Electronic Supplementary Information

One-Step Formation of Four Chemical Bonds toward Dithiophosphinates *via* Multicomponent Reaction

Shangyuan Li,[a] Xiaoyu Yan,[a] Xinyu Cheng,[a] Tianyuan Li,[a] Xiantao Ma,*[a]

[a] College of Chemistry and Chemical Engineering, Green Catalysis & Synthesis Key Laboratory of Xinyang City, Xinyang Normal University, Xinyang, Henan 464000, China

*Email: xiantaoma@126.com

Table of contents

1. General information.....S2

2. Detailed condition screening S3

3. Control experiments for Mechanistic Studies.....S5

3.1 The reaction of allylic alcohols (1a) and S_8.....S5
3.2 The reaction of allylic alcohols (1a) and diphenylphosphine.....S5
3.3 The reaction of diphenylphosphine and S_8.....S5
3.4 The reaction of allylic alcohols (1a) and dithiophosphonic acid (7aa).....S6
3.4.1 The preparation of dithiophosphonic acid (7aa) from diphenylphosphine with elemental sulfur and hydrazine S6
3.4.2 The control reaction of allylic alcohols (1a) with dithiophosphonic acid (7aa).....S6
3.5 The competition experiment of allylic alcohols (1a) with dithiophosphonic acid (7aa) and diphenylphosphine sulfide (8aa).....S7
3.5.1 The preparation of diphenylphosphine sulfide (8aa) from diphenylphosphine with elemental sulfur S7
3.5.2 The competition experiment.....S7
3.6 The reaction of allylic alcohols (1a), S_8 and diphenylphosphine sulfide (8aa).....S8

4. The possible mechanism for reactions involving simple alcohols S9

5. Hammett analysis.....S10

6. Typical Procedure and Characterization of the Products S11

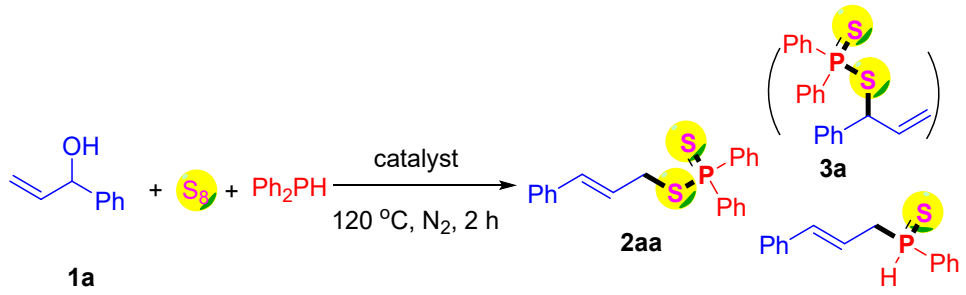
6.Copies of the ^{1}H、^{13}C and ^{31}P NMR Spectra of the Products S26

1. General information

Unless otherwise noted, all chemicals were purchased and used without further purification and all reactions were carried out in sealed Schlenk tubes under N_2 and then monitored by TLC and/or GC-MS. α-Substituted branched allylic alcohols **1** were prepared according to the literature's procedure (*Green Chem.* **2024**, *26*, 10886-10892). ^{1}H、^{13}C and ^{31}P NMR spectra were measured on a JNM-ECZ600R/S3 (Jeol, Japan) (600、151 and 243 MHz for ^{1}H、^{13}C and ^{31}P NMR, respectively) using $CDCl_3$ as the solvent. Chemical shifts for ^{1}H、^{13}C and ^{31}P NMR were referred to internal Me_4Si (0 ppm) as the standard. Mass spectra were measured on an Agilent GC-MS-7890A/5975C Plus spectrometer (EI). HRMS were recorded on a LC-TOF spectrometer (Xevo G2-XS QTof) using ESI techniques

2. Detailed condition screening

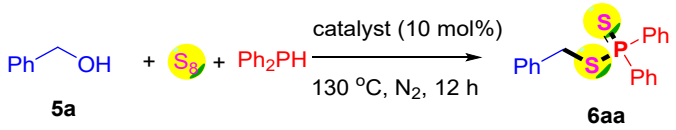
Table S1. Optimization of the reaction conditions for the synthesis of dithiophosphinate from allylic alcohol.[a]



entry	temperature	time	catalyst	**1a**/S/Ph_2PH	solvent	**2aa**/**3a**/**4a**[b]	**2aa**%[c]
1	120 °C	2 h	$Pd(PPh_3)_4$	1.0/1.5/1.0	toluene	95/0/5	52
2	120 °C	2 h	$Pd(PPh_3)_4$	1.0/2.0/1.0	toluene	97/0/3	60
3	120 °C	2 h	$Pd(PPh_3)_4$	1.0/2.2/1.0	toluene	97/0/3	63
4	120 °C	2 h	$Pd(PPh_3)_4$	1.0/3.0/1.0	toluene	97/0/3	55
5	120 °C	2 h	none	1.0/2.2/1.0	toluene	> 99/1/0	80
6	50 °C	2 h	none	1.0/2.2/1.0	toluene	> 99/1/0	trace
7	100 °C	2 h	none	1.0/2.2/1.0	toluene	> 99/1/0	69
8	130 °C	2 h	none	1.0/2.2/1.0	toluene	> 99/1/0	79
9	120 °C	1 h	none	1.0/2.2/1.0	toluene	> 99/1/0	64
10	120 °C	12 h	none	1.0/2.2/1.0	toluene	> 99/1/0	78
11	120 °C	2 h	none	1.0/2.2/1.0	none	> 99/1/0	48
12	120 °C	2 h	none	1.0/2.2/1.0	1,4-dioxane	> 99/1/0	83
13	120 °C	2 h	none	1.0/2.2/1.0	THF	96/4/0	62
14	120 °C	2 h	none	1.0/2.2/1.0	DMF	> 99/1/0	56
15	120 °C	2 h	none	1.0/2.2/1.0	DMSO	---	0
16	120 °C	2 h	none	1.0/2.2/1.0	DCE	> 99/1/0	82
17	120 °C	2 h	none	1.0/2.2/1.0	MeCN	97/3/0	70

[a] Unless otherwise noted, the mixture of **1a** (0.30 mmol), $\mathbf{S_8}$ (0.0825 mmol, 2.2 equiv.), diphenylphosphine (0.30 mmol), catalyst (5 mol%) and a solvent (0.5 mL) sealed under N_2 in a 10 mL Schlenk tube was heated at 120 °C for 2 h and then analyzed by TLC/GC-MS. [b] Determined by GC-MS. [c] Isolated yield based on **1a**.

Table S2. Optimization of the reaction conditions for the synthesis of dithiophosphinates from benzyl alcohol.[a]



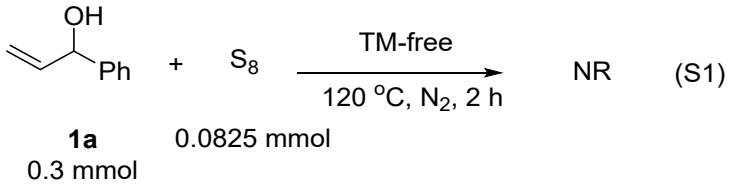
5a **6aa**

entry	cat. (mol%)	solvent	**6aa**%[b]
1	none	none	65
2	$AlCl_3$ (10)	none	86
3	$Sc(OTf)_3$ (10)	none	75
4	$Yb(OTf)_3$ (10)	none	79
5	$BF_3{\cdot}Et_2O$ (10)	none	78
6	ZnI_2 (10)	none	73
7	TsOH (10)	none	66
8	$AlCl_3$ (10)	1,4-dioxane	80
9	$AlCl_3$ (10)	toluene	68
10	$AlCl_3$ (10)	$CHCl_3$	78
11	$AlCl_3$ (10)	xylene	70
12	$AlCl_3$ (10)	DCE	78

[a] Unless otherwise noted, the mixture of **5a** (0.30 mmol), S_8 (0.075 mmol, 2.0 equiv.), diphenylphosphine (0.30 mmol), catalyst (10 mol%) and a solvent (0.5 mL) sealed under N_2 in a 10 mL Schlenk tube was heated at 130 °C for 12 h and then analyzed by TLC/GC-MS. [b]Isolated yield based on **5a**.

3. Control experiments for Mechanistic Studies

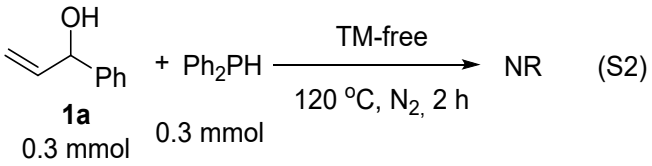
3.1 The reaction of allylic alcohols (1a) and S_8 (Eq. 1 in the text)



Detailed Procedure: The mixture of allylic alcohols **1a** (0.30 mmol), S_8 (0.0825 mmol) and 1,4-dioxane (0.5 mL) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 120 °C for 2 h. The reaction mixture was analyzed by GC-MS and TLC, showing no products were generated.

Result: It is not the initial step of the whole reaction.

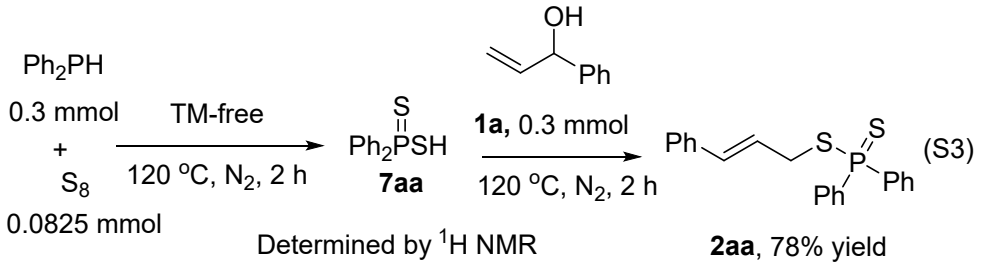
3.2 The reaction of allylic alcohols (1a) and diphenylphosphine (Eq. 1 in the text)



Detailed Procedure: The mixture of allylic alcohols **1a** (0.30 mmol), diphenylphosphine (0.3 mmol) and 1,4-dioxane (0.5 mL) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 120 °C for 2 h. The reaction mixture was analyzed by GC-MS and TLC, showing no product were generated.

Result: It is not the initial step of the whole reaction.

3.3 The reaction of diphenylphosphine and S_8 (Eq. 2 in the text)



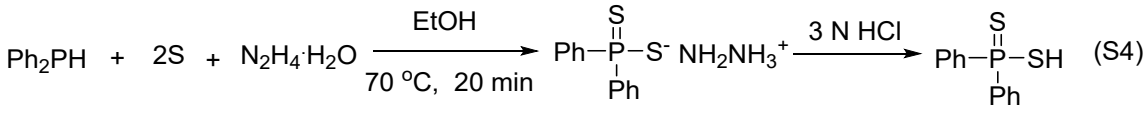
Detailed Procedure: Two parallel experiments were carried out. The mixture of diphenylphosphine (0.30 mmol), S_8 (0.0825 mmol) and 1,4-dioxane (0.5 mL) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 120 °C

for 2 h. As the reaction mixture was cooled, one of the reactions was purified, and analyzed by NMR, showing the generation of dithiophosphonic acid **7aa**. To the other reaction was added allylic alcohols **1a** (0.30 mmol) under nitrogen protection, and stirred at 120 °C for another 2 h. After it was cooled to room temperature, the reaction mixture was analyzed by TLC/GC-MS, and purified by flash column chromatography on silica gel using dichloromethane and petroleum ether (v/v: 0 ~ 1/5) as the eluent, giving **2aa** in 78% isolated yield.

Result: The initial reaction of diphenylphosphine and S_8 may occur to give the key intermediate diphenyl phosphinodithioic acid **7aa**.

3.4 The reaction of allylic alcohols (1a) and dithiophosphonic acid (7aa) (Eq. 3 in the text)

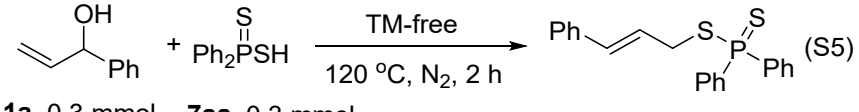
3.4.1 The preparation of dithiophosphonic acid (7aa) from diphenylphosphine with elemental sulfur and hydrazine



7aa, 98% yield

Detailed Procedure: To a 100 ml round-bottom flask, was added elemental sulfur (10 mmol), ethanol (10 mL), hydrazine hydrate (5.5 mmol) and diphenylphosphine (5 mmol) sequentially（Ph_2PH : S: $N_2H_4 \cdot H_2O$ = 1: 2: 1.1). Then the mixture was heated in a 70 °C oil bath for 20 min under air atmosphere, then cooled to room temperature and washed with diethyl ether to remove impurities. And after drying, a white solid was obtained. Finally, the solid was dissolved in 3 N hydrochloric acid and extracted with ethyl acetate. Then the organic solvent was evaporated to obtain dithiophosphonate **7aa** in 98% isolated yield.

3.4.2 The control reaction of allylic alcohols (1a) with dithiophosphonic acid (7aa)



1a, 0.3 mmol **7aa,** 0.3 mmol

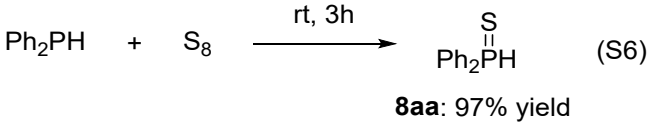
2aa, 80% yield

Detailed Procedure: The mixture of allylic alcohol **1a** (0.30 mmol), dithiophosphonic acid **7aa** (0.30 mmol) and 1,4-dioxane (0.5 mL) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 120 °C for 2 h. The reaction mixture was then analyzed by TLC/GC-MS, and purified by flash column chromatography on silica gel using dichloromethane and petroleum ether (v/v: 0 ~ 1/5) as the eluent, giving **2aa** in 80% isolated yield.

Result: Diphenyl phosphinodithioic acid **7aa** is indeed the key reaction intermediate.

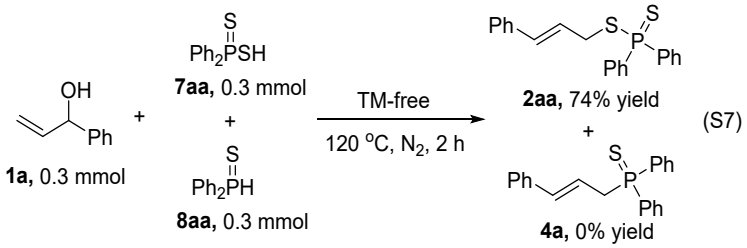
3.5 The competition experiment of allylic alcohols (1a) with dithiophosphonic acid (7aa) and diphenylphosphine sulfide (8aa) (Eq. 4 in the text)

3.5.1 The preparation of diphenylphosphine sulfide (8aa) from diphenylphosphine with elemental sulfur



Detailed Procedure: Under nitrogen atmosphere, a 50 mL Schlenk type sealed tube equipped with S_8 (640 mg, 2.5 mmol) was added toluene (15 mL), diphenylphosphine (20 mmol) and stirred at room temperature for 3 h. The reaction mixture was concentrated in vacuo, and the crude residue was purified by flash column chromatography (DCM/PE = 0 ~ 1/1) to afford the desired diphenylphosphine sulfide (97% yield).

3.5.2 The competition experiment

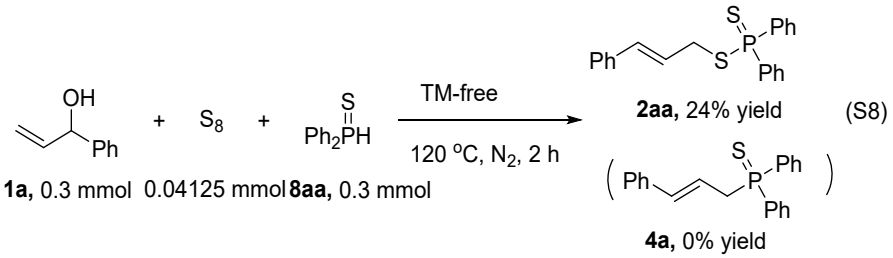


Detailed Procedure: The mixture of allylic alcohol **1a** (0.30 mmol), dithiophosphonic acid **7aa** (0.30 mmol), diphenylphosphine sulfide **8aa** (0.30 mmol) and 1,4-dioxane (0.5 mL) was directly sealed in a Schlenk tube (10 mL) under

nitrogen, and then stirred at 120 °C for 2 h. The reaction mixture was analyzed by TLC/GC-MS and purified by flash column chromatography on silica gel using dichloromethane and petroleum ether (v/v: 0 ~ 1/5) as the eluent, giving only **2aa** in 74% isolated yield.

Result: The reaction of allylic alcohol **1a** with dithiophosphonic acid **7aa** is much faster than that with diphenylphosphine sulfide **8aa,** therefore, the possible byproduct **4a** was not generated under standard conditions.

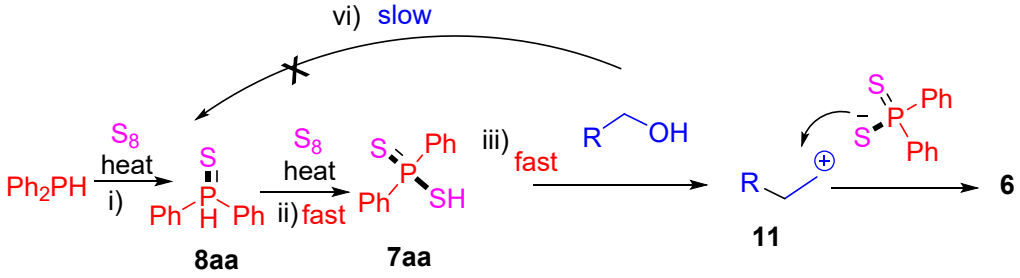
3.6 The reaction of allylic alcohols (1a), S_8 and diphenylphosphine sulfide (8aa)



Detailed Procedure: The mixture of allylic alcohol **1a** (0.30 mmol), diphenylphosphine sulfide **8aa** (0.30 mmol) and 1,4-dioxane (0.5 mL) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 120 °C for 2 h. And purified by flash column chromatography on silica gel using dichloromethane and petroleum ether (v/v: 0 ~ 1/5) as the eluent, giving **2aa** in 24% isolated yield.

Result: The reaction of diphenylphosphine sulfide **8aa** will first react with S_8 to generate **7aa**, and then **7aa** will react with **1a** to generate 24% of the target product, leaving almost no opportunity for **8aa** to react with 1a to generate the byproduct **4a**.

4. The proposed mechanism for reactions involving simple alcohols



Similarly, diphenylphosphine is initially oxidized by S_8 to form diphenylphosphine sulfide (8aa, step i) and subsequently to diphenyl phosphinodithioic acid (**7aa**, step ii). Owing to the acidity of **7aa**, the alcohol (5) is efficiently activated to give carbocation intermediate **11** which reacts more rapidly with phosphinodithioic anion, affording product **6**.

5. Hammett analysis

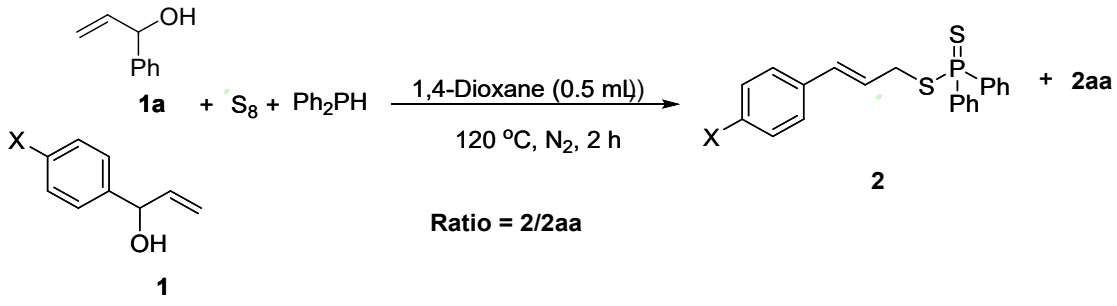


Table S3. Hammett study of Allylic Dithio-Phosphinates of **1** and **2a**

X	Ratio	$\log(k_X/k_H)$
F	0.63:1	-0.2
Cl	0.79:1	-0.1

Me	2.18:1	0.34
MeO	2.47:1	0.39

Following the general procedure: to a 10 mL Schlenk-tube equipped with magnetic stirring was charged with **1a** (0.15 mmol, 0.5 equiv.), **1** (0.15 mmol, 0.5 equiv.) and S_8 (0.0825 mmol, 2.2 equiv.), diphenylphosphine (0.3 mmol, 1.0 equiv.) and 1,4-dioxane (0.5 mL), and the reaction mixture was sealed under N_2 and heated at 120 °C for 2 h. Then the reaction solvents were evaporated, and the crude mixture was directly analyzed by ^{1}H NMR.

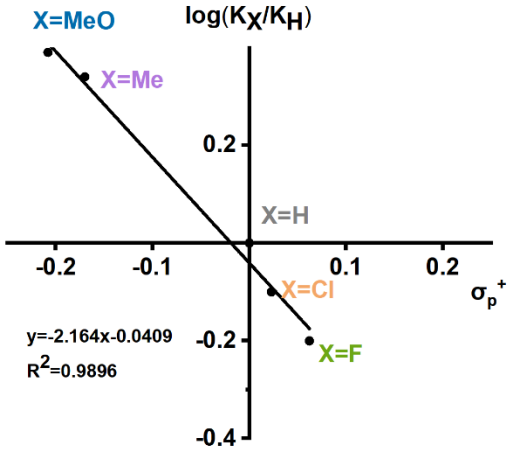
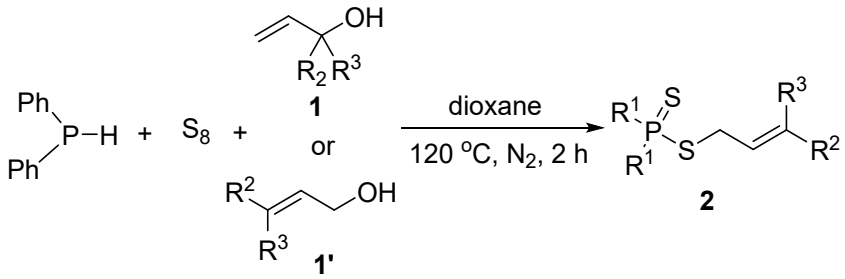
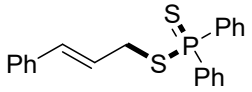


Figure S1. Hammett plot analysis

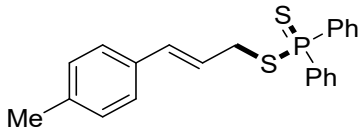
6. Typical Procedure and Characterization of the Products



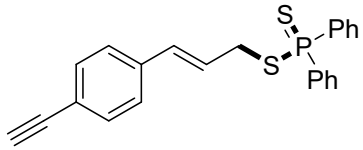
Typical Procedure: The mixture of allylic alcohol **1a** (0.30 mmol), dithiophosphonic acid **7aa** (0.30 mmol), S_8 (0.0825 mmol) and 1,4-dioxane (0.5 mL) was directly sealed in a Schlenk tube (10 mL) under nitrogen, and then stirred at 120 °C for 2 h. The reaction mixture was then analyzed by TLC/GC-MS, and purified by flash column chromatography on silica gel using dichloromethane and petroleum ether (v/v: 0 ~ 1/5) as the eluent, giving target product **2aa** in 83% yield.



Cinnamyl Diphenylphosphinodithioate (2aa), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.90 (m, 4H), 7.49 – 7.39 (m, 6H), 7.23 (dd, J = 7.2, 5.4 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.13 (dd, J = 5.4, 3.6 Hz, 2H), 6.45 (d, J = 15.6 Hz, 1H), 6.08 – 5.93 (m, 1H), 3.83 – 3.76 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 136.4, 134.3 (d, J = 85.0 Hz), 134.0 (d, J = 33.2 Hz), 131.9 (d, J = 2.5 Hz), 131.6 (d, J = 11.4 Hz), 128.7 (d, J = 13.6 Hz), 128.5, 127.8, 126.4, 124.4 (d, J = 4.5 Hz), 34.5. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.5. HRMS (ESI) for $C_{21}H_{20}PS_2^+$ $(M+H)^+$: Calcd: 367.0739; found: 367.0735.

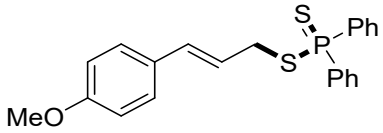


(E)-3-(P-Tolyl) Allyl Aiphenylphosphinodithioate (2ab), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 7.90 (m, 4H), 7.53 – 7.40 (m, 6H), 7.05 (s, 4H), 6.44 (d, J = 15.6 Hz, 1H), 6.04 – 5.92 (m, 1H), 3.79 (dd, J = 13.2, 7.5 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.6, 134.8 (d, J = 84.7 Hz), 133.8, 131.8 (d, J = 2.4 Hz), 131.7, 131.6, 129.2, 128.6 (d, J = 13.6 Hz), 126.4, 123.5 (d, J = 4.9 Hz), 34.6, 21.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.3. HRMS (ESI) for $C_{22}H_{22}PS_2^+$ $(M+H)^+$: Calcd: 381.0896; found: 381.0893.

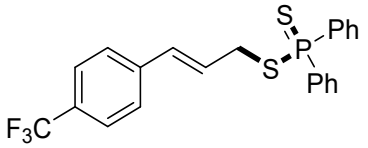


(E)-3-(4-Ethynylphenyl) Allyl Diphenylphosphinodithioate (2ac), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, J = 14.4, 7.2 Hz, 4H), 7.48 – 7.41 (m, 7H), 7.09 (d, J = 5.4 Hz, 1H), 6.88 (dd, J = 4.8, 3.6 Hz, 1H), 6.78 (d, J = 3.6 Hz, 1H), 6.57 (d, J = 15.6 Hz, 1H), 5.82 (m, J = 15.6, 7.8 Hz, 1H), 3.76 (dd, J = 13.2, 7.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.9, 134.3 (d, J = 85.0 Hz), 132.9, 132.2, 132.0, 131.6 (d, J = 11.4 Hz), 128.64 (d, J = 13.2 Hz), 126.3, 125.9 (d, J = 3.9 Hz), 121.2, 83.7, 77.9, 34.4. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.5. HRMS (ESI) for $C_{18}H_{20}PS_2^+$

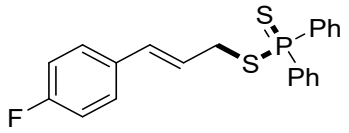
$(M+H)^+$: Calcd: 391.0739; found: 391.0739



(E)-3-(4-Methoxyphenyl) Allyl Diphenylphosphinodithioate (2ad), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (dd, J = 14.4, 7.2 Hz, 4H), 7.48 – 7.37 (m, 6H), 6.77 (d, J = 8.4 Hz, 2H), 6.40 (d, J = 15.6 Hz, 1H), 5.98 – 5.76 (m, 1H), 3.79 (dd, J = 11.4, 6.6 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 134.4 (d, J = 84.6 Hz), 133.4, 131.9 (d, J = 2.4 Hz), 131.6 (d, J = 11.4 Hz), 129.2, 128.7 (d, J = 13.2 Hz), 127.7, 122.1 (d, J = 4.8 Hz), 113.9, 55.4, 34.7. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.3. HRMS (ESI) for $C_{22}H_{22}OPS_2^+$ $(M+H)^+$: Calcd: 397.0845; found: 397.0848.

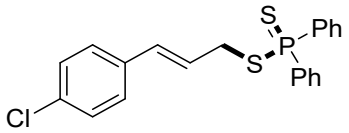


(E)-3-(4-(Frifluoromethyl)Phenyl) Allyl Diphenylphosphinodithioate (2ae), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, J = 14.4, 7.2 Hz, 4H), 7.62 – 7.35 (m, 8H), 7.32 (t, J = 7. Hz, 1H), 6.44 (d, J = 15.6 Hz, 1H), 6.06 – 5.86 (m, 1H), 3.83 (dd, J = 14.8, 7.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.1, 134.2 (d, J = 85.1 Hz), 132.1 (d, J = 29.6 Hz), 131.7 (d, J = 11.4 Hz), 130.8 (q, J = 64.6 Hz), 129.7, 128.9, 128.6 (d, J = 13.3 Hz), 126.7 (d, J = 3.0 Hz), 124.2, 122.9 (d, J = 3.8 Hz), 34.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.4. HRMS (ESI) for $C_{22}H_{19}F_3PS_2^+$ $(M+H)^+$: Calcd: 435.0613; found: 435.0615.

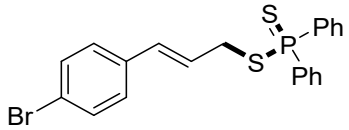


(E)-3-(4-Fluorophenyl) Allyl Diphenylphosphinodithioate (2af), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.83 (m, 4H), 7.52 – 7.37 (m, 6H), 7.07 (dd, J = 8.4, 5.4 Hz, 2H), 6.91 (t, J = 8. Hz, 2H), 6.40 (d, J = 15.6 Hz, 1H), 6.03 – 5.87 (m, 1H), 3.78 (dd, J = 13.8, 7.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4 (d, J = 247.0 Hz), 134.3 (d, J = 85.1 Hz), 132.6, 131.9 (d, J = 2.4 Hz), 131.6 (d, J = 11.0 Hz), 128.7 (d, J = 13.6 Hz), 127.9 (d, J = 8.2 Hz), 124.2, 115.4 (d, J = 21.6 Hz), 34.4. ^{31}P NMR

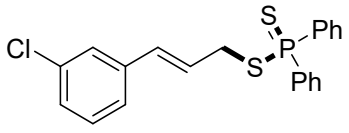
(243 MHz, $CDCl_3$) δ 64.4. HRMS (ESI) for $C_{21}H_{19}FPS_2^+$ $(M+H)^+$: Calcd: 385.0645; found: 385.0648.



(E)-3-(4-Chlorophenyl) Allyl Diphenylphosphinodithioate (2ag), colorless solid. ^1H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 4H), 7.49 – 7.38 (m, 6H), 7.21 – 7.14 (m, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.38 (d, J = 15.6 Hz, 1H), 6.01 – 5.91 (m, 1H), 3.86 – 3.66 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.9 (d, J = 49.8 Hz), 133.7 (d, J = 94.8 Hz), 132.5, 131.9, 131.6 (d, J = 11.4 Hz), 128.7 (d, J = 12.7 Hz), 127.6, 125.2, 34.3. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.4. HRMS (ESI) for $C_{21}H_{19}ClPS_2^+$ $(M+H)^+$: Calcd: 401.0349; found: 401.0343.

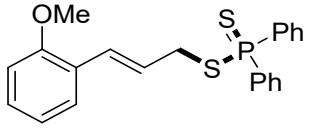


(E)-3-(4-Bromophenyl) Allyl Diphenylphosphinodithioate (2ah), colorless solid. ^1H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.86 (m, 4H), 7.47 – 7.38 (m, 6H), 7.33 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 6.37 (d, J = 15.6 Hz, 1H), 6.08 – 5.89 (m, 1H), 3.84 – 3.72 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.3, 134.6 (d, J = 84.7 Hz), 132.5, 132.0 (d, J = 2.4 Hz), 131.7, 131.6 (d, J = 6.2 Hz), 128.6 (d, J = 13.7 Hz), 127.9, 125.4 (d, J = 3.9 Hz), 121.6, 34.3. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.4. HRMS (ESI) for $C_{21}H_{19}BrPS_2^+$ $(M+H)^+$: Calcd: 444.9844; found: 444.9842.

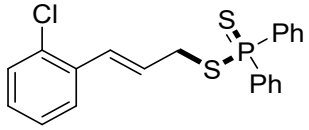


(E)-3-(3-Chlorophenyl) Allyl Diphenylphosphinodithioate (2ai), colorless solid. ^1H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.87 (m, 4H), 7.51 – 7.37 (m, 6H), 7.18 – 7.09 (m, 2H), 7.07 – 6.92 (m, 2H), 6.36 (d, J = 15.6 Hz, 1H), 6.05 – 5.88 (m, 1H), 3.86 – 3.72 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.3, 134.6 (d, J = 29.0 Hz), 134.0, 132.0 (d), 131.7 (d, J = 11.2 Hz), 129.7, 128.7 (d, J = 13.3 Hz), 127.7, 126.2, 124.7, 34.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.4. HRMS (ESI) for $C_{21}H_{19}ClPS_2^+$ $(M+H)^+$: Calcd:

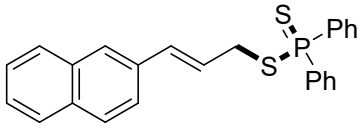
401.0349; found: 401.0341.



(E)-3-(2-Methoxyphenyl) Allyl Diphenylphosphinodithioate (2aj), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (dd, J = 14.4, 7.2 Hz, 4H), 7.48 – 7.40 (m, 6H), 7.17 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 6.82 (t, J = 9.6 Hz, 2H), 6.81 – 6.76 (m, 1H), 6.13 – 5.96 (m, 1H), 3.80 (dd, J = 11.4, 6.6 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 134.5 (d, J = 84.7 Hz), 131.9, 131.6 (d, J = 11.4 Hz), 128.9 (d, J = 22.4 Hz), 128.7 (d, J = 13.5 Hz), 127.0, 125.4, 124.9 (d, J = 5.3 Hz), 120.6, 110.8, 55.5, 35.1. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.2. HRMS (ESI) for $C_{22}H_{22}OPS_2^+$ $(M+H)^+$: Calcd: 397.0845; found: 397.0844.

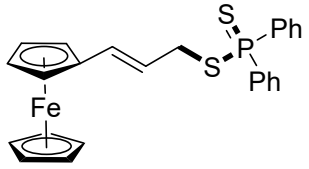


(E)-3-(2-Chlorophenyl) Allyl Diphenylphosphinodithioate (2ak), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 – 7.89 (m, 4H), 7.57 – 7.39 (m, 6H), 7.34 – 7.26 (m, 1H), 7.21 – 7.01 (m, 3H), 6.85 (d, J = 15.6 Hz, 1H), 6.20 – 5.82 (m, 1H), 3.99 – 3.62 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 134.5 (d, J = 21.5 Hz), 134.0, 133.0, 132.0, 131.7 (d, J = 11.5 Hz), 129.7, 128.8 (d, J = 8.4 Hz), 128.6, 127.4 (d, J = 4.5 Hz), 126.8 (d, J = 15.7 Hz), 34.4. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.4. HRMS (ESI) for $C_{21}H_{19}ClPS_2^+$ $(M+H)^+$: Calcd: 401.0349; found: 401.0341.

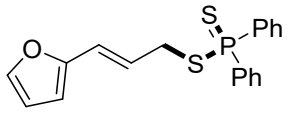


(E)-3-(Naphthalen-2-Yl) Allyl Diphenylphosphinodithioate (2al), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (dd, J = 14.4, 7.2 Hz, 4H), 7.82 – 7.78 (m, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.49 – 7.36 (m, 9H), 7.33 (t, J = 7.2 Hz, 1H), 7.28 – 7.20 (m, 2H), 6.14 – 6.02 (m, 1H), 3.94 (dd, J = 13.8, 7.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.7, 134.1 (d, J = 16.9 Hz), 133.5, 131.9, 131.6 (d, J = 11.0 Hz), 131.0 (d, J = 6.8 Hz), 128.7 (d, J = 13.6 Hz), 128.3 (d, J = 55.2 Hz), 127.5 (d, J = 4.3 Hz),

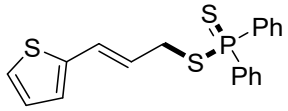
126.1 (d, J = 43.9 Hz), 125.5, 123.9 (d, J = 4.6 Hz), 34.8. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.4. HRMS (ESI) for $C_{25}H_{22}PS_2^+$ $(M+H)^+$: Calcd: 417.0896; found: 417.0894.



Dicyclopentadienyl Iron Allyl Diphenylphosphinodithioate (2am), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 7.88 (m, 4H), 7.54 – 7.36 (m, 6H), 6.26 (d, J = 15.6 Hz, 1H), 5.76 – 5.55 (m, 1H), 4.22 – 4.12 (m, 4H), 4.05 (s, 5H), 3.66 (dd, J = 12.0, 7.8, 0.6 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 134.5 (d, J = 84.8 Hz), 132.1, 132.0, 131.6 (d, J = 11.0 Hz), 128.7 (d, J = 13.1 Hz), 121.2 (d, J = 5.7 Hz), 82.1, 69.4, 69.3, 68.9, 66.9, 34.9. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.2. HRMS (ESI) for $C_{25}H_{24}FePS_2^+$ $(M+H)^+$: Calcd: 475.0401; found: 475.0412.

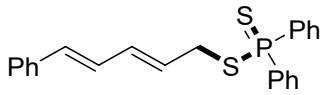


(E)-3-(Furan-2-Yl) Allyl Diphenylphosphinodithioate (2an), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 4H), 7.47 – 7.38 (m, 7H), 6.32 – 6.23 (m, 2H), 6.08 (d, J = 3.6 Hz, 1H), 5.94 (dd, J = 15.6, 7.2 Hz, 1H), 3.75 (dd, J = 13.2, 7.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9, 142.1, 134.2 (d, J = 85.0 Hz), 131.8 (d, J = 2.5 Hz), 131.6 (d, J = 11.4 Hz), 128.6 (d), 122.8 (d, J = 5.1 Hz), 122.2, 111.3, 108.4, 34.3. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.5. HRMS (ESI) for $C_{19}H_{18}OPS_2^+$ $(M+H)^+$: Calcd: 357.0532; found: 357.0534.

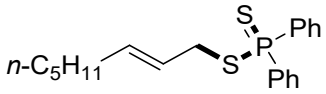


(E)-3-(Thiophen-2-Yl) Allyl Diphenylphosphinodithioate (2ao), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, J = 14.4, 7.2 Hz, 4H), 7.48 – 7.41 (m, 6H), 7.09 (d, J = 5.4 Hz, 1H), 6.88 (dd, J = 4.8, 3.6 Hz, 1H), 6.78 (d, J = 3.6 Hz, 1H), 6.57 (d, J = 15.6 Hz, 1H), 5.91 – 5.73 (m,1H), 3.76 (dd, J = 13.2, 7.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.4, 134.7 (d, J = 84.6 Hz), 131.8 (d, J = 10.8 Hz), 131.6 (d, J = 10.9 Hz), 128.5 (d, J = 13.3 Hz), 127.2, 127.0, 125.8, 124.5, 124.1 (d, J = 5.0 Hz),

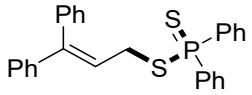
34.3. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.5. HRMS (ESI) for $C_{19}H_{18}PS_3^+$ $(M+H)^+$: Calcd: 373.0303; found: 357.0334.



(2E,4E)-5-Phenylpenta-2,4-Dien-1-Yl Diphenylphosphinodithioate (2ap), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 4H), 7.48 – 7.43 (m, 6H), 7.34 – 7.28 (m, 4H), 7.21 (t, J = 7.2 Hz, 1H), 6.54 – 6.46 (m, 1H), 6.40 (d, J = 15.6 Hz, 1H), 6.26 (dd, J = 14.4, 10.8 Hz, 1H), 5.69 – 5.59 (m, 1H), 3.71 (dd, J = 13.2, 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.1, 134.6, 134.0, 133.0, 131.9, 131.6 (d, J = 11.2 Hz), 128.6 (d, J = 13.3 Hz), 128.2, 127.7 (d, J = 11.5 Hz), 126.5, 34.4.^{31}P NMR (243 MHz, $CDCl_3$) δ 65.0. HRMS (ESI) for $C_{23}H_{22}PS_2^+$ $(M+H)^+$: Calcd: 393.0896; found: 393.0898.

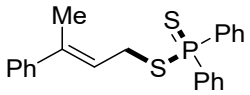


(E)-Oct-2-En-1-Yl Diphenylphosphinodithioate (2aq), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.8, 6.6 Hz, 4H), 7.49 – 7.44 (m, 6H), 5.59 (dt, J = 13.8, 6.6 Hz, 1H), 5.34 – 5.28 (m, 1H), 3.59 – 3.54 (m, 2H), 1.83 – 1.79 (m, 2H), 1.20 – 1.15 (m, 6H), 0.85 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.9, 134.5 (d, J = 85.1 Hz), 131.9 (d, J = 2.5 Hz), 131.6 (d, J = 11.3 Hz), 128.6 (d, J = 13.1 Hz), 124.3 (d, J = 5.3 Hz), 34.2, 32.2, 31.4, 29.8, 22.6, 14.1. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.1. HRMS (ESI) for $C_{10}H_{26}PS_2^+$ $(M+H)^+$: Calcd: 361.1209; found: 361.1208.

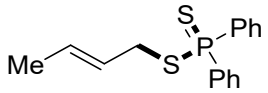


3,3-Diphenylallyl Diphenylphosphinodithioate (2ar), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 7.83 (m, 4H), 7.52 – 7.47 (m, 2H), 7.46 – 7.40 (m, 4H), 7.41 – 7.32 (m, 3H), 7.24 – 7.21 (m, 3H), 7.20 – 7.15 (m, 2H), 7.08 – 7.04 (m, 2H), 6.07 (t, J = 8.4 Hz, 1H), 3.67 (dd, J = 12.0, 8.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.4, 141.7, 138.7, 134.4 (d, J = 84.3 Hz), 132.0 (d, J = 2.3 Hz), 131.6 (d, J = 11.4 Hz), 129.8, 128.7 (d, J = 13.3 Hz), 128.5, 128.2, 127.7 (d, J = 4.8 Hz), 127.5, 123.12 (d, J = 5.7 Hz), 31.7. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.1. HRMS (ESI) for $C_{21}H_{24}PS_2^+$

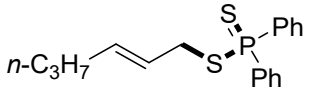
$(M+H)^+$: Calcd: 443.1052; found: 443.1093.



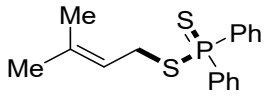
(E)-3-Phenylbut-2-En-1-Yl Diphenylphosphinodithioate (2as), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 4H), 7.50 – 7.43 (m, 6H), 7.29 – 7.21 (m, 3H), 7.18 – 7.14 (m, 2H), 5.81 – 5.66 (m, 1H), 3.79 (dd, J = 12.0, 8.4 Hz, 2H), 2.03 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.6, 139.6, 134.3 (d, J = 84.4 Hz), 131.9 (d, J = 2.5 Hz), 131.6 (d, J = 11.5 Hz), 128.7 (d, J = 13.1 Hz), 128.2, 127.3, 125.8, 122.0 (d, J = 5.7 Hz), 30.4, 16.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.2. HRMS (ESI) for $C_{21}H_{22}PS_2^+$ $(M+H)^+$: Calcd: 381.0896; found: 381.0892.



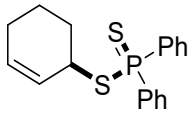
(E)-But-2-En-1-Yl Diphenylphosphinodithioate (2at), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 4H), 7.49 – 7.39 (m, 6H), 5.58 (dd, J = 15.6, 6.6 Hz, 1H), 5.45 – 5.25 (m, 1H), 3.54 (dd, J = 12.6, 7.2 Hz, 2H), 1.48 (d, J = 6.6 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 134.4 (d, J = 84.9 Hz), 131.8 (d, J = 2.5 Hz), 131.6 (d, J = 11.4 Hz), 130.5, 128.6 (d, J = 13.1, 5.5 Hz), 125.6 (d, J = 5.4 Hz), 34.1, 17.7. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.2. This compound is known in the literature: R. F. Cheng, C. J. Li, *Angew. Chem. Int. Ed*., **2023**, *62*, e202301730.



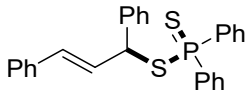
(E)-Hex-2-En-1-Yl Diphenylphosphinodithioate (2au), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 4H), 7.48 – 7.43 (m, 6H), 5.65 – 5.54 (m, 1H), 5.37 – 5.26 (m, 1H), 3.56 (ddd, J = 12.6, 7.2, 0.6 Hz, 2H), 1.83 – 1.77 (m, 2H), 1.22 (dd, J = 14.4, 7.2 Hz, 2H), 0.80 (t, J = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.7, 134.7 (d, J = 84.5 Hz), 131.8 (d, J = 2.6 Hz), 131.6 (d, J = 10.9 Hz), 128.6 (d, J = 13.1 Hz), 124.5 (d, J = 5.5 Hz), 34.3 (d, J = 19.5 Hz), 22.0, 13.7. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.4. HRMS (ESI) for $C_{18}H_{22}PS_2^+$ $(M+H)^+$: Calcd: 333.0896; found: 333.0892.



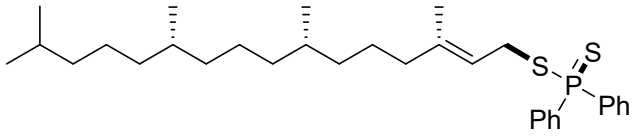
3-Methylbut-2-En-1-Yl Diphenylphosphinodithioate (2av), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 4H), 7.49 – 7.42 (m, 6H), 5.25 – 5.03 (m, 1H), 3.54 (dd, J = 11.4, 8.4 Hz, 2H), 1.58 (d, J = 9.6 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.9, 134.4 (d, J = 84.3 Hz), 131.9 (d, J = 2.5 Hz), 131.7 (d, J = 6.9 Hz), 128.6 (d, J = 13.6 Hz), 118.7 (d, J = 6.5 Hz), 29.9, 25.7, 18.1.^{31}P NMR (243 MHz, $CDCl_3$) δ 63.9. HRMS (ESI) for $C_{17}H_{20}PS_2^+$ $(M+H)^+$: Calcd: 319.0739; found: 319.0733.



Cyclohex-2-En-1-Yl Diphenylphosphinodithioate (2aw), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 7.86 (m, 4H), 7.54 – 7.39 (m, 6H), 5.88 – 5.72 (m, 1H), 5.70 – 5.55 (m, 1H), 4.23 – 4.05 (m, 1H), 2.07 – 1.93 (m, 2H), 1.93 – 1.85 (m, 1H), 1.83 – 1.70 (m, 2H), 1.63 – 1.58 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.3 (d, J = 25.4 Hz), 134.8 (d, J = 24.9 Hz), 131.8, 131.6 (d, J = 11.4 Hz), 131.6 (d, J = 11.4 Hz), 131.0, 128.64 (d, J = 7.7 Hz), 128.56 (d, J = 7.4 Hz), 127.5 (d, J = 6.7 Hz), 44.1, 30.6, 24.7, 19.5. ^{31}P NMR (243 MHz, $CDCl_3$) δ 62.7. HRMS (ESI) for $C_{18}H_{20}PS_2^+$ $(M+H)^+$: Calcd: 331.0739; found: 331.0739

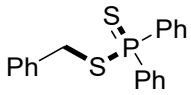


(E)-1,3-Diphenylallyl Diphenylphosphinodithioate (2ax), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.75 (dd, J = 14.4, 7.4 Hz, 2H), 7.39 (d, J = 7.2 Hz, 3H), 7.34 – 7.31 (m, 5H), 7.25 (dd, J = 9.6, 5.4 Hz, 2H), 7.21 – 7.17 (m, 3H), 7.10 – 7.06 (m, 2H), 6.40 (d, J = 15.6 Hz, 1H), 6.29 (dd, J = 15.6, 8.4 Hz, 1H), 5.53 (dd, J = 11.4, 8.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.3, 134.0 (d, J = 84.7 Hz), 132.3, 132.1 (d, J = 11.1 Hz), 131.7 (d, J = 2.5 Hz), 131.4 (d, J = 11.3 Hz), 128.7, 128.6 (d, J = 12.4 Hz), 128.5 (d, J = 2.4 Hz), 128.3 (d, J = 3.4 Hz), 127.7, 126.7, 126.6, 54.3. ^{31}P NMR (243 MHz, $CDCl_3$) δ 63.2. HRMS (ESI) for $C_{27}H_{24}PS_2^+$ $(M+H)^+$: Calcd: 443.1052; found: 443.1055.

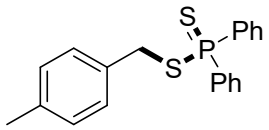


(6S,10S,E)-2,6,10,14-Tetramethylpentadec-1-En-1-Yl

Diphenylphosphinodithioate (2ay), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (dd, J = 13.8, 7.2 Hz, 4H), 7.50 – 7.39 (m, 6H), 5.17 (s, 1H), 3.66 – 3.50 (m, 2H), 1.91 (m, 2H), 1.61 – 1.53 (m, 3H), 1.39 – 1.19 (m, 19H), 0.89 – 0.79 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.9 (d, J = 40.2 Hz), 135.0 (d, J = 84.2 Hz), 131.7 (d, J = 2.3 Hz), 131.5 (d, J = 11.0 Hz), 128.5 (d, J = 13.2 Hz), 119.1 (d, J = 6.6 Hz), 118.4 (d, J = 6.2 Hz), 39.7 (d, J = 47.1 Hz), 37.54 (d, J = 4.2 Hz), 37.45 (d, J = 8.1 Hz), 37.0, 36.7, 32.8 (d, J = 23.9, 18.0 Hz), 32.3, 29.8 (d, J = 30.8 Hz), 28.0, 25.5, 25.1, 24.8, 24.5, 23.3, 22.7 (d, J = 11.7 Hz), 19.8 (d, J = 7.7 Hz), 16.4. ^{31}P NMR (243 MHz, $CDCl_3$) δ 63.7. HRMS (ESI) for $C_{32}H_{50}PS_2^+$ $(M+H)^+$: Calcd: 529.2930; found: 529.2935.

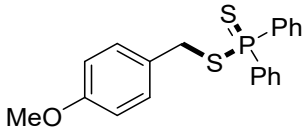


Benzyl Diphenylphosphinodithioate (6aa), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (dd, J = 14.4, 7.7 Hz, 4H), 7.53 – 7.36 (m, 6H), 7.44 (d, J = 8.4 Hz, 5H), 4.14 (d, J = 10.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.8, 134.4 (d, J = 84.8 Hz), 131.9, 131.6 (d, J = 11.2 Hz), 129.4, 128.6, 128.6 (d, J = 2.0 Hz), 127.5, 35.9.^{31}P NMR (243 MHz, $CDCl_3$) δ 64.7. This compound is known in the literature: Burilov, A.R., Drozdova, Y.A., Pudovik, M.A. et al. *Russ Chem Bull*., **1991**,*40*, 1885–1890.

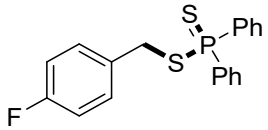


4-Methylbenzyl Diphenylphosphinodithioate (6ab), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (dd, J = 14.4, 7.2 Hz, 4H), 7.57 – 7.35 (m, 6H), 7.16 (d, J = 7.2 Hz, 2H), 7.10 (d, J = 4.1 Hz, 2H), 4.11 (d, J = 10.2 Hz, 2H), 2.35 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 137.2, 134.5, 133.9 , 133.6, 131.8, 131.6 (d, J = 11.4 Hz), 129.3 (d, J = 2.3 Hz), 128.6 (d, J = 13.2 Hz), 35.7, 21.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.4.

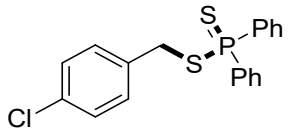
HRMS (ESI) for $C_{20}H_{20}PS_2^+$ $(M+H)^+$: Calcd: 355.0739; found: 355.0731.



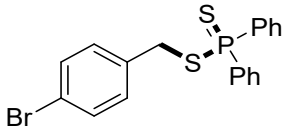
4-Methoxybenzyl Diphenylphosphinodithioate (6ac), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (dd, J = 14.3, 7.7 Hz, 4H), 7.53 – 7.36 (m, 6H), 7.14 (d, J = 8.5 Hz, 2H), 6.69 (d, J = 8.5 Hz, 2H), 4.09 (d, J = 11.8 Hz, 2H), 3.73 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 134.1 (d, J = 84.4 Hz), 131.9 (d, J = 2.4 Hz), 131.5 (d, J = 11.0 Hz), 130.56 , 128.6 (d, J = 13.4 Hz), 113.97, 55.36, 35.52. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.3. HRMS (ESI) for $C_{20}H_{20}OPS_2^+$ $(M+H)^+$: Calcd: 371.0688; found: 371.0687.



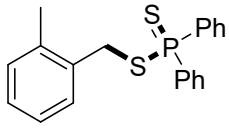
4-Fluorobenzyl Diphenylphosphinodithioate (6ad), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 4H), 7.43 (d, J = 35.4 Hz, 6H), 7.18 (s, 2H), 6.82 (s, 2H), 4.13 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9 (d, J = 246.1 Hz), 134.3 (d, J = 85.0 Hz), 132.6, 132.0, 131.5 (d, J = 11.4 Hz), 131.1 (d, J = 8.2 Hz), 128.7 (d, J = 13.2 Hz), 115.3 (d, J = 21.4 Hz), 35.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.7. HRMS (ESI) for $C_{19}H_{17}FPS_2^+$ $(M+H)^+$: Calcd: 359.0488; found: 359.0481.



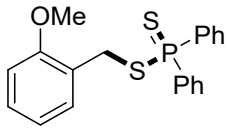
4-Chlorobenzyl Diphenylphosphinodithioate (6ae), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 –7.58 (m, 4H), 7.57 – 7.50 (m, 2H), 7.49 – 7.41 (m, 4H), 7.31 (d, J = 8.4 Hz, 2H), 6.98 (dd, J = 8.4, 2.4 Hz, 2H), 3.60 (d, J = 13.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.4, 134.2, 133.6 (d, J = 54.5 Hz), 131.9 (d, J = 2.6 Hz), 131.6 (d, J = 11.4 Hz), 130.7, 128.6, 128.6 (d, J = 5.0 Hz), 35.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.9. HRMS (ESI) for $C_{19}H_{17}ClPS_2^+$ $(M+H)^+$: Calcd: 359.0488; found: 359.0481.



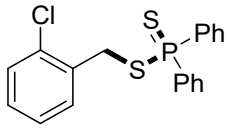
4-Bromobenzyl Diphenylphosphinodithioate (6af), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (dd, J = 14.4, 7.8 Hz, 4H), 7.57 – 7.35 (m, 2H), 7.16 (d, J = 7.2 Hz, 4H), 7.10 (d, J = 4.2 Hz, 2H), 7.03 – 6.95 (m, 2H), 4.11 (d, J = 10.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.0, 134.2 (d, J = 85.2 Hz), 131.9, 131.6, 131.5 (d, J = 4.6 Hz), 131.0, 128.6 (d, J = 13.3 Hz), 121.4, 35.2.^{31}P NMR (243 MHz, $CDCl_3$) δ 64.9. HRMS (ESI) for $C_{19}H_{17}BrPS_2^+$ $(M+H)^+$: Calcd: 418.9688; found: 418.9686.



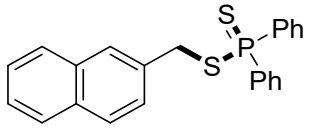
(2-Chlorobenzyl)Diphenylphosphine Oxide(6ag), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (dd, J = 14.4, 7.2 Hz, 4H), 7.57 – 7.35 (m, 6H), 7.16 (d, J = 7.2 Hz, 1H), 7.10 (d, J = 4.2 Hz, 2H), 7.03 – 6.95 (m, 1H), 4.11 (d, J = 10.2 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.0, 134.1 (d, J = 84.2 Hz), 132.0 (d, J = 2.5 Hz), 131.5 (d, J = 11.0 Hz), 130.5 (d, J = 15.2 Hz), 128.6 (d, J = 13.1 Hz), 128.0, 126.2, 34.1, 19.3.^{31}P NMR (243 MHz, $CDCl_3$) δ 64.3. HRMS (ESI) for $C_{20}H_{20}PS_2^+$ $(M+H)^+$: Calcd: 355.0739; found: 355.0739.



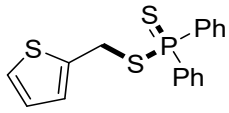
2-Methylbenzyl Diphenylphosphinodithioate (6ah), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 14.4, 7.8 Hz, 4H), 7.48 – 7.35 (m, 6H), 7.20 – 7.05 (m, 2H), 6.77 (d, J = 8.4 Hz, 1H), 6.67 (t, J = 7.2 Hz, 1H), 4.16 (d, J = 12.6 Hz, 2H), 3.78 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 134.3 (d, J = 84.2 Hz), 131.7 (dd, J = 25.2, 6.6 Hz), 129.1, 128.5 (d, J = 13.2 Hz), 125.1, 120.4, 110.4, 55.5, 30.9. ^{31}P NMR (243 MHz, $CDCl_3$) δ 66.0. HRMS (ESI) for $C_{20}H_{20}OPS_2^+$ $(M+H)^+$: Calcd: 371.0688; found: 371.0689.



2-Chlorobenzyl Diphenylphosphinodithioate (6ai), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 – 7.80 (m, 4H), 7.50 – 7.42 (m, 2H), 7.38 (m, J = 7.6, 3.6 Hz, 4H), 7.30 – 7.27 (m, 1H), 7.22 (dd, J = 7.6, 1.4 Hz, 1H), 7.07 (m, J = 7.8, 1.5 Hz, 1H), 6.92 (m, J = 7.5, 0.9 Hz, 1H), 4.28 (d, J = 13.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.7 (d, J = 4.3 Hz), 134.7 (d, J = 84.3 Hz), 131.9, 131.6 (d, J = 8.4 Hz), 131.5, 129.5 (d, J = 77.4 Hz), 128.5 (d, J = 13.8 Hz), 126.7, 33.9.^{31}P NMR (243 MHz, $CDCl_3$) δ 66.1. HRMS (ESI) for $C_{19}H_{17}ClPS_2^+$ $(M+H)^+$: Calcd: 375.0193; found: 375.0193.

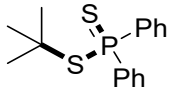


Naphthalen-2-Ylmethyl Diphenylphosphinodithioate (6aj), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (dd, J = 14.4, 7.2 Hz, 4H), 7.57 – 7.35 (m, 1H), 7.16 (d, J = 7.2 Hz, 3H), 7.10 (d, J = 4.2 Hz, 4H), 7.03 – 6.95 (m, 5H), 4.11 (d, J = 10.2 Hz, 2H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.3, 134.1 (d, J = 5.5 Hz), 133.7, 132.9 (d, J = 82.5 Hz), 131.8 (d, J = 2.5 Hz), 131.8 (d, J = 11.0 Hz), 128.6, 128.5 (d, J = 8.7 Hz), 128.3, 127.7 (d, J = 30.8 Hz), 127.2, 126.2 (d, J = 18.2 Hz), 36.3. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.8. HRMS (ESI) for $C_{23}H_{20}PS_2^+$ $(M+H)^+$: Calcd: 391.0739; found: 391.0737.

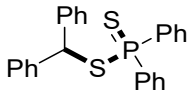


Thiophen-2-Ylmethyl Diphenylphosphinodithioate (6ak), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.79 (m, 4H), 7.54 – 7.36 (m, 6H), 7.11 (d, J = 4.5 Hz, 1H), 6.86 (s, 1H), 6.74 (s, 1H), 4.40 (d, J = 12.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.3 (d, J = 5.6 Hz), 134.3 (d, J = 85.1 Hz), 132.0 (d, J = 2.5 Hz), 131.6 (d, J = 11.5 Hz), 128.6 (d, J = 13.2 Hz), 127.6 (d, J = 108.8 Hz), 125.7, 30.6. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.7. HRMS (ESI) for $C_{17}H_{16}PS_3^+$ $(M+H)^+$: Calcd: 347.0147; found:

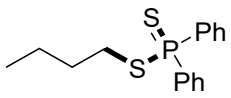
347.0146.



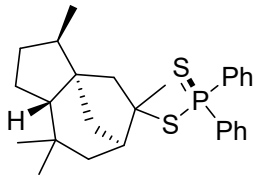
Tert-Butyl Diphenylphosphinodithioate (6al), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (dd, J = 14.4, 7.0 Hz, 4H), 7.58 – 7.38 (m, 6H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.9 (d, J = 84.1 Hz), 131.7 (d, J = 11.3 Hz), 131.6 (d, J = 2.4 Hz), 128.6 (d, J = 13.2 Hz), 53.6 (d, J = 4.0 Hz), 32.7 (d, J = 4.2 Hz), 29.8. ^{31}P NMR (243 MHz, $CDCl_3$) δ 56.8. HRMS (ESI) for $C_{16}H_{20}PS_2^+$ $(M+H)^+$: Calcd: 307.0739; found: 307.0735.



Benzhydryl Diphenylphosphinodithioate (6am), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.63 (m, 4H), 7.41 – 7.35 (m, 2H), 7.34 – 7.27 (m, 8H), 7.17 – 7.12 (m, 4H), 7.12 – 7.07 (m, 2H), 5.94 (d, J = 13.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.8 (d, J = 4.0 Hz), 134.2 (d, J = 85.5 Hz), 131.6 (d, J = 2.8 Hz), 131.5 (d, J = 11.5 Hz), 128.8, 128.4 (d, J = 13.0 Hz), 127.2, 55.3. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.4. HRMS (ESI) for $C_{25}H_{22}PS_2^+$ $(M+H)^+$: Calcd: 417.0896; found: 417.0894.

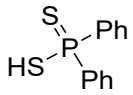


Butyl Diphenylphosphinodithioate (6an), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.87 (m, 4H), 7.54 – 7.34 (m,), 2.96 – 2.76 (m, 2H), 1.62 – 1.46 (m, 2H), 1.42 – 1.28 (m, 2H), 0.82 (t, J = 7.4 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 134.9 (d, J = 84.9 Hz), 131.9 (d, J = 2.5 Hz), 131.5 (d, J = 11.2 Hz), 128.6 (d, J = 13.1 Hz), 32.1 (d, J = 5.1 Hz), 31.5, 21.9, 13.6. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.5. HRMS (ESI) for $C_{16}H_{20}PS_2^+$ $(M+H)^+$: Calcd: 307.0793; found: 307.0792.



(3R,3aR,5R,6R)-3,3a,5,6,8,8,8a-Heptamethyldecahydroazulen-5-Yl

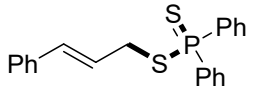
Diphenylphosphinodithioat (6an), white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 7.80 (m, 4H), 7.50 – 7.34 (m, 6H), 1.97 – 1.91 (m, 1H), 1.85 – 1.61 (m, 4H), 1.60 – 1.49 (m, 2H), 1.47 – 1.38 (m, 1H), 1.36 – 1.21 (m, 5H), 1.07 – 0.69 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.9 (d, J = 5.0 Hz), 131.8 (d, J = 10.8 Hz), 131.7 (d, J = 10.7 Hz), 131.6 (d, J = 2.2 Hz), 131.4 (d, J = 11.4 Hz), 128.5 (d, J = 12.7 Hz), 128.4, 125.2, 59.5, 53.7, 52.3, 48.3, 41.6, 40.5, 39.0, 38.9, 36.3, 29.7, 27.6, 25.3, 24.9, 15.3. ^{31}P NMR (243 MHz, $CDCl_3$) δ 64.6. HRMS (ESI) for $C_{27}H_{36}PS_2^+$ $(M+H)^+$: Calcd: 454.1918; found: 454.1907.



Diphenylphosphinodithioic acid (7aa), colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, J = 14.4, 7.2 Hz, 4H), 7.49 – 7.40 (m, 6H), 3.94 (s, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 136.1 (d, J = 90.6 Hz), 132.0 (d, J = 2.3 Hz), 131.0 (d, J = 11.9 Hz), 128.7 (d, J = 13.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 56.9. This compound is known in the literature: Wagner, J.; Ciesielski, M.; Fleckenstein, C. A.; Denecke, H.; Garlichs, F.; Ball, A.; Doering, M. *Org. Process Res. Dev.* **2013**, *17*, 47.

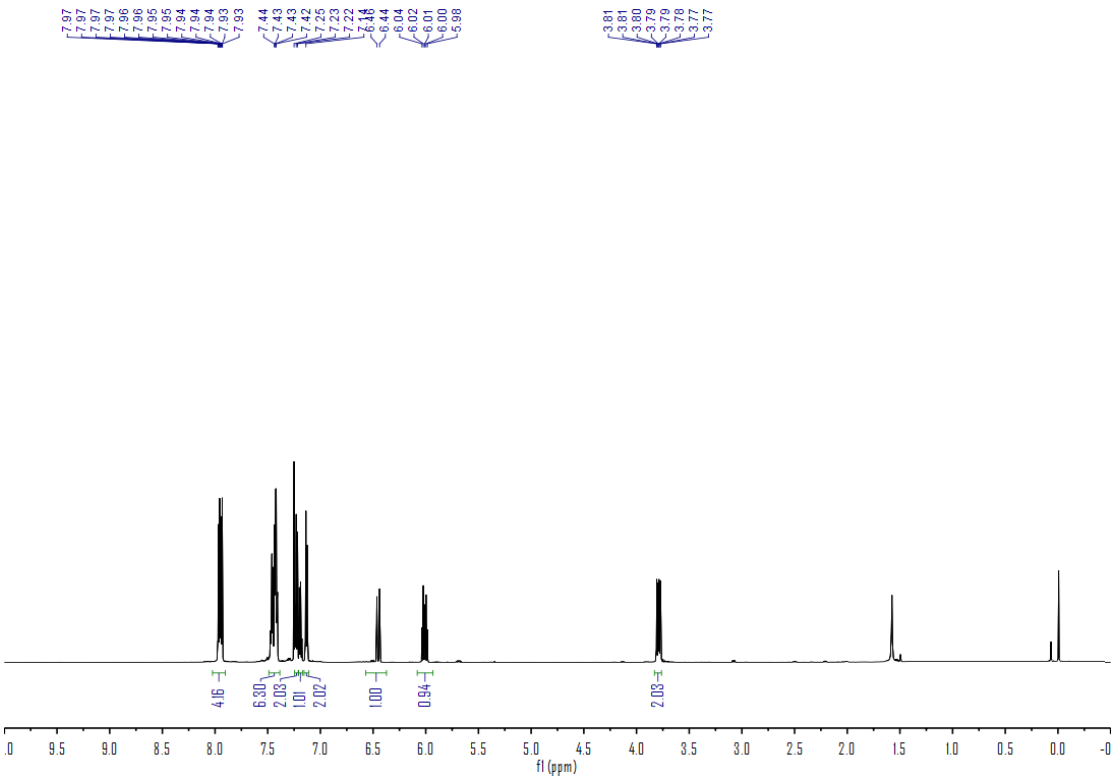
Diphenylphosphine sulfide (8aa), colorless solid. ^{1}H NMR (600 MHz, CDCl3) δ 8.42 (s, 0.5 H), 7.81 – 7.74 (m, 4H), 7.64 (s, 0.5 H), 7.56 – 7.52 (m, 2H), 7.51 – 7.45 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.3 (d, J = 2.5 Hz), 131.4, 131.2 (d, J = 11.6 Hz), 130.8, 129.1 (d, J = 13.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 23.5. This compound is known in the literature: Hirota, E.; Hirashima, S.; Morita, R.; Takase, J.; Matsushima, Y.; Nakashima, K.; Akutsu, H.; Miura, T. *Org. Lett.* **2024**, *26*, 1797.

6.Copies of the ^{1}H、^{13}C and ^{31}P NMR Spectra of the Products

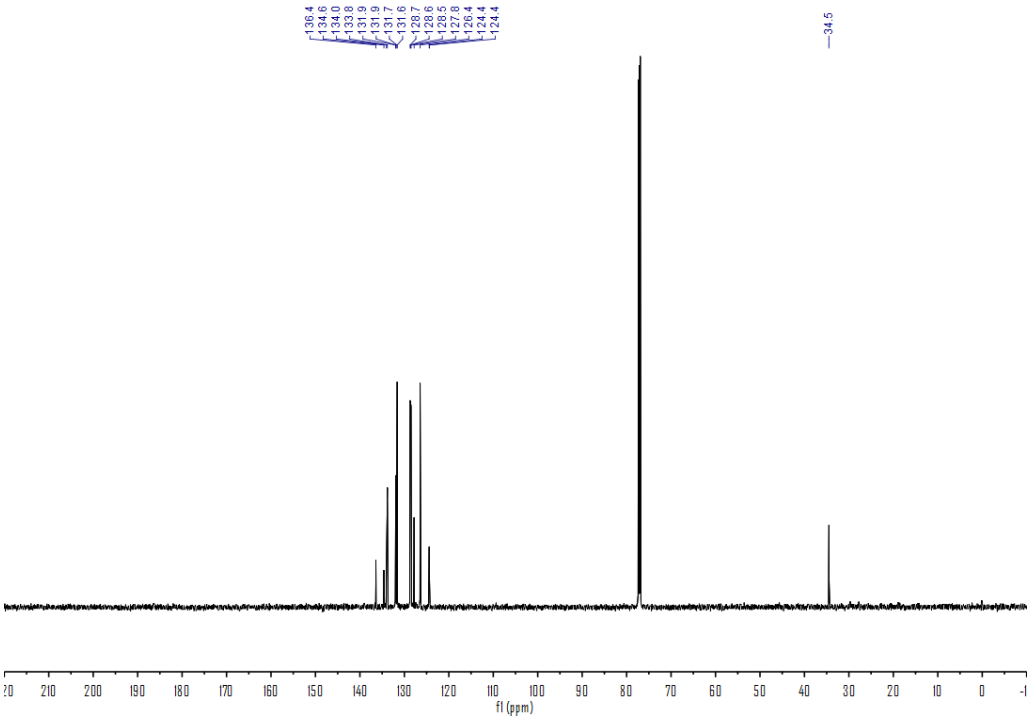


2aa

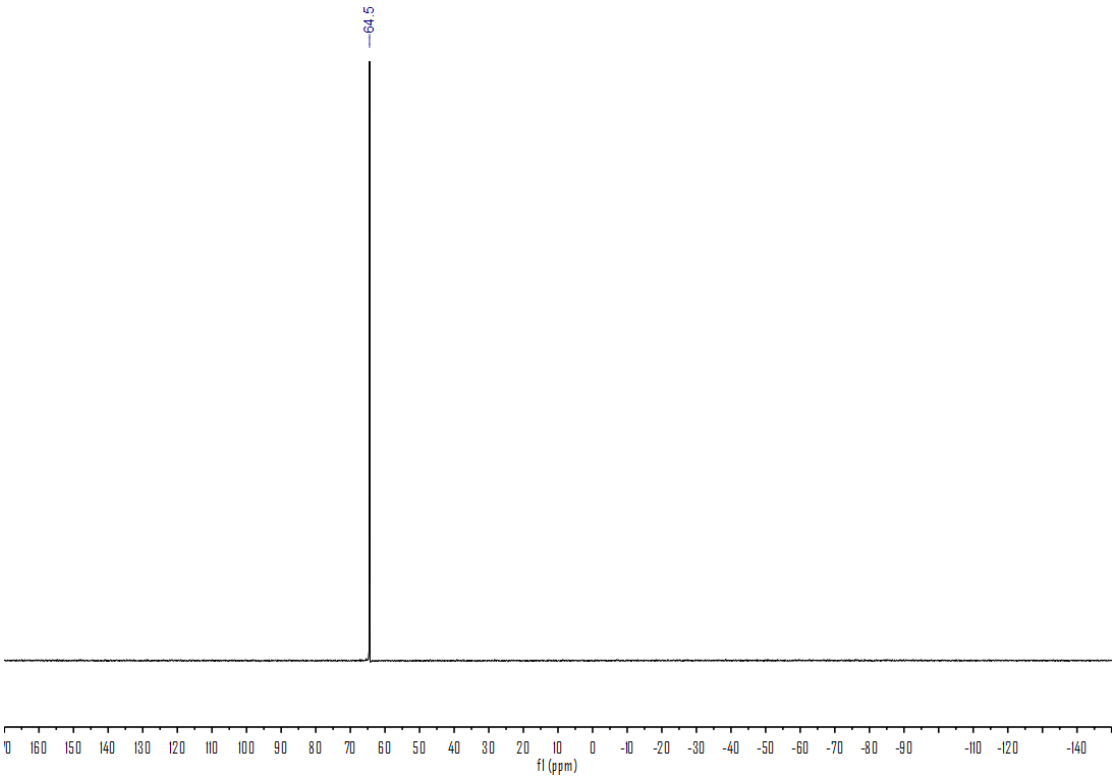
^{1}H NMR (600 MHz, $CDCl_3$)

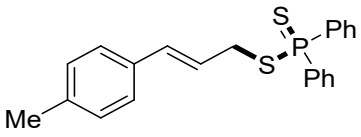


^{13}C NMR (151 MHz, $CDCl_3$)



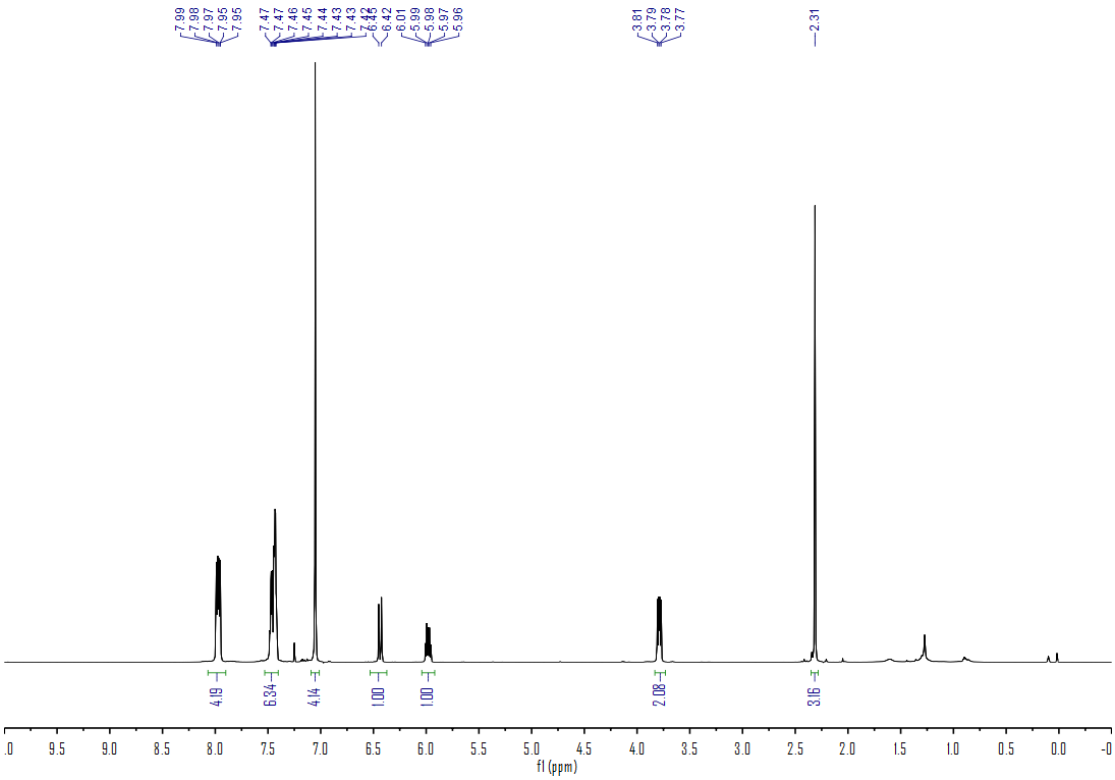
^{31}P NMR (243 MHz, $CDCl_3$)



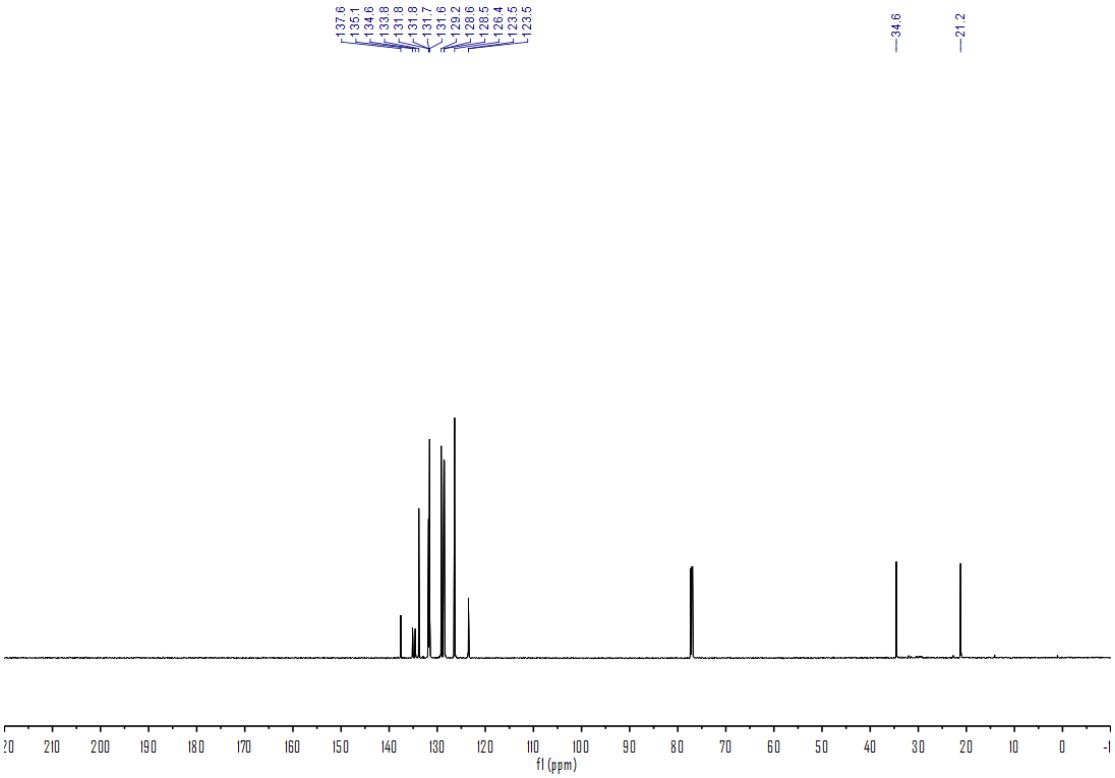


2ab

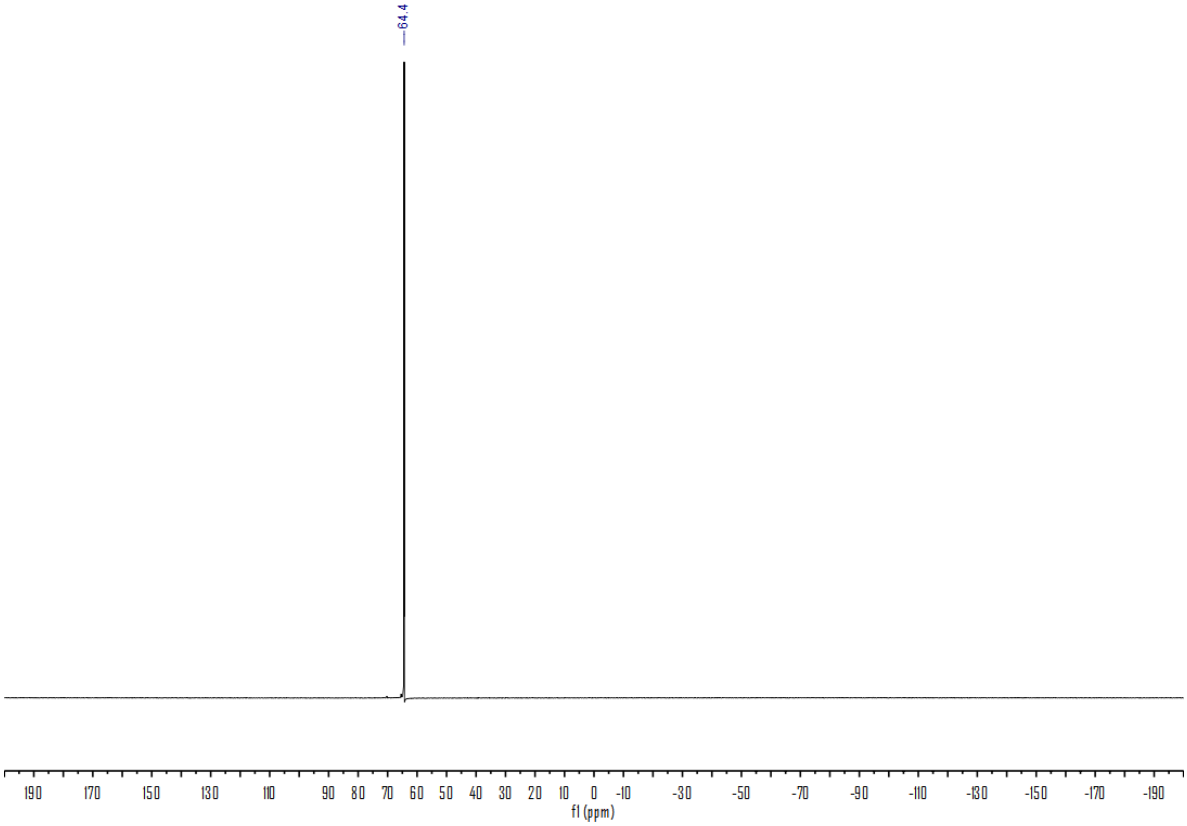
^{1}H NMR (600 MHz, $CDCl_3$)

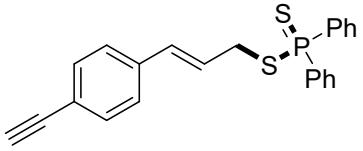


^{13}C NMR (151 MHz, $CDCl_3$)



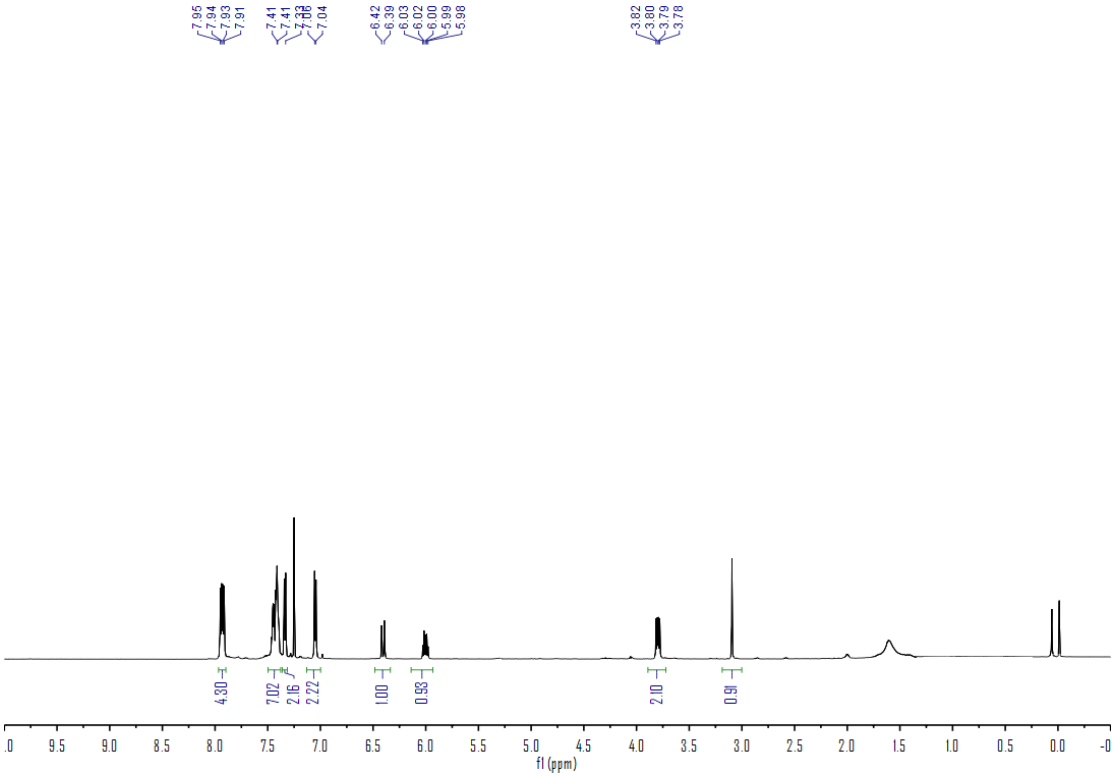
^{31}P NMR (243 MHz, $CDCl_3$)



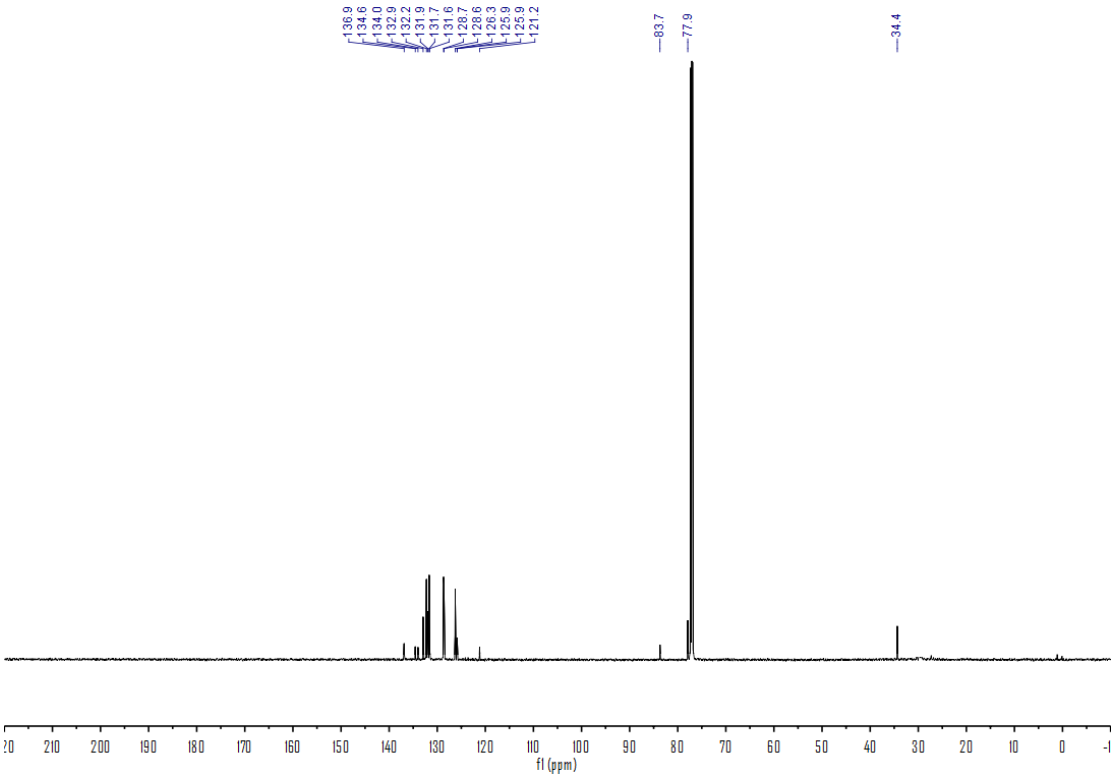


2ac

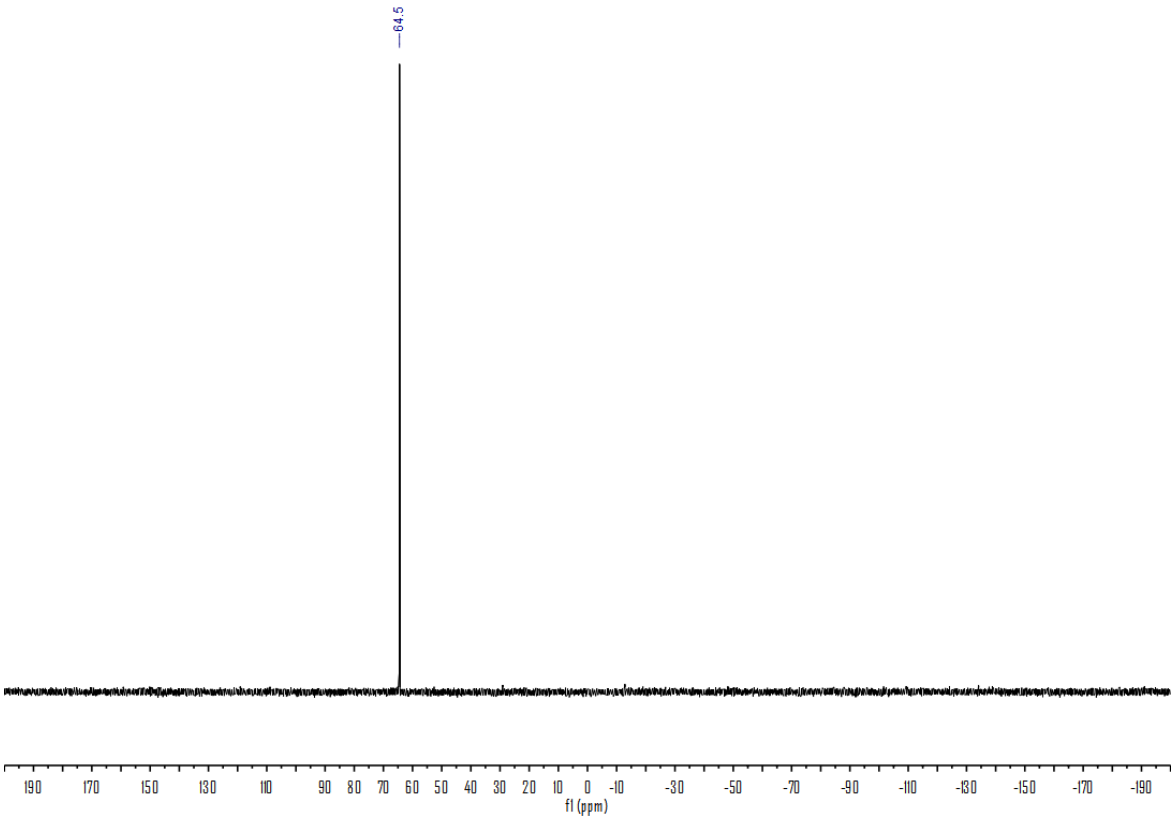
^{1}H NMR (600 MHz, $CDCl_3$)

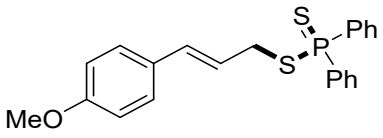


^{13}C NMR (151 MHz, $CDCl_3$)



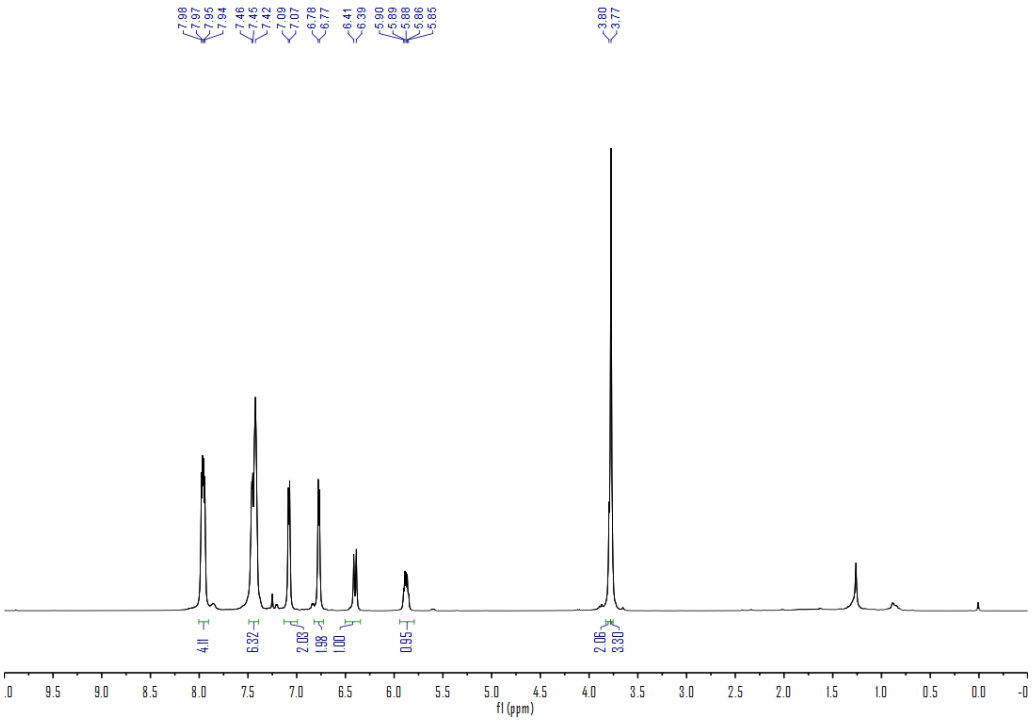
^{31}P NMR (243 MHz, $CDCl_3$)



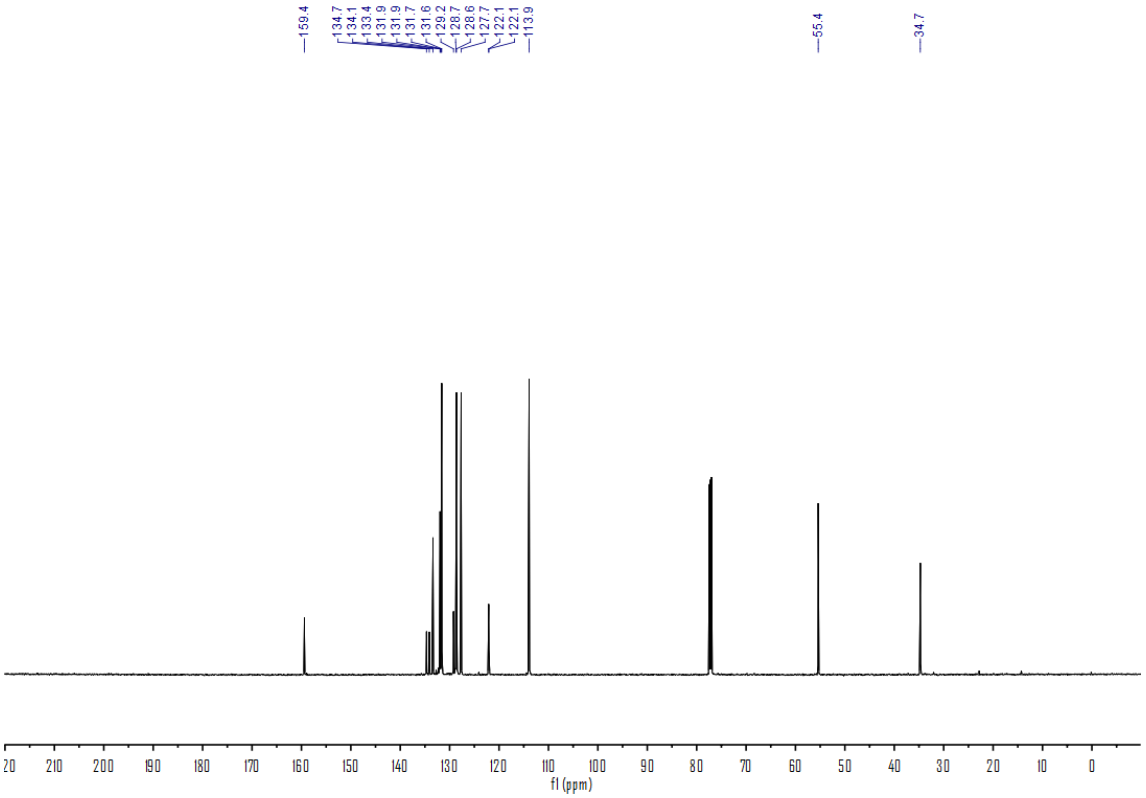


2ad

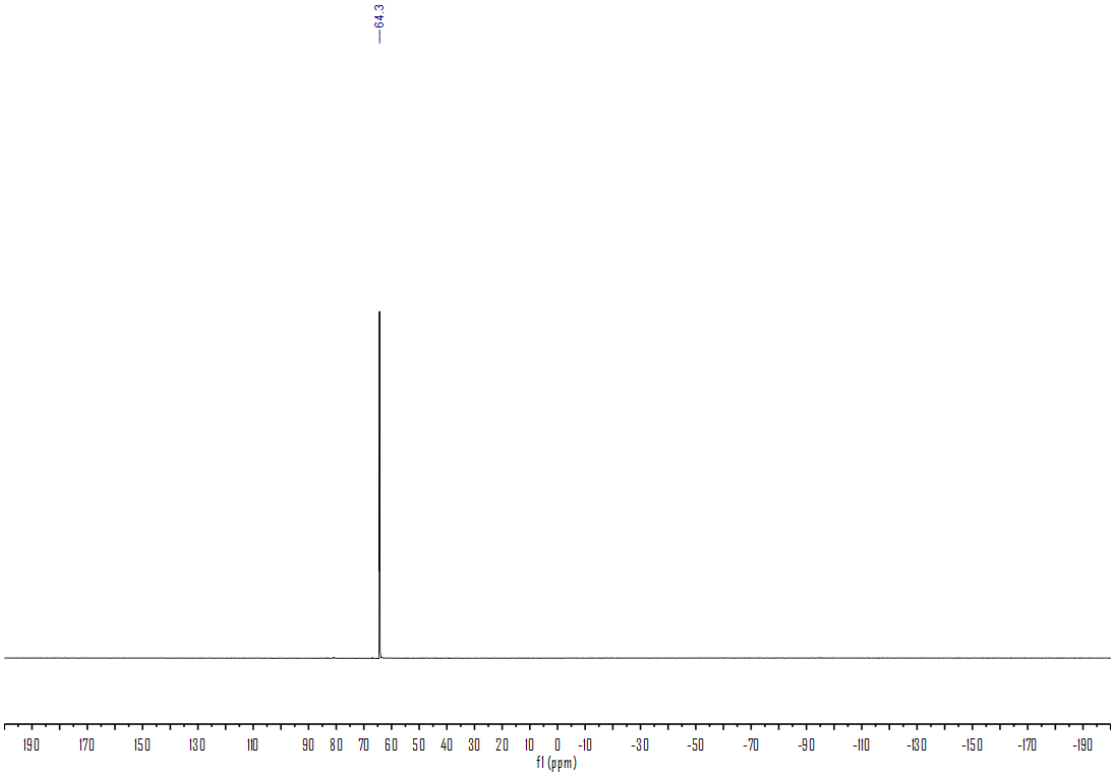
^{1}H NMR (600 MHz, $CDCl_3$)

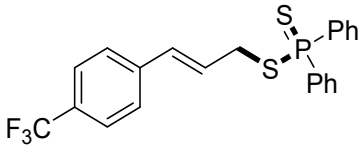


^{13}C NMR (151 MHz, $CDCl_3$)



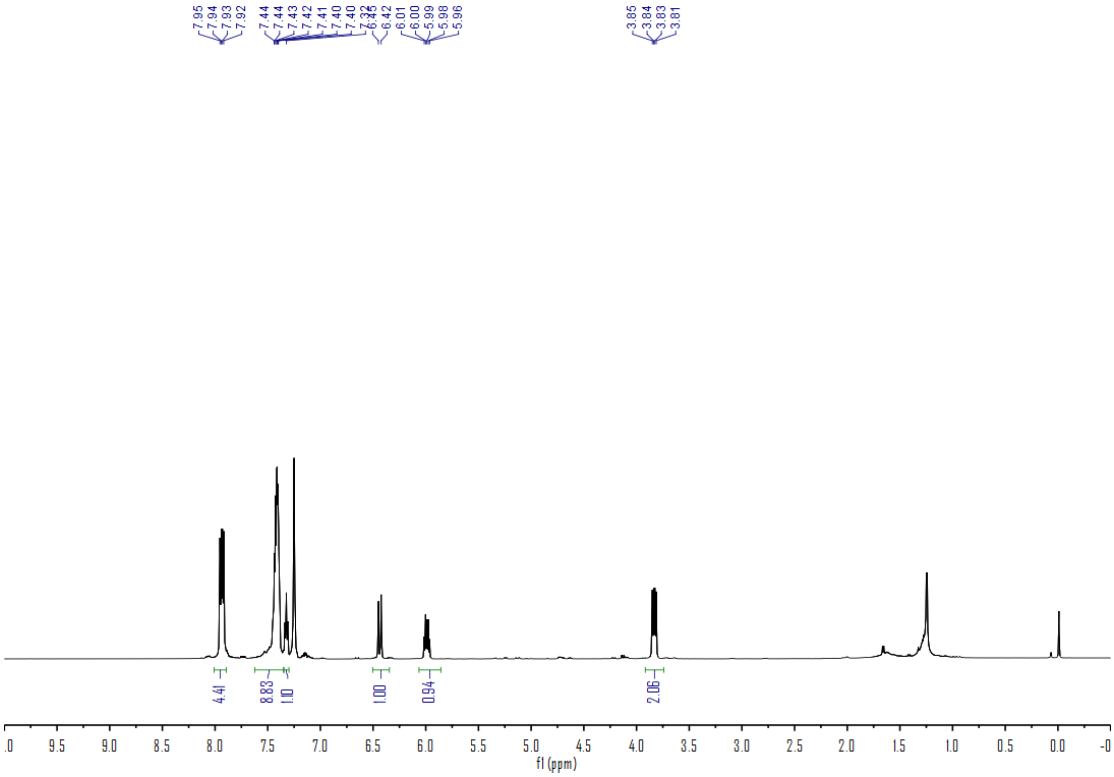
^{31}P NMR (243 MHz, $CDCl_3$)



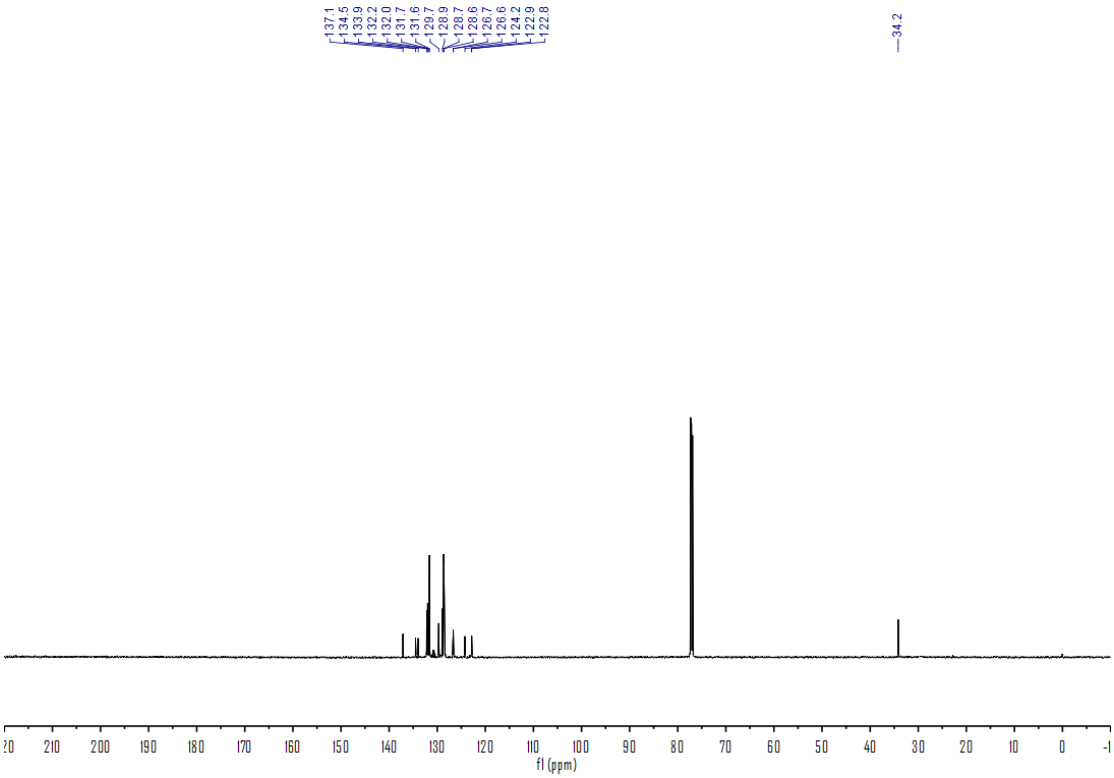


2ae

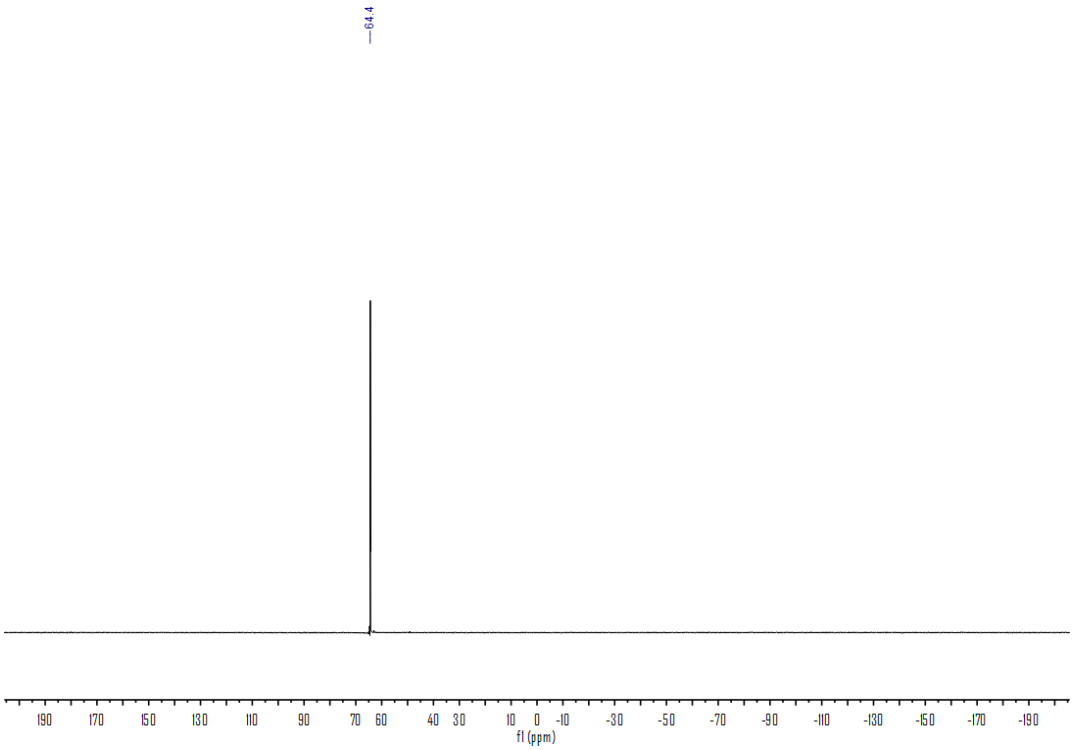
^{1}H NMR (600 MHz, $CDCl_3$)

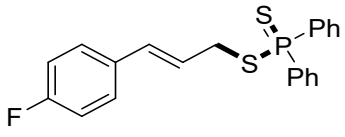


^{13}C NMR (151 MHz, $CDCl_3$)



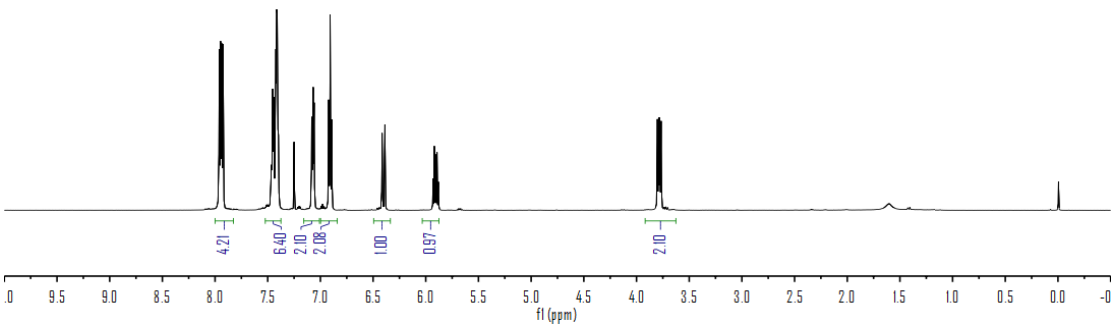
^{31}P NMR (243 MHz, $CDCl_3$)



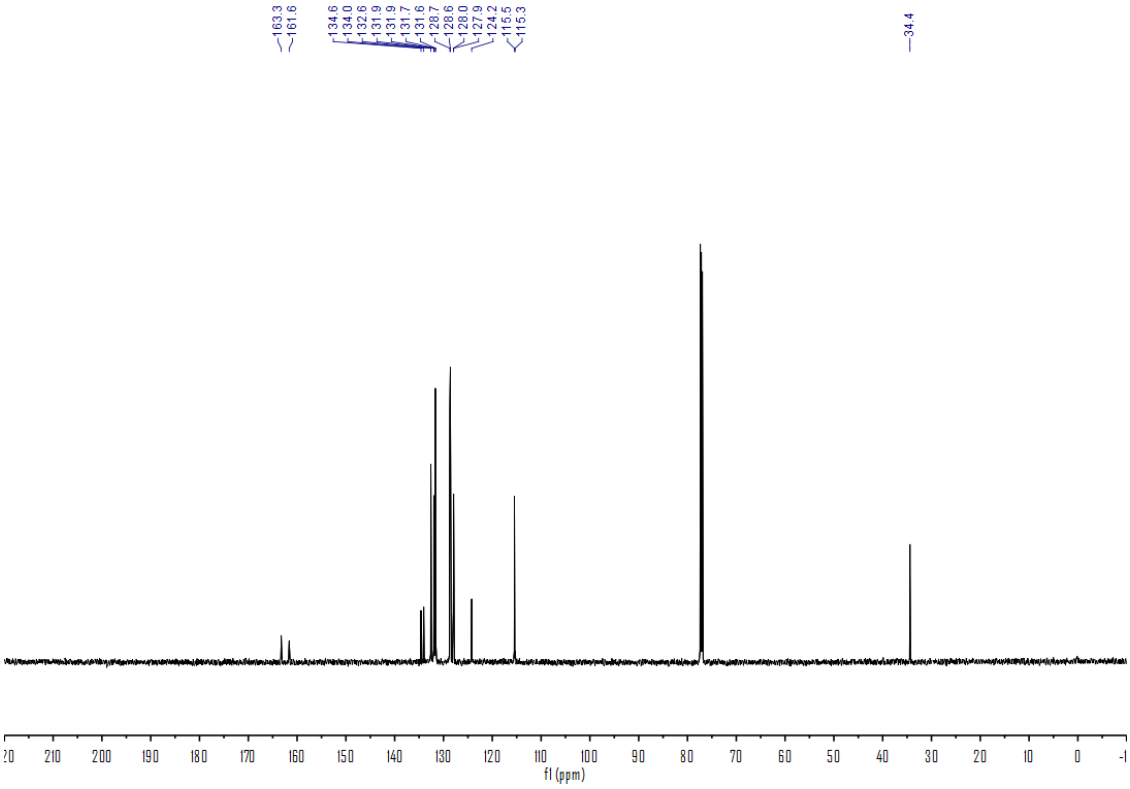


2af

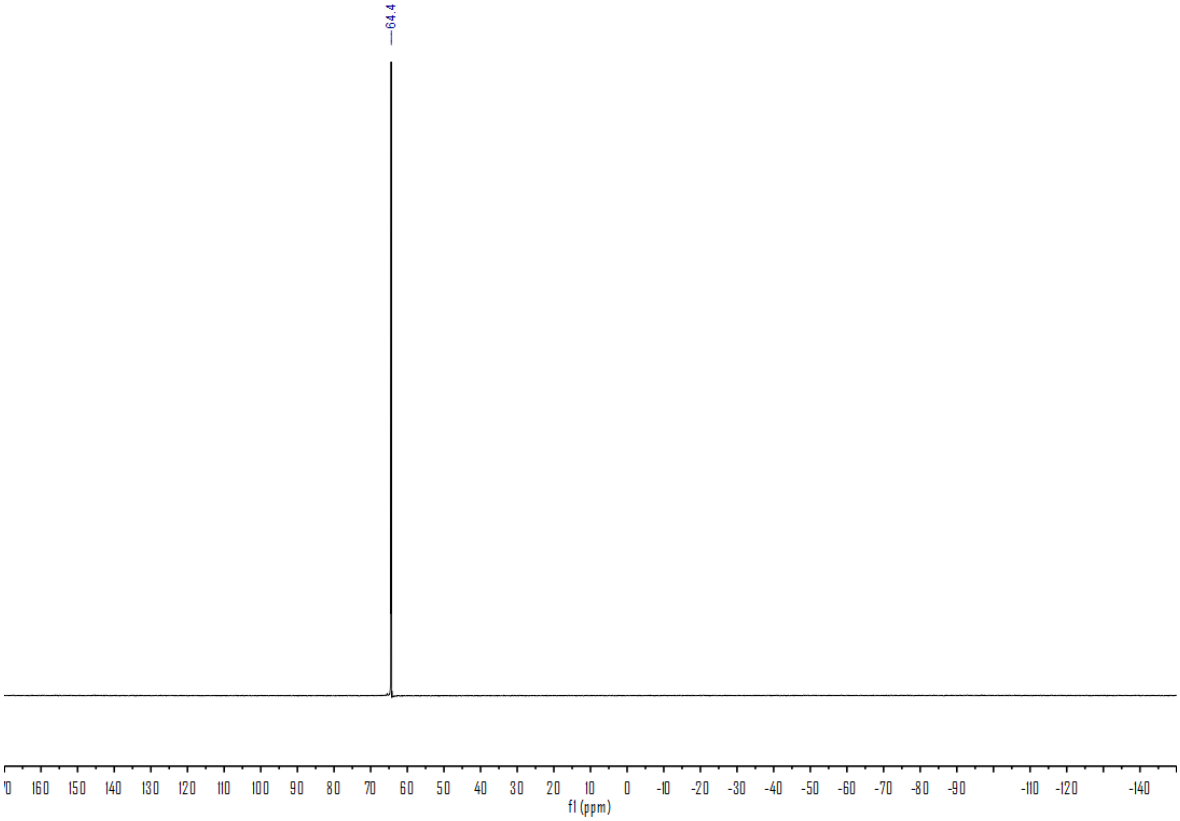
^{1}H NMR (600 MHz, $CDCl_3$)

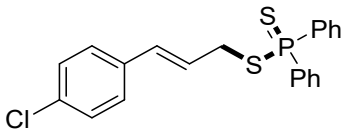


^{13}C NMR (151 MHz, $CDCl_3$)



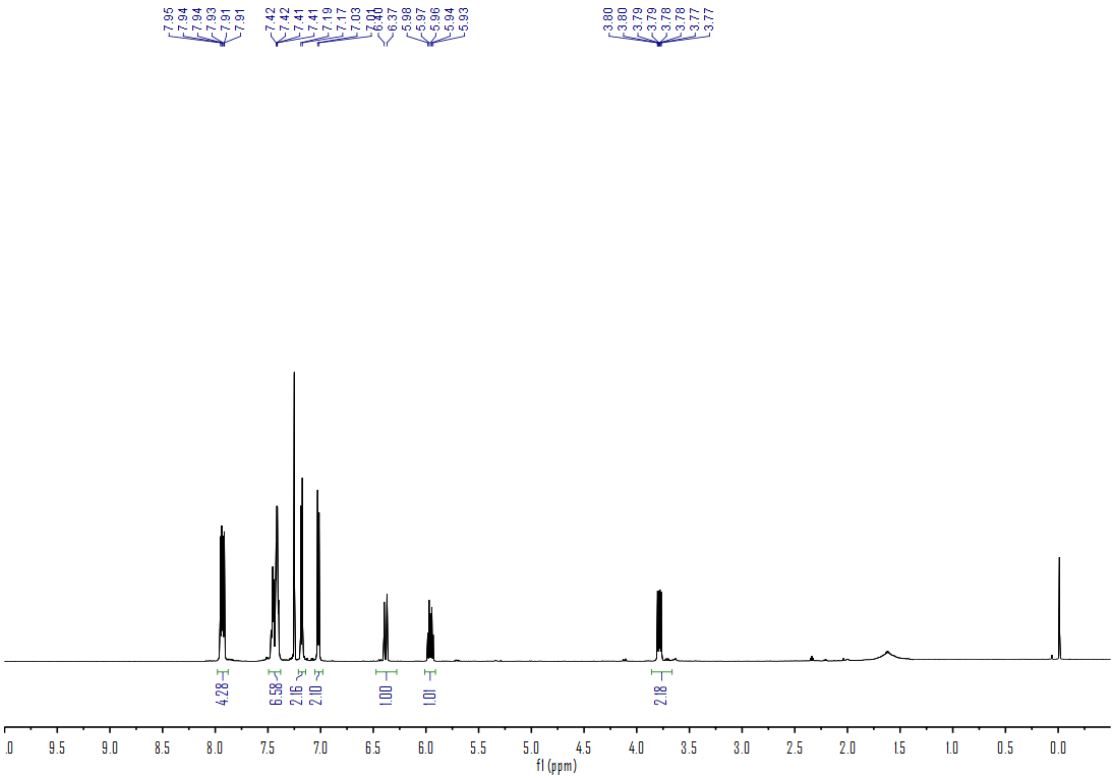
^{31}P NMR (243 MHz, $CDCl_3$)



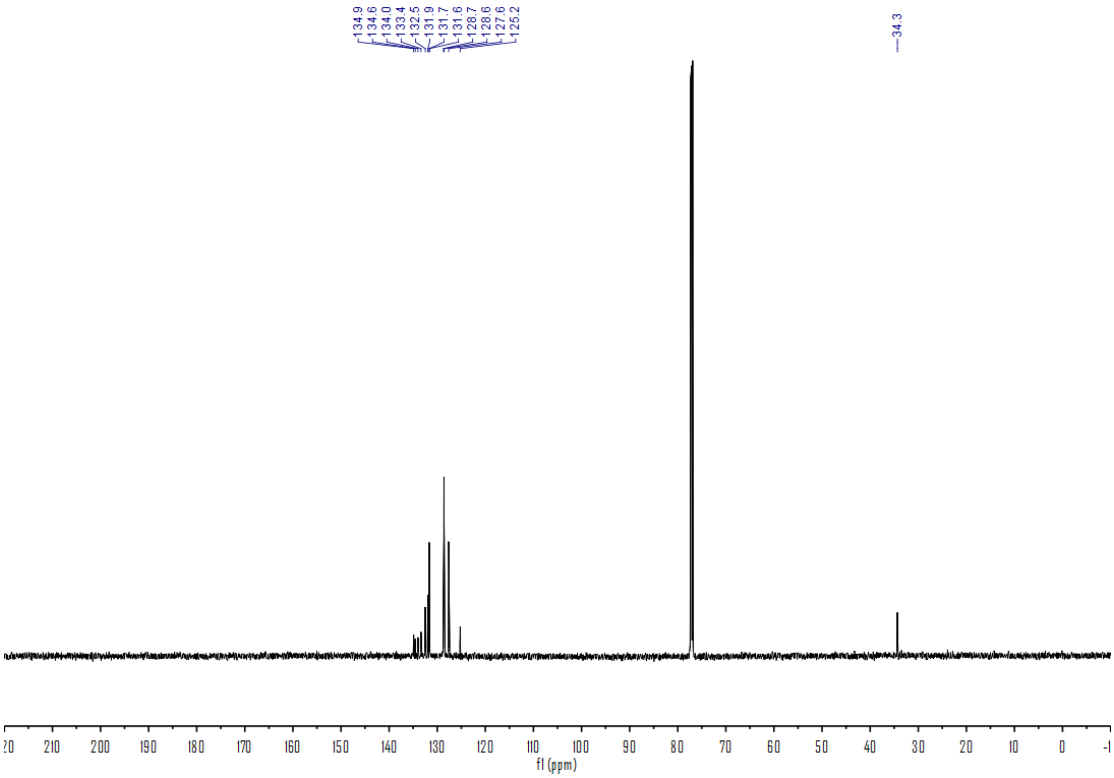


2ag

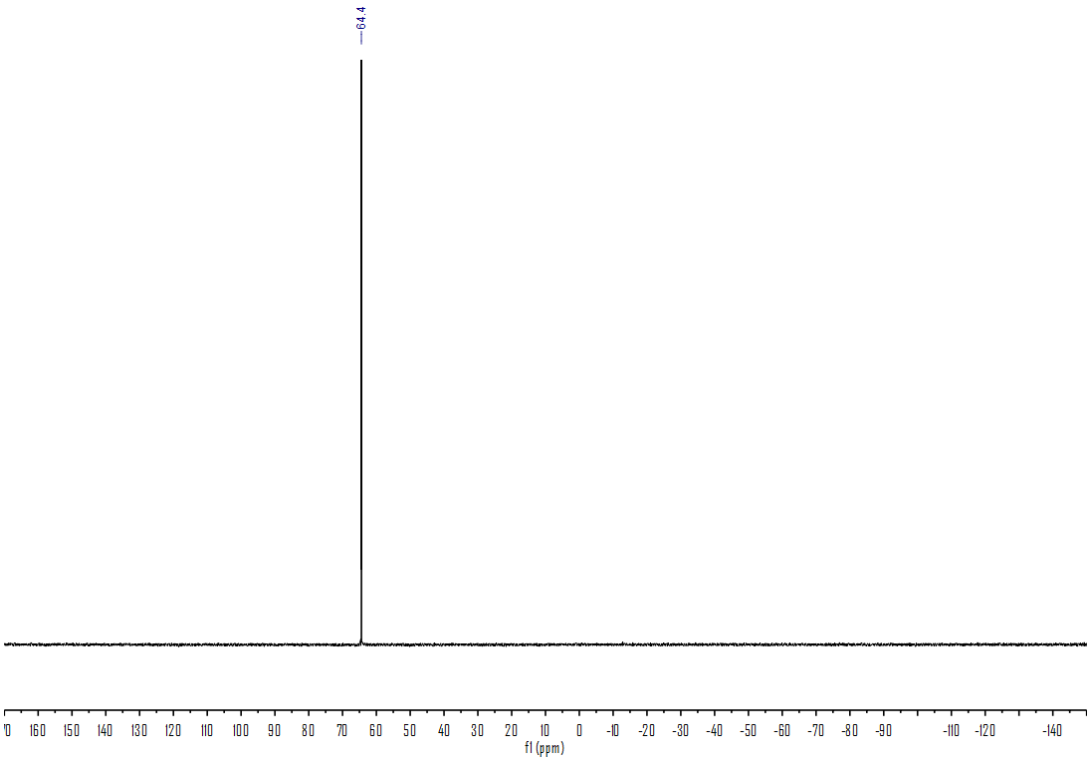
^{1}H NMR (600 MHz, $CDCl_3$)

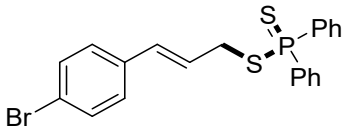


^{13}C NMR (151 MHz, $CDCl_3$)



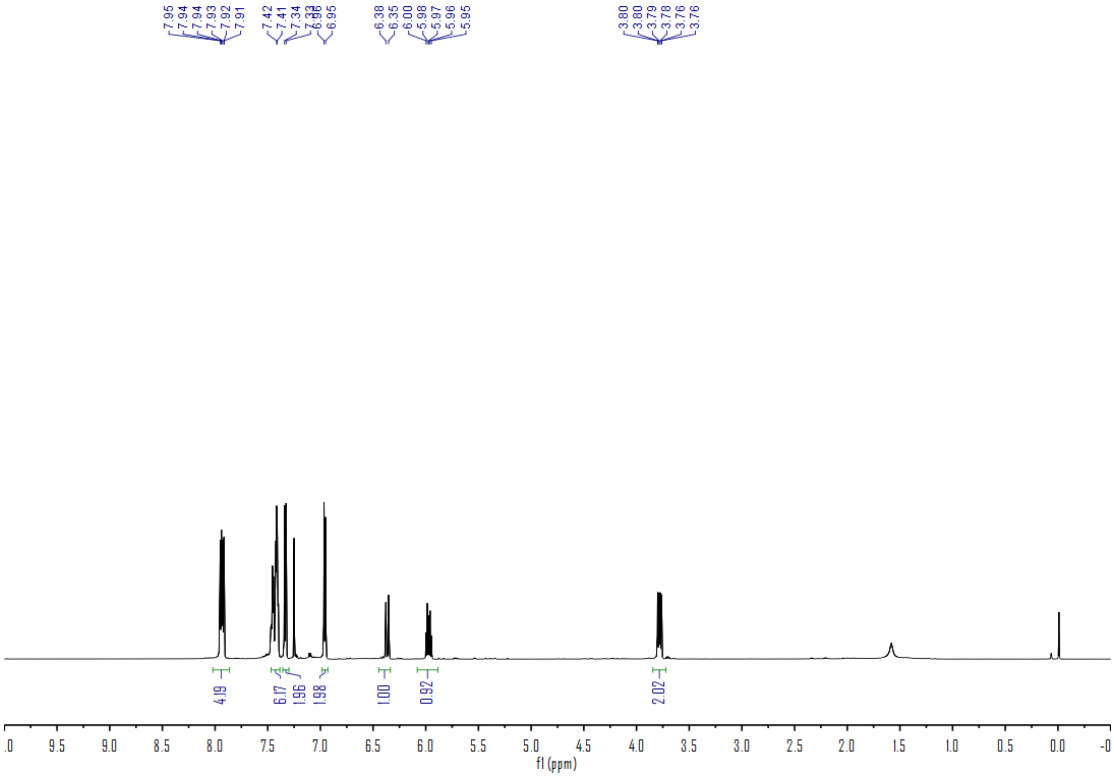
^{31}P NMR (243 MHz, $CDCl_3$)



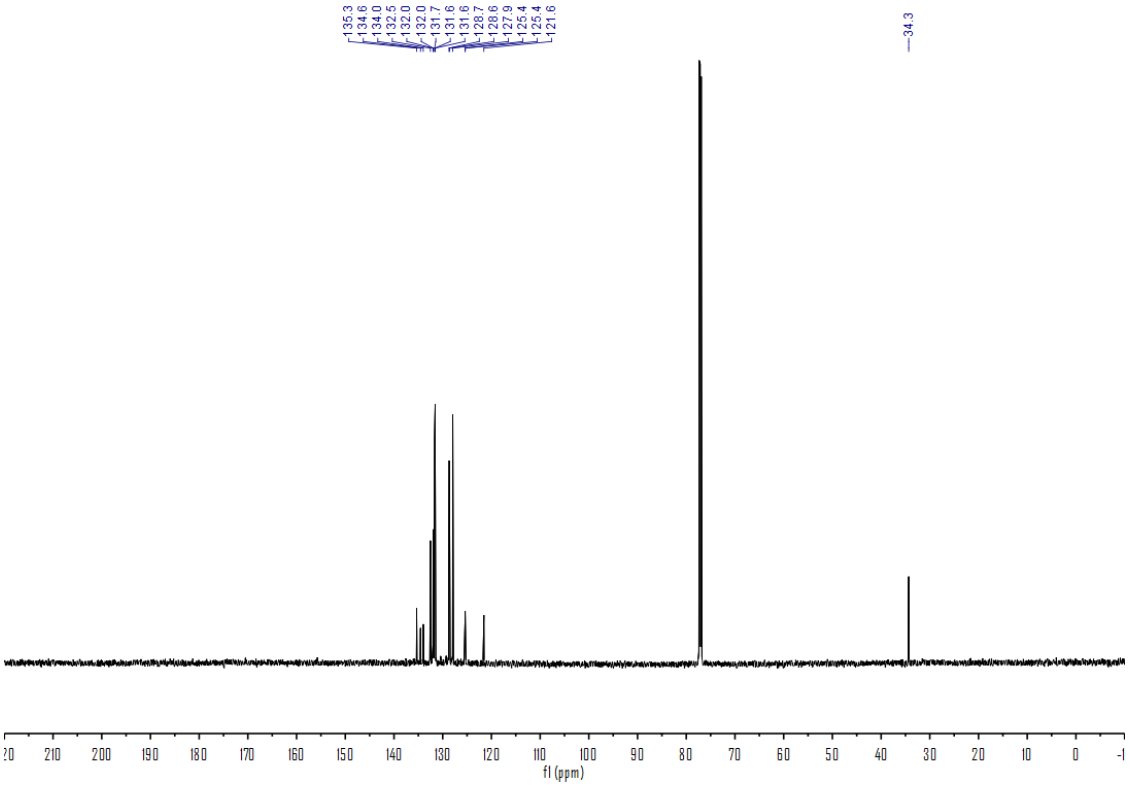


2ah

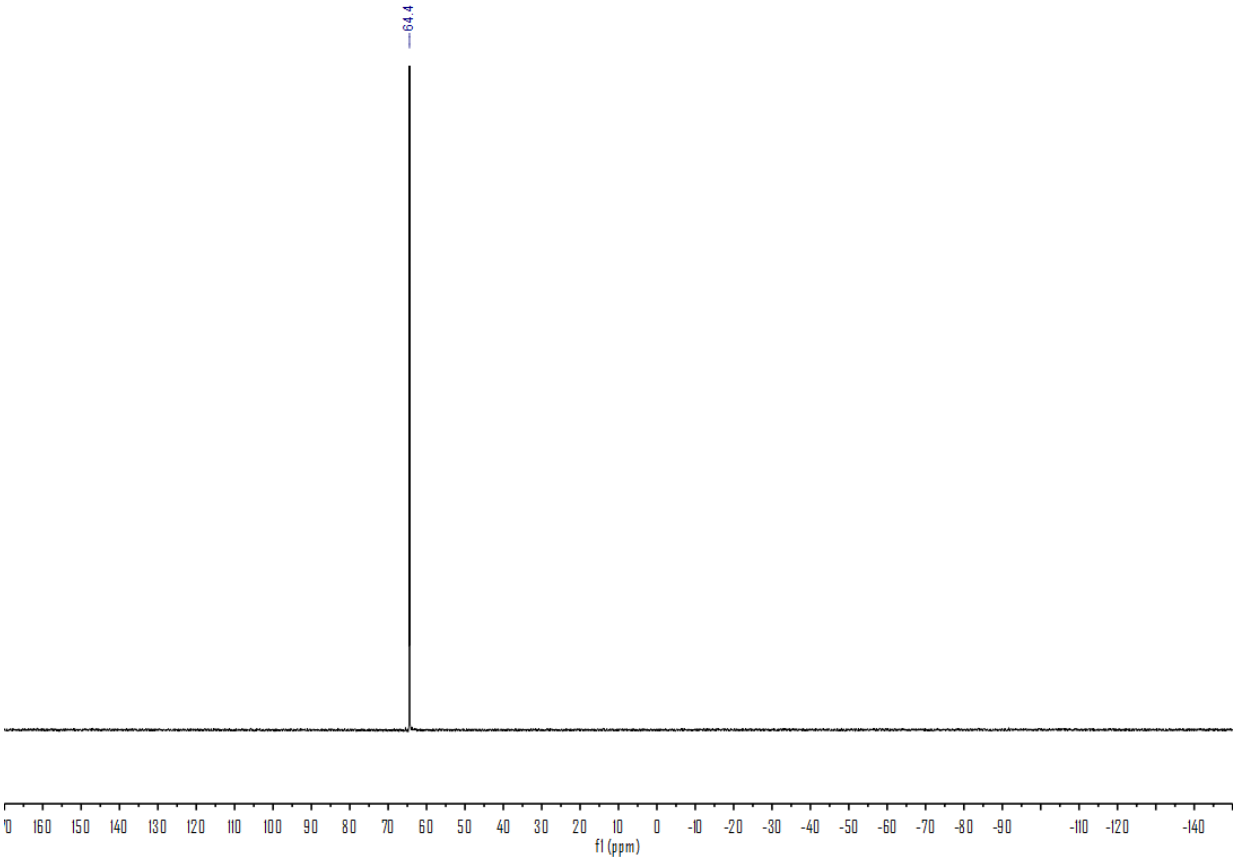
^{1}H NMR (600 MHz, $CDCl_3$)

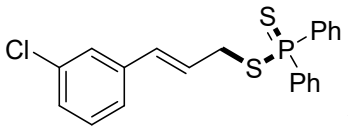


^{13}C NMR (151 MHz, $CDCl_3$)



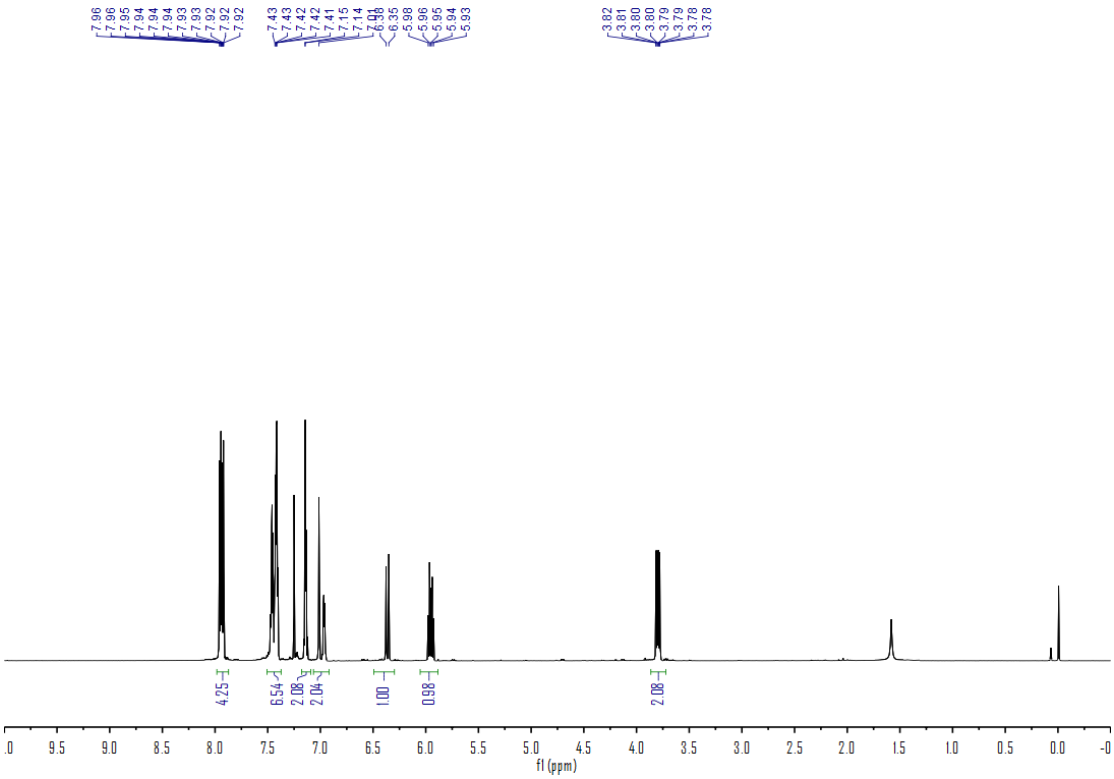
^{31}P NMR (243 MHz, $CDCl_3$)



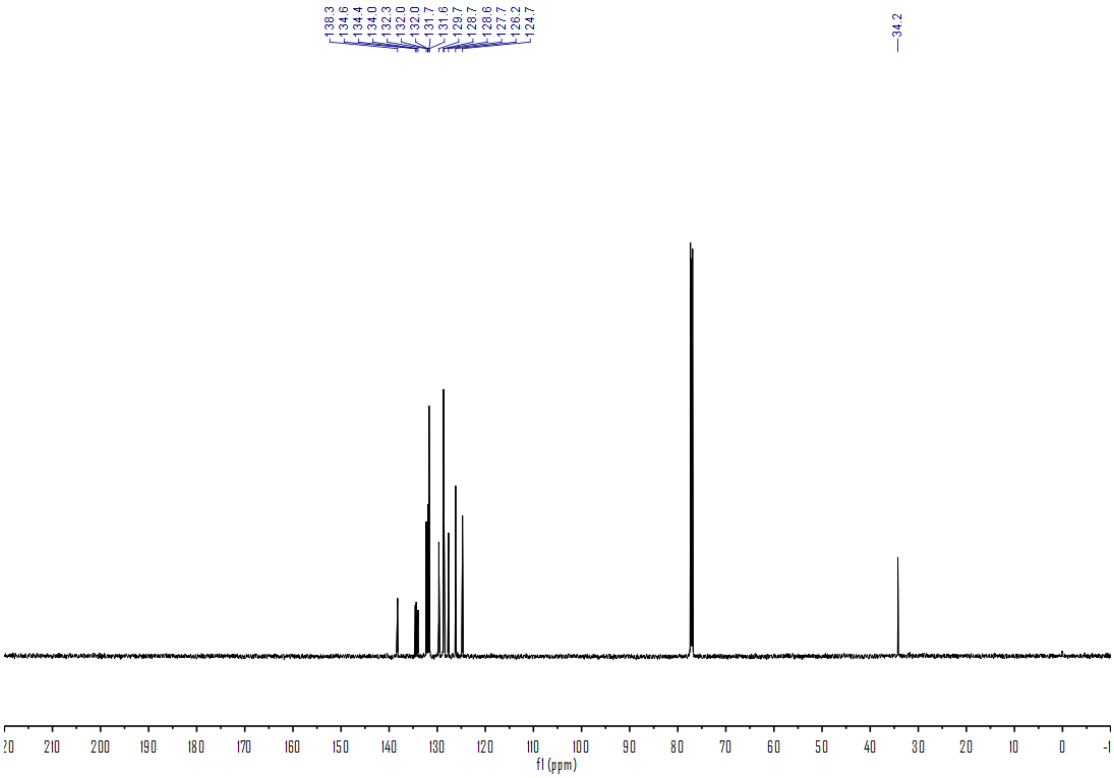


2ai

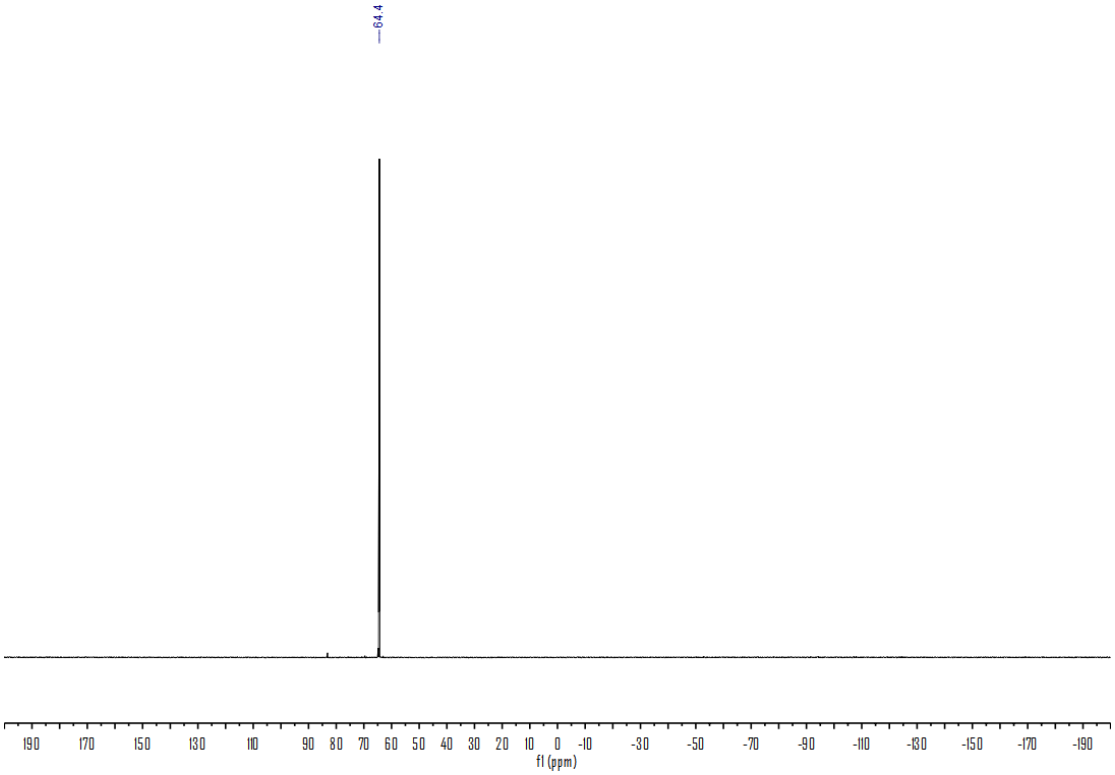
^{1}H NMR (600 MHz, $CDCl_3$)

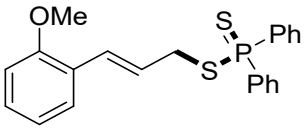


^{13}C NMR (151 MHz, $CDCl_3$)



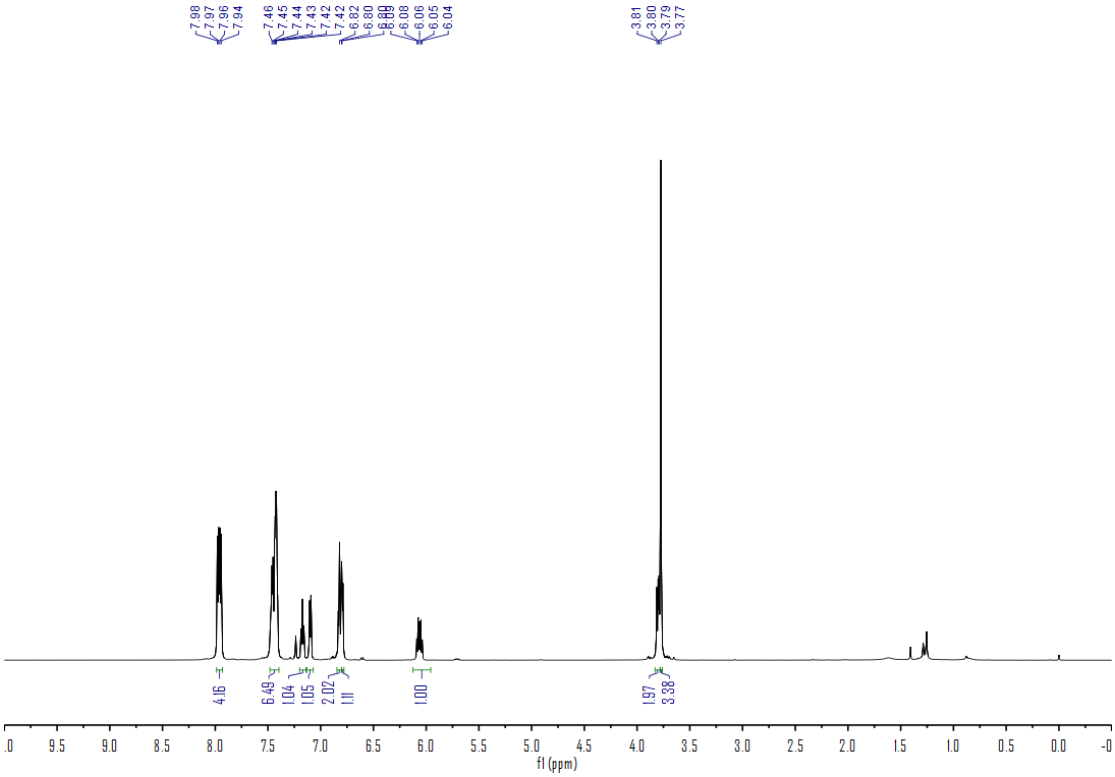
^{31}P NMR (243 MHz, $CDCl_3$)



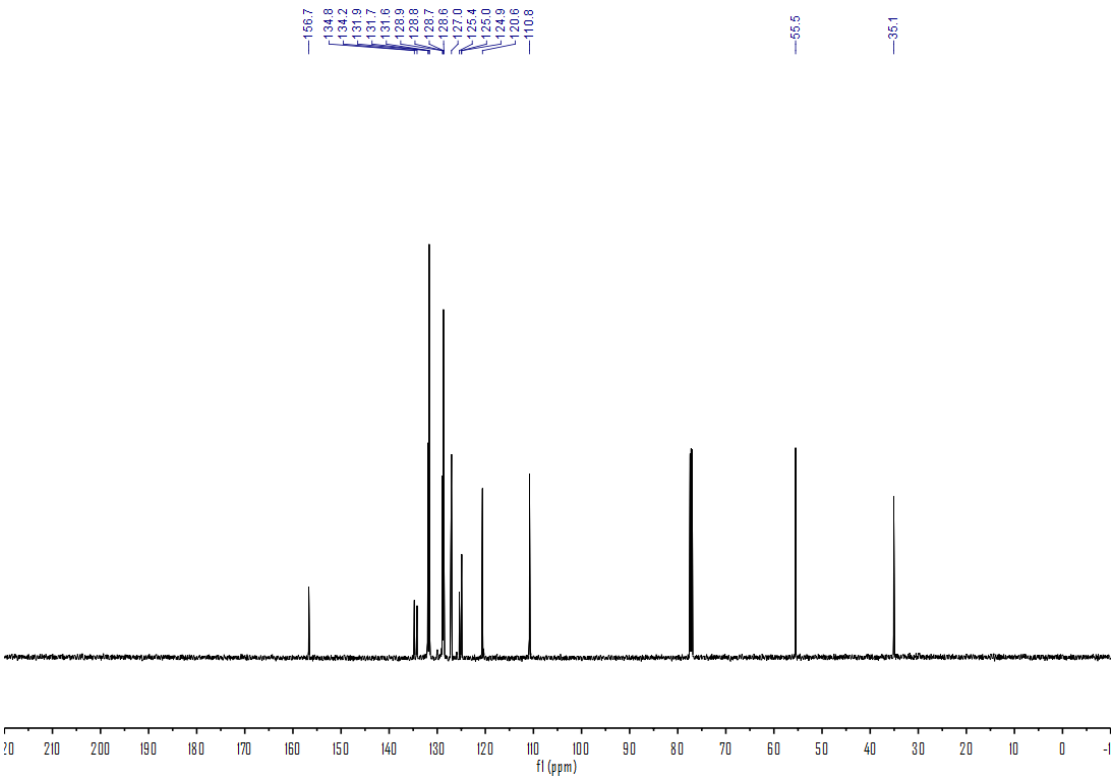


2aj

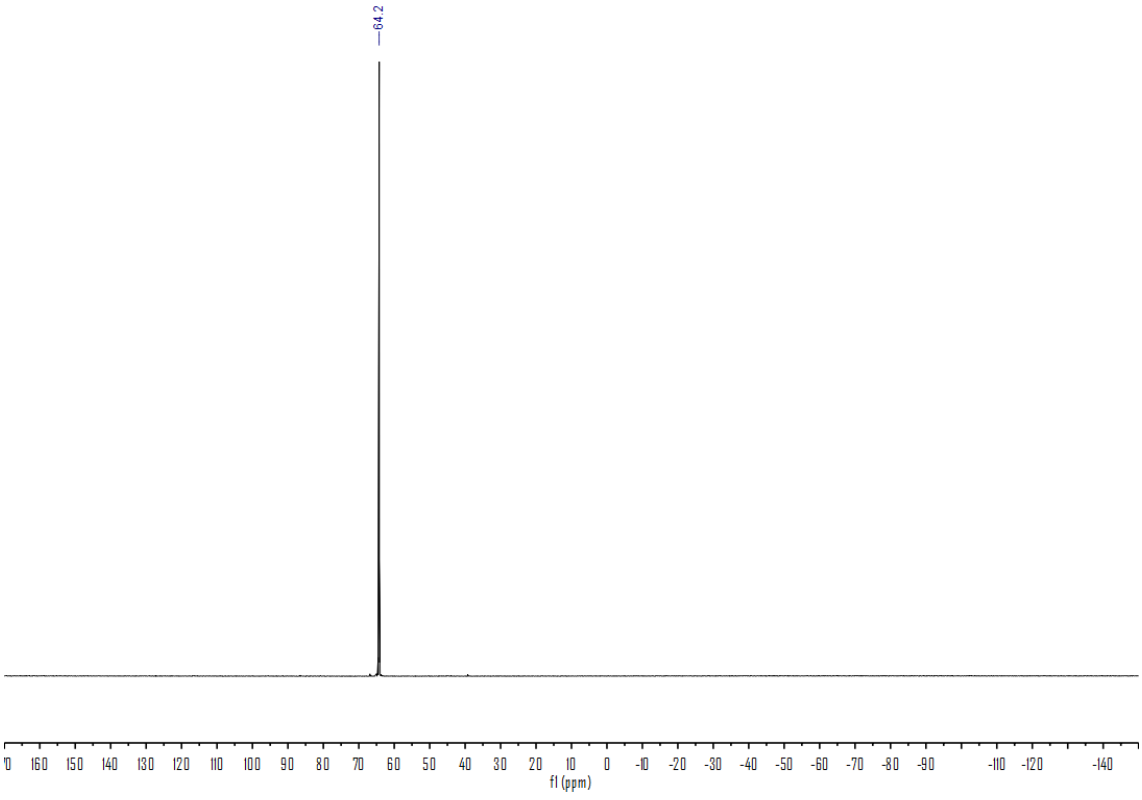
^{1}H NMR (600 MHz, $CDCl_3$)

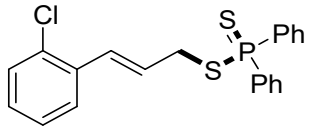


^{13}C NMR (151 MHz, $CDCl_3$)



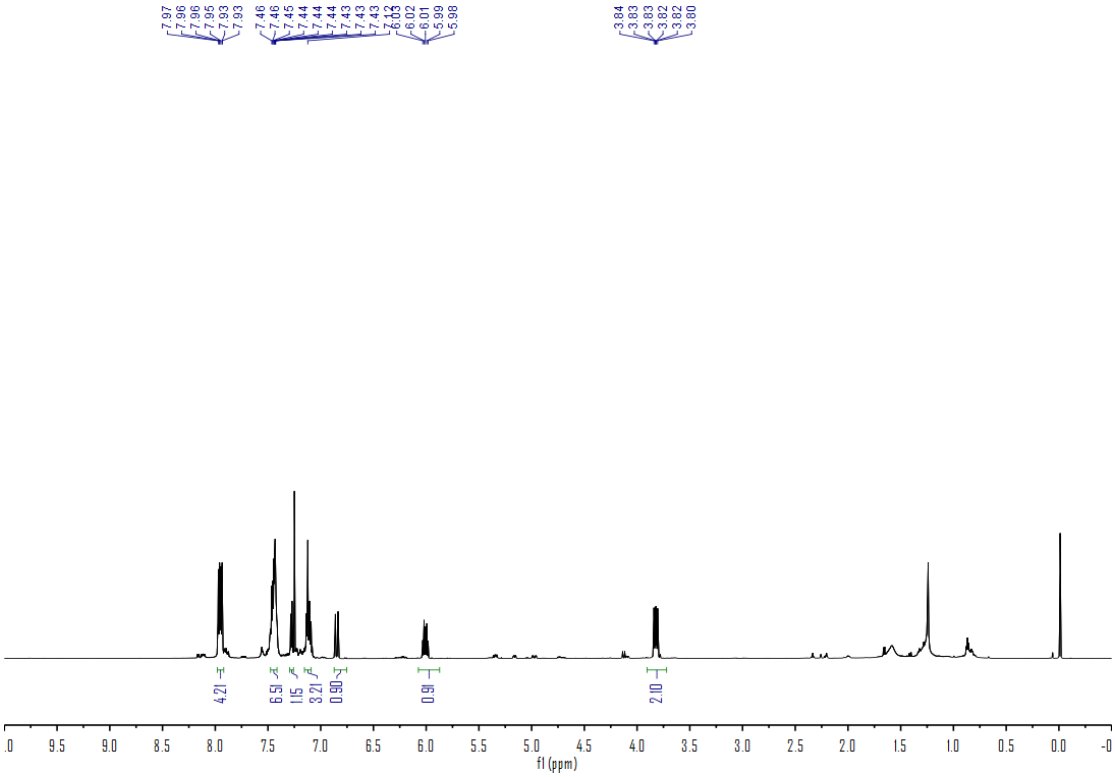
^{31}P NMR (243 MHz, $CDCl_3$)



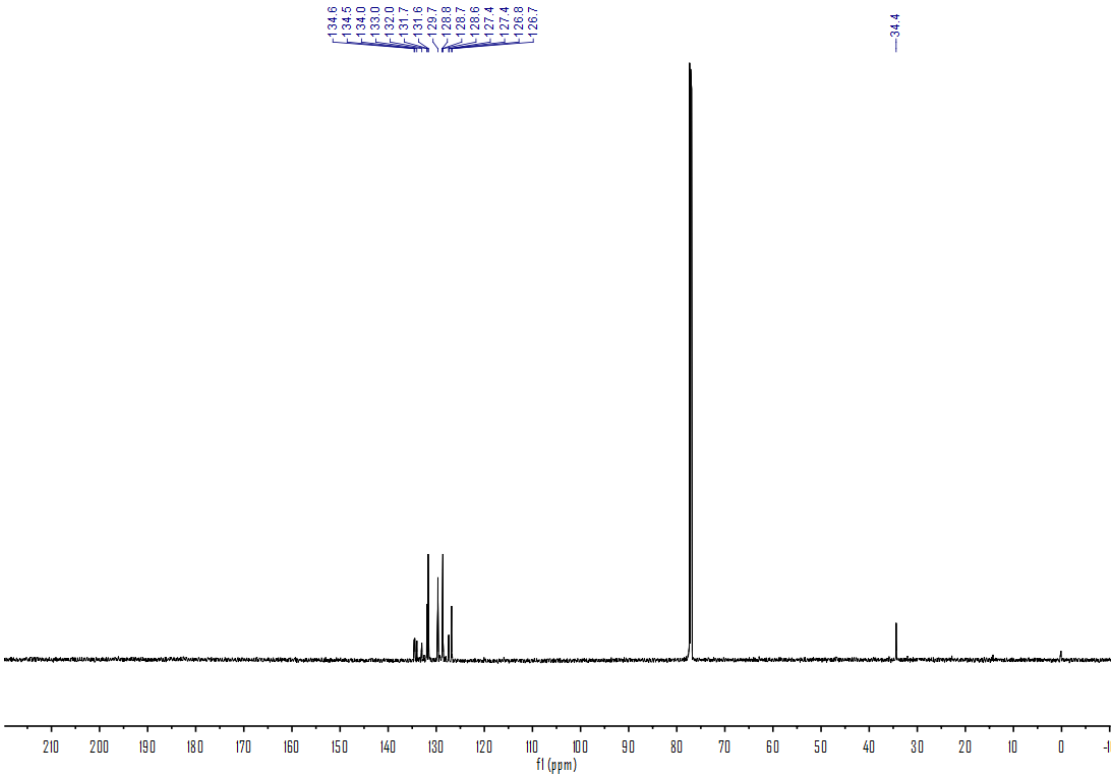


2ak

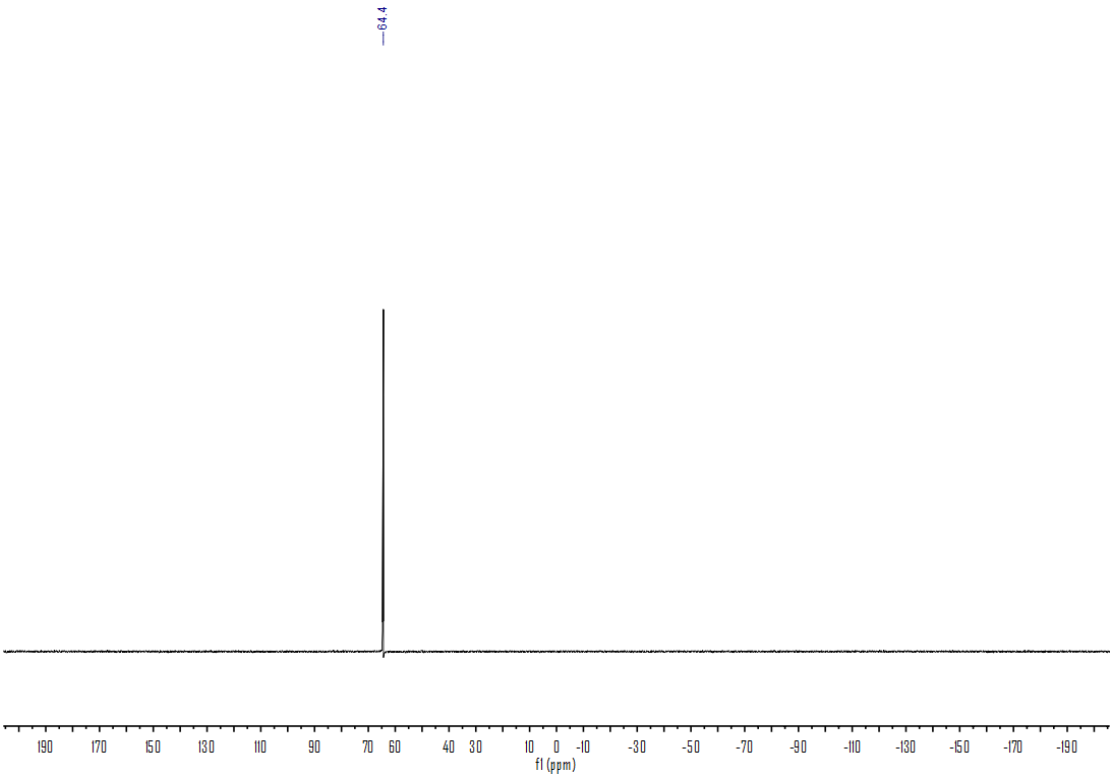
^{1}H NMR (600 MHz, $CDCl_3$)

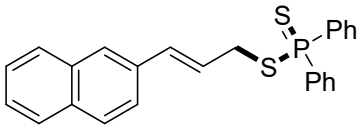


^{13}C NMR (151 MHz, $CDCl_3$)



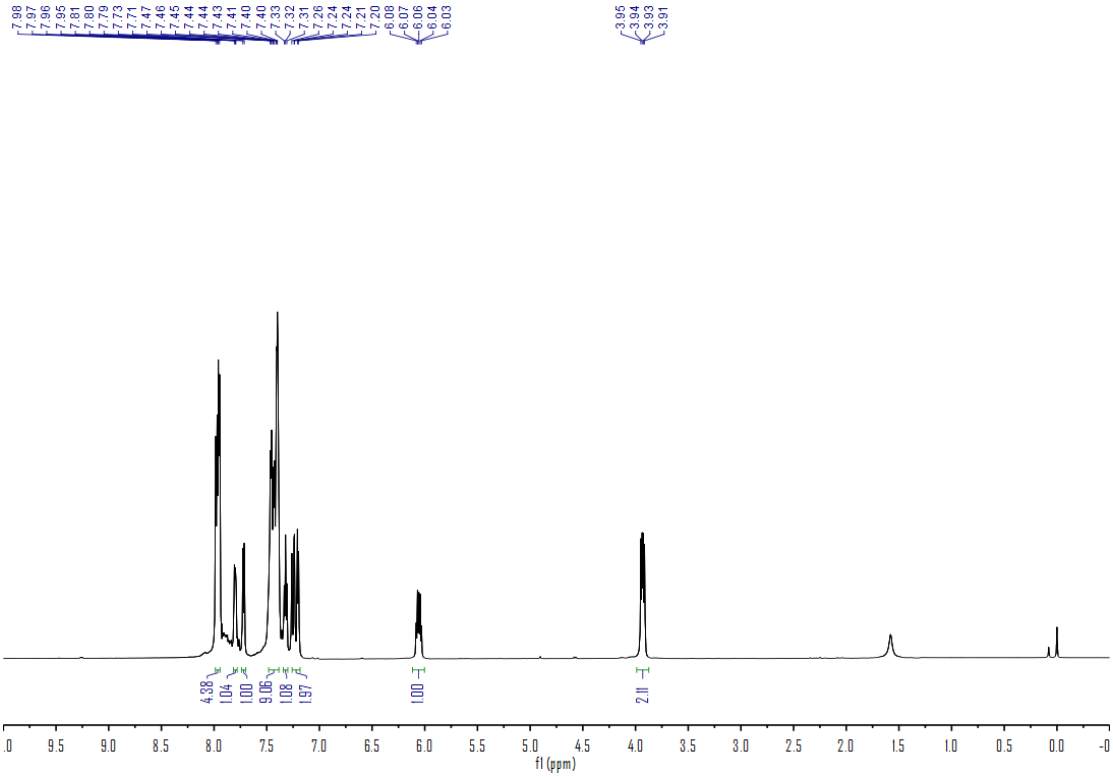
^{31}P NMR (243 MHz, $CDCl_3$)



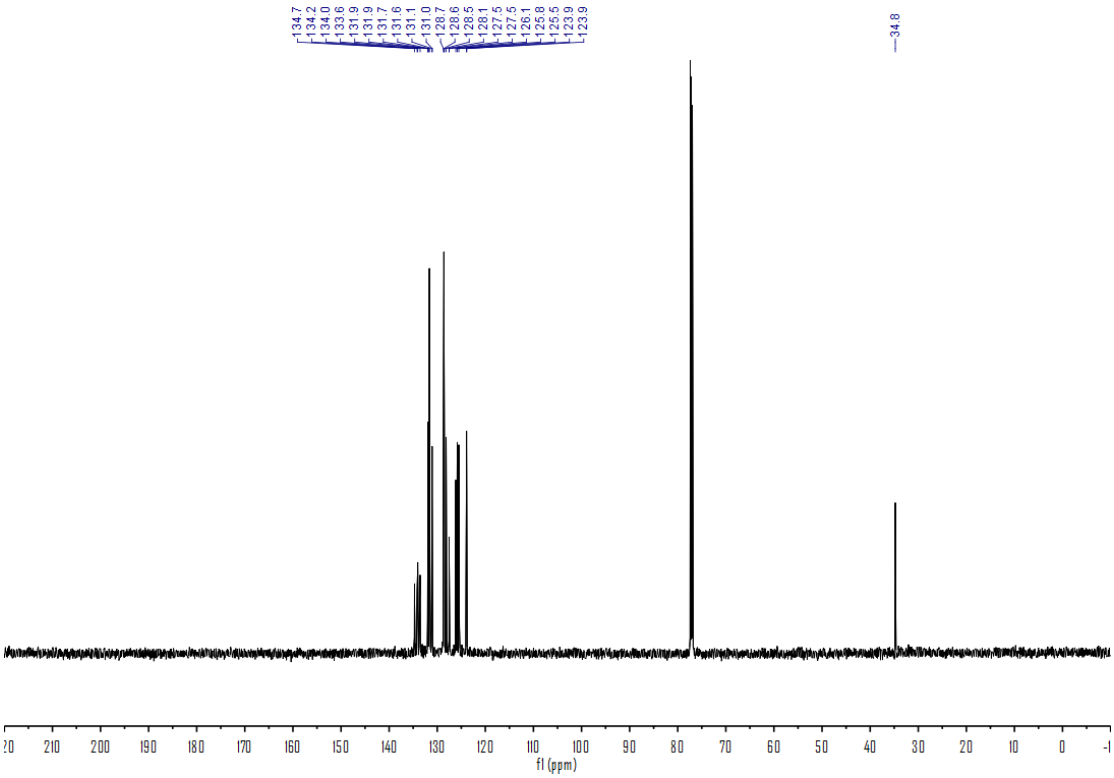


2al

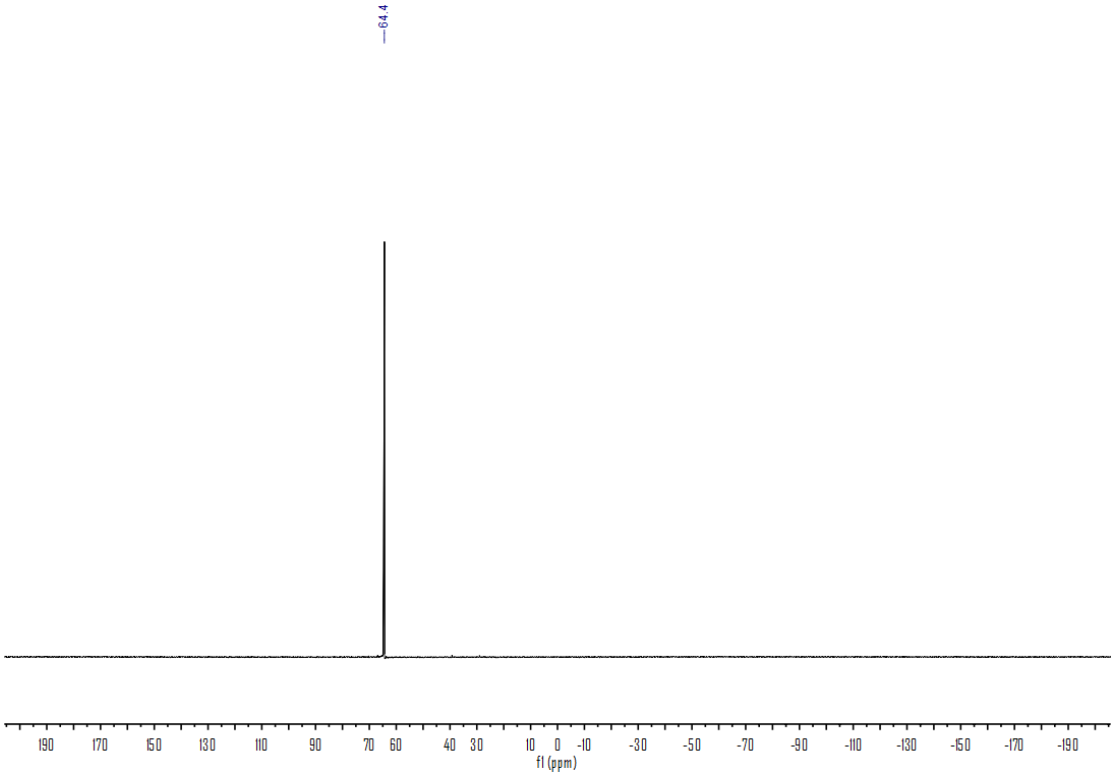
^{1}H NMR (600 MHz, $CDCl_3$)

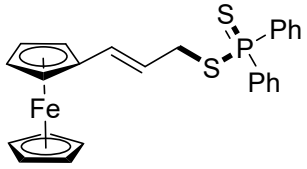


^{13}C NMR (151 MHz, $CDCl_3$)



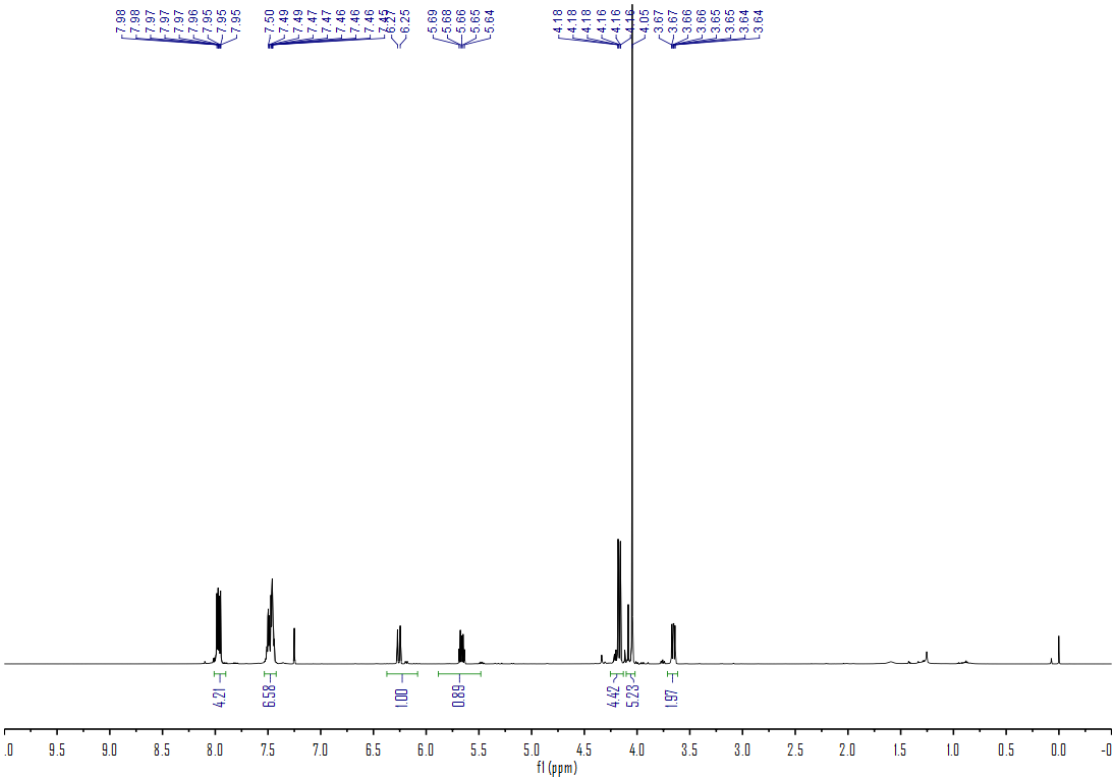
^{31}P NMR (243 MHz, $CDCl_3$)



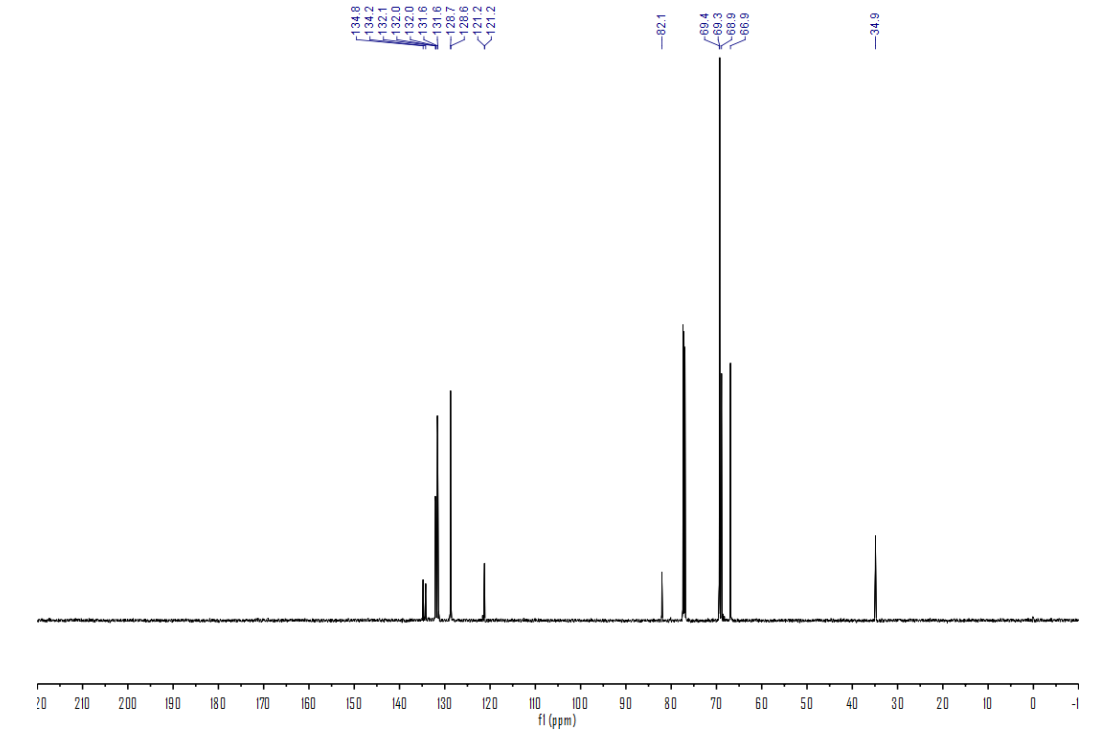


2am

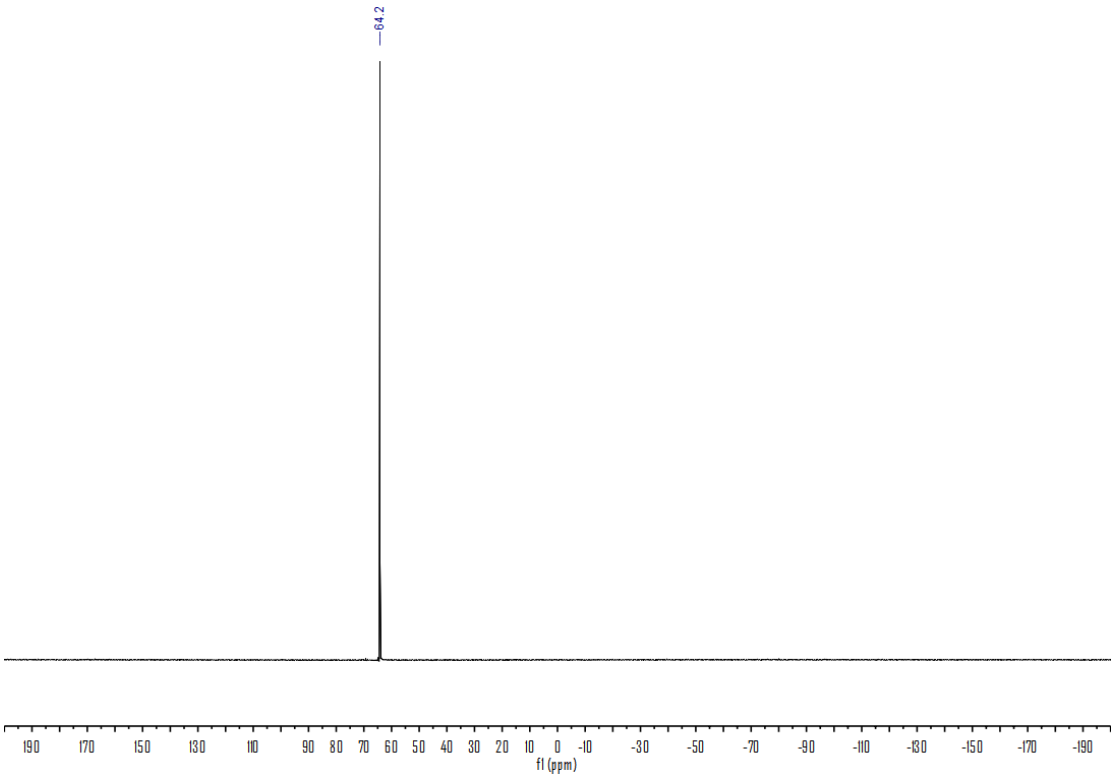
^{1}H NMR (600 MHz, $CDCl_3$)

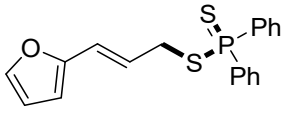


^{13}C NMR (151 MHz, $CDCl_3$)



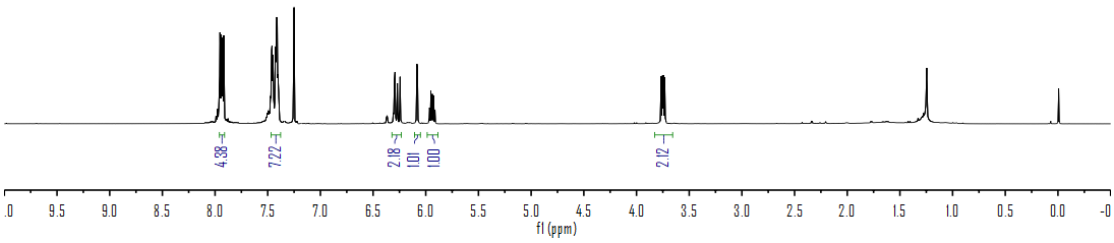
^{31}P NMR (243 MHz, $CDCl_3$)



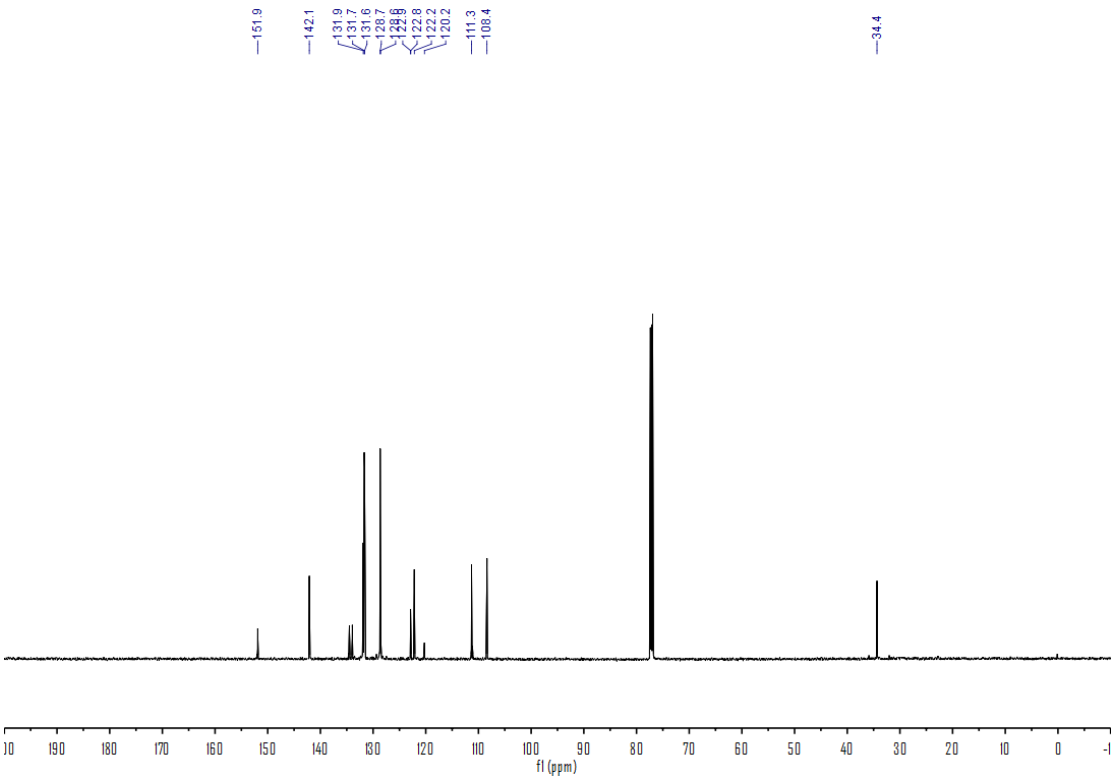


2an

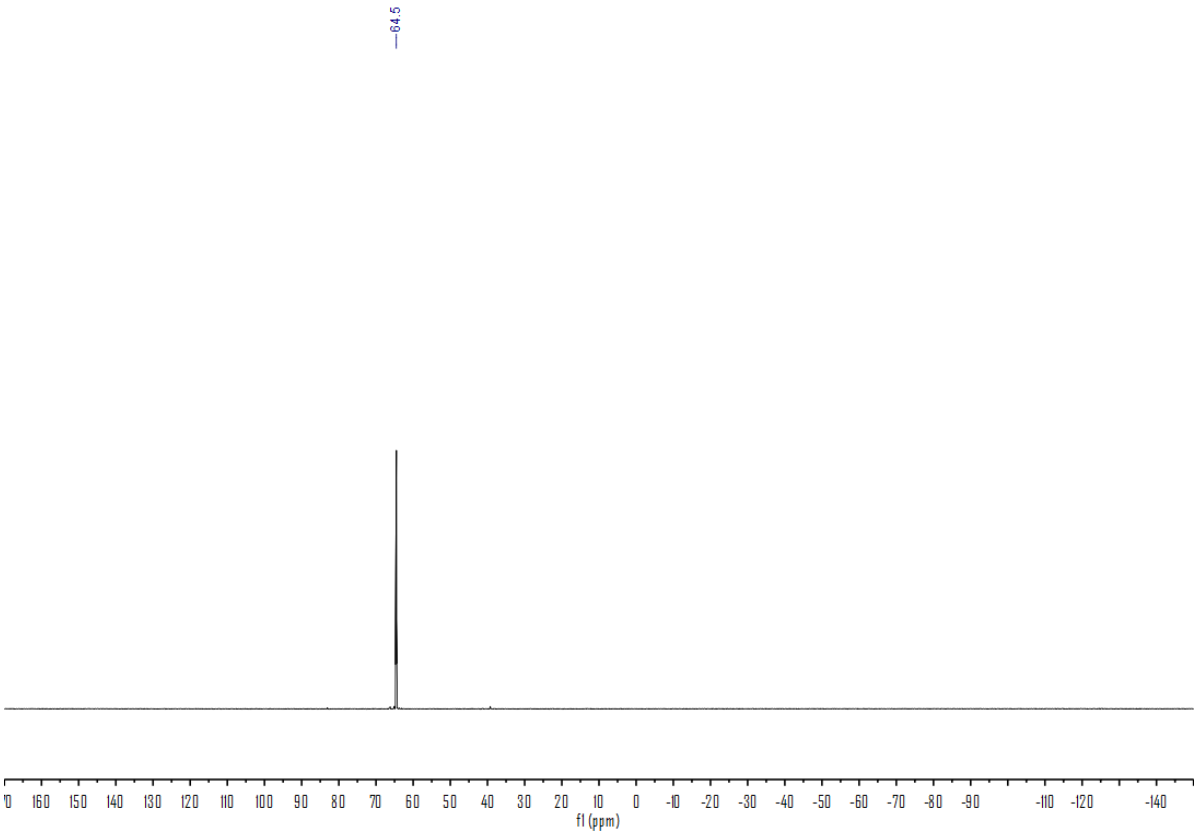
^{1}H NMR (600 MHz, $CDCl_3$)

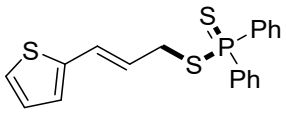


^{13}C NMR (151 MHz, $CDCl_3$)



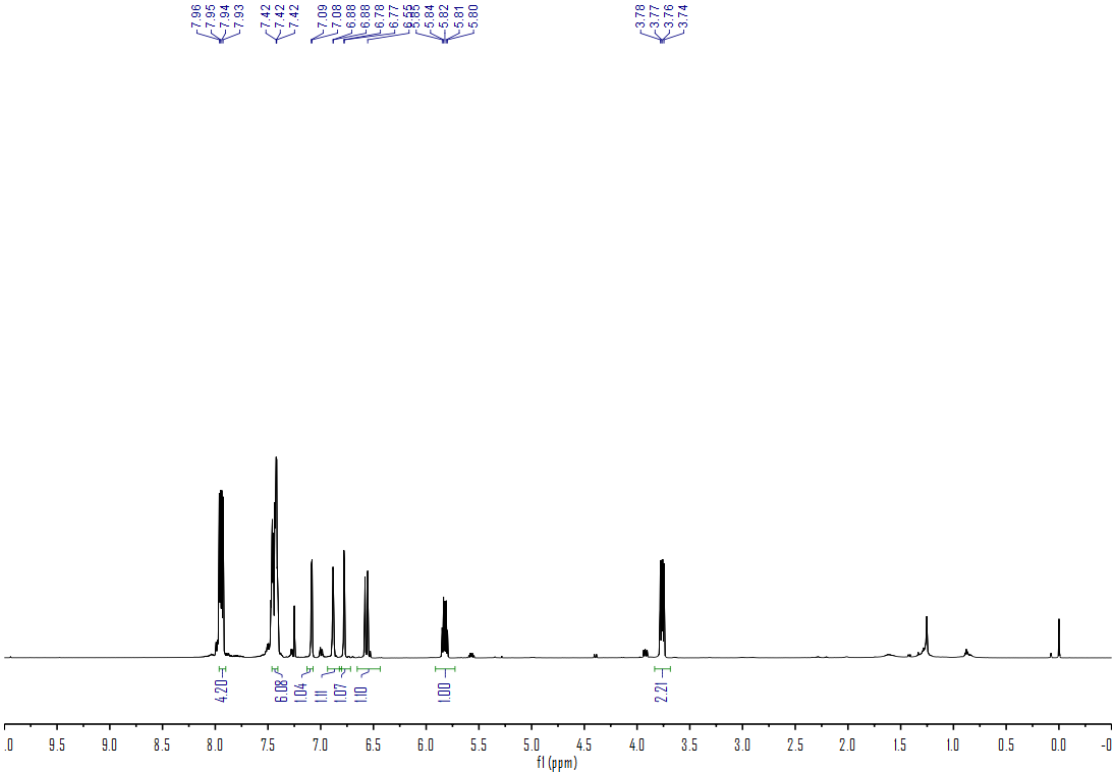
^{31}P NMR (243 MHz, $CDCl_3$)



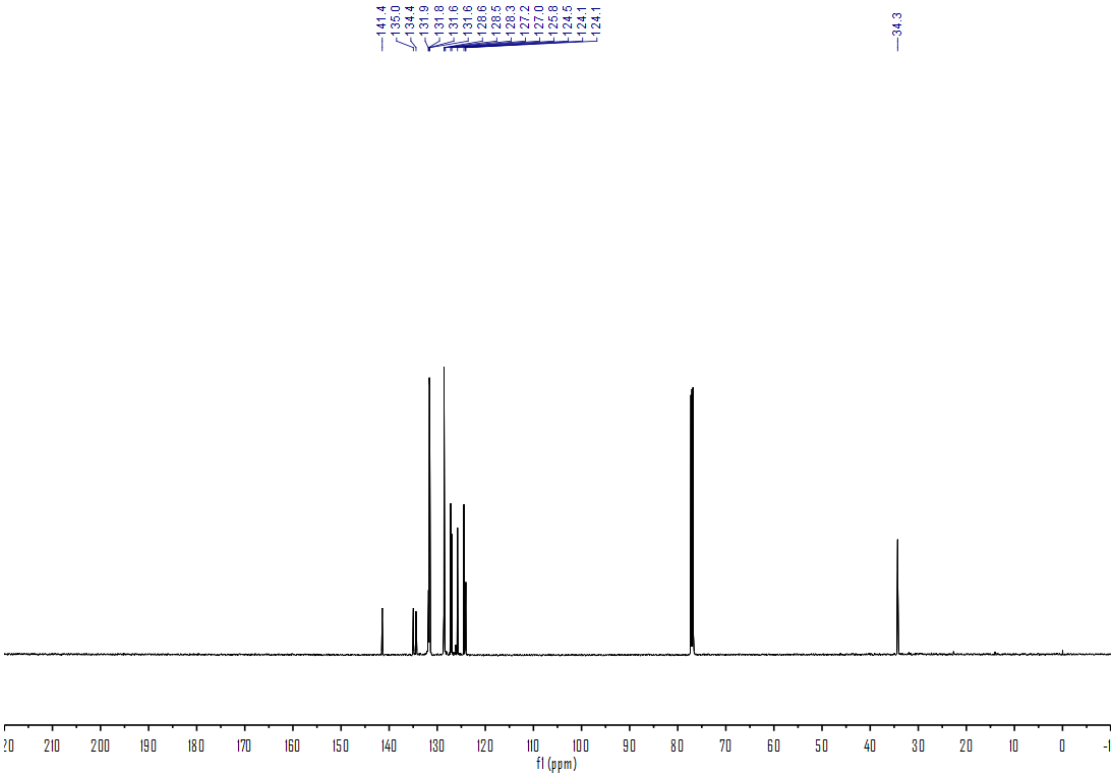


2ao

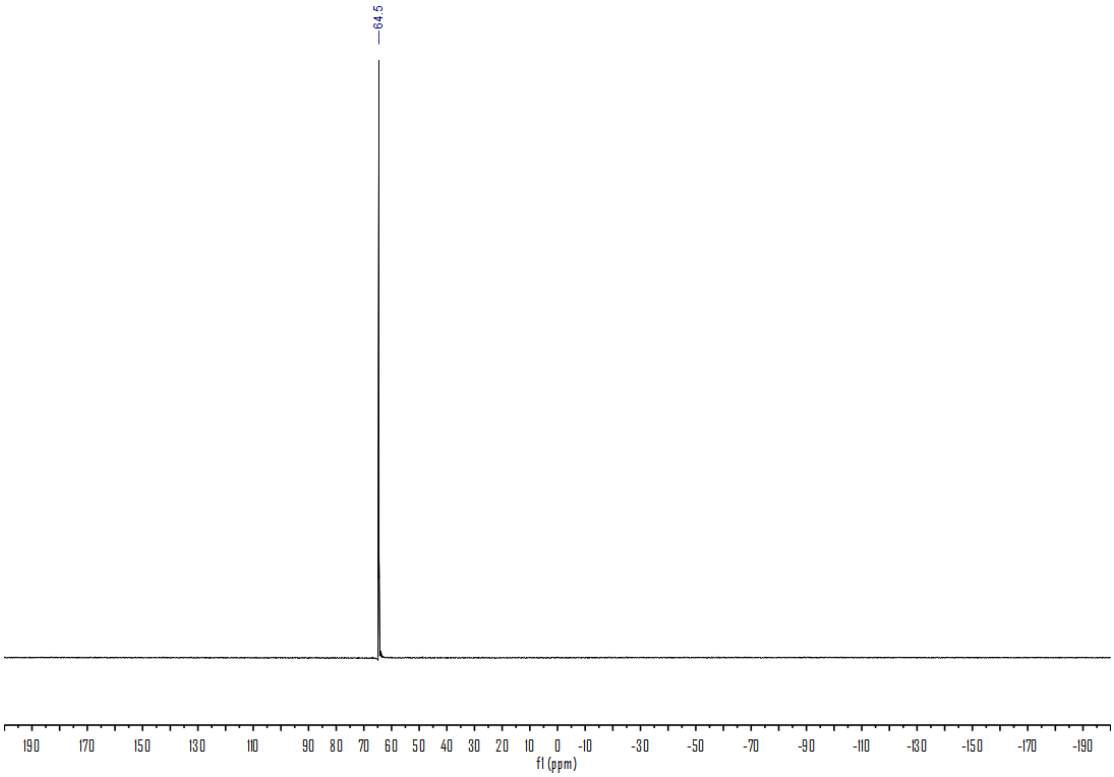
^{1}H NMR (600 MHz, $CDCl_3$)

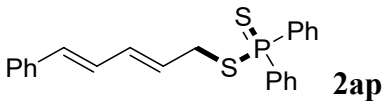


^{13}C NMR (151 MHz, $CDCl_3$)



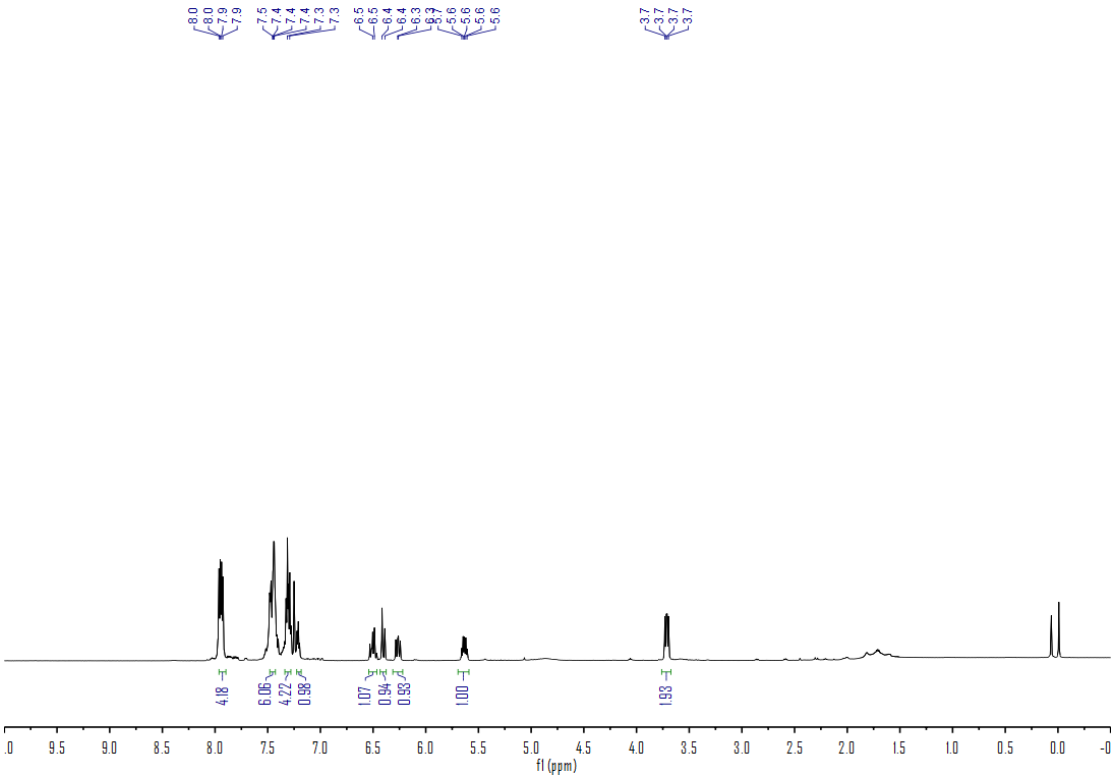
^{31}P NMR (243 MHz, $CDCl_3$)



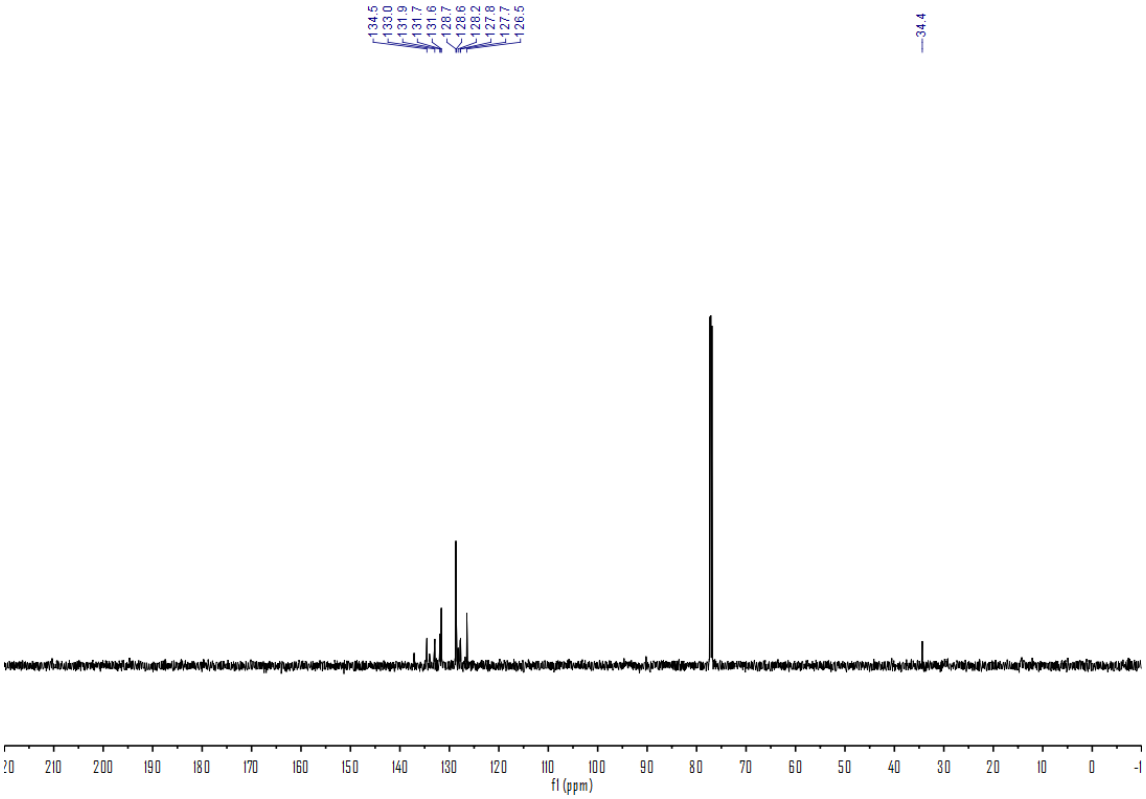


2ap

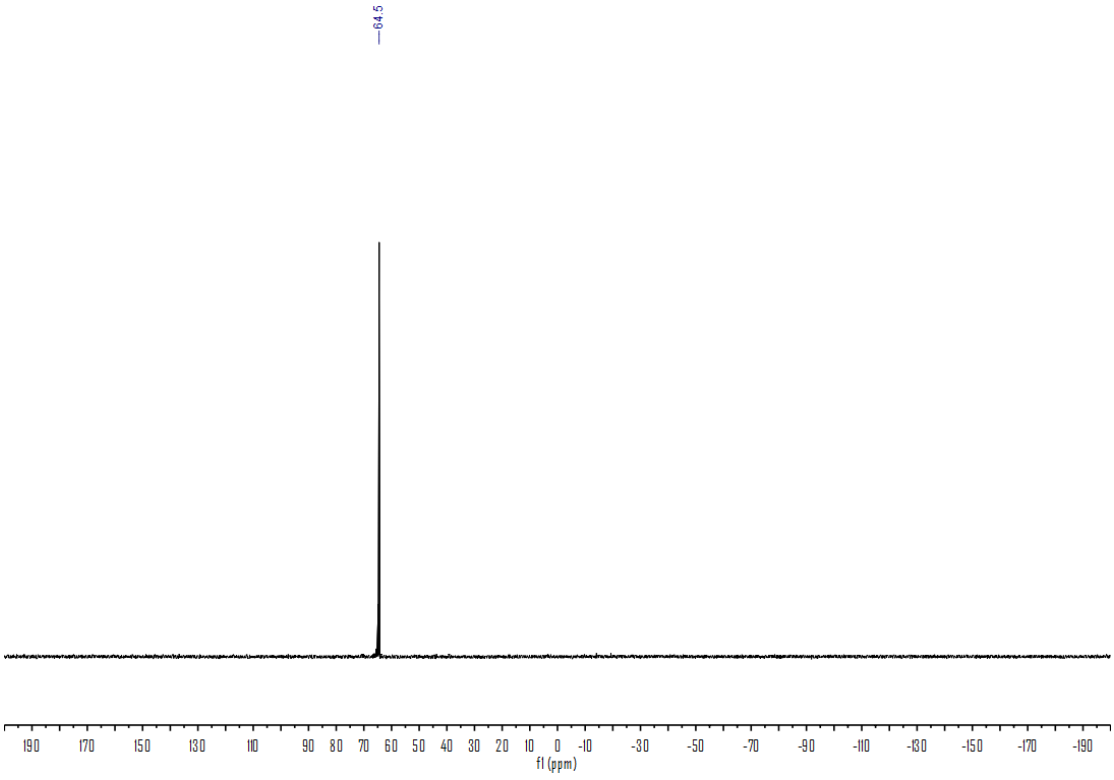
^{1}H NMR (600 MHz, $CDCl_3$)

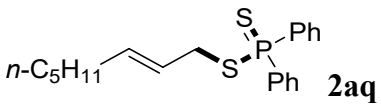


^{13}C NMR (151 MHz, $CDCl_3$)



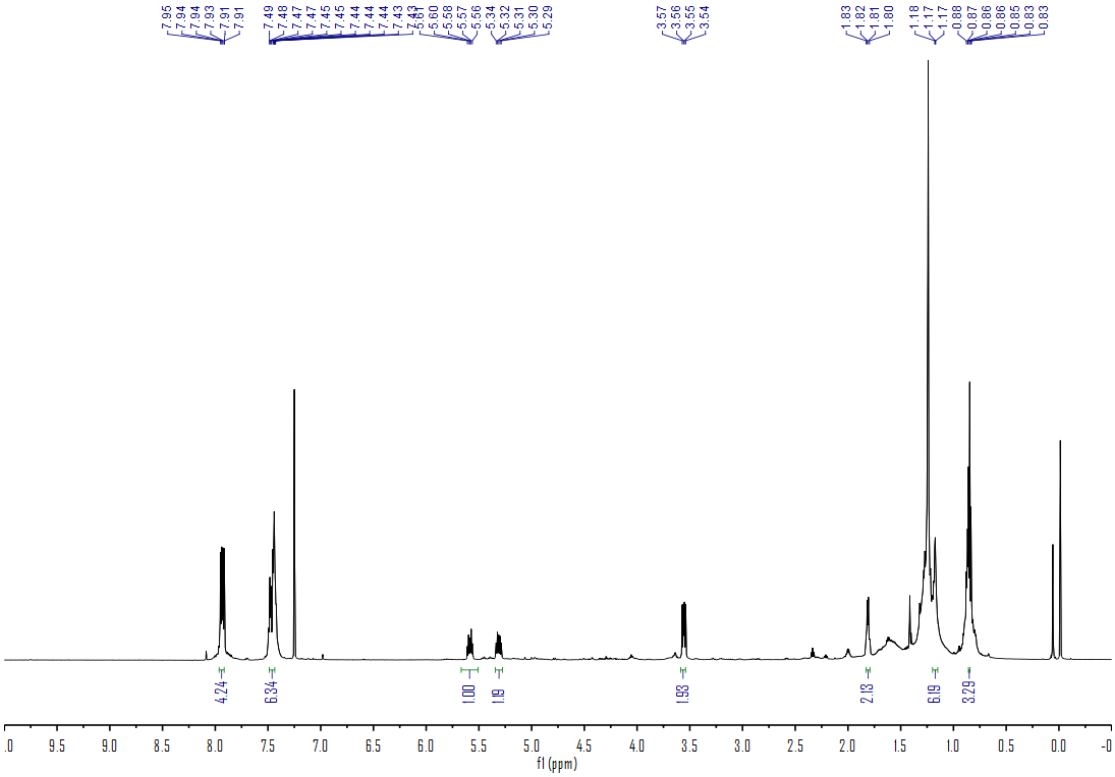
^{31}P NMR (243 MHz, $CDCl_3$)



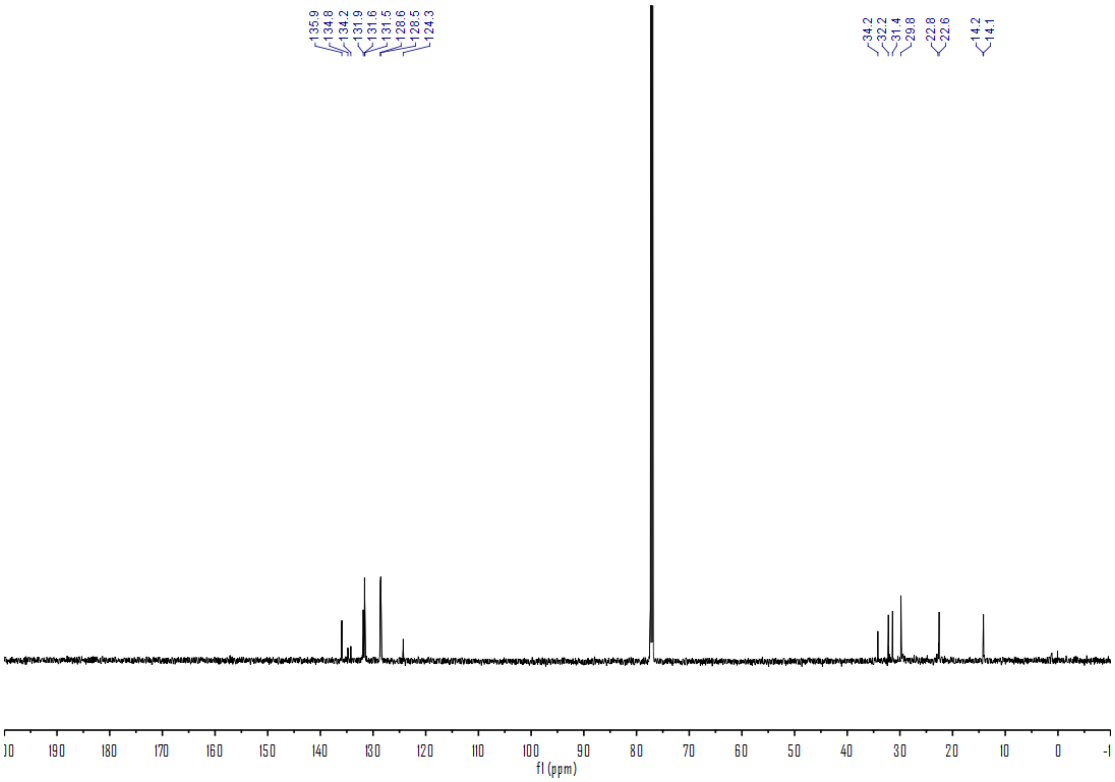


2aq

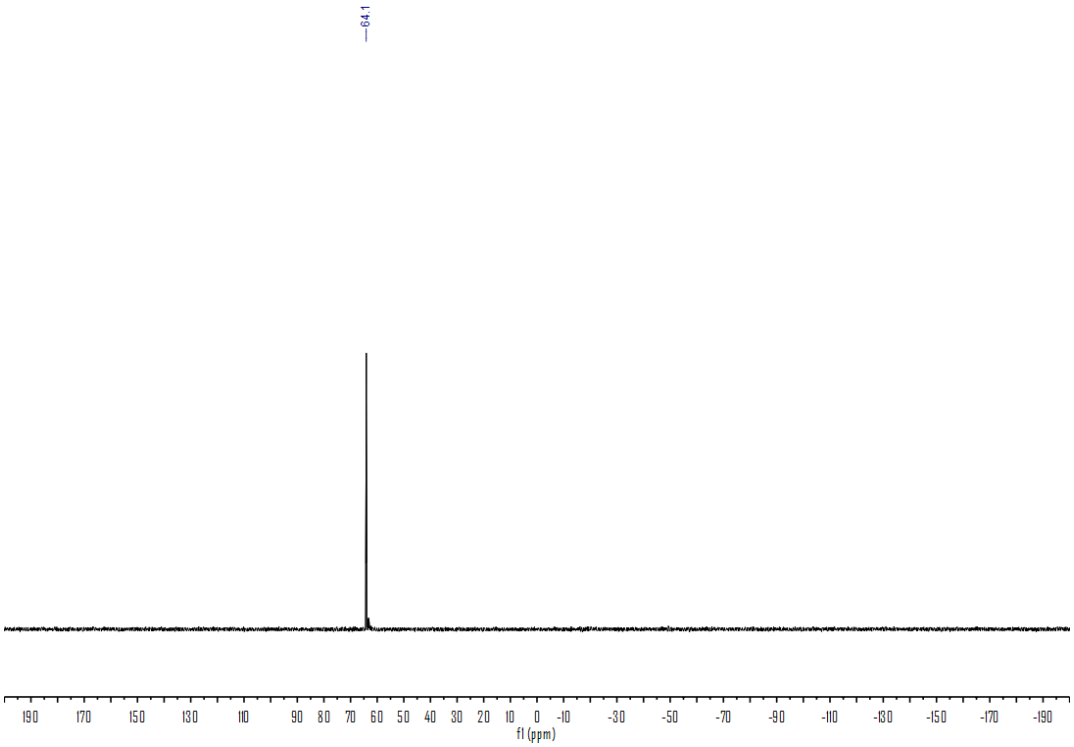
^{1}H NMR (600 MHz, $CDCl_3$)

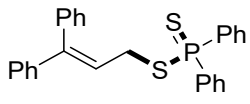


^{13}C NMR (151 MHz, $CDCl_3$)



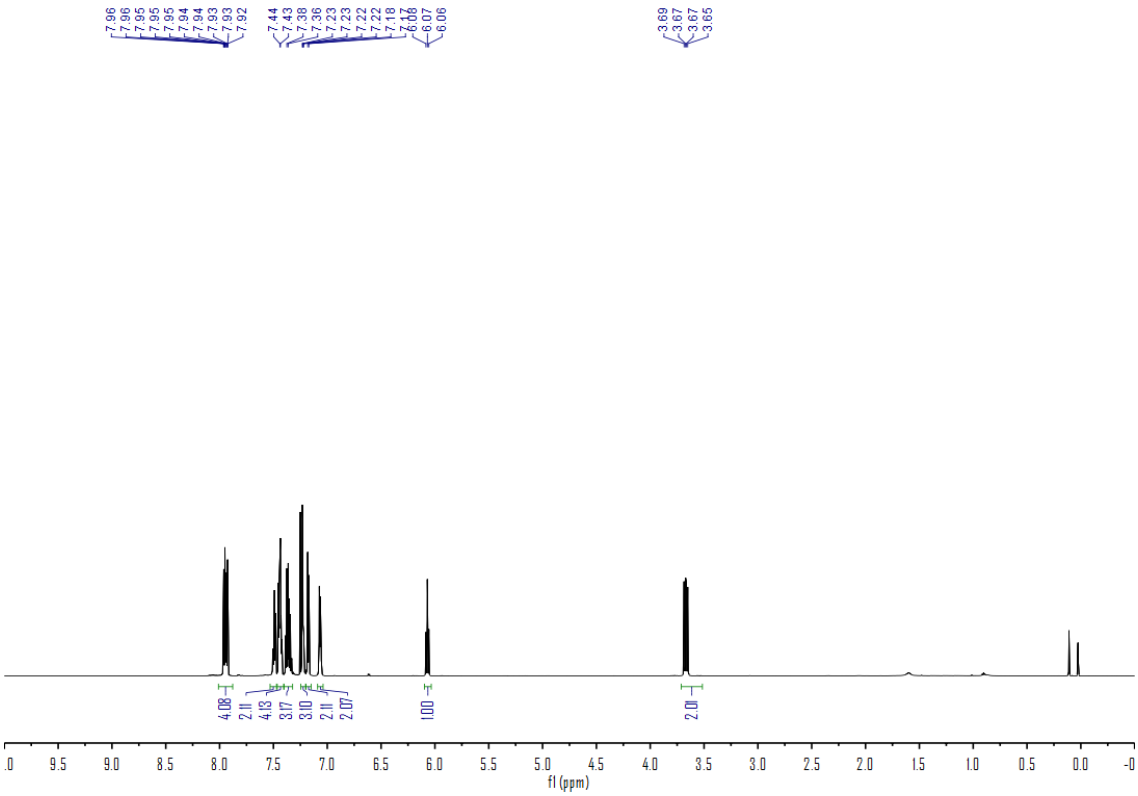
^{31}P NMR (243 MHz, $CDCl_3$)



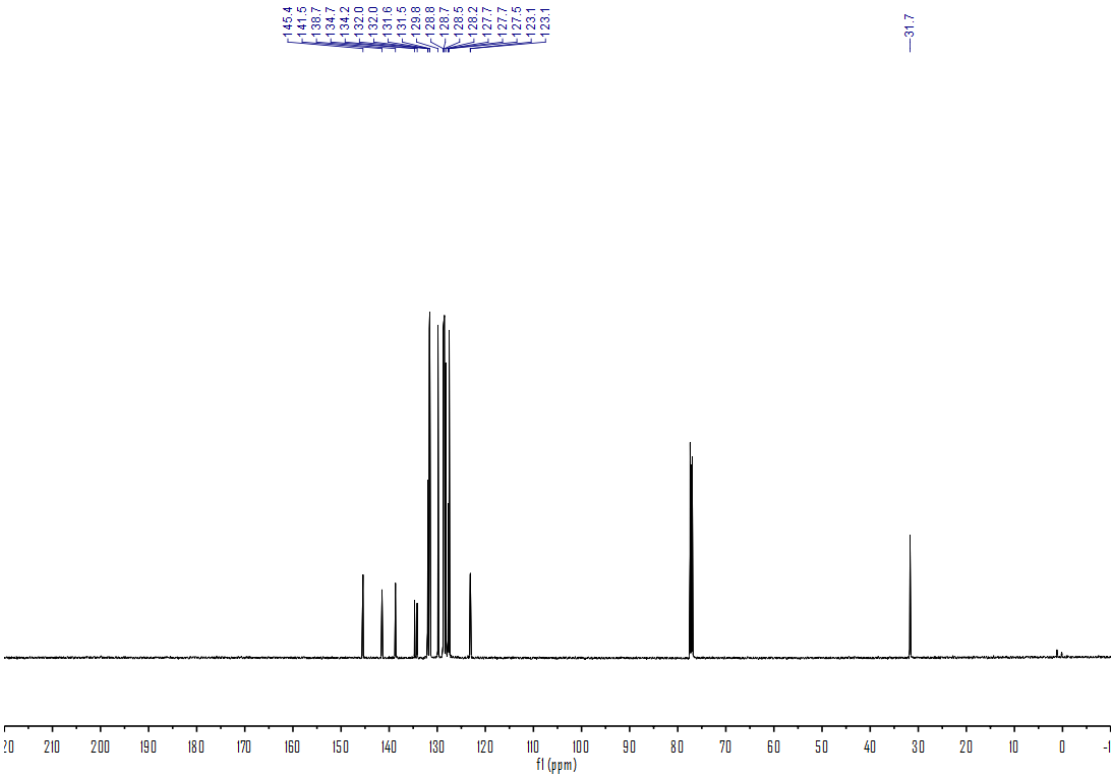


2ar

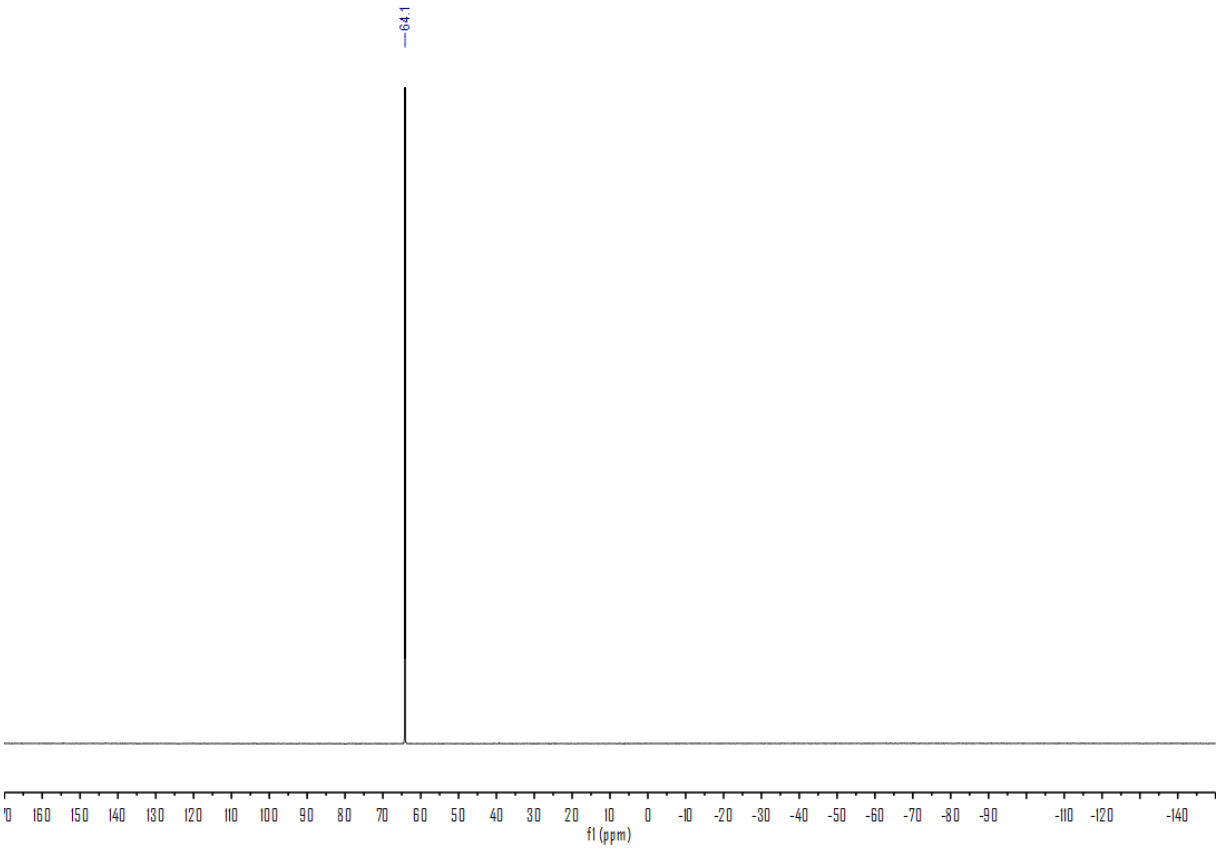
^{1}H NMR (600 MHz, $CDCl_3$)

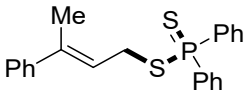


^{13}C NMR (151 MHz, $CDCl_3$)



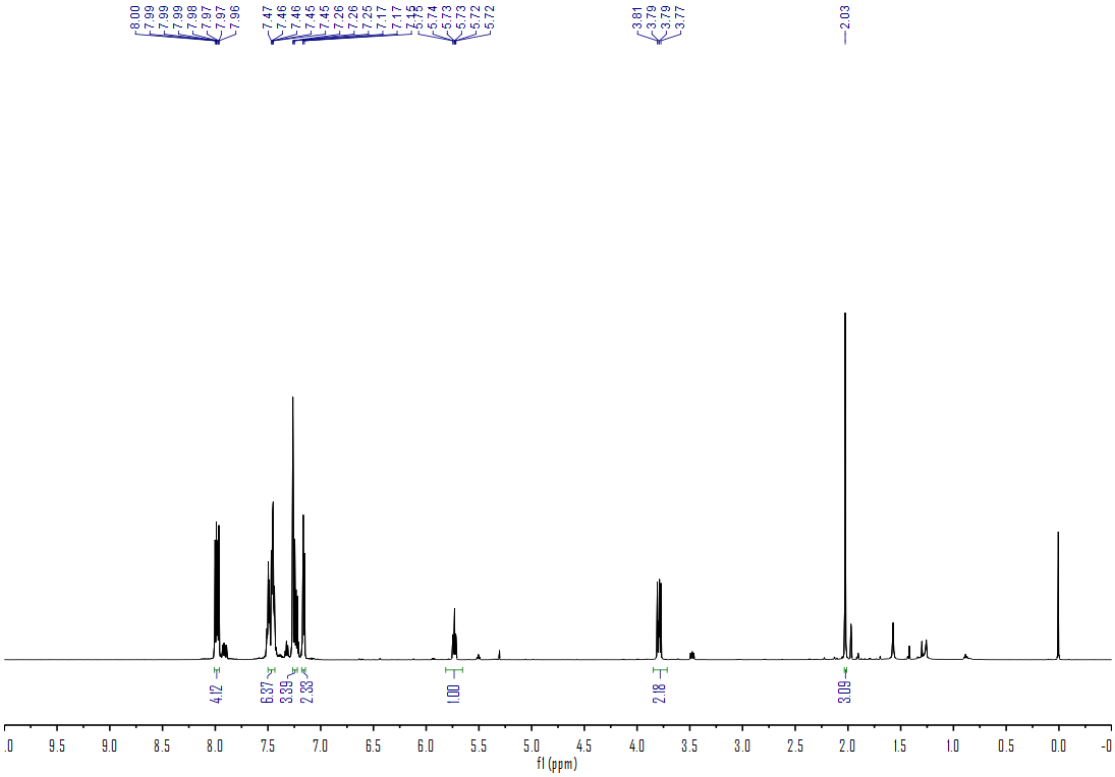
^{31}P NMR (243 MHz, $CDCl_3$)



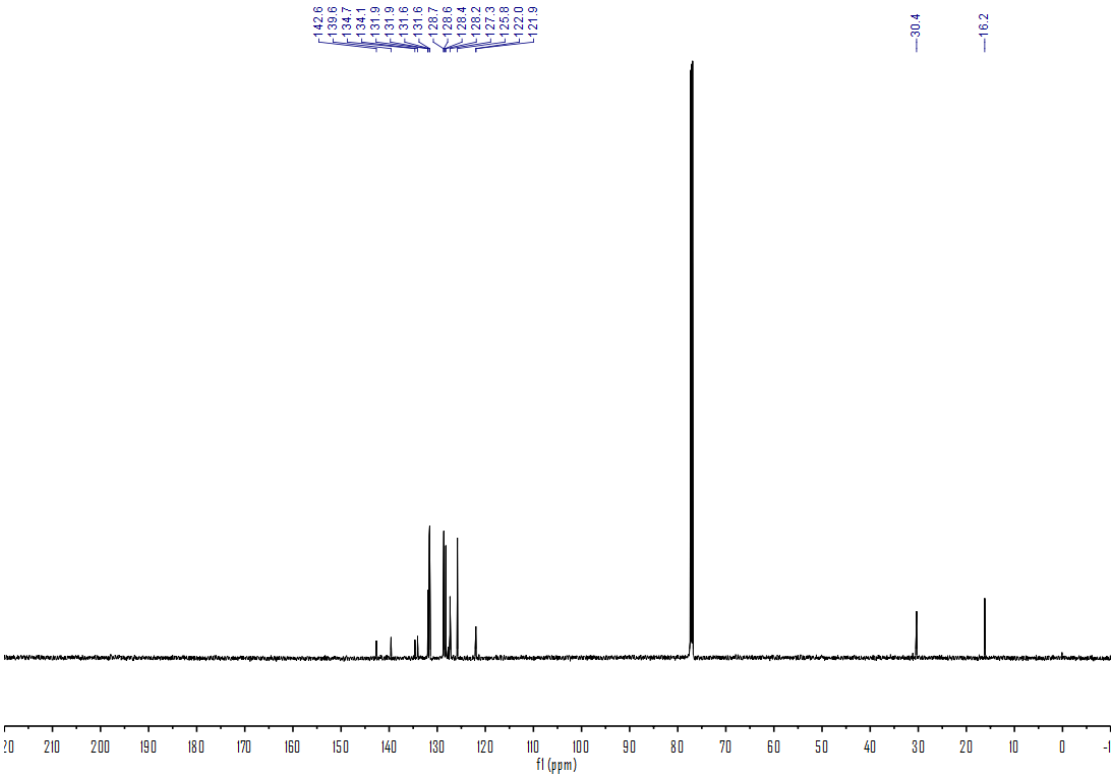


2as

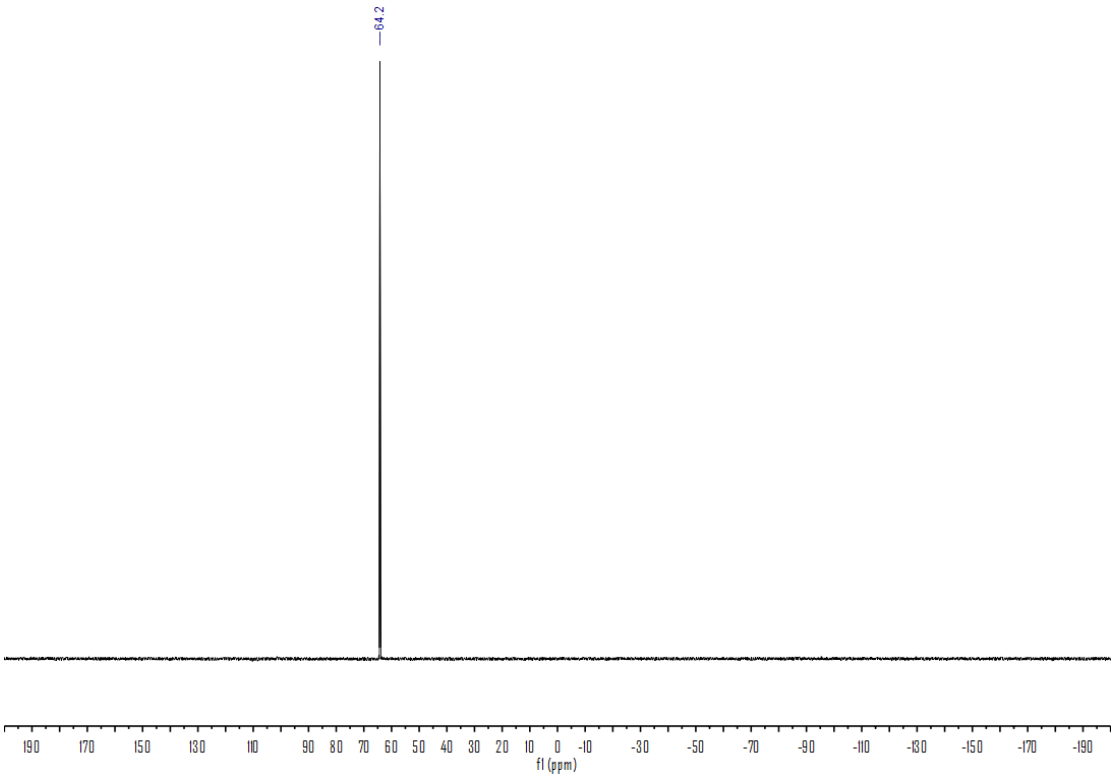
^{1}H NMR (600 MHz, $CDCl_3$)

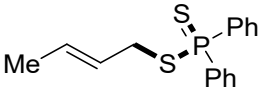


^{13}C NMR (151 MHz, $CDCl_3$)



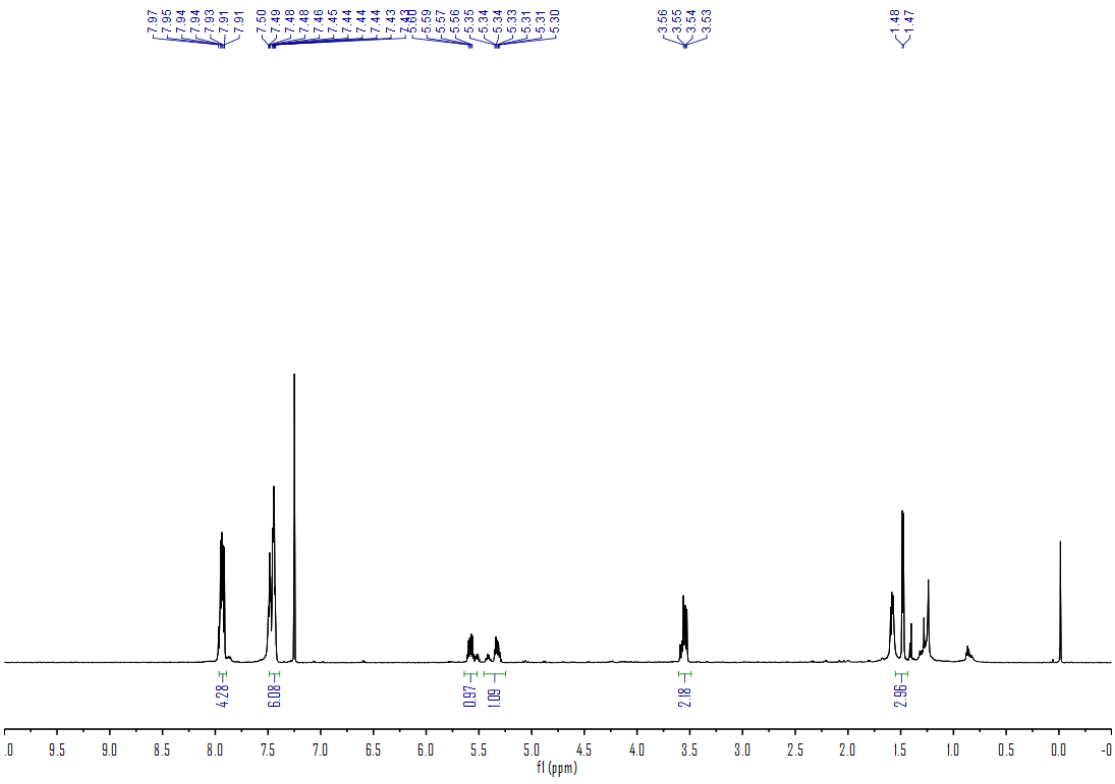
^{31}P NMR (243 MHz, $CDCl_3$)



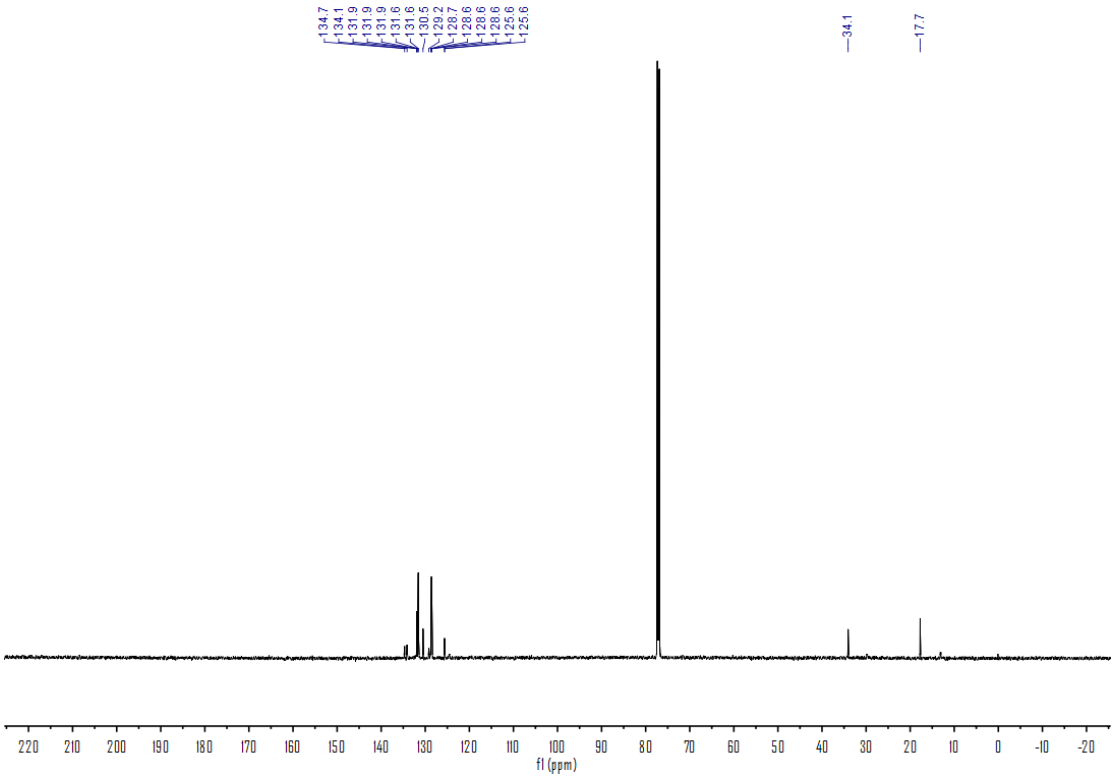


2at

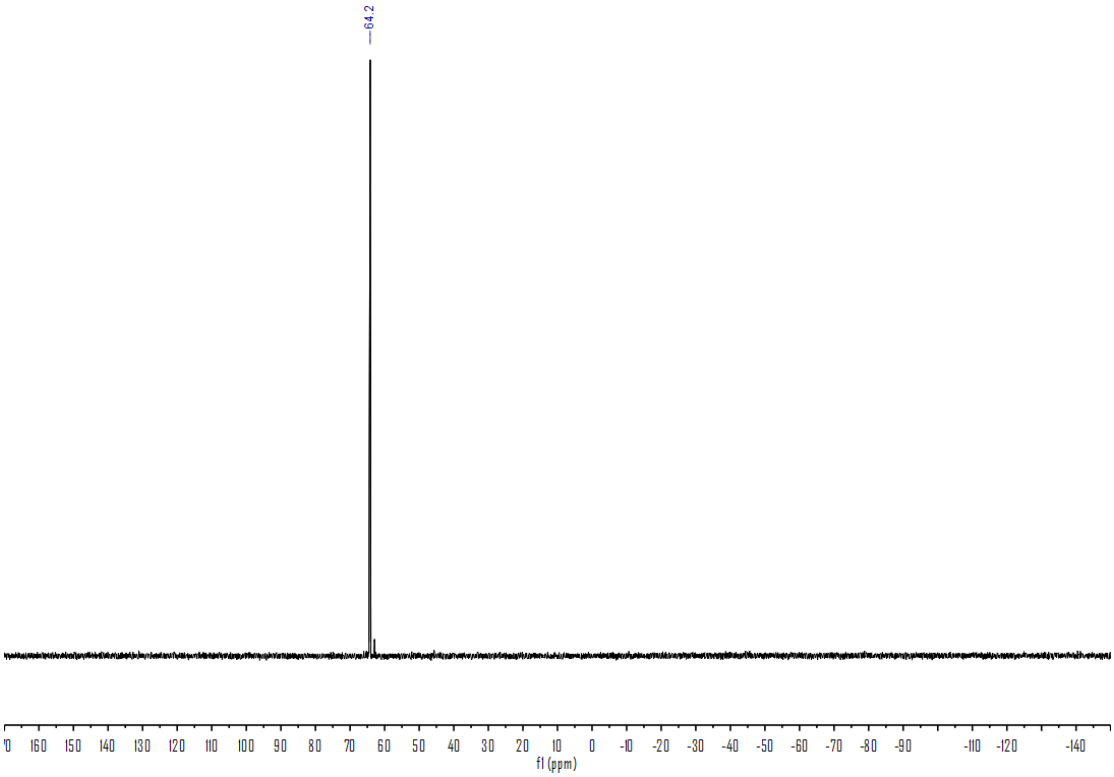
^{1}H NMR (600 MHz, $CDCl_3$)

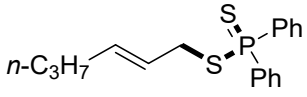


^{13}C NMR (151 MHz, $CDCl_3$)



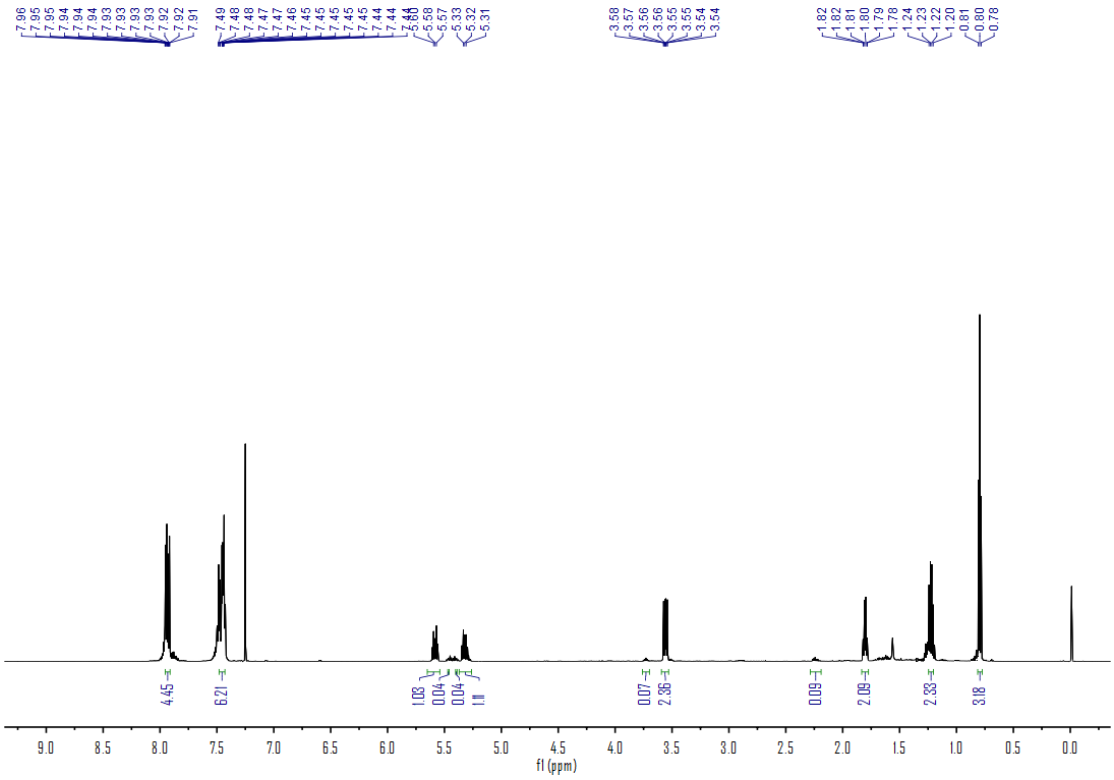
^{31}P NMR (243 MHz, $CDCl_3$)



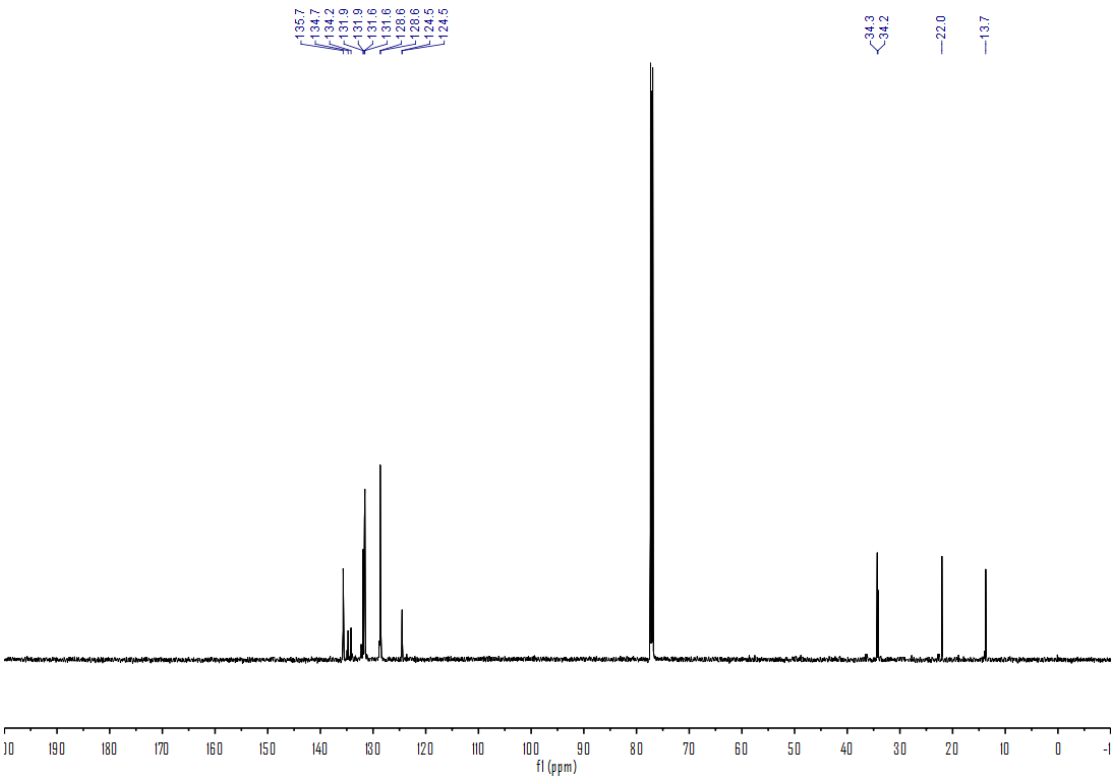


2au

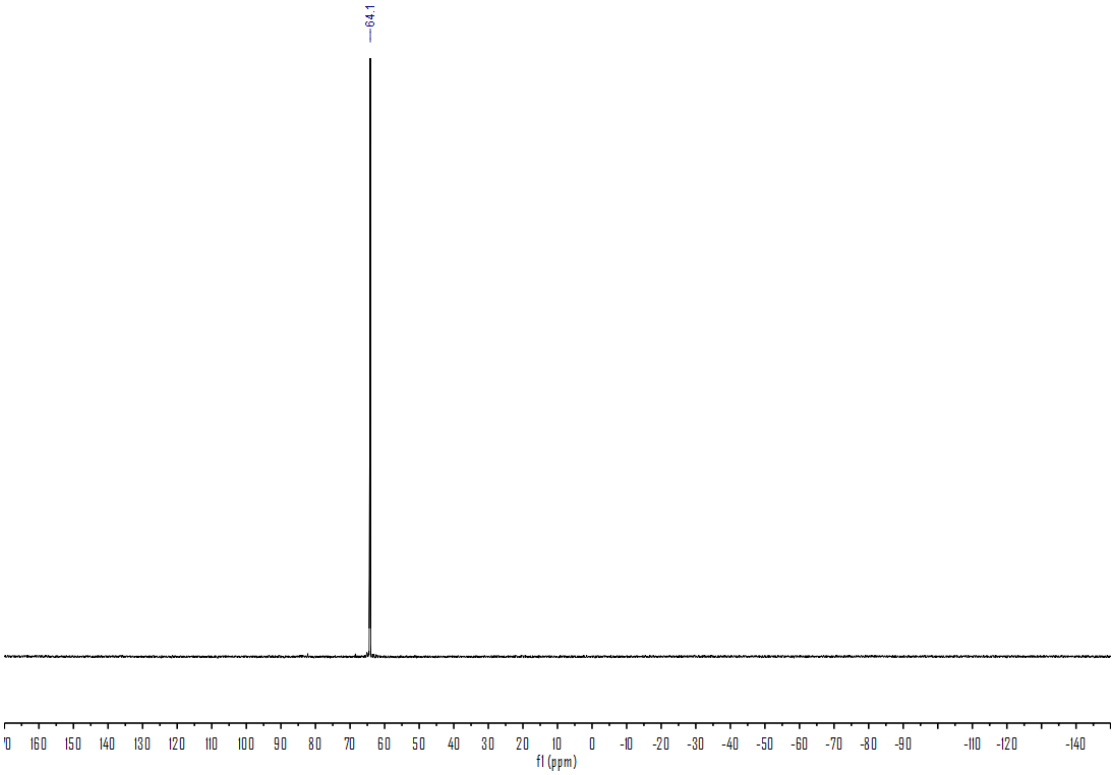
^{1}H NMR (600 MHz, $CDCl_3$)

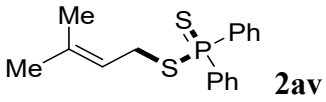


^{13}C NMR (151 MHz, $CDCl_3$)



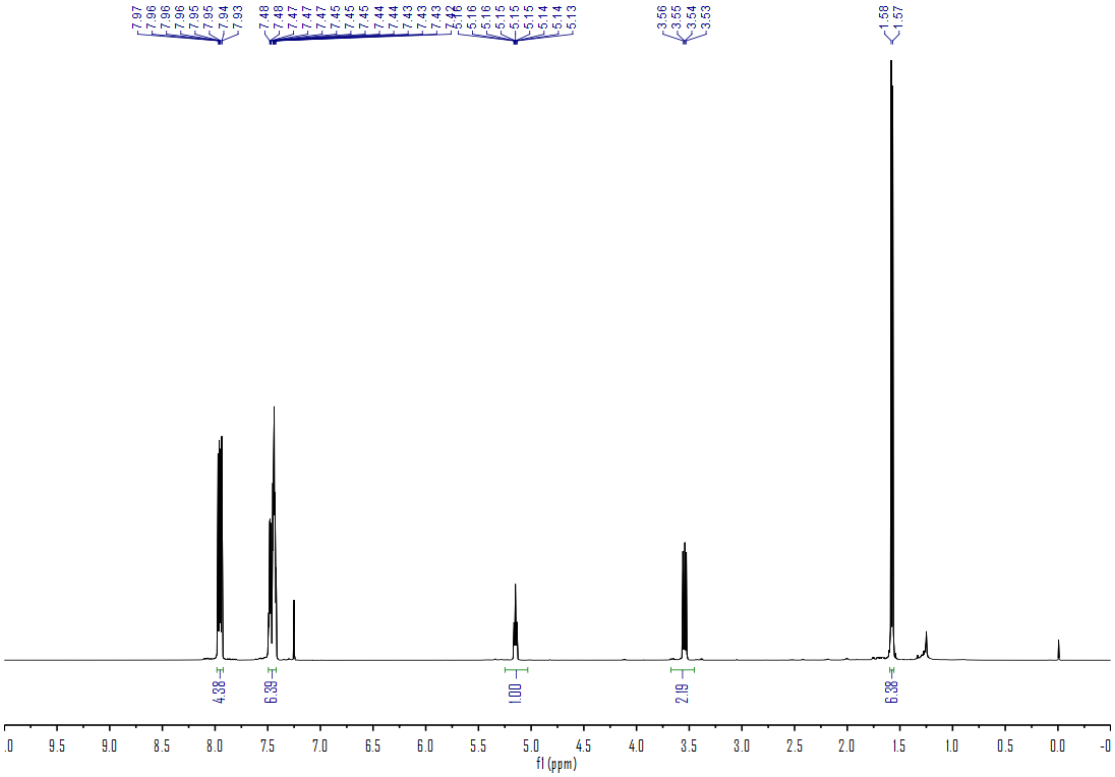
^{31}P NMR (243 MHz, $CDCl_3$)



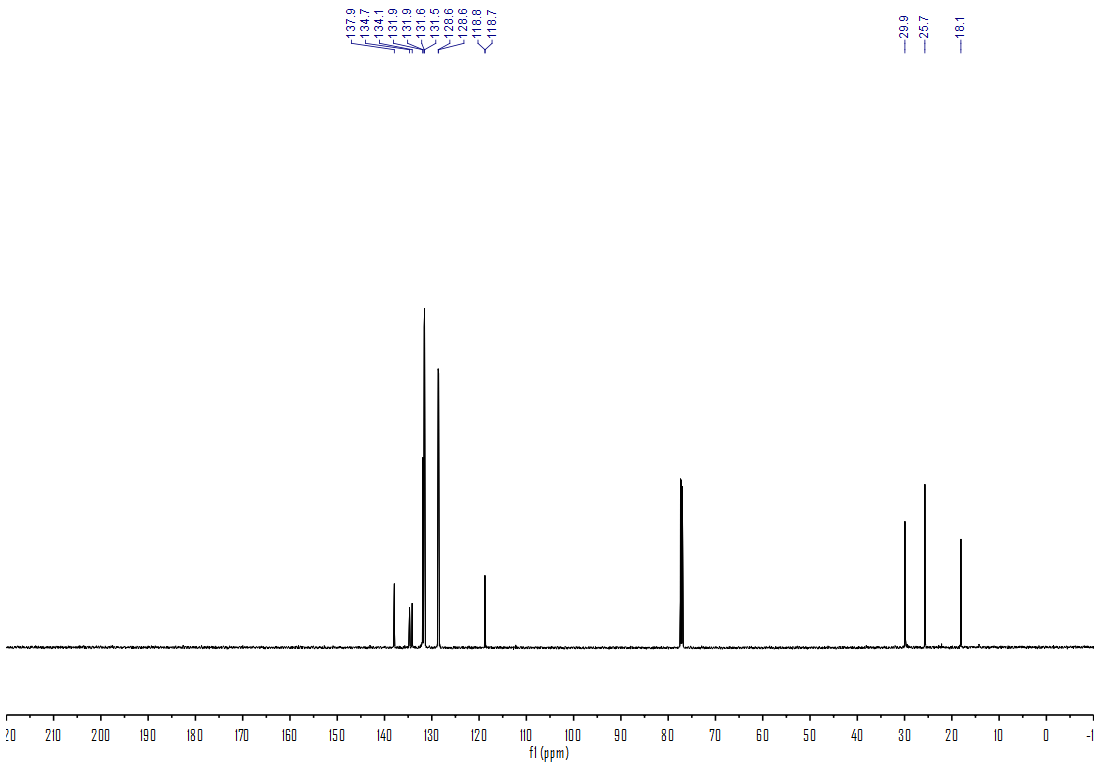


2av

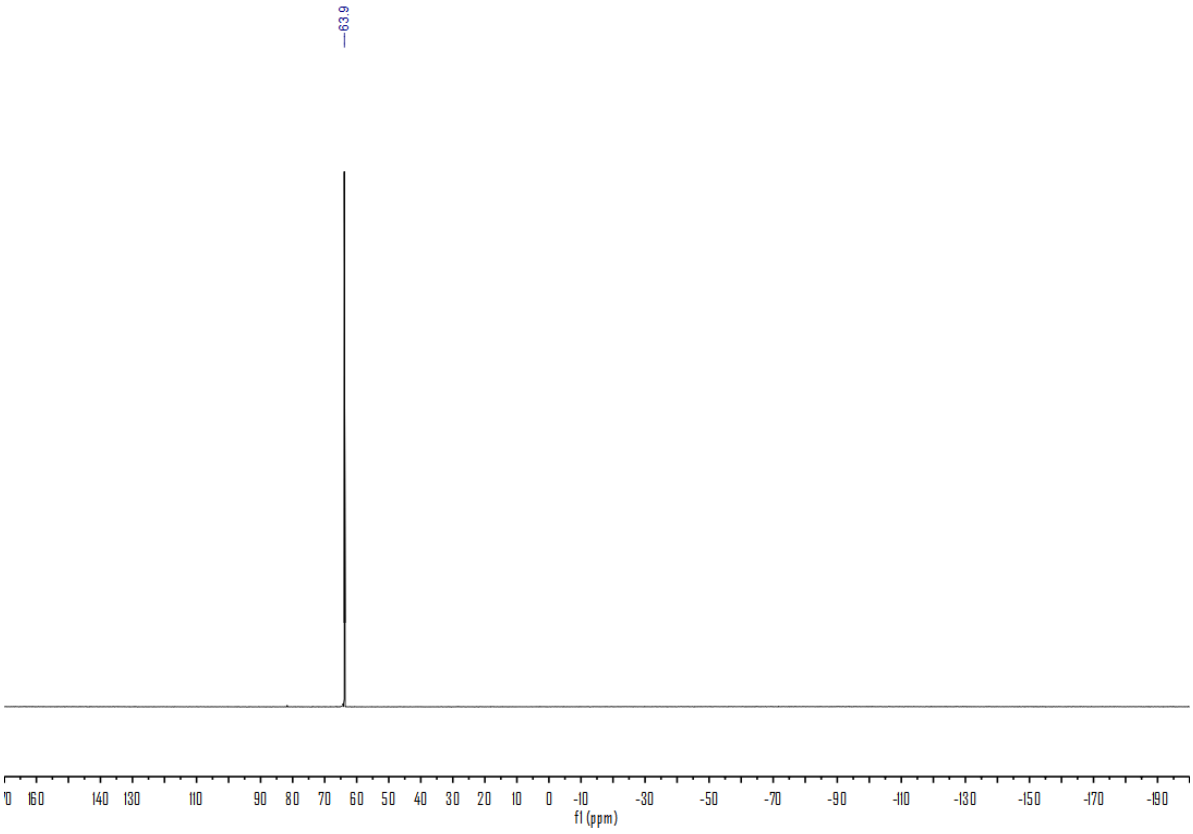
^{1}H NMR (600 MHz, $CDCl_3$)

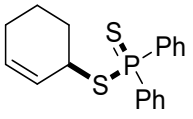


^{13}C NMR (151 MHz, $CDCl_3$)



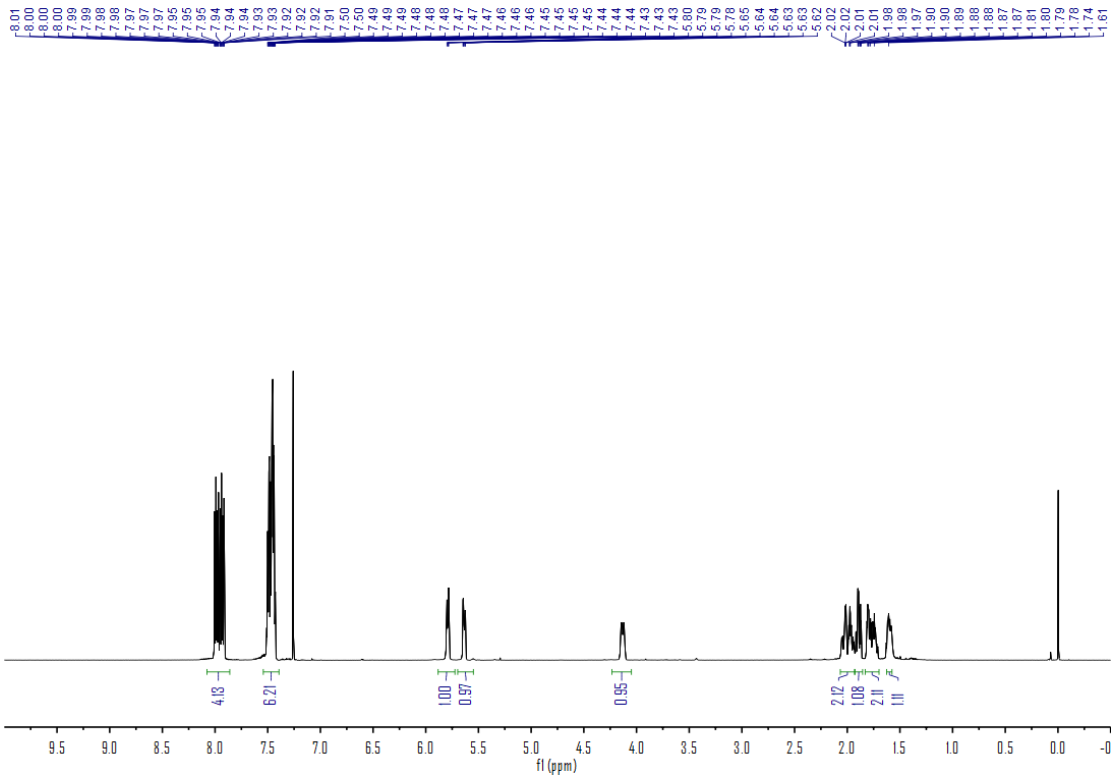
^{31}P NMR (243 MHz, $CDCl_3$)



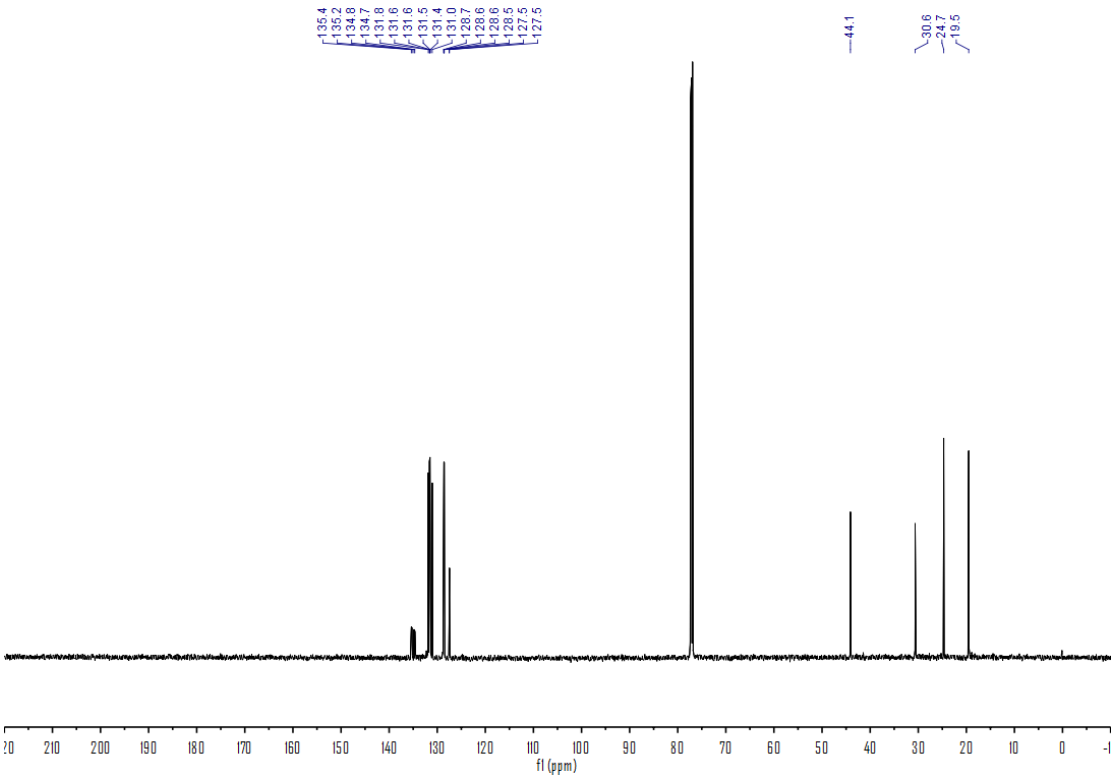


2aw

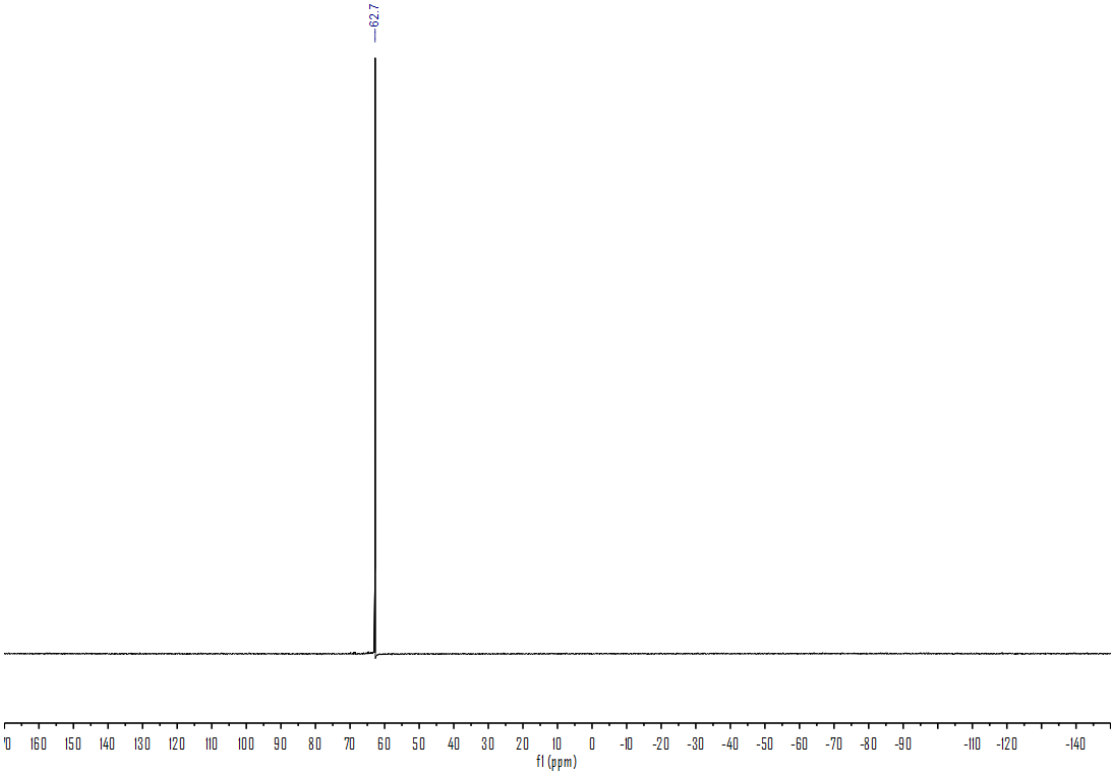
^{1}H NMR (600 MHz, $CDCl_3$)

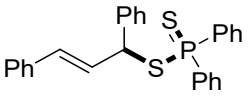


^{13}C NMR (151 MHz, $CDCl_3$)



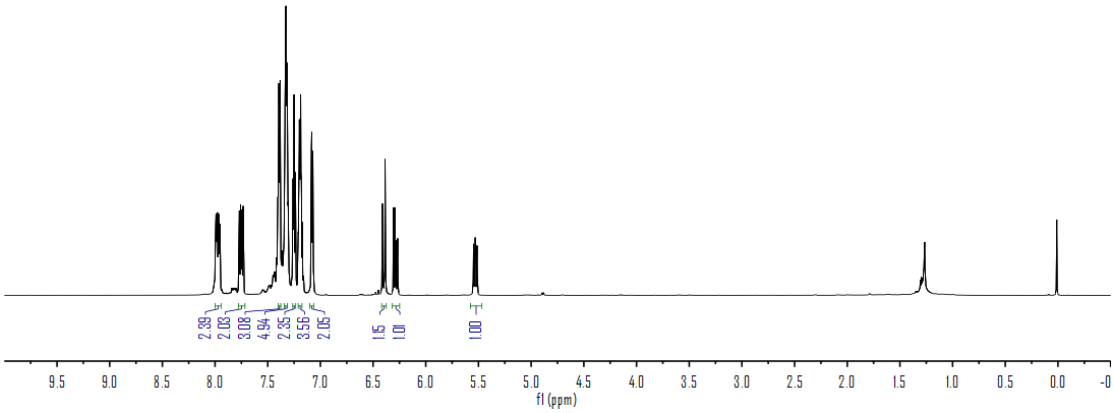
^{31}P NMR (243 MHz, $CDCl_3$)



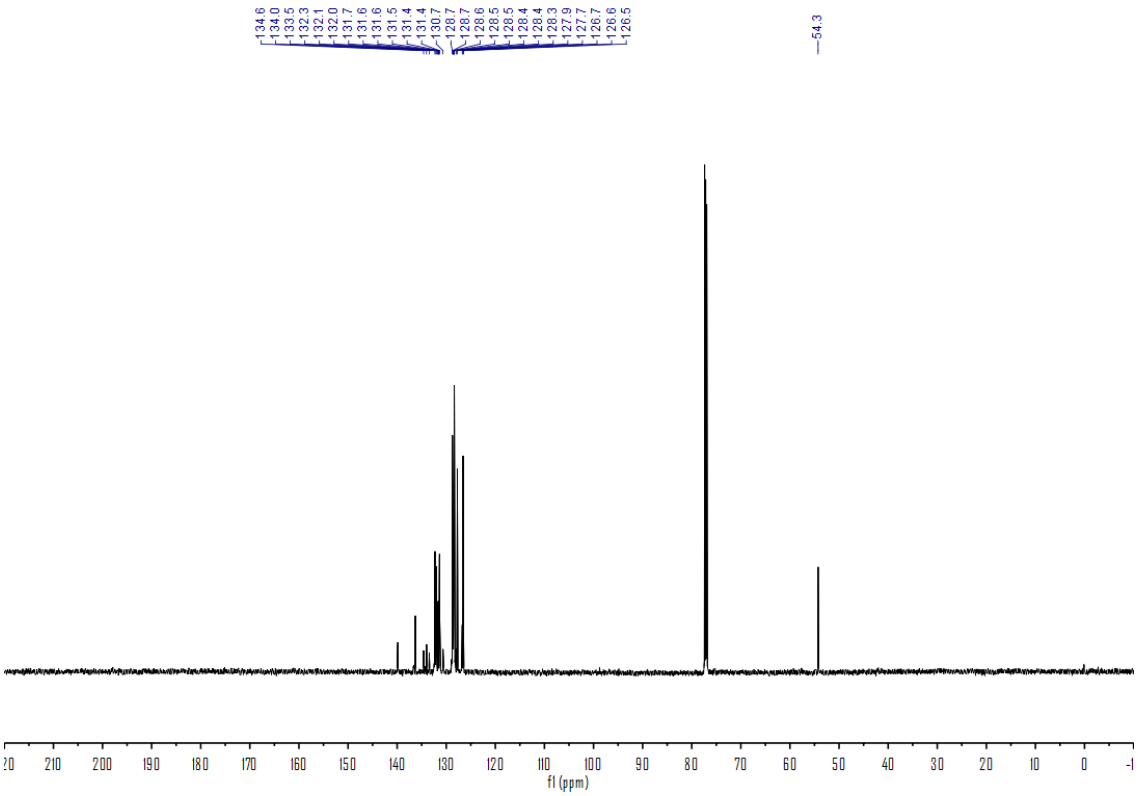


2ax

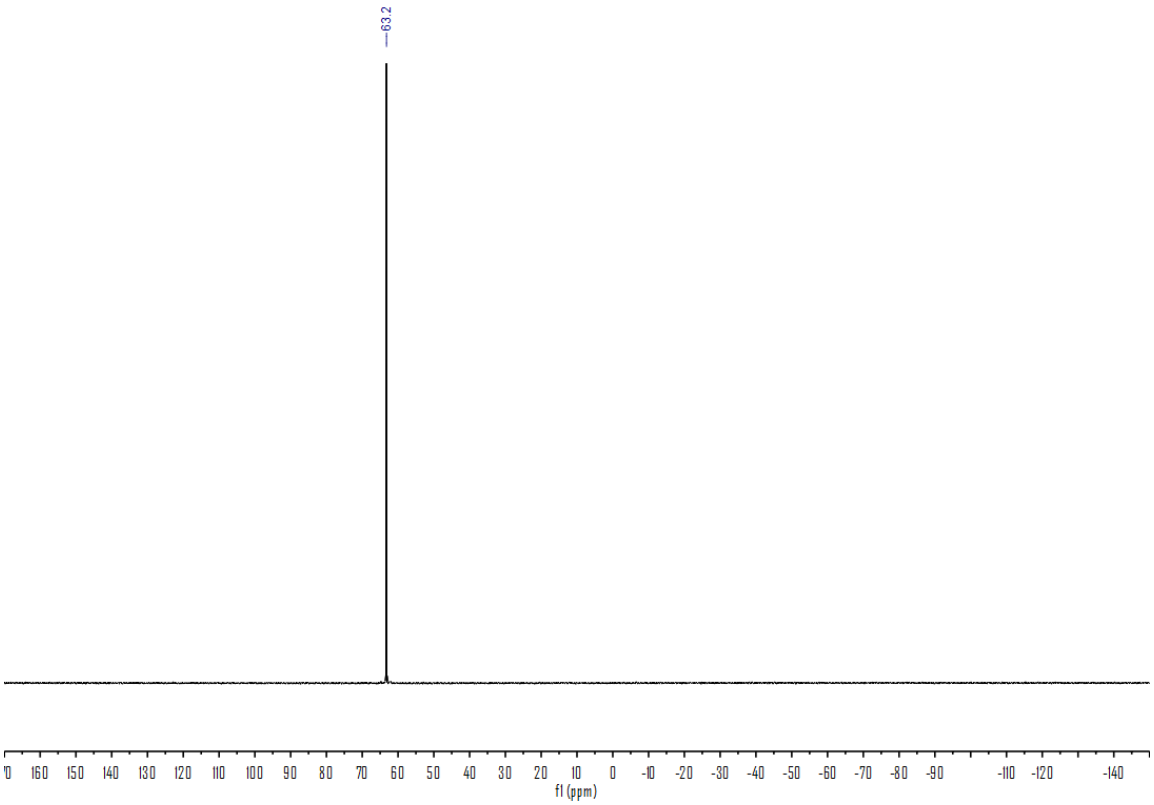
^{1}H NMR (600 MHz, $CDCl_3$)

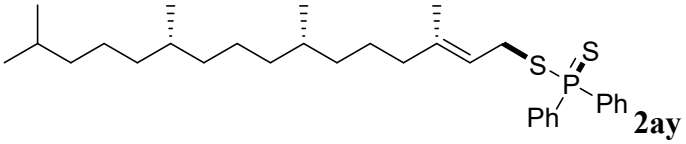


^{13}C NMR (151 MHz, $CDCl_3$)



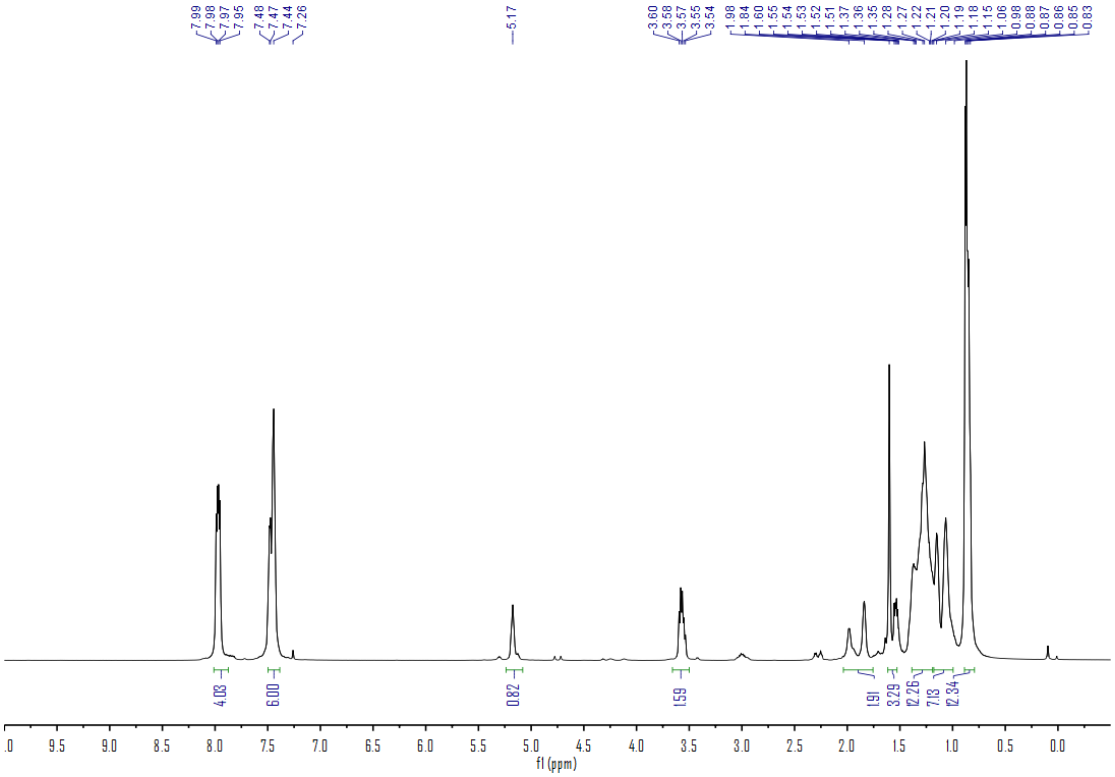
^{31}P NMR (243 MHz, $CDCl_3$)



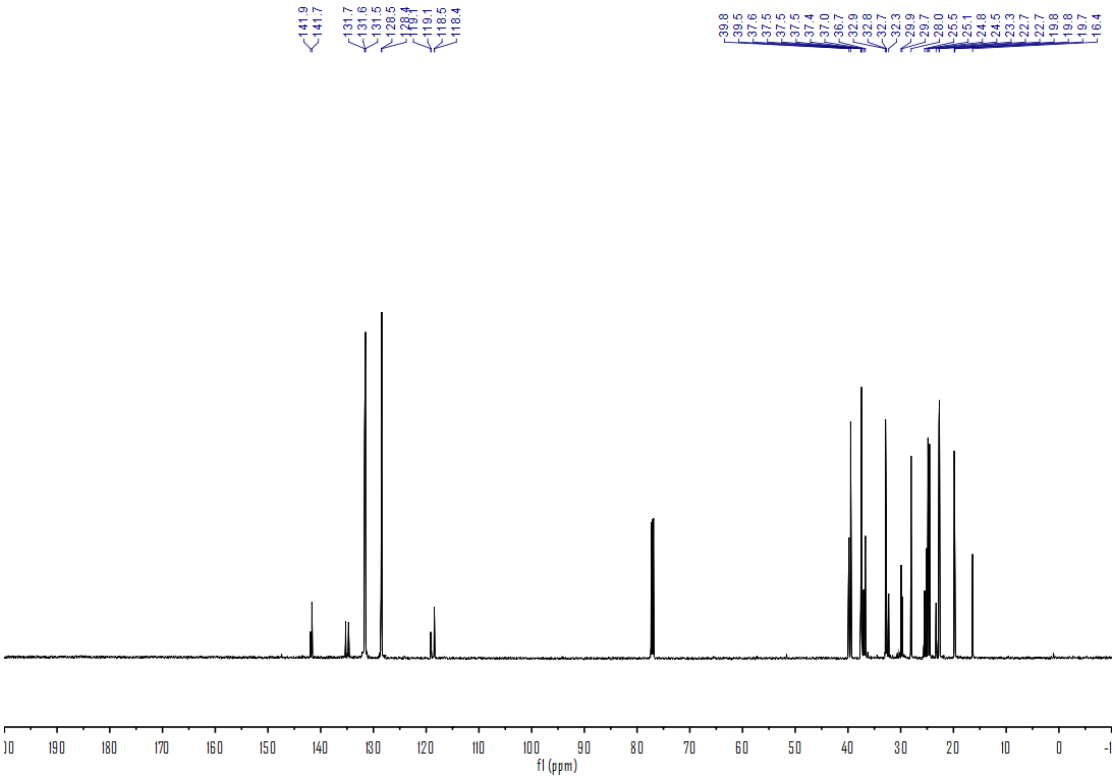


2ay

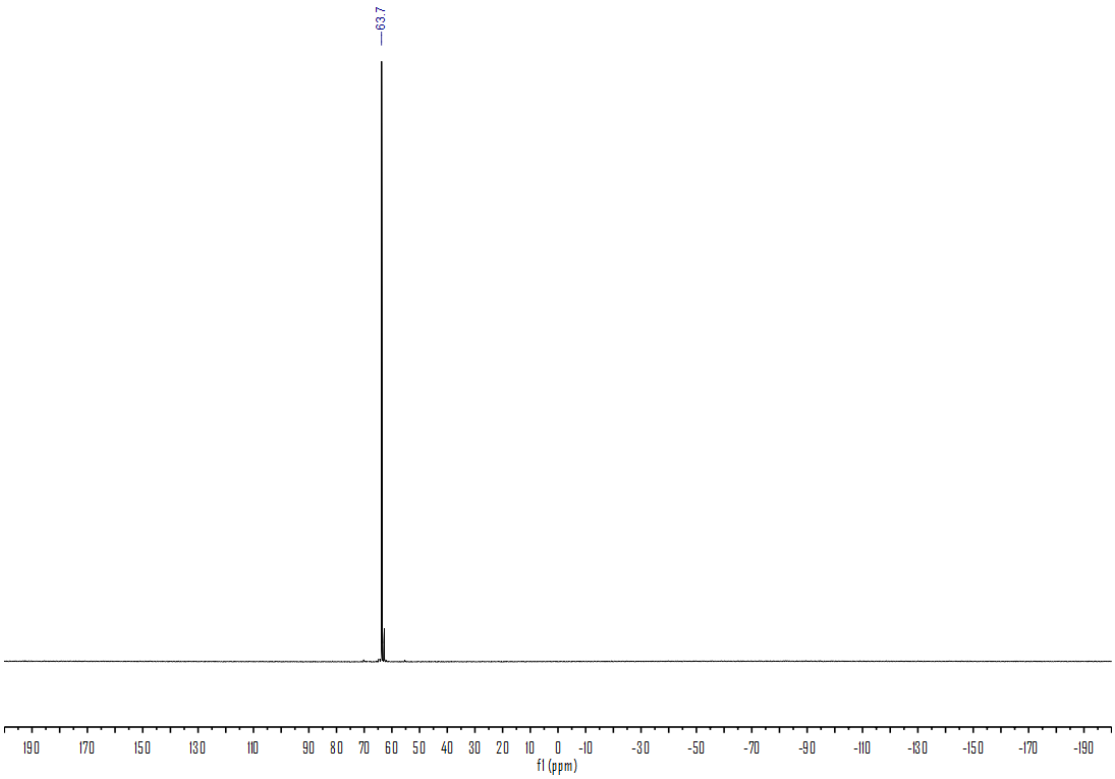
^{1}H NMR (600 MHz, $CDCl_3$)

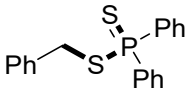


^{13}C NMR (151 MHz, $CDCl_3$)



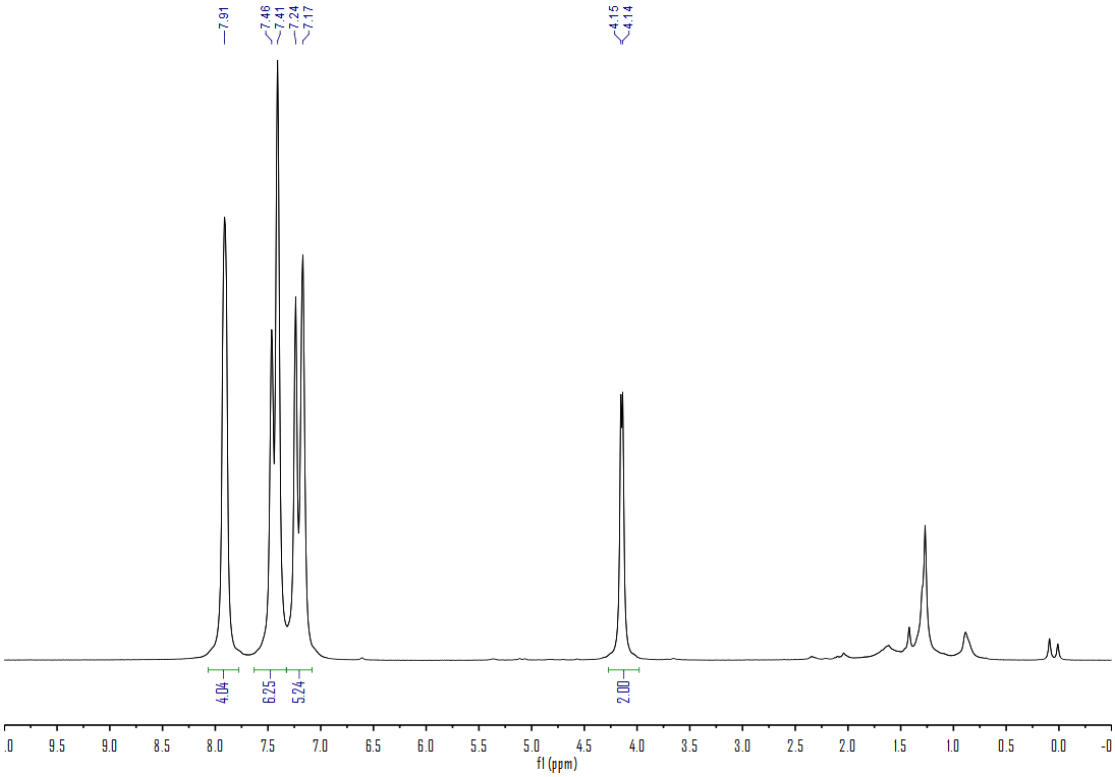
^{31}P NMR (243 MHz, $CDCl_3$)



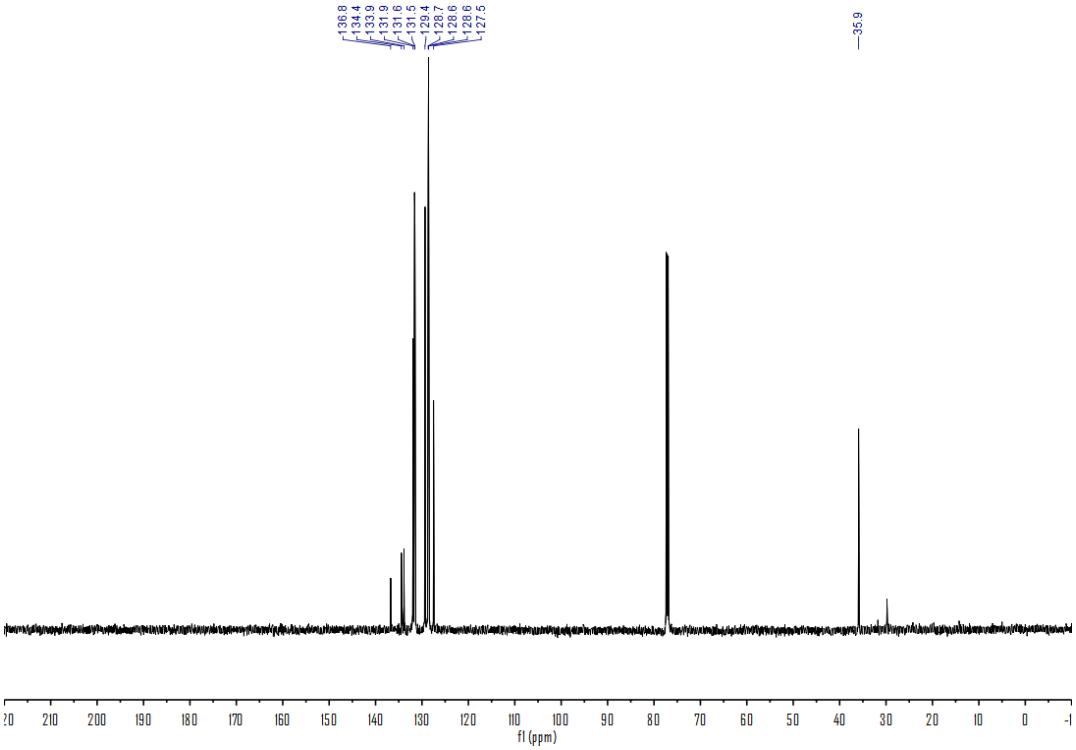


6aa

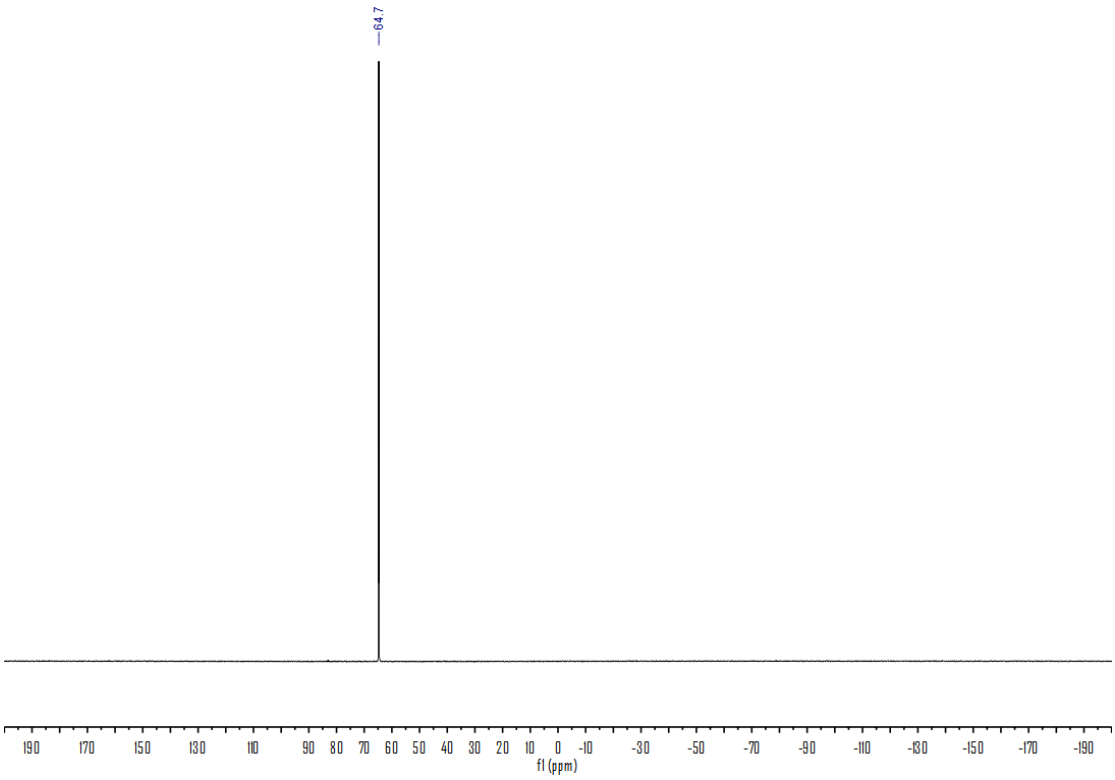
^{1}H NMR (600 MHz, $CDCl_3$)

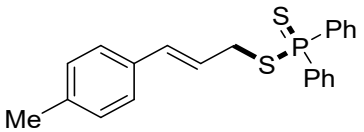


^{13}C NMR (151 MHz, $CDCl_3$)



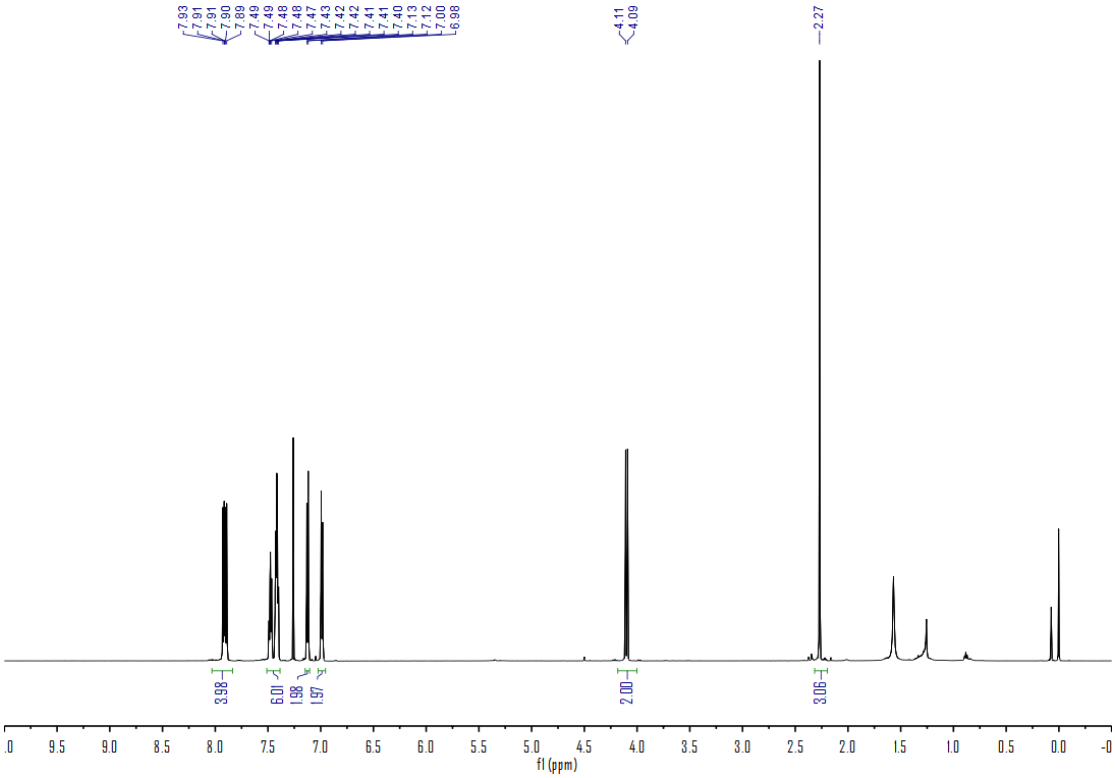
^{31}P NMR (243 MHz, $CDCl_3$)



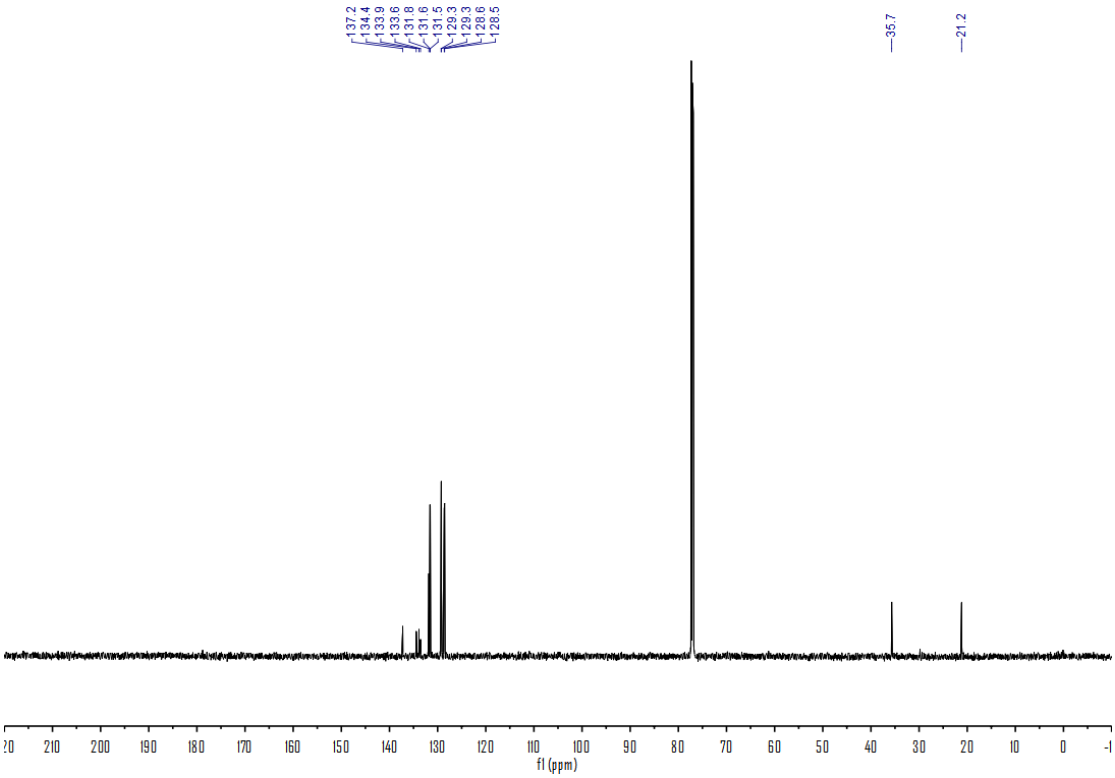


6ab

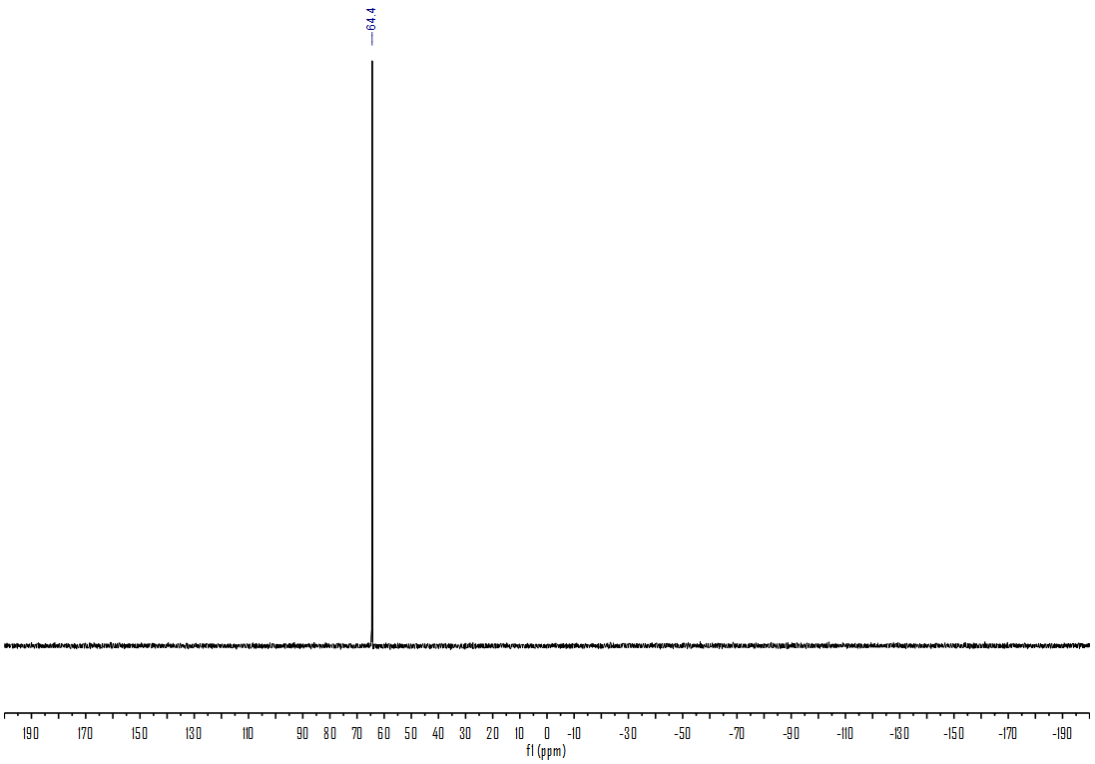
^{1}H NMR (600 MHz, $CDCl_3$)

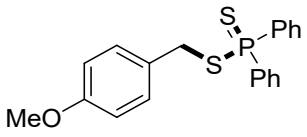


^{13}C NMR (151 MHz, $CDCl_3$)



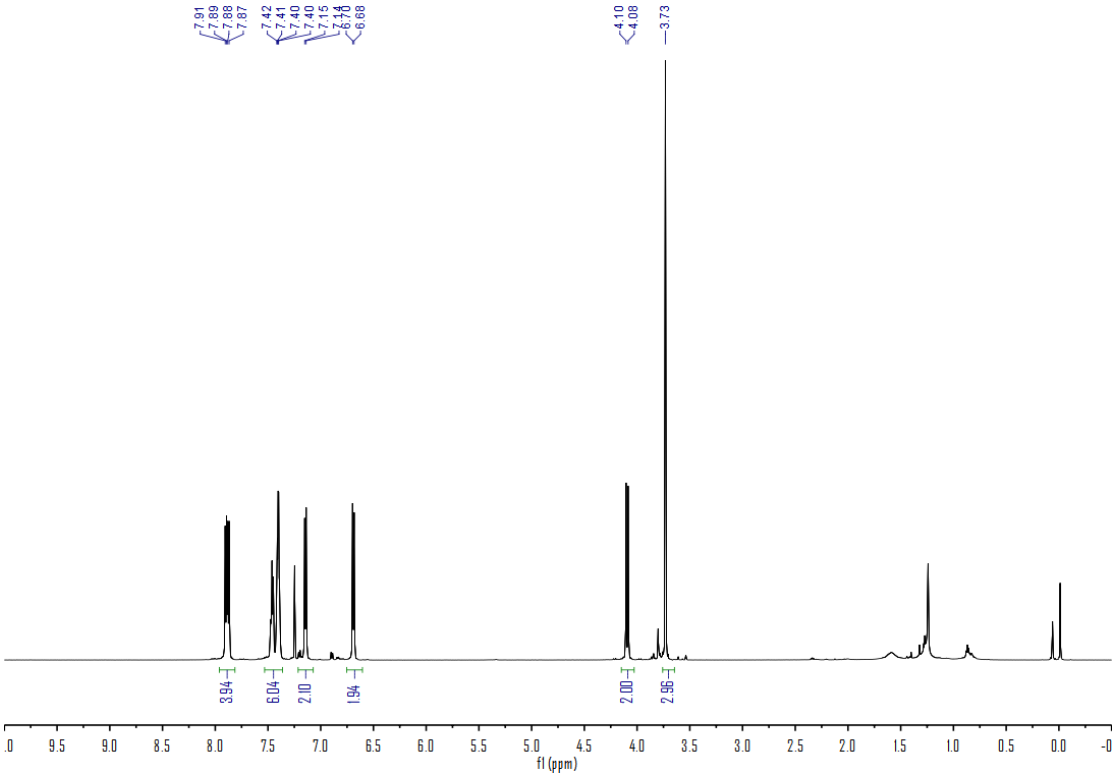
^{31}P NMR (243 MHz, $CDCl_3$)



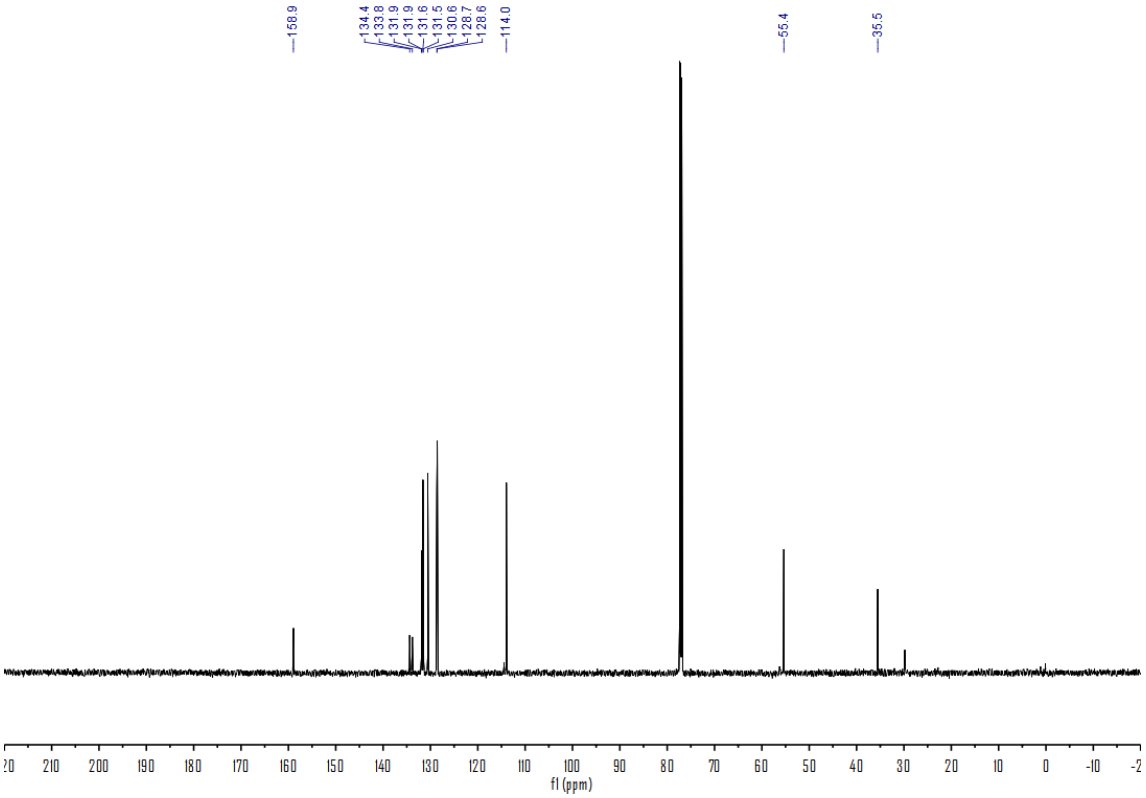


6ac

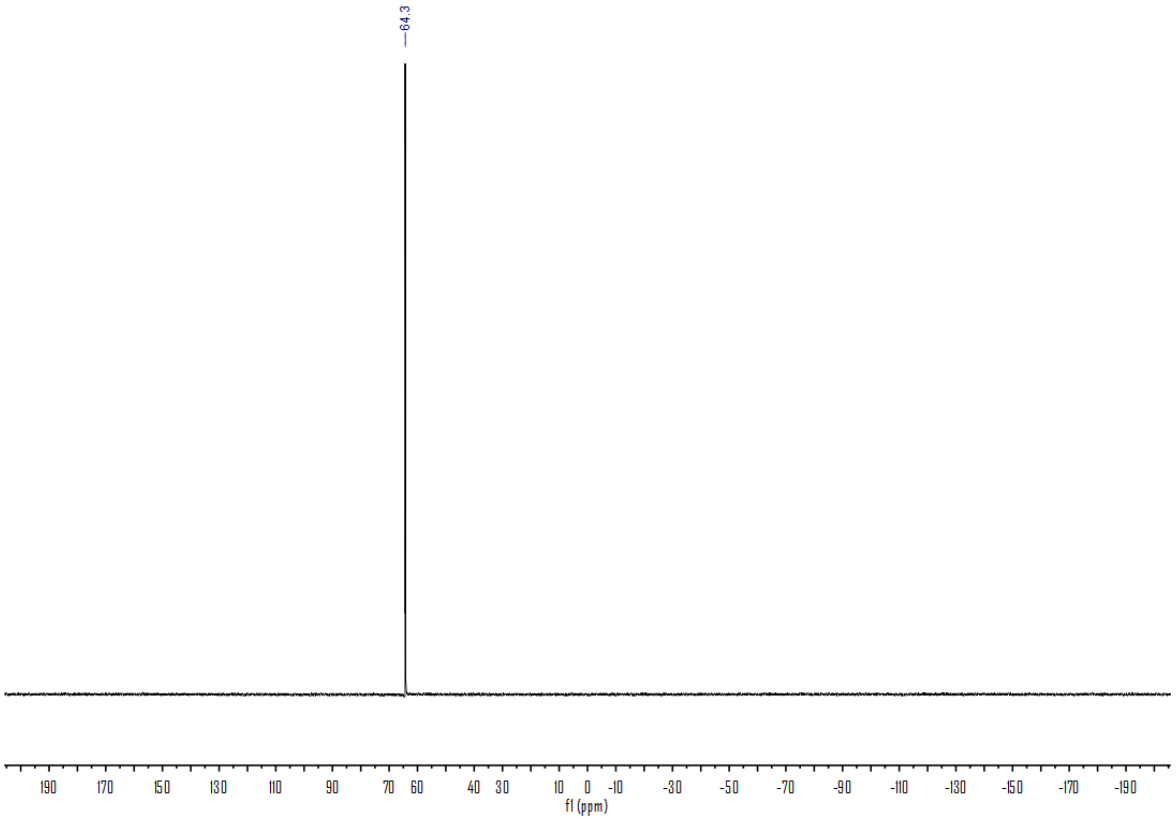
^{1}H NMR (600 MHz, $CDCl_3$)

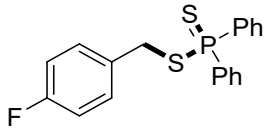


^{13}C NMR (151 MHz, $CDCl_3$)



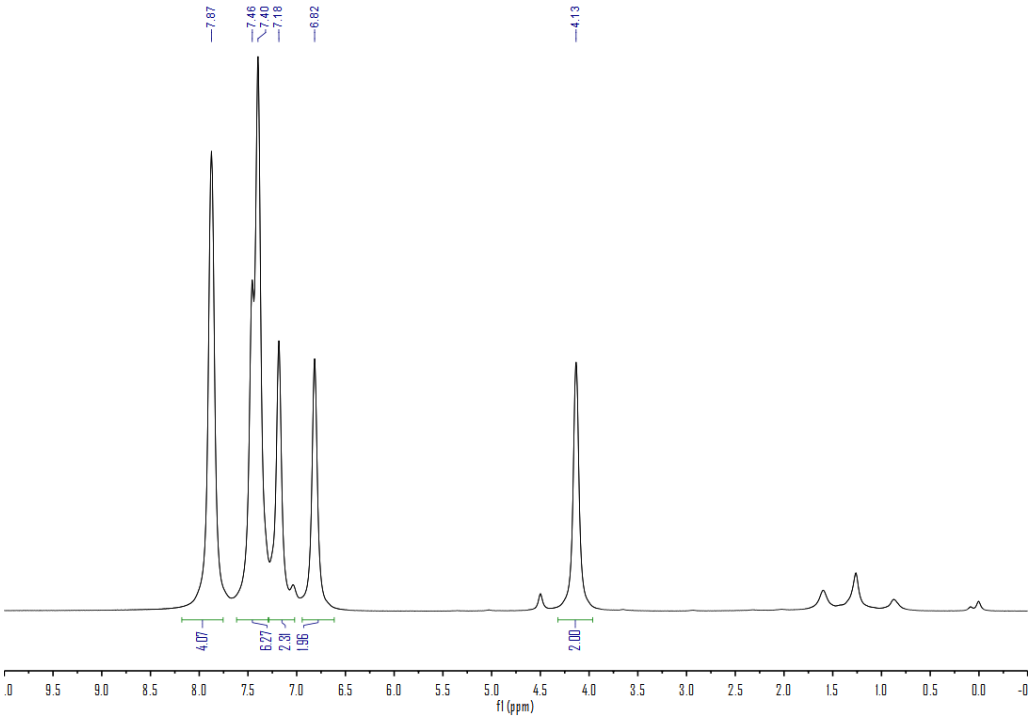
^{31}P NMR (243 MHz, $CDCl_3$)



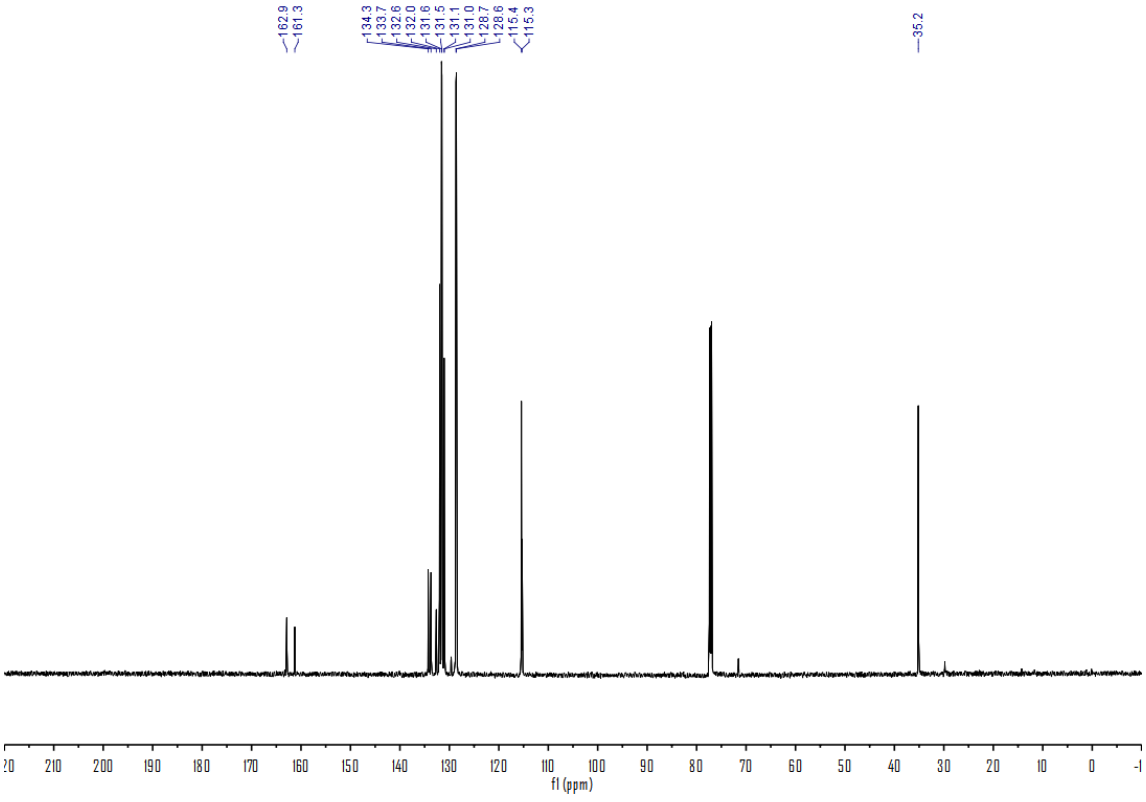


6ad

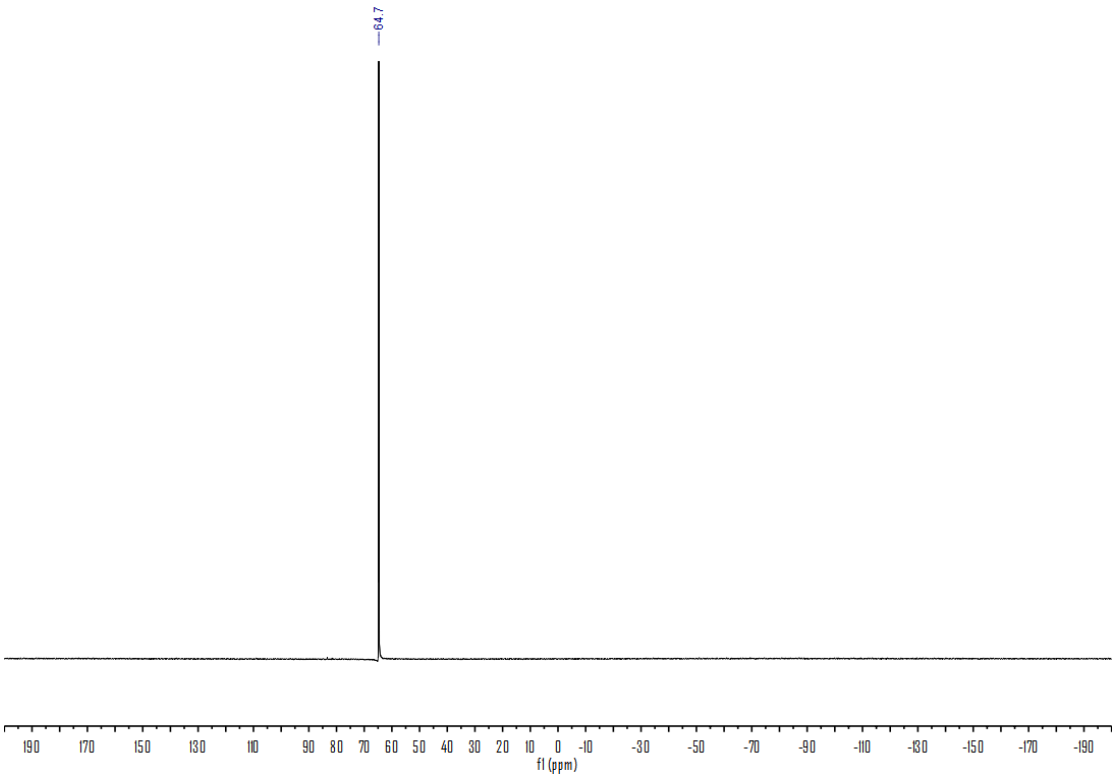
^{1}H NMR (600 MHz, $CDCl_3$)

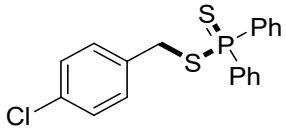


^{13}C NMR (151 MHz, $CDCl_3$)



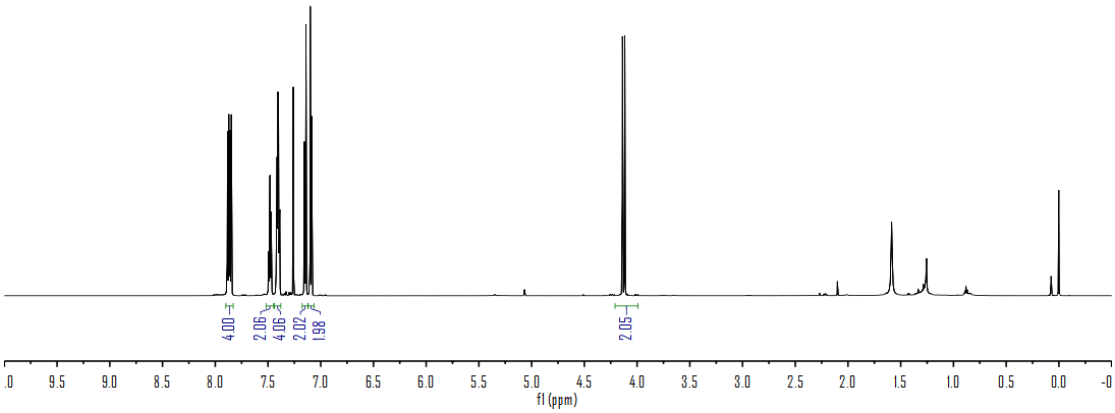
^{31}P NMR (243 MHz, $CDCl_3$)



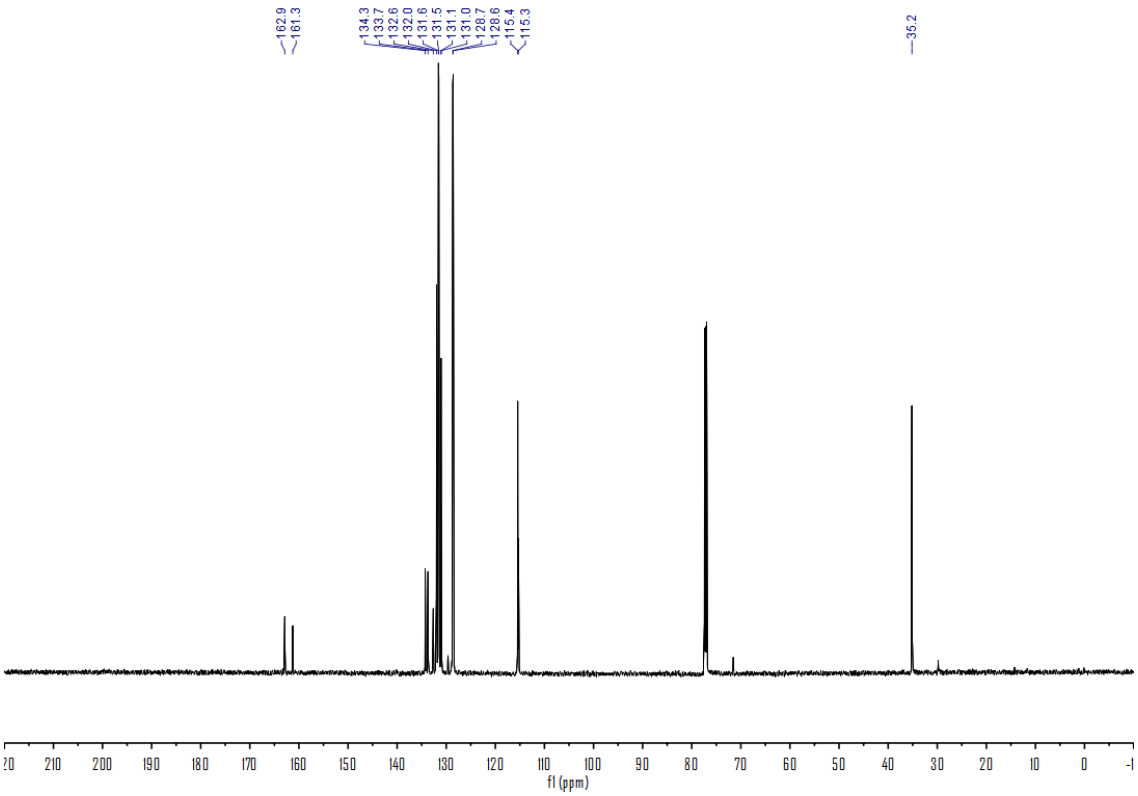


6ae

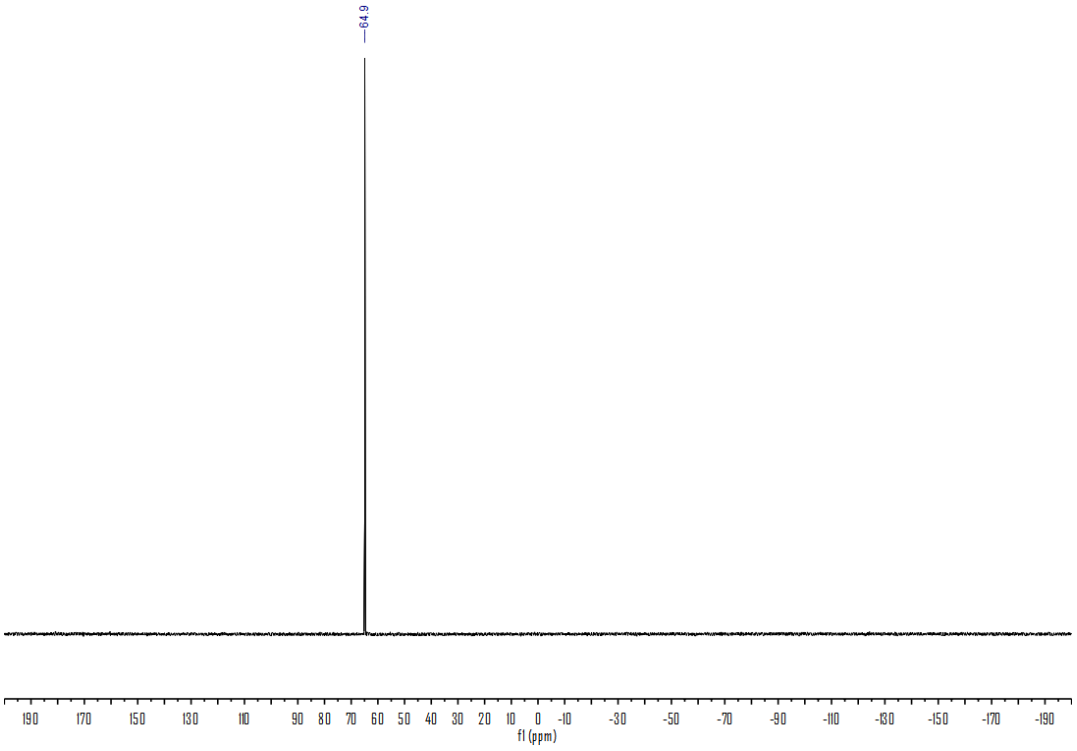
^{1}H NMR (600 MHz, $CDCl_3$)

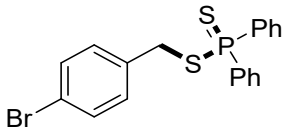


^{13}C NMR (151 MHz, $CDCl_3$)



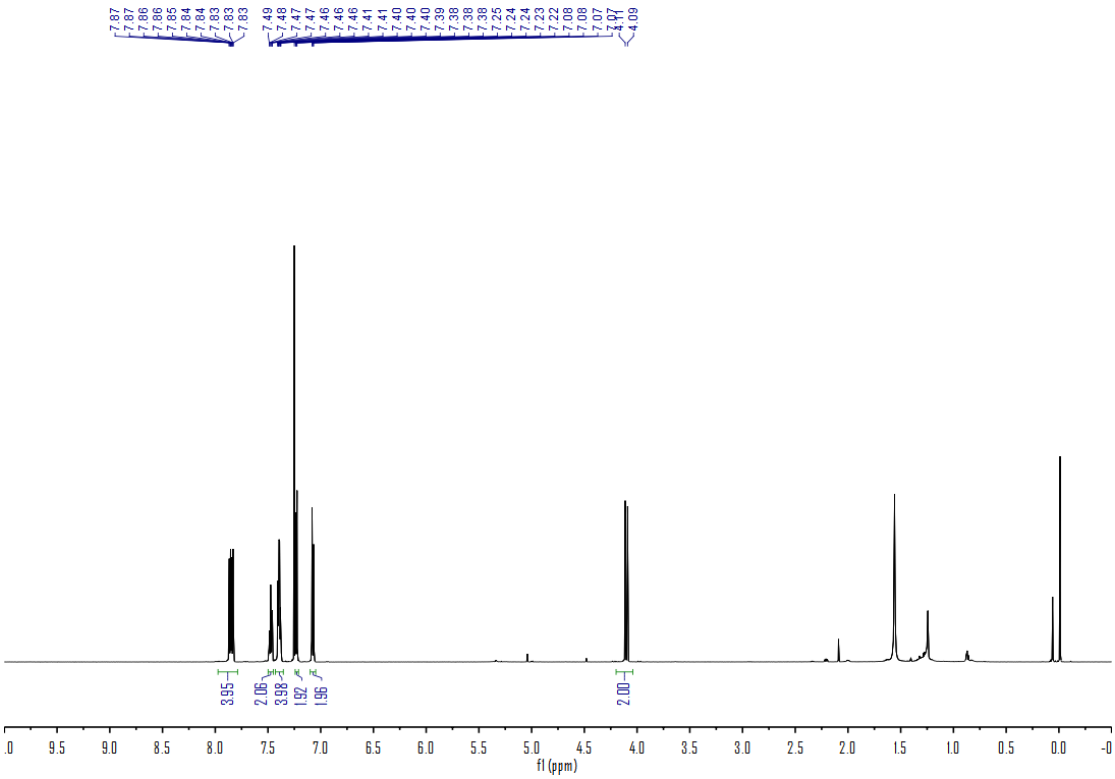
^{31}P NMR (243 MHz, $CDCl_3$)



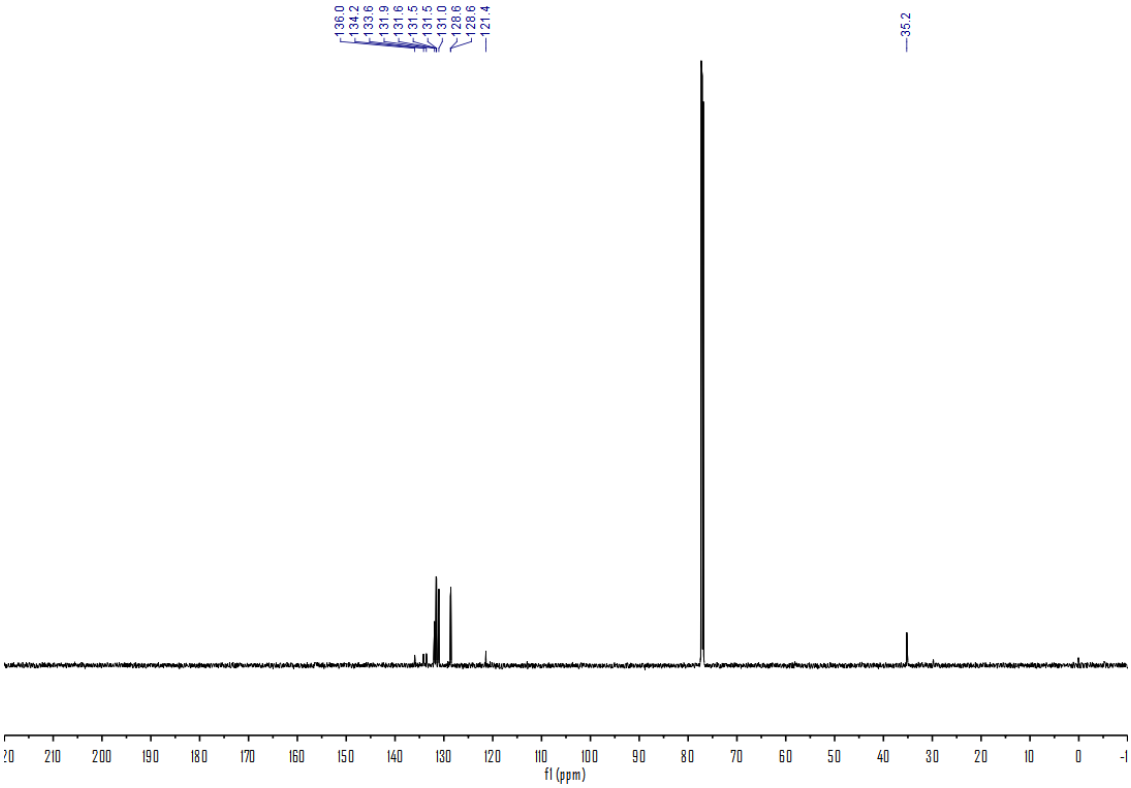


6af

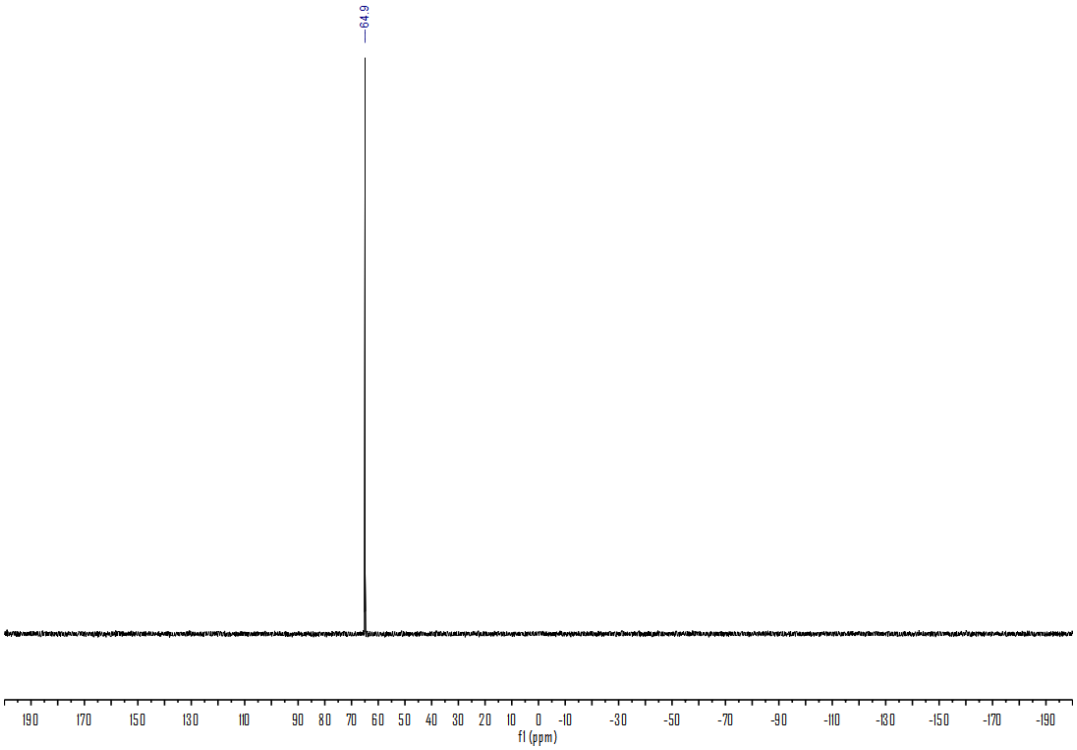
^{1}H NMR (600 MHz, $CDCl_3$)

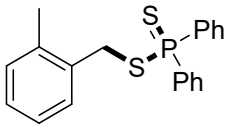


^{13}C NMR (151 MHz, $CDCl_3$)



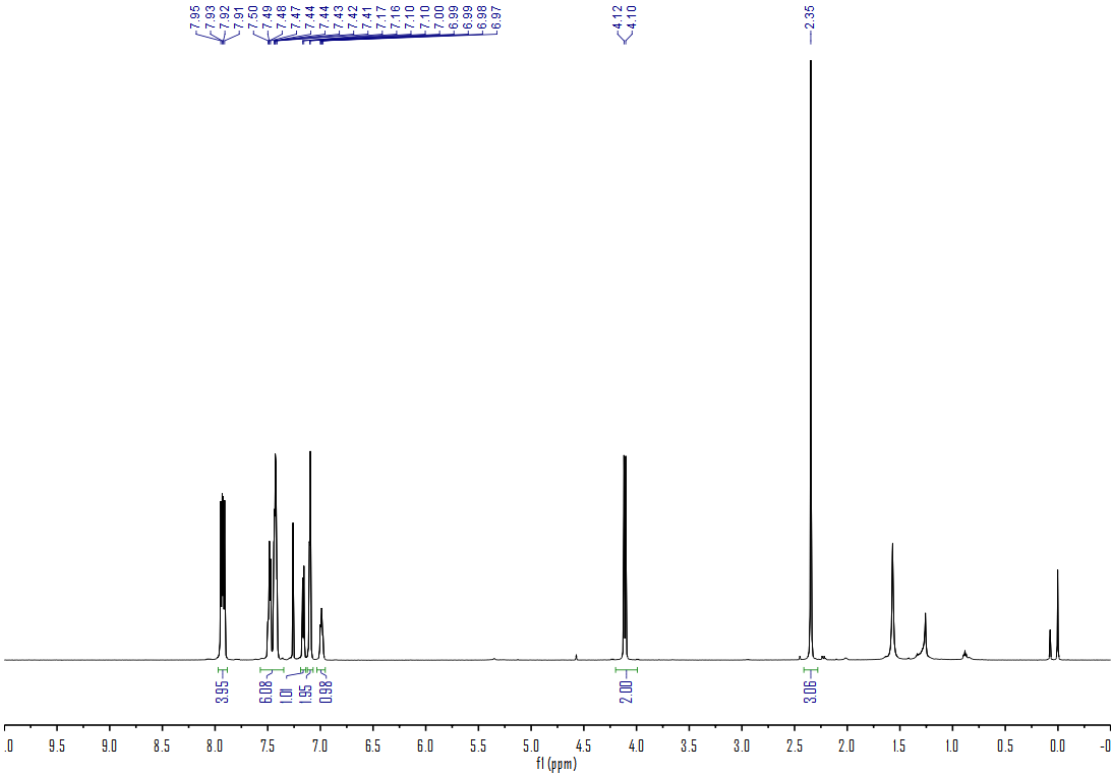
^{31}P NMR (243 MHz, $CDCl_3$)



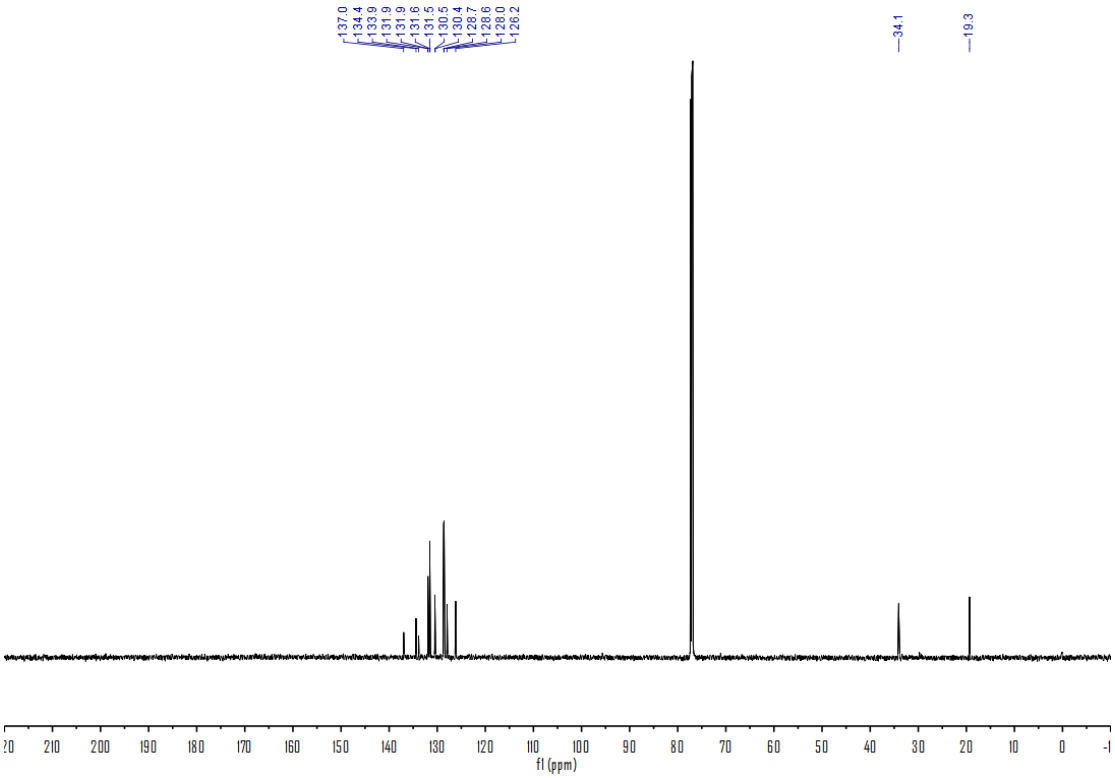


6ag

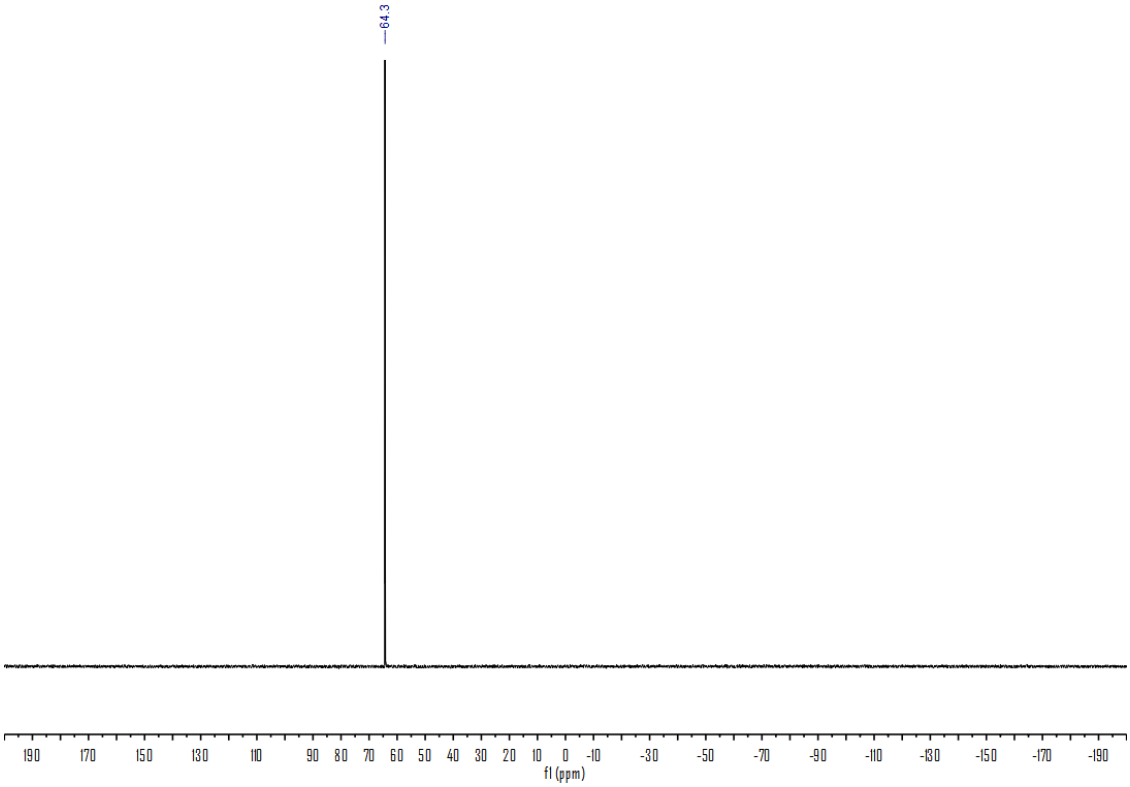
^{1}H NMR (600 MHz, $CDCl_3$)

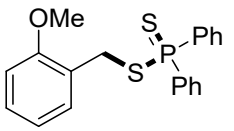


^{13}C NMR (151 MHz, $CDCl_3$)



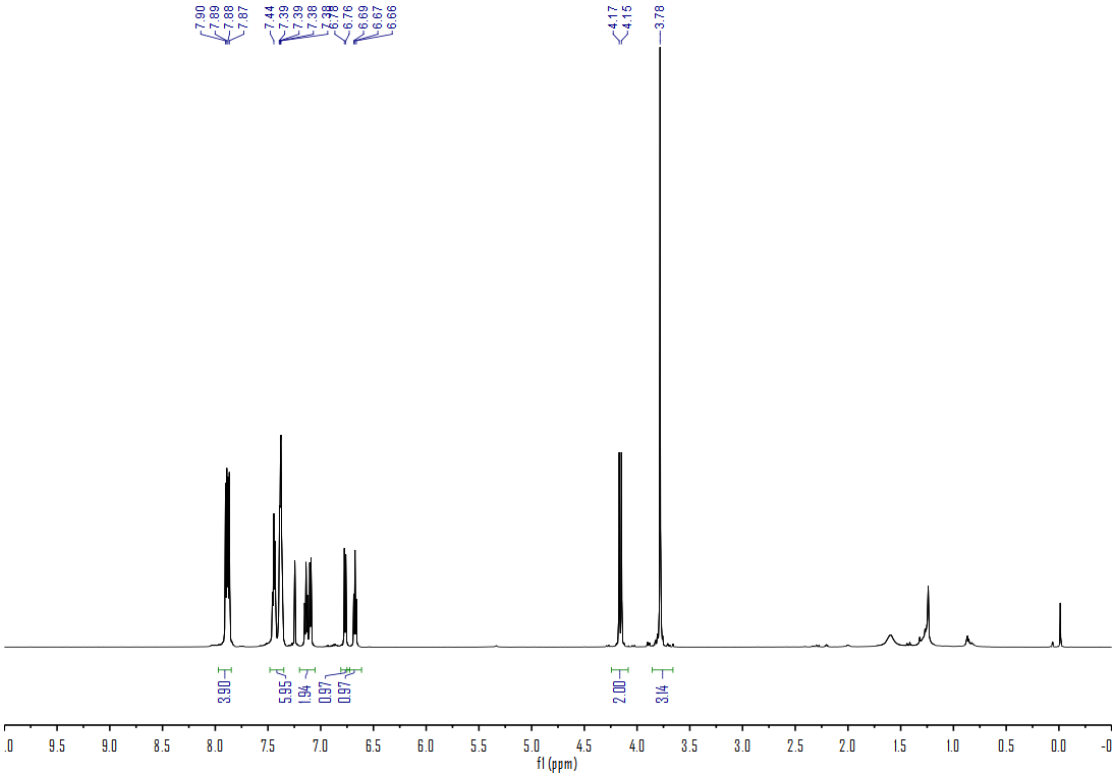
^{31}P NMR (243 MHz, $CDCl_3$)



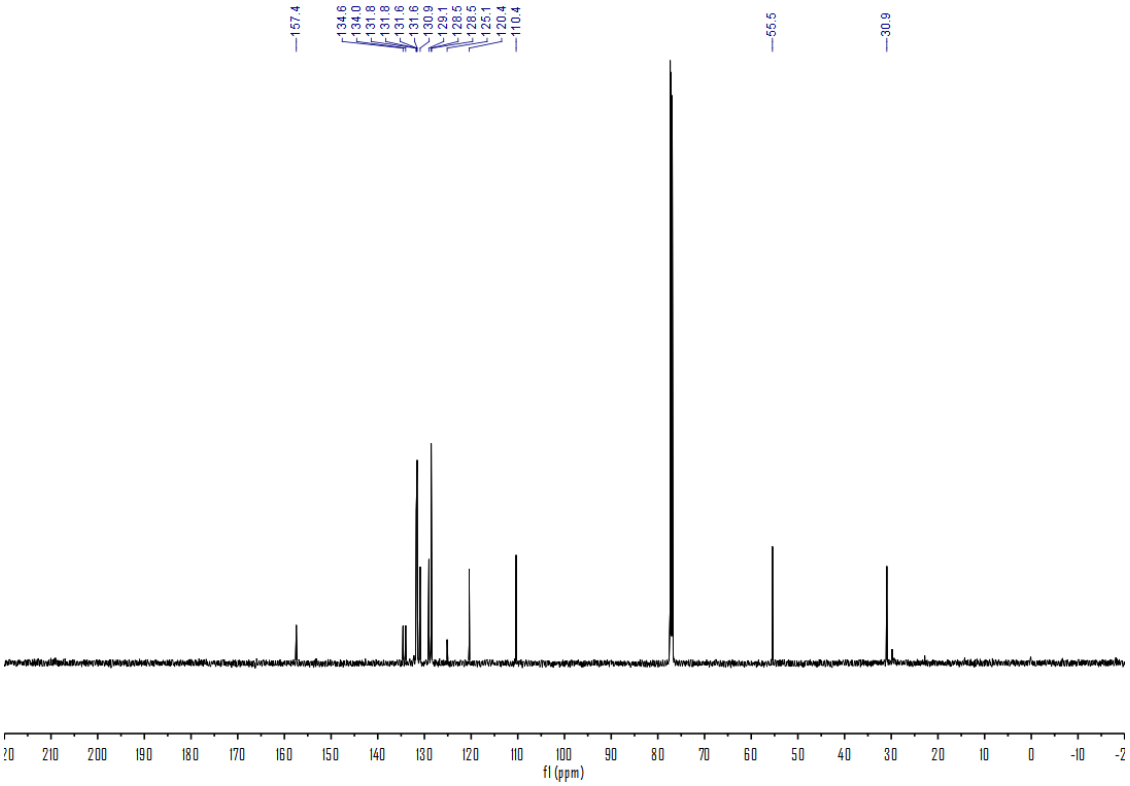


6ah

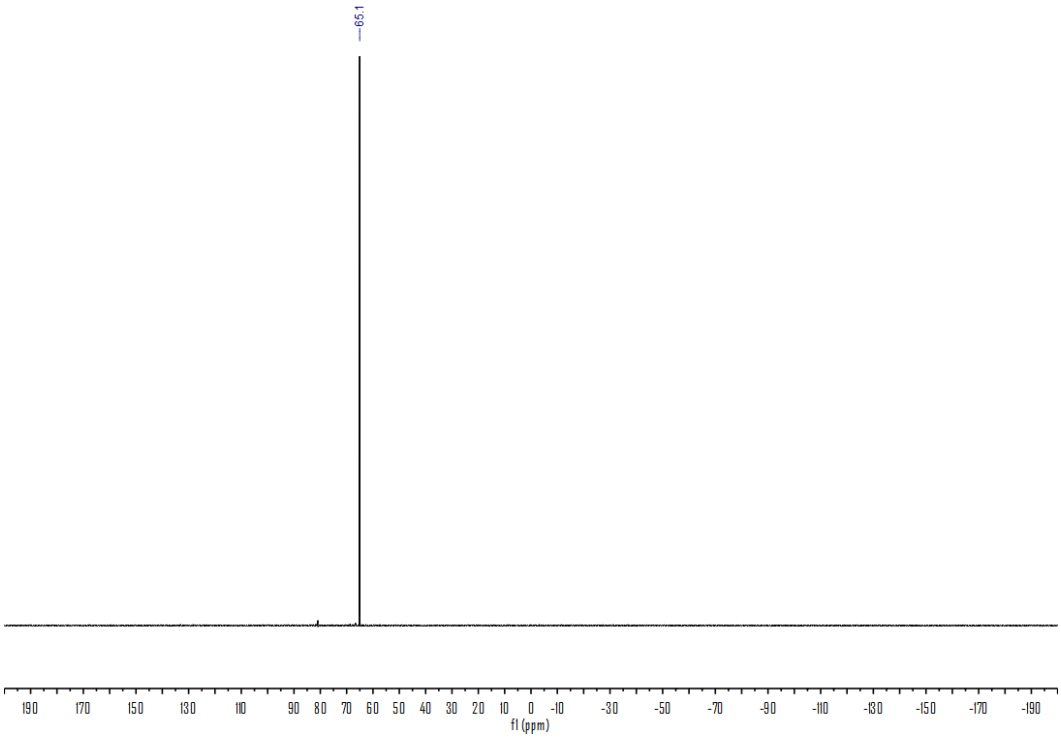
^{1}H NMR (600 MHz, $CDCl_3$)

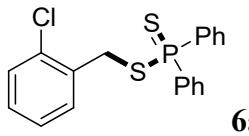


^{13}C NMR (151 MHz, $CDCl_3$)



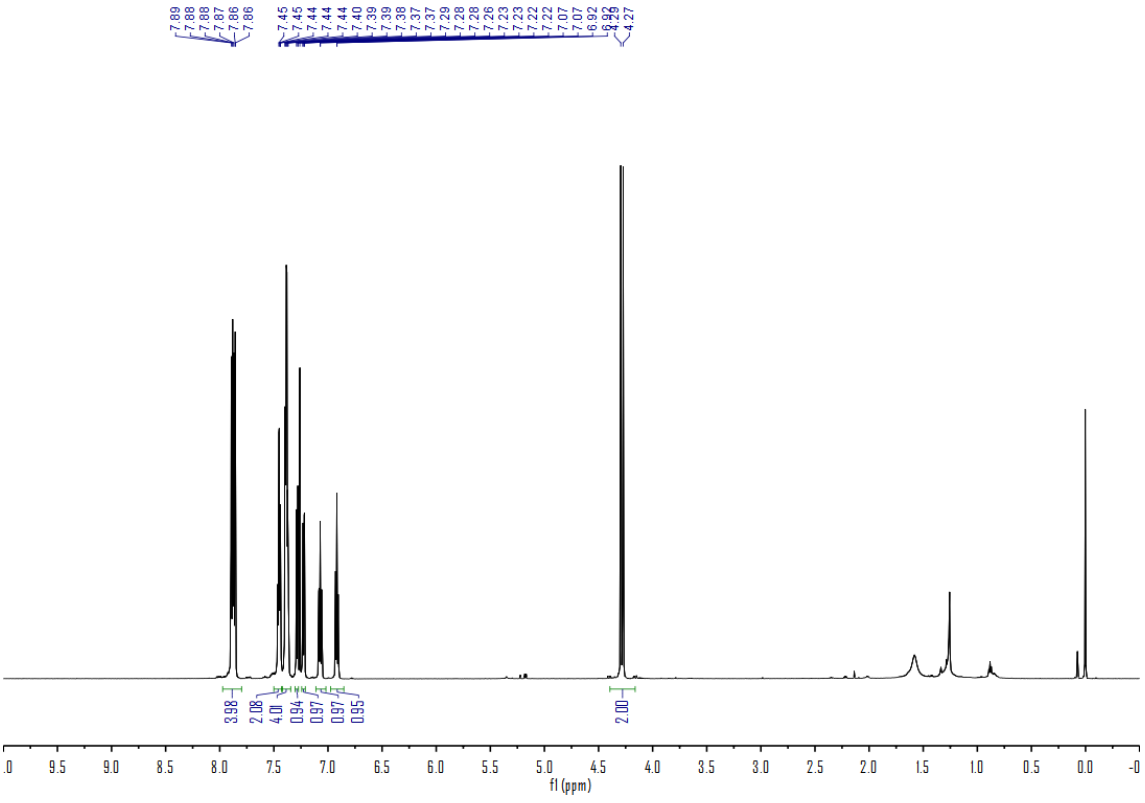
^{31}P NMR (243 MHz, $CDCl_3$)



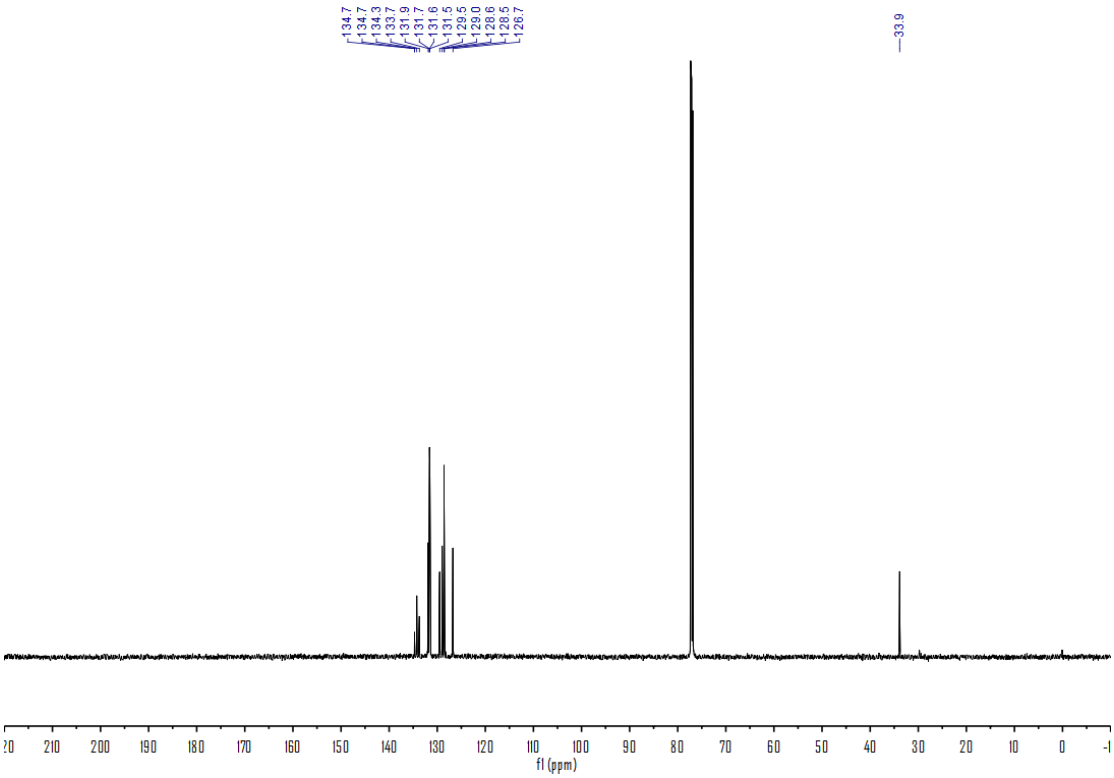


6ai

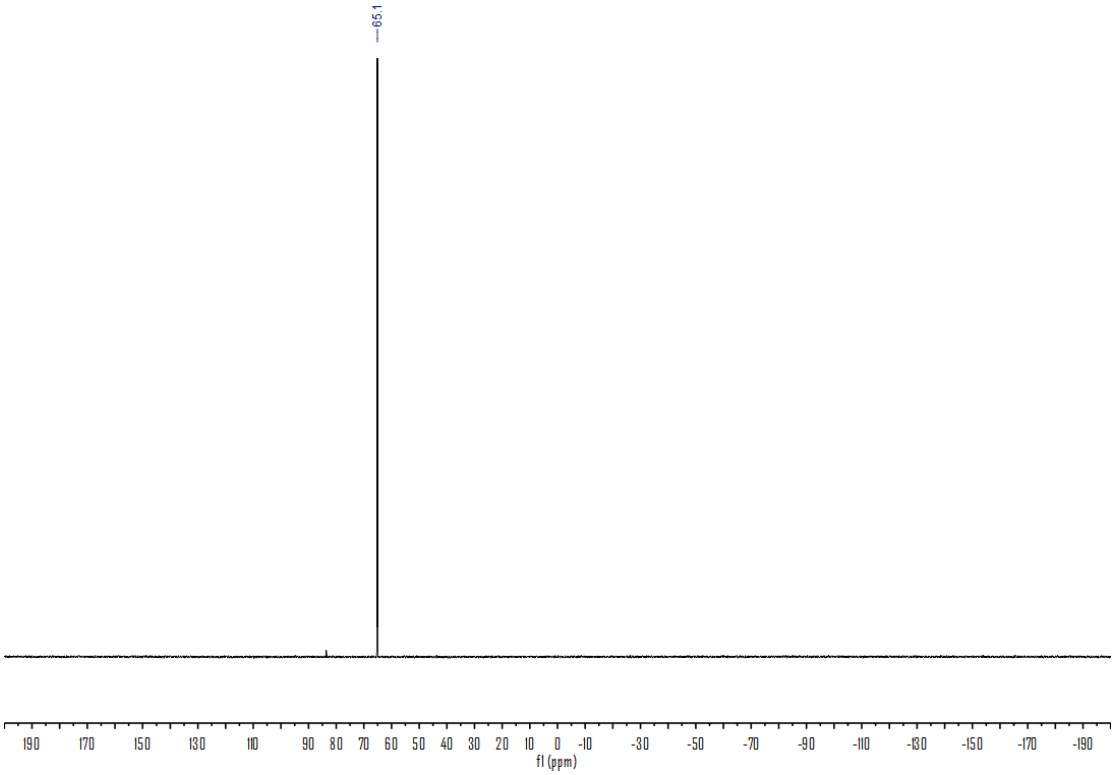
^{1}H NMR (600 MHz, $CDCl_3$)

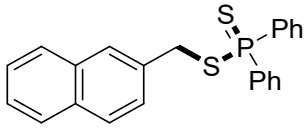


^{13}C NMR (151 MHz, $CDCl_3$)



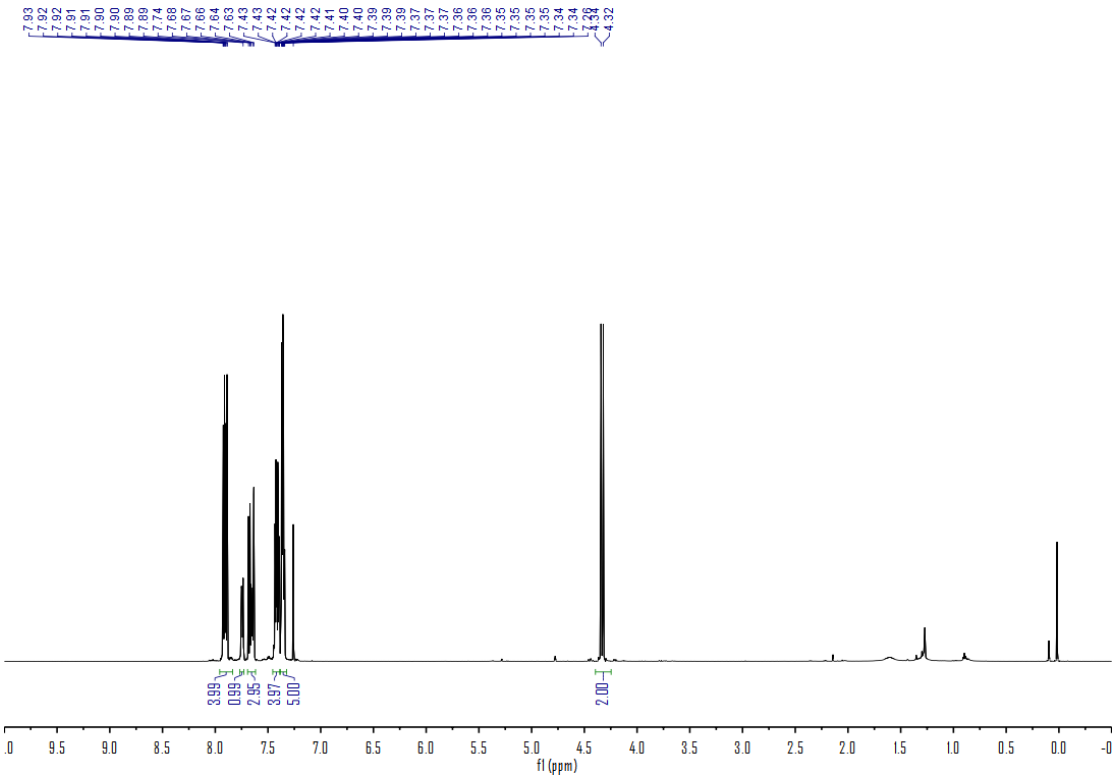
^{31}P NMR (243 MHz, $CDCl_3$)



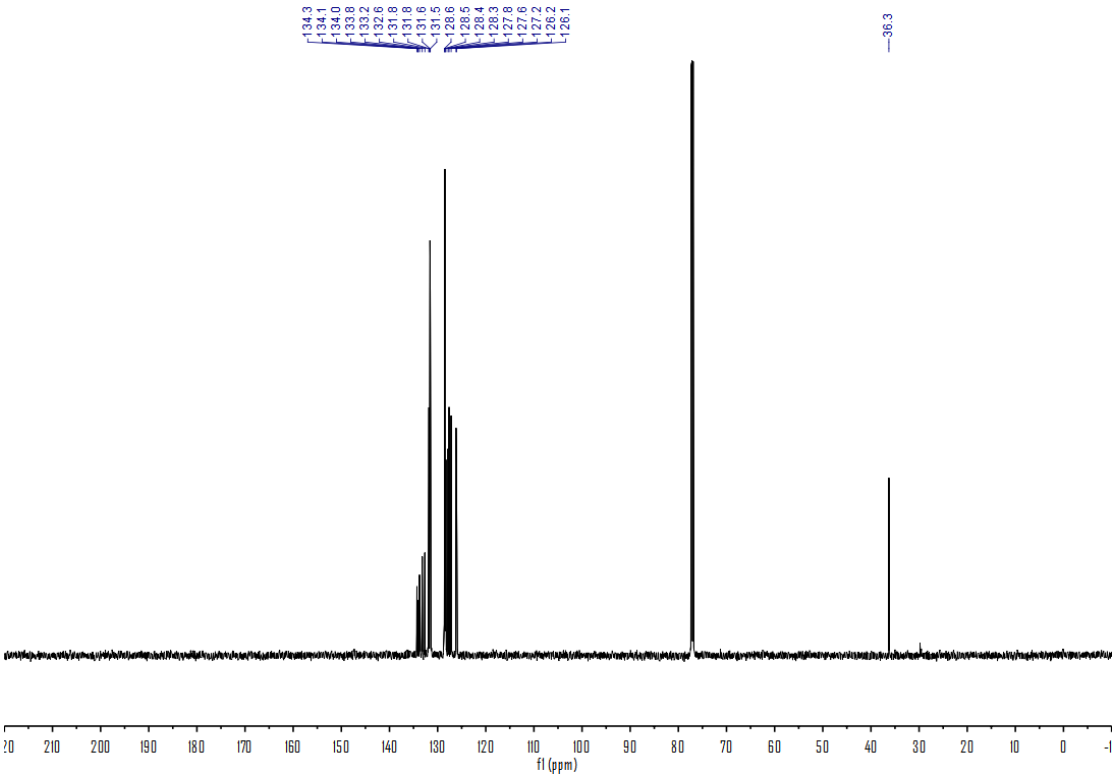


6aj

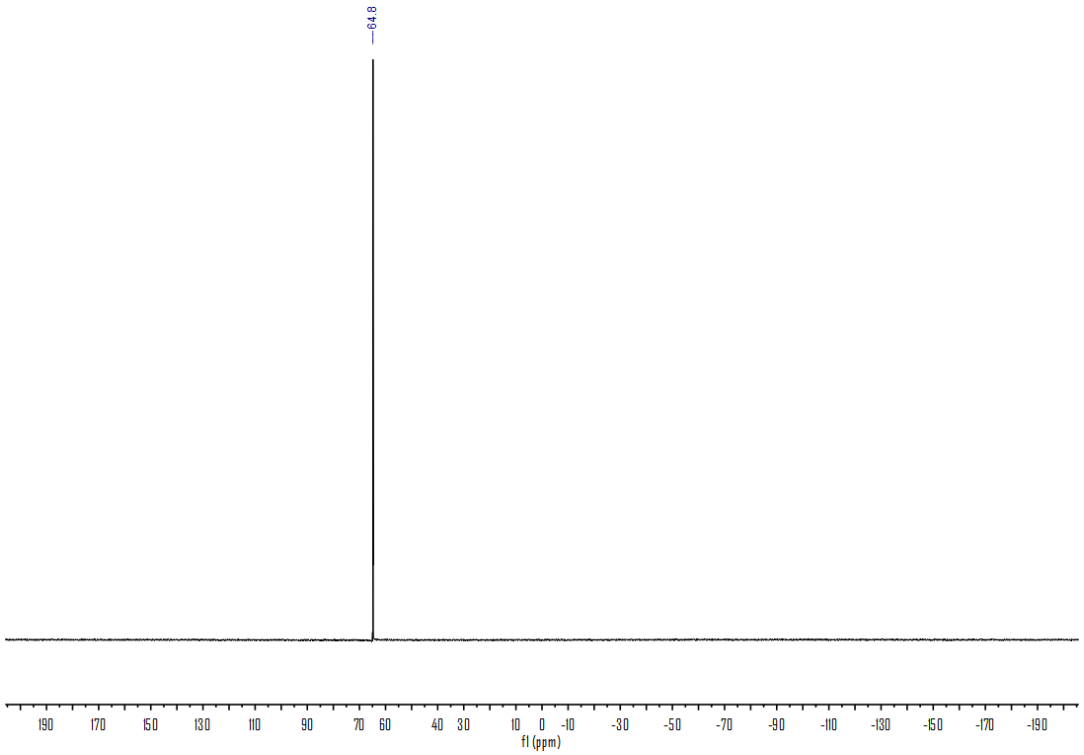
^{1}H NMR (600 MHz, $CDCl_3$)

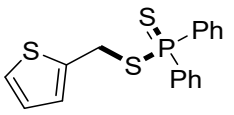


^{13}C NMR (151 MHz, $CDCl_3$)



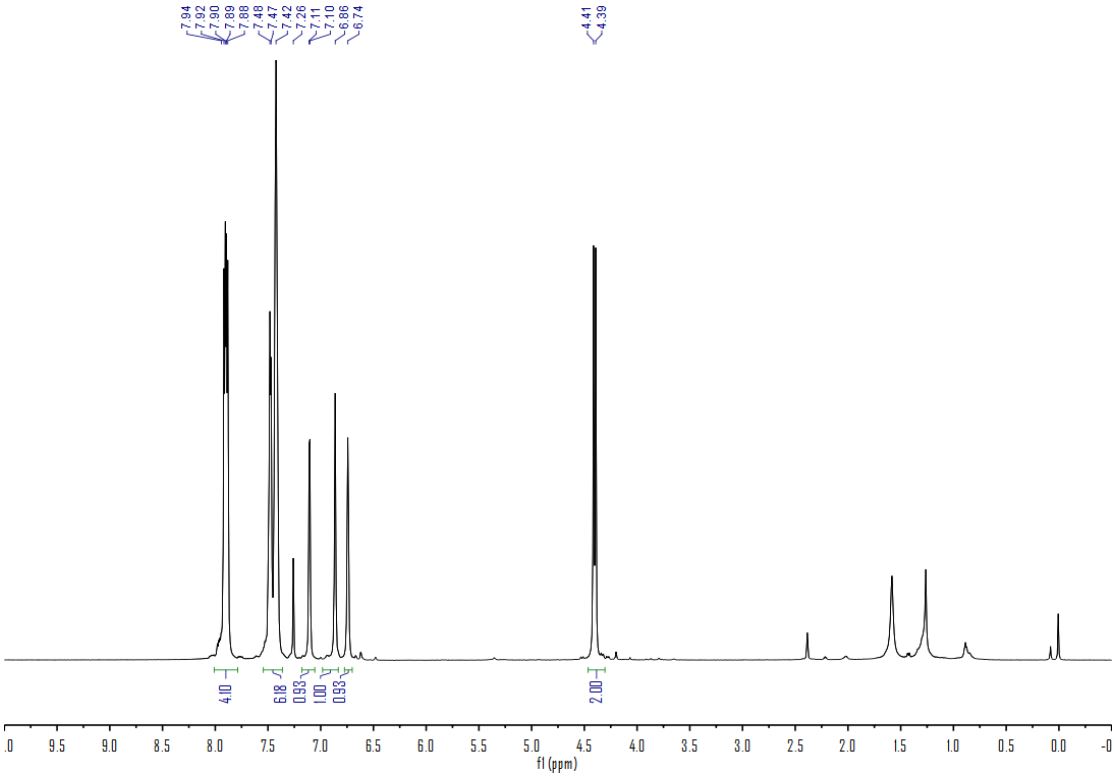
^{31}P NMR (243 MHz, $CDCl_3$)



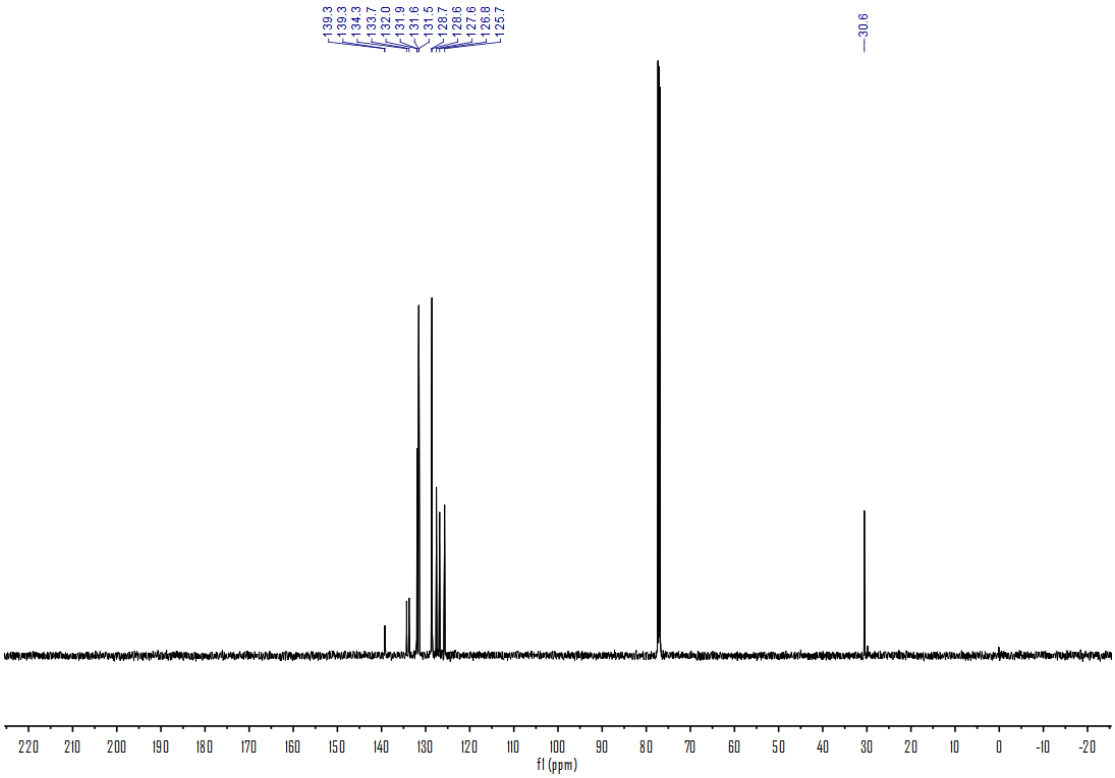


6ak

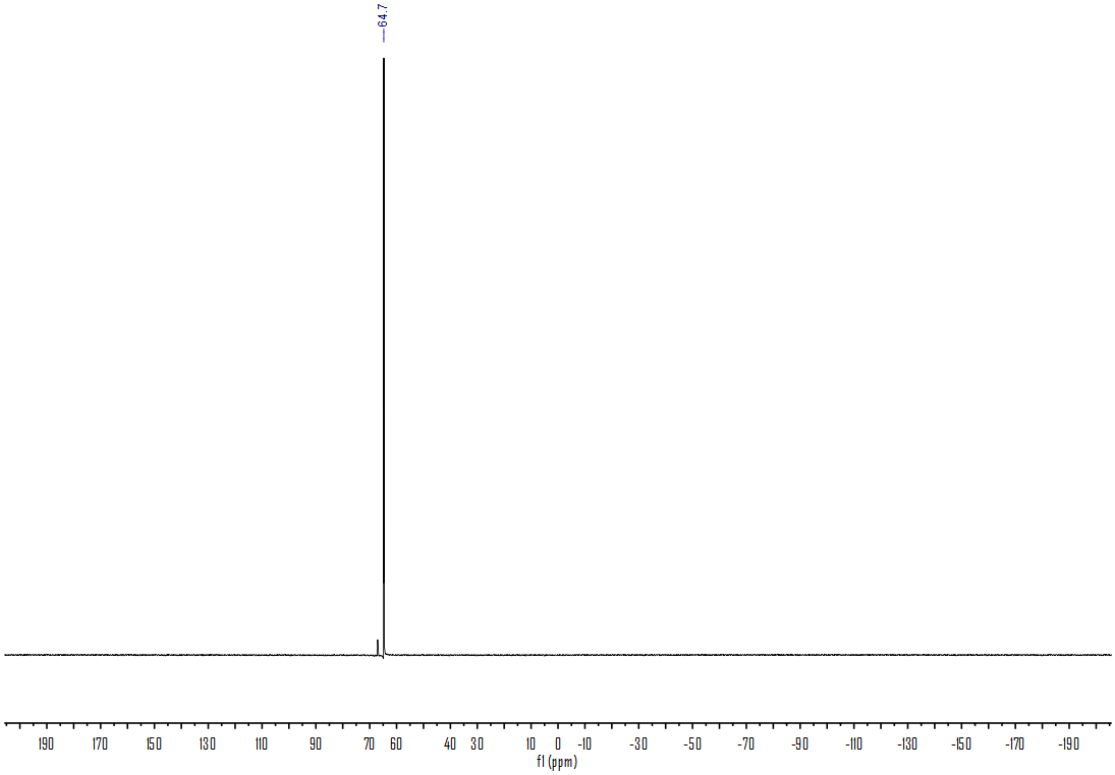
^{1}H NMR (600 MHz, $CDCl_3$)

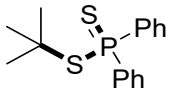


^{13}C NMR (151 MHz, $CDCl_3$)



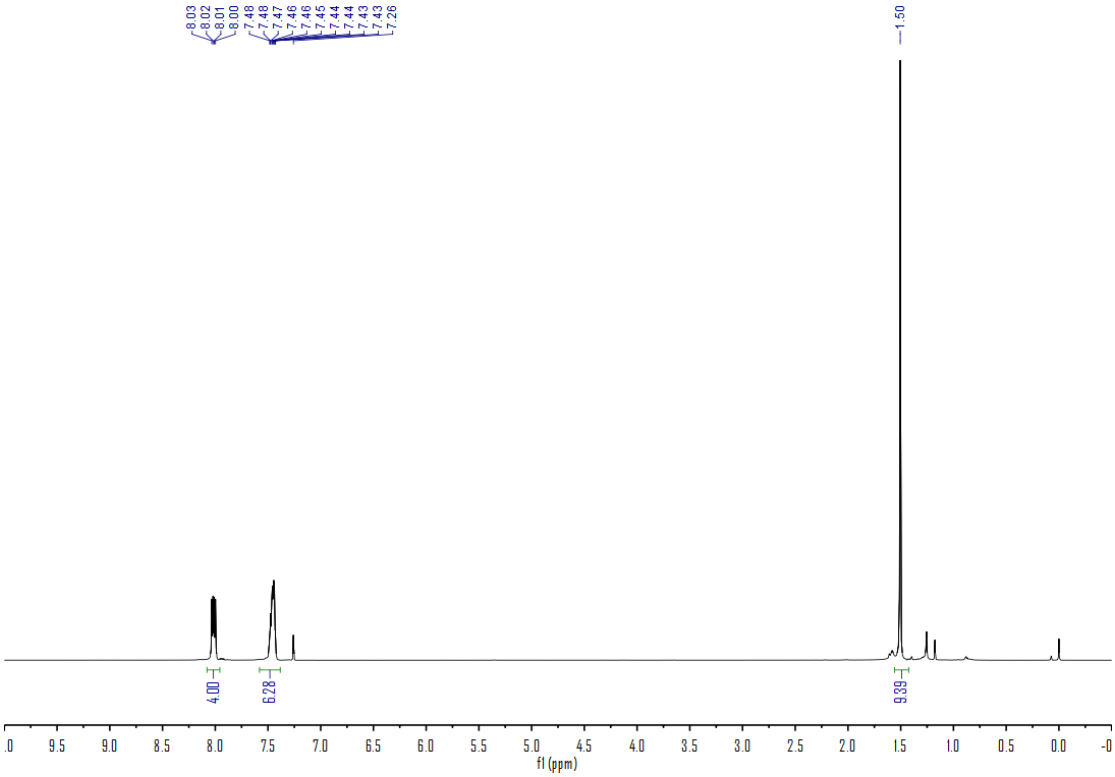
^{31}P NMR (243 MHz, $CDCl_3$)



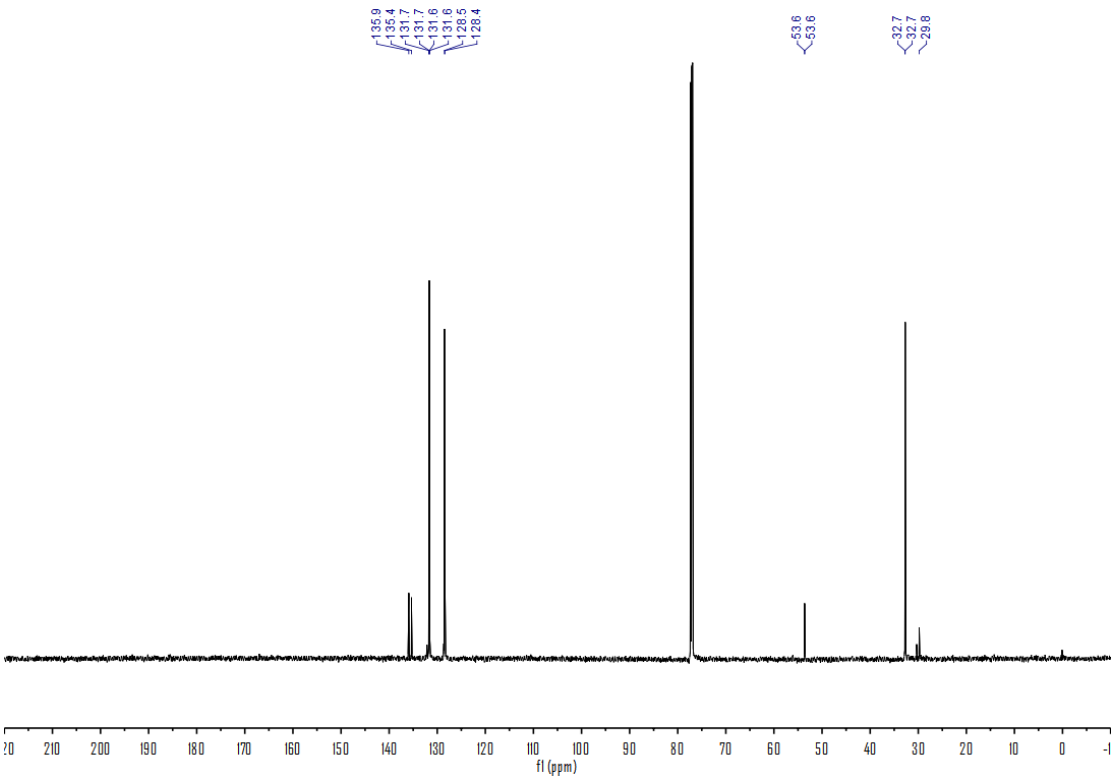


6al

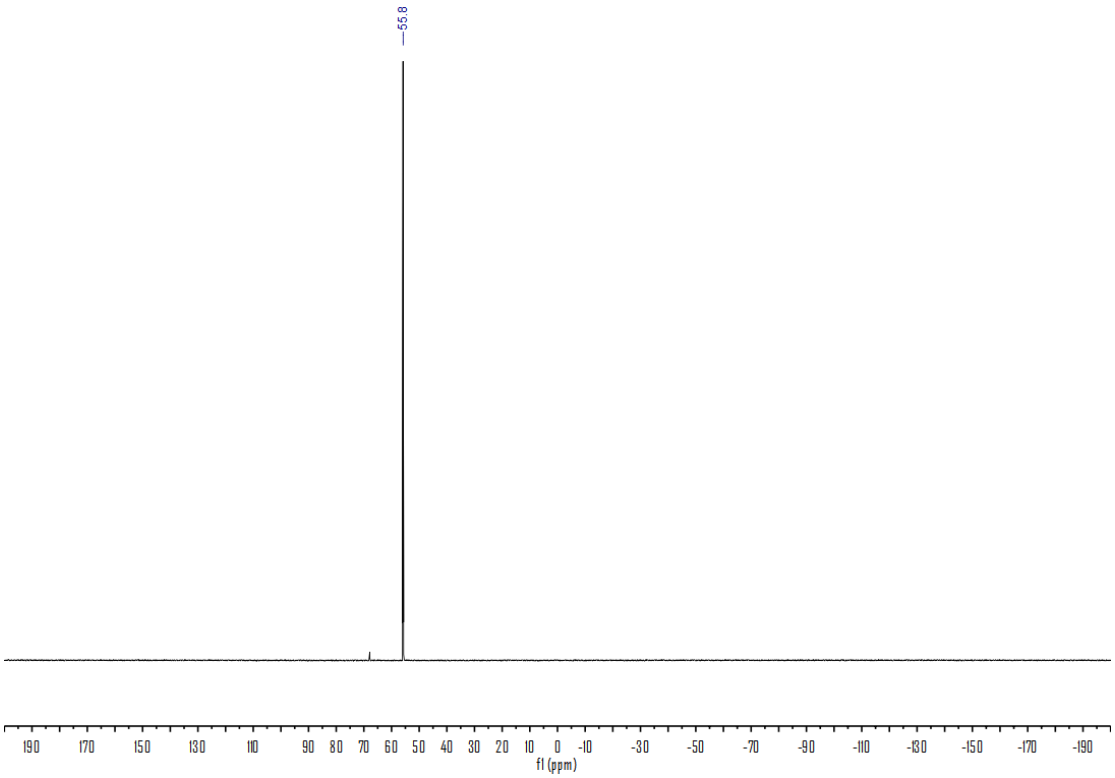
^{1}H NMR (600 MHz, $CDCl_3$)

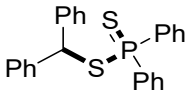


^{13}C NMR (151 MHz, $CDCl_3$)



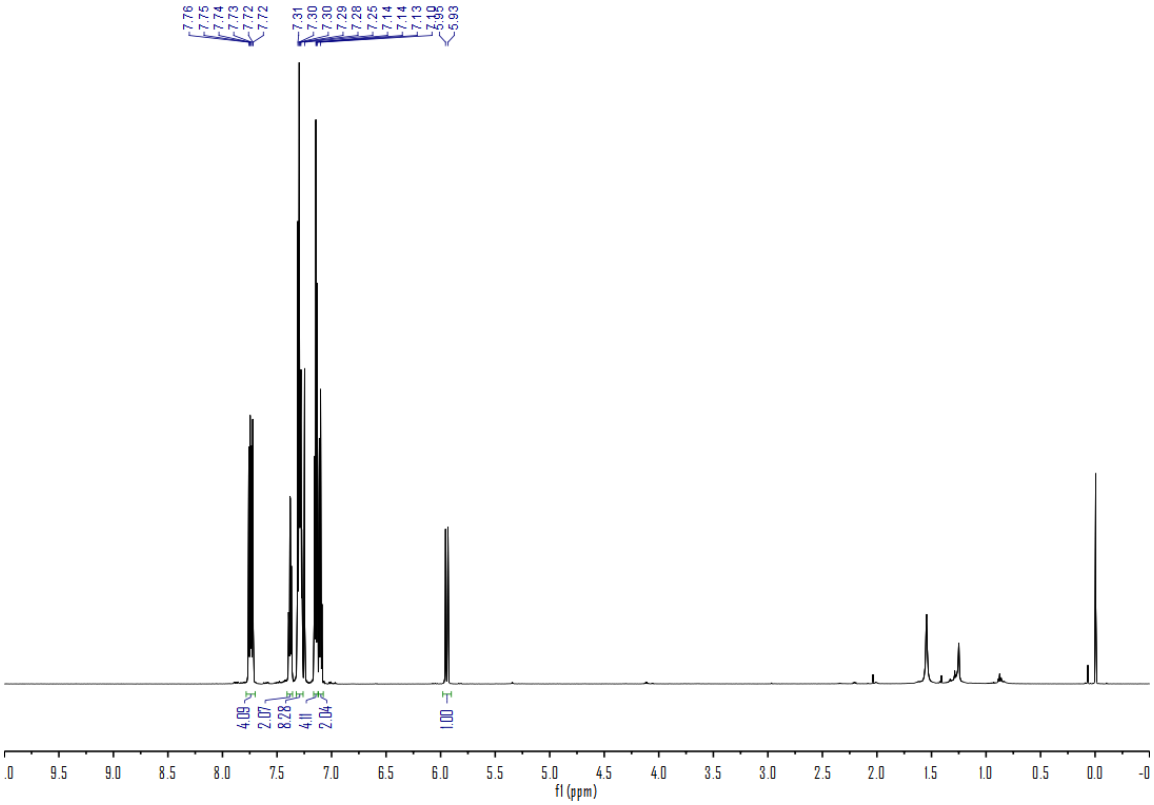
^{31}P NMR (243 MHz, $CDCl_3$)



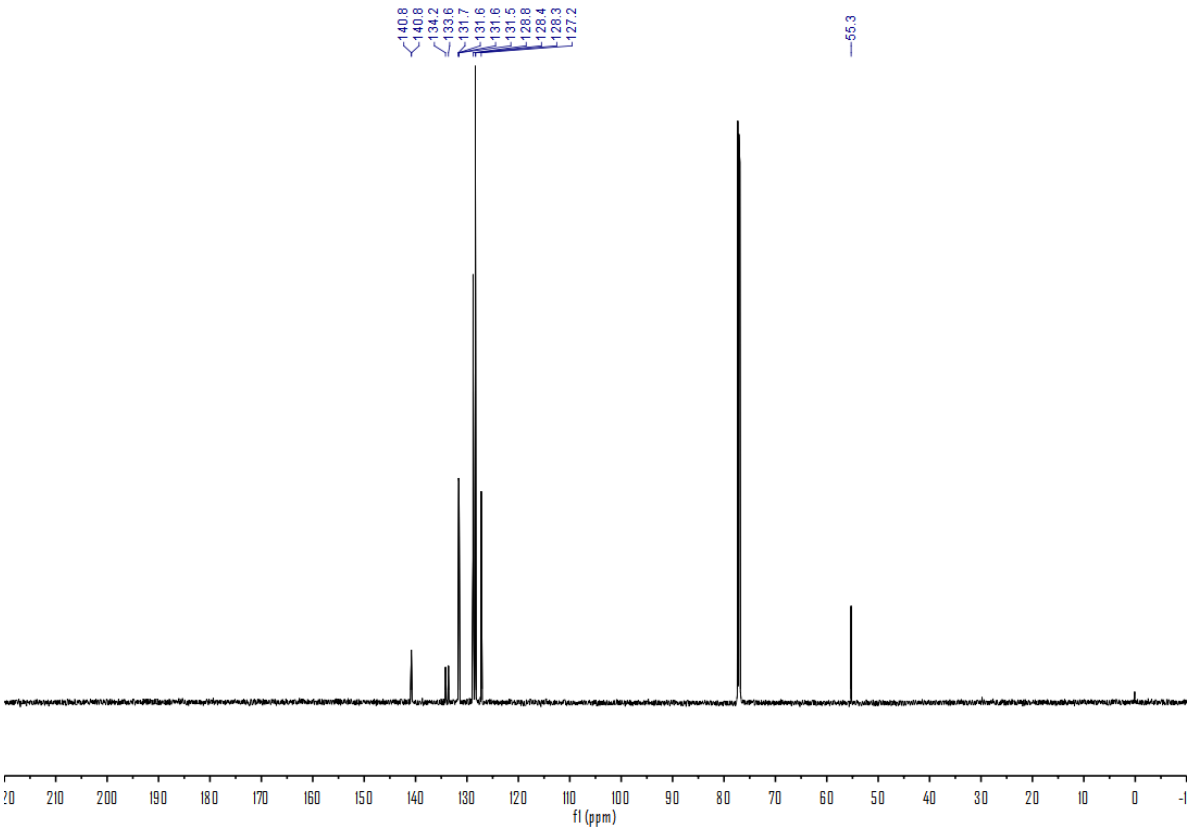


6am

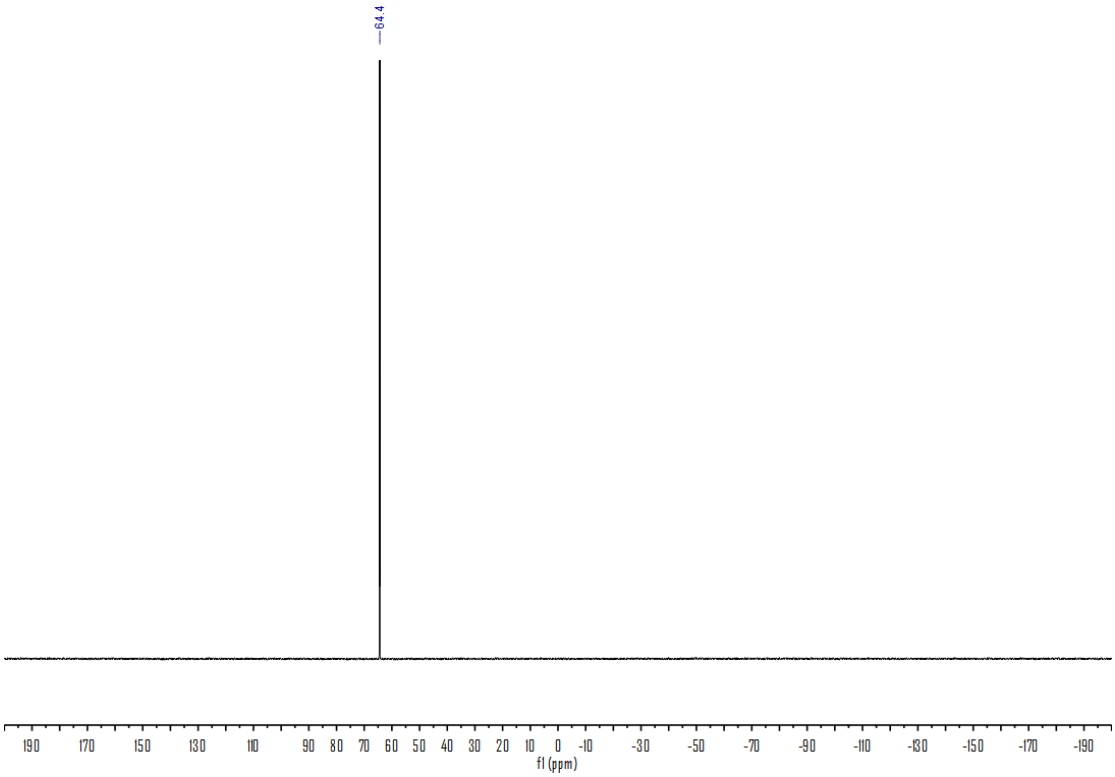
^{1}H NMR (600 MHz, $CDCl_3$)

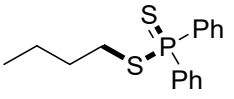


^{13}C NMR (151 MHz, $CDCl_3$)



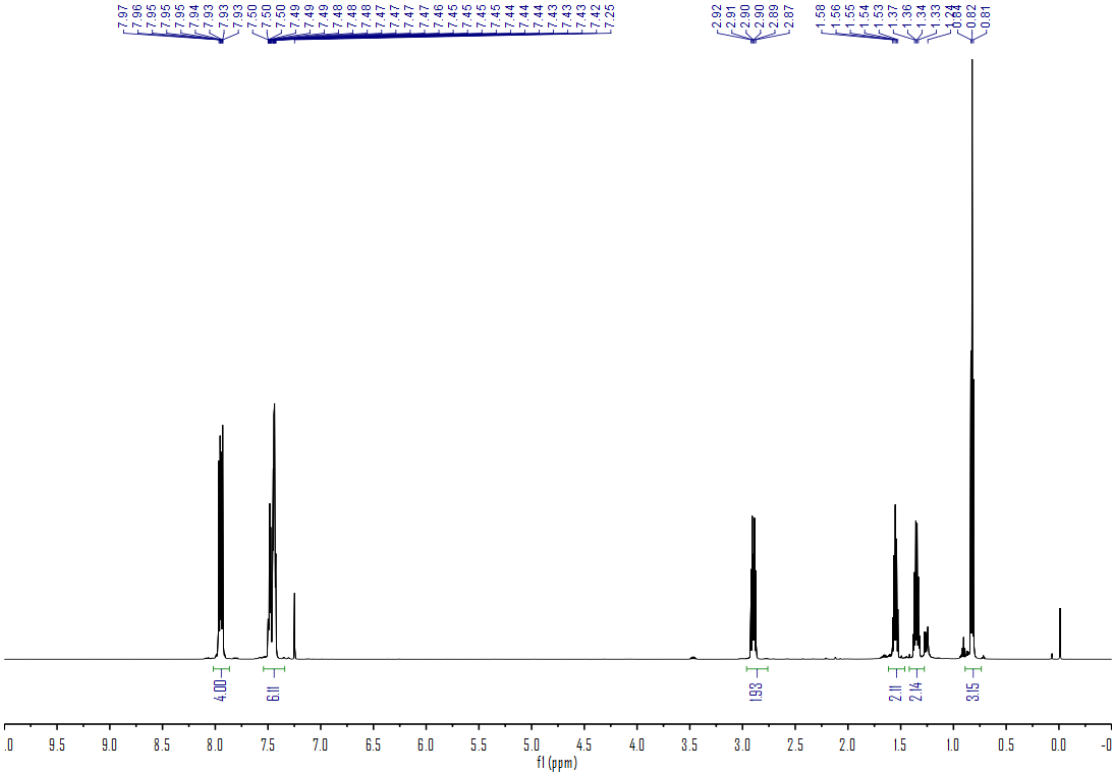
^{31}P NMR (243 MHz, $CDCl_3$)



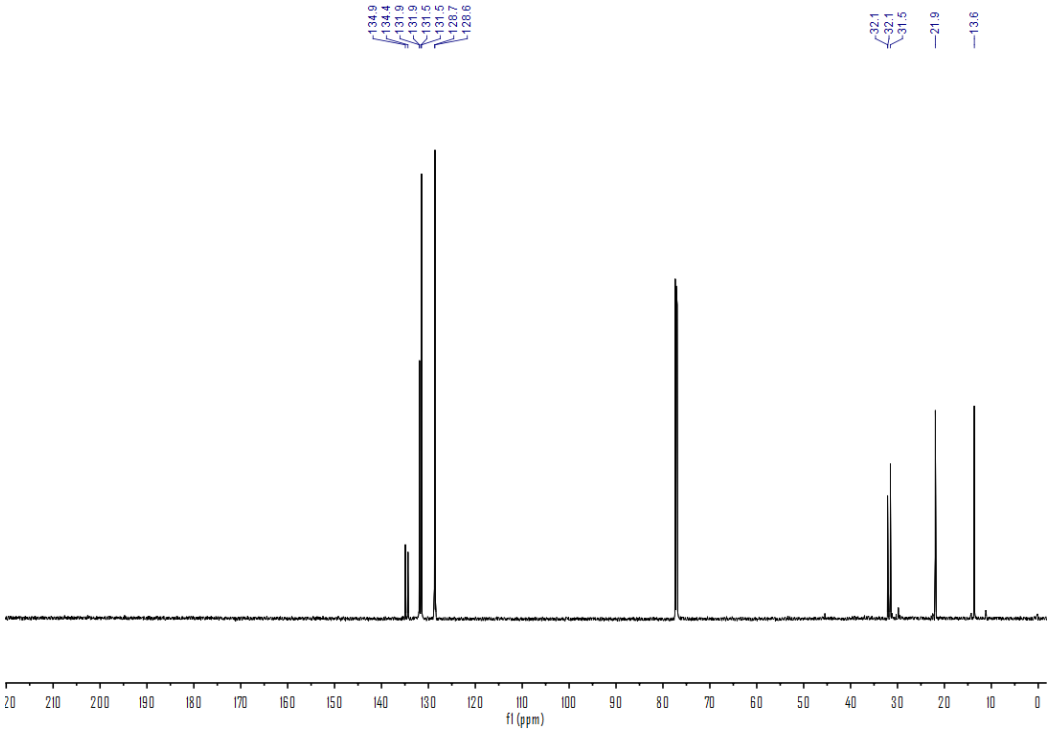


6an

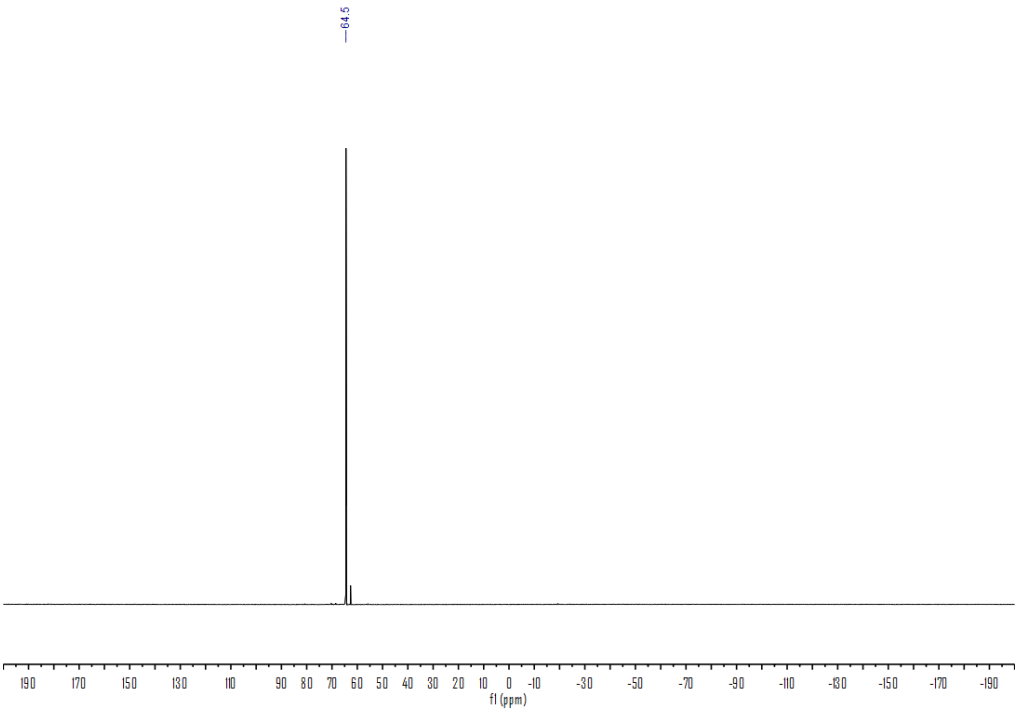
^{1}H NMR (600 MHz, $CDCl_3$)

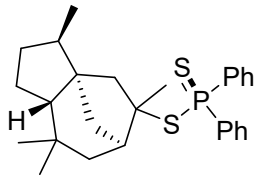


^{13}C NMR (151 MHz, $CDCl_3$)



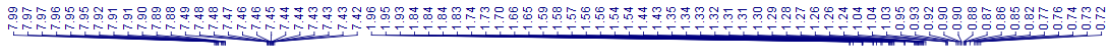
^{31}P NMR (243 MHz, $CDCl_3$)

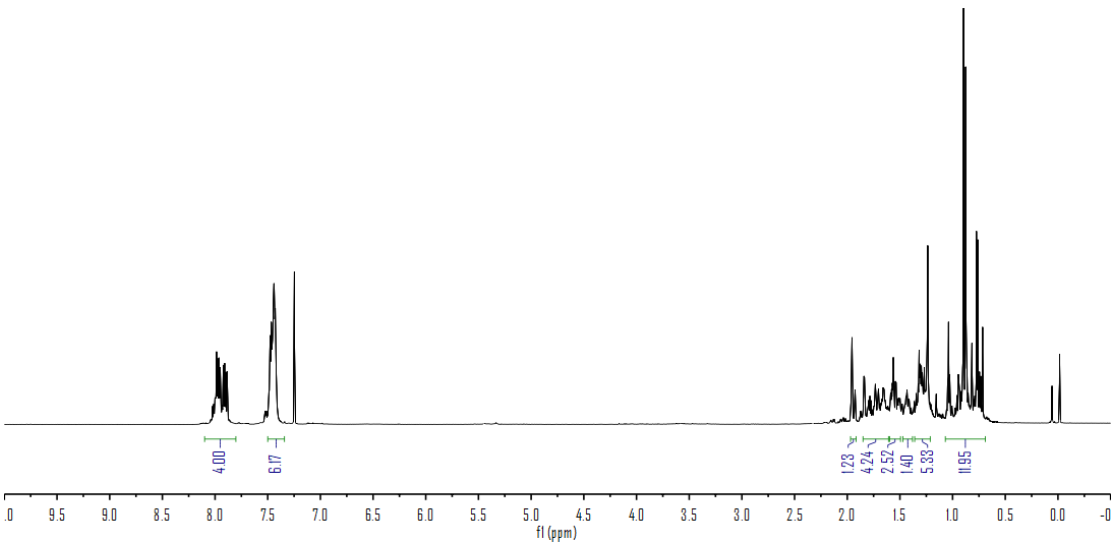




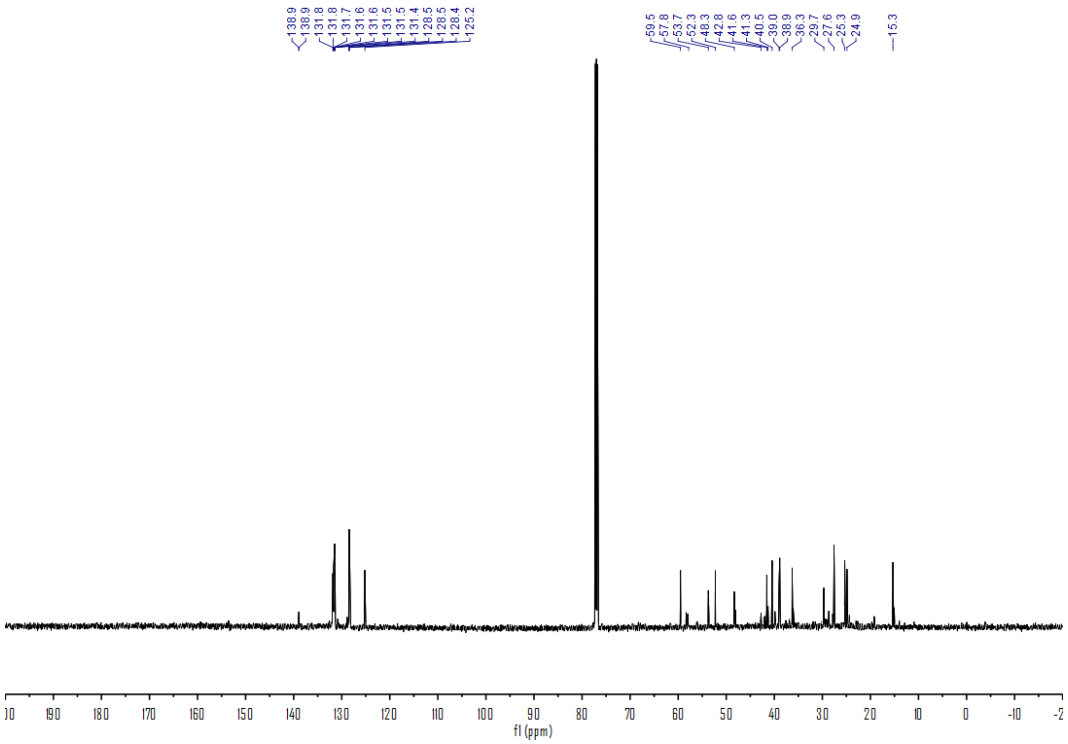
6ao

^{1}H NMR (600 MHz, $CDCl_3$)

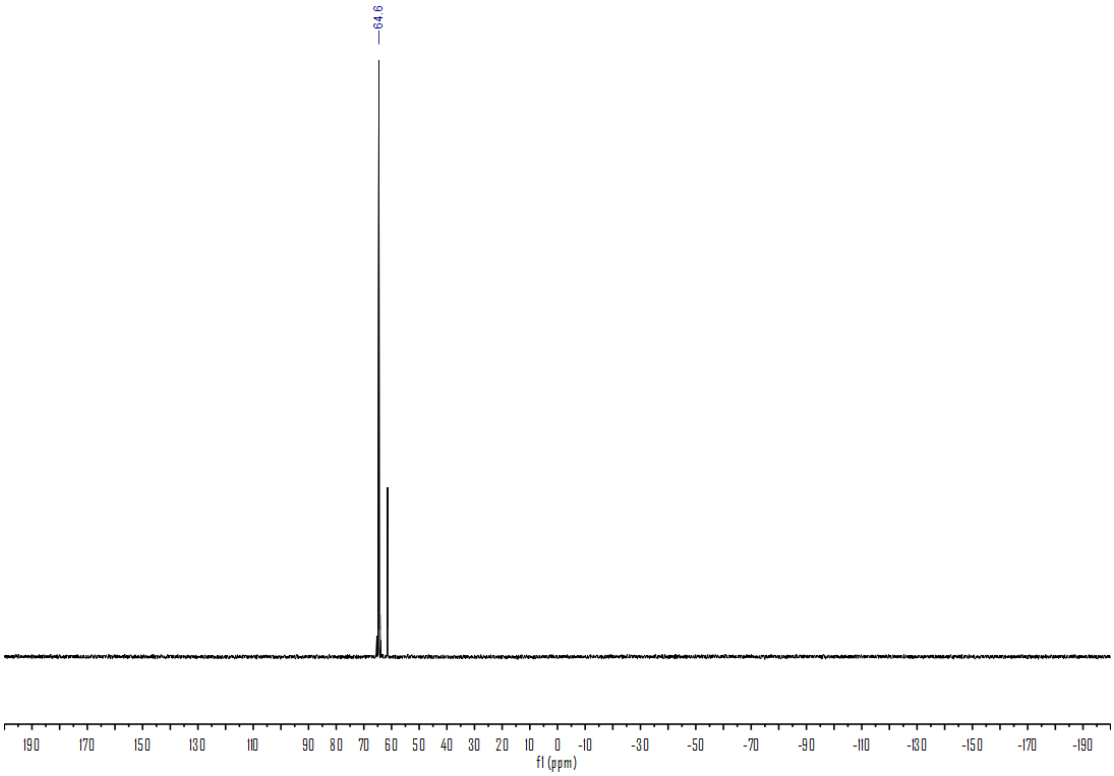


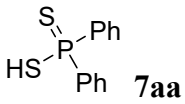


^{13}C NMR (151 MHz, $CDCl_3$)



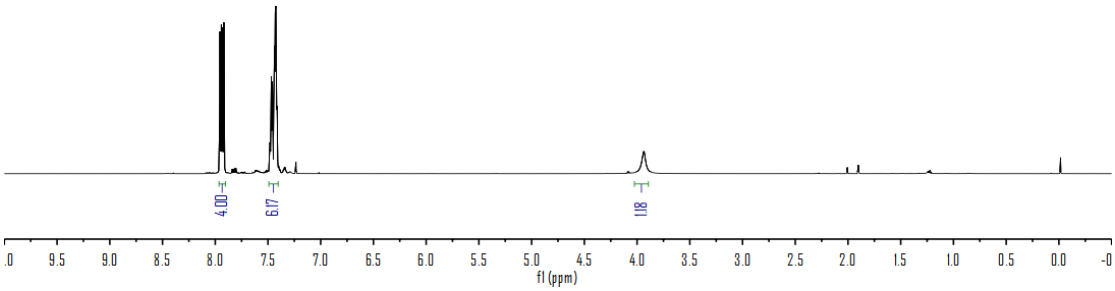
^{31}P NMR (243 MHz, $CDCl_3$)



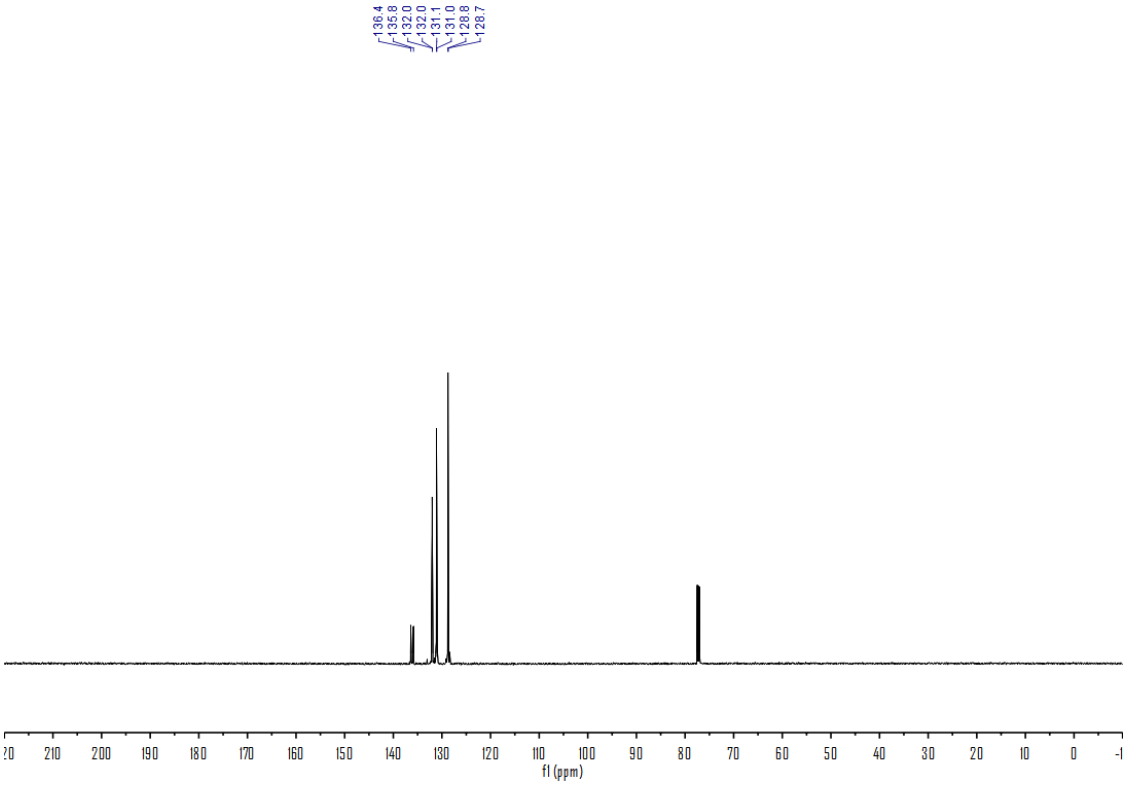


7aa

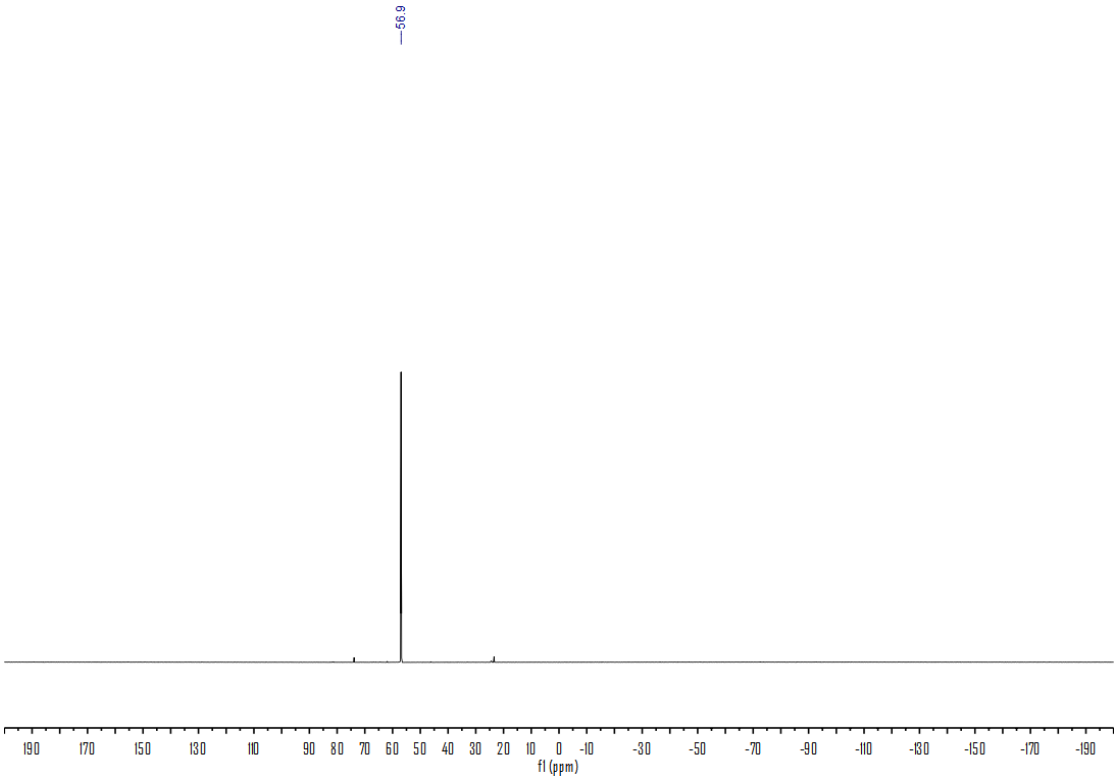
^{1}H NMR (600 MHz, $CDCl_3$)

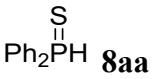


^{13}C NMR (151 MHz, $CDCl_3$)



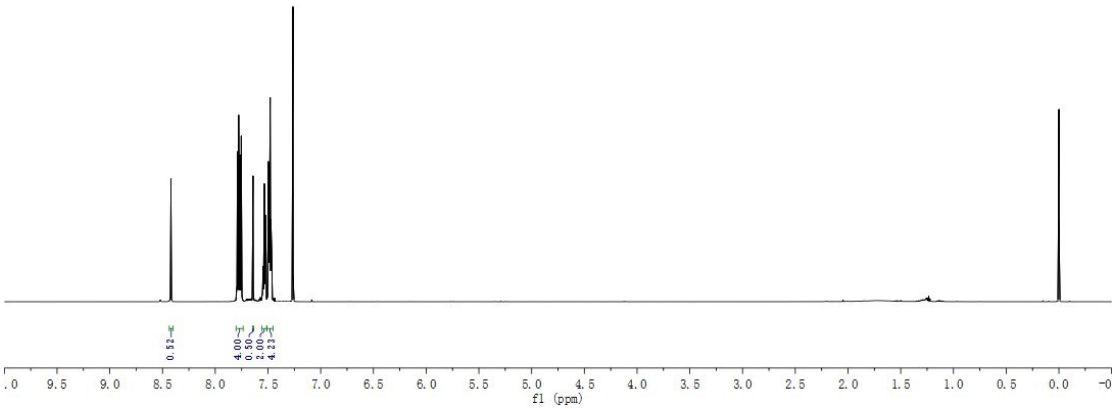
^{31}P NMR (243 MHz, $CDCl_3$)



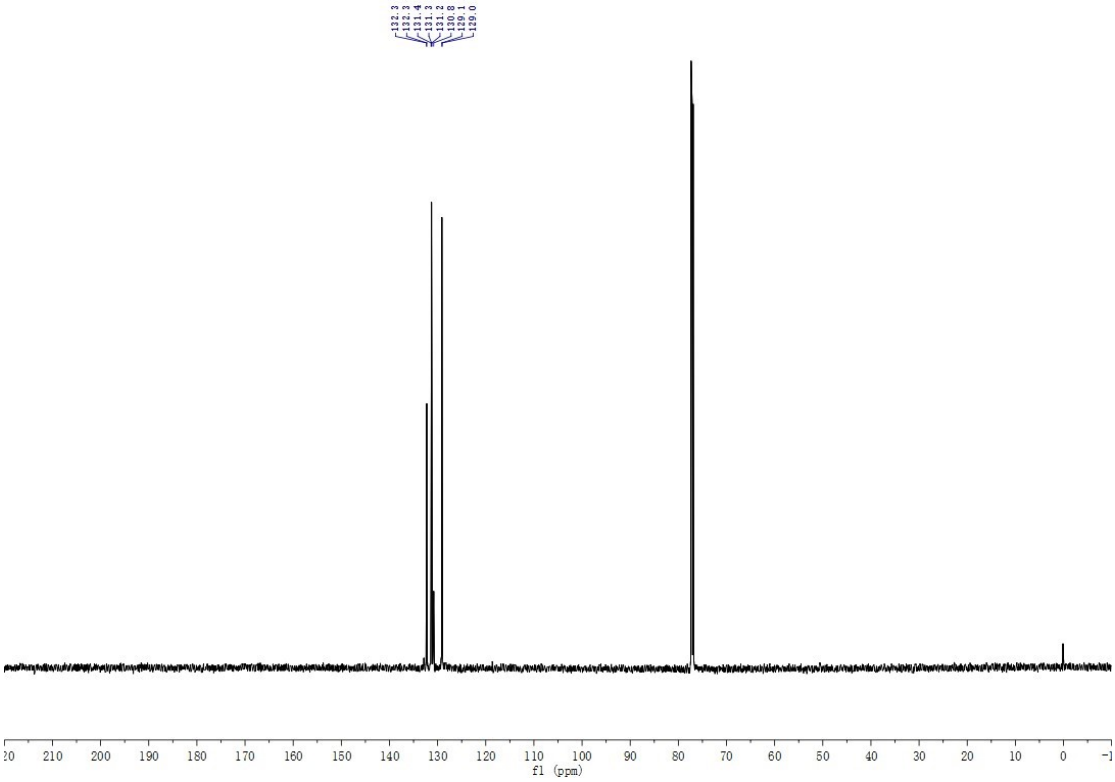


8aa

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



^{31}P NMR (243 MHz, $CDCl_3$)