Supporting Information for

Photochemical Halogen-Bonding Assisted Carbothiophosphorylation Reactions of Alkenyl and 1,3-Dienyl Bromides

Helena F. Piedra,† Victoria Gebler,† Carlos Valdés,† and Manuel Plaza*,†

† Departamento de Química Orgánica e Inorgánica, Instituto Universitario de Química Organometálica "Enrique Moles" and Centro de Innovación en Química Avanzada (ORFEO-CINQA). Universidad de Oviedo. Julián Clavería 8. 33006 Oviedo, Spain.

Corresponding author: plazamanuel@uniovi.es

CONTENTS

1. General considerations……..**2**
2. Continuous flow protocol.……...…….**4**
3. General procedure for the synthesis and characterization data for the compounds **3** and **5**……**6**
4. UV-Vis spectra……..……..……**35**
5. Computational studies……**36**
6. NMR titration experiments……..……**41**
7. Copies of the NMR spectra……**44**

1. General considerations

All of the vinyl bromides **1** and phosphorothioates **2** were prepared following previously reported methodologies.[1,2] The different reagents employed during the development of this work are commercially available from Sigma Aldrich Chemical co., Acros Organics Chemical co. and Alfa Aesar Chemical co. Dry DMSO stored with molecular sieves acquired from Sigma Aldrich Chemical co. was used for the photochemical reactions.

A Kessil® PR160 Rig equipped with different lamps (PR160-366nm, PR160-390nm, PR160-427nm, PR160-440nm and PR160-456nm) and a cooling fan was used as the photochemistry setup. A PR time controller was additionally used to select the irradiation time. 5 mL glass vials purchased in VWR® were used to run the photochemical reactions. The vials were sealed with a cap after adding the chemicals and solvent and placed at a distance of approximately 5 cm away from the lamp prior to irradiation at maximum intensity (100% power) of the Kessil lamp. Figures SI-1 to SI-3 illustrate relevant photophysical properties of the lamps.

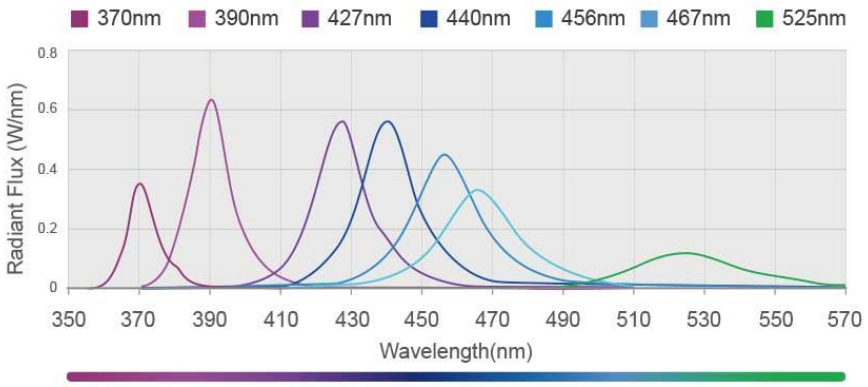


Figure SI-1. Emission spectrums of the different Kessil® lamps.

Power Consumption	370nm (max 43W), 390nm (max 52W), 427nm & 440nm (max 45W), 456nm (max 50W), 467nm (max 44W), 525nm (max 44W)
Input Voltage	100-240 VAC
Operating Temperature	0 - 40°C / 32 - 104°F
Beam Angle	56°
Wavelength Options	370nm, 390nm, 427nm, 440nm, 456nm, 467nm, 525nm
Average Intensity of PR160 series	352mW/cm2 (measured from 1 cm distance)
Dimensions (H x D)	4.49" x 2.48" / 11.4cm x 6.3cm

Figure SI-2. Technical specifications of the Kessil® lamps.

[1] a) For the synthesis of the vinyl bromides **1**, we followed a two-step sequence based on a dibromoolefination reaction of the corresponding aldehyde precursor (A. R. Silva, E. C. Polo, N. C. Martins, Correia, D. C. Roque. *Adv. Synth. Catal.* **2018**, *360*, 346.) followed by a dehalogenation reaction (Y. Ye, H. Chen, K. Yao, H. Gong. *Org. Lett.* **2020**, *22*, 2070.). b) The *cis*-configured vinyl bromide **1a'** was synthesized following this procedure: K. G. Tang, G. T. Kent, I. Erden, W. Wu. *Tetrahedron Lett.* **2017**, *58*, 3894.

[2] S. Sarkar, M. Kalek *Org. Lett.* **2023**, *25*, 671.

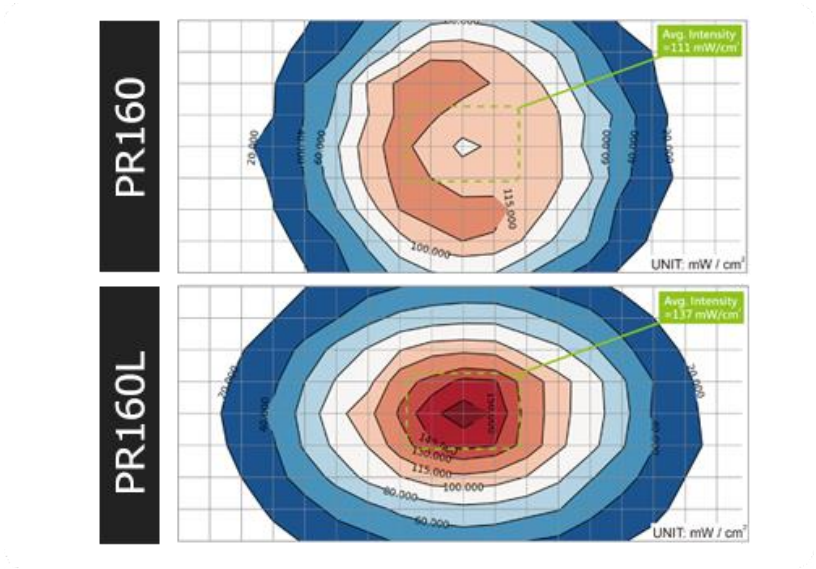


Figure SI-3. Intensity map of the Kessil® lamps.

NMR spectra were recorded in $CDCl_3$ at 600 MHz and 300 MHz for ^{1}H, 75 MHz, 100 MHz and 150 MHz for ^{13}C and 282 MHz for ^{19}F, with tetramethylsilane as internal standard for ^{1}H and the residual solvent signals as standard for ^{13}C. The data is being reported as s = singlet, bs = broad singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quatriplet, p = quintuplet and m = multiplet or unresolved, chemical shifts in ppm and coupling constant(s) in Hz. The values of the chemical shift of the signals in the NMR reports are in ppms. HRMS were measured in ESI, EI or APCI mode, and the mass analyser of the HRMS was TOF (Bruker model Impact II).

Melting points were measured in a Gallenkamp apparatus.

2. Continuous flow protocol

The Photochemical flow reactor

The flow reactor was constructed using 0.8 mm internal diameter PTFE tubing wound around a transparent, colourless polystyrene sheet measuring 10cm x 10cm. Two different panels connected in tandem were employed having a total volume of 10 mL, utilizing 20 meters of PTFE tubing. The end of the photoreactor was attached to a 20 psi back pressure regulator (BPR) through a flangeless fitting. The BPR's exit was linked to a collector flask. The initial end of the PTFE tubing in the flow reactor was connected via a flangeless fitting to a syringe containing the solution. This syringe pump was used to push the reaction solution through the reactor to the collector flask.

To provide lighting for the flow reactor, two Kessil® PR160L lamps with 390 nm wavelength were positioned at a distance of 3-7 cm from the photoreactor. These lamps were attached to a PR160 Rig with Fan Kit by Kessil to prevent overheating of the reaction due to radiation (refer to figures SI-13 and SI-14 for details).

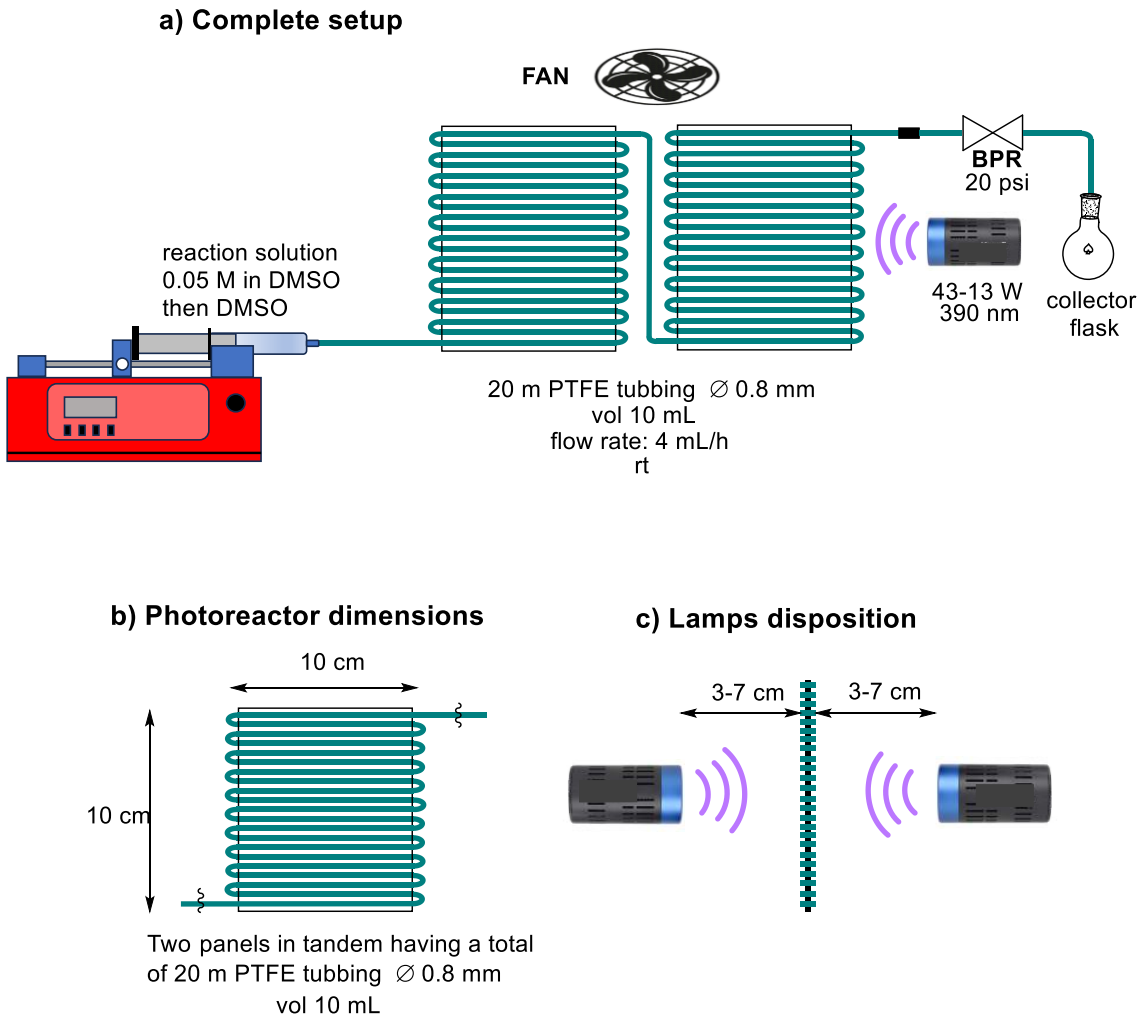


Figure SI-13. Scheme of the set up for the continuos flow reactions.

- Materials:

PTFE tubing: Ø 0.8 mm from BOLA (ref. S 1810-10)

Back pressure regulator: P-763 BPR Cartridge from IDEX health and science

LED lamps: PR160L 390 nm.

Fan kit: Kessil PR160 Rig with Fan Kit

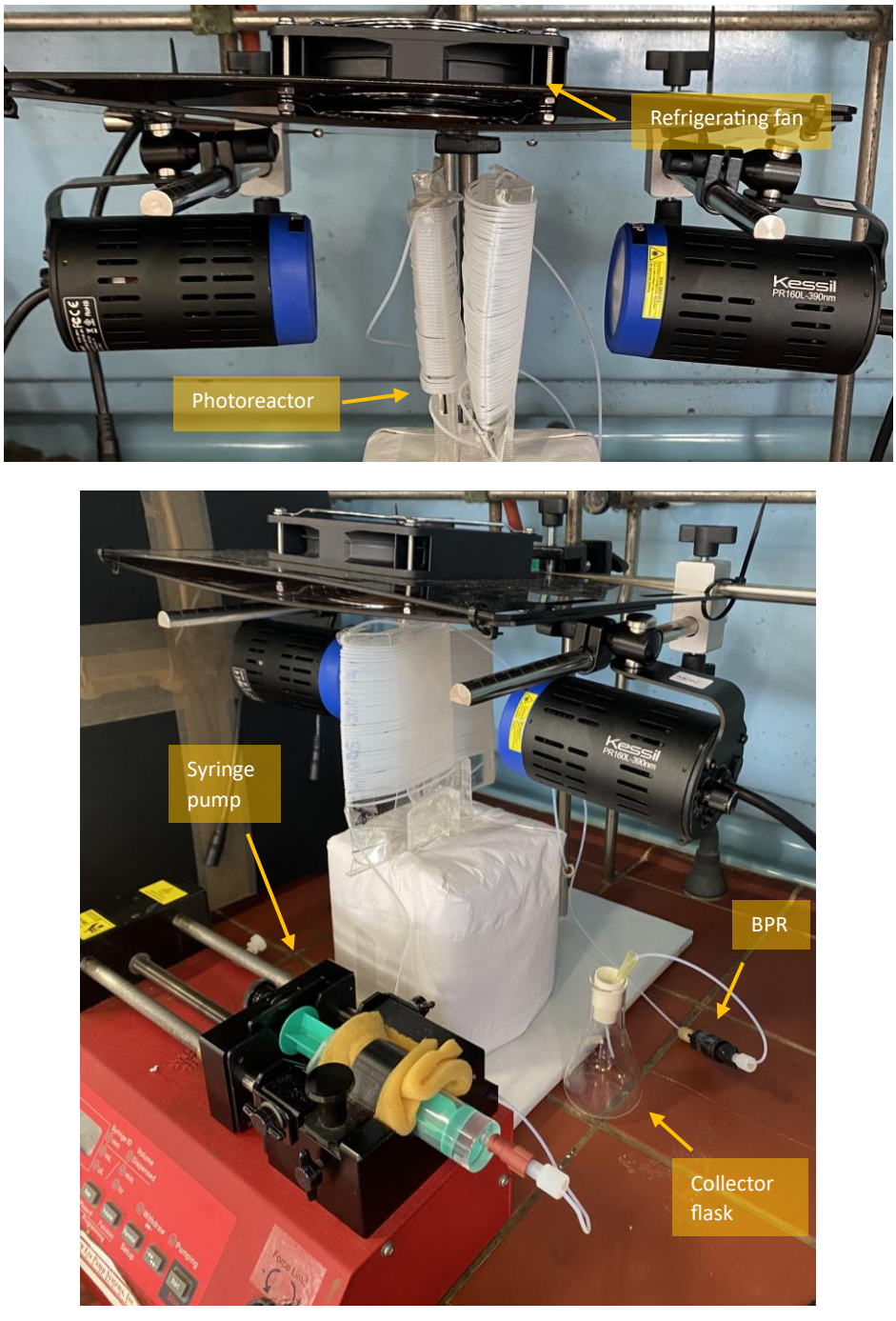
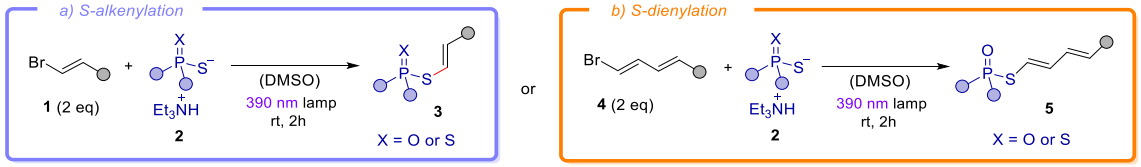


Figure SI-14. Pictures of the setup used.

3. General procedures for the synthesis and characterization data for the compounds 3 and 5.

General procedure A (under batch conditions)



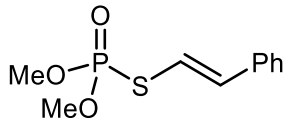
The corresponding vinyl bromide **1** (0.30 mmol), phosphorothioate **2** (0.15 mmol), and dry DMSO (3 mL) were combined in a 5 mL glass vial. The vial was sealed and positioned approximately 5 cm in front of the 390 nm Kessil® lamp. The lamp and cooling fan were turned on, and the reaction mixture was stirred at room temperature for 2 hours to ensure complete conversion. To quench the reaction, 2 mL of water was added, resulting in a heterogeneous mixture that was then diluted with 5 mL of Et_2O and transferred to a separating funnel. The aqueous phase was extracted three times with 5 mL of Et_2O, while the combined organic phases were washed with 10 mL of brine and dried using Na_2SO_4. The crude reaction was concentrated under reduced pressure and then analysed by ^{1}H-NMR or GC/MS to determine the *trans/cis* ratio. Subsequently, it underwent flash chromatography (using a Hex/EtOAc system) to yield the corresponding phosphorothioate **3**.

General procedure B (under continuous flow conditions)

A solution containing the corresponding vinyl bromide **1** (0.6 mmol) and phosphorothioate **2** (0.3 mmol) in dry DMSO (6 mL) was introduced in a syringe, placed in a high-pressure syringe pump, and linked to the photoreactor. The reaction is pumped thought the system at a rate of 4 mL/h while both lamps (two Kessil lamps PRL160 390 nm) are turned on. After the solution is introduced into the reactor, DMSO is pumped to push the reaction through the system into the collector flask. Once the reaction is collected, it is quenched by adding 15 mL of water resulting in a heterogeneous mixture. This mixture was then further diluted with 15 mL of diethyl ether (Et_2O) and subsequently transferred to a separation funnel. The aqueous phase underwent extraction three times, each with 15 mL of Et_2O, while the combined organic phases were subjected to a 20 mL brine wash and then dried using sodium sulfate (Na_2SO_4). The solvents were removed under reduced pressure and the crude reaction was purified by flash chromatography (Hexane/EtOAc) to yield the corresponding phosphorothioate **3**.

Characterization data for the compounds 3 and 5

(*E*)-*O,O*-dimethyl *S*-styryl phosphorothioate (3aa)



Following the general procedure A, a 10:1 *trans/cis* mixture of vinyl bromide **1a** (38 µL, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (26 mg, 70% isolated yield, *d.r.:* 6.8:1 *trans/cis*).

Rf = 0.38 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 6.8:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

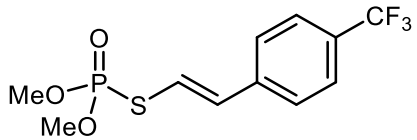
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.57 – 7.21 (m, 5H, + *cis* isom.), 6.90 (dd, *J* = 15.5, 2.3 Hz, 1H), 6.81 (d, *J* = 10.4 Hz, *cis* isom.), 6.64 (dd, *J* = 15.5, 8.3 Hz, 1H), 6.38 (dd, *J* = 12.9, 10.4 Hz, *cis* isom.), 3.86 (d, *J* = 12.9 Hz, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 137.6 (d, $^{2}J_{C\text{-}P}$ = 12.5 Hz, CH), 135.6 (C), 128.5 (CH), 128.5 (CH), 126.4 (CH), 114.0 (d,$^{3}J_{C\text{-}P}$ = 6.0 Hz, CH), 54.2 (d, $^{2}J_{C\text{-}P}$ = 5.7 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 26.6, 26.6.

HRMS [APCI(+)]: calcd. For ($[C_{10}H_{13}O_3PS]+H)^+$: 245.0396, found: 245.0398.

(*E*)-*O,O*-dimethyl *S*-(4-(trifluoromethyl)styryl) phosphorothioate (3ab)



Following the general procedure A, a 7:1 *trans/cis* mixture of vinyl bromide **1b** (75.3 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (27 mg, 58% isolated yield, *d.r.:* 6.6:1 *trans/cis*).

Rf = 0.35 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 6.6:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.57 (d, *J* = 8.2 Hz, 2H, + *cis* isom.), 7.44 (d, *J* = 8.1 Hz, 2H, + *cis* isom.), 6.95 – 6.72 (m, 2H, + *cis* isom.), 6.53 (dd, J = 13.2, 10.5 Hz, *cis* isom.), 3.86 (d, *J* = 12.9 Hz, 6H, + *cis* isom.).

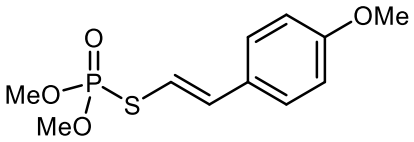
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 138.9 (C), 134.9 (d, $^{3}J_{C\text{-}P}$ = 12.8 Hz, CH), 130.0 (q, $^{2}J_{C\text{-}F}$ = 31.5 Hz, C), 126.4 (CH), 125.7 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz, CH), 118.0 (d, $^{2}J_{C\text{-}P}$ = 5.6 Hz, CH), 54.3 (d, $^{2}J_{C\text{-}P}$ = 5.8 Hz, CH_3).

^{19}F NMR (282 MHz, $CDCl_3$, 300K) δ -62.6, -62.6.

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 25.9, 25.7.

HRMS [APCI(+)]: calcd. For ($[C_{11}H_{12}F_3O_3PS]+H)^+$: 313.0207, found: 313.0273.

(*E*)-*S*-(4-methoxystyryl) *O,O*-dimethyl phosphorothioate (3ac)



Following the general procedure A, a 9:1 *trans/cis* mixture of vinyl bromide **1c** (63.9 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (25 mg, 61% isolated yield, *d.r.:* 4.6:1 *trans/cis*).

Rf = 0.27 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 4.6:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

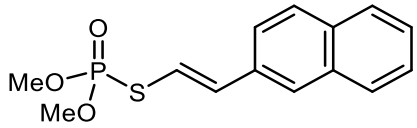
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.30 (m, 2H, + *cis* isom.), 6.98 – 6.81 (m, 3H, + *cis* isom.), 6.75 (d, *J* = 10.3 Hz, *cis* isom.), 6.45 (dd, *J* = 15.4, 7.6 Hz, 1H), 6.21 (dd, *J* = 12.4, 10.3 Hz, *cis* isom.), 3.91 – 3.79 (m, 9H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 159.9 (C), 138.0 (d, $^{3}J_{C\text{-}P}$ = 12.3 Hz, CH), 130.3 (C), 127.8 (CH), 114.1 (CH), 110.6 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, CH), 55.3 (CH_3), 54.1 (d, $^{2}J_{C\text{-}P}$ = 5.7 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 25.5, 25.2.

HRMS [APCI(+)]: calcd. For ($[C_{11}H_{15}O_4PS]+H)^+$: 275.0501, found: 275.0502.

(*E*)-*O,O*-dimethyl *S*-(2-(naphthalen-2-yl)vinyl) phosphorothioate (3ad)



Following the general procedure A, a 8.7:1 *trans/cis* mixture of vinyl bromide **1d** (69.9 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as an orange oil (44 mg, 99% isolated yield, *d.r.:* 4.6:1 *trans/cis*).

Rf = 0.39 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 4.6:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

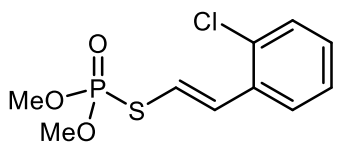
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.99 (s, *cis* isom.), 7.92 – 7.77 (m, 3H, + *cis* isom.), 7.73 (s, 1H), 7.68 – 7.41 (m, 3H, + *cis* isom.), 7.06 (dd, *J* = 15.5, 2.2 Hz, 1H), 6.96 (d, *J* = 10.4 Hz, *cis* isom.), 6.78 (dd, *J* = 15.5, 8.4 Hz, 1H), 6.47 (d, *J* = 12.9, 10.4 Hz, *cis* isom.), 3.89 (q, *J* = 13.0 Hz, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 137.6 (d, $^{2}J_{C\text{-}P}$ = 12.6 Hz, CH), 133.4 (C), 133.3 (C), 133.3 (C), 133.1 (C), 128.5 (CH), 128.2 (CH), 127.7 (CH), 126.6 (CH), 126.5 (CH), 126.4 (CH), 123.1 (CH), 114.3 (d, $^{3}J_{C\text{-}P}$ = 6.1 Hz, CH), 54.2 (d, $^{2}J_{C\text{-}P}$ = 5.7 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 26.6, 26.5.

HRMS [APCI(+)]: calcd. For ($[C_{14}H_{15}O_3PS]+H)^+$: 295.0552, found: 295.0558.

(*E*)-*S*-(2-chlorostyryl) *O,O*-dimethyl phosphorothioate (3ae)



Following the general procedure A, a 7.2:1 *trans/cis* mixture of vinyl bromide **1e** (65.2 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (29 mg, 69% isolated yield, *d.r.:* 2.7:1 *trans/cis*).

Rf = 0.45 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 2.7:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

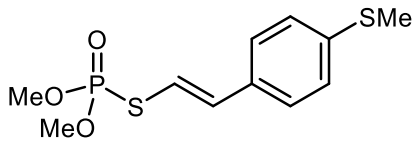
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.66 – 7.14 (m, 4H, + *cis* isom.), 7.01 (d, J = 10.3 Hz, *cis* isom.), 6.69 (dd, J = 15.5, 8.9 Hz, 1H), 6.53 (dd, J = 12.1, 10.2 Hz, *cis* isom.), 3.87 (d, J = 12.9 Hz, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 133.8 (C), 133.1 (d, $^{2}J_{C\text{-}P}$ = 12.8 Hz, CH), 132.7 (C), 129.8 (CH), 129.4 (CH), 127.0 (CH), 126.8 (CH), 117.6 (d, $^{3}J_{C\text{-}P}$ = 5.7 Hz, CH), 54.2 (d, $^{2}J_{C\text{-}P}$ = 5.6 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 26.3, 26.2.

HRMS [APCI(+)]: calcd. For $([C_{10}H_{12}ClO_3PS]+H)^+$: 279.0006, found: 279.0009.

(*E*)-*O,O*-dimethyl *S*-(4-(methylthio)styryl) phosphorothioate (3af)



Following the general procedure A, a 8:2 *trans/cis* mixture of vinyl bromide **1f** (68.7 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (23 mg, 53% isolated yield, *d.r.:* 1.8:1 *trans/cis*).

Rf = 0.38 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 1.8:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

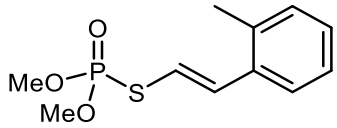
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.37 – 7.10 (m, 4H, + *cis* isom.), 6.84 (dd, *J* = 15.5, 2.3 Hz, 1H), 6.74 (d, *J* = 10.4 Hz, *cis* isom.), 6.58 (dd, *J* = 15.5, 8.2 Hz, 1H), 6.31 (dd, J = 12.7, 10.4 Hz, *cis* isom.), 3.86 (d, *J* = 12.8 Hz, 6H, + *cis* isom.), 2.50 (s, 3H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 139.3 (C), 137.1 (d, $^{2}J_{C\text{-}P}$ = 12.4 Hz, CH), 132.4 (C), 126.7 (CH), 126.3 (CH), 112.99 (d, $^{3}J_{C\text{-}P}$ = 6.1 Hz, CH), 54.20 (d, $^{2}J_{C\text{-}P}$ = 5.6 Hz, CH_3), 15.49 (CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 26.6, 26.4.

HRMS [APCI(+)]: calcd. For $([C_{11}H_{15}O_3PS_2]+H)^+$: 291.0273, found: 291.0275.

(*E*)-*O,O*-dimethyl *S*-(2-methylstyryl) phosphorothioate (3ag)



Following the general procedure A, a 4.8:1 *trans/cis* mixture of vinyl bromide **1g** (59.1 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (21 mg, 54% isolated yield, *d.r.:* 4.3:1 *trans/cis*).

Rf =0.49 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 4.3:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

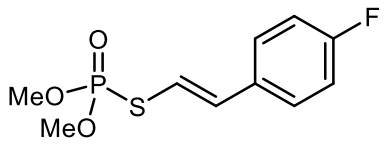
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.45 – 7.06 (m, 4H, *cis* isom.), 6.90 (d, *J* = 10.0 Hz, *cis* isom.), 6.58 – 6.36 (m, 1H, + *cis* isom.), 3.83 (d, *J* = 12.8 Hz, 6H, + *cis* isom.), 2.31 (s, 3H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 135.9 (d, $^{2}J_{C\text{-}P}$ = 12.2 Hz), 135.3 (C), 134.8 (C), 130.5 (CH), 128.4 (CH), 126.3 (CH), 125.7 (CH), 114.90 (d, $^{3}J_{C\text{-}P}$ = 6.1 Hz), 54.14 (d, $^{2}J_{C\text{-}P}$ = 5.5 Hz, CH_3), 19.78 (CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 27.2, 26.8.

HRMS [APCI(+)]: calcd. For $([C_{11}H_{15}O_3PS]+H)^+$: 259.0552, found: 259.0554.

(*E*)-*S*-(4-fluorostyryl) *O,O*-dimethyl phosphorothioate (3ah)



Following the general procedure A, a 7:1 *trans/cis* mixture of vinyl bromide **1h** (60.4 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (37 mg, 95% isolated yield, *d.r.:* 4.9:1 *trans/cis*).

Rf = 0.37 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 4.9:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.54 – 7.23 (m, 2H, + *cis* isom.), 7.14 – 6.95 (m, 2H, + *cis* isom.), 6.84 (dd, *J* = 15.5, 2.3 Hz, 1H), 6.74 (d, *J* = 10.4 Hz, *cis* isom.), 6.54 (dd, *J* = 15.5, 8.2 Hz, 1H), 6.33 (d, *J* = 12.7, 10.4 Hz, *cis* isom.), 3.84 (d, *J* = 12.8, 6H, + *cis* isom.).

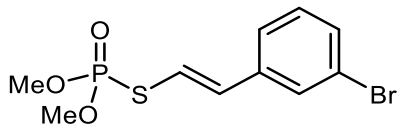
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 162.8 (d, $^{1}J_{C\text{-}F}$ = 248.8 Hz, C), 136.4 (d, $^{2}J_{C\text{-}P}$ = 12.5 Hz, CH), 131.9 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz, C), 128.0 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz, CH), 115.8 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, CH), 113.7 (dd, $^{3}J_{C\text{-}P}$ = 6.2, $^{5}J_{C\text{-}F}$ =2.6 Hz, CH), 54.2 (d, $^{2}J_{C\text{-}P}$ = 5.8 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 26.5, 26.2.

^{19}F NMR (282 MHz, $CDCl_3$, 300K) δ -112.6, -112.7.

HRMS [APCI(+)]: calcd. For ($[C_{10}H_{12}FO_3PS]+H)^+$: 263.0302, found: 263.0302.

(*E*)-*S*-(3-bromostyryl) *O,O*-dimethyl phosphorothioate (3ai)



Batch reaction: Following the general procedure A, a 7.2:1 *trans/cis* mixture of vinyl bromide **1i** (78.6 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1

Hex/EtOAc), the product was obtained as a yellow oil (20 mg, 40% isolated yield, *d.r.:* 3.6:1 *trans/cis*).

Continuous flow reaction: Using procedure B, a 7.2:1 *trans/cis* mixture of vinyl bromide **1i** (157.2 mg, 0.6 mmol) and the phosphorothioate **2a** (73.2 mg, 0.3 mmol) were dissolved in 6 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (52 mg, 54% isolated yield, *d.r.:* 3.2:1 *trans/cis*).

Rf = 0.52 (1:1 Hex/EtOAc) [UV] [Vanillin]

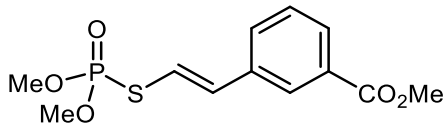
A 3.6:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.63 (s, *cis* isom.), 7.49 (s, 1H), 7 7.45 – 7.34 (m, 1H, + *cis* isom.), 7.31 – 7.15 (m, 2H, + *cis* isom.), 6.79 (d, *J* = 15.7 Hz, 1H), 6.74 – 6.59 (m, 1H, + *cis* isom.), 6.44 (dd, *J* = 13.0, 10.4 Hz, *cis* isom.), 3.85 (d, *J* = 12.6 Hz, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 137.6 (C), 135.3 (d, $^{2}J_{C-P}$ = 12.7 Hz, CH), 131.2 (CH), 130.3 (CH), 129.1 (CH), 125.0 (CH), 122.9 (C), 116.4 (d, $^{3}J_{C-P}$ = 5.8 Hz, CH), 54.7 (d, $^{2}J_{C-P}$ = 5.8 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 26.1, 25.9.

Methyl (*E*)-3-(2-((dimethoxyphosphoryl)thio)vinyl)benzoate (3aj)



Following the general procedure A, a 5.7:1 *trans/cis* mixture of vinyl bromide **1j** (72.3 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (22 mg, 48% isolated yield, *d.r.:* 3.6:1 *trans/cis*).

Rf = 0.33 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 3.6:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

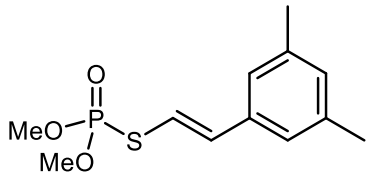
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 8.18 – 7.91 (m, 2H, + *cis* isom.), 7.60 – 7.24 (m, 2H, + *cis* isom.), 6.91 (dd, *J* = 15.6, 1.9 Hz, 1H), 6.86 – 6.80 (m, *cis* isom.), 6.74 (dd, *J* = 15.5, 8.5 Hz, 1H), 6.47 (dd, *J* = 12.9, 10.4 Hz, *cis* isom.), 3.94 (s, 3H, + *cis* isom.), 3.89 (d, *J* = 12.8 Hz, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 166.7 (C), 136.1 (d, $^{2}J_{C\text{-}P}$ = 12.6 Hz, CH), 135.9 (C), 130.6 (CH), 129.3 (CH), 128.9 (CH), 127.3 (CH), 115.9 (d, $^{3}J_{C\text{-}P}$ = 5.9 Hz, CH), 54.2 (d, $^{2}J_{C\text{-}P}$ = 5.8 Hz, CH_3), 52.3 (CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 26.2, 26.1.

HRMS [APCI(+)]: calcd. For $([C_{12}H_{15}O_5PS]+H)^+$: 303.0451, found: 303.0452.

(*E*)-*S*-(3,5-dimethylstyryl) *O,O*-dimethyl phosphorothioate (3ak)



Batch reaction: Following the general procedure A, a 8.6:1 *trans/cis* mixture of vinyl bromide **1k** (63.3 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (14 mg, 33% isolated yield, *d.r.:* 4.8:1 *trans/cis*).

Continuous flow reaction: Using procedure B, a 8.6:1 *trans/cis* mixture of vinyl bromide **1k** (126.6 mg, 0.6 mmol) and the phosphorothioate **2a** (73.2 mg, 0.3 mmol) were dissolved in 6 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (51 mg, 61% isolated yield, *d.r.:* 8.6:1 *trans/cis*).

Rf = 0.48 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 4.8:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.14 (s, 1H), 7.03 – 6.92 (m, 2H, + *cis* isom.), 6.84 (dd, *J* = 15.5, 2.3 Hz, 1H), 6.74 (d, *J* = 10.4 Hz, *cis* isom.), 6.60 (dd, *J* = 15.5, 8.1 Hz,

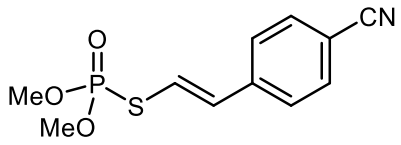
1H), 6.31 (dd, *J* = 13.0, 10.4 Hz, *cis* isom.), 3.88 (d, *J* = 12.8 Hz, 6H, + *cis* isom.), 2.32 (s, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 138.3 (C), 138.0 (d, $^2J_{C\text{-}P}$ = 12.4 Hz, CH), 135.5 (C), 130.3 (CH), 124.2 (CH), 113.2 (d, $^3J_{C\text{-}P}$ = 6.1 Hz, CH), 54.1 (d, $^2J_{C\text{-}P}$ = 5.5 Hz, CH_3), 21.2 (CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 26.9.

HRMS [APCI(+)]: calcd. For $([C_{12}H_{17}O_3PS]+H)^+$: 273.0709, found: 273.0713.

(*E*)-*S*-(4-cyanostyryl) *O,O*-dimethyl phosphorothioate (3al)



Following the general procedure A, a 10:1 *trans/cis* mixture of vinyl bromide **1l** (62.4 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (14 mg, 35% isolated yield, *d.r.:* 7:1 *trans/cis*).

Rf = 0.22 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 7:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

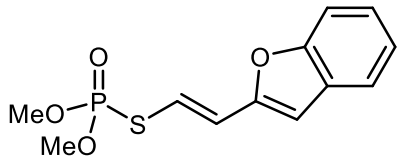
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.73 – 7.56 (m, 2H, + *cis* isom.), 7.45 (d, *J* = 8.4 Hz, 2H, + *cis* isom.), 6.95 – 6.81 (m, 2H), 6.79 (d, *J* = 10.6 Hz, *cis* isom.), 6.62 (dd, *J* = 13.4, 10.6 Hz, *cis* isom.), 3.89 (d, *J* = 12.9 Hz, 12H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 139.9 (C), 134.0 (d, $^2J_{C\text{-}P}$ = 12.9 Hz, CH), 132.6 (CH), 126.7 (CH), 120.0 (d, $^3J_{C\text{-}P}$ = 5.4 Hz, CH), 118.7 (C), 111.5 (C), 54.4 (d, $^2J_{C\text{-}P}$ = 5.8 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 25.5, 25.2.

HRMS [APCI(+)]: calcd. For $([C_{11}H_{12}NO_3PS]+H)^+$: 270.0348, found: 270.0352.

(*E*)-*S*-(2-(benzofuran-2-yl)vinyl) *O,O*-dimethyl phosphorothioate (3am)



Following the general procedure A, a 2.8:1 *trans/cis* mixture of vinyl bromide **1m** (70 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (21 mg, 50% isolated yield, *d.r.:* 3.5:1 *trans/cis*).

Rf = 0.36 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 3.5:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

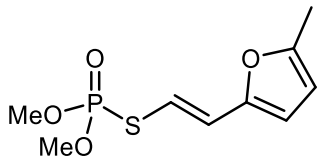
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.71 – 7.42 (m, 2H, + *cis* isom.), 7.42 – 7.14 (m, 2H, + *cis* isom.), 7.04 – 6.68 (m, 2H, + *cis* isom.), 6.61 (s, 1H, + *cis* isom.), 6.58 – 6.43 (m, *cis* isom.), 3.91 (d, *J* = 12.7 Hz, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 154.9 (C), 152.7 (C), 128.5 (C), 125.1 (CH), 124.5 (d, $^{2}J_{C\text{-}P}$ = 13.2 Hz, CH), 123.1 (CH), 121.2 (CH), 116.6 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, CH), 111.1 (CH), 105.5 (CH), 54.3 (d, $^{2}J_{C\text{-}P}$ = 5.5 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 26.3, 25.7.

HRMS [APCI(+)]: calcd. For $([C_{12}H_{13}O_3PS])^{+}$: 284.0272, found: 284.0269.

(*E*)-*O,O*-dimethyl *S*-(2-(5-methylfuran-2-yl)vinyl) phosphorothioate (3an)



Following the general procedure A, a 1.4:1 *trans/cis* mixture of vinyl bromide **1n** (56.1 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (12 mg, 33% isolated yield, *d.r.:* 2:1 *trans/cis*).

Rf = 0.43 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 2:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

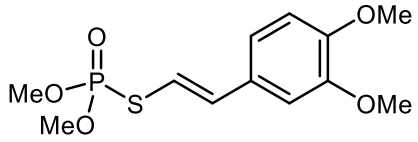
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 6.60 (dd, *J* = 15.2, 2.6 Hz, 1H), 6.54 (d, *J* = 10.5 Hz, *cis* isom.), 6.47 (d, *J* = 3.4 Hz, *cis* isom.), 6.38 (dd, *J* = 15.2, 8.3 Hz, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 6.13 – 6.03 (m, 1H, + *cis* isom.), 5.99 – 5.94 (m, 1H), 3.85 (d, *J* = 12.8 Hz, 6H, + *cis* isom.), 2.29 (s, 3H, + *cis* isom.).

^{13}C NMR (101 MHz, $CDCl_3$, 300K) δ 153.3 (C), 149.7 (d, $^{4}J_{C\text{-}P}$ = 1.5 Hz, C), 126.4 (d, $^{2}J_{C\text{-}P}$ = 12.8 Hz, CH), 110.7 (d, $^{5}J_{C\text{-}P}$ = 1.4 Hz, CH), 109.5 (d, $^{3}J_{C\text{-}P}$ = 7.0 Hz, CH), 107.6 (CH), 54.1 (d, $^{2}J_{C\text{-}P}$ = 5.5 Hz, CH_3), 13.7 (CH_3).

^{31}P NMR (162 MHz, $CDCl_3$, 300K) δ 26.8, 26.4.

HRMS [APCI(+)]: calcd. For ($[C_9H_{13}O_4PS]+H)^+$: 249.0345, found: 249.0344.

(*E*)-*S*-(3,4-dimethoxystyryl) *O,O*-dimethyl phosphorothioate (3ao)



Batch reaction: Following the general procedure A, a 12:1 *trans/cis* mixture of vinyl bromide **1o** (72.9 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as an orange oil (23 mg, 49% isolated yield, *d.r.:* 1.6:1 *trans/cis*).

Continuous flow reaction: Using procedure B, a 12:1 *trans/cis* mixture of vinyl bromide **1o** (145.9 mg, 0.6 mmol) and the phosphorothioate **2a** (73.2 mg, 0.3 mmol) were dissolved in 6 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (49 mg, 54% isolated yield, *d.r.:* 1.2:1 *trans/cis*).

Rf = 0.23 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 1.6:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

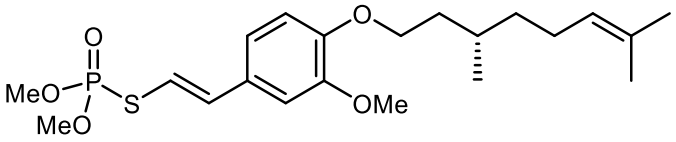
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.15 – 7.02 (m, 1H, + *cis* isom.), 6.93 – 6.77 (m, 3H, + *cis* isom.), 6.71 (d, J = 10.4 Hz, *cis* isom.), 6.44 (dd, J = 15.4, 7.7 Hz, 1H), 6.20 (dd, J = 12.6, 10.3 Hz, *cis* isom.), 3.99 – 3.76 (m, 12H, + *cis* isom.).

^{13}C NMR (101 MHz, $CDCl_3$, 300K) δ 149.6 (C), 149.1 (C), 138.2 (d, $^{2}J_{C\text{-}P}$ = 12.4 Hz, CH), 128.7 (C), 120.0 (CH), 111.0 (CH), 110.9 (d, $^{3}J_{C\text{-}P}$ = 6.9 Hz, CH), 108.6 (CH), 55.9 (CH_3), 55.9 (CH_3), 54.2 (d, $^{2}J_{C\text{-}P}$ = 5.8 Hz, CH_3).

^{31}P NMR (162 MHz, $CDCl_3$, 300K) δ 26.9, 26.6.

HRMS [APCI(+)]: calcd. For ($[C_{12}H_{17}O_5PS]+H)^+$: 305.0607, found: 305.0613.

(*E*)-*S*-(4-((3,7-dimethyloct-6-en-1-yl)oxy)-3-methoxystyryl) *O,O*-dimethyl phosphorothioate (3ap)



Batch reaction: Following the general procedure A, a 9.6:1 *trans/cis* mixture of vinyl bromide **1p** (110.2 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained a yellow oil (32 mg, 50% isolated yield, *d.r.:* 3:1 *trans/cis*).

Continuous flow reaction: Using procedure B, a 9.6:1 *trans/cis* mixture of vinyl bromide **1p** (220.4 mg, 0.6 mmol) and the phosphorothioate **2a** (73.2 mg, 0.3 mmol) were dissolved in 6 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (70 mg, 54% isolated yield, *d.r.:* 4.3:1 *trans/cis*).

Rf = 0.41 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 3:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.15 – 6.99 (m, 1H, + *cis* isom.), 6.95 – 6.77 (m, 3H, + *cis* isom.), 6.73 (d, *J* = 10.4 Hz, *cis* isom.), 6.46 (dd, *J* = 15.4, 7.6 Hz, 1H), 6.21 (dd, *J* = 12.6, 10.3 Hz, *cis* isom.), 5.17 – 5.05 (m, 1H, + *cis* isom.), 4.15 – 3.97 (m, 2H, + *cis* isom.), 3.95 – 3.74 (m, 9H, + *cis* isom.), 2.20 – 1.78 (m, 4H, + *cis* isom.), 1.70 (s, 3H, +

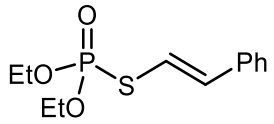
cis isom.), 1.62 (s, 3H, + *cis* isom.), 1.53 – 1.10 (m, 3H, + *cis* isom.), 0.97 (d, *J* = 6.3 Hz, 3H, + *cis* isom.)

^{13}C NMR (101 MHz, $CDCl_3$, 300K) δ 149.5 (C), 149.2 (C), 138.3 (d, $^2J_{C\text{-}P}$ = 12.3 Hz, CH), 131.3 (C), 128.6 (C), 124.6 (CH), 120.0 (CH), 112.5 (CH), 110.67 (d, $^3J_{C\text{-}P}$ = 6.4 Hz, CH), 109.1 (CH), 67.4 (CH_2), 56.1 (CH_3), 54.2 (d, $^2J_{C\text{-}P}$ = 5.7 Hz, CH_3), 37.1 (CH_2), 35.9 (CH_2), 29.6 (CH), 25.7 (CH_3), 25.4 (CH_2), 19.6 (CH_3), 17.7 (CH_3).

^{31}P NMR (162 MHz, $CDCl_3$, 300K) δ 26.7, 26.7.

HRMS [APCI(+)]: calcd. For ($[C_{21}H_{33}O_5PS]+H)^+$: 429.1860, found: 429.1855.

(*E*)-*O,O*-diethyl *S*-styryl phosphorothioate (3ba)



Following the general procedure A, a 10:1 *trans/cis* mixture of vinyl bromide **1a** (38 µL, 0.3 mmol) and the phosphorothioate **2b** (40.7 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as an orange oil (35 mg, 86% isolated yield, *d.r.:* 5.8:1 *trans/cis*).

Rf = 0.49 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 5.8:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

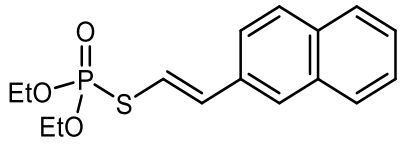
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.57 – 7.21 (m, 5H, + *cis* isom.), 6.87 (dd, *J* = 15.5, 2.1 Hz, 1H), 6.78 (d, *J* = 10.5 Hz, *cis* isom.), 6.68 (dd, *J* = 15.5, 8.4 Hz, 1H), 6.41 (dd, *J* = 13.0, 10.4 Hz, *cis* isom.), 4.38 – 4.12 (m, 4H, + *cis* isom.), 1.39 (t, *J* = 7.0 Hz, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 137.0 (d, $^2J_{C\text{-}P}$ = 12.6 Hz, CH), 135.8 (C), 128.7 (CH), 128.4 (CH), 126.3 (CH), 114.8 (CH) (d, $^3J_{C\text{-}P}$ = 6.0 Hz, CH), 64.1 (d, $^2J_{C\text{-}P}$ = 5.7 Hz, CH_2), 16.1 (d, $^3J_{C\text{-}P}$ = 7.0 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 23.1, 23.0.

HRMS [APCI(+)]: calcd. For ($[C_{12}H_{17}O_3PS]+H)^+$: 273.0709, found: 273.0713.

(*E*)-*O,O*-diethyl *S*-2-(naphthalen-2-yl)vinyl) phosphorothioate (3bd)



Following the general procedure A, a 8.7:1 *trans/cis* mixture of vinyl bromide **1d** (69.9 mg, 0.3 mmol) and the phosphorothioate **2b** (40.7 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as an orange oil (37 mg, 77% isolated yield, *d.r.:* 1.7:1 *trans/cis*).

Rf = 0.50 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 1.7:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

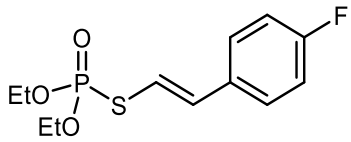
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.99 (s, *cis* isom.), 7.93 – 7.77 (m, 3H, + *cis* isom.), 7.73 (s, 1H), 7.69 – 7.44 (m, 3H, + *cis* isom.), 7.04 (dd, *J* = 15.5, 2.1 Hz, 1H), 6.94 (d, *J* = 10.5 Hz, *cis* isom.), 6.82 (dd, *J* = 15.5, 8.5 Hz, 1H), 6.51 (dd, *J* = 13.1, 10.4 Hz, *cis* isom.), 4.41 – 4.12 (m, 4H, + *cis* isom.), 1.46 – 1.38 (m, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 137.0 (d, $^{2}J_{C\text{-}P}$ = 12.4 Hz, CH), 133.4 (C), 133.2 (C), 133.2 (C), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.7 (CH), 126.6 (CH), 126.5 (CH), 123.1 (CH) , 115.1 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, CH), 64.1 (d, $^{2}J_{C\text{-}P}$ = 5.6 Hz, CH_2), 16.1 (d, $^{3}J_{C\text{-}P}$ = 6.9 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 23.1, 22.9.

HRMS [APCI(+)]: calcd. For $([C_{16}H_{19}O_3PS]+H)^+$: 323.0865, found: 323.0870.

(*E*)-*O,O*-diethyl *S*-(4-fluorostyryl) phosphorothioate (3bh)



Following the general procedure A, a 7:1 *trans/cis* mixture of vinyl bromide **1h** (60.4 mg, 0.3 mmol) and the phosphorothioate **2b** (40.7 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as an orange oil (20 mg, 45% isolated yield, *d.r.:* 6.1:1 *trans/cis*).

Rf = 0.45 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 6.1:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.54 – 7.29 (m, 2H, + *cis* isom.), 7.14 – 6.96 (m, 2H, + *cis* isom.), 6.84 (dd, *J* = 15.5, 2.1 Hz, 1H), 6.74 (d, *J* = 10.5 Hz, *cis* isom.), 6.60 (dd, *J* = 15.5, 8.4 Hz, 1H), 6.39 (dd, *J* = 12.8, 10.5 Hz, *cis* isom.), 4.38 – 4.11 (m, 2H, + *cis* isom.), 1.40 (td, *J* = 7.1, 0.7 Hz, 8H, + *cis* isom.).

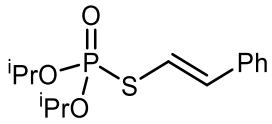
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 162.7 (d, $^{1}J_{C\text{-}F}$ = 248.4 Hz, C), 135.9 (d, $^{2}J_{C\text{-}P}$ = 12.4 Hz, CH), 132.0 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz, C), 127.9 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz, CH), 115.7 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, CH), 114.5 (dd, $^{3}J_{C\text{-}P}$ = 6.0, $^{5}J_{C\text{-}F}$ = 2.5 Hz, CH), 64.1 (d, $^{2}J_{C\text{-}P}$ = 5.7 Hz, CH_2), 16.1 (d, $^{3}J_{C\text{-}P}$ = 7.2 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 23.0, 22.7.

^{19}F NMR (282 MHz, $CDCl_3$, 300K) δ -112.8, -112.9.

HRMS [APCI(+)]: calcd. For $([C_{12}H_{16}FO_3PS]+H)^+$: 291.0615, found: 291.0619.

(*E*)-*O,O*-diisopropyl *S*-styryl phosphorothioate (3ca)



Batch reaction: Following the general procedure A, a 10:1 *trans/cis* mixture of vinyl bromide **1a** (38 µL, 0.3 mmol) and the phosphorothioate **2c** (44.9 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (11 mg, 24% isolated yield, *d.r.:* 6.6:1 *trans/cis*).

Continuous flow reaction: Using procedure B, a 10:1 *trans/cis* mixture of vinyl bromide **1a** (77 µL, 0.6 mmol) and the phosphorothioate **2c** (89.8 mg, 0.3 mmol) were dissolved in 6 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (62 mg, 68% isolated yield, *d.r.:* 6.1:1 *trans/cis*).

Rf = 0.43 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 6.6:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

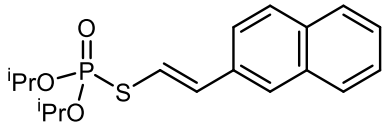
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.45 – 7.22 (m, 5H, + *cis* isom.), 6.86 (dd, *J* = 15.6, 1.9 Hz, 1H), 6.78 (d, *J* = 10.3 Hz, *cis* isom.), 6.71 (dd, *J* = 15.6, 8.6 Hz, 1H), 6.44 (dd, *J* = 13.3, 10.5 Hz, *cis* isom.), 4.95 – 4.72 (m, 2H), 1.40 (dd, *J* = 11.7, 6.2 Hz, 12H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 136.3 (d, $^{2}J_{C\text{-}P}$ = 12.5 Hz, CH), 136.0 (C), 128.7 (CH), 128.2 (CH), 126.2 (CH), 115.8 (d, $^{3}J_{C\text{-}P}$ = 5.8 Hz, CH), 73.2 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, CH), 23.9 (d, $^{3}J_{C\text{-}P}$ = 4.0 Hz, CH_3), 23.6 (d, $^{3}J_{C\text{-}P}$ = 5.7 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ. 20.5, 20.4.

HRMS [APCI(+)]: calcd. For $([C_{14}H_{21}O_3PS]+H)^+$: 301.1022, found: 301.1022.

(*E*)-*O,O*-diisopropyl *S*-2-(naphthalen-2-yl)vinyl) phosphorothioate (3cd)



Batch reaction: Following the general procedure A, a 8.7:1 *trans/cis* mixture of vinyl bromide **1d** (69.9 mg, 0.3 mmol) and the phosphorothioate **2c** (44.9 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as an orange oil (18 mg, 35% isolated yield, *d.r.:* 1.8:1 *trans/cis*).

Continuous flow reaction: Using procedure B, a 8.7:1 *trans/cis* mixture of vinyl bromide **1d** (139.8 mg, 0.6 mmol) and the phosphorothioate **2c** (89.8 mg, 0.3 mmol) were dissolved in 6 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a orange oil (85 mg, 81% isolated yield, *d.r.:* 1:1 *trans/cis*).

Rf = 0.40 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 1.8:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

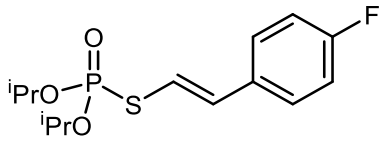
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.99 (s, *cis* isom.), 7.91 – 7.77 (m, 3H, + *cis* isom.), 7.72 (s, 1H), 7.68 – 7.40 (m, 3H, + *cis* isom.), 7.01 (dd, *J* = 15.6, 1.9 Hz, 1H), 6.92 (d, *J* = 10.5 Hz, *cis* isom.), 6.85 (dd, *J* = 15.6, 8.8 Hz, 1H), 6.53 (dd, *J* = 13.3, 10.5 Hz, *cis* isom.), 4.86 (m, 2H, + *cis* isom.), 1.48 – 1.33 (m, 12H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 136.3 (d, $^2J_{C-P}$ = 12.4 Hz), 133.5, 133.4, 133.2 (d, $^4J_{C-P}$ = 2.4 Hz), 128.5, 128.1, 127.7, 126.5, 126.4, 126.3, 123.1, 116.1 (d, $^3J_{C-P}$ = 5.7 Hz), 73.3 (d, $^2J_{C-P}$ = 5.8 Hz), 23.9 (d, $^3J_{C-P}$ = 3.8 Hz), 23.6 (d, $^3J_{C-P}$ = 5.7 Hz).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 20.4, 20.3.

HRMS [APCI(+)]: calcd. For ($[C_{18}H_{23}O_3PS]+H)^+$: 351.1178, found: 351.1179.

(*E*)-*S*-(4-fluorostyryl) *O,O*-diisopropyl phosphorothioate (3ch)



Batch reaction: Following the general procedure A, a 7:1 *trans/cis* mixture of vinyl bromide **1h** (60.4 mg, 0.3 mmol) and the phosphorothioate **2c** (44.9 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (21 mg, 43% isolated yield, *d.r.:* 6.1:1 *trans/cis*).

Continuous flow reaction: Using procedure B, a 7:1 *trans/cis* mixture of vinyl bromide **1h** (120.6 mg, 0.6 mmol) and the phosphorothioate **2c** (89.8 mg, 0.3 mmol) were dissolved in 6 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (60 mg, 63% isolated yield, *d.r.:* 3.8:1 *trans/cis*).

Rf = 0.43 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 6.1:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.41 – 7.27 (m, 2H, + *cis* isom.), 7.13 – 6.96 (m, 2H, + *cis* isom.), 6.81 (dd, *J* = 15.6, 2.0 Hz, 1H), 6.72 (d, *J* = 10.5 Hz, *cis* isom.), 6.63 (dd, *J* = 15.6, 8.7 Hz, 1H), 6.41 (dd, *J* = 13.1, 10.5 Hz, *cis* isom.), 5.01 – 4.68 (m, 2H), 1.40 (dd, *J* = 11.7, 6.2 Hz, 12H, + *cis* isom.).

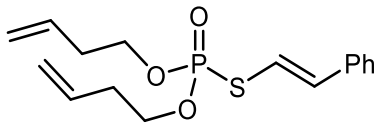
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 162.6 (d, $^1J_{C-F}$ = 248.2 Hz, C), 135.1 (d, $^2J_{C-P}$ = 12.5 Hz, CH), 132.2 (d, $^4J_{C-F}$ = 3.4 Hz, C), 127.8 (d, $^3J_{C-F}$ = 8.1 Hz, CH), 115.7 (d, $^2J_{C-F}$ = 21.8 Hz, CH), 115.5 – 115.3 (m, CH), 73.3 (d, $^2J_{C-P}$ = 6.2 Hz, CH), 23.9 (d, $^3J_{C-P}$ = 4.0 Hz, CH_3), 23.6 (d, $^3J_{C-P}$ = 5.8 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ. 20.4, 20.1.

^{19}F NMR (282 MHz, $CDCl_3$, 300K) δ -113.1, -113.1.

HRMS [APCI(+)]: calcd. For $([C_{14}H_{20}FO_3PS]+H)^+$: 319.0928, found: 319.0932.

(*E*)-*O,O*-di(but-3-en-1-yl) *S*-styryl phosphorothioate (3da)



Following the general procedure A, a 10:1 *trans/cis* mixture of vinyl bromide **1a** (38 µL, 0.3 mmol) and the phosphorothioate **2d** (48.5 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a colourless oil (13 mg, 26% isolated yield, *d.r.:* 4.2:1 *trans/cis*).

Rf = 0.55 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 4.2:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

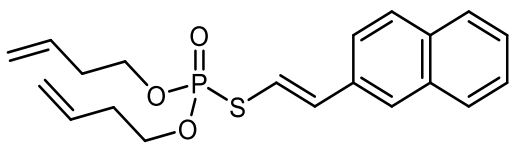
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.55 – 7.22 (m, 5H, + *cis* isom.), 6.88 (dd, *J* = 15.5, 2.2 Hz, 1H), 6.80 (d, *J* = 10.4 Hz, *cis* isom.), 6.66 (dd, *J* = 15.5, 8.4 Hz, 1H), 6.40 (dd, *J* = 13.0, 10.4 Hz, *cis* isom.), 5.91 – 5.69 (m, 2H, + *cis* isom.), 5.22 – 5.06 (m, 4H, + *cis* isom.), 4.34 – 4.07 (m, 4H, + *cis* isom.), 2.57 – 2.42 (m, 4H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 137.3 (d, $^{2}J_{C\text{-}P}$ = 12.5 Hz, CH), 135.7, (C), 133.1 (CH), 128.7 (CH), 128.4 (CH), 126.3 (CH), 118.0 (CH_2), 114.4 (d, $^{3}J_{C\text{-}P}$ = 6.2 Hz, CH), 66.9 (d, $^{2}J_{C\text{-}P}$ = 6.1 Hz, CH_2), 34.5 (d, $^{3}J_{C\text{-}P}$ = 7.1 Hz, CH_2).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 23.4, 23.3.

HRMS [APCI(+)]: calcd. For $([C_{16}H_{21}O_3PS]+H)^+$: 325.1022, found: 325.1020.

(*E*)-*O,O*-di(but-3-en-1-yl) *S*-(2-(naphthalen-2-yl)vinyl) phosphorothioate (3dd)



Following the general procedure A, a 8.7:1 *trans/cis* mixture of vinyl bromide **1d** (69.9 mg, 0.3 mmol) and the phosphorothioate **2d** (48.5 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a colourless oil (14 mg, 25% isolated yield, *d.r.:* 1.7:1 *trans/cis*).

Rf = 0.51 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 1.7:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

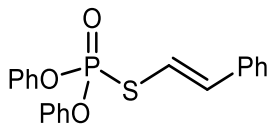
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.98 (s, *cis* isom.), 7.90 – 7.79 (m, 3H, + *cis* isom.), 7.73 (s, 1H), 7.69 – 7.43 (m, 3H, + *cis* isom.), 7.03 (dd, *J* = 15.5, 2.2 Hz, 1H), 6.95 (d, *J* = 10.4 Hz, *cis* isom.), 6.79 (dd, *J* = 15.5, 8.6 Hz, 1H), 6.48 (dd, *J* = 13.0, 10.4 Hz, *cis* isom.), 5.92 – 5.70 (m, 2H, + *cis* isom.), 5.24 – 5.06 (m, 4H, + *cis* isom.), 4.38 – 4.02 (m, 4H, + *cis* isom.), 2.59 – 2.43 (m, 4H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 137.3 (d, $^{2}J_{C\text{-}P}$ = 12.6 Hz, CH), 133.4 (C), 133.2 (C), 133.2 (CH), 132.7 (C), 128.5 (CH), 128.1 (CH), 127.7 (CH), 126.6 (CH), 126.5 (CH), 126.4 (CH), 123.1 (CH), 118.1 (CH_2), 114.8 (d, $^{3}J_{C\text{-}P}$ = 6.1 Hz, CH), 67.0 (d, $^{2}J_{C\text{-}P}$ = 6.3 Hz, CH_2), 34.5 (d, $^{3}J_{C\text{-}P}$ = 7.2 Hz, CH_2).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 23.4, 23.3.

HRMS [APCI(+)]: calcd. For $([C_{20}H_{23}O_3PS]+H)^+$:375.1178, found: 375.1182.

(*E*)-*O,O*--diphenyl *S*-styryl phosphorothioate (3fa)



Continuous flow reaction: Using procedure B, a 10:1 *trans/cis* mixture of vinyl bromide **1a** (77 µL, 0.6 mmol) and the phosphorothioate **2c** (110 mg, 0.3 mmol) were dissolved in 6 mL of dry DMSO. After purification by column chromatography (10:1 Hex/EtOAc), the product was obtained as a yellow oil (37 mg, 33% isolated yield, *d.r.:* 3.3:1 *trans/cis*).

Rf = 0.18 (10:1 Hex/EtOAc) [UV] [Vanillin]

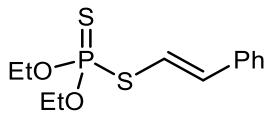
A 3.3:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.46 – 7.19 (m, 15H + *cis* isom.), 6.96 – 6.79 (m, 1H + *cis* isom.), 6.69 (dd, *J* = 15.4, 7.7 Hz, 1H), 6.52 (dd, *J* = 12.8, 10.3 Hz, *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 150.1 (d, $^{2}J_{C\text{-}P}$ = 8.0 Hz, C), 139.7 (d, $^{2}J_{C\text{-}P}$ = 13.2 Hz, CH), 135.4 (C), 129.9 (CH), 128.8 (CH), 126.5 (CH), 125.9 (CH), 120.7 (d, $^{3}J_{C\text{-}P}$ = 4.9 Hz, CH), 112.6 (d, $^{3}J_{C\text{-}P}$ = 7.1 Hz, CH).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 16.3, 15.7.

(*E*)-*O,O*-diethyl *S*-styryl phosphorodithioate (3ea)



Following the general procedure A, a 10:1 *trans/cis* mixture of vinyl bromide **1a** (38 µL, 0.3 mmol) and the dithiophosphate **2e** (30.5 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (10:1 Hex/EtOAc), the product was obtained as a colourless oil (27 mg, 62% isolated yield, *d.r.:* 4.6:1 *trans/cis*).

Rf = 0.39 (10:1 Hex/EtOAc) [UV] [Vanillin]

A 4.6:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

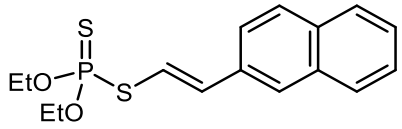
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.55 – 7.23 (m, 5H, + *cis* isom.), 6.86 (dd, *J* = 15.5, 2.5 Hz, 1H), 6.81 – 6.67 (m, 1H, + *cis* isom.), 6.45 (dd, *J* = 14.5, 10.5 Hz, *cis* isom.), 4.40 – 4.10 (m, 4H, + *cis* isom.), 1.41 (td, *J* = 7.1, 0.8 Hz, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 136.7 (d, $^{2}J_{C\text{-}P}$ = 11.7 Hz, CH), 135.8 (C), 128.8 (CH), 128.4 (CH), 126.4 (CH), 116.7 (d, $^{3}J_{C\text{-}P}$ = 6.1 Hz, CH), 64.3 (d, $^{2}J_{C\text{-}P}$ = 5.4 Hz, CH_2), 15.9 (d, $^{3}J_{C\text{-}P}$ = 8.4 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 88.8, 88.6

HRMS [APCI(+)]: calcd. For $([C_{12}H_{17}O_2PS_2]+H)^{+}$: 288.0480, found: 288.0485.

(*E*)-*O,O*-diethyl *S*-(2-(naphthalen-2-yl)vinyl) phosphorodithioate (3ed)



Following the general procedure A, a 8.7:1 *trans/cis* mixture of vinyl bromide **1d** (69.9 mg, 0.3 mmol) and the dithiophosphate **2e** (30.5 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (10:1 Hex/EtOAc), the product was obtained as a yellow oil (28 mg, 55% isolated yield, *d.r.:* 2.1:1 *trans/cis*).

Rf = 0.36 (10:1 Hex/EtOAc) [UV] [Vanillin]

A 2.1:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

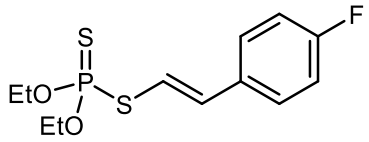
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.97 (s, *cis* isom.), 7.92 – 7.79 (m, 3H, + *cis* isom.), 7.74 (s, 1H), 7.70 – 7.43 (m, 3H, + *cis* isom.), 7.01 (dd, *J* = 15.5, 2.6 Hz, 1H), 6.95 – 6.78 (m, 1H, + *cis* isom.), 6.53 (dd, *J* = 14.6, 10.6 Hz, *cis* isom.), 4.42 – 4.09 (m, 4H, + *cis* isom.), 1.42 (td, *J* = 7.1, 0.8 Hz, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 136.7 (d, $^{2}J_{C\text{-}P}$ = 11.8 Hz, CH), 133.4 (C), 133.3 (C), 133.2 (C), 128.5 (CH), 128.1 (CH), 127.7 (CH), 126.7 (CH), 126.6 (CH), 126.4 (CH), 123.1 (CH), 117.0 (d, $^{3}J_{C\text{-}P}$ = 6.1 Hz, CH), 64.3 (d, $^{2}J_{C\text{-}P}$ = 5.2 Hz, CH_2), 15.92 (d, $^{3}J_{C\text{-}P}$ = 8.0 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 88.7, 88.5.

HRMS [APCI(+)]: calcd. For $([C_{16}H_{19}O_2PS_2]+H)^+$: 339.0637, found: 339.0643.

(*E*)-*O,O*-diethyl *S*-(4-fluorostyryl) phosphorodithioate (3eh)



Following the general procedure A, a 7:1 *trans/cis* mixture of vinyl bromide **1h** (60.4 mg, 0.3 mmol) and the dithiophosphate **2e** (30.5 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (10:1 Hex/EtOAc), the product was obtained as a colourless oil (27 mg, 60% isolated yield, *d.r.:* 3:1 *trans/cis*).

Rf = 0.40 (10:1 Hex/EtOAc) [UV] [Vanillin]

A 3:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.54 – 7.29 (m, 2H, + *cis* isom.), 7.13 – 6.99 (m, 2H, + *cis* isom.), 6.81 (dd, *J* = 15.5, 2.8 Hz, 1H), 6.72 (d, *J* = 10.6 Hz, *cis* isom.), 6.63 (dd, *J* = 15.5, 8.5 Hz, 1H), 6.42 (dd, *J* = 14.2, 10.5 Hz, *cis* isom.), 4.39 – 4.07 (m, 4H, + *cis* isom.), 1.40 (td, *J* = 7.0, 0.8 Hz, 6H, + *cis* isom.).

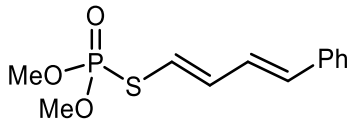
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 162.7 (d, $^{1}J_{C\text{-}F}$ = 248.6 Hz, C), 135.5 (d, $^{2}J_{C\text{-}P}$ = 11.9 Hz, CH), 132.1 (C), 128.0 (d, $^{4}J_{C\text{-}F}$ = 8.1 Hz, CH), 116.4 (dd, $^{3}J_{C\text{-}P}$ = 5.8, $^{5}J_{C\text{-}F}$ = 2.1 Hz, CH), 115.8 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz, CH), 64.3 (d, $^{2}J_{C\text{-}P}$ = 5.7 Hz, CH_2), 15.9 (d, $^{3}J_{C\text{-}P}$ = 8.0 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 88.8, 88.3

^{19}F NMR (282 MHz, $CDCl_3$, 300K) δ -112.7, 112.9.

HRMS [APCI(+)]: calcd. For $([C_{12}H_{16}FO_2PS_2]+H)^+$: 307.0386, found: 307.0394.

***O,O*-dimethyl *S*-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl) phosphorothioate (5ap)**



Batch reaction: Following the general procedure A, a 2.7:1 *trans/cis* mixture of vinyl bromide **1p** (62.7 mg, 0.3 mmol) and the phosphorothioate **2a** (36.6 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (26 mg, 65% isolated yield, *d.r.:* 1.8:1 *trans/cis*).

Continuous flow reaction: Using procedure B, a 2.7:1 *trans/cis* mixture of vinyl bromide **1p** (125.4 mg, 0.6 mmol) and the phosphorothioate **2a** (73.2 mg, 0.3 mmol) were dissolved in 6 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (69 mg, 71% isolated yield, *d.r.:* 1.1:1 *trans/cis*).

Rf = 0.45 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 1.8:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

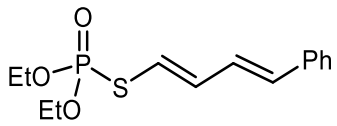
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.52 – 7.05 (m, 5H, + *cis* isom.), 6.84 – 6.50 (m, 3H, + *cis* isom.), 6.30 – 6.18 (m, 1H), 6.12 – 6.01 (m, *cis* isom.), 3.85 (d, *J* = 12.8 Hz, 6H, + *cis* isom).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 138.3 (d, $^{2}J_{C\text{-}P}$ = 12.5 Hz, CH), 136.5 (C), 136.1 (CH), 133.9 (d, $^{4}J_{C\text{-}P}$ = 2.3 Hz, CH), 128.7 (CH), 126.6 (CH), 123.1 (CH), 116.6 (d, $^{3}J_{C\text{-}P}$ = 6.6 Hz, CH), 54.2 (d, $^{2}J_{C\text{-}P}$ = 5.6 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 26.5, 26.4, 26.2.

HRMS [APCI(+)]: calcd. For $([C_{12}H_{15}O_3PS]+H)^+$: 271.0552, found: 271.0554.

***O,O*-diethyl *S*-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl) phosphorothioate (5bp)**



Batch reaction: Following the general procedure A, a 2.7:1 *trans/cis* mixture of vinyl bromide **1p** (62.7 mg, 0.3 mmol) and the phosphorothioate **2b** (40.7 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (19 mg, 43% isolated yield, *d.r.:* 2:1 *trans/cis*).

Continuous flow reaction: Using procedure B, a 2.7:1 *trans/cis* mixture of vinyl bromide **1p** (125.4 mg, 0.6 mmol) and the phosphorothioate **2b** (81.4 mg, 0.3 mmol) were dissolved in 6 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (69 mg, 77% isolated yield, *d.r.:* 1.7:1 *trans/cis*).

Rf = 0.65 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 2:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

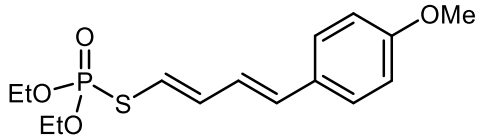
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.53 – 7.05 (m, 5H + *cis* isom.), 6.87 – 6.50 (m, 3H + *cis* isom.), 6.36 – 6.23 (m, 1H), 6.13 (t, *J* = 9.4 Hz, *cis* isom.), 4.37 – 4.12 (m, 4H + *cis* isom.), 1.46 – 1.34 (m, 6H + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 137.7 (d, $^{2}J_{C\text{-}P}$ = 12.5 Hz, CH), 136.6 (C), 135.8 (CH), 133.6 (d, $^{4}J_{C\text{-}P}$ = 2.1 Hz, CH), 128.7 (CH), 126.6 (CH), 123.3 (CH), 117.4 (d, $^{3}J_{C\text{-}P}$ = 6.4 Hz, CH), 64.0 (d, $^{2}J_{C\text{-}P}$ = 5.7 Hz, CH_2), 16.08 (d, J = 7.2 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 22.9, 22.8, 22.7.

HRMS [APCI(+)]: calcd. For ($[C_{14}H_{19}O_3PS]+H)^+$: 299.0865, found: 299.0866.

S-((1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl) *O,O*-diethyl phosphorothioate (5bq)



Batch reaction: Following the general procedure A, a 1.8:1 *trans/cis* mixture of vinyl bromide **1q** (71.7 mg, 0.3 mmol) and the phosphorothioate **2b** (40.7 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as an orange oil (18 mg, 35% isolated yield, *d.r.:* 1.3:1 *trans/cis*).

Continuous flow reaction: Using procedure B, a 1.8:1 *trans/cis* mixture of vinyl bromide **1q** (143.4 mg, 0.6 mmol) and the phosphorothioate **2b** (81.4 mg, 0.3 mmol) were dissolved in 6 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (67 mg, 68% isolated yield, *d.r.:* 1.7:1 *trans/cis*).

Rf = 0.48 (1:1 Hex/EtOAc) [UV] [Vanillin]

A 1.3:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

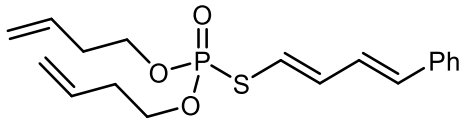
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.45 – 7.21 (m, 2H + *cis* isom.), 7.07 – 6.78 (m, 2H + *cis* isom.), 6.73 – 6.38 (m, 3H + *cis* isom.), 6.26 – 6.16 (m, 1H), 6.03 (t, J = 9.2 Hz, *cis* isom.), 4.36 – 4.11 (m, 4H + *cis* isom.), 3.82 (s, 3H + *cis* isom.), 1.45 – 1.33 (m, 6H + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 159.6 (C), 138.5 (d, $^2J_{C-P}$ = 12.5 Hz, CH), 135.5 (CH),129.3 (C), 127.9 (CH), 124.8 (d, $^4J_{C-P}$ = 2.3 Hz, CH), 115.6 (d, $^3J_{C-P}$ = 6.8 Hz, CH), 114.2 (CH), 64.0 (d, $^2J_{C-P}$ = 5.6 Hz, CH_2), 55.3 (CH_3), 16.1 (d, $^3J_{C-P}$ = 7.4 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 23.2, 23.0, 22.9, 22.8.

HRMS [APCI(+)]: calcd. For ($[C_{15}H_{21}O_4PS]+H)^+$: 329.0971, found: 329.0974.

***O,O*-di(but-3-en-1-yl) *S*-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl) phosphorothioate (5dp)**



Following the general procedure A, a 2.7:1 *trans/cis* mixture of vinyl bromide **1p** (62.7 mg, 0.3 mmol) and the phosphorothioate **2d** (48.5 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (5:1 Hex/EtOAc), the product was obtained as a yellow oil (25 mg, 47% isolated yield, *d.r.:* 1.8:1 *trans/cis*).

Rf = 0.25 (5:1 Hex/EtOAc) [UV] [Vanillin]

A 1.8:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

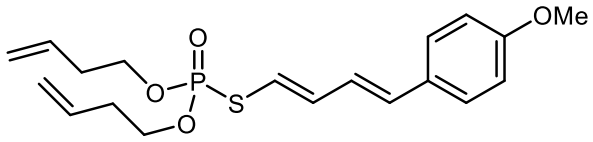
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.53 – 7.06 (m, 5H, + *cis* isom.), 6.86 – 6.46 (m, 3H, + *cis* isom.), 6.28 (dd, *J* = 14.4, 9.0 Hz, 1H), 6.12 (dd, *J* = 9.3, 9.3 Hz, *cis* isom.), 5.91 – 5.70 (m, 2H, + *cis* isom.), 5.24 – 5.09 (m, 4H, + *cis* isom.), 4.32 – 4.07 (m, 4H, + *cis* isom.), 2.57 – 2.43 (m, 4H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 138.0 (d, $^2J_{C-P}$ = 12.6 Hz, CH), 136.6 (C), 135.9 (CH), 133.7 (d, $^4J_{C-P}$ = 2.4 Hz, CH), 133.1 (CH), 128.7 (CH), 126.6 (CH), 123.2 (CH), 118.0 (CH_2), 117.1 (d, $^3J_{C-P}$ = 6.6 Hz, CH), 66.9 (d, $^2J_{C-P}$ = 6.1 Hz, CH_2), 34.5 (d, $^3J_{C-P}$ = 6.7 Hz, CH_2).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 23.2, 23.1, 23.0.

HRMS [APCI(+)]: calcd. For ($[C_{18}H_{23}O_3PS]+H)^+$: 351.1178, found: 351.1179.

***O,O*-di(but-3-en-1-yl) *S*-((1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl) phosphorothioate (5dq)**



Following the general procedure A, a 1.8:1 *trans/cis* mixture of vinyl bromide **1q** (71.7 mg, 0.3 mmol) and the phosphorothioate **2d** (48.5 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (5:1 Hex/EtOAc), the product was obtained as an orange oil (17 mg, 30% isolated yield, *d.r.:* 1.8:1 *trans/cis*).

Rf = 0.21 (5:1 Hex/EtOAc) [UV] [Vanillin]

A 1.8:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

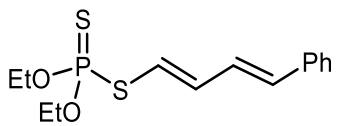
^{1}H NMR (600 MHz, $CDCl_3$, 300K) δ 7.42 (d, *J* = 8.7 Hz, *cis* isom.), 7.35 (d, *J* = 8.7 Hz, 2H), 7.06 – 6.83 (m, 2H, + *cis* isom.), 6.70 – 6.42 (m, 3H, + *cis* isom.), 6.31 (dd, *J* = 14.8, 9.2 Hz, *trans* isom.), 6.24 – 6.14 (m, 1H), 6.03 (dd, *J* = 9.3, 9.1 Hz, *cis* isom.), 5.87 – 5.75 (m, 2H, + *cis* isom.), 5.22 – 5.09 (m, 2H, + *cis* isom.), 4.28 – 4.06 (m, 4H, + *cis* isom.), 3.85 (s, *cis* isom.), 3.84 (s, 3H), 2.54 – 2.46 (m, 4H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 159.7 (C), 138.8 (d, $^{2}J_{C\text{-}P}$ = 12.4 Hz, CH), 135.6 (CH), 133.1 (CH), 129.3 (C), 127.9 (CH), 124.8 (d, $^{4}J_{C\text{-}P}$ = 2.3 Hz, CH), 118.0 (CH_2), 115.3 (d, $^{3}J_{C\text{-}P}$ = 6.8 Hz, CH), 114.2 (CH), 66.9 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, CH_2), 55.3 (CH_3), 34.5 (d, $^{3}J_{C\text{-}P}$ = 7.3 Hz, CH_2)

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 23.4, 23.2, 23.2, 23.1.

HRMS [APCI(+)]: calcd. For ($[C_{19}H_{25}O_4PS]+H)^+$: 381.1284, found: 381.1284.

***O,O*-diethyl *S*-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl) phosphorodithioate (5ep)**



Following the general procedure A, a 2.7:1 *trans/cis* mixture of vinyl bromide **1p** (62.7 mg, 0.3 mmol) and the dithiophosphate **2e** (30.5 mg, 0.15 mmol) were dissolved in 3 mL

of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a colourless oil (42 mg, 89% isolated yield, *d.r:* 1.8:1 *trans/cis*).

Rf = 0.43 (10:1 Hex/EtOAc) [UV] [Vanillin]

A 1.8:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

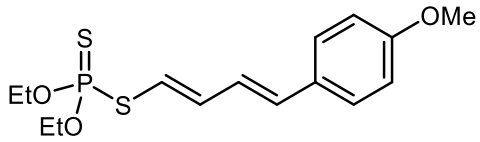
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.56 – 7.03 (m, 5H, + *cis* isom.), 6.90 – 6.51 (m, 3H, + *cis* isom.), 6.33 (dd, *J* = 14.7, 9.2 Hz, 1H), 6.17 (dd, J = 9.7, 9.7 Hz, *cis* isom.), 1H), 4.39 – 4.10 (m, 4H, + *cis* isom.), 1.49 – 1.34 (m, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 137.5 (d, $^{2}J_{C\text{-}P}$ = 11.9 Hz, CH), 136.6 (C), 135.9 (CH), 134.0 (d, $^{4}J_{C\text{-}P}$ = 2.5 Hz, CH), 128.7 (CH), 126.6 (CH), 123.5 (CH), 119.2 (d, $^{3}J_{C\text{-}P}$ = 6.6 Hz, CH), 64.2 (d, $^{2}J_{C\text{-}P}$ = 5.3 Hz, CH_2), 15.9 (d, $^{3}J_{C\text{-}P}$ = 8.3 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 88.4, 87.8.

HRMS [APCI(+)]: calcd. For ($[C_{14}H_{19}O_2PS_2]$+H)$^{+}$: 315.0637, found: 315.0636.

O,O-diethyl *S*-((1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl) phosphorodithioate (5eq)



Following the general procedure A, a 1.8:1 *trans/cis* mixture of vinyl bromide **1q** (71.7 mg, 0.3 mmol) and the dithiophosphate **2e** (30.5 mg, 0.15 mmol) were dissolved in 3 mL of dry DMSO. After purification by column chromatography (1:1 Hex/EtOAc), the product was obtained as a yellow oil (45 mg, 87% isolated yield, *d.r.:* 1.7:1 *trans/cis*).

Rf = 0.35 (10:1 Hex/EtOAc) [UV] [Vanillin]

A 1.7:1 *trans/cis* isomeric mixture was obtained. For simplicity, the integrals in the spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.49 – 7.31 (m, 2H,+ *cis* isom.), 7.09 – 6.83 (m, 3H, + *cis* isom.), 6.77 – 6.41 (m, 2H, + *cis* isom.), 6.31 – 6.17 (m, 1H), 6.07 (dd, *J* = 9.8, 9.2

Hz, *cis* isom.), 4.38 – 4.09 (m, 4H, + *cis* isom.), 3.84 (s, *cis* isom.), 3.83 (s, 3H), 1.46 – 1.30 (m, 6H, + *cis* isom.).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 159.7 (C), 138.4 (d, $^{2}J_{C\text{-}P}$ = 11.9 Hz, CH), 135.7(CH), 129.3 (C), 127.9 (CH), 124.9 (d, $^{4}J_{C\text{-}P}$ = 2.9 Hz, CH), 117.4 (d, $^{3}J_{C\text{-}P}$ = 7.0 Hz, CH), 114.2 (CH), 64.40 – 64.05 (m, CH_2), 55.3 (CH_3), 15.9 (d, $^{3}J_{C\text{-}P}$ = 8.3 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$, 300K) δ 88.6, 88.4, 88.0, 87.9.

HRMS [APCI(+)]: calcd. For $([C_{15}H_{22}O_3PS_2]+H)^+$:345.0743, found: 345.0743.

4. UV/Vis spectra

The measurements involved were carried out by dissolving the appropriate reagents in DMSO at a concentration of 0.05 mM. When the mixture of **1a + 2a** was examined, a red-shifted bathochromic shift was observed. This shift provides evidence for the formation of a halogen bonding (HB) complex between **1a** and the phosphorothioate anion **2a**. Consequently, this complex can be selectively excited using a 390 nm lamp.

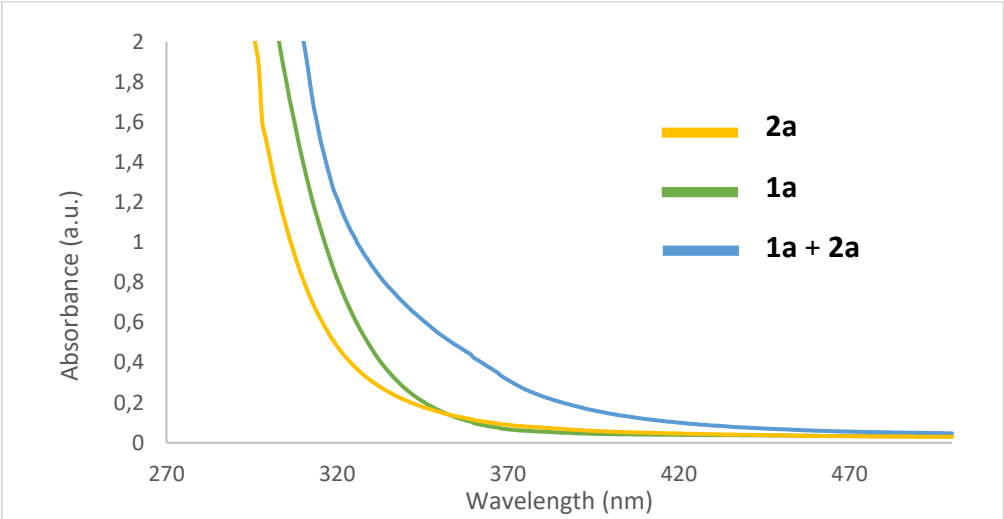


Figure SI-4. UV-Vis spectra of compounds **1a** (green line), **2a** (yellow line), and a equimolar mixture of **1a + 2a** (blue line).

5. Computational studies

The Gaussian 09 software was used for performing the computational calculations. The geometry optimizations were carried out using the wB97x-D functional, which incorporates dispersion corrections and has proven to yield reliable outcomes for non-bonding interactions.[3] The Def2-TZVPP basis set with polarization correction was employed for all atoms. Analytical frequency calculations were performed to characterize the optimized structures as energy minima in the potential energy surface. Single point energy calculations on the optimized structures were conducted using the CMCD (DMSO) model at the same theoretical level to consider solvation effects. The three-dimensional model was visualized using Cylview 2.0.[4] For the representation of the electrostatic potential map, Gaussview 5.0 was used based on a model obtained from Gaussian 09 at the wB97x-D/Def2-TZVPP level. The electrostatic potential was mapped over a $4x10^{-4}$ atomic units (au) isodensity surface. The modeling studies provide evidence for the presence of a minimum in the potential energy surface, indicating the existence of a halogen-bonded complex (HB-complex) between vinyl bromide **1a** and phosphorothioate **2a**. The halogen bond interaction between the bromine and sulfur atoms exhibits significant directionality, as demonstrated by a dihedral angle of 178.6° between the Csp^2-Br-S bonds. This arrangement gives rise to a nearly linear structure for the halogen-bonding complex. Notably, the electrostatic potential surface reveals that the positively charged bromine σ-hole zone is positioned near the center of the C-Br axis. This linear geometry, with dihedral angles ranging from 160° to 180° for the HB complex, aligns with previously reported observations on similar complexes. Furthermore, our findings indicate that the distance between the bromine and sulfur atoms in the halogen-bonding complex is 3.35 Å, which is shorter than the sum of the Van der Waals radii of sulfur and bromine atoms (3.65 Å). This observation supports the existence of a non-covalent weak interaction between these atoms, likely resulting from the formation of a halogen bond. Based on the computations, the complexation process is found to be exothermic, with a ΔH of -108.1 $kcal \cdot mol^{-1}$, and exergonic with a ΔG of -9.3 $kcal \cdot mol^{-1}$.

[3] Y.-S. Lin, G.-D. Li, S. P. Mao, J.-D. Chai Long-Range Corrected Hybrid Density Functionals with Improved Dispersion Corrections *J. Chem. Theory Comput.* **2013**, *9*, 1, 263.
[4] CYLview20; Legault, C. Y., Université de Sherbrooke, 2020 (http://www.cylview.org).

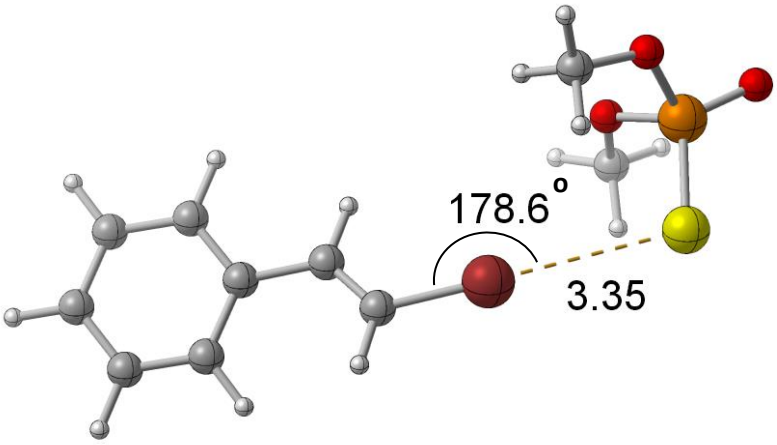


Figure SI-5. HB complex between **1a** and **2a** calculated at the wB97x-D/Def2TZVPP.

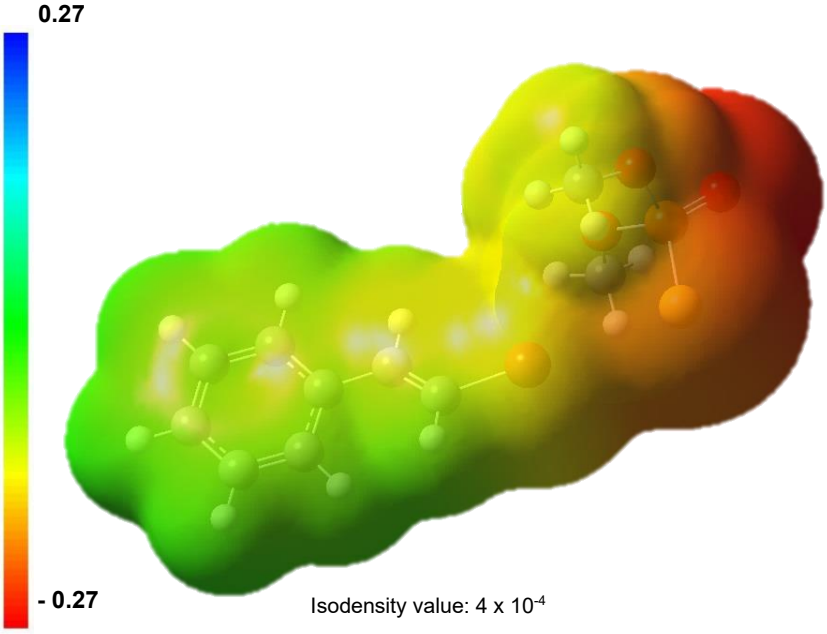
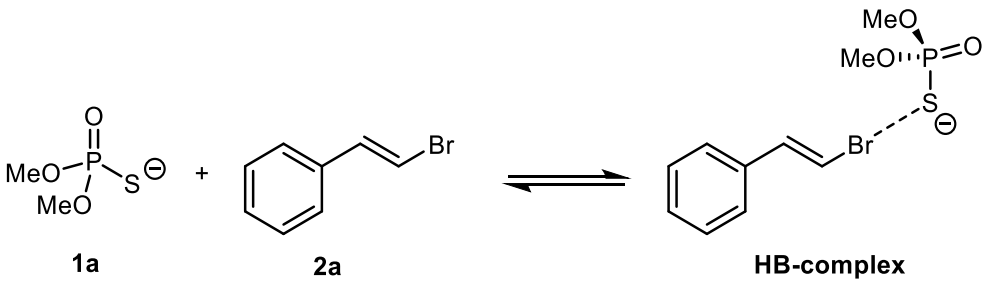


Figure SI-6. Calculated electrostatic potential map (red = negative electrostatic potential) on the 0.0004 au isodensity surface.



$$\Delta H = -180.1\ kcal \cdot mol^{-1};\ \Delta G(solv) = -9.3\ kcal \cdot mol^{-1}$$

Cartesian Coordinates and energy data

- β-bromostyrene **1a**

C	1.116212	0.422628	-0.083875	C	-1.818751	1.096414	0.078922
H	0.947304	1.465540	-0.304211	C	-1.286418	-0.194123	0.063024
C	0.156670	-0.469797	0.108556	H	-1.772349	-2.279987	-0.001711
H	0.434454	-1.500492	0.298317	H	-4.204599	-1.922099	-0.109210
C	-2.168599	-1.272043	0.002422	H	-5.120251	0.376006	-0.105328
C	-3.537899	-1.071388	-0.060133	H	-3.579771	2.305043	0.030530
C	-4.051699	0.215036	-0.056933	H	-1.162563	1.953432	0.154356
C	-3.185249	1.297610	0.015405	Br	2.946062	-0.015527	-0.010488

SCF energy: -2883.26439080 Hartree

Gibbs free energy: -2883.174132 Hartree

SCF energy (CPCM-dmso): -2883.26882569 Hartree

Gibbs free energy (CPCM-dmso): -2883.17413 Hartree

- O,O-dimethyl phosphorothioate **2a**

C	-2.615024	-0.224725	-0.319180	H	0.884060	3.156496	-0.843880
H	-2.662899	0.769092	-0.769691	P	0.025280	-0.201706	0.246748
H	-2.795625	-0.142301	0.755061	O	-1.335203	-0.838120	-0.580693
H	-3.363526	-0.872798	-0.772713	O	0.044349	1.311737	-0.615110
C	1.014698	2.287622	-0.200153	O	-0.354378	0.105344	1.754116
H	2.029680	1.895765	-0.318788	S	1.714599	-1.335361	-0.246550
H	0.859352	2.576038	0.843094				

SCF energy: -1044.98146190 Hartree

Gibbs free energy: -1044.926698 Hartree

SCF energy (CPCM-dmso): -1045.32876507 Hartree

Gibbs free energy (CPCM-dmso): -1045.27400 Hartree

- HB complex

C	2.584942	0.926828	2.193971		C	-2.457010	0.084932	-0.083123
H	2.428470	-0.145535	2.335575		H	-1.874113	0.989036	-0.222243
H	1.686101	1.354488	1.740586		C	-4.442101	1.541242	0.098623
H	2.759416	1.403423	3.160095		C	-5.809655	1.757005	0.149575
C	2.361476	1.062182	-2.128026		C	-6.688183	0.690846	0.039113
H	3.206693	1.366294	-2.752919		C	-6.181127	-0.590461	-0.131272
H	1.480535	1.643626	-2.405580		C	-4.815505	-0.803881	-0.184306
H	2.159696	0.000167	-2.298870		C	-3.916012	0.257828	-0.057524
P	3.867659	0.508894	-0.071094		H	-3.761212	2.378837	0.188075
O	3.718876	1.169935	1.398255		H	-6.190156	2.762436	0.277021
O	2.624664	1.313006	-0.770621		H	-7.756986	0.855256	0.078878
O	5.154411	0.940768	-0.644053		H	-6.857848	-1.429600	-0.231677
S	3.403695	-1.422872	-0.019378		H	-4.442282	-1.807416	-0.340052
C	-1.813636	-1.065013	0.080996		Br	0.059777	-1.222760	0.052947
H	-2.327231	-2.000570	0.257592					

SCF energy: -3928.53656667 Hartree

Gibbs free energy: -3928.370352 Hartree

SCF energy (CPCM-dmso): -3928.62923586 Hartree

Gibbs free energy (CPCM-dmso): -3928.46302 Hartree

6. NMR titration experiments.

To conduct these experiments, various solutions were prepared, each containing an increasing quantity of vinyl bromide **1a** while keeping the amount of phosphorothioate **2a** constant. All the samples were prepared in d^6-DMSO to facilitate direct NMR analysis and dimethylphosphite was used as reference. Throughout the titration process, a progressive downfield shift of the phosphorus signal in the phosphorothioate **2a** was observed. The composition of each sample and its corresponding ^{31}P-NMR spectra are presented here:

- Sample 1

Preparation: **2a** (36.6 mg, 0.15 mmol) was dissolved in 0.4 mL of d^6-DMSO in a 5 mL vial with dimethylphosphite as reference.

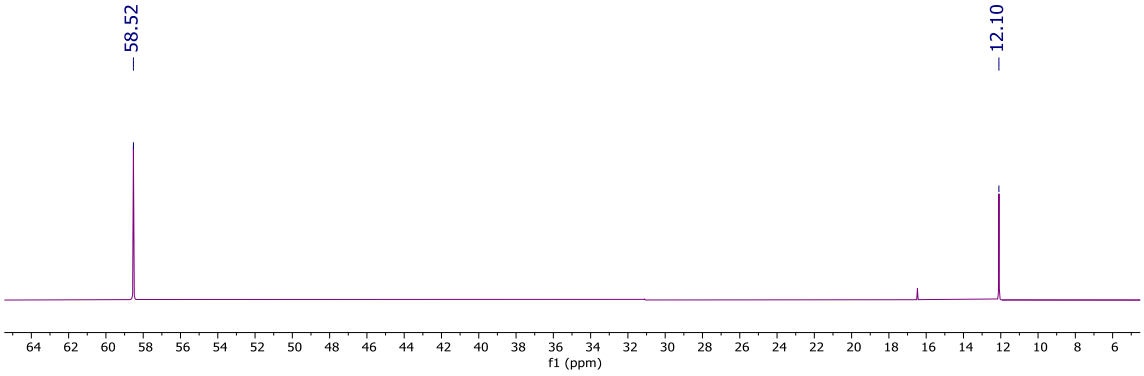


Figure SI-7. ^{31}P-NMR spectra recorded for the Sample 1 in d^6-DMSO.

Chemical shift: 58.52 ppm.

- Sample 2

Preparation: **1a** (18 µL, 0.15 mmol) and **2a** (36.6 mg, 0.15 mmol) were dissolved in 0.4 mL of d^6-DMSO in a 5 mL vial with dimethylphosphite as reference.

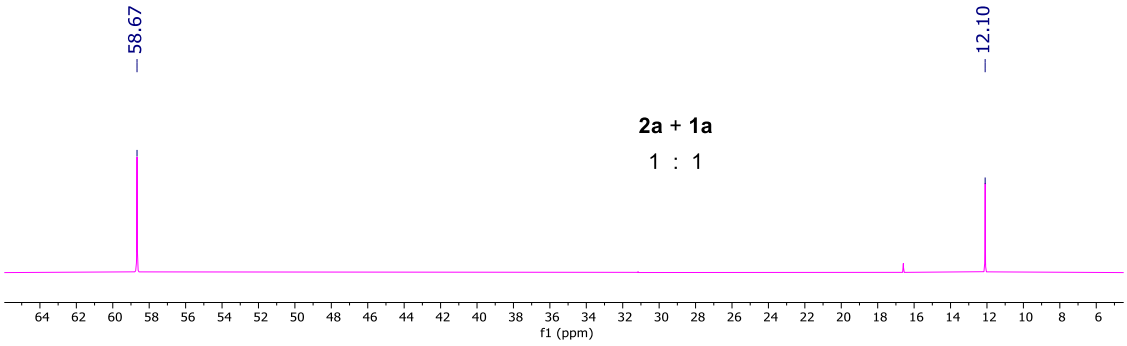


Figure SI-8. ^{31}P-NMR spectra recorded for the Sample 2 in d^6-DMSO.

Chemical shift: 58.67 ppm.

- Sample 3

Preparation: **1a** (38 µL, 0.30 mmol) and **2a** (36.6 mg, 0.15 mmol) were dissolved in 0.4 mL of d^6-DMSO in a 5 mL vial with dimethylphosphite as reference.

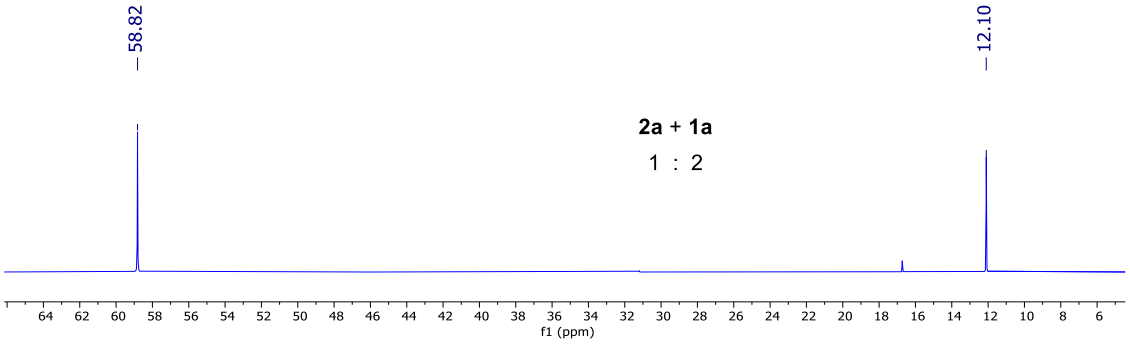


Figure SI-9. ^{31}P-NMR spectra recorded for the Sample 3 in d^6-DMSO.

Chemical shift: 58.82 ppm.

- Sample 4

Preparation: **1a** (72 µL, 0.60 mmol) and **2a** (36.6 mg, 0.15 mmol) were dissolved in 0.4 mL of d^6-DMSO in a 5 mL vial with dimethylphosphite as reference.

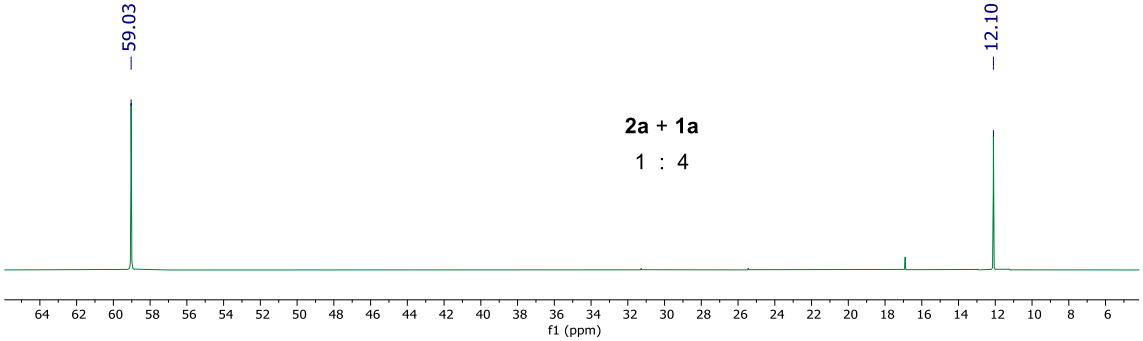


Figure SI-10. ^{31}P-NMR spectra recorded for the Sample 4 in d^6-DMSO.

Chemical shift: 59.03 ppm.

- Sample 5

Preparation: **1a** (108 µL, 0.90 mmol) and **2a** (36.6 mg, 0.15 mmol) were dissolved in 0.4 mL of d^6-DMSO in a 5 mL vial with dimethylphosphite as reference.

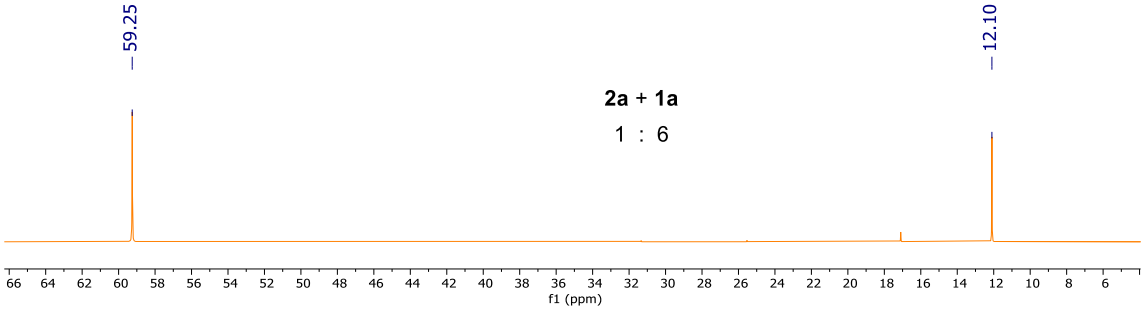


Figure SI-11. ^{31}P-NMR spectra recorded for the Sample 5 in d^6-DMSO.

Chemical shift: 59.25 ppm.

- Sample 6

Preparation: **1a** (180 µL, 1.5 mmol) and **2a** (36.6 mg, 0.15 mmol) were dissolved in 0.4 mL of d^6-DMSO in a 5 mL vial with dimethylphosphite as reference.

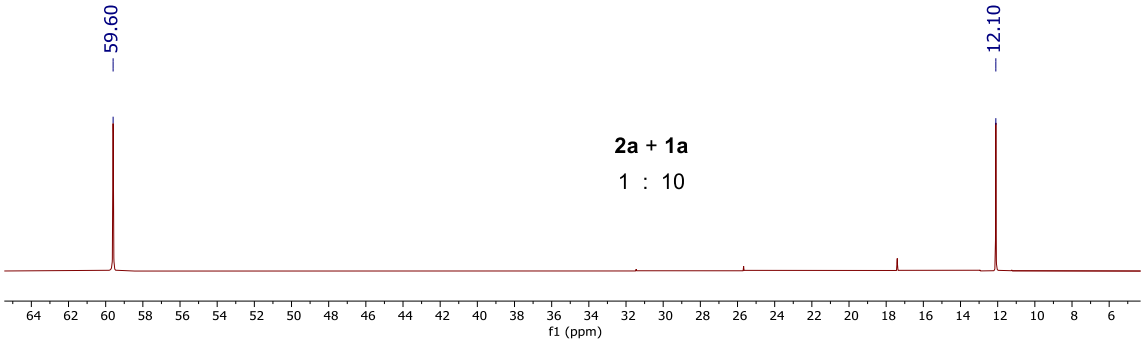
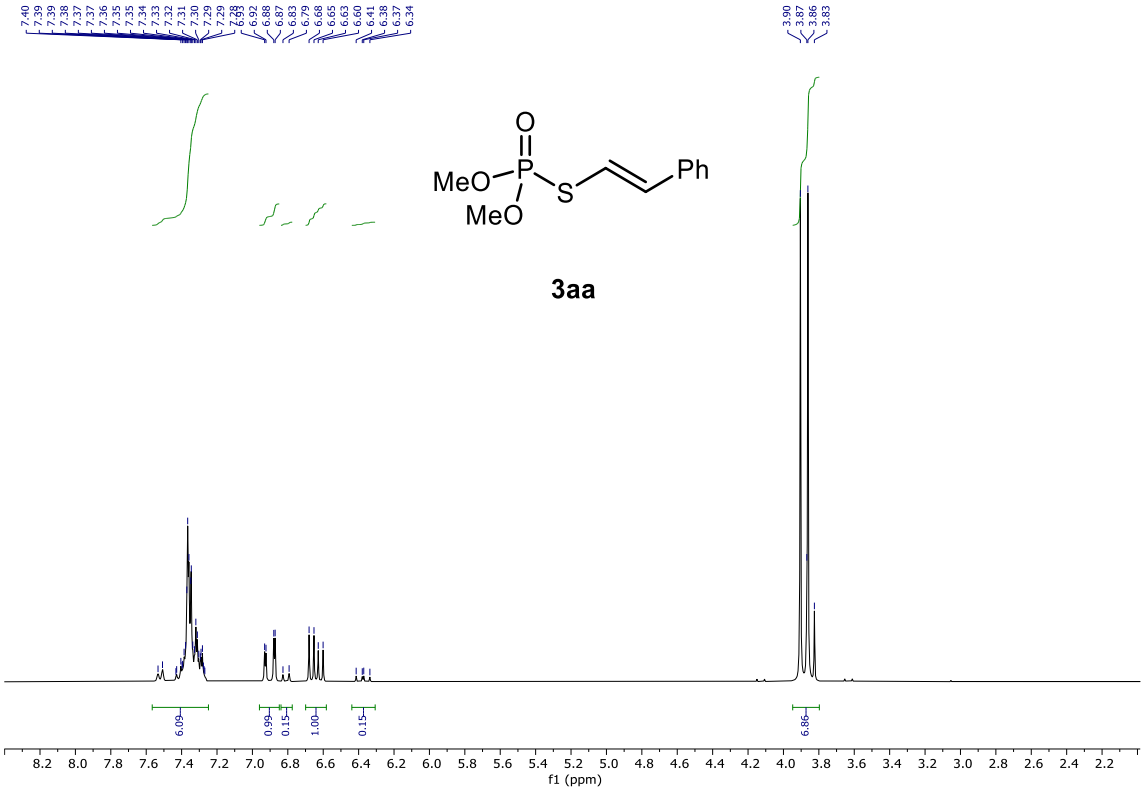
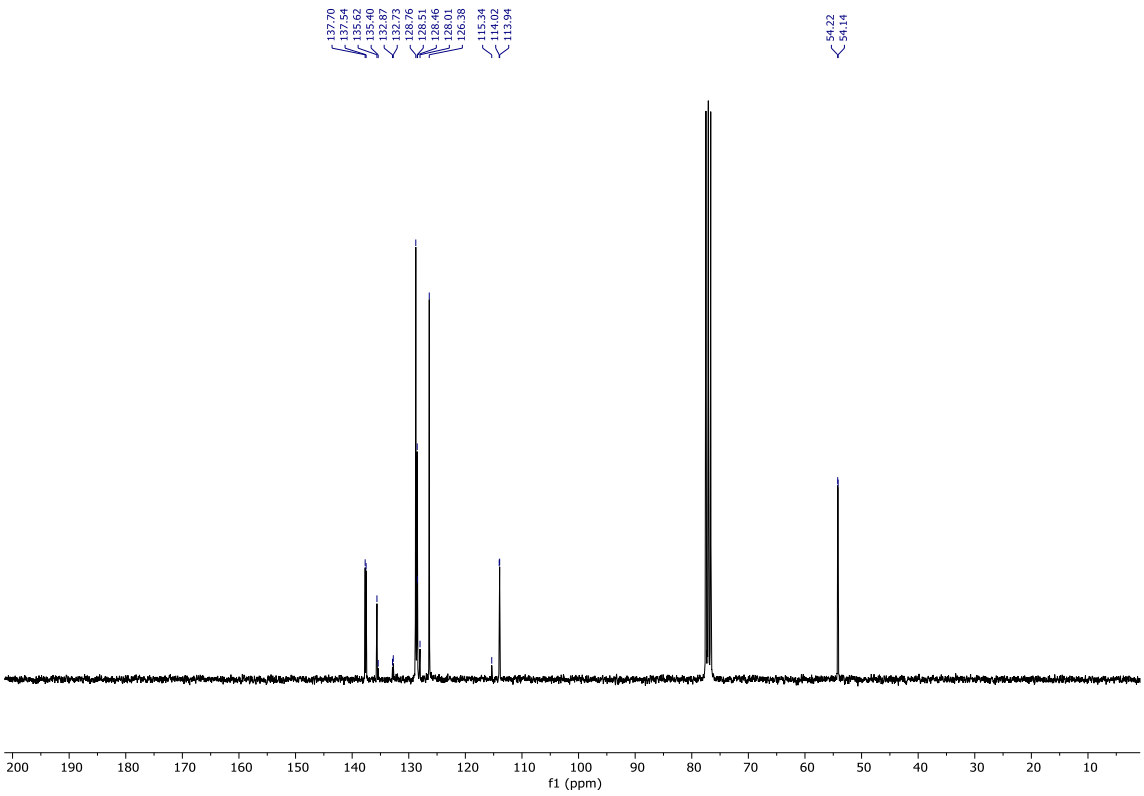


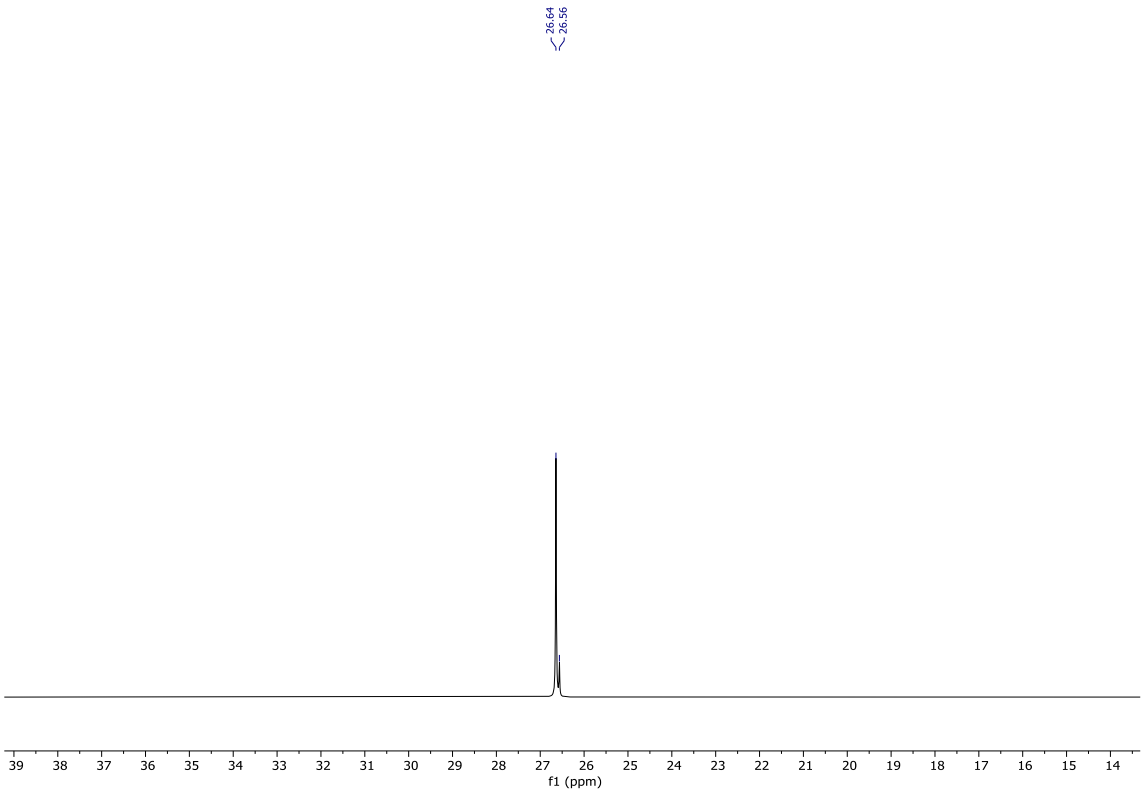
Figure SI-12. ^{31}P-NMR spectra recorded for the Sample 6 in d^6-DMSO. Chemical shift: 59.60 ppm.

7. Copies of the NMR spectra

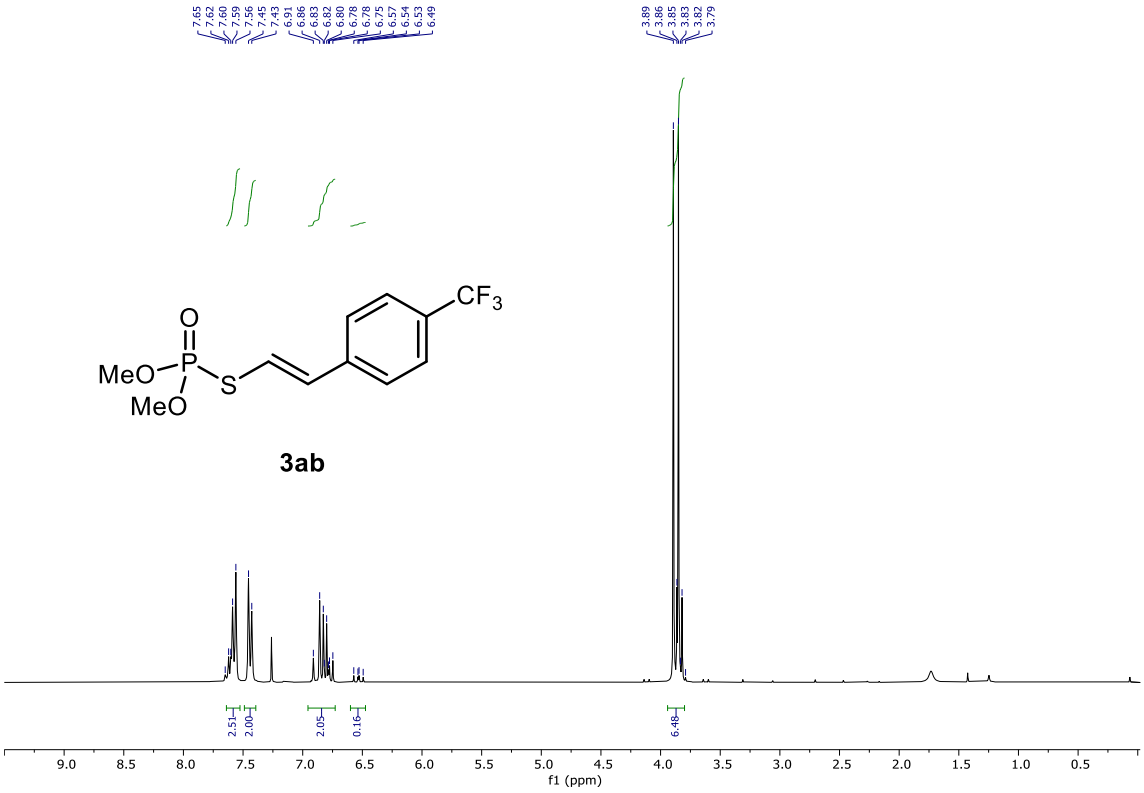
(*E*)-*O,O*-dimethyl *S*-styryl phosphorothioate (3aa)

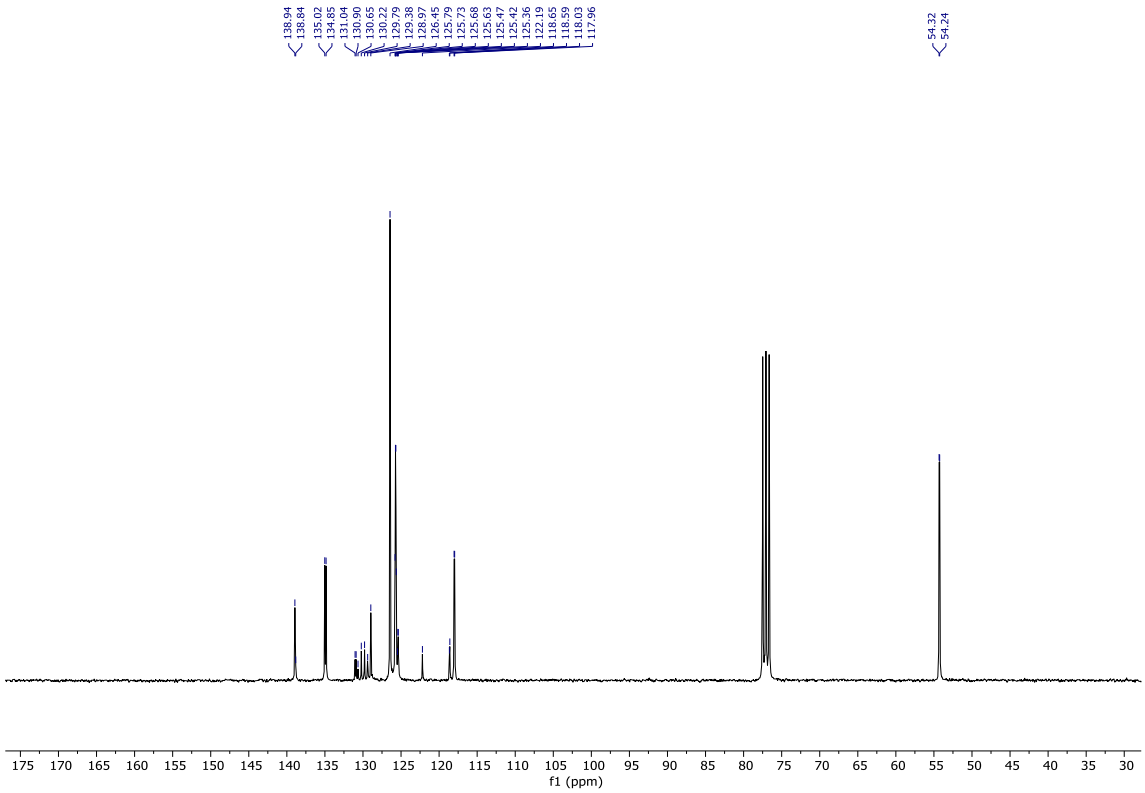


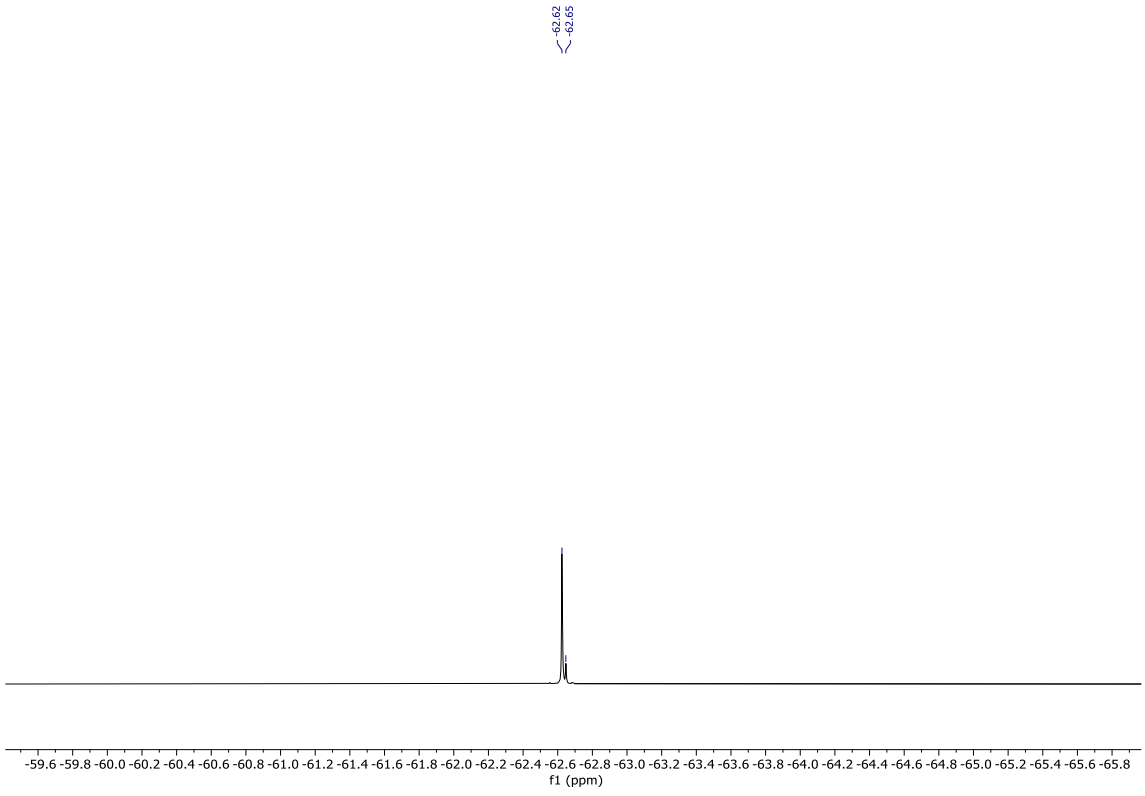


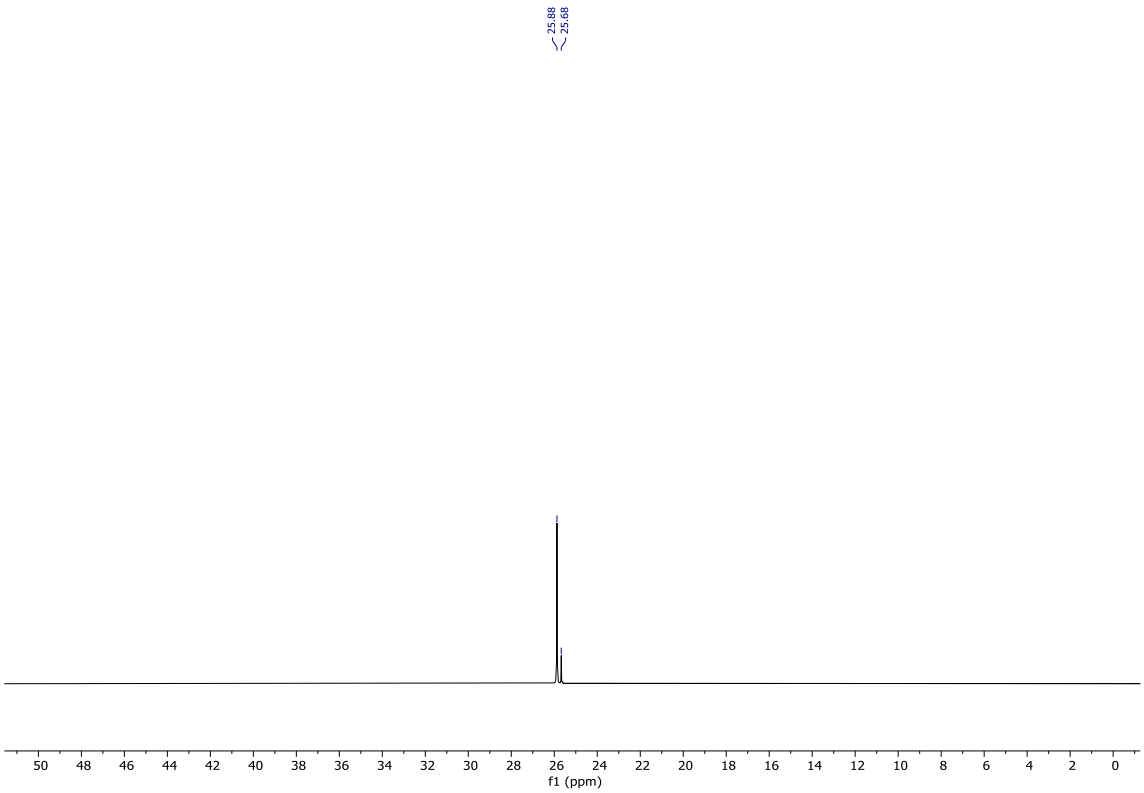


(*E*)-*O,O*-dimethyl *S*-(4-(trifluoromethyl)styryl) phosphorothioate (3ab)

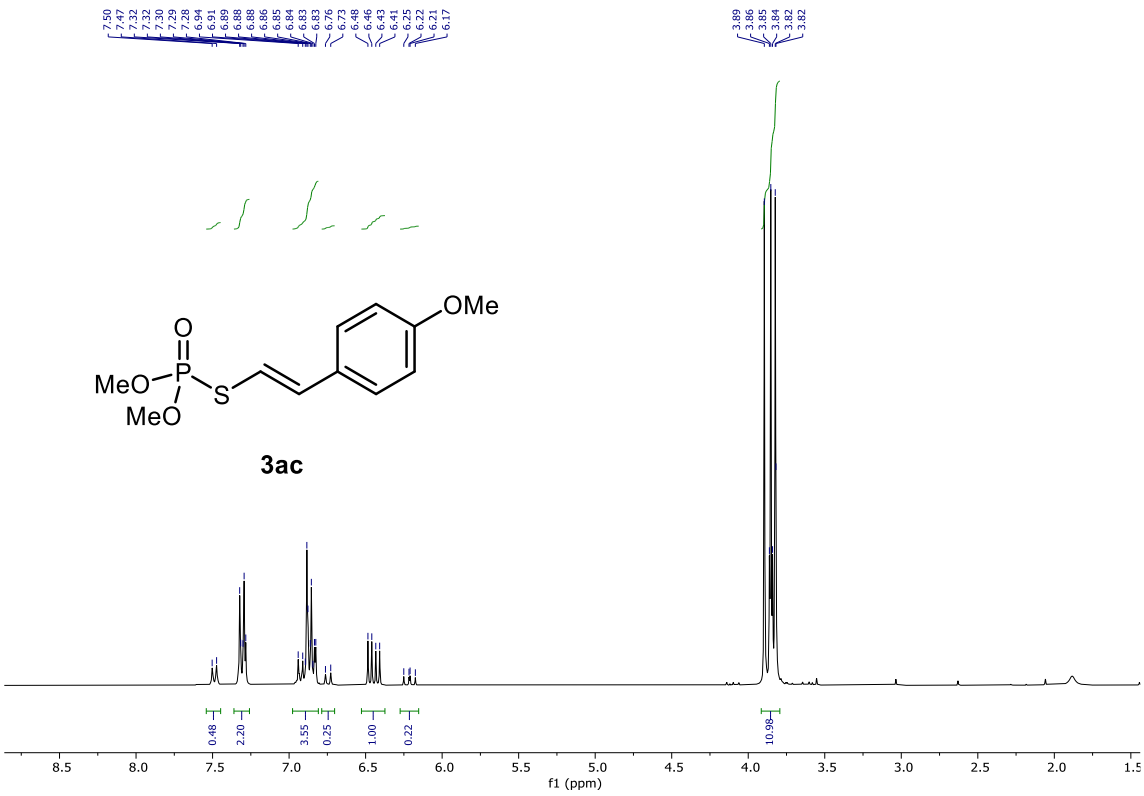


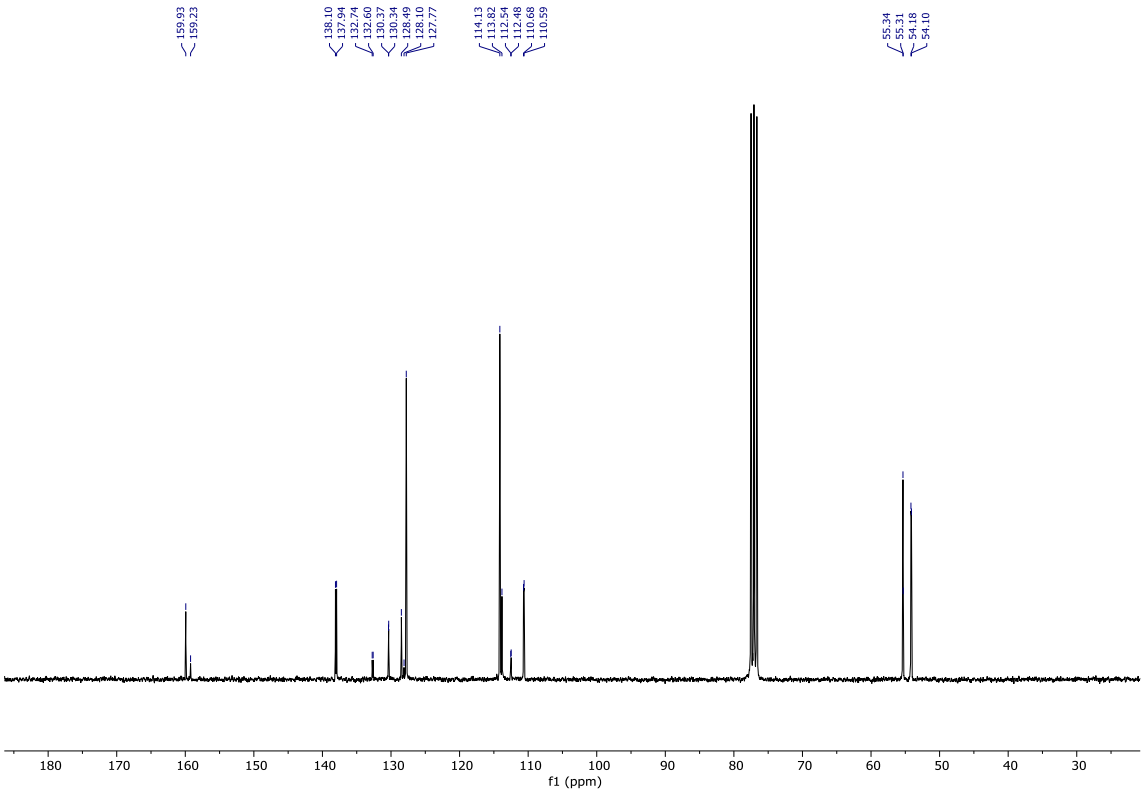

138.94
138.84
135.02
134.85
131.04
130.90
130.65
130.22
129.79
129.38
128.97
126.45
125.79
125.73
125.68
125.63
125.47
125.42
125.36
122.19
118.65
118.59
118.03
117.96
54.32
54.24
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30
f1 (ppm)

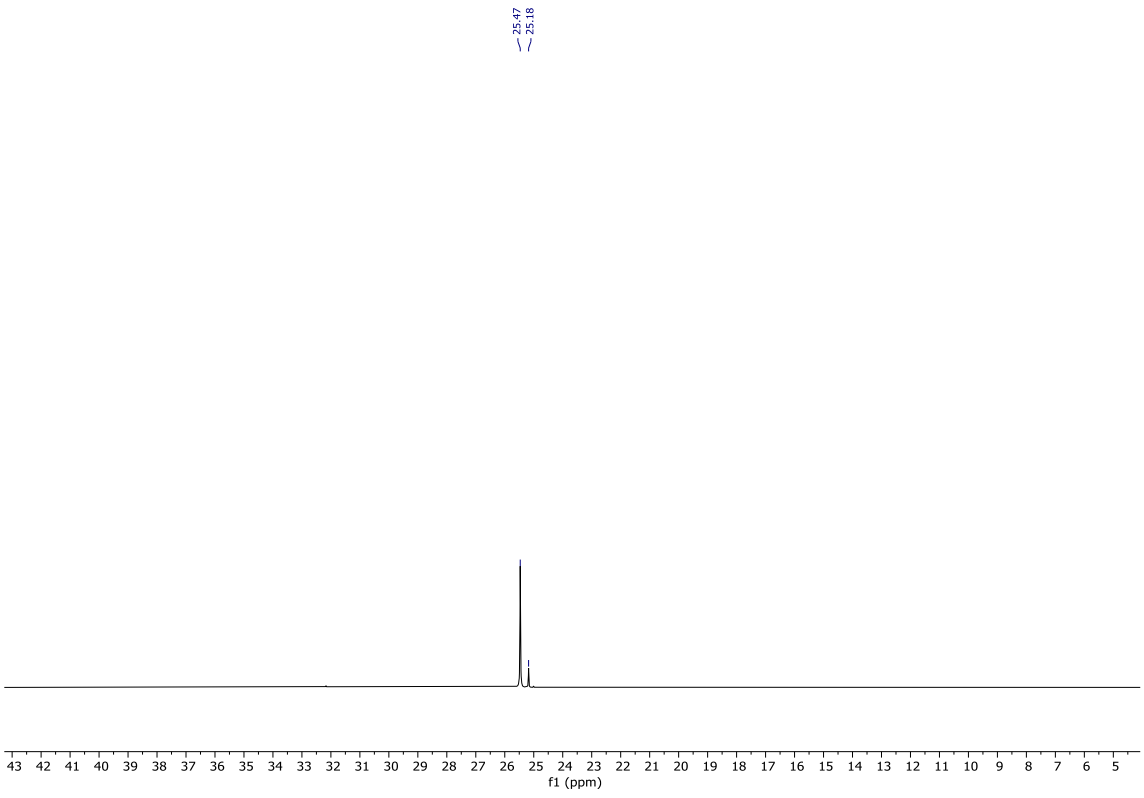

-62.62
-62.65
-59.6 -59.8 -60.0 -60.2 -60.4 -60.6 -60.8 -61.0 -61.2 -61.4 -61.6 -61.8 -62.0 -62.2 -62.4 -62.6 -62.8 -63.0 -63.2 -63.4 -63.6 -63.8 -64.0 -64.2 -64.4 -64.6 -64.8 -65.0 -65.2 -65.4 -65.6 -65.8
f1 (ppm)



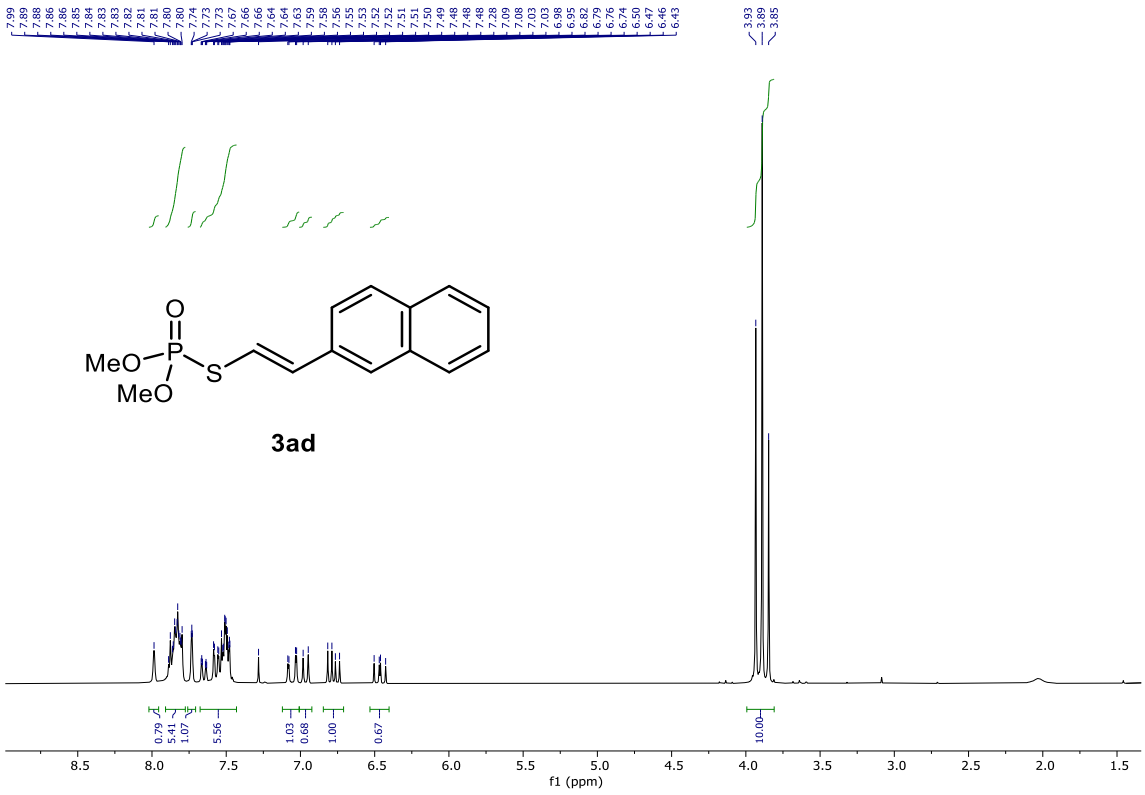
(*E*)-*S*-(4-methoxystyryl) *O,O*-dimethyl phosphorothioate (3ac)

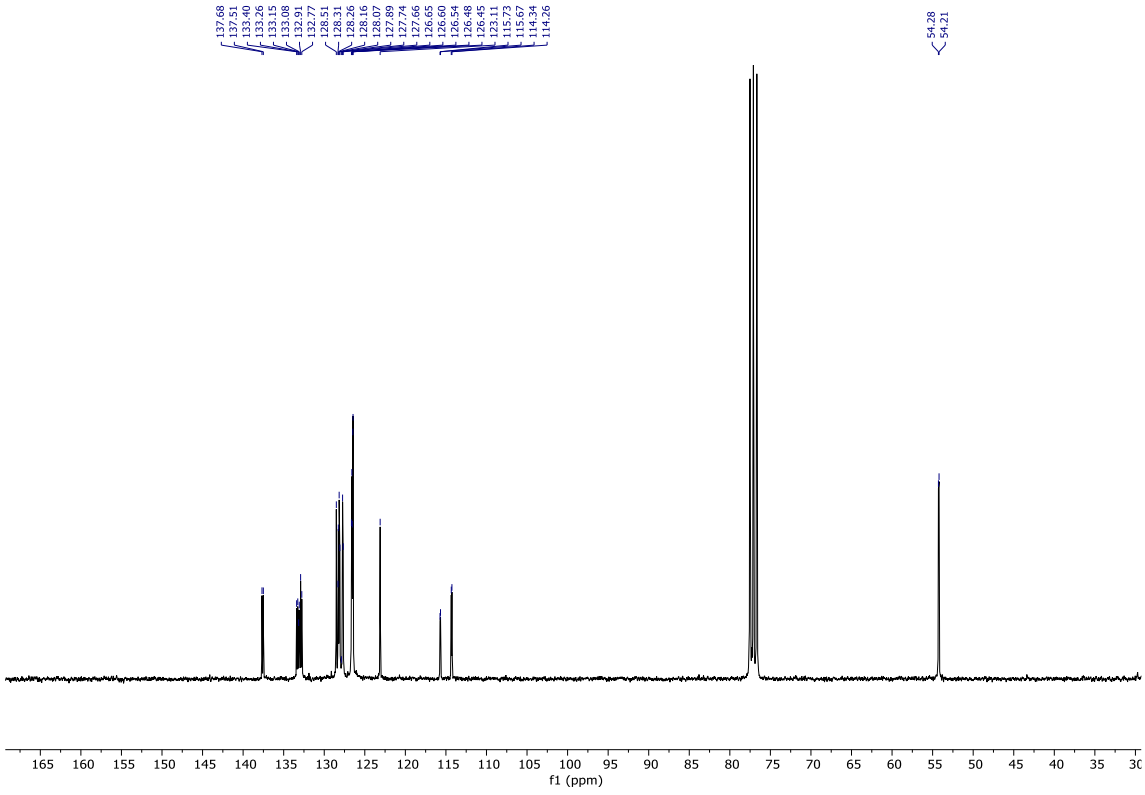


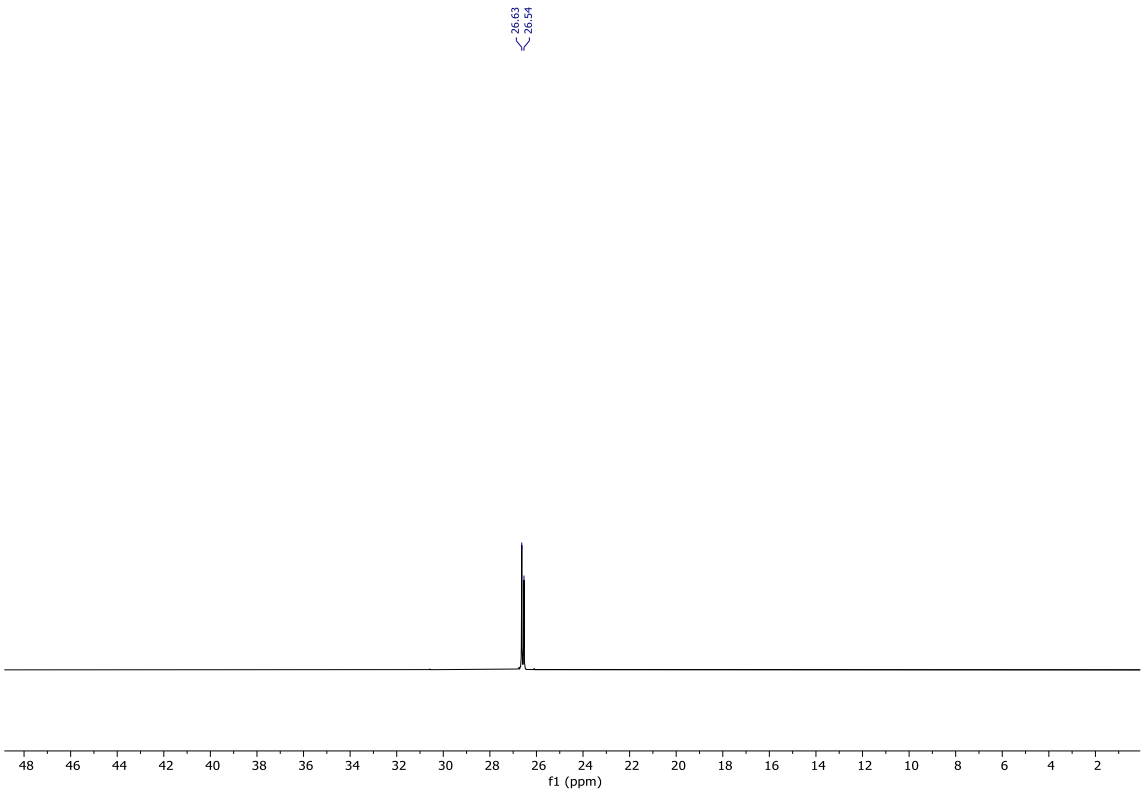

159.93
159.23
138.10
137.94
132.74
132.60
130.37
130.34
129.49
128.10
127.77
114.13
113.92
113.54
112.48
110.68
110.59
55.34
55.31
54.18
54.10
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)


25.47
25.18
43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5
f1 (ppm)

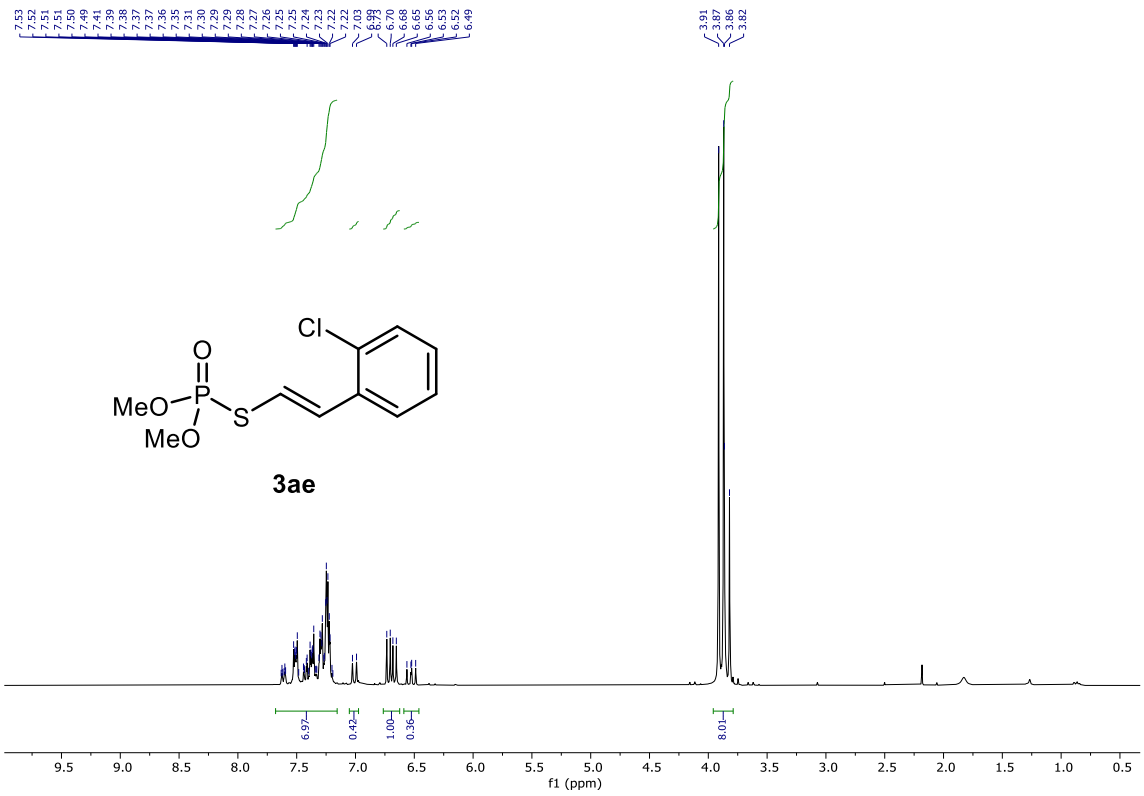
(*E*)-*O,O*-dimethyl *S*-(2-(naphthalen-2-yl)vinyl) phosphorothioate (3ad)

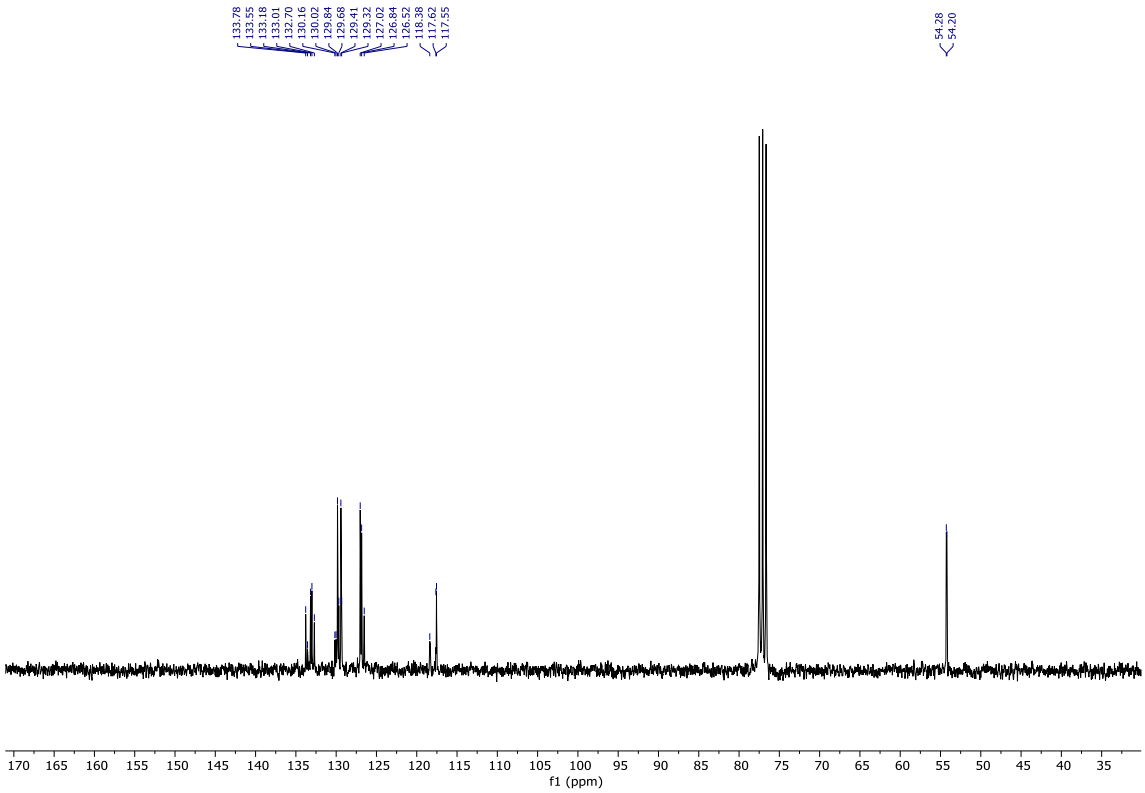


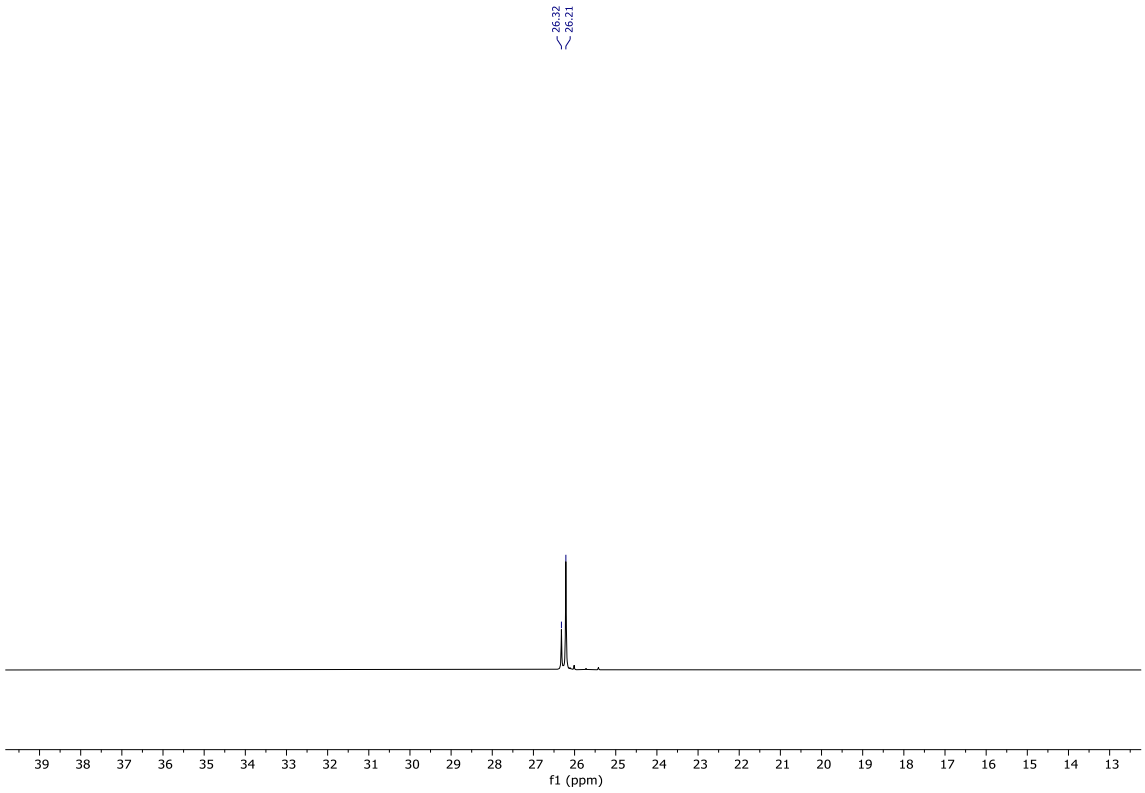




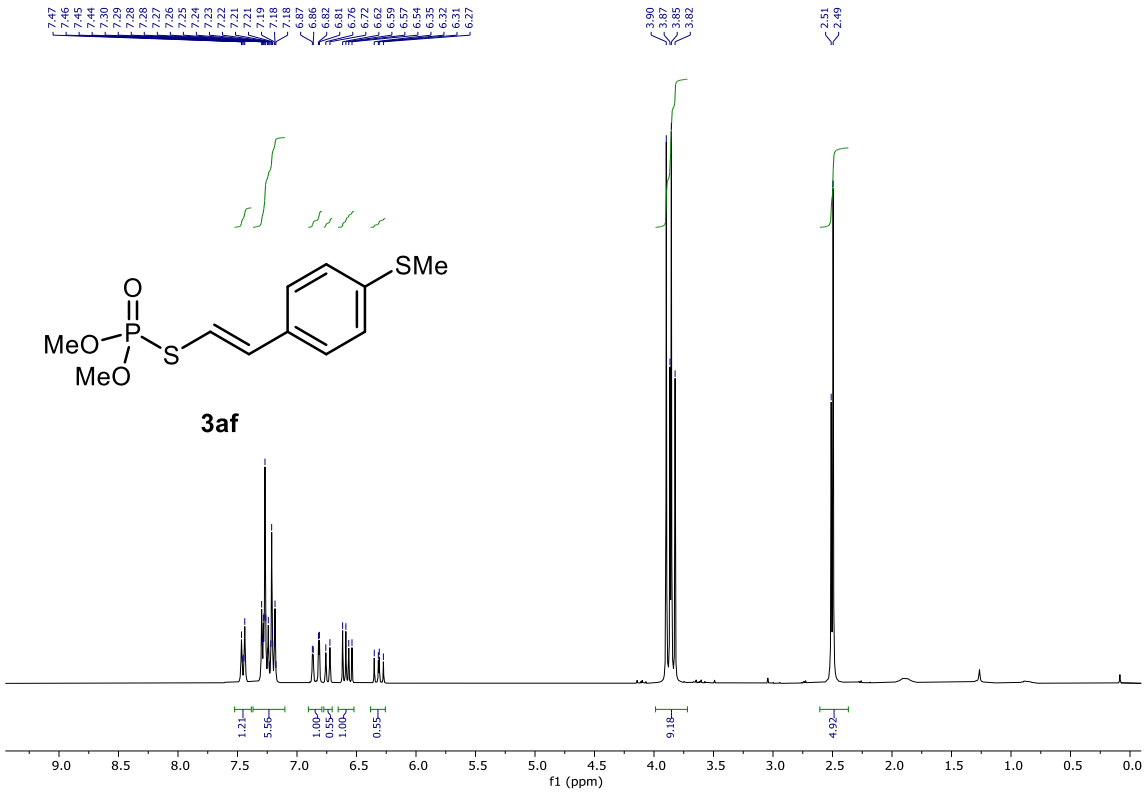
(*E*)-*S*-(2-chlorostyryl) *O,O*-dimethyl phosphorothioate (3ae)

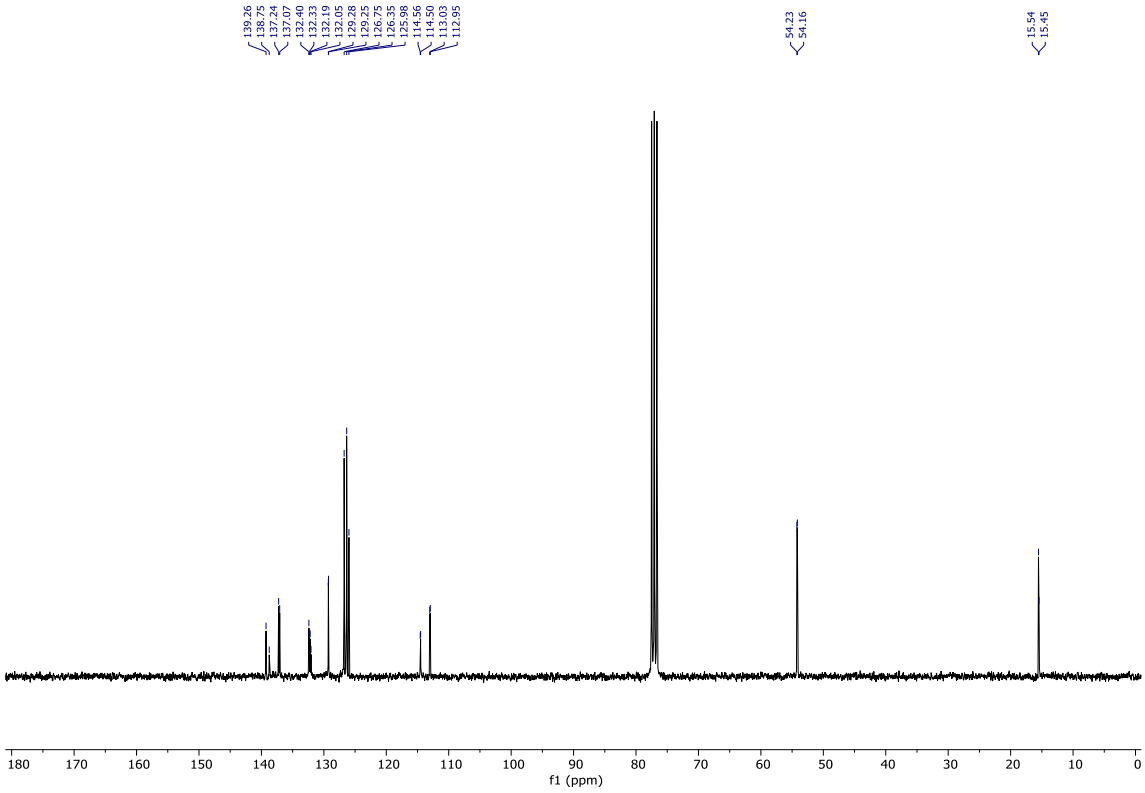


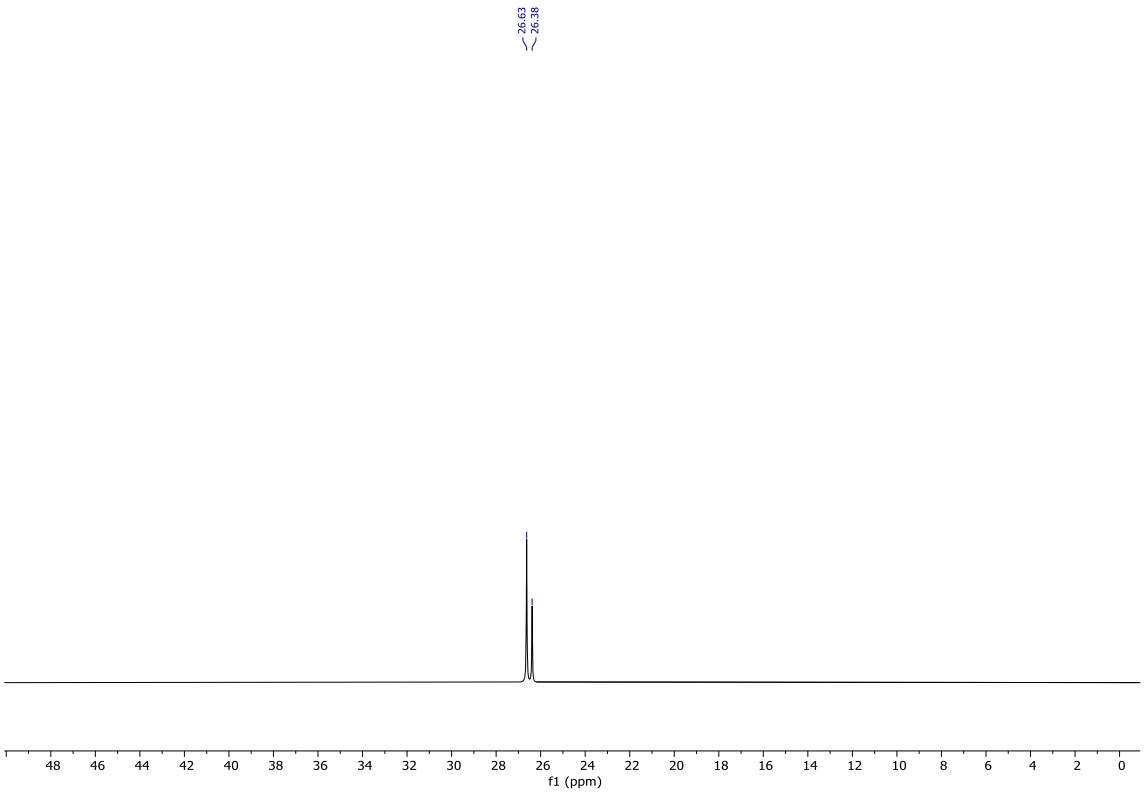

133.78
133.55
133.18
133.01
132.70
130.16
130.02
129.84
129.68
129.41
129.32
127.02
126.84
126.52
118.38
117.62
117.55
54.28
54.20
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)


26.32
26.21
39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13
f1 (ppm)

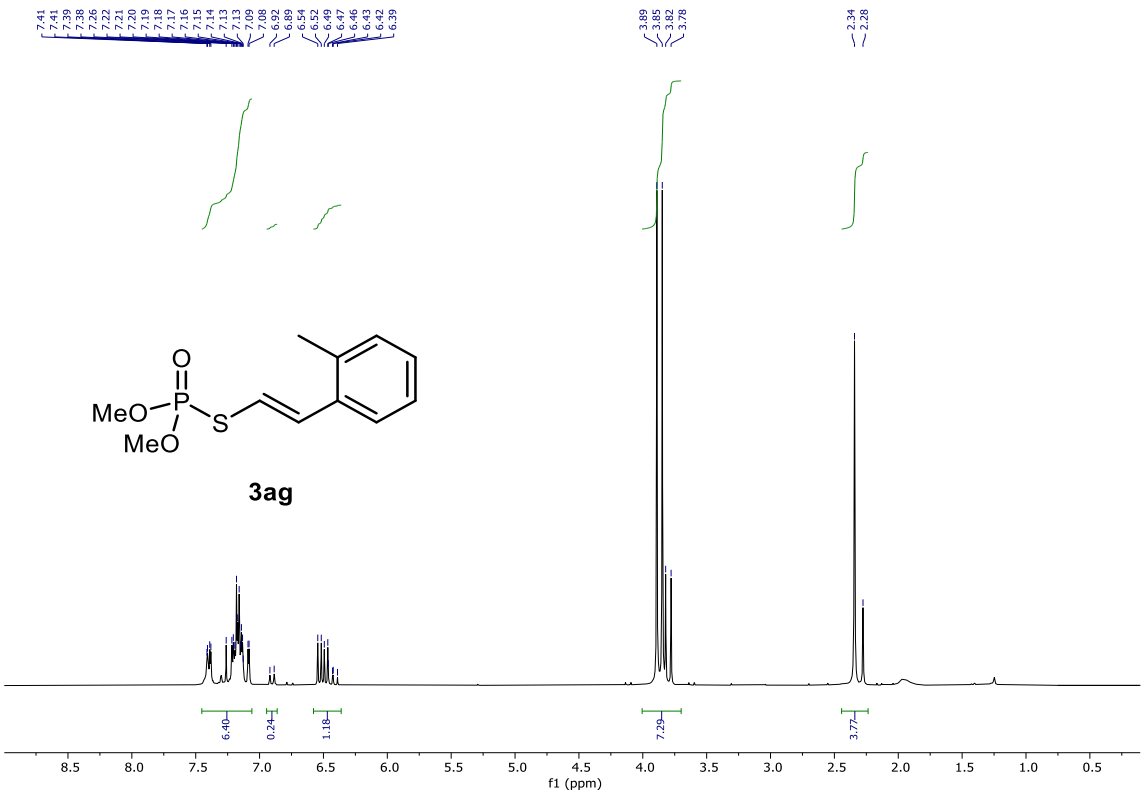
(*E*)-*O,O*-dimethyl *S*-(4-(methylthio)styryl) phosphorothioate (3af)

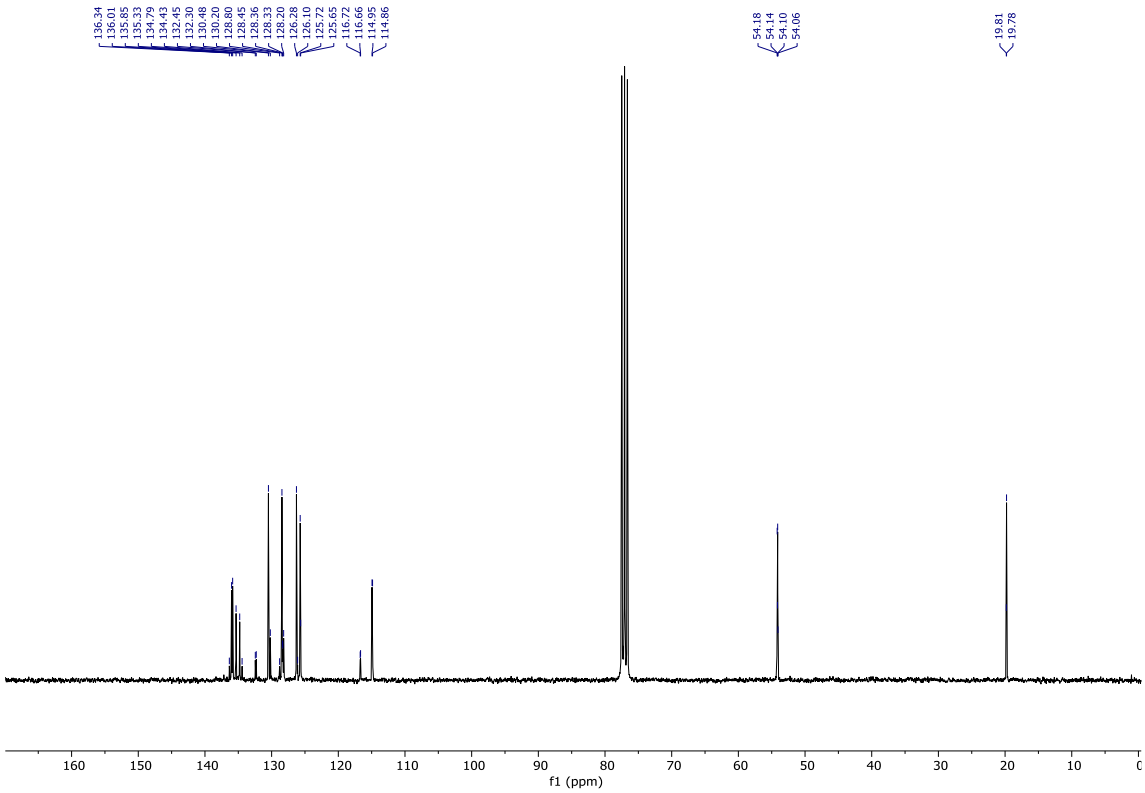


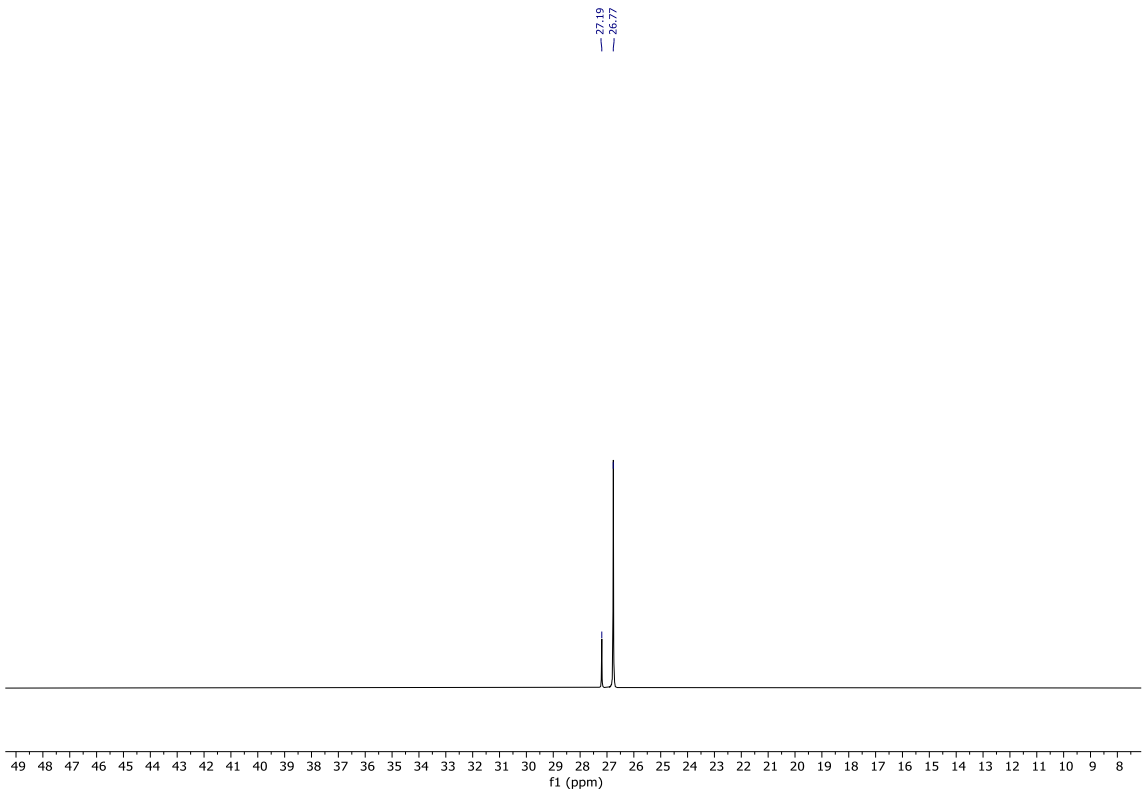




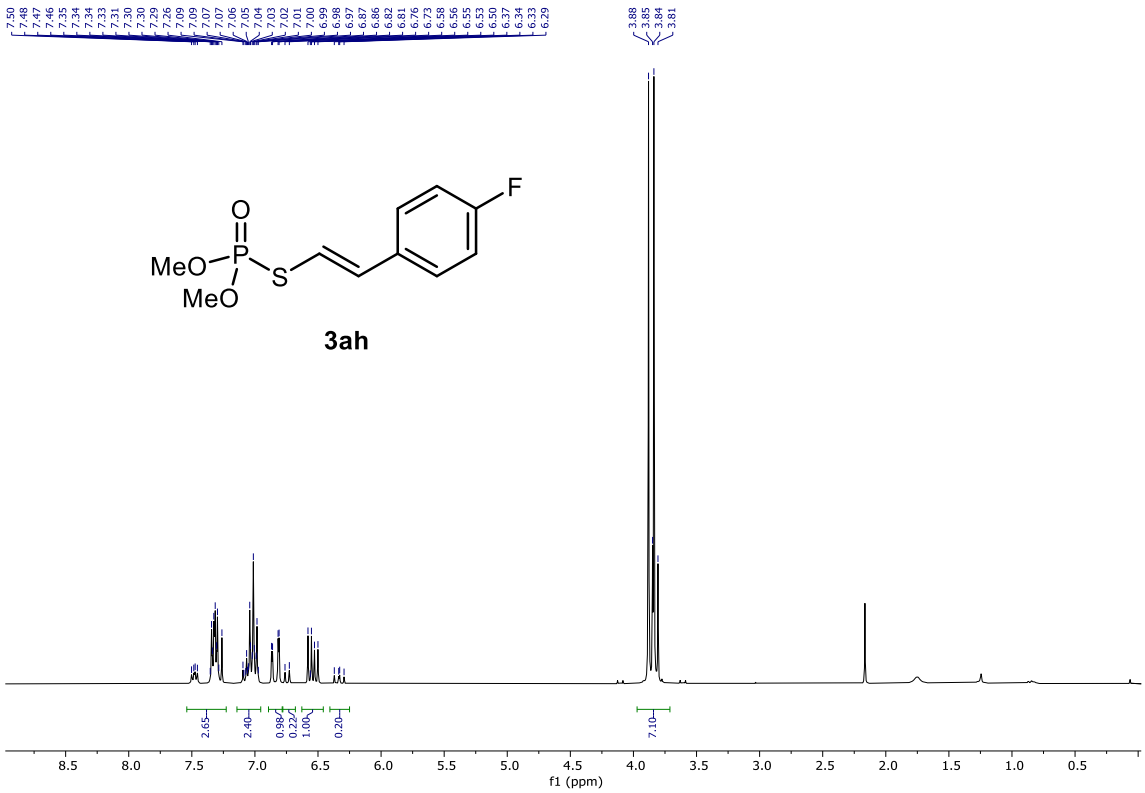
(*E*)-*O,O*-dimethyl *S*-(2-methylstyryl) phosphorothioate (3ag)

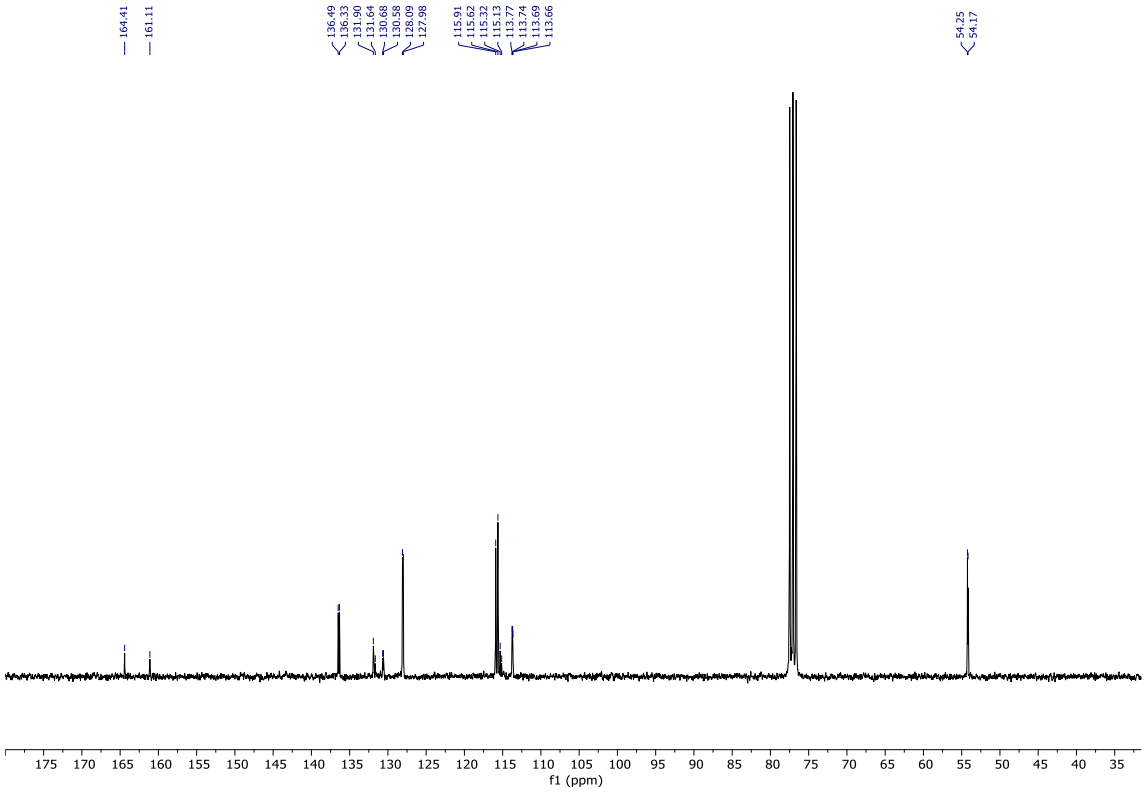


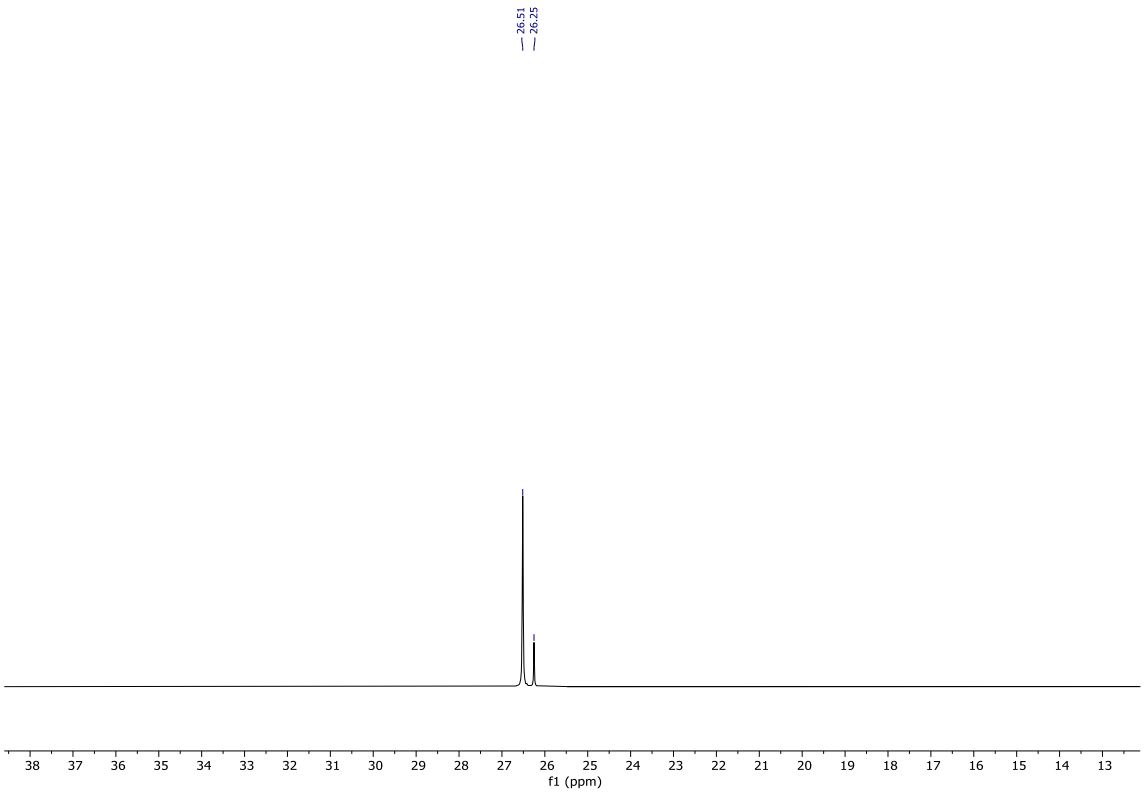

136.34
136.01
135.85
135.33
134.79
134.43
132.45
132.30
130.48
130.20
128.80
128.45
128.36
128.23
128.20
126.28
126.10
125.72
125.65
116.72
116.66
114.95
114.86
54.18
54.14
54.10
54.06
19.81
19.78
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

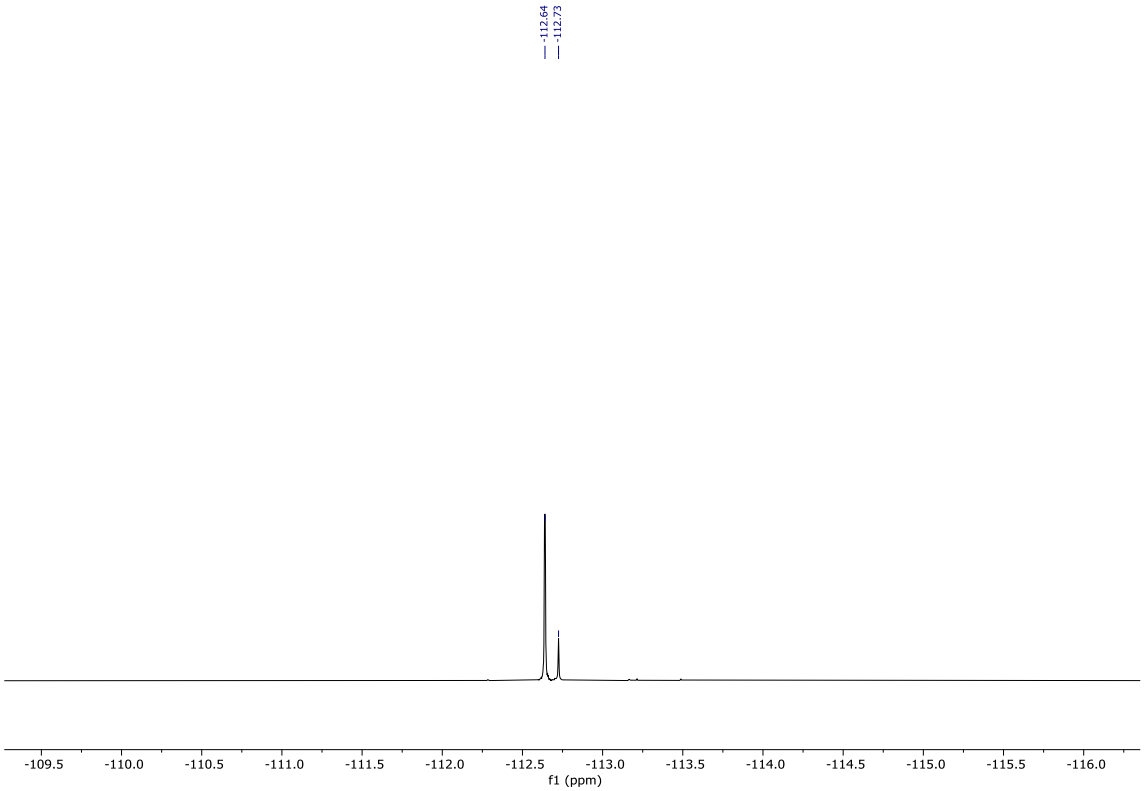

27.19
26.77
49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8
f1 (ppm)

(*E*)-*S*-(4-fluorostyryl) *O,O*-dimethyl phosphorothioate (3ah)

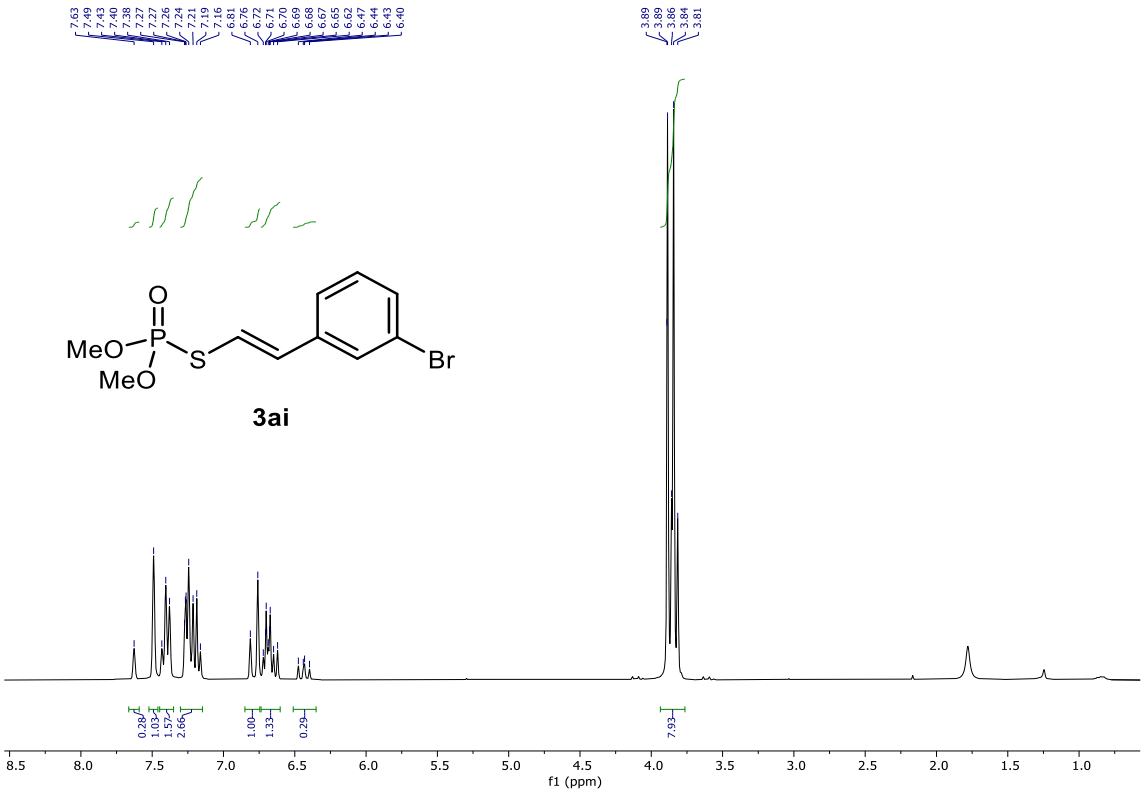


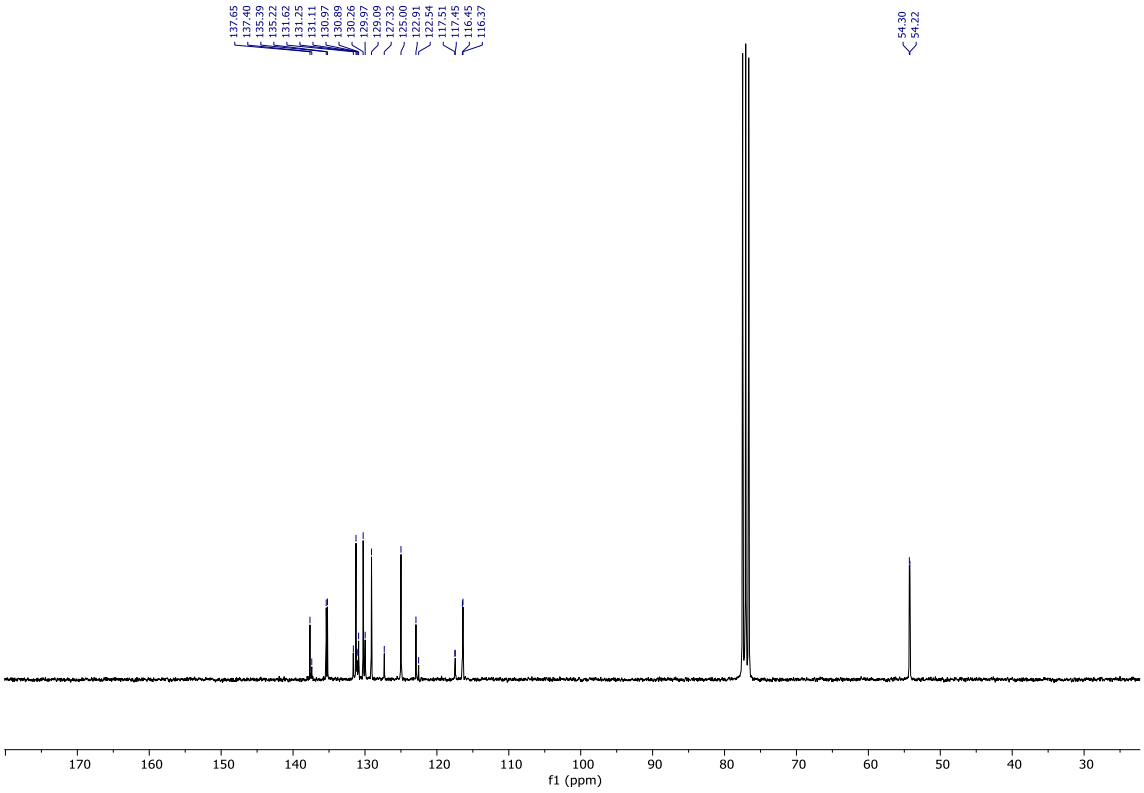


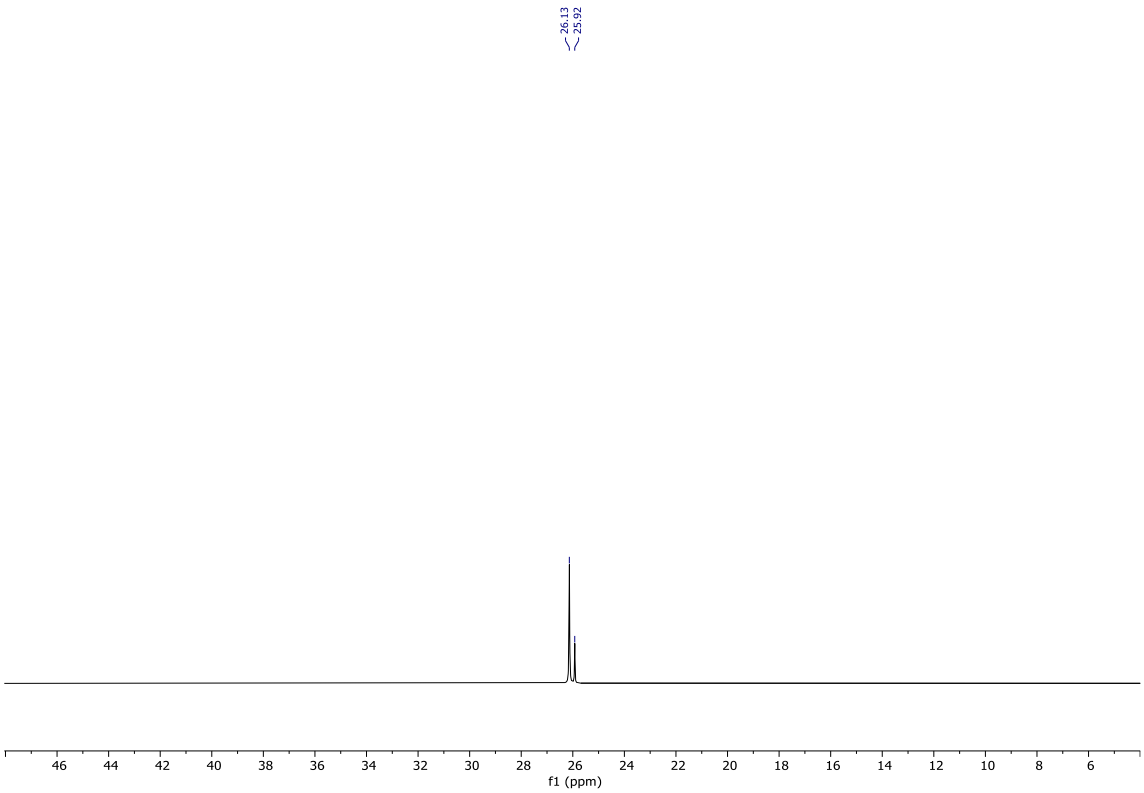

26.51
26.25
38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13
f1 (ppm)


-112.64
-112.73
-109.5 -110.0 -110.5 -111.0 -111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0 -115.5 -116.0
f1 (ppm)

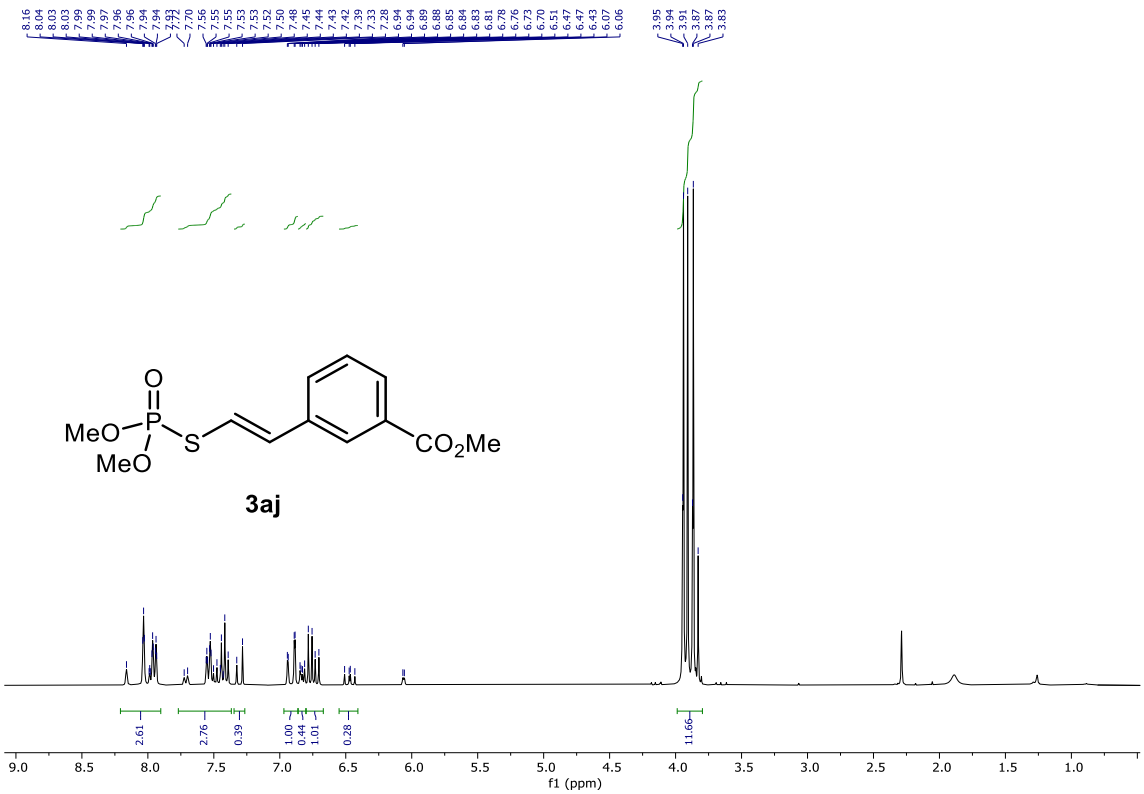
(*E*)-*S*-(3-bromostyryl) *O,O*-dimethyl phosphorothioate (3ai)

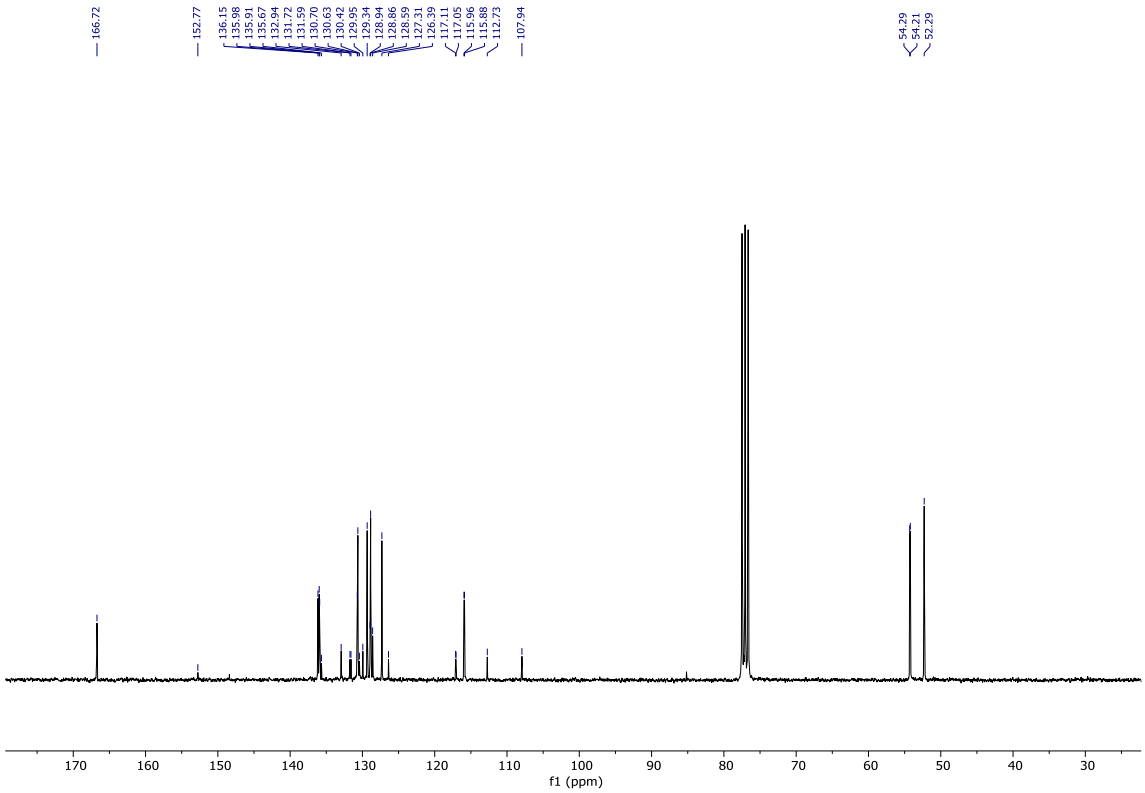


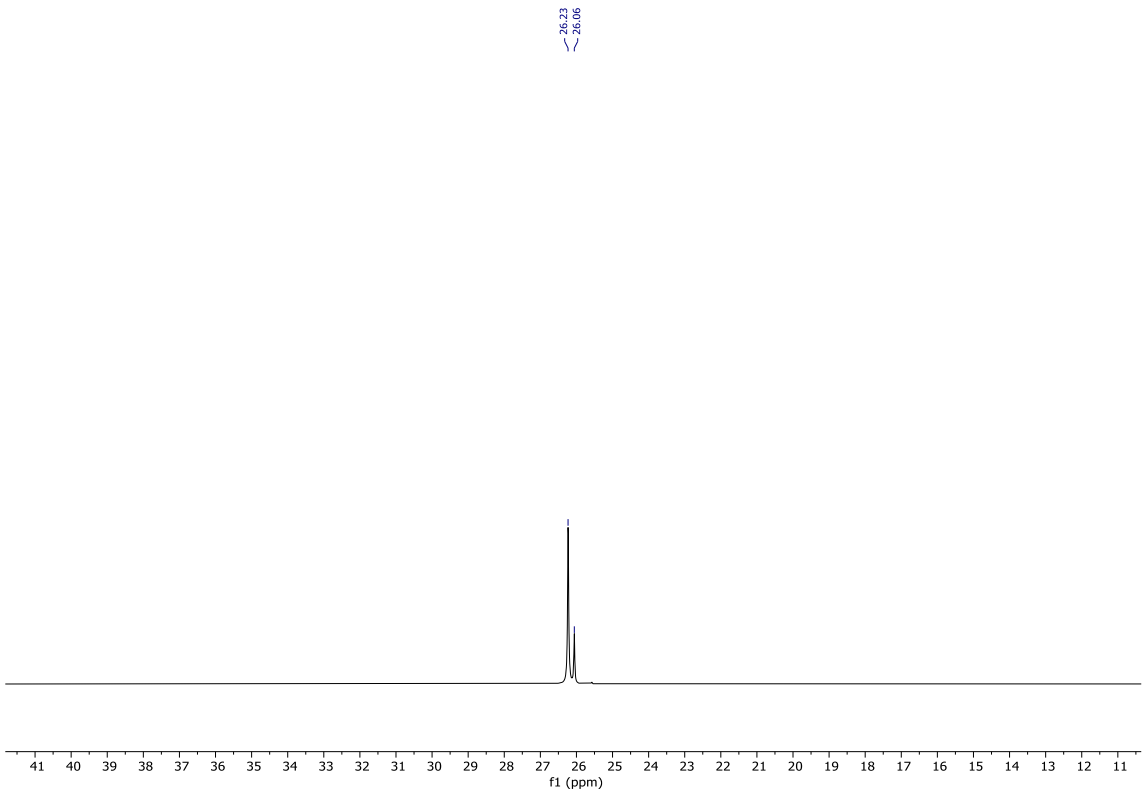




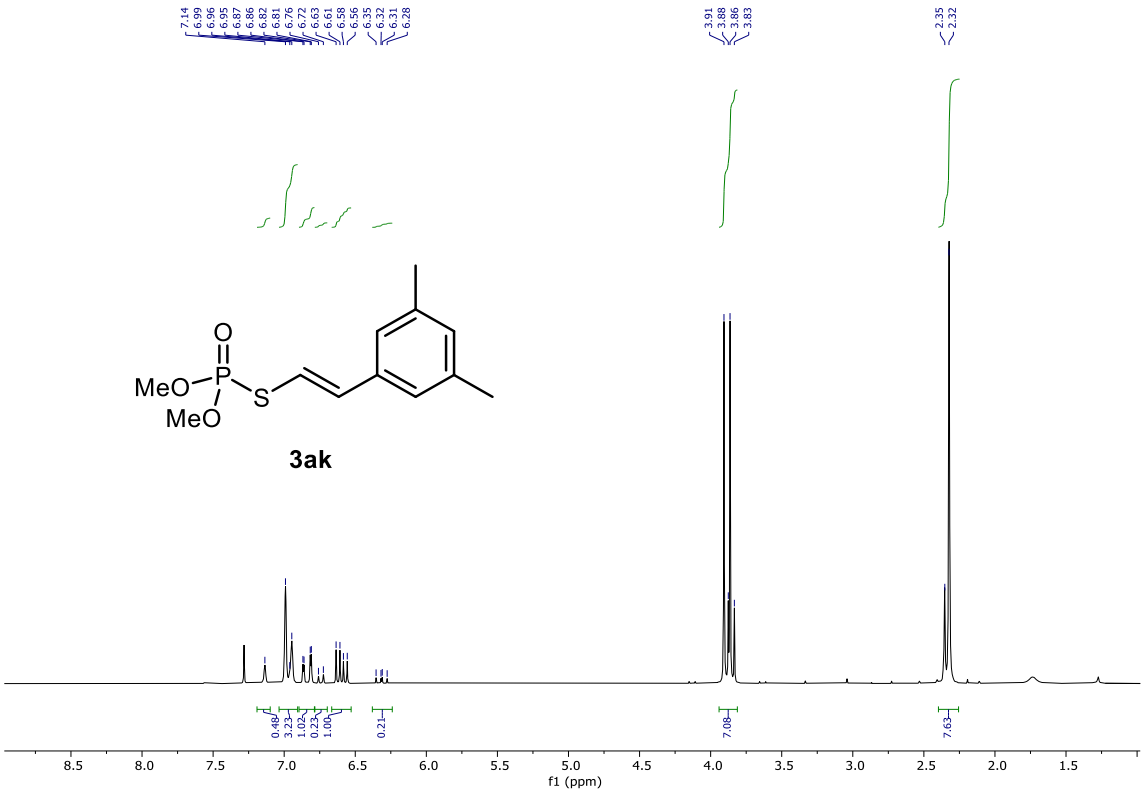
Methyl (*E*)-3-(2-((dimethoxyphosphoryl)thio)vinyl)benzoate (3aj)

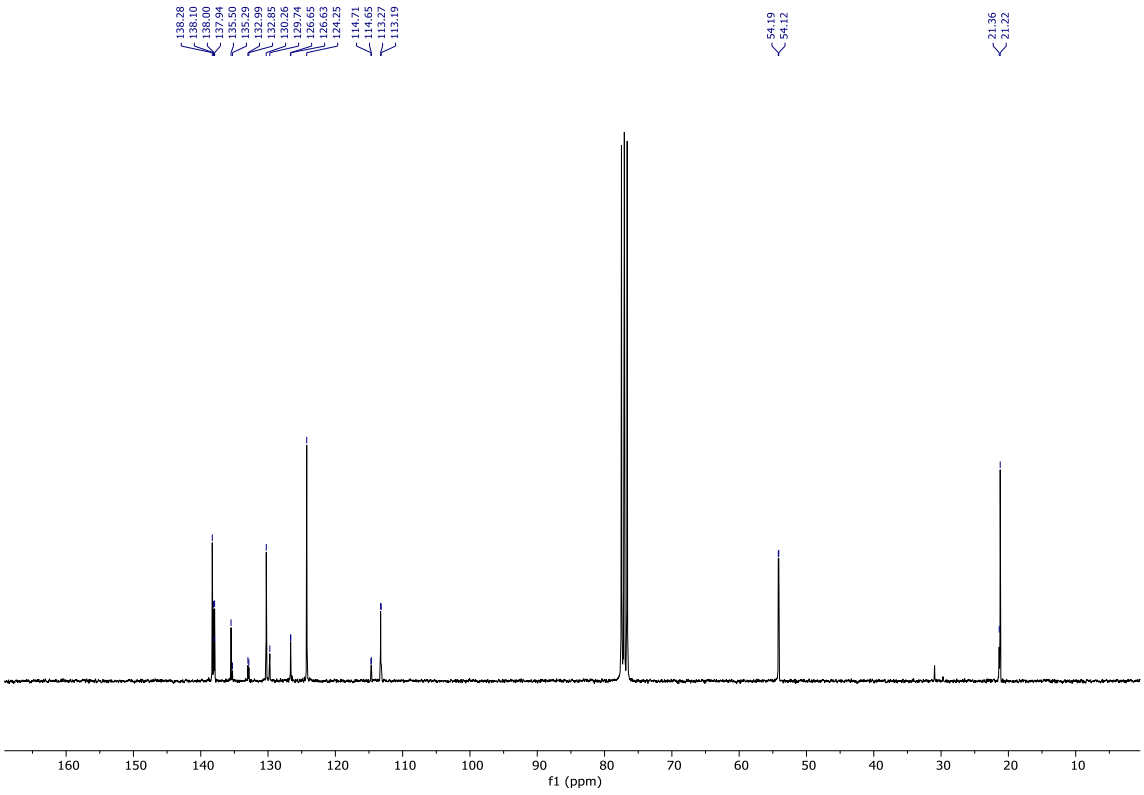


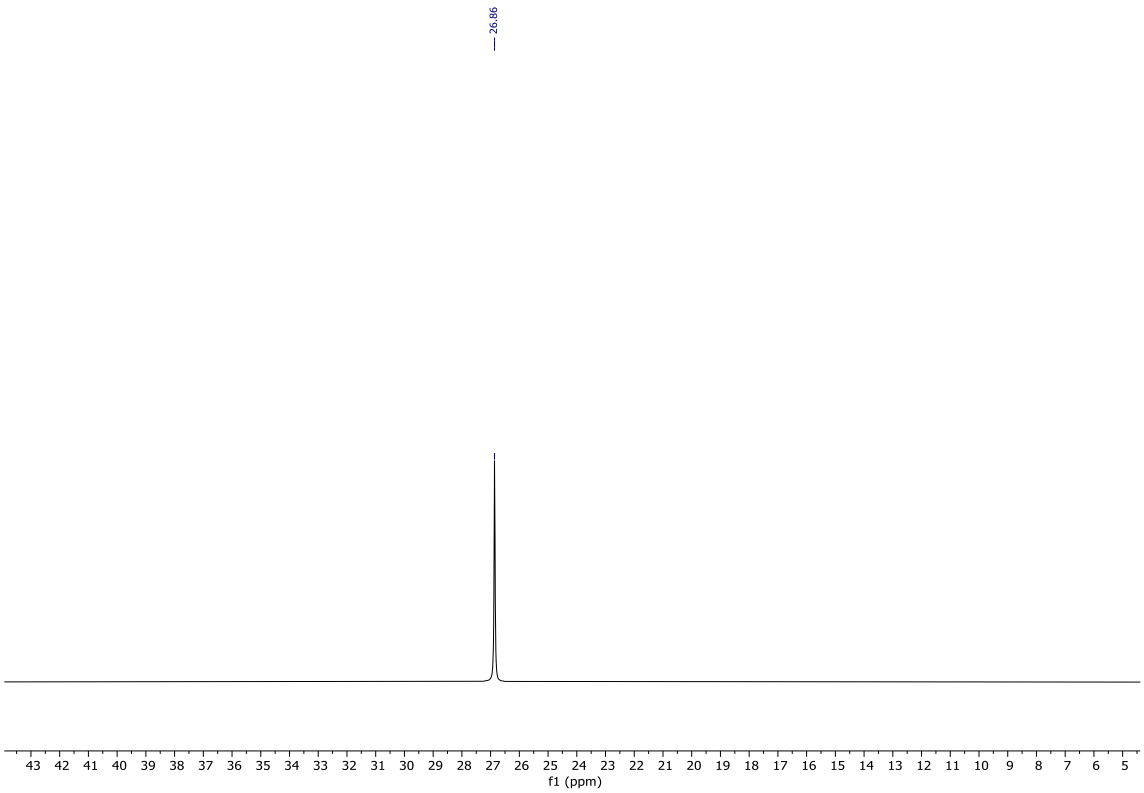

166.72
152.77
136.15
135.98
135.91
135.67
132.94
131.72
131.59
130.70
130.63
130.42
129.95
129.34
128.94
128.86
128.59
127.31
126.39
117.11
117.05
115.96
115.88
112.73
107.94
54.29
54.21
52.29
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)


26.23
26.06
41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11
f1 (ppm)

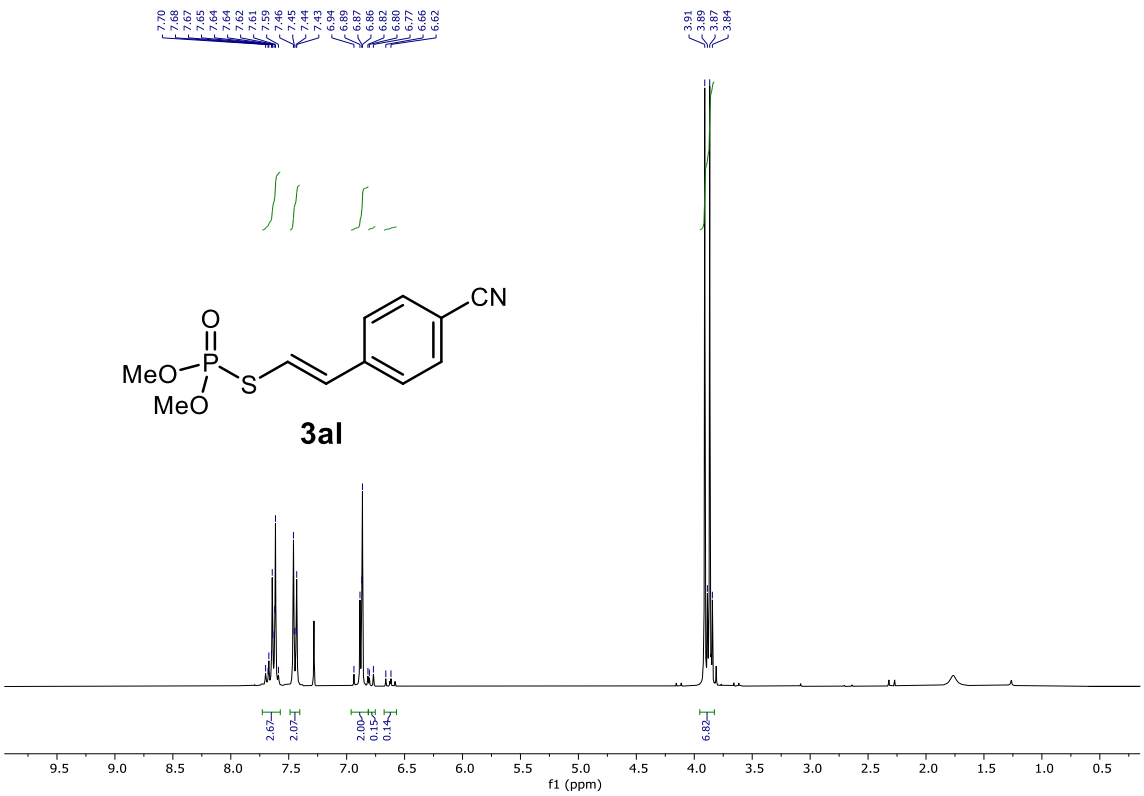
(*E*)-*S*-(3,5-dimethylstyryl) *O,O*-dimethyl phosphorothioate (3ak)

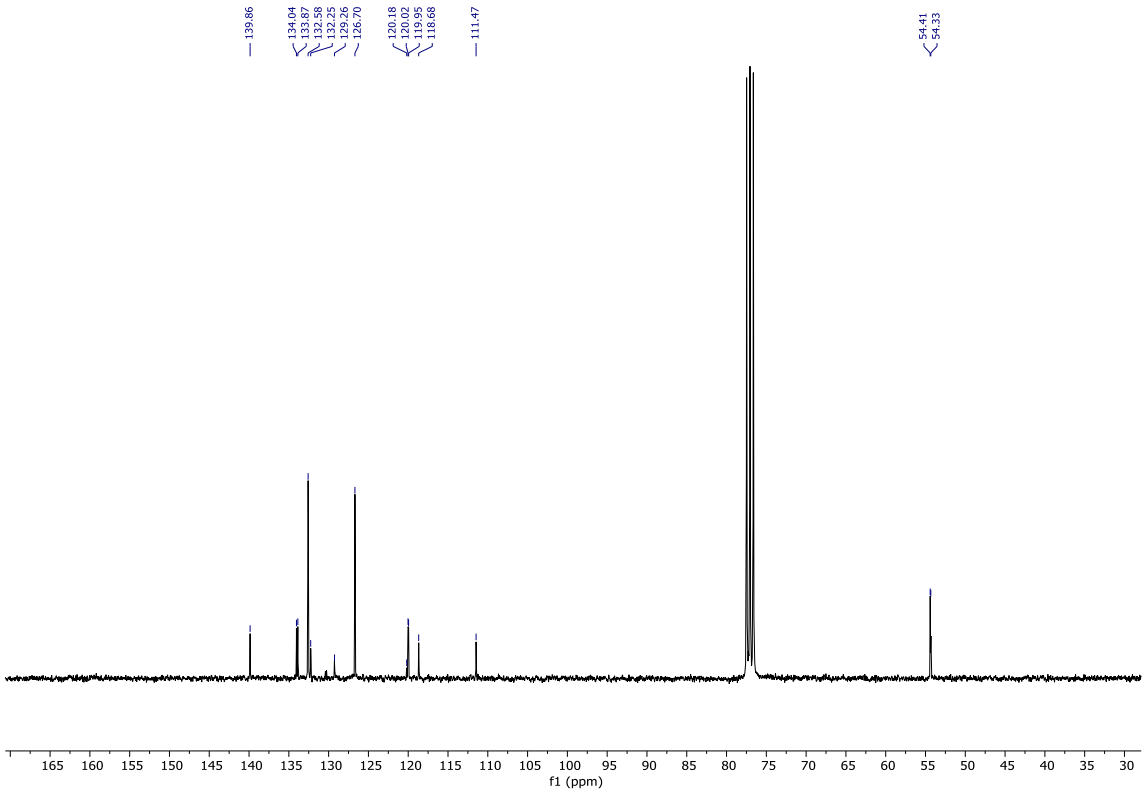


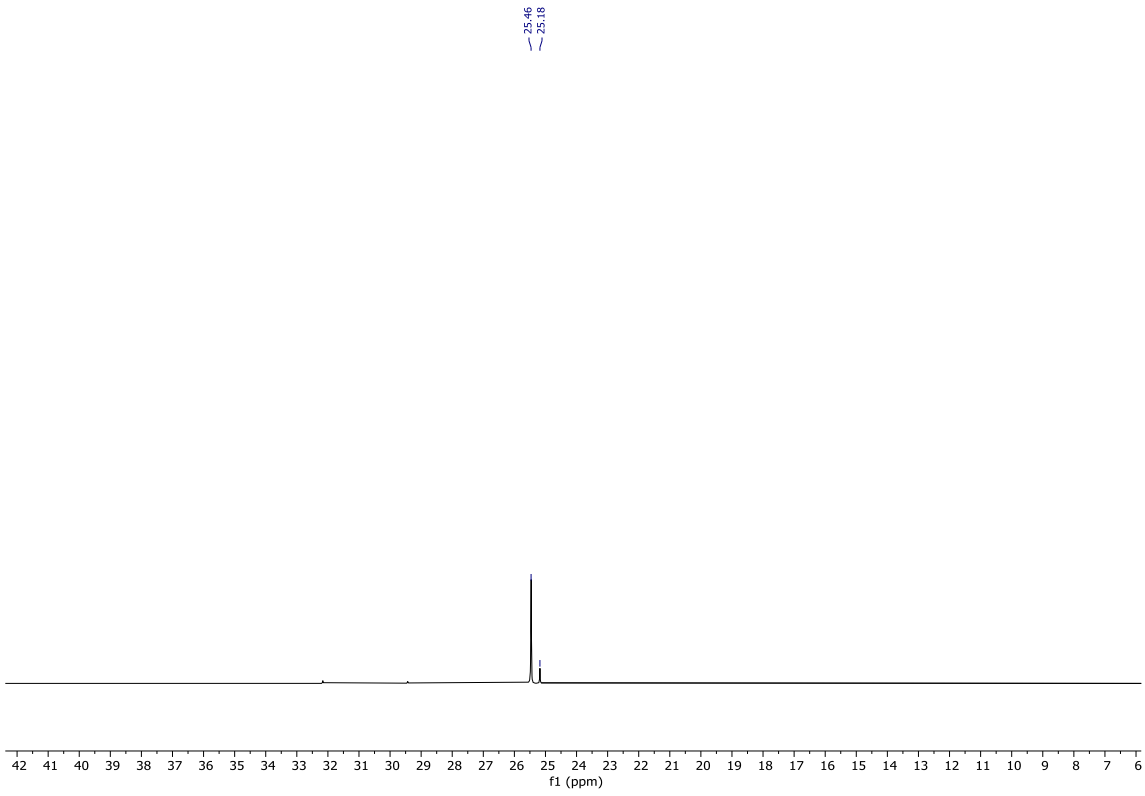




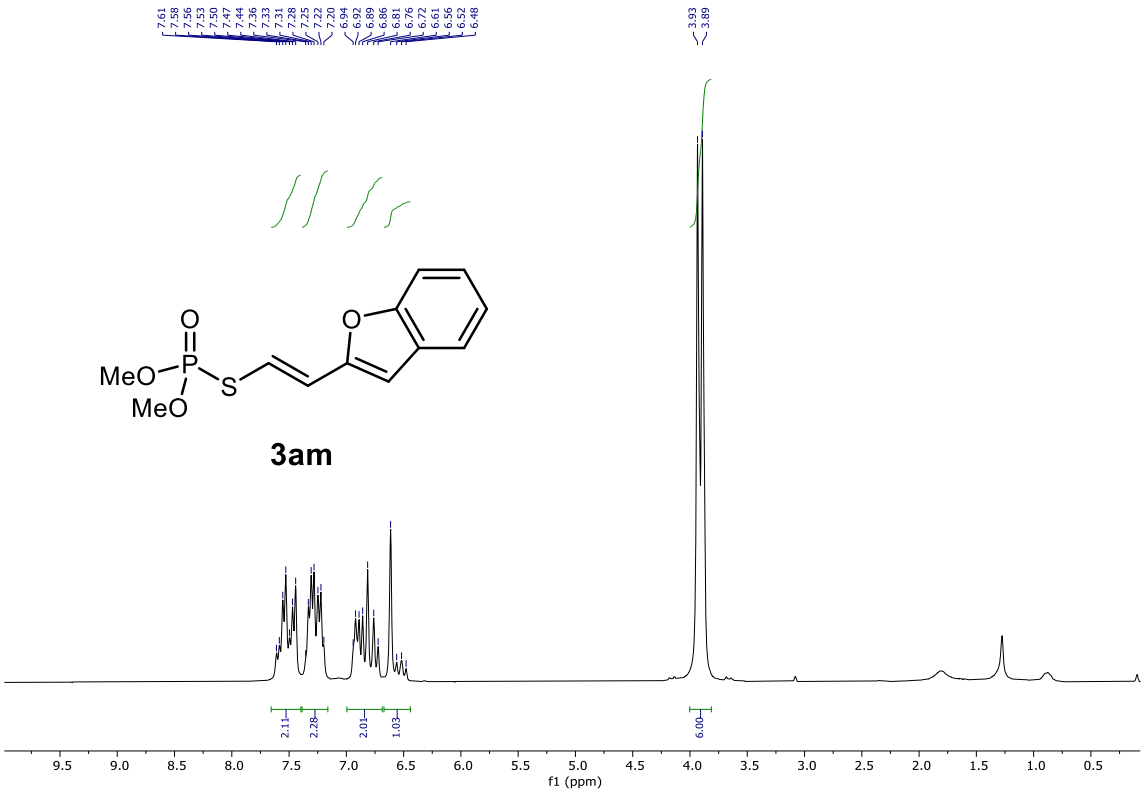
(*E*)-*S*-(4-cyanostyryl) *O,O*-dimethyl phosphorothioate (3al)

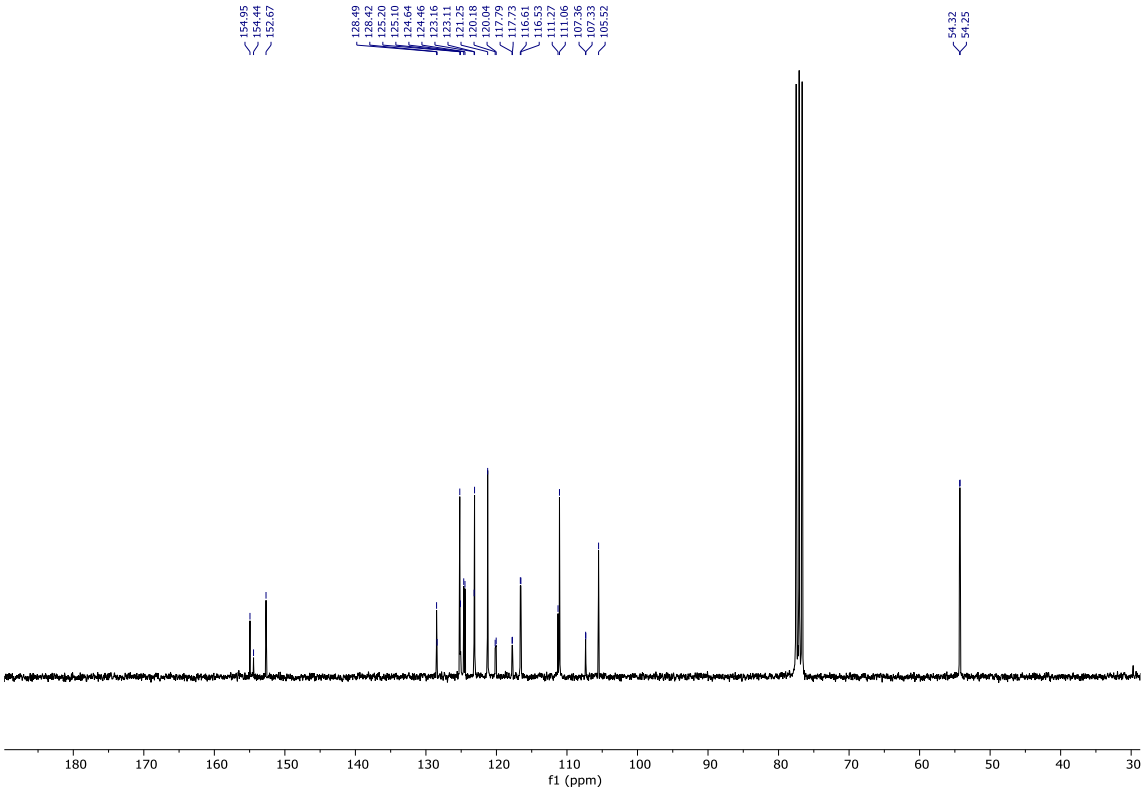


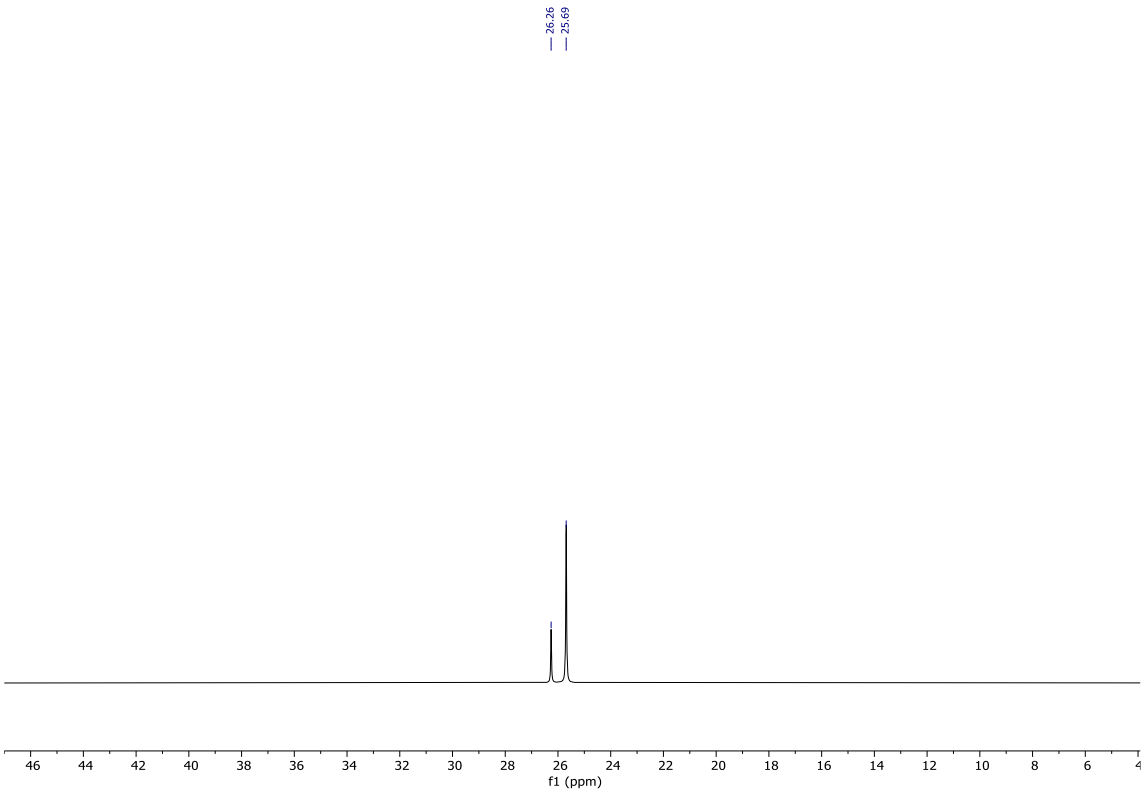

139.86
134.04
133.87
132.58
132.25
129.26
126.70
120.18
120.02
119.95
118.68
111.47
54.41
54.33
f1 (ppm)


25.46
25.18
f1 (ppm)

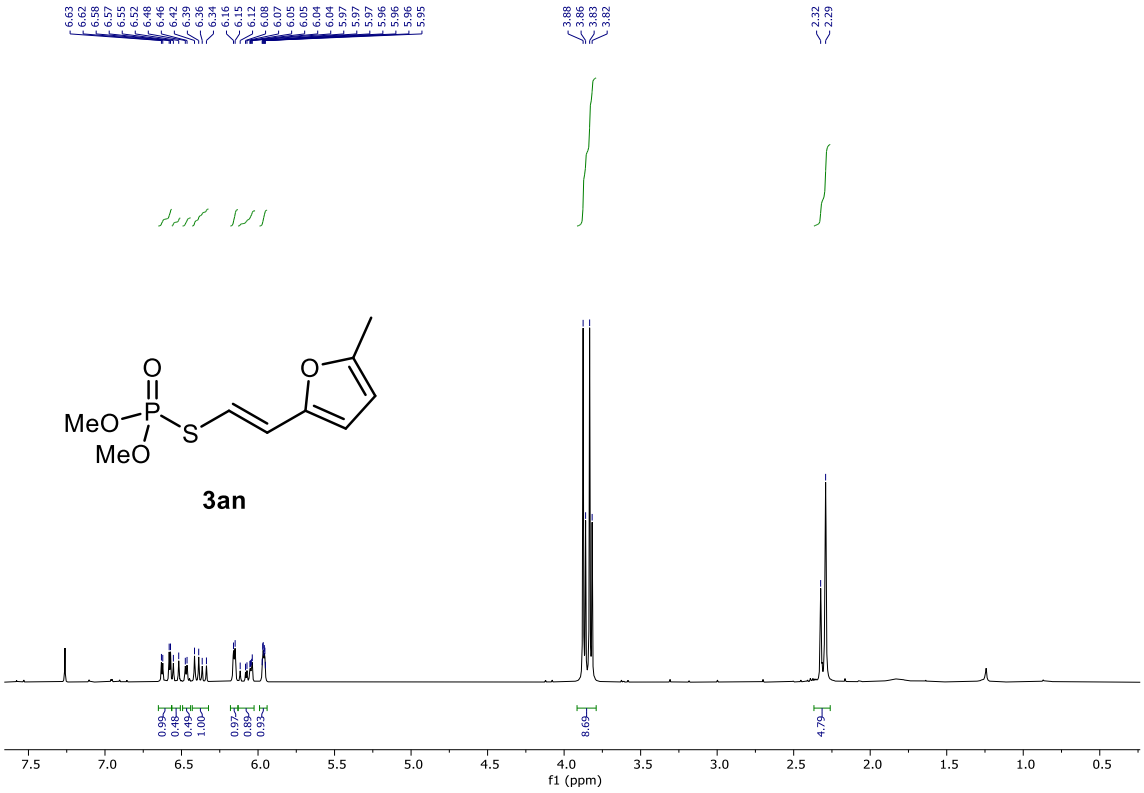
(*E*)-*S*-(2-(benzofuran-2-yl)vinyl) *O,O*-dimethyl phosphorothioate (3am)

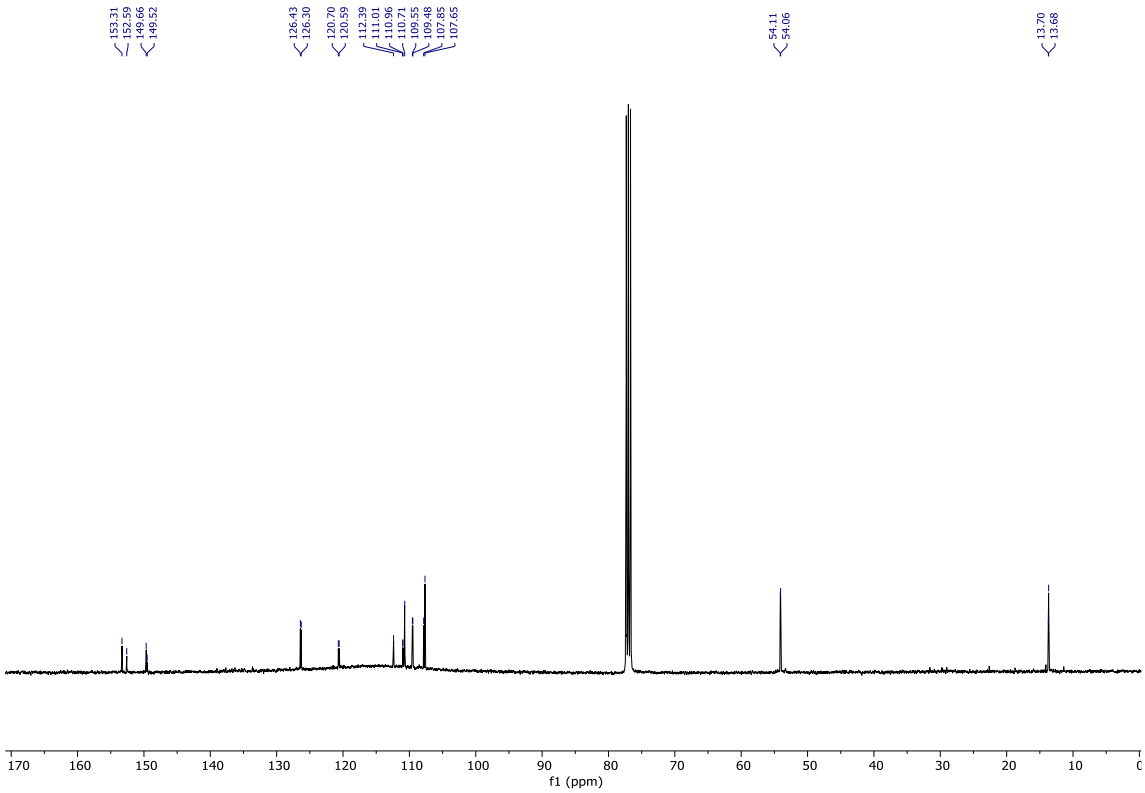


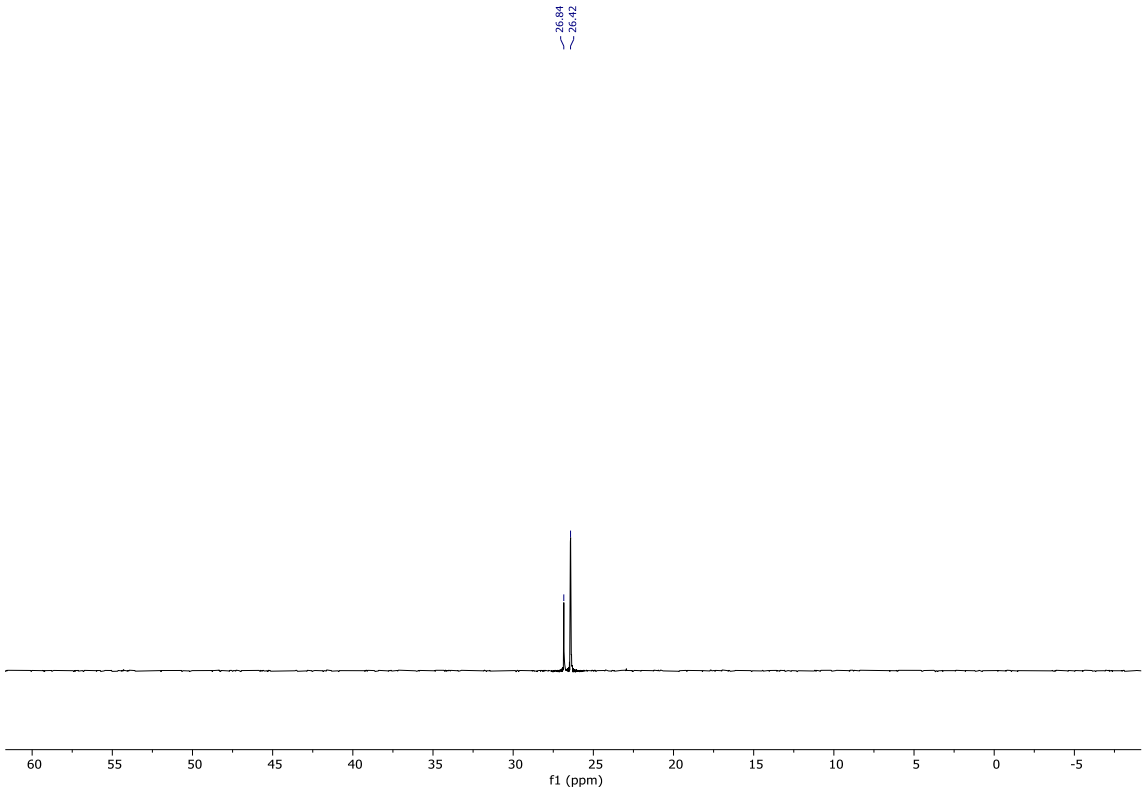




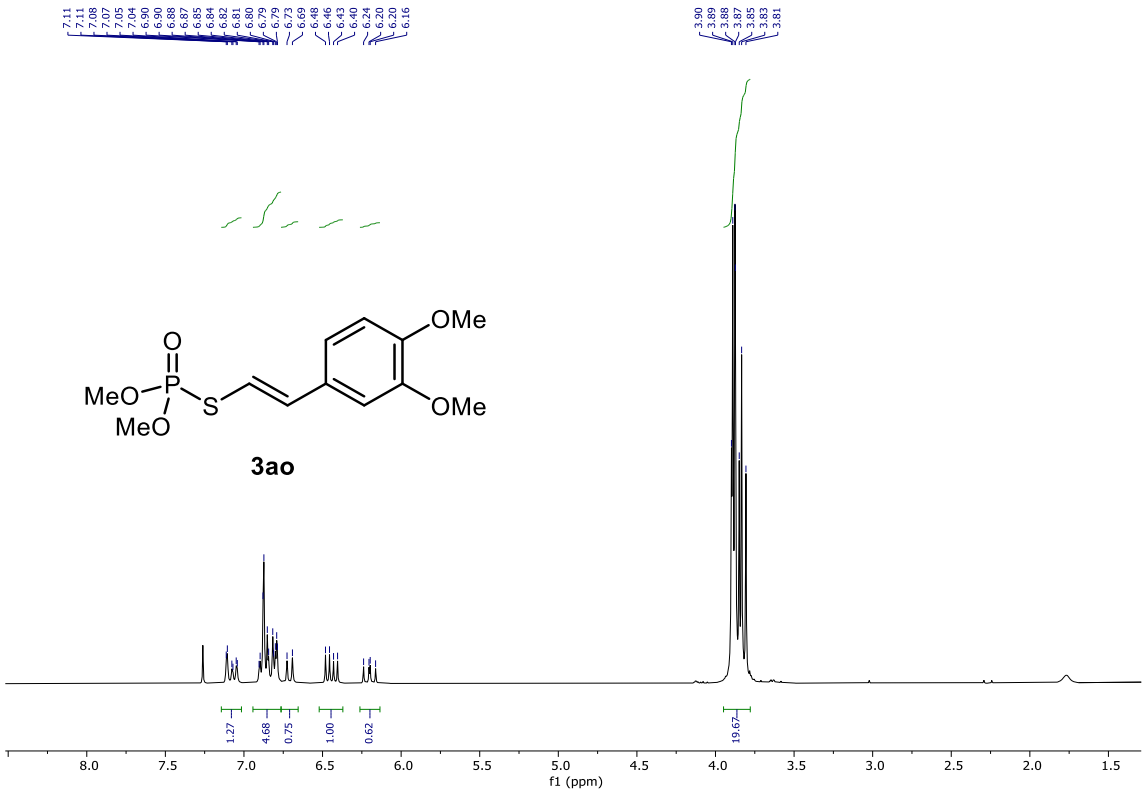
(*E*)-*O,O*-dimethyl *S*-(2-(5-methylfuran-2-yl)vinyl) phosphorothioate (3an)

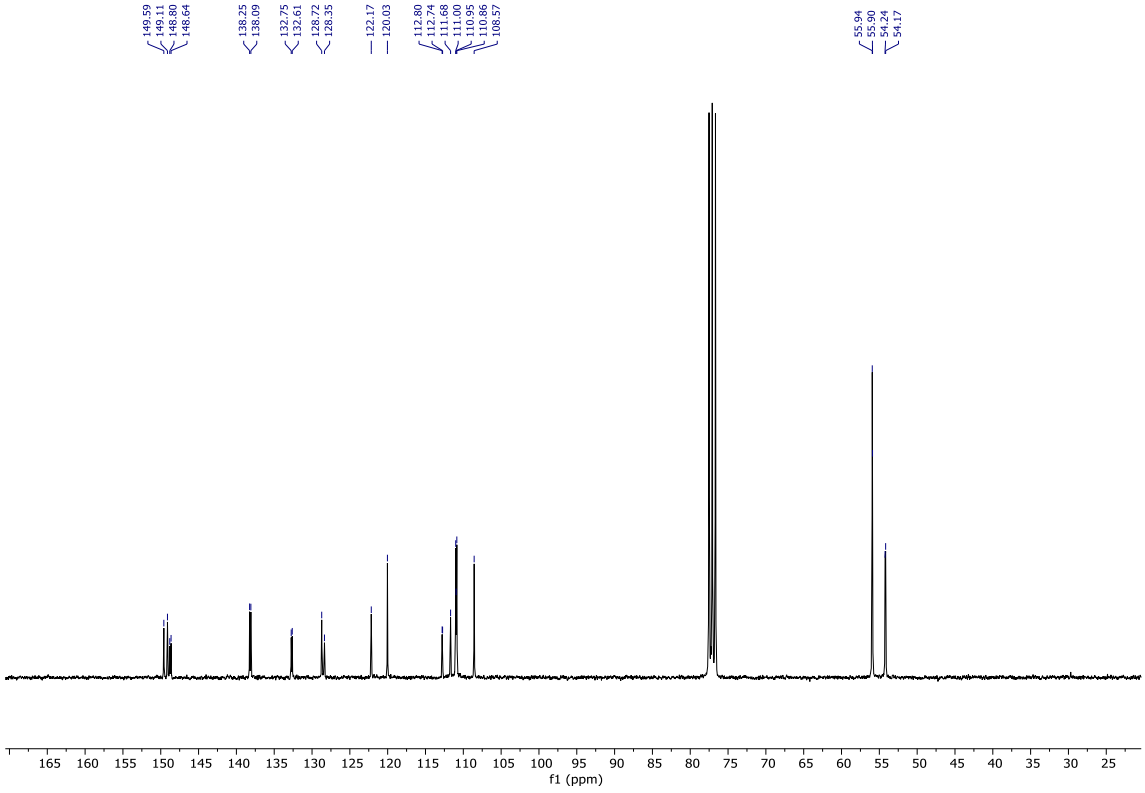


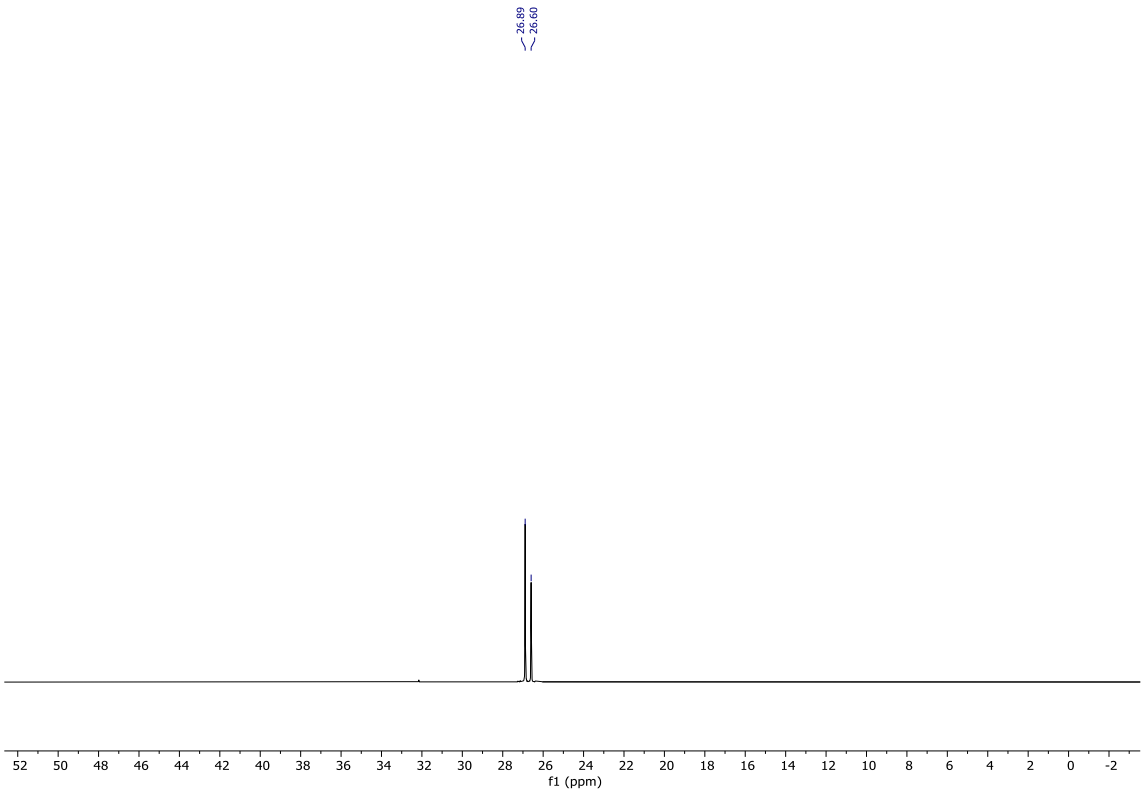

153.31
152.59
149.66
149.52
126.43
126.30
120.70
120.59
112.39
111.01
110.96
110.71
109.55
109.48
107.85
107.65
54.11
54.06
13.70
13.68
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


26.84
26.42
60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

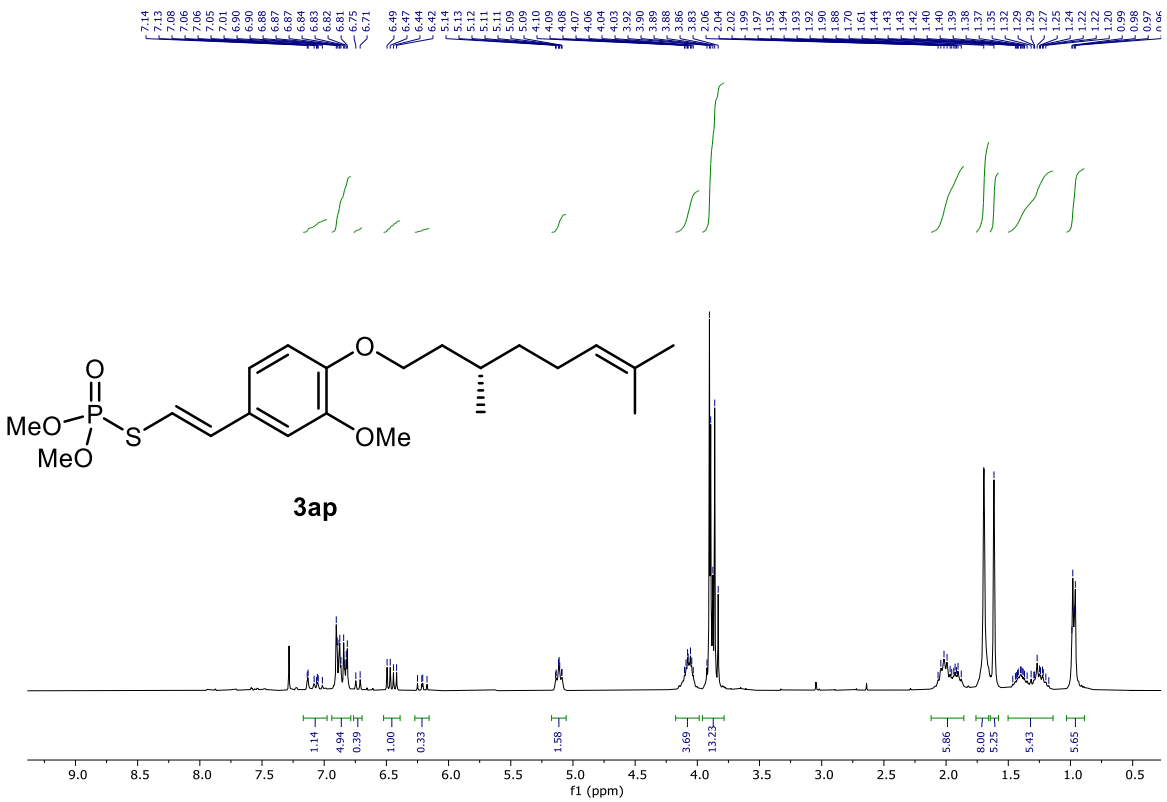
(*E*)-*S*-(3,4-dimethoxystyryl) *O,O*-dimethyl phosphorothioate (3o)

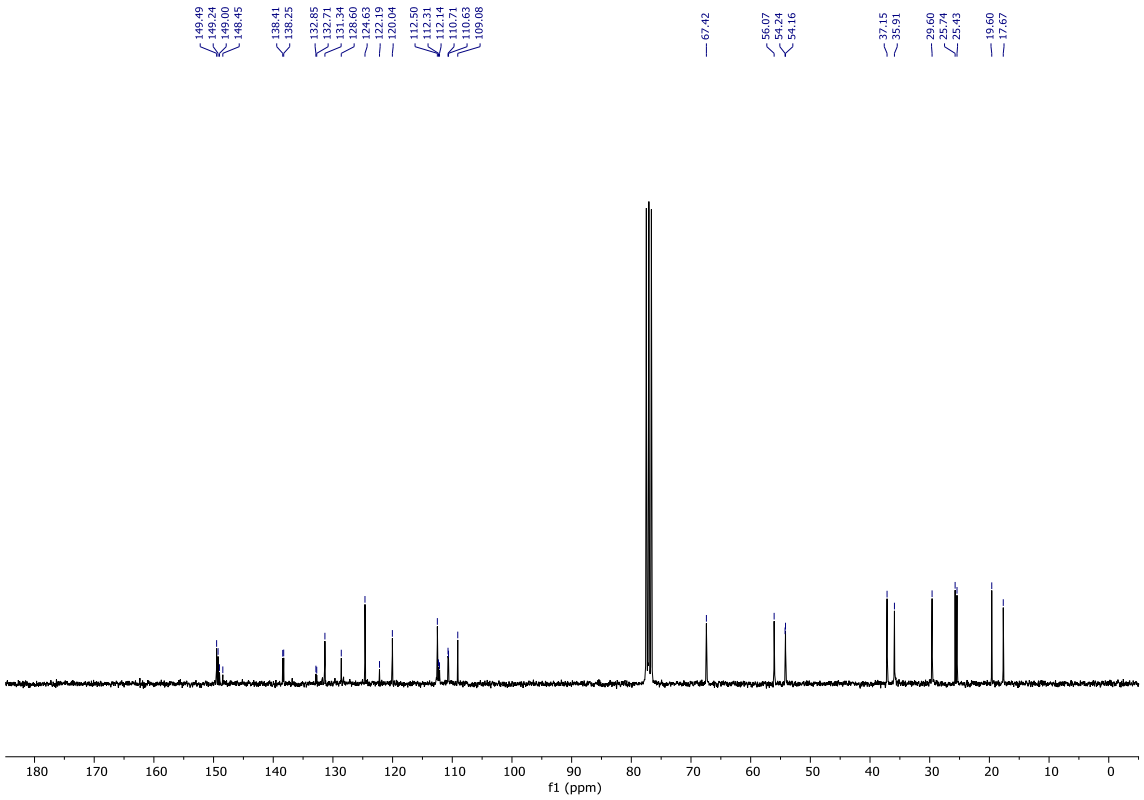


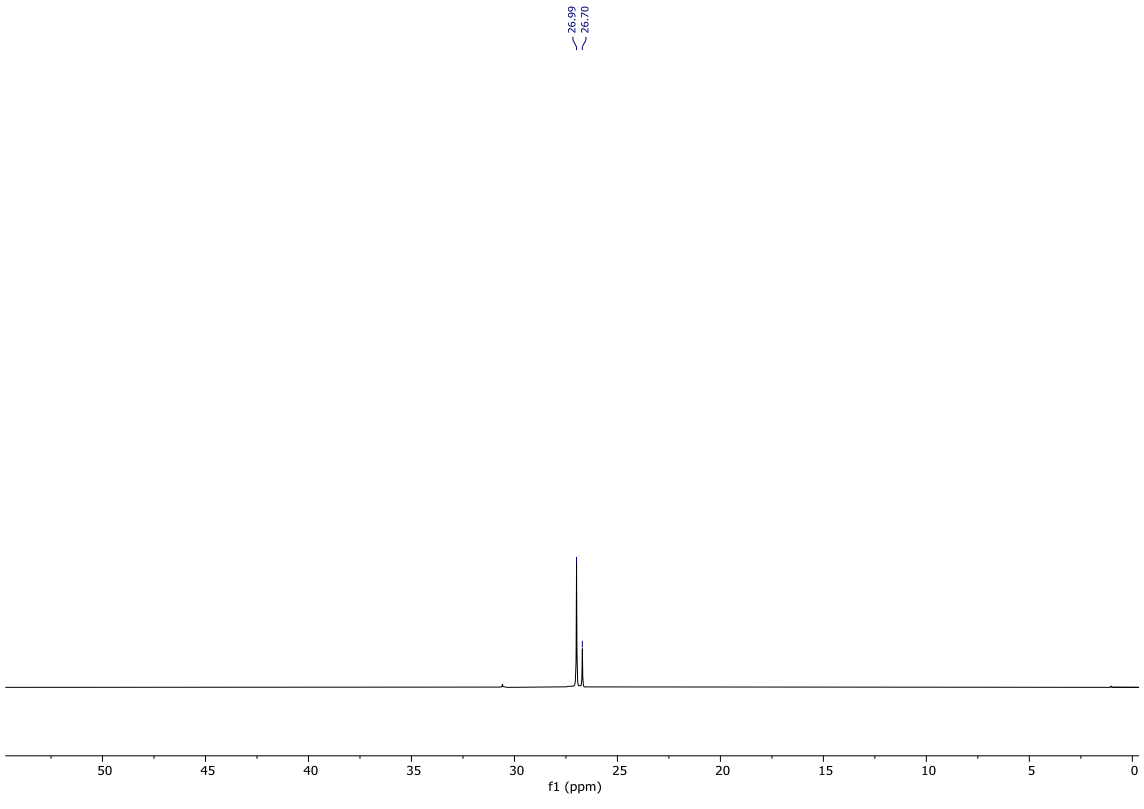




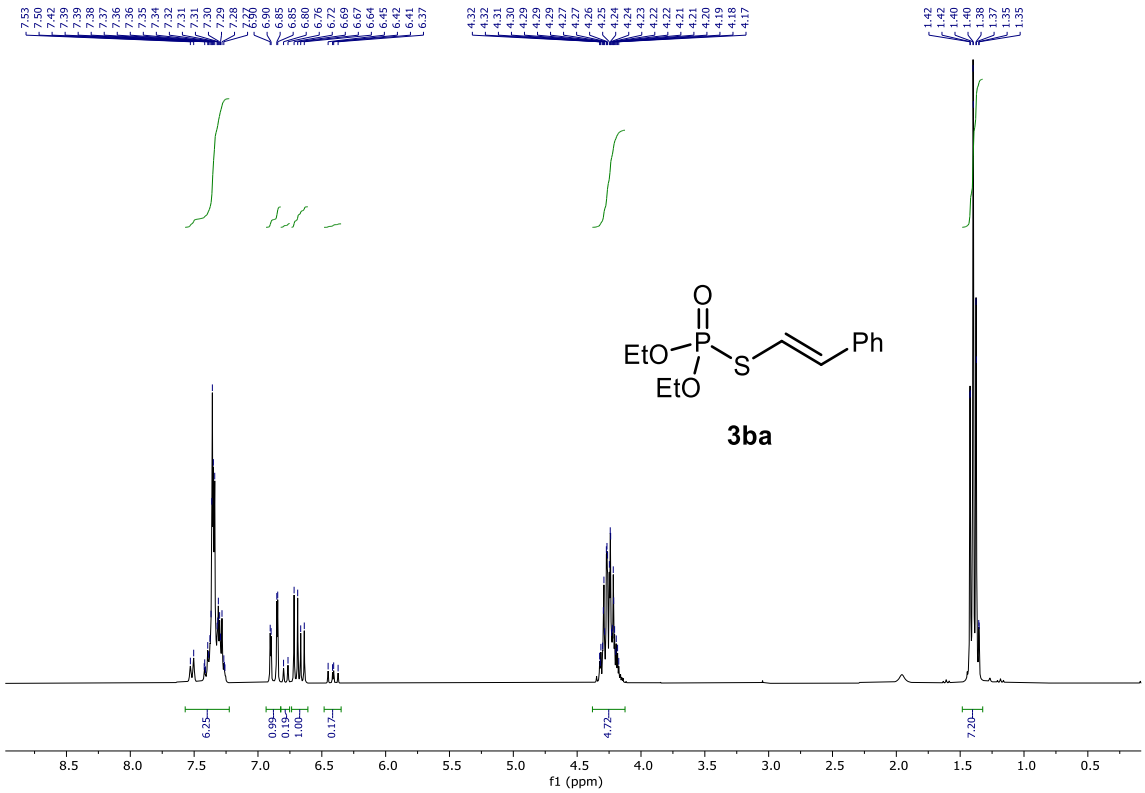
(*E*)-*S*-(4-((3,7-dimethyloct-6-en-1-yl)oxy)-3-methoxystyryl) *O,O*-dimethyl phosphorothioate (3ap)

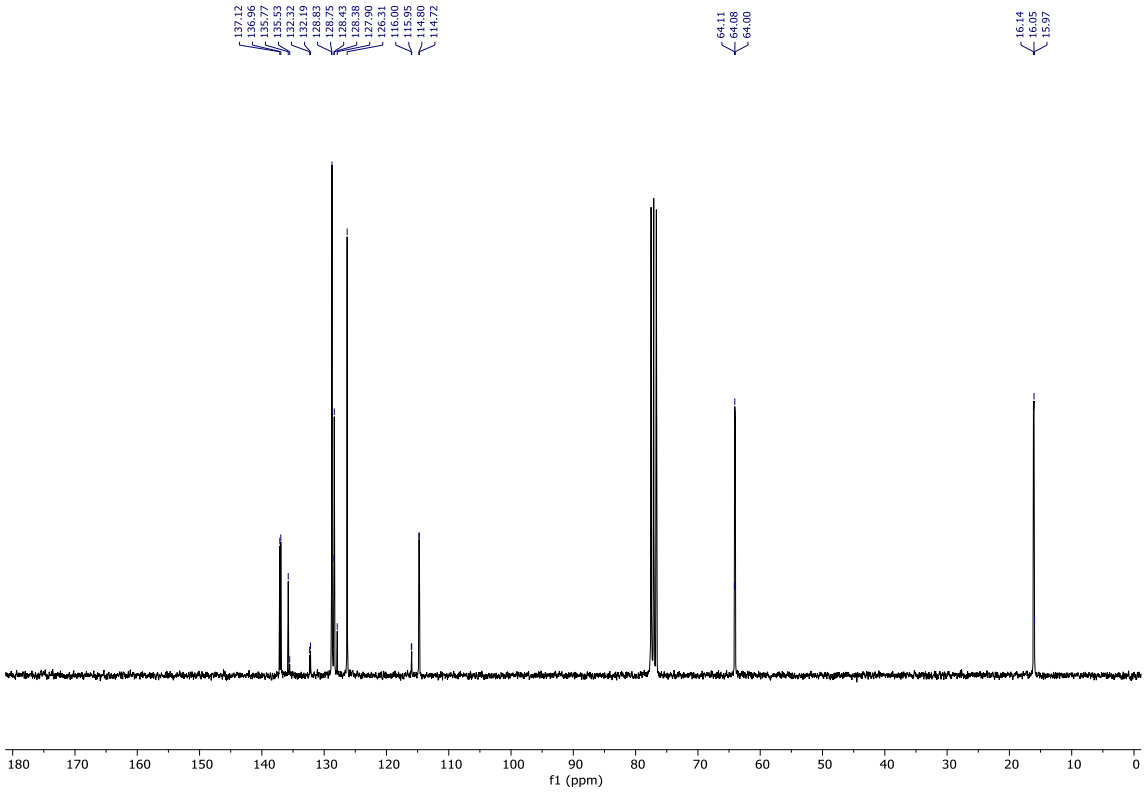


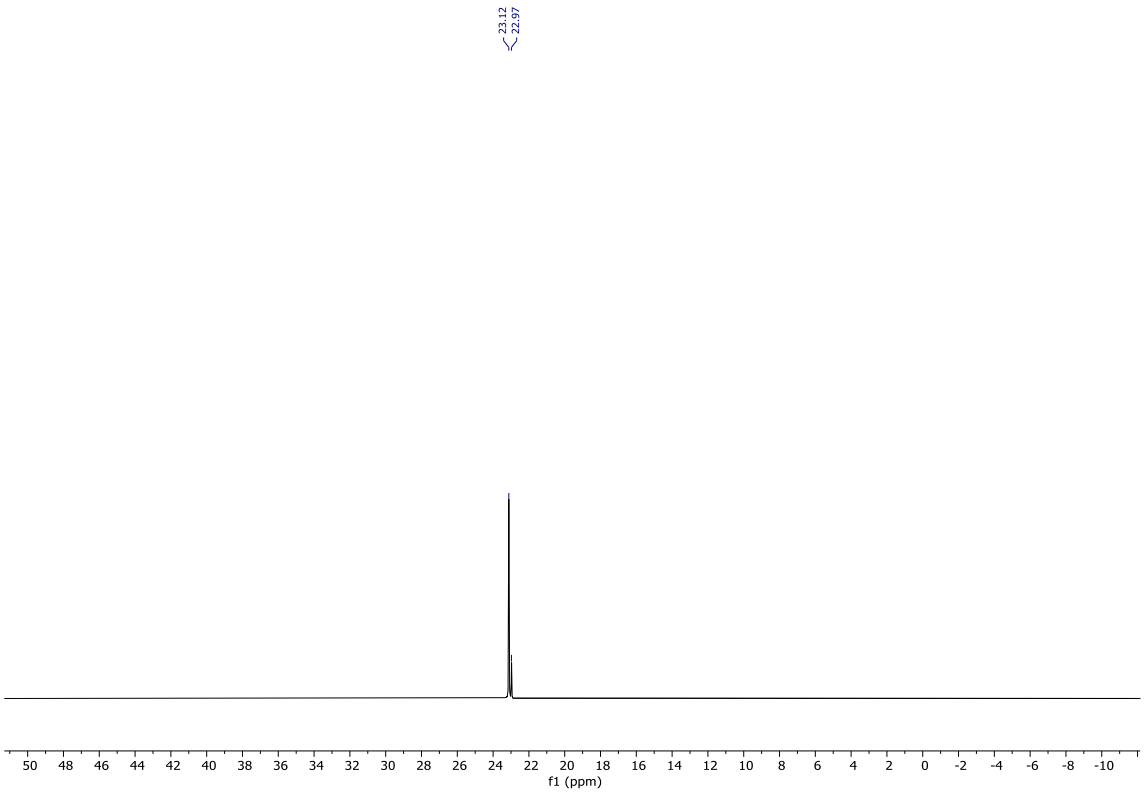

149.49
149.24
149.00
148.45
138.41
138.25
132.85
132.71
131.34
128.60
124.63
122.19
120.04
112.50
112.31
112.14
110.71
110.63
109.08
67.42
56.07
54.24
54.16
37.15
35.91
29.60
25.74
25.43
19.60
17.67
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


26.99
26.70
50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

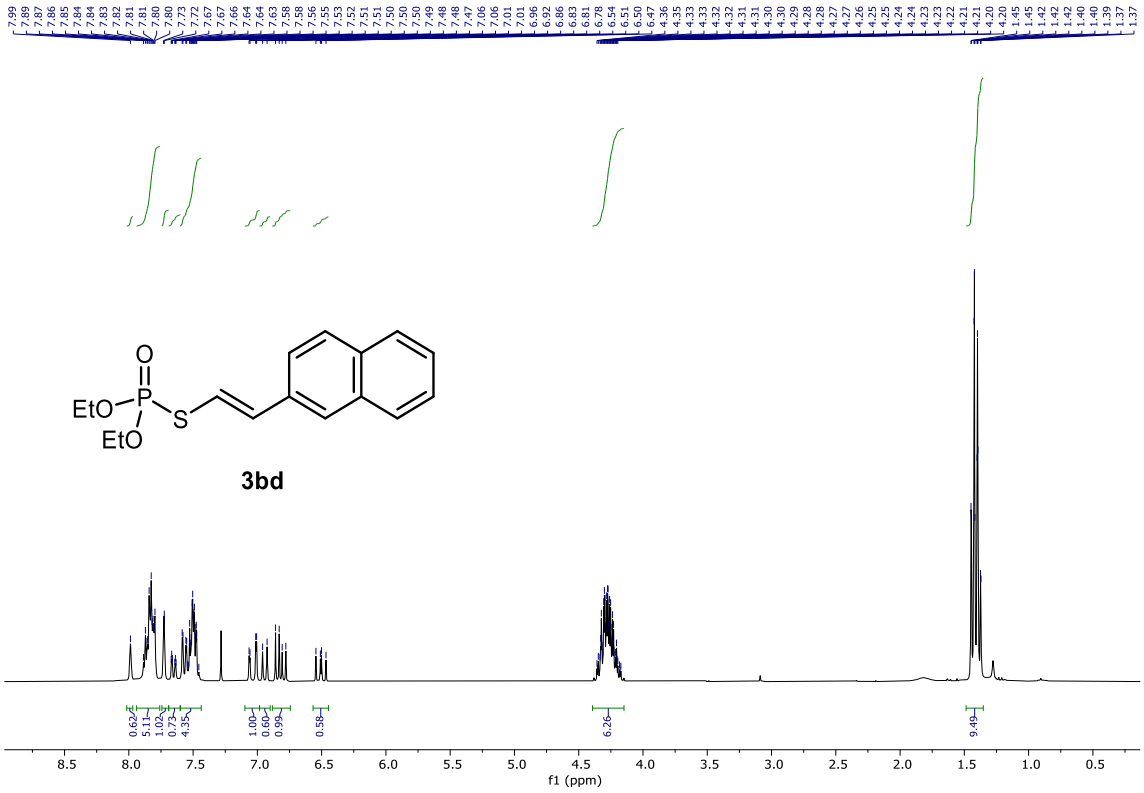
(*E*)-*O,O*-diethyl *S*-styryl phosphorothioate (3ba)

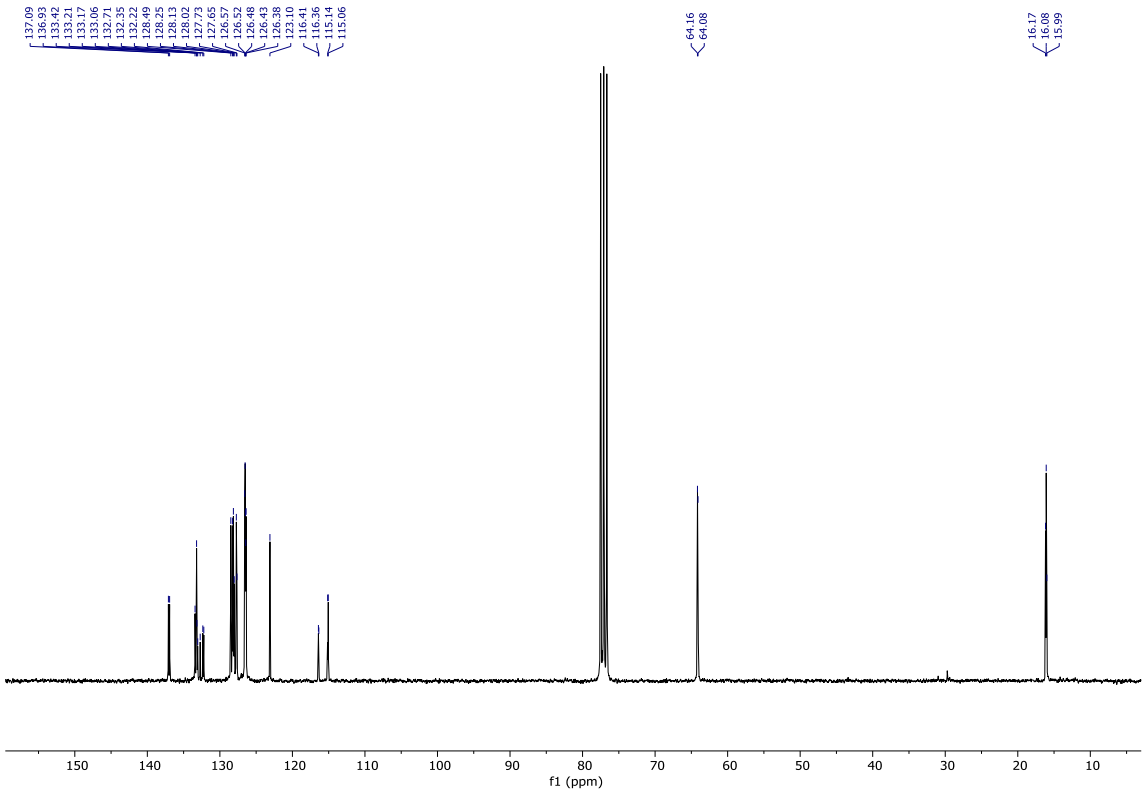


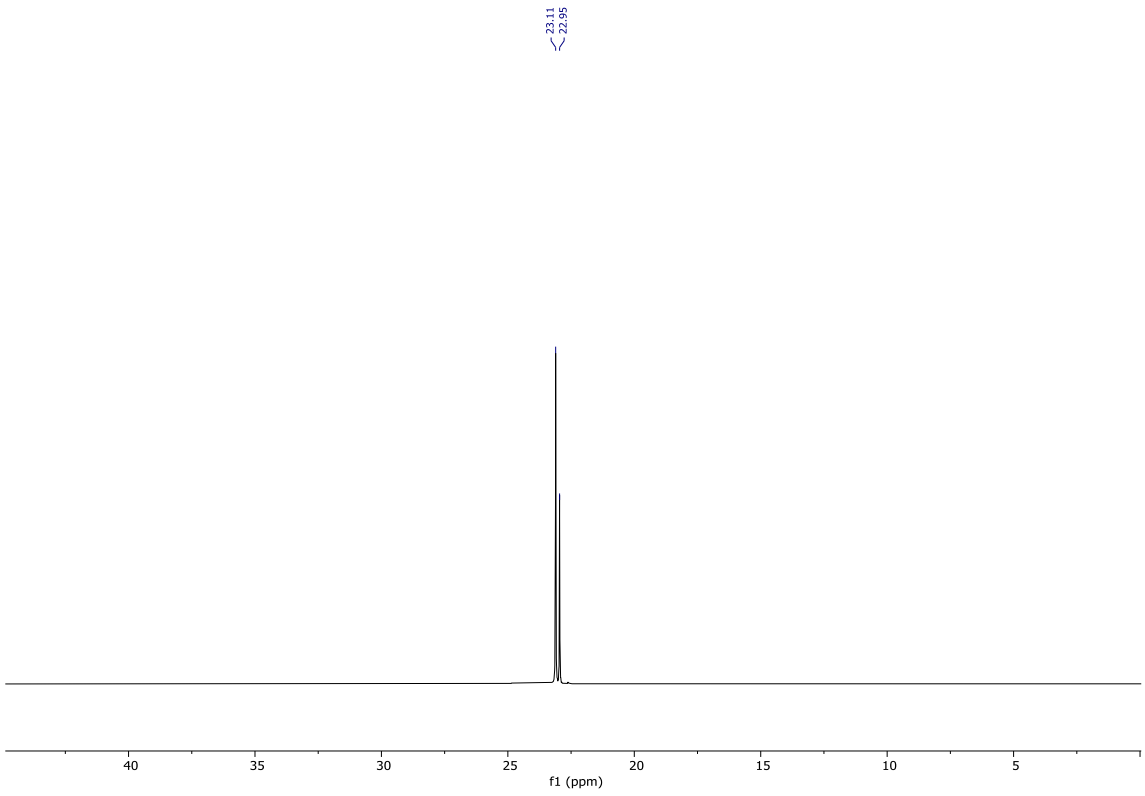




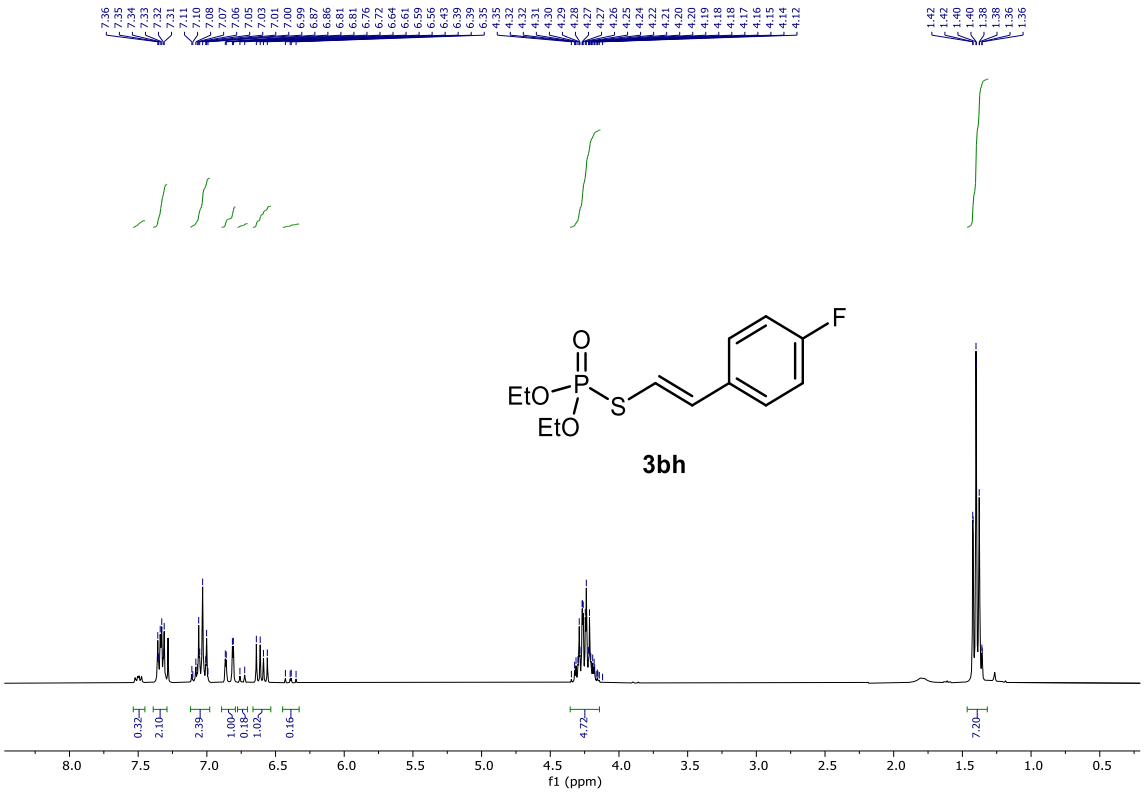
(*E*)-*O,O*-diethyl *S*-2-(naphthalen-2-yl)vinyl) phosphorothioate (3bd)

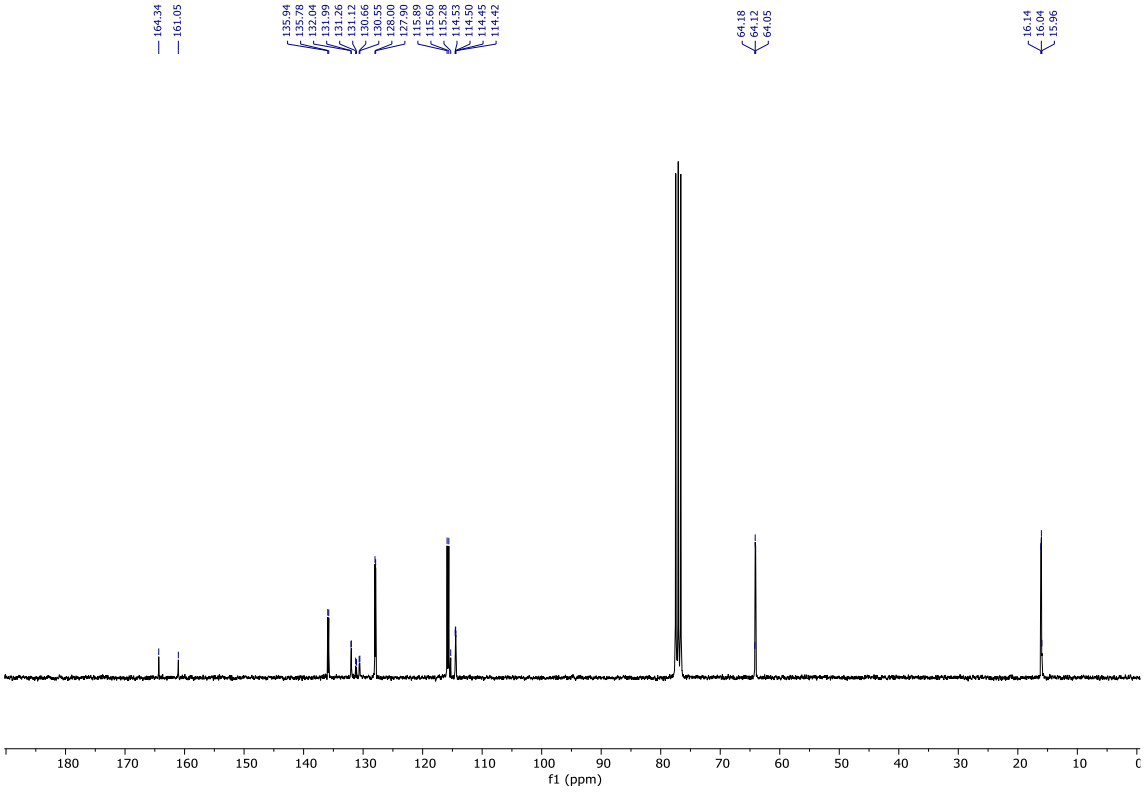


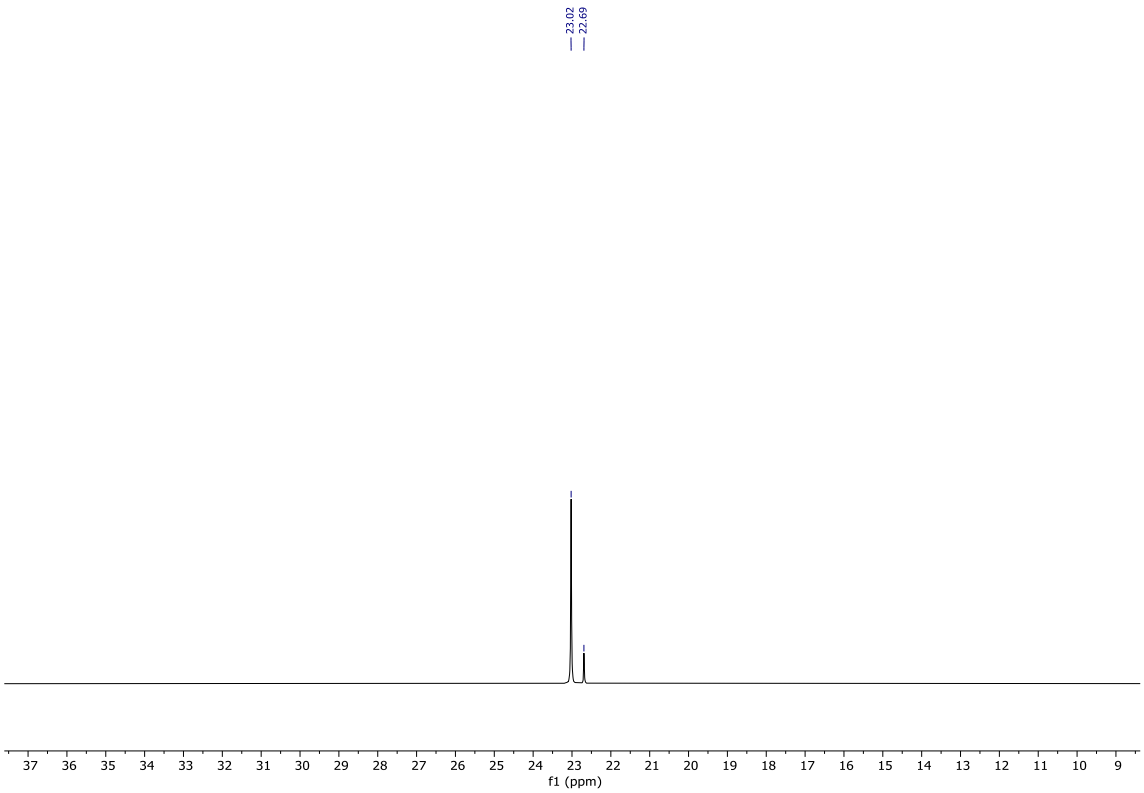

137.09
136.93
133.42
133.21
133.17
133.06
132.71
132.35
132.22
128.49
128.25
128.13
128.02
127.73
127.65
126.57
126.52
126.48
126.43
126.38
123.10
116.41
116.36
115.14
115.06
64.16
64.08
16.17
16.08
15.99
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

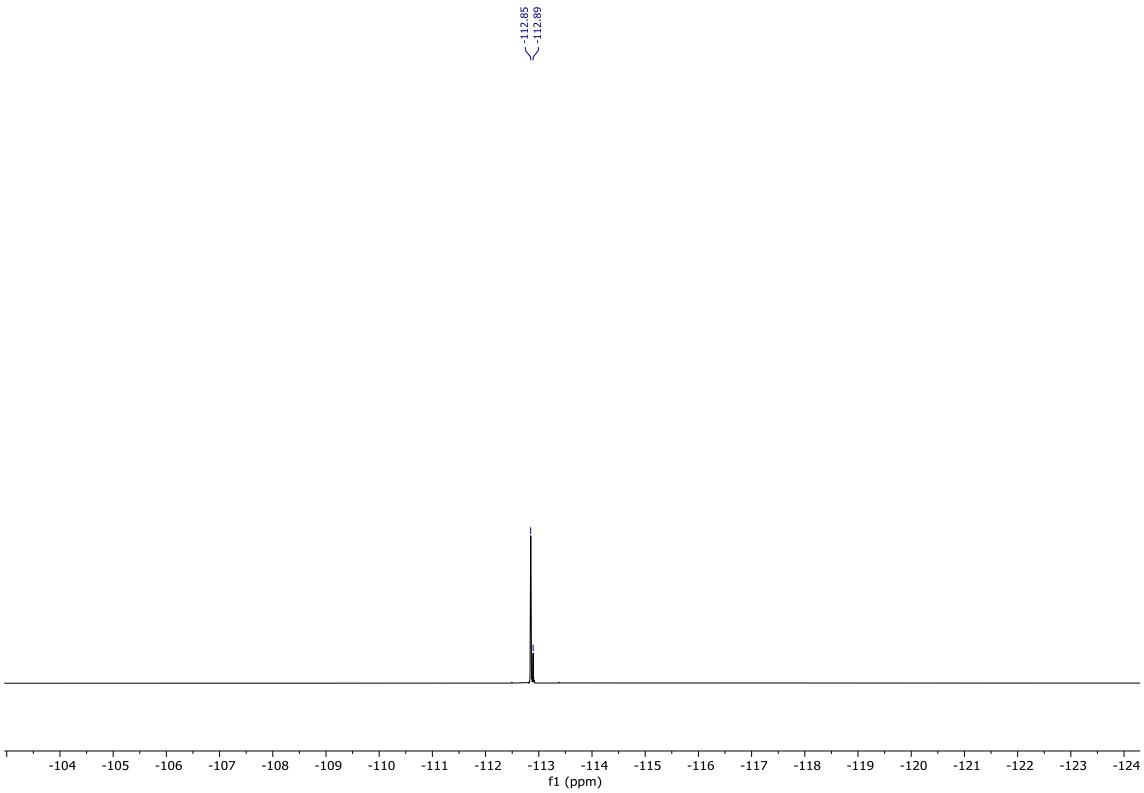

23.11
22.95
40
35
30
25
20
15
10
5
f1 (ppm)

(*E*)-*O,O*-diethyl *S*-(4-fluorostyryl) phosphorothioate (3bh)

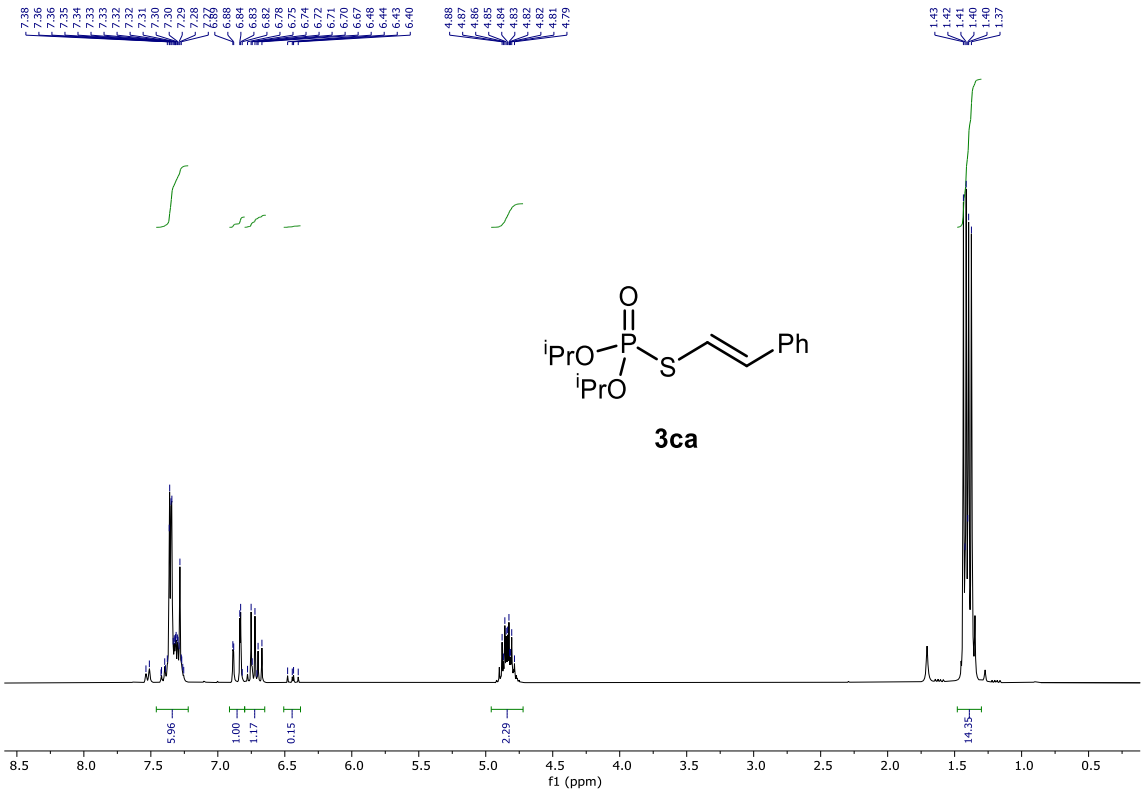


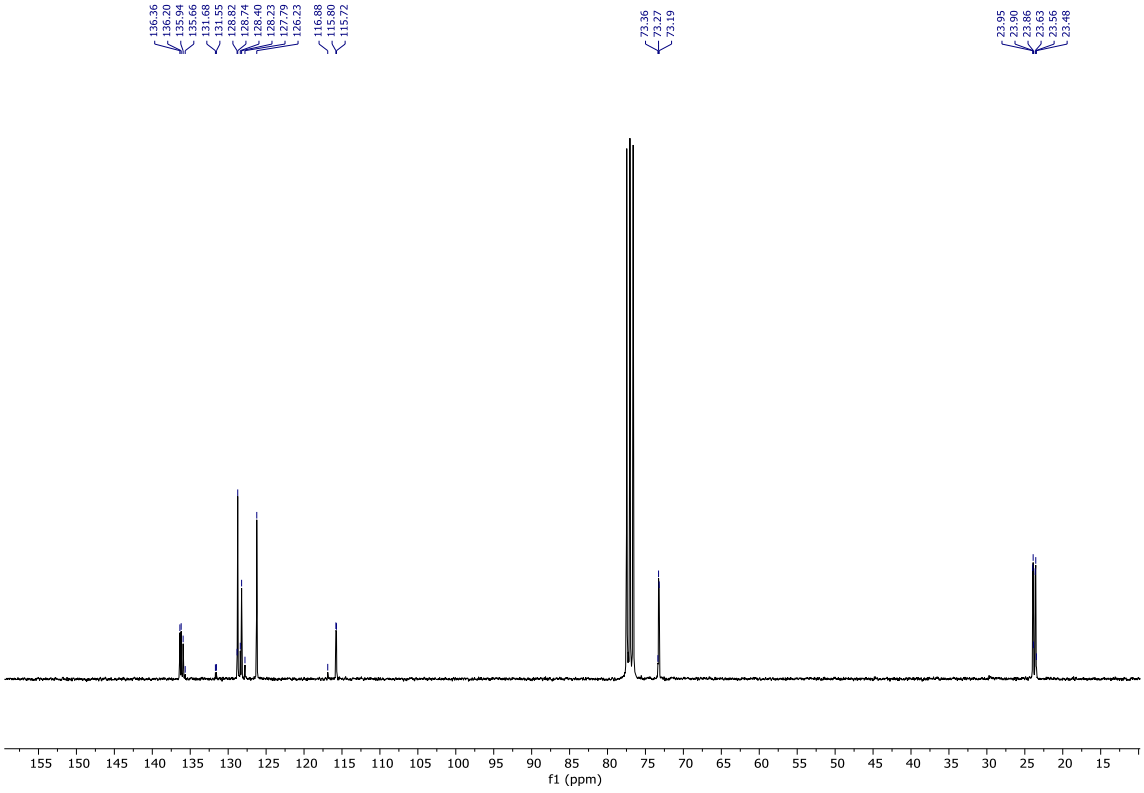


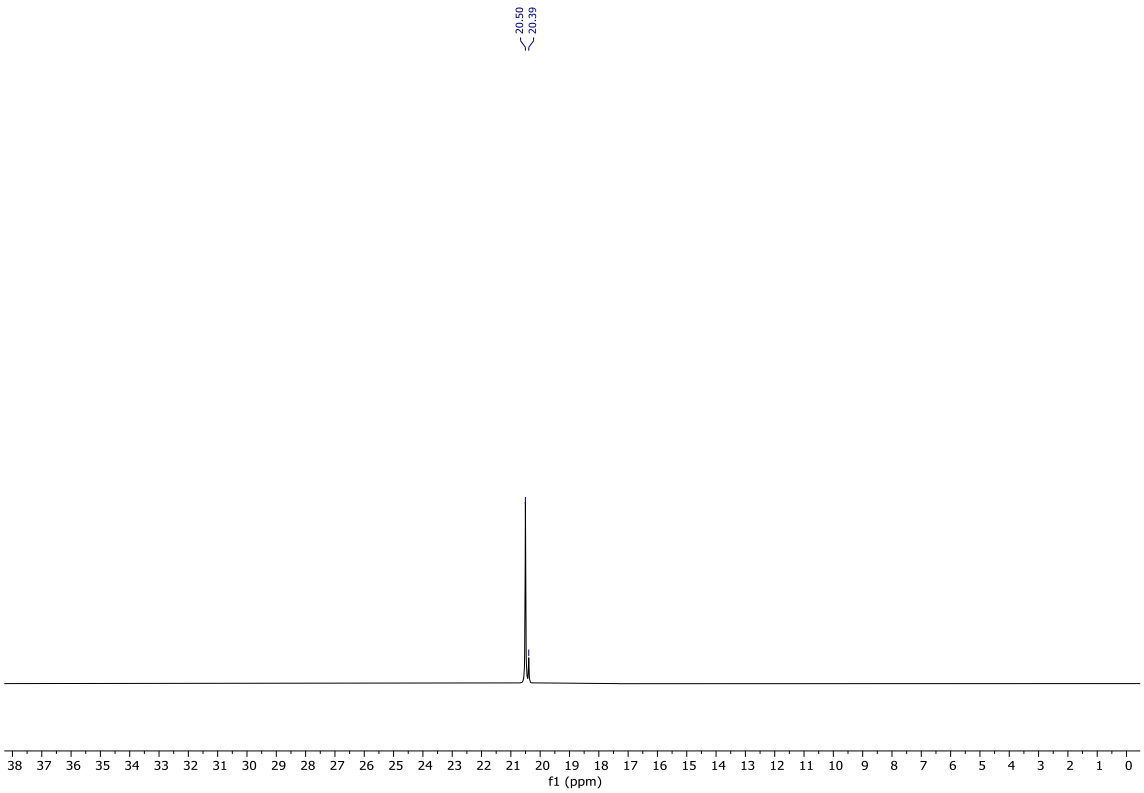

23.02
22.69
37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9
f1 (ppm)


-112.85
-112.89
-104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124
f1 (ppm)

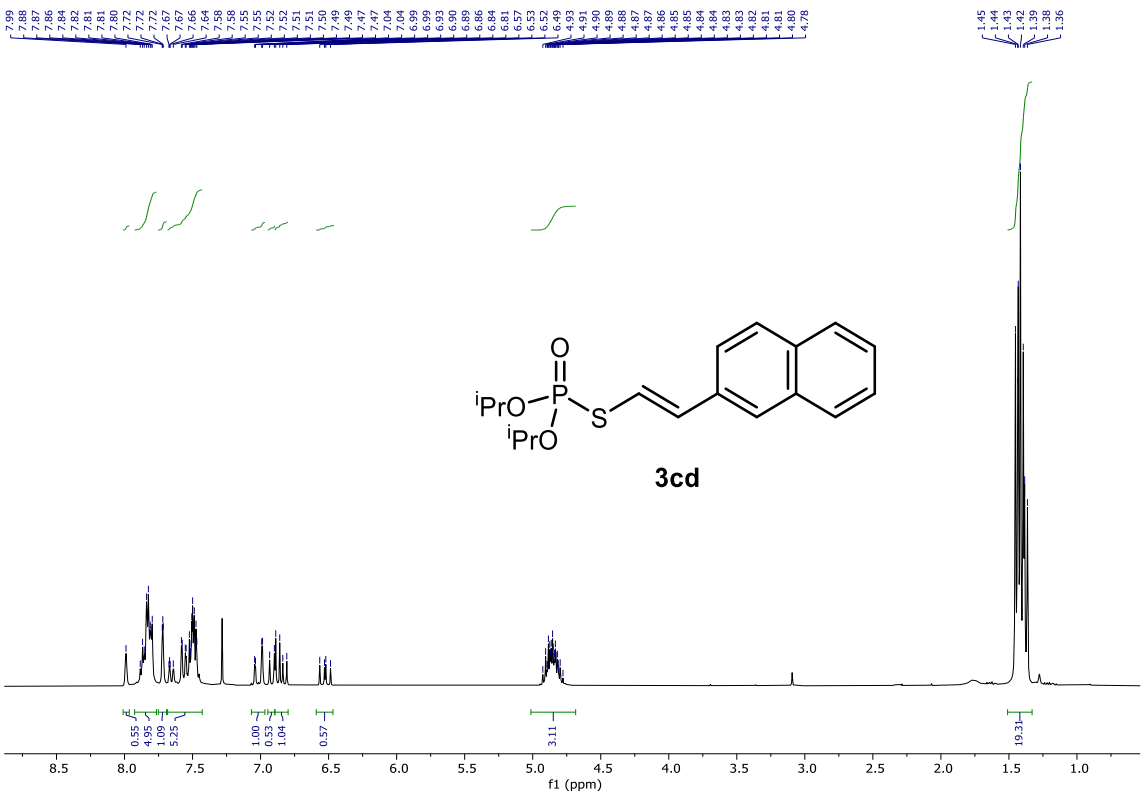
(*E*)-*O,O*-diisopropyl *S*-styryl phosphorothioate (3ca)

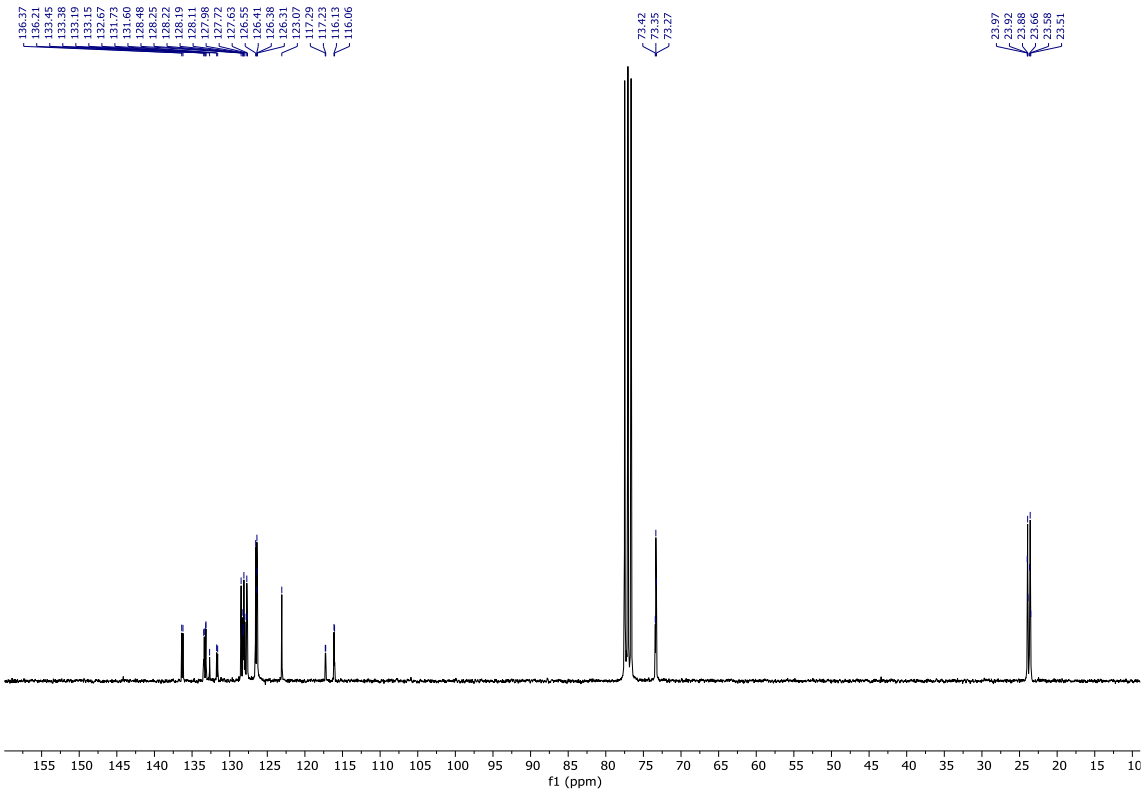


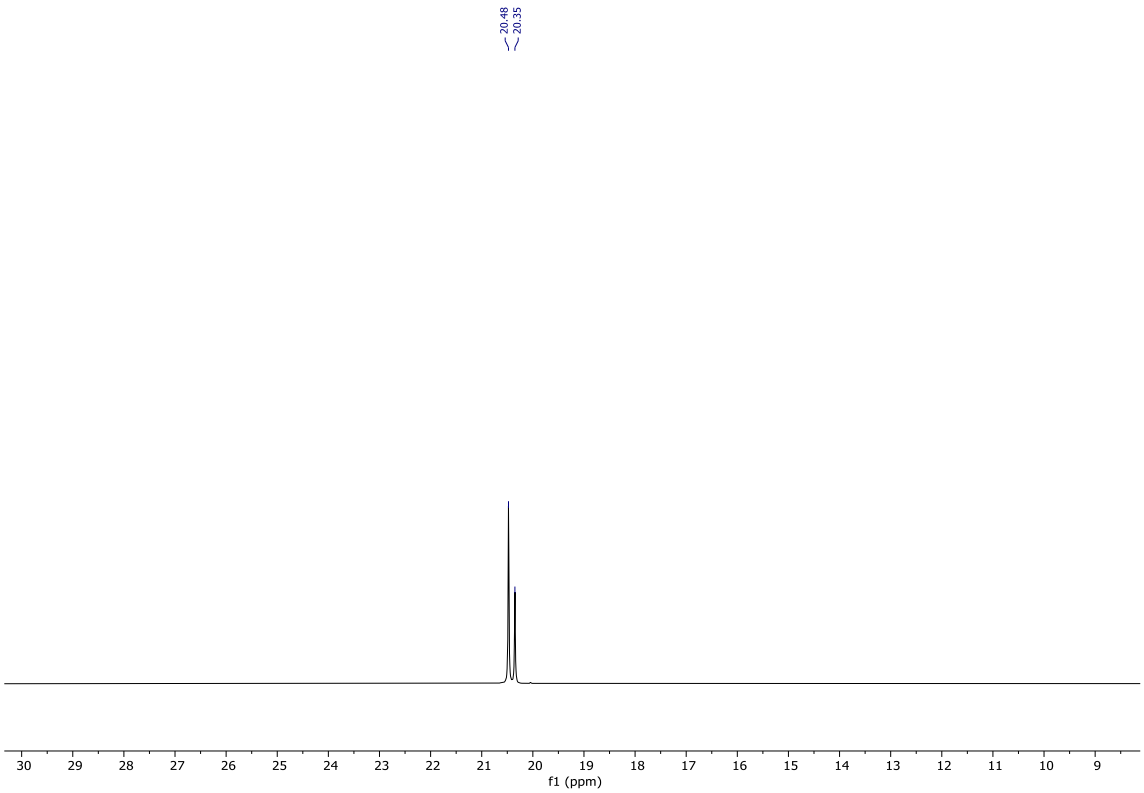




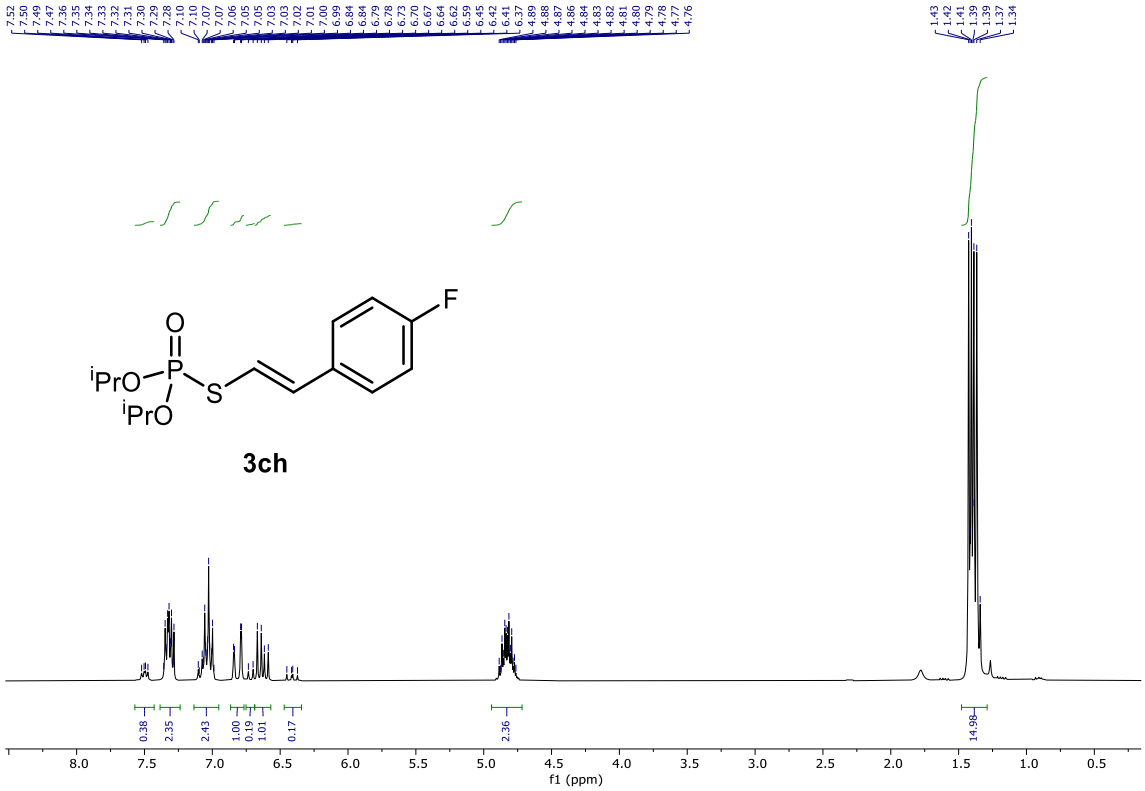
(*E*)-*O,O*-diisopropyl *S*-2-(naphthalen-2-yl)vinyl) phosphorothioate (3cd)

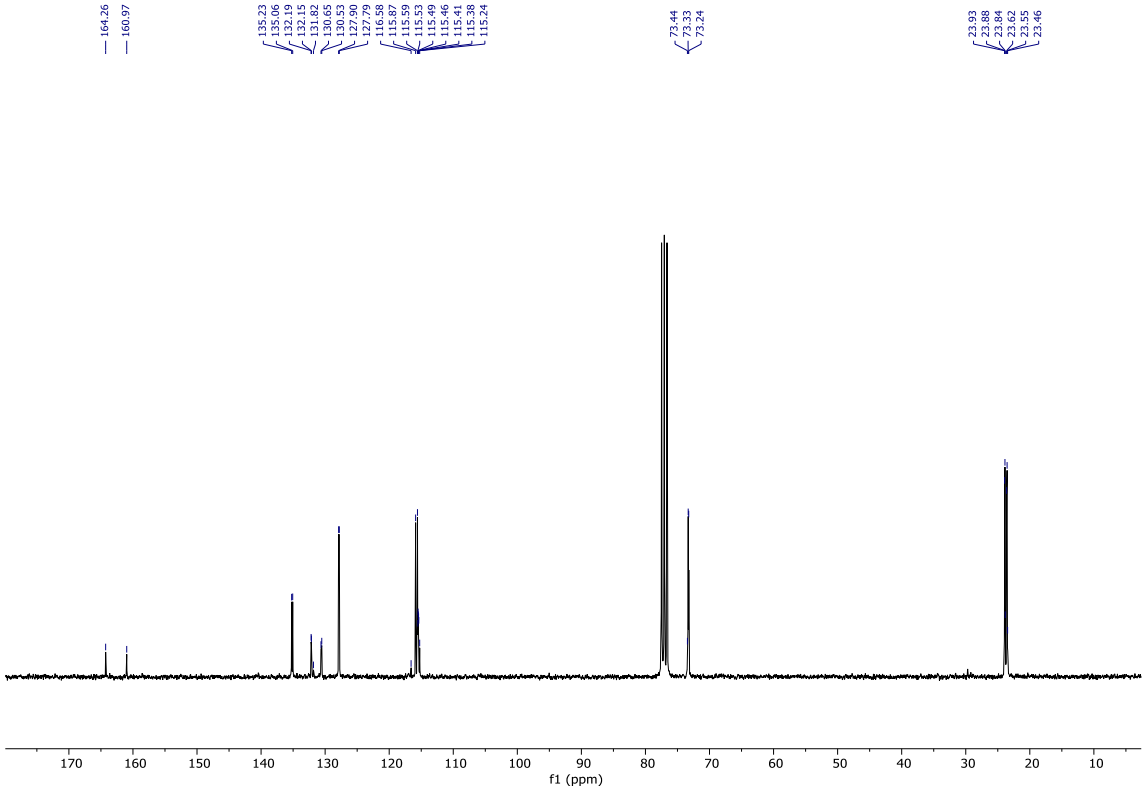


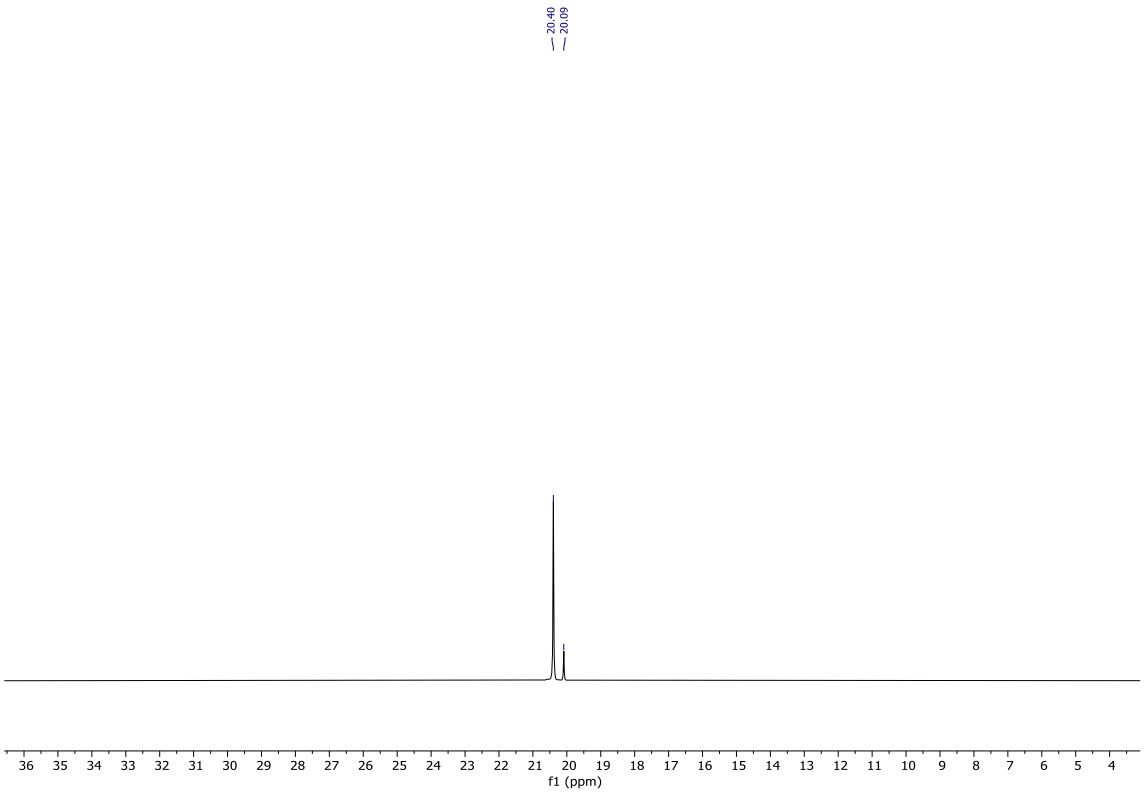

136.37
136.21
133.45
133.38
133.19
133.15
132.67
131.73
131.60
128.48
128.25
128.22
128.19
128.11
127.98
127.72
127.63
126.55
126.41
126.38
126.31
123.07
117.29
117.23
116.13
116.06
73.42
73.35
73.27
23.97
23.92
23.88
23.66
23.58
23.51
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

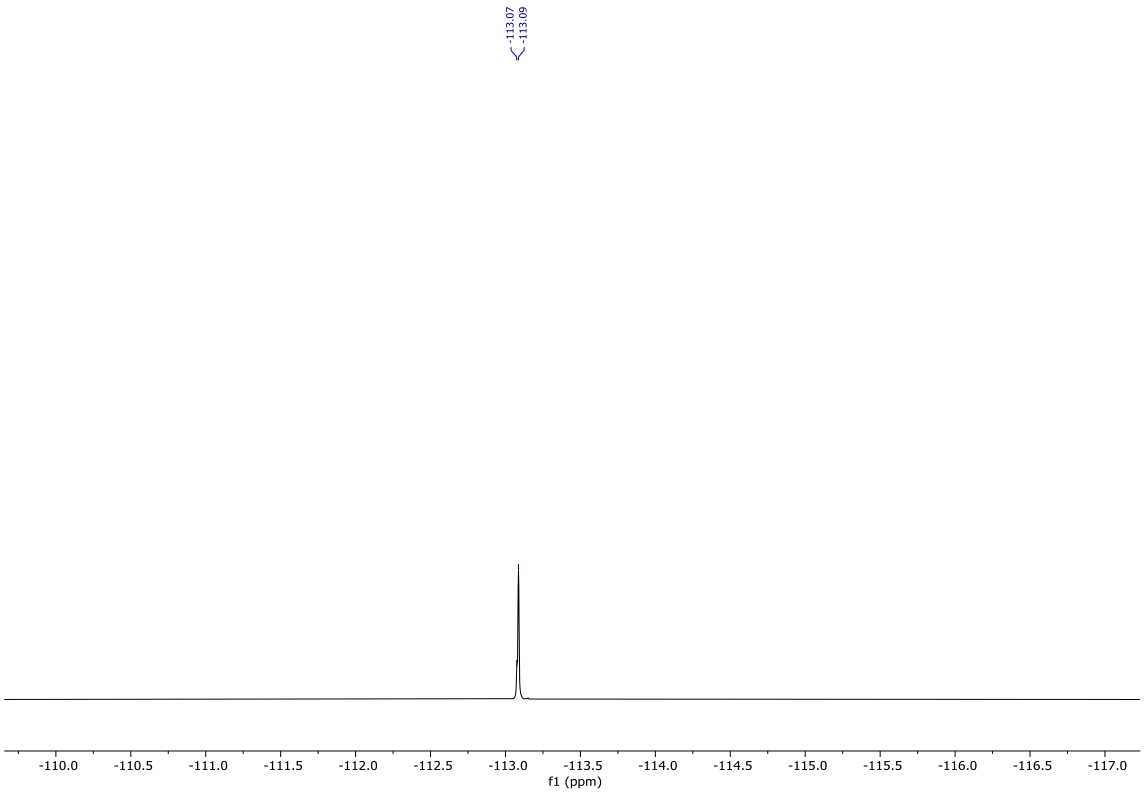

20.48
20.35
30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9
f1 (ppm)

(*E*)-*S*-(4-fluorostyryl) *O,O*-diisopropyl phosphorothioate (3ch)

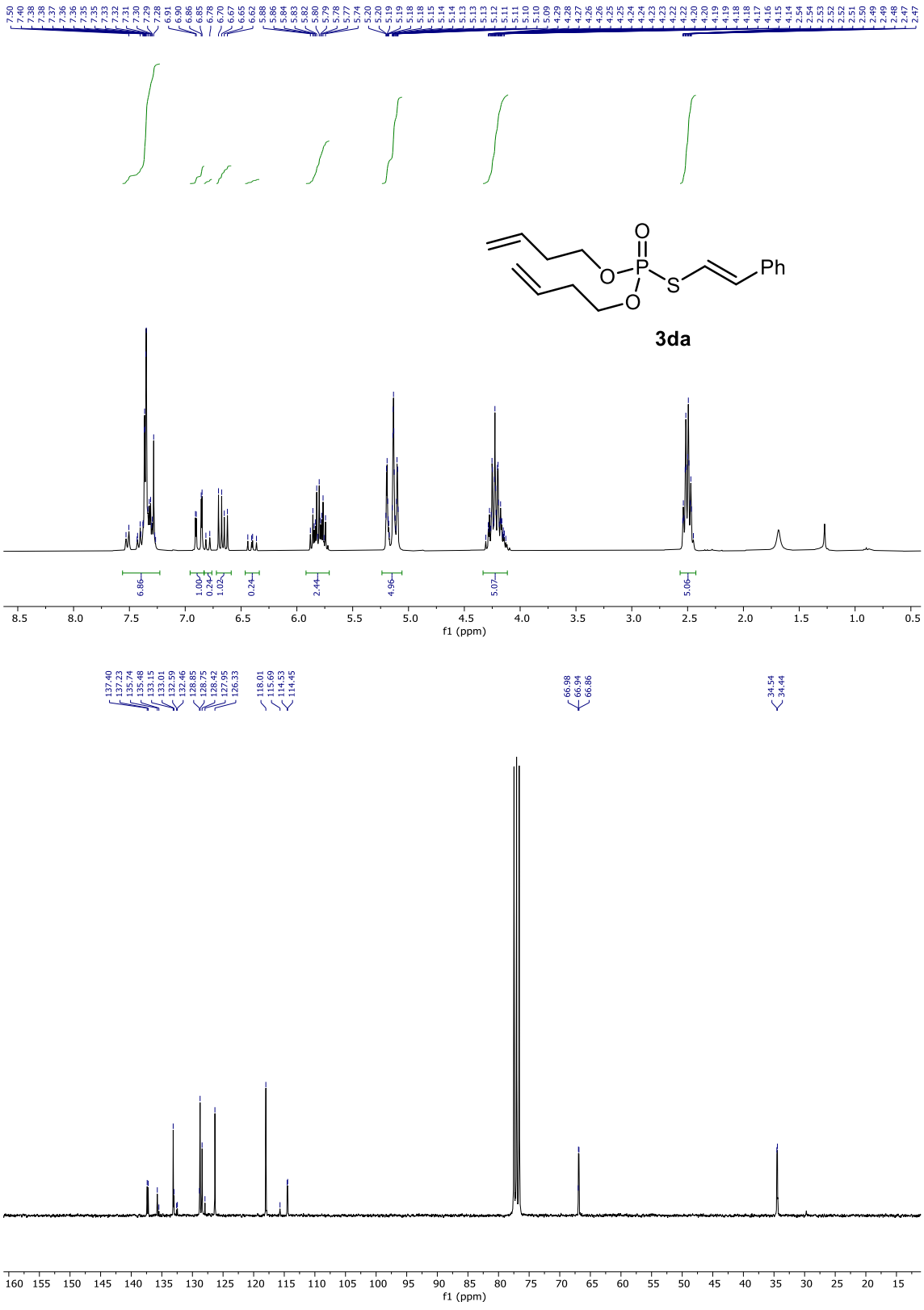


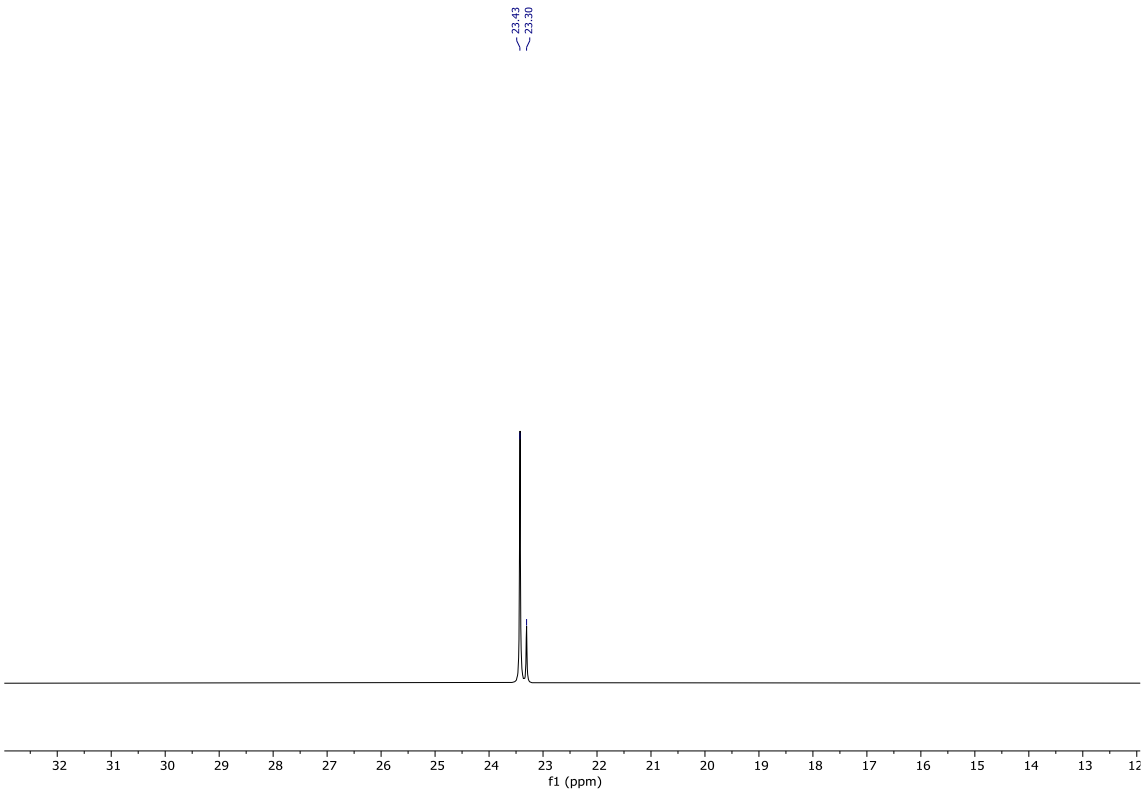



20.40
20.09
36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4
f1 (ppm)

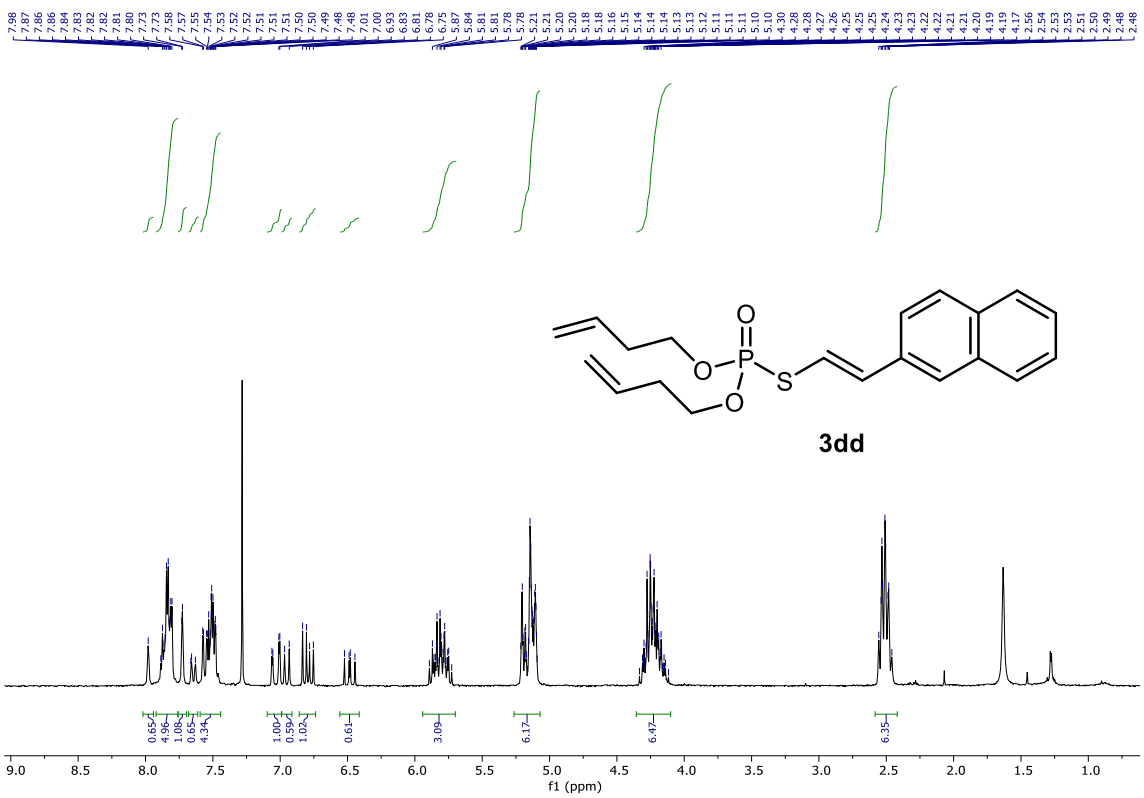

-113.07
-113.09
-110.0 -110.5 -111.0 -111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0 -115.5 -116.0 -116.5 -117.0
f1 (ppm)

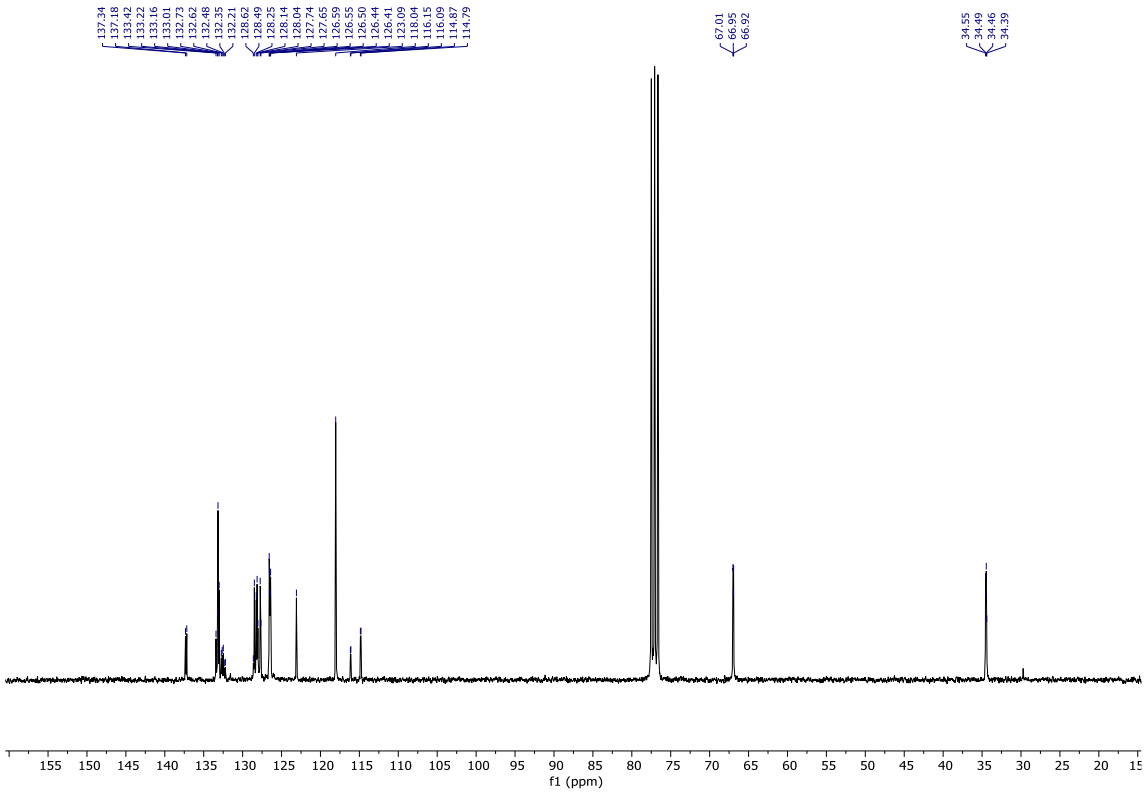
(*E*)-*O,O*-di(but-3-en-1-yl) *S*-styryl phosphorothioate (3da)

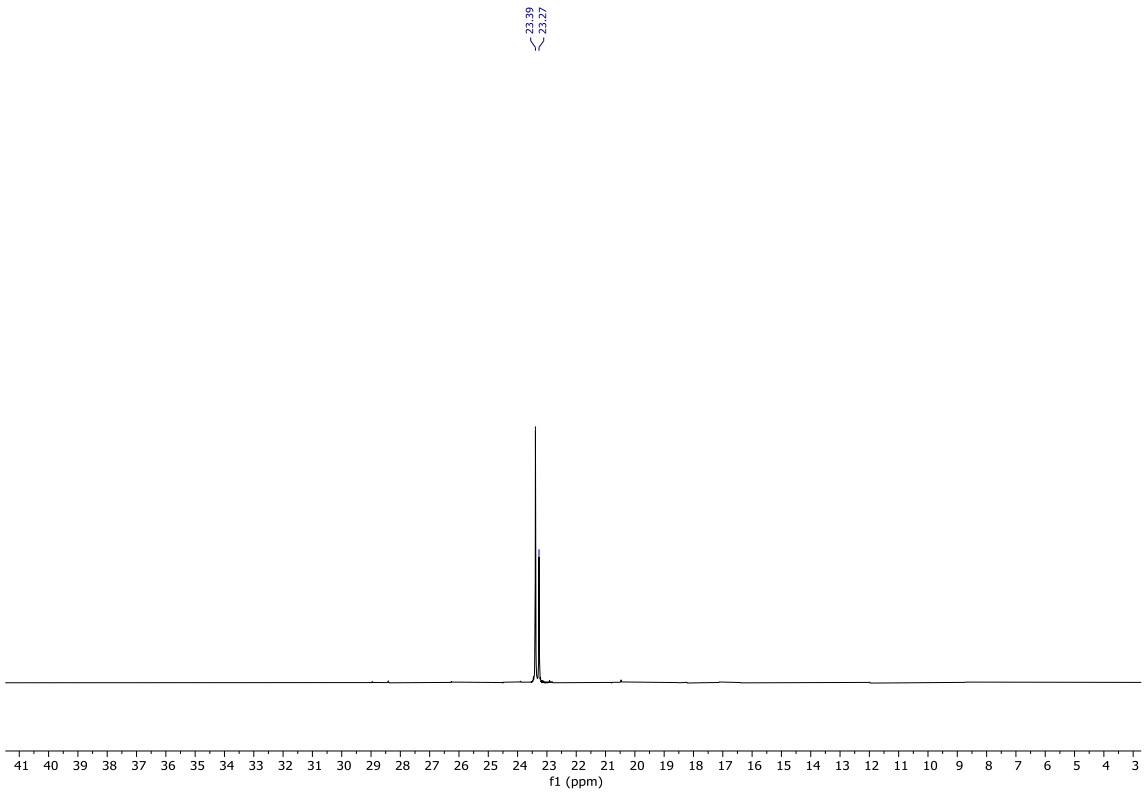




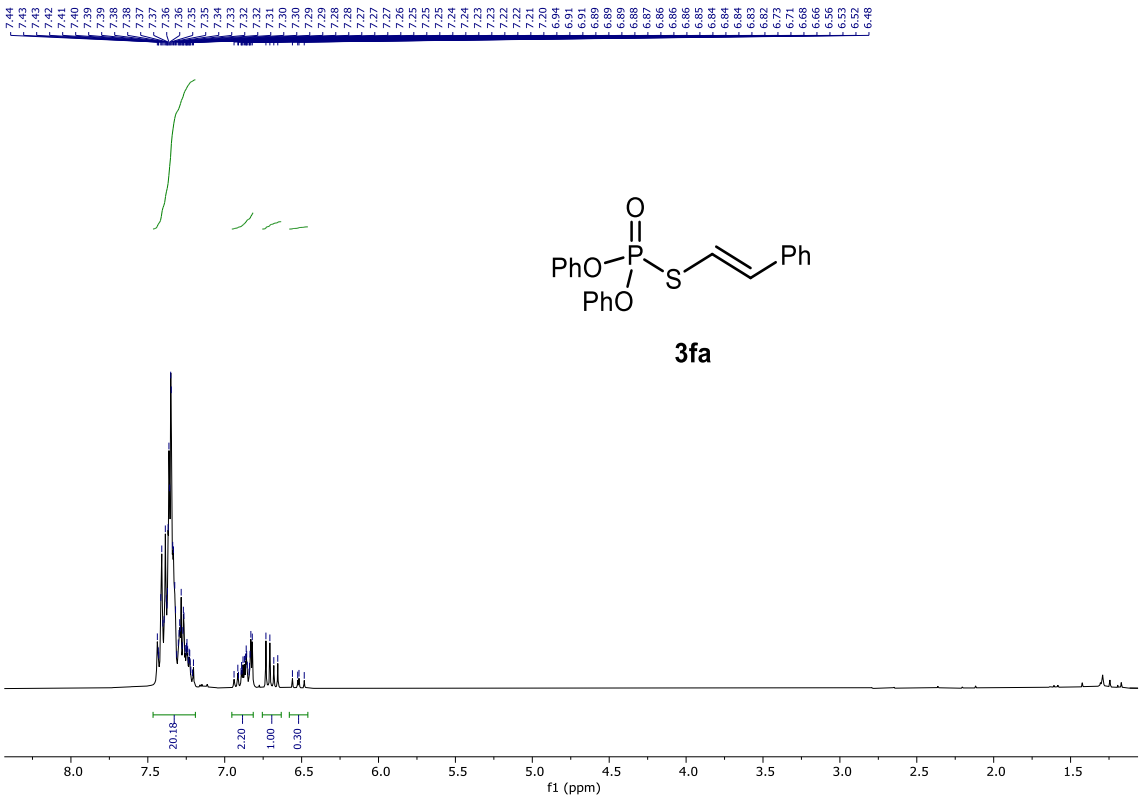
(*E*)-*O,O*-di(but-3-en-1-yl) *S*-(2-(naphthalen-2-yl)vinyl) phosphorothioate (3dd)

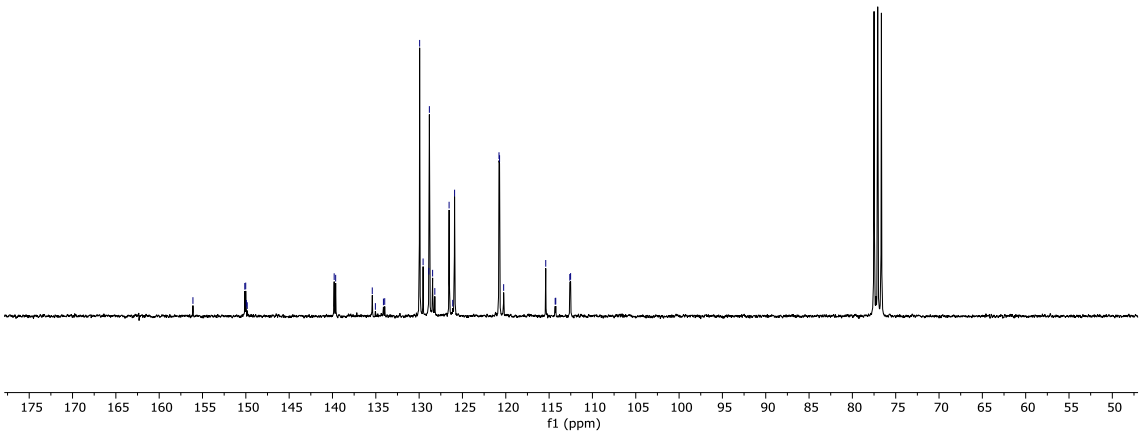


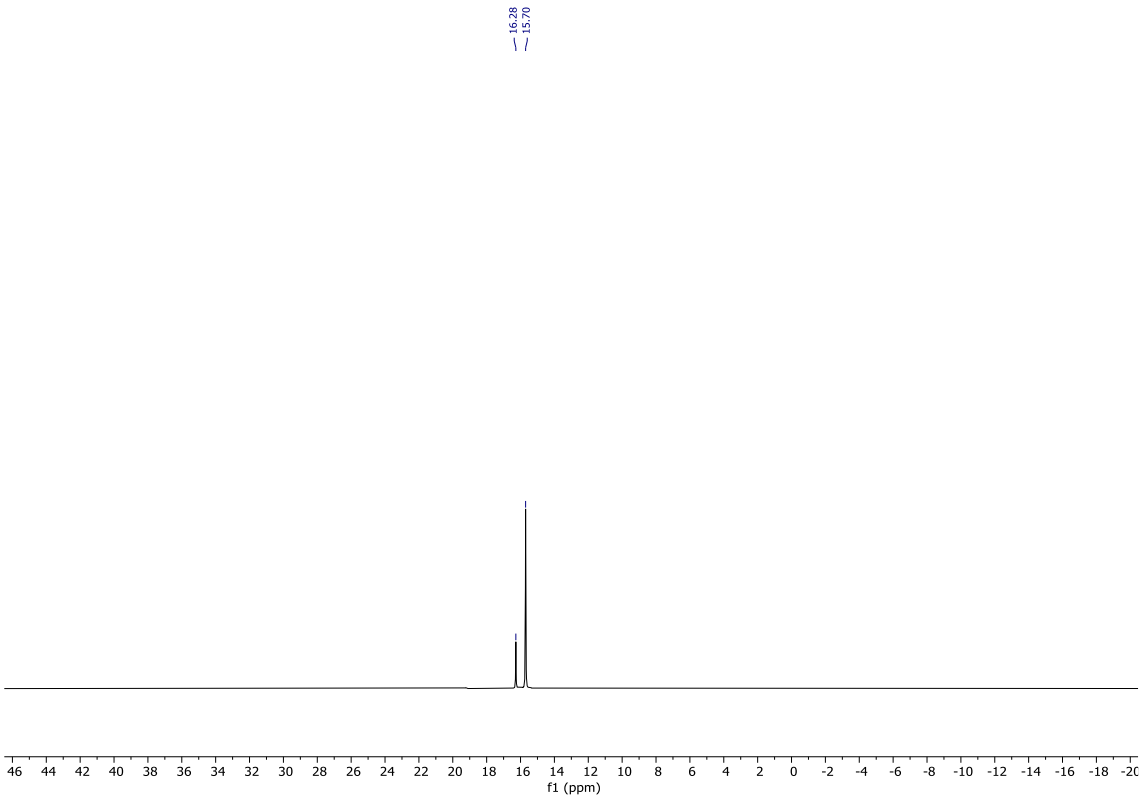

137.34
137.18
133.42
133.22
133.16
133.01
132.73
132.62
132.48
132.35
132.21
128.62
128.49
128.25
128.14
128.04
127.74
127.65
126.59
126.55
126.50
126.44
126.41
123.09
118.04
116.15
116.09
114.87
114.79
67.01
66.95
66.92
34.55
34.49
34.46
34.39
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)


23.39
23.27
41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3
f1 (ppm)

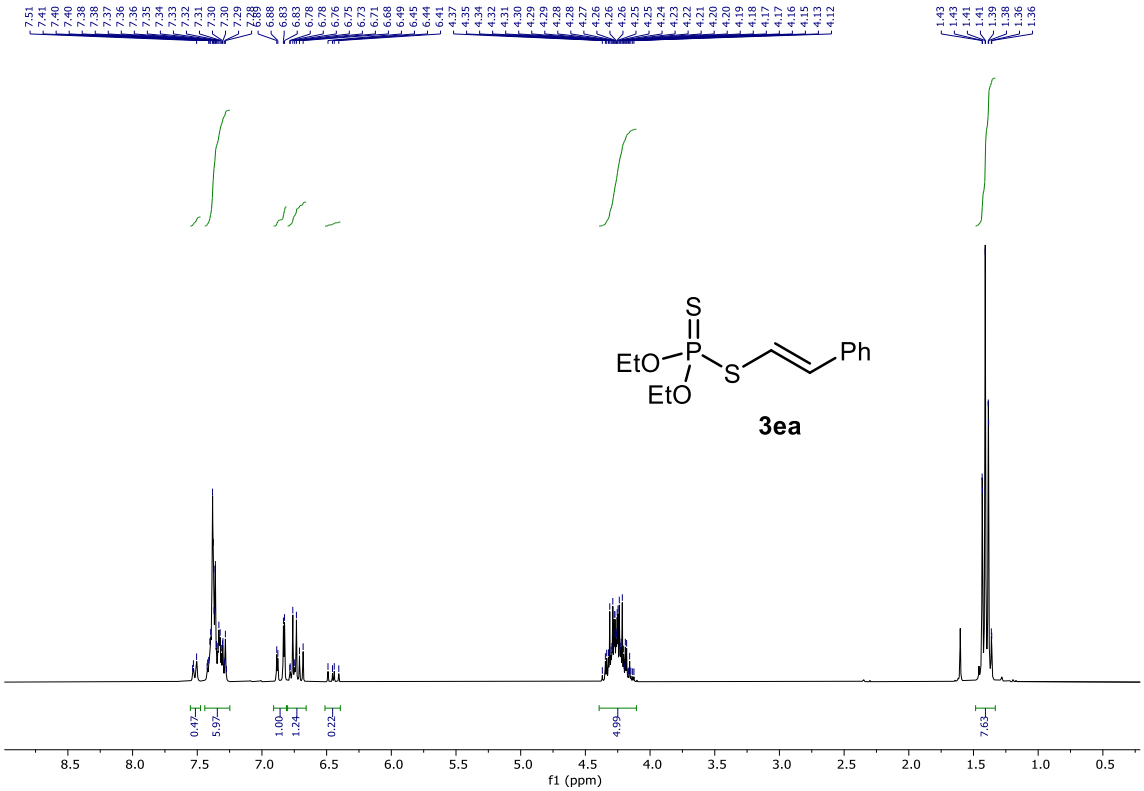
(*E*)-*O,O*--diphenyl *S*-styryl phosphorothioate (3fa)

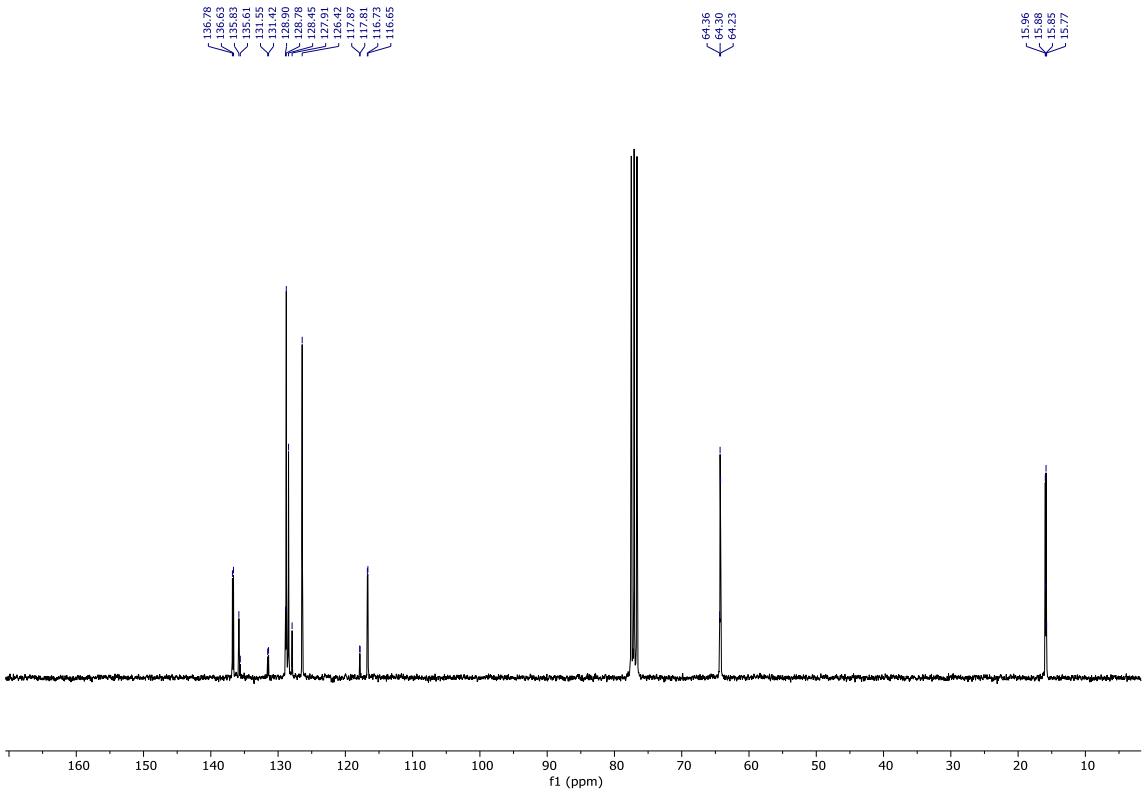


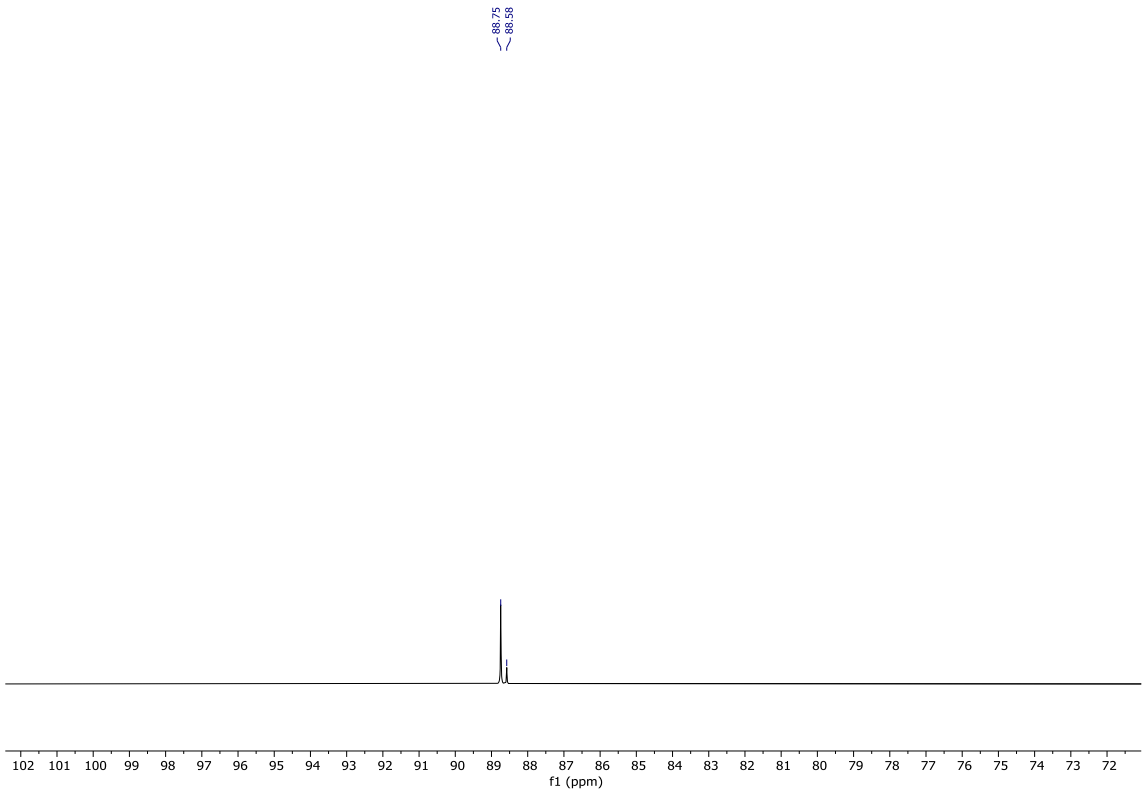




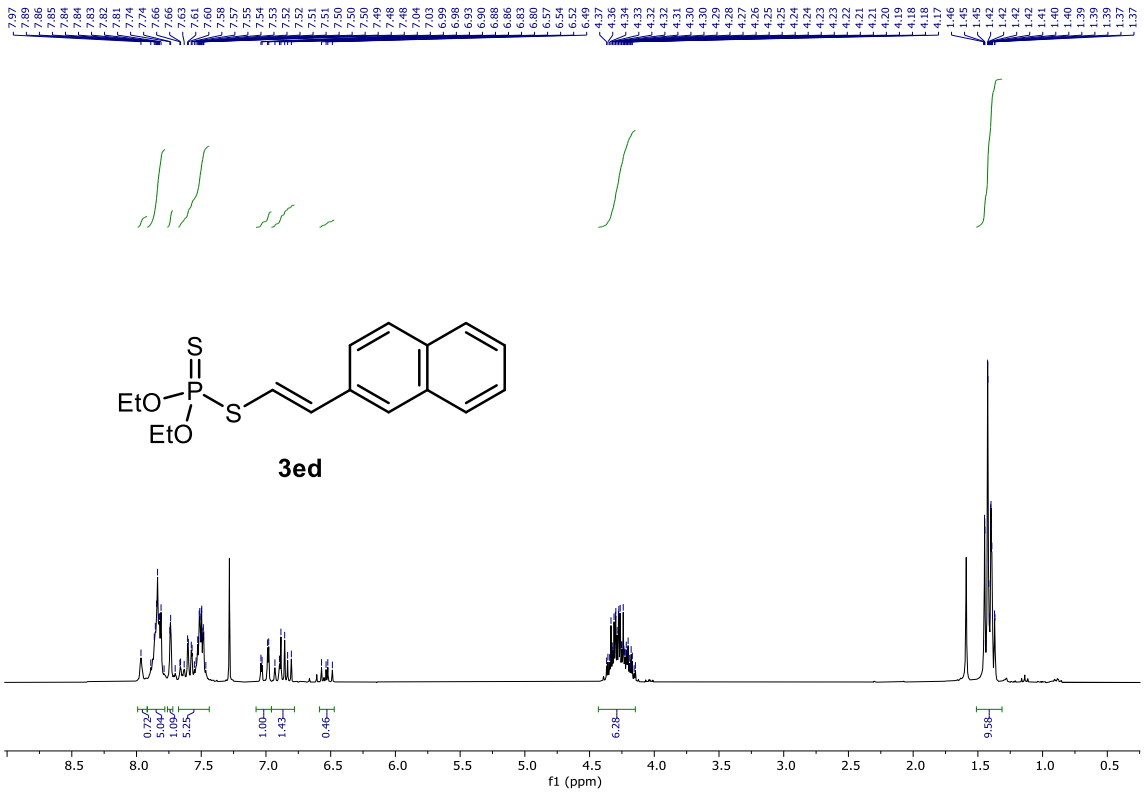
(*E*)-*O,O*-diethyl *S*-styryl phosphorodithioate (3ea)



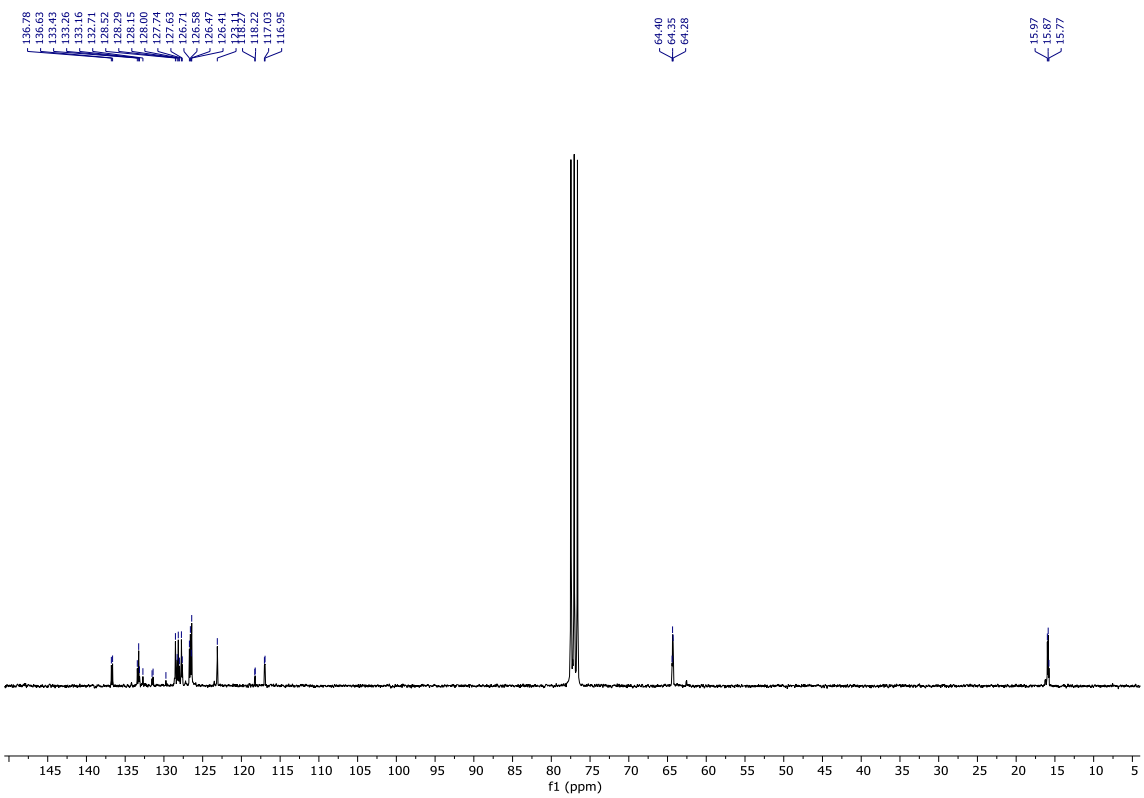


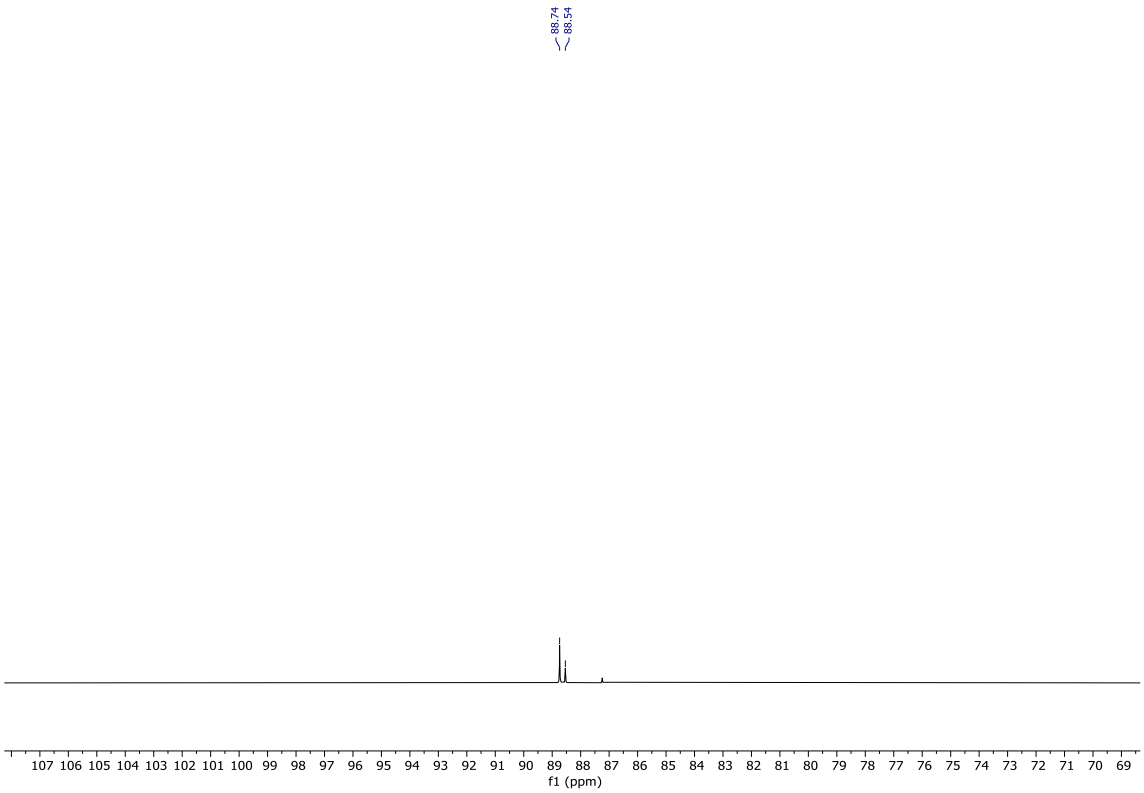


(*E*)-*O,O*-diethyl *S*-(2-(naphthalen-2-yl)vinyl) phosphorodithioate (3ed)

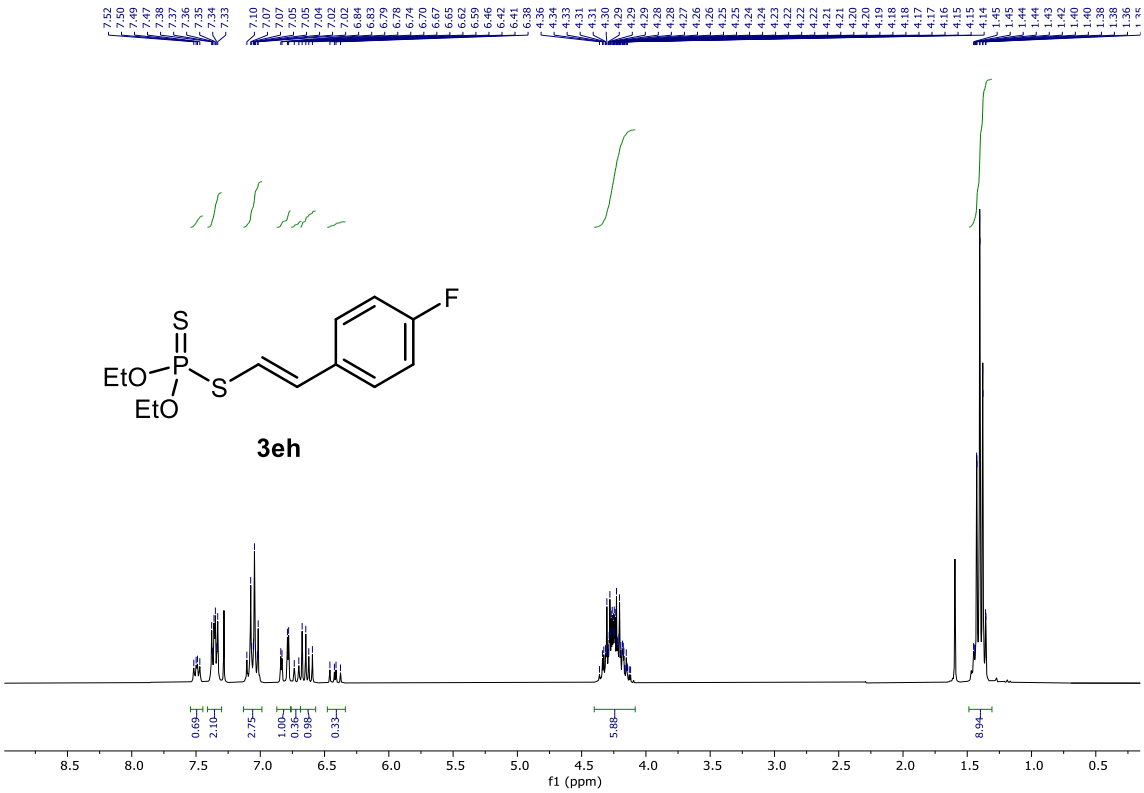


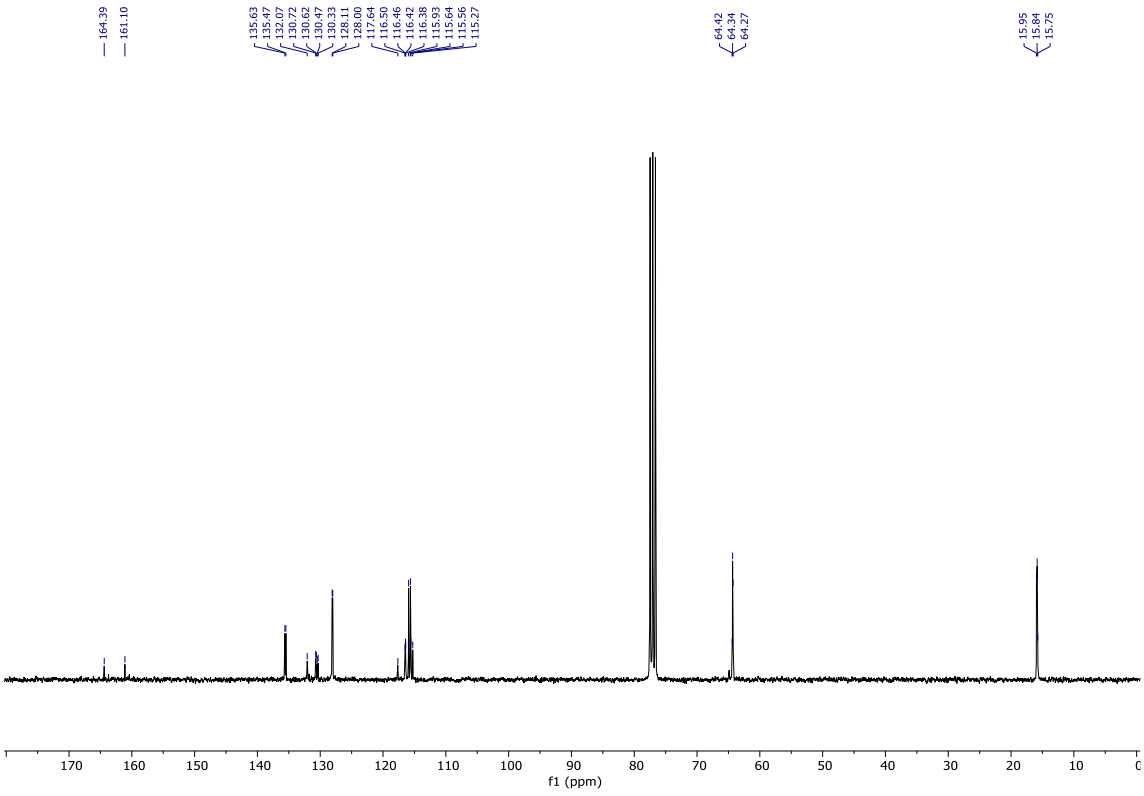
3ed

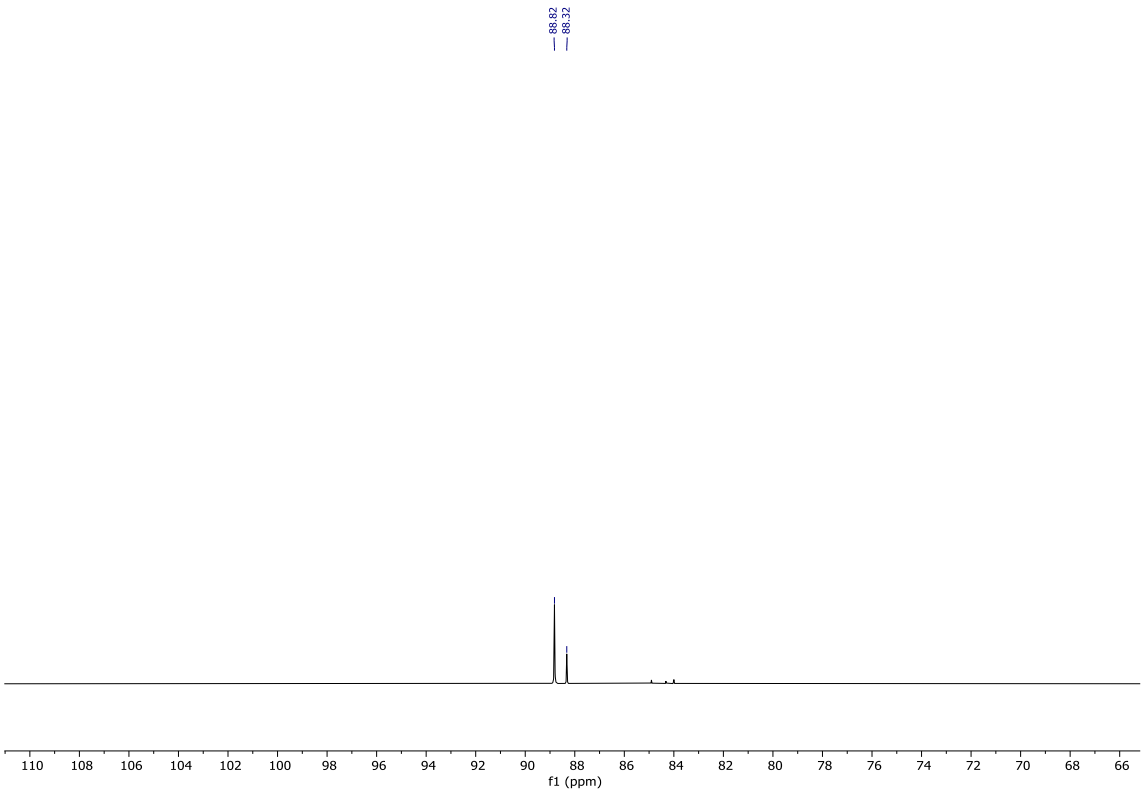


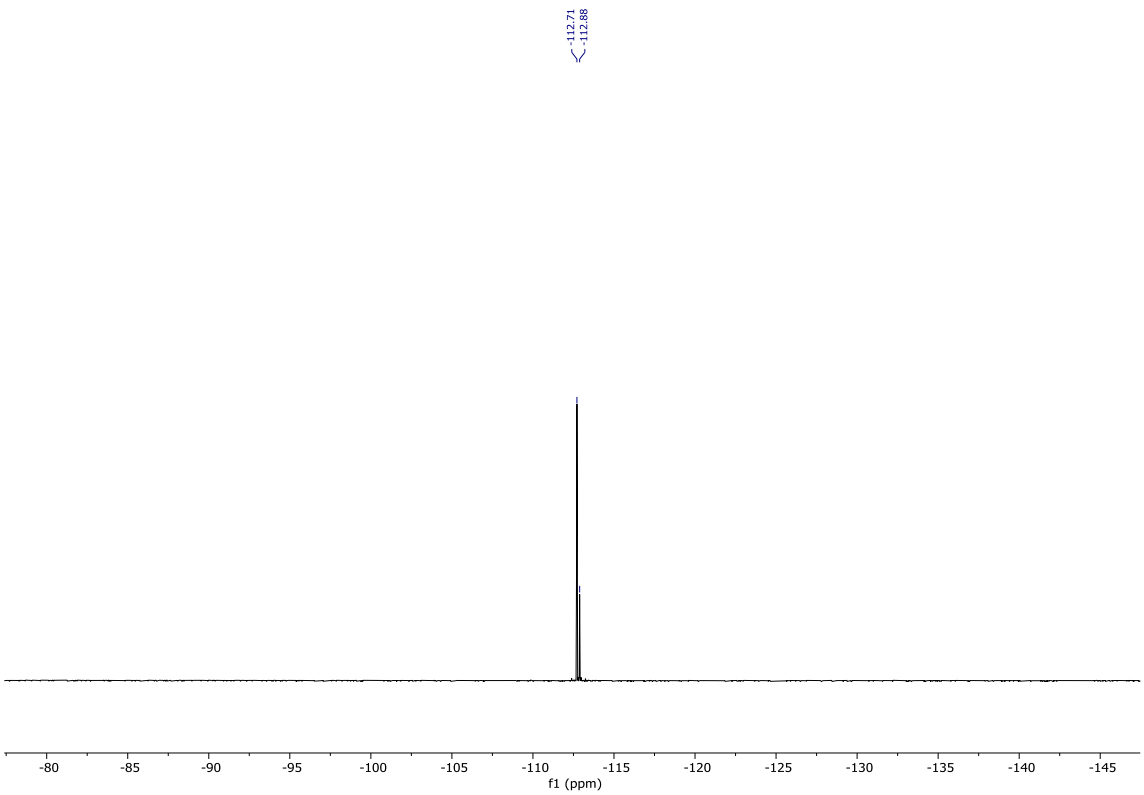


(*E*)-*O,O*-diethyl *S*-(4-fluorostyryl) phosphorodithioate (3eh)

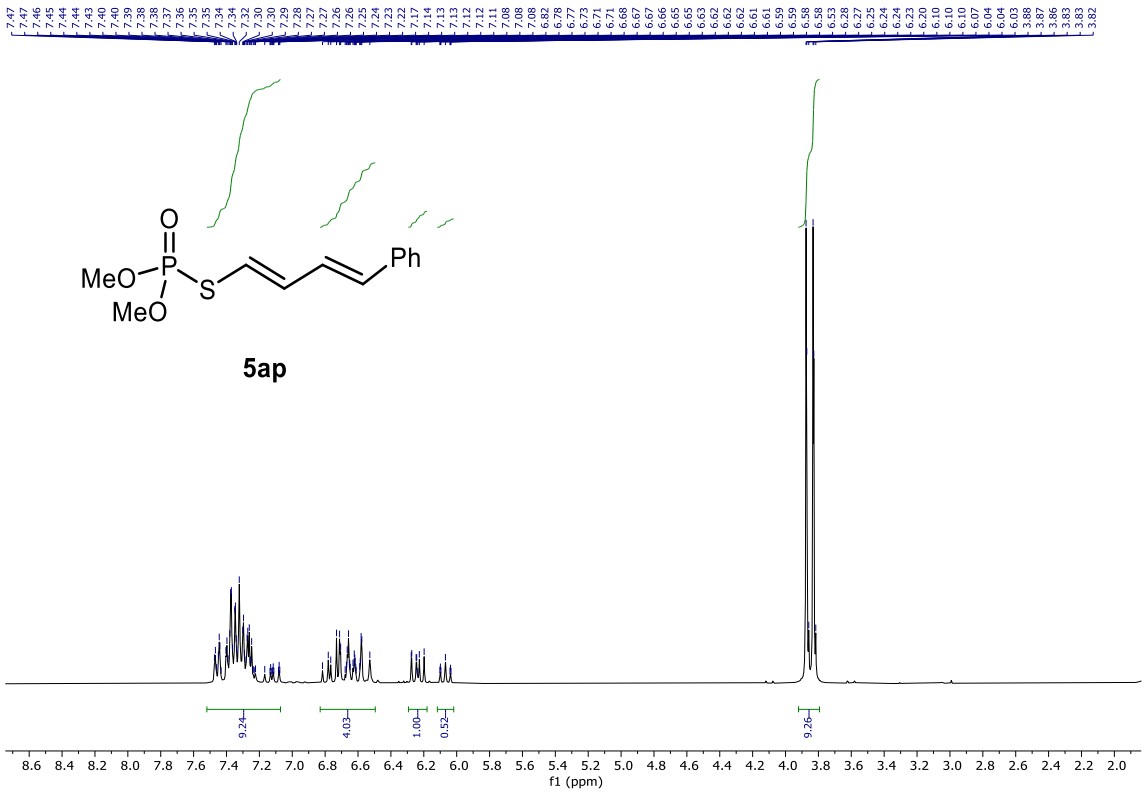

F
S
EtO
P
S
EtO
3eh
f1 (ppm)

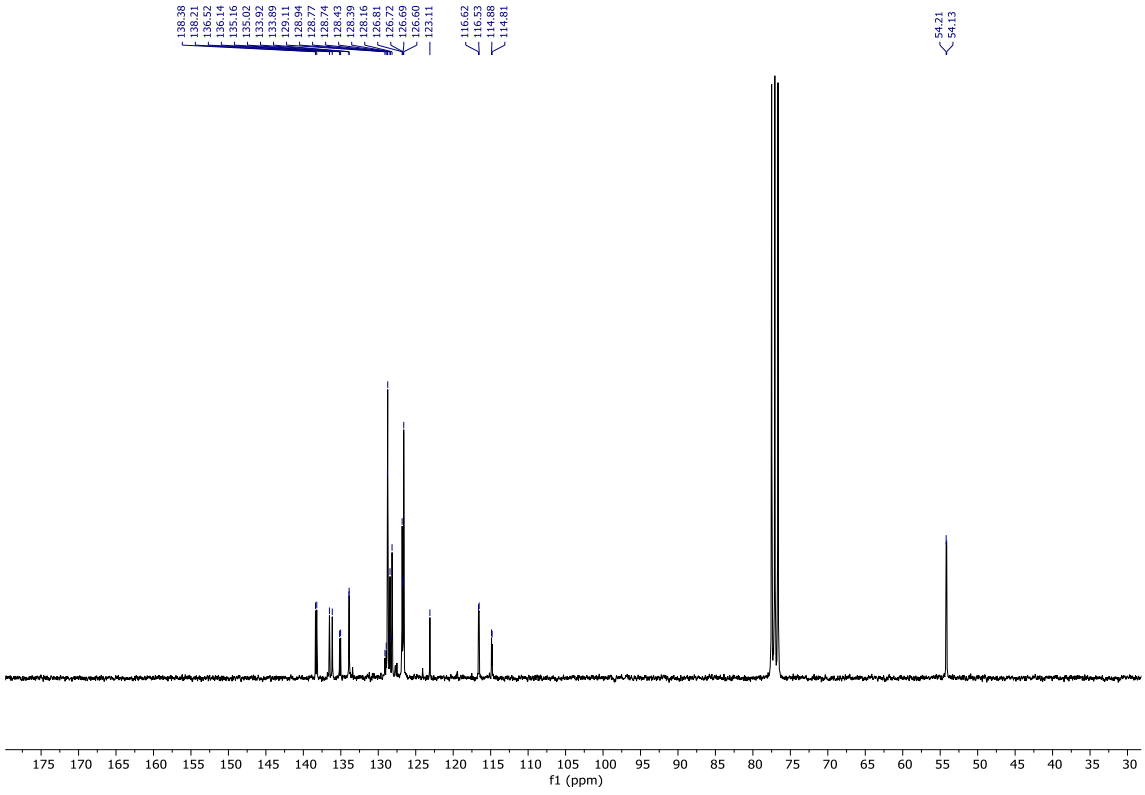

f1 (ppm)

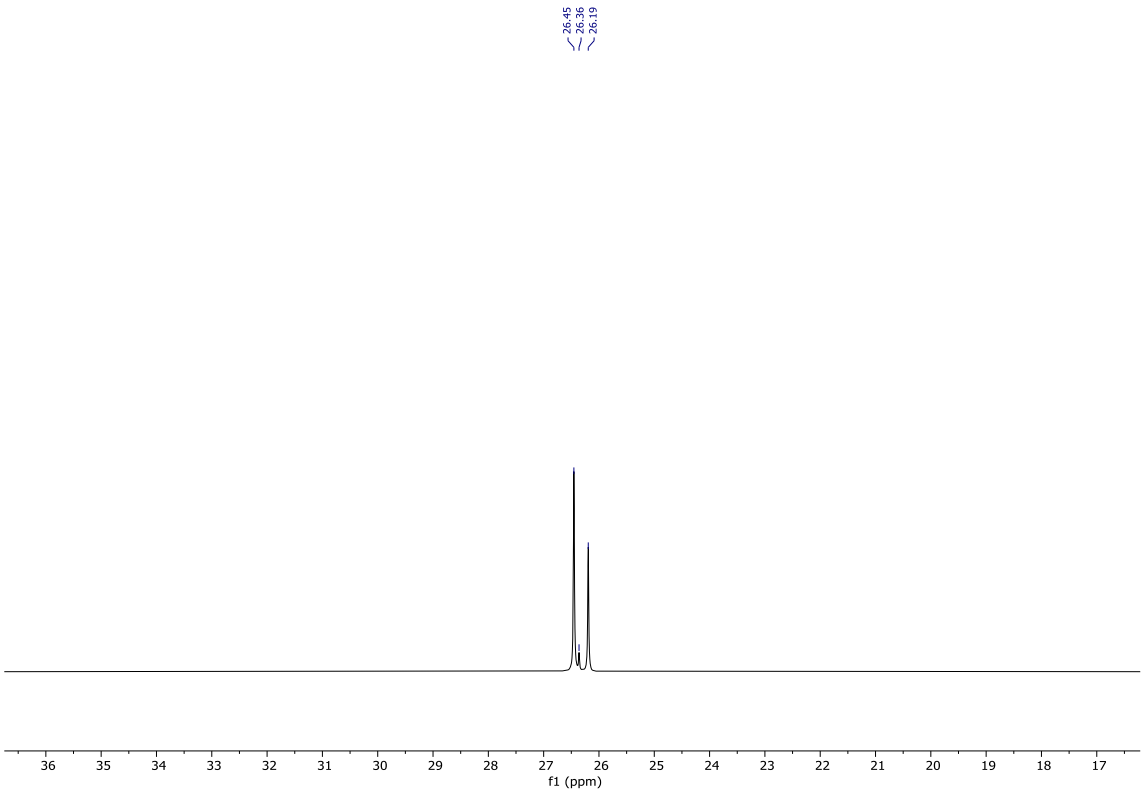

88.82
88.32
110 108 106 104 102 100 98 96 94 92 90 88 86 84 82 80 78 76 74 72 70 68 66
f1 (ppm)


-112.71
-112.88
-80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)

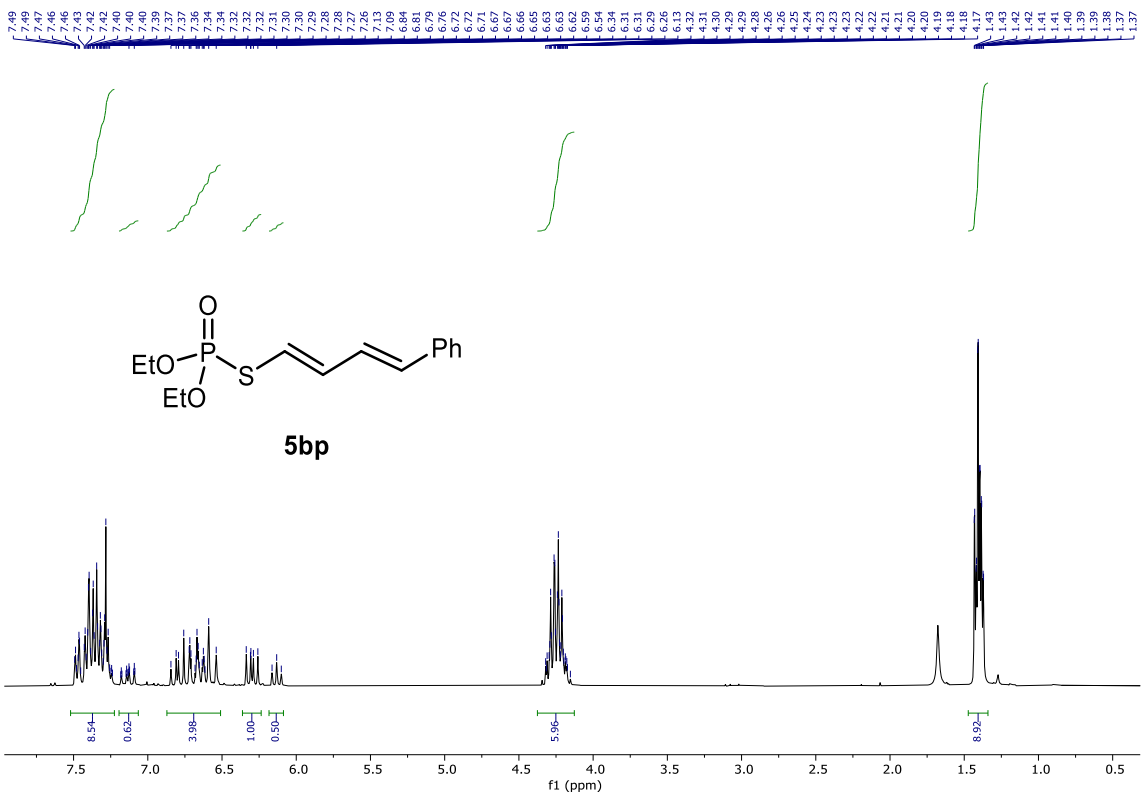
O,O-dimethyl *S*-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl) phosphorothioate (5ap)

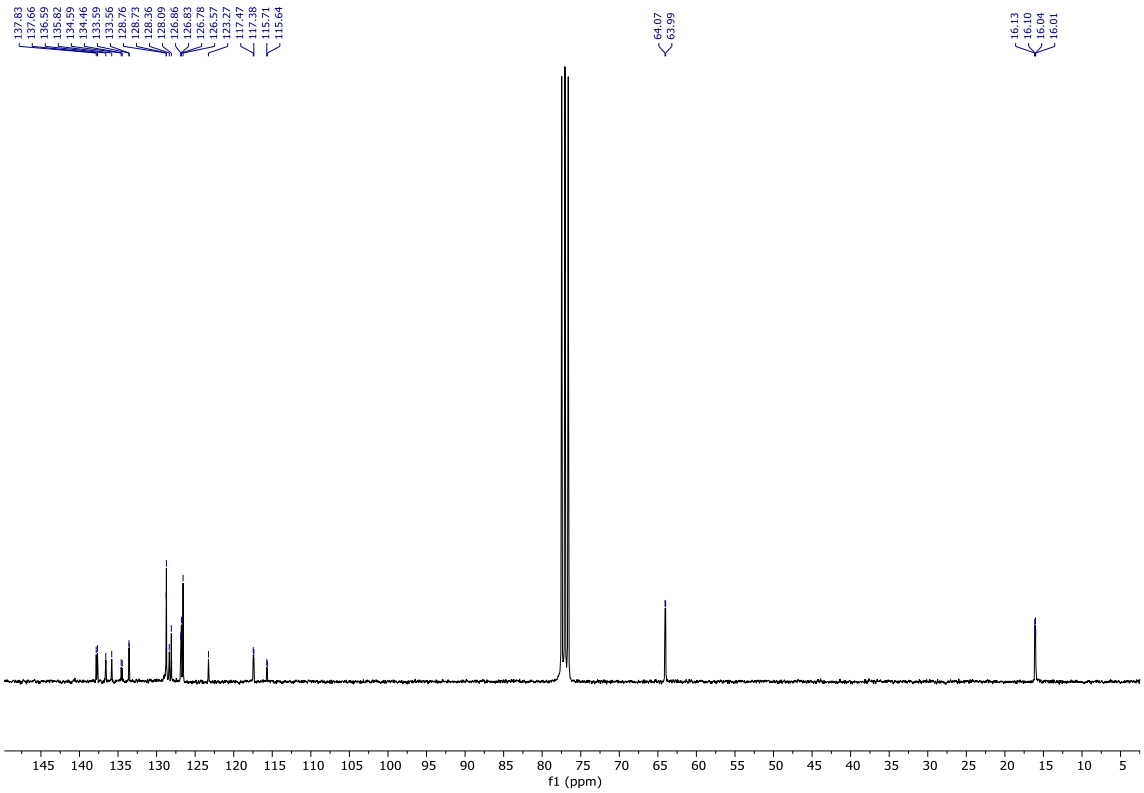


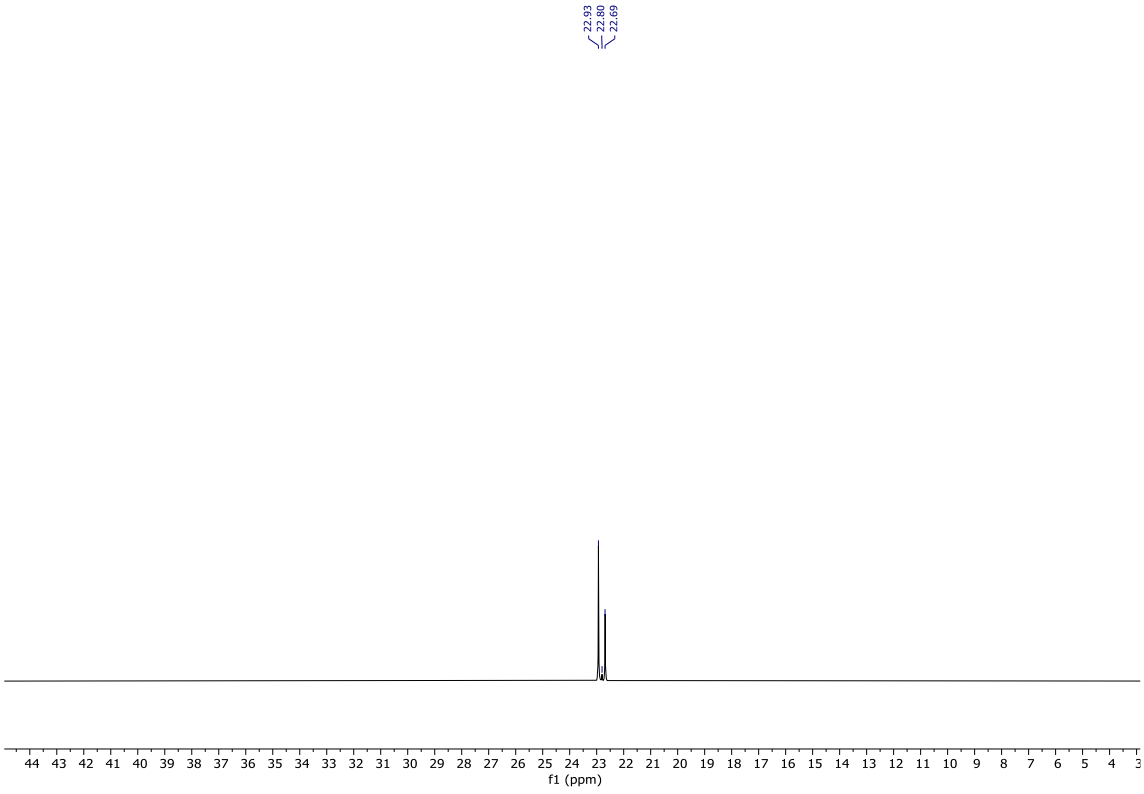




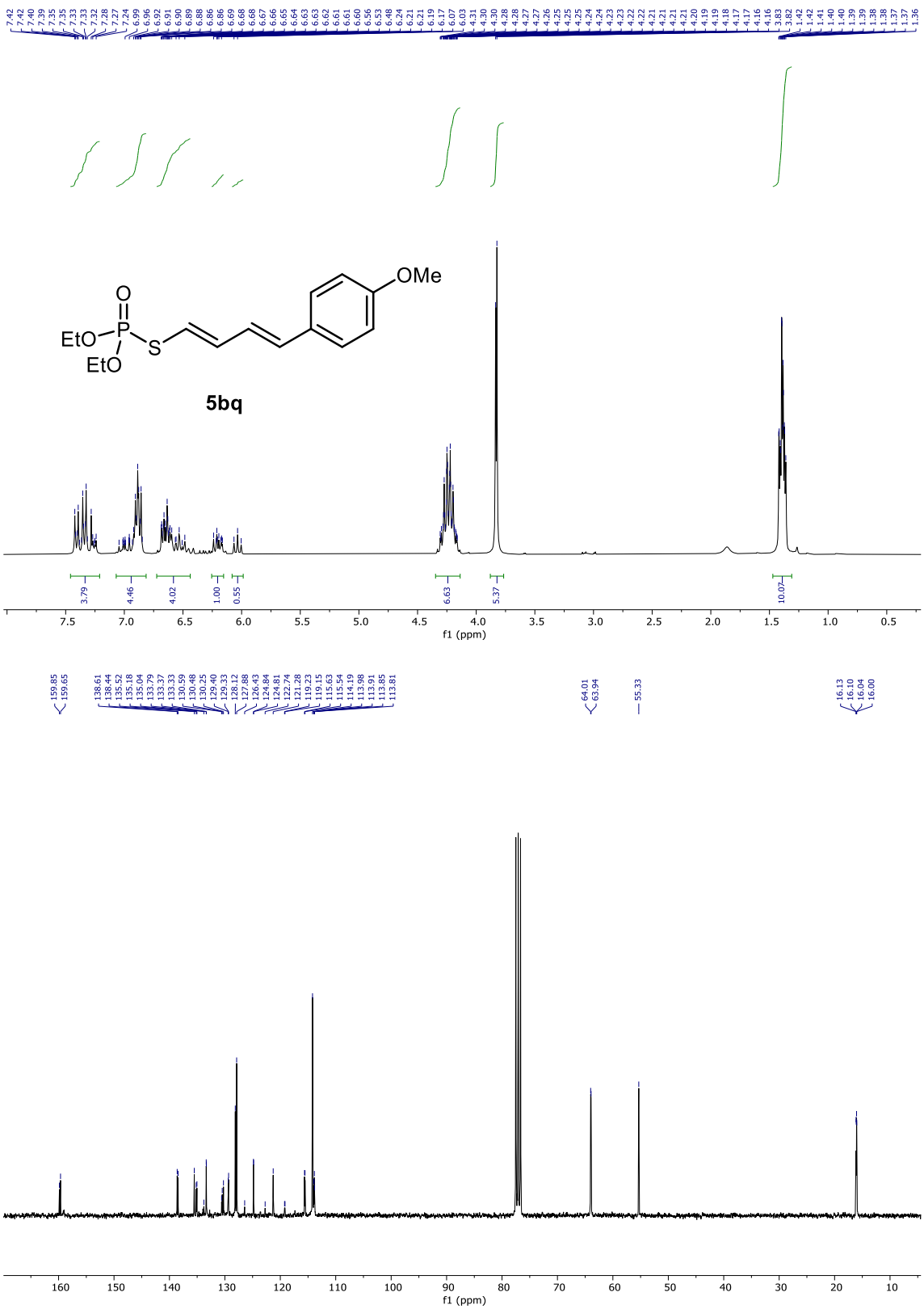
***O,O*-diethyl *S*-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl) phosphorothioate (5bp)**

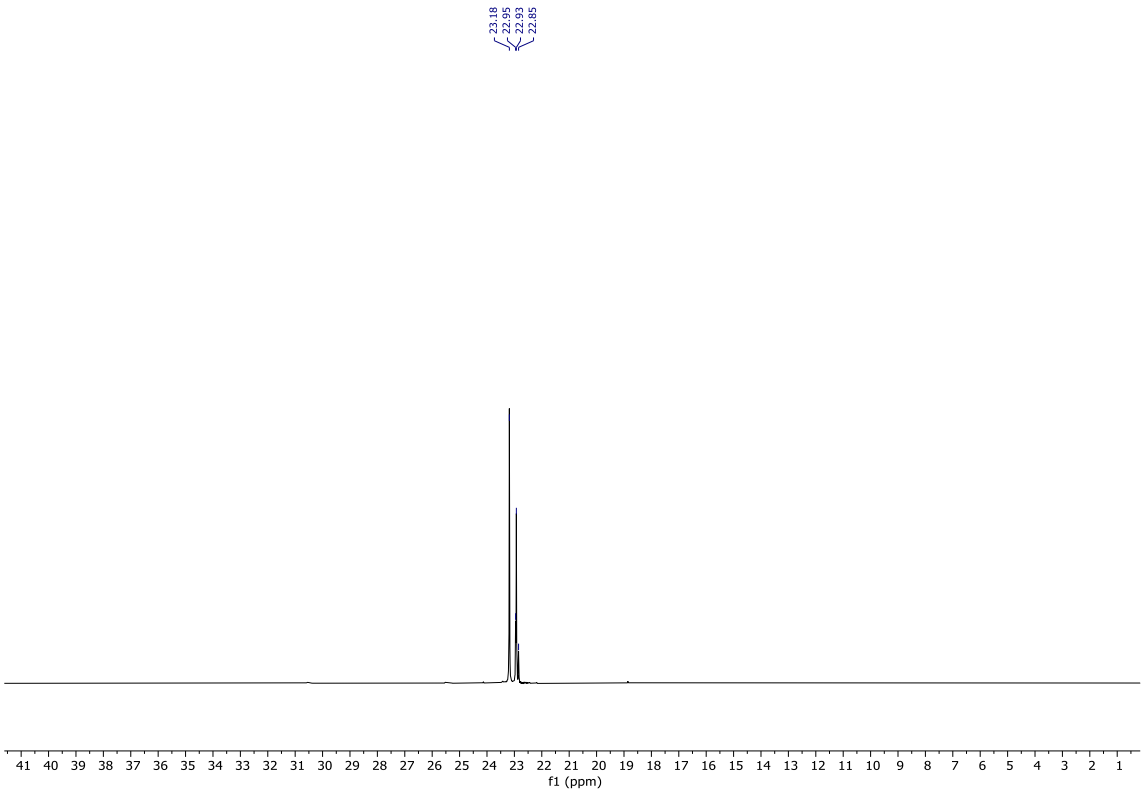



137.83
137.66
136.59
136.02
135.63
134.46
133.59
133.56
128.76
128.73
128.36
128.09
126.86
126.83
126.78
126.57
123.27
117.47
117.38
115.71
115.64
64.07
63.99
16.13
16.10
16.04
16.01
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

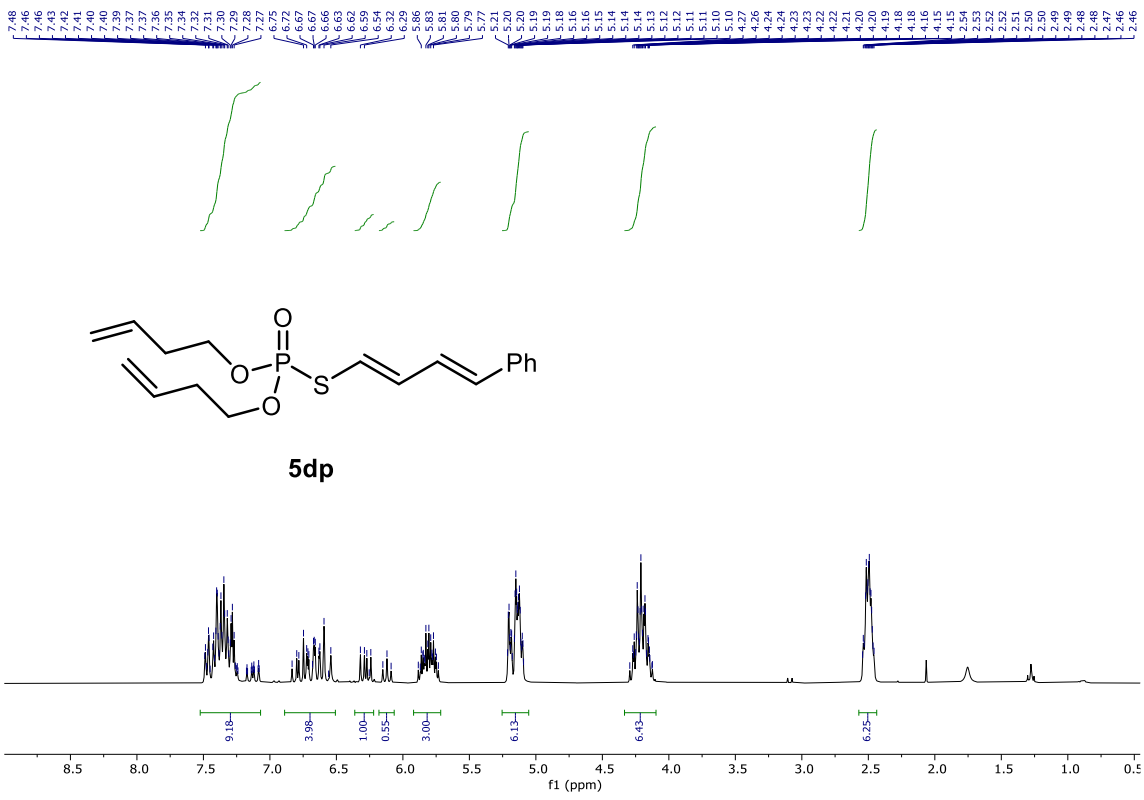

22.93
22.80
22.69
44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3
f1 (ppm)

_S_-((1_E_,3_E_)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl) _O,O_-diethyl phosphorothioate (5bq)

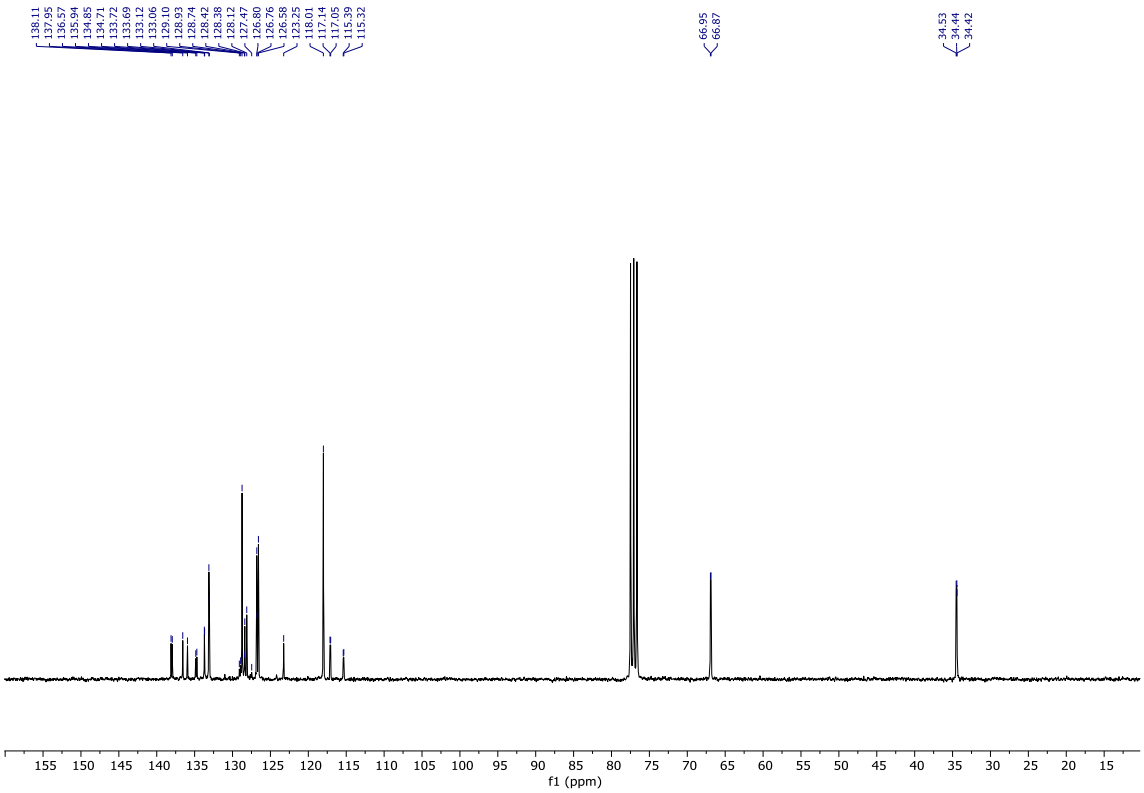


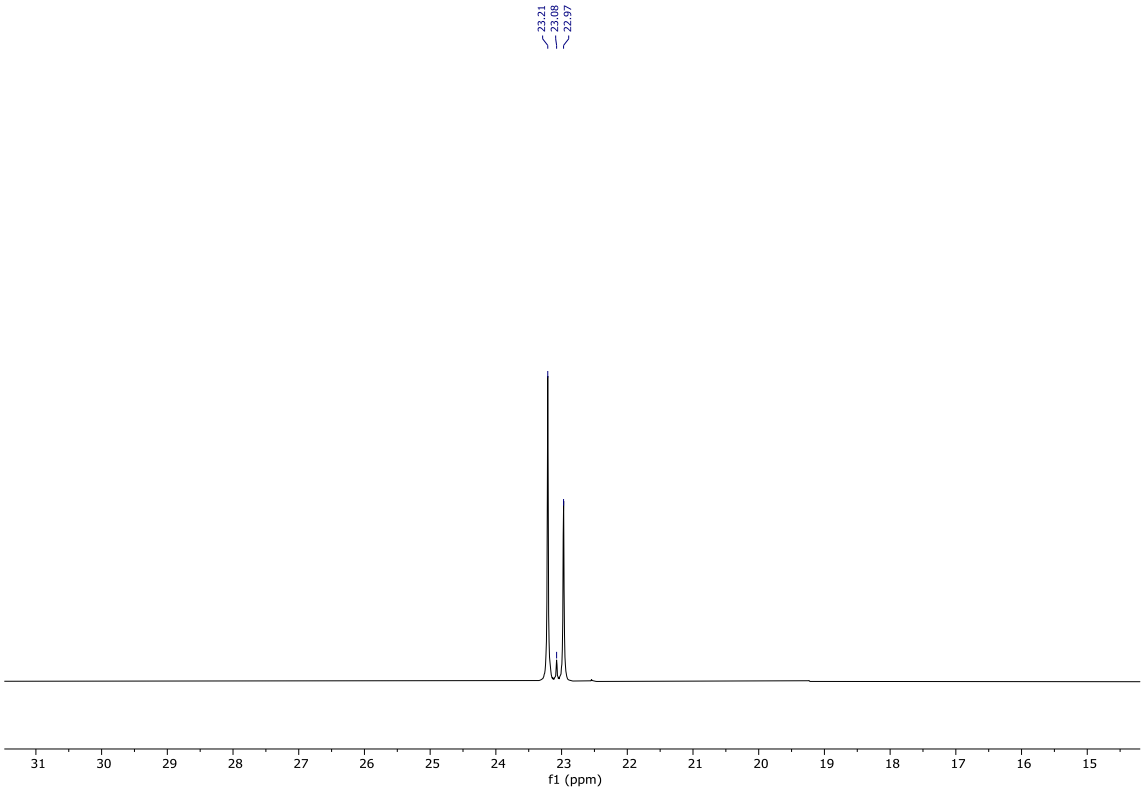


***O,O*-di(but-3-en-1-yl) *S*-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl) phosphorothioate (5dp)**

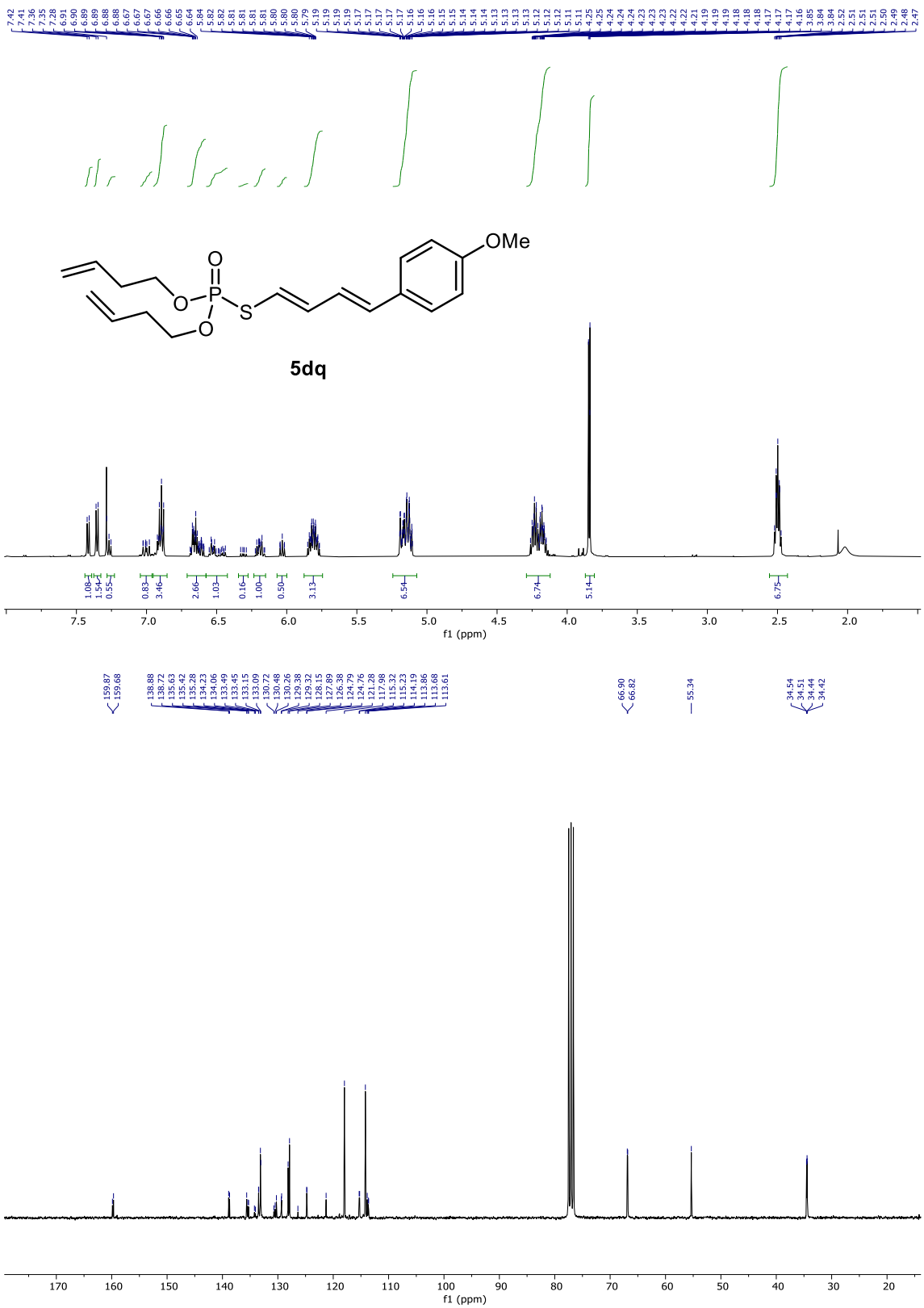


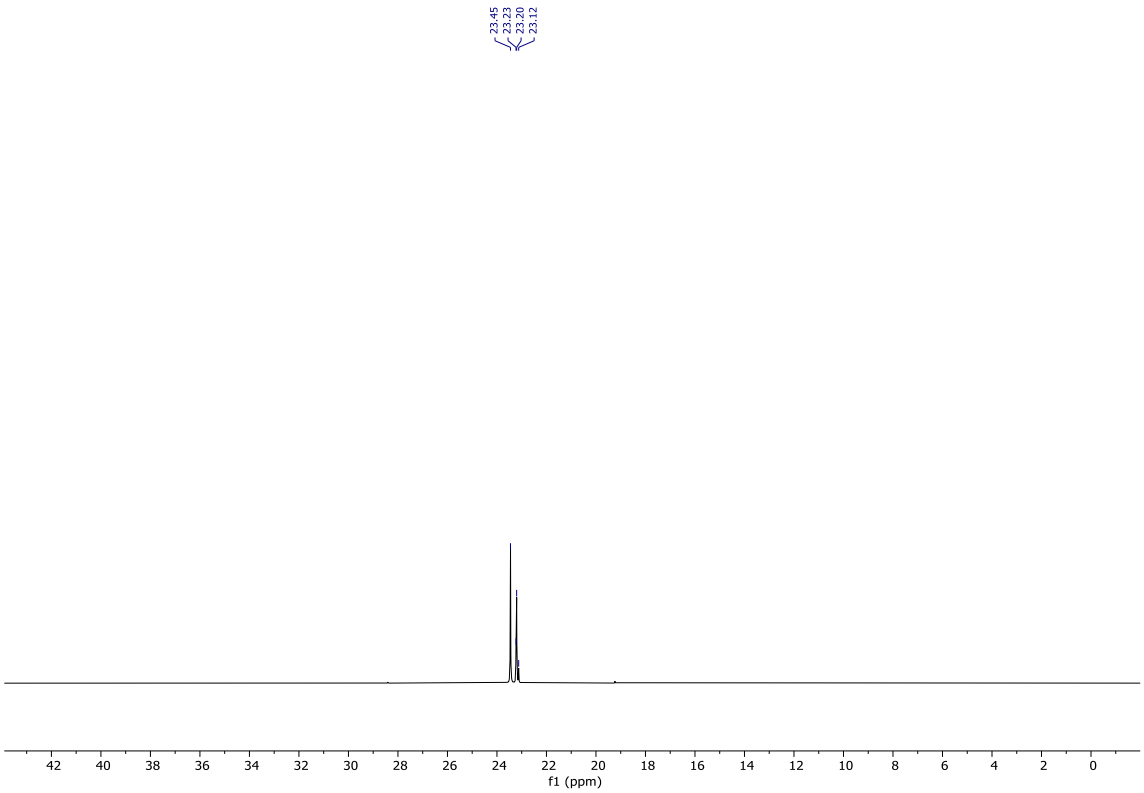
5dp


138.11
137.95
136.57
135.94
134.85
134.71
133.72
133.69
133.12
133.06
129.10
128.93
128.74
128.42
128.38
128.12
127.47
126.80
126.76
126.58
123.25
119.01
117.14
117.05
115.39
115.32
66.95
66.87
34.53
34.44
34.42
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

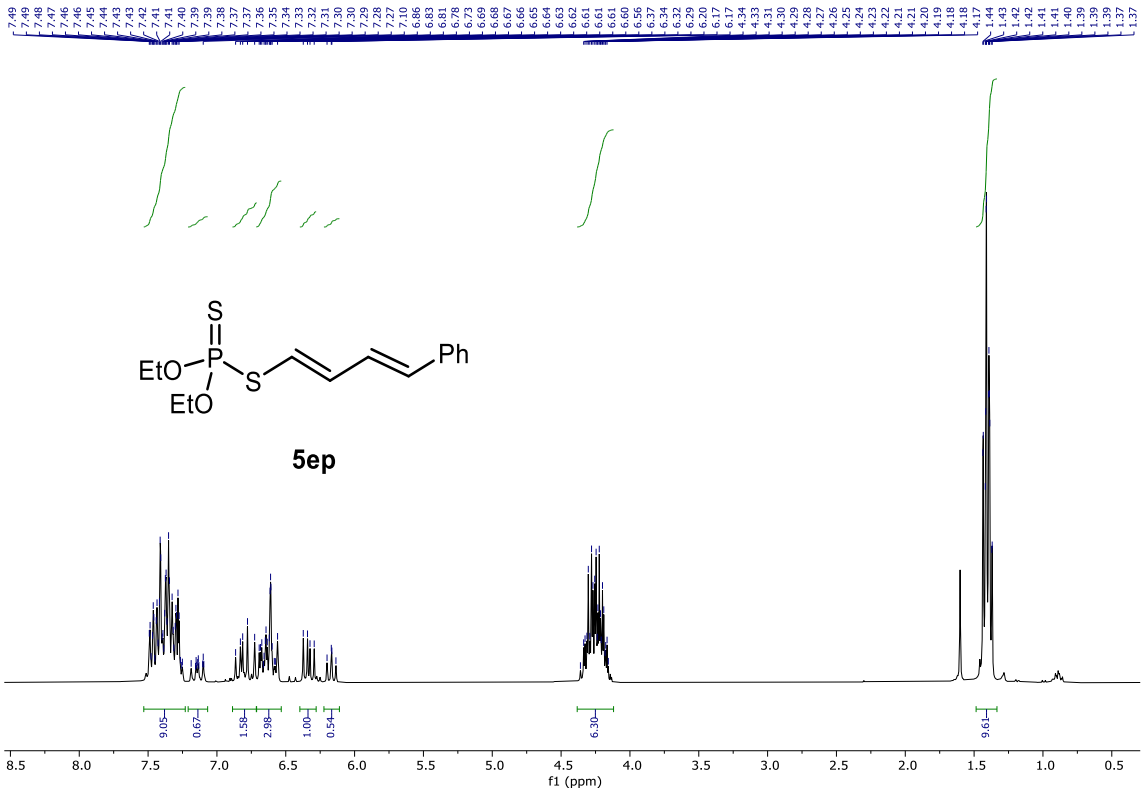

23.21
23.08
22.97
31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15
f1 (ppm)

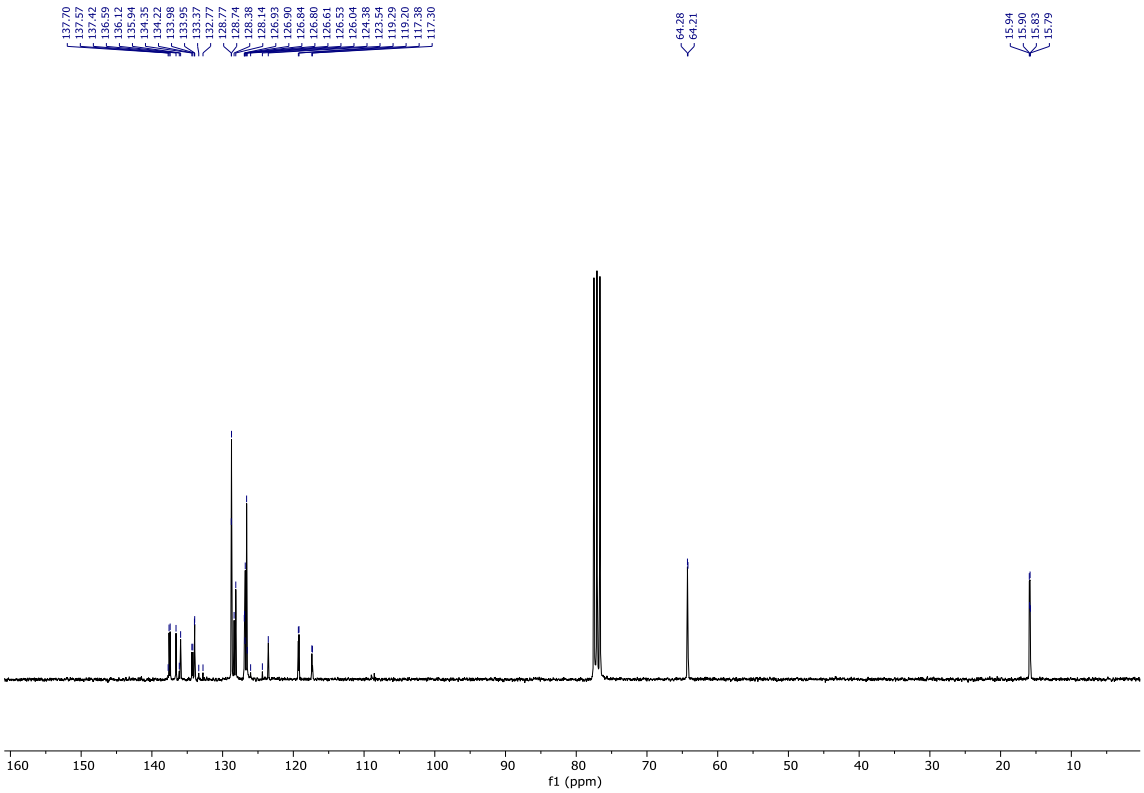
***O,O*-di(but-3-en-1-yl) *S*-((1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl) phosphorothioate (5dq)**

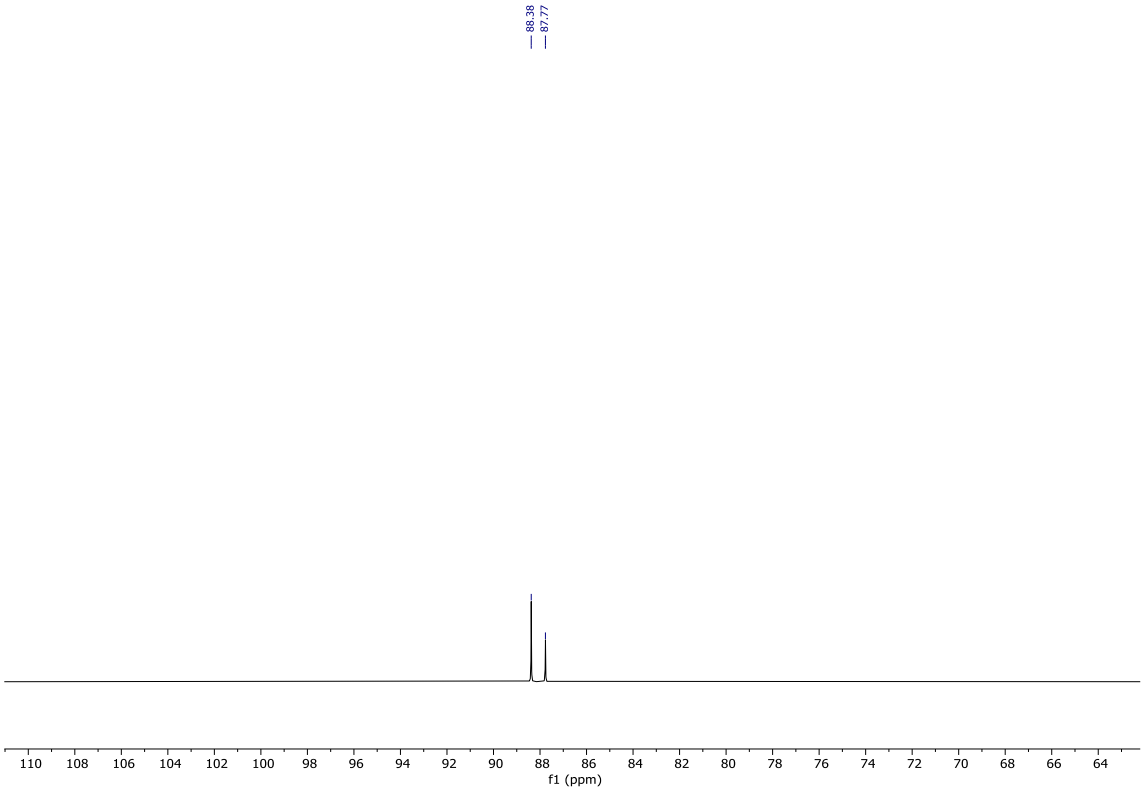




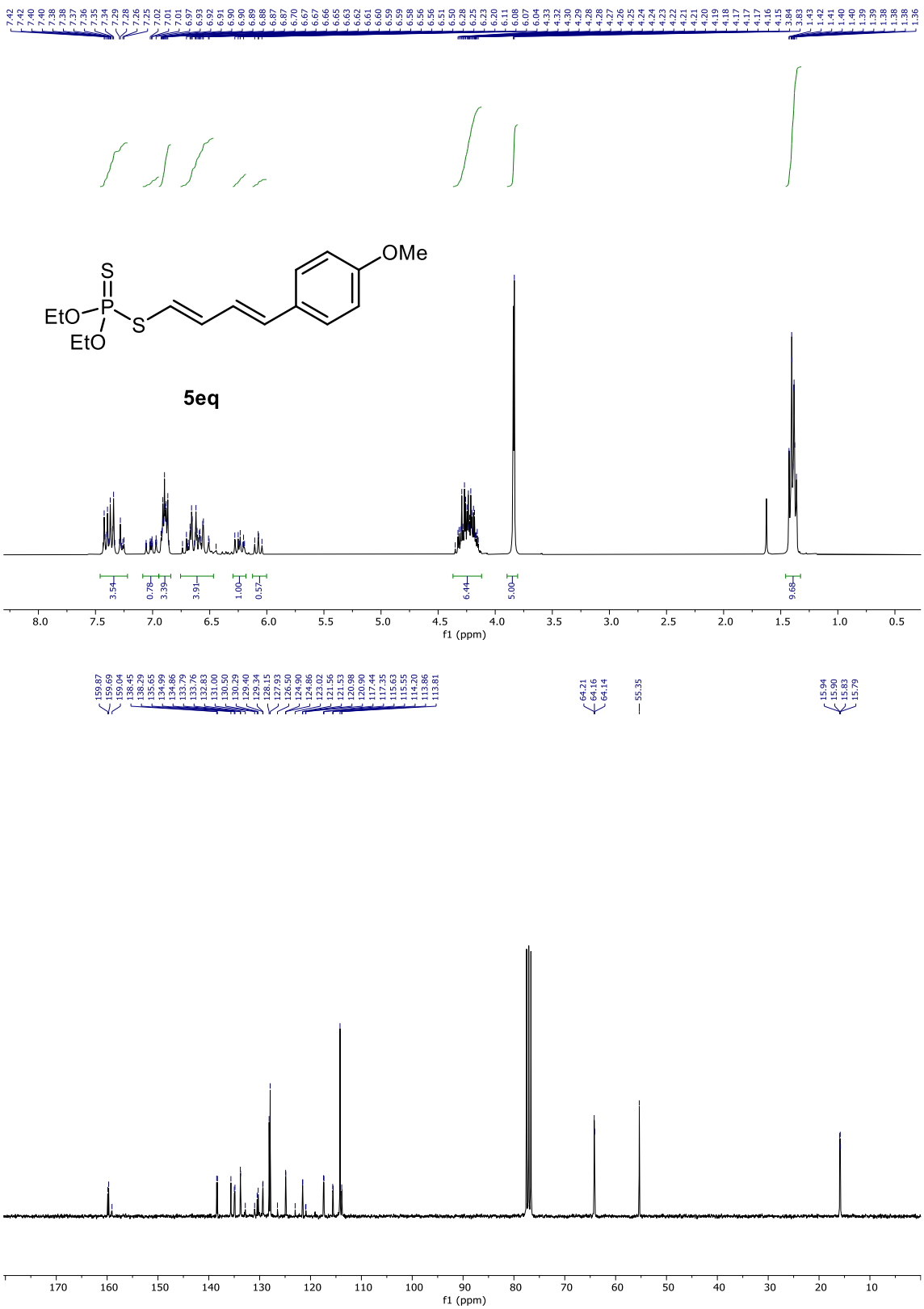
***O,O*-diethyl *S*-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl) phosphorodithioate (5ep)**

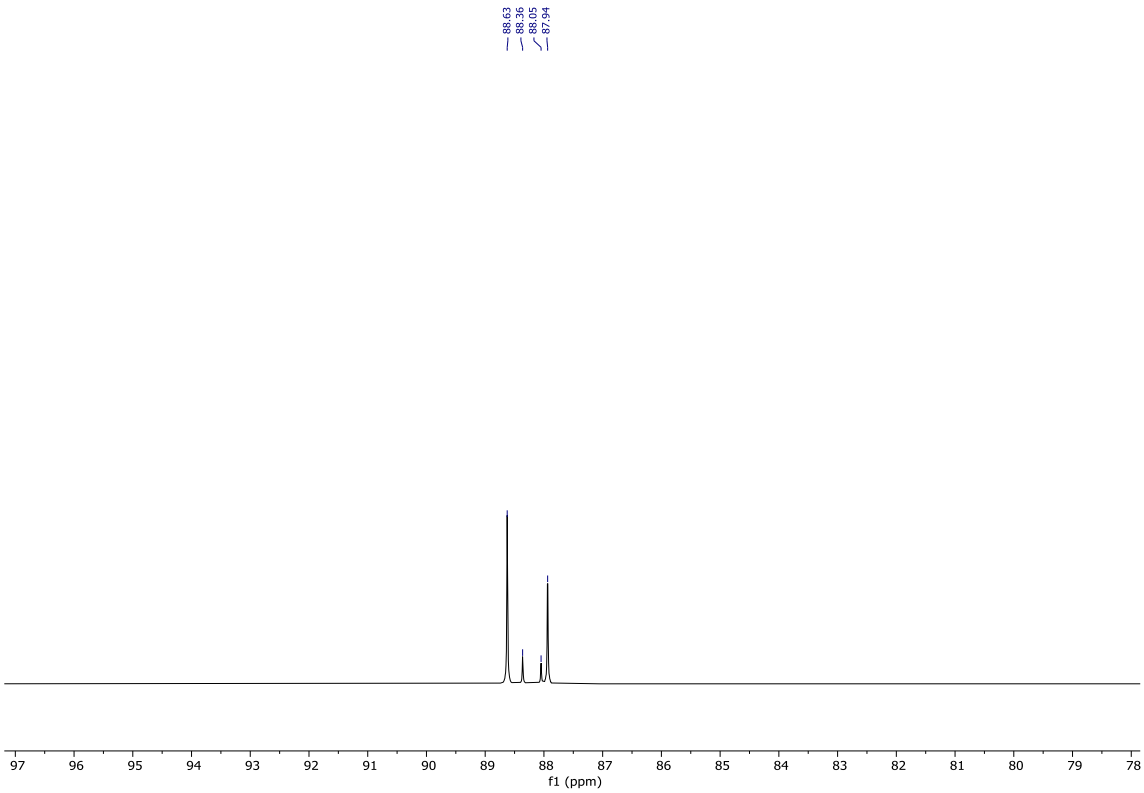



137.70
137.57
137.42
136.59
136.12
135.94
134.35
134.22
133.98
133.95
133.37
132.77
126.77
128.74
128.38
128.14
126.93
126.90
126.84
126.80
126.61
126.53
126.04
125.38
125.04
119.29
119.20
117.38
117.30
64.28
64.21
15.94
15.90
15.83
15.79
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


88.38
87.77
110
108
106
104
102
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
f1 (ppm)

***O,O*-diethyl *S*-((1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl) phosphorodithioate (5eq)**




88.63
88.36
88.05
87.94
97
96
95
94
93
92
91
90
89
88
87
86
85
84
83
82
81
80
79
78
f1 (ppm)