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Graphical Abstract

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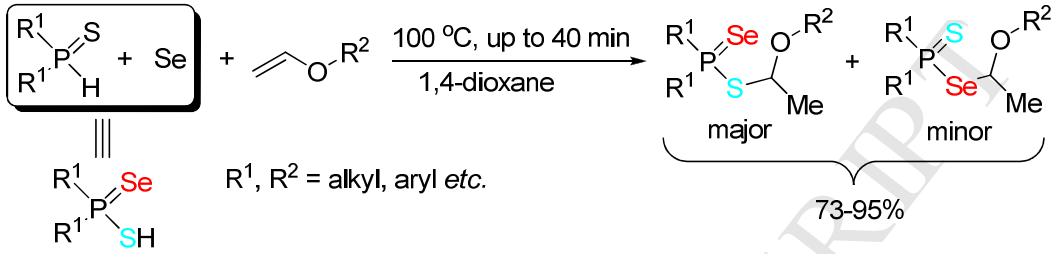

Three-component reaction between secondary phosphine sulfides, elemental selenium and vinyl ethers: the first examples of Markovnikov addition of thioselenophosphinic acids to double bond

Ludmila A. Oparina,[a] Alexander V. Artem'ev,[a] Oksana V. Vysotskaya,[a] Nikita A. Kolyvanov,[a] Irina Yu. Bagryanskaya,[b] Evgeniya P. Doronina[a] and Nina K. Gusarova[a*]

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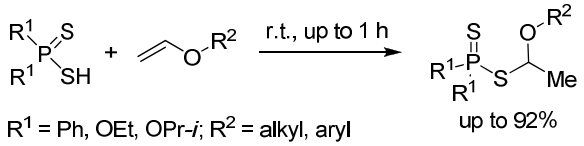
Abstract. Thioselenophosphinic acids, $R_2P(Se)SH$, generated *in situ* from secondary phosphine sulfides and elemental selenium, easily add to various vinyl ethers (equimolar ratio, 100 °C, 1,4-dioxane, up to 40 min) to give earlier unknown *S*- and *Se*-[1-(organyloxy)ethyl]thioselenophosphinates, i.e. $R_2P(Se)SCH(Me)OR'$ and $R_2P(S)SeCH(Me)OR'$ (R, R′ = alkyl, aralkyl, hetaralkyl and aryl), the *S*-esters being predominant (73-95% total yield).

Keywords: vinyl ethers, secondary phosphine sulfides, selenium, thioselenophosphinic acids

1. Introduction

Currently, vinyl ethers attract increasing attention of researchers as monomers for the preparation of functional polymer materials,[1] precursors for design of pharmaceuticals[2] and convenient building blocks for the synthesis of, in particular, hemilabile mono-[3] and diphosphine ligands.[4] The vinyl ethers as substrates can participate in many reactions such as cycloadditions,[5] metathesis,[6] Claisen rearrangement,[7] metallation,[8] addition of diverse X-H-acids (X = O, N, S, *etc.*)[9] and Heck-type arylation.[10] One of the most powerful and atom-economic methods for functionalization of vinyl ethers is electrophilic addition of OH-compounds, for example, various acids to the vinyloxy group.[11] This reaction usually proceeds under the mild conditions and creates real prerequisites for direct and controlled modification of vinyl ethers by diverse functional moieties. For instance, the electrophilic addition of carboxylic acids[12] and their thio-analogs[13] to vinyl ethers is shown to provide a direct, efficient and facile short-cut to acetals including functional and optically active ones.

However, little is known about the addition of organophosphorus acids and its thio- or selenoanalogs to vinyl ethers. Phosphinic acids, $R_2P(O)OH$, do not add to the vinyloxy group, nevertheless, dithiophosphinic and -phosphoric acids easily react with vinyl ethers (room temperature, without catalyst and solvent) to give regioselectively the corresponding Markovnikov-type adducts in quantitative yields[14] (Scheme 1).



R^1 = Ph, OEt, OPr-*i*; R^2 = alkyl, aryl

Scheme 1. Electrophilic addition of dithiophosphinic and -phosphoric acids to vinyl ethers.

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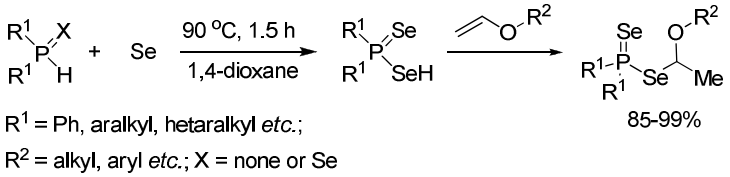
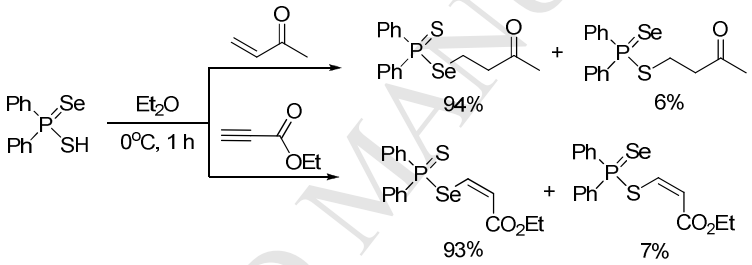
Recently,[15] it has been shown that diselenophosphinic acids, generated *in situ* from secondary phosphines (or their selenides) and elemental selenium (90 °C, 1,4-dioxane), add to a diverse array of vinyl ethers to afford previously unknown diselenophosphinic esters in high yields (Scheme 2).



Scheme 2. One-pot synthesis of *Se*-[1-(organyloxy)ethyl]diselenophosphinates.

At the same time, precedent for the addition of thioselenophosphinic acids, $R_2P(Se)SH$ or $R_2P(S)SeH$, to vinyl ethers is absent in the literature. It is pertinent to note that until recently only two examples of such acids, namely $Ph_2P(Se)SH$ and *t*-Bu(Ph)P(Se)SH, have been prepared (both by acidification of the corresponding salts with HCl).[16] Murai et al. have demonstrated that $Ph_2P(Se)SH$ acids add selectively to methyl vinyl ketone or ethyl propiolate in an anti-Markovnikov fashion to afford *Se*-esters with a small amount of the *S*-isomers (up to 7%), Scheme 3.[16]



Scheme 3. Nucleophilic addition of thioselenophosphinic acids to methyl vinyl ketone and ethyl propiolate.

In the present work we have implemented for first time the electrophilic addition of thioselenophosphinic acids to alkenes (on example of vinyl ethers). For this purpose, we have studied the reaction of secondary phosphine sulfides with selenium in the presence of vinyl ethers aiming at (i) the development of an atom-economic route to a thioselenophosphinic esters and (ii) the investigation of the competition between thioselenophosphinic *S*- and *Se*-esters formation.

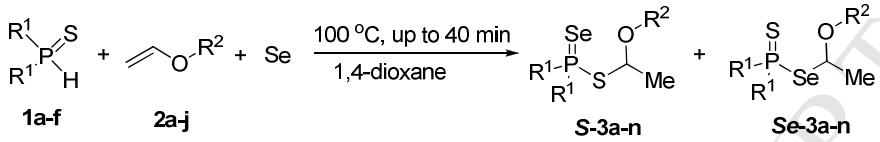
2. Results and Discussion

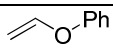
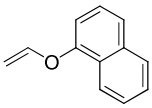
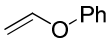
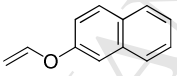
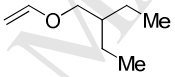
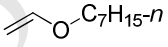
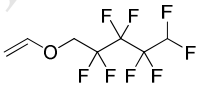
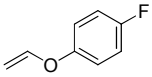
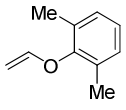
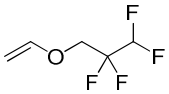
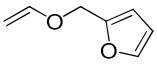
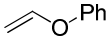
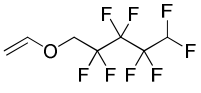
We have found that the thioselenophosphinic esters may be successfully synthesized *via* the three-component reaction between secondary phosphine sulfides, elemental selenium and vinyl ethers. Experiments have shown that the thioselenophosphinic acids, $R_2P(Se)SH$, generated *in situ* from secondary phosphine sulfides **1a-f** and elemental selenium, easily add to various vinyl ethers **2a-j** in a Markovnikov fashion (1,4-dioxane, 100 °C, up to 40 min) to give a mixture of thioselenophosphinic *S*-

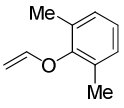
and *Se*-esters **3a-n** in high yield (^{31}P NMR data). The isolated yields of the products **3a-n** and ratio of *S*- and *Se*-esters in the reaction mixtures are presented in Table 1.

Table 1

One-pot synthesis of thioselenophosphinic *S*- and *Se*-esters **3a-n**



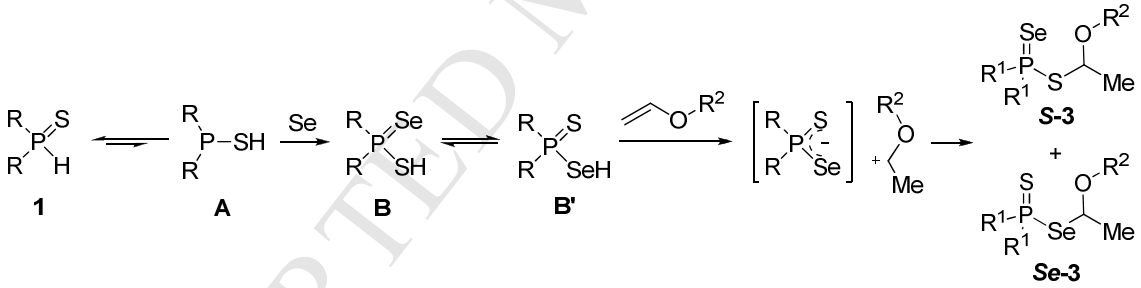
Entry	Phosphine sulfide	R^1	Vinyl ether	Product	Molar ratio of *S*-/*Se*-ester[a]	Overall yield[b] (%)
1	**1a**	Cy	 **(2a)**	**3a**	58:42	93
2	**1a**	Cy	 **(2b)**	**3b**	50:50	93
3	**1b**	$(CH_2)_2Ph$	 **(2a)**	**3c**	70:30	90
4	**1b**	$(CH_2)_2Ph$	 **(2c)**	**3d**	63:37	95
5	**1c**	$(CH_2)_2(4\text{-}MeOC_6H_4)$	 **(2d)**	**3e**	75:25	73
6	**1c**	$(CH_2)_2(4\text{-}MeOC_6H_4)$	 **(2e)**	**3f**	72:28	90
7	**1c**	$(CH_2)_2(4\text{-}MeOC_6H_4)$	 **(2f)**	**3g**	62:38	93
8	**1c**	$(CH_2)_2(4\text{-}MeOC_6H_4)$	 **(2g)**	**3h**	61:39	91
9	**1c**	$(CH_2)_2(4\text{-}MeOC_6H_4)$	 **(2h)**	**3i**	53:47	80
10	**1d**	$(CH_2)_2(4\text{-}ClC_6H_4)$	 **(2i)**	**3j**	69:31	81
11	**1d**	$(CH_2)_2(4\text{-}ClC_6H_4)$	 **(2j)**	**3k**	80:20	82
12	**1e**	$(CH_2)_2(2\text{-Furyl})$	 **(2a)**	**3l**	73:27	93
13	**1f**	Ph	 **(2f)**	**3m**	64:36	90

14	**1f**	Ph	 (**2h**)	**3n**	69:31	83

[a]Determined by ^{1}H and ^{31}P NMR.
[b]Isolated yield.

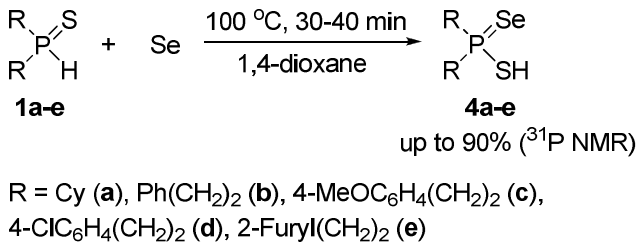
The results (Table 1) reveal that this reaction is applicable for a diverse range of aryl- and alkyl vinyl ethers as well as a secondary phosphine sulfides bearing alkyl, aralkyl, hetaralkyl and aryl groups. Indeed, a variety of substituents (Me, Ph, naphth, F, Cl and OMe), including acid-sensitive groups (2-furyl), tolerates to reaction conditions.

Apparently, the mechanism of thioselenophosphinates **3a-n** formation in the present three-component reaction involves oxidation of the corresponding trivalent tautomeric form **A** of secondary phosphine sulfides **1** by elemental selenium. The resulting thioselenophosphinic *S*-acid **B** (or its tautomeric form **B'**) adds to electron-rich double bond of vinyl ether to give the *S*- and *Se*-esters **3** (Scheme 4). Certainly, this type of addition is electrophilic in nature and proceeds regioselectively in agreement with the Markovnikov's rule that allows thioselenophosphinates **3** with the XCH(OR^2)Me (X = S or Se) structural unit to be prepared. Therefore, the equimolar mixture of secondary phosphine sulfide with elemental selenium in this three-component reaction acts as synthetic equivalent of the thioselenophosphinic acids.



Scheme 4. Proposed mechanism for the three-component reaction between secondary phosphine sulfides, vinyl ethers and selenium.

The mechanism proposed is in compliance with our recent finding[18] that secondary phosphine sulfides **1a-e** react with elemental selenium in equimolar ratio (100 ^{o}C, 30-40 min) to give selectively thioselenophosphinic *S*-acids **4a-e** in a yield of up to 90% (Scheme 5). Notably, in solution these acids exist solely as SH-tautomers (NMR data).[17]

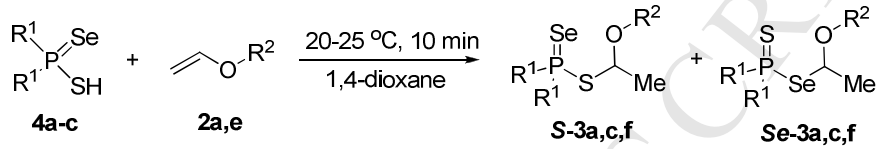


Scheme 5. Synthesis of thioselenophosphinic *S*-acids **4a-e**.

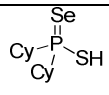
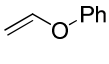
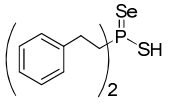
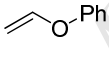
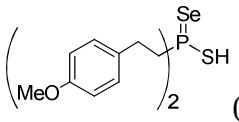
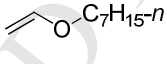
The thioselenophosphinic *S*-acids **4a-c**, prepared in this way (Scheme 5), readily react with vinyl ethers **2a, e** under exceptionally mild conditions (20-25 °C, 1,4-dioxane, 10 min) to give *S*- and *Se*-adducts **3a, c, f** (with a predominance of *S*-esters) in high yields (Table 2). Analysis of the crude reaction mixtures by ^{1}H and ^{31}P NMR spectroscopy indicates nearly the same ratio of the *S*- and *Se*-esters **3a, c, f** as in the three-component reaction (Table 1).

Table 2

Electrophilic addition of thioselenophosphinic *S*-acids **4a-c** to vinyl ethers **2a, e**



4a-c **2a,e** ***S*-3a,c,f** ***Se*-3a,c,f**

Entry	Acid	Ether	Product	Molar ratio of *S*-/*Se*-esters[a]	Overall yield[b] (%)
1	 (**4a**)	 (**2a**)	**3a**	57:43	84
2	 (**4b**)	 (**2a**)	**3c**	70:30	81
3	 (**4c**)	 (**2e**)	**3f**	79:21	79

[a]Determined by ^{31}P NMR.
[b]Isolated yield.

It is noteworthy that the employment of a one-pot protocol (Table 1) significantly facilitates the preparation of thioselenophosphinic esters because it allows avoiding handling thioselenophosphinic acids **4a-e**, which are air-sensitive and unstable compounds.[16,17]

With regard to the ratio of *S*- and *Se*-isomer, in almost all the cases (Tables 1 and 2) the major isomer is *S*-ester. The only exception is the addition of di(cyclohexyl)thioselenophosphinic acid (**4a**), generated from $Cy_2P(S)H$ (**1a**) and selenium, to (1-naphthyl)vinyl ether (**2b**), which results in the formation of equimolar amounts of both isomeric esters **3b** (Table 1, entry 2).

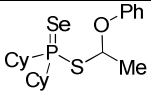
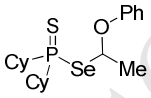
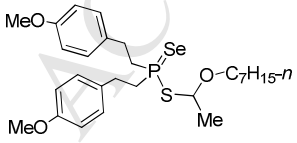
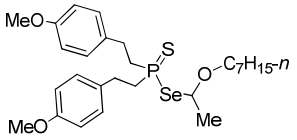
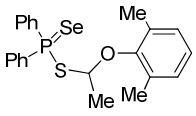
For a rational explanation of the observed outcome we have analyzed the local philicity indexes[18] (ω_k^{α}) of model intermediates, i.e. $[Cy_2PSeS]^-$ anion and $Me(PhO)HC^+$ cation, formed *via* the proton transfer from acid Cy_2PSeSH to phenyl vinyl ether (according to the electrophilic character of the addition). The geometries of these ions have been optimized by the B3LYP/6-311++G(d,p) method for 1,4-dioxane solution (C-PCM).[19] The calculated [HF/6-31G(d)] NBO[20] values of the local nucleophilicity indexes, ω_k^- (Equation S1 in Supporting Materials), for sulfur (ω_S^- = 0.180) and

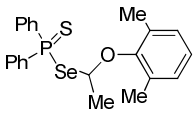
selenium (ω_{Se}^{-} = 0.053) atoms of $[Cy_2PSeS]^{-}$ as well as local electrophilicity index, ω_k^{+}, for cationic carbon (ω_C^{+} = 1.773) in $Me(PhO)HC^{+}$ unambiguously (ω_C^{+} - ω_S^{-} < ω_C^{+} - ω_{Se}^{-}) indicate that this carbocation predominantly will be attacked by the S atom of *S*,*Se*-ambident $[Cy_2PSeS]^{-}$ anion. Moreover, the Gibbs free energy calculations [MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p)] of two model isomers, i.e. $Cy_2P(Se)SCH(Me)OPh$ and $Cy_2P(S)SeCH(Me)OPh$, have confirmed that the *S*-ester is more stable than the *Se*-isomer by 1.28 kcal/mol. Interestingly, the alkylation of the ambident $[R_2PSeS]^{-}$ thioselenophosphinate anions (in form of alkali metal salts) by diverse organic halides takes place exclusively at the Se atom to afford corresponding *Se*-esters in high yields.[16,21]

The structures of isomeric *S*- and *Se*-esters **3a-n** have been unambiguously established by the ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR techniques as well as by X-ray diffraction analysis. Some characteristic NMR properties of the selected esters (**3a, f, n**) are summarized in Table 3. In the ^{31}P NMR spectra of *S*-esters, the resonance of phosphorus atoms is observed as a sharp singlet at 52.68-85.93 ppm flanked by single set of ^{77}Se satellites with $^{1}J_{PSe}$ = 756-789 Hz indicating the presence of the P=Se double bond. The ^{77}Se NMR spectra of the *S*-esters comprise of a downfield doublet at (–367)-(–196) ppm ($^{1}J_{PSe}$ = 756-789 Hz). The ^{31}P NMR spectra of *Se*-esters show a sharp singlet at 50.89-85.90 ppm flanked by one set of ^{77}Se satellites ($^{1}J_{PSe}$ = 347-362 Hz), while the ^{77}Se NMR spectra contain a doublet at 230-397 ppm with characteristic one-bond ^{31}P-^{77}Se coupling of 347-362 Hz.

Table 3

The selected NMR data of *S*- and *Se*-esters **3a, f, n**

Compound		δ, ppm		$^{1}J_{PSe}$, Hz	δ(**Me**CH), ppm		δ(O**CH**Ch), ppm	
		^{31}P NMR	^{77}Se NMR		^{1}H NMR[a]	^{13}C NMR[b]	^{1}H NMR[c]	^{13}C NMR[d]
3a		84.62	–367	762	1.86	25.2	5.86	86.9
		85.91	230	352	2.06	26.8	5.94	85.2
3f		60.38	–266	762	1.75	25.3	5.34	89.9
		61.14	319	362	1.93	26.9	5.54	91.5
3n		52.68	–206	789	1.98	25.1	5.79	89.2

	51.09	397	369	2.13	25.8	6.01	88.6

[a] A doublet with $^3J_{HH}$ = 6.0-6.2 Hz.
[b] A doublet with $^3J_{CP}$ = 2.4-4.8 Hz.
[c] A multiplet.
[d] A singlet.

The molecular structures of *S*- and *Se*-esters **3b**, which form co-crystals (1:1), have been determined by single-crystal X-ray diffraction analysis (Figure 1).[22] It appears that the sulfur and selenium atoms of the co-crystallized esters **3b** are disordered over the two positions with Se1/S2:Se2/S1 occupancy ratio of 0.580:0.420(2).

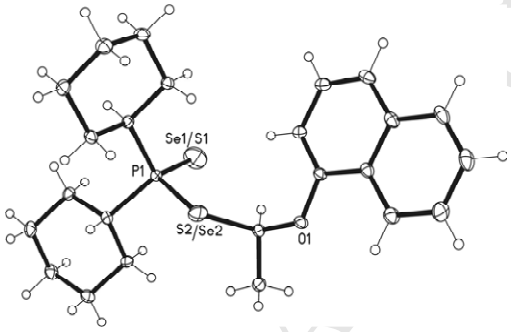
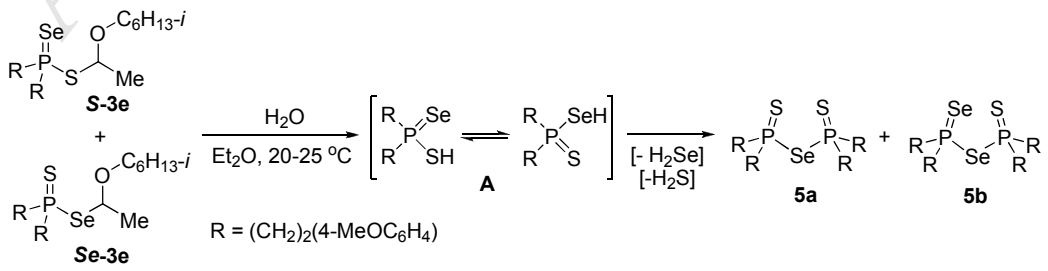


Figure 1. Perspective view of molecular structure of the esters ***S*-3b** and ***Se*-3b** in its co-crystal (30% thermal ellipsoid).

Esters **3a-n** are stable up to ~ 110 °C (at this temperature, the molar ratio of the isomeric *S*- and *Se*-esters does not change). We have found *S*- and *Se*-**3c** decompose upon heating up to 150 °C (*in vacuo*, 1 Torr) to give phenol and 1,1-bis(phenoxy)ethane as well as a complex mixture of organophosphorus compounds. Among the latter, selenoanhydrides, $(R_2P{=}S)_2Se$ and $(R_2P{=}S)Se(Se{=}PR_2)$, were detectable (^{31}P NMR).

Notably, the esters **3e-g, j, k, m** bearing aliphatic R^2 substituents are quite easily hydrolyzed. So, the storage of thioselenophosphinates ***S*-3e** and ***Se*-3e** solution (their ratio is *ca.* 75:25) in wet ether (20-25 °C, 1 week) yields co-crystals (1:1) of selenides **5a, b** (Scheme 6). Apparently, the formation of these selenides proceeds *via* hydrolysis of the esters **3e** followed by the intermolecular condensation of the generated SH- and/or SeH-acids **A**.



Scheme 6. Hydrolysis of thioselenophosphinates ***S*-3e** and ***Se*-3e**.

The molecular structures of the selenides **5a, b** are supported by X-ray diffraction analysis of their co-crystal (Figure 2).[23] The sulfur and selenium atoms in the co-crystal are disordered over two positions with Se1/S2:Se2/S1 occupancy ratio of 0.776:0.224(5). Also, the disordering one of the bridging CH_2 groups over the two positions is observed, the C30:C30A occupancy ratio being 0.65:0.35(1).

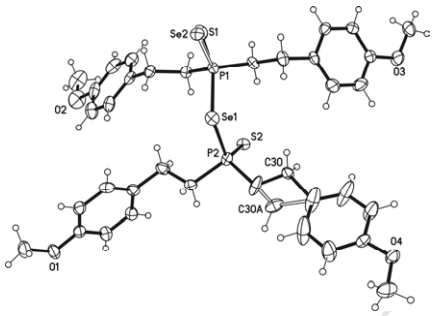


Figure 2. Perspective view of molecular structures of the selenides **5a, b** in its co-crystal (30% thermal ellipsoid).

Our numerous attempts to isolate the individual *S*- and *Se*-esters **3a-n** from their mixtures by chromatographic methods (such as column and TLC) were unsuccessful. According to experimental data, both *S*- and *Se*-esters **3a, d, g, n** have virtually identical R_f values without reference to polarity of the eluent used. Apparently, the similarity of physical proprieties of individual *S*- and *Se*-esters makes it impossible to separate these isomers.

3. Conclusion

In summary, we have disclosed for the first time that the electrophilic addition of thioselenophosphinic acids, readily generated from secondary phosphine sulfides and elemental selenium, to a diverse range of vinyl ethers. The reaction proceeds with the formation of Markovnikov adducts, i.e. *S*- and *Se*-esters of thioselenophosphinic acids, in high yields. In practically all examples, the major isomers were *S*-esters, the ratio of which depends on the structures of the initial vinyl ethers and thioselenophosphinic acids.

4. Experimental section

4.1. General

All reactions were performed under an atmosphere of dry argon. 1,4-Dioxane was dried and freshly distilled over sodium/benzophenone prior to use. Dicyclohexilphosphine sulfide (**1a**) and diphenylphosphine sulfide (**1f**) were prepared by oxidation of commercially available phosphines (Aldrich) with powdered sulfur (S_8) in an ethanol solution. Phosphine sulfides **1b-e** were prepared according to known procedure from red phosphorus, elemental sulfur and styrene, 4-methoxystyrene, 4-chlorostyrene or 2-vinylfuran.[24] Vinyl ethers **2a-j** were prepared according to a published method.[25] The ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectra were recorded in $CDCl_3$ solutions on a Bruker DPX 400 and

Bruker AV-400 spectrometers (400.13, 100.62, 161.98 and 76.31 MHz, respectively) Chemical shifts were reported in δ (ppm) relative to $CDCl_3$ (^1H, ^{13}C) as internal standard or H_3PO_4 (^{31}P) and Me_2Se (^{77}Se NMR) as external standard. Infrared (IR-FT) spectra were taken on a Bruker Vertex 70 spectrometer. The microanalyses were performed on a Flash EA 1112 Series elemental analyzer.

The crystallographic data were obtained on a Bruker Kappa Apex II CCD diffractometer using *φ,ω*-scans of narrow (0.5°) frames with MoK_α radiation (λ = 0.71073 Å) and a graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares method against all F^2 in anisotropic approximation using the *SHELX-97* programs set.[26] The hydrogen atoms positions were calculated with the riding model. Absorption correction was applied empirically using *SADABS* programs.[27]

CCDC 894978 (co-crystal of ***S*-3b** and ***Se*-3b**) and 901600 (co-crystal of **5a, b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

4.2. Synthesis

4.2.1. (1-Phenoxyethyl)dicyclohexylphosphinoselenothioate (***3a***). Dicyclohexylphosphine sulfide (**1a**; 230 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of phenyl vinyl ether (**2a**; 120 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 °C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 °C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3a** as yellowish powder (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 58:42). Yield: 399 mg (93%); IR (KBr) 3055, 2996, 2929, 2873, 2852, 1592, 1497, 1445, 1372, 1343, 1326, 1293, 1268, 1249, 1223, 1178, 1112, 1091, 1073, 1046, 1029, 1014, 1002, 930, 895, 885, 850, 819, 794, 753, 691, 644, 630, 602, 566, 541, 514, 466, 457, 438, 406 cm^{-1}. Anal. Calcd for $C_{20}H_{31}OPSSe$ (429.46): C, 55.93; H, 7.28; P, 7.21; S, 4.47; Se, 18.39. Found: C, 56.01; H, 7.45; P, 7.28; S, 4.87; Se, 17.98; (***S*-3a**): ^1H NMR (400.13 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2 H, PhO), 7.10-7.00 (m, 3 H, PhO), 5.86 (m, 1 H, CHS), 2.03-1.96 (m, 2 H, Cy), 1.96-1.86 (m, 2 H, Cy), 1.86 (d, $^3J_{HH}$=6.0 Hz, 3 H, *Me*CH), 1.82-1.69 (m, 4 H, Cy), 1.67-1.58 (m, 2 H, Cy), 1.58-1.42 (m, 2 H, Cy), 1.31-1.14 (m, 10 H, Cy); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 156.0 (C^1 in PhO), 129.2 ($C^{3,5}$ in PhO), 122.5 ($C^{2,6}$ in PhO), 118.3 (C^4 in PhO), 86.9 (CHS), 42.1 (d, $^1J_{PC}$=39.2 Hz, CHP), 40.0 (d, $^1J_{PC}$=41.9 Hz, CHP), 26.3, 26.2, 26.1, 25.7, 25.6 (Cy), 25.2 (d, $^3J_{PC}$=4.8 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 84.62 (s, $^1J_{P=Se}$=762 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ **–**367 (d, $^1J_{P=Se}$=762 Hz); (***Se*-3a**): ^1H NMR (400.13 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2 H, PhO), 7.10-7.00 (m, 3 H, PhO), 5.94 (m, 1 H, CHSe), 2.06 (d, $^3J_{HH}$=6.0 Hz, 3 H, *Me*CH), 2.03-1.96 (m, 2 H, Cy), 1.96-1.86 (m, 2 H, Cy), 1.82-1.68 (m, 4 H, Cy),

1.67-1.58 (m, 2 H, Cy), 1.58-1.42 (m, 2 H, Cy), 1.31-1.14 (m, 10 H, Cy); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 156.0 (C^1 in PhO), 129.1 ($C^{3,5}$ in PhO), 122.4 ($C^{2,6}$ in PhO), 117.9 (C^4 in PhO), 85.2 (CHSe), 42.4 (d, $^1J_{PC}$=41.9 Hz, CHP), 26.8 (d, $^3J_{PC}$=2.6 Hz, *Me*CH), 26.3, 26.2, 26.1, 25.7, 25.6 (Cy); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 85.91 (s, $^1J_{P\text{-}Se}$=352 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 230 (d, $^1J_{P\text{-}Se}$=352 Hz).

*4.2.2. [1-(1-Naphthhyloxy)ethyl]dicyclohexylphosphinoselenothioate (**3b**).* Dicyclohexylphosphine sulfide (**1a**; 230 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of 1-naphthyl vinyl ether (**2b**; 170 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 ^{o}C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3b** as yellowish solid (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 50:50). Yield: 446 mg (93%); IR (KBr) 3010, 2954, 2930, 2850, 1596, 1576, 1507, 1461, 1448, 1394, 1376, 1344, 1301, 1292, 1267, 1240, 1178, 1157, 1099, 1047, 1017. 1002, 962, 926, 894, 884, 848, 818, 793, 775, 752, 734, 691, 642, 629, 571, 562, 541, 513, 505, 475, 465, 437, 419, 400 cm^{-1}. Anal. Calcd for $C_{24}H_{33}OPSSe$ (479.52): C, 60.11; H, 6.94; P, 6.69; S, 6.69; Se, 16.47. Found: C, 60.42; H, 6.60; P, 6.72; S, 6.78; Se, 16.21; (***S*-3b**): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 8.18 (m, 1 H, naphth), 7.77 (m, 1 H, naphth), 7.49-7.44 (m, 3 H, naphth), 7.38 (t, $^3J_{HH}$=7.9 Hz, 1 H, naphth), 7.29 (t, $^3J_{HH}$=7.9 Hz, 1 H, naphth), 6.08 (m, 1 H, CHS), 1.96 (d, $^3J_{HH}$=6.0 Hz, 3 H, *Me*CH), 1.91-1.82 (m, 4 H, Cy), 1.76-1.64 (m, 4 H, Cy), 1.63-1.58 (m, 2 H, Cy), 1.56-1.48 (m, 2 H, Cy), 1.28-1.17 (m, 6 H, Cy), 1.12-0.98 (m, 4 H, Cy); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 151.5, 134.5, 128.8, 126.1, 125.6, 125.3 (naphth), 122.2-121.8, 111.0 (m), 87.0 (CHS), 41.9 (d, $^1J_{PC}$=41.9 Hz, CHP), 41.0 (d, $^1J_{PC}$=41.6 Hz, CHP), 26.3, 26.2, 26.1 (Cy), 25.5 (d, $^3J_{PC}$=4.8 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 85.93 (s, $^1J_{P=Se}$=762 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ –366 (d, $^1J_{P=Se}$=762 Hz); (***Se*-3b**): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 8.18 (m, 1 H, naphth), 7.77 (m, 1 H, naphth), 7.49-7.44 (m, 3 H, naphth), 7.38 (t, $^3J_{HH}$=7.9 Hz, 1 H, naphth), 7.29 (t, $^3J_{HH}$=7.9 Hz, 1 H, naphth), 6.13 (m, 1 H, CHSe), 2.17 (d, $^3J_{HH}$=6.0 Hz, 3 H, *Me*CH), 1.91-1.82 (m, 4 H, Cy), 1.76-1.64 (m, 4 H, Cy), 1.63-1.58 (m, 2 H, Cy), 1.56-1.48 (m, 2 H, Cy), 1.28-1.17 (m, 6 H, Cy), 1.12-0.98 (m, 4 H, Cy); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 151.5, 134.5, 128.8, 126.1, 125.6, 125.3 (naphth), 122.2-121.8 (m), 110.7, 84.9 (CHSe), 42.8-40.7 (m, CHP), 26.3, 26.2, 26.1 (Cy), 25.2 (d, $^3J_{PC}$=2.8 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 86.81 (s, $^1J_{P\text{-}Se}$=352 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 241 (d, $^1J_{P\text{-}Se}$=352 Hz).

*4.2.3. 1-Phenoxyethyl diphenethylphosphinoselenothioate (**3c**).* Diphenethylphosphine sulfide (**1b**; 274 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a

solution of phenyl vinyl ether (**2a**; 120 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 ^{o}C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3c** as yellowish oil (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 70:30). Yield: 426 mg (90%); IR (KBr) 3104, 3085, 3062, 3027, 3001, 2973, 2926, 2859, 1597, 1591, 1496, 1442, 1396, 1376, 1333, 1291, 1220, 1173, 1155, 1128, 1112, 1089, 1071, 1028, 1013, 945, 928, 907, 797, 753, 696, 636, 614, 576, 550, 526, 494, 434, 415 cm^{-1}. Anal. Calcd for $C_{24}H_{27}OPSSe$ (473.47): C, 60.88; H, 5.75; P, 6.54; S, 6.77; Se, 16.68. Found: C, 60.71; H, 5.60; P, 6.72; S, 6.78; Se, 17.01; (***S-3c***):^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.20-7.08 (m, 12 H, Ph, PhO), 6.99-6.94 (m, 3 H, PhO), 5.96 (dq, 1 H, $^{3}J_{HH}$=6.1 Hz, $^{2}J_{PH}$=11.4 Hz, CHS), 3.04-2.83 (m, 4 H, CH_2Ph), 2.41-2.29 and 2.27-2.14 (m, 4 H, CH_2P), 1.86 (d, $^{3}J_{HH}$=6.2 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 155.6 (C^{1} in PhO), 139.8 (d, $^{3}J_{PC}$=16.8 Hz, *i*-C, Ph), 129.3 (C^{3,5} in PhO), 128.5, 128.4, 128.1, 128.0, 126.3, 126.2 (*o*-, *m*-, *p*-C, Ph), 122.8, 118.2 (C^{2,4,6} in PhO), 86.6 (CHS), 39.5 (d, $^{1}J_{PC}$=40.0 Hz, CH_2P), 38.6 (d, $^{1}J_{PC}$=43.1 Hz, CH_2P), 29.3, 29.2 (*C*H_2Ph), 24.5 (d, $^{3}J_{PC}$=4.8 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 63.45 (s, $^{1}J_{P=Se}$=766 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ –268 (d, $^{1}J_{P=Se}$=766 Hz); (***Se-3c***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.20-7.08 (m, 12 H, Ph, PhO), 6.99-6.94 (m, 3 H, PhO), 6.07 (dq, 1 H, $^{3}J_{HH}$=6.1 Hz, $^{2}J_{PH}$=8.8 Hz, CHSe), 3.04-2.83 (m, 4 H, CH_2Ph), 2.41-2.29 and 2.27-2.14 (m, 4 H, CH_2P), 2.07 (d, $^{3}J_{HH}$=6.1 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 155.8 (C^{1} in PhO), 139.9 (d, $^{3}J_{PC}$=16.8 Hz, *i*-C, Ph), 129.2 (C^{3,5} in PhO), 128.5, 128.4, 128.1, 128.0, 126.3, 126.2 (*o*-, *m*-, *p*-C, Ph), 122.8, 118.0 (C^{2,4,6} in PhO), 86.1 (CHSe), 40.2 (d, $^{1}J_{PC}$=41.2 Hz, CH_2P), 39.6 (d, $^{1}J_{PC}$ = 44.3 Hz, CH_2P), 29.2, 28.9 (*C*H_2Ph), 26.4 (d, $^{3}J_{PC}$=2.8 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 64.45 (s, $^{1}J_{P\text{-}Se}$=350 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 317 (d, $^{1}J_{P\text{-}Se}$=350 Hz).

*4.2.4. [1-(2-Naphthhyloxy)ethyl] diphenethylphosphinoselenothioate (**3d**).* Diphenethylphosphine sulfide (**1b**; 274 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of 2-naphthyl vinyl ether (**2c**; 170 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 ^{o}C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3d** as yellowish oil (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 63:37). Yield: 497 mg (95%); IR (KBr): 3084, 3060, 3026, 3001, 2955, 2925, 2853, 1629, 1600, 1510, 1496, 1466, 1454, 1442, 1389, 1377, 1357, 1333, 1288, 1254, 1211, 1180, 1121, 1180, 1121, 1109, 1082, 1029, 1007, 966, 946, 932, 887, 874, 850, 812, 748, 698, 638, 623, 613, 576, 551, 527, 494, 476, 434, 414 cm^{-1}. Anal. Calcd for $C_{28}H_{29}OPSSe$ (523.53): C, 64.24; H, 5.58; P, 5.92; S, 6.12; Se, 15.08. Found: C, 64.41; H, 5.49; P, 6.05; S, 5.93; Se, 15.38; (***S-3d***): ^{1}H NMR

(400.13 MHz, $CDCl_3$) δ 7.88-7.85 (m, 1 H, naphth), 7.81 (d, $^3J_{HH}$=8.7 Hz, 2 H, naphth), 7.70 (s, 1 H, naphth), 7.51-7.40 (m, 2 H, Ph), 7.34-7.22 (m, 6 H, Ph, naphth), 7.17-7.15 (m, 3 H, Ph), 6.81 (m, 2 H, naphth), 6.20 (dq, 1 H, $^3J_{HH}$=6.1 Hz, $^2J_{PH}$=11.9 Hz, CHS), 3.11-2.98 and 2.83-2.70 (m, 4 H, CH_2Ph), 2.50-2.44 and 2.31-2.26 (m, 4 H, CH_2P), 2.03 (d, $^3J_{HH}$=6.1 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 153.6 (C^2 in naphth), 140.1 (d, $^3J_{PC}$=16.9 Hz, *i*-C, Ph), 134.2, 130.0, 129.6 (naphth), 128.8, 128.5 (*o*-, *m*-C, Ph), 127.7, 127.3, 126.6 (naphth), 126.3 (*p*-C, Ph), 124.6, 119.8, 112.8 (naphth), 86.6 (CHS), 39.9 (d, $^1J_{PC}$=43.6 Hz, CH_2P), 38.1 (d, $^1J_{PC}$=43.1 Hz, CH_2P), 29.8, 29.5 (*C*H_2Ph), 25.0 (d, $^3J_{PC}$=4.8 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 62.45 (s, $^1J_{P=Se}$=766 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ –266 (d, $^1J_{P=Se}$=758 Hz); (***Se-3d***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.88-7.85 (m, 1 H, Naphth), 7.81 (d, $^3J_{HH}$=8.7 Hz, 2 H, naphth), 7.74 (s, 1 H, naphth), 7.51-7.40 (m, 2 H, Ph), 7.34-7.22 (m, 6 H, Ph, naphth), 7.17-7.15 (m, 3 H, Ph), 6.81 (m, 2 H, naphth), 6.30 (m, 1 H, CHSe), 3.11-2.98 and 2.83-2.70 (m, 4 H, CH_2Ph), 2.50-2.44 and 2.31-2.26 (m, 4 H, CH_2P), 2.25 (d, $^3J_{HH}$=6.1 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 153.7 (C^2 in naphth), 139.8 (d, $^3J_{PC}$=16.8 Hz, *i*-C, Ph), 134.2, 130.0, 129.5 (naphth), 128.5, 128.4 (*o*-, *m*-C, Ph), 127.7, 127.5, 126.6 (naphth), 126.3 (*p*-C, Ph), 124.6, 119.78, 112.6 (naphth), 85.8 (CHSe), 40.5 (d, $^1J_{PC}$=43.5 Hz, CH_2P), 39.9 (d, $^1J_{PC}$=43.5 Hz, CH_2P), 29.3, 29.2 (*C*H_2Ph), 26.8 (d, $^3J_{PC}$=2.6 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 63.52 (s, $^1J_{P\text{-}Se}$=356 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 319 (d, $^1J_{P\text{-}Se}$=356 Hz).

*4.2.5. [1-(2-Ethylbutoxy)ethyl] bis(4-methoxyphenethyl)phosphinoselenothioate (**3e**).* Bis(4-methoxyphenethyl)phosphine sulfide (**1c**; 334 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of 2-ethylbutyl vinyl ether (**2d**; 128 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 ^{o}C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3e** as yellowish oil (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 75:25). Yield: 395 mg (73%); IR (KBr) 3162, 3126, 3100, 3061, 3030, 2995, 2959, 2931, 2874, 2834, 1612, 1584, 1513,1464, 1441, 1397, 1374, 1301, 1265, 1247, 1178, 1119, 1103, 1036, 948, 874, 820, 796, 735, 636, 621, 611, 550, 518 cm^{-1}. Anal. Calcd for $C_{24}H_{35}OPSSe$ (541.59): C, 57.66; H, 7.26; P, 5.72; S, 5.92; Se, 14.58. Found: C, 57.78; H, 7.32; P, 5.84; S, 5.74; Se, 14.43; (***S-3e***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.10-7.08 and 6.83-6.80 (m, 8 H, in Ar), 5.30 (dq, $^3J_{HH}$=6.0 Hz, $^2J_{PH}$=11.0 Hz, 1 H, CHS), 3.77 (c, 6 H, OMe), 3.66-3.62 and 3.46-3.38 (m, each 1 H, OCH_2), 3.05-2.78 (m, 4 H, CH_2Ar), 2.56-2.31 (m, 4 H, CH_2P), 1.74 (d, $^3J_{HH}$=6.0 Hz, 3 H, *Me*CH), 1.47-1.39 (m, 1 H, CH), 1.38-1.27 (m, 4 H, CH_2), 0.86 (t, $^3J_{HH}$=7.0 Hz, 6 H, Me); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 158.3 (C^1 in Ar), 132.1 (d, $^3J_{PC}$=15.6 Hz, C^1 in Ar), 129.3, 114.2, ($C^{2,3,4,6}$ in Ar), 90.4 (CHS), 67.9 (OCH_2), 55.2 (OMe), 40.8 (CH), 40.8 (d, $^1J_{PC}$=36.0 Hz, CH_2P), 39.4 (d, $^1J_{PC}$ = 42.3 Hz, CH_2P), 28.2 (*C*H_2Ar), 25.2 (d, $^3J_{PC}$=4.4 Hz, *Me*CH), 23.3 (CH_2), 11.0 (Me);

^{31}P NMR (161.98 MHz, $CDCl_3$) δ 60.77 (s, $^1J_{P=Se}$=762 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ –262 (d, $^1J_{P=Se}$=763 Hz); (***Se-3e***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.10-7.08 and 6.83- 6.80 (m, 8 H, in Ar), 5.50 (dq, 1 H, $^3J_{HH}$=6.0 Hz, $^2J_{PH}$=8.6 Hz, CHSe), 3.77 (c, 6 H, OMe), 3.66-3.62 and 3.46-3.38 (m, each 1 H, OCH_2), 3.05-2.78 (m, 4 H, C*H*$_2$Ar), 2.56-2.31 (m, 4 H, CH_2P), 1.93 (d, $^3J_{HH}$=6.0 Hz, 3 H, *Me*CH), 1.47-1.39 (m, 1 H, CH), 1.38-1.27 (m, 4 H, CH_2), 0.87 (t, $^3J_{HH}$=6.9 Hz, 6 H, Me); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 158.21 (C^4 in Ar); 131.7 (d, $^3J_{PC}$=14.4 Hz, C^1 in Ar), 129.2, 114.0 (C^{2,3,4,6} in Ar), 91.4 (CHSe), 71.1 (OCH_2), 55.2 (OMe), 43.5 (d, $^1J_{PC}$=43.6 Hz, CH_2P), 41.0 (d, $^1J_{PC}$=39.5 Hz, CH_2P), 40.8 (CH), 28.7 (*C*H$_2$Ar), 26.6 (d, $^3J_{PC}$=2.4 Hz, *Me*CH), 26.1, 23.3 (CH_2), 11.0 (Me); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 61.56 (s, $^1J_{P\text{-}Se}$=362 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 316 (d, $^1J_{P\text{-}Se}$=362 Hz).

*4.2.6. [1-(Heptyloxy)ethyl] bis(4-methoxyphenethyl)phosphinoselenothioate (**3f**).* Bis(4-methoxyphenethyl)phosphine sulfide (**1c**; 334 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of heptyl vinyl ether (**2e**; 142 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 ^{o}C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3f** as yellowish oil (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 72:28). Yield: 501 mg (90%); IR (KBr) 3061, 3030, 2995, 2953, 2930, 2856, 2835, 1612, 1584, 1513, 1465, 1441, 1421, 1397, 1373, 1301, 1247, 1178, 1118, 1037, 947, 888, 872, 847, 820, 795, 734, 622, 550, 517, 460 cm^{-1}. Anal. Calcd for $C_{17}H_{41}O_3PSSe$ (555.61): C, 58.37; H, 7.44; P, 5.57; S, 5.77; Se, 14.21. Found: C, 58.18; H, 7.60; P, 5.72; S, 5.78; Se, 14.43; (***S-3f***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.11-7.08 and 6.83-6.81 (m, 8 H, in Ar), 5.34 (dq, $^3J_{HH}$=6.1 Hz, $^2J_{PH}$=11.1 Hz, 1 H, CHS), 3.78 (c, 6 H, OMe), 3.77-3.61 and 3.45-3.38 (m, 2 H, OCH_2), 3.01-2.81 (m, 4 H, C*H*$_2$Ar), 2.56-2.46 and 2.44-2.34 (m, 4 H, CH_2P), 1.75 (d, $^3J_{HH}$=6.2 Hz, 3 H, *Me*CH), 1.59-1.53 (m, 2 H, CH_2), 1.30-1.26 (m, 8 H, CH_2), 0.87 (t, $^3J_{HH}$=6.9 Hz, 3 H, Me); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 158.4 (C^1 in Ar), 132.2 (d, $^3J_{PC}$=16.8 Hz, C^1 in Ar), 129.3, 114.2 (C^{2,3,4,6} in Ar), 89.9 (CHS), 68.9 (OCH_2), 55.3 (OMe), 40.0 (d, $^1J_{PC}$=39.9 Hz, CH_2P), 39.4 (d, $^1J_{PC}$=41.9 Hz, CH_2P), 31.8, 29.5, 29.1 (CH_2), 28.8 (*C*H$_2$Ar), 25.3 (d, $^3J_{PC}$=4.1 Hz, *Me*CH), 22.63 (CH_2), 14.1 (Me); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 60.38 (s, $^1J_{P=Se}$=762 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ –266 (d, $^1J_{P=Se}$=762 Hz); (***Se-3f***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.11-7.08 and 6.83-6.81 (m, 8 H, in Ar), 5.54 (dq, $^3J_{HH}$=6.1 Hz, $^2J_{PH}$=8.7 Hz, 1 H, CHSe), 3.78 (c, 6 H, OMe), 3.77-3.61 and 3.45-3.38 (m, 2 H, OCH_2), 3.01-2.81 (m, 4 H, C*H*$_2$Ar), 2.56-2.46 and 2.44-2.34 (m, 4 H, CH_2P), 1.93 (d, $^3J_{HH}$=6.1 Hz, 3 H, *Me*CH), 1.59-1.53 (m, 2 H, CH_2), 1.30-1.26 (m, 8 H, CH_2), 0.87 (t, $^3J_{HH}$=6.9 Hz, 3 H, Me); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 158.4 (C^4 in Ar), 132.5 (d, $^3J_{PC}$=16.8 Hz, C^1 in Ar), 129.3, 114.2 (C^{2,3,4,6} in Ar), 91.5 (CHSe), 70.2 (OCH_2), 55.3 (OMe), 41.0 (d, $^1J_{PC}$=42.3 Hz, CH_2P), 40.5 (d, $^1J_{PC}$=42.3 Hz, CH_2P), 31.8, 29.5, 29.1, (CH_2), 28.5 (*C*H$_2$Ar), 26.9 (d, $^3J_{PC}$=2.4 Hz, *Me*CH), 26.1, 22.6

(CH_2), 14.1 (Me); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 61.14 (s, $^1J_{P\text{-}Se}$=362 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 319 (d, $^1J_{P\text{-}Se}$=362 Hz).

*4.2.7. 1-[(2,2,3,3,4,4,5,5-Octafluoropentyl)oxy]ethyl bis(4-methoxyphenethyl)phosphino-selenothioate (**3g**).* Bis(4-methoxyphenethyl)phosphine sulfide (**1c**; 334 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of 2,2,3,3,4,4,5,5-octafluoropentyl vinyl ether (**2f**; 258 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 ^{o}C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3g** as yellowish oil (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 62:38). Yield: 624 mg (93%); IR (KBr) 3061, 3031, 2997, 2954, 2935, 2913, 2861, 2837, 1612, 1584, 1513, 1466, 1443, 1420, 1400, 1378, 1301, 1248, 1178. 1131, 1036, 991, 955, 903, 874, 848, 819, 759, 736, 637, 611, 548, 519, 463 cm^{-1}. Anal. Calcd for $C_{25}H_{29}F_8O_3PSSe$ (671.48): C, 44.72; H, 4.35; F, 22.63; P, 4.61; S, 4.78; Se, 11.76. Found: C, 44.71; F, 22.64; H, 3.60; P, 4.78; S, 4.58; Se, 12.01; (***S*-3g**): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.13-7.09 and 6.86-6.83 (m, 8 H, in Ar), 6.05 (tt, $^2J_{HF}$=52.0 Hz, $^3J_{HF}$=5.7 Hz, CHF_2), 5.46 (dq, $^3J_{HH}$=6.2 Hz, $^2J_{PH}$=12.1 Hz, 1 H, CHS), 4.24-4.11 (m, 2 H, OCH_2), 3.80 (c, 6 H, OMe), 3.06-2.92 and 2.90-2.77 (m, 4 H, C*H*$_2$Ar), 2.55-2.35 (m, 4 H, CH_2P), 1.81 (d, $^3J_{HH}$=6.2 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 155.4 (C^1 in Ar), 132.1 (d, $^3J_{PC}$=16.0 Hz, C^4 in Ar), 129.3, 114.2 ($C^{2,3,5,6}$ in Ar), 113.5-110.1 [m, $(CF_2)_3$], 107.6 (tt, $^1J_{CF}$=254.0 Hz, $^2J_{CF}$=31.9 Hz, CHF_2), 89.9 (CHS), 64.9 (t, $^3J_{CF}$=26.3 Hz, OCH_2), 55.3 (OMe), 39.9 (d, $^1J_{PC}$=40.8 Hz, CH_2P), 39.3 (d, $^1J_{PC}$=42.8 Hz, CH_2P), 28.8 (*C*H_2Ar), 24.6 (d, $^3J_{PC}$=4.8 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 63.30 (s, $^1J_{P=Se}$=766 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ –259 (d, $^1J_{P=Se}$=761 Hz); (***Se*-3g**): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.13-7.09 and 6.86-6.83 (m, 8 H, in Ar), 6.05 (tt, $^2J_{HF}$=52.0 Hz, $^3J_{HF}$=5.7 Hz, CHF_2), 5.61 (dq, $^3J_{HH}$=6.3 Hz, $^2J_{PH}$=9.5 Hz, 1 H, CHSe), 4.24-4.11 (m, 2 H, OCH_2), 3.80 (c, 6 H, Me), 3.06-2.92 and 2.90-2.77 (m, 4 H, C*H*$_2$Ar), 2.55-2.35 (m, 4 H, CH_2P), 1.98 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 155.4 (C^1 in Ar), 131.8 (d, $^3J_{PC}$=14.7 Hz, C^4 in Ar), 129.3, 114.2 ($C^{2,3,5,6}$ in Ar), 113.5-110.1 [m, $(CF_2)_3$], 107.6 (tt, $^1J_{CF}$=254.0 Hz, $^2J_{CF}$=31.9 Hz, CHF_2), 89.4 (CHSe), 65.8 (t, $^3J_{CF}$=26.4 Hz, OCH_2), 55.3 (OMe), 41.2 (d, $^1J_{PC}$=43.5 Hz, CH_2P), 40.4 (d, $^1J_{PC}$=43.1 Hz, CH_2P), 28.4 (*C*H_2Ar), 26.0 (d, $^3J_{PC}$=2.6 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 63.69 (s, $^1J_{P\text{-}Se}$=343 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 321 (d, $^1J_{P\text{-}Se}$=347 Hz).

*4.2.8. [1-(4-Fluorophenoxy)ethyl] bis(4-methoxyphenethyl)phosphinoselenothioate (**3h**).* Bis(4-methoxyphenethyl)phosphine sulfide (**1c**; 334 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of 4-fluorophenyl vinyl ether (**2g**; 138 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100

^{o}C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3h** as yellowish oil (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 61:39). Yield: 502 mg (91%); IR (KBr) 3064, 3031, 2996, 2953, 2932, 2910, 2858, 2835, 1611, 1584, 1513, 1465, 1441, 1421, 1367, 1377, 1301, 1247, 1178. 1130, 1081, 1036, 1010, 933, 915, 873, 822, 747, 735, 635, 611, 551, 518, 461 cm^{-1}. Anal. Calcd for $C_{26}H_{30}FO_3PSSe$ (551.51): C, 56.62; H, 5.48; P, 5.62; S, 5,81; Se, 14.32; F, 3.44. Found: C, 56.71; H, 5.60; P, 5.94; S, 5.78; Se, 14.01; F, 3.44; (***S-3h***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.16-7.12 (m, 4 H, Ar), 7.04-6.98 (m, 4 H, in Ar), 6.88-6.82 (m, 4 H, C_6H_4F), 5.96 (dq, 1 H, $^{3}J_{HH}$=6.1 Hz, $^{2}J_{PH}$=12.4 Hz, CHS), 3.83 (s, 6 H, MeO), 3.05-2.87 and 2.83-2.64 (m, 4 H, C*H*$_2$Ar), 2.45-2.35 and 2.29-2.18 (m, 4 H, CH_2P), 1.92 (d, $^{3}J_{HH}$=6.1 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 158.7 (d, $^{1}J_{CF}$ = 241.7 Hz, C^4-F), 158.4 (C^4 in Ar), 151.9 (C^1 in C_6H_4F), 131.9 (d, $^{3}J_{PC}$=15.6 Hz, C^1 in Ar), 129.3 (C^{2,6} in Ar), 120.1 (d, $^{3}J_{CF}$=8.0 Hz, C^{2,6} in C_6H_4F), 116.0 (d, $^{2}J_{CF}$=23.2 Hz, C^{3,5} in C_6H_4F), 114.2 (C^{3,5} in Ar), 87.6 (CHS), 55.3 (OMe), 38.9 (d, $^{1}J_{PC}$=38.7 Hz, CH_2P), 38.1 (d, $^{1}J_{PC}$=42.3 Hz, CH_2P), 29.0, 28.6 (*C*H$_2$Ar), 24.7 (d, $^{3}J_{PC}$=4.8 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 62.52 (s, $^{1}J_{P=Se}$=765 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ –265 (d, $^{1}J_{P=Se}$=765 Hz); (***Se-3h***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.16-7.12 (m, 4 H, in Ar), 7.04-6.98 (m, 4 H, in Ar), 6.88-6.82 (m, 4 H, C_6H_4F), 6.06 (m, 1 H, CHSe), 3.82 (s, 6 H, MeO), 3.05-2.87 and 2.83-2.64 (m, 4 H, C*H*$_2$Ar), 2.45-2.35 and 2.29-2.18 (m, 4 H, CH_2P), 2.14 (d, $^{3}J_{HH}$=6.1 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 158.7 (d, $^{1}J_{CF}$ = 241.7 Hz, C^4-F), 158.3 (C^4 in Ar), 152.1 (C^1 in C_6H_4F), 132.2 (d, $^{3}J_{PC}$=14.8 Hz, C^1 in Ar), 129.2 (C^{2,6} in Ar), 119.7 (d, $^{3}J_{CF}$=8.0 Hz, C^{2,6} in C_6H_4F), 115.9 (d, $^{2}J_{CF}$=23.2 Hz, C^{3,5} in C_6H_4F), 114.1 (C^{3,5} in Ar), 87.1 (CHSe), 55.3 (OMe), 40.7 (d, $^{1}J_{PC}$=42.8 Hz, CH_2P), 40.0 (d, $^{1}J_{PC}$=43.5 Hz, CH_2P), 28.6, 28.3 (*C*H$_2$Ar), 26.6 (d, $^{3}J_{PC}$=2.4 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 63.49 (s, $^{1}J_{P\text{-}Se}$=349 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 317 (d, $^{1}J_{P\text{-}Se}$=349 Hz).

*4.2.9. [1-(2,6-Dimethylphenoxy)ethyl] bis(4-methoxyphenethyl)phosphinoselenothioate (**3i**).* Bis(4-methoxyphenethyl)phosphine sulfide (**1c**; 334 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of 2,6-dimethylphenyl vinyl ether (**2h**; 148 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 ^{o}C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3i** as colorless oil (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 53:47). Yield: 331 mg (80%); IR (KBr) 3125, 3100, 3061, 3029, 2995, 2953, 2929, 2858, 2834, 1612, 1584, 1513, 1465, 1441, 1397, 1375, 1318, 1301, 1247, 1193, 1178, 1131, 1079, 1036, 1009, 949, 917, 866, 847, 818, 772, 733, 696, 678, 637, 610, 572, 546, 517, 466 cm^{-1}. Anal. Calcd for $C_{28}H_{35}OPSSe$: Anal. Calcd for $C_{28}H_{35}O_3PSSe$

(413.37): C, 59.89; H, 6.28; P, 5.52; S, 5.71; Se, 14.06. Found: C, 60.01; H, 5.80; P, 5.50; S, 5.78; Se, 14.01; (***S-3i***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.16-7.00 and 6.91-6.85(m, each 4 H, in Ar), 6.80-6.75 (m, 3 H, C_6H_3O), 5.78 (dq, $^{3}J_{HH}$=6.2 Hz, $^{2}J_{PH}$=12.3 Hz, 1 H, CHS), 3.05-2.76 (m, 4 H, C*H*$_2$Ar), 2.47-2.28 and 2.27-2.14 (m, 4 H, CH_2P), 1.94 (d, $^{3}J_{HH}$=6.2 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 157.6 (C^4 in Ar), 152.7 (C^1 in C_6H_3O), 131.7 (d, $^{3}J_{PC}$=15.3 Hz, C^1 in Ar), 130.8 ($C^{2,6}$ in C_6H_3O), 128.6 ($C^{2,6}$ in Ar), 128.5 ($C^{3,5}$ in C_6H_3O), 124.2 (C^4 in C_6H_3O), 113.2 ($C^{3,5}$ in Ar), 90.4 (CHS), 54.6 (OMe), 40.2 (d, $^{1}J_{PC}$=41.8 Hz, CH_2P), 39.8 (d, $^{1}J_{PC}$=38.7 Hz, CH_2P), 28.0, 27.9 (*C*H$_2$Ar), 25.0 (d, $^{3}J_{PC}$=4.3 Hz, *Me*CH), 17.0 (Me); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 63.52 (s, $^{1}J_{P=Se}$=767 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ –266 (d, $^{1}J_{P=Se}$=767 Hz); (***Se-3i***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.16-7.00 and 6.91-6.85 (m, each 4 H, in Ar), 6.80-6.75 (m, 3 H, C_6H_3O), 6.00 (dq, $^{3}J_{HH}$=6.2 Hz, $^{2}J_{PH}$=9.5 Hz, 1 H, CHSe), 3.05-2.76 (m, 4 H, C*H*$_2$Ar), 2.47-2.28 and 2.27-2.14 (m, 4 H, CH_2P), 2.11 (d, $^{3}J_{HH}$=6.2 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 157.8 (C^4 in Ar), 152.3 (C^1 in C_6H_3O), 131.6 (d, $^{3}J_{PC}$=16.2 Hz, C^1 in Ar), 130.4 ($C^{2,6}$ in C_6H_3O), 128.6 ($C^{2,6}$ in Ar), 128.4 ($C^{3,5}$ in C_6H_3O), 124.1 (C^4 in C_6H_3O), 113.4 ($C^{3,5}$ in Ar), 89.8 (CHSe), 54.6 (OMe), 38.3 (d, $^{1}J_{PC}$=45.2 Hz, CH_2P), 36.8 (d, $^{1}J_{PC}$=43.3 Hz, CH_2P), 27.6, 27.5 (*C*H$_2$Ar), 25.8 (d, $^{3}J_{PC}$=3.4 Hz, *Me*CH), 16.9 (Me); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 63.34 (s, $^{1}J_{P\text{-}Se}$=351 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 325 (d, $^{1}J_{P\text{-}Se}$=351 Hz).

*4.2.10. 1-[(2,2,3,3-Tetrafluoropropyl)oxy]ethyl bis(4-chlorophenethyl)phosphinoselenothioate (**3j**).* Bis(4-chlorophenethyl)phosphine sulfide (**1d**; 343 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of 2,2,3,3-tetrafluoropropyl vinyl ether (**2i**; 158 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 ^{o}C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3j** as yellowish oil (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 69:31). Yield: 470 mg (81%); IR (KBr) 3099, 3084, 3062, 3041, 3026, 3008, 2985, 2926, 2904, 2891, 2850, 1492, 1435, 1407, 1395, 1352, 1276, 1255, 1237, 1205, 1183, 1131, 1117, 1045, 1014, 991, 972, 941, 904, 873, 836, 811, 771, 736, 705, 685, 653, 601, 549, 532, 509, 489, 464, 400 cm^{-1}. Anal. Calcd for $C_{21}H_{23}Cl_2F_4PSSe$ (580.31): C, 43.46; H, 3.99; Cl, 12.22; P, 5.34; S, 5.53; Se, 13.61. Found: C, 43.71; H, 3.65; Cl, 12.51; P, 5.70; S, 5.79; Se, 16.21; (***S-3j***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.23-7.19 and 7.11-7.04 (m, 8 H, in Ar), 5.83 (tt, $^{2}J_{HF}$=53.0 Hz, $^{3}J_{HF}$=4.6 Hz, 1 H, CHF_2), 5.37 (dq, $^{3}J_{HH}$=6.2 Hz, $^{2}J_{PH}$=9.8 Hz, 1 H, CHS), 4.02 and 3.93 (dt, $^{2}J_{HH}$=12.6 Hz, $^{3}J_{HF}$=12.4 Hz, 2 H, OCH_2), 3.04-2.88 and 2.84-2.73 (m, 4 H, C*H*$_2$Ar), 2.49-2.27 (m, 4 H, PCH_2), 1.72 (d, $^{3}J_{HH}$=6.2 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 138.1 (d, $^{3}J_{PC}$=16.8 Hz, C^1 in Ar), 132.5 (C^4 in Ar), 129.5, 128.5 ($C^{2,3,5,6}$ in Ar), 114.5 (m, CF_2), 109.0 (tt, $^{1}J_{CF}$=249.6 Hz, $^{2}J_{CF}$=34.1 Hz, CHF_2), 89.8 (CHS), 64.8 (t, $^{3}J_{CF}$=29.1 Hz, OCH_2), 39.2 (d, $^{1}J_{PC}$=41.8 Hz,

CH_2P), 39.0 (d, $^1J_{PC}$=42.2 Hz, CH_2P), 29.0 (d, $^2J_{PC}$=11.9 Hz, *C*H_2Ar), 24.1 (d, $^3J_{PC}$=5.0 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 62.72 (s, $^1J_{P=Se}$=769 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ –263 (d, $^1J_{P=Se}$ = 769 Hz); (***Se-3j***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.23-7.19 and 7.11-7.04 (m, 8 H, in Ar), 5.83 (tt, $^2J_{HF}$=53.0 Hz, $^3J_{HF}$=4.6 Hz, 1 H, CHF_2), 5.50 (dq, $^3J_{HH}$=6.2 Hz, $^2J_{PH}$=9.8 Hz, 1 H, CHSe), 4.02 and 3.93 (dt, $^2J_{HH}$=12.6 Hz, $^3J_{HF}$=12.4 Hz, 2 H, OCH_2), 3.04-2.88 and 2.84-2.73 (m, 4 H, C*H*$_2$Ar), 2.49-2.27 (m, 4 H, PCH_2), 1.90 (d, $^3J_{HH}$=6.2 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 138.3 (d, $^3J_{PC}$=16.5 Hz, C^1 in Ar), 132.46 (C^4 in Ar), 129.5, 128.5 (C^{2,3,5,6} in Ar), 114.5 (m, CF_2), 109.0 (tt, $^1J_{CF}$=249.6 Hz, $^2J_{CF}$=34.1 Hz, CHF_2), 89.8 (CHSe), 65.9 (t, $^3J_{CF}$=28.4 Hz, OCH_2), 40.5 (d, $^1J_{PC}$=44.9 Hz, CH_2P), 40.1 (d, $^1J_{PC}$=44.5 Hz, CH_2P), 28.6 (d, $^2J_{PC}$=13.0 Hz, *C*H_2Ar), 25.8 (d, $^3J_{PC}$=3.8 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 62.72 (s, $^1J_{P\text{-}Se}$=348 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 321 (d, $^1J_{P\text{-}Se}$=348 Hz).

*4.2.11. 1-(2-Furylmethoxy)ethyl bis(4-chlorophenethyl)phosphinoselenothioate (**3k**).* Bis(4-chlorophenethyl)phosphine sulfide (**1d**; 343 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of 2-furylmethyl vinyl ether (**2j**; 124 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 ^{o}C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3k** as yellowish oil (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 80:20). Yield: 448 mg (82%); IR (KBr) 3117, 3085, 3026, 2960, 2914, 2889, 2854, 1492, 1453, 1445, 1408, 1366, 1333, 1289, 1254, 1225, 1218, 1180, 1150, 1121, 1083, 1048, 1015, 949, 937, 914, 888, 874, 847, 807, 744, 706, 656, 613, 600, 514, 491, 449, 396 cm^{-1}. Anal. Calcd for $C_{23}H_{25}Cl_2O_2PSSe$ (546.35): C, 50.56; H, 4.61; Cl, 12.98; P, 5.67; S, 5.87; Se, 14.45. Found: C, 50.74; H, 4.90; P, 5.73; S, 5.71; Se, 13.99; (***S-3k***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.29 (br s, 1 H, CH^5 in Fur), 7.22-7.18 and 7.10-7.04 (m, 8 H, in Ar), 6.31 and 6.27 (each d, $^3J_{HH}$=3.0 Hz, 2 H, CH^{3,4} in Fur), 5.39 (dq, $^3J_{HH}$=6.2 Hz, $^2J_{PH}$=12.4 Hz, 1 H, CHS), 4.60 (dd, $^2J_{HH}$=12.5 Hz, $^3J_{PH}$=19.4 Hz, 2 H, OCH_2), 3.03-2.79 (m, 4 H, C*H*$_2$Ar), 2.57-2.28 (m, 4 H, CH_2P), 1.71 (d, $^3J_{HH}$=6.2 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 150.4 (C^2 in Fur), 142.9 (C^5 in Fur), 138.4 (d, $^3J_{PC}$=16.8 Hz, C^1 in Ar), 132.3 (C^4 in Ar), 129.6, 128.7 (C^{2,3,5,6} in Ar), 110.3, 109.9 (C^{3,4} in Fur), 88.4 (CHS), 62.3 (OCH_2), 39.3 (d, $^1J_{PC}$=41.0 Hz, CH_2P), 38.6 (d, $^1J_{PC}$=42.5 Hz, CH_2P), 29.2, 28.9 (*C*H_2Ar), 24.5 (d, $^3J_{PC}$=5.0 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 59.31 (s, $^1J_{P=Se}$=768 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ –264 (d, $^1J_{P=Se}$=766 Hz); (***Se-3k***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.32 (br s, 1 H, CH^5 in Fur), 7.22-7.18 and 7.10-7.04 (m, 8 H, Ar), 6.35 and 6.24 (each d, $^3J_{HH}$=3.0 Hz, 2 H, CH^{3,4} in Fur), 5.57 (dq, $^3J_{HH}$=6.2 Hz, $^2J_{PH}$=9.0 Hz, 1 H, CHSe), 4.50 (dd, $^2J_{HH}$=12.5 Hz, $^3J_{PH}$=12.5 Hz, 2 H, OCH_2), 3.03-2.79 (m, 4 H, C*H*$_2$Ar), 2.57-2.28 (m, 4 H, CH_2P), 1.90 (d, $^3J_{HH}$=6.2 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 150.4 (C^2 in Fur), 142.9 (C^5 in Fur),

138.4 (d, $^{3}J_{PC}$=16.8 Hz, C^{1} in Ar), 132.3 (C^{4} in Ar), 129.6, 128.7 ($C^{2,3,5,6}$ in Ar), 110.2, 110.0 ($C^{3,4}$ in Fur), 89.9 (CHSe), 63.4 (OCH_2), 40.4 (d, $^{1}J_{PC}$=44.5 Hz, CH_2P), 40.2 (d, $^{1}J_{PC}$=43.7 Hz, CH_2P), 28.8, 28.6 (CH_2Ar), 26.4 (d, $^{3}J_{PC}$=3.4 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 59.75 (s, $^{1}J_{P\text{-}Se}$=358 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 309 (d, $^{1}J_{P\text{-}Se}$ = 359 Hz).

*4.2.12. (1-Phenoxy)ethyl bis(2-furylethyl)phosphinoselenothioate (**3l**).* Bis[2-(2-furyl)ethyl]phosphine sulfide (**1e**; 254 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of phenyl vinyl ether (**2a**; 120 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 °C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 °C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3l** as yellowish oil (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 73:27). Yield: 421 mg (93%); IR (KBr) 3146, 3115, 3062, 3040, 2974, 2920, 2851, 1596, 1506, 1488, 1454, 1437, 1400, 1378, 1334, 1291, 1218, 1174, 1147, 1112, 1089, 1071, 1008, 951, 936, 916, 885, 851, 799, 754, 732, 692, 637, 612, 599, 528, 460 cm^{-1}. Anal. Calcd for $C_{20}H_{23}O_2PSSe$ (453.40): C, 52.98; H, 5.11; P, 6.83; S, 7.07; Se, 17.42. Found: C, 52.70; H, 5.03; P, 6.72; S, 6.78; Se, 17.11; (***S*-3l**): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.30-7.24 (m, 4 H, PhO, CH^{5} in Fur), 7.12-7.10 and 7.04-7.00 (m, 3 H, PhO), 6.27-6.23 (m, 2 H, CH^{4} in Fur), 6.10-6.01 (m, 1 H, CH^{3} in Fur), 5.98-5.89 (m, 2 H, CHS, CH^{3} in Fur), 3.09-2.68 (m, 4 H, CH_2Fur), 2.49-2.19 (m, 4 H, CH_2P), 1.87 (d, $^{3}J_{HH}$=6.1 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 155.84 (C^{1} in PhO), 153.16 (d, $^{3}J_{PC}$=18.4 Hz, C^{2} in Fur), 141.50, 141.37 (C^{5} in Fur), 129.50, 123.12, 118.48 (PhO), 110.97, 110.93, 105.97, 105.93 ($C^{3,4}$ in Fur), 86.94 (CHS), 36.43 (d, $^{1}J_{PC}$=42.0 Hz, CH_2P), 34.20 (d, $^{1}J_{PC}$=45.2 Hz, CH_2P), 24.65 (d, $^{3}J_{PC}$=4.6 Hz, *Me*CH), 22.66 (d, $^{2}J_{PC}$=30.8 Hz, CH_2Fur); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 61.55 (s, $^{1}J_{P=Se}$=762 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ –268 (d, $^{1}J_{P=Se}$=762 Hz); (***Se*-3l**): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.30-7.24 (m, 4 H, PhO, CH^{5} in Fur), 7.12-7.10 and 7.04-7.00 (m, 3 H, PhO), 6.27-6.23 (m, 2 H, CH^{4} in Fur), 6.10-6.01 (m, 1 H, CH^{3} in Fur), 5.98-5.89 (m, 2 H, CHSe, CH^{3} in Fur), 3.09-2.68 (m, 4 H, CH_2Fur), 2.49-2.19 (m, 4 H, CH_2P), 1.99 (d, $^{3}J_{HH}$=6.1 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 156.02 (C^{1} in PhO), 153.16 (d, $^{3}J_{PC}$=18.4 Hz, C^{2} in Fur), 141.50, 141.37 (C^{5} in Fur), 129.45, 123.18, 118.27 (PhO), 110.97, 110.93, 105.89, 105.83 ($C^{3,4}$ in Fur), 86.53 (CHSe), 39.86 (d, $^{1}J_{PC}$=45.5 Hz, CH_2P), 36.13 (d, $^{1}J_{PC}$=46.3 Hz, CH_2P), 26.60 (d, $^{3}J_{PC}$=2.6 Hz, *Me*CH), 21.17 (d, $^{2}J_{PC}$=23.0 Hz, CH_2Fur); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 61.85 (s, $^{1}J_{P=Se}$=352 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 323 (d, $^{1}J_{P=Se}$=352 Hz).

*4.2.13. 1-[(2,2,3,3-Tetrafluoropropyl)oxy]ethyl diphenylphosphinoselenothioate (**3m**).* Diphenylphosphine sulfide (**1f**; 218 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of 2,2,3,3,4,4,5,5-octafluoropentyl vinyl ether (**2f**; 258 mg, 1.0

mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 ^{o}C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3m** as yellowish oil (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 64:36). Yield: 499 mg (90%); IR (KBr) 3075, 3057, 2962, 2929, 2890, 2856, 1481, 1454, 1437, 1403, 1378, 1333, 1308, 1288, 1255, 1225, 1129, 1046, 1027, 998, 975, 958, 902, 890, 874, 809, 747, 716, 690, 648, 615, 561, 520, 482, 440 cm^{-1}. Anal. Calcd for $C_{19}H_{17}F_8OPSSe$ (555.33): C, 41.09; H, 3.09; F, 27.37; P, 5.58; S, 5.77; Se, 14.22. Found: C, 41.31; H, 2.60; P, 5.72; S, 5.78; Se, 14.10; (***S*-*3m***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 8.01-7.88 (m, 4 H, Ph), 7.54-7.46 (m, 6 H, Ph), 6.00 (tt, $^{3}J_{HH}$=5.6 Hz, $^{2}J_{HF}$=52.0 Hz, 1 H, CHF_2), 5.46 (dq, $^{3}J_{HH}$=6.2 Hz, $^{2}J_{PH}$=12.4 Hz, 1 H, CHS), 3.93 (t, $^{3}J_{HF}$=13.8 Hz, 2 H, CH_2O), 1.71 (d, $^{3}J_{HH}$=6.2 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 133.8 and 133.6 (d, $^{1}J_{PC}$=75.1 and 76.6 Hz, *i*-C, Ph), 132.1 (d, $^{4}J_{CP}$=3.0 Hz, *p*-C, Ph), 131.9 and 131.7 (d, $^{2}J_{CP}$=13.4 Hz, *o*-C, Ph), 128.6 (d, $^{3}J_{CP}$=13.4 Hz, *m*-C, Ph), 114.9 (tt, $^{1}J_{CF}$=255.7 Hz, $^{2}J_{CF}$=31.4 Hz, CF_2), 107.69 (tt, $^{1}J_{CF}$=254.0 Hz, $^{2}J_{CF}$=30.7 Hz, CHF_2), 89.4 (CHS), 65.4 (t, $^{2}J_{CF}$=25.7 Hz, CH_2O), 24.5 (d, $^{3}J_{PC}$=5.4 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 53.18 (s, $^{1}J_{P=S}$=784 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ −196 (d, $^{1}J_{P=Se}$=784 Hz); (***Se*-*3m***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 8.01-7.88 (m, 4 H, Ph), 7.54-7.46 (m, 6 H, Ph), 6.00 (tt, $^{3}J_{HH}$=5.6 Hz, $^{2}J_{HF}$=52.0 Hz, 1 H, CHF_2), 5.61 (dq, $^{3}J_{HH}$=6.2 Hz, $^{2}J_{PH}$=9.4 Hz, 1 H, CHSe), 3.93 (t, $^{3}J_{HF}$=13.8 Hz, 2 H, CH_2O), 1.88 (d, $^{3}J_{HH}$=6.2 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 135.2 and 135.0 (d, $^{1}J_{PC}$=78.2 and 79.0 Hz, *i*-C, Ph), 132.2 (d, $^{4}J_{CP}$=3.0 Hz, *p*-C, Ph), 131.4 and131.3 (d, $^{2}J_{CP}$=13.4 Hz, *o*-C, Ph), 128.6 (d, $^{3}J_{CP}$=13.4 Hz, *m*-C, Ph), 114.9 (tt, $^{1}J_{CF}$ =255.7 Hz, $^{2}J_{CF}$ =31.4 Hz, CF_2), 107.6 (tt, $^{1}J_{CF}$ =254.0 Hz, $^{2}J_{CF}$ =30.7 Hz, CHF_2), 89.3 (CHSe), 66.1 (t, $^{2}J_{CF}$=25.7 Hz, CH_2O), 25.5 (d, $^{3}J_{PC}$ =4.6 Hz, *Me*CH); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 50.89 (s, $^{1}J_{P\text{-}Se}$=359 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 408 (d, $^{1}J_{P\text{-}Se}$ 359 Hz).

*4.2.14. [1-(2,6-Dimethylphenoxy)ethyl] diphenylphosphinoselenothioate (**3n**)* Diphenylphosphine sulfide (**1f**; 218 mg, 1.0 mmol) and powdered grey selenium (79 mg, 1.0 mmol) were added consecutively to a solution of 2,6-dimethylphenyl vinyl ether (**2h**; 148 mg, 1.0 mmol) in 1,4-dioxane (5 mL) at ambient temperature (in argon atmosphere). The suspension was stirred at 100 ^{o}C until dissolution of selenium residue to give a light yellow transparent solution. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compound **3n** as colorless oil (isomeric mixture of the *S*- and *Se*-esters, the molar ratio being 69:31). Yield: 370 mg (83%); IR (KBr) 3144, 3055, 3020, 3044, 2956, 2922, 2887, 2854, 1588, 1574, 1478, 1436, 1375, 1333, 1308, 1287, 1262, 1190, 1161, 1120, 1093, 1027, 1009, 999, 918, 888, 874, 846, 815, 770, 746, 715, 689, 647, 615, 559, 519, 481, 438 cm^{-1}. Anal. Calcd for $C_{22}H_{23}OPSSe$ (445.42): C, 59.30; H, 5.02; P, 6.95; S, 7.20; Se, 17.73. Found: C,

59.62; H, 5.02; P, 6.52; S, 7.78; Se, 17.54; (***S-3n***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.73 (dd, $^{3}J_{PH}$=14.4 Hz, $^{3}J_{HH}$=7.5 Hz, 2 H, Ph), 7.51 (dd, $^{3}J_{PH}$=14.6 Hz, $^{3}J_{HH}$=7.5 Hz, 2 H, Ph), 7.46-7.34 (m, 4 H, Ph), 7.25-7.20 (m, 2 H, Ph), 6.83 (m, 3 H, OAr), 5.79 (dq, $^{2}J_{PH}$=12.0 Hz, $^{3}J_{HH}$=6.1 Hz, 1 H, CHS), 2.21 (s, 6 H, Me), 1.98 (d, $^{3}J_{HH}$=6.1 Hz, 3 H, *Me*CH);^{13}C NMR (100.62 MHz, $CDCl_3$) δ 152.1 (C^{1} in OAr), 132.7 (d, $^{1}J_{PC}$=79.0 Hz, *i*-C, Ph), 131.1 (*p*-C, Ph), 130.7 (d, $^{2}J_{CP}$=11.2 Hz, *o*-C, Ph), 128.3 ($C^{2,5}$ in OAr), 127.5 (d, $^{3}J_{CP}$=13.4 Hz, *m*-C, Ph), 123.8 (C^{4} in OAr), 89.2 (CHS), 25.1 (d, $^{3}J_{PC}$=3.4 Hz, *Me*CH), 16.8 (Me); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 52.68 (s, $^{1}J_{P=Se}$=789 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ –206 (d, $^{1}J_{P=Se}$=789 Hz); (***Se-3n***): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.73 (dd, $^{3}J_{PH}$=14.4 Hz, $^{3}J_{HH}$=7.5 Hz, 2 H, Ph), 7.51 (dd, $^{3}J_{PH}$=14.6 Hz, $^{3}J_{HH}$=7.5 Hz, 2 H, Ph), 7.46-7.34 (m, 4 H, Ph), 7.25-7.20 (m, 2 H, Ph), 6.83 (m, 3 H, OAr), 6.01 (m, 1 H, CHSe), 2.21 (s, 6 H, Me), 2.13 (d, $^{3}J_{HH}$=6.1 Hz, 3 H, *Me*CH); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 152.5 (C^{1} in OAr), 133.9 (d, $^{1}J_{PC}$=79.4 Hz, *i*-C, Ph), 131.2 (*p*-C, Ph), 130.7 (d, $^{2}J_{CP}$=11.5 Hz, *o*-C, Ph), 128.4 ($C^{2,5}$ in OAr), 127.8 (d, $^{3}J_{CP}$=13.4 Hz, *m*-C, Ph), 123.8 (C^{4} in OAr), 88.6 (CHSe), 25.8 (d, $^{3}J_{PC}$=2.4 Hz, *Me*CH), 16.8 (Me); ^{31}P NMR (161.98 MHz, $CDCl_3$) δ 51.09 (s, $^{1}J_{P\text{-}Se}$=369 Hz); ^{77}Se NMR (76.31 MHz, $CDCl_3$) δ 397 (d, $^{1}J_{P\text{-}Se}$=369 Hz).

*Electrophilic addition of thioselenophosphinic S-acid **4a-c** to vinyl ethers **2a, e** (Table 2).* A solution of secondary phosphine sulfide **1a-c** (1.0 mmol) in 1,4-dioxane (5 mL) and amorphous grey selenium (79 mg, 1.0 mmol) were placed into a vial filled with argon. The vial was sealed, and the suspension stirred at 100 ^{o}C until the dissolution of selenium residue (*ca.* 30-40 min). The ^{31}P NMR analysis of the resulting solution revealed the formation of thioselenophosphinic *S*-acid **4a-c** in yields up to 90%. To a prepared solution of acid **4a-c**, the corresponding vinyl ether **2a, e** (1.0 mmol) was added and mixture was stirred at ambient temperature for 10 min. The solvent was removed under reduced pressure (1 Torr, 40-45 ^{o}C), and the residue was purified by flash-chromatography (3 cm of neutral Al_2O_3; $CHCl_3$-hexane, 3:1) to give compounds **3a, c, f**.

*Co-crystals (1:1) of selenides **5a, b***. The thioselenophosphinates S-/Se-**3e** (271 mg, 0.5 mmol; ratio was *ca*. 75:25) were stored in wet diethyl ether (20-25 ^{o}C, 1 week). The solvent was distilled at lowered pressure. The remaining yellow residue was triturated with hexane, decanted and dried in *vacuo* (1 Torr) to give of selenides **5a, b** (97 mg) as a light yellow solid. The co-crystals (1:1) of the selenides were grown by the storage of their ether solution within a several days. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 71.03 and 71.14 (s, $^{1}J_{P\text{-}Se}$ = 360 Hz) in ratio of ~ 1:3.

Supplementary Material

Supplementary data (^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectra as well as computational details) associated with this article can be found in the online version, at … .

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22. Co-crystals of esters ***S*-3b** and ***Se*-3b**: $C_{24}H_{33}OPSSe$, M = 479.49, T = 150(2) K, monoclinic, space group $P2_1/c$, a = 13.9744(8) Å, b = 10.4250(5) Å and c = 15.9755(8) Å, β = 94.959(2), V = 2318.6(2) Å^3, Z = 4, d_{calc} = 1.374 g/cm^{-3}, μ(MoK$_\alpha$) = 1.791 mm^{-1}, $(\theta)_{max}$ = 60.22°, reflections collected 49847, independent reflections 6806 [R(int) = 0.0452], data/restraints/parameters: 6806/0/272, final R indexes [I>=2σ (I)]: R_1 = 0.0318, wR_2 = 0.0692, final R indexes [all data]: R_1 = 0.0471, wR_2 = 0.0763.

23. Co-crystals of selenides **5a** and **5b**: $C_{36}H_{42}O_4P_2S_{1.77}Se_{1.23}$, M = 754.27, T = 200(2) K, monoclinic, space group $P2_1/c$, a = 6.0832(3) Å, b = 31.8970(17) Å and c = 19.4135(11) Å, β = 96.163(2), V = 3745.1(3) Å^3, Z = 4, d_{calc} = 1.338 g/cm^{-3}, μ(MoK$_\alpha$) = 1.441 mm^{-1}, $(\theta)_{max}$ = 50.76°, reflections collected 62160, independent reflections 6744 [R(int) = 0.0923], data/restraints/parameters 6744/0/426, final R indexes [I>=2σ (I)]: R_1 = 0.0512, wR_2 = 0.1407, final R indexes [all data]: R_1 = 0.0890, wR_2 = 0.1672.
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Supporting Information

Three-component reaction between secondary phosphine sulfides, elemental selenium and vinyl ethers: the first examples of Markovnikov addition of thioselenophosphinic acids to double bond

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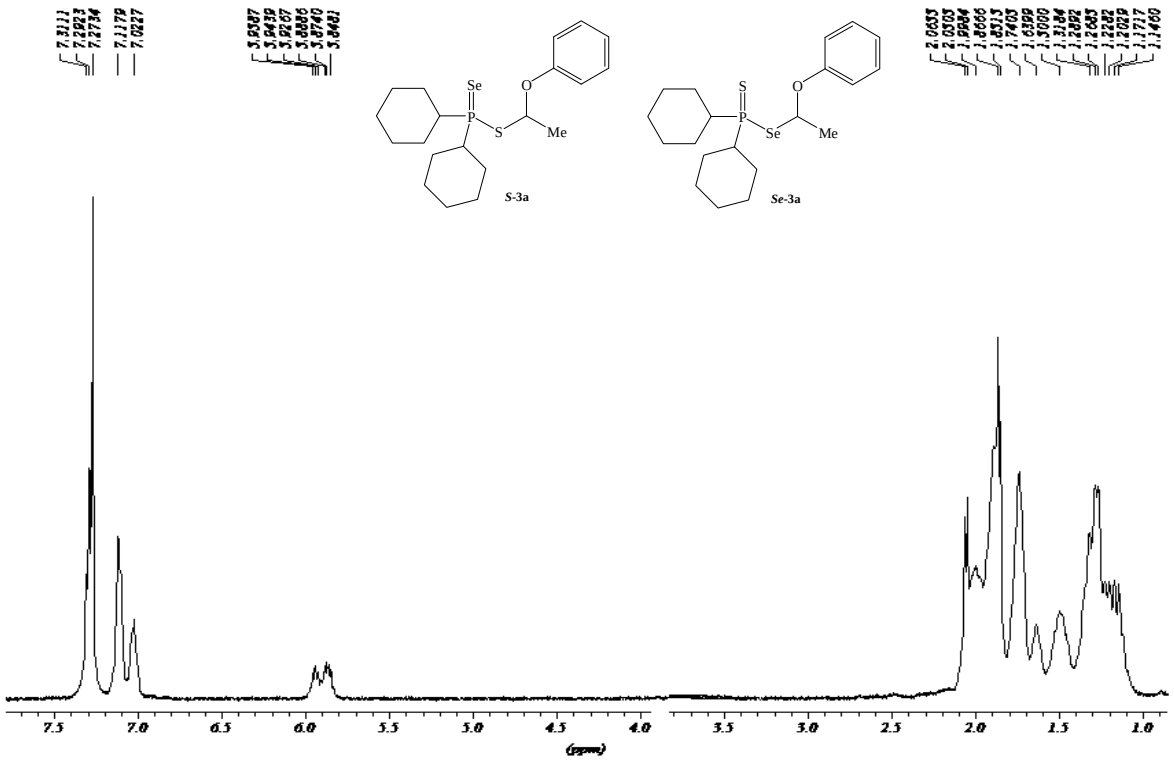
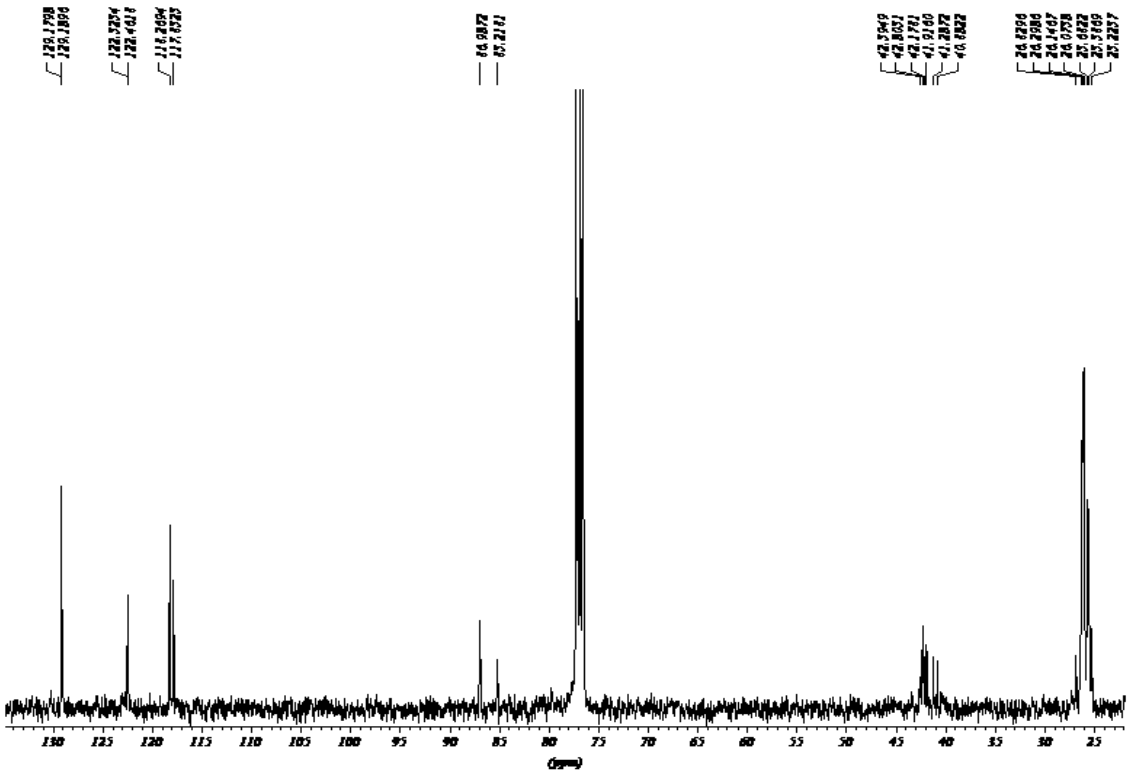
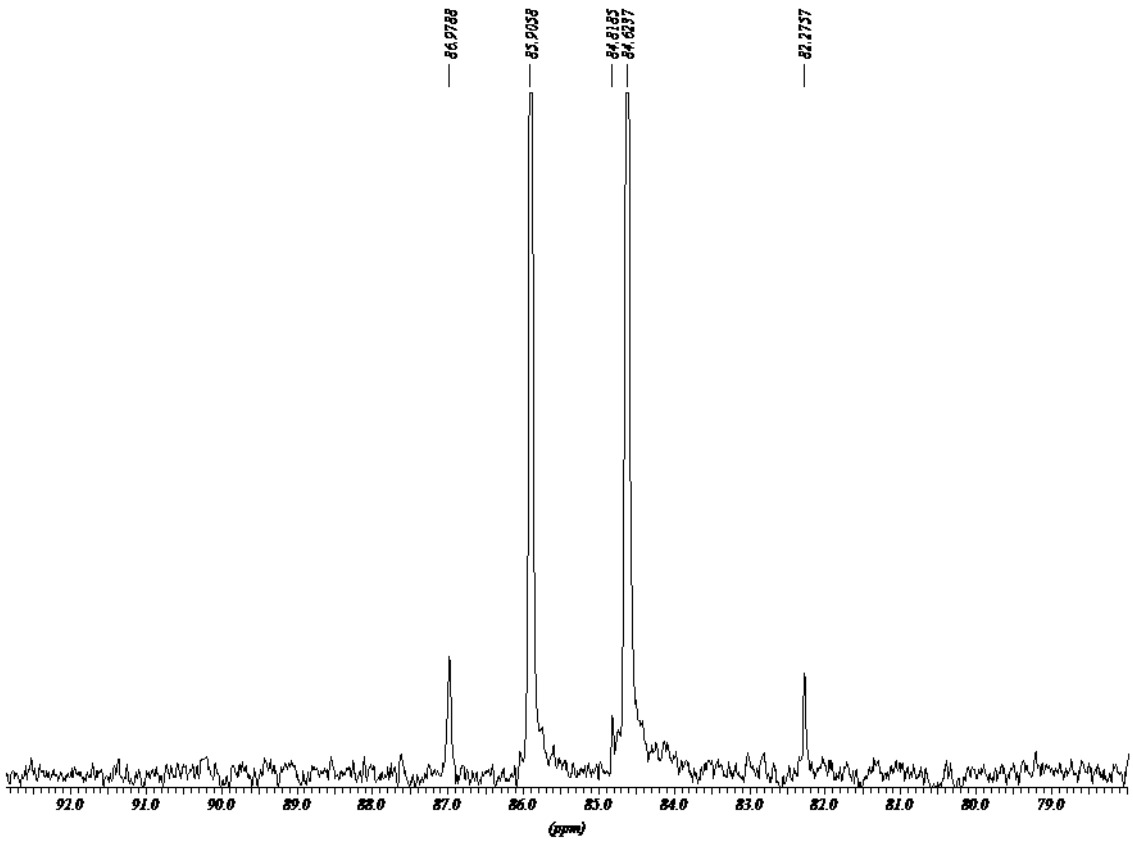
Table of Contents

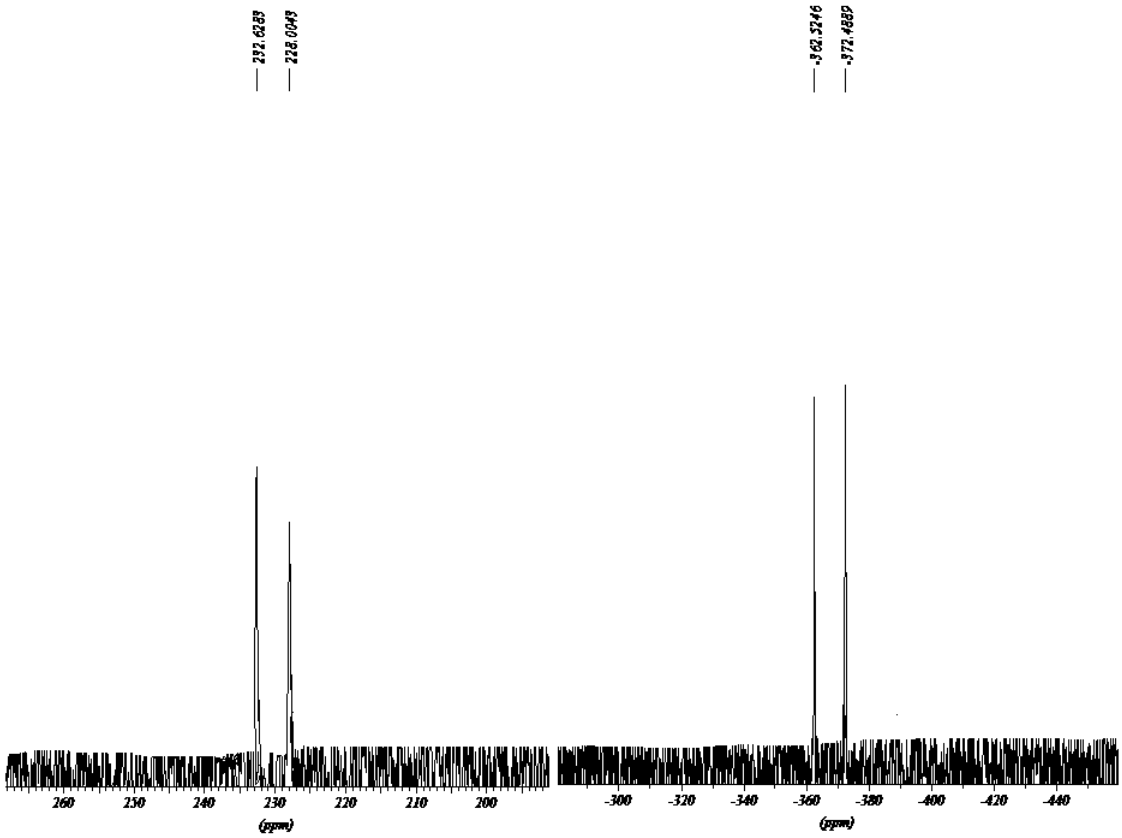
^{1}H, ^{13}C, ^{31}P and ^{77}Se spectra of the synthesized products

(1-Phenoxyethyl)dicyclohexylphosphinoselenothioate (3a)









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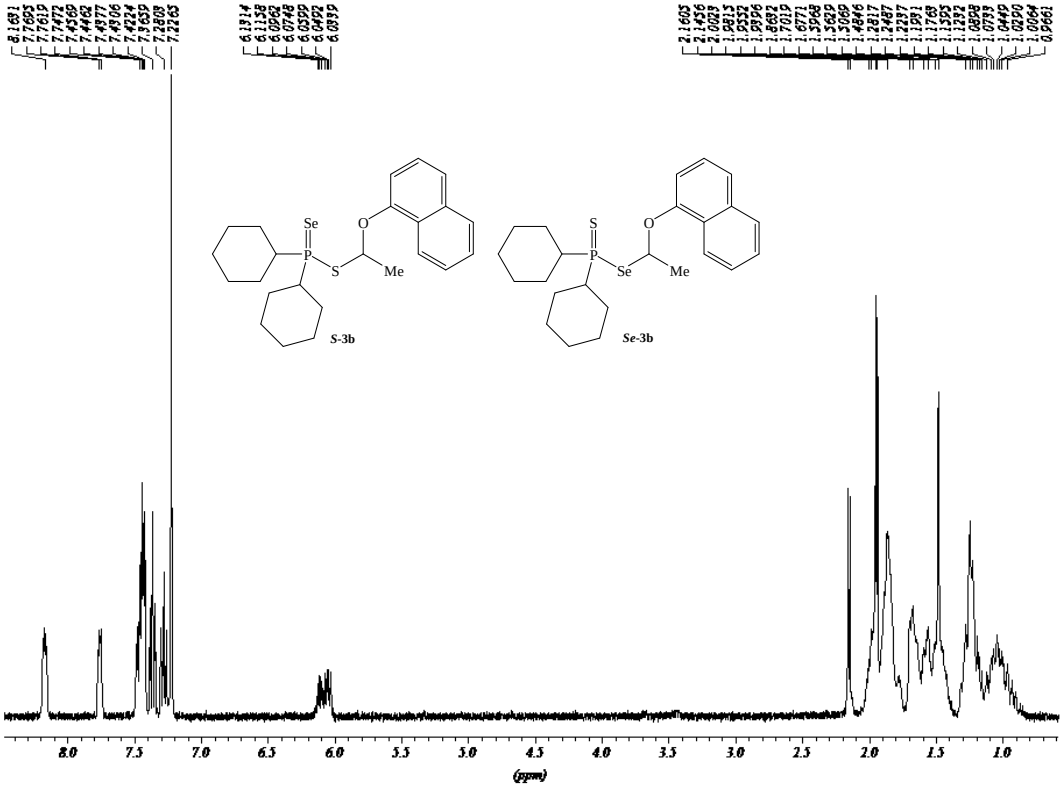

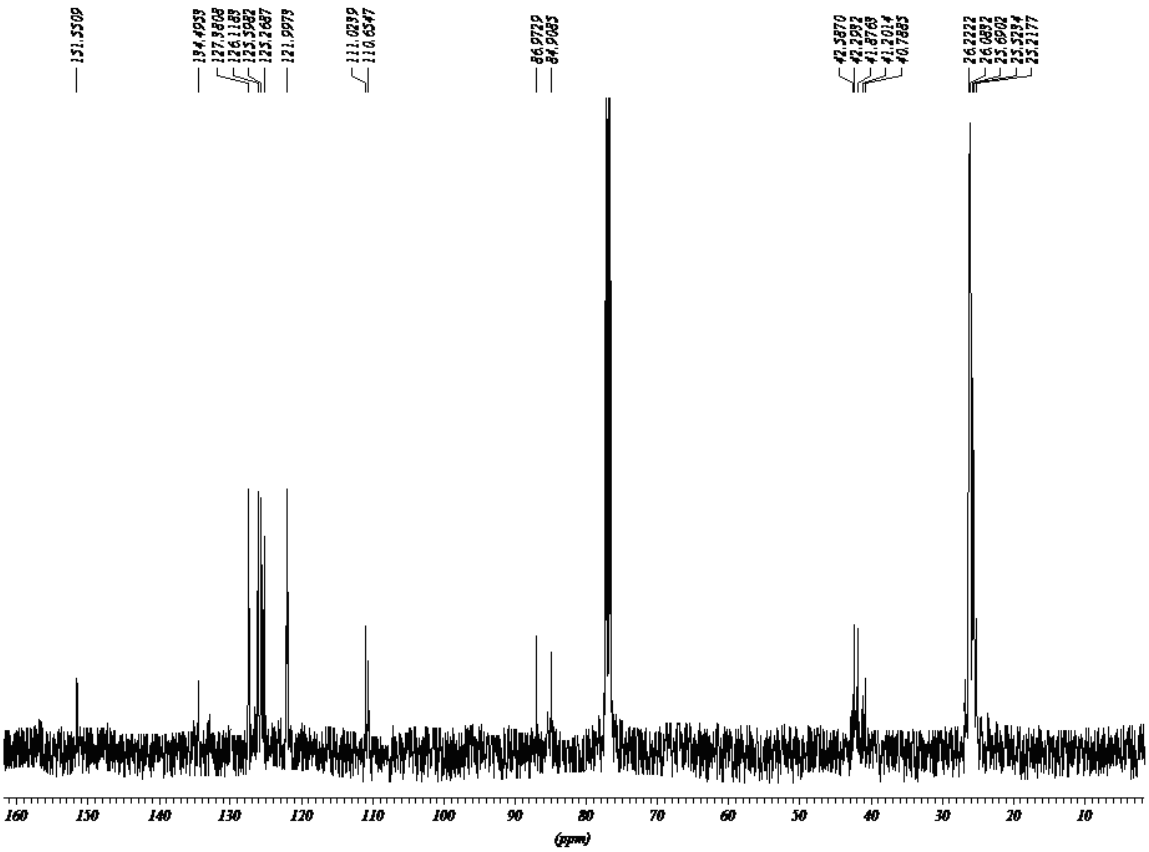
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126.1183
125.5962
125.2687
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86.9729
84.9085
42.3870
42.1592
41.8768
41.2014
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26.2222
26.0892
25.6902
25.3274
25.2177
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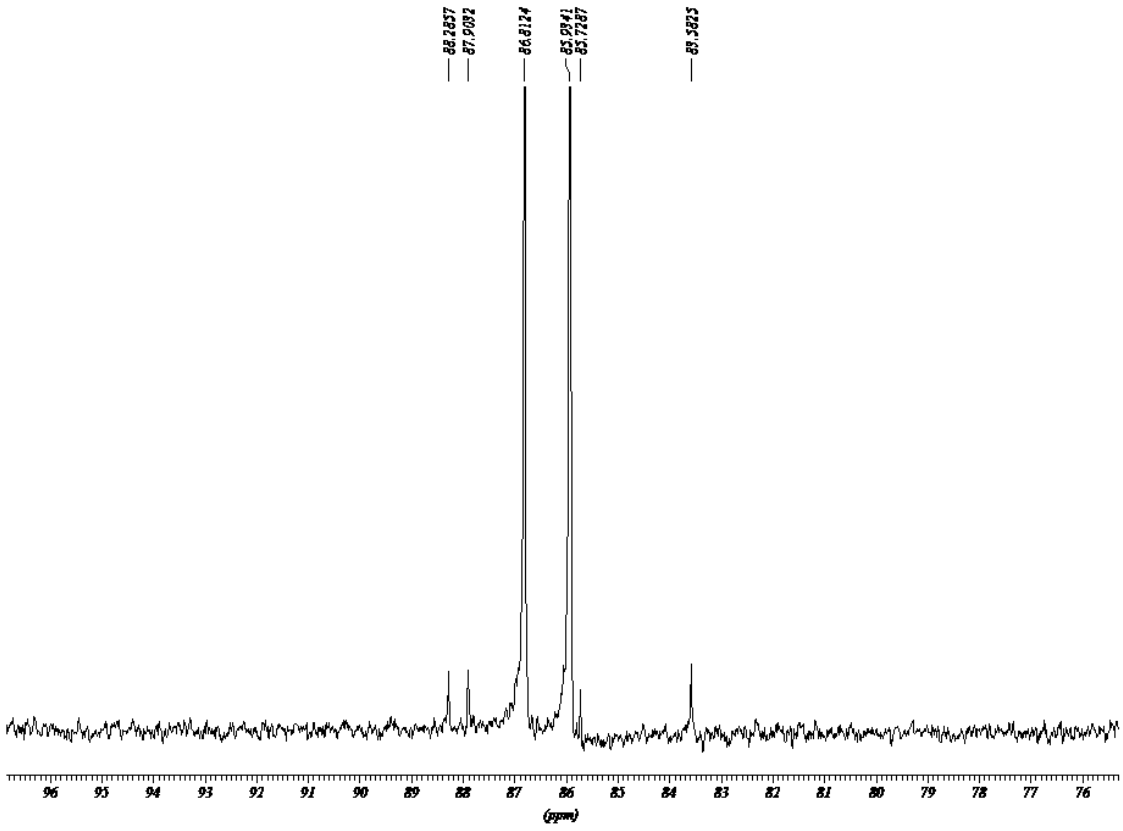
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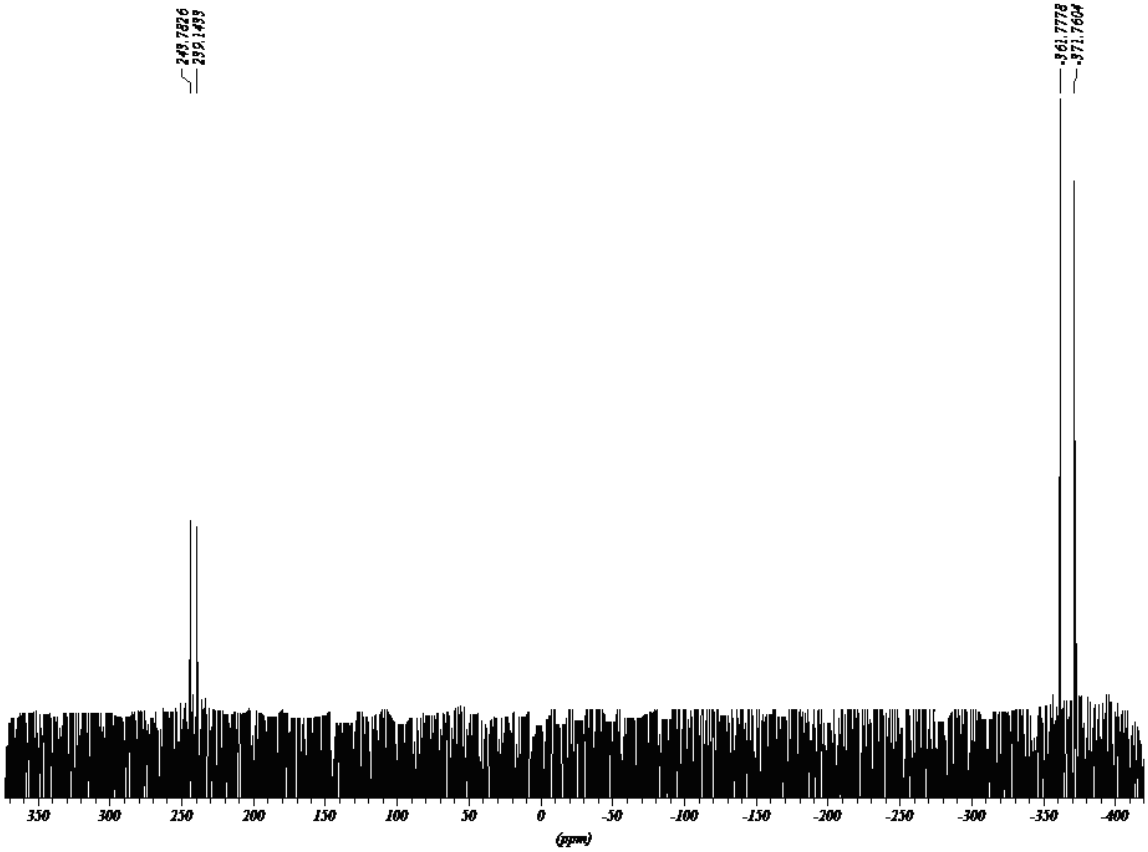
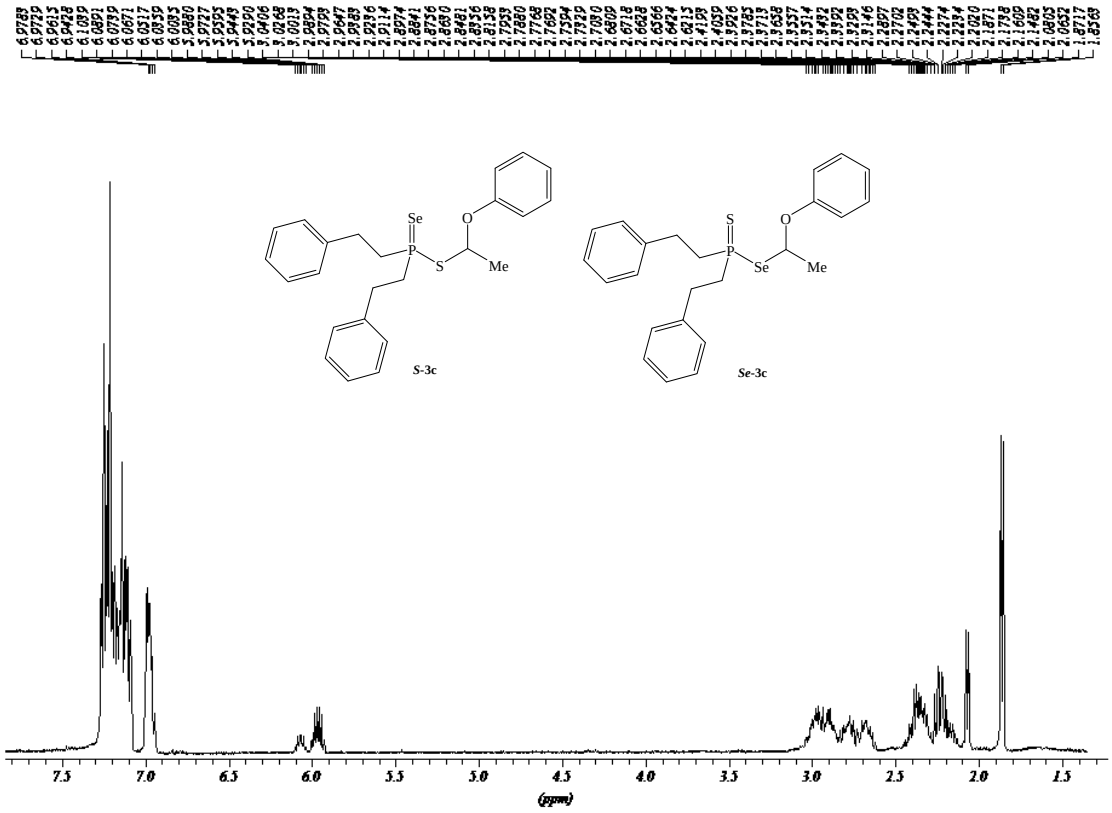
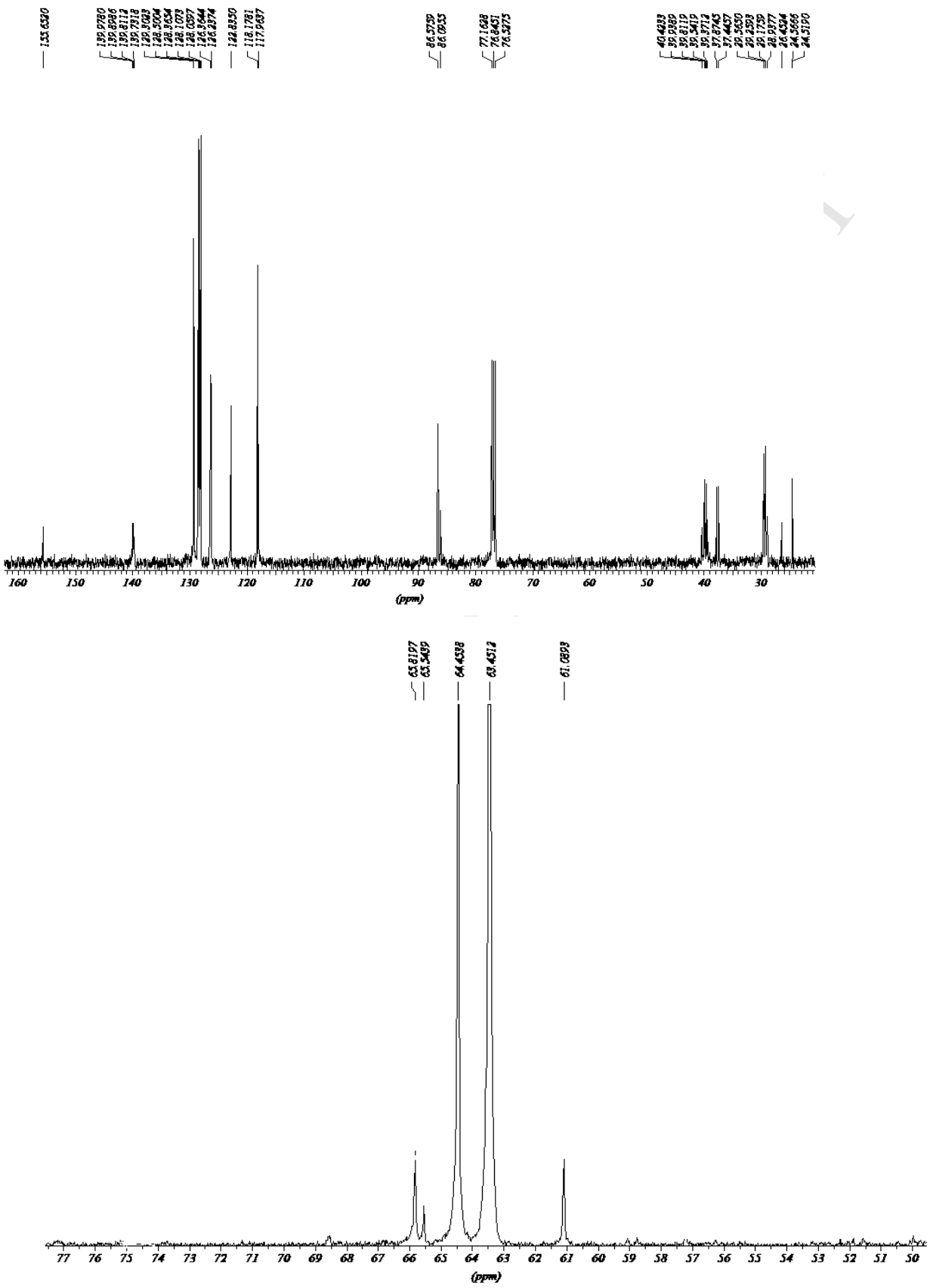
(ppm)



1-Phenoxyethyl diphenethylphosphinoselenothioate (3c)

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126.9544
126.8374
122.8350
118.1781
117.9697
86.5739
86.0855
77.1628
76.8451
76.5275
40.4233
39.9989
39.8119
39.5419
39.3721
37.8745
37.4457
29.5650
29.4393
29.1755
28.9977
26.4204
24.3666
24.3190
160 150 140 130 120 110 100 90 80 70 60 50 40 30
(ppm)
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63.4513
61.0859
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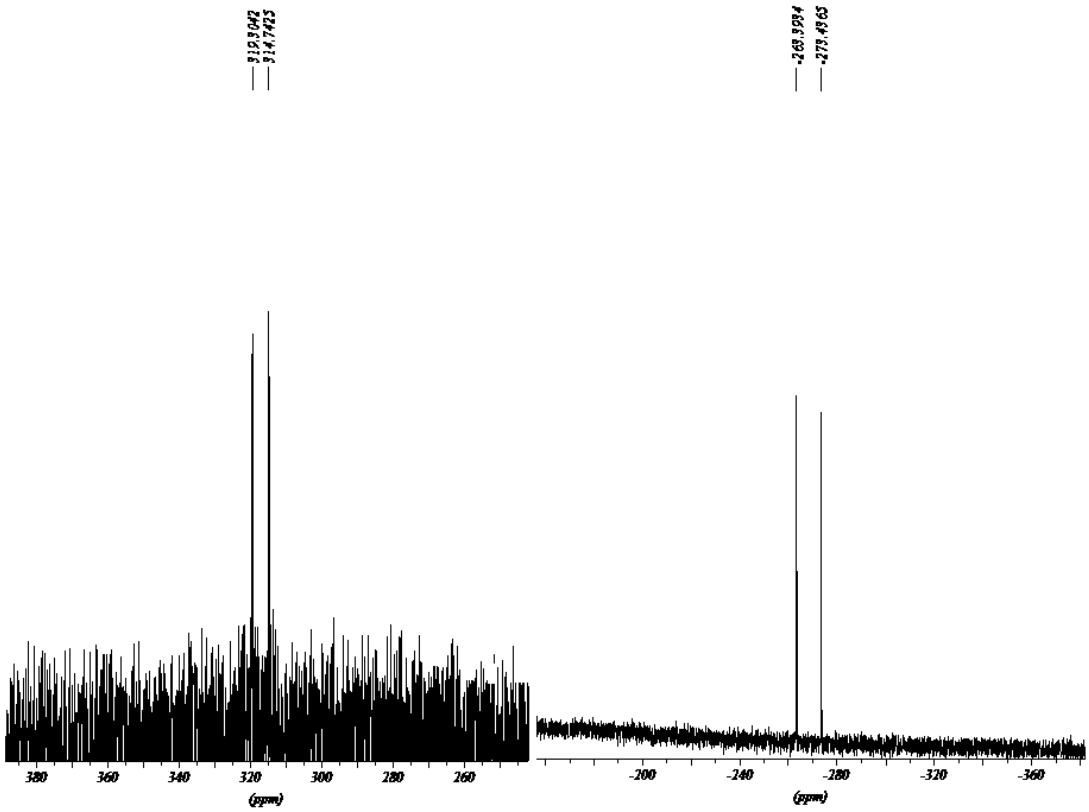
(ppm)



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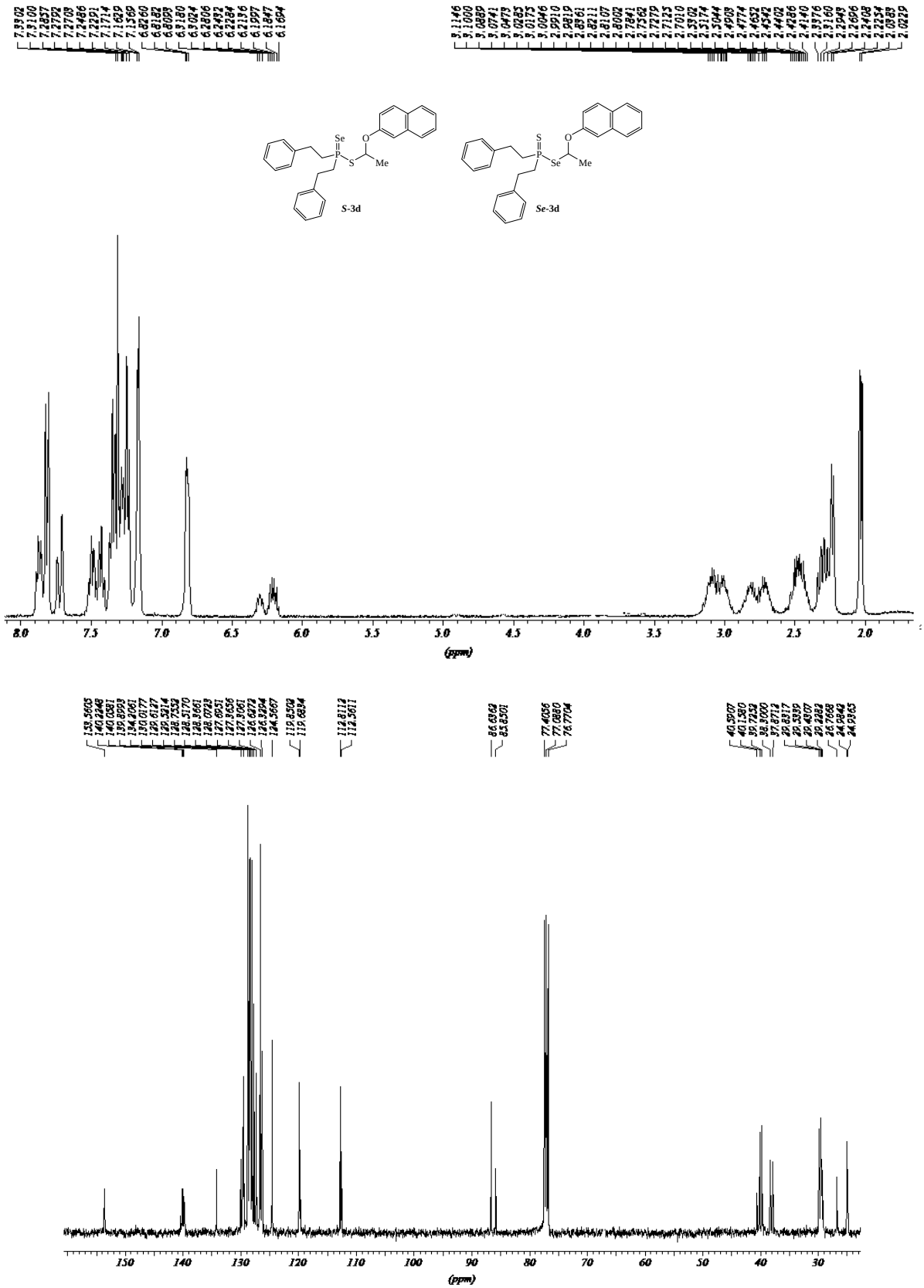
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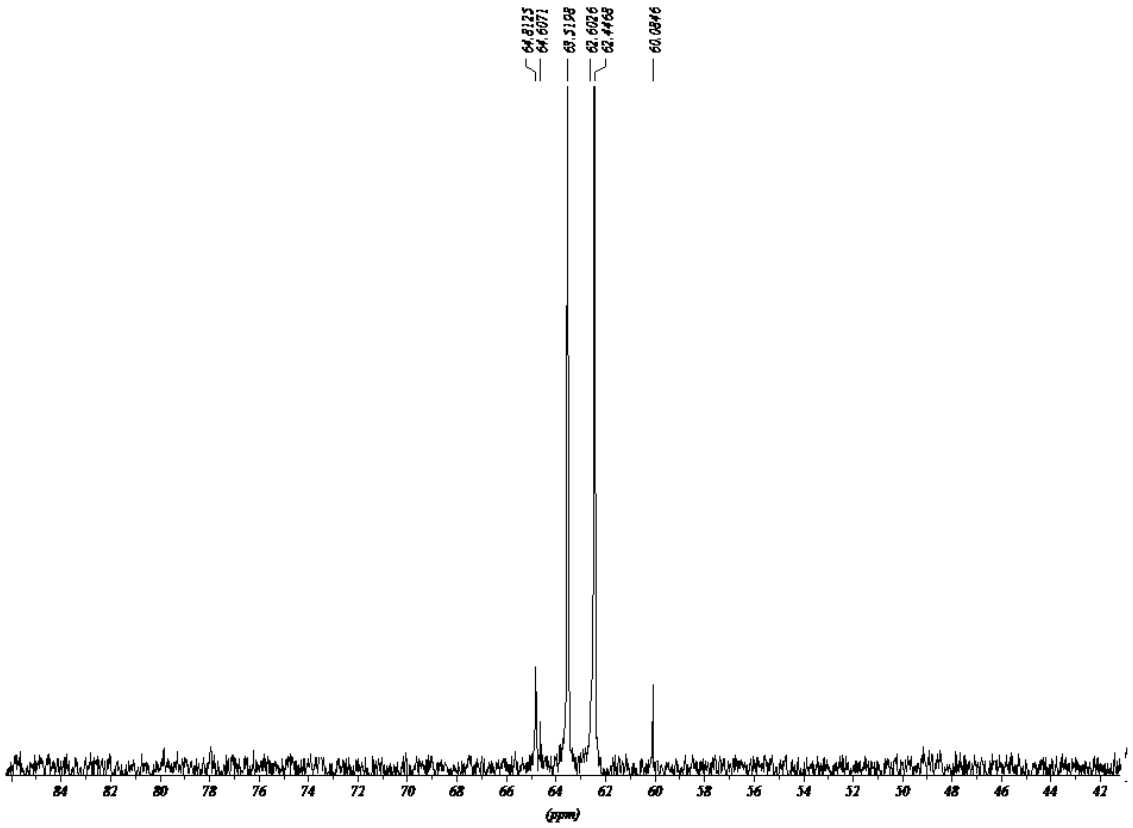
O
P
S
Me
S-3d
S
O
P
Se
Me
Se-3d
(ppm)
(ppm)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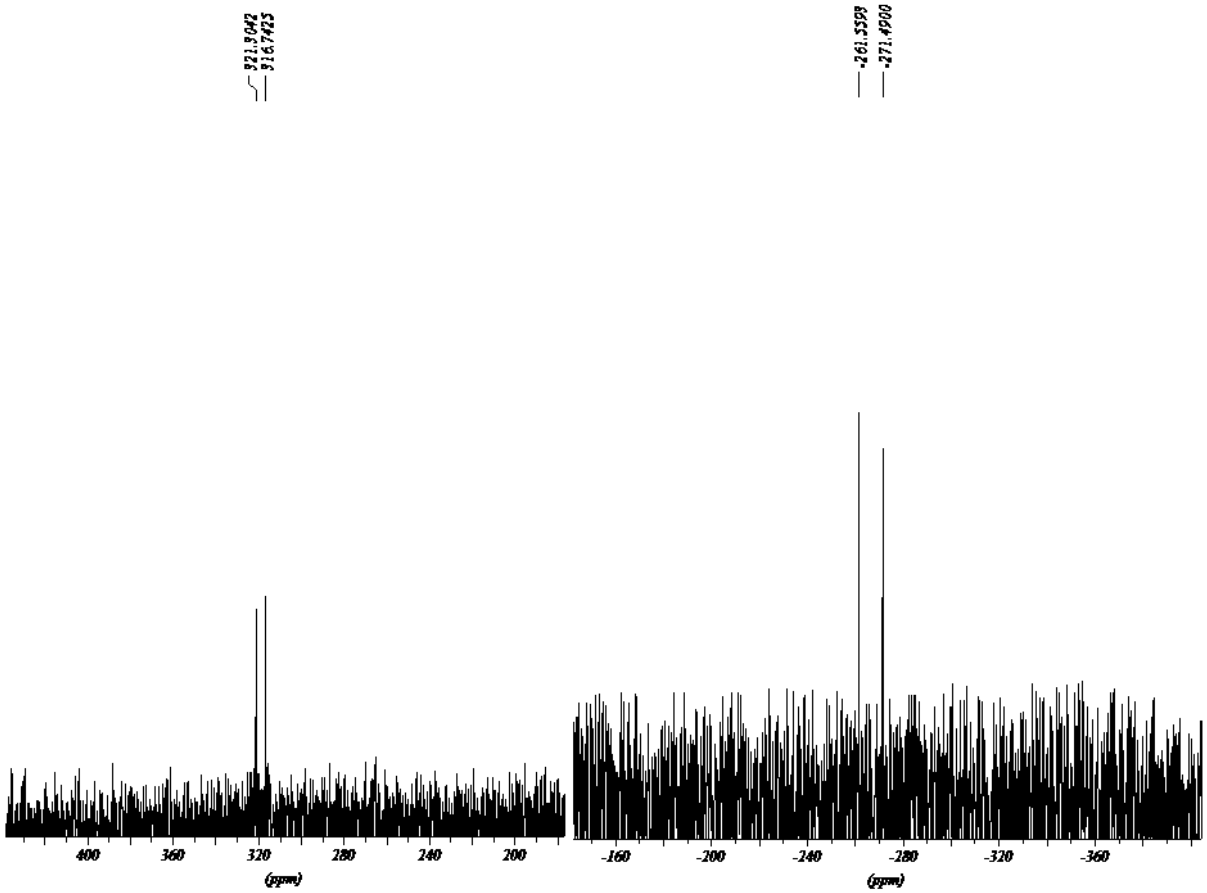
(ppm)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-261.5593
-271.4900
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(ppm)

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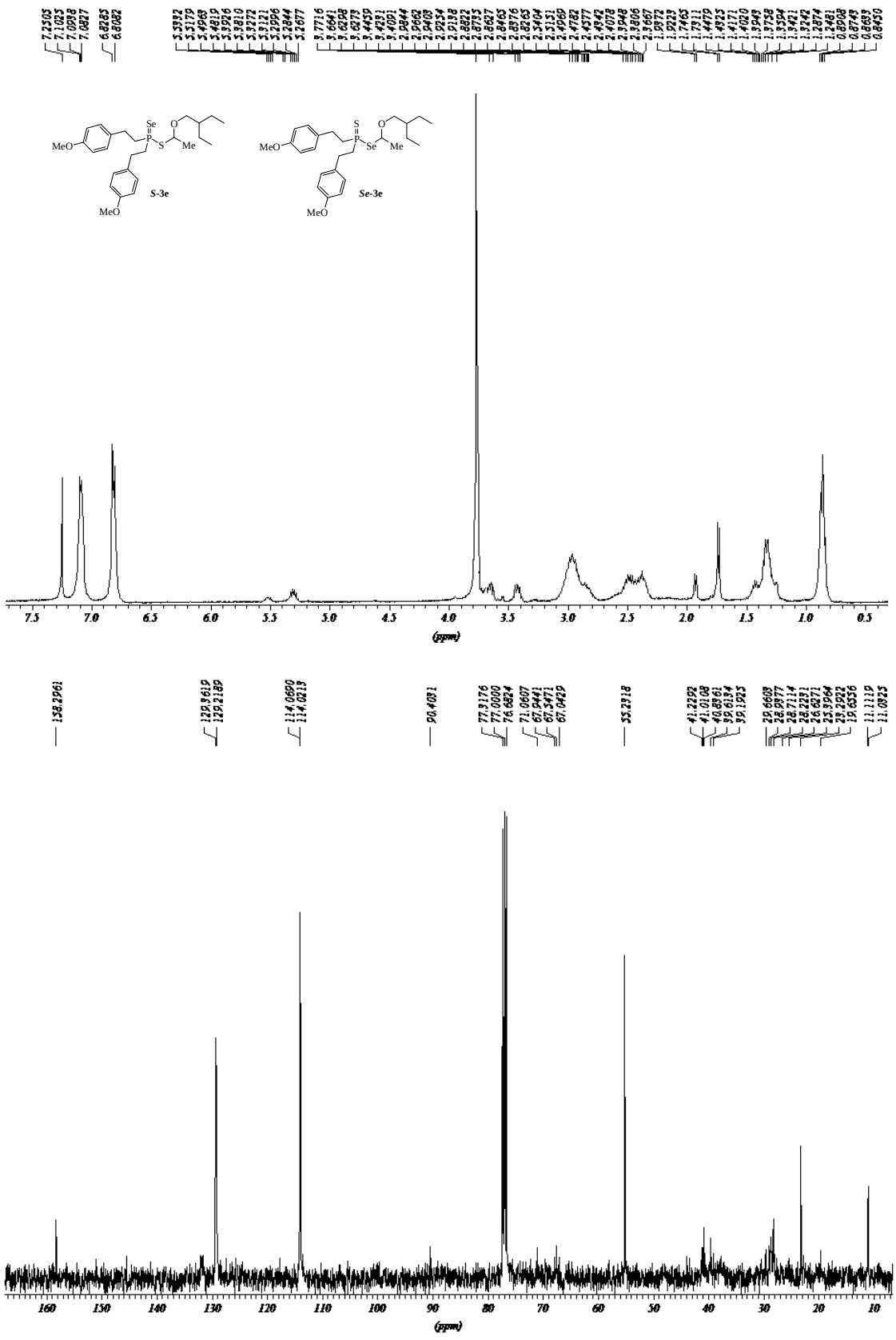

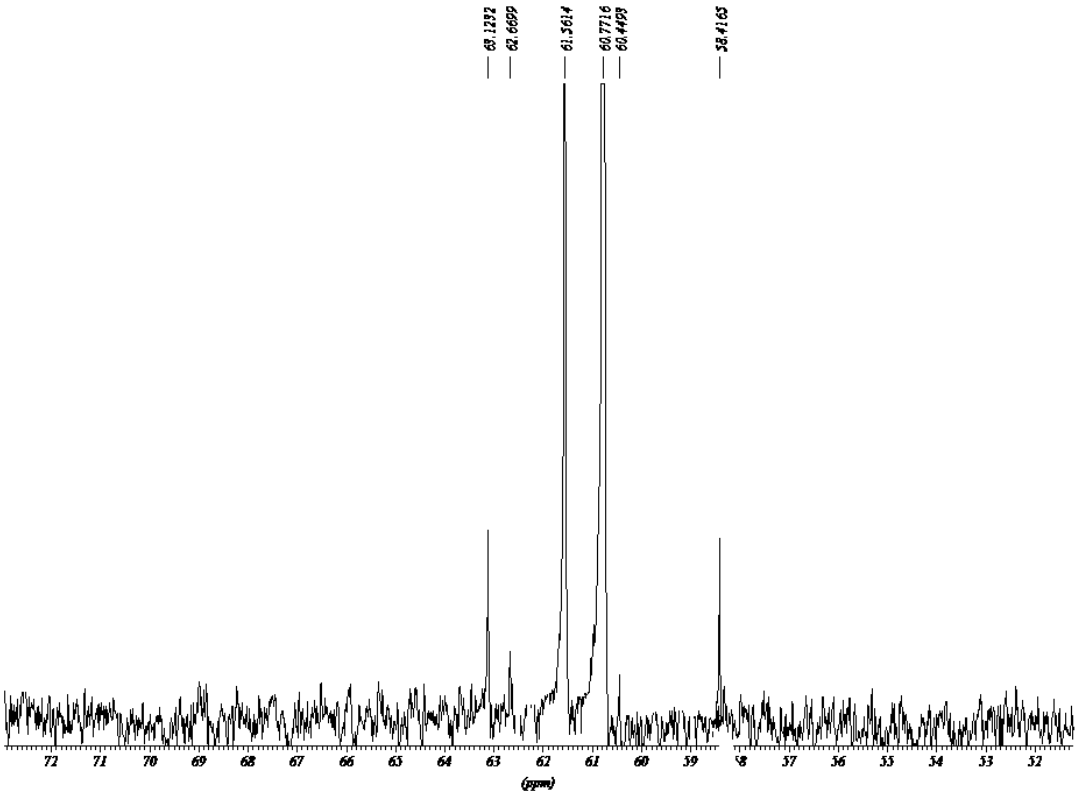
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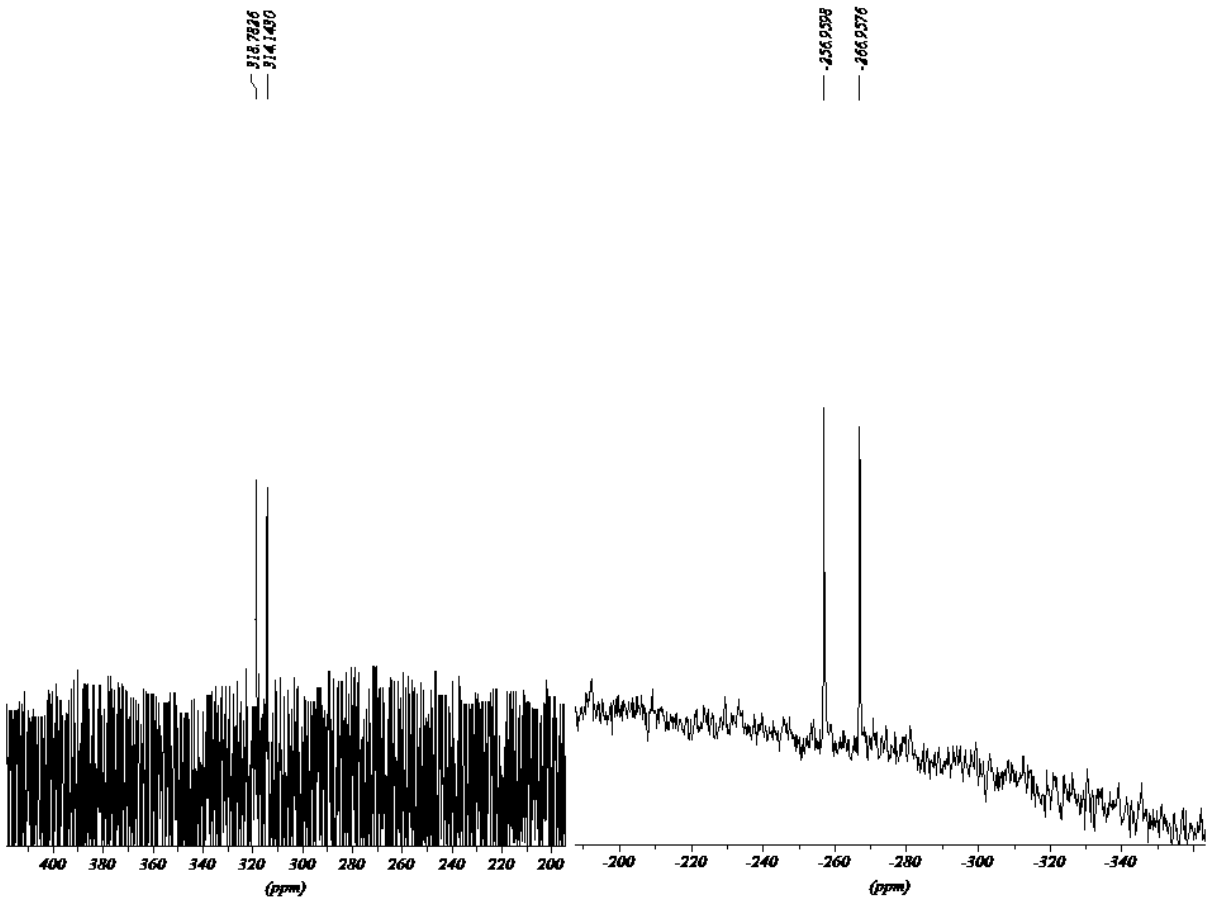
(ppm)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-266.9576
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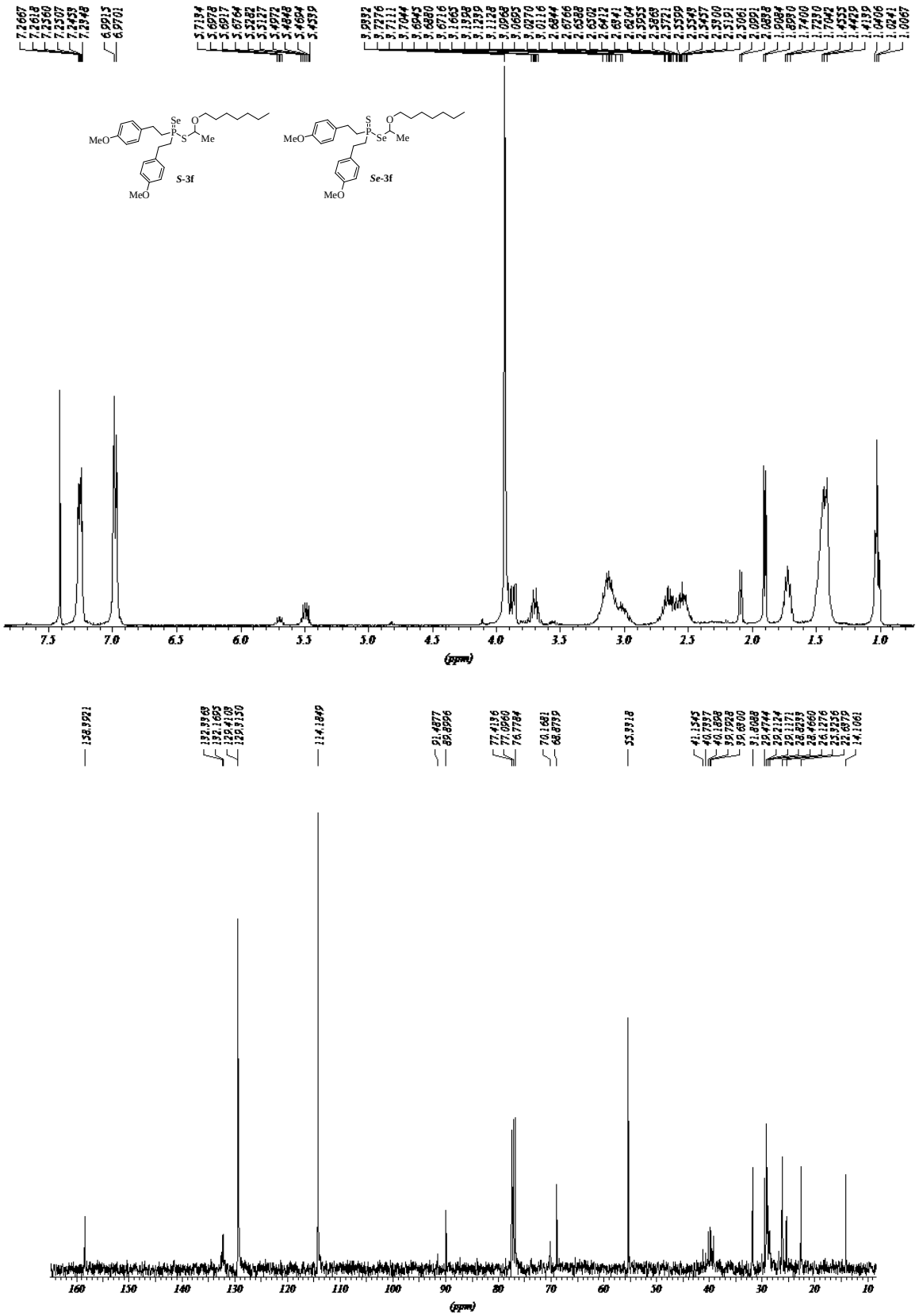
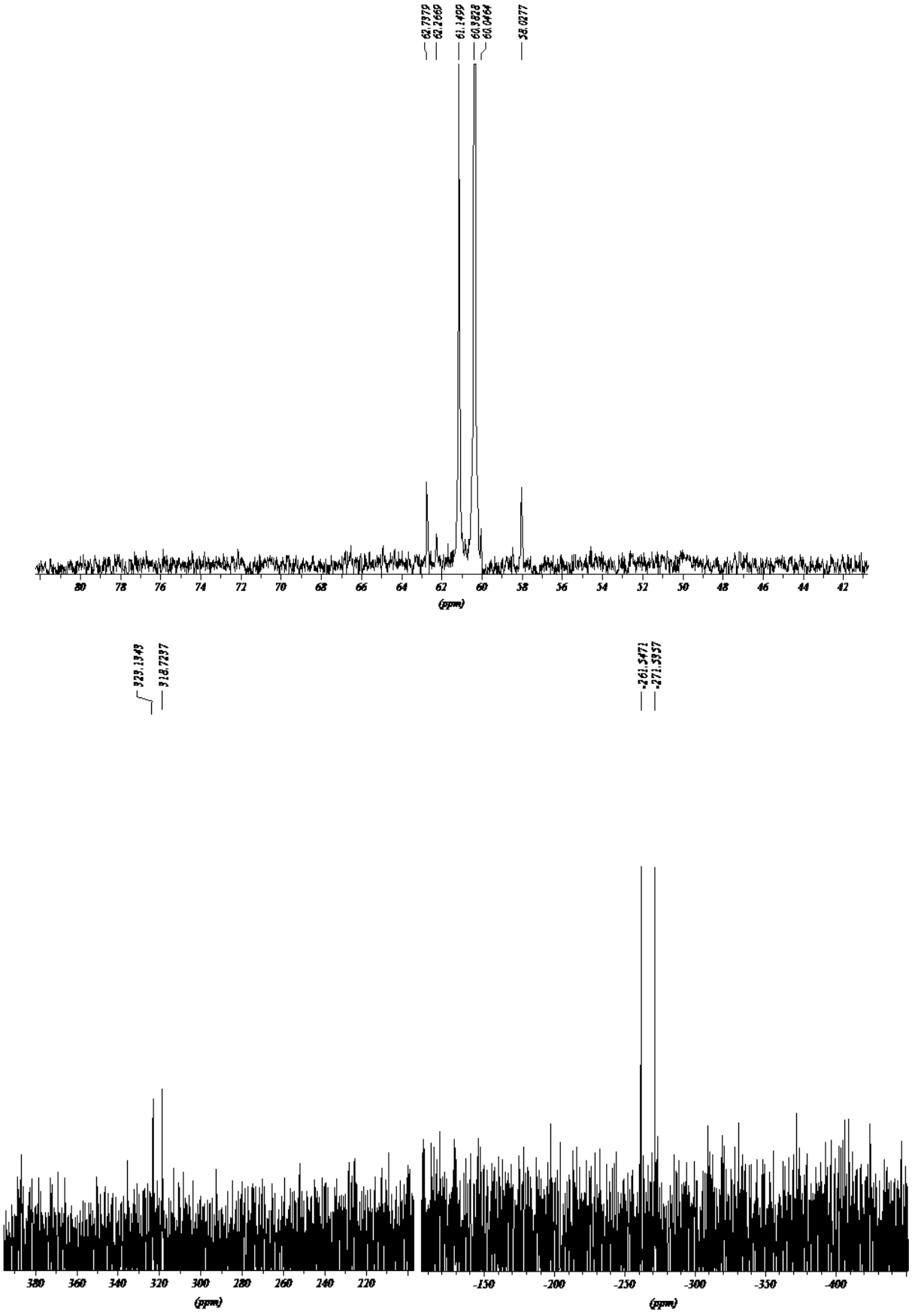
(ppm)

[1-(Heptyloxy)ethyl] bis(4-methoxyphenethyl)phosphinoselenothioate (3f)

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60.0464
58.0277
80 78 76 74 72 70 68 66 64 62 60 58 56 54 52 50 48 46 44 42
(ppm)
323.1343
318.7297
-261.5471
-271.5957
380 360 340 320 300 280 260 240 220
(ppm)
-150 -200 -250 -300 -350 -400
(ppm)

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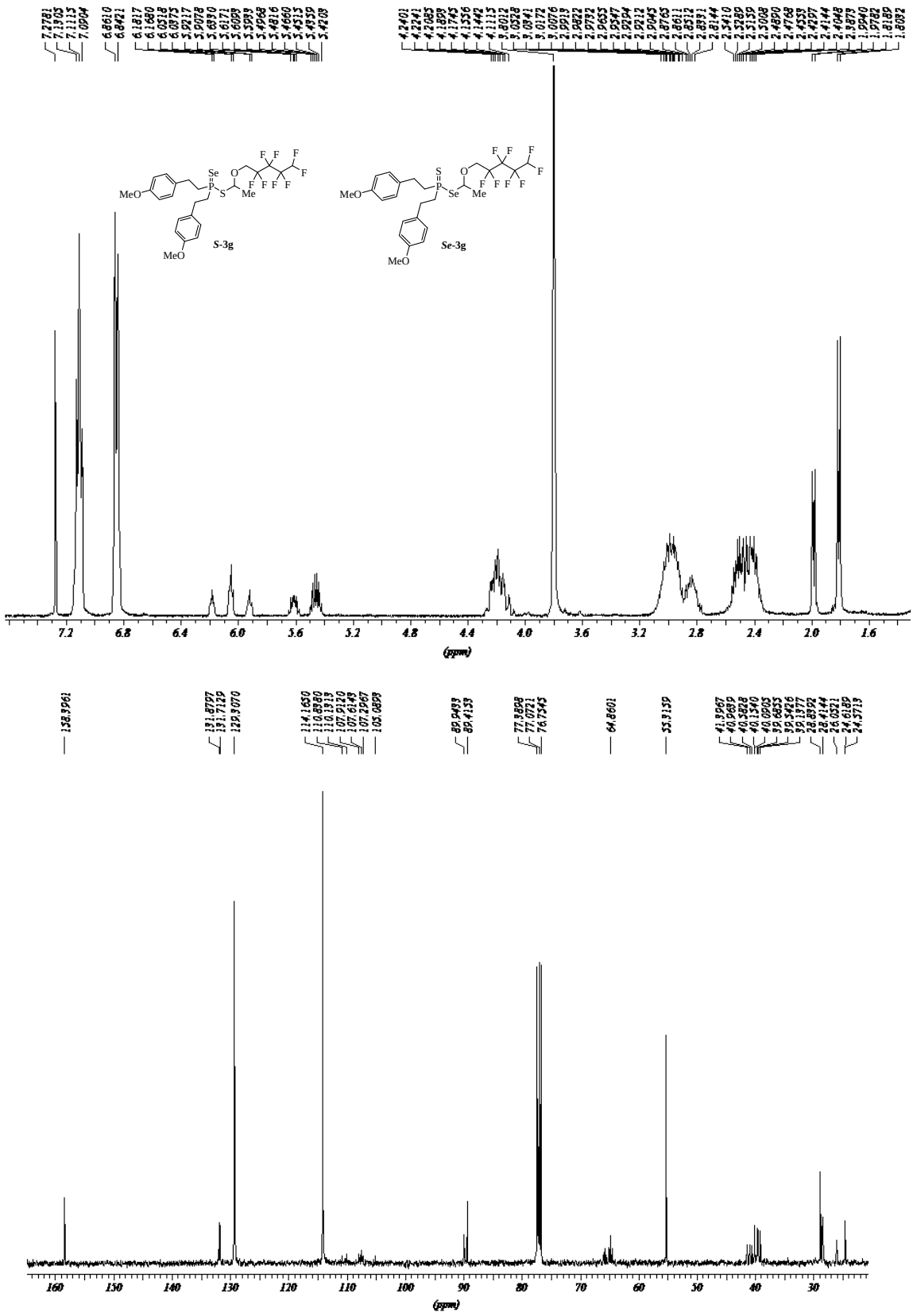

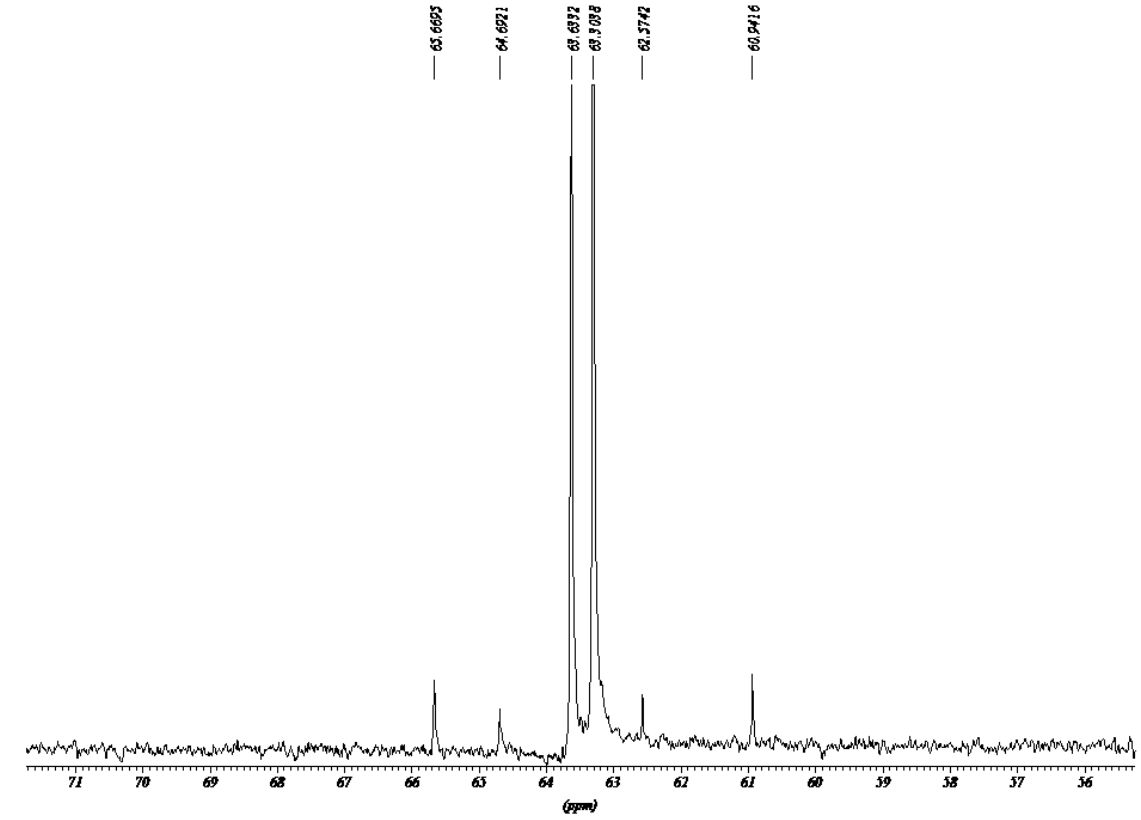
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68
67
66
65
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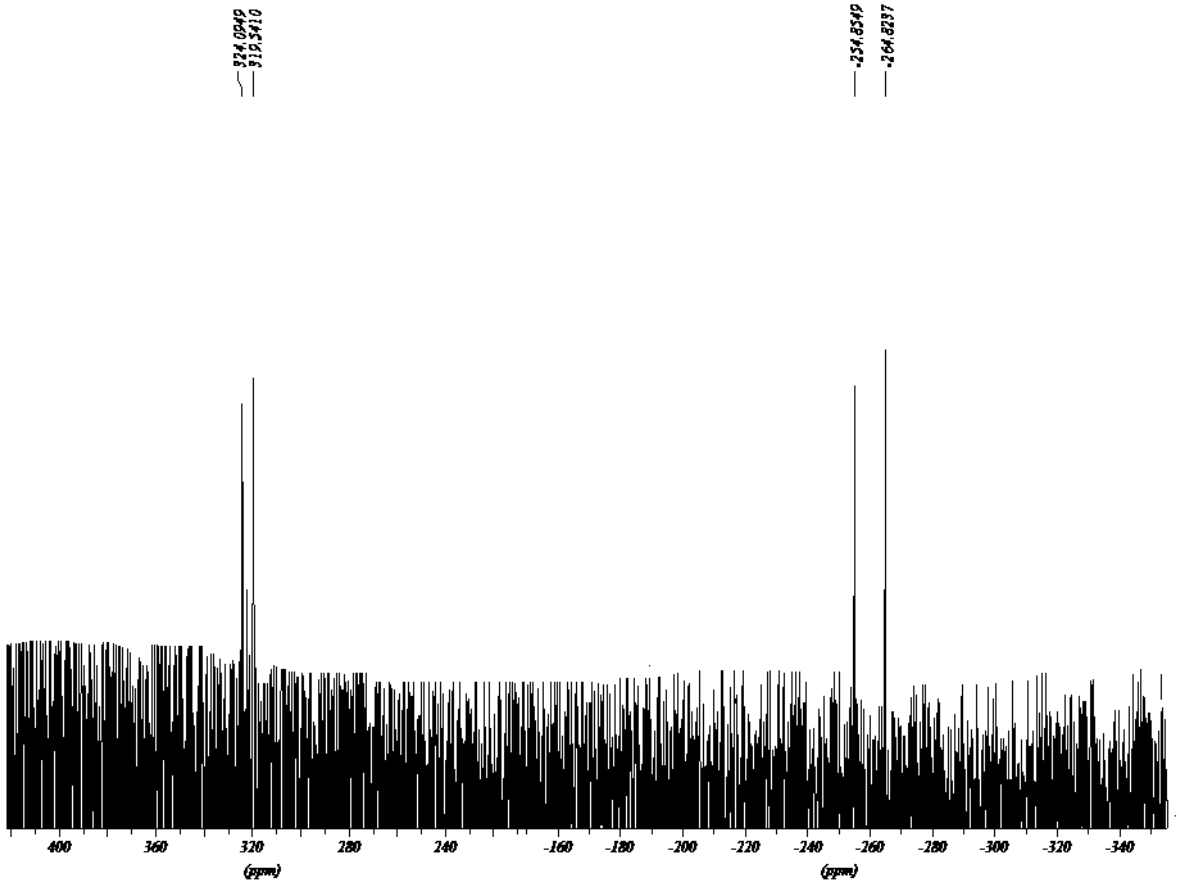
63
62
61
60
59
58
57
56
(ppm)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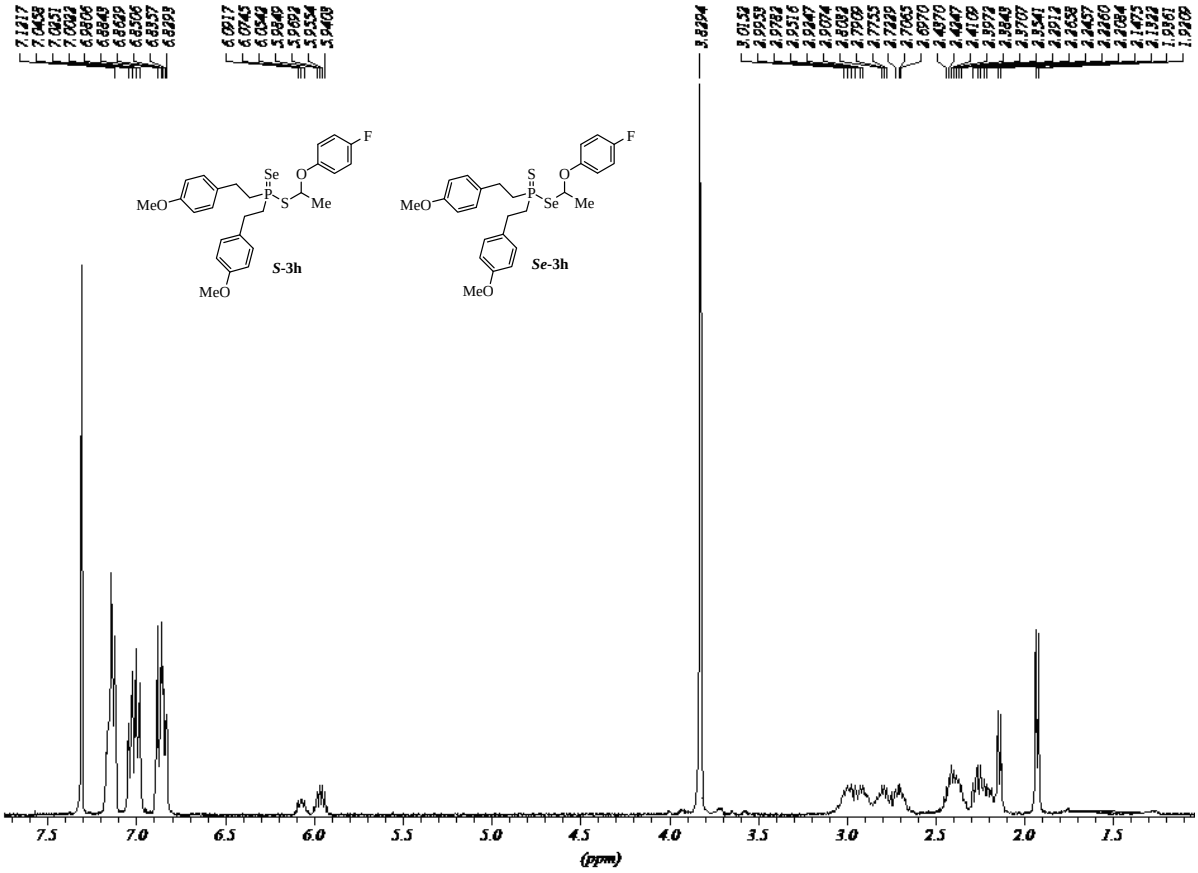
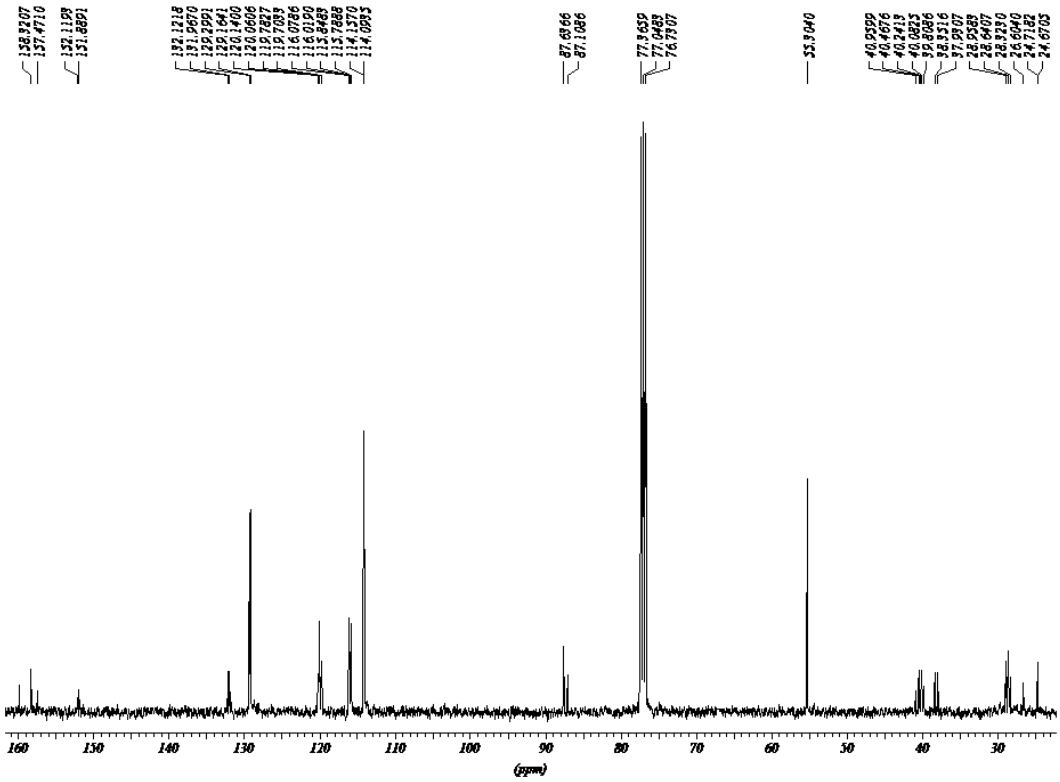
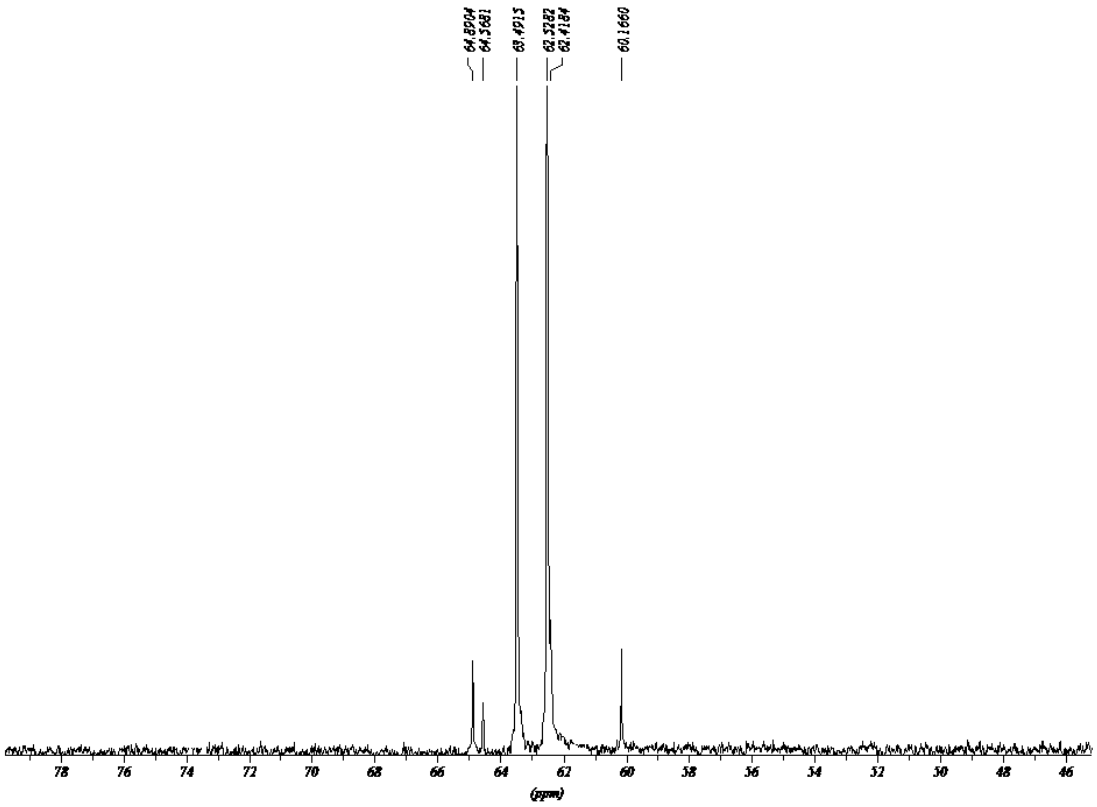
400
360
320
280
240
-160
-180
-200
-220
-240
-260
-280
-300
-320
-340
(ppm)
(ppm)

[1-(4-Fluorophenoxy)ethyl] bis(4-methoxyphenethyl)phosphinoselenothioate (3h)



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74
72
70
68
66
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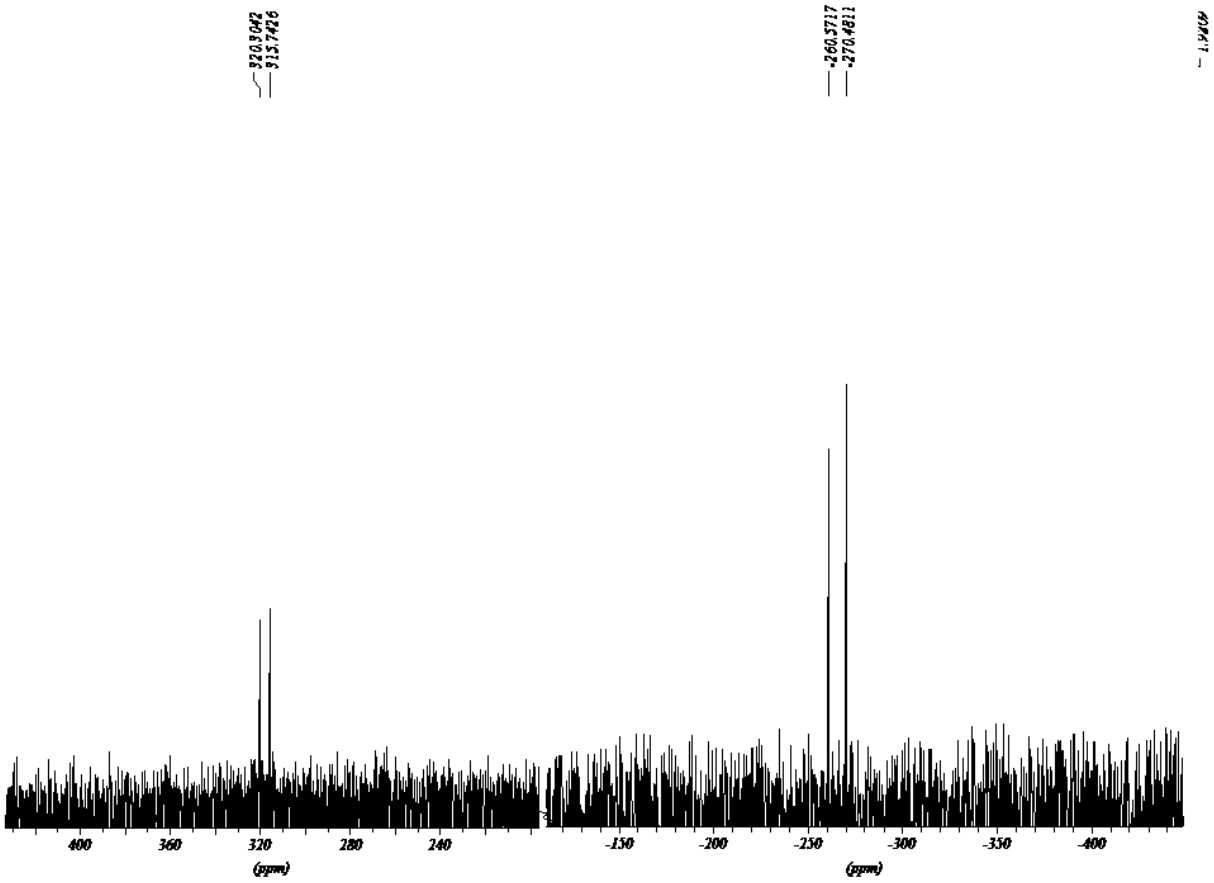
60
58
56
54
52
50
48
46
(ppm)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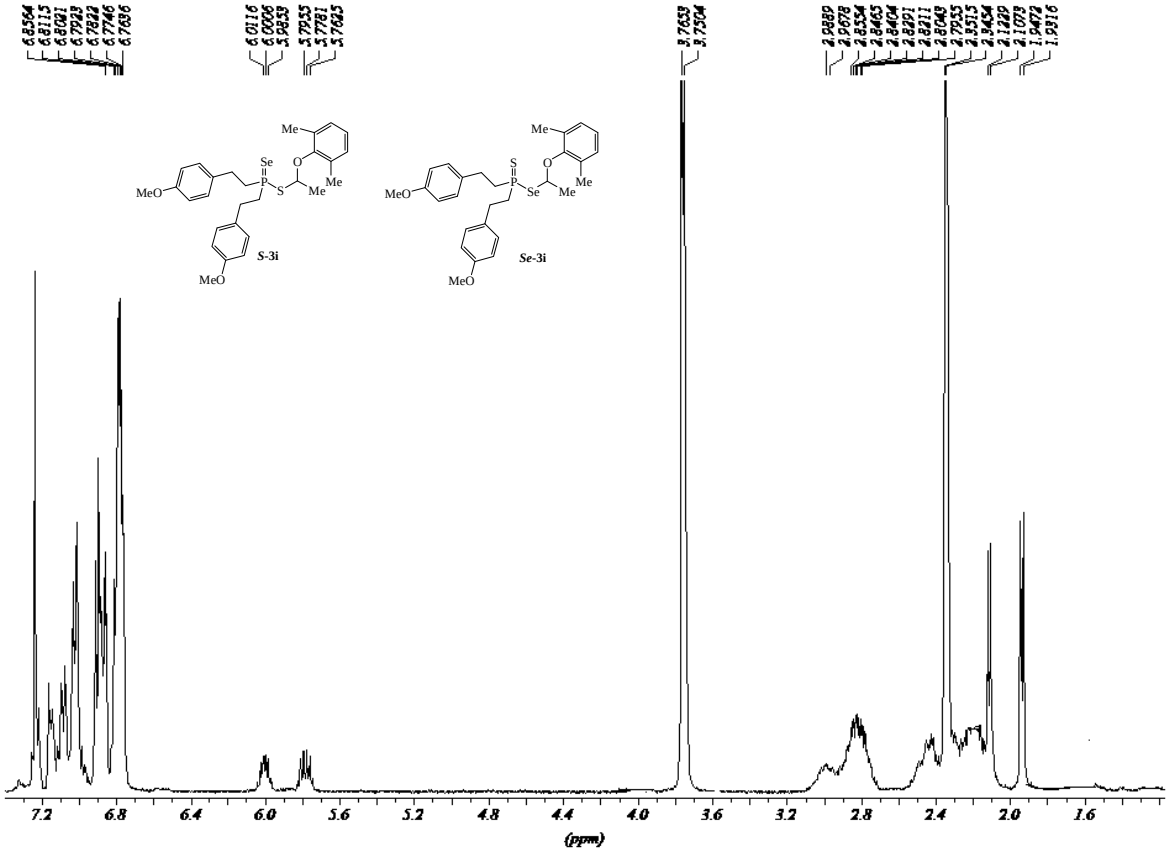
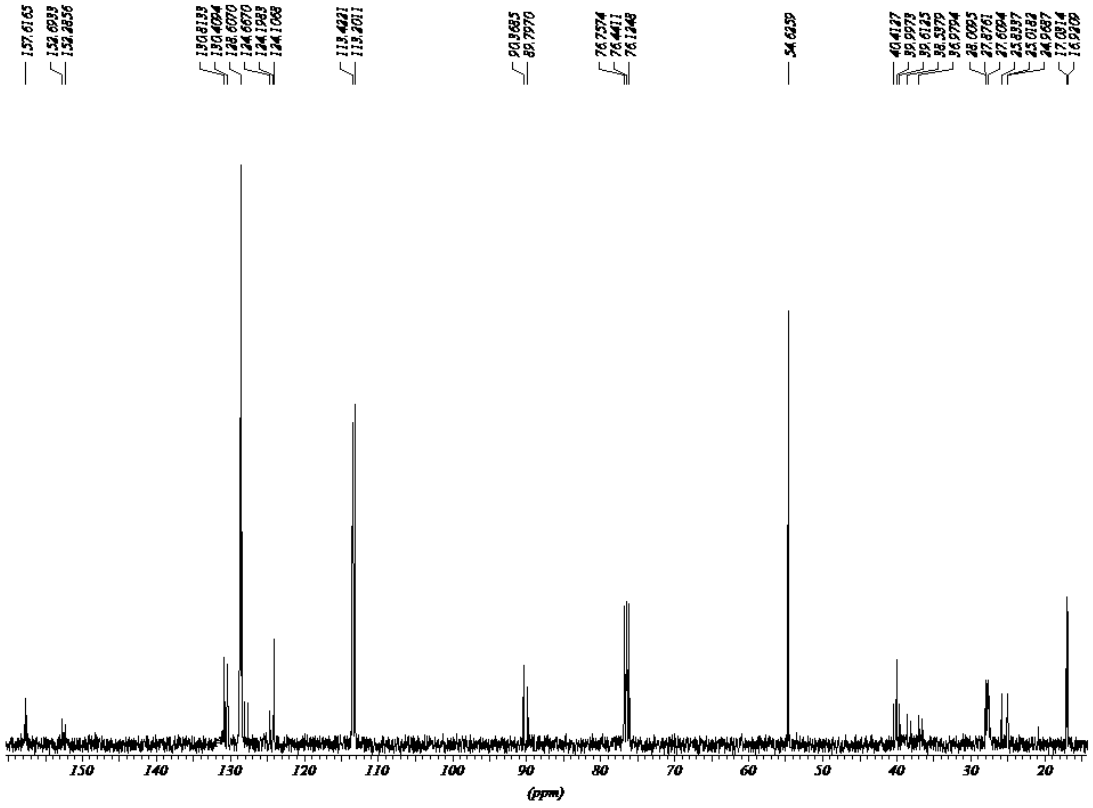
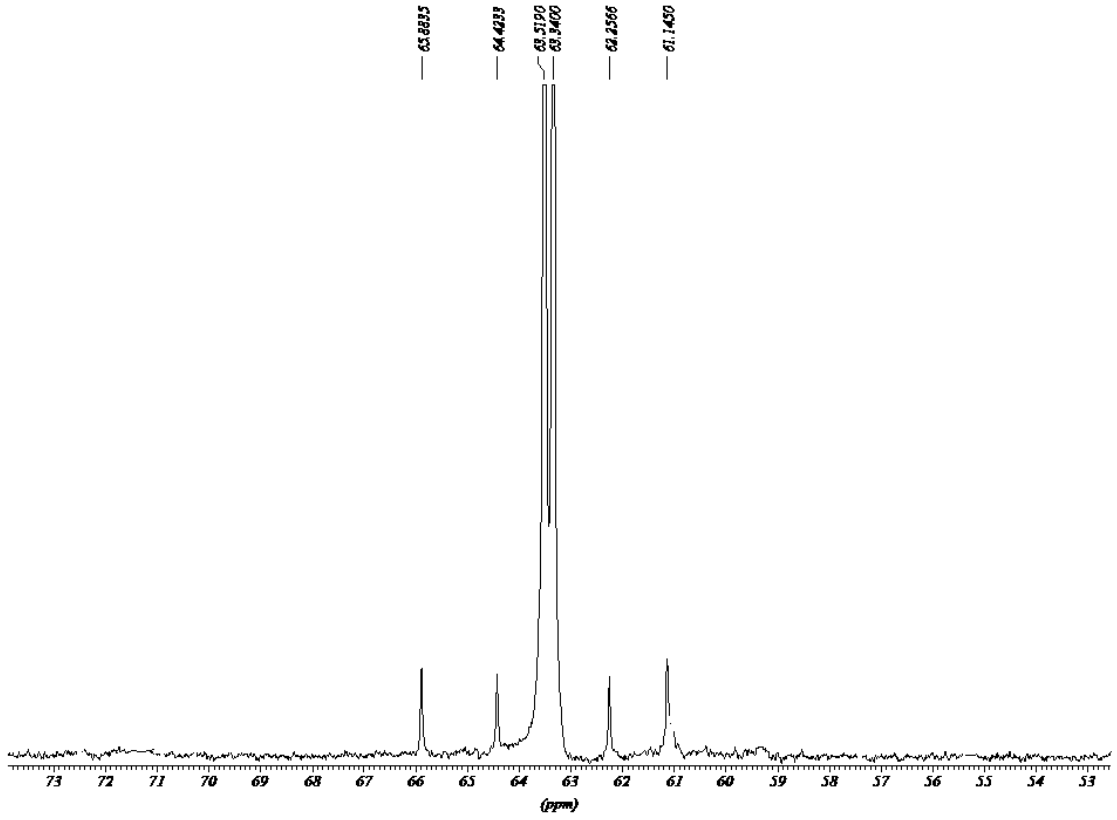
315.7426
-260.5717
-270.4811
400
360
320
280
240
-150
-200
-250
-300
-350
-400
(ppm)
(ppm)

[1-(2,6-Dimethylphenoxy)ethyl] bis(4-methoxyphenethyl)phosphinoselenothioate (3i)



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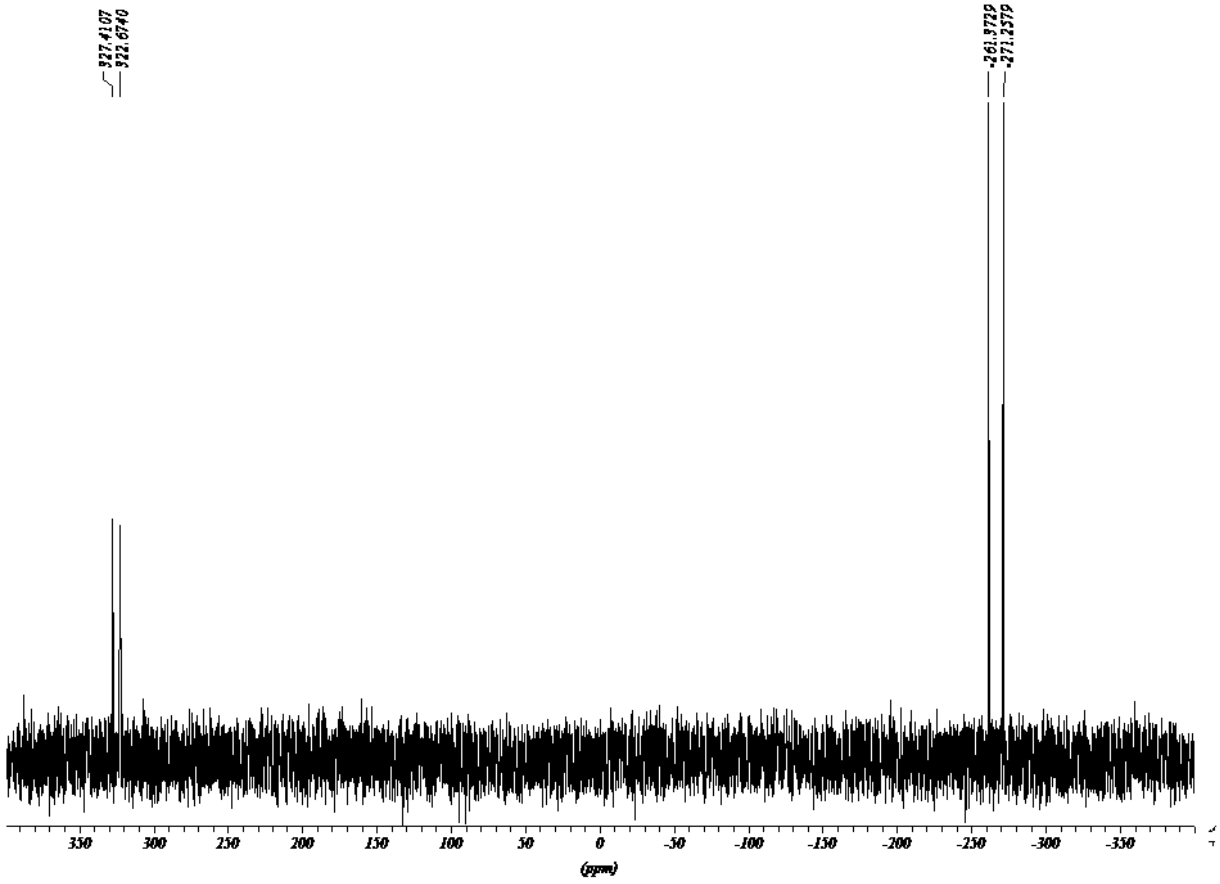
(ppm)


327.4107
322.6740
-261.8729
-271.2579
350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
(ppm)

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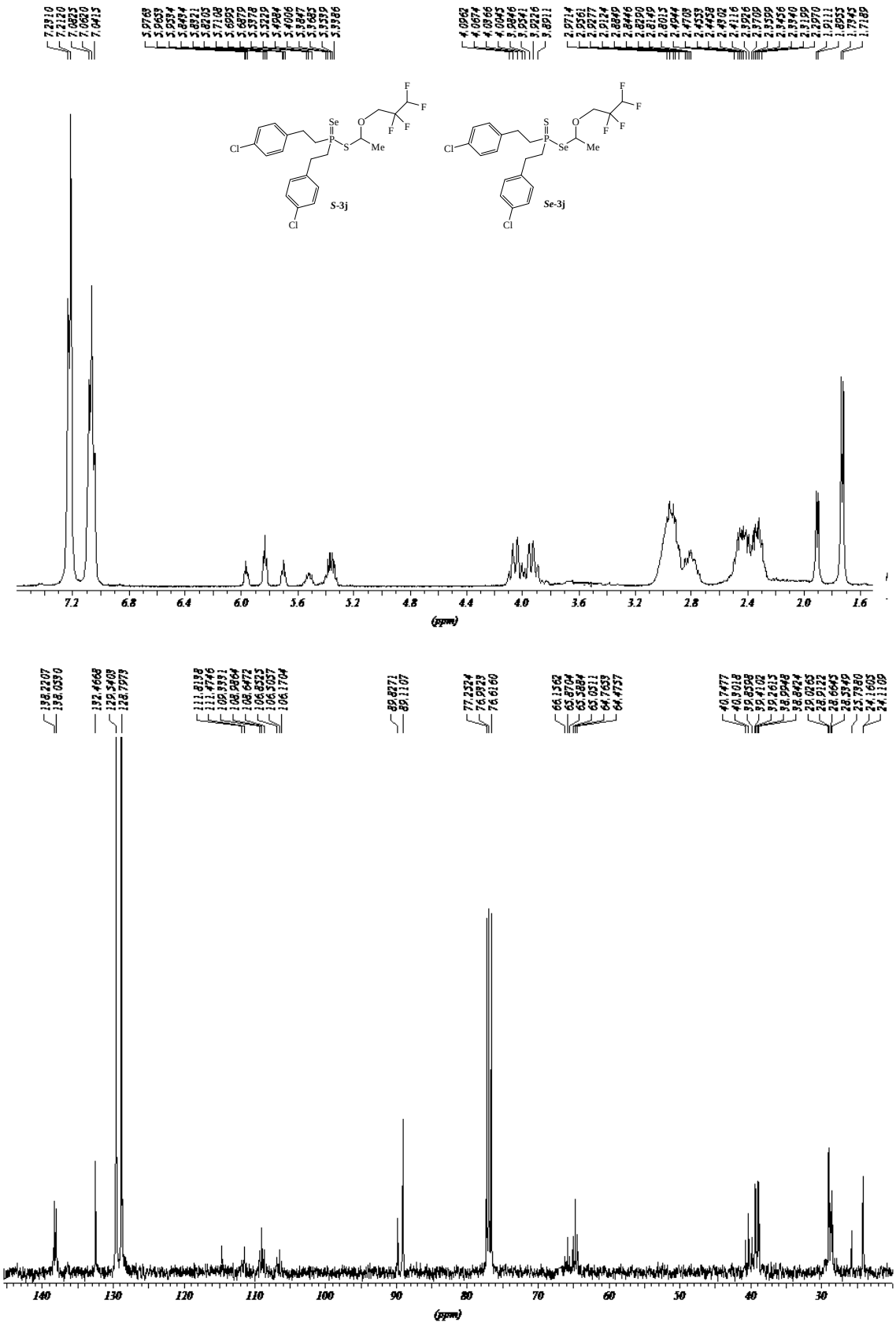
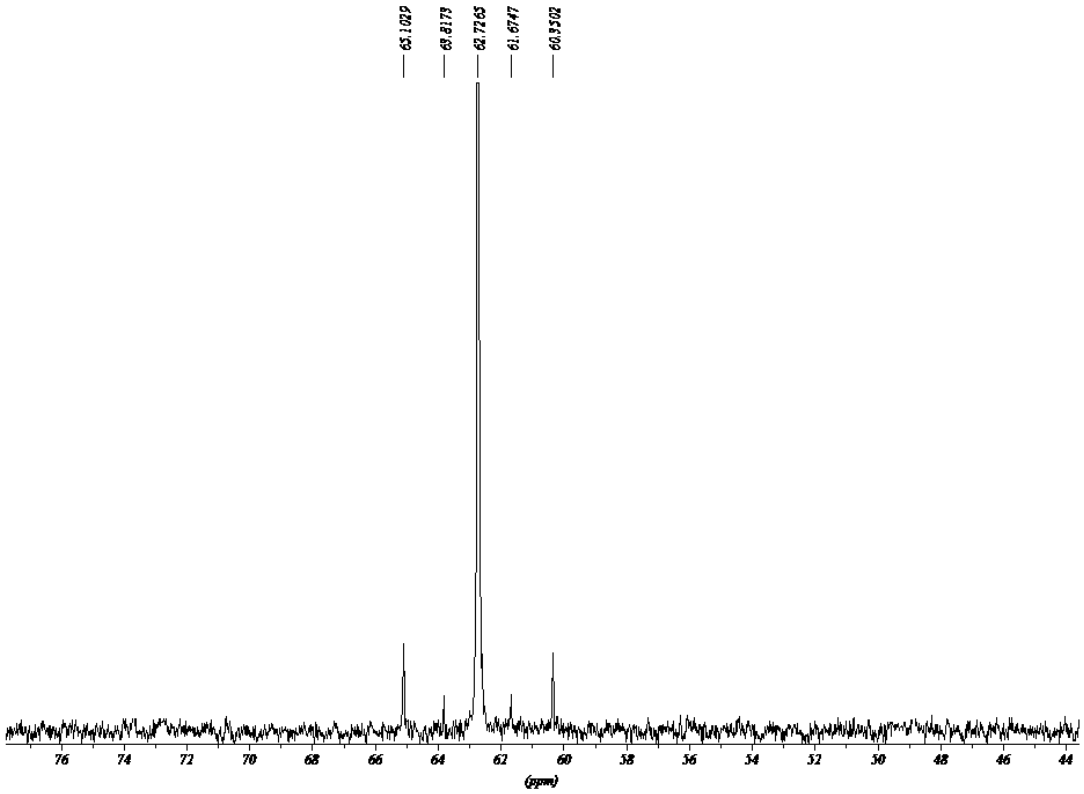
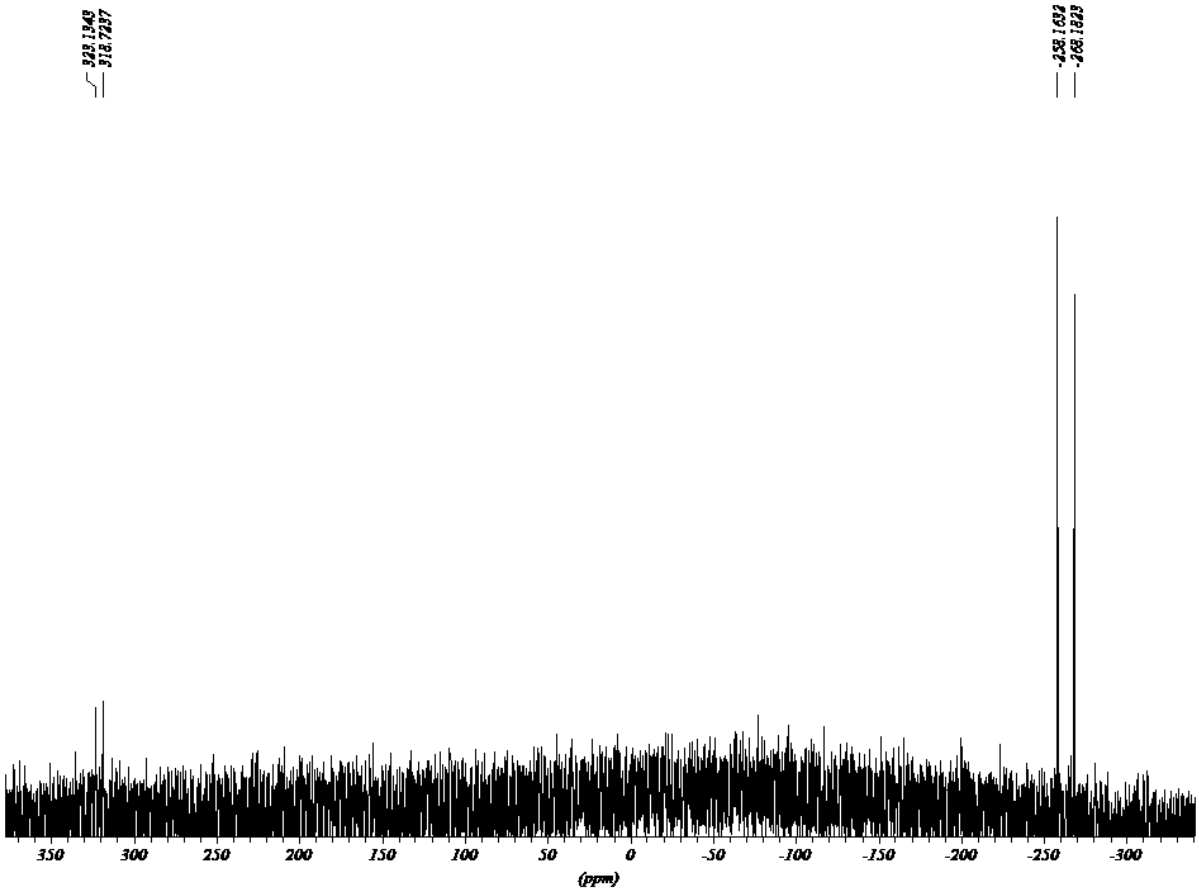
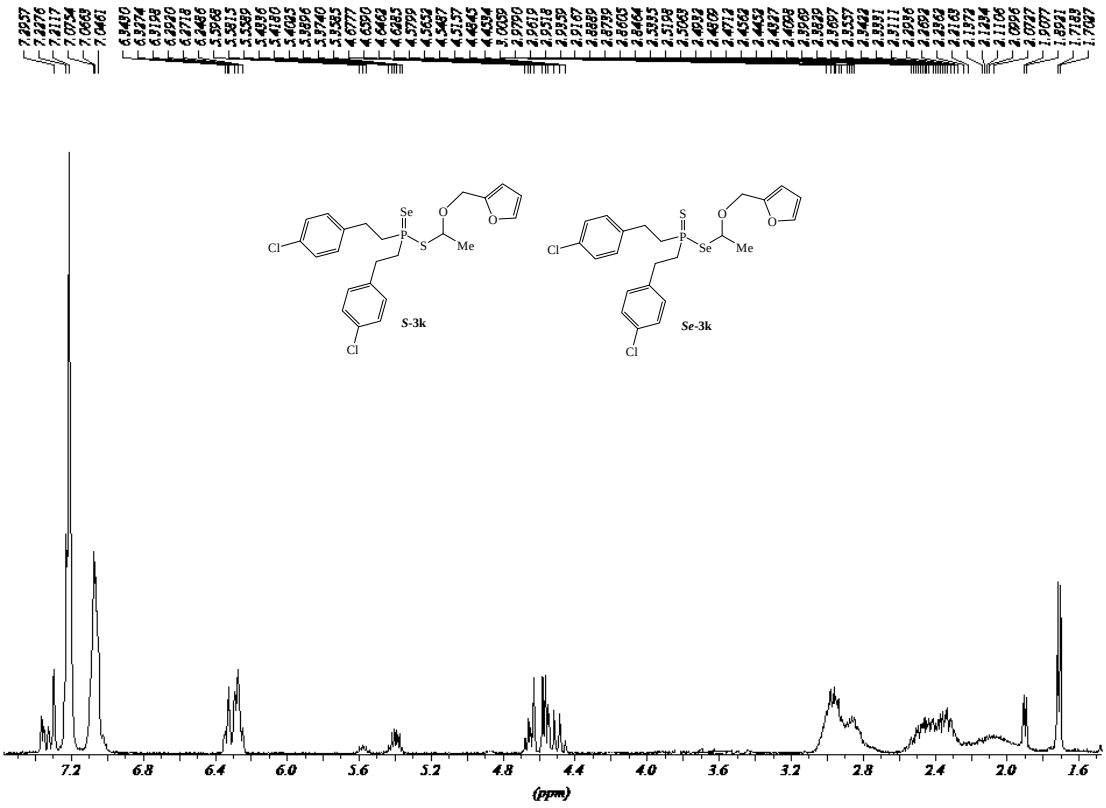
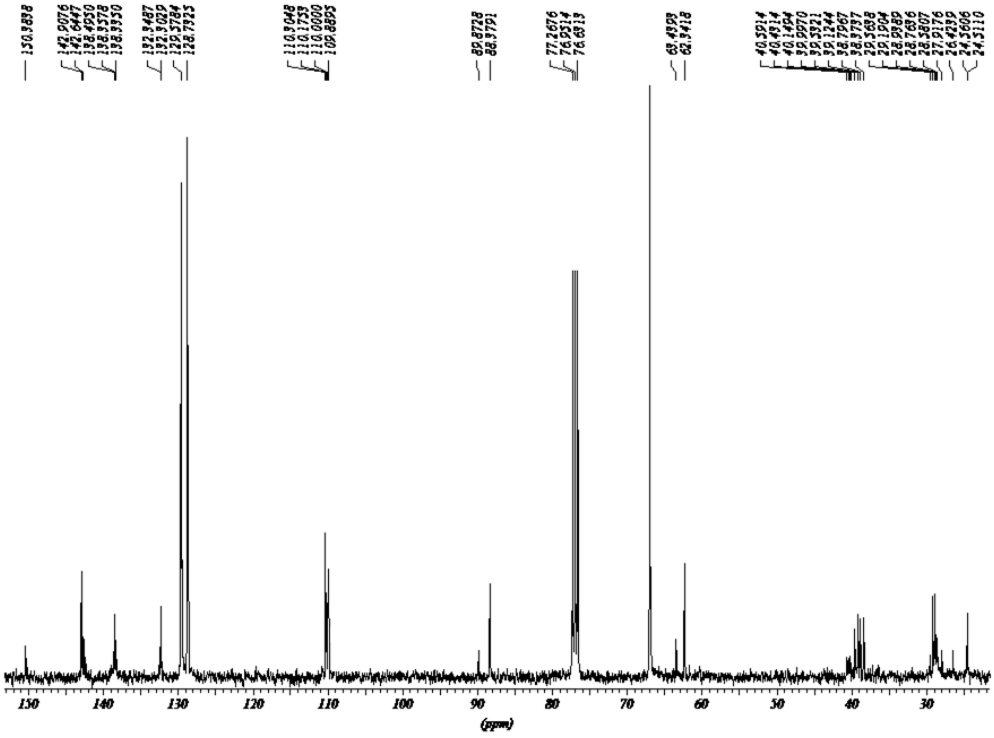


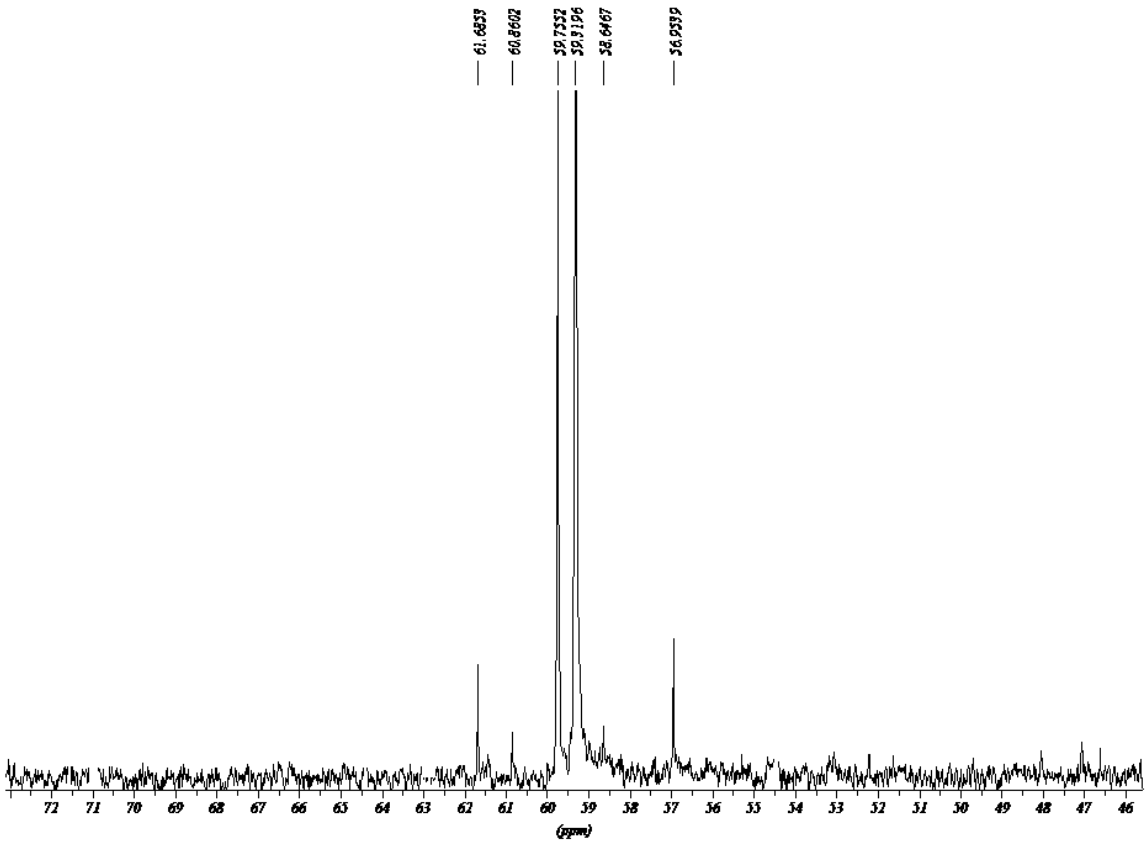

65.1029
63.8173
62.7265
61.6747
60.5502
76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
(ppm)

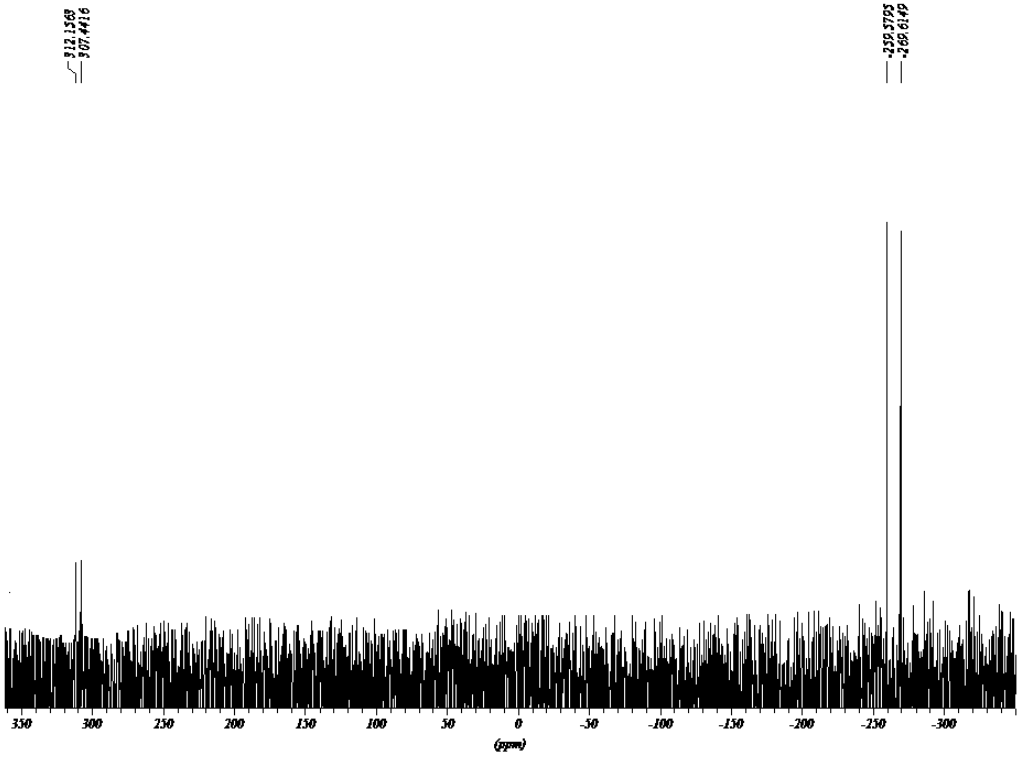

328.1349
318.7237
-258.1693
-268.1823
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
(ppm)

1-(2-Furylmethoxy)ethyl bis(4-chlorophenethyl)phosphinoselenothioate (3k)

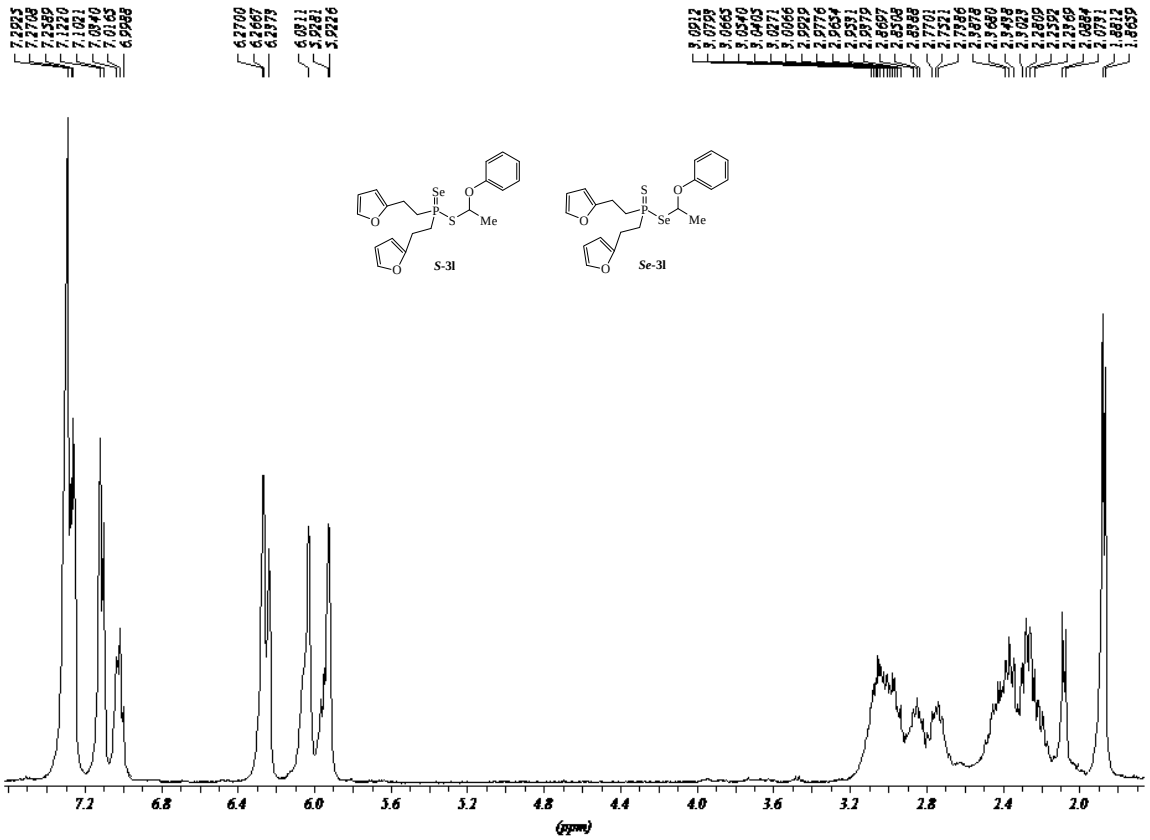


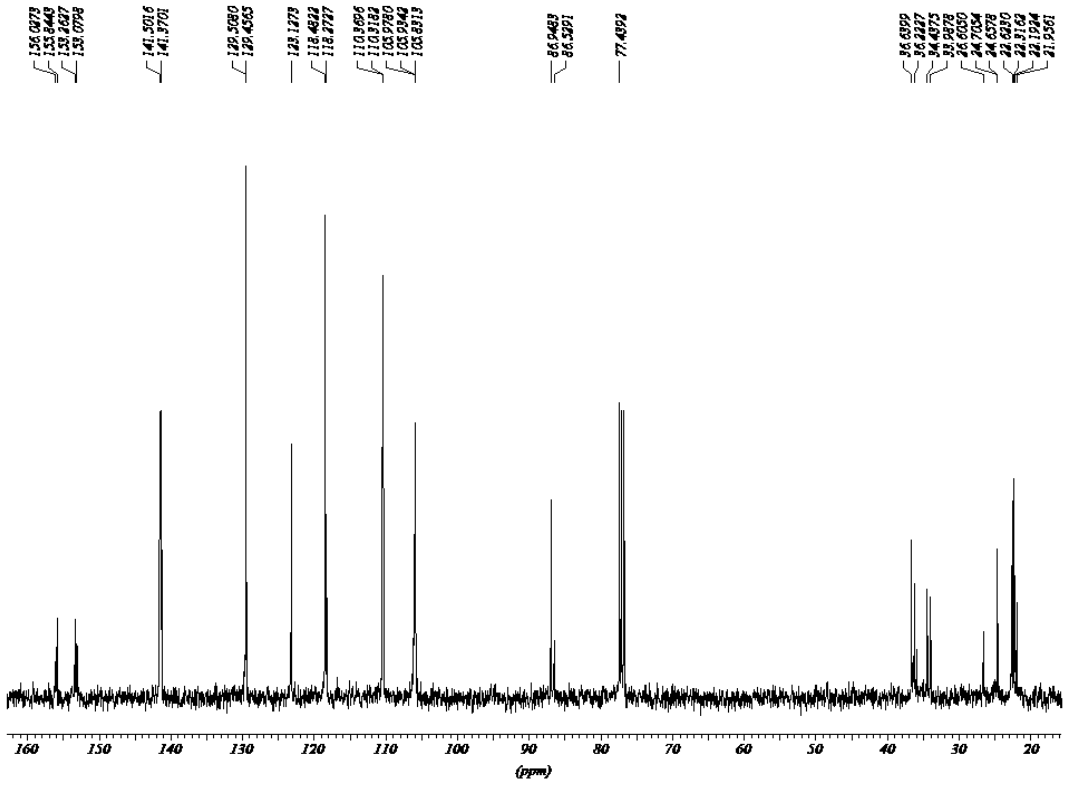


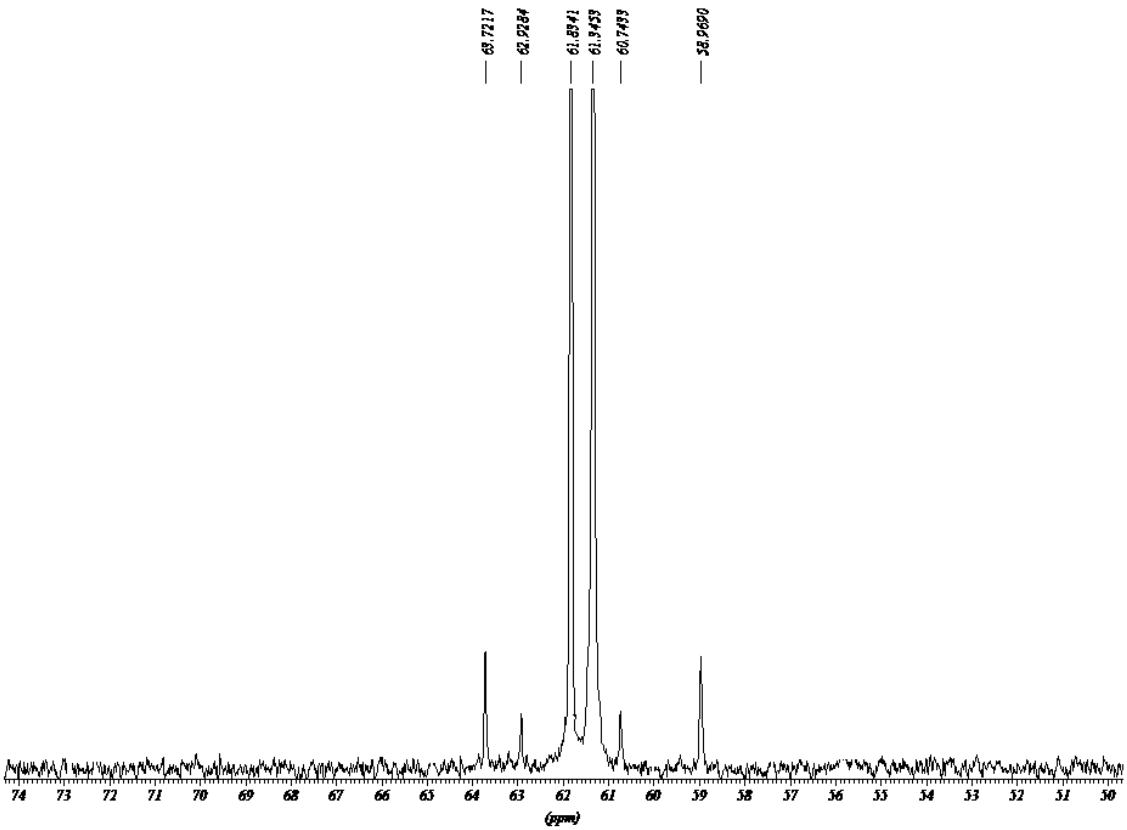

61.6853
60.8602
59.7552
59.3196
58.6467
56.9559
72 71 70 69 68 67 66 65 64 63 62 61 60 59 58 57 56 55 54 53 52 51 50 49 48 47 46
(ppm)

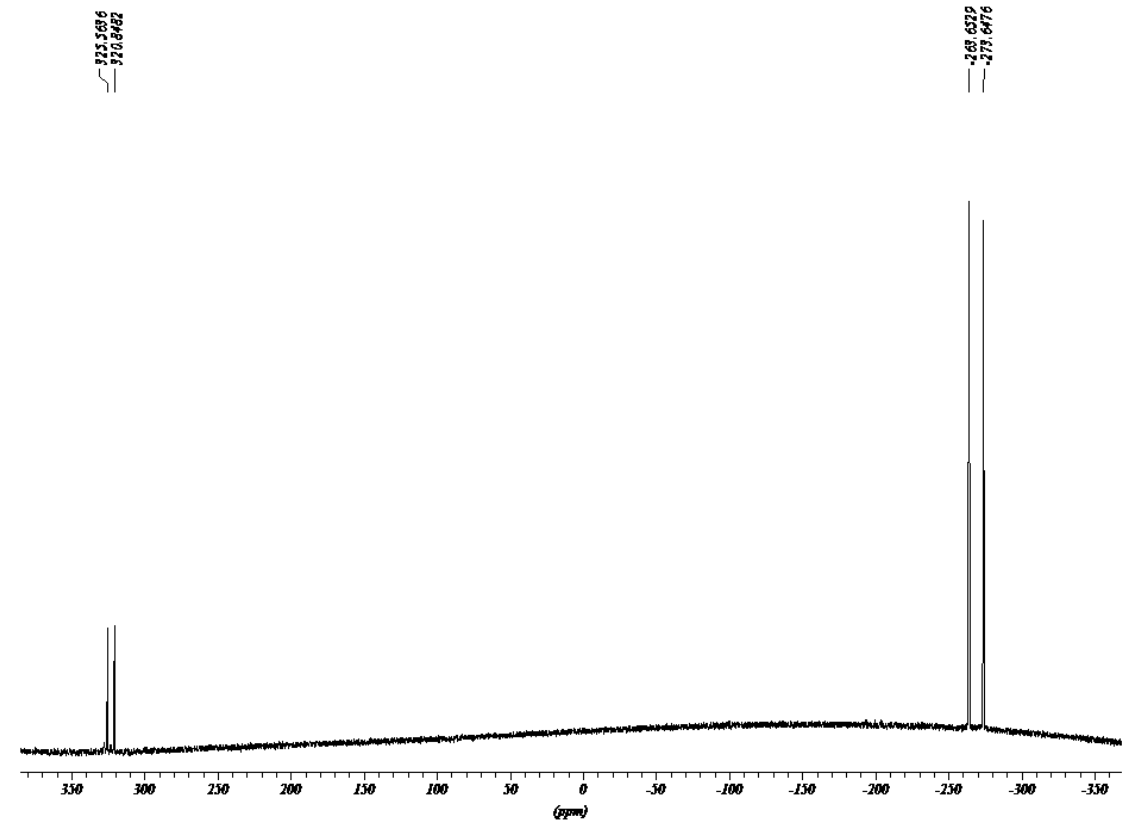

912.1569
907.4416
-259.3795
-269.6149
350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300
(ppm)

(1-Phenoxy)ethyl bis(2-furylethyl)phosphinoselenothioate (3l)

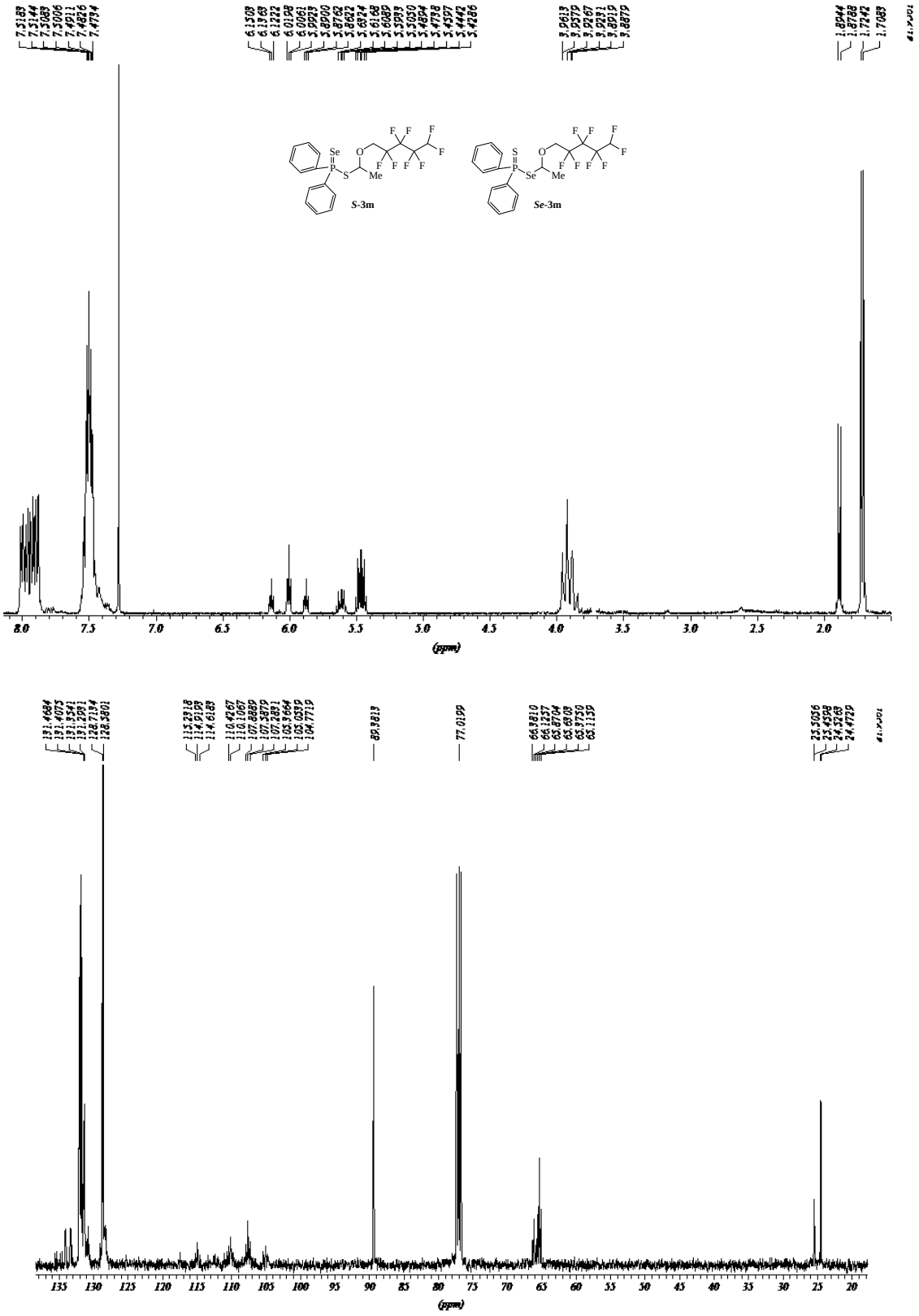


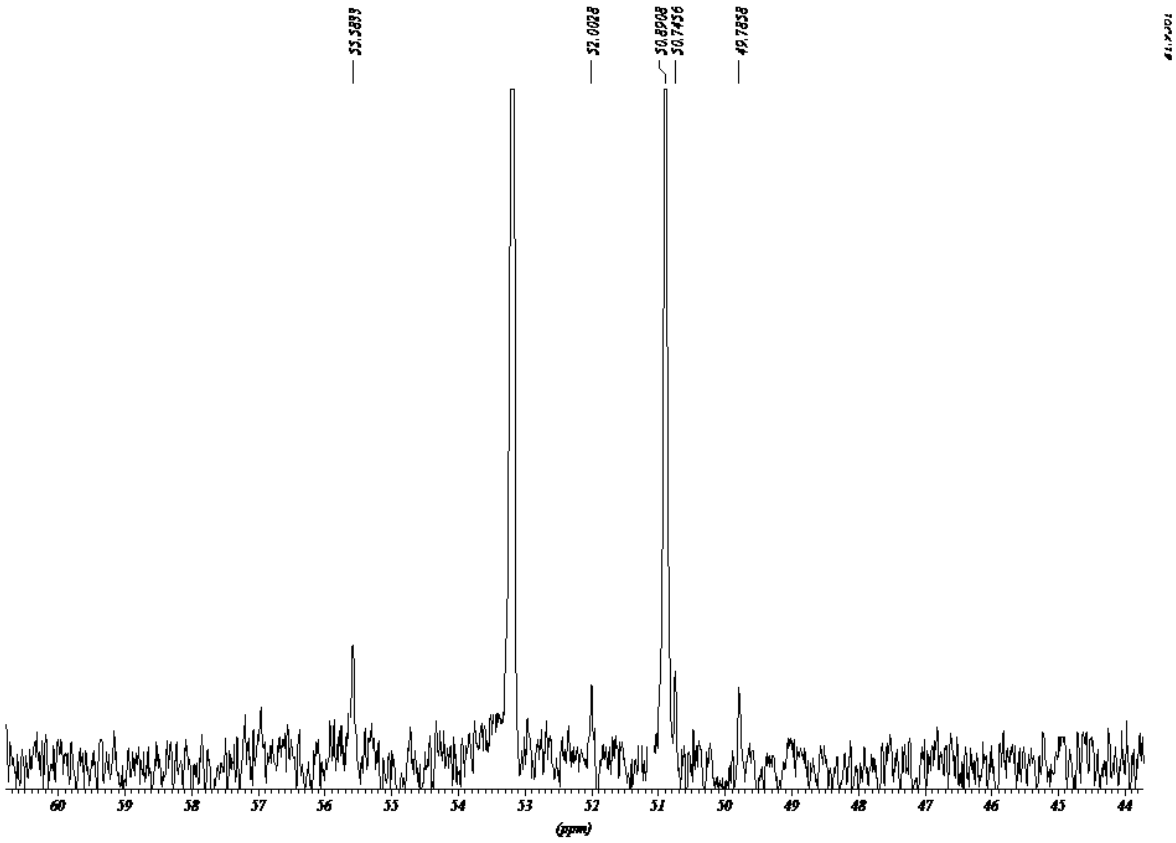



63.7217
62.9284
61.8541
61.3453
60.7493
58.9690
74 73 72 71 70 69 68 67 66 65 64 63 62 61 60 59 58 57 56 55 54 53 52 51 50
(ppm)


335.5686
320.8492
-268.6529
-273.6476
350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
(ppm)

1-[(2,2,3,3-Tetrafluoropropyl)oxy]ethyl diphenylphosphinoselenothioate (3m)

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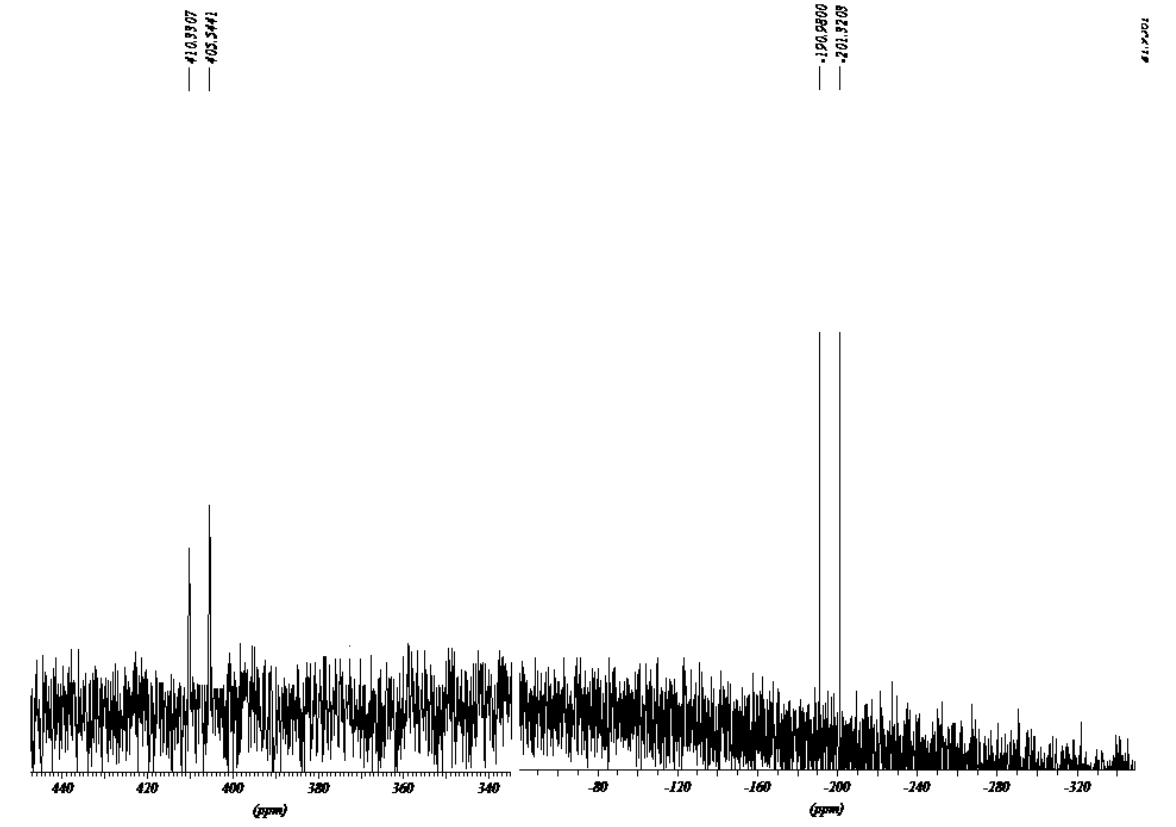
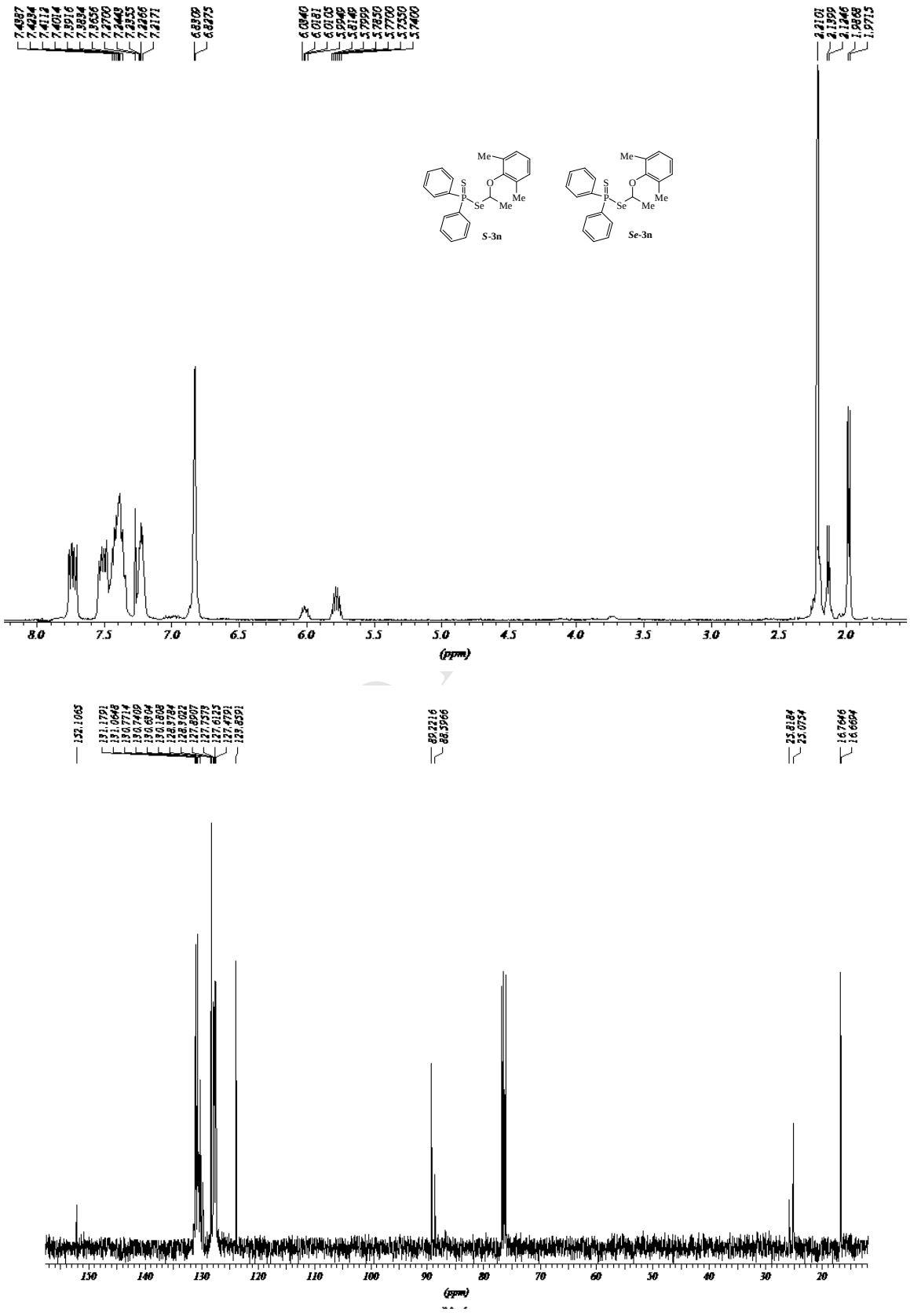
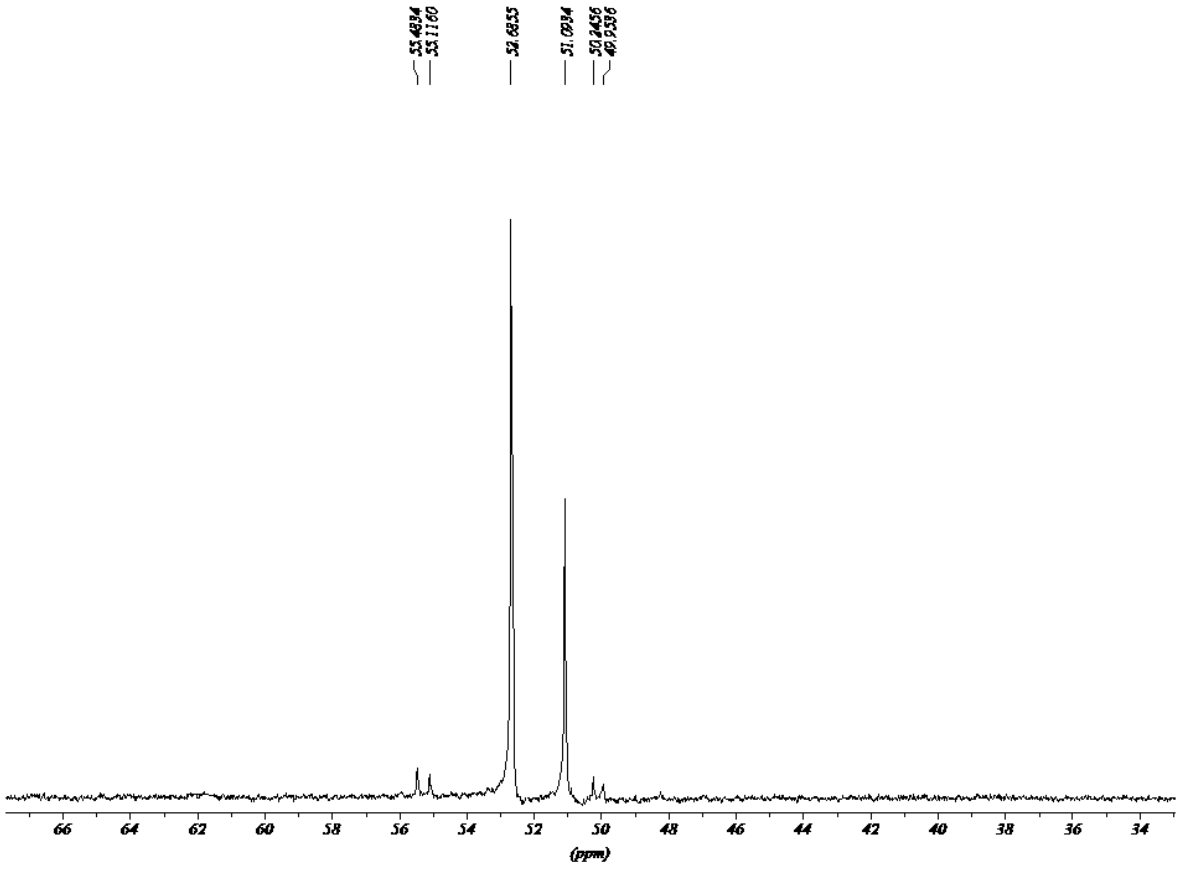
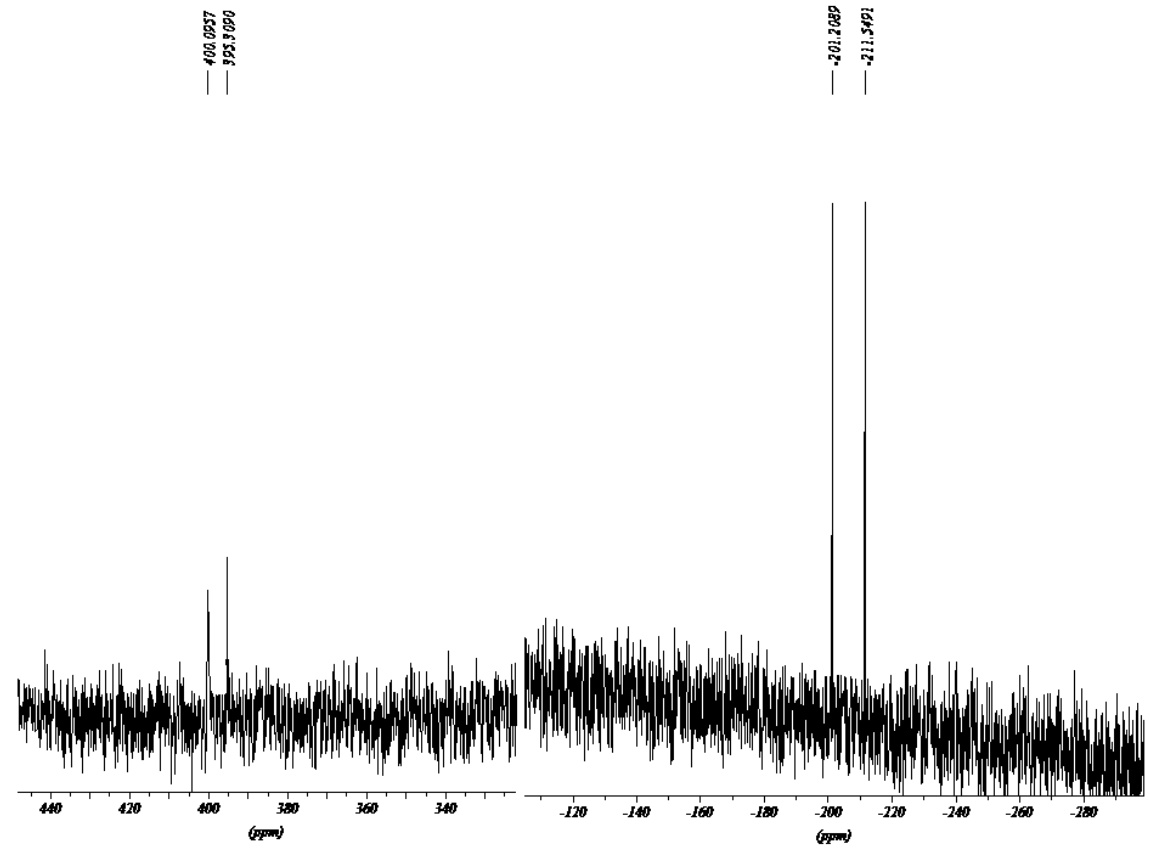
52.0028
50.8508
50.7456
49.7858
60
59
58
57
56
55
54
53
52
51
50
49
48
47
46
45
44
(ppm)


410.8507
405.5441
-190.9800
-201.9208
440
420
400
380
360
340
-80
-120
-160
-200
-240
-280
-320
(ppm)

[1-(2,6-Dimethylphenoxy)ethyl] diphenylphosphinoselenothioate (3n)




55.4834
55.1160
54.6855
51.0934
50.2456
49.9536
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
(ppm)


400.0957
399.5090
-201.2089
-211.5491
440
420
400
380
360
340
(ppm)
-120
-140
-160
-180
-200
-220
-240
-260
-280
(ppm)

Computational details

$$\omega_k^- = f_k^- \frac{\mu^2}{2\eta} \qquad \text{(a)}$$

$$\omega_k^+ = f_k^+ \frac{\mu^2}{2\eta} \qquad \text{(b)}$$

Equation S1. Here, $f_k^- = q_k(N) - q_k(N-1)$ and $f_k^+ = q_k(N+1) - q_k(N)$ are the Fukui functions at the atom *k* for electrophilic and nucleophilic attacks, respectively, q_k are atom charges in the $N-1$, N and $N+1$ electron systems with the same geometry of molecule. $\mu = (\varepsilon_{HOMO} + \varepsilon_{LUMO})/2$ is the electronic chemical potential, and $\eta = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ is the chemical hardness.

Table S1. The values [eV] of energies of the frontier orbitals (ε_{HOMO}, ε_{LUMO}), electronic chemical potentials (μ), chemical hardness (η), global electrophilicity indexes (ω), atomic charges (q_k), Fukui functions (f_k^α) and local philicity indexes (ω_k^α) (calculated using NBO [HF/6-31G(d)] analysis) for $[Cy_2PSeS]^-$ anion and $Me(PhO)HC^+$ cation

Ion	ε_{HOMO}	ε_{LUMO}	μ	η	ω	Atom	q_k	f_k^α	ω_k^α
$[Cy_2PSeS]^-$	-3.506	8.372	2.433	11.878	0.249	S	-0.814	-0.721	0.180
						Se	-0.753	-0.213	0.053
$Me(PhO)HC^+$	-13.312	-3.339	-8.325	9.972	3.475	C	0.677	-0.511	1.773

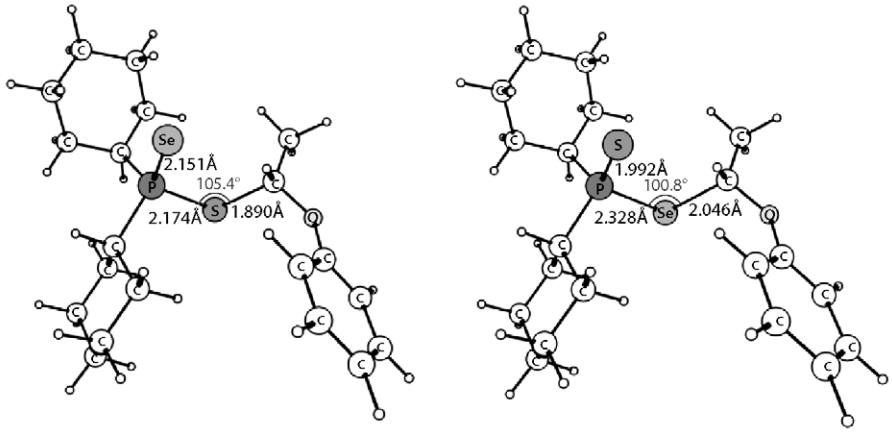


Figure S1. B3LYP/6-311++G(d,p) optimized structures of the *S*- and *Se*-esters **3a**, $Cy_2P(Se)SC(H)(Me)(OPh)$ and $Cy_2P(S)SeC(H)(Me)(OPh)$, in 1,4-dioxane solution

References

[1] Sheldrick, G. M. // SHELX-97 – Programs for Crystal Structure Analysis (Release 97-2). – University of Göttingen, Germany. – 1997.

[2] Sheldrick, G. M. SADABS.Version 2.01. Bruker AXS Inc. Madison, Wisconsin, USA, 2004.