Supporting Information

Halide-Free and Metal-Free Allylic Thiolation/ Selenation of P(O)H Compounds with Sulfur/Selenium and Allylic Alcohols

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Contents

1. Experimental Section

1.1 General information

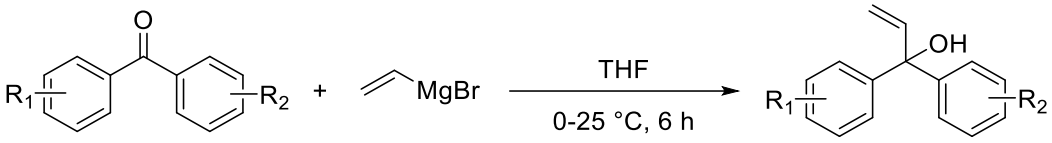
All solvents used in the reactions were freshly distilled. The other reagents were recrystallized or distilled as necessary. All reactions were performed under an atmosphere of dry nitrogen unless specified otherwise. ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (100 MHz), $^{31}P\{^{1}H\}$ (162 MHz), $^{19}F\{^{1}H\}$ (376 MHz) were recorded on a 400 MHz spectrometer in $CDCl_3$. ^{1}H NMR chemical shifts were reported using TMS as the internal standard while $^{13}C\{^{1}H\}$ NMR chemical shifts were reported relative to $CDCl_3$. The electron ionization method was used for HRMS measurements, and the mass analyzer type used for the HRMS measurement is Q Exactive Orbitrap.

1.2 General procedure for the synthesis of 3, 4 and 5

To a Schlenk tube charged with a magnetic stirring bar, sulfur powder (0.2 mmol, 6.4 mg) or selenium (0.2 mmol, 15.8 mg) was added. The reaction tube was vacuumed with a pump and backfilled with nitrogen for three times. Following this, a solution of allylic alcohols (**1**, 0.2 mmol) and P(O)−H compound (**2**, 0.20 mmol) in CH_3CN (1 mL) was introduced into the setup under N_2 conditions. The mixture was then allowed to stir at 100 ºC for 12 hours. After the substrate was completely consumed, the reaction mixture was quenched with water (3 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layer was then washed with saturated sodium chloride solution (5 mL) and dried using anhydrous Na_2SO_4. Following filtration and concentration in vacuo, the obtained residue was subjected to flash column chromatography with petroleum ether/ethyl acetate (2:1) as an eluent to isolate the pure product.

2. Preparation of the starting materials

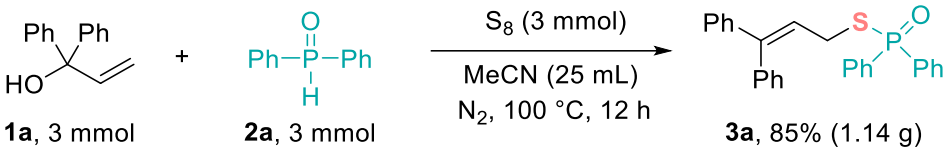
2.1 Preparation of allyl alcohols



According to the reported method,[1] to a two-neck bottle equipped with a magnetic stirrer, diaryl ketone (20 mmol) was added was added. The reaction bottle was vacuumed with a pump and backfilled with nitrogen for three cycles. Subsequently, under a nitrogen atmosphere at 0 °C, 20 mL anhydrous THF was added to the bottle and stirred to dissolve the diaryl ketone. Following the dissolution process, 40 mL of vinyl magnesium bromide (1 M in THF) was added to the reaction bottle in a slow, controlled manner via a titration funnel over a period of 30 minutes. After the addition of the vinyl magnesium bromide was completed, the reaction mixture was stirred at 0 °C for 30 minutes and then allowed to react at room temperature for 6 hours. The reaction solution was then quenched with 20 mL of saturated NH_4Cl solution, followed by extraction with ethyl acetate for three times (50 mL x 3). The combined organic phase was subsequently dried by adding an appropriate amount of anhydrous sodium sulfate, followed by filtration and concentration using a rotary evaporator. Finally, the concentrated residue was subjected to flash column chromatography for separation and purification, resulting in the target compound as a colorless oil, utilizing a mixture of petroleum ether and EtOAc in a ratio of 10:1 (v:v) as the eluent.

3. Large-scale synthesis and late-stage functionalization

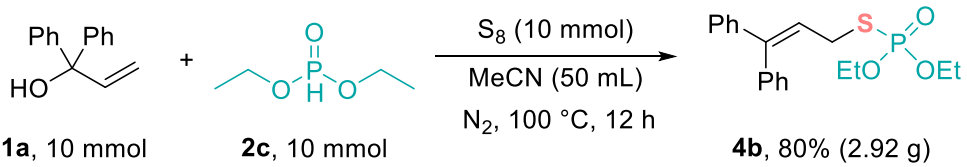
3.1 Gram-scale synthesis of 3a



1a, 3 mmol **2a**, 3 mmol **3a**, 85% (1.14 g)

In a 100 mL reaction tube equipped with a magnetic stir bar, sulfur powder (96.0 mg, 3 mmol) was added. The reaction tube was vacuumed with a pump and backfilled with nitrogen for three cycles. Subsequently, in the nitrogen atmosphere, diphenyl allyl alcohol (**1a**, 630.2 mg, 3 mmol), diphenylphosphine oxide (**2a**, 606.6 mg, 3 mmol), and 25 mL MeCN were added. The reaction mixture was then vigorously stirred in an oil bath at 100 °C for 12 hours. Following TLC monitoring, the reaction mixture was concentrated under vacuum, washed with brine, and extracted with ethyl acetate for three cycles. The combined mixture was concentrated using a rotary vacuum evaporator and separated on a flash silica gel column with a petroleum ether/ethyl acetate eluent (v:v = 2:1) to yield **3a** (1.14 g, 85% yield).

3.2 Gram-scale synthesis of 4b

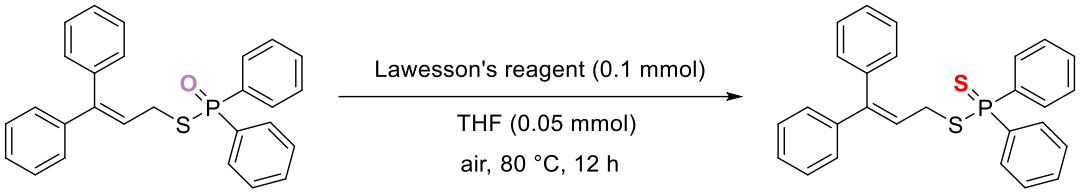


1a, 10 mmol **2c**, 10 mmol **4b**, 80% (2.92 g)

In a 100 mL reaction tube equipped with a magnetic stir bar, sulfur powder (320.0 mg, 10 mmol) was added. The reaction tube was vacuumed with a pump and backfilled with nitrogen for three cycles. Subsequently, in the nitrogen atmosphere, diphenyl allyl alcohol (**1a**, 2.1 g, 10 mmol), diethyl phosphonate (**2c**, 1.3 mL, 10 mmol), and 50 mL MeCN were added. The reaction mixture was then vigorously stirred in an oil bath at 100 °C for 12 hours. Following TLC monitoring, the reaction mixture was concentrated under vacuum, washed with brine, and extracted with ethyl acetate for three cycles. The

combined mixture was concentrated using a rotary vacuum evaporator and separated on a flash silica gel column with a petroleum ether/ethyl acetate eluent (v:v = 2:1) to yield **4b** (2.92 g, yield 80%).

3.3 Late-stage functionalization of 3a



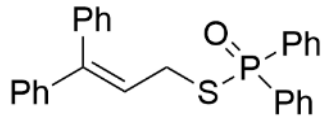
3a, 2.2 eq

7a, 82%

Following a modified procedure,[2] THF (0.05 M, 6 mL) as a solvent was added to a 25 mL reaction tube containing Lawesson's reagent (0.1 mmol, 44.0 mg) and **3a** (2.2 eq, 0.22 mmol, 98.0 mg). The reaction was conducted at 80 °C for 12 hours. The obtained mixture was concentrated using a rotary vacuum evaporator and separated on a flash silica gel column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 10:1) to yield **7a** (36.3 mg, 0.082 mmol, 82%, based on Lawesson's reagent) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 14.3, 8.0 Hz, 4H), 7.44 – 7.33 (m, 5H), 7.31 – 7.23 (m, 3H), 7.20 – 7.05 (m, 6H), 6.97 (dd, J = 4.8, 2.8 Hz, 2H), 5.97 (t, J = 8.0 Hz, 1H), 3.61 – 3.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 141.5, 138.7, 134.9, 134.0, 132.0 (d, J = 3.2 Hz), 131.6 (d, J = 11.3 Hz), 129.3 (d, J = 107.9 Hz), 128.6, 128.5, 128.2, 127.7 (d, J = 2.9 Hz), 127.5, 123.1 (d, J = 5.8 Hz), 31.7 (d, J = 1.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}PS_2$ 443.1052; Found 443.1049.

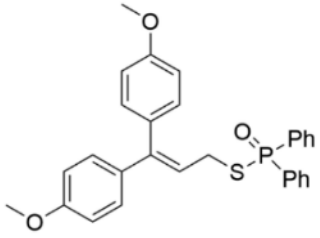
4. Analytical data for the compounds

S-(3,3-diphenylallyl) diphenylphosphinothioate (3a)



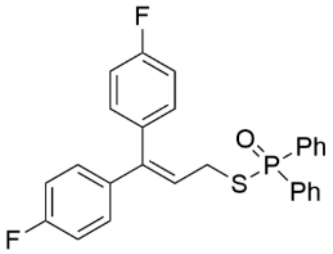
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3a** (78.4 mg, 0.184 mmol, 92%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 4H), 7.54 – 7.49 (m, 2H), 7.42 – 7.47 (m, 4H), 7.36 – 7.31 (m, 3H), 7.25 – 7.20 (m, 3H), 7.10 – 7.13 (m, 4H), 6.10 (t, *J* = 8.1 Hz, 1H), 3.53 (dd, *J* = 9.8, 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 141.5, 138.6, 133.3 (d, *J* = 106.9 Hz), 132.4 (d, *J* = 2.9 Hz), 131.6 (d, *J* = 10.5 Hz), 129.8, 128.9, 128.7, 128.5, 128.2, 127.8, 127.7, 127.6, 123.5 (d, *J* = 5.1 Hz), 29.2 (d, *J* = 1.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{27}H_{24}OPS$ 427.1280; Found 427.1283.

S-(3,3-bis(4-methoxyphenyl)allyl) diphenylphosphi nothioate (3b)



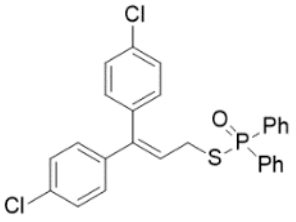
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3b** (89.5 mg, 0.184 mmol, 92%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 12.9, 7.9 Hz, 4H), 7.43 – 7.31 (m, 6H), 6.98 – 6.92 (m, 4H), 6.80 – 6.75 (m, 2H), 6.70 – 6.64 (m, 2H), 5.84 (dd, *J* = 8.2, 7.2 Hz, 1H), 3.71 (dd, *J* = 22.3, 1.4 Hz, 6H), 3.46 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 159.0, 144.5, 134.4, 133.16 (d, *J* = 107.3 Hz), 132.4 (d, *J* = 2.9 Hz), 131.6(d, *J* = 10.6 Hz), 131.0, 130.9, 130.8, 130.1, 128.8 (d, *J* = 4.1 Hz), 128.7, 128.4, 127.9, 127.8, 121.1 (d, *J* = 5.4 Hz), 113.8, 113.5, 55.3 (d, *J* = 1.1 Hz), 29.5 (d, *J* = 1.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{29}H_{28}O_3PS$ 487.1491; Found 487.1489.

S-(3,3-bis(4-fluorophenyl)allyl) diphenylphosphinothioate (3c)



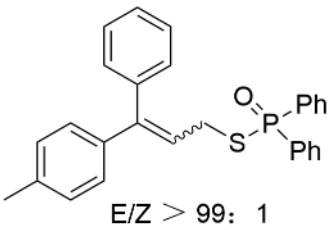
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3c** (87.9 mg, 0.190 mmol, 95%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 13.0, 8.1 Hz, 4H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.40 – 7.33 (m, 4H), 7.01 – 6.91 (m, 6H), 6.81 -6.85 (m 2H), 5.96 (t, *J* = 7.9 Hz, 1H), 3.42 (t, *J* = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 247.5 Hz), 162.3 (d, *J* = 247.2 Hz) 143.0, 137.4 (d, *J* = 3.1 Hz), 134.3 (d, *J* = 3.5 Hz), 133.2(d, J = 107.2 Hz), 132.4 (d, *J* = 2.9 Hz), 131.6, 131.5, 131.4, 131.3, 129.1 (d, *J* = 8.1 Hz), 128.8, 128.7, 123.8 (d, *J* = 4.5 Hz), 115.7, 115.4, 115.2, 115.0, 29.1 (d, *J* = 1.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.0, -114.3. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{22}F_2OPS$ 463.1092; Found 463.1090.

S-(3,3-bis(4-chlorophenyl)allyl) diphenylphosphinothioate (3d)



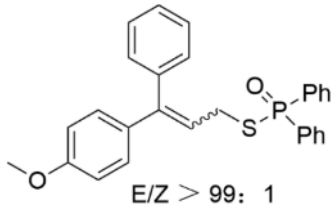
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3d** (93.1 mg, 0.188 mmol, 94%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 12.6, 7.8 Hz, 4H), 7.49 – 7.34 (m, 6H), 7.24 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.12 (dd, *J* = 8.4, 1.5 Hz, 2H), 6.94 (dd, *J* = 11.2, 4.4 Hz, 4H), 6.02 (dd, *J* = 8.1, 7.1 Hz, 1H), 3.42 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 139.5, 136.6, 133.9 (d, *J* = 3.0 Hz), 133.1 (d, J = 107.3 Hz), 132.5 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 10.5 Hz), 131.1, 128.9 (d, *J* = 2.7 Hz), 128.8 (d, *J* = 1.0 Hz), 128.5, 124.7 (d, *J* = 4.8 Hz), 29.0 (d, *J* = 1.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.9. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{22}Cl_2OPS$ 495.0501; Found 495.0500.

S-(3-phenyl-3-(p-tolyl)allyl) diphenylphosphinothioate (3e)



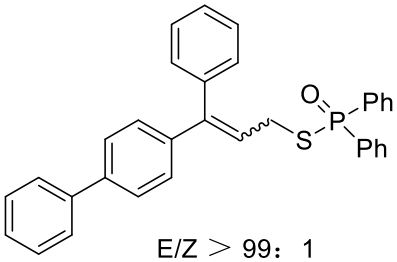
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3e** (82.8 mg, 0.188 mmol, 94%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 4H), 7.53 – 7.39 (m, 6H), 7.34 – 7.08 (m, 7H), 7.00 (dd, *J* = 10.9, 5.0 Hz, 2H), 6.03 (t, *J* = 8.0 Hz, 1H), 3.58 – 3.47 (m, 2H), 2.34 (d, *J* = 26.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.24, 145.2, 141.7, 138.8, 138.6, 137.6, 137.3, 135.6, 133.2 (d, *J* = 107.2 Hz), 132.4, 131.6 (d, *J* = 10.6 Hz), 131.0, 129.7 (d, *J* = 8.4 Hz), 129.2, 128.9 (d, *J* = 7.9 Hz), 128.7, 128.4, 128.2, 127.6 (d, *J* = 8.1 Hz), 127.4, 123.2 (d, *J* = 5.1 Hz), 122.4 (d, *J* = 5.2 Hz), 29.3, 21.3 (d, *J* = 17.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.2. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{28}H_{26}OPS$ 441.1437; Found 441.1438.

S-(3-(4-methoxyphenyl)-3-phenylallyl) diphenylphosphinothioate (3f)



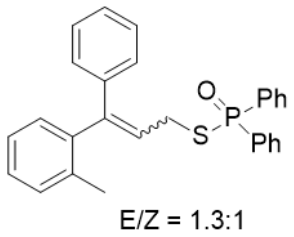
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3f** (84.0 mg, 0.184 mmol, 92%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 4H), 7.53 – 7.42 (m, 6H), 7.23 – 7.03 (m, 7H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.02 (dd, *J* = 18.1, 8.5 Hz, 1H), 3.80 (d, *J* = 23.1 Hz, 3H), 3.49 – 3.59 (m 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 159.1, 144.9, 144.7, 141.9, 138.8, 134.1, 133.3 (d, *J* = 106.9 Hz), 132.3, 131.6 (d, *J* = 10.4 Hz), 131.0, 130.8, 129.7, 128.8, 128.7, 128.4, 128.1, 127.7, 127.6, 127.59, 123.1 (d, *J* = 5.2 Hz), 121.5 (d, *J* = 5.0 Hz), 113.8, 113.6, 55.3, 29.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{28}H_{26}O_2PS$ 457.1386; Found 457.1388.

S-(3-([1,1'-biphenyl]-4-yl)-3-phenylallyl) diphenylphosphinothioate (3g)



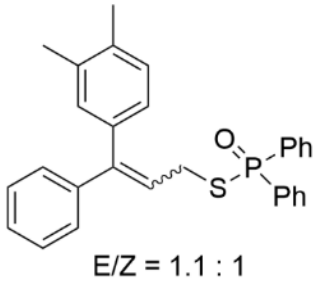
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3g** (90.5 mg, 0.180 mmol, 90%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 13.0, 8.0 Hz, 4H), 7.56 – 7.52 (m, 1H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.43 – 7.22 (m, 12H), 7.18 – 7.04 (m, 5H), 6.09 – 5.98 (m, 1H), 3.52 – 3.44 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.8, 141.4, 140.7, 140.7, 140.5, 140.4, 140.3, 138.5, 137.6, 133.1 (d, *J* = 107.5 Hz), 133.0 (d, *J* = 107.4 Hz), 132.4 (d, *J* = 2.5 Hz), 131.6 (d, *J* = 10.5 Hz), 131.0, 130.9, 130.2, 129.7, 128.94, 128.9, 128.7, 128.5, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.1 (d, *J* = 1.4 Hz), 127.1, 126.9, 123.5 (d, *J* = 5.3 Hz), 123.4 (d, *J* = 5.1 Hz), 29.3 (d, *J* = 4.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{33}H_{28}OPS$ 503.1593; Found 503.1595.

S-(3-phenyl-3-(o-tolyl)allyl) diphenylphosphinothioate (3h)



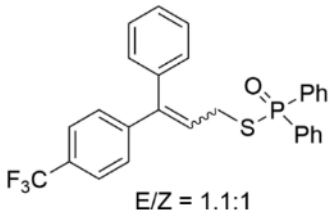
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3h** (77.5 mg, 0.176 mmol, 88%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 4H), 7.51 – 7.43 (m, 6H), 7.29 – 7.02 (m, 9H), 6.24 – 5.72 (m, 1H), 3.75 – 3.32 (m, 2H), 1.98 (d, *J* = 12.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 144.4, 142.6, 139.9, 138.8, 137.7, 136.6, 136.1, 133.9, 133.2 (d, *J* = 107.2 Hz), 132.4, 132.42, 132.39, 131.6 (d, *J* = 10.5 Hz), 130.4, 130.37, 130.0, 129.9, 129.2, 128.9, 128.7, 128.4, 128.3, 127.9, 127.7, 127.6, 127.5, 126.5, 126.0, 125.6 (d, *J* = 3.4 Hz), 123.24 (d, *J* = 5.0 Hz), 29.0 (d, *J* = 2.0 Hz), 28.8 (d, *J* = 1.8 Hz), 20.5, 19.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.3, 43.1. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{28}H_{26}OPS$ 441.1437; Found 441.1434.

S-(3-(3,4-dimethylphenyl)-3-phenylallyl) diphenylphosphinothioate (3i)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3i** (85.5 mg, 0.188 mmol, 94%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 4H), 7.55 – 7.41 (m, 6H), 7.34 – 7.09 (m, 5H), 7.07 – 6.74 (m, 3H), 6.03 (t, *J* = 8.0 Hz, 1H), 3.57 – 3.49 (m, 2H), 2.31 – 2.15 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3 (d, *J* = 4.7 Hz), 141.8, 139.1, 138.8, 136.6, 136.3, 136.0, 135.99, 133.4 (d, *J* = 107.7 Hz), 132.4, 132.37, 132.3, 131.6 (d, *J* = 10.5 Hz), 130.8, 129.7 (d, *J* = 5.8 Hz), 129.5, 128.8 (d, *J* = 2.5 Hz), 128.7 (d, *J* = 2.6 Hz), 128.6, 128.4, 128.1, 127.6 (d, *J* = 5.3 Hz), 127.2, 125.1, 123.1 (d, *J* = 5.2 Hz), 122.3 (d, *J* = 5.2 Hz), 29.3 (d, *J* = 1.6 Hz), 29.2 (d, *J* = 1.8 Hz), 19.9 (d, *J* = 2.5 Hz), 19.7, 19.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.2, 43.1. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{29}H_{28}OPS$ 455.1593; Found 455.1598.

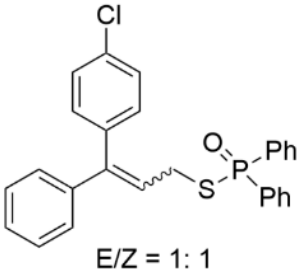
S-(3-phenyl-3-(4-(trifluoromethyl)phenyl)allyl) diphenylphosphinothioate (3j)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3j** (89.0 mg, 0.180 mmol, 90%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 4H), 7.62 – 7.49 (m, 4H), 7.46 – 7.43 (m, 2H), 7.35 (d, *J* = 5.7 Hz, 2H), 7.28 – 7.17 (m, 5H), 7.12 – 7.05 (m, 2H), 6.16 (t, *J* = 8.2 Hz, 1H), 3.57 – 3.44 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 143.8, 142.4, 139.2 (q, *J* = 282.1 Hz), 133.6, 132.9 (d, J = 107.6 Hz), 132.6, 132.56, 132.5,131.7 (d, *J* = 3.8 Hz), 131.6 (d, *J* = 3.9 Hz), 130.9, 130.2, 129.7, 128.9, 128.8, 128.7, 128.4, 128.1, 128.06, 127.8, 127.5, 125.9, 125.5 (d, *J* = 3.8 Hz), 125.2 (d, *J* = 3.8 Hz), 124.4 (d, *J* = 5.3 Hz), 31.6 (d, *J* = 7.0 Hz), 30.3 (d, *J* = 5.5 Hz)., 29.1. ^{31}P NMR (162 MHz, $CDCl_3$)

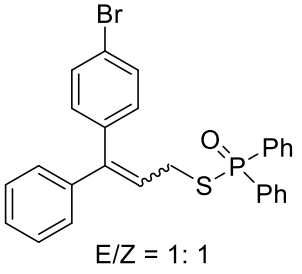
δ 43.5, 43.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47, -62.48. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{23}F_3OPS$ 495.1154; Found 495.1157.

S-(3-(4-chlorophenyl)-3-phenylallyl) diphenylphosphinothioate (3k)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3k** (85.7 mg, 0.186 mmol, 93%) as a clear colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 4H), 7.54 – 7.43 (m, 6H), 7.35 – 7.17 (m, 5H), 7.13 – 6.98 (m, 4H), 6.15 – 6.04 (m, 1H), 3.51 (dd, *J* = 17.6, 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 143.9, 141.0, 140.0, 138.2, 137.0, 133.7, 133.6, 133.3 (d, *J* = 107.3 Hz), 133.2 (d, *J* = 107.2 Hz), 132.5, 132.47, 132.4, 131.7 (d, *J* = 1.7 Hz), 131.6 (d, *J* = 1.6 Hz), 131.2, 129.7, 128.9 (d, J = 4.7 Hz), 128.8, 128.6, 128.4 (d, *J* = 3.5 Hz), 128.0, 127.9, 127.5, 124.2 (d, *J* = 4.7 Hz), 124.0 (d, *J* = 5.3 Hz), 29.14 (d, *J* = 2.2 Hz), 29.10 (d, *J* = 2.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.0, 42.9. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{23}ClOPS$ 461.0890; Found 461.0894.

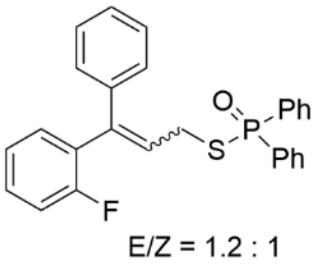
S-(3-(4-bromophenyl)-3-phenylallyl) diphenylphosphinothioate (3l)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3l** (89.0 mg, 0.176 mmol, 88%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.74 (m, 4H), 7.55 – 7.43 (m, 6H), 7.38 – 7.22 (m, 5H), 7.13 – 6.93 (m, 4H), 6.15 – 6.05 (m, 1H), 3.51 (dd, *J* = 18.0, 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 143.9, 140.5, 140.00, 133.4 (d, *J* = 107.1 Hz), 132.5, 132.48, 132.4, 131.73, 131.7 (d, *J* = 1.8 Hz), 131.6 (d, *J* = 1.7 Hz), 131.5, 131.3, 131.2, 129.2, 128.90, 128.86, 128.8, 128.6, 128.4 (d, *J* = 3.4 Hz),

127.9 (d, J = 7.5 Hz), 127.5, 31.6, 30.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.93, 42.90. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{23}BrOPS$ 505.0385; Found 505.0387.

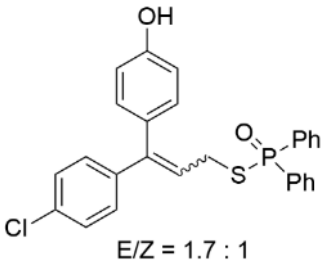
S-(3-(2-fluorophenyl)-3-phenylallyl) diphenylphosphinothioate (3m)



E/Z = 1.2 : 1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3m** (83.6 mg, 0.188 mmol, 94%) as a clear colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 12.9, 8.0 Hz, 4H), 7.56 – 7.20 (m, 10H), 7.18 – 6.88 (m, 5H), 6.23 – 6.01 (m, 1H), 3.66 – 3.42 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (d, J = 236.4 Hz), 160.2 (d, J = 250.3 Hz), 140.2, 140.0, 138.7, 138.6, 133.3 (d, J = 107.3 Hz), 133.2 (d, J = 107.2Hz), 132.4 (d, J = 3.0 Hz), 131.9 (d, J = 3.5 Hz), 131.6 (d, J = 10.6 Hz), 131.3 (d, J = 3.3 Hz), 130.1, 130.0, 129.9, 129.3, 129.26, 129.1, 128.9, 128.7, 128.4 (d, J = 2.2 Hz), 127.9, 127.8 – 127.7 (m), 127.4, 126.8, 125.9, 125.7 (d, J = 4.4 Hz), 124.3 (d, J = 3.6 Hz), 123.9 (d, J = 3.7 Hz), 116.1 (d, J = 6.0 Hz), 115.9 (d, J = 6.5 Hz), 29.0 (d, J = 1.3 Hz), 28.8 (d, J = 2.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.2, 43.1. ^{19}F NMR (376 MHz, CDCl3) δ -113.3, -113.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{23}FOPS$ 445.1186; Found 445.1181.

S-(3-(4-chlorophenyl)-3-(4-hydroxyphenyl)allyl) diphenylphosphinothioate (3n)

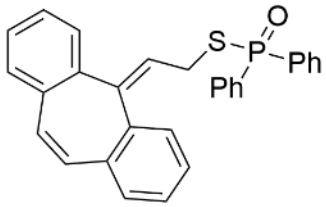


E/Z = 1.7 : 1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1)gave product **3n** (76.3 mg, 0.160 mmol, 80%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.98 – 7.74 (m, 4H), 7.57 – 7.37 (m, 6H), 7.27 (d, J = 8.2 Hz, 1H), 7.20 – 7.11 (m, 1H), 7.06 – 6.86 (m, 5H), 6.77 (d, J = 8.6 Hz, 1H), 6.15 – 5.86 (m, 1H), 3.40 – 3.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 157.0, 144.4, 143.7, 140.6, 137.5, 133.5, 133.2, 132.9 (d, J = 124.5

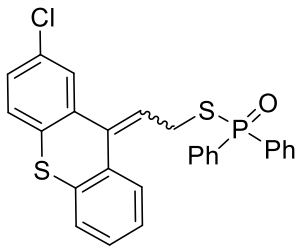
Hz), 132.7 (d, J = 2.6 Hz), 131.6 (d, J = 10.7 Hz), 131.2, 131.0, 129.0, 128.9, 128.7, 128.6, 128.2, 122.8 (d, J = 4.5 Hz), 115.7, 115.5, 29.7 (d, J = 27.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.7, 44.7. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{27}H_{23}ClO_2PS$ 477.0839; Found 477.0835.

S-(2-(5H-dibenzo[a,d][7]annulen-5-ylidene)ethyl) diphenylphosphinothioate (3o)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3o** (83.8 mg, 0.186 mmol, 93%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.82 (m, 4H), 7.54 – 7.41 (m, 6H), 7.34 – 7.16 (m, 8H), 6.87 – 6.75 (m, 2H), 5.59 (t, J = 8.2 Hz, 1H), 3.52 – 3.44 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 141.3, 135.8, 134.8, 133.82, 133.8, 133.4 (d, J = 107.1 Hz), 132.7, 132.4 (d, J = 3.0 Hz), 131.6 (d, J = 10.5 Hz), 131.2, 131.0, 128.9, 128.87 (d, J = 2.3 Hz), 128.84, 128.7 (d, J = 2.3 Hz), 128.4, 128.3 (d, J = 2.9 Hz), 128.0, 127.9, 127.5 (d, J = 1.4 Hz), 127.3, 28.1 (d, J = 1.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.9. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{29}H_{24}OPS$ 451.1280; Found 451.1281.

S-(2-(1-chloro-9H-thioxanthen-9-ylidene)ethyl) diphenylphosphinothioate (3p)

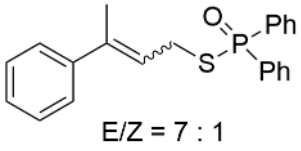


E/Z = 1.2 : 1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3p** (68.7 mg, 0.140 mmol, 70%) as a yellow oil. ^{1}H NMR (400 MHz, CDCl3) δ 7.93 (dd, J = 13.0, 8.1 Hz, 4H), 7.61 – 7.45 (m, 7H), 7.39 – 7.31 (m, 1H), 7.29 – 7.11 (m, 5H), 5.95 – 5.74 (m, 1H), 3.93 – 3.67 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 137.6, 137.3, 136.7, 133.5, 133.4 (d, J = 98.3 Hz), 132.8 (d, J = 3.4 Hz), 132.6 (d, J = 2.5 Hz), 131.7 (d, J = 10.7Hz), 130.4, 129.0, 128.9, 128.6, 128.2, 128.1, 128.0, 127.8, 127.6, 127.3, 127.0, 126.9, 126.7, 126.6, 126.0, 125.9, 125.7, 28.7 (d, J = 2.1 Hz), 28.6 (d, J = 2.0 Hz). ^{31}P NMR (162

MHz, $CDCl_3$) δ 43.0, 42.7. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{21}ClOPS_2$ 491.0454; Found 491.0451.

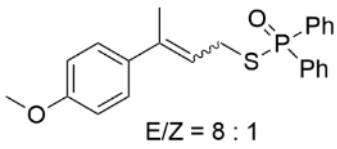
S-(3-phenylbut-2-en-1-yl) diphenylphosphinothioate (3q)



E/Z = 7 : 1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3q** (47.4 mg, 0.130 mmol, 65%) as a white oil. ^{1}H NMR (400 MHz, CDCl3) δ 7.86 – 7.71 (m, 4H), 7.47 – 7.33 (m, 6H), 7.27 – 7.09 (m, 5H), 5.70 – 5.43 (m, 1H), 3.80 – 2.94 (m, 2H), 1.88 (dd, *J* = 5.9, 1.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 139.4, 133.5 (d, *J* = 107.1 Hz), 132.4 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 4.6 Hz), 131.5 (d, *J* = 4.6 Hz), 128.8 (d, *J* = 4.7 Hz), 128.7 (d, *J* = 4.6 Hz), 128.2, 127.7, 127.4, 127.3, 127.0 (d, *J* = 241.09 Hz), 122.2 (d, *J* = 5.1 Hz), 27.8 (d, *J* = 2.1 Hz), 15.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.9, 42.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{22}OPS$ 365.1123; Found 365.1121.

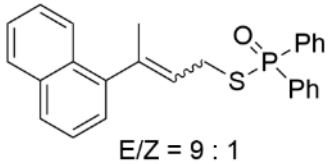
S-(3-(4-methoxyphenyl)but-2-en-1-yl) diphenylphosphinothioate (3r)



E/Z = 8 : 1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3r** (67.1 mg, 0.170 mmol, 85%) as a yellow oil. ^{1}H NMR (400 MHz, CDCl3) δ 8.02 – 7.74 (m, 4H), 7.60 – 7.40 (m, 6H), 7.21 – 7.02 (m, 2H), 6.88 – 6.76 (m, 2H), 5.47 – 5.71 (m, 1H), 3.80 (d, J = 4.9 Hz, 3H), 3.73 – 3.33 (m, 2H), 1.94 (dd, J = 7.8, 1.0 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 141.0, 138.8, 135.0, 133.3 (d, *J* = 107.2 Hz), 132.4 (d, *J* = 3.1 Hz), 131.7 (d, *J* = 3.9 Hz), 131.6 (d, *J* = 3.8 Hz), 128.9, 128.85, 128.8, 128.7 (d, *J* = 4.3 Hz), 126.9, 124.6, 120.4 (d, *J* = 5.3 Hz), 113.7, 113.5, 55.4 (d, *J* = 2.3 Hz), 27.9 (d, *J* = 1.9 Hz), 15.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.0, 42.8. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{24}O_2PS$ 395.1229; Found 395.1232.

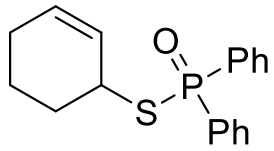
S-(3-(naphthalen-1-yl)but-2-en-1-yl) diphenylphosphinothioate (3s)



E/Z = 9 : 1

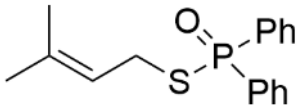
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3s** (58.0 mg, 0.140 mmol, 70%) as a yellow oil. ^{1}H NMR (400 MHz, CDCl3) δ 7.98 – 7.85 (m, 4H), 7.85 – 7.64 (m, 3H), 7.64 – 7.27 (m, 9H), 7.18 – 6.99 (m, 1H), 5.97 – 5.42 (m, 1H), 3.75 – 3.07 (m, 2H), 2.04 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 140.4, 133.8, 133.2 (d, *J* = 107.6 Hz), 132.5 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 10.6 Hz), 130.9 (d, *J* = 4.4 Hz), 128.9, 128.8, 128.76, 128.6, 128.5, 128.4, 128.1, 127.9, 127.4, 126.0, 125.8, 125.7, 125.4, 124.9 (d, *J* = 3.7 Hz), 27.4 (d, *J* = 2.0 Hz), 19.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.9, 43.5. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{26}H_{24}OPS$ 415.1280; Found 415.1276.

S-(cyclohex-2-en-1-yl) diphenylphosphinothioate (3t)



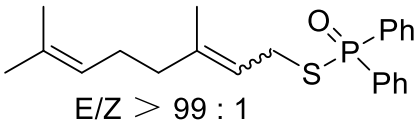
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3t** (44.0 mg, 0.140 mmol, 70%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.85 (m, 4H), 7.57 – 7.43 (m, 6H), 5.76 (dd, *J* = 8.5, 4.8 Hz, 1H), 5.64 (dd, *J* = 9.9, 1.9 Hz, 1H), 3.94 (d, *J* = 5.5 Hz, 1H), 2.04 – 1.88 (m, 4H), 1.83 – 1.73 (m, 1H), 1.65 – 1.56 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.9 (d, *J* = 106.8 Hz), 133.8 (d, *J* = 106.7 Hz), 132.3 (dd, *J* = 2.8, 1.8 Hz), 131.7 (d, *J* = 10.4 Hz), 131.5, 131.4, 130.7, 128.8 (d, *J* = 5.0 Hz), 128.7 (d, *J* = 5.0 Hz), 127.9 (d, *J* = 5.5 Hz), 41.4 (d, *J* = 1.8 Hz), 31.2 (d, *J* = 2.3 Hz), 24.6, 19.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.3. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{19}H_{22}OPS$ 315.0984; Found 315.0989.

S-(3-methylbut-2-en-1-yl) diphenylphosphinothioate (3u)



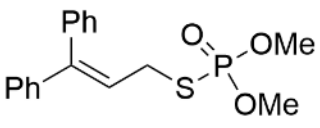
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3u** (39.3 mg, 0.130 mmol, 65%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 4H), 7.55 – 7.43 (m, 6H), 5.16 (t, *J* = 8.0 Hz, 1H), 3.45 (t, *J* = 8.6 Hz, 2H), 1.56 (d, *J* = 21.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 133.3 (d, *J* = 107.3 Hz), 132.3 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 10.5 Hz), 131.0 (d, *J* = 11.3 Hz), 128.8, 128.7, 128.1, 127.9, 119.1 (d, *J* = 5.7 Hz), 27.5 (d, *J* = 1.9 Hz), 25.7, 17.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.2. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{20}OPS$ 303.0967; Found 303.0966.

S-(3,7-dimethylocta-2,6-dien-1-yl) diphenylphosphinothioate (3v)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3v** (55.6 mg, 0.150 mmol, 75%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 12.9, 7.3 Hz, 4H), 7.55 – 7.44 (m, 6H), 5.19 (s, 1H), 5.02 (t, *J* = 6.3 Hz, 1H), 3.48 (t, *J* = 8.5 Hz, 2H), 2.00 –1.87 (m, 4H), 1.66 (s, 3H), 1.57 (d, *J* = 4.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 133.6 (d, *J* = 106.9 Hz), 132.3 (d, *J* = 3.0 Hz), 131.8, 131.6 (d, *J* = 10.5 Hz), 128.8, 128.6, 123.9, 118.9 (d, *J* = 5.6 Hz), 39.5, 27.3 (d, *J* = 2.1 Hz), 26.3, 25.8, 17.8, 16.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.7. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{22}H_{28}OPS$ 371.1593; Found 371.1591.

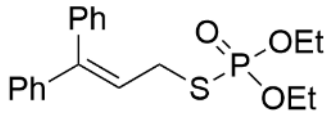
S-(3,3-diphenylallyl) O,O-dimethyl phosphorothioate (4a)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **4a** (56.8 mg, 0.170 mmol, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$)

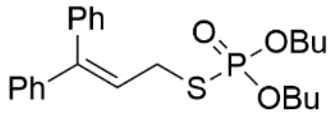
δ 7.41 – 7.21 (m, 10H), 6.21 (t, *J* = 8.0 Hz, 1H), 3.76 (dd, *J* = 12.7, 1.0 Hz, 6H), 3.53 (dd, *J* = 13.3, 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 141.4, 138.6, 129.2 (d, *J* = 126.1 Hz), 128.4, 128.0, 127.9, 127.6, 123.1 (d, *J* = 6.1 Hz), 53.9 (d, *J* = 5.7 Hz), 30.6 (d, *J* = 3.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.77 (s). HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{20}O_3PS$ 335.0865; Found 335.0869.

S-(3,3-diphenylallyl) O,O-diethyl phosphorothioate (4b)



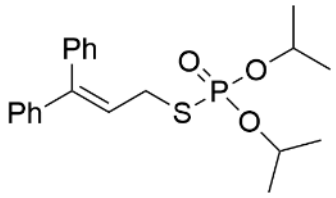
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4b** (63.8 mg, 0.176 mmol, 88%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 3H), 7.28 – 7.20 (m, 7H), 6.22 (t, *J* = 8.1 Hz, 1H), 4.20 – 4.05 (m, 4H), 3.53 (dd, *J* = 12.8, 8.1 Hz, 2H), 1.30 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 141.44, 138.6, 129.8, 128.5, 128.3, 127.9, 127.8, 127.5, 123.2 (d, *J* = 6.4 Hz), 63.6 (d, *J* = 5.7 Hz), 30.6 (d, *J* = 3.7 Hz), 16.1 (d, *J* = 7.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.1. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{19}H_{24}O_3PS$ 363.1178; Found 363.1173.

O,O-dibutyl S-(3,3-diphenylallyl) phosphorothioate (4c)



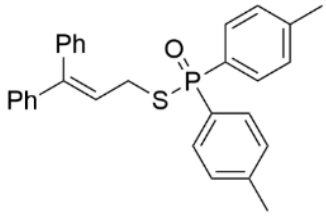
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4c** (77.8 mg, 0.186 mmol, 93%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 3H), 7.30 – 7.18 (m, 7H), 6.21 (t, *J* = 8.1 Hz, 1H), 4.12 – 3.99 (m, 4H), 3.52 (dd, *J* = 12.9, 8.1 Hz, 2H), 1.61 (dd, *J* = 14.6, 6.9 Hz, 4H), 1.39 – 1.32 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 141.5, 138.7, 129.8, 128.5, 128.3, 127.9, 127.8, 127.6, 123.3(d, *J* =6.5 Hz), 67.4 (d, *J* = 6.2 Hz), 32.2 (d, *J* = 7.4 Hz), 30.6 (d, *J* = 3.7 Hz), 18.8, 13.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.3. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{23}H_{32}O_3PS$ 419.1804; Found 419.1803.

S-(3,3-diphenylallyl) O,O-diisopropyl phosphorothioate (4d)



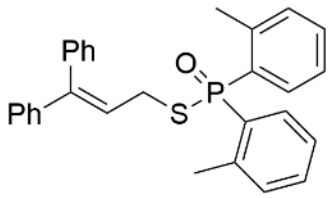
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4d** (64.8 mg, 0.166 mmol, 83%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 3H), 7.28 – 7.19 (m, 7H), 6.22 (t, *J* = 8.1 Hz, 1H), 4.75 – 4.67 (m, 2H), 3.54 (dd, *J* = 12.0, 8.2 Hz, 2H), 1.35 – 1.31 (m, 6H), 1.28 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 141.5, 138.7, 129.8, 128.5, 128.3, 127.9, 127.8, 127.6, 123.3 (d, *J* = 7.3 Hz), 72.8 (d, *J* = 6.2 Hz), 30.9 (d, *J* = 3.6 Hz), 24.0 (d, *J* = 4.0 Hz), 23.7 (d, *J* = 5.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.5. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{21}H_{28}O_3PS$ 391.1491; Found 391.1494.

S-(3,3-diphenylallyl) di-p-tolylphosphinothioate (4e)



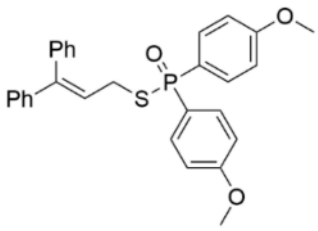
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4e** (86.4 mg, 0.190 mmol, 95%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 12.8, 8.0 Hz, 4H), 7.33 (d, *J* = 7.1 Hz, 3H), 7.27 – 7.20 (m, 7H), 7.15 – 7.07 (m, 4H), 6.07 (t, *J* = 8.1 Hz, 1H), 3.51 (dd, *J* = 9.8, 8.3 Hz, 2H), 2.38 (s, 6H). ^{13}C NMR (101 MHz, CH_2Cl_2) δ 144.9, 142.9 (d, *J* = 3.0 Hz), 141.5, 138.6, 131.6 (d, *J* = 10.9 Hz), 130.2 (d, *J* = 109.8 Hz), 129.8, 129.6, 129.4, 128.4, 128.2, 127.7, 127.6 (d, *J* = 2.9 Hz), 123.8 (d, *J* = 5.0 Hz), 29.2, 21.7 (d, *J* = 1.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{29}H_{28}OPS$ 455.1593; Found 455.1591.

S-(3,3-diphenylallyl) di-o-tolylphosphinothioate (4f)



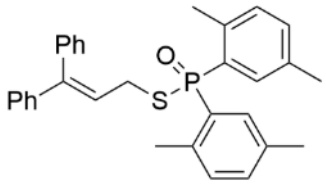
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4f** (77.3 mg, 0.170 mmol, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 15.2, 7.6 Hz, 2H), 7.43 – 7.32 (m, 5H), 7.26 – 7.11 (m, 11H), 6.17 (t, *J* = 8.2 Hz, 1H), 3.63 (t, *J* = 8.8 Hz, 2H), 2.40 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 142.0 (d, *J* = 10.0 Hz), 141.5, 138.7, 132.8 (d, *J* = 12.3 Hz), 132.4 (d, *J* = 2.8 Hz), 132.1, 132.0, 131.1, 129.1 (d, *J* = 130.9 Hz), 128.2, 127.7 (d, *J* = 4.7 Hz), 127.50, 125.7 (d, *J* = 13.4 Hz), 123.6 (d, *J* = 5.1 Hz), 29.1 (d, *J* = 1.6 Hz), 21.6 (d, *J* = 4.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 46.2. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{29}H_{28}OPS$ 455.1593; Found 455.1591.

S-(3,3-diphenylallyl) bis(4-methoxyphenyl)phosphinothioate (4g)



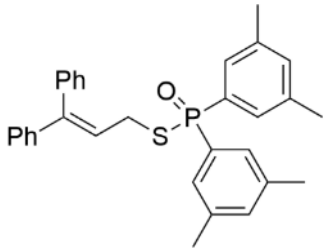
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **4g** (87.7 mg, 0.180 mmol, 90%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 4H), 7.37 – 7.29 (m, 3H), 7.26 – 7.20 (m, 3H), 7.16 – 7.09 (m, 4H), 6.96 – 6.90 (m, 4H), 6.08 (t, *J* = 8.1 Hz, 1H), 3.82 (s, 6H), 3.50 (dd, *J* = 9.9, 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, *J* = 3.0 Hz), 144.8, 141.5, 138.6, 133.5 (d, *J* = 12.0 Hz), 129.1 (d, *J* = 130.9 Hz), 128.2, 127.6, 127.5 (d, *J* = 4.2 Hz), 124.7 (d, *J* = 114.7 Hz), 123.8 (d, *J* = 5.0 Hz), 114.2 (d, *J* = 14.3 Hz), 55.5, 29.3 (d, *J* = 1.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.9. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{29}H_{28}O_3PS$ 487.1491; Found 487.1487.

S-(3,3-diphenylallyl) bis(2,5-dimethylphenyl)phosphinothioate (4h)



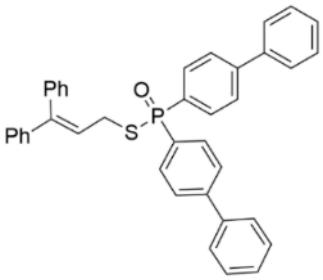
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **4h** (88.8 mg, 0.184 mmol, 92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 15.4 Hz, 2H), 7.40 – 7.30 (m, 3H), 7.25 – 7.11 (m, 10H), 7.11 – 7.05 (m, 1H), 6.18 (t, *J* = 8.2 Hz, 1H), 3.63 (dd, *J* = 9.6, 8.4 Hz, 2H), 2.30 (d, *J* = 8.8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 141.6, 138.8, 138.5 (d, *J* = 10.2 Hz), 135.3 (d, *J* = 13.2 Hz), 133.2, 133.12, 133.1, 133.06, 131.9 (d, *J* = 12.6 Hz), 131.8 (d, *J* = 102.1 Hz), 129.8, 128.5, 128.2, 127.6 (d, *J* = 1.8 Hz), 127.5, 124.1 (d, *J* = 4.6 Hz), 29.0 (d, *J* = 1.7 Hz), 21.1 (d, *J* = 4.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{31}H_{32}OPS$ 483.1906; Found 483.1911.

S-(3,3-diphenylallyl) bis(3,5-dimethylphenyl)phosphinothioate (4i)



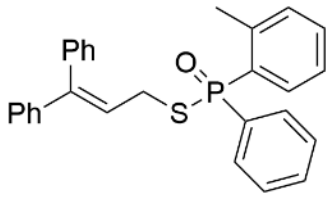
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **4i** (80.1 mg, 0.166 mmol, 83%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.30 (m, 8H), 7.24 – 7.21 (m, 2H), 7.11 (dd, *J* = 11.2, 3.9 Hz, 6H), 6.09 (t, *J* = 8.2 Hz, 1H), 3.52 (dd, *J* = 9.9, 8.3 Hz, 2H), 2.32 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 141.6, 138.7, 138.5 (d, *J* = 13.8 Hz), 134.2 (d, *J* = 3.0 Hz), 133.2 (d, *J* = 106.0 Hz), 129.8, 129.2, 129.1, 128.4, 128.2, 127.6 (d, *J* = 4.5 Hz), 127.5, 123.9 (d, *J* = 4.7 Hz), 29.1 (d, *J* = 1.7 Hz), 21.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 44.0. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{31}H_{32}OPS$ 483.1906; Found 483.1912.

S-(3,3-diphenylallyl) di([1,1'-biphenyl]-4-yl)phosphinothioate (4j)



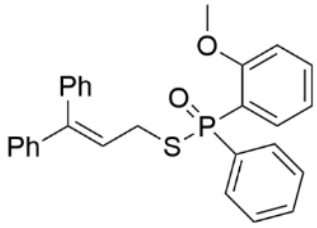
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4j** (111.1 mg, 0.192 mmol, 96%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 12.6, 8.0 Hz, 4H), 7.67 (dd, *J* = 8.0, 2.9 Hz, 4H), 7.60 – 7.55 (m, 4H), 7.45 (t, *J* = 7.7 Hz, 4H), 7.38 (dd, *J* = 10.7, 3.8 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.19 (dd, *J* = 4.3, 2.0 Hz, 3H), 7.12 (t, *J* = 7.1 Hz, 4H), 6.13 (t, *J* = 8.1 Hz, 1H), 3.65 – 3.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2 (d, *J* = 3.0 Hz), 145.1, 141.4, 139.8, 138.6, 132.1 (d, *J* = 10.9 Hz), 131.9 (d, *J* =108.8 Hz), 129.7, 129.0, 128.4, 128.3, 128.2, 127.7 (d, *J* = 6.9 Hz), 127.5 (d, *J* = 3.5 Hz), 127.4 (d, *J* = 3.8 Hz), 123.5 (d, *J* = 4.9 Hz), 29.3 (d, *J* = 1.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{39}H_{32}OPS$ 579.1906; Found 579.1904.

S-(3,3-diphenylallyl) phenyl(o-tolyl)phosphinothioate (4k)



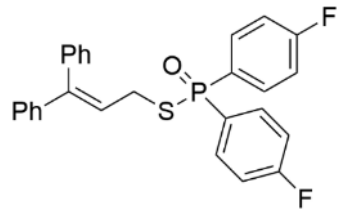
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4k** (76.7 mg, 0.174 mmol, 87%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.68 (m, 3H), 7.55 – 7.49 (m, 1H), 7.48 – 7.32 (m, 6H), 7.27 – 7.20 (m, 5H), 7.18 – 7.10 (m, 4H), 6.14 (t, *J* = 8.2 Hz, 1H), 3.65 – 3.52 (m, 2H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 142.6 (d, *J* = 9.7 Hz), 141.5, 138.7, 133.9 (d, *J* = 105.7 Hz), 133.0, 132.9, 132.5 (d, *J* = 2.8 Hz), 132.3 (d, *J* = 3.4 Hz), 132.1, 131.6 (d, *J* = 10.9 Hz), 131.1 (d, *J* = 104.6 Hz), 129.8, 128.8 (d, *J* = 13.2 Hz), 128.5, 128.2, 127.7 (d, *J* = 4.8 Hz), 127.6, 125.7 (d, *J* = 13.5 Hz), 123.6 (d, *J* = 5.1 Hz), 29.2 (d, *J* = 1.9 Hz), 21.8 (d, *J* = 4.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.3. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{26}OPS$ 441.1437; Found 441.1436.

S-(3,3-diphenylallyl) (2-methoxyphenyl)(phenyl)phosphinothioate (4l)



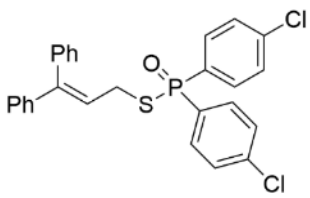
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4l** (77.6 mg, 0.170 mmol, 85%) as a colorless oil. ^{1}H NMR (400 MHz, CDCl3) δ 7.85 – 7.98 (m, 3H), 7.57 – 7.27 (m, 8H), 7.25 – 7.19 (m, 3H), 7.18 – 7.03 (m, 5H), 6.12 (t, *J* = 8.2 Hz, 1H), 3.71 (s, 3H), 3.60 (dd, *J* = 10.2, 8.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2 (d, *J* = 4.2 Hz), 144.5, 141.6, 138.7, 134.4 (d, *J* = 1.6 Hz), 133.8, 133.7, 131.7 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 11.2 Hz), 129.2 (d, *J* = 143.6 Hz), 128.2, 128.1, 128.09 (d, *J* = 2.0 Hz), 127.5, 124.3 (d, *J* = 5.1 Hz), 122.3, 121.7 (d, *J* = 106.9 Hz), 120.9 (d, *J* = 12.4 Hz), 111.5(d, *J* = 7.3 Hz), 55.5, 28.5 (d, *J* = 2.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{28}H_{26}O_2PS$ 457.1386; Found 457.1389.

S-(3,3-diphenylallyl) bis(4-fluorophenyl)phosphinothioate (4m)



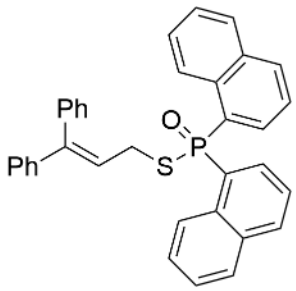
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4m** (88.8 mg, 0.192 mmol, 96%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.74 (m, 4H), 7.38 – 7.07 (m, 14H), 6.09 (t, *J* = 8.1 Hz, 1H), 3.58 – 3.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4 (d, *J* = 254.6 Hz), 165.3 (d, *J* = 254.6 Hz).145.5, 141.2, 138.4, 134.14 (d, *J* =12.3 Hz), 134.05 (d, *J* = 12.1 Hz), 129.7, 129.60, 129.56, 128.4 (d, *J* = 23.1 Hz), 127.8 (d, *J* = 12.5 Hz), 127.5, 122.9 (d, *J* = 5.4 Hz), 116.3 (d, *J* = 21.5 Hz), 116.2 (d, *J* = 21.6 Hz)., 29.4 (d, *J* = 2.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.60, -105.61. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{27}H_{22}OPS$ 463.1092; Found 463.1093.

S-(3,3-diphenylallyl) bis(4-chlorophenyl)phosphinothioate (4n)



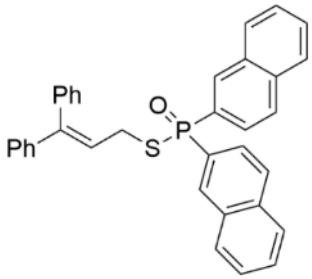
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4n** (94.1 mg, 0.190 mmol, 95%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 12.5, 8.4 Hz, 4H), 7.34 (dd, *J* = 8.5, 2.7 Hz, 4H), 7.27 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.18 – 7.16 (m, 3H), 7.04 – 7.01 (m, 4H), 5.99 (t, *J* = 8.1 Hz, 1H), 3.46 (dd, *J* = 10.1, 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 141.3, 139.4 (d, *J* = 3.6 Hz), 138.5, 132.9 (d, *J* = 11.5 Hz), 131.5 (d, *J* = 109.5 Hz), 129.7, 129.4, 129.2, 128.5, 128.3, 127.9, 127.8, 127.5, 122.9 (d, *J* = 3.3 Hz), 29.5 (d, *J* = 1.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.9. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{22}Cl_2OPS$ 495.0501; Found 495.0498

S-(3,3-diphenylallyl) naphthalen-1-yl(naphthalen-2-yl)phosphinothioate (4o)



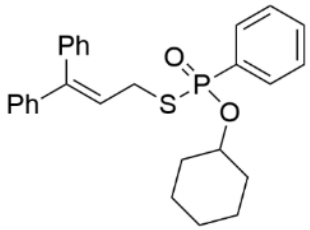
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4o** (94.8 mg, 0.180 mmol, 90%) as a white solid. mp: 170.0-170.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 – 8.81 (m, 2H), 8.05 – 7.85 (m, 6H), 7.56 – 7.49 (m, 4H), 7.45 – 7.38 (m, 2H), 7.33 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.22 (dd, *J* = 6.6, 3.6 Hz, 3H), 7.15 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.12 – 7.08 (m, 2H), 6.18 (t, *J* = 8.2 Hz, 1H), 3.76 (dd, *J* = 9.6, 8.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 141.5, 138.7, 134.2 (d, *J* = 10.0 Hz), 133.9 (d, *J* = 3.1 Hz), 133.5, 133.4, 130.0, 129.8, 129.0, 128.5, 127.7 (d, *J* = 4.6 Hz), 127.5 (d, *J* = 2.4 Hz), 127.3 (d, *J* = 5.1 Hz), 126.7, 124.6 (d, *J* = 15.5 Hz), 123.6 (d, *J* =5.2 Hz), 29.9 (d, *J* = 2.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.0. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{35}H_{28}OPS$ 527.1593; Found 527.1597.

S-(3,3-diphenylallyl) di(naphthalen-2-yl)phosphinothioate (4p)



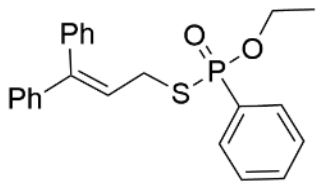
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4p** (97.0 mg, 0.184 mmol, 92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 14.9 Hz, 2H), 7.94 – 7.81 (m, 8H), 7.63 – 7.52 (m, 4H), 7.29 – 7.21 (m, 3H), 7.20 – 7.12 (m, 3H), 7.09 – 7.01 (m, 4H), 6.11 (t, *J* = 8.1 Hz, 1H), 3.61 (dd, *J* = 10.2, 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 141.4, 138.5, 135.0 (d, *J* = 2.5 Hz), 133.8 (d, *J* = 9.7 Hz), 132.6 (d, *J* = 14.3 Hz), 131.0, 129.9, 129.7, 129.2, 128.8, 128.7, 128.6, 128.4, 128.2, 127.7 (d, *J* = 6.4 Hz), 127.6 (d, *J* = 79.5 Hz), 127.5, 126.3 (d, *J* = 11.7 Hz), 123.6 (d, *J* = 4.9 Hz), 29.4 (d, *J* = 1.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.9. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{35}H_{28}OPS$ 527.1593; Found 527.1597.

O-cyclohexyl S-(3,3-diphenylallyl) phenylphosphonothioate (4q)



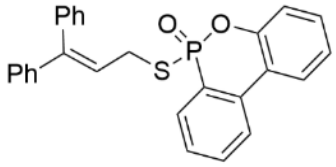
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4q** (62.8 mg, 0.140 mmol, 70%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 2H), 7.53 – 7.50 (m, 1H), 7.45 – 7.41 (m, 2H), 7.37 – 7.29 (m, 3H), 7.21 (dd, *J* = 6.5, 3.7 Hz, 3H), 7.15 – 7.06 (m, 4H), 6.01 (t, *J* = 8.1 Hz, 1H), 4.69 – 4.60 (m, 1H), 3.51 – 3.37 (m, 2H), 1.92 (d, *J* = 12.4 Hz, 2H), 1.79 – 1.64 (m, 3H), 1.61 – 1.36 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 141.5, 138.6, 133.5 (d, *J* = 150.8 Hz), 132.4 (d, *J* = 3.2 Hz), 131.2 (d, *J* = 10.9 Hz), 129.7, 128.6, 128.4 (d, *J* = 7.2 Hz), 128.2, 127.7 (d, *J* = 5.7 Hz), 127.5, 123.5 (d, *J* = 5.6 Hz), 76.5 (d, *J* = 7.2 Hz), 34.0 (d, *J* = 3.0 Hz), 33.7 (d, *J* = 4.5 Hz), 30.3 (d, *J* = 2.4 Hz), 25.2, 23.7 (d, *J* = 7.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.2. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{27}H_{30}O_2PS$ 449.1699; Found 449.1701.

S-(3,3-diphenylallyl) O-ethyl phenylphosphonothioate (4r)



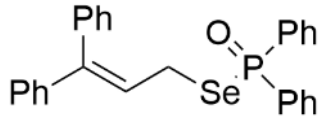
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **4r** (64.7 mg, 0.164 mmol, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 13.8, 8.1 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.39 – 7.30 (m, 3H), 7.27 – 7.20 (m, 3H), 7.17 – 7.06 (m, 4H), 6.04 (t, *J* = 8.0 Hz, 1H), 4.33 – 4.15 (m, 2H), 3.47 – 3.40 (m, 2H), 1.35 (dd, *J* = 7.7, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 141.5, 138.6, 132.8 (d, *J* = 150.5 Hz), 132.6 (d, *J* = 3.2 Hz), 131.3 (d, *J* = 11.0 Hz), 129.8, 128.7 (d, *J* =14.8 Hz), 128.4 (d, *J* = 23.5 Hz), 127.8 (d, *J* = 5.7 Hz), 127.6, 123.5 (d, *J* = 5.4 Hz), 62.3 (d, *J* = 6.9 Hz), 30.2 (d, *J* = 2.5 Hz), 16.5 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.9. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{23}H_{24}O_2PS$ 395.1229; Found 395.1226.

6-((3,3-diphenylallyl)thio)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (4s)



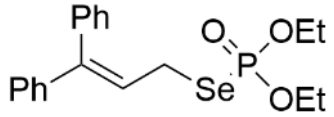
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **4s** (79.3 mg, 0.180 mmol, 90%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.86 (m, 3H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.45 – 7.50 (m, 1H), 7.37 – 7.22 (m, 9H), 7.19 – 7.10 (m, 3H), 7.07 (dd, *J* = 6.5, 3.0 Hz, 1H), 6.13 (t, *J* = 8.1 Hz, 1H), 3.66 – 3.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6 (d, *J* = 9.5 Hz), 145.5, 141.4, 138.4, 136.2 (d, *J* = 7.4 Hz), 133.9 (d, *J* = 2.5 Hz), 130.8, 130.6 (d, *J* = 11.1 Hz), 129.7, 128.7 (d, *J* = 15.0 Hz), 128.4 (d, *J* =20.8 Hz), 127.8 (d, *J* = 14.0 Hz), 127.6, 125.8 (d, *J* = 135.5 Hz), 125.2 (d, *J* =1.0 Hz), 125.0, 123.9 (d, *J* = 11.2 Hz), 123.1 (d, *J* = 5.2 Hz), 122.3 (d, *J* = 12.1 Hz), 120.6 (d, *J* = 6.7 Hz), 30.1 (d, *J* = 3.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.7. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{27}H_{22}O_2PS$ 441.1073; Found 441.1075.

Se-(3,3-diphenylallyl) diphenylphosphinotselenoate (5a)



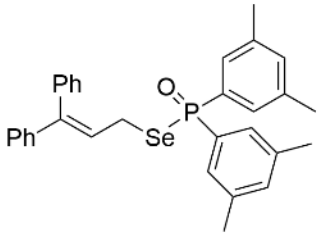
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **5a** (90.1 mg, 0.190 mmol, 95%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 4H), 7.46 – 7.33 (m, 6H), 7.29 – 7.23 (m, 3H), 7.13 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.07 – 6.98 (m, 4H), 6.09 (t, *J* = 8.5 Hz, 1H), 3.50 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 141.4, 138.6, 134.4 (d, *J* = 97.7 Hz), 132.3 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 10.9 Hz), 129.7, 128.8, 128.7, 128.5, 128.2, 127.6 (d, *J* = 4.2 Hz), 127.4, 124.0 (d, *J* = 4.0 Hz), 24.9 (d, *J* = 2.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.1. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{24}OPSe$ 475.0725; Found 475.0728.

Se-(3,3-diphenylallyl) O,O-diethyl phosphoroselenoate (5b)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **6a** (74.8 mg, 0.182 mmol, 91%) as a faint yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 3H), 7.28 – 7.20 (m, 7H), 6.33 (t, *J* = 8.5 Hz, 1H), 4.20 – 4.04 (m, 4H), 3.59 (dd, *J* = 11.4, 8.5 Hz, 2H), 1.35 – 1.29 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 141.5, 138.7, 129.8, 128.6, 128.3, 127.8, 127.7, 127.5, 123.9 (d, *J* = 5.5 Hz), 63.5 (d, *J* = 5.5 Hz), 25.7 (d, *J* = 4.4 Hz), 16.1 (d, *J* = 7.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.6. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{24}O_3PSe$ 411.0632; Found 411.0627.

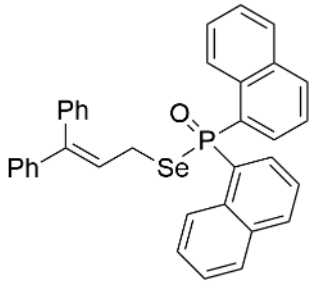
Se-(3,3-diphenylallyl) bis(3,5-dimethylphenyl)phosphinoselenoate (5c)



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **6c** (69.0 mg, 0.130 mmol, 65%) as a faint yellow oil.

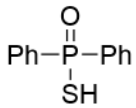
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 12.5 Hz, 4H), 7.30 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.27 – 7.26 (m, 3H), 7.21 (dd, *J* = 6.9, 3.0 Hz, 2H), 7.12 (s, 2H), 7.07 (dd, *J* = 6.4, 3.2 Hz, 2H), 6.26 (t, *J* = 6.9 Hz, 1H), 4.61 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 141.6, 138.6, 138.3 (d, J = 13.8 Hz), 134.0 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 135.3 Hz), 129.7, 129.4, 129.3, 128.4, 128.3, 128.0, 127.8, 123.9 (d, *J* = 7.1 Hz), 29.8, 21.4 (d, *J* = 0.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{31}H_{32}OPSe$ 531.1351; Found 531.1349.

Se-(3,3-diphenylallyl) naphthalen-1-yl(naphthalen-2-yl)phosphinoselenoate (5d)



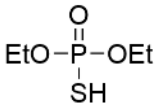
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 1:1) gave product **6d** (91.9 mg, 0.160 mmol, 80%) as a white solid. mp: 153.0-154.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 – 8.76 (m, 2H), 8.01 (dd, *J* = 18.2, 7.4 Hz, 4H), 7.87 (d, *J* = 6.7 Hz, 2H), 7.49 (p, *J* = 6.1 Hz, 4H), 7.40 (td, *J* = 7.5, 2.3 Hz, 2H), 7.33 (d, *J* = 6.1 Hz, 3H), 7.26 – 7.19 (m, 4H), 7.17 – 7.14 (m, 2H), 7.10 (d, *J* = 3.5 Hz, 1H), 6.26 (t, *J* = 8.6 Hz, 1H), 3.77 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.84, 141.47, 138.7, 134.2, 134.1, 133.8 (d, *J* = 3.2 Hz), 133.4, 133.2, 133.1, 133.0, 130.8, 129.8, 129.0 (d, *J* = 1.2 Hz), 128.5, 128.3 (d, *J* = 3.1 Hz), 128.2, 127.8, 127.7, 127.6 (d, *J* = 3.8 Hz), 127.5, 127.4, 127.2 (d, *J* = 5.2 Hz), 126.7, 124.5 (d, *J* = 15.6 Hz), 124.1 (d, *J* = 4.1 Hz), 26.0 (d, *J* = 2.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.6. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{35}H_{28}OPSe$ 575.1038; Found 575.1041.

diphenylphosphinothioic S-acid (6a)



Following the general method,[3] without further purification, diphenylphosphinothioic *S*-acid (**6a**) was obtained as a yellow oil. ^{31}P NMR (162 MHz, $CDCl_3$) δ 71.2.

O,O-diethyl S-hydrogen phosphorothioate (6b)



Following the general method,[3] without further purification, *O*,*O*-diethyl *S*-hydrogen phosphorothioate (**6b**) was obtained as a yellow oil. ^{31}P NMR (162 MHz, $CDCl_3$) δ 61.2.

5. References

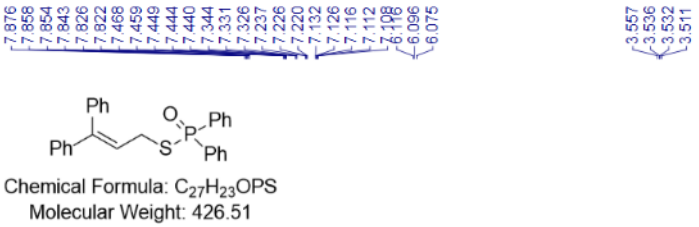
(1) Xiong, B.; Shi, C.; Ren, Y.; Xu, W.; Liu, Y.; Zhu, L.; Cao, F.; Tang, K.-W.; Yin, S.-F. Zn-Catalyzed Dehydroxylative Phosphorylation of Allylic Alcohols with P(III)-Nucleophiles. *J. Org. Chem.* **2024**, *89*, 3033-3048.

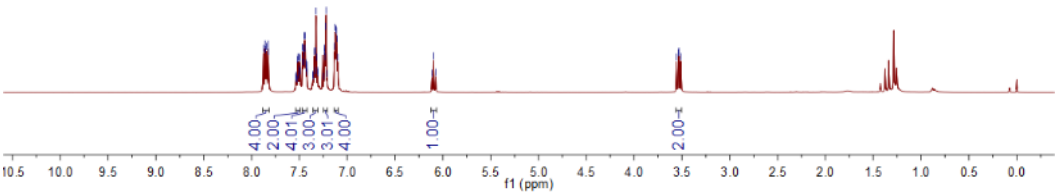
(2) Wang, X.-L.; Chen, J.-X.; Jia, X.-S.; Yin, L. Synthesis of α,β-Unsaturated Phosphine Sulfides. *Synthesis* **2019**, *52*, 141-149.

(3) Shi, S.; Chen, J.; Zhuo, S.; Wu, Z. a.; Fang, M.; Tang, G.; Zhao, Y. Iodide-Catalyzed Phosphorothiolation of Heteroarenes Using P(O)H Compounds and Elemental Sulfur. *Adv. Synth. Catal.* **2019**, *361*, 3210-3216. Xu, J.; Zhang, L.; Li, X.; Gao, Y.; Tang, G.; Zhao, Y. Phosphorothiolation of Aryl Boronic Acids Using P(O)H Compounds and Elemental Sulfur. *Org. Lett.* **2016**, *18*, 1266-1269.

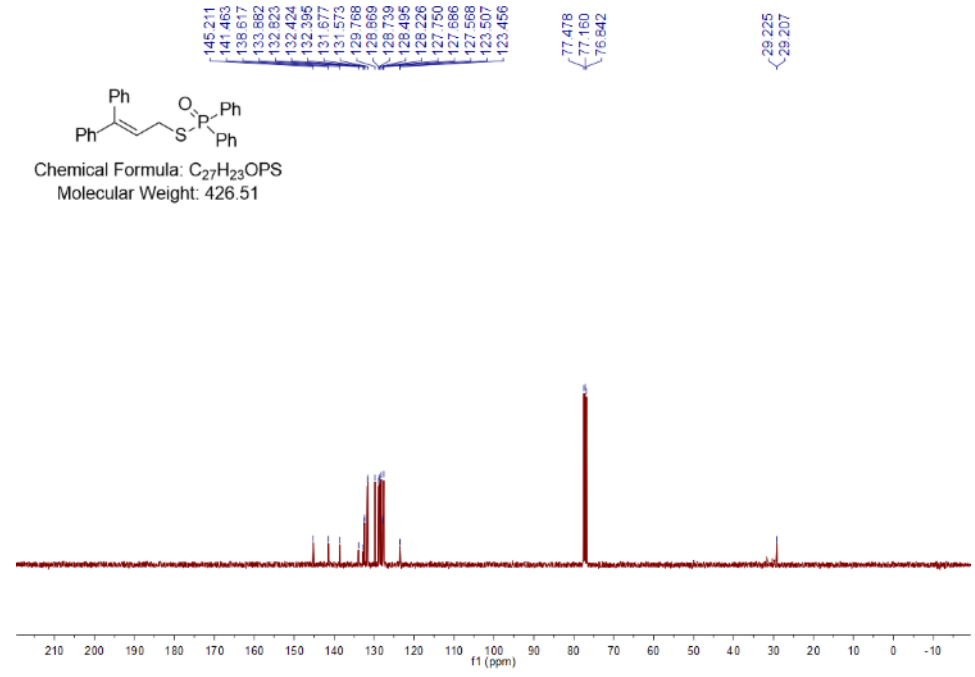
6. Copies of ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra of isolated compounds

S-(3,3-diphenylallyl) diphenylphosphinothioate (3a)

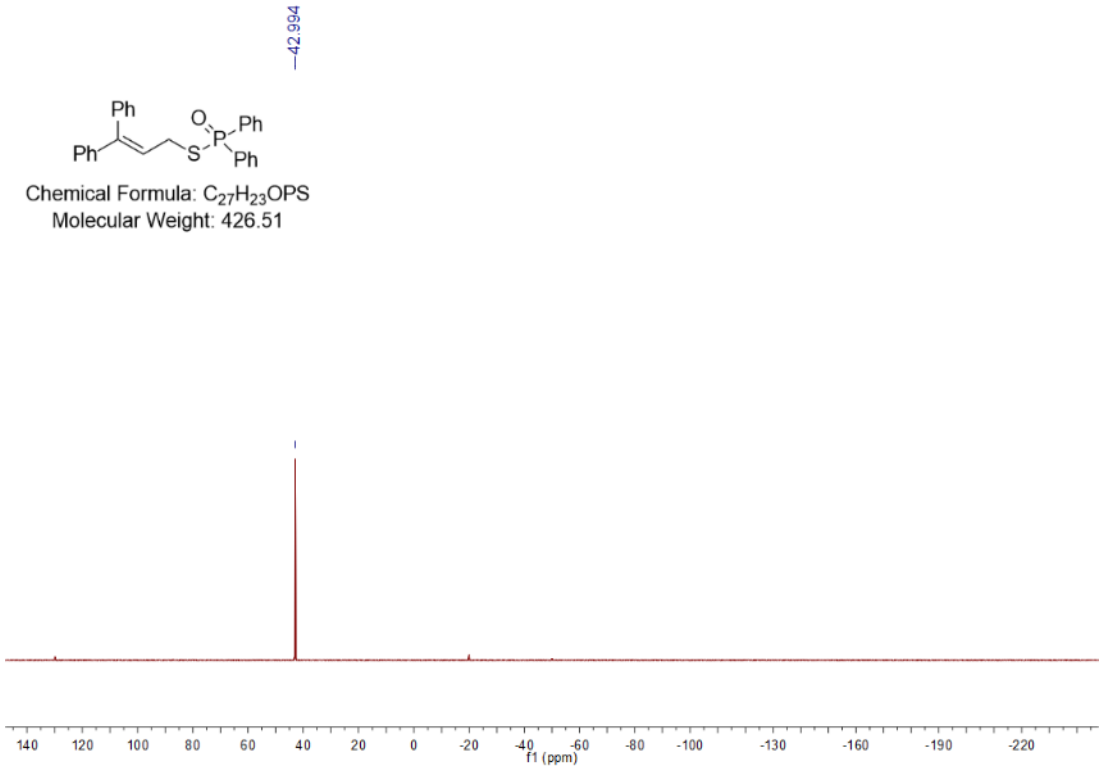




^{1}H NMR spectrum, 400 MHz, $CDCl_3$

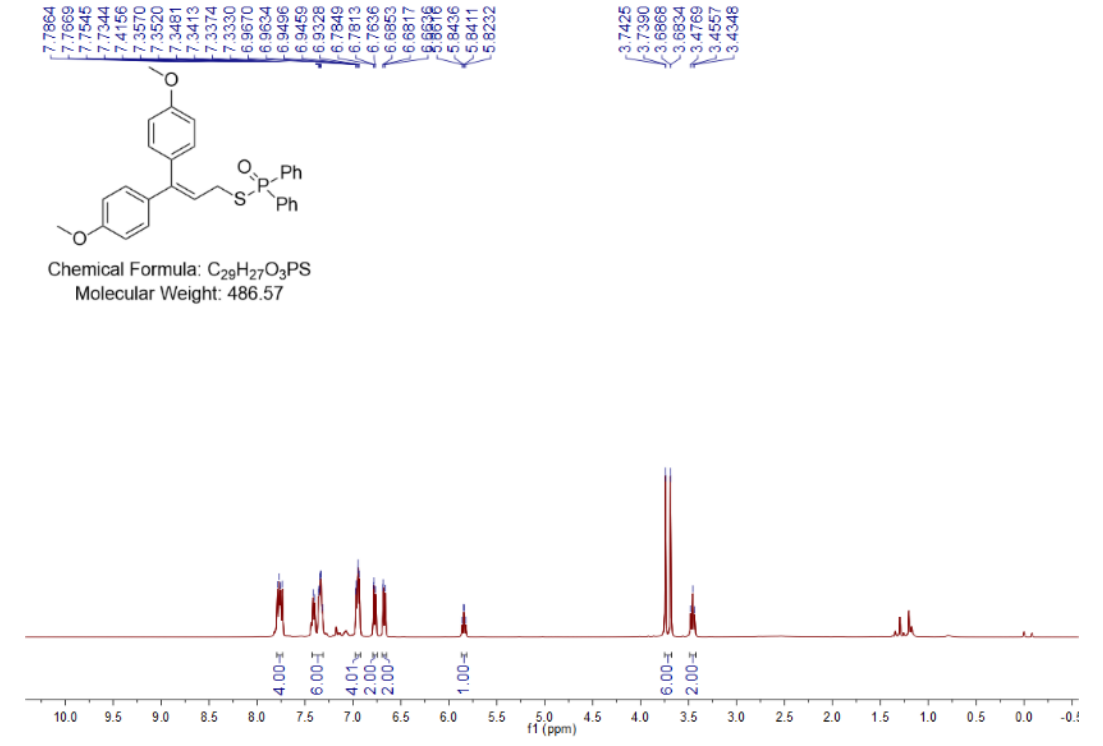


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

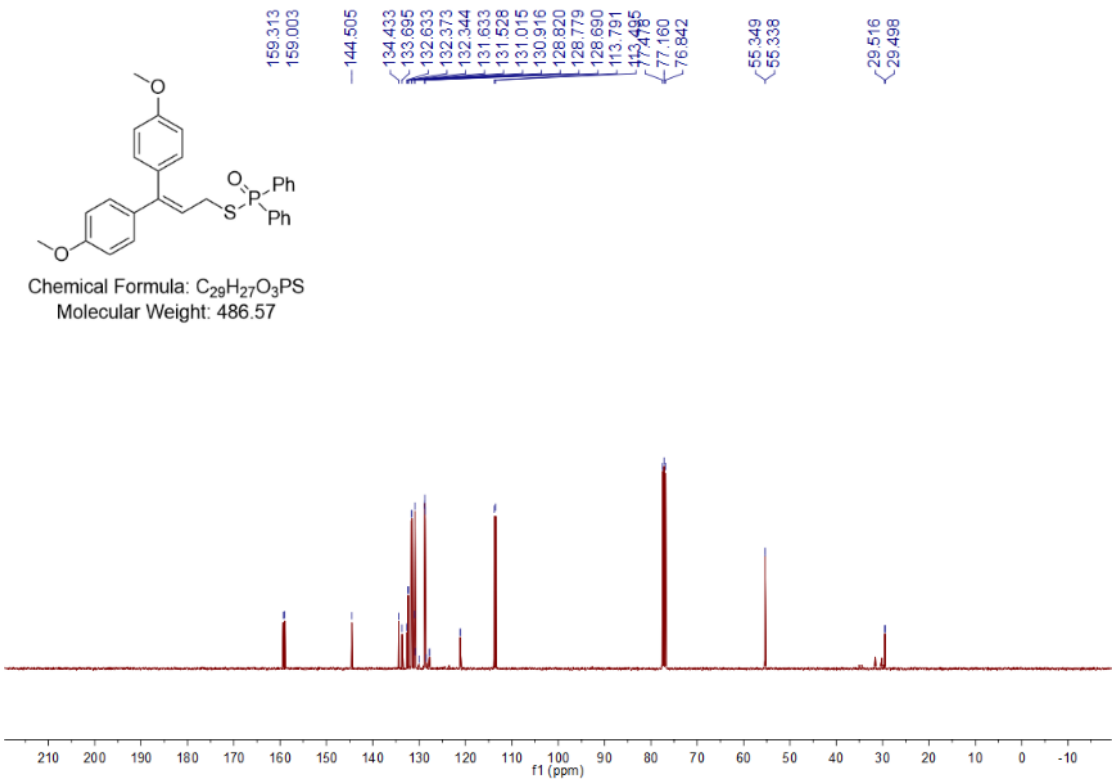


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

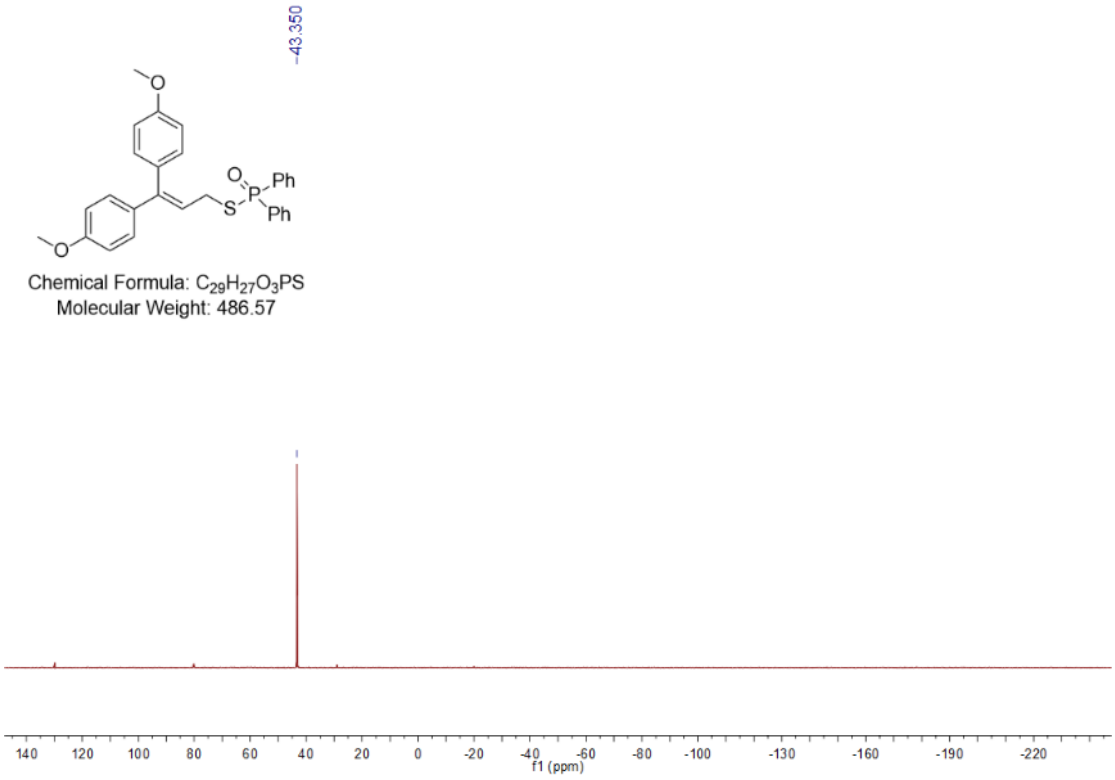
S-(3,3-bis(4-methoxyphenyl)allyl) diphenylphosphinothioate (3b)



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

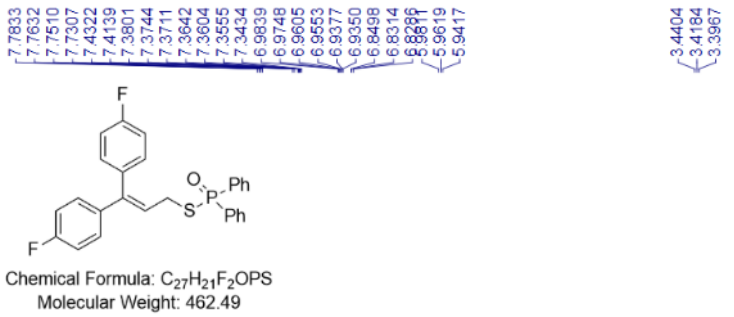


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

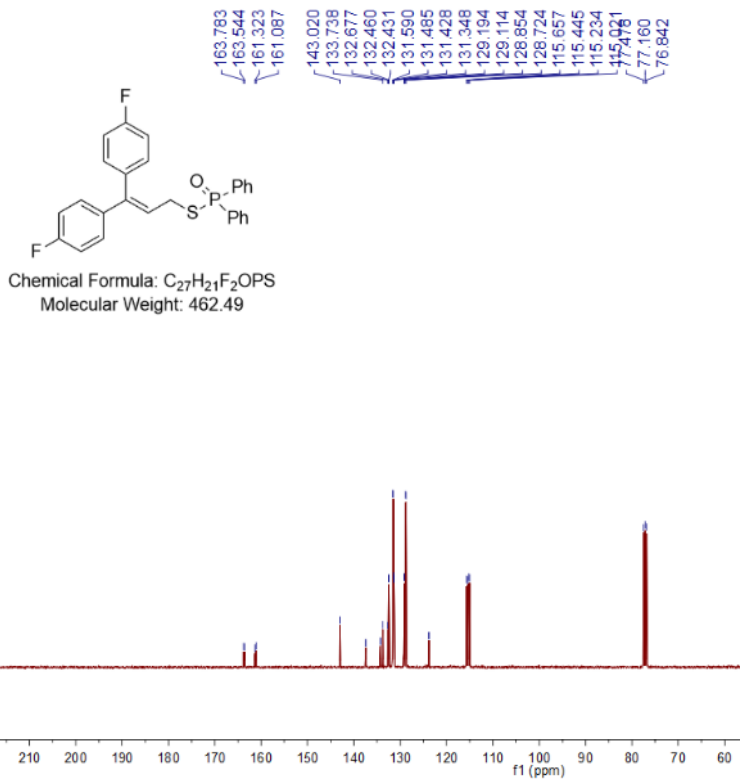


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

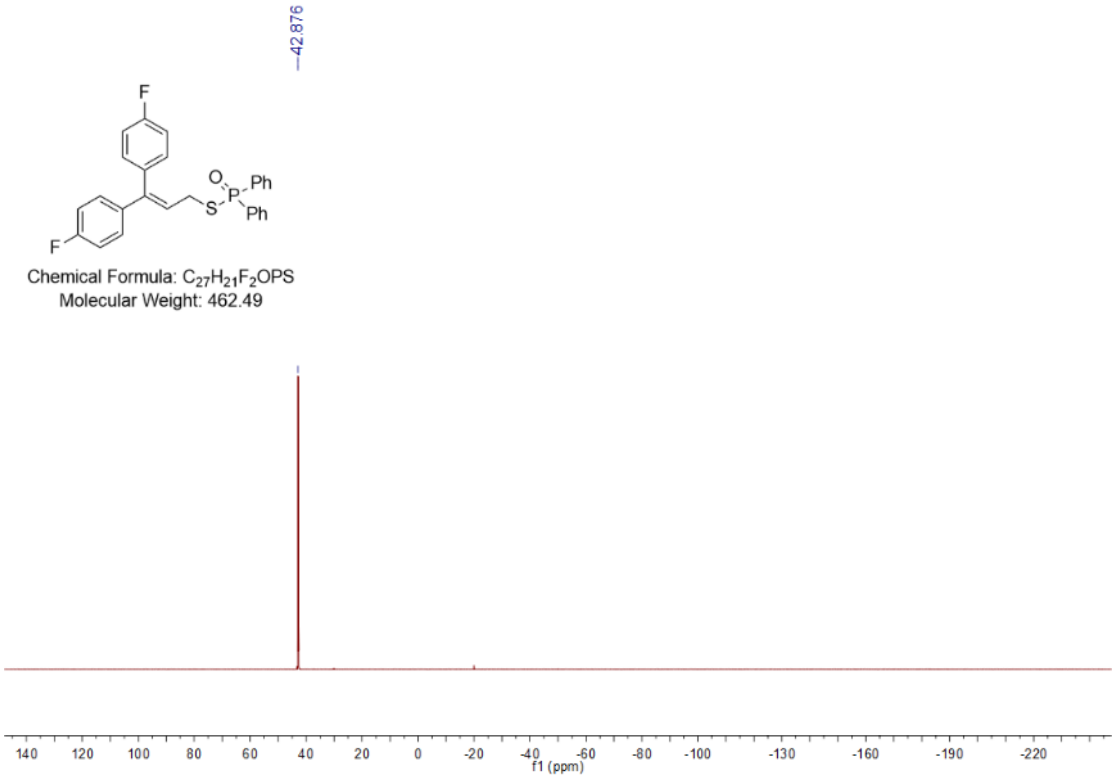
S-(3,3-bis(4-fluorophenyl)allyl) diphenylphosphinothioate (3c)



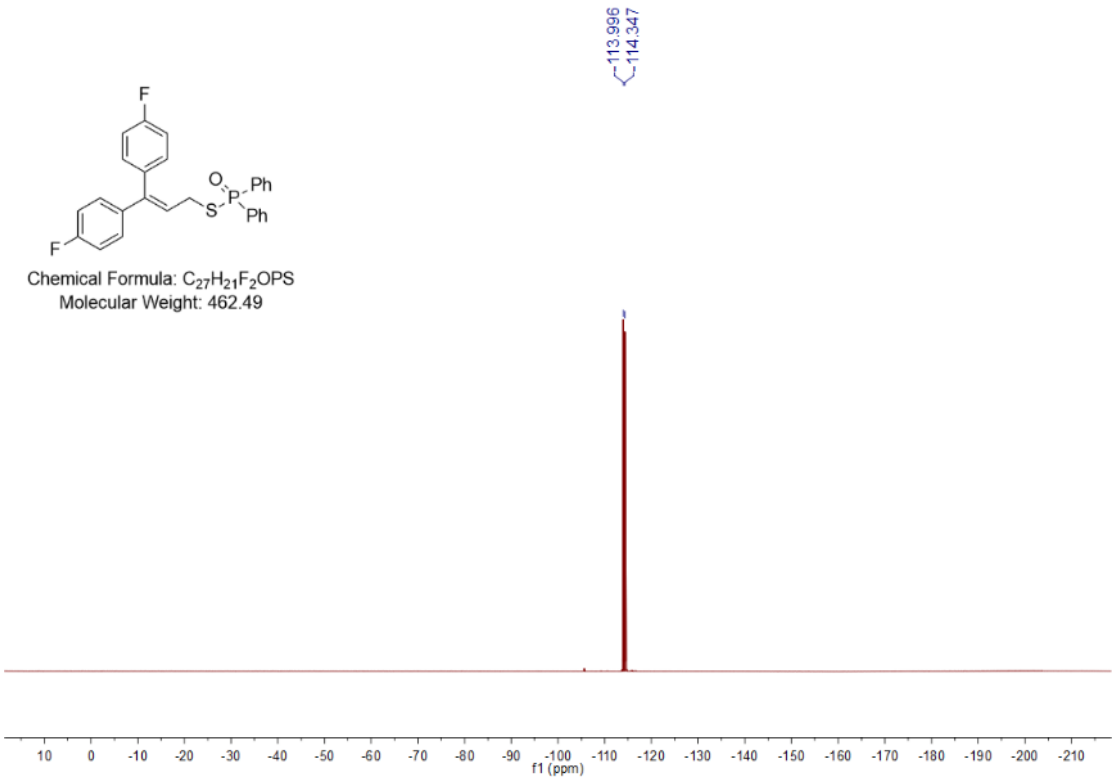
^{1}H NMR spectrum, 400 MHz, $CDCl_3$



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

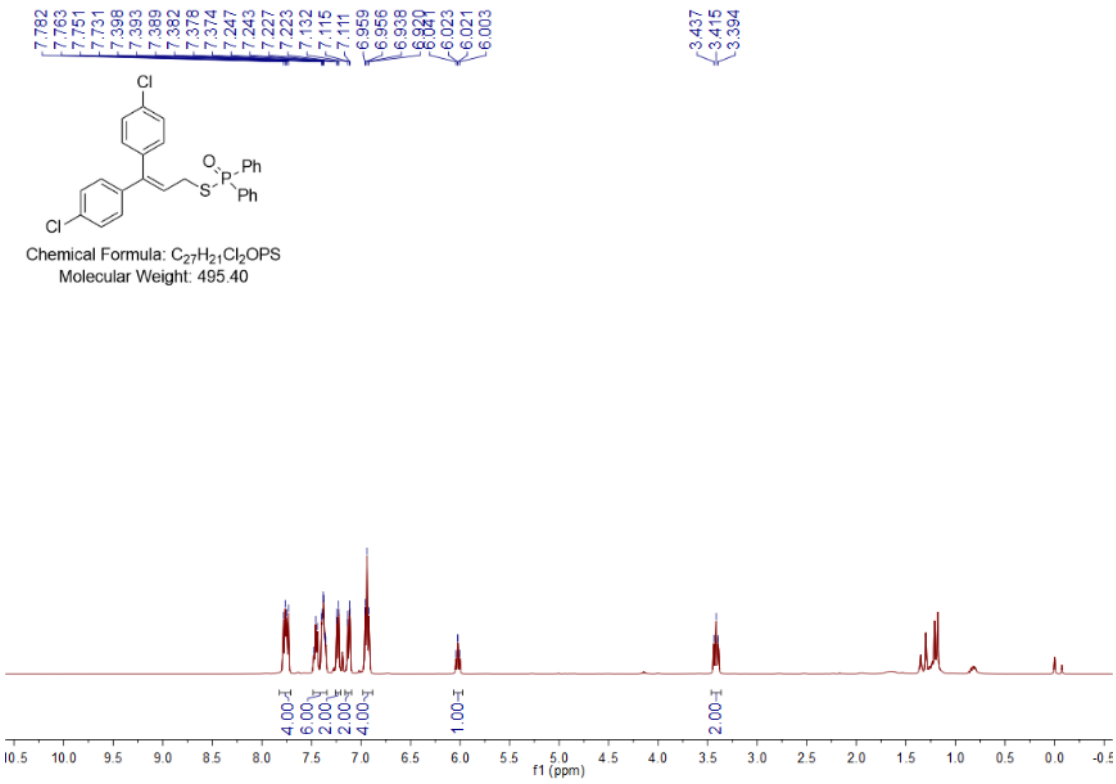


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

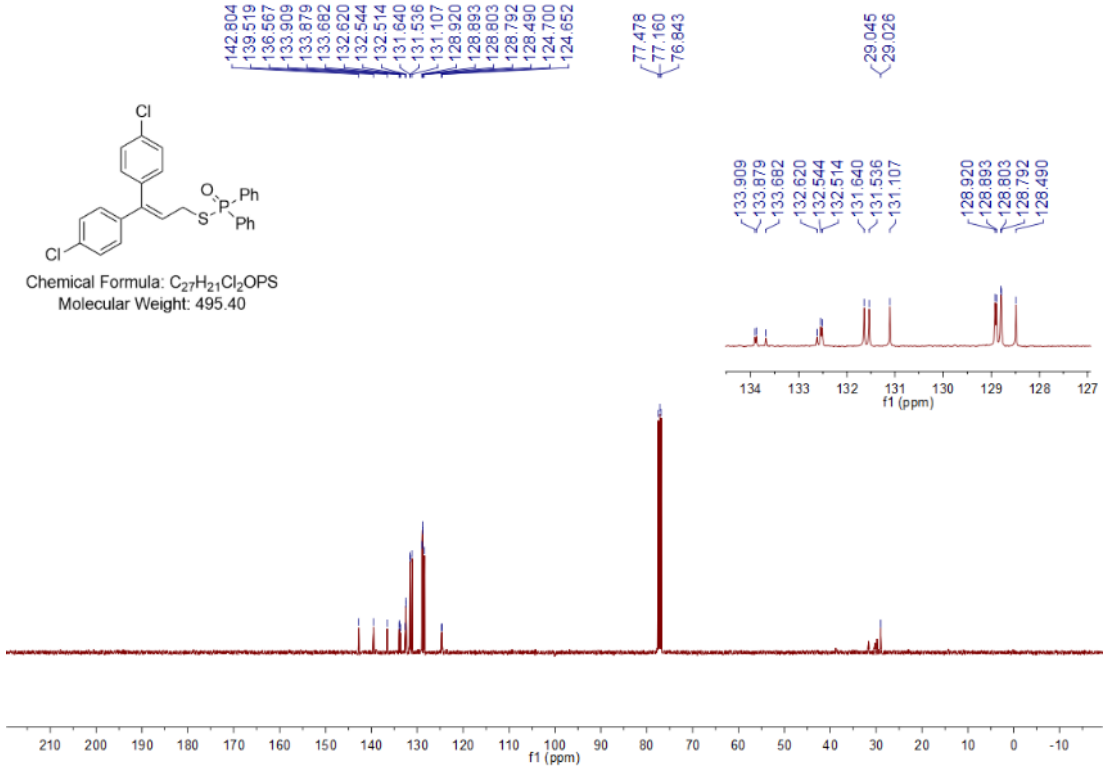


^{19}F NMR spectrum, 376 MHz, $CDCl_3$

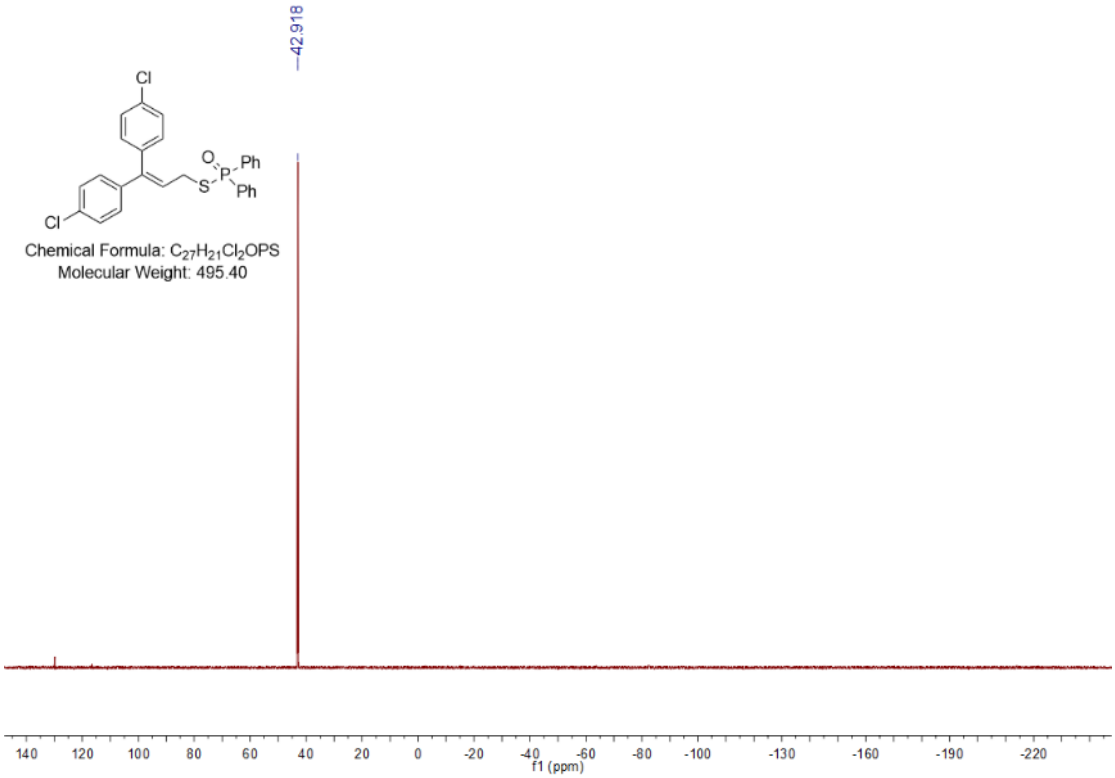
S-(3,3-bis(4-chlorophenyl)allyl) diphenylphosphinothioate (3d)



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

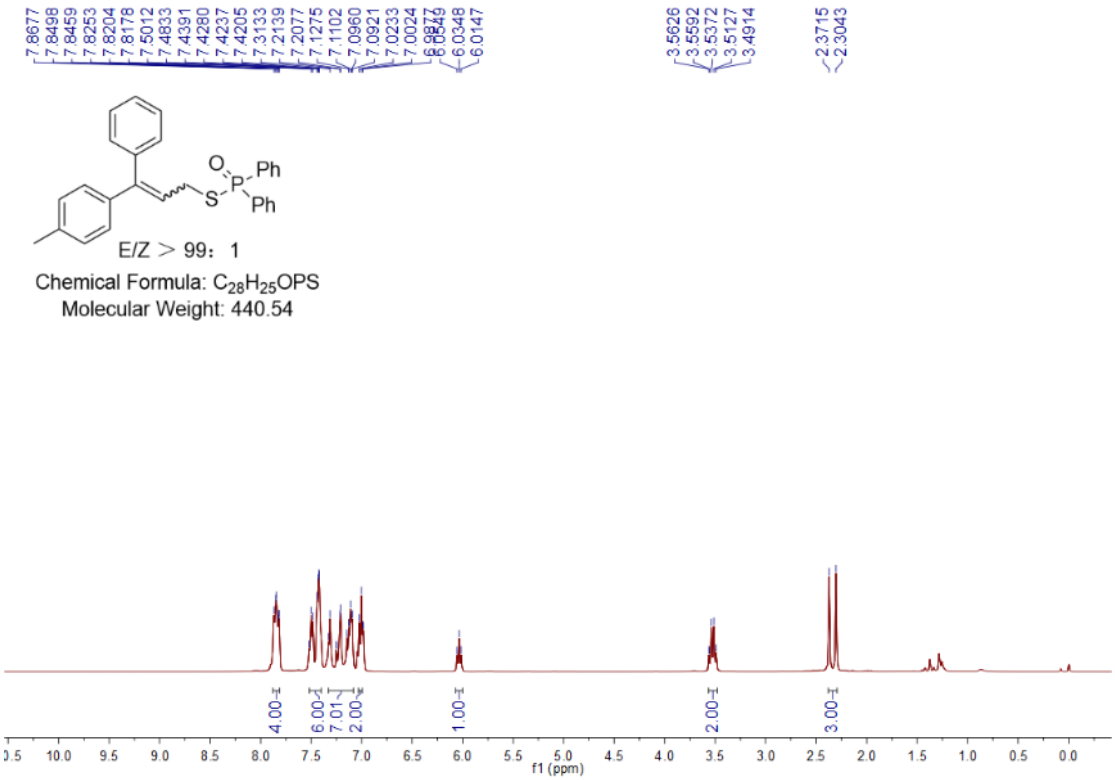


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

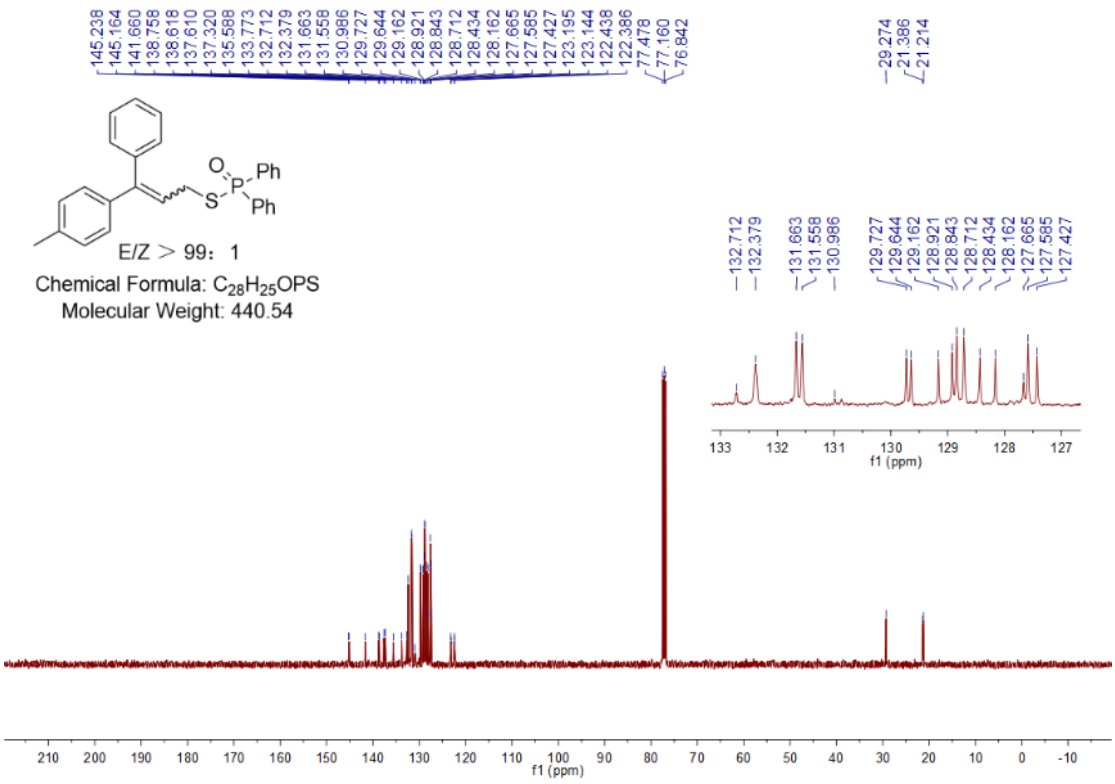


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

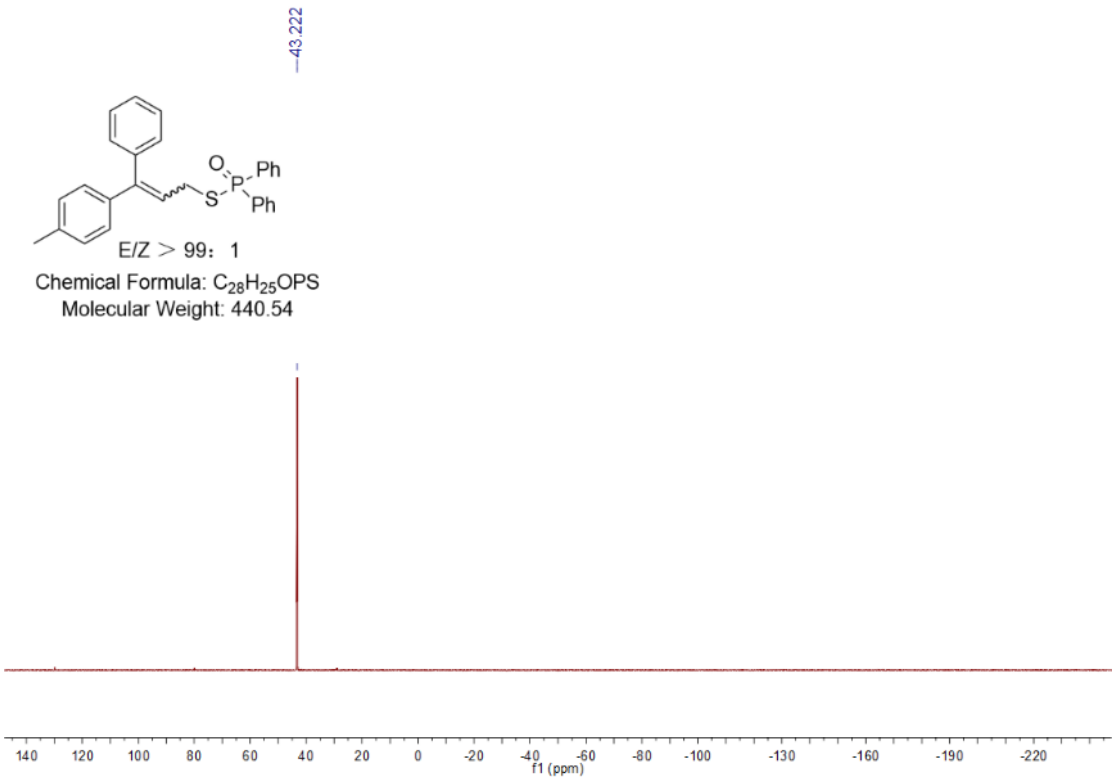
S-(3-phenyl-3-(p-tolyl)allyl) diphenylphosphinothioate (3e)



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

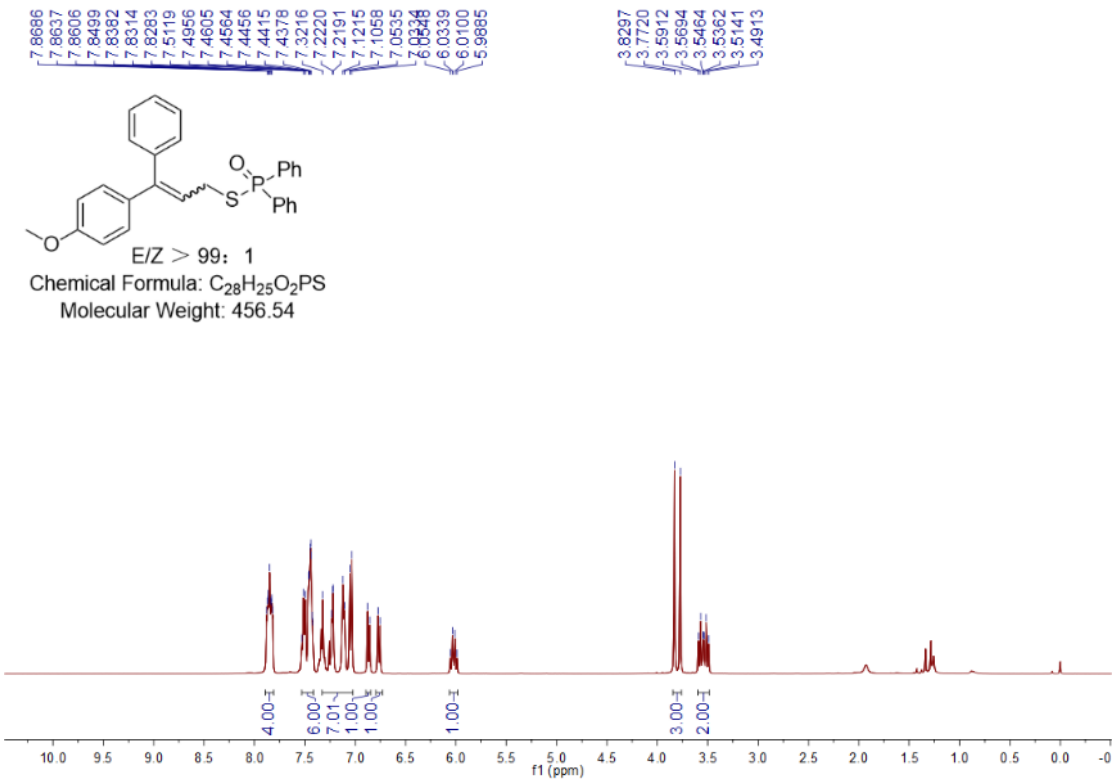


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

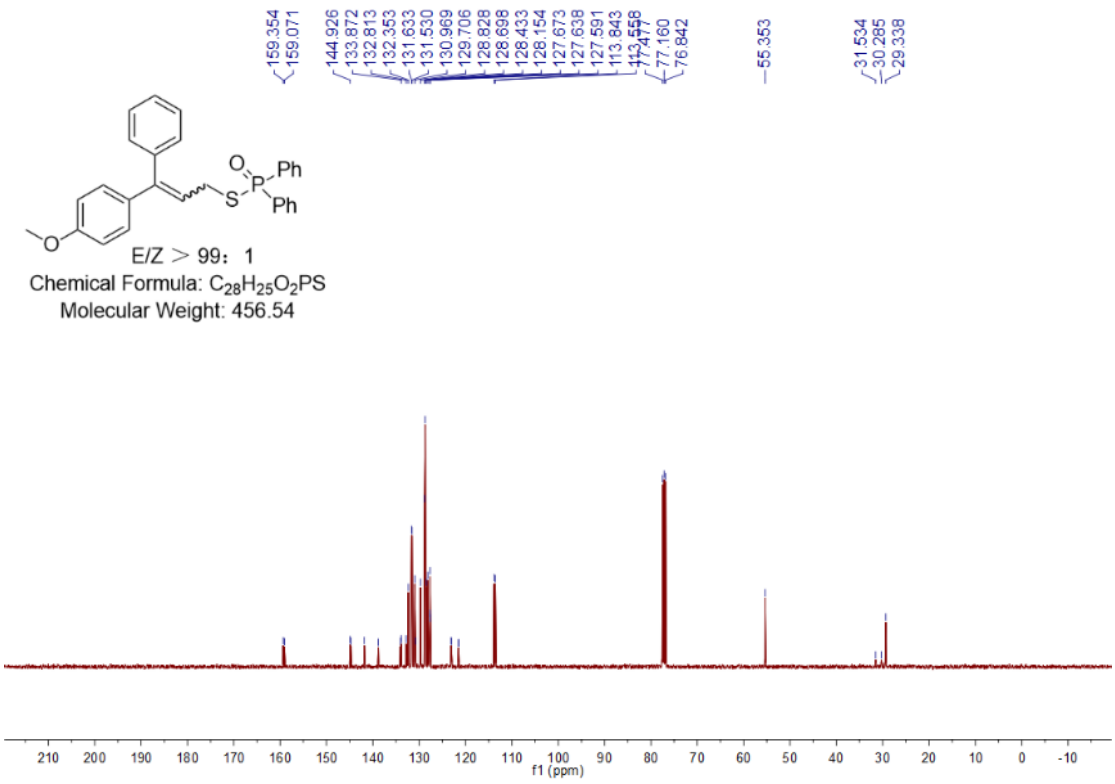


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

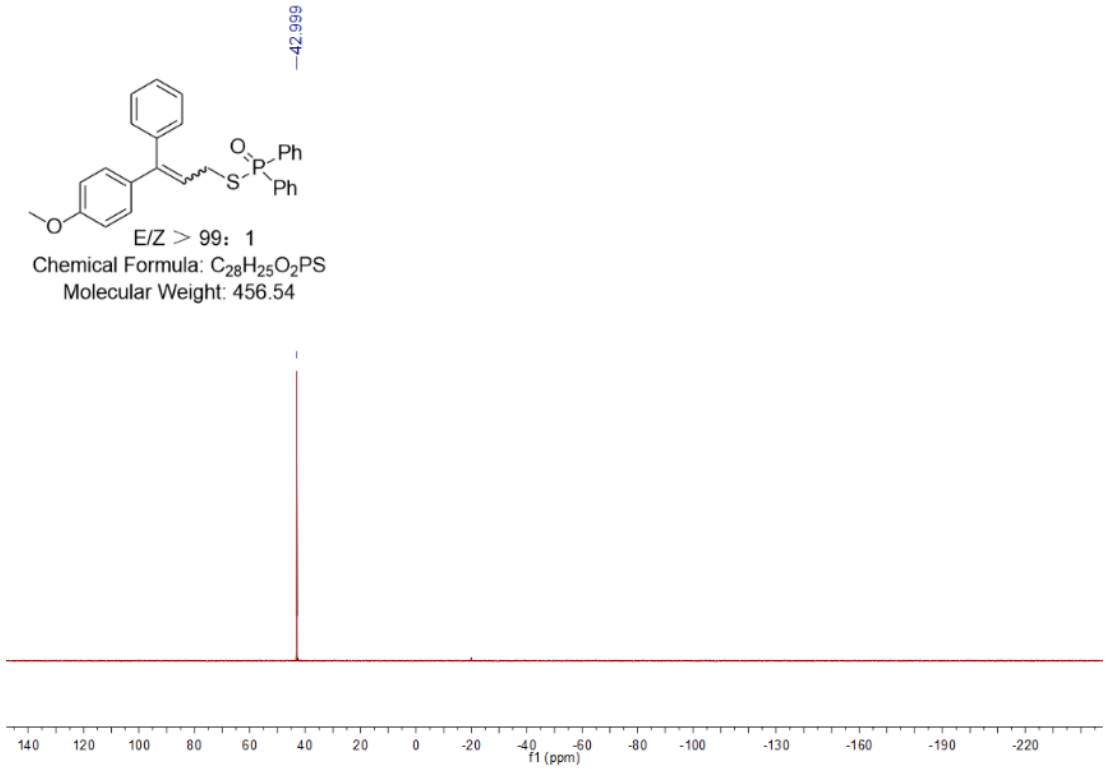
S-(3-(4-methoxyphenyl)-3-phenylallyl) diphenylphosphinothioate (3f)



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

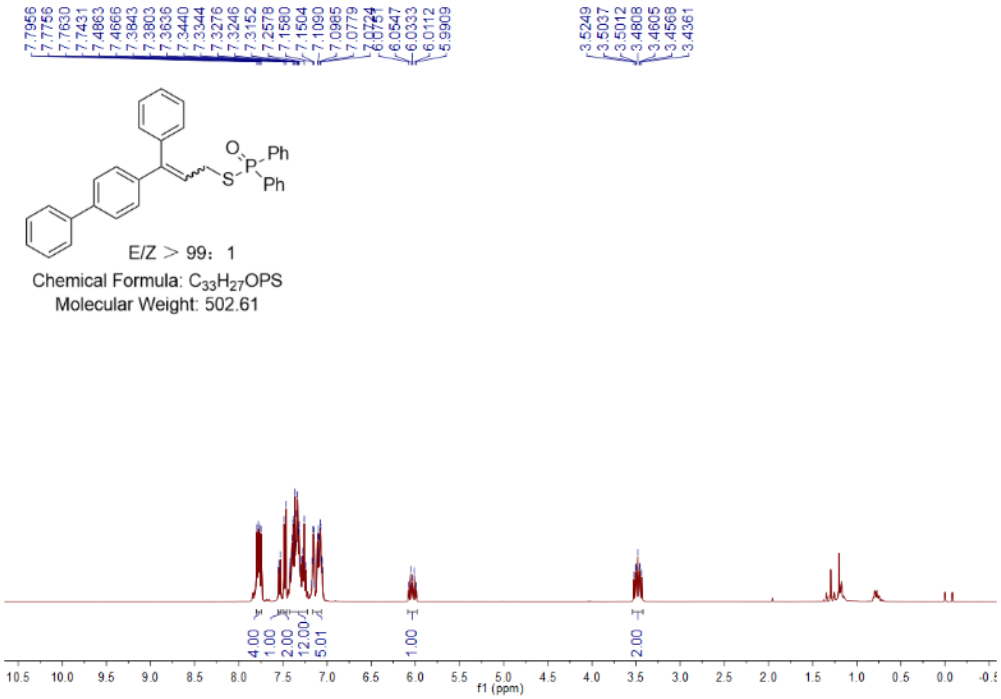


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

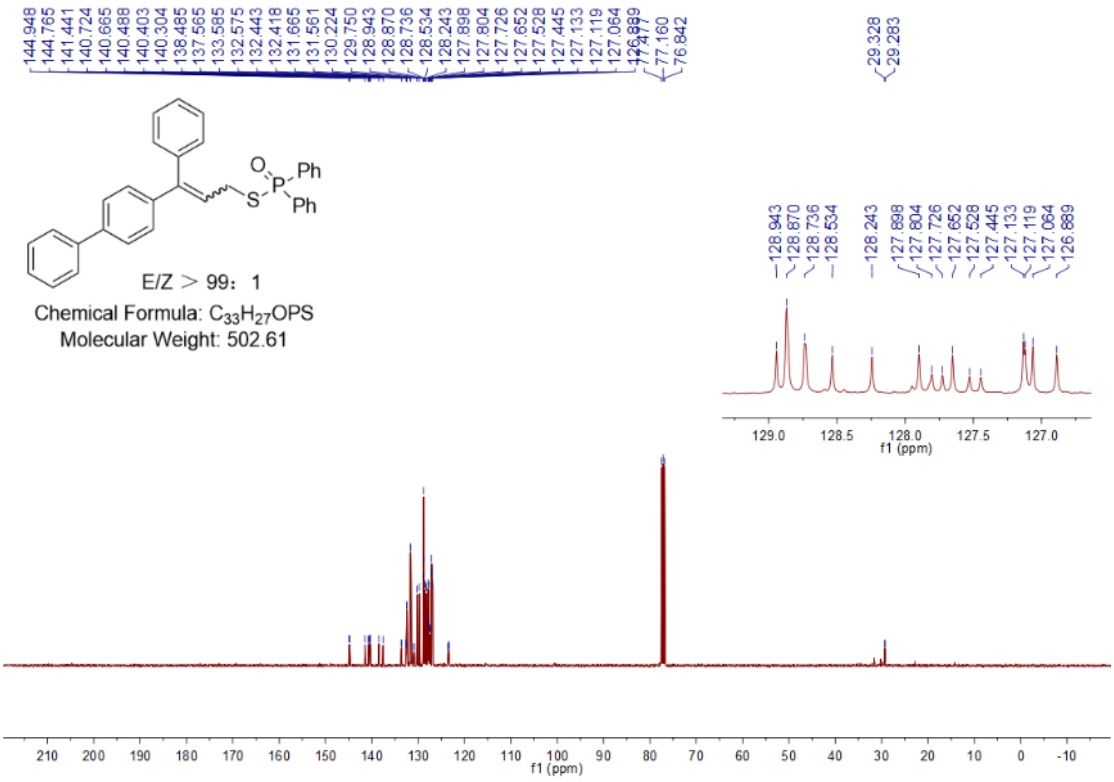


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

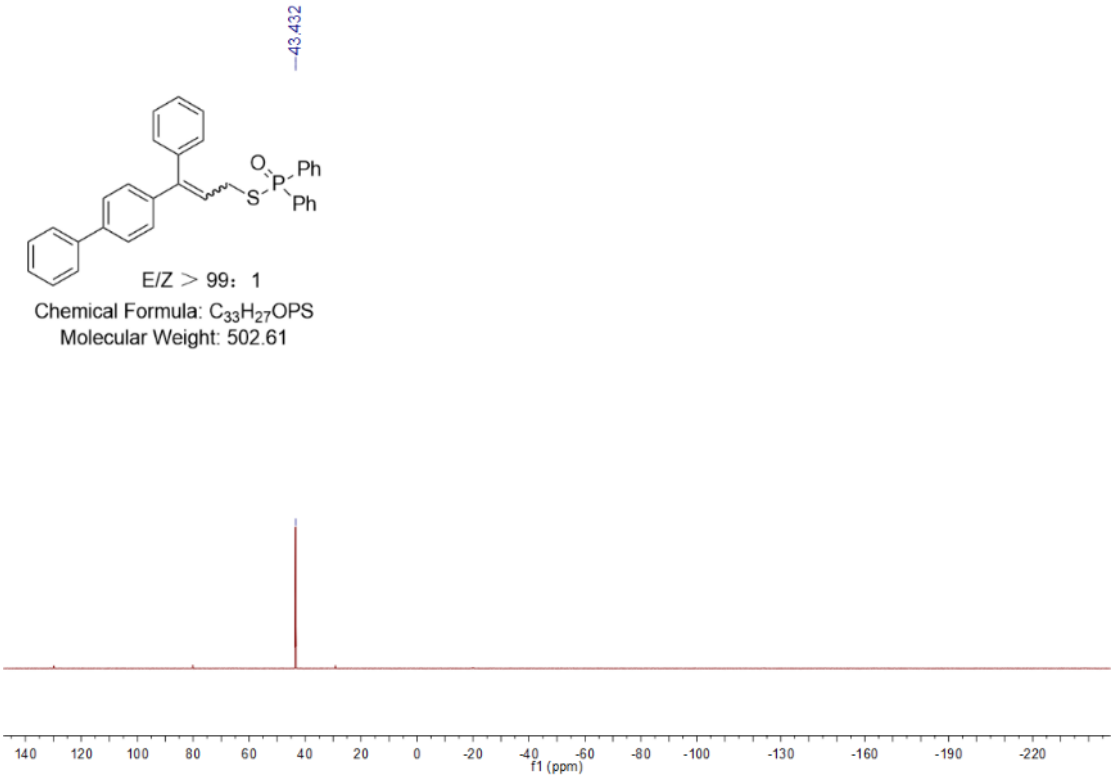
S-(3-([1,1'-biphenyl]-4-yl)-3-phenylallyl) diphenylphosphinothioate (3g)



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

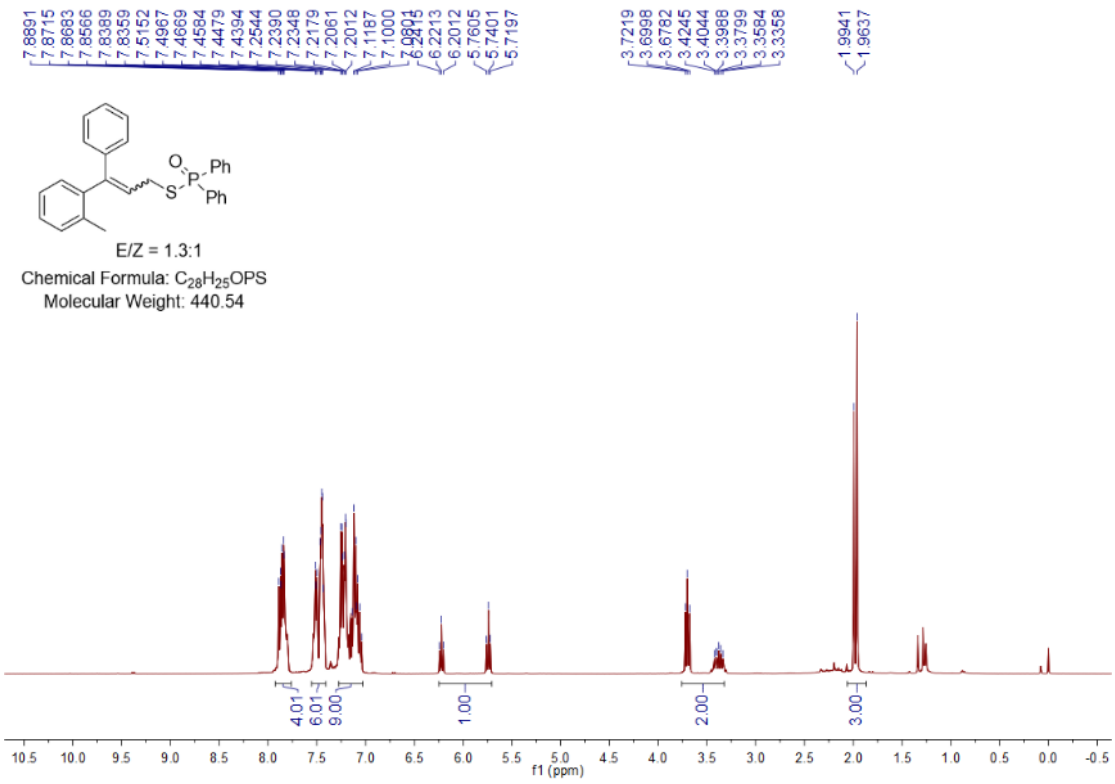


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

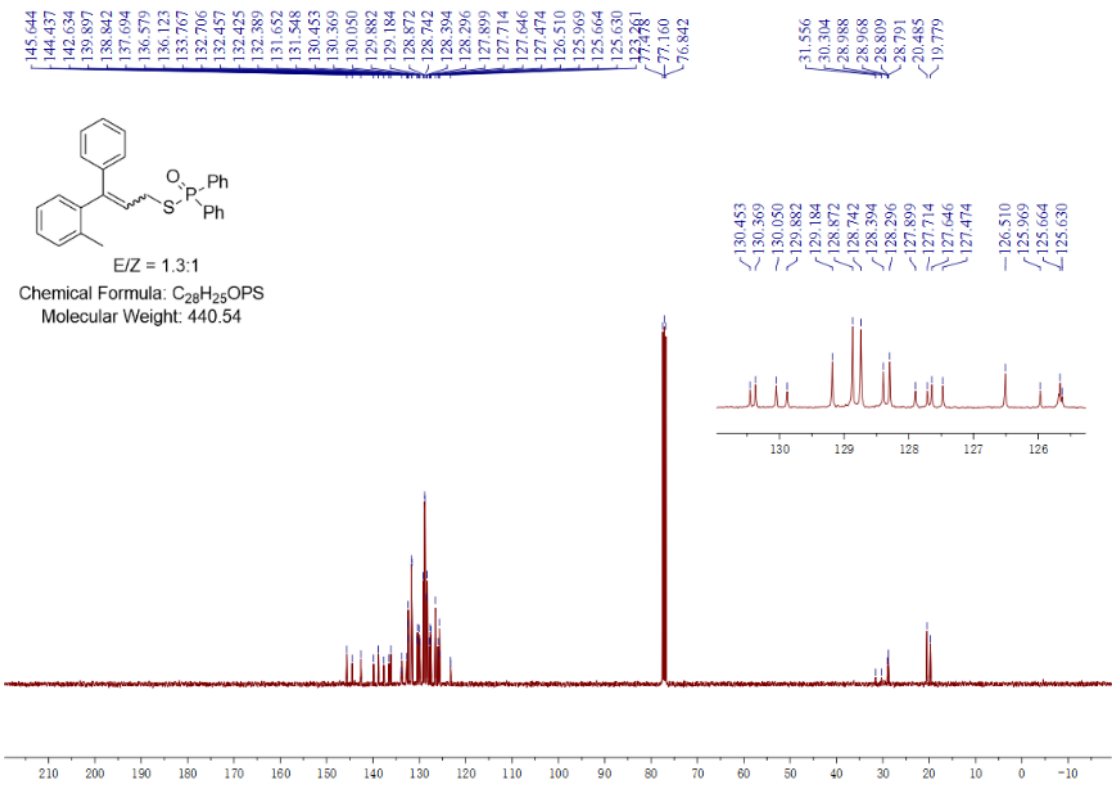


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

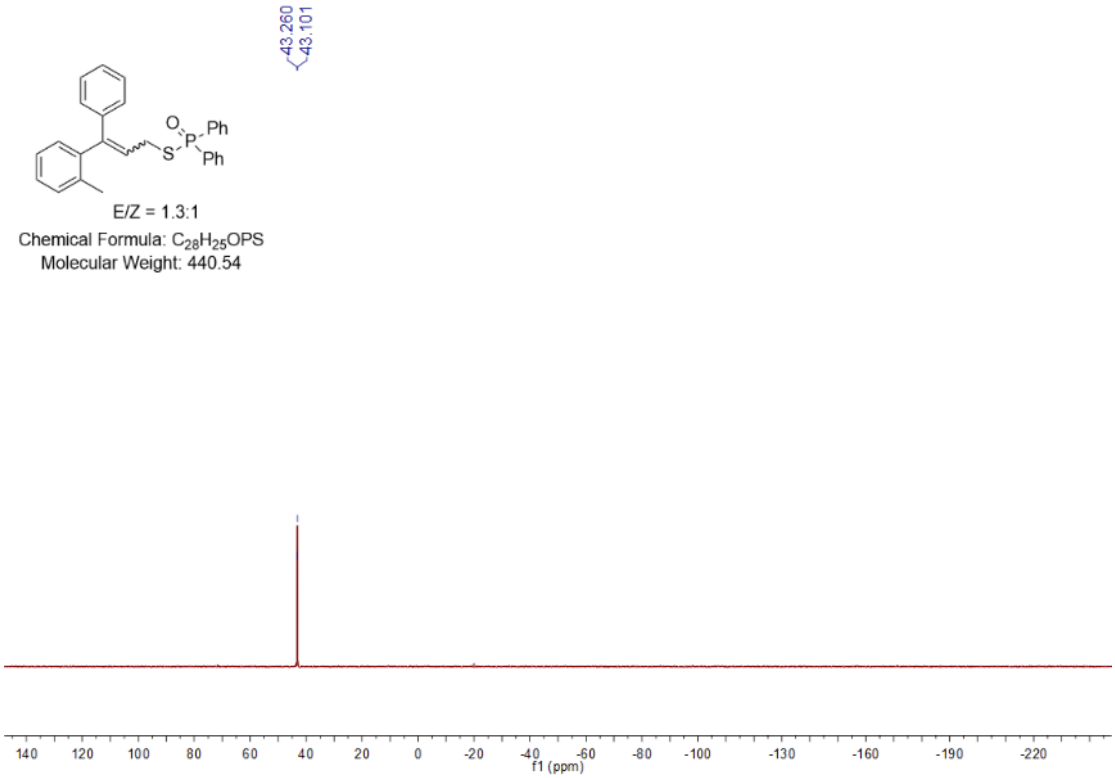
S-(3-phenyl-3-(o-tolyl)allyl) diphenylphosphinothioate (3h)



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

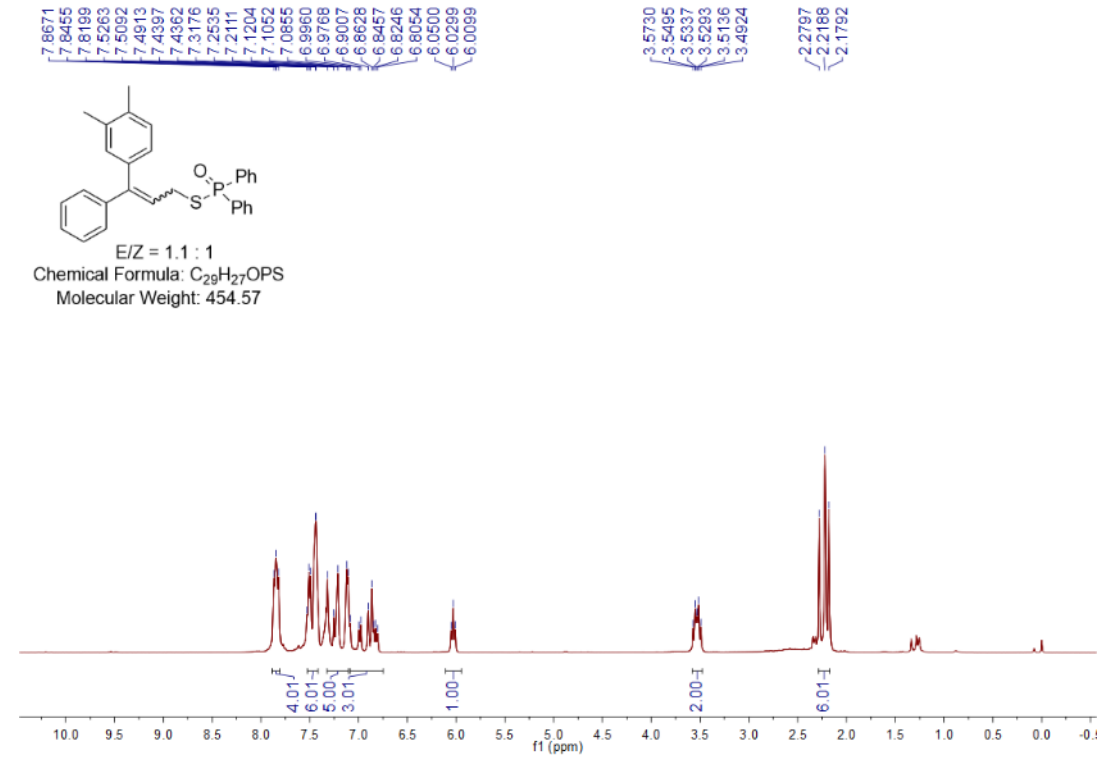


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

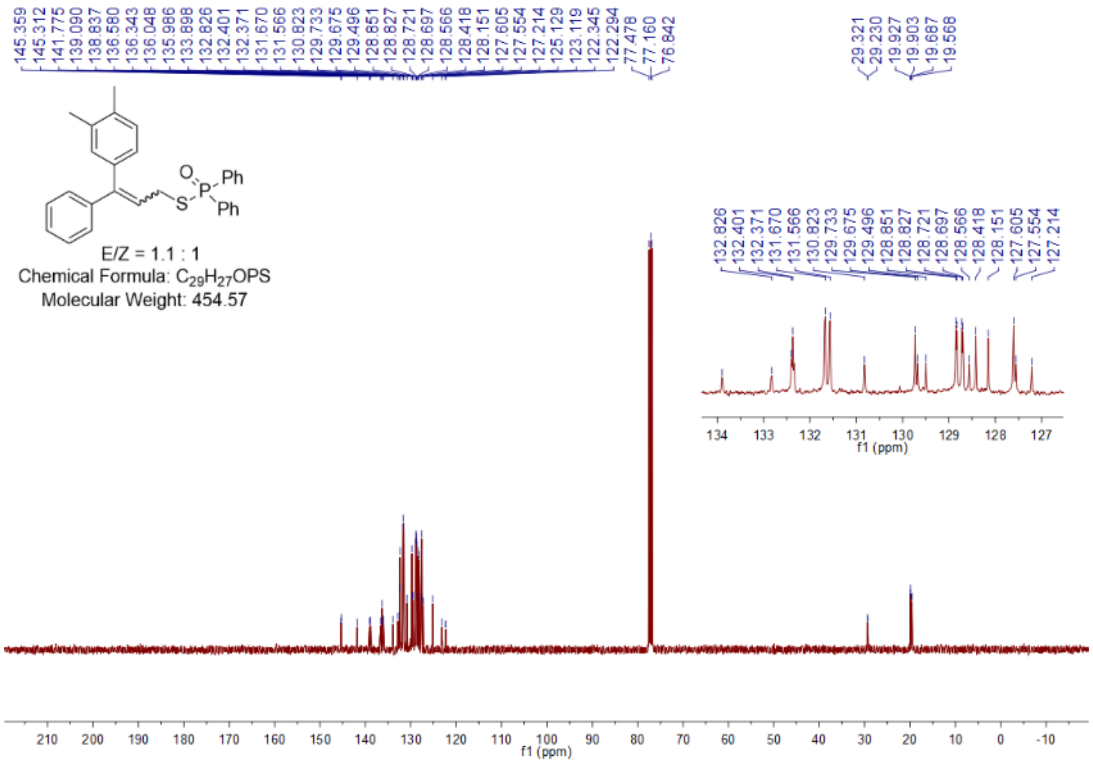


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

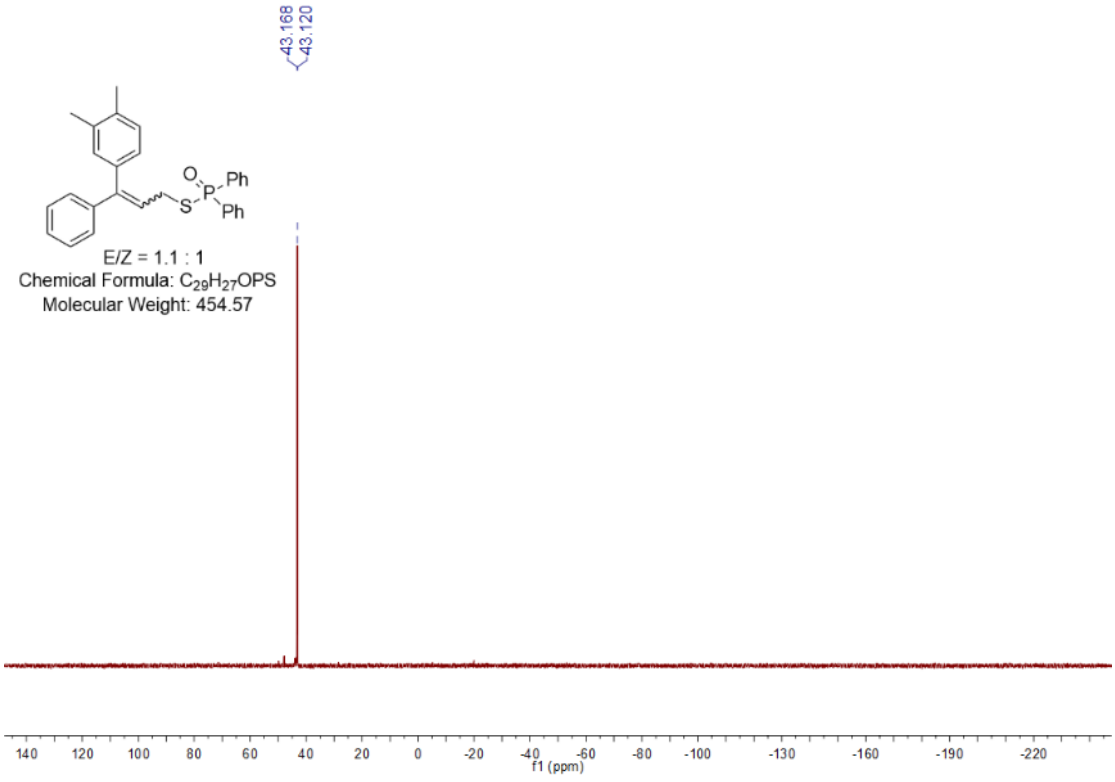
S-(3-(3,4-dimethylphenyl)-3-phenylallyl) diphenylphosphinothioate (3i)



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

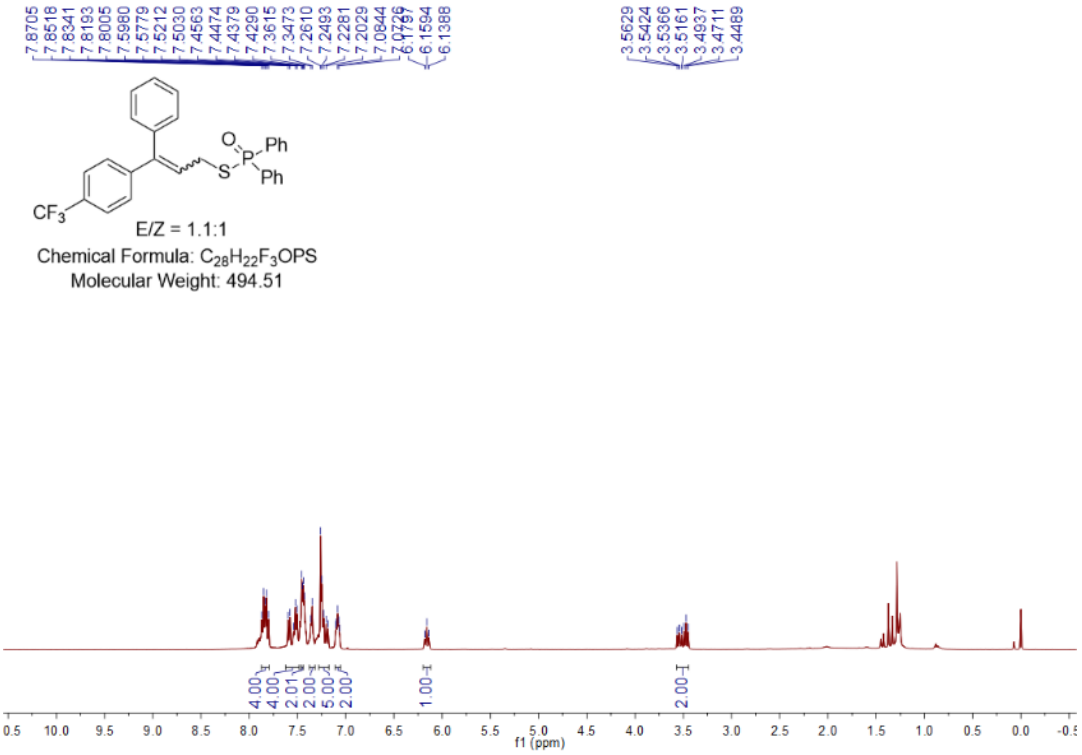


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

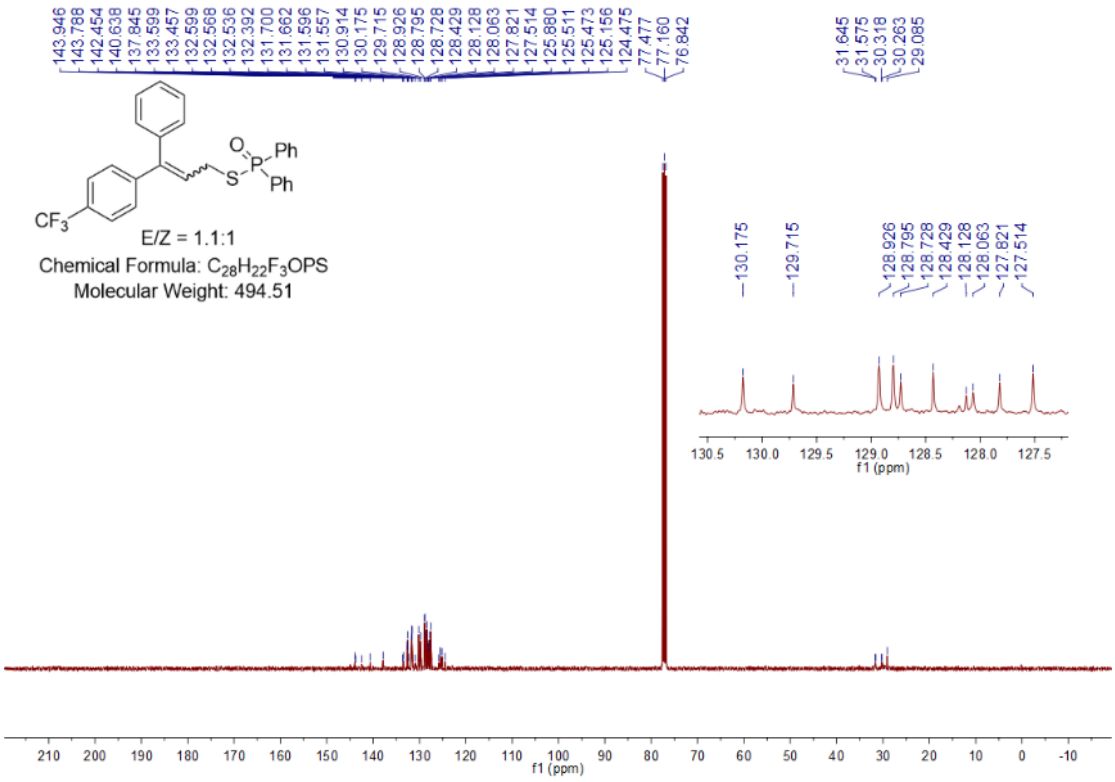


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

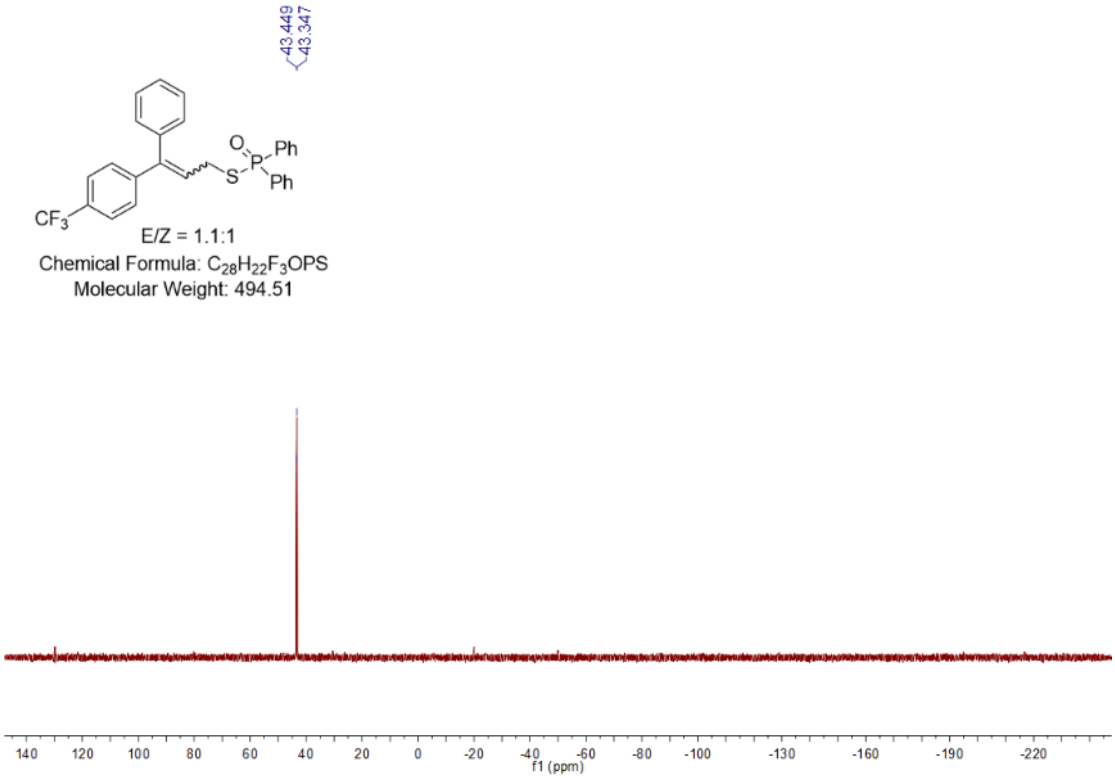
S-(3-phenyl-3-(4-(trifluoromethyl)phenyl)allyl) diphenylphosphinothioate (3j)



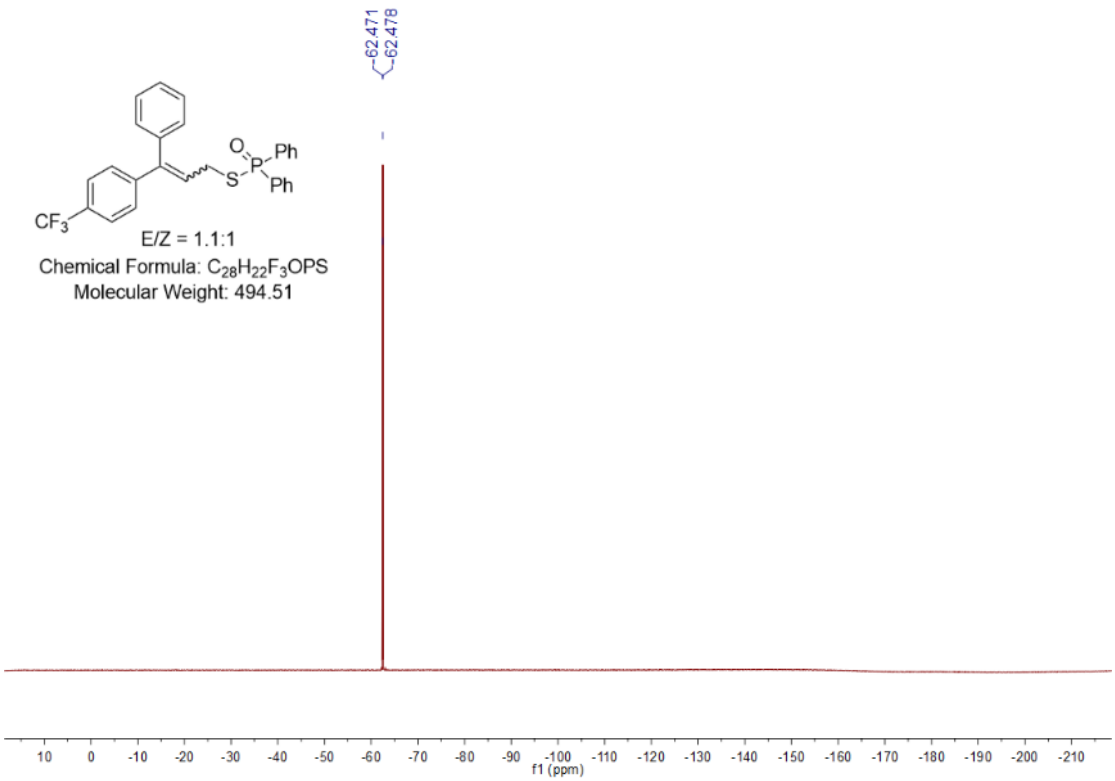
^{1}H NMR spectrum, 400 MHz, $CDCl_3$



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

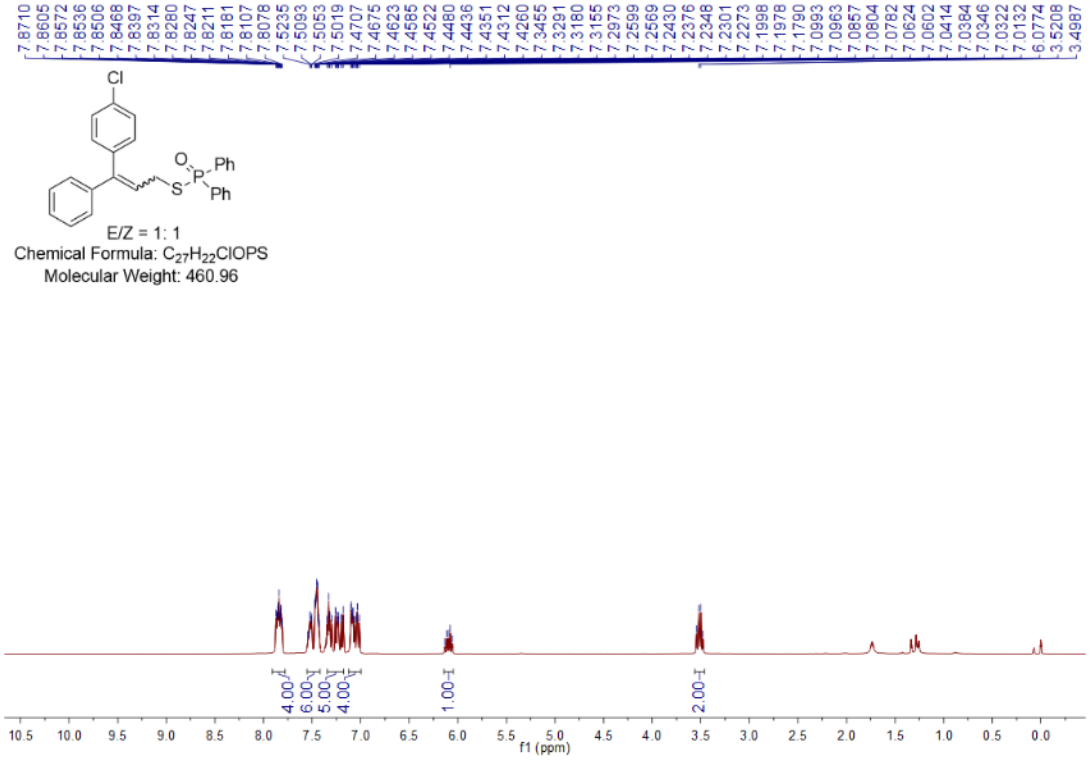


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

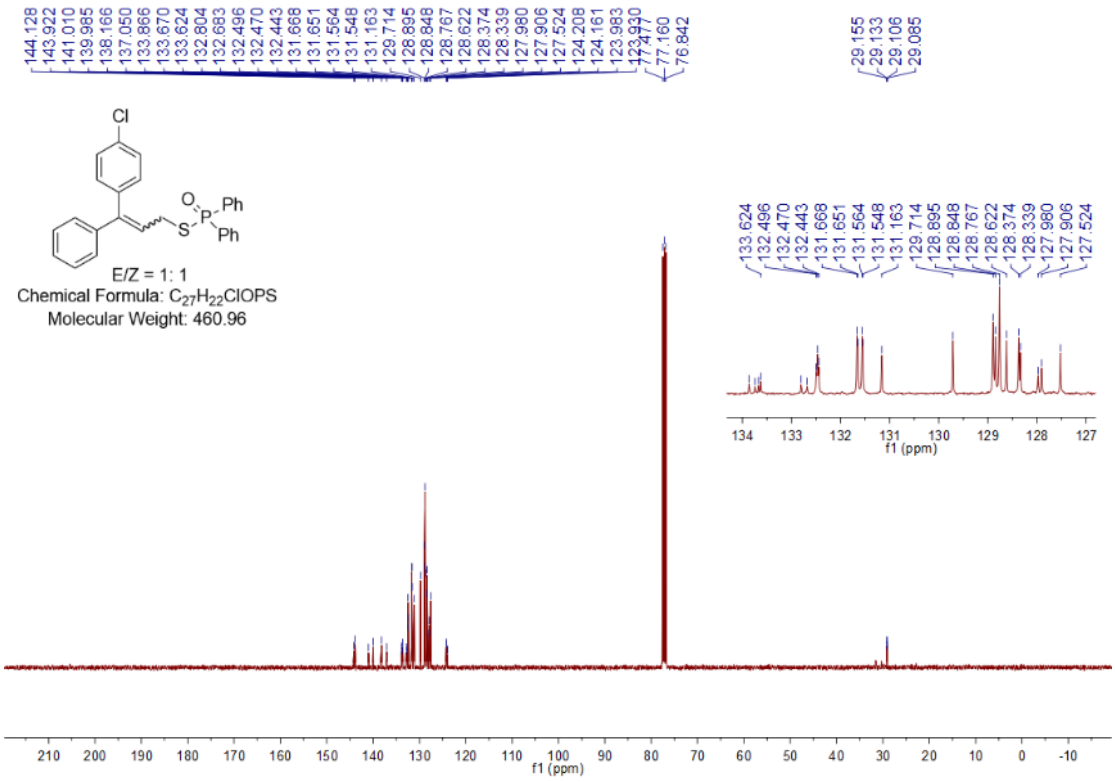


^{19}F NMR spectrum, 376 MHz, $CDCl_3$

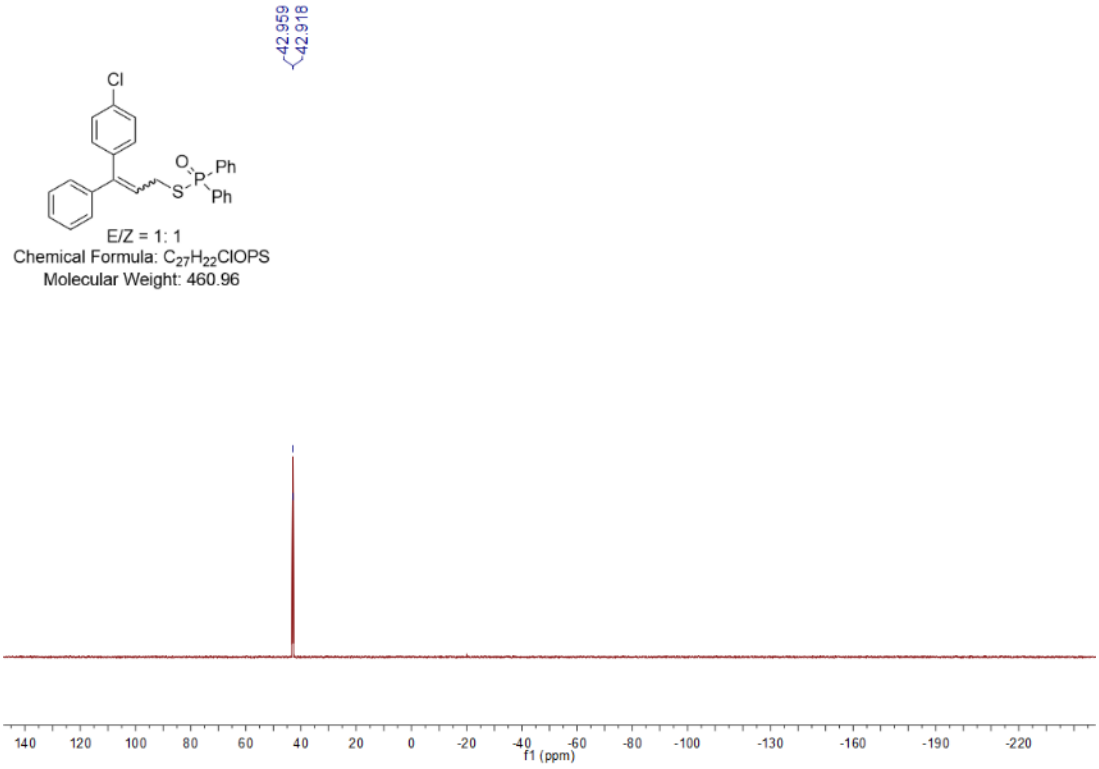
S-(3-(4-chlorophenyl)-3-phenylallyl) diphenylphosphinothioate (3k)



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

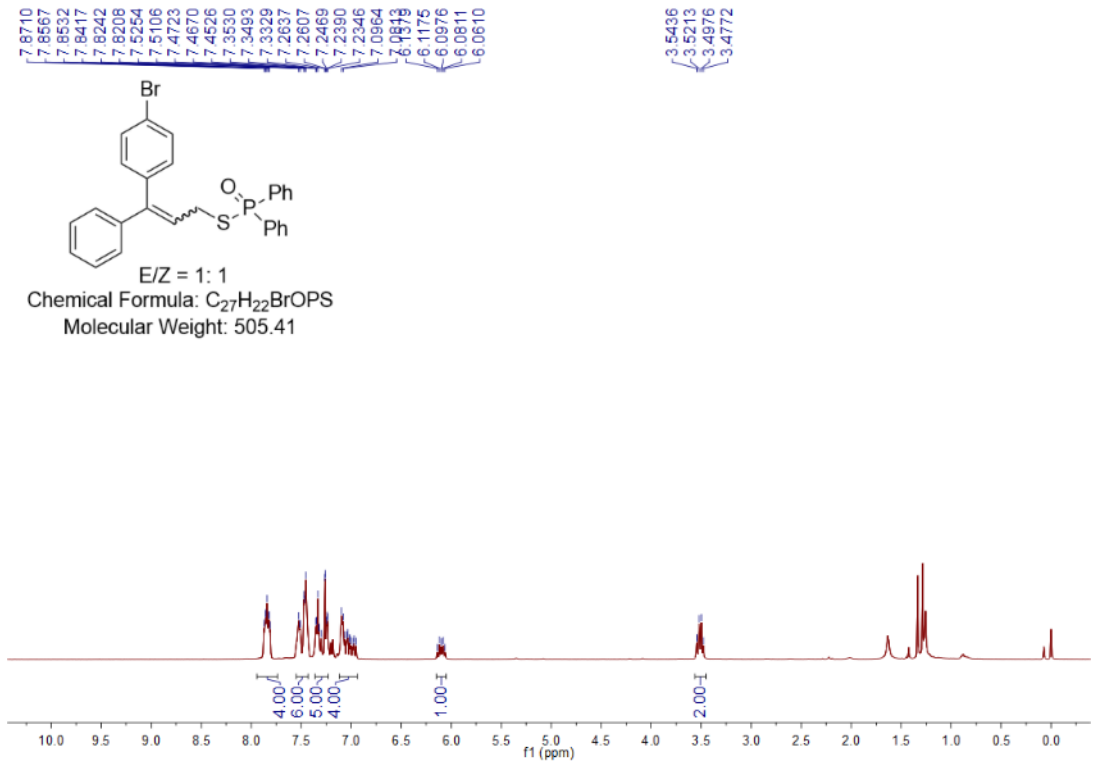


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

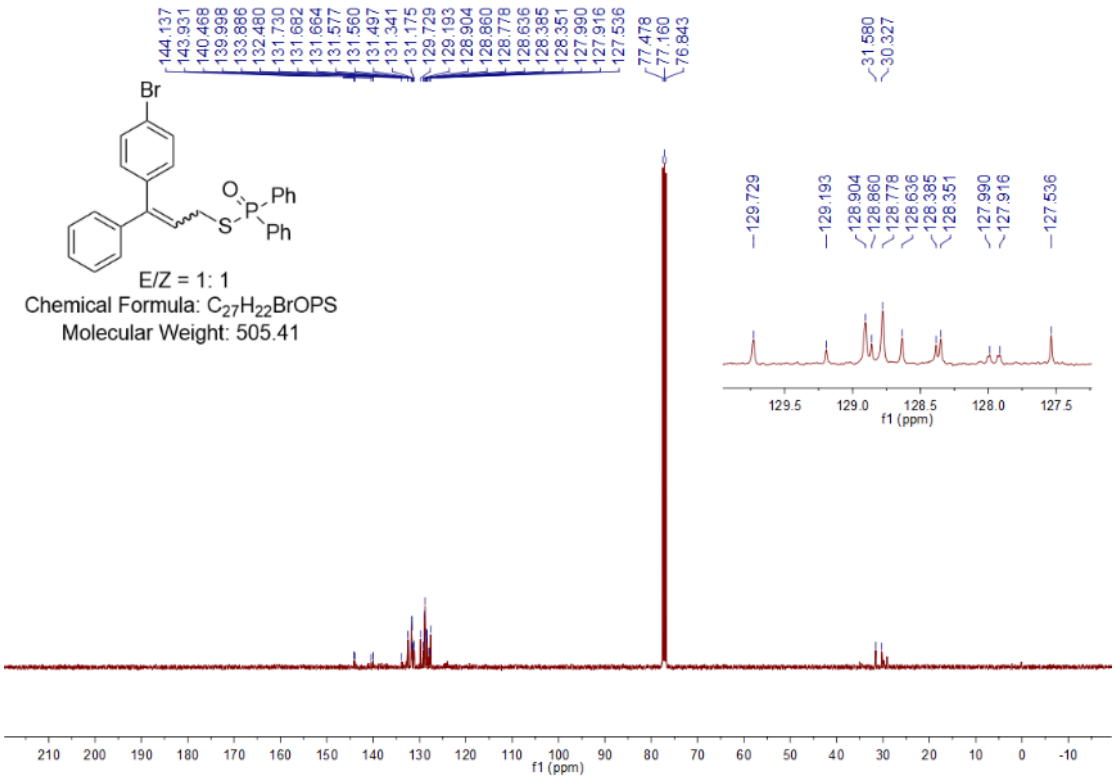


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

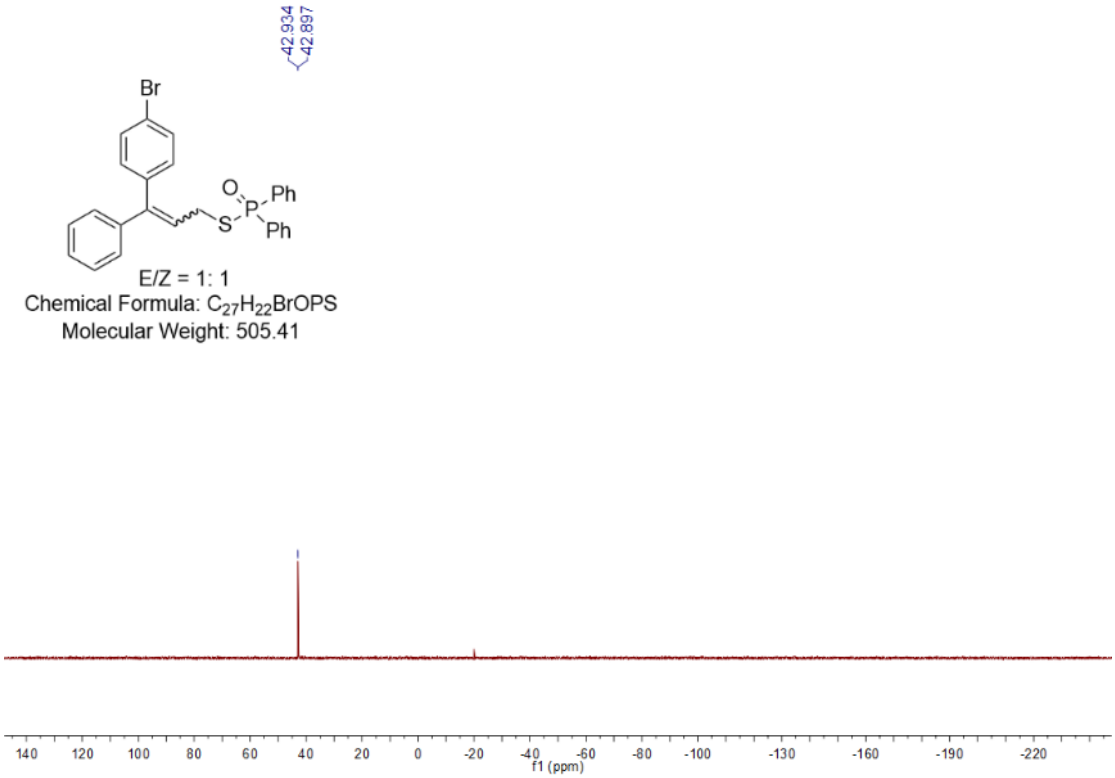
S-(3-(4-bromophenyl)-3-phenylallyl) diphenylphosphinothioate (3l)



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

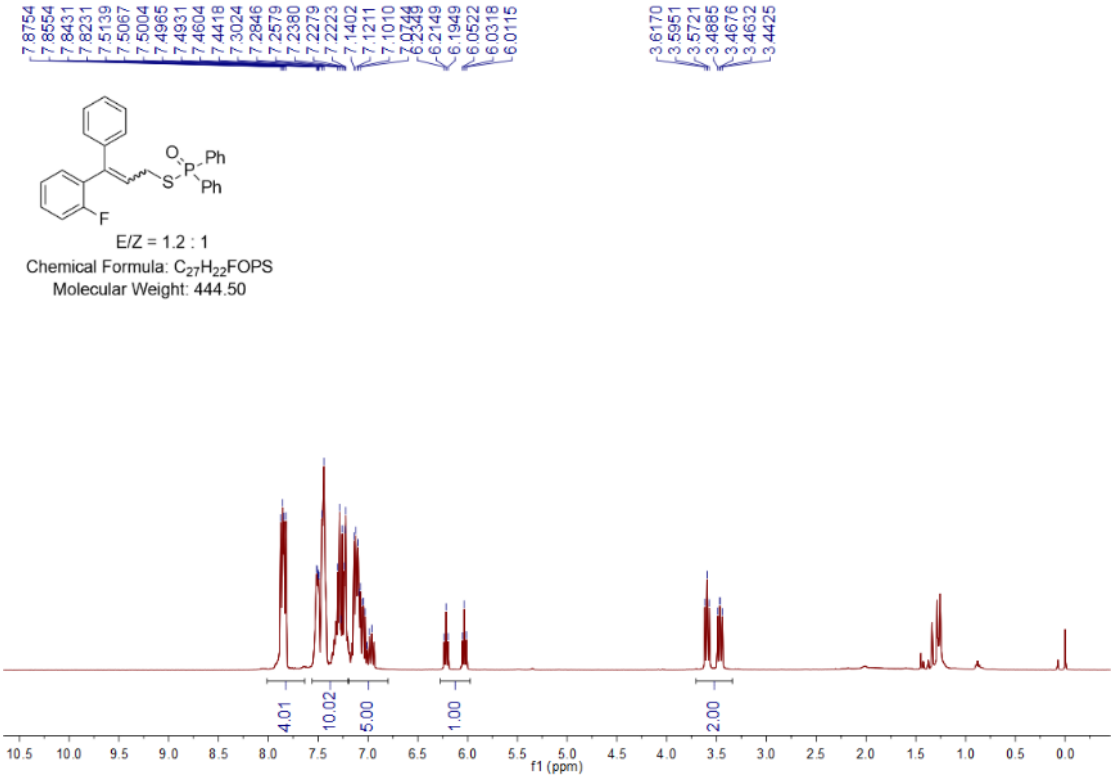


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

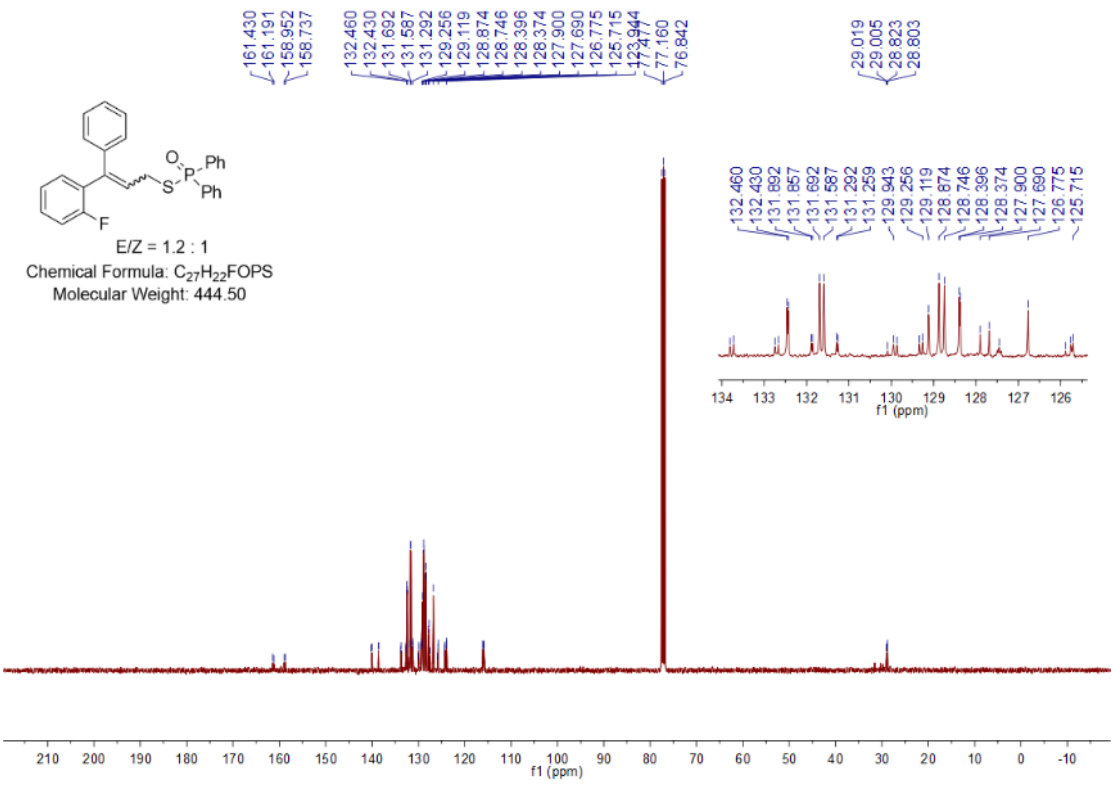


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

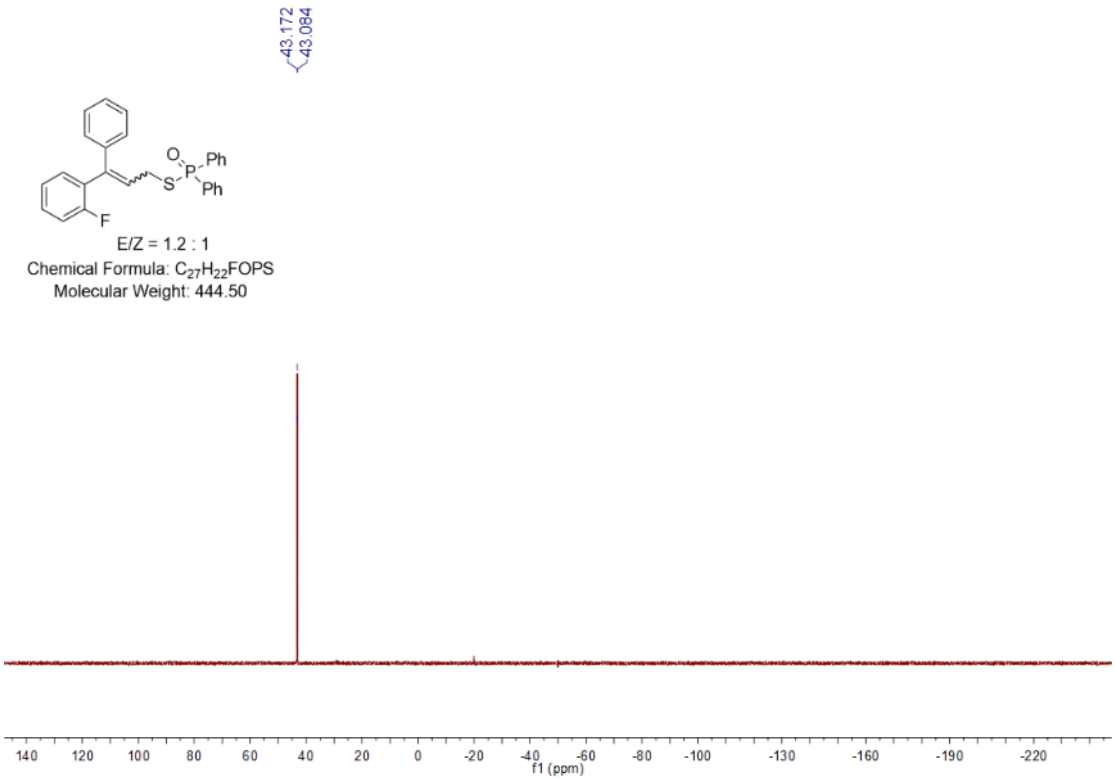
S-(3-(2-fluorophenyl)-3-phenylallyl) diphenylphosphinothioate (3m)



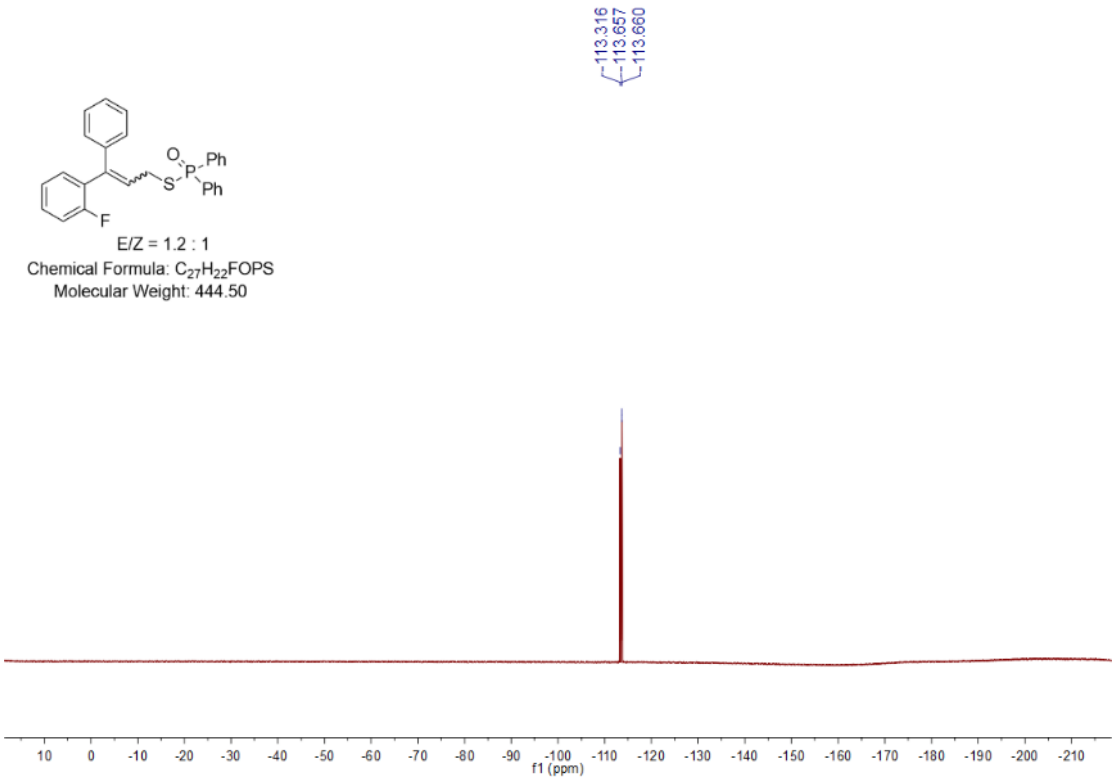
^{1}H NMR spectrum, 400 MHz, $CDCl_3$



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

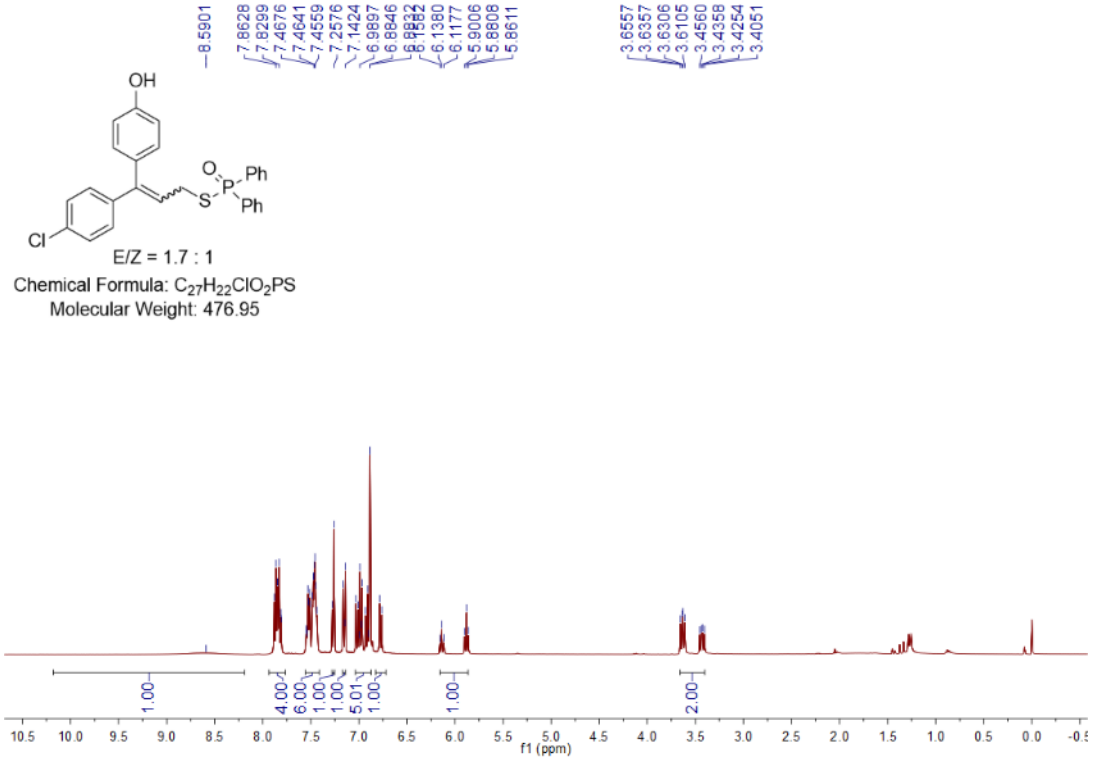


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

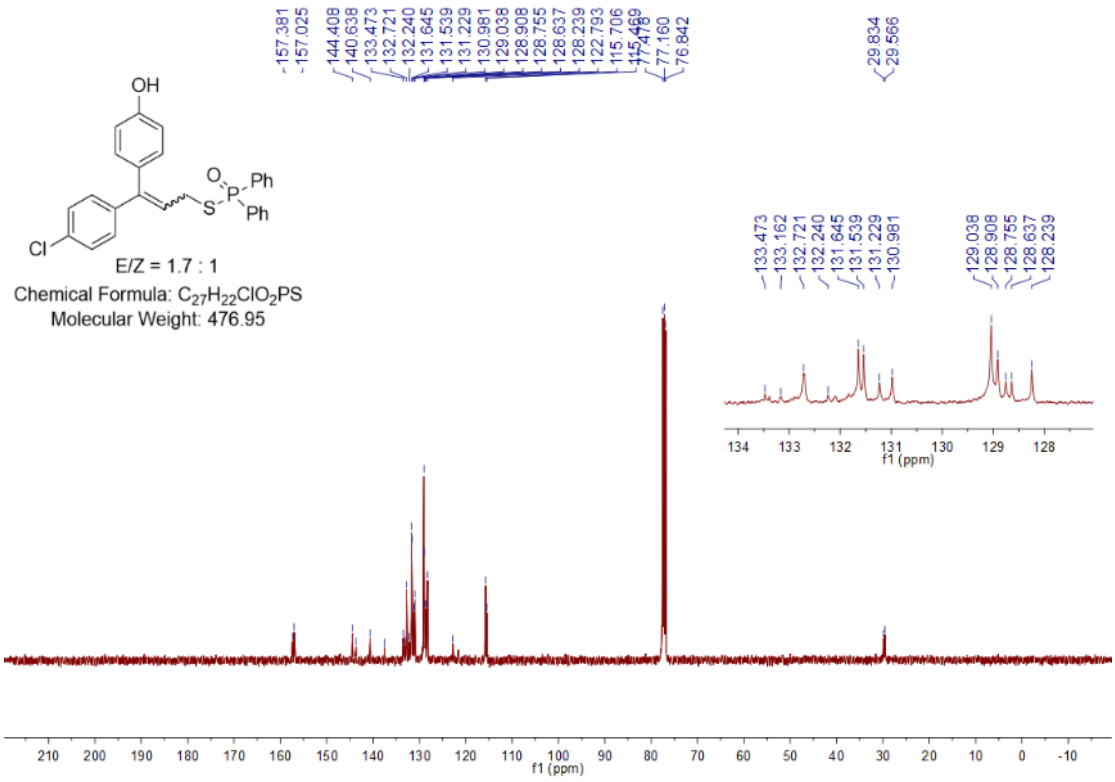


^{19}F NMR spectrum, 376 MHz, $CDCl_3$

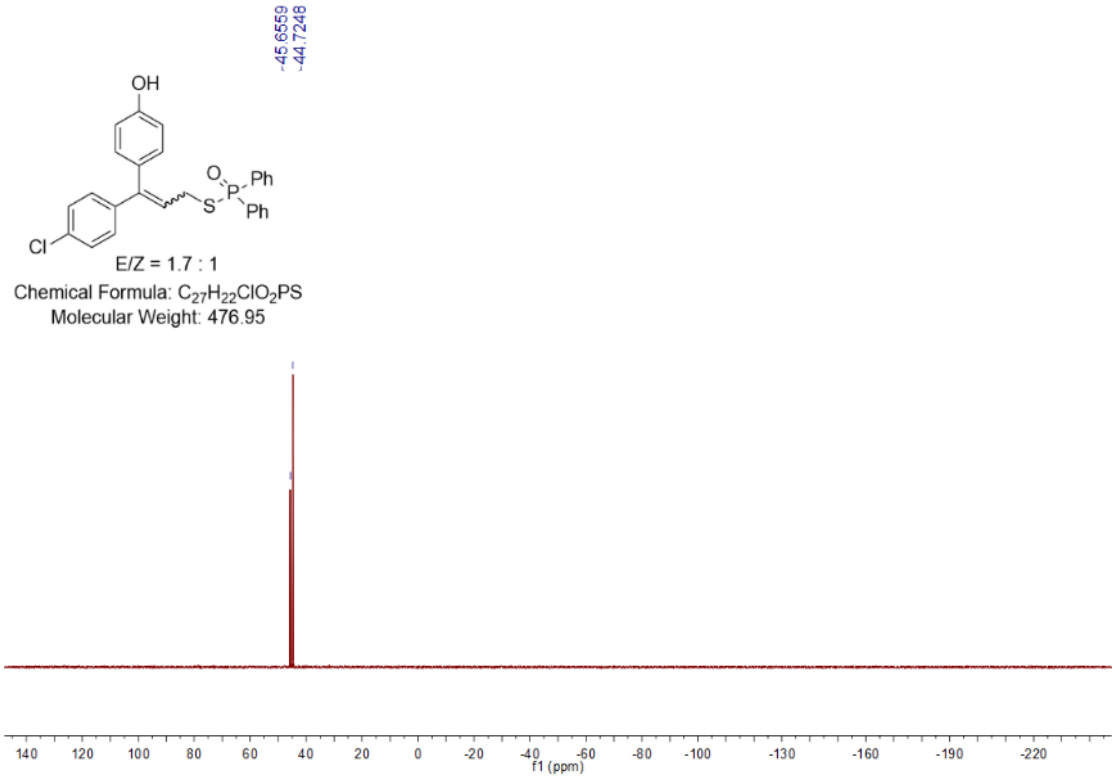
S-(3-(4-chlorophenyl)-3-(4-hydroxyphenyl)allyl) diphenylphosphinothioate (3n)



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

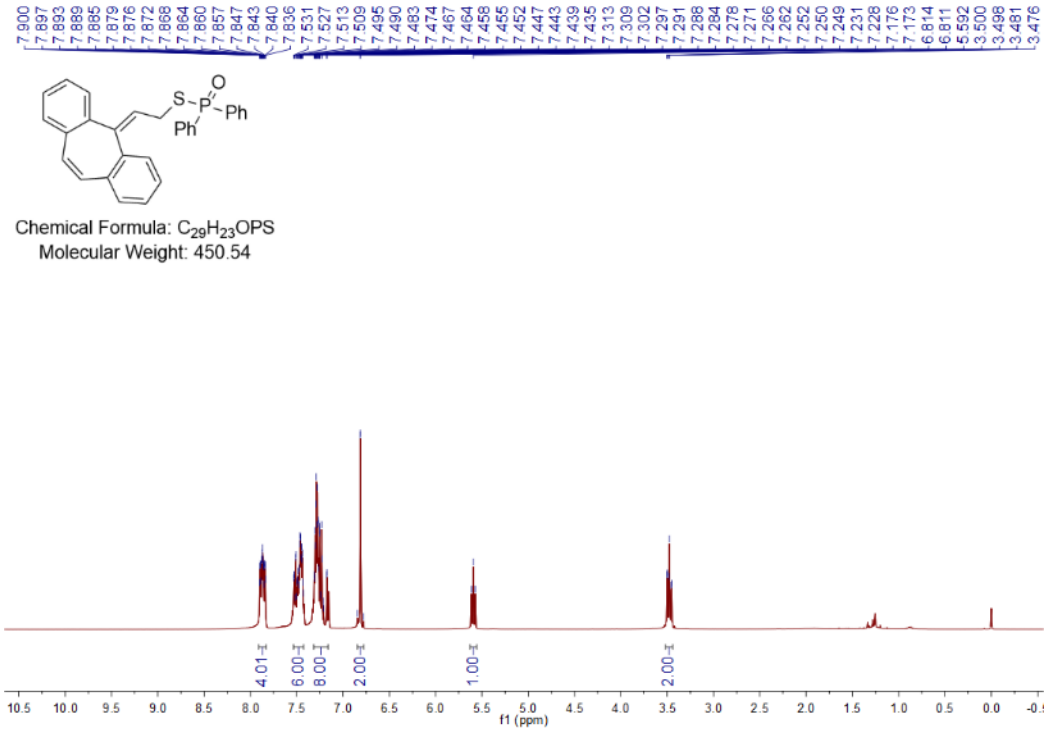


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

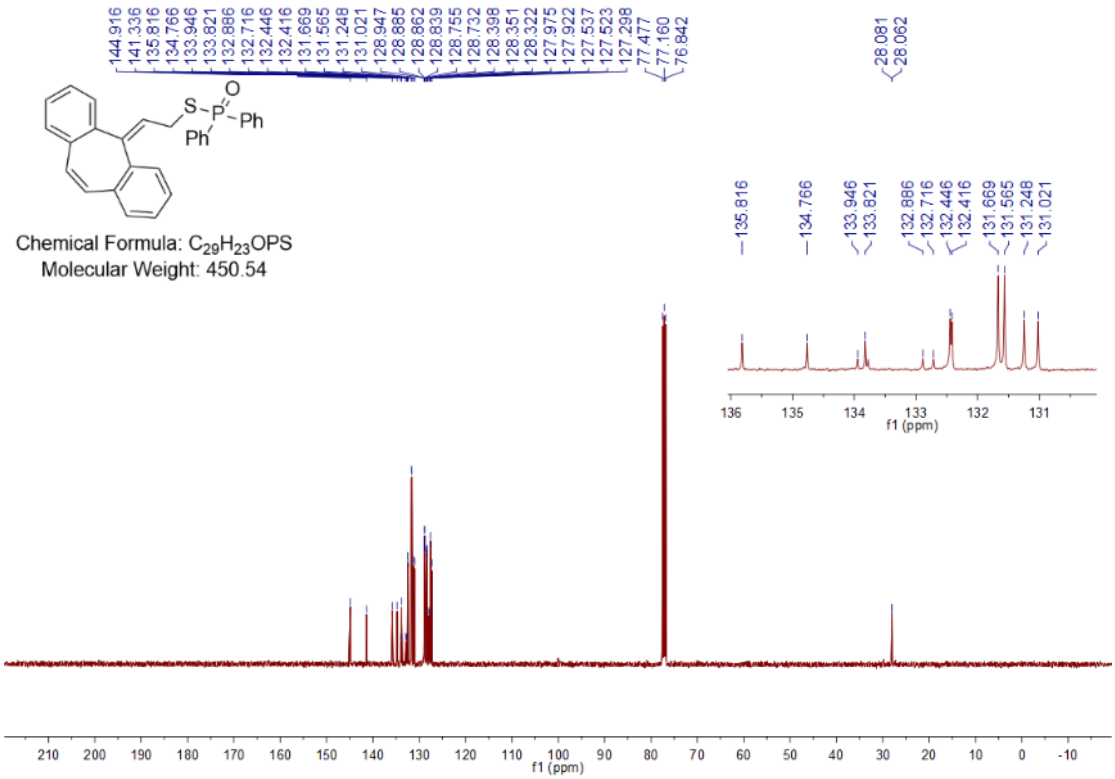


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

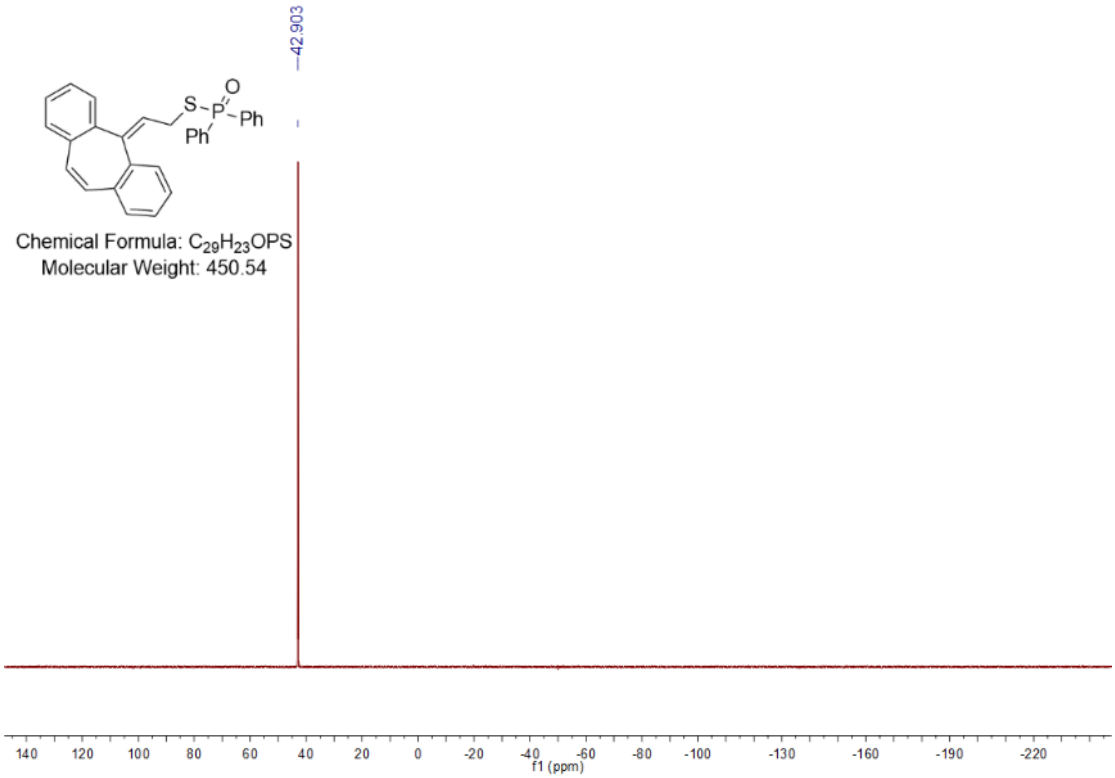
S-(2-(5H-dibenzo[a,d][7]annulen-5-ylidene)ethyl) diphenylphosphinothioate (3o)



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

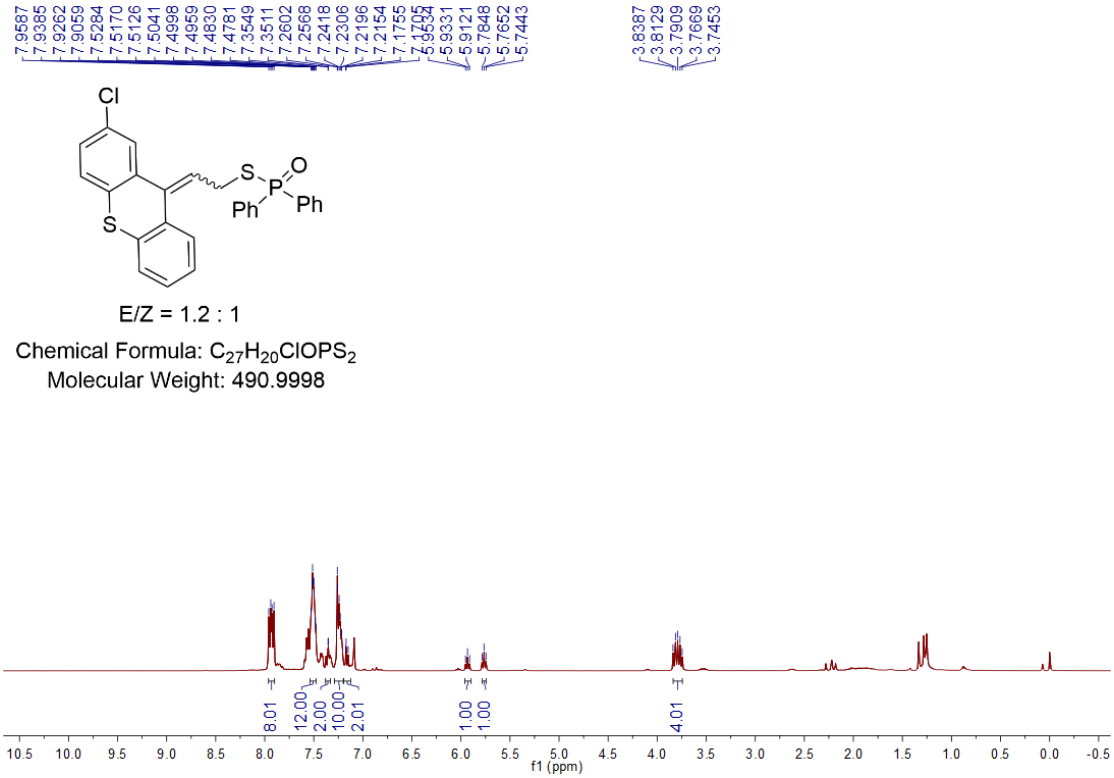


^{13}C NMR spectrum, 100 MHz, $CDCl_3$



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

S-(2-(1-chloro-9H-thioxanthen-9-ylidene)ethyl) diphenylphosphinothioate (3p)

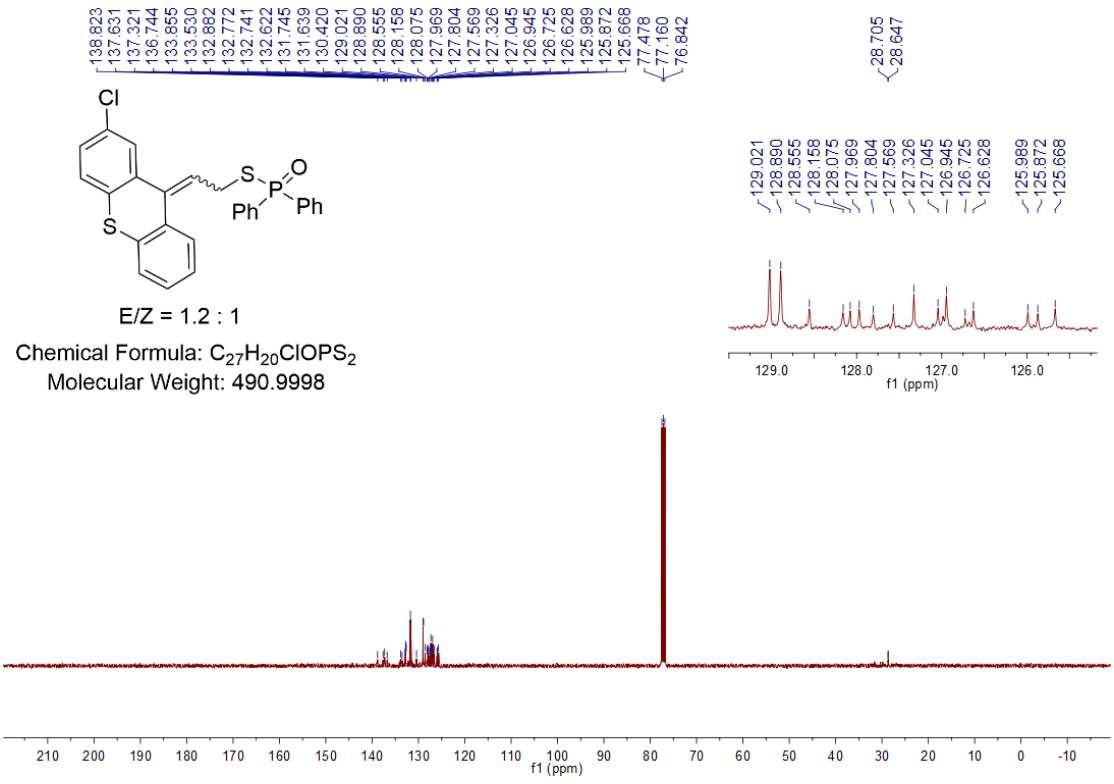


E/Z = 1.2 : 1

Chemical Formula: $C_{27}H_{20}ClOPS_2$

Molecular Weight: 490.9998

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

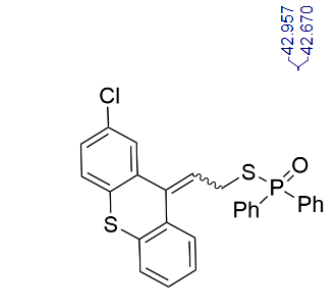


E/Z = 1.2 : 1

Chemical Formula: $C_{27}H_{20}ClOPS_2$

Molecular Weight: 490.9998

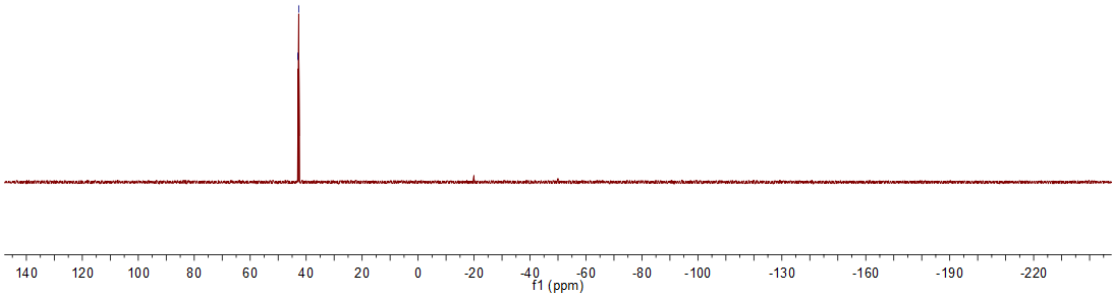
^{13}C NMR spectrum, 100 MHz, $CDCl_3$



E/Z = 1.2 : 1

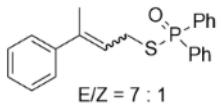
Chemical Formula: $C_{27}H_{20}ClOPS_2$

Molecular Weight: 490.9998



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

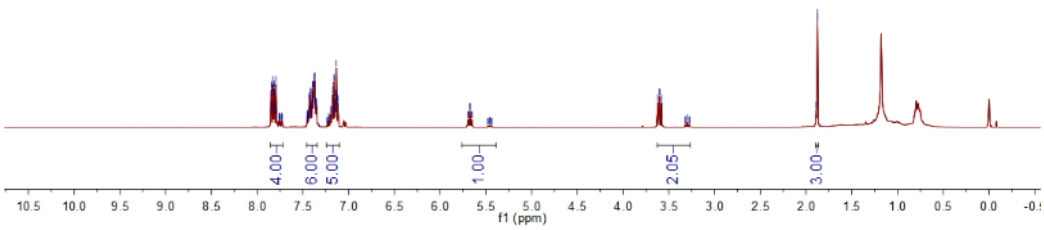
S-(3-phenylbut-2-en-1-yl) diphenylphosphinothioate (3q)



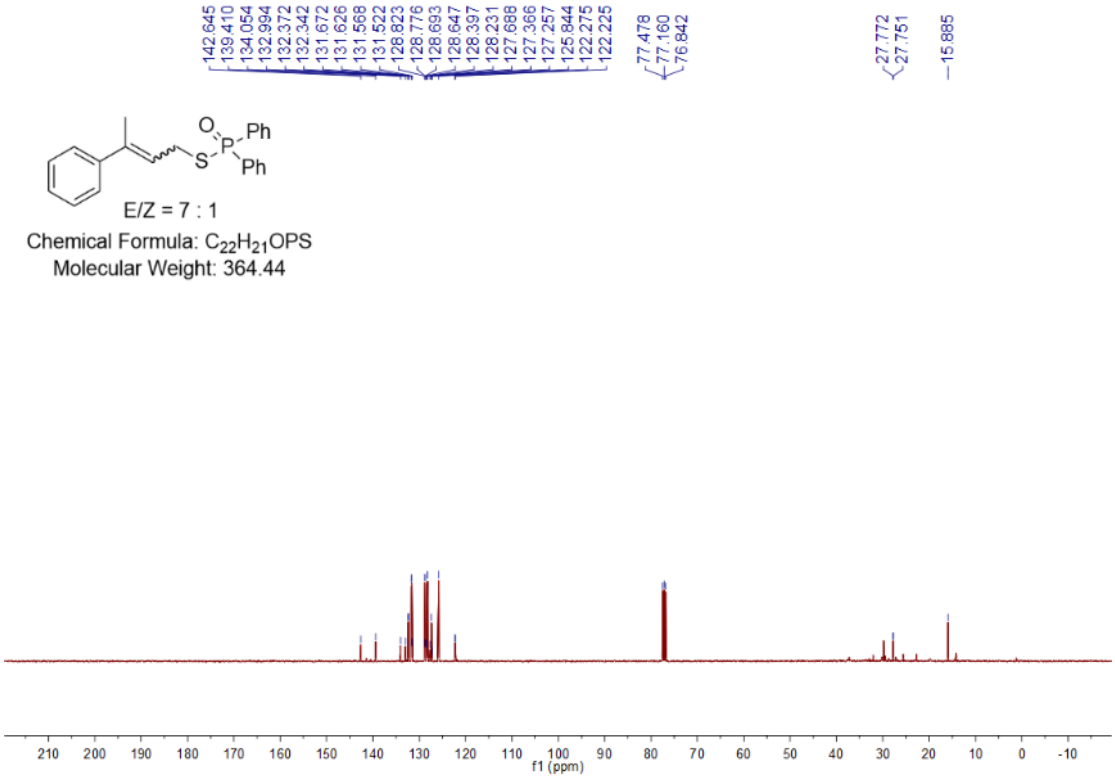
E/Z = 7 : 1

Chemical Formula: $C_{22}H_{21}OPS$

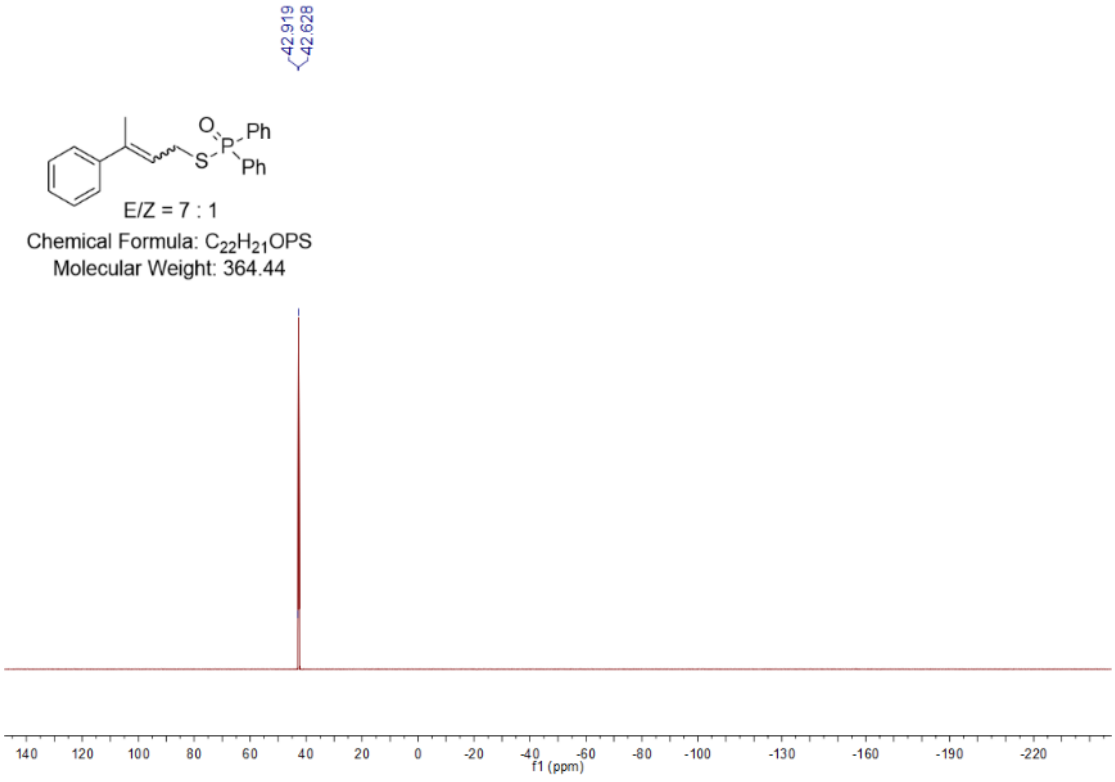
Molecular Weight: 364.44



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

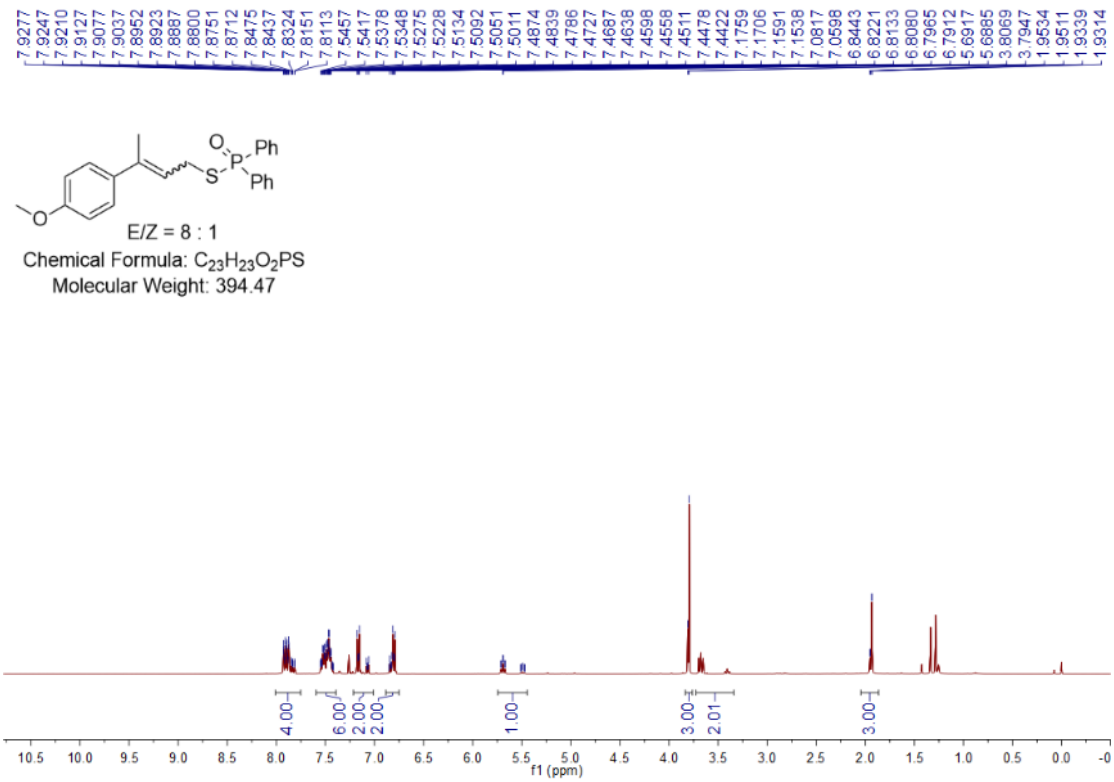


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

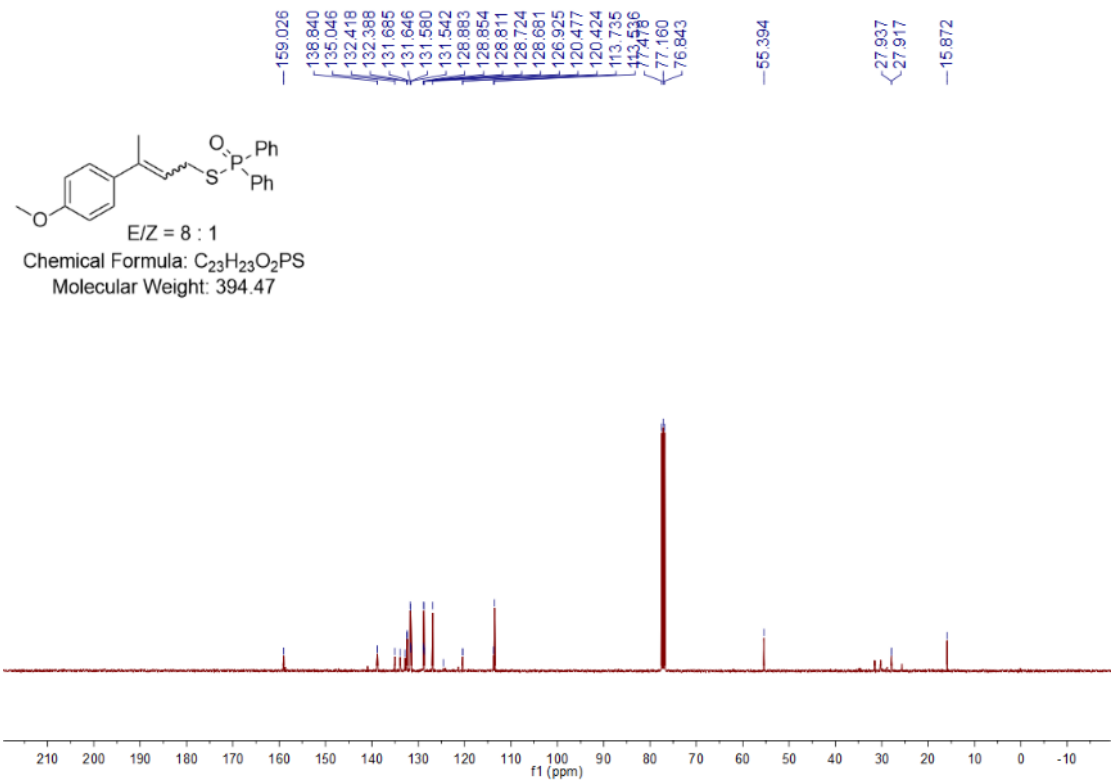


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

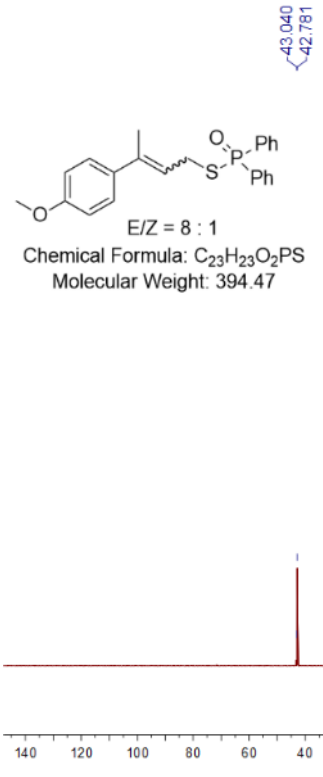
S-(3-(4-methoxyphenyl)but-2-en-1-yl) diphenylphosphinothioate (3r)



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

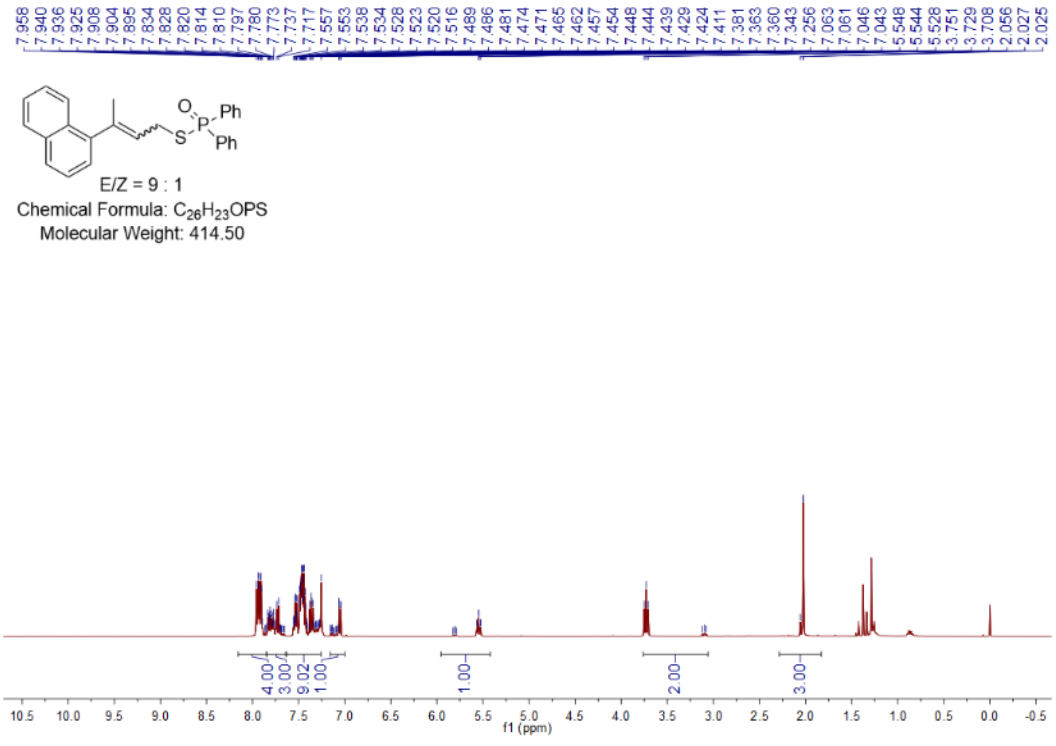


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

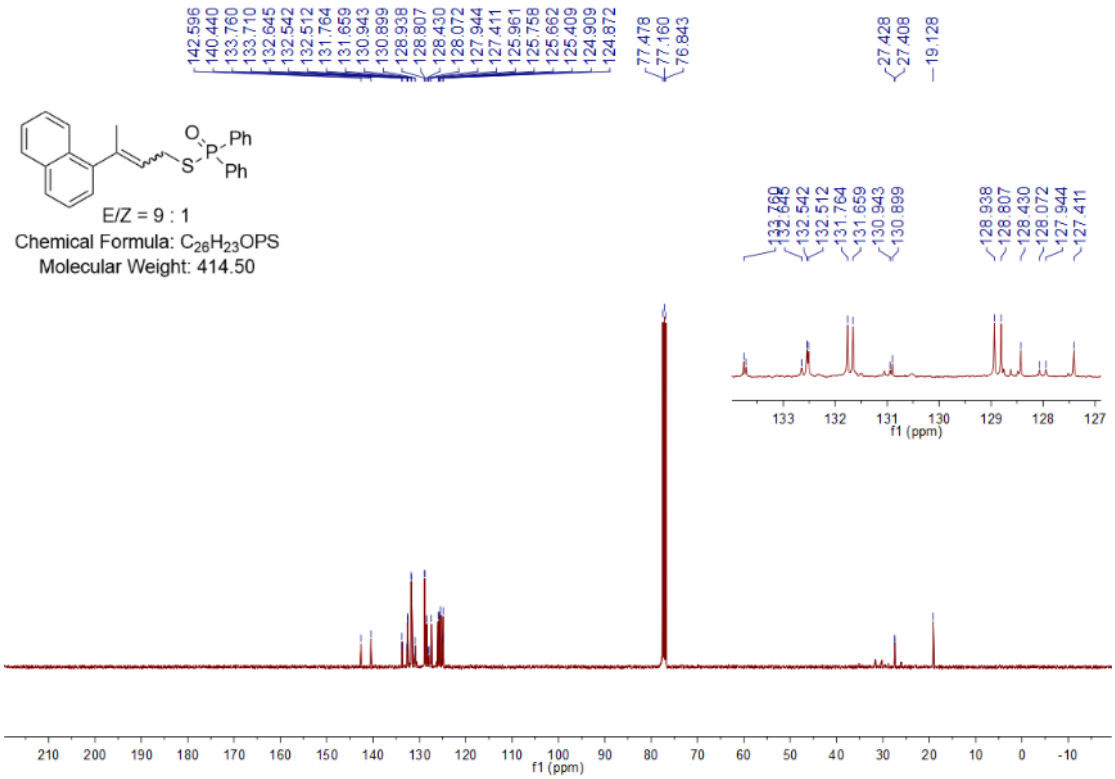


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

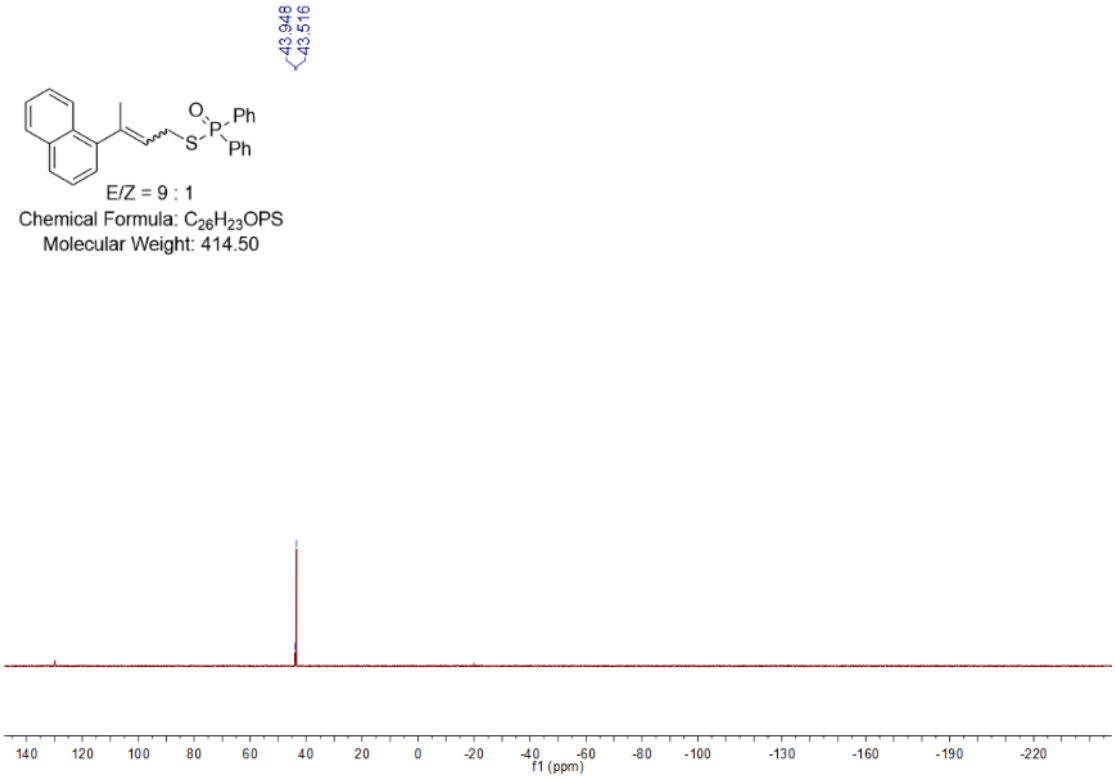
S-(3-(naphthalen-1-yl)but-2-en-1-yl) diphenylphosphinothioate (3s)



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

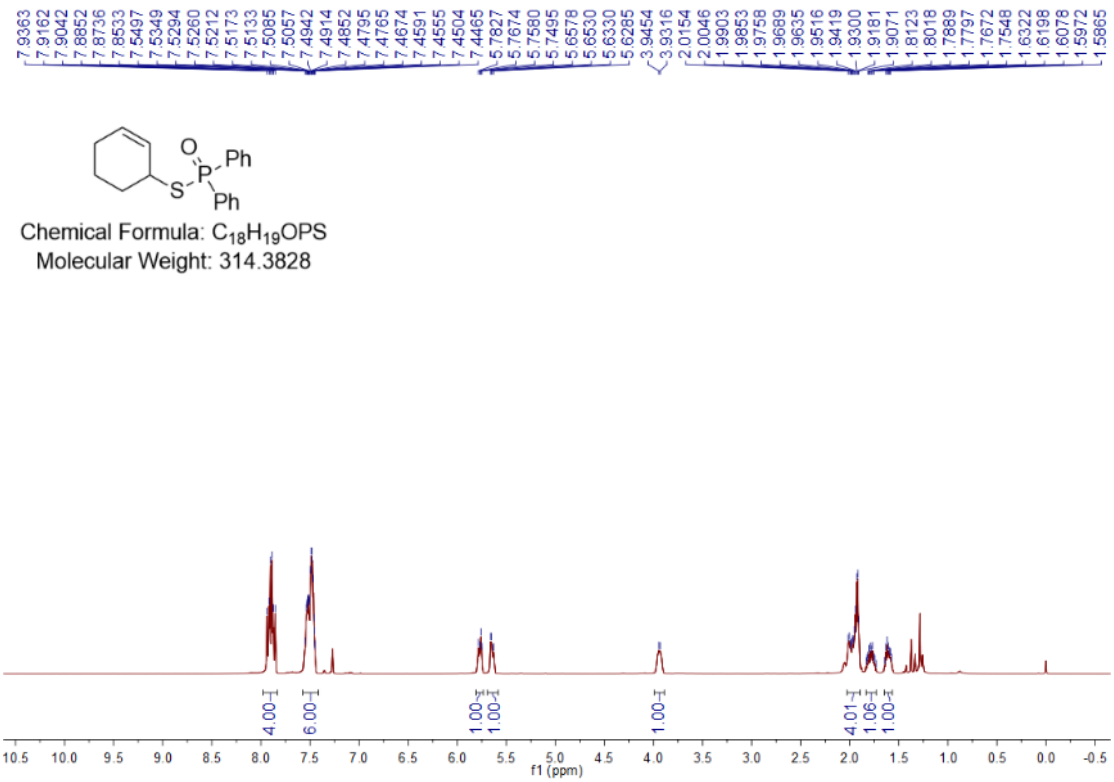


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

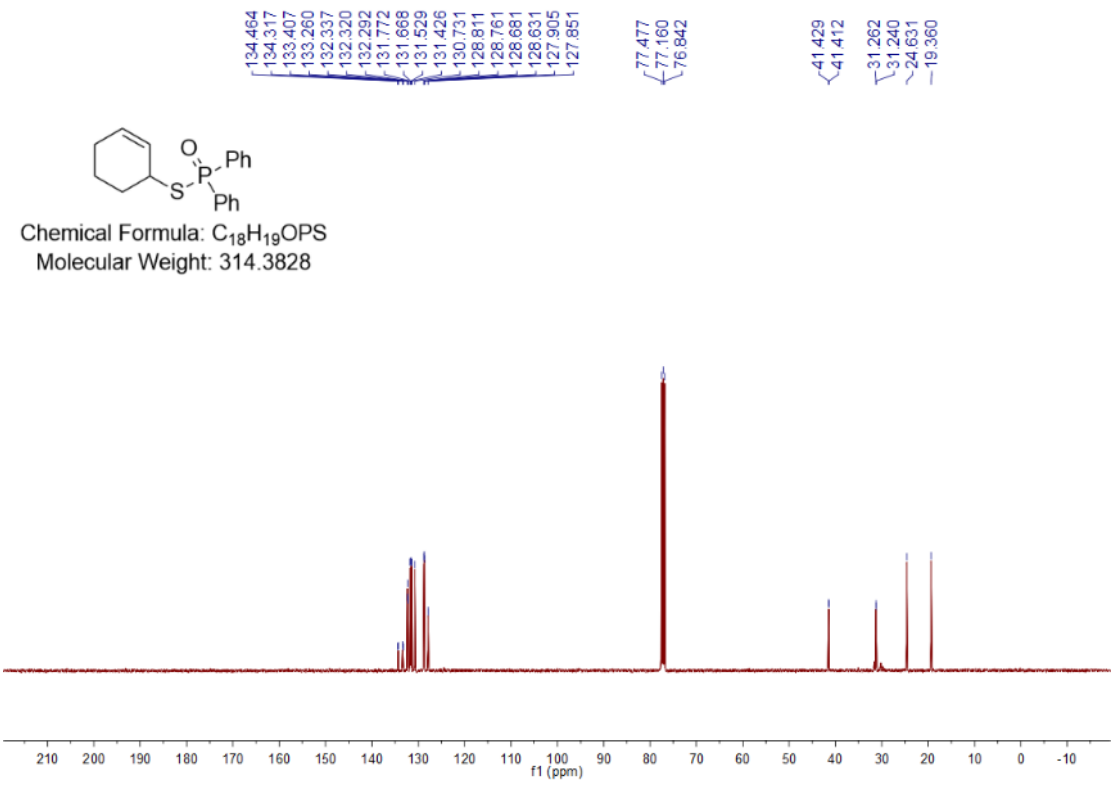


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

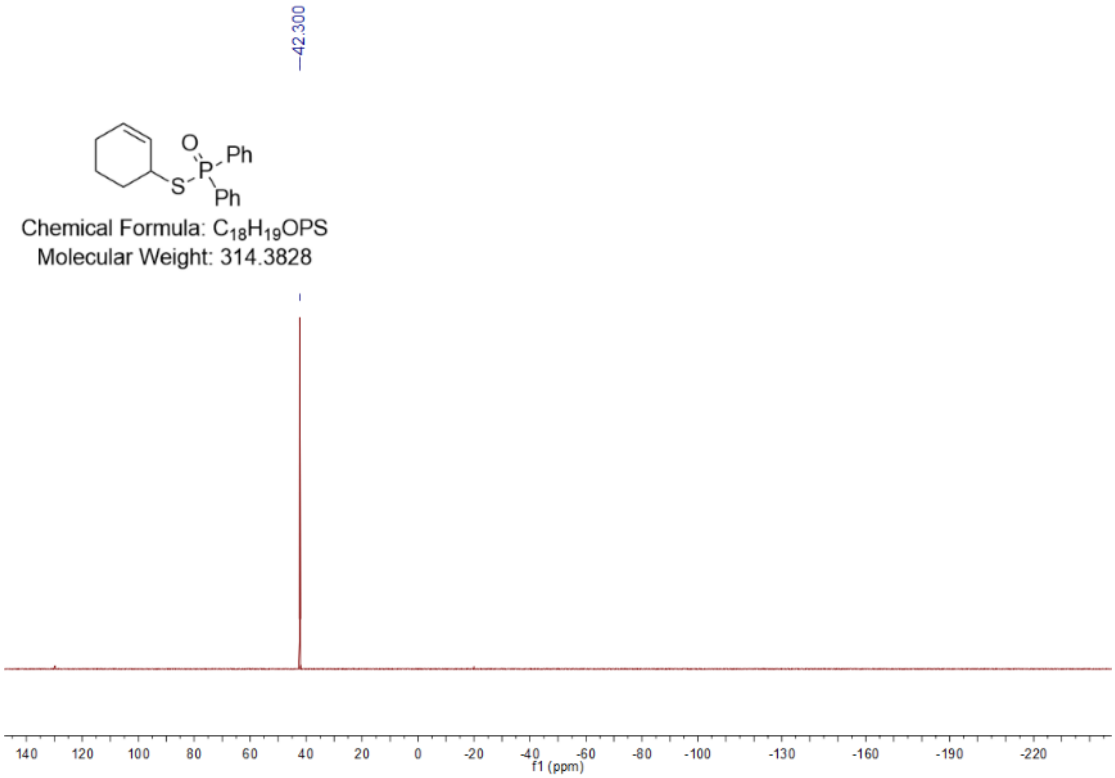
S-(cyclohex-2-en-1-yl) diphenylphosphinothioate (3t)



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

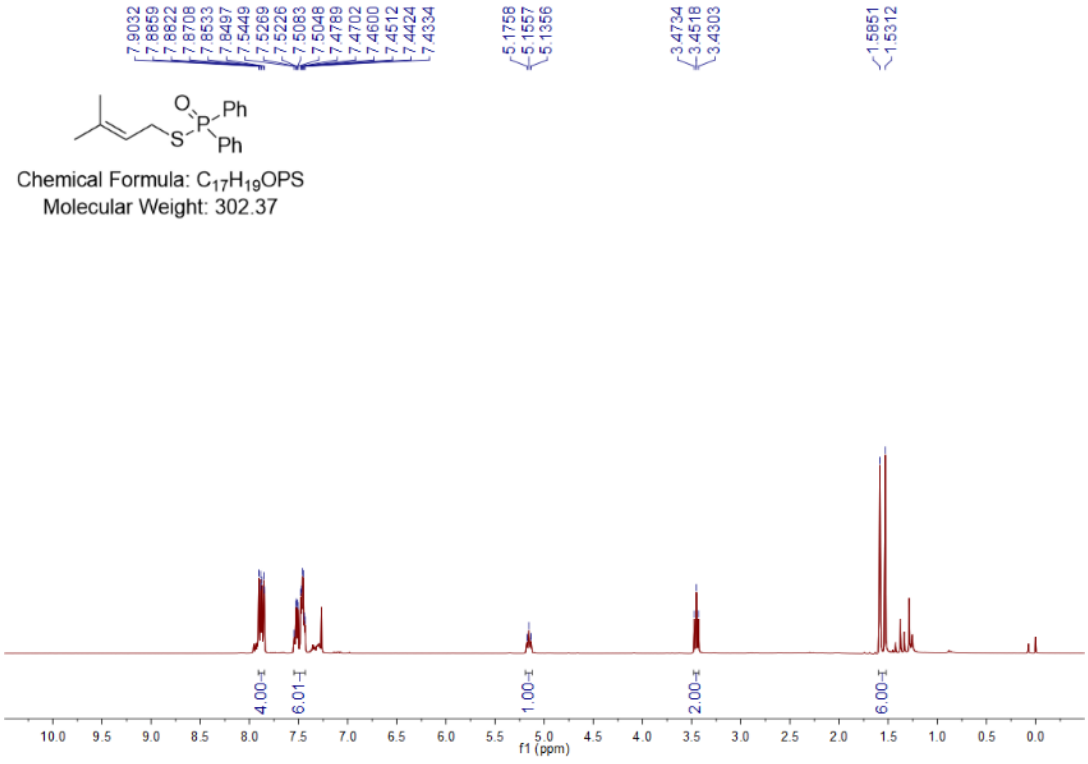


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

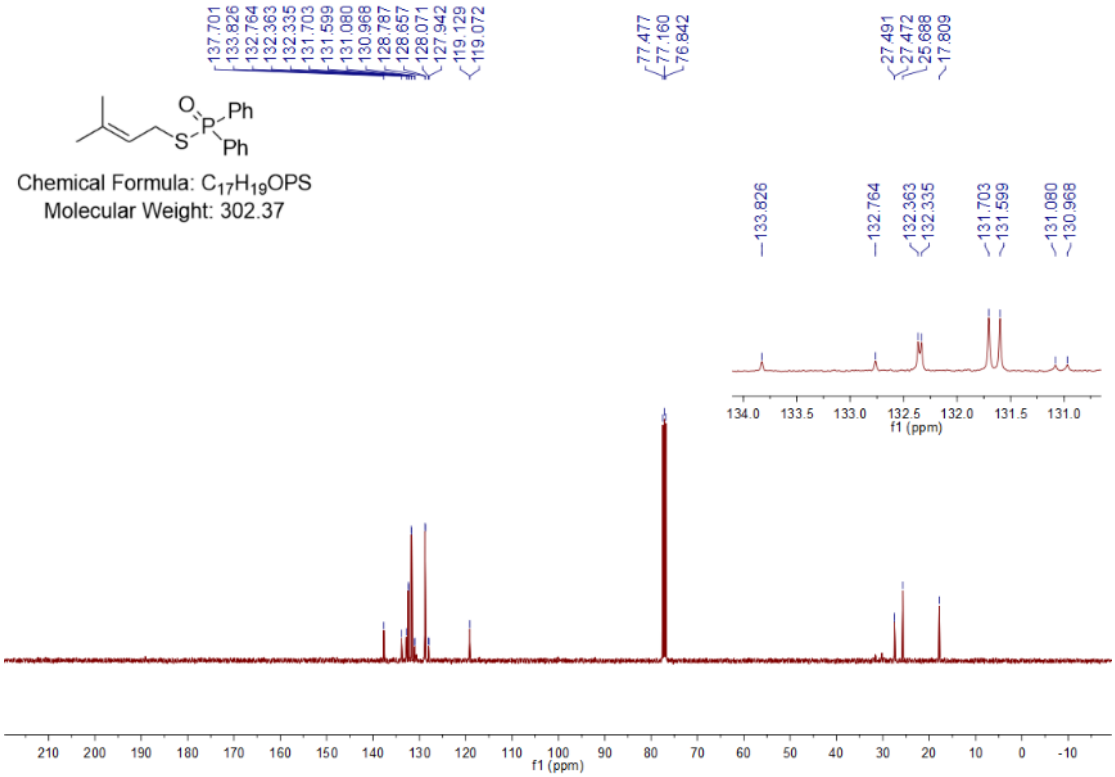


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

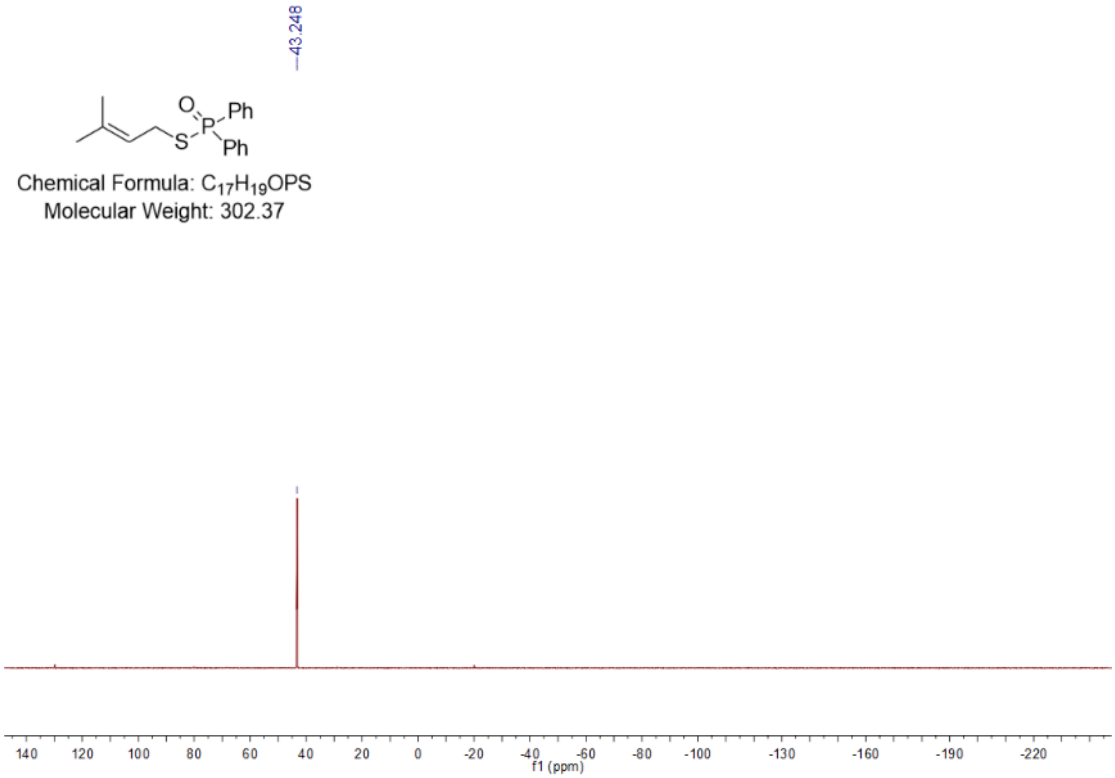
S-(3-methylbut-2-en-1-yl) diphenylphosphinothioate (3u)



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

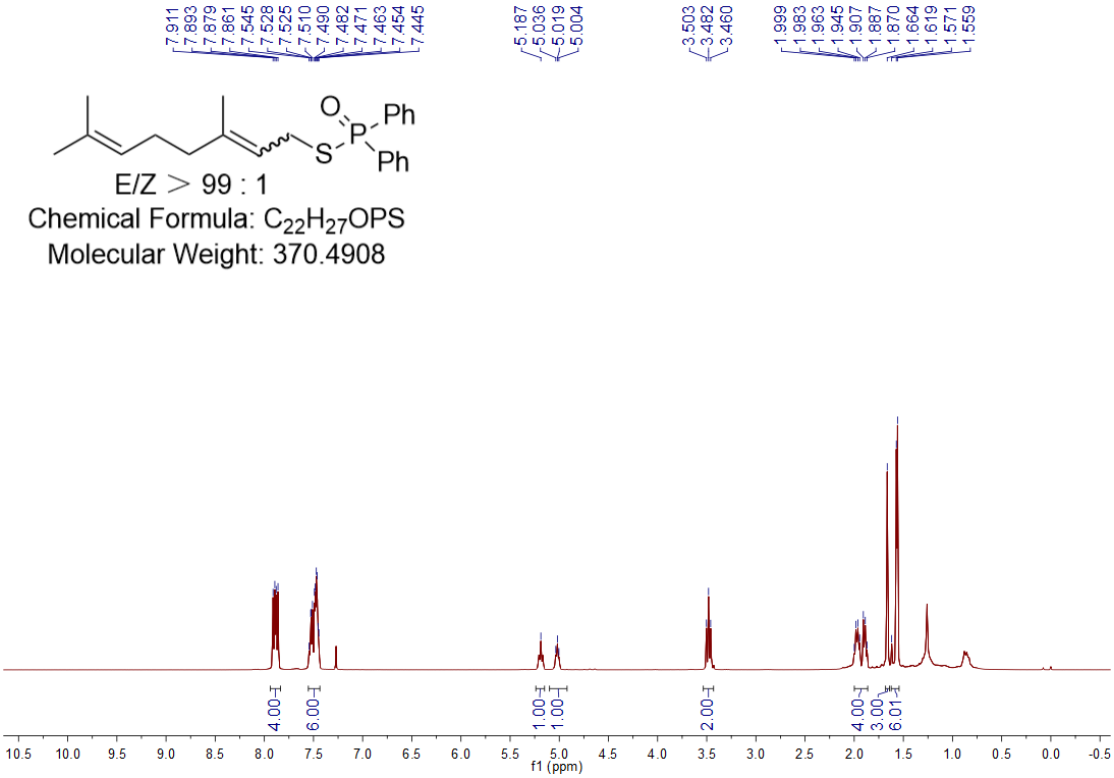


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

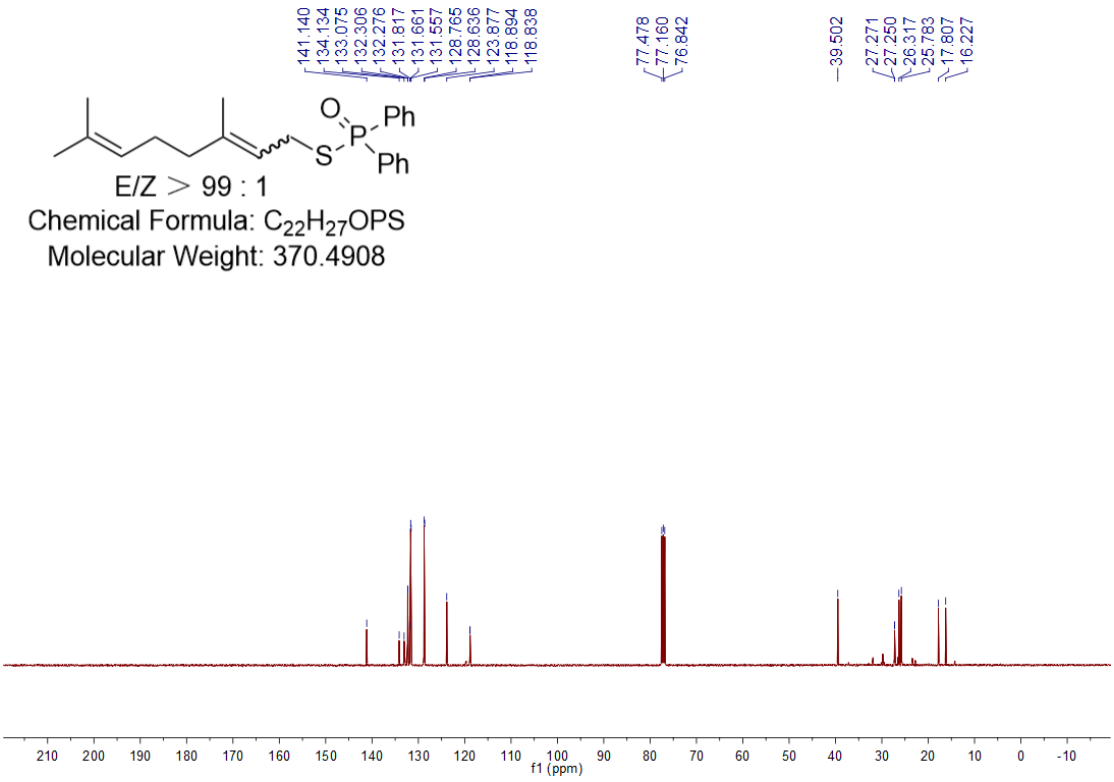


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

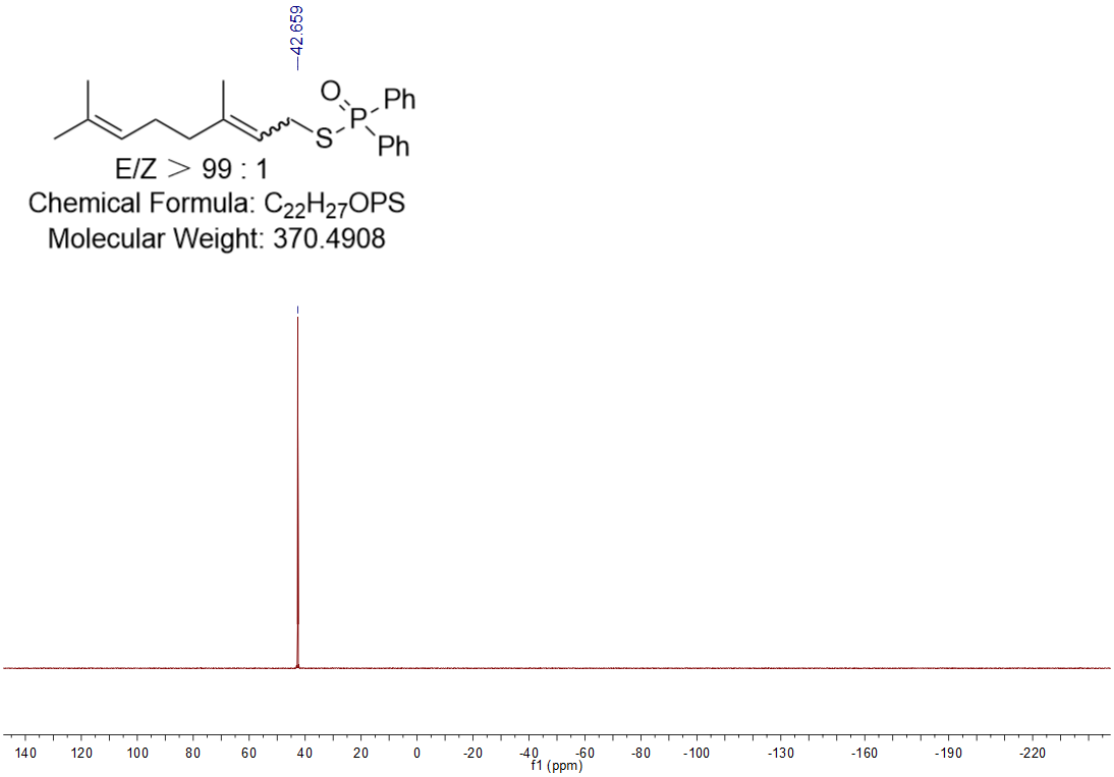
S-(3,7-dimethylocta-2,6-dien-1-yl) diphenylphosphinothioate (3v)



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

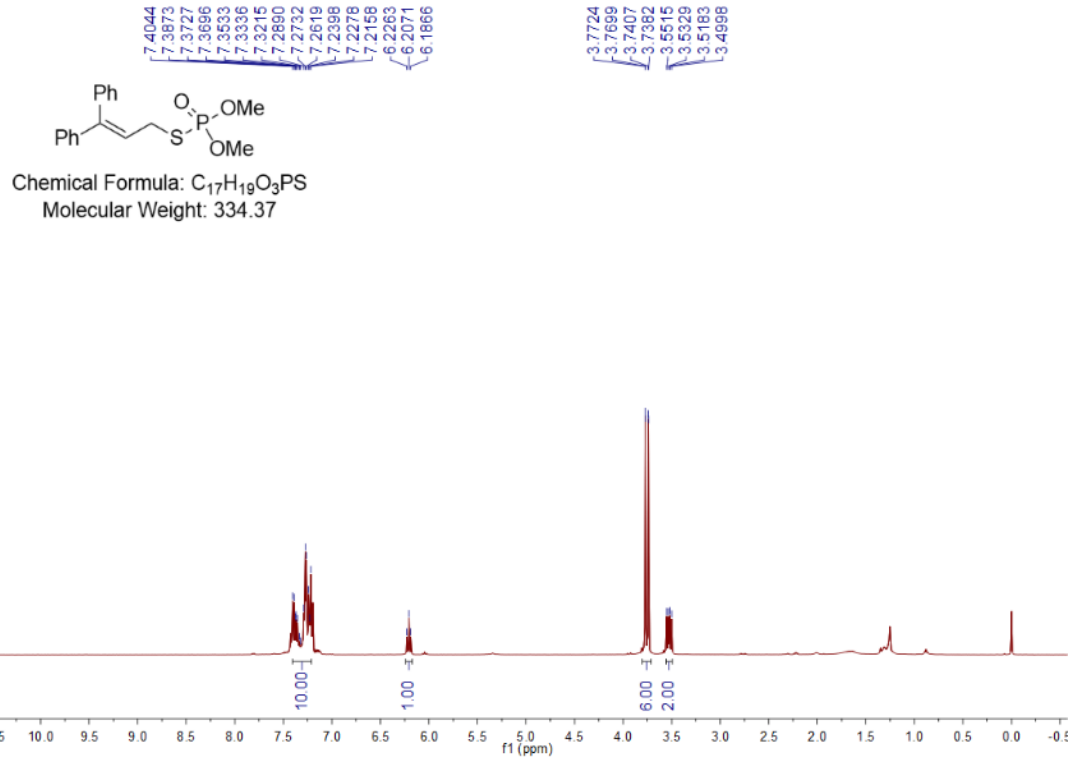


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

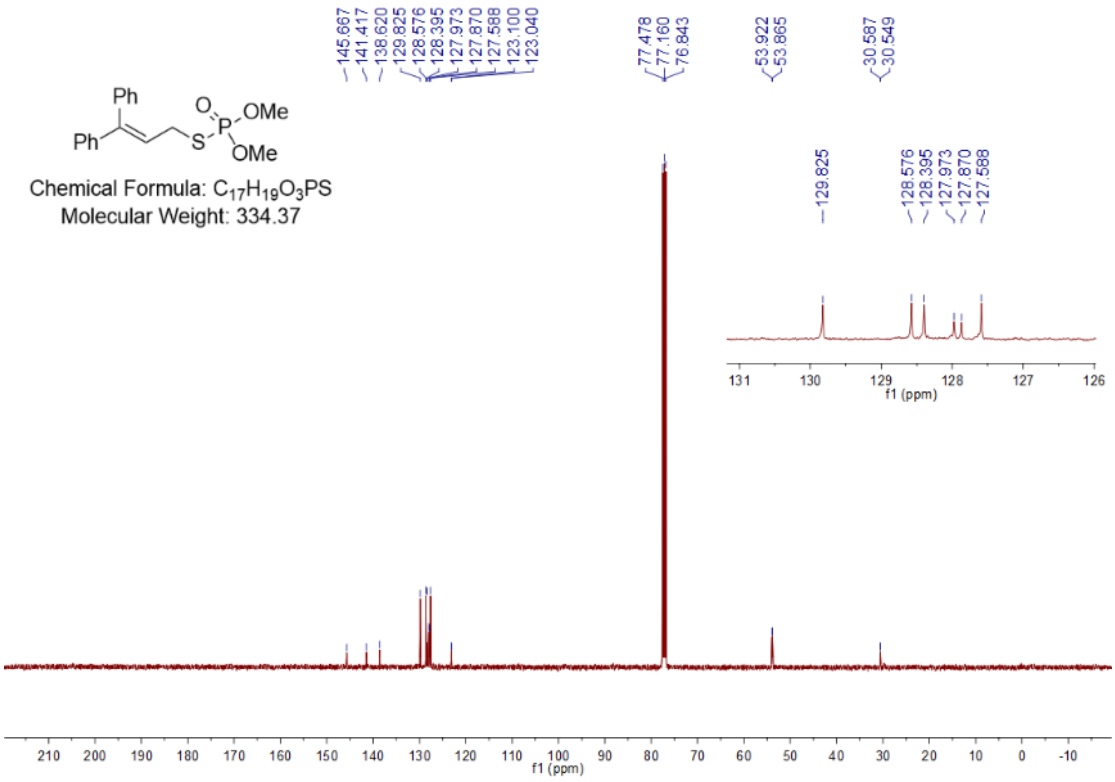


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

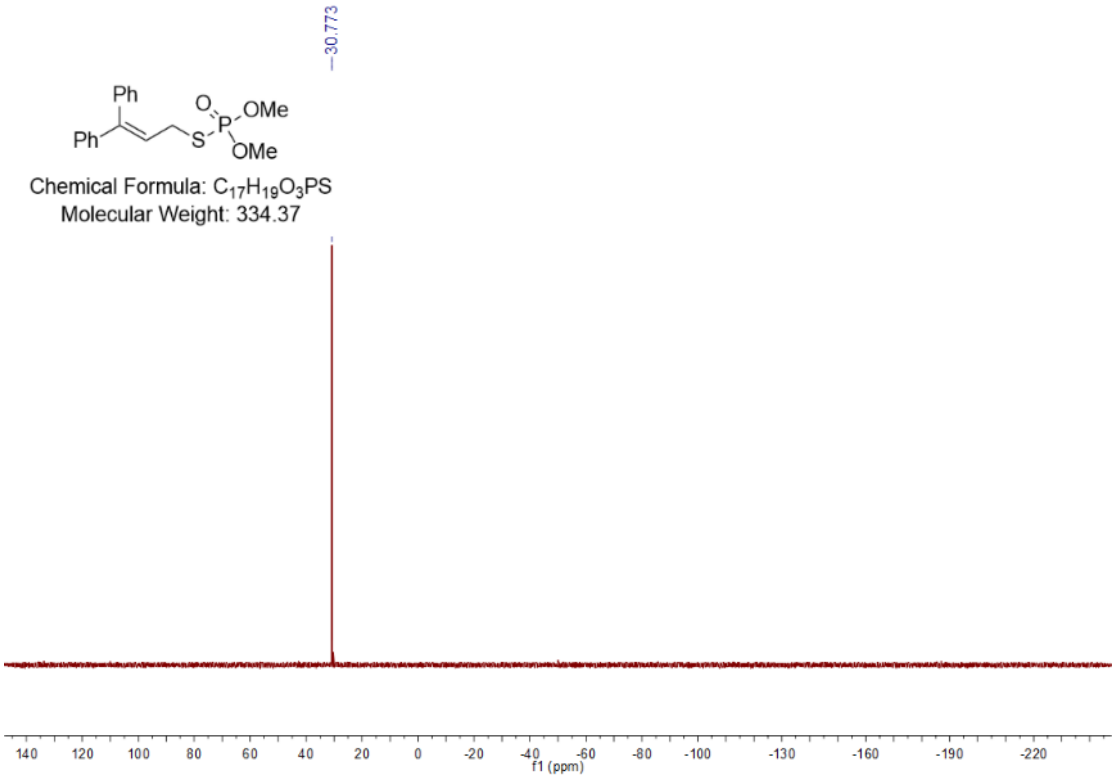
S-(3,3-diphenylallyl) O,O-dimethyl phosphorothioate (4a)



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

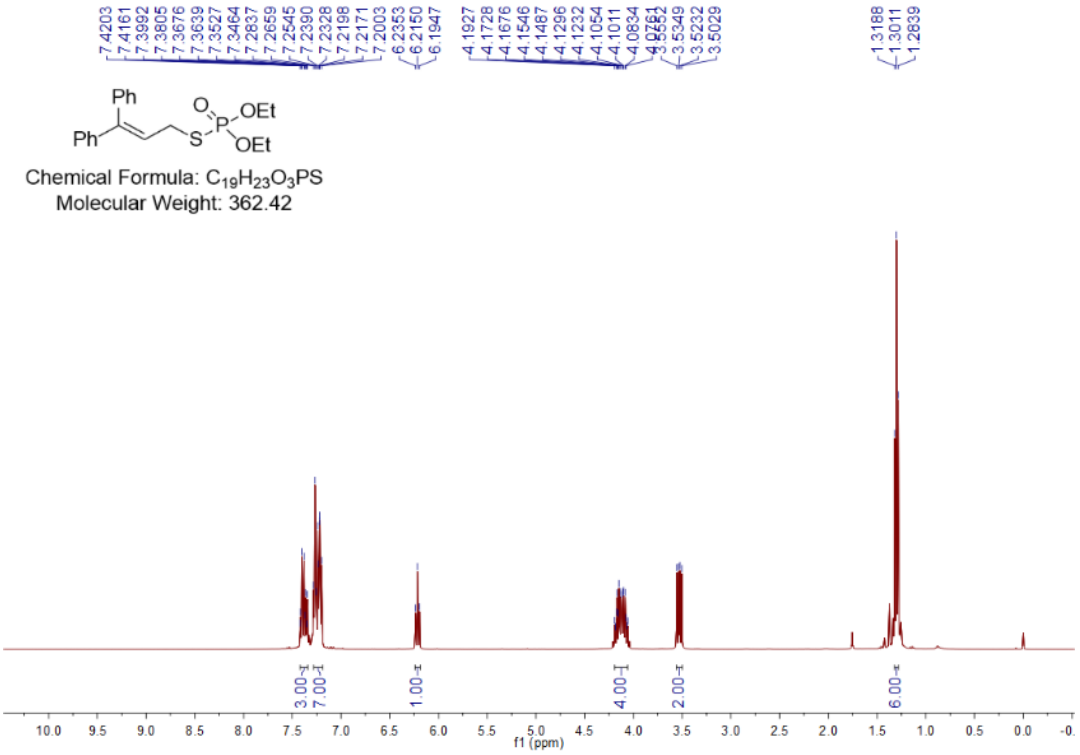


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

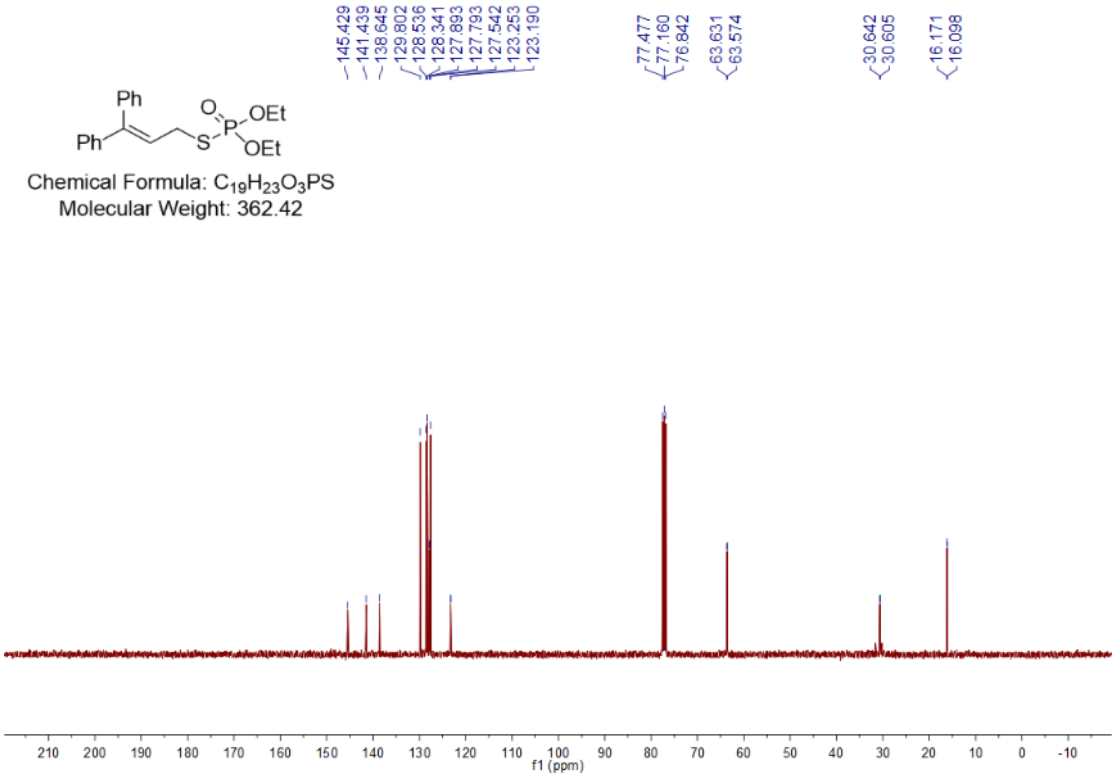


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

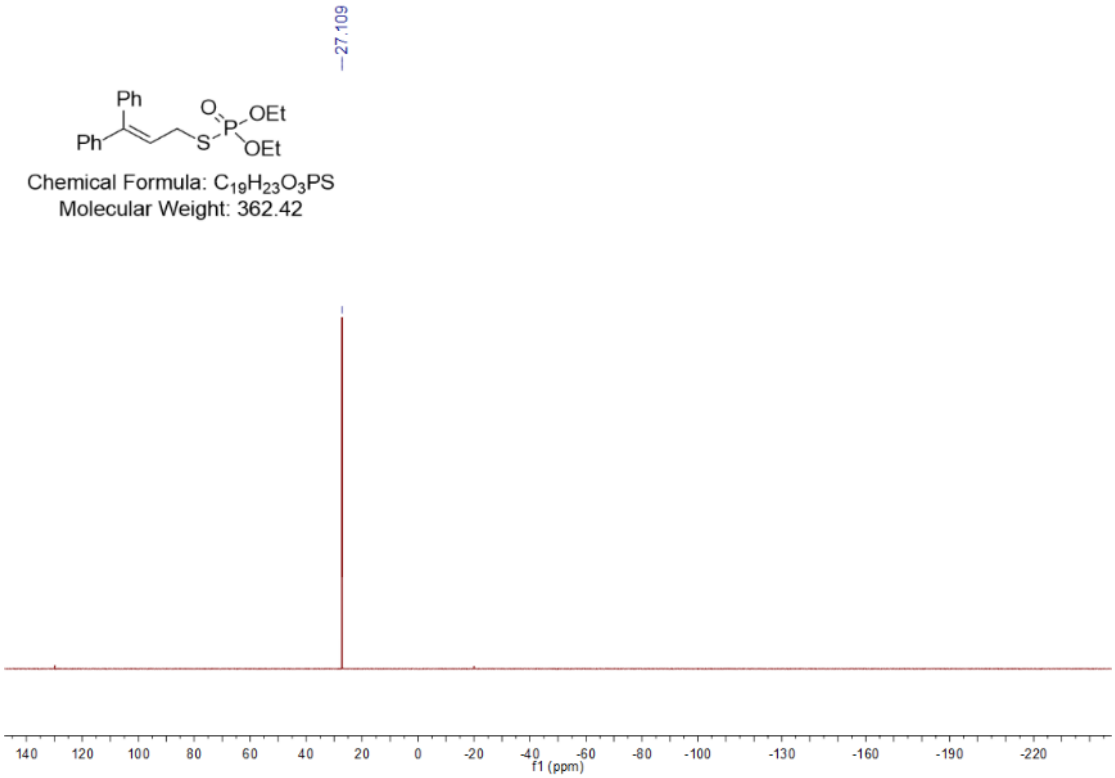
S-(3,3-diphenylallyl) O,O-diethyl phosphorothioate (4b)



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

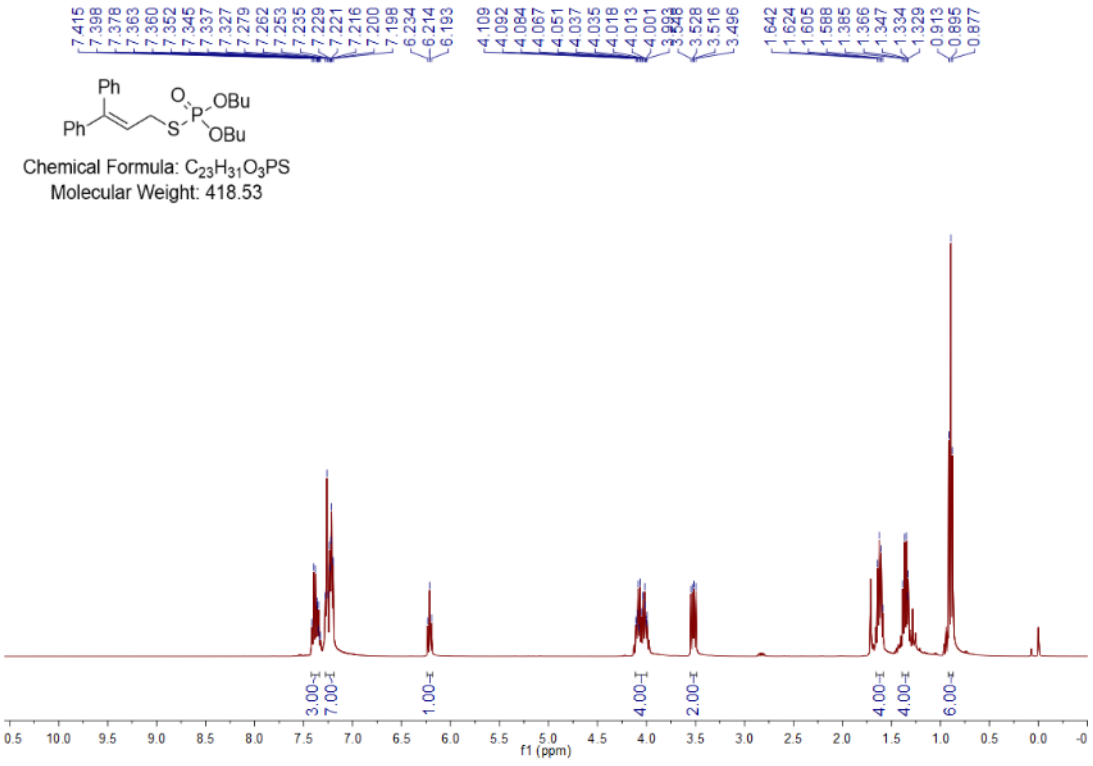


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

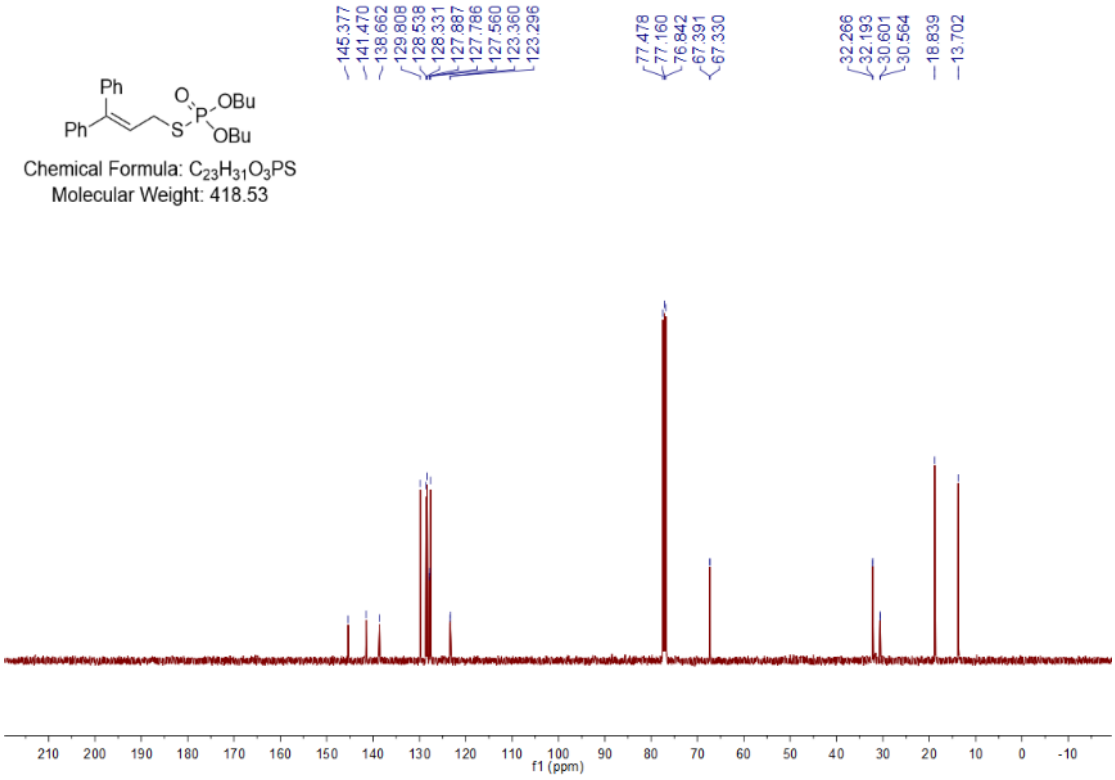


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

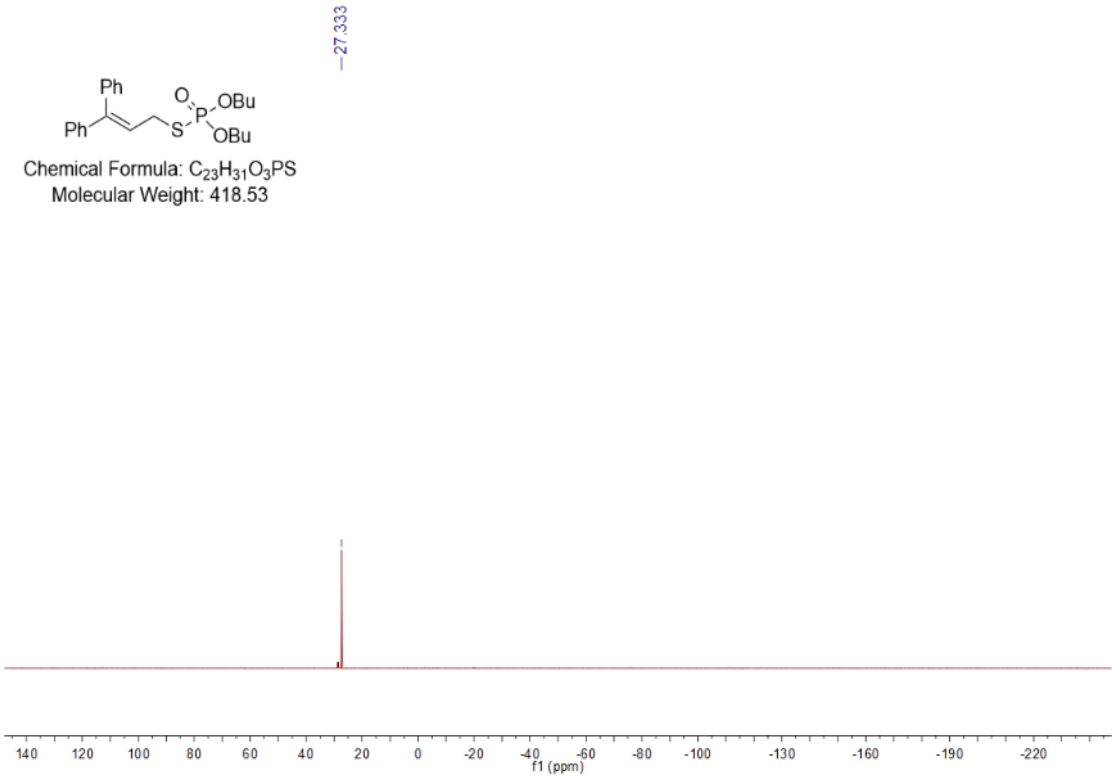
O,O-dibutyl S-(3,3-diphenylallyl) phosphorothioate (4c)



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

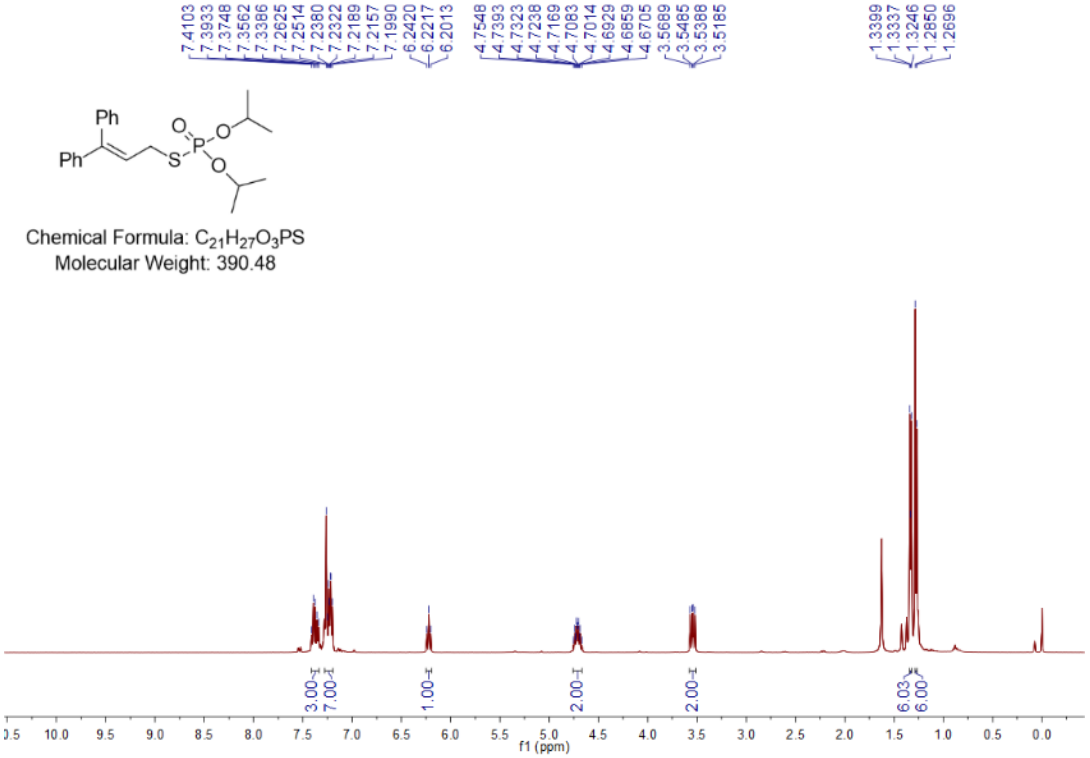


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

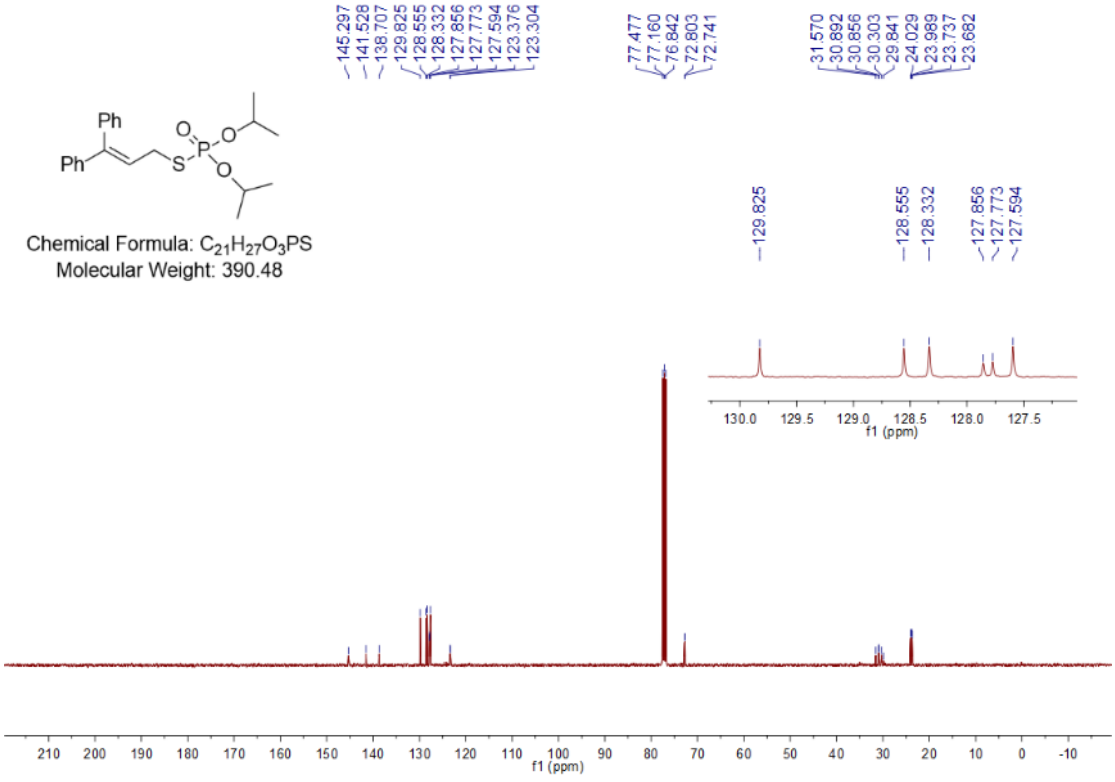


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

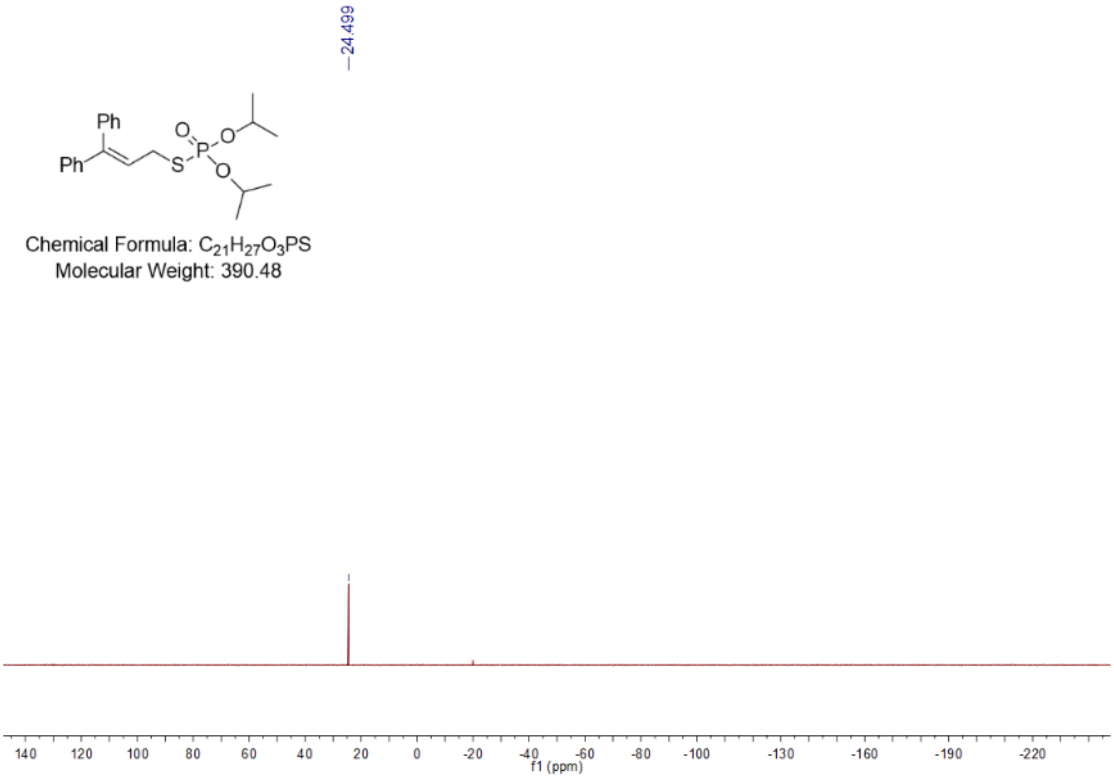
S-(3,3-diphenylallyl) O,O-diisopropyl phosphorothioate (4d)



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

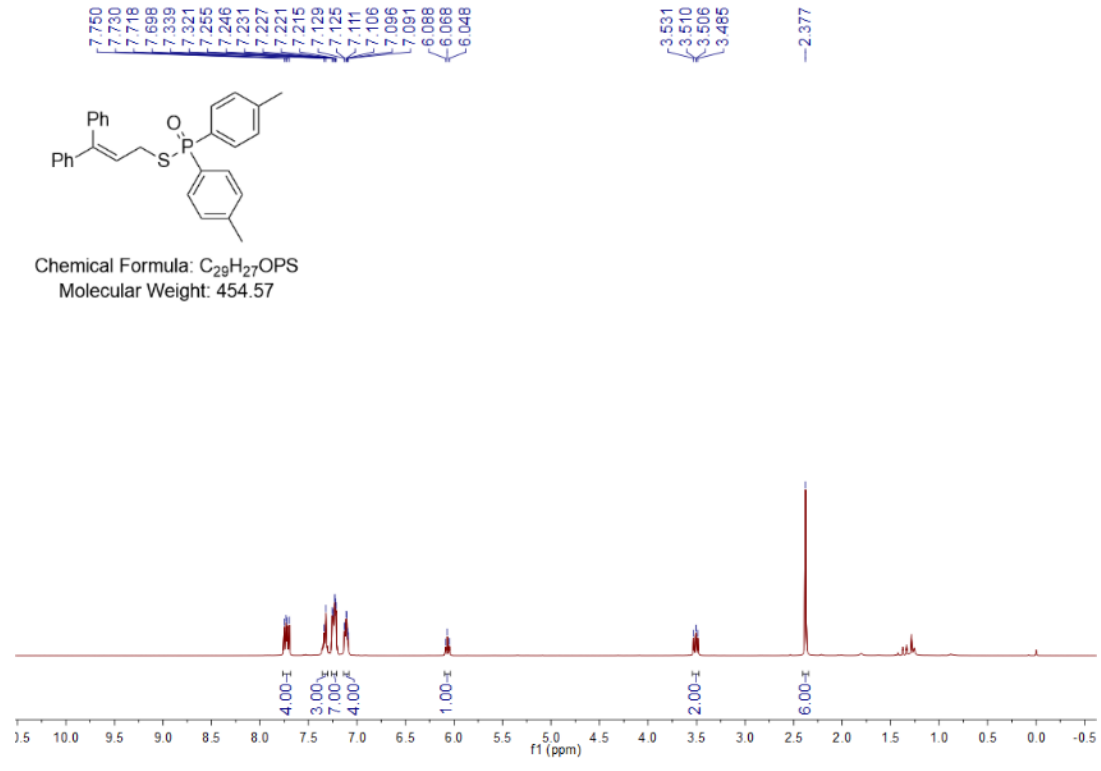


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

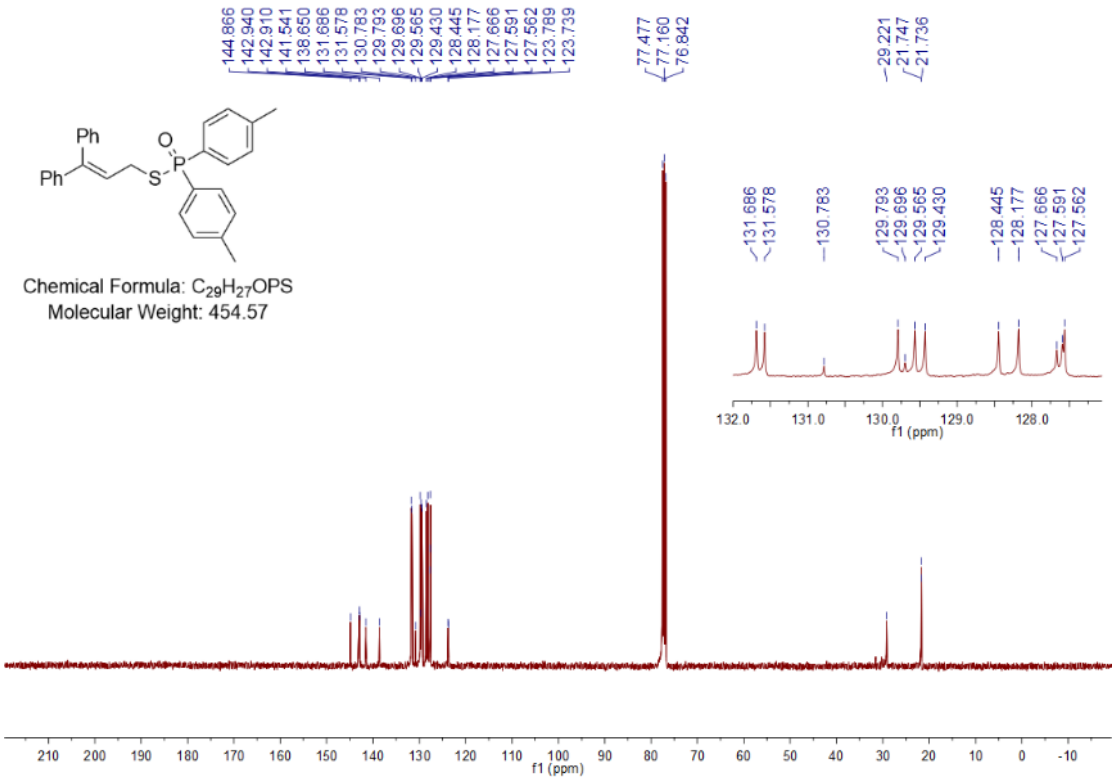


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

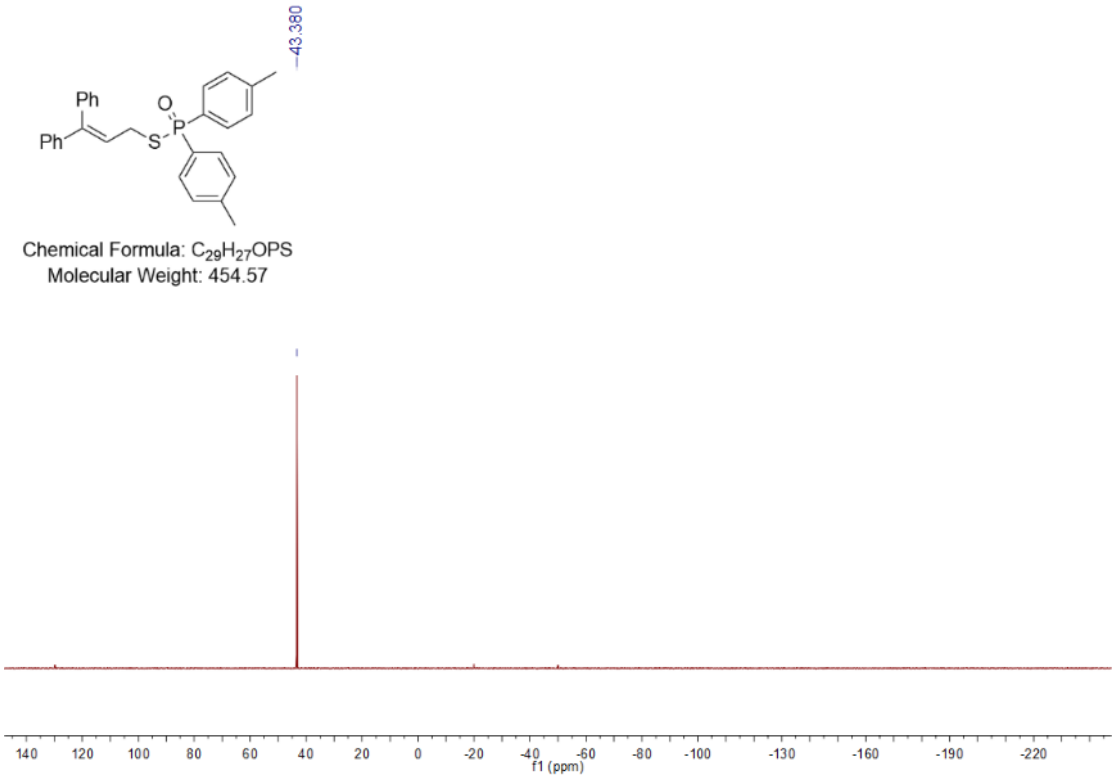
S-(3,3-diphenylallyl) di-p-tolylphosphinothioate (4e)



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

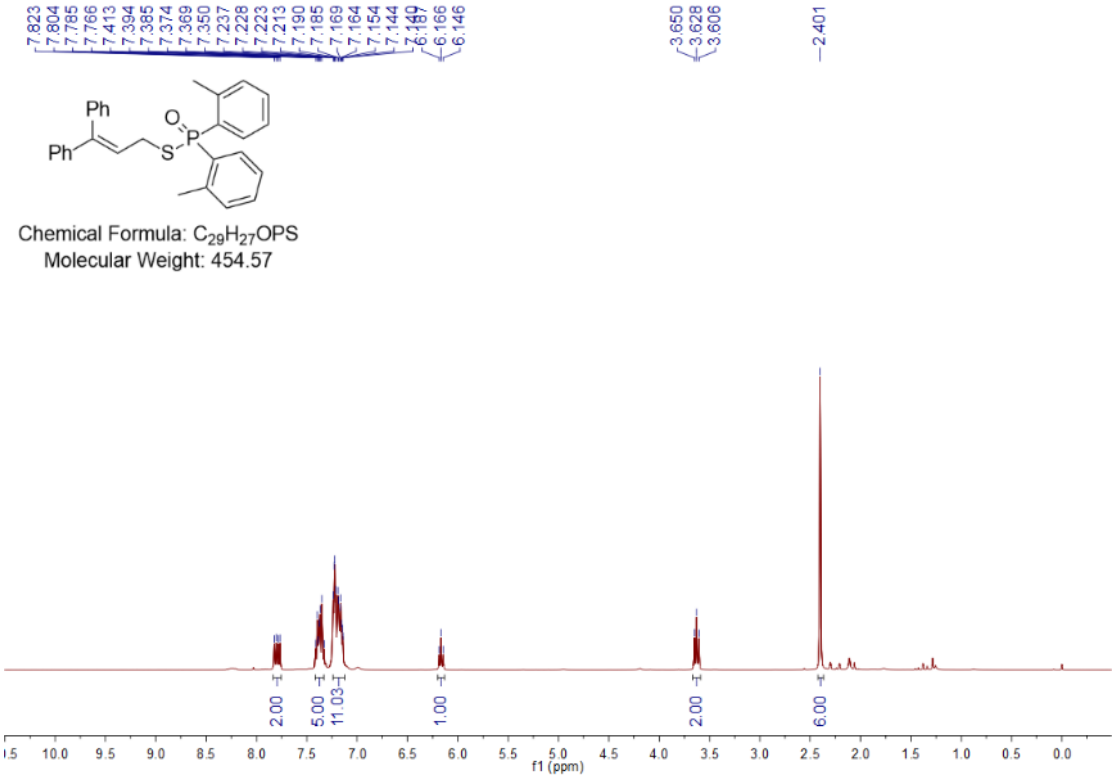


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

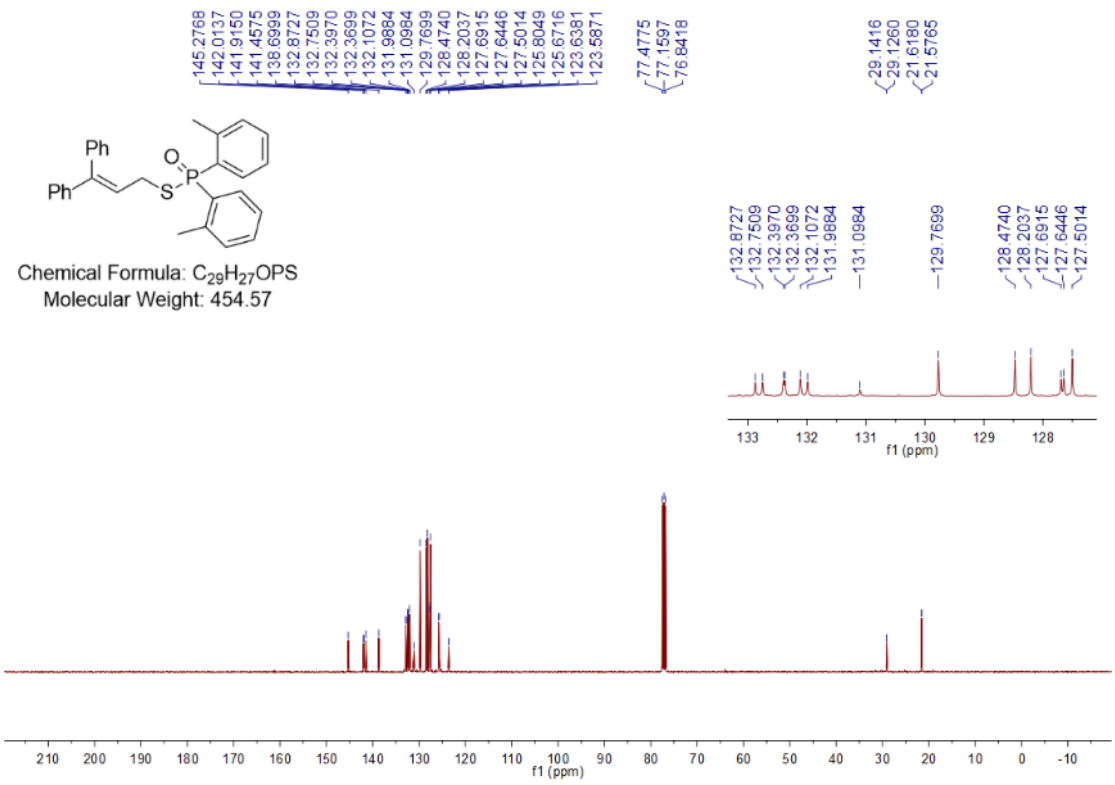


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

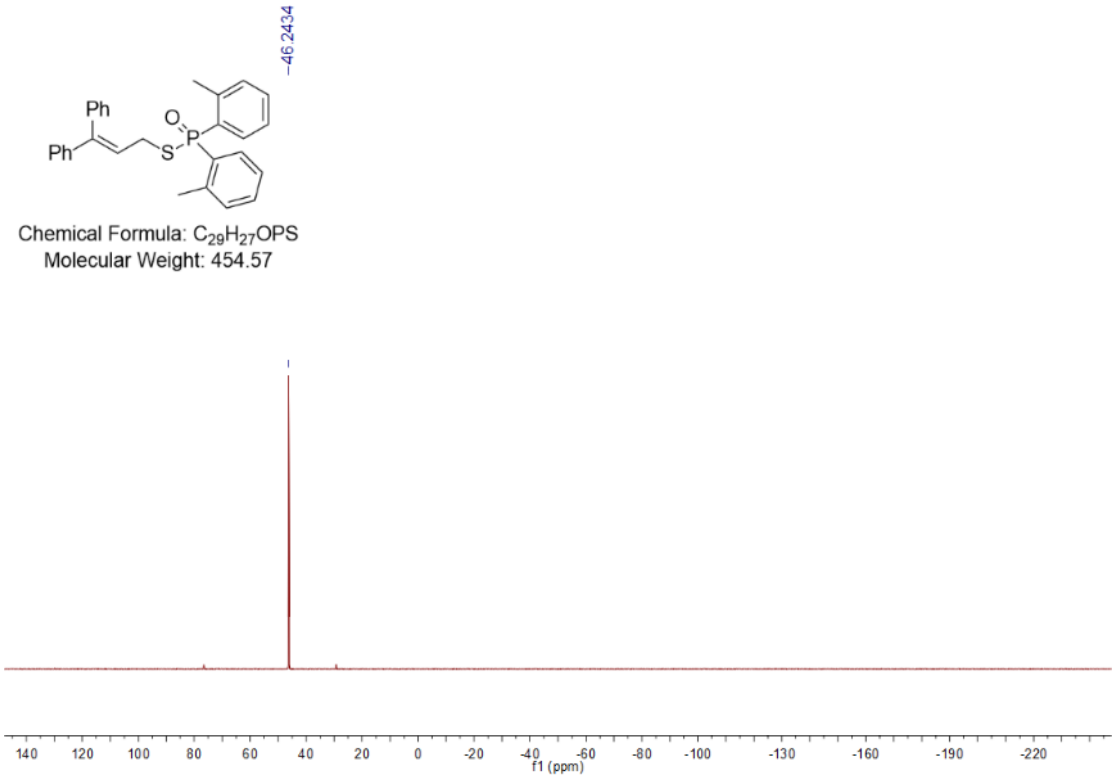
S-(3,3-diphenylallyl) di-o-tolylphosphinothioate (4f)



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

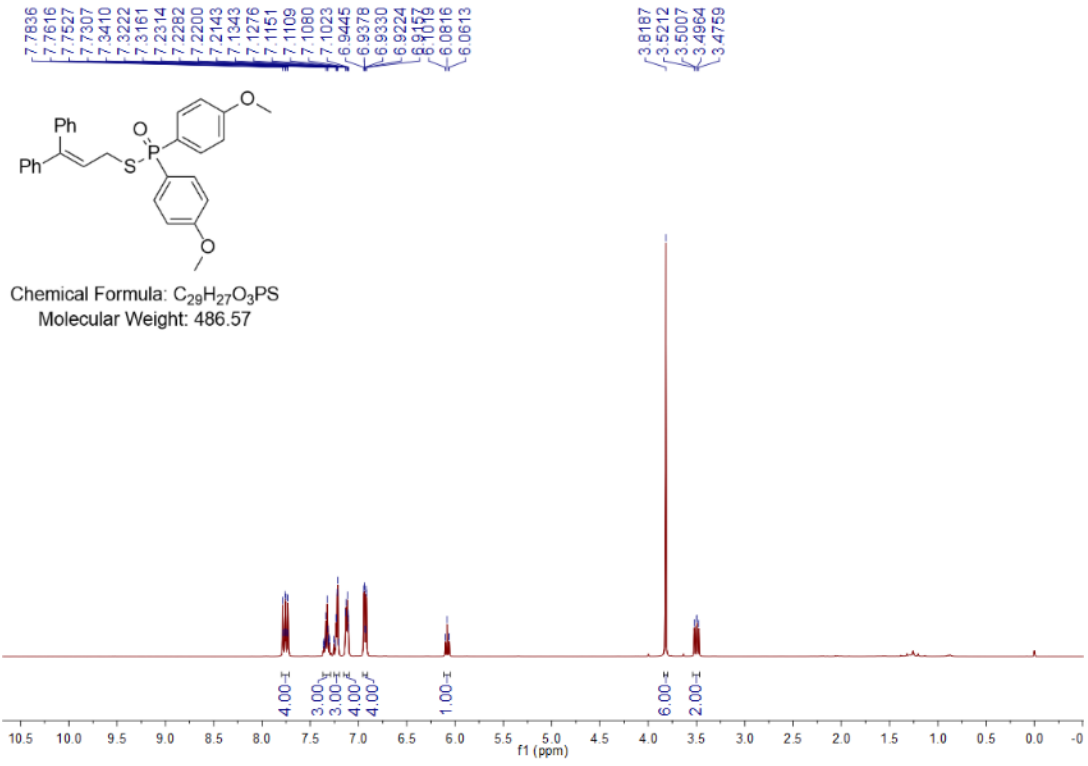


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

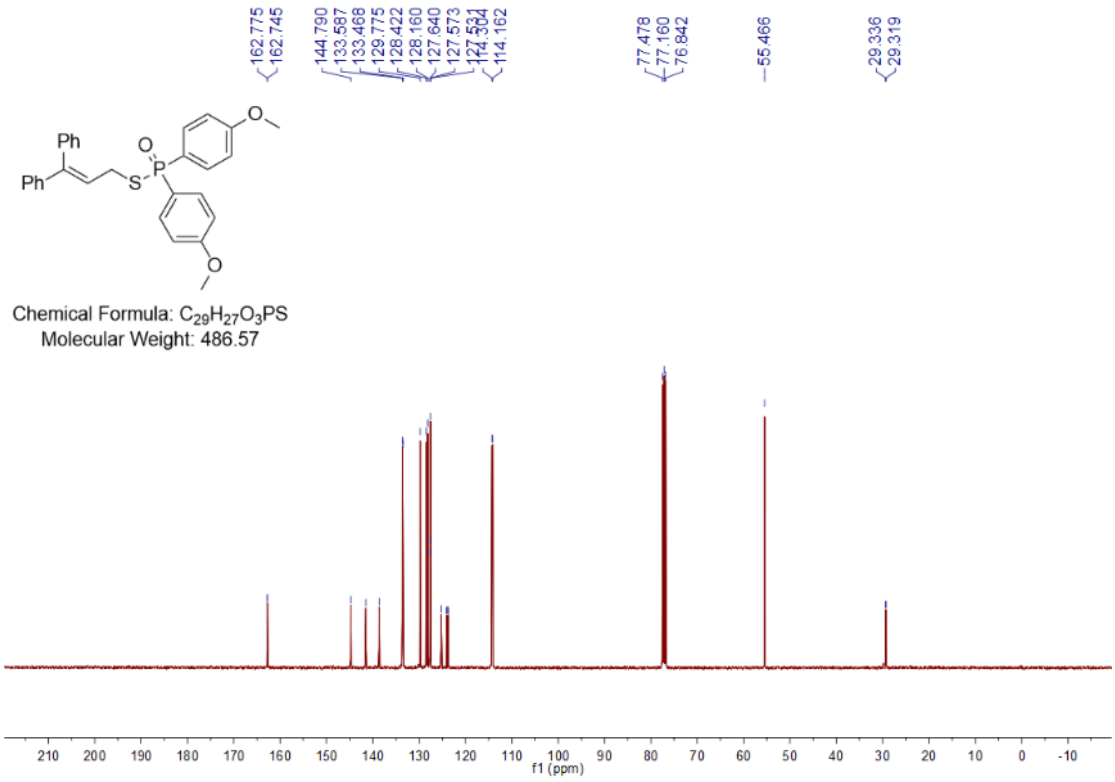


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

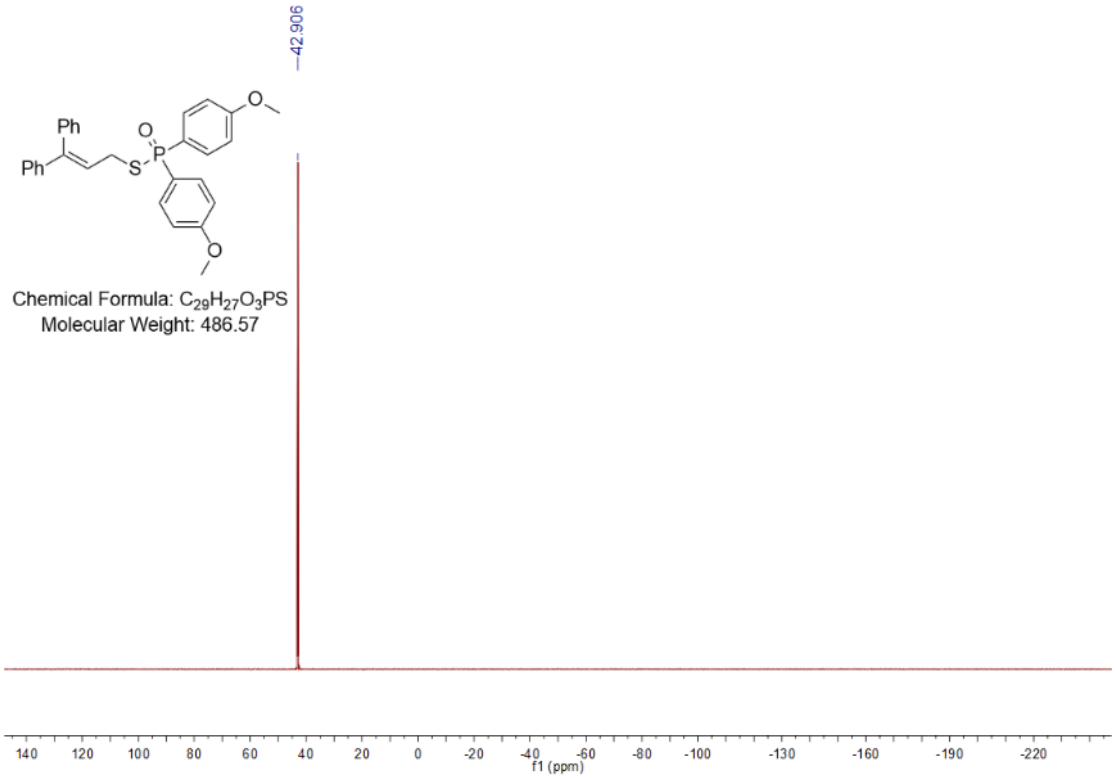
S-(3,3-diphenylallyl) bis(4-methoxyphenyl)phosphinothioate (4g)



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

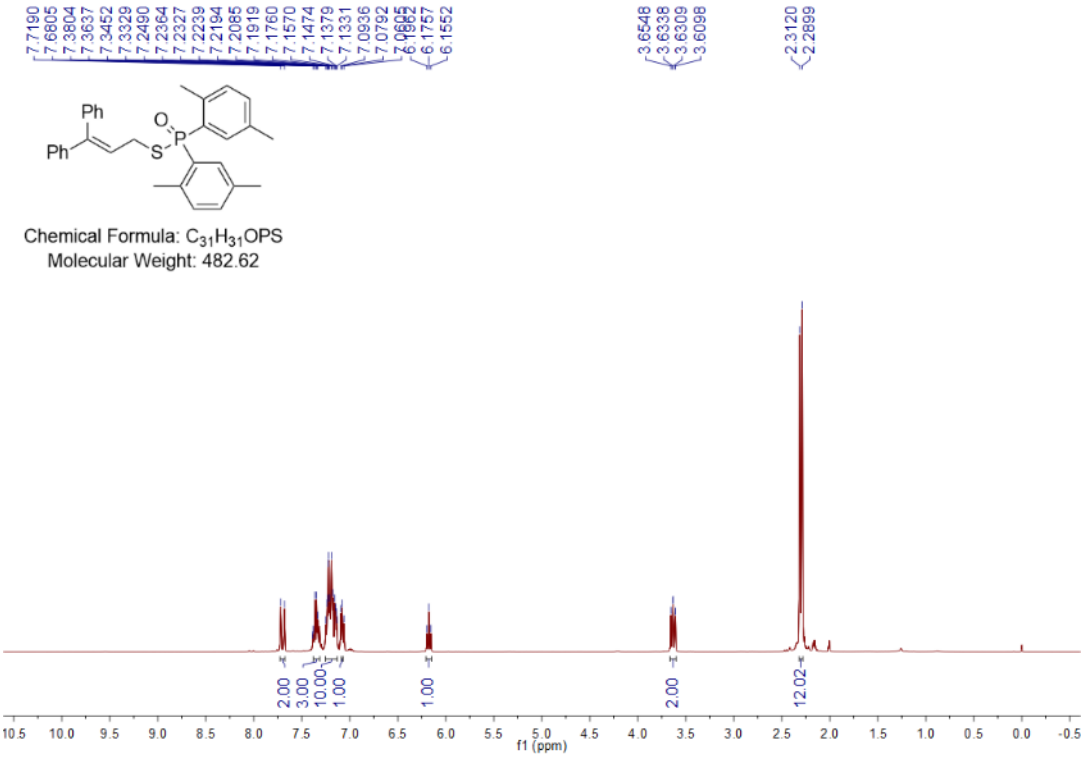


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

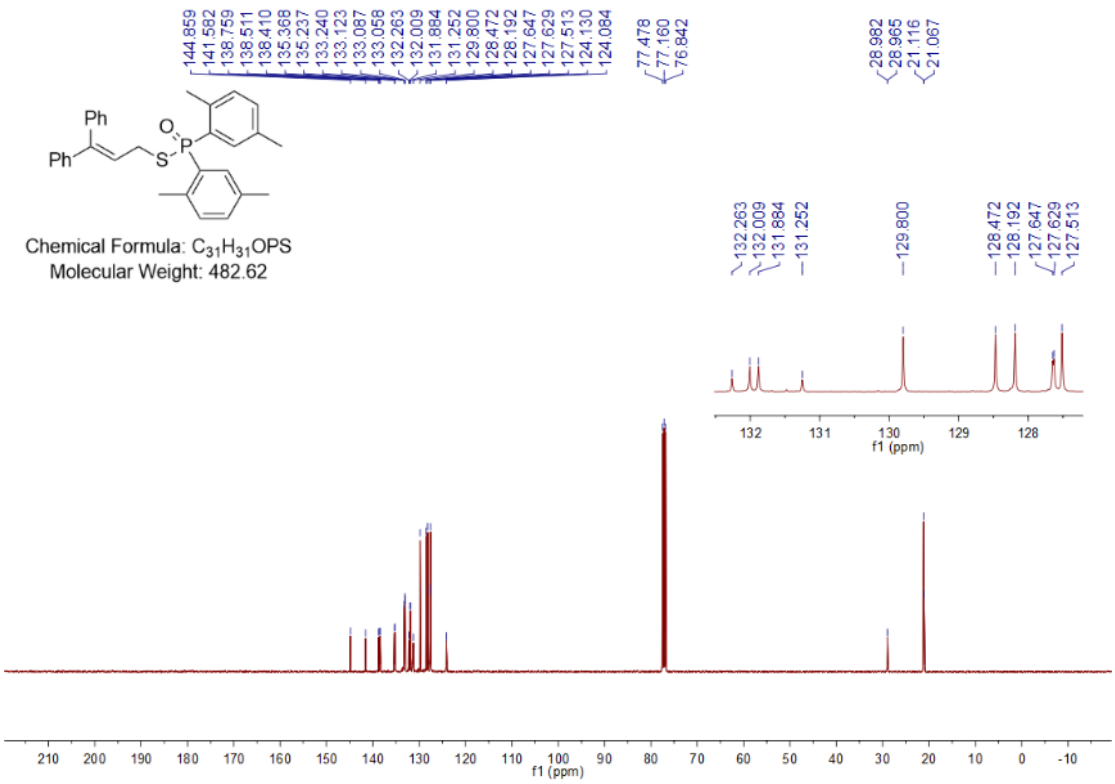


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

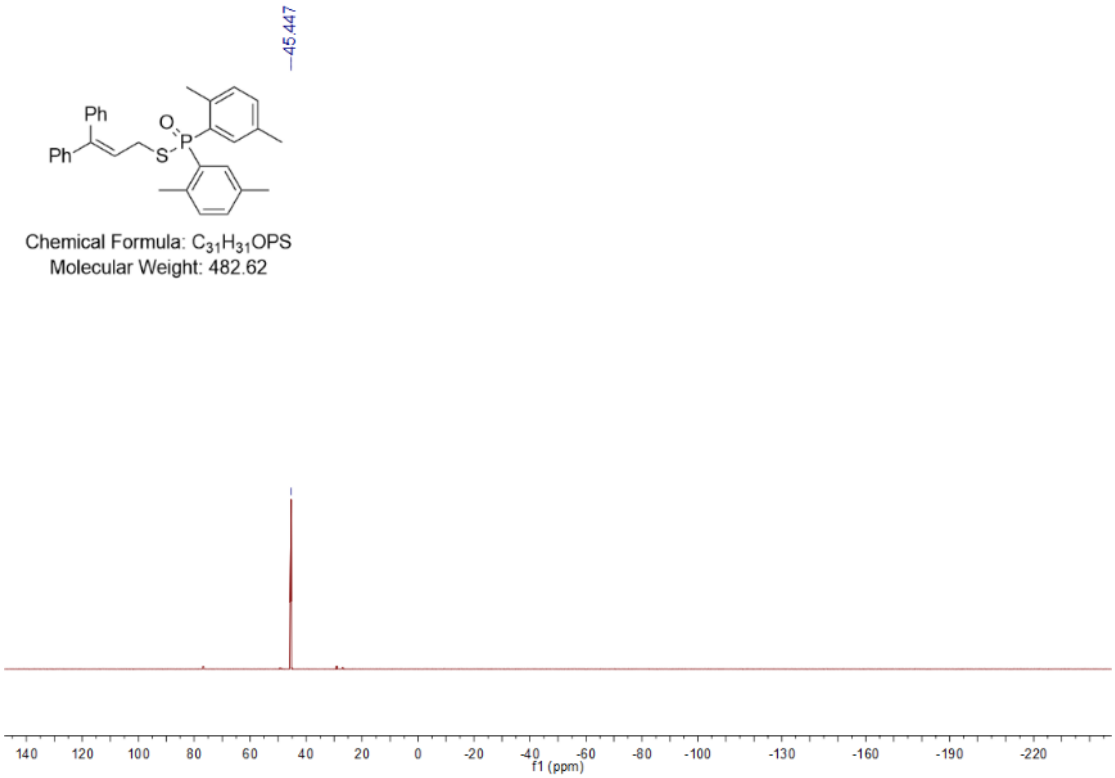
S-(3,3-diphenylallyl) bis(2,5-dimethylphenyl)phosphinothioate (4h)



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

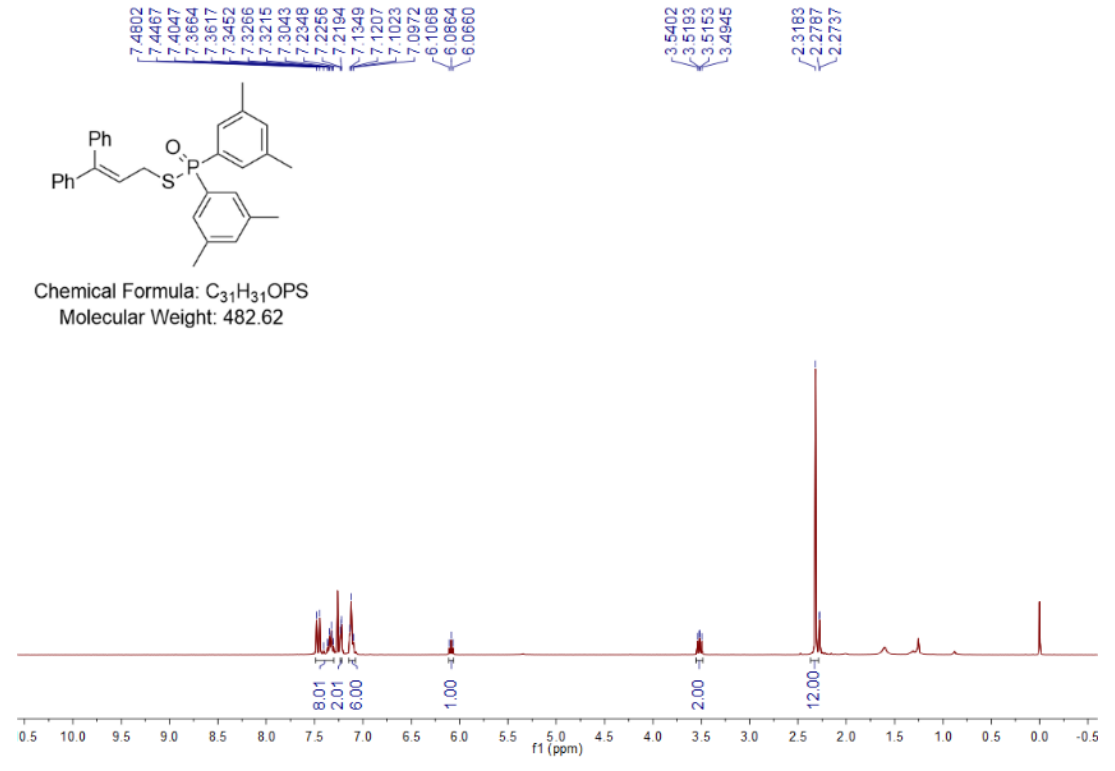


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

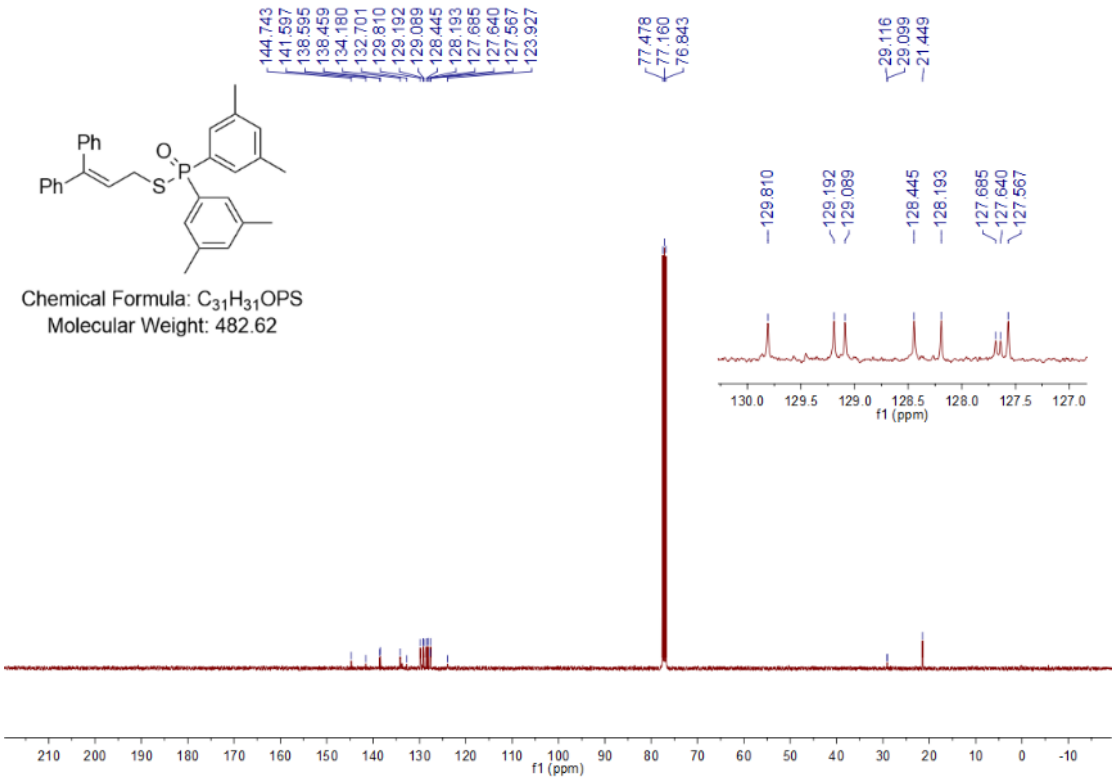


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

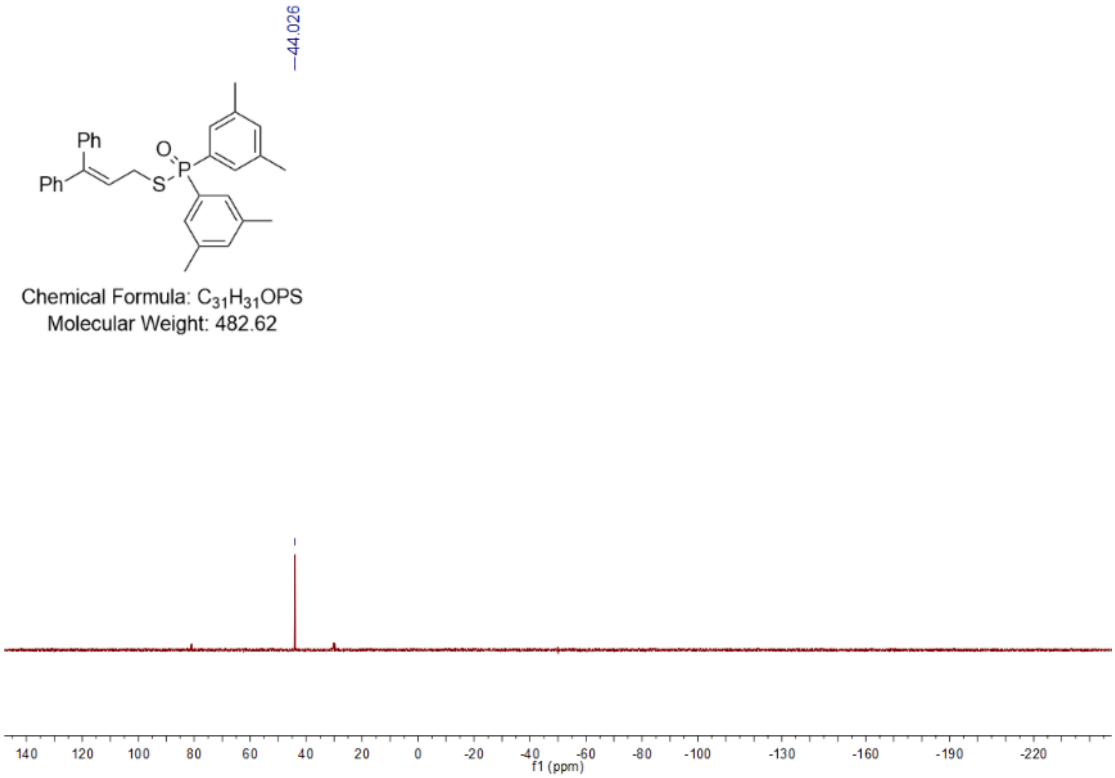
S-(3,3-diphenylallyl) bis(3,5-dimethylphenyl)phosphinothioate (4i)



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

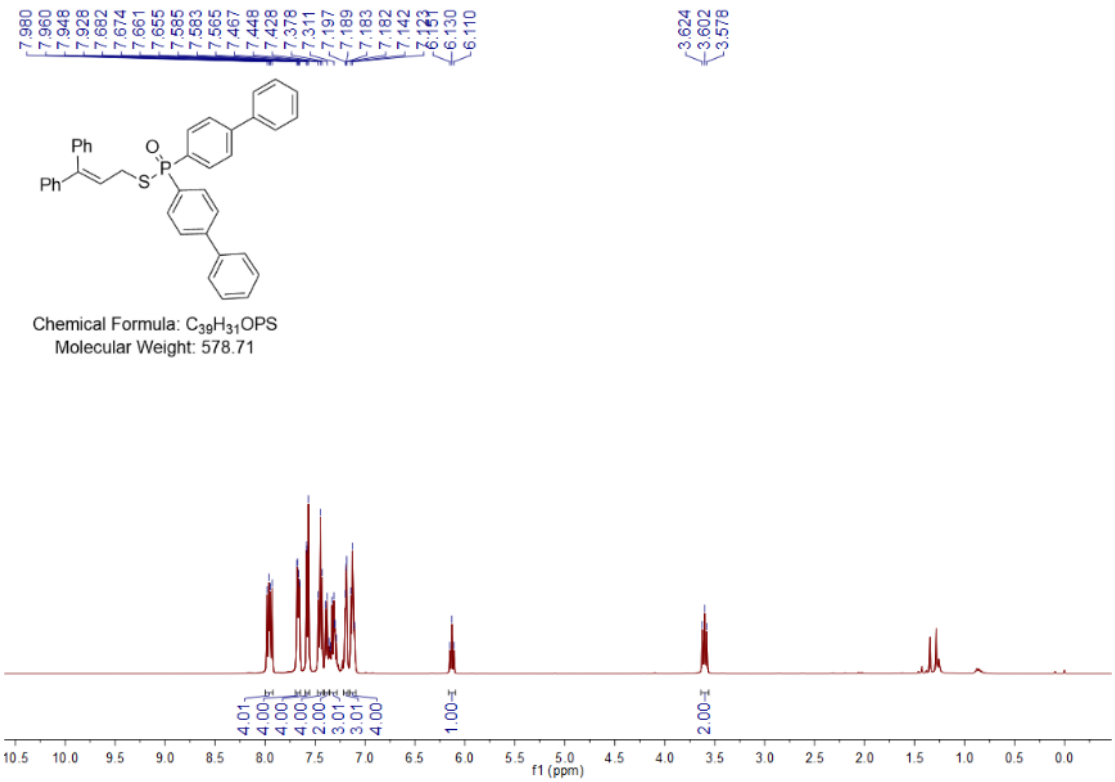


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

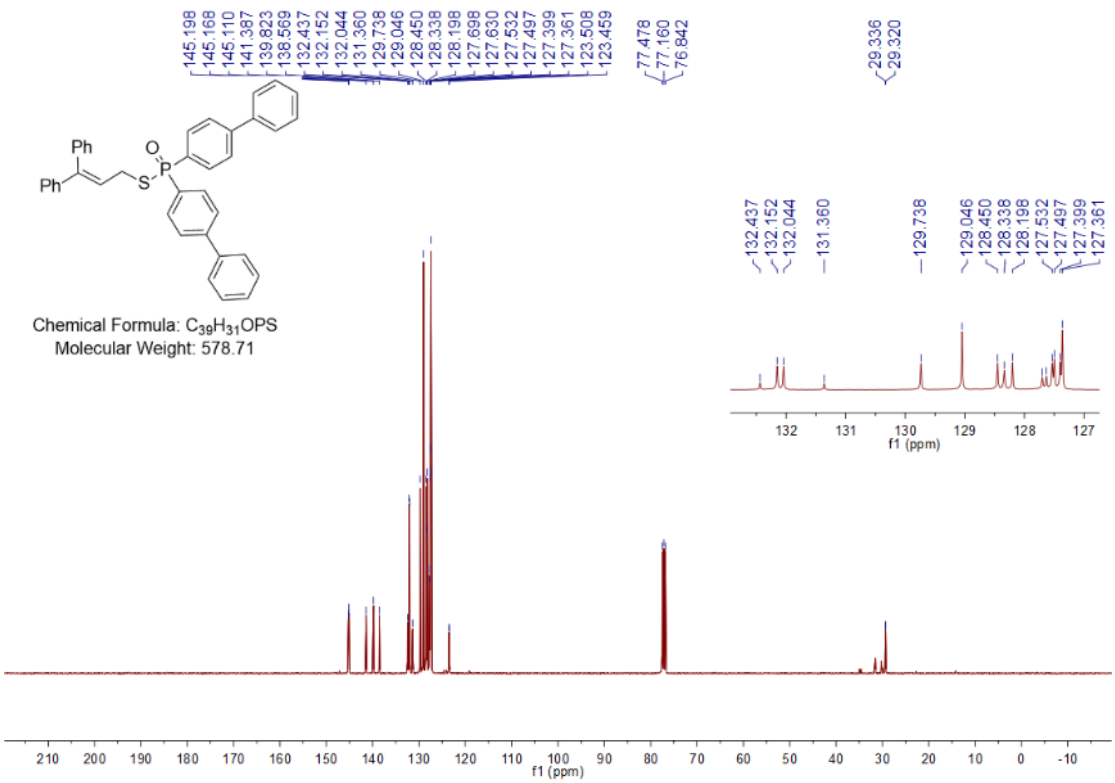


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

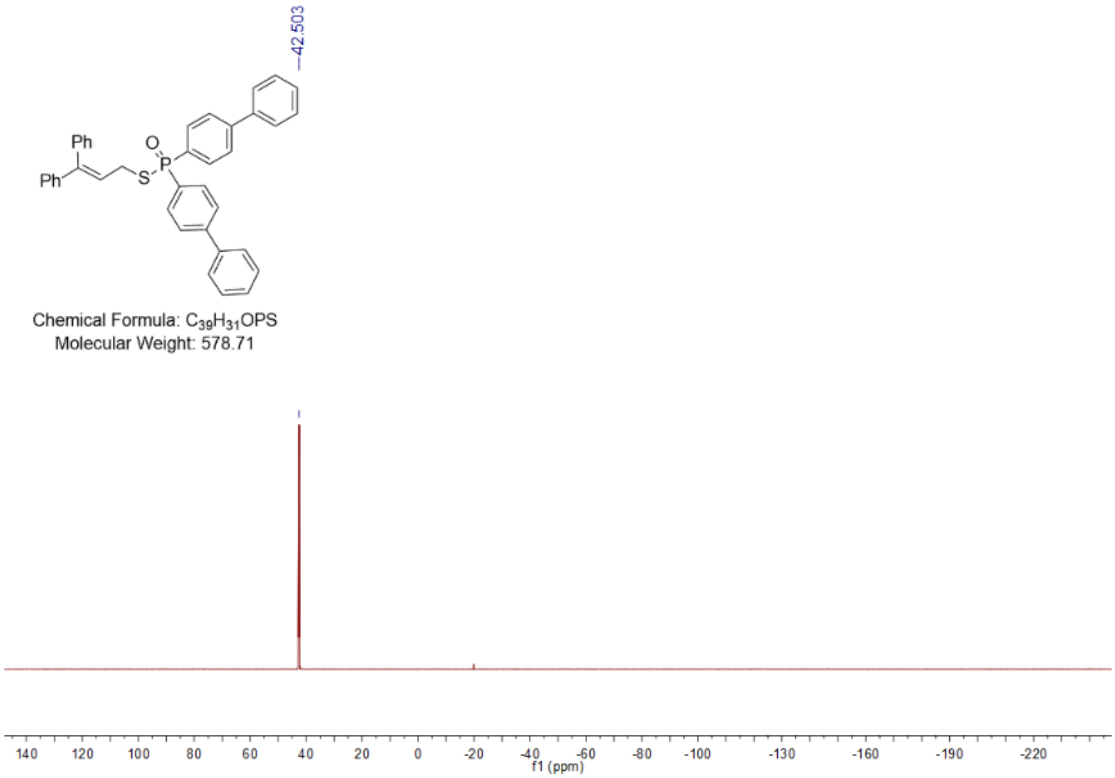
S-(3,3-diphenylallyl) di([1,1'-biphenyl]-4-yl)phosphinothioate (4j)



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

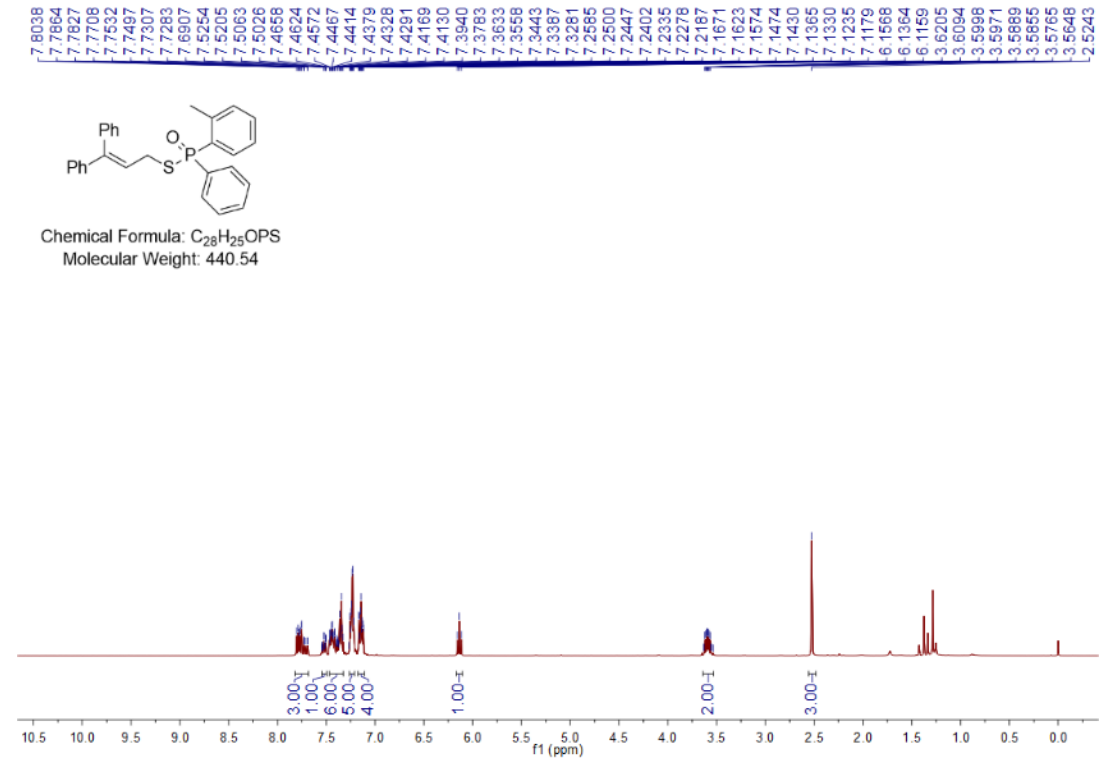


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

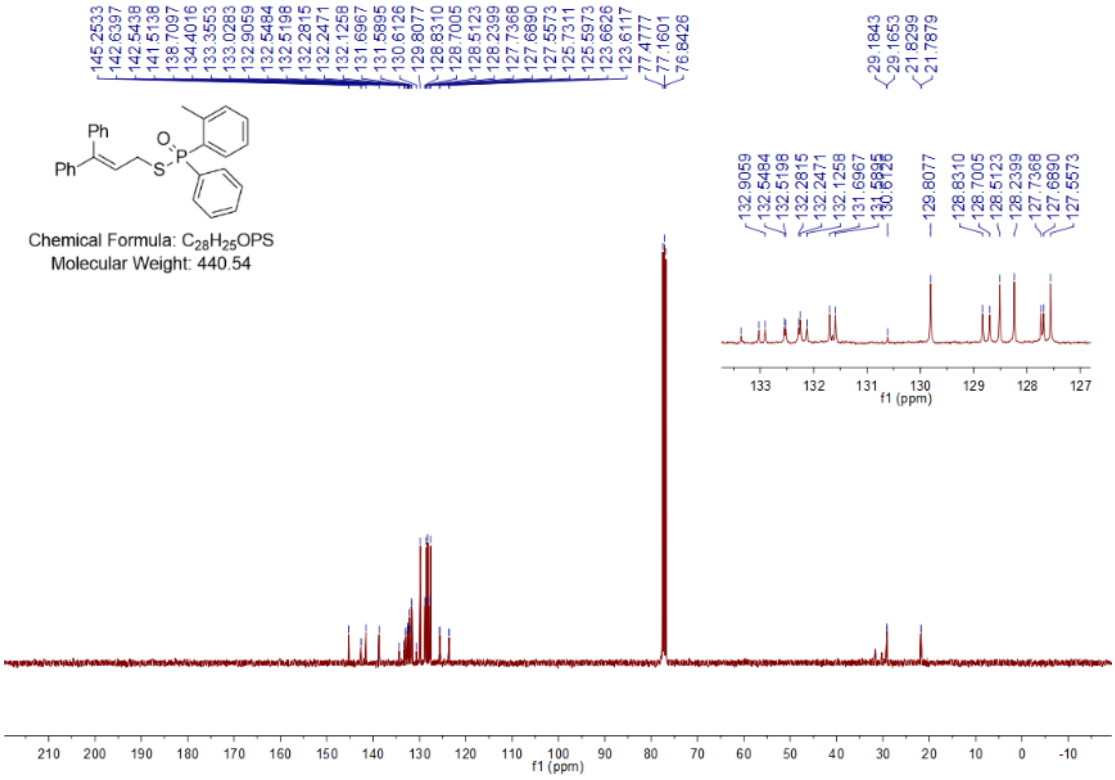


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

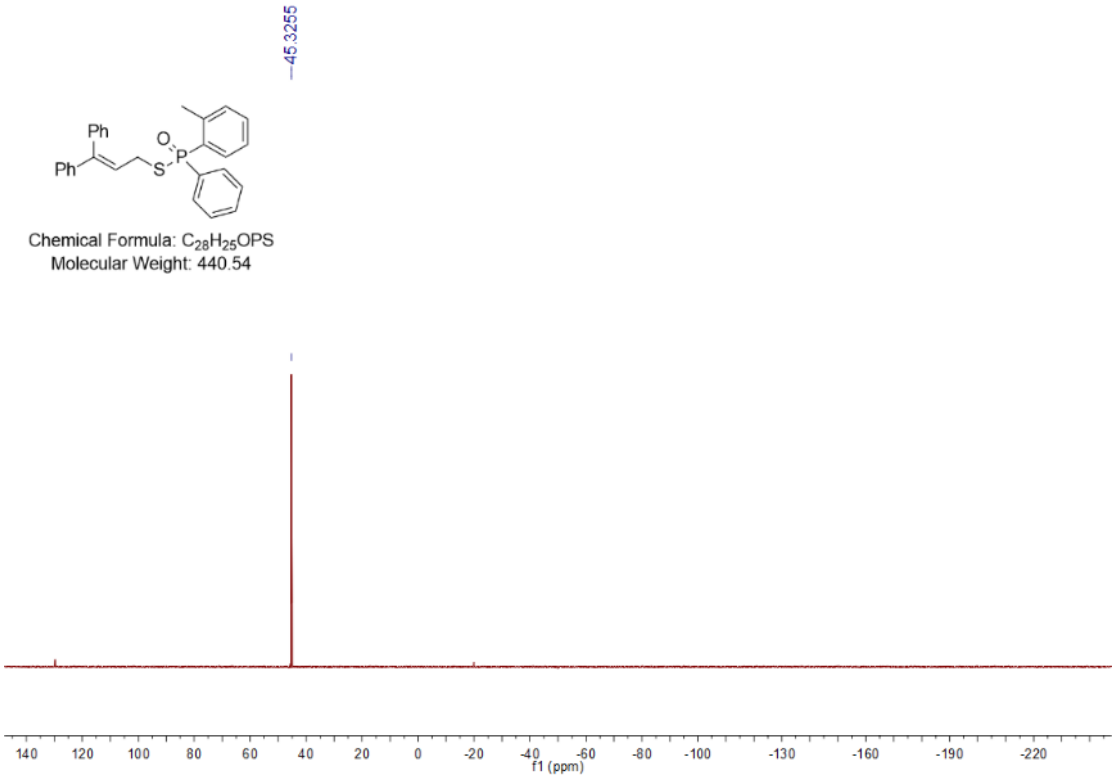
S-(3,3-diphenylallyl) phenyl(o-tolyl)phosphinothioate (4k)



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

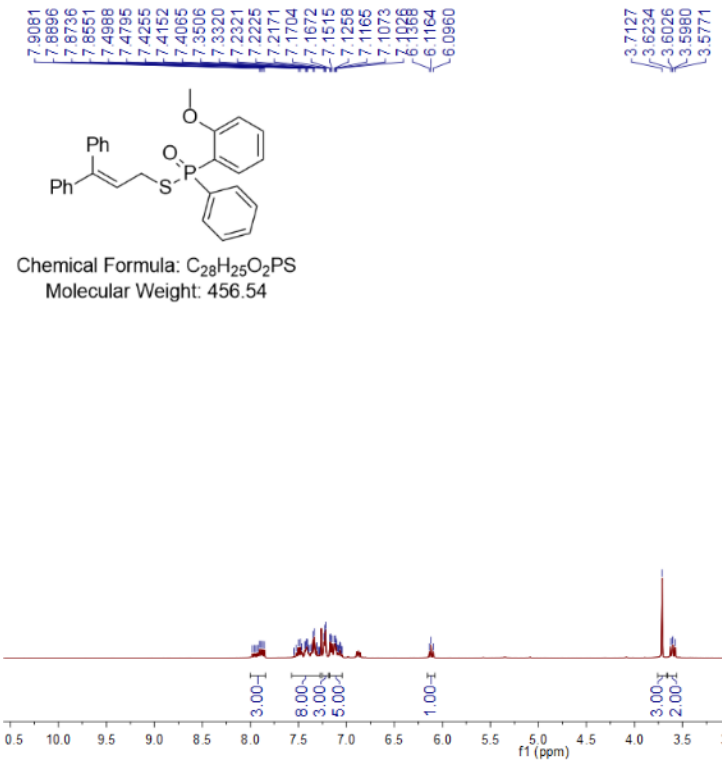


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

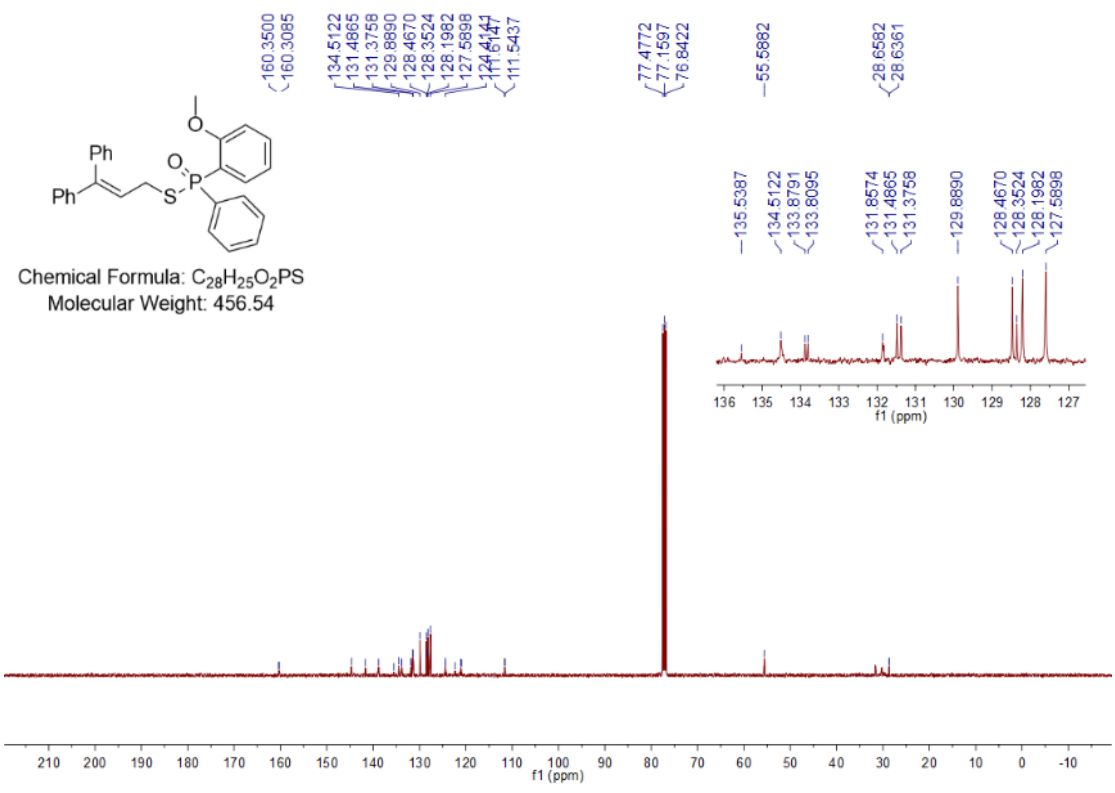


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

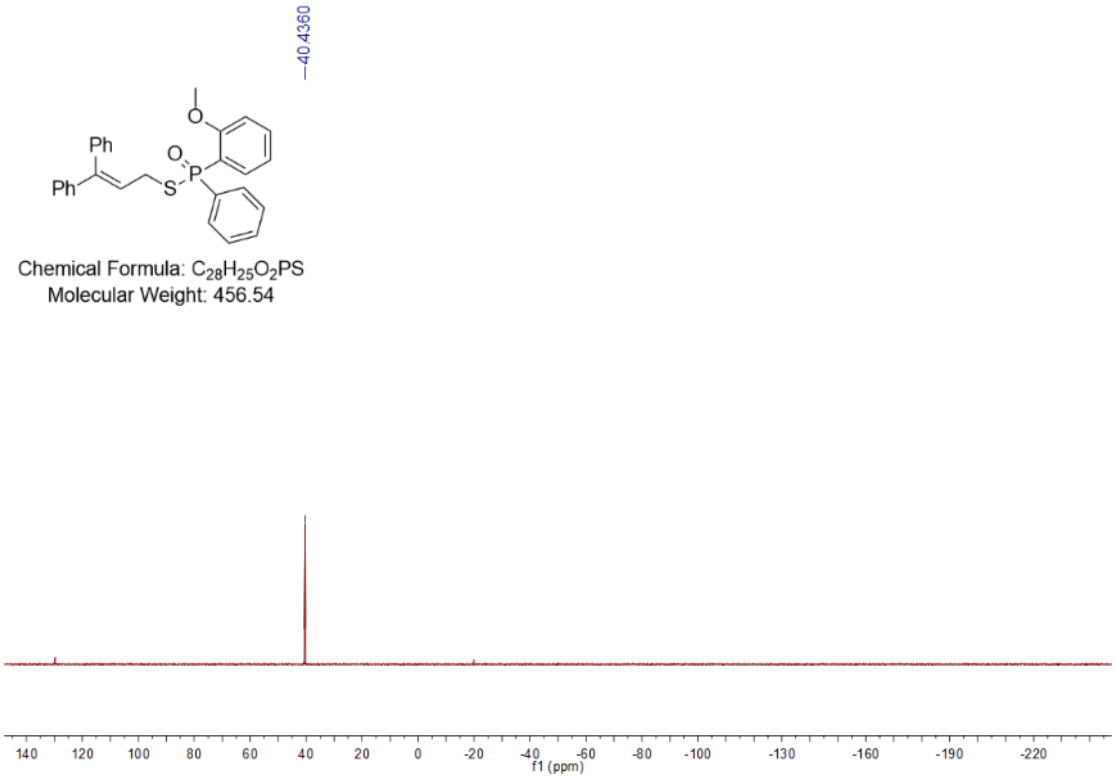
S-(3,3-diphenylallyl) (2-methoxyphenyl)(phenyl)phosphinothioate (4l)



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

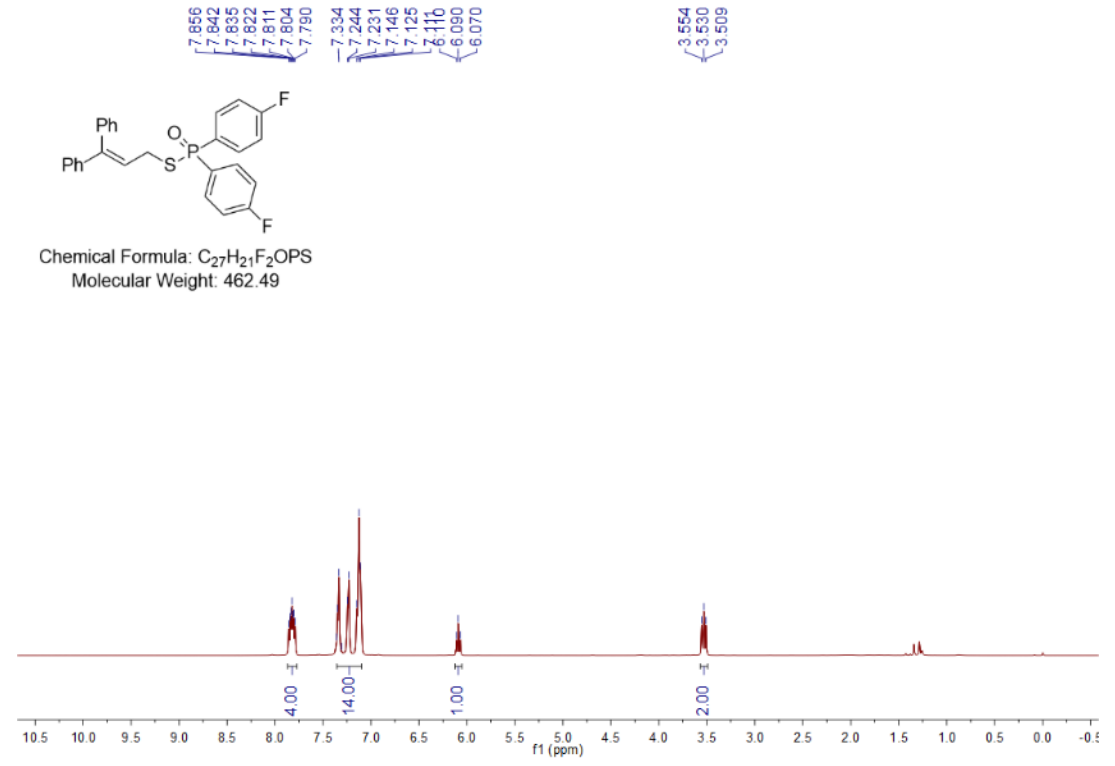


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

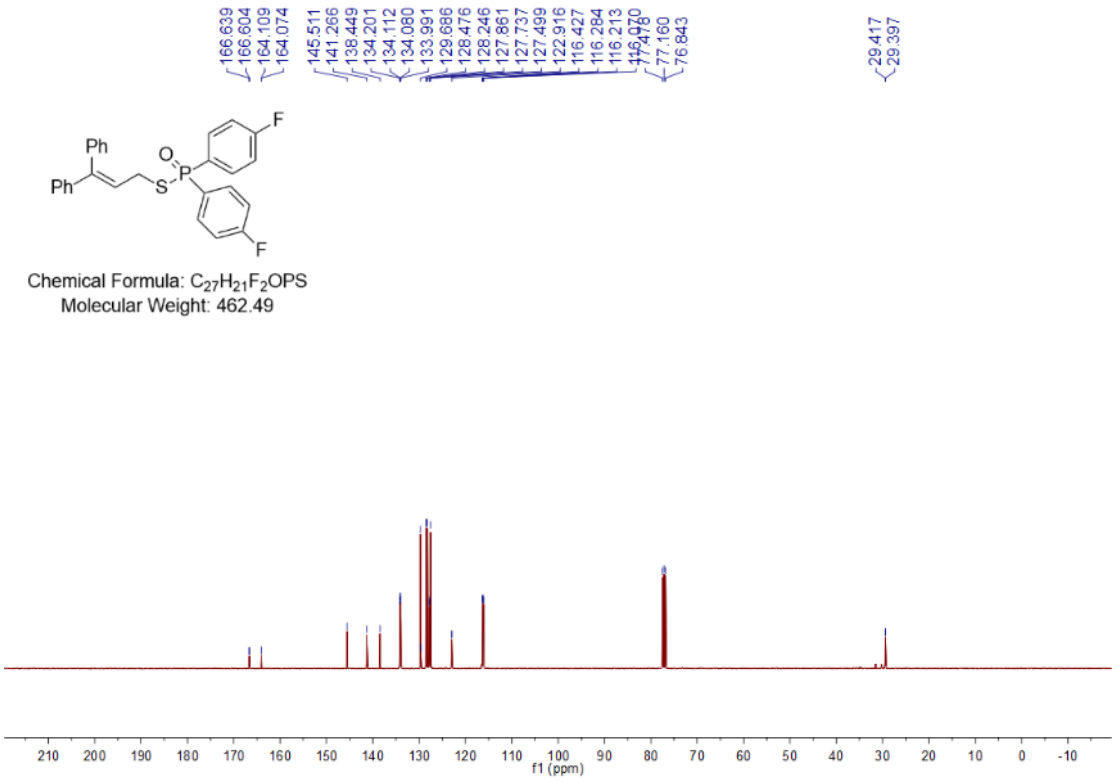


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

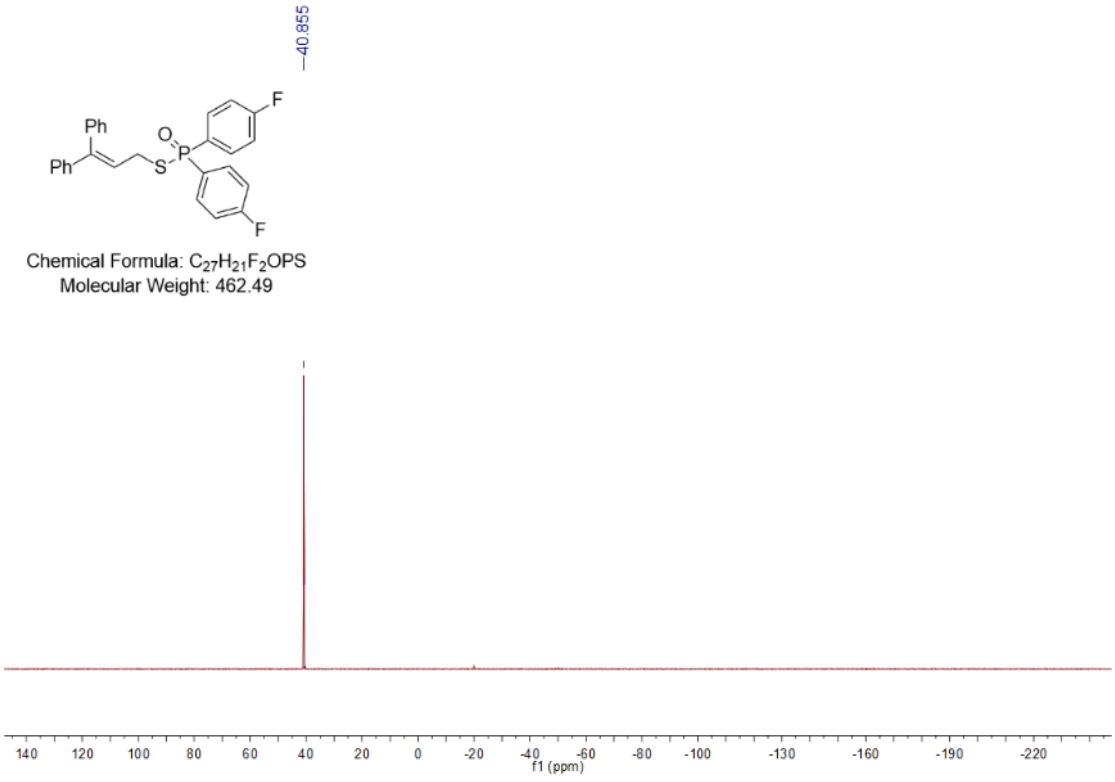
S-(3,3-diphenylallyl) bis(4-fluorophenyl)phosphinothioate (4m)



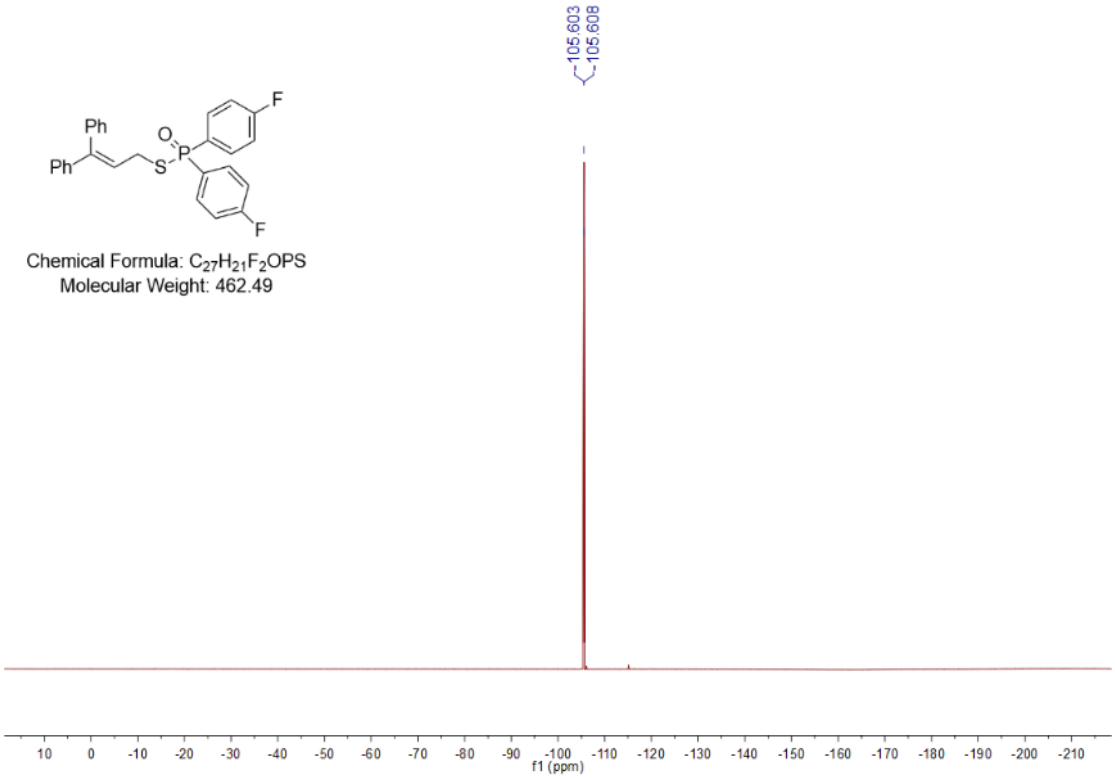
^{1}H NMR spectrum, 400 MHz, $CDCl_3$



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

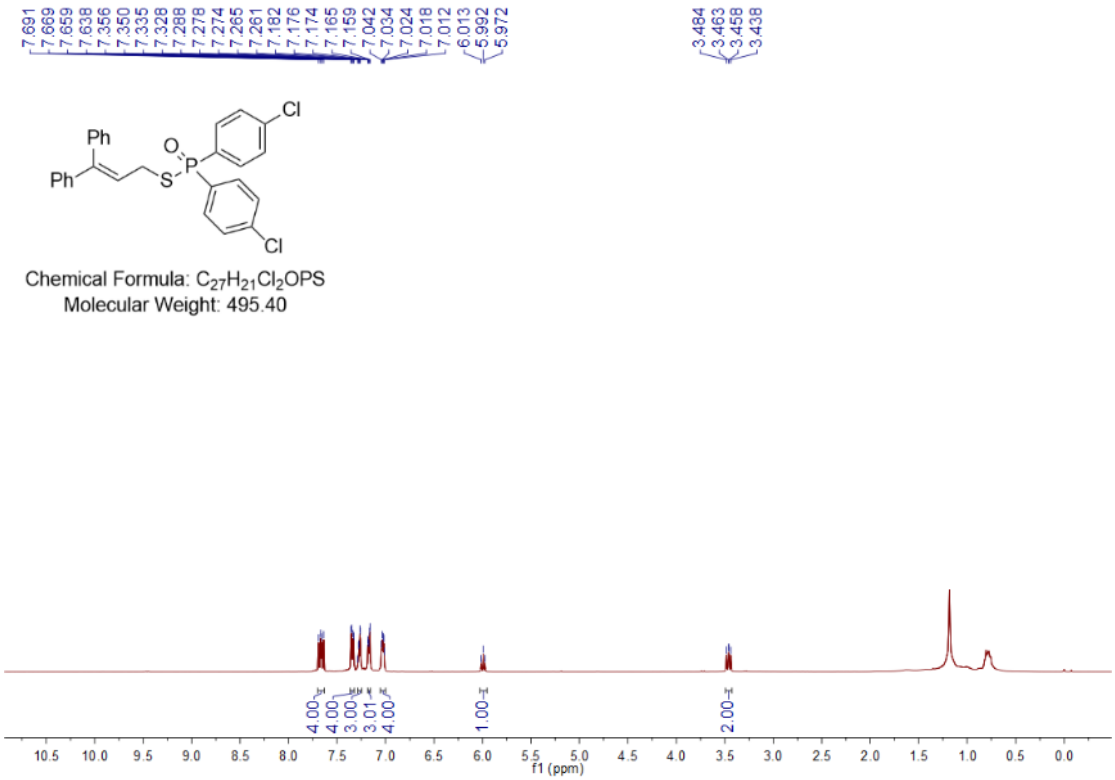


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

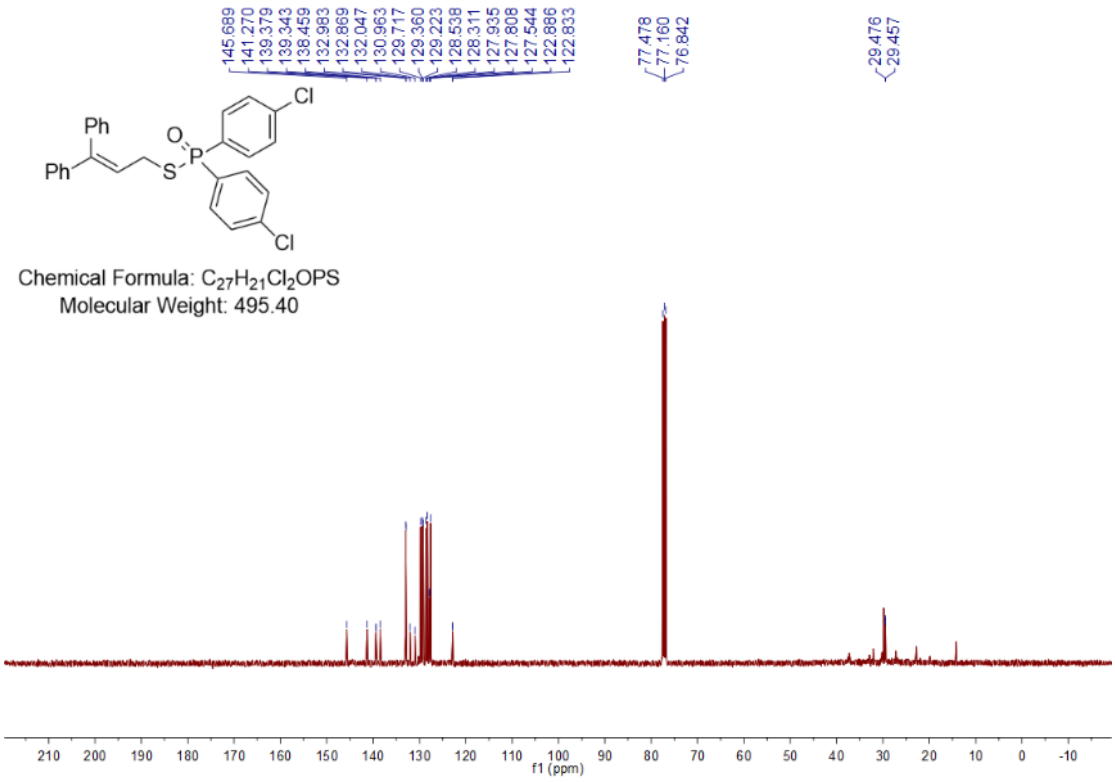


^{19}F NMR spectrum, 376 MHz, $CDCl_3$

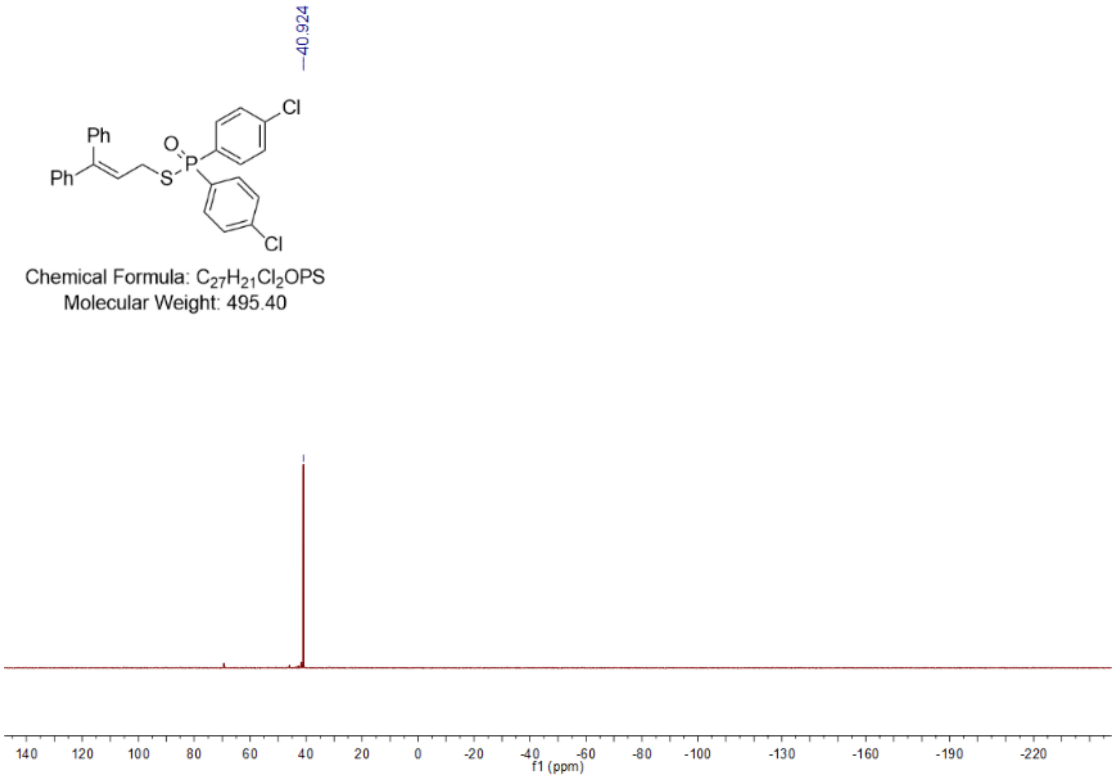
S-(3,3-diphenylallyl) bis(4-chlorophenyl)phosphinothioate (4n)



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

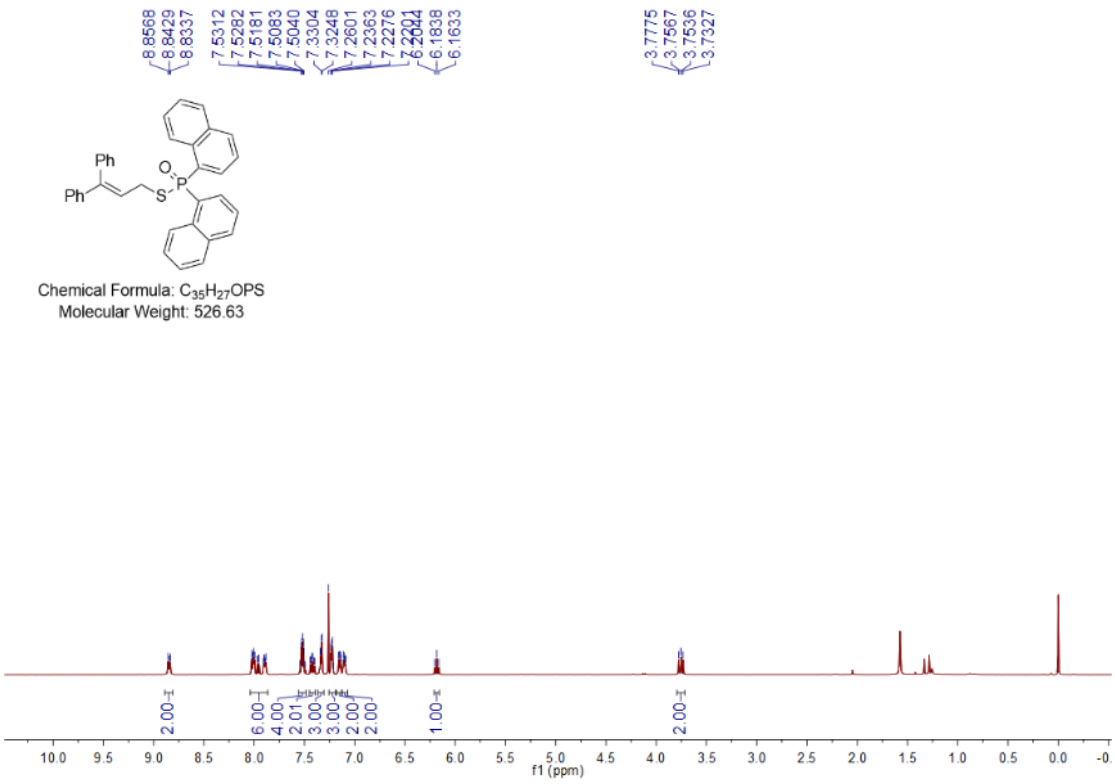


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

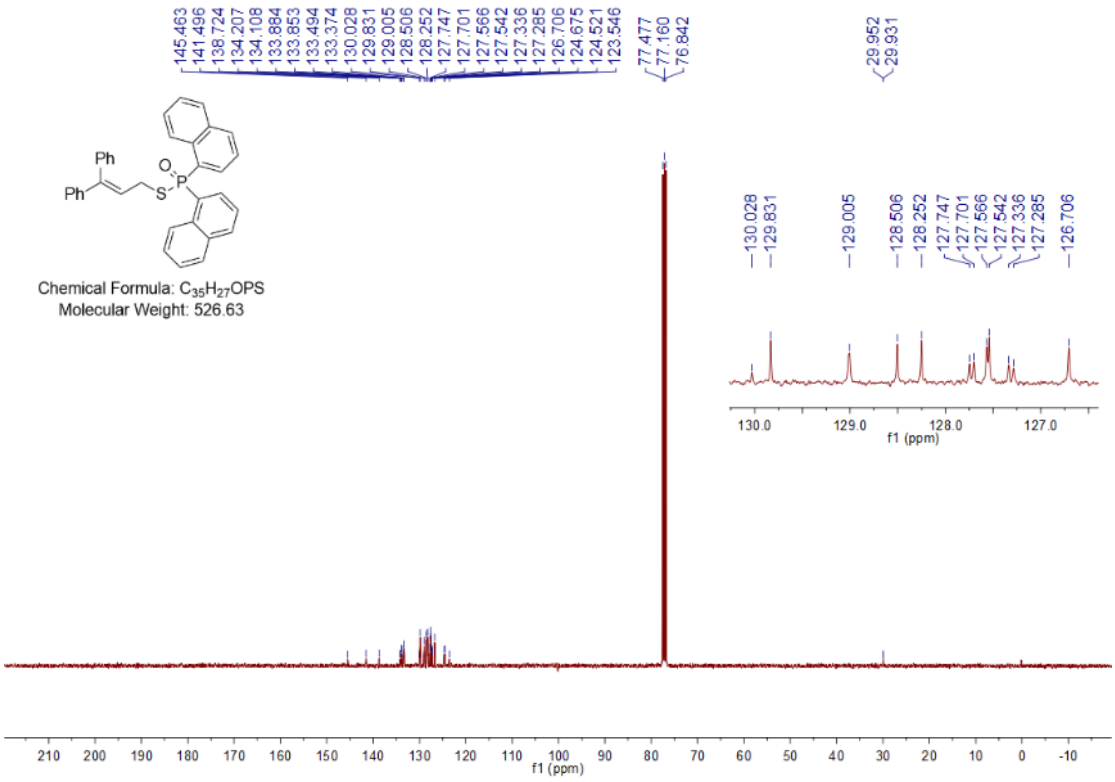


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

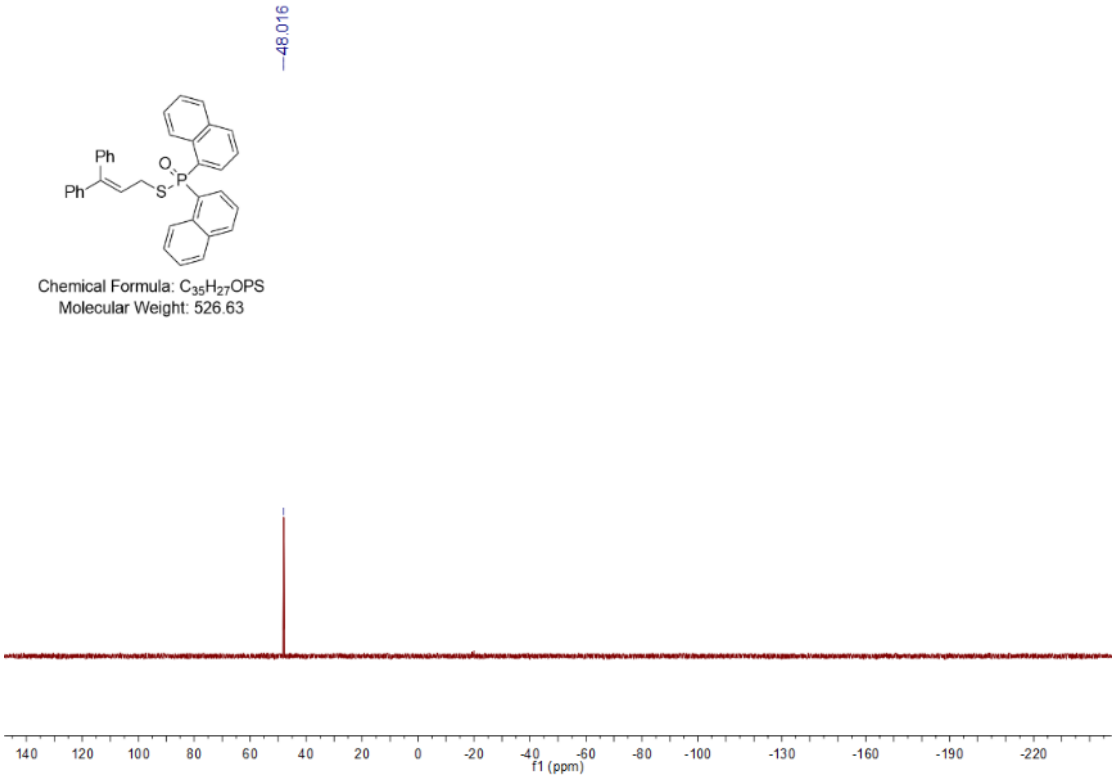
S-(3,3-diphenylallyl) naphthalen-1-yl(naphthalen-2-yl)phosphinothioate (4o)



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

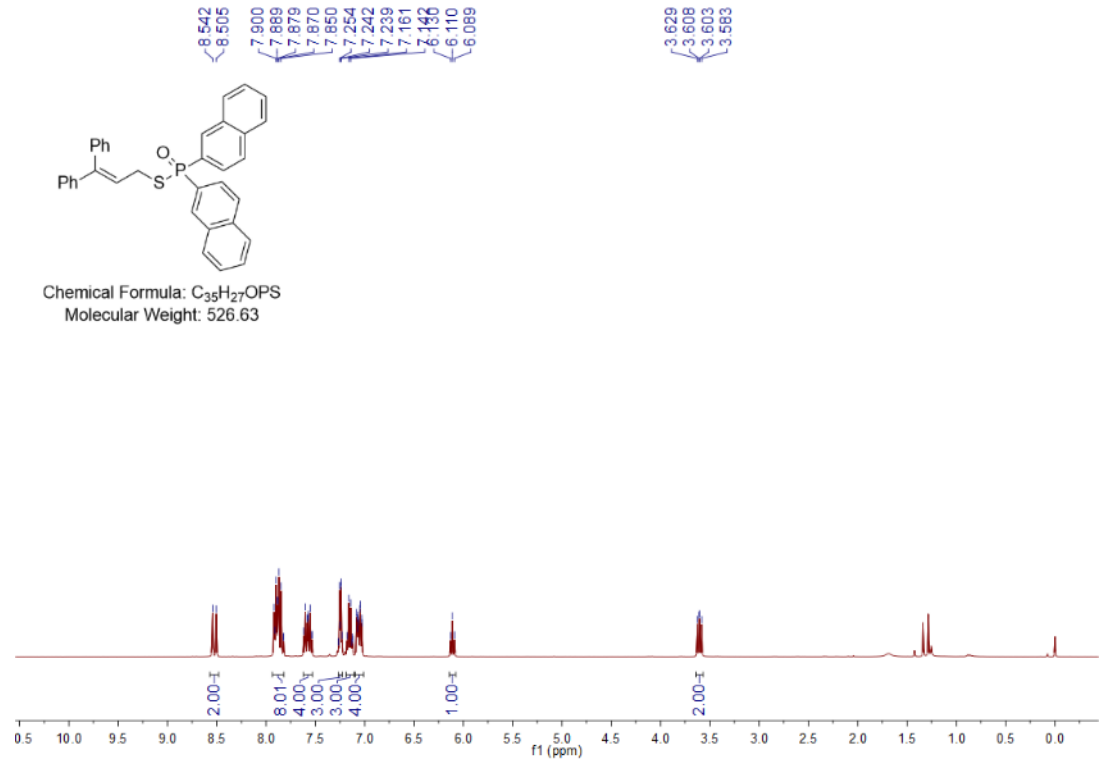


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

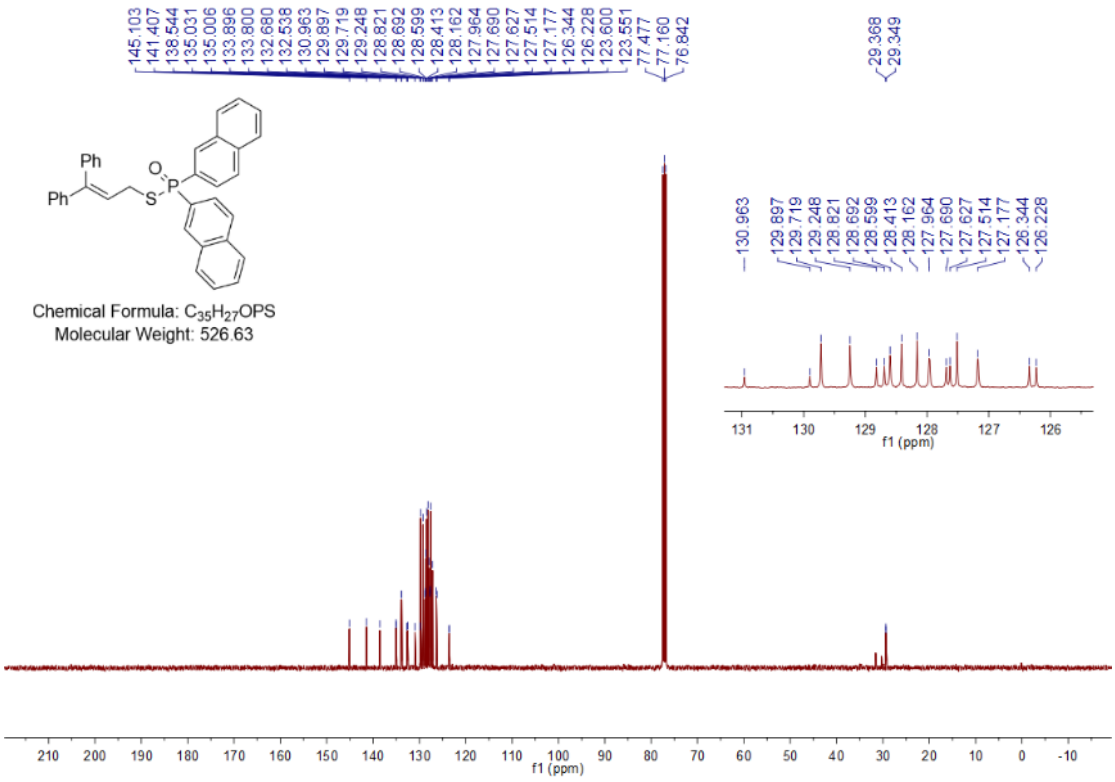


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

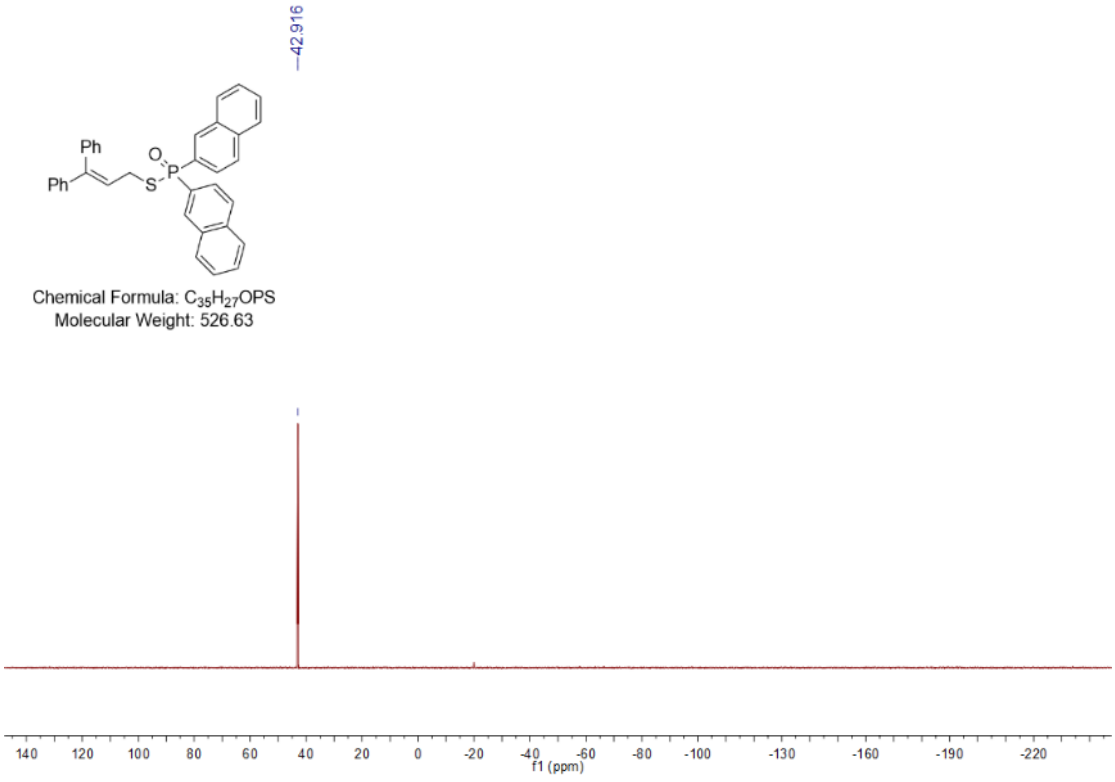
S-(3,3-diphenylallyl) di(naphthalen-2-yl)phosphinothioate (4p)



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

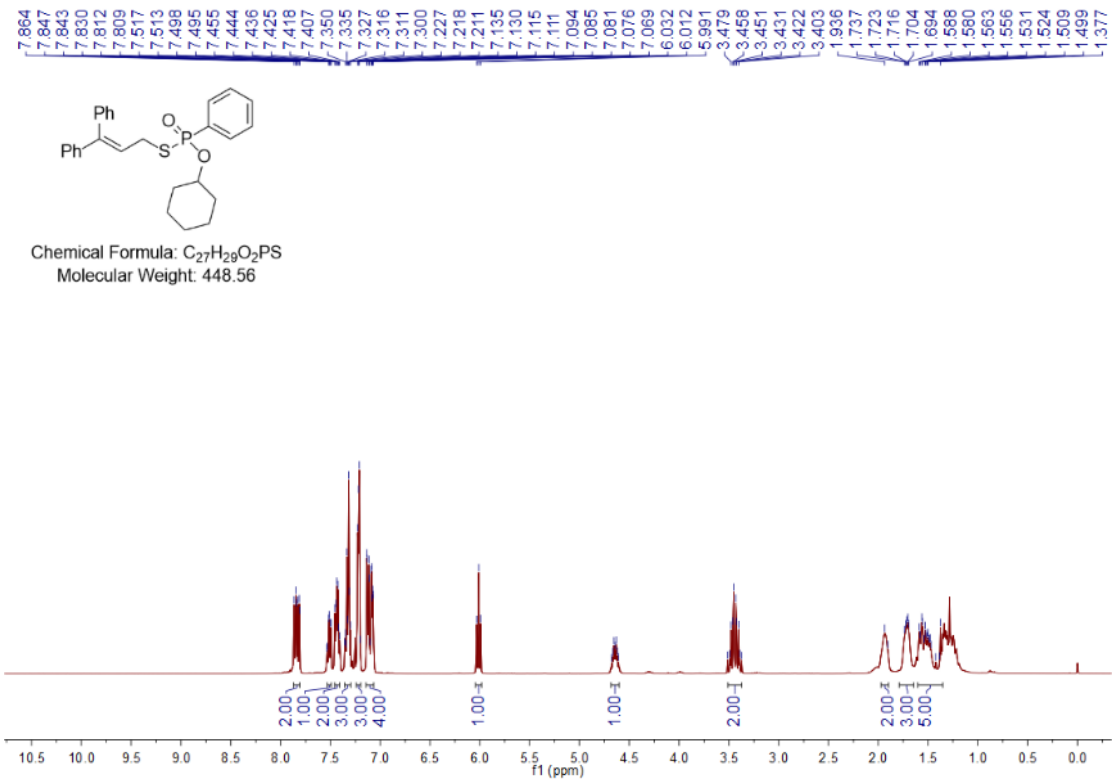


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

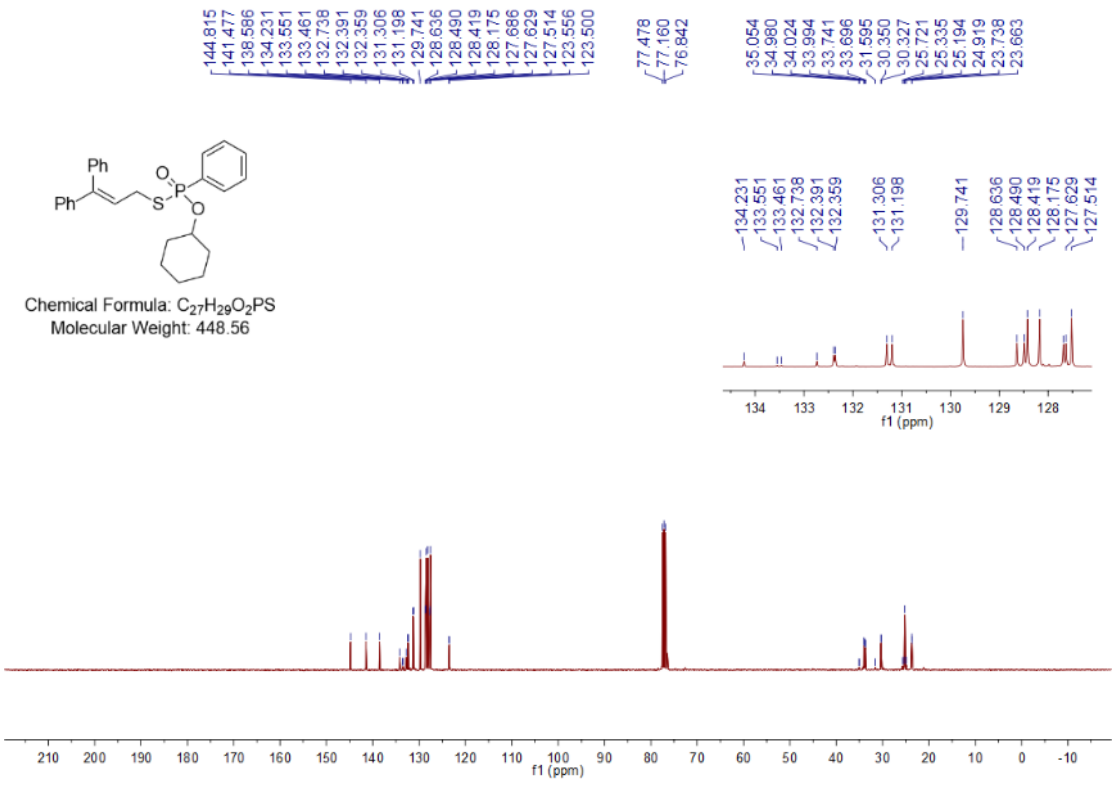


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

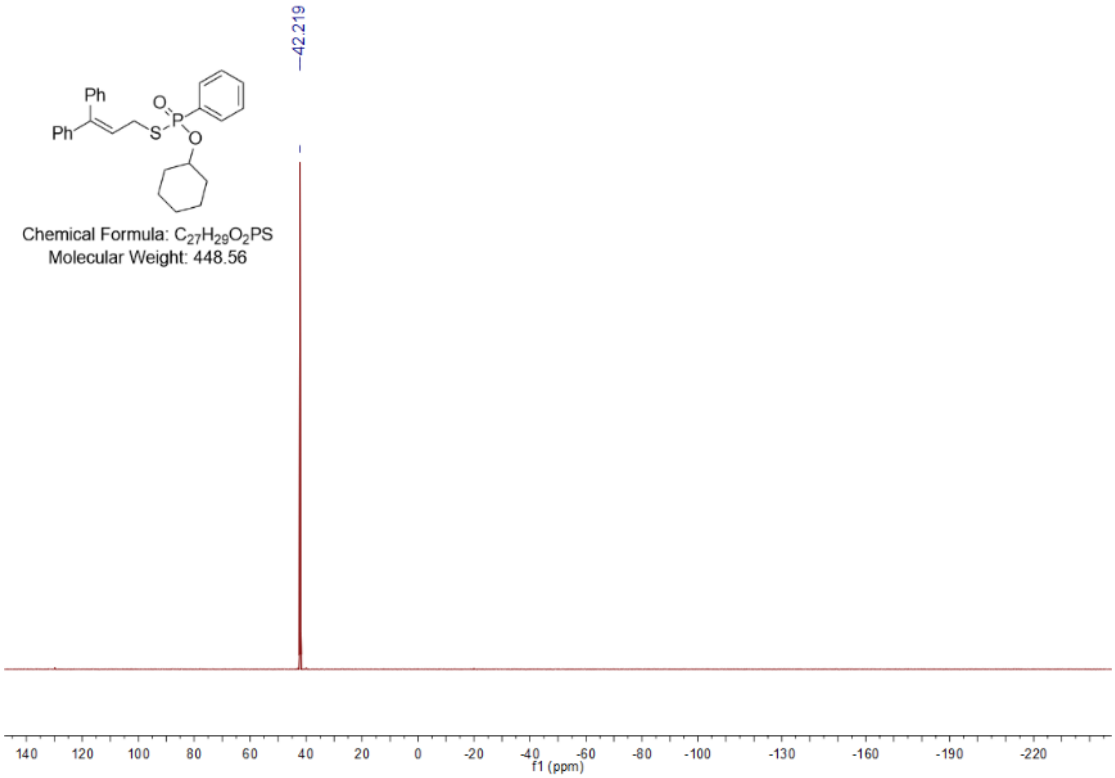
O-cyclohexyl S-(3,3-diphenylallyl) phenylphosphonothioate (4q)



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

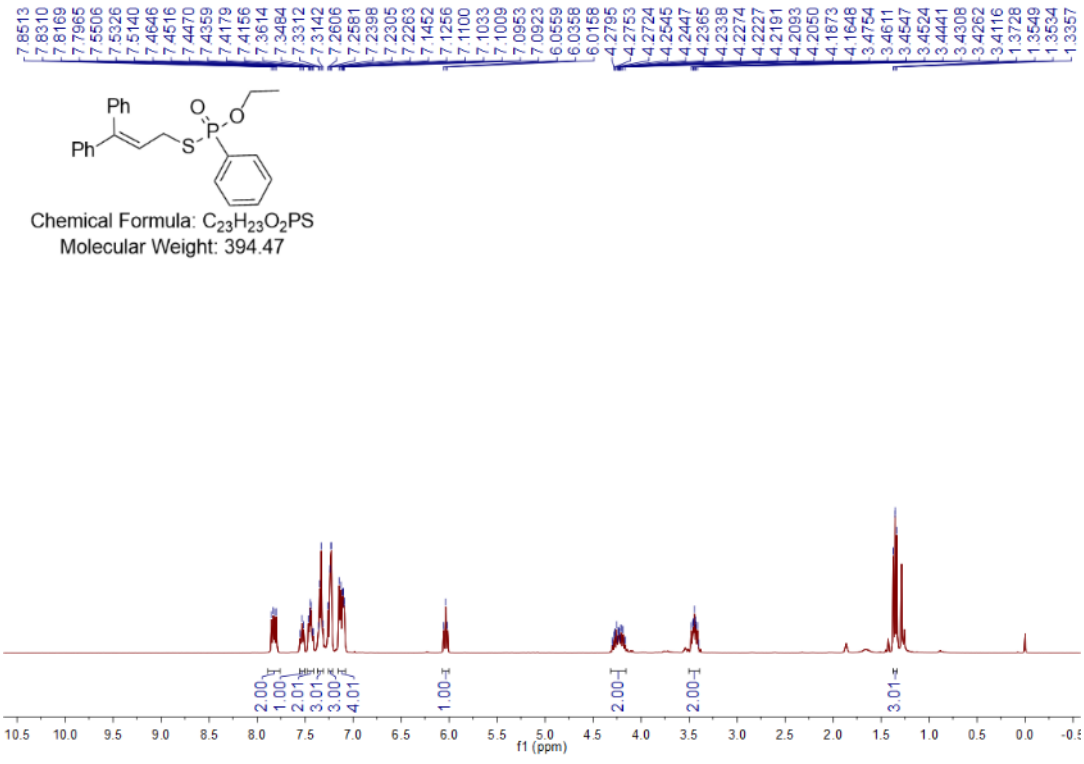


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

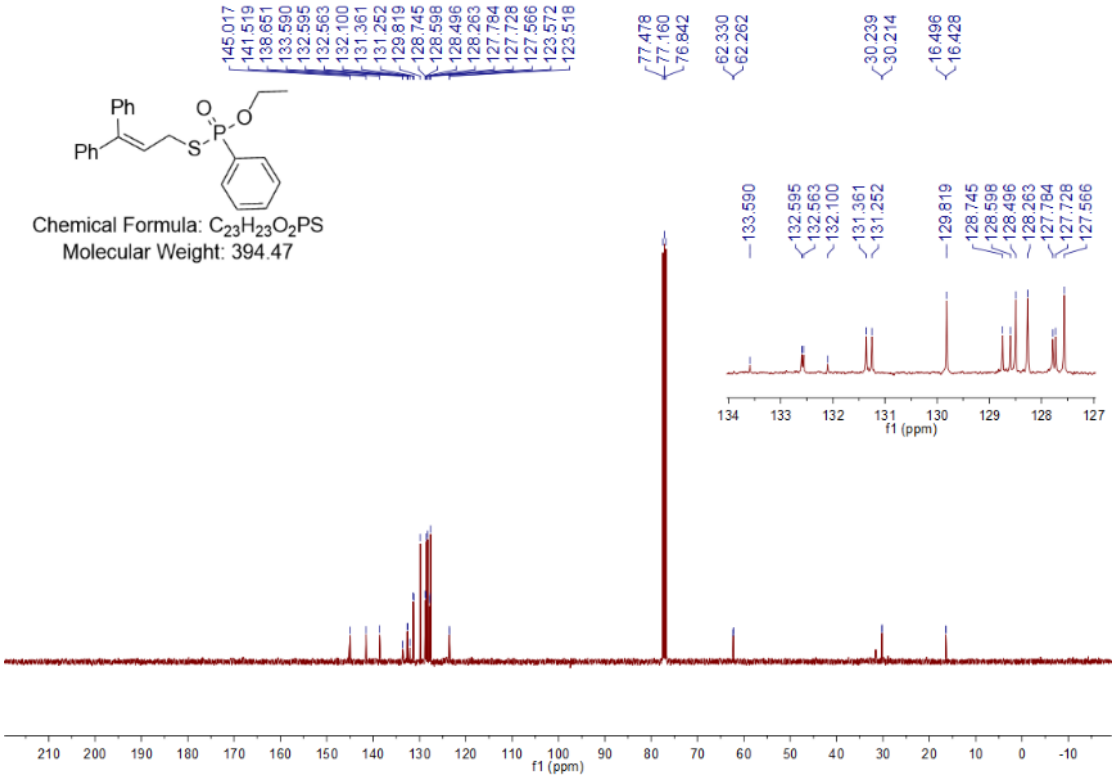


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

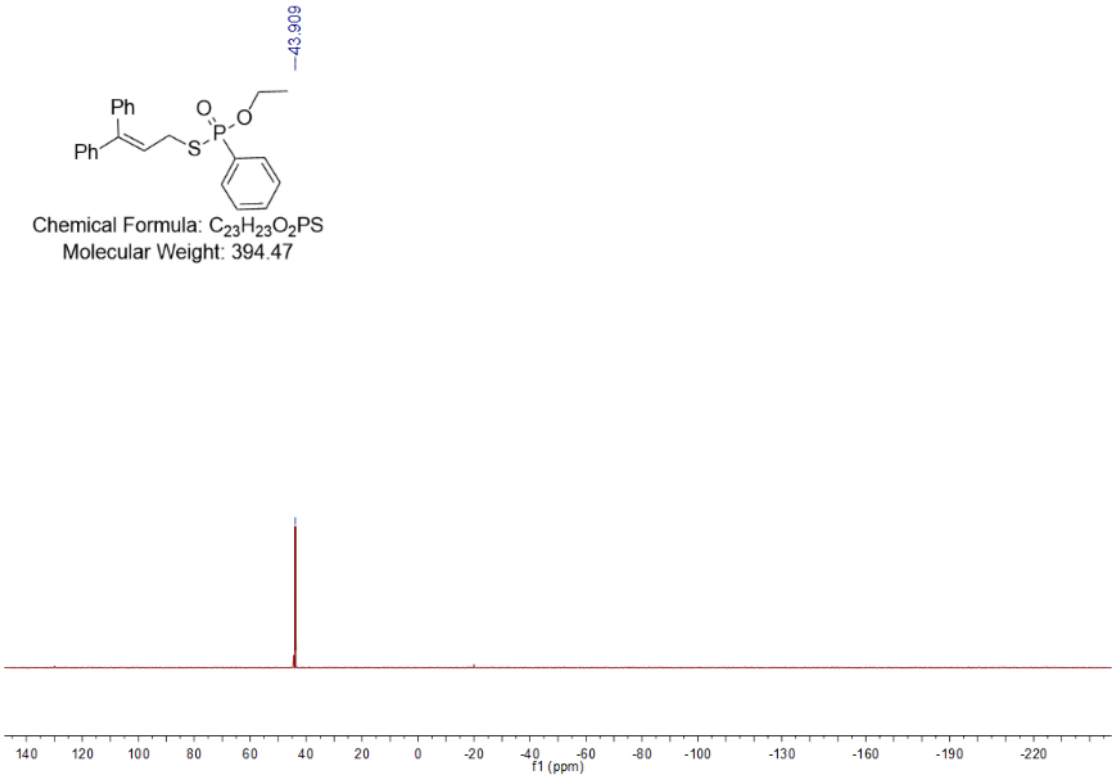
S-(3,3-diphenylallyl) O-ethyl phenylphosphonothioate (4r)



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

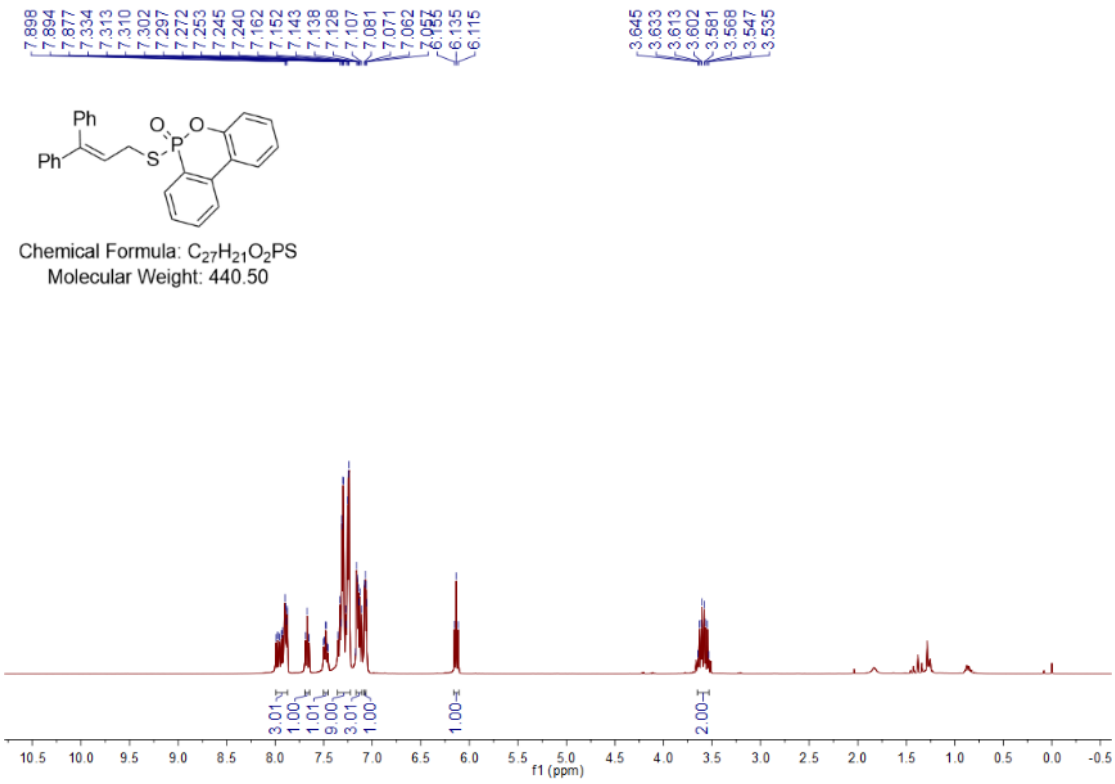


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

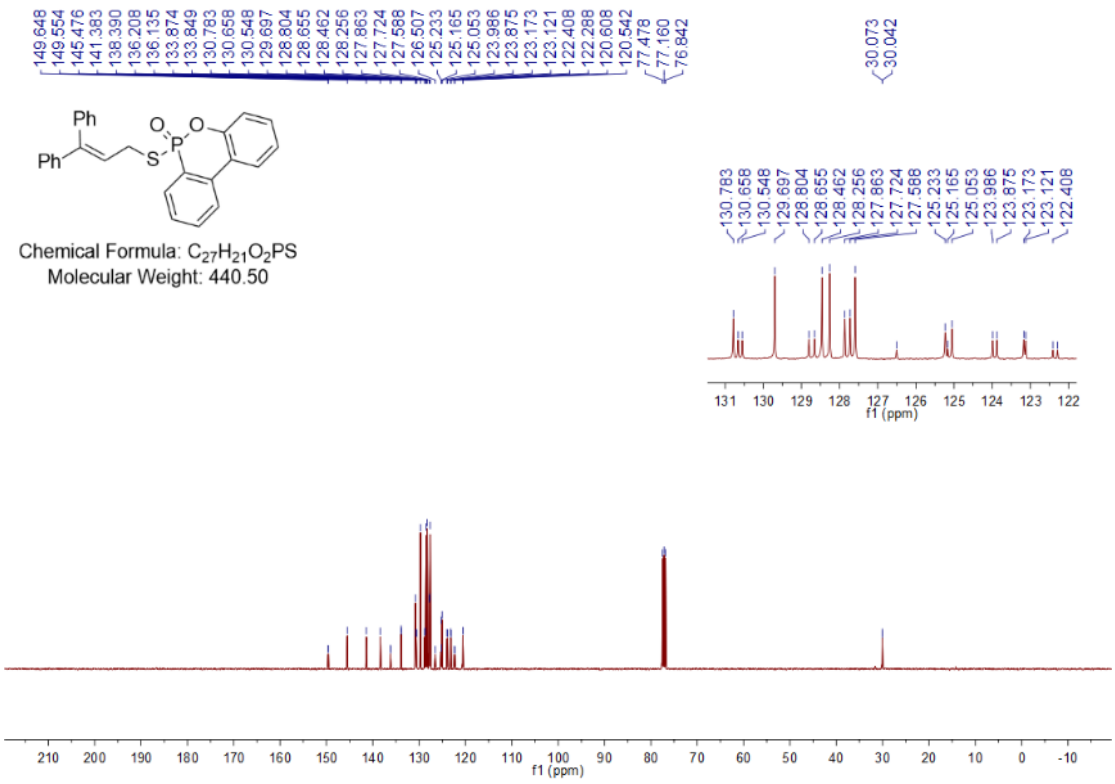


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

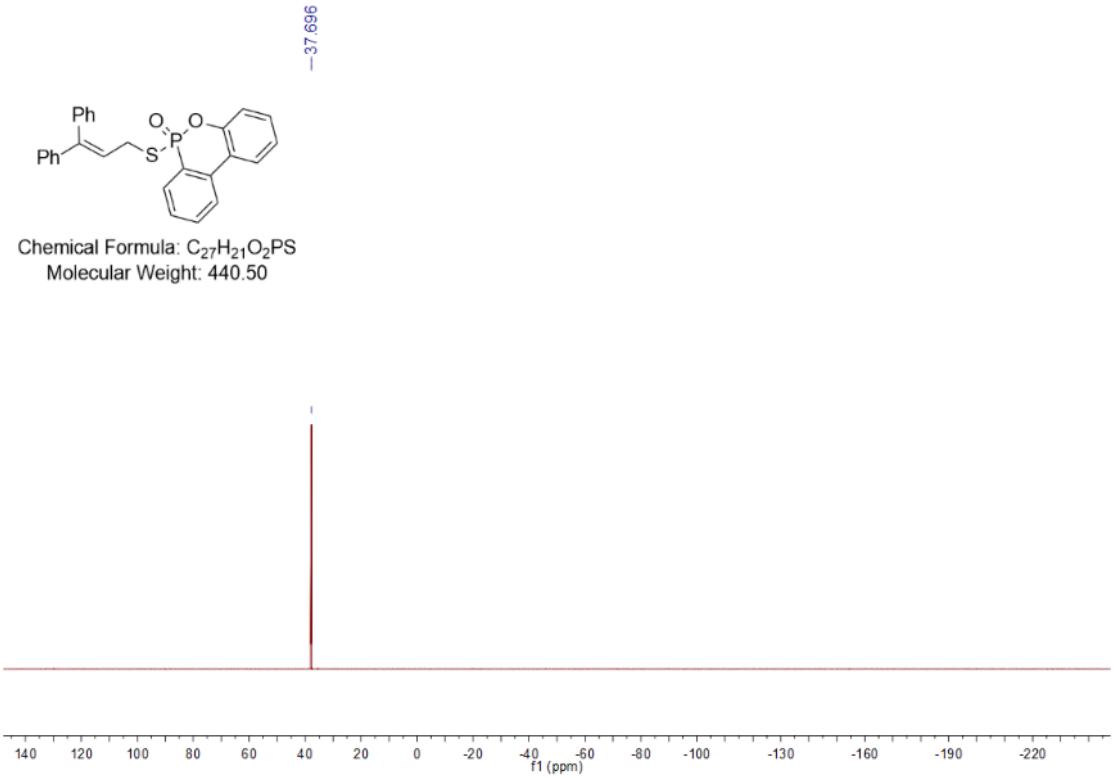
6-((3,3-diphenylallyl)thio)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (4s)



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

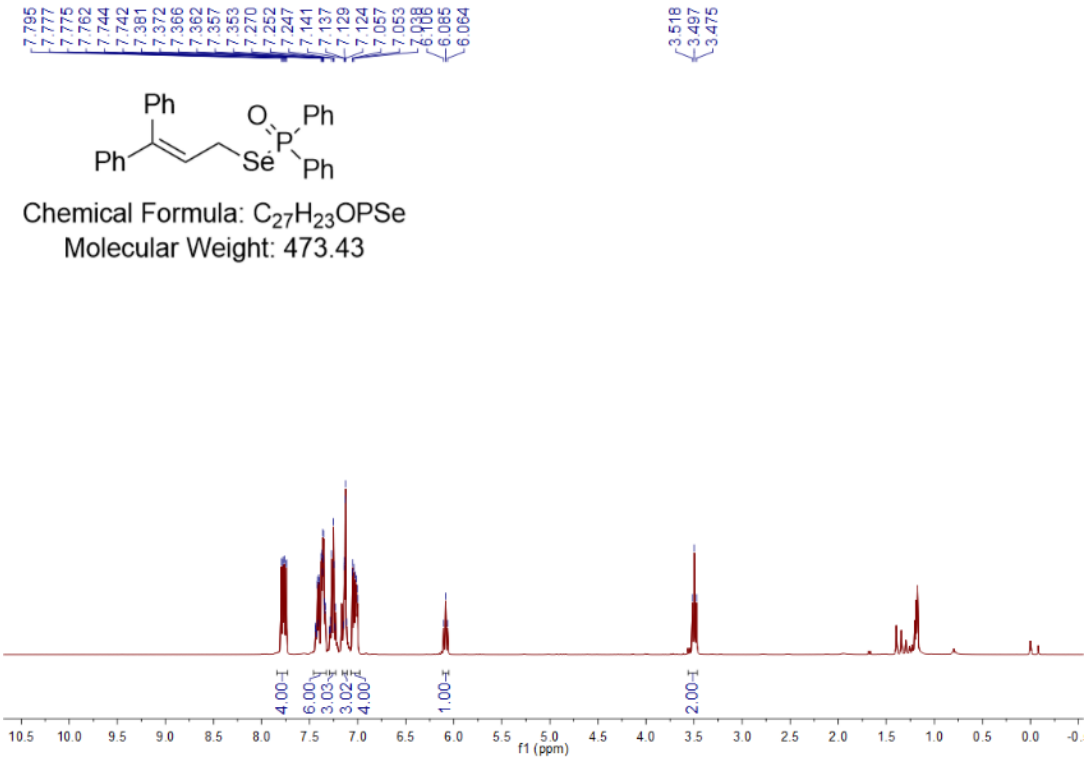


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

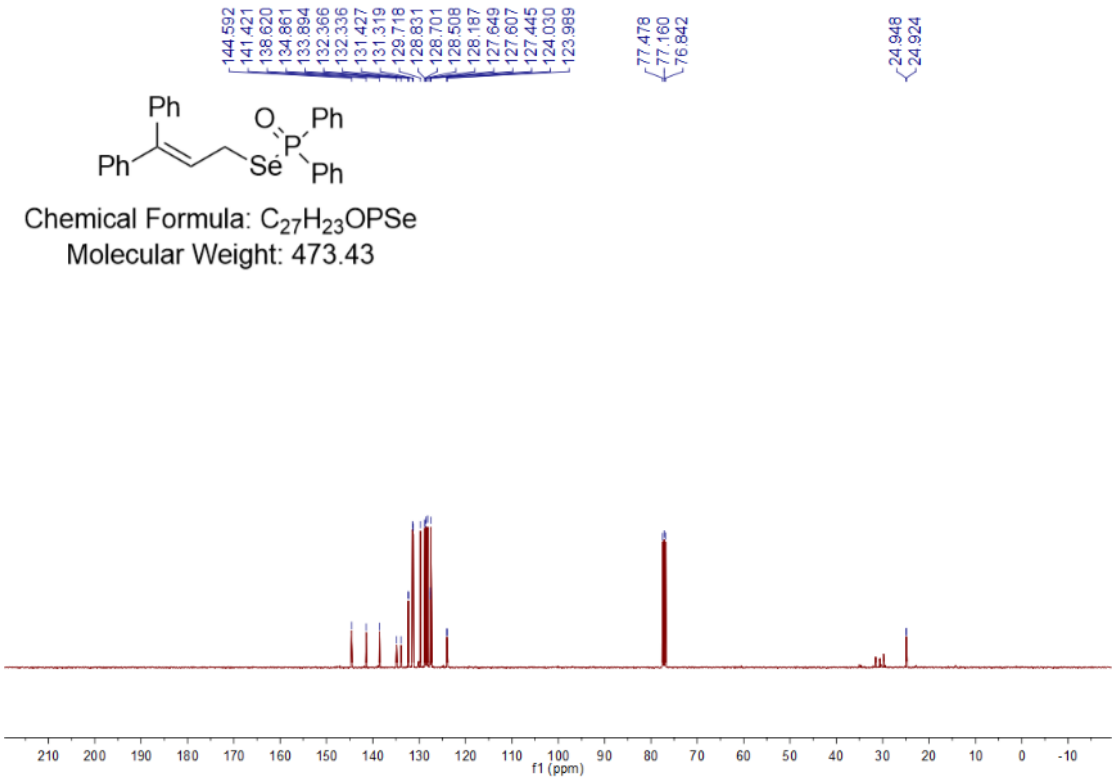


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

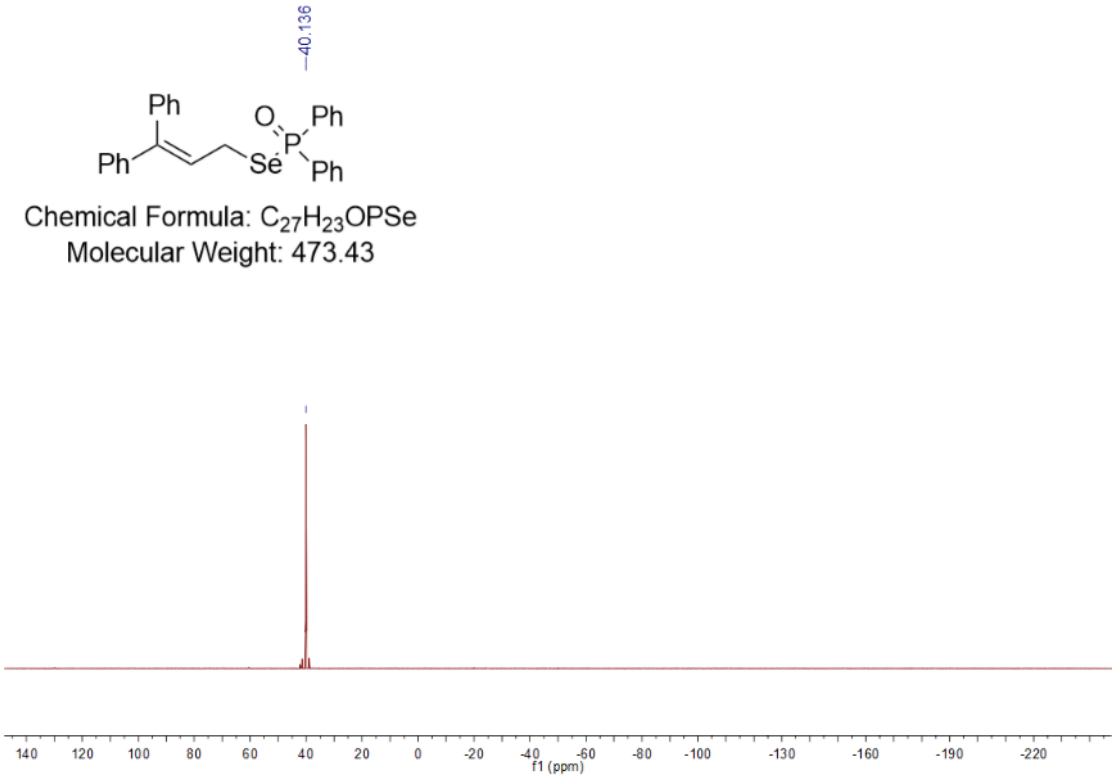
Se-(3,3-diphenylallyl) diphenylphosphinotselenoate (5a)



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

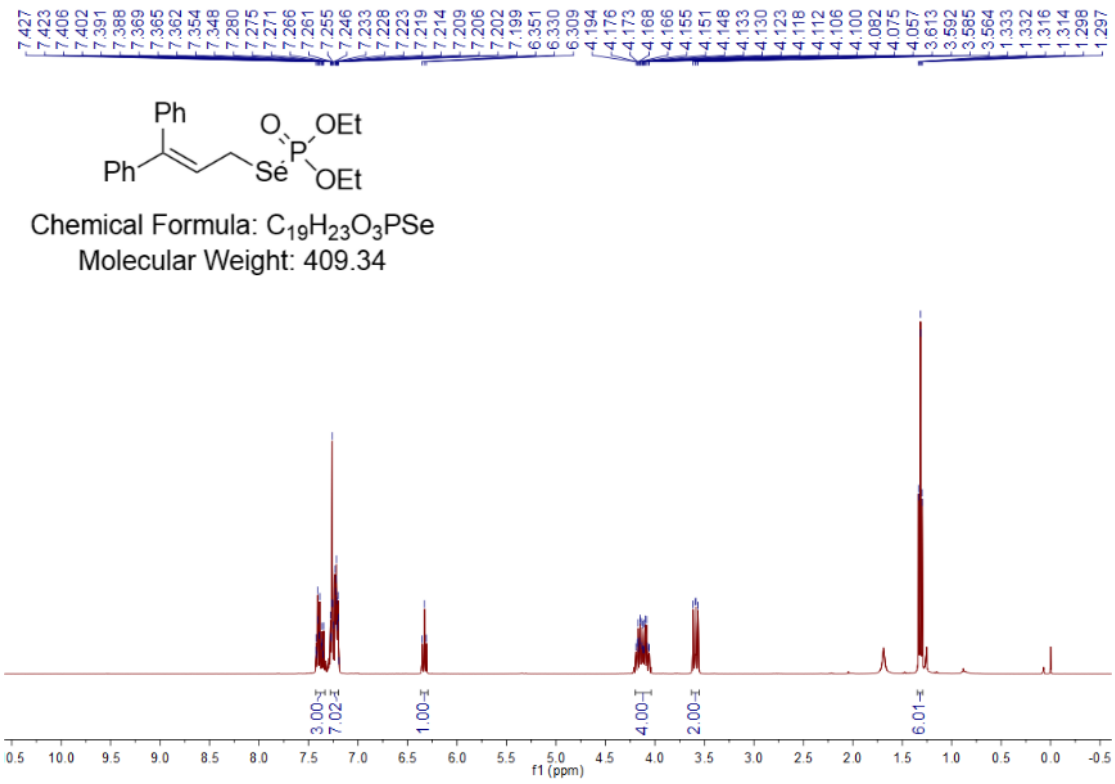


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

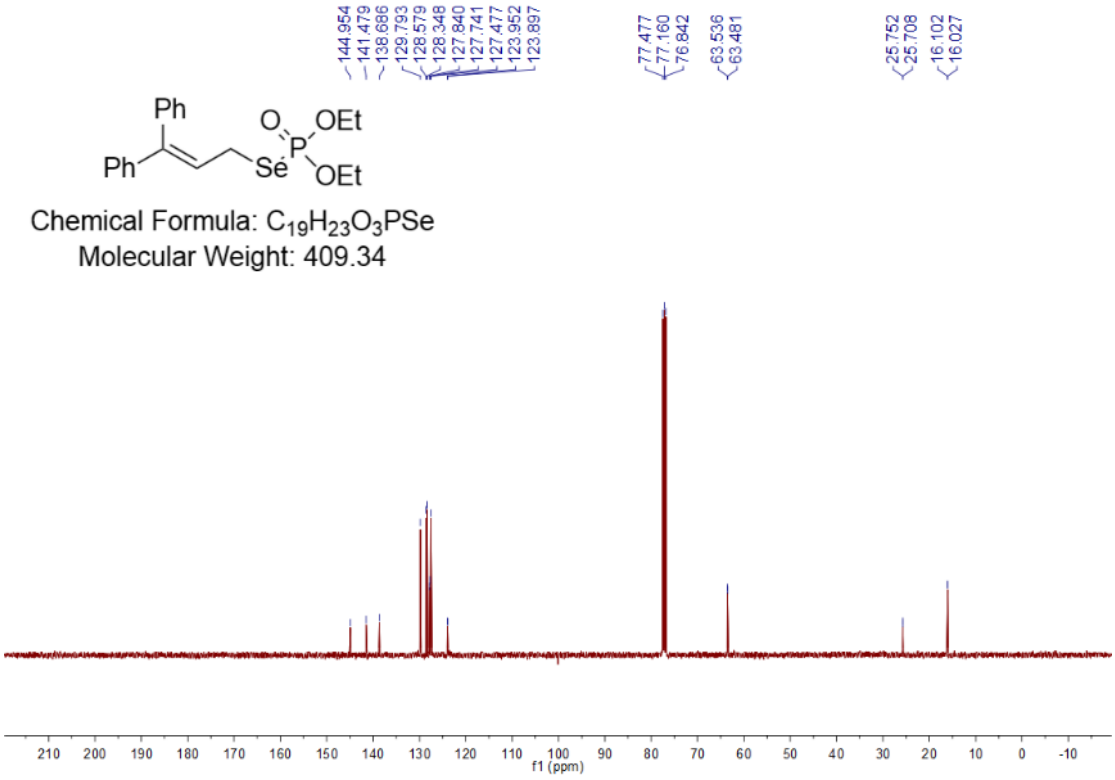


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

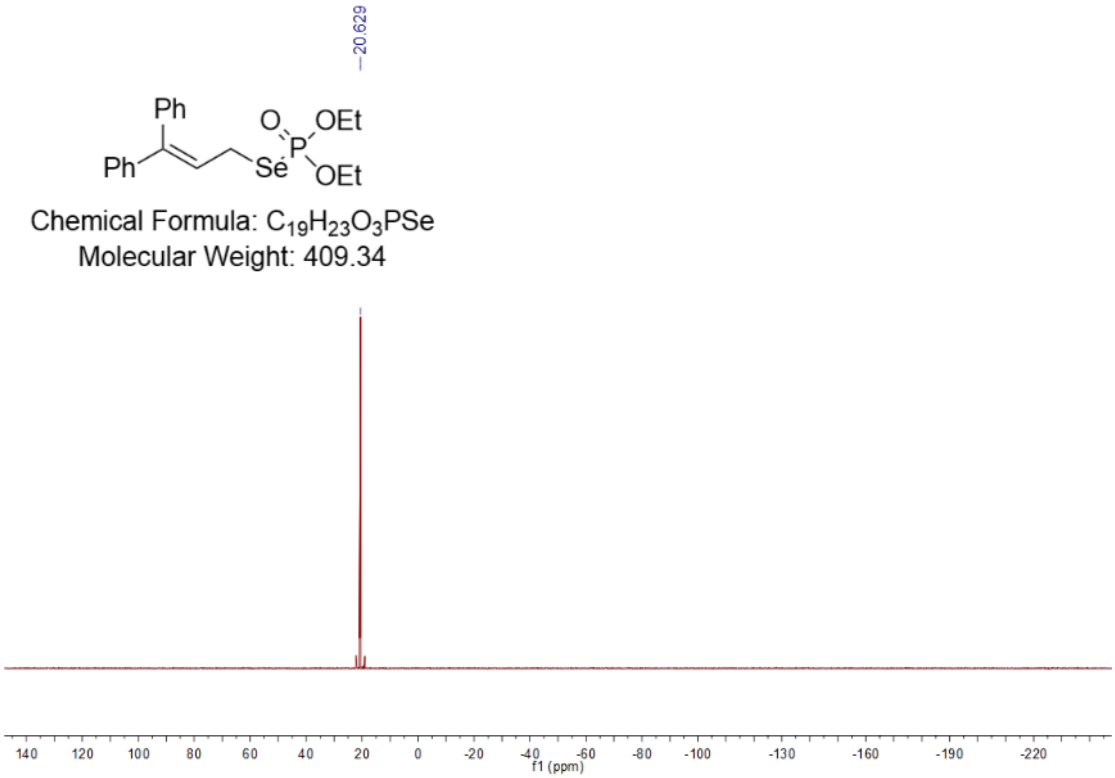
Se-(3,3-diphenylallyl) O,O-diethyl phosphoroselenoate (5b)



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

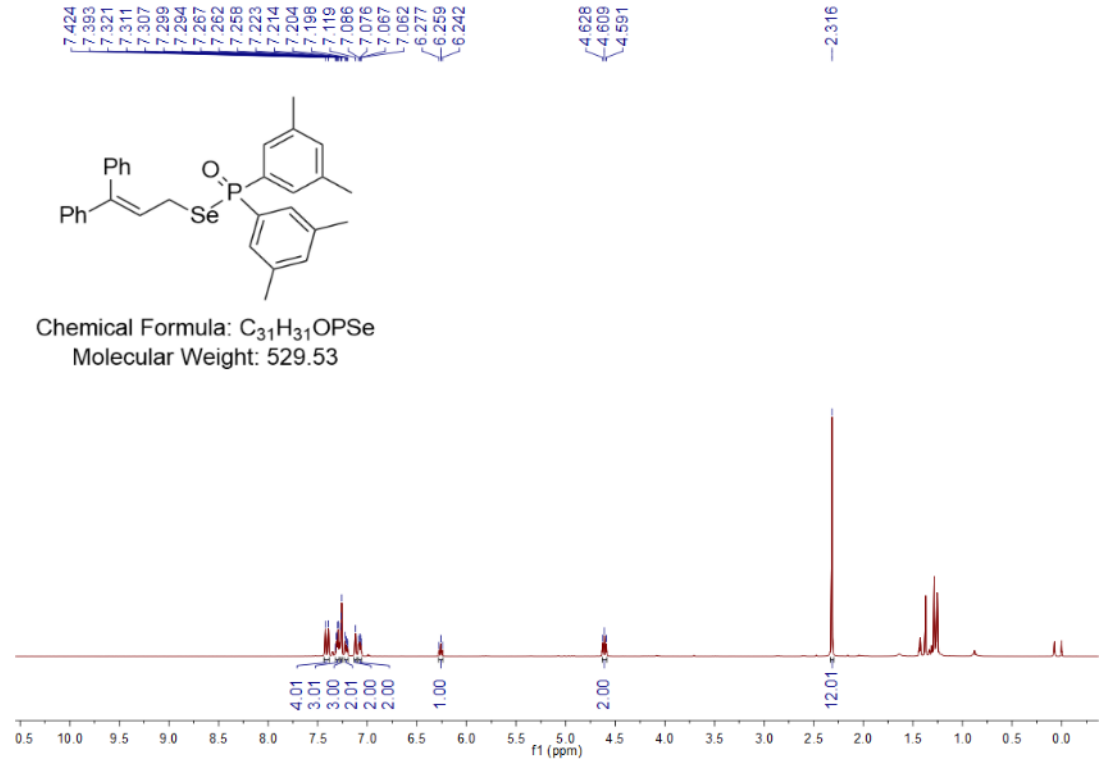


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

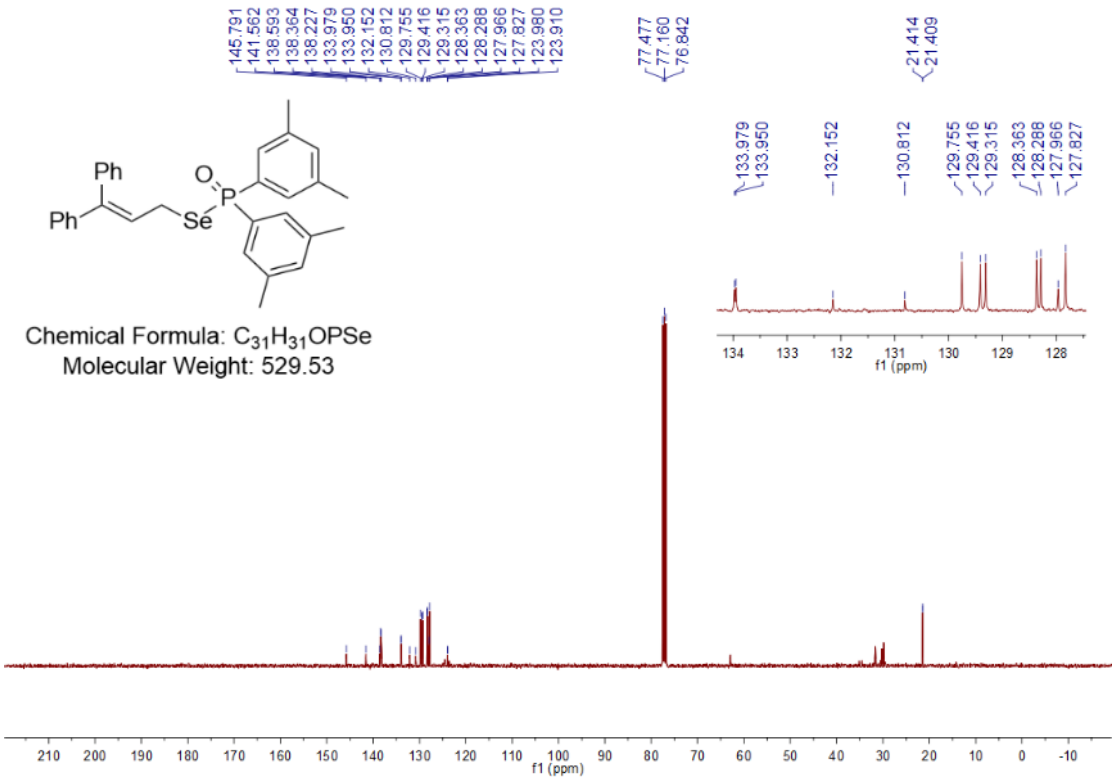


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

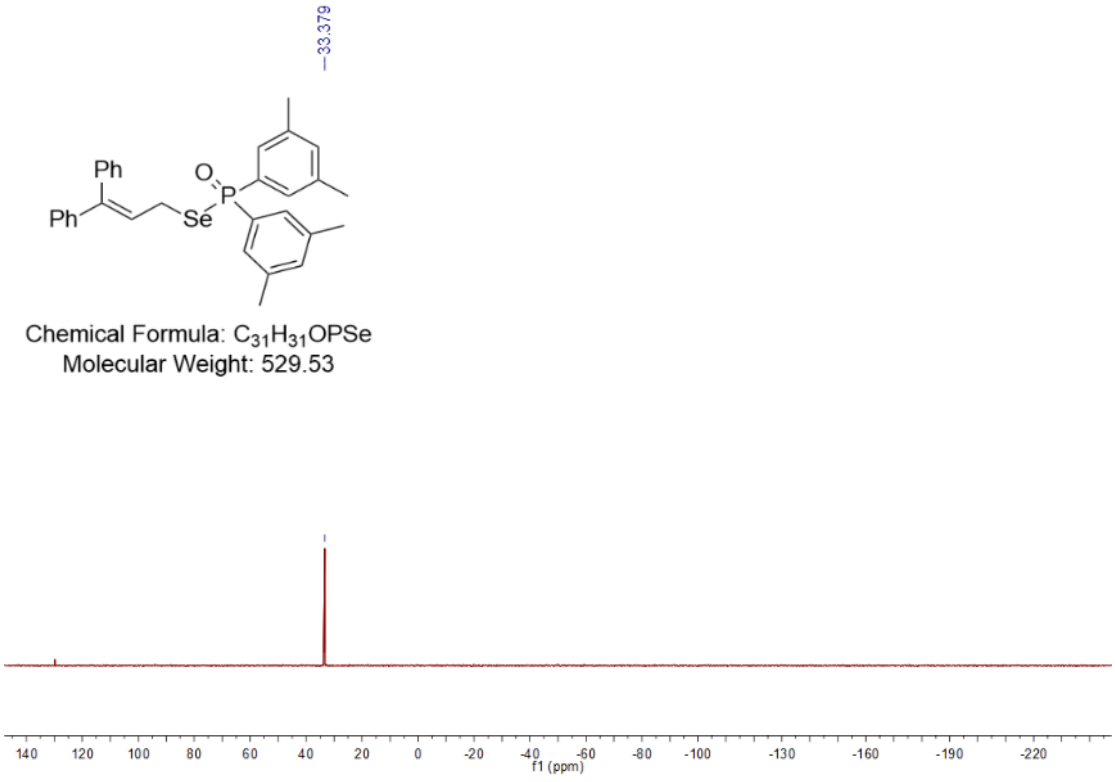
Se-(3,3-diphenylallyl) bis(3,5-dimethylphenyl)phosphinothioate (5c)



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

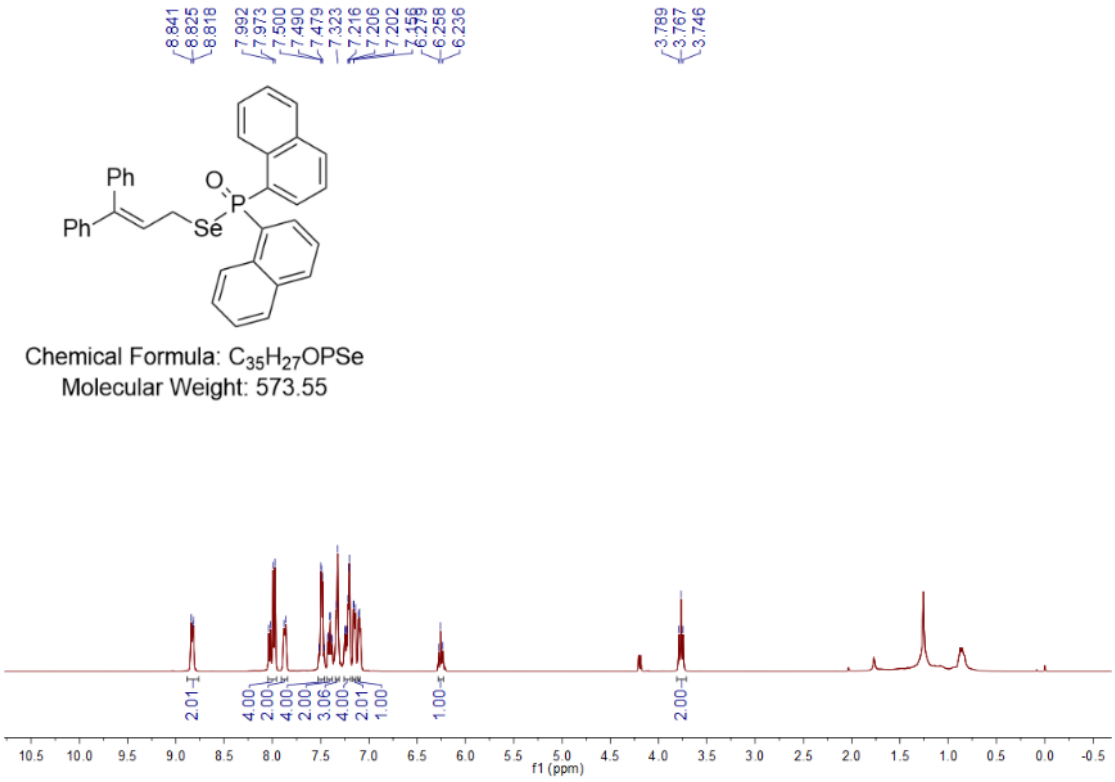


^{13}C NMR spectrum, 100 MHz, $CDCl_3$

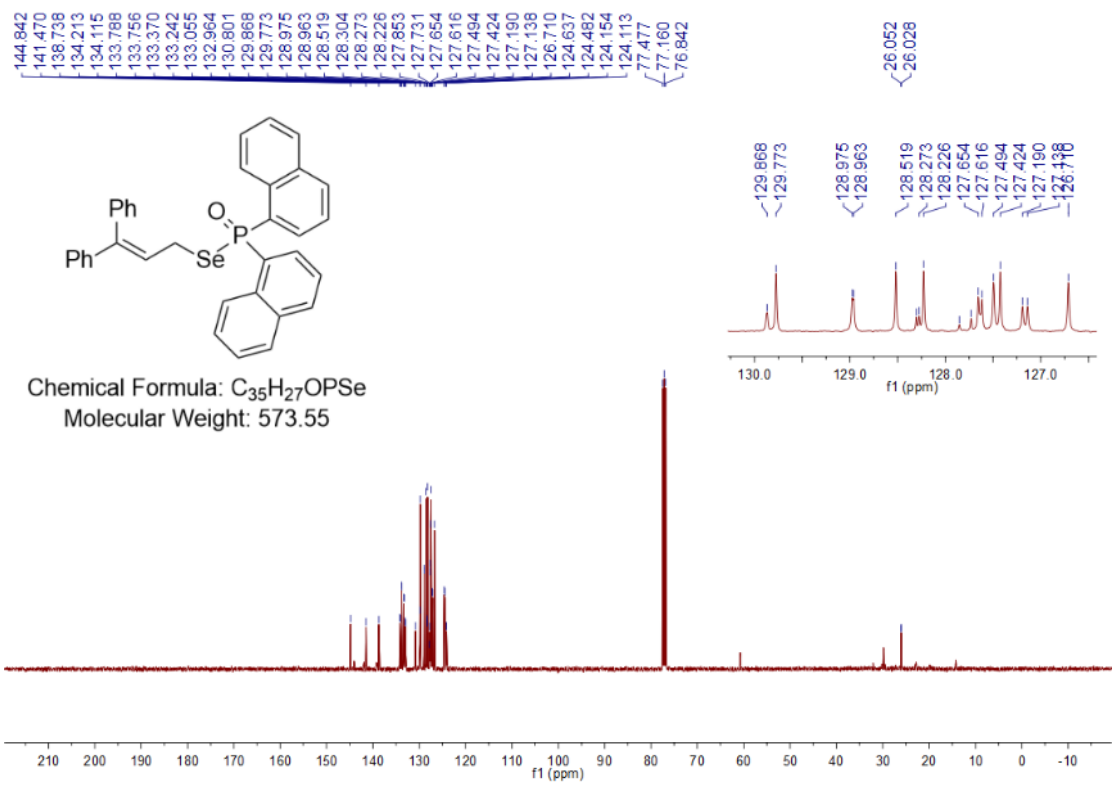


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

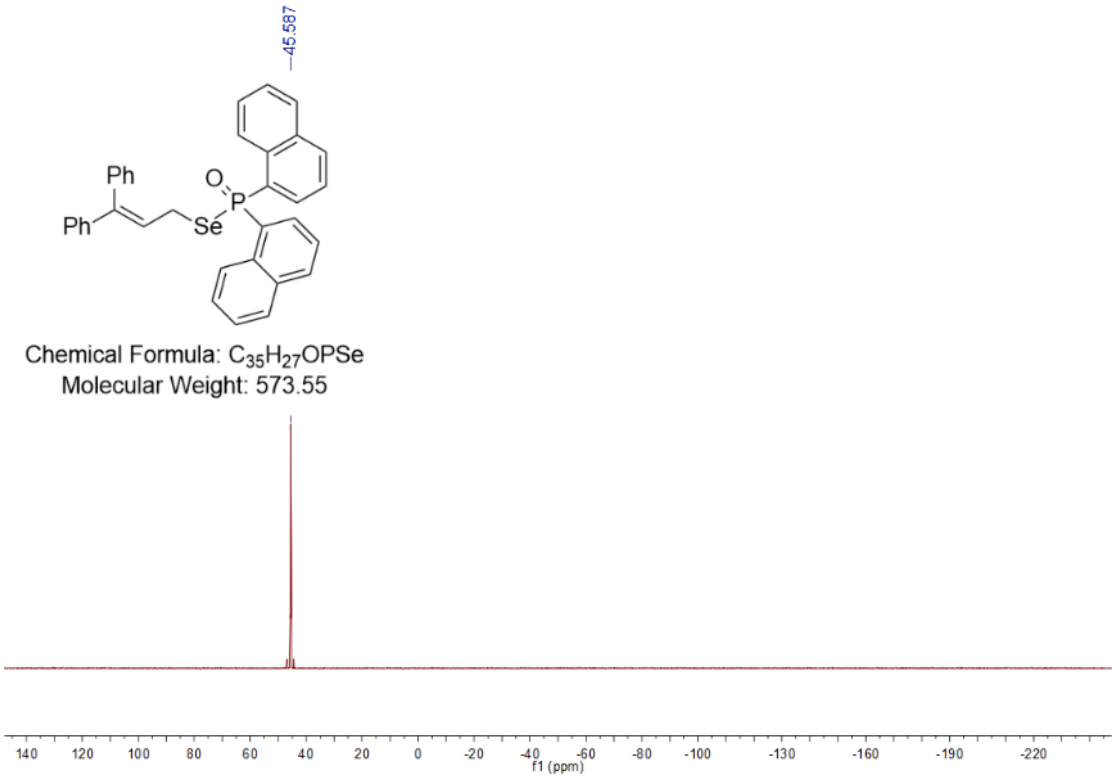
Se-(3,3-diphenylallyl) naphthalen-1-yl(naphthalen-2-yl)phosphinoselenoate (5d)



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

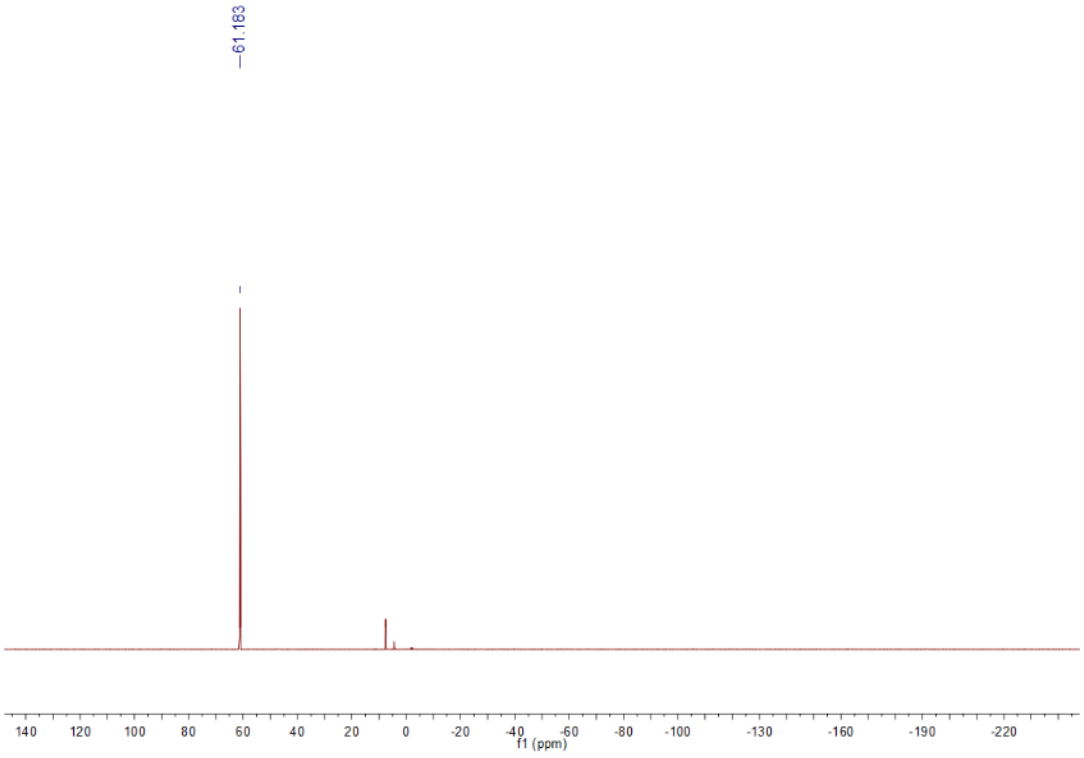


^{13}C NMR spectrum, 100 MHz, $CDCl_3$



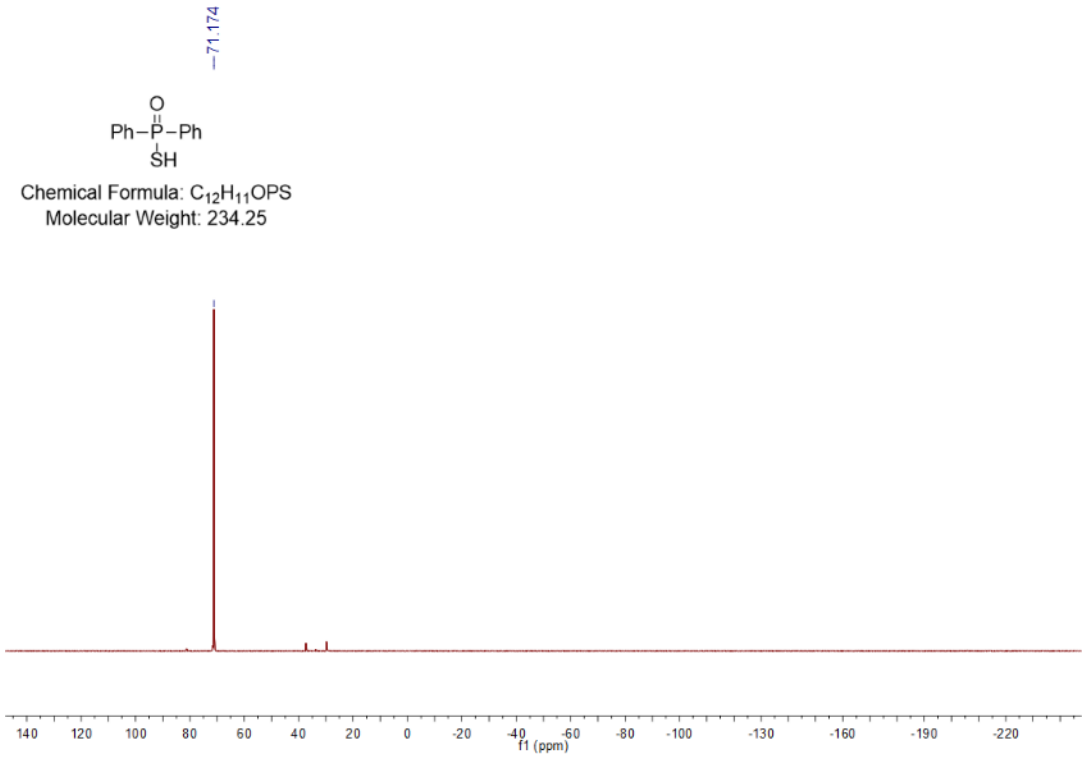
^{31}P NMR spectrum, 162 MHz, $CDCl_3$

diphenylphosphinothioic S-acid (6a)



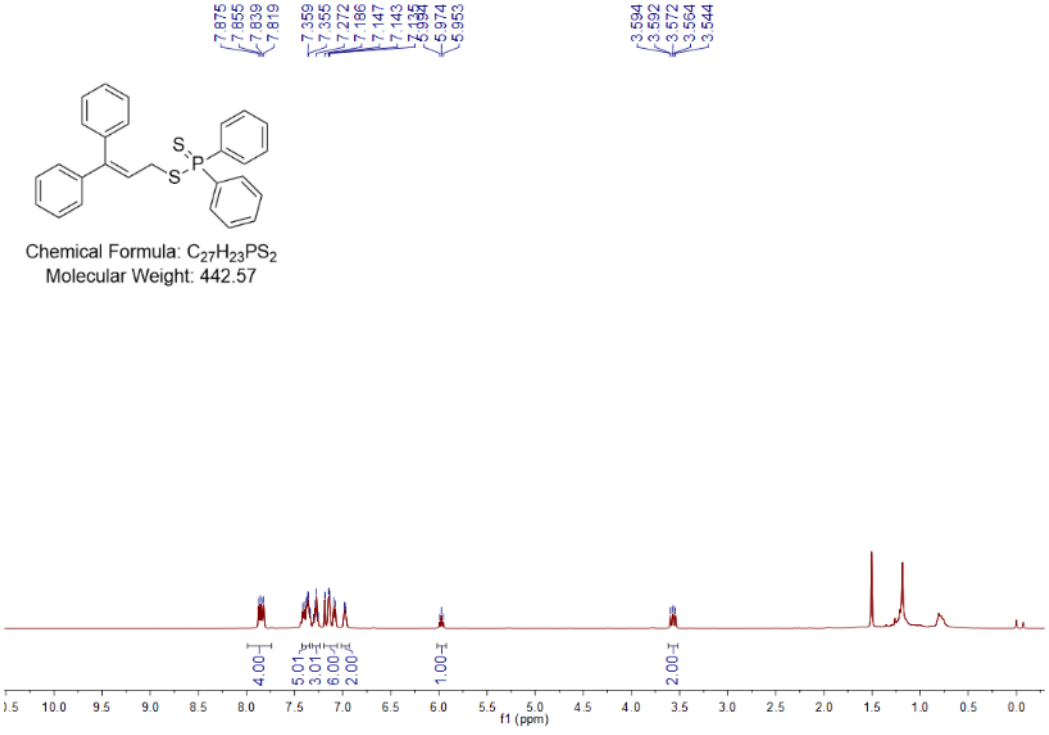
^{31}P NMR spectrum, 162 MHz, $CDCl_3$

O,O-diethyl S-hydrogen phosphorothioate (6b)

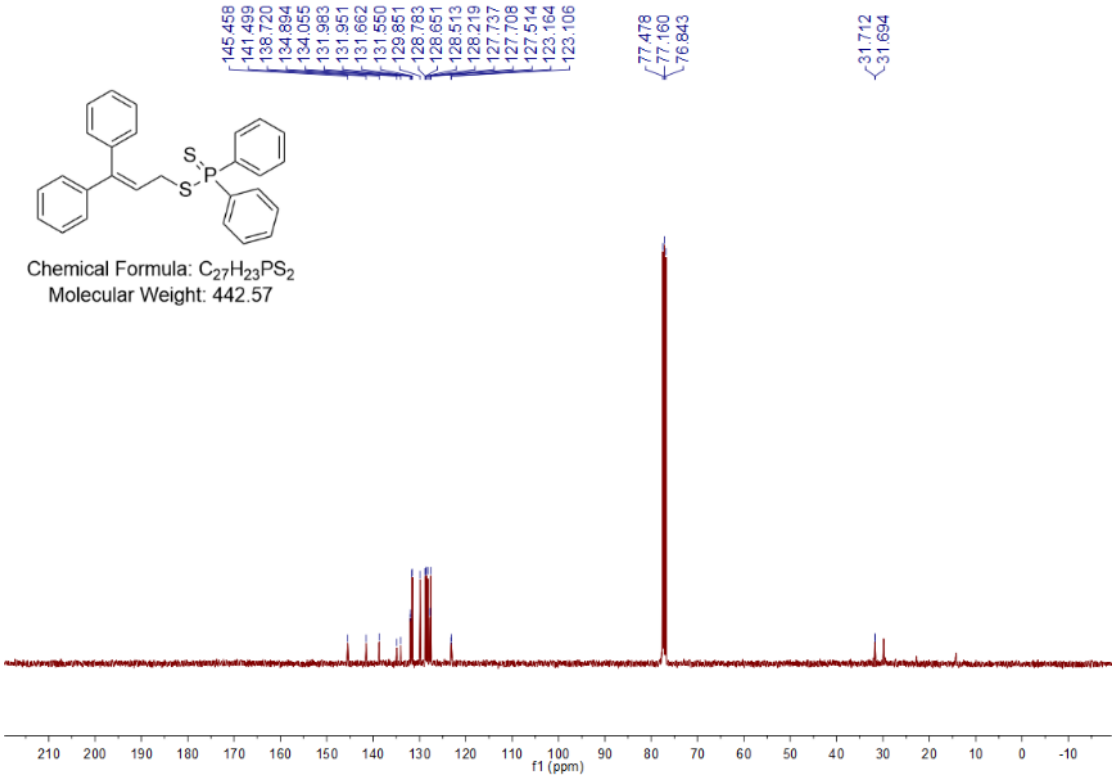


^{31}P NMR spectrum, 162 MHz, $CDCl_3$

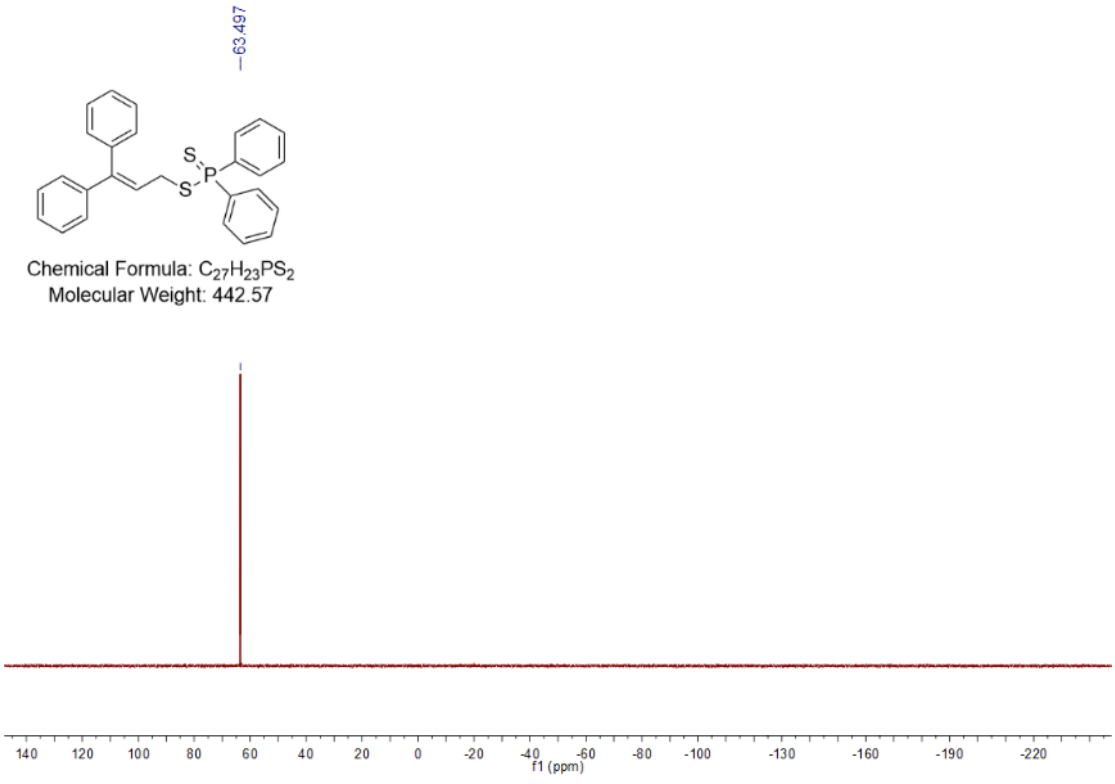
3,3-diphenylallyl diphenylphosphinodithioate (7a)



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



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



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