Supporting Information

Synchronous recognition of P–intermediates and nucleophiles empowers diversified trivalent phosphorus synthesis

Xue Liu[1‡], Jingcheng Hu[1‡], Chengbiao Zhu[1], Dake Wang[1], Jia Yan[1], Jinyu Wang[3], Zhenwei Wei[1]*, Yong Yuan[2]*, Hong Yi[1]*, Aiwen Lei[1]*

[1] The Institute for Advanced Studies (IAS), College of Chemistry and Molecular Sciences; Wuhan University; Wuhan, 430072, P. R. China.
[2] College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, 730070, P. R. China.
[3] State Key Laboratory of Chemistry for NBC Hazards Protection；Beijing，102205，P. R. China.

‡These authors contributed equally to this work.
* Aiwen Lei. aiwenlei@whu.edu.cn, hong.yi@whu.edu.cn, yuanyong@nwnu.edu.cn, weizw2021@whu.edu.cn

Contents

1. General Information

1.1. Reagents, solvents and experimental conditions

All reactions were carried out under an atmosphere of argon in oven-dried glassware, unless otherwise noted. The solvent uses innochem's ultra-dry acetonitrile. Except where stated, all starting materials were commercially available and used without further purification.

1.2. Analytical techniques

Chronoamperometry and cyclic voltammograms were obtained on a CorrTest® CS2350H bipotentiostat. Hydrogen gas content was analyzed by gas chromatography (GC9790 Plus, Fuli, China, TCD, N_2 as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector). GC yields were recorded by SHIMADZU™ GC-2014 gas chromatography. Molecular weights of products were determined by SHIMADZU™ GCMS-QP2010 SE gas chromatgraphy mass spectrometrometry. All new compounds were characterized by high resolution mass spectra (HRMS). All undivided cells were purchased from Jiehengda® limited liability company (https://www.whjiehengda.com).

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform, 39.60 ppm, dimethylsulfoxide), respectively.

1.3. Compound purification

Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm). Flash chromatography columns were packed with 200-300 silica gel in petroleum (b.p. 60-90 °C).

1.4. Electrochemical set-up

The instrument for electrolysis was Current (HSPY-120-01) (made in China).

2. Importance of Bidentate Phosphine Ligands (III)

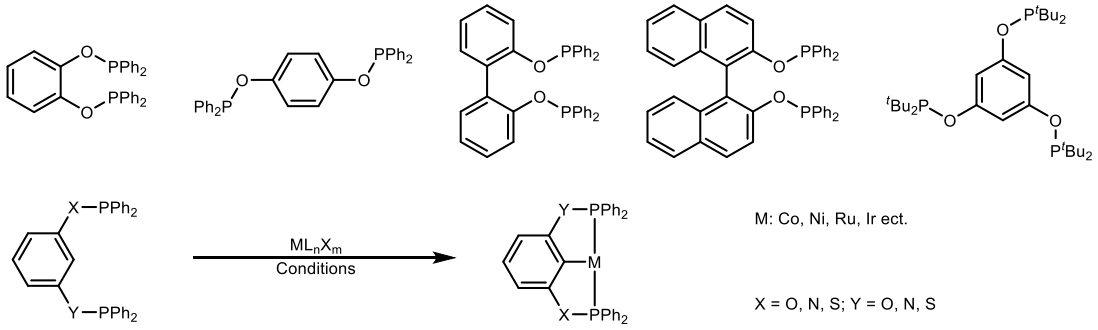
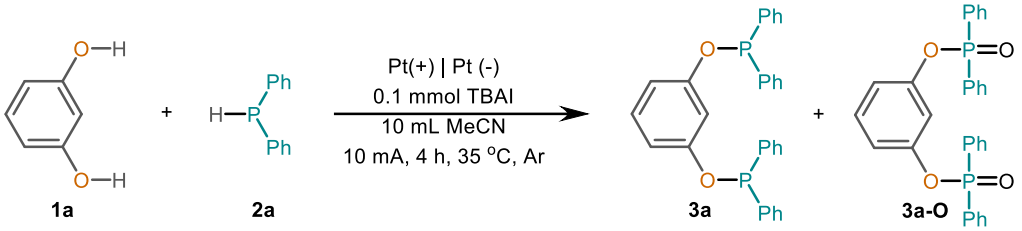


Fig. S1 Importance of bidentate phosphine ligands (III)

Organic molecules bearing X–Y bonds are pervasive. A particularly consequential family comprises trivalent phosphines with P–X units, which are central ligands across transition-metal catalysis and have propelled advances in organometallic chemistry. Chelating (bi- and multidentat) phosphines incorporating P–X motifs are widely paired with Rh, Ir, Co and Ni; notably, 1,3-disubstituted arenes preorganize scaffolds that serve as privileged pincer precursors.

3. Experimental Procedures for the Electrolysis

3.1. The condition optimized for the synthesis of 3a

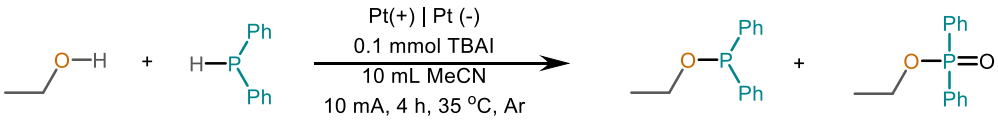


1a **2a** **3a** **3a-O**

entry	variation from standard conditions	yield of **3a**[a]	yield of **3a-O**[a]
1	none	91% (90%)[b]	1%
2	DMF instead of MeCN	12%	10%
3	DCM instead of MeCN	45%	8%
4	TEAI instead of TBAI	75%	5%
5	NH_4I instead of TBAI	16%	14%
6	NaI instead of TBAI	63%	2%
7	KI instead of TBAI	83%	2%
8	TBAB instead of TBAI	26%	7%
9	TBACl instead of TBAI	n.d.	n.d.
10	$TBABF_4$ instead of TBAI	11%	11%
11	CC(+) instead of Pt(+)	61%	13%
12	CF(+) instead of Pt(+)	65%	2%
13	CP(+) instead of Pt(+)	36%	5%
14	CC(-) instead of Pt(-)	58%	7%
15	SS(-) instead of Pt(-)	2%	1%
16	r.t. instead of 35 °C	85%	4%
17	45 °C instead of 35 °C	90%	5%
18	5 mA, 8 h instead of 10 mA, 4 h	88%	6%
19	20 mA, 2 h instead of 10 mA, 4 h	65%	6%
20	no electricity	n.d.	n.d.

Table S1. [a] Reaction conditions: platinum plate (15 mm × 15 mm × 0.3 mm) as the anode, platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode, undivided cell, **1a** (0.25 mmol), **2a** (0.7 mmol), TBAI (0.1 mmol), MeCN (10.0 mL), Ar, 35 °C, 10.0 mA, 4 h, yield was determined by assure ^{31}P NMR with triethyl phosphate oxide as internal standard. [b] Isolated yield.

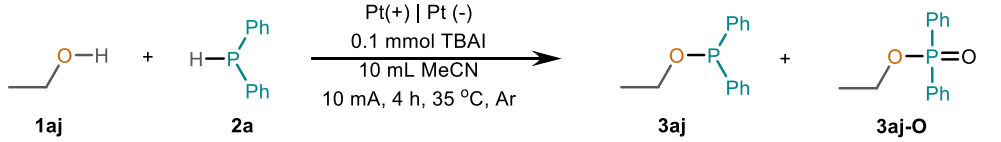
3.2. The condition optimized for the synthesis of 3aj



1aj **2a** **3aj** **3aj-O**

entry	variation from standard conditions	yield of **3aj**[a]	yield of **3aj-O**[a]
1	none	79%	17%
2	CC(+) instead of Pt(+)	23%	21%
3	CP(-) instead of Pt(-)	10%	11%
4	20 mA, 2 h instead of 10 mA, 4 h	54%	21%
5	15 mA, 2 h 40 min instead of 10 mA, 4 h	61%	20%
6	5 mA, 8 h instead of 10 mA, 4 h	27%	12%
7	KI instead of TBAI	54%	44%

Table S2. [a] Reaction conditions: platinum plate (15 mm × 15 mm × 0.3 mm) as the anode, platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode, undivided cell, **1aj** (1.0 mmol), **2a** (0.5 mmol), TBAI (0.1 mmol), MeCN (10.0 mL), Ar, 35 °C, 10.0 mA, 4 h, yield was determined by assure ^{31}P NMR with triethyl phosphate oxide as internal standard.



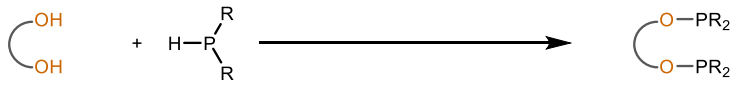
1aj **2a** **3aj** **3aj-O**

Entry	Variation	Yield of **3aj**[a]	Yield of **3aj-O**[a]
1	none	79%	17%
2	AC, 1/20 Hz	97%	3%

Table S3. [a] Reaction conditions: platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode, platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode, undivided cell, **1aj** (1.0 mmol), **2a** (0.5 mmol), TBAI (0.1 mmol), MeCN (10.0 mL), AC power (10 mA, D = 50%), Ar, 35 °C, 4 h. Yield was determined by assure ^{31}P NMR with triethyl phosphate oxide as internal standard.

4. Experimental Procedures and Characterization Data

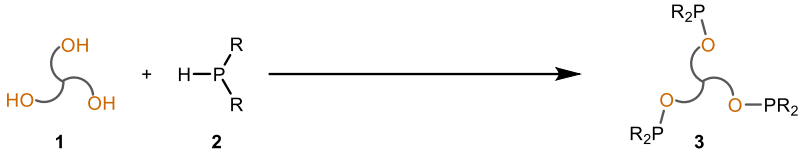
4.1. Synthesis of compound 3



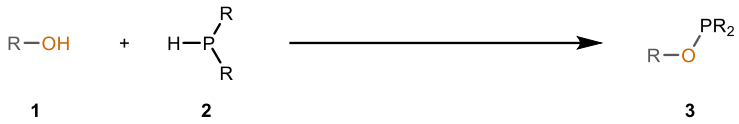
1 **2** **3**

Method A for the preparation of compound 3 (3a-3p,3s-3u): In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. Bisphenol (**1**, 0.25 mmol), TBAI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane or di-tert-butylphosphine (**2**, 0.7 mmol) and extra

dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 4 h (J = 4.4 mA/cm^2, 6.0 F/mol).



Method B for the preparation of compound 3 (3q-3r): Otherwise above method A, diphenylphosphane (**2a**, 1.00 mmol) was added, the mixtures were stirred at a constant current of 10 mA at 35 ºC for 5 h (J = 4.4 mA/cm^2, 7.5 F/mol).



Method C for the preparation of compound 3 (3v-3ai): In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. Phenol (**1**, 1.0 mmol), TBAI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane (**2a**, 0.5 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 3 h (J = 4.4 mA/cm^2, 2.2 F/mol).

Method D for the preparation of compound 3 (3aj-3at): Otherwise above method C, Then the mixture was stirred at an alternating current of 10 mA (1/20 Hz, duty ratio (D) = 50%) at 35 °C for 4 h (J = 4.4 mA/cm^2, 3.0 F/mol).

Method E for the preparation of compound 3 (3au-3av): Otherwise above method D, secondary alcohol (**1**, 6.0 mmol) added.

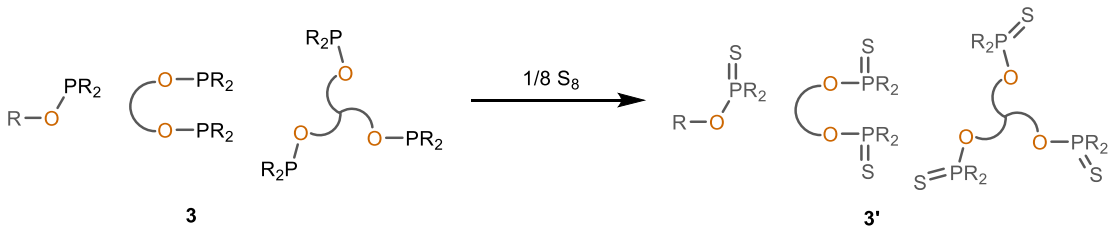
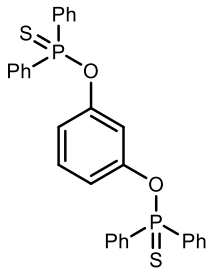


Fig. S2 Method for determining separation yield

Because the products are readily oxidized upon exposure to air, isolating them in pure form by routine methods such as flash chromatography proved challenging. To preserve product integrity, S_8 (1/8 equiv. per P atom) was added to the reaction mixture upon completion, and the mixture was stirred for 30 minutes to suppress oxidation. The desired products were then obtained in pure form after purification by flash chromatography on 200–300 mesh silica gel (petroleum: EtOAc = 50: 1).

O,O'-(1,3-phenylene) bis(diphenylphosphinothioate) (**3a'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and resorcinol (27.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (122.0 mg, yield 90%).

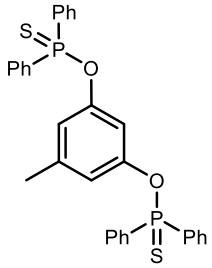
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.83 (m, 8H), 7.53 – 7.47 (m, 4H), 7.47 – 7.40 (m, 8H), 7.05 (t, *J* = 8.2 Hz, 1H), 6.88 (q, *J* = 1.9 Hz, 1H), 6.86 – 6.80 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.88 (d, *J* = 8.9 Hz), 133.94 (d, *J* = 111.0 Hz), 132.07 (d, *J* = 3.1 Hz), 131.29 (d, *J* = 11.5 Hz), 129.32, 128.48 (d, *J* = 13.8 Hz), 118.13 (dd, *J* = 5.1, 1.5 Hz), 115.74 (t, *J* = 5.2 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.62.

HRMS (ESI, m/z): calcd for $C_{30}H_{24}O_2P_2S_2$ $[M+H]^+$: 543.0766 found: 543.0763.

O,O'-(5-methyl-1,3-phenylene) bis(diphenylphosphinothioate) (**3b'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and 5-methylbenzene-1,3-diol (31.0 mg, 0.25 mmol), followed by further purification to obtained a white solid (104.3 mg, yield 75%).

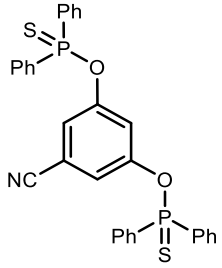
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.83 (m, 9H), 7.53 – 7.43 (m, 4H), 7.46 – 7.37 (m, 8H), 6.69 – 6.62 (m, 3H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.51 (d, *J* = 9.4 Hz), 139.93, 134.02 (d, *J* = 111.1 Hz), 131.98 (d, *J* = 3.1 Hz), 131.21 (d, *J* = 11.6 Hz), 128.41 (d, *J* = 13.7 Hz), 118.92 (dd, *J* = 5.0, 1.7 Hz), 112.52 (t, *J* = 5.1 Hz), 21.30.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.26.

HRMS (ESI, m/z): calcd for $C_{31}H_{26}O_2P_2S_2$ $[M+H]^+$: 557.0922 found: 557.0925.

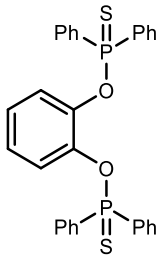
O,O'-(5-cyano-1,3-phenylene) bis(diphenylphosphinothioate) (**3c'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and 3,5-dihydroxybenzonitrile

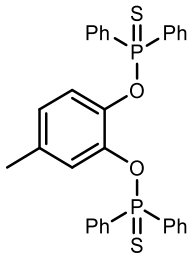
(33.8 mg, 0.25 mmol), followed by further purification to obtained a white solid (46.8 mg, yield 33%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.83 (m, 8H), 7.59 – 7.51 (m, 4H), 7.51 – 7.43 (m, 8H), 7.17 (p, *J* = 1.9 Hz, 1H), 7.09 (q, *J* = 1.6 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.22 (d, *J* = 9.0 Hz), 133.14 (d, *J* = 110.6 Hz), 132.50 (d, *J* = 3.1 Hz), 131.24 (d, *J* = 11.8 Hz), 128.69 (d, *J* = 13.9 Hz), 121.77 (dd, *J* = 5.1, 1.5 Hz), 121.09 (t, *J* = 5.1 Hz), 117.17, 113.13.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 85.00.
HRMS (ESI, m/z): calcd for $C_{31}H_{23}NO_2P_2S_2$ $[M+H]^+$: 568.0718 found: 568.0716.

O,O'-(1,2-phenylene) bis(diphenylphosphinothioate) (**3d'**)



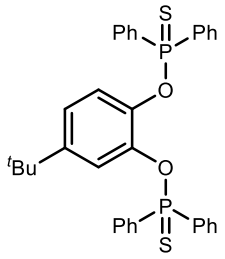
Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and pyrocatechol (27.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (117.9 mg, yield 87%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.89 (m, 8H), 7.50 – 7.41 (m, 4H), 7.37 – 7.28 (m, 8H), 7.11 – 7.04 (m, 2H), 6.91 – 6.82 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.48 (dd, *J* = 8.4, 5.8 Hz), 134.07 (d, *J* = 110.8 Hz), 131.97 (d, *J* = 3.1 Hz), 131.45 (d, *J* = 11.8 Hz), 128.41 (d, *J* = 13.7 Hz), 124.51, 121.93 (d, *J* = 5.4 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.87.
HRMS (ESI, m/z): calcd for $C_{30}H_{24}O_2P_2S_2$ $[M+H]^+$: 543.0766 found: 543.0764.

O,O'-(4-methyl-1,2-phenylene) bis(diphenylphosphinothioate) (**3e'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and 4-methylbenzene-1,2-diol (31.0 mg, 0.25 mmol), followed by further purification to obtained a white solid (108.4 mg, yield 78%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.88 (m, 8H), 7.46 – 7.40 (m, 4H), 7.35 – 7.26 (m, 8H), 6.94 – 6.87 (m, 2H), 6.69 – 6.62 (m, 1H), 2.07 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.03 (dd, *J* = 8.4, 5.7 Hz), 140.01 (dd, *J* = 8.4, 5.6 Hz), 134.66 (d, *J* = 1.4 Hz), 134.49, 133.56 (d, *J* = 1.2 Hz), 131.88 (d, *J* = 3.1 Hz), 131.43 (d, *J* = 2.2 Hz), 131.31 (d, *J* = 2.2 Hz), 128.61, 128.40, 128.26, 125.05, 122.51 (d, *J* = 5.2 Hz), 121.41 (d, *J* = 5.3 Hz), 20.80.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.79, 82.71.
HRMS (ESI, m/z): calcd for $C_{31}H_{26}O_2P_2S_2$ $[M+H]^+$: 557.0922 found: 557.0917.

O,O'-(4-(tert-butyl)-1,2-phenylene) bis(diphenylphosphinothioate) (**3f'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and 4-(tert-butyl)benzene-1,2-diol (41.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (145.0 mg, yield 97%).

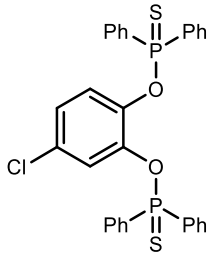
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.90 (m, 8H), 7.52 – 7.40 (m, 4H), 7.37 – 7.28 (m, 9H), 7.06 – 7.01 (m, 1H), 6.97 – 6.90 (m, 1H), 6.88 – 6.81 (m, 1H), 1.06 – 1.01 (m, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.62, 141.74 (dd, *J* = 8.5, 5.8 Hz), 140.18 – 139.06 (m), 134.70 (d, *J* = 37.5 Hz), 133.60 (d, *J* = 37.1 Hz), 131.90 (t, *J* = 2.7 Hz), 131.63, 131.50 (d, *J* = 3.7 Hz), 131.36, 128.41 (d, *J* = 6.1 Hz), 128.28 (d, *J* = 6.1 Hz), 121.07, 120.88 (d, *J* = 5.5 Hz), 119.62 (d, *J* = 5.5 Hz), 34.23, 30.91.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.41, 82.19.

HRMS (ESI, m/z): calcd for $C_{34}H_{32}O_2P_2S_2$ $[M+H]^+$: 599.1392 found: 599.1378.

O,O'-(4-chloro-1,2-phenylene) bis(diphenylphosphinothioate) (**3g'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and 4-chlorocyclohexa-2,4-diene-1,2-diol (36.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (106.6 mg, yield 74%).

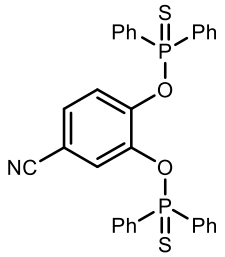
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.86 (m, 8H), 7.50 – 7.41 (m, 4H), 7.37 – 7.28 (m, 8H), 7.12 – 7.07 (m, 1H), 7.02 – 6.97 (m, 1H), 6.87 – 6.81 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.82 (dd, *J* = 8.5, 5.6 Hz), 141.33 (dd, *J* = 8.3, 5.6 Hz), 134.14 (d, *J* = 9.2 Hz), 133.04 (d, *J* = 9.2 Hz), 132.13 (d, *J* = 7.9 Hz), 132.13 (d, *J* = 1.8 Hz), 131.92 (d, *J* = 2.2 Hz), 131.39 (d, *J* = 1.9 Hz), 131.27 (d, *J* = 2.0 Hz), 129.16 (d, *J* = 1.7 Hz), 128.51 (d, *J* = 1.6 Hz), 128.37 (d, *J* = 1.5 Hz), 124.56, 122.40 (dd, *J* = 11.1, 5.4 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 84.29, 83.88.

HRMS (ESI, m/z): calcd for $C_{30}H_{23}ClO_2P_2S_2$ $[M+H]^+$: 577.0376 found: 577.0363.

O,O'-(4-cyano-1,2-phenylene) bis(diphenylphosphinothioate) (**3h'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and 3,4-dihydroxybenzonitrile (33.8 mg, 0.25 mmol), followed by further purification to obtained a white solid (110.6 mg, yield 78%). 83%

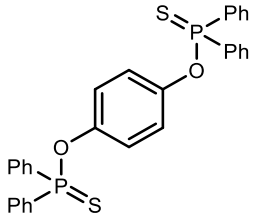
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.85 (m, 8H), 7.56 – 7.44 (m, 4H), 7.41 – 7.29 (m, 9H), 7.26 – 7.17 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.85 (dd, *J* = 8.0, 5.2 Hz), 142.74 (dd, *J* = 8.4, 5.9 Hz), 133.74 (d, *J* = 10.7 Hz), 132.65 (d, *J* = 11.0 Hz), 132.38 (d, *J* = 6.7 Hz), 132.38, 131.37 (d, *J* = 3.5 Hz), 131.25 (d, *J* = 3.4 Hz), 128.92, 128.66 (d, *J* = 3.2 Hz), 128.52 (d, *J* = 3.3 Hz), 125.60 (d, *J* = 5.3 Hz), 122.54 (d, *J* = 5.9 Hz), 117.57, 107.86.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 85.47, 84.73.

HRMS (ESI, m/z): calcd for $C_{31}H_{23}NO_2P_2S_2$ $[M+H]^+$: 568.0718 found: 568.0715.

O,O'-(1,4-phenylene) bis(diphenylphosphinothioate) (**3i'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and hydroquinone (27.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (88.1 mg, yield 65%).

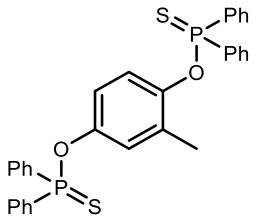
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.87 (m, 8H), 7.58 – 7.49 (m, 4H), 7.49 – 7.40 (m, 8H), 6.91 – 6.87 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.50 – 146.84 (m), 134.10 (d, *J* = 111.0 Hz), 132.19 – 131.98 (m), 131.34 (d, *J* = 11.8 Hz), 128.49 (d, *J* = 13.9 Hz), 122.48 – 122.28 (m).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.54.

HRMS (ESI, m/z): calcd for $C_{30}H_{24}O_2P_2S_2$ $[M+H]^+$: 543.0766 found: 543.0765.

O,O'-(2-methyl-1,4-phenylene) bis(diphenylphosphinothioate) (**3j'**)



Synthesized by following method A using diphenylphosphane (135 μL, 0.7 mmol) and 2-methylbenzene-1,4-diol (31.0 mg, 0.25 mmol), followed by further purification to obtained a white solid (108.4 mg, yield

78%).

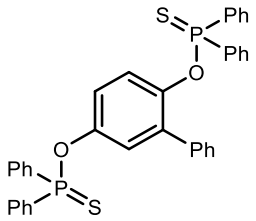
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.87 (m, 8H), 7.54 – 7.38 (m, 12H), 6.89 (d, *J* = 2.9 Hz, 1H), 6.78 – 6.71 (m, 1H), 6.66 – 6.58 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.68 (dd, *J* = 9.0, 1.9 Hz), 146.11 (dd, *J* = 9.0, 2.0 Hz), 134.91 (d, *J* = 39.1 Hz), 133.81 (d, *J* = 39.0 Hz), 131.99 (d, *J* = 3.1 Hz), 131.93 (d, *J* = 1.4 Hz), 131.88 (d, *J* = 1.3 Hz), 131.16 (d, *J* = 24.3 Hz), 131.16 (d, *J* = 1.3 Hz), 128.50 (d, *J* = 6.5 Hz), 128.37 (d, *J* = 6.5 Hz), 124.26 (d, *J* = 4.9 Hz), 121.10 (dd, *J* = 4.5, 1.5 Hz), 119.21 (dd, *J* = 4.9, 1.5 Hz), 17.33.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.22, 81.43 (d, *J* = 2.6 Hz).

HRMS (ESI, m/z): calcd for $C_{31}H_{26}O_2P_2S_2$ $[M+H]^+$: 557.0922 found: 557.0914.

O,O'-([1,1'-biphenyl]-2,5-diyl) bis(diphenylphosphinothioate) (**3k'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and [1,1'-biphenyl]-2,5-diol (46.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (139.1 mg, yield 90%).

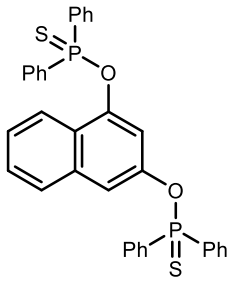
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.86 (m, 4H), 7.67 – 7.56 (m, 4H), 7.53 – 7.46 (m, 2H), 7.46 – 7.36 (m, 6H), 7.33 – 7.21 (m, 9H), 7.20 – 7.15 (m, 1H), 7.05 – 7.00 (m, 1H), 6.87 – 6.79 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.73 (dd, *J* = 8.8, 1.7 Hz), 144.69 (dd, *J* = 8.8, 1.9 Hz), 136.85, 135.70 (d, *J* = 5.1 Hz), 134.51 (d, *J* = 5.1 Hz), 133.41 (d, *J* = 5.3 Hz), 132.07 (d, *J* = 3.0 Hz), 131.79 (d, *J* = 3.1 Hz), 131.22 (d, *J* = 24.3 Hz), 131.22 (d, *J* = 1.3 Hz), 129.61, 128.45 (d, *J* = 13.6 Hz), 128.20 (d, *J* = 13.8 Hz), 127.90, 127.36, 124.22 (d, *J* = 5.0 Hz), 122.01 (d, *J* = 4.8 Hz), 120.80 (d, *J* = 4.6 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.86, 82.73.

HRMS (ESI, m/z): calcd for $C_{36}H_{28}O_2P_2S_2$ $[M+H]^+$: 619.1079 found: 619.1058.

O,O'-(naphthalene-1,3-diyl) bis(diphenylphosphinothioate) (**3l'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and naphthalene-1,3-diol (40.0 mg, 0.25 mmol), followed by further purification to obtained a white solid (106.6 mg, yield 72%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.84 (m, 9H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.36 (m, 13H), 7.36 – 7.28 (m, 2H), 7.10 (d, *J* = 2.2 Hz, 1H).

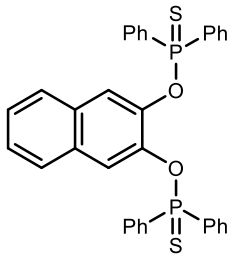
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.29 (d, *J* = 9.2 Hz), 147.16 (dd, *J* = 8.9, 1.6 Hz), 134.50

(d, *J* = 15.1 Hz), 134.02 (d, *J* = 1.4 Hz), 133.40 (d, *J* = 15.0 Hz), 132.13 (d, *J* = 3.1 Hz), 132.00 (d, *J* = 3.1 Hz), 131.27 (d, *J* = 10.3 Hz), 131.16 (d, *J* = 10.6 Hz), 128.59 (d, *J* = 13.9 Hz), 128.44 (d, *J* = 13.9 Hz), 127.41, 127.10, 125.37, 125.07 (d, *J* = 4.6 Hz), 122.04, 115.03 (d, *J* = 5.6 Hz), 112.71 – 111.84 (m).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.94, 82.65.

HRMS (ESI, m/z): calcd for $C_{34}H_{26}O_2P_2S_2$ $[M+H]^+$: 593.0922 found: 593.0910.

O,O'-(naphthalene-2,3-diyl) bis(diphenylphosphinothioate) (**3m'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and naphthalene-2,3-diol (40.0 mg, 0.25 mmol), followed by further purification to obtained a white solid (115.4 mg, yield 78%).

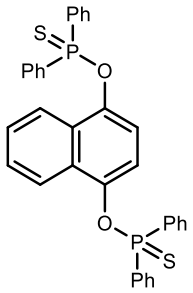
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.93 (m, 8H), 7.52 – 7.44 (m, 8H), 7.38 – 7.31 (m, 8H), 7.31 – 7.27 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.46 (dd, *J* = 8.5, 5.5 Hz), 133.95 (d, *J* = 110.9 Hz), 132.05 (d, *J* = 3.0 Hz), 131.52 (d, *J* = 11.8 Hz), 130.11, 128.48 (d, *J* = 13.7 Hz), 127.18, 125.65, 118.88 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 83.21.

HRMS (ESI, m/z): calcd for $C_{34}H_{26}O_2P_2S_2$ $[M+H]^+$: 593.0922 found: 593.0908.

O,O'-(naphthalene-1,4-diyl) bis(diphenylphosphinothioate) (**3n'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and naphthalene-1,4-diol (40.0 mg, 0.25 mmol), followed by further purification to obtained a white solid (127.3 mg, yield 86%).

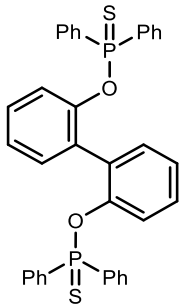
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.96 (m, 10H), 7.53 – 7.38 (m, 14H), 6.88 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.41 (dd, *J* = 9.3, 1.9 Hz), 134.34 (d, *J* = 110.9 Hz), 132.14, 132.11, 131.19 (d, *J* = 11.8 Hz), 128.59 (d, *J* = 13.7 Hz), 126.64, 122.28, 115.45 – 114.27 (m).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.28.

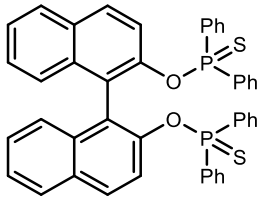
HRMS (ESI, m/z): calcd for $C_{34}H_{26}O_2P_2S_2$ $[M+H]^+$: 593.0922 found: 593.0907.

O,O'-([1,1'-biphenyl]-2,2'-diyl) bis(diphenylphosphinothioate) (**3o'**)



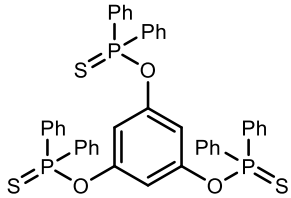
Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and [1,1'-biphenyl]-2,2'-diol (46.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (115.9 mg, yield 75%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.50 (m, 6H), 7.38 – 7.30 (m, 6H), 7.26 – 7.13 (m, 12H), 7.03 (t, *J* = 7.4 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.62 (d, *J* = 8.5 Hz), 134.25 (d, *J* = 111.4 Hz), 131.71, 131.60 (d, *J* = 3.1 Hz), 131.02 (d, *J* = 11.7 Hz), 130.64 (d, *J* = 5.7 Hz), 128.40, 128.17 (d, *J* = 13.6 Hz), 124.22, 120.53 (d, *J* = 5.2 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 81.05.
HRMS (ESI, m/z): calcd for $C_{36}H_{28}O_2P_2S_2$ $[M+H]^+$: 619.1079 found: 619.1064.

O,O'-([1,1'-binaphthalene]-2,2'-diyl) bis(diphenylphosphinothioate) (**3p'**)



Synthesized by method A using diphenylphosphane (135 μL, 0.7 mmol) and [1,1'-binaphthalene]-2,2'-diol (71.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (93.3 mg, yield 52%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.76 (m, 4H), 7.72 – 7.66 (m, 2H), 7.58 – 7.48 (m, 4H), 7.37 – 7.25 (m, 8H), 7.25 – 7.17 (m, 6H), 7.16 – 7.08 (m, 4H), 7.07 – 7.00 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.38 (d, *J* = 8.4 Hz), 134.94 (d, *J* = 52.2 Hz), 133.83 (d, *J* = 50.5 Hz), 133.65, 131.45 (dd, *J* = 14.3, 3.0 Hz), 130.97 (d, *J* = 11.7 Hz), 130.67 (d, *J* = 11.9 Hz), 130.56, 129.06, 128.05 (dd, *J* = 29.7, 13.9 Hz), 126.75, 125.66 (d, *J* = 110.1 Hz), 123.04 (d, *J* = 6.6 Hz), 120.50 (d, *J* = 5.1 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 80.06.
HRMS (ESI, m/z): calcd for $C_{44}H_{32}O_2P_2S_2$ $[M+H]^+$: 719.1392 found: 719.1374.

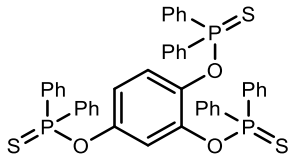
O,*O',O''*-(benzene-1,3,5-triyl) tris(diphenylphosphinothioate) (**3q'**)



Synthesized by method B using diphenylphosphane (190 μL, 1.0 mmol) and benzene-1,3,5-triol (31.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (129.6 mg, yield 67%).

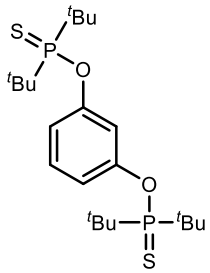
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.77 (m, 12H), 7.53 – 7.46 (m, 6H), 7.46 – 7.37 (m, 12H), 6.71 (q, *J* = 1.3 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.82 (d, *J* = 8.6 Hz), 133.65 (d, *J* = 110.8 Hz), 132.09 (d, *J* = 3.1 Hz), 131.27 (d, *J* = 11.7 Hz), 128.50 (d, *J* = 13.7 Hz), 112.23 (d, *J* = 6.1 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 83.12.
HRMS (ESI, m/z): calcd for $C_{42}H_{33}O_3P_3S_3$ $[M+H]^+$: 775.0877 found: 775.0865

O,O',O''-(benzene-1,2,4-triyl) tris(diphenylphosphinothioate) (**3r'**)



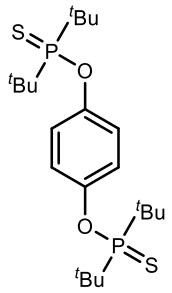
Synthesized by method B using diphenylphosphane (190 μL, 1.0 mmol) and benzene-1,2,4-triol (31.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (139.3 mg, yield 72%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.76 (m, 12H), 7.52 – 7.37 (m, 10H), 7.35 – 7.26 (m, 8H), 7.00 (d, *J* = 2.7 Hz, 1H), 6.93 (d, *J* = 9.1 Hz, 1H), 6.63 (d, *J* = 9.2, 2.0 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.46, 134.45, 134.25 (d, *J* = 6.7 Hz), 133.35, 133.15 (d, *J* = 6.6 Hz), 132.05, 132.02, 131.99, 131.48, 131.36, 131.24, 128.53, 128.49, 128.40, 128.36, 121.56 (d, *J* = 5.3 Hz), 117.56, 115.90.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 83.55, 83.13, 82.89.
HRMS (ESI, m/z): calcd for $C_{42}H_{33}O_3P_3S_3$ $[M+H]^+$: 775.0877 found: 775.0862

O,O'-(1,3-phenylene) bis(di-tert-butylphosphinothioate) (**3s'**)



Synthesized by method A using Di-tert-butylphosphine (102.2 mg, 0.7 mmol) and resorcinol (27.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (92.4 mg, yield 80%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (tt, *J* = 2.3, 1.1 Hz, 1H), 7.20 (t, *J* = 8.2 Hz, 1H), 7.06 – 6.99 (m, 2H), 1.43 (d, 36H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.80 (d, *J* = 11.7 Hz), 128.67, 117.23 (d, *J* = 4.1 Hz), 115.46 (t, *J* = 4.0 Hz), 41.20 (d, *J* = 58.4 Hz), 27.45 (d, *J* = 1.3 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 128.24.
HRMS (ESI, m/z): calcd for $C_{22}H_{40}O_2P_2S_2$ $[M+H]^+$: 463.2018 found: 463.2010

O,O'-(1,4-phenylene) bis(di-tert-butylphosphinothioate) (**3t'**)



Synthesized by method A using Di-tert-butylphosphine (102.2 mg, 0.7 mmol) and hydroquinone (27.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (101.6 mg, yield 88%).

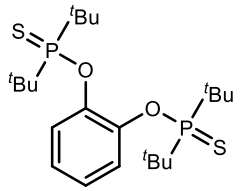
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (s, 4H), 1.43 (d, *J* = 16.3 Hz, 36H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.74 (dd, *J* = 12.0, 1.5 Hz), 126.65 – 116.12 (m), 41.10 (d, *J* = 58.6 Hz), 27.43.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 127.71.

HRMS (ESI, m/z): calcd for $C_{22}H_{40}O_2P_2S_2$ $[M+H]^+$: 463.2018 found: 463.2008

O,O'-(1,2-phenylene) bis(di-tert-butylphosphinothioate) (**3u'**)



Synthesized by method A using Di-tert-butylphosphine (102.2 mg, 0.7 mmol) and pyrocatechol (27.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (90.1 mg, yield 78%).

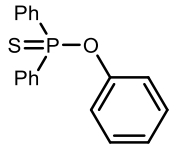
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 – 8.09 (m, 2H), 7.02 – 6.93 (m, 2H), 1.44 (d, *J* = 16.5 Hz, 36H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.15 (dd, *J* = 11.0, 4.9 Hz), 123.00 (d, *J* = 4.7 Hz), 122.93, 41.58 (d, *J* = 57.7 Hz), 27.54 (d, *J* = 1.2 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 131.37.

HRMS (ESI, m/z): calcd for $C_{22}H_{40}O_2P_2S_2$ $[M+H]^+$: 463.2018 found: 463.2007

O-phenyl diphenylphosphinothioate (**3v'**) [1]



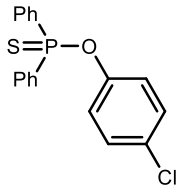
Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and phenol (94 mg, 1.0 mmol), followed by further purification to obtained a yellow solid (147.3 mg, yield 95%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (dd, *J* = 13.8, 7.5 Hz, 4H), 7.45 (ddd, *J* = 17.5, 8.8, 4.1 Hz, 6H), 7.20 (t, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 9.4 Hz, 2H), 7.04 – 6.98 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.38, 134.21 (d, *J* = 111.0 Hz), 131.97 (d, *J* = 3.1 Hz), 131.27 (d, *J* = 11.5 Hz), 129.22 (d, *J* = 1.3 Hz), 128.39 (d, *J* = 13.6 Hz), 124.72 (d, *J* = 1.8 Hz), 121.60 (d, *J* = 4.9 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.03.

O-(4-chlorophenyl) diphenylphosphinothioate (**3w'**)



Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and 4-chlorophenol (128 mg, 1.0 mmol), followed by further purification to obtained a yellow solid (165.1 mg, yield 96%).

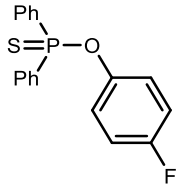
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.90 (m, 4H), 7.58 – 7.42 (m, 6H), 7.22 – 7.14 (m, 2H), 7.00 – 6.92 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.96 (d, *J* = 8.8 Hz), 133.87 (d, *J* = 110.9 Hz), 132.22 (d, *J* = 3.1 Hz), 131.35 (d, *J* = 11.6 Hz), 130.22 (d, *J* = 2.2 Hz), 129.32 (d, *J* = 1.4 Hz), 128.54 (d, *J* = 13.6 Hz), 123.06 (d, *J* = 4.8 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 83.15.

HRMS (ESI, m/z): calcd for $C_{18}H_{14}ClOPS$ $[M+H]^+$: 345.0264 found: 345.0261.

O-(4-fluorophenyl) diphenylphosphinothioate (**3x'**)



Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and 4-fluorophenol (112 mg, 1.0 mmol), followed by further purification to obtained a yellow solid (139.4 mg, yield 85%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.51 (m, 4H), 7.44 – 7.36 (m, 2H), 7.34 (t, *J* = 3.2 Hz, 6H), 6.90 (t, *J* = 8.7 Hz, 2H).

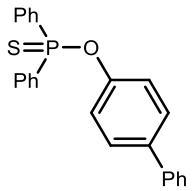
^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.22 (dd, *J* = 247.2, 2.0 Hz), 137.18 (d, *J* = 23.8 Hz), 134.21 (d, *J* = 6.7 Hz), 134.13 (d, *J* = 6.7 Hz), 132.65 (d, *J* = 20.9 Hz), 129.37, 128.57 (d, *J* = 6.5 Hz), 116.01 (d, *J* = 22.0 Hz).

^{19}F NMR (377 MHz, Chloroform-*d*) δ -114.39 (d, *J* = 3.0 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 35.87 (d, *J* = 2.9 Hz).

HRMS (ESI, m/z): calcd for $C_{18}H_{14}FOPS$ $[M+H]^+$: 329.0552 found: 329.0560.

O-([1,1'-biphenyl]-4-yl) diphenylphosphinothioate (**3y'**)

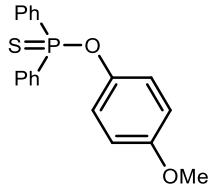


Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and [1,1'-biphenyl]-4-ol (170 mg, 1.0 mmol), followed by further purification to obtained a yellow solid (179.5 mg, yield 93%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.94 (m, 4H), 7.51 – 7.39 (m, 10H), 7.39 – 7.31 (m, 2H), 7.31 – 7.25 (m, 1H), 7.13 – 7.07 (m, 2H).

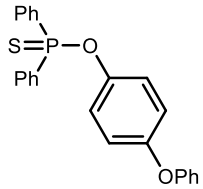
^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.91 (d, *J* = 8.8 Hz), 140.12, 137.74 (d, *J* = 1.8 Hz), 134.19 (d, *J* = 110.9 Hz), 132.05 (d, *J* = 3.1 Hz), 131.32 (d, *J* = 11.6 Hz), 128.58 (d, *J* = 11.4 Hz), 128.39, 127.91 (d, *J* = 1.4 Hz), 127.10, 126.84, 121.87 (d, *J* = 5.0 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.28.
HRMS (ESI, m/z): calcd for $C_{24}H_{19}OPS$ $[M+H]^+$: 387.0967 found: 387.0967.

O-(4-methoxyphenyl) diphenylphosphinothioate (**3z'**) [1]



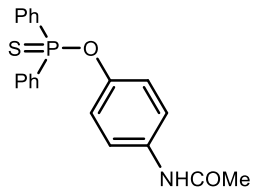
Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and 4-methoxyphenol (124 mg, 1.0 mmol), followed by further purification to obtained a yellow solid (159.8 mg, yield 94%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.90 (m, 4H), 7.53 – 7.37 (m, 6H), 6.98 – 6.85 (m, 2H), 6.77 – 6.63 (m, 2H), 3.70 – 3.62 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.45 (d, *J* = 1.8 Hz), 143.76 (d, *J* = 9.0 Hz), 134.18 (d, *J* = 110.8 Hz), 131.94 (d, *J* = 3.0 Hz), 131.29 (d, *J* = 11.4 Hz), 128.35 (d, *J* = 13.5 Hz), 122.47 (d, *J* = 4.6 Hz), 114.18 (d, *J* = 1.6 Hz), 55.34.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 36.38.

O-(4-phenoxyphenyl) diphenylphosphinothioate (**3aa'**)



Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and 4-phenoxyphenol (186 mg, 1.0 mmol), followed by further purification to obtained a white solid (174.9 mg, yield 87%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.83 (m, 4H), 7.48 – 7.33 (m, 6H), 7.29 – 7.21 (m, 2H), 6.99 – 6.91 (m, 1H), 6.91 – 6.81 (m, 2H), 4.40 – 4.31 (m, 2H), 4.22 – 4.14 (m, 2H).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.93 (m, 4H), 7.54 – 7.39 (m, 6H), 7.22 – 7.15 (m, 1H), 7.07 – 6.88 (m, 3H), 6.00 – 5.85 (m, 1H), 5.06 – 4.92 (m, 2H), 3.44 – 3.37 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.54, 134.38 (d, *J* = 110.5 Hz), 131.99 (d, *J* = 3.0 Hz), 131.31 (d, *J* = 11.4 Hz), 129.60, 128.52 (d, *J* = 13.5 Hz), 121.22, 114.73.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.89.
HRMS (ESI, m/z): calcd for $C_{24}H_{19}O_2PS$ $[M+H]^+$: 403.0916 found: 403.0912.

O-(4-acetamidophenyl) diphenylphosphinothioate (**3ab'**)



Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and N-(4-hydroxyphenyl)acetamide (151 mg, 1.0 mmol), followed by further purification to obtained a white solid (143.1 mg, yield 78%).

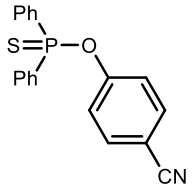
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.89 (m, 5H), 7.54 – 7.40 (m, 6H), 7.35 – 7.28 (m, 2H), 6.94 – 6.87 (m, 2H), 2.03 – 1.97 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.65, 146.38 (d, *J* = 8.9 Hz), 134.99 – 134.37 (m), 133.34, 132.11 (d, *J* = 3.0 Hz), 131.25 (d, *J* = 11.6 Hz), 128.45 (d, *J* = 13.6 Hz), 121.82 (d, *J* = 4.8 Hz), 120.85 (d, *J* = 1.4 Hz), 24.14.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.62.

HRMS (ESI, m/z): calcd for $C_{20}H_{18}NO_2PS$ $[M+H]^+$: 368.0869 found: 368.0857.

O-(4-cyanophenyl) diphenylphosphinothioate (**3ac'**)



Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and 4-hydroxybenzonitrile (119 mg, 1.0 mmol), followed by further purification to obtained a yellow liquid (157.5 mg, yield 94%).

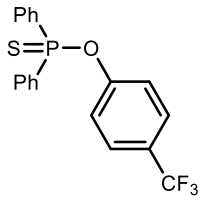
1H NMR (400 MHz, CDCl3) δ 8.01 – 7.90 (m, 4H), 7.58 – 7.44 (m, 8H), 7.20 – 7.11 (m, 2H).

13C NMR (101 MHz, CDCl3) δ 153.87 (d, J = 8.5 Hz), 133.47, δ 133.23 (d, J = 110.8 Hz), 132.39 (d, J = 3.1 Hz), 131.13 (d, J = 11.7 Hz), 128.58 (d, J = 13.7 Hz), 122.50 (d, J = 5.4 Hz), 118.16, 108.36 (d, J = 1.6 Hz).

31P NMR (162 MHz, $CDCl_3$) δ 83.87.

HRMS (ESI, m/z): calcd for $C_{19}H_{14}NOPS$ $[M+H]^+$: 336.0607 found: 336.0602.

O-(4-(trifluoromethyl)phenyl) diphenylphosphinothioate (**3ad'**)



Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and 4-(trifluoromethyl)phenol (162 mg, 1.0 mmol), followed by further purification to obtained a white solid (181.4 mg, yield 96%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.88 (m, 4H), 7.56 – 7.45 (m, 8H), 7.19 – 7.13 (m, 2H).

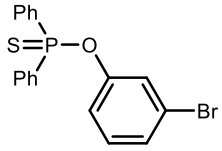
^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.12 (d, *J* = 8.4 Hz), 133.72 (d, *J* = 111.1 Hz), 132.34 (d, *J* = 3.0 Hz), 131.31 (d, *J* = 11.7 Hz), 128.62 (d, *J* = 13.7 Hz), 126.65 (t, *J* = 3.7 Hz), 121.98 (d, *J* = 5.1 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 83.26.

^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.02.

HRMS (ESI, m/z): calcd for $C_{19}H_{14}F_3OPS$ $[M+H]^+$: 379.0528 found: 379.0524.

O-(3-bromophenyl) diphenylphosphinothioate (**3ae'**) [2]



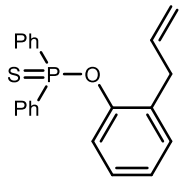
Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and 3-bromophenol (171 mg, 1.0 mmol), followed by further purification to obtained a white solid (189.6 mg, yield 98%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.85 (m, 4H), 7.55 – 7.39 (m, 6H), 7.26 – 7.17 (m, 2H), 7.09 – 7.01 (m, 1H), 7.01 – 6.94 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.92 (d, *J* = 8.6 Hz), 133.75 (d, *J* = 111.0 Hz), 132.20 (d, *J* = 3.1 Hz), 131.22 (d, *J* = 11.7 Hz), 130.20 (d, *J* = 1.3 Hz), 128.49 (d, *J* = 13.8 Hz), 127.93 (d, *J* = 1.7 Hz), 125.08 (d, *J* = 5.1 Hz), 122.15 (d, *J* = 1.4 Hz), 120.39 (d, *J* = 4.9 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 83.26.

O-(2-allylphenyl) diphenylphosphinothioate (**3af'**)



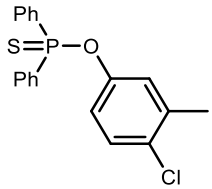
Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and 2-allylphenol (134 mg, 1.0 mmol), followed by further purification to obtained a white solid (159.3 mg, yield 91%).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.91 (d, *J* = 8.8 Hz), 136.05, 134.68 (d, *J* = 111.1 Hz), 131.95 (d, *J* = 3.1 Hz), 131.12 (d, *J* = 11.6 Hz), 130.47, 128.45 (d, *J* = 13.6 Hz), 126.91 (d, *J* = 1.3 Hz), 124.63 (d, *J* = 1.5 Hz), 120.62 (d, *J* = 5.1 Hz), 116.05, 34.72.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 81.01.

HRMS (ESI, m/z): calcd for $C_{21}H_{19}OPS$ $[M+H]^+$: 351.0969 found: 351.0961.

O-(4-chloro-3-methylphenyl) diphenylphosphinothioate (**3ag'**)



Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and 4-chloro-3-methylphenol (142 mg, 1.0 mmol), followed by further purification to obtained a white solid (162.9 mg, yield 91%).

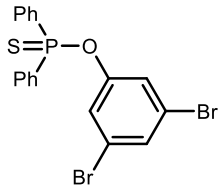
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.90 (m, 4H), 7.54 – 7.39 (m, 6H), 7.17 – 7.11 (m, 1H), 6.96 – 6.91 (m, 1H), 6.81 – 6.74 (m, 1H), 2.26 – 2.21 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.72 (d, *J* = 8.8 Hz), 137.14 (d, *J* = 1.4 Hz), 133.97 (d, *J* = 111.0 Hz), 132.10 (d, *J* = 3.1 Hz), 131.25 (d, *J* = 11.5 Hz), 130.30 (d, *J* = 2.1 Hz), 129.42 (d, *J* = 1.4 Hz), 128.44 (d, *J* = 13.6 Hz), 124.07 (d, *J* = 4.9 Hz), 120.21 (d, *J* = 4.8 Hz), 20.08.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.74.

HRMS (ESI, m/z): calcd for $C_{19}H_{16}ClOPS$ $[M+H]^+$: 359.0421 found: 359.0418.

O-(3,5-dibromophenyl) diphenylphosphinothioate (**3ah'**)



Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and 3,5-dibromophenol (245 mg, 1.0 mmol), followed by further purification to obtained a white solid (210.2 mg, yield 90%).

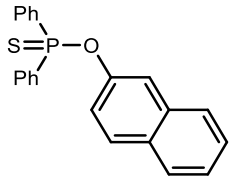
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.88 (m, 4H), 7.57 – 7.37 (m, 7H), 7.22 – 7.12 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.19 (d, *J* = 8.8 Hz), 133.35 (d, *J* = 110.8 Hz), 132.39 (d, *J* = 3.1 Hz), 131.19 (d, *J* = 11.7 Hz), 130.64 (d, *J* = 1.6 Hz), 128.58 (d, *J* = 13.7 Hz), 124.03 (d, *J* = 4.9 Hz), 122.49 (d, *J* = 1.6 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 84.51.

HRMS (ESI, m/z): calcd for $C_{18}H_{13}Br_2OPS$ $[M+H]^+$: 468.8844 found: 468.8829.

O-(naphthalen-2-yl) diphenylphosphinothioate (**3ai'**)



Synthesized by method C using diphenylphosphane (89 μL, 0.5 mmol) and naphthalen-2-ol (144 mg, 1.0 mmol), followed by further purification to obtained a yellow solid (158.4 mg, yield 88%).

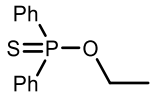
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.09 (m, 4H), 7.88 – 7.81 (m, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.65 – 7.51 (m, 7H), 7.51 – 7.43 (m, 2H), 7.37 – 7.30 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.12 (d, *J* = 9.0 Hz), 134.18 (d, *J* = 111.0 Hz), 133.59 (d, *J* = 1.4 Hz), 132.03 (d, *J* = 3.0 Hz), 131.31 (d, *J* = 11.5 Hz), 130.70 (d, *J* = 1.3 Hz), 129.24, 128.43 (d, *J* = 13.6 Hz), 127.54, 127.36, 126.34, 125.21, 121.51 (d, *J* = 4.5 Hz), 118.26 (d, *J* = 5.6 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.44.

HRMS (ESI, m/z): calcd for $C_{22}H_{17}OPS$ $[M+H]^+$: 361.0811 found: 361.0802.

O-ethyl diphenylphosphinothioate (**3aj'**)



Synthesized by method D using diphenylphosphane (89 μL, 0.5 mmol) and ethanol (46 mg, 1.0 mmol), followed by further purification to obtained a colorless liquid (127.1 mg, yield 97%).

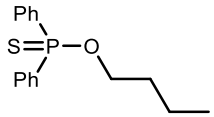
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.83 (m, 4H), 7.50 – 7.36 (m, 6H), 4.15 – 4.03 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.55 (d, *J* = 110.4 Hz), 131.62 (d, *J* = 3.0 Hz), 130.98 (d, *J* = 11.3 Hz), 128.26 (d, *J* = 13.4 Hz), 60.98 (d, *J* = 5.6 Hz), 16.10 (d, *J* = 8.0 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 81.02.

HRMS (ESI, m/z): calcd for $C_{14}H_{15}OPS$ $[M+H]^+$: 263.0654 found: 263.0649.

O-butyl diphenylphosphinothioate (**3ak'**)



Synthesized by method D using diphenylphosphane (89 μL, 0.5 mmol) and butan-1-ol (74 mg, 1.0 mmol), followed by further purification to obtained a colorless liquid (123.1 mg, yield 83%).

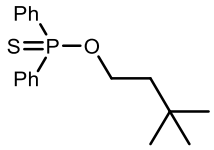
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.82 (m, 4H), 7.52 – 7.38 (m, 6H), 4.07 – 3.97 (m, 2H), 1.76 – 1.64 (m, 2H), 1.50 – 1.36 (m, 2H), 0.95 – 0.87 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.64 (d, *J* = 110.4 Hz), 131.68 (d, *J* = 3.0 Hz), 131.10 (d, *J* = 11.3 Hz), 128.33 (d, *J* = 13.3 Hz), 64.63 (d, *J* = 6.0 Hz), 32.30 (d, *J* = 8.0 Hz), 18.93, 13.62.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 80.90.

HRMS (ESI, m/z): calcd for $C_{16}H_{19}OPS$ $[M+H]^+$: 291.0967 found: 291.0961.

O-(3,3-dimethylbutyl) diphenylphosphinothioate (**3al'**)



Synthesized by method D using diphenylphosphane (89 μL, 0.5 mmol) and 3,3-dimethylbutan-1-ol (102 mg, 1.0 mmol), followed by further purification to obtained a colorless liquid (111.3 mg, yield 70%).

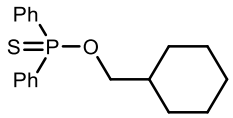
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.82 (m, 4H), 7.56 – 7.33 (m, 6H), 4.16 – 4.00 (m, 2H), 1.92 – 1.38 (m, 2H), 0.97 – 0.86 (m, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.55 (d, *J* = 110.3 Hz), 131.64 (d, *J* = 3.0 Hz), 131.02 (d, *J* = 11.3 Hz), 128.29 (d, *J* = 13.3 Hz), 62.53 (d, *J* = 5.9 Hz), 43.56 (d, *J* = 7.4 Hz), 29.59.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 81.27.

HRMS (ESI, m/z): calcd for $C_{18}H_{23}OPS$ $[M+H]^+$: 319.1280 found: 319.1272.

O-(cyclohexylmethyl) diphenylphosphinothioate (**3am'**)



Synthesized by method D using diphenylphosphane (89 μL, 0.5 mmol) and cyclohexylmethanol (114 mg, 1.0 mmol), followed by further purification to obtained a yellow liquid (102.3 mg, yield 62%).

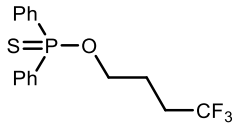
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.80 (m, 4H), 7.50 – 7.37 (m, 6H), 3.83 – 3.75 (m, 2H), 1.83 – 1.61 (m, 6H), 1.31 – 1.06 (m, 3H), 1.06 – 0.92 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.70 (d, *J* = 110.3 Hz), 131.77, 131.20 (d, *J* = 11.3 Hz), 128.43 (d, *J* = 13.3 Hz), 69.77 (d, *J* = 6.3 Hz), 38.40 (d, *J* = 8.1 Hz), 29.59, 26.42, 25.69.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 80.75.

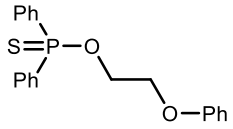
HRMS (ESI, m/z): calcd for $C_{19}H_{23}OPS$ $[M+H]^+$: 331.1280 found: 331.1279.

O-(4,4,4-trifluorobutyl) diphenylphosphinothioate (**3an'**) [1]



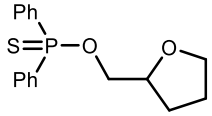
Synthesized by method D using diphenylphosphane (89 μL, 0.5 mmol) and 4,4,4-trifluorobutan-1-ol (128 mg, 1.0 mmol), followed by further purification to obtained a yellow liquid (154.7 mg, yield 90%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.81 (m, 4H), 7.53 – 7.39 (m, 6H), 4.12 – 4.02 (m, 2H), 2.29 – 2.15 (m, 2H), 2.02 – 1.92 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.05 (d, *J* = 110.3 Hz), 131.92 (d, *J* = 3.0 Hz), 131.00 (d, *J* = 11.3 Hz), 128.44 (d, *J* = 13.4 Hz), 125.48, 62.91 (d, *J* = 5.3 Hz), 30.49 (q, *J* = 29.3 Hz), 23.06 (dt, *J* = 6.1, 2.9 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.51.
^{19}F NMR (377 MHz, Chloroform-*d*) δ -66.27.

O-(2-phenoxyethyl) diphenylphosphinothioate (**3ao'**)



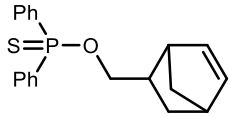
Synthesized by method D using diphenylphosphane (89 μL, 0.5 mmol) and 2-phenoxyethan-1-ol (138 mg, 1.0 mmol), followed by further purification to obtained a white solid (145.3 mg, yield 87%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.83 (m, 4H), 7.50 – 7.32 (m, 6H), 7.30 – 7.19 (m, 2H), 6.99 – 6.81 (m, 3H), 4.43 – 4.28 (m, 2H), 4.26 – 4.12 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.30, 134.14 (d, *J* = 110.5 Hz), 131.75 (d, *J* = 3.0 Hz), 131.07 (d, *J* = 11.4 Hz), 129.36, 128.28 (d, *J* = 13.5 Hz), 120.98, 114.50, 66.76 (d, *J* = 8.4 Hz), 63.14 (d, *J* = 5.4 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.89.
HRMS (ESI, m/z): calcd for $C_{20}H_{19}O_2PS$ $[M+H]^+$: 335.0916 found: 335.0911.

O-((tetrahydrofuran-2-yl)methyl) diphenylphosphinothioate (**3ap'**)



Synthesized by method D using diphenylphosphane (89 μL, 0.5 mmol) and (tetrahydrofuran-2-yl)methanol (102 mg, 1.0 mmol), followed by further purification to obtained a white solid (116.1 mg, yield 73%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.84 (m, 4H), 7.52 – 7.37 (m, 6H), 4.25 – 4.13 (m, 1H), 4.10 – 4.00 (m, 1H), 3.97 – 3.88 (m, 1H), 3.89 – 3.74 (m, 2H), 2.06 – 1.93 (m, 1H), 1.92 – 1.81 (m, 2H), 1.77 – 1.67 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.26 (dd, *J* = 110.7, 12.5 Hz), 131.74 (d, *J* = 3.1 Hz), 131.14 (dd, *J* = 11.3, 6.7 Hz), 128.33 (d, *J* = 13.3 Hz), 77.38 (d, *J* = 9.0 Hz), 68.40, 66.40 (d, *J* = 6.0 Hz), 27.77, 25.60.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.54.
HRMS (ESI, m/z): calcd for $C_{17}H_{19}O_2PS$ $[M+H]^+$: 319.0916 found: 319.0912.

O-(bicyclo[2.2.1]hept-5-en-2-ylmethyl) diphenylphosphinothioate (**3aq'**)



Synthesized by method D using diphenylphosphane (89 μL, 0.5 mmol) and bicyclo[2.2.1]hept-5-en-2-ylmethanol (124 mg, 1.0 mmol), followed by further purification to obtained a white solid (135.9, yield 80%).

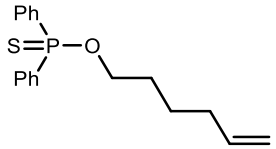
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.84 (m, 4H), 7.55 – 7.40 (m, 6H), 4.22 – 4.09 (m, 0.5H), 3.95 (q, *J* = 9.1 Hz, 0.5H), 3.90 – 3.81 (m, 0.5H), 3.65 – 3.53 (m, 0.5H), 3.02 (s, 0.5H), 2.89 – 2.78 (m, 1.5H), 1.93 – 1.78 (m, 1H), 1.50 – 1.46 (m, 0.5H), 1.40 – 1.25 (m, 2.5H), 1.24 – 1.16 (m, 0.5H), 0.60 – 0.51 (m, 0.5H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.50, 136.90, 136.08, 135.37 – 133.70 (m), 131.97, 131.63 (dt, *J* = 5.1, 2.4 Hz), 131.27 – 130.81 (m), 128.56 – 127.93 (m), 68.28 (dd, *J* = 80.9, 6.1 Hz), 49.19, 44.80, 43.72, 43.43, 42.13, 41.44, 39.35 (t, *J* = 7.6 Hz), 29.36, 28.67.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 80.88, 80.23.

HRMS (ESI, m/z): calcd for $C_{20}H_{21}OPS$ $[M+H]^+$: 341.1124 found: 341.1120.

O-(hex-5-en-1-yl) diphenylphosphinothioate (**3ar'**)



Synthesized by method D using diphenylphosphane (89 μL, 0.5 mmol) and hex-5-en-1-ol (100 mg, 1.0 mmol), followed by further purification to obtained a white solid (142.1 mg, yield 84%).

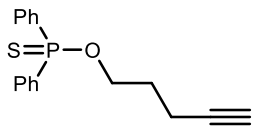
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.83 (m, 4H), 7.53 – 7.35 (m, 6H), 5.85 – 5.69 (m, 1H), 5.08 – 4.91 (m, 2H), 4.08 – 3.97 (m, 2H), 2.12 – 2.02 (m, 2H), 1.78 – 1.67 (m, 2H), 1.61 – 1.44 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.18, 134.51 (d, *J* = 110.4 Hz), 131.64 (d, *J* = 3.1 Hz), 131.02 (d, *J* = 11.1 Hz), 128.28 (d, *J* = 13.2 Hz), 114.74, 64.60 (d, *J* = 5.9 Hz), 33.06, 29.57 (d, *J* = 7.9 Hz), 24.85.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 81.07.

HRMS (ESI, m/z): calcd for $C_{20}H_{19}OPS$ $[M+H]^+$: 339.0967 found: 339.0964.

O-(pent-4-yn-1-yl) diphenylphosphinothioate (**3as'**)



Synthesized by method D using diphenylphosphane and pent-4-yn-1-ol (84 mg, 1.0 mmol), followed by further purification to obtained a yellow liquid (112.5 mg, yield 75%).

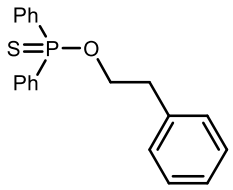
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.82 (m, 4H), 7.53 – 7.36 (m, 6H), 4.94 – 4.84 (m, 1H), 1.32 – 1.24 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.57 (d, *J* = 111.0 Hz), 131.51 (d, *J* = 3.0 Hz), 131.06 (d, *J* = 11.4 Hz), 128.20 (d, *J* = 13.3 Hz), 70.45 (d, *J* = 5.8 Hz), 24.00 (d, *J* = 4.4 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 78.58.

HRMS (ESI, m/z): calcd for $C_{17}H_{17}OPS$ $[M+H]^+$: 301.0811 found: 301.0806.

O-phenethyl diphenylphosphinothioate (**3at'**)



Synthesized by method D using diphenylphosphane and 2-phenylethan-1-ol (122 mg, 1.0 mmol), followed by further purification to obtained a yellow liquid (157.2 mg, yield 93%).

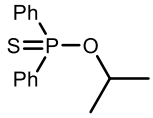
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.70 (m, 4H), 7.50 – 7.38 (m, 6H), 7.36 – 7.12 (m, 5H), 4.26 – 4.15 (m, 2H), 3.06 – 2.95 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.53, 134.31 (d, *J* = 110.3 Hz), 131.63 (d, *J* = 3.0 Hz), 130.99 (d, *J* = 11.3 Hz), 129.01, 128.34 (d, *J* = 4.0 Hz), 128.18, 126.50, 65.29 (d, *J* = 5.7 Hz), 36.74 (d, *J* = 8.2 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 81.41.

HRMS (ESI, m/z): calcd for $C_{20}H_{19}OPS$ $[M+H]^+$: 339.0967 found: 339.0961.

O-isopropyl diphenylphosphinothioate (**3au'**) [1]



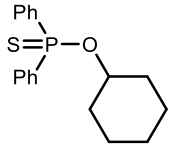
Synthesized by method E using diphenylphosphane and propan-2-ol (0.35 mL, 6.0 mmol), followed by further purification to obtained a yellow liquid (96.7 mg, yield 72%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (ddt, *J* = 13.5, 8.1, 1.3 Hz, 4H), 7.60 – 7.37 (m, 6H), 5.02 – 4.83 (m, 1H), 1.40 – 1.26 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.57 (d, *J* = 111.0 Hz), 131.51 (d, *J* = 3.0 Hz), 131.06 (d, *J* = 11.4 Hz), 128.20 (d, *J* = 13.3 Hz), 70.45 (d, *J* = 5.8 Hz), 24.00 (d, *J* = 4.4 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 78.58.

O-cyclohexyl diphenylphosphinothioate (**3av'**)



Synthesized by method E using diphenylphosphane and cyclohexanol (0.64 mL, 6.0 mmol), followed by further purification to obtained a yellow liquid (94.9 mg, yield 60%).

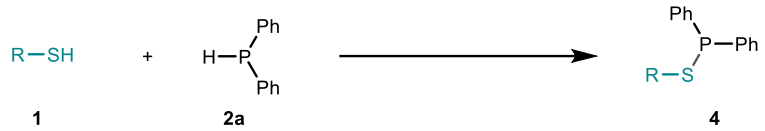
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 7.65 (m, 4H), 7.51 – 7.27 (m, 6H), 4.70 – 4.57 (m, 1H), 1.90 – 1.78 (m, 2H), 1.76 – 1.64 (m, 2H), 1.62 – 1.40 (m, 3H), 1.39 – 1.17 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.71 (d, *J* = 111.0 Hz), 131.42 (d, *J* = 3.1 Hz), 130.94 (d, *J* = 11.3 Hz), 128.12 (d, *J* = 13.4 Hz), 75.09 (d, *J* = 6.2 Hz), 33.57 (d, *J* = 4.0 Hz), 25.11, 23.52.

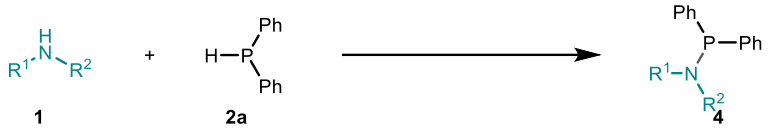
^{31}P NMR (162 MHz, Chloroform-*d*) δ 78.35.

HRMS (ESI, m/z): calcd for $C_{18}H_{21}OPS$ $[M+H]^+$: 317.1123 found: 317.1119.

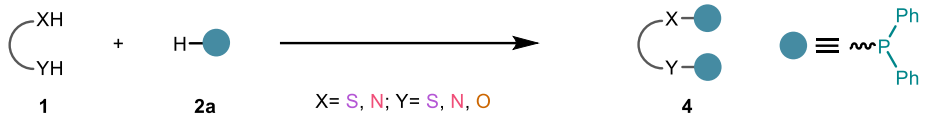
4.2. Synthesis of compound 4



Method F for the preparation of compound 4 (4a-4w): In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. Thiols or thiophenol (**1'**, 0.5 mmol), TBAI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane (96 μL, 0.5 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 4 h (J = 4.4 mA/cm^2, 3.0 F/mol).



Method G for the preparation of compound 4 (4ab-4aj): In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. Aniline (**1'**, 1.0 mmol), TBAI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane (96 μL, 0.5 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 4 h (J = 4.4 mA/cm^2, 3.0 F/mol).



Method H for the preparation of compound 4 (4x-4aa,3ak-3ap): In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. **1'** (0.25 mmol), TBAI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane or Di-tert-butylphosphine (**2a**, 0.7 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 4 h (J = 4.4 mA/cm^2, 6.0 F/mol).

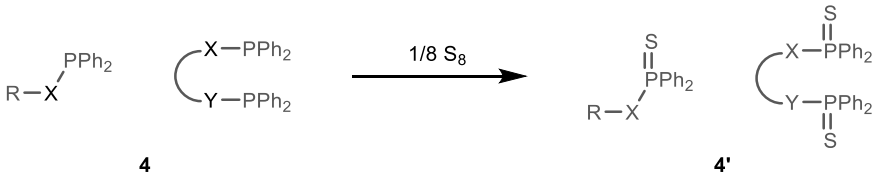
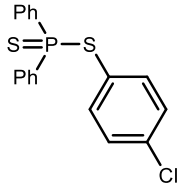


Fig. S3 Method for determining separation yield

Due to the easy oxidation of the product in air, was difficult to separate the pure products during the separation process such as flash chromatography. In order to ensure the purity of these products, we added S_8 (1/8 equiv. of P atom) to the tube at the end of reaction to avoid oxidation and the

mixtures were stirred for 30 minutes. Then the desired products were obtained after purification by flash chromatography on 200-300 silica gel (petroleum: EtOAc = 50: 1).

4-Chlorophenyl diphenylphosphinodithioate (**4a'**) [3]



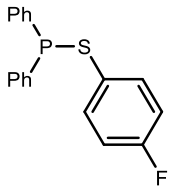
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and 4-Chlorothiophenol (74 mg, 0.5 mmol), followed by further purification to obtained a yellow solid (154.8 mg, yield 86%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.89 (m, 4H), 7.53 – 7.39 (m, 6H), 7.29 – 7.22 (m, 2H), 7.22 – 7.14 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.45 (d, *J* = 3.9 Hz), 136.17 (d, *J* = 3.7 Hz), 133.16 (d, *J* = 83.9 Hz), 131.98 (d, *J* = 3.2 Hz), 131.64 (d, *J* = 11.0 Hz), 129.03 (d, *J* = 2.6 Hz), 128.46 (d, *J* = 13.2 Hz), 125.12 (d, *J* = 5.5 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 66.00.

((4-Fuorophenyl)thio)diphenylphosphane (**4b**) [4]



Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and 4-fluorobenzenethiol (55 μL, 0.5 mmol), followed by further purification to obtained a yellow solid (137.3 mg, yield 88%)

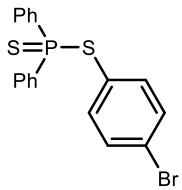
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.53 (m, 4H), 7.45 – 7.39 (m, 2H), 7.39 – 7.29 (m, 6H), 6.98 – 6.79 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.22 (dd, *J* = 247.2, 2.0 Hz), 137.18 (d, *J* = 23.8 Hz), 134.21 (d, *J* = 6.7 Hz), 134.13 (d, *J* = 6.7 Hz), 132.65 (d, *J* = 20.9 Hz), 129.37, 128.57 (d, *J* = 6.5 Hz), 116.01 (d, *J* = 22.0 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 35.87 (d, *J* = 2.9 Hz).

^{19}F NMR (377 MHz, Chloroform-*d*) δ -114.39 (d, *J* = 3.0 Hz).

4-Bromophenyl diphenylphosphinodithioate (**4c'**)

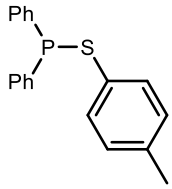


Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and 4-Bromothiophenoll (63 μL, 0.5 mmol), followed by further purification to obtained a white solid (171.3 mg, yield 85%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.87 (m, 4H), 7.54 – 7.39 (m, 6H), 7.38 – 7.29 (m, 2H), 7.25 – 7.13 (m, 2H).

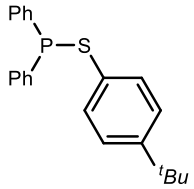
^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.72 (d, *J* = 3.8 Hz), 133.20 (d, *J* = 84.0 Hz), 132.04 (d, *J* = 2.9 Hz), 131.69 (d, *J* = 11.0 Hz), 128.51 (d, *J* = 13.3 Hz), 125.82 (d, *J* = 5.6 Hz), 124.61 (d, *J* = 3.8 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 65.85.
HRMS (ESI, m/z): calcd for $C_{18}H_{14}BrPS_2$ $[M+H]^+$: 404.9531 found: 404.9519

Diphenyl(p-tolylthio)phosphane (**4d)** [4]



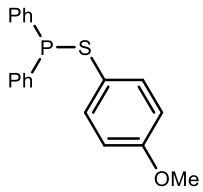
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and 2-methylbenzenethiol (63 mg, 0.5 mmol), followed by further purification to obtained a white solid (126.3 mg, yield 82%)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.52 (m, 4H), 7.41 – 7.27 (m, 8H), 7.06 – 6.99 (m, 2H), 2.28 – 2.24 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.61 (d, *J* = 23.8 Hz), 137.00 (d, *J* = 1.9 Hz), 132.64 (d, *J* = 20.9 Hz), 132.13 (d, *J* = 7.2 Hz), 131.58 (d, *J* = 10.1 Hz), 131.16 (d, *J* = 14.2 Hz), 129.45 (d, *J* = 52.9 Hz), 128.48 (d, *J* = 6.4 Hz), 21.00.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 34.03.

((4-(Tert-butyl)phenyl)thio)diphenylphosphane (**4e**) [4]



Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and 4-(tert-butyl)benzenethiol (88 μL, 0.5 mmol), followed by further purification to obtained a yellow liquid (145.3 mg, yield 83%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (dtt, *J* = 7.9, 5.2, 2.8 Hz, 4H), 7.50 (dq, *J* = 8.4, 1.4 Hz, 2H), 7.49 – 7.42 (m, 6H), 7.36 (dd, *J* = 8.6, 2.4 Hz, 2H), 1.37 (d, *J* = 2.6 Hz, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.16 (d, *J* = 1.8 Hz), 137.62 (d, *J* = 23.5 Hz), 132.67 (d, *J* = 20.9 Hz), 131.63 (d, *J* = 7.4 Hz), 131.38 (d, *J* = 14.2 Hz), 129.21, 128.51 (d, *J* = 6.5 Hz), 126.05, 34.46, 31.23.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 32.92.

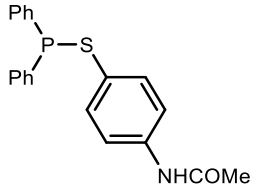
((4-Methoxyphenyl)thio)diphenylphosphane (**4f**) [4]



Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and 4-methoxy thiophenol (72 mg, 0.5 mmol), followed by further purification to obtained a white solid (153.1 mg, yield 86%).

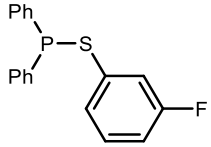
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.51 (m, 4H), 7.42 – 7.25 (m, 8H), 6.87 – 6.63 (m, 2H), 3.80 – 3.62 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.24 (d, *J* = 1.8 Hz), 137.68 (d, *J* = 24.5 Hz), 134.33 (d, *J* = 5.8 Hz), 132.64 (d, *J* = 20.8 Hz), 129.17, 128.46 (d, *J* = 6.3 Hz), 124.89 (d, *J* = 14.2 Hz), 114.59, 55.22.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 36.38.

N-(4-((diphenylphosphaneyl)thio)phenyl)acetamide (**4g**)



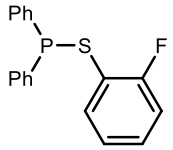
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and N-(4-mercaptophenyl)acetamide (34 mg, 0.5 mmol), followed by further purification to obtained a white solid (136.9 mg, yield 78%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 – 8.58 (m, 1H), 7.61 – 7.52 (m, 4H), 7.45 – 7.39 (m, 2H), 7.38 – 7.32 (m, 8H), 2.11 – 2.01 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.03, 137.50 (d, *J* = 1.9 Hz), 137.25 (d, *J* = 23.9 Hz), 132.79 (d, *J* = 6.9 Hz), 132.52 (d, *J* = 20.9 Hz), 129.18, 128.41 (d, *J* = 6.4 Hz), 120.42, 63.69 (d, *J* = 5.9 Hz), 24.15.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 34.68.
HRMS (ESI, m/z): calcd for $C_{20}H_{18}NOPS$ $[M+H]^+$: 352.0919 found: 329.0907.

((3-Fluorophenyl)thio)diphenylphosphane (**4h**) [4]



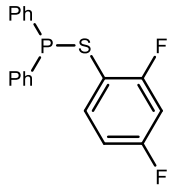
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and 3-fluorobenzenethiol (55 μL, 0.5 mmol), followed by further purification to obtained a yellow solid (101.4 mg, yield 65%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.52 (m, 4H), 7.41 – 7.32 (m, 6H), 7.27 – 7.14 (m, 3H), 6.93 – 6.83 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.55 (d, *J* = 248.7 Hz), 137.30 (dd, *J* = 14.7, 7.8 Hz), 136.79 (d, *J* = 23.0 Hz), 132.68 (d, *J* = 21.2 Hz), 130.07 (d, *J* = 8.5 Hz), 129.48, 128.63 (d, *J* = 6.6 Hz), 127.02 (dd, *J* = 8.3, 3.0 Hz), 118.23 (dd, *J* = 23.0, 9.1 Hz), 113.87 (dd, *J* = 21.3, 1.5 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 32.04.
^{19}F NMR (377 MHz, Chloroform-*d*) δ -111.94.

((2-Fluorophenyl)thio)diphenylphosphane (**4i**) [4]



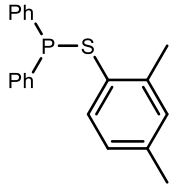
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and 2-Fluorothiophenol (55 μL, 0.5 mmol), followed by further purification to obtained a yellow solid (124.8 mg, yield 80%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (ddq, *J* = 9.0, 5.6, 3.1 Hz, 4H), 7.50 (tt, *J* = 7.5, 2.1 Hz, 1H), 7.35 (tq, *J* = 5.0, 3.2, 2.3 Hz, 6H), 7.23 – 7.13 (m, 1H), 7.06 – 6.96 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.93 (dd, *J* = 246.2, 2.6 Hz), 137.15 (d, *J* = 23.6 Hz), 134.47 (d, *J* = 10.8 Hz), 132.69 (d, *J* = 21.1 Hz), 129.39, 129.12 (dd, *J* = 7.8, 1.9 Hz), 128.55 (d, *J* = 6.4 Hz), 124.49 (d, *J* = 3.8 Hz), 121.92 (dd, *J* = 17.9, 14.7 Hz), 115.81 (d, *J* = 22.7 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 34.20 (d, *J* = 11.9 Hz).
^{19}F NMR (377 MHz, Chloroform-*d*) δ -107.19 (d, *J* = 12.2 Hz).

((2,4-Difluorophenyl)thio)diphenylphosphane (**4j**) [4]



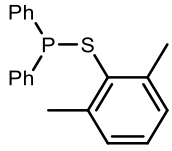
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and 2,4-difluorobenzenethiol (73 mg, 0.5 mmol), followed by further purification to obtained a yellow solid (133.7 mg, yield 81%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.54 (m, 4H), 7.47 – 7.40 (m, 1H), 7.40 – 7.30 (m, 6H), 6.85 – 6.69 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.78 (ddd, *J* = 29.6, 11.7, 2.3 Hz), 161.73 – 160.66 (m), 137.03 (d, *J* = 23.9 Hz), 136.04 (td, *J* = 8.9, 2.2 Hz), 132.67 (d, *J* = 21.1 Hz), 129.46, 128.57 (d, *J* = 6.4 Hz), 117.12 (ddd, *J* = 19.0, 15.1, 4.1 Hz), 111.86 (dd, *J* = 21.4, 3.9 Hz), 104.48 (t, *J* = 26.3 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 37.45 (dd, *J* = 12.7, 3.8 Hz).
^{19}F NMR (377 MHz, Chloroform-*d*) δ -101.67 (dd, *J* = 12.6, 8.5 Hz), -109.41 (dd, *J* = 8.3, 3.4 Hz).

((2,4-Dimethylphenyl)thio)diphenylphosphane (**4k**) [4]



Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and 2,4-dimethylbenzenethiol (69 mg, 0.5 mmol), followed by further purification to obtained a yellow solid (132.0 mg, yield 82%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.54 (m, 4H), 7.45 – 7.31 (m, 7H), 7.02 – 6.97 (m, 1H), 6.91 – 6.85 (m, 1H), 2.41 – 2.33 (m, 3H), 2.29 – 2.22 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.10 (d, *J* = 2.5 Hz), 137.90 (d, *J* = 24.2 Hz), 137.41 (d, *J* = 2.2 Hz), 133.37 (d, *J* = 10.9 Hz), 132.70 (d, *J* = 20.9 Hz), 131.22, 130.29 (d, *J* = 13.2 Hz), 129.16, 128.46 (d, *J* = 6.4 Hz), 127.35, 21.32, 20.94.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 32.32.

((2,6-Dimethylphenyl)thio)diphenylphosphane (**4l**) [4]



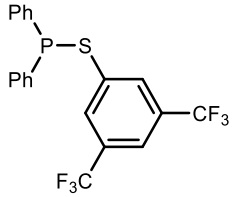
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and 2,6-dimethylbenzenethiol (69 mg, 0.5 mmol), followed by further purification to obtained a yellow solid (124.0 mg, yield 77%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.55 (m, 4H), 7.38 – 7.27 (m, 6H), 7.12 – 7.01 (m, 3H), 2.42 – 2.37 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.29 (d, *J* = 3.2 Hz), 138.90 (d, *J* = 25.2 Hz), 132.73 (d, *J* = 21.0 Hz), 132.41 (d, *J* = 12.3 Hz), 129.09, 128.39 (d, *J* = 6.5 Hz), 128.20 (d, *J* = 1.8 Hz), 128.09 (d, *J* = 2.8 Hz), 22.96 (d, *J* = 2.5 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 34.69.

((3,5-Bis(trifluoromethyl)phenyl)thio)diphenylphosphane (**4m**) [4]



Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and 3,5-bis(trifluoromethyl)benzenethiol (123 mg, 0.5 mmol), followed by further purification to obtained a yellow solid (144.1 mg, yield 67%).

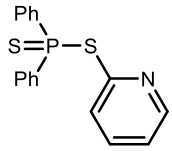
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.88 (m, 2H), 7.71 – 7.67 (m, 1H), 7.61 – 7.53 (m, 4H), 7.45 – 7.34 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.82 (d, *J* = 15.3 Hz), 135.85 (d, *J* = 22.3 Hz), 132.77 (d, *J* = 21.2 Hz), 132.03 (d, *J* = 33.4 Hz), 131.08 (d, *J* = 5.3 Hz), 129.92, 128.83 (d, *J* = 6.7 Hz), 124.33, 121.61, 120.50.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 34.34

^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.97.

Pyridin-2-yl diphenylphosphinodithioate (**4n'**)



Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and pyridine-2-thiol (56 mg, 0.5 mmol), followed by further purification to obtained a yellow solid (126.3 mg, yield 77%).

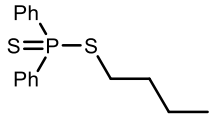
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 – 8.37 (m, 1H), 8.06 – 7.96 (m, 4H), 7.65 – 7.58 (m, 1H), 7.56 – 7.50 (m, 1H), 7.50 – 7.39 (m, 6H), 7.20 – 7.09 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.23 (d, *J* = 5.0 Hz), 150.09, 136.77 (d, *J* = 1.3 Hz), 133.47 (d, *J* = 85.2 Hz), 131.86 (d, *J* = 3.3 Hz), 131.63 (d, *J* = 11.3 Hz), 130.29 (d, *J* = 3.6 Hz), 128.39 (d, *J* = 13.5 Hz), 123.22 (d, *J* = 2.0 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 64.93

HRMS (ESI, m/z): calcd for $C_{17}H_{14}NPS_2$ $[M+H]^+$: 328.0378 found: 328.0373.

Butyl diphenylphosphinodithioate (**4o'**) [5]



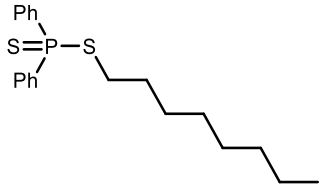
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and butane-1-thiol (45 mg, 0.5 mmol), followed by further purification to obtained a colorless liquid (114.8 mg, yield 75%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.85 (m, 4H), 7.52 – 7.37 (m, 6H), 2.96 – 2.85 (m, 2H), 1.61 – 1.50 (m, 2H), 1.42 – 1.30 (m, 2H), 0.91 – 0.78 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.46 (d, *J* = 84.8 Hz), 131.63 (d, *J* = 3.2 Hz), 131.21 (d, *J* = 11.3 Hz), 128.37 (d, *J* = 13.2 Hz), 31.84 (d, *J* = 5.4 Hz), 31.25 (d, *J* = 2.4 Hz), 21.64, 13.34.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 63.82.

Octyl diphenylphosphinodithioate (**4p'**) [5]



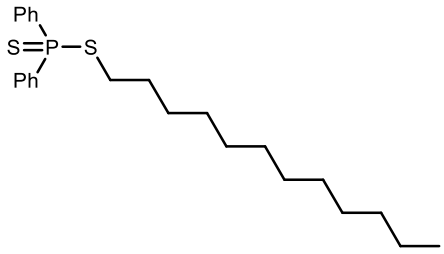
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and octane-1-thiol (73 mg, 0.5 mmol), followed by further purification to obtained a colorless liquid (135.8 mg, yield 75%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.90 (m, 4H), 7.51 – 7.37 (m, 6H), 2.96 – 2.85 (m, 2H), 1.61 – 1.51 (m, 2H), 1.38 – 1.15 (m, 10H), 0.90 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.53 (d, *J* = 84.7 Hz), 131.62 (d, *J* = 3.2 Hz), 131.25 (d, *J* = 11.3 Hz), 128.37 (d, *J* = 13.2 Hz), 31.66 – 31.51 (m), 29.87, 29.82, 28.91, 28.79, 28.52, 22.47, 13.97.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 63.77.

Dodecyl diphenylphosphinodithioate (**4q'**) [5]



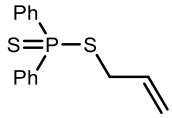
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and dodecane-1-thiol (101 mg, 0.5 mmol), followed by further purification to obtained a colorless liquid (148.4 mg, yield 71%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.91 (m, 4H), 7.52 – 7.39 (m, 6H), 2.96 – 2.85 (m, 2H), 1.63 – 1.51 (m, 2H), 1.40 – 1.12 (m, 20H), 0.92 – 0.84 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.58 (d, *J* = 84.8 Hz), 131.65 (d, *J* = 3.2 Hz), 131.29 (d, *J* = 11.3 Hz), 128.40 (d, *J* = 13.3 Hz), 31.81, 31.66 (d, *J* = 2.2 Hz), 29.91, 29.86, 29.52, 29.42, 29.29, 29.24, 28.88, 28.57, 22.59, 14.04.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 63.77.

Allyl diphenylphosphinodithioate (**4r'**) [6]



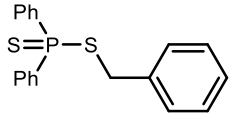
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and prop-2-ene-1-thiol (37 mg, 0.5 mmol), followed by further purification to obtained a colorless liquid (113.1 mg, yield 78%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.66 (m, 4H), 7.56 – 7.35 (m, 6H), 5.91 – 5.74 (m, 1H), 5.36 – 4.96 (m, 2H), 3.67 – 3.18 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.20 (d, *J* = 80.3 Hz), 131.39 (d, *J* = 3.0 Hz), 131.12 (d, *J* = 9.9 Hz), 128.40 (dd, *J* = 12.3, 2.4 Hz), 127.18 (d, *J* = 8.4 Hz), 121.03 (d, *J* = 13.0 Hz), 38.96 (d, *J* = 54.4 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 40.43.

Benzyl diphenylphosphinodithioate (**4s'**) [7]



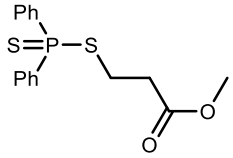
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and thiophene-2-thiol (63 mg, 0.5 mmol), followed by further purification to obtained a colorless liquid (110.5 mg, yield 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.84 (m, 4H), 7.46 – 7.40 (m, 2H), 7.40 – 7.32 (m, 4H), 7.23 – 7.20 (m, 2H), 7.18 – 7.09 (m, 3H), 4.16 – 4.09 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.46 (d, *J* = 5.6 Hz), 133.87 (d, *J* = 84.8 Hz), 131.67 (d, *J* = 3.2 Hz), 131.28 (d, *J* = 11.3 Hz), 129.09, 128.43, 128.32 (d, *J* = 3.4 Hz), 127.26 (d, *J* = 2.2 Hz), 35.65 (d, *J* = 2.0 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 64.14.

Methyl 3-((diphenylphosphorothioyl)thio)propanoate (**4t'**) [8]



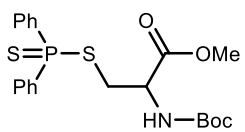
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and methyl 3-mercaptopropanoate (60 mg, 0.5 mmol), followed by further purification to obtained a colorless liquid (110.9 mg, yield 66%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.46 (m, 4H), 7.40 – 7.31 (m, 6H), 3.67 – 3.63 (m, 3H), 3.08 – 2.96 (m, 2H), 2.74 – 2.66 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.03, 137.68 (d, *J* = 20.8 Hz), 132.54 (d, *J* = 20.7 Hz), 129.12, 128.48 (d, *J* = 6.6 Hz), 51.72, 36.26 (d, *J* = 6.1 Hz), 28.42 (d, *J* = 24.7 Hz).

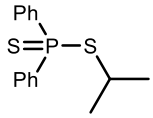
^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.50.

Methyl N-(tert-butoxycarbonyl)-S-(diphenylphosphorothioyl)cysteinate (**4u'**)



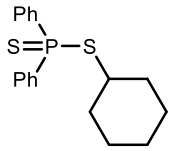
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and methyl acetylcysteinate (89 mg, 0.5 mmol), followed by further purification to obtained a white solid (193.9 mg, yield 86%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.47 (m, 4H), 7.46 – 7.25 (m, 6H), 5.43 – 5.18 (m, 1H), 4.81 – 4.53 (m, 1H), 3.84 – 3.66 (m, 3H), 3.45 – 3.23 (m, 2H), 1.49 – 1.43 (m, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.87, 132.46 (dd, *J* = 21.0, 9.3 Hz), 129.15 (d, *J* = 15.0 Hz), 128.50, 128.36, 79.91, 54.20, 52.39, 36.32 (d, *J* = 24.7 Hz), 28.23.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 33.17.
HRMS (ESI, m/z): calcd for $C_{21}H_{26}NO_4PS_2$ $[M+H]^+$: 452.1114 found: 452.1104.

Isopropyl diphenylphosphinodithioate (**4v'**) [9]



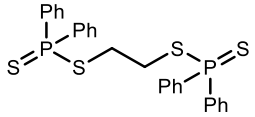
Synthesized by method F using diphenylphosphane (89 μL, 0.5 mmol) and propane-2-thiol (50 mg, 0.5 mmol), followed by further purification to obtained a colorless liquid (105.1 mg, yield 72%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.90 (m, 4H), 7.56 – 7.30 (m, 6H), 3.68 – 3.54 (m, 1H), 1.34 – 1.24 (m, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.91 (d, *J* = 84.9 Hz), 131.59 (d, *J* = 3.2 Hz), 131.29 (d, *J* = 11.3 Hz), 128.35 (d, *J* = 13.2 Hz), 39.08 (d, *J* = 2.2 Hz), 24.99 (d, *J* = 5.0 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 61.52.

Cyclohexyl diphenylphosphinodithioate (**4w'**) [10]



Synthesized by method A using diphenylphosphane (89 μL, 0.5 mmol) and cyclohexanethiol (58 mg, 0.5 mmol), followed by further purification to obtained a colorless liquid (117.9 mg, yield 71%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.90 (m, 4H), 7.52 – 7.38 (m, 6H), 3.71 – 3.31 (m, 1H), 1.94 – 1.86 (m, 2H), 1.70 – 1.61 (m, 2H), 1.54 – 1.46 (m, 2H), 1.40 – 1.31 (m, 2H), 1.29 – 1.22 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.26 (d, *J* = 84.8 Hz), 131.61 (d, *J* = 3.2 Hz), 131.35 (d, *J* = 11.1 Hz), 128.41 (d, *J* = 13.2 Hz), 46.84 (d, *J* = 2.2 Hz), 34.89 (d, *J* = 4.4 Hz), 25.80, 25.32.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 61.73.

Ethane-1,2-diyl bis(diphenylphosphinodithioate) (**4x'**)



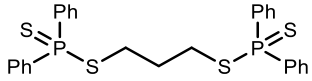
Synthesized by method H using diphenylphosphane (135 μL, 0.7 mmol) and ethane-1,2-dithiol (23.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (93.4 mg, yield 71%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.78 (m, 8H), 7.58 – 7.37 (m, 12H), 3.19 – 3.03 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.23 (d, *J* = 85.0 Hz), 131.94 (d, *J* = 3.3 Hz), 131.39 (d, *J*

= 11.4 Hz), 128.59 (d, *J* = 13.5 Hz), 32.05 (dd, *J* = 3.6, 1.9 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 64.15.

HRMS (ESI, m/z): calcd for $C_{26}H_{24}P_2S_4$ $[M+H]^+$: 527.0309 found: 527.0295.

Propane-1,3-diyl bis(diphenylphosphinodithioate) (**4y'**)



Synthesized by method H using diphenylphosphane (135 μL, 0.7 mmol) and propane-1,3-dithiol (27.0 mg, 0.25 mmol), followed by further purification to obtained a white solid (106.7 mg, yield 79%).

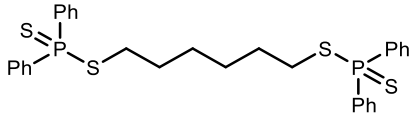
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.85 (m, 8H), 7.51 – 7.30 (m, 12H), 3.04 – 2.84 (m, 4H), 1.83 (p, *J* = 7.0 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.20 (d, *J* = 85.0 Hz), 131.79 (d, *J* = 3.2 Hz), 131.24 (d, *J* = 11.3 Hz), 128.46 (d, *J* = 13.3 Hz), 30.15 (d, *J* = 2.2 Hz), 30.06 (d, *J* = 4.5 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 64.11.

HRMS (ESI, m/z): calcd for $C_{27}H_{26}P_2S_4$ $[M+H]^+$: 541.0465 found: 541.0452.

Hexane-1,6-diyl bis(diphenylphosphinodithioate) (**4z'**)



Synthesized by method H using diphenylphosphane (135 μL, 0.7 mmol) and hexane-1,6-dithiol (37.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (131.0 mg, yield 90%).

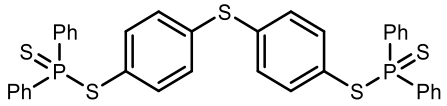
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.79 – 6.68 (m, 8H), 6.32 – 6.17 (m, 12H), 1.73 – 1.58 (m, 4H), 0.33 – 0.22 (m, 4H), 0.11 – -0.03 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.39 (d, *J* = 84.9 Hz), 131.68 (d, *J* = 3.2 Hz), 131.21 (d, *J* = 11.3 Hz), 128.40 (d, *J* = 13.2 Hz), 31.38 (d, *J* = 2.3 Hz), 29.50 (d, *J* = 5.2 Hz), 27.71.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 63.83.

HRMS (ESI, m/z): calcd for $C_{30}H_{32}P_2S_4$ $[M+H]^+$: 583.0935 found: 583.0917.

Thiobis(4,1-phenylene) bis(diphenylphosphinodithioate) (**4aa'**)



Synthesized by method H using diphenylphosphane (135 μL, 0.7 mmol) and 4,4'-thiodibenzenethiol (62.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (68.2 mg, yield 40%).

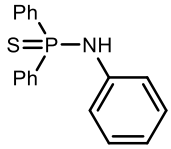
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.89 (m, 8H), 7.54 – 7.40 (m, 12H), 7.30 – 7.20 (m, 4H), 7.14 – 7.04 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.26 (d, *J* = 3.3 Hz), 136.86 (d, *J* = 3.9 Hz), 133.30 (d, *J* = 83.7 Hz), 132.00 (d, *J* = 3.2 Hz), 131.71 (d, *J* = 11.0 Hz), 130.96 (d, *J* = 2.5 Hz), 128.48 (d, *J* = 13.2 Hz), 125.75 (d, *J* = 5.7 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 65.88.

HRMS (ESI, m/z): calcd for $C_{36}H_{28}P_2S_5$ $[M+H]^+$: 683.0343 found: 683.0321.

N,P,P-triphenylphosphinothioic amide (**4ab'**) [1]



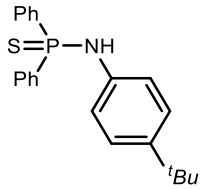
Synthesized by method G using diphenylphosphane (89 μL, 0.5 mmol) and aniline (93 mg, 1.0 mmol), followed by further purification to obtained a white solid (92.7 mg, yield 60%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 7.96 (m, 4H), 7.64 – 7.41 (m, 6H), 7.22 – 7.09 (m, 2H), 6.99 – 6.80 (m, 3H), 4.93 – 4.87 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.04, 133.61 (d, *J* = 103.1 Hz), 132.02 (d, *J* = 3.1 Hz), 131.62 (d, *J* = 11.4 Hz), 129.07, 128.75 (d, *J* = 13.2 Hz), 121.77, 118.81 (d, *J* = 7.0 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 52.51.

N-(4-(tert-butyl)phenyl)-*P,P*-diphenylphosphinothioic amide (**4ac'**) [1]



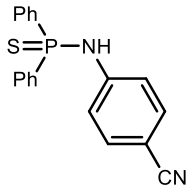
Synthesized by method G using diphenylphosphane (89 μL, 0.5 mmol) and 4-(tert-butyl)aniline (149 mg, 1.0 mmol), followed by further purification to obtained a white solid (87.6 mg, yield 48%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.94 (m, 4H), 7.54 – 7.39 (m, 6H), 7.19 – 7.10 (m, 2H), 6.86 – 6.75 (m, 2H), 4.87 (d, *J* = 6.3 Hz, 1H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.40, 137.27 (d, *J* = 2.0 Hz), 133.74 (d, *J* = 103.2 Hz), 131.89 (d, *J* = 3.1 Hz), 131.56 (d, *J* = 11.4 Hz), 128.65 (d, *J* = 13.2 Hz), 125.86, 118.43 (d, *J* = 6.8 Hz), 34.00, 31.30.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 52.45.

N-(4-cyanophenyl)-*P,P*-diphenylphosphinothioic amide (**4ad'**)



Synthesized by method G using diphenylphosphane (89 μL, 0.5 mmol) and 4-aminobenzonitrile (118 mg, 1.0 mmol), followed by further purification to obtained a white solid (85.1 mg, yield 51%).

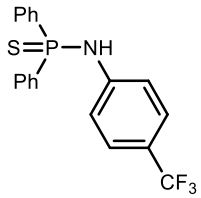
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.83 (d, *J* = 9.1 Hz, 1H), 8.03 – 7.90 (m, 4H), 7.67 – 7.52 (m, 8H), 7.16 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 146.39, 133.04, 132.93 (d, *J* = 102.5 Hz), 132.32 (d, *J* = 3.0 Hz), 131.44 (d, *J* = 11.4 Hz), 128.95 (d, *J* = 13.0 Hz), 119.40, 118.79 (d, *J* = 8.2 Hz), 102.26.

^{31}P NMR (162 MHz, DMSO-d_6) δ 50.02.

HRMS (ESI, m/z): calcd for $C_{17}H_{14}NPS_2$ $[M+H]^+$: 335.0755 found: 335.0755.

P,P-diphenyl-*N*-(4-(trifluoromethyl)phenyl)phosphinothioic amide (**4ae'**) [1]



Synthesized by method G using diphenylphosphane (89 μL, 0.5 mmol) and 4-(trifluoromethyl)aniline (161 mg, 1.0 mmol), followed by further purification to obtained a white solid (86.7 mg, yield 46%).

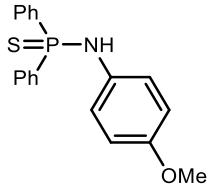
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.93 (m, 4H), 7.61 – 7.42 (m, 6H), 6.98 (d, *J* = 8.4 Hz, 2H), 5.28 (d, *J* = 6.9 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.33, 132.83 (d, *J* = 107.1 Hz), 132.31 (d, *J* = 3.3 Hz), 131.50 (d, *J* = 11.5 Hz), 128.89 (d, *J* = 13.4 Hz), 126.26 (q, *J* = 3.7 Hz), 124.25 (d, *J* = 271.2 Hz), 123.46 (q, *J* = 32.8 Hz), 118.26 (d, *J* = 7.3 Hz).

^{19}F NMR (377 MHz, Chloroform-*d*) δ -61.76.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 52.65.

N-(4-methoxyphenyl)-*P,P*-diphenylphosphinothioic amide (**4af'**) [1]



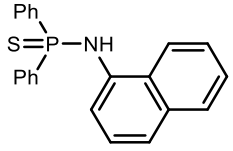
Synthesized by method G using diphenylphosphane (89 μL, 0.5 mmol) and 4-methoxyaniline (123 mg, 1.0 mmol), followed by further purification to obtained a white solid (67.8 mg, yield 40%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.97 (m, 4H), 7.56 – 7.41 (m, 6H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.70 (d, *J* = 8.3 Hz, 2H), 4.71 (d, *J* = 5.8 Hz, 1H), 3.70 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.05, 133.77 (d, *J* = 103.1 Hz), 133.02 (d, *J* = 2.3 Hz), 131.92 (d, *J* = 3.0 Hz), 131.66 (d, *J* = 11.3 Hz), 128.65 (d, *J* = 13.2 Hz), 120.98 (d, *J* = 6.5 Hz), 114.42, 55.42.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 53.52.

N-(naphthalen-1-yl)-*P,P*-diphenylphosphinothioic amide (**4ag'**)



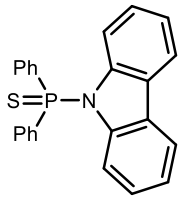
Synthesized by method G using diphenylphosphane (89 μL, 0.5 mmol) and naphthalen-1-amine (143 mg, 1.0 mmol), followed by further purification to obtained a white solid (113.1 mg, yield 63%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.02 (m, 4H), 7.86 – 7.79 (m, 2H), 7.55 – 7.41 (m, 9H), 7.38 – 7.32 (m, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 5.39 (d, *J* = 6.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.19 (d, *J* = 2.0 Hz), 134.27, 133.56 (d, *J* = 103.4 Hz), 133.40 (t, *J* = 5.4 Hz), 132.03 (d, *J* = 3.0 Hz), 131.64 (d, *J* = 11.3 Hz), 128.96, 128.76 (d, *J* = 13.3 Hz), 128.32 – 127.88 (m), 126.11 (d, *J* = 7.1 Hz), 125.65, 122.62, 119.79, 115.81 (d, *J* = 5.9 Hz).

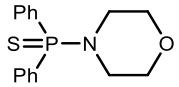
^{31}P NMR (162 MHz, Chloroform-*d*) δ 53.42.

(9H-carbazol-9-yl)diphenylphosphine sulfide (**4ah'**) [1]



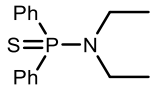
Synthesized by method G using diphenylphosphane (89 μL, 0.5 mmol) and 9H-carbazole (167 mg, 1.0 mmol), followed by further purification to obtained a white solid (136.0 mg, yield 71%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.91 (m, 6H), 7.65 – 7.56 (m, 2H), 7.54 – 7.45 (m, 4H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.11 – 7.02 (m, 2H), 6.73 (d, *J* = 8.5 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.33 (d, *J* = 2.7 Hz), 132.68 (d, *J* = 3.2 Hz), 132.55 (d, *J* = 11.7 Hz), 132.46 (d, *J* = 101.8 Hz), 129.02 (d, *J* = 13.7 Hz), 126.83 (d, *J* = 5.5 Hz), 125.79, 121.81, 119.89, 115.29 (d, *J* = 2.3 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 56.34.

Morpholinodiphenylphosphine sulfide (**4ai'**) [11]



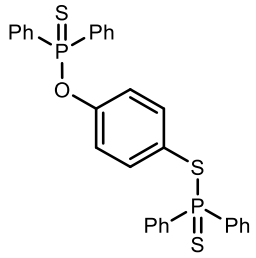
Synthesized by method G using diphenylphosphane (89 μL, 0.5 mmol) and morpholine (87 mg, 1.0 mmol), followed by further purification to obtained a white solid (100.0 mg, yield 66%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (ddd, *J* = 13.1, 7.6, 1.9 Hz, 4H), 7.46 (dt, *J* = 7.2, 4.5 Hz, 6H), 3.74 (t, *J* = 4.7 Hz, 4H), 2.87 (q, *J* = 5.3 Hz, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.88 (d, *J* = 10.5 Hz), 131.67 (d, *J* = 2.9 Hz), 131.57 (d, *J* = 103.1 Hz), 128.40 (d, *J* = 12.8 Hz), 66.47 (d, *J* = 10.3 Hz), 44.85 (d, *J* = 1.6 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 67.58.

N,N-diethyl-*P,P*-diphenylphosphinothioic amide (**4aj'**) [12]



Synthesized by method G using diphenylphosphane (89 μL, 0.5 mmol) and diethylamine (73 mg, 1.0 mmol), followed by further purification to obtained a white solid (121.4 mg, yield 84%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.93 (m, 4H), 7.50 – 7.37 (m, 6H), 3.11 – 2.98 (m, 4H), 1.08 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 133.65 (d, *J* = 103.1 Hz), 131.87 (d, *J* = 10.6 Hz), 131.27 (d, *J* = 2.9 Hz), 128.14 (d, *J* = 12.7 Hz), 40.27 (d, *J* = 3.2 Hz), 13.52 (d, *J* = 5.4 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 68.42.

O-(4-((diphenylphosphorothioyl)thio)phenyl) diphenylphosphinothioate (**4ak'**)



Synthesized by method H using diphenylphosphane (135 μL, 0.7 mmol) and 4-mercaptophenol (31.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (104.6 mg, yield 75%).

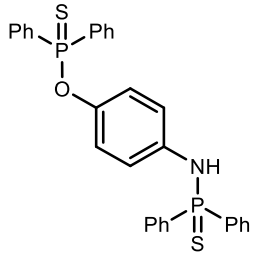
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.83 (m, 8H), 7.56 – 7.38 (m, 12H), 7.21 – 7.15 (m, 2H), 6.95 – 6.87 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.53, 137.50, 134.11 (d, *J* = 78.0 Hz), 133.14 (d, *J* = 50.7 Hz), 132.19 (d, *J* = 3.0 Hz), 131.93 (d, *J* = 3.3 Hz), 131.72 (d, *J* = 11.0 Hz), 131.31 (d, *J* = 11.7 Hz), 128.57 (d, *J* = 7.3 Hz), 128.43 (d, *J* = 6.8 Hz), 122.34 (d, *J* = 2.5 Hz), 122.29 (d, *J* = 2.6 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.71 (d, *J* = 3.0 Hz), 65.66 (d, *J* = 3.7 Hz).

HRMS (ESI, m/z): calcd for $C_{30}H_{24}OP_2S_3$ $[M+H]^+$: 559.0537 found: 559.0536.

O-(4-((diphenylphosphorothioyl)amino)-2-methylphenyl) diphenylphosphinothioate (**4al'**)



Synthesized by method H using diphenylphosphane (135 μL, 0.7 mmol) and 4-aminophenol (27.3 mg, 0.25 mmol), followed by further purification to obtained a white solid (86.7 mg, yield 64%).

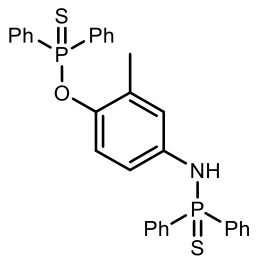
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.85 (m, 8H), 7.54 – 7.39 (m, 12H), 6.85 – 6.73 (m, 4H), 4.84 (d, *J* = 6.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.18 (d, *J* = 9.0 Hz), 136.88, 134.36 (d, *J* = 91.1 Hz), 133.30 (d, *J* = 83.3 Hz), 132.03 (d, *J* = 6.3 Hz), 132.03, 131.58 (d, *J* = 11.4 Hz), 131.33 (d, *J* = 11.5 Hz), 128.74 (d, *J* = 13.4 Hz), 128.44 (d, *J* = 13.6 Hz), 122.22 (d, *J* = 4.8 Hz), 119.75 (d, *J* = 6.5 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.10, 52.98.

HRMS (ESI, m/z): calcd for $C_{30}H_{25}NOP_2S_2$ $[M+H]^+$: 542.0926 found: 542.0911.

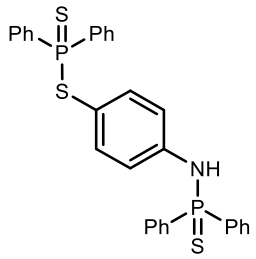
O-(4-((diphenylphosphorothioyl)amino)phenyl) diphenylphosphinothioate (**4am'**)



Synthesized by method H using diphenylphosphane (135 μL, 0.7 mmol) and 4-amino-2-methylphenol

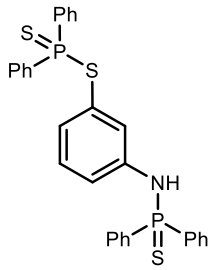
(30.8 mg, 0.25 mmol), followed by further purification to obtained a white solid (88.8 mg, yield 64%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.87 (m, 8H), 7.55 – 7.40 (m, 12H), 6.73 (d, *J* = 2.8 Hz, 1H), 6.64 (dd, *J* = 8.7, 1.5 Hz, 1H), 6.52 (dd, *J* = 8.8, 2.9 Hz, 1H), 4.79 (d, *J* = 6.2 Hz, 1H), 2.11 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.27 (d, *J* = 9.1 Hz), 136.50, 134.80 (d, *J* = 111.1 Hz), 133.55 (d, *J* = 103.2 Hz), 131.95 (d, *J* = 6.3 Hz), 131.95, 131.55 (d, *J* = 11.4 Hz), 131.43, 131.17 (d, *J* = 11.5 Hz), 128.69 (d, *J* = 13.2 Hz), 128.47 (d, *J* = 13.6 Hz), 121.89 (d, *J* = 7.1 Hz), 121.06 (d, *J* = 4.6 Hz), 116.93 (d, *J* = 6.3 Hz), 17.41.
^{31}P NMR (162 MHz, Chloroform-*d*) δ 80.91, 52.98.
HRMS (ESI, m/z): calcd for $C_{31}H_{27}NOP_2S_2$ $[M+H]^+$: 556.1082 found: 556.1067.

4-((Diphenylphosphorothioyl)amino)phenyl diphenylphosphinodithioate (**4an'**)



Synthesized by method H using diphenylphosphane (135 μL, 0.7 mmol) and 4-aminobenzenethiol (31.3 mg, 0.25 mmol), followed by further purification to obtained a white solid (107.2 mg, yield 77%).
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 (d, *J* = 8.6 Hz, 1H), 8.00 – 7.84 (m, 8H), 7.64 – 7.48 (m, 12H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 142.43 (d, *J* = 2.3 Hz), 133.81 (d, *J* = 54.7 Hz), 132.88 (d, *J* = 35.3 Hz), 132.18 (dd, *J* = 35.5, 3.0 Hz), 131.42 (d, *J* = 11.3 Hz), 131.25 (d, *J* = 11.0 Hz), 128.92 (d, *J* = 13.1 Hz), 128.75 (d, *J* = 12.9 Hz), 127.77 (d, *J* = 4.0 Hz), 126.42 (d, *J* = 5.6 Hz).
^{31}P NMR (162 MHz, DMSO-d_6) δ 64.66, 49.92.
HRMS (ESI, m/z): calcd for $C_{30}H_{25}NP_2S_3$ $[M+H]^+$: 558.0697 found: 558.0705.

3-((Diphenylphosphorothioyl)amino)phenyl diphenylphosphinodithioate (**4ao'**)



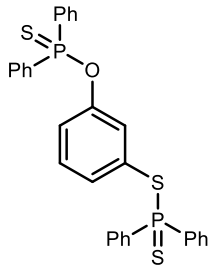
Synthesized by method H using diphenylphosphane (135 μL, 0.7 mmol) and 3-aminobenzenethiol (31.3 mg, 0.25 mmol), followed by further purification to obtained a white solid (87.7 mg, yield 63%).
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 (d, *J* = 8.9 Hz, 1H), 7.97 – 7.83 (m, 8H), 7.64 – 7.47 (m, 12H), 7.12 – 7.05 (m, 2H), 6.98 – 6.91 (m, 2H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 143.62, 136.64 (d, *J* = 3.4 Hz), 133.62 (d, *J* = 45.6 Hz), 132.70 (d, *J* = 25.2 Hz), 132.35 (d, *J* = 3.1 Hz), 132.13 (d, *J* = 2.9 Hz), 131.43 (d, *J* = 7.9 Hz), 131.32 (d, *J*

= 7.4 Hz), 128.94 (d, *J* = 6.6 Hz), 128.81 (d, *J* = 6.7 Hz), 119.12 (d, *J* = 8.0 Hz), 116.11 (d, *J* = 5.5 Hz).

^{31}P NMR (162 MHz, DMSO-d_6) δ 64.90, 49.62.

HRMS (ESI, m/z): calcd for $C_{30}H_{25}NP_2S_3$ $[M+H]^+$: 558.0697 found: 558.0691.

O-(3-((diphenylphosphorothioyl)thio)phenyl) diphenylphosphinothioate (**4ap'**)



Synthesized by method H using diphenylphosphane (135 μL, 0.7 mmol) and 3-mercaptophenol (31.5 mg, 0.25 mmol), followed by further purification to obtained a white solid (103.4 mg, yield 74%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.84 (m, 8H), 7.53 – 7.36 (m, 12H), 7.16 (p, *J* = 1.9 Hz, 1H), 7.11 – 6.97 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.39 (dd, *J* = 8.8, 2.6 Hz), 134.07 (d, *J* = 78.1 Hz), 133.10 (d, *J* = 51.1 Hz), 132.53 (dd, *J* = 4.0, 1.7 Hz), 132.08 (d, *J* = 3.1 Hz), 131.89 (d, *J* = 3.2 Hz), 131.64 (d, *J* = 11.0 Hz), 131.25 (d, *J* = 11.7 Hz), 129.30 (d, *J* = 4.4 Hz), 129.25 (d), 127.97 (d, *J* = 5.5 Hz), 122.92 (dd, *J* = 4.8, 3.0 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 82.89, 65.69.

HRMS (ESI, m/z): calcd for $C_{30}H_{24}OP_2S_3$ $[M+H]^+$: 559.0537 found: 559.0529.

4.3. Synthesis of intermediates

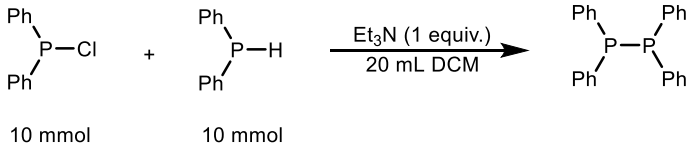


Fig. S4 Synthesis of 1,1,2,2-tetraphenyldiphosphane

Diphenylphosphine (1.8 g, 10 mmol) and chlorodiphenylphosphine (2.2 g, 10 mmol) were placed in a 20 mL microwave vessel in the glovebox filled with nitrogen. Et_3N (1.4 mL, 10 mmol) and THF (10 mL) were added to the vessel at 0 °C, and the solution was stirred at room temperature for 12 h. After the mixture was filtered through a pad of Celite and washed by degassed n-hexane in the glovebox, the solvent was removed under reduced pressure to give an analytically pure tetraphenyldiphosphane in 79% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.33 (m, 8H), 7.27 – 7.12 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.63 (t, *J* = 5.0 Hz), 134.28 (t, *J* = 12.9 Hz), 128.63, 128.18 (t, *J* = 3.5 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ -14.92.[13]

4.4. Gram scale experiment

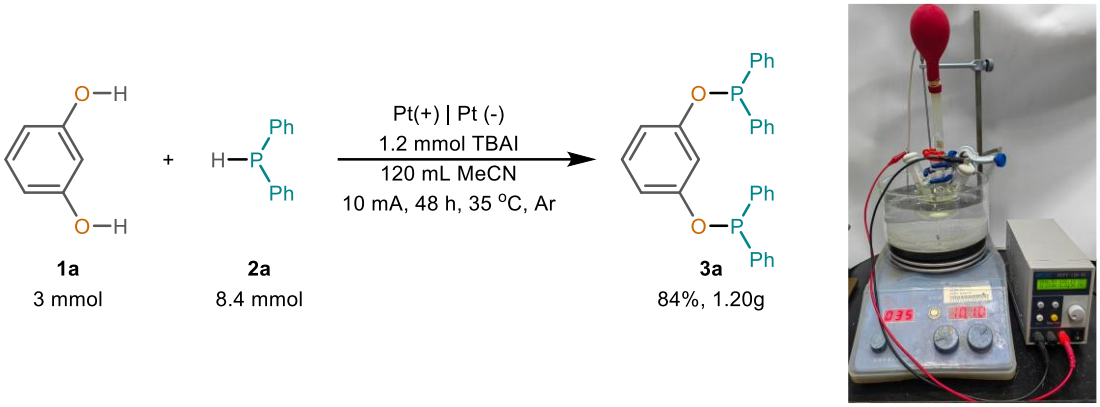


Fig. S5 Gram scale experiment

In an oven-dried three-necked flask equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. M-diphenol (**1a**, 330.0 mg, 3.0 mmol), TBAI (442.8 mg, 1.2 mmol) were added. This was followed by the addition of diphenylphosphane (**2a**, 1.62 mL, 8.4 mmol) and extra dry acetonitrile (120 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 48 h. The yield was then determined by assured 31P NMR. Because trivalent products are easy to oxidize in air, the products are easy to deteriorate in the separation process of column chromatography. In order to ensure the purity of the product, after the reaction, add S_8 (96.0 mg, 6.00 mmol, calculated according to S atom) into the reaction tube to stabilize the trivalent phosphorus, stirred for 30 min, and then purified by column chromatography (200-300 mesh silica gel, petroleum ether (PE): ethyl acetate (EA)=50:1), to obtain the required product of 1.2 g.

4.5. Unsuccessful examples

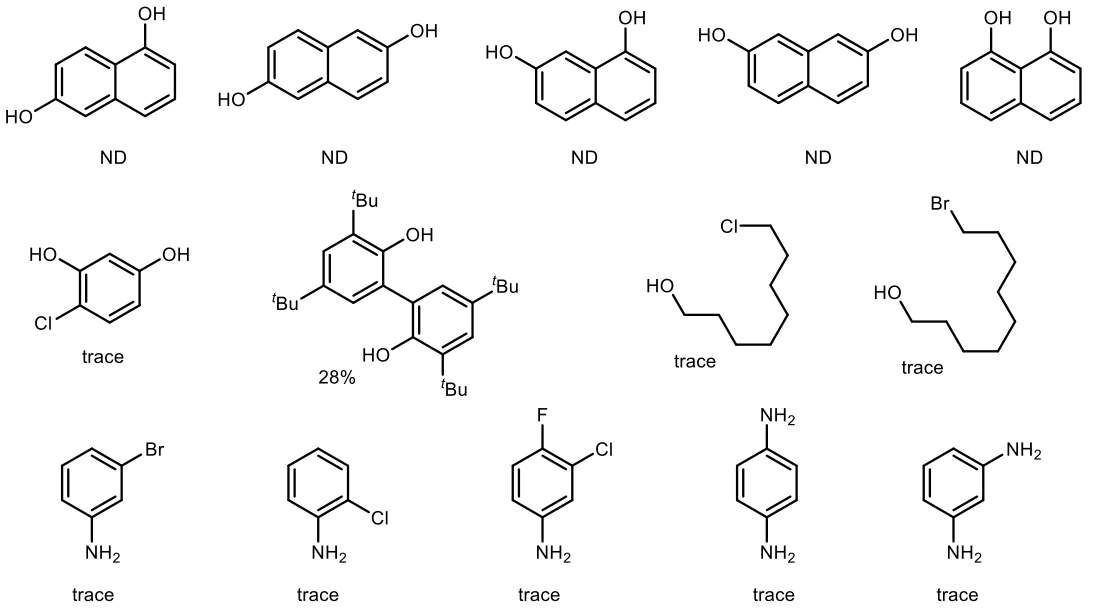


Table S4. Unsuccessful example

5. Experimental Procedures for Control Experiment

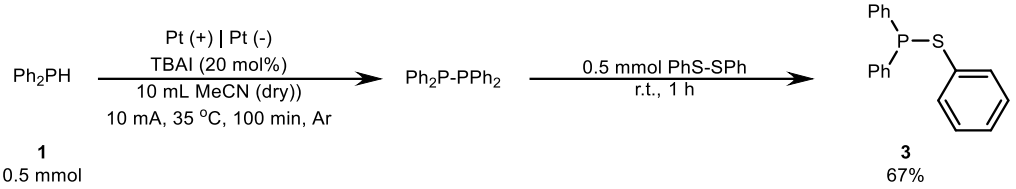
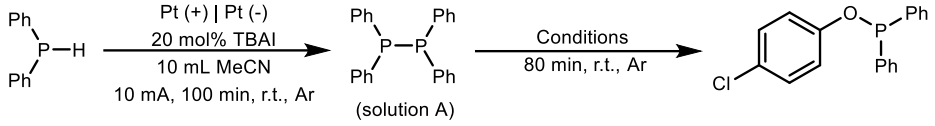


Table S5. Control experiment for P-S bonding

In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. TBAI (36.9 mg, 0.1 mmol) was added. This was followed by the addition of diphenylphosphane (89 μL, 0.5 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 100 minutes. Then diphenyl disulfide (54.6 mg, 0.25 mmol) was added to the system and stirred for 1 h. Then the yield was determined by assure ^{31}P NMR.



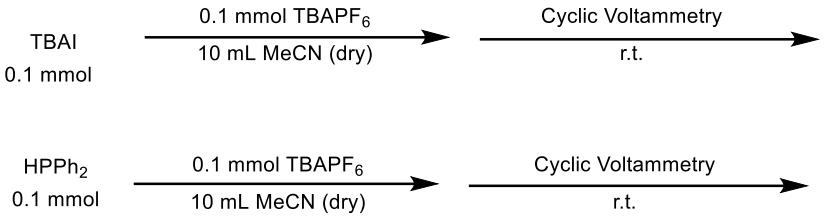
Entry	Conditions	Yield of **3w**
1	4-Cl-PhOH as substrate, Pt (+) | Pt (-), 10 mA	52%
2	4-Cl-PhOH as substrate, no electricity	n.d.
3	4-Cl-PhONa as substrate, no electricity	n.d.

Table S6. Control experiment for P-O bonding

In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. TBAI (36.9 mg, 0.1 mmol) was added. This was followed by the addition of diphenylphosphane (89 μL, 0.5 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 100 minutes. After electrolysis, for entry 1, *p*-chlorophenylthiophenol was added to the solution and was stirred at a constant current of 10.0 mA at 35 °C for 80 minutes; for entries 2-3, *p*-chlorophenylthiophenol or sodium *p*-chlorophenylthiophenol was added to the solution and was sitrred for 80 minutes. Then the yield was determined by assure ^{31}P NMR.

6. Electrochemical Procedures for Cyclic Voltammetry

Cyclic voltammograms were recorded with a CorrTest® CS2350H bipotentiostat at room temperature. $TBAPF_6$ (38.9 mg, 0.10 mmol) was used as the supporting electrolyte. The scan rate was 100 mV / s. The scan range is between 0 V to 2.0 V.



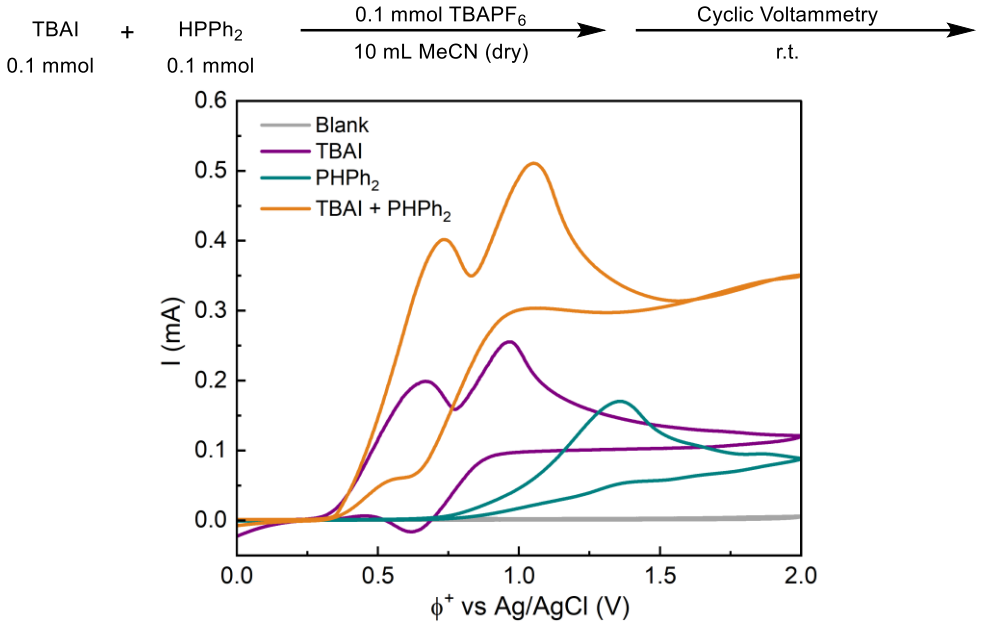
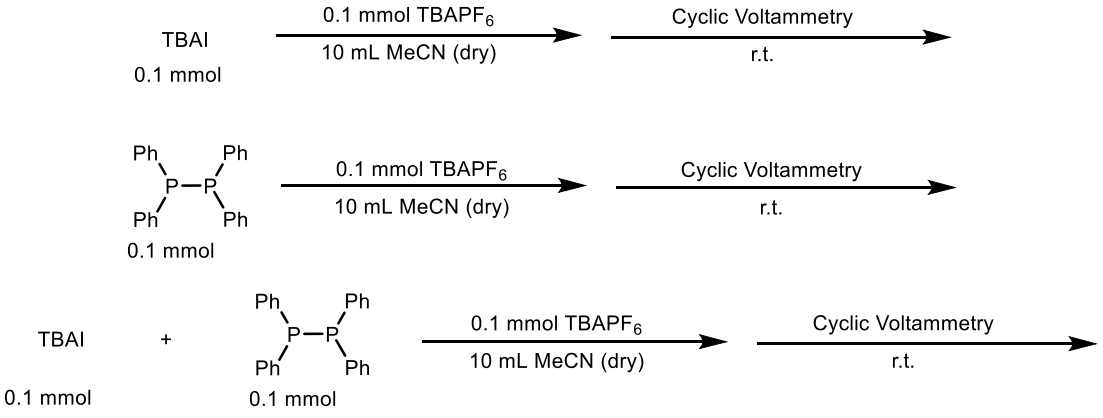


Fig. S6 Cyclic voltammetry curve for diphenylphosphine and TBAI

In an undivided cell equipped with a stir bar, $TBAPF_6$ (38.9 mg, 0.10 mmol), TBAI (36.9 mg, 0.10 mmol), or diphenylphosphine (18.6 mg, 0.10 mmol) was added as required, followed by MeCN (10 mL). The undivided cell was equipped with glassy-carbon disk working electrode (diameter, 3.0 mm) and Pt wire auxiliary electrode. All potentials are referenced against the Ag/AgCl reference electrode.



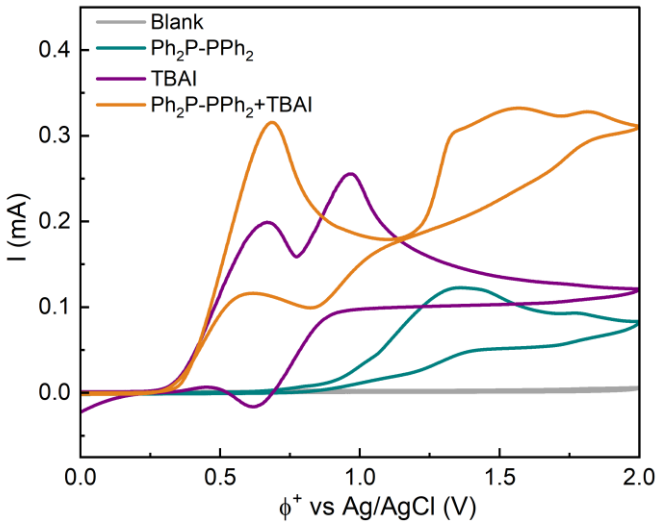
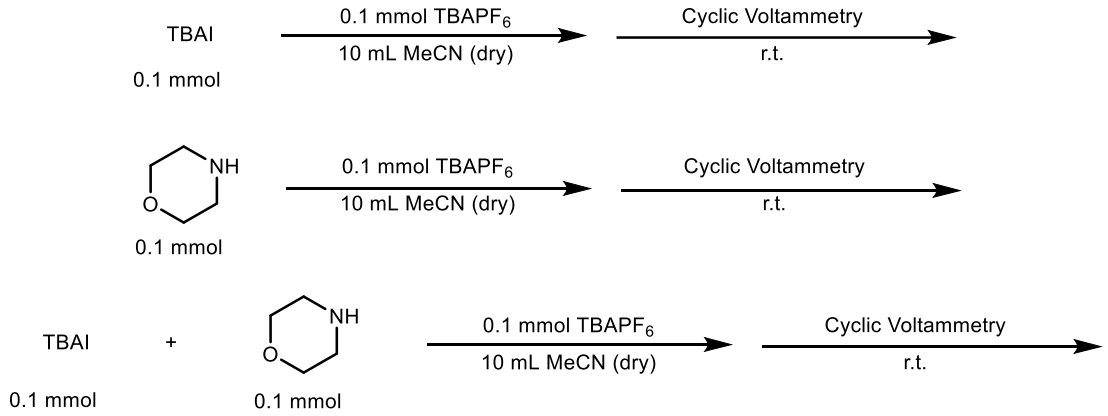


Fig. S7 Cyclic voltammetry curve for TBAI and 1,1,2,2-tetraphenyldiphosphane

In an undivided cell equipped with a stir bar, $TBAPF_6$ (38.9 mg, 0.10 mmol), TBAI (36.9 mg, 0.10 mmol), or 1,1,2,2-tetraphenyldiphosphane (37.0 mg, 0.10 mmol) was added as required, followed by MeCN (10 mL). The undivided cell was equipped with glassy-carbon disk working electrode (diameter, 3.0 mm) and Pt wire auxiliary electrode. All potentials are referenced against the Ag/AgCl reference electrode.



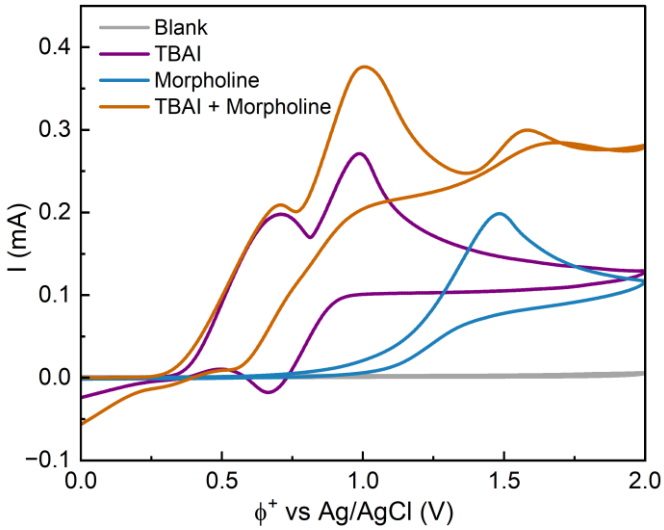


Fig. S8 Cyclic voltammetry curve for TBAI and morpholine

In an undivided cell equipped with a stir bar, $TBAPF_6$ (38.9 mg, 0.10 mmol), TBAI (36.9 mg, 0.10 mmol), or morpholine (8.2 mg, 0.10 mmol) was added as required, followed by MeCN (10 mL). The undivided cell was equipped with glassy-carbon disk working electrode (diameter, 3.0 mm) and Pt wire auxiliary electrode. The scan range was 0 V to 2.0 V. All potentials are referenced against the Ag/AgCl reference electrode.

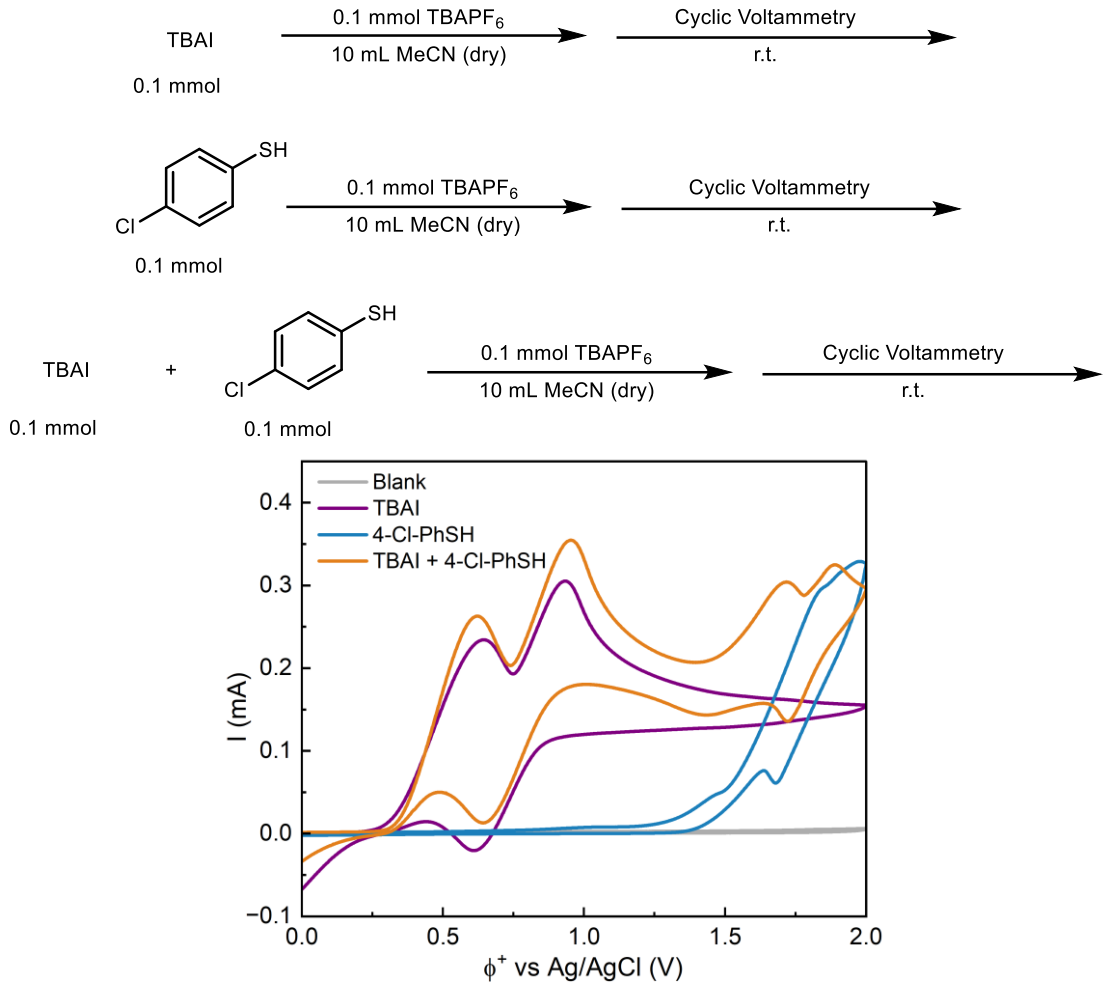


Fig. S9 Cyclic voltammetry curve for TBAI and phenylthiophenol

In an undivided cell equipped with a stir bar, $TBAPF_6$ (38.9 mg, 0.10 mmol), TBAI (36.9 mg, 0.10 mmol), or 4-chlorothiophenol (12.8 mg, 0.10 mmol) was added as required, followed by MeCN (10 mL). The undivided cell was equipped with glassy-carbon disk working electrode (diameter, 3.0 mm) and Pt wire auxiliary electrode. The scan range was 0 V to 2.0 V. All potentials are referenced against the Ag/AgCl reference electrode.

7. Experimental Procedures for Sampling Experiment

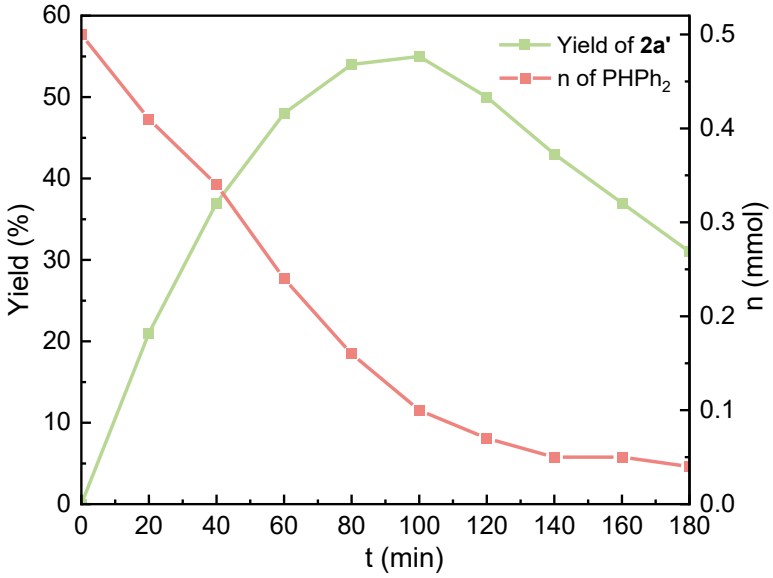


Fig. S10 Sampling test for P-P bonding reaction

In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. Triphenyl phosphate (81.5 mg, 0.25 mmol), TBAI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane (89 μL, 0.5 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 3 h. The samples were taken into the NMR tubes in the glove box every 20 minutes. Then the samples were subjected to assure ^{31}P NMR testing. After the testing was finished, the samples were transformed back to the reaction.

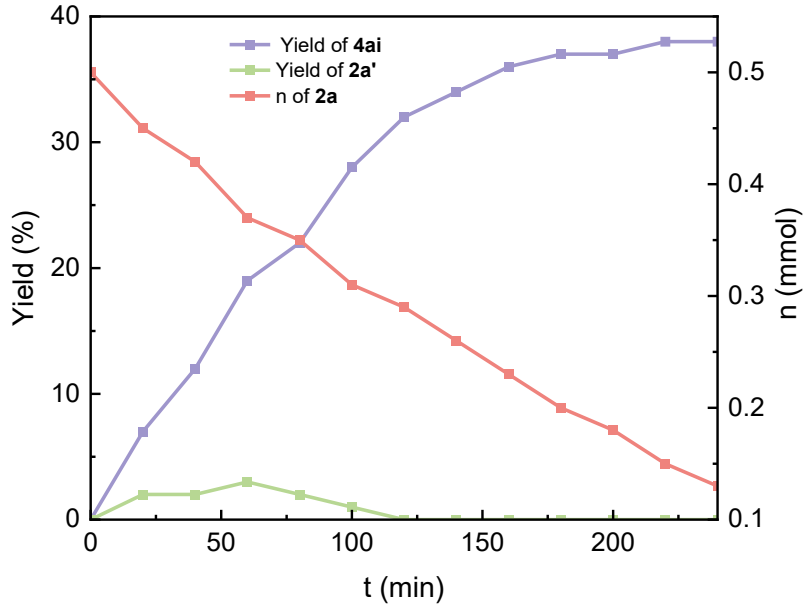


Fig. S11 Sampling test for P-N bonding reaction

In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. Triphenyl phosphate (81.5 mg, 0.25 mmol),

morpholine (87 mg, 1.0 mmol), TBAI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane (89 μL, 0.5 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 4 h. The samples were taken into the NMR tubes in the glove box every 20 minutes. Then the samples were subjected to assure ^{31}P NMR testing. After the testing was finished, the samples were transformed back to the reaction.

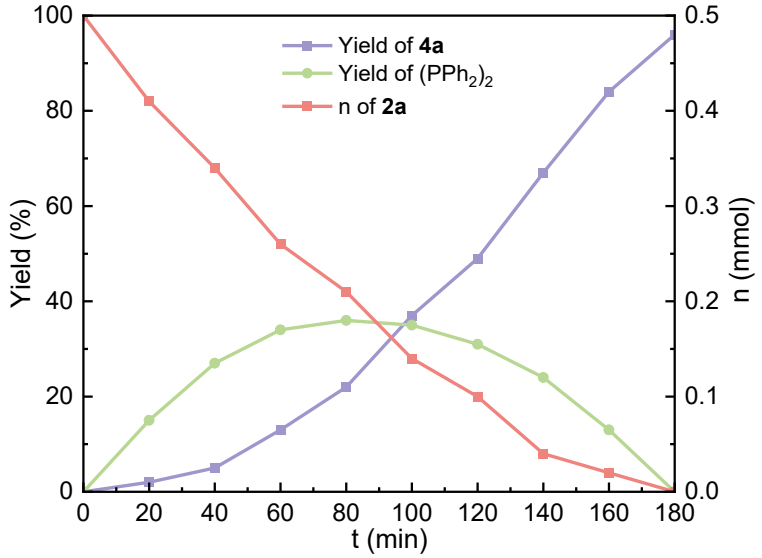


Fig. S12 Sampling test for P-S bonding reaction

In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. Triphenyl phosphate (81.5 mg, 0.25 mmol), 4-chlorothiophenol (73 mg, 0.5 mmol), TBAI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane (89 μL, 0.5 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 3 h. The samples were taken into the NMR tubes in the glove box every 20 minutes. Then the samples were subjected to assure ^{31}P NMR testing. After the testing was finished, the samples were transformed back to the reaction.

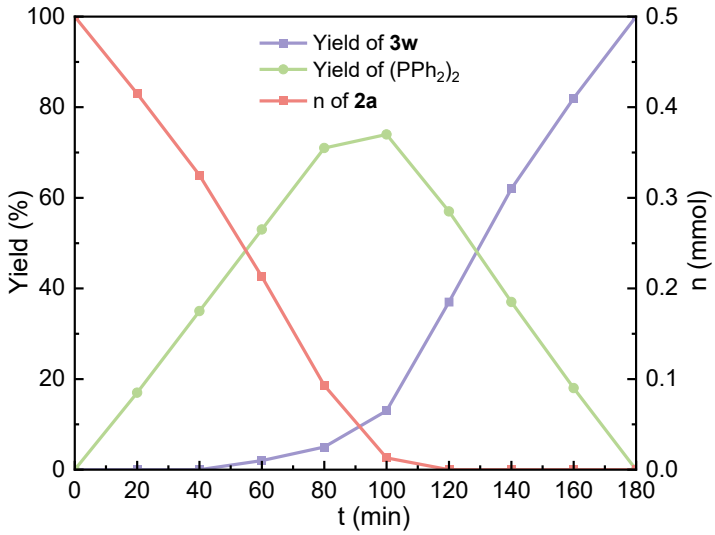


Fig. S13 Sampling test for P-O bonding reaction

In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. Triphenyl phosphate (81.5 mg, 0.25 mmol), 4-Chlorophenol (128 mg, 1.0 mmol), TBAI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane (89 μL, 0.5 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 3 h. The samples were taken into the NMR tubes in the glove box every 20 minutes. Then the samples were subjected to assure ^{31}P NMR testing. After the testing was finished, the samples were transformed back to the reaction.

8. Experimental Procedures for Electron Paramagnetic Resonance (EPR) Experiment

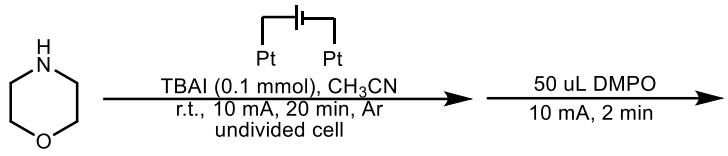


Fig. S14 EPR testing of nitrogen radicals

The adduct of nitrogen radical to DMPO

In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with two platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode and the anode. The distance of electrodes is 0.6 cm. $^{n}Bu_4NBF_4$ (32.9 mg, 0.1 mmol) were added. This was followed by the addition of morphline (87 μL, 1.0 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixture was stirred at a constant current of 10.0 mA at 25 °C for 5 minutes. After that, 50 μL DMPO was added and electrolysis for 5 minutes. After that, an aliquot was taken for EPR analysis.

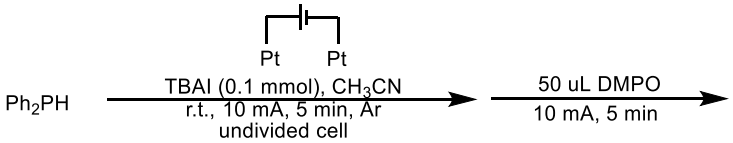


Fig. S15 EPR testing of phosphine radicals

The adduct of phosphorus radical to DMPO

In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with two platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode and the anode. The distance of electrodes is 0.6 cm. $^{n}Bu_4NI$ (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane (89 μL, 0.5 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixture was stirred at a constant current of 10.0 mA at 25 °C for 5 minutes. After that, 50 μL DMPO was added and electrolysis for 5 minutes. After that, an aliquot was taken for EPR analysis.

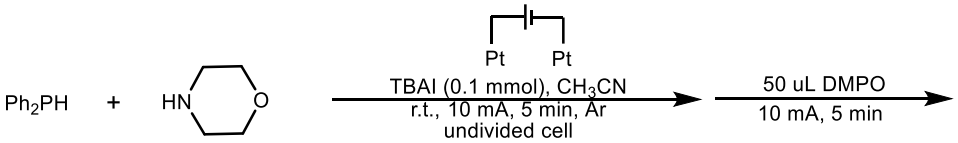


Fig. S16 EPR testing of phosphorus free radicals in the presence of morpholine

The adduct of phosphorus radical to DMPO

In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with two platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode and the anode. The distance of electrodes is 0.6 cm. ^{n}Bu$_4$NI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane (89 μL, 0.5 mmol), morpholine (87 μL, 1.0 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixture was stirred at a constant current of 10.0 mA at 25 °C for 5 minutes. After that, 50 μL DMPO was added and electrolysis for 5 minutes. After that, an aliquot was taken for EPR analysis.

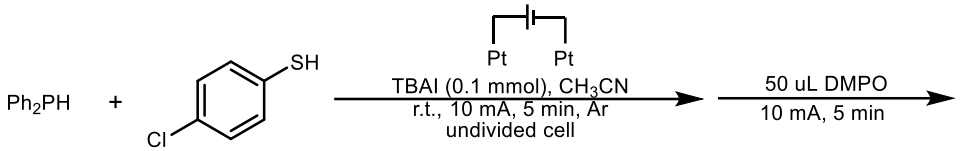


Fig. S17 EPR testing of phosphorus radicals in the presence of 4-chlorothiophenol

The adduct of phosphorus radical to DMPO

In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with two platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode and the anode. The distance of electrodes is 0.6 cm. ^{n}Bu$_4$NI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane (89 μL, 0.5 mmol), 4-chlorothiophenol (72.3 mg, 0.5 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixture was stirred at a constant current of 10.0 mA at 25 °C for 5 minutes. After that, 50 μL DMPO was added and electrolysis for 5 minutes. After that, an aliquot was taken for EPR analysis.

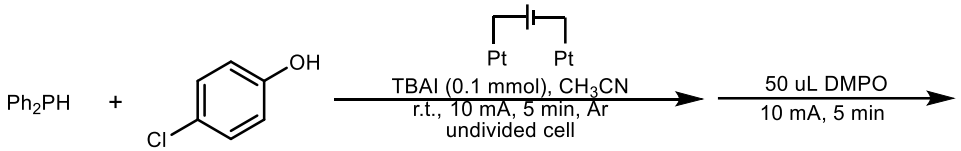


Fig. S18 EPR testing of phosphorus radicals in the presence of 4-chlorophenol

The adduct of phosphorus radical to DMPO

In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with two platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode and the anode. The distance of electrodes is 0.6 cm. ^{n}Bu$_4$NI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane (89 μL, 0.5 mmol), 4-chlorophenol (128 mg, 1.0 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). The mixture was stirred at a constant current of 10.0 mA at 25 °C for 5 minutes. After that, 50 μL DMPO was added and electrolysis for 5 minutes. After that, an aliquot was taken for EPR analysis.

9. Experimental Procedures for Radical Capture Experiment

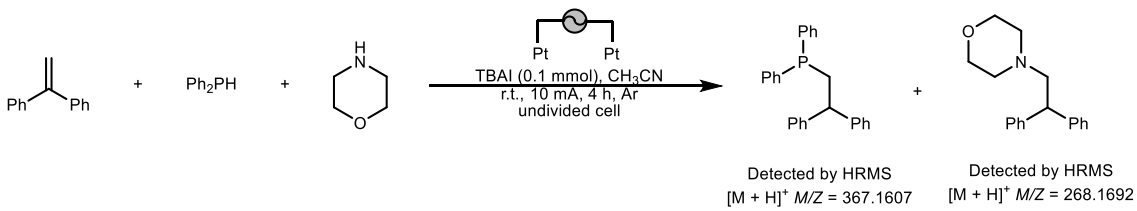


Fig. S19 Radical capture experiment

In an oven-dried undivided tube (25.0 mL) equipped with a stir bar. The tube was equipped with a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the anode and a platinum plate (1.5 × 1.5 × 0.03 cm^3) as the cathode. The distance of electrodes is 0.6 cm. 1,1-Diphenylethylene (180 μL, 1.0 mmol), morpholine (87 μL, 1.0 mmol), TBAI (36.9 mg, 0.1 mmol) were added. This was followed by the addition of diphenylphosphane (**2a**, 0.5 mmol) and extra dry acetonitrile (10 mL) in a glovebox (H_2O and O_2 < 0.1 ppm). Then the mixture was stirred at a constant current of 10.0 mA at 35 °C for 3 h (J = 4.4 mA/cm^2, 2.2 F/mol). After the reaction was completed, the product was detected by HRMS.

10. Experimental Procedures for Operando EC-MS

10.1. Reagents and materials

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Platinum wire (φ: 0.1 mm). The borosilicate glass tube (O.D.: 1.5 mm, I.D.: 0.86 mm, Length: 10 cm) was purchased from SUTTER Instrument Co., Ltd., USA.

10.2. Electrospray ionization source emitters

Electrospray ionization source (ESI) emitters were pulled from borosilicate glass tube by using a P-97 microelectrode puller (Sutter Instrument, Co., Ltd., USA). For the parameters optimization and performance evaluation experiments, emitter with tip diameter of ca. 20 μm was used. The pulling parameters for this emitter are as follows:

HEAT = 529, PULL = 10, VEL = 11, TIME = 250, P = 500

10.3. Mass spectrometry

MS data were acquired by LTQ Velos Orbitrap Elite mass spectrometer (Thermo Fisher Scientific Co., Ltd., USA). The temperature of the ion transmission tube was set to 275°C; the energy of the S-lens was set to 60%; the number of micro scan was set to 1. MS/MS data were acquired by setting isolation window at 1.0 Da and normalized collision energies from 20 to 35 (units were defined by the instrument manufacturer, the collision gas was helium). The resolution of MS was set to 60000. All MS data were analyzed through the Qual browser (Xcalibur workstation, version 4.2.47). The spray voltage was supplied by a high voltage power supply (Dongwen High Voltage Power Supply Co., Ltd., Tianjin). Both the mass spectrometer and the external high voltage power supply were well grounded.

10.4. Online electrochemical reactions

Herein, we employ the FE-ESI (floating electrochemical electrospray ionization) device to achieve real-time monitoring of the reaction process. Based on the original setup, a potential controller was integrated, enabling the device to stably provide a broad output voltage range from –12 V to +12 V under floating conditions, with a voltage regulation precision reaching 1 mV. A photograph of the actual device is shown in Figure S19. Ag/AgCl was used as the reference electrode, a platinum wire as the counter electrode, and a platinum wire as the counter electrode as the working electrode. (It is important to note that the platinum wire of the counter electrode and working electrode should be sleeved with a polyimide capillary tube (I.D. 150 μm, O.D. 365 μm) to prevent a short circuit with the reference electrode.) The distance between the working electrode, reference electrode, and counter electrode was maintained at 2 mm. We had placed WE very close (≈ 200 μm) to the exit of the emitter (O.D. ≈ 20 μm) to ensure electrode reaction products transferred to MS quickly. The spray voltage was set at 1.5~2.5 kV. The parameter settings for the floating electrochemical system were as follows: The electrochemical method adopts a rapid output mode at

constant potential, with the potential set at 0 V from 0 to 0.4 minutes, 0.6 V from 0.4 to 0.8 minutes, and 1 V from 0.8 to 1.2 minutes. The application of the electrochemical method and data collection begin 0.2 minutes after the initiation of mass spectrometry data acquisition. Chemical structure of the intermediate was verified by using high resolution tandem mass spectrometry (HRMS).

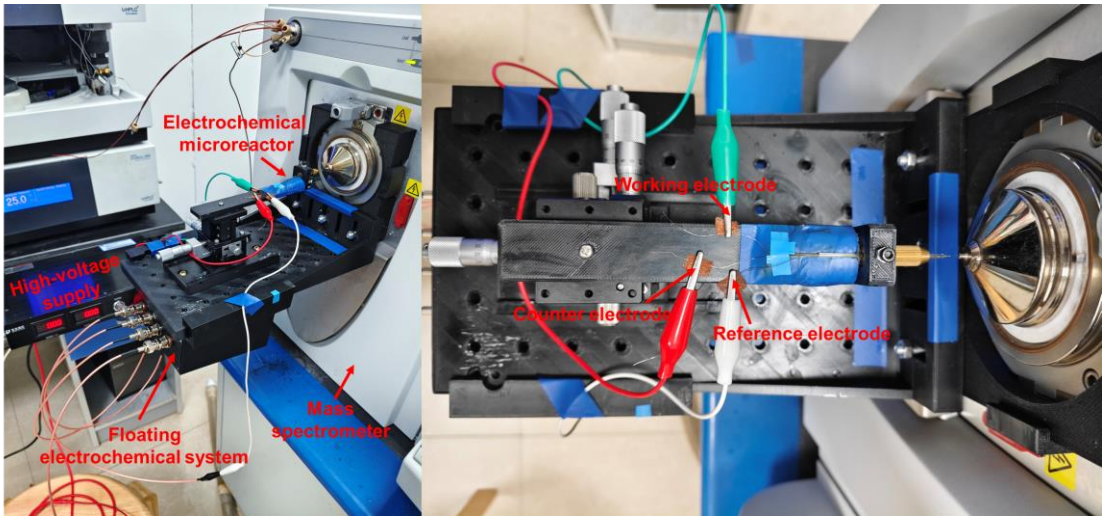


Fig. S20 The full view of the EC-MS platform

10.5. EC oxidation of 2a' to 2a'' observed in positive mode HRMS

For the monitoring of EC oxidation of **2a'** to **2a''** in positive ESI mode, the solution of MeCN (10.0 mL) containing 1.0 mmol NaI and 0.2 mmol **2a'** were loaded into the ESI emitter (Platinum wire (φ: 0.1 mm) as anode, Platinum wire (φ: 0.1 mm) as cathode). The spray voltage was set at 2.5 kV. Chemical structure of the intermediate was verified by using high resolution tandem mass spectrometry (HRMS)

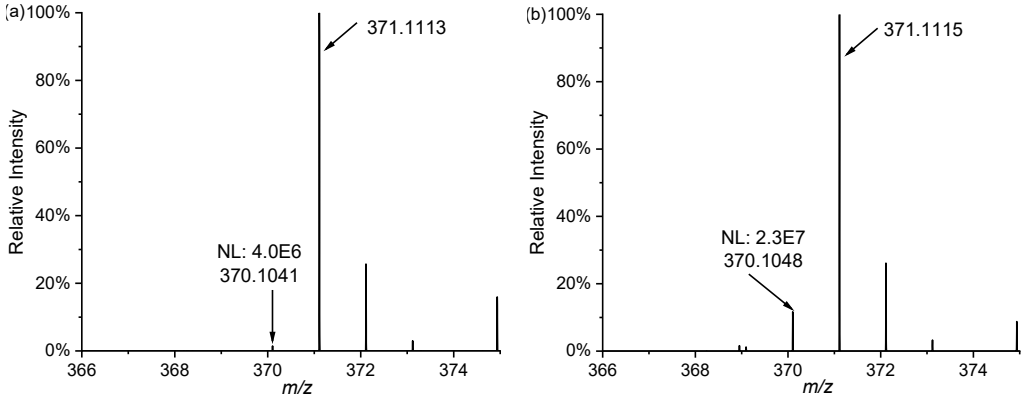


Fig. S21 (a) 1,1,2,2-Tetraphenyldiphosphane high-resolution mass spectrum before electrolysis (control experiment), (b) 1,1,2,2-tetraphenyldiphosphane high-resolution mass spectrum of electrolysis

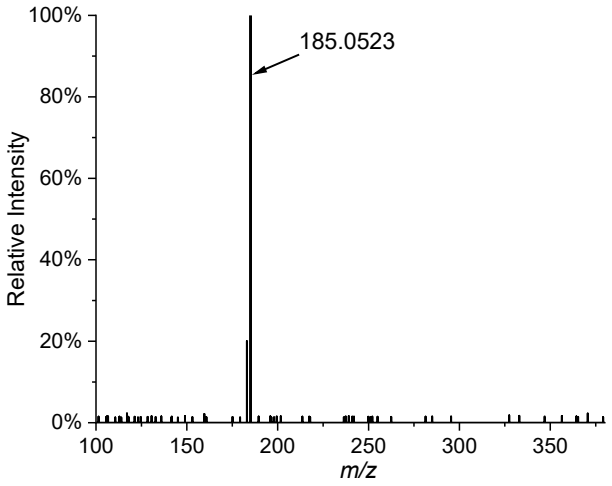


Fig. S22 tandem MS of the parent ion 185.0523

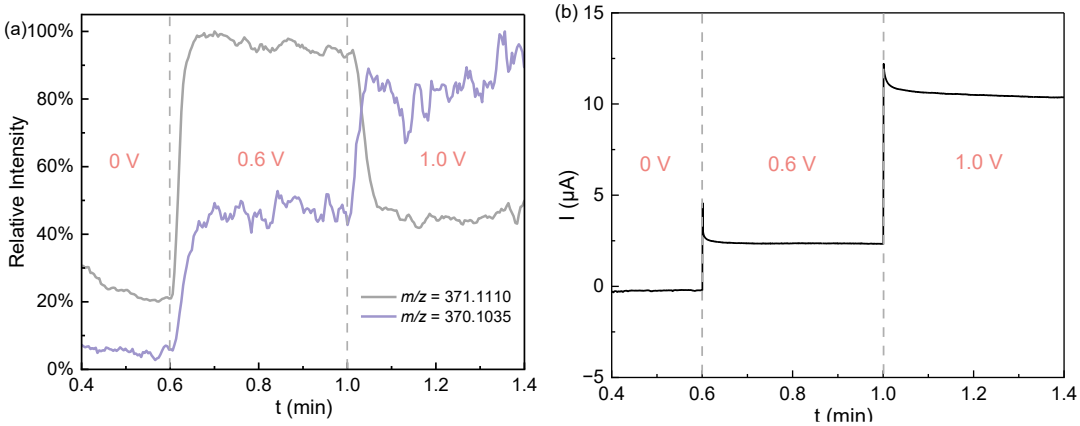


Fig. S23 (a) Extracted ion chromatograms (EICs) of the 1,1,2,2-tetraphenyldiphosphane ([M+H$^+$]) and 1,1,2,2-tetraphenyldiphosphane radical cations; (b) Current during electrolysis.

11. References

[1] Ohta, H., Asahara, R., Ikeda, R., Sakamoto, T. & Hayashi, M. A Protocol for the Synthesis of Organophosphorus(V) Compounds with P–N and P–O Bonds by Umpolung Strategy Using Hydroxymethylphosphine Sulfides. *The Journal of Organic Chemistry* **90**, 824-829 (2025). https://doi.org/10.1021/acs.joc.4c01832.

[2] Baranskii, V. A.; Eliseeva, G. D.; Sukhorukova. N. A Bases of reactivity of phosphoryl and thiophosphoryl compounds. *Zhurnal Obshchei Khimii* **58**, 777-83 (1988).

[3] Li, S. *et al.* Electrochemical Cross-Dehydrogenative Coupling of P(O)–H/P–H Bonds with Heteroatom Nucleophiles: Access to P(O)–N and P(S)–X Compounds. *The Journal of Organic Chemistry* **90**, 8269-8282 (2025). https://doi.org/10.1021/acs.joc.5c00760

[4] 1Zhang, C.-P., Wang, T.-Z., Yang, Z.-J. & Liang, Y.-F. Manganese Promoted Reductive Cross-Coupling of Phosphine Chlorides with Disulfides for the Synthesis of Thiophosphanes. *Advanced Synthesis & Catalysis* **367**, e202401395 (2025). https://doi.org/10.1002/adsc.202401395

[5] Yoshifuji, M., Hanafusa, F. & Inamoto, N. Synthetic Method of Functionalized Unsymmetrical Sulfides and Disulfides Using Diphenylphosphinodithioates. *Chemistry Letters* **8**, 723-726 (1979). https://doi.org/10.1246/cl.1979.723

[6] Majewski, M. *et al.* Product Subclass 12: Allyllithium Compounds. *Science of Synthesis* **8a**, 1 (2006). https://doi.org/ 10.1055/sos-SD-008-00184

[7] Ni, H. *et al.* Cyclical palmitoylation regulates TLR9 signalling and systemic autoimmunity in mice. *Nature Communications* **15**, 1 (2024). https://doi.org/10.1038/s41467-023-43650-z

[8] Horner, L., Gehring, R. & Lindel, H. PHOSPHORORGANISCHE VERBINDUNGEN 97: Die Diphenylphosphinyl- und die Diphenylthiophosphinylgruppe als selektive Schutzgruppe für die Mercaptofunktion. Nucleophile Ablösung der Thioloestergruppe aus Thiophosphin-, Thiophosphon-und Thiophosphorsäure-S-estern durch nicht solvatisierte Fluoridionen. *Phosphorus and Sulfur and the Related Elements* **11**, 349-356 (1981). https://doi.org/10.1080/03086648108077434

[9] Murav'ev, I. V.; Fedorovich, I. S. Arylation of the acid halides of di- and triphosphoric acid esters. *Zhurnal Obshchei Khimii* **46**, 789-91 (1976).

[10] Yamamoto, Y. *et al.* Photoinduced Syntheses and Reactivities of Phosphorus-Containing Interelement Compounds. *The Journal of Organic Chemistry* **85**, 14708-14719 (2020). https://doi.org/10.1021/acs.joc.0c02014

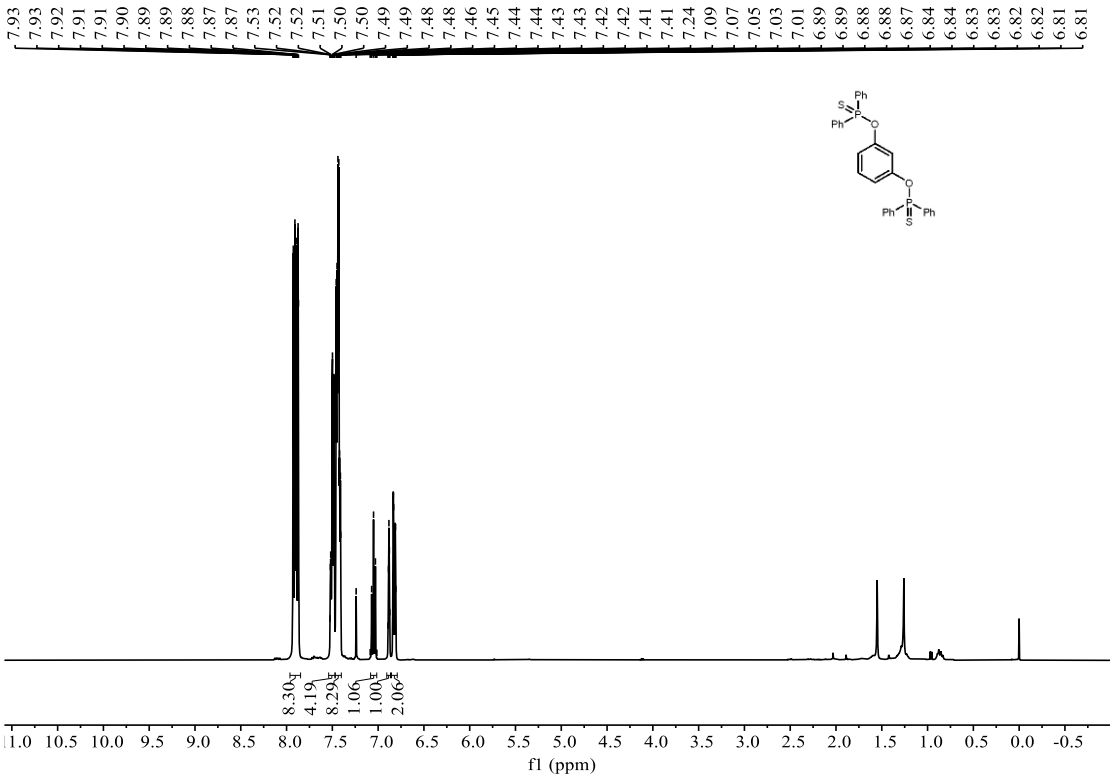
[11] Liu, K. *et al.* Tunable synthesis of chalcophosphinic amides and tertiary phosphinates using tert-butyl N,N-dialkylperoxyamidate. *Organic Chemistry Frontiers* **8**, 4860-4864 (2021). https://doi.org/10.1039/D1QO00542A

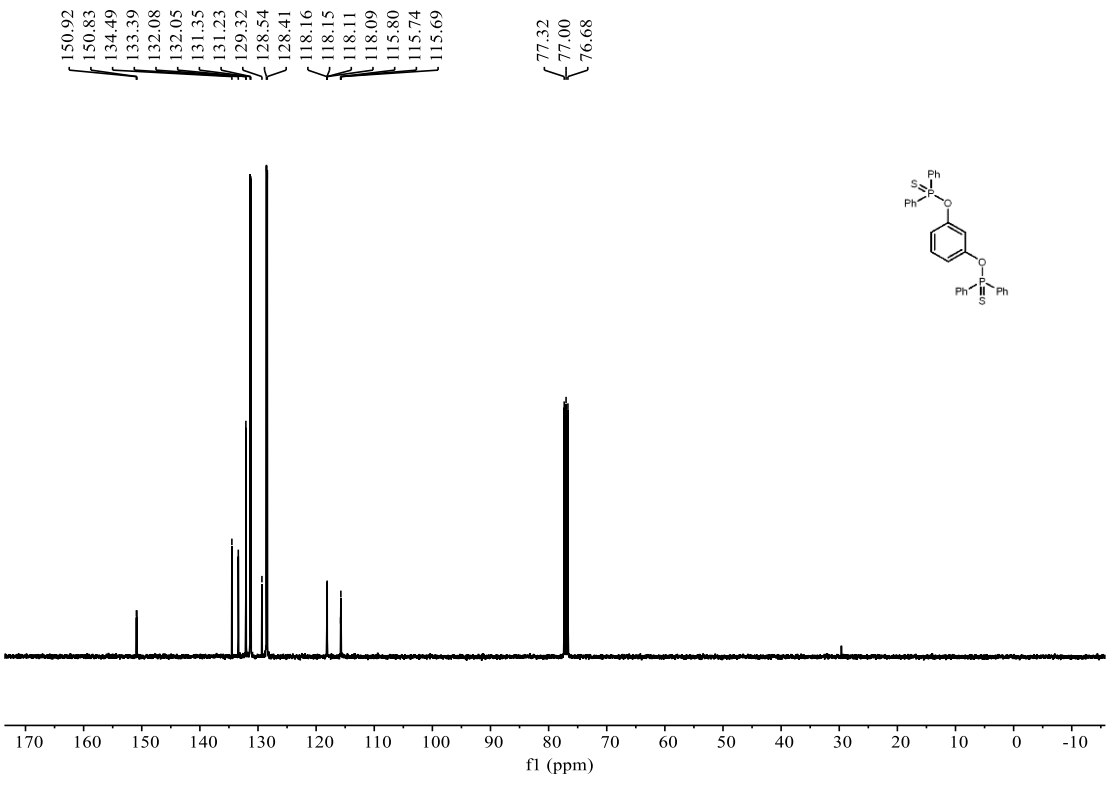
[12] Yoshida, S., Igawa, K. & Tomooka, K. Nucleophilic Substitution Reaction at the Nitrogen of Arylsulfonamides with Phosphide Anion. *Journal of the American Chemical Society* **134**, 19358-19361 (2012). https://doi.org/10.1021/ja309642r

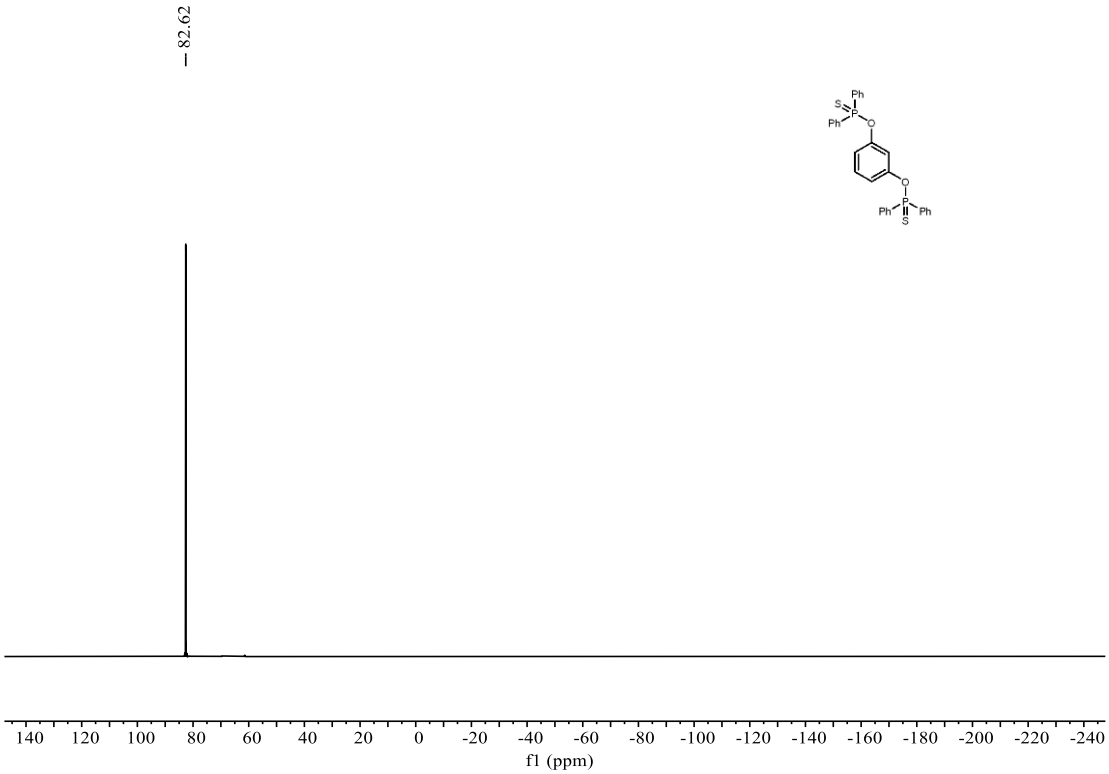
[13] Xia, G.-D., Liu, Z.-K., Zhao, Y.-L., Jia, F.-C. & Hu, X.-Q. Radical Phosphorylation of Aliphatic C–H Bonds via Iron Photocatalysis. *Organic Letters* **25**, 5279-5284 (2023). https://doi.org/10.1021/acs.orglett.3c01824

12. Spectral Data

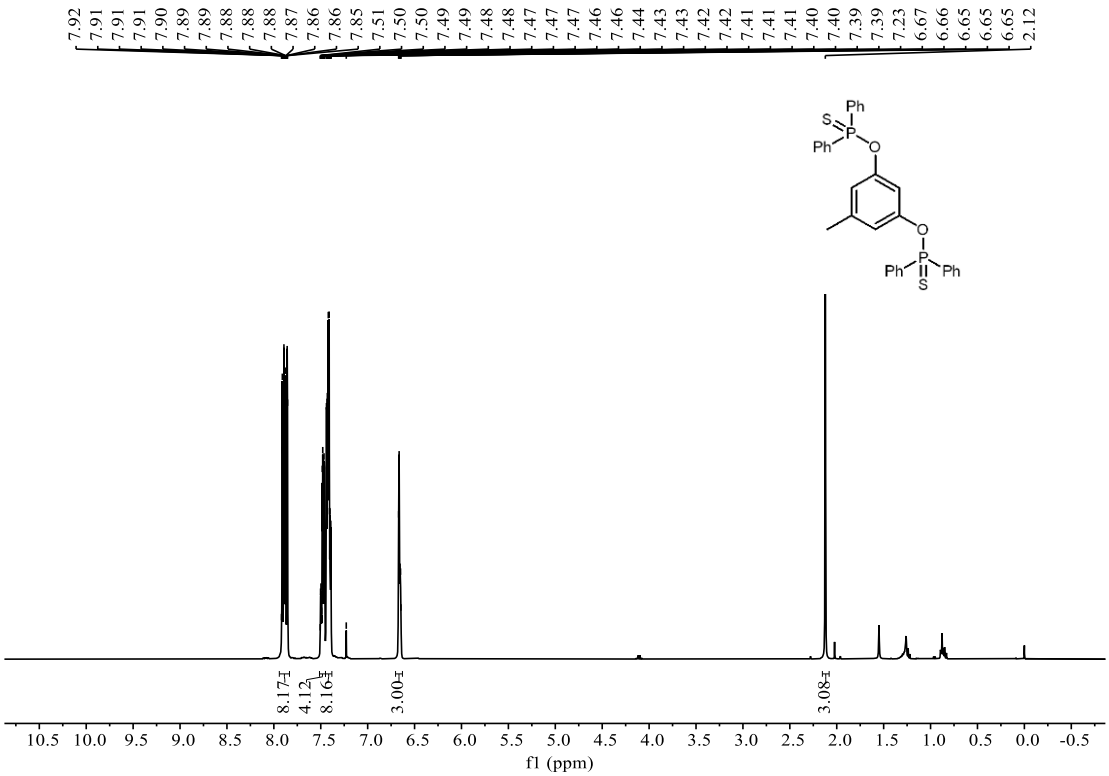
O-(3-((diphenylphosphorothioyl)thio)phenyl) diphenylphosphinothioate (**3a'**)

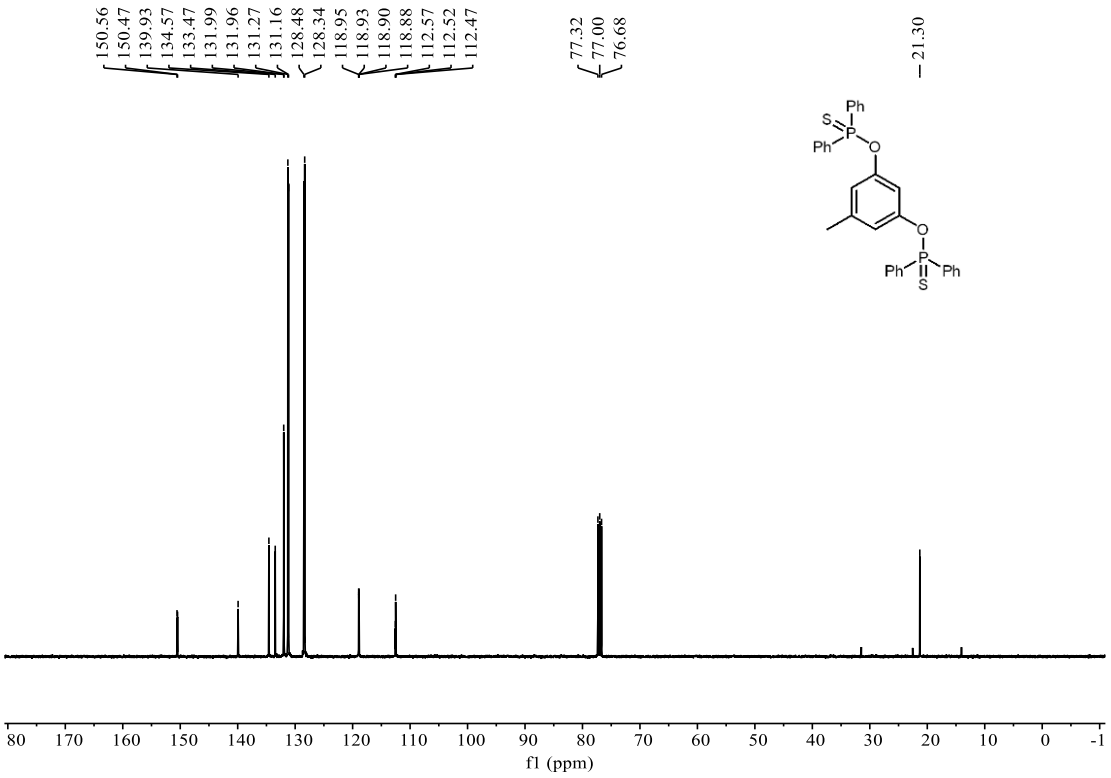


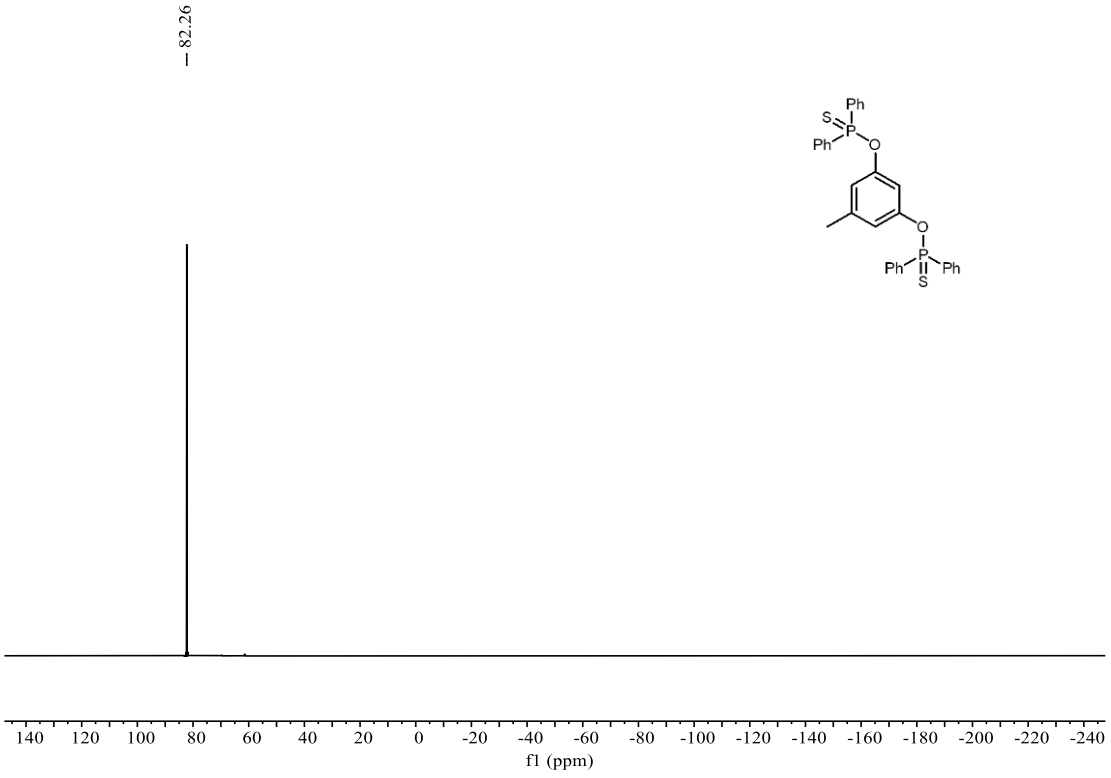




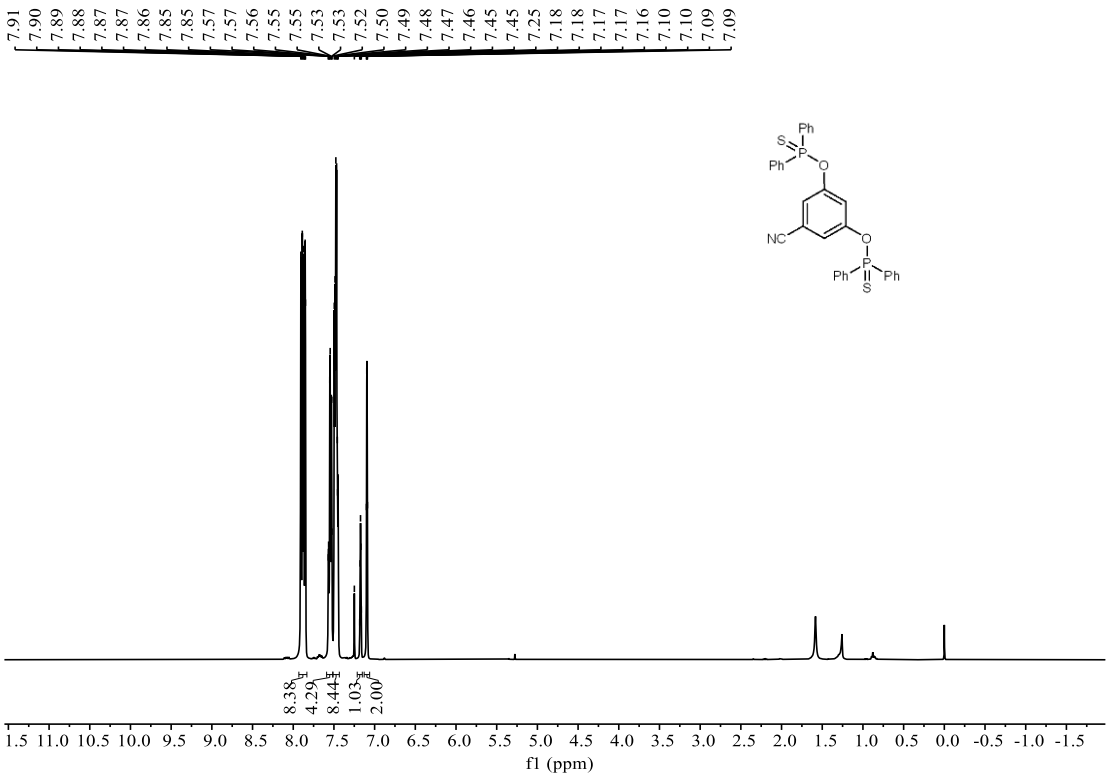
O,O'-(5-methyl-1,3-phenylene) bis(diphenylphosphinothioate) (**3b'**)

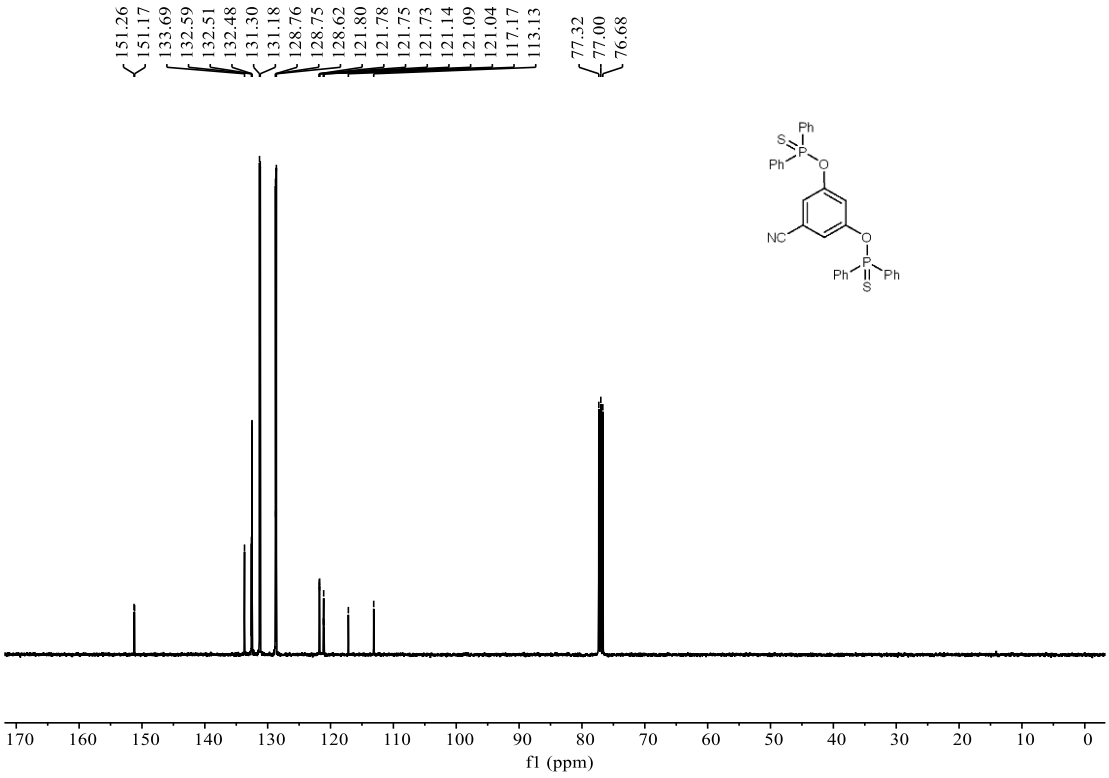


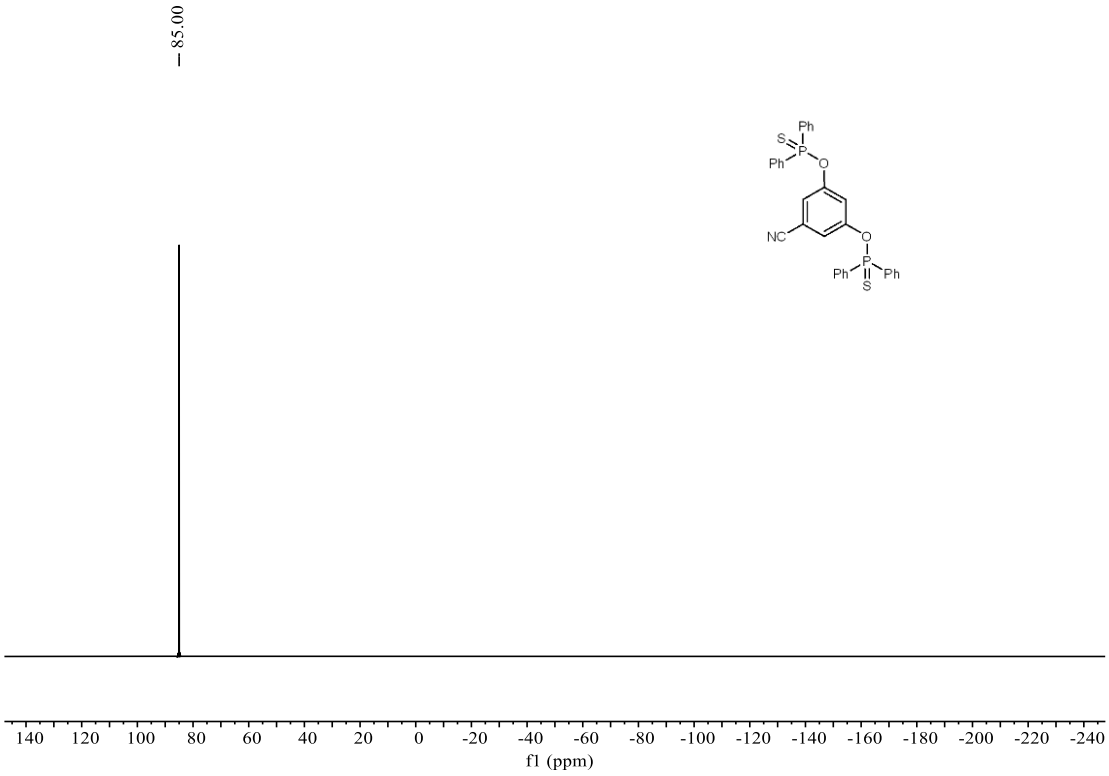

150.56
150.47
139.93
134.57
133.47
131.99
131.96
131.27
131.16
128.48
128.34
118.95
118.93
118.90
118.88
112.57
112.52
112.47
77.32
77.00
76.68
21.30
Ph
S
P
Ph
O
O
P
Ph
Ph
S
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


82.26
Ph
S
P
Ph
O
O
P
Ph
Ph
S
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

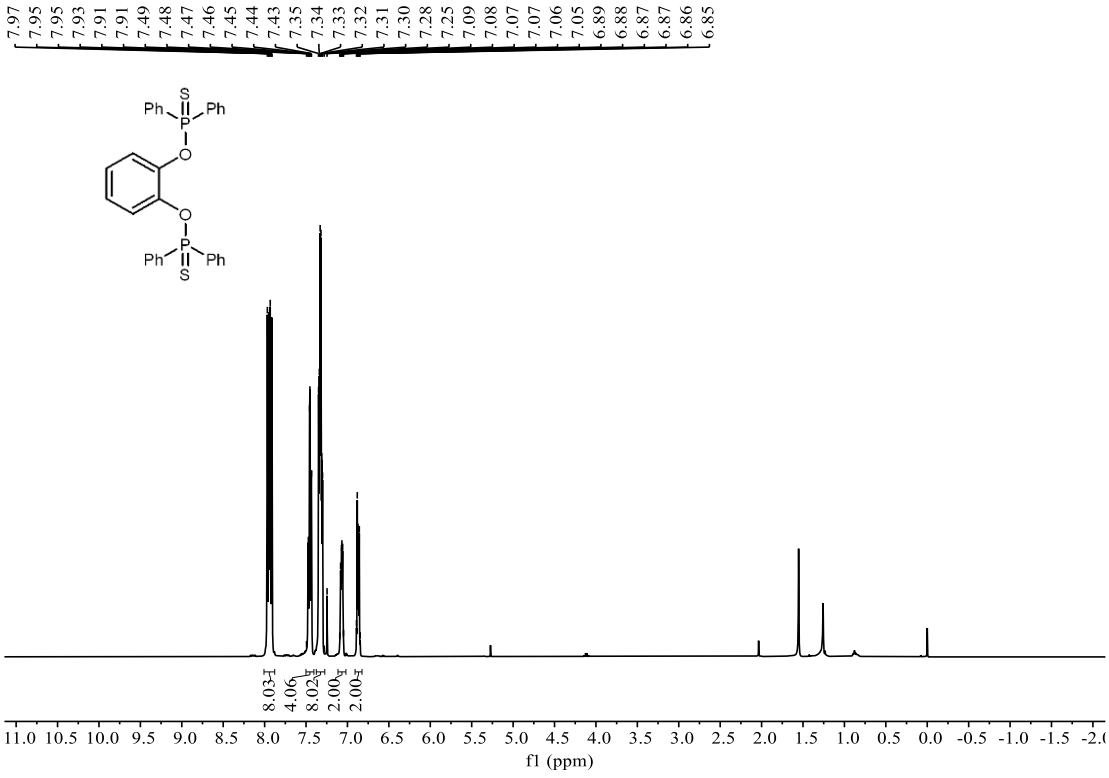
O,O'-(5-cyano-1,3-phenylene) bis(diphenylphosphinothioate) (**3c'**)

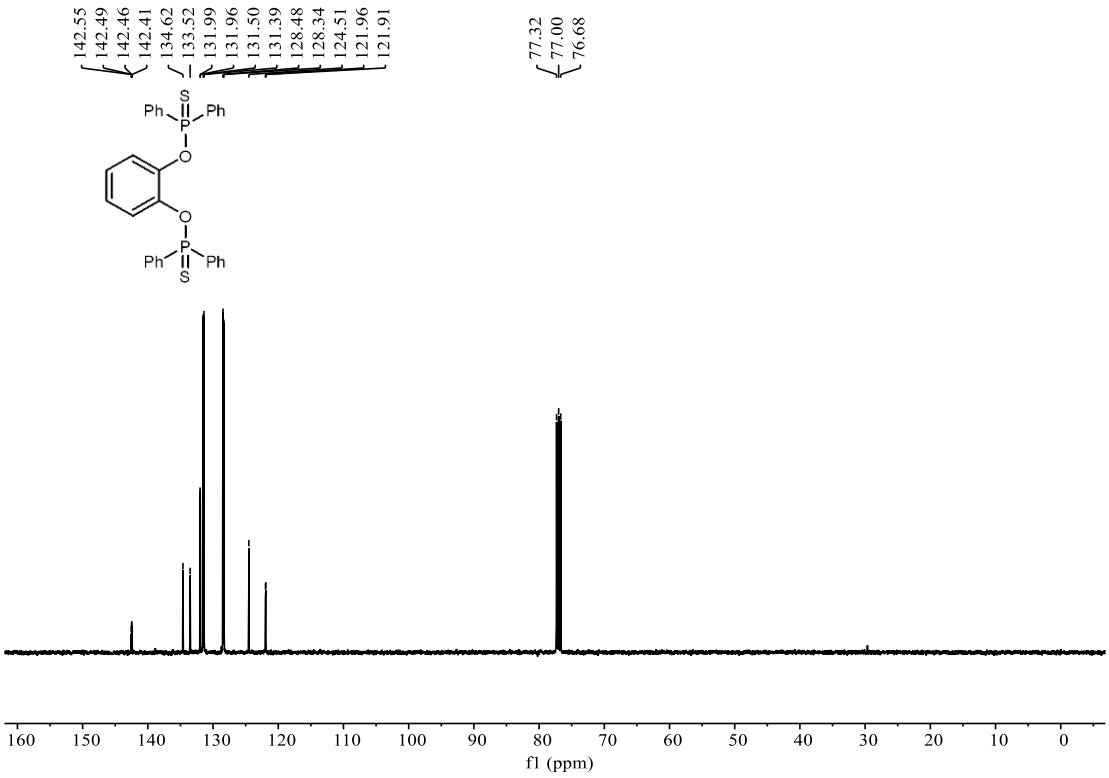


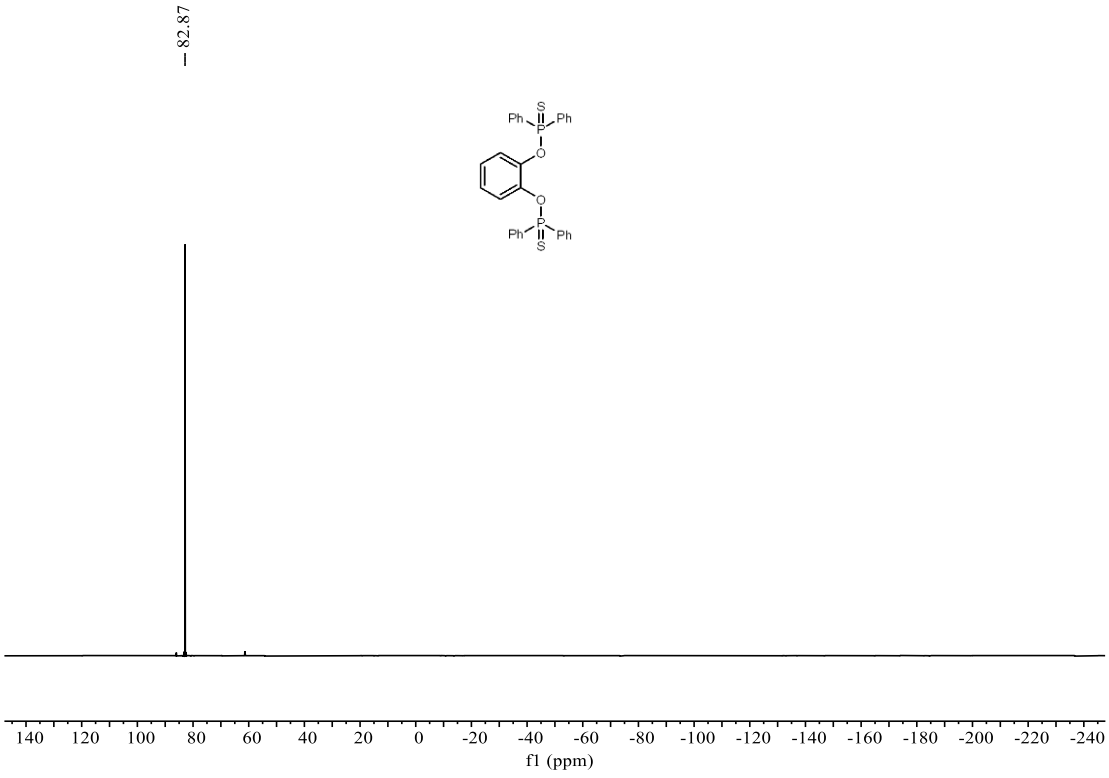




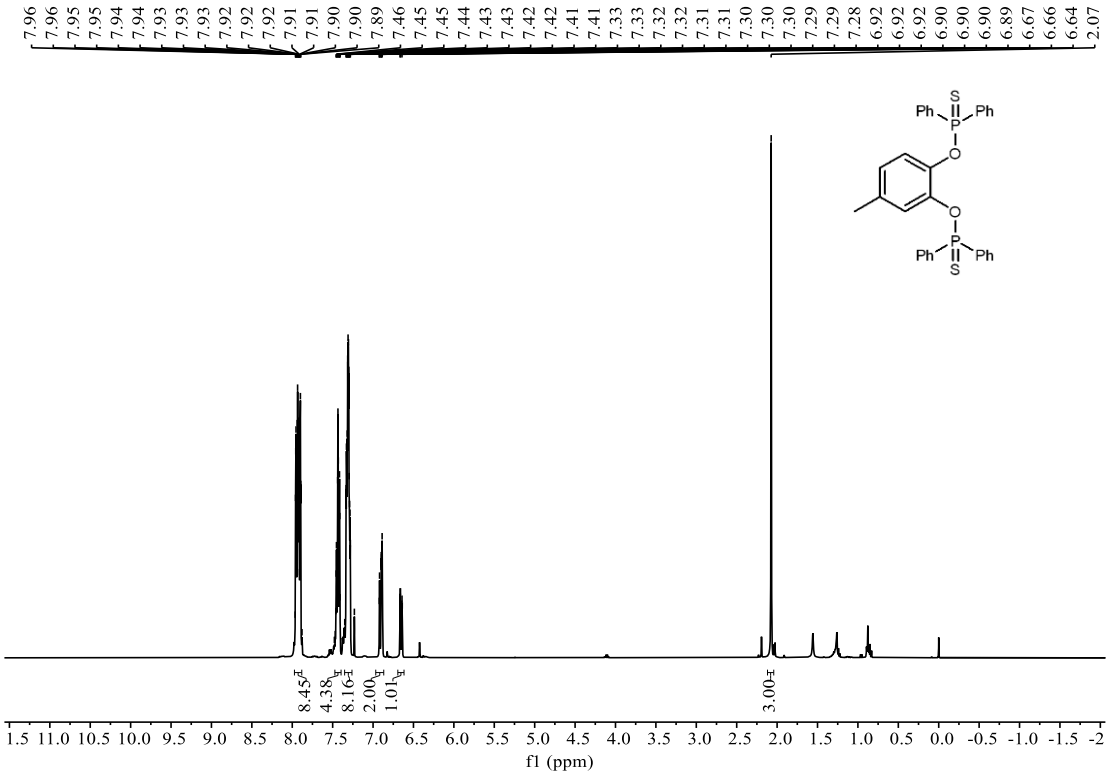
O,O'-(1,2-phenylene) bis(diphenylphosphinothioate) (**3d'**)

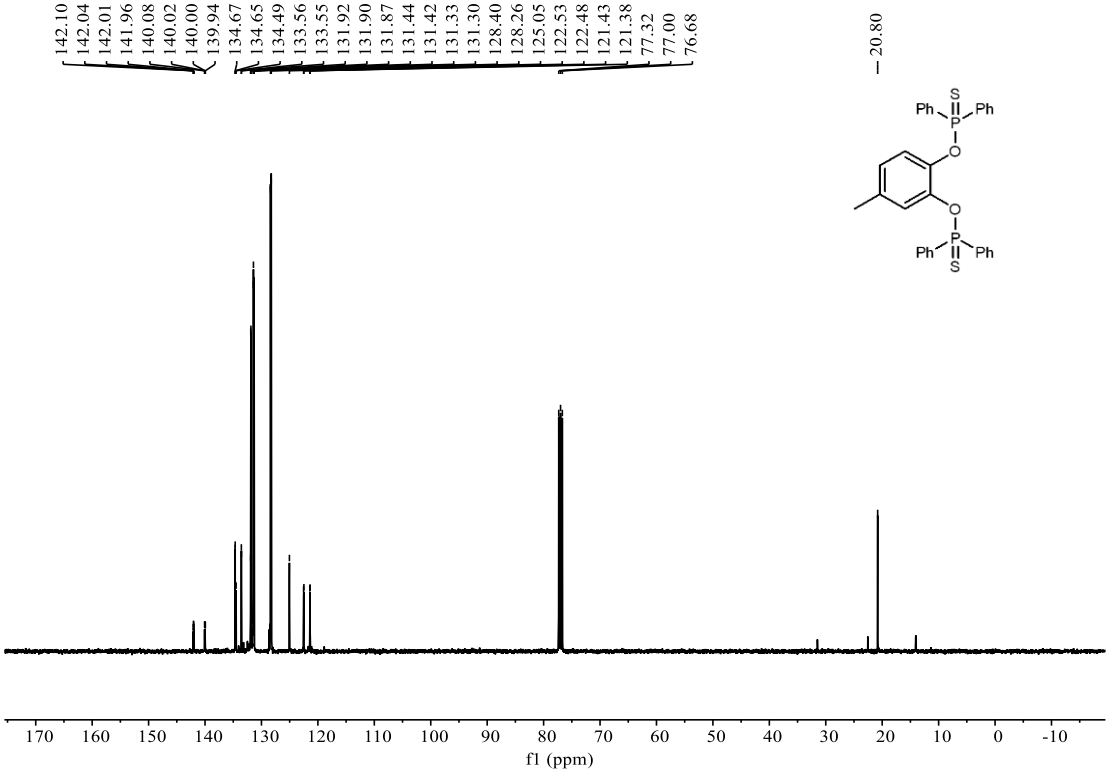


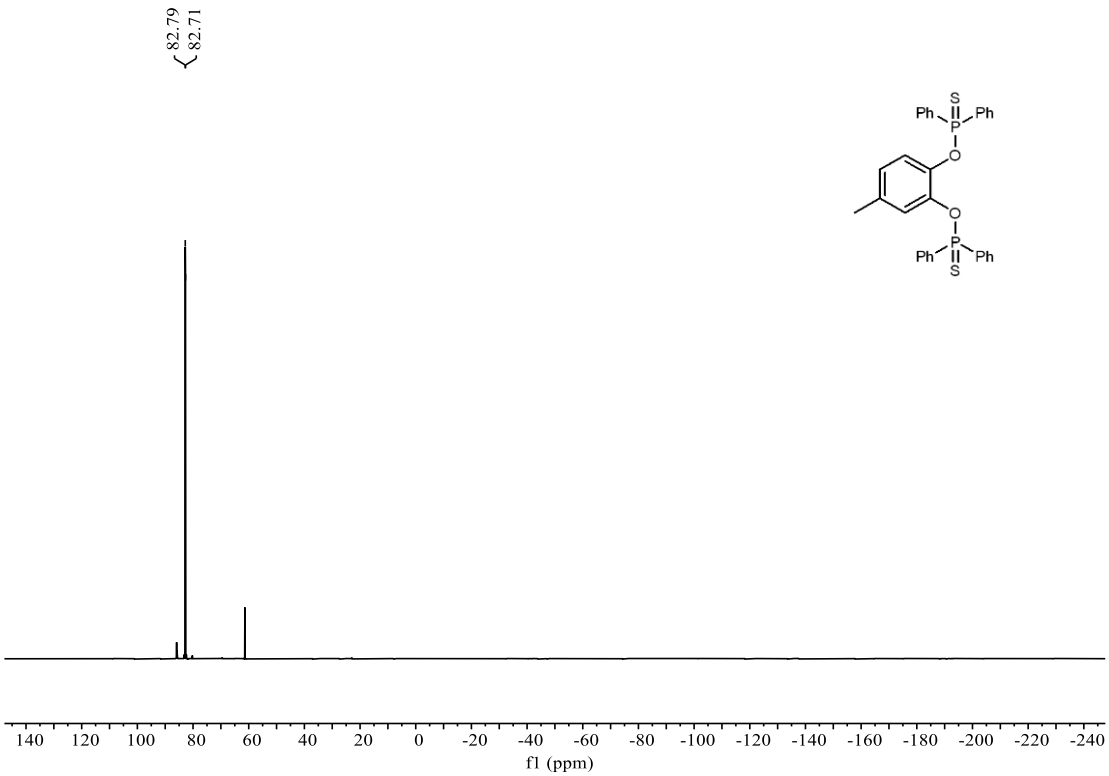

142.55
142.49
142.46
142.41
134.62
133.52
131.99
131.96
131.50
131.39
128.48
128.34
124.51
121.96
121.91
77.32
77.00
76.68
Ph
Ph
Ph
Ph
S
S
O
O
P
P
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


82.87
Ph
Ph
Ph
Ph
S
S
O
O
P
P
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

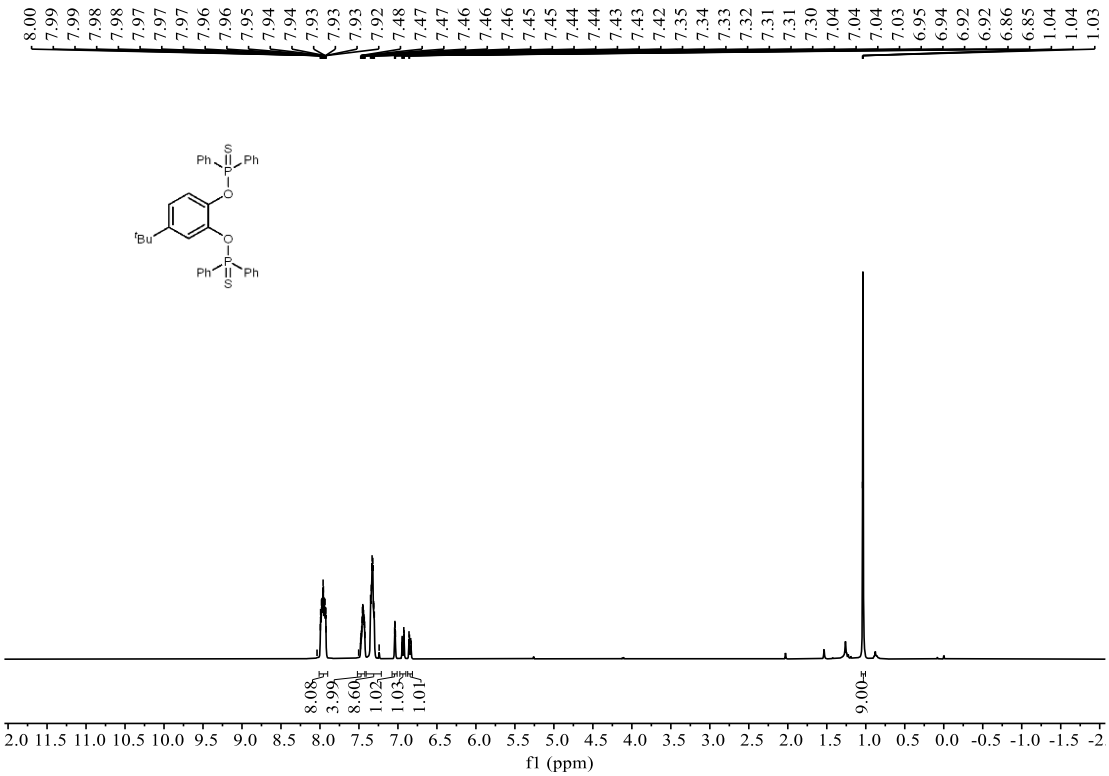
O,O'-(4-methyl-1,2-phenylene) bis(diphenylphosphinothioate) (**3e'**)

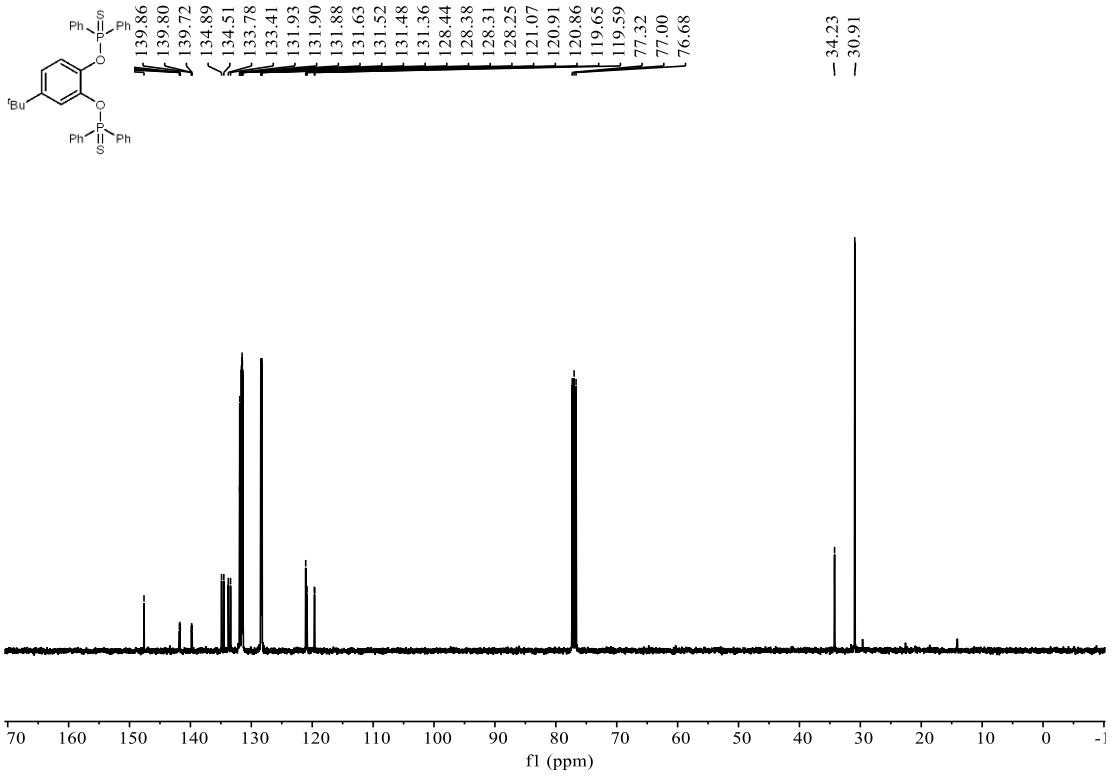


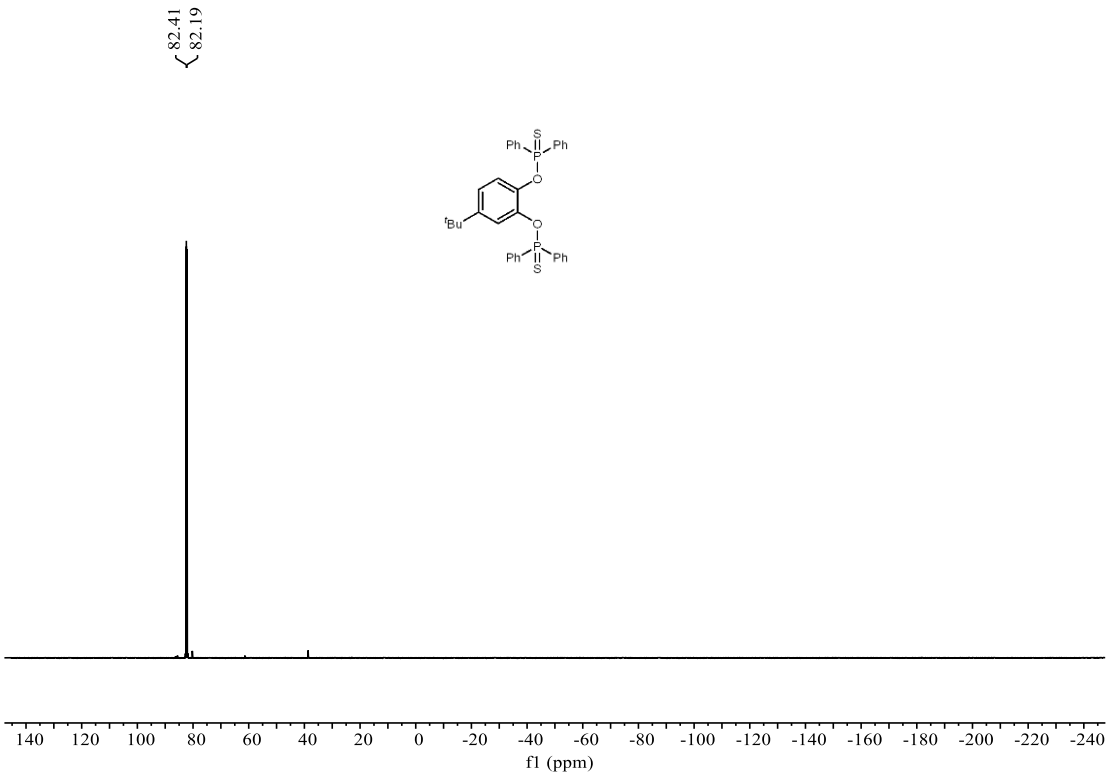




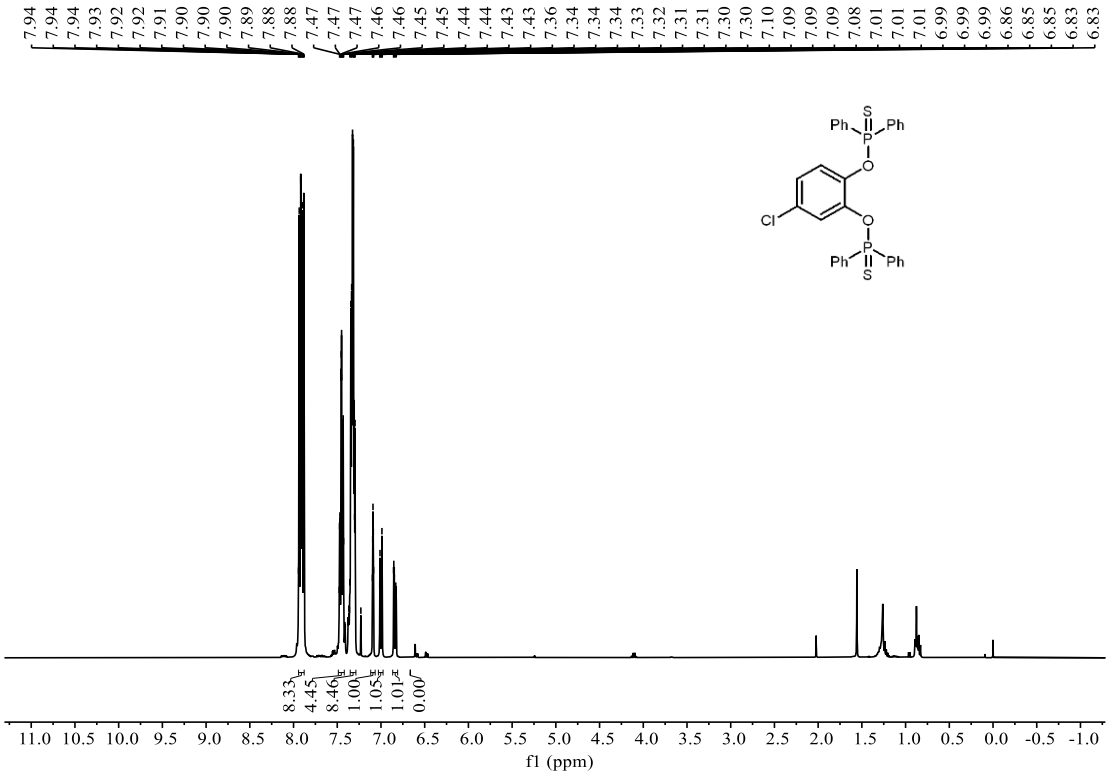
O,O'-(4-(tert-butyl)-1,2-phenylene) bis(diphenylphosphinothioate) (**3f'**)

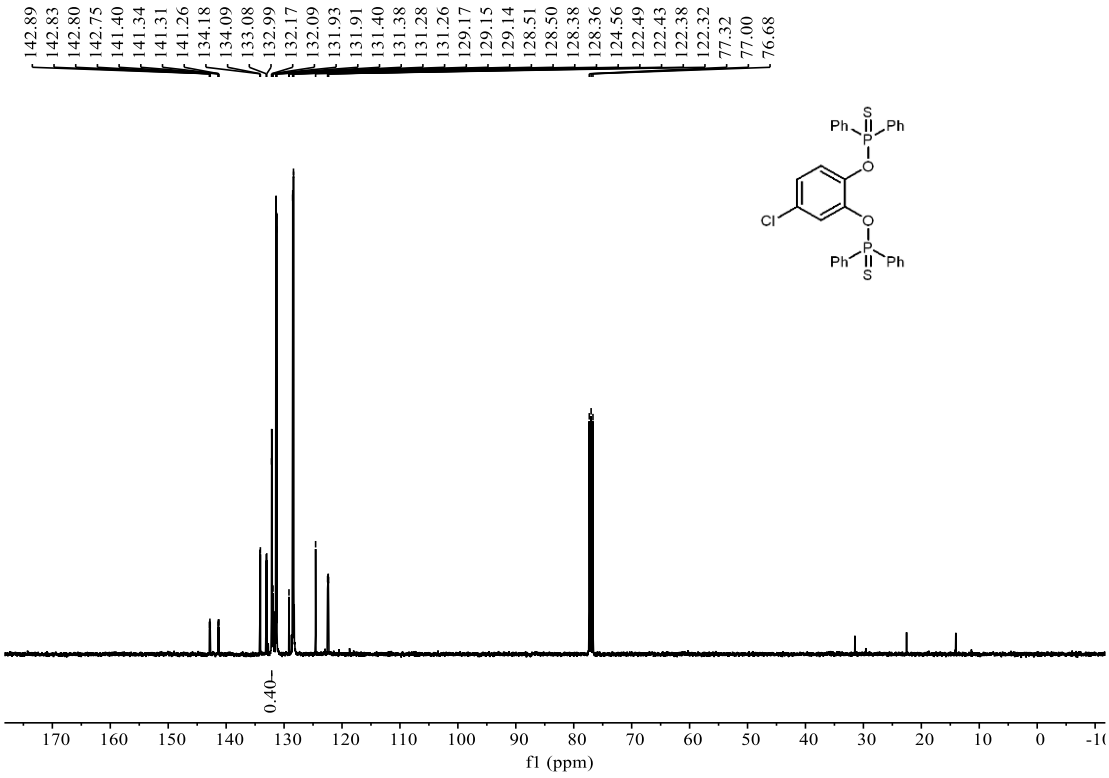


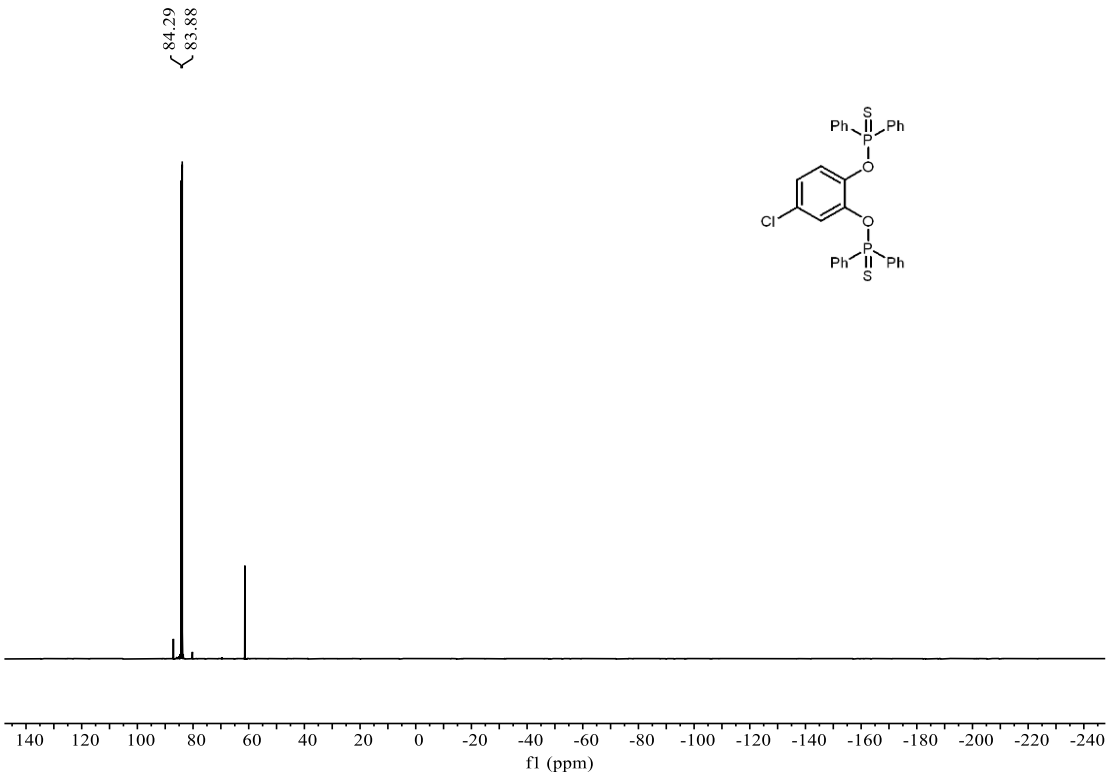

139.86
139.80
139.72
134.89
134.51
133.78
133.41
131.93
131.90
131.88
131.63
131.52
131.48
131.36
128.44
128.38
128.31
128.25
121.07
120.91
120.86
119.65
119.59
77.32
77.00
76.68
34.23
30.91
f1 (ppm)


82.41
82.19
f1 (ppm)

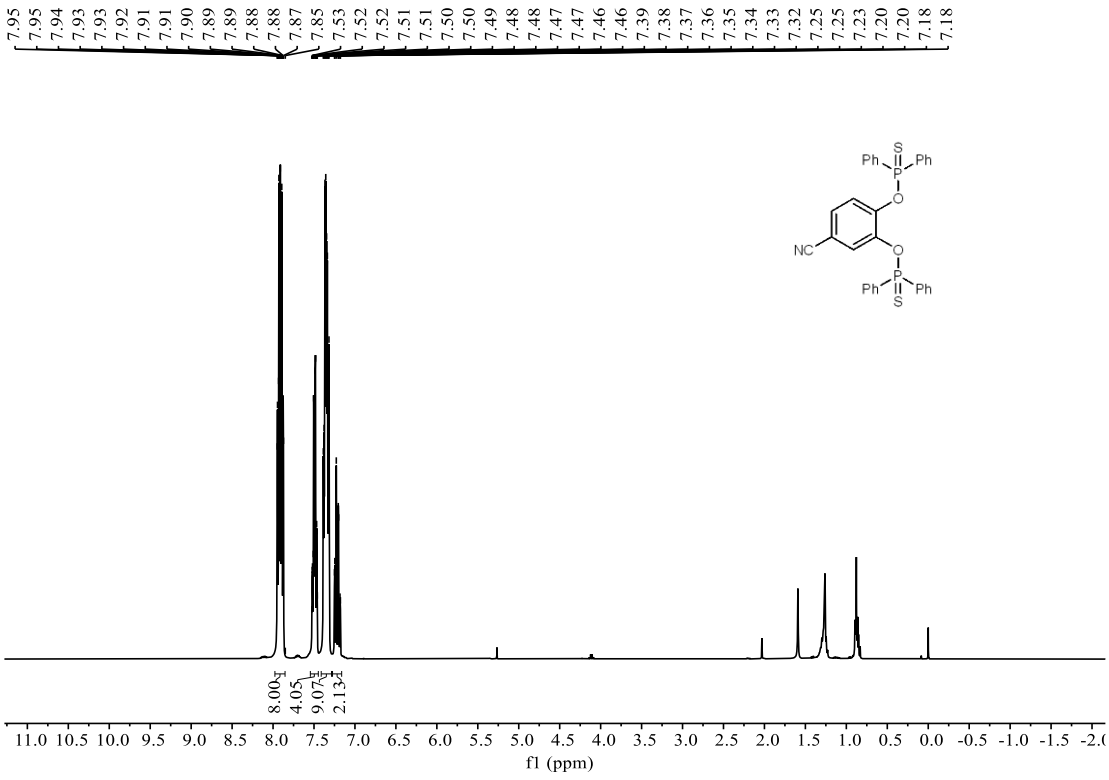
O,O'-(4-chloro-1,2-phenylene) bis(diphenylphosphinothioate) (**3g'**)

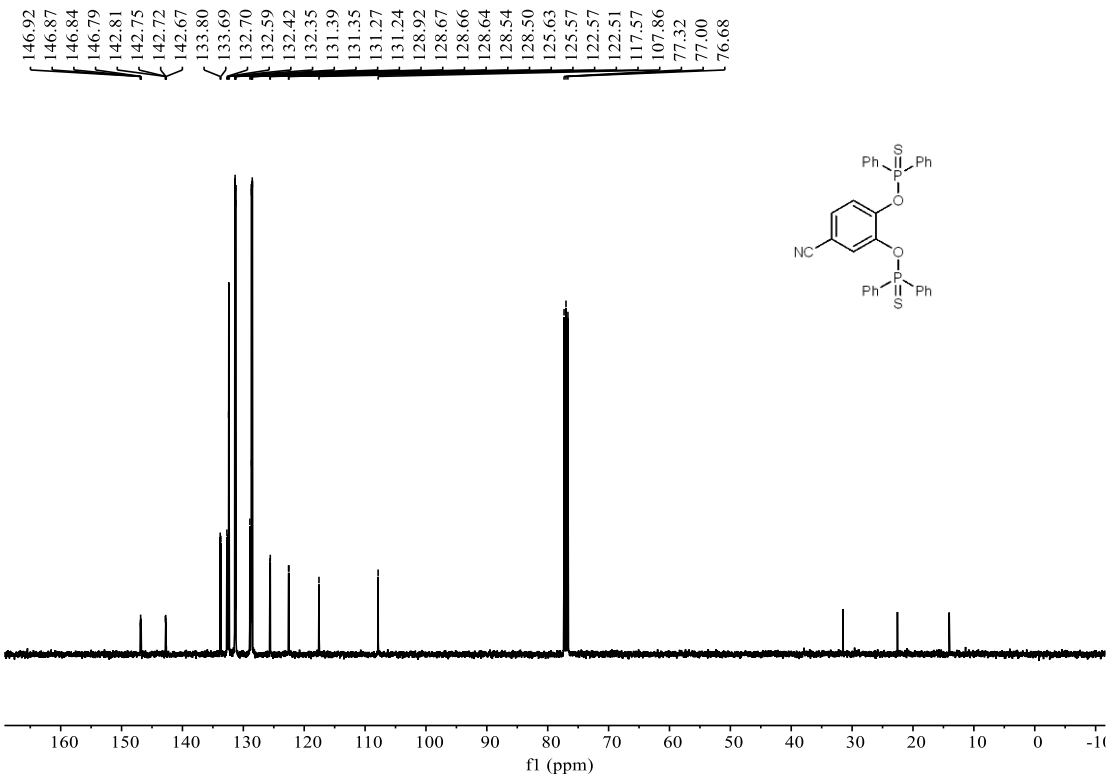


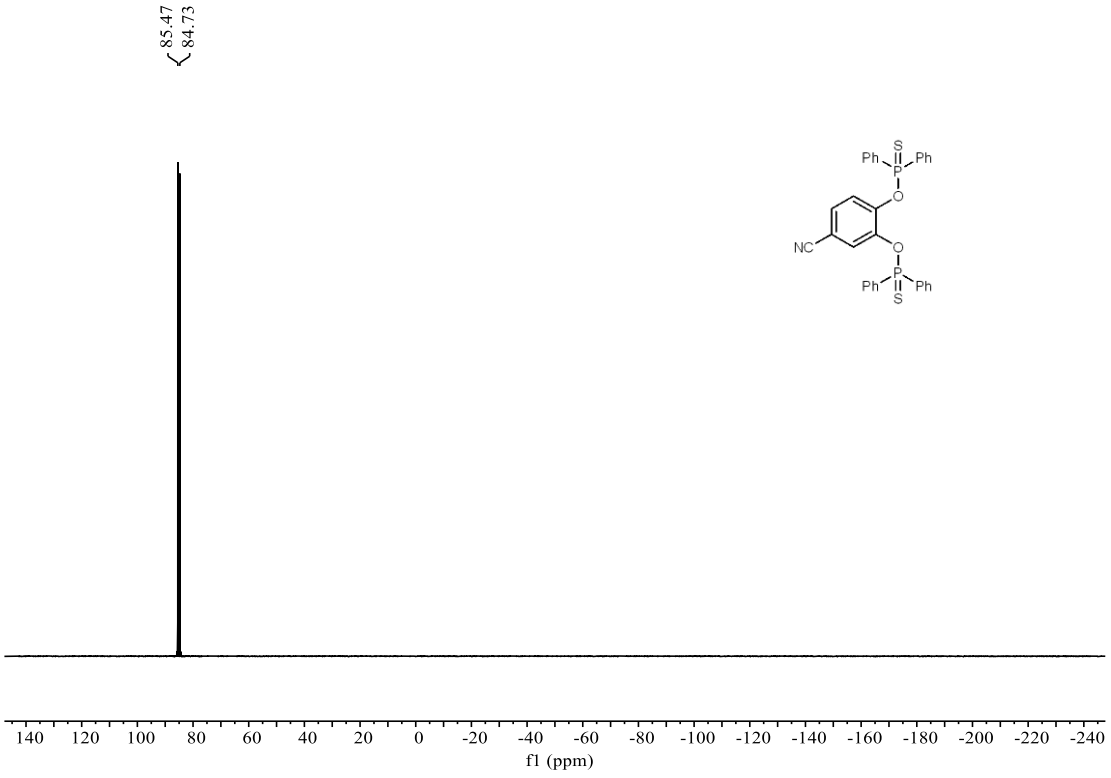




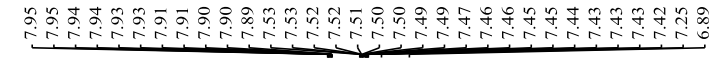
O,O'-(4-cyano-1,2-phenylene) bis(diphenylphosphinothioate) (**3h'**)

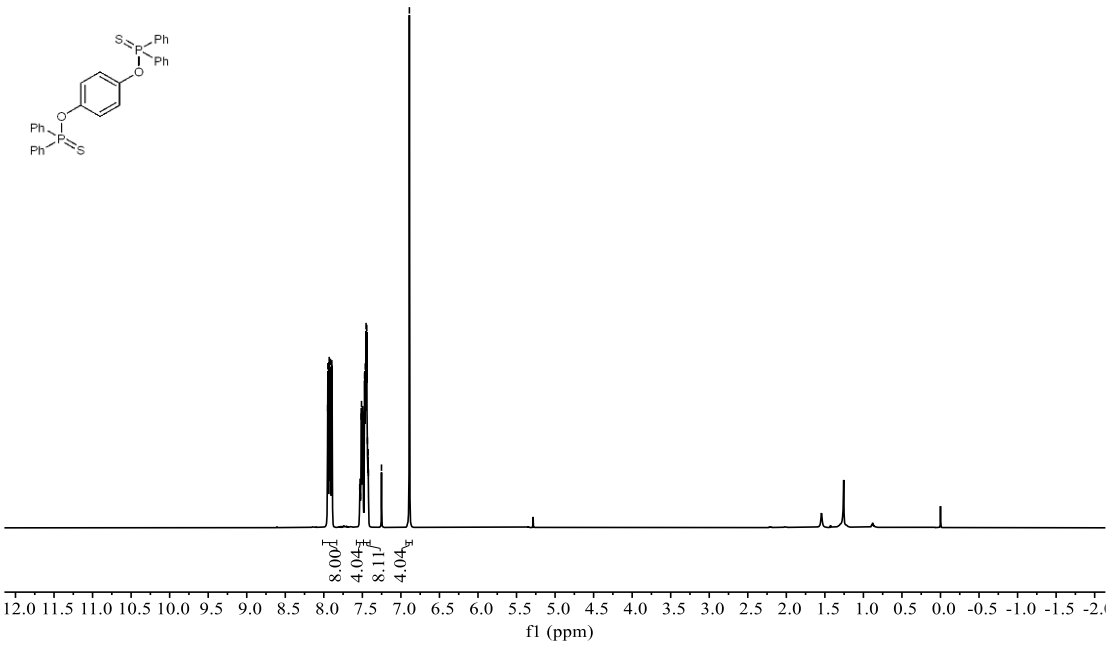


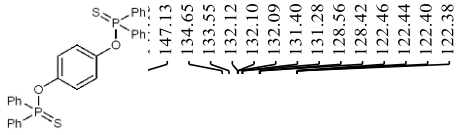

146.92
146.87
146.84
146.79
142.81
142.75
142.72
142.67
133.80
133.69
132.70
132.59
132.42
132.35
131.39
131.35
131.27
131.24
128.92
128.67
128.66
128.64
128.54
128.50
125.63
125.57
122.57
122.51
117.57
107.86
77.32
77.00
76.68
S
Ph
Ph
P
O
NC
O
P
Ph
Ph
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

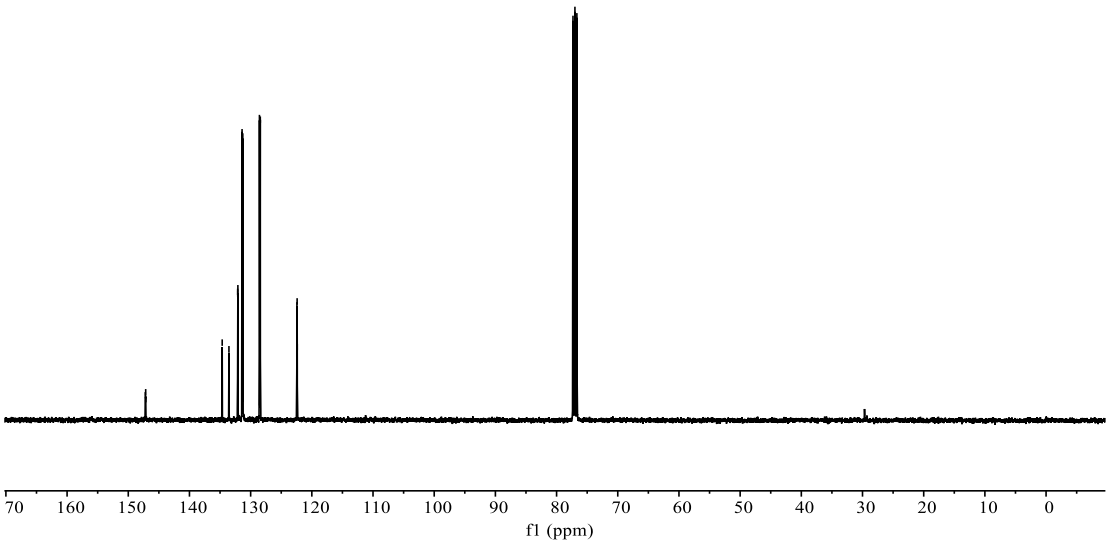

85.47
84.73
S
Ph
Ph
P
O
NC
O
P
Ph
Ph
S
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

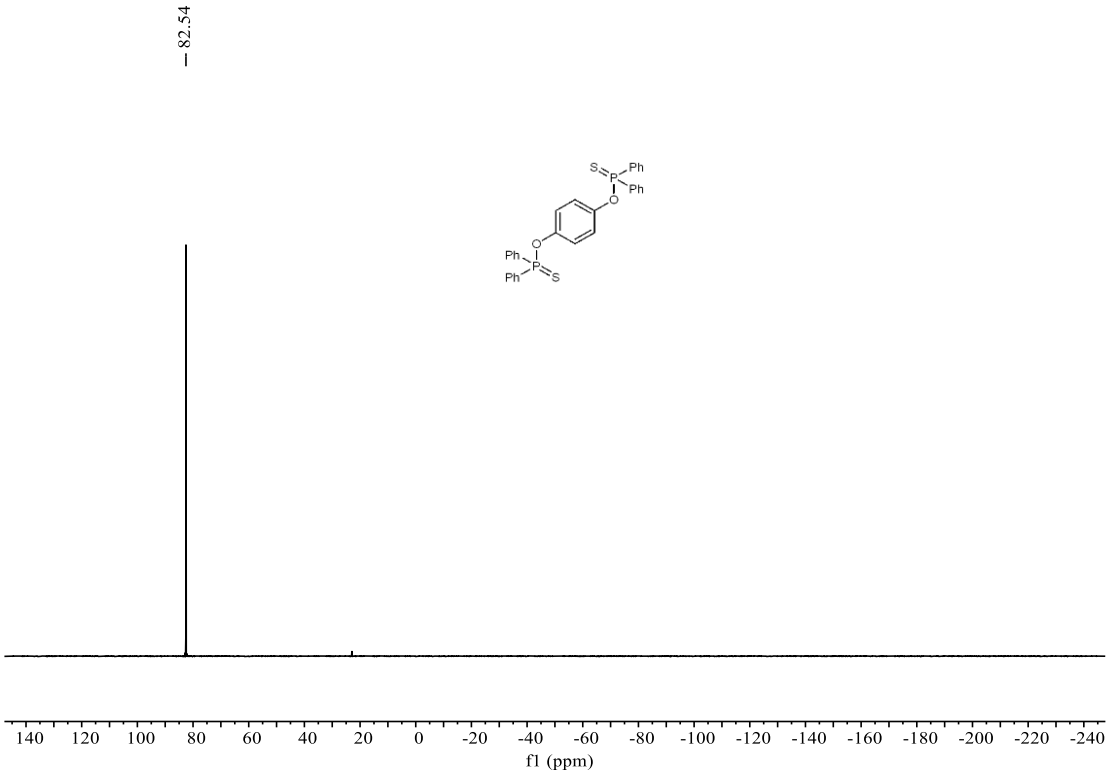
O,O'-(1,4-phenylene) bis(diphenylphosphinothioate) (**3i'**)



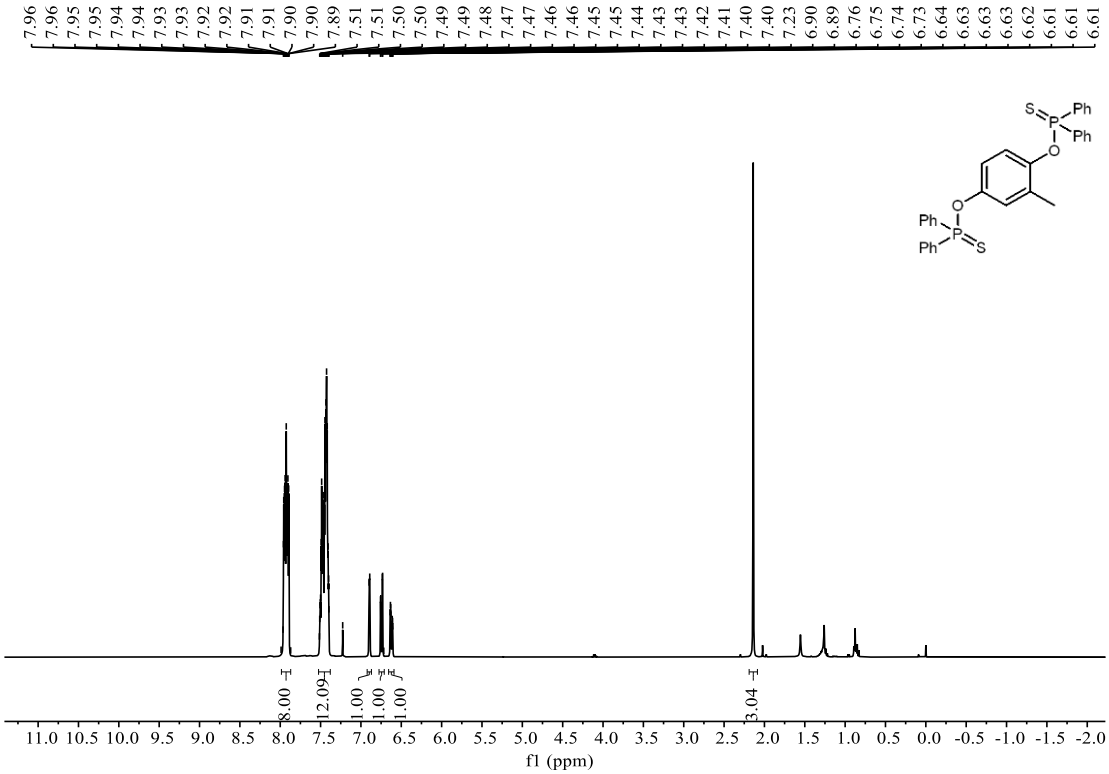


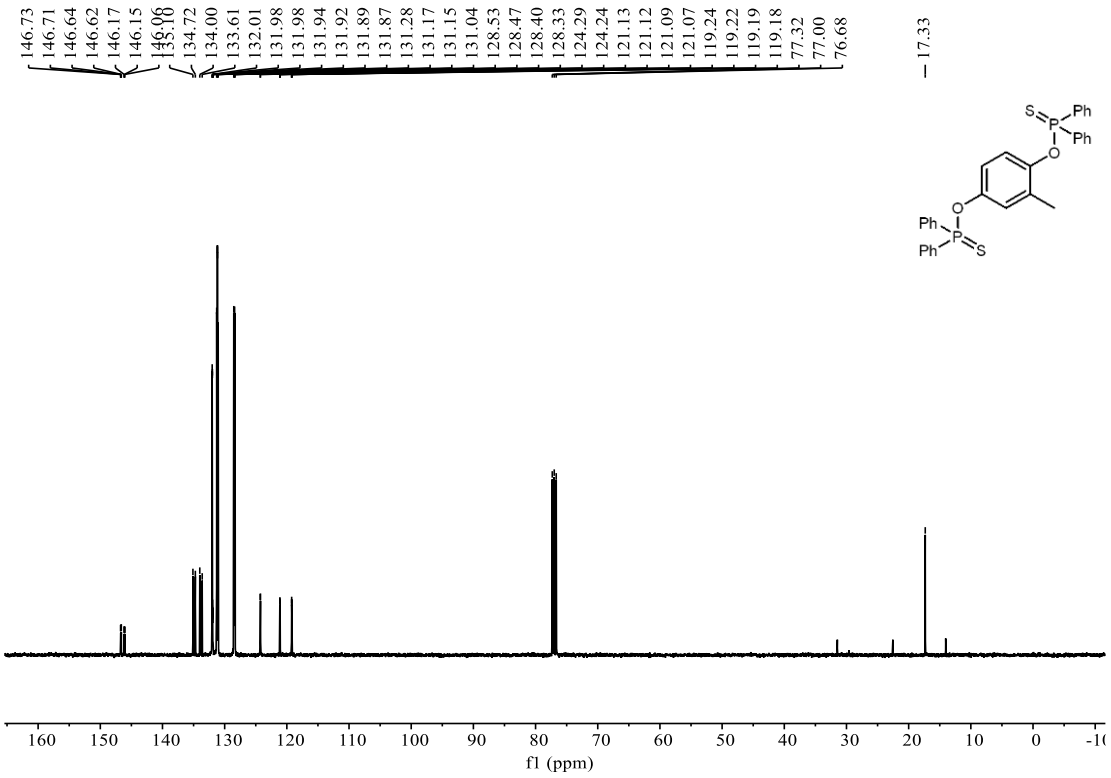


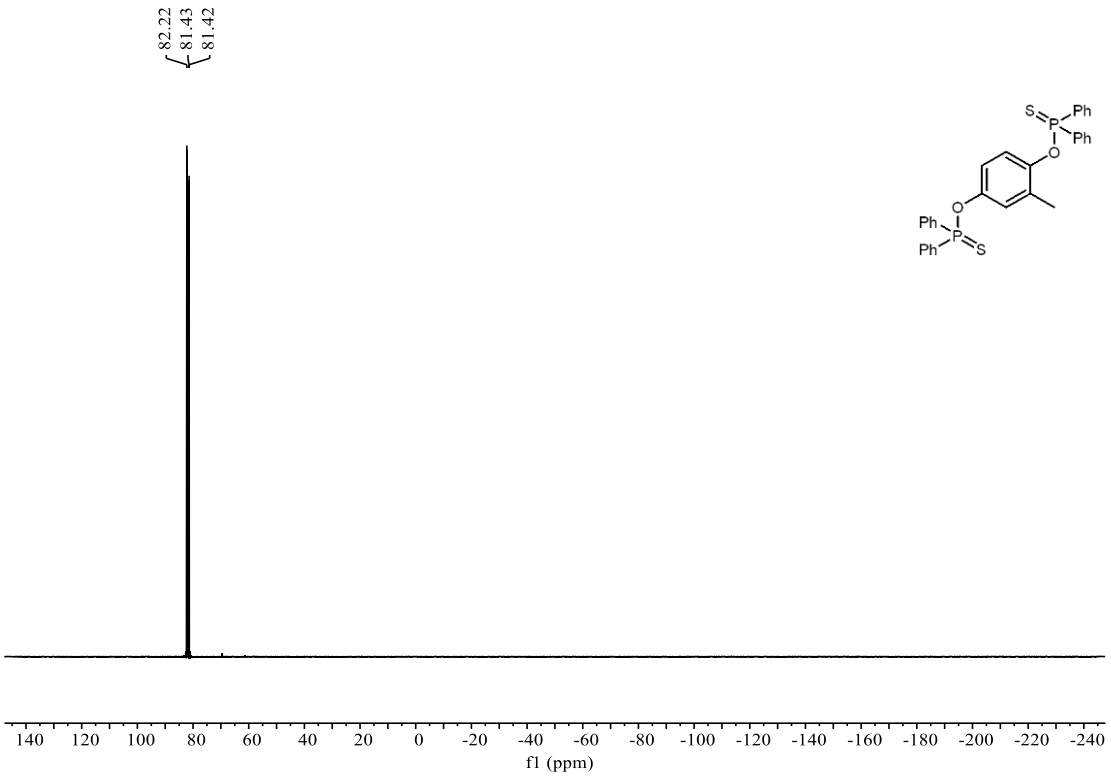




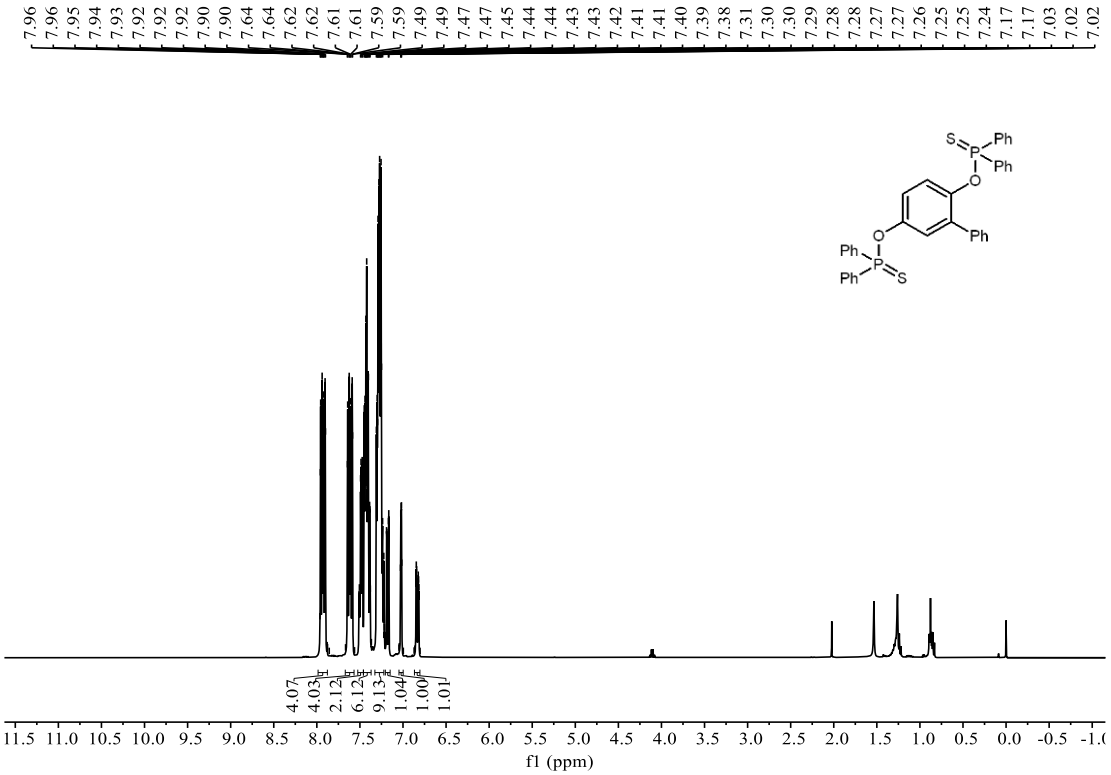
O,O'-(2-methyl-1,4-phenylene) bis(diphenylphosphinothioate) (**3j'**)

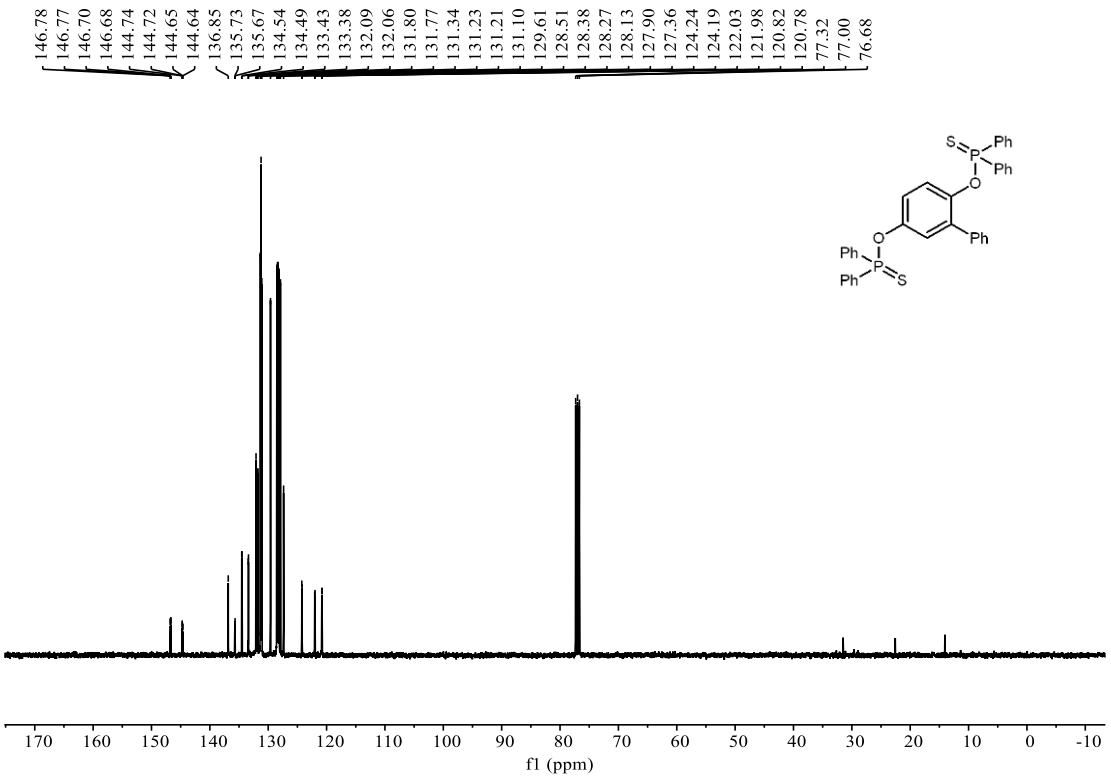


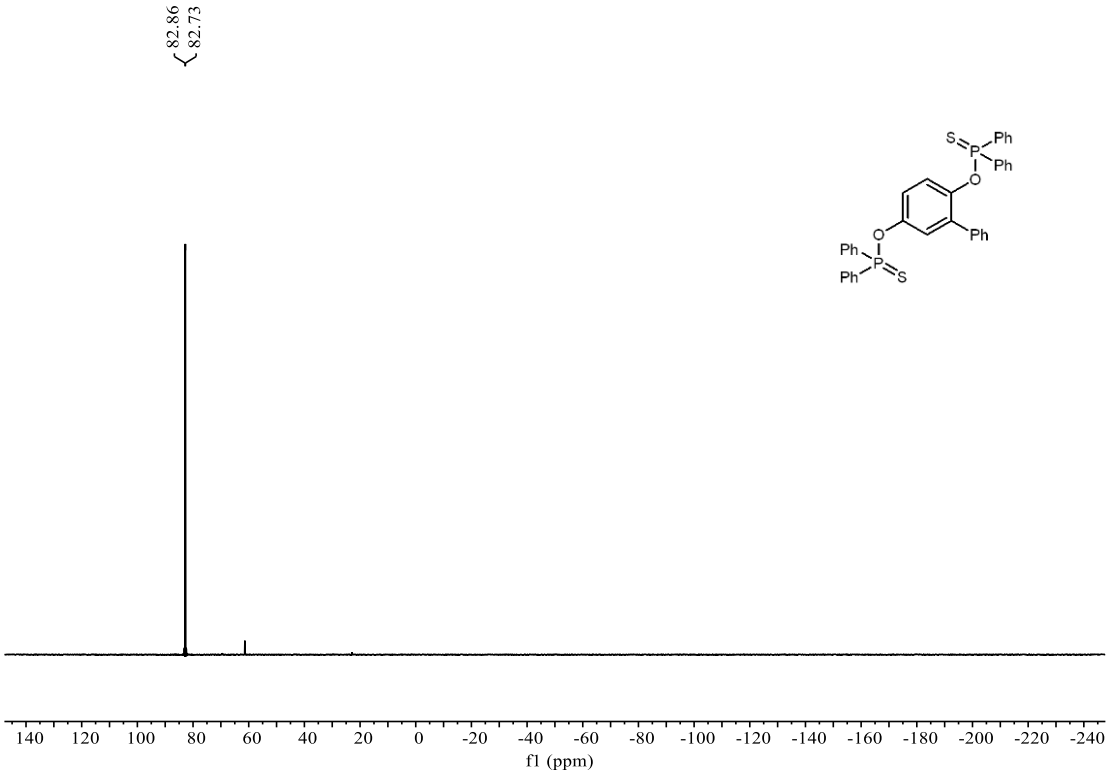

146.73
146.71
146.64
146.62
146.17
146.15
146.06
135.10
134.72
134.00
133.61
132.01
131.98
131.98
131.94
131.92
131.89
131.87
131.28
131.17
131.15
131.04
128.53
128.47
128.40
128.33
124.29
124.24
121.13
121.12
121.09
121.07
119.24
119.22
119.19
119.18
77.32
77.00
76.68
17.33
Ph
S
P
Ph
O
O
Ph
P
Ph
S
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


82.22
81.43
81.42
Ph
S
P
Ph
O
O
Ph
P
Ph
S
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

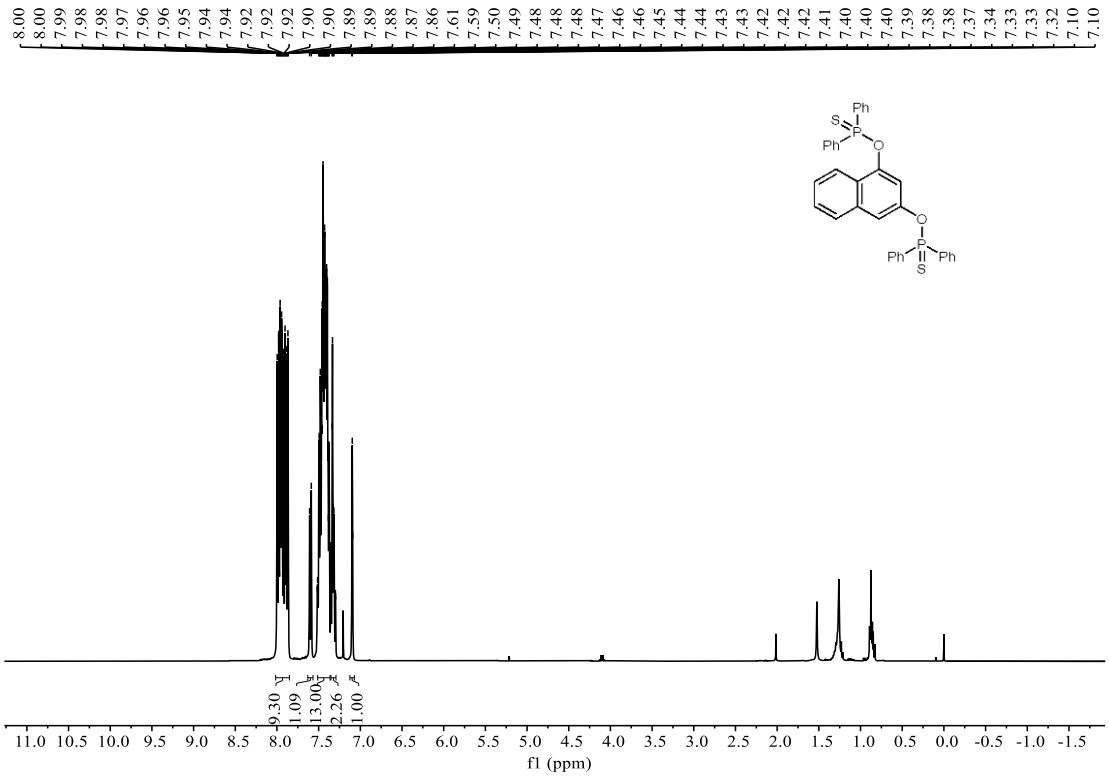
O,O'-([1,1'-biphenyl]-2,5-diyl) bis(diphenylphosphinothioate) (**3k'**)

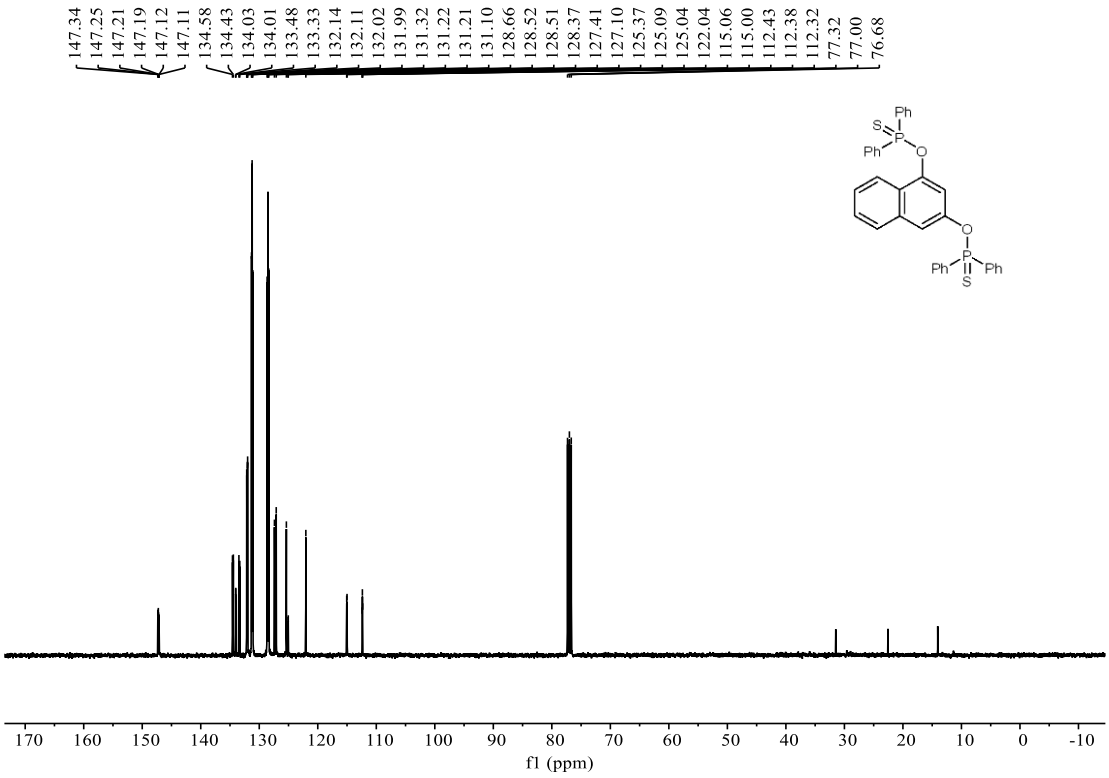


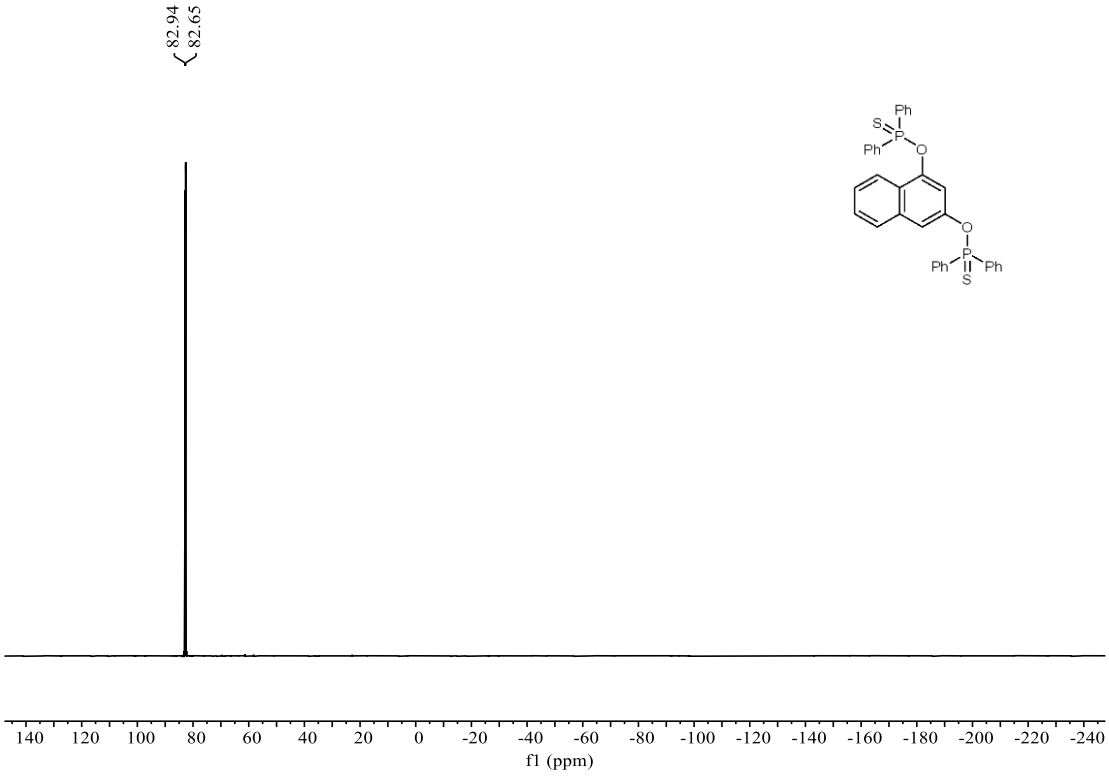




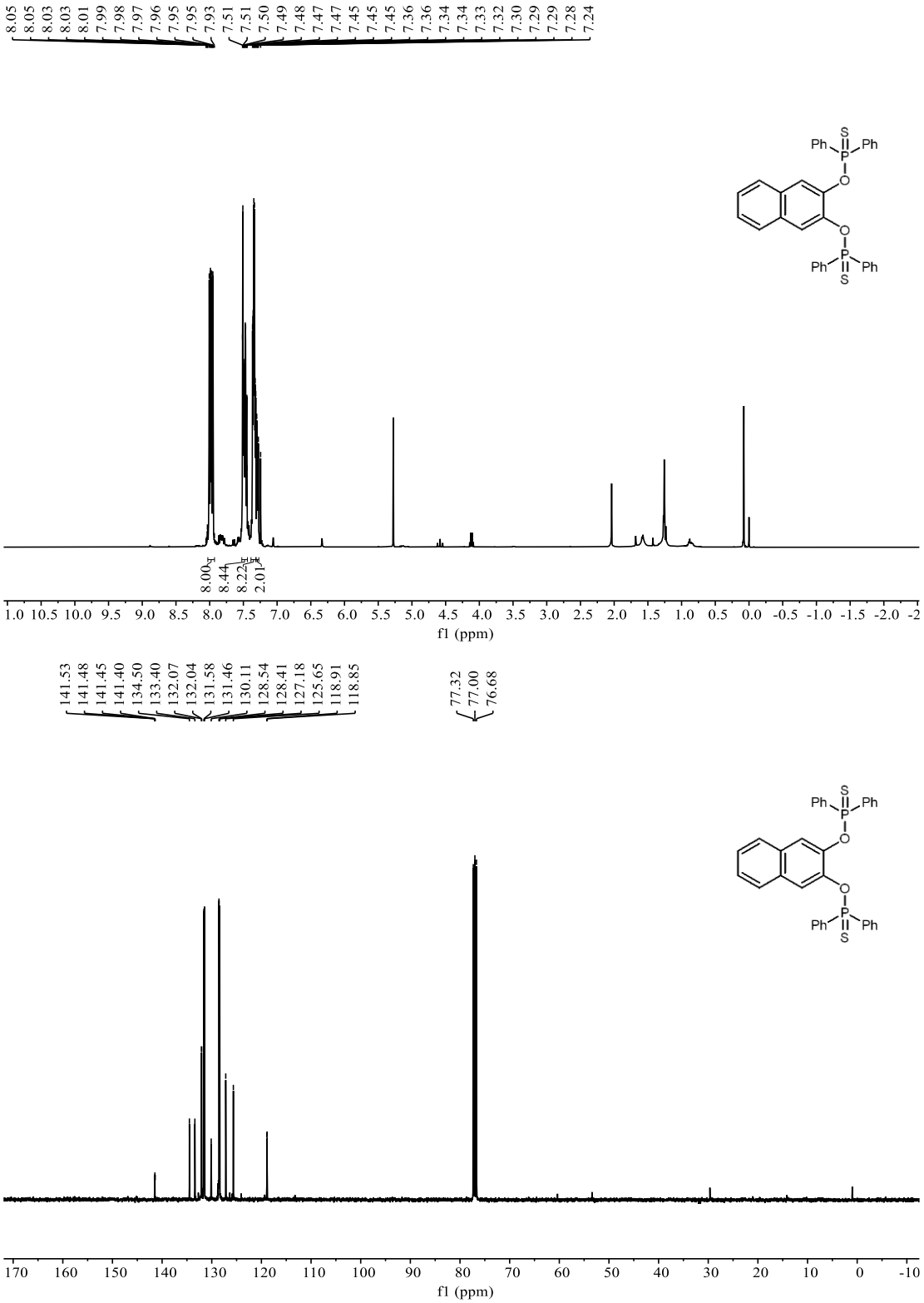
O,O'-(naphthalene-1,3-diyl) bis(diphenylphosphinothioate) (**3l'**)

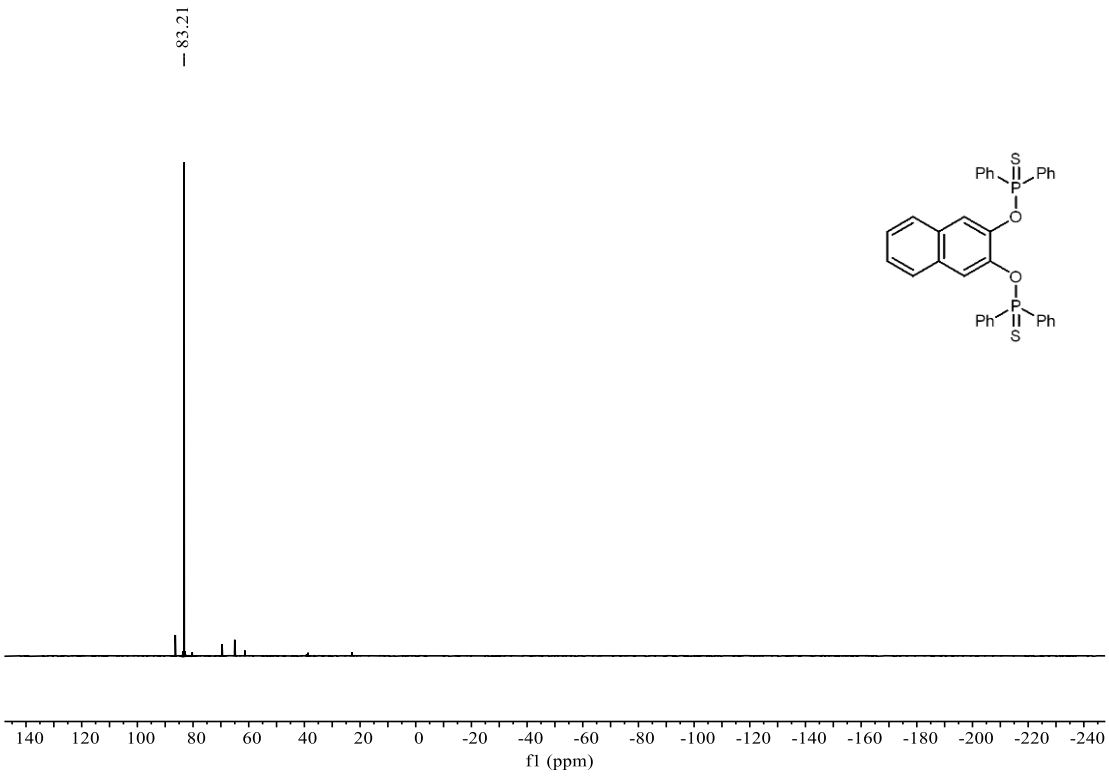



147.34
147.25
147.21
147.19
147.12
147.11
134.58
134.43
134.03
134.01
133.48
133.33
132.14
132.11
132.02
131.99
131.32
131.22
131.21
131.10
128.66
128.52
128.51
128.37
127.41
127.10
125.37
125.09
125.04
122.04
115.06
115.00
112.43
112.38
112.32
77.32
77.00
76.68
Ph
S
P
Ph
O
O
P
Ph
Ph
S
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

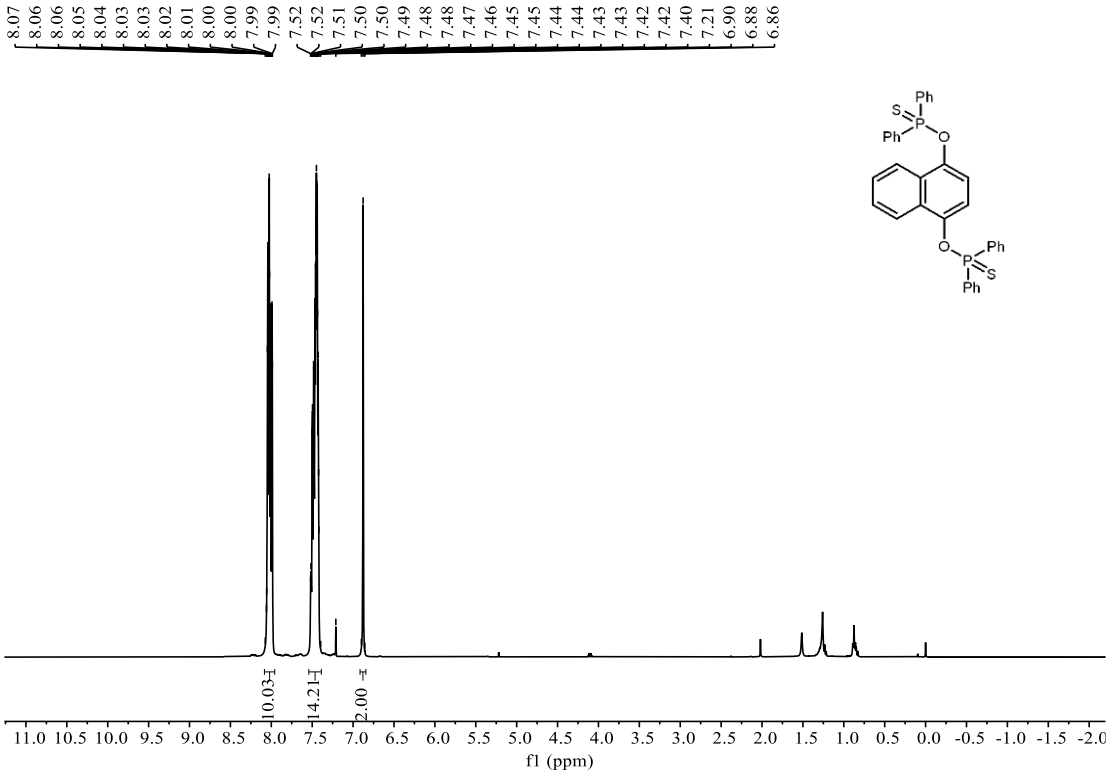

82.94
82.65
Ph
S
P
Ph
O
O
P
Ph
Ph
S
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

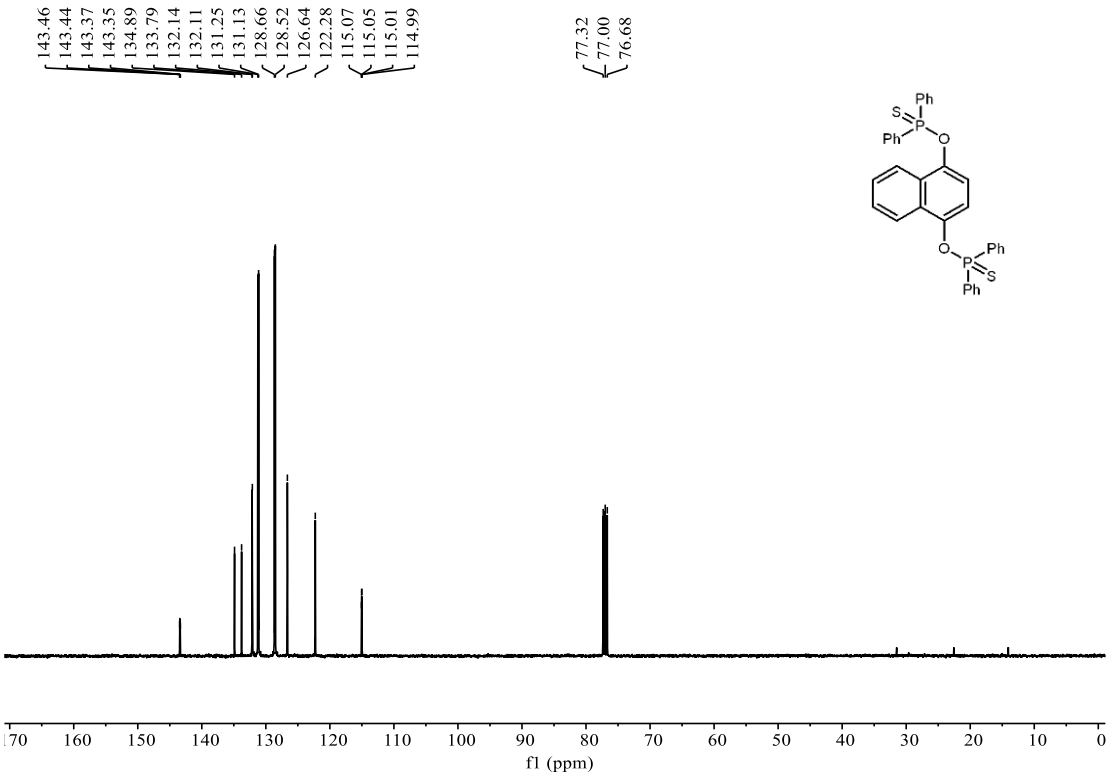
O,O'-(naphthalene-2,3-diyl) bis(diphenylphosphinothioate) (**3m'**)

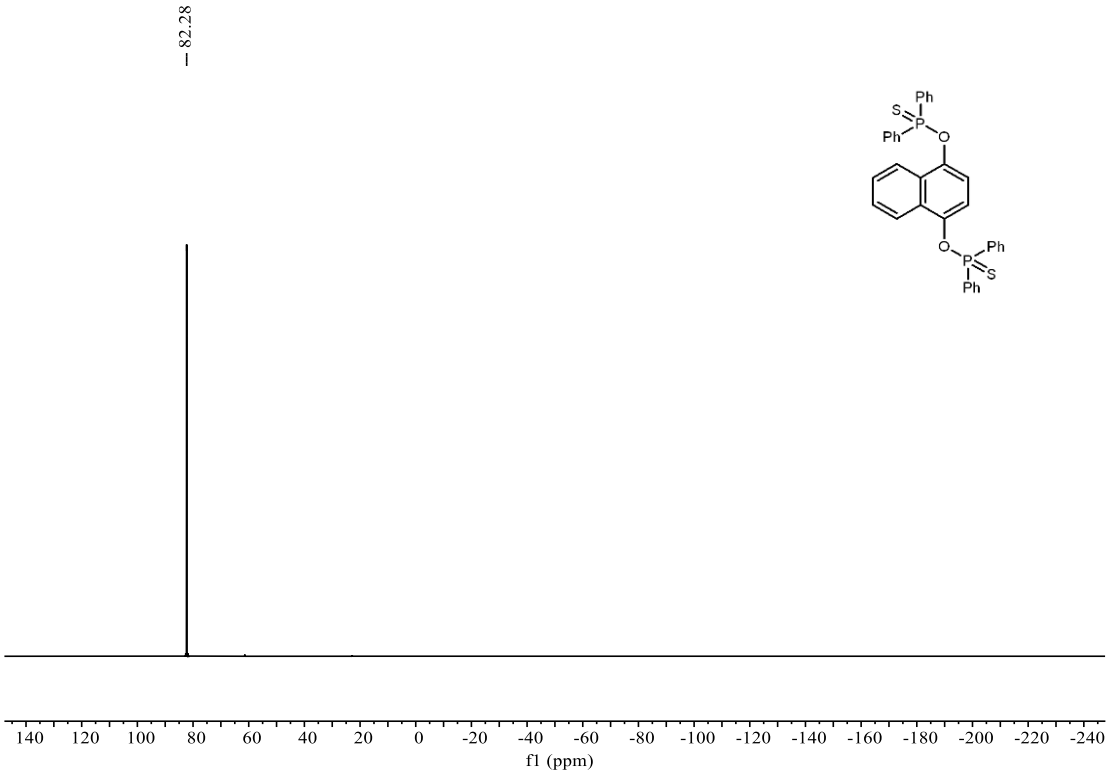




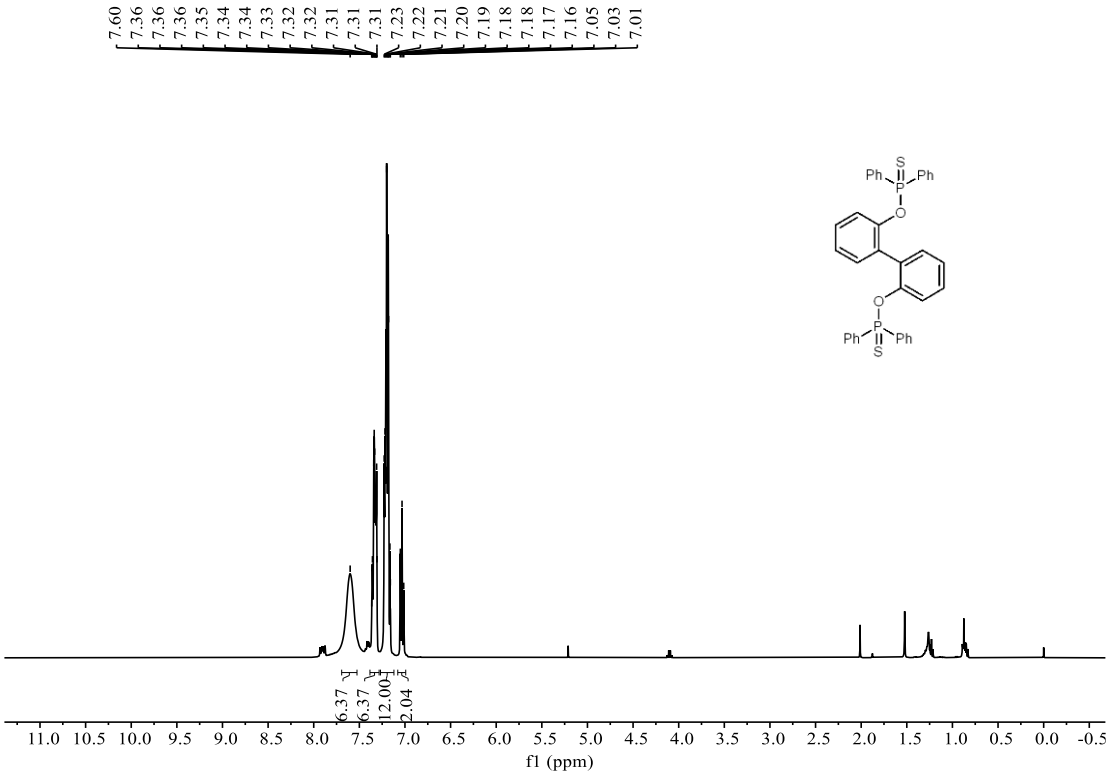
O,O'-(naphthalene-1,4-diyl) bis(diphenylphosphinothioate) (**3n'**)

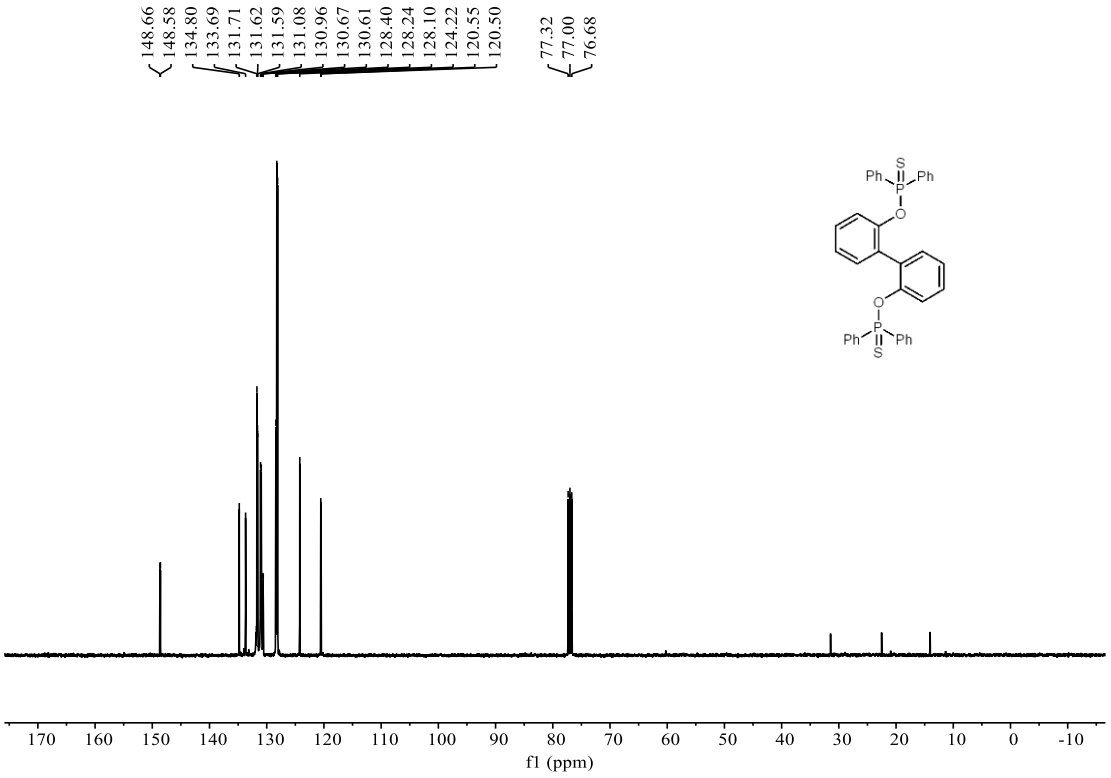


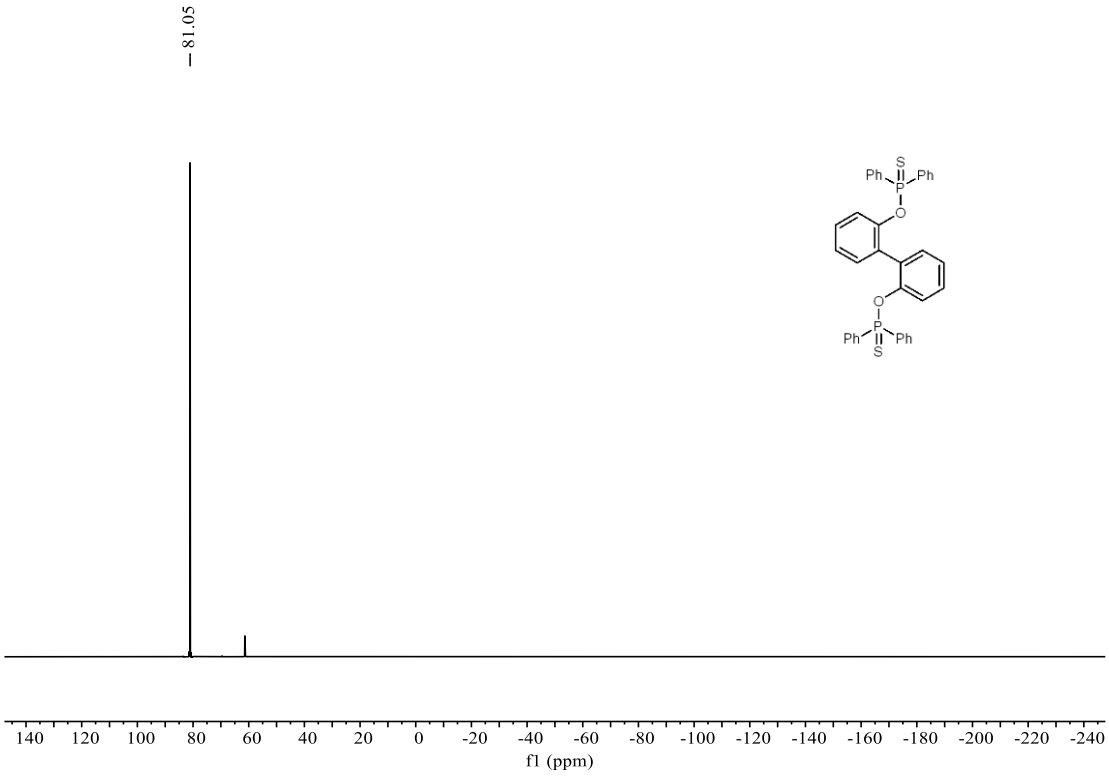

143.46
143.44
143.37
143.35
134.89
133.79
132.14
132.11
131.25
131.13
128.66
128.52
126.64
122.28
115.07
115.05
115.01
114.99
77.32
77.00
76.68
Ph
S
P
Ph
O
O
P
Ph
S
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


82.28
Ph
S
P
Ph
O
O
P
Ph
S
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

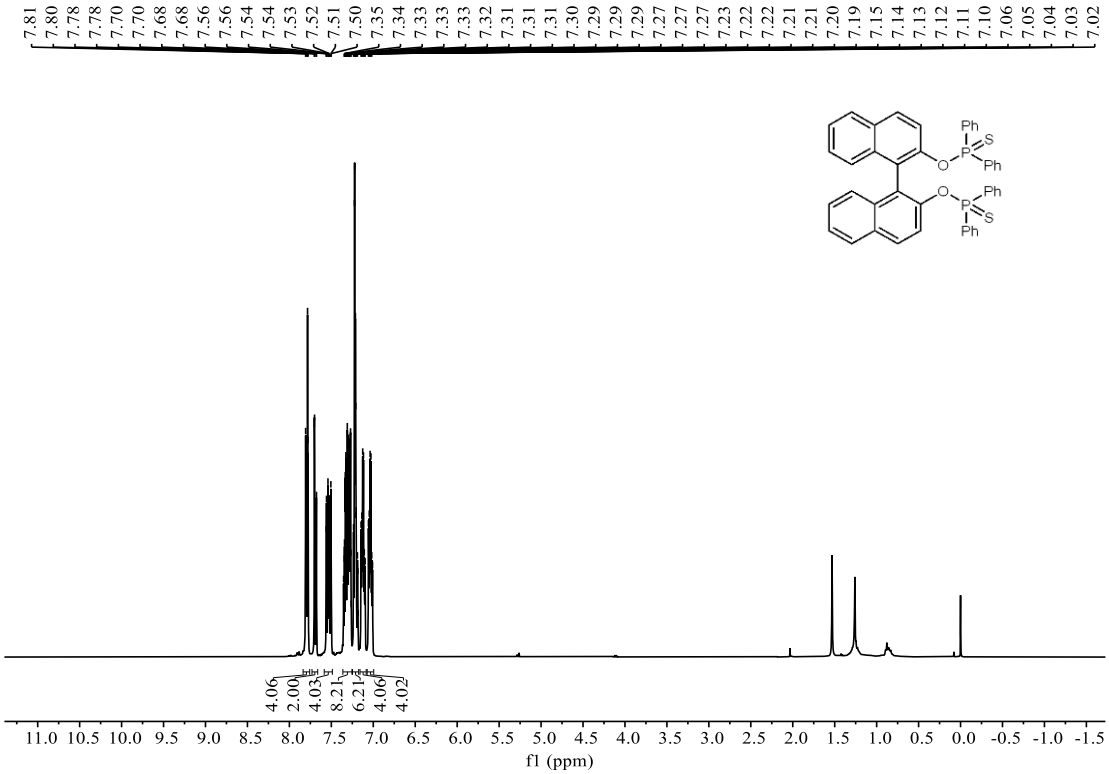
O,O'-([1,1'-biphenyl]-2,2'-diyl) bis(diphenylphosphinothioate) (**3o'**)

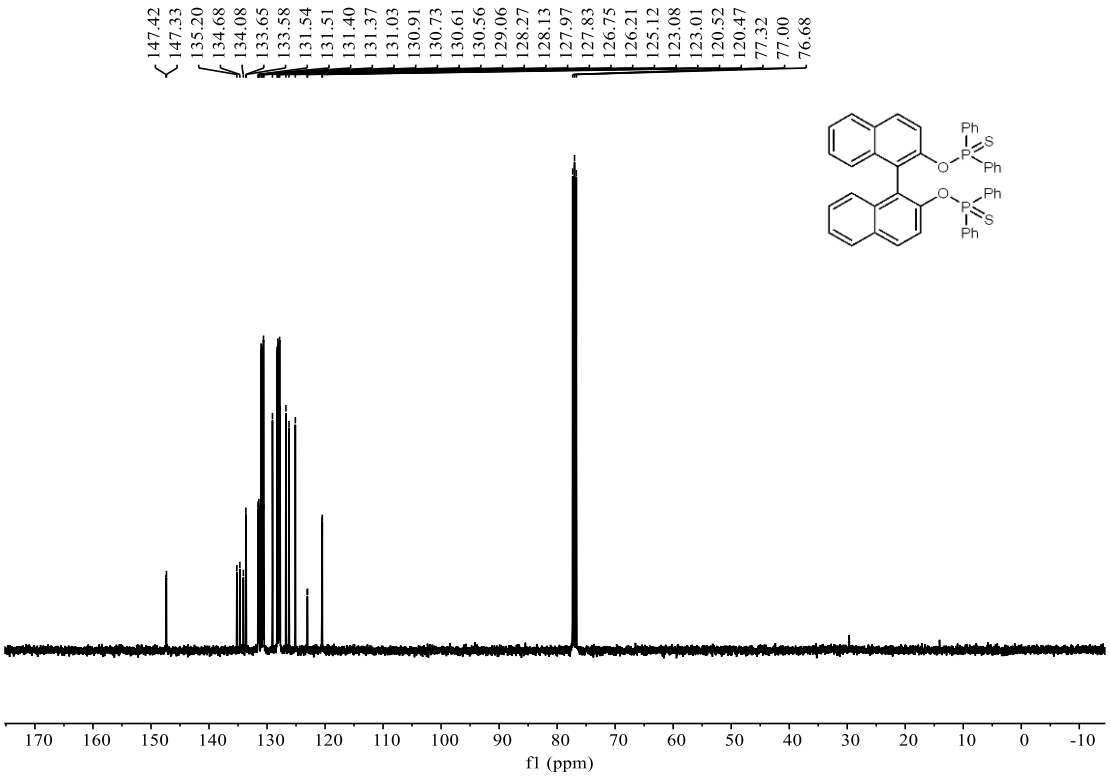


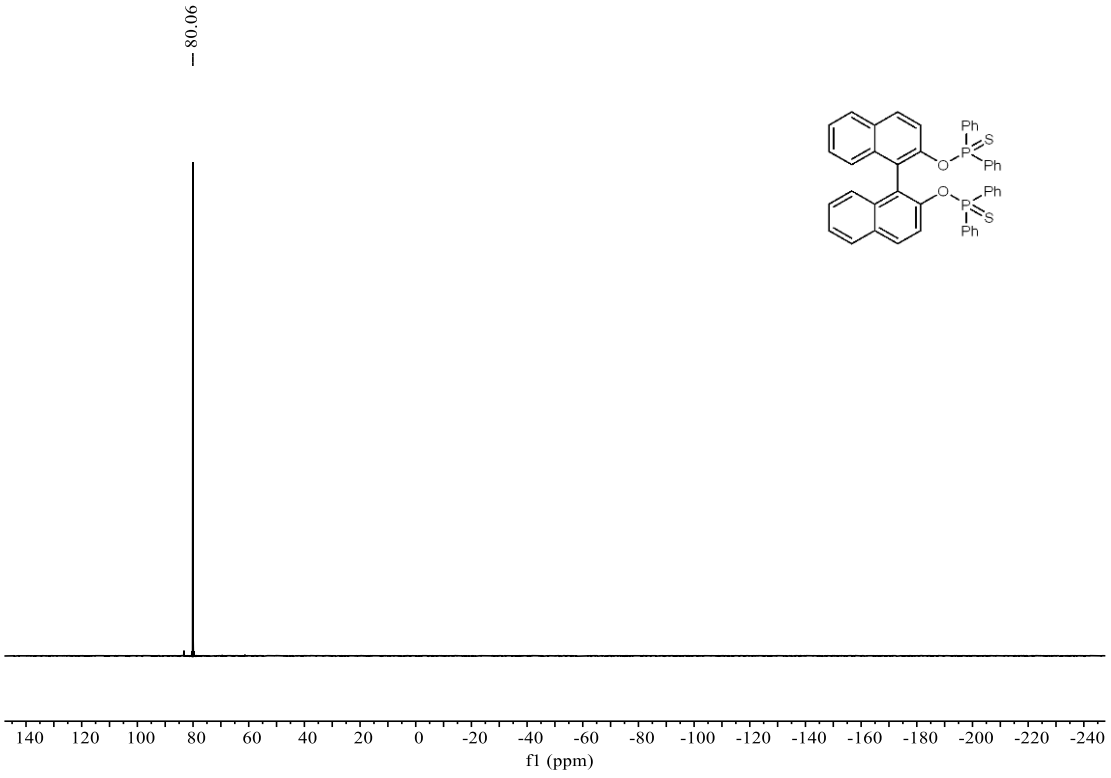




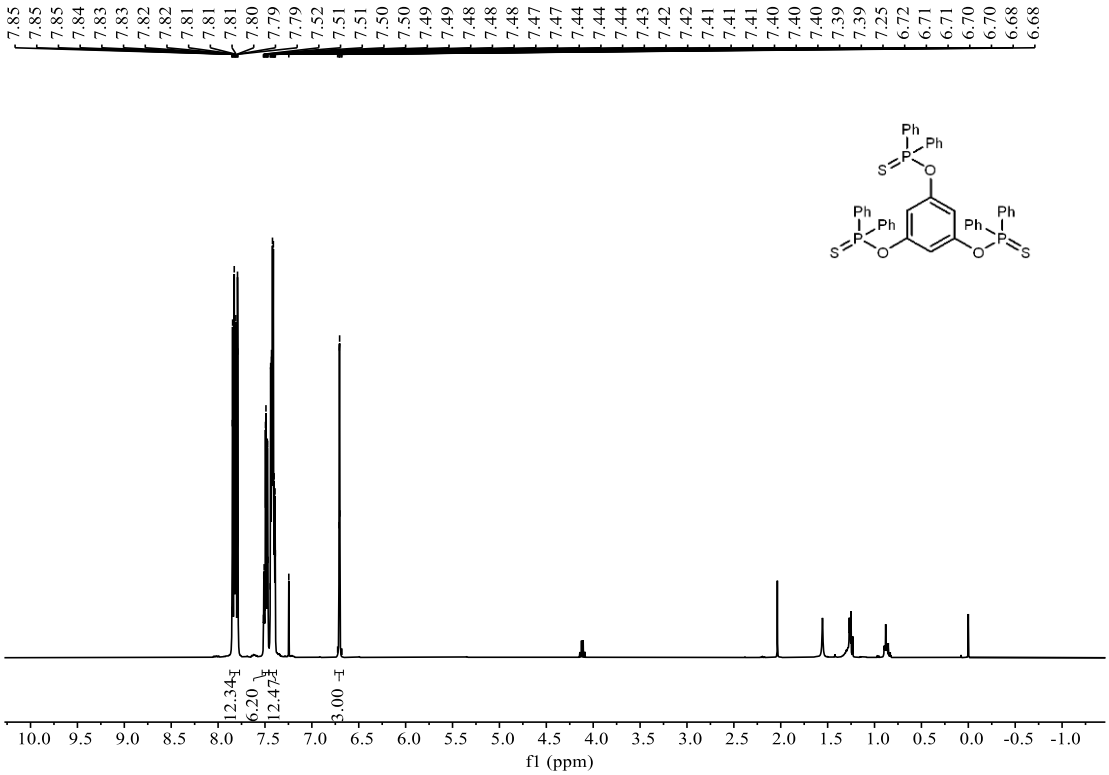
O,O'-([1,1'-binaphthalene]-2,2'-diyl) bis(diphenylphosphinothioate) (**3p'**)

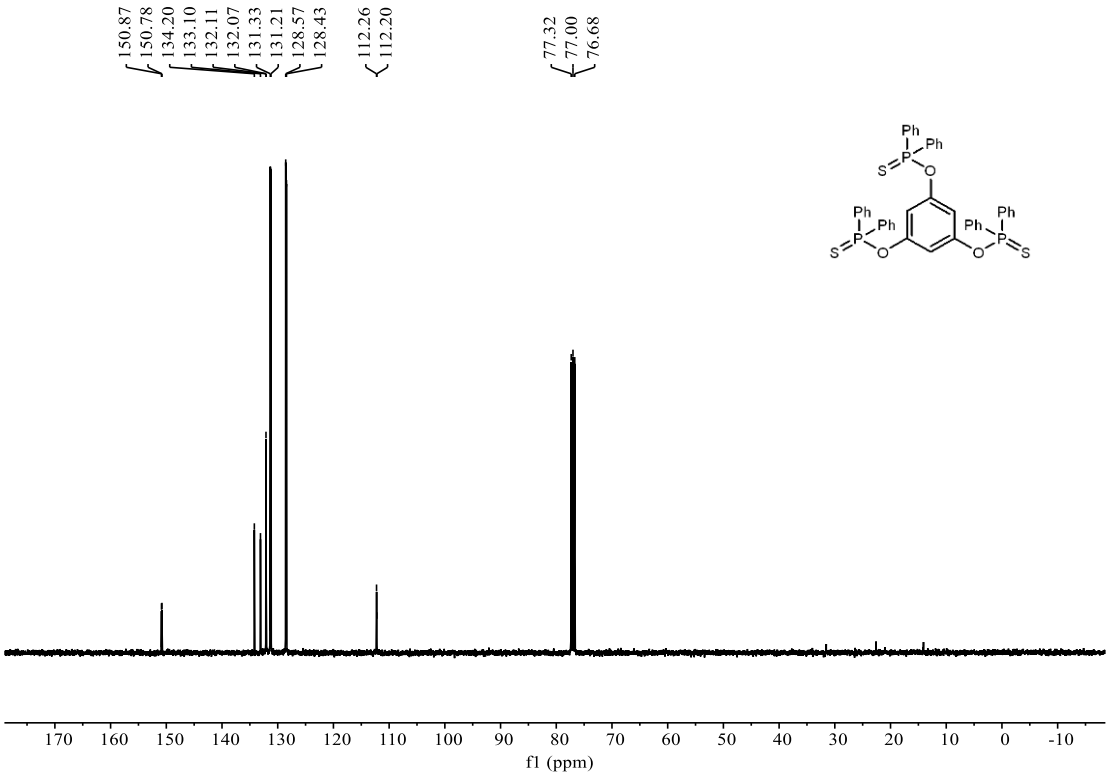


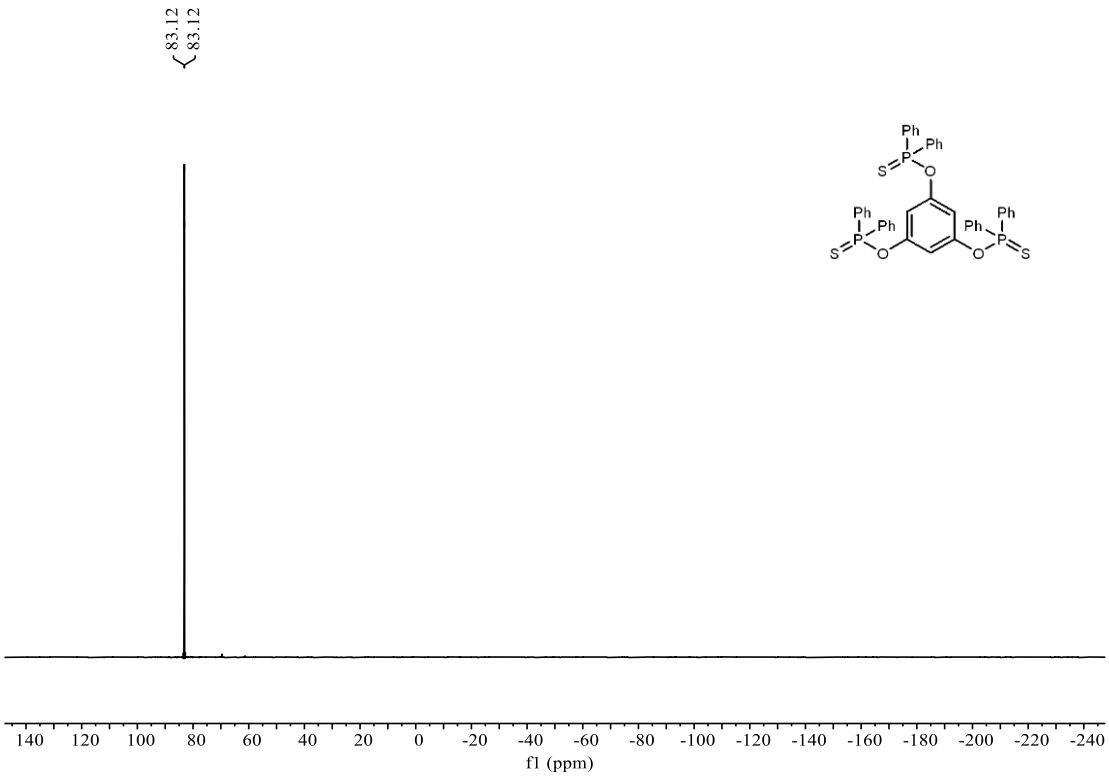

147.42
147.33
135.20
134.68
134.08
133.65
133.58
131.54
131.51
131.40
131.37
131.03
130.91
130.73
130.61
130.56
129.06
128.27
128.13
127.97
127.83
126.75
126.21
125.12
123.08
123.01
120.52
120.47
77.32
77.00
76.68
Ph
S
P
O
Ph
Ph
P
O
S
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


80.06
Ph
S
P
O
Ph
Ph
P
O
S
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

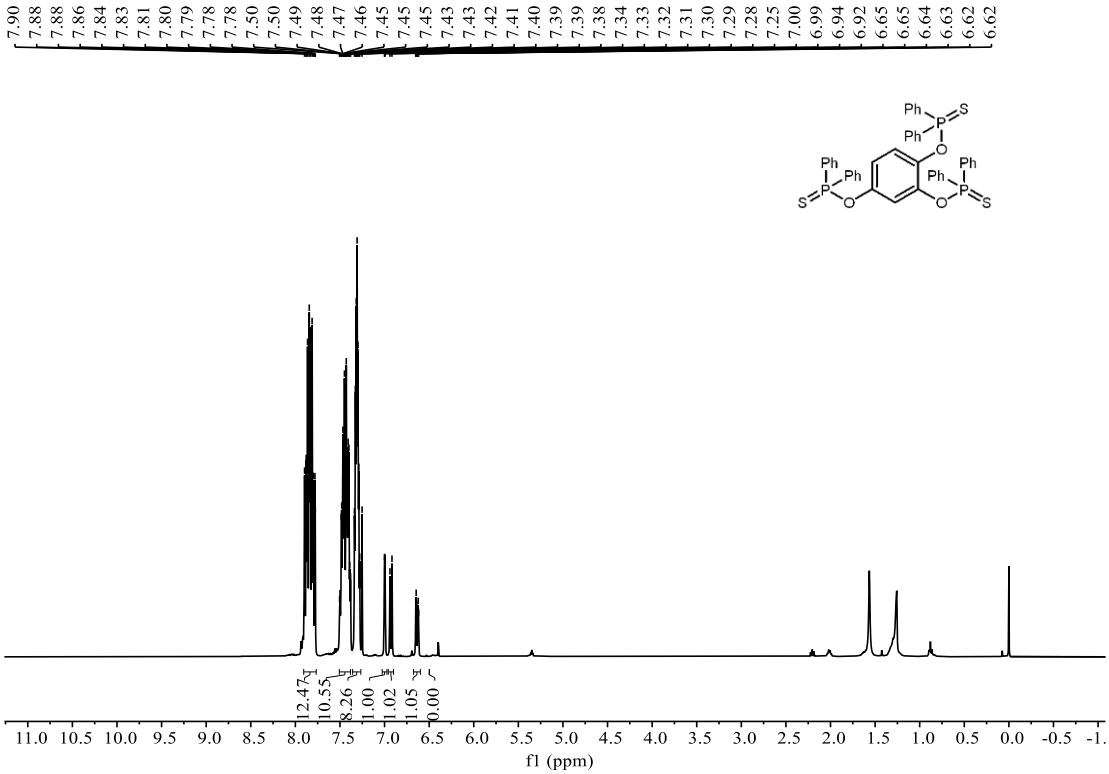
O,O',O''-(benzene-1,3,5-triyl) tris(diphenylphosphinothioate) (**3q'**)

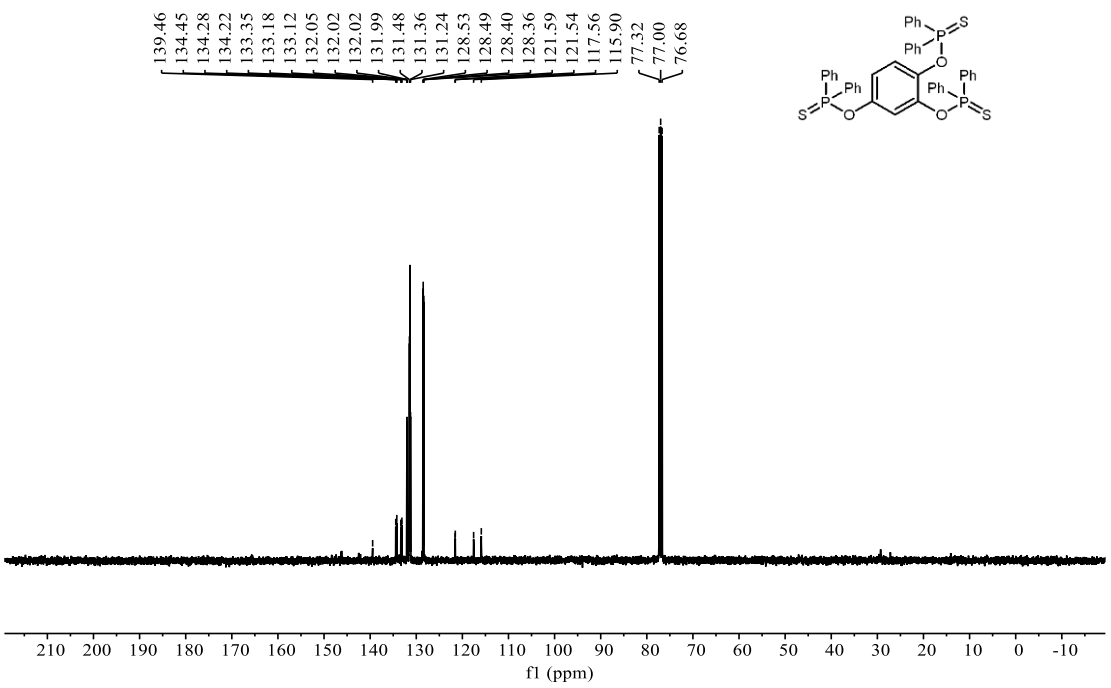


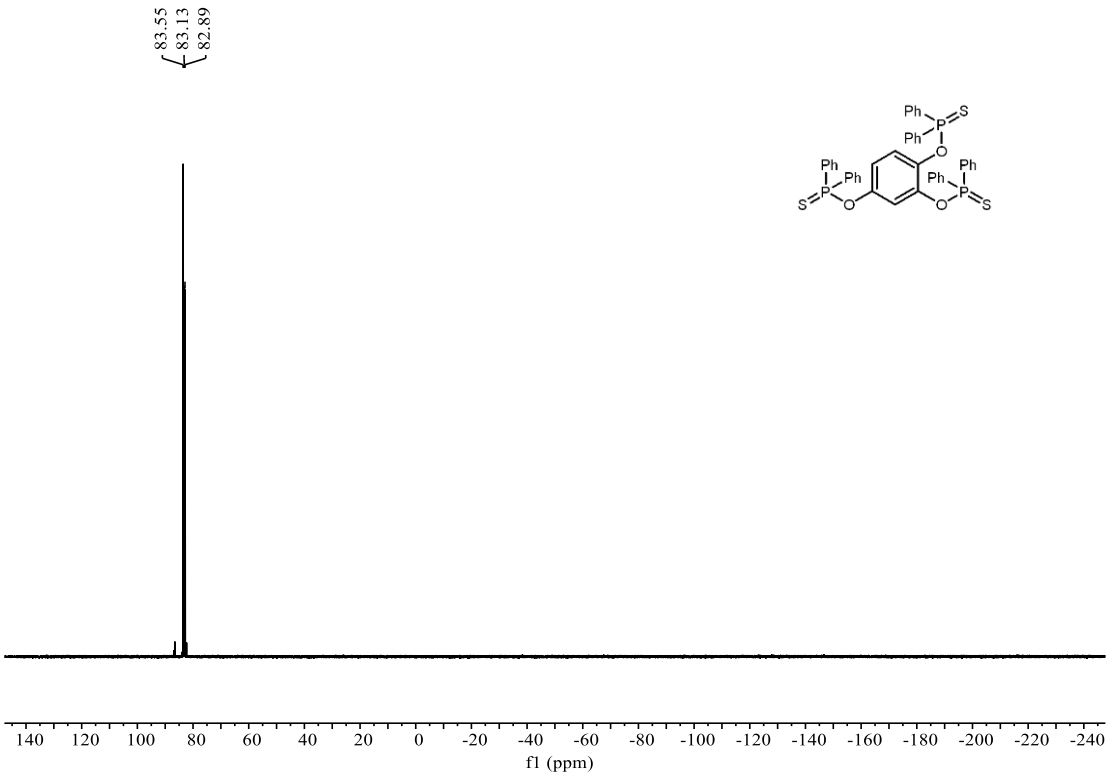




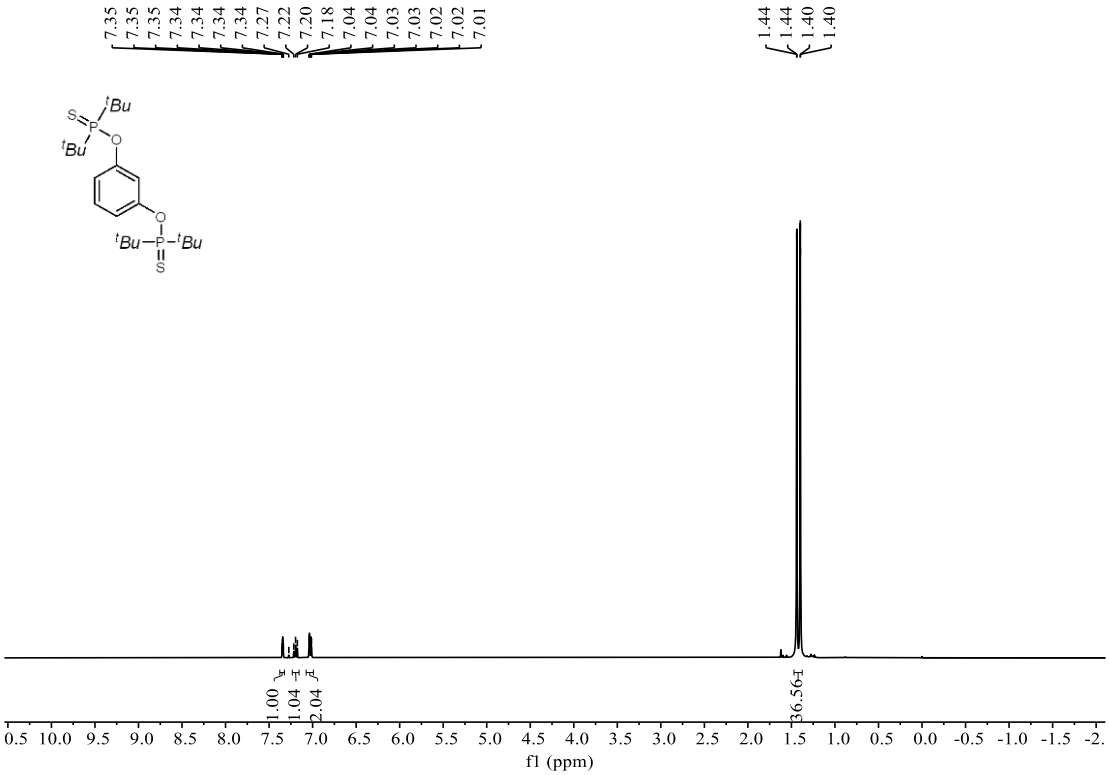
O,O',O''-(benzene-1,2,4-triyl) tris(diphenylphosphinothioate) (**3r'**)

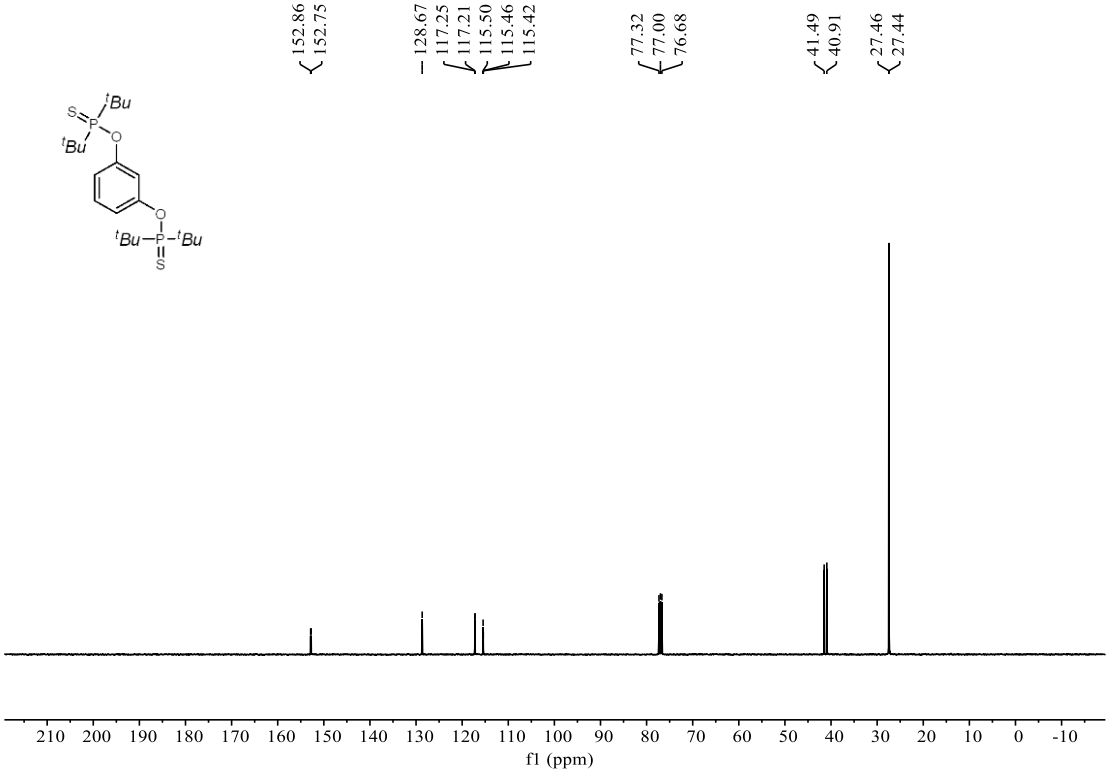


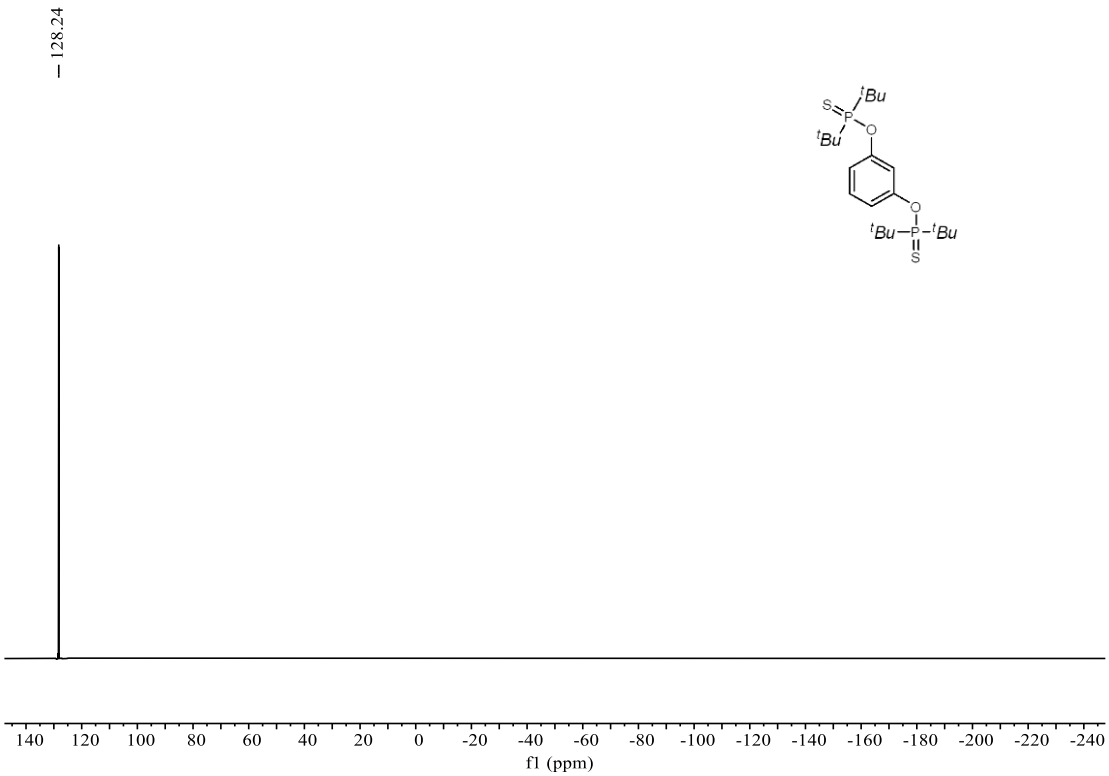

139.46
134.45
134.28
134.22
133.35
133.18
133.12
132.05
132.02
132.02
131.99
131.48
131.36
131.24
128.53
128.49
128.40
128.36
121.59
121.54
117.56
115.90
77.32
77.00
76.68
Ph
Ph
P
S
O
Ph
Ph
P
S
O
Ph
Ph
P
S
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


83.55
83.13
82.89
Ph
Ph
P
S
O
Ph
Ph
P
S
O
Ph
Ph
P
S
O
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

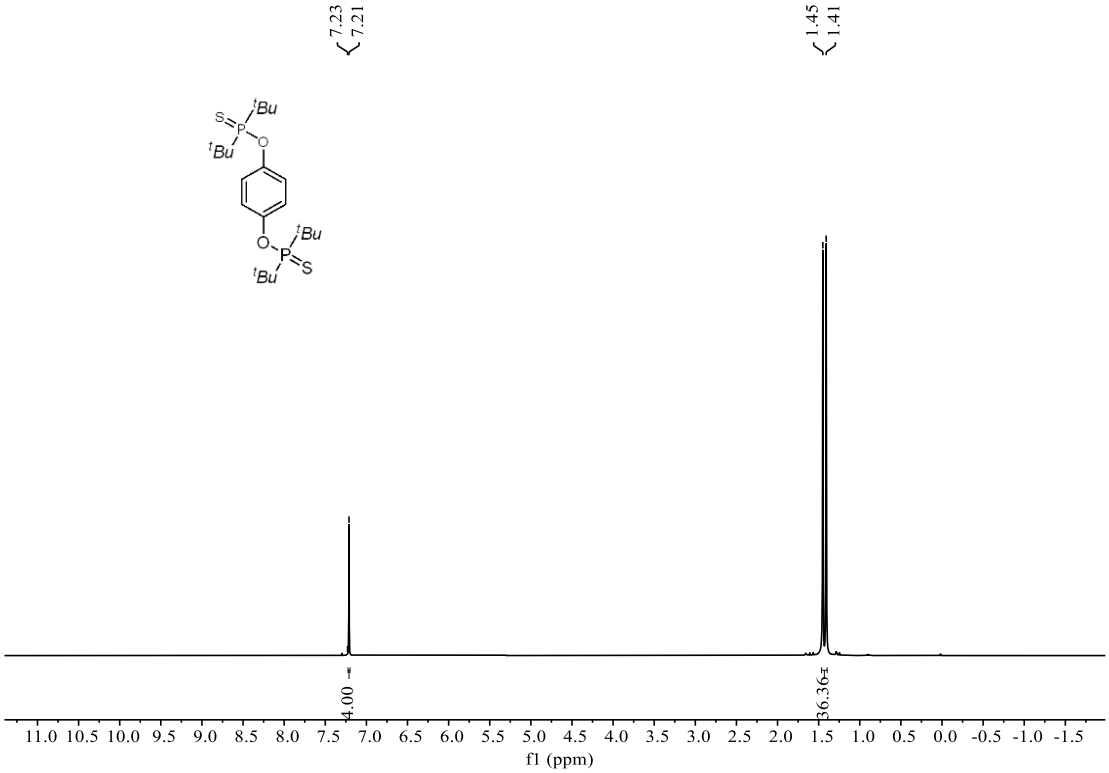
O,O'-(1,3-phenylene) bis(di-tert-butylphosphinothioate) (**3s'**)

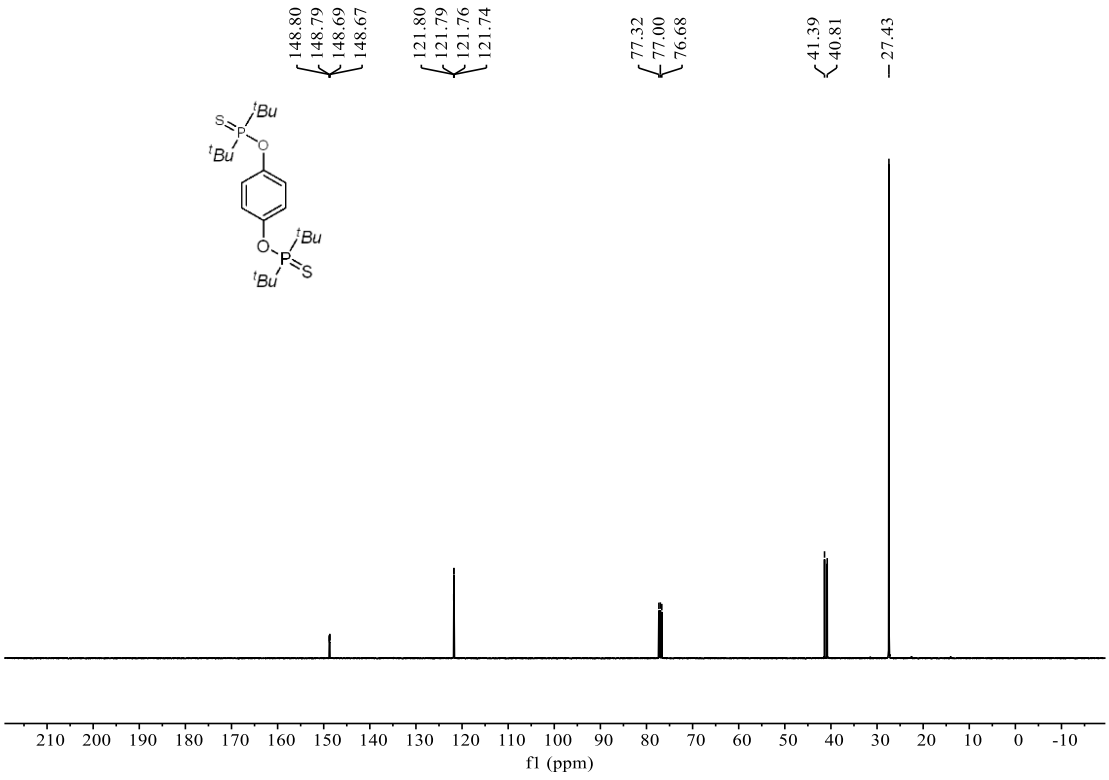


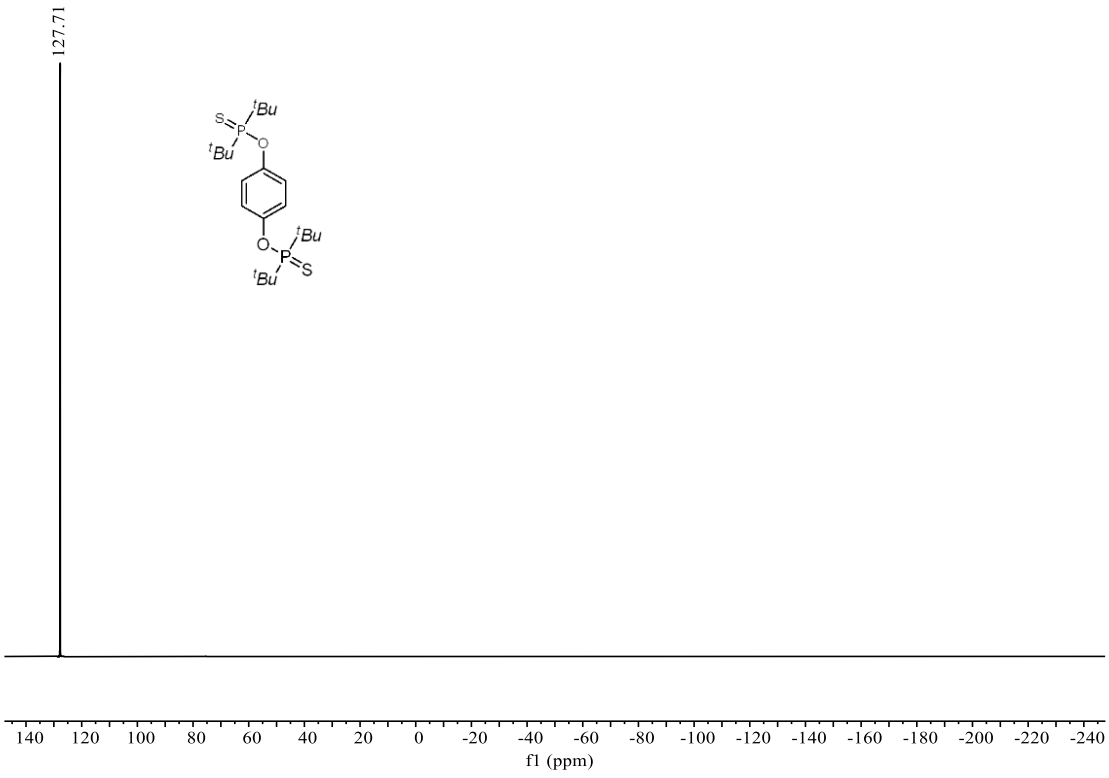




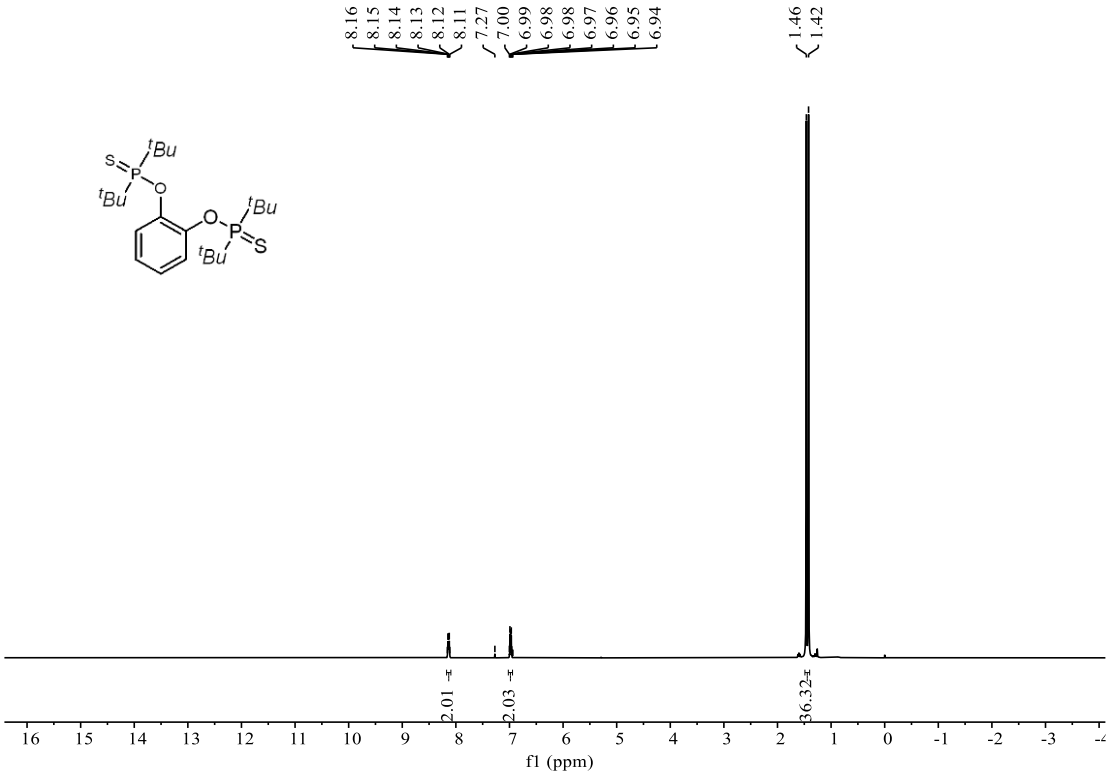
O,O'-(1,4-phenylene) bis(di-tert-butylphosphinothioate) (**3t'**)

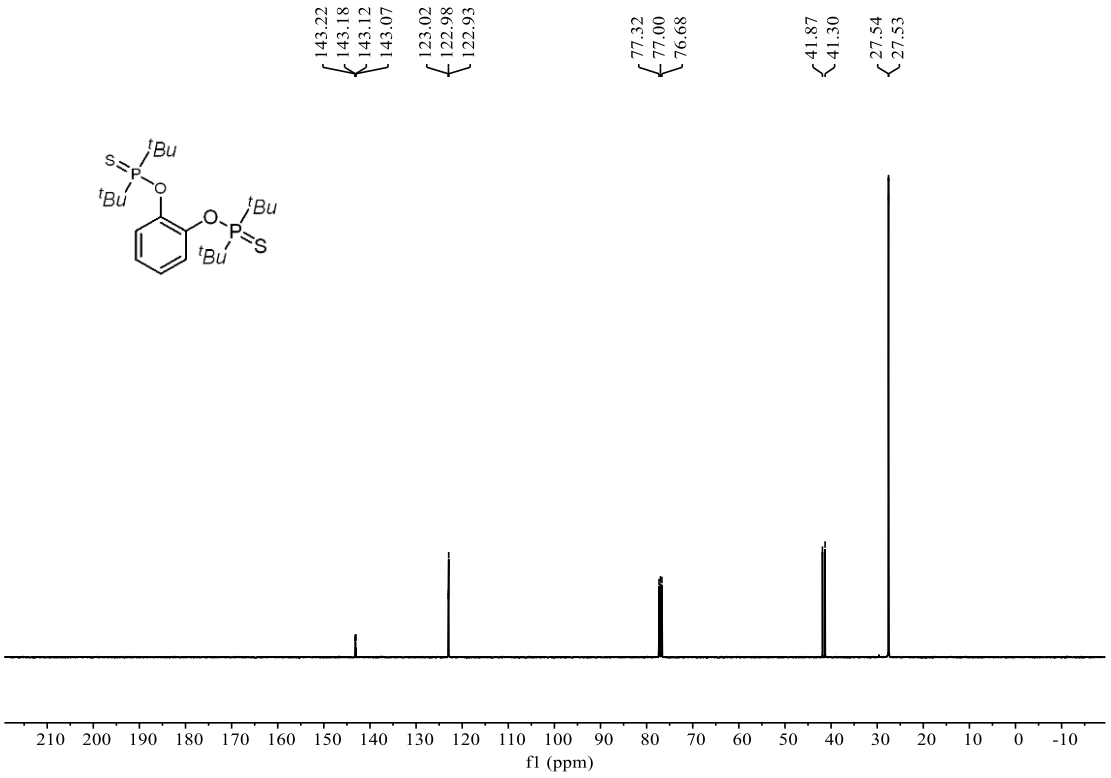


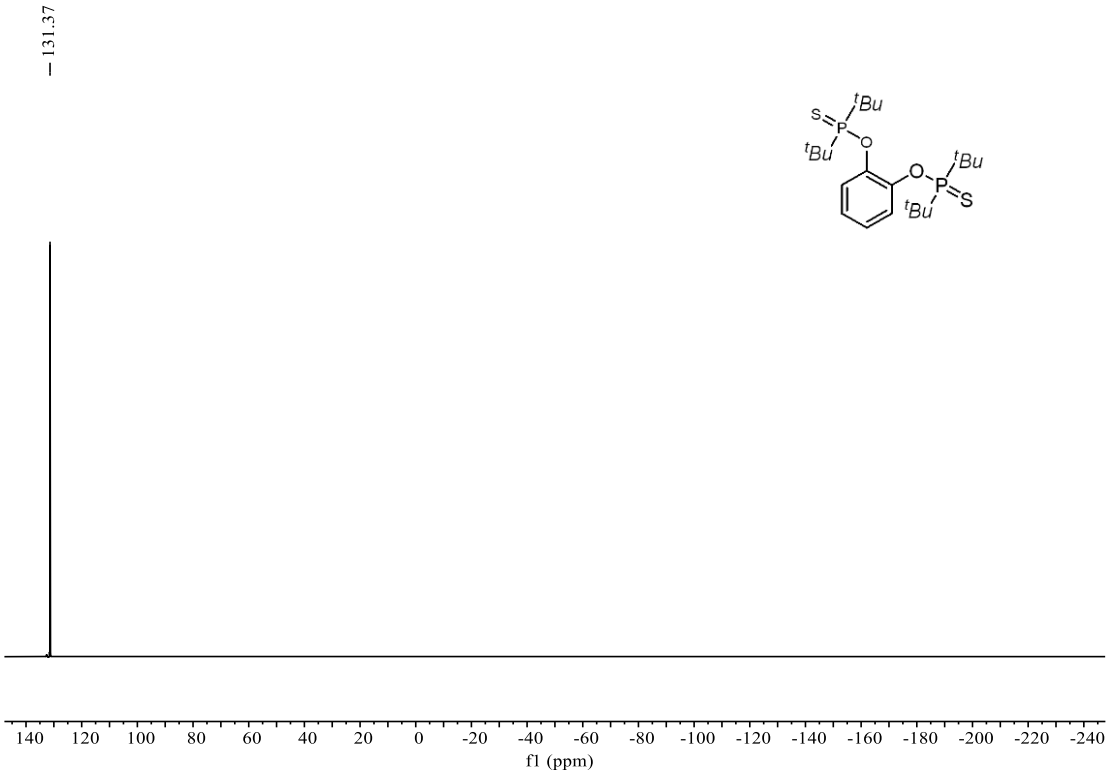

148.80
148.79
148.69
148.67
121.80
121.79
121.76
121.74
77.32
77.00
76.68
41.39
40.81
27.43
tBu
tBu
S
P
O
tBu
tBu
O
P
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


127.71
tBu
tBu
S
P
O
tBu
tBu
O
P
S
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

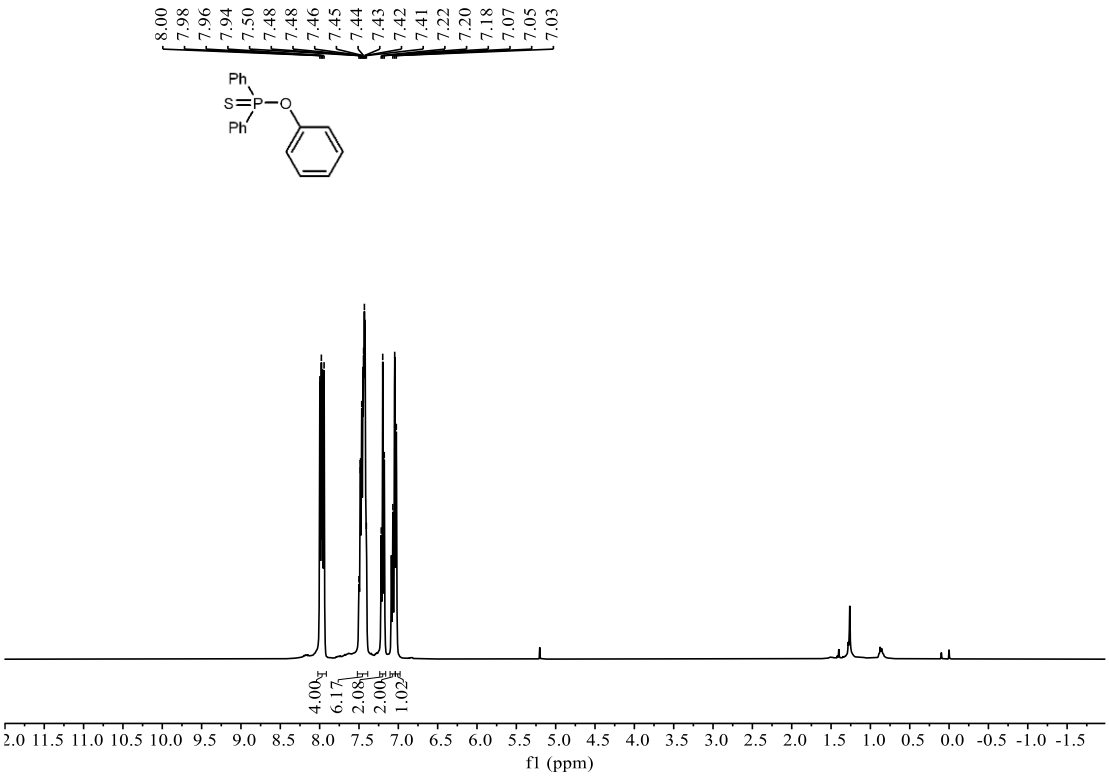
O,O'-(1,2-phenylene) bis(di-tert-butylphosphinothioate) (**3u'**)

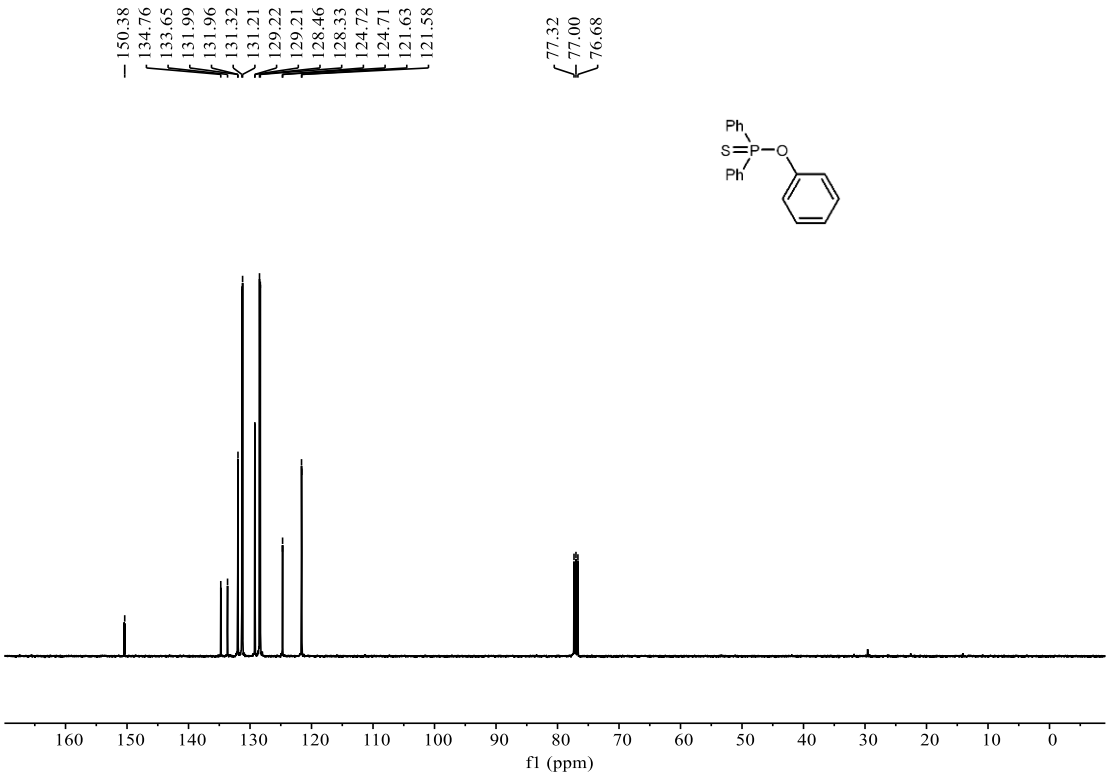


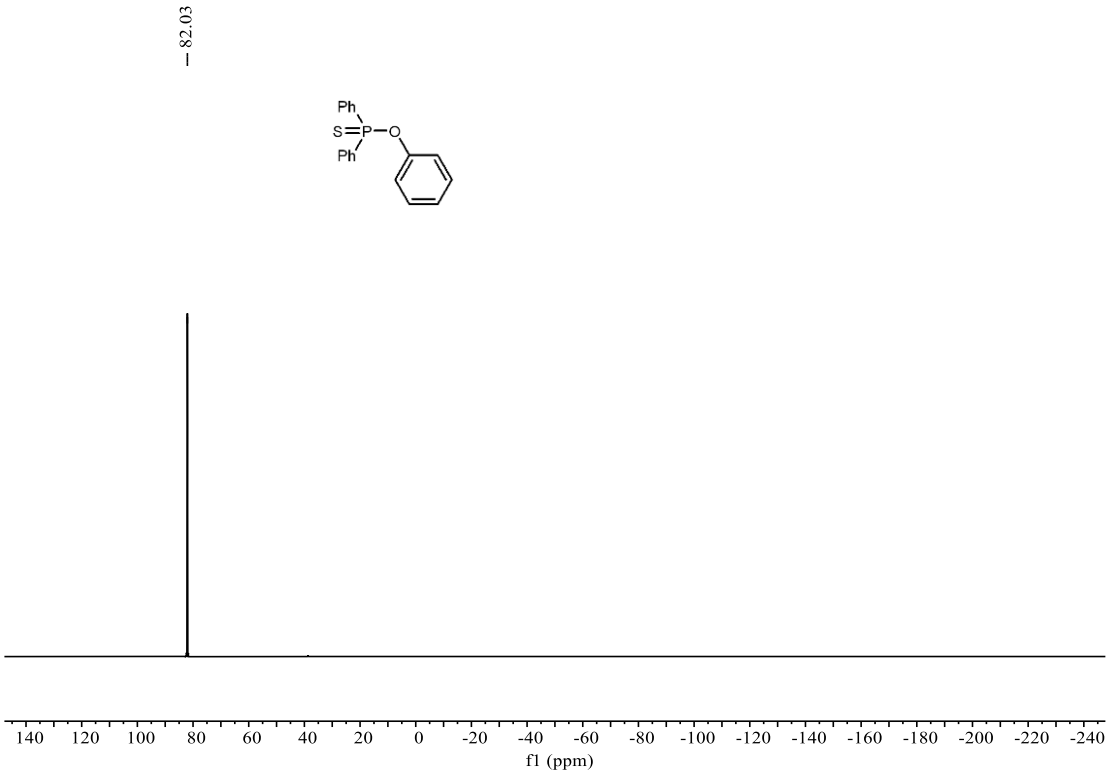




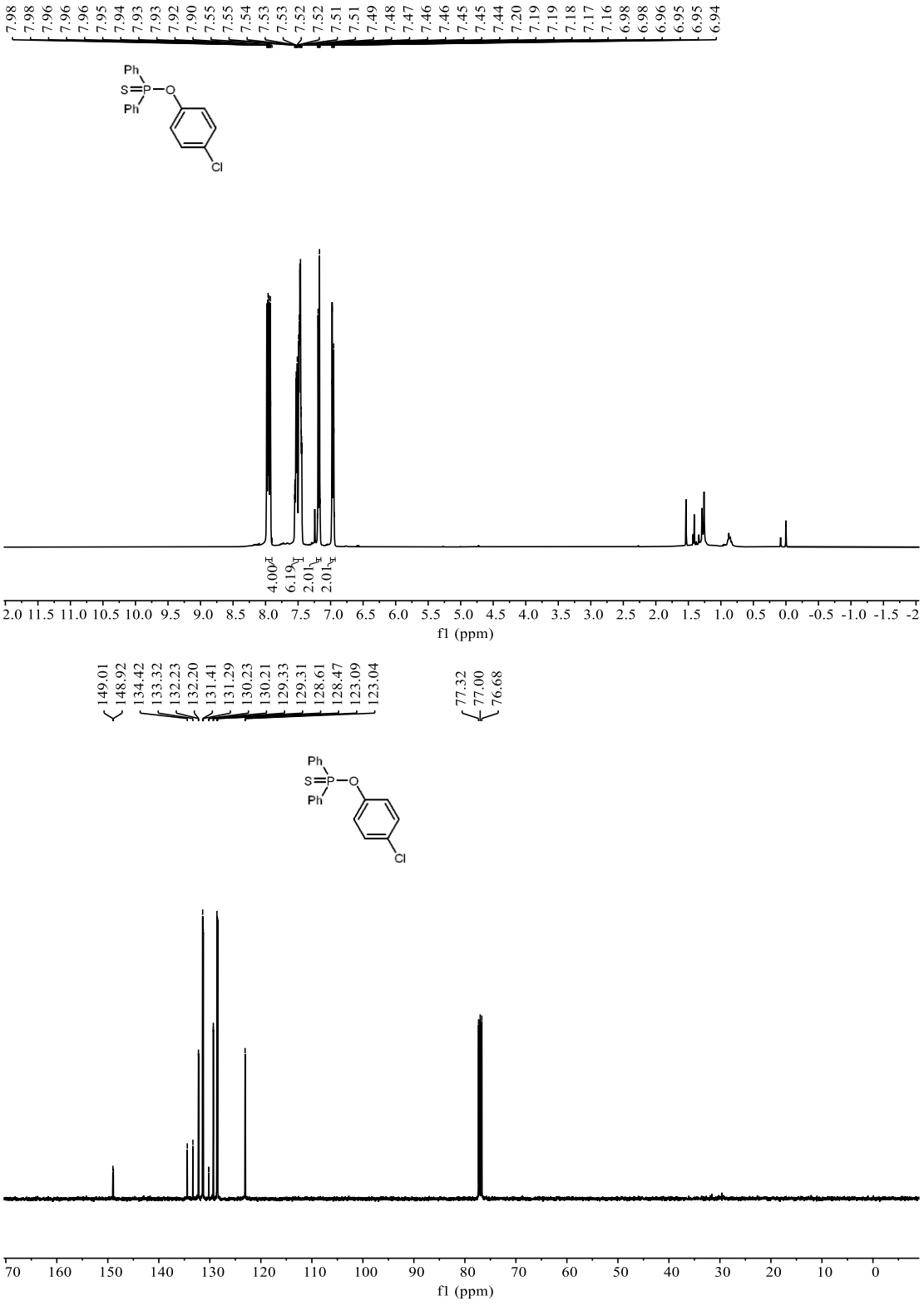
O-phenyl diphenylphosphinothioate (**3v'**)

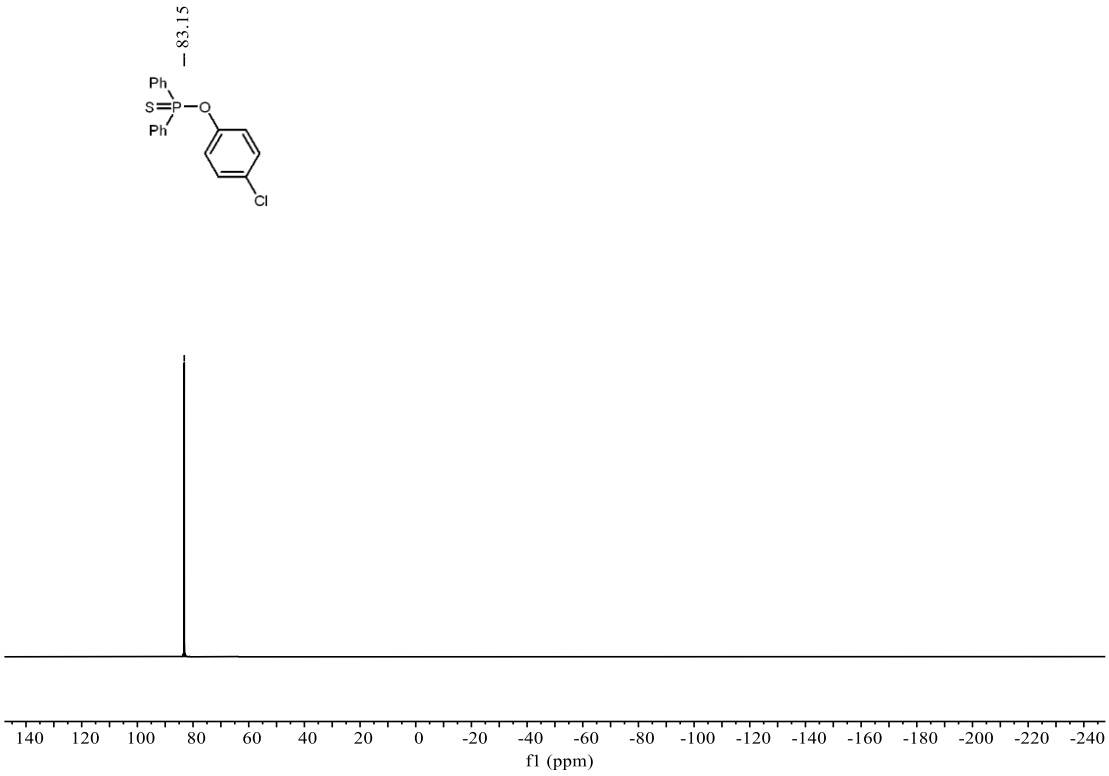



150.38
134.76
133.65
131.99
131.96
131.32
131.21
129.22
129.21
128.46
128.33
124.72
124.71
121.63
121.58
77.32
77.00
76.68
Ph
S
P
O
Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

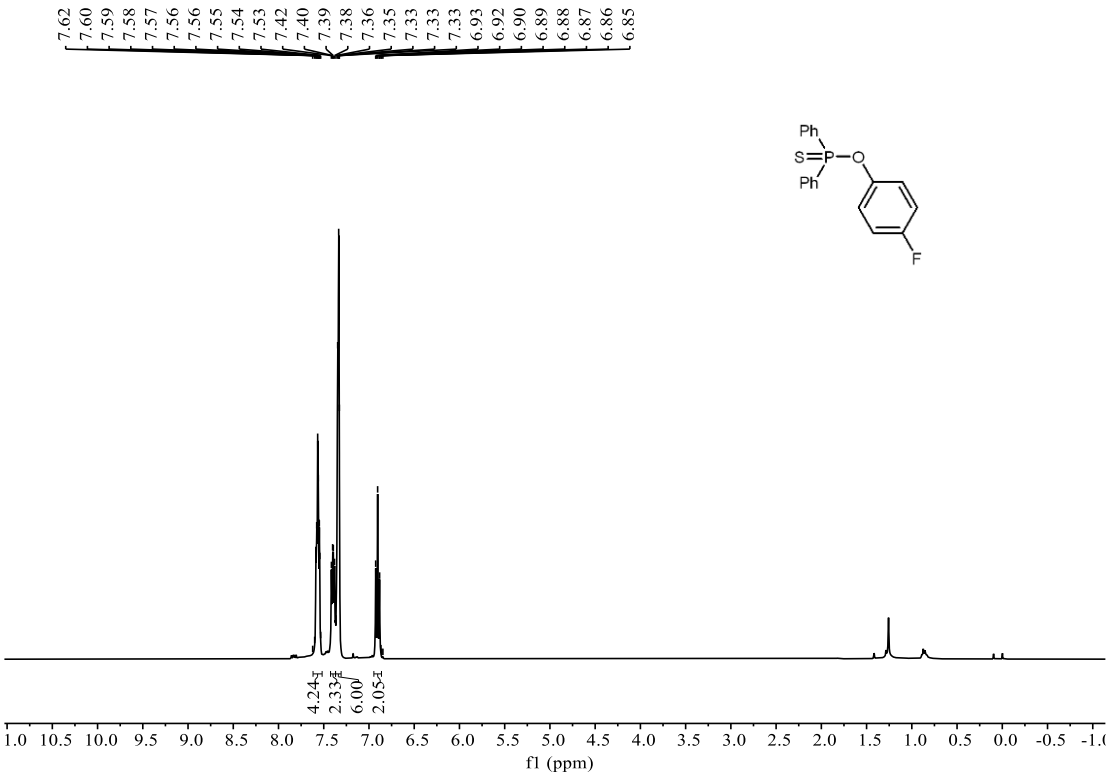

82.03
Ph
S
P
O
Ph
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

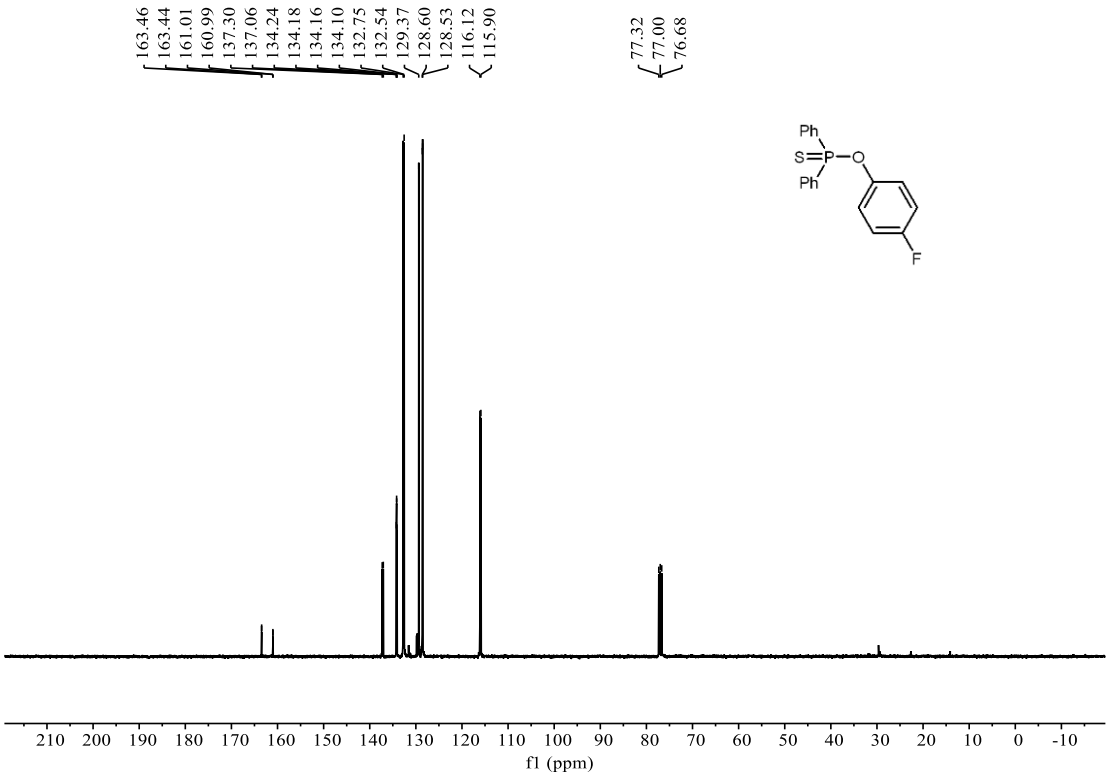
O-(4-chlorophenyl) diphenylphosphinothioate (**3w'**)

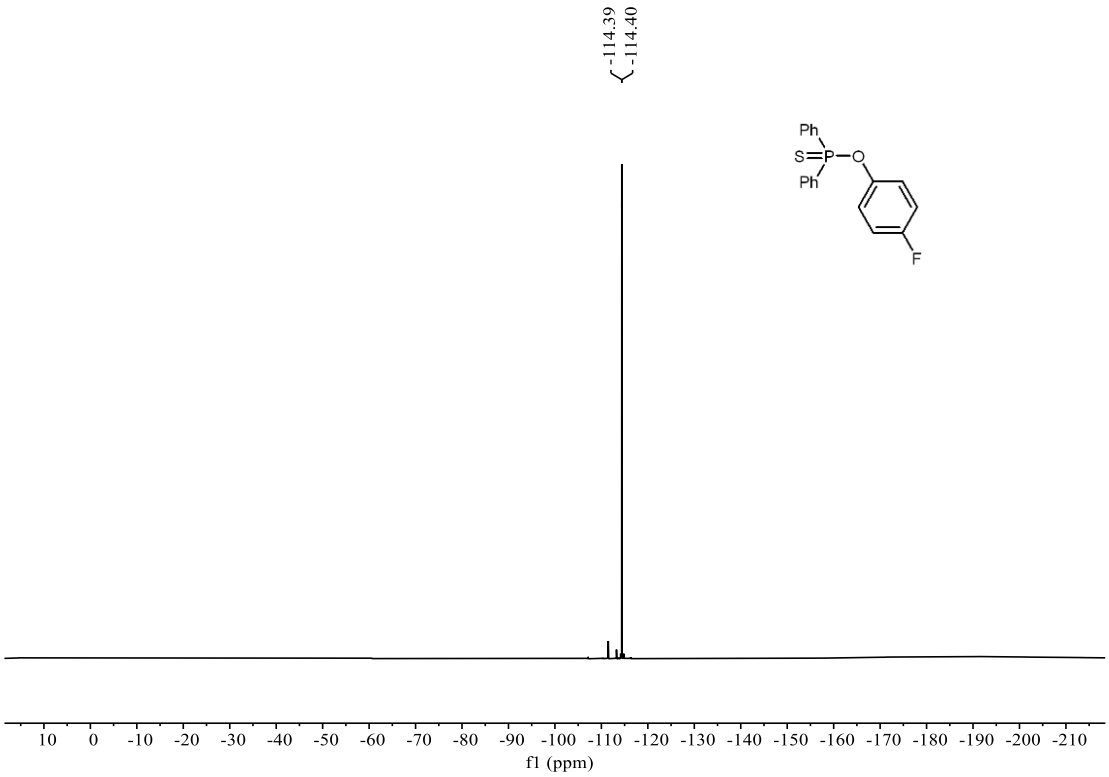


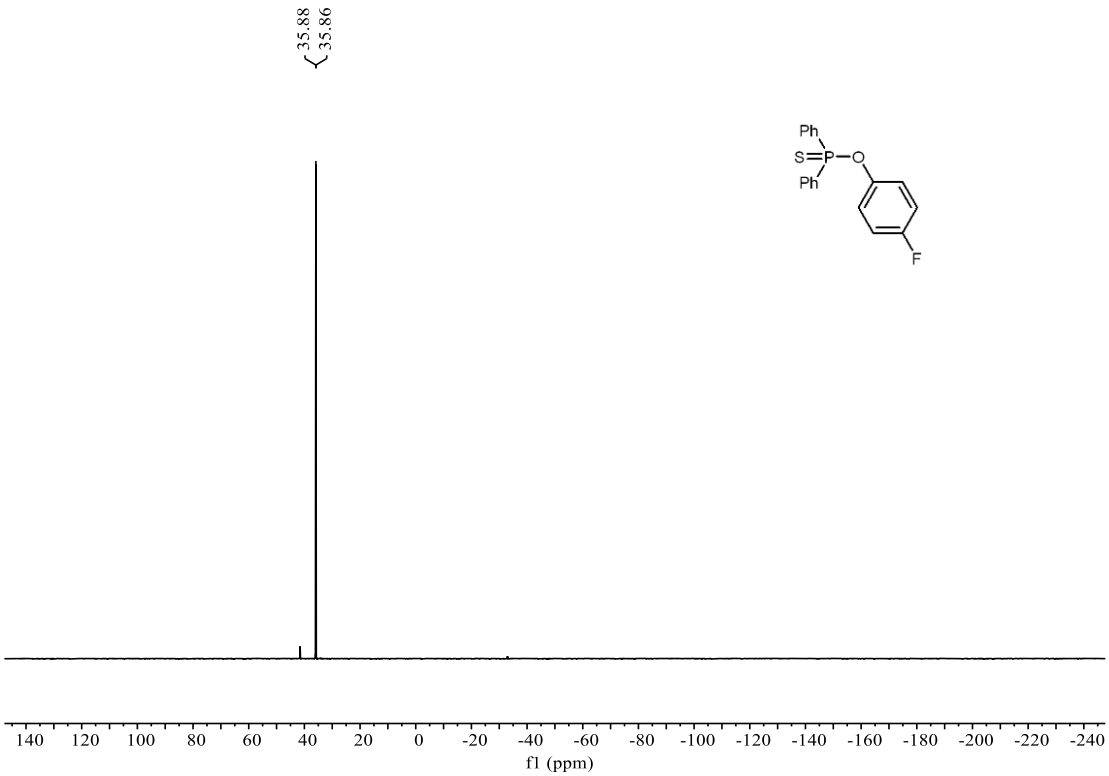


O-(4-fluorophenyl) diphenylphosphinothioate (**3x'**)

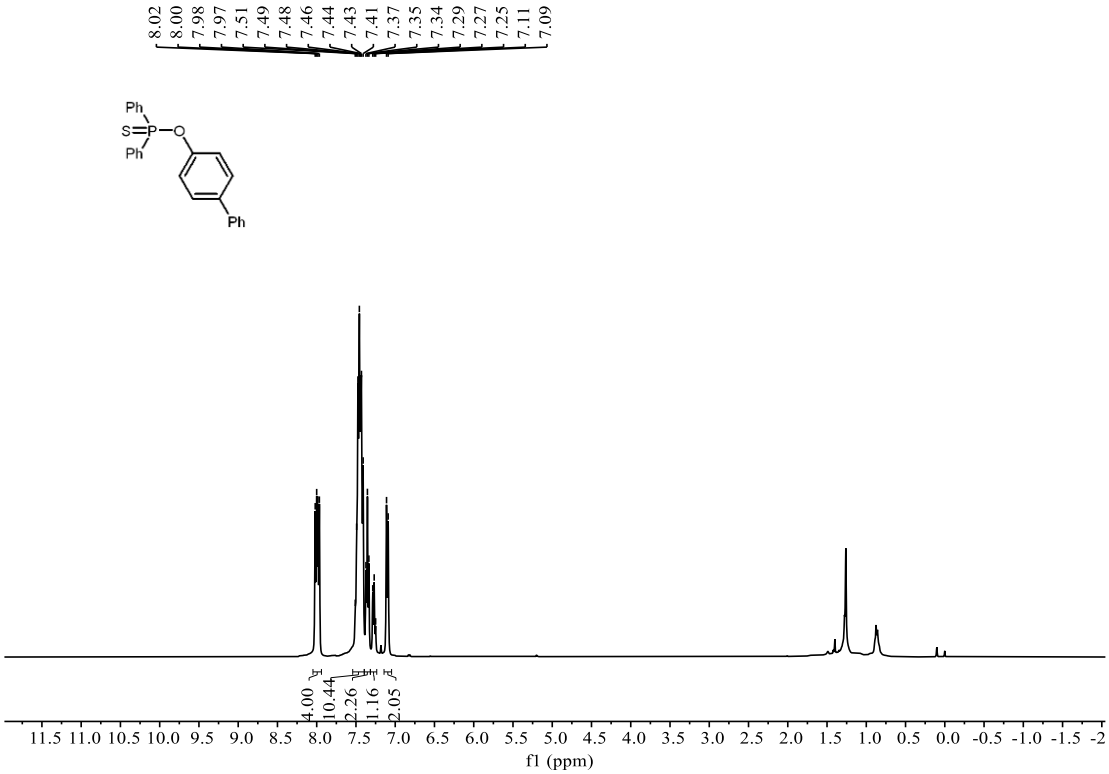


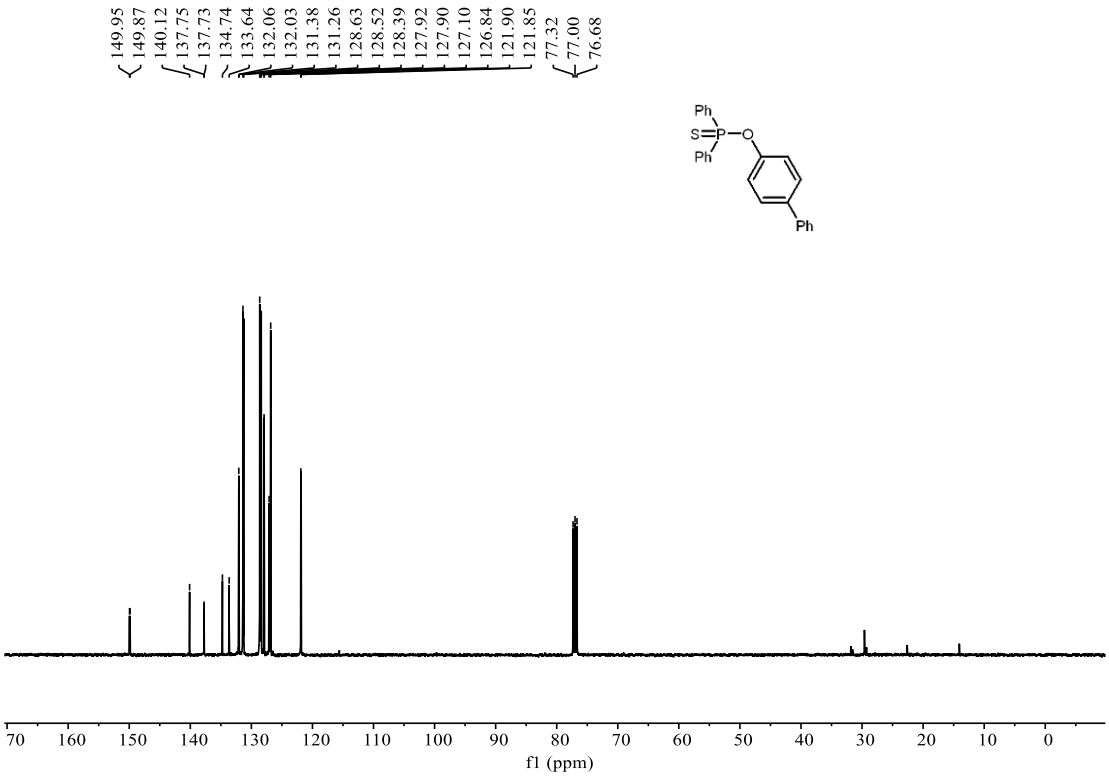

163.46
163.44
161.01
160.99
137.30
137.06
134.24
134.18
134.16
134.10
132.75
132.54
129.37
128.60
128.53
116.12
115.90
77.32
77.00
76.68
Ph
S
P
O
Ph
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

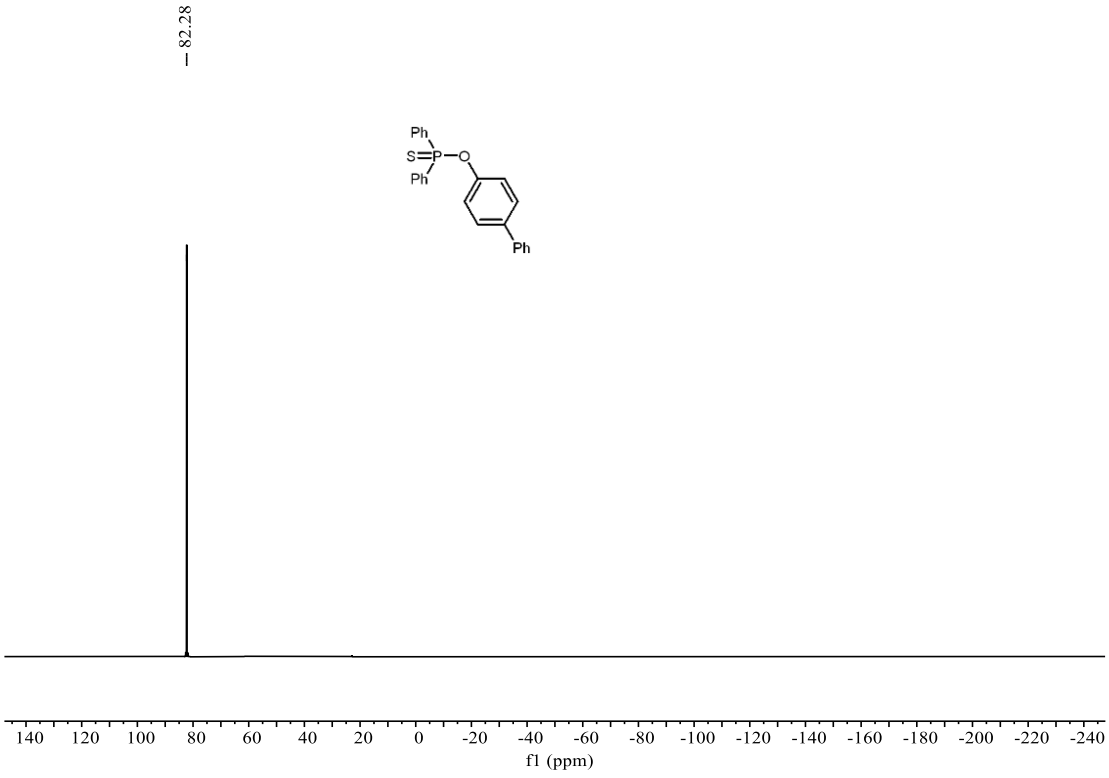

-114.39
-114.40
Ph
S
P
O
Ph
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



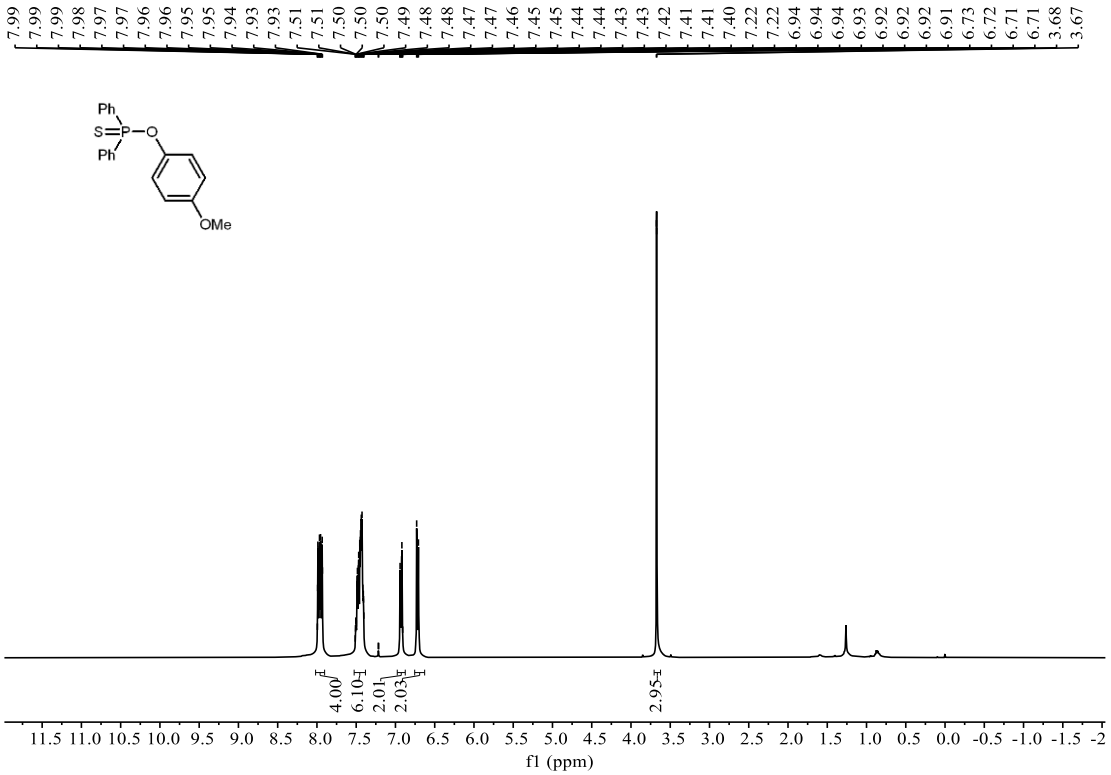
O-([1,1'-biphenyl]-4-yl) diphenylphosphinothioate (**3y'**)

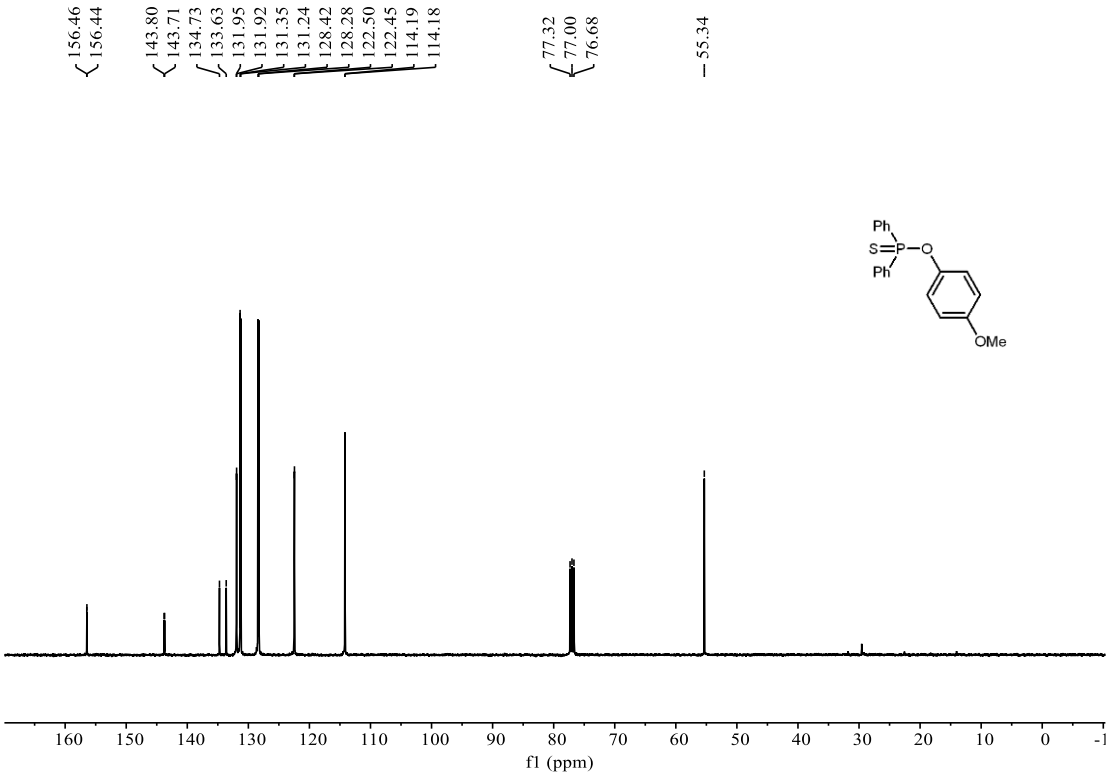


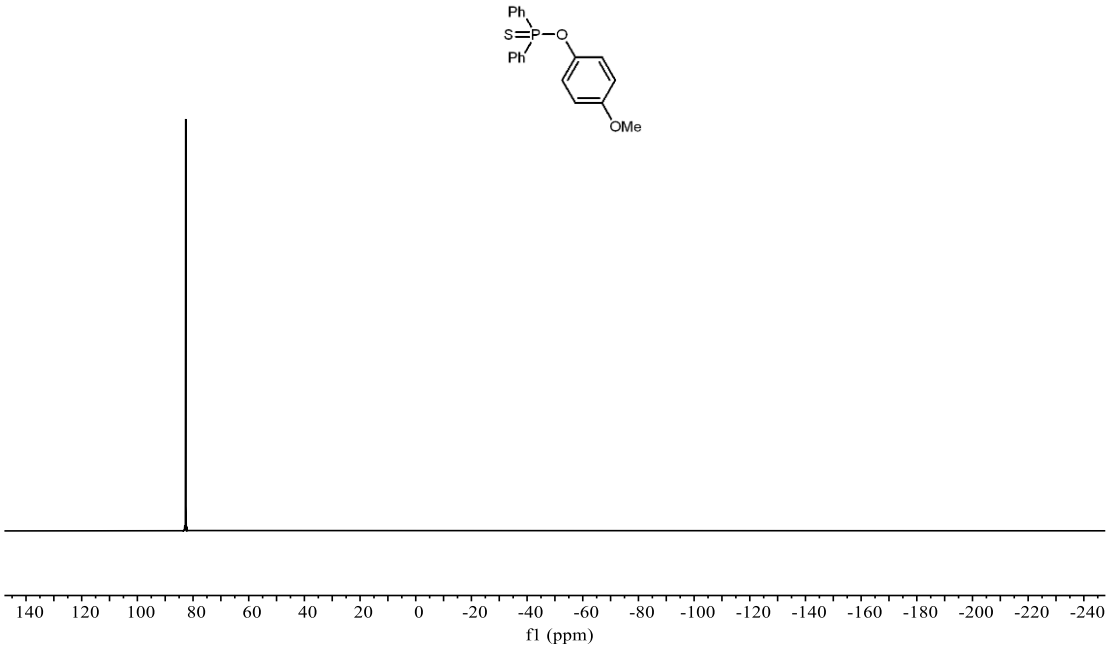

149.95
149.87
140.12
137.75
137.73
134.74
133.64
132.06
132.03
131.38
131.26
128.63
128.52
128.39
127.92
127.90
127.10
126.84
121.90
121.85
77.32
77.00
76.68
Ph
S
P
O
Ph
Ph
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


82.28
Ph
S
P
O
Ph
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

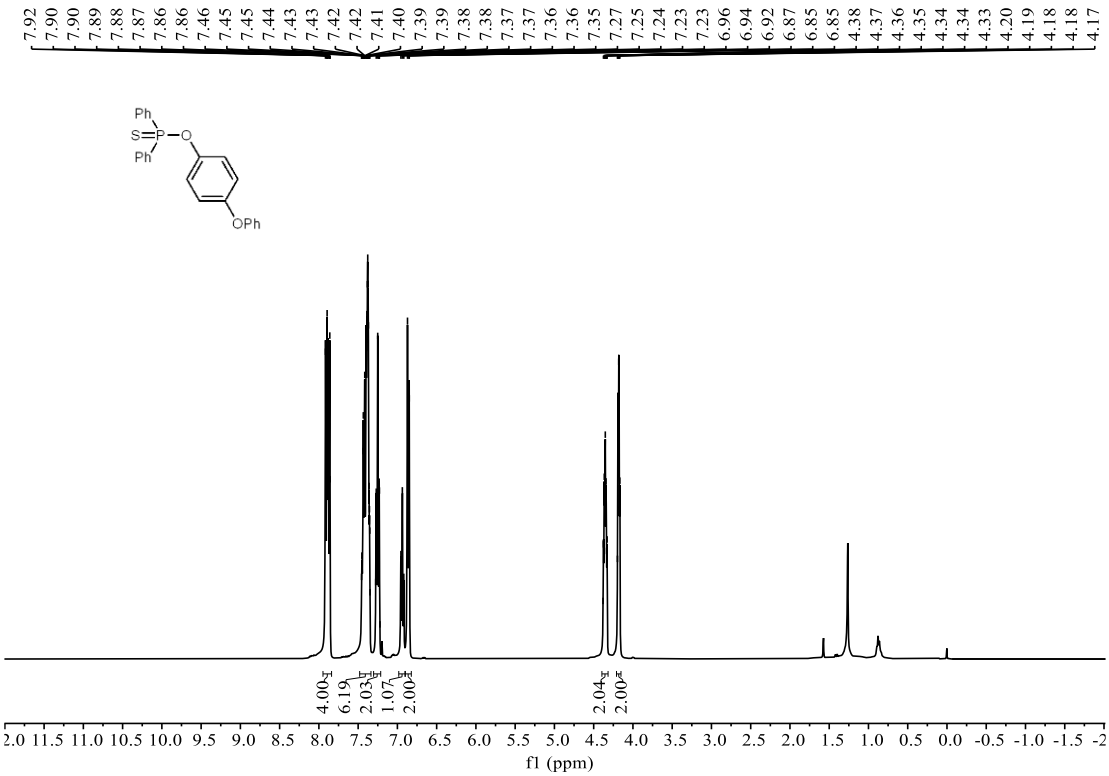
O-(4-methoxyphenyl) diphenylphosphinothioate (**3z'**)

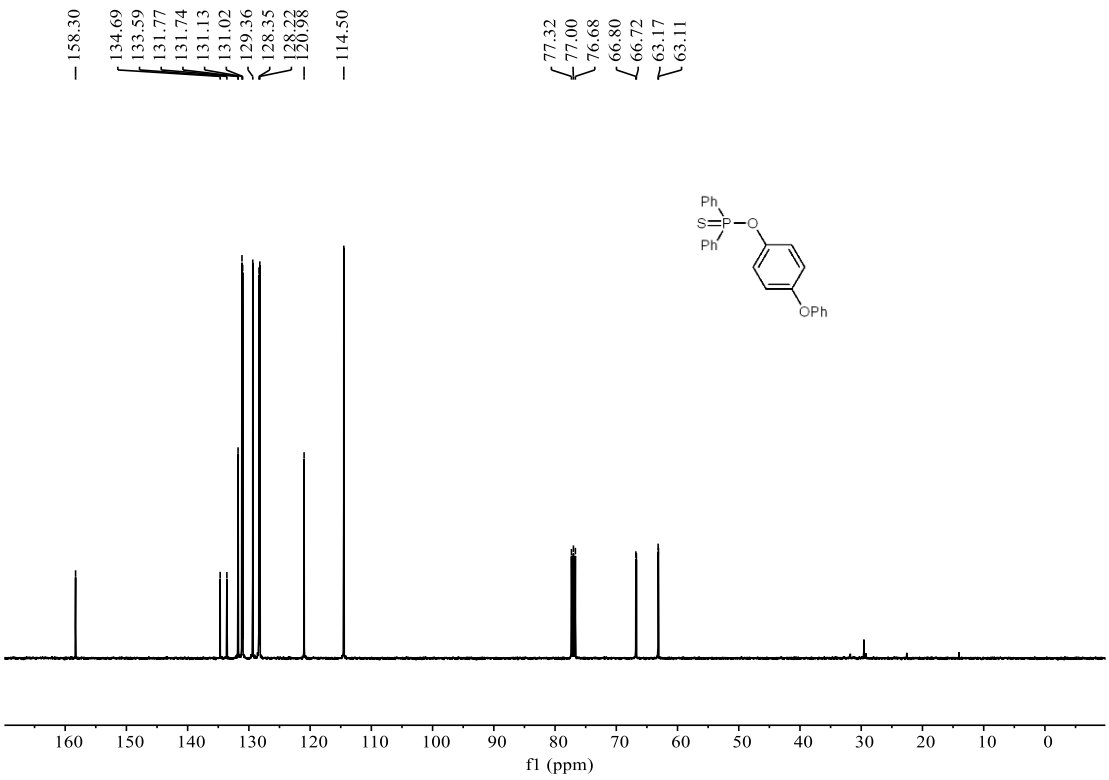


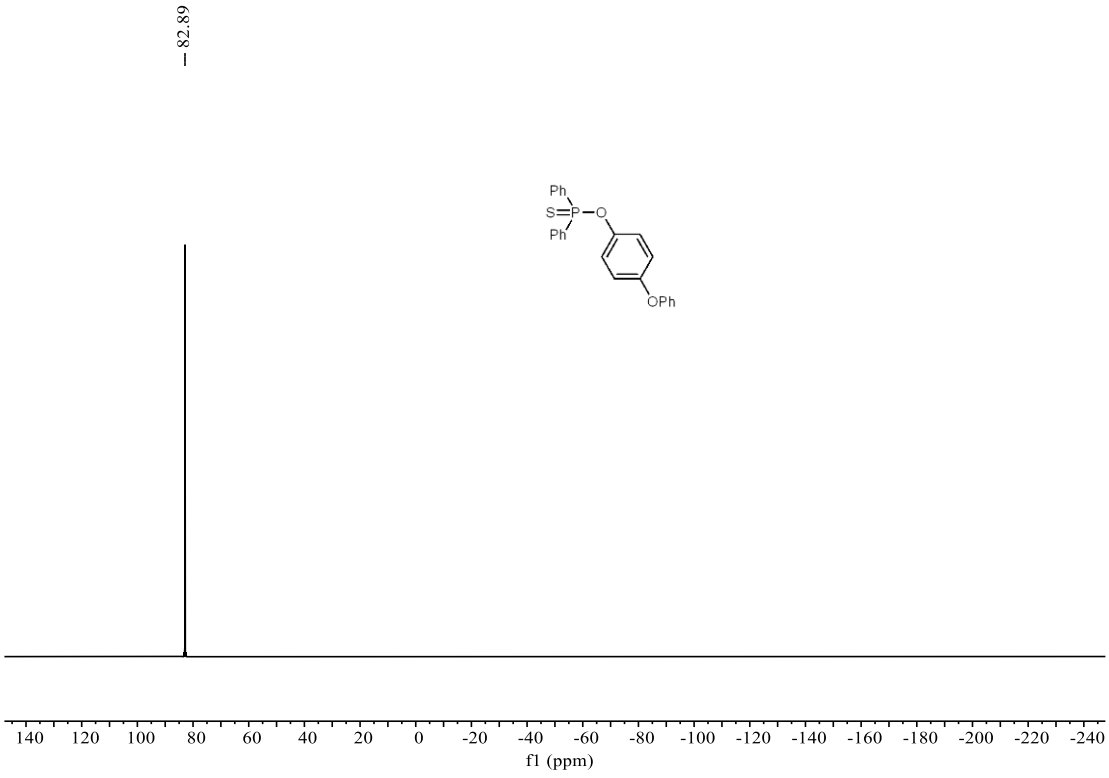




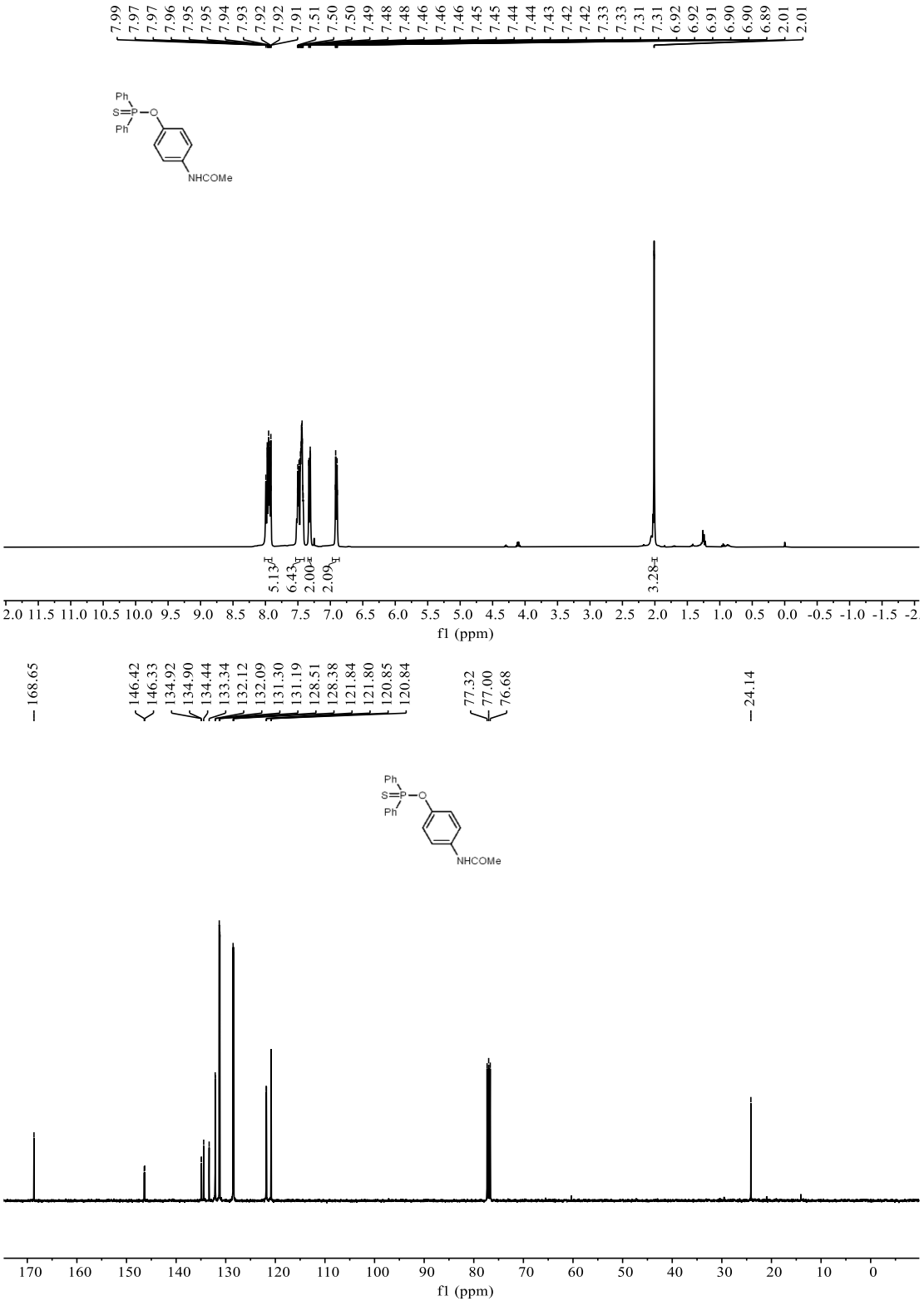
O-(4-phenoxyphenyl) diphenylphosphinothioate (**3aa'**)

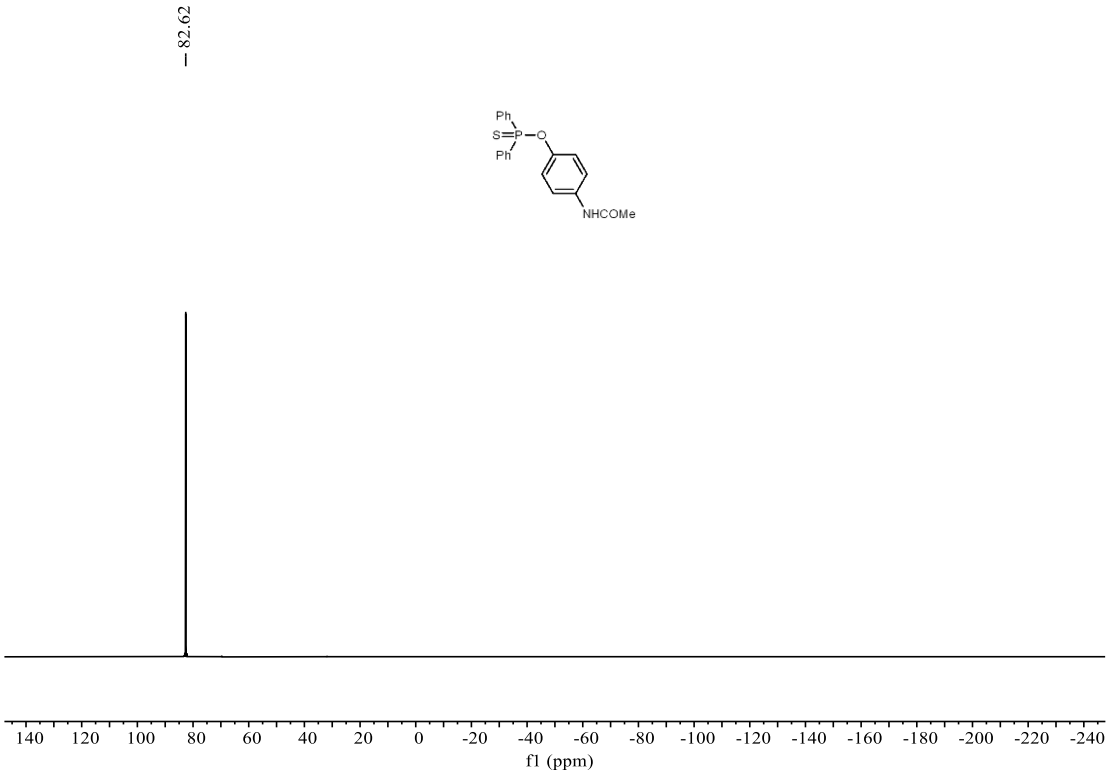



158.30
134.69
133.59
131.77
131.74
131.13
131.02
129.36
128.35
128.22
120.98
114.50
77.32
77.00
76.68
66.80
66.72
63.17
63.11
Ph
S
P
O
Ph
OPh
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

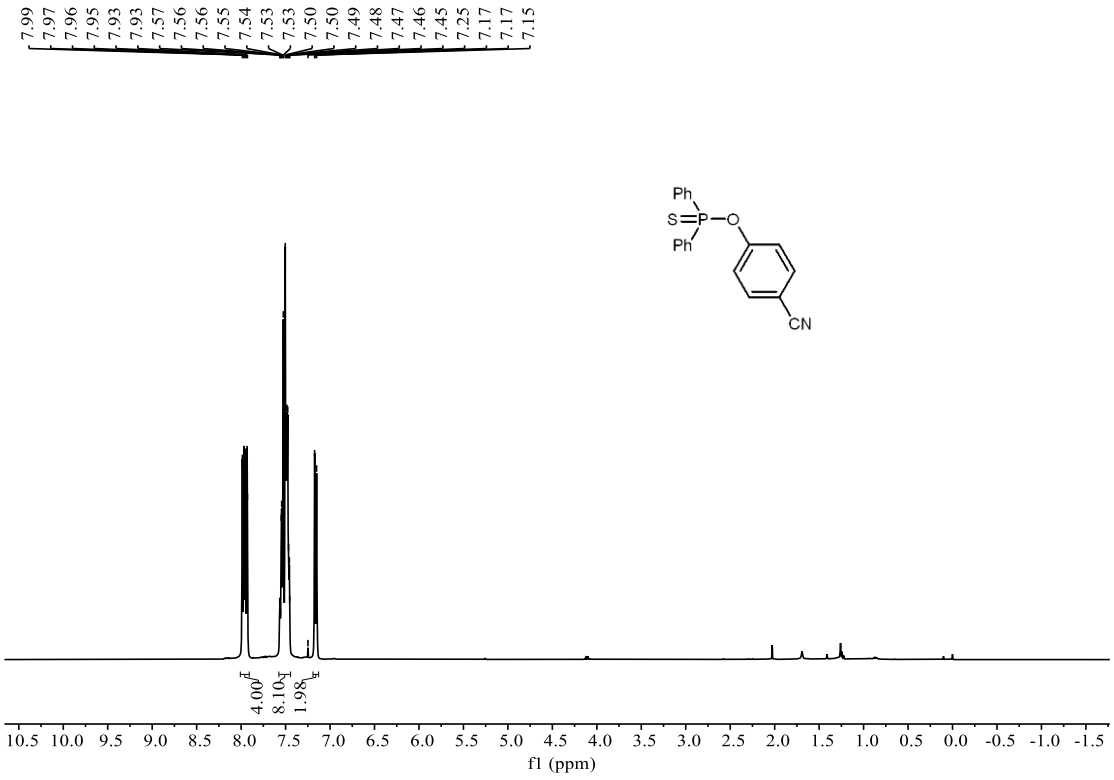

82.89
Ph
S
P
O
Ph
OPh
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

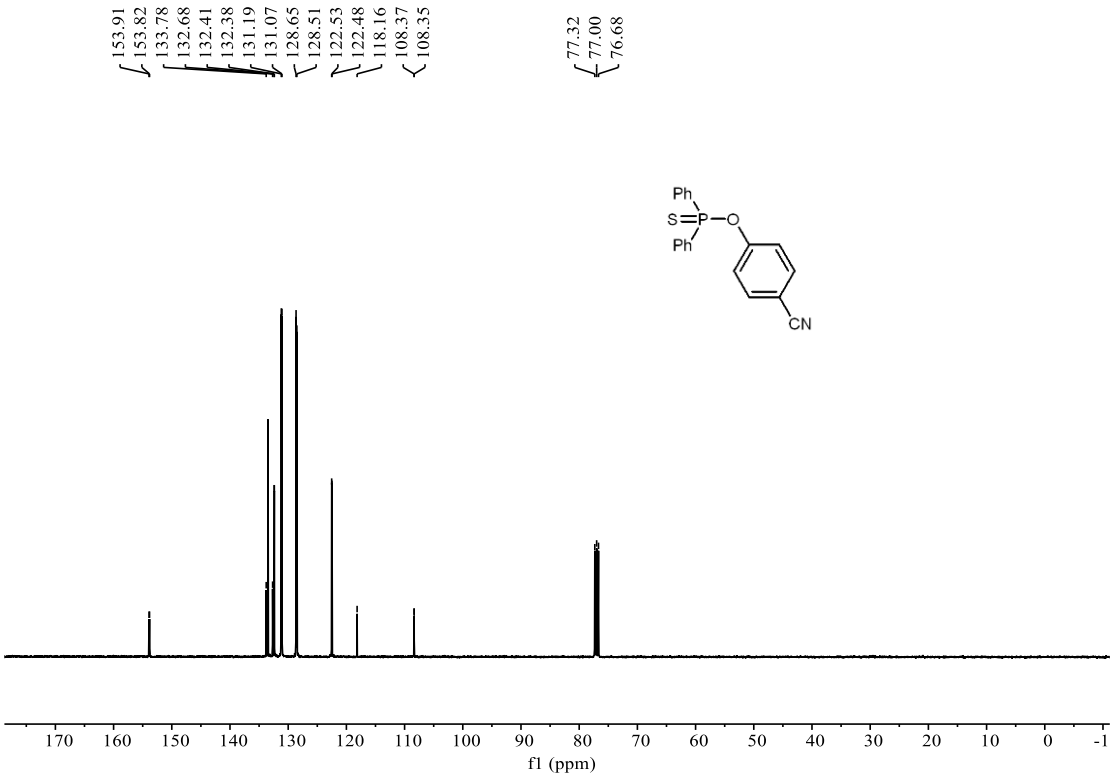
O-(4-acetamidophenyl) diphenylphosphinothioate (**3ab'**)

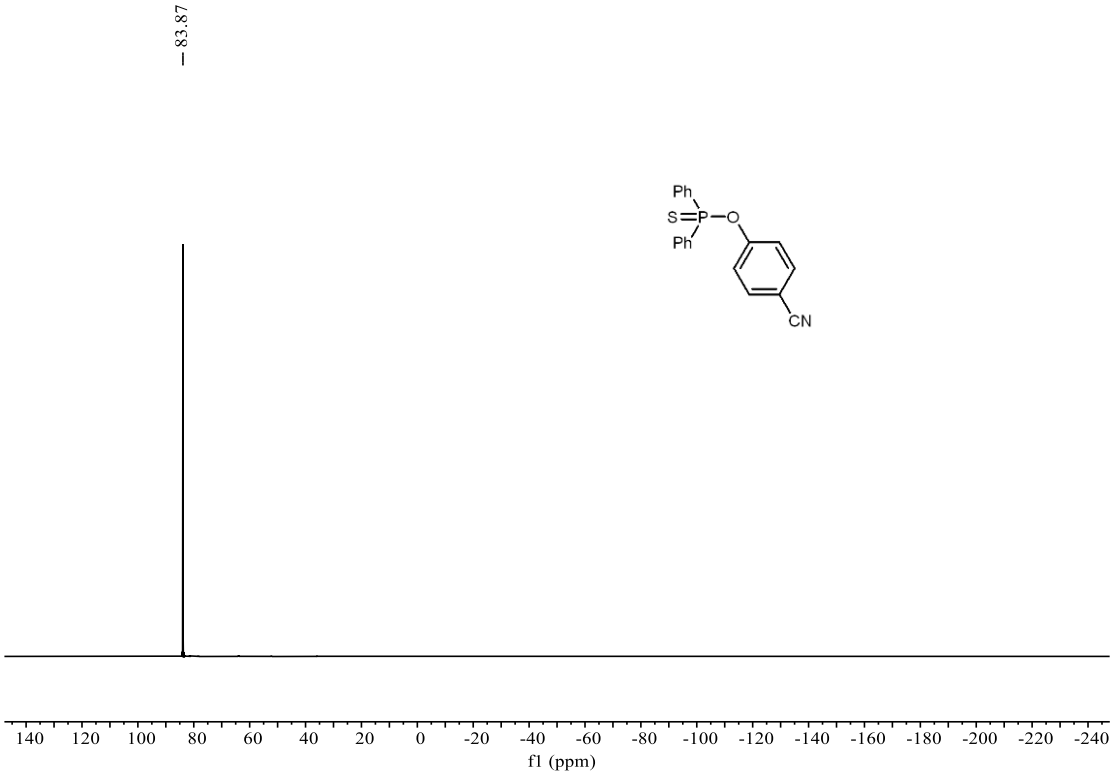




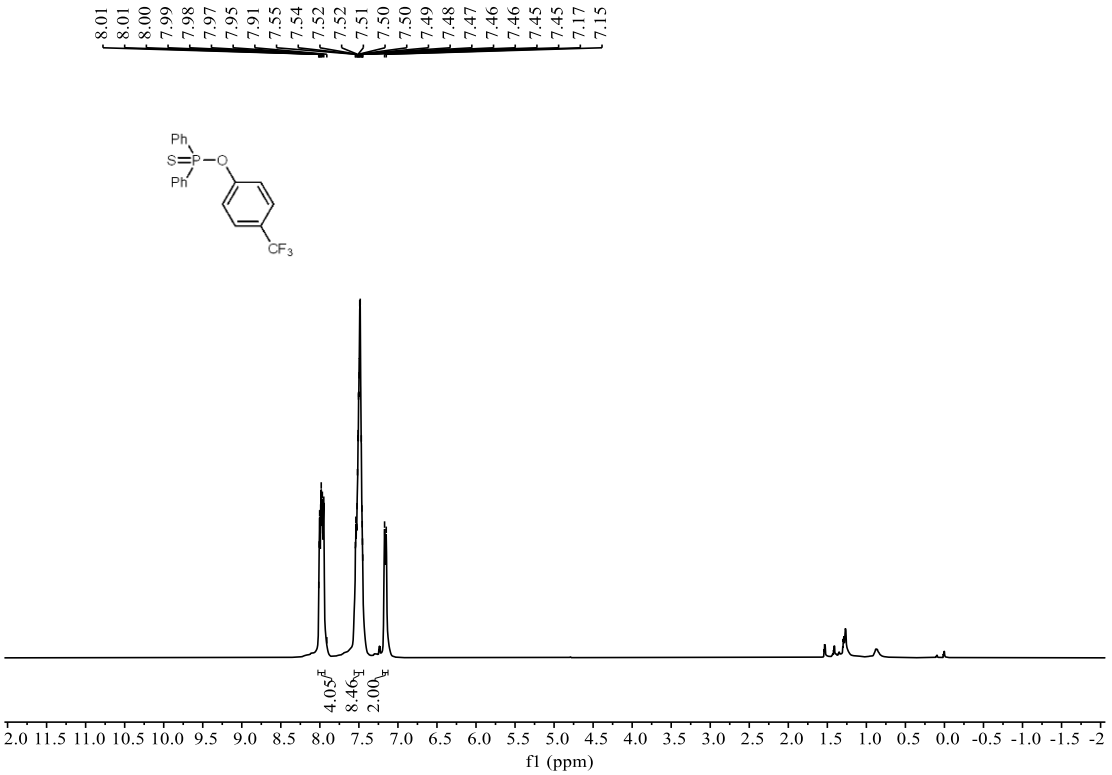
O-(4-cyanophenyl) diphenylphosphinothioate (**3ac'**)

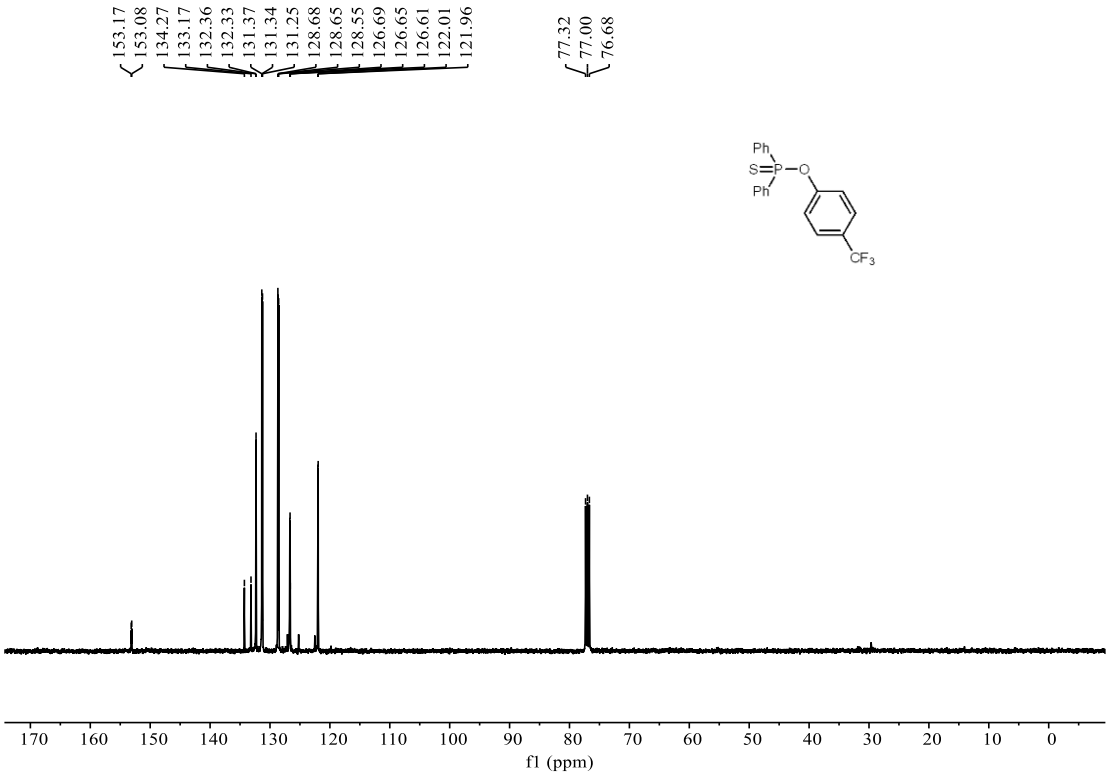


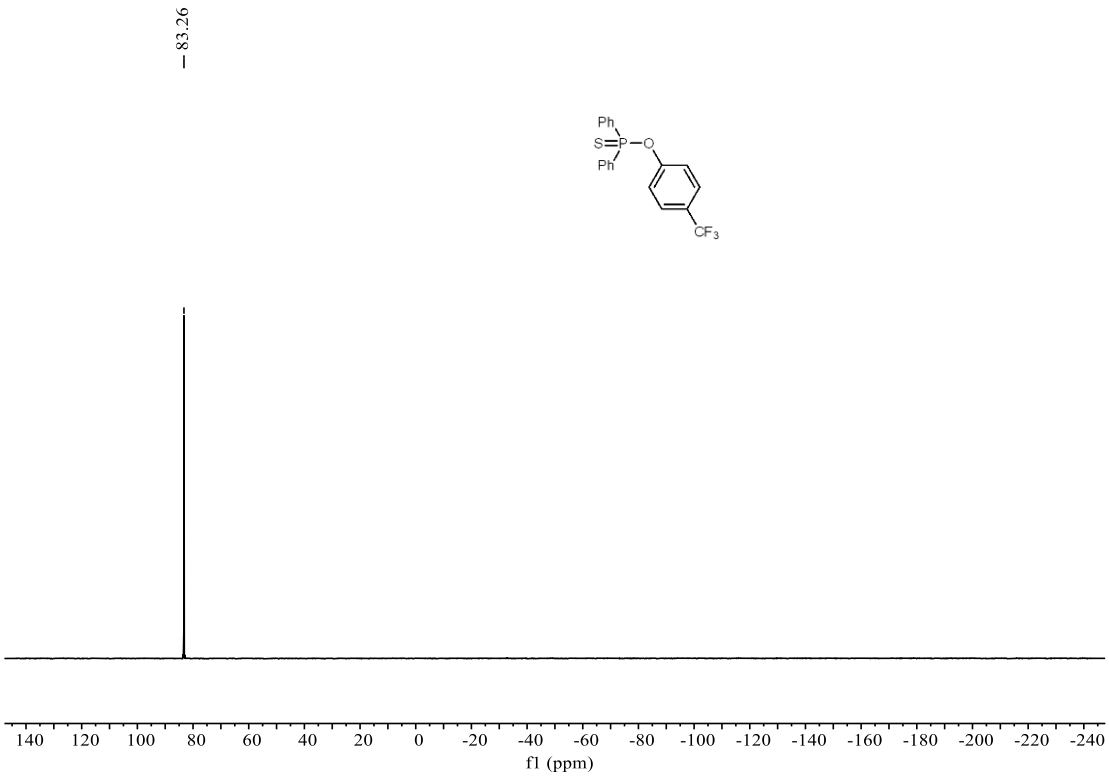

153.91
153.82
133.78
132.68
132.41
132.38
131.19
131.07
128.65
128.51
122.53
122.48
118.16
108.37
108.35
77.32
77.00
76.68
Ph
S
P
O
Ph
CN
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

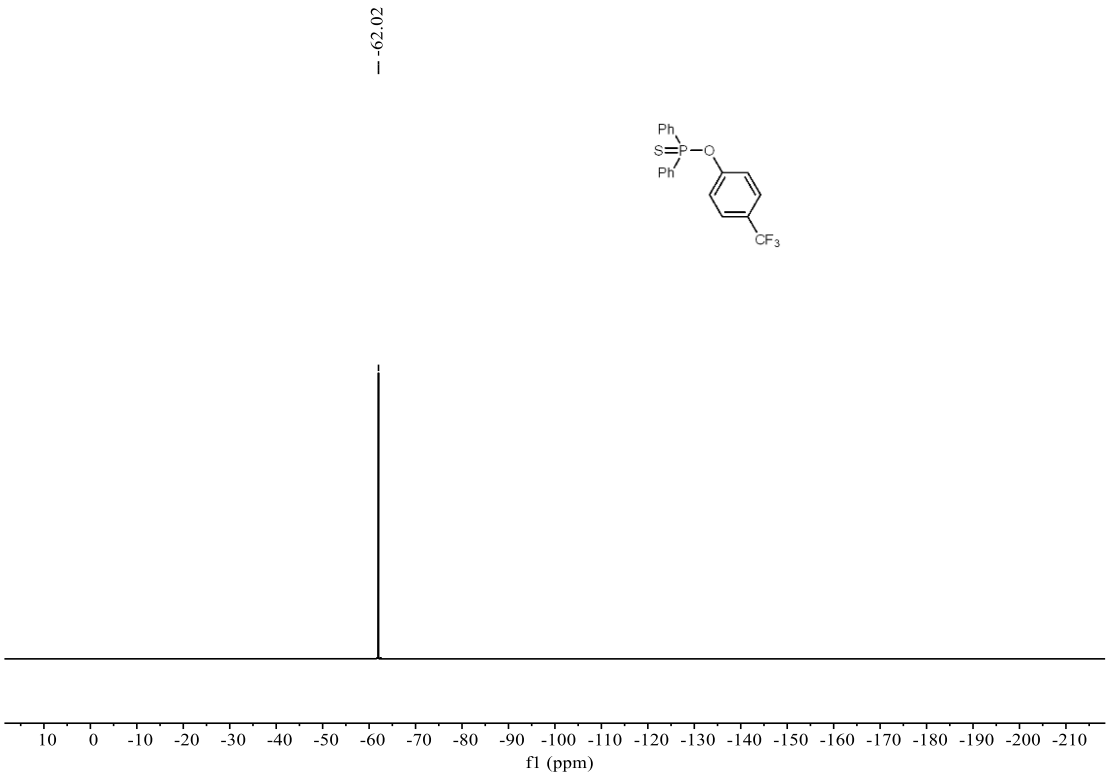

83.87
Ph
S
P
O
Ph
CN
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

O-(4-(trifluoromethyl)phenyl) diphenylphosphinothioate (**3ad'**)

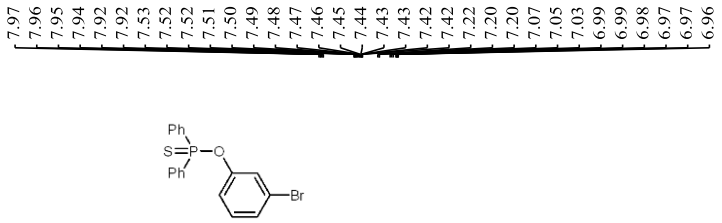


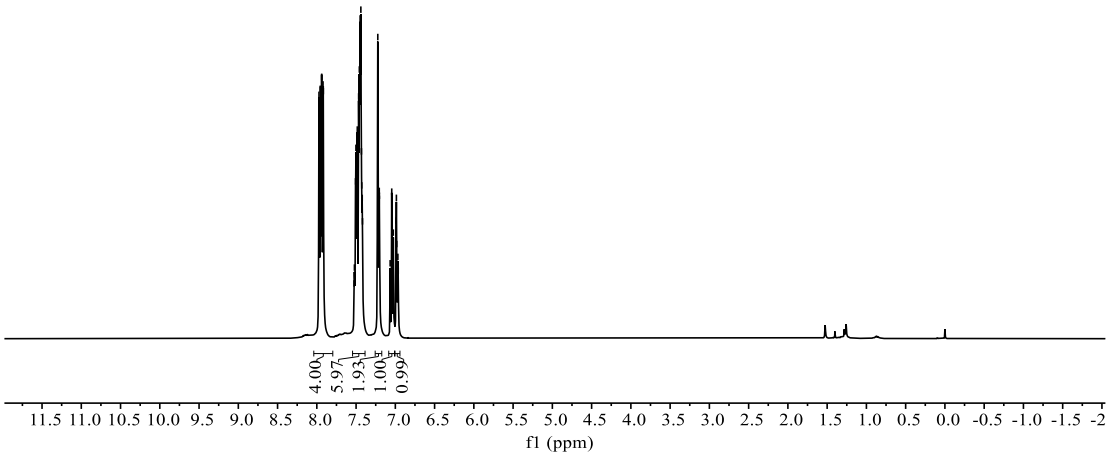


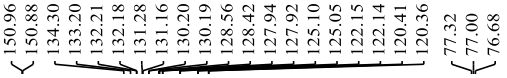

83.26
Ph
S
P
O
Ph
CF3
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

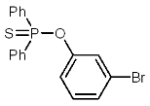

-62.02
Ph
S
P
O
Ph
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

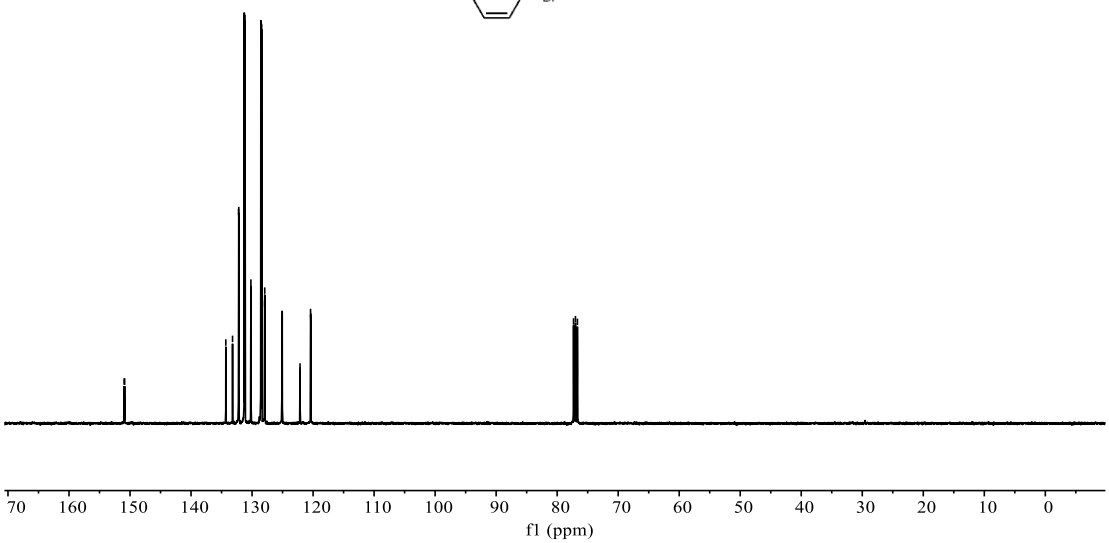
O-(3-bromophenyl) diphenylphosphinothioate (**3ae'**)

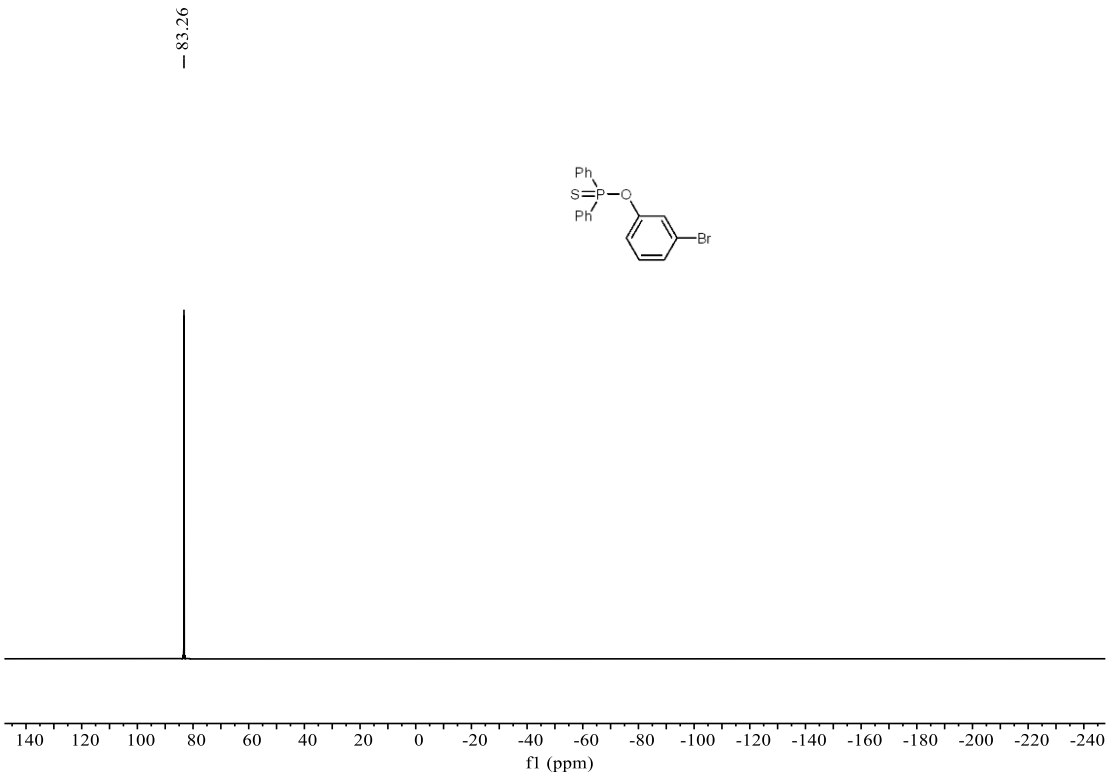




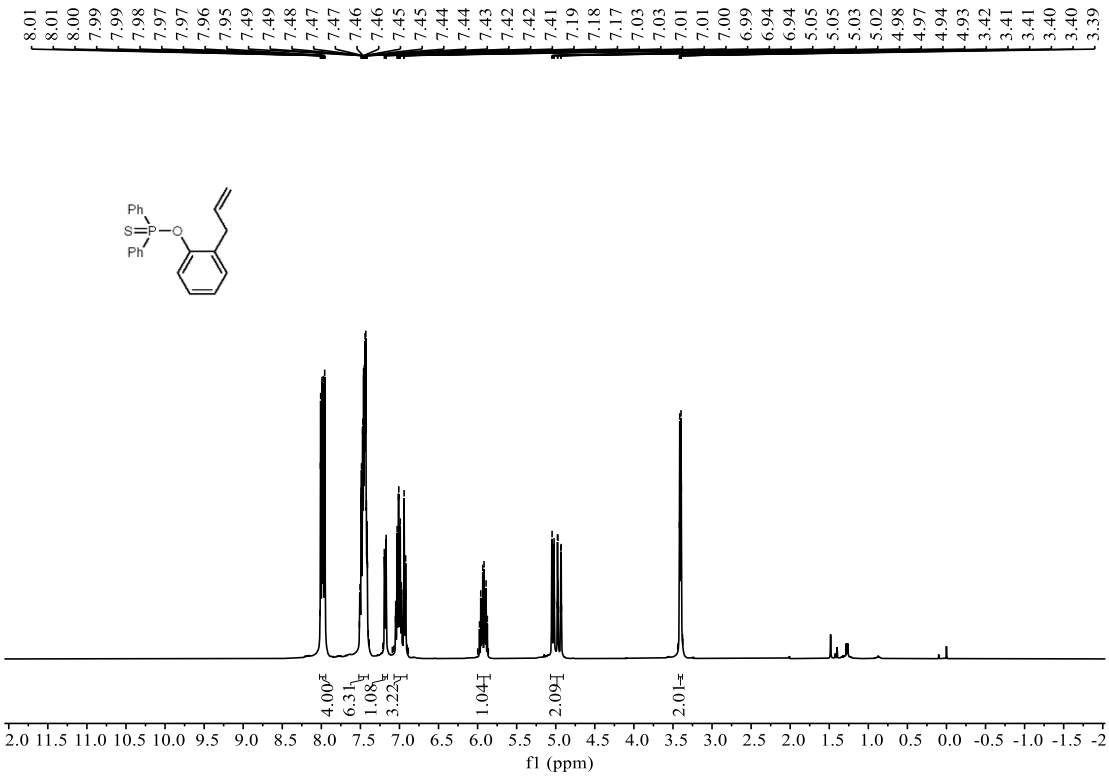


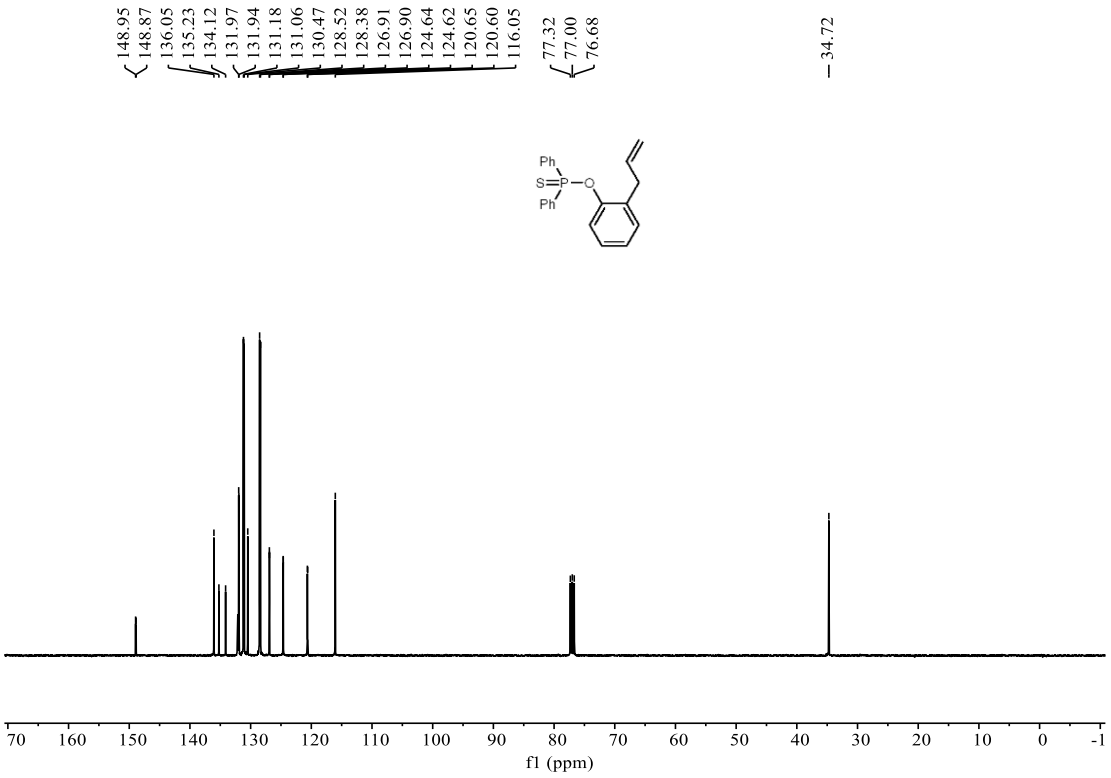


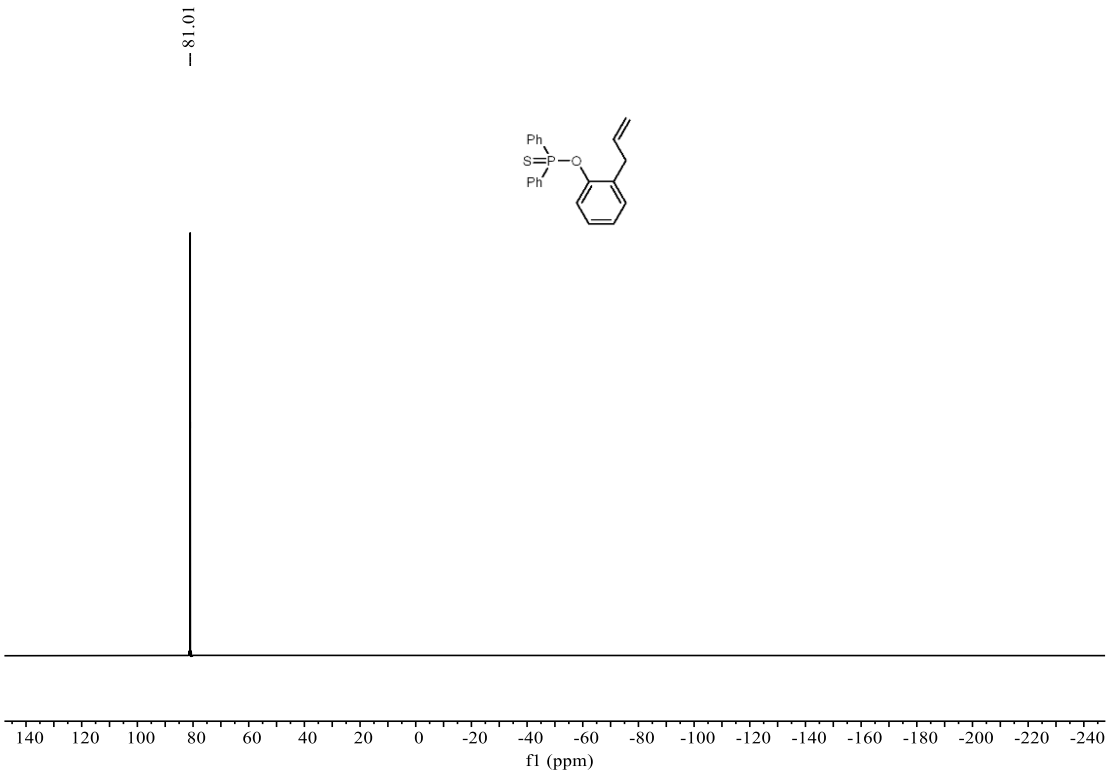




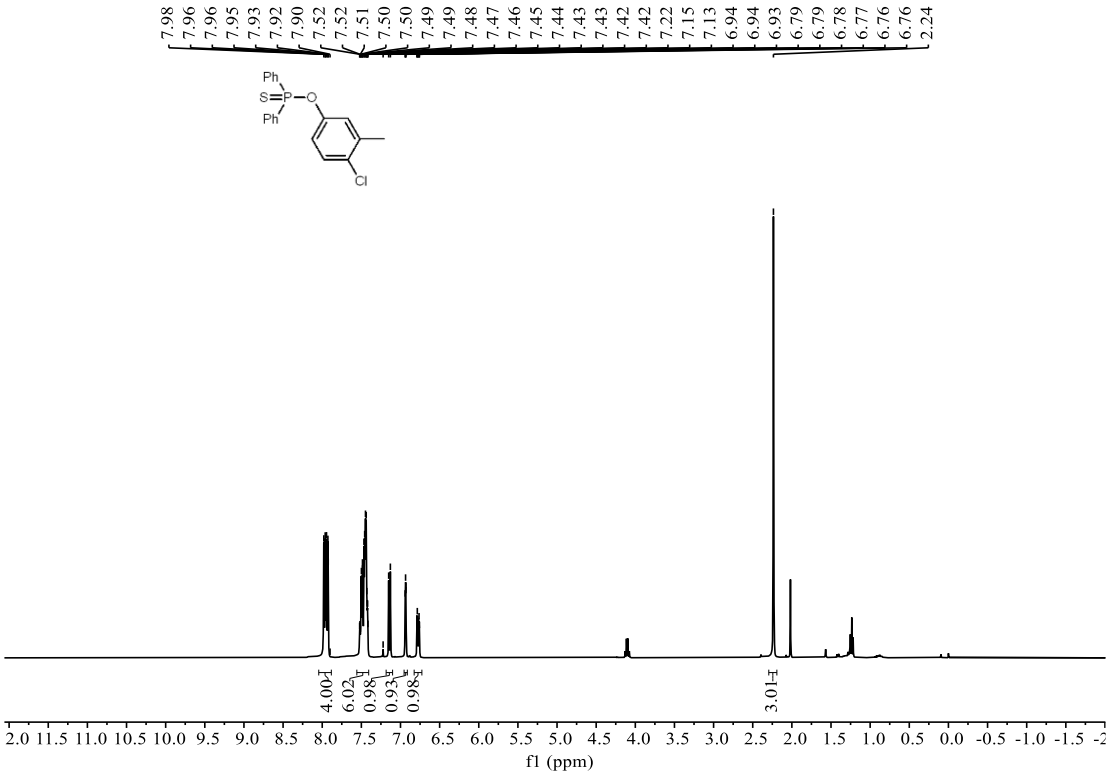
O-(2-allylphenyl) diphenylphosphinothioate (**3af'**)

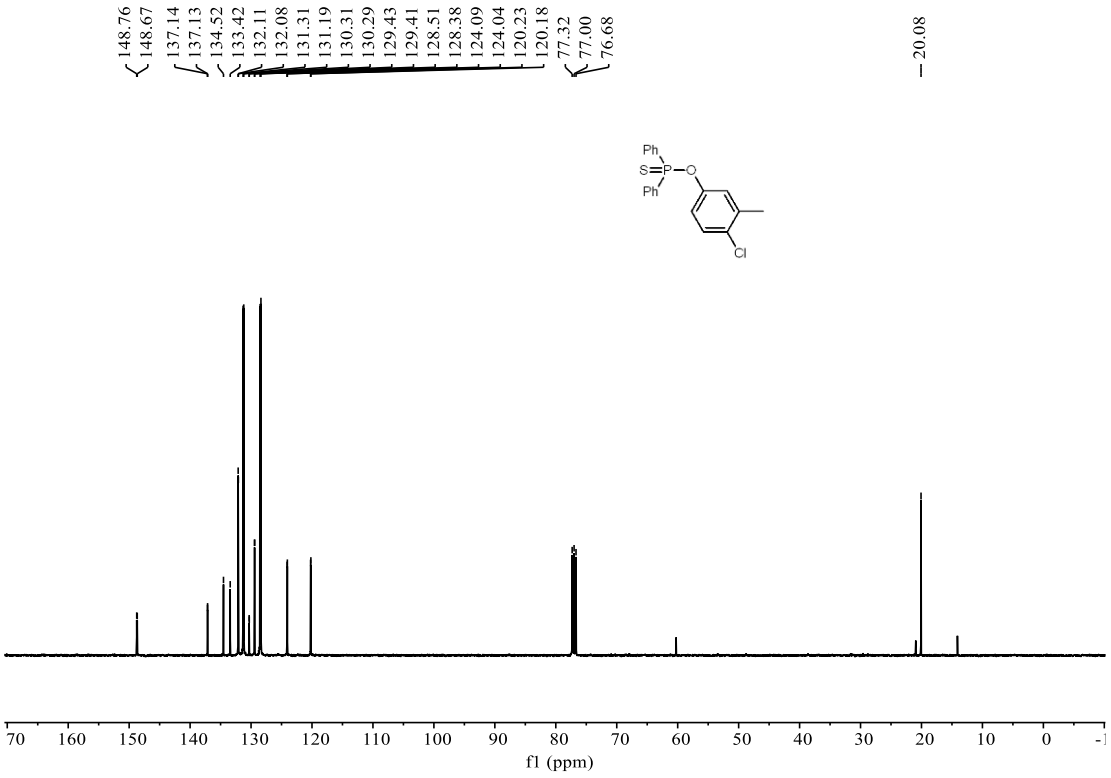


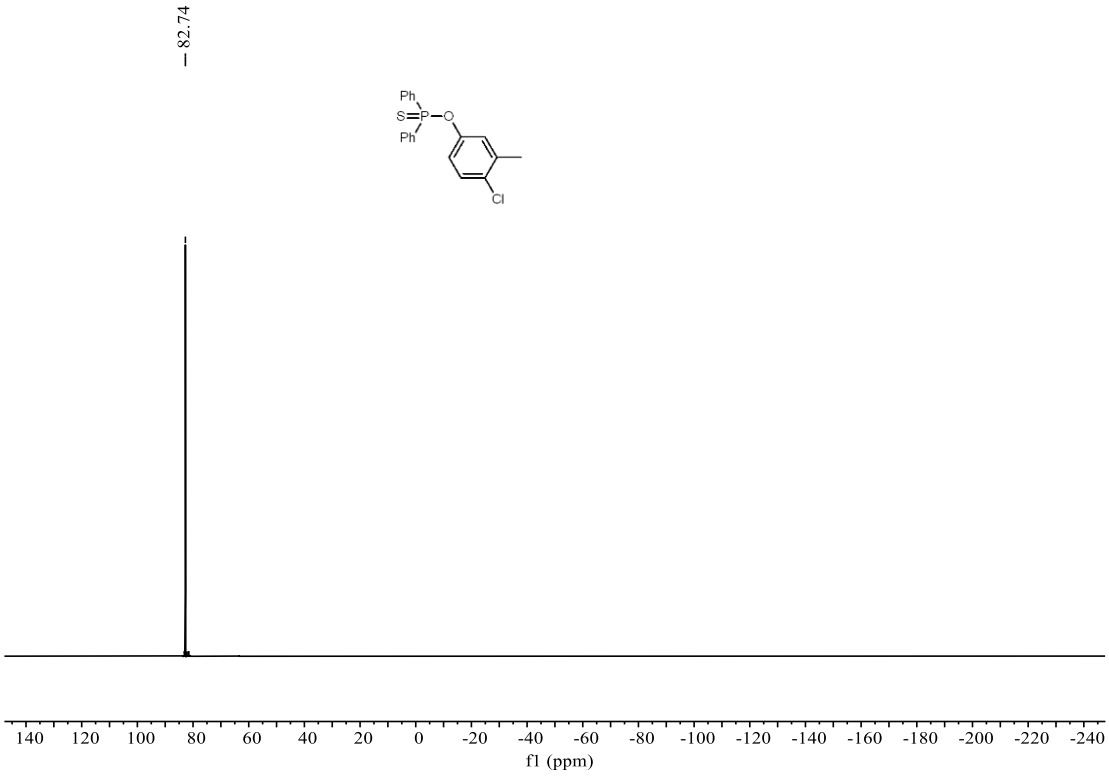

148.95
148.87
136.05
135.23
134.12
131.97
131.94
131.18
131.06
130.47
128.52
128.38
126.91
126.90
124.64
124.62
120.65
120.60
116.05
77.32
77.00
76.68
34.72
Ph
S
P
O
Ph
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


81.01
Ph
S
P
O
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

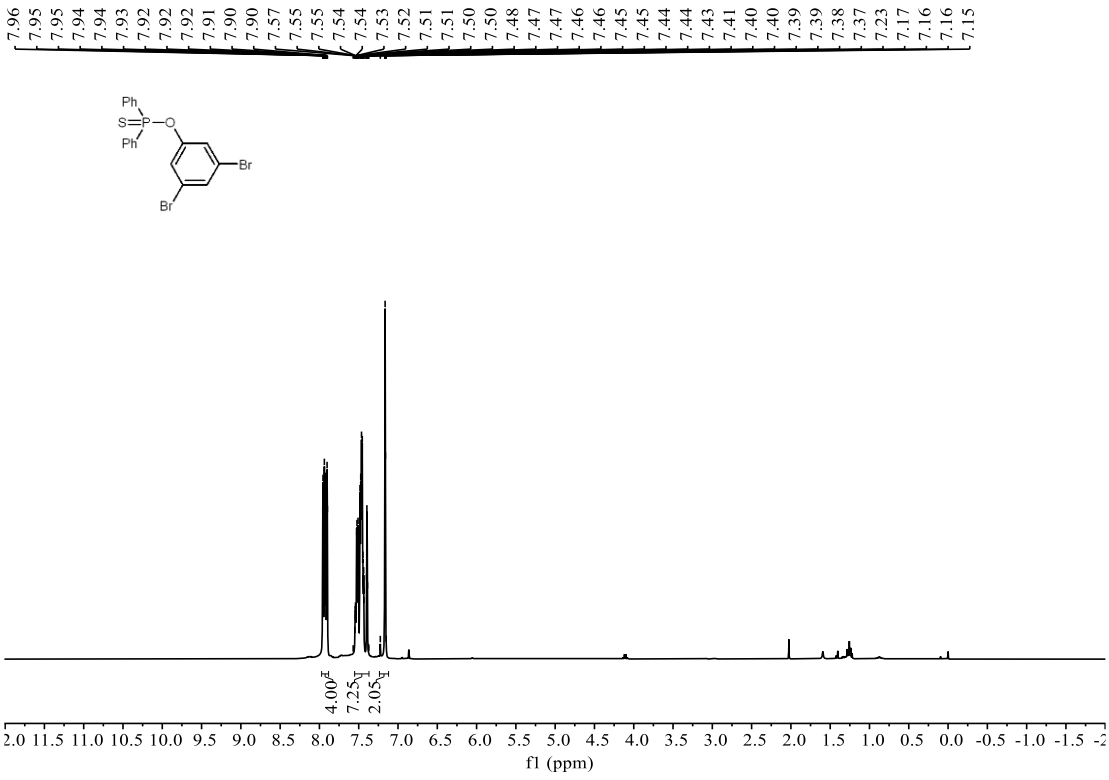
O-(4-chloro-3-methylphenyl) diphenylphosphinothioate (**3ag'**)

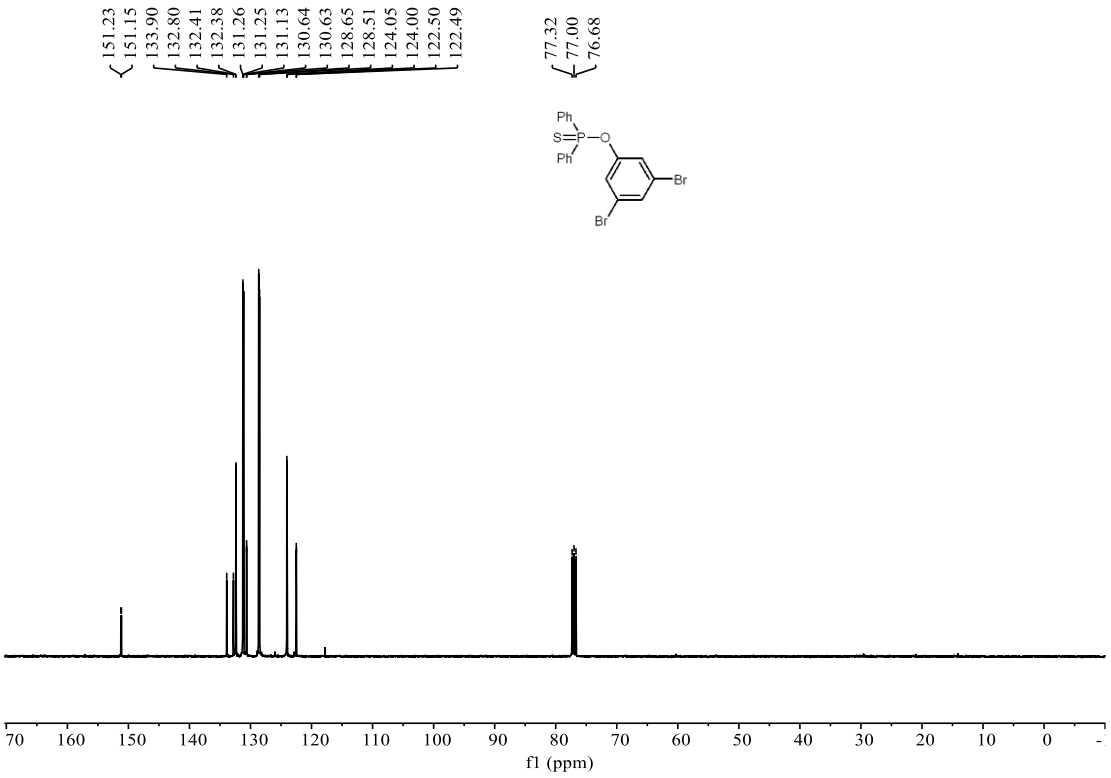


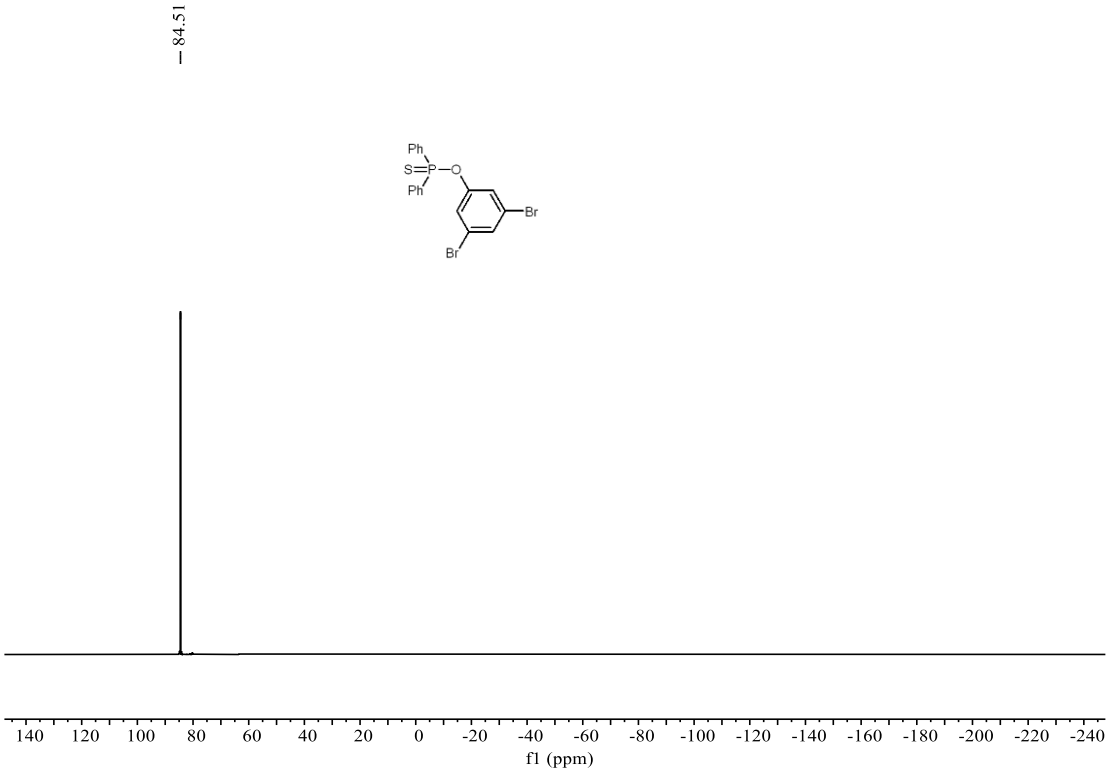




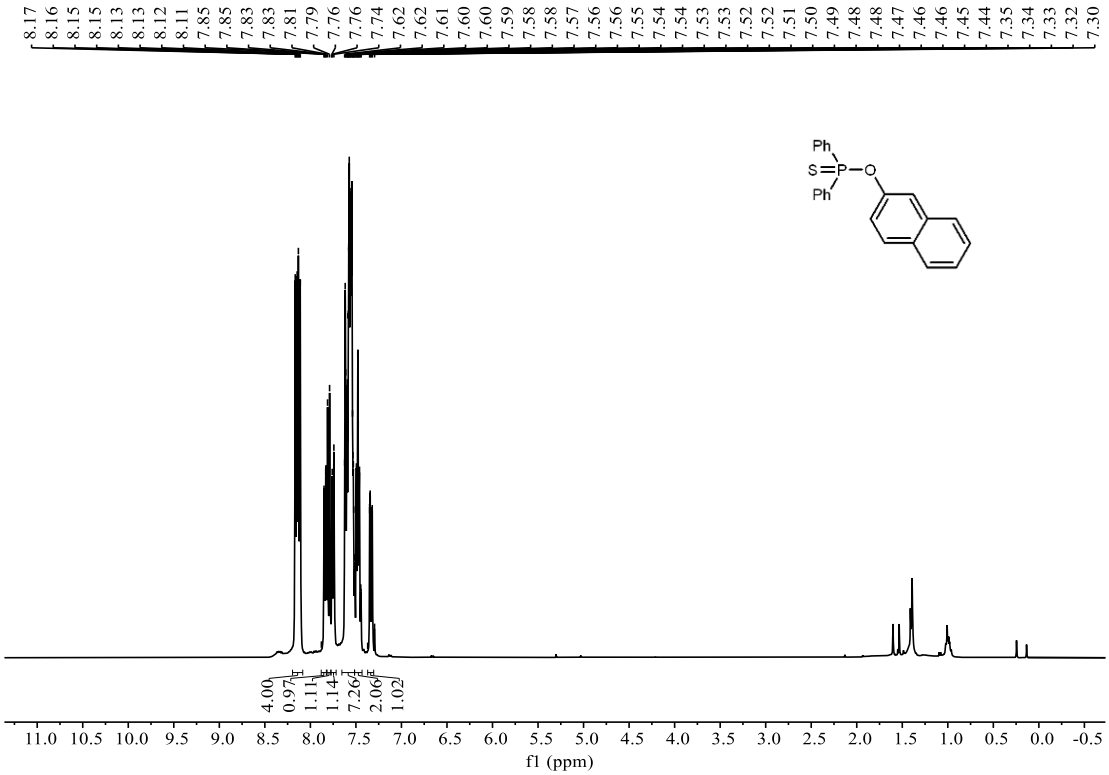
O-(3,5-dibromophenyl) diphenylphosphinothioate (**3ah'**)

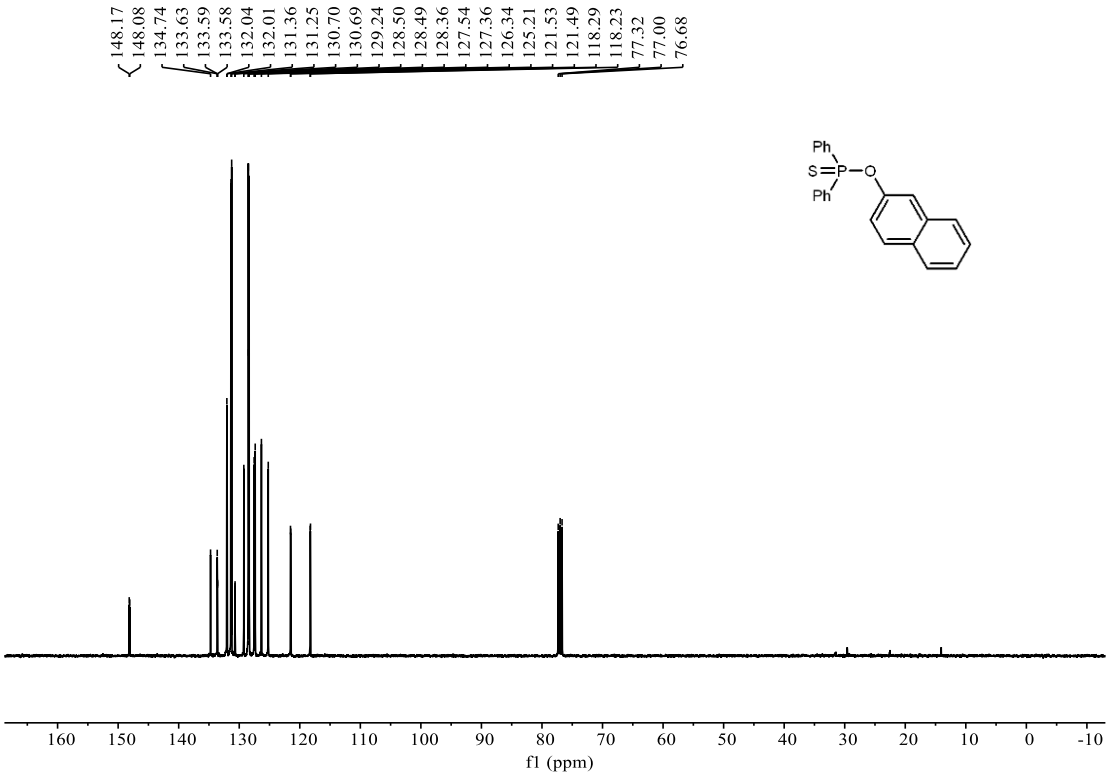


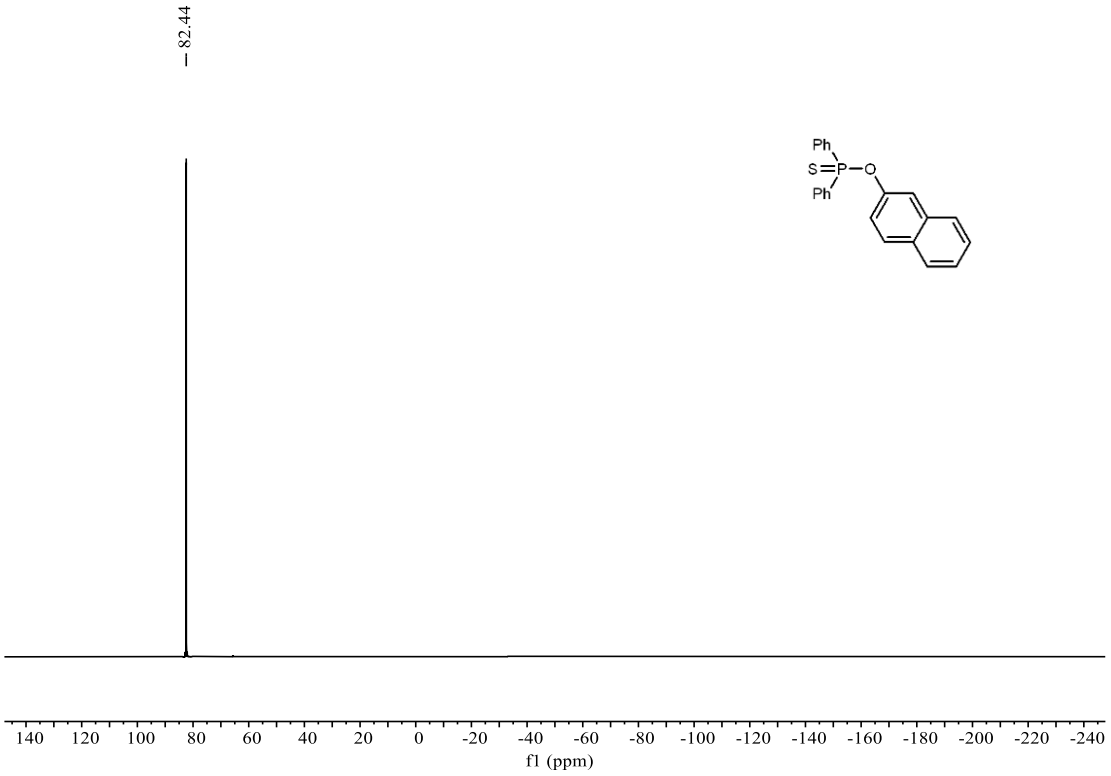

151.23
151.15
133.90
132.80
132.41
132.38
131.26
131.25
131.13
130.64
130.63
128.65
128.51
124.05
124.00
122.50
122.49
77.32
77.00
76.68
Ph
S
P
O
Ph
Br
Br
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)


84.51
Ph
S
P
O
Ph
Br
Br
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

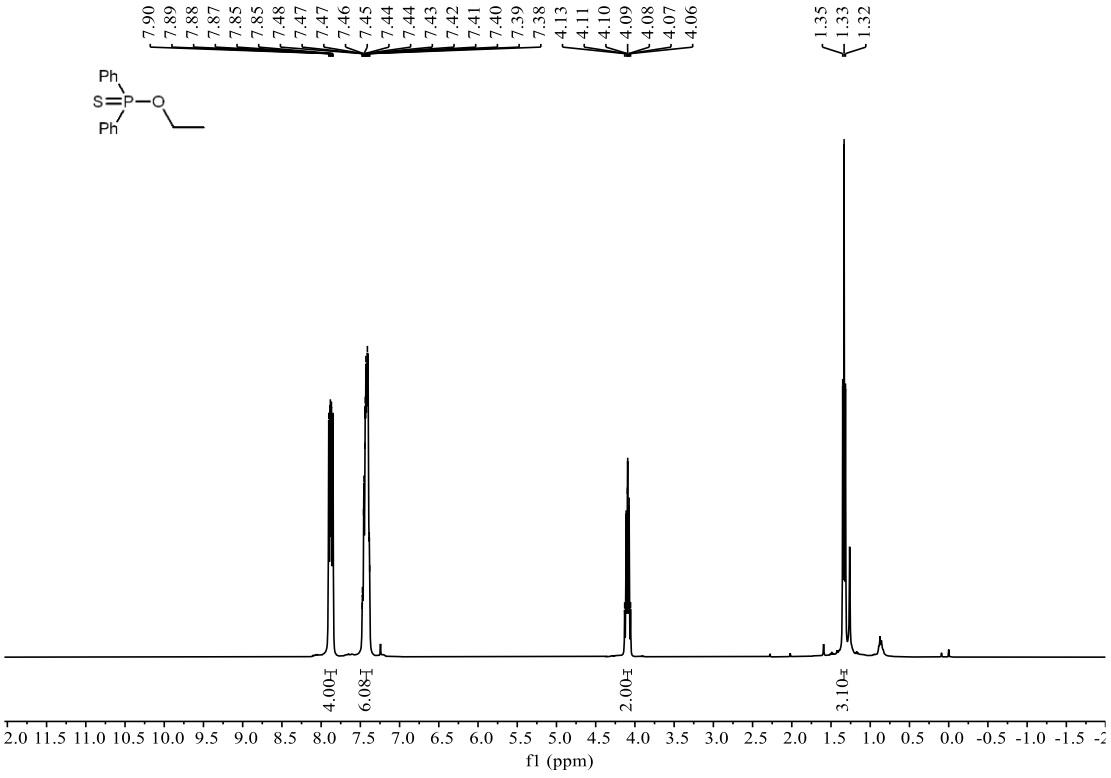
O-(naphthalen-2-yl) diphenylphosphinothioate (**3ai'**)

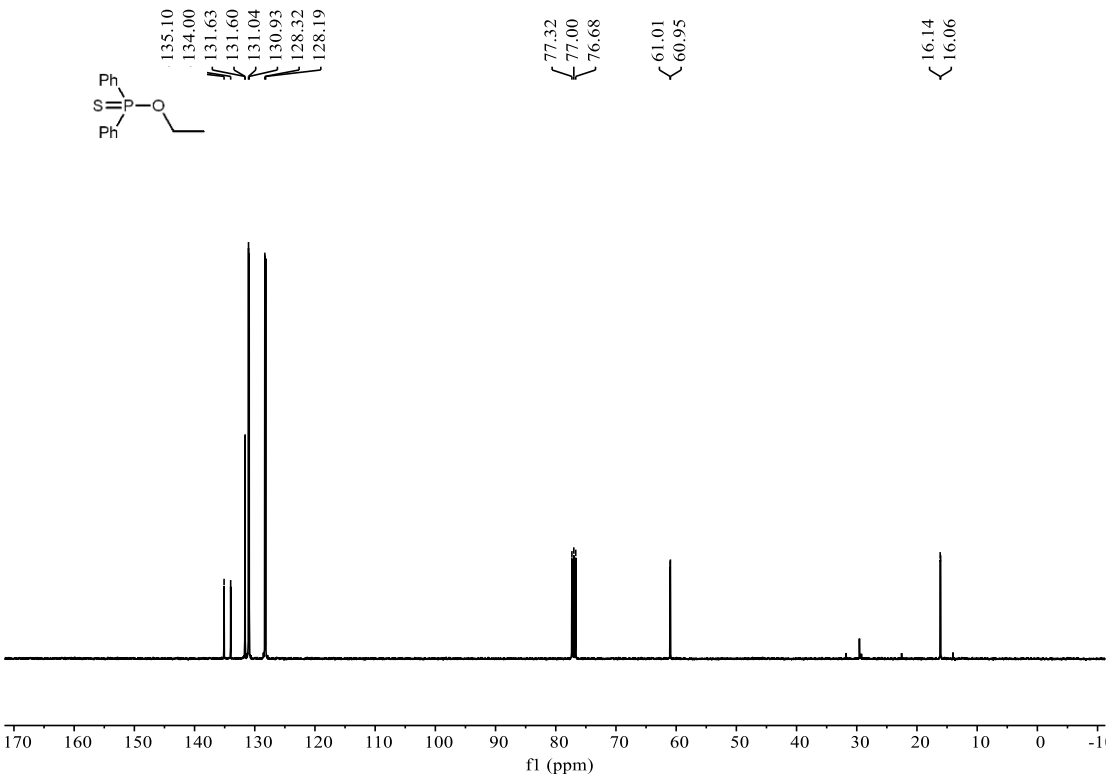


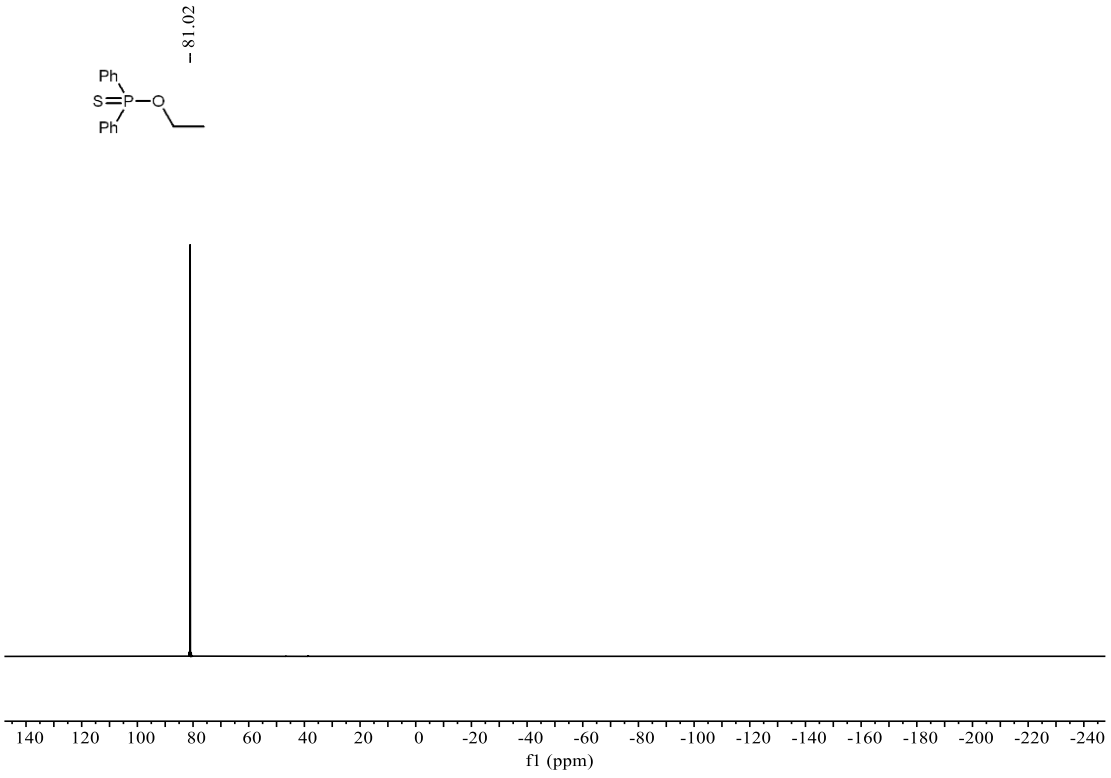




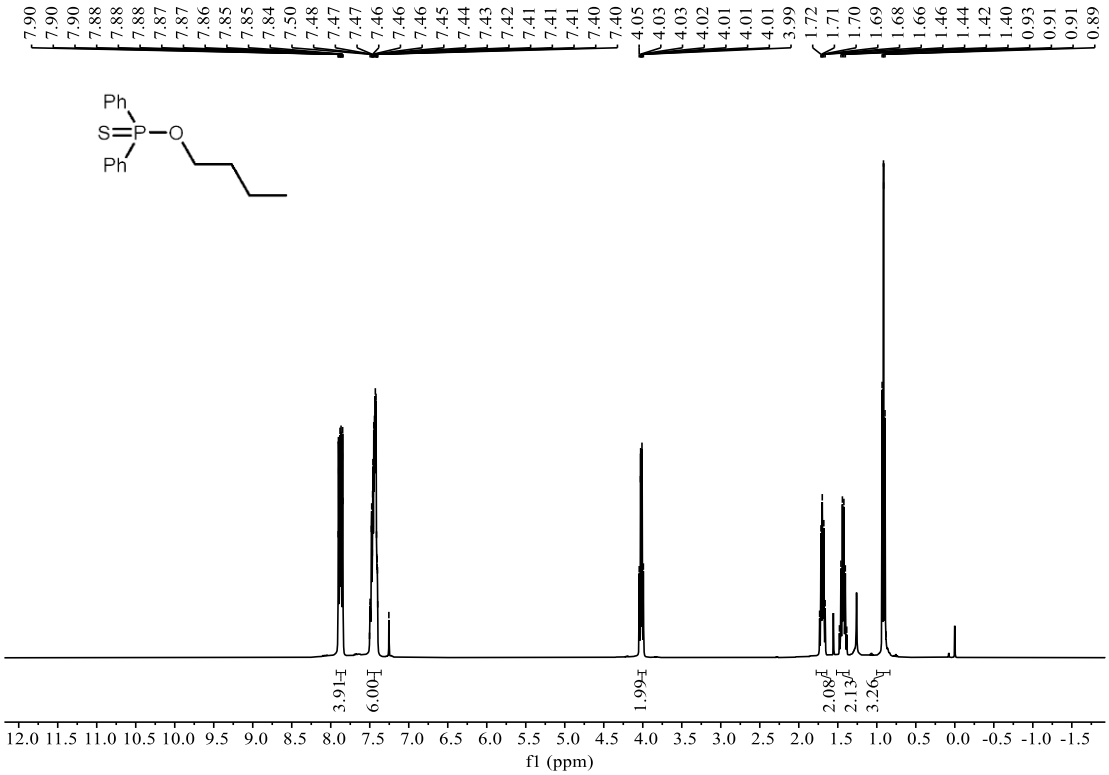
O-ethyl diphenylphosphinothioate (**3aj'**)

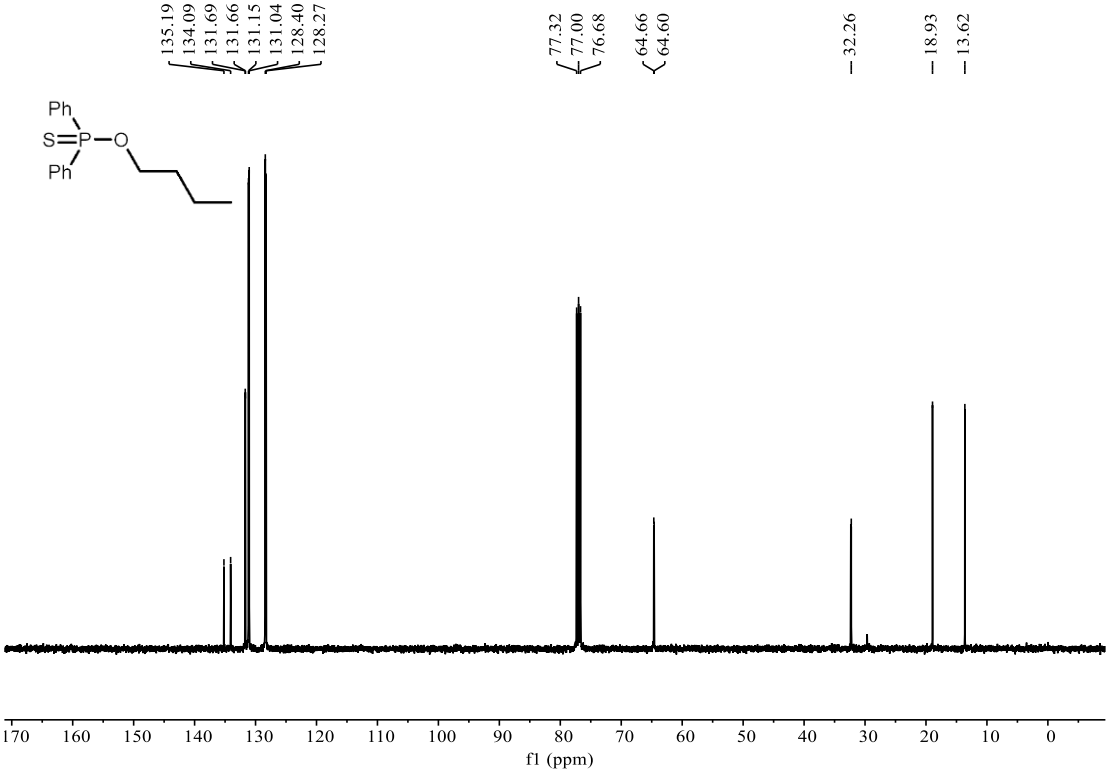


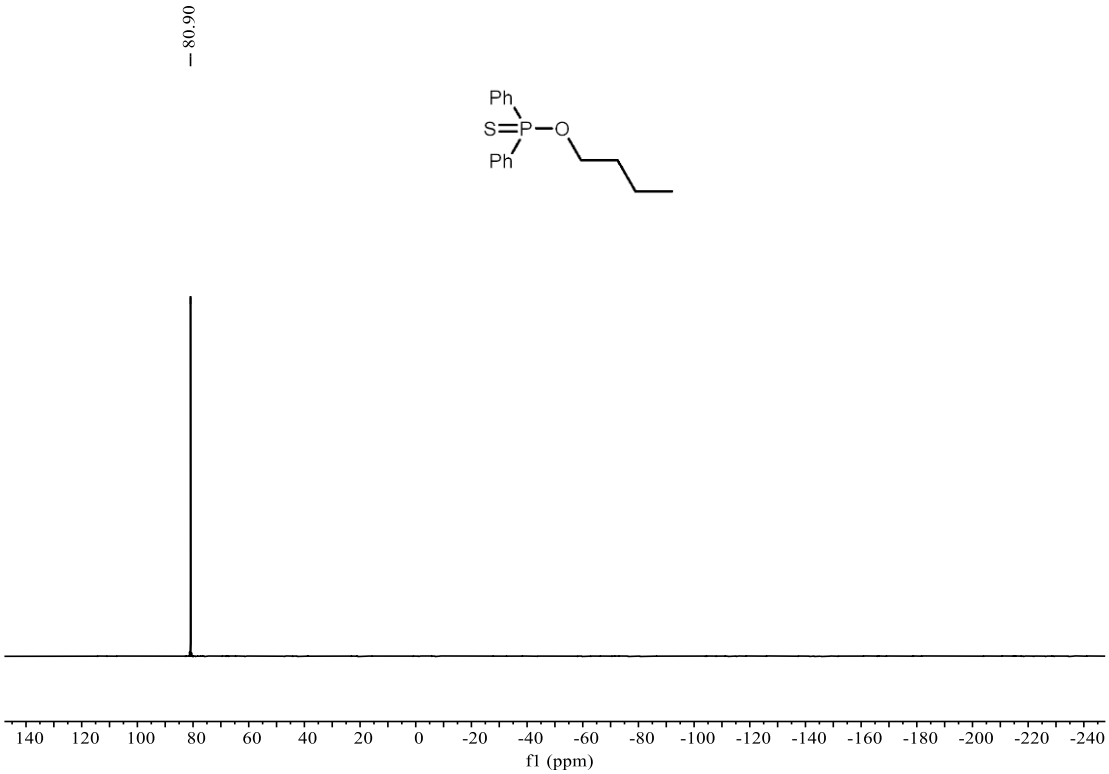

135.10
134.00
131.63
131.60
131.04
130.93
128.32
128.19
77.32
77.00
76.68
61.01
60.95
16.14
16.06
Ph
S
P
O
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


81.02
Ph
S
P
O
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

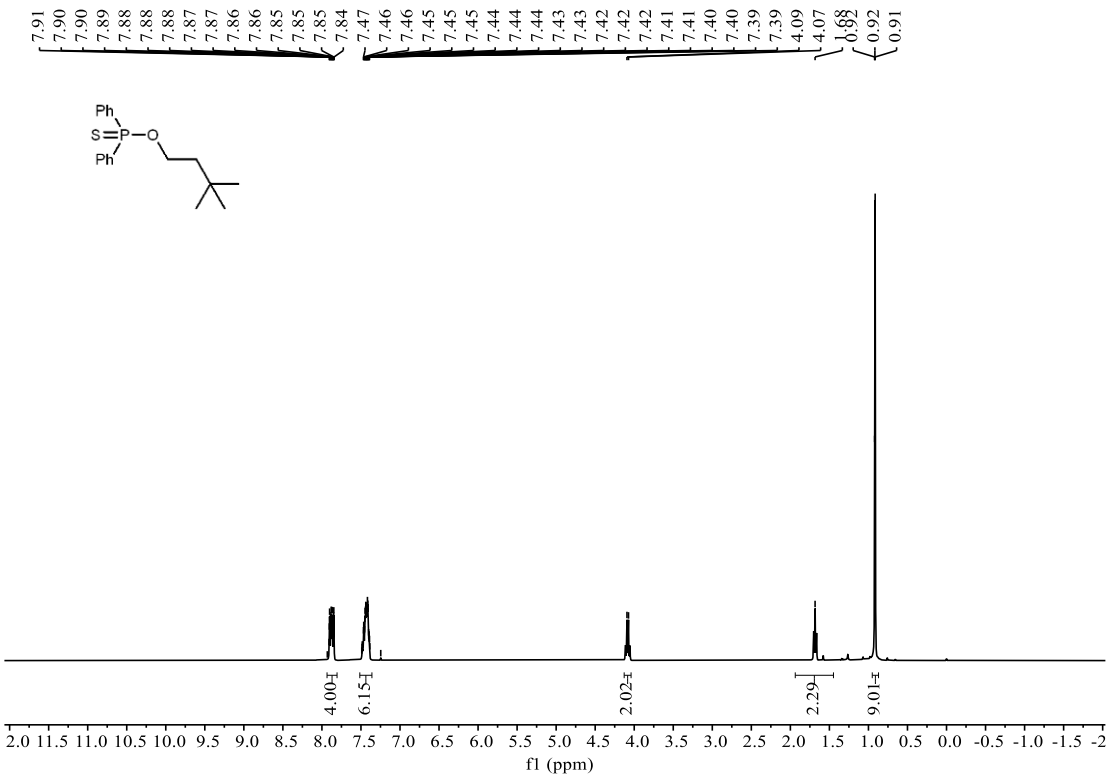
O-butyl diphenylphosphinothioate (**3ak'**)

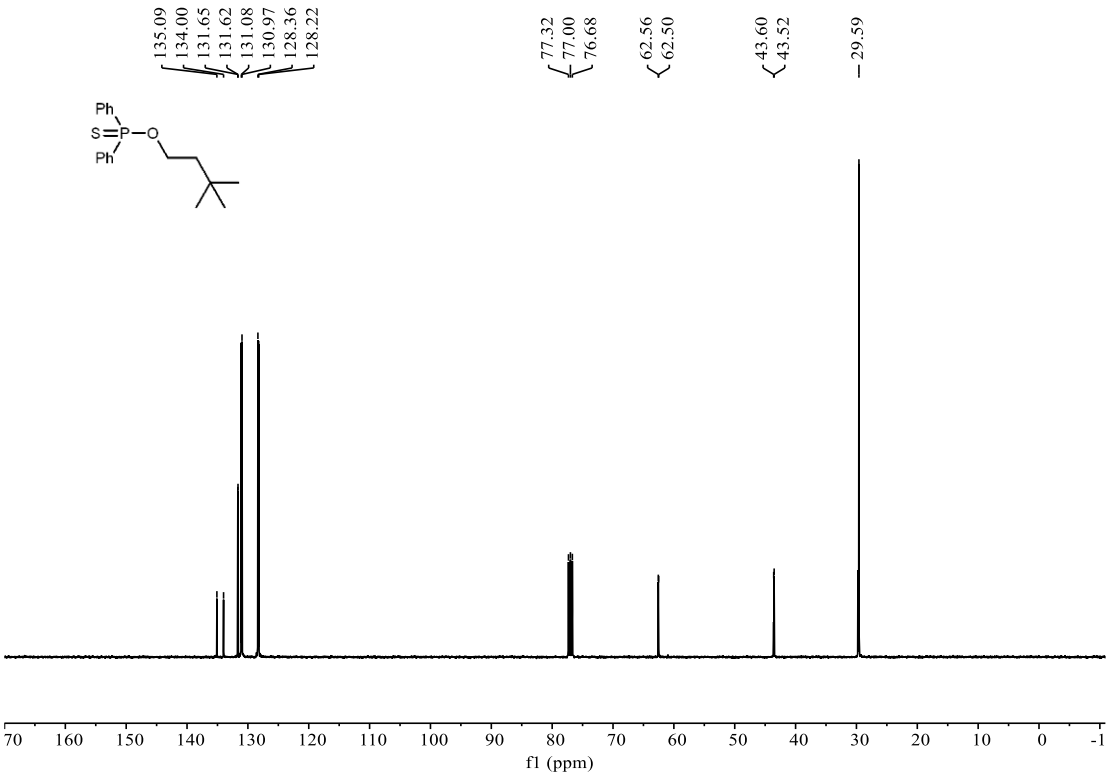


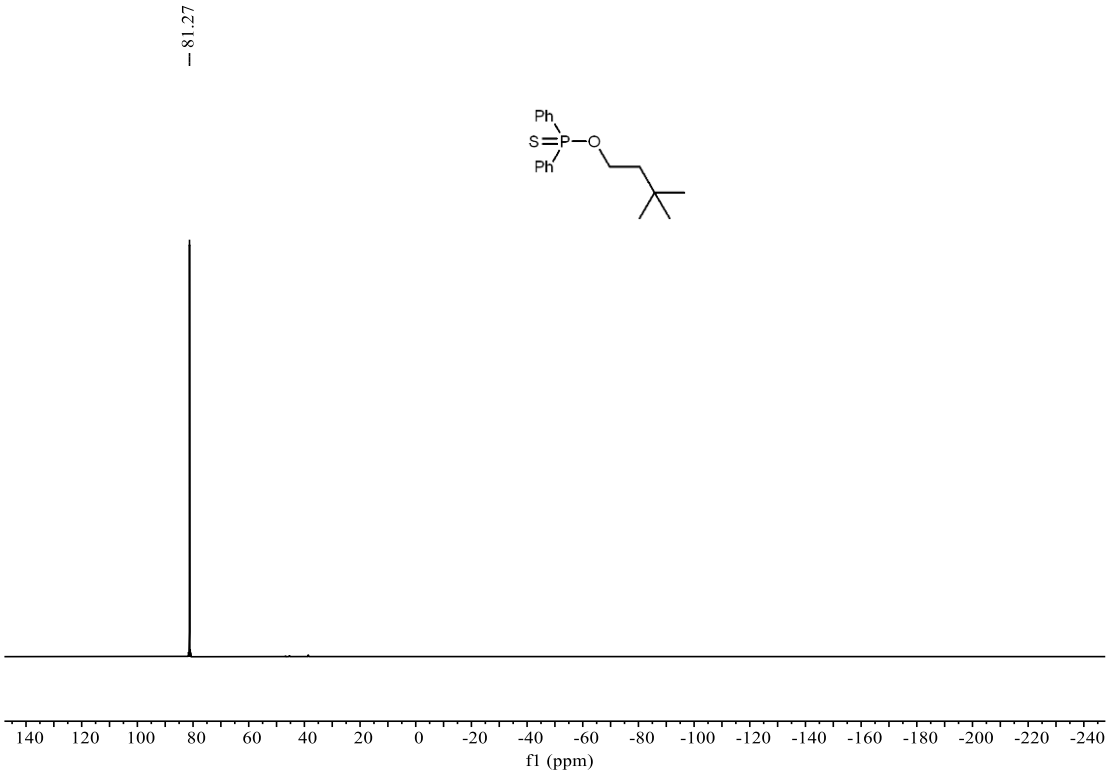




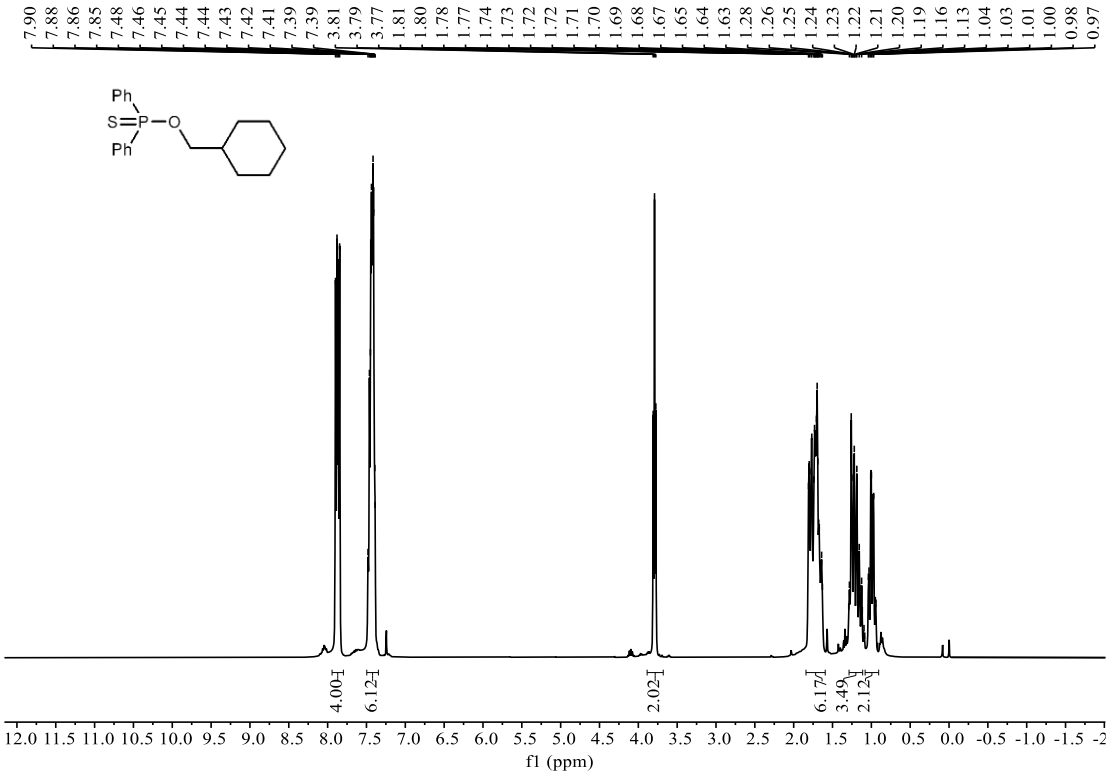
O-(3,3-dimethylbutyl) diphenylphosphinothioate (**3al'**)

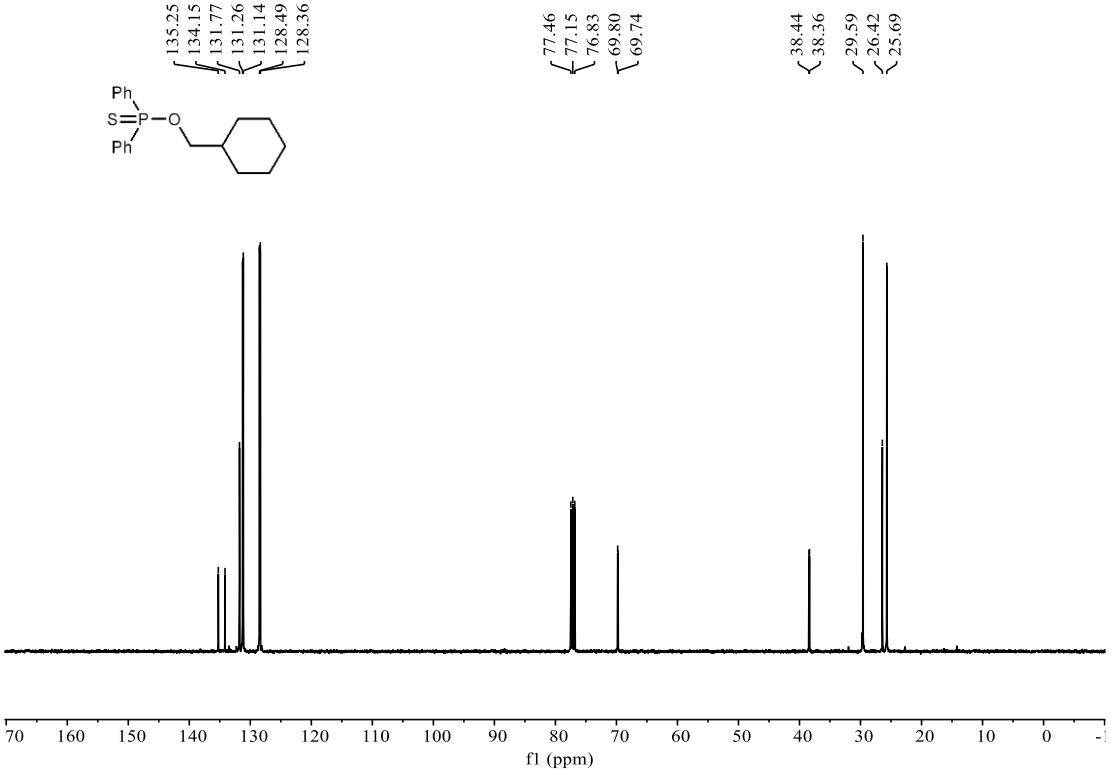


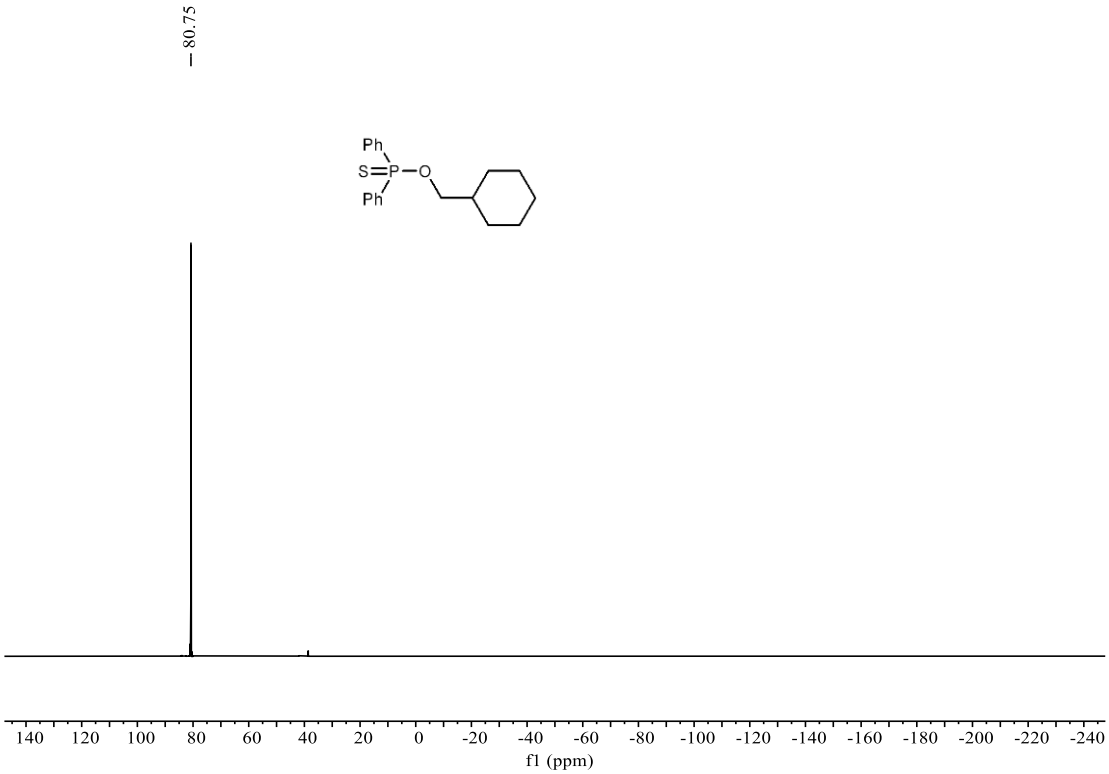

135.09
134.00
131.65
131.62
131.08
130.97
128.36
128.22
77.32
77.00
76.68
62.56
62.50
43.60
43.52
29.59
Ph
S=P—O
Ph
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


81.27
Ph
S=P—O
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

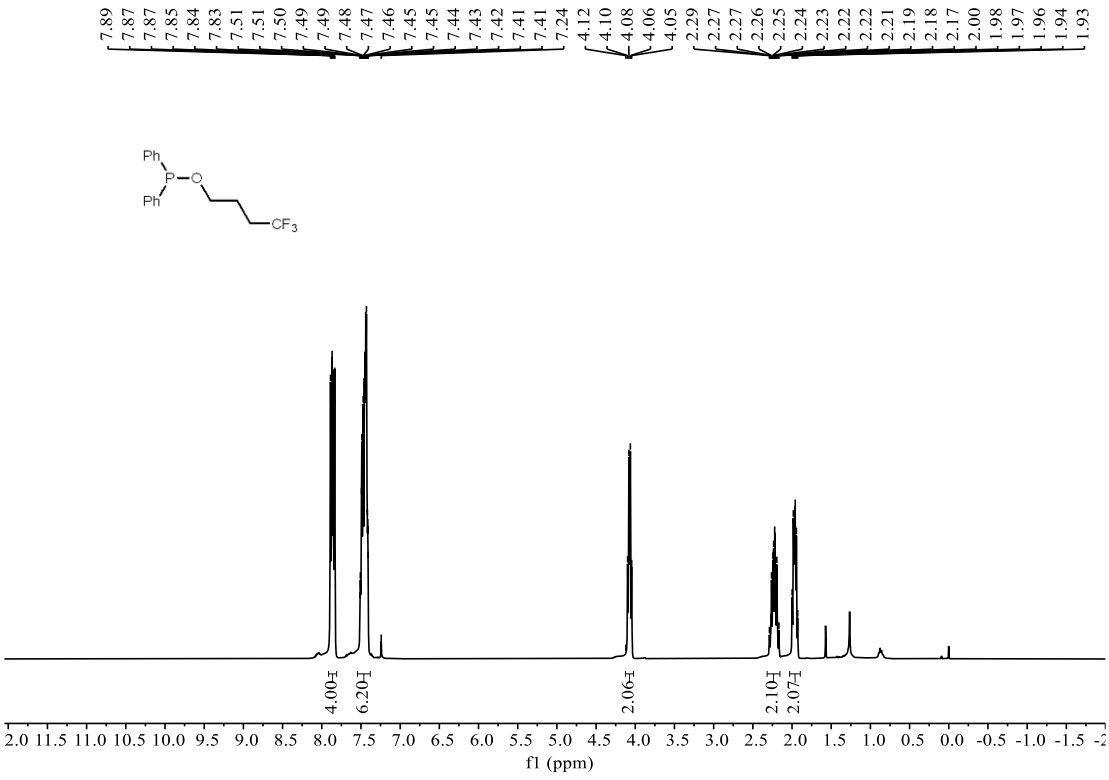
O-(cyclohexylmethyl) diphenylphosphinothioate (**3am'**)

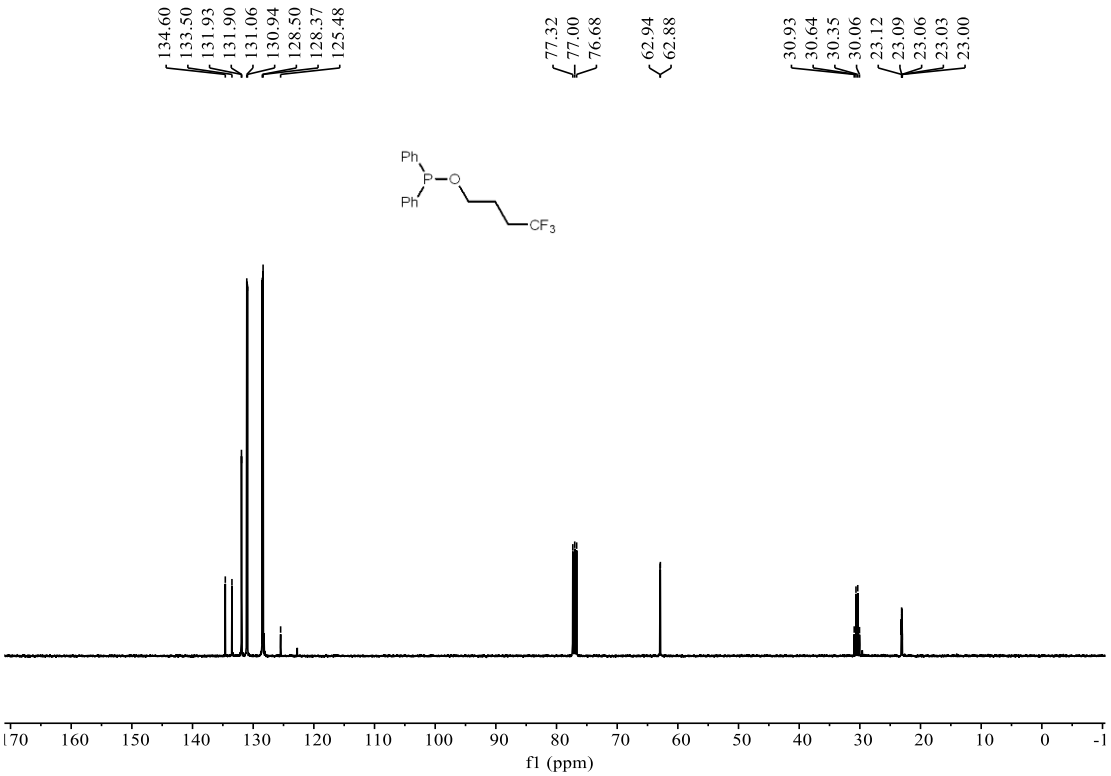


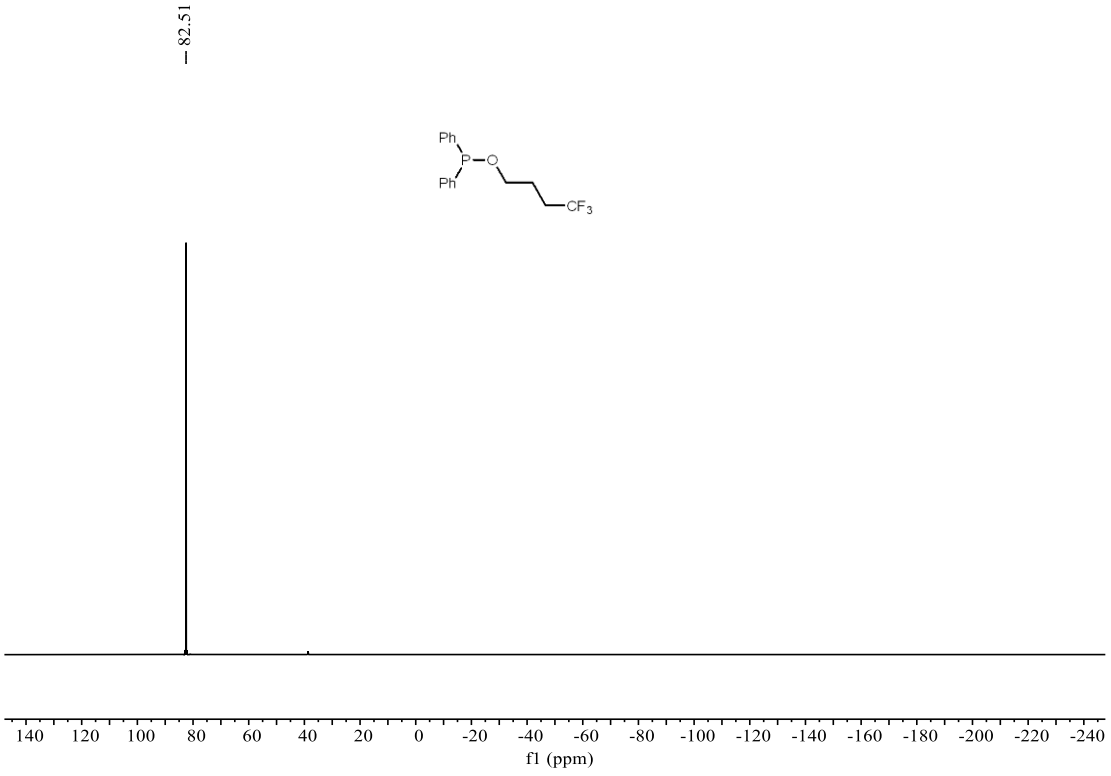


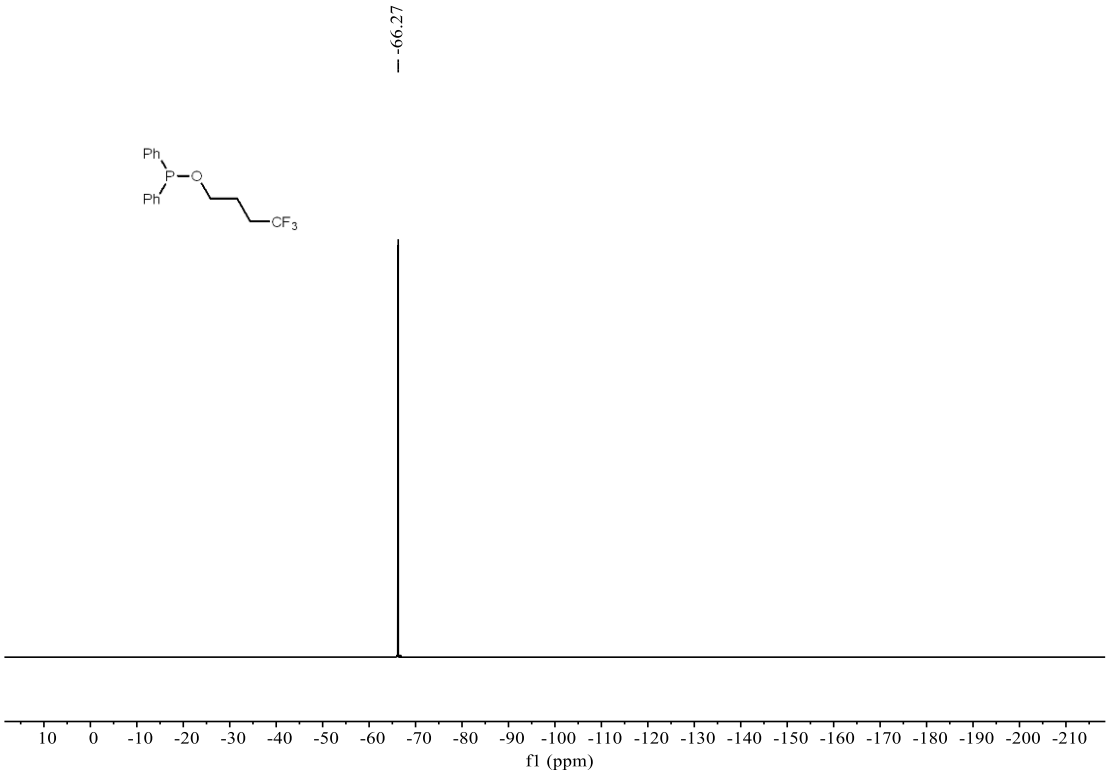


diphenyl(4,4,4-trifluorobutoxy)phosphane (**3an'**)

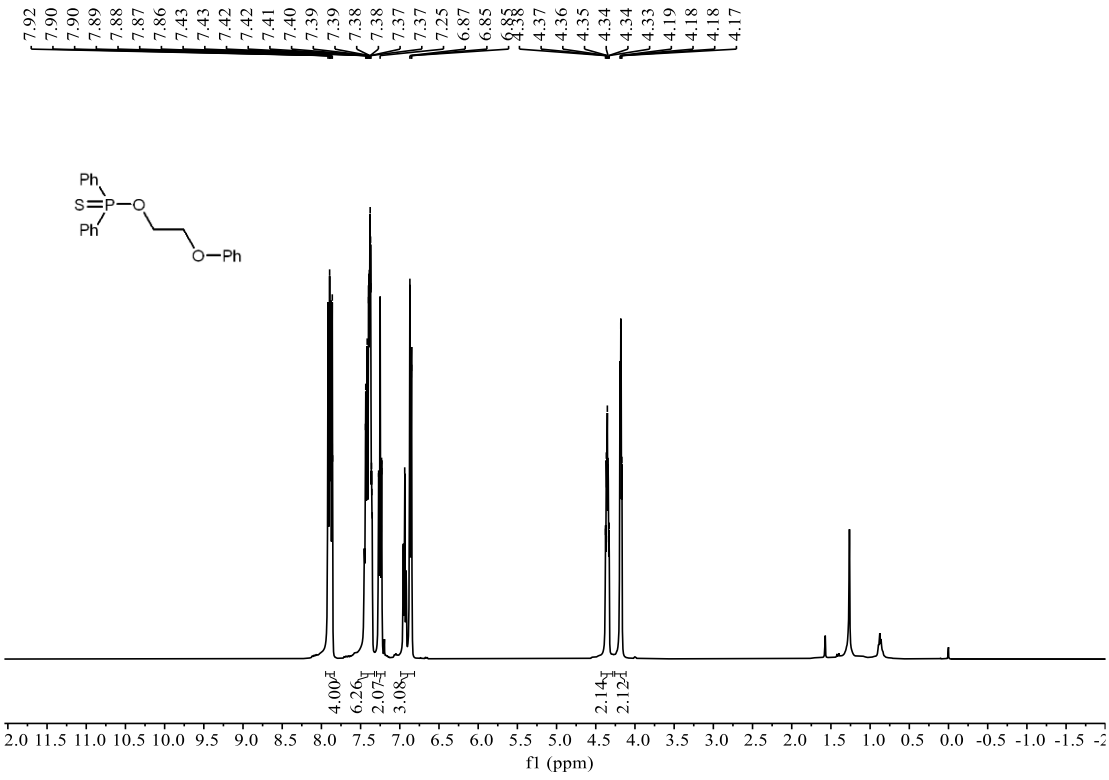


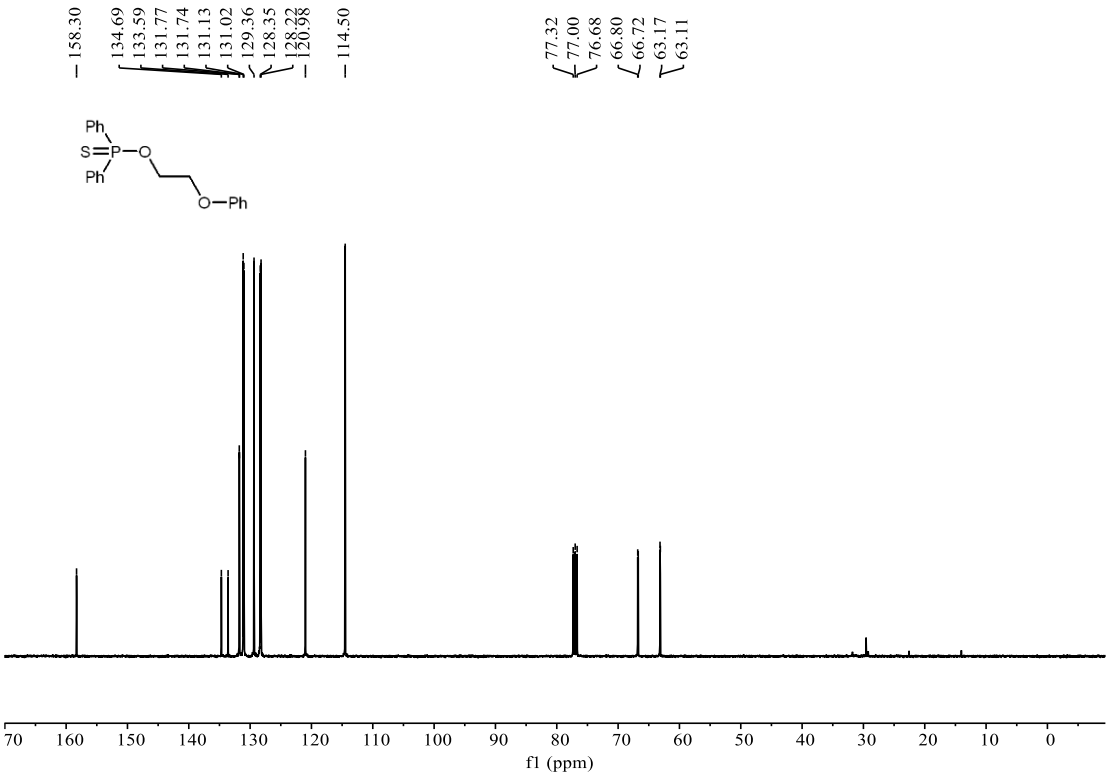

134.60
133.50
131.93
131.90
131.06
130.94
128.50
128.37
125.48
77.32
77.00
76.68
62.94
62.88
30.93
30.64
30.35
30.06
23.12
23.09
23.06
23.03
23.00
Ph
P
O
Ph
CF3
f1 (ppm)

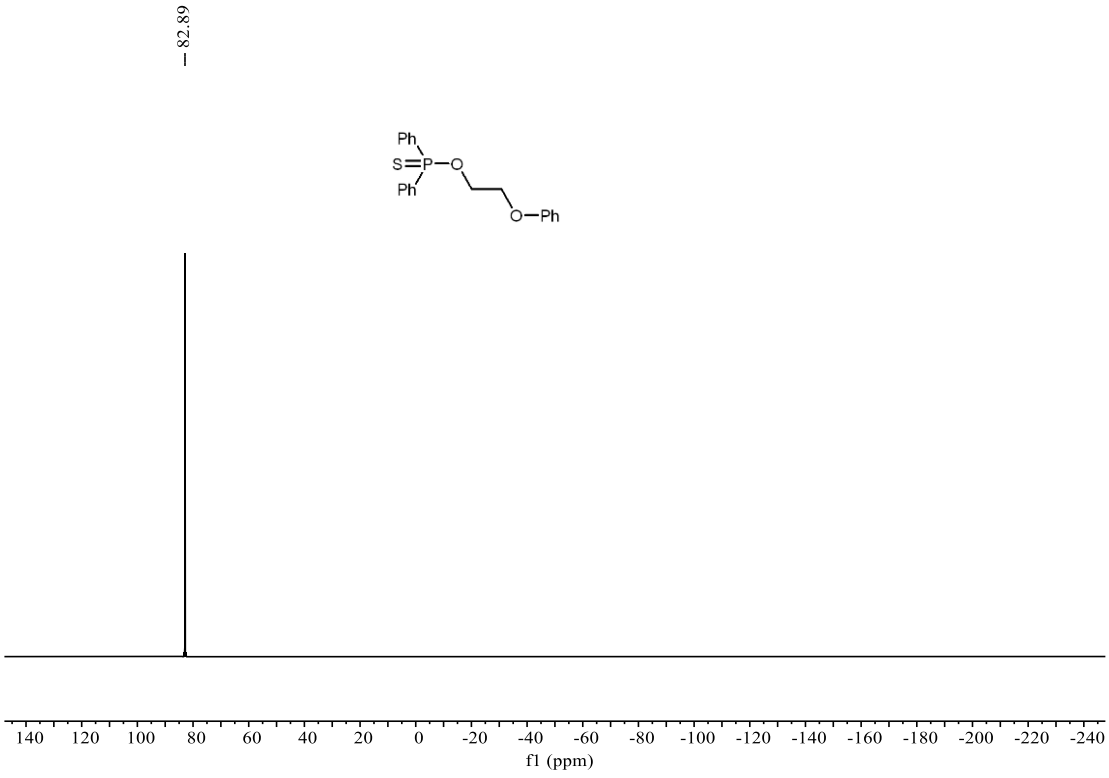

82.51
Ph
P
O
Ph
CF3
f1 (ppm)



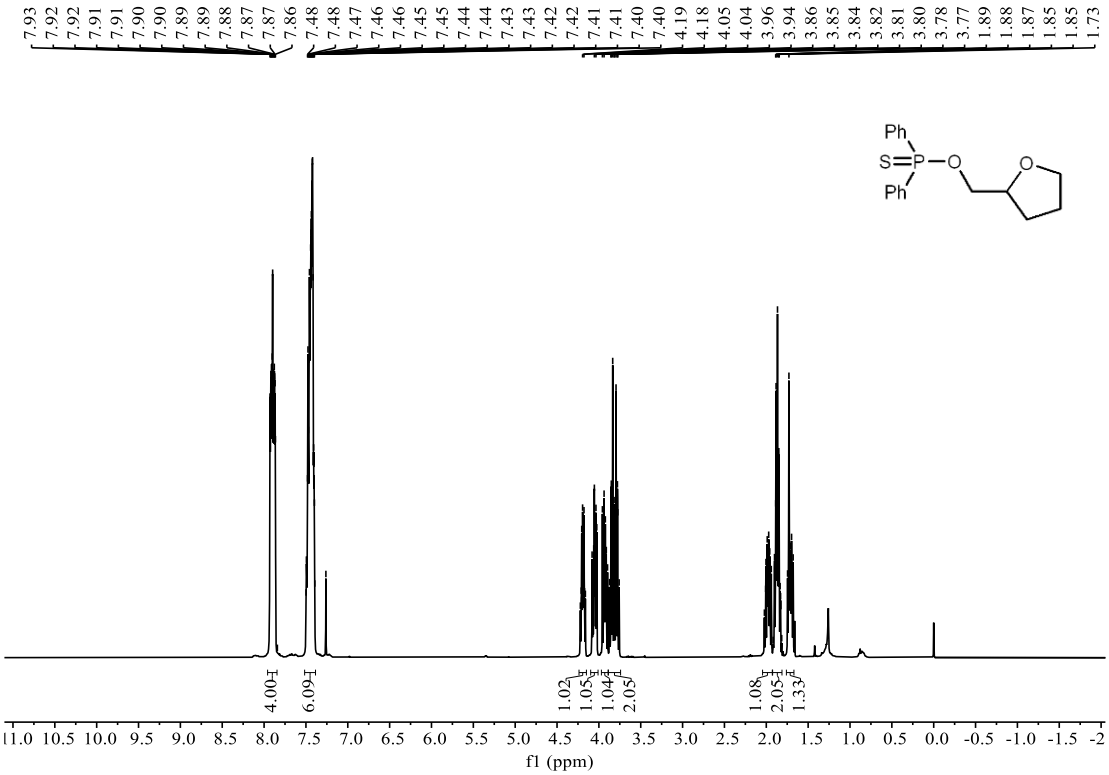
O-(2-phenoxyethyl) diphenylphosphinothioate (**3ao'**)

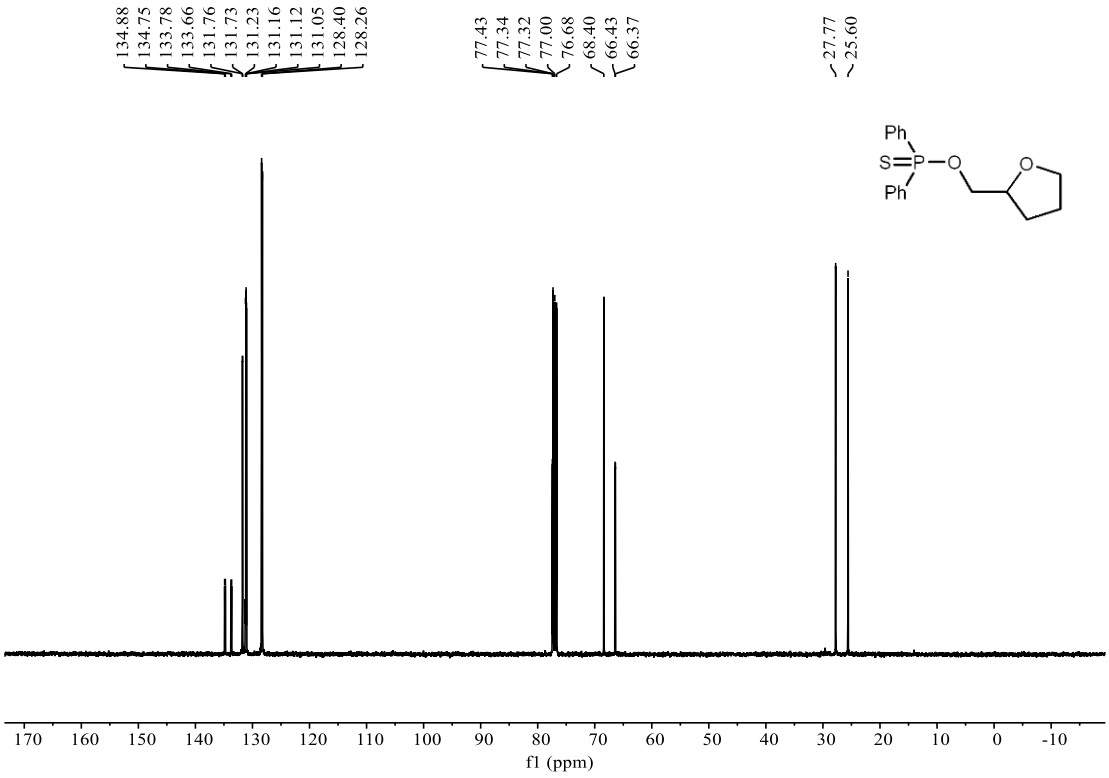


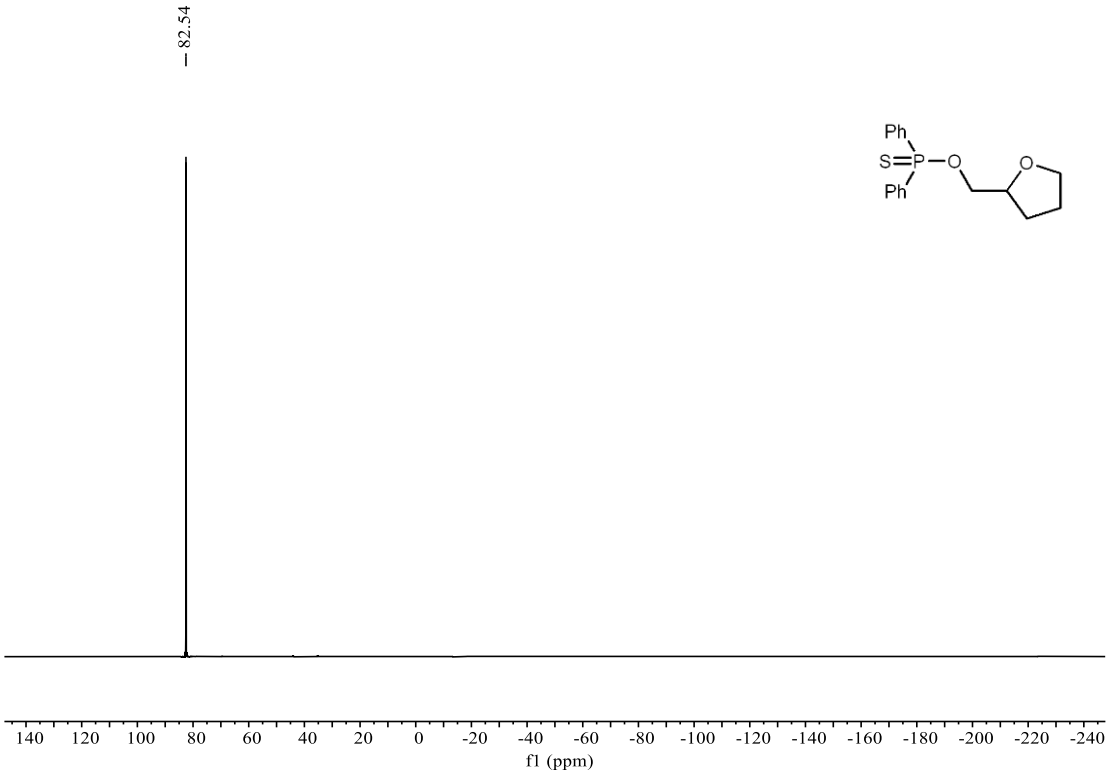

158.30
134.69
133.59
131.77
131.74
131.13
131.02
129.36
128.35
128.22
120.98
114.50
77.32
77.00
76.68
66.80
66.72
63.17
63.11
Ph
S
P
O
Ph
O
Ph
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


82.89
Ph
S
P
O
Ph
O
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

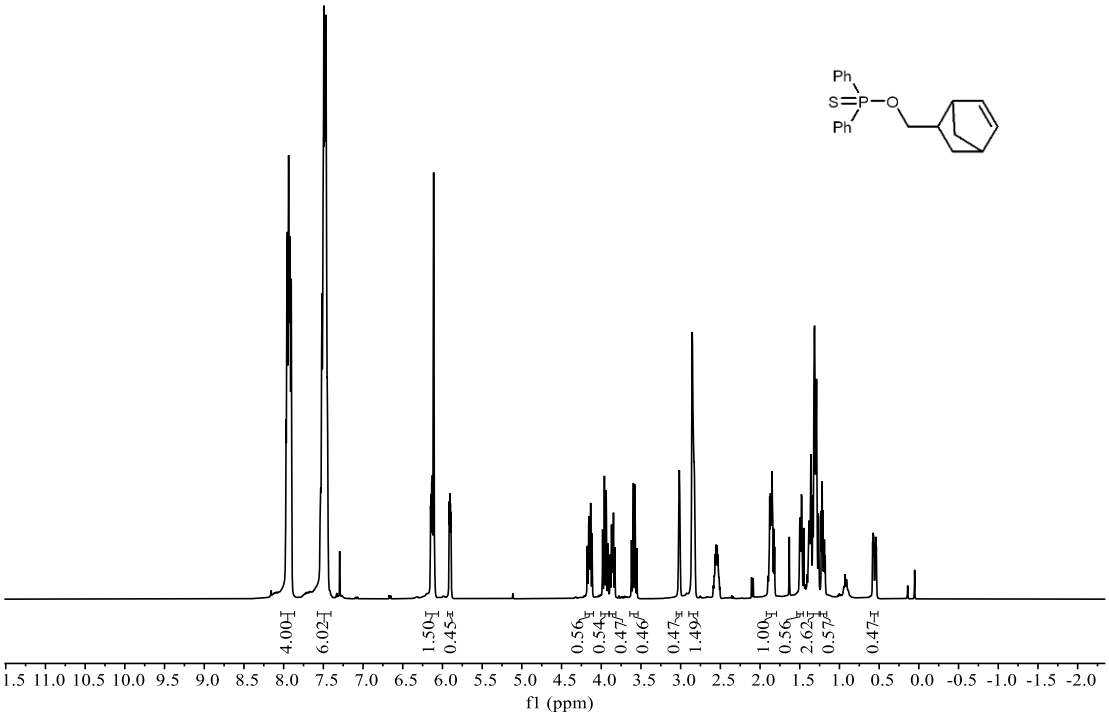
O-((tetrahydrofuran-2-yl)methyl) diphenylphosphinothioate (**3ap'**)

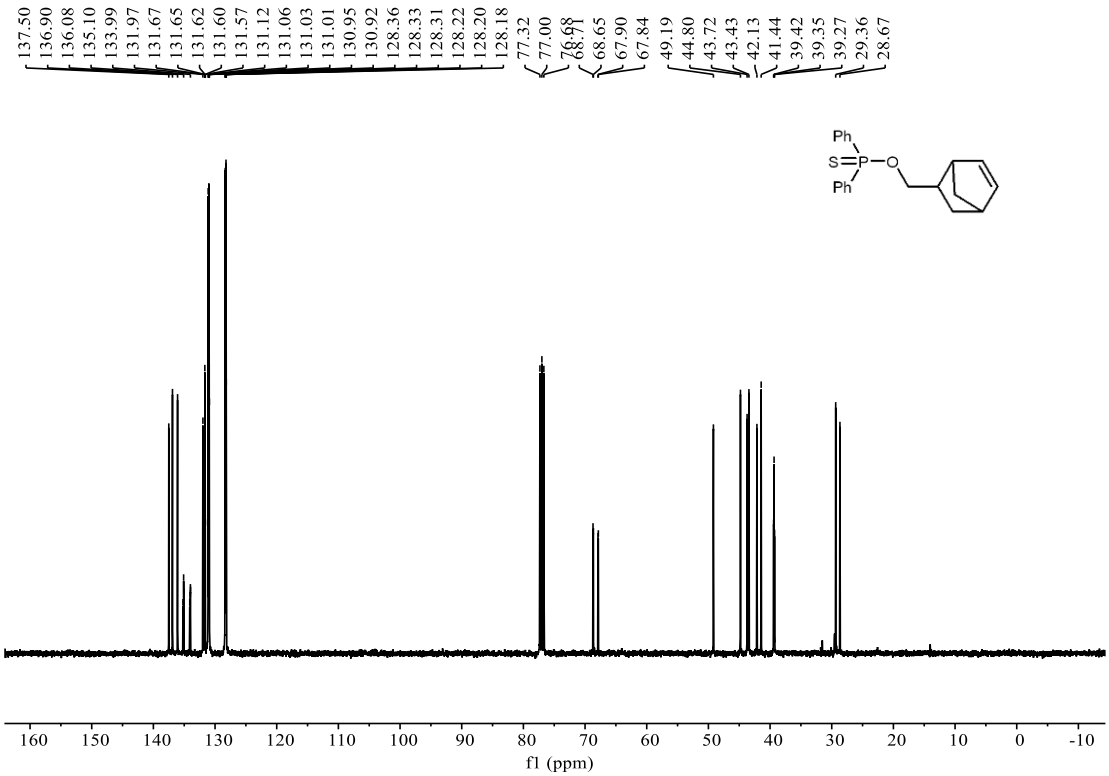


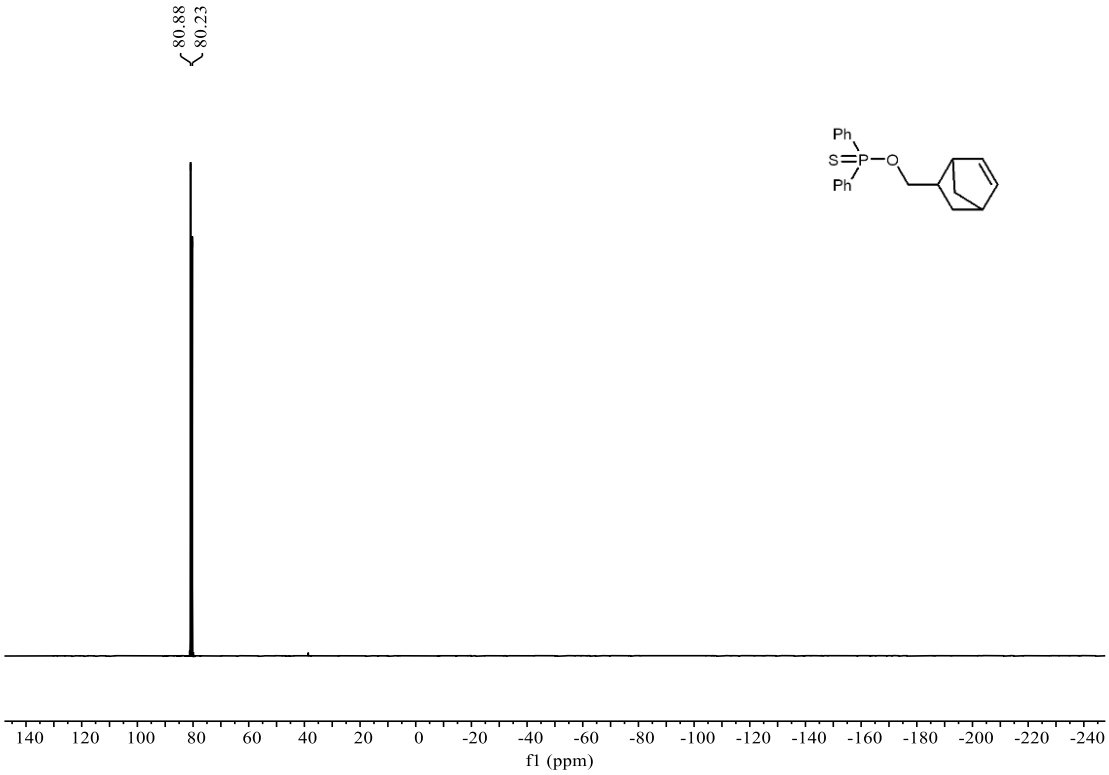




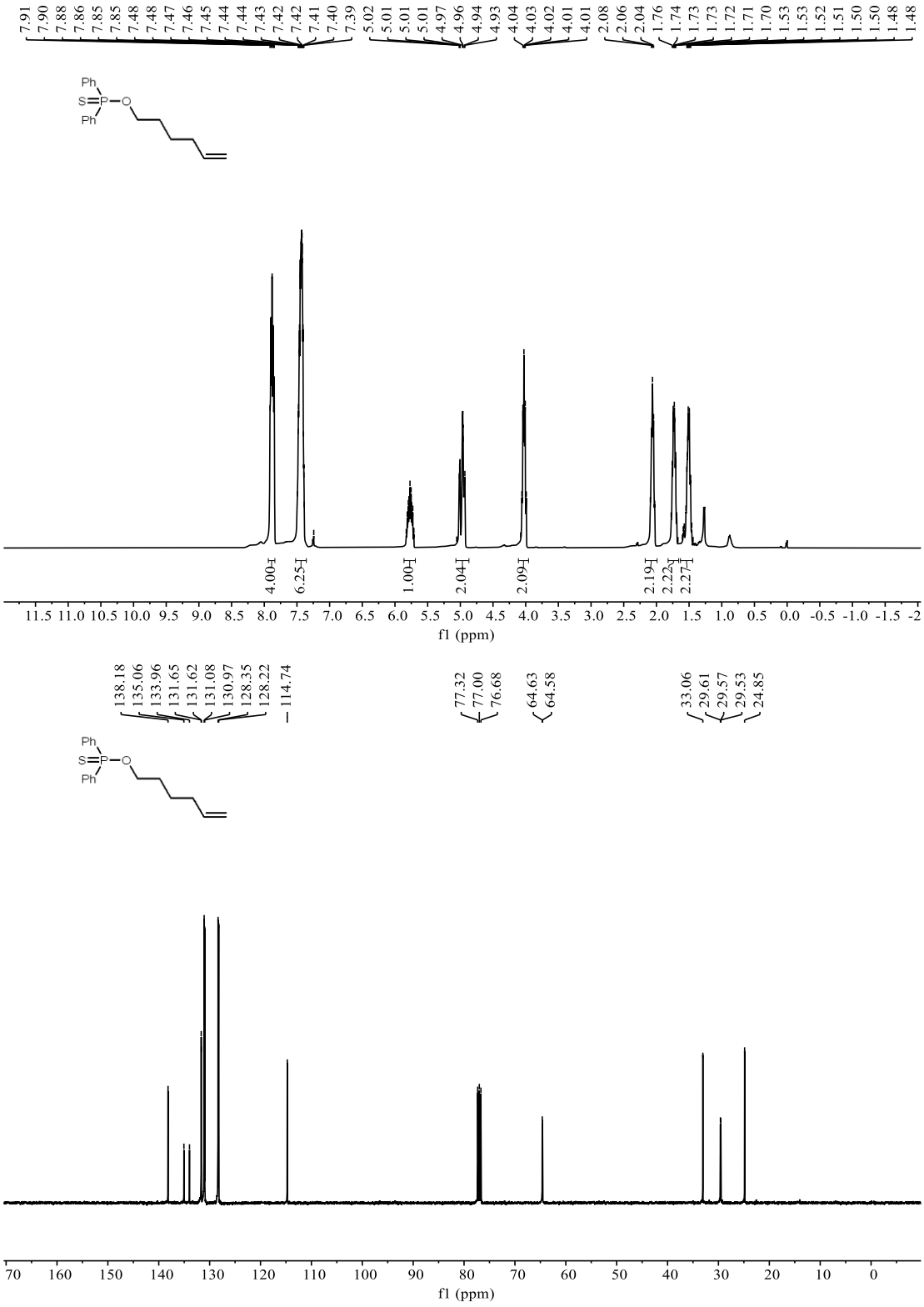
O-(bicyclo[2.2.1]hept-5-en-2-ylmethyl) diphenylphosphinothioate (**3aq'**)

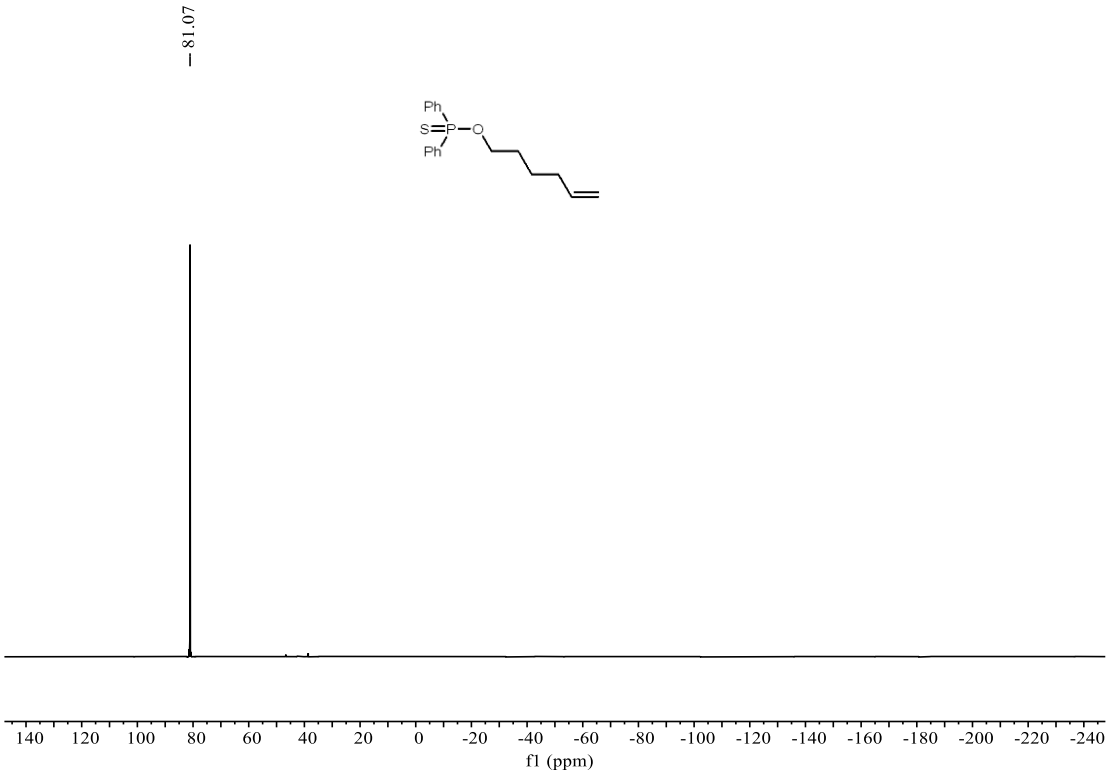



137.50
136.90
136.08
135.10
133.99
131.97
131.67
131.65
131.62
131.60
131.57
131.12
131.06
131.03
131.01
130.95
130.92
128.36
128.33
128.31
128.22
128.20
128.18
77.32
77.00
76.68
68.71
68.65
67.90
67.84
49.19
44.80
43.72
43.43
42.13
41.44
39.42
39.35
39.27
29.36
28.67
Ph
S
P
O
Ph
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

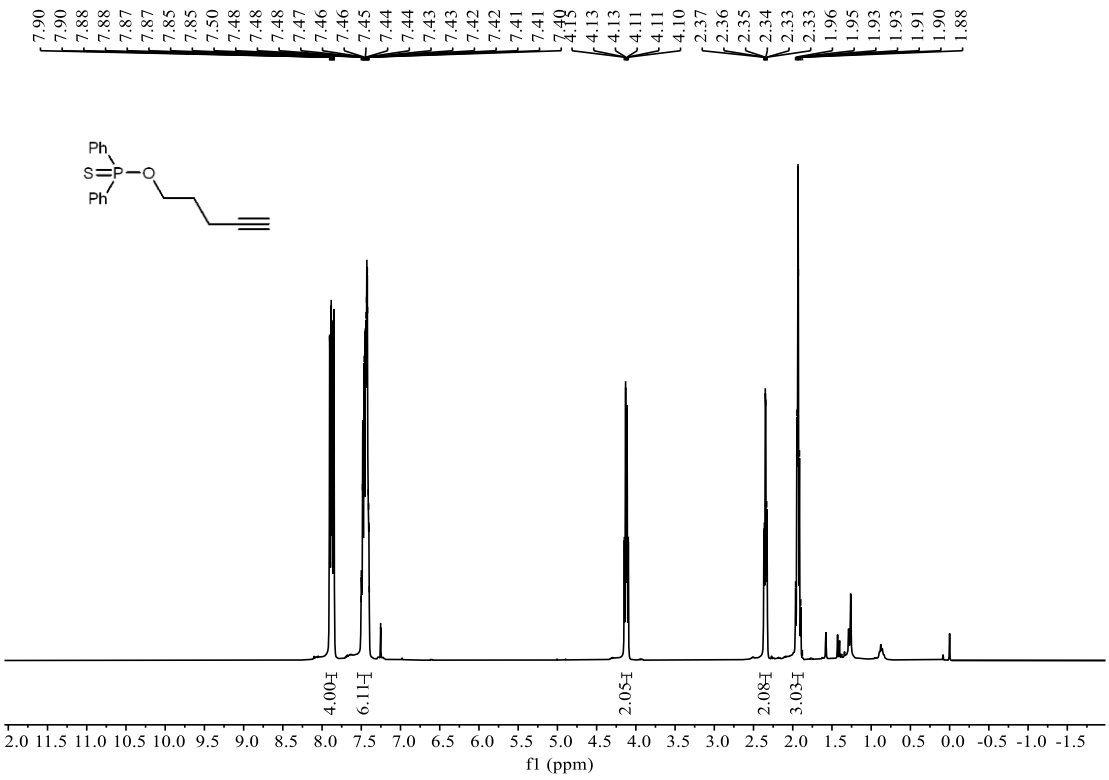

80.88
80.23
Ph
S
P
O
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

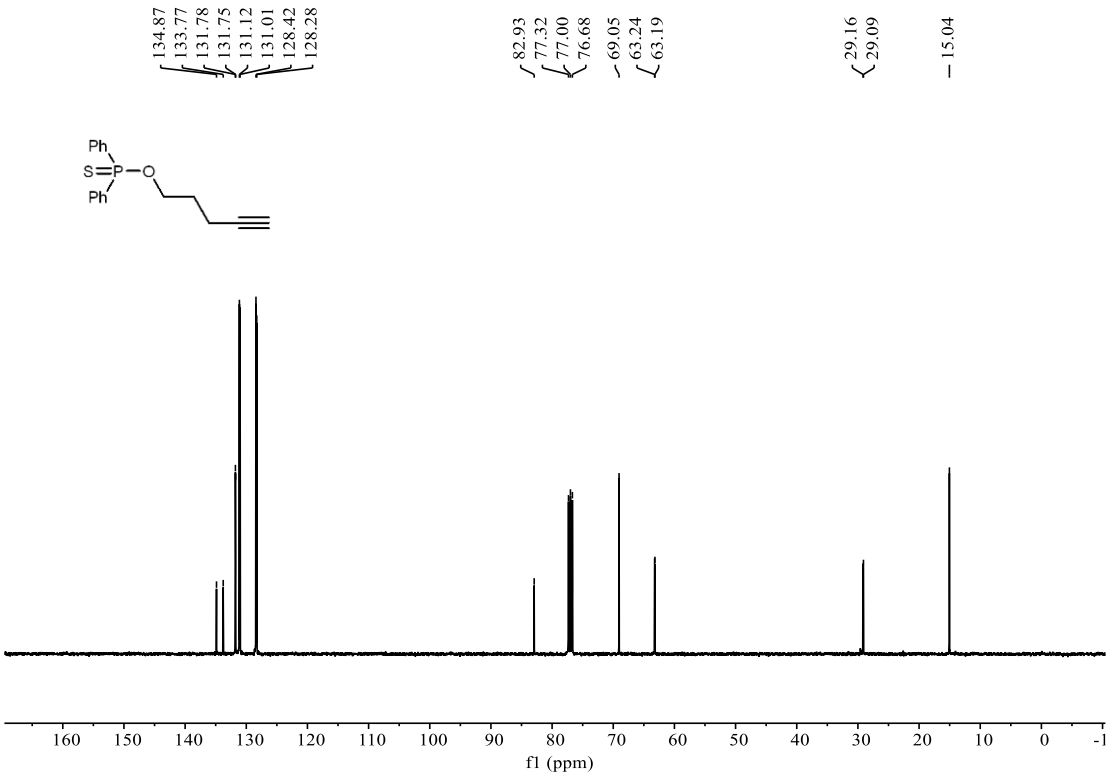
O-(hex-5-en-1-yl) diphenylphosphinothioate (**3ar'**)

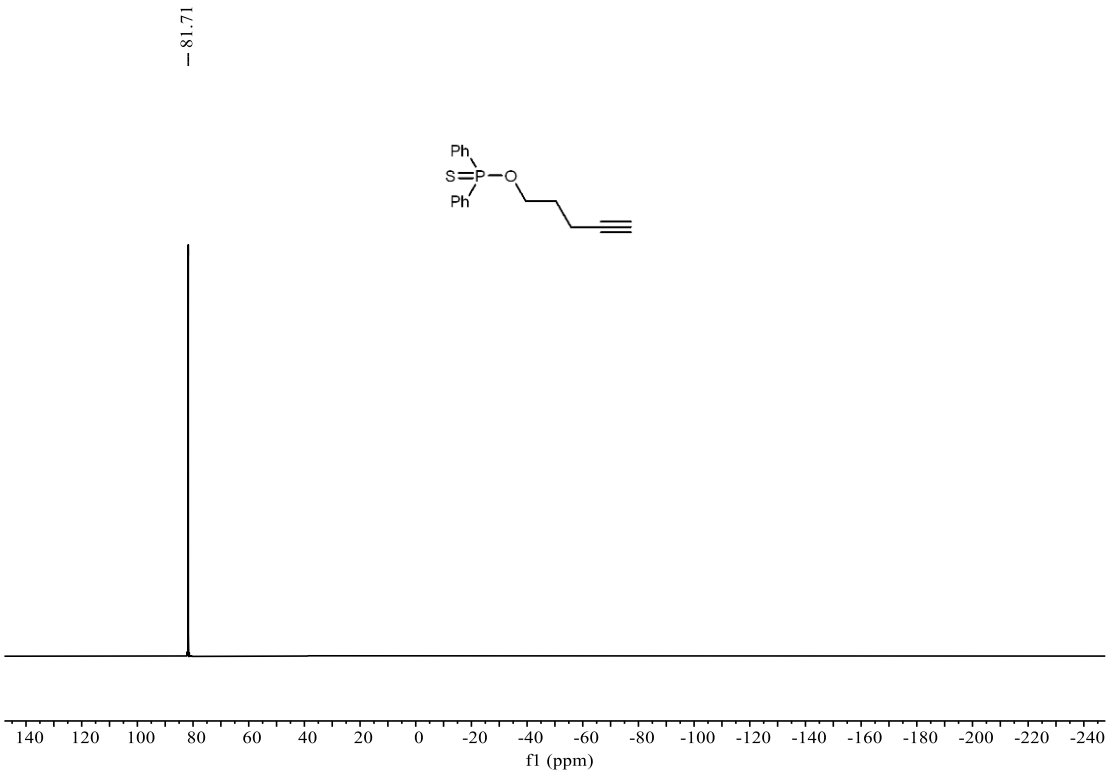




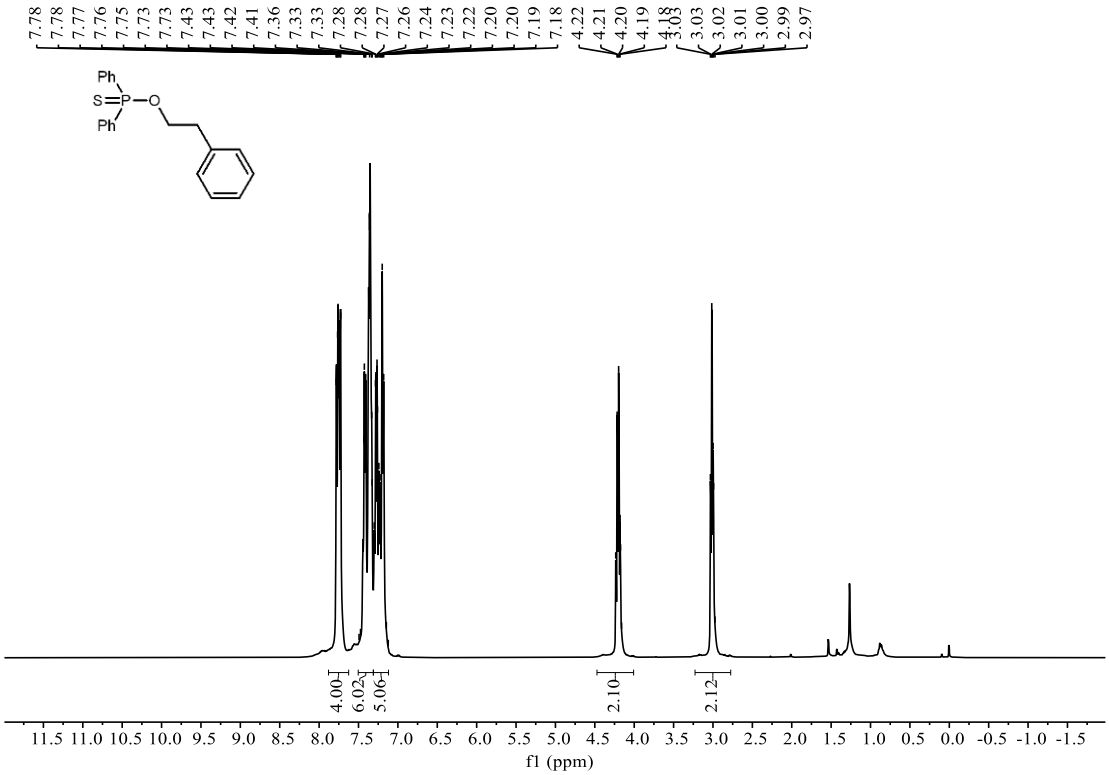
O-(pent-4-yn-1-yl) diphenylphosphinothioate (**3as'**)

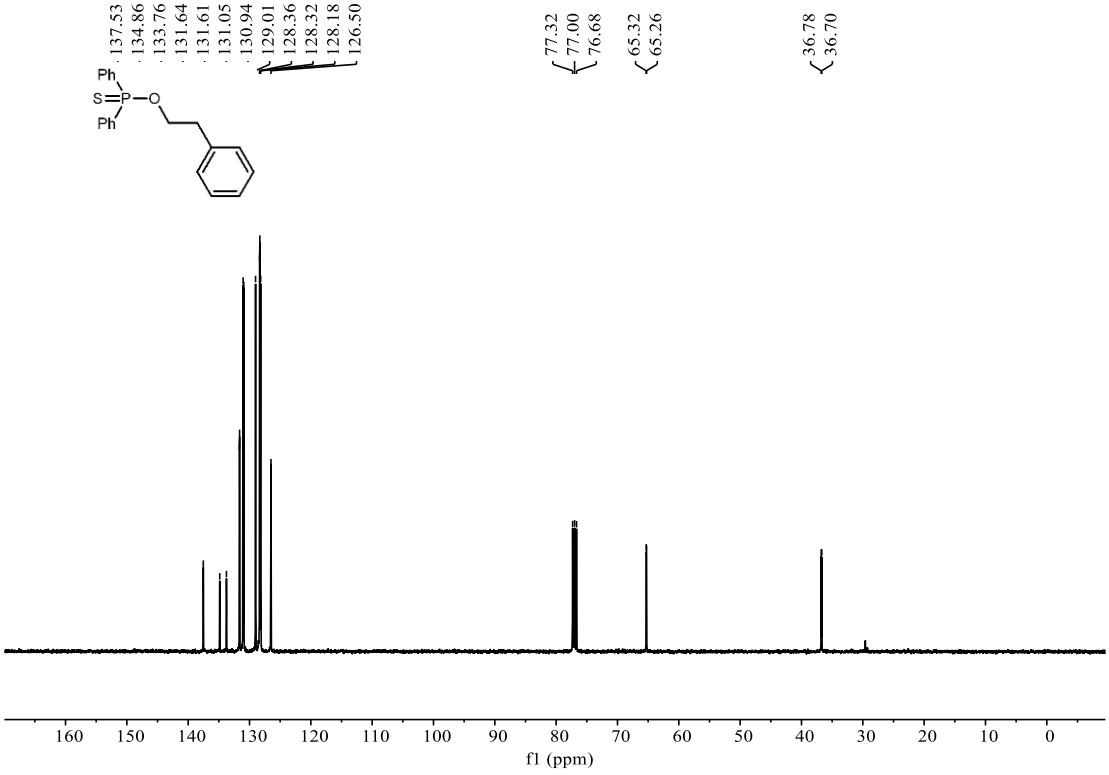


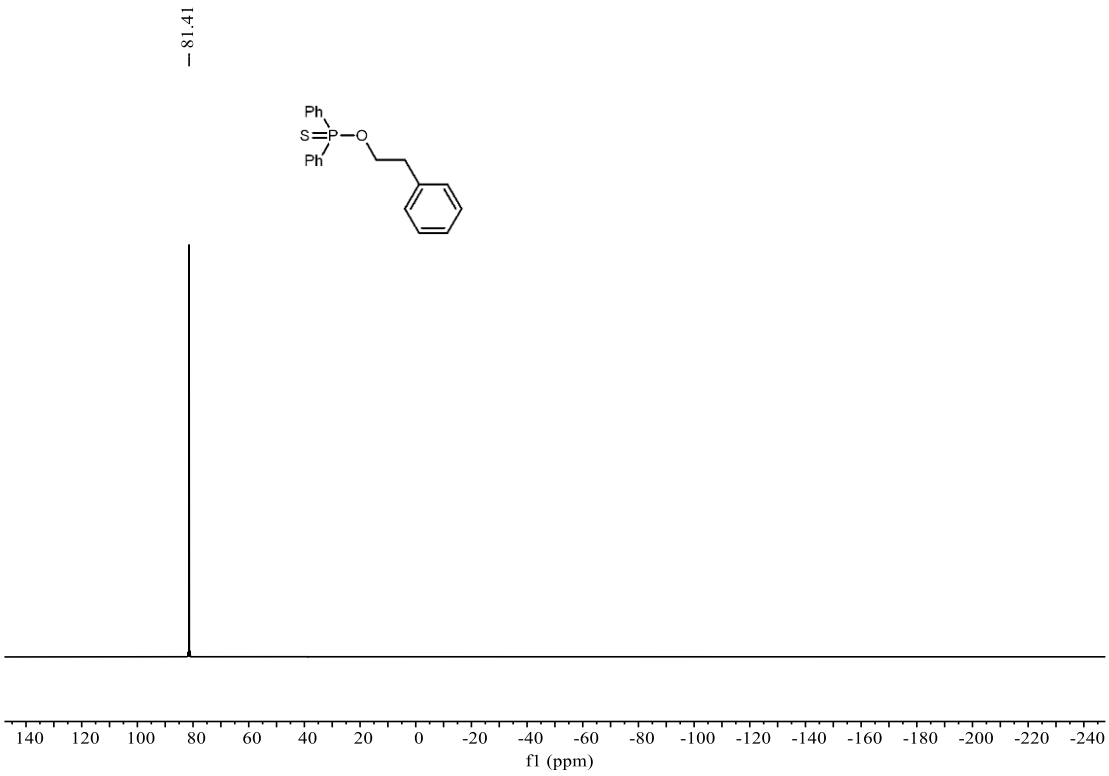

134.87
133.77
131.78
131.75
131.12
131.01
128.42
128.28
82.93
77.32
77.00
76.68
69.05
63.24
63.19
29.16
29.09
15.04
Ph
S
P
O
Ph
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


81.71
Ph
S
P
O
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

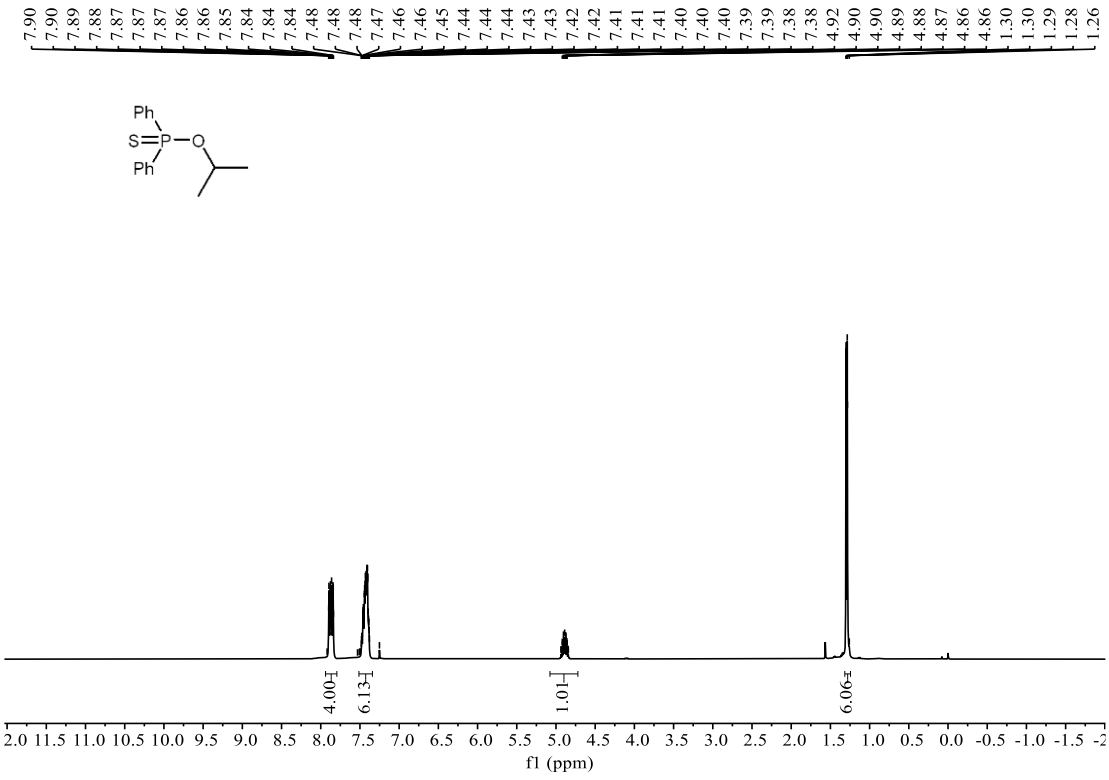
O-phenethyl diphenylphosphinothioate (**3at'**)

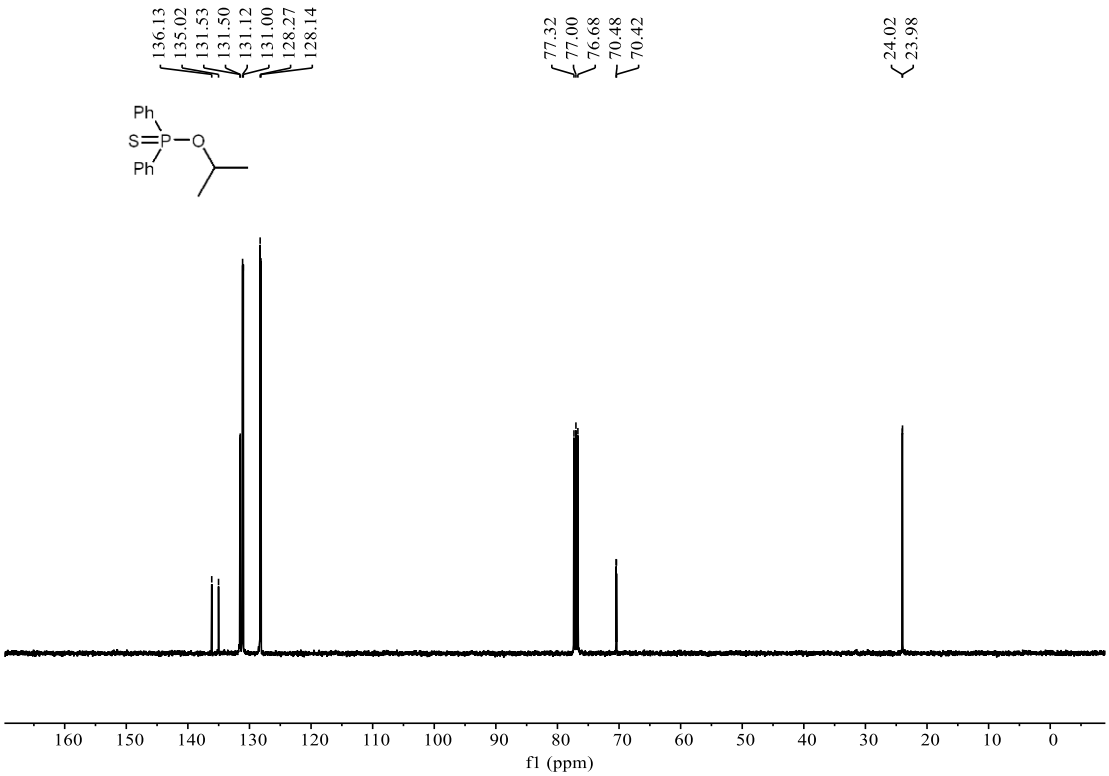


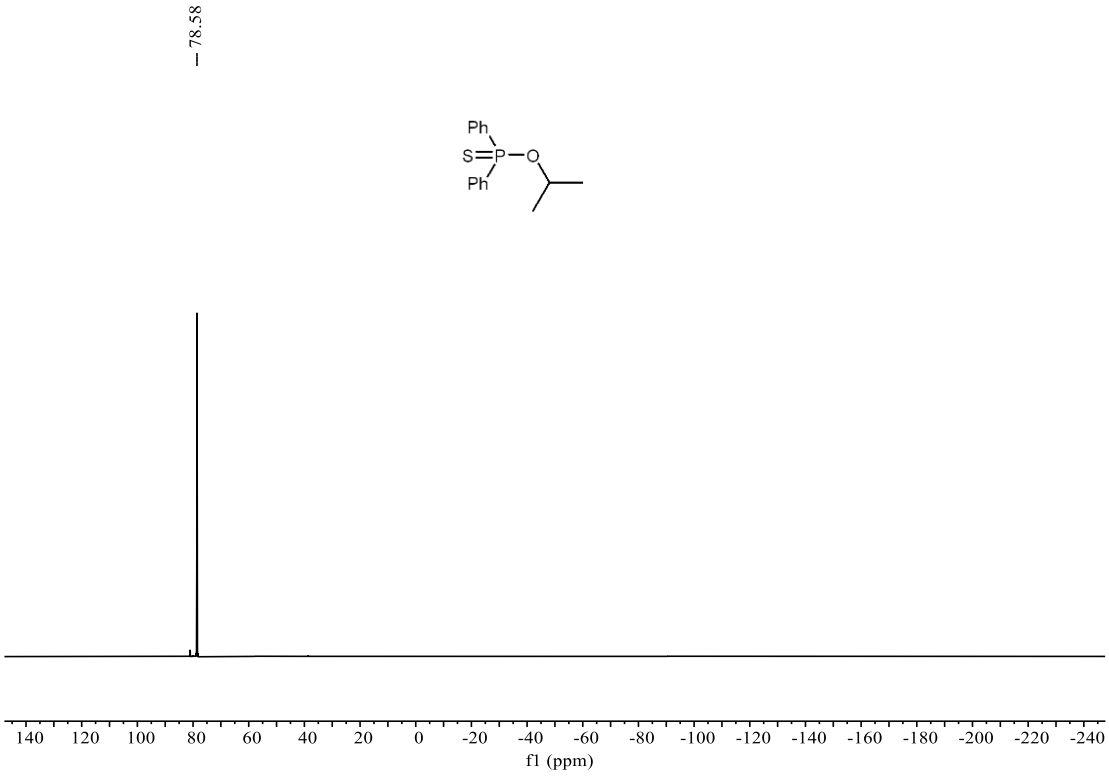




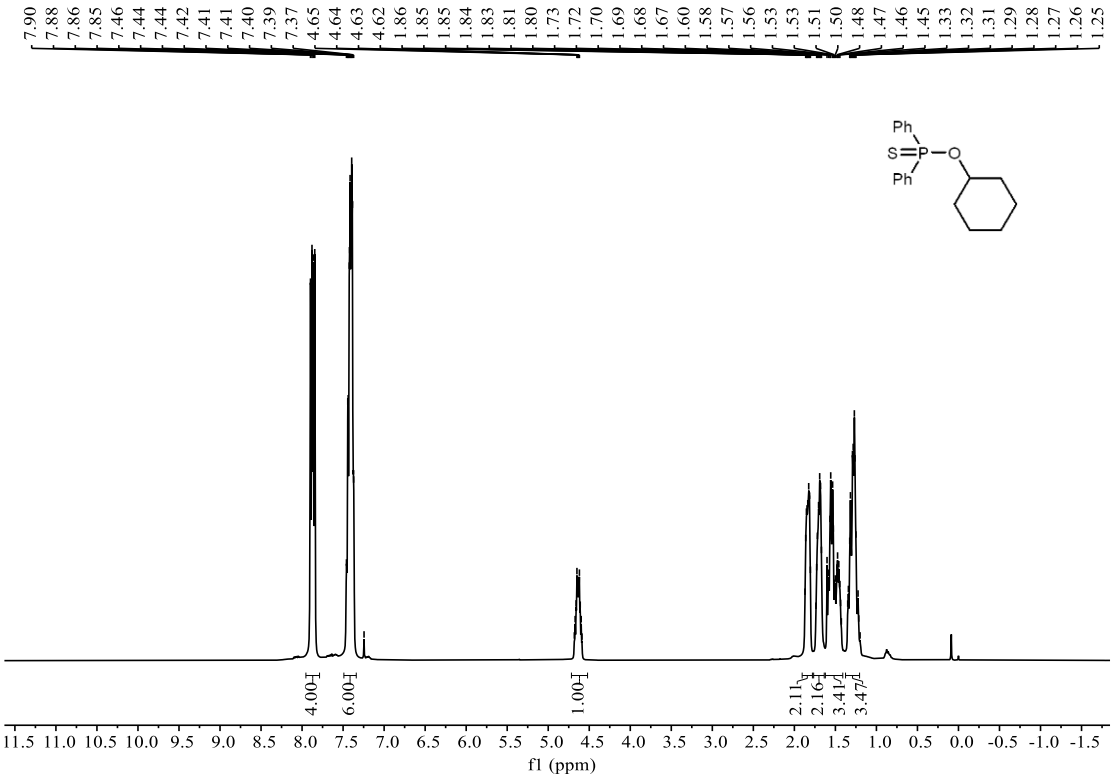
O-isopropyl diphenylphosphinothioate (**3au'**)

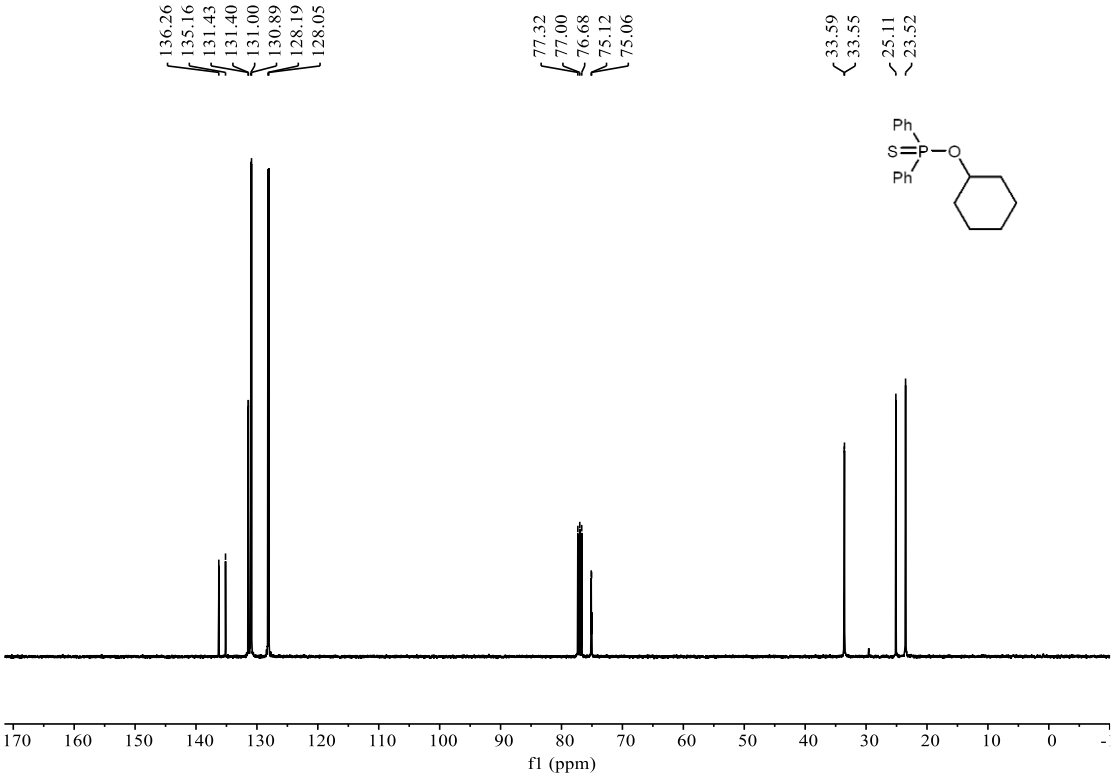


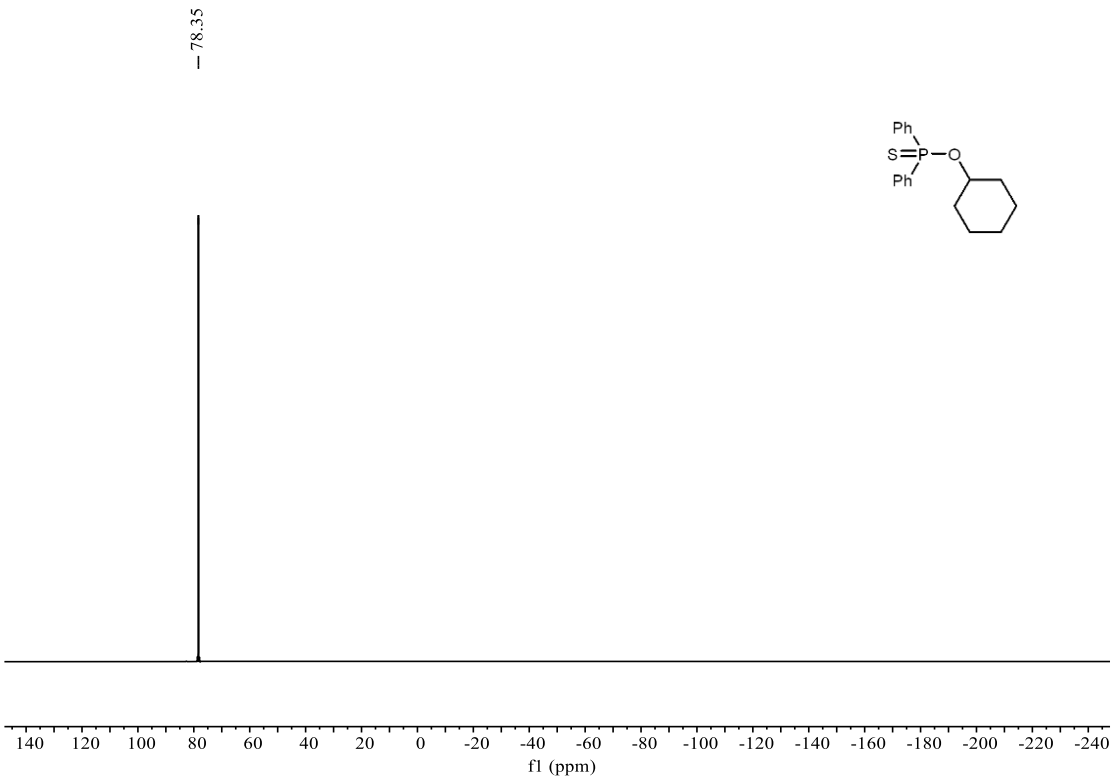

136.13
135.02
131.53
131.50
131.12
131.00
128.27
128.14
77.32
77.00
76.68
70.48
70.42
24.02
23.98
Ph
S
P
O
Ph
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


78.58
Ph
S
P
O
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

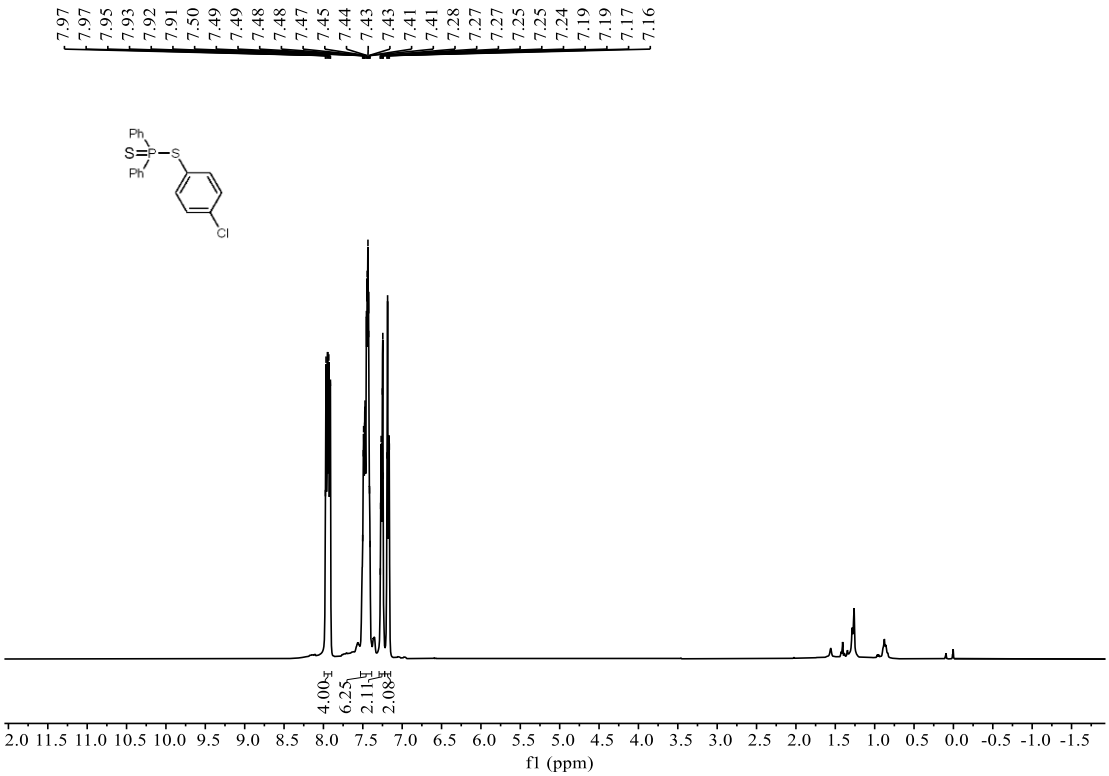
O-cyclohexyl diphenylphosphinothioate (**3av'**)

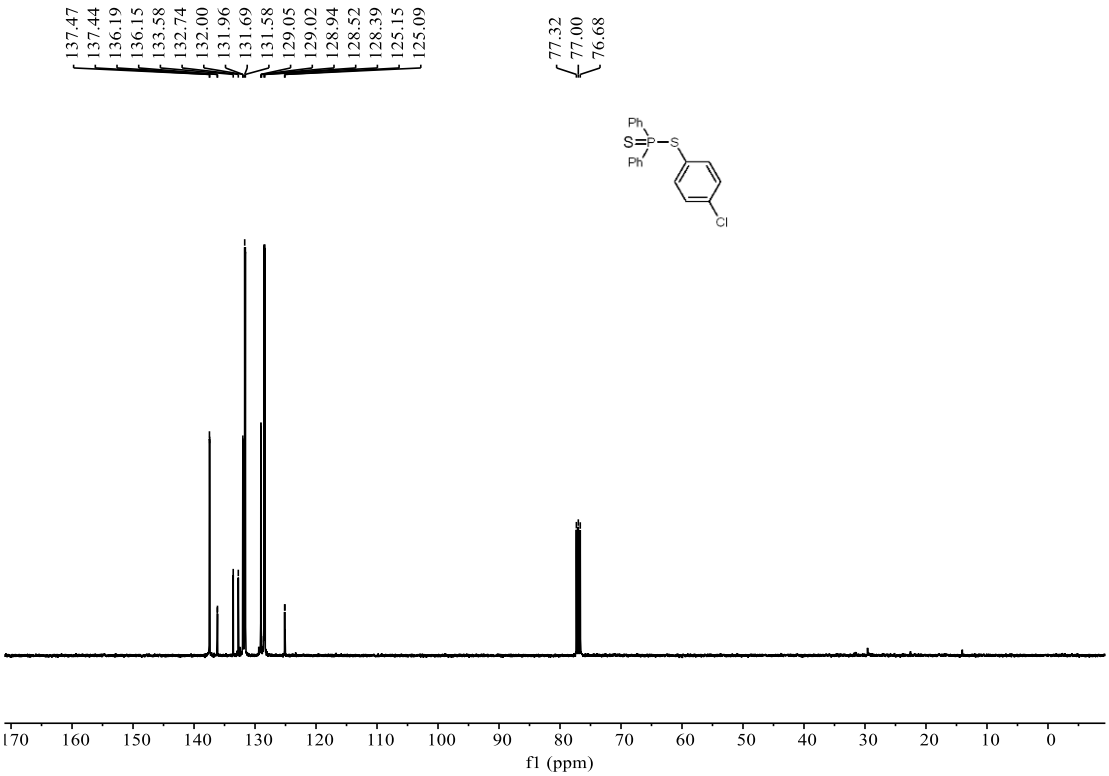


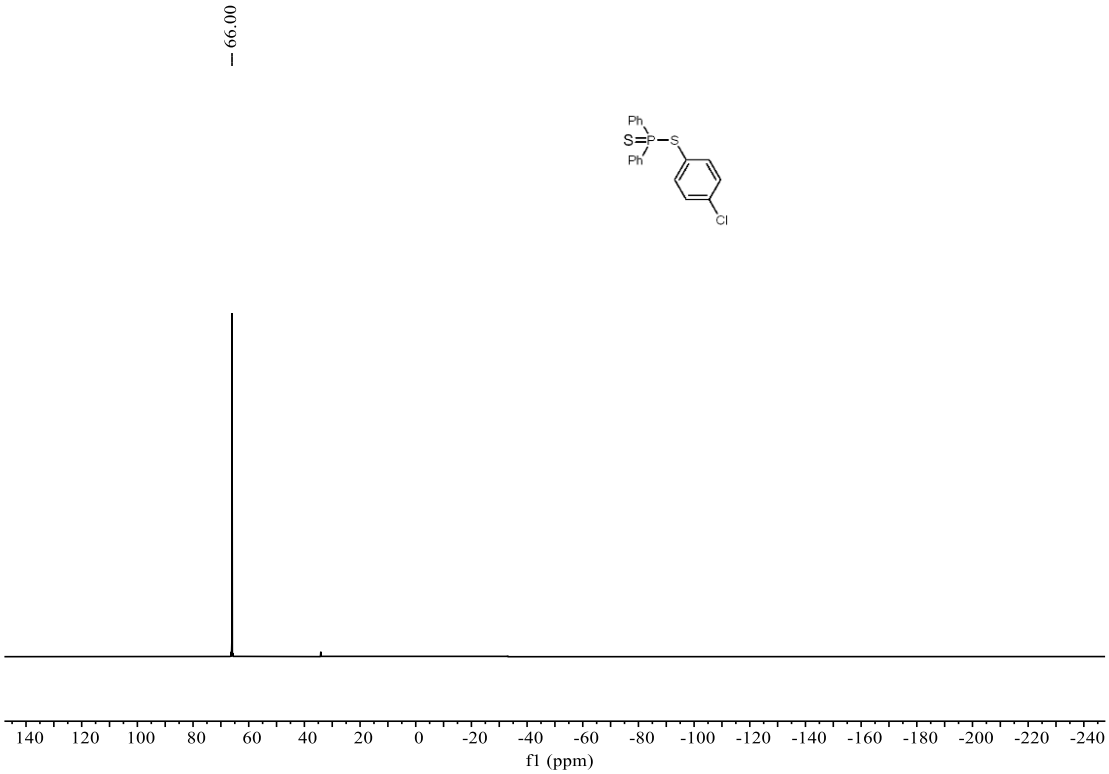




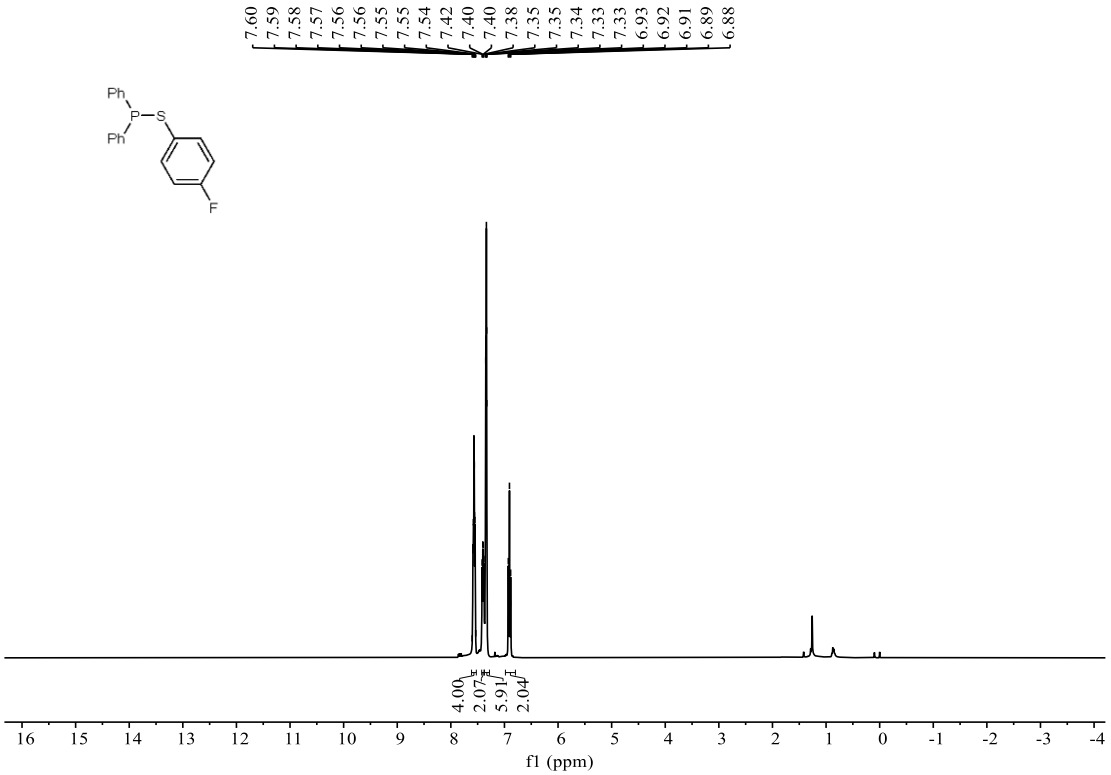
4-chlorophenyl diphenylphosphinodithioate (**4a'**)

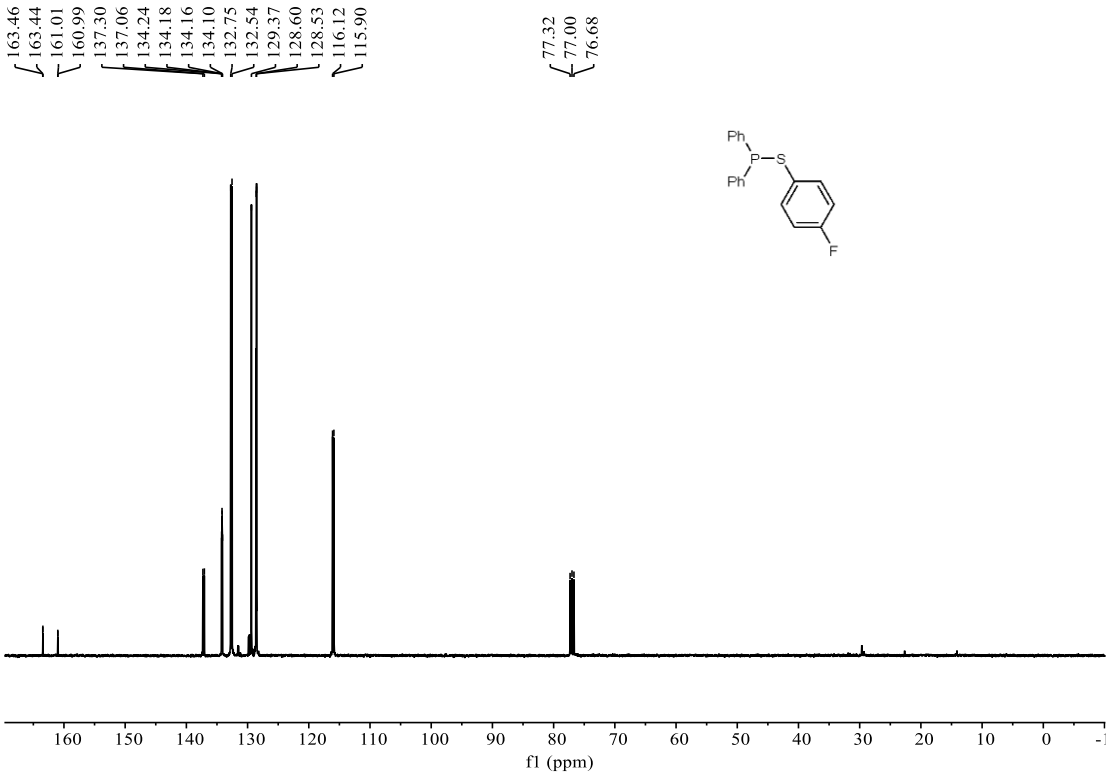


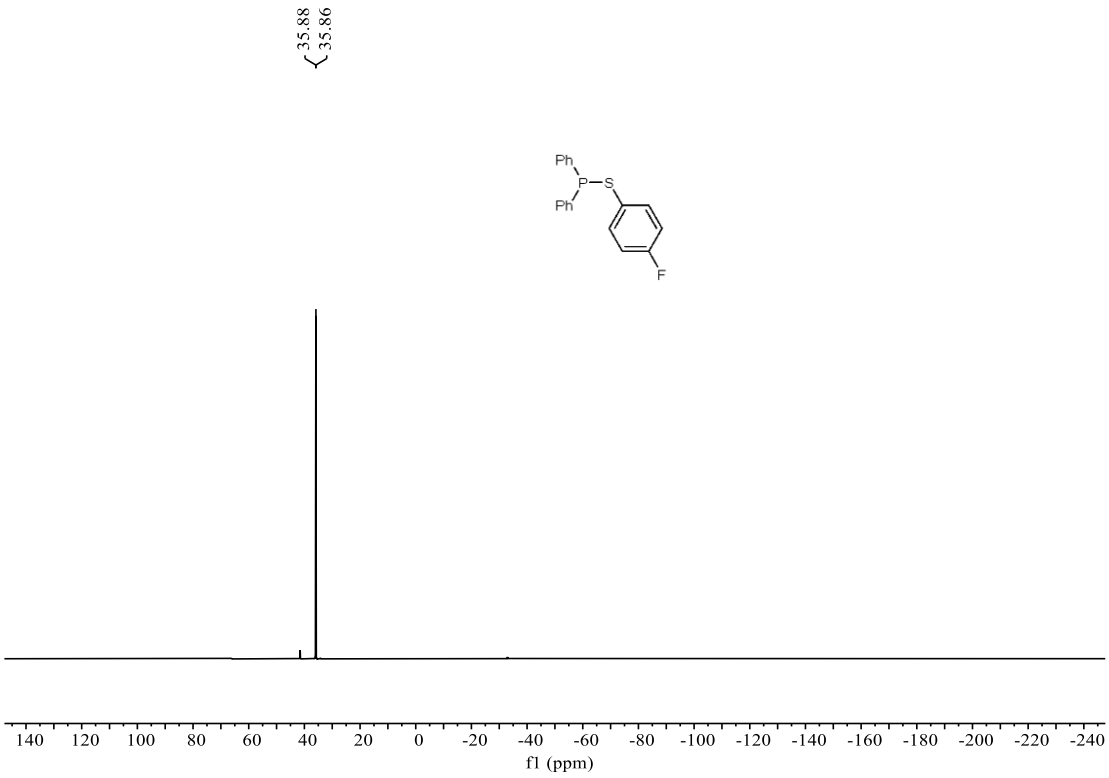

137.47
137.44
136.19
136.15
133.58
132.74
132.00
131.96
131.69
131.58
129.05
129.02
128.94
128.52
128.39
125.15
125.09
77.32
77.00
76.68
Ph
S
P
S
Ph
Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

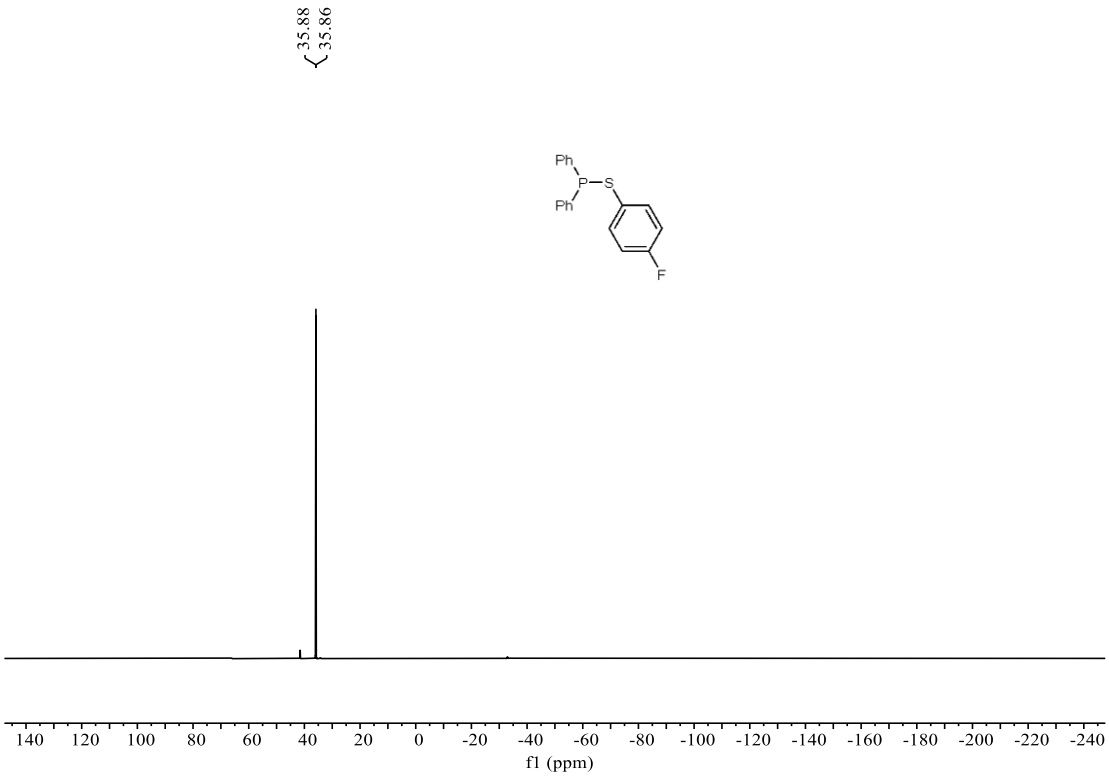

66.00
Ph
S
P
S
Ph
Cl
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

((4-Fluorophenyl)thio)diphenylphosphane (**4b'**)

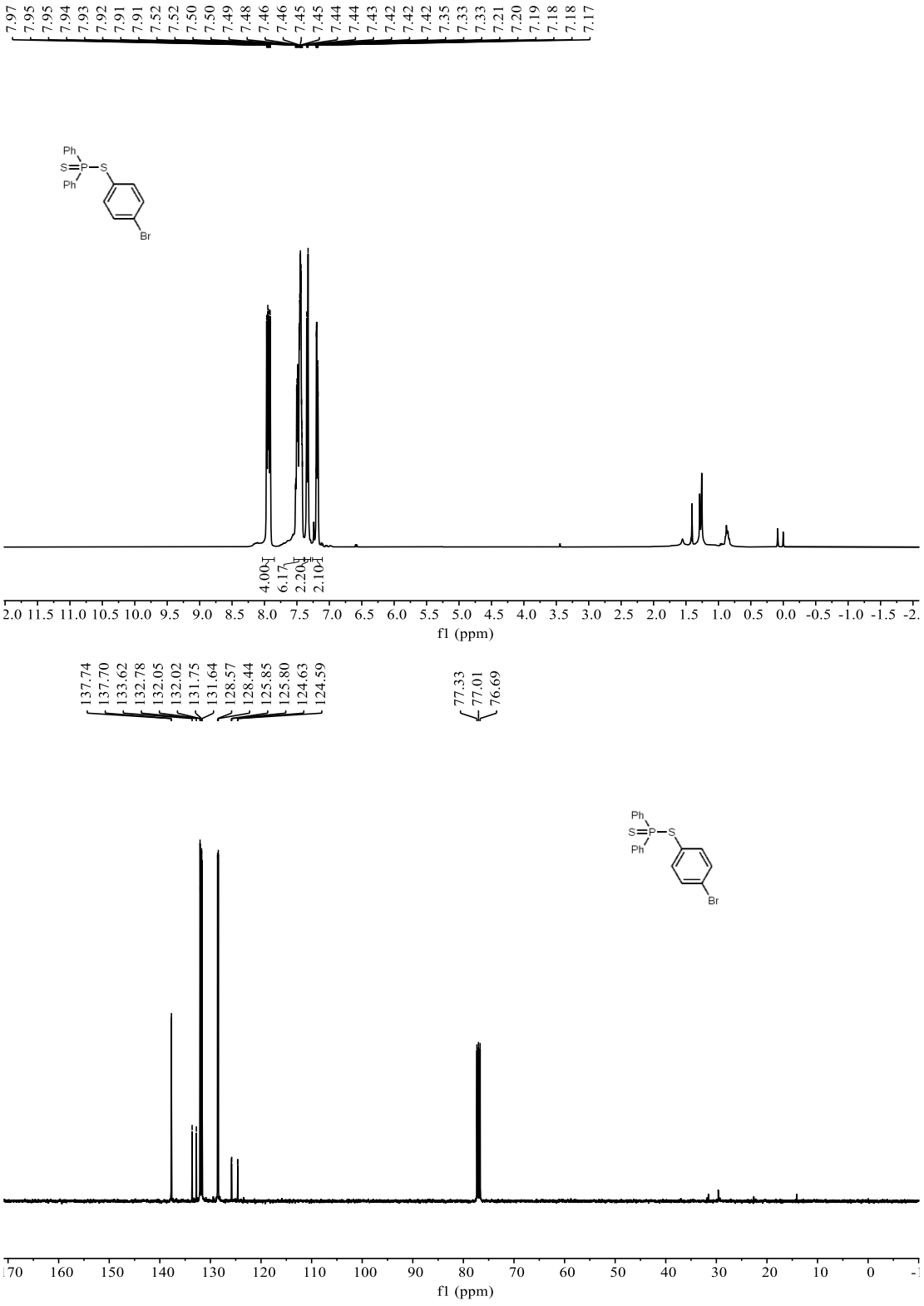


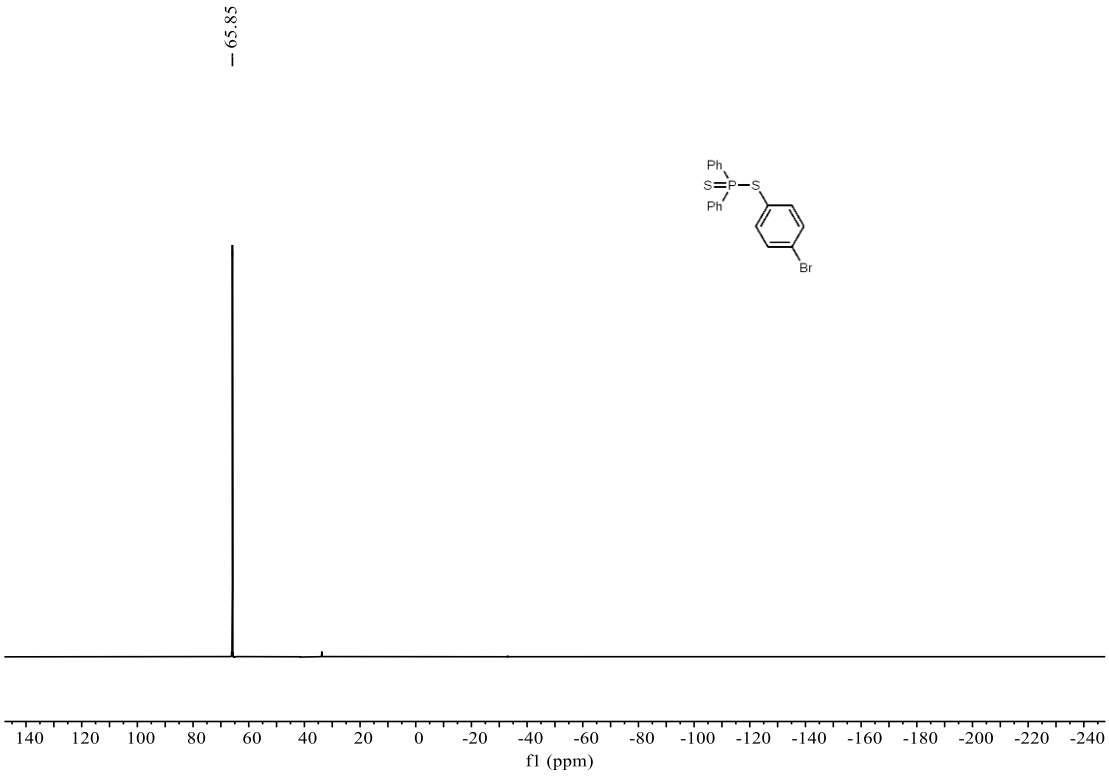



35.88
35.86
Ph
P
S
Ph
F
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

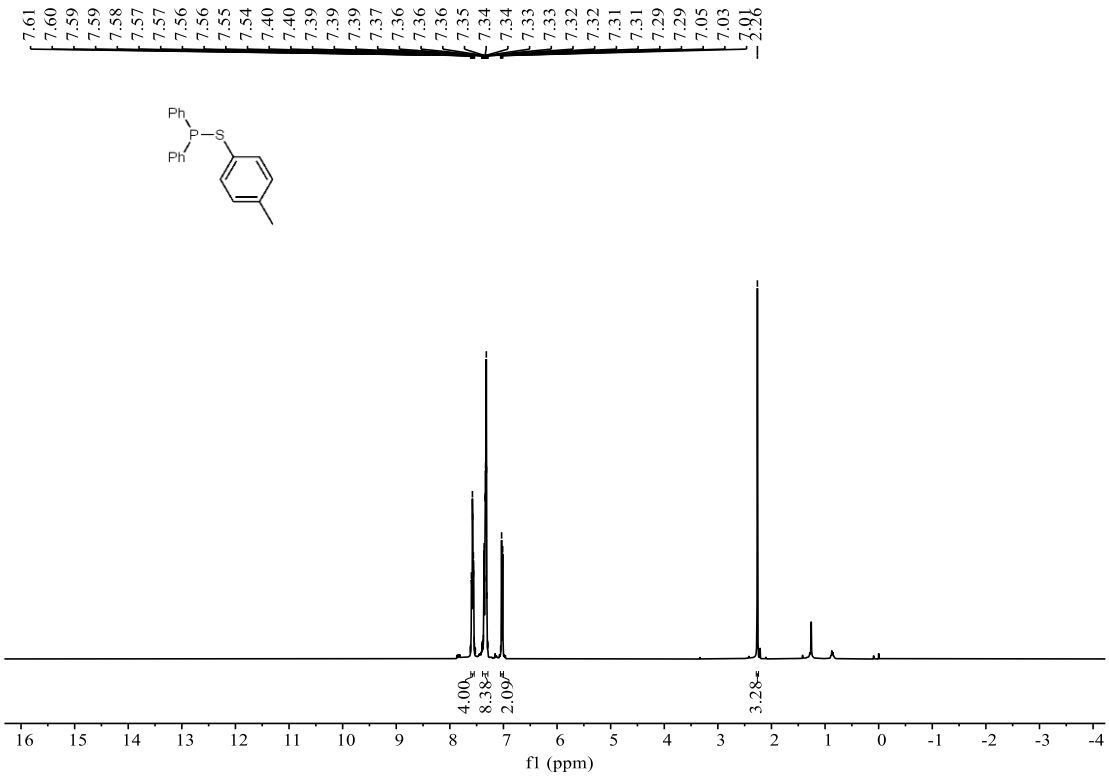

35.88
35.86
Ph
P
S
Ph
F
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

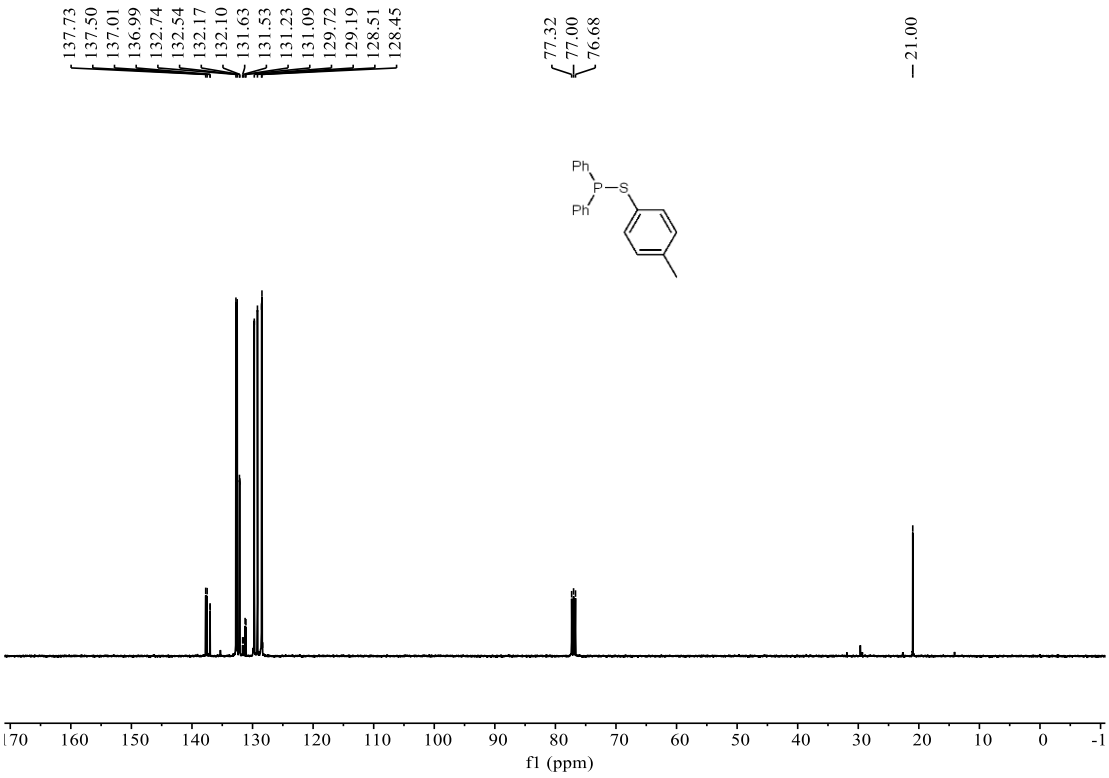
4-Bromophenyl diphenylphosphinodithioate (**4c'**)

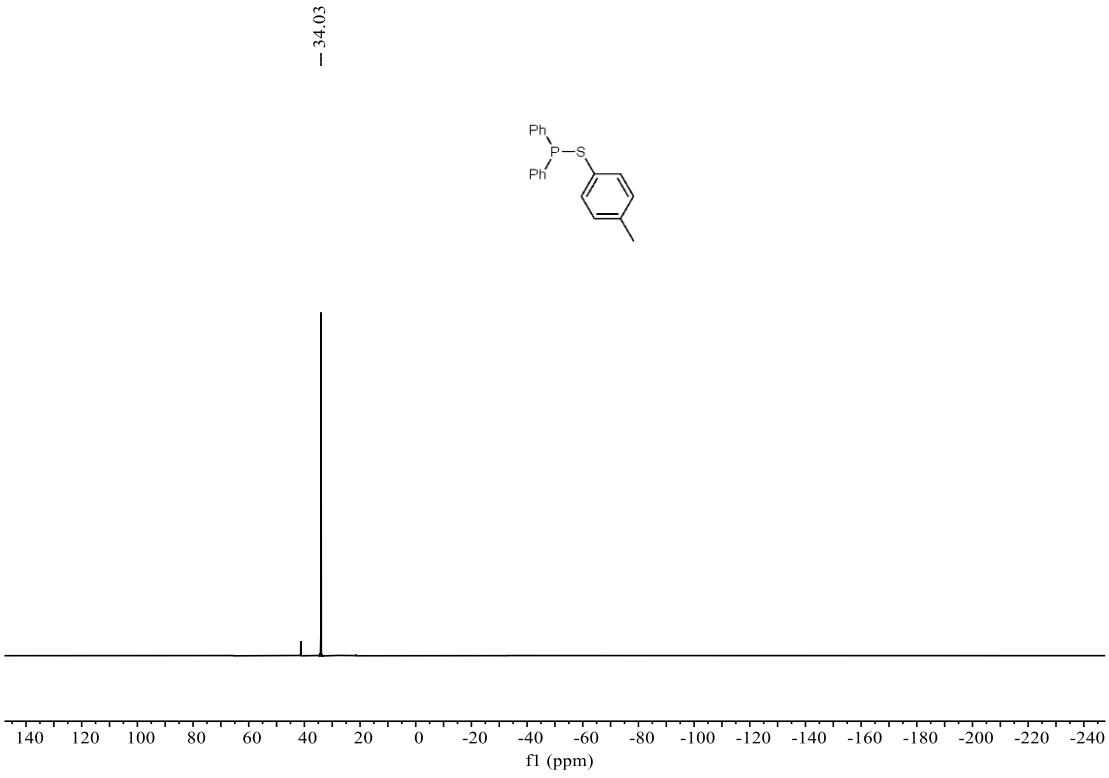




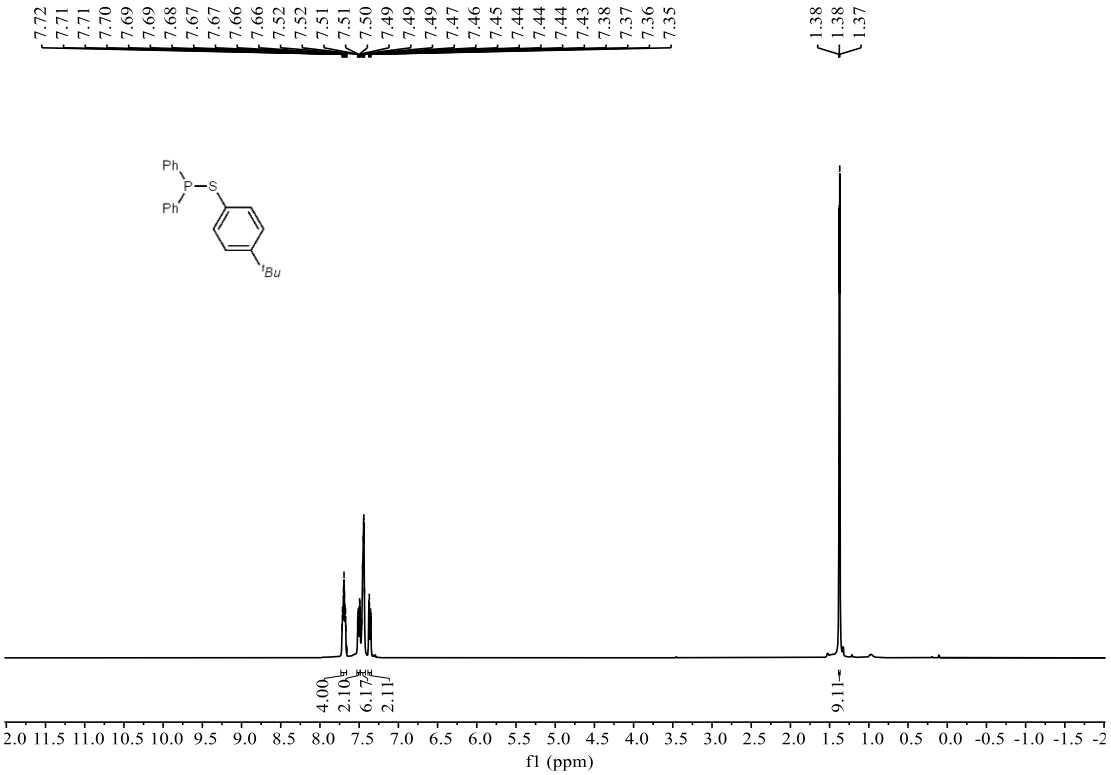
Diphenyl(p-tolylthio)phosphane (**4d)**

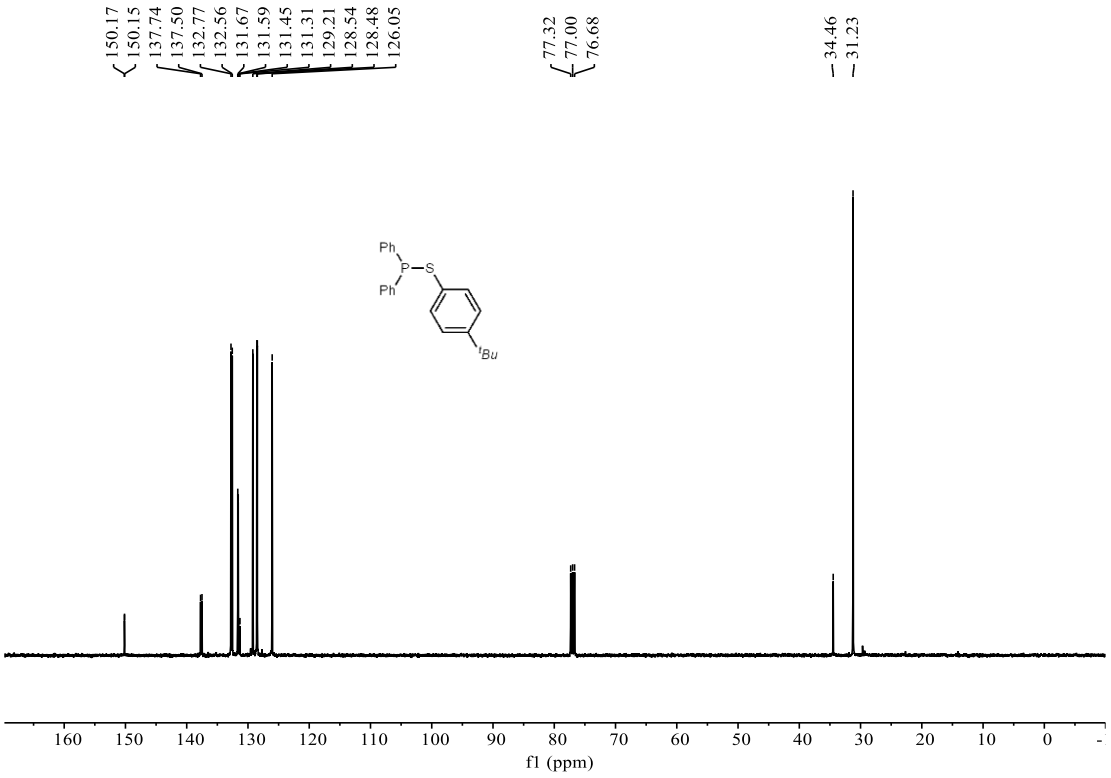


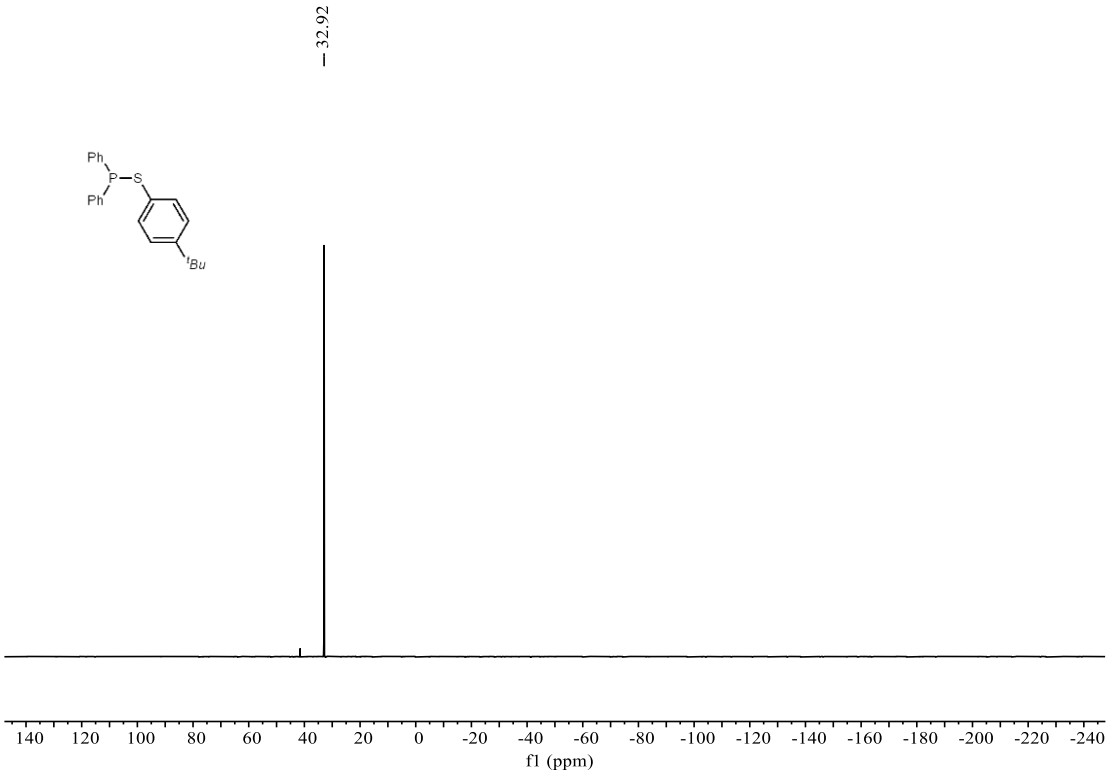

137.73
137.50
137.01
136.99
132.74
132.54
132.17
132.10
131.63
131.53
131.23
131.09
129.72
129.19
128.51
128.45
77.32
77.00
76.68
21.00
Ph
P
S
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


34.03
Ph
P
S
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

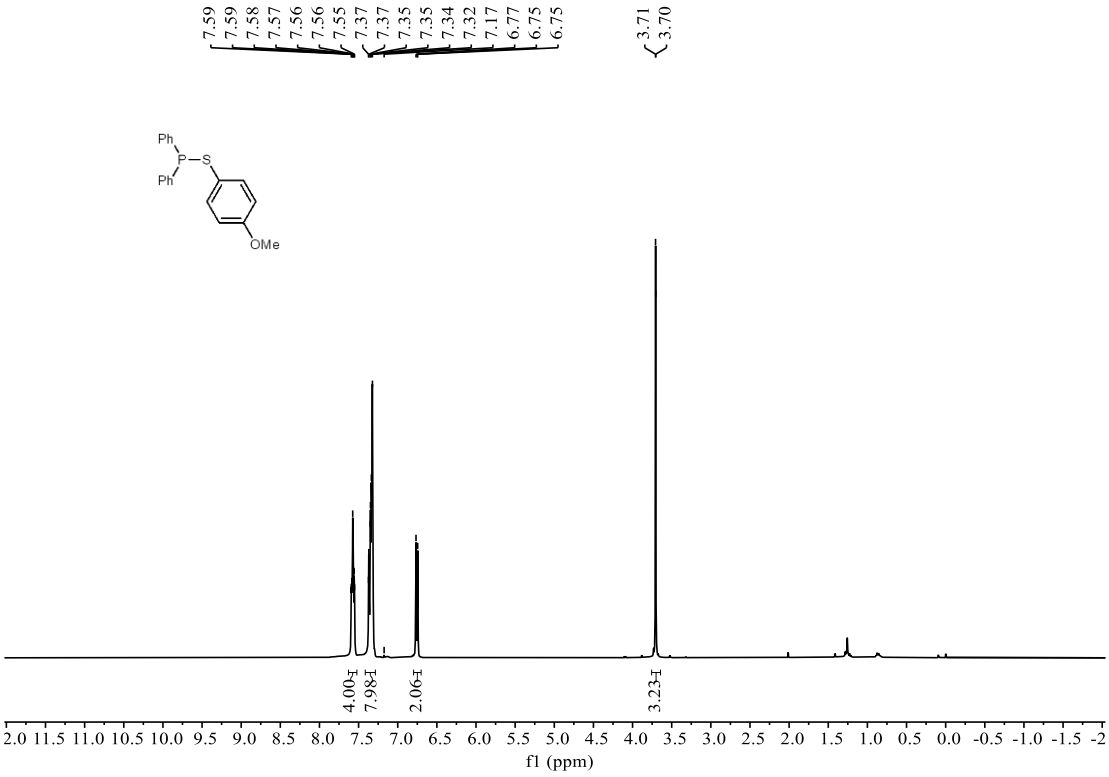
((4-(Tert-butyl)phenyl)thio)diphenylphosphane (**4e**)

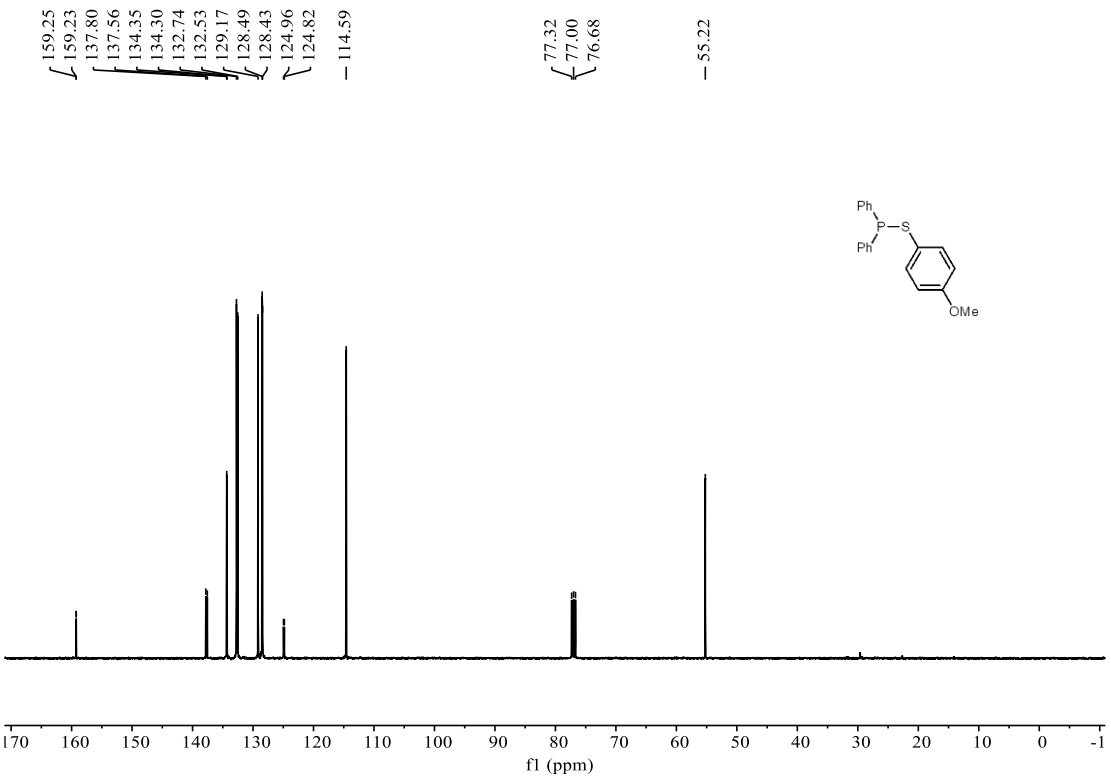


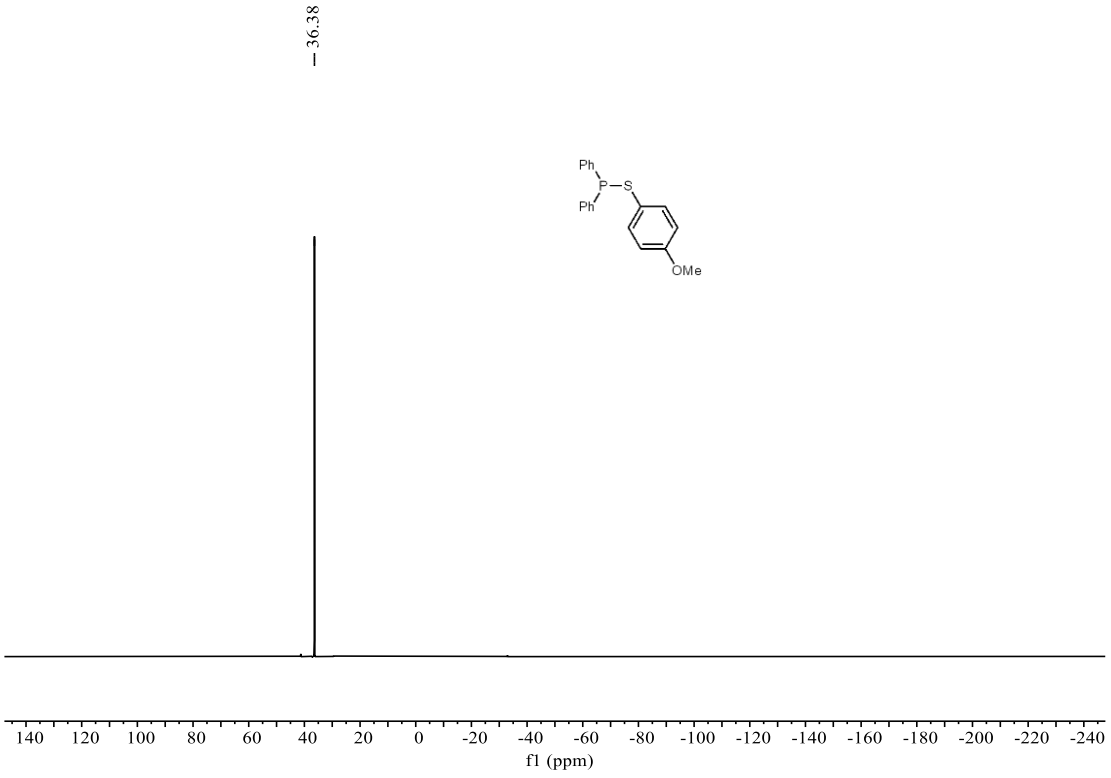




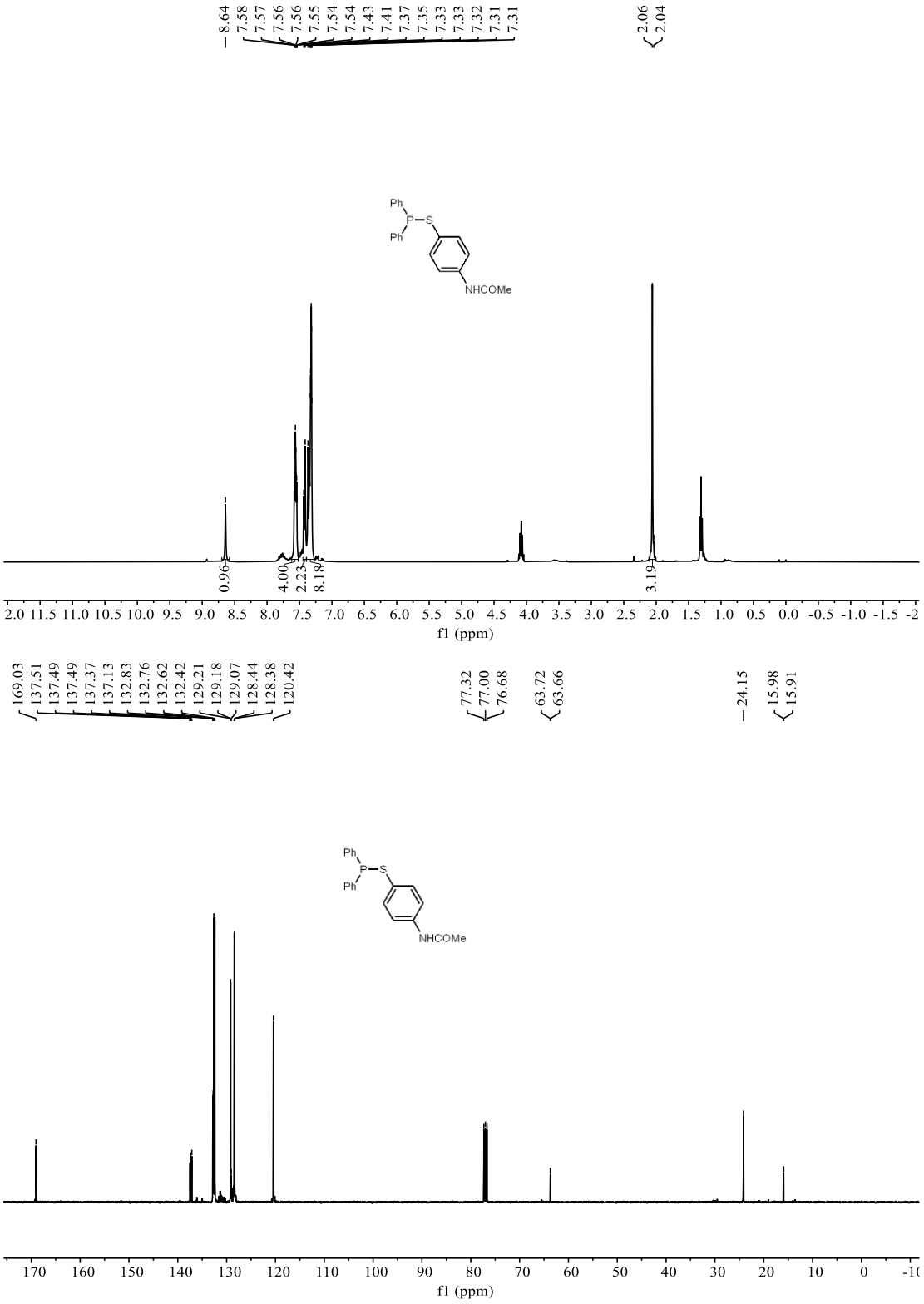
((4-Methoxyphenyl)thio)diphenylphosphane (**4f**)

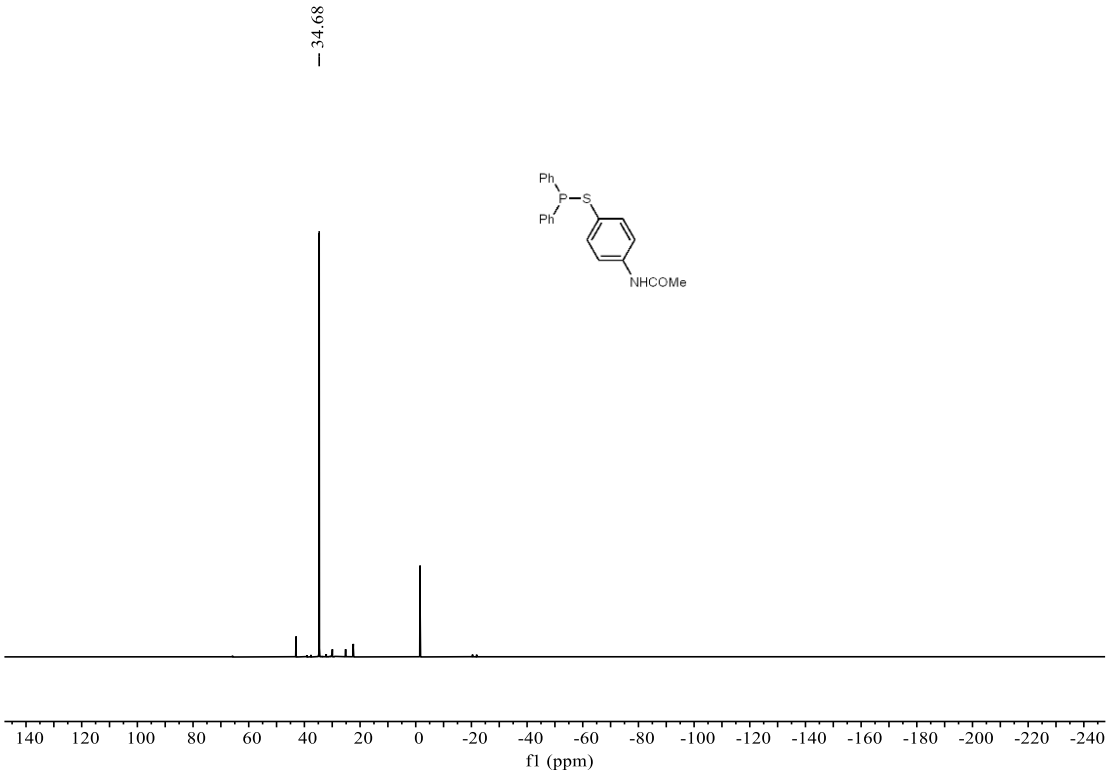



159.25
159.23
137.80
137.56
134.35
134.30
132.74
132.53
129.17
128.49
128.43
124.96
124.82
114.59
77.32
77.00
76.68
55.22
Ph
P
S
Ph
OMe
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

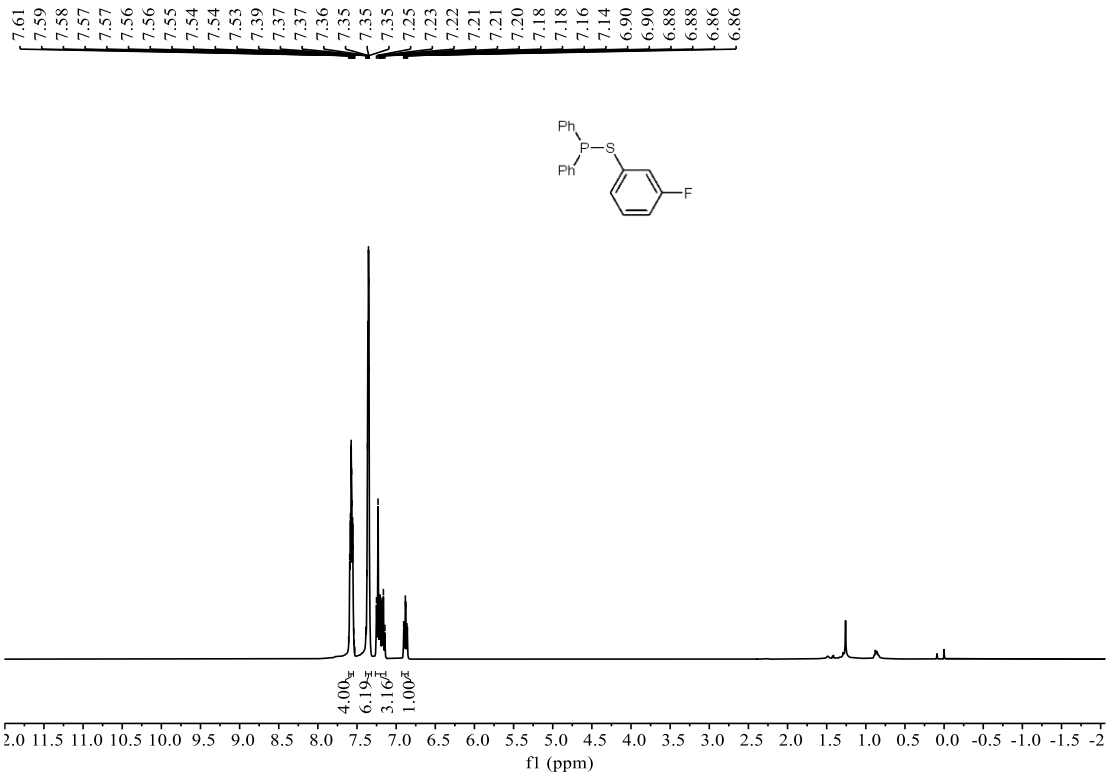

36.38
Ph
P
S
Ph
OMe
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

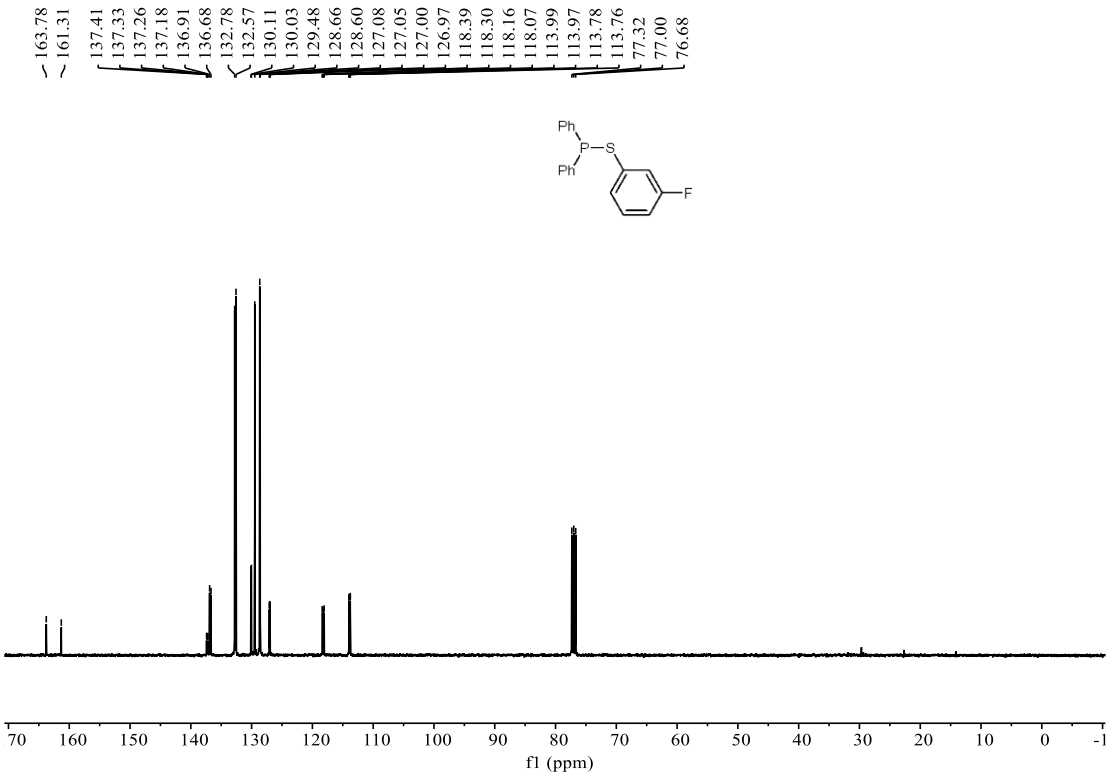
N-(4-((diphenylphosphaneyl)thio)phenyl)acetamide (**4g**)

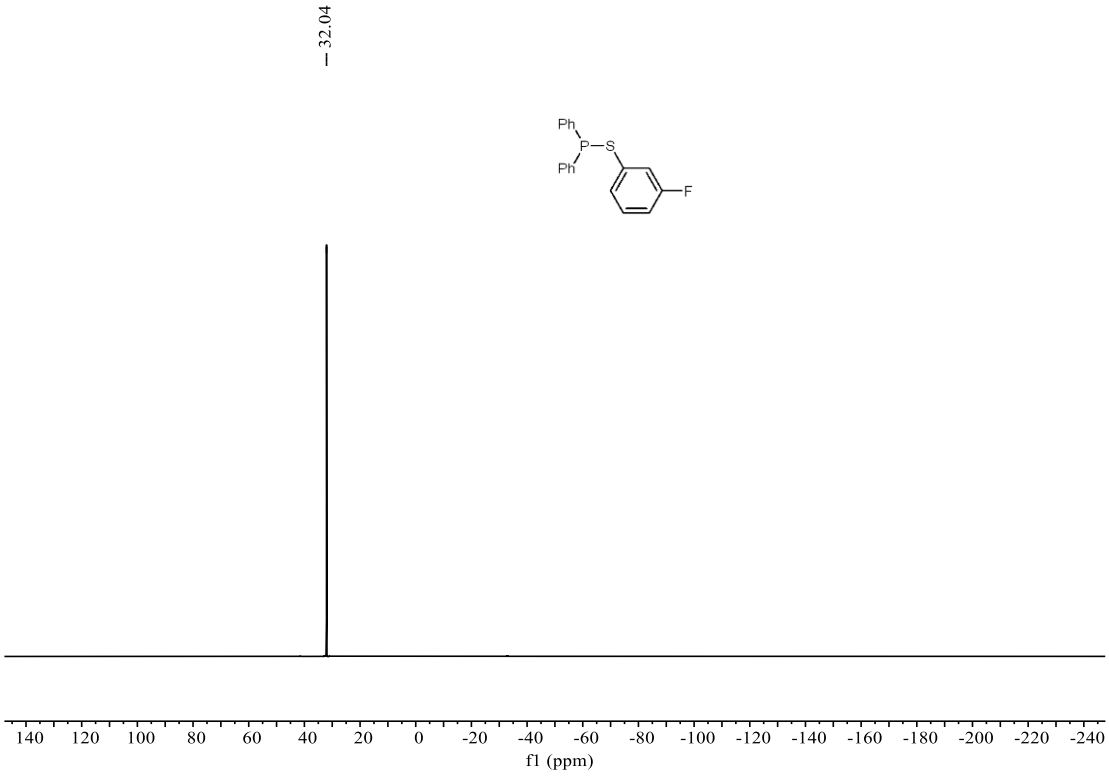


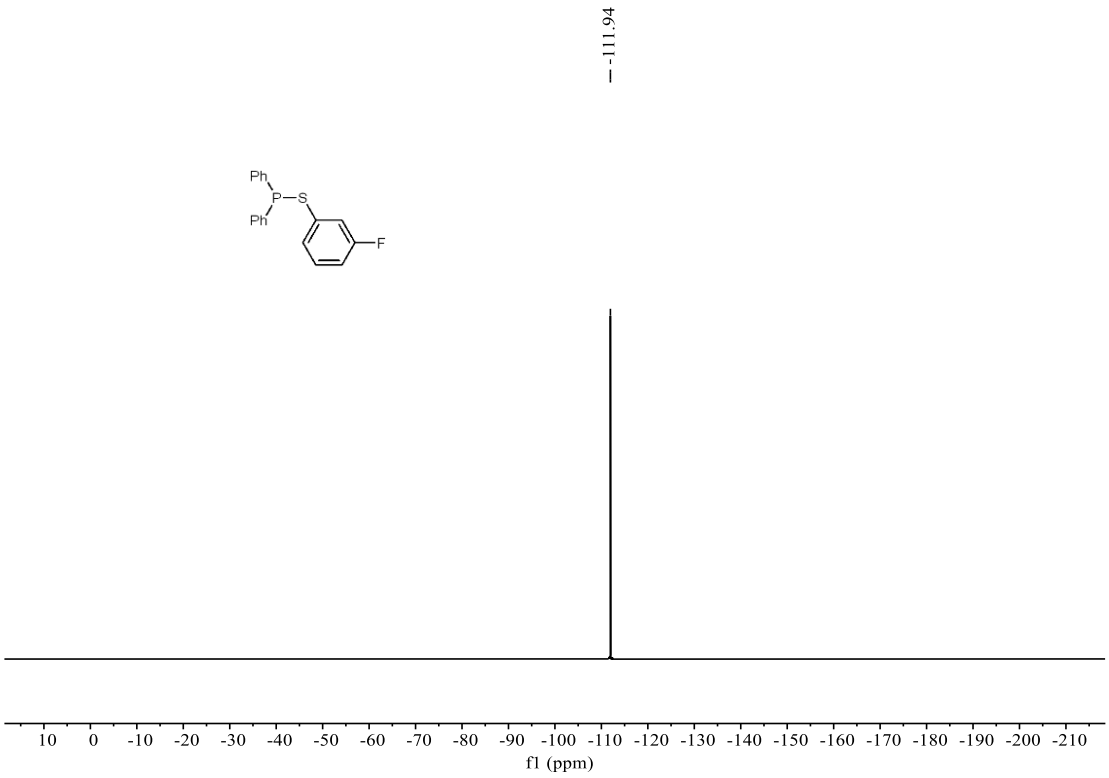


((3-Fluorophenyl)thio)diphenylphosphane (**4h**)

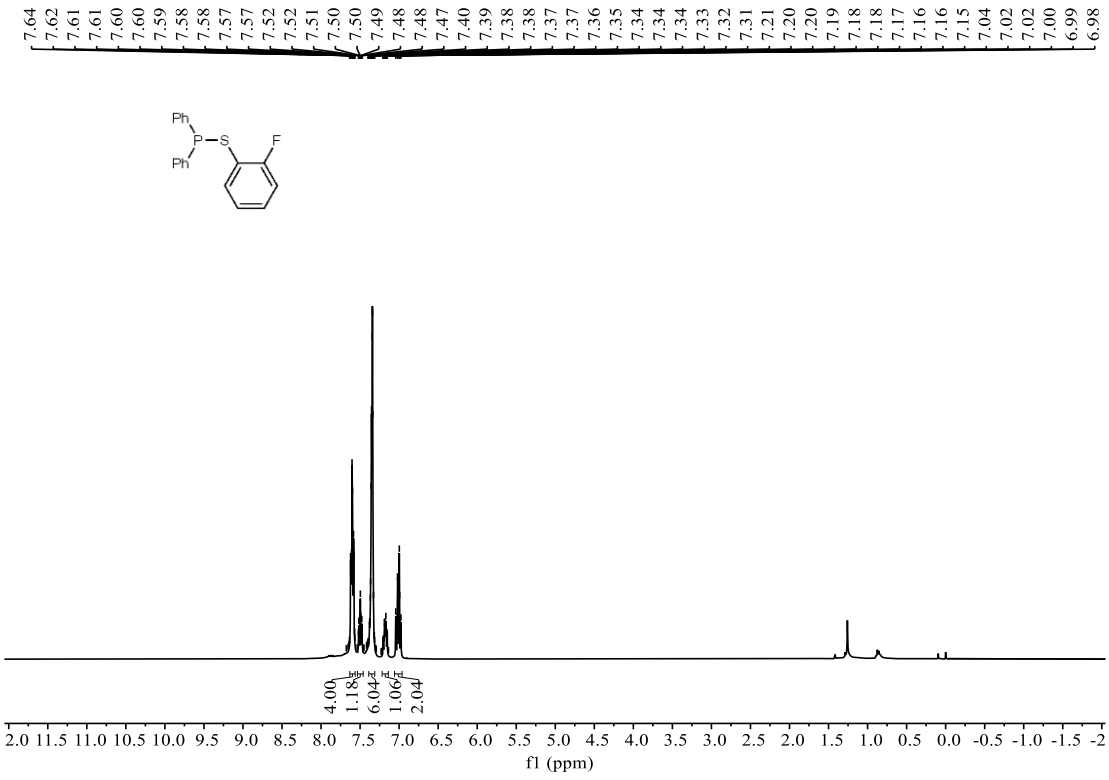


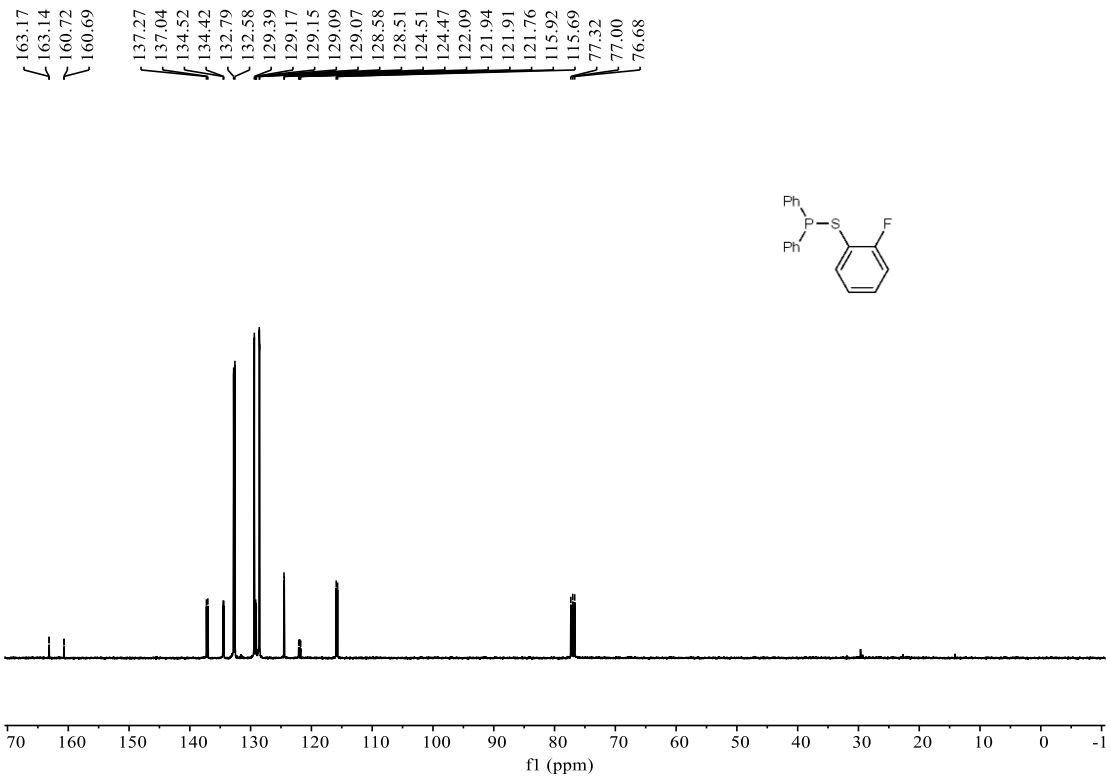

163.78
161.31
137.41
137.33
137.26
137.18
136.91
136.68
132.78
132.57
130.11
130.03
129.48
128.66
128.60
127.08
127.05
127.00
126.97
118.39
118.30
118.16
118.07
113.99
113.97
113.78
113.76
77.32
77.00
76.68
Ph
P
S
Ph
F
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

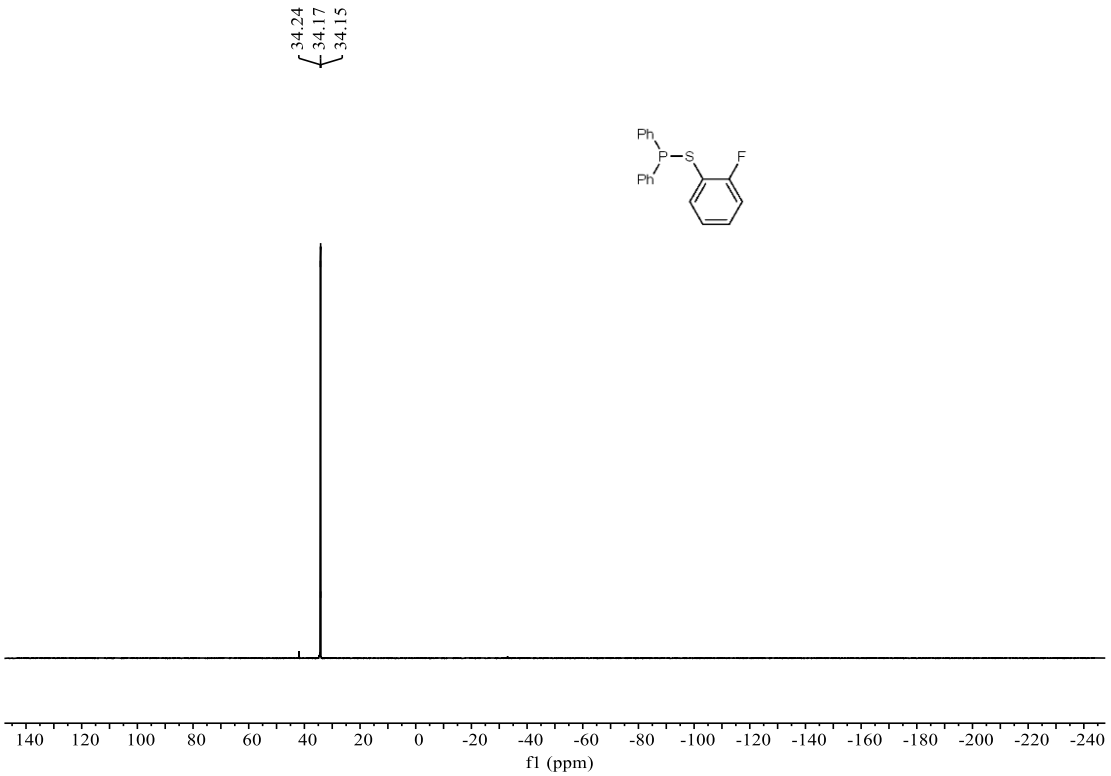

32.04
Ph
P
S
Ph
F
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

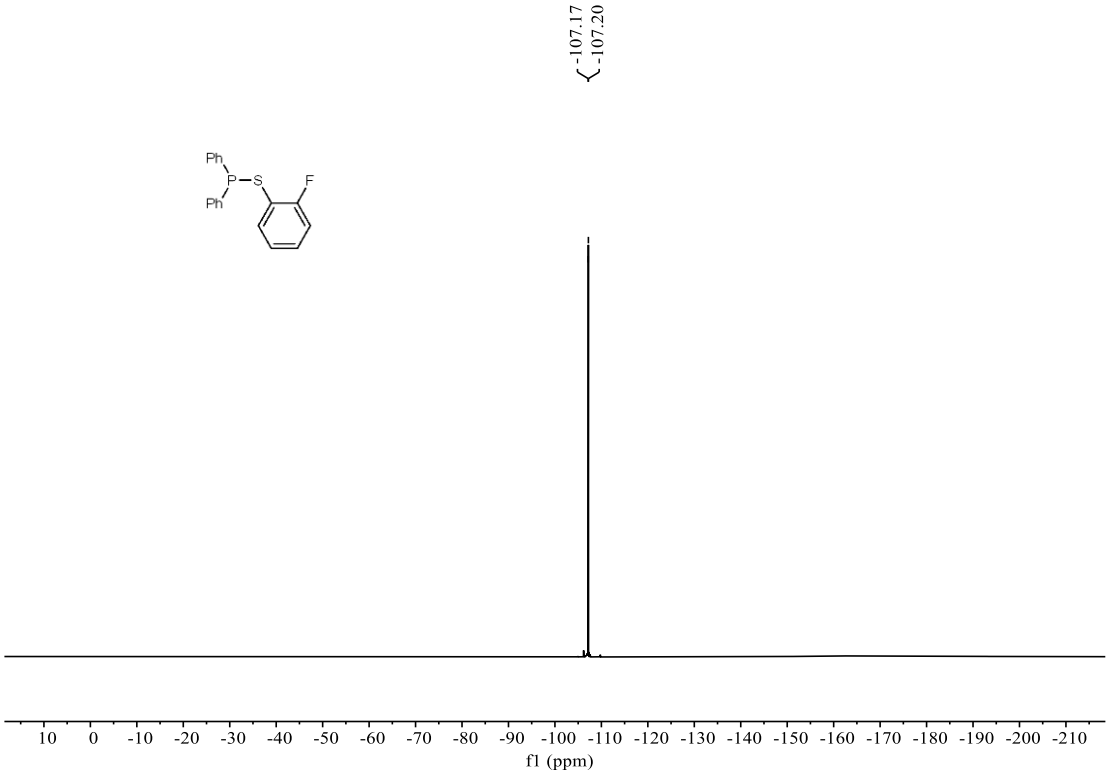


((2-Fluorophenyl)thio)diphenylphosphane (**4i**)

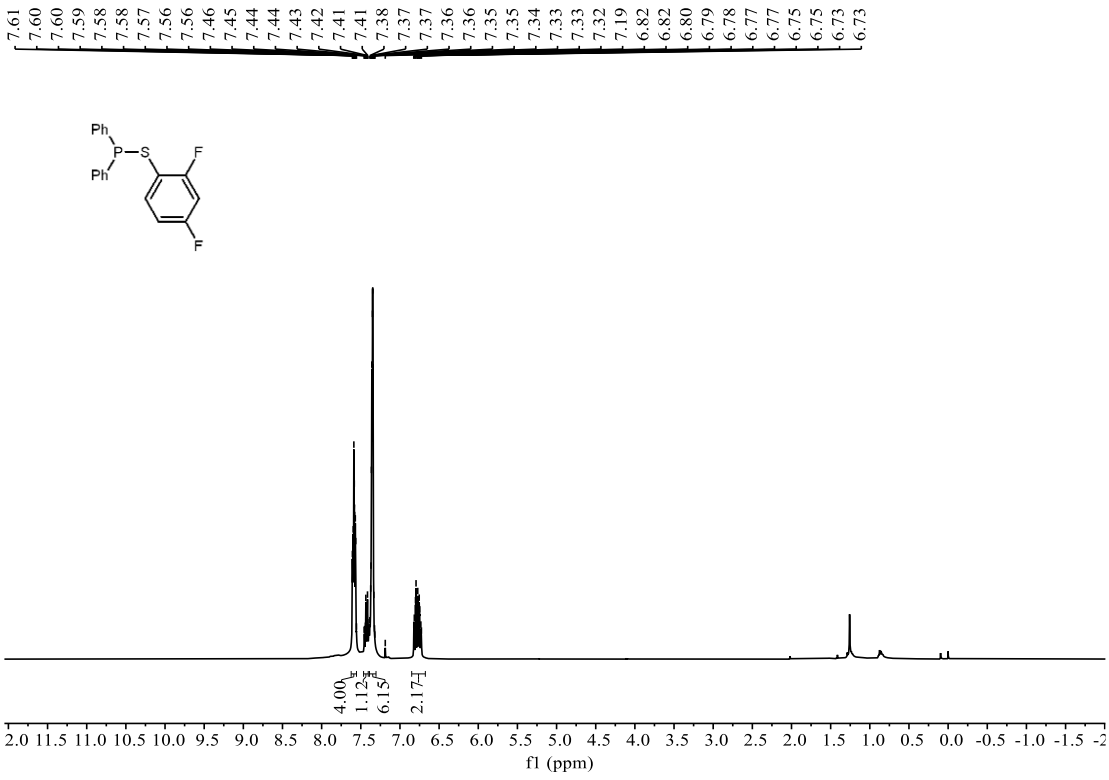


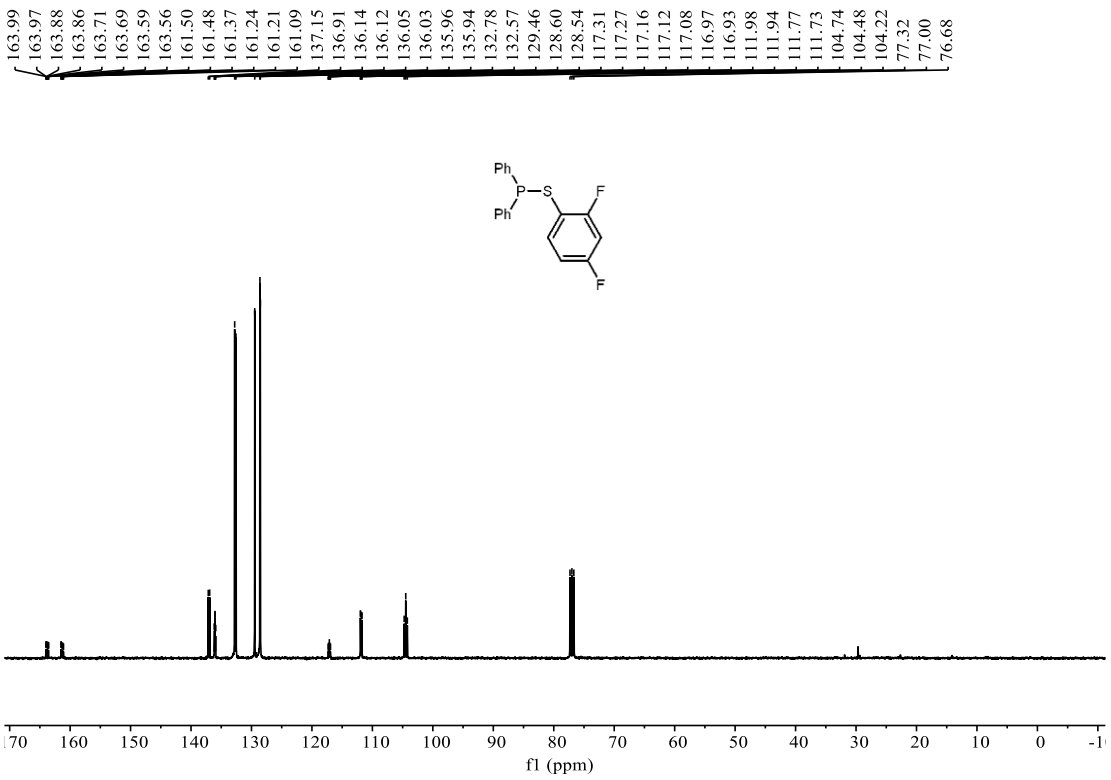

163.17
163.14
160.72
160.69
137.27
137.04
134.52
134.42
132.79
132.58
129.39
129.17
129.15
129.09
129.07
128.58
128.51
124.51
124.47
122.09
121.94
121.91
121.76
115.92
115.69
77.32
77.00
76.68
Ph
P
S
F
Ph
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

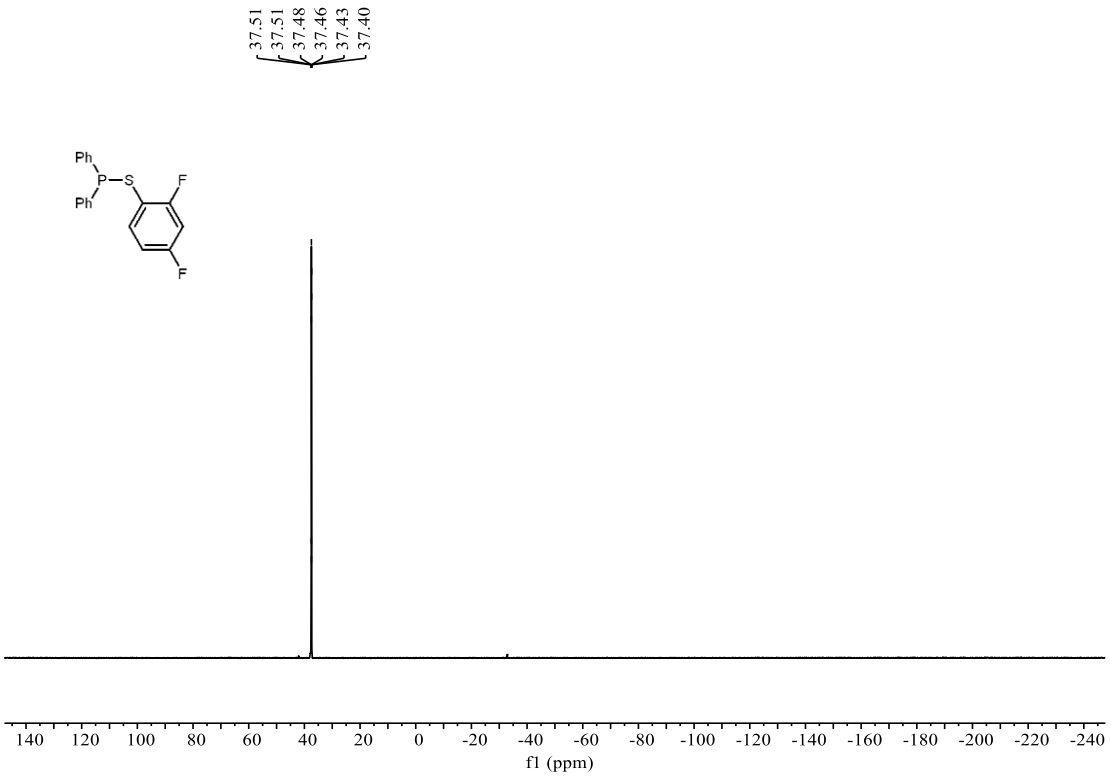

34.24
34.17
34.15
Ph
P
S
F
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

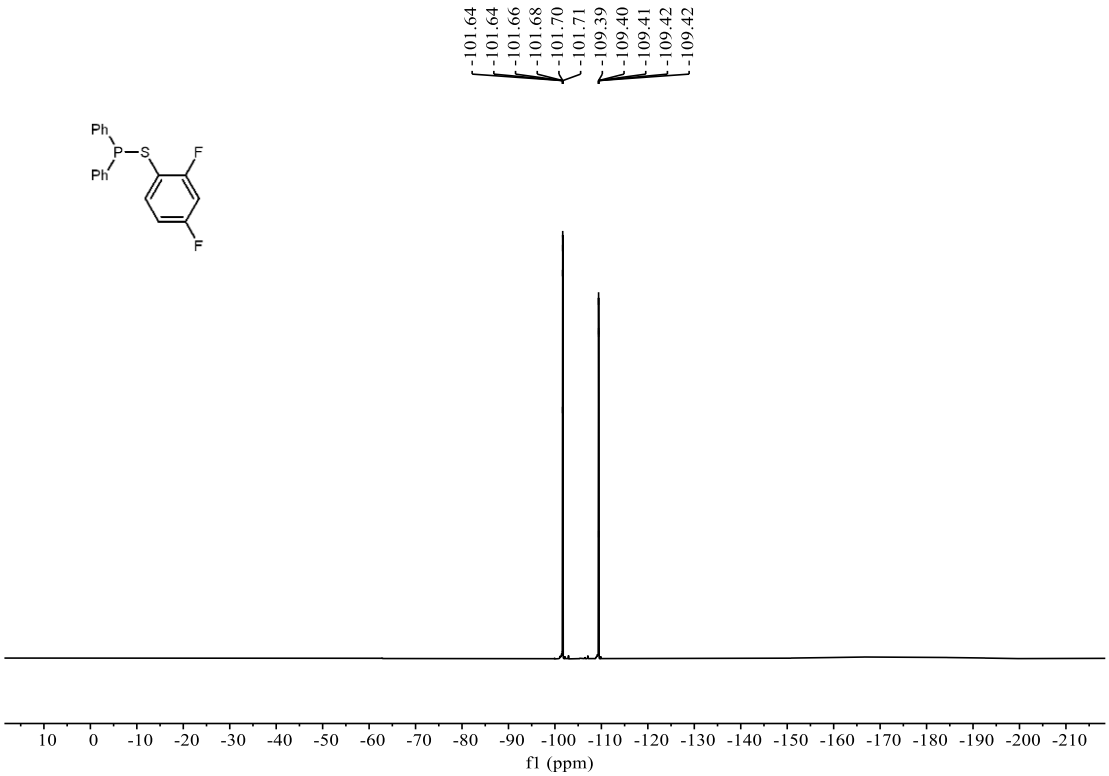


((2,4-Difluorophenyl)thio)diphenylphosphane (**4j**)

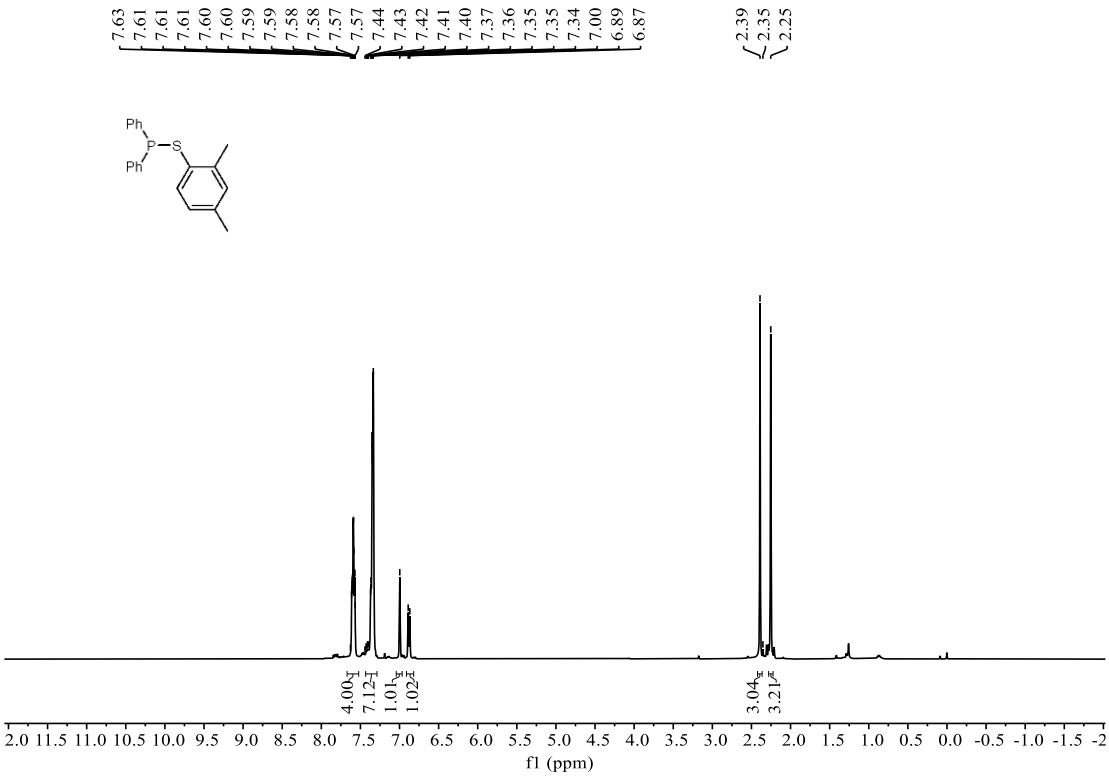


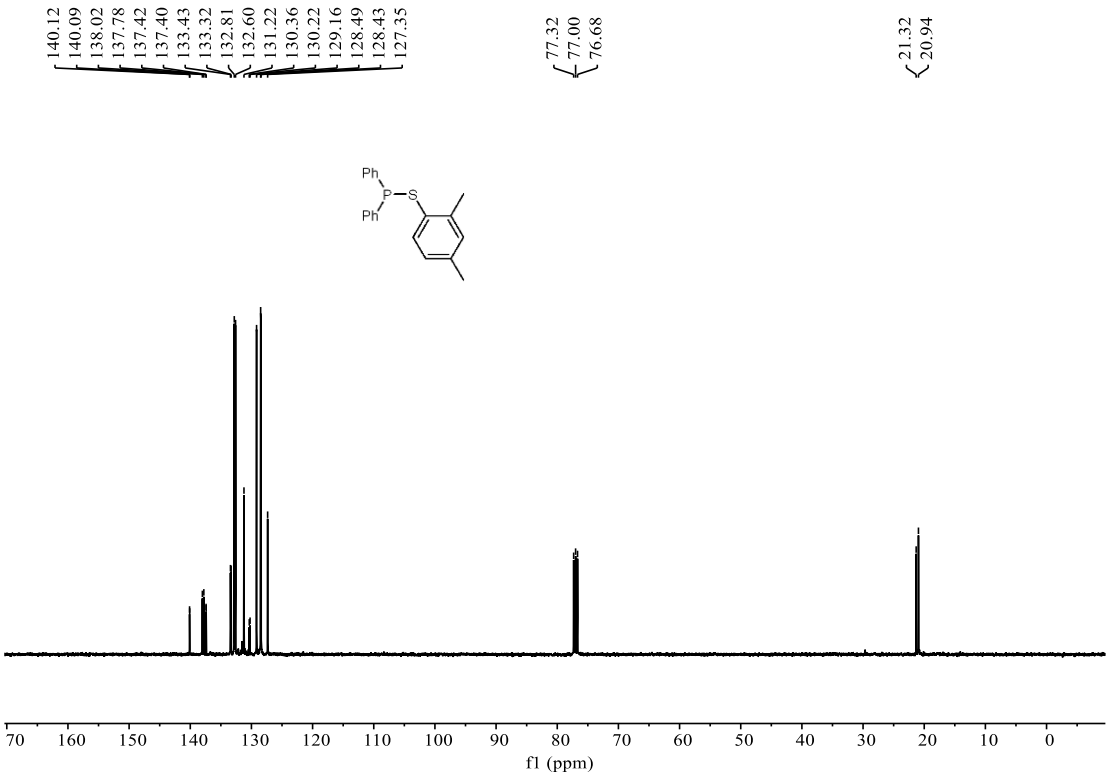

163.99
163.97
163.88
163.86
163.71
163.69
163.59
163.56
161.50
161.48
161.37
161.24
161.21
161.09
137.15
136.91
136.14
136.12
136.05
136.03
135.96
135.94
132.78
132.57
129.46
128.60
128.54
117.31
117.27
117.16
117.12
117.08
116.97
116.93
111.98
111.94
111.77
111.73
104.74
104.48
104.22
77.32
77.00
76.68
Ph
P
S
F
Ph
F
f1 (ppm)

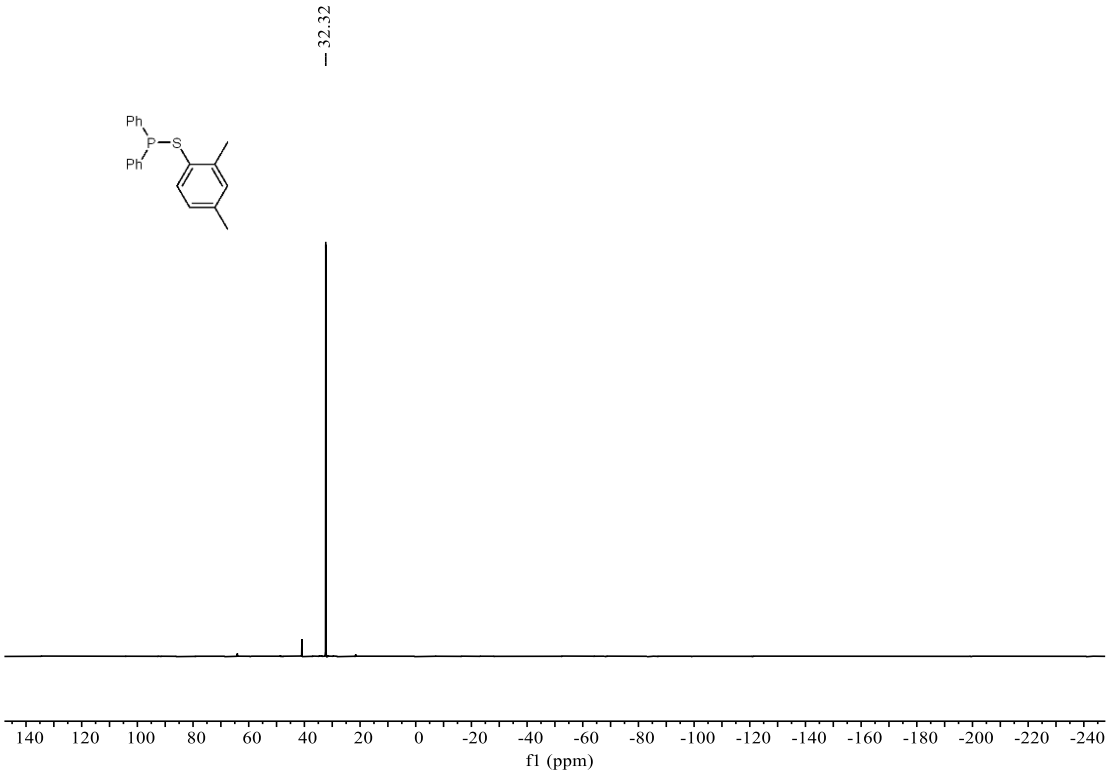

37.51
37.51
37.48
37.46
37.43
37.40
Ph
P
S
F
Ph
F
f1 (ppm)



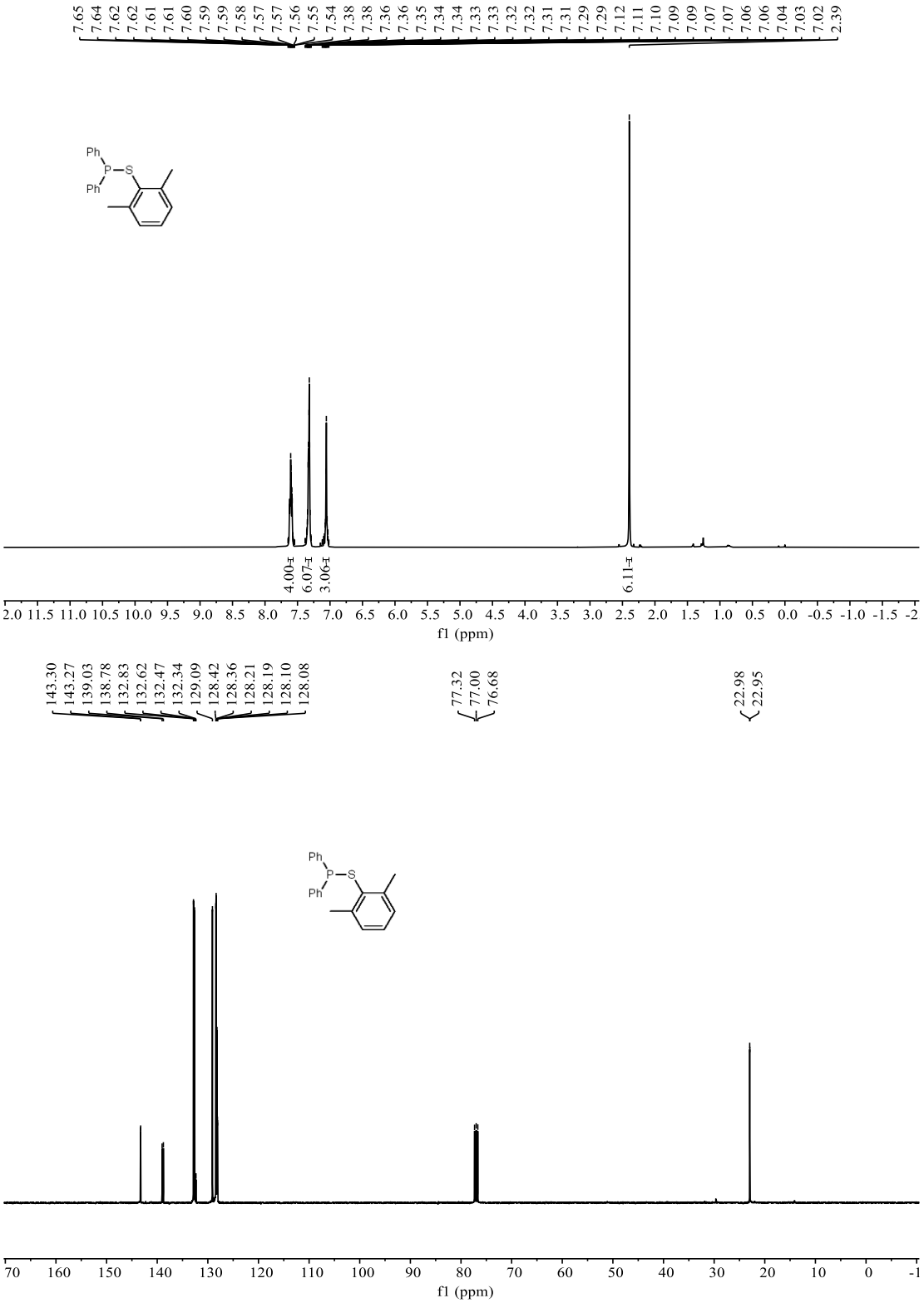
((2,4-Dimethylphenyl)thio)diphenylphosphane (**4k**)

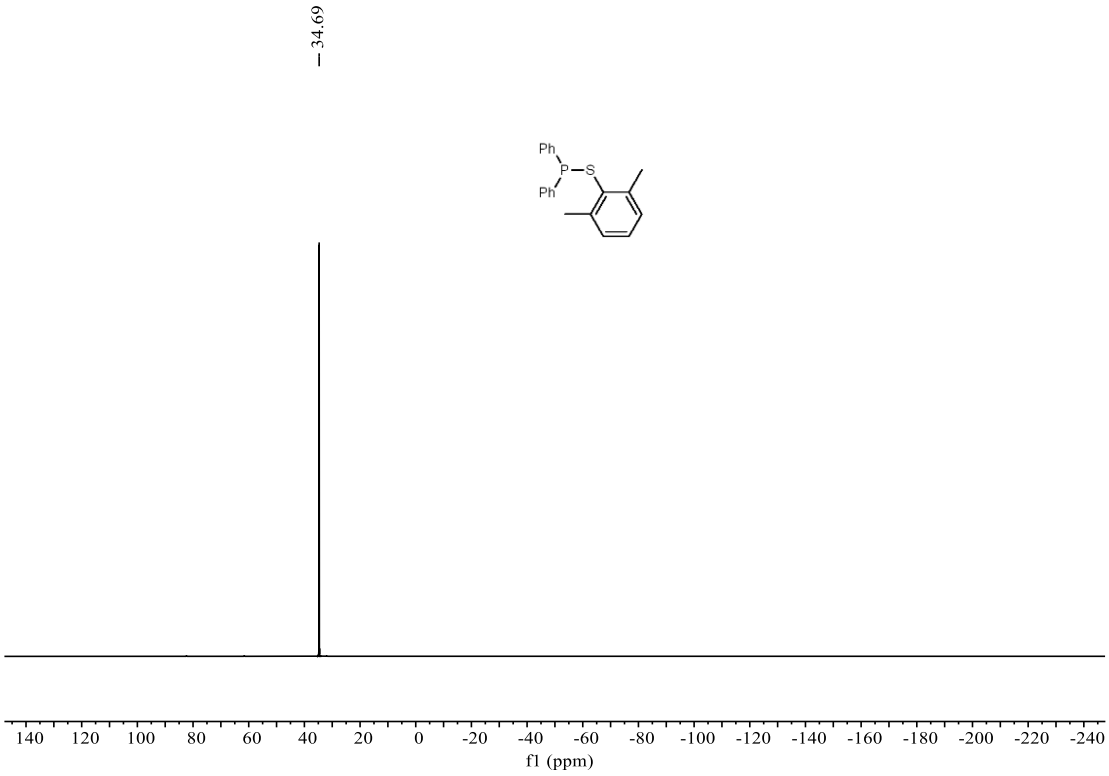



140.12
140.09
138.02
137.78
137.42
137.40
133.43
133.32
132.81
132.60
131.22
130.36
130.22
129.16
128.49
128.43
127.35
77.32
77.00
76.68
21.32
20.94
Ph
P
S
Ph
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

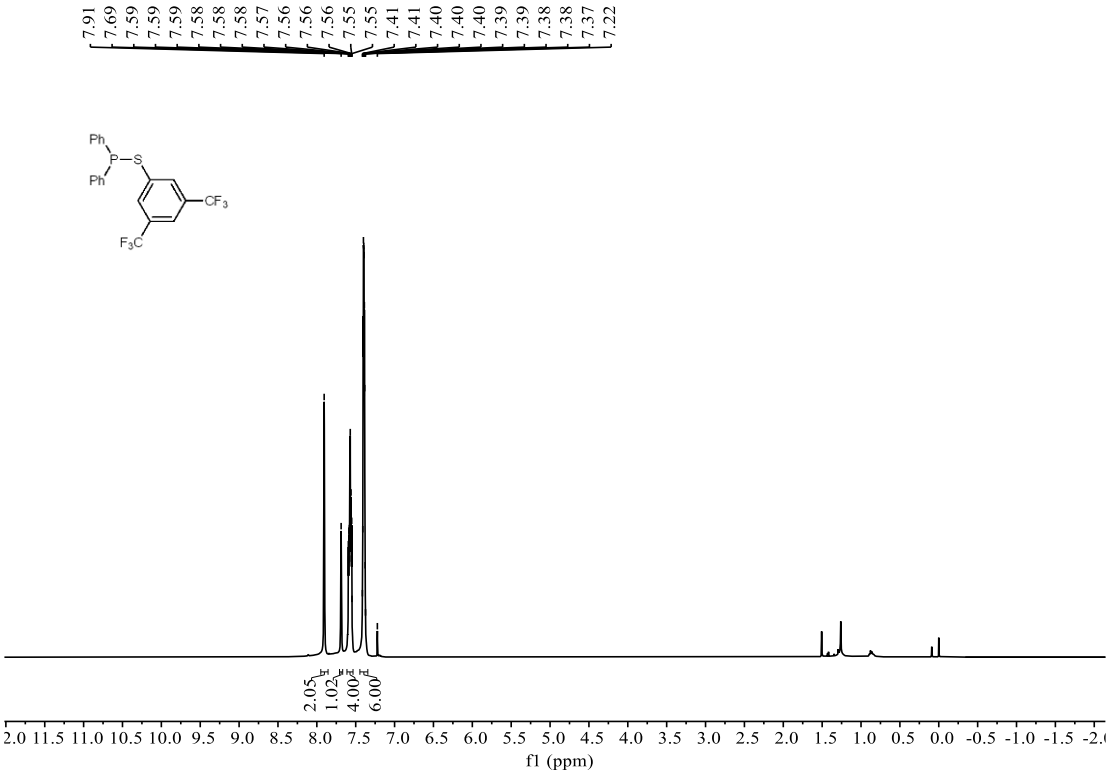

32.32
Ph
P
S
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

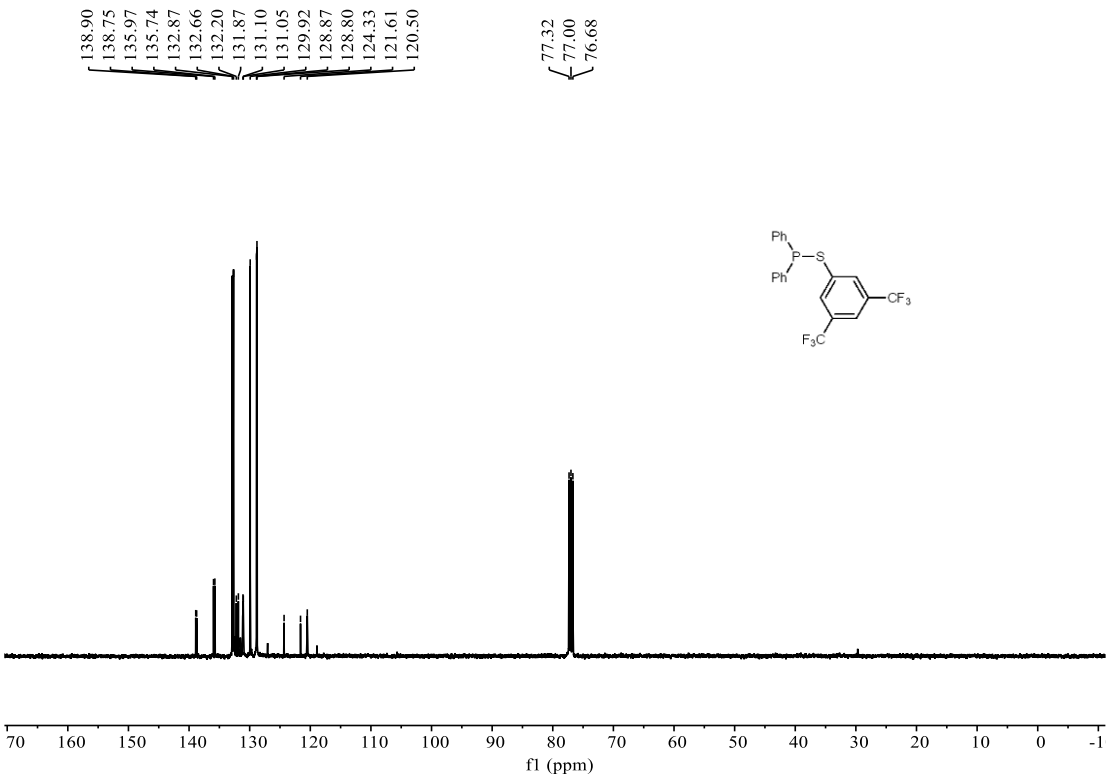
((2,6-Dimethylphenyl)thio)diphenylphosphane (**4l**)

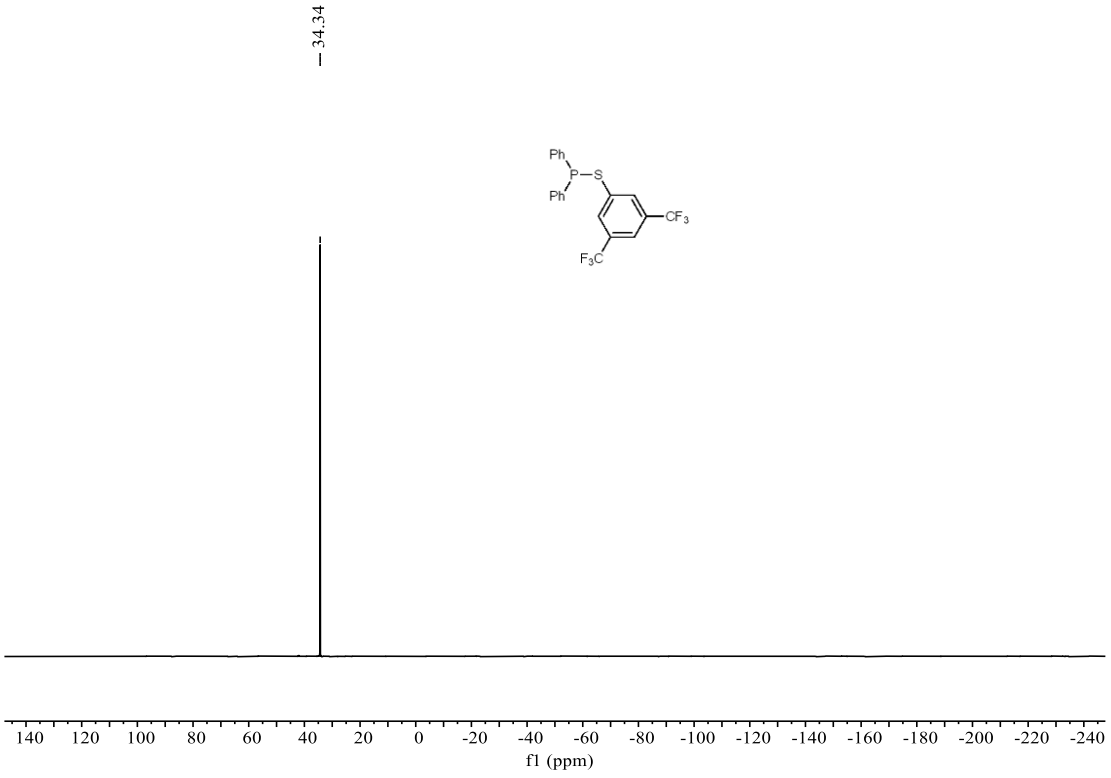


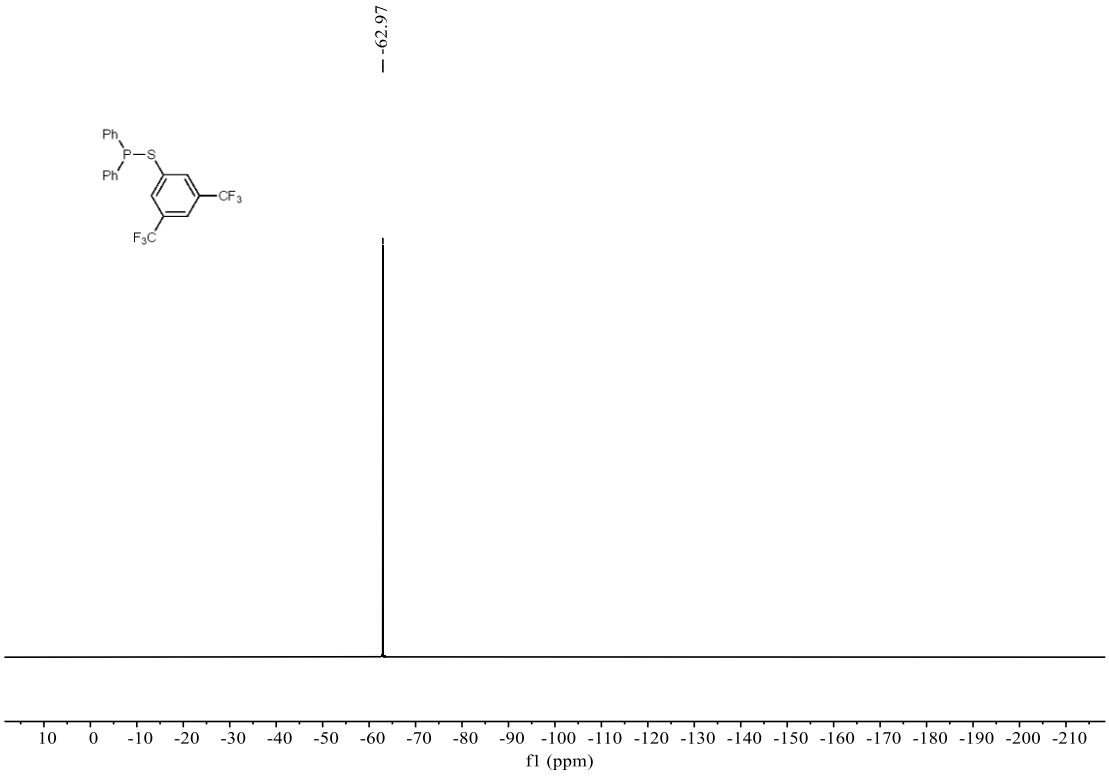


((3,5-Bis(trifluoromethyl)phenyl)thio)diphenylphosphane (**4m**)

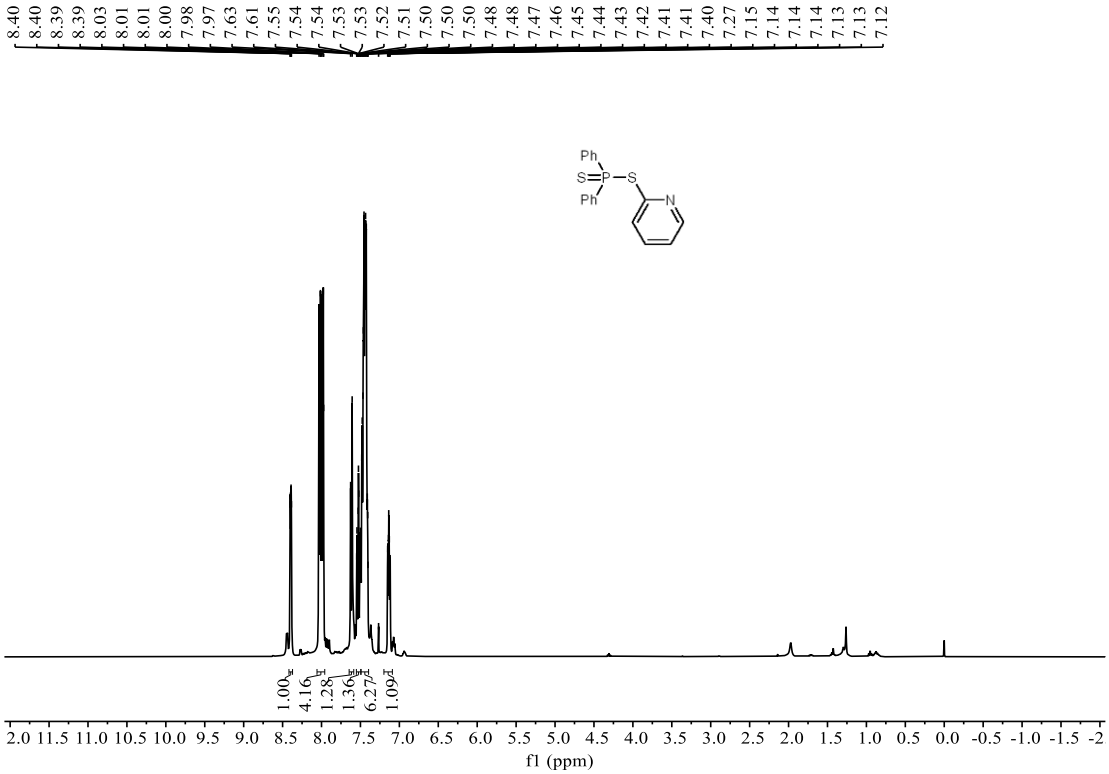


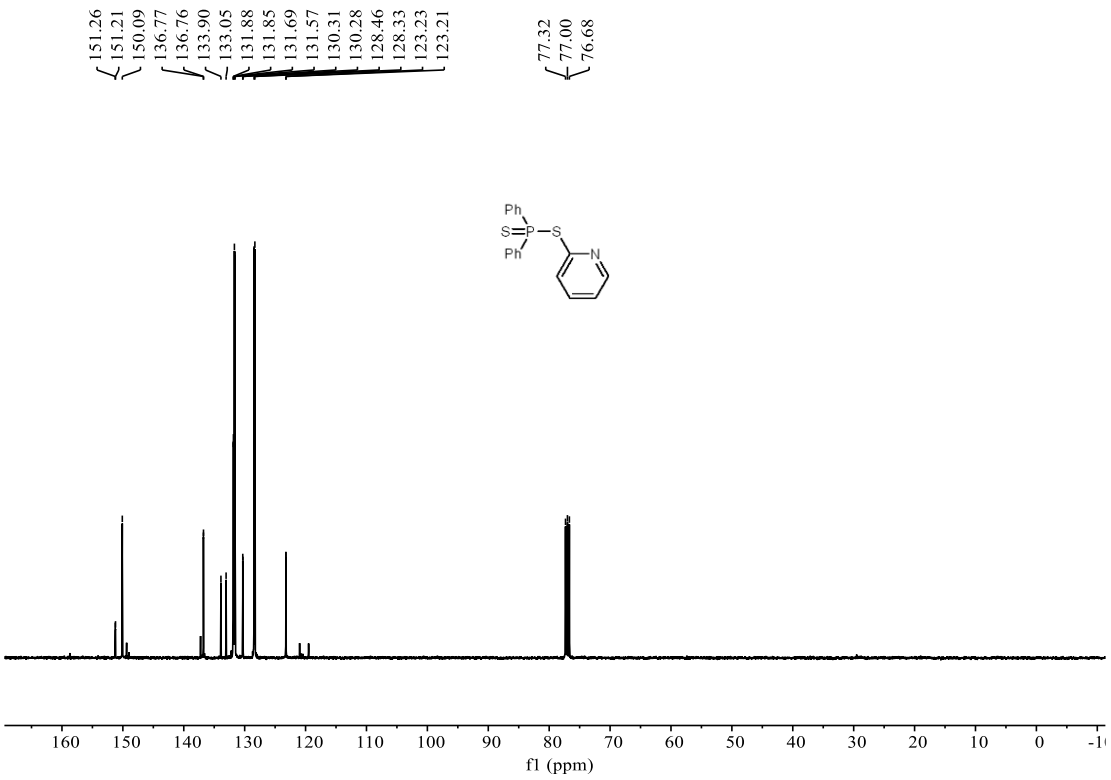

138.90
138.75
135.97
135.74
132.87
132.66
132.20
131.87
131.10
131.05
129.92
128.87
128.80
124.33
121.61
120.50
77.32
77.00
76.68
Ph
P
S
Ph
CF3
F3C
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

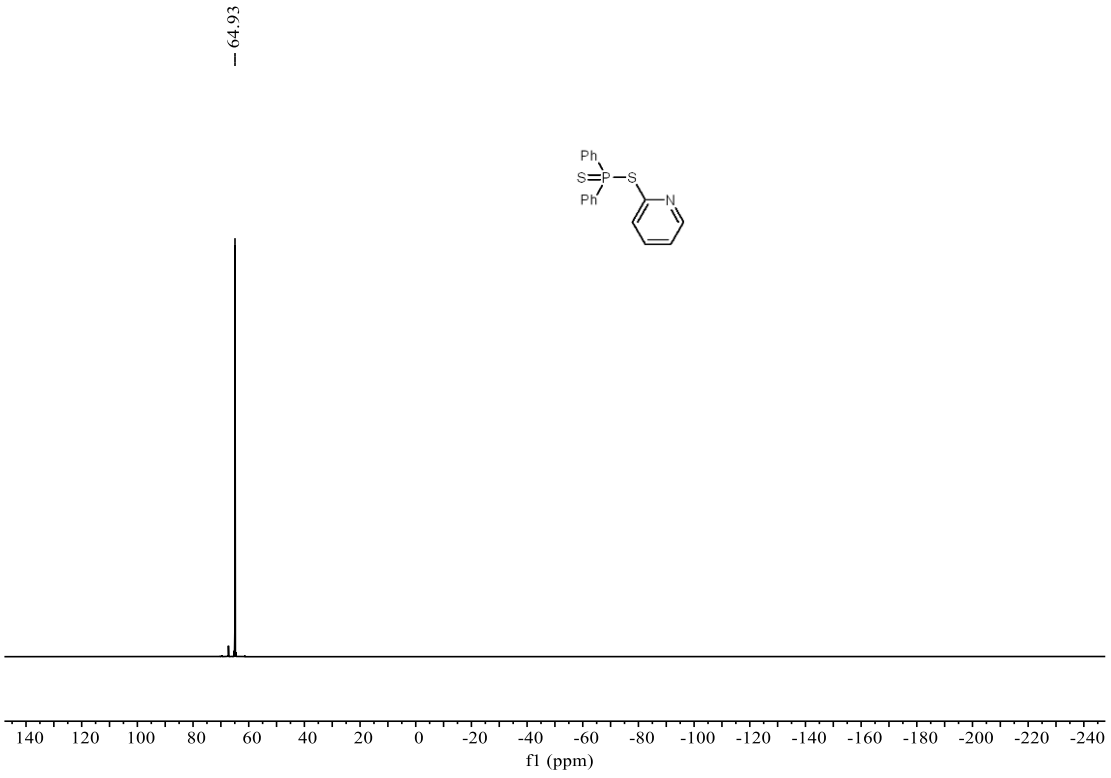

34.34
Ph
P
S
Ph
CF3
F3C
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)



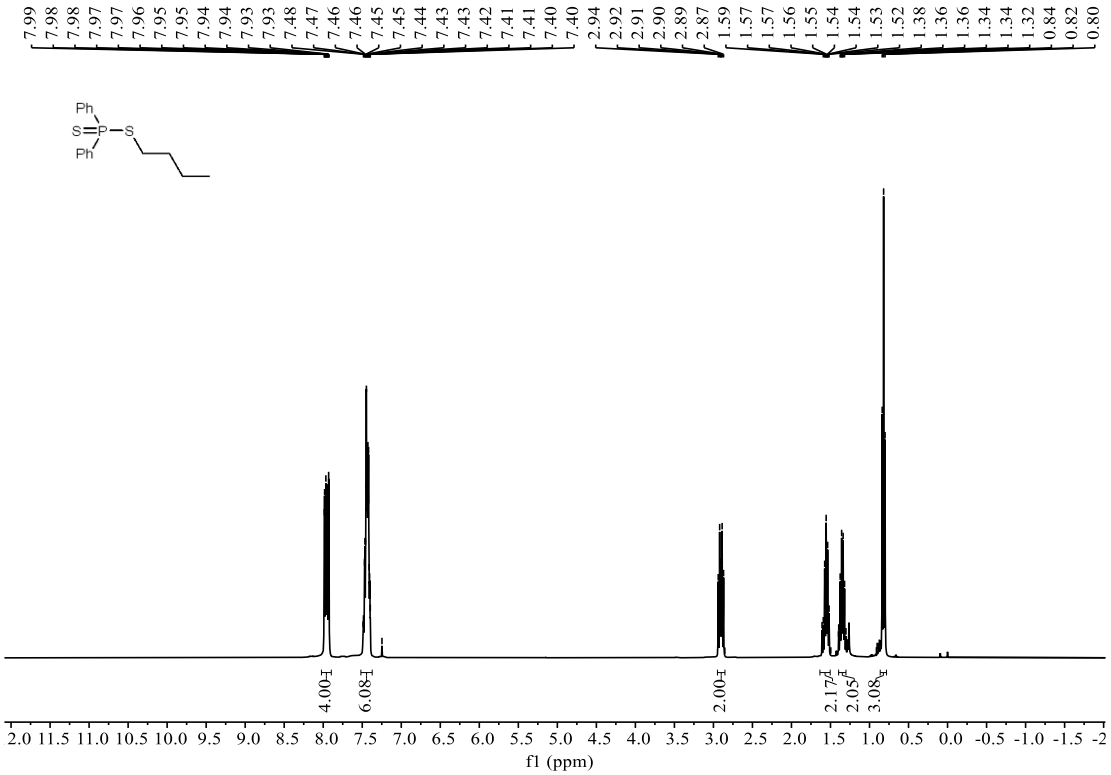
Pyridin-2-yl diphenylphosphinodithioate (**4n'**)

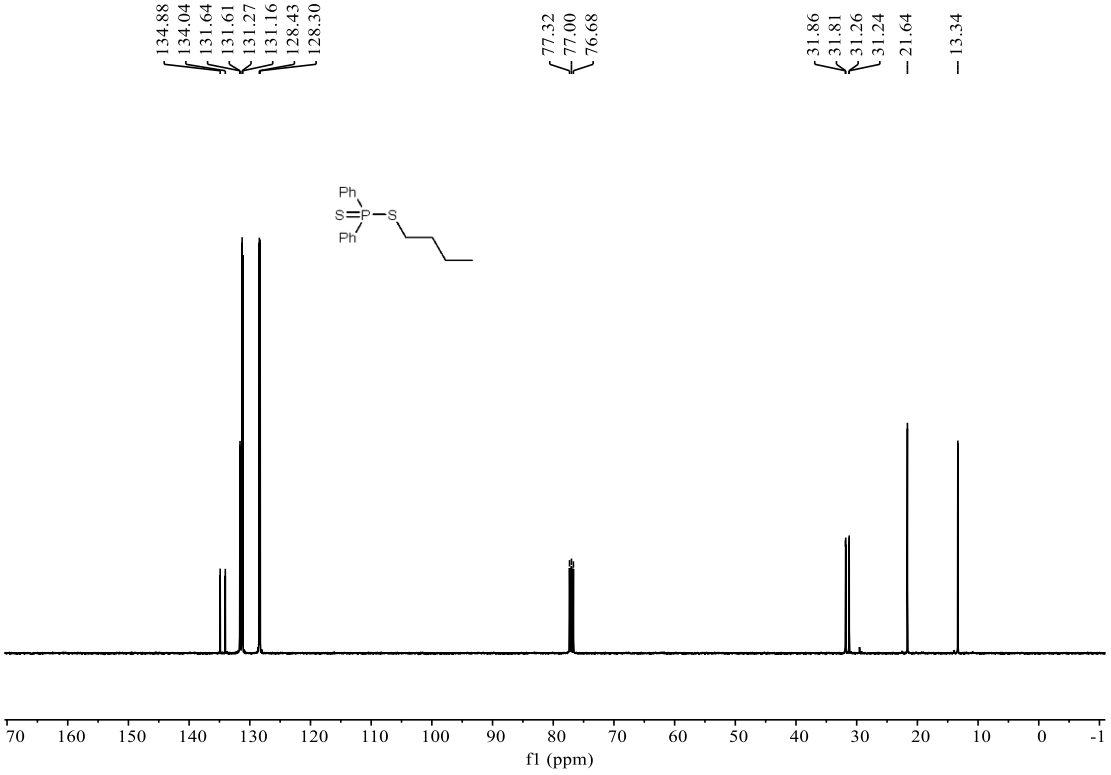


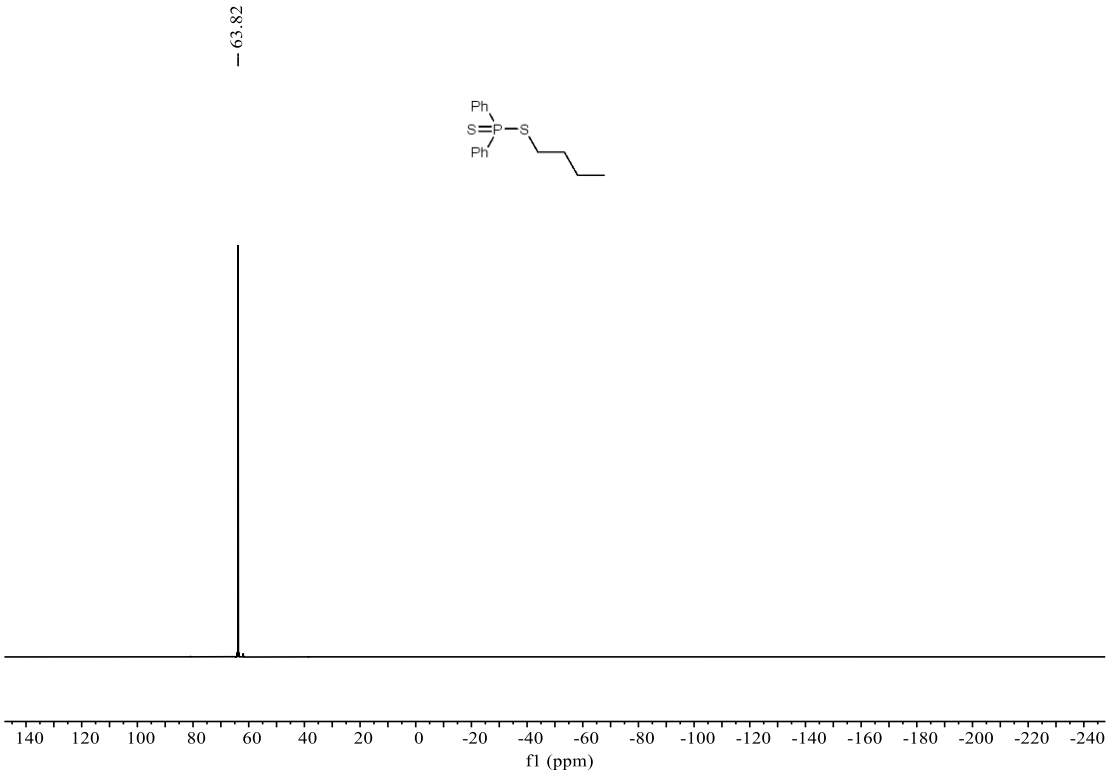

151.26
151.21
150.09
136.77
136.76
133.90
133.05
131.88
131.85
131.69
131.57
130.31
130.28
128.46
128.33
123.23
123.21
77.32
77.00
76.68
Ph
S
P
S
Ph
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


64.93
Ph
S
P
S
Ph
N
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

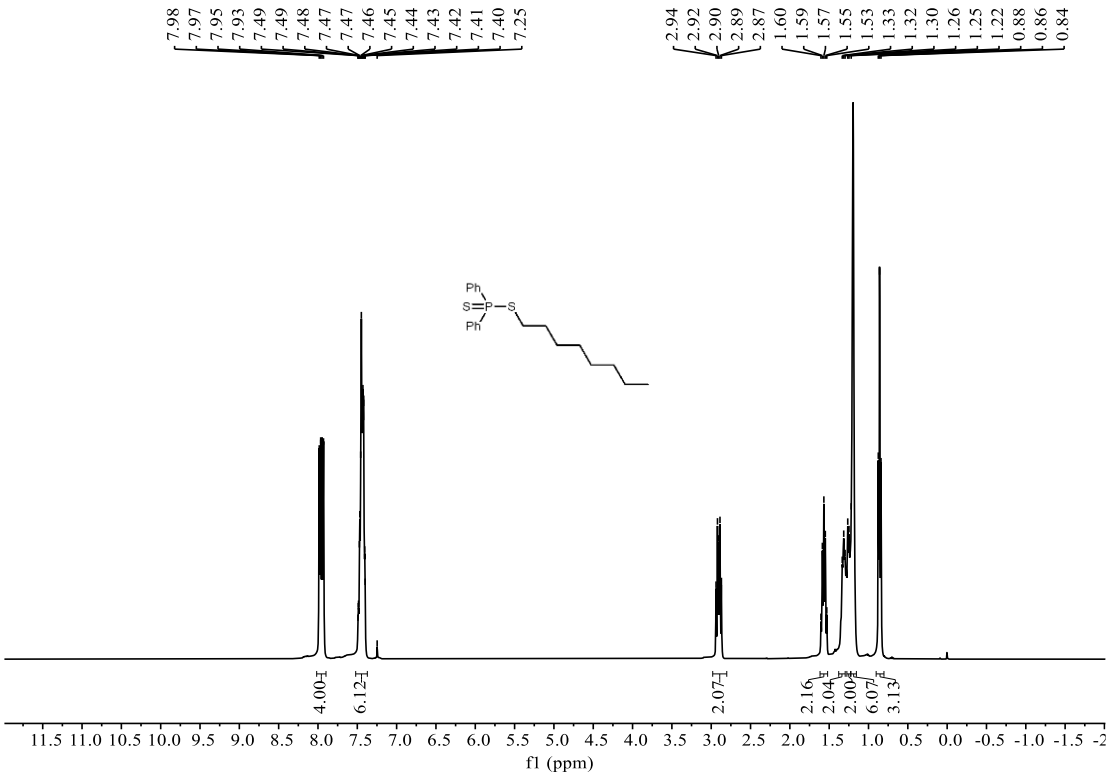
Butyl diphenylphosphinodithioate (**4o'**)

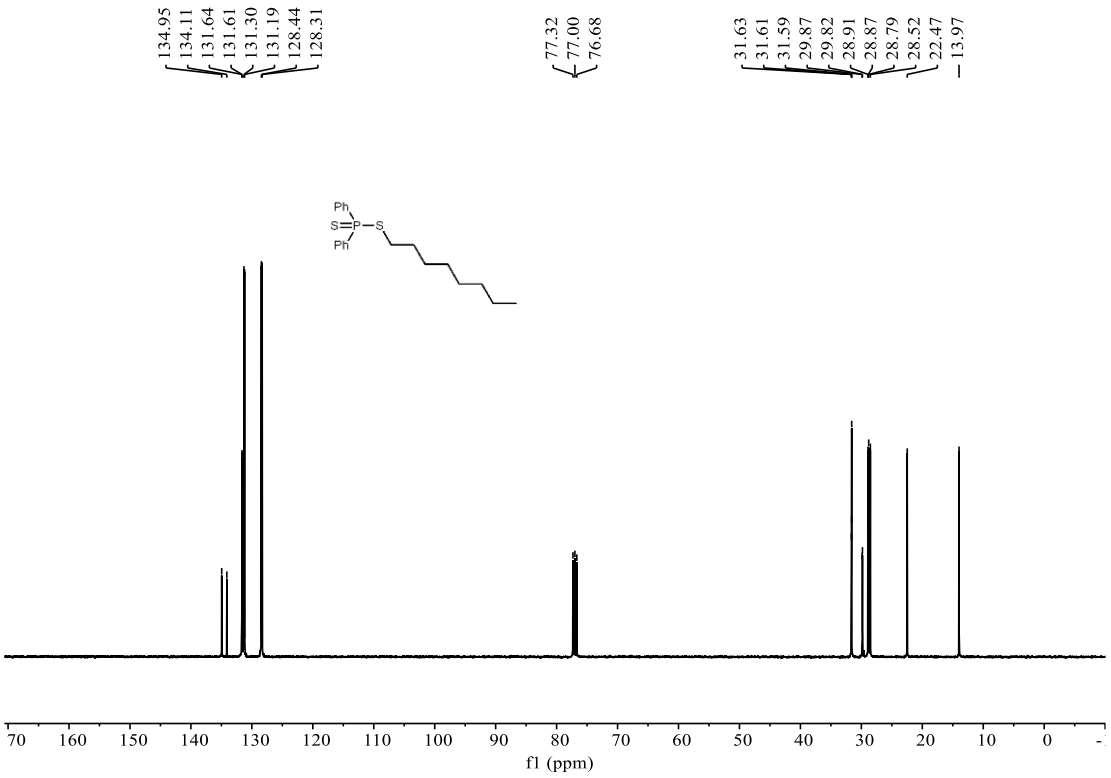


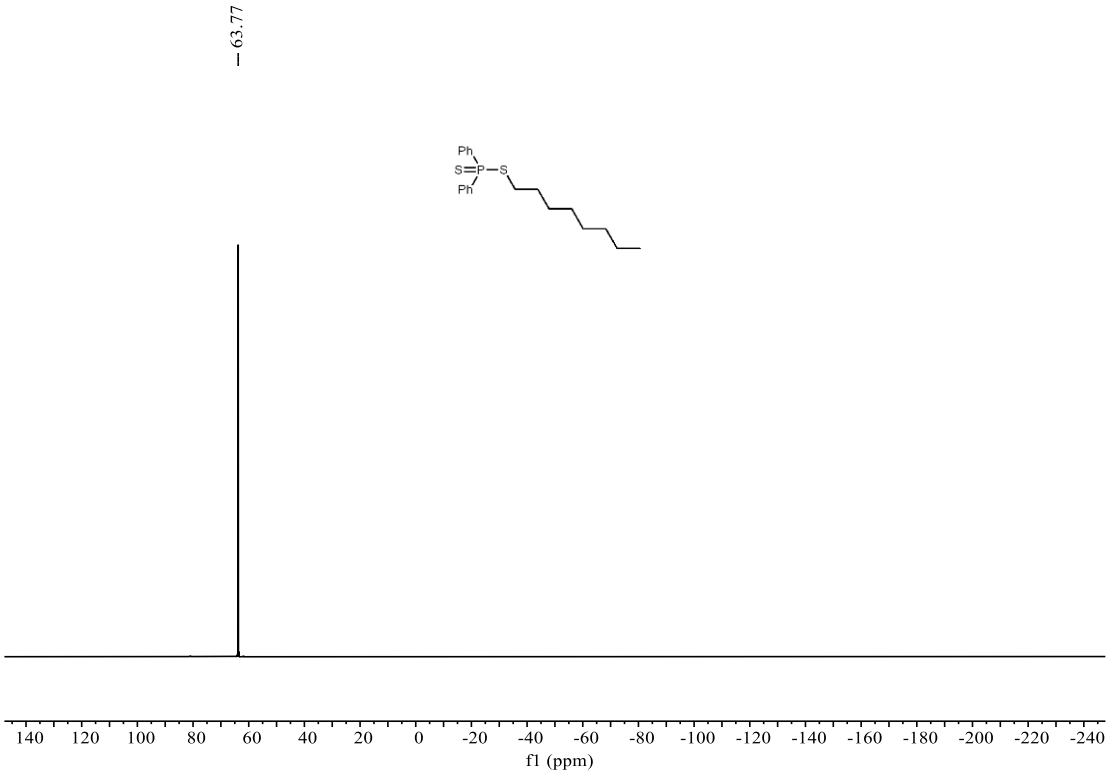




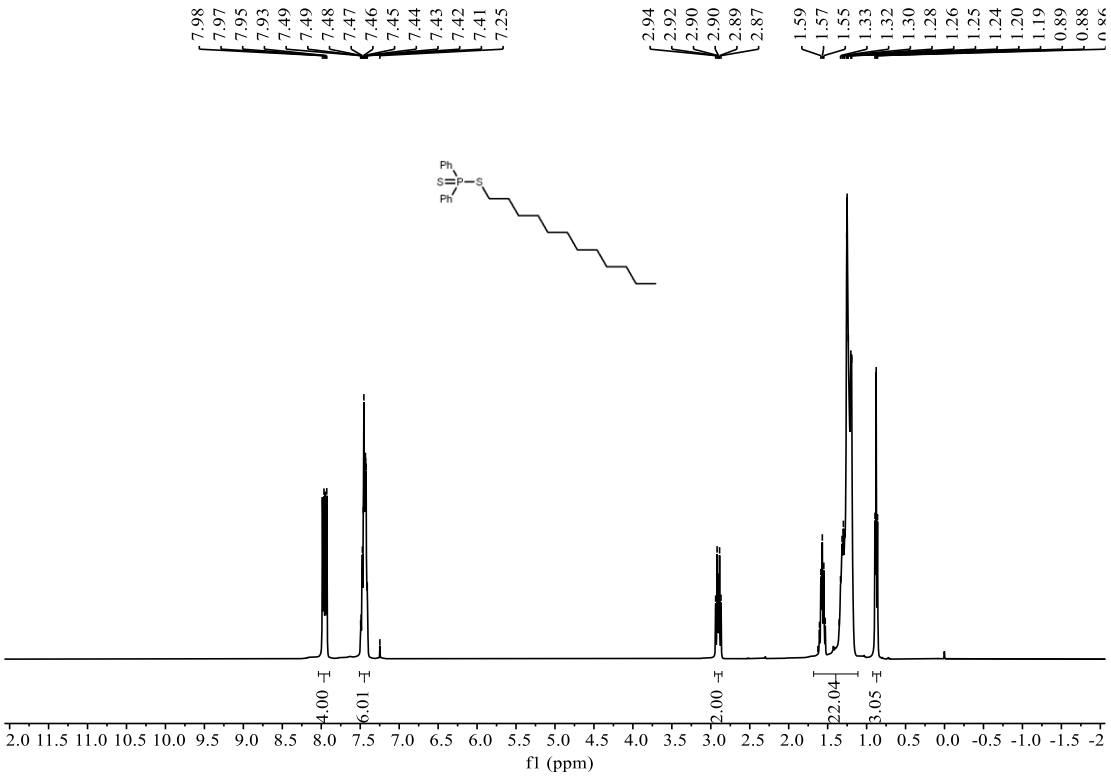
Octyl diphenylphosphinodithioate (**4p'**)

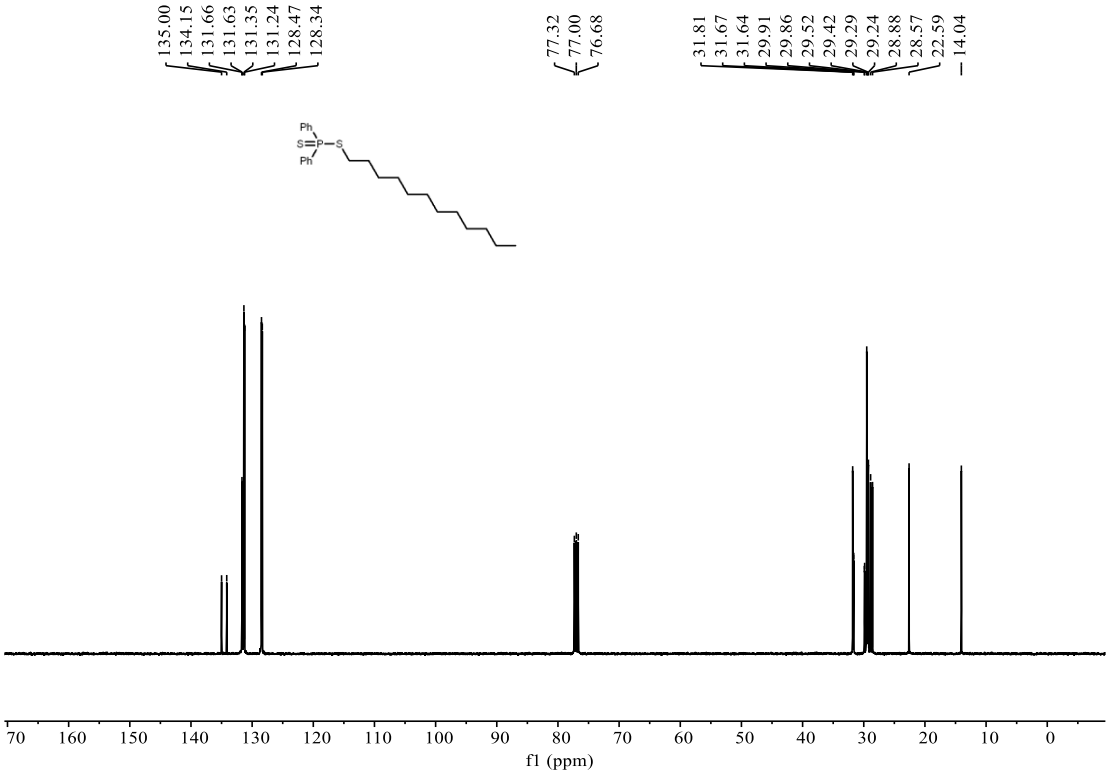


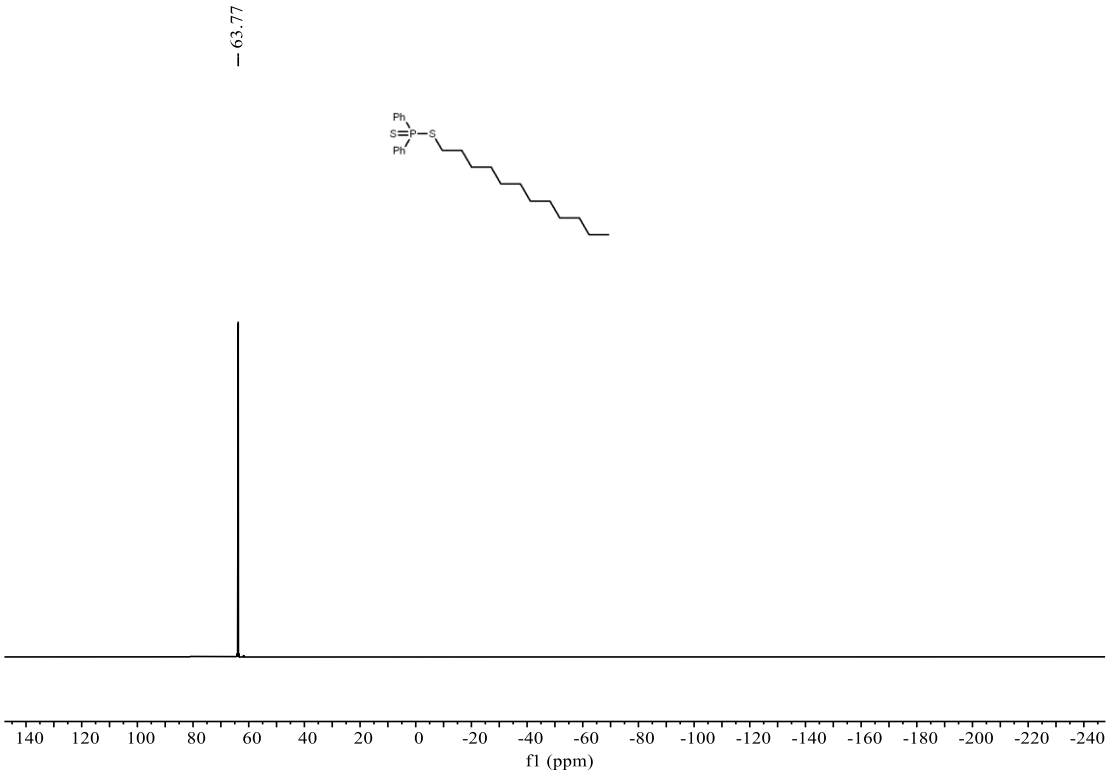




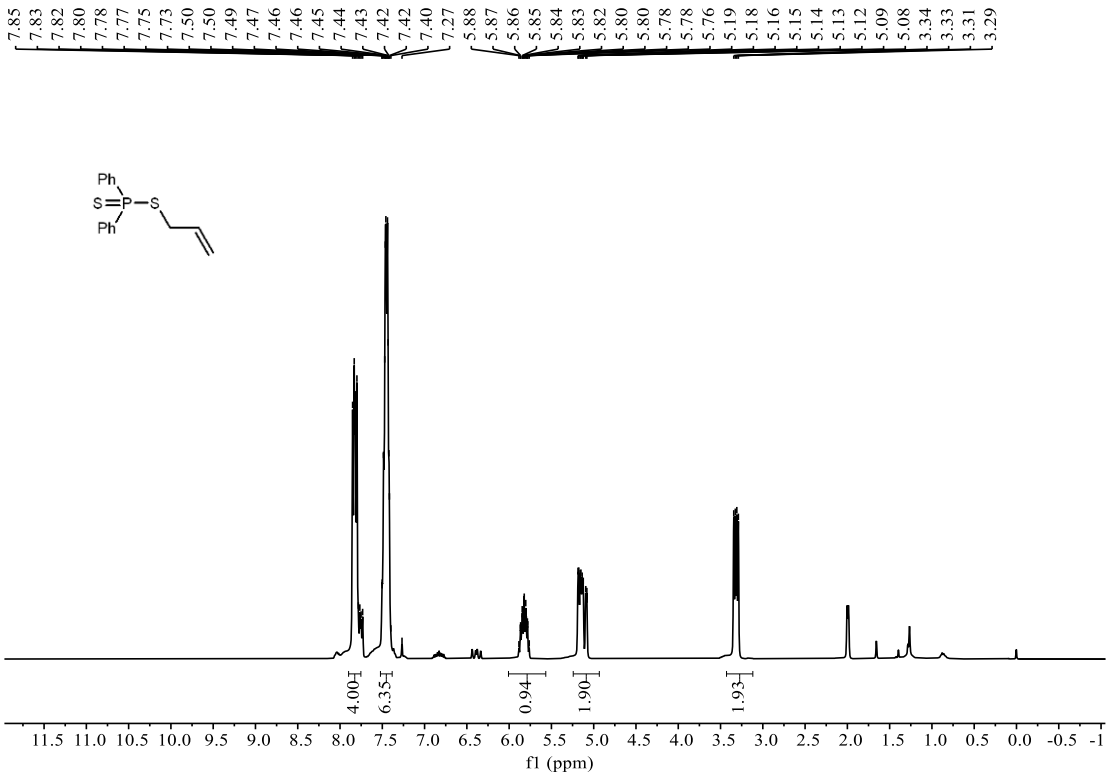
Dodecyl diphenylphosphinodithioate (**4q'**)

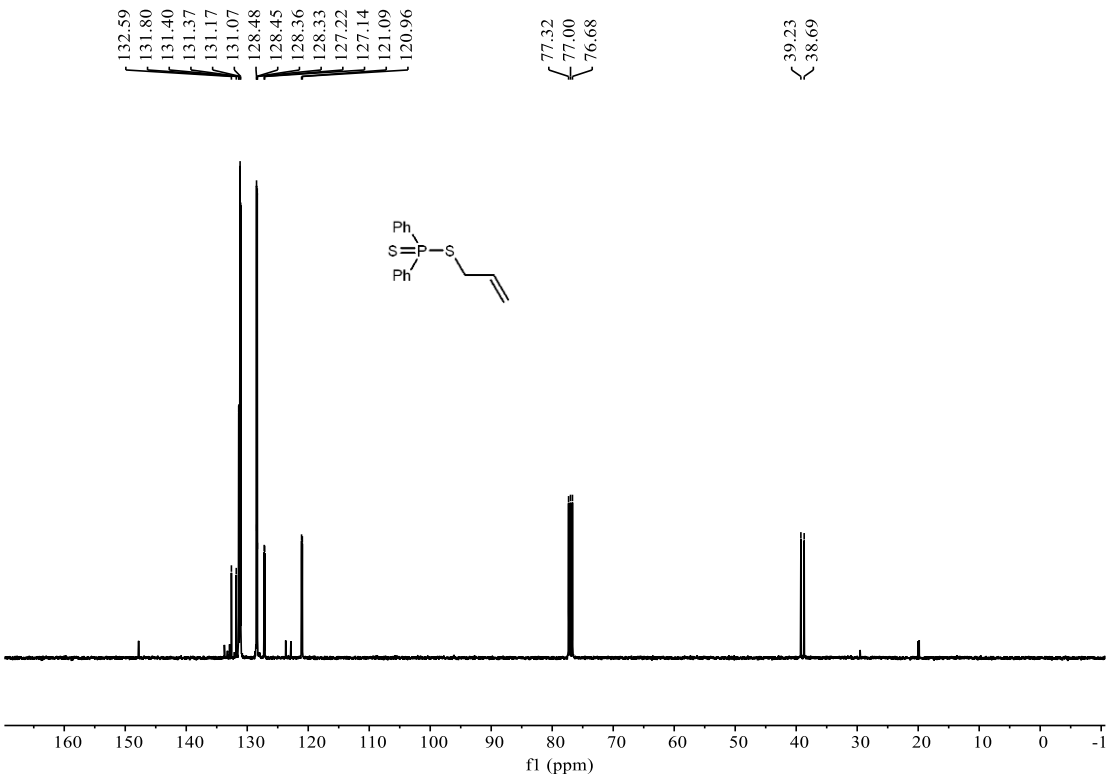

7.98
7.97
7.95
7.93
7.49
7.49
7.48
7.47
7.46
7.45
7.44
7.43
7.42
7.41
7.25
2.94
2.92
2.90
2.90
2.89
2.87
1.59
1.57
1.55
1.33
1.32
1.30
1.28
1.26
1.25
1.24
1.20
1.19
0.89
0.88
Ph
S
P
S
Ph
4.00
6.01
2.00
22.04
3.05
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2
f1 (ppm)

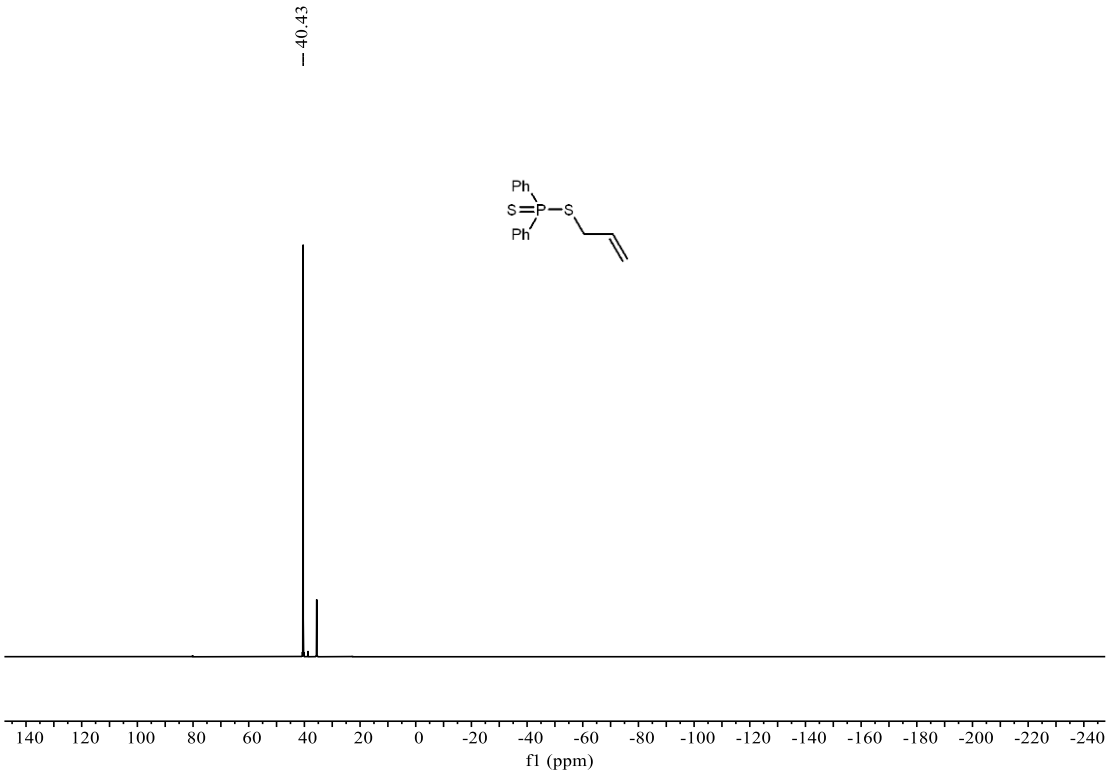

135.00
134.15
131.66
131.63
131.35
131.24
128.47
128.34
77.32
77.00
76.68
31.81
31.67
31.64
29.91
29.86
29.52
29.42
29.29
29.24
28.88
28.57
22.59
14.04
Ph
S
P
S
Ph
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



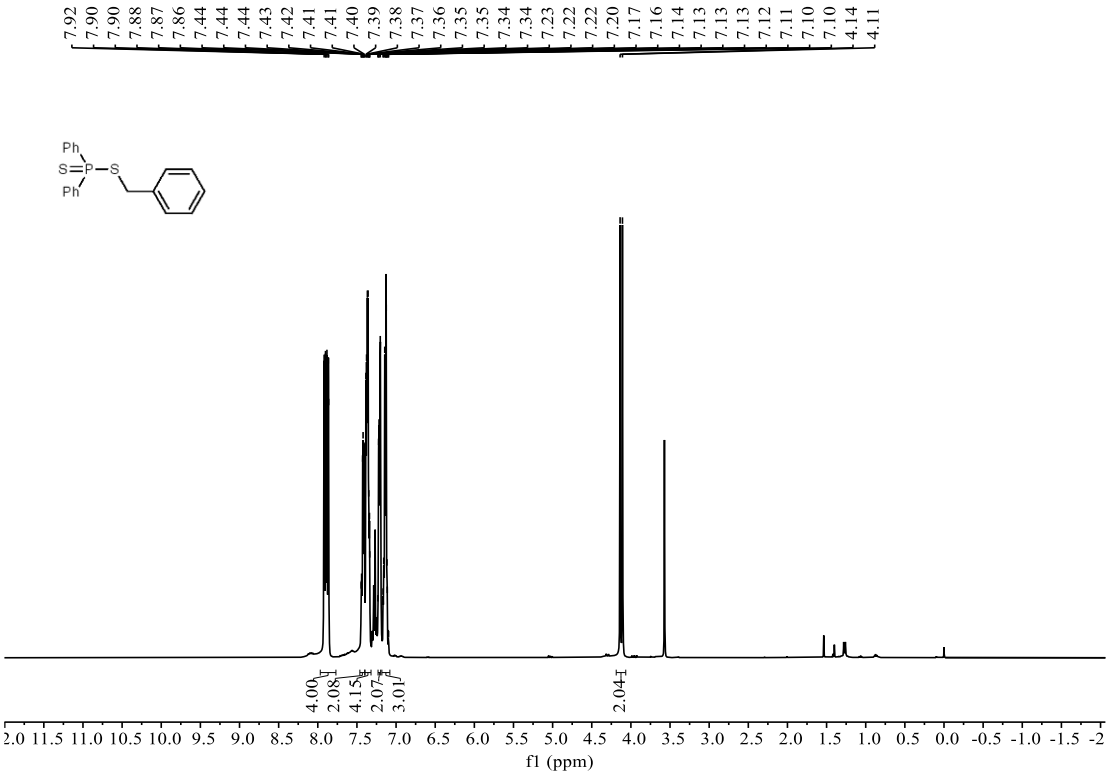
Allyl diphenylphosphinodithioate (**4r**)

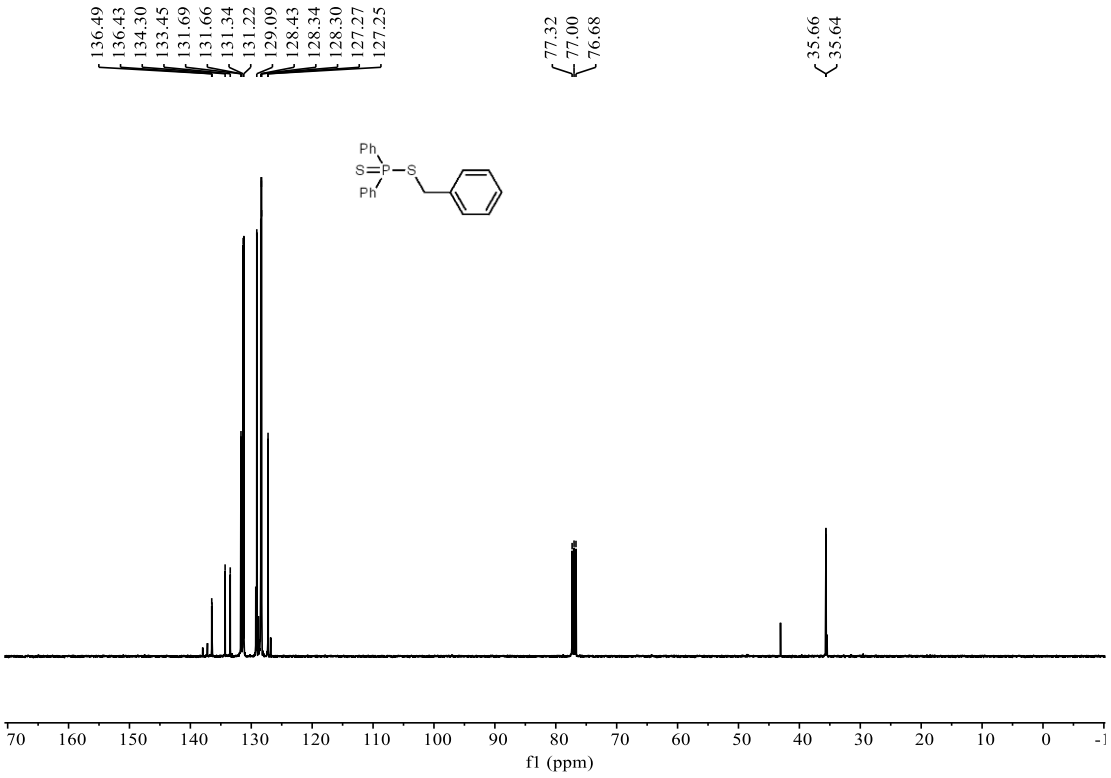


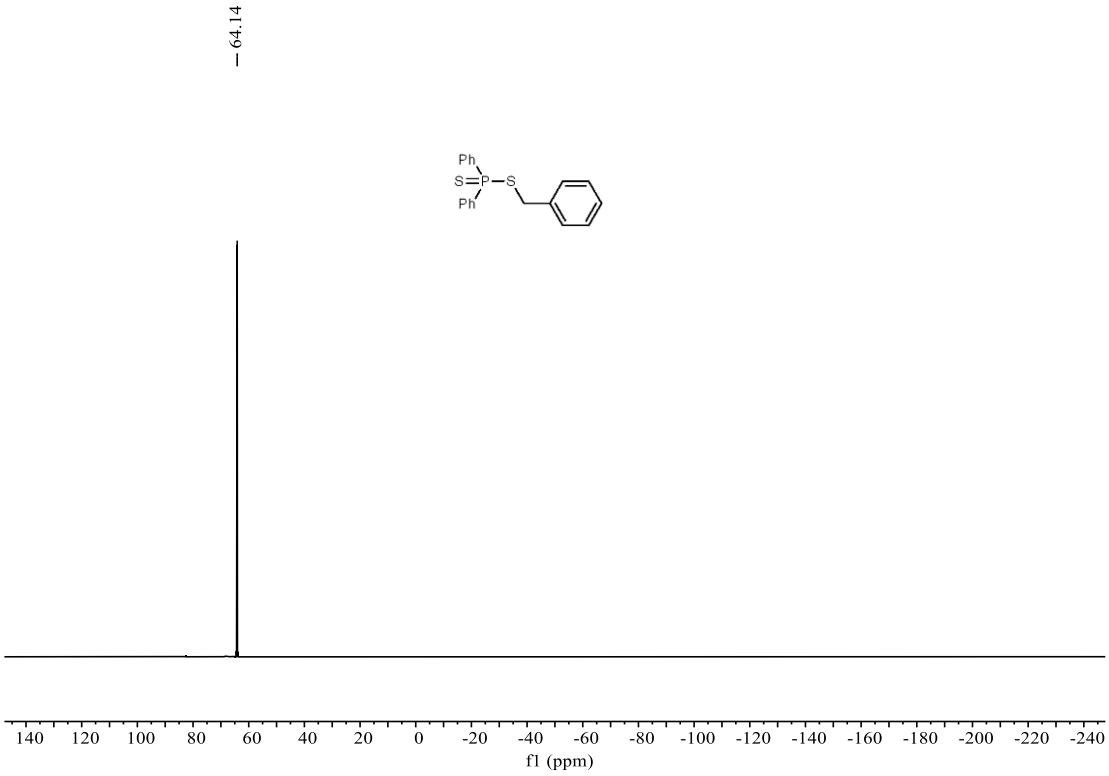

132.59
131.80
131.40
131.37
131.17
131.07
128.48
128.45
128.36
128.33
127.22
127.14
121.09
120.96
77.32
77.00
76.68
39.23
38.69
Ph
S
P
S
Ph
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


40.43
Ph
S
P
S
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

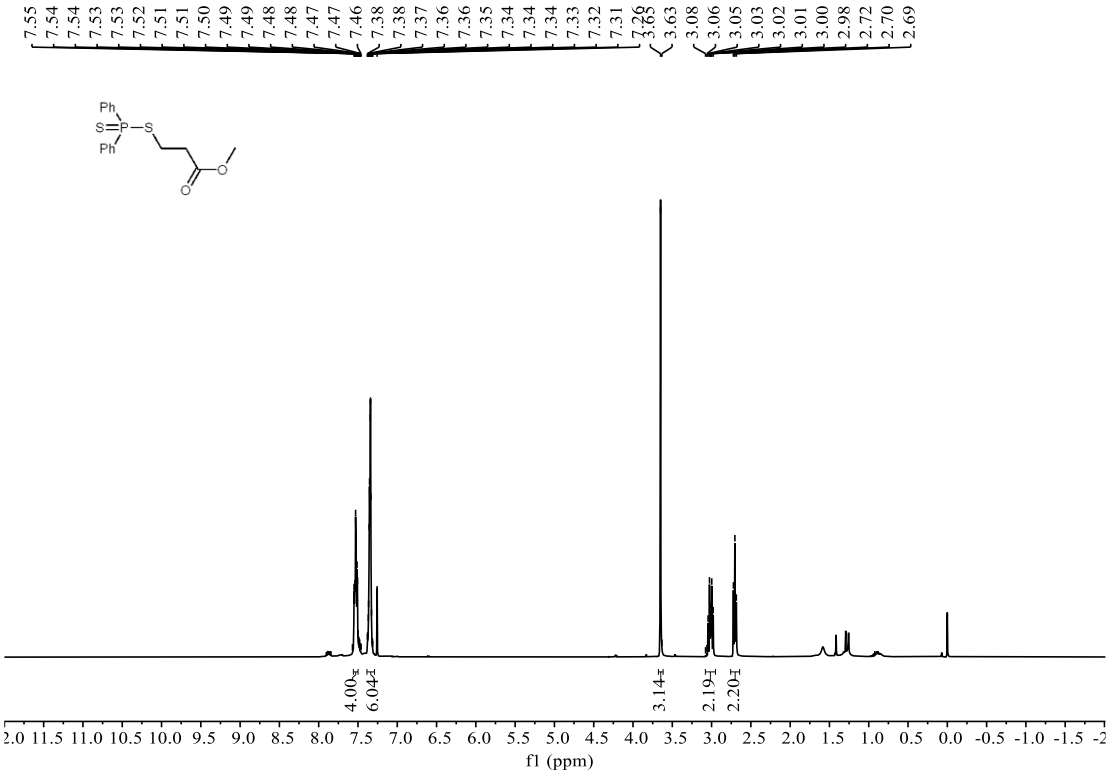
Benzyl diphenylphosphinodithioate (**4s'**)

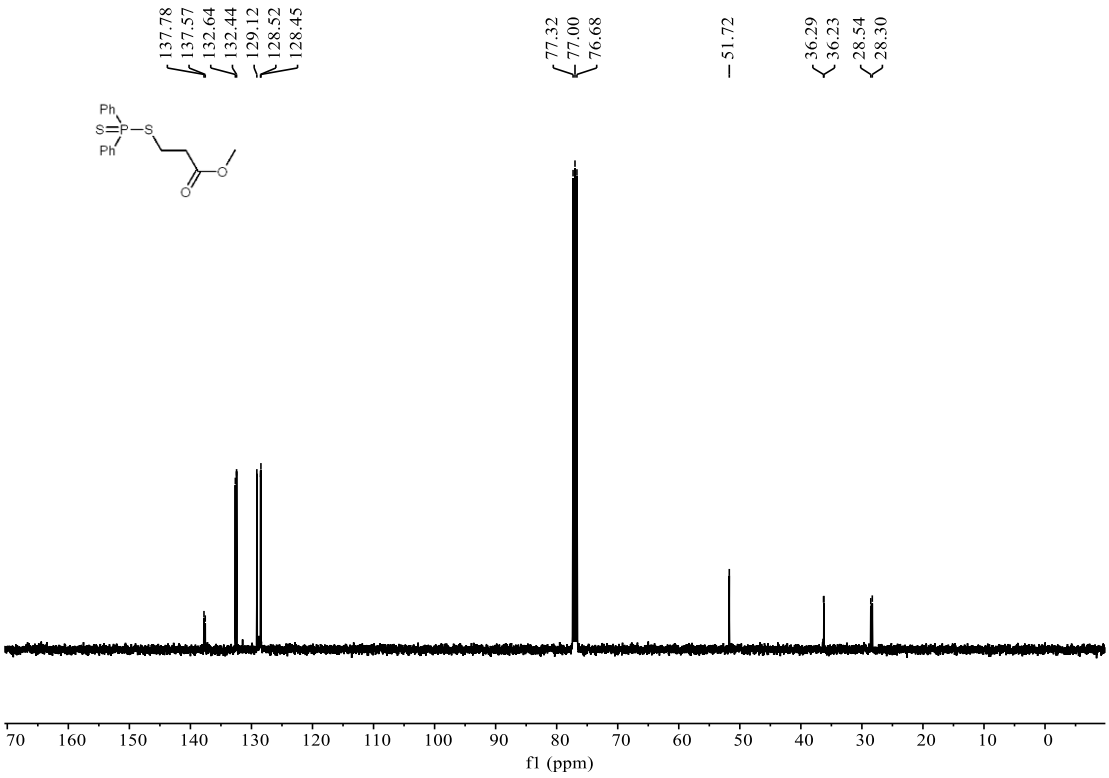


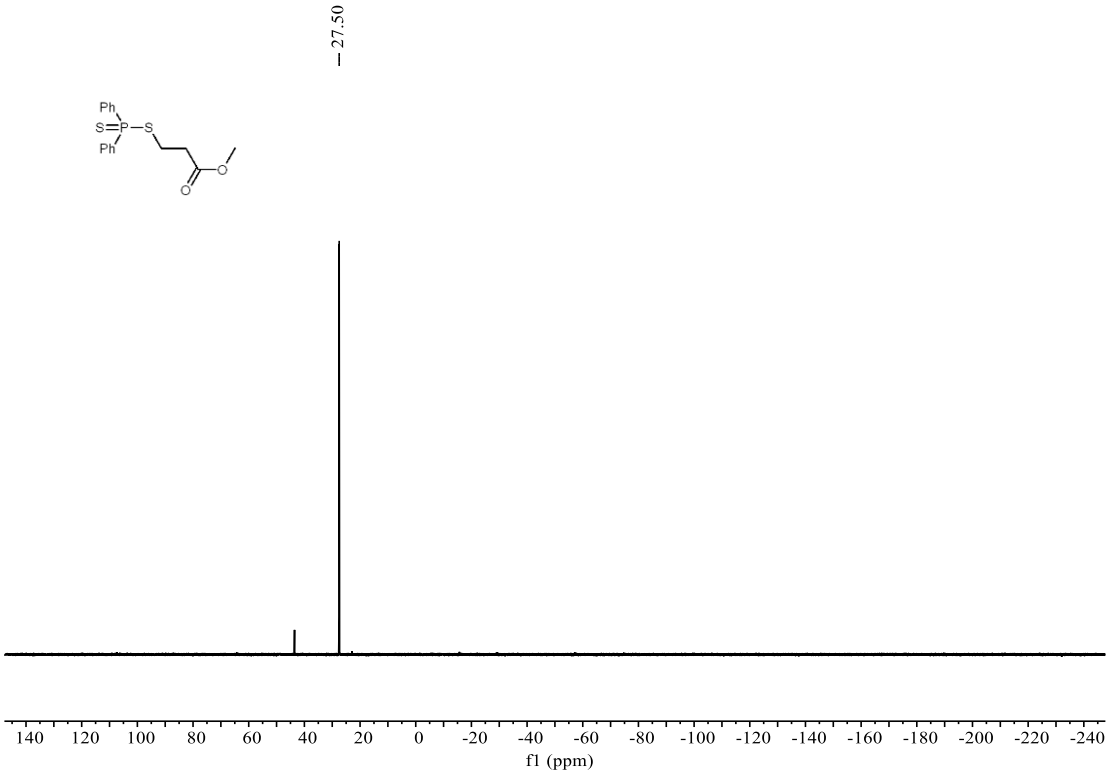




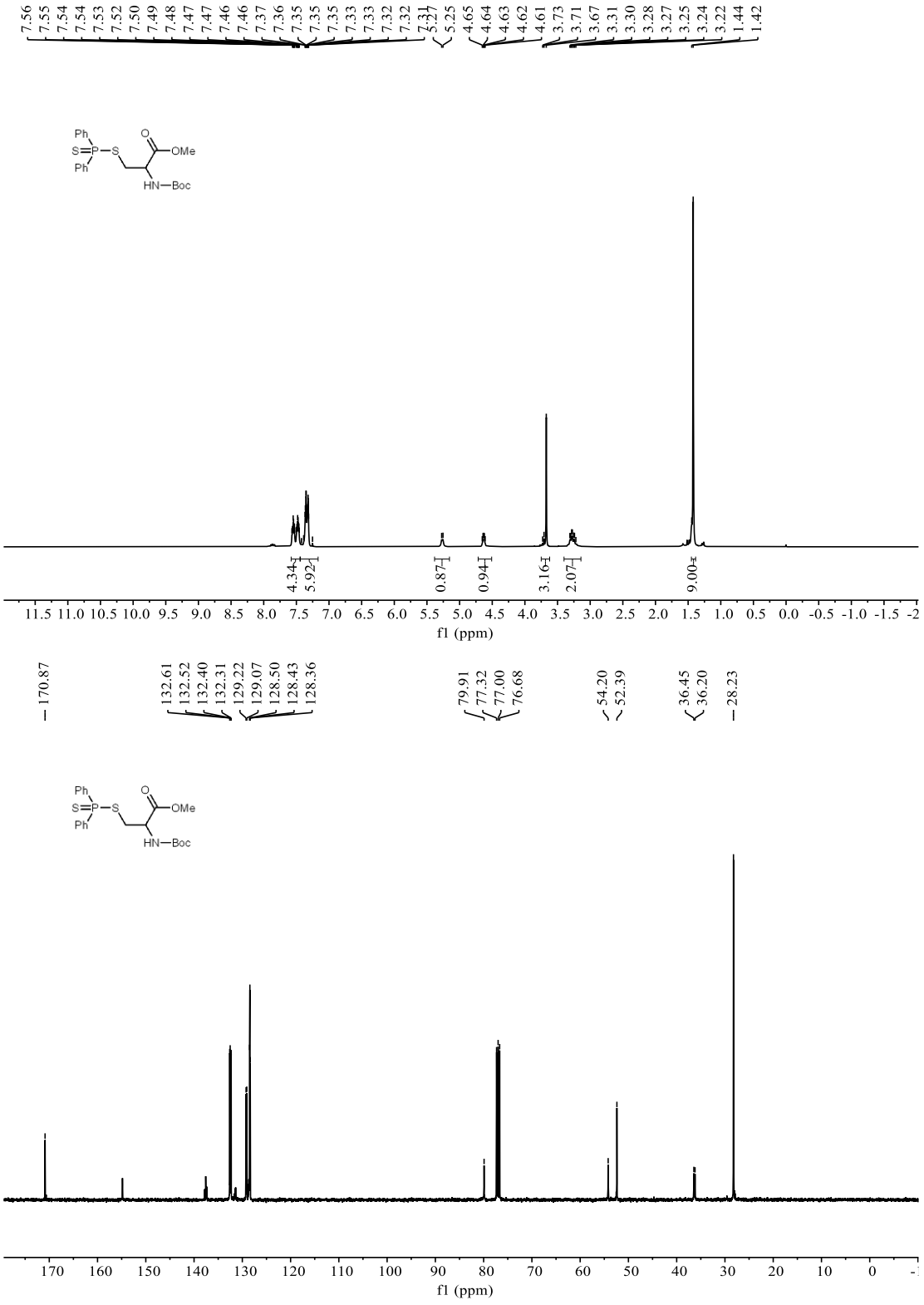
Methyl 3-((diphenylphosphorothioyl)thio)propanoate (**4t'**)

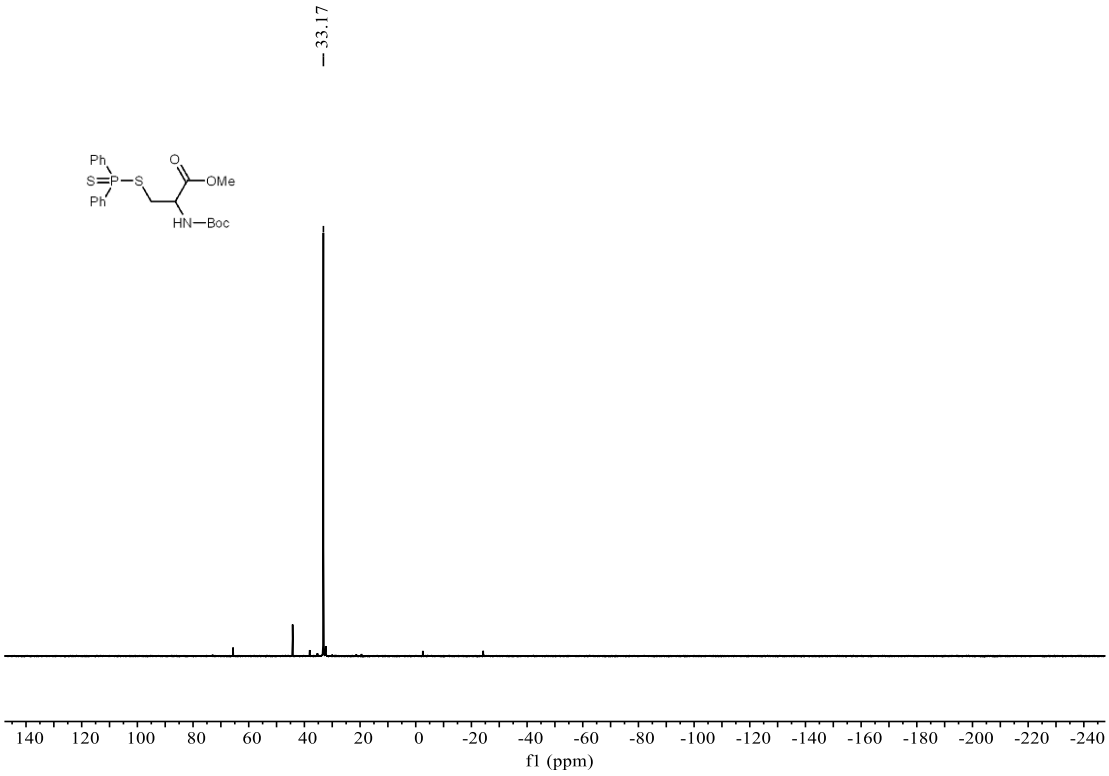



137.78
137.57
132.64
132.44
129.12
128.52
128.45
77.32
77.00
76.68
51.72
36.29
36.23
28.54
28.30
Ph
S=P—S
Ph
O
O
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

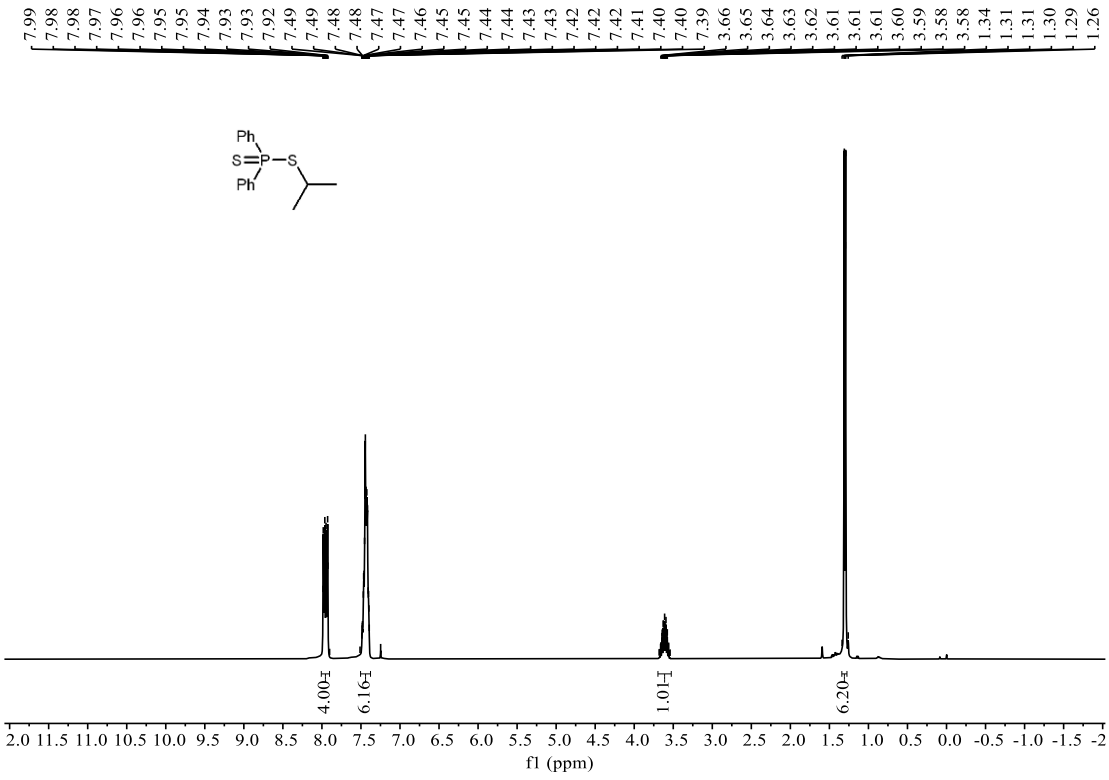

27.50
Ph
S=P—S
Ph
O
O
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

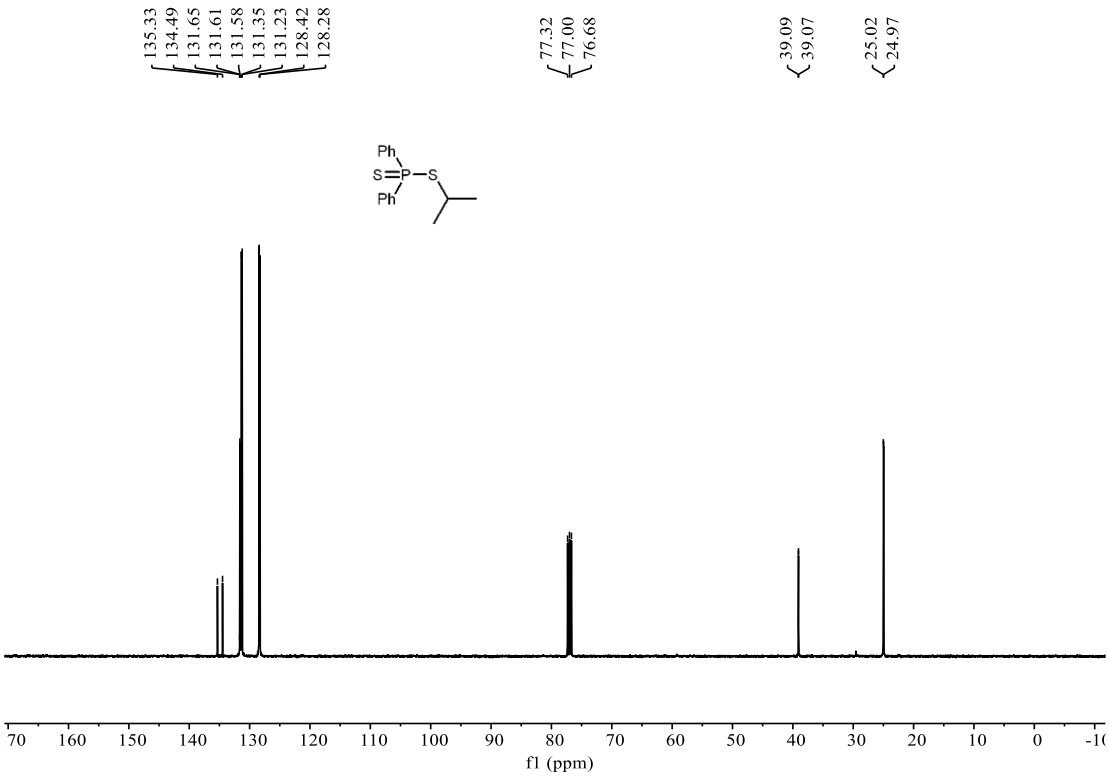
Methyl N-(tert-butoxycarbonyl)-S-(diphenylphosphorothioyl)cysteinate (**4u'**)

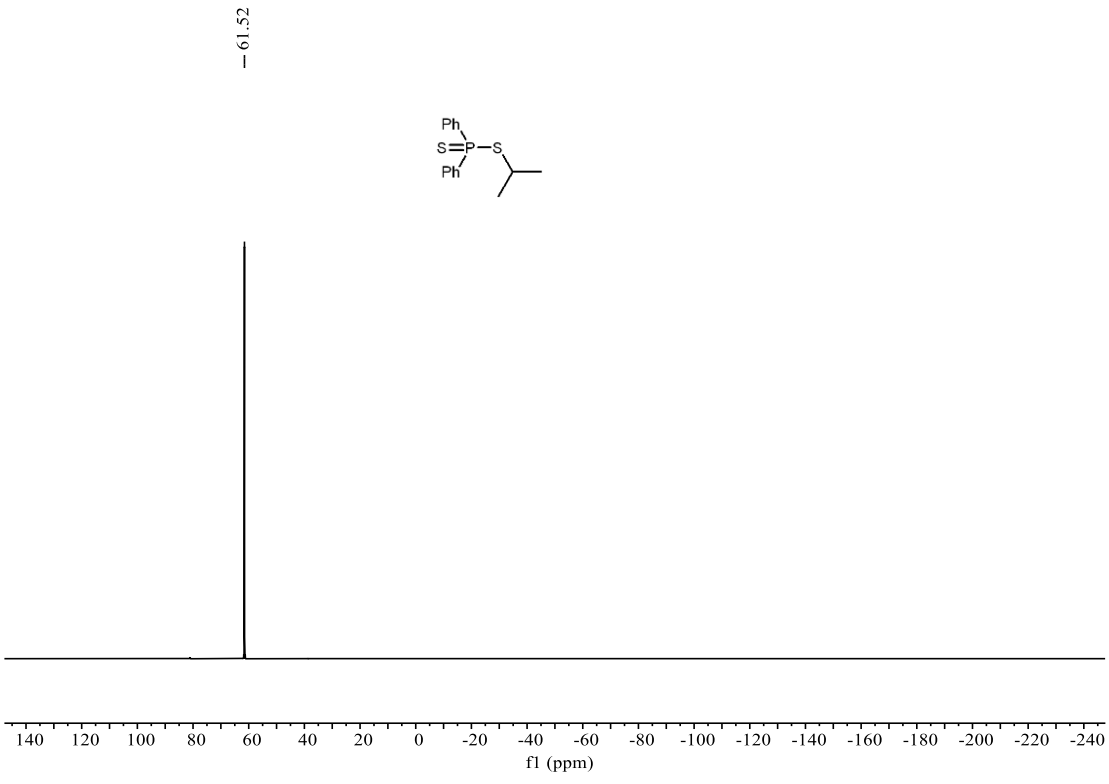




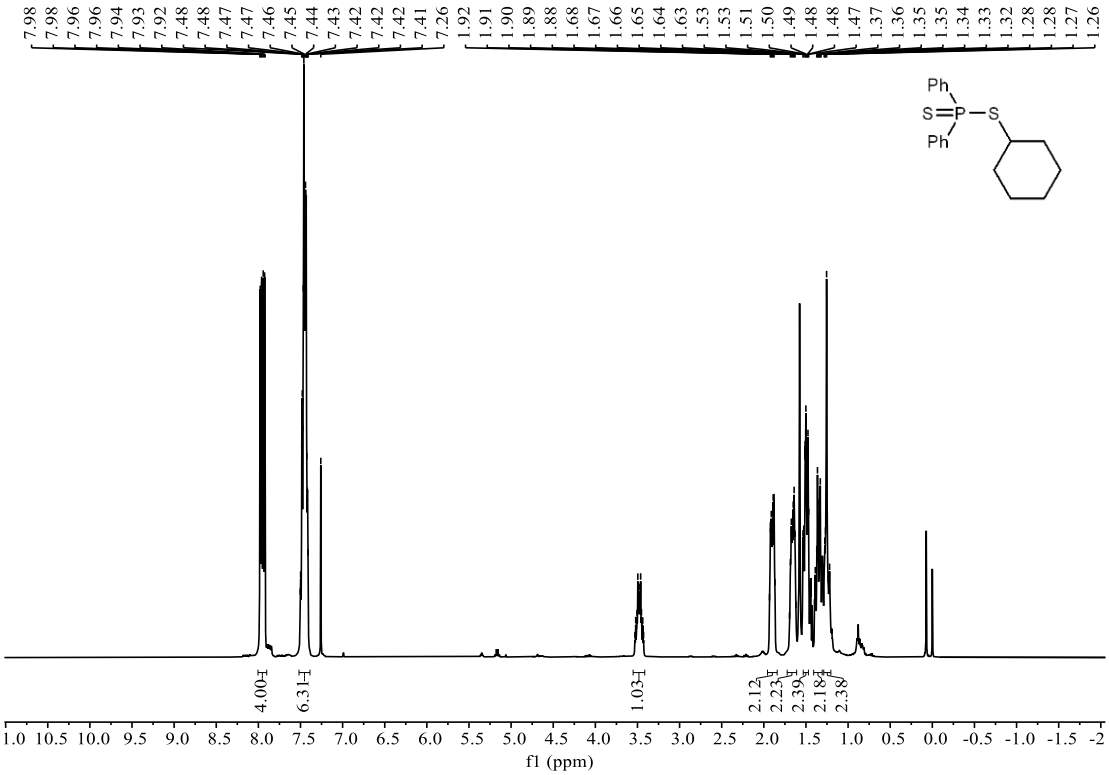
Isopropyl diphenylphosphinodithioate (**4v'**)

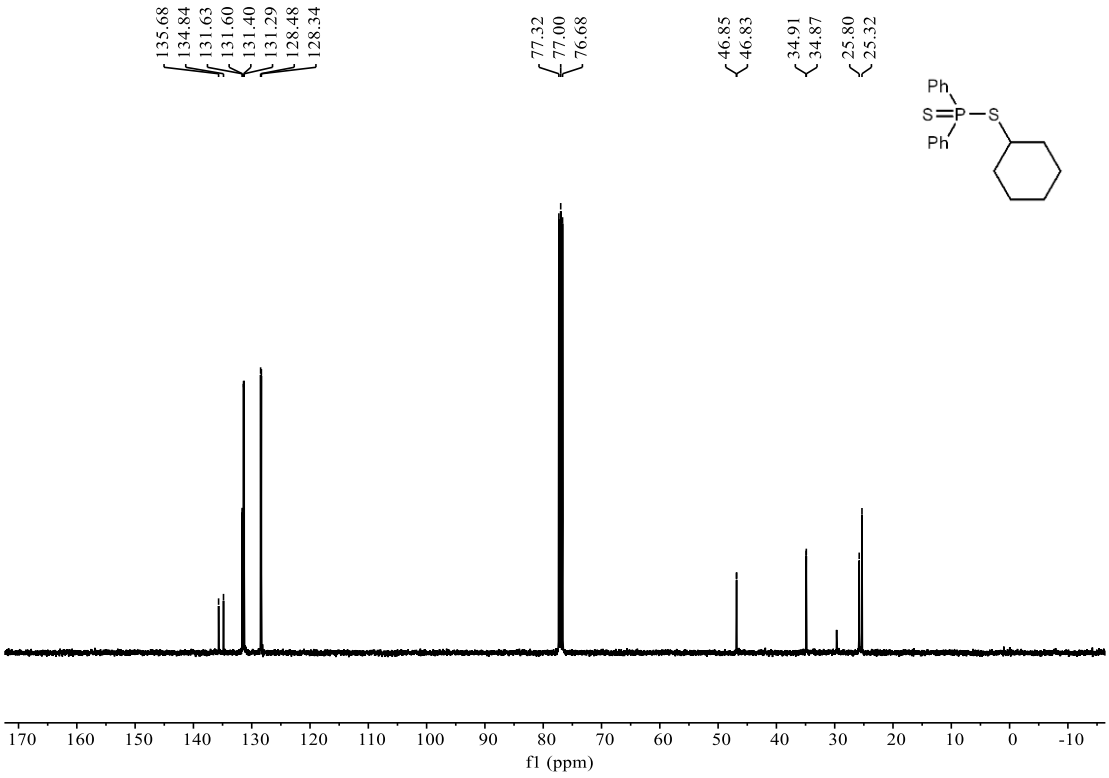


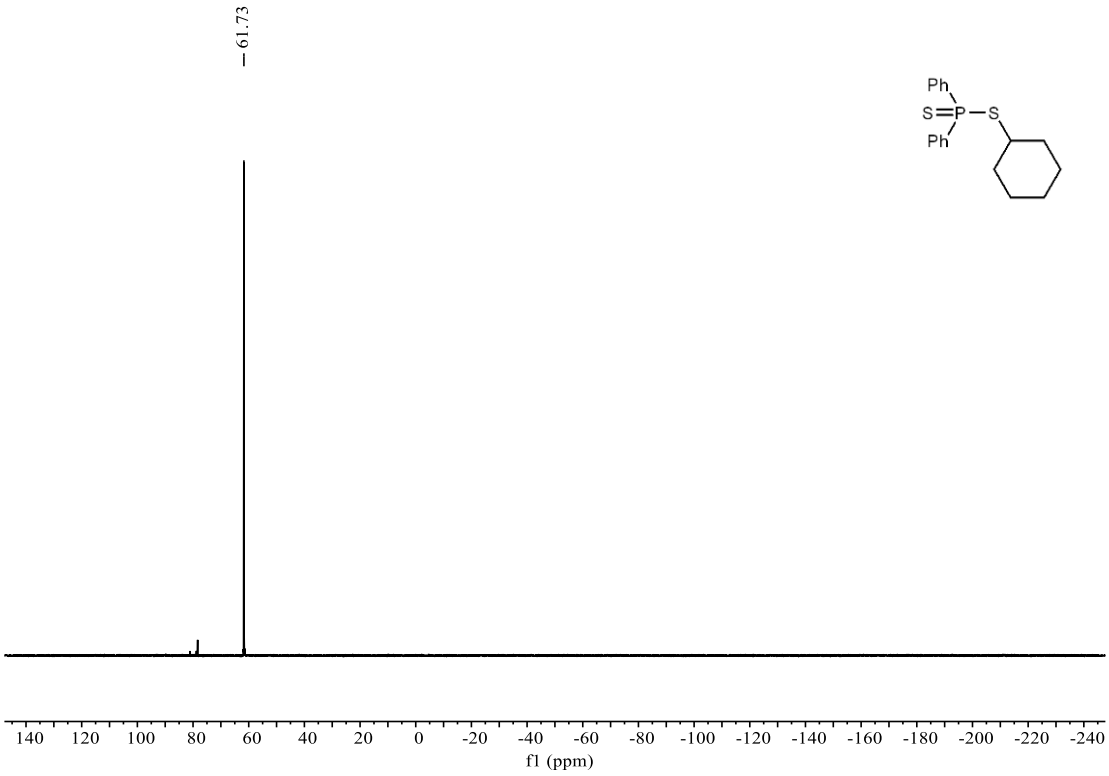

135.33
134.49
131.65
131.61
131.58
131.35
131.23
128.42
128.28
77.32
77.00
76.68
39.09
39.07
25.02
24.97
Ph
S
P
S
Ph
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


61.52
Ph
S
P
S
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

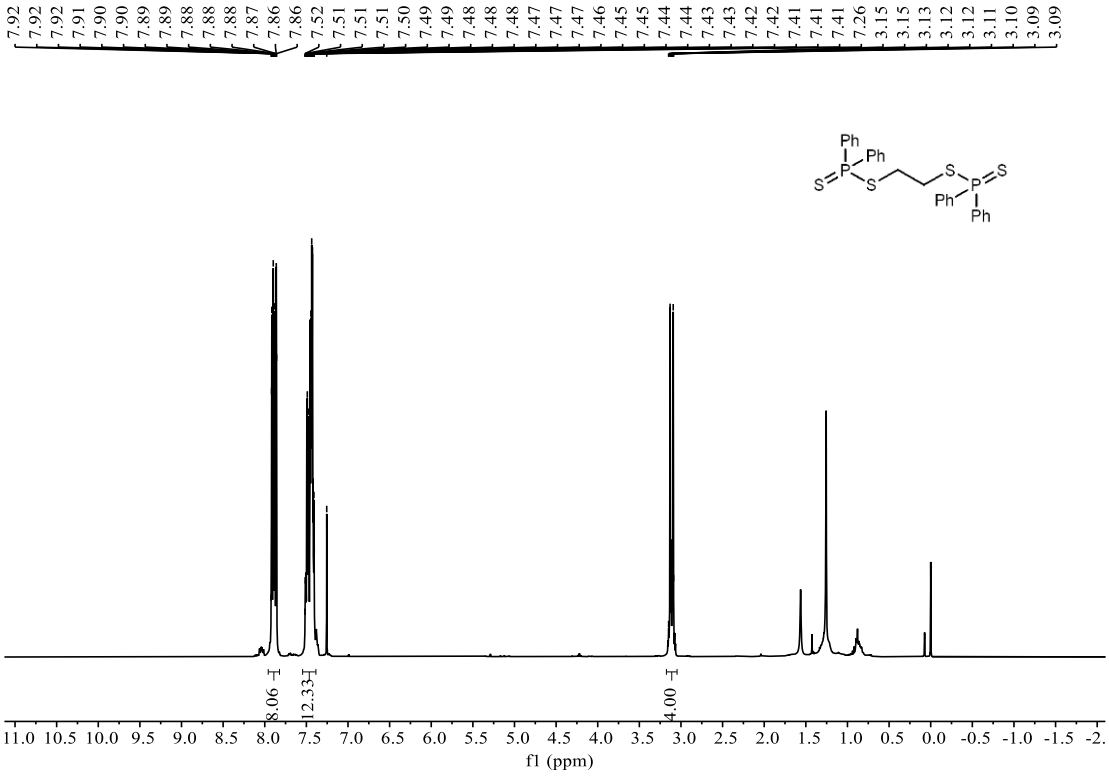
Cyclohexyl diphenylphosphinodithioate (**4w'**)

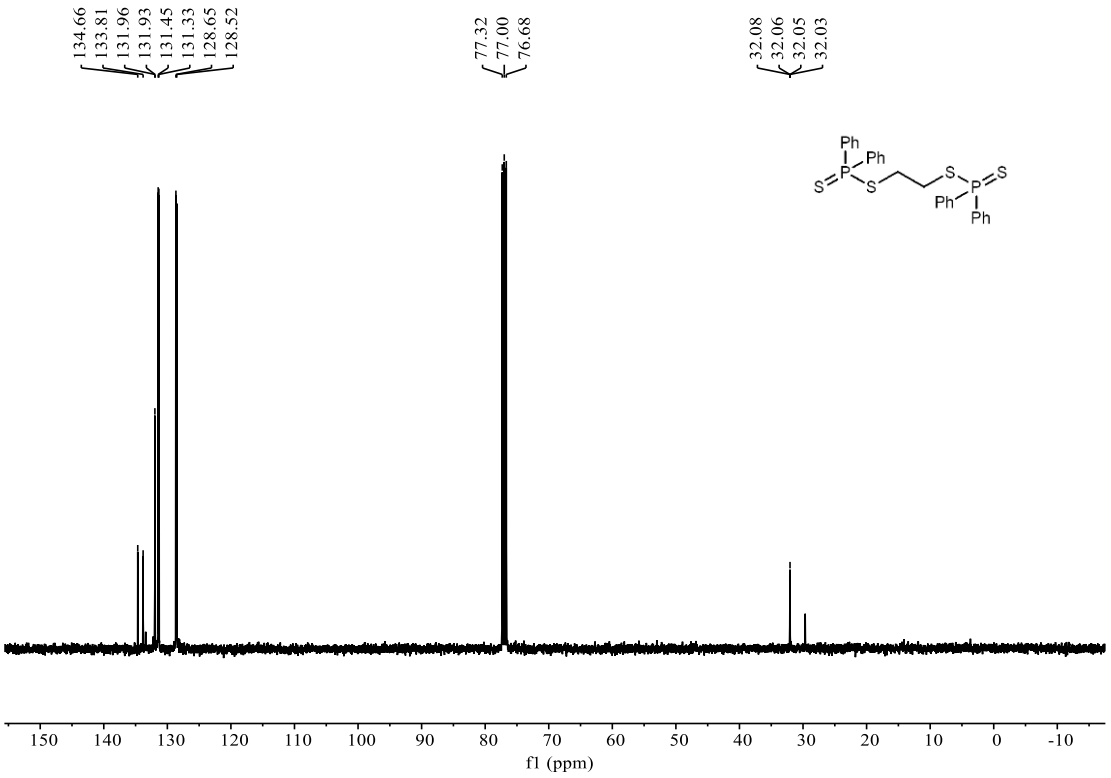


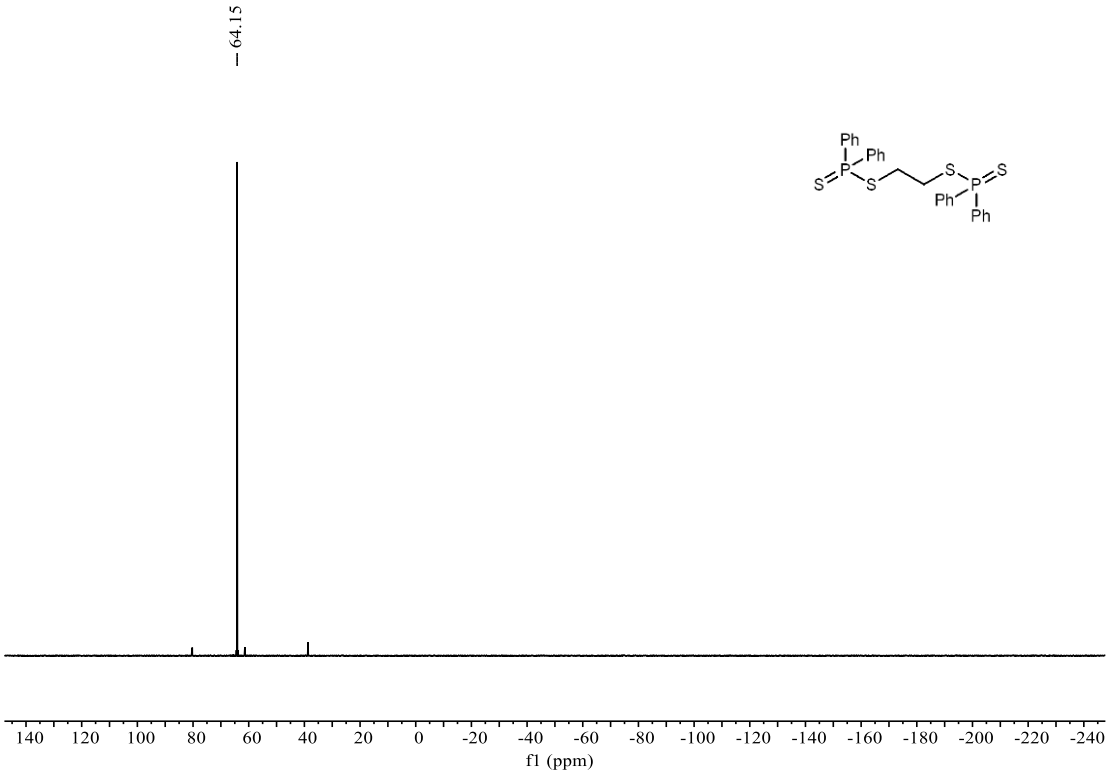




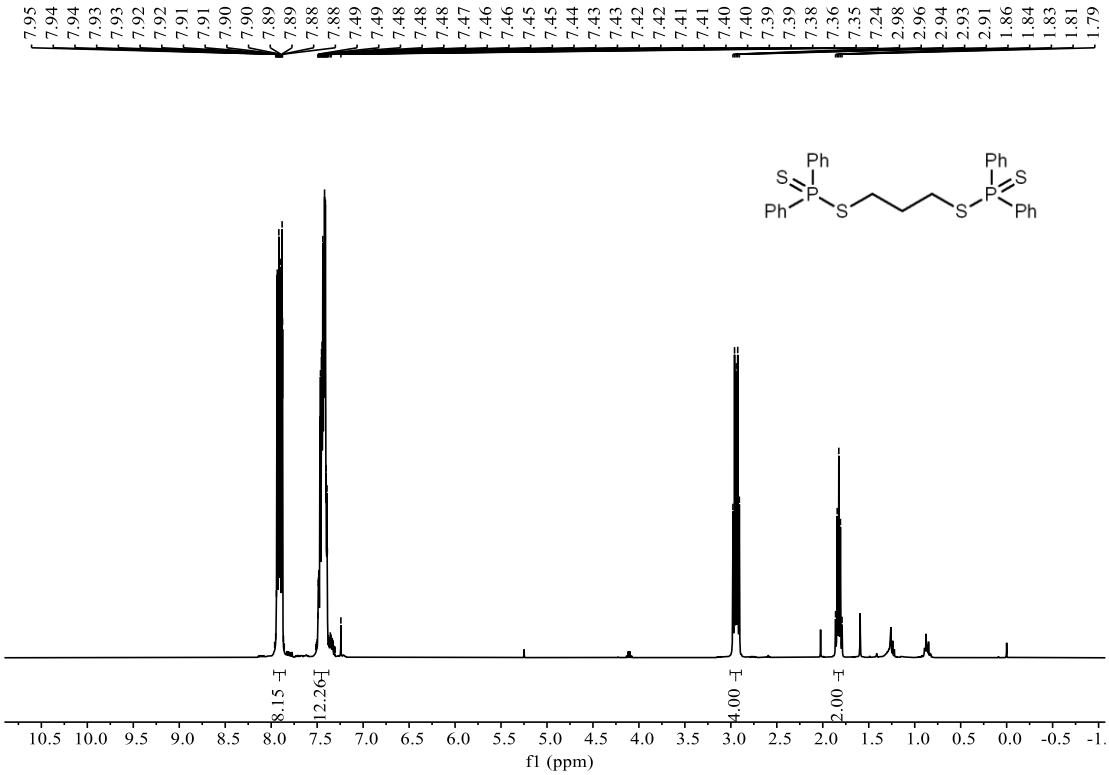
Ethane-1,2-diyl bis(diphenylphosphinodithioate) (**4x'**)

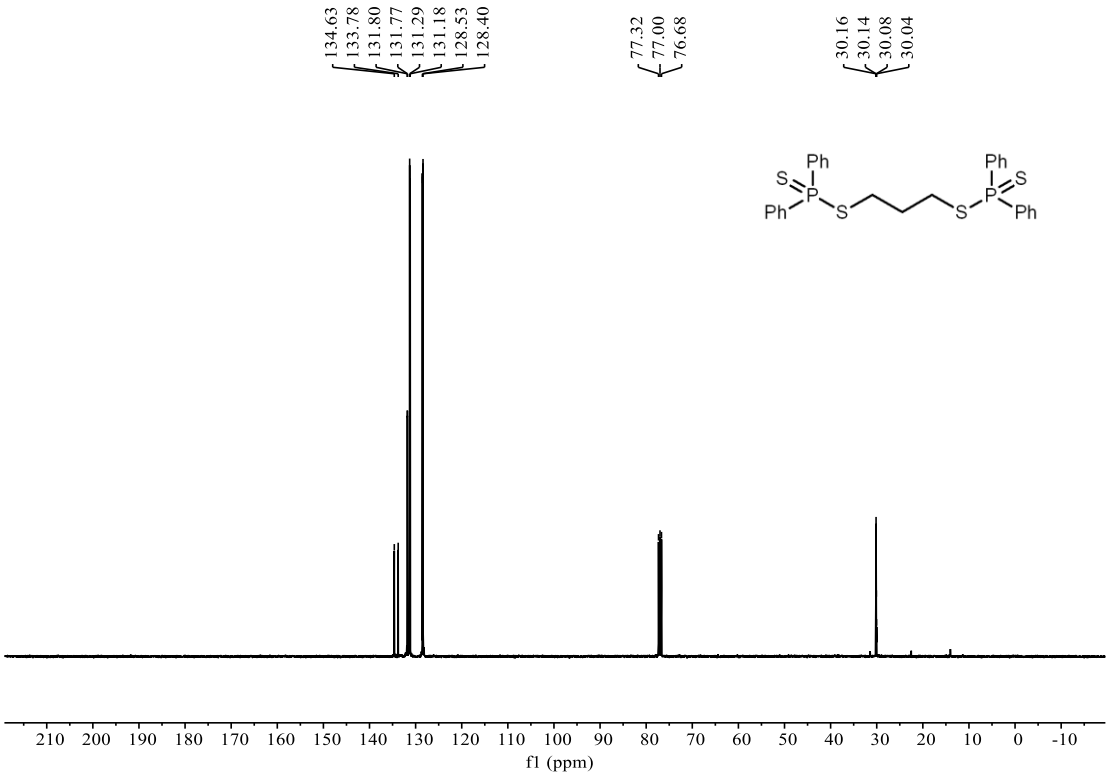


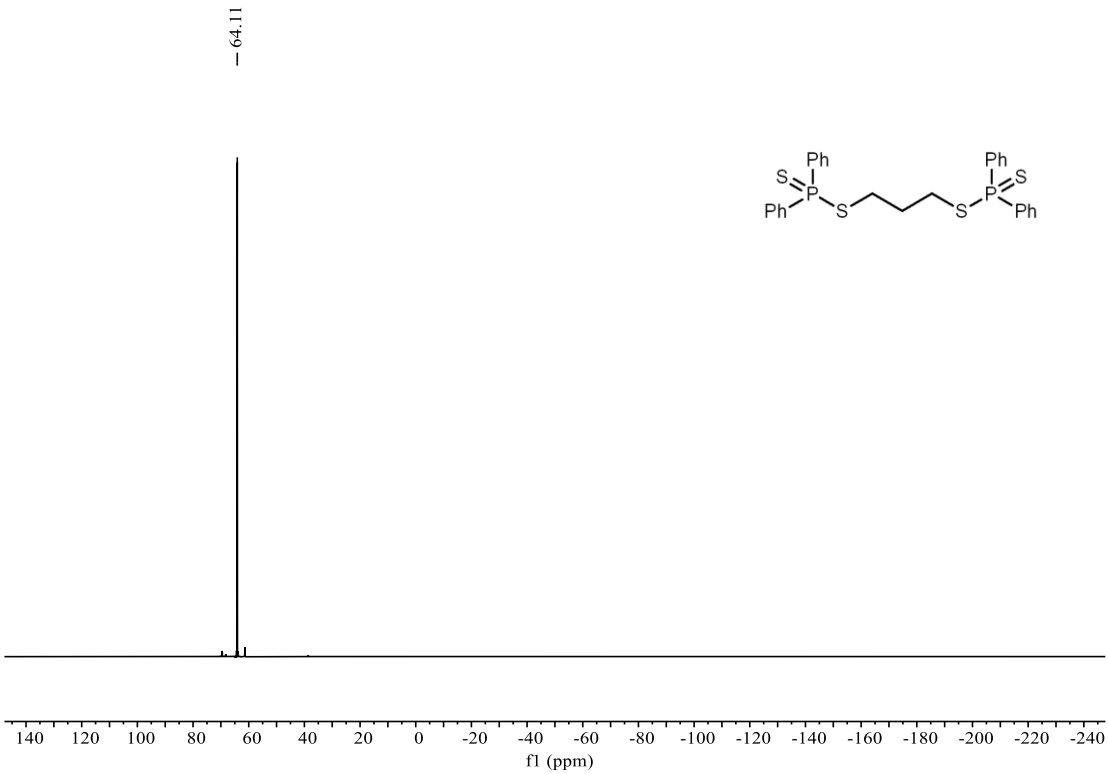

134.66
133.81
131.96
131.93
131.45
131.33
128.65
128.52
77.32
77.00
76.68
32.08
32.06
32.05
32.03
Ph
Ph
S
P
S
S
P
S
Ph
Ph
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


64.15
Ph
Ph
S
P
S
S
P
S
Ph
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

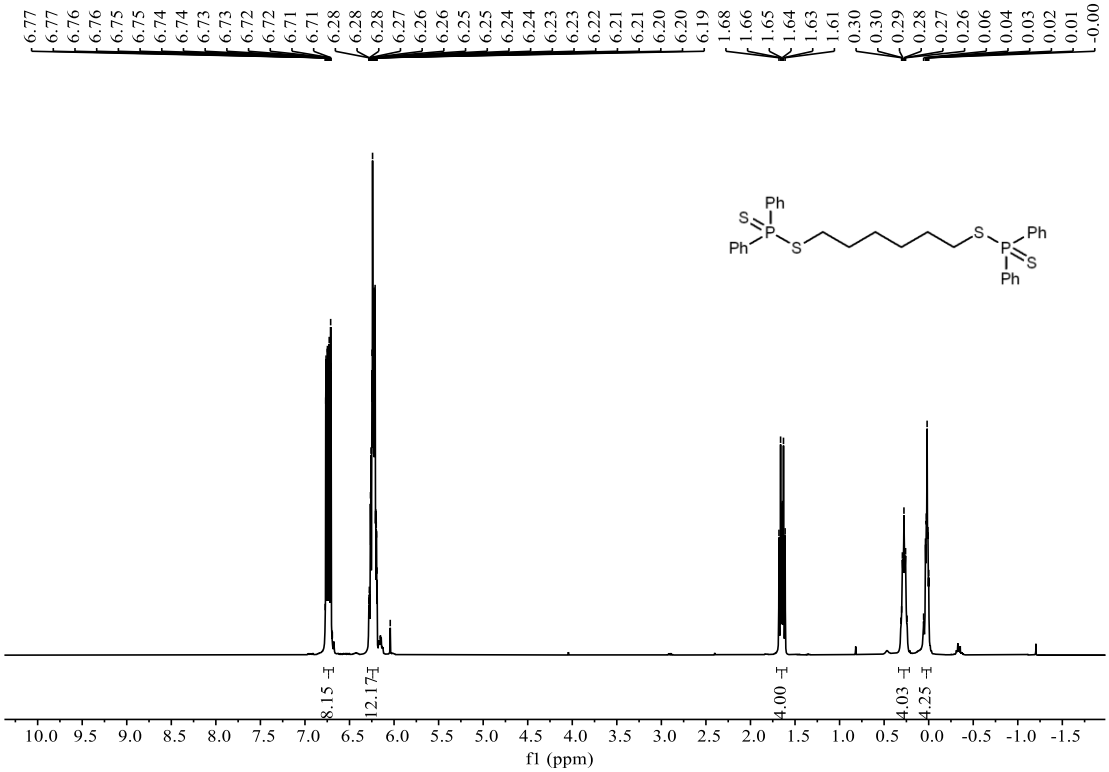
Propane-1,3-diyl bis(diphenylphosphinodithioate) (**4y'**)

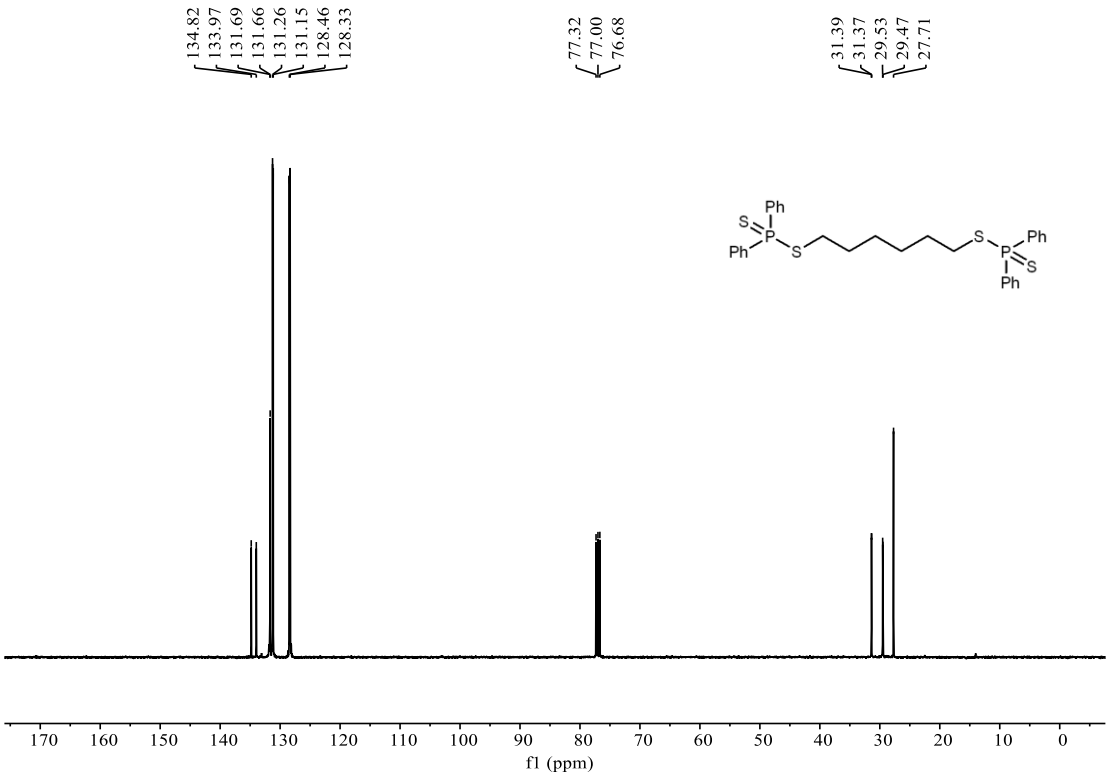


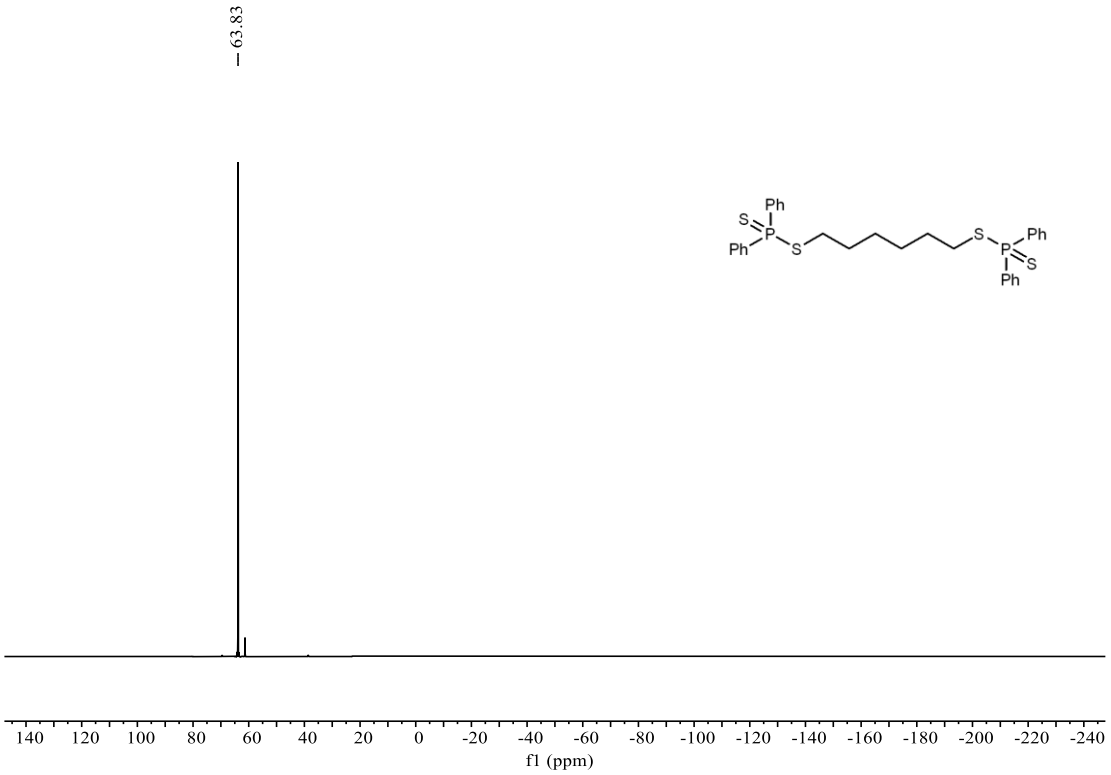




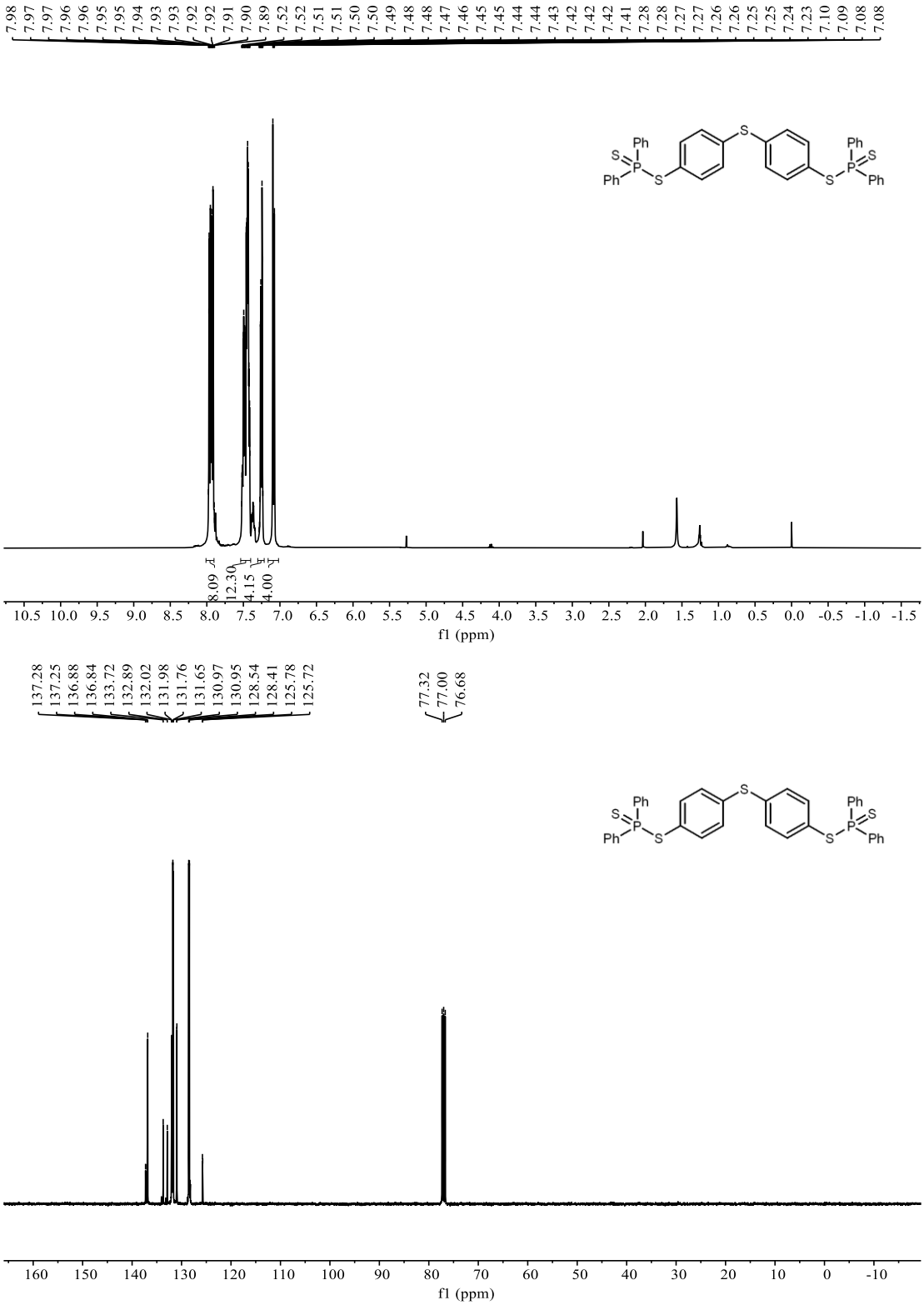
Hexane-1,6-diyl bis(diphenylphosphinodithioate) (**4z'**)

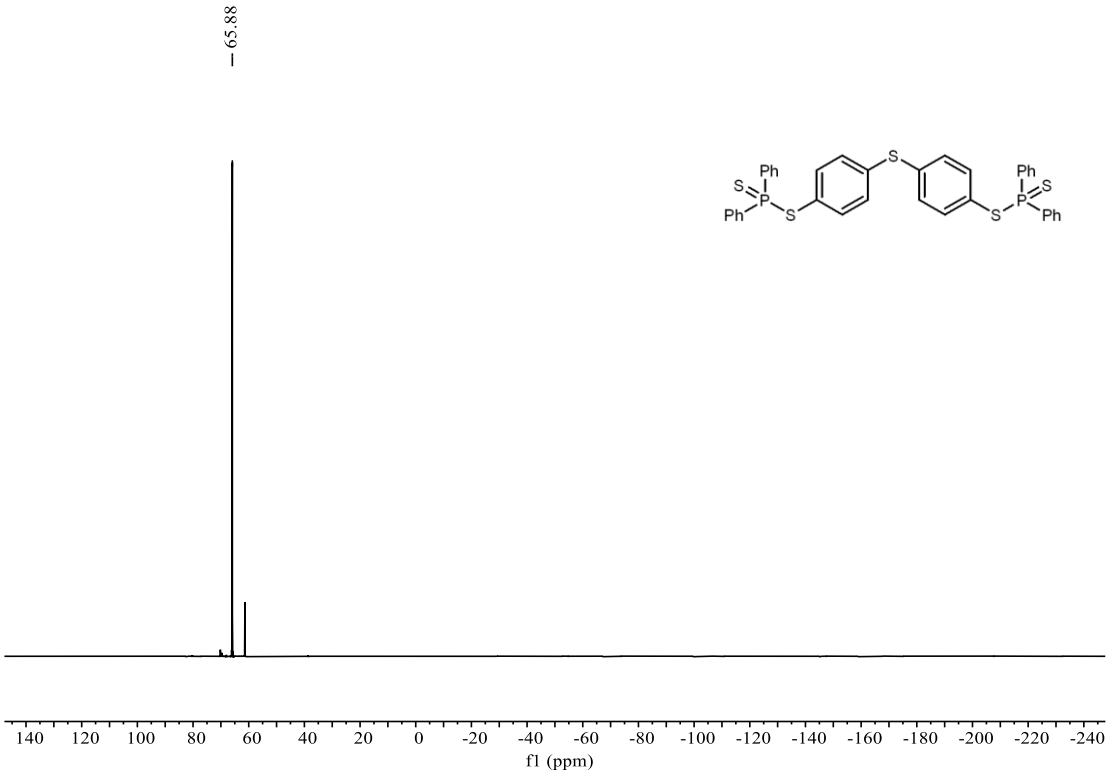



134.82
133.97
131.69
131.66
131.26
131.15
128.46
128.33
77.32
77.00
76.68
31.39
31.37
29.53
29.47
27.71
Ph
S
P
Ph
S
S
P
Ph
S
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

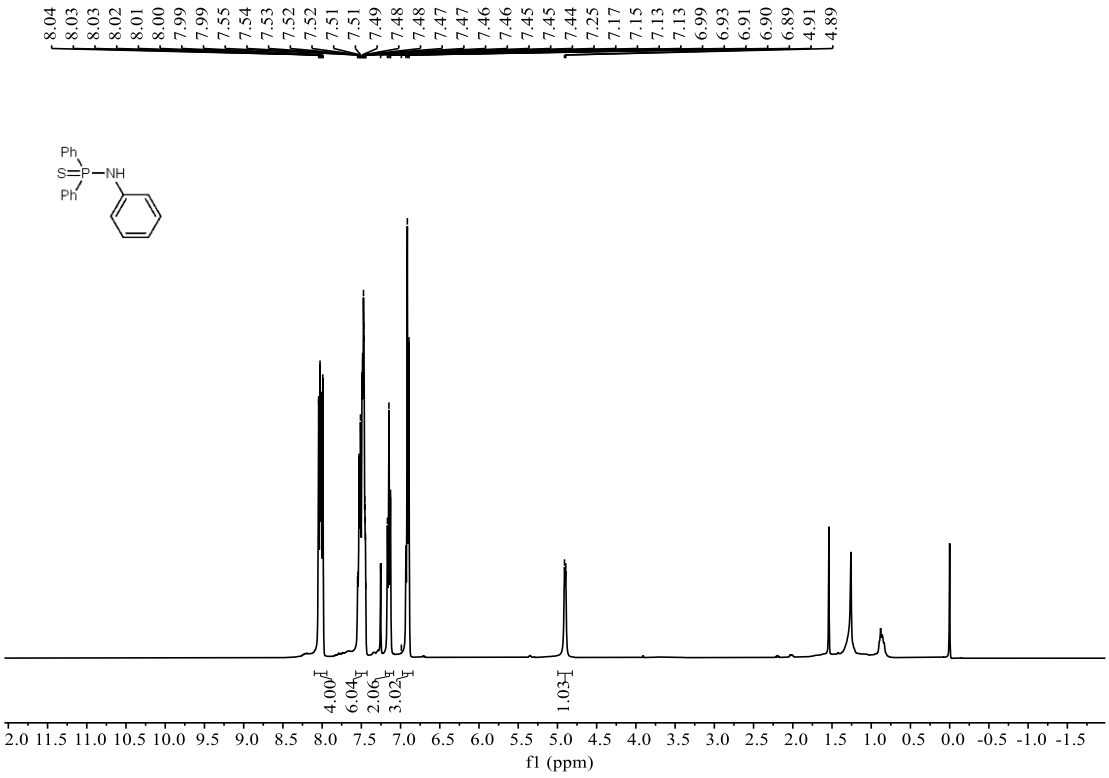

63.83
Ph
S
P
Ph
S
S
P
Ph
S
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

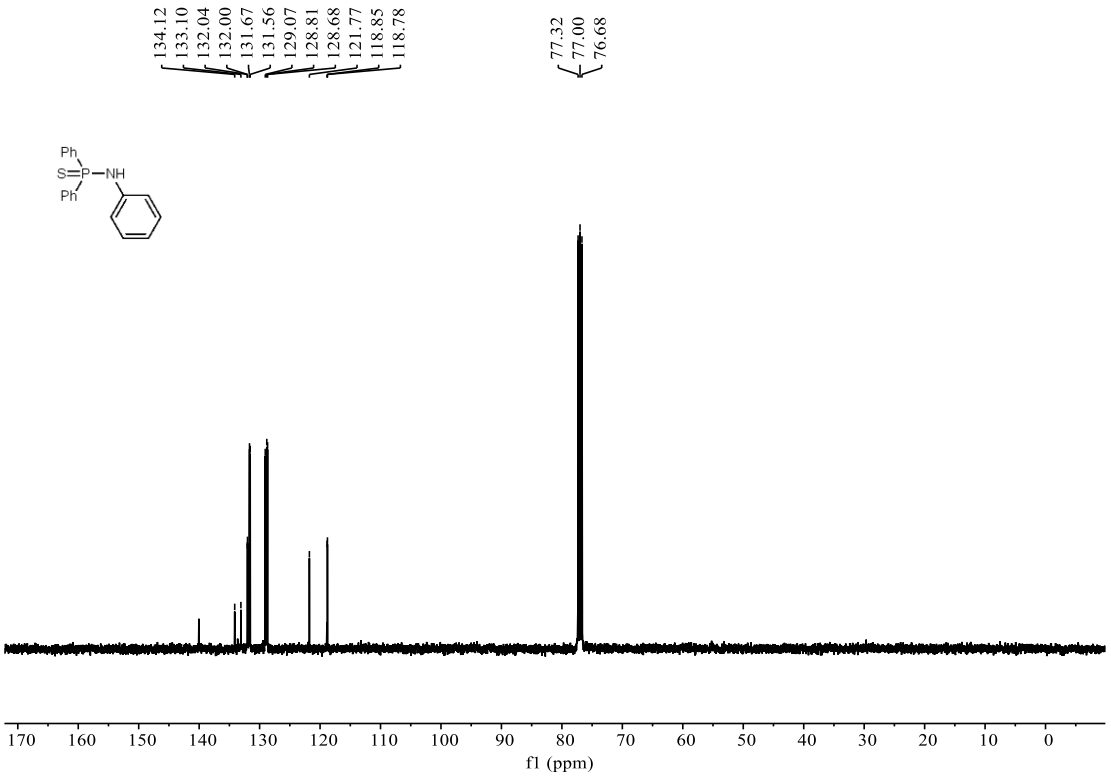
Thiobis(4,1-phenylene) bis(diphenylphosphinodithioate) (**4aa'**)

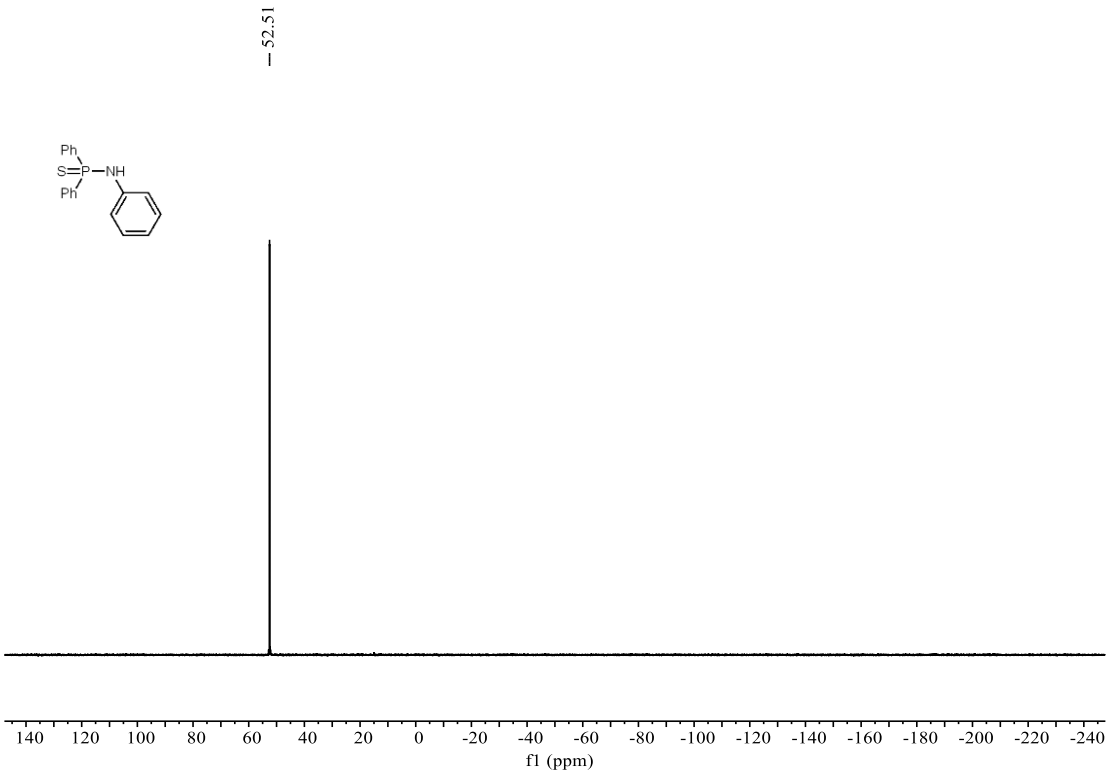




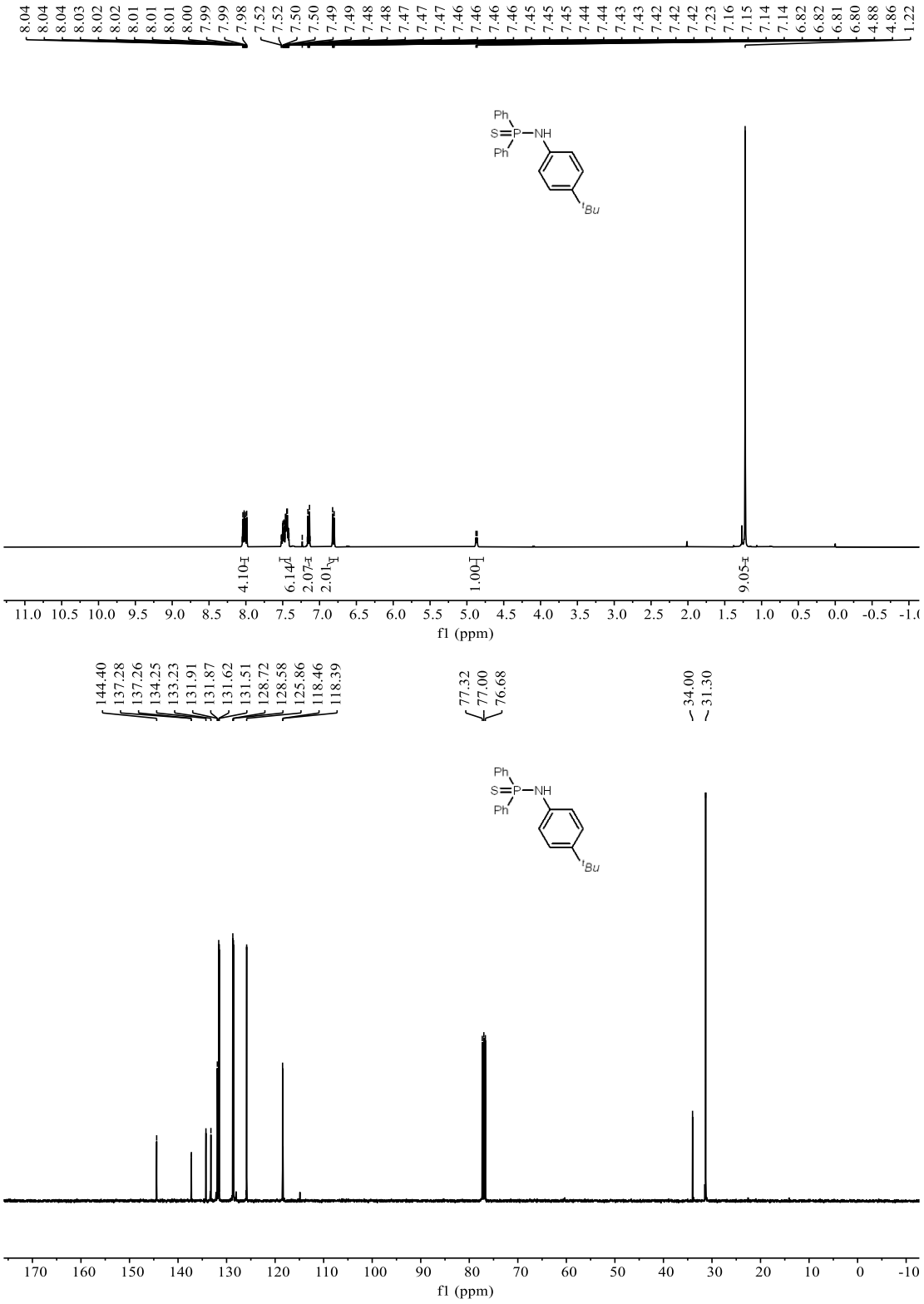
N,P,P-triphenylphosphinothioic amide (**4ab'**)

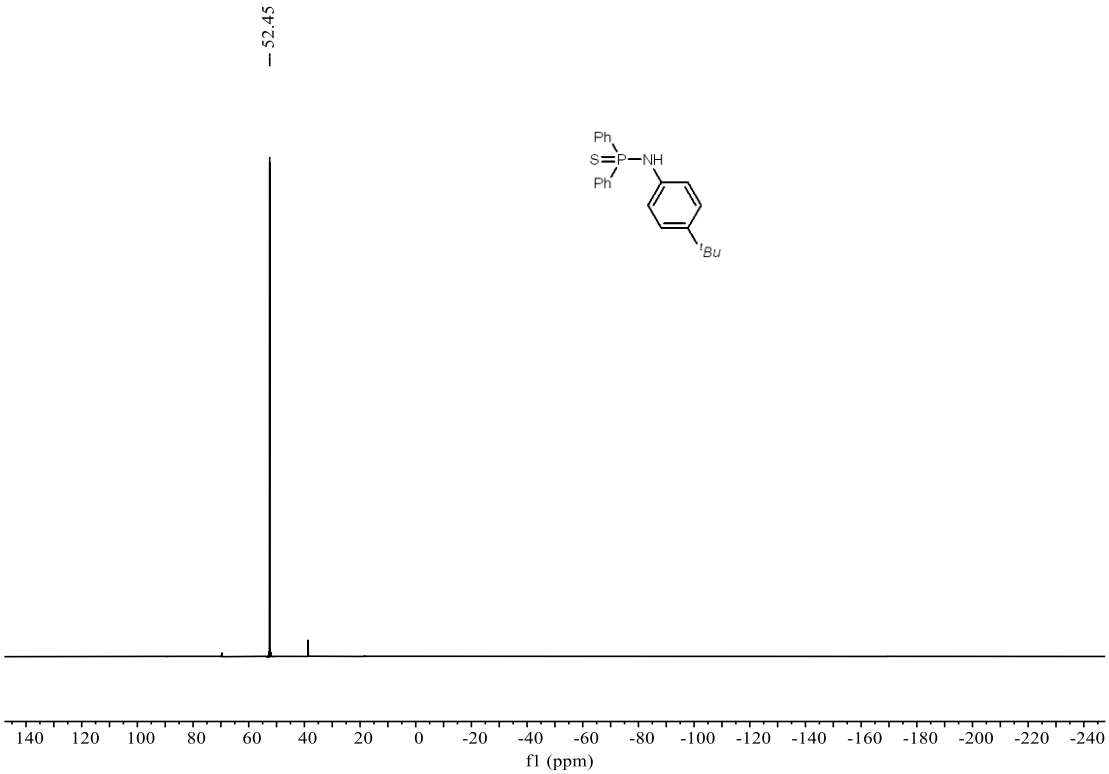



134.12
133.10
132.04
132.00
131.67
131.56
129.07
128.81
128.68
121.77
118.85
118.78
77.32
77.00
76.68
Ph
S=P–NH
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

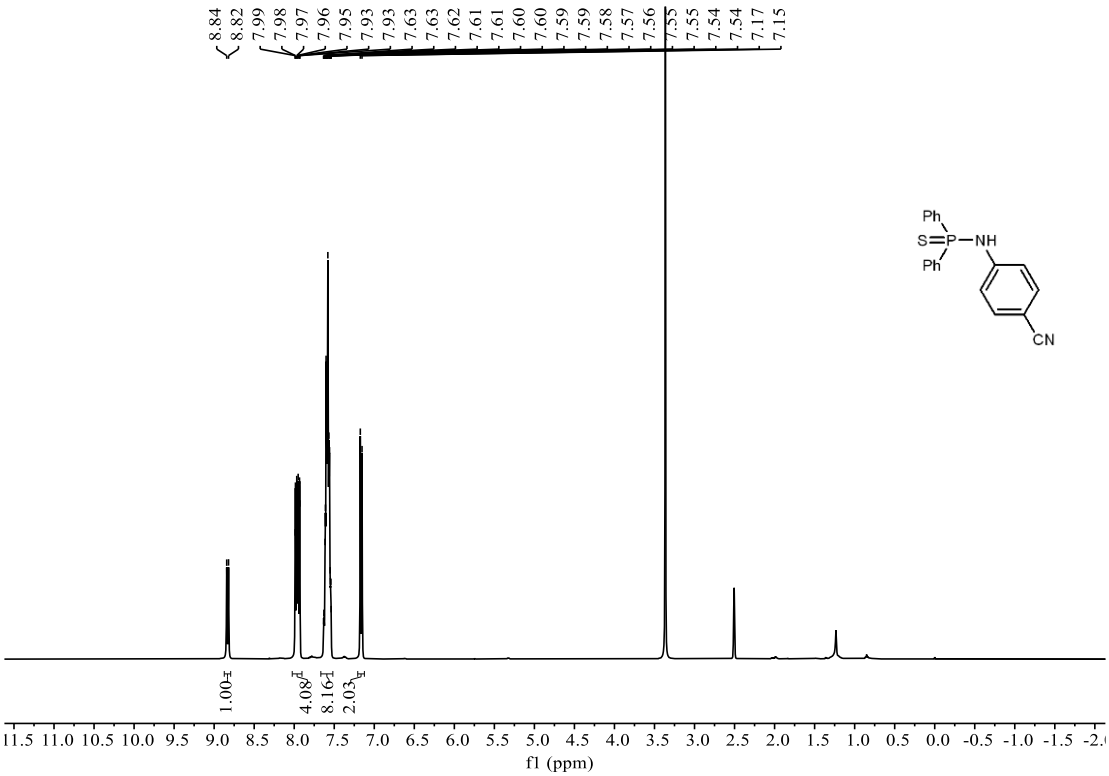

52.51
Ph
S=P–NH
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

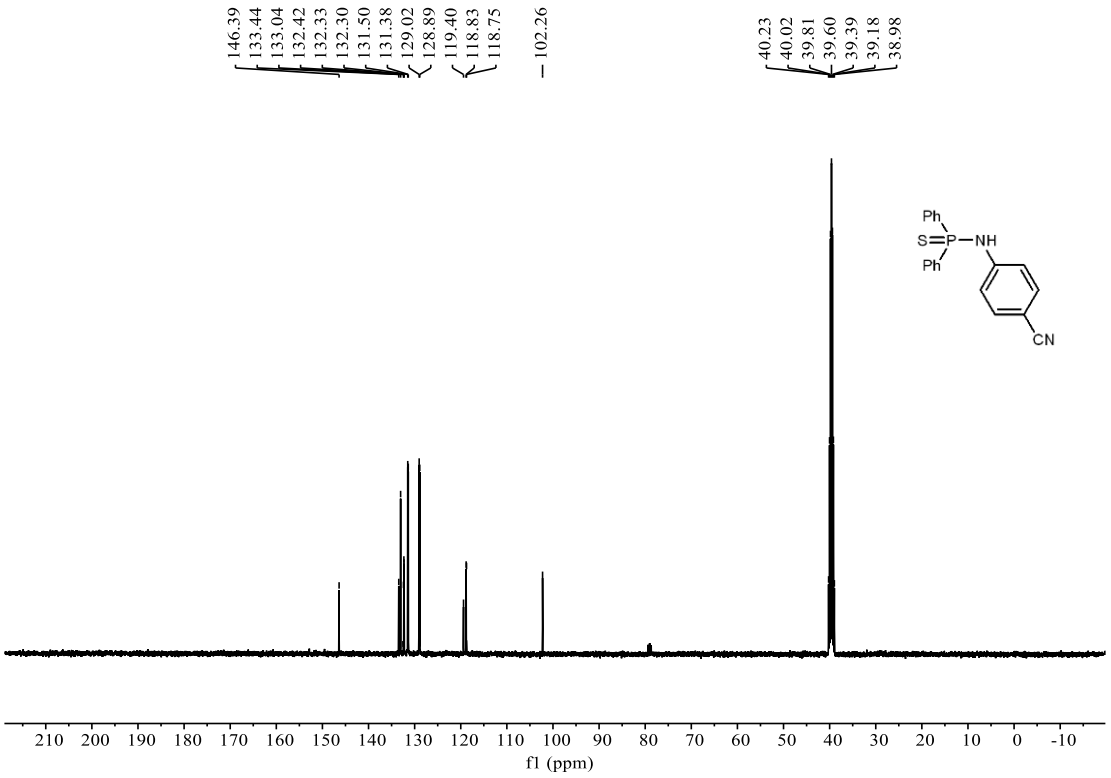
N-(4-(tert-butyl)phenyl)-P,P-diphenylphosphinothioic amide (**4ac'**)

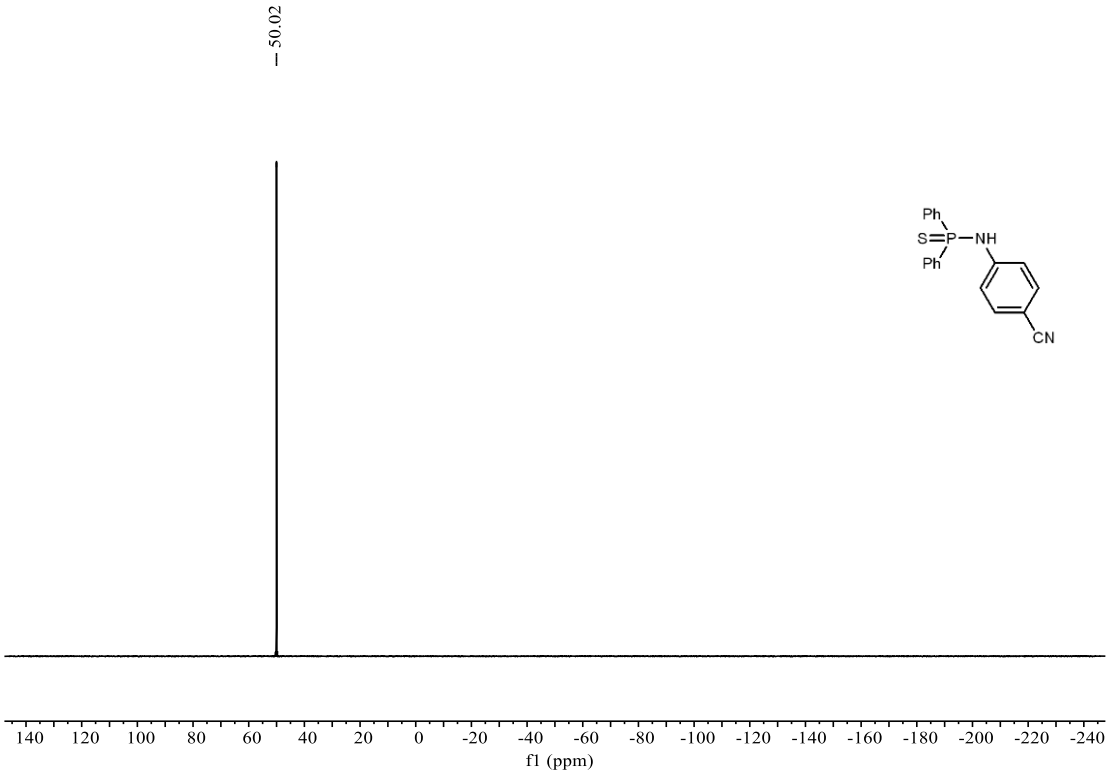




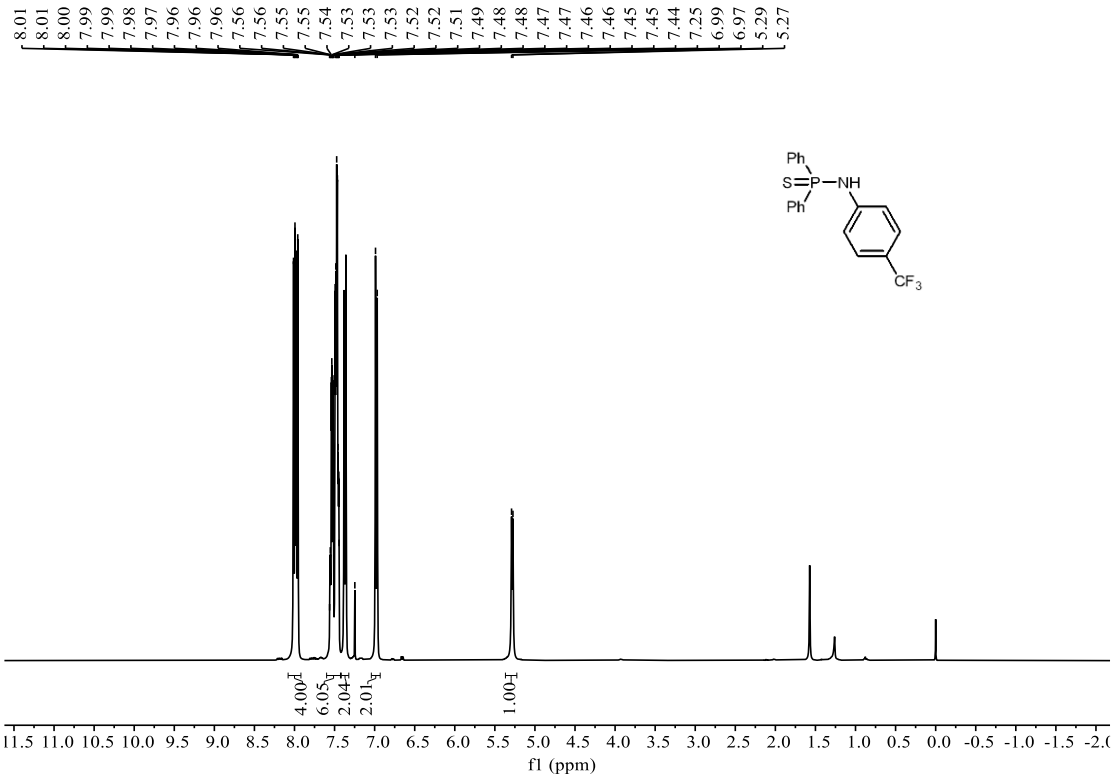
N-(4-cyanophenyl)-P,P-diphenylphosphinothioic amide (**4ad'**)

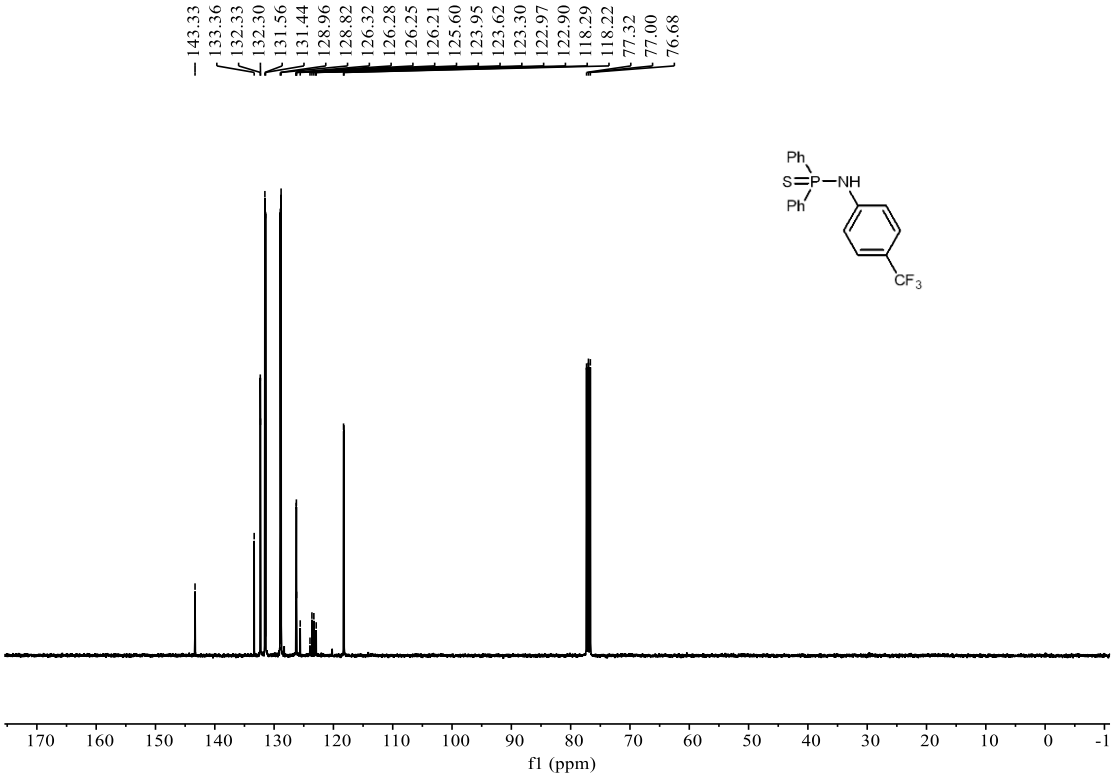


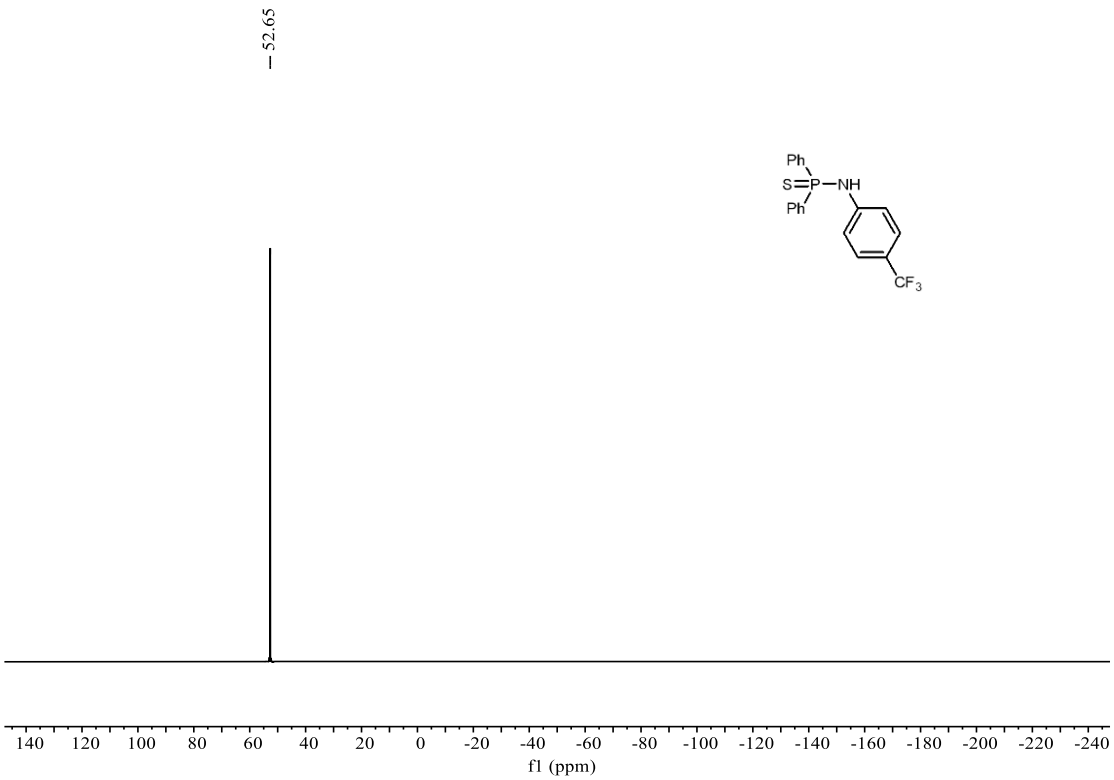

146.39
133.44
133.04
132.42
132.33
132.30
131.50
131.38
129.02
128.89
119.40
118.83
118.75
102.26
40.23
40.02
39.81
39.60
39.39
39.18
38.98
Ph
S=P—NH
Ph
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

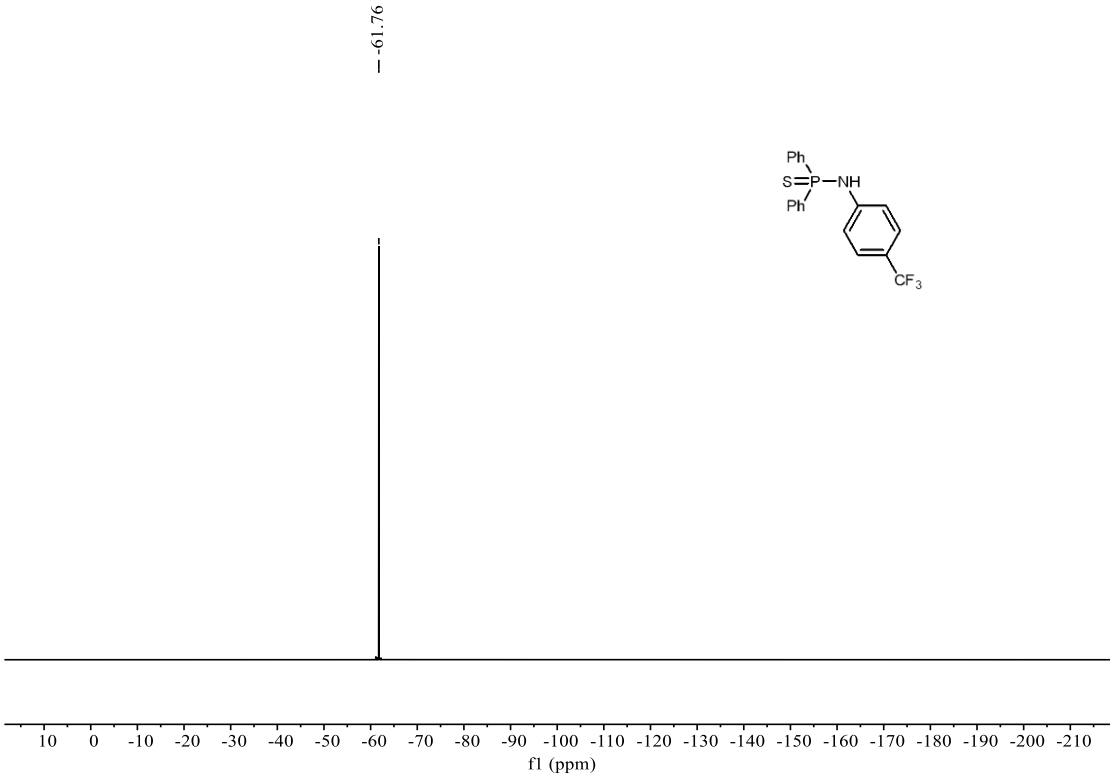

50.02
Ph
S=P—NH
Ph
CN
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

P,P-diphenyl-N-(4-(trifluoromethyl)phenyl)phosphinothioic amide (**4ae'**)

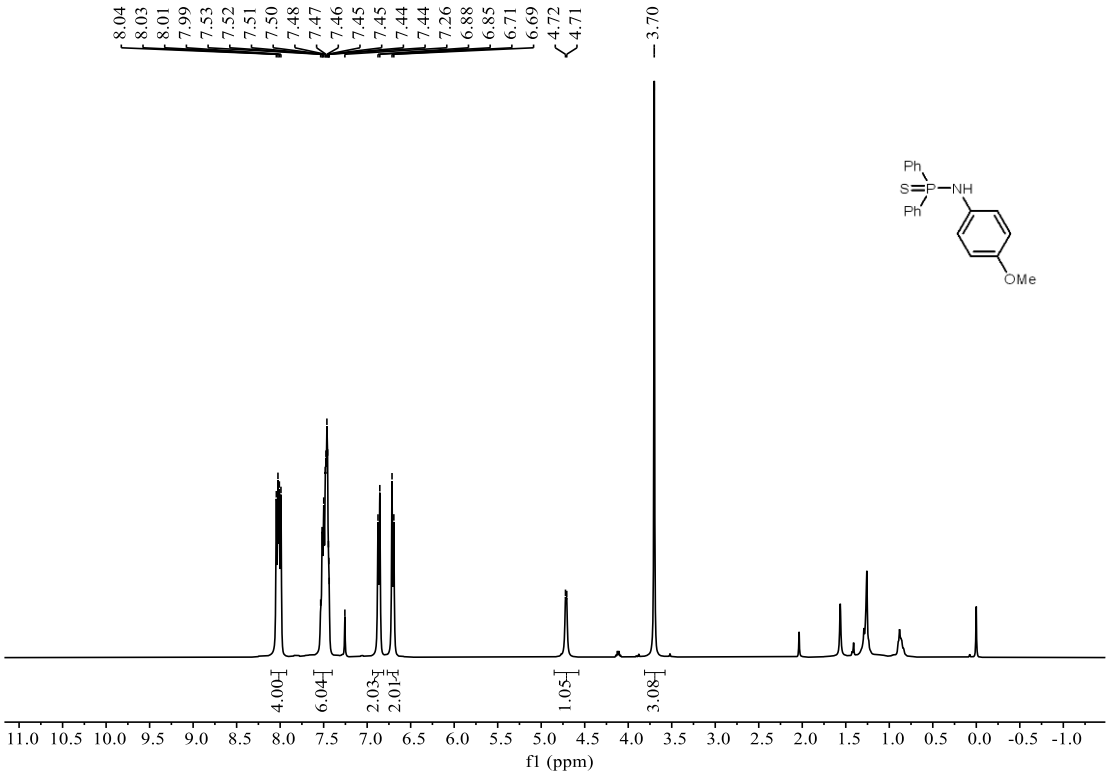


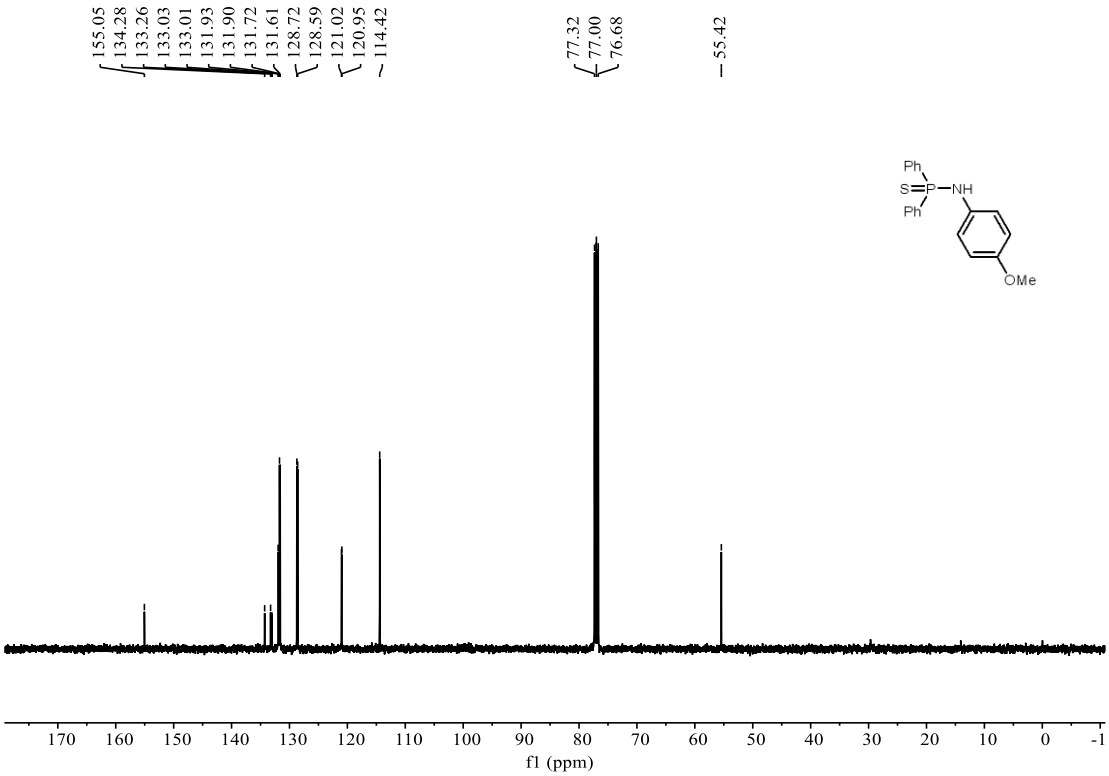


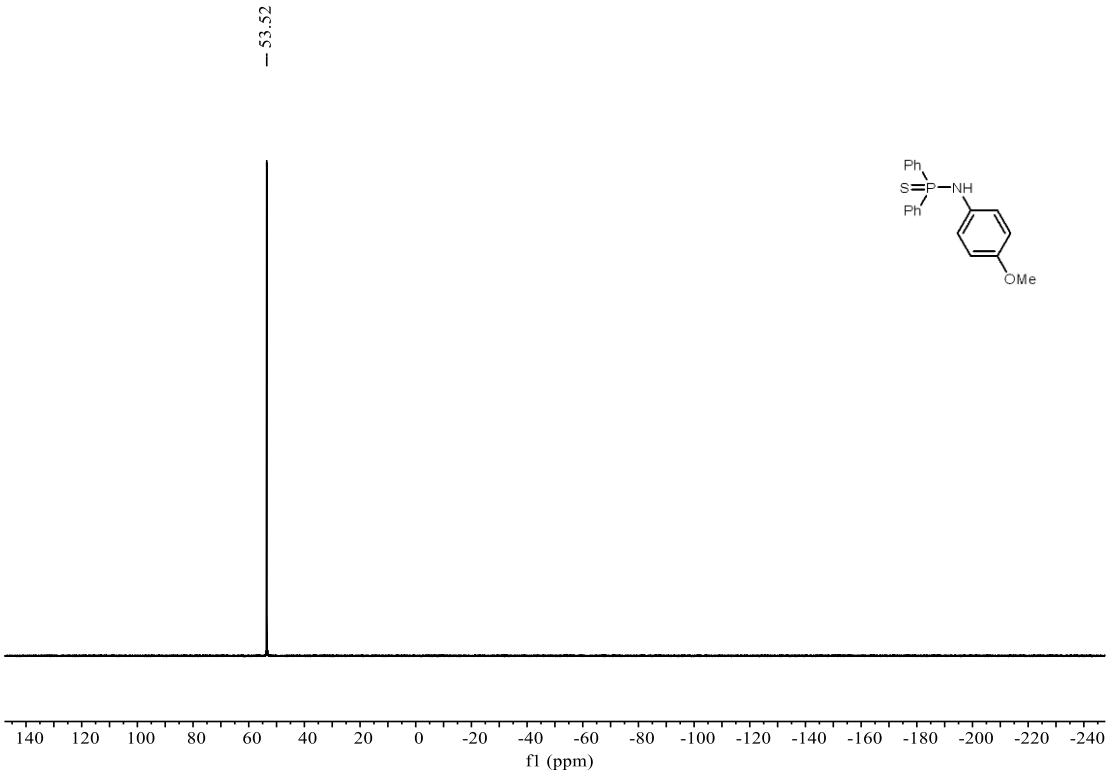

52.65
Ph
S
P
NH
Ph
CF3
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)


-61.76
Ph
S
P
NH
Ph
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

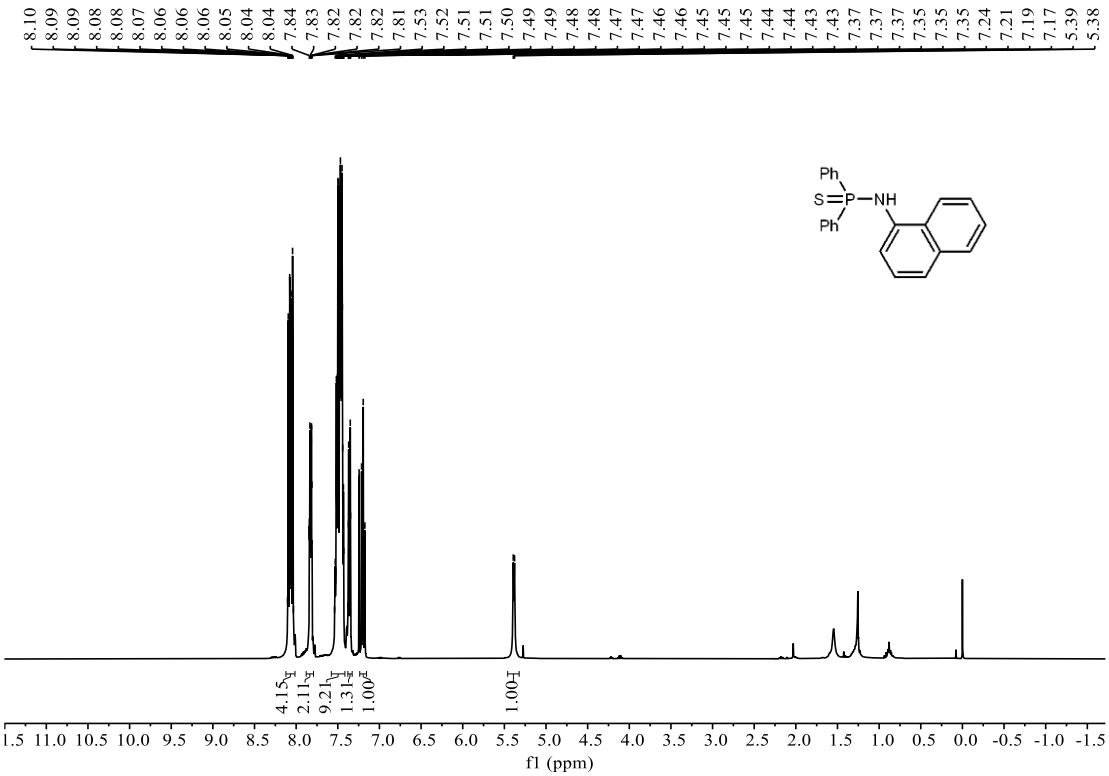
N-(4-methoxyphenyl)-P,P-diphenylphosphinothioic amide (**4af'**)

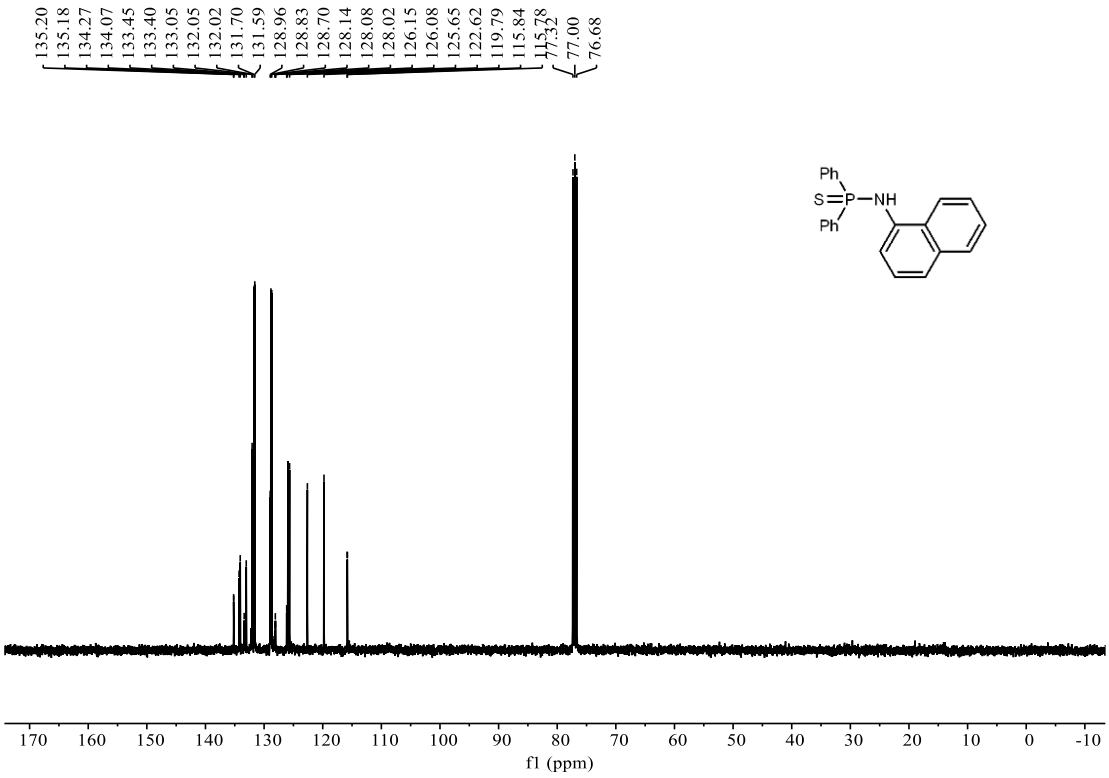


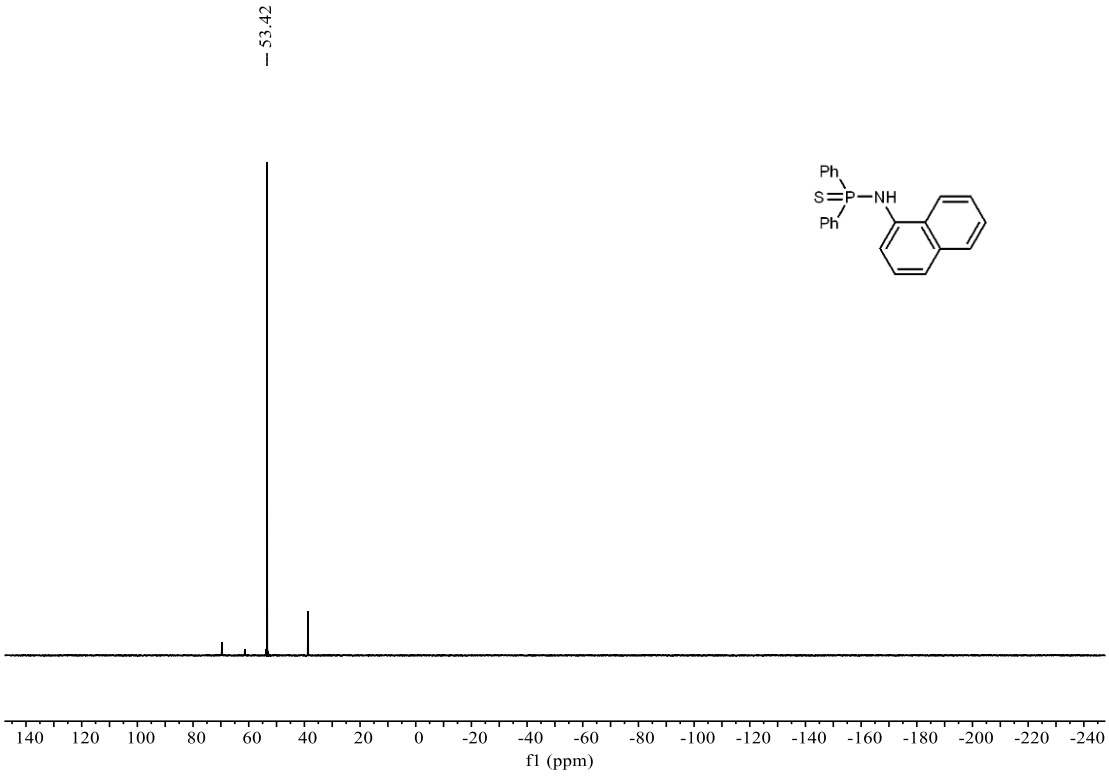




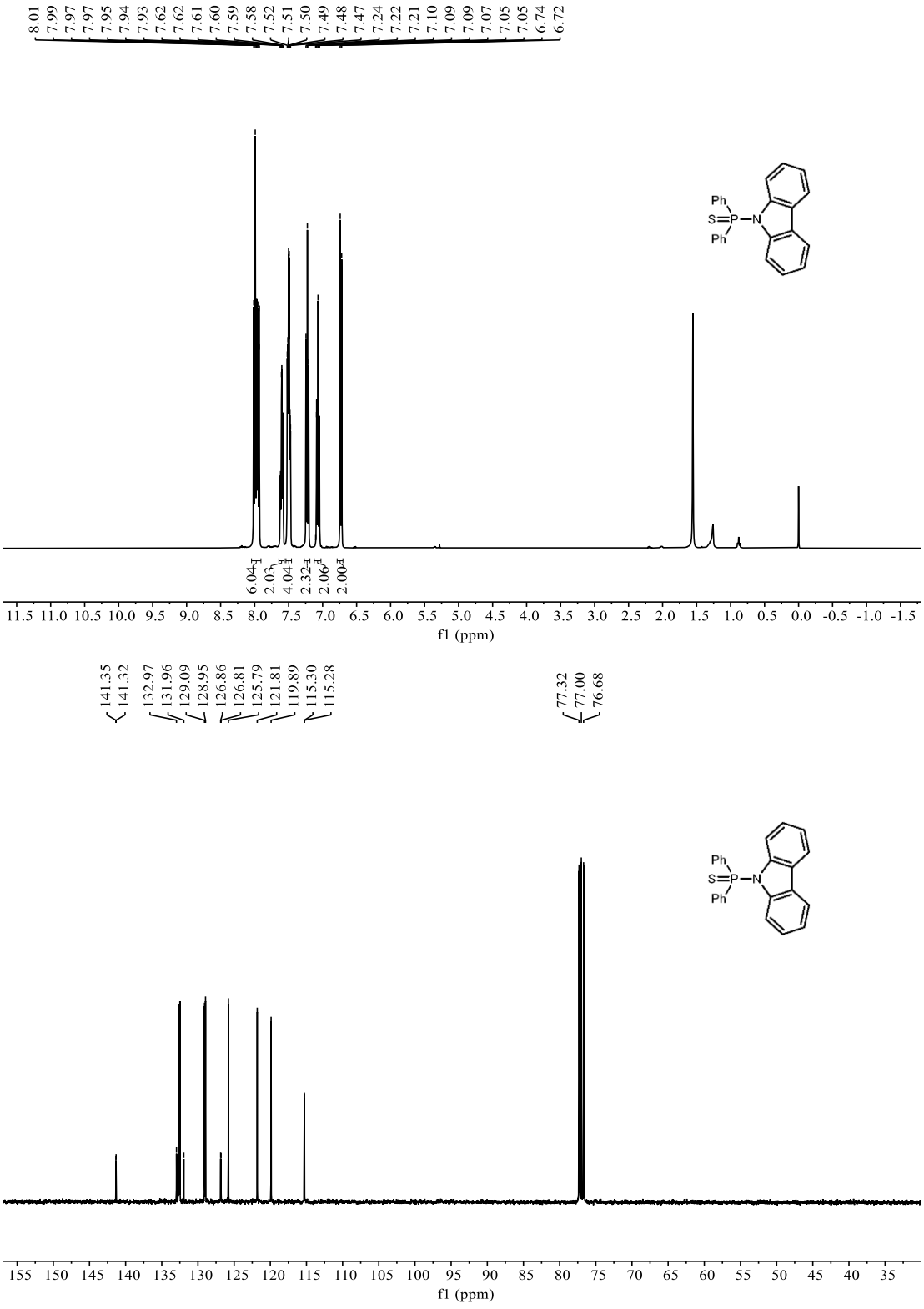
N-(naphthalen-1-yl)-P,P-diphenylphosphinothioic amide (**4ag'**)

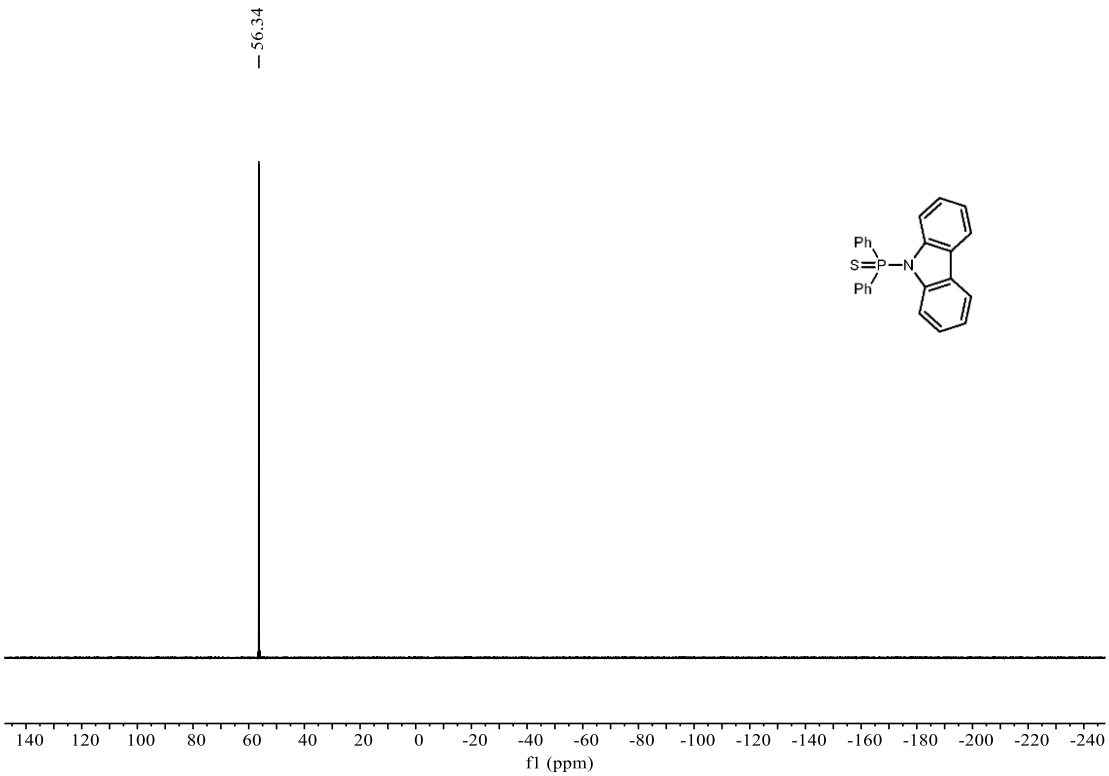



135.20
135.18
134.27
134.07
133.45
133.40
133.05
132.05
132.02
131.70
131.59
128.96
128.83
128.70
128.14
128.08
128.02
126.15
126.08
125.65
122.62
119.79
115.84
115.78
77.32
77.00
76.68
Ph
S=P–NH
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

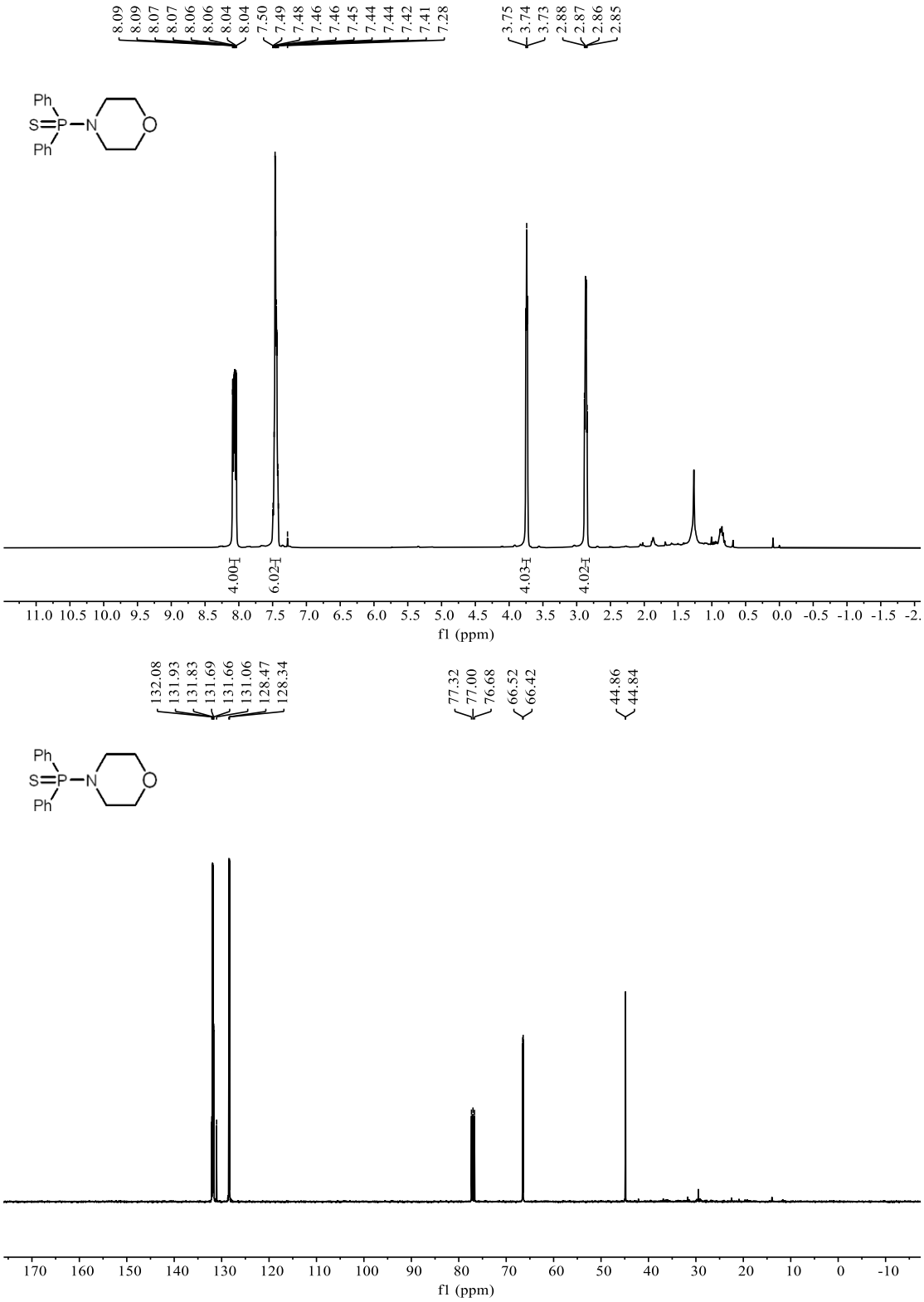

53.42
Ph
S=P–NH
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

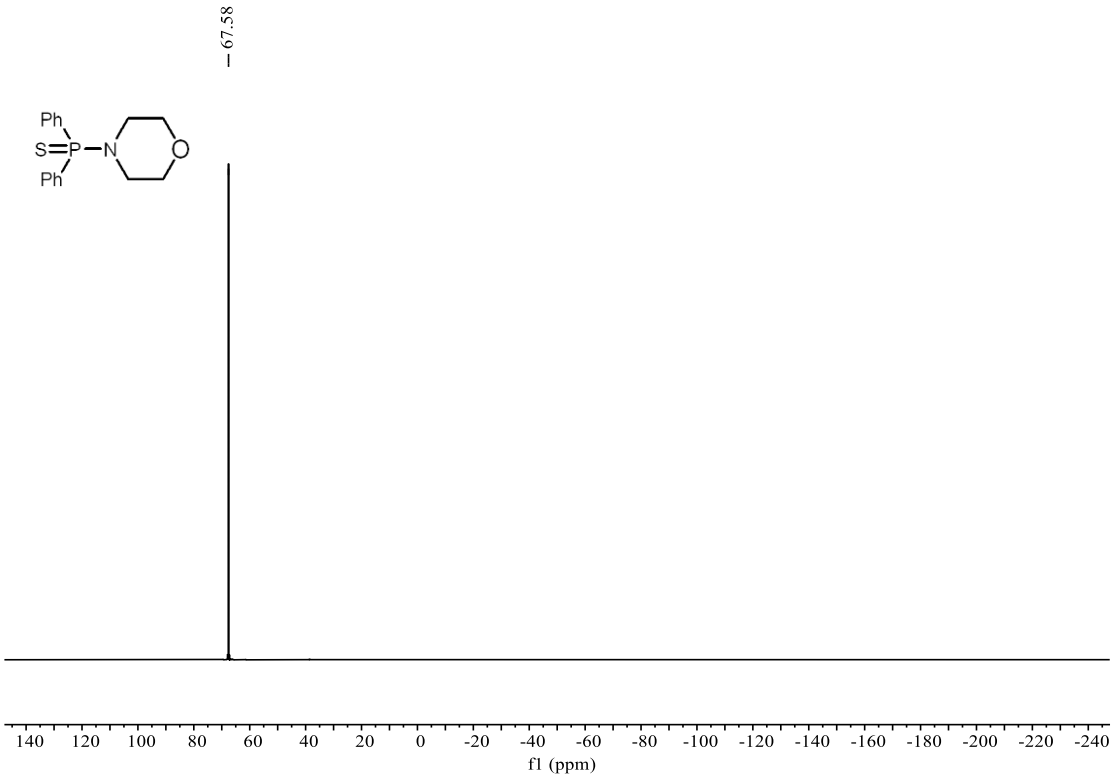
(9H-carbazol-9-yl)diphenylphosphine sulfide (**4ah'**)



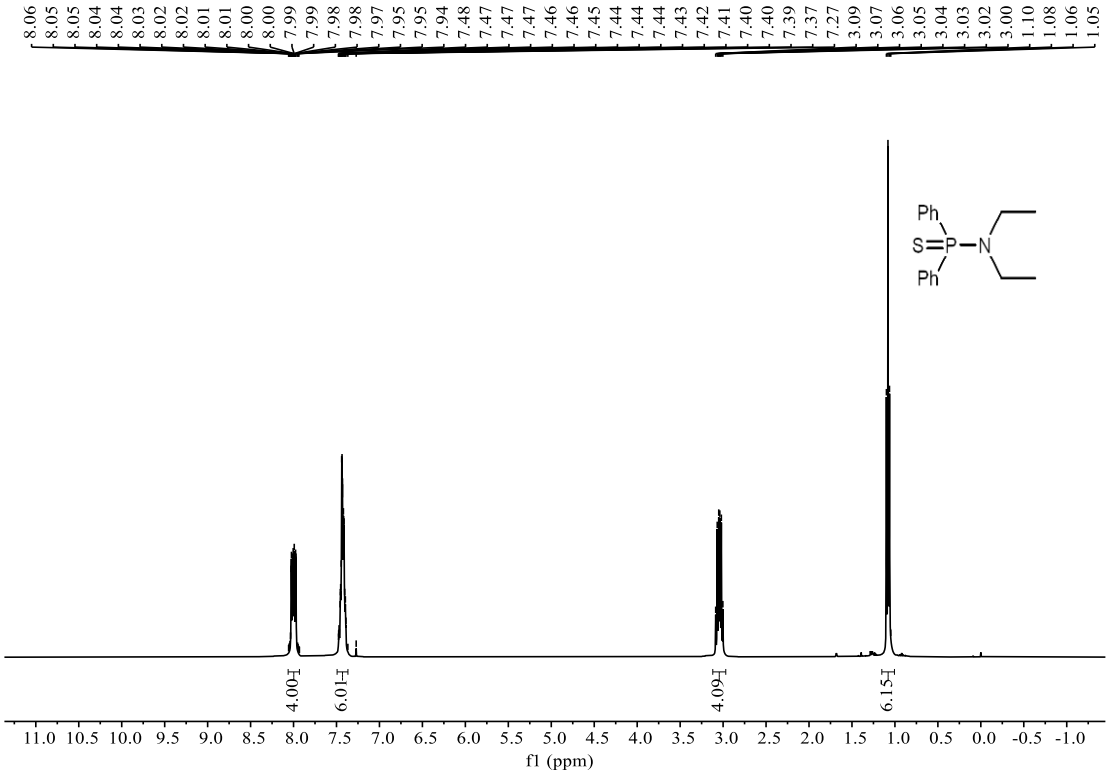

56.34
Ph
S
P
N
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

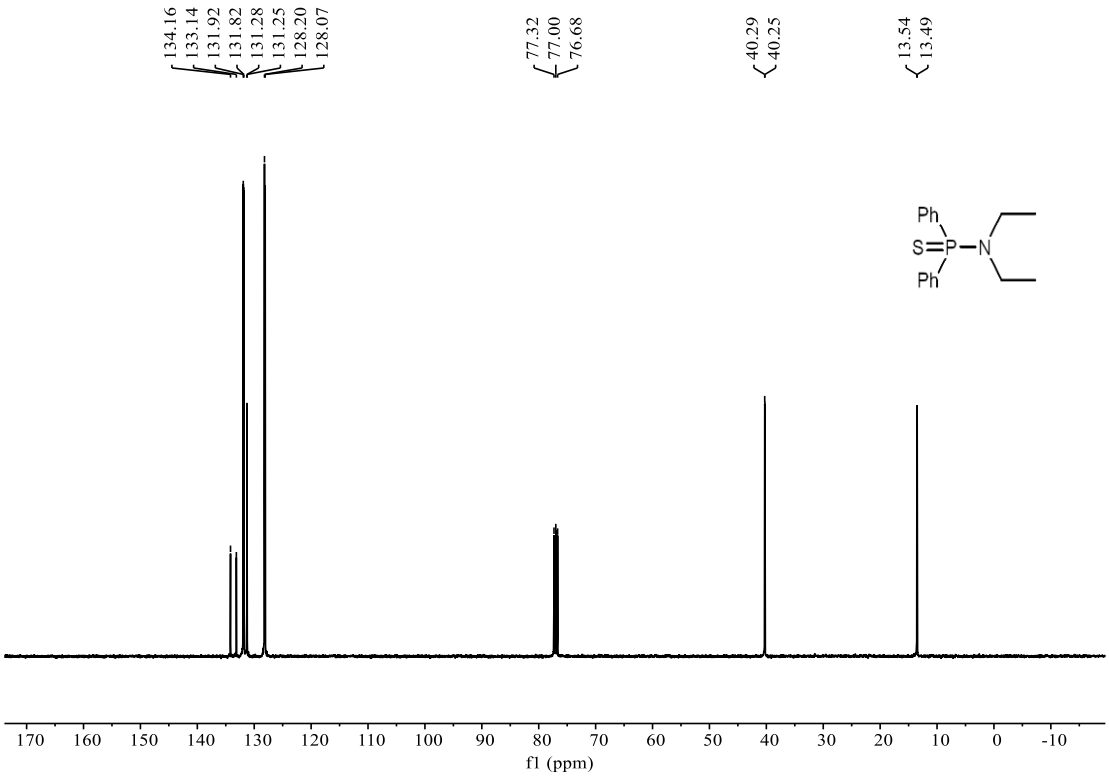
Morpholinodiphenylphosphine sulfide (**4ai'**)

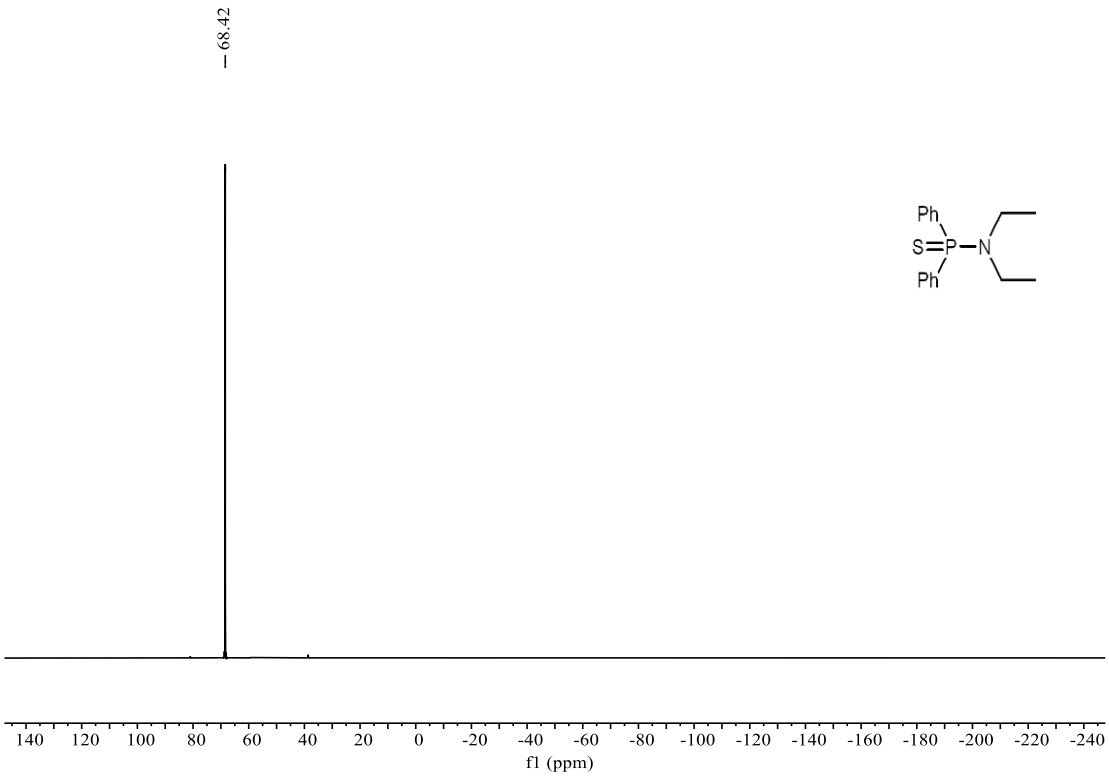




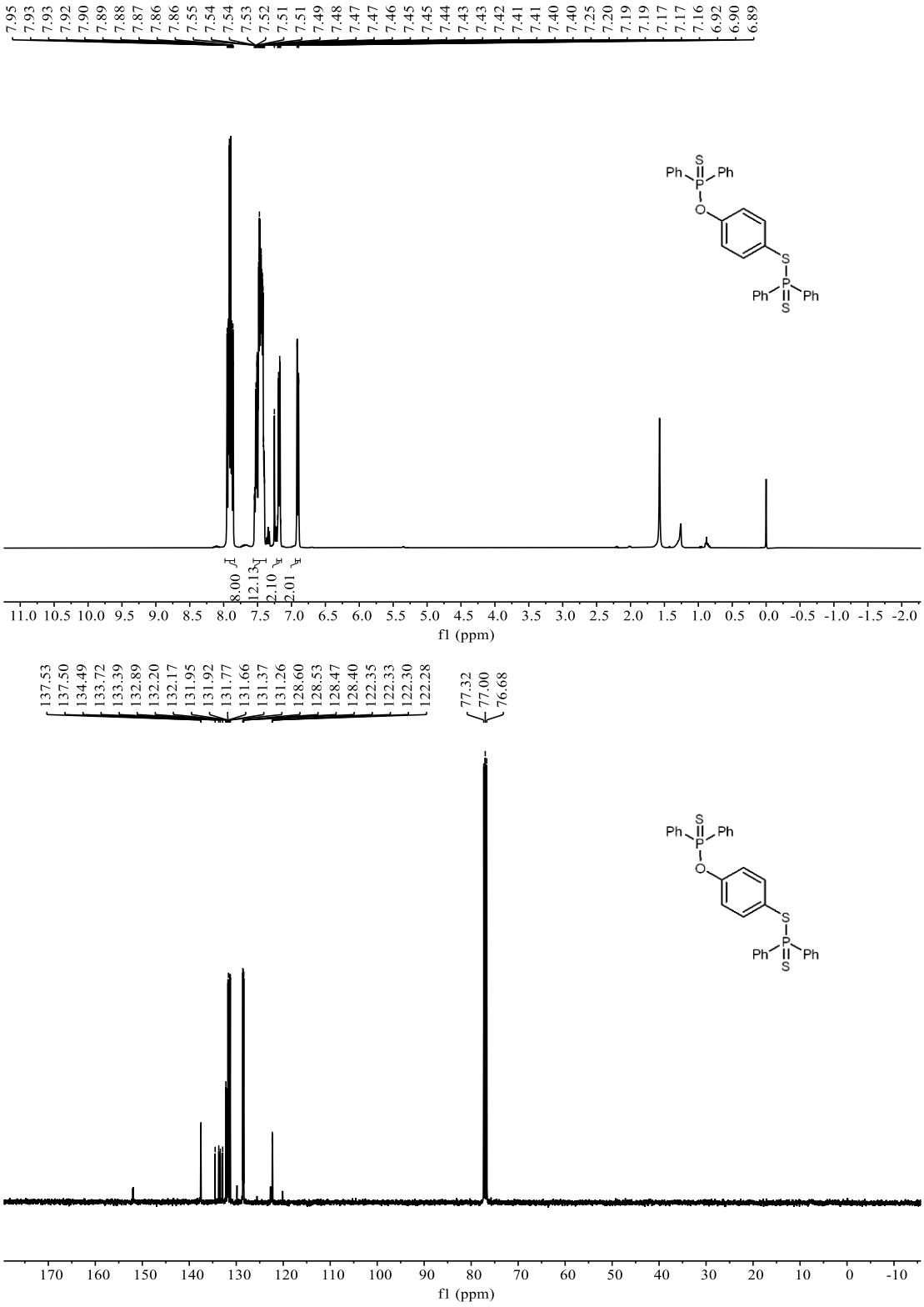
N,N-diethyl-P,P-diphenylphosphinothioic amide (**4aj'**)

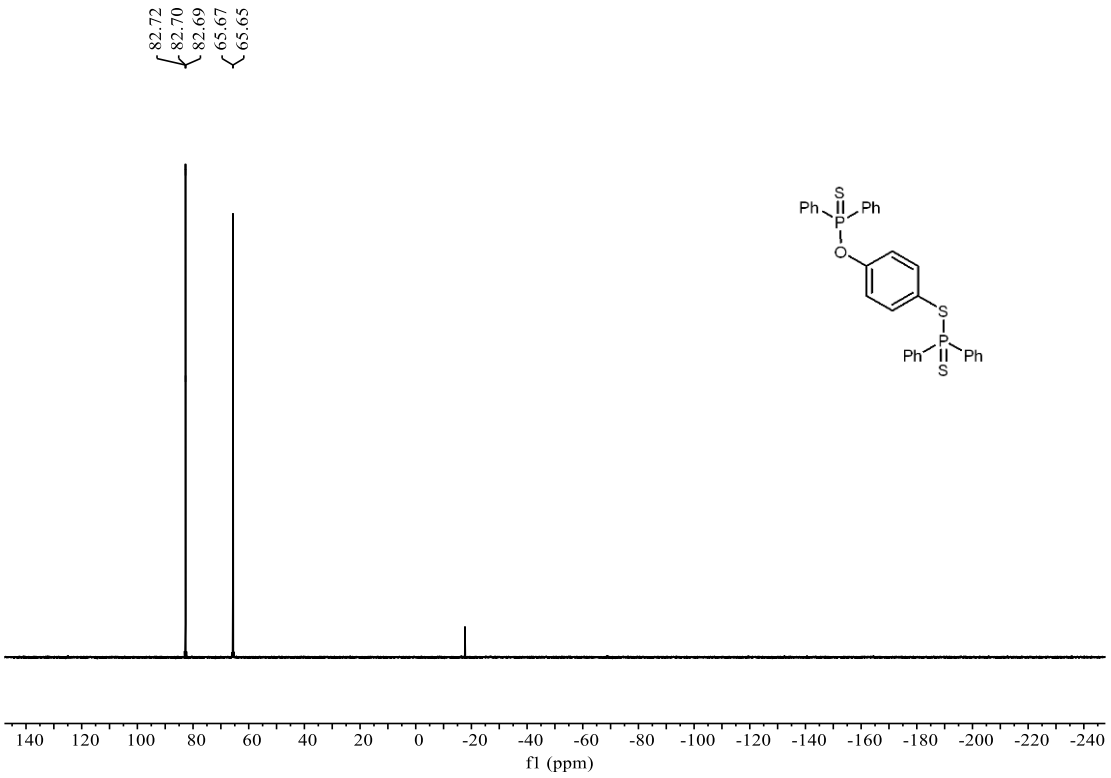



134.16
133.14
131.92
131.82
131.28
131.25
128.20
128.07
77.32
77.00
76.68
40.29
40.25
13.54
13.49
Ph
S=P–N
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

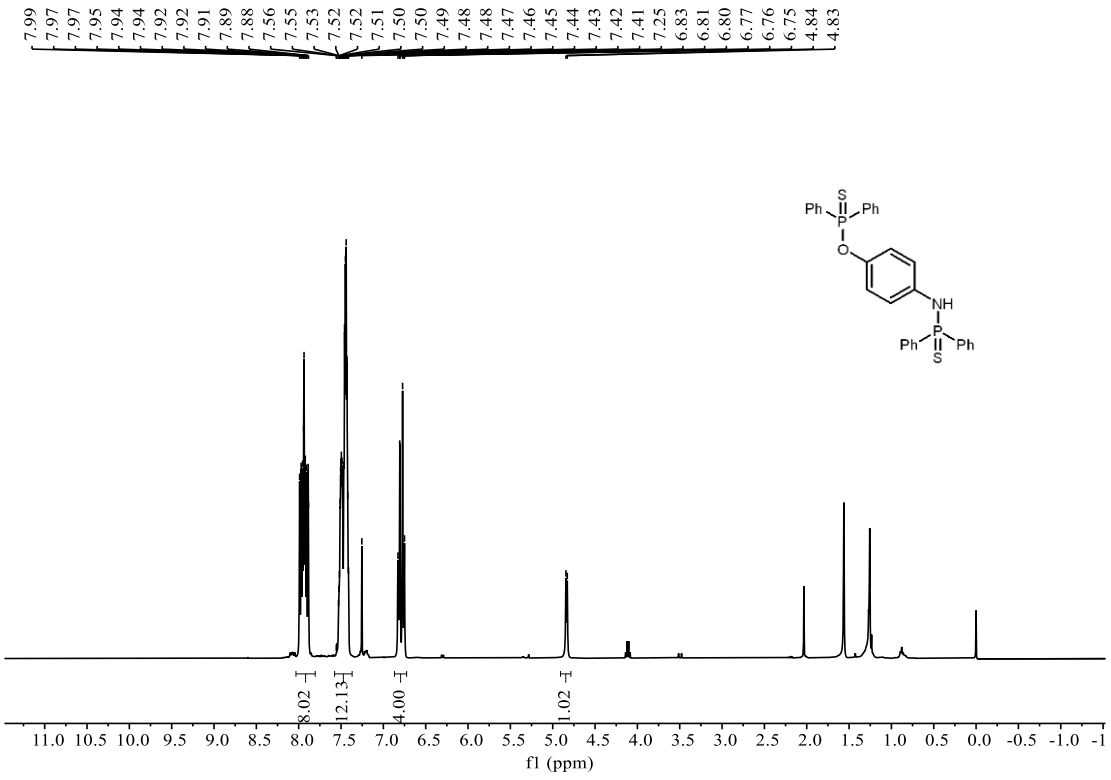

68.42
Ph
S=P–N
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

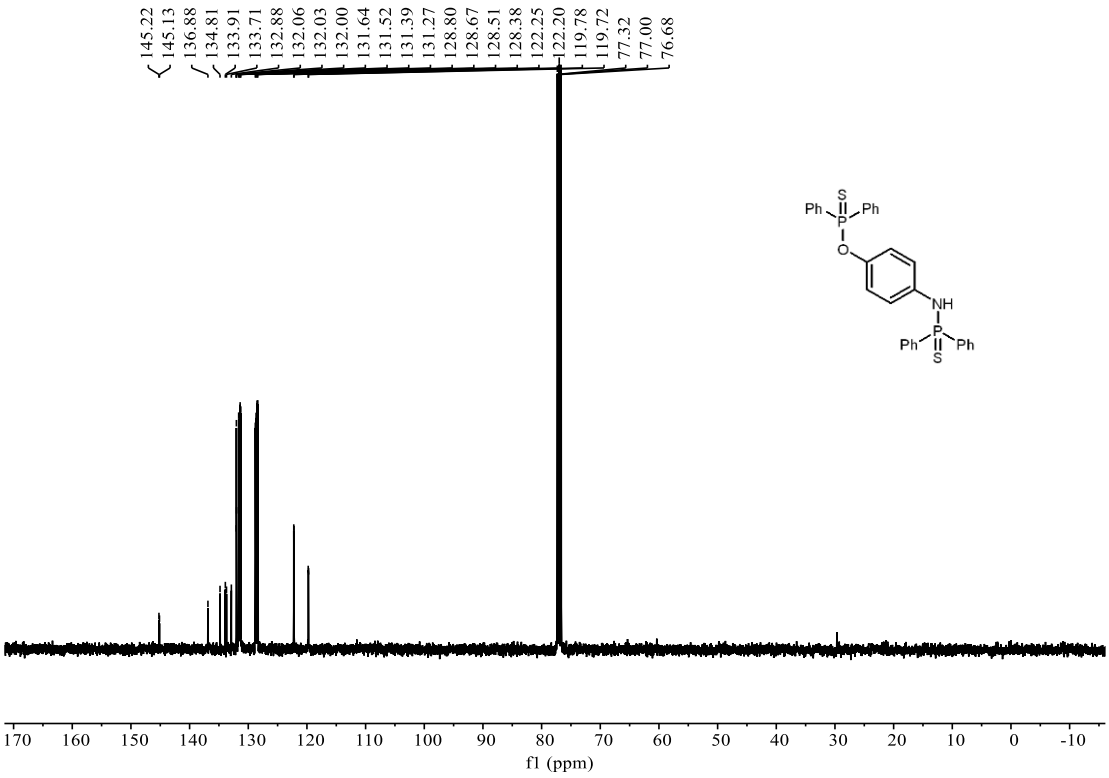
O-(4-((diphenylphosphorothioyl)thio)phenyl) diphenylphosphinothioate (**4ak'**)

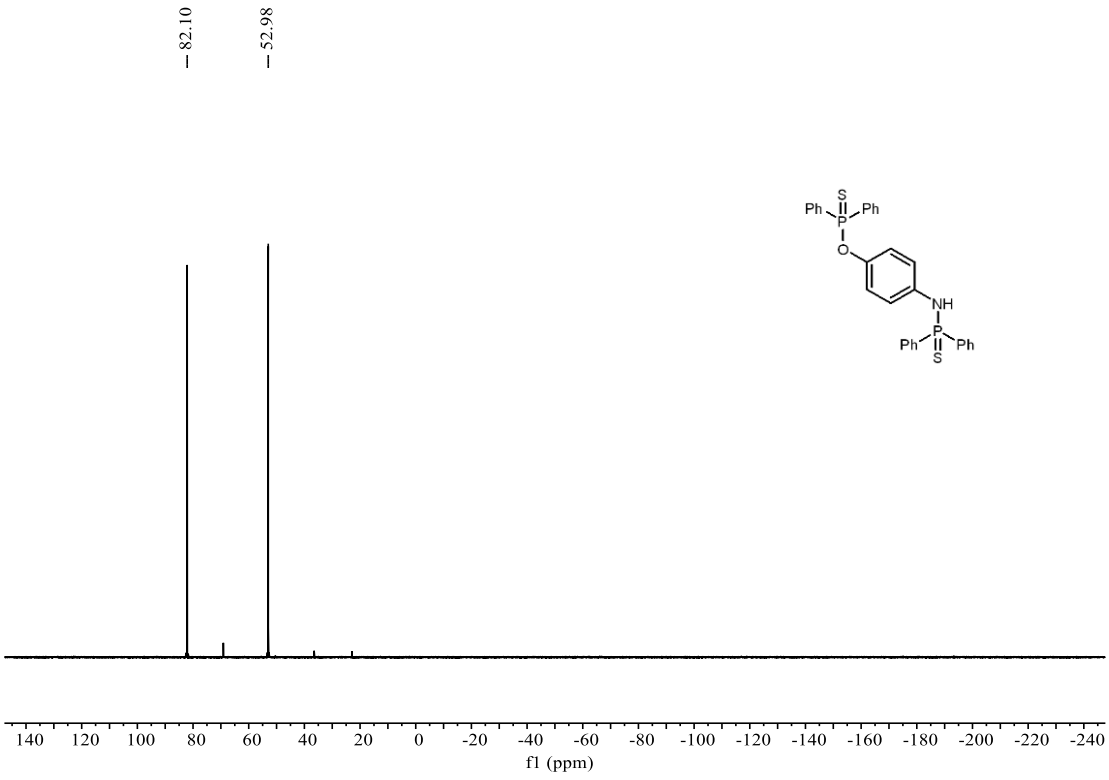




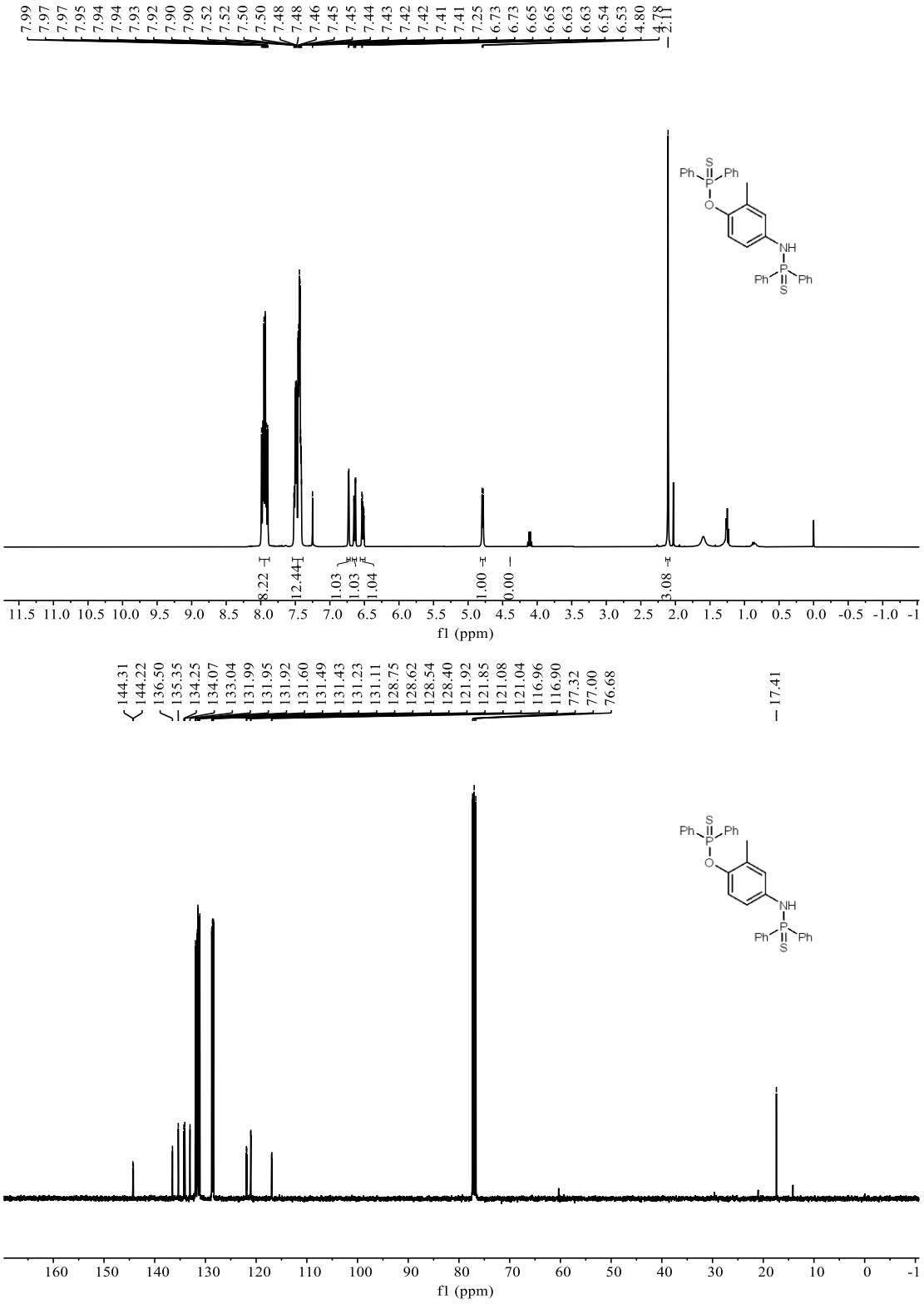
O-(4-((diphenylphosphorothioyl)amino)-2-methylphenyl) diphenylphosphinothioate (**4al'**)

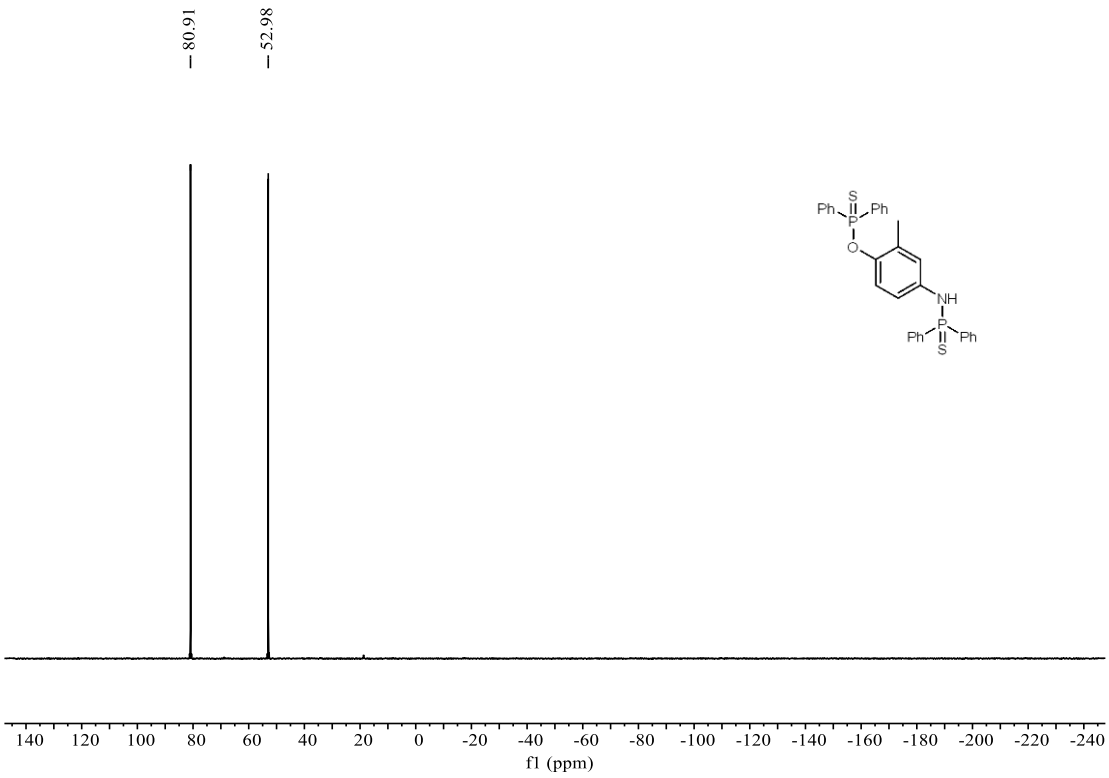



145.22
145.13
136.88
134.81
133.91
133.71
132.88
132.06
132.03
132.00
131.64
131.52
131.39
131.27
128.80
128.67
128.51
128.38
122.25
122.20
119.78
119.72
77.32
77.00
76.68
Ph
S
P
Ph
O
NH
Ph
P
Ph
S
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

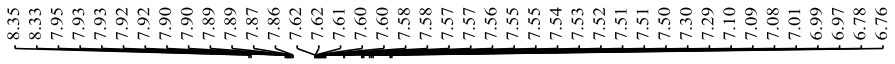

82.10
52.98
Ph
S
P
Ph
O
NH
Ph
P
Ph
S
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

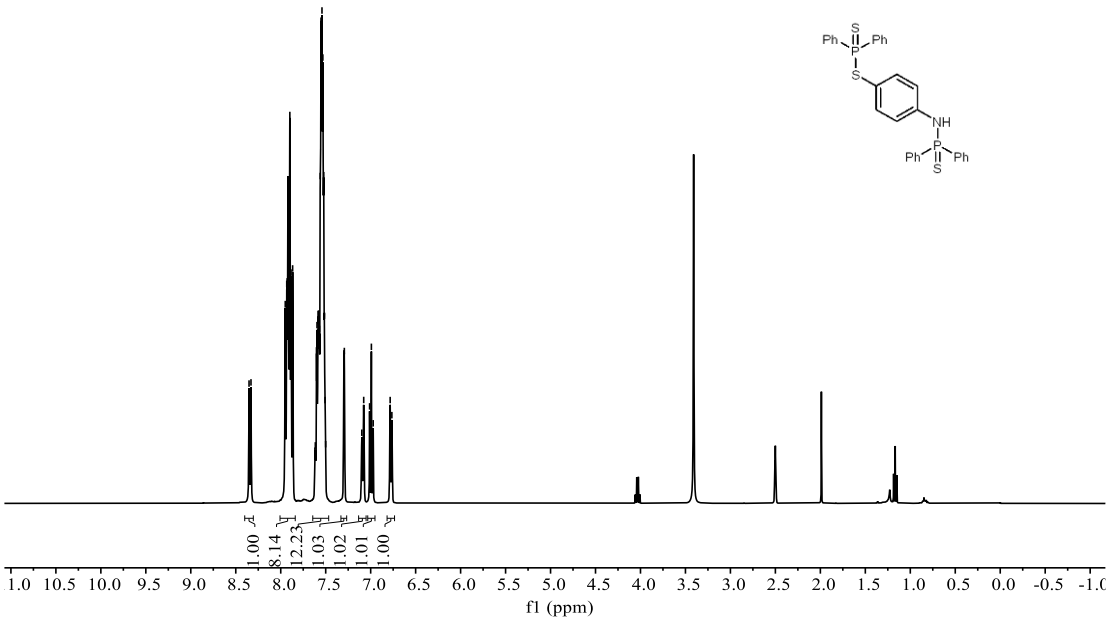
O-(4-((diphenylphosphorothioyl)amino)phenyl) diphenylphosphinothioate (**4am'**)

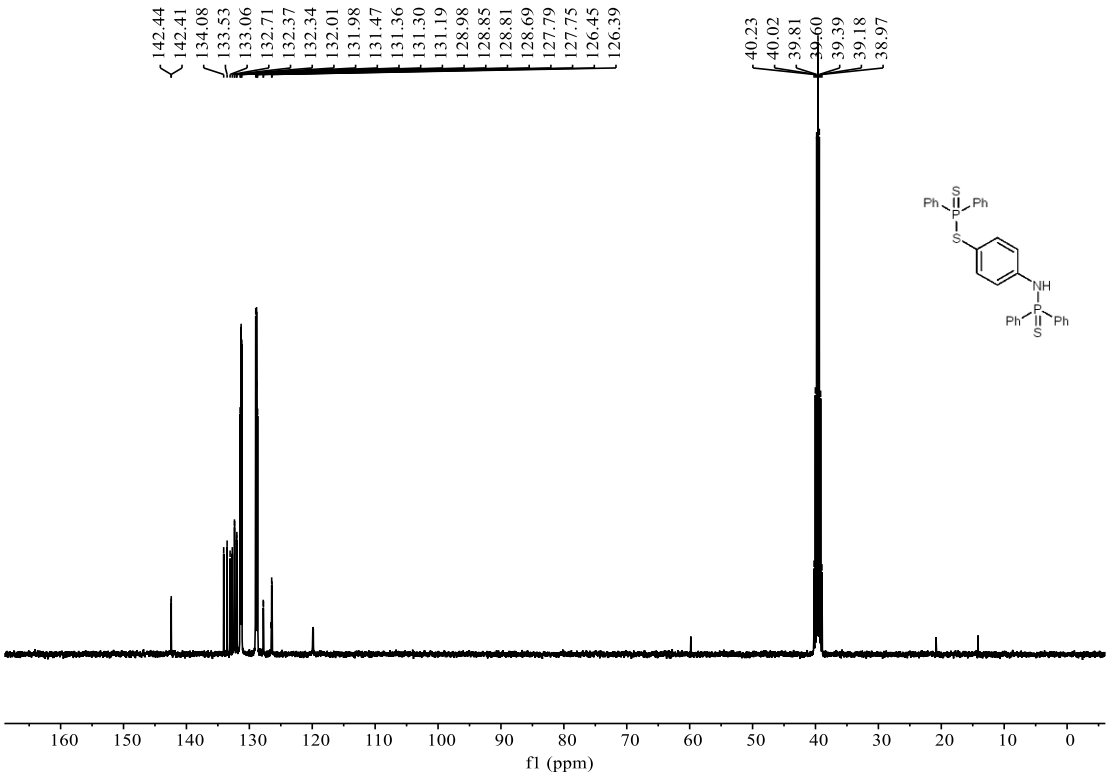


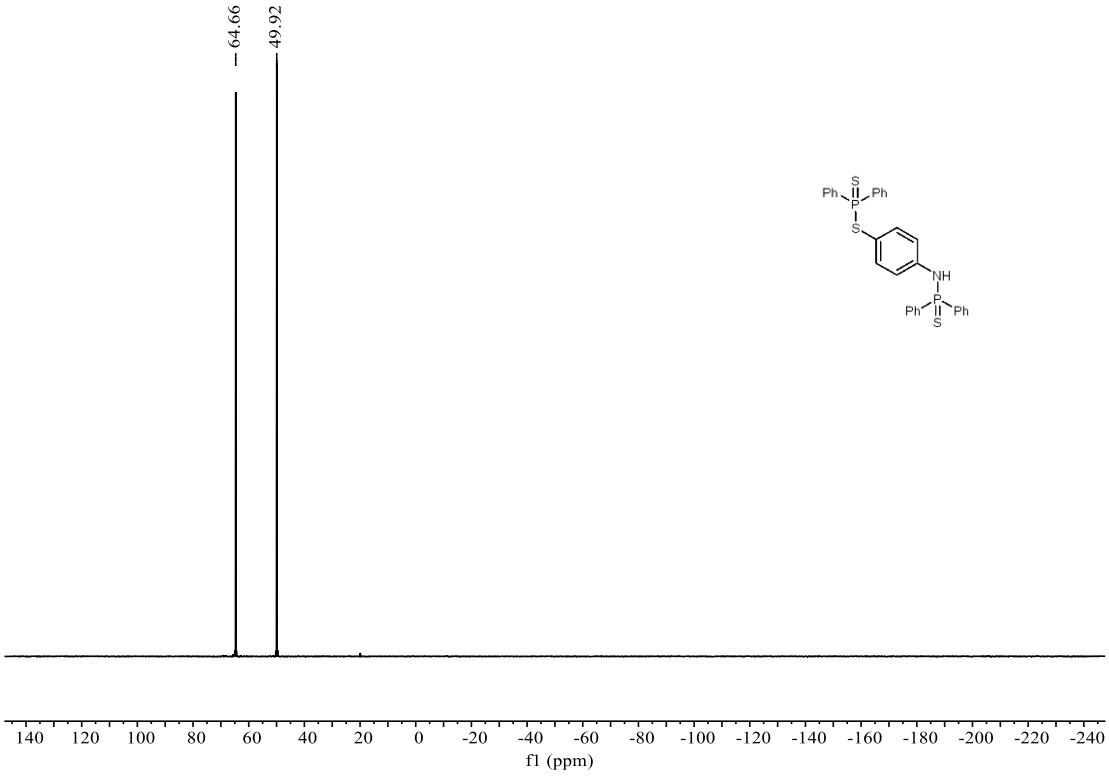


4-((Diphenylphosphorothioyl)amino)phenyl diphenylphosphinodithioate (**4an'**)

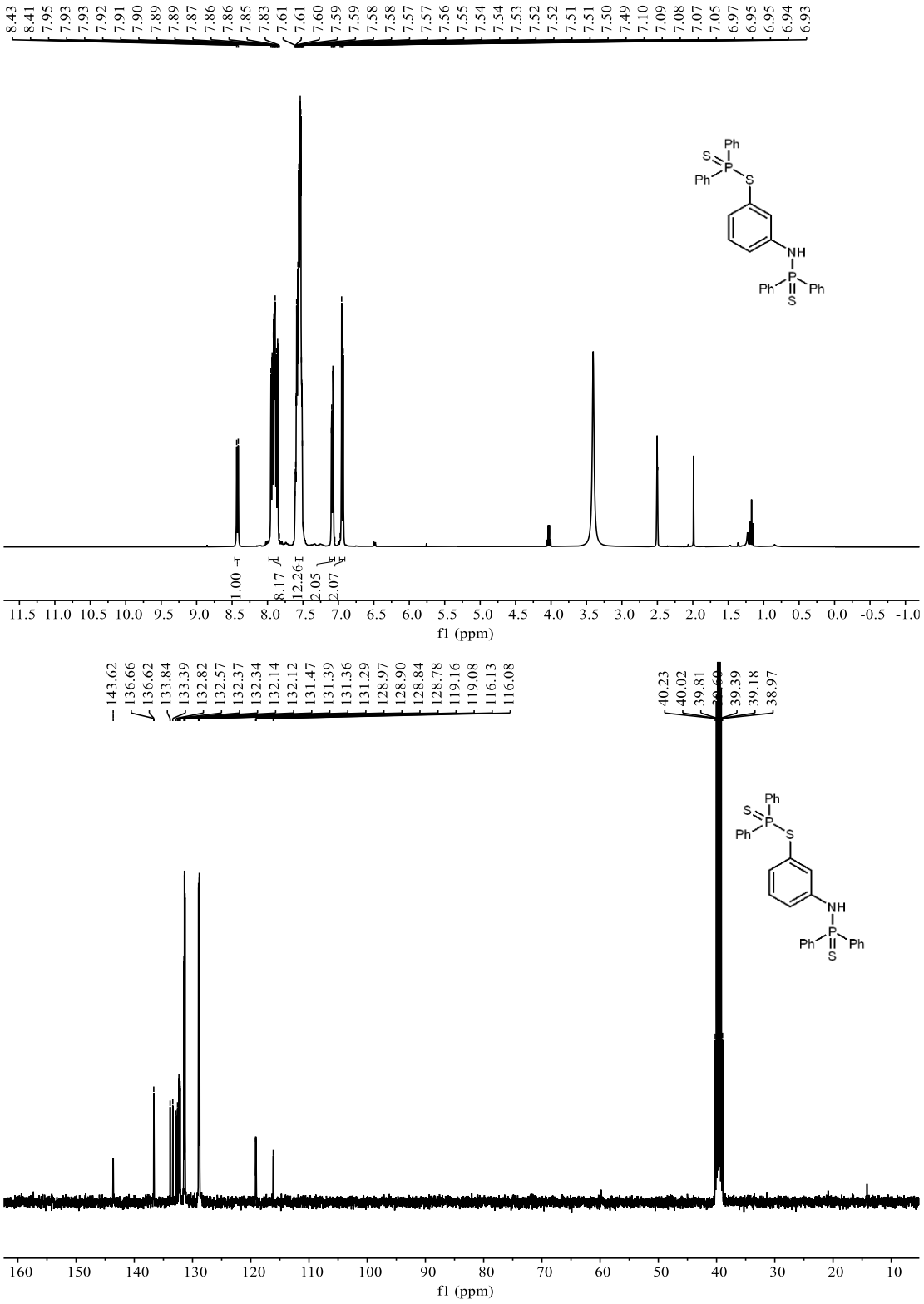


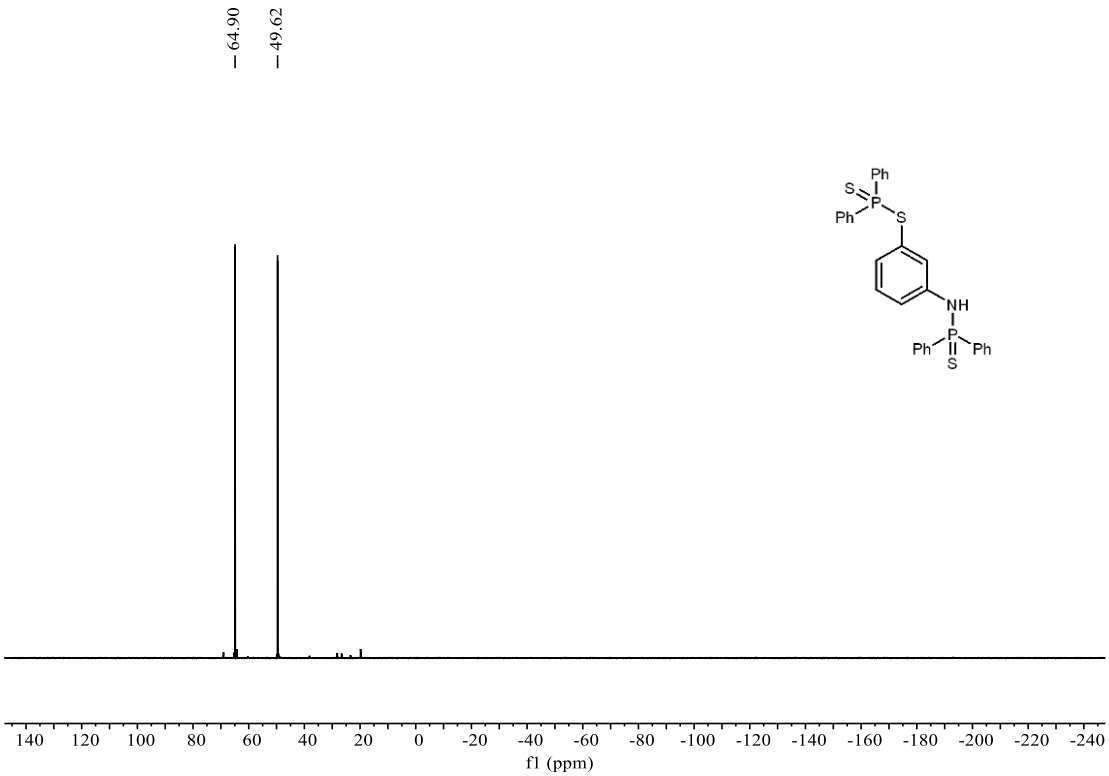



142.44
142.41
134.08
133.53
133.06
132.71
132.37
132.34
132.01
131.98
131.47
131.36
131.30
131.19
128.98
128.85
128.81
128.69
127.79
127.75
126.45
126.39
40.23
40.02
39.81
39.60
39.39
39.18
38.97
Ph
S
P
Ph
S
NH
Ph
P
Ph
S
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

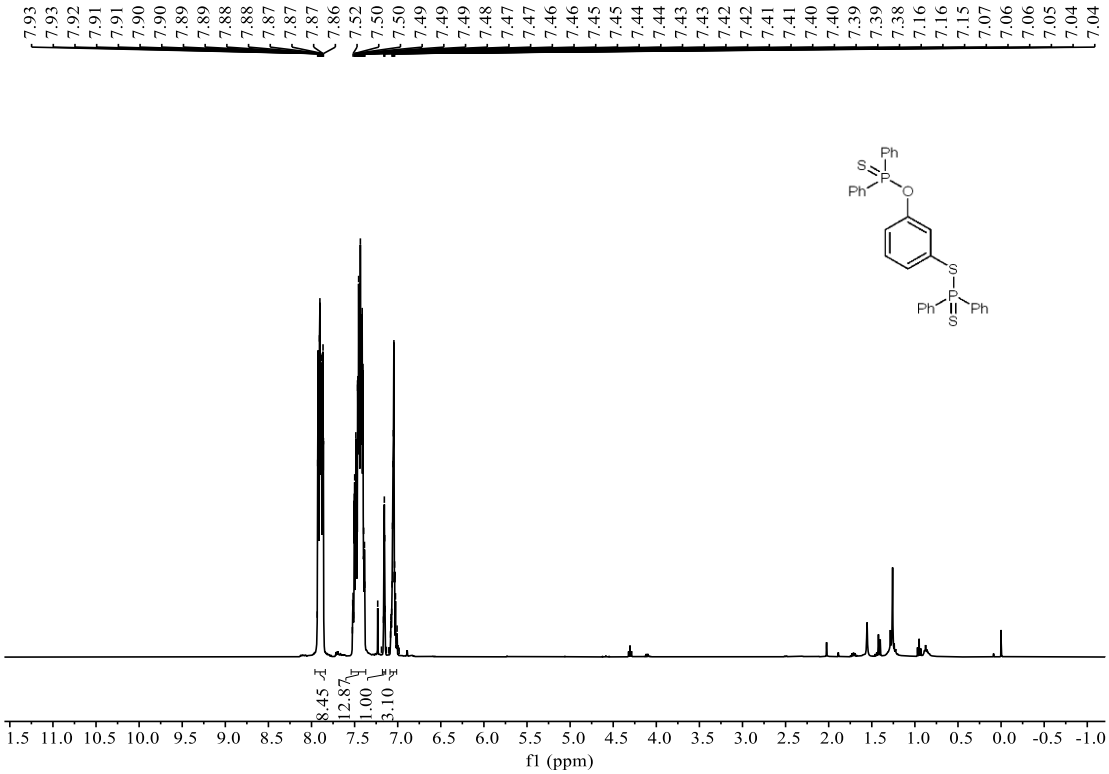

64.66
49.92
Ph
S
P
Ph
S
NH
Ph
P
Ph
S
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

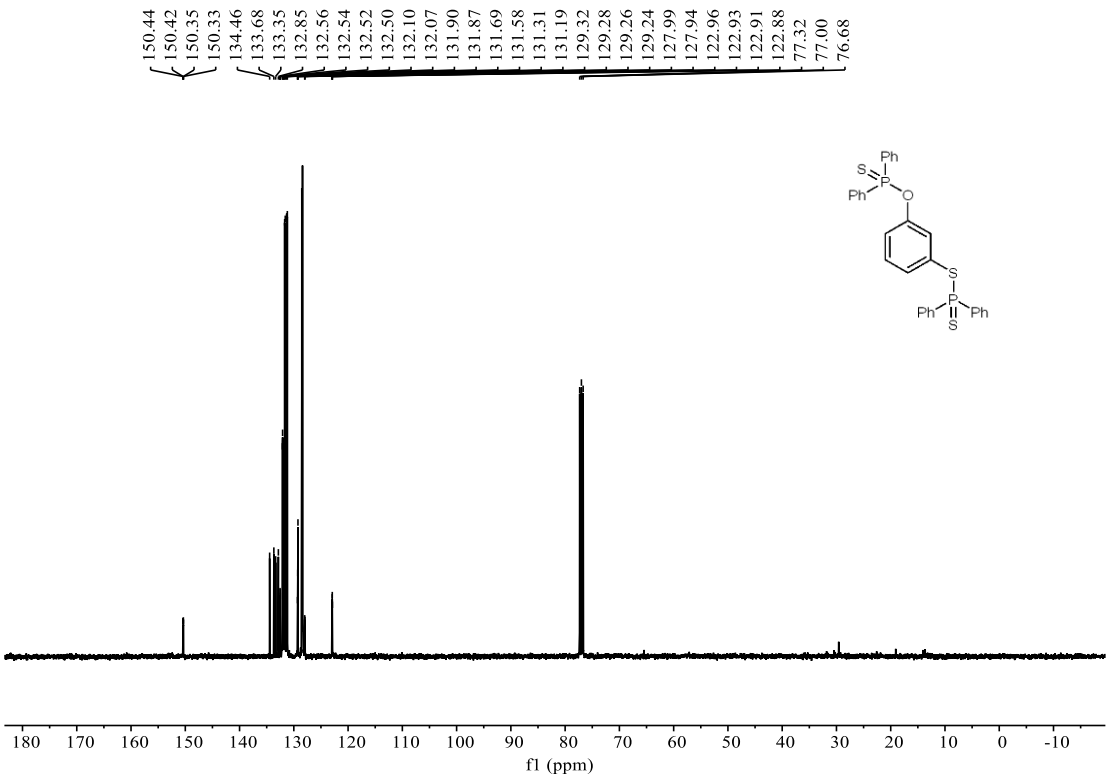
3-((Diphenylphosphorothioyl)amino)phenyl diphenylphosphinodithioate (**4ao'**)

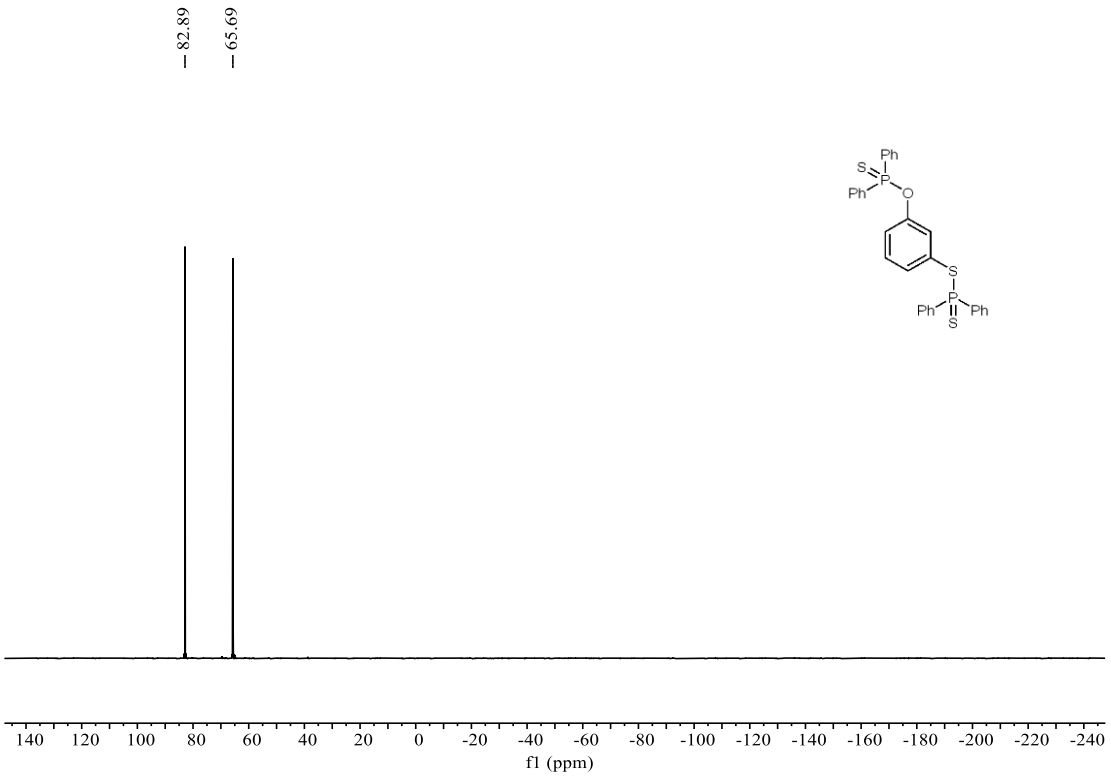




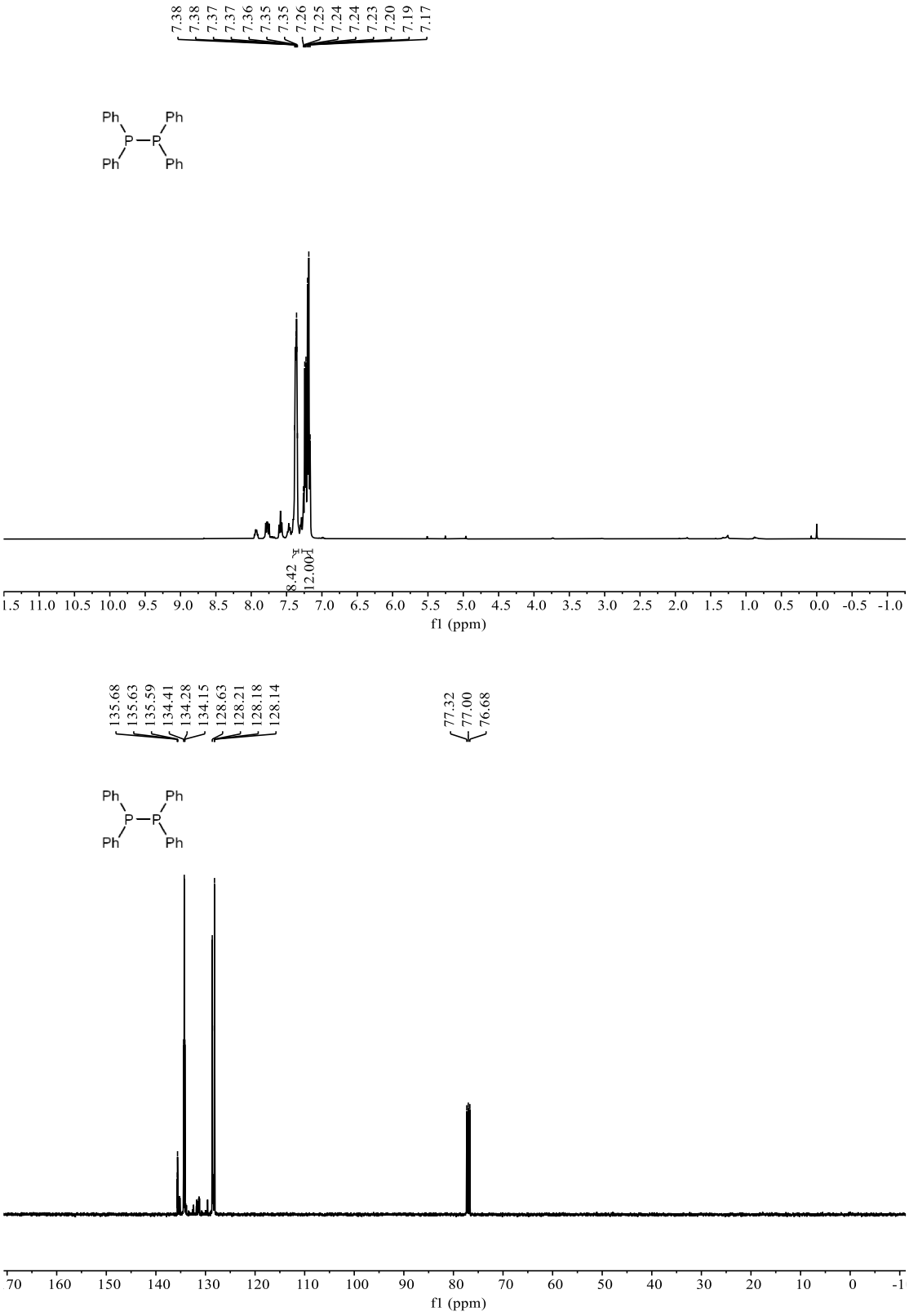
O-(3-((diphenylphosphorothioyl)thio)phenyl) diphenylphosphinothioate (**4ap'**)

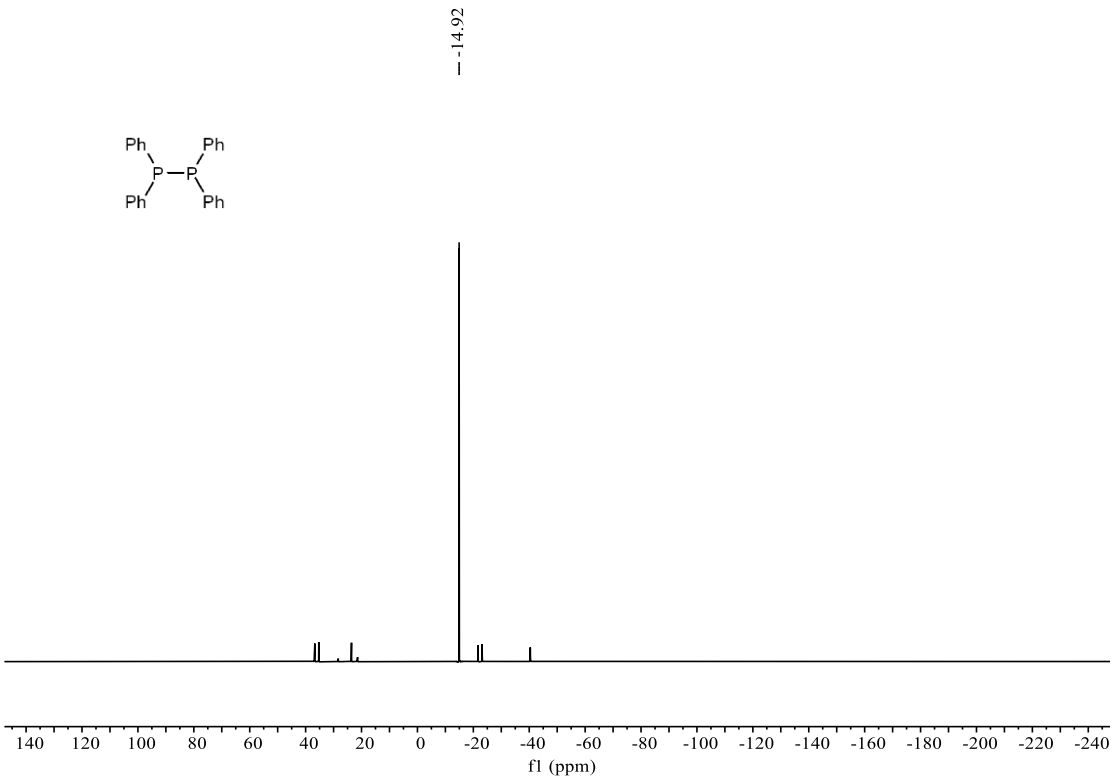



150.44
150.42
150.35
150.33
134.46
133.68
133.35
132.85
132.56
132.54
132.52
132.50
132.10
132.07
131.90
131.87
131.69
131.58
131.31
131.19
129.32
129.28
129.26
129.24
127.99
127.94
122.96
122.93
122.91
122.88
77.32
77.00
76.68
Ph
S
P
O
Ph
S
P
Ph
Ph
S
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


82.89
65.69
Ph
S
P
O
Ph
S
P
Ph
Ph
S
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

1,1,2,2-Tetraphenyldiphosphane (**2a'**)




-14.92
Ph
Ph
P
P
Ph
Ph
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)