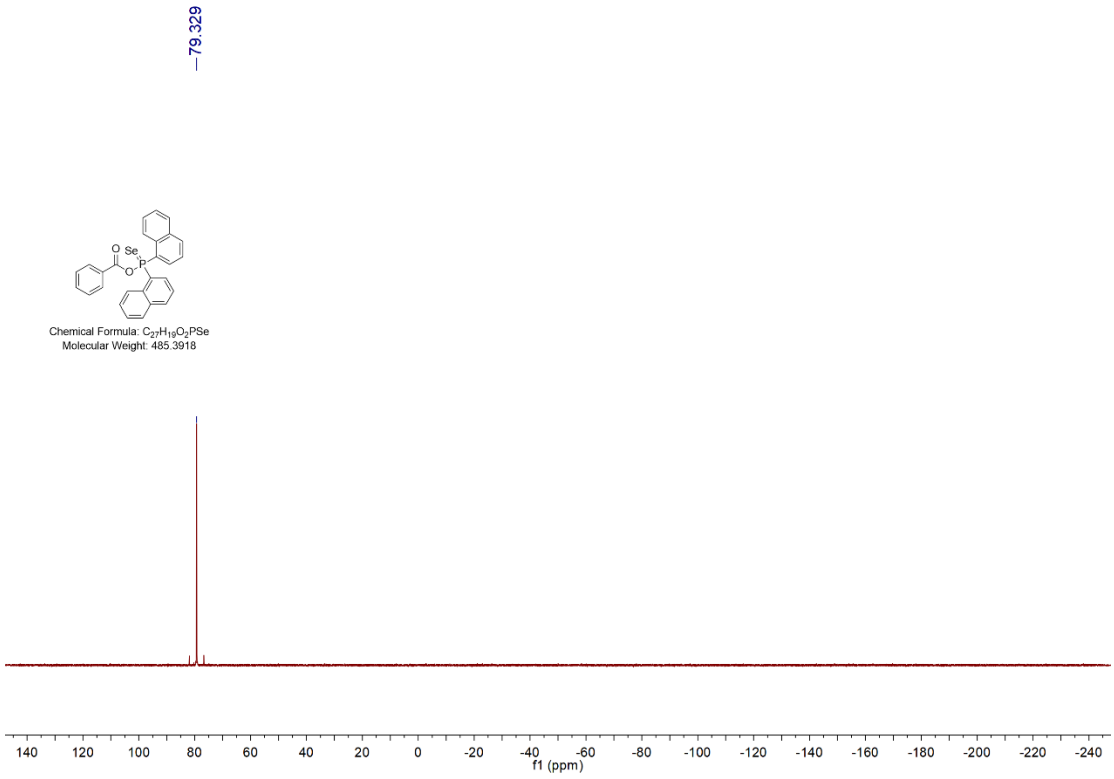
Benzoic di(naphthalen-1-yl)phosphinoselenoic anhydride (5k)



^{1}H NMR spectrum of 5k, 400 MHz, $CDCl_3$

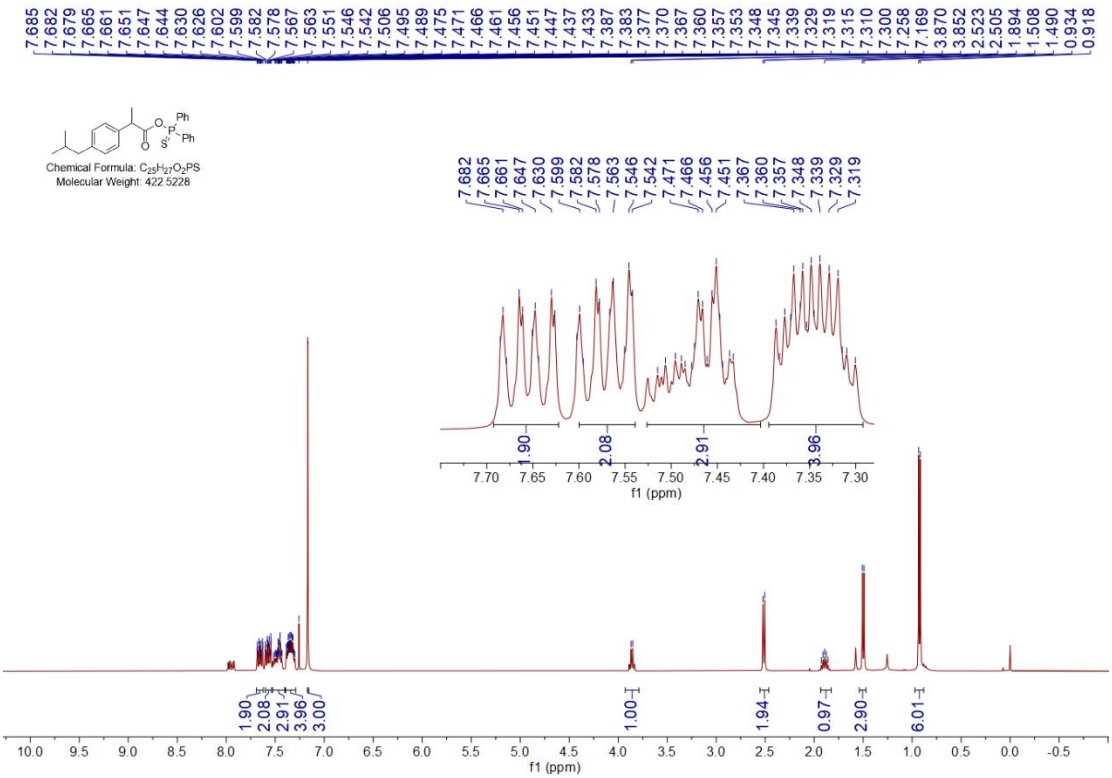


^{13}C NMR spectrum of 5k, 100 MHz, $CDCl_3$

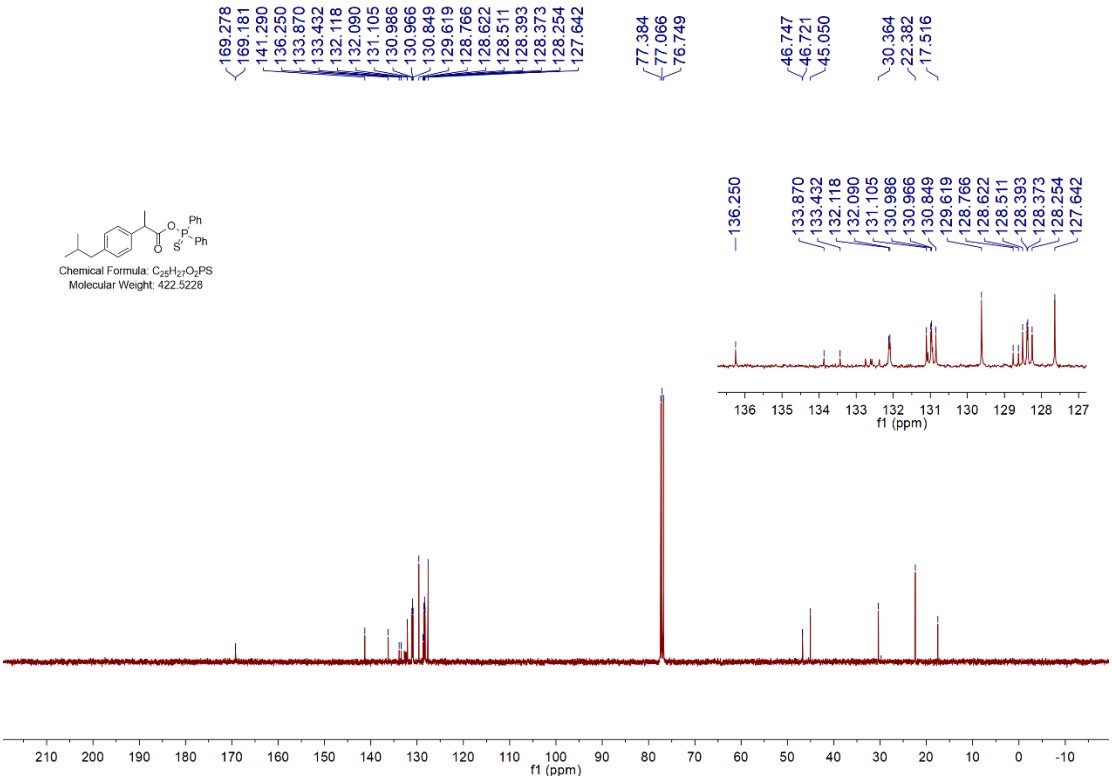


^{31}P NMR spectrum of 5k, 162 MHz, $CDCl_3$

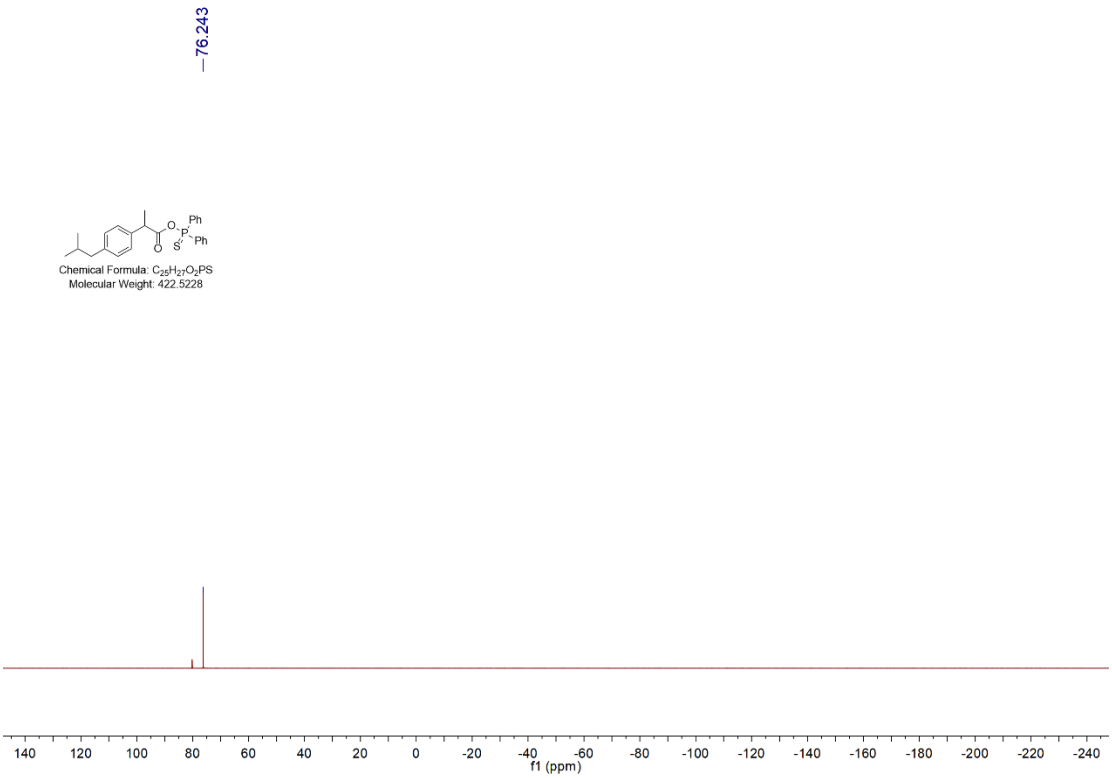
2-(4-Isobutylphenyl)propanoic diphenylphosphinothioic anhydride (6a)



^{1}H NMR spectrum of 6a, 400 MHz, $CDCl_3$

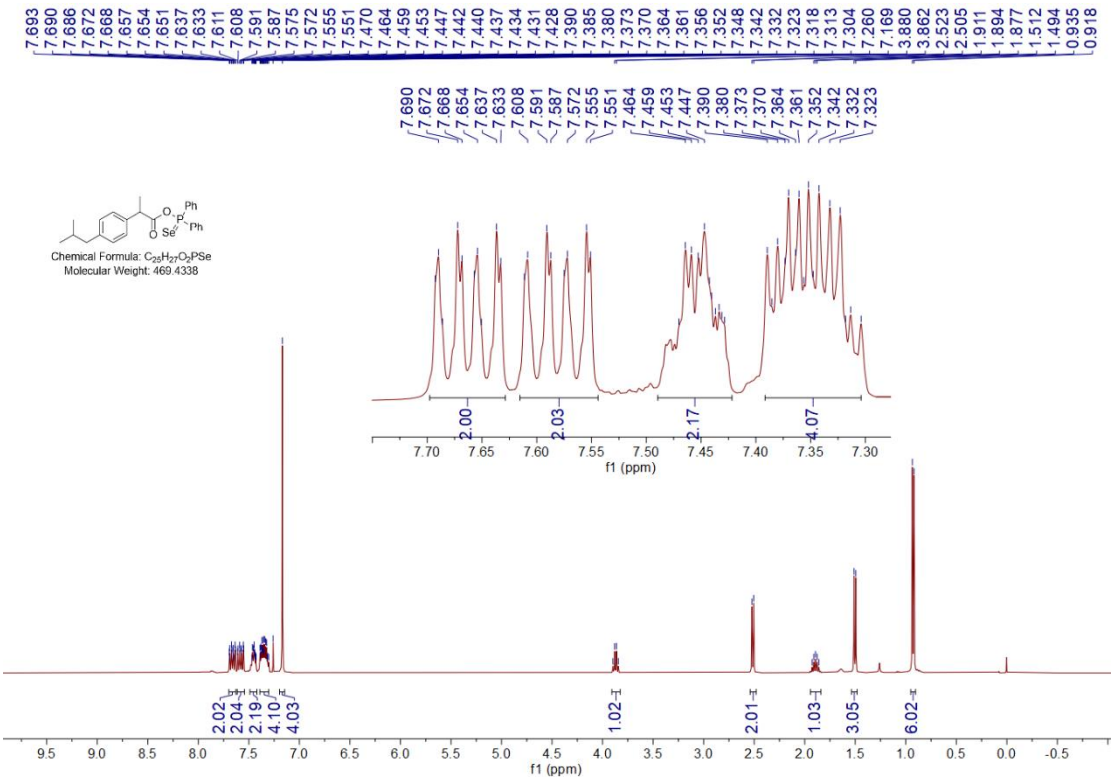


^{13}C NMR spectrum of 6a, 100 MHz, $CDCl_3$

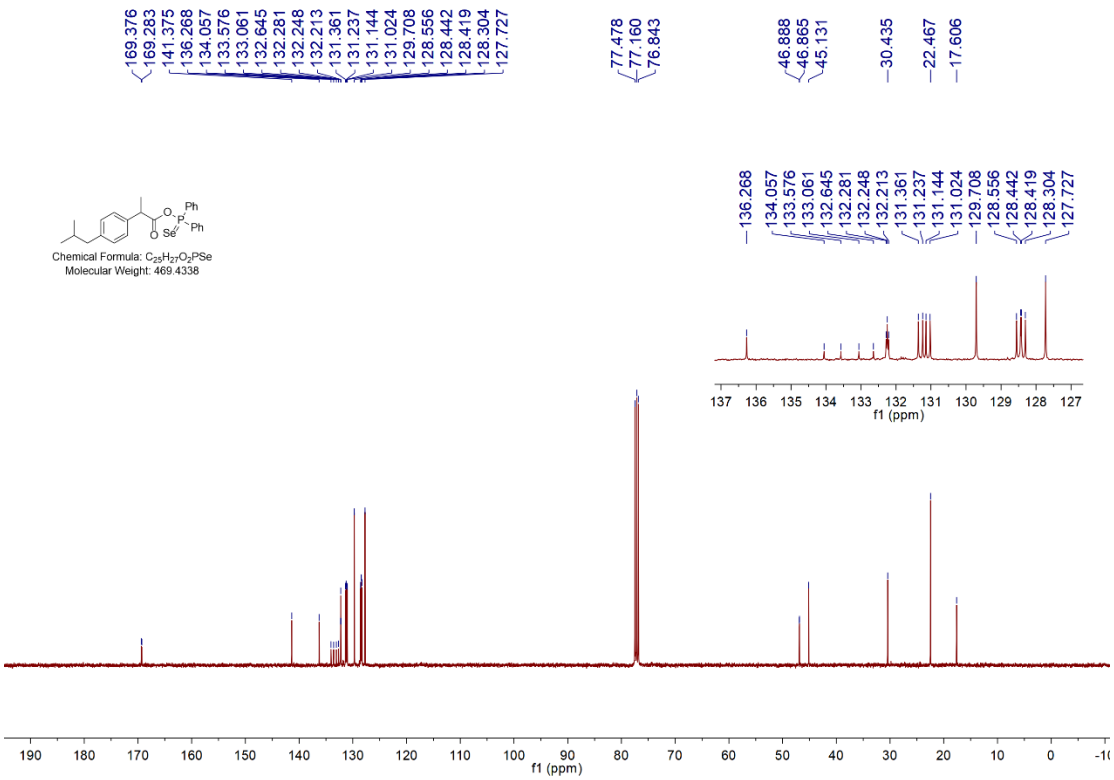


^{31}P NMR spectrum of 6a, 162 MHz, $CDCl_3$

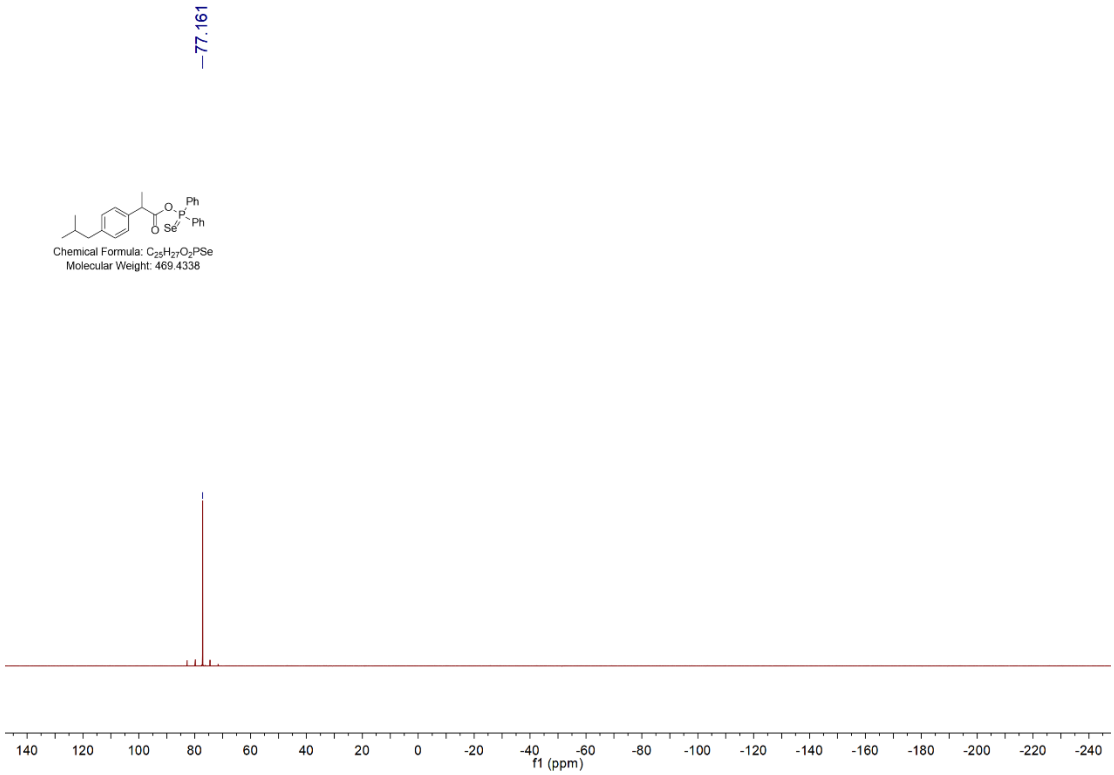
3-(4-Isobutylphenyl)propanoic diphenylphosphinoselenoic anhydride (6b)



^{1}H NMR spectrum of 6b, 400 MHz, $CDCl_3$



^{13}C NMR spectrum of 6b, 100 MHz, $CDCl_3$



^{31}P NMR spectrum of 6b, 162 MHz, $CDCl_3$

11. References

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