Supporting Information

Deoxygenative 1,3-Carbophosphination of Allylic Alcohols enabled by Manganese Pincer Catalyst

Xin Chen, Guanbo Li, Hui Ma, Sheng-Yin Zhao* and Weiping Liu*

Key Laboratory of Science and Technology of Eco-Textile, Ministry of Education, College of Chemistry and Chemical Engineering, Donghua University, Shanghai, 201620, P. R. China

*E-mail: syzhao8@dhu.edu.cn, weipingliu@dhu.edu.cn

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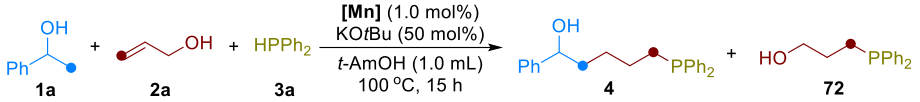
General information

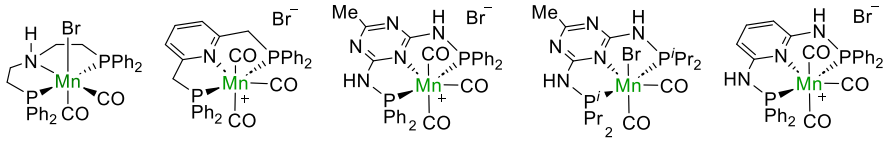
All catalytic reactions were performed under inert atmosphere using standard Schlenk techniques. Unless stated otherwise, all commercially available reagents were used without further purification. Dry solvents were prepared according to standard procedures and kept in the glove box after degassing. Bis(4-methylphenyl) phosphine, bis(4-methoxyphenyl) phosphine, bis(4-fluorophenyl) phosphine, bis(4-chlorophenyl) phosphine, di(naphthalen-2-yl) phosphine were synthesized according to reported methods[1]. Column chromatography was performed using silica gel (100-200 mesh). Visualization of the compounds was accomplished with UV light (254 nm) or basic $KMnO_4$. ^{1}H NMR, ^{31}P NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III instrument (600 MHz, 243 MHz, 565 MHz and 150 MHz, respectively). Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent $CDCl_3$ (7.26 ppm) referenced to the deuterated solvent signals in $CDCl_3$ (77.1 ppm). Chemical shifts are reported in δ (parts per million) values. Coupling constants J are reported in Hz. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), multiple (m). HRMS was measured on a Thermo Scientific Q Exactive HF Orbitrap-FTMS and Aglient 7250 & JEOL-JMS-T100LP AccuTOF apparatus.

Evaluation of the manganese catalysts

Table S1. Evaluation of the manganese catalysts [a]

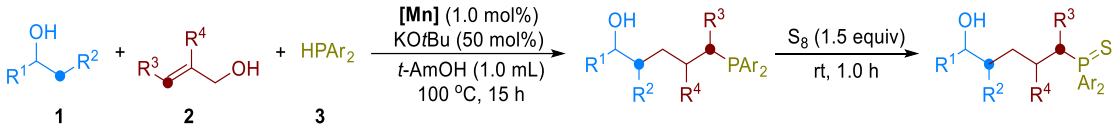


Entry	Catalyst	**1a (%)**	Yield of **4** (%)	Yield of **72** (%)
1	**[Mn]**	1	94	8
2	**Mn-1**	>99	<1	<1
3	**Mn-2**	85	7	44
4	**Mn-3**	50	42	26
5	**Mn-4**	88	5	17



[a] Condition: **1a** (0.5 mmol), **2a** (0.6 mmol), **3a** (0.6 mmol), Catalyst (1.0 mol%), KO*t*Bu (50 mol%), and *t*-AmOH (1.0 mL) in a sealed tube stirred at 100 °C for 15 h. Yields were determined by ^{1}H-NMR analysis using mesitylene as an internal standard.

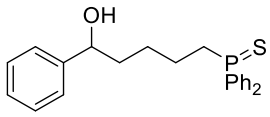
General procedure for preparation of ε-hydroxy phosphine



In a nitrogen-filled glove box, an oven-dried Schlenk pressure tube (10 mL) containing a stirring bar was charged with [**Mn**] (1.0 mol%). Dry and degassed *t*-AmOH (1.0 mL) and KO*t*Bu (50 mol%) were added and stirred at room temperature for 5.0 min. Then **2** (0.6 mmol, 1.2 equiv), secondary phosphine **3** (0.6 mmol, 1.2 equiv) and **1** (0.5 mmol, 1.0 equiv) were added in sequence. The tube was brought out of the glovebox and heated at 100 °C for 15 h. Upon reaction completion, S_8 (0.75 mmol, 1.5 equiv) was added and further stirred at room temperature for 1.0 h in N_2 atmosphere. The mixture was purified by column chromatography on silica gel (100-200 mesh) using PE/ EA as an eluent to afford final product.

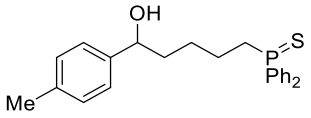
Characterization data of the isolated products

(5-Hydroxy-5-phenylpentyl) diphenylphosphine sulfide ([S]-4)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-4** (169.1 mg, 87%) as white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.85 – 7.74 (m, 4H), 7.52 – 7.41 (m, 6H), 7.35 – 7.23 (m, 5H), 4.64 – 4.60 (m, 1H), 2.47 – 2.36 (m, 2H), 1.88 – 1.74 (m, 2H), 1.72 – 1.59 (m, 3H), 1.55 – 1.45 (m, 1H), 1.44 – 1.34 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.6, 133.14 (d, J = 80.3 Hz), 133.06 (d, J = 79.9 Hz), 131.5 (d, J = 3.1 Hz), 131.11 (d, J = 10.0 Hz), 131.09 (d, J = 10.0 Hz), 128.7 (d, J = 12.1), 128.5, 127.6, 125.8, 74.2, 38.4, 32.5 (d, J = 56.8 Hz), 26.7 (d, J = 16.8 Hz), 22.1 (d, J = 2.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{23}H_{26}OPS$ $[M + H]^+$ 381.1437, found 381.1438.

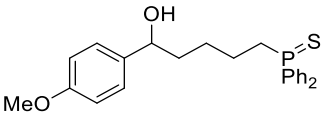
(5-Hydroxy-5-(*p*-tolyl) pentyl) diphenylphosphine sulfide ([S]-5)



The procedure was followed using 1-(*p*-tolyl) ethan-1-ol (0.5 mmol, 68.1 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-5** (167.1 mg, 85%) as white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.84 – 7.76 (m, 4H), 7.51 – 7.40 (m, 6H), 7.18 – 7.10 (m, 4H), 4.60 – 4.55 (m, 1H), 2.45 – 2.38 (m, 2H), 2.33 (s, 3H), 1.85 (s, 1H), 1.81 – 1.72 (m, 1H), 1.71 – 1.59 (m, 3H), 1.56 – 1.46 (m, 1H), 1.40 – 1.30 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 141.6, 137.3, 133.2 (d, J = 80.4 Hz), 133.1 (d, J

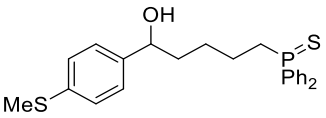
= 80.2 Hz), 131.5 (d, *J* = 3.1 Hz), 131.1 (d, *J* = 9.9 Hz), 131.0 (d, *J* = 10.1 Hz), 129.2, 128.7 (d, *J* = 12.1 Hz), 125.8, 74.0, 38.4, 32.5 (d, *J* = 56.4 Hz), 26.8 (d, *J* = 16.8 Hz), 22.1 (d, *J* = 2.6 Hz), 21.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{24}H_{28}OPS$ $[M + H]^+$ 395.1593, found 395.1590.

(5-Hydroxy-5-(4-methoxyphenyl) pentyl) diphenylphosphine sulfide ([S]-6)



The procedure was followed using 1-(4-methoxyphenyl) ethan-1-ol (0.5 mmol, 76.1 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-6** (170.3 mg, 83%) as white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.81 – 7.75 (m, 4H), 7.50 – 7.39 (m, 6H), 7.19 – 7.14 (m, 2H), 6.84 – 6.80 (m, 2H), 4.54 – 4.49 (m, 1H), 3.76 (s, 3H), 2.44 – 2.34 (m, 2H), 2.23 (s, 1H), 1.79 – 1.68 (m, 1H), 1.69 – 1.56 (m, 3H), 1.51 – 1.41 (m, 1H), 1.36 – 1.28 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.0, 136.8, 133.1 (d, *J* = 79.5 Hz), 133.0 (d, *J* = 79.8 Hz), 131.5 (d, *J* = 2.9 Hz), 131.1 (d, *J* = 10.2 Hz), 131.0 (d, *J* = 10.0 Hz), 128.7 (d, *J* = 12.0 Hz), 127.1, 113.8, 73.7, 55.3, 38.4, 32.4 (d, *J* = 56.6 Hz), 26.8 (d, *J* = 16.9 Hz), 22.1 (d, *J* = 2.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{24}H_{26}OPS$ $[M + H - H_2O]^+$ 393.1436, found 393.1435.

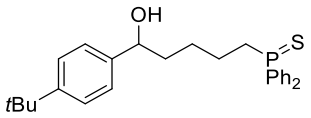
(5-Hydroxy-5-(4-(methylthio) phenyl) pentyl) diphenylphosphine sulfide ([S]-7)



The procedure was followed using 1-(4-(methylthio) phenyl) ethan-1-ol (0.5 mmol, 84.2 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-7** (180.1

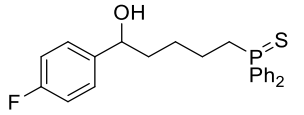
mg, 85%) as yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97 – 7.66 (m, 4H), 7.61 – 7.34 (m, 6H), 7.23 – 6.99 (m, 4H), 4.63 – 4.35 (m, 1H), 2.52 (s, 1H), 2.42 (s, 3H), 2.41 – 2.34 (m, 2H), 1.75 – 1.65 (m, 1H), 1.64 – 1.55 (m, 3H), 1.48 – 1.38 (m, 1H), 1.36 – 1.29 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 141.6, 137.3, 133.1 (d, J = 79.0 Hz), 133.0 (d, J = 79.8 Hz), 131.5 (d, J = 2.9 Hz), 131.1 (d, J = 10.6 Hz), 131.0 (d, J = 10.2 Hz), 128.7 (d, J = 11.9 Hz), 126.6, 126.5, 73.5, 38.4, 32.4 (d, J = 56.7 Hz), 26.7 (d, J = 16.7 Hz), 22.1 (d, J = 2.4 Hz), 16.0. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{24}H_{26}PS_2$ $[M + H - H_2O]^+$ 409.1208, found 409.1201.

(5-(4-(*tert*-Butyl) phenyl)-5-hydroxypentyl) diphenylphosphine sulfide ([S]-8)



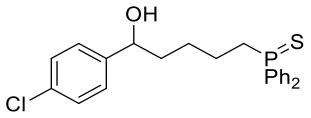
The procedure was followed using 1-(4-(*tert*-butyl) phenyl) ethan-1-ol (0.5 mmol, 89.2 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-8** (175.7 mg, 81%) as white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 – 7.74 (m, 4H), 7.47 – 7.37 (m, 6H), 7.34 – 7.29 (m, 2H), 7.20 – 7.15 (m, 2H), 4.58 – 4.46 (m, 1H), 2.45 – 2.36 (m, 2H), 2.25 (s, 1H), 1.79 – 1.69 (m, 1H), 1.67 – 1.56 (m, 3H), 1.55 – 1.44 (m, 1H), 1.42 – 1.34 (m, 1H), 1.29 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 150.4, 141.7, 133.2 (d, J = 79.7 Hz), 133.1 (d, J = 79.7 Hz), 131.5 (d, J = 3.0 Hz), 131.2 (d, J = 10.1 Hz), 131.1 (d, J = 10.3 Hz), 128.7 (d, J = 11.9 Hz), 125.6, 125.4, 73.8, 38.4, 34.5, 32.5 (d, J = 56.6 Hz), 31.5, 26.8 (d, J = 16.9 Hz), 22.1 (d, J = 2.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. HR-MS (ESI) m/z calcd for $C_{27}H_{34}OPS$ $[M + H]^+$ 437.2063, found 437.2065.

(5-(4-Fluorophenyl)-5-hydroxypentyl) diphenylphosphine sulfide ([S]-9)



The procedure was followed using 1-(4-fluorophenyl) ethan-1-ol (0.5 mmol, 70.1 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-9** (145.6 mg, 73%) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.82 – 7.78 (m, 4H), 7.51 – 7.47 (m, 2H), 7.46 – 7.43 (m, 4H), 7.25 – 7.22 (m, 2H), 7.01 – 6.97 (m, 2H), 4.62 – 4.58 (m, 1H), 2.44 – 2.39 (m, 2H), 1.98 (s, 1H), 1.78 – 1.73 (m, 1H), 1.68 – 1.61 (m, 3H), 1.51 – 1.45 (m, 1H), 1.40 – 1.33 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 162.1 (d, J = 245.4 Hz), 140.3 (d, J = 3.0 Hz), 133.1 (d, J = 80.0 Hz), 133.0 (d, J = 79.8 Hz), 131.5 (d, J = 3.1 Hz), 131.1 (d, J = 9.7 Hz), 131.0 (d, J = 10.4 Hz), 128.7 (d, J = 12.1 Hz), 127.5 (d, J = 8.0 Hz), 115.3 (d, J = 21.5 Hz), 73.5, 38.5, 32.4 (d, J = 56.6 Hz), 26.7 (d, J = 16.5 Hz), 22.0 (d, J = 2.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ = -115.0. HR-MS (ESI) m/z calcd for $C_{23}H_{25}FOPS$ $[M + H]^+$ 399.1343, found 399.1344.

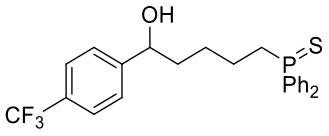
(5-(4-Chlorophenyl)-5-hydroxypentyl) diphenylphosphine sulfide ([S]-10)



The procedure was followed using 1-(4-chlorophenyl) ethan-1-ol (0.5 mmol, 78.3 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-10** (190.8 mg, 92%) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.81 – 7.77 (m, 4H), 7.51 – 7.47 (m, 2H), 7.46 – 7.42 (m, 4H), 7.29 – 7.26 (m, 2H), 7.22 – 7.19 (m, 2H), 4.63 – 4.56 (m, 1H), 2.45 – 2.38 (m, 2H), 2.03 (s, 1H), 1.77 – 1.70 (m, 1H), 1.66 – 1.59 (m, 3H), 1.51 – 1.42 (m, 1H), 1.40 – 1.33 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 143.2, 133.0 (d, J = 80.0 Hz), 132.9, 132.4 (d, J = 80.1 Hz), 131.6 (d, J = 3.0 Hz), 131.1 (d, J = 9.8 Hz), 131.0 (d, J = 10.0 Hz), 128.7 (d, J = 11.9 Hz), 128.5, 127.3, 73.2, 38.5, 32.3 (d, J = 56.4 Hz), 26.6 (d, J = 16.6 Hz), 22.0 (d, J = 1.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$)

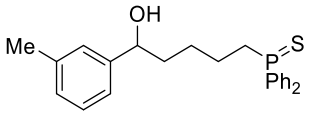
δ = 42.6. HR-MS (ESI) m/z calcd for $C_{23}H_{25}ClOPS$ $[M + H]^+$ 415.1047, found 415.1041.

(5-Hydroxy-5-(4-(trifluoromethyl) phenyl) pentyl) diphenylphosphine sulfide ([S]-11)



The procedure was followed using 1-(4-(trifluoromethyl) phenyl) ethan-1-ol (0.5 mmol, 95.1 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-11** (159.8 mg, 72%) as yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.80 – 7.75 (m, 4H), 7.59 – 7.50 (m, 2H), 7.49 – 7.40 (m, 6H), 7.37 – 7.32 (m, 2H), 4.66 – 4.62 (m, 1H), 2.64 (s, 1H), 2.44 – 2.36 (m, 2H), 1.74 – 1.68 (m, 1H), 1.68 – 1.59 (m, 3H), 1.48 – 1.42 (m, 1H), 1.40 – 1.35 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 148.7, 133.0 (d, J = 80.0 Hz), 132.3 (d, J = 80.1 Hz), 131.6 (d, J = 2.8 Hz), 131.1 (d, J = 10.1 Hz), 131.0 (d, J = 10.2 Hz), 129.5 (q, J = 32.3 Hz), 128.7 (d, J = 12.1 Hz), 126.1, 125.7, 125.3 (q, J = 3.7 Hz), 124.2 (q, J = 272.0 Hz), 73.2, 38.5, 32.3 (d, J = 56.5 Hz), 26.4 (d, J = 16.3 Hz), 22.0 (d, J = 2.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ = -62.3. HR-MS (ESI) m/z calcd for $C_{24}H_{25}F_3OPS$ $[M + H]^+$ 449.1311, found 449.1306.

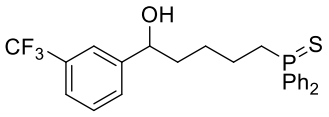
(5-Hydroxy-5-(*m*-tolyl) pentyl) diphenylphosphine sulfide ([S]-12)



The procedure was followed using 1-(*m*-tolyl) ethan-1-ol (0.5 mmol, 68.1 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-12** (168.0 mg, 85%)

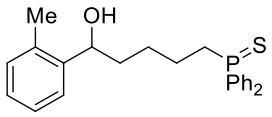
as white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.86 – 7.79 (m, 4H), 7.53 – 7.42 (m, 6H), 7.24 – 7.18 (m, 1H), 7.13 – 7.04 (m, 3H), 4.62 – 4.46 (m, 1H), 2.48 – 2.39 (m, 2H), 2.35 (s, 3H), 2.34 – 2.20 (m, 1H), 1.81 – 1.72 (m, 1H), 1.72 – 1.58 (m, 3H), 1.56 – 1.45 (m, 1H), 1.44 – 1.32 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.6, 138.1, 133.1 (d, J = 79.6 Hz), 133.0 (d, J = 80.2 Hz), 131.5 (d, J = 3.0 Hz), 131.1 (d, J = 10.1 Hz), 131.0 (d, J = 10.0 Hz), 128.7 (d, J = 12.0 Hz), 128.4, 128.3, 126.6, 123.0, 74.1, 38.5, 32.4 (d, J = 56.5 Hz), 26.8 (d, J = 16.9 Hz), 22.1 (d, J = 2.7 Hz), 21.5. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. HR-MS (ESI) m/z calcd for $C_{24}H_{28}OPS$ $[M + H]^+$ 395.1593, found 395.1591.

(5-Hydroxy-5-(3-(trifluoromethyl) phenyl) pentyl) diphenylphosphine sulfide ([S]-13)



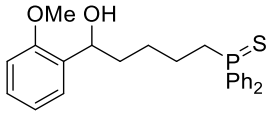
The procedure was followed using 1-(3-(trifluoromethyl) phenyl) ethan-1-ol (0.5 mmol, 95.1 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-13** (177.2 mg, 79%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 – 7.70 (m, 4H), 7.57 – 7.48 (m, 1H), 7.47 – 7.34 (m, 9H), 4.62 – 4.58 (m, 1H), 2.81 (s, 1H), 2.45 – 2.34 (m, 2H), 1.72 – 1.64 (m, 1H), 1.64 – 1.54 (m, 3H), 1.51 – 1.42 (m, 1H), 1.41 – 1.32 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 145.8, 133.0 (d, J = 80.0 Hz), 132.3 (d, J = 79.7 Hz), 131.6 (d, J = 2.8 Hz), 131.1 (d, J = 10.2 Hz), 131.0 (d, J = 10.3 Hz), 130.5 (q, J = 32.1 Hz), 129.3, 128.9, 128.7 (d, J = 12.0 Hz), 125.1 (q, J = 272.9 Hz), 124.2 (q, J = 3.8 Hz), 122.6 (q, J = 3.7 Hz), 73.2, 38.6, 32.3 (d, J = 56.5 Hz), 26.5 (d, J = 16.6 Hz), 22.0 (d, J = 2.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ = -62.3. HR-MS (ESI) m/z calcd for $C_{24}H_{25}F_3OPS$ $[M + H]^+$ 449.1311, found 449.1311.

(5-Hydroxy-5-(*o*-tolyl) pentyl) diphenylphosphine sulfide ([S]-14)



The procedure was followed using 1-(*o*-tolyl) ethan-1-ol (0.5 mmol, 68.1 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-14** (136.0 mg, 69%) as yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.84 – 7.75 (m, 4H), 7.48 – 7.36 (m, 7H), 7.18 – 7.14 (m, 1H), 7.13 – 7.09 (m, 1H), 7.09 – 7.05 (m, 1H), 4.84 – 4.81 (m, 1H), 2.44 – 2.36 (m, 2H), 2.24 (s, 3H), 2.04 (s, 1H), 1.74 – 1.48 (m, 5H), 1.49 – 1.37 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 142.8, 134.4, 133.2 (d, *J* = 79.3 Hz), 133.1 (d, *J* = 79.9 Hz), 131.5 (d, *J* = 3.2 Hz), 131.1 (d, *J* = 10.2 Hz), 131.0 (d, *J* = 10.0 Hz), 130.4, 128.7 (d, *J* = 12.0 Hz), 127.2, 126.3, 125.2, 70.2, 37.5, 32.5 (d, *J* = 56.6 Hz), 26.9 (d, *J* = 16.7 Hz), 22.2 (d, *J* = 2.8 Hz), 19.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{24}H_{28}OPS$ $[M + H]^+$ 395.1593, found 395.1600.

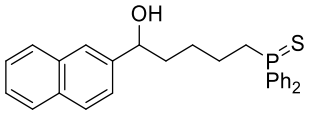
(5-Hydroxy-5-(2-methoxyphenyl) pentyl) diphenylphosphine sulfide ([S]-15)



The procedure was followed using 1-(2-methoxyphenyl) ethan-1-ol (0.5 mmol, 76.1 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-15** (141.3 mg, 69%) as white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.85 – 7.75 (m, 4H), 7.49 – 7.39 (m, 6H), 7.27 – 7.17 (m, 2H), 6.95 – 6.88 (m, 1H), 6.86 – 6.81 (m, 1H), 4.83 – 4.79 (m, 1H), 3.78 (s, 3H), 2.60 (s, 1H), 2.49 – 2.36 (m, 2H), 1.80 – 1.69 (m, 2H), 1.68 – 1.59 (m, 2H), 1.59 – 1.50 (m, 1H), 1.47 – 1.38 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 156.4, 133.3 (d, *J* = 79.9 Hz), 133.2 (d, *J* = 79.7 Hz), 132.4, 131.4 (d, *J* = 3.0 Hz), 131.1 (d, *J* = 10.1 Hz), 131.0 (d, *J* = 10.3 Hz), 128.6 (d, *J* = 11.8 Hz), 128.3, 126.8,

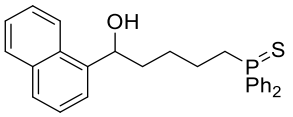
120.7, 110.5, 70.4, 55.3, 36.7, 32.6 (d, J = 56.5 Hz), 27.0 (d, J = 17.1 Hz), 22.1 (d, J = 2.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. HR-MS (ESI) m/z calcd for $C_{24}H_{28}O_2PS$ $[M + H]^+$ 411.1542, found 411.1539.

(5-Hydroxy-5-(naphthalen-2-yl) pentyl) diphenyl phosphine sulfide ([S]-16)



The procedure was followed using 1-(naphthalen-2-yl) ethan-1-ol (0.5 mmol, 86 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-16** (193.8 mg, 91%) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.84 – 7.75 (m, 7H), 7.73 – 7.70 (m, 1H), 7.50 – 7.39 (m, 9H), 4.82 – 4.77 (m, 1H), 2.44 – 2.37 (m, 2H), 1.98 (s, 1H), 1.91 – 1.82 (m, 1H), 1.82 – 1.73 (m, 1H), 1.72 – 1.60 (m, 2H), 1.56 – 1.47 (m, 1H), 1.45 – 1.37 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 141.9, 133.2, 133.14 (d, J = 79.6 Hz), 133.09 (d, J = 79.3 Hz), 133.0, 131.4 (d, J = 2.9 Hz), 131.10 (d, J = 10.0 Hz), 131.08 (d, J = 9.8 Hz), 128.6 (d, J = 12.1 Hz), 128.4, 127.9, 127.7, 126.2, 125.9, 124.6, 124.0, 74.3, 38.3, 32.5 (d, J = 56.5 Hz), 26.7 (d, J = 16.7 Hz), 22.1 (d, J = 2.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.5. HR-MS (ESI) m/z calcd for $C_{27}H_{28}OPS$ $[M + H]^+$ 431.1593, found 431.1583.

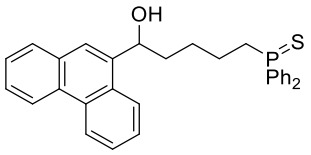
(5-Hydroxy-5-(naphthalen-1-yl) pentyl) diphenyl phosphine sulfide ([S]-17)



The procedure was followed using 1-(naphthalen-1-yl) ethan-1-ol (0.5 mmol, 86 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-17** (204.5 mg, 95%) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.08 – 8.03 (m, 1H), 7.90 – 7.83 (m,

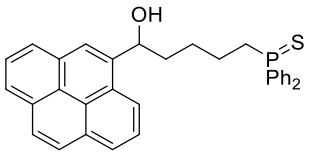
1H), 7.83 – 7.75 (m, 5H), 7.61 – 7.57 (m, 1H), 7.54 – 7.40 (m, 9H), 5.47 – 5.41 (m, 1H), 2.47 – 2.36 (m, 2H), 1.99 – 1.82 (m, 3H), 1.78 – 1.49 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 140.2, 133.8, 133.1 (d, J = 79.7 Hz), 133.0 (d, J = 79.7 Hz), 131.5 (d, J = 2.8 Hz), 131.1 (d, J = 10.0 Hz), 131.0 (d, J = 9.9 Hz). 130.3, 129.0, 128.6 (d, J = 12.0 Hz), 128.0, 126.1, 125.6, 125.4, 123.1, 122.9, 70.9, 37.6, 32.5 (d, J = 56.5 Hz), 27.0 (d, J = 16.6 Hz), 22.1 (d, J = 2.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{27}H_{28}OPS$ $[M + H]^+$ 431.1593, found 431.1594.

(5-Hydroxy-5-(phenanthren-9-yl) pentyl) diphenyl phosphine sulfide ([S]-18)



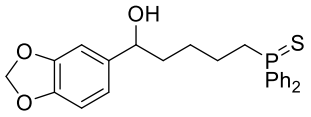
The procedure was followed using 1-(phenanthren-9-yl) ethan-1-ol (0.5 mmol, 111 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-18** (218.6 mg, 91%) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.76 – 8.72 (m, 1H), 8.67 – 8.63 (m, 1H), 8.10 – 8.06 (m, 1H), 7.89 – 7.83 (m, 2H), 7.82 – 7.74 (m, 4H), 7.69 – 7.56 (m, 4H), 7.50 – 7.38 (m, 6H), 5.47 – 5.42 (m, 1H), 2.46 – 2.37 (m, 2H), 2.08 – 1.97 (m, 2H), 1.95 – 1.86 (m, 1H), 1.78 – 1.68 (m, 1H), 1.68 – 1.56 (m, 2H), 1.39 – 1.23 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 138.3, 133.1 (d, J = 79.6 Hz), 132.5 (d, J = 79.1 Hz), 131.43 (d, J = 3.0 Hz), 131.37, 131.1 (d, J = 10.1 Hz), 131.0 (d, J = 10.0 Hz), 130.8, 130.0, 129.5, 128.8, 128.6 (d, J = 11.9 Hz), 126.8, 126.69, 126.67, 126.4, 123.8, 123.6, 123.4, 122.5, 71.1, 37.2, 32.5 (d, J = 56.4 Hz), 27.0 (d, J = 16.5 Hz), 22.1 (d, J = 2.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{31}H_{30}OPS$ $[M + H]^+$ 481.1750, found 481.1744.

(5-Hydroxy-5-(pyren-4-yl) pentyl) diphenyl phosphine sulfide ([S]-19)



The procedure was followed using 1-(pyren-4-yl) ethan-1-ol (0.5 mmol, 123 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-19** (213.2 mg, 85%) as yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.27 – 8.22 (m, 1H), 8.19 – 8.09 (m, 4H), 8.08 – 7.96 (m, 4H), 7.79 – 7.72 (m, 4H), 7.48 – 7.35 (m, 6H), 5.72 – 5.68 (m, 1H), 2.43 – 2.33 (m, 2H), 2.22 (s, 1H), 2.06 – 1.93 (m, 2H), 1.71 – 1.48 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 137.9, 133.1 (d, J = 79.6 Hz), 133.0 (d, J = 79.4 Hz), 132.9, 131.41 (d, J = 2.9 Hz), 131.38, 131.1 (d, J = 10.1 Hz), 131.0 (d, J = 10.1 Hz), 130.6, 128.6 (d, J = 12.0 Hz), 127.7, 127.48, 127.46, 127.3, 126.0, 125.3, 125.1, 125.0, 124.9, 124.8, 123.3, 122.4, 70.9, 38.4, 32.5 (d, J = 56.5 Hz), 27.0 (d, J = 16.5 Hz), 22.1 (d, J = 2.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{33}H_{28}PS$ $[M + H - H_2O]^+$ 487.1644, found 487.1638.

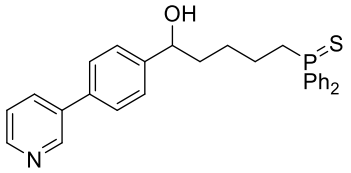
(5-(Benzo[*d*] [1,3] dioxol-5-yl)-5-hydroxypentyl) diphenyl phosphine sulfide ([S]-20)



The procedure was followed using 1-(benzo[*d*] [1,3] dioxol-5-yl) ethan-1-ol (0.5 mmol, 83 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-20** (161.4 mg, 76%) as pink solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 – 7.77 (m, 4H), 7.52 – 7.42 (m, 6H), 6.81 – 6.78 (m, 1H), 6.76 – 6.69 (m, 2H), 5.94 (s, 2H), 4.55 – 4.50 (m, 1H), 2.45 – 2.38 (m, 2H), 1.83 (s, 1H), 1.79 – 1.70 (m, 1H), 1.68 – 1.61 (m,

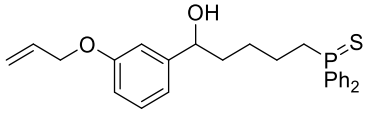
3H), 1.52 – 1.41 (m, 1H), 1.39 – 1.30 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 147.8, 146.9, 138.6, 133.1 (d, J = 79.5 Hz), 133.0 (d, J = 80.0 Hz), 131.5 (d, J = 2.9 Hz), 131.11 (d, J = 9.9 Hz), 131.08 (d, J = 9.8 Hz), 128.7 (d, J = 11.9 Hz), 119.3, 108.1, 106.3, 101.0, 74.1, 38.4, 32.5 (d, J = 56.7 Hz), 26.8 (d, J = 16.7 Hz), 22.0 (d, J = 2.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{24}H_{25}O_3PSNa$ $[M + Na]^+$ 447.1154, found 447.1158.

(5-Hydroxy-5-(4-(pyridin-3-yl) phenyl) pentyl) diphenyl phosphine sulfide ([S]-21)



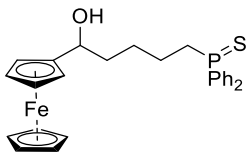
The procedure was followed using 1-(4-(pyridin-3-yl) phenyl) ethan-1-ol (0.5 mmol, 100 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 3/1) yielded **[S]-21** (209.8 mg, 92%) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.69 – 8.65 (m, 1H), 7.93 – 7.89 (m, 2H), 7.84 – 7.66 (m, 6H), 7.50 – 7.41 (m, 6H), 7.38 – 7.34 (m, 2H), 7.25 – 7.20 (m, 1H), 4.69 – 4.64 (m, 1H), 2.49 – 2.26 (m, 3H), 1.84 – 1.75 (m, 1H), 1.75 – 1.58 (m, 3H), 1.55 – 1.45 (m, 1H), 1.45 – 1.36 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 157.2, 149.7, 145.5, 138.6, 136.9, 133.13 (d, J = 79.8 Hz), 133.06 (d, J = 79.4 Hz), 131.5 (d, J = 2.8 Hz), 131.10 (d, J = 10.4 Hz), 131.08 (d, J = 10.1 Hz), 128.7 (d, J = 12.0 Hz), 127.0, 126.3, 122.2, 120.6, 73.8, 38.5, 32.5 (d, J = 56.8 Hz), 26.7 (d, J = 16.8 Hz), 22.1 (d, J = 2.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{28}H_{29}NOPS$ $[M + H]^+$ 458.1702, found 458.1695.

(5-(3-(Allylicoxy) phenyl)-5-hydroxypentyl) diphenylphosphine sulfide ([S]-22)



The procedure was followed using 1-(3-(allylicoxy) phenyl) ethan-1-ol (0.5 mmol, 89 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-22** (153.0 mg, 70%) as pink solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.86 – 7.77 (m, 4H), 7.52 – 7.42 (m, 6H), 7.26 – 7.20 (m, 1H), 6.89 – 6.84 (m, 2H), 6.84 – 6.79 (m, 1H), 6.10 – 6.01 (m, 1H), 5.45 – 5.38 (m, 1H), 5.31 – 5.26 (m, 1H), 4.62 – 4.58 (m, 1H), 4.55 – 4.51 (m, 2H), 2.46 – 2.38 (m, 2H), 1.85 – 1.82 (m, 1H), 1.81 – 1.72 (m, 1H), 1.71 – 1.57 (m, 3H), 1.55 – 1.45 (m, 1H), 1.45 – 1.32 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 158.8, 146.3, 133.2, 133.13 (d, J = 79.9 Hz), 133.05 (d, J = 79.8 Hz), 131.5 (d, J = 2.9 Hz), 131.11 (d, J = 10.1 Hz), 131.09 (d, J = 10.1 Hz), 129.5, 128.7 (d, J = 11.8 Hz), 118.3, 117.7, 113.8, 112.1, 74.1, 68.8, 38.4, 32.5 (d, J = 56.6 Hz), 26.7 (d, J = 16.7 Hz), 22.0 (d, J = 2.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{26}H_{30}O_2PS$ $[M + H]^+$ 437.1699, found 437.1703.

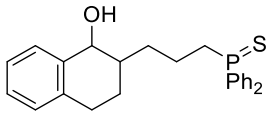
(5-Hydroxy-5-(ferrocenyl)) diphenyl phosphine ([S]-23)



The procedure was followed using KO*t*Bu (80 mol%), 1-(ferrocenyl) ethanol (0.5 mmol, 115 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-23** (158.6 mg, 65%) as yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.85 – 7.77 (m, 4H), 7.52 – 7.41 (m, 6H), 4.28 – 4.24 (m, 1H), 4.21 – 4.09 (m, 9H), 2.48 – 2.38 (m, 2H), 1.95 (s, 1H), 1.76 – 1.49 (m, 5H), 1.47 – 1.38 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.2 (d, J = 80.0 Hz), 133.1 (d, J = 79.4 Hz), 131.5 (d, J = 3.0 Hz), 131.12 (d, J = 9.9 Hz), 131.10 (d, J = 9.9 Hz), 128.7 (d, J = 11.8 Hz), 94.2, 69.3, 68.3, 68.0, 67.8, 67.2, 65.1, 37.6, 32.6 (d, J = 56.4 Hz), 27.0 (d, J = 17.1 Hz), 22.2 (d, J = 2.7 Hz). ^{31}P NMR

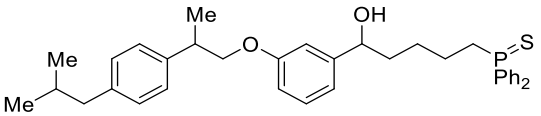
(243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{27}H_{28}FePS$ $[M + H - H_2O]^+$ 471.0993, found 471.0988.

(3-(1-Hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl) propyl) diphenylphosphine sulfide ([S]-24)



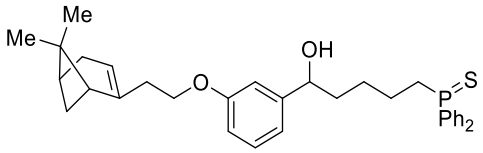
The procedure was followed using KO*t*Bu (80 mol%), 1,2,3,4-tetrahydronaphthalen-1-ol (0.5 mmol, 74 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-24** (151.3 mg, 67%, *d. r.* = 1: 1.1) as white solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.86 – 7.79 (m, 4H), 7.50 – 7.40 (m, 6H), 7.28 – 7.23 (m, 1H), 7.20 – 7.12 (m, 2H), 7.09 – 7.01 (m, 1H), 4.55 – 4.52 (m, 0.5H), 4.34 – 4.30 (m, 0.5H), 2.85 – 2.62 (m, 2H), 2.57 – 2.36 (m, 2H), 2.08 – 1.91 (m, 1H), 1.91 – 1.51 (m, 5H), 1.50 – 1.20 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 138.7, 138.5, 136.9, 136.8, 133.3 (d, J = 79.9 Hz), 133.2 (d, J = 79.8 Hz), 132.7 (d, J = 79.7 Hz), 132.6 (d, J = 79.7 Hz), 131.50 (d, J = 2.8 Hz), 131.49 (d, J = 2.7 Hz), 131.14 (d, J = 10.1 Hz), 131.12 (d, J = 9.9 Hz), 131.06 (d, J = 10.1 Hz), 131.0 (d, J = 10.1 Hz), 130.0, 129.1, 128.74, 128.71 (d, J = 11.6 Hz) x 2C, 128.3, 127.9, 127.3, 126.2, 126.1, 73.2, 69.6, 41.6, 39.2, 32.8 (d, J = 56.2 Hz), 32.7 (d, J = 16.1 Hz), 32.5 (d, J = 16.1 Hz), 32.4 (d, J = 56.6 Hz), 29.1, 27.7, 24.7, 22.9, 19.9 (d, J = 2.7 Hz), 19.8 (d, J = 2.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.8, 42.7. HR-MS (ESI) m/z calcd for $C_{25}H_{26}PS$ $[M + H - H_2O]^+$ 429.1412, found 429.1409.

(5-Hydroxy-5-(3-(2-(4-isobutylphenyl) propoxy) phenyl) pentyl) diphenylphosphine sulfide ([S]-25)



The procedure was followed using 1-(3-(2-(4-isobutylphenyl) propoxy) phenyl) ethan-1-ol (0.5 mmol, 156 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-25** (235.0 mg, 82%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.82 – 7.75 (m, 4H), 7.49 – 7.39 (m, 6H), 7.21 – 7.14 (m, 3H), 7.12 – 7.08 (m, 2H), 6.84 – 6.74 (m, 3H), 4.56 – 4.52 (m, 1H), 4.07 – 4.02 (m, 1H), 3.93 – 3.87 (m, 1H), 3.22 – 3.16 (m, 1H), 2.47 – 2.36 (m, 4H), 2.02 (s, 1H), 1.89 – 1.80 (m, 1H), 1.77 – 1.68 (m, 1H), 1.68 – 1.58 (m, 3H), 1.51 – 1.43 (m, 1H), 1.41 – 1.32 (m, 4H), 0.90 (d, J = 6.7 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.2, 146.3, 140.8, 140.0, 133.2 (d, J = 79.9 Hz), 133.1 (d, J = 79.4 Hz), 131.5 (d, J = 3.3 Hz), 131.13 (d, J = 10.0 Hz), 131.11 (d, J = 10.4 Hz), 129.5, 129.3, 128.7 (d, J = 12.1 Hz), 127.2, 118.1, 113.7, 111.9, 74.1, 73.6, 45.1, 39.2, 38.4, 32.5 (d, J = 56.7 Hz), 30.3, 26.7 (d, J = 16.5 Hz), 22.5, 22.1 (d, J = 2.6 Hz), 18.3 (d, J = 1.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{36}H_{44}O_2PS$ $[M + H]^+$ 571.2794, found 571.2791.

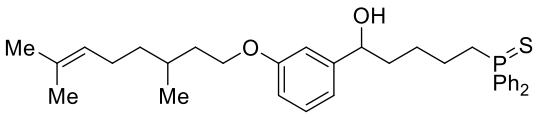
(5-(3-(2-(6,6-Dimethylbicyclo [3.1.1] hept-2-en-2-yl) ethoxy) phenyl)-5-hydroxypentyl) diphenyl phosphine sulfide ([S]-26)



The procedure was followed using 1-(3-(2-(6,6-dimethylbicyclo [3.1.1] hept-2-en-2-yl) ethoxy) phenyl) ethan-1-ol (0.5 mmol, 143 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-26** (209.0 mg, 80%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 – 7.77 (m, 4H), 7.51 – 7.41 (m, 6H), 7.24 – 7.18 (m, 1H), 6.85 – 6.81 (m, 2H), 6.80 – 6.75 (m, 1H), 5.35 – 5.33 (m, 1H), 4.60 – 4.56 (m, 1H), 3.98 – 3.93 (m, 2H), 2.48 – 2.34 (m, 5H), 2.31 – 2.25 (m, 1H), 2.23 – 2.17 (m,

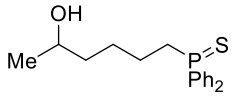
1H), 2.11 – 2.07 (m, 2H), 1.89 – 1.86 (m, 1H), 1.81 – 1.71 (m, 1H), 1.69 – 1.59 (m, 3H), 1.55 – 1.45 (m, 1H), 1.44 – 1.34 (m, 1H), 1.27 (s, 3H), 1.21 – 1.15 (m, 1H), 0.83 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.1, 146.2, 144.5, 133.2 (d, J = 79.6 Hz), 133.1 (d, J = 79.9 Hz), 131.5 (d, J = 3.0 Hz), 131.11 (d, J = 10.1 Hz), 131.09 (d, J = 10.0 Hz), 129.5, 128.7 (d, J = 12.1 Hz), 118.6, 118.0, 113.5, 112.1, 74.1, 66.3, 45.9, 40.7, 38.4, 38.1, 36.6, 32.5 (d, J = 56.8 Hz), 31.7, 31.4, 26.7 (d, J = 16.8 Hz), 26.3, 22.1 (d, J = 2.6 Hz), 21.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{34}H_{41}O_2PSNa$ $[M + Na]^+$ 567.2457, found 567.2460.

(5-(3-((3,7-Dimethyloct-6-en-1-yl) oxy) phenyl)-5-hydroxypentyl) diphenylphosphine sulfide ([S]-27)



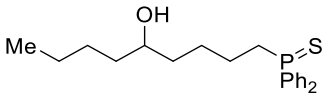
The procedure was followed using 1-(3-((3,7-dimethyloct-6-en-1-yl) oxy) phenyl) ethan-1-ol (0.5 mmol, 138 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-27** (208.7 mg, 78%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.82 – 7.75 (m, 4H), 7.48 – 7.39 (m, 6H), 7.21 – 7.15 (m, 1H), 6.86 – 6.74 (m, 3H), 5.13 – 5.08 (m, 1H), 4.57 – 4.51 (m, 1H), 4.01 – 3.91 (m, 2H), 2.43 – 2.36 (m, 2H), 2.20 (s, 1H), 2.08 – 1.93 (m, 2H), 1.89 – 1.78 (m, 1H), 1.71 – 1.54 (m, 12H), 1.53 – 1.32 (m, 3H), 1.30 – 1.17 (m, 1H), 0.94 (d, J = 6.7 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.3, 146.4, 133.2 (d, J = 79.9 Hz), 133.1 (d, J = 79.9 Hz), 131.4 (d, J = 2.8 Hz), 131.3, 131.12 (d, J = 10.0 Hz), 131.10 (d, J = 10.1 Hz), 129.4, 128.7 (d, J = 11.8 Hz), 124.7, 118.0, 113.5, 112.0, 74.0, 66.3, 38.4, 37.2, 36.2, 32.5 (d, J = 56.5 Hz), 29.6, 26.7 (d, J = 16.6 Hz), 25.8, 25.5, 22.1 (d, J = 2.6 Hz), 19.6, 17.8. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{33}H_{44}O_2PS$ $[M + H]^+$ 535.2794, found 535.2790.

(5-Hydroxyhexyl) diphenylphosphine sulfide ([S]-28)



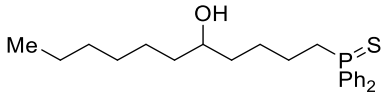
The procedure was followed using propan-2-ol (0.5 mmol, 30 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-28** (120.4 mg, 76%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 – 7.77 (m, 4H), 7.53 – 7.40 (m, 6H), 3.79 – 3.68 (m, 1H), 2.52 – 2.40 (m, 2H), 1.73 – 1.57 (m, 2H), 1.59 – 1.48 (m, 2H), 1.48 – 1.35 (m, 3H), 1.14 (d, J = 6.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.13 (d, J = 79.8 Hz), 133.07 (d, J = 79.6 Hz), 131.5 (d, J = 2.8 Hz), 131.11 (d, J = 10.0 Hz), 131.09 (d, J = 10.2 Hz), 128.7 (d, J = 11.8 Hz), 67.7, 38.6, 32.5 (d, J = 56.5 Hz), 26.7 (d, J = 16.6 Hz), 23.6, 22.2 (d, J = 2.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{18}H_{24}OPS$ $[M + H]^+$ 319.1280, found 319.1273.

(5-Hydroxynonyl) diphenylphosphine sulfide ([S]-29)



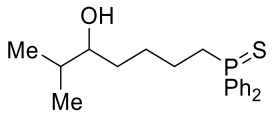
The procedure was followed using hexan-2-ol (0.5 mmol, 51 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-29** (127.1 mg, 71%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.82 (m, 4H), 7.52 – 7.40 (m, 6H), 5.30 – 5.26 (m, 1H), 3.58 – 3.45 (m, 1H), 2.50 – 2.42 (m, 2H), 1.69 – 1.50 (m, 4H), 1.49 – 1.32 (m, 5H), 1.33 – 1.21 (m, 3H), 0.91 – 0.85 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.2 (d, J = 79.6 Hz), 132.5 (d, J = 79.5 Hz), 131.5 (d, J = 2.9 Hz), 131.1 (d, J = 9.9 Hz), 131.0 (d, J = 10.0 Hz), 128.7 (d, J = 12.0 Hz), 71.4, 37.2, 36.8, 32.5 (d, J = 56.5 Hz), 27.8, 26.7 (d, J = 16.5 Hz), 22.7, 22.2 (d, J = 2.7 Hz), 14.1. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. HR-MS (ESI) m/z calcd for $C_{21}H_{30}OPS$ $[M + H]^+$ 361.1750, found 361.1743.

(5-Hydroxyundecyl) diphenylphosphine sulfide ([S]-30)



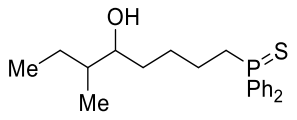
The procedure was followed using octan-2-ol (0.5 mmol, 65 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-30** (142.0 mg, 73%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 – 7.77 (m, 4H), 7.51 – 7.42 (m, 6H), 3.57 – 3.47 (m, 1H), 2.53 – 2.41 (m, 2H), 1.73 – 1.49 (m, 4H), 1.49 – 1.33 (m, 6H), 1.33 – 1.18 (m, 7H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.2 (d, J = 80.1 Hz), 132.6 (d, J = 80.4 Hz), 131.5 (d, J = 3.1 Hz), 131.1 (d, J = 10.4 Hz), 131.0 (d, J = 10.0 Hz), 128.7 (d, J = 11.8 Hz), 71.5, 37.6, 36.8, 32.5 (d, J = 56.4 Hz), 31.8, 29.4, 26.7 (d, J = 16.6 Hz), 25.6, 22.6, 22.2 (d, J = 2.6 Hz), 14.1. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.6. HR-MS (ESI) m/z calcd for $C_{23}H_{34}OPS$ $[M + H]^+$ 389.2063, found 389.2054.

(5-Hydroxy-6-methylheptyl) diphenylphosphine sulfide ([S]-31)



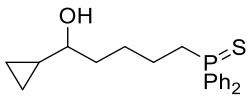
The procedure was followed using 3-methylbutan-2-ol (0.5 mmol, 44 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-31** (130.2 mg, 75%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.89 – 7.77 (m, 4H), 7.56 – 7.38 (m, 6H), 3.32 – 3.26 (m, 1H), 2.53 – 2.40 (m, 2H), 1.75 – 1.65 (m, 1H), 1.64 – 1.50 (m, 4H), 1.49 – 1.27 (m, 3H), 0.90 – 0.80 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.2 (d, J = 79.7 Hz), 132.5 (d, J = 79.6 Hz), 131.5 (d, J = 3.1 Hz), 131.1 (d, J = 10.2 Hz), 131.0 (d, J = 9.9 Hz), 128.7 (d, J = 11.9 Hz), 76.3, 33.6, 32.5 (d, J = 56.4 Hz), 27.2 (d, J = 16.7 Hz), 22.3 (d, J = 2.7 Hz), 18.8, 17.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. HR-MS (ESI) m/z calcd for $C_{20}H_{27}OPSNa$ $[M + Na]^+$ 369.1412, found 369.1411.

(5-Hydroxy-6-methyloctyl) diphenylphosphine sulfide ([S]-32)



The procedure was followed using 3-methylpentan-2-ol (0.5 mmol, 51 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-32** (138.8 mg, 77%, *d. r.* = 1: 1) as yellow oil. Diastereomeric ratio was determined by HPLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 – 7.78 (m, 4H), 7.53 – 7.38 (m, 6H), 3.46 – 3.40 (m, 1H), 2.50 – 2.43 (m, 2H), 1.76 – 1.51 (m, 4H), 1.50 – 1.24 (m, 5H), 1.20 – 1.04 (m, 1H), 0.89 – 0.84 (m, 3H), 0.84 – 0.80 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.2 (d, J = 79.5 Hz), 132.5 (d, J = 79.7 Hz), 131.5 (d, J = 2.9 Hz), 131.1 (d, J = 10.0 Hz), 131.0 (d, J = 10.0 Hz), 128.7 (d, J = 12.0 Hz), 75.3, 74.5, 40.6, 40.1, 33.9, 32.8, 32.7 (d, J = 56.7 Hz), 32.3 (d, J = 56.3 Hz), 27.4 (d, J = 16.6 Hz), 27.2 (d, J = 16.6 Hz), 25.9, 24.6, 22.3 (d, J = 2.7 Hz), 22.3 (d, J = 2.7 Hz), 14.7, 13.3, 11.9, 11.8. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. HR-MS (ESI) m/z calcd for $C_{21}H_{30}OPS$ $[M + H]^+$ 361.1750, found 361.1749.

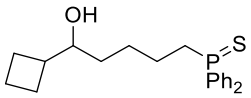
(5-Cyclopropyl-5-hydroxypentyl) diphenylphosphine sulfide ([S]-33)



The procedure was followed using 1-cyclopropylethan-1-ol (0.5 mmol, 43 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-33** (131.4 mg, 76%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 – 7.77 (m, 4H), 7.51 – 7.39 (m, 6H), 2.83 – 2.73 (m, 1H), 2.51 – 2.42 (m, 2H), 1.83 (s, 1H), 1.73 – 1.45 (m, 6H), 0.86 – 0.78 (m, 1H), 0.51 – 0.39 (m, 2H), 0.25 – 0.18 (m, 1H), 0.18 – 0.09 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.2 (d, J = 80.0 Hz), 132.6 (d, J = 80.0 Hz), 131.5 (d,

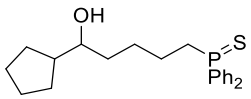
J = 3.0 Hz), 131.1 (d, J = 10.0 Hz), 131.0 (d, J = 10.0 Hz), 128.7 (d, J = 11.8 Hz), 76.4, 36.6, 32.5 (d, J = 56.7 Hz), 26.7 (d, J = 16.7 Hz), 22.3 (d, J = 2.7 Hz), 17.9, 2.8, 2.6. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. HR-MS (ESI) m/z calcd for $C_{20}H_{25}OPSNa$ [M + Na]$^+$ 367.1256, found 367.1257.

(5-Cyclobutyl-5-hydroxypentyl) diphenylphosphine sulfide ([S]-34)



The procedure was followed using 1-cyclobutylethan-1-ol (0.5 mmol, 50 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-34** (127.1 mg, 71%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 – 7.78 (m, 4H), 7.52 – 7.40 (m, 6H), 3.45 – 3.39 (m, 1H), 2.51 – 2.39 (m, 2H), 2.30 – 2.20 (m, 1H), 2.01 – 1.93 (m, 1H), 1.92 – 1.49 (m, 9H), 1.47 – 1.33 (m, 2H), 1.30 – 1.18 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.2 (d, J = 80.6 Hz), 132.5 (d, J = 80.1 Hz), 131.5 (d, J = 2.9 Hz), 131.1 (d, J = 10.0 Hz), 131.0 (d, J = 10.0 Hz), 128.7 (d, J = 11.8 Hz), 75.4, 41.4, 33.9, 32.5 (d, J = 56.5 Hz), 26.7 (d, J = 16.8 Hz), 24.4, 24.3, 22.3 (d, J = 2.8 Hz), 17.9. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. HR-MS (ESI) m/z calcd for $C_{21}H_{28}OPS$ [M + H]$^+$ 359.1593, found 359.1585.

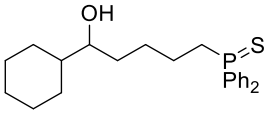
(5-Cyclopentyl-5-hydroxypentyl) diphenylphosphine sulfide ([S]-35)



The procedure was followed using 1-cyclopentylethan-1-ol (0.5 mmol, 57 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-35** (119.1 mg, 64%) as white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 – 7.78 (m, 4H), 7.54 – 7.40 (m, 6H),

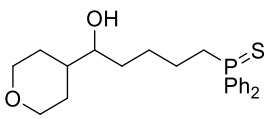
3.37 – 3.30 (m, 1H), 2.51 – 2.41 (m, 2H), 1.84 – 1.78 (m, 1H), 1.77 – 1.66 (m, 2H), 1.66 – 1.41 (m, 10H), 1.39 – 1.23 (m, 2H), 1.18 – 1.09 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.2 (d, J = 79.8 Hz), 132.6 (d, J = 79.2 Hz), 131.4 (d, J = 2.9 Hz), 131.1 (d, J = 10.1 Hz), 131.0 (d, J = 9.9 Hz), 128.7 (d, J = 11.8 Hz), 75.6, 46.4, 35.6, 32.5 (d, J = 56.5 Hz), 29.2, 28.6, 26.9 (d, J = 16.7 Hz), 25.7, 25.6, 22.3 (d, J = 2.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. HR-MS (ESI) m/z calcd for $C_{22}H_{30}OPS$ $[M + H]^+$ 373.1750, found 373.1748.

(5-Cyclohexyl-5-hydroxypentyl) diphenylphosphine sulfide ([S]-36)



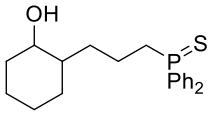
The procedure was followed using 1-cyclohexylethan-1-ol (0.5 mmol, 64 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 3/1) yielded **[S]-36** (144.5 mg, 75%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.86 – 7.78 (m, 4H), 7.52 – 7.42 (m, 6H), 3.32 – 3.26 (m, 1H), 2.53 – 2.39 (m, 2H), 1.79 – 1.53 (m, 8H), 1.50 – 1.32 (m, 4H), 1.30 – 1.08 (m, 4H), 1.06 – 0.89 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.2 (d, J = 79.6 Hz), 132.6 (d, J = 79.1 Hz), 131.4 (d, J = 2.9 Hz), 131.1 (d, J = 10.3 Hz), 131.0 (d, J = 10.0 Hz), 128.7 (d, J = 12.0 Hz), 75.8, 43.7, 33.6, 32.5 (d, J = 56.4 Hz), 29.2, 27.8, 27.0 (d, J = 16.6 Hz), 26.5, 26.3, 26.2, 22.3 (d, J = 2.8 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. HR-MS (ESI) m/z calcd for $C_{23}H_{32}OPS$ $[M + H]^+$ 387.1906, found 387.1900.

(5-Hydroxy-5-(tetrahydro-2*H*-pyran-4-yl) pentyl) diphenylphosphine sulfide ([S]-37)



The procedure was followed using 1-(tetrahydro-2*H*-pyran-4-yl) ethan-1-ol (0.5 mmol, 65 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 2/1) yielded **[S]-37** (126.1 mg, 65%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.89 – 7.76 (m, 4H), 7.55 – 7.38 (m, 6H), 4.09 – 3.84 (m, 2H), 3.51 – 3.16 (m, 3H), 2.56 – 2.34 (m, 2H), 1.83 – 1.14 (m, 11H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.1 (d, J = 79.9 Hz), 132.7 (d, J = 80.2 Hz), 131.5 (d, J = 2.9 Hz), 131.1 (d, J = 9.9 Hz), 131.0 (d, J = 10.0 Hz), 128.7 (d, J = 11.8 Hz), 68.1, 41.1, 33.5, 32.5 (d, J = 56.4 Hz), 29.2, 28.3, 26.8 (d, J = 16.1 Hz), 22.3 (d, J = 2.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. HR-MS (ESI) m/z calcd for $C_{22}H_{30}O_2PS$ $[M + H]^+$ 389.1699, found 389.1697.

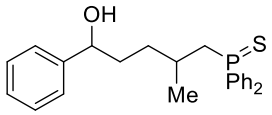
(3-(2-Hydroxy-3-methylcyclohexyl) propyl) diphenylphosphine sulfide ([S]-38)



The procedure was followed using cyclohexanol (0.5 mmol, 50 mg), allylic alcohol (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-38** (86.5 mg (major diastereomer); 52.5 mg (minor diastereomer)), 78%, *d. r.* = 1: 1.5) as colorless oil. Diastereomeric ratio was determined by NMR analysis of the crude mixture. Major diastereomer product: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 – 7.77 (m, 4H), 7.55 – 7.39 (m, 6H), 3.83 – 3.78 (m, 1H), 2.52 – 2.37 (m, 2H), 1.78 – 1.47 (m, 6H), 1.46 – 1.23 (m, 7H), 1.23 – 1.11 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.3 (d, J = 79.7 Hz), 132.7 (d, J = 80.0 Hz), 131.4 (d, J = 3.3 Hz), 131.1 (d, J = 10.0 Hz), 131.0 (d, J = 10.0 Hz), 128.6 (d, J = 12.1 Hz), 68.9, 40.9, 33.1, 32.9 (d, J = 16.7 Hz), 32.6 (d, J = 56.4 Hz), 26.6, 25.1, 20.4, 19.8 (d, J = 2.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. Minor diastereomer product: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.86 – 7.74 (m, 4H), 7.56 – 7.37 (m, 6H), 3.20 – 3.11 (m, 1H), 2.56 – 2.33 (m, 2H), 1.93 – 1.52 (m, 8H), 1.34 – 1.05 (m,

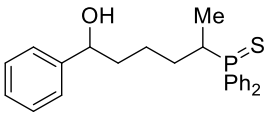
6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 133.4 (d, J = 79.3 Hz), 132.6 (d, J = 79.3 Hz), 131.4 (d, J = 3.3 Hz), 131.1 (d, J = 10.0 Hz), 131.0 (d, J = 10.1 Hz), 128.7 (d, J = 11.7 Hz), 74.4, 44.7, 35.9, 33.2 (d, J = 15.9 Hz), 32.6 (d, J = 56.4 Hz), 30.0, 25.5, 24.8, 19.3 (d, J = 2.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.7. HR-MS (ESI) m/z calcd for $C_{21}H_{28}OPS$ $[M + H]^+$ 359.1593, found 359.1590.

(5-Hydroxy-2-methyl-5-phenylpentyl) diphenylphosphine sulfide ([S]-39)



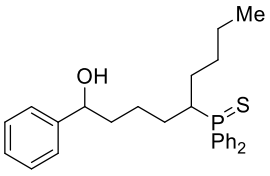
The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 2-methylprop-2-en-1-ol (0.6 mmol, 43.3 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-39** (160.5 mg, 57%, *d. r.* = 1: 1) as white oil. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 – 7.76 (m, 4H), 7.49 – 7.37 (m, 6H), 7.33 – 7.27 (m, 2H), 7.27 – 7.21 (m, 3H), 4.56 – 4.51 (m, 0.5H), 4.53 – 4.48 (m, 0.48H), 2.50 – 2.30 (m, 2.39H), 2.28 – 2.13 (m, 1.47H), 1.74 – 1.57 (m, 2H), 1.52 – 1.39 (m, 1H), 1.34 – 1.22 (m, 1H), 0.85 (d, J = 6.7 Hz, 1.52H), 0.82 (d, J = 6.7 Hz, 1.55H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.7, 144.6, 134.2 (d, J = 79.5 Hz), 134.1 (d, J = 79.8 Hz), 133.7 (d, J = 78.1 Hz), 133.2 (d, J = 79.2 Hz), 131.42 (d, J = 3.0 Hz), 131.39 (d, J = 3.0 Hz), 131.37 (d, J = 3.0 Hz), 131.3 (d, J = 2.9 Hz), 131.2 (d, J = 10.0 Hz), 131.1 (d, J = 10.0 Hz), 131.0 (d, J = 10.0 Hz) x 2C, 128.7 (d, J = 12.0 Hz), 128.64 (d, J = 12.1 Hz), 128.58 (d, J = 11.7 Hz), 128.5 (d, J = 11.9 Hz), 128.43, 128.42, 127.5, 127.4, 125.93, 125.86, 74.5, 73.8, 38.8 (d, J = 55.0 Hz), 38.3 (d, J = 55.5 Hz), 36.0, 35.9, 34.4 (d, J = 11.0 Hz), 34.0 (d, J = 10.0 Hz), 28.5 (d, J = 2.6 Hz), 28.1 (d, J = 2.6 Hz), 21.24 (d, J = 6.6 Hz), 21.17 (d, J = 7.8 Hz). HR-MS (ESI) m/z calcd for $C_{24}H_{26}PS$ $[M + H – H_2O]^+$ 377.1487, found 377.1486.

(6-Hydroxy-6-phenylhexan-2-yl) diphenylphosphine sulfide ([S]-40)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), but-2-en-1-ol (0.6 mmol, 43.3 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-40** (157.7 mg, 80%, *d. r.* = 1: 1) as white solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97 – 7.86 (m, 4H), 7.51 – 7.39 (m, 6H), 7.35 – 7.21 (m, 5H), 4.61 – 4.49 (m, 1H), 2.75 – 2.62 (m, 1H), 1.92 (s, 1H), 1.77 – 1.48 (m, 5H), 1.35 – 1.03 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.6, 144.5, 132.1 (d, J = 79.6 Hz), 132.0 (d, J = 79.3 Hz), 131.6 (d, J = 79.8 Hz), 131.5 (d, J = 79.6 Hz), 131.42 (d, J = 3.0 Hz), 131.41 (d, J = 3.1 Hz), 131.40 (d, J = 3.0 Hz), 131.39 (d, J = 3.0 Hz), 131.38 (d, J = 9.9 Hz), 131.36 (d, J = 10.0 Hz), 131.33 (d, J = 9.9 Hz), 131.31 (d, J = 9.9 Hz), 128.7 (d, J = 11.2 Hz), 128.60 (d, J = 11.1 Hz), 128.58 (d, J = 11.5 Hz), 128.53 (d, J = 11.2 Hz), 128.50, 128.49, 127.63, 127.60, 125.9, 125.8, 74.2, 74.1, 38.6, 38.5, 33.0 (d, J = 55.8 Hz), 32.6 (d, J = 55.7 Hz), 29.1 x 2C, 23.6 (d, J = 14.1 Hz), 23.5 (d, J = 14.3 Hz), 12.5 (d, J = 2.2 Hz), 12.4 (d, J = 2.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 53.0, 52.9. HR-MS (ESI) m/z calcd for $C_{24}H_{28}OPS$ $[M + H]^+$ 395.1593, found 395.1589.

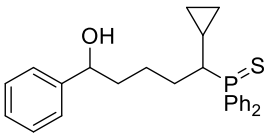
(1-Hydroxy-1-phenylnonan-5-yl) diphenylphosphine sulfide ([S]-41)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), hept-2-en-1-ol (0.6 mmol, 69 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification

by column chromatography (PE/EA = 5/1) yielded **[S]-41** (171.0 mg, 81%, *d. r.* = 1: 1.1) as white solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.96 – 7.87 (m, 4H), 7.48 – 7.36 (m, 6H), 7.32 – 7.26 (m, 2H), 7.26 – 7.16 (m, 3H), 4.51 – 4.44 (m, 1H), 2.55 – 2.47 (m, 1H), 2.06 (s, 1H), 1.76 – 1.27 (m, 8H), 1.25 – 1.01 (m, 4H), 0.76 – 0.67 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.6, 144.5, 132.7 (d, *J* = 75.7 Hz) x 2C, 132.6 (d, *J* = 76.4 Hz), 132.0 (d, *J* = 76.4 Hz), 131.5 (d, *J* = 9.3 Hz), 131.44 (d, *J* = 9.4 Hz), 131.40 (d, *J* = 9.1 Hz), 131.36 (d, *J* = 9.2 Hz), 131.32 (d, *J* = 2.6 Hz) x 2C, 131.29 (d, *J* = 2.7 Hz) x 2C, 128.6 (d, *J* = 11.6 Hz), 128.53 (d, *J* = 11.6 Hz) x 2C, 128.48 (d, *J* = 11.7 Hz), 128.43, 128.41, 127.51, 127.48, 125.9, 125.8, 73.93, 73.92, 39.0, 38.9, 38.0 (d, *J* = 53.8 Hz) x 2C, 30.8 (d, *J* = 10.5 Hz), 30.7 (d, *J* = 10.8 Hz), 29.03, 28.98, 28.8, 24.8 (d, *J* = 10.6 Hz), 24.6 (d, *J* = 10.8 Hz), 22.7 (d, *J* = 3.0 Hz) x 2C, 13.8. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 52.4, 52.3. HR-MS (ESI) m/z calcd for $C_{27}H_{34}OPS$ $[M + H]^+$ 437.2063, found 437.2068.

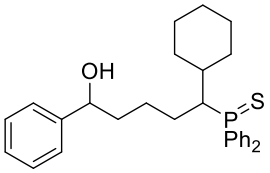
(1-Cyclopropyl-5-hydroxy-5-phenylpentyl) diphenylphosphine sulfide ([S]-42)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 3-cyclopropylprop-2-en-1-ol (0.6 mmol, 59 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-42** (143.0 mg, 68%, *d. r.* = 1: 1) as white solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.79 – 8.64 (m, 4H), 8.31 – 8.20 (m, 4H), 8.20 – 8.14 (m, 2H), 8.14 – 8.07 (m, 2H), 8.06 – 8.00 (m, 3H), 5.41 – 5.31 (m, 1H), 2.79 (s, 1H), 2.72 – 2.57 (m, 2H), 2.56 – 2.44 (m, 3H), 2.43 – 2.33 (m, 1H), 2.15 – 2.01 (m, 1H), 1.88 – 1.71 (m, 1H), 1.36 – 1.20 (m, 1H), 1.00 – 0.85 (m, 1H), 0.86 – 0.77 (m, 1H), 0.17 – 0.10 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.7, 144.6, 132.84 (d, *J* = 76.3 Hz), 132.81 (d, *J* = 75.7 Hz), 132.18 (d, *J* = 75.6

Hz), 132.15 (d, J = 75.2 Hz), 131.9 (d, J = 10.1 Hz), 131.8 (d, J = 9.8 Hz), 131.5 (d, J = 3.2 Hz), 131.4 (d, J = 3.2 Hz), 131.2 (d, J = 3.0 Hz), 128.7 (d, J = 11.2 Hz), 128.6 (d, J = 11.2 Hz), 128.4, 128.14, 128.07, 127.5 (d, J = 3.2 Hz), 125.9, 125.8, 74.12, 74.08, 44.1 (d, J = 53.6 Hz), 43.6 (d, J = 53.7 Hz), 39.1, 39.0, 30.3, 30.2, 24.1 (d, J = 12.5 Hz), 24.0 (d, J = 12.2 Hz), 10.6, 10.4, 4.9 (d, J = 14.9 Hz), 4.7 (d, J = 15.4 Hz), 4.5. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 51.6, 51.5. HR-MS (ESI) m/z calcd for $C_{26}H_{30}OPS$ $[M + H]^+$ 421.1750, found 421.1740.

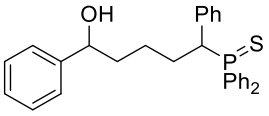
(1-Cyclohexyl-5-hydroxy-5-phenylpentyl) diphenylphosphine sulfide ([S]-43)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 3-cyclohexylprop-2-en-1-ol (0.6 mmol, 84 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 ℃ for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-43** (161.7 mg, 70%, *d. r.* = 1: 0.9) as colorless oil. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.01 – 7.87 (m, 4H), 7.48 – 7.35 (m, 6H), 7.31 – 7.26 (m, 2H), 7.26 – 7.21 (m, 1H), 7.21 – 7.18 (m, 1H), 7.18 – 7.14 (m, 1H), 4.47 – 4.43 (m, 1H), 2.52 – 2.45 (m, 1H), 2.17 – 2.08 (m, 1H), 2.01 (s, 1H), 1.79 – 1.43 (m, 9H), 1.41 – 1.12 (m, 3H), 1.12 – 0.92 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.54, 144.49, 133.4 (d, J = 75.0 Hz), 133.1 (d, J = 76.5 Hz), 132.9 (d, J = 74.4 Hz), 132.5 (d, J = 76.5 Hz), 131.33 (d, J = 9.3 Hz), 131.29 (d, J = 9.6 Hz), 131.27 (d, J = 9.3 Hz), 131.2 (d, J = 9.5 Hz), 131.14 (d, J = 2.6 Hz), 131.09 (d, J = 2.8 Hz), 128.54 (d, J = 11.1 Hz), 128.48 (d, J = 11.3 Hz), 128.4, 127.5, 125.89, 125.87, 74.0, 73.7, 43.1 (d, J = 51.7 Hz), 42.7 (d, J = 51.3 Hz), 39.0, 38.9, 38.3, 38.2, 35.0 (d, J = 12.7 Hz), 34.8 (d, J = 12.8 Hz), 29.14 (d, J = 2.5 Hz), 29.11 (d, J = 2.3 Hz), 27.20, 27.17, 26.42, 26.38, 26.21, 26.18, 26.2 (d, J = 10.7 Hz),

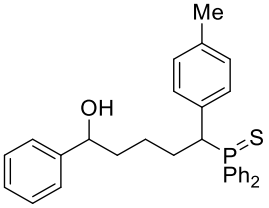
26.0 (d, J = 10.7 Hz), 25.5, 25.3. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 51.3, 51.2. HR-MS (ESI) m/z calcd for $C_{29}H_{36}OPS$ $[M + H]^+$ 463.2219, found 463.2211.

(5-Hydroxy-1,5-diphenylpentyl) diphenylphosphine sulfide ([S]-44)



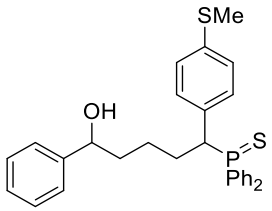
The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 3-phenylprop-2-en-1-ol (0.6 mmol, 81 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-44** (174.5 mg, 77%, *d. r.* = 1: 0.8) as white solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.12 – 8.07 (m, 2H), 7.58 – 7.51 (m, 3H), 7.44 – 7.38 (m, 2H), 7.31 – 7.08 (m, 13H), 4.50 – 4.43 (m, 1H), 3.83 – 3.71 (m, 1H), 2.34 – 2.21 (m, 1H), 1.90 – 1.51 (m, 4H), 1.39 – 1.07 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.6, 144.4, 134.7 (d, J = 4.7 Hz), 134.7 (d, J = 4.4 Hz), 132.2 (d, J = 79.4 Hz), 132.2 (d, J = 80.0 Hz), 132.0 (d, J = 9.0 Hz), 131.7 (d, J = 3.2 Hz), 131.5 (d, J = 9.6 Hz), 131.0 (d, J = 2.9 Hz), 130.9, 129.9 (d, J = 5.7 Hz), 128.8 (d, J = 11.4 Hz), 128.7 (d, J = 11.6 Hz), 128.5, 128.4, 127.91 (d, J = 3.9 Hz), 127.89 (d, J = 2.9 Hz), 127.84 (d, J = 6.4 Hz), 127.83 (d, J = 6.1 Hz), 127.6, 127.34 (d, J = 3.0 Hz), 127.30 (d, J = 3.4 Hz), 125.9, 125.8, 74.1, 74.0, 47.2 (d, J = 49.9 Hz), 46.7 (d, J = 50.4 Hz), 38.4, 38.2, 29.4, 29.3, 24.0 (d, J = 14.3 Hz), 23.8 (d, J = 14.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 50.5, 50.4. HR-MS (ESI) m/z calcd for $C_{29}H_{30}OPS$ $[M + H]^+$ 457.1750, found 457.1753.

(5-Hydroxy-5-phenyl-1-(*p*-tolyl) pentyl) diphenylphosphine sulfide ([S]-45)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 3-(*p*-tolyl) prop-2-en-1-ol (0.6 mmol, 89 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-45** (191.7 mg, 82%, *d. r.* = 1: 1.1) as white solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.11 – 8.00 (m, 2H), 7.57 – 7.48 (m, 3H), 7.48 – 7.41 (m, 2H), 7.30 – 7.13 (m, 8H), 7.10 – 7.01 (m, 2H), 6.96 – 6.90 (m, 2H), 4.49 – 4.40 (m, 1H), 3.81 – 3.71 (m, 1H), 2.24 (s, 3H), 1.88 – 1.47 (m, 4H), 1.39 – 1.06 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.6, 144.5, 136.94 (d, *J* = 3.5 Hz), 136.89 (d, *J* = 3.7 Hz), 132.3 (d, *J* = 79.3 Hz), 132.0, 131.9, 131.8 (d, *J* = 79.9 Hz), 131.60 (d, *J* = 3.4 Hz), 131.56 (d, *J* = 9.4 Hz), 131.5 (d, *J* = 9.4 Hz), 131.1, 131.0 (d, *J* = 3.0 Hz), 129.82, 129.79, 128.78 (d, *J* = 11.7 Hz), 128.75 (d, *J* = 11.4 Hz), 128.65 (d, *J* = 4.4 Hz), 128.60 (d, *J* = 4.4 Hz), 128.5, 128.4, 127.9 (d, *J* = 2.1 Hz), 127.8 (d, *J* = 2.0 Hz), 127.5, 125.9, 125.8, 74.1, 74.0, 46.8 (d, *J* = 50.5 Hz), 46.3 (d, *J* = 50.1 Hz), 38.4, 38.3, 29.3, 29.2, 23.9 (d, *J* = 14.4 Hz), 23.8 (d, *J* = 14.1 Hz), 21.1. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 50.4, 50.3. HR-MS (ESI) m/z calcd for $C_{30}H_{32}OPS$ $[M + H]^+$ 471.1906, found 471.1904.

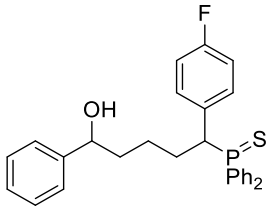
(5-Hydroxy-1-(4-(methylthio) phenyl)-5-phenylpentyl) diphenylphosphine sulfide ([S]-46)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 3-(4-(methylthio) phenyl) prop-2-en-1-ol (0.6 mmol, 108 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-46** (210.4 mg, 84%, *d. r.* = 1: 0.7) as yellow solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ =

8.10 – 8.04 (m, 2H), 7.59 – 7.50 (m, 3H), 7.48 – 7.41 (m, 2H), 7.33 – 7.13 (m, 8H), 7.12 – 7.05 (m, 2H), 7.03 – 6.97 (m, 2H), 4.48 – 4.41 (m, 1H), 3.82 – 3.71 (m, 1H), 2.40 (s, 3H), 2.26 – 2.16 (m, 1H), 1.88 – 1.74 (m, 2H), 1.73 – 1.49 (m, 2H), 1.37 – 1.08 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.5, 144.4, 137.4 (d, J = 4.0 Hz), 137.3 (d, J = 3.9 Hz), 132.1 (d, J = 79.9 Hz), 131.9 (d, J = 8.9 Hz), 131.7 (d, J = 2.9 Hz), 131.6 (d, J = 80.7 Hz), 131.5 (d, J = 9.3 Hz), 131.4, 131.1 (d, J = 2.9 Hz), 130.9, 130.3 (d, J = 5.7 Hz), 128.8 (d, J = 11.7 Hz), 128.7 (d, J = 11.2 Hz), 128.46, 128.45, 128.0 (d, J = 12.2 Hz), 127.9 (d, J = 11.8 Hz), 127.59, 127.58, 125.9, 125.84, 125.76, 74.1, 74.0, 46.7 (d, J = 50.2 Hz), 46.2 (d, J = 50.6 Hz), 38.4, 38.2, 29.3, 29.2, 23.9 (d, J = 14.2 Hz), 23.7 (d, J = 14.3 Hz), 15.69, 15.67. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 50.3, 50.2. HR-MS (ESI) m/z calcd for $C_{30}H_{32}OPS_2$ $[M + H]^+$ 503.1627, found 503.1624.

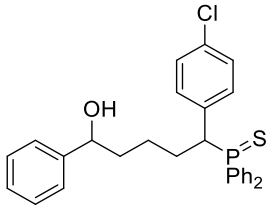
(1-(4-Fluorophenyl)-5-hydroxy-5-phenylpentyl) diphenylphosphine sulfide ([S]-47)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 3-(4-fluorophenyl) prop-2-en-1-ol (0.6 mmol, 91 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-47** (193.5 mg, 82%, *d. r.* = 1: 0.9) as white solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.12 – 8.04 (m, 2H), 7.59 – 7.51 (m, 3H), 7.46 – 7.39 (m, 2H), 7.33 – 7.08 (m, 10H), 6.85 – 6.77 (m, 2H), 4.49 – 4.43 (m, 1H), 3.81 – 3.75 (m, 1H), 2.25 – 2.16 (m, 1H), 1.84 – 1.75 (m, 2H), 1.74 – 1.50 (m, 2H), 1.36 – 1.17 (m, 1.53H), 1.13 – 1.04 (m, 0.49H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 162.1 (d, J = 246.1 Hz), 144.5, 144.4, 132.0 (d, J = 80.4 Hz), 131.9 (d, J = 9.0 Hz), 131.8 (d, J = 2.8 Hz), 131.5 (d, J = 79.9 Hz), 131.4 (d, J = 9.5 Hz), 131.3, 131.1 (d, J = 2.9 Hz), 130.7, 128.9 (d, J = 2.8 Hz), 128.8

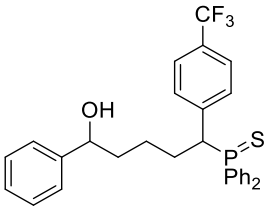
(d, J = 2.8 Hz), 128.48, 128.47, 128.03 (d, J = 12.0 Hz), 127.95 (d, J = 12.3 Hz), 127.65, 127.62, 125.9, 125.8, 114.9 (d, J = 5.5 Hz), 114.8 (d, J = 5.3 Hz), 114.72 (d, J = 5.3 Hz), 114.70 (d, J = 5.5 Hz), 74.15, 74.06, 46.4 (d, J = 50.8 Hz), 45.8 (d, J = 50.3 Hz), 38.3, 38.1, 29.4, 29.3, 23.9 (d, J = 14.4 Hz), 23.7 (d, J = 14.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 50.5 (d, J = 5.9 Hz), 50.4 (d, J = 5.8 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ = -114.99 – -115.06 (m), -115.06 – -115.13 (m). HR-MS (ESI) m/z calcd for $C_{29}H_{29}FOPS$ $[M + H]^+$ 475.1656, found 475.1655.

(1-(4-Chlorophenyl)-5-hydroxy-5-phenylpentyl) diphenylphosphine sulfide ([S]-48)



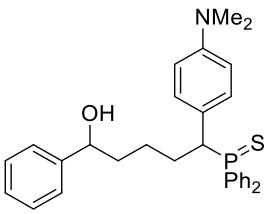
The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 3-(4-chlorophenyl) prop-2-en-1-ol (0.6 mmol, 101 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-48** (195.2 mg, 80%, *d. r.* = 1: 0.7) as yellow solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.13 – 8.02 (m, 2H), 7.60 – 7.50 (m, 3H), 7.48 – 7.41 (m, 2H), 7.35 – 7.05 (m, 12H), 4.51 – 4.41 (m, 1H), 3.81 – 3.72 (m, 1H), 2.27 – 2.13 (m, 1H), 1.88 – 1.74 (m, 2H), 1.75 – 1.48 (m, 2H), 1.36 – 1.16 (m, 1H), 1.14 – 1.03 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.5, 144.3, 133.3 (d, J = 80.3 Hz), 133.2 (d, J = 80.2 Hz), 131.9 (d, J = 9.0 Hz), 131.8 (d, J = 2.9 Hz), 131.4 (d, J = 9.5 Hz), 131.21 (d, J = 3.1 Hz), 131.15, 131.1, 130.6, 128.9 (d, J = 11.6 Hz), 128.8 (d, J = 11.6 Hz), 128.5, 128.1 (d, J = 6.0 Hz), 128.0 (d, J = 5.6 Hz), 127.7, 127.6, 125.8, 125.7, 74.1, 74.0, 46.6 (d, J = 50.1 Hz), 46.1 (d, J = 50.7 Hz), 38.3, 38.1, 29.3, 29.2, 23.9 (d, J = 14.2 Hz), 23.7 (d, J = 14.0 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 50.3, 50.2. HR-MS (ESI) m/z calcd for $C_{29}H_{29}ClOPS$ $[M + H]^+$ 491.1360, found 491.1350.

(5-Hydroxy-5-phenyl-1-(4-(trifluoromethyl) phenyl) pentyl) diphenylphosphine sulfide ([S]-49)



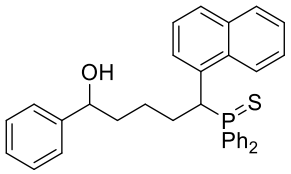
The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 3-(4-(trifluoromethyl) phenyl) prop-2-en-1-ol (0.6 mmol, 121 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-49** (188.0 mg, 72%, *d. r.* = 1: 1) as white solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.13 – 8.03 (m, 2H), 7.61 – 7.51 (m, 3H), 7.45 – 7.40 (m, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.11 (m, 10H), 4.49 – 4.40 (m, 1H), 3.93 – 3.82 (m, 1H), 2.32 – 2.21 (m, 1H), 1.88 (s, 1H), 1.87 – 1.77 (m, 1H), 1.74 – 1.50 (m, 2H), 1.33 – 1.24 (m, 1H), 1.23 – 1.15 (m, 0.52H), 1.13 – 1.02 (m, 0.49H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.4, 144.3, 139.1 (d, J = 14.7 Hz), 139.0 (d, J = 14.4 Hz), 131.9 (d, J = 90.8 Hz), 131.7 (d, J = 80.5 Hz), 131.3 (d, J = 91.1 Hz), 130.9 (d, J = 77.3 Hz), 130.2 (d, J = 5.4 Hz), 129.4 (q, J = 31.7 Hz).129.0 (d, J = 11.6 Hz), 128.9 (d, J = 11.5 Hz), 128.48, 128.46, 128.1 (d, J = 11.9 Hz), 127.7, 127.6, 125.8, 125.7, 125.0 (q, J = 271.9 Hz), 124.7 (q, J = 6.3 Hz), 74.1, 74.0, 47.2 (d, J = 49.9 Hz), 46.6 (d, J = 49.5 Hz), 38.3, 38.1, 29.3, 29.1, 23.9 (d, J = 14.3 Hz), 23.7 (d, J = 13.9 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 50.5, 50.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ = -62.41, -62.43. HR-MS (ESI) m/z calcd for $C_{30}H_{29}F_3OPS$ $[M + H]^+$ 525.1624, found 525.1621.

(1-(4-(Dimethylamino) phenyl)-5-hydroxy-5-phenylpentyl) diphenylphosphine sulfide ([S]-50)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 3-(4-(dimethylamino) phenyl) prop-2-en-1-ol (0.6 mmol, 106 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-50** (188.5 mg, 76%, *d. r.* = 1: 0.8) as white solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.11 – 8.02 (m, 2H), 7.58 – 7.47 (m, 3H), 7.48 – 7.40 (m, 2H), 7.33 – 7.15 (m, 8H), 7.06 – 6.97 (m, 2H), 6.54 – 6.46 (m, 2H), 4.51 – 4.42 (m, 1H), 3.74 – 3.66 (m, 1H), 2.87 (s, 6H), 2.25 – 2.13 (m, 1H), 1.86 – 1.51 (m, 4H), 1.42 – 1.32 (m, 0.51H), 1.31 – 1.24 (m, 1H), 1.17 – 1.07 (m, 0.48H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.63, 144.55, 132.6 (d, J = 79.6 Hz), 132.5 (d, J = 79.1 Hz), 132.03 (d, J = 1.8 Hz), 131.98 (d, J = 1.6 Hz), 131.8, 130.65 (d, J = 9.4 Hz), 131.57 (d, J = 9.4 Hz), 131.5 (d, J = 1.8 Hz), 131.3, 130.8 (d, J = 2.9 Hz), 130.60, 130.56, 128.7 (d, J = 4.1 Hz), 128.6 (d, J = 4.0 Hz), 128.44, 128.42, 127.9 (d, J = 11.9 Hz), 127.8 (d, J = 11.6 Hz), 127.5, 125.9, 125.8, 112.1, 74.2, 74.1, 46.3 (d, J = 51.0 Hz), 45.9 (d, J = 50.3 Hz), 40.6, 40.5, 38.5, 38.3, 29.2, 29.1, 23.9 (d, J = 14.4 Hz), 23.8 (d, J = 14.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 50.3, 50.2. HR-MS (ESI) m/z calcd for $C_{31}H_{35}NOPS$ $[M + H]^+$ 500.2172, found 500.2168.

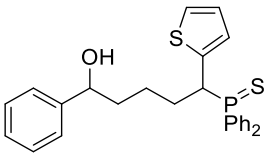
(5-Hydroxy-1-(naphthalen-1-yl)-5-phenylpentyl) diphenylphosphine sulfide ([S]-51)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 3-(naphthalen-2-yl) prop-2-en-1-ol (0.6 mmol, 111 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-51** (176.6 mg, 70%, *d. r.* = 1: 0.9) as white solid. Diastereomeric ratio was

determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.28 – 8.16 (m, 2H), 8.15 – 8.07 (m, 1H), 7.72 – 7.55 (m, 6H), 7.52 – 7.45 (m, 1H), 7.32 – 7.26 (m, 1H), 7.25 – 7.07 (m, 7H), 7.06 – 6.99 (m, 1H), 6.98 – 6.91 (m, 1H), 6.84 – 6.75 (m, 2H), 4.84 – 4.77 (m, 1H), 4.38 – 4.33 (m, 1H), 2.46 – 2.35 (m, 1H), 2.09 – 1.94 (m, 1H), 1.77 – 1.47 (m, 3H), 1.37 – 1.08 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.5, 144.3, 133.4, 132.8 (d, J = 80.1 Hz), 132.3 (d, J = 9.0 Hz), 132.2 (d, J = 9.2 Hz), 132.1 (d, J = 80.8 Hz), 131.8 (d, J = 2.9 Hz), 131.2, 131.1, 130.7 (d, J = 2.1 Hz), 128.93 (d, J = 11.5 Hz), 128.90 (d, J = 11.0 Hz), 128.9, 128.4, 128.3, 127.9, 127.50, 127.46, 127.4, 127.0, 126.8, 125.8, 125.73, 125.72, 125.3 (d, J = 3.6 Hz), 124.9 (d, J = 6.3 Hz), 121.9 (d, J = 3.4 Hz), 74.03, 73.96, 39.6 (d, J = 51.0 Hz), 39.1 (d, J = 50.6 Hz), 38.7, 38.4, 31.1, 30.9, 24.0 (d, J = 14.0 Hz), 23.8 (d, J = 14.0 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 51.5, 51.4. HR-MS (ESI) m/z calcd for $C_{33}H_{32}OPS$ $[M + H]^+$ 507.1906, found 507.1900.

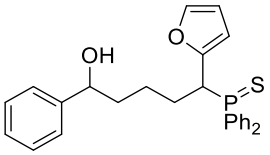
(5-Hydroxy-5-phenyl-1-(thiophen-2-yl) pentyl) diphenylphosphine sulfide ([S]-52)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 3-(thiophen-2-yl) prop-2-en-1-ol (0.6 mmol, 84 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-52** (160.5 mg, 70%, *d. r.* = 1: 0.8) as yellow solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.13 – 7.99 (m, 2H), 7.65 – 7.48 (m, 5H), 7.38 – 7.16 (m, 8H), 7.13 – 7.01 (m, 1H), 6.89 – 6.75 (m, 2H), 4.54 – 4.44 (m, 1H), 4.19 – 4.08 (m, 1H), 2.21 – 2.10 (m, 1H), 1.92 – 1.51 (m, 4H), 1.50 – 1.11 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.6, 144.5, 137.3 (d, J = 5.9 Hz), 137.2 (d, J = 5.7 Hz), 131.9 (d, J = 9.1 Hz), 131.8 (d, J = 79.5 Hz), 131.5 (d, J = 9.4 Hz), 131.3 (d, J = 79.2 Hz), 131.2, 130.7, 128.9 (d, J = 11.4 Hz), 128.8 (d, J = 11.9

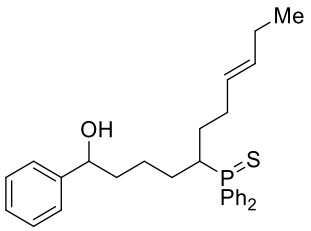
Hz), 128.5, 128.1, 128.0, 127.6 (d, J = 3.1 Hz), 127.5 (d, J = 3.9 Hz), 126.3, 125.9, 125.8, 125.0 (d, J = 3.5 Hz), 124.9 (d, J = 3.4 Hz), 74.1, 74.0, 43.4 (d, J = 53.2 Hz), 42.9 (d, J = 52.5 Hz), 38.4, 38.2, 31.24, 31.16, 23.9 (d, J = 13.5 Hz), 23.8 (d, J = 13.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 50.0, 49.9. HR-MS (ESI) m/z calcd for $C_{27}H_{28}OPS_2$ $[M + H]^+$ 463.1314, found 463.1316.

(1-(Furan-2-yl)-5-hydroxy-5-phenylpentyl) diphenylphosphine sulfide ([S]-53)



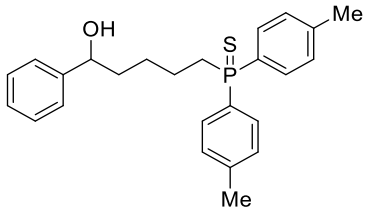
The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), 3-(furan-2-yl) prop-2-en-1-ol (0.6 mmol, 75 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-53** (146.8 mg, 66%, *d. r.* = 1: 0.8) as green solid. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.01 – 7.88 (m, 2H), 7.65 – 7.55 (m, 2H), 7.56 – 7.42 (m, 3H), 7.41 – 7.33 (m, 1H), 7.33 – 7.09 (m, 8H), 6.32 – 6.11 (m, 2H), 4.54 – 4.36 (m, 1H), 4.07 – 3.95 (m, 1H), 2.21 – 2.03 (m, 2H), 1.90 – 1.48 (m, 3H), 1.45 – 1.11 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 149.4 (d, J = 8.6 Hz), 144.6, 144.5, 141.7, 131.8 (d, J = 9.7 Hz), 131.7 (d, J = 10.1 Hz), 131.6 (d, J = 10.0 Hz), 131.4 (d, J = 2.6 Hz), 130.98 (d, J = 79.1 Hz), 130.95 (d, J = 79.8 Hz), 128.8 (d, J = 11.5 Hz), 128.7 (d, J = 11.5 Hz), 128.4, 128.1 (d, J = 12.1 Hz) x 2C, 127.6, 127.5, 125.9, 125.8, 110.8, 109.28 (d, J = 5.4 Hz), 109.23 (d, J = 5.4 Hz), 74.2, 74.0, 42.5 (d, J = 53.7 Hz), 42.1 (d, J = 53.1 Hz), 38.3, 38.2, 28.72, 28.68, 24.1 (d, J = 14.0 Hz), 24.0 (d, J = 14.0 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 48.7, 48.6. HR-MS (ESI) m/z calcd for $C_{27}H_{28}O_2PS$ $[M + H]^+$ 447.1542, found 447.1540.

(1-Hydroxy-1-phenylundec-8-en-5-yl) diphenylphosphine sulfide ([S]-54)



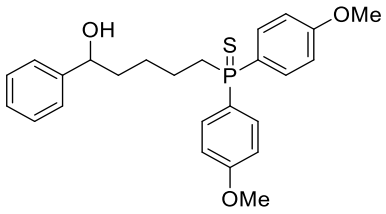
The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), cucumber alcohol (0.6 mmol, 87 mg) and diphenylphosphine (0.6 mmol, 105 μL) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-54** (200.2 mg, 87%, *d. r.* = 1: 0.8) as colorless oil. Diastereomeric ratio was determined by NMR analysis of the crude mixture. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98 – 7.88 (m, 4H), 7.48 – 7.38 (m, 6H), 7.33 – 7.27 (m, 2H), 7.29 – 7.18 (m, 3H), 5.37 – 5.28 (m, 1H), 5.15 – 5.05 (m, 1H), 4.53 – 4.43 (m, 1H), 2.59 – 2.52 (m, 1H), 2.05 – 1.35 (m, 12H), 1.26 – 1.15 (m, 0.65H), 1.13 – 1.04 (m, 0.51H), 0.89 – 0.81 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.53, 144.46, 132.8, 132.6 (d, J = 77.2 Hz), 132.4 (d, J = 76.2 Hz), 131.53 (d, J = 3.1 Hz), 131.47 (d, J = 3.1 Hz), 131.39 (d, J = 8.4 Hz), 131.38 (d, J = 8.3 Hz), 131.34 (d, J = 8.4 Hz), 131.32 (d, J = 8.2 Hz), 128.61 (d, J = 11.8 Hz), 128.59 (d, J = 11.7 Hz) x 2C, 128.52 (d, J = 11.5 Hz), 128.46, 127.69, 127.66, 127.56, 127.55, 125.84, 125.83, 73.98, 73.97, 39.0, 38.9, 37.3 (d, J = 54.2 Hz) x 2C, 29.2, 29.0, 28.9, 25.9 (d, J = 10.9 Hz), 25.8 (d, J = 10.7 Hz), 24.6 (d, J = 10.3 Hz), 24.5 (d, J = 10.3 Hz), 20.5, 14.4. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 52.2, 52.0. HR-MS (ESI) m/z calcd for $C_{29}H_{36}OPS$ $[M + H]^+$ 463.2219, found 463.2212.

((5-Hydroxy-5-phenylpentyl) di-*p*-tolylphosphine sulfide ([S]-55)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), allylic alcohol (0.6 mmol, 42 μL) and di-*p*-tolylphosphane (0.6 mmol, 129 mg) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-55** (180.3 mg, 88%) as yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.71 – 7.59 (m, 4H), 7.31 – 7.15 (m, 9H), 4.60 – 4.50 (m, 1H), 2.47 – 2.23 (m, 9H), 1.77 – 1.67 (m, 1H), 1.68 – 1.53 (m, 3H), 1.51 – 1.40 (m, 1H), 1.40 – 1.28 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.7, 141.9 (d, J = 2.9 Hz), 131.1 (d, J = 10.5 Hz), 131.0 (d, J = 10.7 Hz), 130.0 (d, J = 82.5 Hz), 129.9 (d, J = 82.0 Hz), 129.4 (d, J = 12.2 Hz), 128.4, 127.5, 125.9, 74.1, 38.5, 32.6 (d, J = 56.9 Hz), 26.8 (d, J = 17.0 Hz), 22.1 (d, J = 2.7 Hz), 21.5. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.0. HR-MS (ESI) m/z calcd for $C_{25}H_{30}OPS$ $[M + H]^+$ 409.1750, found 409.1745.

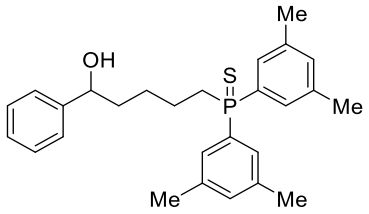
(5-Hydroxy-5-phenylpentyl) bis(4-methoxyphenyl) phosphine sulfide ([S]-56)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), allylic alcohol (0.6 mmol, 42 μL) and bis(4-methoxyphenyl) phosphane (0.6 mmol, 148 mg) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-56** (189.2 mg, 86%) as yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.74 – 7.65 (m, 4H), 7.33 – 7.21 (m, 5H), 7.03 – 6.84 (m, 4H), 4.63 – 4.50 (m, 1H), 3.80 (s, 6H), 2.41 – 2.20 (m, 3H), 1.79 – 1.71 (m, 1H), 1.69 – 1.54 (m, 3H), 1.51 – 1.41 (m, 1H), 1.40 – 1.31 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 162.0 (d, J = 2.8 Hz), 144.7, 132.9 (d, J = 11.8 Hz), 132.8 (d, J = 11.6 Hz), 128.4, 127.5, 125.9, 124.5 (d, J = 86.2 Hz), 123.8 (d, J = 85.4 Hz), 114.1 (d, J = 12.9 Hz), 74.1, 55.4, 38.5, 33.0 (d, J = 57.4 Hz), 26.7 (d, J =

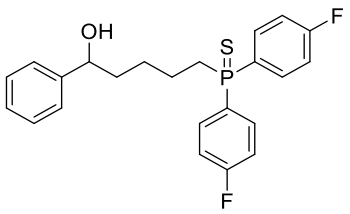
16.9 Hz), 22.2 (d, J = 2.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 41.1. HR-MS (ESI) m/z calcd for $C_{25}H_{30}O_3PS$ $[M + H]^+$ 441.1648, found 441.1639.

Bis(3,5-dimethylphenyl) (5-hydroxy-5-phenylpentyl) phosphine sulfide ([S]-57)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), allylic alcohol (0.6 mmol, 42 μL) and bis(3,5-dimethylphenyl) phosphane (0.6 mmol, 145 mg) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-57** (206.8 mg, 94%) as white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.40 – 7.35 (m, 4H), 7.35 – 7.23 (m, 5H), 7.11 – 7.08 (m, 2H), 4.66 – 4.58 (m, 1H), 2.43 – 2.35 (m, 2H), 2.33 (s, 12H), 1.86 (s, 1H), 1.83 – 1.75 (m, 1H), 1.73 – 1.58 (m, 3H), 1.55 – 1.46 (m, 1H), 1.44 – 1.34 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.6, 138.3 (d, J = 12.7 Hz), 133.2 (d, J = 3.0 Hz), 133.0 (d, J = 80.0 Hz), 132.4 (d, J = 79.0 Hz), 128.7 (d, J = 10.4 Hz), 128.6 (d, J = 10.0 Hz), 128.5, 127.6, 125.9, 74.3, 38.5, 32.3 (d, J = 56.5 Hz), 26.8 (d, J = 16.6 Hz), 22.0 (d, J = 2.5 Hz), 21.4. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.4. HR-MS (ESI) m/z calcd for $C_{27}H_{34}OPS$ $[M + H]^+$ 437.2063, found 437.2055.

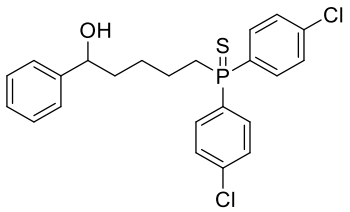
Bis(4-fluorophenyl) (5-hydroxy-5-phenylpentyl) phosphine sulfide ([S]-58)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), allylic alcohol (0.6 mmol, 42 μL) and bis(4-fluorophenyl) phosphane (0.6 mmol, 133 mg) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature

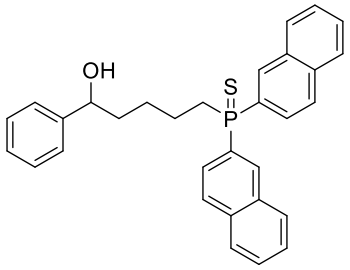
for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-58** (156.2 mg, 75%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.82 – 7.73 (m, 4H), 7.31 – 7.20 (m, 5H), 7.16 – 7.07 (m, 4H), 4.64 – 4.46 (m, 1H), 2.45 – 2.30 (m, 3H), 1.78 – 1.69 (m, 1H), 1.68 – 1.54 (m, 3H), 1.51 – 1.42 (m, 1H), 1.40 – 1.30 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 165.6 (d, J = 254.1 Hz), 163.9 (d, J = 253.7 Hz), 144.6, 133.6 (d, J = 9.0 Hz), 133.56 (d, J = 8.9 Hz), 133.54 (d, J = 8.8 Hz), 133.4 (d, J = 8.9 Hz), 128.9 (d, J = 83.0 Hz), 128.8 (d, J = 82.5 Hz), 128.5, 128.4 (d, J = 82.5 Hz), 128.3 (d, J = 82.5 Hz), 127.6, 125.9, 116.1 (d, J = 13.3 Hz), 116.0 (d, J = 13.2 Hz), 74.0, 38.4, 32.7 (d, J = 57.1 Hz), 26.7 (d, J = 16.7 Hz), 22.1 (d, J = 2.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 41.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ = -107.4. HR-MS (ESI) m/z calcd for $C_{23}H_{24}F_2OPS$ $[M + H]^+$ 417.1248, found 417.1249.

Bis(4-chlorophenyl) (5-hydroxy-5-phenylpentyl) phosphine sulfide ([S]-59)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), allylic alcohol (0.6 mmol, 42 μL) and bis(4-chlorophenyl) phosphane (0.6 mmol, 153 mg) stirred at 100 °C for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-59** (179.2 mg, 80%) as yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.75 – 7.64 (m, 4H), 7.46 – 7.37 (m, 4H), 7.32 – 7.18 (m, 5H), 4.62 – 4.51 (m, 1H), 2.42 – 2.31 (m, 2H), 2.27 (s, 1H), 1.79 – 1.70 (m, 1H), 1.68 – 1.52 (m, 3H), 1.52 – 1.41 (m, 1H), 1.40 – 1.31 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.5, 138.3 (d, J = 3.6 Hz), 132.5 (d, J = 11.2 Hz), 132.4 (d, J = 11.3 Hz), 131.4 (d, J = 81.4 Hz), 130.8 (d, J = 81.0 Hz), 129.1 (d, J = 12.6 Hz), 128.5, 127.6, 125.9, 74.1, 38.4, 32.3 (d, J = 56.9 Hz), 26.7 (d, J = 16.9 Hz), 22.0 (d, J = 2.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 41.7. HR-MS (ESI) m/z calcd for $C_{23}H_{24}Cl_2OPS$ $[M + H]^+$ 449.0657, found 449.0649.

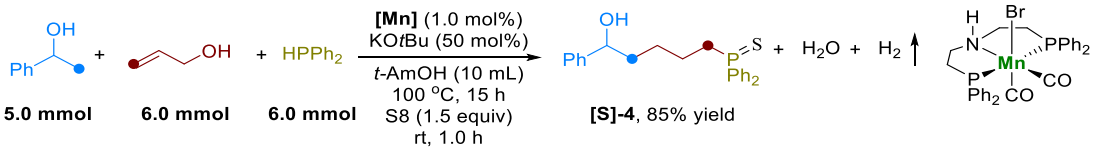
(5-Hydroxy-5-phenylpentyl) di(naphthalen-2-yl) phosphine sulfide ([S]-60)



The procedure was followed using 1-phenylethanol (0.5 mmol, 61 mg), allylic alcohol (0.6 mmol, 42 μL) and di(naphthalen-2-yl) phosphane (0.6 mmol, 172 mg) stirred at 100 ℃ for 15 h. Treated with S_8 (1.5 equiv) and stirred at room temperature for 1.0 h. Purification by column chromatography (PE/EA = 5/1) yielded **[S]-60** (215.1 mg, 90%) as pink solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.51 – 8.41 (m, 2H), 7.95 – 7.82 (m, 6H), 7.76 – 7.69 (m, 2H), 7.61 – 7.52 (m, 4H), 7.32 – 7.19 (m, 5H), 4.63 – 4.54 (m, 1H), 2.66 – 2.56 (m, 2H), 1.89 (s, 1H), 1.81 – 1.62 (m, 4H), 1.58 – 1.48 (m, 1H), 1.47 – 1.37 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.5, 134.4 (d, J = 2.2 Hz), 133.1 (d, J = 10.1 Hz), 133.0 (d, J = 10.1 Hz), 132.6, 132.5, 130.2 (d, J = 80.7 Hz), 129.6 (d, J = 80.7 Hz), 129.0, 128.6 (d, J = 11.6 Hz), 128.5, 128.2, 127.8, 127.6, 127.1, 125.9 (d, J = 10.5 Hz), 125.8, 74.2, 38.4, 32.2 (d, J = 56.7 Hz), 26.8 (d, J = 16.8 Hz), 22.1 (d, J = 2.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.9. HR-MS (ESI) m/z calcd for $C_{31}H_{30}OPS$ $[M + H]^+$ 481.1750, found 481.1751.

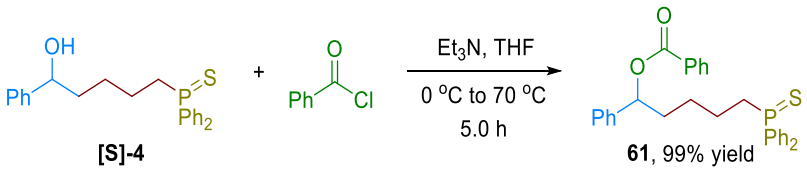
Gram scale reaction and derivatizations of product

Gram-scale reaction



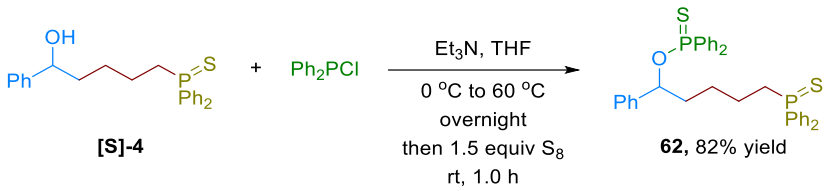
In a nitrogen-filled glove box, an oven-dried Schlenk pressure tube (100 mL) containing a stirring bar was charged with [**Mn**] (1.0 mol%, 32 mg). Dry and degassed *t*-AmOH (10 mL) and KO*t*Bu (50 mol%, 280 mg) were added and stirred at room temperature for 5.0 min. Then allylic alcohol (6.0 mmol, 420 μL), diphenylphosphine (6.0 mmol, 1.05 mL) and 1-phenylethanol (5.0 mmol, 610 mg) were added in sequence. The tube was brought out of the glovebox and heated at 100 °C for 15 h. Upon reaction completion, S_8 (7.5 mmol, 1.5 equiv) was added and further stirred at room temperature for 1.0 h in N_2 atmosphere. The mixture was purified by column chromatography on silica gel (100-200 mesh) using PE/EA (5/1) as an eluent to afford desired product **[S]-4** (1.49 g, 85%).

Derivatizations of product

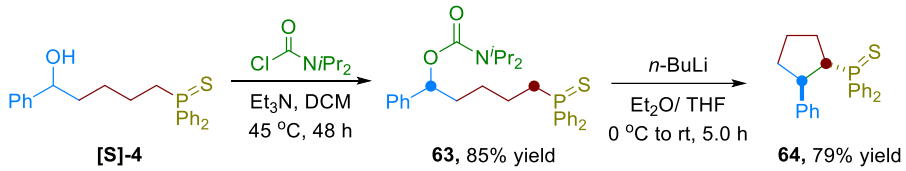


To a 10 mL Schlenk tube with a stir bar was added **[S]-4** (190 mg, 0.5 mmol), Et_3N (139 μL, 1.0 mmol) and THF (2.0 mL). The solution was added benzoyl chloride (117 μL, 1.0 mmol) dropwise at 0 °C and then stirred at 70 °C for 5.0 h. Upon reaction completion, the mixture was extracted with DCM and H_2O. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography over silica gel (PE/EA = 5/1) to afford **61** (240.0 mg, 99%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.13 – 8.03 (m, 2H), 7.83 – 7.75 (m, 4H), 7.61 – 7.51 (m, 1H), 7.46 – 7.38 (m, 8H), 7.36 – 7.28 (m, 4H), 7.28 – 7.23 (m, 1H), 5.95 – 5.90 (m, 1H), 2.48 – 2.36 (m, 2H), 2.09 – 1.99 (m, 1H), 1.93 – 1.83 (m,

1H), 1.74 – 1.64 (m, 2H), 1.56 – 1.46 (m, 1H), 1.46 – 1.36 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 165.8, 140.5, 133.1, 132.6 (d, J = 79.3 Hz), 132.5 (d, J = 79.7 Hz), 131.5 (d, J = 2.6 Hz), 131.13 (d, J = 9.8 Hz), 131.11 (d, J = 10.0 Hz), 130.4, 129.7, 128.73, 128.72, 128.65, 128.64 (d, J = 11.9 Hz), 128.5, 128.0, 126.4, 76.4, 36.1, 32.5 (d, J = 56.7 Hz), 26.7 (d, J = 16.8 Hz), 22.2 (d, J = 2.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.5. HR-MS (ESI) m/z calcd for $C_{30}H_{30}O_2PS$ $[M + H]^+$ 485.1699, found 485.1708.



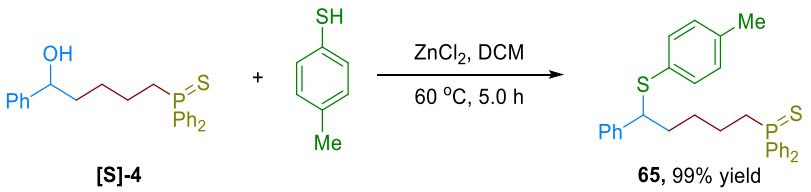
To a 50 mL Schlenk tube with a stir bar was added **[S]-4** (380 mg, 1.0 mmol), Et_3N (555 μL, 4.0 mmol), and THF (5.0 mL). The solution was then cooled to 0 °C and added chlorodiphenylphosphine (330 mg, 1.5 mmol) dropwise. The resulting mixture was kept at 0 °C and stirred for 30 min. Then the reaction was heated to 60 °C and stirred overnight. Upon reaction completion, S_8 (1.5 equiv) was added to the solution and further stirred at room temperature for 1.0 h. Then the crude product was purified by column chromatography over silica gel (PE/EA = 3/1) to afford the pure product **62** (485.5 mg, 82% yield) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.94 – 7.89 (m, 2H), 7.88 – 7.79 (m, 4H), 7.64 – 7.57 (m, 2H), 7.52 – 7.41 (m, 9H), 7.36 – 7.31 (m, 1H), 7.26 – 7.15 (m, 7H), 5.60 – 5.52 (m, 1H), 2.51 – 2.40 (m, 1H), 2.37 – 2.28 (m, 1H), 2.14 – 2.06 (m, 1H), 1.91 – 1.84 (m, 1H), 1.70 – 1.56 (m, 2H), 1.48 – 1.29 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 140.2 (d, J = 3.4 Hz), 135.4 (d, J = 115.0 Hz), 134.3 (d, J = 106.6 Hz), 133.2 (d, J = 79.6 Hz), 132.4 (d, J = 79.9 Hz), 131.8 (d, J = 2.9 Hz), 131.52 (d, J = 3.1 Hz), 131.49, 131.46, 131.4 (d, J = 11.5 Hz), 131.2 (d, J = 10.0 Hz), 131.1 (d, J = 10.0 Hz), 131.0 (d, J = 11.1 Hz), 128.7 (d, J = 11.7 Hz), 128.6 (d, J = 11.6 Hz), 128.5, 128.4, 128.3, 128.00, 127.99, 127.9, 126.9, 78.0 (d, J = 5.8 Hz), 37.2 (d, J = 4.7 Hz), 32.4 (d, J = 56.7 Hz), 26.1 (d, J = 17.2 Hz), 21.9 (d, J = 2.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 81.3, 42.6. HR-MS (ESI) m/z calcd for $C_{35}H_{35}OP_2S_2$ $[M + H]^+$ 597.1599, found 597.1597.



A solution of **[S]-4** (380 mg, 1.0 mmol), (dimethylamino)acetyl chloride (200 mg, 1.2 equiv) and Et_3N (168 μL, 1.2 equiv) in dry DCM (2.0 mL) was heated under reflux for 48 h. Upon reaction completion, the mixture was extracted with DCM and H_2O. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography over silica gel (PE/EA = 3/1) to afford **63** (431.0 mg, 85%) as yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.84 – 7.72 (m, 4H), 7.51 – 7.38 (m, 6H), 7.35 – 7.17 (m, 5H), 5.63 (t, J=6.8 Hz, 1H), 4.15 – 4.00 (m, 1H), 3.87 – 3.69 (m, 1H), 2.49 – 2.31 (m, 2H), 1.99 – 1.89 (m, 1H), 1.82 – 1.73 (m, 1H), 1.69 – 1.54 (m, 2H), 1.49 – 1.40 (m, 1H), 1.37 – 1.28 (m, 1H), 1.26 – 1.09 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 155.0, 141.3, 133.1 (d, J = 79.8 Hz), 132.5 (d, J = 79.4 Hz), 131.46 (d, J = 4.9 Hz), 131.45, 131.1 (d, J = 9.8 Hz), 131.0 (d, J = 10.0 Hz), 128.6 (d, J = 12.0 Hz), 128.4, 127.6, 126.5, 76.4, 36.4, 32.6 (d, J = 56.6 Hz), 26.7 (d, J = 17.0 Hz), 22.2 (d, J = 2.4 Hz), 21.8, 20.6. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.5. HR-MS (ESI) m/z calcd for $C_{30}H_{39}NO_2PS$ $[M + H]^+$ 508.2434, found 508.2431.

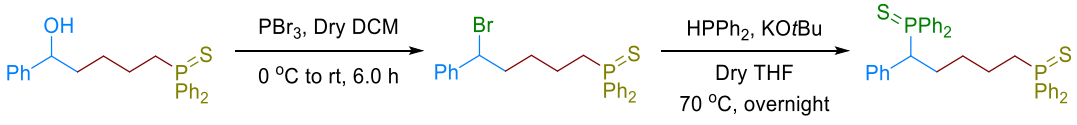
Compound **63** (102 mg, 0.2 mmol) and *n*-BuLi (1.6 M solution in hexanes, 1.5 equiv) in dry diethyl ether (0.5 mL) and THF (0.5 mL) were stirred for 1.0 h at 0 °C. After stirring for additional 4.0 h at room temperature and purification by column chromatography over silica gel (PE/EA = 5/1) to afford the pure product **64** (57.0 mg, 79% yield) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.93 – 7.84 (m, 2H), 7.63 – 7.52 (m, 2H), 7.49 – 7.36 (m, 3H), 7.24 – 7.16 (m, 1H), 7.12 – 7.04 (m, 2H), 7.02 – 6.95 (m, 3H), 6.91 – 6.82 (m, 2H), 3.61 – 3.46 (m, 1H), 3.38 – 3.20 (m, 1H), 2.27 – 2.14 (m, 2H), 2.08 – 1.97 (m, 1H), 1.94 – 1.86 (m, 2H), 1.85 – 1.77 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 145.2 (d, J = 3.2 Hz), 133.7 (d, J = 78.2 Hz), 131.6 (d, J = 10.0 Hz), 131.5 (d, J = 77.8 Hz), 131.2 (d, J = 3.4 Hz), 131.1 (d, J = 10.0 Hz), 130.8 (d, J = 3.0 Hz), 128.5 (d, J = 11.6 Hz), 128.1, 127.8 (d, J = 12.1 Hz), 127.4, 125.8, 46.8, 45.7 (d, J = 56.3 Hz), 38.0 (d, J = 9.4 Hz), 29.1, 26.8 (d, J = 7.2 Hz). ^{31}P NMR (243 MHz,

$CDCl_3$) δ = 52.0. HR-MS (ESI) m/z calcd for $C_{23}H_{24}PS$ $[M + H]^+$ 363.1331, found 363.1322.



[S]-4 **65**, 99% yield

A mixture of (5-hydroxy-5-phenylpentyl) diphenylphosphine sulfide **[S]-4** (190 mg, 0.5 mmol), 4-methylbenzenethiol (62.1 mg, 0.5 mmol), $ZnCl_2$ (10 mol%) and dry DCM (1.5 mL) was placed in a 10 mL Schlenk tube. The reaction contents were stirred magnetically at 60 °C for 5.0 h. Upon reaction completion, the mixture was quenched with H_2O and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent removed under vacuum to get crude product, which was purified by column chromatography (PE/EA = 5/1) to yield **65** (240.0 mg, 99% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.80 – 7.73 (m, 4H), 7.48 – 7.44 (m, 2H), 7.44 – 7.40 (m, 4H), 7.24 – 7.20 (m, 2H), 7.19 – 7.16 (m, 1H), 7.16 – 7.12 (m, 2H), 7.12 – 7.09 (m, 2H), 6.99 – 6.95 (m, 2H), 3.99 – 3.95 (m, 1H), 2.39 – 2.29 (m, 2H), 2.25 (s, 3H), 1.96 – 1.81 (m, 2H), 1.65 – 1.53 (m, 2H), 1.45 – 1.29 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 142.0, 137.4, 133.2, 133.1 (d, J = 80.1 Hz), 133.1 (d, J = 79.5 Hz), 131.5 (d, J = 3.2 Hz), 131.2 (d, J = 10.0 Hz), 131.0 (d, J = 10.4 Hz), 129.5, 128.7 (d, J = 12.1 Hz), 128.4, 127.8, 127.1, 126.0, 53.7, 35.5, 32.4 (d, J = 56.5 Hz), 28.5 (d, J = 17.0 Hz), 21.8 (d, J = 2.6 Hz), 21.2. ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.5. HR-MS (ESI) m/z calcd for $C_{30}H_{32}PS_2$ $[M + H]^+$ 487.1678, found 487.1670.

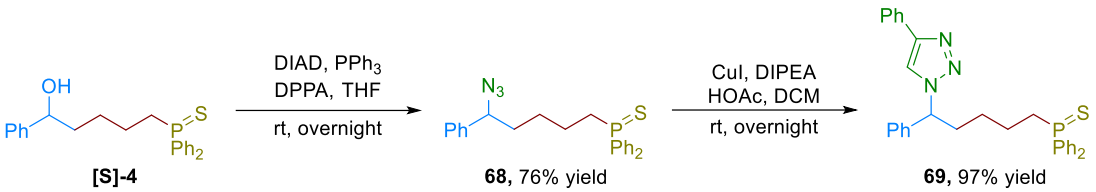


[S]-4 **66**, 70% yield **67**, 96% yield

To a 10 mL Schlenk tube with a stir bar was added **[S]-4** (380 mg, 1.0 mmol) and dry DCM (2.0 mL). The solution was added PBr_3 (104 μL, 1.1 mmol) dropwise at 0 °C and then stirred at room temperature for 6.0 h. Upon reaction completion, the mixture was

quenched with H_2O at 0 ºC and neutralized with saturated $NaHCO_3$ solution. Then the mixture was extracted with DCM and the organic phase was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography over silica gel (PE/EA = 5/1) to afford **66** (310.1 mg, 70%) as a white oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 – 7.78 (m, 4H), 7.52 – 7.47 (m, 2H), 7.47 – 7.40 (m, 4H), 7.33 – 7.25 (m, 5H), 4.90 – 4.84 (m, 1H), 2.46 – 2.37 (m, 2H), 2.34 – 2.18 (m, 1H), 2.14 – 2.06 (m, 1H), 1.71 – 1.62 (m, 3H), 1.45 – 1.35 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 141.9, 133.0 (d, J = 80.4 Hz), 132.4 (d, J = 79.7 Hz), 131.5 (d, J = 3.1 Hz), 131.1 (d, J = 10.0 Hz), 131.0 (d, J = 10.6 Hz), 128.74 (d, J = 11.9 Hz), 128.66, 128.4, 127.2, 55.1, 39.5, 32.4 (d, J = 56.5 Hz), 29.2 (d, J = 16.8 Hz), 21.6 (d, J = 2.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.5. HR-MS (ESI) m/z calcd for $C_{23}H_{25}BrPS$ [M + H^+] 443.0593, found 443.0593.

To a 10 mL Schlenk tube with a stir bar was added **66** (200 mg, 0.45 mmol), diphenylphosphine (94 μL, 1.2 equiv), KO*t*Bu (101 mg, 2.0 equiv) and THF (1.5 mL). And the resulting reaction mixture was stirred at 70 ºC overnight under nitrogen atmosphere. Upon reaction completion, S_8 (1.5 equiv) was added to the solution and further stirred at room temperature for 1.0 h. Then the residue mixture was concentrated under vacuum and purified by column chromatography over silica gel (PE/EA = 3/1) to afford the pure product **67** (251.1 mg, 96% yield) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.00 – 7.89 (m, 4H), 7.63 – 7.53 (m, 4H), 7.49 – 7.33 (m, 12H), 7.15 – 7.07 (m, 3H), 7.02 – 6.97 (m, 2H), 2.95 – 2.88 (m, 2H), 2.73 – 2.65 (m, 1H), 2.07 – 1.94 (m, 2H), 1.90 – 1.78 (m, 1H), 1.67 – 1.56 (m, 1H), 1.29 – 1.15 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 139.3 (d, J = 14.4 Hz), 132.9 (d, J = 79.9 Hz), 132.8 (d, J = 79.7 Hz), 132.4 (d, J = 75.9 Hz), 132.3 (d, J = 71.7 Hz), 131.6 (d, J = 2.8 Hz), 131.5 (d, J = 2.9 Hz), 131.4 (d, J = 9.5 Hz), 131.3 (d, J = 10.0 Hz), 131.0 (d, J = 12.1 Hz), 130.9 (d, J = 12.1 Hz), 129.0, 128.71 (d, J = 12.0 Hz), 128.69 (d, J = 11.9 Hz), 128.63 (d, J = 12.4 Hz), 128.61 (d, J = 11.6 Hz), 126.5, 40.2 (d, J = 53.4 Hz), 35.6, 32.5 (d, J = 56.5 Hz), 29.9 (d, J = 17.7 Hz), 21.6 (d, J = 9.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 51.9, 42.0. HR-MS (ESI) m/z calcd for $C_{35}H_{35}P_2S_2$ [M + H] $^+$ 581.1650, found 581.1643.

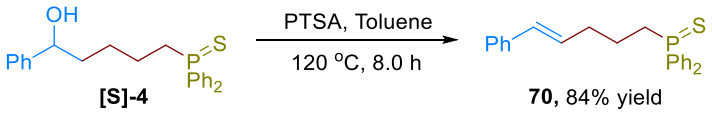


[S]-4 **68**, 76% yield **69**, 97% yield

To a cooled solution of DIAD (122 mg, 0.6 mmol) in THF (3.5 mL) was added the (5-hydroxy-5-phenylpentyl) diphenylphosphine sulfide **[S]-4** (190 mg, 0.5 mmol) and PPh_3 (160 mg, 0.6 mmol). After 30 min, Diphenylphosphoryl azide (DPPA, 165 mg, 0.6 mmol) was added and the reaction mixture was allowed to warm to room temperature. After stirring overnight, the solvent was removed in vacuum to give yellow oil. The crude product was purified by flash column chromatography (PE/EA = 10/1) to give the desired product **68** (154.0 mg, 76%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 – 7.77 (m, 4H), 7.52 – 7.41 (m, 6H), 7.36 – 7.28 (m, 3H), 7.26 – 7.20 (m, 2H), 4.37 – 4.33 (m, 1H), 2.47 – 2.37 (m, 2H), 1.84 – 1.75 (m, 1H), 1.75 – 1.59 (m, 3H), 1.52 – 1.41 (m, 1H), 1.41 – 1.31 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 139.5, 133.0 (d, J = 79.5 Hz), 133.0 (d, J = 79.6 Hz), 131.5 (d, J = 2.9 Hz), 131.1 (d, J = 10.0 Hz), 131.0 (d, J = 10.1 Hz), 128.8, 128.7 (d, J = 11.9 Hz), 128.3, 126.9, 66.0, 35.7, 32.4 (d, J = 56.8 Hz), 27.2 (d, J = 16.7 Hz), 21.9 (d, J = 2.5 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.5. HR-MS (ESI) m/z calcd for $C_{23}H_{25}N_3PS$ $[M + H]^+$ 406.1502, found 406.1498.

To a mixture of CuI (0.08 mg, 0.004 mmol), DIPEA (1.04 mg, 0.008 mmol), and HOAc (0.48 mg, 0.008 mmol) in DCM (1.0 mL) was added a mixture of ethynylbenzene (20.5 mg, 0.2 mmol) and (5-azido-5-phenylpentyl) diphenylphosphine sulfide **68** (85.2 mg, 0.21 mmol) at room temperature. The resultant mixture was stirred until the alkyne disappeared. Purification by column chromatography (PE/EA = 2/1) yielded **69** (98.1 mg, 97%) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 – 7.75 (m, 6H), 7.70 – 7.64 (m, 1H), 7.49 – 7.26 (m, 14H), 5.57 – 5.51 (m, 1H), 2.54 – 2.45 (m, 1H), 2.45 – 2.35 (m, 2H), 2.29 – 2.20 (m, 1H), 1.79 – 1.62 (m, 2H), 1.49 – 1.30 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 147.7, 138.7, 132.93 (d, J = 79.4 Hz), 132.88 (d, J = 80.3 Hz), 131.5 (d, J = 2.9 Hz), 131.1 (d, J = 10.1 Hz), 131.0 (d, J = 10.0 Hz), 130.6, 129.1, 128.8, 128.73 (d, J = 12.2 Hz), 128.69, 128.2, 126.9, 125.7, 118.8, 65.0, 34.7,

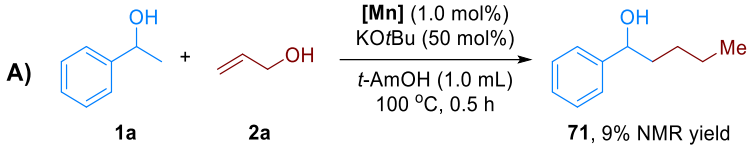
32.2 (d, J = 56.7 Hz), 27.3 (d, J = 16.3 Hz), 21.8 (d, J = 2.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.5. HR-MS (ESI) m/z calcd for $C_{31}H_{31}N_3PS$ $[M + H]^+$ 508.1971, found 508.1974.



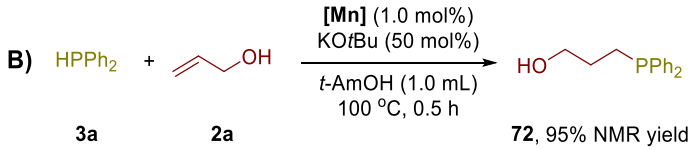
[S]-4 **70**, 84% yield

To a solution of **[S]-4** (190 mg, 0.5 mmol) in toluene (2.0 mL) was added PTSA (17.2 mg, 20 mol%). The mixture was stirred under 120 °C for 8.0 h, then diluted with DCM, and washed with H_2O and brine. The combined organic layers were added Na_2SO_4, filtered, and then evaporated under reduced pressure. The crude product was purified by column chromatography on gel using PE/EA = 10/1 as eluent to give final product **70** (152.2 mg, 84%) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.43 – 7.40 (m, 4H), 7.33 – 7.30 (m, 8H), 7.30 – 7.27 (m, 2H), 7.20 – 7.17 (m, 1H), 6.39 – 6.33 (m, 1H), 6.20 – 6.12 (m, 1H), 2.36 – 2.30 (m, 2H), 2.12 – 2.05 (m, 2H), 1.67 – 1.57 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 137.4, 132.8 (d, J = 79.9 Hz), 131.5 (d, J = 3.0 Hz), 131.2, 131.1 (d, J = 10.1 Hz), 129.1, 128.7, 128.6 (d, J = 12.6 Hz), 127.2, 126.0, 33.6 (d, J = 16.7 Hz), 31.9 (d, J = 56.6 Hz), 21.9 (d, J = 2.2 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 42.8. HR-MS (ESI) m/z calcd for $C_{23}H_{24}PS$ $[M + H]^+$ 363.1331, found 363.1322.

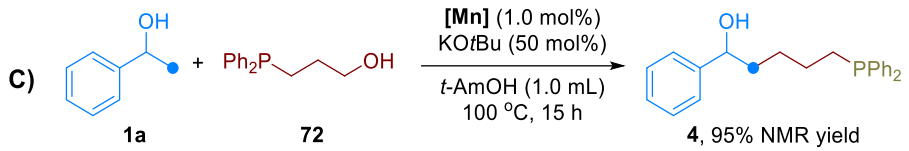
Control experiments



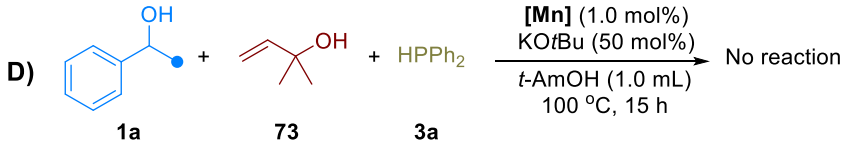
In a nitrogen-filled glove box, an oven-dried Schlenk pressure tube (10 mL) containing a stirring bar was charged with [**Mn**] (1.0 mol%, 3.2 mg). Dry and degassed *t*-AmOH (1.0 mL) and KO*t*Bu (50 mol%, 28 mg) were added and stirred at room temperature for 5.0 min. Then 1-phenylethanol **1a** (0.5 mmol, 61 mg) and allylic alcohol **2a** (0.6 mmol, 42 μL) were added in sequence. The tube was brought out of the glovebox and heated at 100 °C for 0.5 h. Upon reaction completion, the vessel was cooled to ambient temperature, and the excess organic solvent was removed under vacuum. Then mesitylene (0.25 mmol, 30.0 mg) was added as an internal standard to the reaction mixture, and it was analyzed by NMR spectroscopy immediately.



In a nitrogen-filled glove box, an oven-dried Schlenk pressure tube (10 mL) containing a stirring bar was charged with [**Mn**] (1.0 mol%, 3.2 mg). Dry and degassed *t*-AmOH (1.0 mL) and KO*t*Bu (50 mol%, 28 mg) were added and stirred at room temperature for 5.0 min. Then allylic alcohol **2a** (0.6 mmol, 42 μL) and diphenylphosphine (0.6 mmol, 105 μL) were added in sequence. The tube was brought out of the glovebox and heated at 100 °C for 0.5 h. Upon reaction completion, the vessel was cooled to ambient temperature, and the excess organic solvent was removed under vacuum. Then mesitylene (0.25 mmol, 30.0 mg) was added as an internal standard to the reaction mixture, and it was analyzed by NMR spectroscopy immediately.



In a nitrogen-filled glove box, an oven-dried Schlenk pressure tube (10 mL) containing a stirring bar was charged with [**Mn**] (1.0 mol%, 3.2 mg). Dry and degassed *t*-AmOH (1.0 mL) and KO*t*Bu (50 mol%, 28 mg) were added and stirred at room temperature for 5.0 min. Then 1-phenylethanol (0.5 mmol, 61 mg) and compound **72** (0.6 mmol, 146.5 mg) were added in sequence. The tube was brought out of the glovebox and heated at 100 °C for 15 h. Upon reaction completion, the vessel was cooled to ambient temperature, and the excess organic solvent was removed under vacuum. Then mesitylene (0.5 mmol, 60.1 mg) was added as an internal standard to the reaction mixture, and it was analyzed by NMR spectroscopy immediately.



In a nitrogen-filled glove box, an oven-dried Schlenk pressure tube (10 mL) containing a stirring bar was charged with [**Mn**] (1.0 mol%, 3.2 mg). Dry and degassed *t*-AmOH (1.0 mL) and KO*t*Bu (50 mol%, 28 mg) were added and stirred at room temperature for 5.0 min. Then compound **73** (0.6 mmol, 51.7 mg), diphenylphosphine (0.6 mmol, 105 μL) and 1-phenylethanol (0.5 mmol, 61 mg) were added in sequence. The tube was brought out of the glovebox and heated at 100 °C for 15 h. Upon reaction completion, the vessel was cooled to ambient temperature. No product was detected by GCMS.

Kinetic studies

Time course experiment

In a nitrogen-filled glove box, oven-dried Schlenk pressure tubes (10 mL) containing stirring bars were charged with [**Mn**] (1.0 mol%). Dry and degassed *t*-AmOH (1.0 mL) and KO*t*Bu (50 mol%) were added and stirred at room temperature for 5.0 min. Then allylic alcohol **2a** (0.6 mmol, 42 μL), diphenylphosphine **3a** (0.6 mmol, 105 μL) and 1-phenylethanol **1a** (0.5 mmol, 61 mg) were added in sequence. The tubes were brought out of the glovebox and heated at 100 °C. The pressure tube was taken out of the heated alloy plate after 0.5 h, 1.0 h, 2.0 h, 4.0 h, 6.0 h, 8.0 h, 10 h, 12 h, 15 h. Upon reaction completion, the vessel was cooled to ambient temperature, and the excess organic solvent was removed under vacuum. Then mesitylene (0.25 mmol, 30.0 mg) was added as an internal standard to the reaction mixture, and it was analyzed by NMR spectroscopy immediately.

Table S2 Data of reaction monitoring [a].

Time	1a (%)	4 (%)	71 (%)	72 (%)
0.5 h	84	15	0	94
1.0 h	62	35	0	64
2.0 h	39	56	0	34
4.0 h	22	72	2	21
6.0 h	14	83	2	17
8.0 h	10	85	3	14
10 h	6	90	3	11
12 h	1	94	3	9
15 h	1	94	3	8

[a] Reaction condition: **1a** (0.5 mmol), **2a** (0.6 mmol), **3a** (0.6 mmol), [**Mn**] (1.0 mol%),

KO*t*Bu (50 mol%), and *t*-AmOH (1.0 mL) in a 10 mL sealed tube, 100 °C. Yields were based on 0.5 mmol and determined by ^{1}H-NMR analysis using mesitylene as an internal standard.

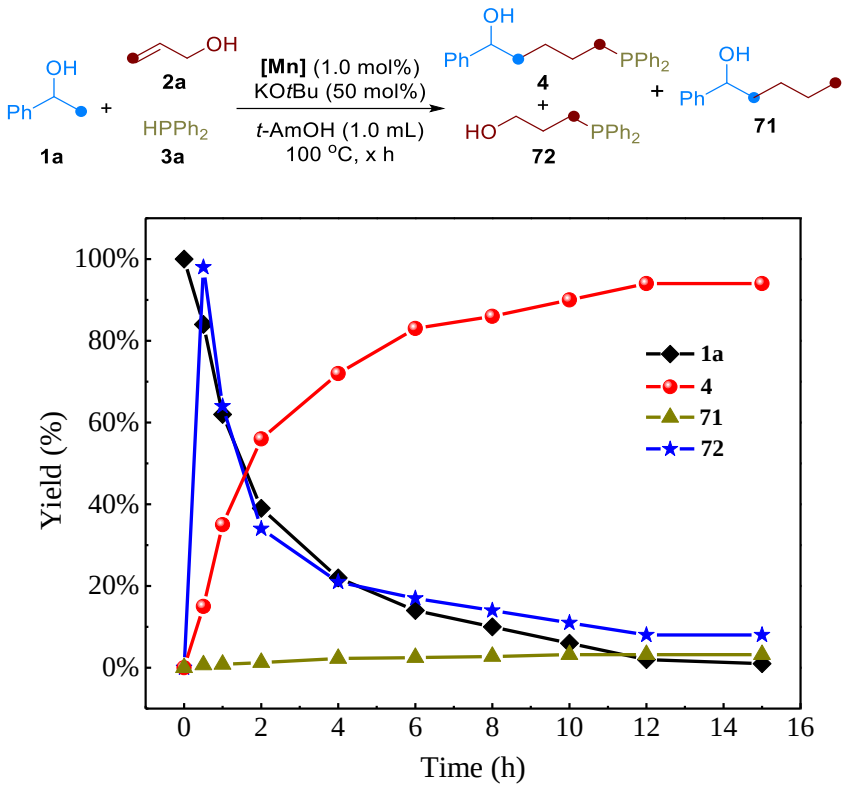


Figure S1 Line chart of reaction monitoring.

General procedure and data of kinetic studies

According to the general procedure of reaction monitoring, oven-dried pressure tubes (10 mL) were charged with 1-phenylethanol (**1a**), allylic alcohol (**2a**), diphenylphosphine (**3a**), **[Mn]** in several different equivalents and KO*t*Bu (50 mol%), *t*-AmOH (1.0 mL) under 100 °C for 15 min, 30 min, 45 min, 60 min, and cooled to room temperature immediately. The excess organic solvent was removed under vacuum. Then mesitylene (0.25 mmol, 30.0 mg) was added as an internal standard to the reaction mixture, and it was analyzed by NMR spectroscopy immediately.

Table S3 The molar concentration of product **4** in different concentration of 1-phenylethanol (**1a**) at different time interval.

Time (min)	0.1287554 M (**1a**)	0.2124044 M (**1a**)	0.2938707 M (**1a**)	0.3740648 M (**1a**)
15	0.0170815	0.0180544	0.0225021	0.0273067
30	0.0272961	0.0345794	0.0486986	0.0617623
45	0.0383262	0.0497876	0.0738455	0.1019119
60	0.0456652	0.0670773	0.0998321	0.1358271

Table S4 The k_{in} value of product **4** in different concentration of 1-phenylethanol (**1a**).

1a (M)	k_{in} (Mmin^{-1})	R^2	b
0.1287554	0.0006	0.9935	0.0079
0.2124044	0.0011	0.9995	0.0018
0.2938707	0.0017	0.9999	-0.0031
0.3740648	0.0024	0.9989	-0.0097

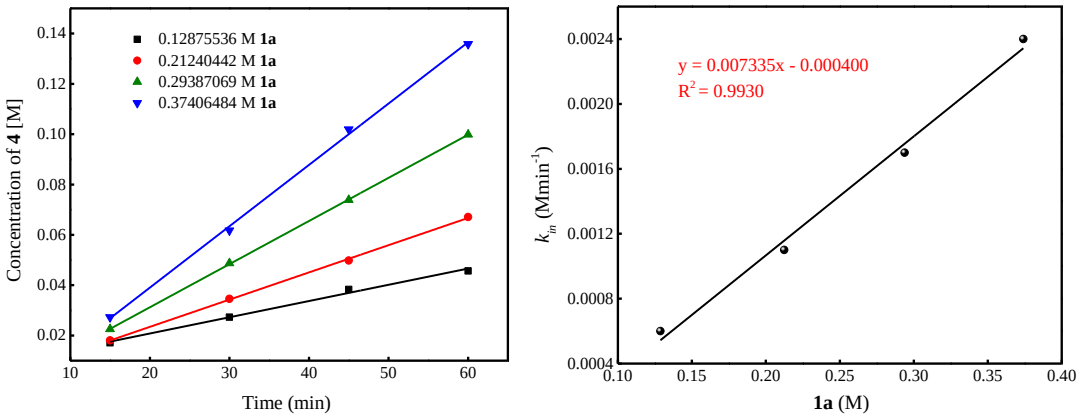


Figure S2 (a) Plot of the rise of product **4** from the reaction of **2a** (0.6 mmol), **3a** (0.6 mmol), **[Mn]** (1.0 mol%) with 0.1287554 M, 0.2124044 M, 0.2938707 M, 0.3740648 M of **1a** in different time interval. The curve depicts the results of an unweighted least-square fit to y = k*x + b. (b) Plot of k_{in} versus **1a** from the reaction of **2a** (0.6 mmol), **3a** (0.6 mmol), **[Mn]** (1.0 mol%) with 0.1287554 M, 0.2124044 M, 0.2938707 M, 0.3740648 M of **1a**. The curve depicts the results of an unweighted least-square fit to y = k*x + b.

Table S5 The molar concentration of product **4** in different concentration of allylic alcohol (**2a**) at different time interval.

Time (min)	0.2527380 M (**2a**)	0.3350084 M (**2a**)	0.3757515 M (**2a**)	0.4163197 M (**2a**)
15	0.0112047	0.0176298	0.0221276	0.0258951
30	0.0255687	0.0345477	0.0387442	0.0423813
45	0.0418703	0.0501675	0.0596610	0.0616570
60	0.0594777	0.0680067	0.0723113	0.0768526

Table S6 The k_{in} value of product **4** in different concentration of allylic alcohol (**2a**).

2a (M)	k_{in} ($Mmin^{-1}$)	R^2	b
0.2527380	0.001114	0.9979	-0.0058
0.3350084	0.001112	0.9994	0.0009
0.3757515	0.001123	0.9920	0.0053
0.4163197	0.001138	0.9981	0.0087

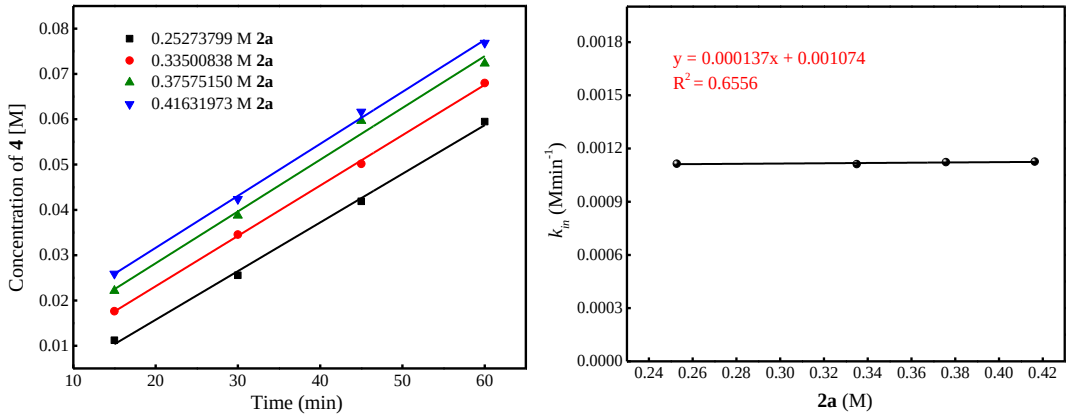


Figure S3 (a) Plot of the rise of product **4** from the reaction of **1a** (0.5 mmol), **3a** (0.6 mmol), **[Mn]** (1.0 mol%) with 0.2527380 M, 0.3350084 M, 0.3757515 M, 0.4163197 M of **2a** in different time interval. The curve depicts the results of an unweighted least-square fit to y = *k**x + b. (b) Plot of k_{in} versus **2a** from the reaction of **1a** (0.5 mmol), **3a** (0.6 mmol), **[Mn]** (1.0 mol%) with 0.2527380 M, 0.3350084 M, 0.3757515 M, 0.4163197 M of **2a**. The curve depicts the results of an unweighted least-square fit to y

= k*x + b.

Table S7 The molar concentration of product **4** in different concentration of diphenylphosphine (**3a**) at different time interval.

Time (min)	0.1755926 M (**3a**)	0.2595156 M (**3a**)	0.3407155 M (**3a**)	0.4194631 M (**3a**)
15	0.0108867	0.0197664	0.0276406	0.0375420
30	0.0343284	0.0416522	0.0541312	0.0647651
45	0.0565408	0.0682958	0.0761499	0.0902265
60	0.0845478	0.0903114	0.1023424	0.1114513

Table S8 The k_{in} value of product **4** in different concentration of diphenylphosphine (**3a**).

3a (M)	k_{in} (Mmin^{-1})	R^2	b
0.1755926	0.00162	0.9974	-0.0142
0.2595156	0.00159	0.9984	-0.0046
0.3407155	0.00164	0.9988	0.0035
0.4194631	0.00165	0.9970	0.0142

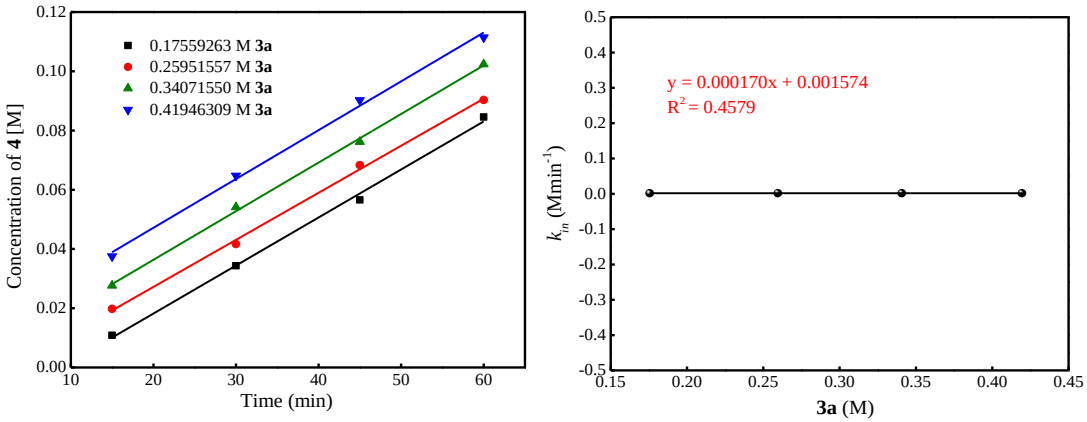


Figure S4 (a) Plot of the rise of product **4** from the reaction of **1a** (0.5 mmol), **2a** (0.6 mmol), **[Mn]** (1.0 mol%) with 0.1755926 M, 0.2595156 M, 0.3407155 M, 0.4194631 M of **3a** in different time interval. The curve depicts the results of an unweighted least-

square fit to y = k*x + b. (b) Plot of k_{in} versus **3a** from the reaction of **1a** (0.5 mmol), **2a** (0.6 mmol), **[Mn]** (1.0 mol%) with 0.1755926 M, 0.2595156 M, 0.3407155 M, 0.4194631 M of **3a**. The curve depicts the results of an unweighted least-square fit to y = k*x + b.

Table S9 The molar concentration of product **4** in different concentration of **[Mn]** at different time interval.

Time (min)	0.0016543 M ([**Mn**])	0.0024814 M ([**Mn**])	0.0033085 M ([**Mn**])	0.0041356 M ([**Mn**])
15	0.0083540	0.0109595	0.0138958	0.0238627
30	0.0163772	0.0279983	0.0391232	0.0573201
45	0.0248966	0.0441274	0.0619107	0.0899917
60	0.0330438	0.0586435	0.0846567	0.1209677

Table S10 The k_{in} value of product **4** in different concentration of **[Mn]**.

[Mn] (M)	k_{in} (Mmin^{-1})	R^2	b
0.0016543	0.0006	0.9999	0.0002
0.0024814	0.0011	0.9987	-0.0044
0.0033085	0.0016	0.9993	-0.0089
0.0041356	0.0022	0.9997	-0.0080

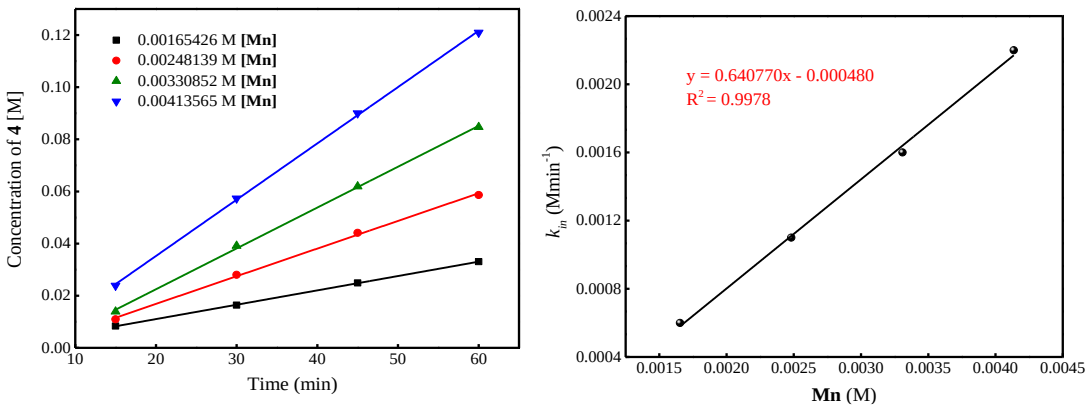


Figure S5 (a) Plot of the rise of product **4** from the reaction of **1a** (0.5 mmol), **2a** (0.6 mmol), **3a** (0.6 mmol) with 0.0016543 M, 0.0024814 M, 0.0033085 M, 0.0041356 M

of **[Mn]** in different time interval. The curve depicts the results of an unweighted least-square fit to y = *k**x + b. (b) Plot of k_{in} versus **[Mn]** from the reaction of **1a** (0.5 mmol), **2a** (0.6 mmol), **3a** (0.6 mmol) with 0.0016543 M, 0.0024814 M, 0.0033085 M, 0.0041356 M of **[Mn]**. The curve depicts the results of an unweighted least-square fit to y = *k**x + b.

Hammett studies

In a nitrogen-filled glove box, an oven-dried Schlenk pressure tube (10 mL) containing a stirring bar was charged with [**Mn**] (1.0 mol%). Dry and degassed *t*-AmOH (1.0 mL) and KO*t*Bu (50 mol%) were added and stirred at room temperature for 5.0 min. Then allylic alcohol **2a** (0.6 mmol, 1.2 equiv), diphenylphosphine **3a** (0.6 mmol, 1.2 equiv) and **1** (0.5 mmol, 1.0 equiv) were added in sequence. All Schlenk pressure tubes were placed on preheated (100 °C) aluminum heating block and stirred for defined time. These samples were then analyzed by ^{1}H NMR and the corresponding products were measured relative to the internal standard of mesitylene. Initial rate kinetics were obtained and these rates were compared against one another.

Table S11 Kinetics experiment.

	ln (1/1-α)						
Time (min)	**OMe**	***t*-Bu**	**Me**	**H**	**F**	**Cl**	**CF_3**
10	0.0457	0.0466	0.0571	0.0413	0.0593	0.0600	0.0288
20	0.1312	0.1135	0.1411	0.1114	0.1150	0.1024	0.0620
30	0.2275	0.2024	0.2115	0.1980	0.1619	0.1576	0.0983
40	0.3888	0.2671	0.3223	0.2504	0.2527	0.1991	0.1381
α = initial concentration conversion of substrates.							

Table S12 Equation parameters.

Equation	y = a + b*x						
Draw	**OMe**	***t*-Bu**	**Me**	**H**	**F**	**Cl**	**CF_3**
Intercept	-0.0830	-0.0302	-0.0335	-0.0282	-0.0095	0.0116	-0.0093
Slope	0.0113	0.0075	0.0087	0.0071	0.0063	0.0047	0.0036
Pearson's r	0.98773	0.99809	0.99569	0.99597	0.98883	0.99842	0.99918
Adj. R-Square	0.96342	0.99427	0.9871	0.98792	0.96667	0.99527	0.99754
R^2	0.9757	0.9962	0.9914	0.9920	0.9778	0.9968	0.9983

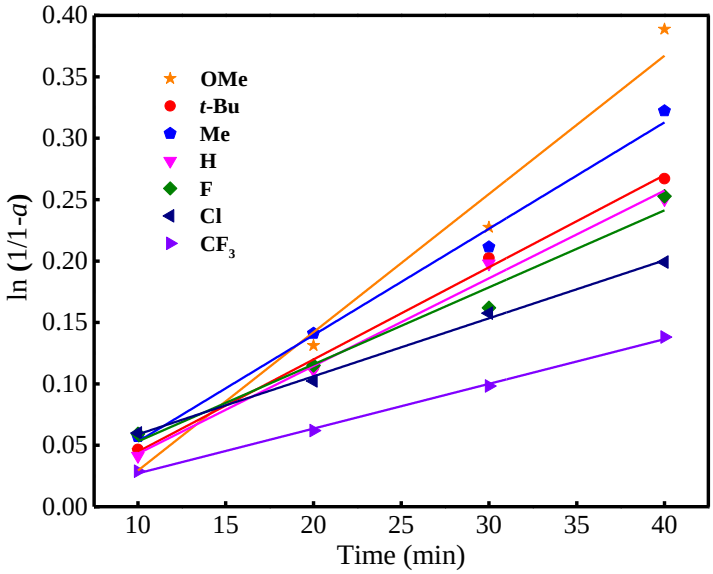
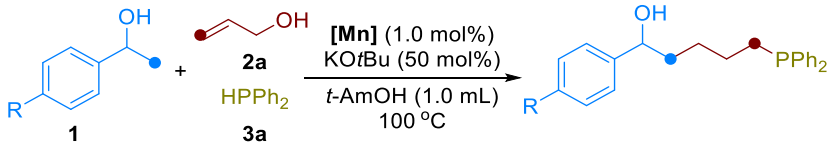


Figure S6 Substituent effect.

Table S13 Hammett plot kinetic study.



Entry	R_{para}	$lg(k_x/k_0)$	σ_{para}
1	H	0	0
2	OMe	0.2018	-0.27
3	*t*-Bu	0.0238	-0.20
4	Me	0.0883	-0.17
5	F	-0.0519	0.06
6	Cl	-0.1792	0.23
7	CF_3	-0.2950	0.54

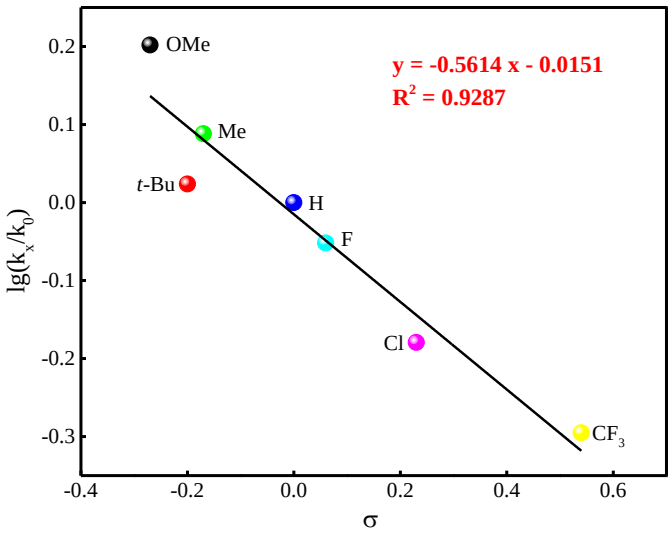
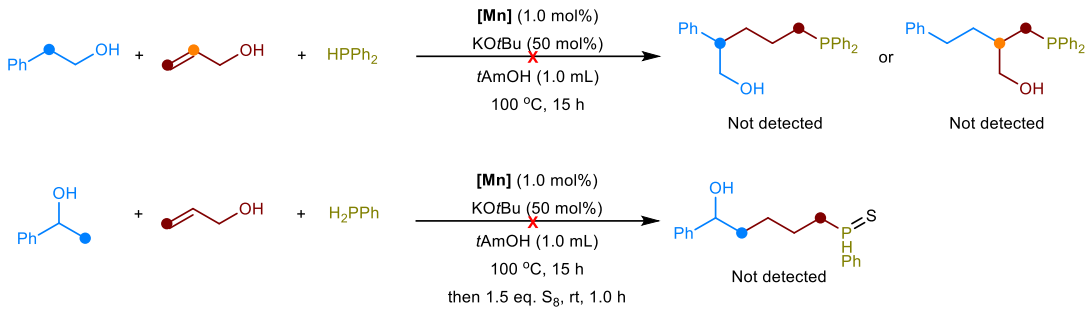


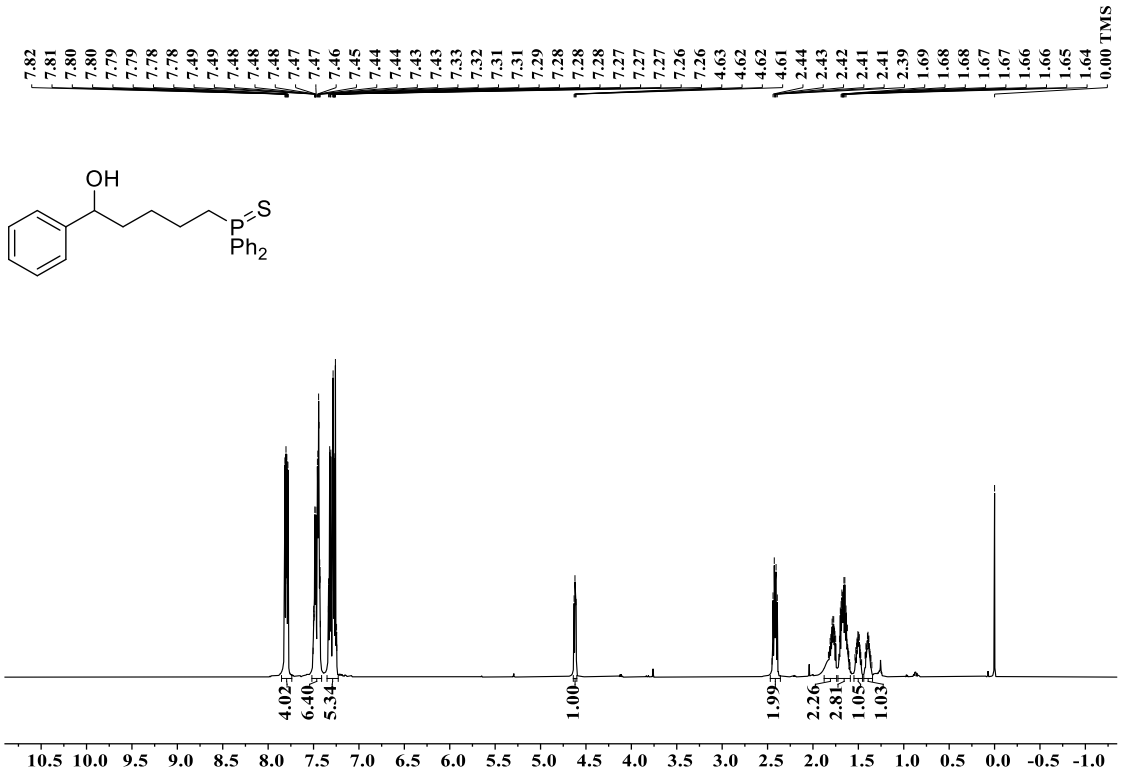
Figure S7 Hammett plot.

Unsuccessful substrates

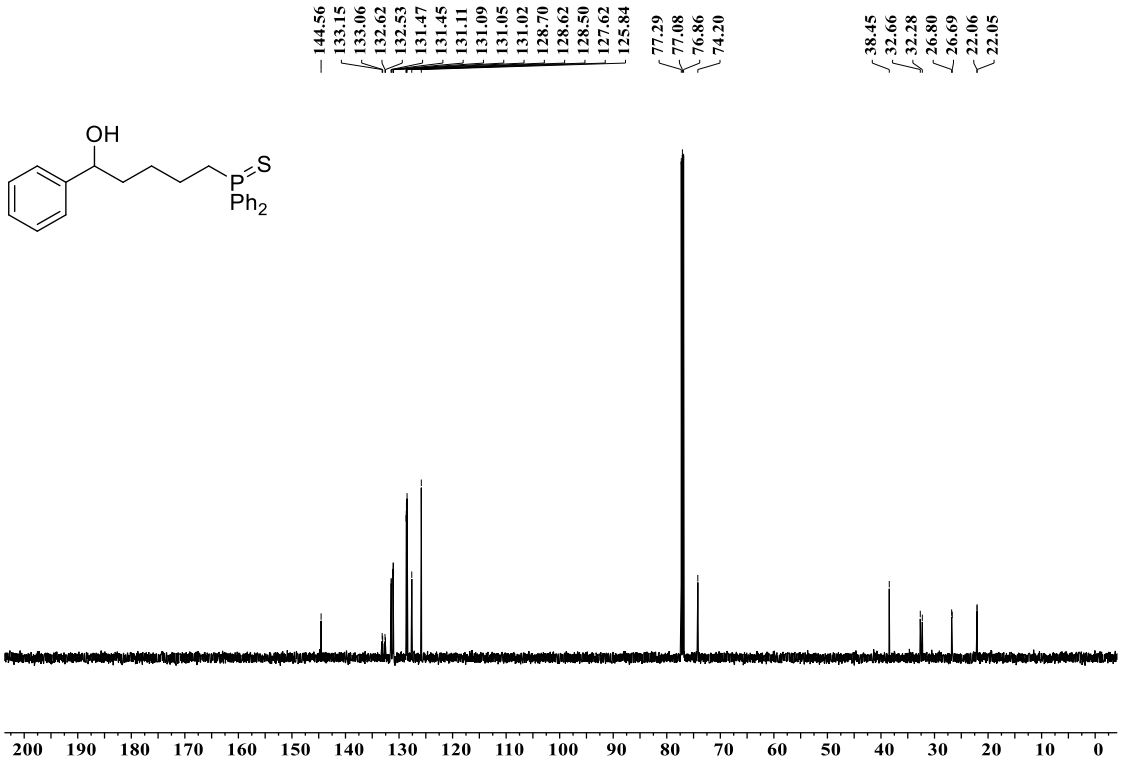


NMR spectra

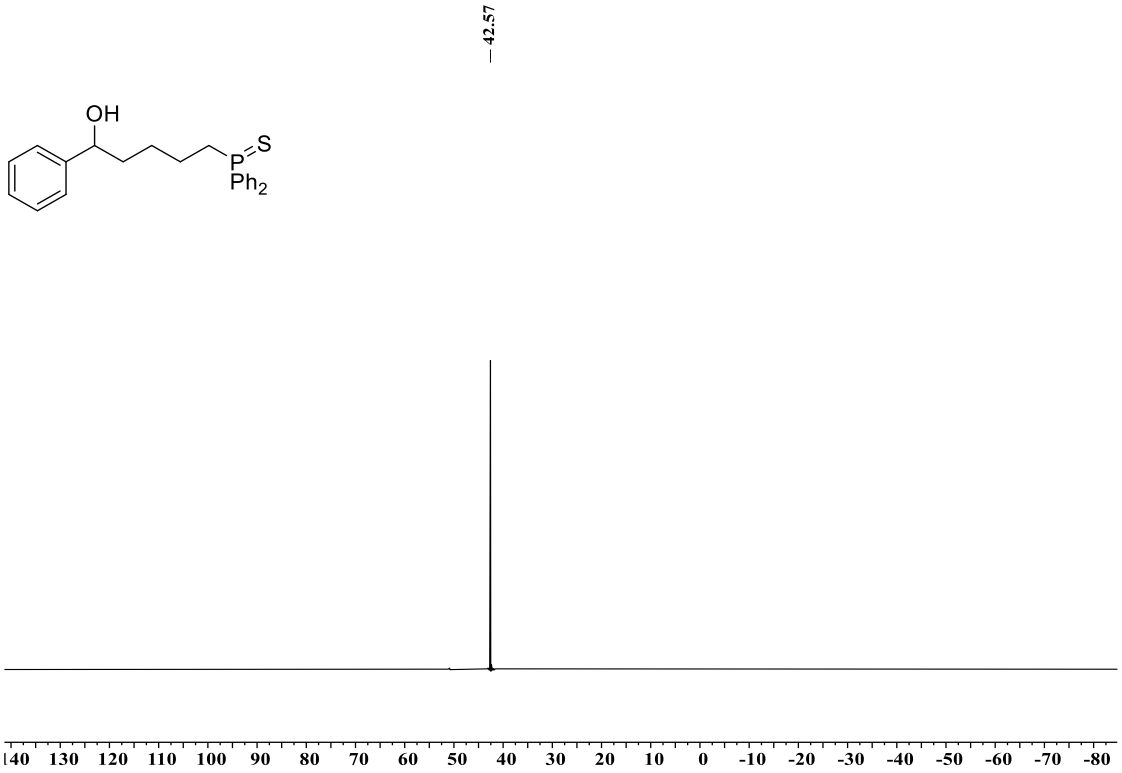
^{1}H NMR spectrum of **[S]-4** (600 MHz, $CDCl_3$)



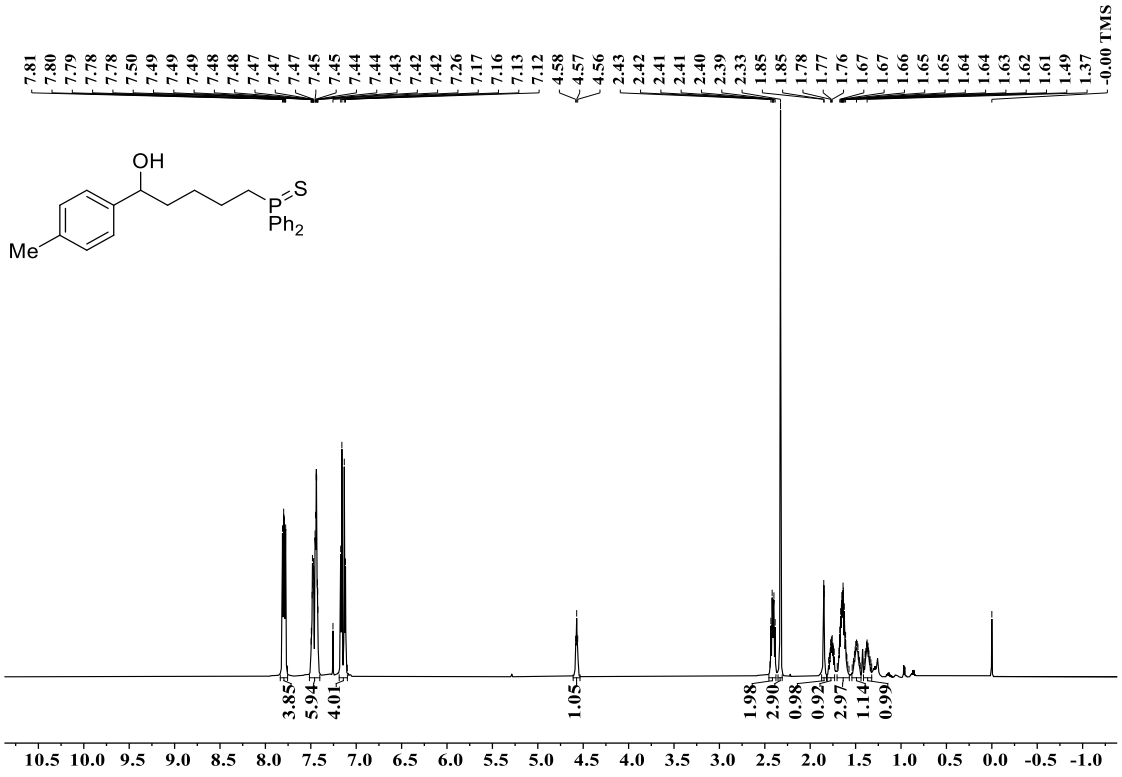
^{13}C NMR spectrum of **[S]-4** (150 MHz, $CDCl_3$)



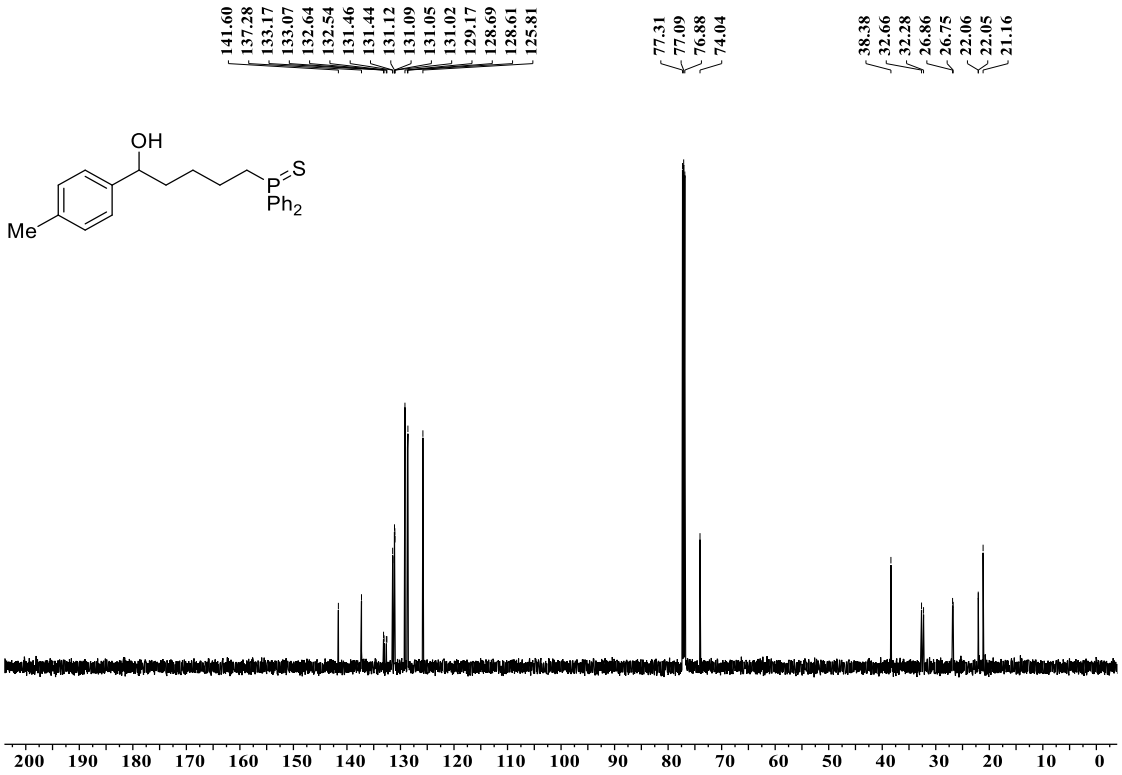
^{31}P NMR spectrum of **[S]-4** (243 MHz, $CDCl_3$)



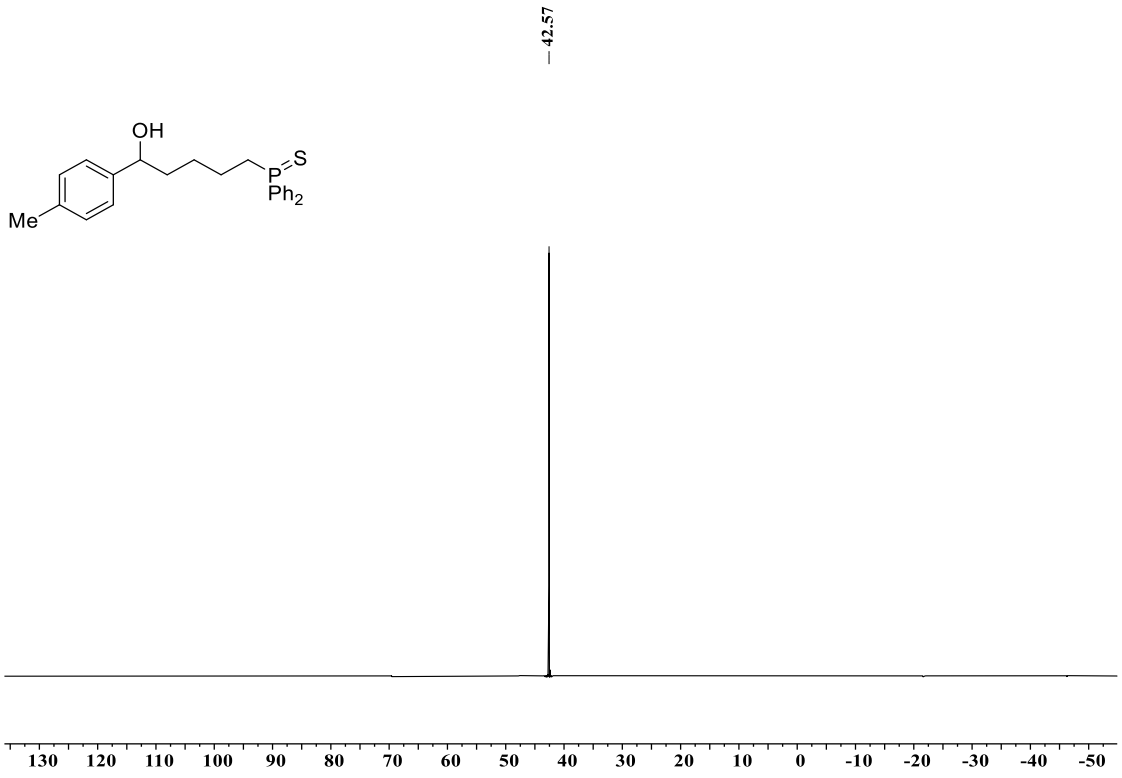
^{1}H NMR spectrum of **[S]-5** (600 MHz, $CDCl_3$)



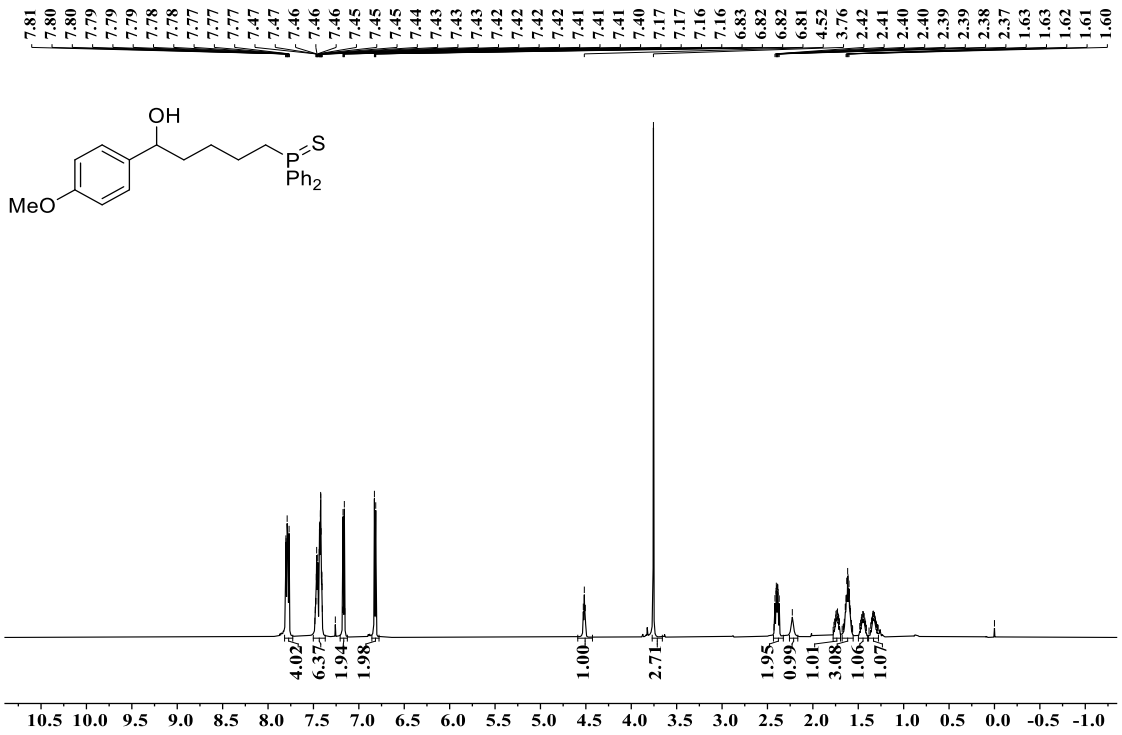
^{13}C NMR spectrum of **[S]-5** (150 MHz, $CDCl_3$)



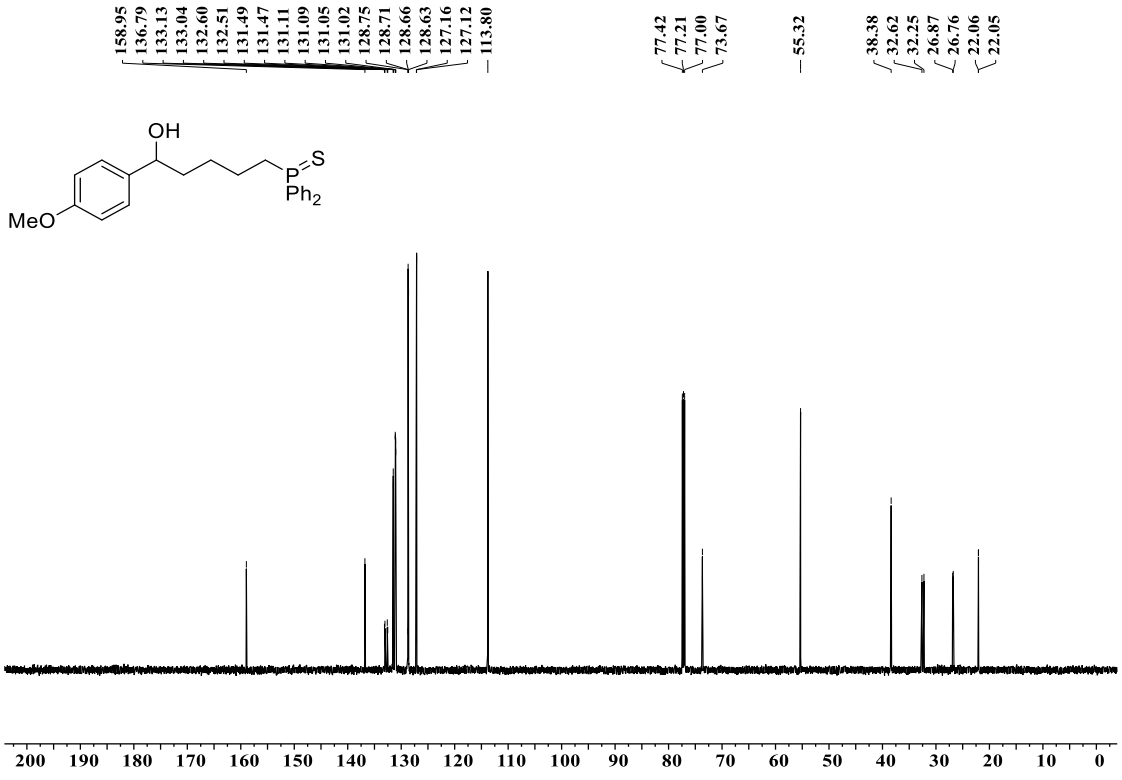
^{31}P NMR spectrum of **[S]-5** (243 MHz, $CDCl_3$)



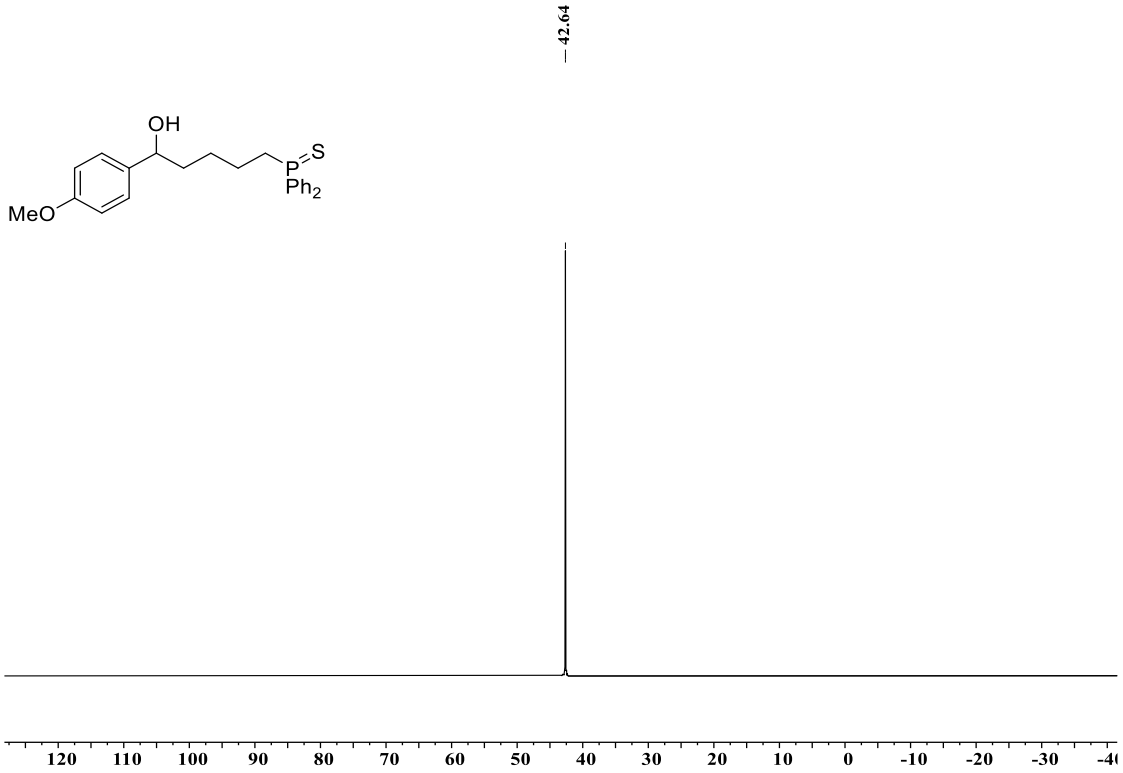
^{1}H NMR spectrum of **[S]-6** (600 MHz, $CDCl_3$)



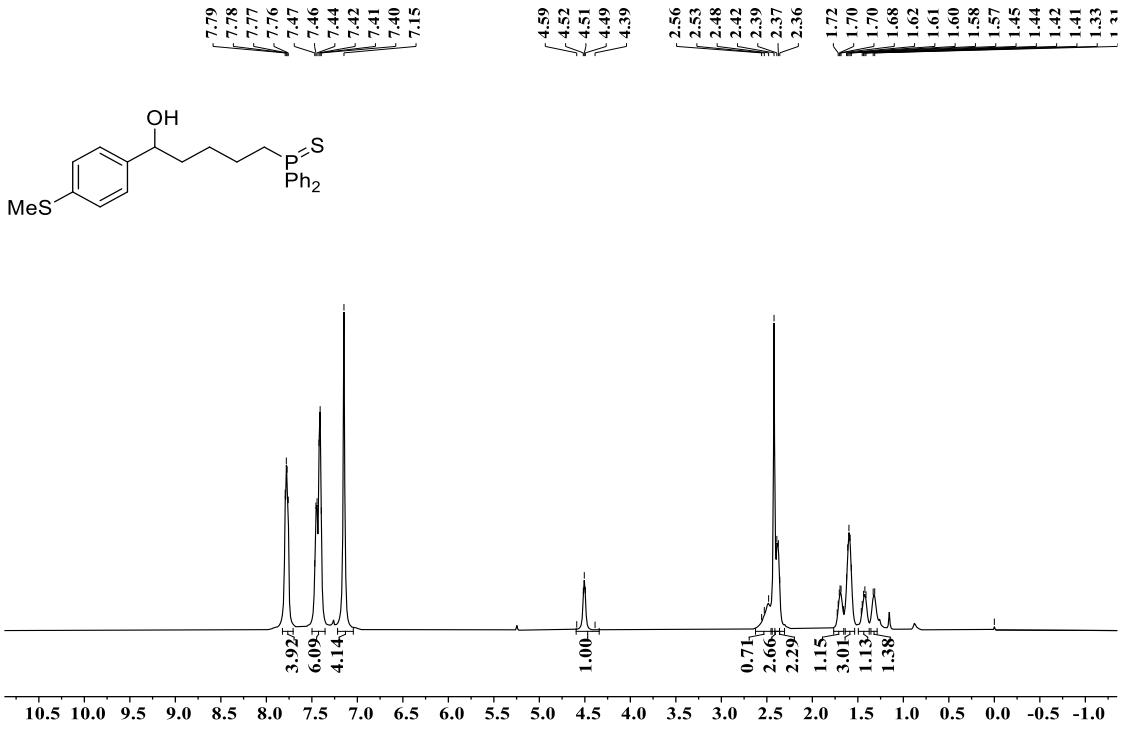
^{13}C NMR spectrum of **[S]-6** (150 MHz, $CDCl_3$)



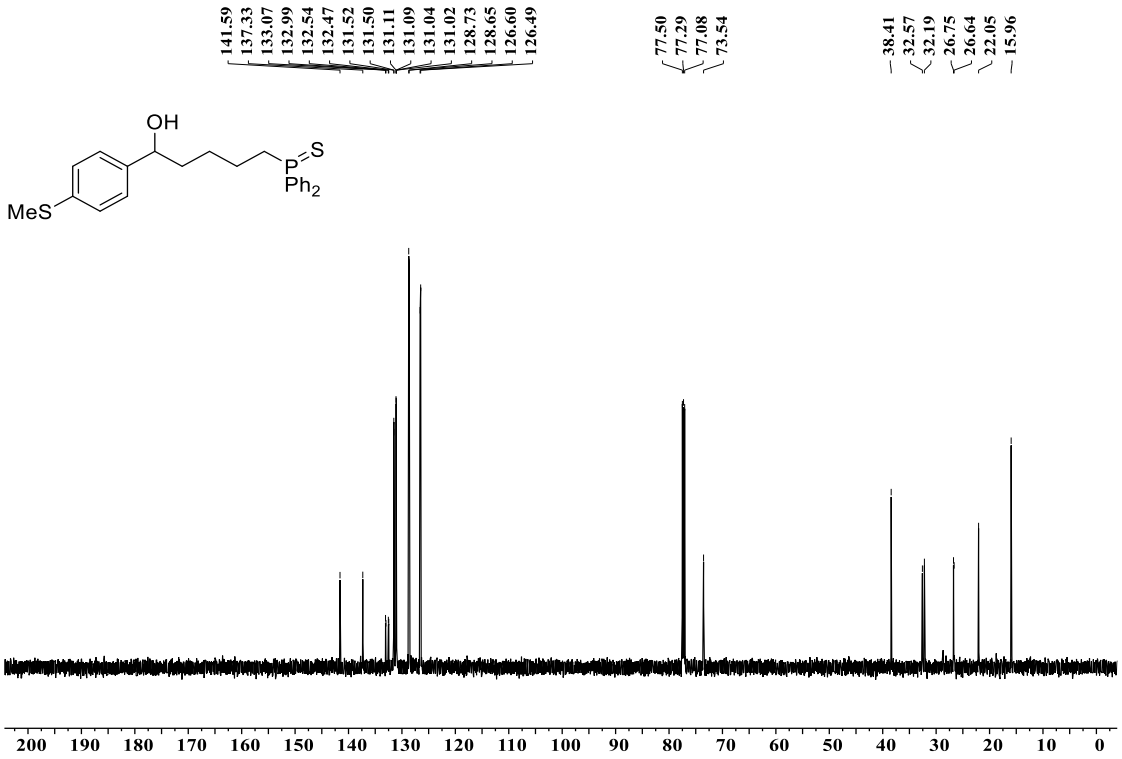
^{31}P NMR spectrum of **[S]-6** (243 MHz, $CDCl_3$)



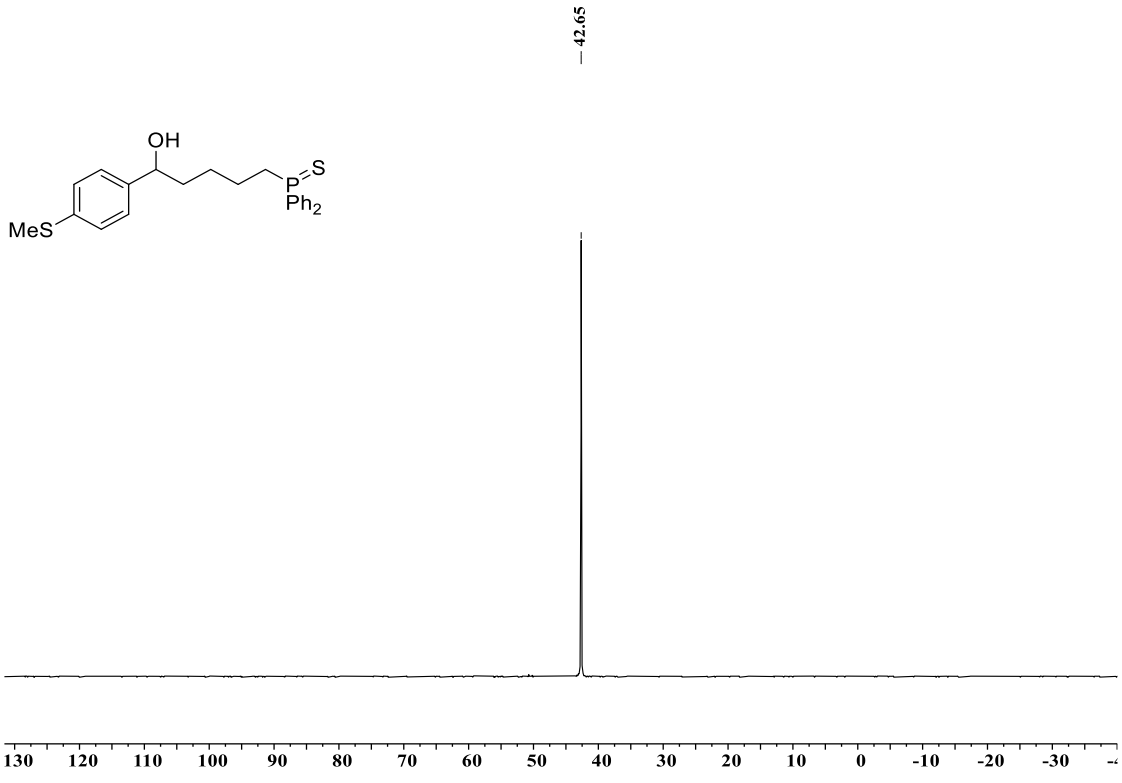
^{1}H NMR spectrum of **[S]-7** (600 MHz, $CDCl_3$)



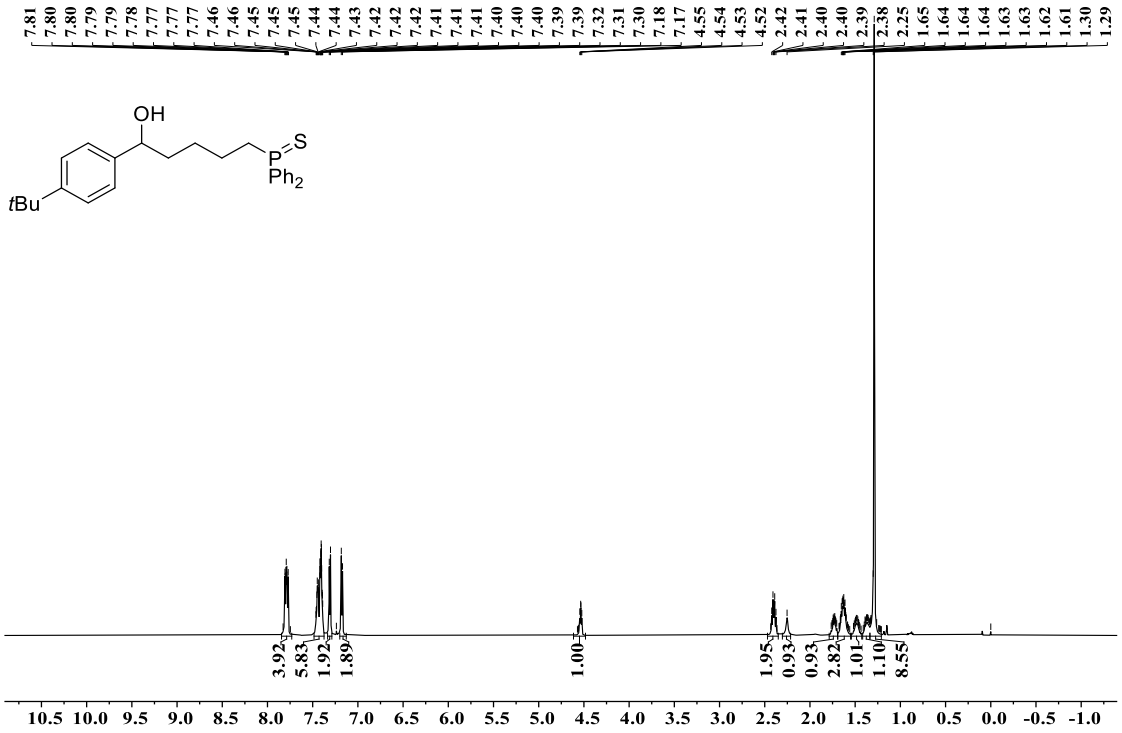
^{13}C NMR spectrum of **[S]-7** (150 MHz, $CDCl_3$)



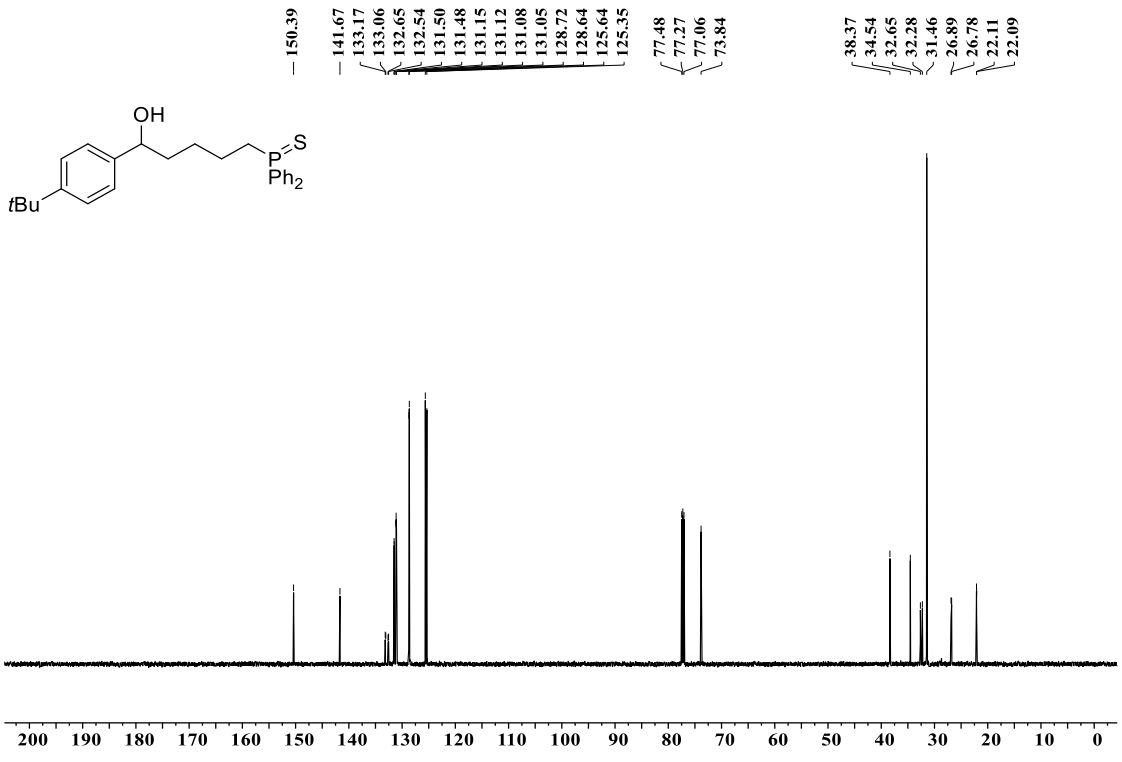
^{31}P NMR spectrum of **[S]-7** (243 MHz, $CDCl_3$)



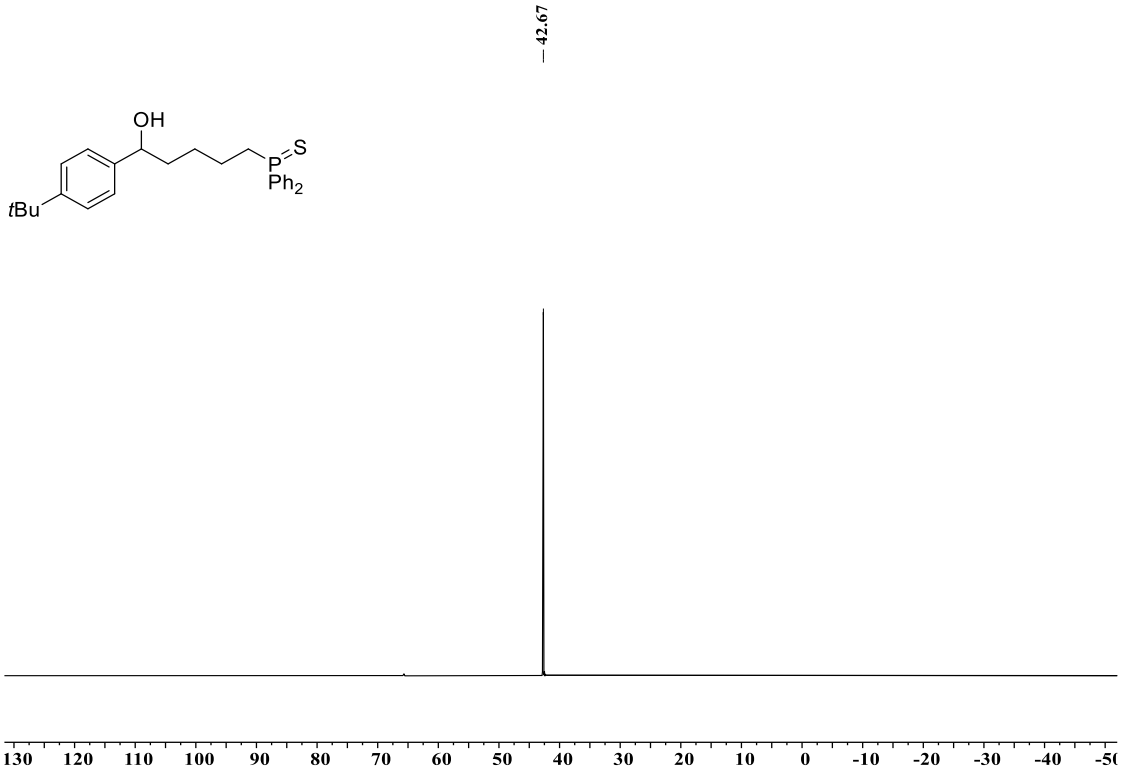
^{1}H NMR spectrum of **[S]-8** (600 MHz, $CDCl_3$)



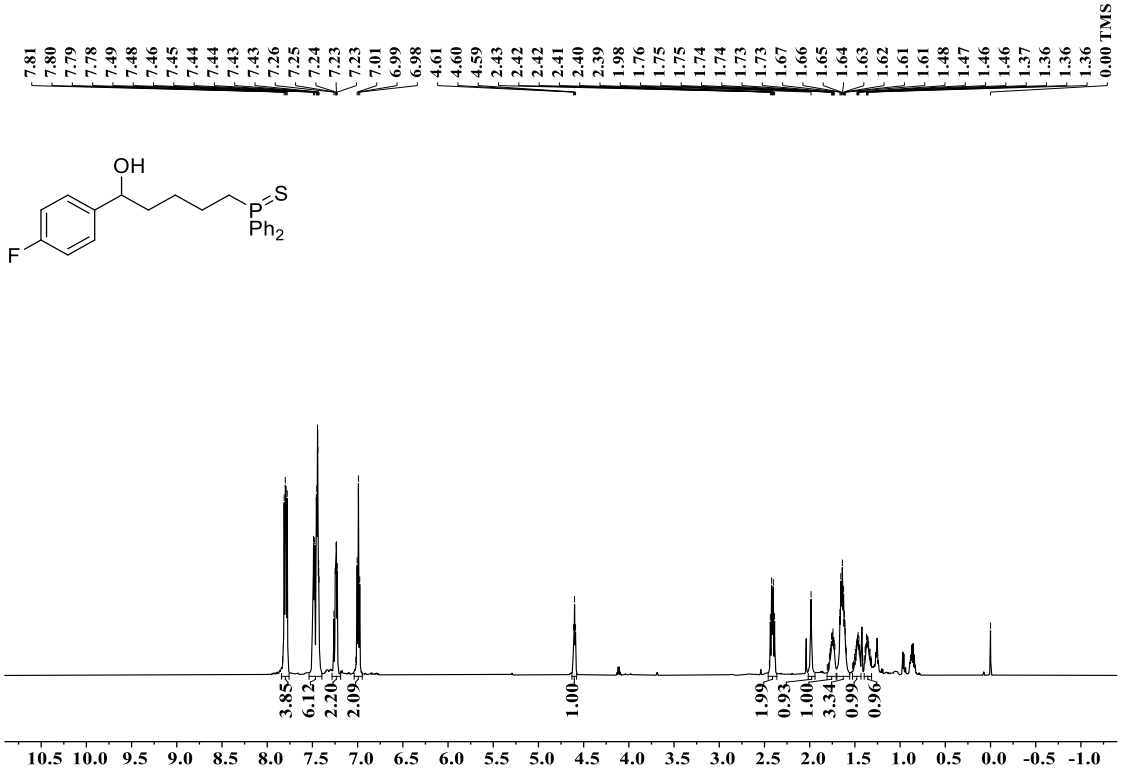
^{13}C NMR spectrum of **[S]-8** (150 MHz, $CDCl_3$)



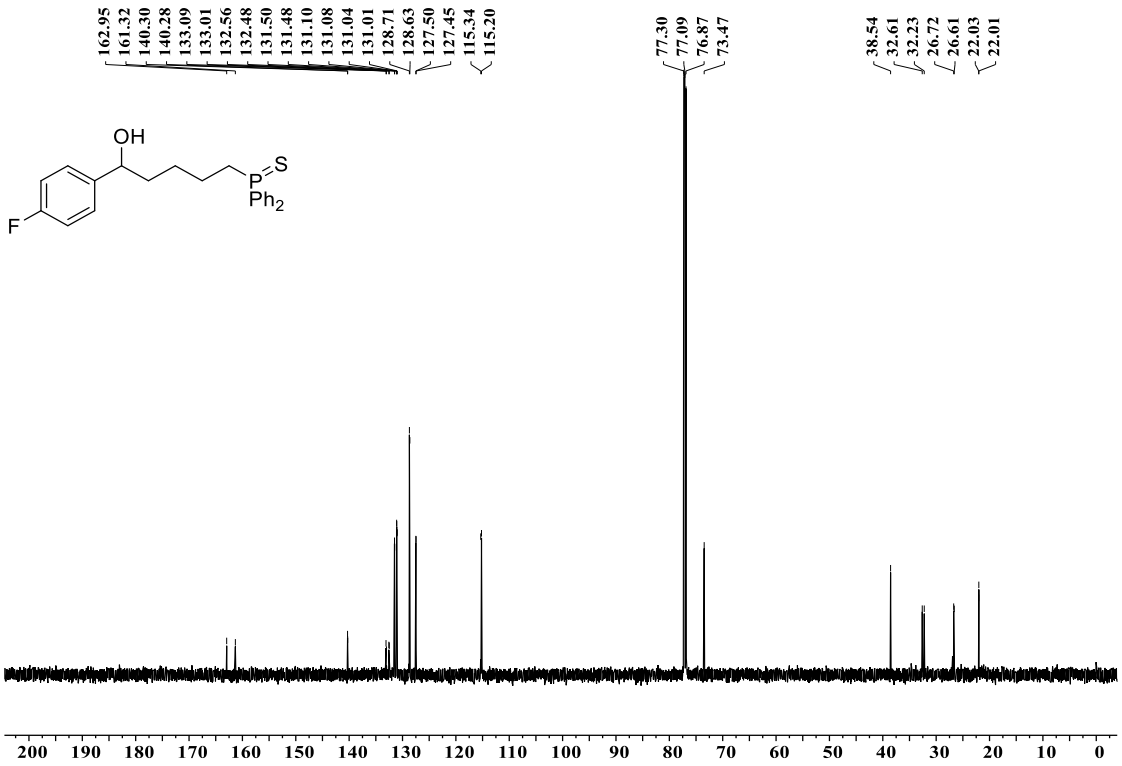
^{31}P NMR spectrum of **[S]-8** (243 MHz, $CDCl_3$)



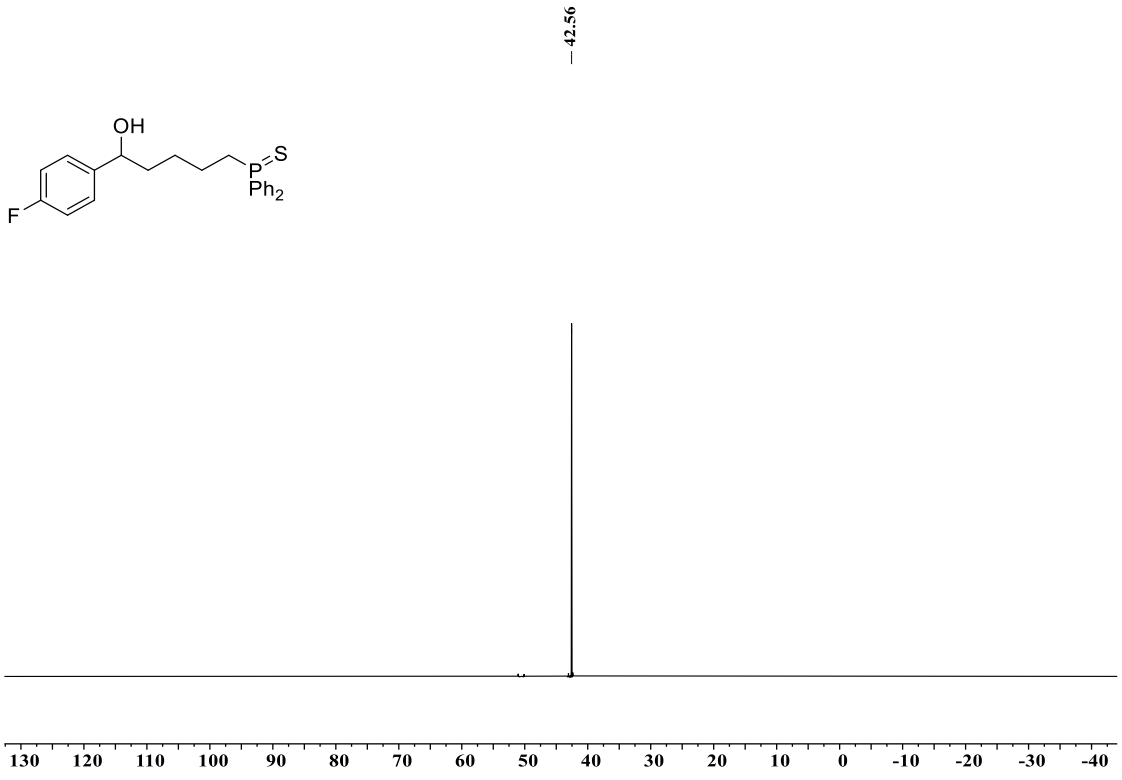
^{1}H NMR spectrum of **[S]-9** (600 MHz, $CDCl_3$)



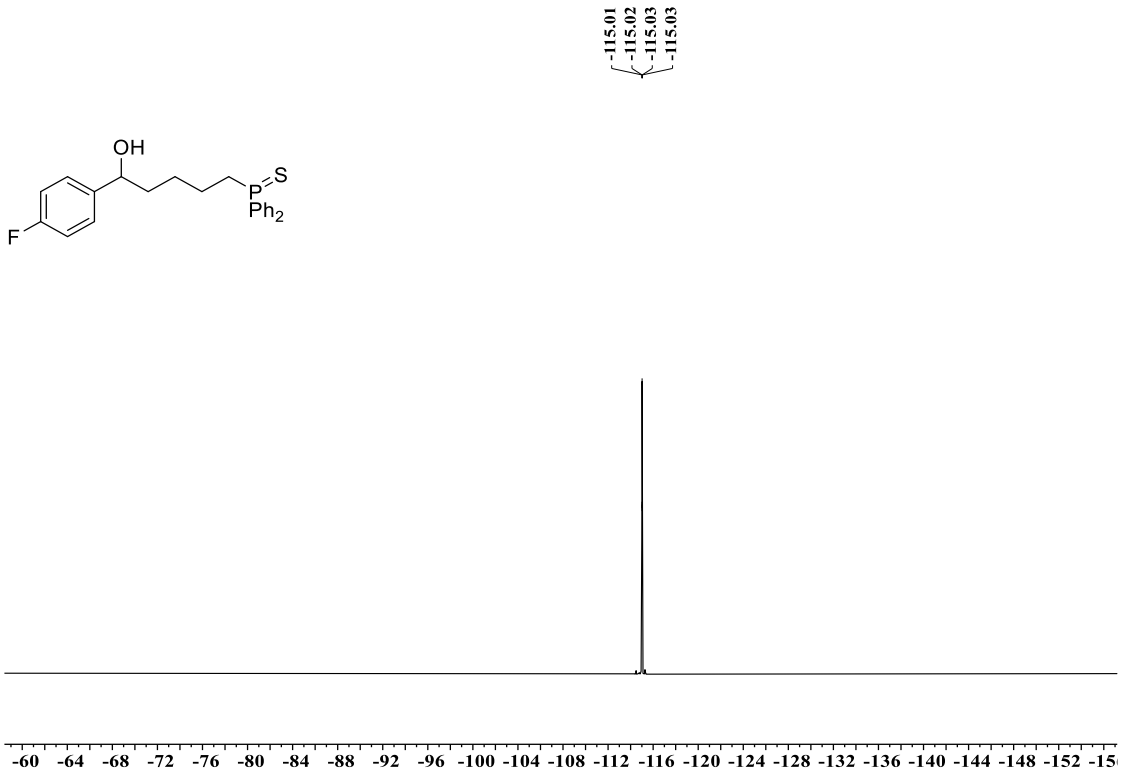
^{13}C NMR spectrum of **[S]-9** (150 MHz, $CDCl_3$)



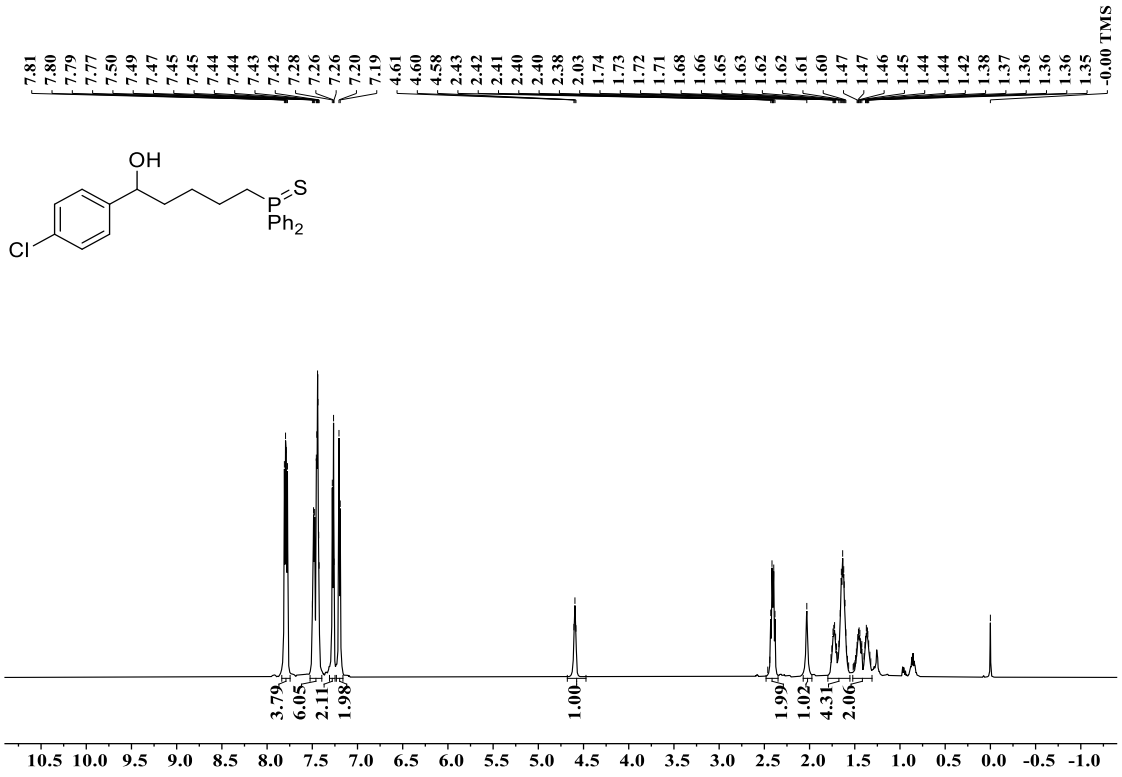
^{31}P NMR spectrum of **[S]-9** (243 MHz, $CDCl_3$)



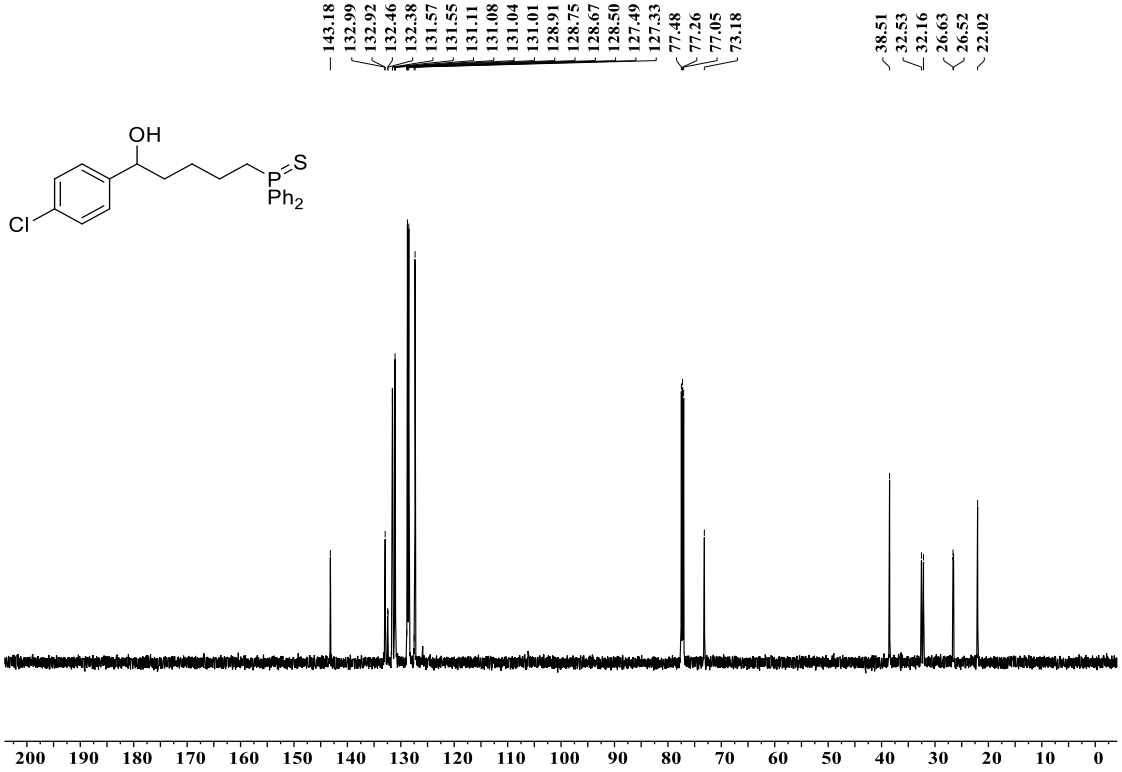
^{19}F NMR spectrum of **[S]-9** (565 MHz, $CDCl_3$)



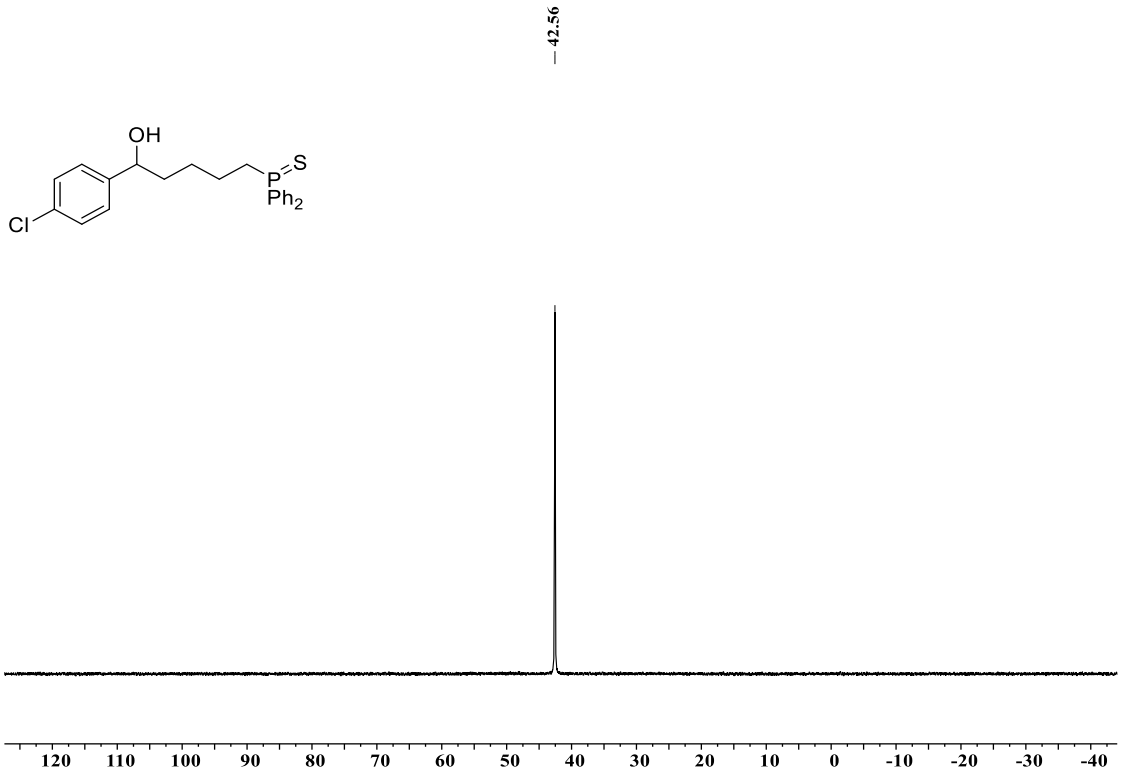
^{1}H NMR spectrum of **[S]-10** (600 MHz, $CDCl_3$)



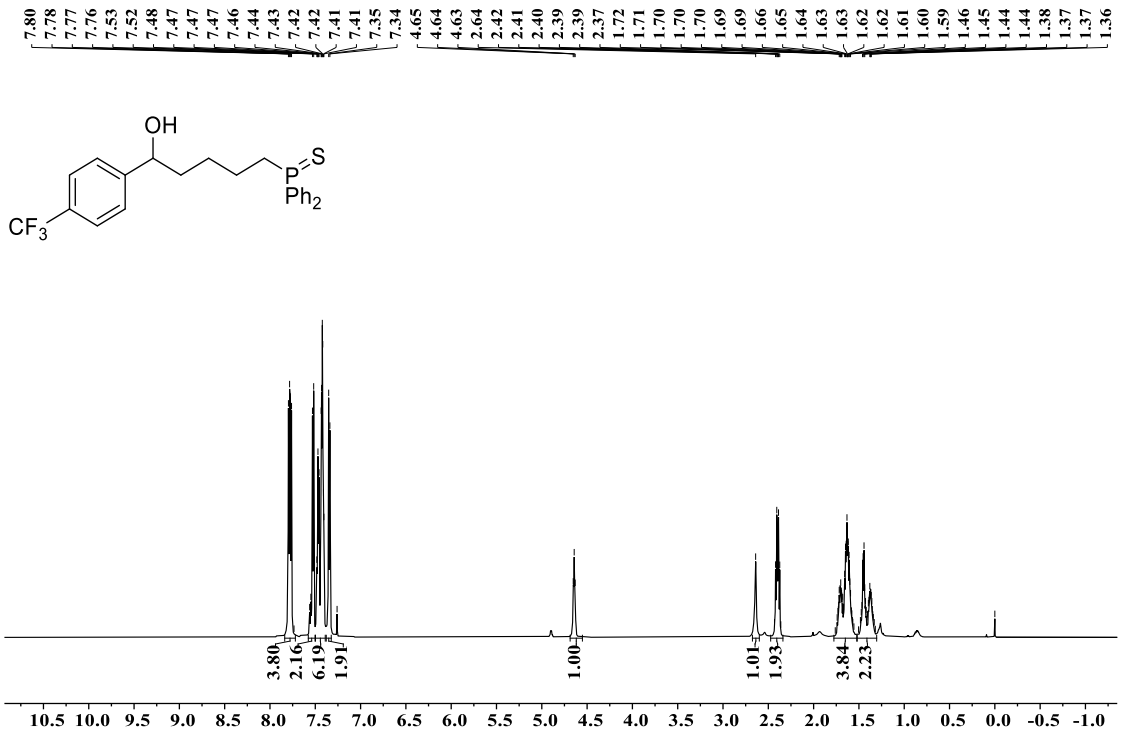
^{13}C NMR spectrum of **[S]-10** (150 MHz, $CDCl_3$)



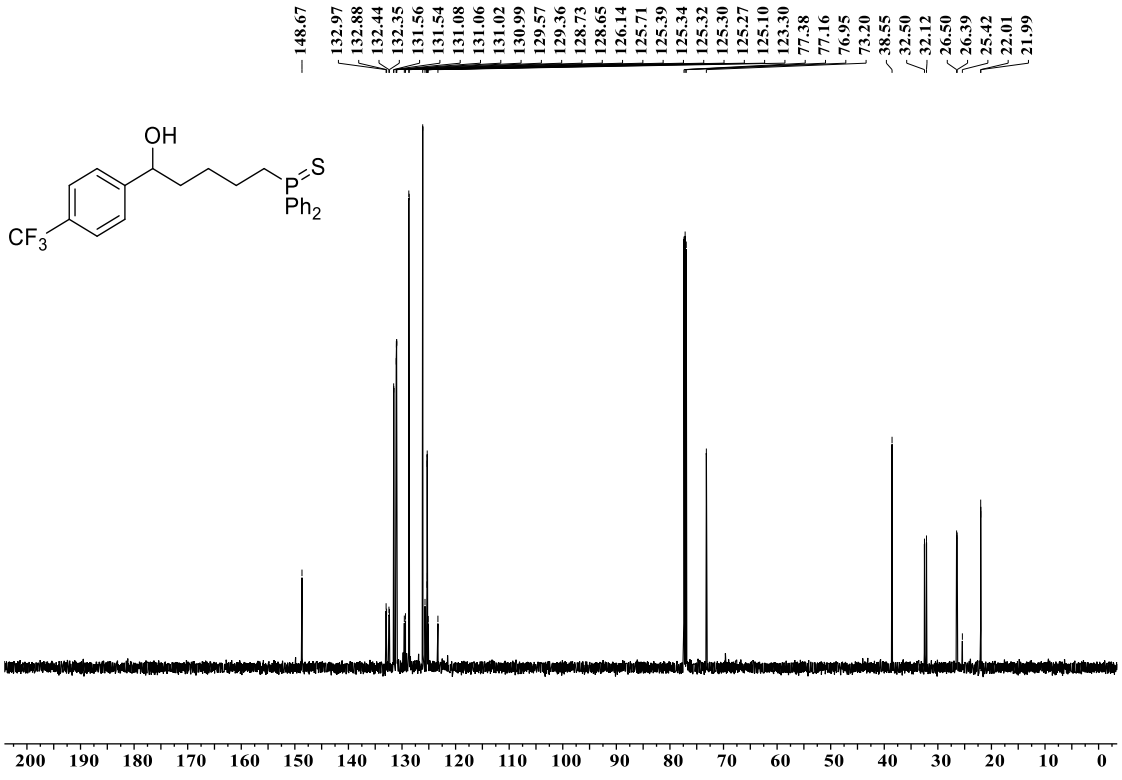
^{31}P NMR spectrum of **[S]-10** (243 MHz, $CDCl_3$)



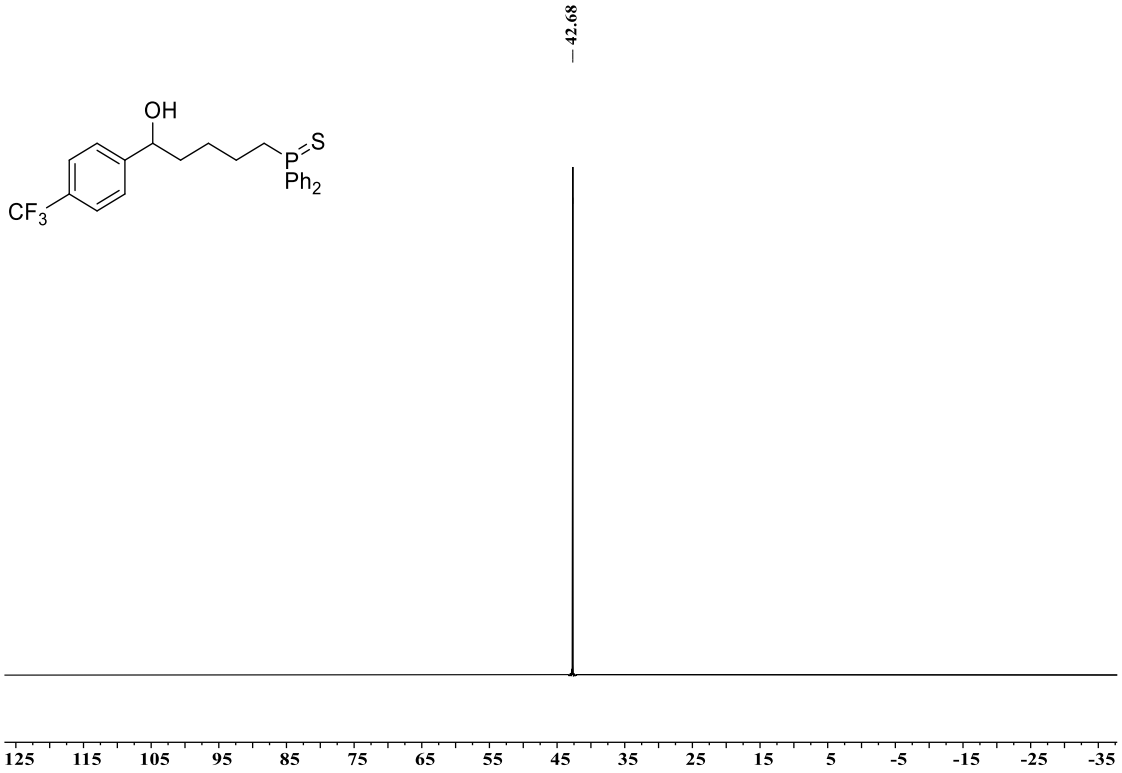
^{1}H NMR spectrum of **[S]-11** (600 MHz, $CDCl_3$)



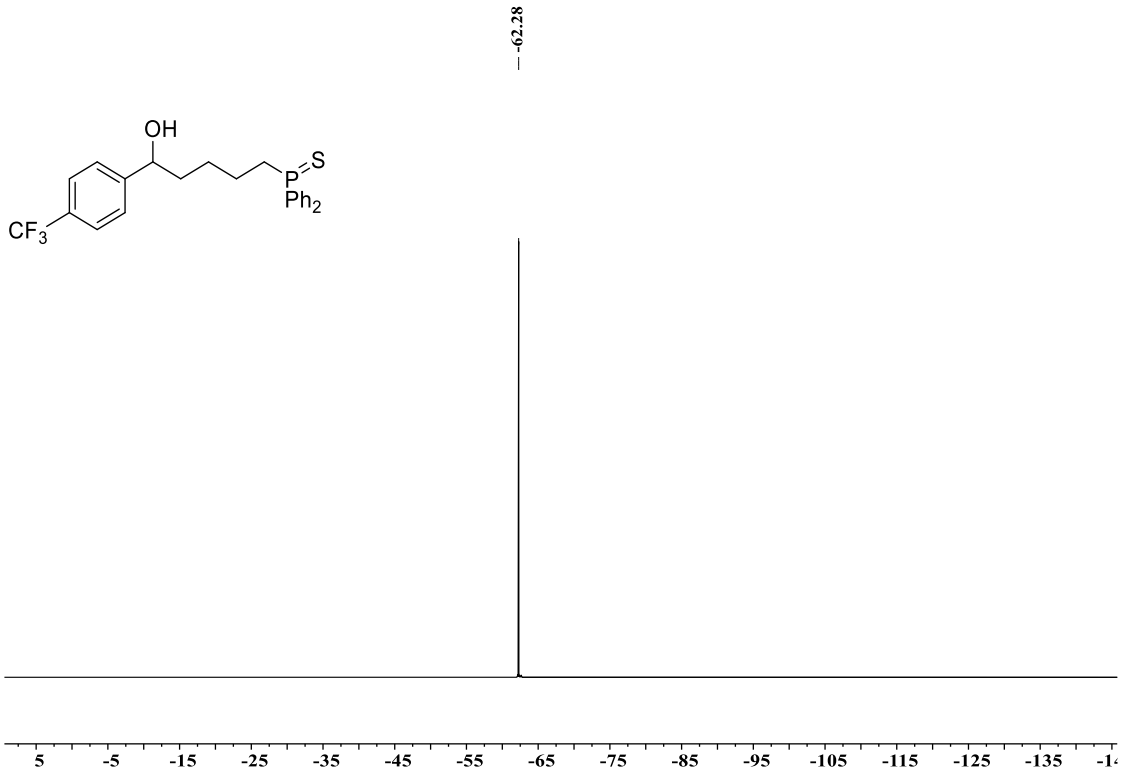
^{13}C NMR spectrum of **[S]-11** (150 MHz, $CDCl_3$)



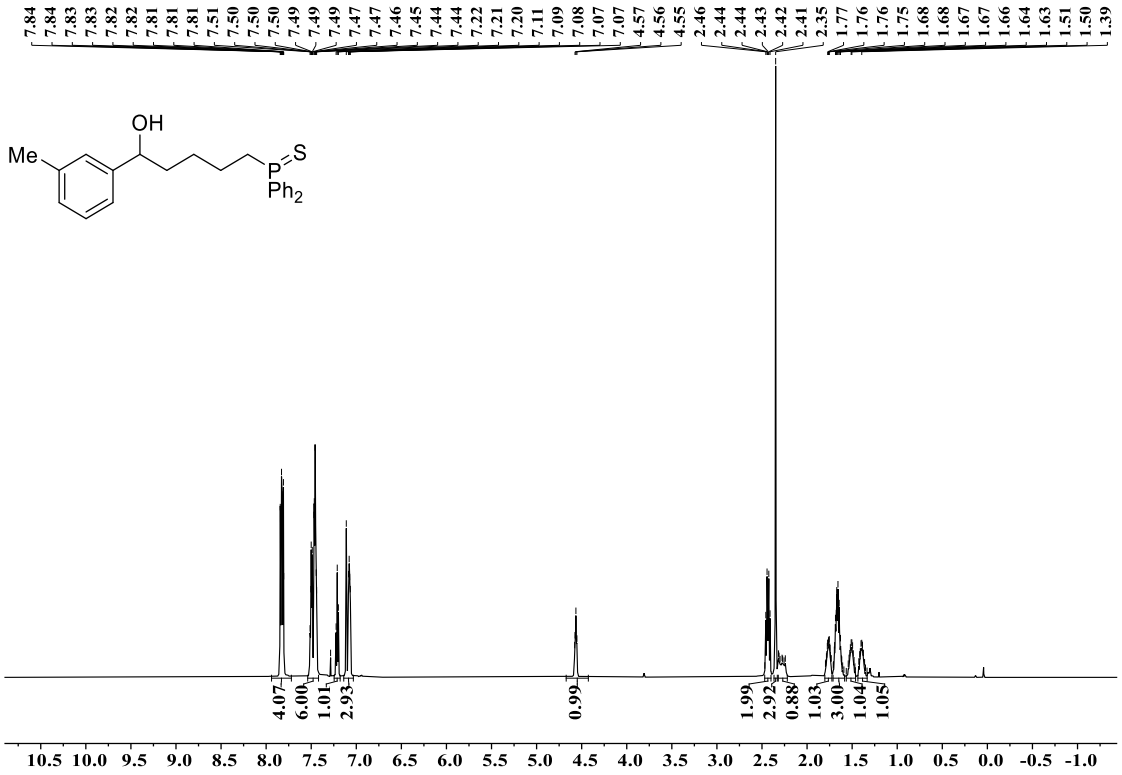
^{31}P NMR spectrum of **[S]-11** (243 MHz, $CDCl_3$)



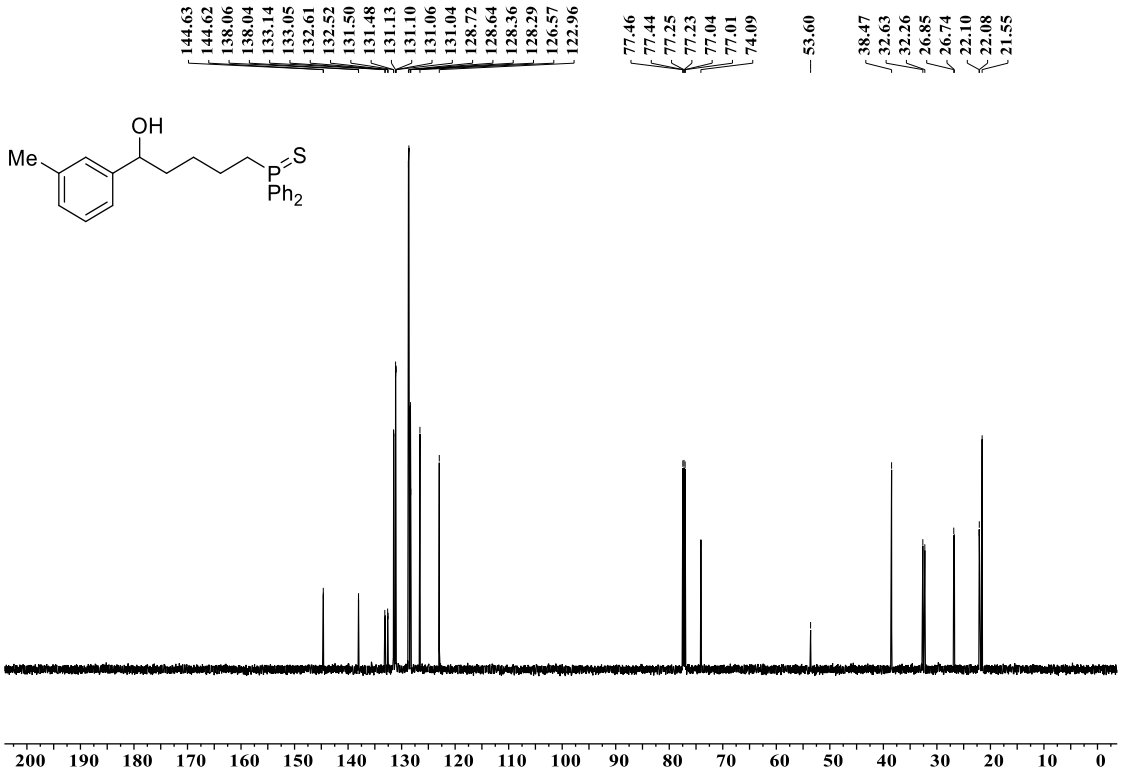
^{19}F NMR spectrum of **[S]-11** (565 MHz, $CDCl_3$)



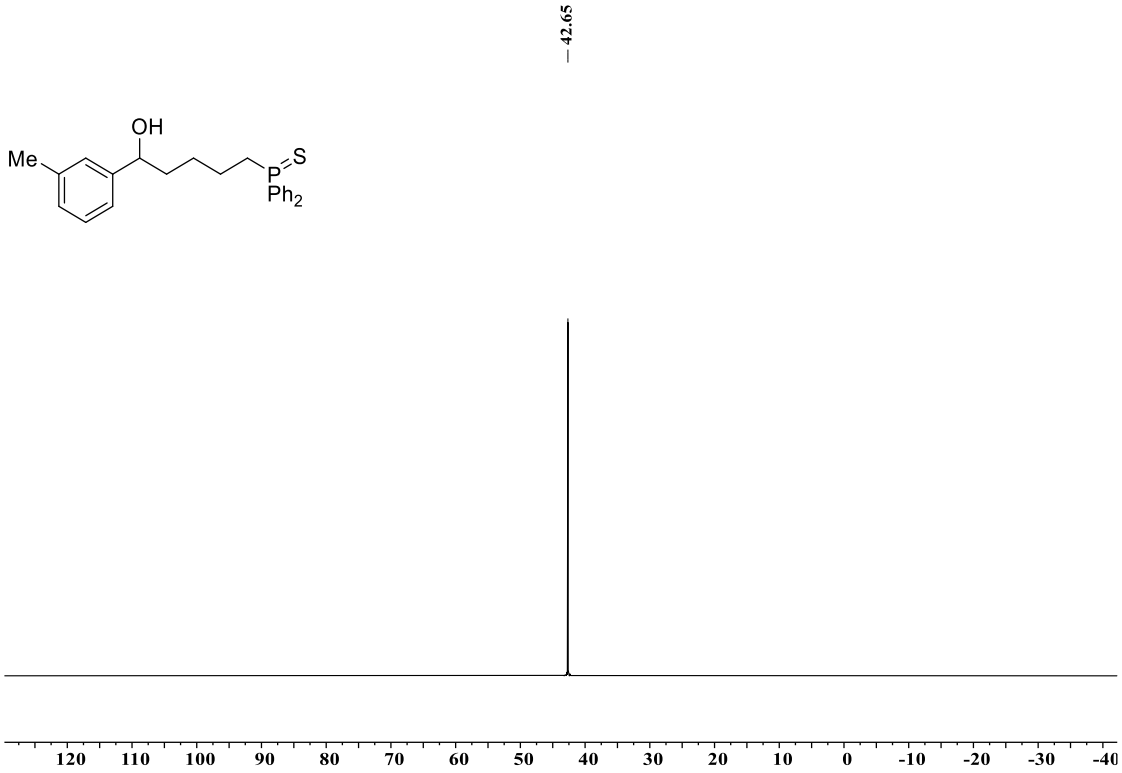
^{1}H NMR spectrum of **[S]-12** (600 MHz, $CDCl_3$)



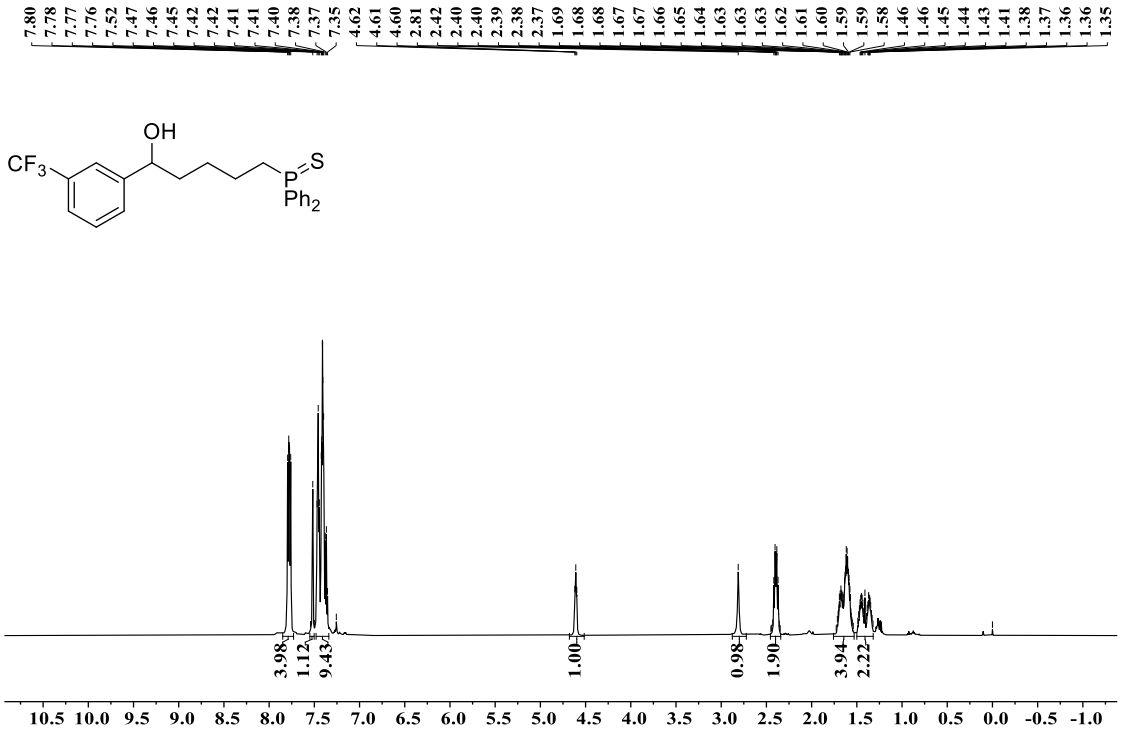
^{13}C NMR spectrum of **[S]-12** (150 MHz, $CDCl_3$)



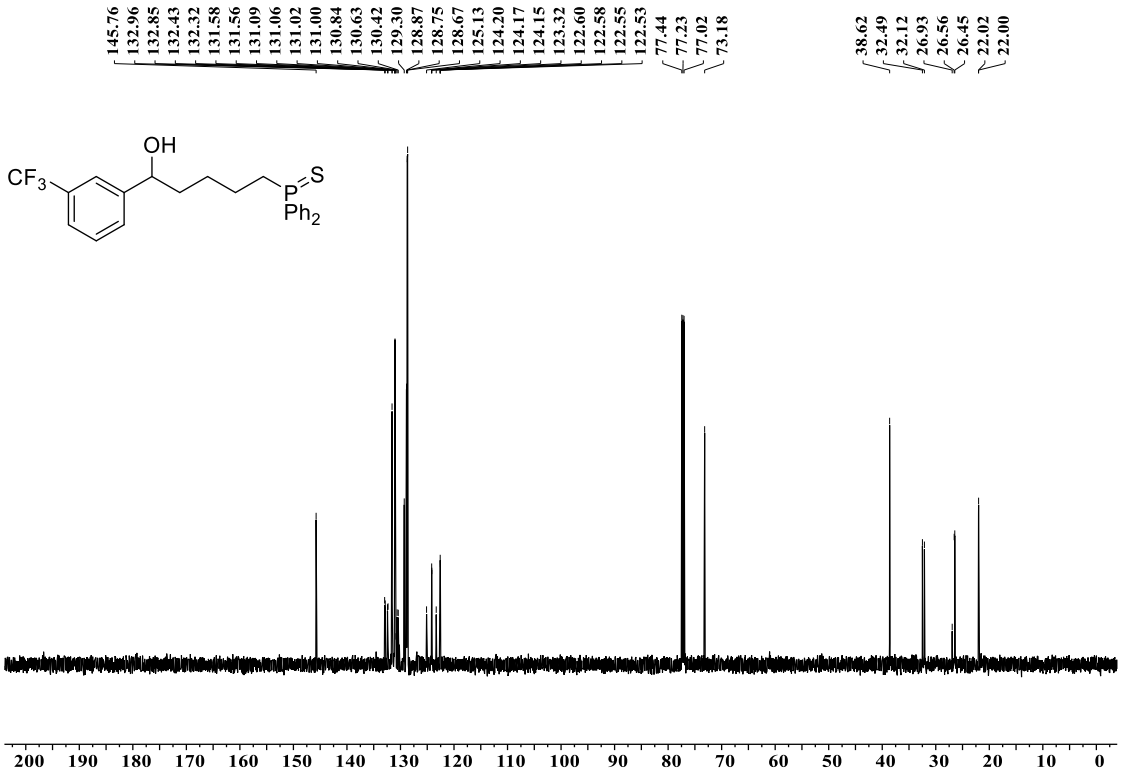
^{31}P NMR spectrum of **[S]-12** (243 MHz, $CDCl_3$)



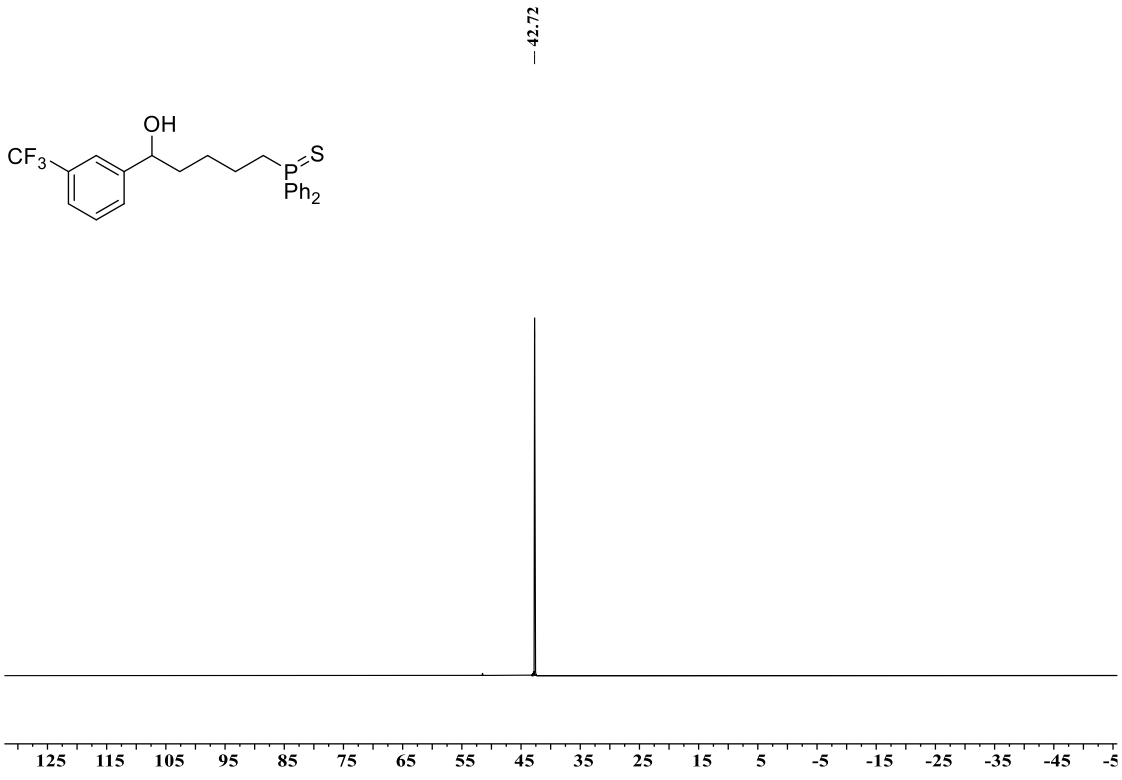
^{1}H NMR spectrum of **[S]-13** (600 MHz, $CDCl_3$)



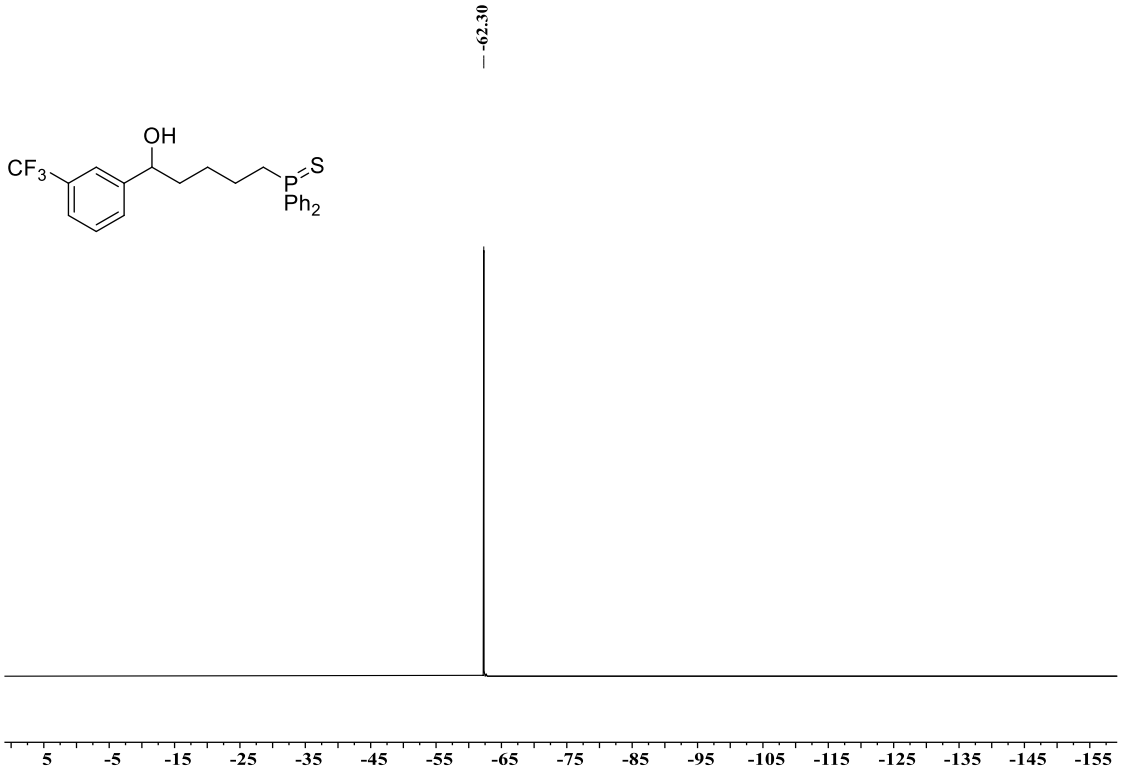
^{13}C NMR spectrum of **[S]-13** (150 MHz, $CDCl_3$)



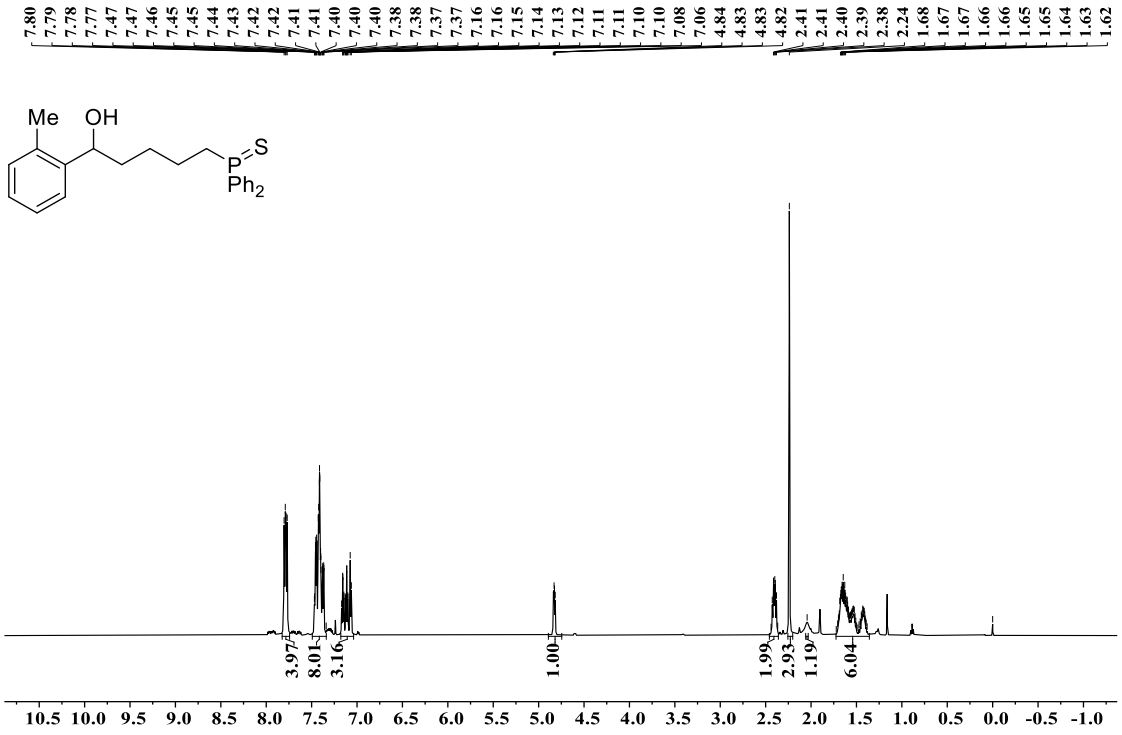
^{31}P NMR spectrum of **[S]-13** (243 MHz, $CDCl_3$)



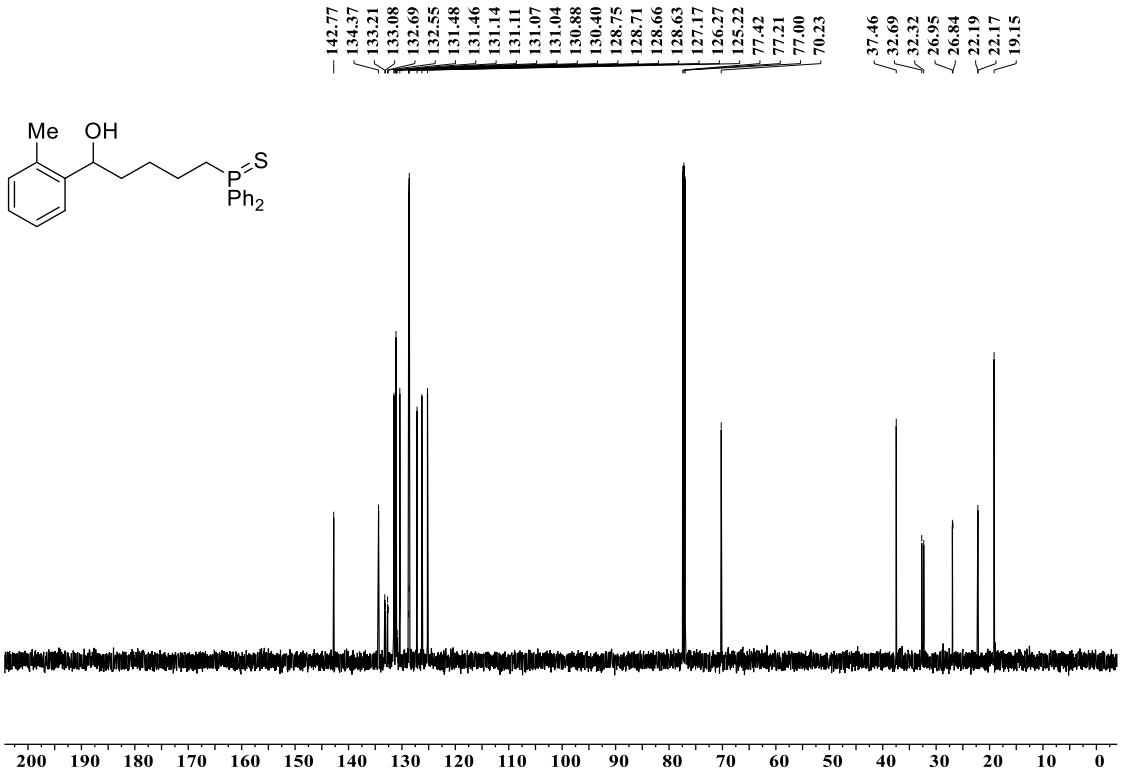
^{19}F NMR spectrum of **[S]-13** (565 MHz, $CDCl_3$)



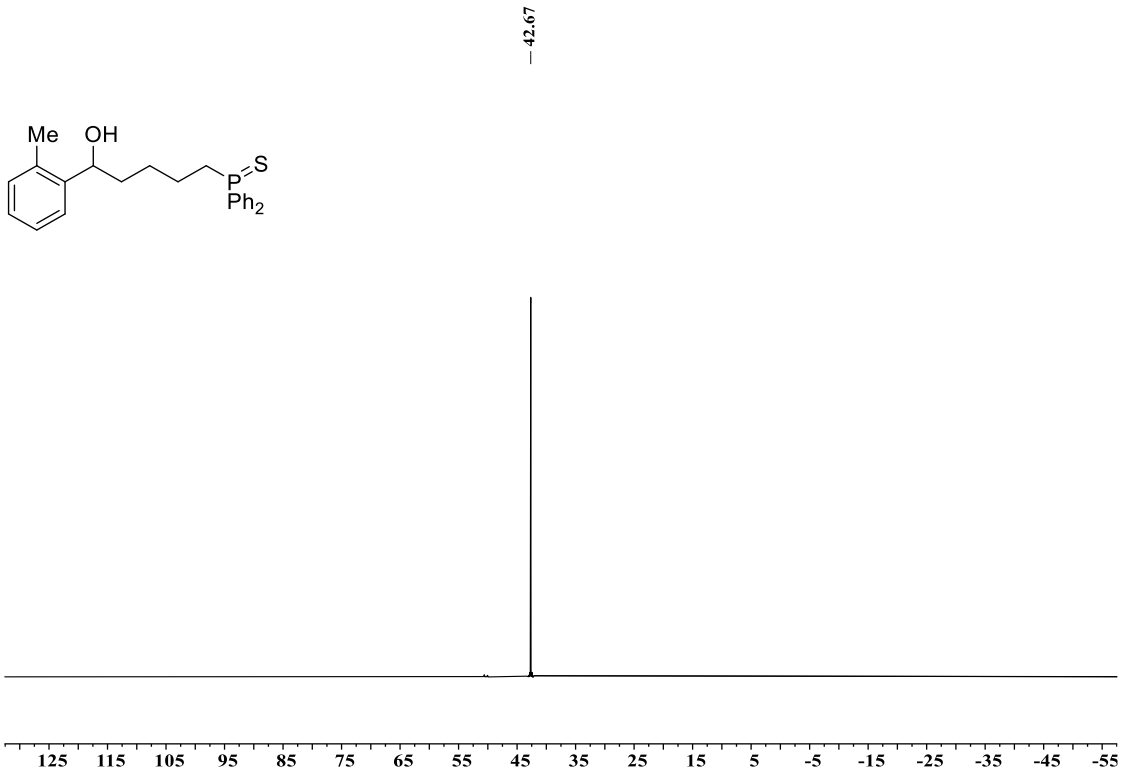
^{1}H NMR spectrum of **[S]-14** (600 MHz, $CDCl_3$)



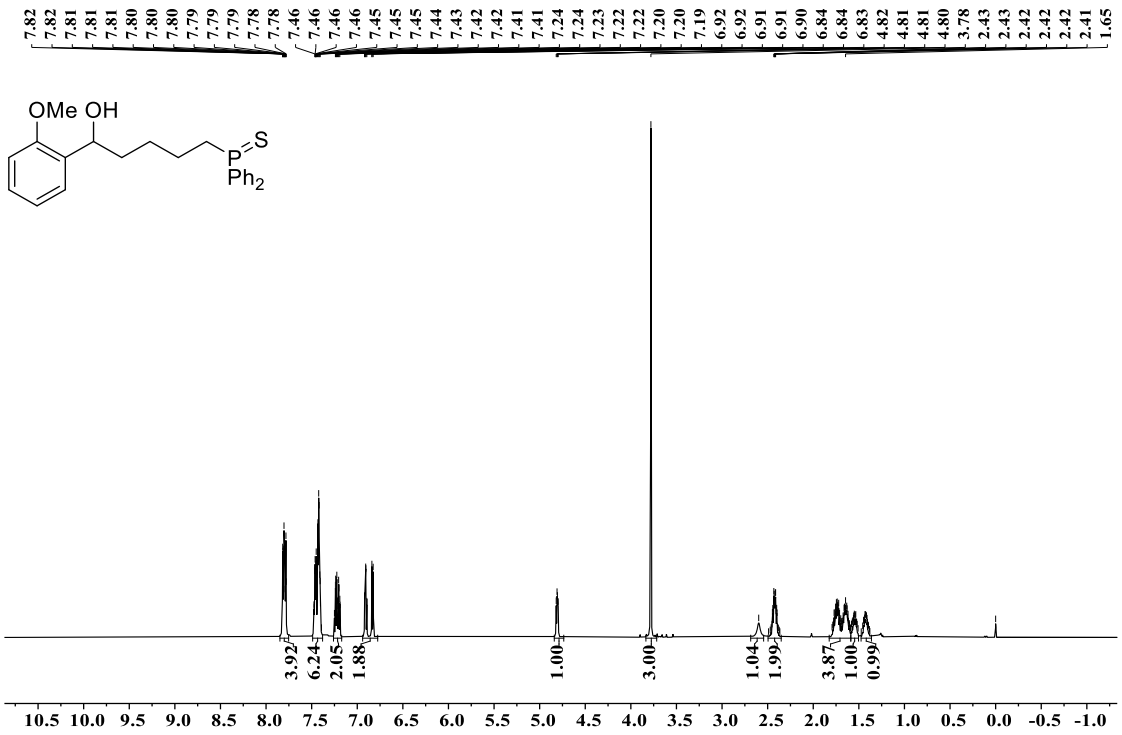
^{13}C NMR spectrum of **[S]-14** (150 MHz, $CDCl_3$)



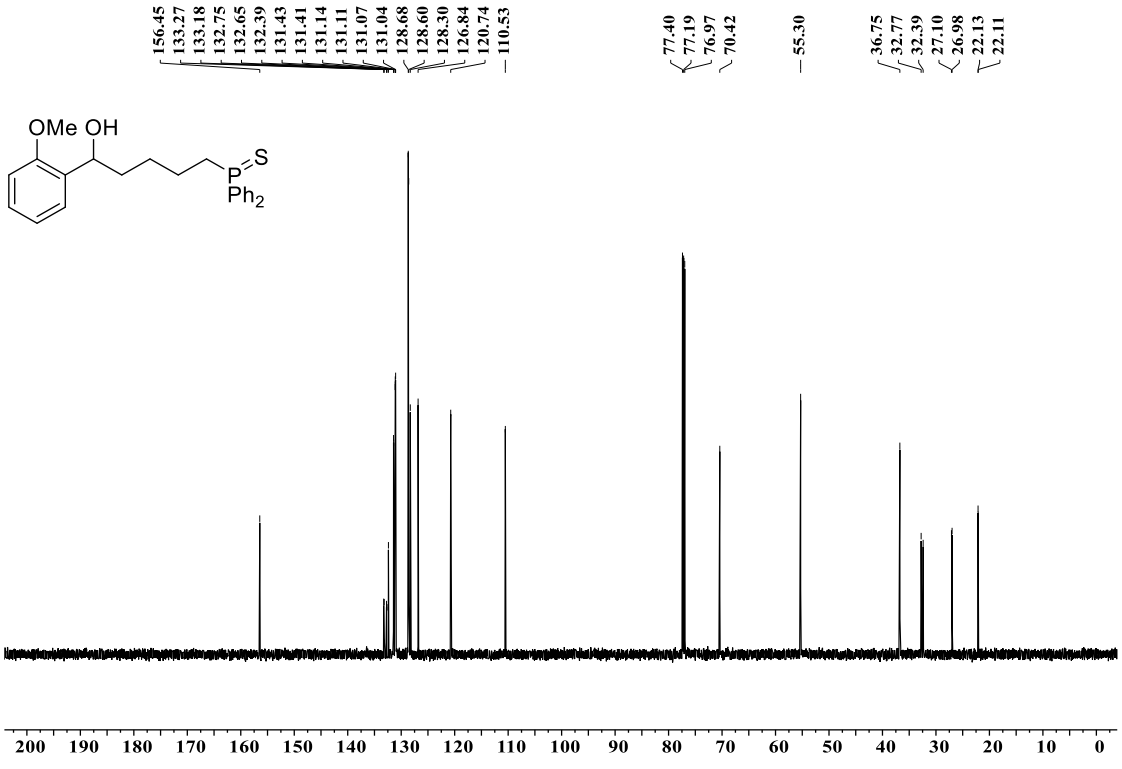
^{31}P NMR spectrum of **[S]-14** (243 MHz, $CDCl_3$)



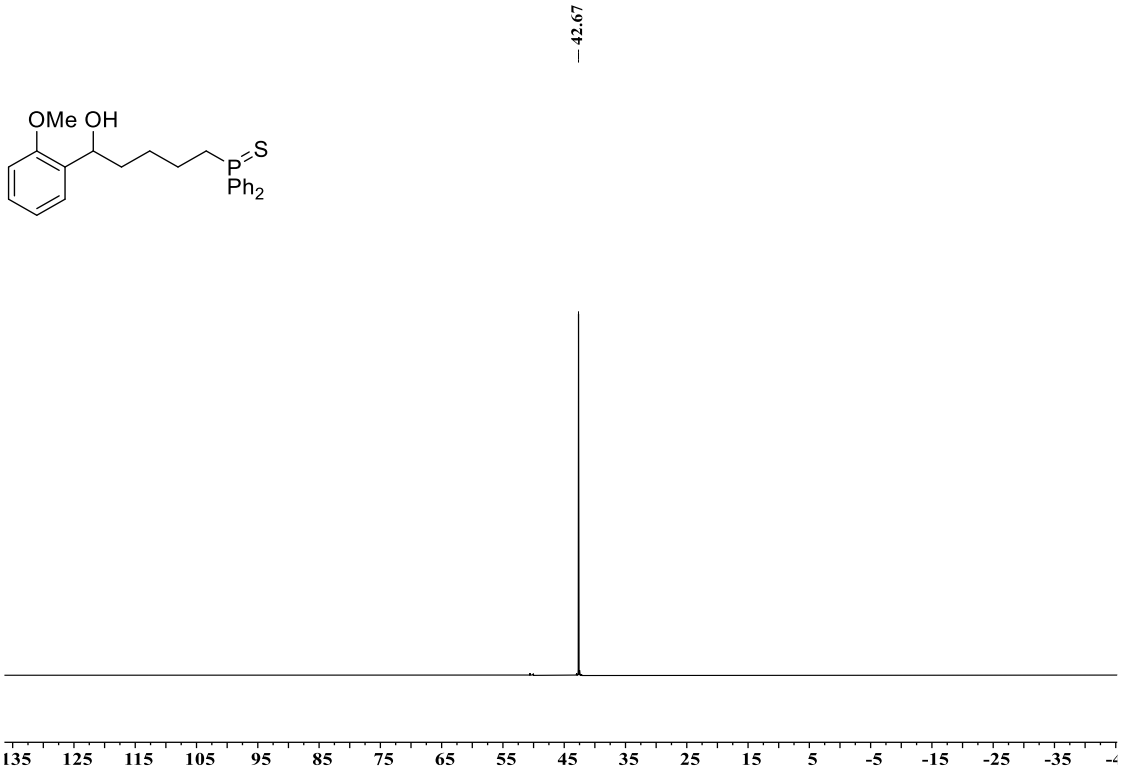
^{1}H NMR spectrum of **[S]-15** (600 MHz, $CDCl_3$)



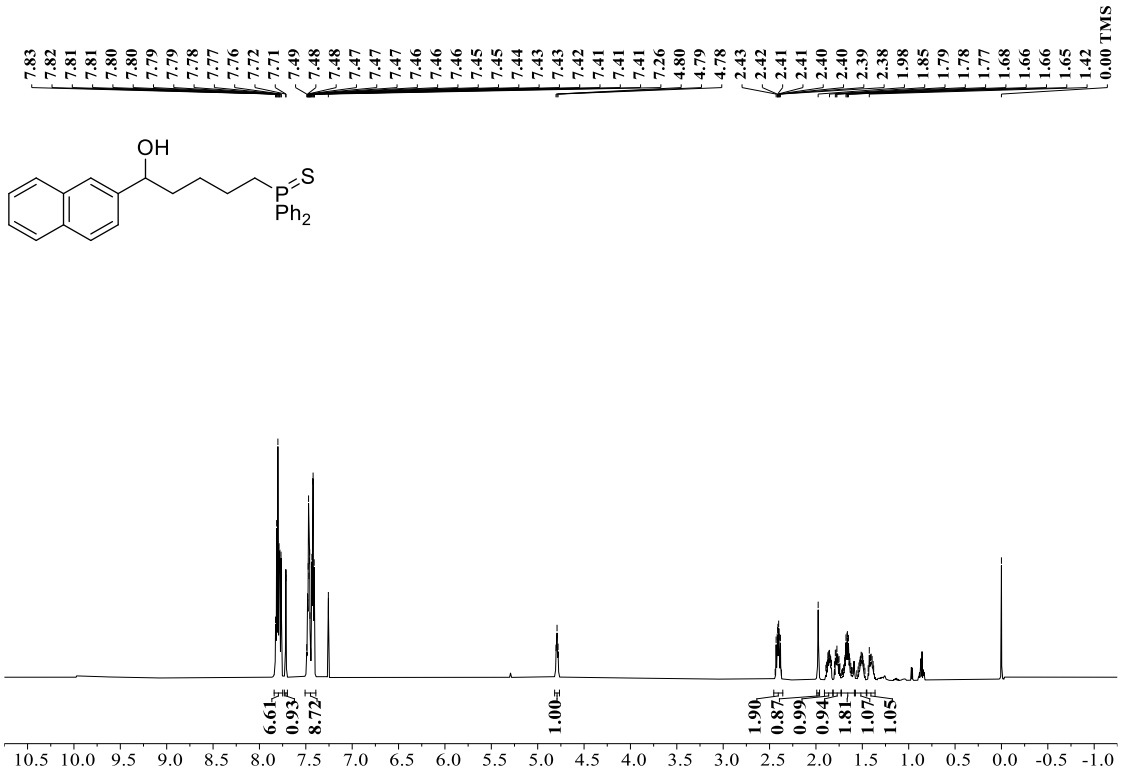
^{13}C NMR spectrum of **[S]-15** (150 MHz, $CDCl_3$)



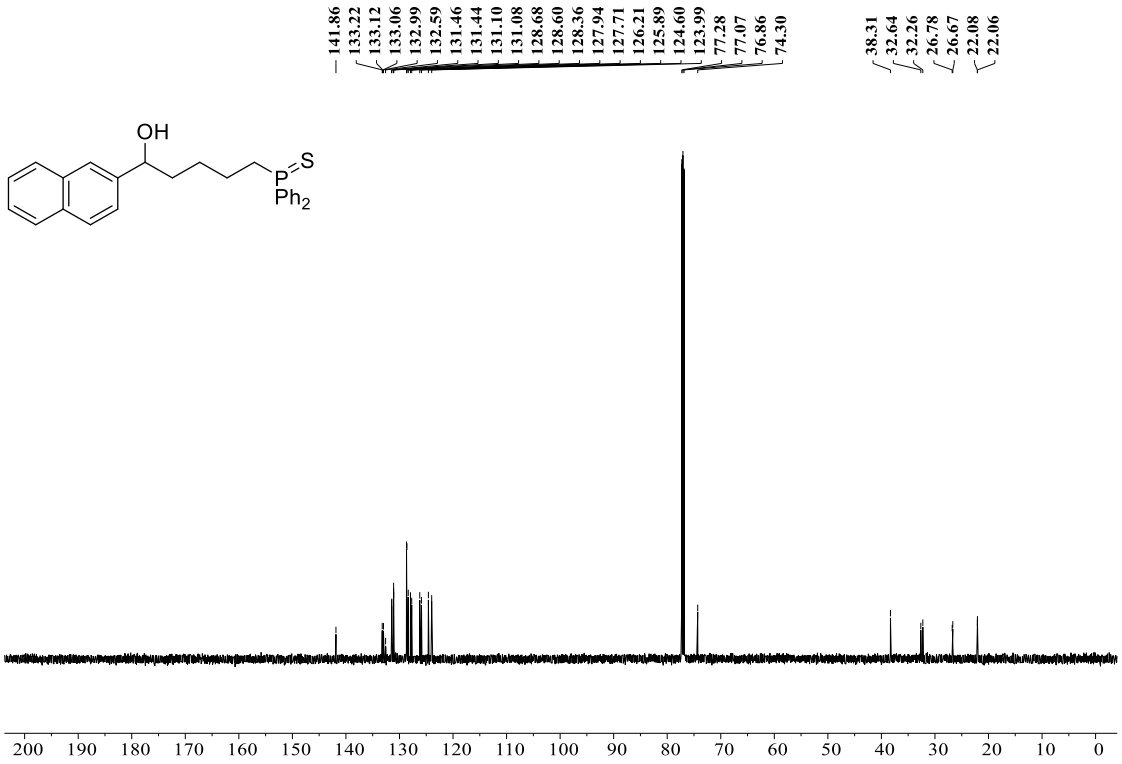
^{31}P NMR spectrum of **[S]-15** (243 MHz, $CDCl_3$)



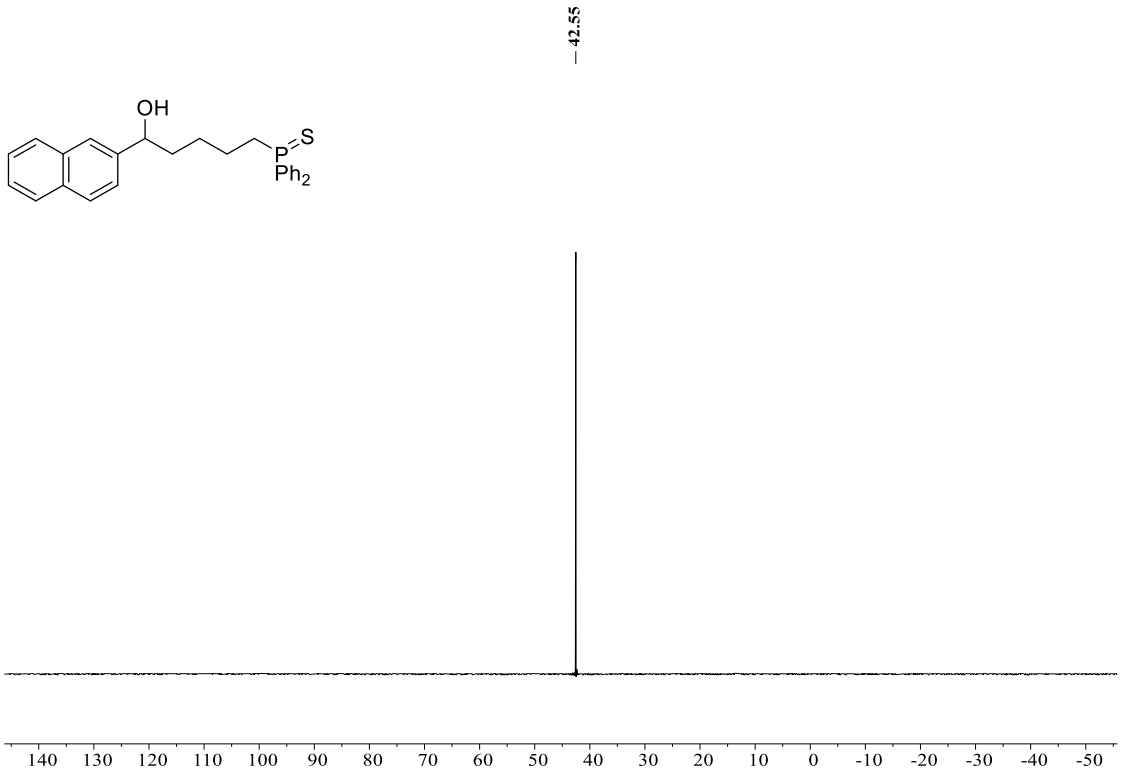
^{1}H NMR spectrum of **[S]-16** (600 MHz, $CDCl_3$)



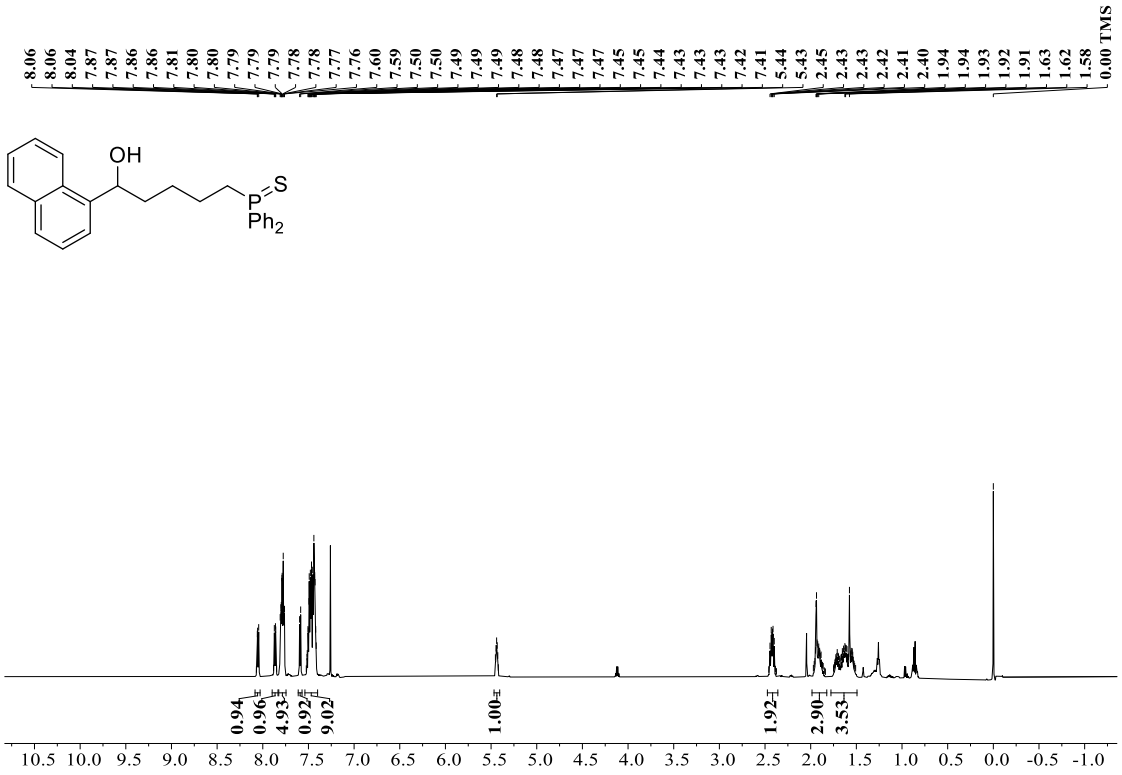
^{13}C NMR spectrum of **[S]-16** (150 MHz, $CDCl_3$)



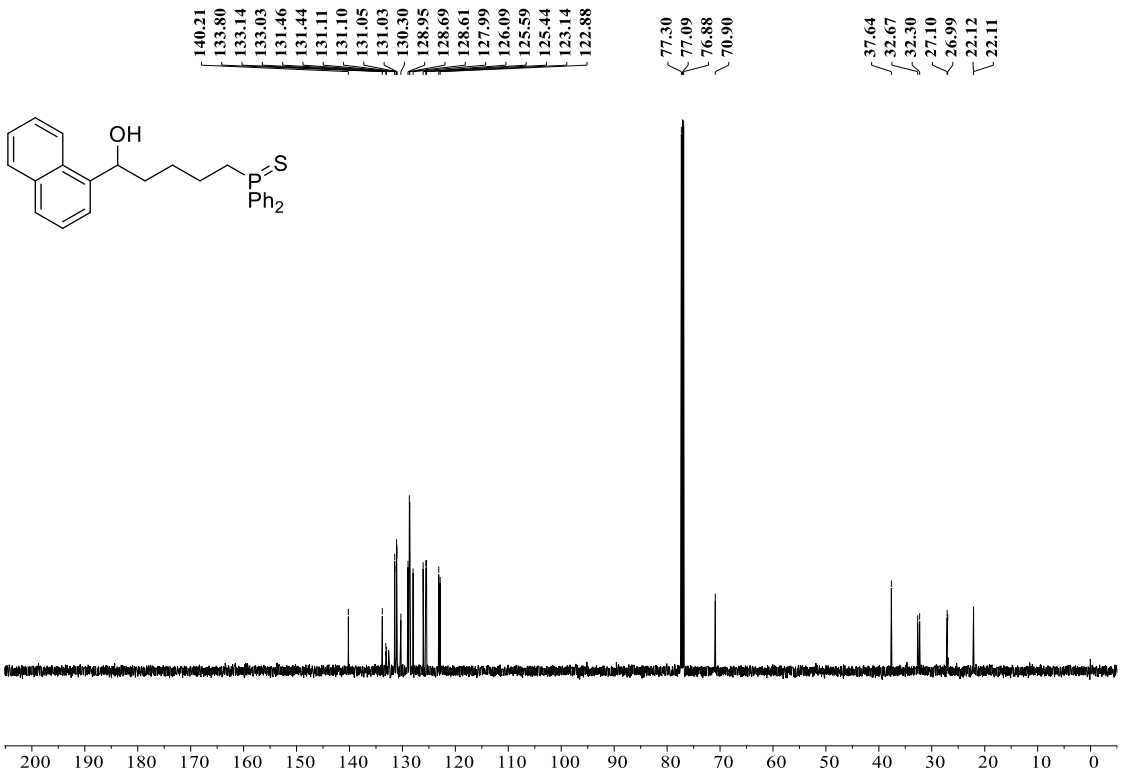
^{31}P NMR spectrum of **[S]-16** (243 MHz, $CDCl_3$)



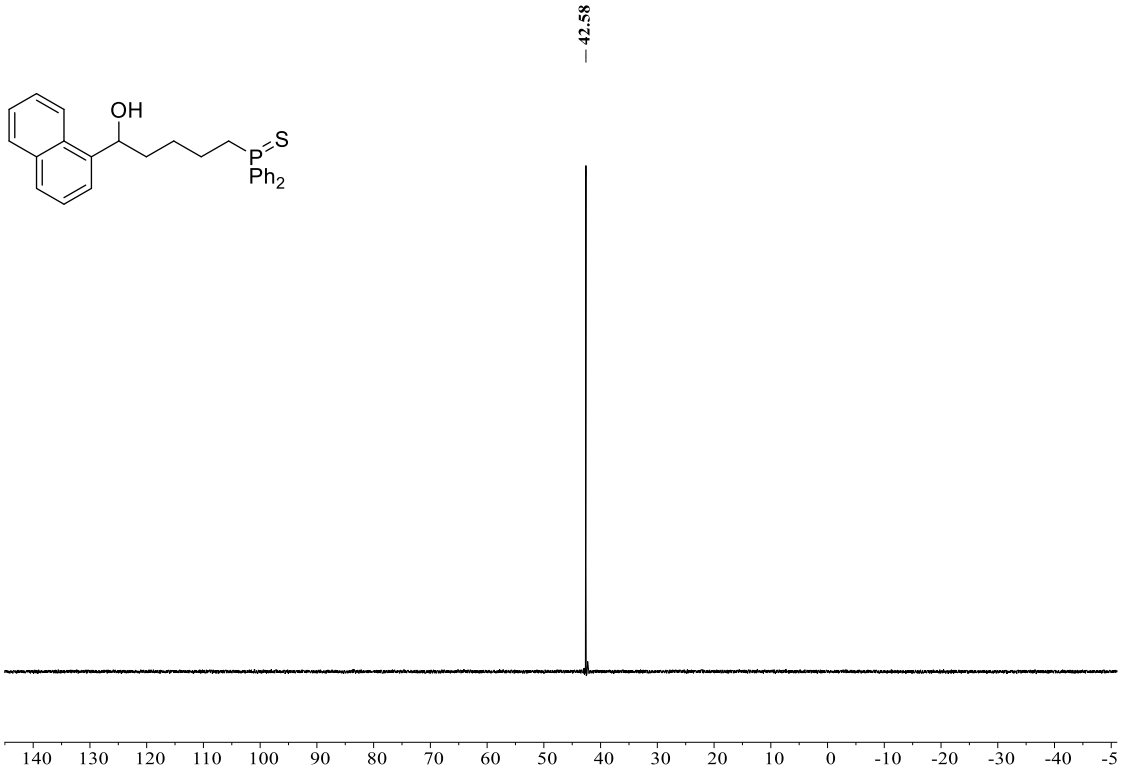
^{1}H NMR spectrum of **[S]-17** (600 MHz, $CDCl_3$)



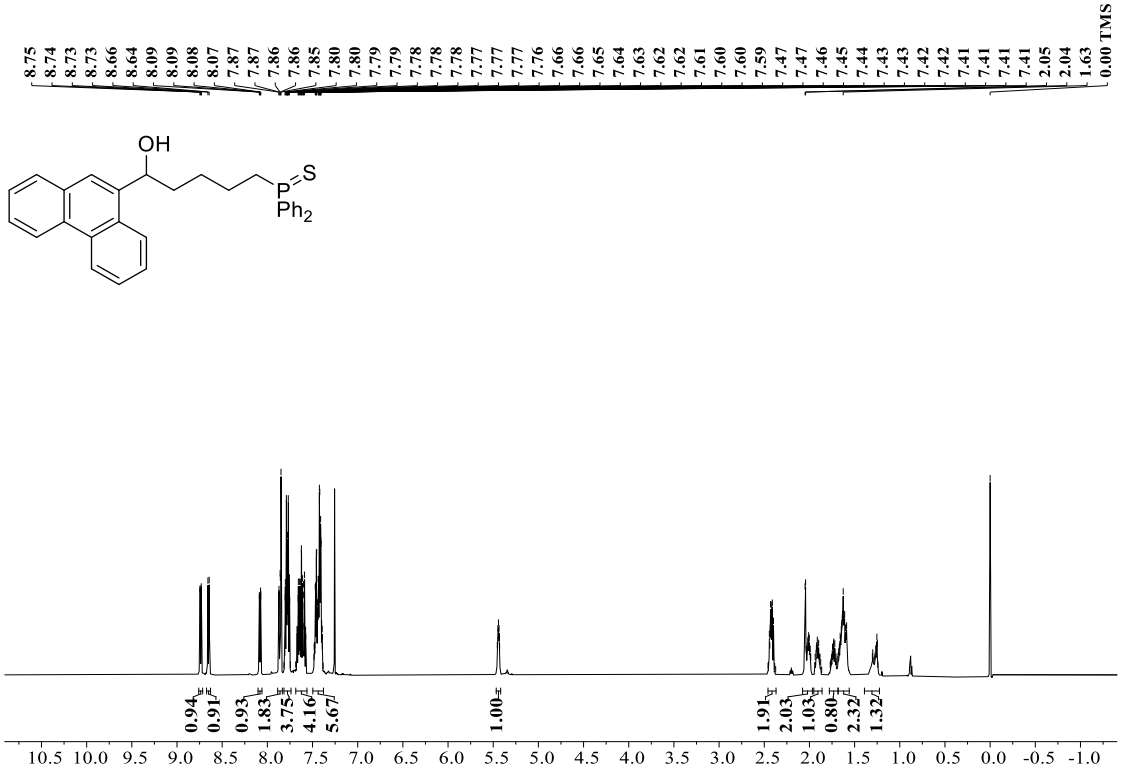
^{13}C NMR spectrum of **[S]-17** (150 MHz, $CDCl_3$)



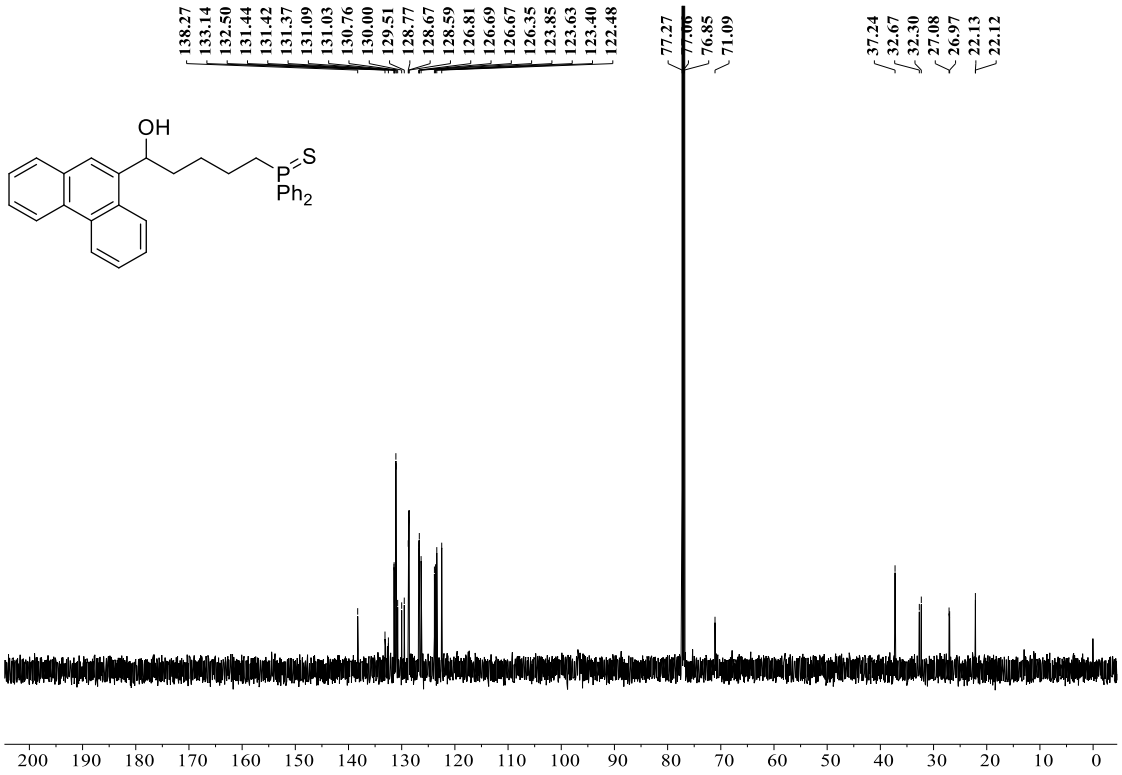
^{31}P NMR spectrum of **[S]-17** (243 MHz, $CDCl_3$)



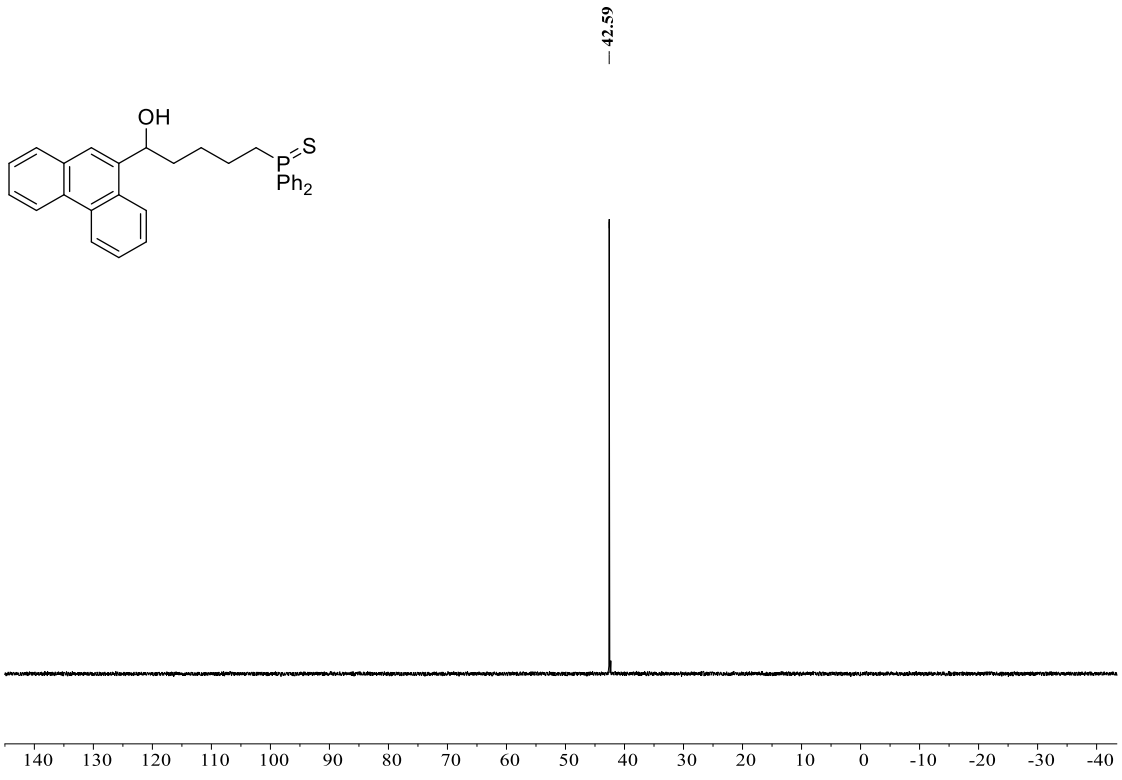
^{1}H NMR spectrum of **[S]-18** (600 MHz, $CDCl_3$)



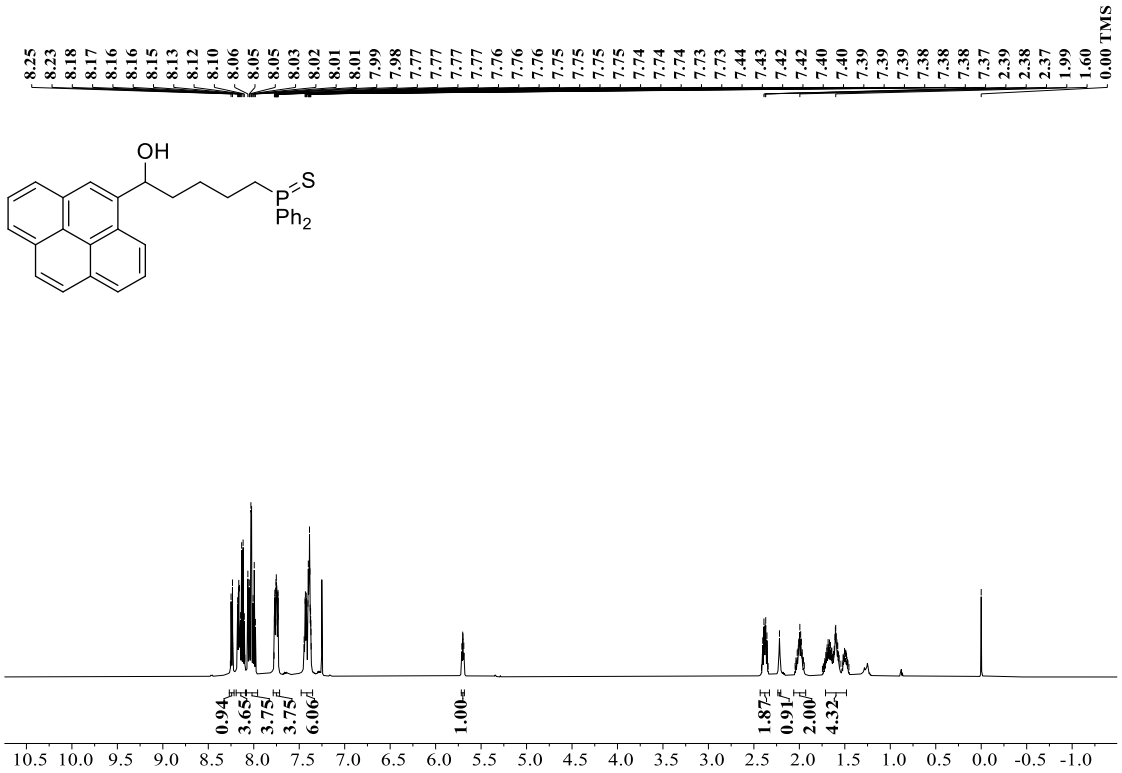
^{13}C NMR spectrum of **[S]-18** (150 MHz, $CDCl_3$)



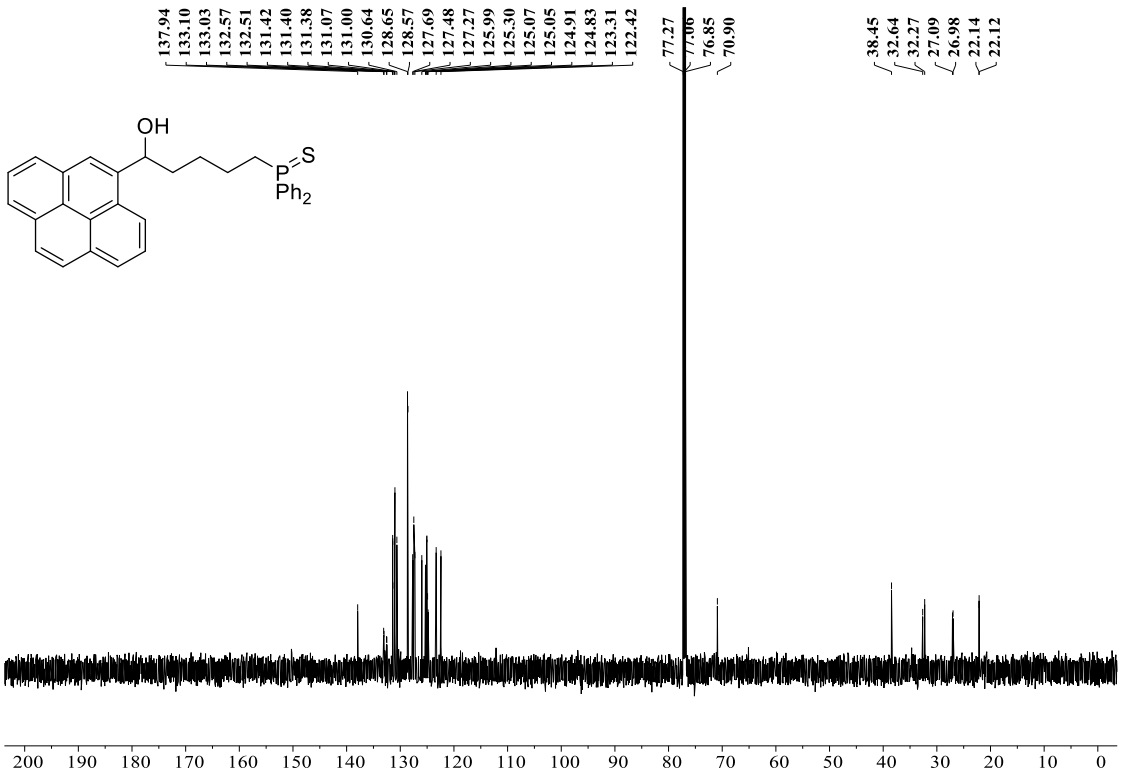
^{31}P NMR spectrum of **[S]-18** (243 MHz, $CDCl_3$)



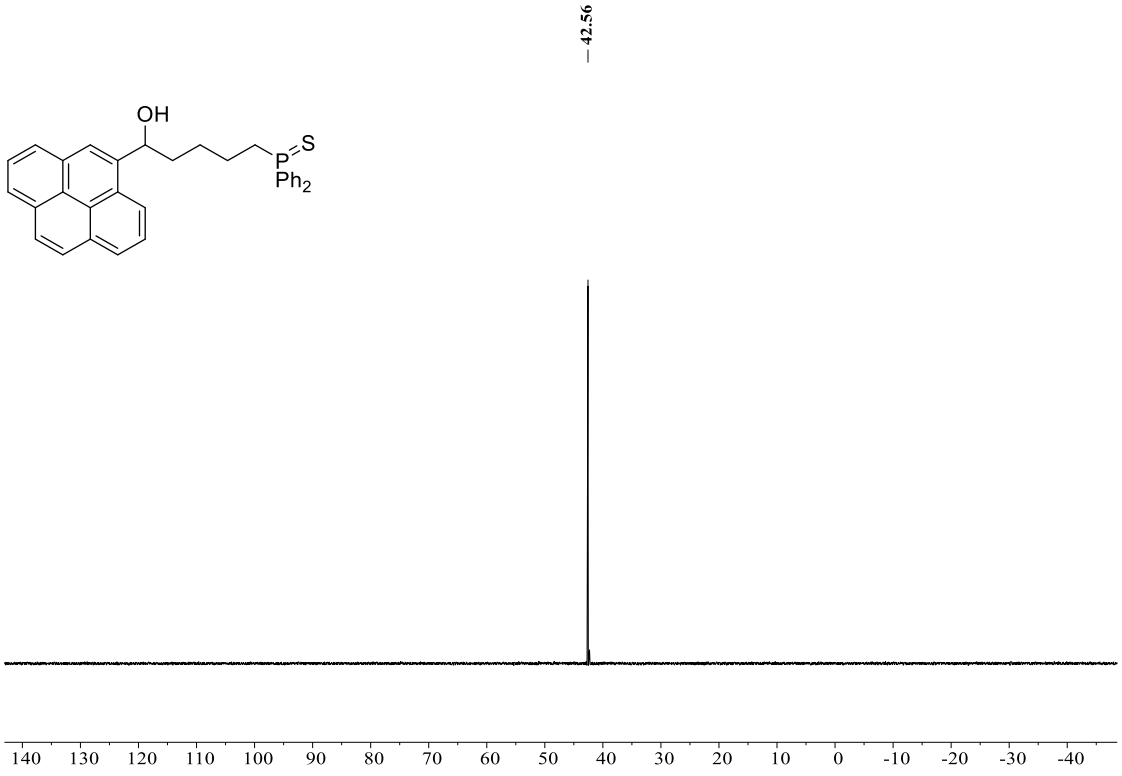
^{1}H NMR spectrum of **[S]-19** (600 MHz, $CDCl_3$)



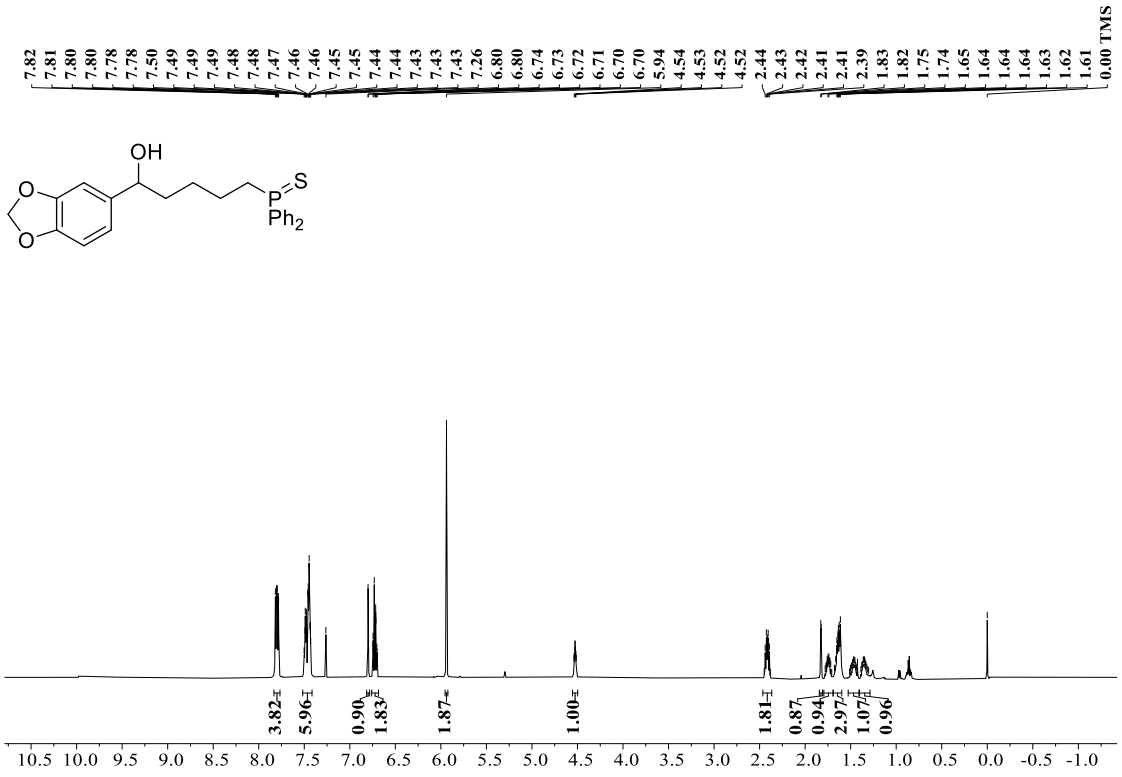
^{13}C NMR spectrum of **[S]-19** (150 MHz, $CDCl_3$)



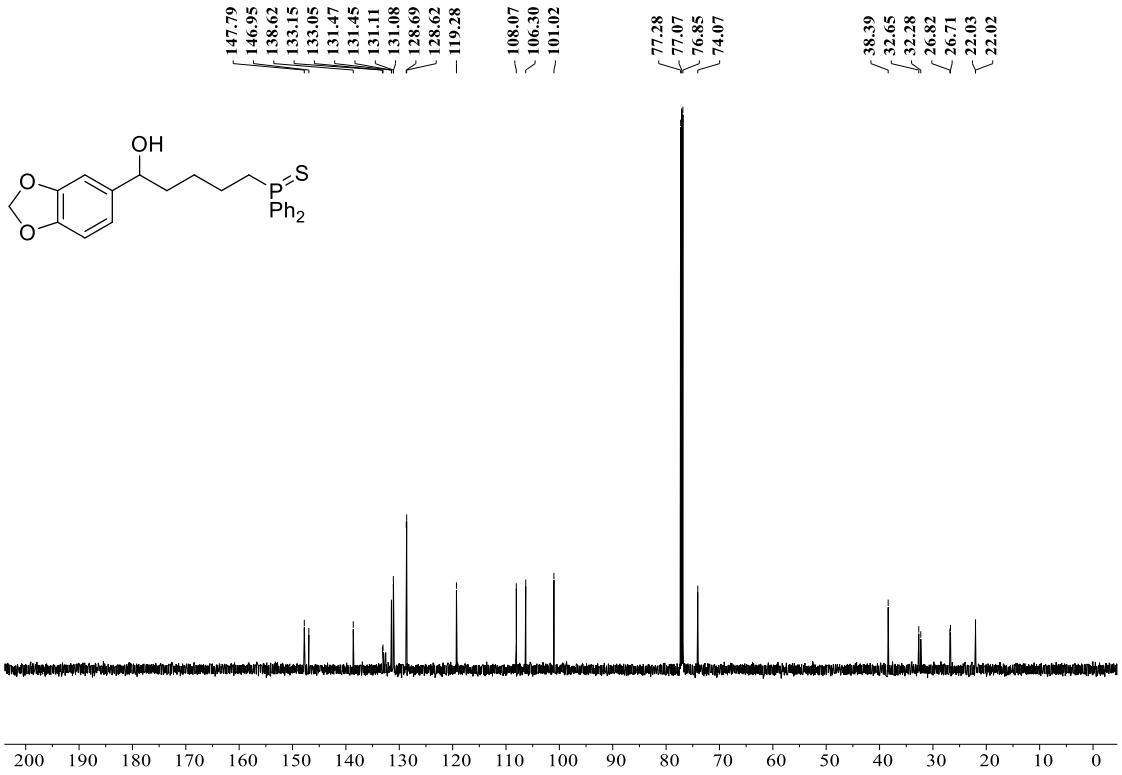
^{31}P NMR spectrum of **[S]-19** (243 MHz, $CDCl_3$)



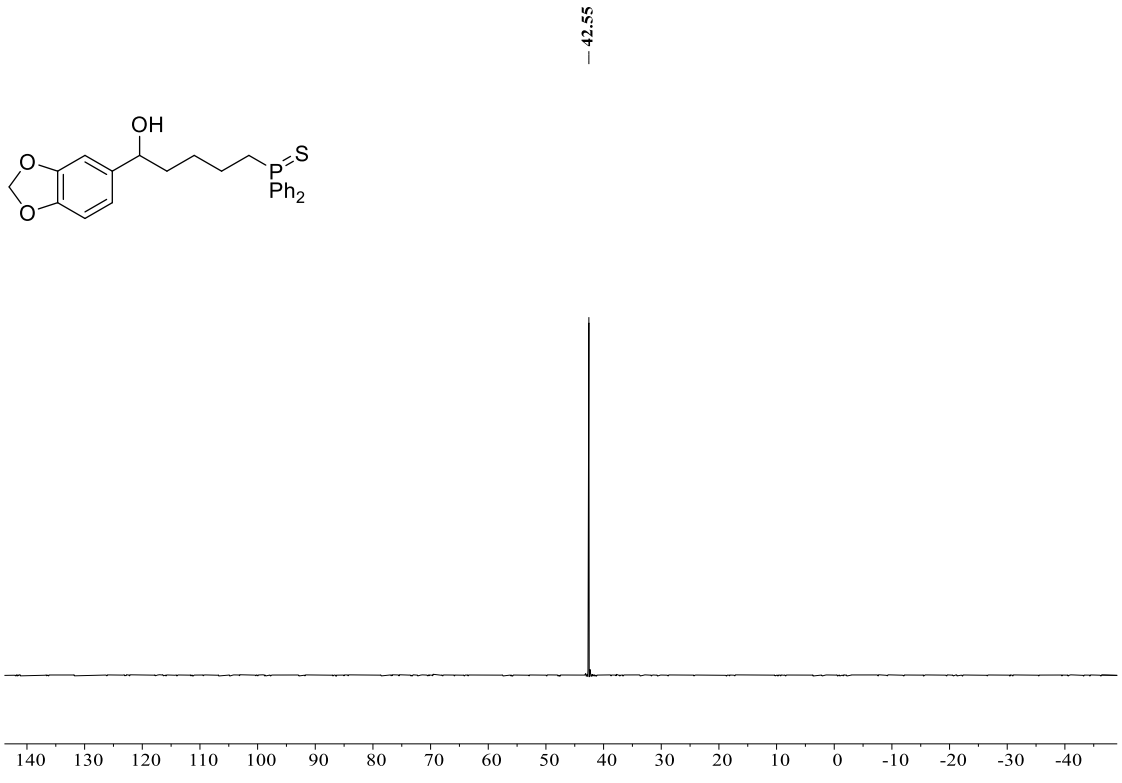
^{1}H NMR spectrum of **[S]-20** (600 MHz, $CDCl_3$)



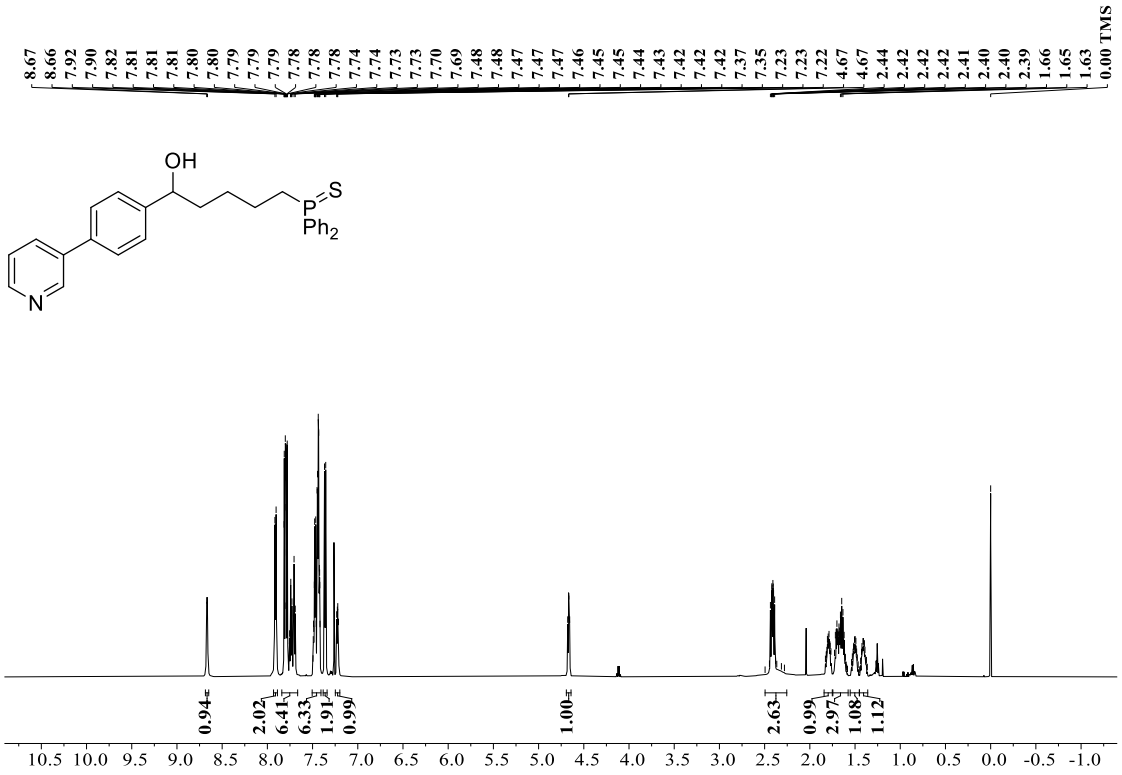
^{13}C NMR spectrum of **[S]-20** (150 MHz, $CDCl_3$)



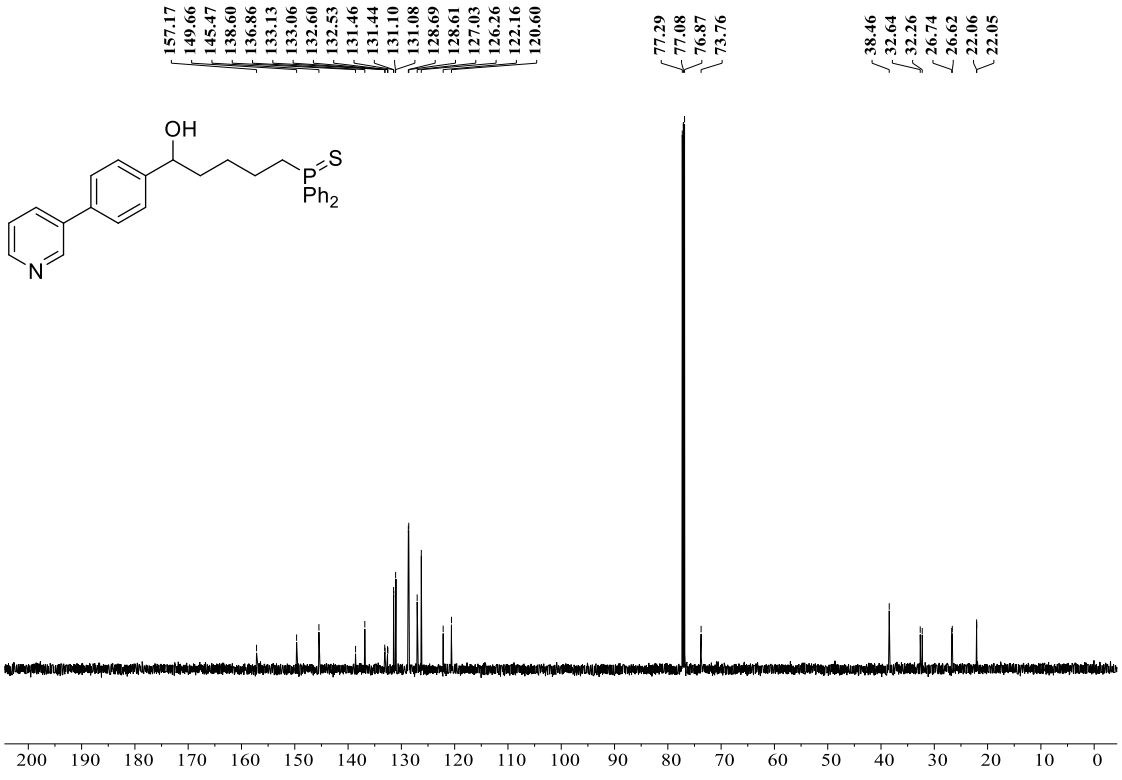
^{31}P NMR spectrum of **[S]-20** (243 MHz, $CDCl_3$)



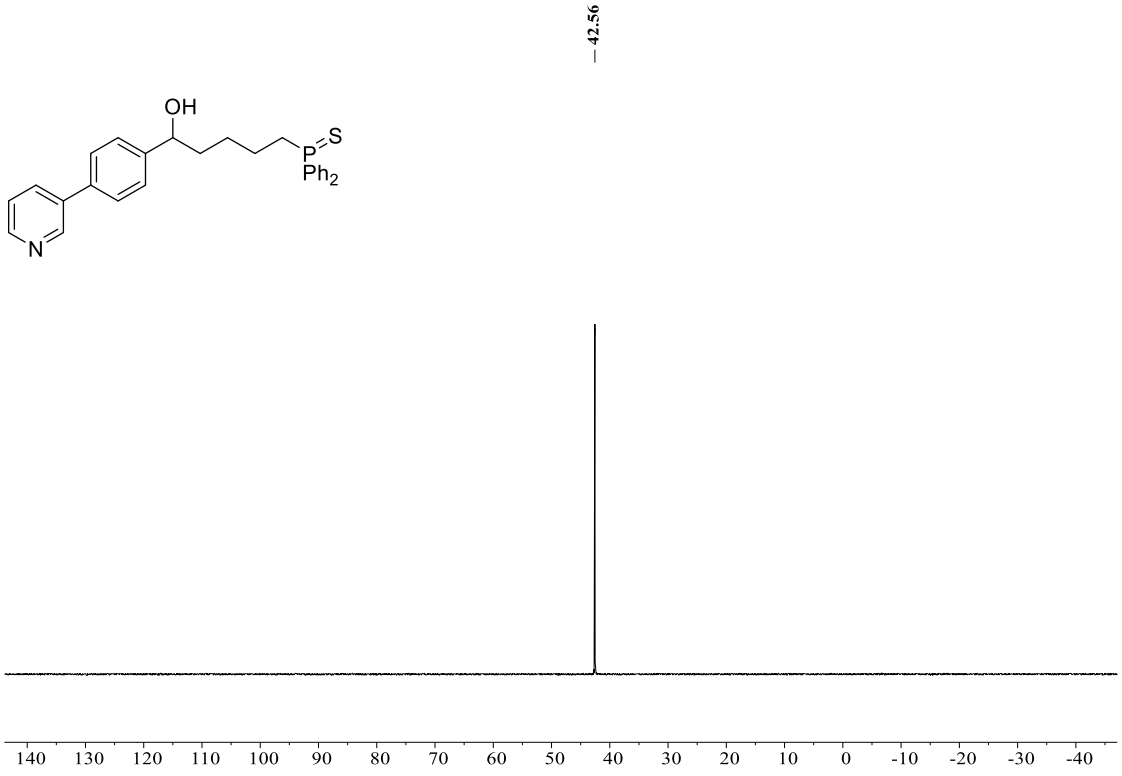
^{1}H NMR spectrum of **[S]-21** (600 MHz, $CDCl_3$)



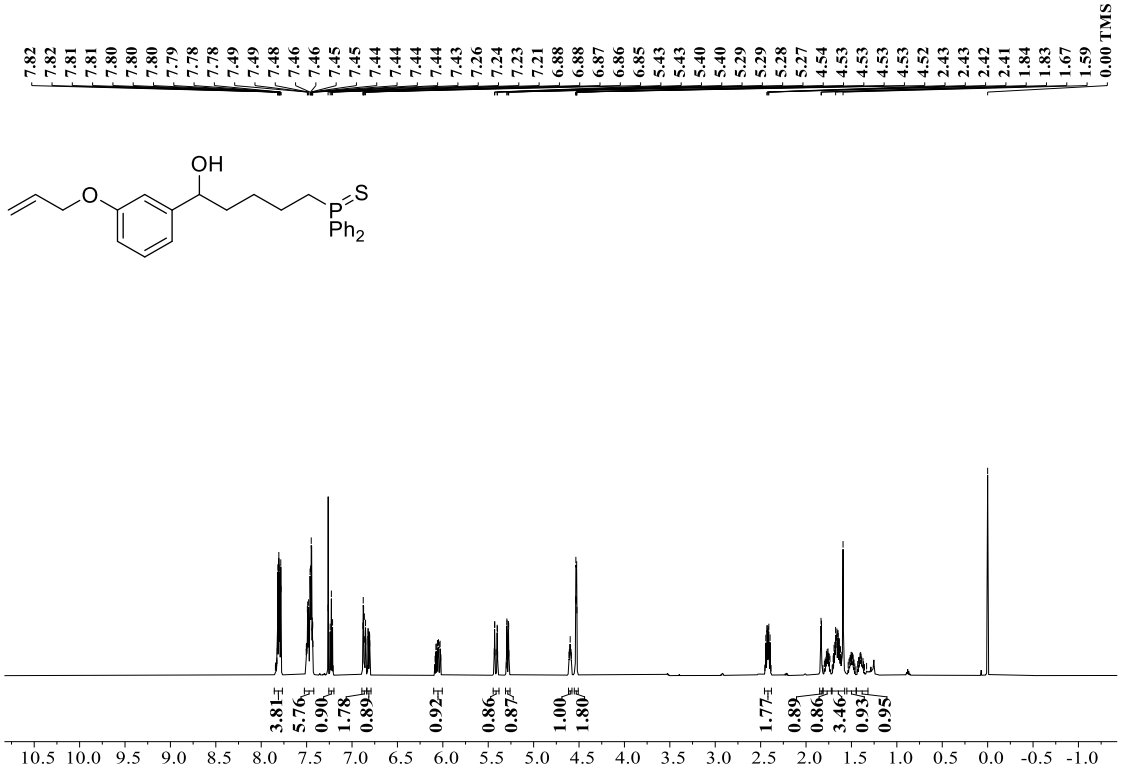
^{13}C NMR spectrum of **[S]-21** (150 MHz, $CDCl_3$)



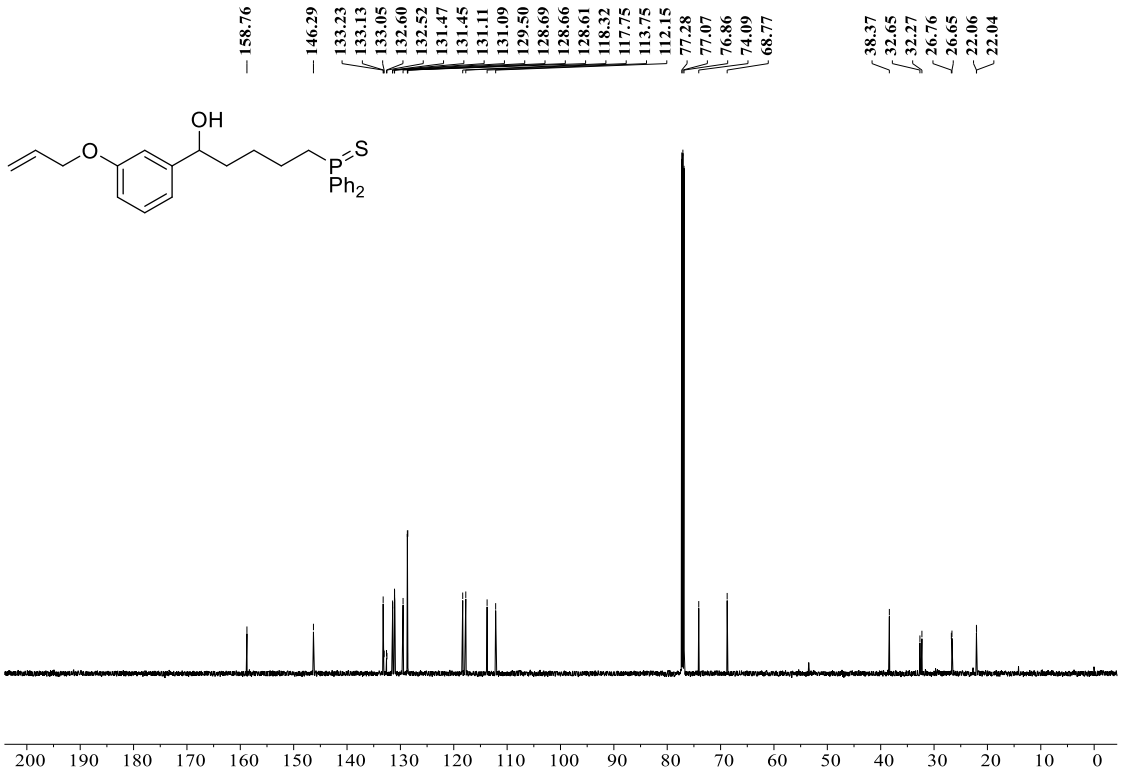
^{31}P NMR spectrum of **[S]-21** (243 MHz, $CDCl_3$)



^{1}H NMR spectrum of **[S]-22** (600 MHz, $CDCl_3$)

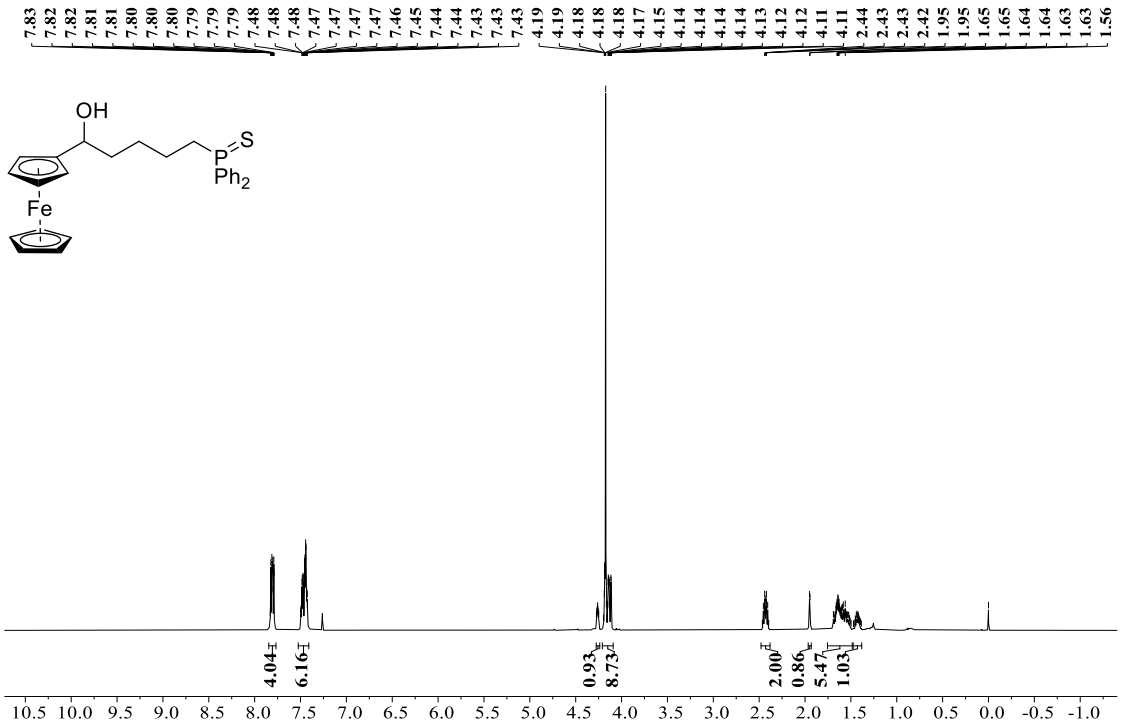


^{13}C NMR spectrum of **[S]-22** (150 MHz, $CDCl_3$)

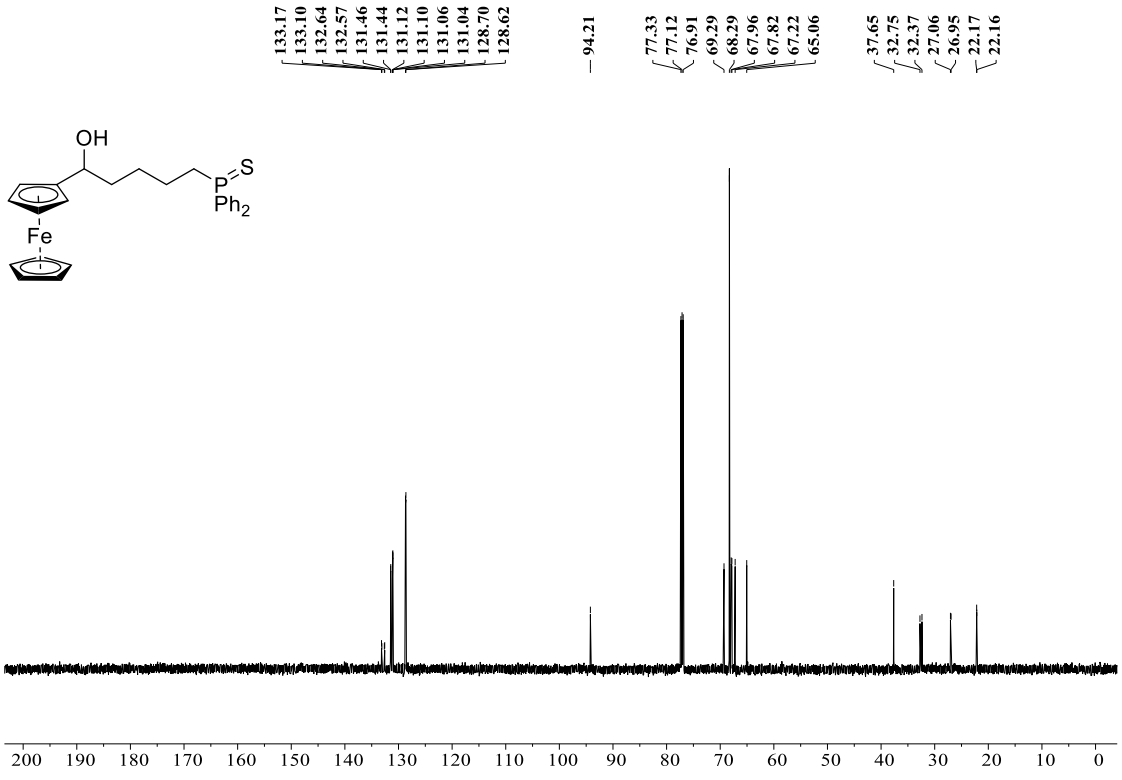


^{31}P NMR spectrum of **[S]-22** (243 MHz, $CDCl_3$)

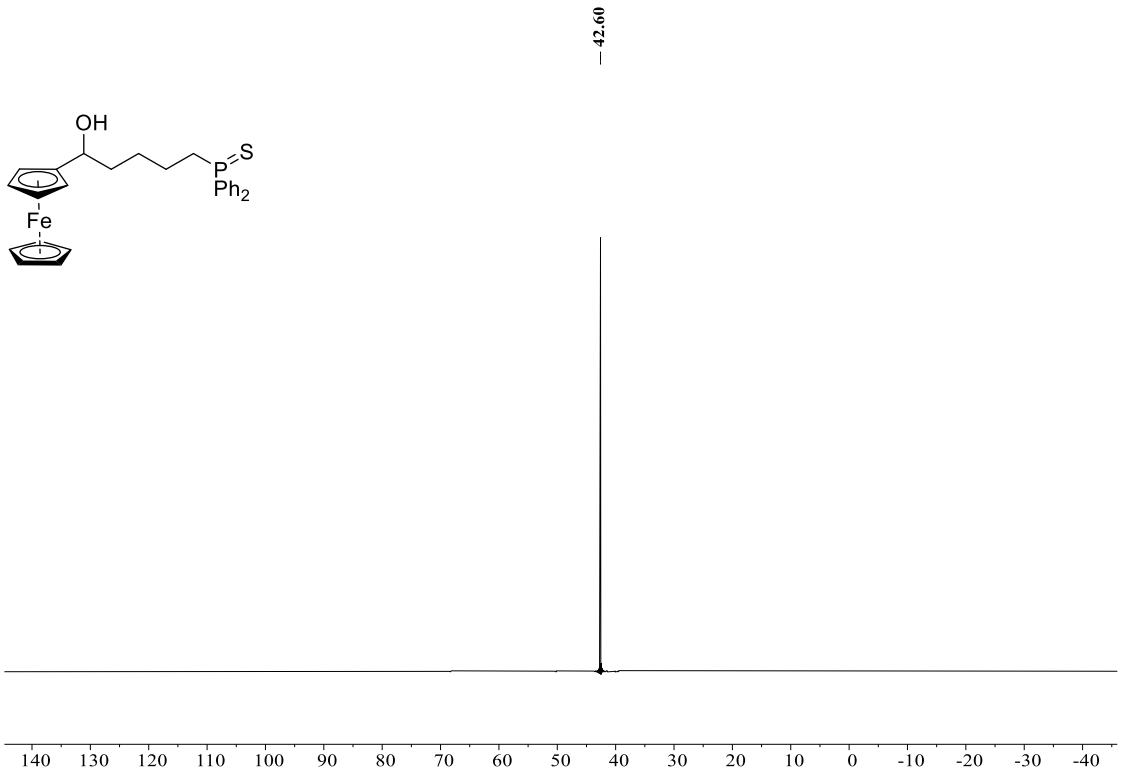
^{1}H NMR spectrum of **[S]-23** (600 MHz, $CDCl_3$)



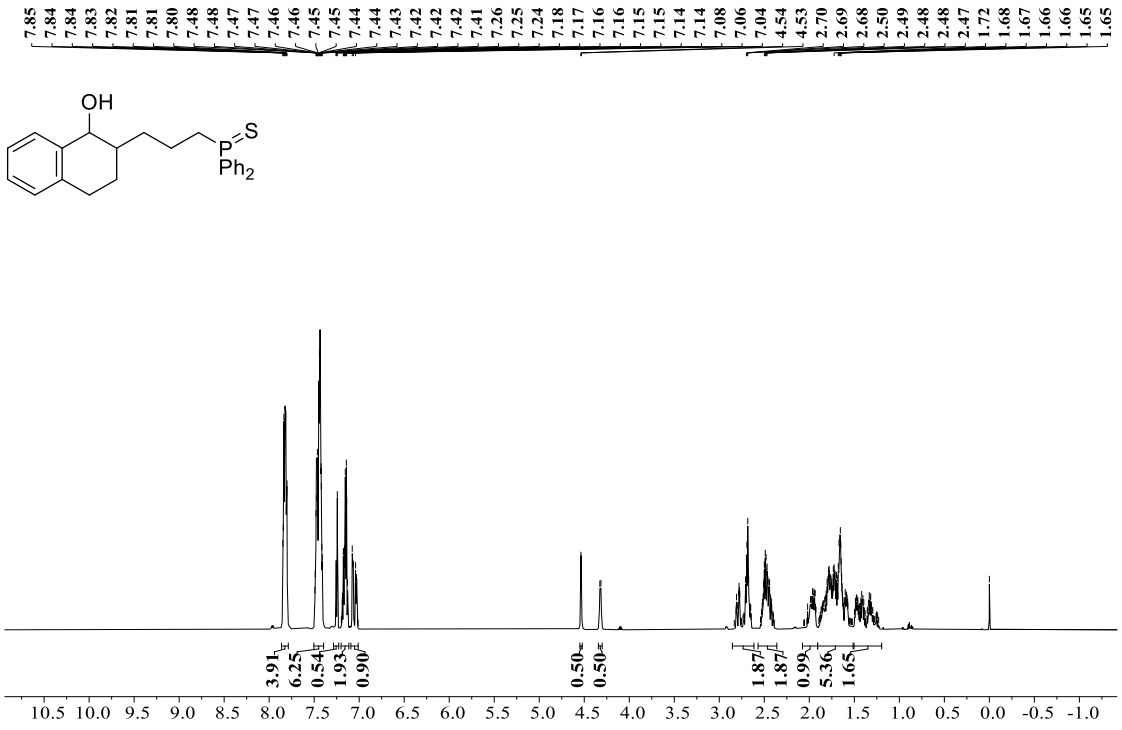
^{13}C NMR spectrum of **[S]-23** (150 MHz, $CDCl_3$)



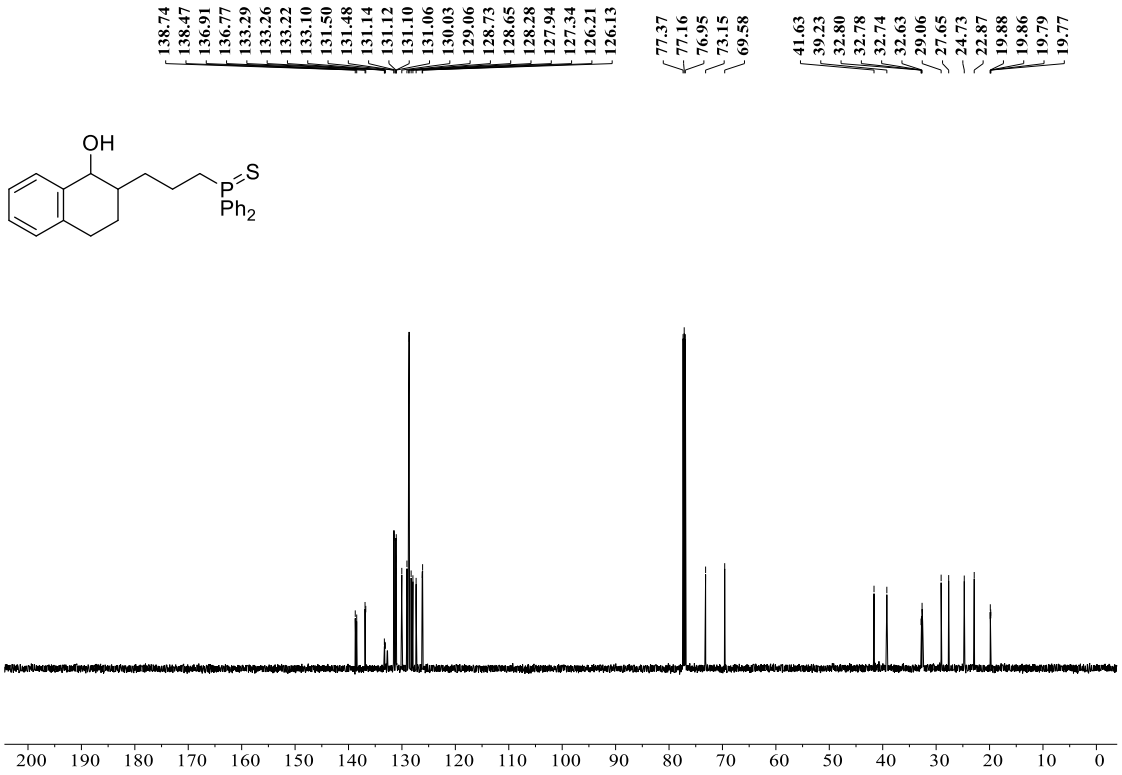
^{31}P NMR spectrum of **[S]-23** (243 MHz, $CDCl_3$)



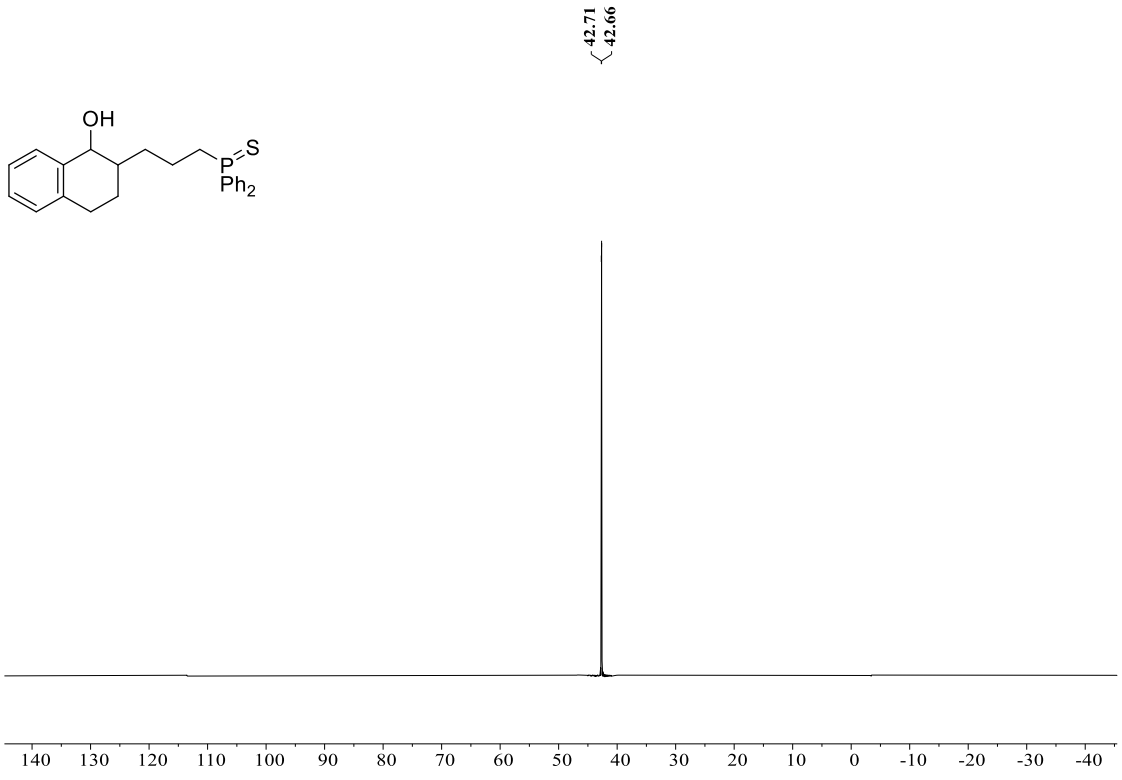
^{1}H NMR spectrum of **[S]-24** (600 MHz, $CDCl_3$)



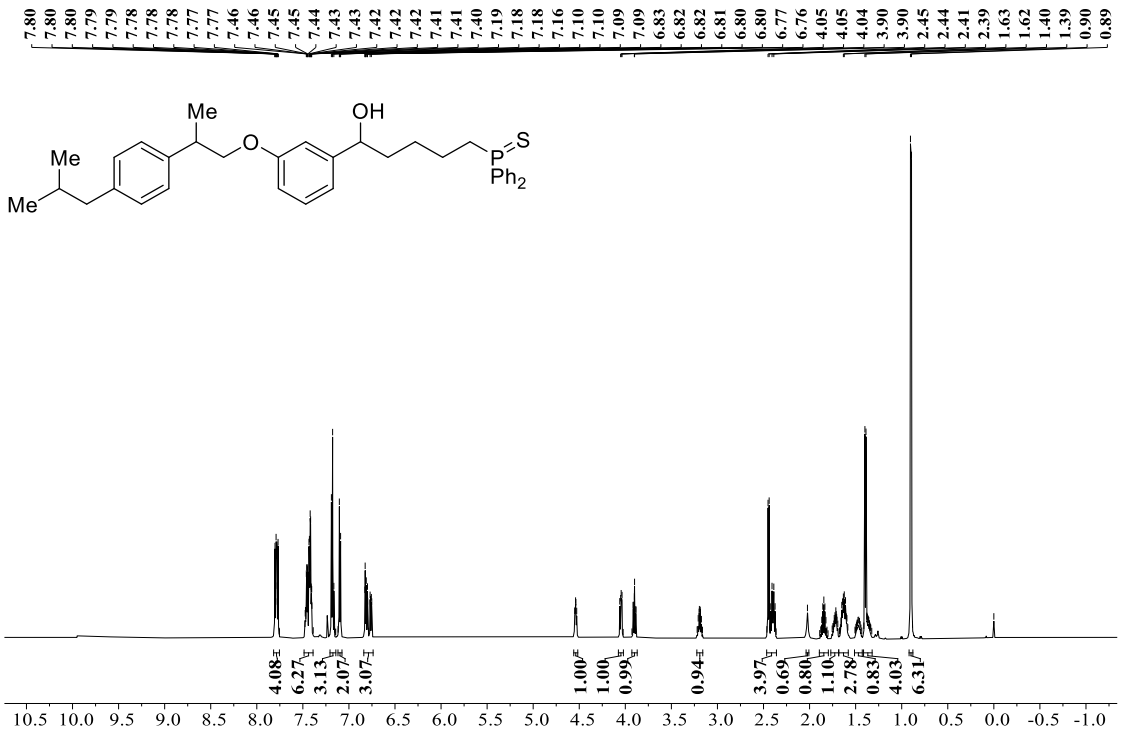
^{13}C NMR spectrum of **[S]-24** (150 MHz, $CDCl_3$)



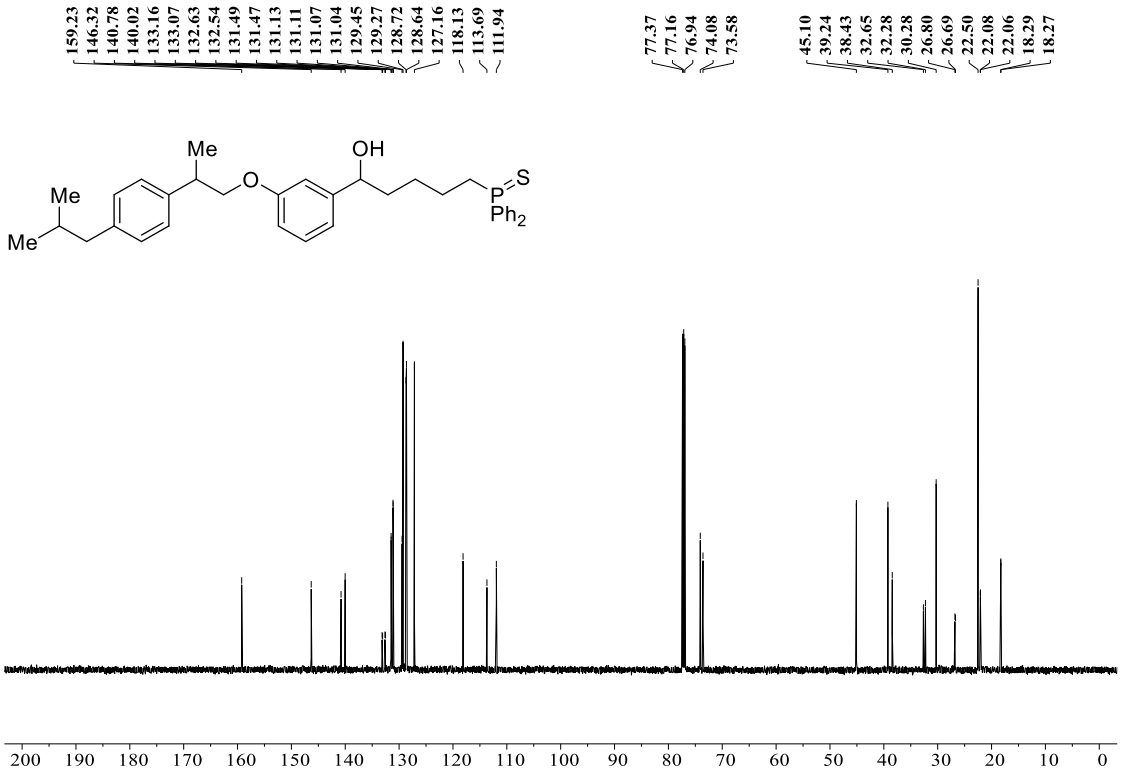
^{31}P NMR spectrum of **[S]-24** (243 MHz, $CDCl_3$)



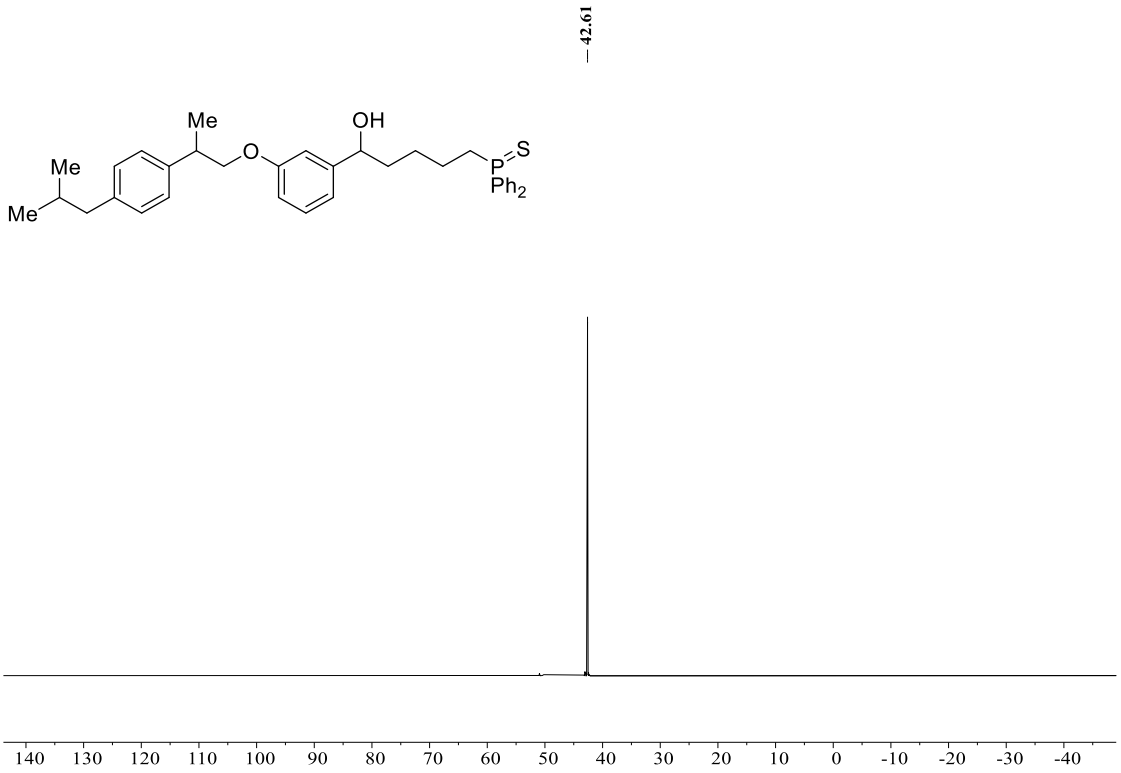
^{1}H NMR spectrum of **[S]-25** (600 MHz, $CDCl_3$)



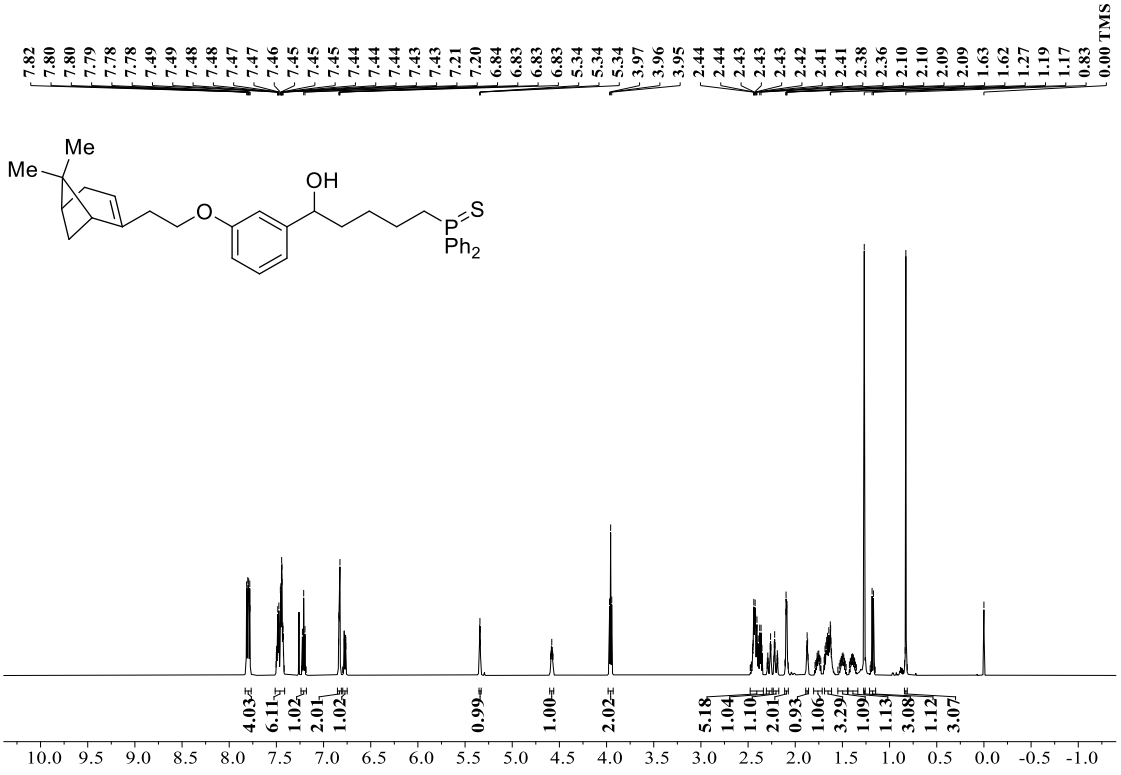
^{13}C NMR spectrum of **[S]-25** (150 MHz, $CDCl_3$)



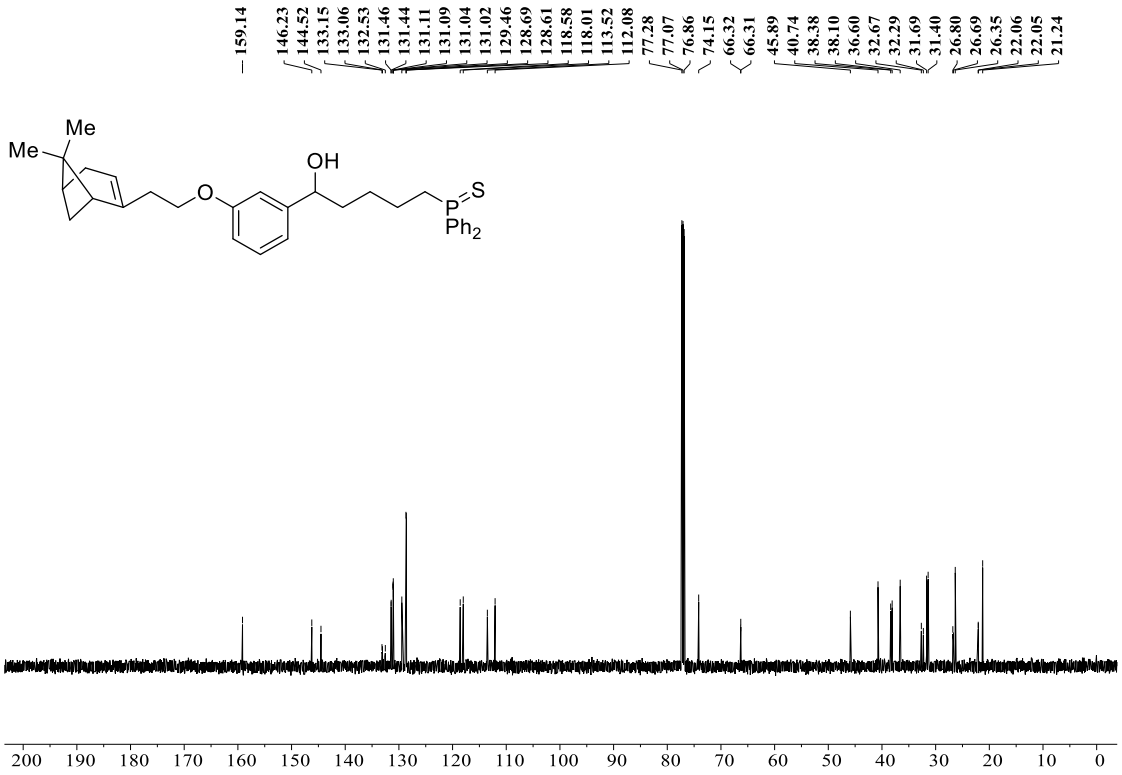
^{31}P NMR spectrum of **[S]-25** (243 MHz, $CDCl_3$)



^{1}H NMR spectrum of **[S]-26** (600 MHz, $CDCl_3$)

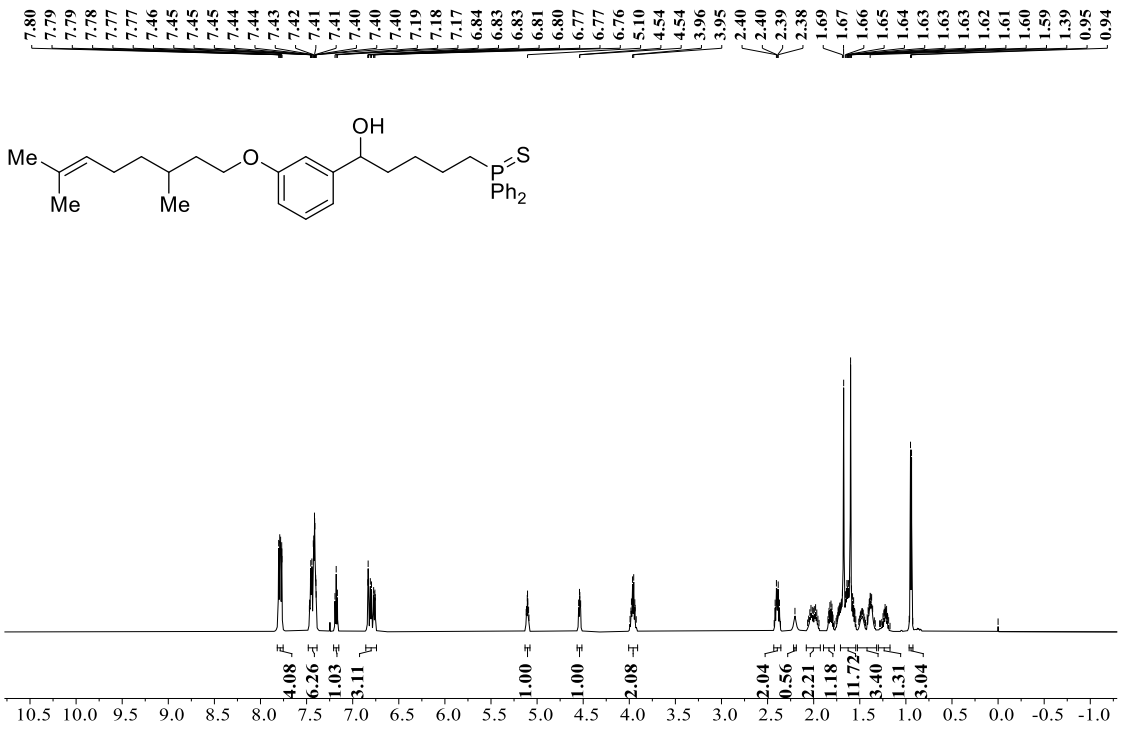


^{13}C NMR spectrum of **[S]-26** (150 MHz, $CDCl_3$)

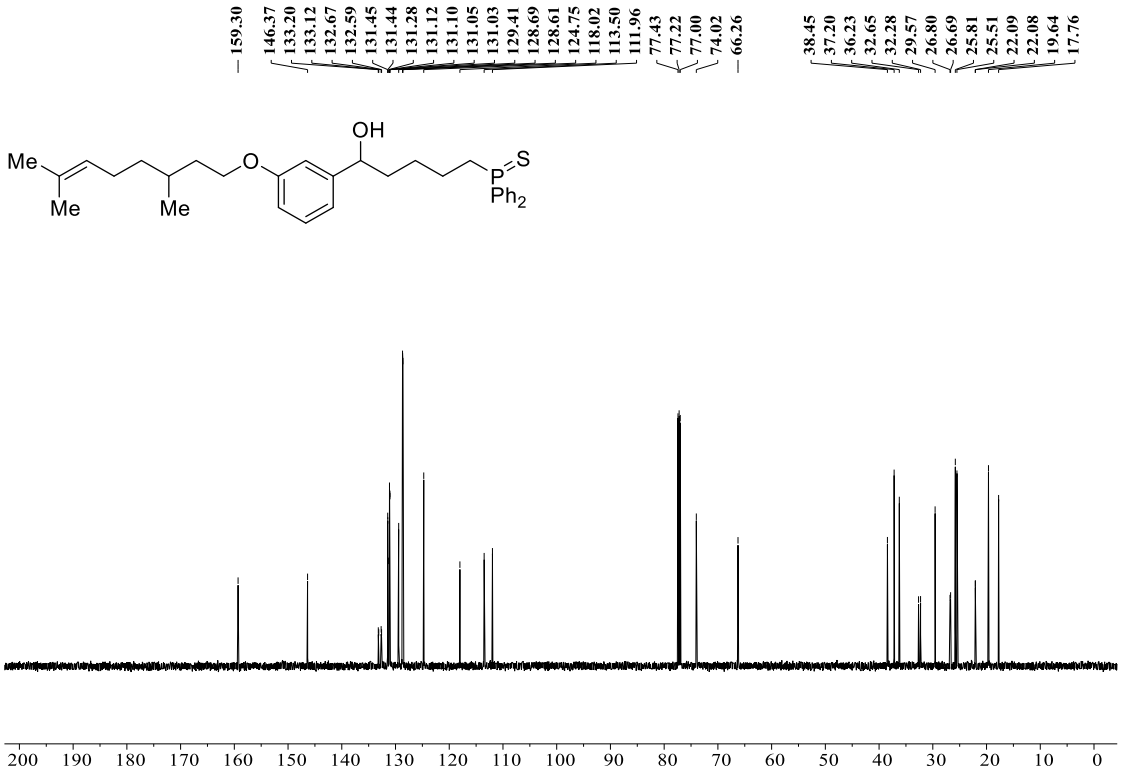


^{31}P NMR spectrum of **[S]-26** (243 MHz, $CDCl_3$)

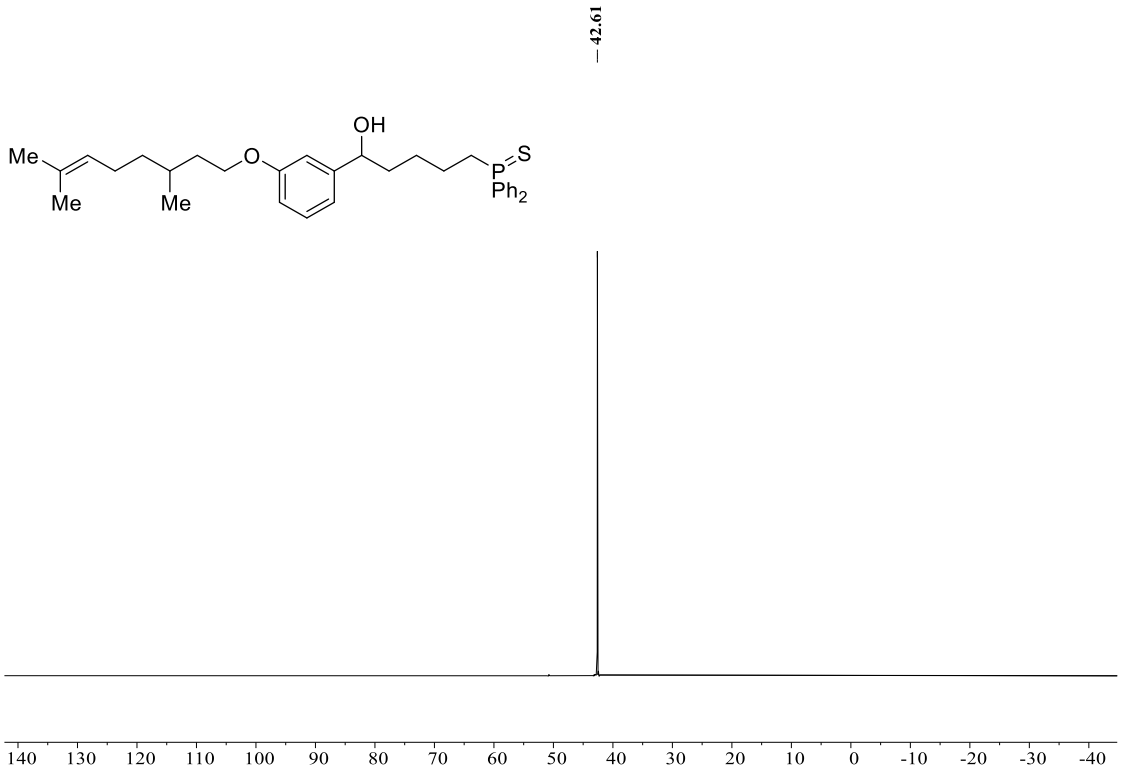
^{1}H NMR spectrum of **[S]-27** (600 MHz, $CDCl_3$)



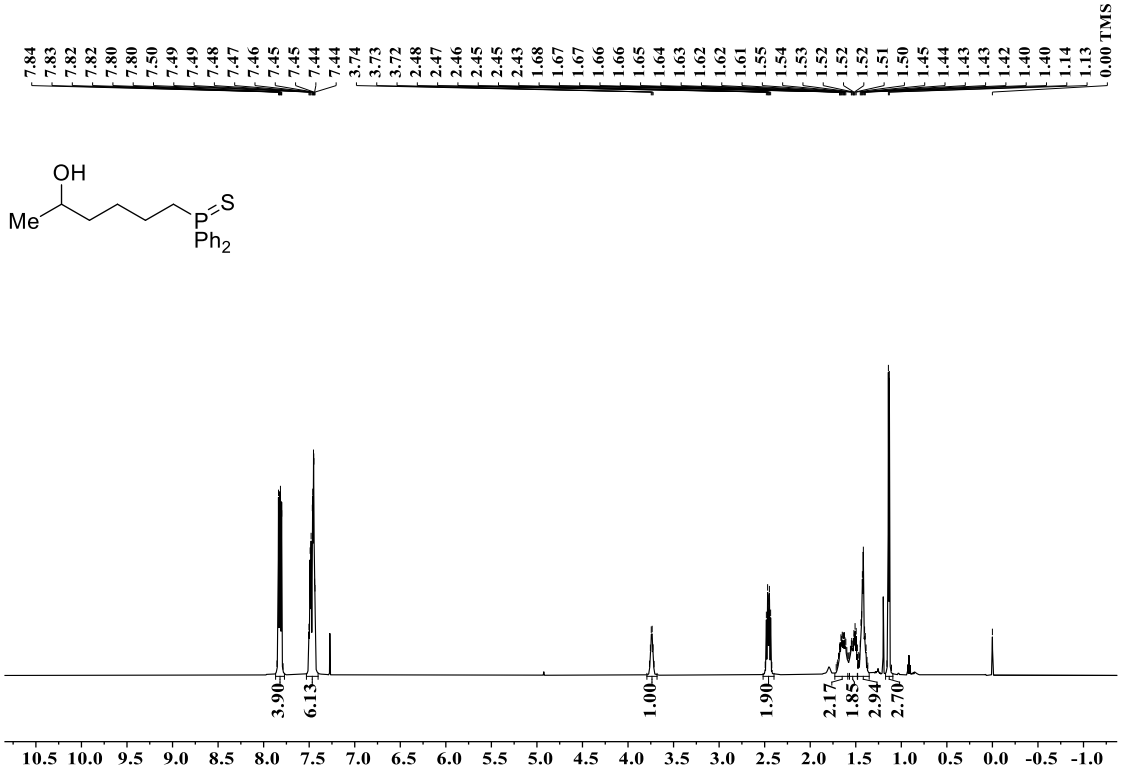
^{13}C NMR spectrum of **[S]-27** (150 MHz, $CDCl_3$)



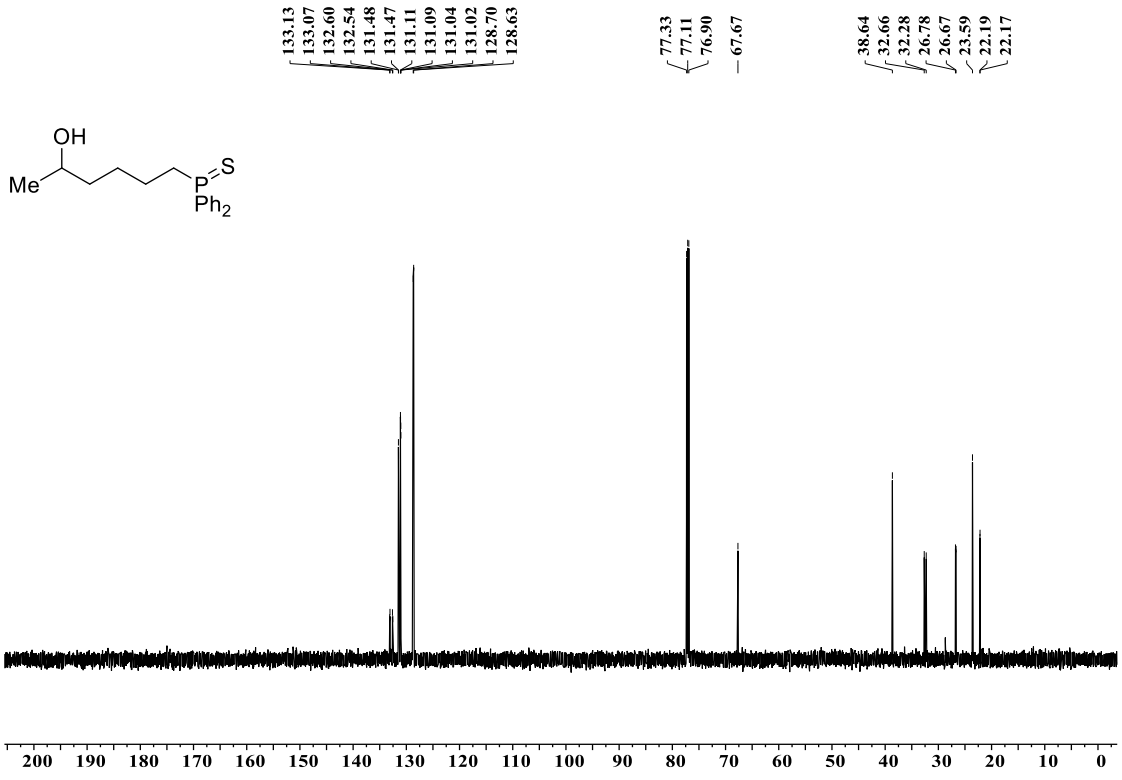
^{31}P NMR spectrum of **[S]-27** (243 MHz, $CDCl_3$)



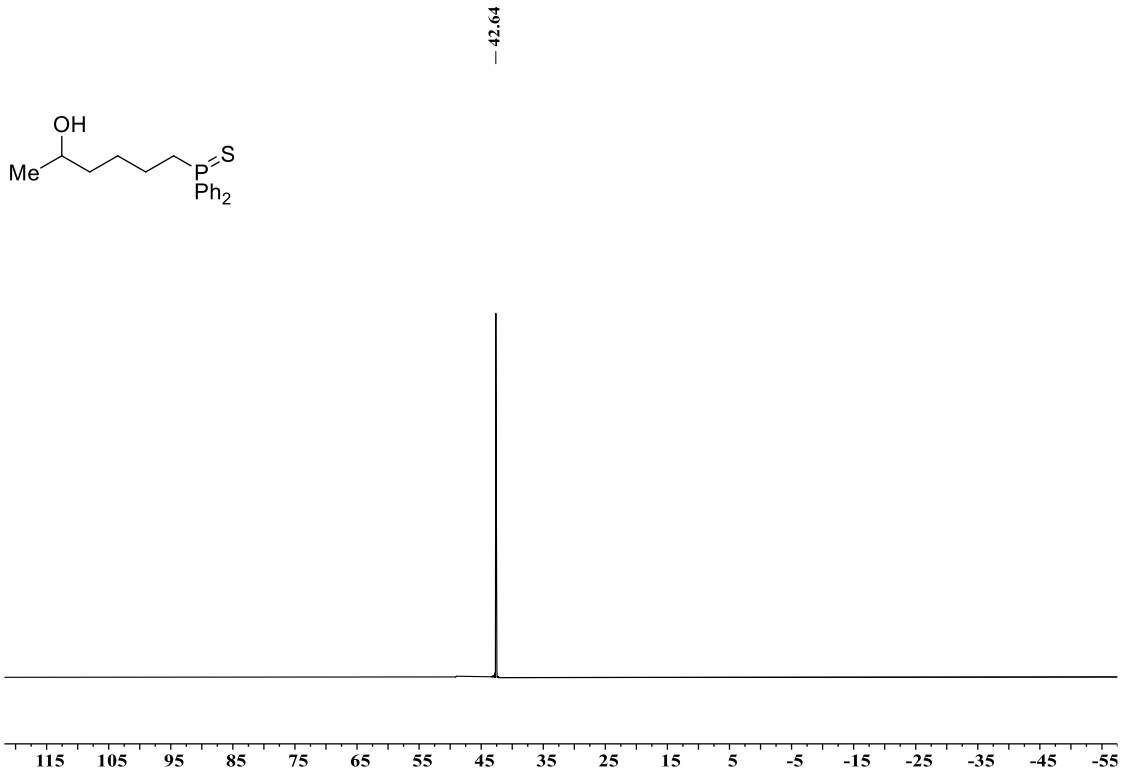
^{1}H NMR spectrum of **[S]-28** (600 MHz, $CDCl_3$)



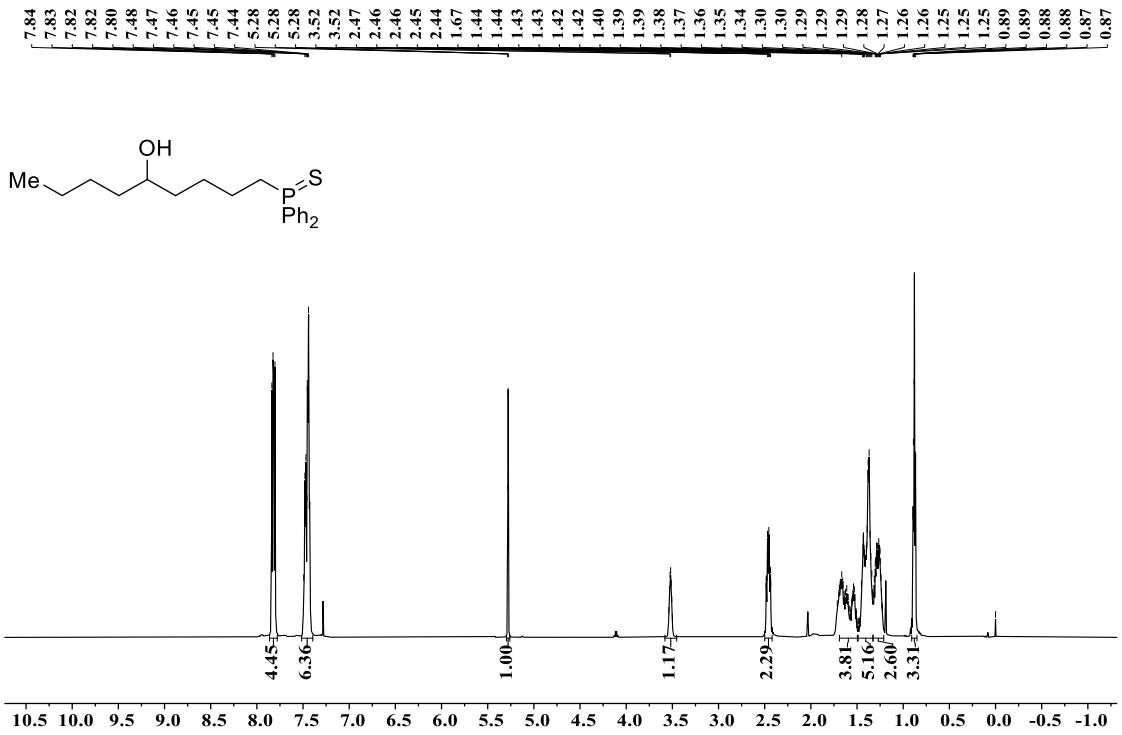
^{13}C NMR spectrum of **[S]-28** (150 MHz, $CDCl_3$)



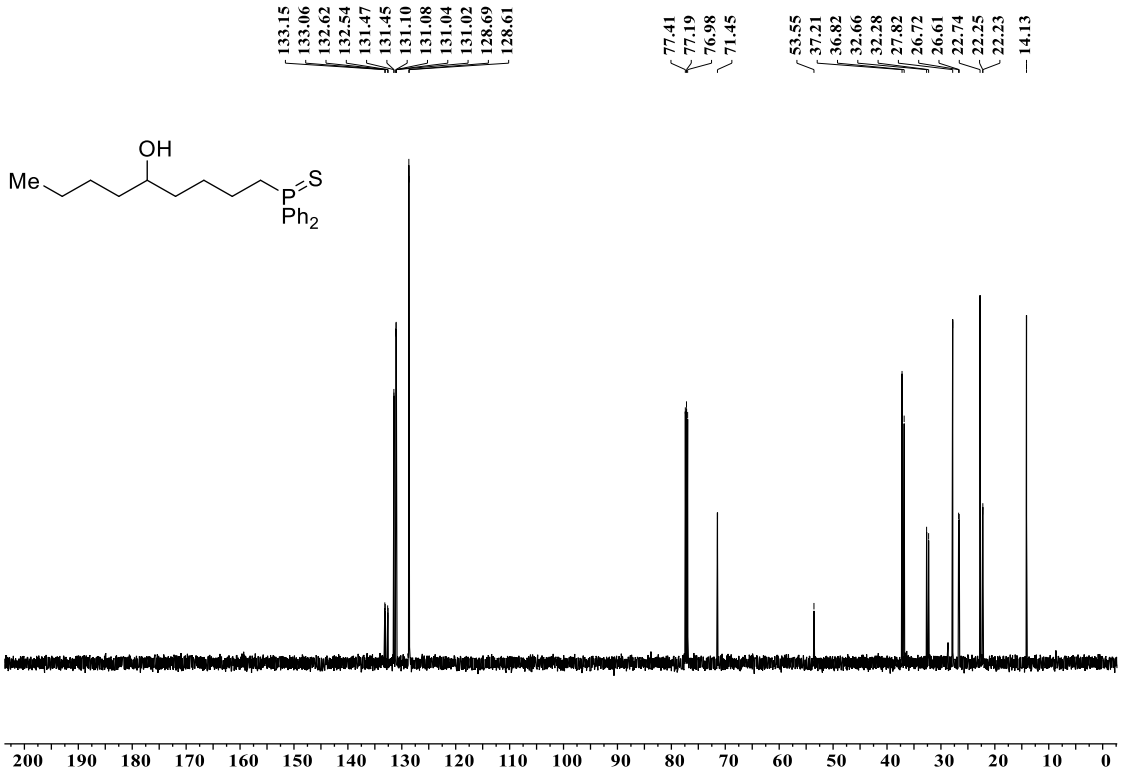
^{31}P NMR spectrum of **[S]-28** (243 MHz, $CDCl_3$)



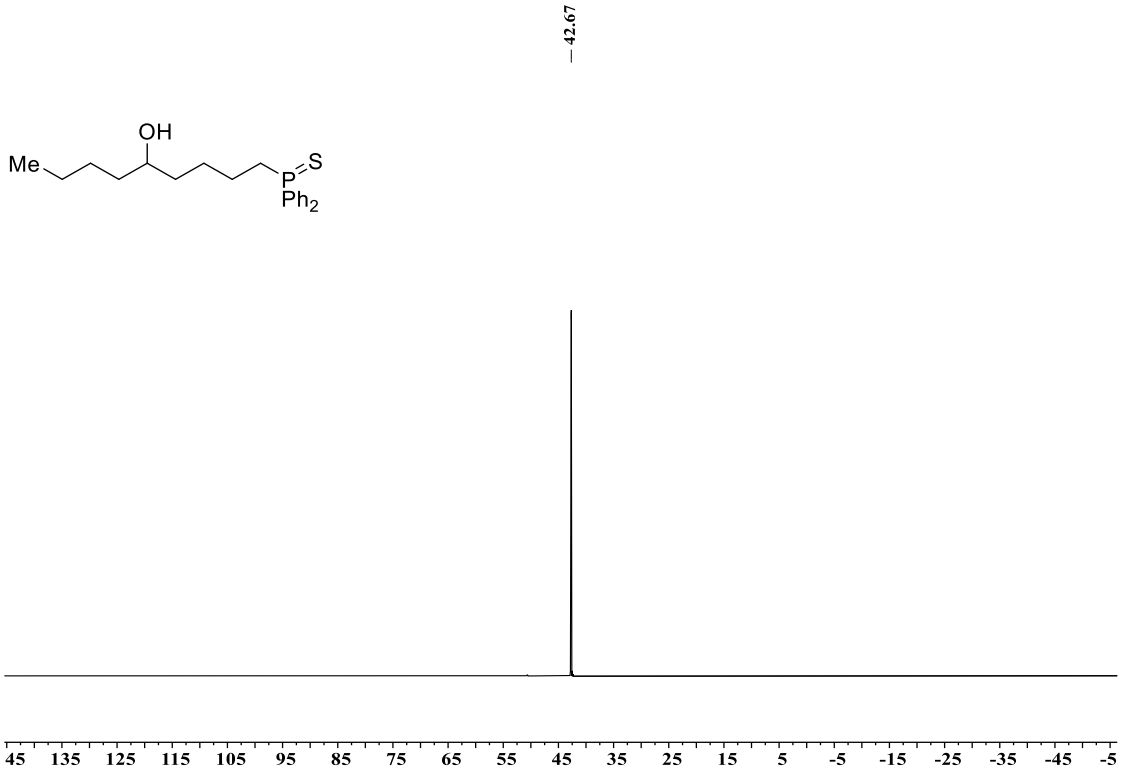
^{1}H NMR spectrum of **[S]-29** (600 MHz, $CDCl_3$)



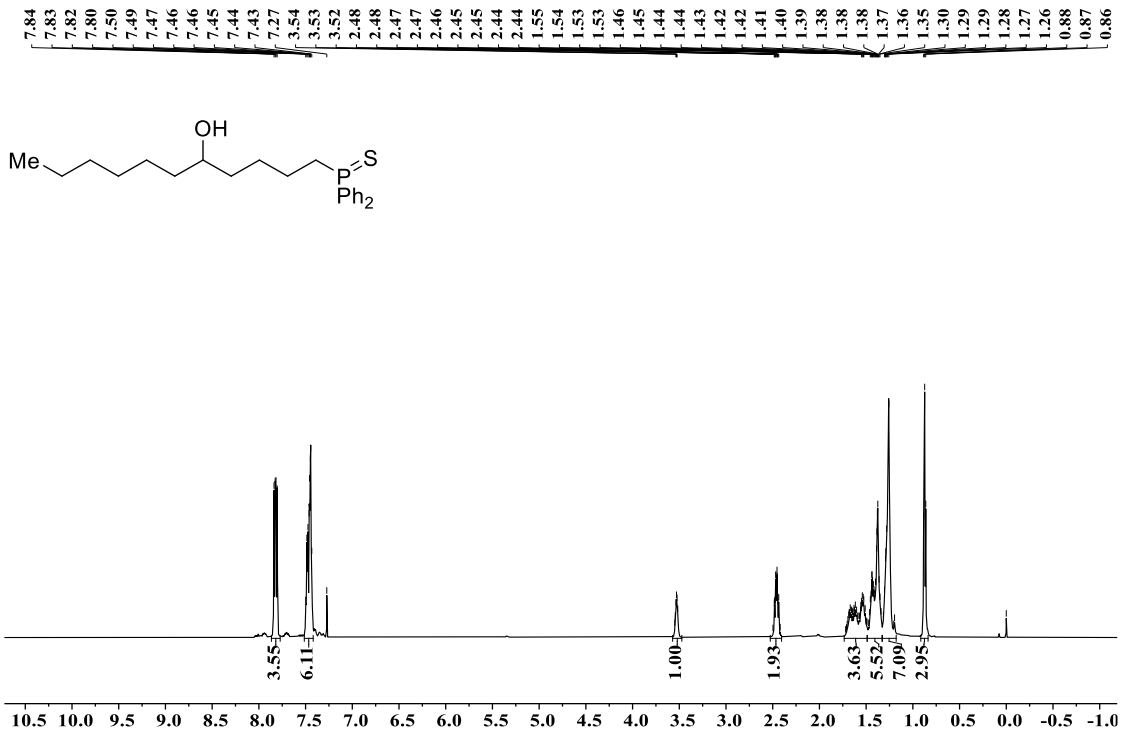
^{13}C NMR spectrum of **[S]-29** (150 MHz, $CDCl_3$)



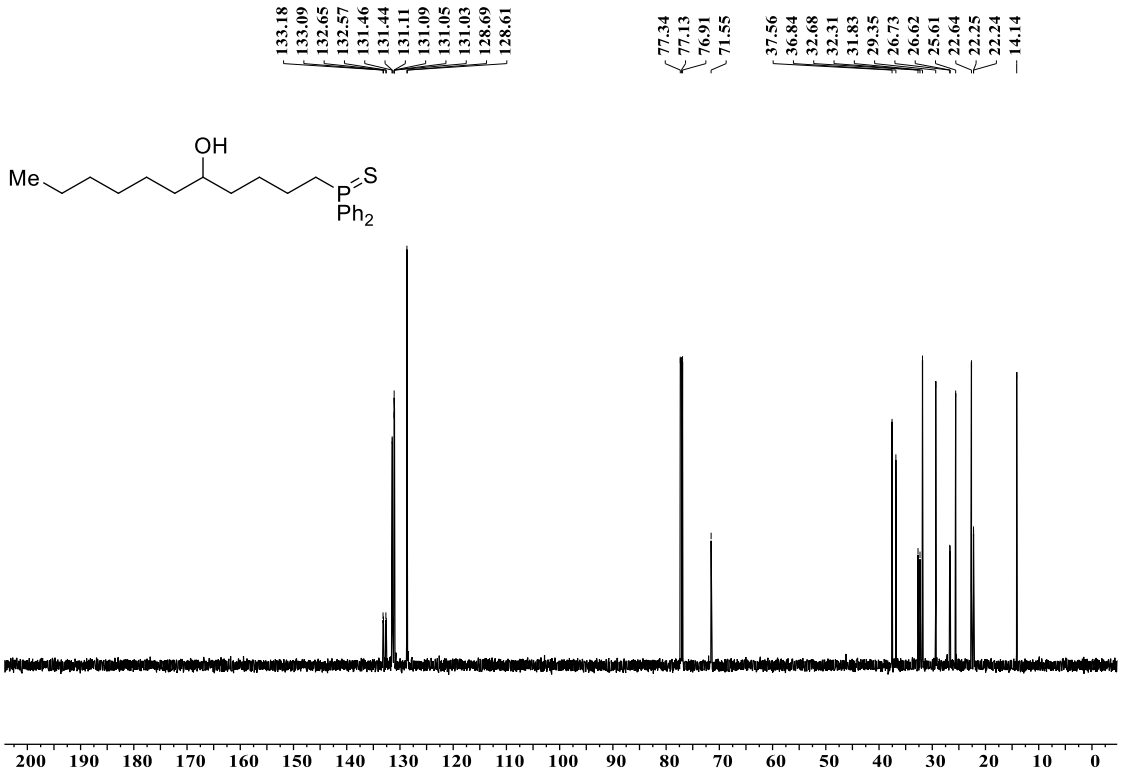
^{31}P NMR spectrum of **[S]-29** (243 MHz, $CDCl_3$)



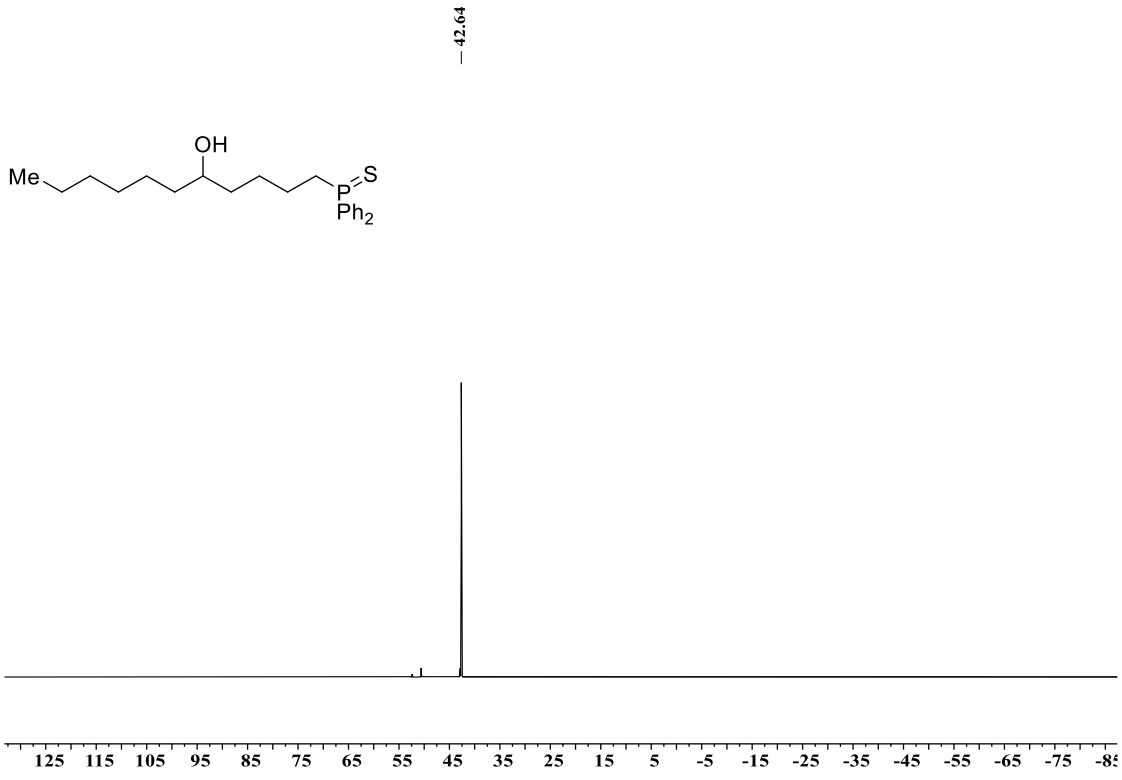
^{1}H NMR spectrum of **[S]-30** (600 MHz, $CDCl_3$)



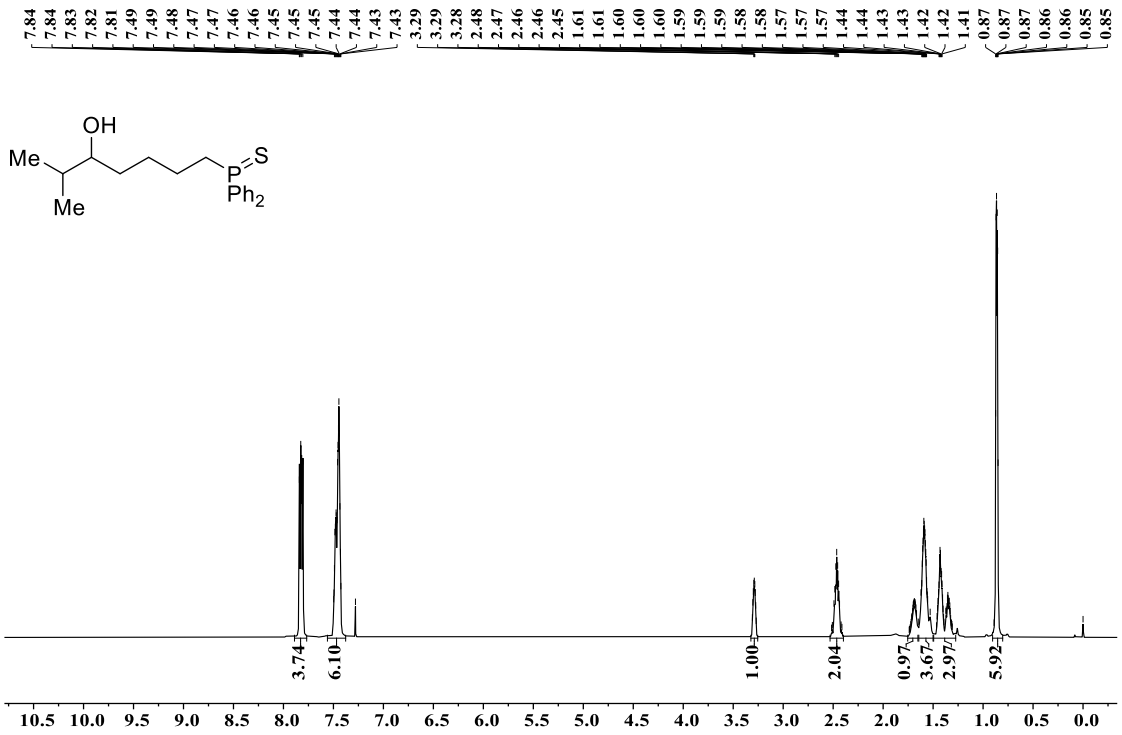
^{13}C NMR spectrum of **[S]-30** (150 MHz, $CDCl_3$)



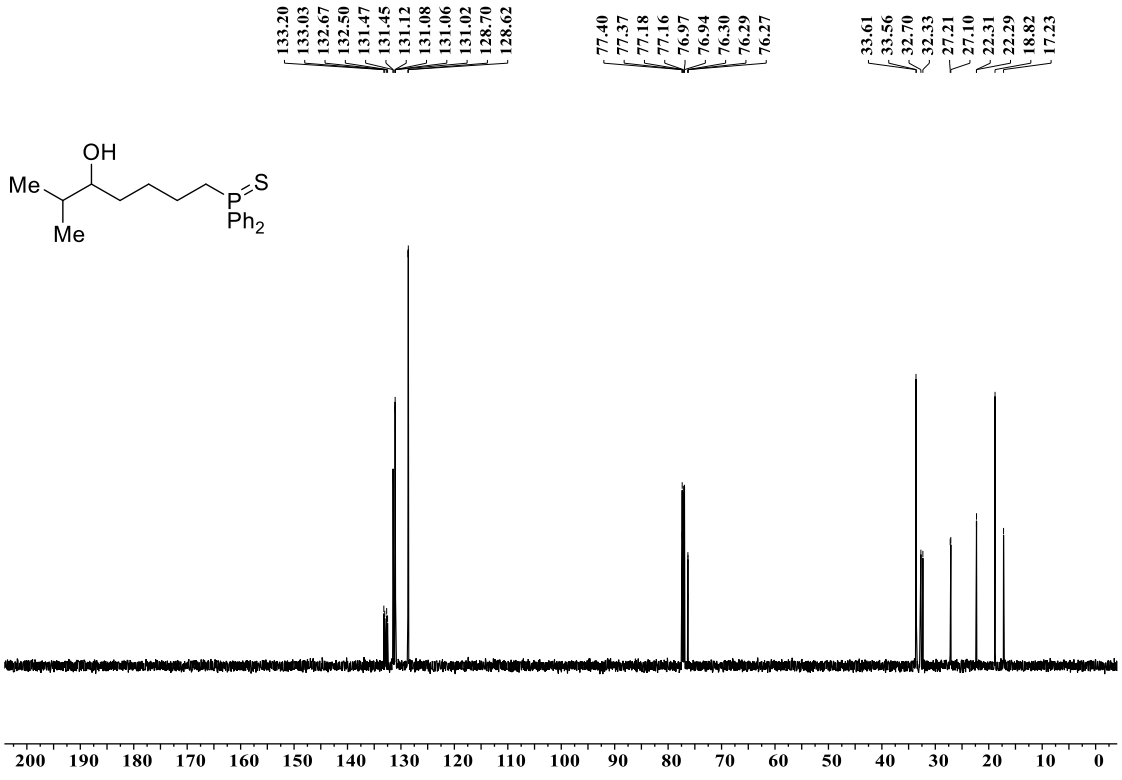
^{31}P NMR spectrum of **[S]-30** (243 MHz, $CDCl_3$)



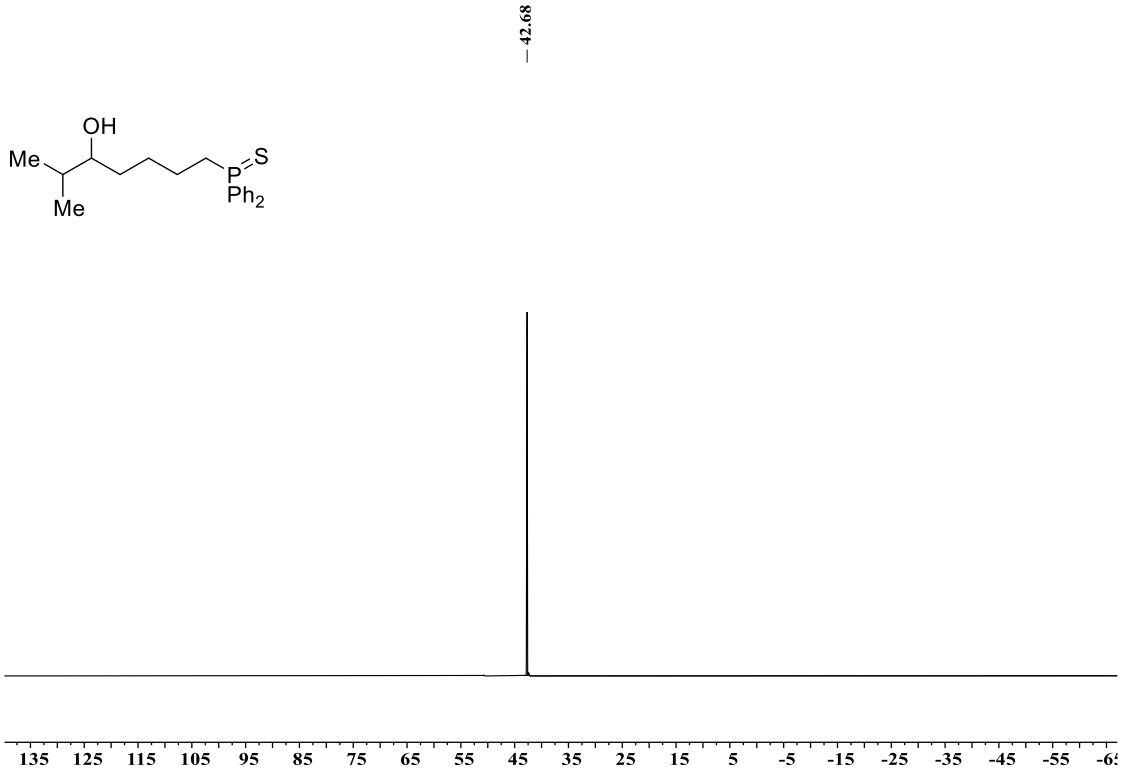
^{1}H NMR spectrum of **[S]-31** (600 MHz, $CDCl_3$)



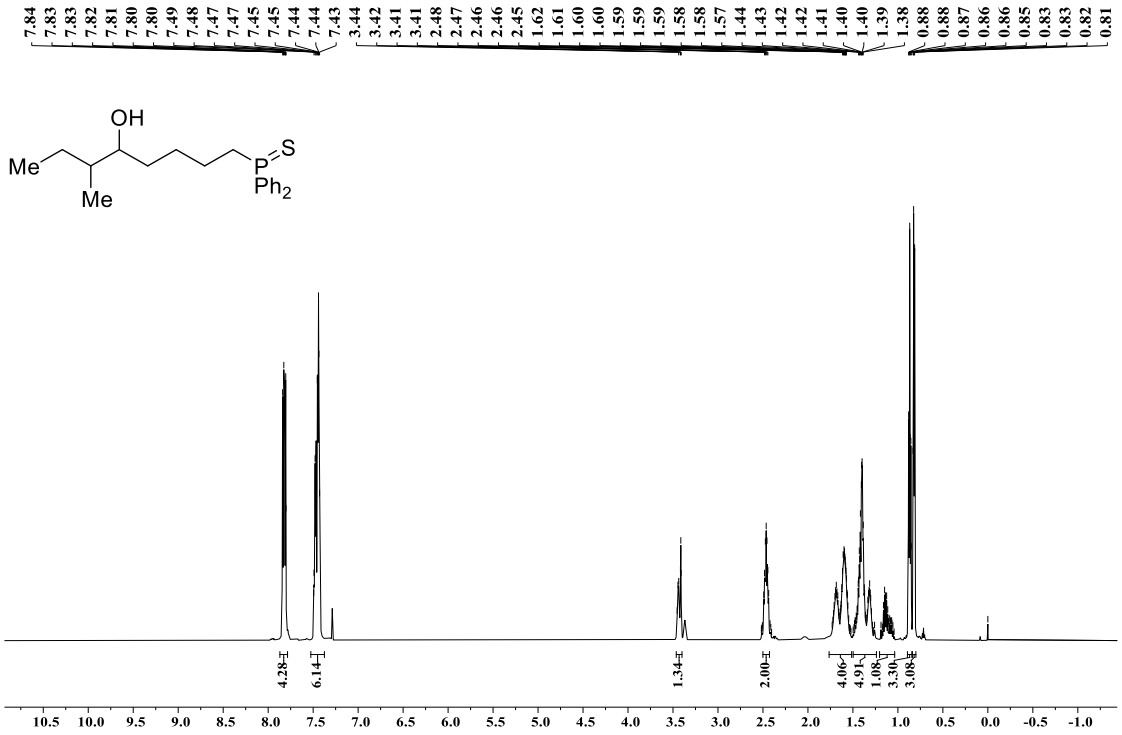
^{13}C NMR spectrum of **[S]-31** (150 MHz, $CDCl_3$)



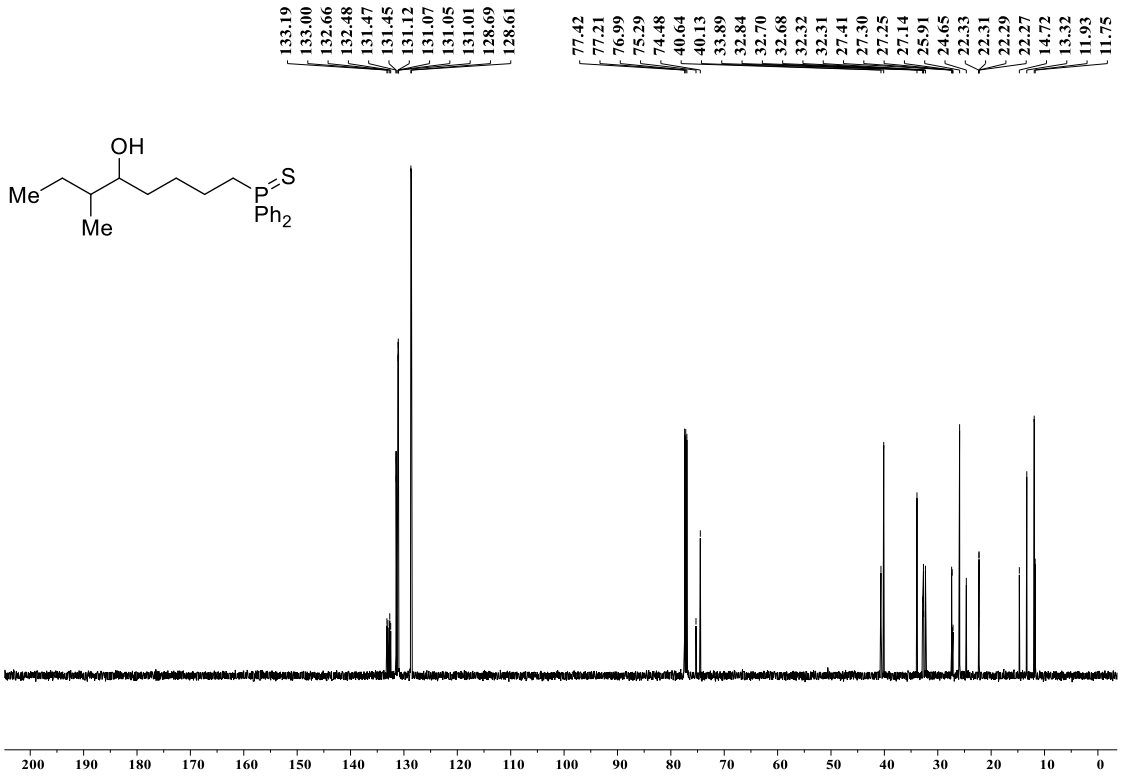
^{31}P NMR spectrum of **[S]-31** (243 MHz, $CDCl_3$)



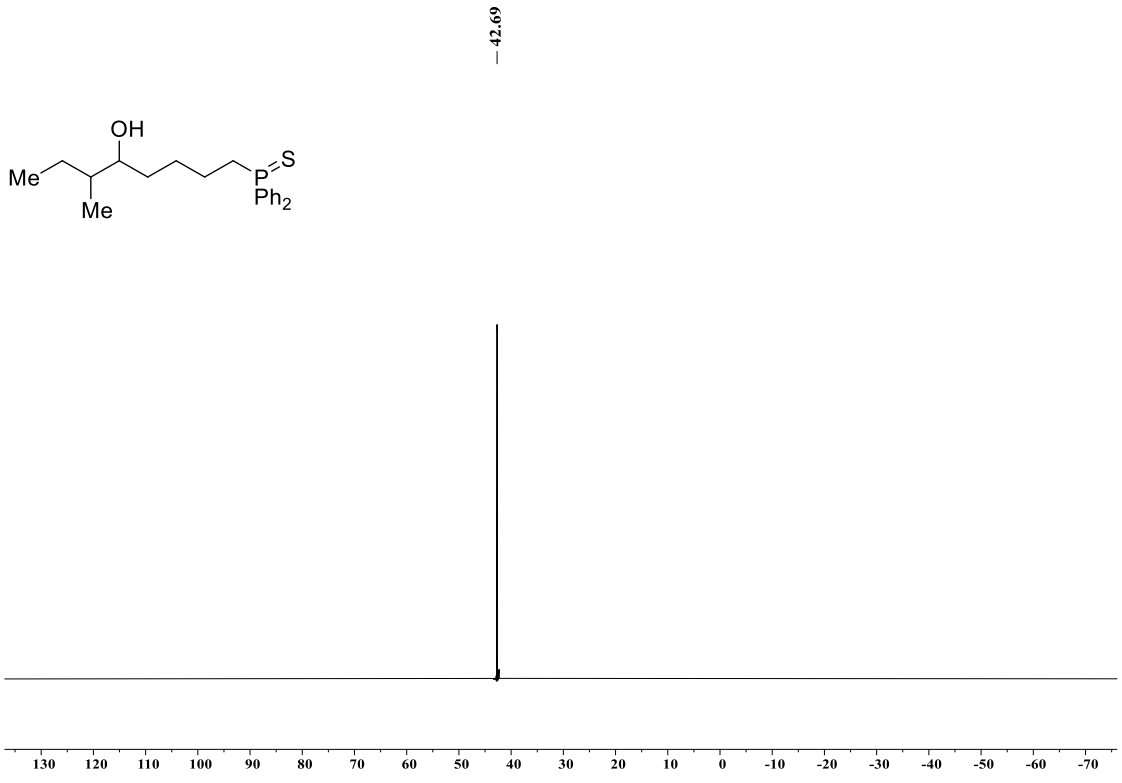
^{1}H NMR spectrum of **[S]-32** (600 MHz, $CDCl_3$)



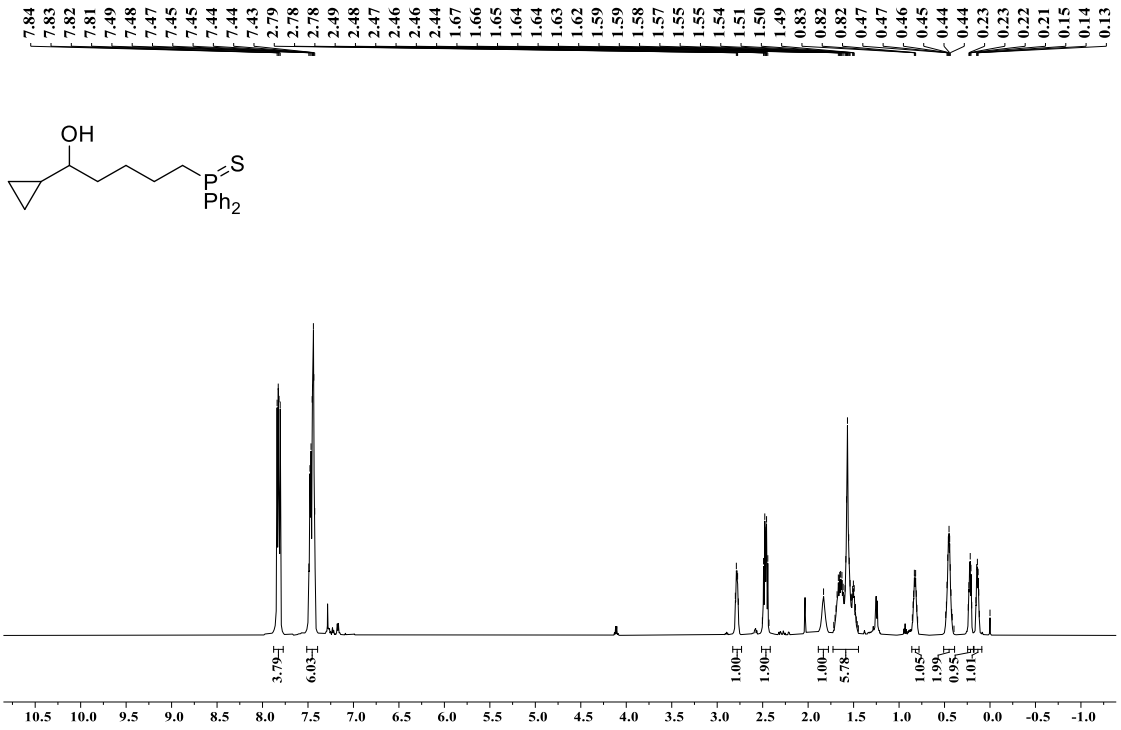
^{13}C NMR spectrum of **[S]-32** (150 MHz, $CDCl_3$)



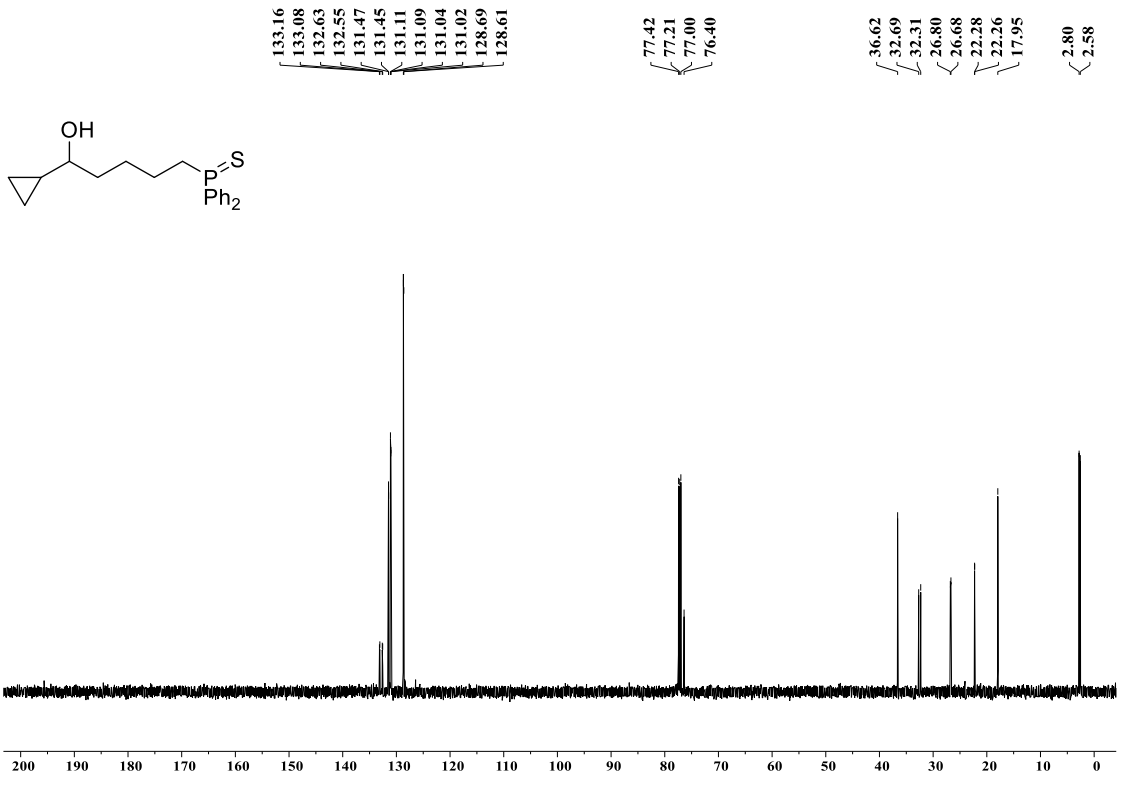
^{31}P NMR spectrum of **[S]-32** (243 MHz, $CDCl_3$)



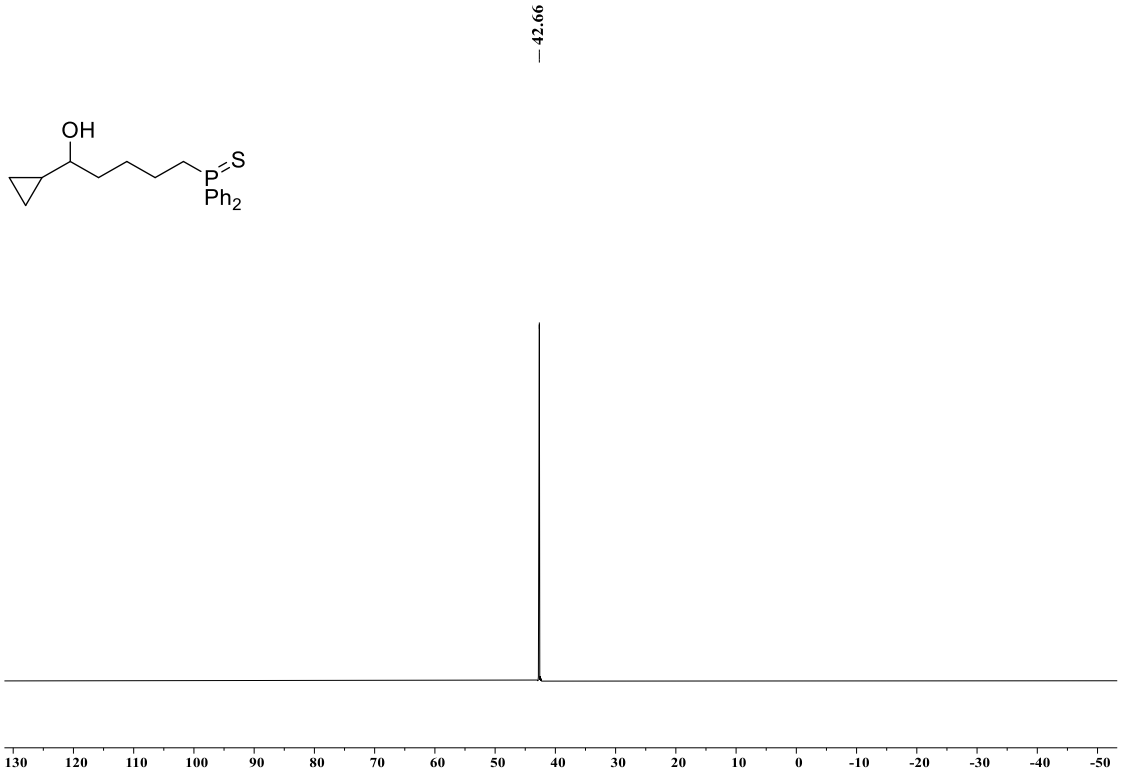
^{1}H NMR spectrum of **[S]-33** (600 MHz, $CDCl_3$)



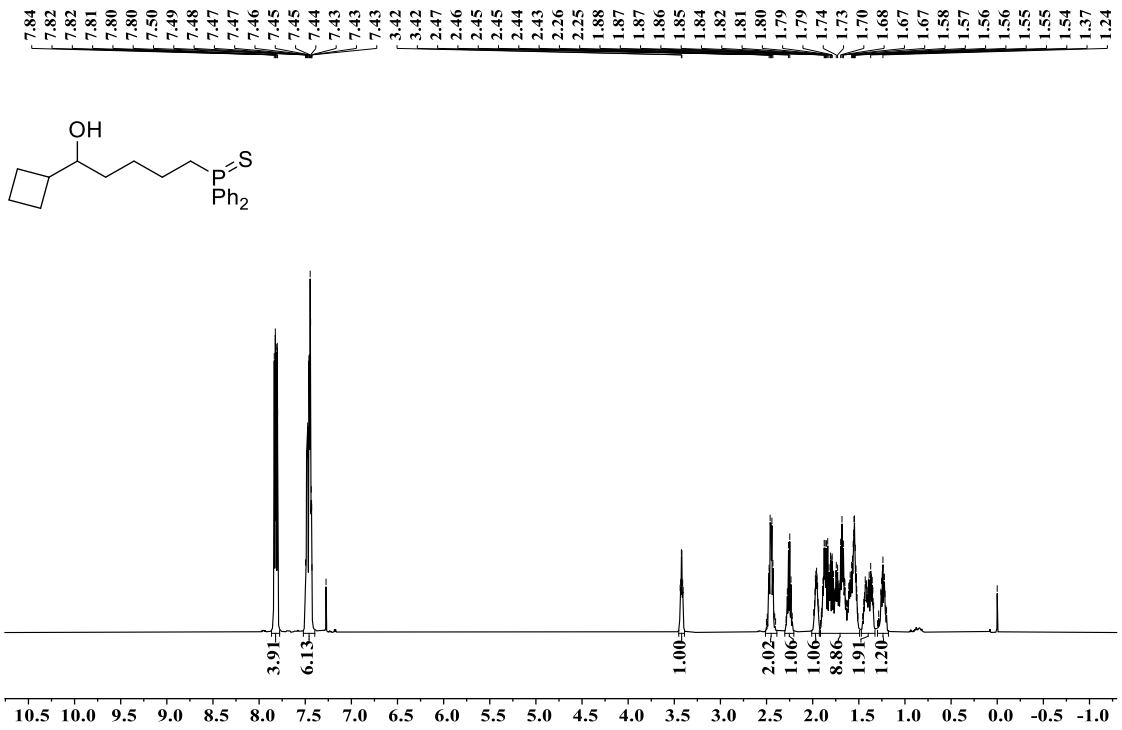
^{13}C NMR spectrum of **[S]-33** (150 MHz, $CDCl_3$)



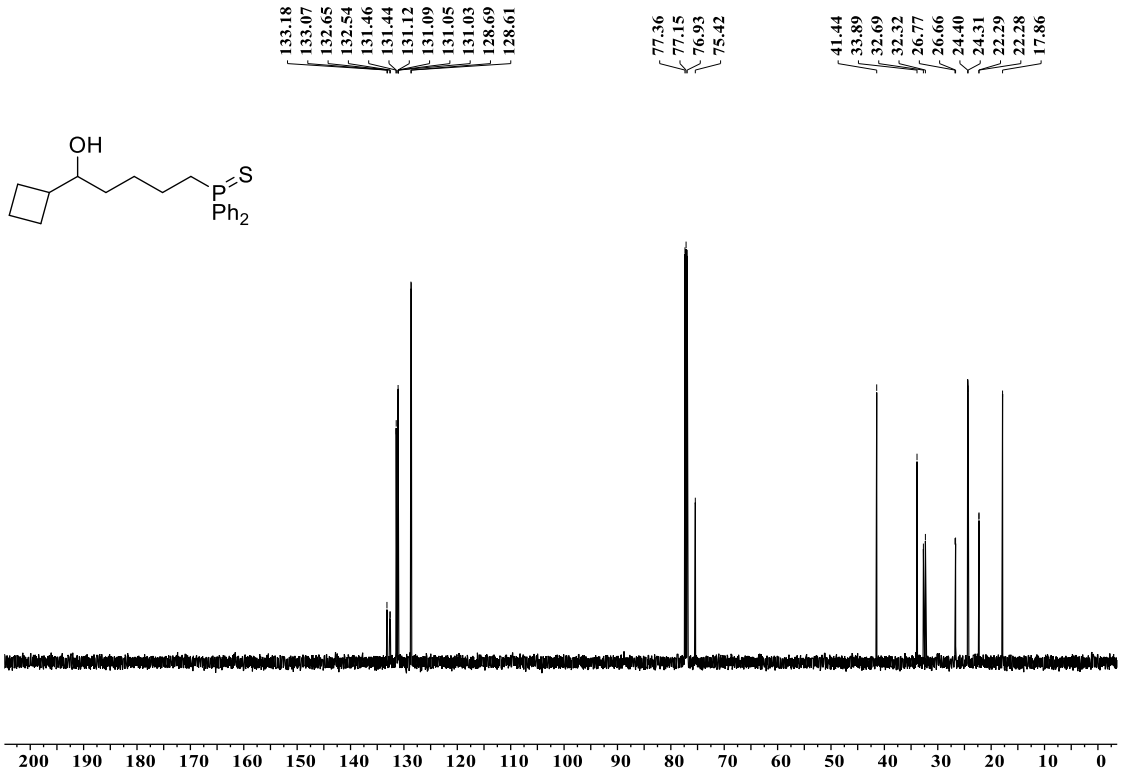
^{31}P NMR spectrum of **[S]-33** (243 MHz, $CDCl_3$)



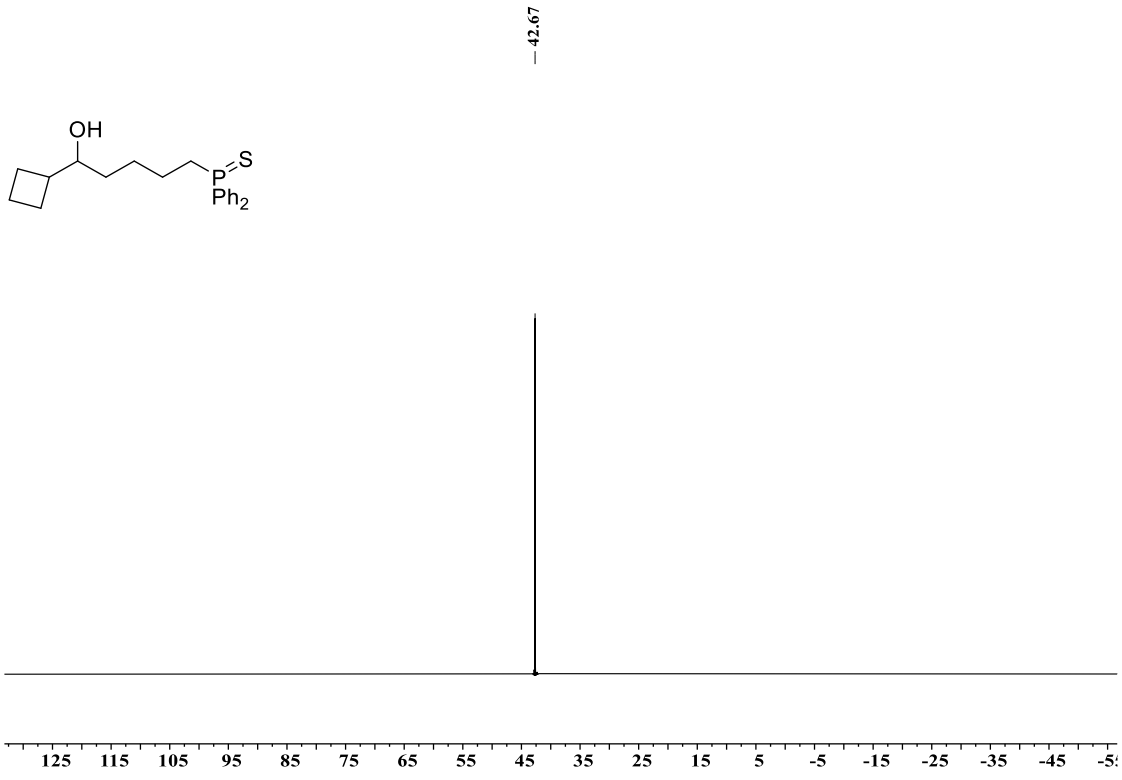
^{1}H NMR spectrum of **[S]-34** (600 MHz, $CDCl_3$)



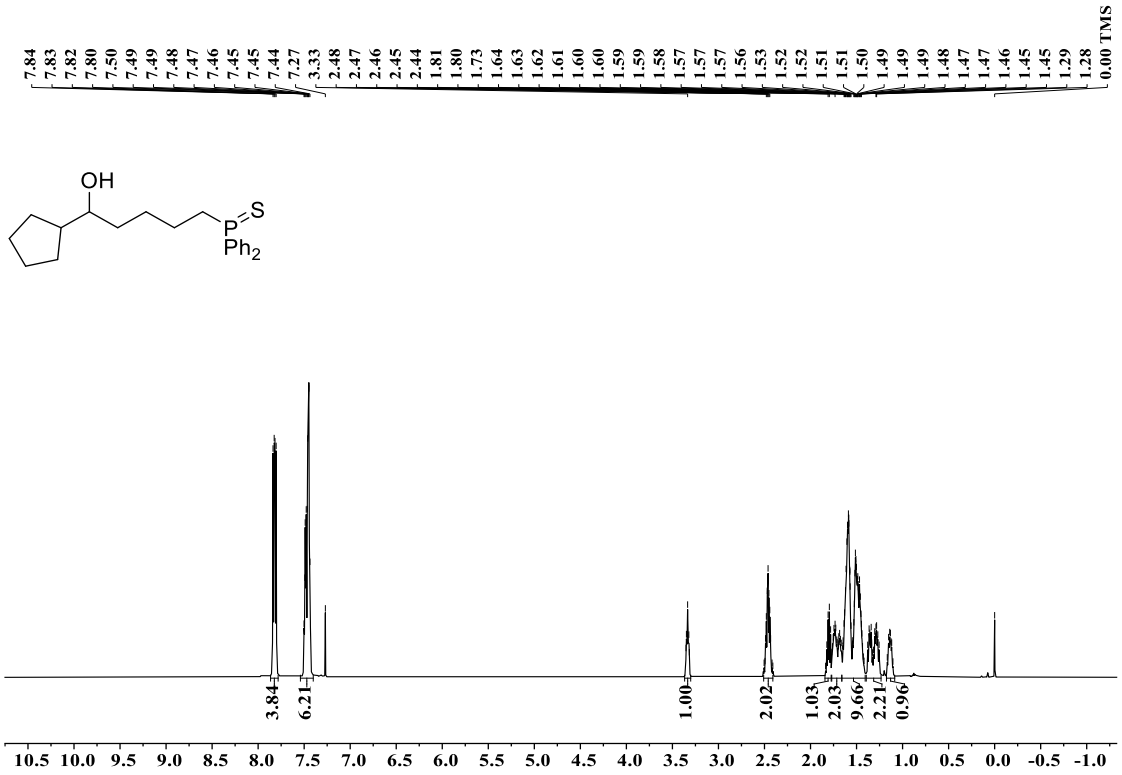
^{13}C NMR spectrum of **[S]-34** (150 MHz, $CDCl_3$)



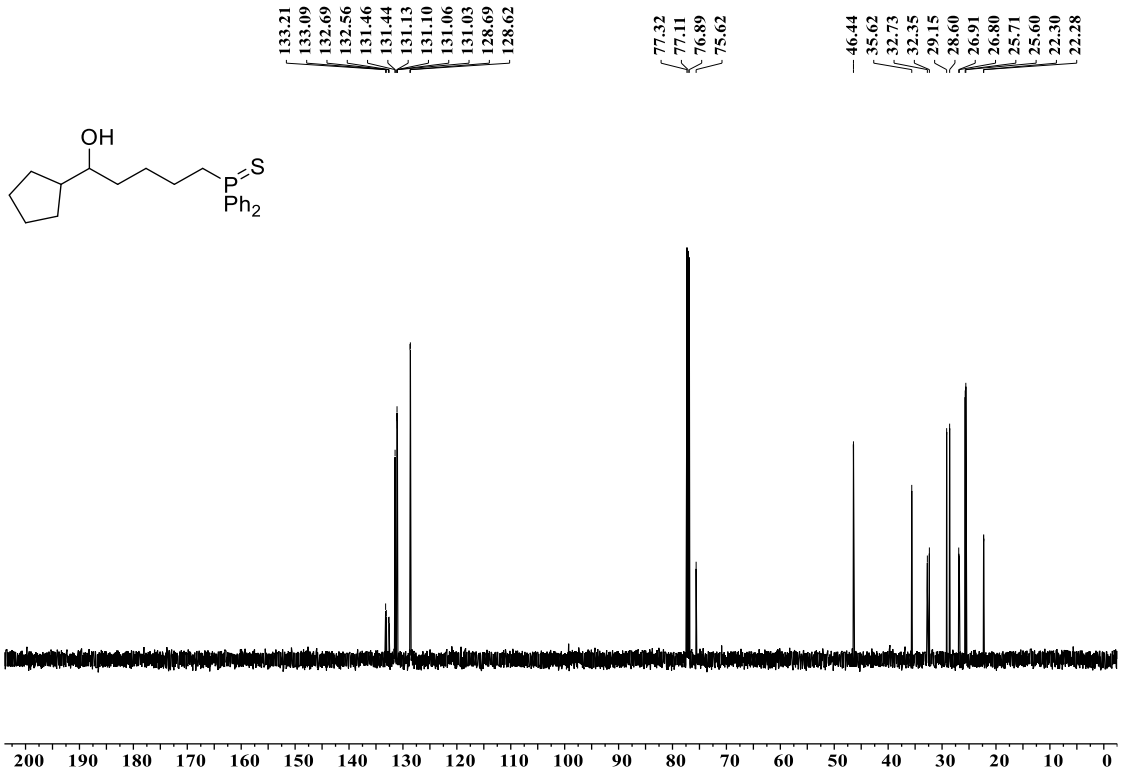
^{31}P NMR spectrum of **[S]-34** (243 MHz, $CDCl_3$)



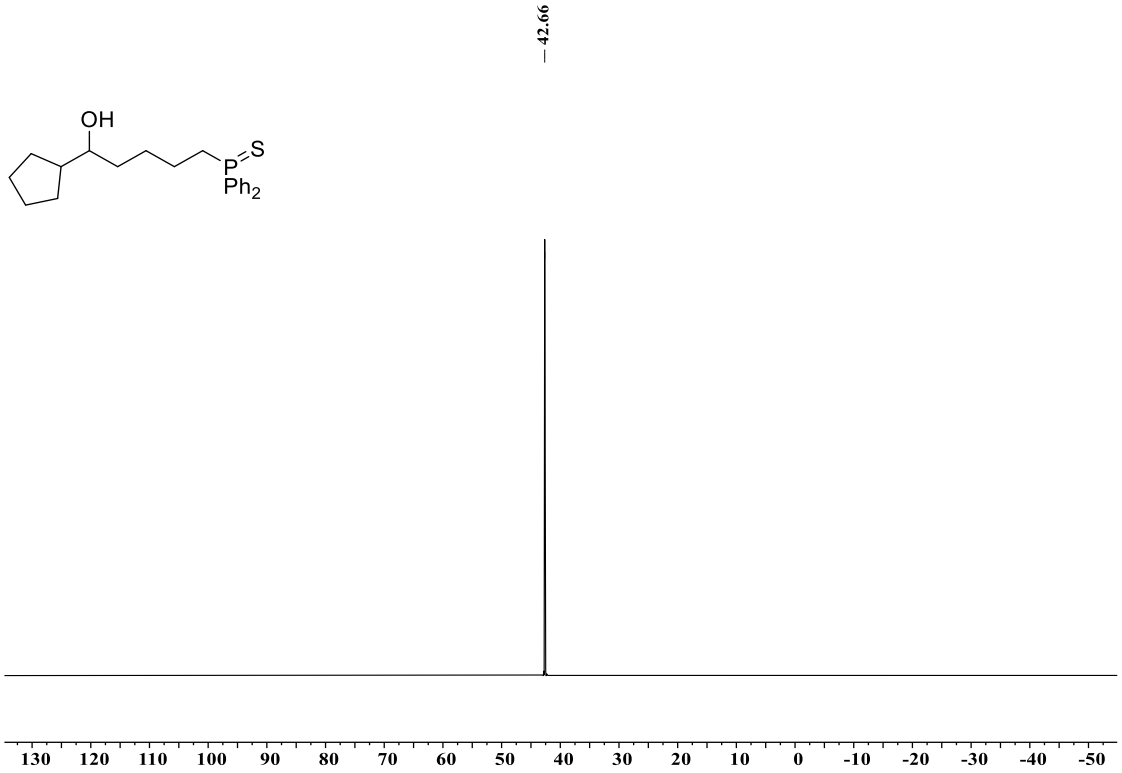
^{1}H NMR spectrum of **[S]-35** (600 MHz, $CDCl_3$)



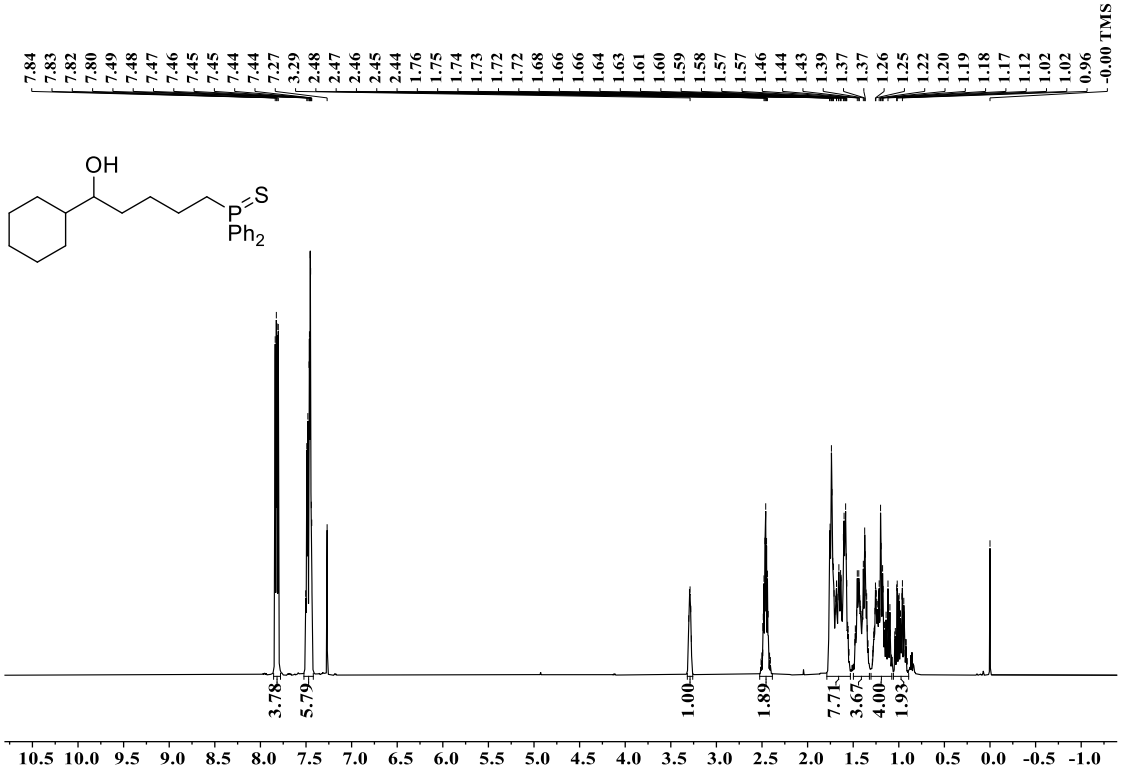
^{13}C NMR spectrum of **[S]-35** (150 MHz, $CDCl_3$)



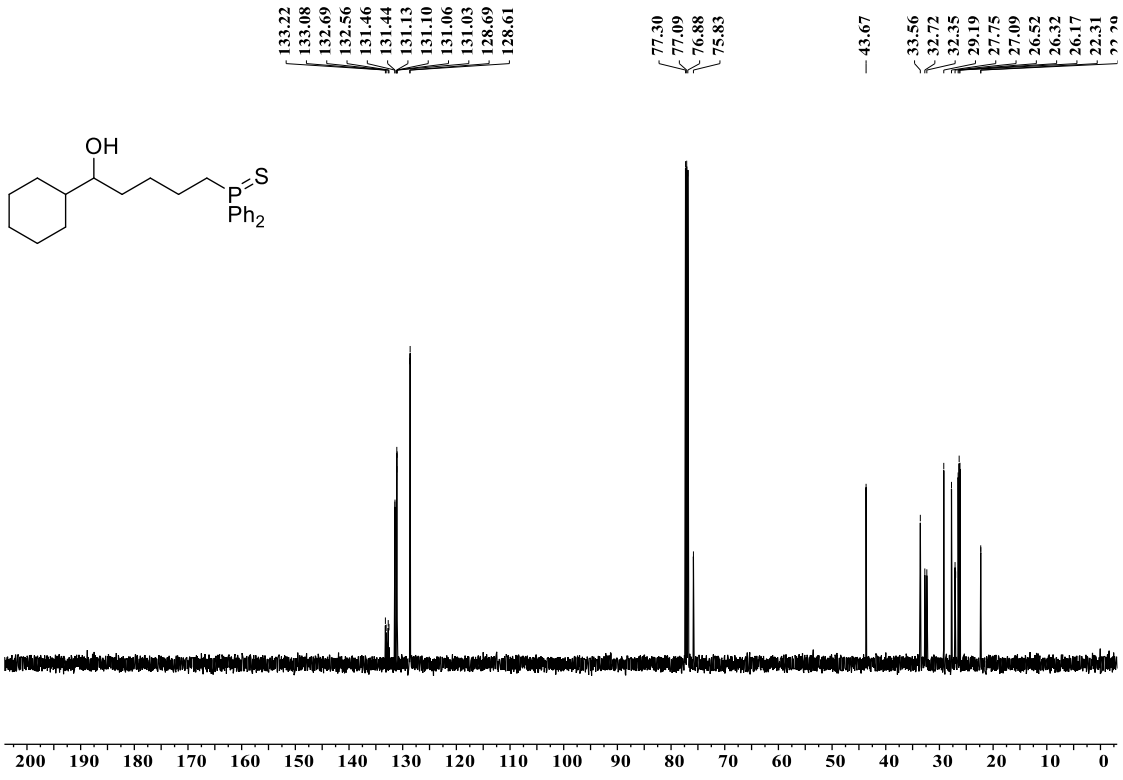
^{31}P NMR spectrum of **[S]-35** (243 MHz, $CDCl_3$)



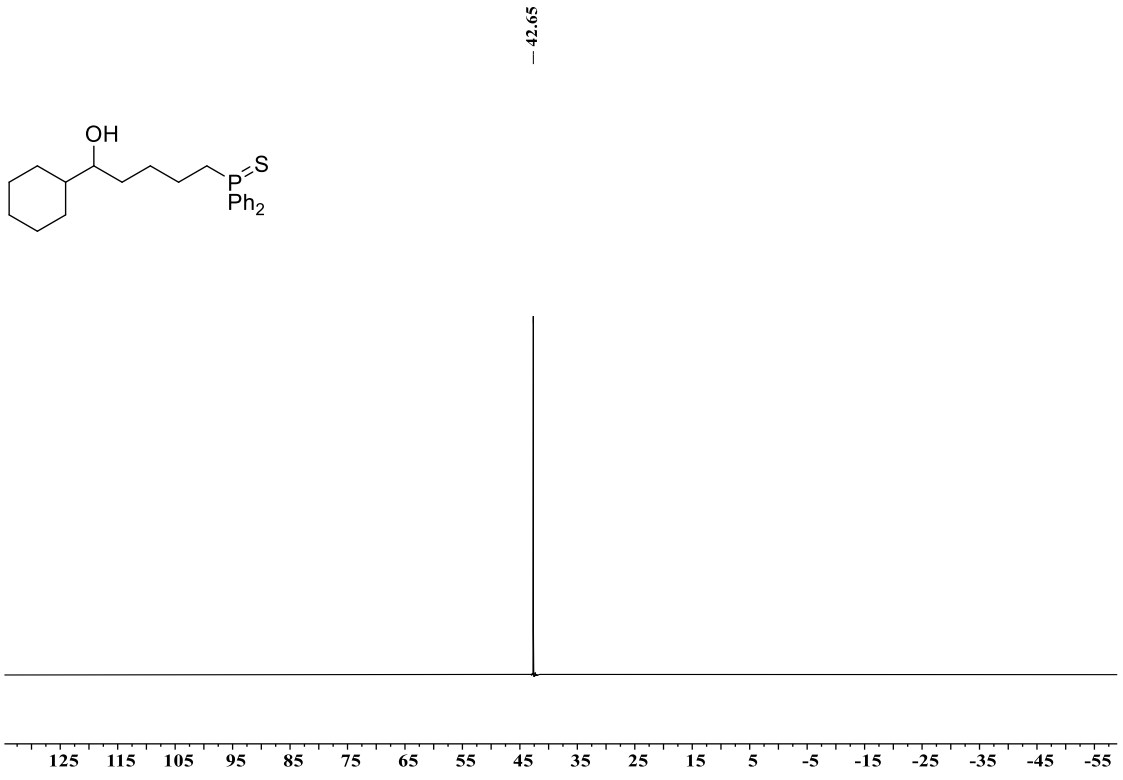
^{1}H NMR spectrum of **[S]-36** (600 MHz, $CDCl_3$)



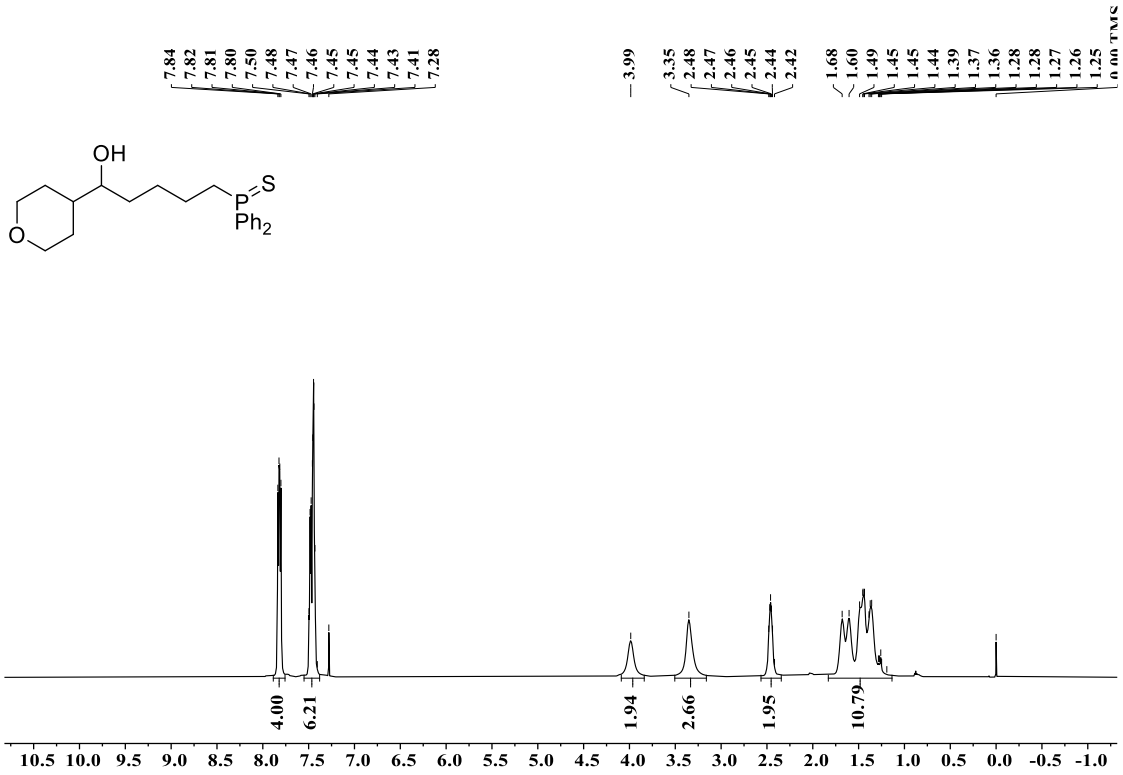
^{13}C NMR spectrum of **[S]-36** (150 MHz, $CDCl_3$)



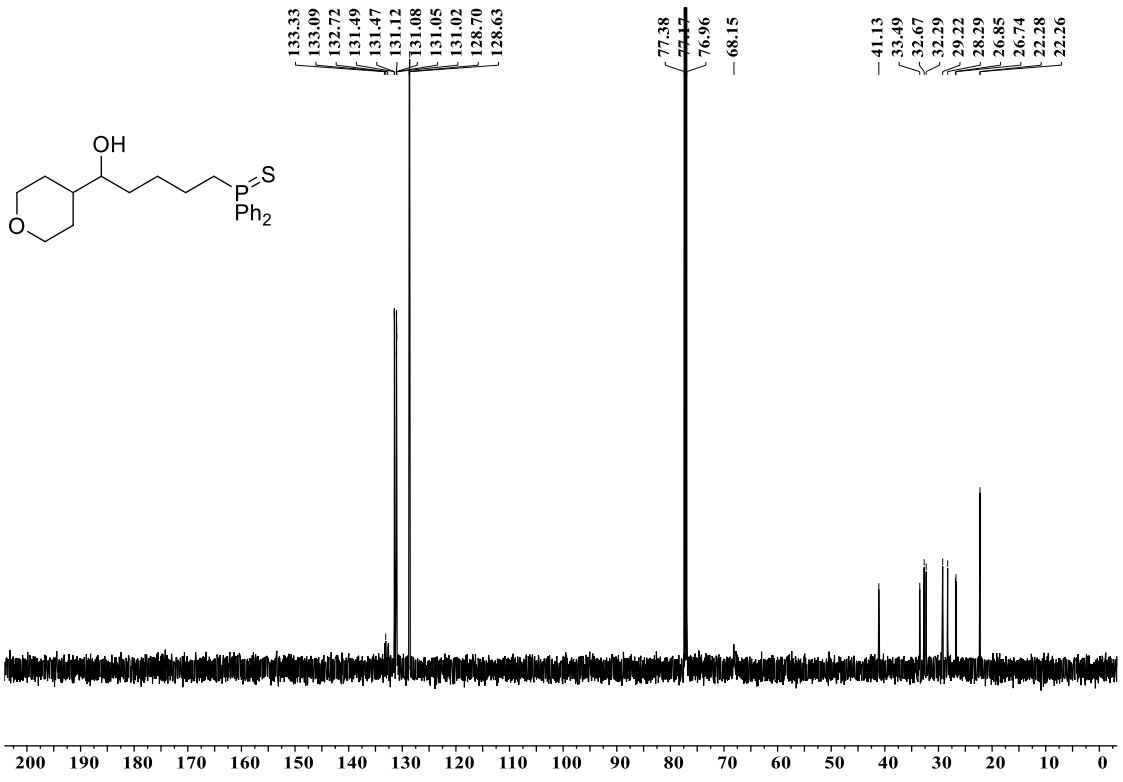
^{31}P NMR spectrum of **[S]-36** (243 MHz, $CDCl_3$)



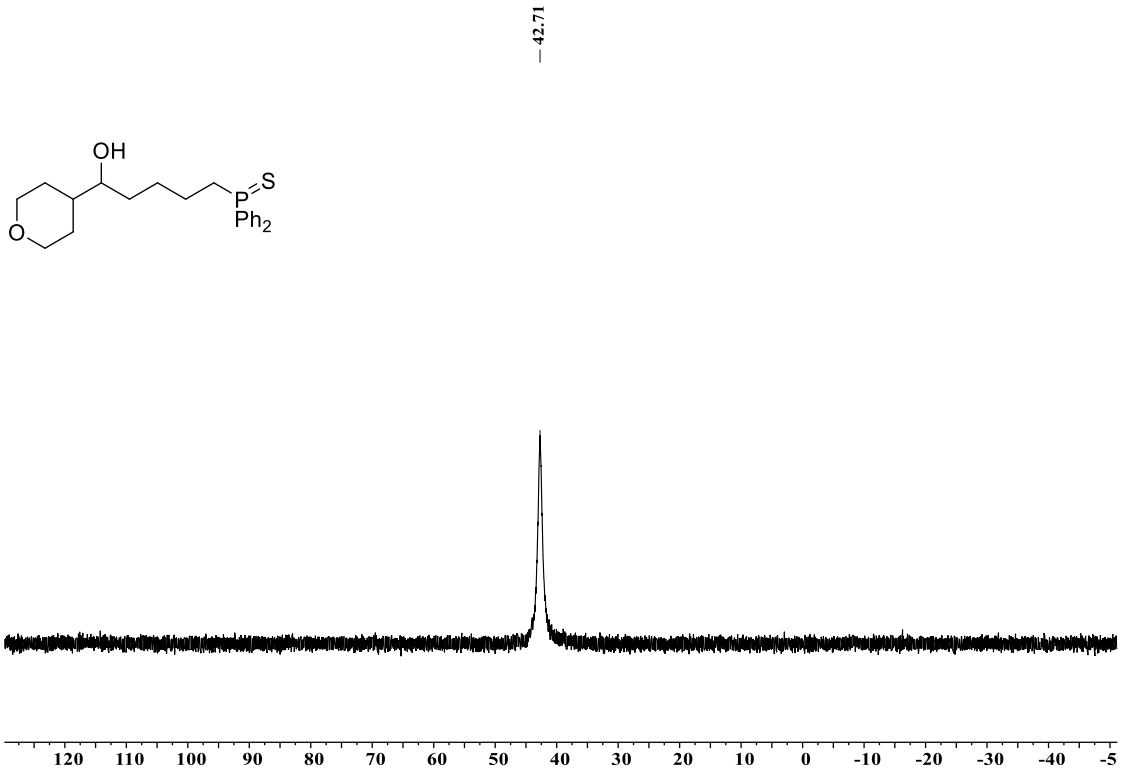
^{1}H NMR spectrum of **[S]-37** (600 MHz, $CDCl_3$)



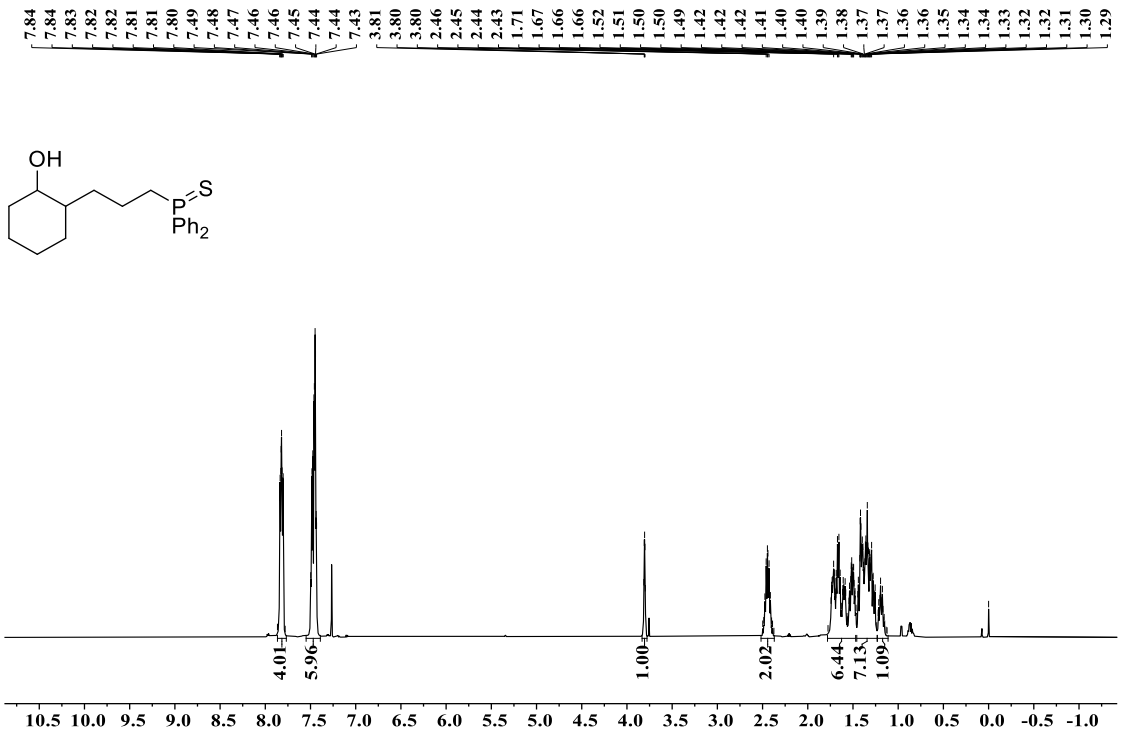
^{13}C NMR spectrum of **[S]-37** (150 MHz, $CDCl_3$)



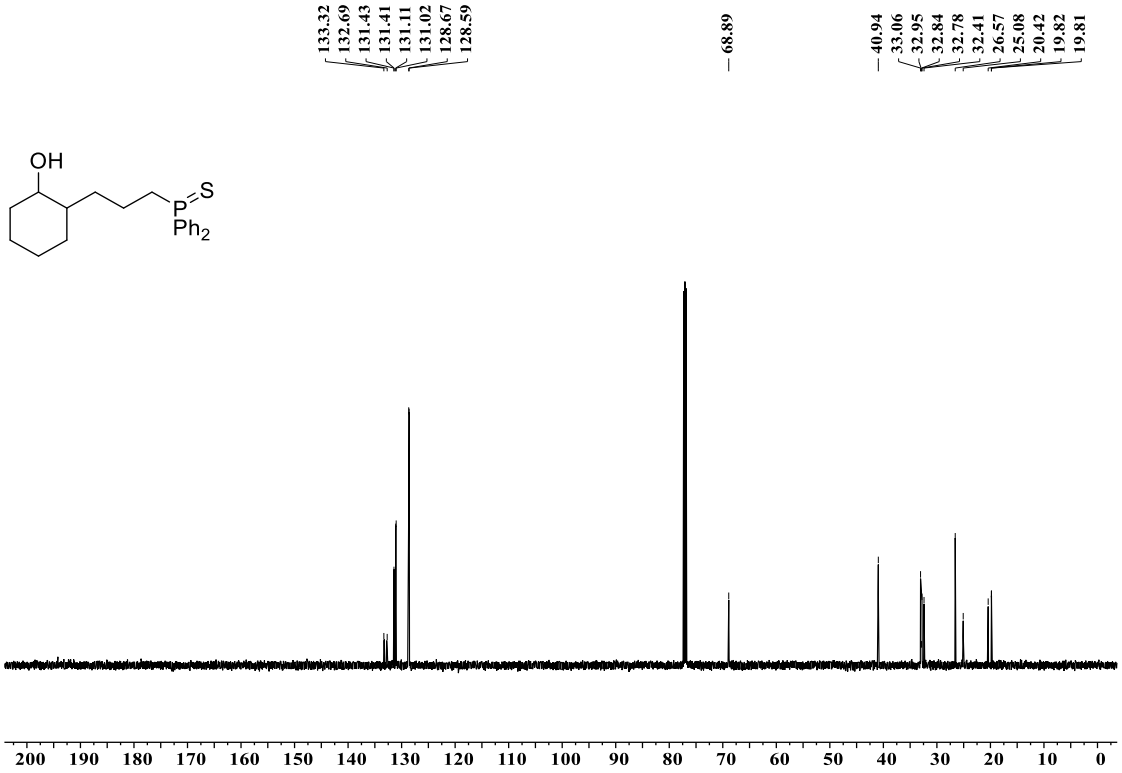
^{31}P NMR spectrum of **[S]-37** (243 MHz, $CDCl_3$)



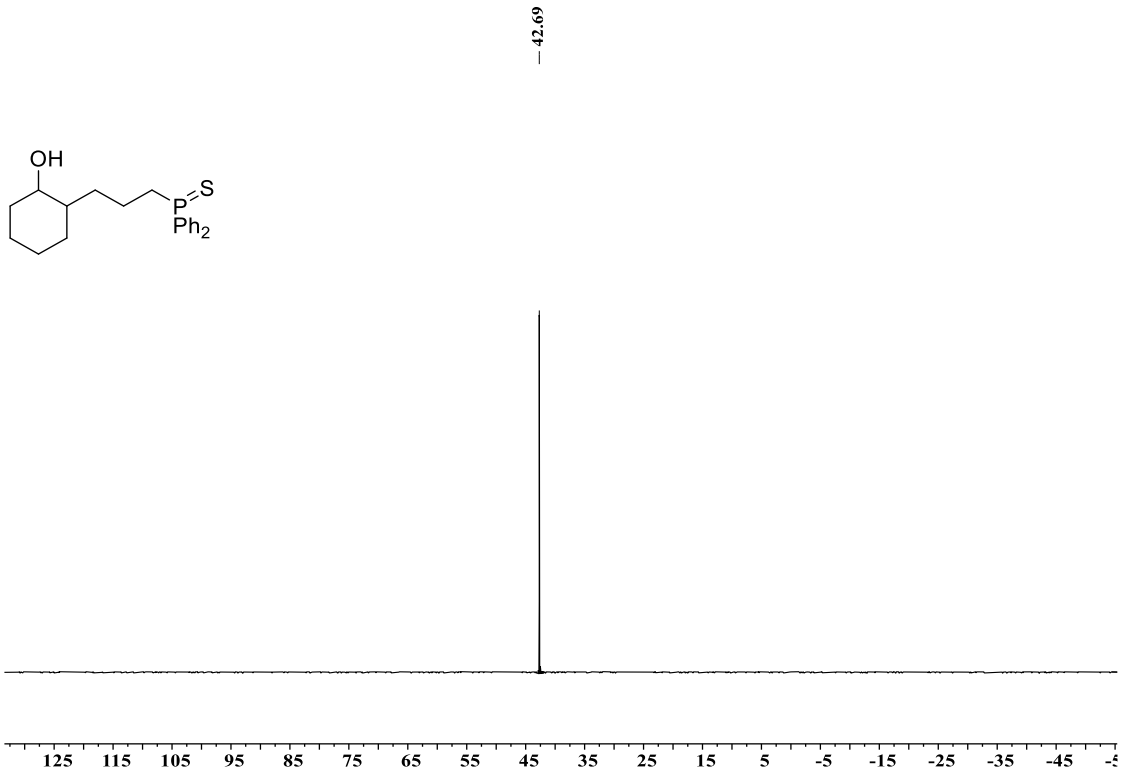
^{1}H NMR spectrum of **[S]-38** (Major diastereomer product) (600 MHz, $CDCl_3$)



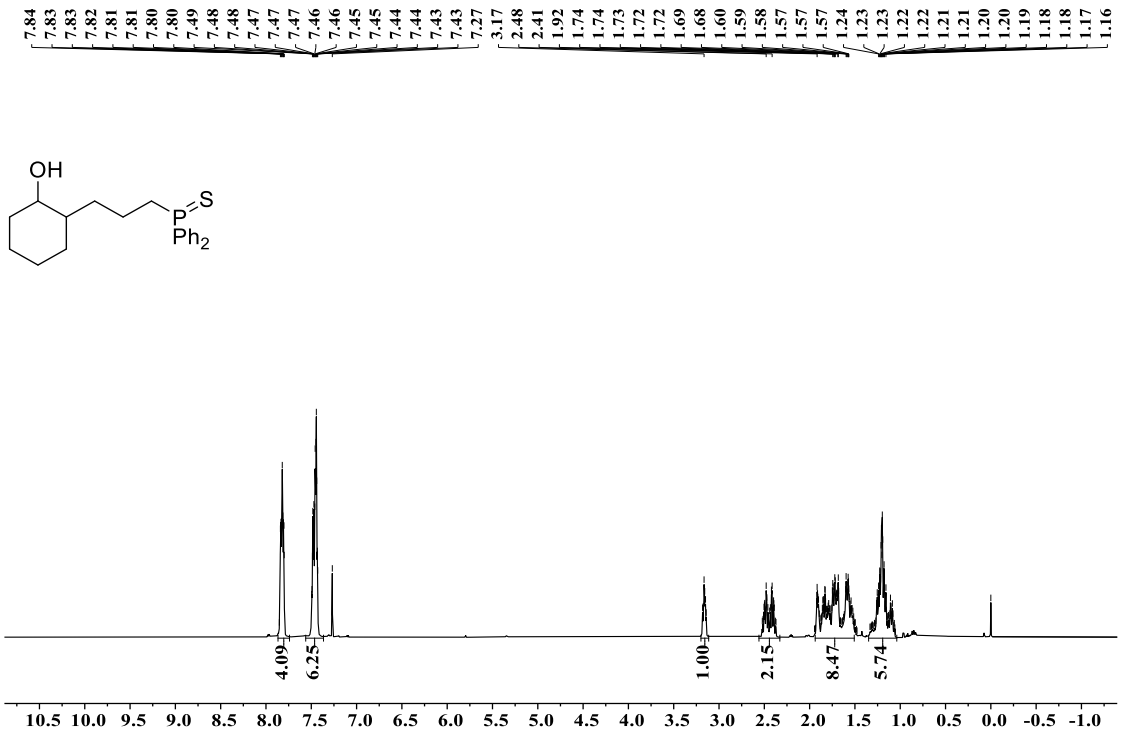
^{13}C NMR spectrum of **[S]-38** (Major diastereomer product) (150 MHz, $CDCl_3$)



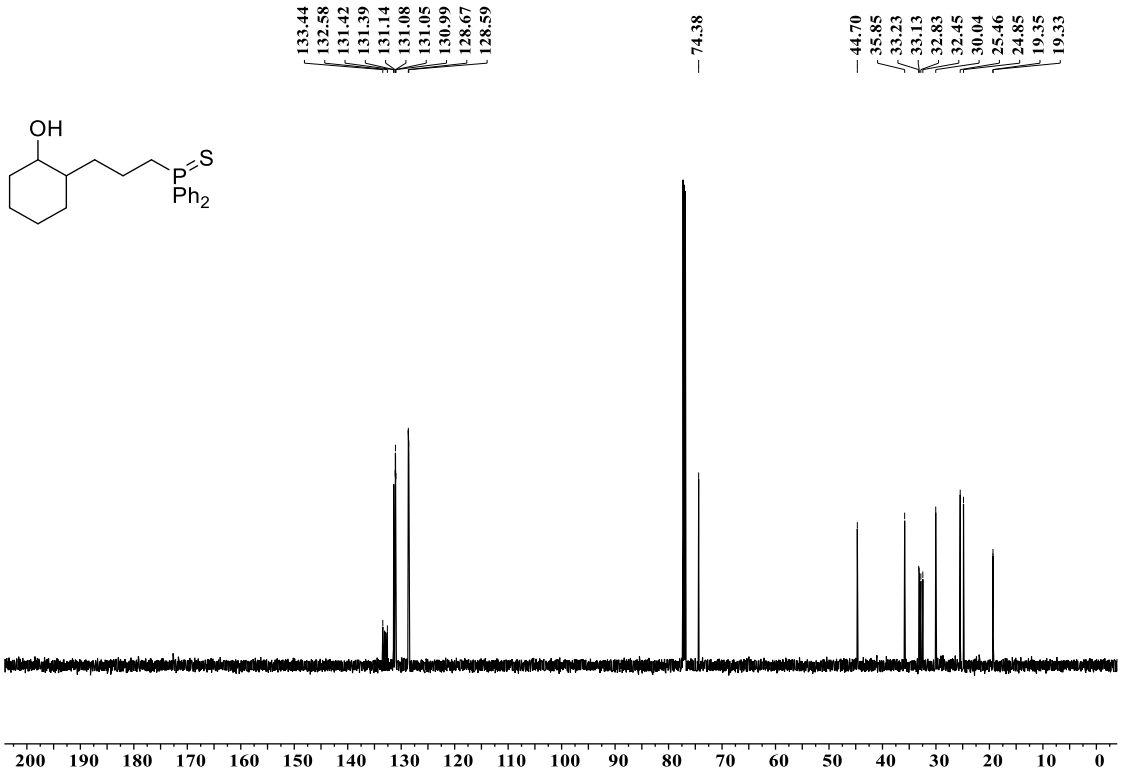
^{31}P NMR spectrum of **[S]-38** (Major diastereomer product) (243 MHz, $CDCl_3$)



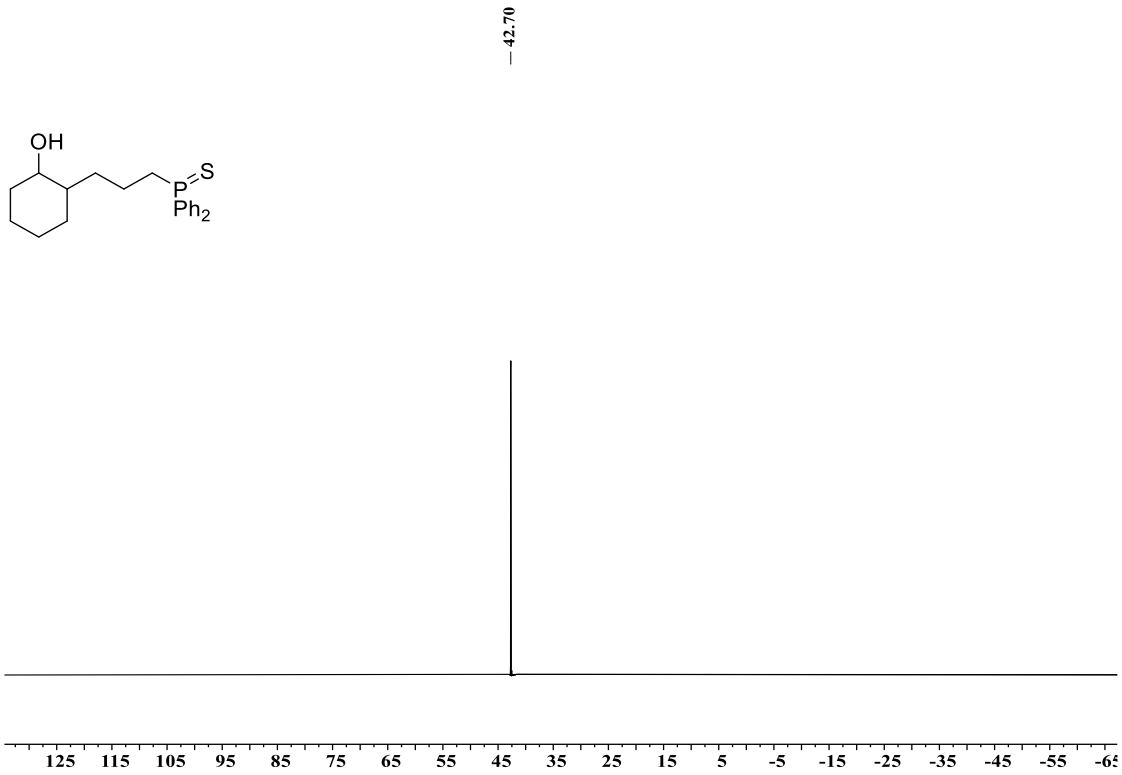
^{1}H NMR spectrum of **[S]-38** (Minor diastereomer product) (600 MHz, $CDCl_3$)



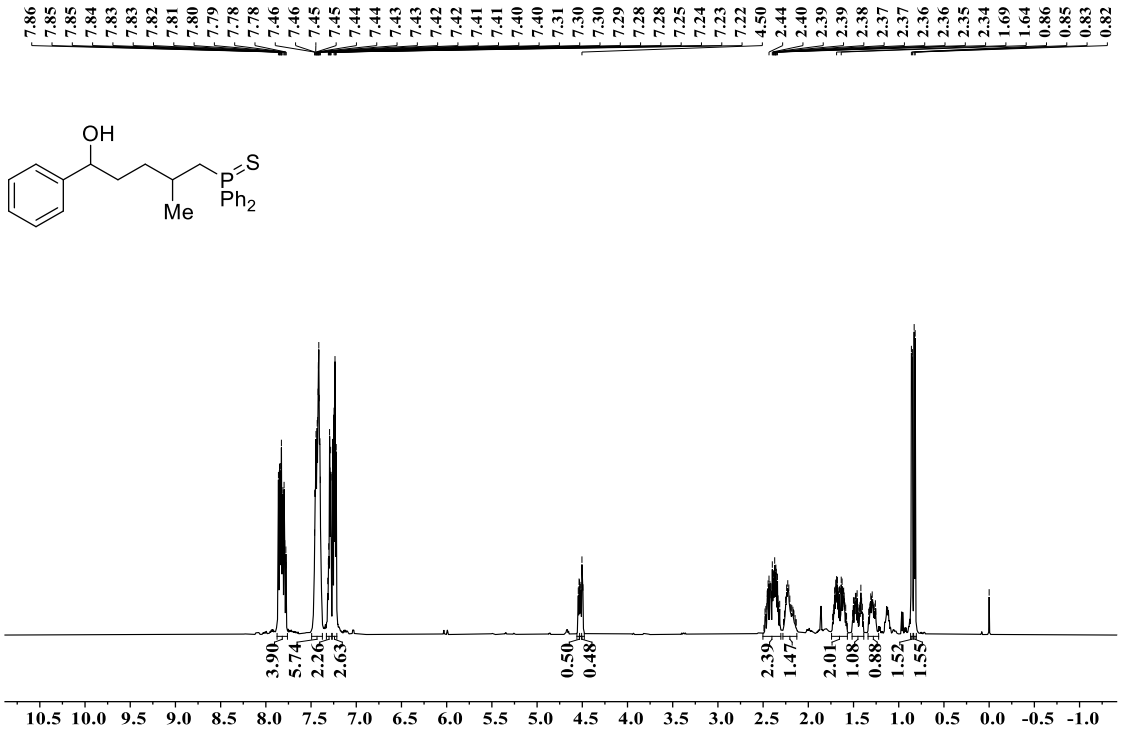
^{13}C NMR spectrum of **[S]-38** (Minor diastereomer product) (150 MHz, $CDCl_3$)



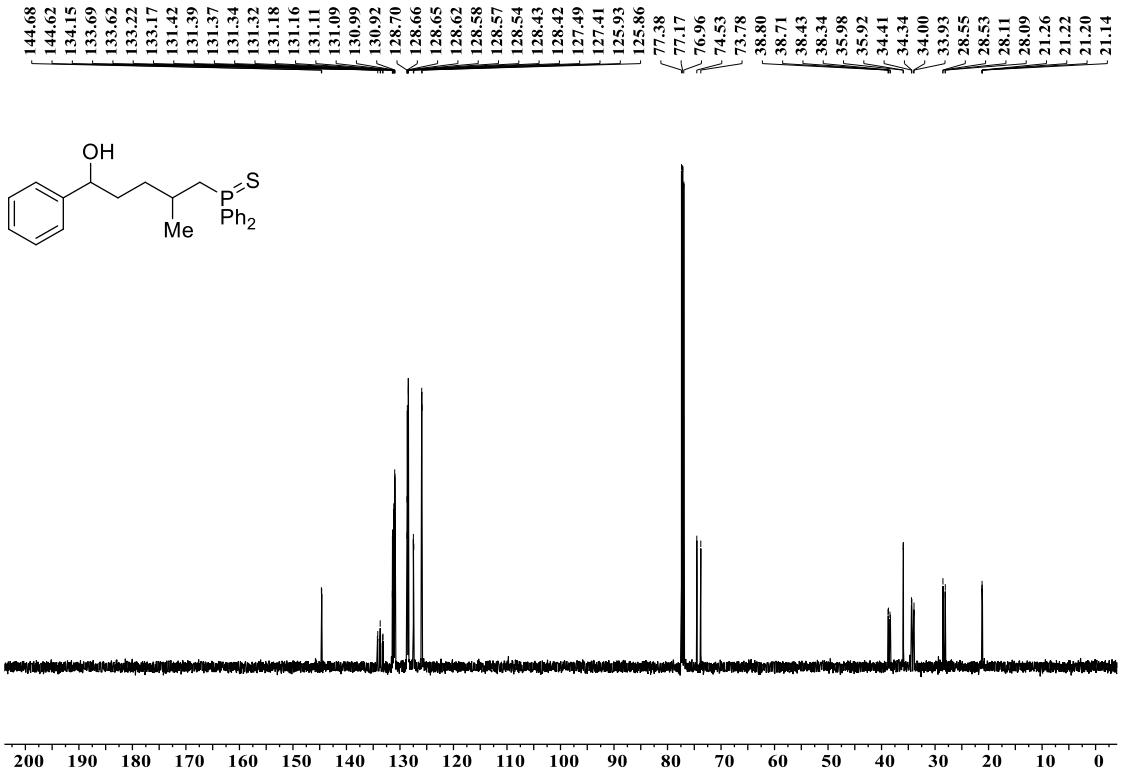
^{31}P NMR spectrum of **[S]-38** (Minor diastereomer product) (243 MHz, $CDCl_3$)



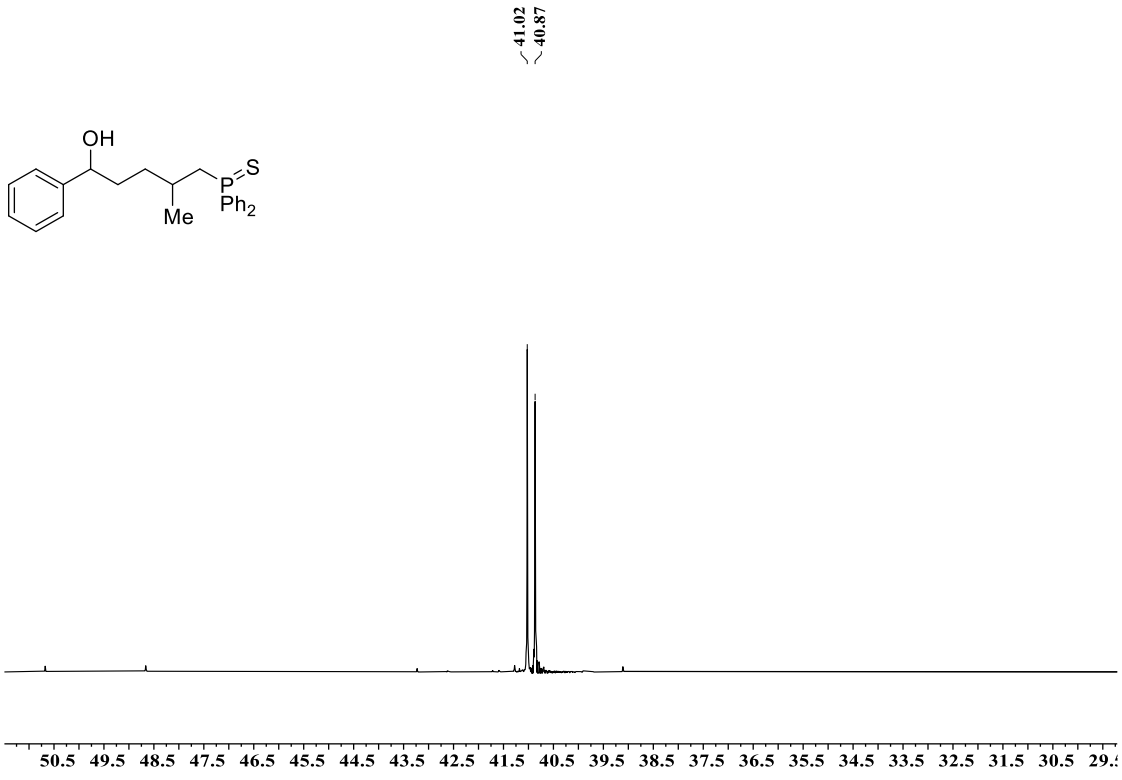
^{1}H NMR spectrum of **[S]-39** (600 MHz, $CDCl_3$)



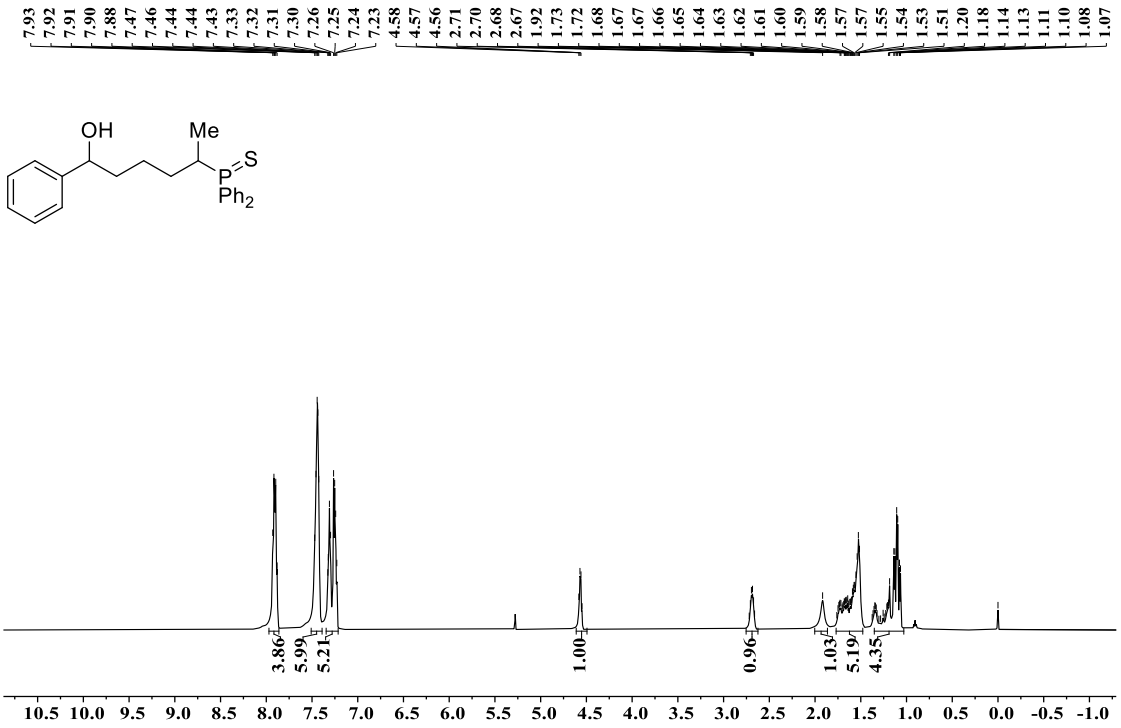
^{13}C NMR spectrum of **[S]-39** (150 MHz, $CDCl_3$)



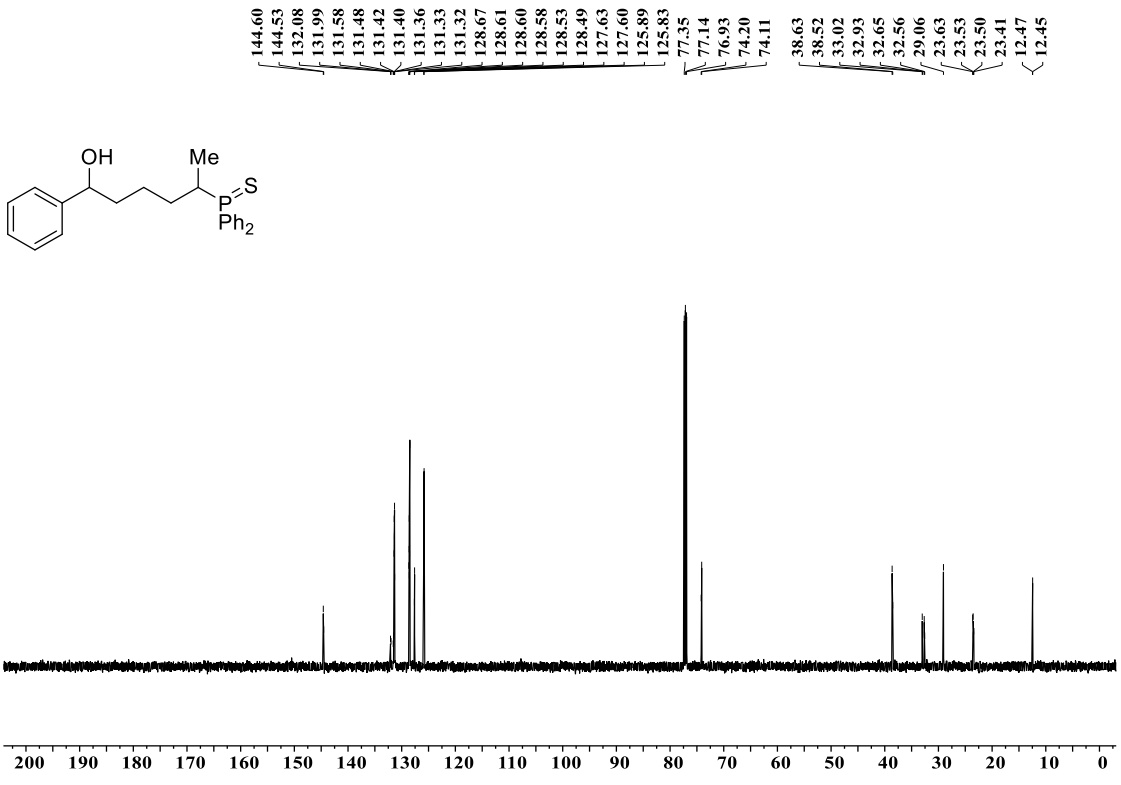
^{31}P NMR spectrum of **[S]-39** (243 MHz, $CDCl_3$)



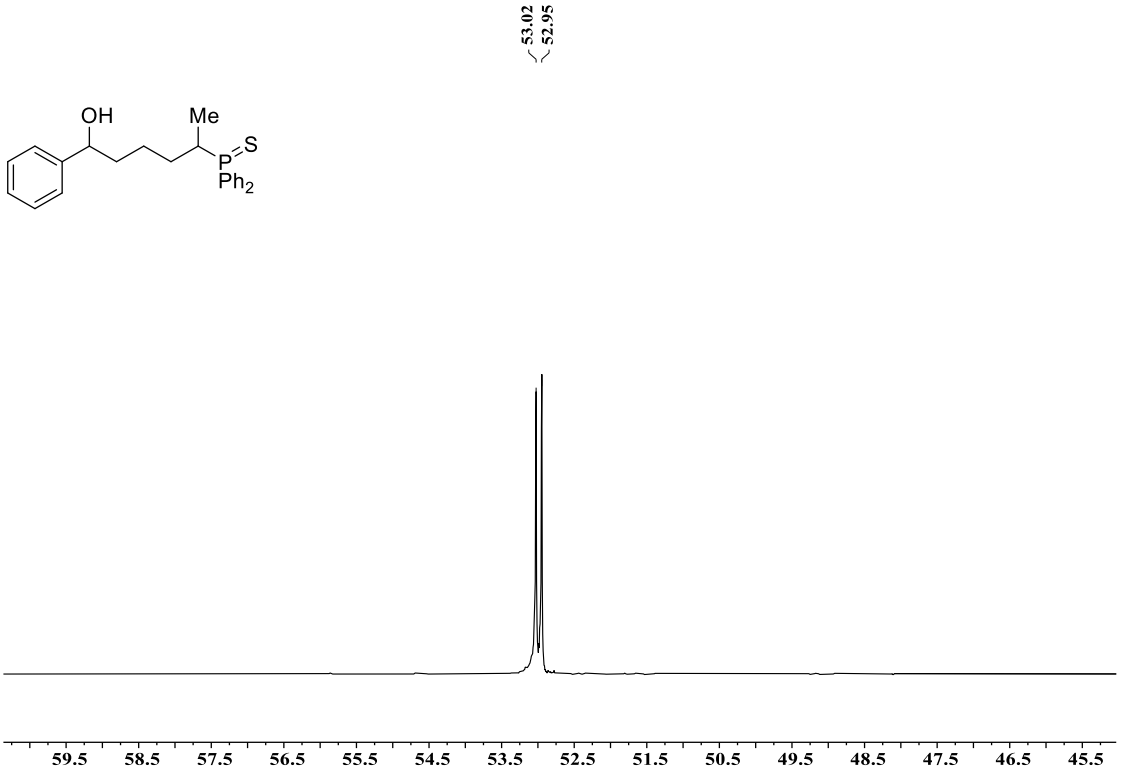
^{1}H NMR spectrum of **[S]-40** (600 MHz, $CDCl_3$)



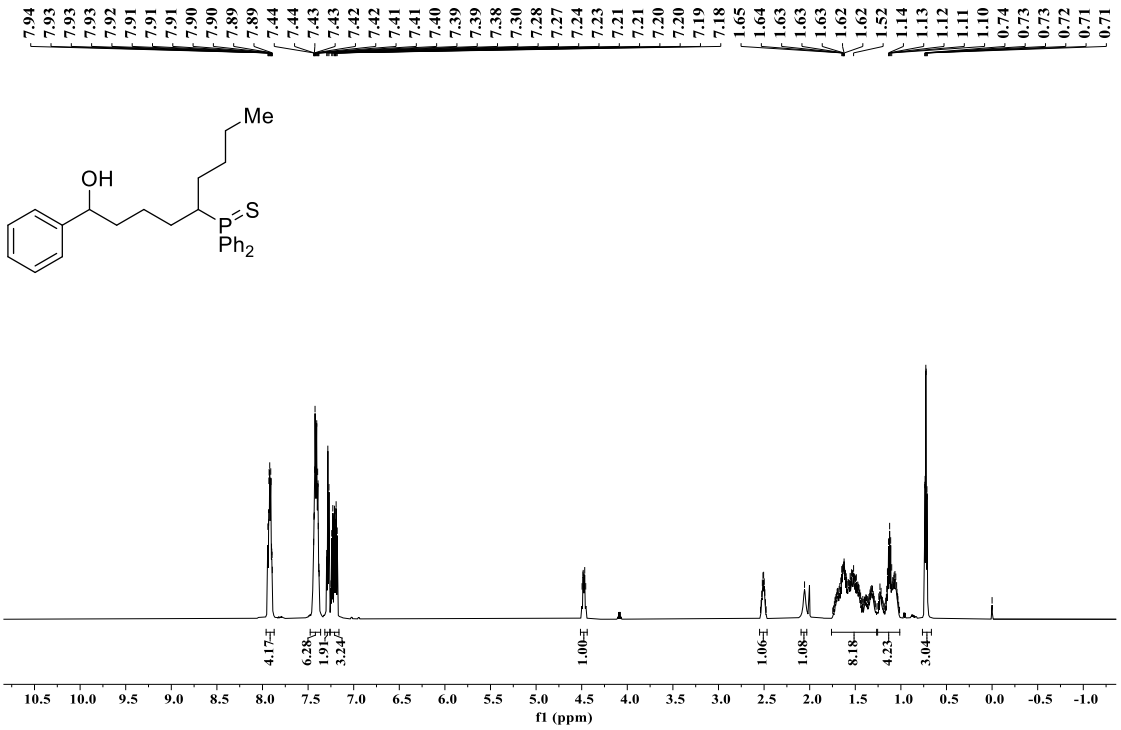
^{13}C NMR spectrum of **[S]-40** (150 MHz, $CDCl_3$)



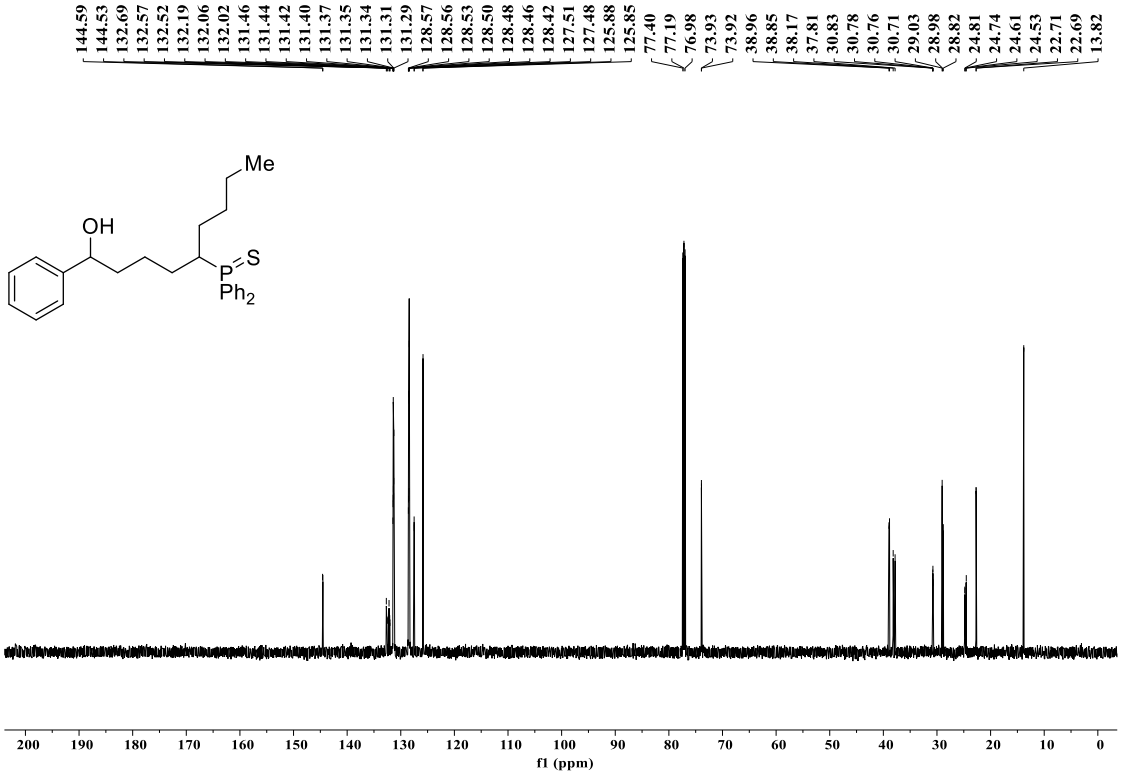
^{31}P NMR spectrum of **[S]-40** (243 MHz, $CDCl_3$)



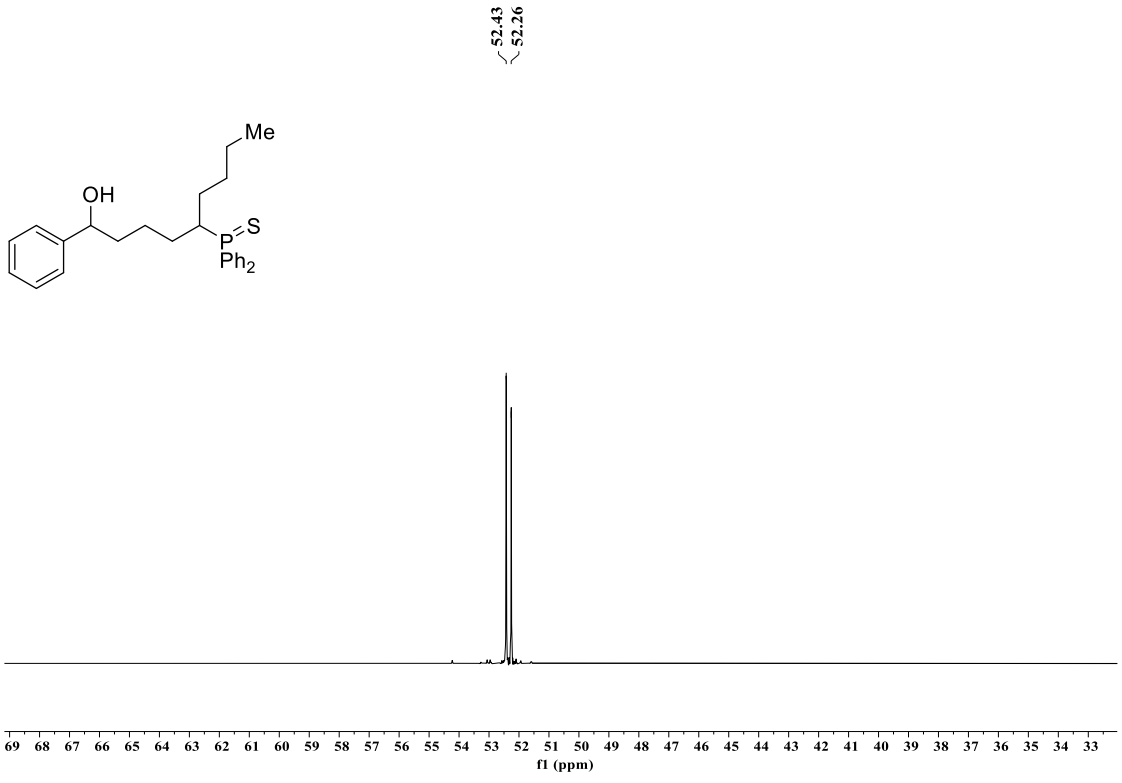
^{1}H NMR spectrum of **[S]-41** (600 MHz, $CDCl_3$)



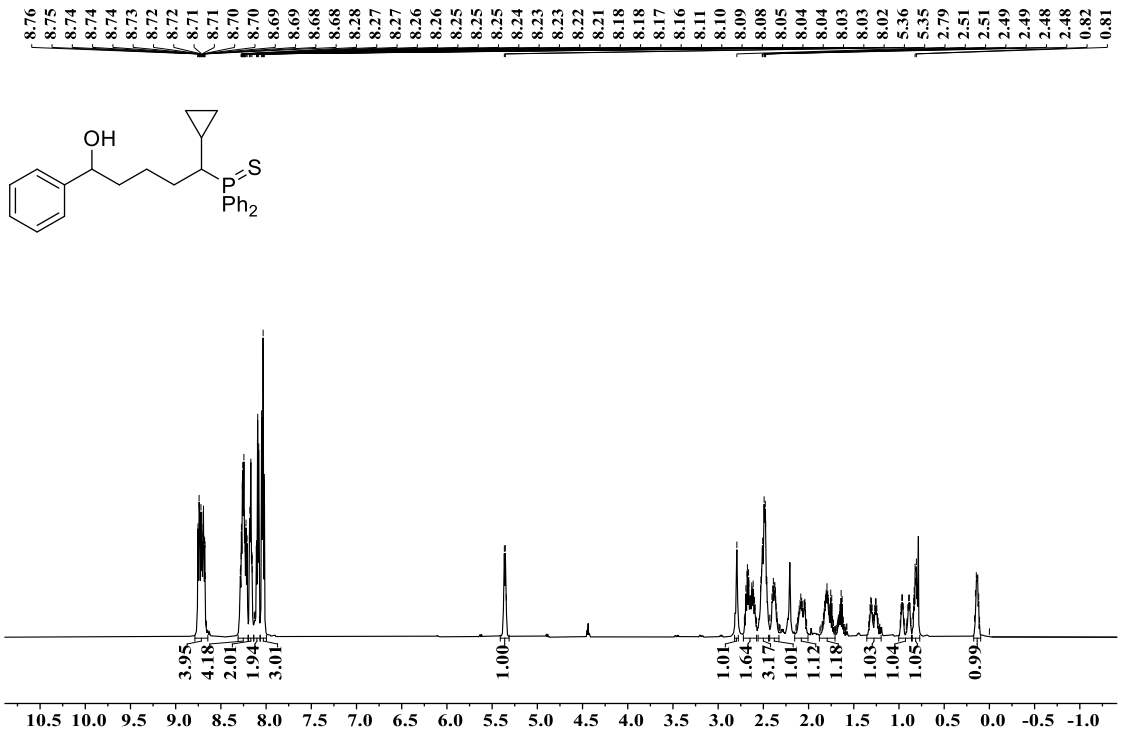
^{13}C NMR spectrum of **[S]-41** (150 MHz, $CDCl_3$)



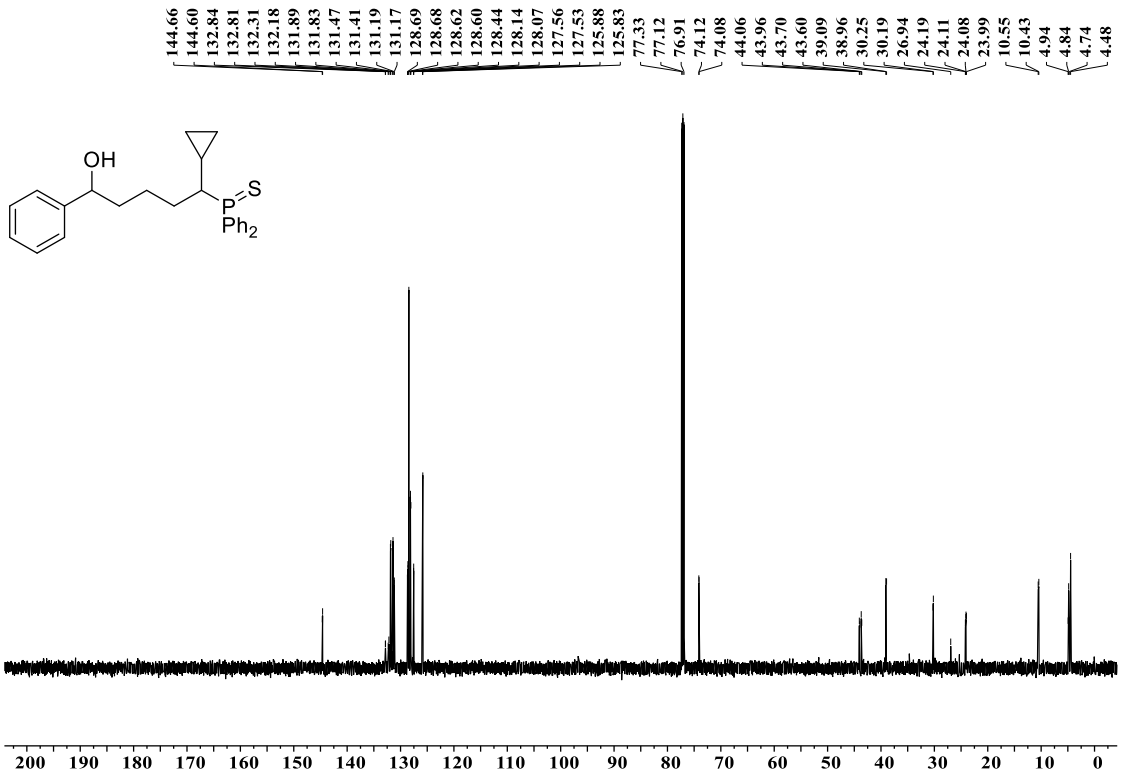
^{31}P NMR spectrum of **[S]-41** (243 MHz, $CDCl_3$)



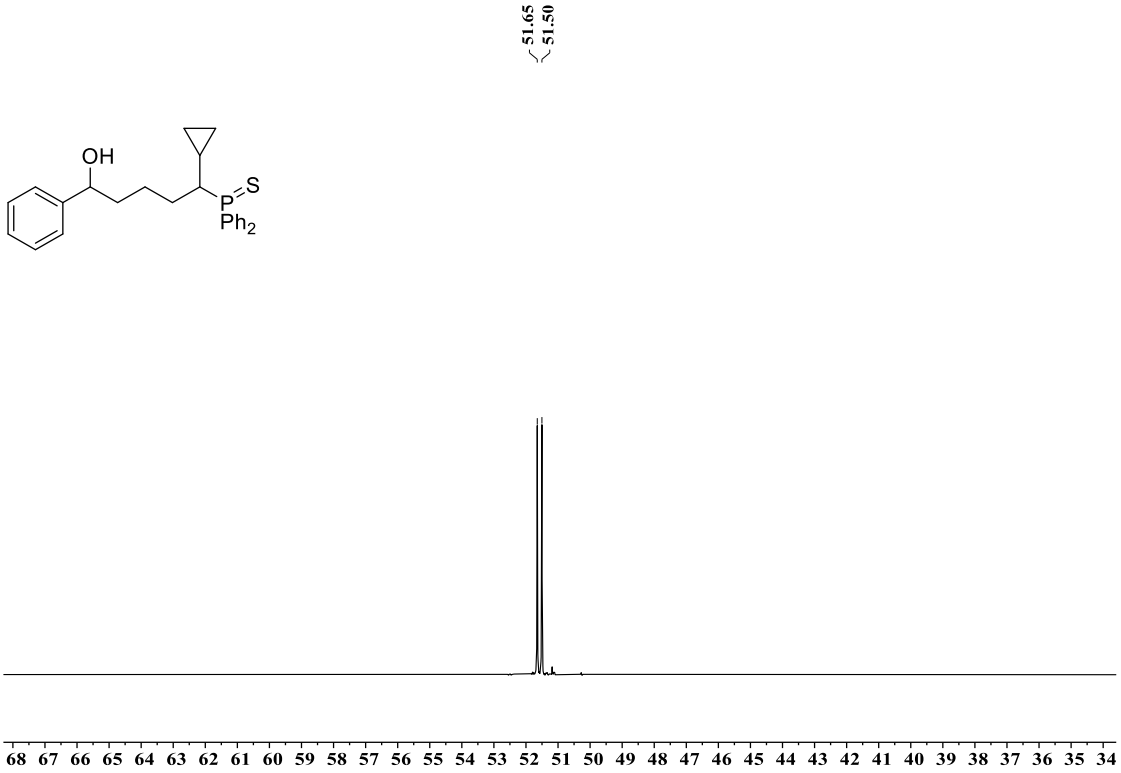
^{1}H NMR spectrum of **[S]-42** (600 MHz, $CDCl_3$)



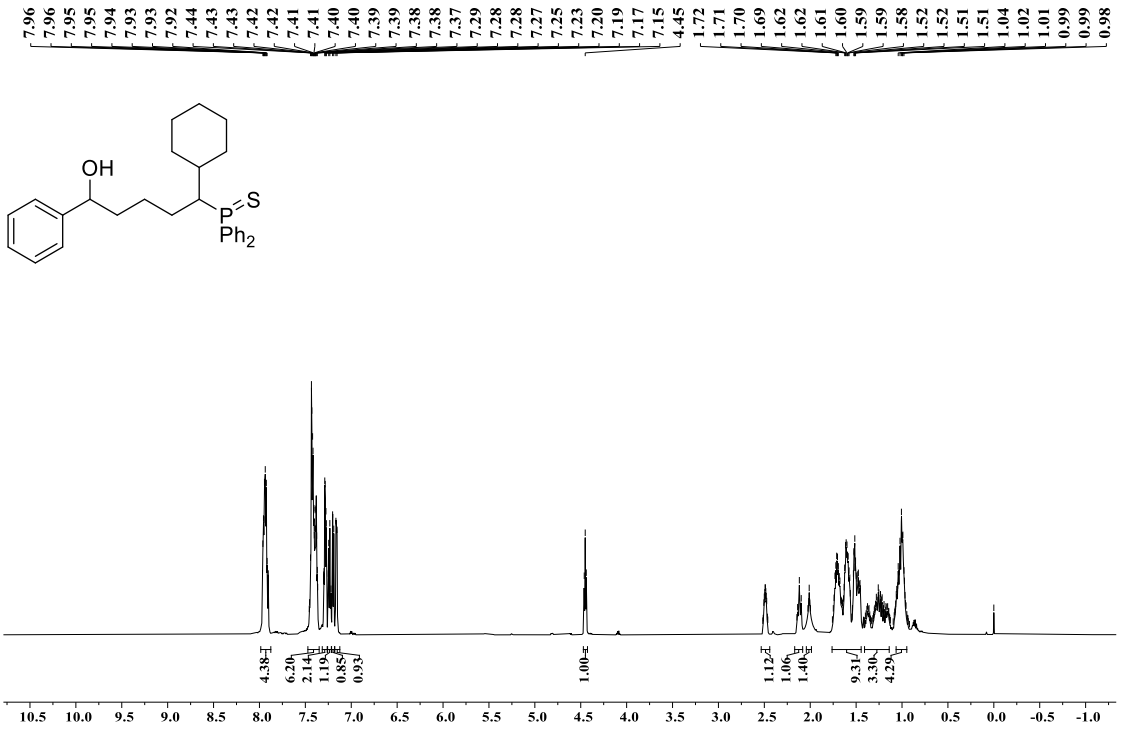
^{13}C NMR spectrum of **[S]-42** (150 MHz, $CDCl_3$)



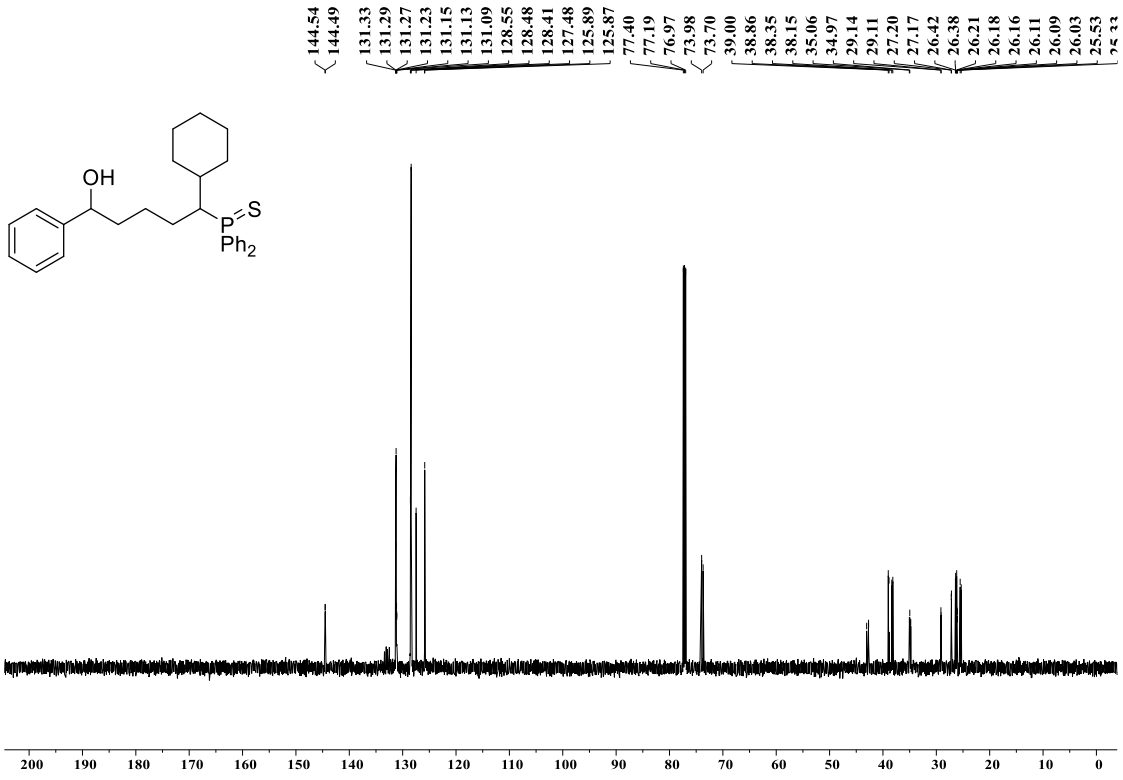
^{31}P NMR spectrum of **[S]-42** (243 MHz, $CDCl_3$)



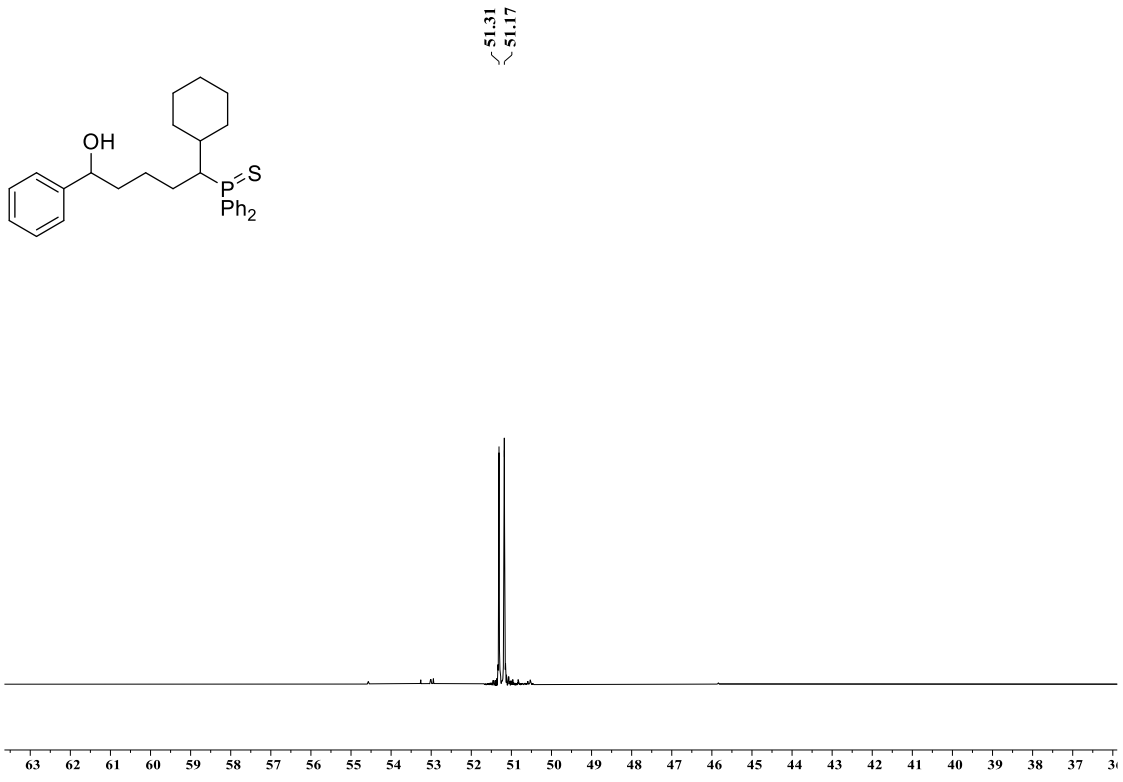
^{1}H NMR spectrum of **[S]-43** (600 MHz, $CDCl_3$)



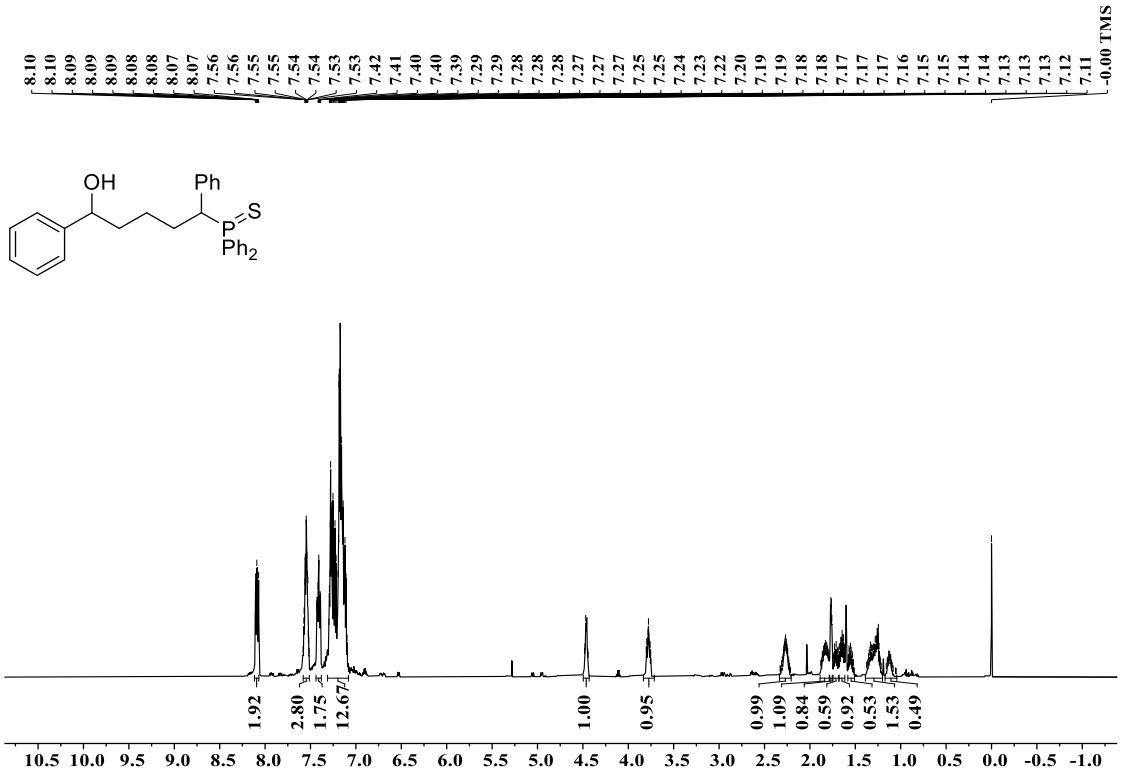
^{13}C NMR spectrum of **[S]-43** (150 MHz, $CDCl_3$)



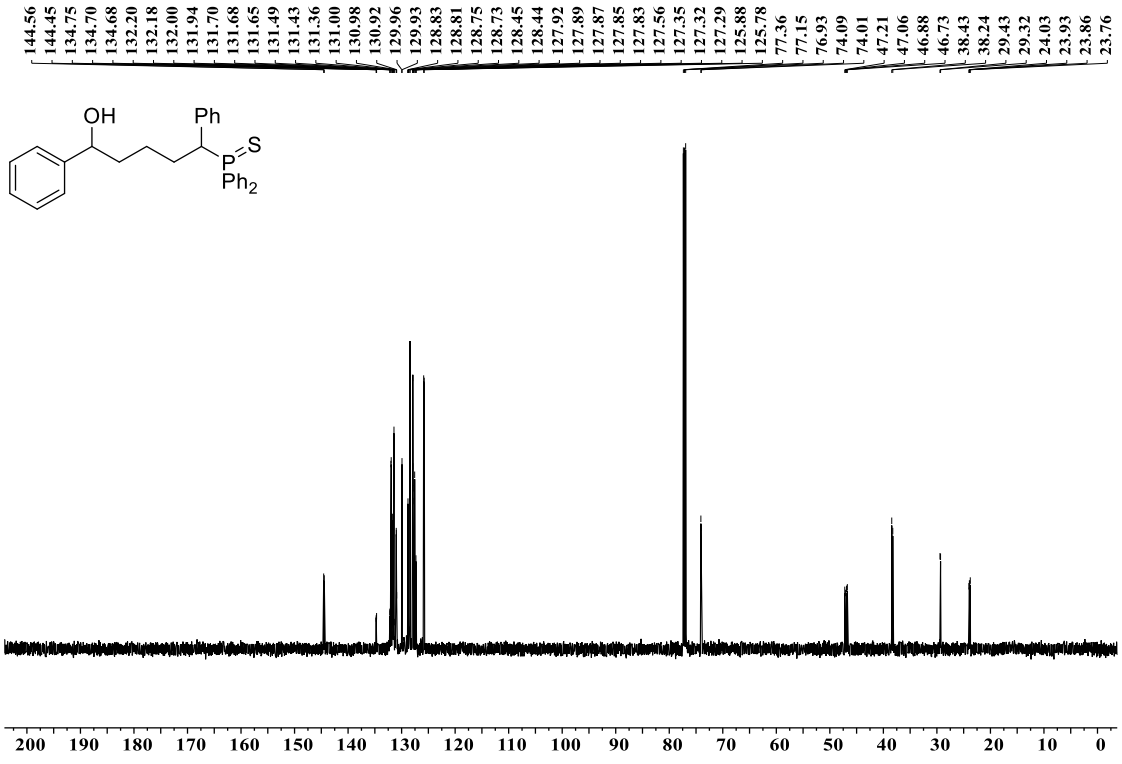
^{31}P NMR spectrum of **[S]-43** (243 MHz, $CDCl_3$)



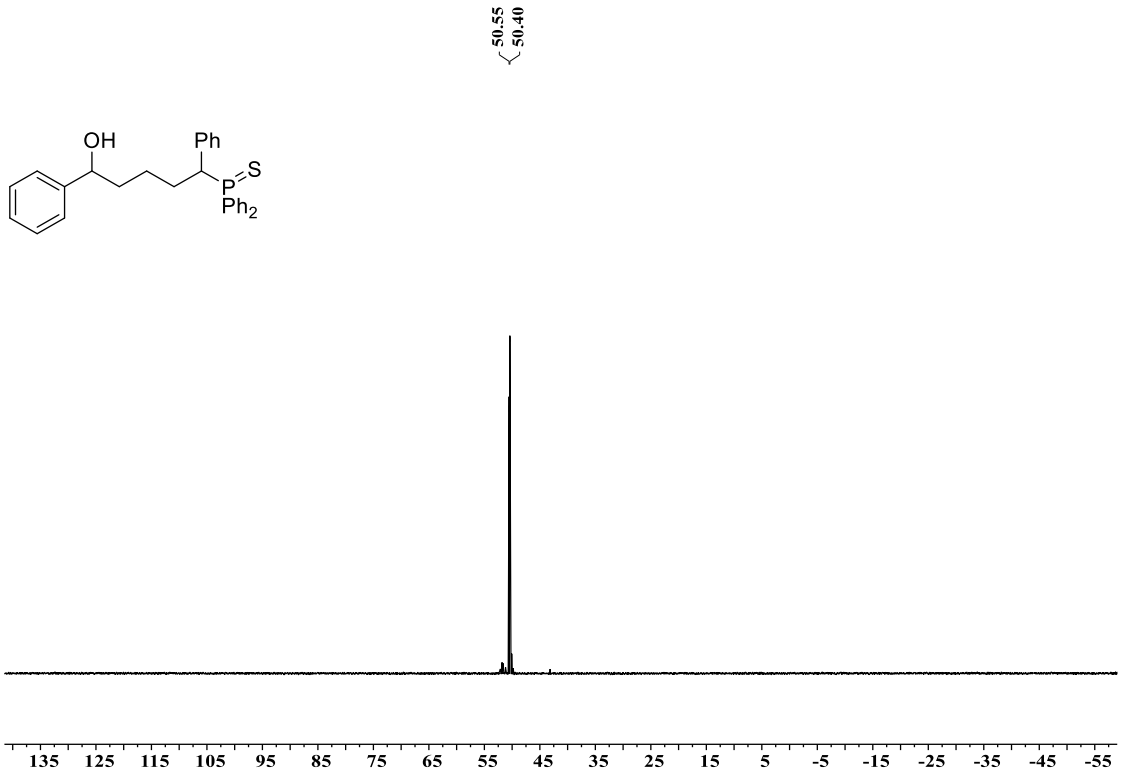
^{1}H NMR spectrum of **[S]-44** (600 MHz, $CDCl_3$)



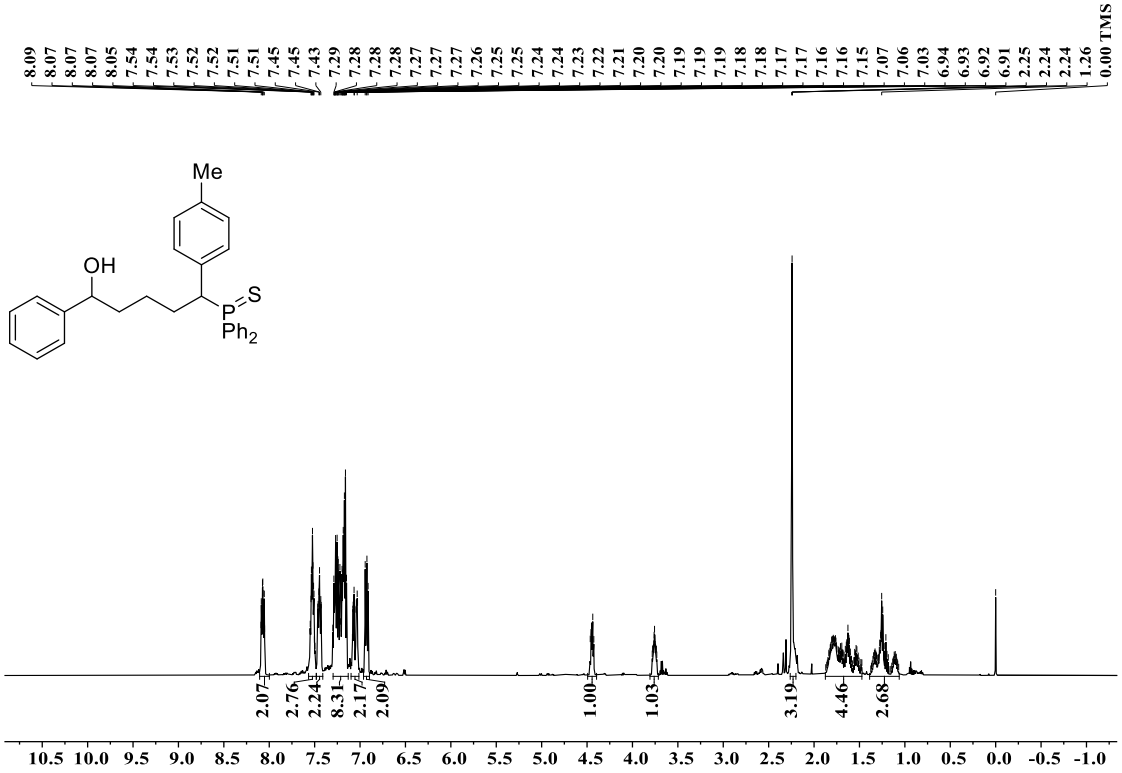
^{13}C NMR spectrum of **[S]-44** (150 MHz, $CDCl_3$)



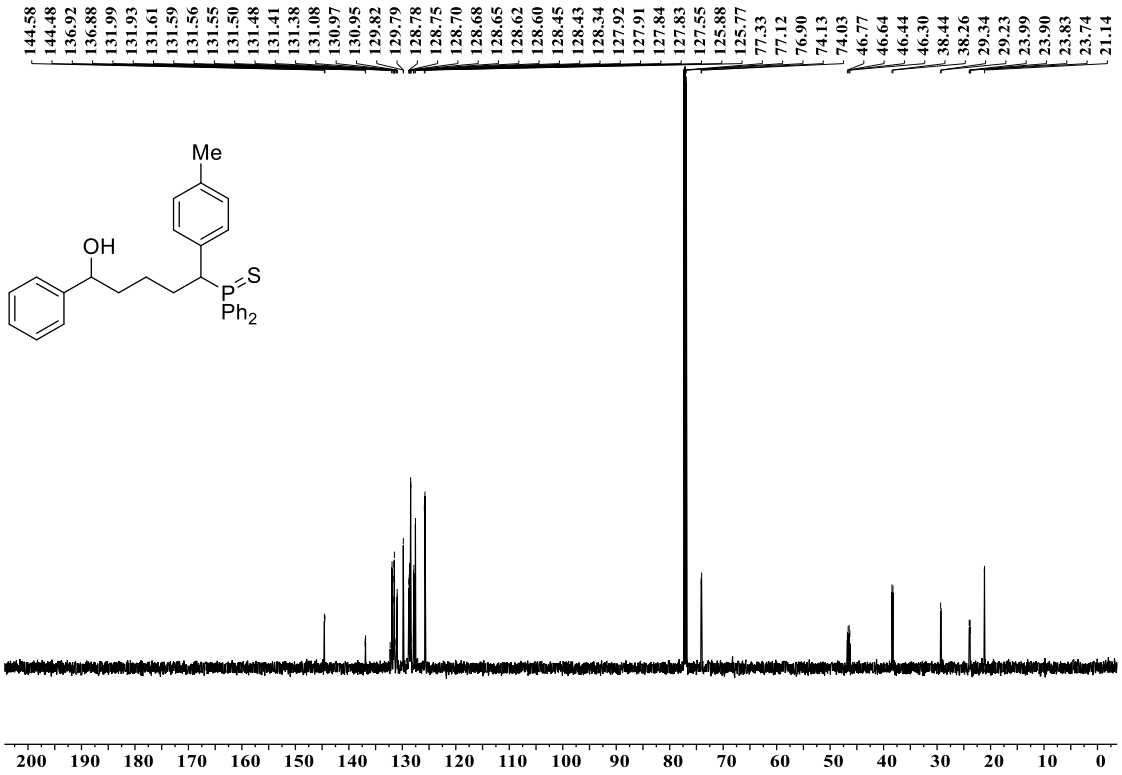
^{31}P NMR spectrum of **[S]-44** (243 MHz, $CDCl_3$)



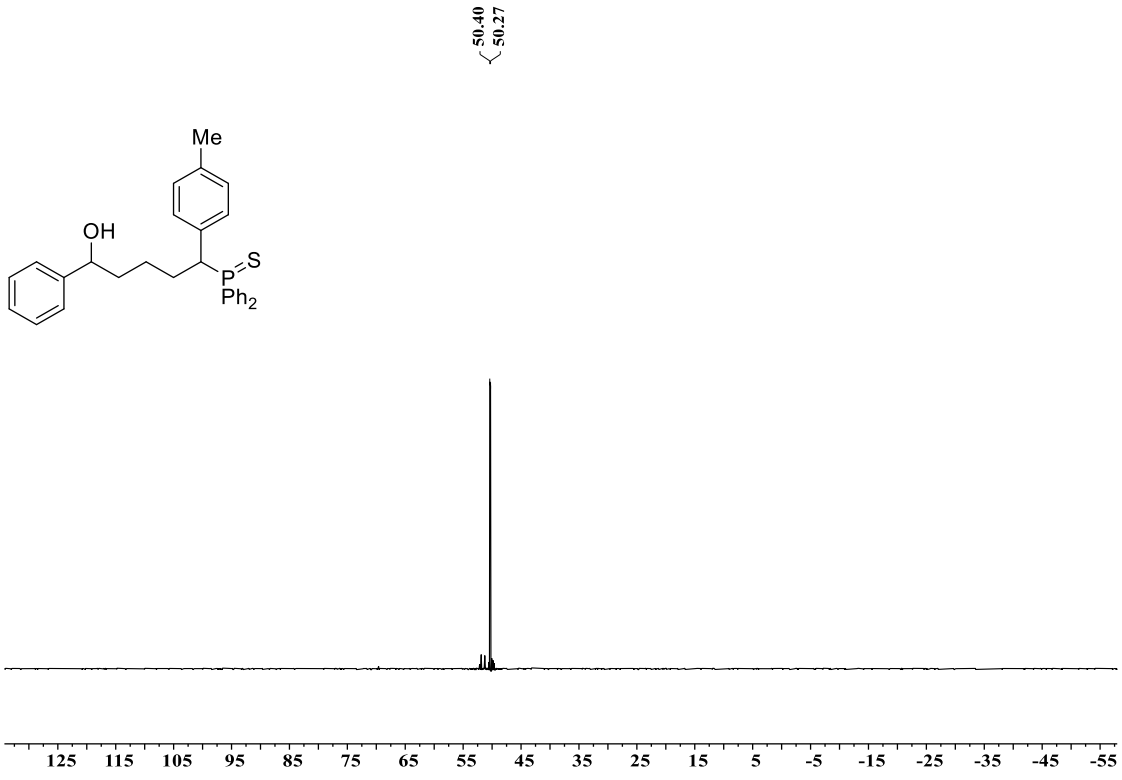
^{1}H NMR spectrum of **[S]-45** (600 MHz, $CDCl_3$)



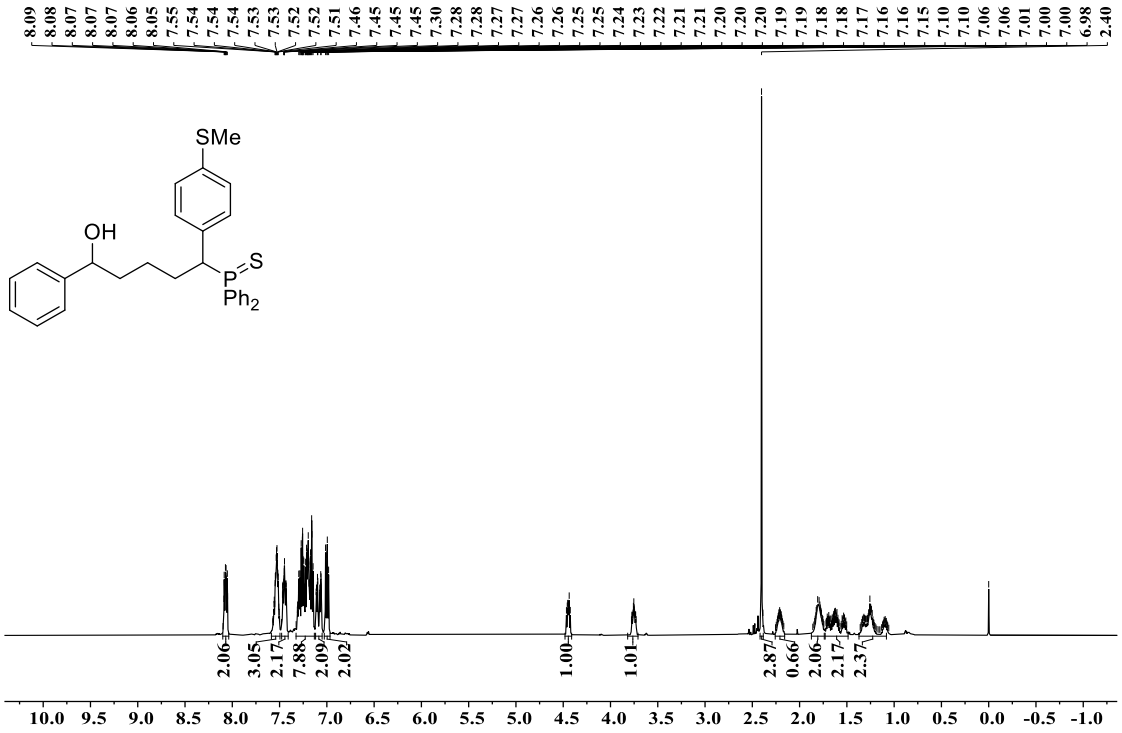
^{13}C NMR spectrum of **[S]-45** (150 MHz, $CDCl_3$)



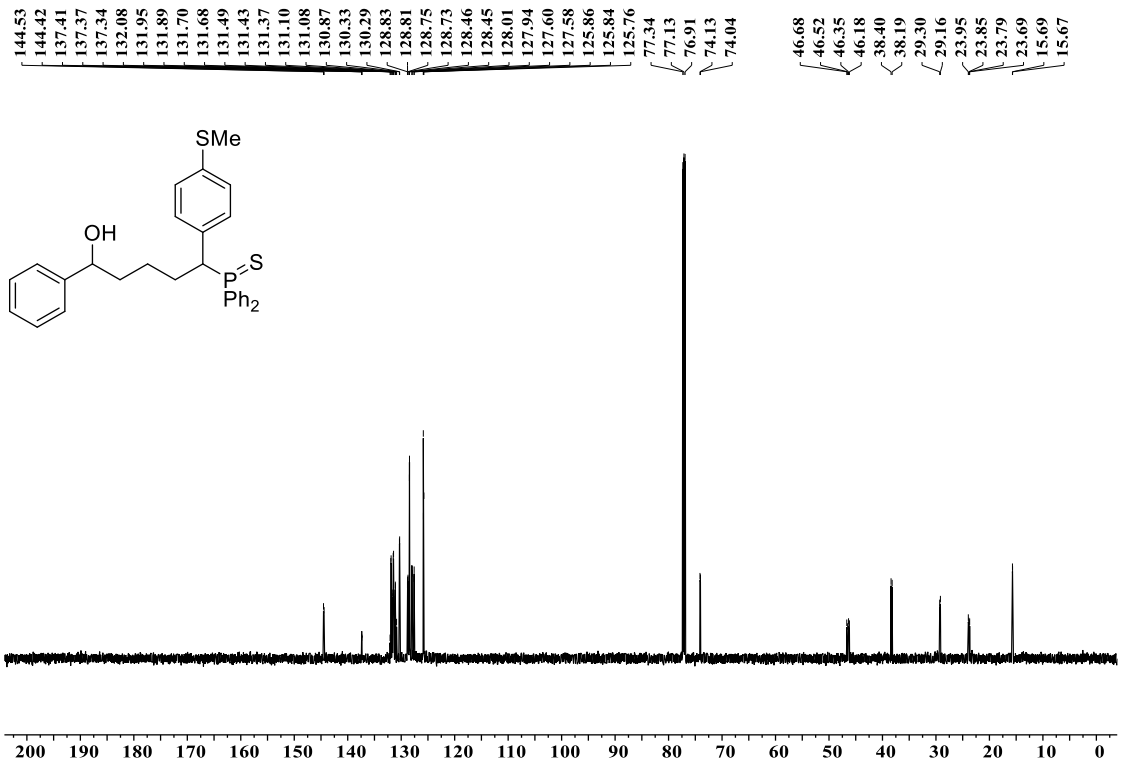
^{31}P NMR spectrum of **[S]-45** (243 MHz, $CDCl_3$)



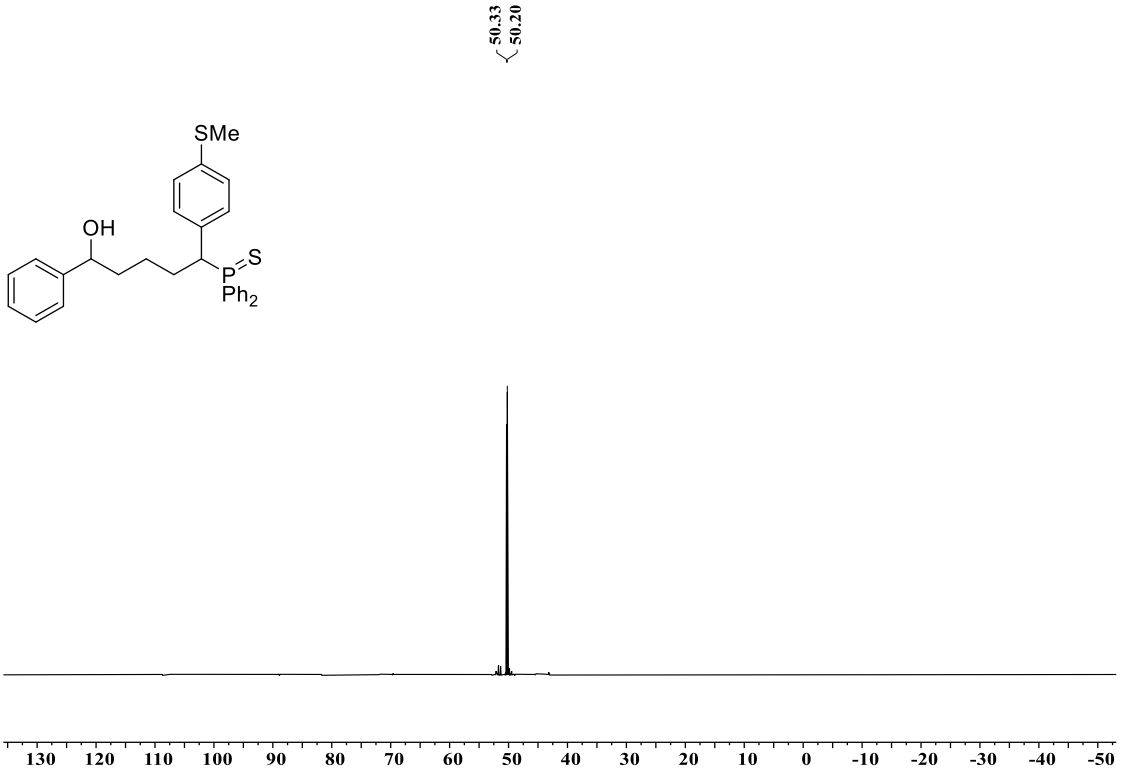
^{1}H NMR spectrum of **[S]-46** (600 MHz, $CDCl_3$)



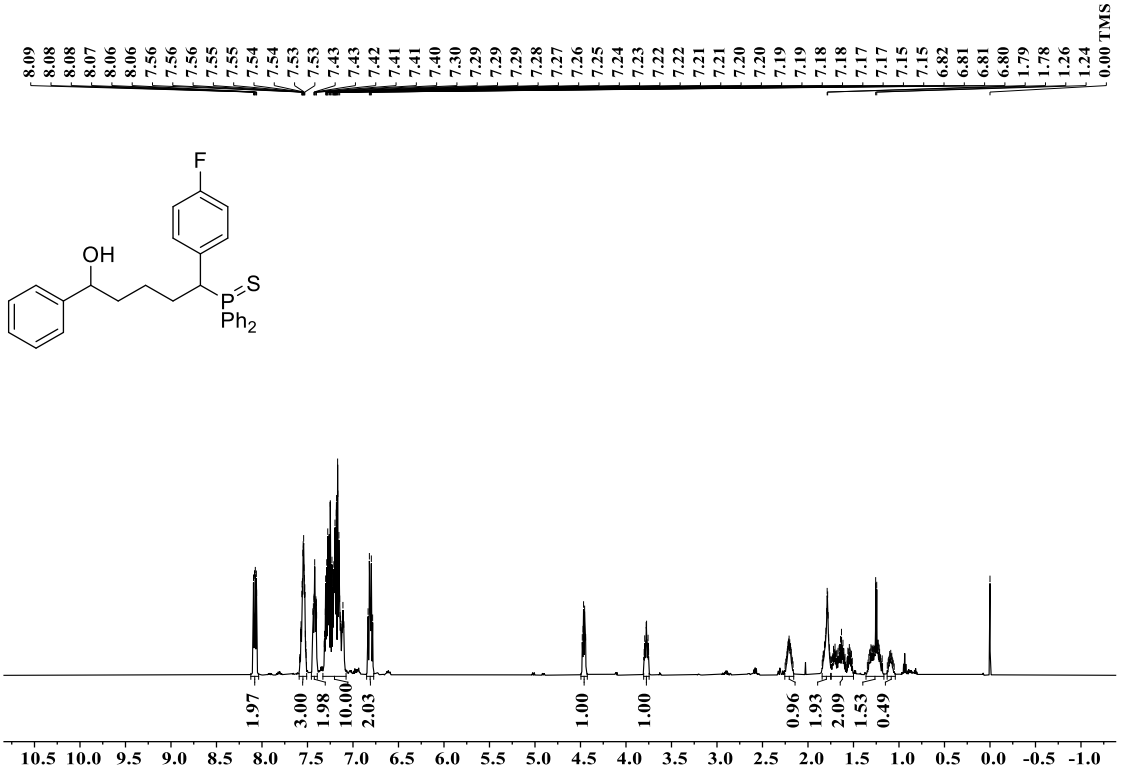
^{13}C NMR spectrum of **[S]-46** (150 MHz, $CDCl_3$)



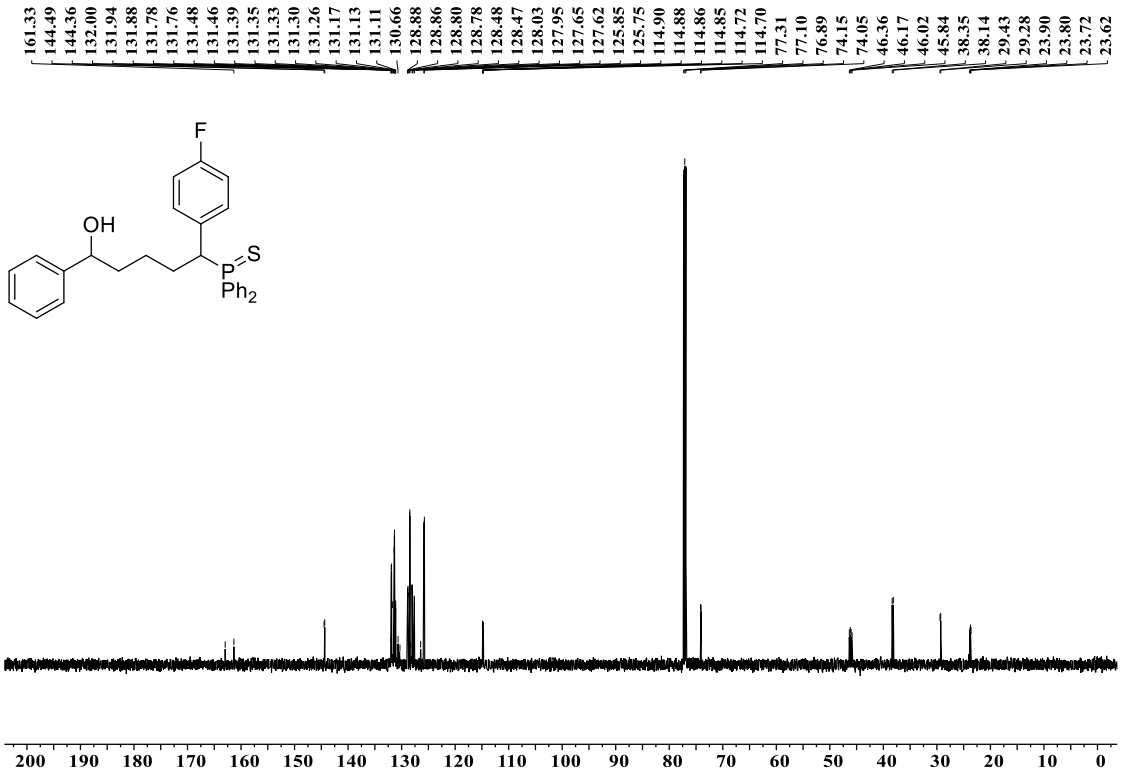
^{31}P NMR spectrum of **[S]-46** (243 MHz, $CDCl_3$)



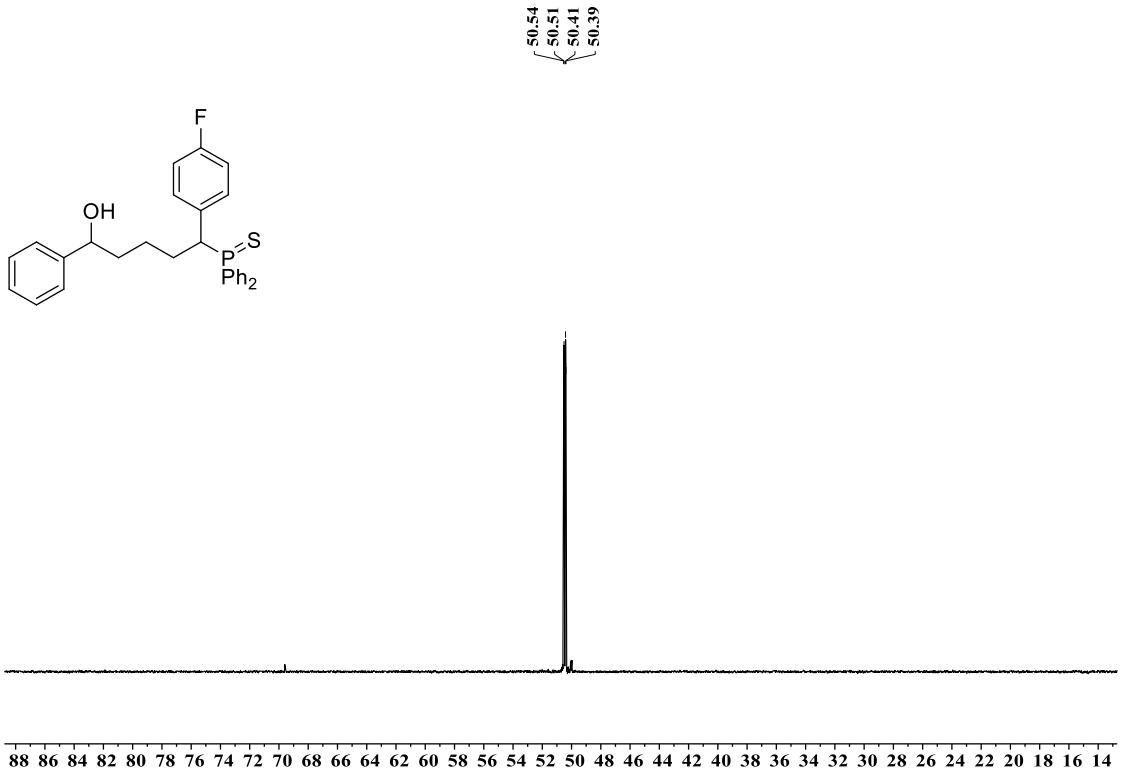
^{1}H NMR spectrum of **[S]-47** (600 MHz, $CDCl_3$)



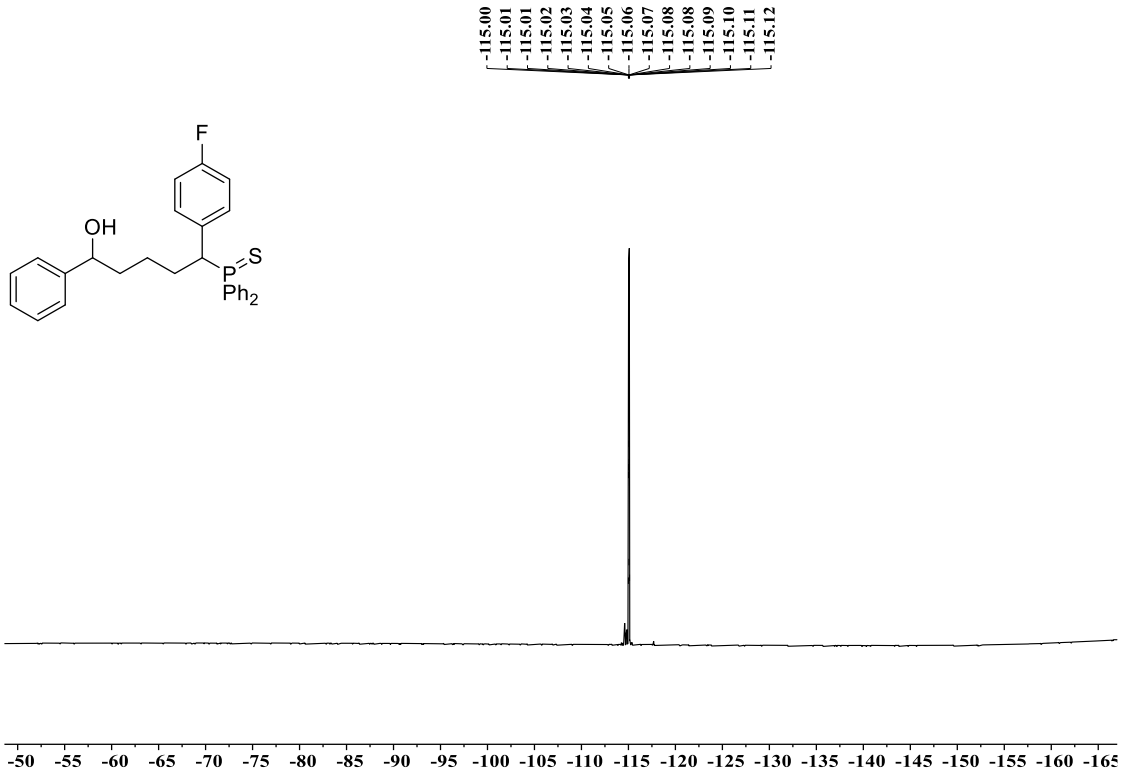
^{13}C NMR spectrum of **[S]-47** (150 MHz, $CDCl_3$)



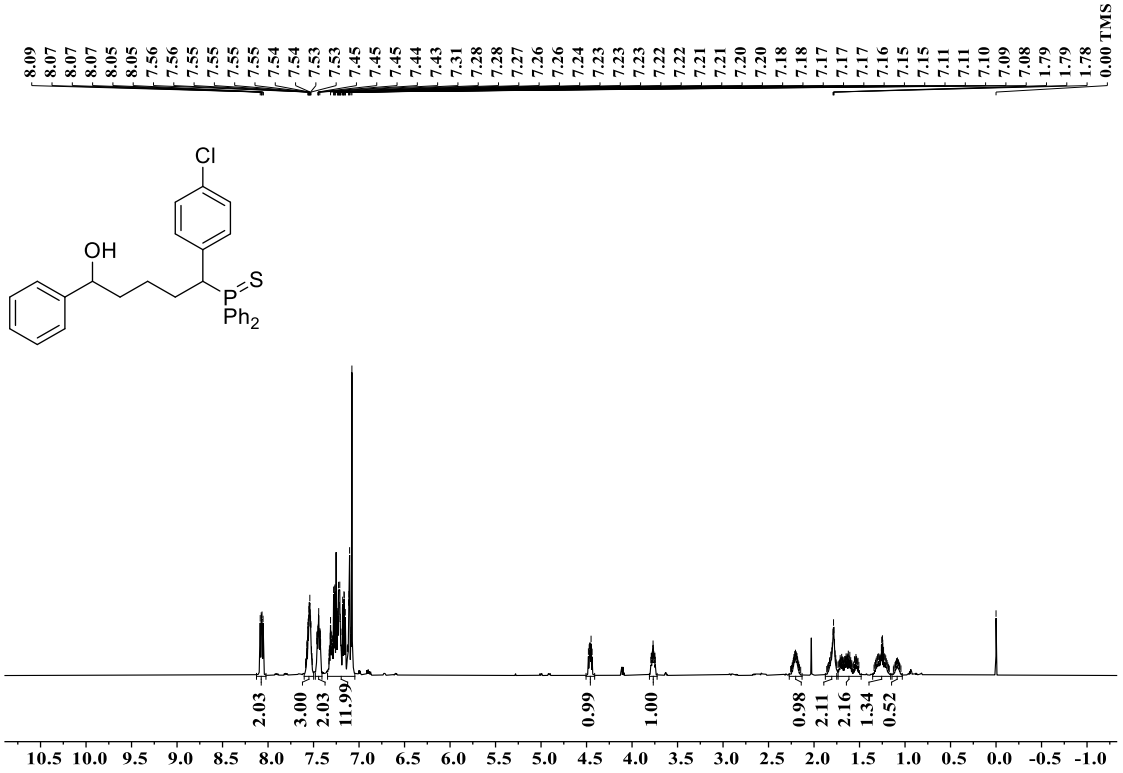
^{31}P NMR spectrum of **[S]-47** (243 MHz, $CDCl_3$)



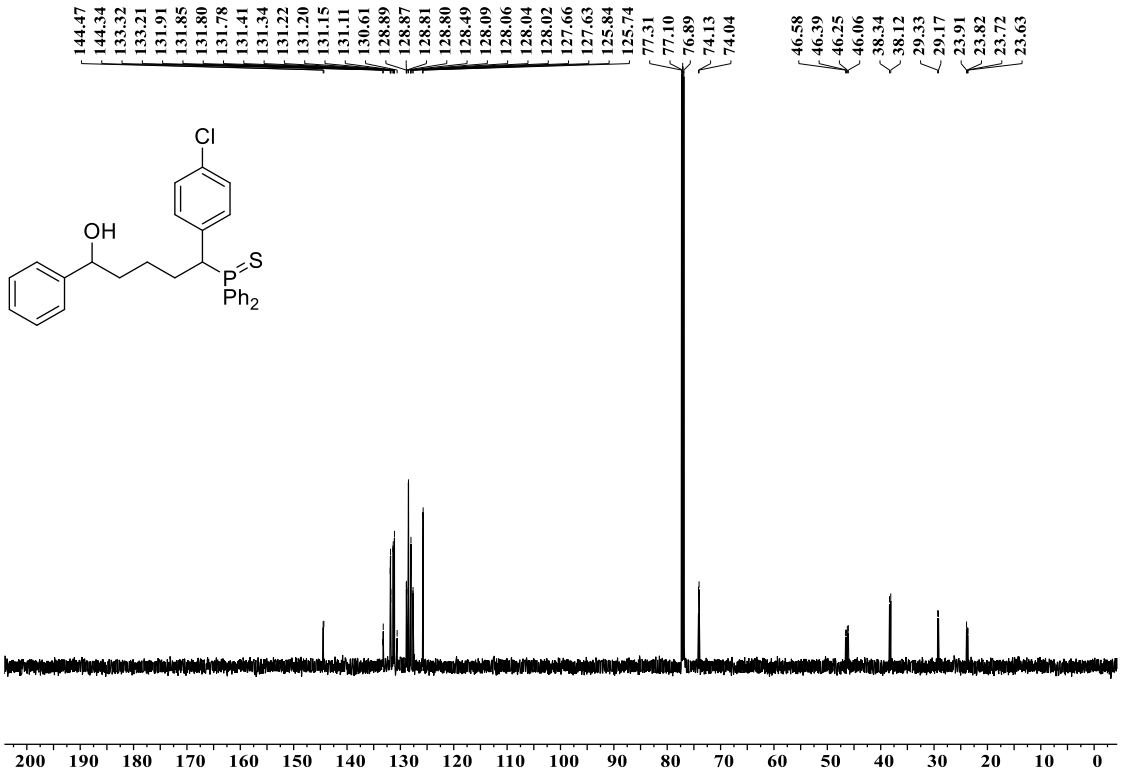
^{19}F NMR spectrum of **[S]-47** (565 MHz, $CDCl_3$)



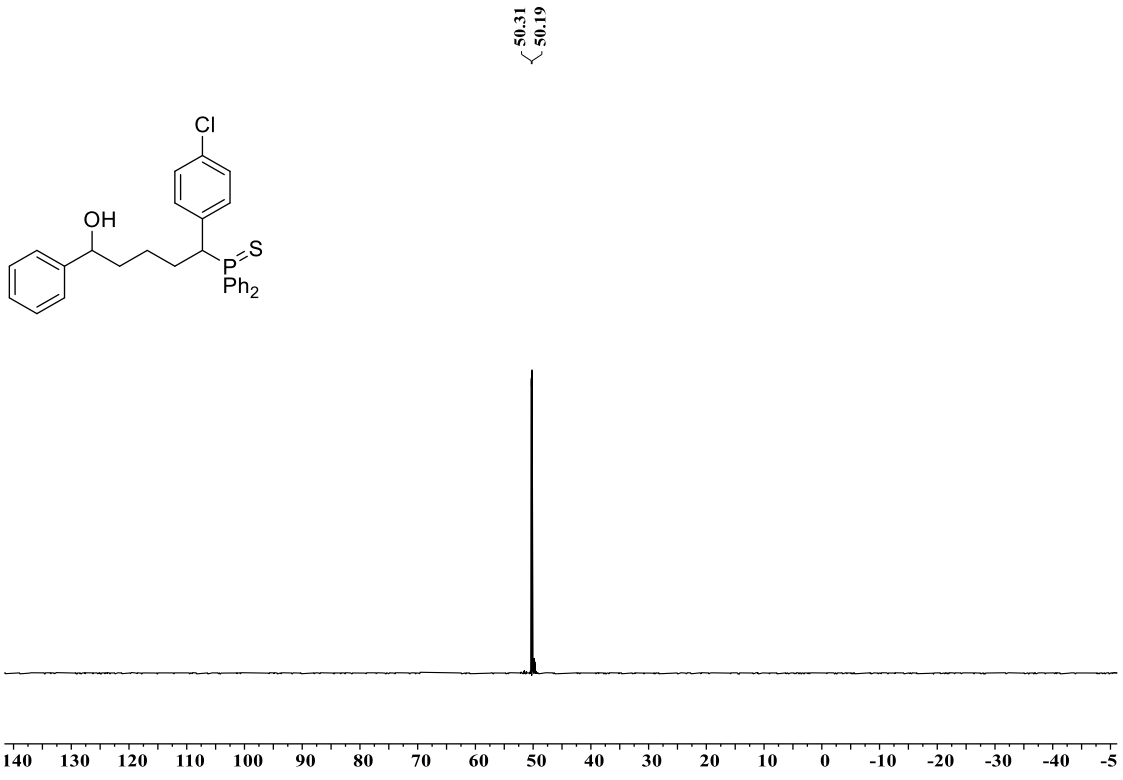
^{1}H NMR spectrum of **[S]-48** (600 MHz, $CDCl_3$)



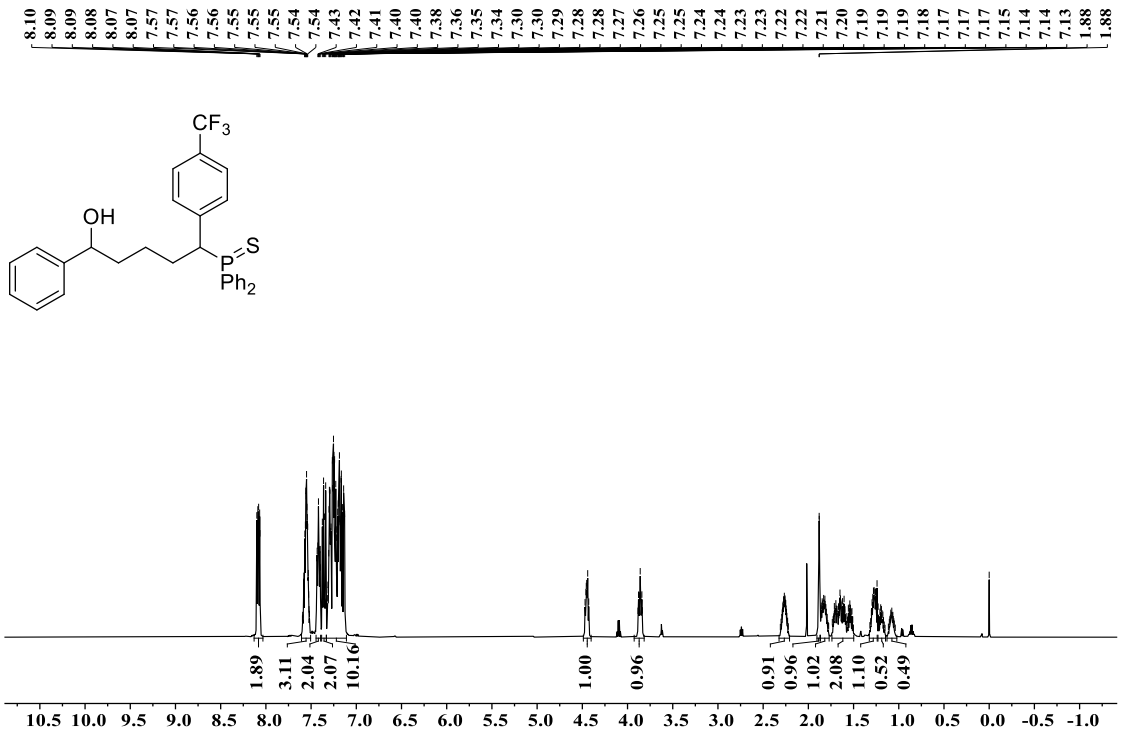
^{13}C NMR spectrum of **[S]-48** (150 MHz, $CDCl_3$)



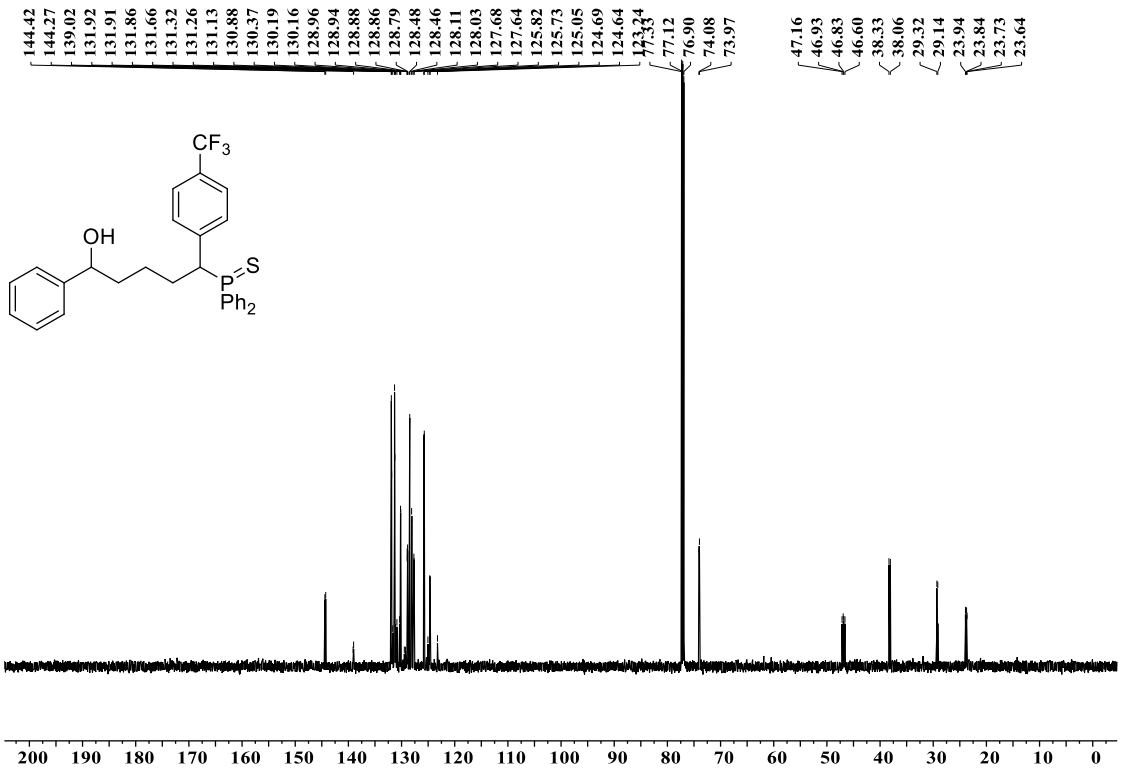
^{31}P NMR spectrum of **[S]-48** (243 MHz, $CDCl_3$)



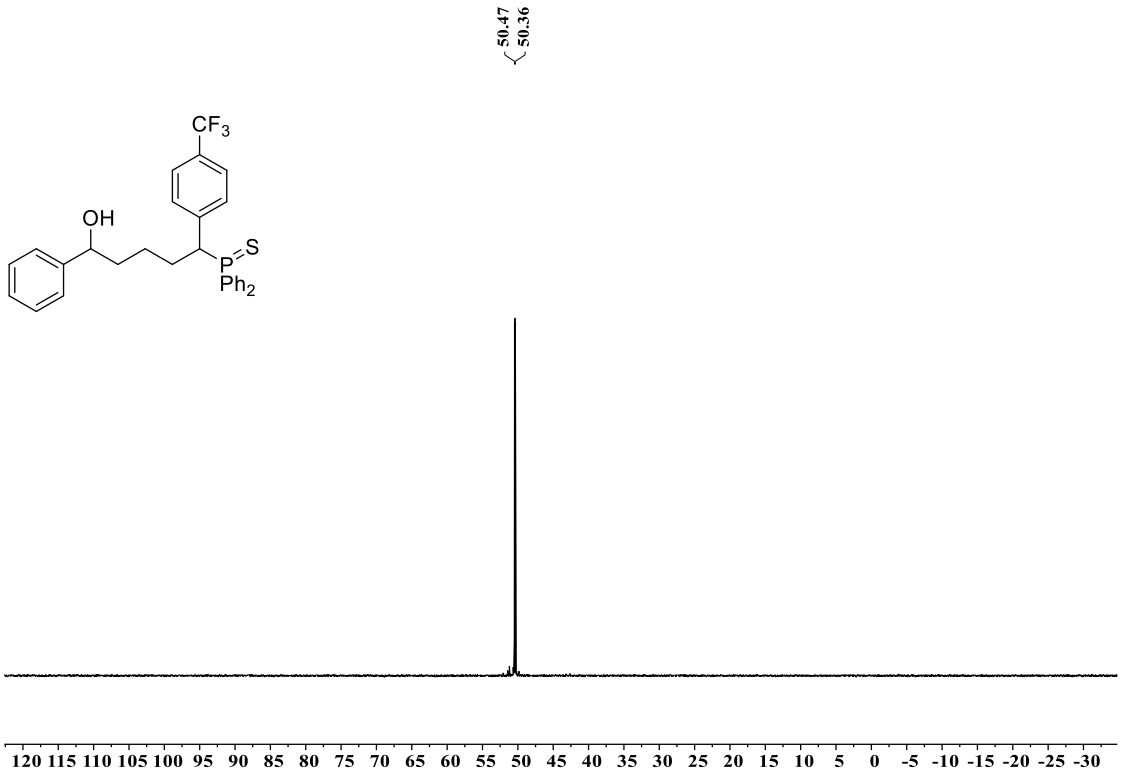
^{1}H NMR spectrum of **[S]-49** (600 MHz, $CDCl_3$)



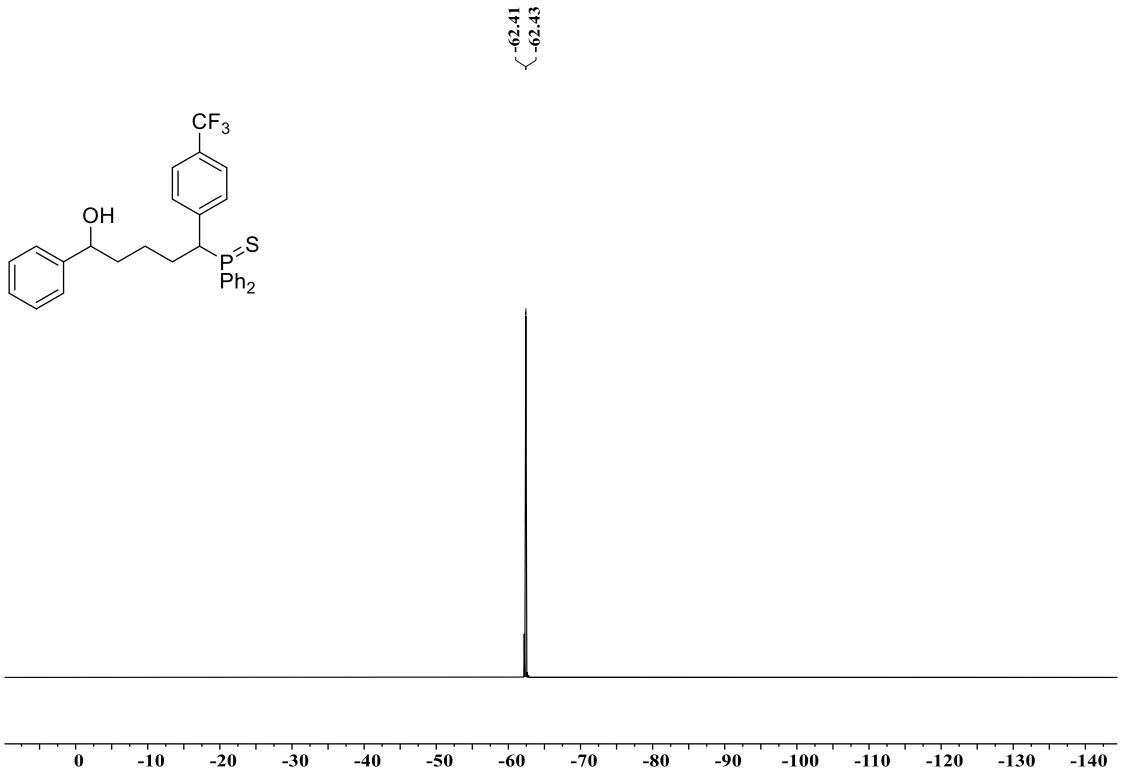
^{13}C NMR spectrum of **[S]-49** (150 MHz, $CDCl_3$)



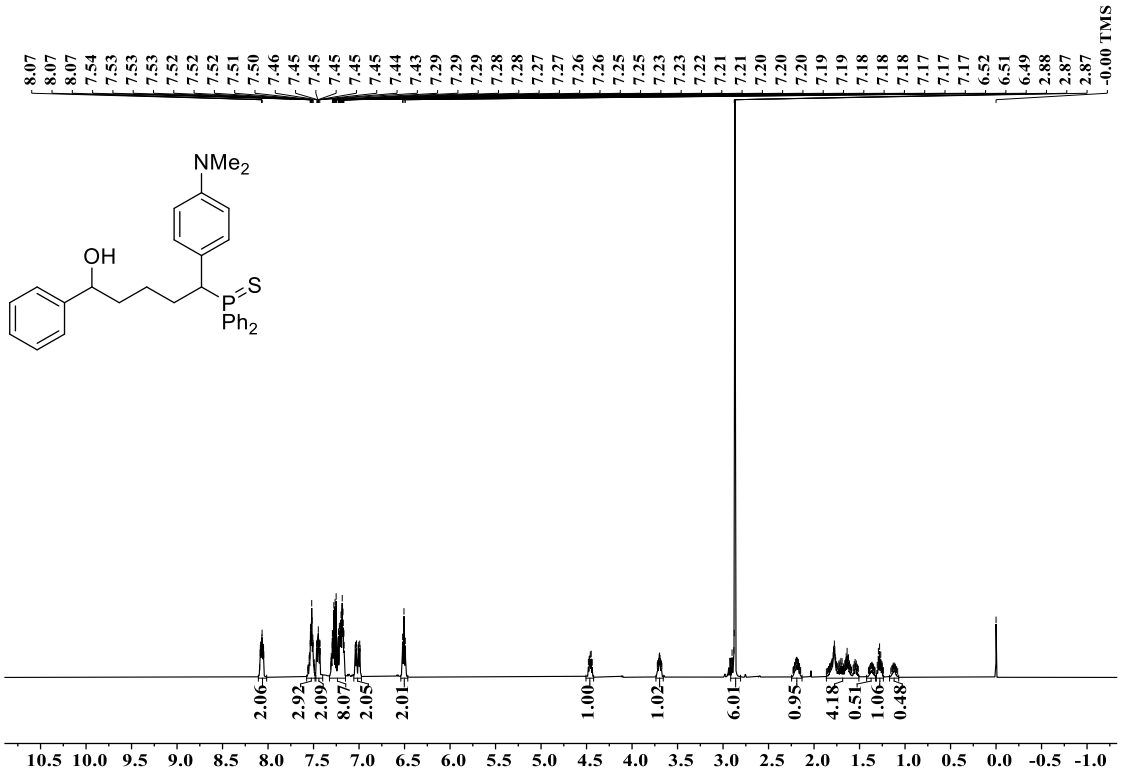
^{31}P NMR spectrum of **[S]-49** (243 MHz, $CDCl_3$)



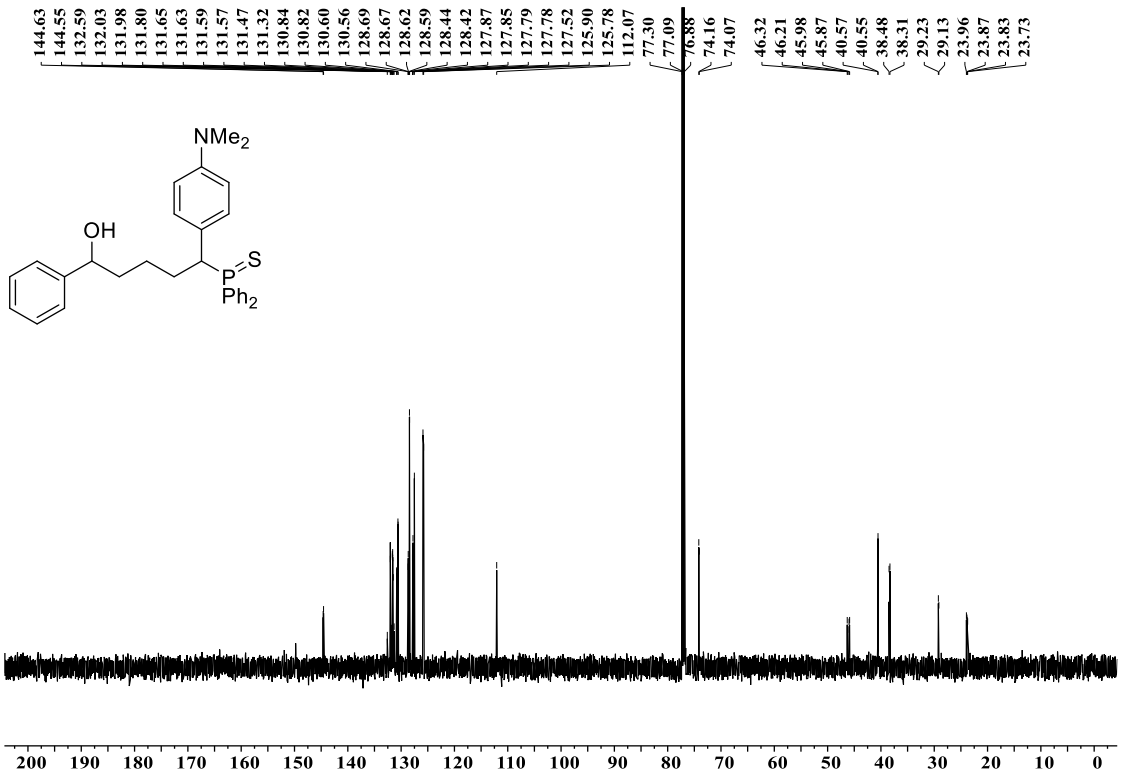
^{19}F NMR spectrum of **[S]-49** (565 MHz, $CDCl_3$)



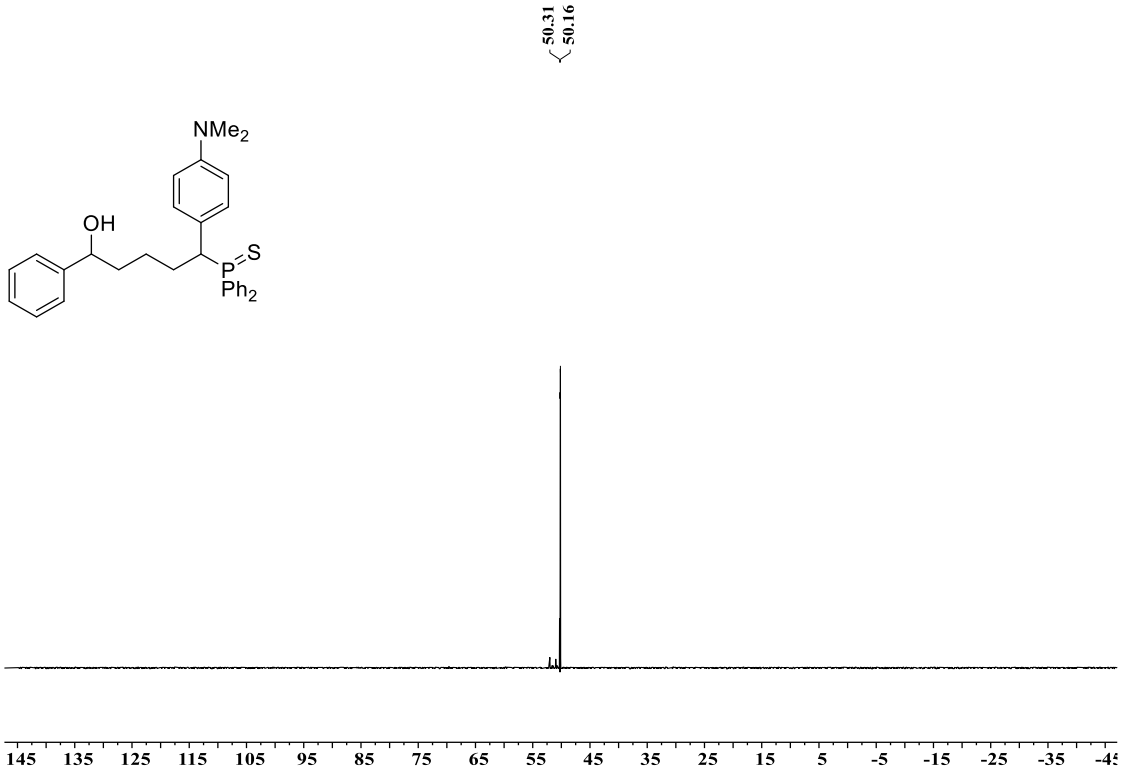
^{1}H NMR spectrum of **[S]-50** (600 MHz, $CDCl_3$)



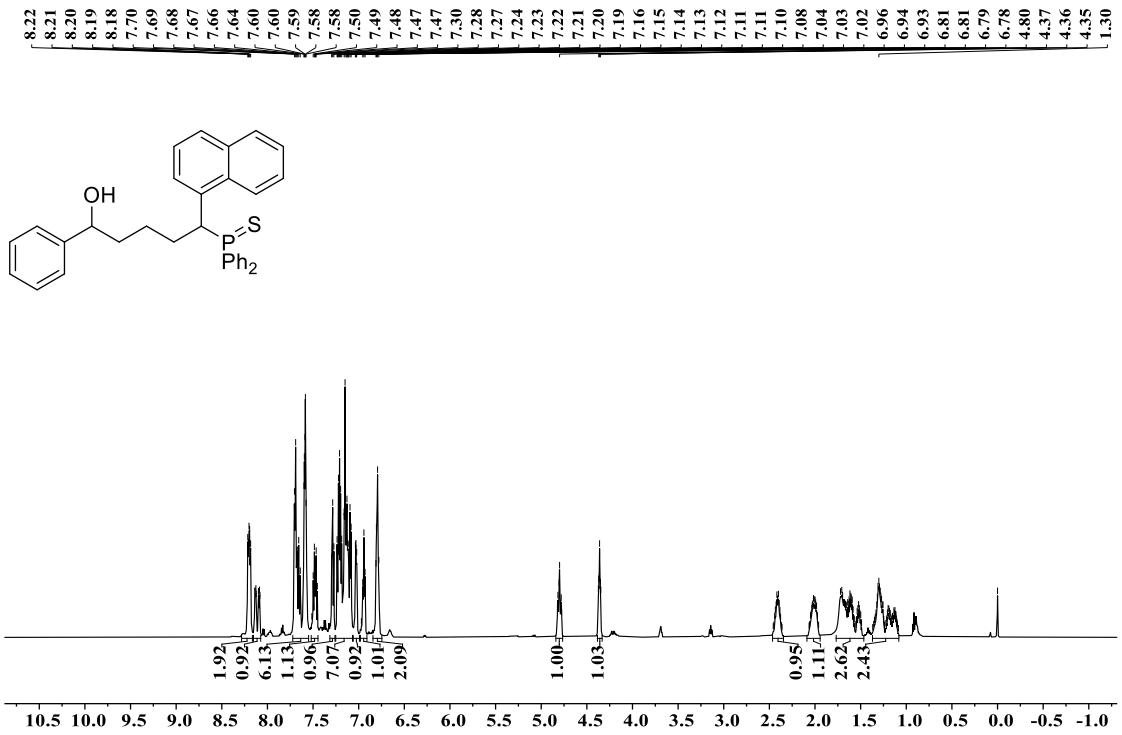
^{13}C NMR spectrum of **[S]-50** (150 MHz, $CDCl_3$)



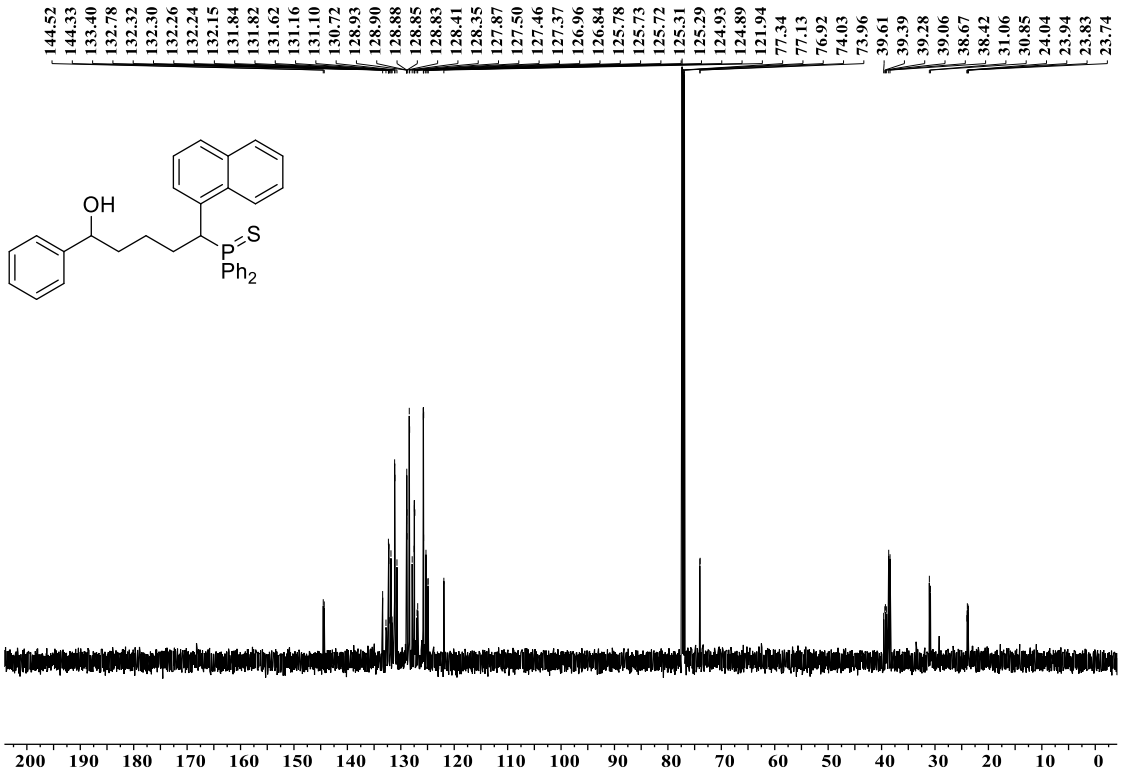
^{31}P NMR spectrum of **[S]-50** (243 MHz, $CDCl_3$)



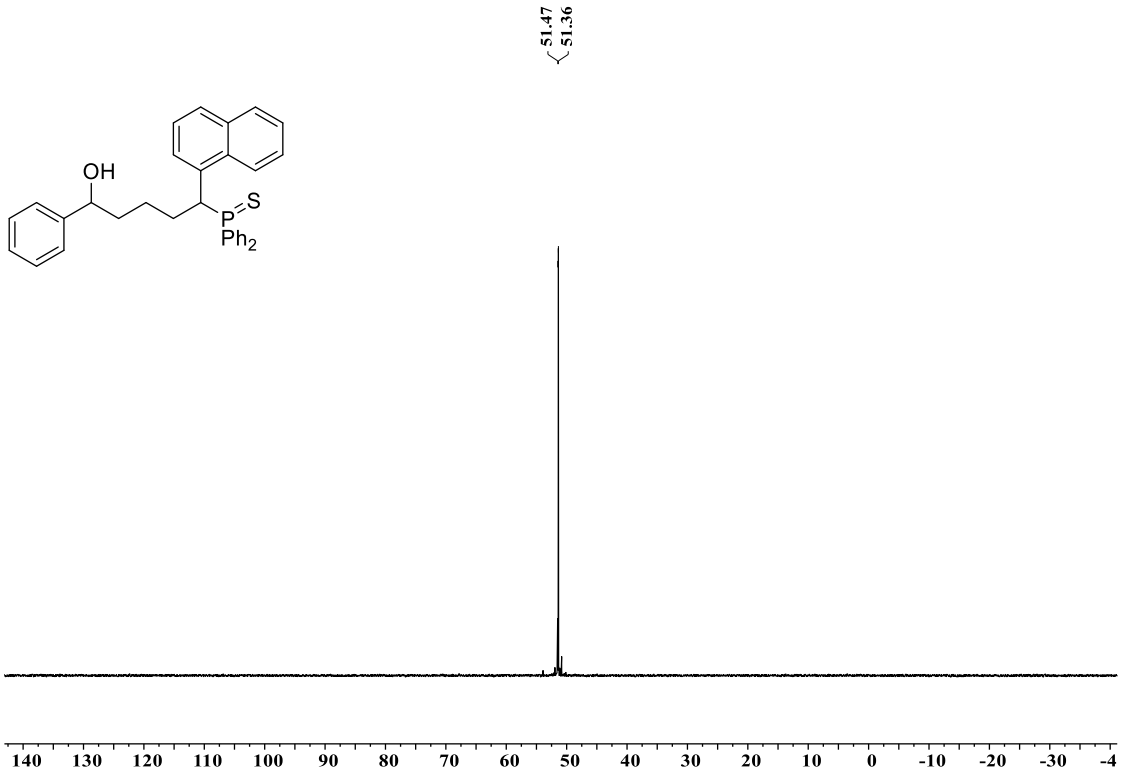
^{1}H NMR spectrum of **[S]-51** (600 MHz, $CDCl_3$)



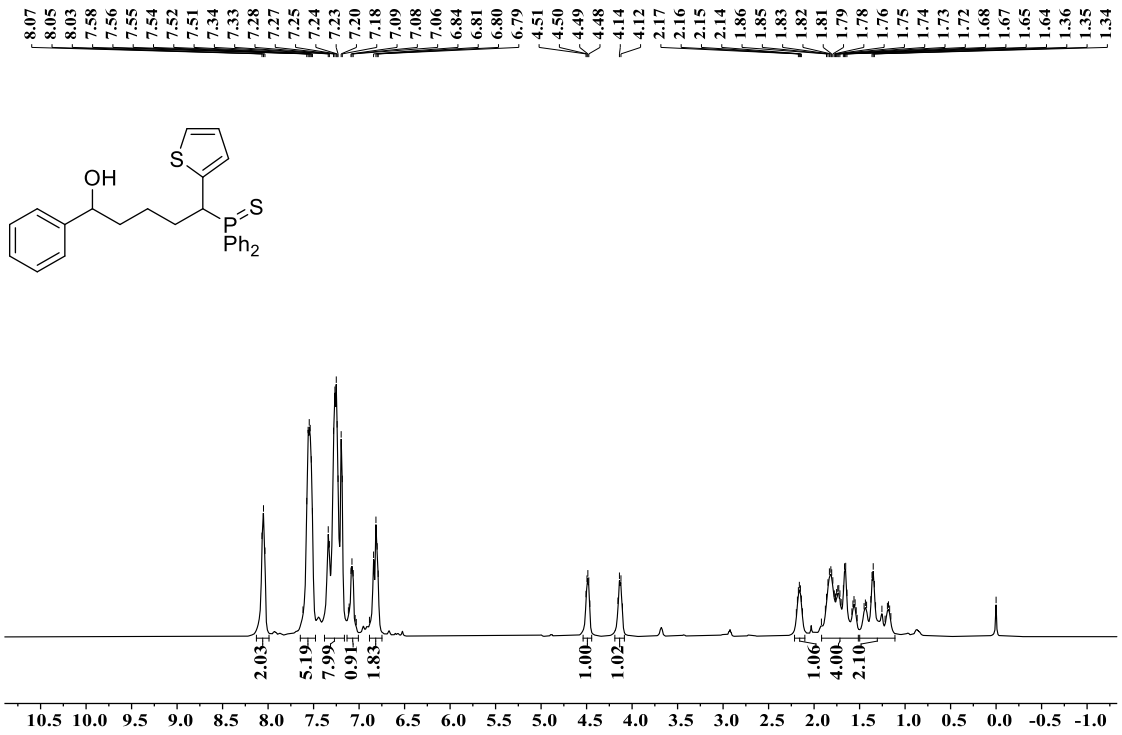
^{13}C NMR spectrum of **[S]-51** (150 MHz, $CDCl_3$)



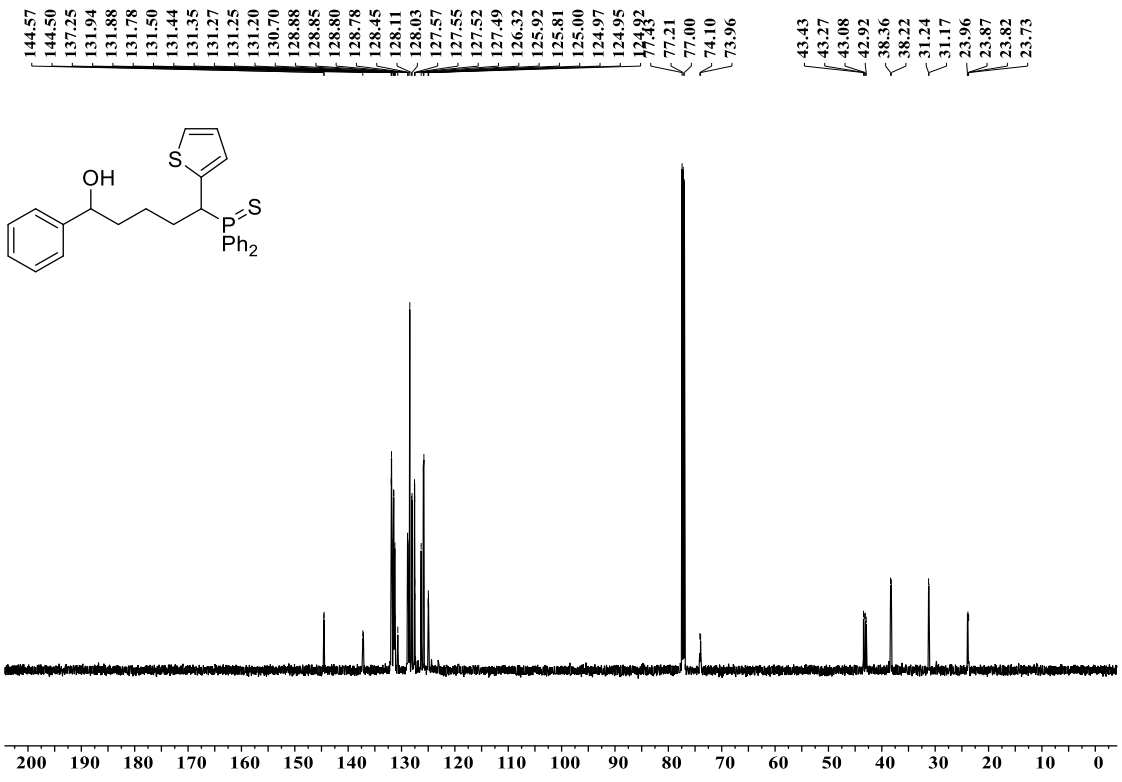
^{31}P NMR spectrum of **[S]-51** (243 MHz, $CDCl_3$)



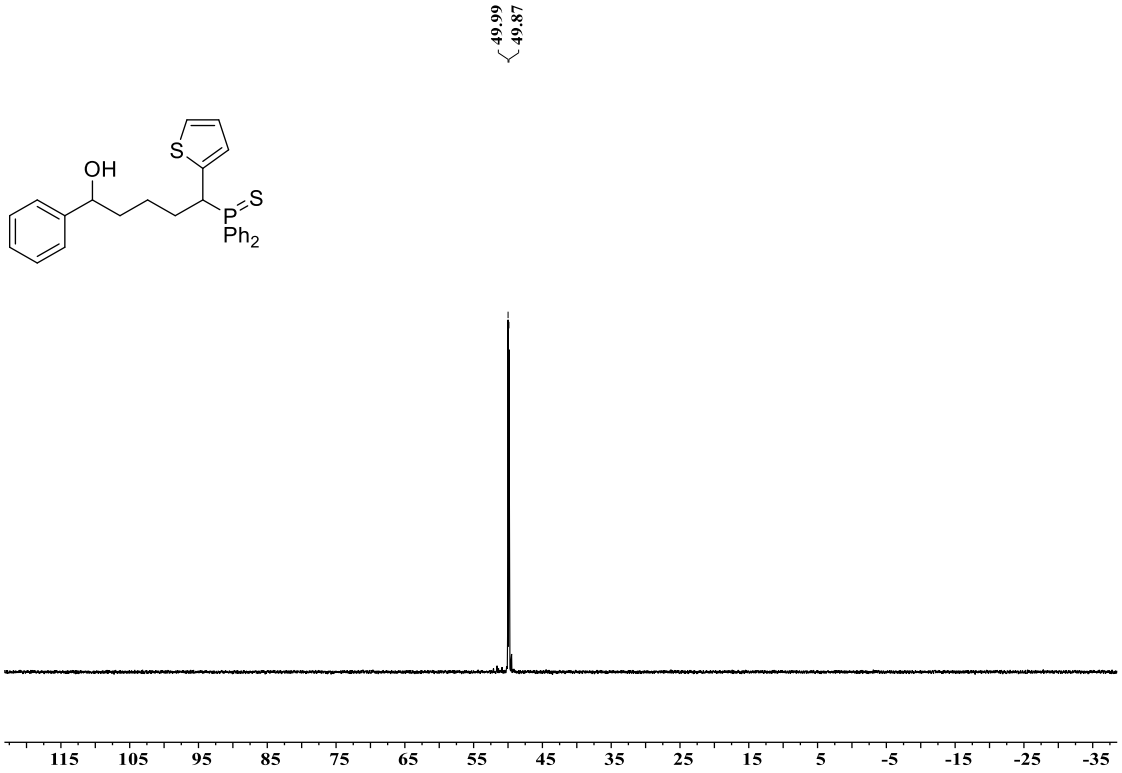
^{1}H NMR spectrum of **[S]-52** (600 MHz, $CDCl_3$)



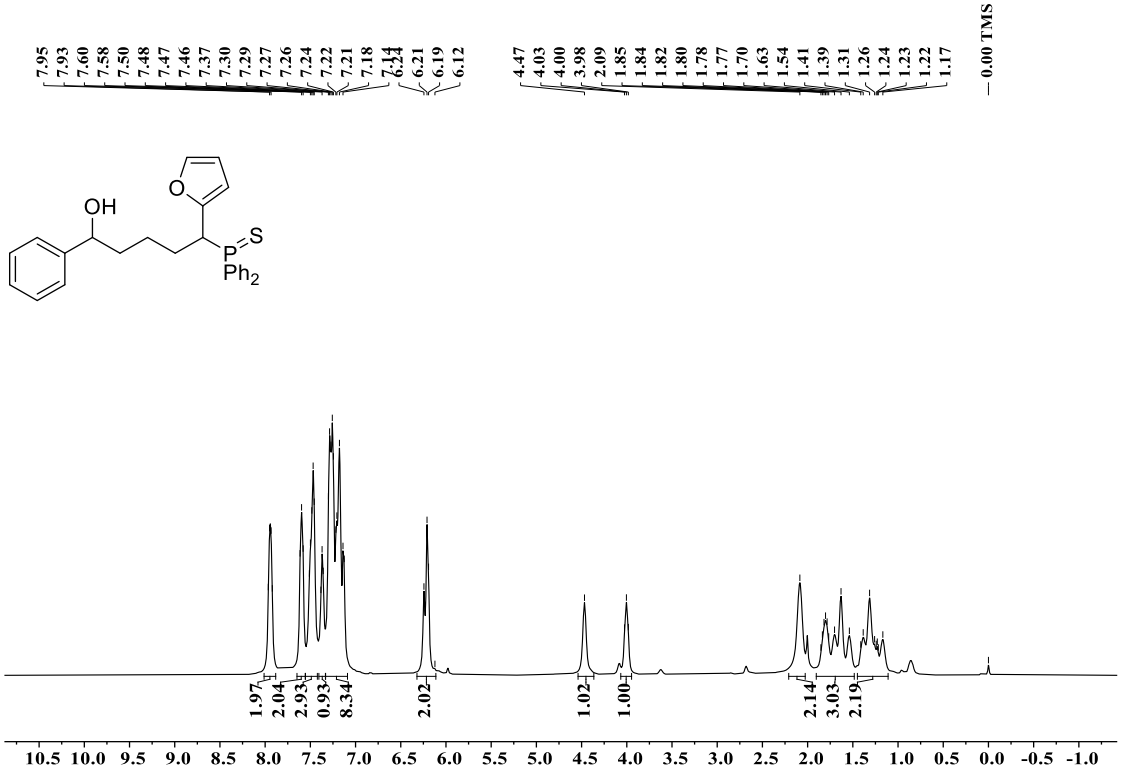
^{13}C NMR spectrum of **[S]-52** (150 MHz, $CDCl_3$)



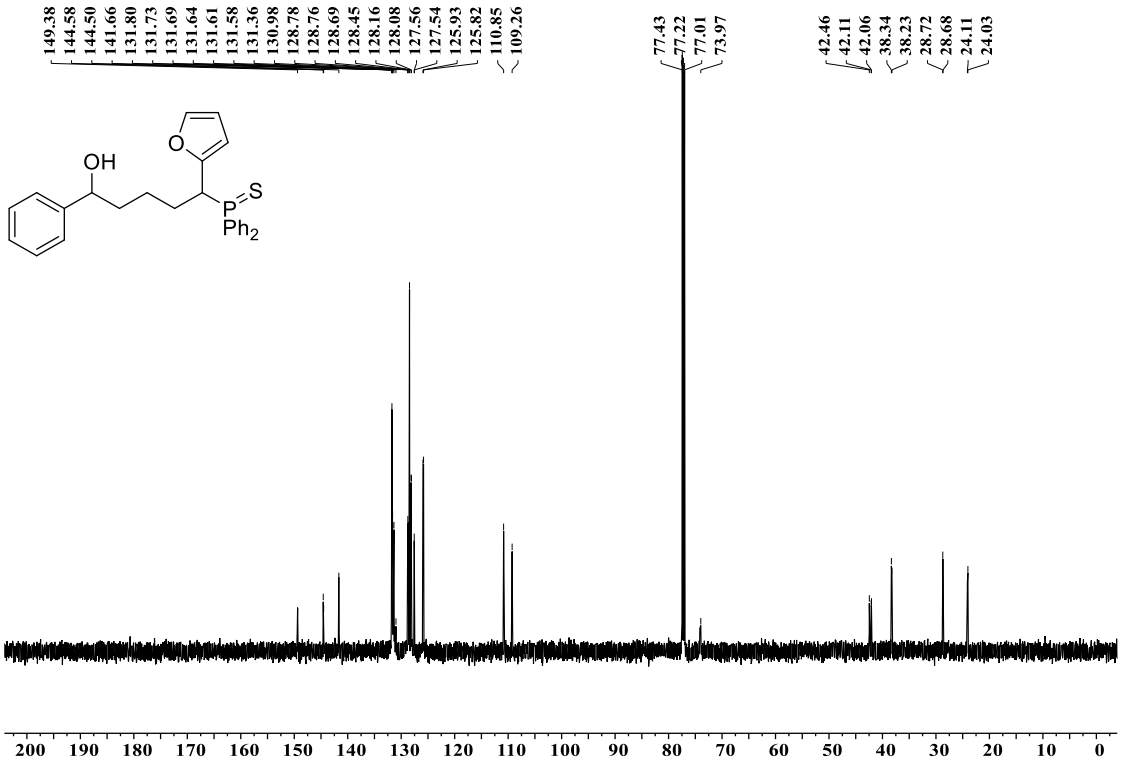
^{31}P NMR spectrum of **[S]-52** (243 MHz, $CDCl_3$)



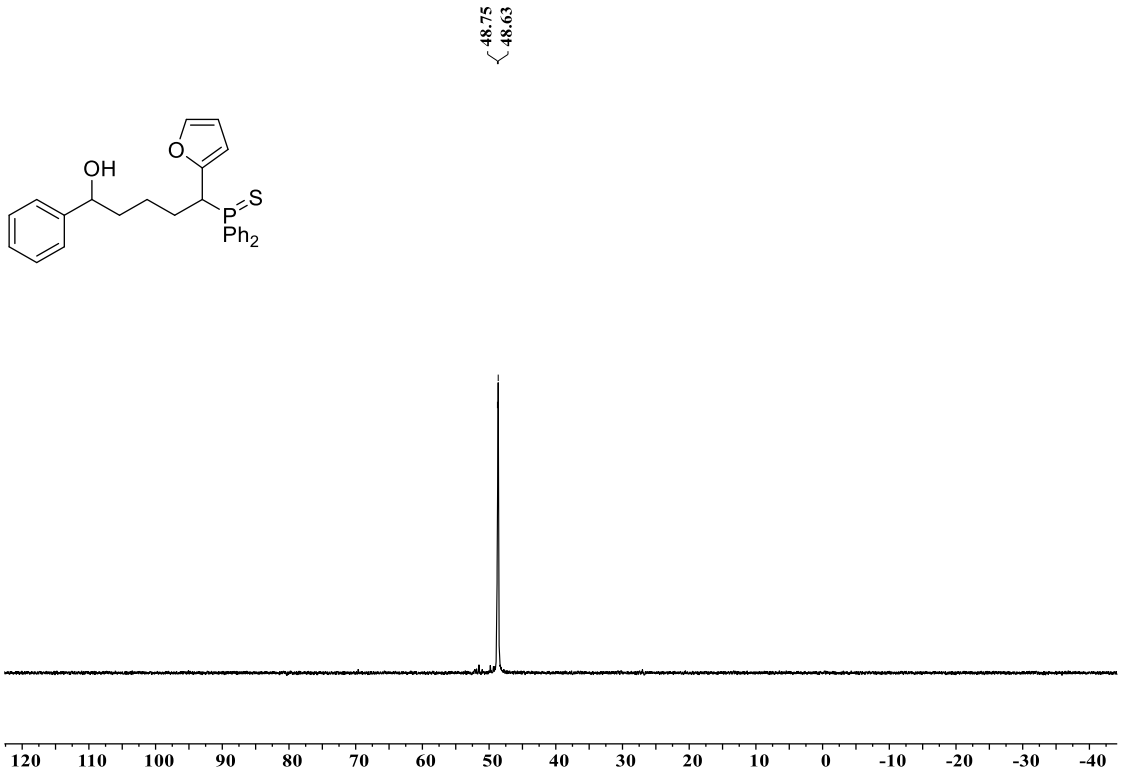
^{1}H NMR spectrum of **[S]-53** (600 MHz, $CDCl_3$)



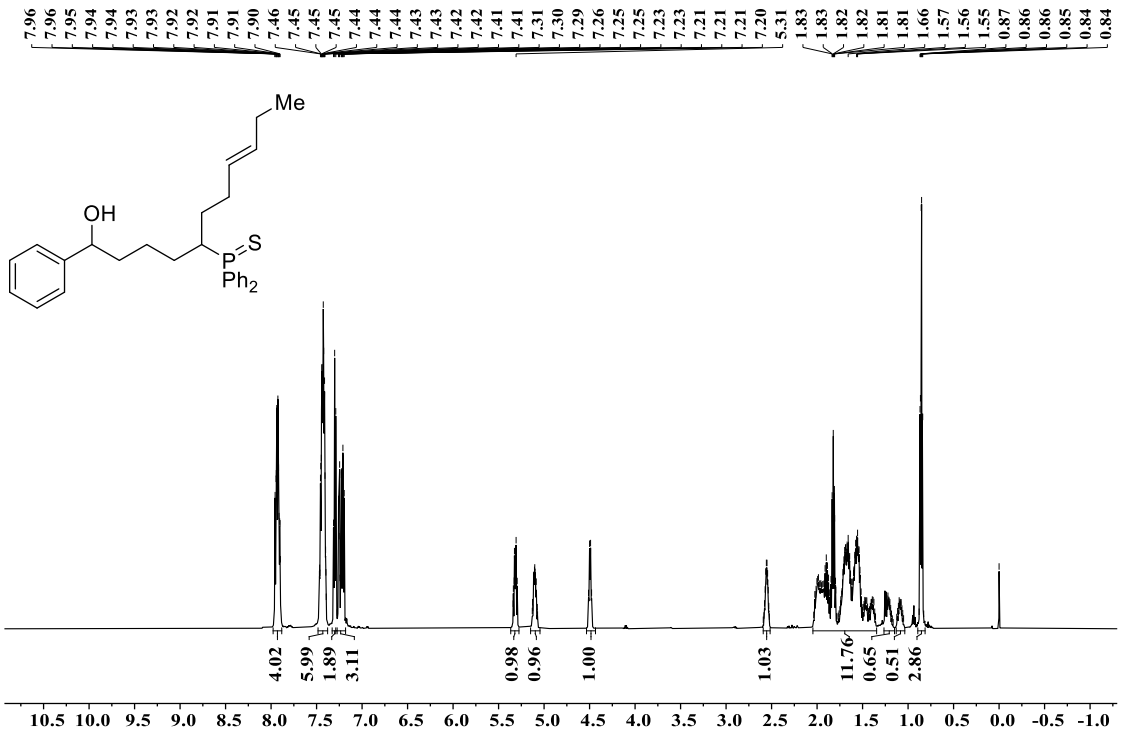
^{13}C NMR spectrum of **[S]-53** (150 MHz, $CDCl_3$)



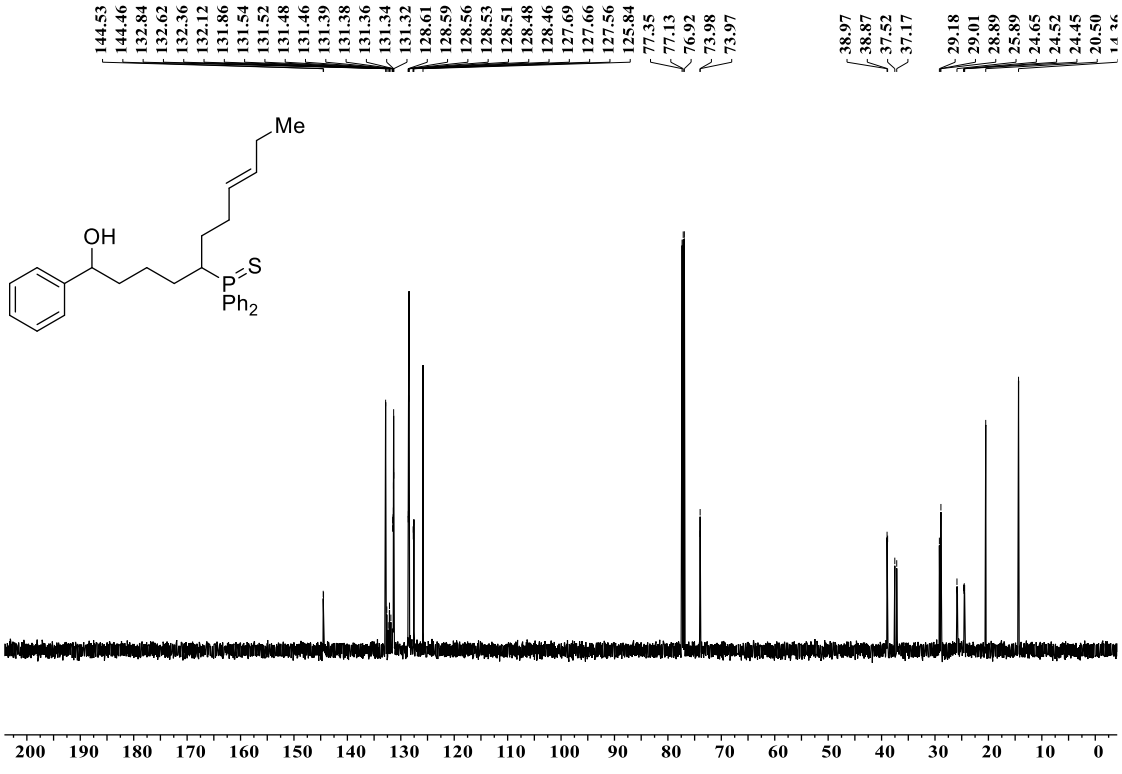
^{31}P NMR spectrum of **[S]-53** (243 MHz, $CDCl_3$)



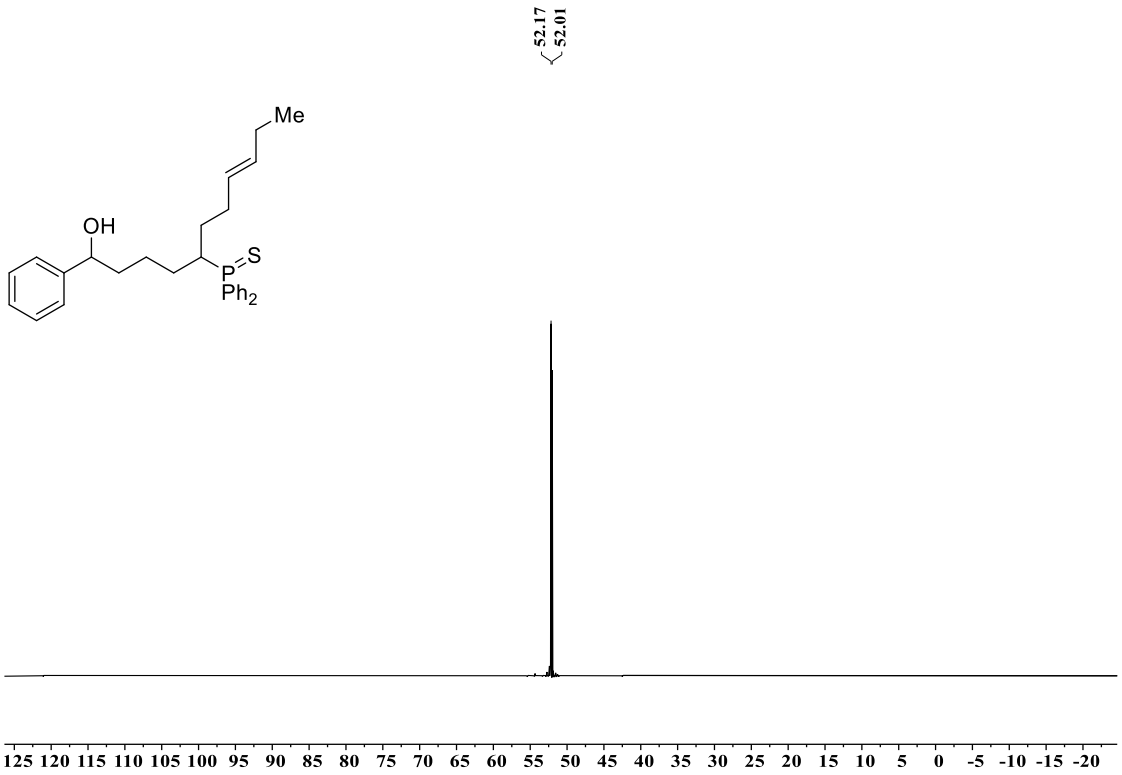
^{1}H NMR spectrum of **[S]-54** (600 MHz, $CDCl_3$)



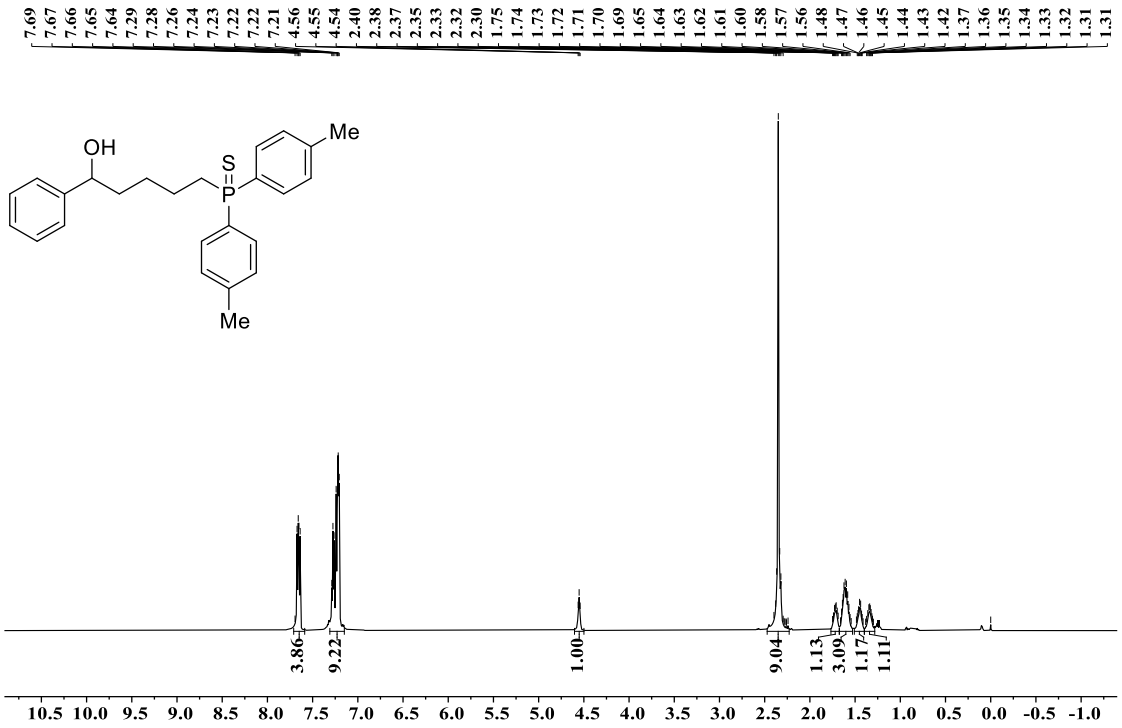
^{13}C NMR spectrum of **[S]-54** (150 MHz, $CDCl_3$)



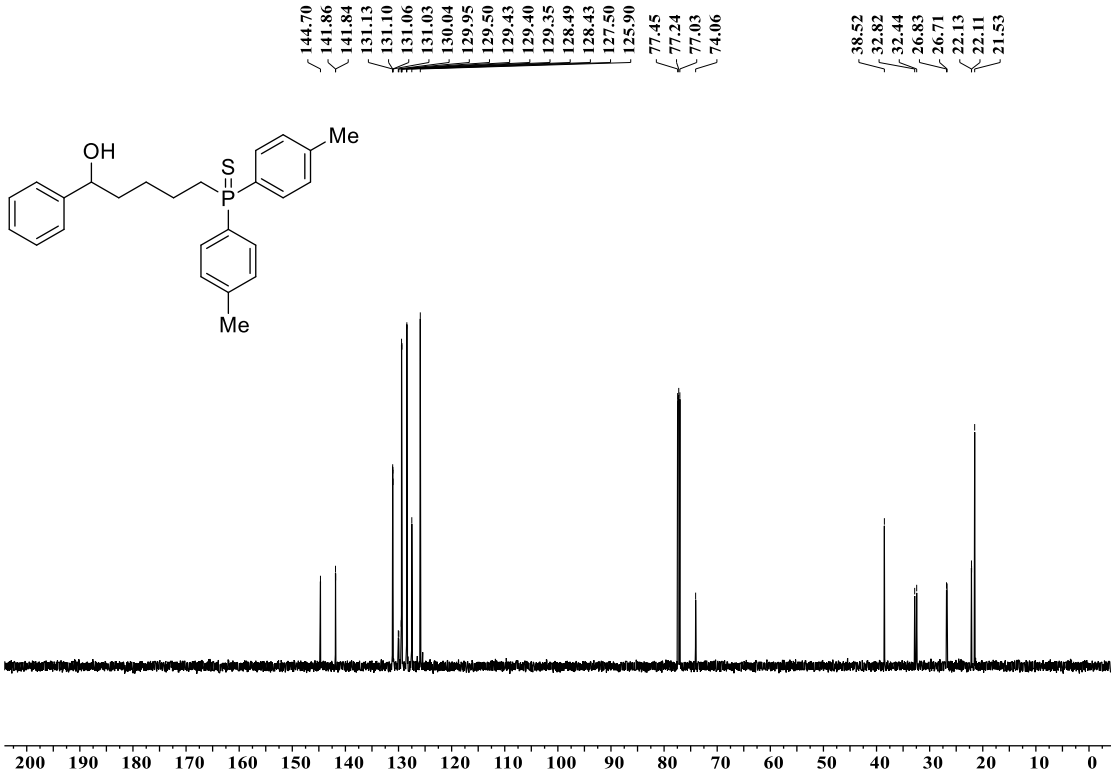
^{31}P NMR spectrum of **[S]-54** (243 MHz, $CDCl_3$)



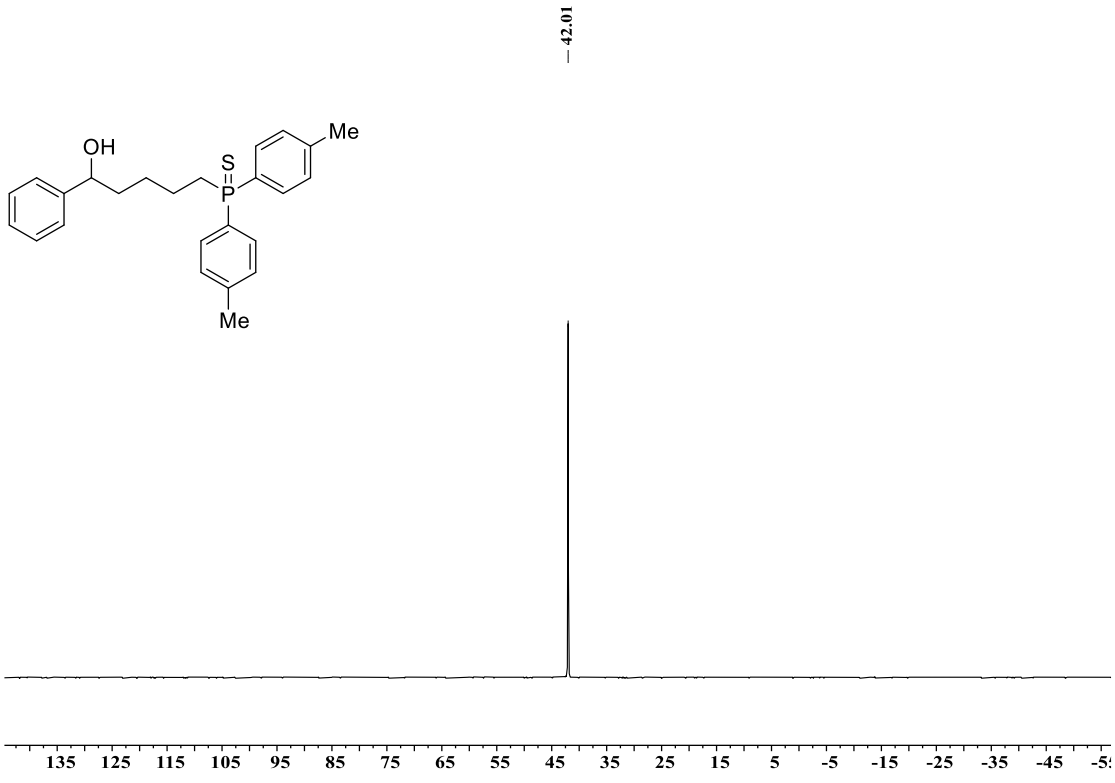
^{1}H NMR spectrum of **[S]-55** (600 MHz, $CDCl_3$)



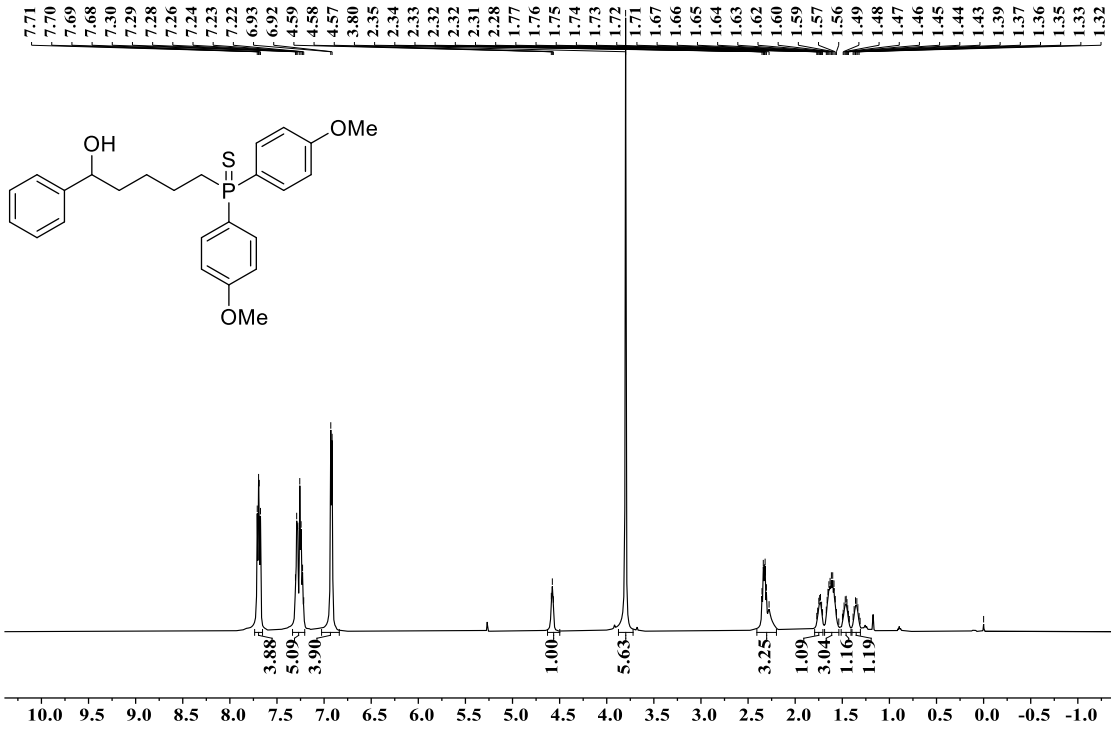
^{13}C NMR spectrum of **[S]-55** (150 MHz, $CDCl_3$)



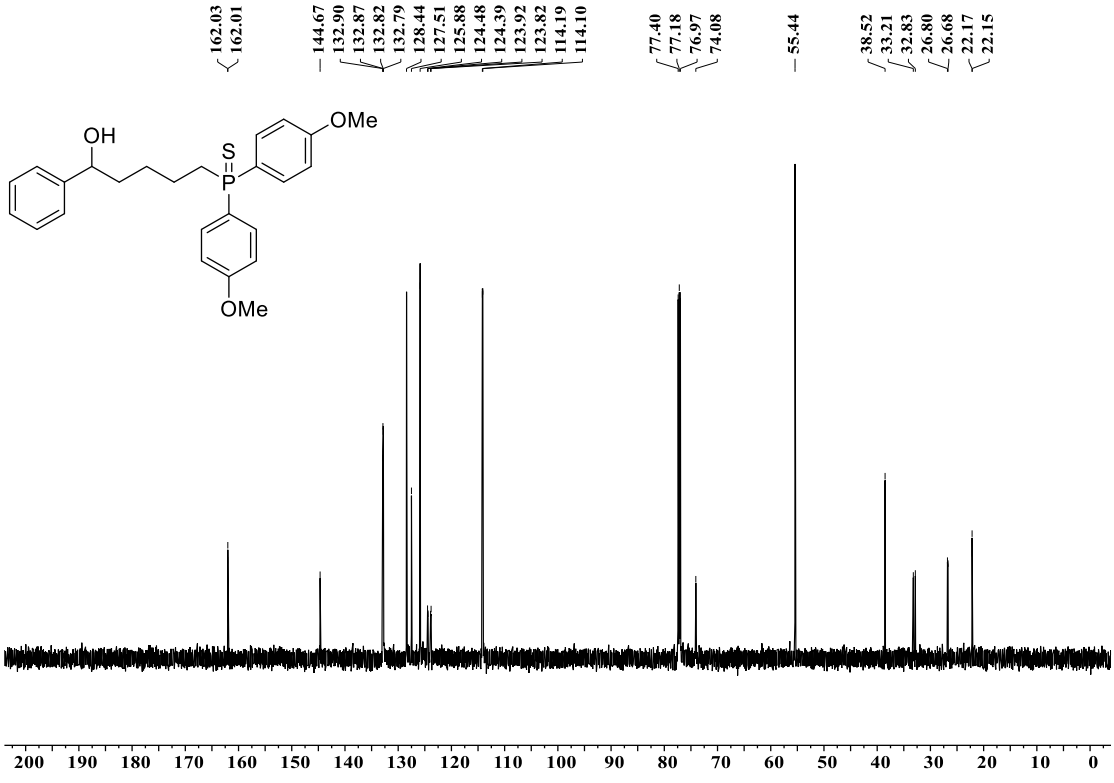
^{31}P NMR spectrum of **[S]-55** (243 MHz, $CDCl_3$)



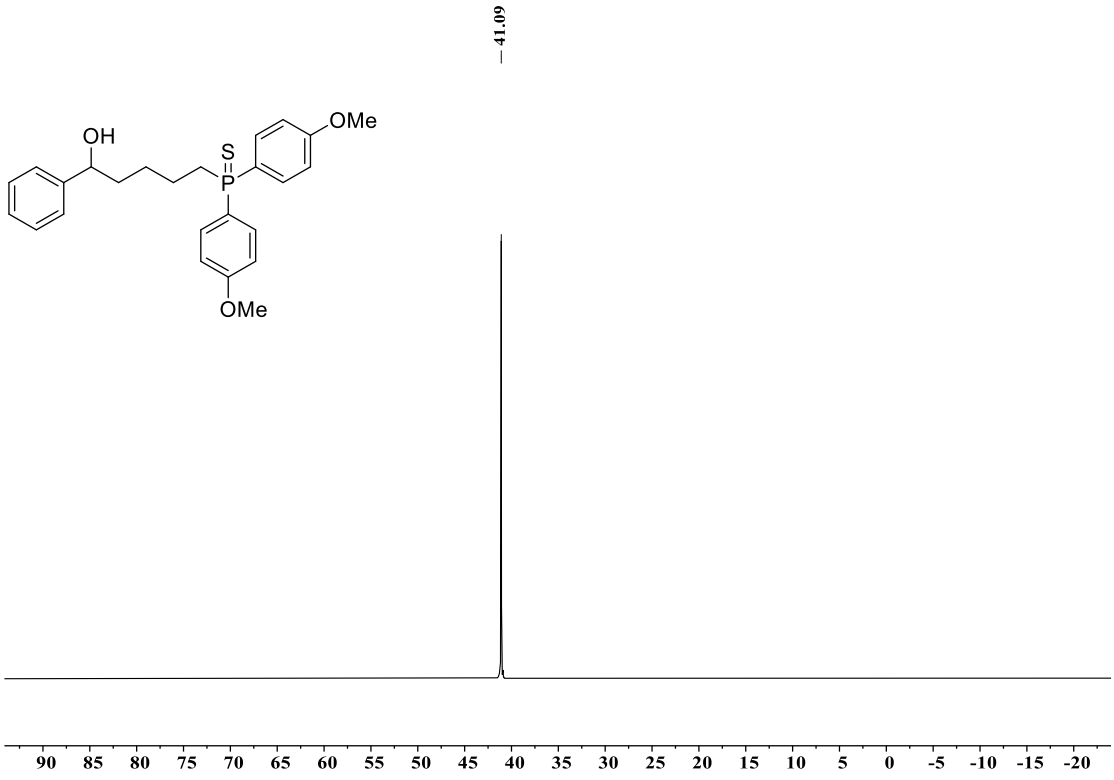
^{1}H NMR spectrum of **[S]-56** (600 MHz, $CDCl_3$)



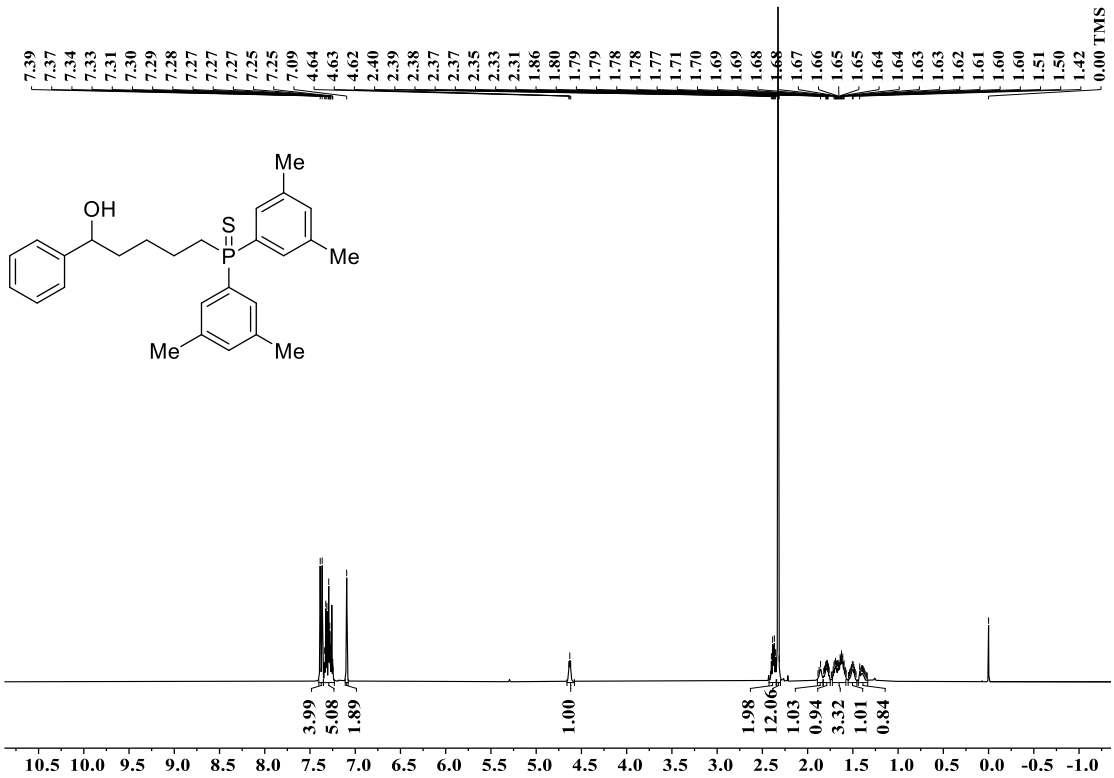
^{13}C NMR spectrum of **[S]-56** (150 MHz, $CDCl_3$)



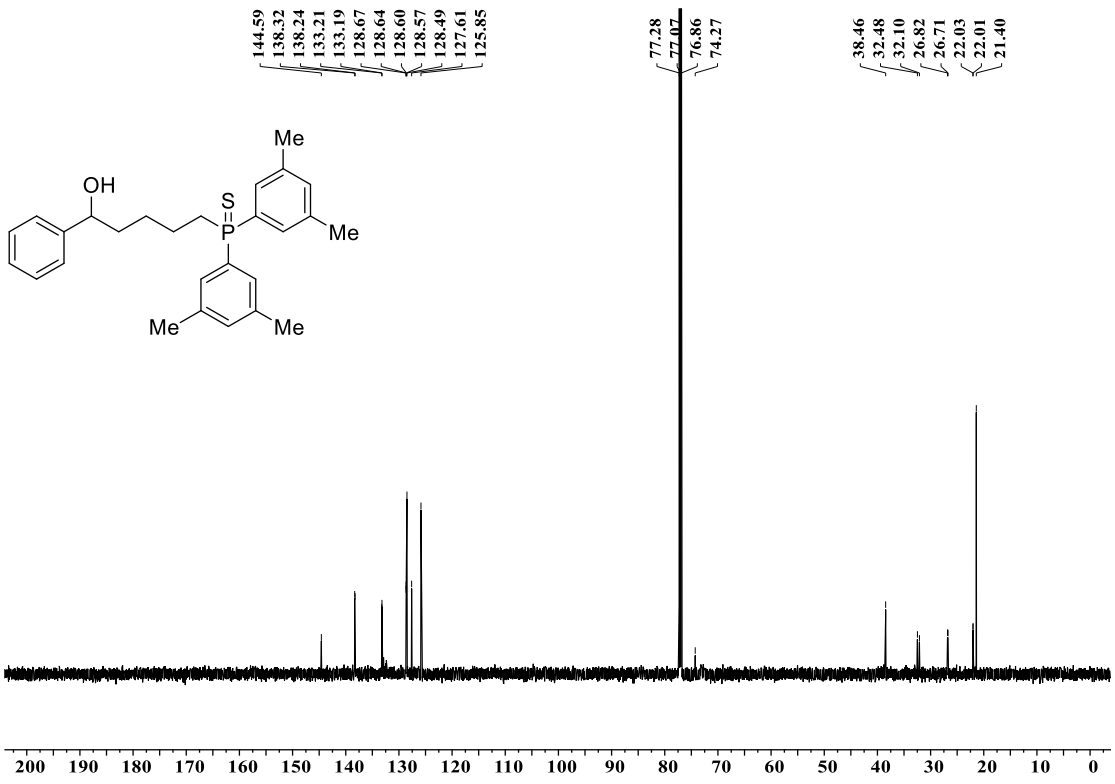
^{31}P NMR spectrum of **[S]-56** (243 MHz, $CDCl_3$)



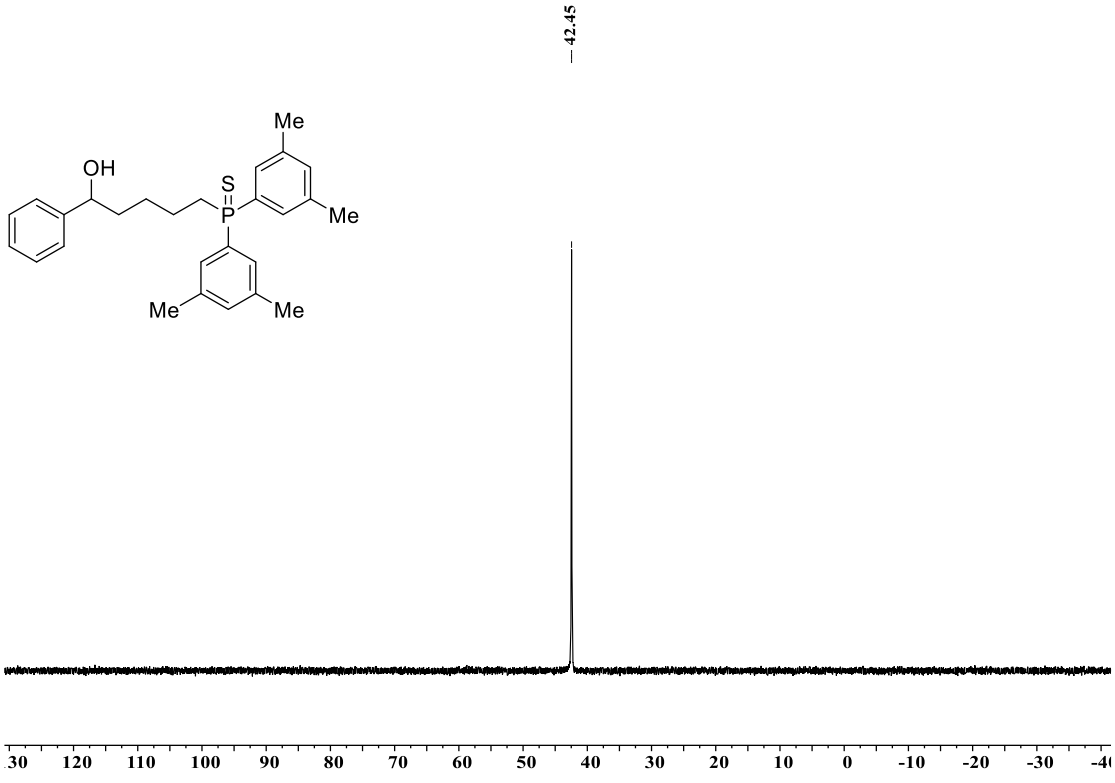
^{1}H NMR spectrum of **[S]-57** (600 MHz, $CDCl_3$)



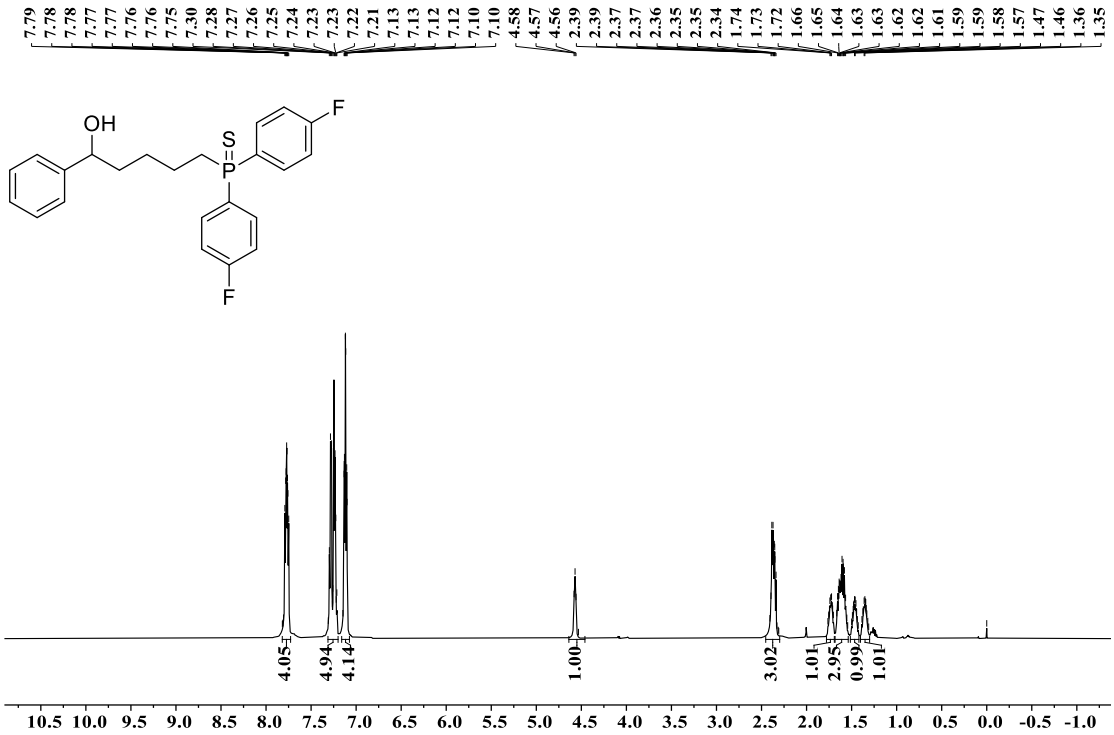
^{13}C NMR spectrum of **[S]-57** (150 MHz, $CDCl_3$)



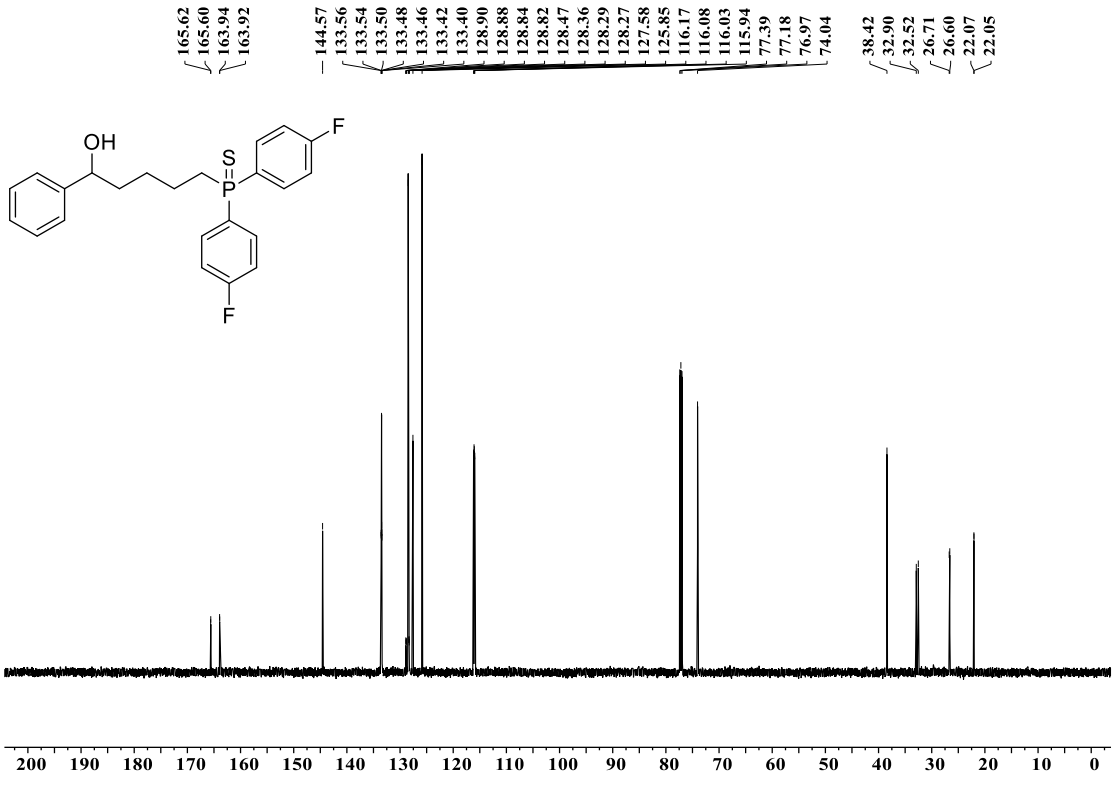
^{31}P NMR spectrum of **[S]-57** (243 MHz, $CDCl_3$)



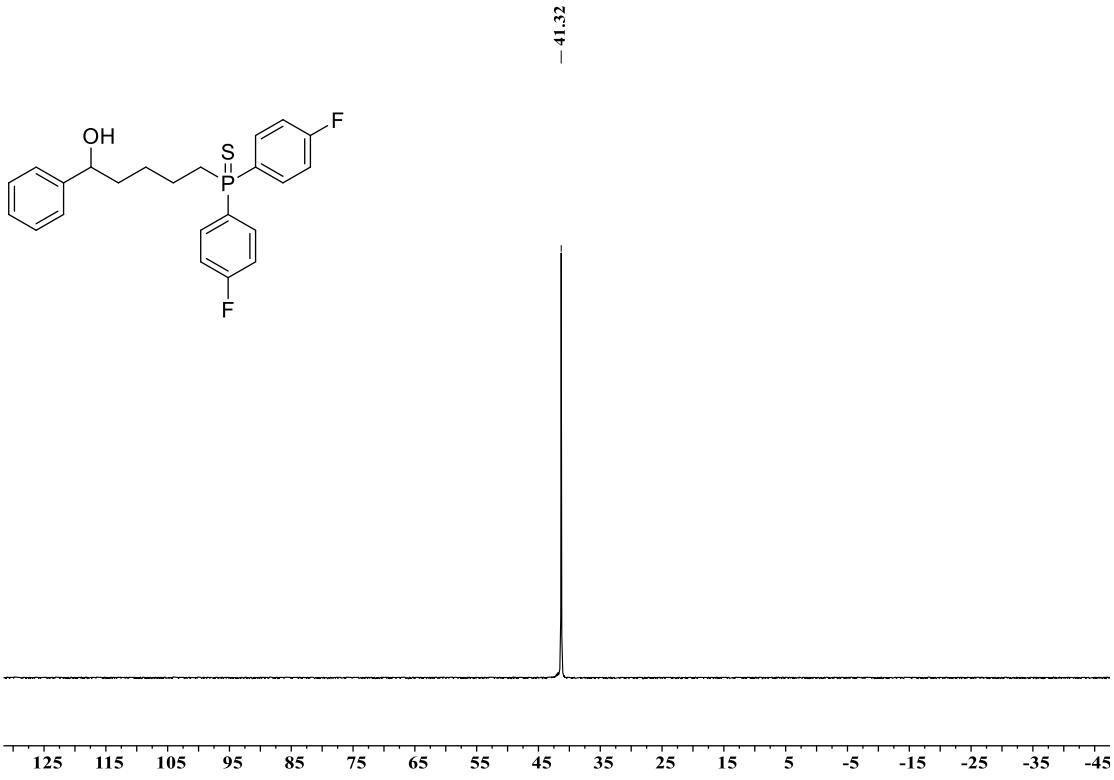
^{1}H NMR spectrum of **[S]-58** (600 MHz, $CDCl_3$)



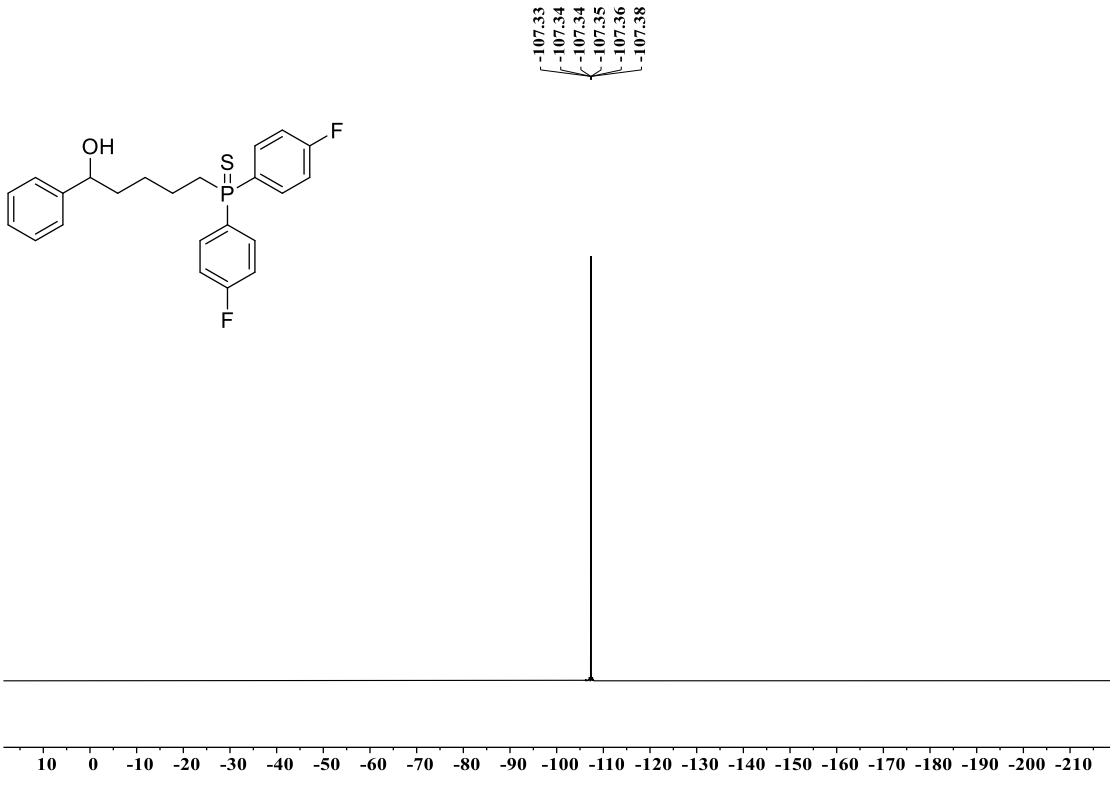
^{13}C NMR spectrum of **[S]-58** (150 MHz, $CDCl_3$)



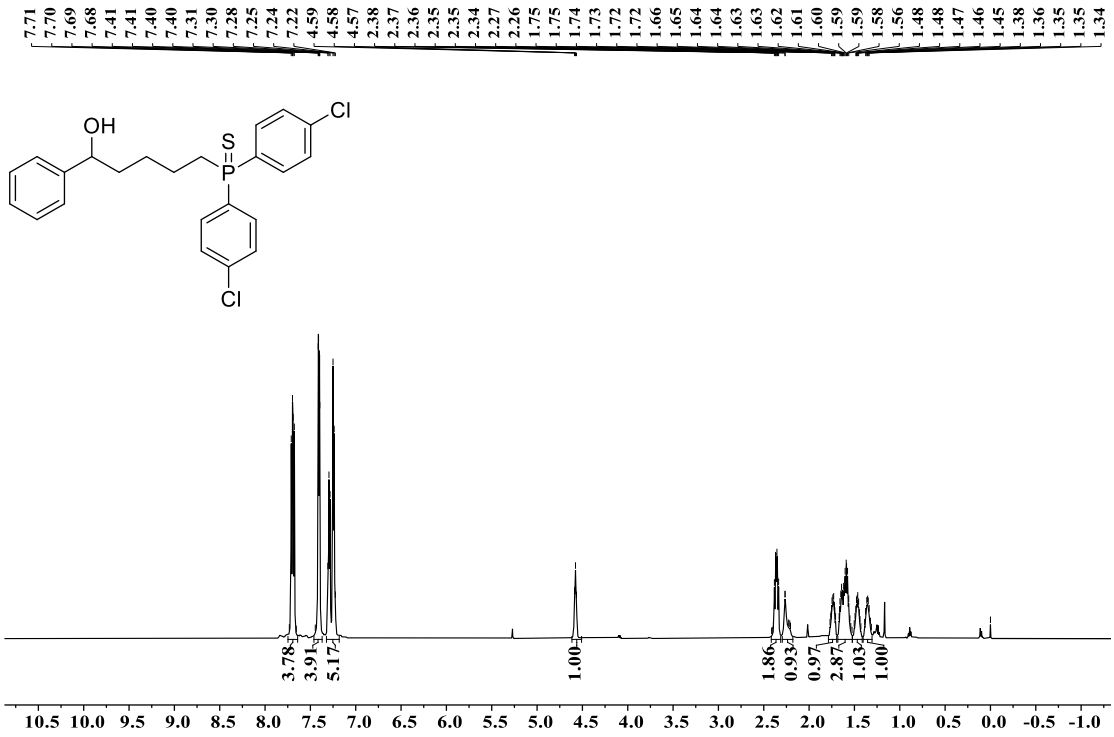
^{31}P NMR spectrum of **[S]-58** (243 MHz, $CDCl_3$)



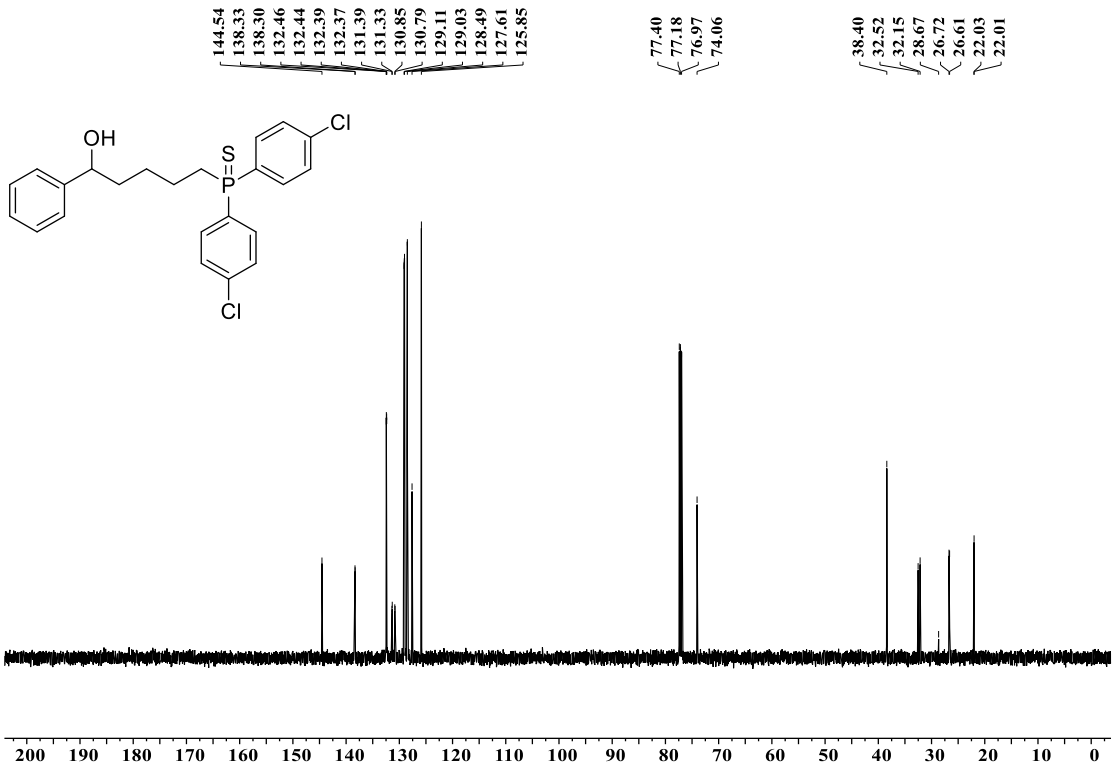
^{19}F NMR spectrum of **[S]-58** (565 MHz, $CDCl_3$)



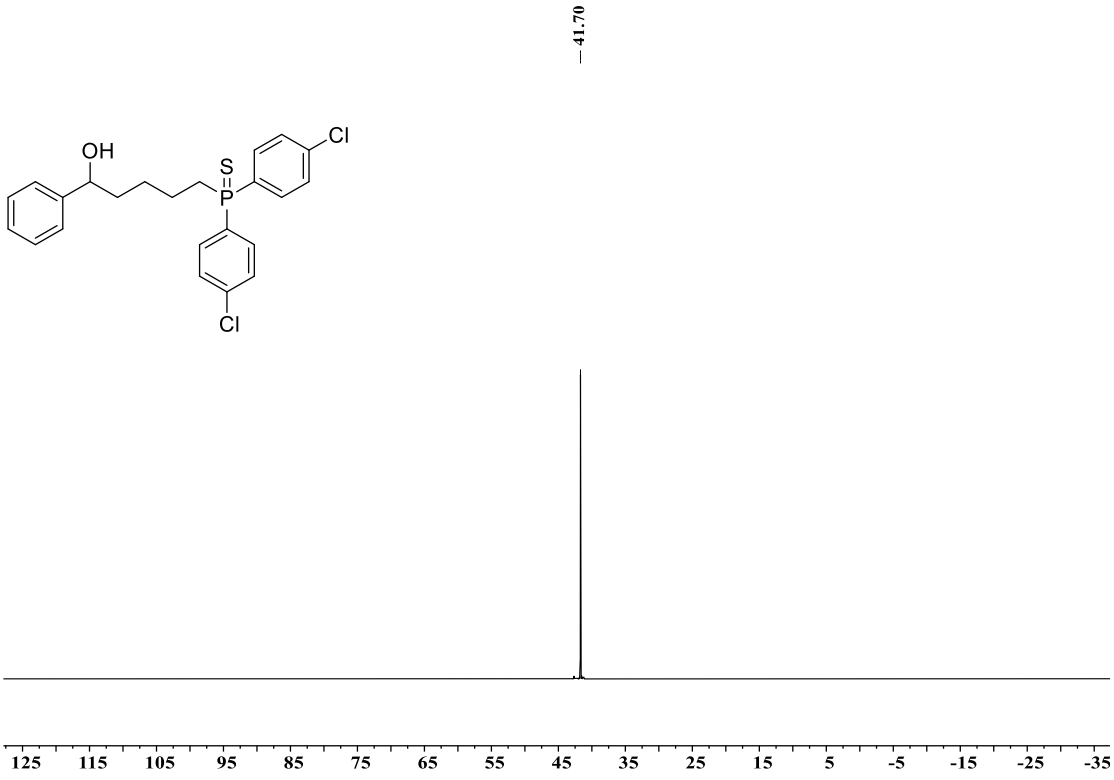
^{1}H NMR spectrum of **[S]-59** (600 MHz, $CDCl_3$)



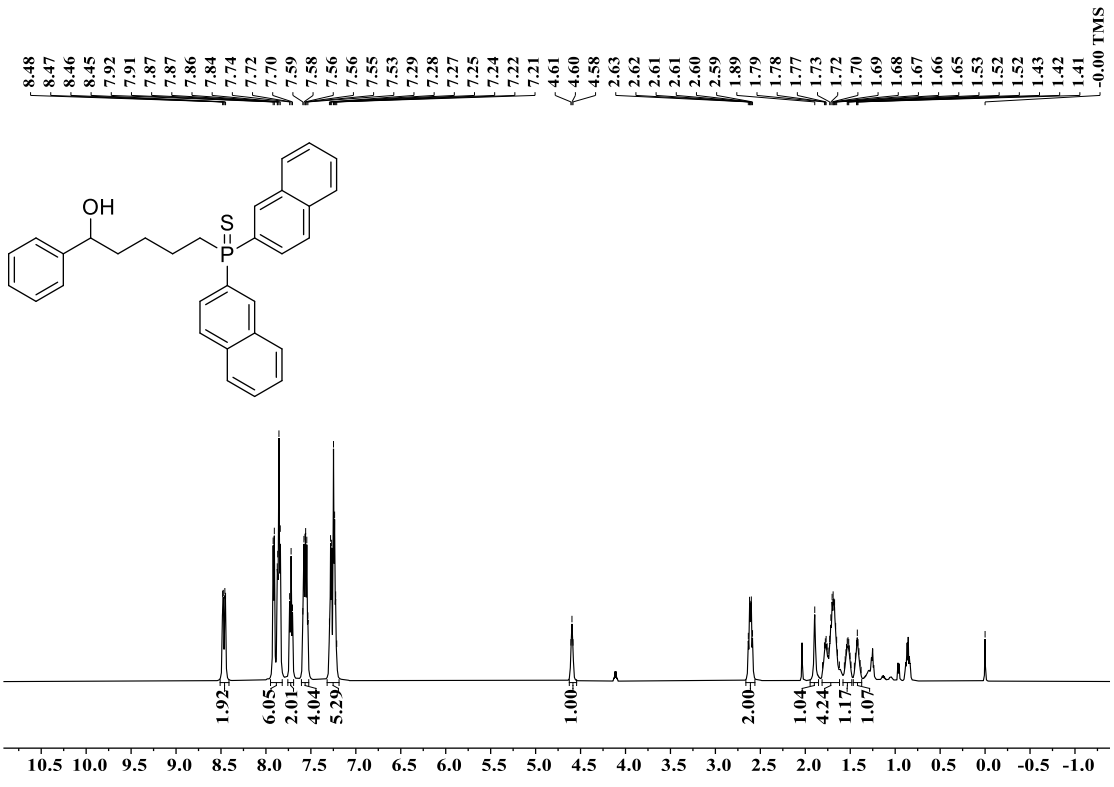
^{13}C NMR spectrum of **[S]-59** (150 MHz, $CDCl_3$)



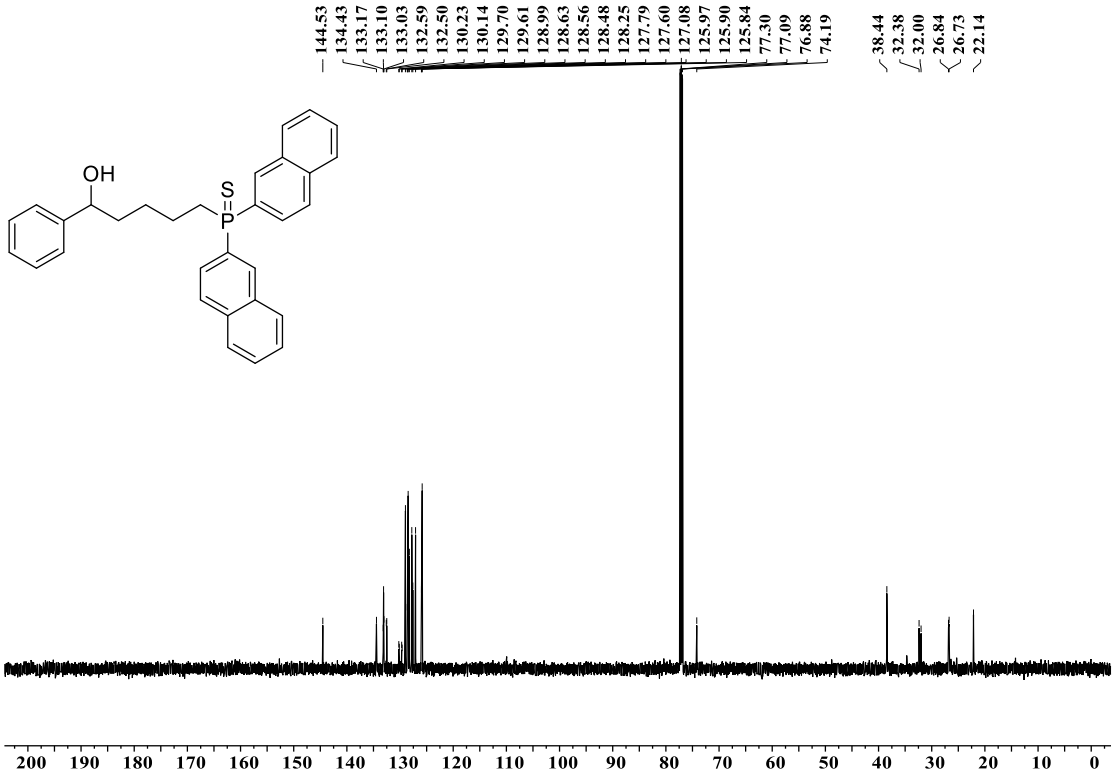
^{31}P NMR spectrum of **[S]-59** (243 MHz, $CDCl_3$)



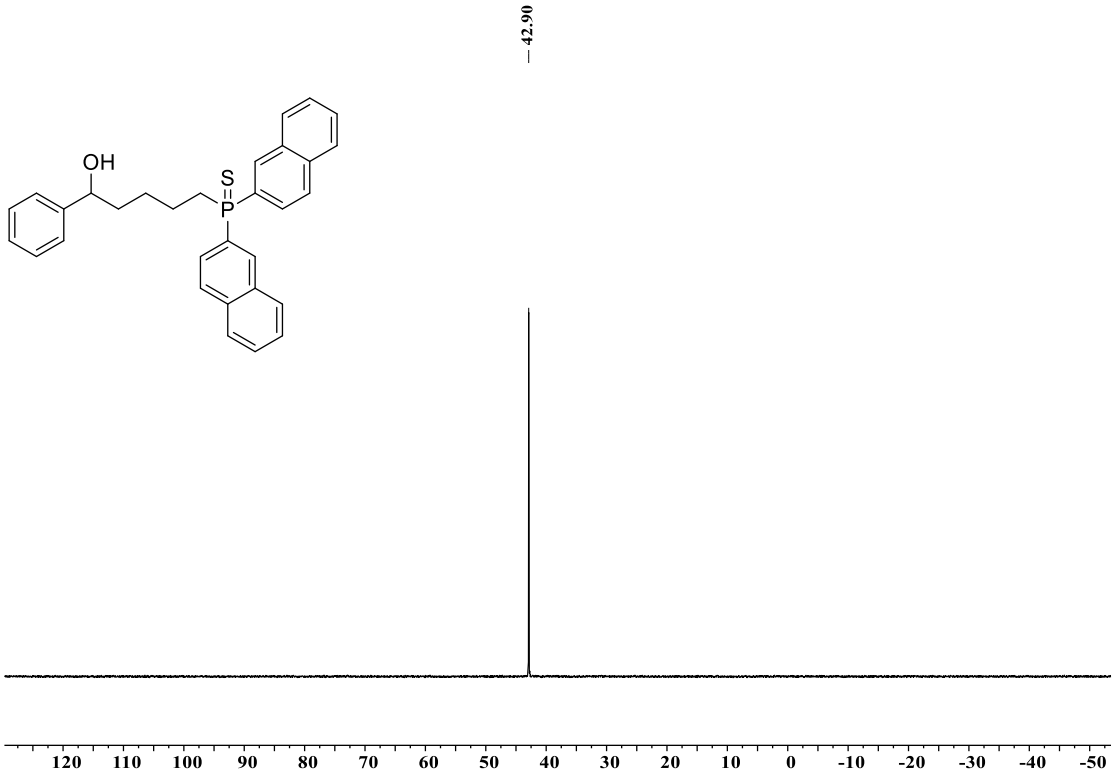
^{1}H NMR spectrum of **[S]-60** (600 MHz, $CDCl_3$)



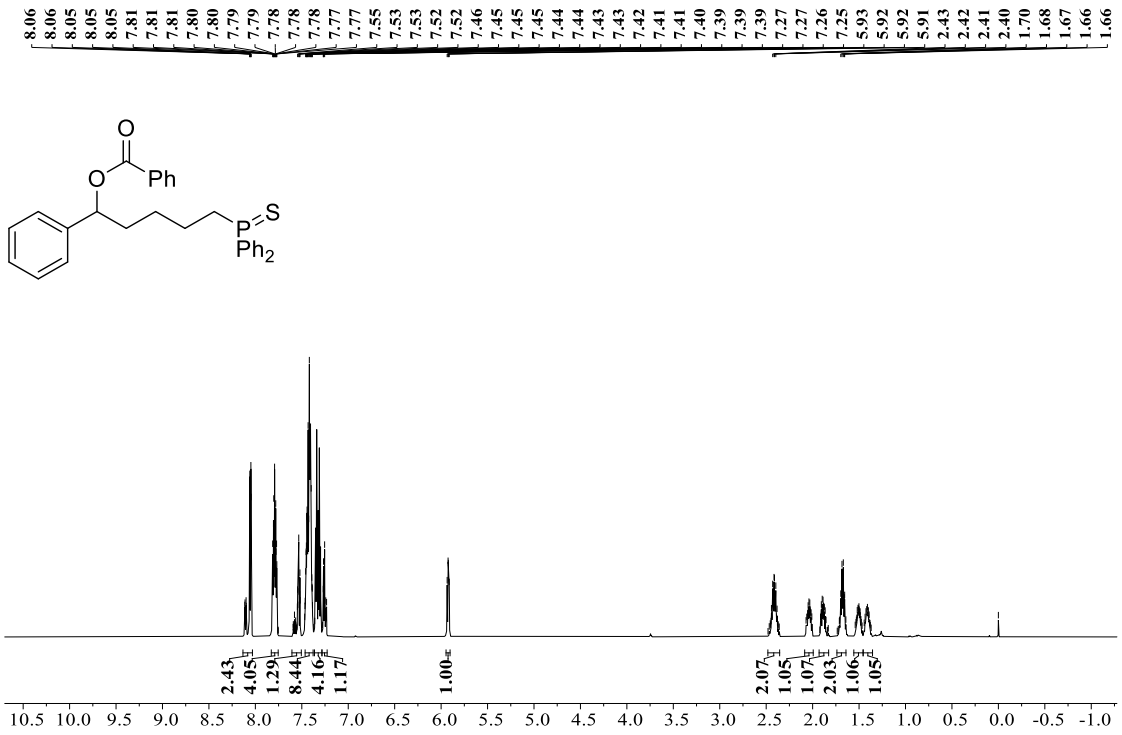
^{13}C NMR spectrum of **[S]-60** (150 MHz, $CDCl_3$)



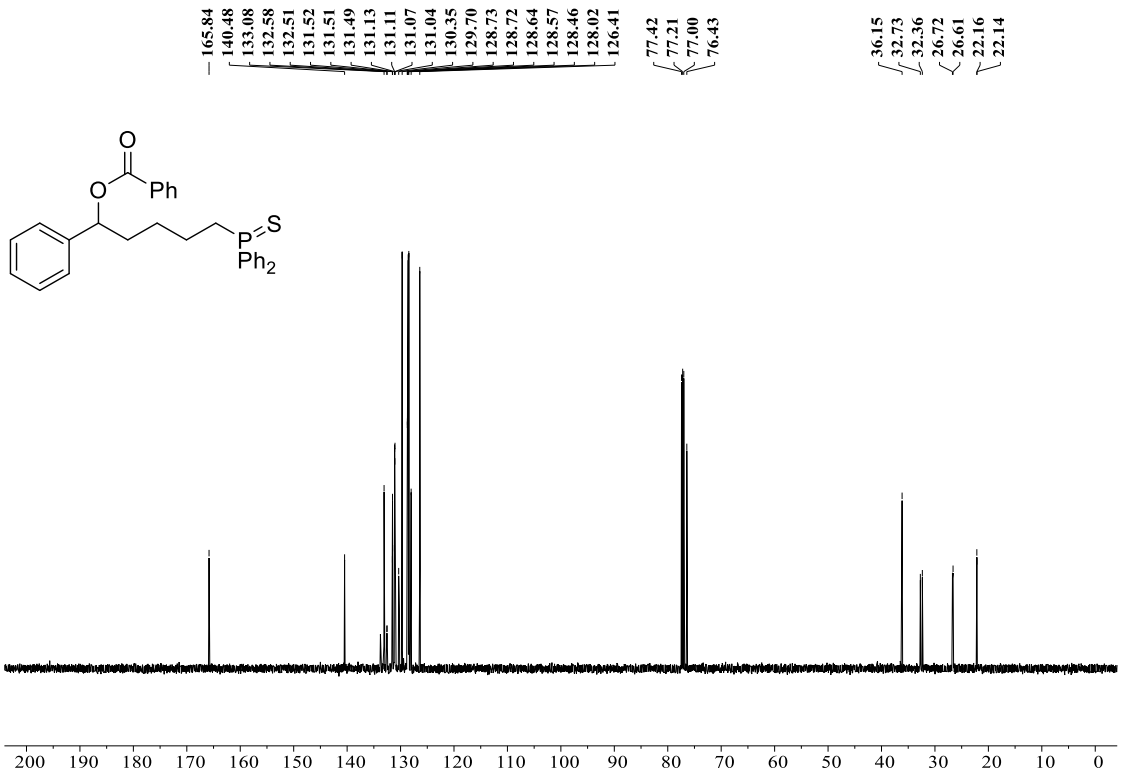
^{31}P NMR spectrum of **[S]-60** (243 MHz, $CDCl_3$)



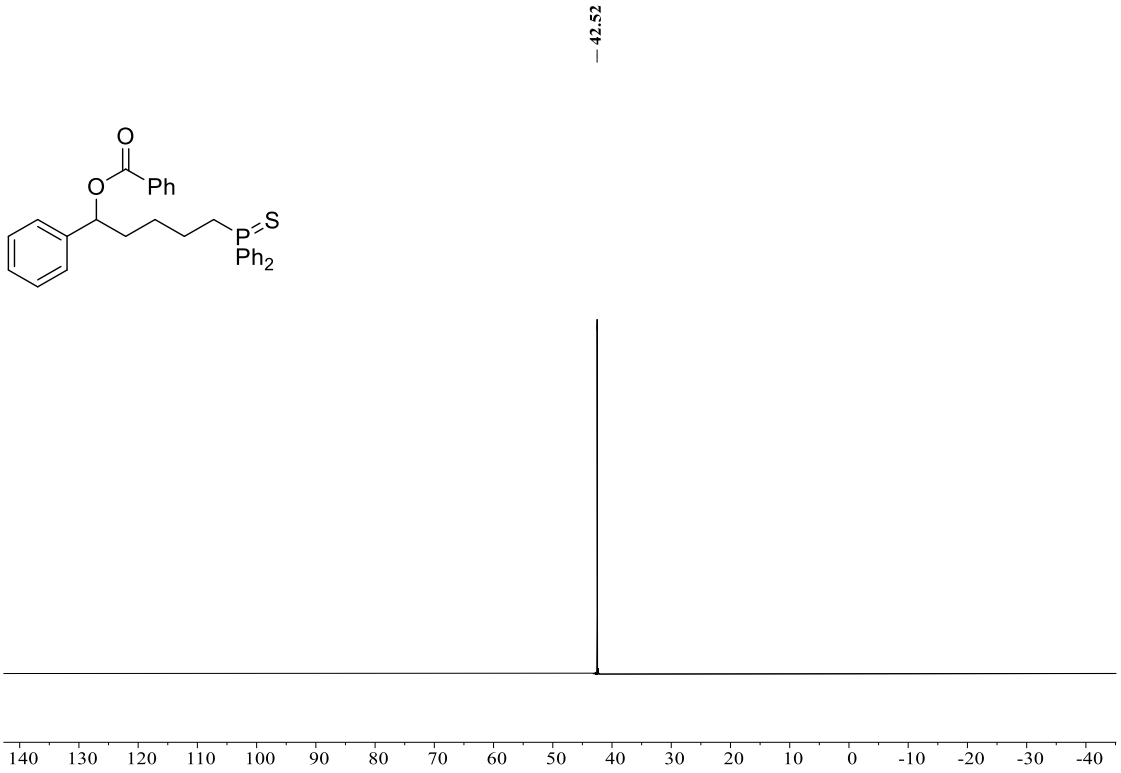
^{1}H NMR spectrum of **61** (600 MHz, $CDCl_3$)



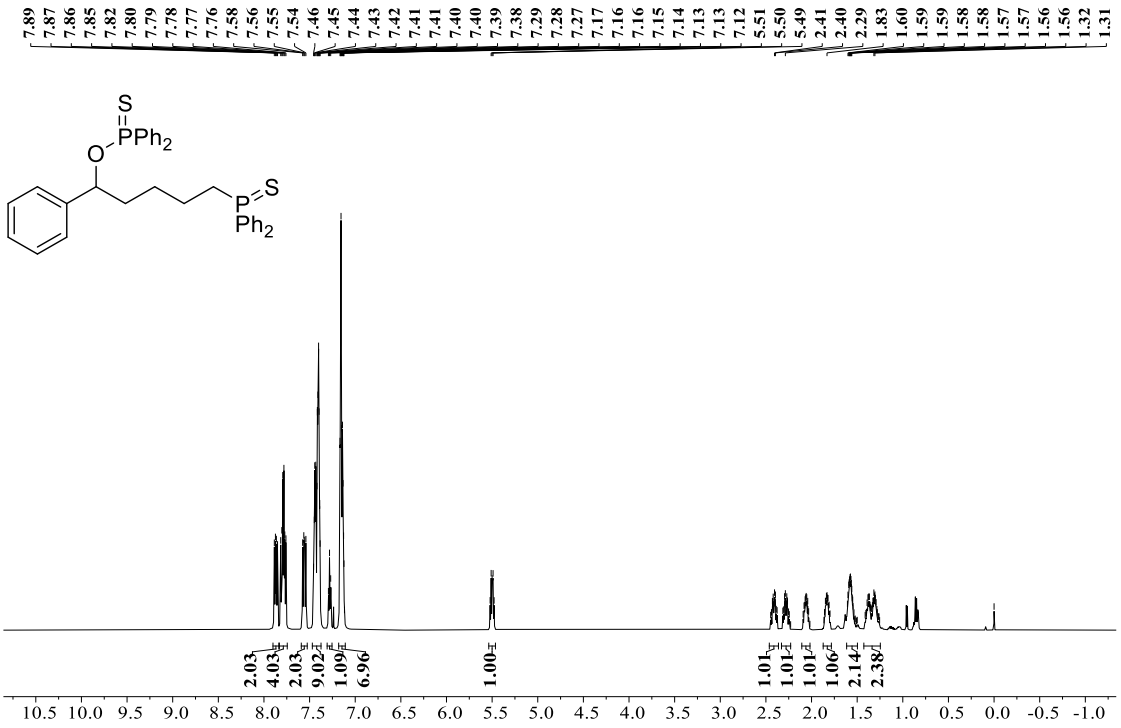
^{13}C NMR spectrum of **61** (150 MHz, $CDCl_3$)



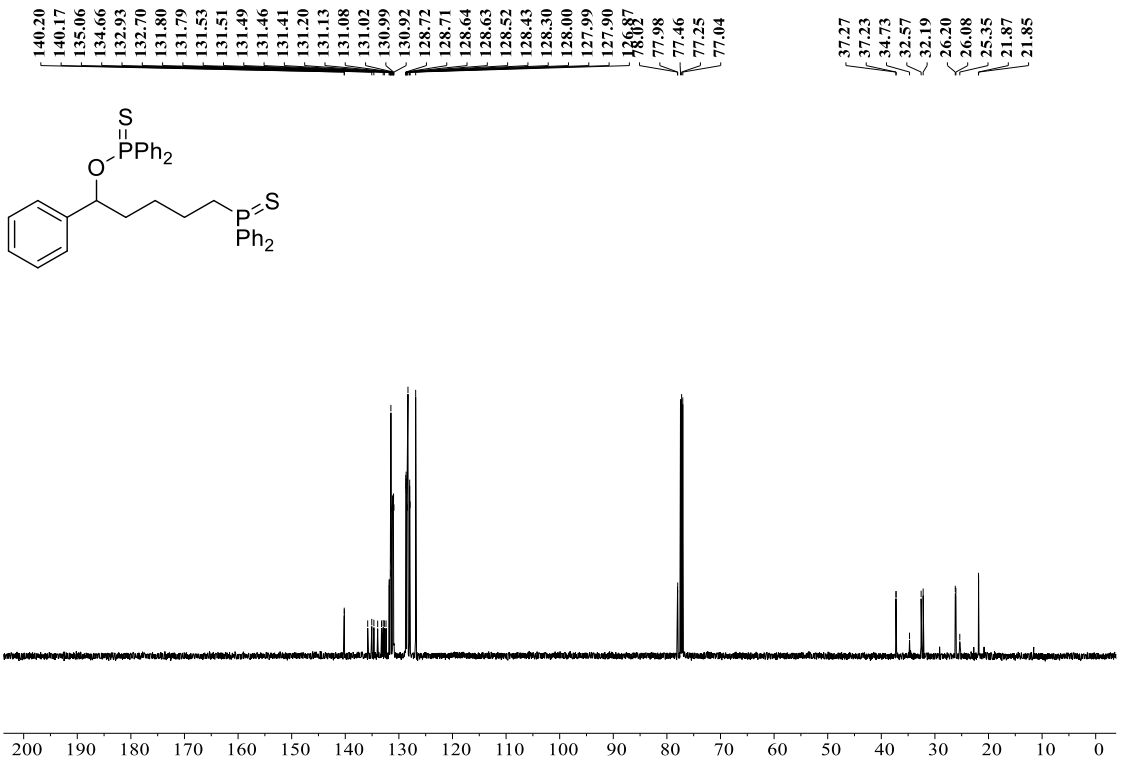
^{31}P NMR spectrum of **61** (243 MHz, $CDCl_3$)



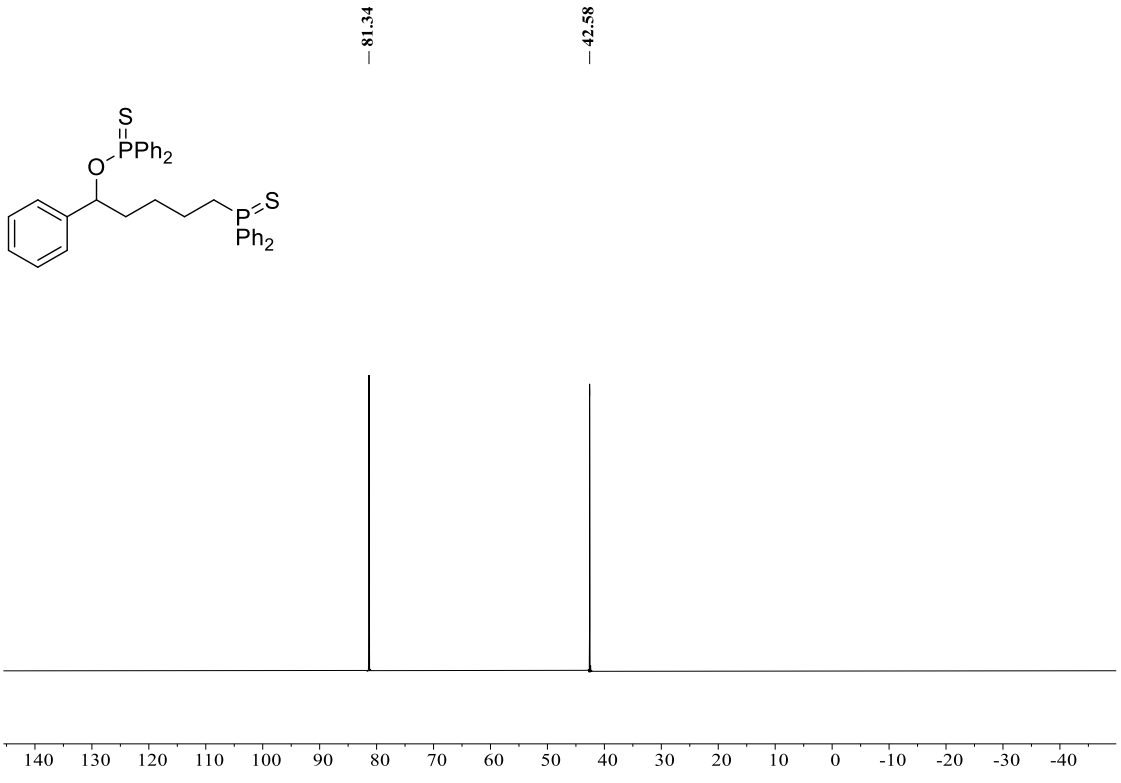
^{1}H NMR spectrum of **62** (600 MHz, $CDCl_3$)



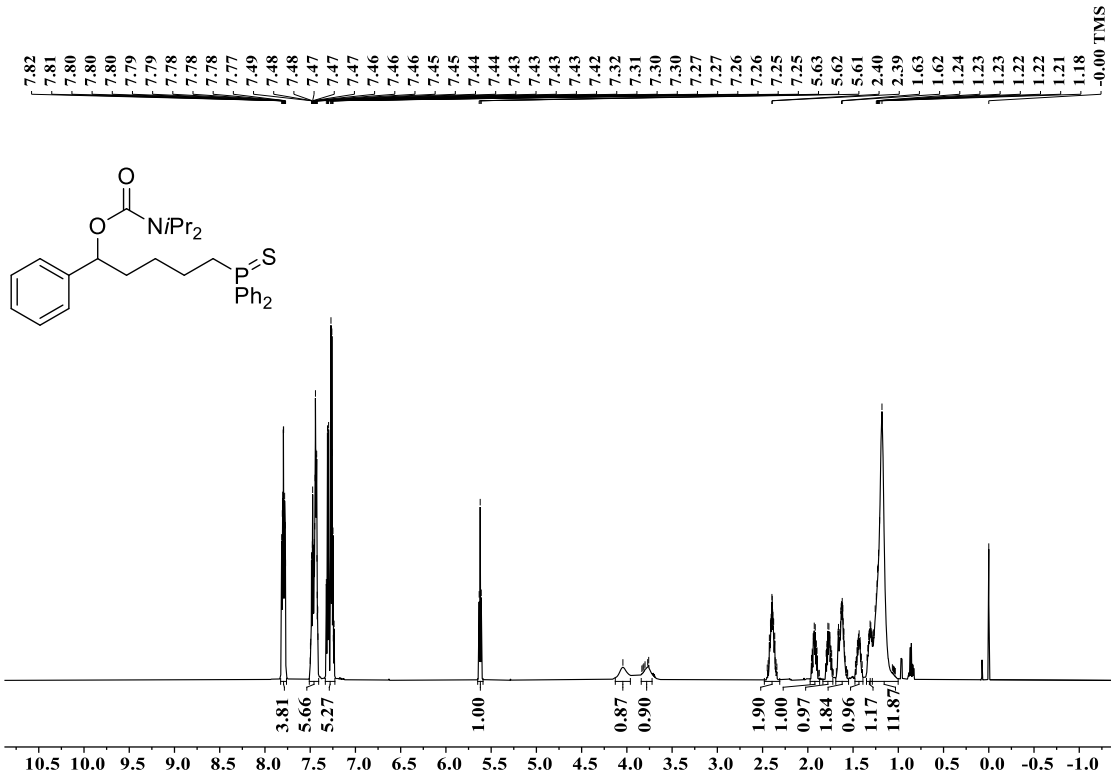
^{13}C NMR spectrum of **62** (150 MHz, $CDCl_3$)



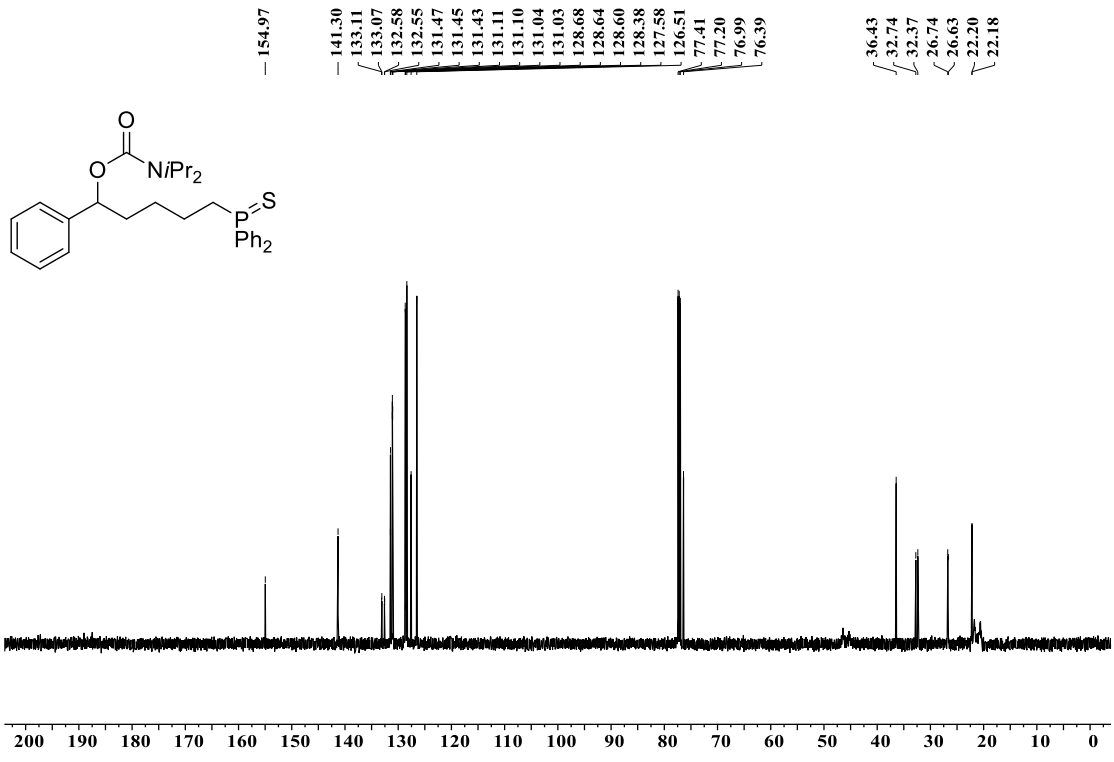
^{31}P NMR spectrum of **62** (243 MHz, $CDCl_3$)



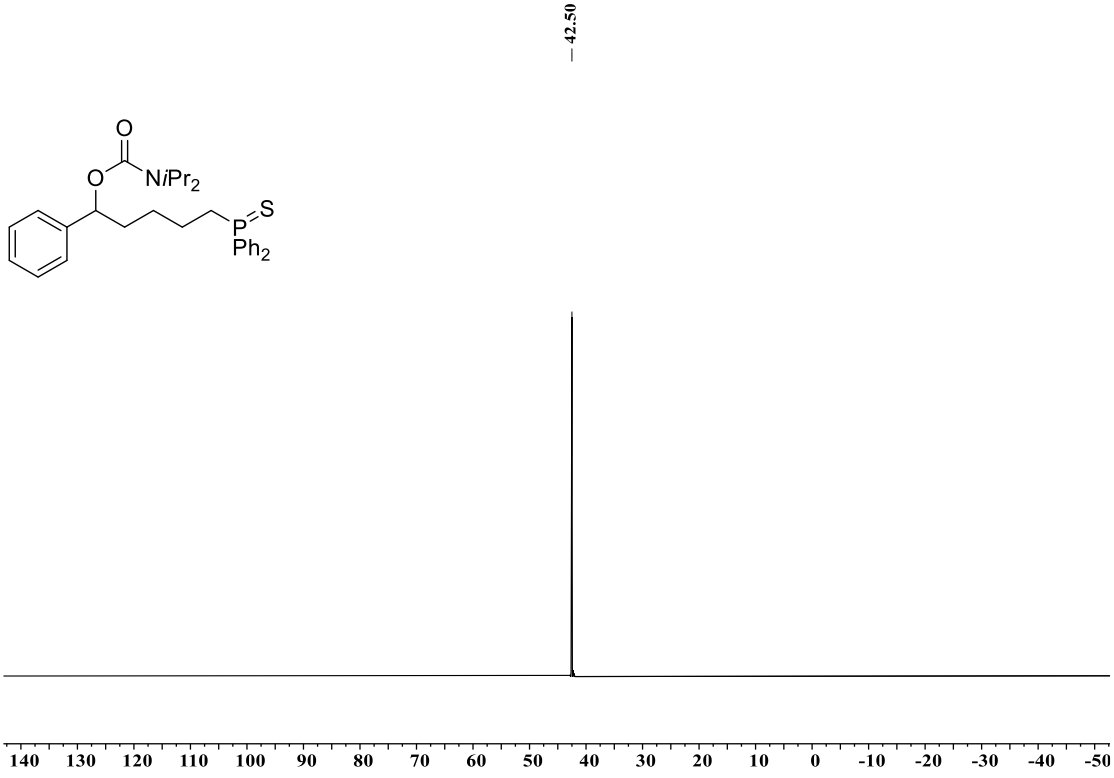
^{1}H NMR spectrum of **63** (600 MHz, $CDCl_3$)



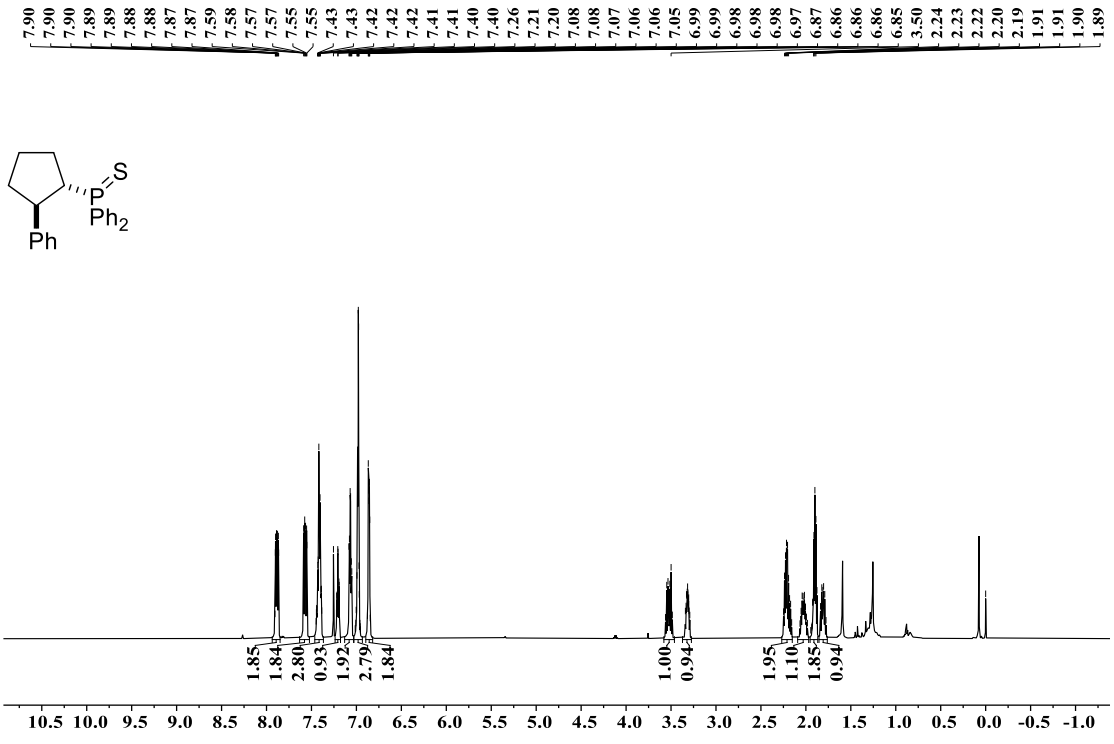
^{13}C NMR spectrum of **63** (150 MHz, $CDCl_3$)



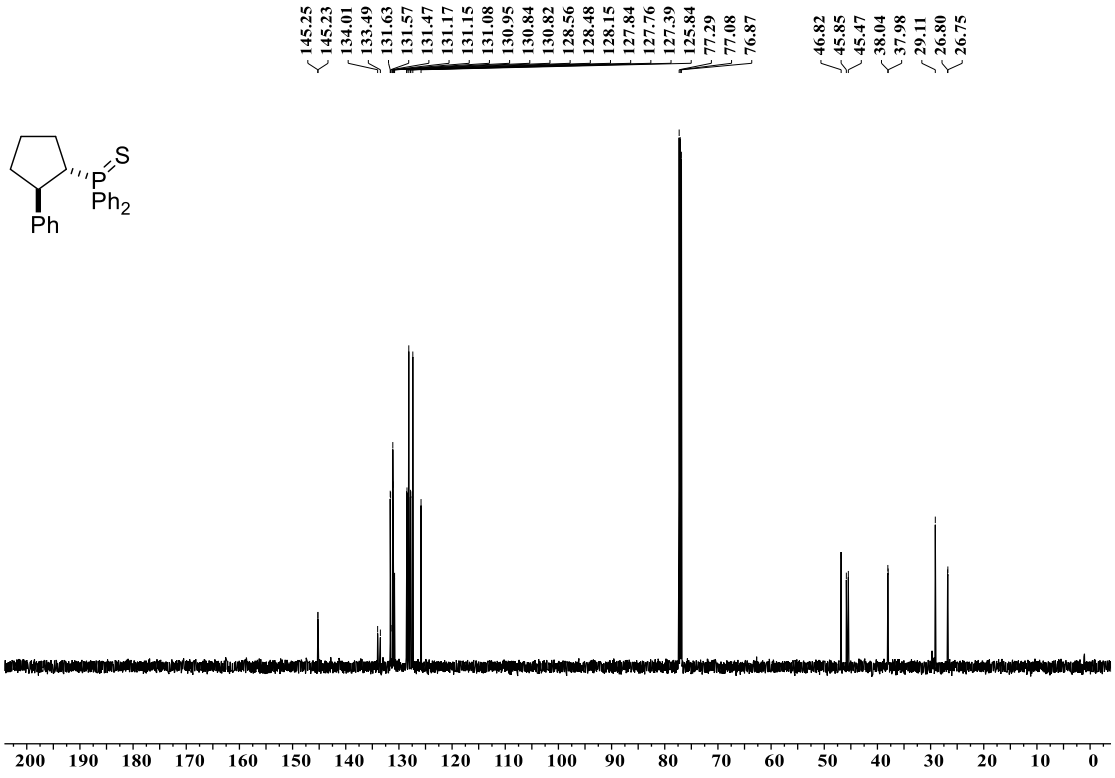
^{31}P NMR spectrum of **63** (243 MHz, $CDCl_3$)



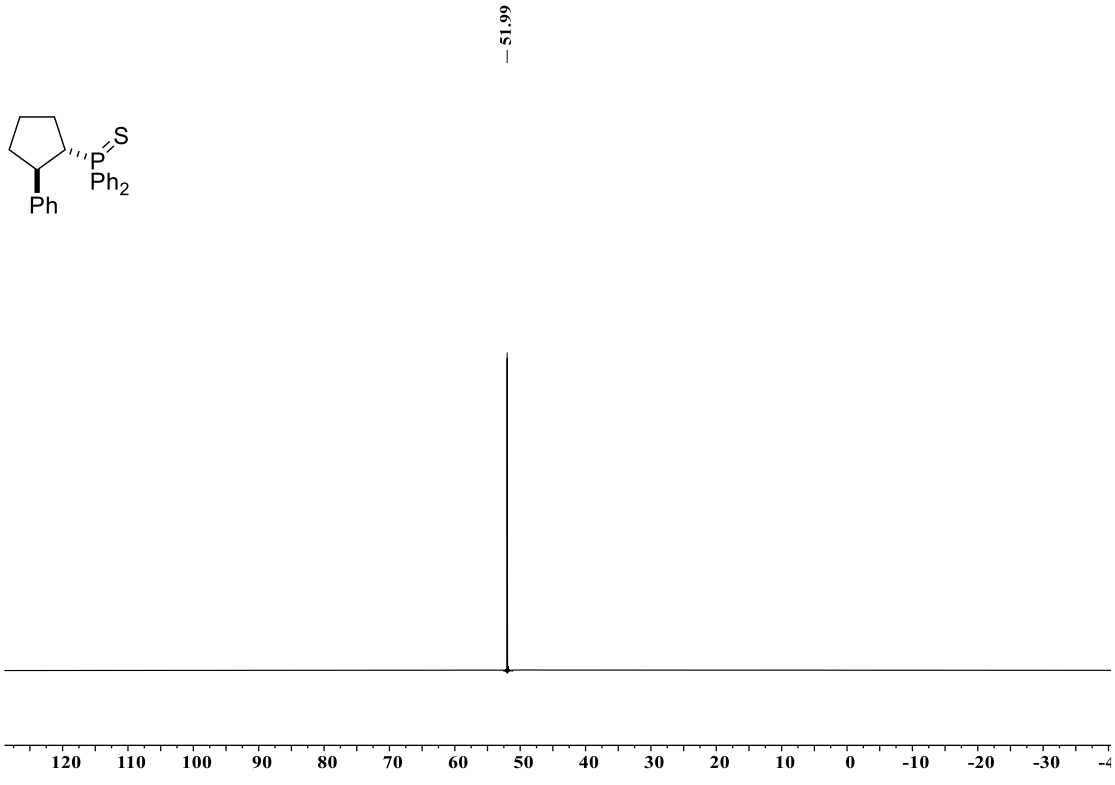
^{1}H NMR spectrum of **64** (600 MHz, $CDCl_3$)



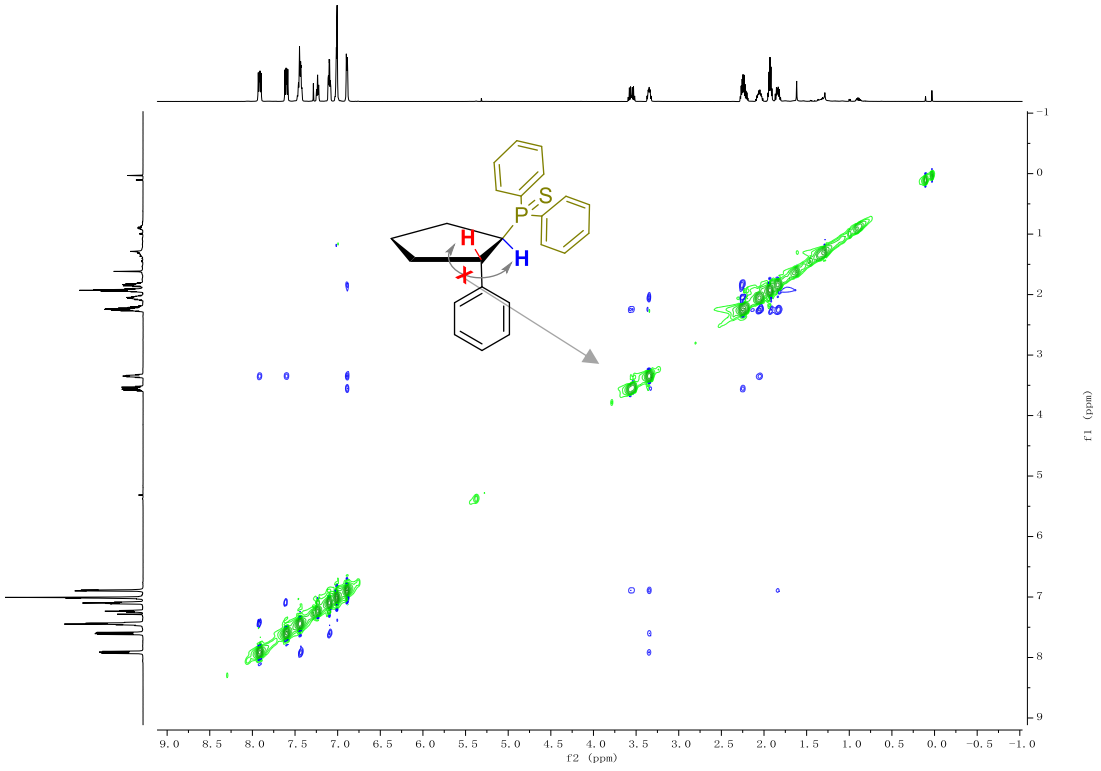
^{13}C NMR spectrum of **64** (150 MHz, $CDCl_3$)



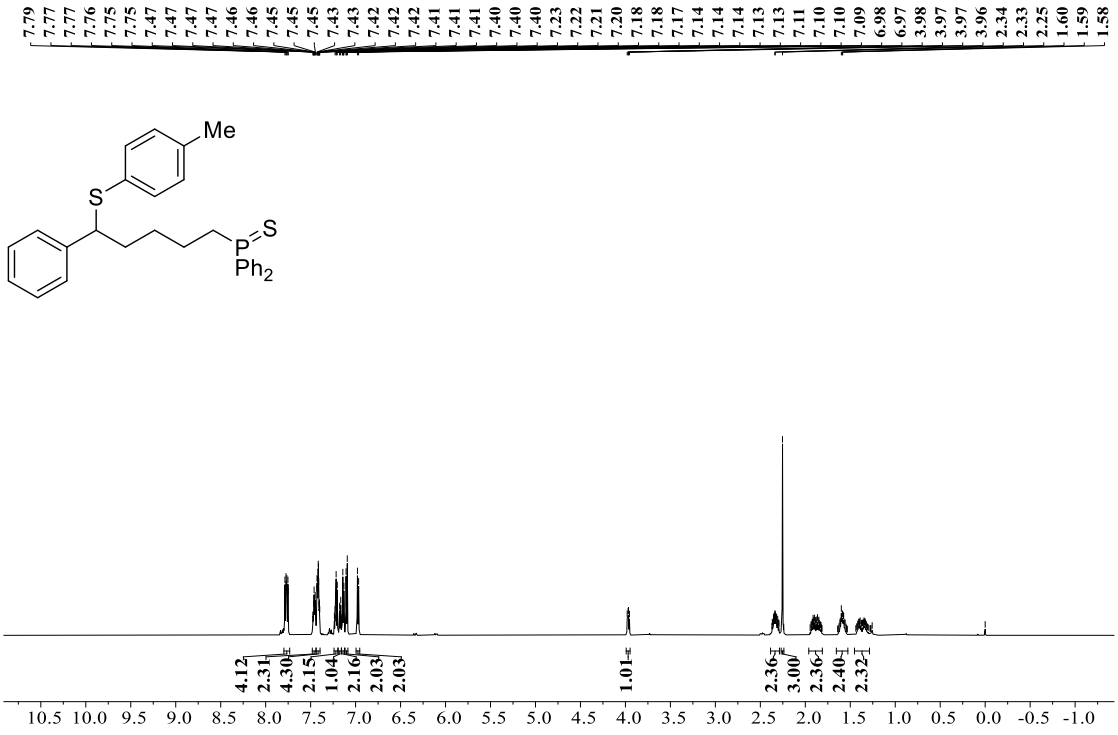
^{31}P NMR spectrum of **64** (243 MHz, $CDCl_3$)



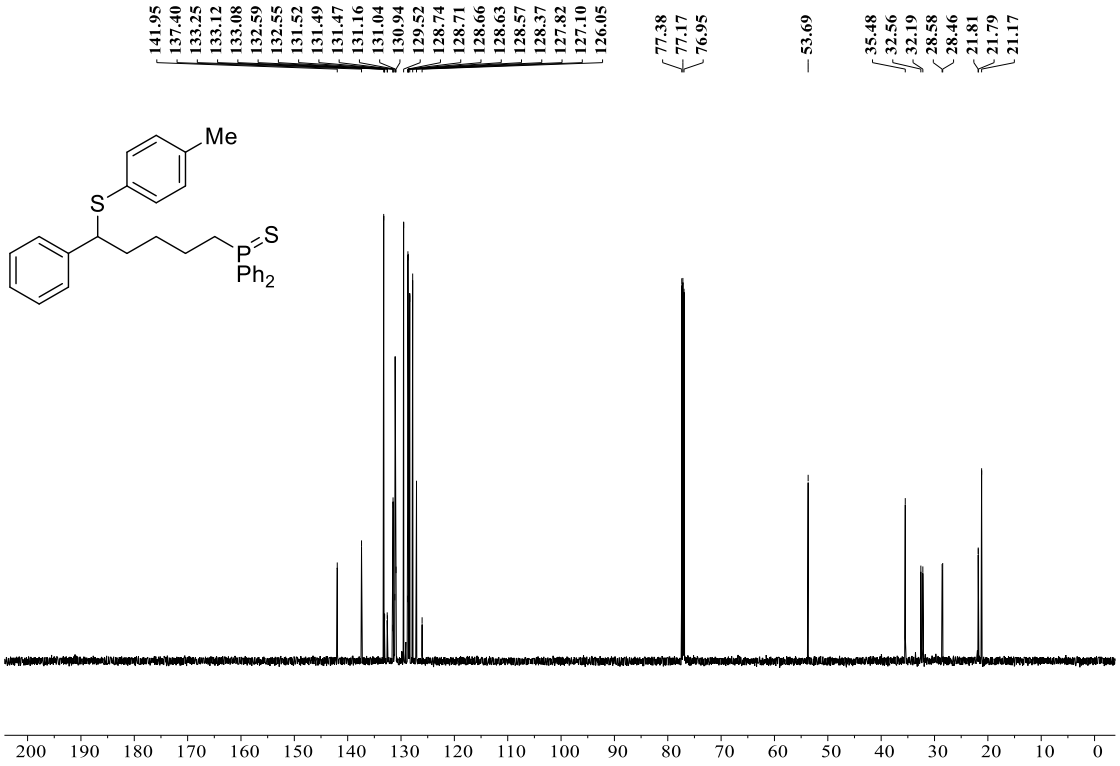
^{1}H NOE NMR spectrum of **64** (600 MHz, $CDCl_3$)



^{1}H NMR spectrum of **65** (600 MHz, $CDCl_3$)

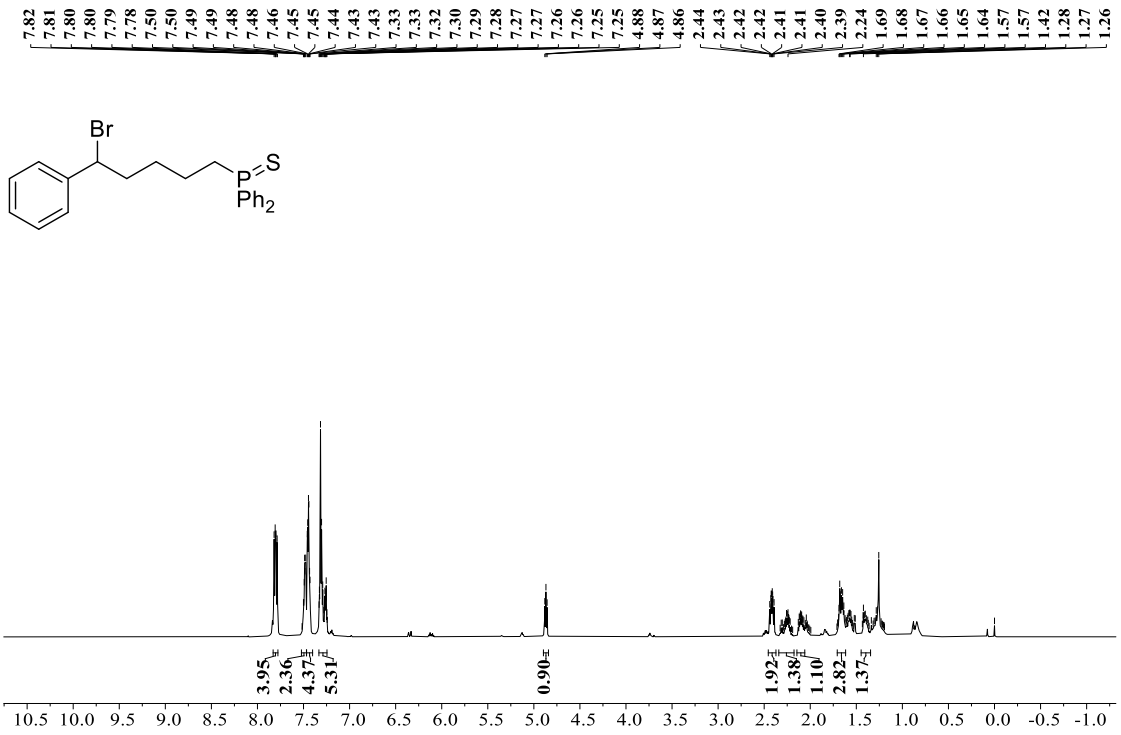


^{13}C NMR spectrum of **65** (150 MHz, $CDCl_3$)

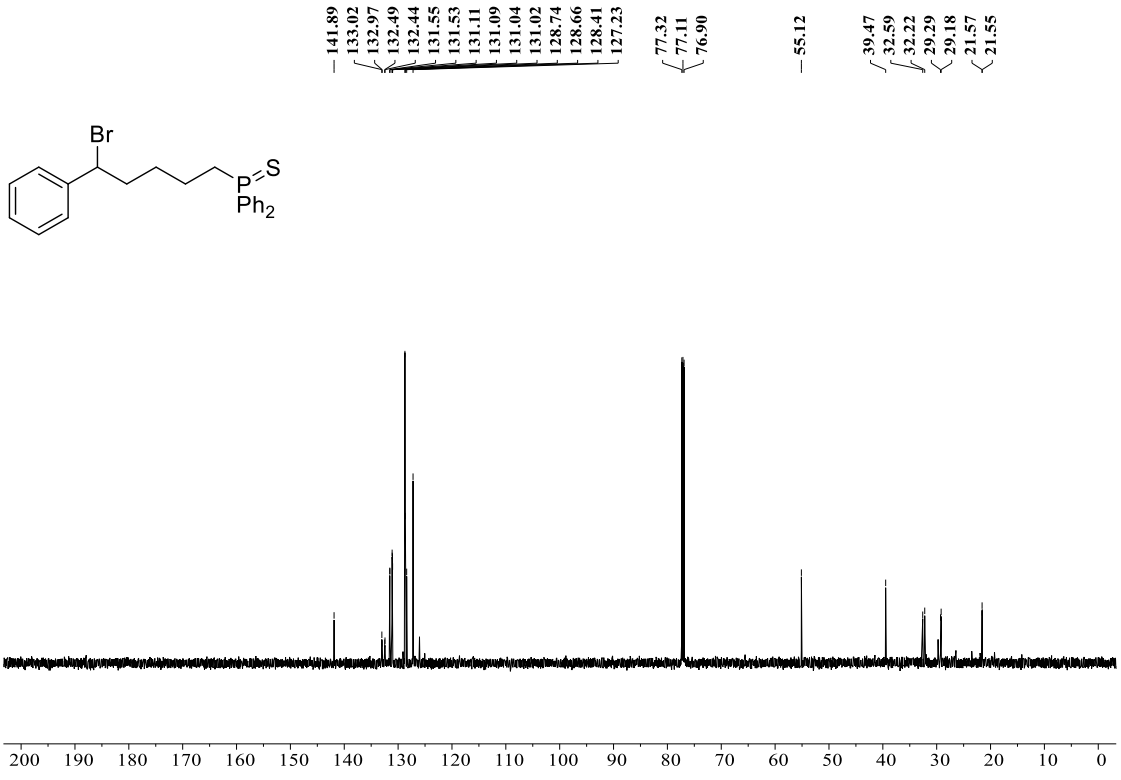


^{31}P NMR spectrum of **65** (243 MHz, $CDCl_3$)

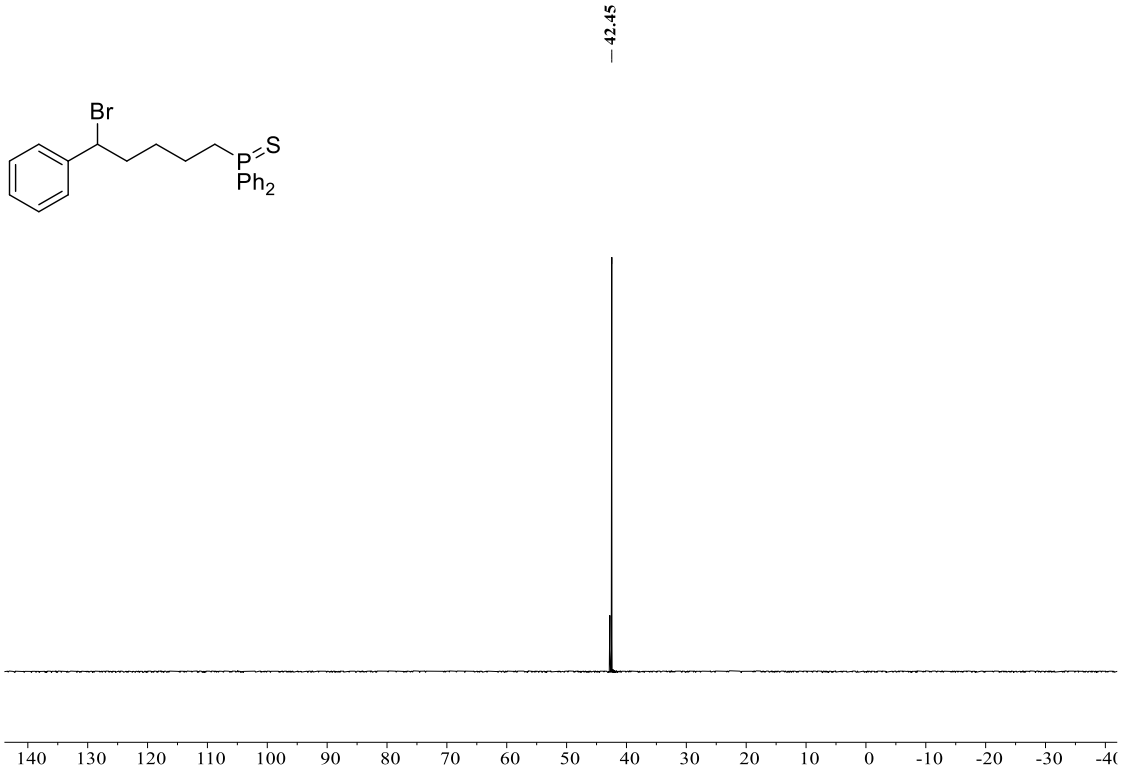
^{1}H NMR spectrum of **66** (600 MHz, $CDCl_3$)



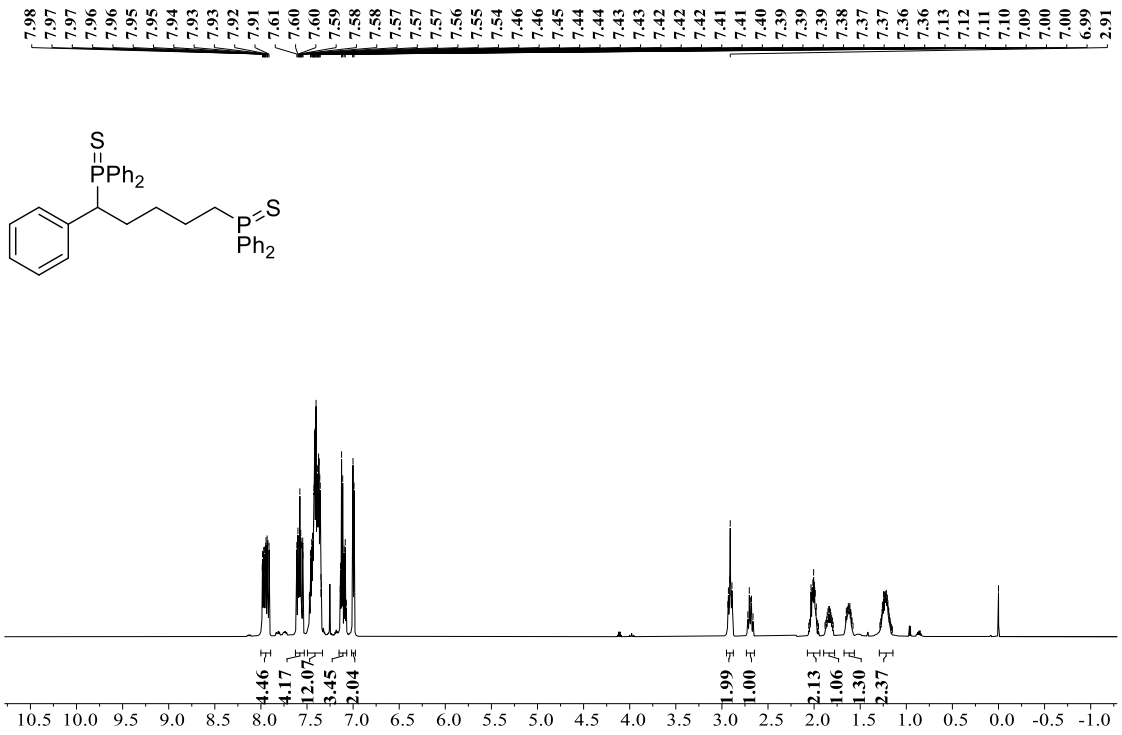
^{13}C NMR spectrum of **66** (150 MHz, $CDCl_3$)



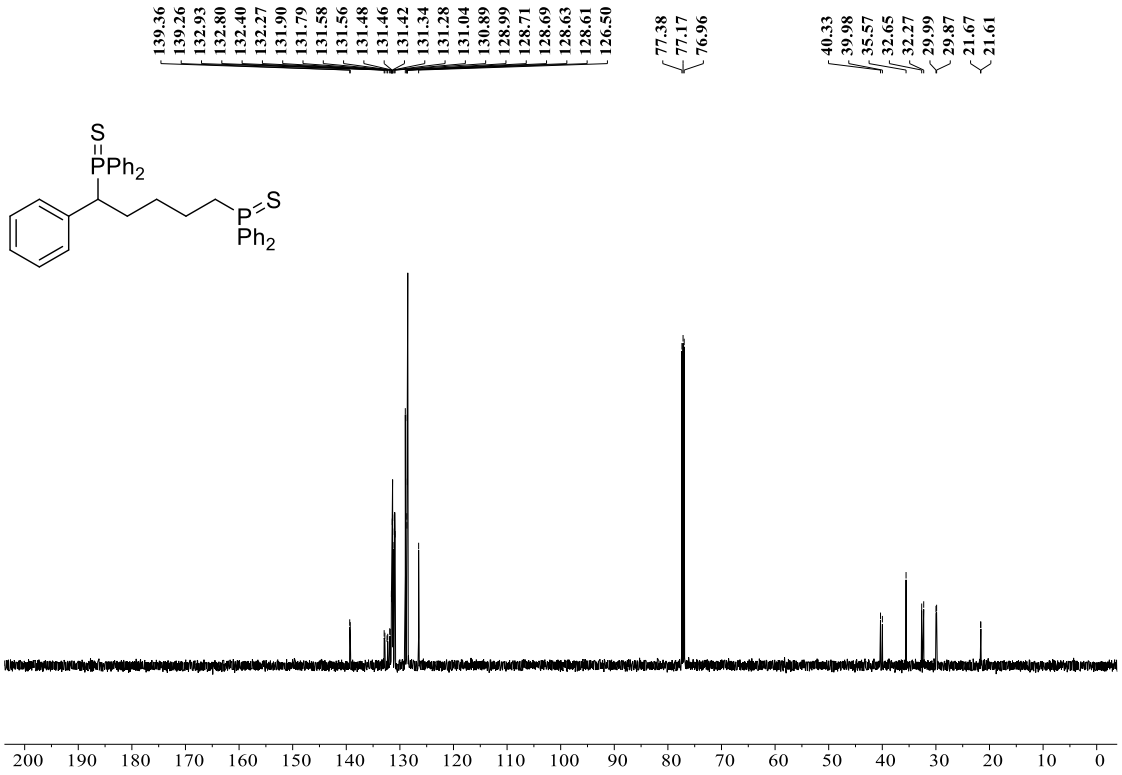
^{31}P NMR spectrum of **66** (243 MHz, $CDCl_3$)



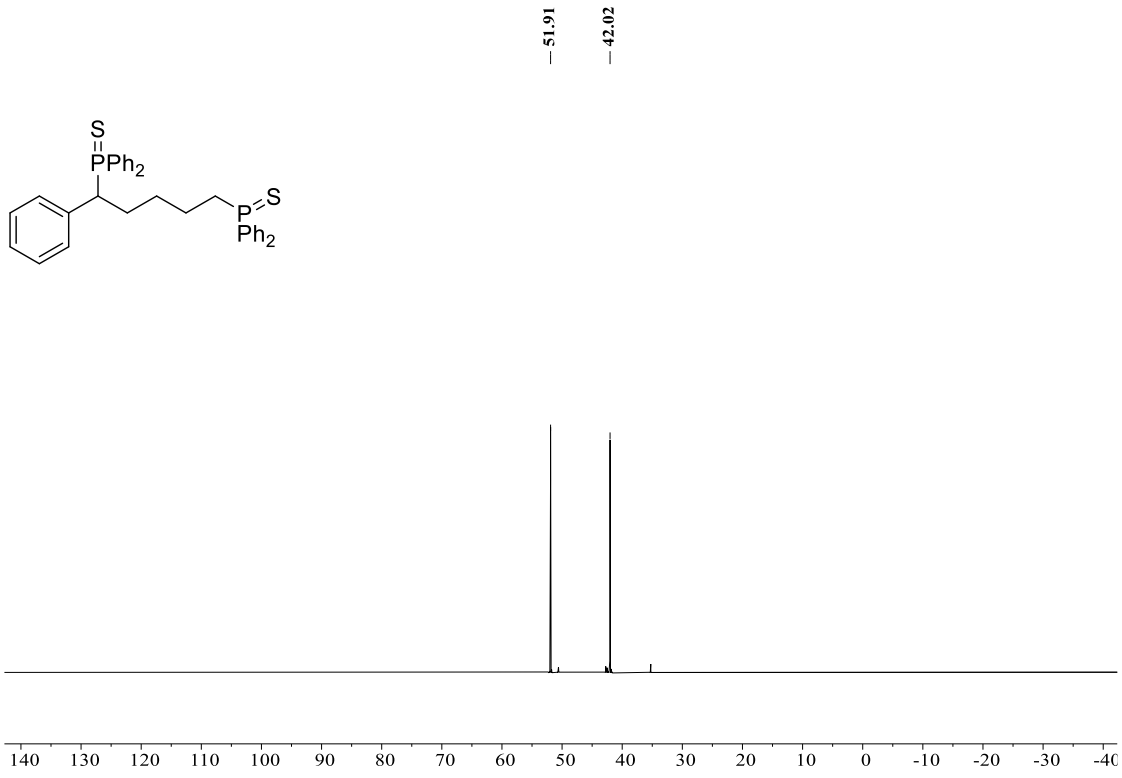
^{1}H NMR spectrum of **67** (600 MHz, $CDCl_3$)



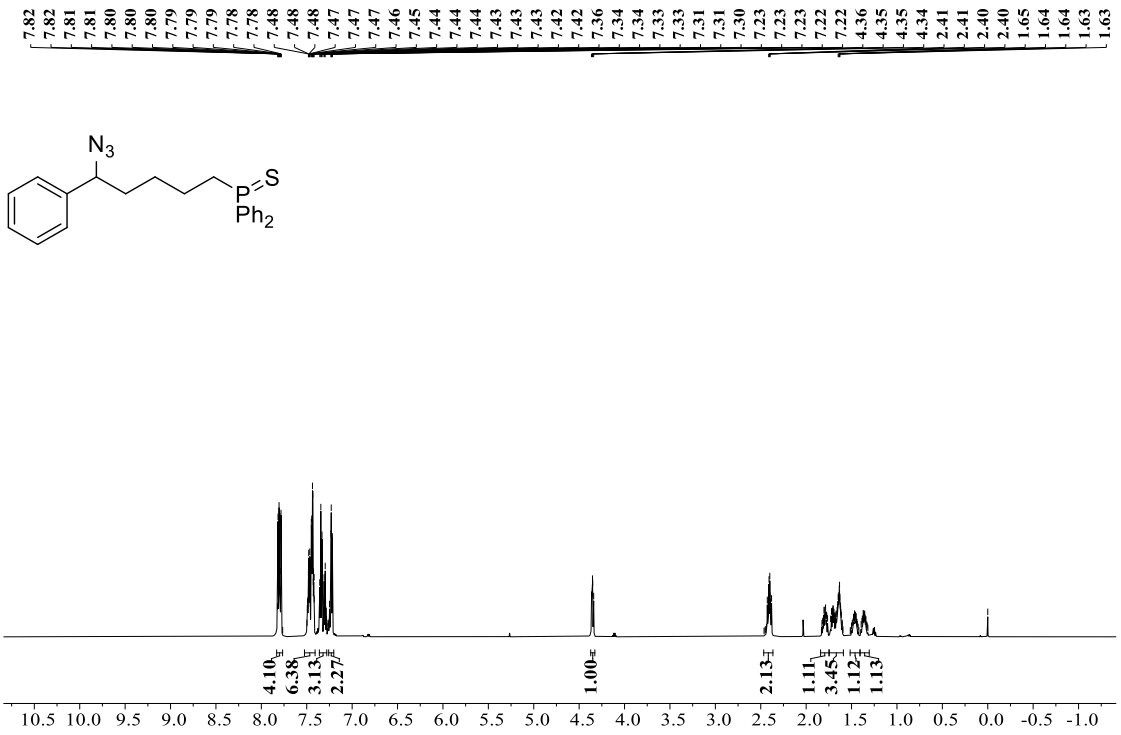
^{13}C NMR spectrum of **67** (150 MHz, $CDCl_3$)



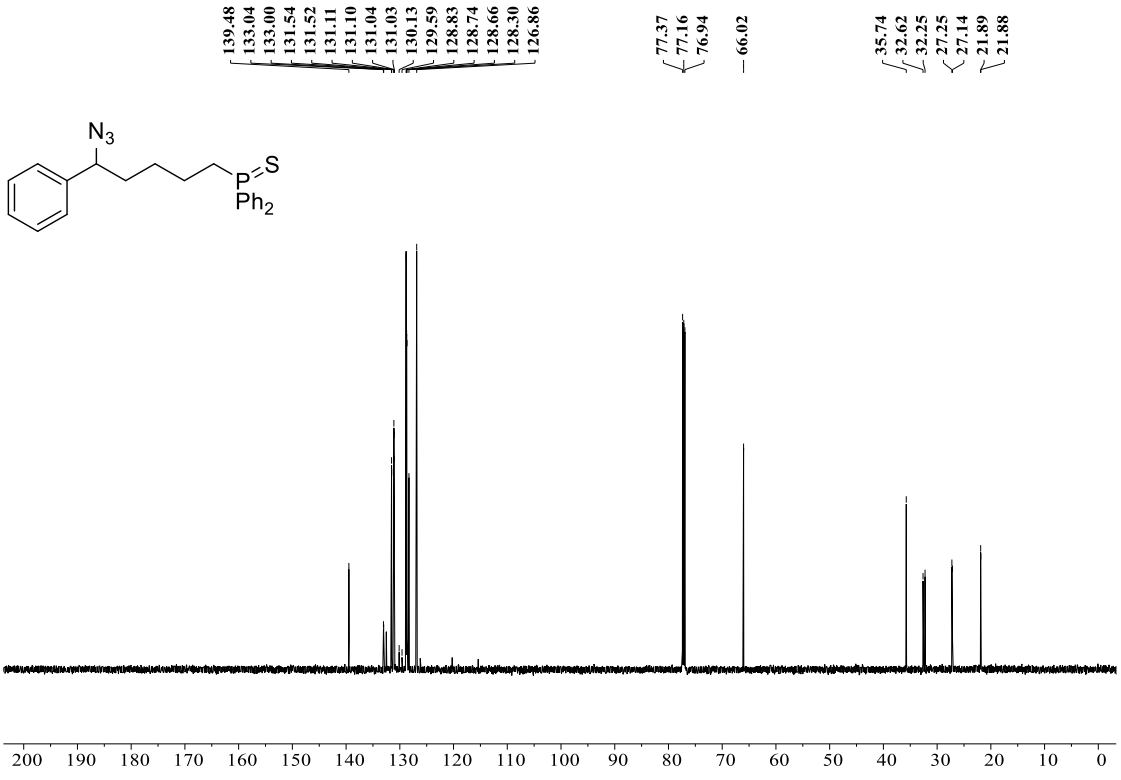
^{31}P NMR spectrum of **67** (243 MHz, $CDCl_3$)



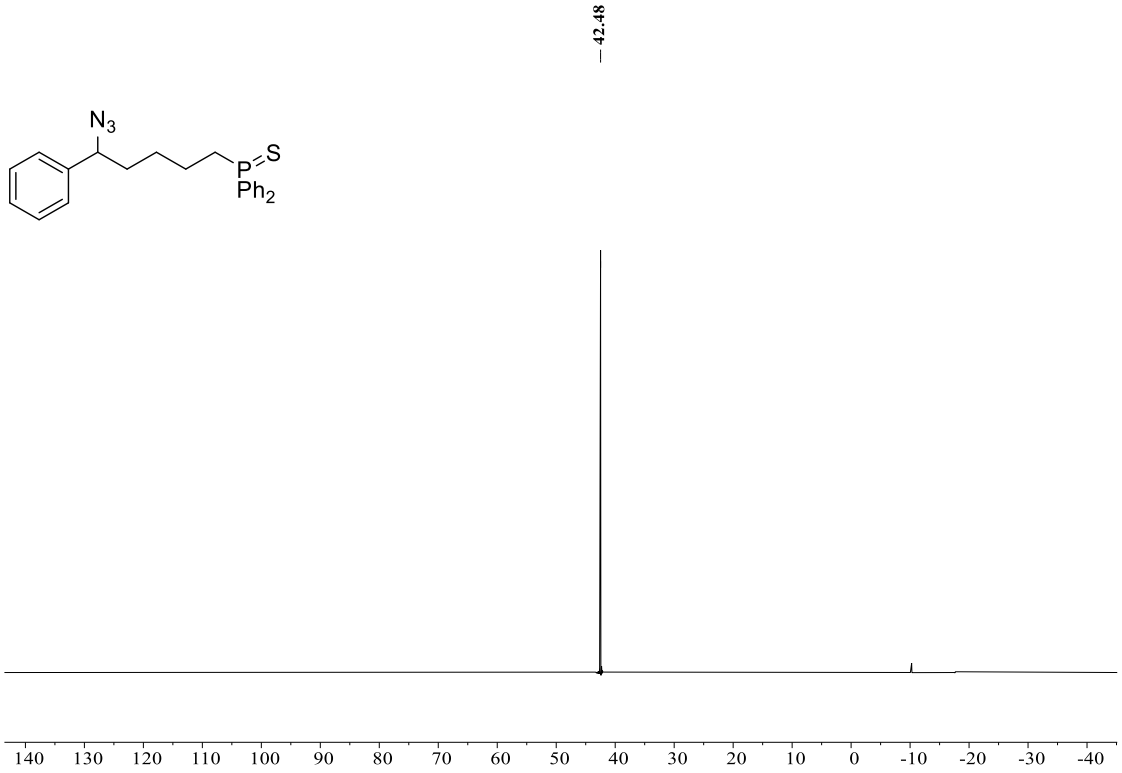
^{1}H NMR spectrum of **68** (600 MHz, $CDCl_3$)



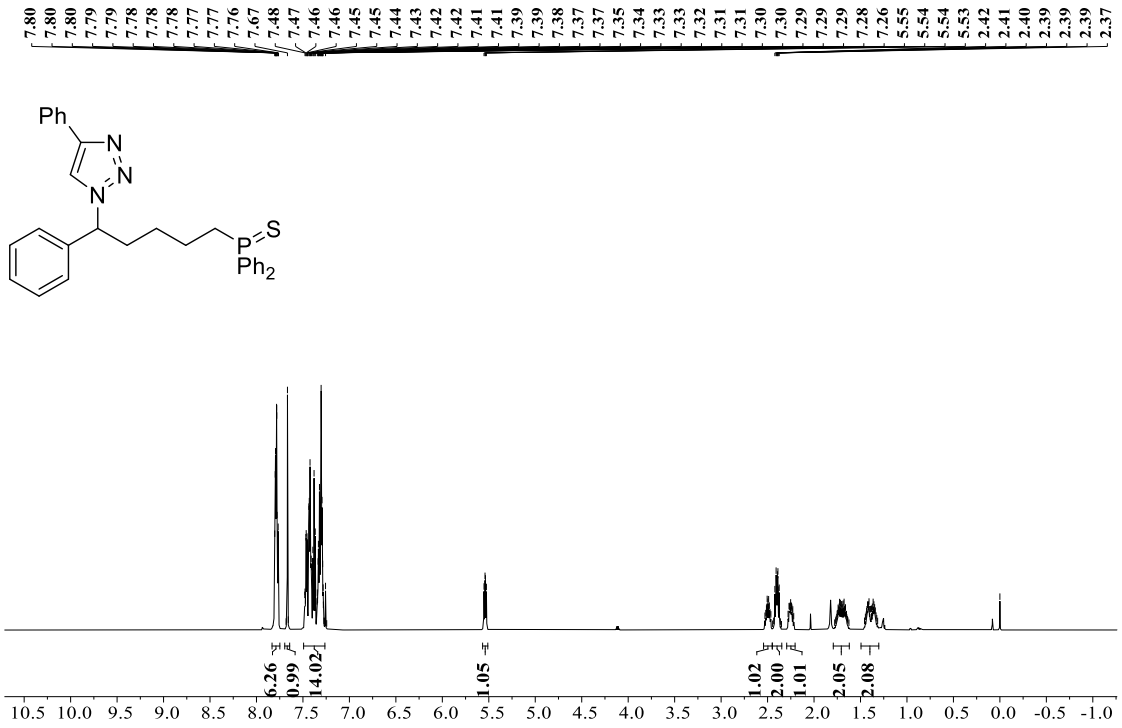
^{13}C NMR spectrum of **68** (150 MHz, $CDCl_3$)



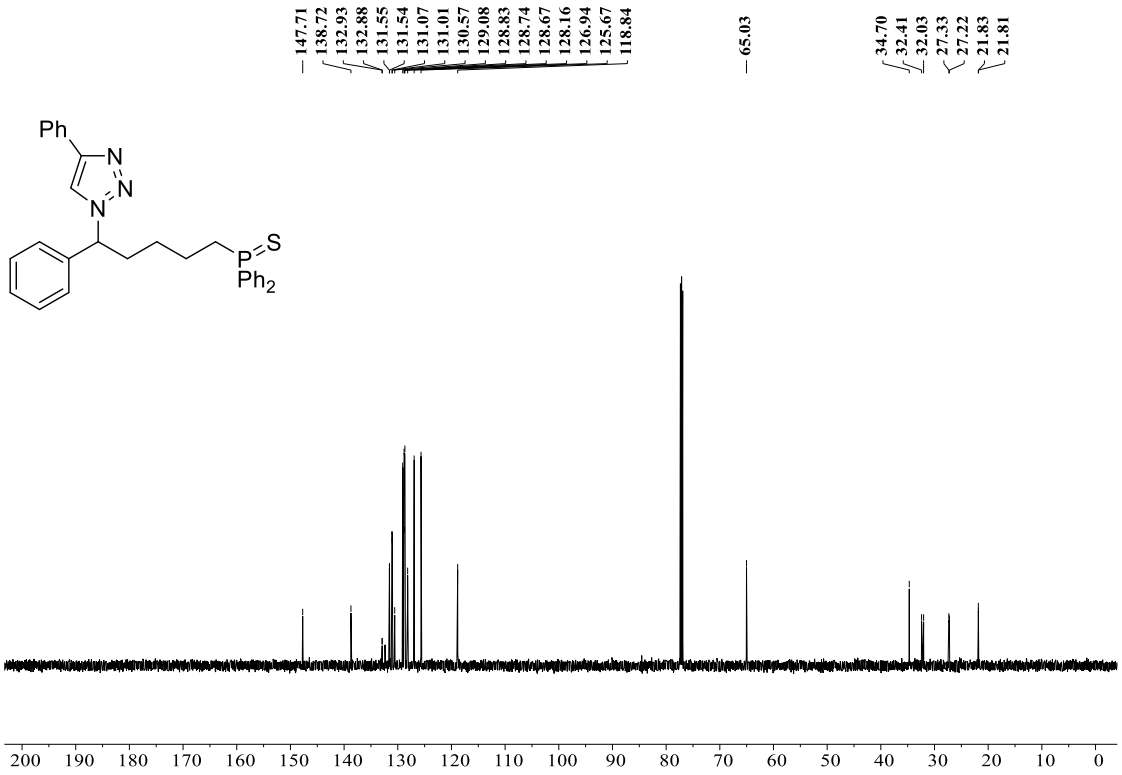
^{31}P NMR spectrum of **68** (243 MHz, $CDCl_3$)



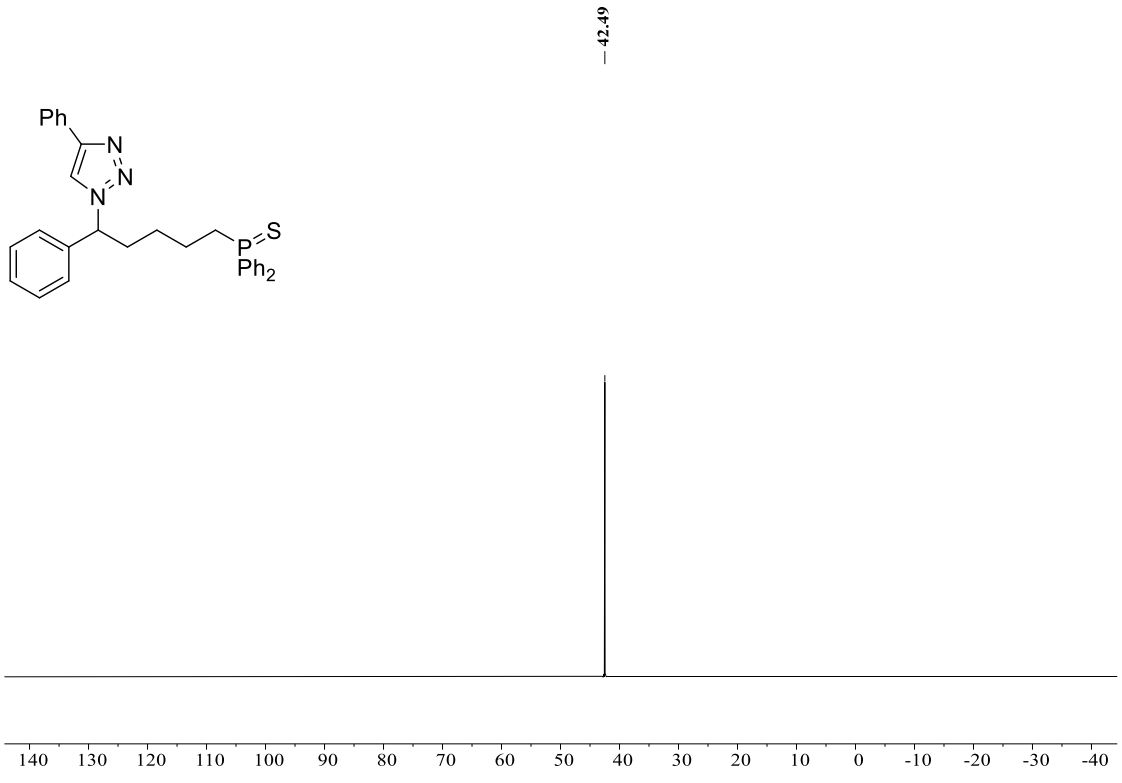
^{1}H NMR spectrum of **69** (600 MHz, $CDCl_3$)



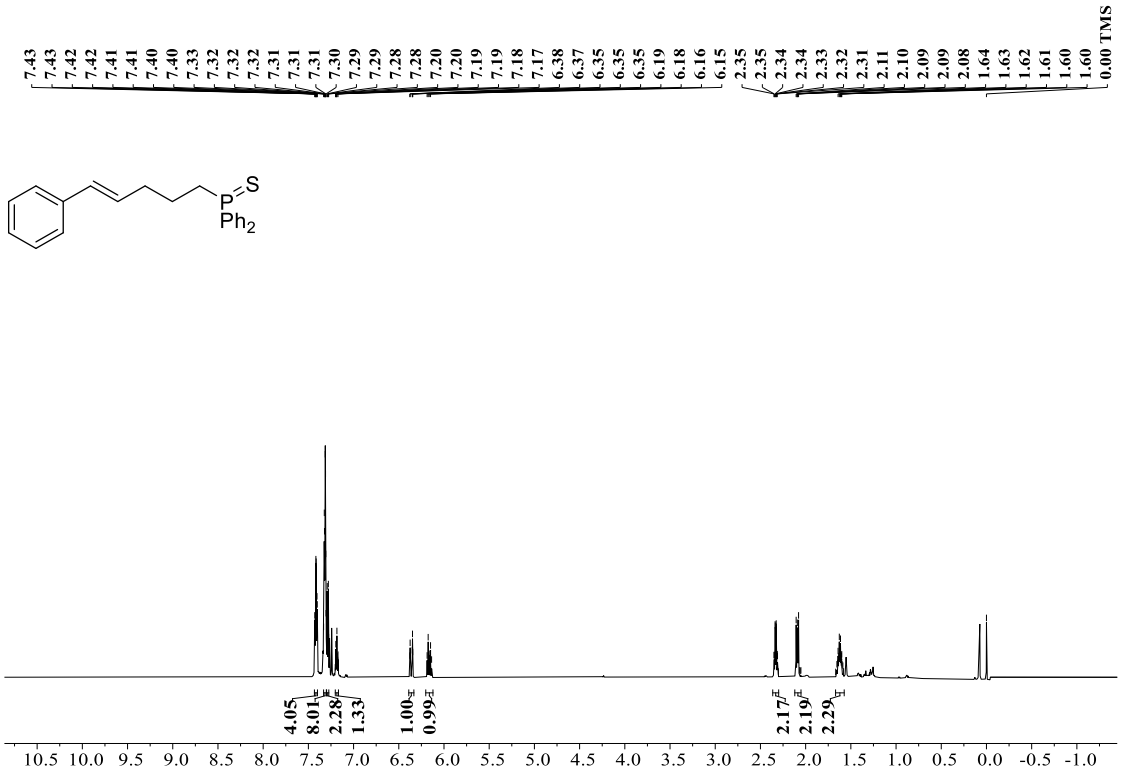
^{13}C NMR spectrum of **69** (150 MHz, $CDCl_3$)



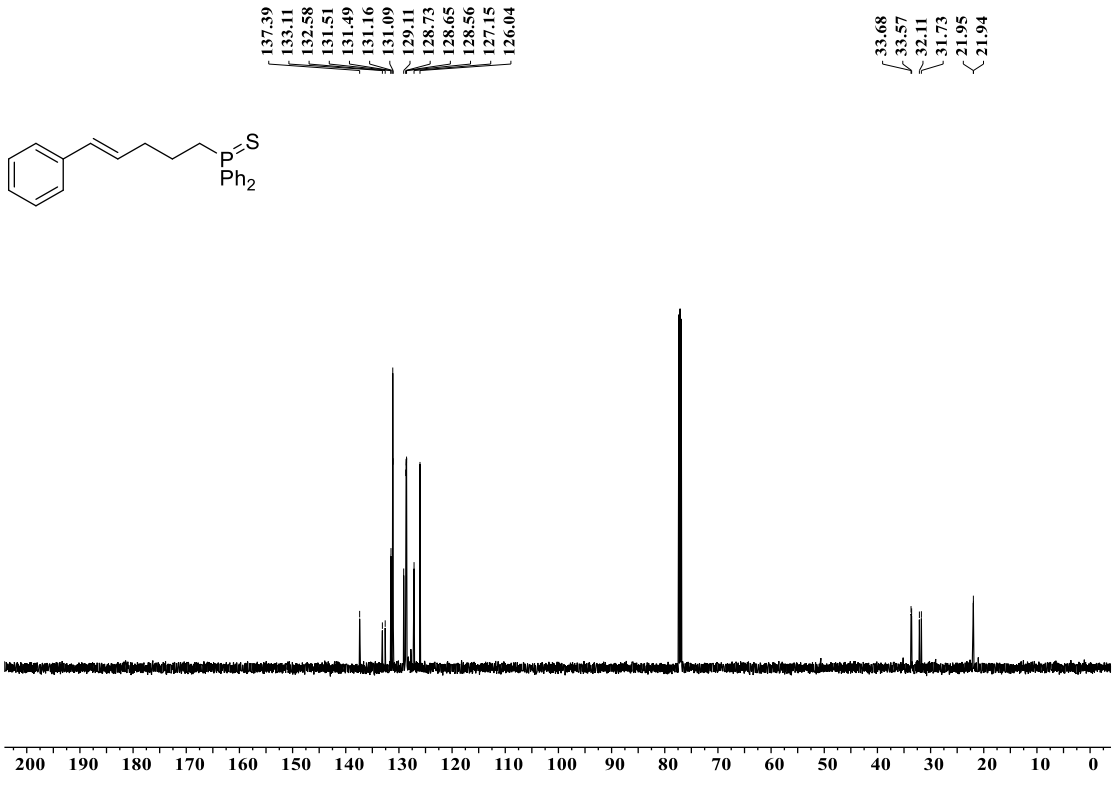
^{31}P NMR spectrum of **69** (243 MHz, $CDCl_3$)



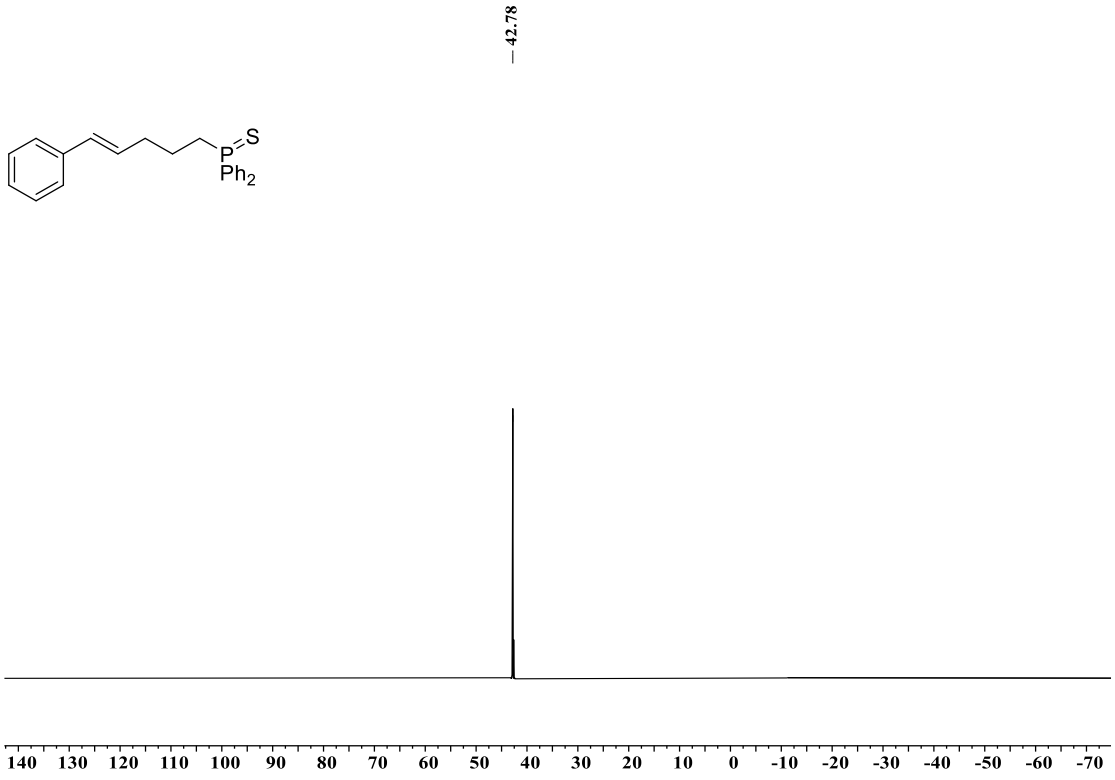
^{1}H NMR spectrum of **70** (600 MHz, $CDCl_3$)



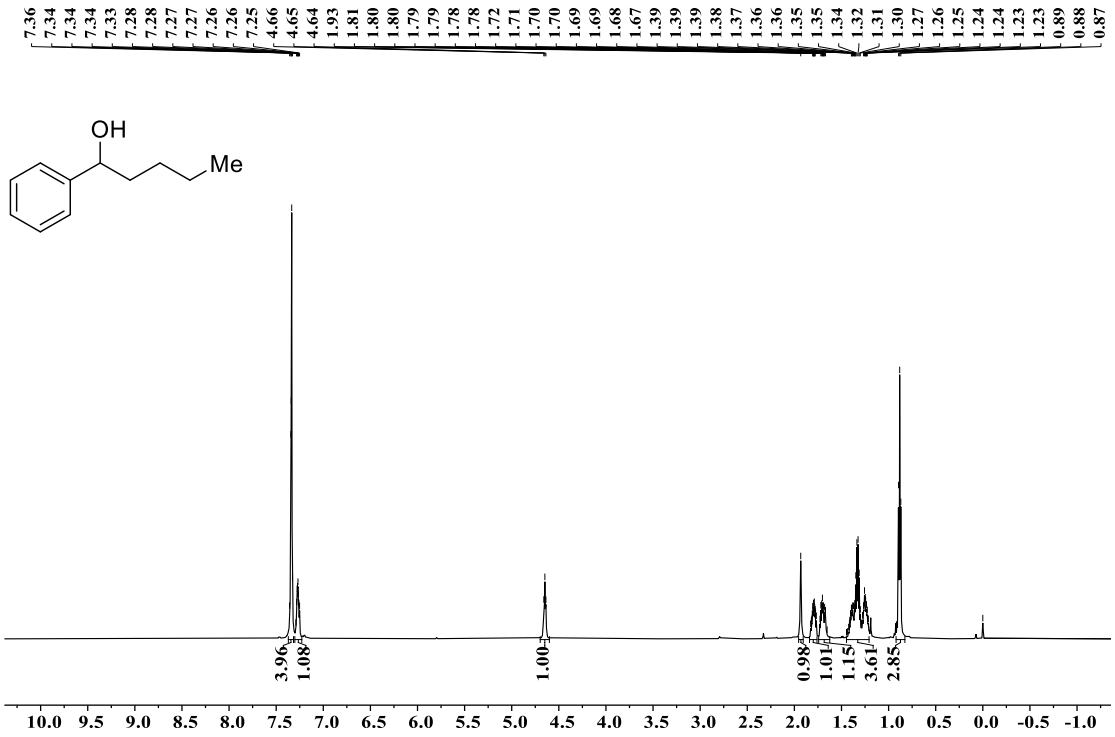
^{13}C NMR spectrum of **70** (150 MHz, $CDCl_3$)



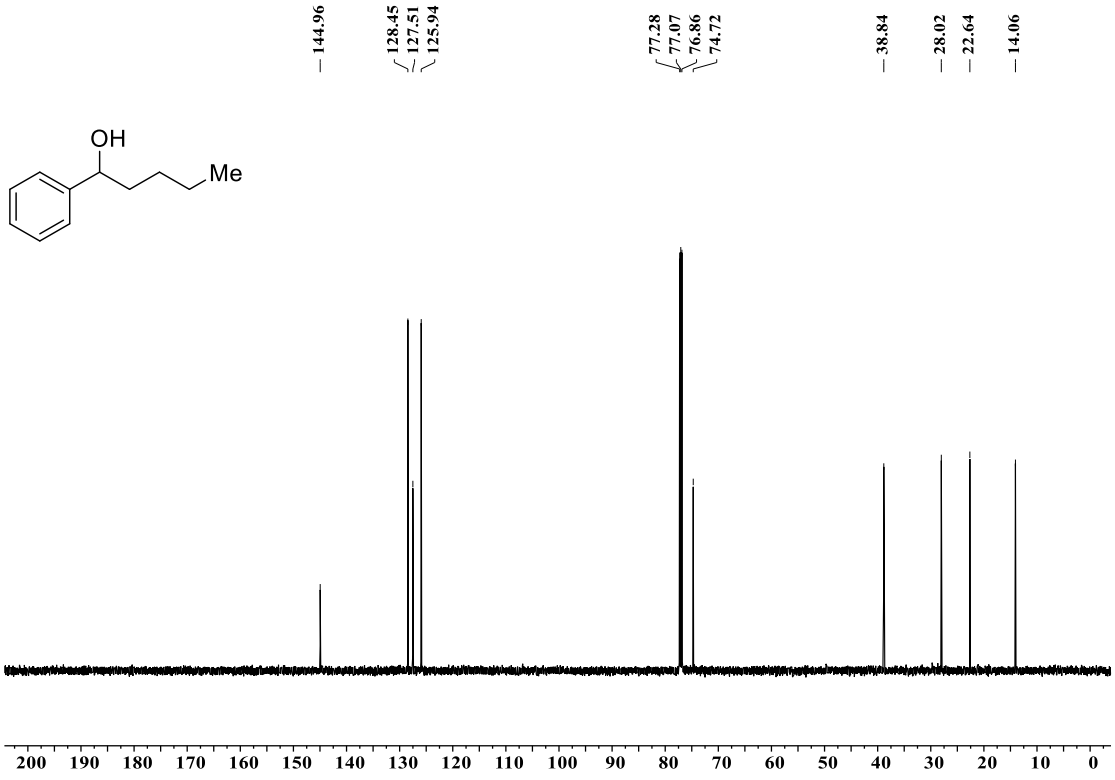
^{31}P NMR spectrum of **70** (243 MHz, $CDCl_3$)



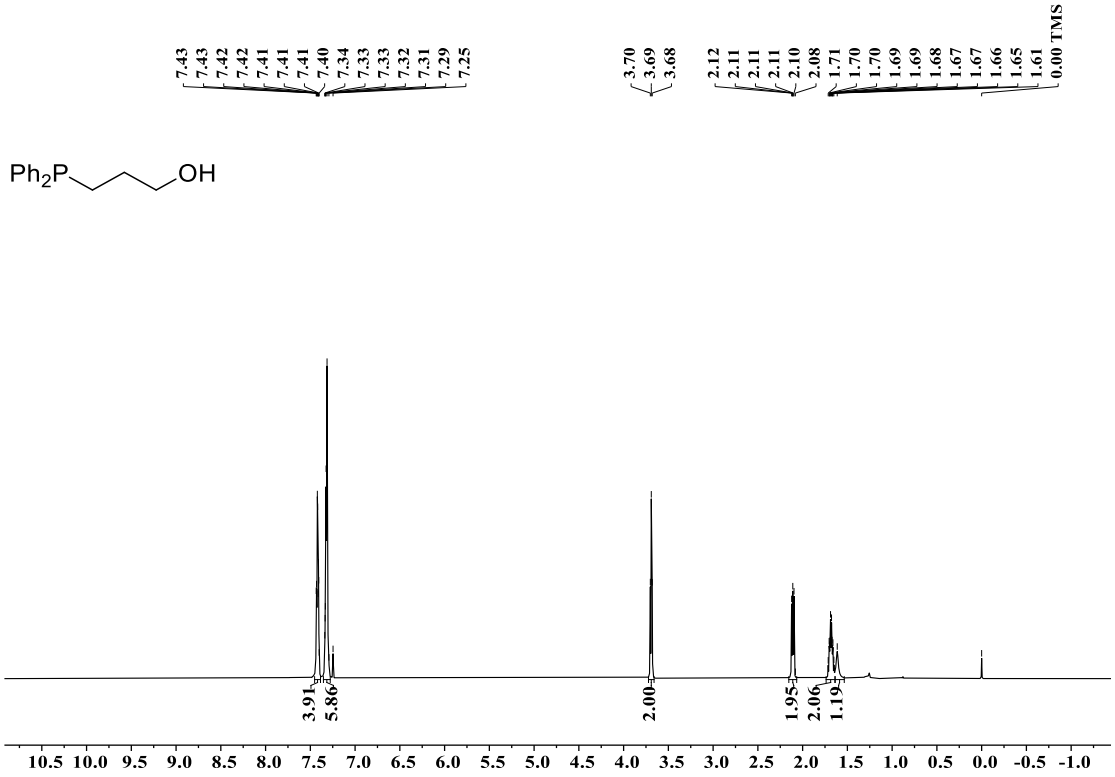
^{1}H NMR spectrum of **71** (600 MHz, $CDCl_3$)



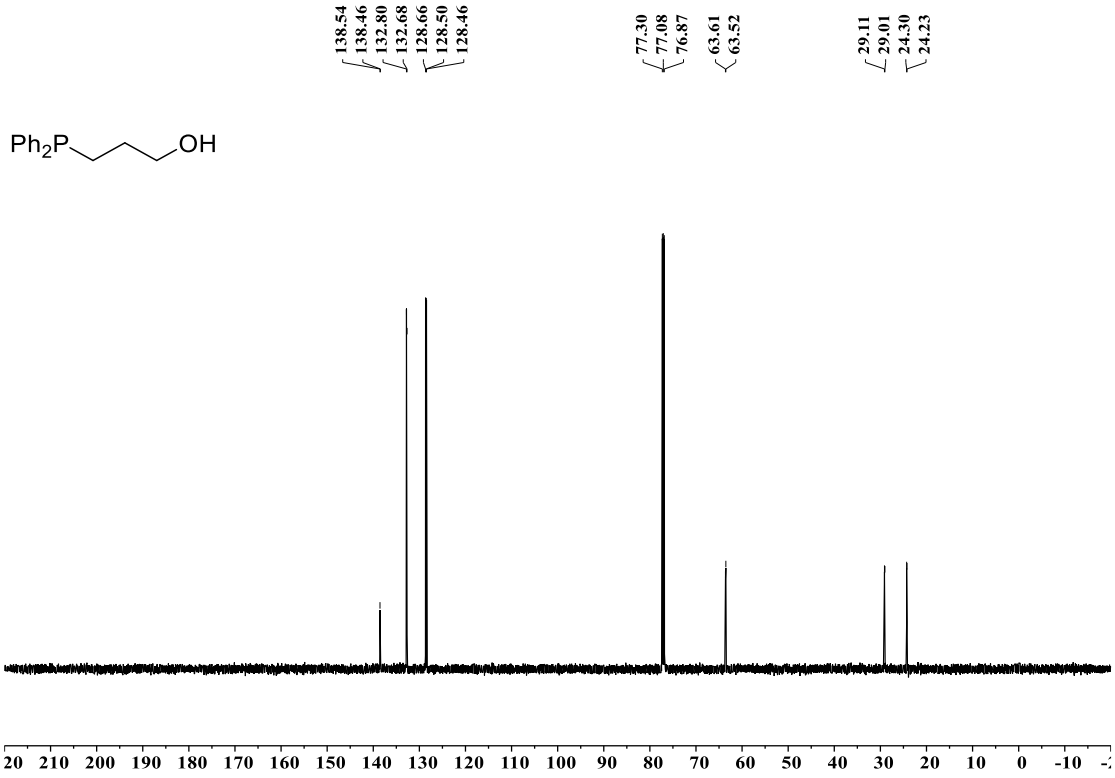
^{13}C NMR spectrum of **71** (150 MHz, $CDCl_3$)



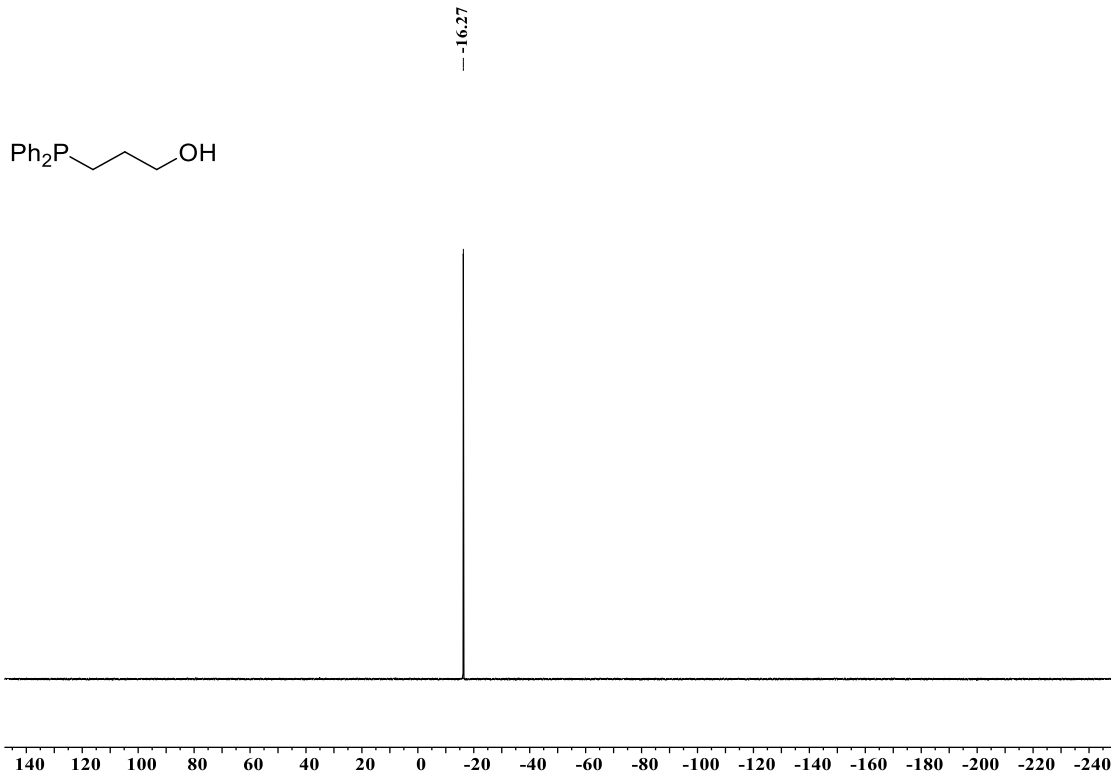
^{1}H NMR spectrum of **72** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of **72** (150 MHz, $CDCl_3$)



^{31}P NMR spectrum of **72** (243 MHz, $CDCl_3$)



Reference

1. C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, A superior method for the reduction of secondary phosphine oxides. *Org. Lett.* **2005**, *7*, 4277-4280.