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Supporting Information

Bromide ion promoted practical synthesis of phosphinothioates of sulfinic acid derivatives with H-phosphine oxides

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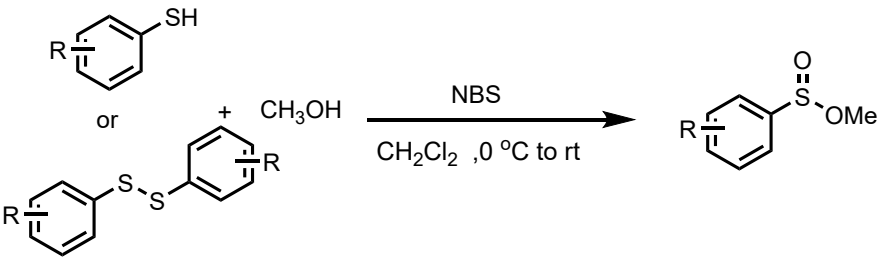
CONTENTS

1. General information

The reagents used for experiments were commercially available and used as received unless otherwise noted. ^{1}H NMR, ^{13}C NMR,^{31}P NMR and ^{19}F NMR were recorded in $CDCl_3$ on a Bruker Avance III 400 spectrometer with TMS as internal standard (400 MHz ^{1}H, 101 MHz ^{13}C, 162 MHz ^{31}P and 376 MHz ^{19}F) at room temperature. Column chromatography was performed on silica gel (300-400 mesh).

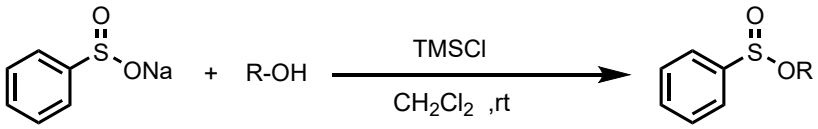
2. General procedure

1. General sulfinate synthesis from thiols or disulfides



Solid N-bromosuccinimide powder (2.0 equiv.) was added in one portion to a 0°C, methanol:dichloromethane solution (1:1 by volume) of the thiol (1equiv.). The cold bath was removed and, after 1 h, the mixture was poured into 0°C, saturated $NaHCO_3$ solution. The biphasic mixture was transferred to a separation funnel and shaken until discoloration. The phases were separated and the aqueous layer was extracted with dichloromethane (x3). The combined organic extract was washed with brine, dried (Na_2SO_4), and concentrated to afford a yellowish crude sulfinate. The crude sulfinate was purified by flash chromatography on silica gel (200–300 mesh) to afford pure methyl sulfinate.

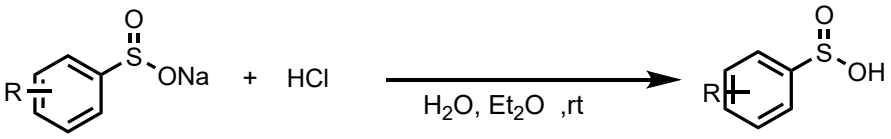
2. General sulfinate synthesis from sodium arylsulfinate



The mixture of an alcohol (10 mmol), a sodium arylsulfinate (5 mmol) and TMSCl (10 mmol) in CH_2Cl_2 (20.0 mL) was stirred at 25 °C for 1 h, then water (10 mL) and dichloromethane (20 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3×20 mL). The combined organic extracts were washed by brine, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography

on silica gel (200–300 mesh) to afford the desired sulfinate.

3. General sulfinic acids synthesis from sodium arylsulfinate



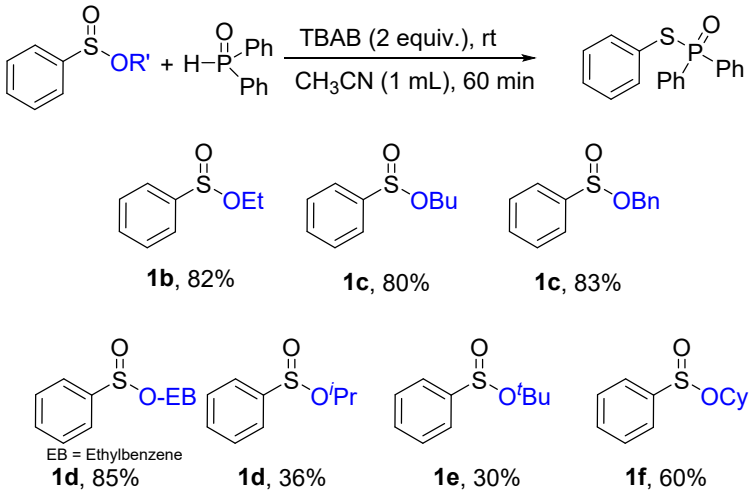
Add sodium arylsulfinates (10 mmol) dissolved in H_2O (12.5 mL) and diethyl ether (12.5 mL) and HCl (37%, 0.9 mL) to a 100 mL round flask equipped with a stirring bar. Stir the reaction mixture during 1 h at room temperature. Extract the reaction mixture with diethyl ether (3x10 mL). Dry the organic layer over anhydrous Na_2SO_4. Filter the organic layer with diethyl ether. Remove the half of the diethyl ether to obtain thick residue under reducing pressure. Add petroleum ether (20 mL) to the mixture. Filter the mixture to afford arylsulfinic acids.

4. General procedure for generation of 3a

A round bottom flask equipped with a magnetic stir bar was charged with **1a** (0.2 mmol), **2a** (0.5 mmol, 2.5 equiv.), TBAB (0.4 mmol, 2.0 equiv.), then CH_3CN (1.0 mL) was added into the mixture. Later, reaction system kept stirring at room temperature for 1 h. After that, the mixture was purified by column chromatography on silica gel to afford the corresponding product.

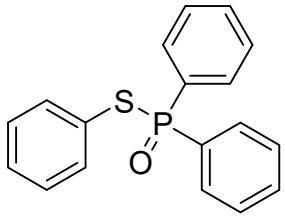
Gram-scale synthesis: The mixture of **1a** (4.0 mmol), **2a** (10 mmol) and TBAB (8 mmol) in CH_3CN (10 mL) was stirred at room temperature for 4 h. After that, the mixture was purified by column chromatography on silica gel to afford the corresponding product **3a** (1.14g, 92%).

5. Screening the alkyl benzenesulfinates



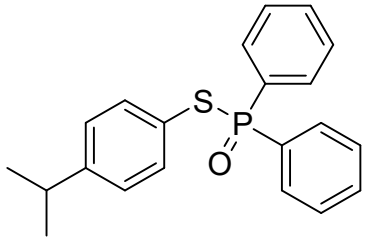
3. Characterization and analytical data of products

S-phenyl diphenylphosphinothioate (3a)



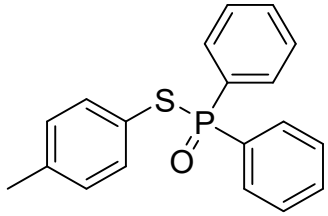
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.81 (m, 4H), 7.53 – 7.40 (m, 8H), 7.27 – 7.16 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4 (d, *J* = 3.7 Hz), 133.1 (d, *J* = 108.1 Hz), 132.4 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 10.2 Hz), 129.1 (d, *J* = 1.4 Hz), 129.0 (d, *J* = 2.1 Hz), 128. 6 (d, *J* = 13.1 Hz), 126.1 (d, *J* = 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.53.

S-(4-isopropylphenyl) diphenylphosphinothioate (3b)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 12.0, 8.0 Hz, 4H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.42 (dt, *J* = 12.0, 4.0 Hz, 4H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 2.83–2.73 (m, 1H), 1.15 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0 (d, *J* = 2.5 Hz), 135.5 (d, *J* = 3.7 Hz), 132.7 (d, *J* = 107.1 Hz)，132.3 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 10.1 Hz), 128.5 (d, *J* = 13.1 Hz), 127.4 (d, *J* = 2.0 Hz), 122.5 (d, *J* = 5.3 Hz), 33.8, 23.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.61.

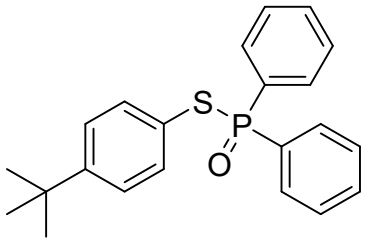
S-(*p*-tolyl) diphenylphosphinothioate (3c)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white

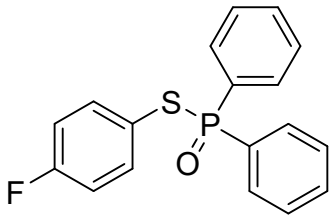
solid in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.74 (m, 4H), 7.53 – 7.46 (m, 2H), 7.46 – 7.37 (m, 4H), 7.33 – 7.27 (m, 2H), 6.99 (d, *J* = 8.0Hz, 2H), 2.24 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2 (d, *J* = 3.0 Hz), 135.4 (d, *J* = 4.0 Hz), 132.7 (d, *J* = 107.1 Hz), 132.3 (d, *J* = 4.0 Hz), 131.7 (d, *J* = 10.1 Hz), 130.0 (d, *J* = 2.0 Hz), 128.5 (d, *J* = 13.1 Hz), 122.3 (d, *J* = 5.1 Hz), 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.33.

S-(4-(tert-butyl)phenyl) diphenylphosphinothioate (3d)



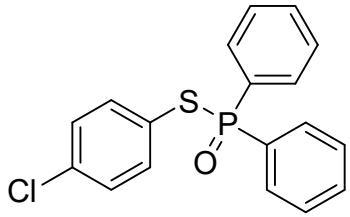
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.80 (m, 4H), 7.52 – 7.46 (m, 2H), 7.45-7.39 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3 (d, *J* = 2.0 Hz), 135.2 (d, *J* = 4.0 Hz), 132.7 (d, *J* = 107.1 Hz), 132.3 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 10.1 Hz), 128.5 (d, *J* = 13.1 Hz), 126.3 (d, *J* = 2.0 Hz), 122.3 (d, *J* = 5.1 Hz), 34.6, 31.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.59.

S-(4-fluorophenyl) diphenylphosphinothioate (3e)



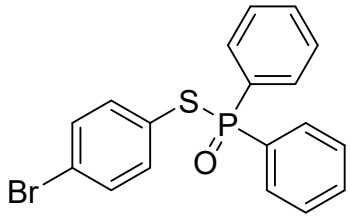
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 4H), 7.55 – 7.50 (m, 2H), 7.48 – 7.42 (m, 4H), 7.29 – 7.25 (m, 1H), 7.20 – 7.14 (m, 2H), 6.98 – 6.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (dd, *J* = 250.5, 2.0 Hz),132.6 (d, *J* = 4.0 Hz), 132.2 (d, *J* = 108.1 Hz), 131.6 (d, *J* = 10.1 Hz), 131.0 (t, *J* = 3.0 Hz), 130.3 (dd, *J* = 8.1, 2.0 Hz), 128.7 (d, *J* = 13.1 Hz), 128.3 (dd, *J* = 8.1, 5.1 Hz), 122.1 (dd, *J* = 23.2, 4.0 Hz), 116.2 (dd, *J* = 21.2, 2.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.59; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.36.

S-(4-chlorophenyl) diphenylphosphinothioate (3f)



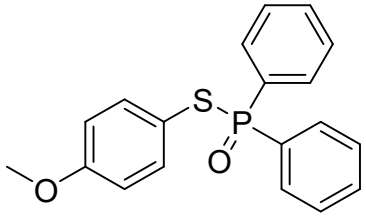
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.78 (m, 4H), 7.54 – 7.48 (m, 2H), 7.43 (m, 4H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6 (d, *J* = 3.0 Hz), 135.6 (d, *J* = 3.0 Hz), 132.7, 132.5 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 10.1 Hz), 129.4 (d, *J* = 2.0 Hz), 128. 7 (d, *J* = 13.1 Hz), 124.7 (d, *J* = 4.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.60.

S-(4-bromophenyl) diphenylphosphinothioate (3g)



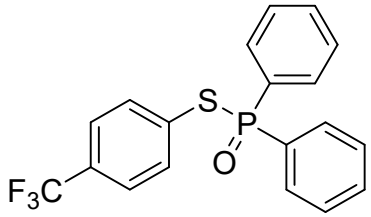
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a colorless oil in 83% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 4H), 7.56 – 7.50 (m, 2H), 7.49 – 7.41 (m, 4H), 7.35 – 7.28 (m, 4H);^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8 (d, *J* = 4.0 Hz), 132.7, 132.5 (d, *J* = 3.0 Hz), 132.3 (d, *J* = 1.0 Hz), 131.6 (d, *J* = 10.1 Hz), 128.7 (d, *J* = 13.1 Hz), 125.4 (d, *J* = 5.1 Hz), 123.8 (d, *J* = 2.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.43.

S-(4-methoxyphenyl) diphenylphosphinothioate (3h)



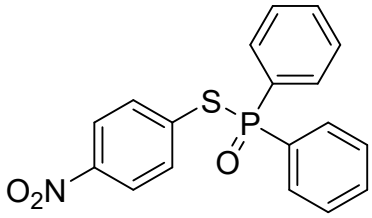
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 4H), 7.55 – 7.48 (m, 2H), 7.47 – 7.39 (m, 4H), 7.36 – 7.30 (m, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 3.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5 (d, *J* = 2.0 Hz), 137.1 (d, *J* = 4.0 Hz), 132.6 (d, *J* = 106.1 Hz), 132.3(d, *J* = 3.0 Hz), 131.7 (d, *J* = 10.1 Hz), 128.5 (d, *J* = 13.1 Hz), 116.0 (d, *J* = 5.1 Hz), 114.8 (d, *J* = 2.0 Hz), 55.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.35.

S-(4-(trifluoromethyl)phenyl) diphenylphosphinothioate (3i)



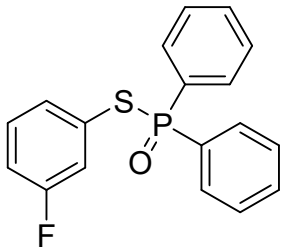
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 4H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.50 – 7.42 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2 (d, *J* = 4.0 Hz), 132.7 (d, *J* = 3.0 Hz), 132.0 (d, *J* = 107.6 Hz), 131.6 (d, *J* = 10.1 Hz), 130.9 (dd, *J* = 32.3, 2.0 Hz), 128.74 (d, *J* = 13.1 Hz), 125.9 (q, *J* = 2.0 Hz), 125.1, 122.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.73; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.88.

S-(4-nitrophenyl) diphenylphosphinothioate (3j)



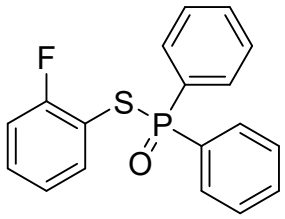
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.90 – 7.82 (m, 4H), 7.70 – 7.66 (m, 2H), 7.59 – 7.53 (m, 2H), 7.52 – 7.45 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 136.1(d, *J* = 5.1 Hz), 135.2 (d, *J* = 4.0 Hz), 132.9 (d, *J* = 3.0Hz), 131.7 (d, *J* = 108.1 Hz), 131.6 (d, *J* = 10.1 Hz), 128.87 (d, *J* = 13.1 Hz), 123.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.96.

S-(3-fluorophenyl) diphenylphosphinothioate (3k)



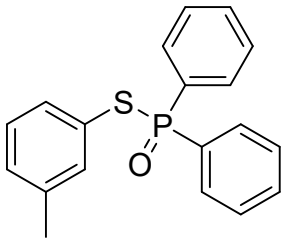
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 4H), 7.55 – 7.50 (m, 2H), 7.48 – 7.42 (m, 4H), 7.29 – 7.25 (m, 1H), 7.20 – 7.14 (m, 2H), 6.98 – 6.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (dd, *J* = 250.5, 2.0 Hz),132.6 (d, *J* = 4.0 Hz), 132.2 (d, *J* = 108.1 Hz), 131.6 (d, *J* = 10.1 Hz), 131.0 (t, *J* = 3.0 Hz), 130.3 (dd, *J* = 8.1, 2.0 Hz), 128.7 (d, *J* = 13.1 Hz), 128.3 (dd, *J* = 8.1, 5.1 Hz), 122.1 (dd, *J* = 23.2, 4.0 Hz), 116.2 (dd, *J* = 21.2, 2.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.59;^{19}F NMR (376 MHz, $CDCl_3$) δ -111.36.

S-(2-fluorophenyl) diphenylphosphinothioate (3l)



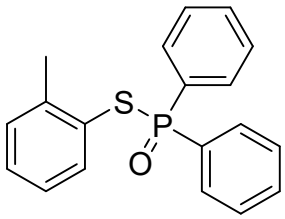
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.80 (m, 4H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.46 – 7.42 (m, 4H), 7.25 – 7.20 (m, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (dd, *J* = 249.5, 4.0 Hz), 137.9 (d, *J* = 3.0 Hz), 132.5 (d, *J* = 3.0 Hz), 132.3 (d, *J* = 108.1.0 Hz), 131.6 (d, *J* = 11.1 Hz), 131.3 (dd, *J* = 8.1, 2.0 Hz), 128.6 (d, *J* = 13.1 Hz), 124.7 (dd, *J* = 4.0, 2.0 Hz), 116.0 (dd, *J* = 23.2, 2.0 Hz), 113.5 (dd, *J* = 18.2, 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.00; ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.32.

S-(m-tolyl) diphenylphosphinothioate (3m)



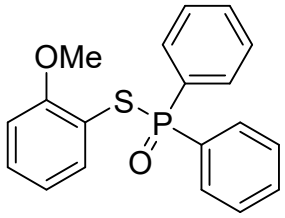
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 4H), 7.53 – 7.48 (m, 2H), 7.47 – 7.41 (m, 4H), 7.25 – 7.21 (m, 2H), 7.11 – 7.02 (m, 2H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0 (d, *J* = 2.0 Hz), 136.1 (d, *J* = 4.0 Hz), 132.7 (d, *J* = 107.1 Hz), 132.4 (d, *J* = 4.0 Hz), 132.3 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 10.1 Hz), 129.8 (d, *J* = 2.0 Hz), 128.9 (d, *J* = 1.0 Hz), 128.5 (d, *J* = 13.1 Hz), 125.7 (d, *J* = 5.1 Hz), 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.34.

S-(o-tolyl) diphenylphosphinothioate (3n)



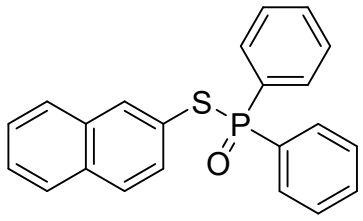
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 82% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 4H), 7.54 – 7.48 (m, 2H), 7.47 – 7.39 (m, 5H), 7.19 – 7.10 (m, 2H), 7.03 – 6.99 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9 (d, *J* = 3.0 Hz), 136.8 (d, *J* = 4.0 Hz), 133.3, 132.3 (d, *J* = 4.0 Hz), 131.5 (d, *J* = 10.1 Hz), 130.7 (d, *J* = 1.0 Hz), 129.3 (d, *J* = 2.0 Hz), 128.5 (d, *J* = 13.1 Hz), 126.5 (d, *J* = 2.0 Hz), 125.4 (d, *J* = 5.1 Hz), 21.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.06.

S-(2-methoxyphenyl) diphenylphosphinothioate (3o)



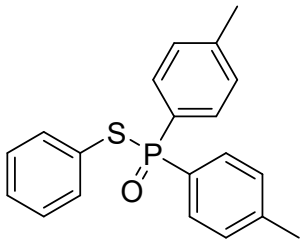
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/10) to afford a white solid in 54% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 4H), 7.75 – 7.70 (m, 1H), 7.59 – 7.40 (m, 7H), 7.36 – 7.30 (m, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 3.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8 (d, *J* = 4.0 Hz), 139.5 (d, *J* = 4.0 Hz), 133.4 (d, *J* = 2.0Hz), 132.8(d, *J* = 107.1 Hz), 132.4 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 11.1 Hz), 128.4 (d, *J* = 13.1Hz), 116.4 (d, *J* = 4.0Hz), 112.7 (d, *J* = 2.0 Hz), 112.55 (d, *J* = 2.0 Hz), 55.83. ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.43.

S-(naphthalen-2-yl) diphenylphosphinothioate (3p)



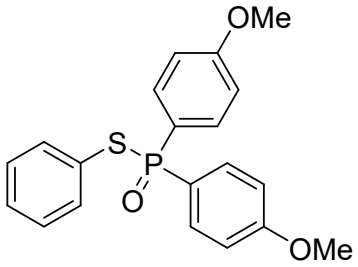
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a light yellow solid in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.92 – 7.82 (m, 4H), 7.75 – 7.67 (m, 2H), 7.65 (d, *J* = 12.0 Hz, 1H), 7.51 – 7.39 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4 (d, *J* = 4.0 Hz), 133.5 (d, *J* = 2.0 Hz), 133.0 (d, *J* = 2.0 Hz), 132.6 (d, *J* = 107.8 Hz), 132.4 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 10.1 Hz), 131.6 (d, *J* = 4.0 Hz), 128.7 (d, *J* = 1.0 Hz), 128.6 (d, *J* = 13.1 Hz), 127.8, 127.6, 126.9, 126.5, 123.5 (d, *J* = 6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.51.

S-phenyl di-p-tolylphosphinothioate (3r)



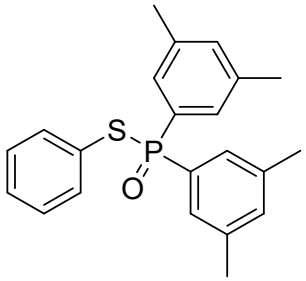
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 12.0, 8.0 Hz, 4H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 20.0, 8.0 Hz, 7H), 2.37 (s, 6H);^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8 (d, *J* = 3.0 Hz), 135.2 (d, *J* = 4.0 Hz), 131.6 (d, *J* = 10.1 Hz), 130.0 (d, *J* = 1.0 Hz), 129.2 (d, *J* = 13.1 Hz), 129.0 (d, *J* = 1.0 Hz), 128.7 (d, *J* = 2.0 Hz), 126.6 (d, *J* = 5.1 Hz), 21.6 (d, *J* = 1.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.05.

S-phenyl bis(4-methoxyphenyl)phosphinothioate (3s)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 12.0, 8.0 Hz, 4H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 20.0, 8.0 Hz, 7H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8 (d, *J* = 3.0 Hz), 135.2 (d, *J* = 4.0 Hz), 131.6 (d, *J* = 10.1 Hz), 130.0 (d, *J* = 1.0 Hz), 129.2 (d, *J* = 13.1 Hz), 129.0 (d, *J* = 1.0 Hz), 128.7 (d, *J* = 2.0 Hz), 126.6 (d, *J* = 5.1 Hz), 21.6 (d, *J* = 1.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.05.

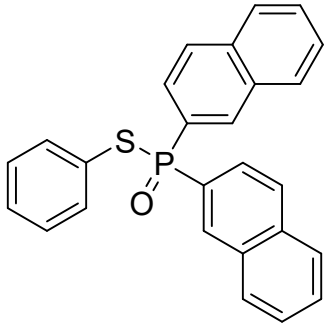
S-phenyl bis(3,5-dimethylphenyl)phosphinothioate (3t)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2/1) to afford a white solid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 13.3 Hz, 6H), 7.21 (m, 3H), 7.12 (s, 2H), 2.32 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2 (d, *J* = 14.1 Hz), 135.3 (d, *J* = 3.0Hz), 134.0 (d, *J* = 3.0

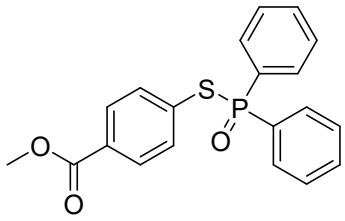
Hz), 132.3 (d, J = 106.1 Hz), 129.1 (d, J = 10.1 Hz), 129.0 (d, J = 1.0 Hz), 128.8 (d, J = 2.0 Hz), 126.6 (d, J = 5.1 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.69.

S-phenyl di(naphthalen-2-yl)phosphinothioate (3u)



The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/10) to afford a white solid in 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 16.0 Hz, 2H), 7.92–7.83 (m, 8H), 7.61–7.48 (m, 6H), 7.22–7.12 (m, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4 (d, J = 4.0 Hz), 134.8 (d, J = 2.0 Hz), 134.0 (d, J = 9.1 Hz), 132.4 (d, J = 14.1 Hz), 130.1, 129.2 (d, J = 1.0 Hz), 129.1, 129.0 (d, J = 2.0 Hz), 128.5, 128.5, 128.4, 127.8, 127.0, 126.2 (d, J = 12.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.61.

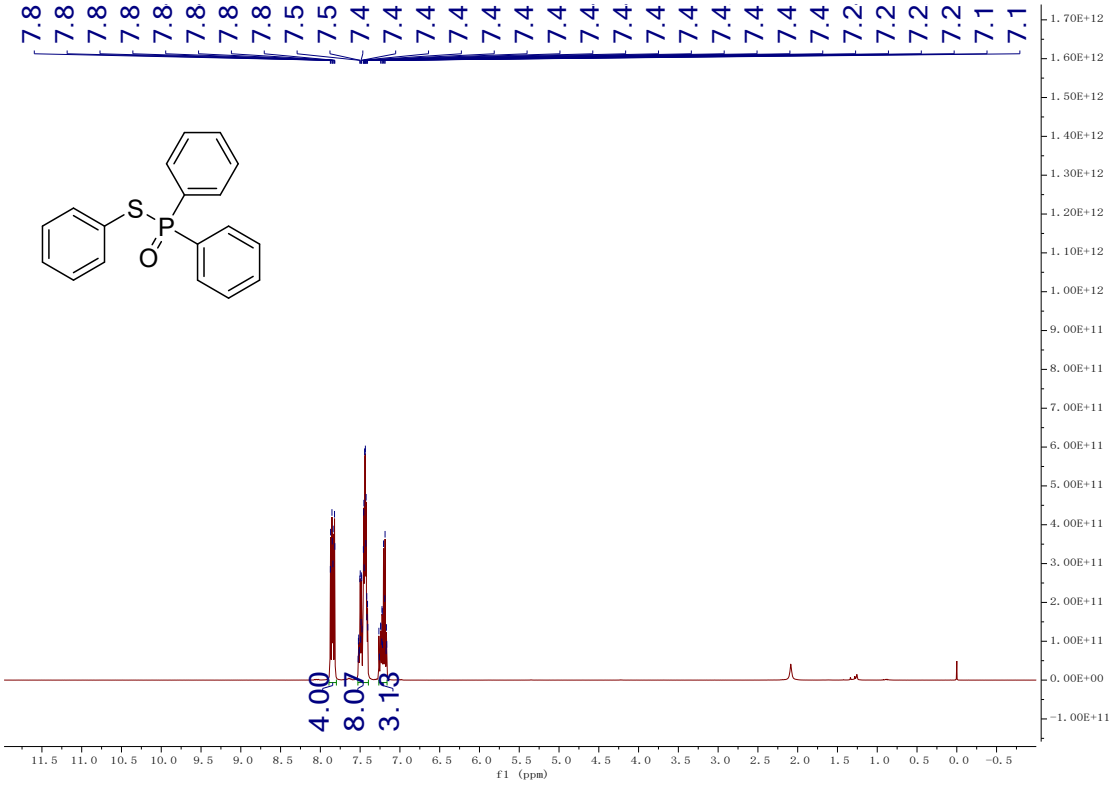
methyl 4-((diphenylphosphoryl)thio)benzoate (3w)

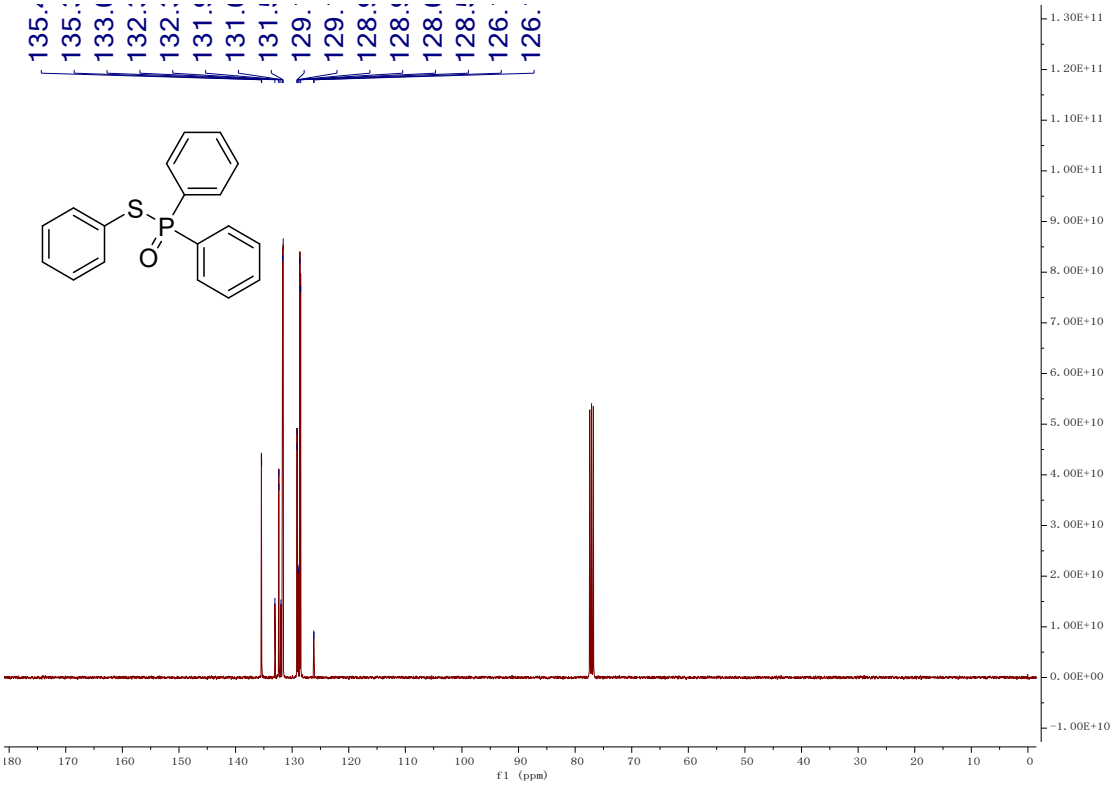


The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1) to afford a white solid in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 6H), 7.56 – 7.48 (m, 4H), 7.47 – 7.40 (m, 4H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 134.7 (d, J = 4.0 Hz), 132.6 (d, J = 4.0 Hz), 131.6 (d, J = 11.1 Hz), 130.0 (d, J = 2.0 Hz), 128.7 (d, J = 14.1 Hz), 52.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.77. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}O_3PS^+$:369.0709; Found: 369.0709

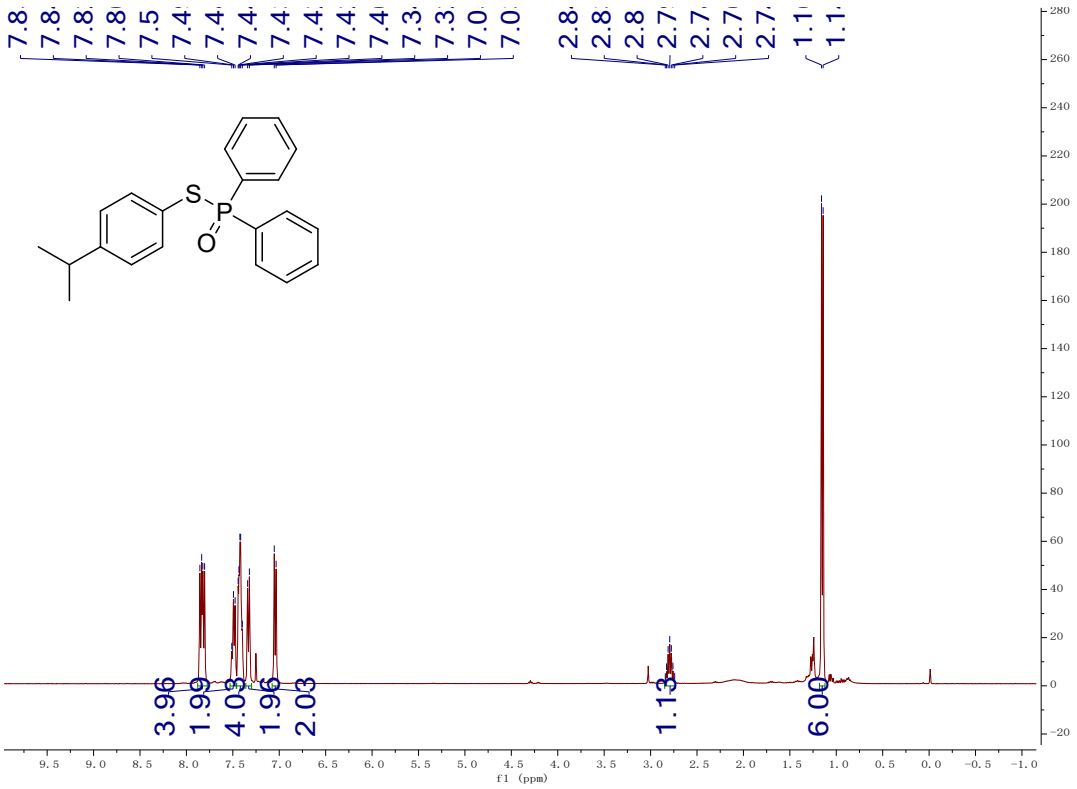
4. Copies of product ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, ^{19}F NMR

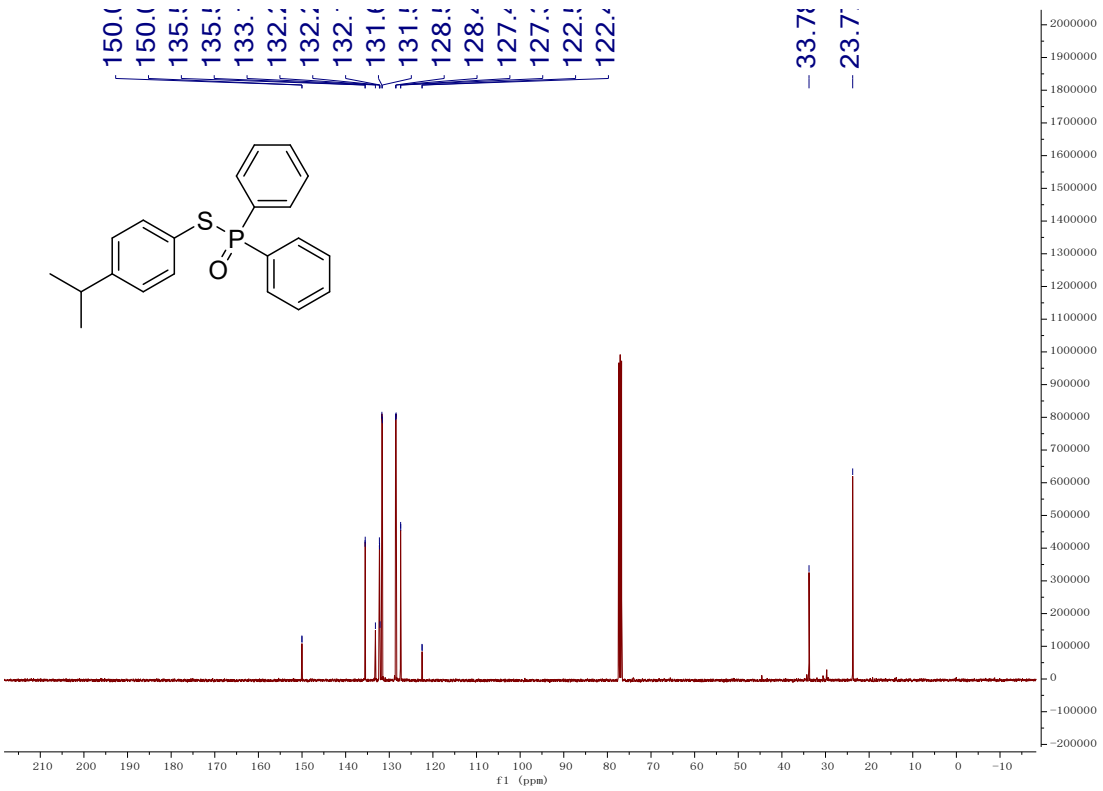
S-phenyl diphenylphosphinothioate (3a)

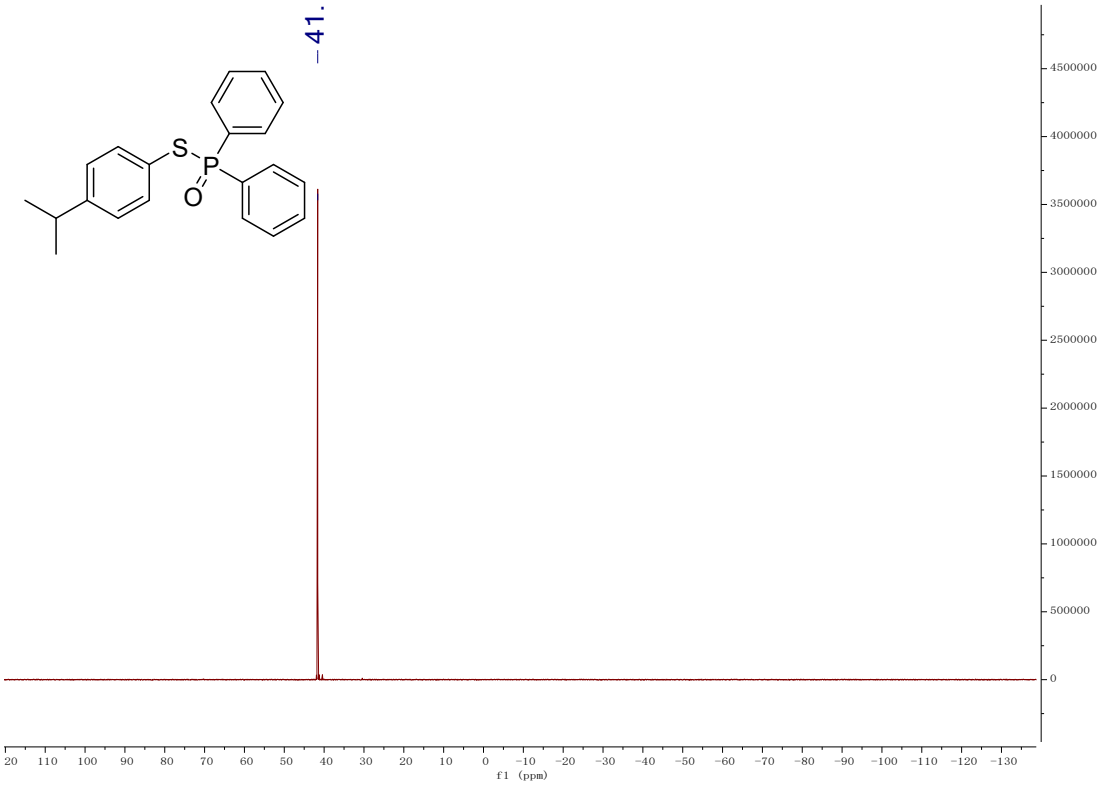




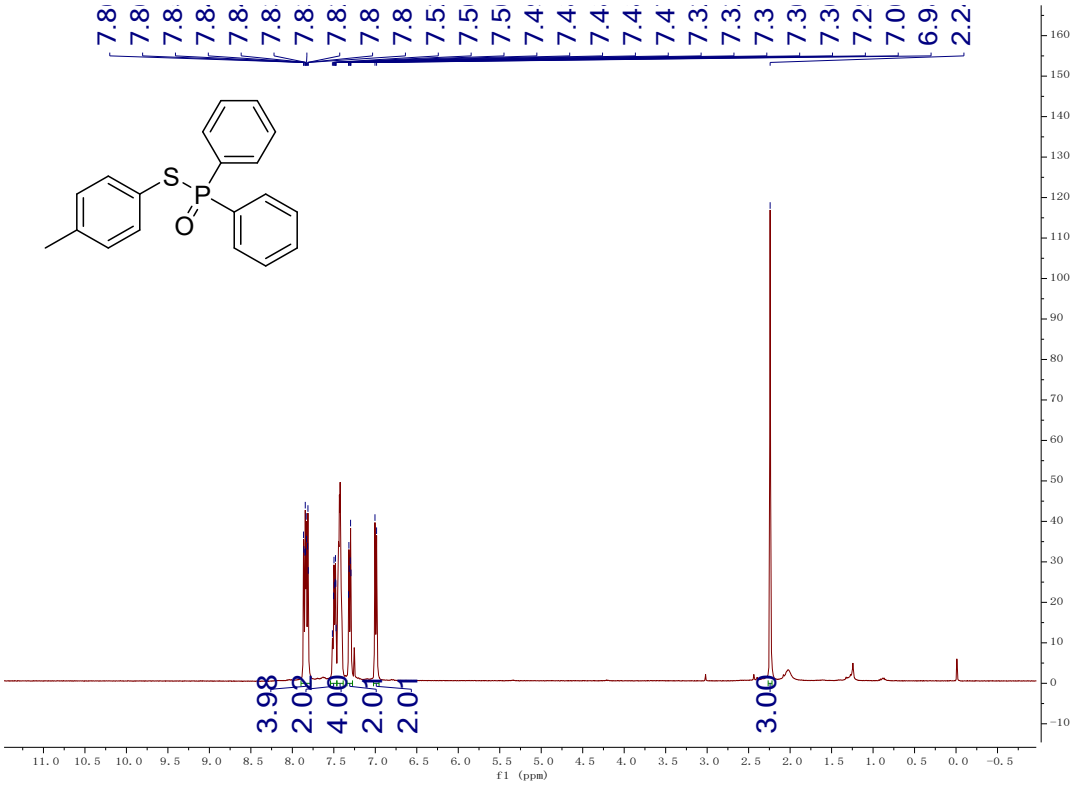
S-(4-isopropylphenyl) diphenylphosphinothioate (3b)

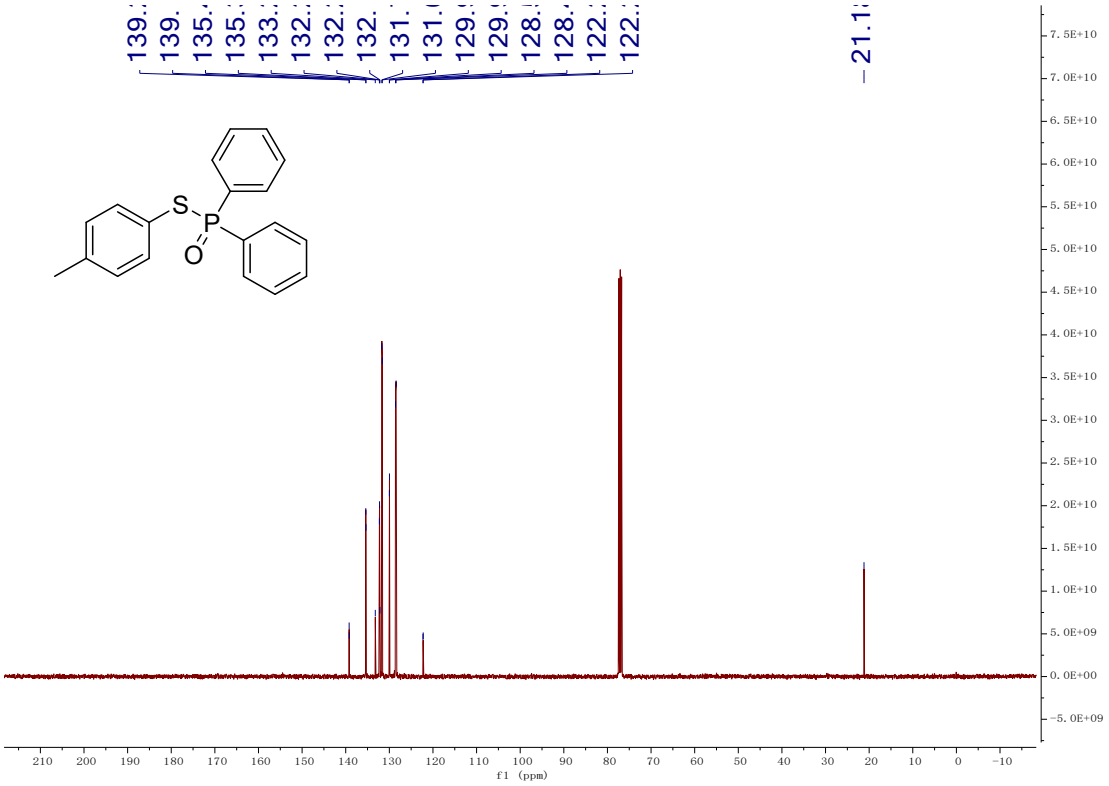

S
P
O
3.96
1.99
4.03
1.96
2.03
1.13
6.00
f1 (ppm)

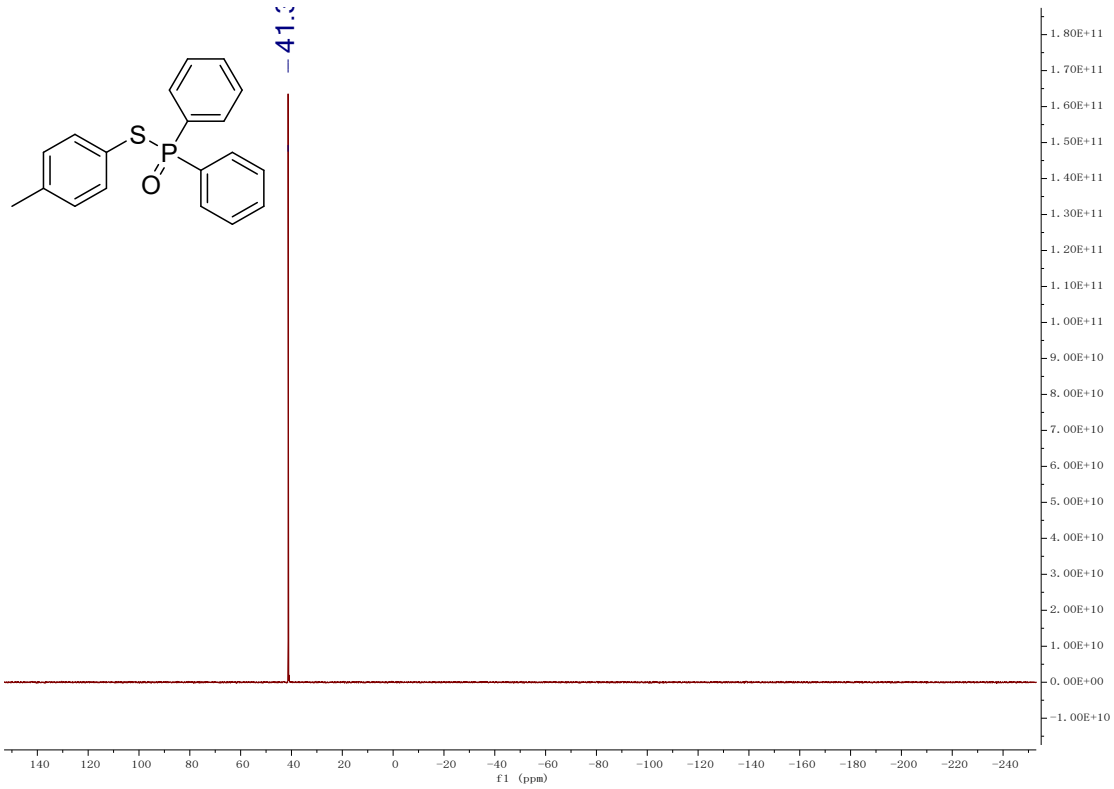

S
P
O
f1 (ppm)



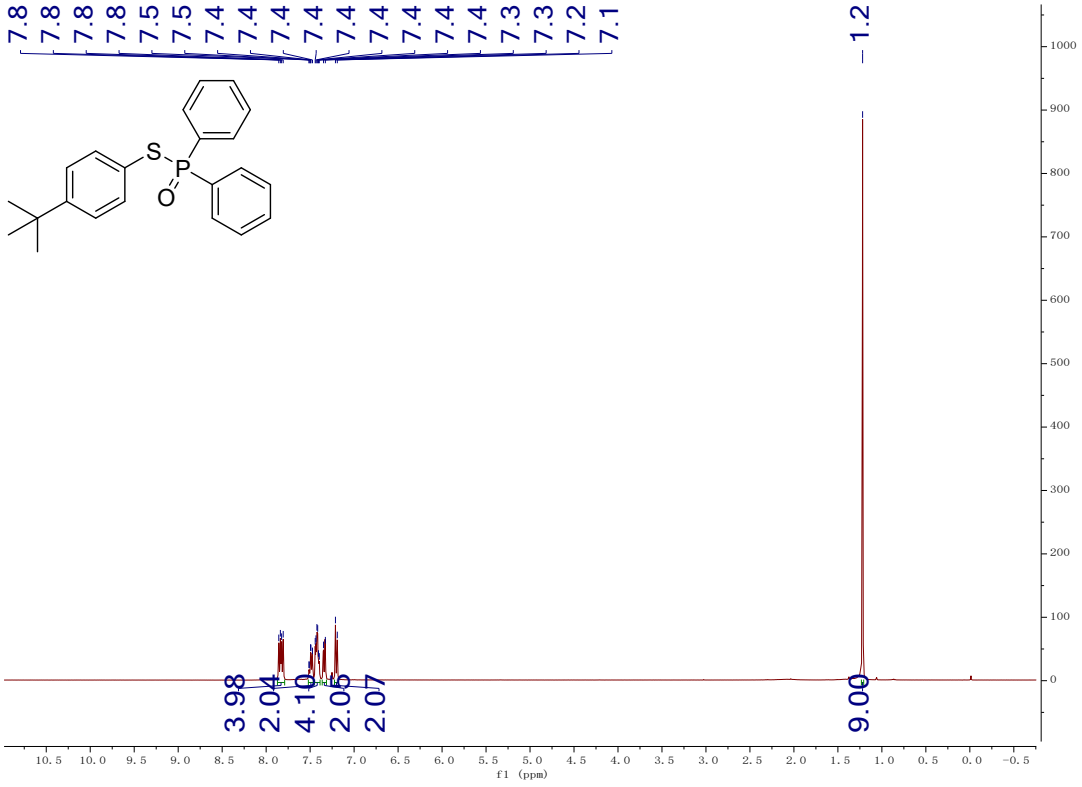
S-(*p*-tolyl) diphenylphosphinothioate (3c)

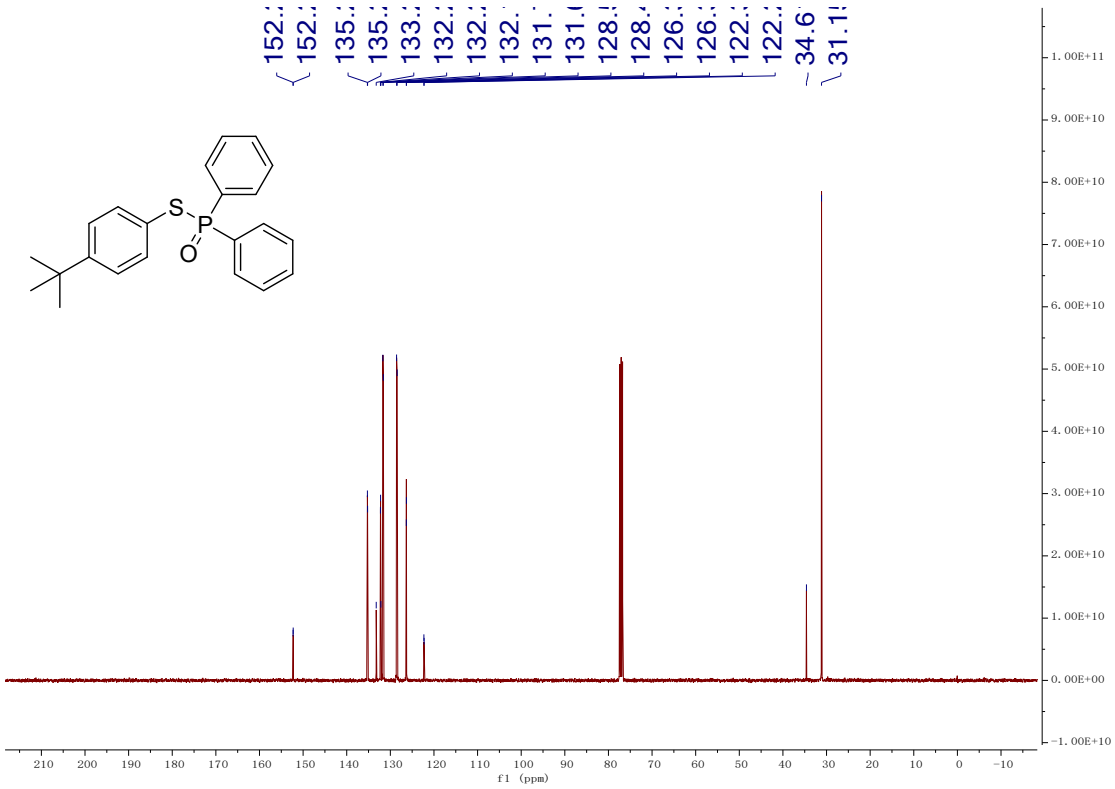


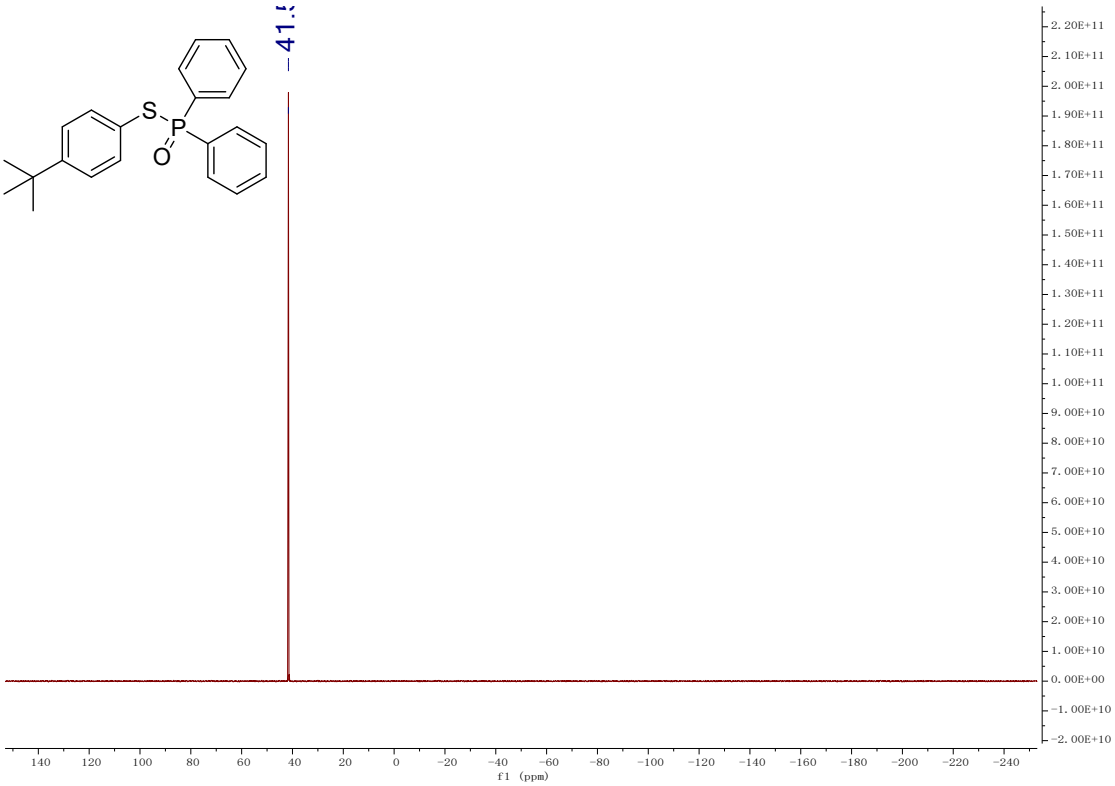

139.
139.
135.
135.
133.
132.
132.
132.
131.
131.
129.
129.
128.
128.
122.
122.
21.1
S
P
O
7.5E+10
7.0E+10
6.5E+10
6.0E+10
5.5E+10
5.0E+10
4.5E+10
4.0E+10
3.5E+10
3.0E+10
2.5E+10
2.0E+10
1.5E+10
1.0E+10
5.0E+09
0.0E+00
-5.0E+09
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



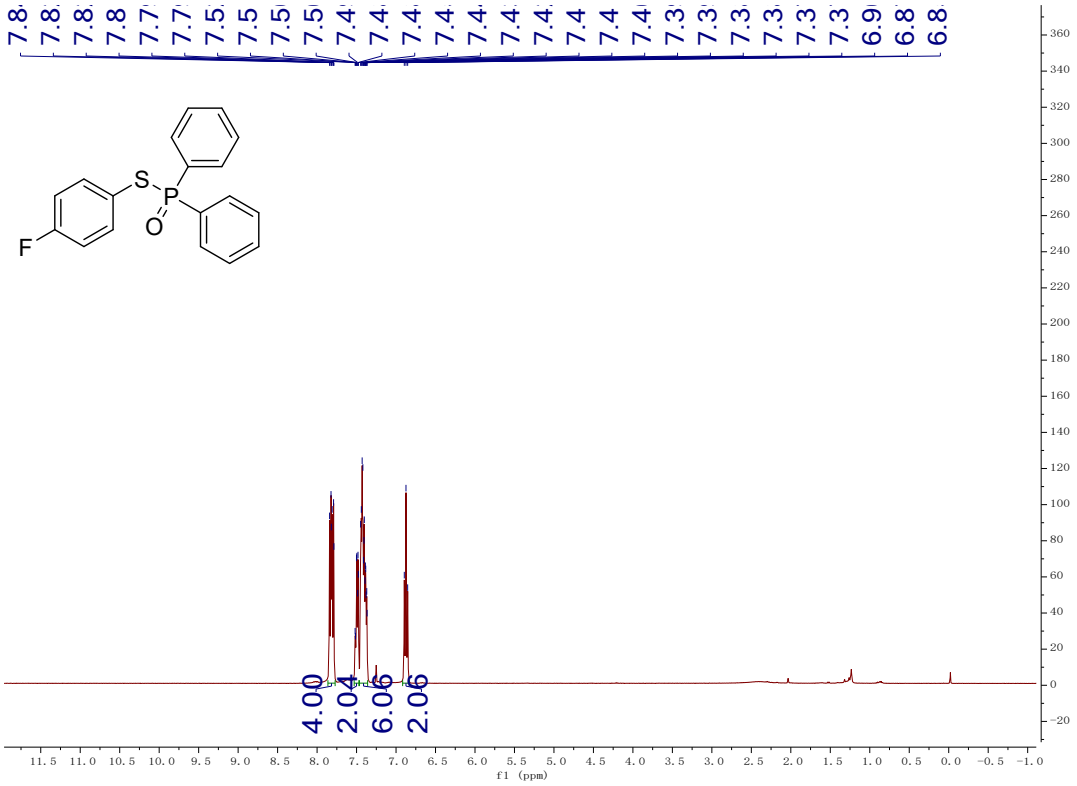
Diphenyl(4-(tert-Butyl)phenyl)phosphine Oxide (3d)

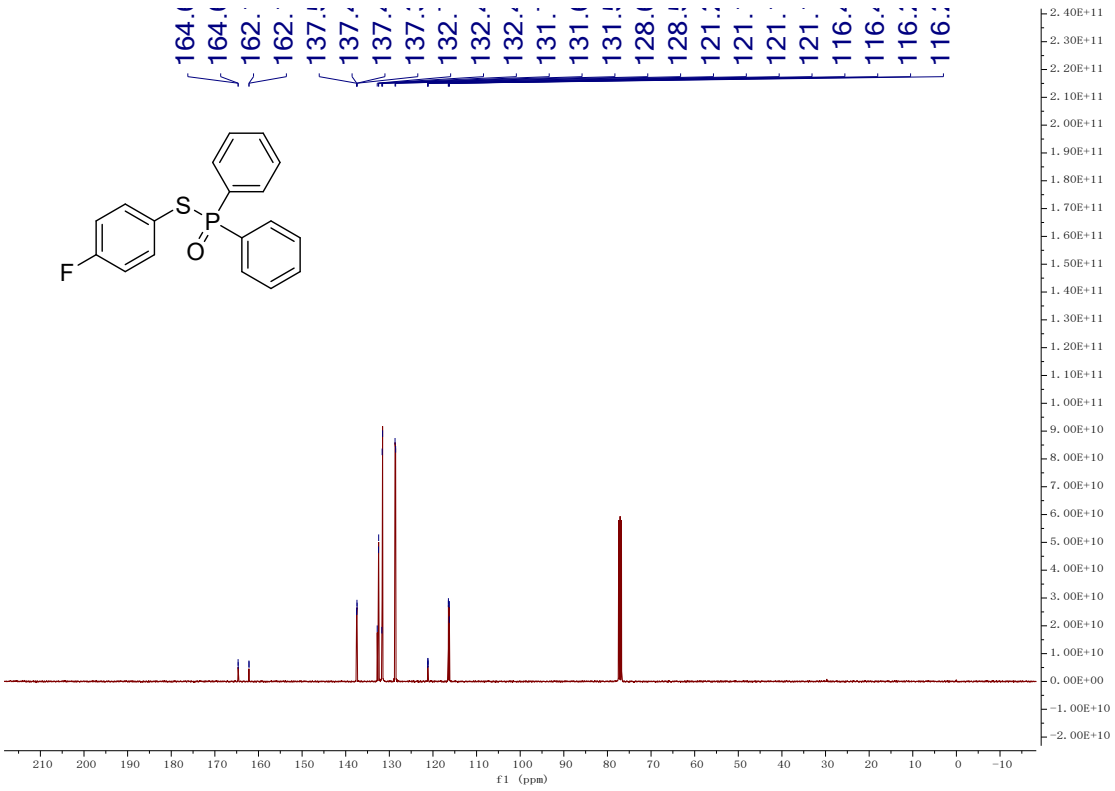


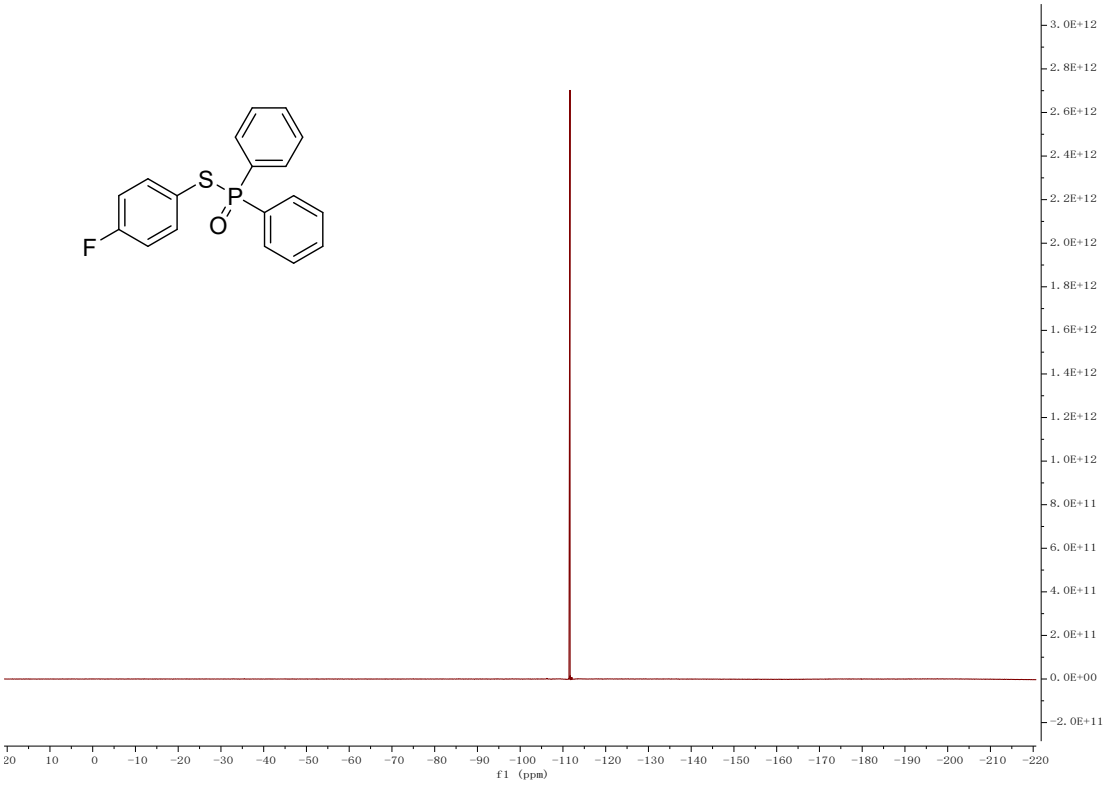

34.6
31.1
S
P
O
f1 (ppm)


41.5
S
P
O
f1 (ppm)

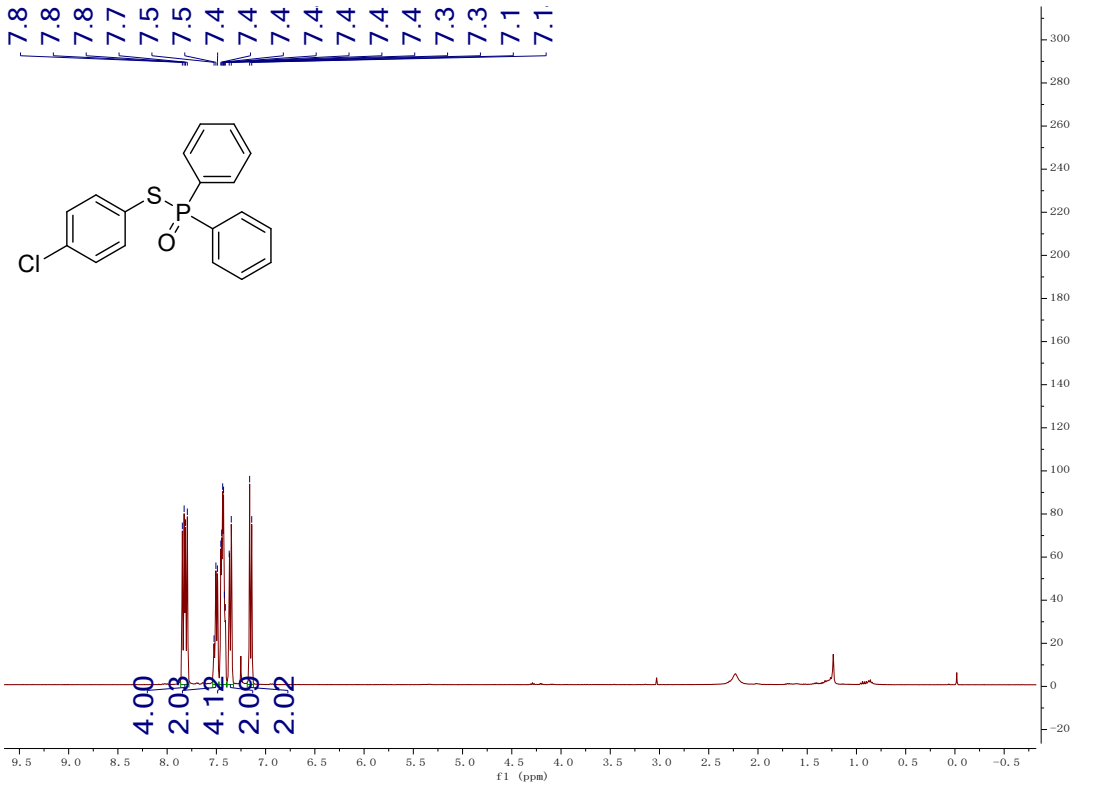
S-(4-fluorophenyl) diphenylphosphinothioate (3e)

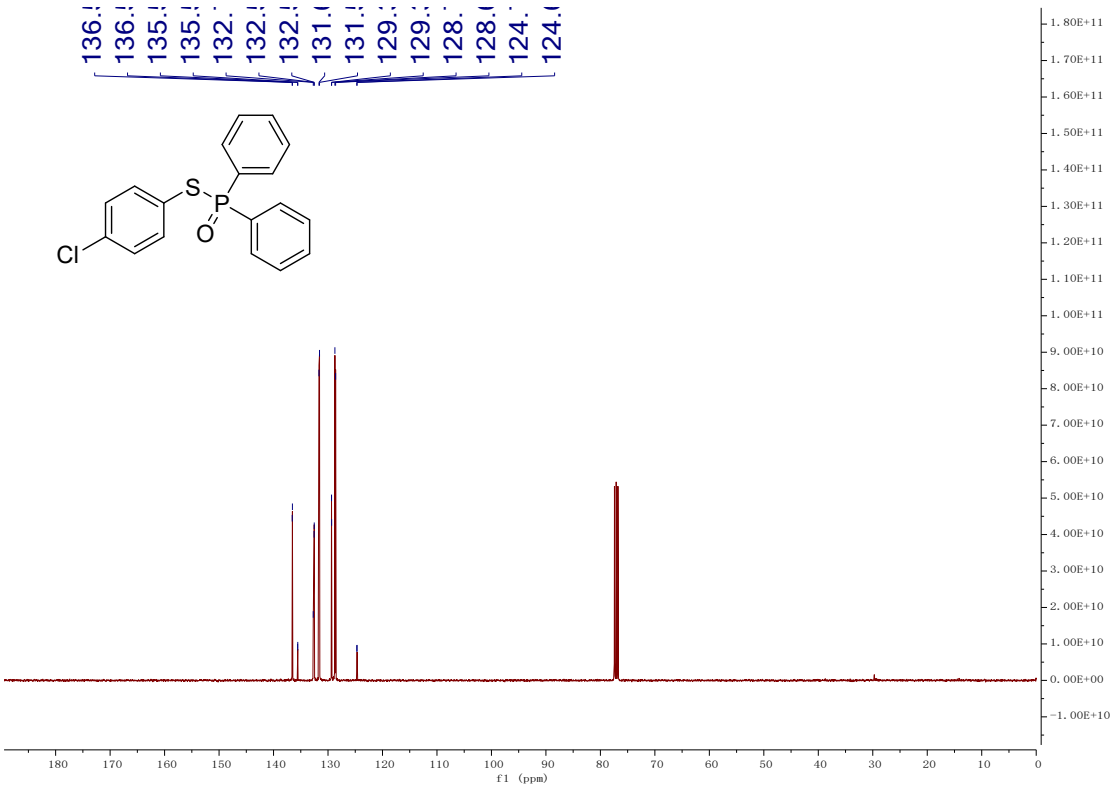


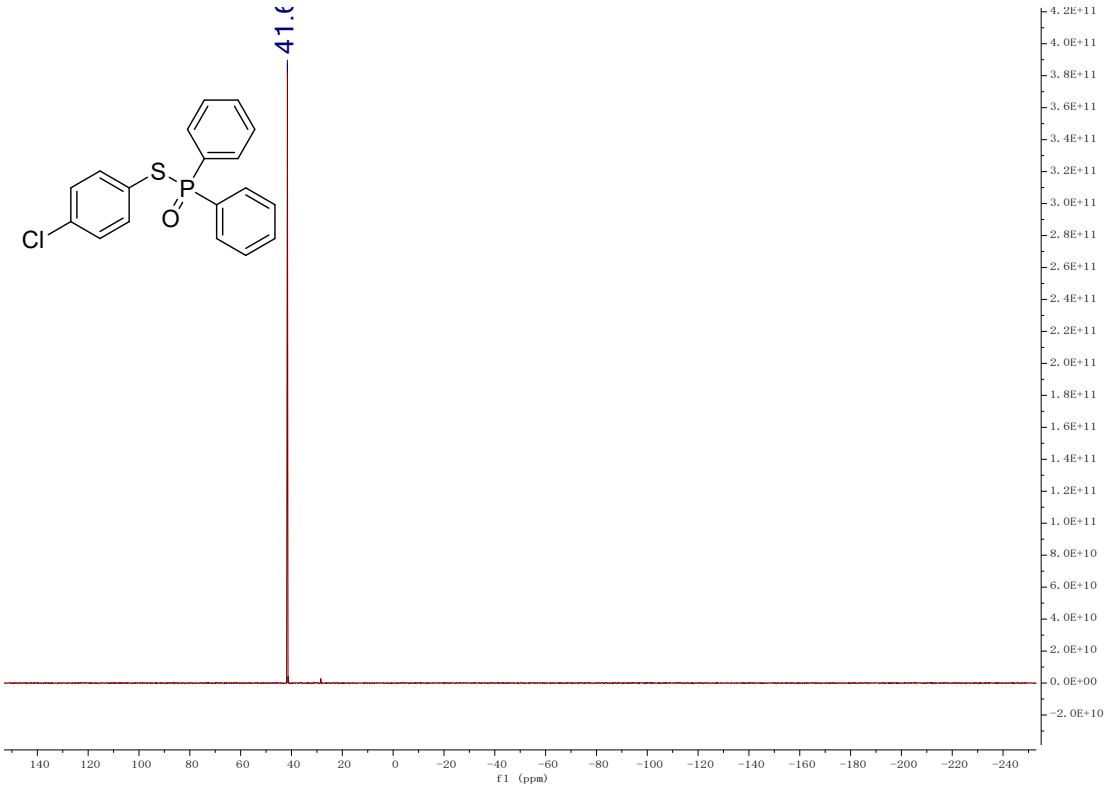




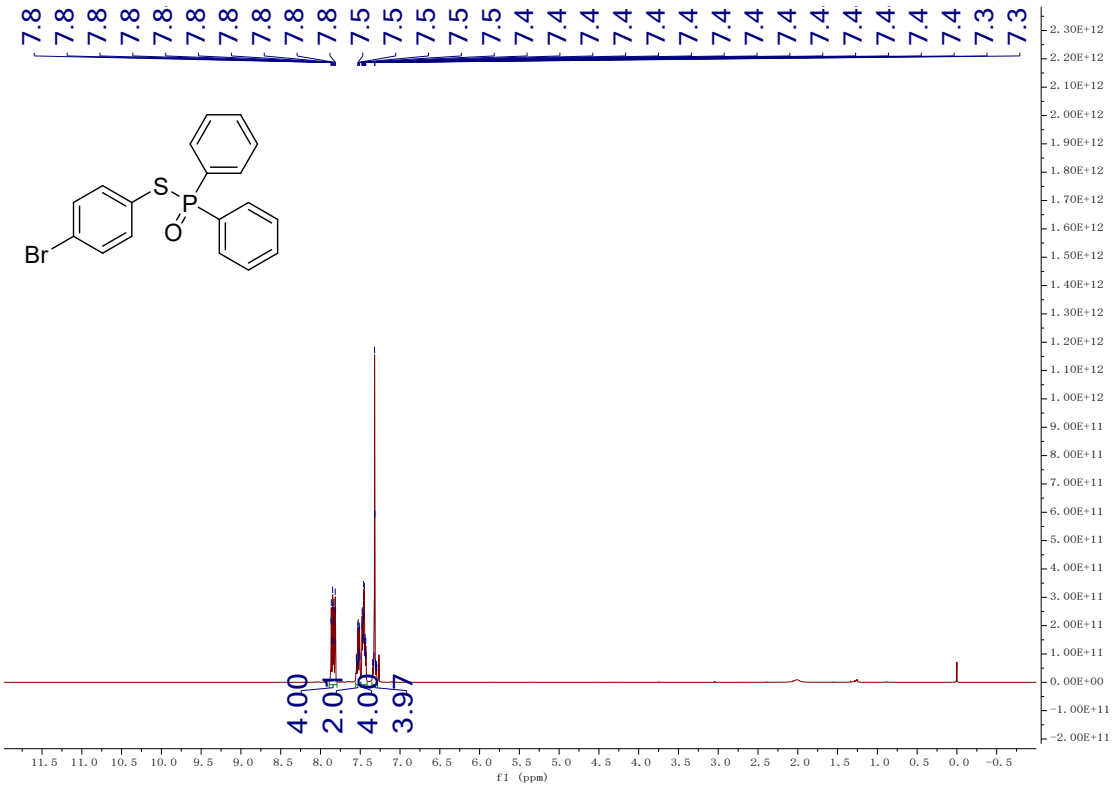
S-(4-chlorophenyl) diphenylphosphinothioate (3f)

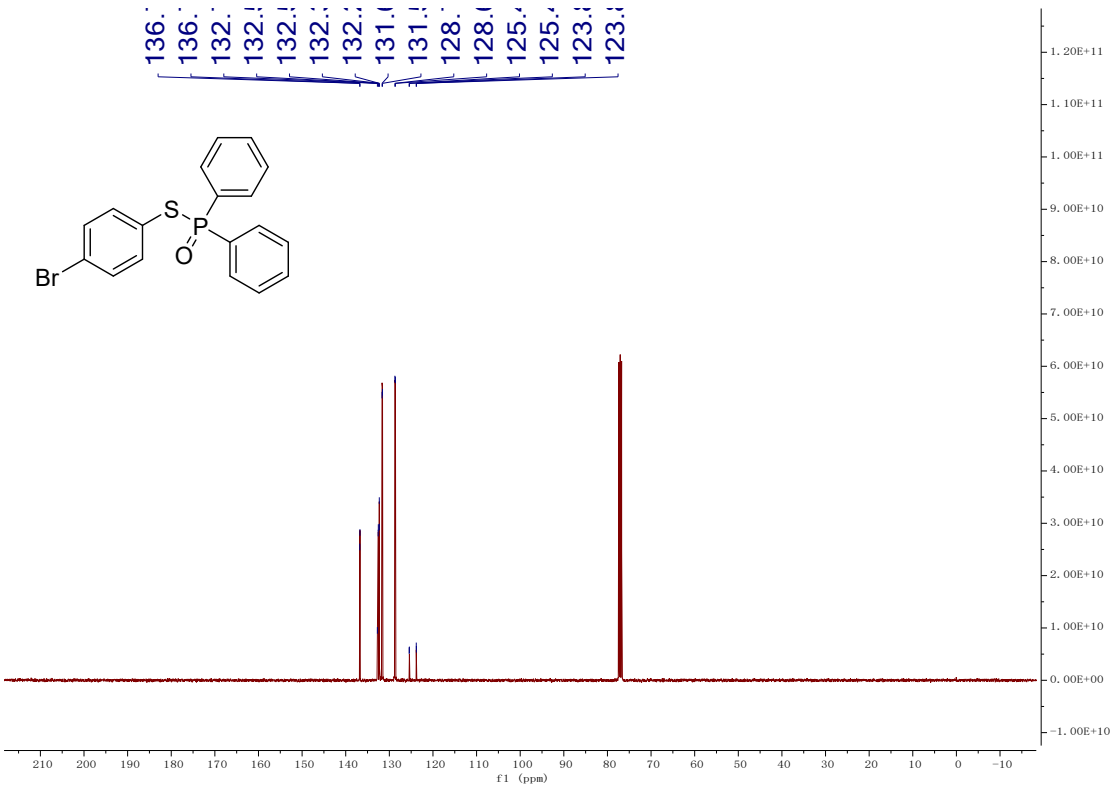

7.8
7.8
7.8
7.7
7.5
7.5
7.4
7.4
7.4
7.4
7.4
7.4
7.4
7.3
7.3
7.1
7.1
S
P
O
Cl
4.00
2.03
4.11
2.09
2.02
f1 (ppm)

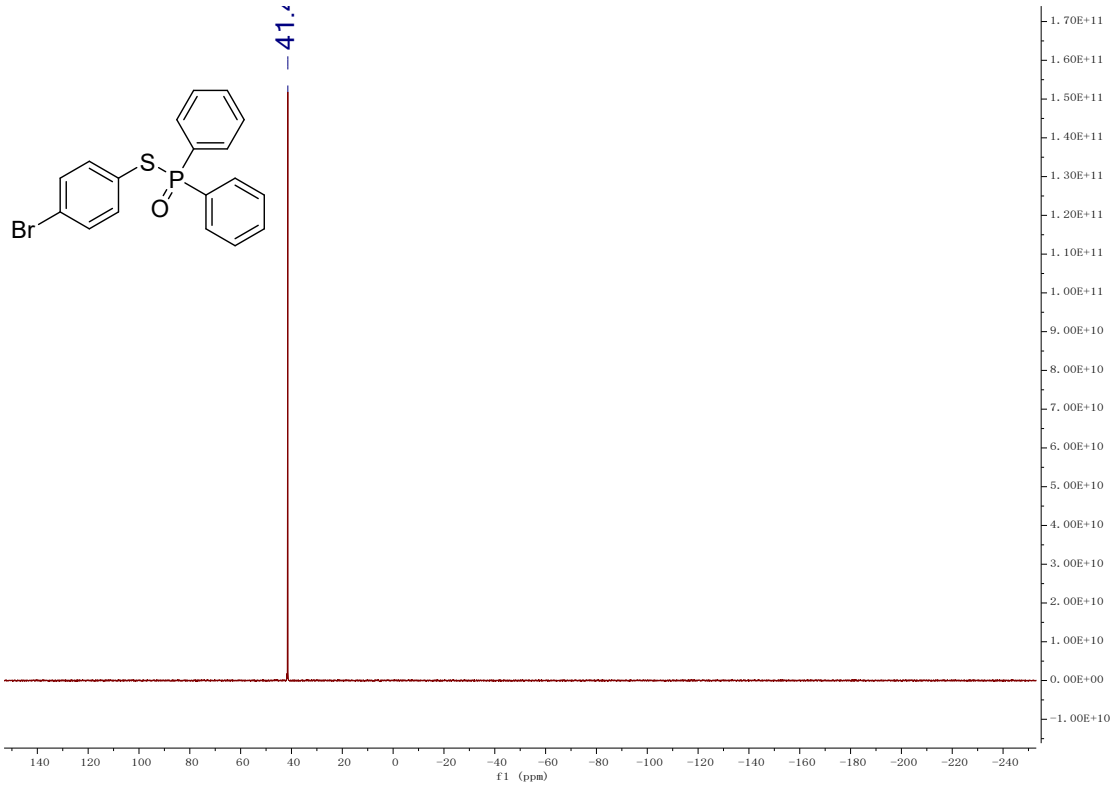

S
P
O
Cl
f1 (ppm)



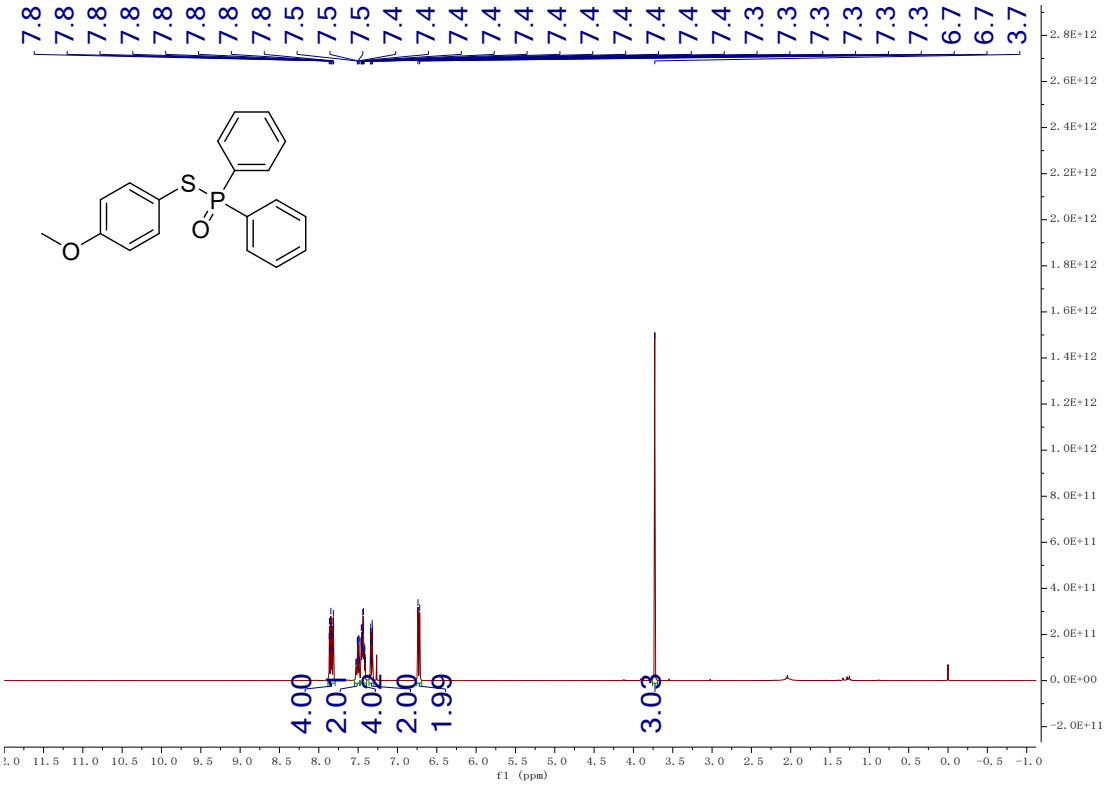
S-(4-bromophenyl) diphenylphosphinothioate (3g)

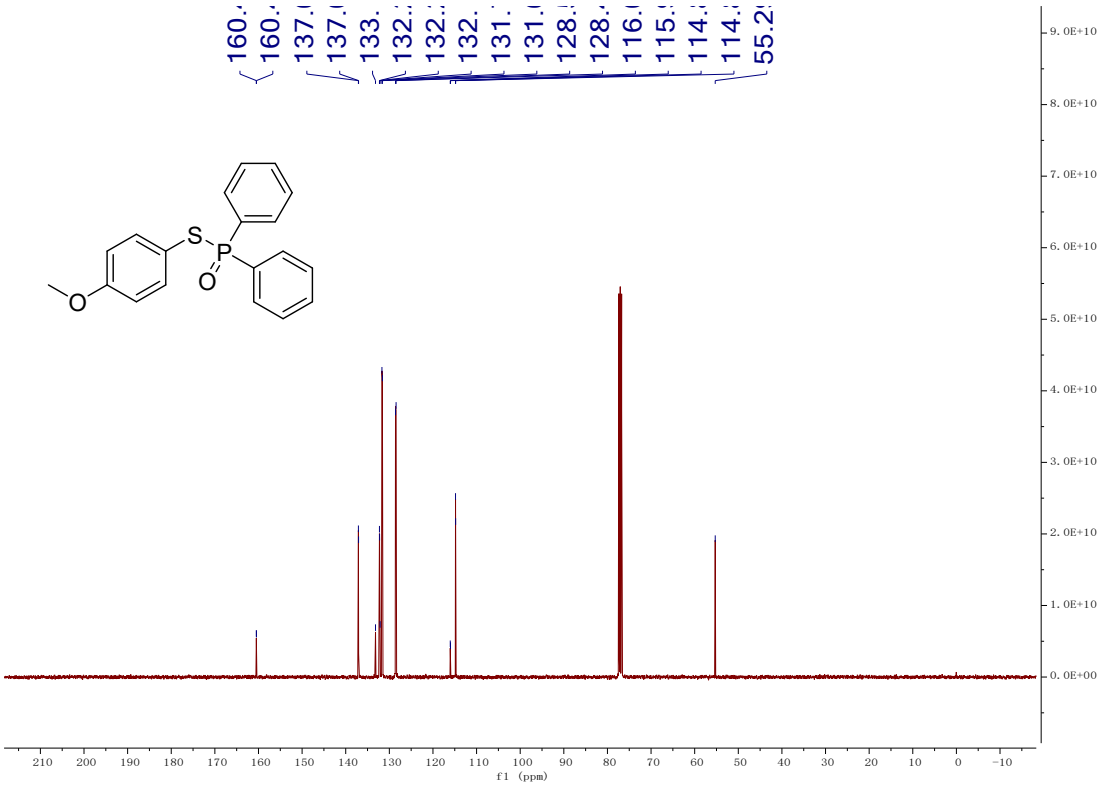


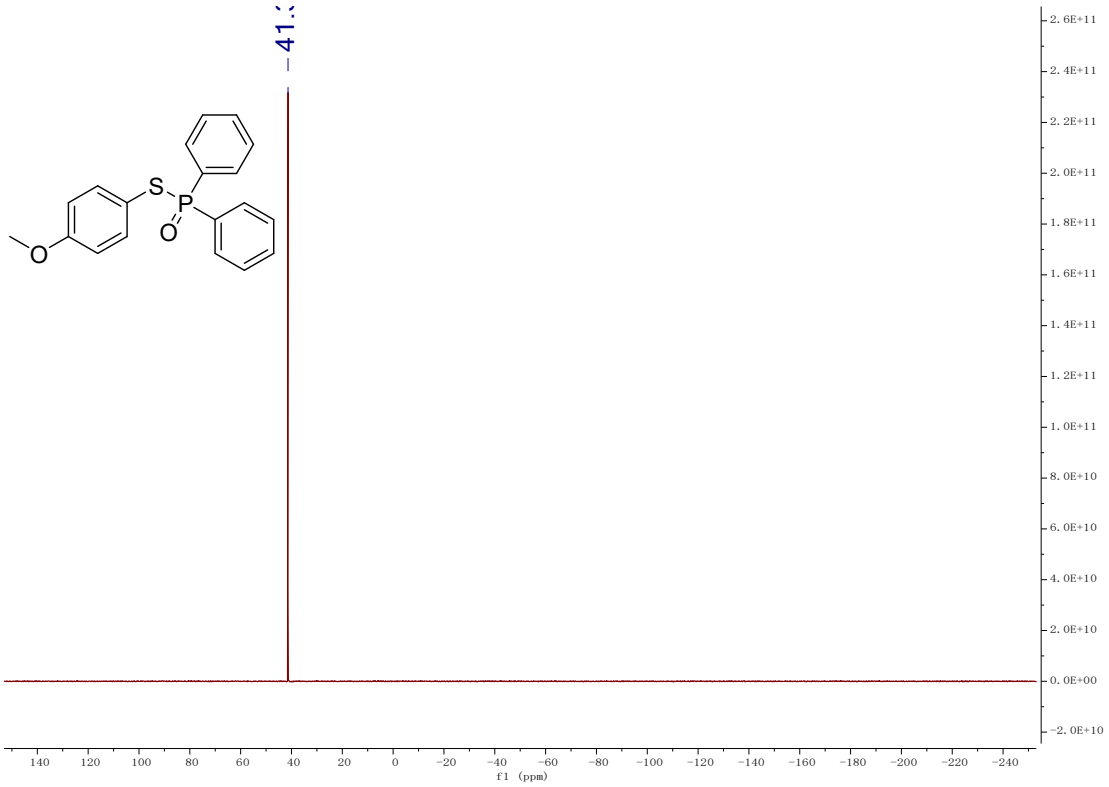

Br
S
P
O
f1 (ppm)


Br
S
P
O
f1 (ppm)

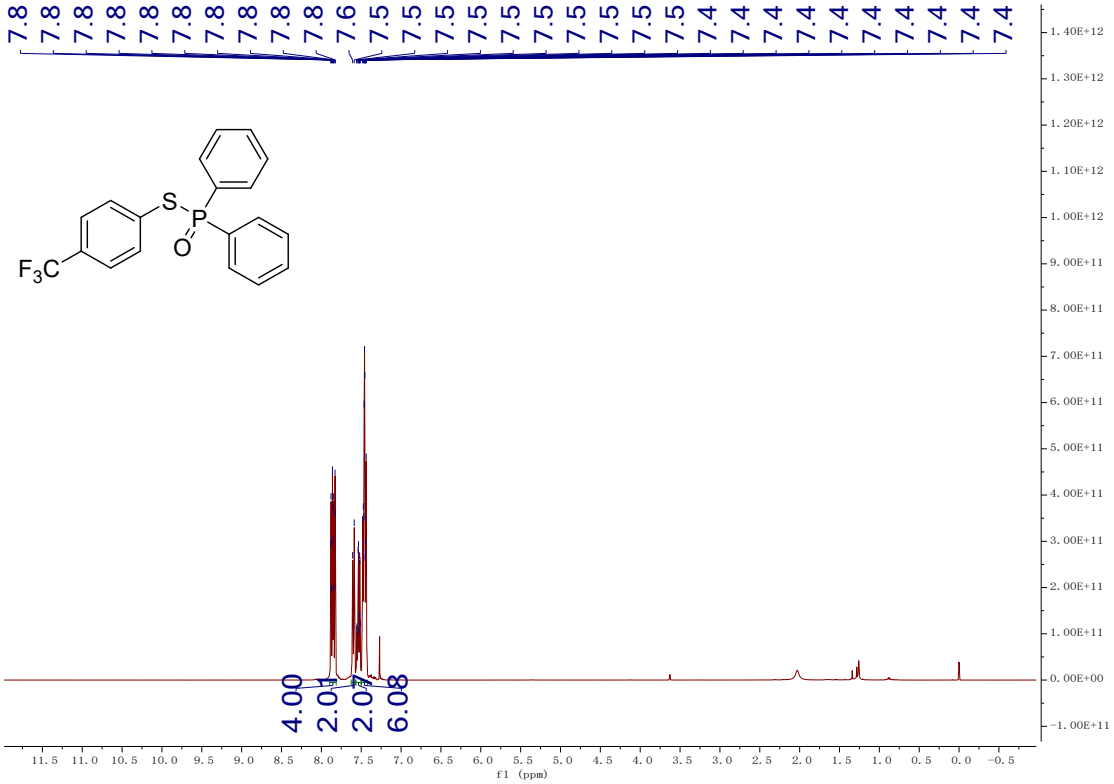
S-(4-methoxyphenyl) diphenylphosphinothioate (3h)

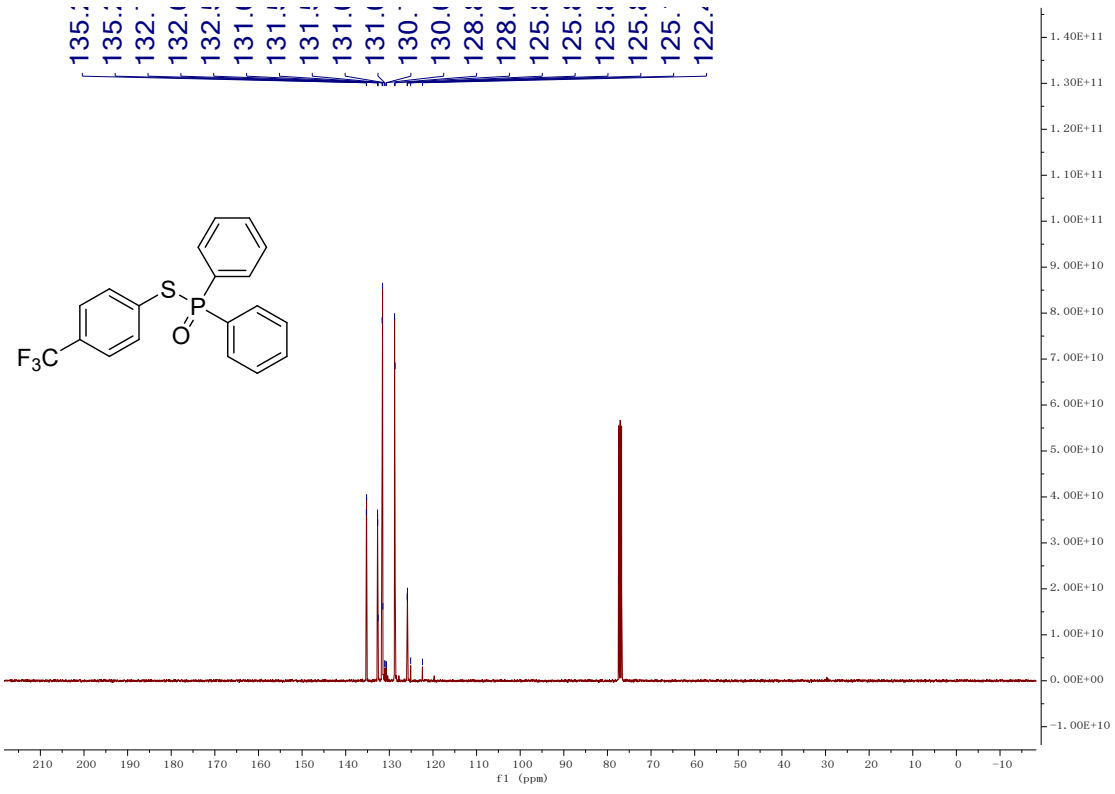


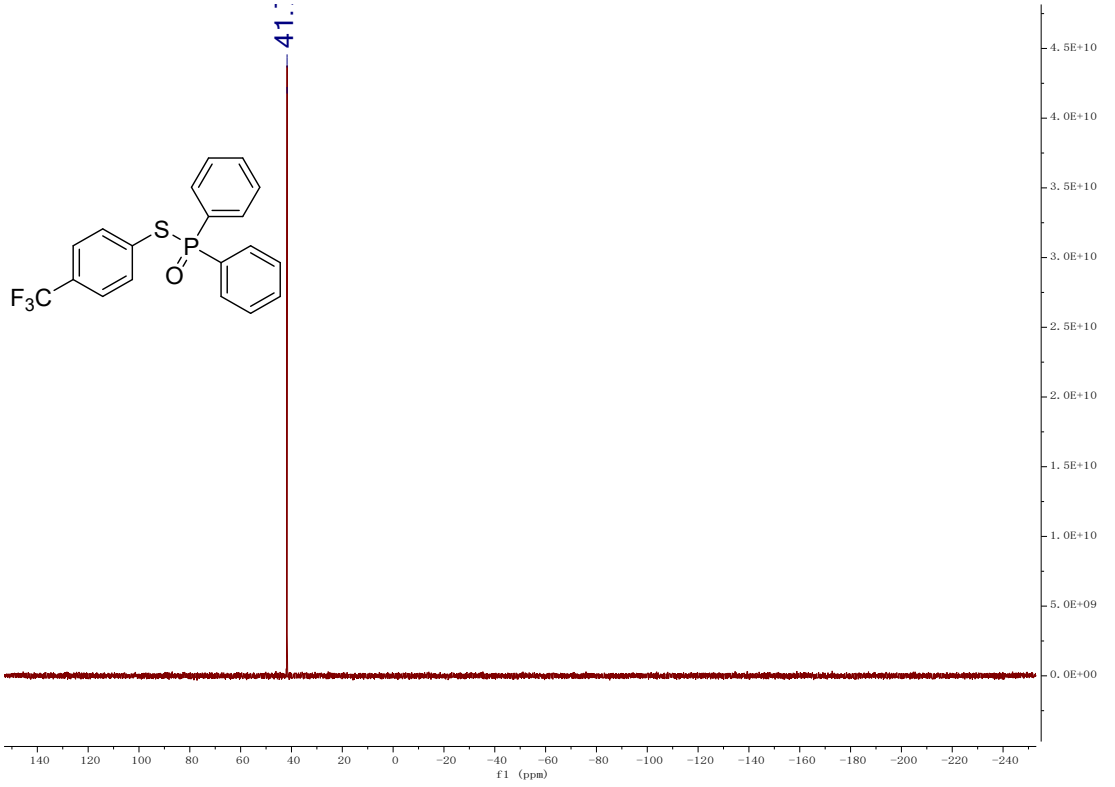


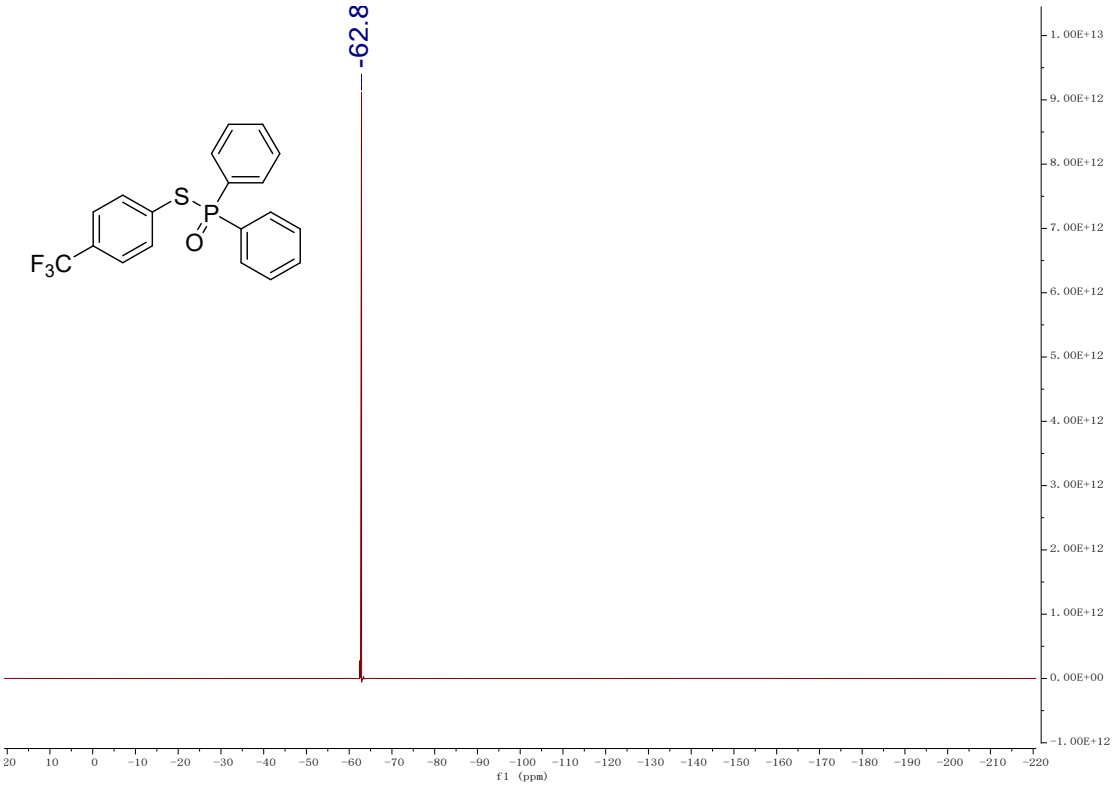


S-(4-(trifluoromethyl)phenyl) diphenylphosphinothioate (3i)

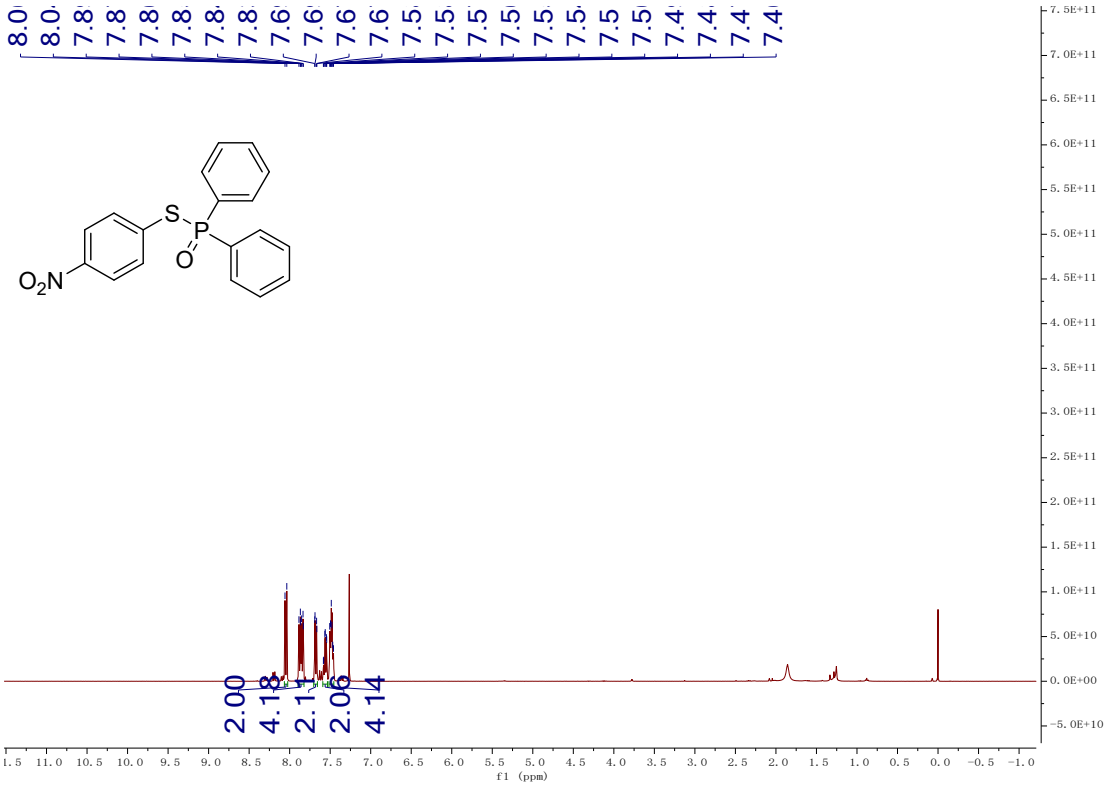


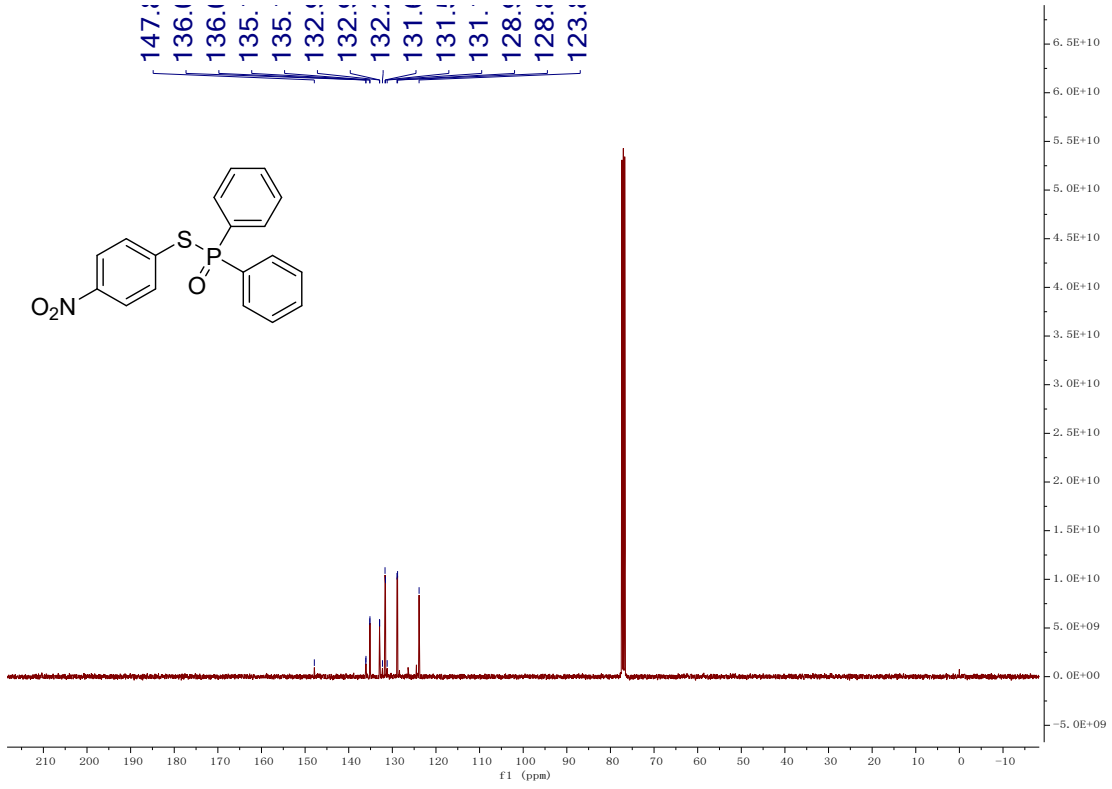

F3C
S
P
O
f1 (ppm)

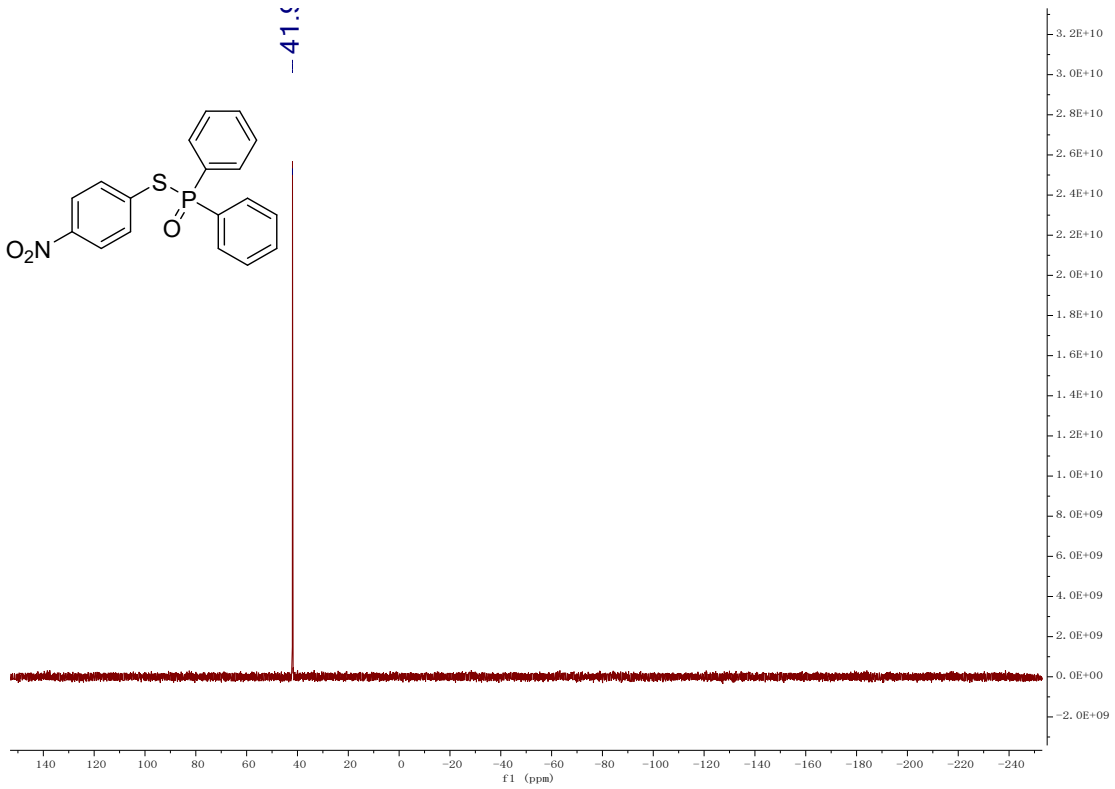

F3C
S
P
O
f1 (ppm)



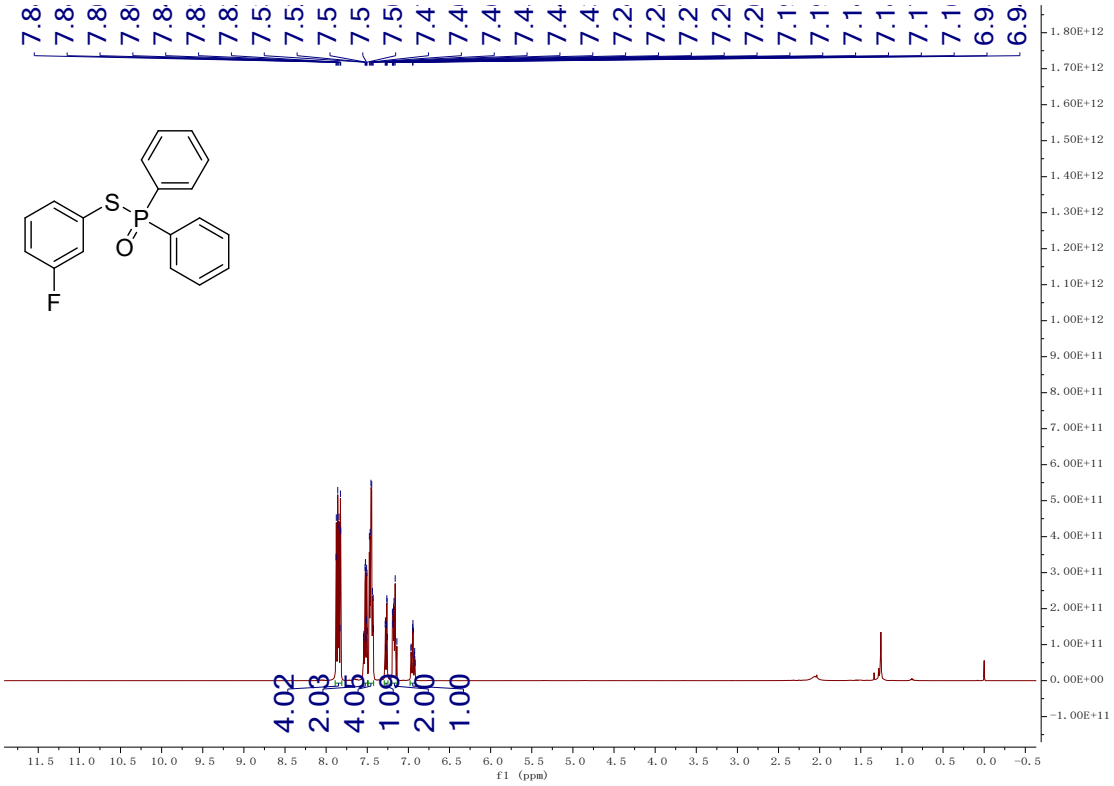
S-(4-nitrophenyl) diphenylphosphinothioate (3j)

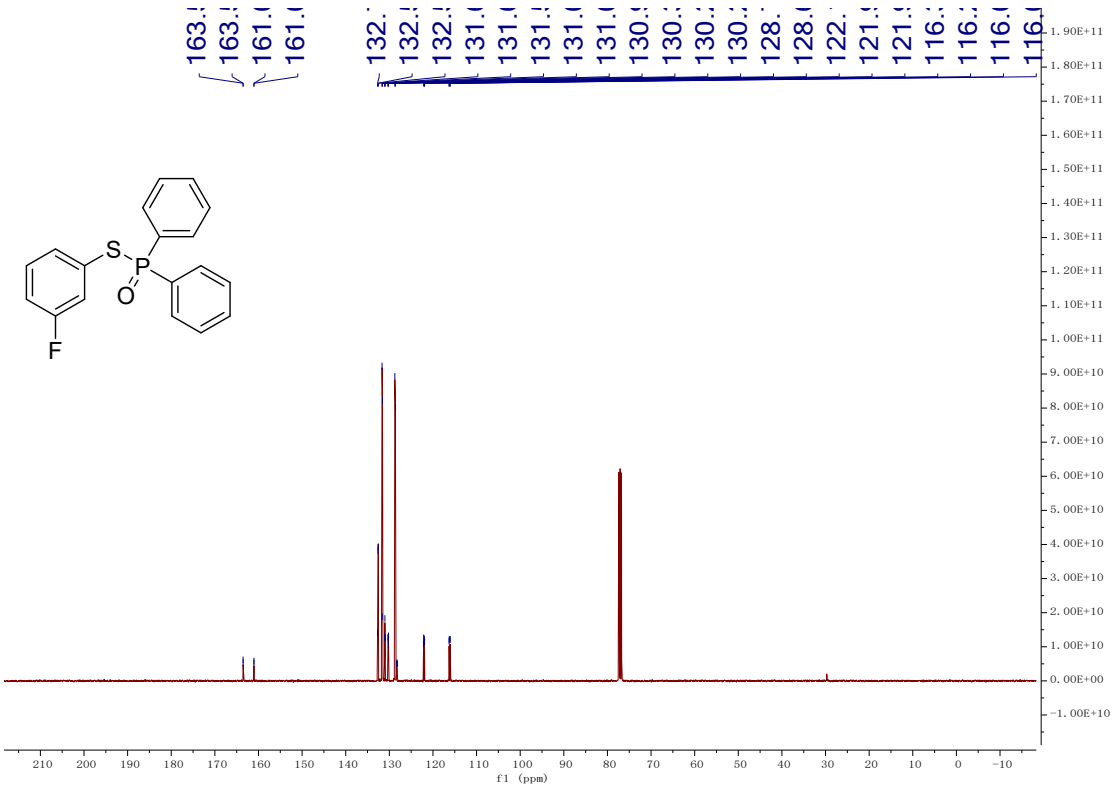


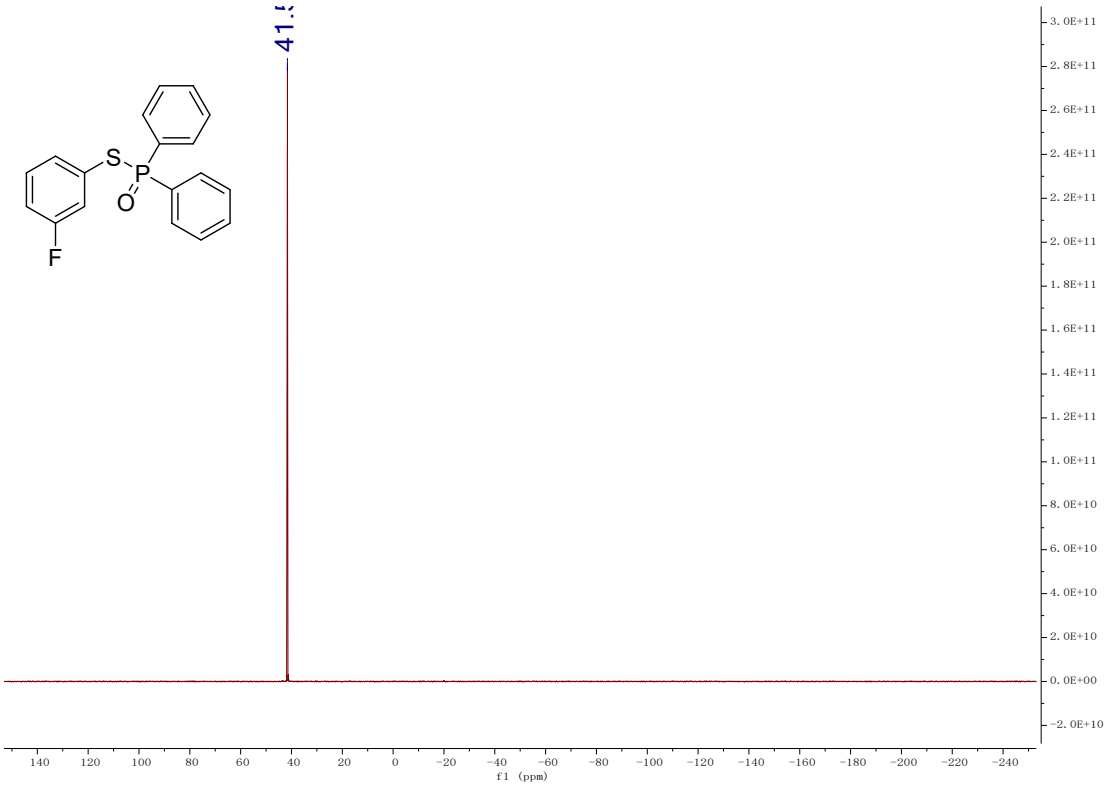

147.
136.
136.
135.
135.
132.
132.
132.
131.
131.
131.
128.
128.
123.
S
P
O
O2N
6. 5E+10
6. 0E+10
5. 5E+10
5. 0E+10
4. 5E+10
4. 0E+10
3. 5E+10
3. 0E+10
2. 5E+10
2. 0E+10
1. 5E+10
1. 0E+10
5. 0E+09
0. 0E+00
-5. 0E+09
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

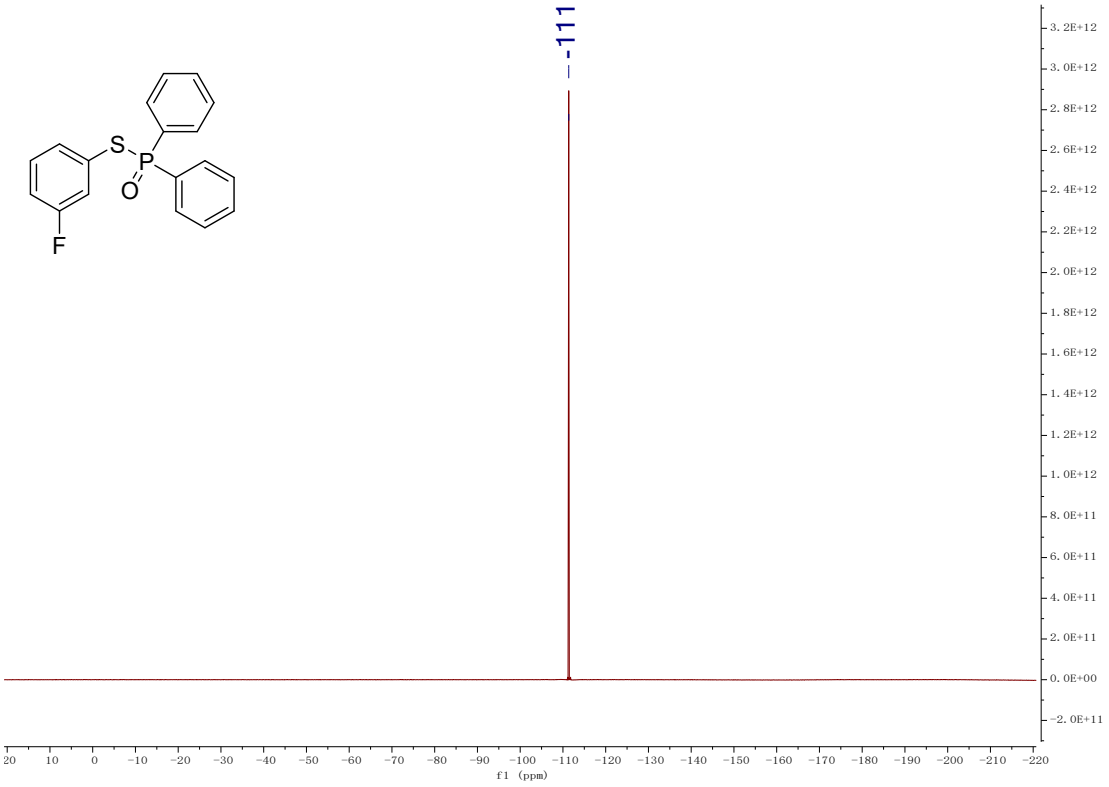

41.
S
P
O
O2N
3. 2E+10
3. 0E+10
2. 8E+10
2. 6E+10
2. 4E+10
2. 2E+10
2. 0E+10
1. 8E+10
1. 6E+10
1. 4E+10
1. 2E+10
1. 0E+10
8. 0E+09
6. 0E+09
4. 0E+09
2. 0E+09
0. 0E+00
-2. 0E+09
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

S-(3-fluorophenyl) diphenylphosphinothioate (3k)

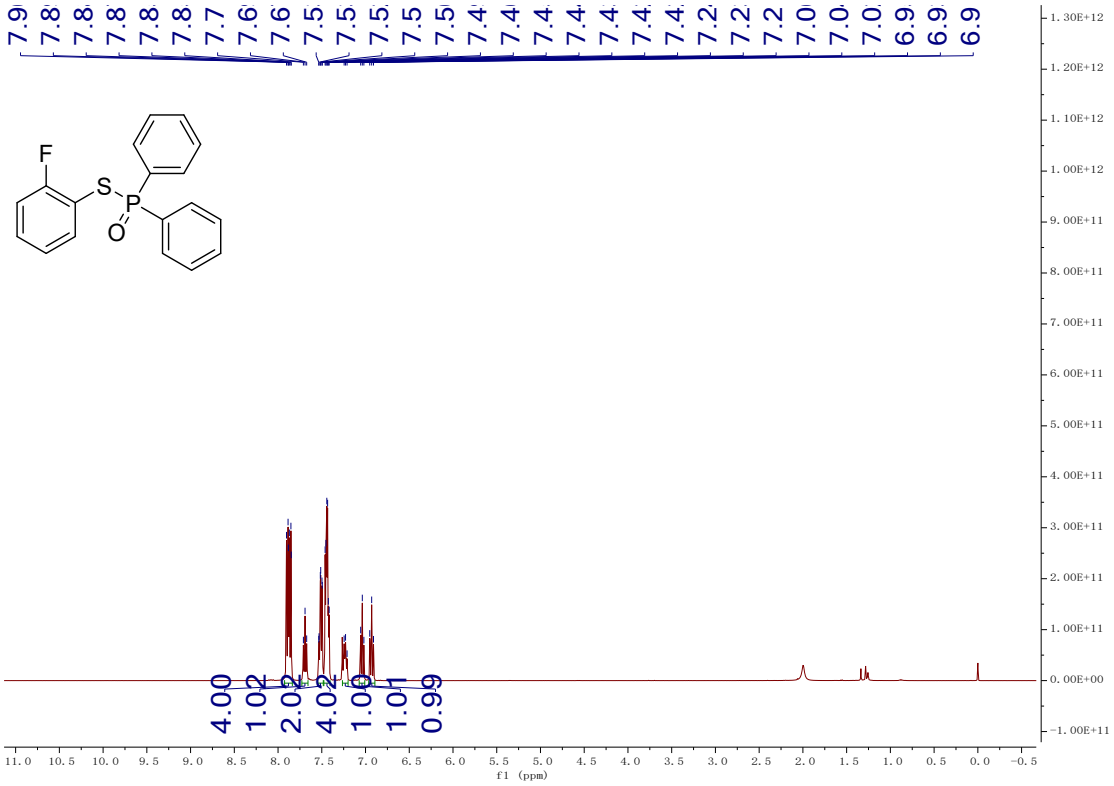


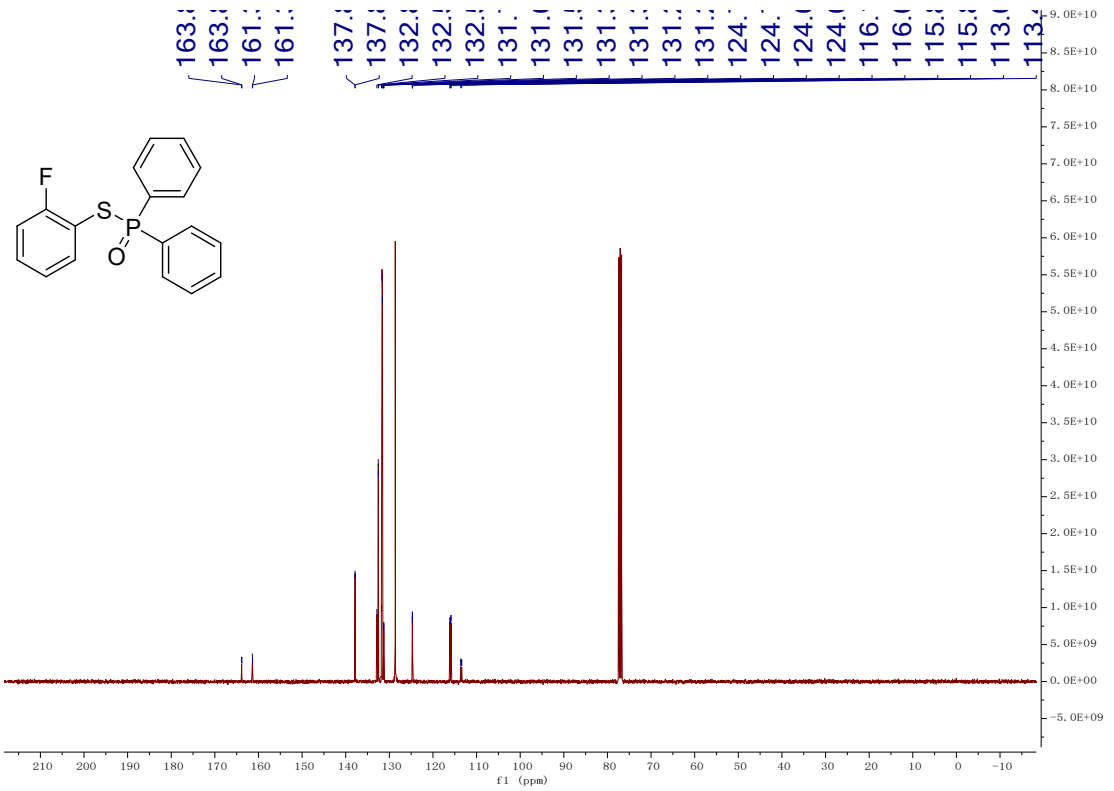


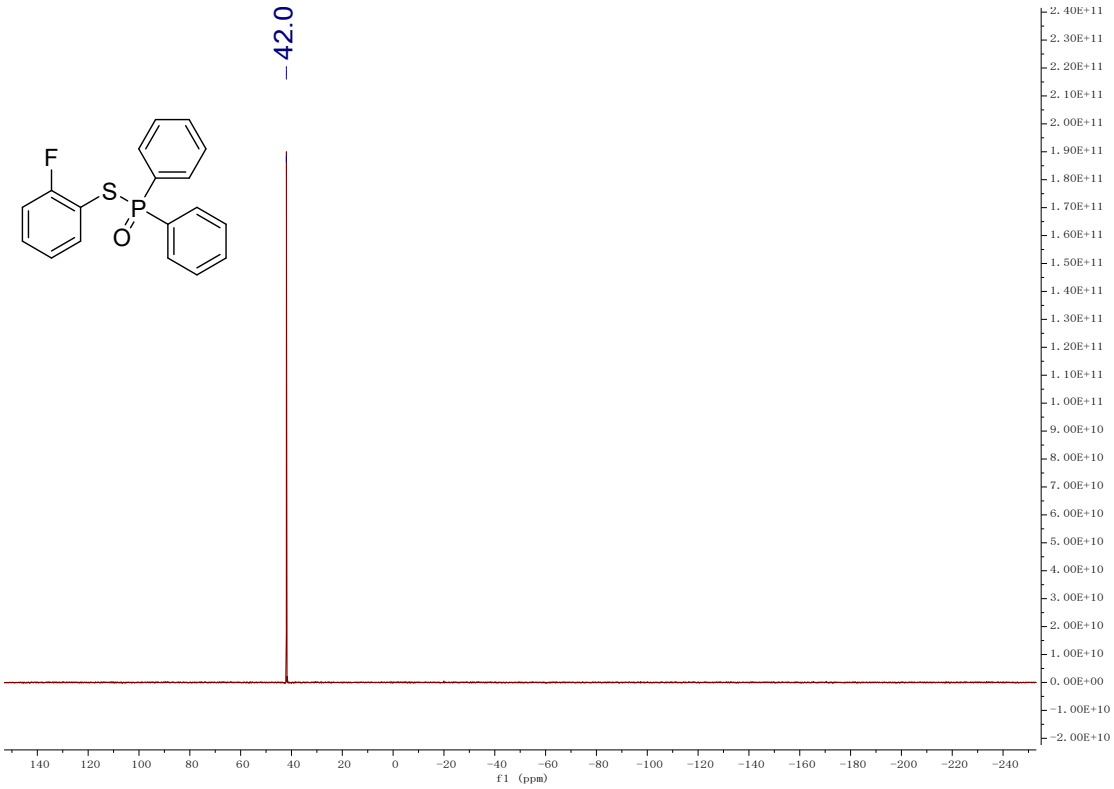

41.5
S
P
O
F
3.0E+11
2.8E+11
2.6E+11
2.4E+11
2.2E+11
2.0E+11
1.8E+11
1.6E+11
1.4E+11
1.2E+11
1.0E+11
8.0E+10
6.0E+10
4.0E+10
2.0E+10
0.0E+00
-2.0E+10
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

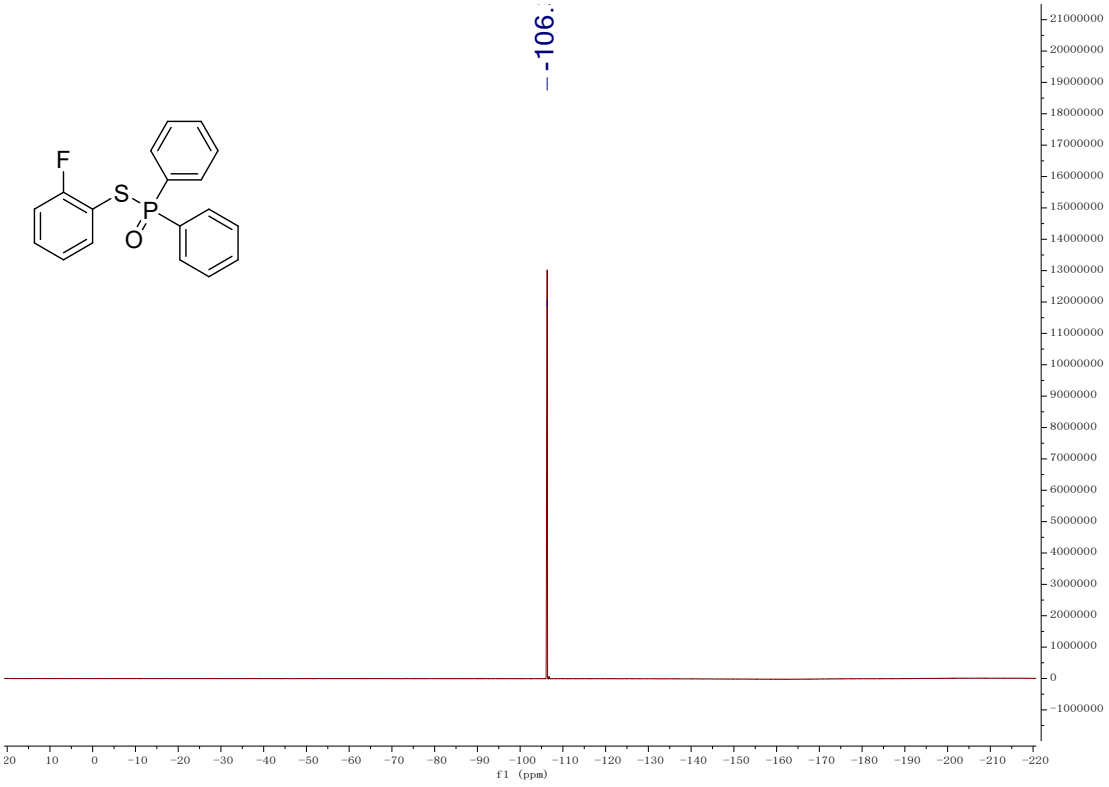

-111
S
P
O
F
3.2E+12
3.0E+12
2.8E+12
2.6E+12
2.4E+12
2.2E+12
2.0E+12
1.8E+12
1.6E+12
1.4E+12
1.2E+12
1.0E+12
8.0E+11
6.0E+11
4.0E+11
2.0E+11
0.0E+00
-2.0E+11
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

S-(2-fluorophenyl) diphenylphosphinothioate (3l)

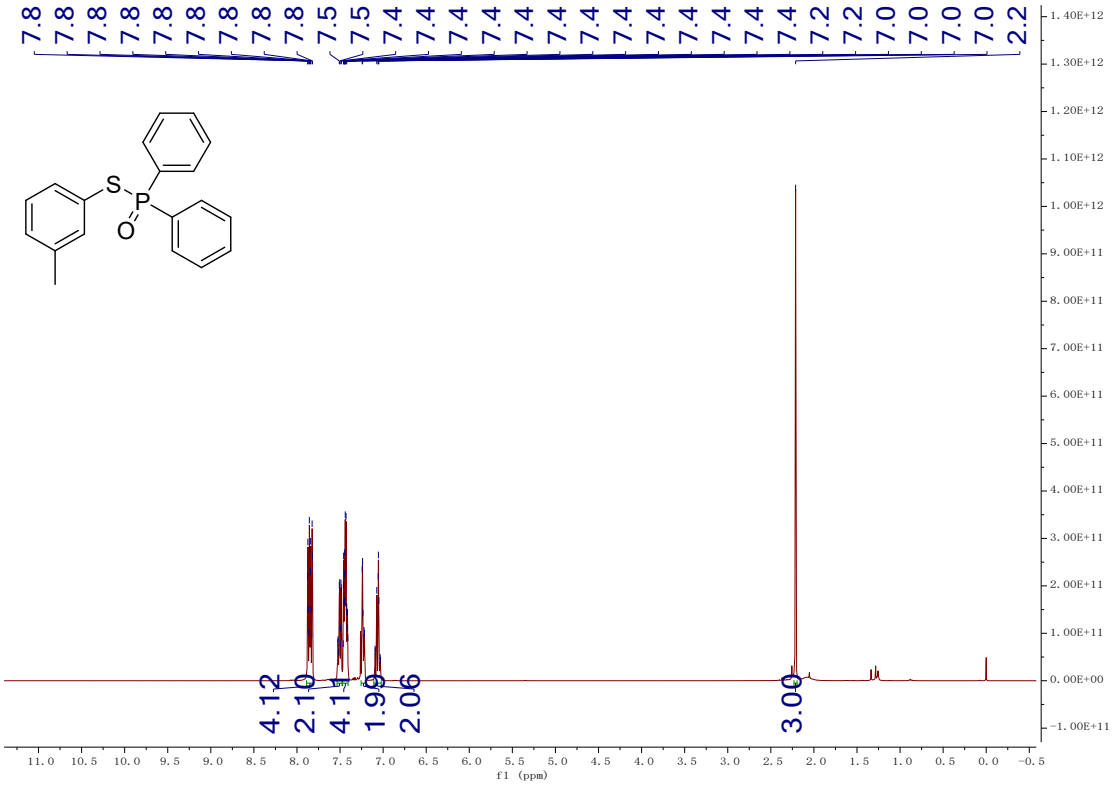


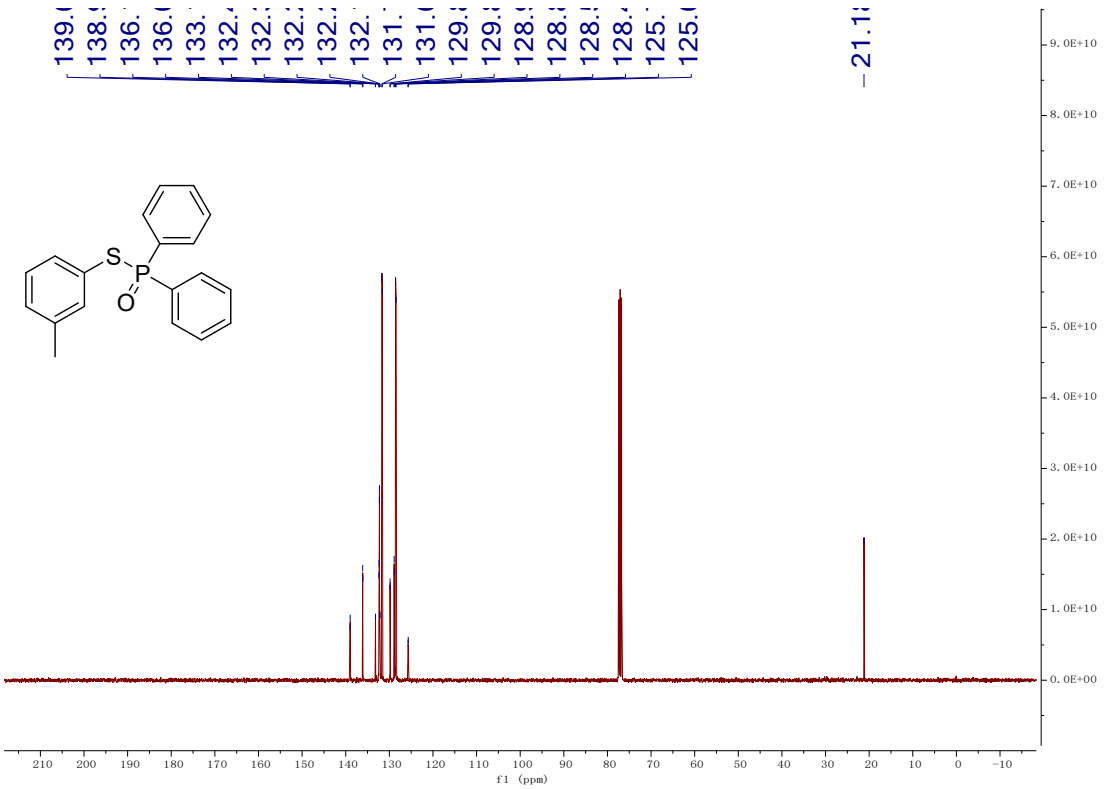


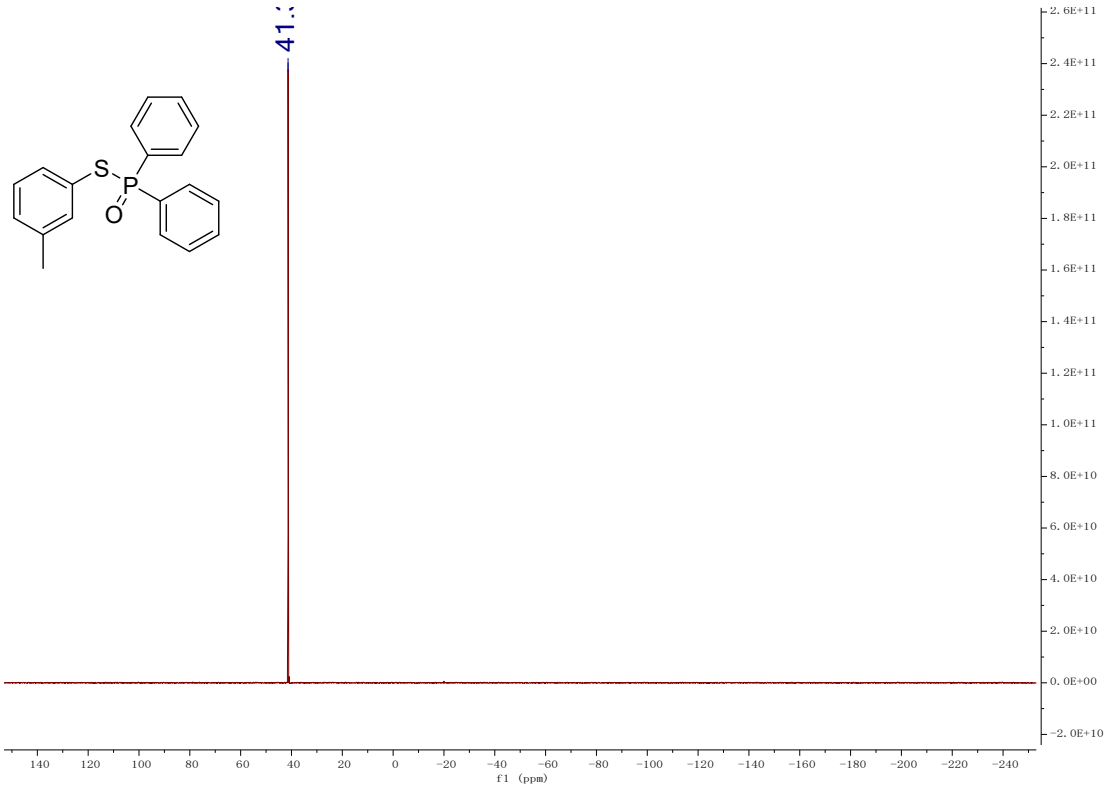

-42.0
F
S
P
O
f1 (ppm)


-106.
F
S
P
O
f1 (ppm)

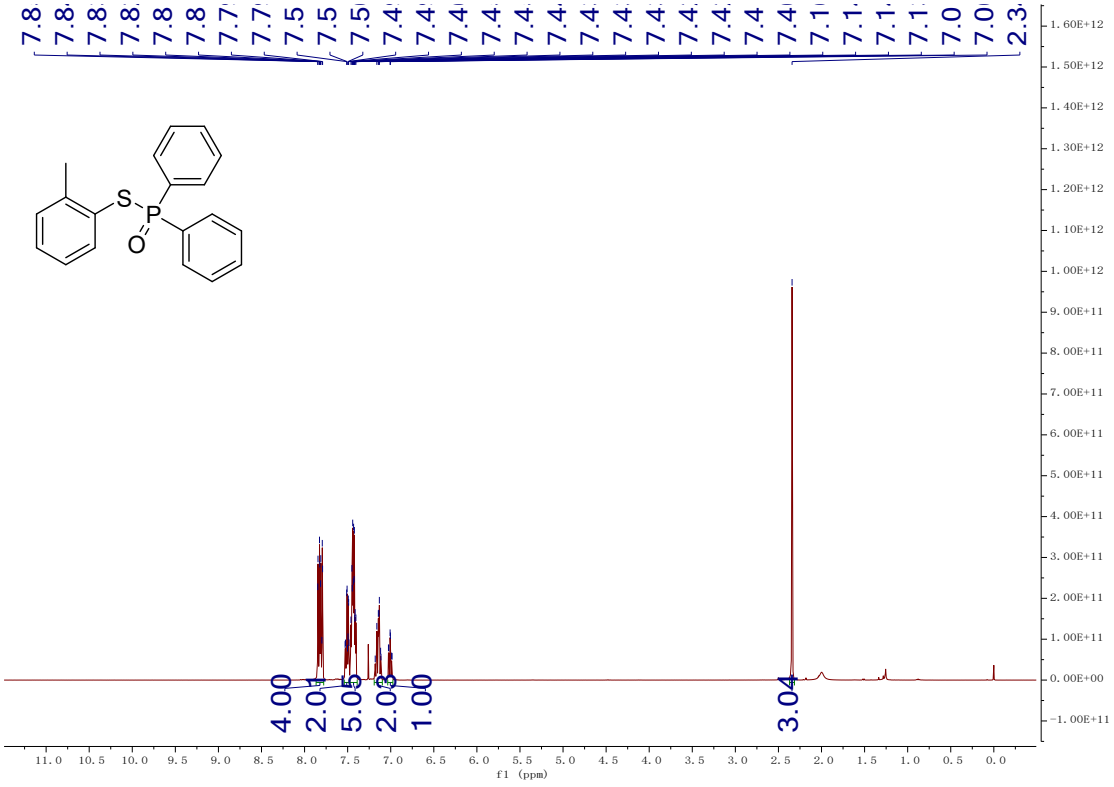
S-(m-tolyl) diphenylphosphinothioate (3m)

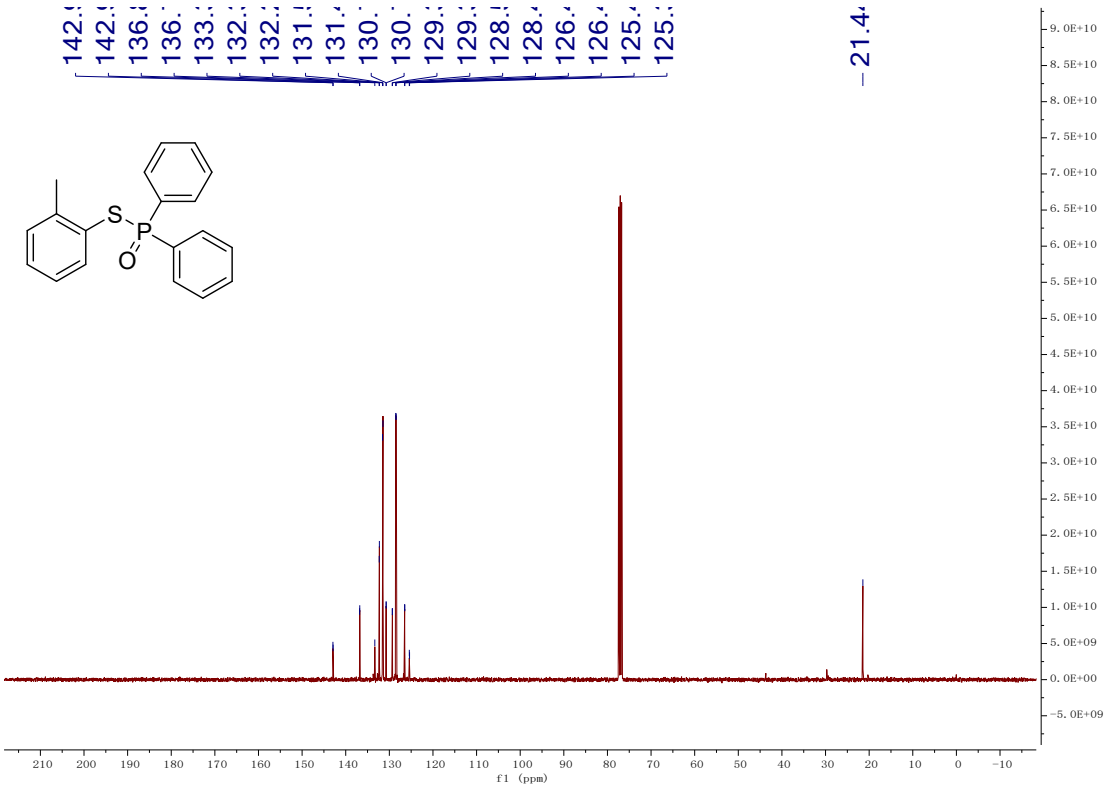


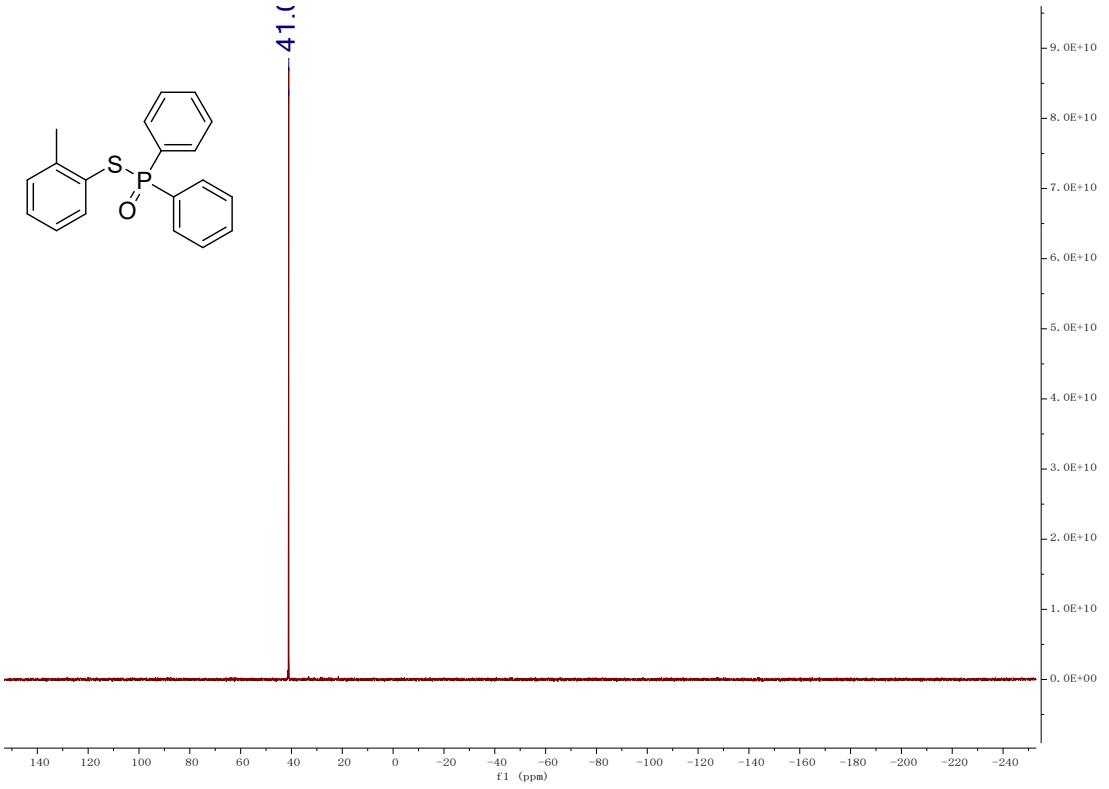




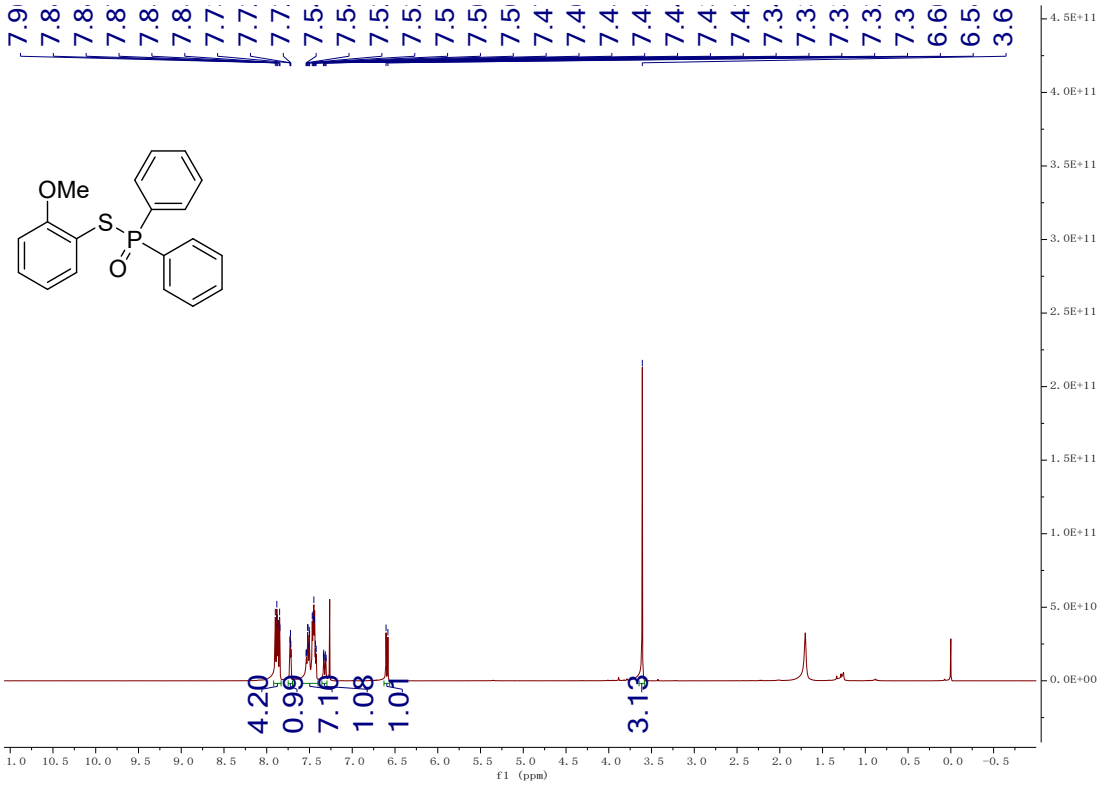
S-(o-tolyl) diphenylphosphinothioate (3n)

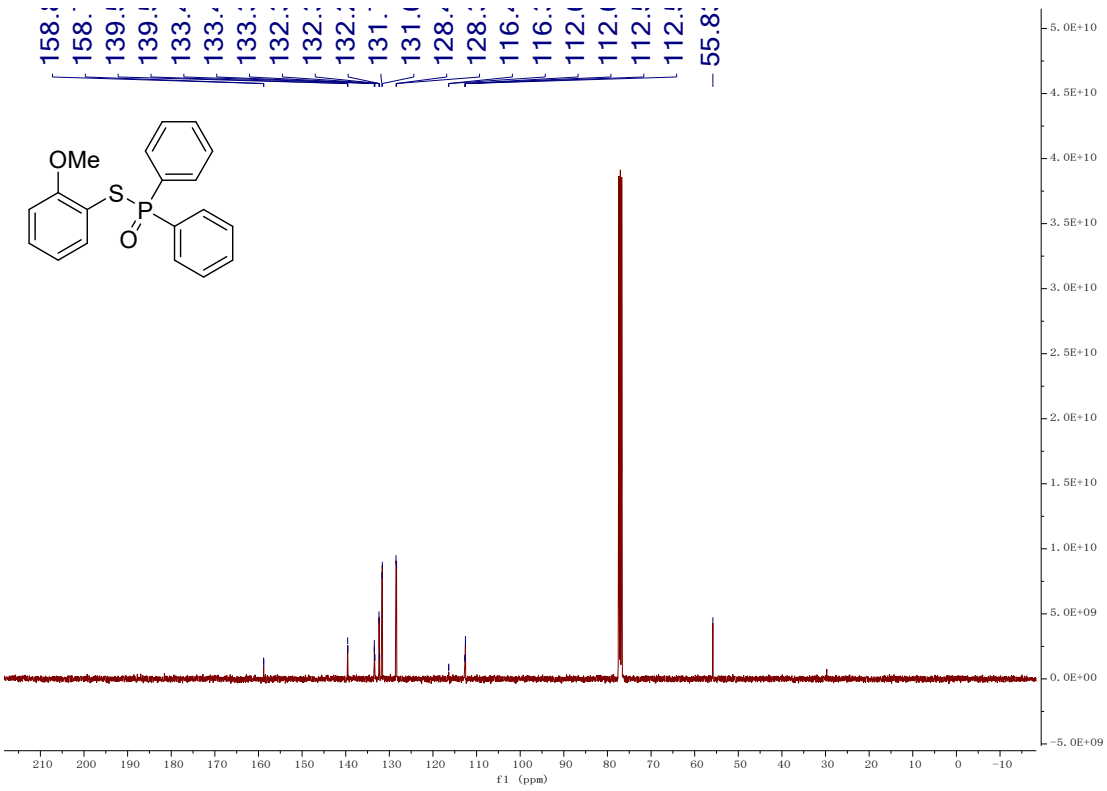


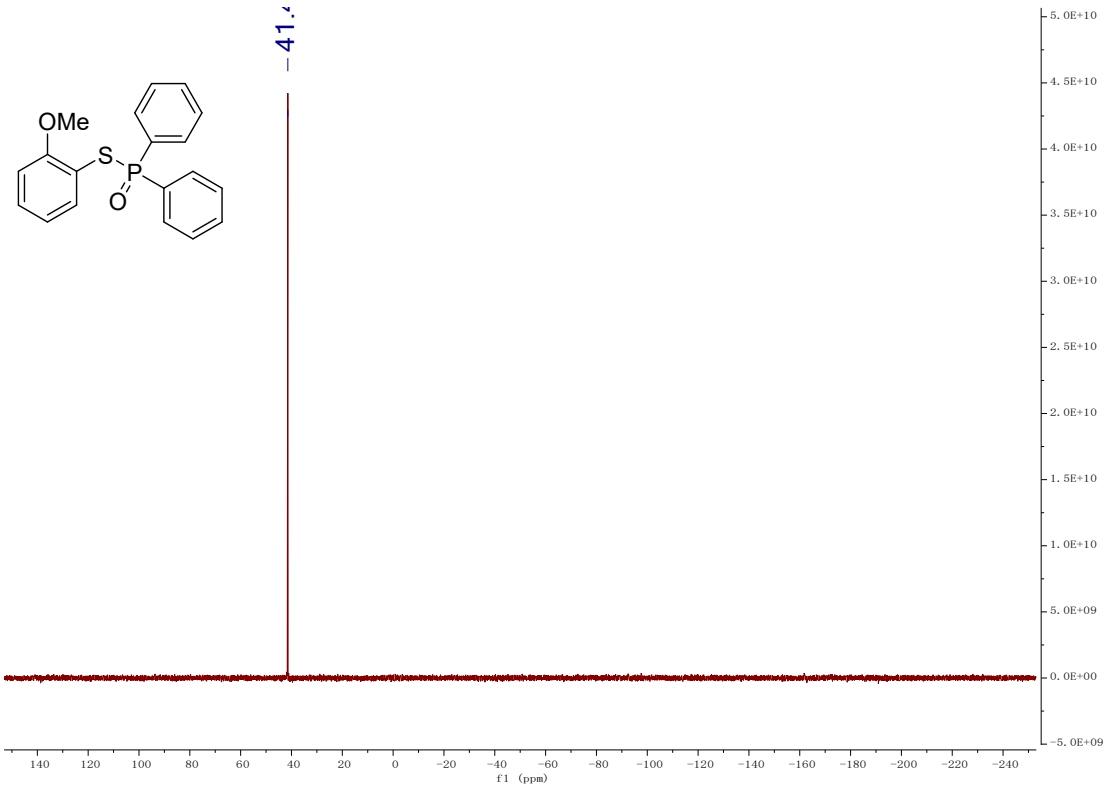

142.
142.
136.
136.
133.
132.
132.
131.
131.
130.
130.
129.
129.
128.
128.
126.
126.
125.
125.
21.4
S
P
O
9.0E+10
8.5E+10
8.0E+10
7.5E+10
7.0E+10
6.5E+10
6.0E+10
5.5E+10
5.0E+10
4.5E+10
4.0E+10
3.5E+10
3.0E+10
2.5E+10
2.0E+10
1.5E+10
1.0E+10
5.0E+09
0.0E+00
-5.0E+09
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


41.
S
P
O
9.0E+10
8.0E+10
7.0E+10
6.0E+10
5.0E+10
4.0E+10
3.0E+10
2.0E+10
1.0E+10
0.0E+00
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

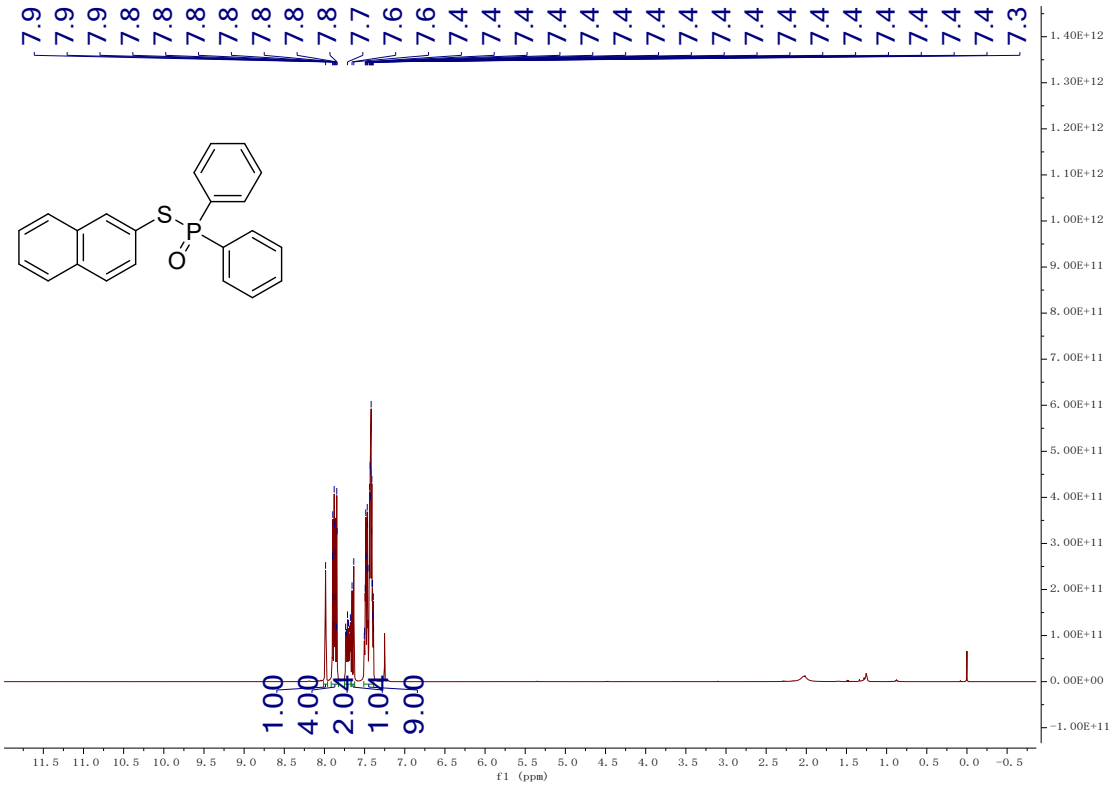
S-(2-methoxyphenyl) diphenylphosphinothioate (3o)

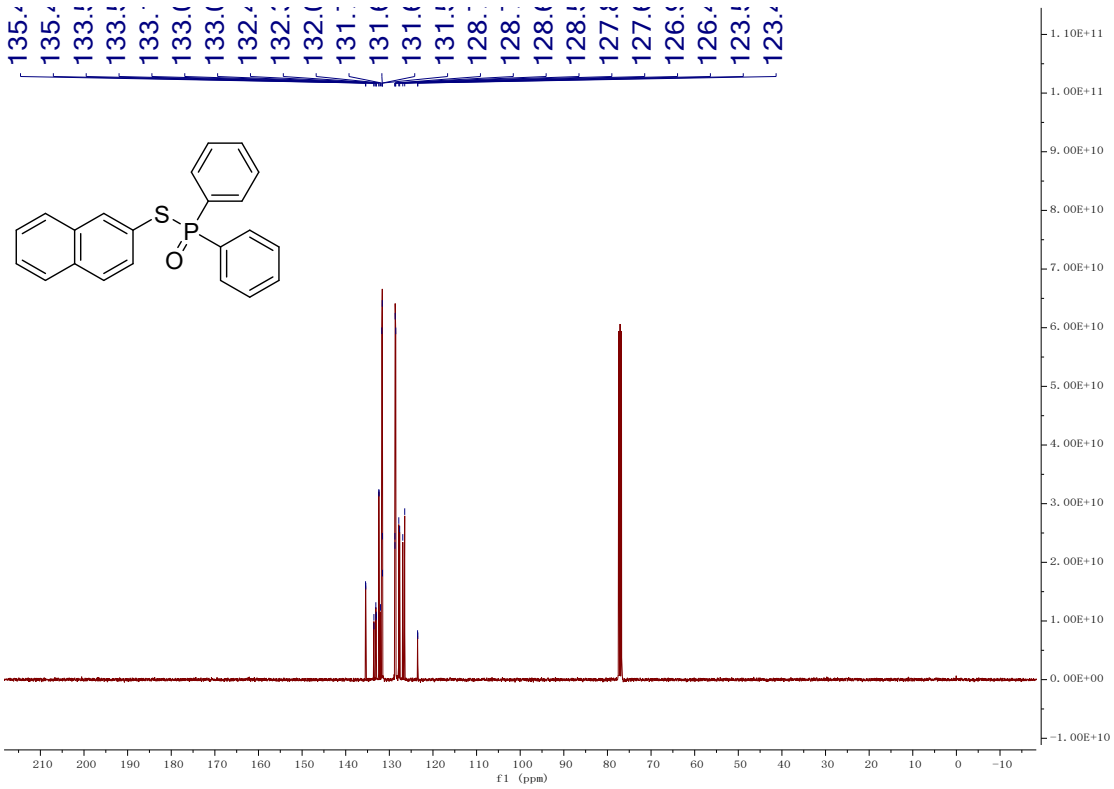


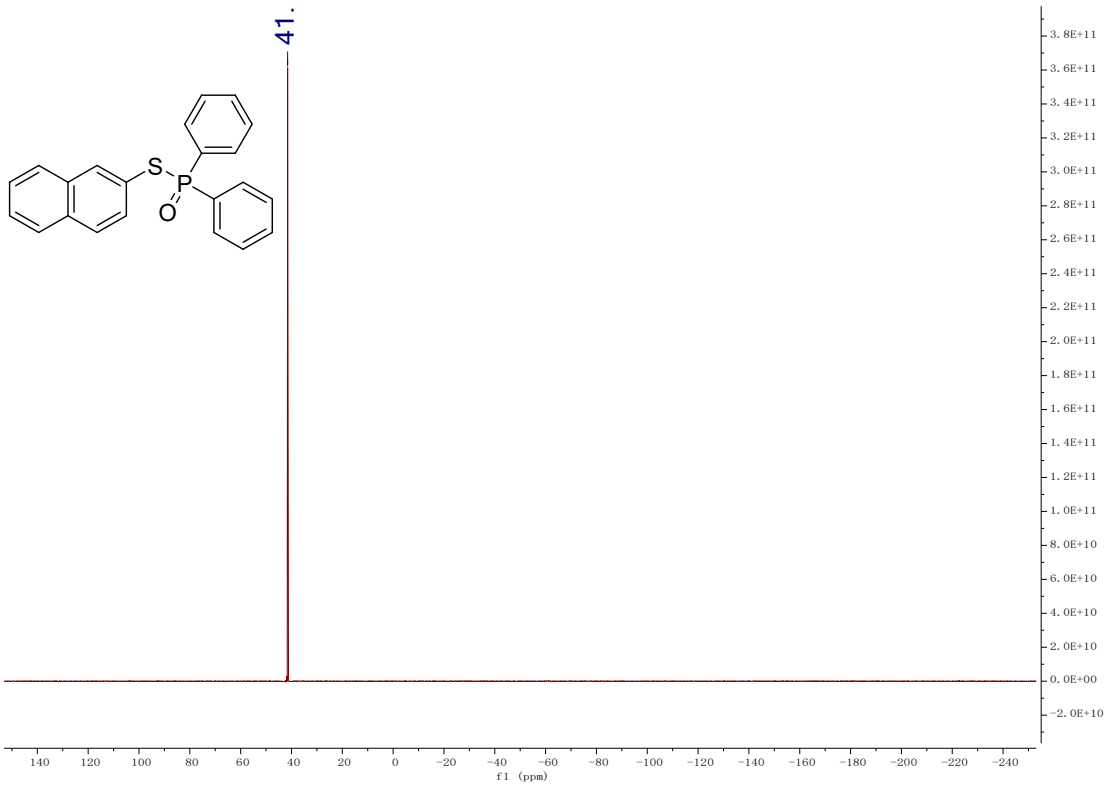




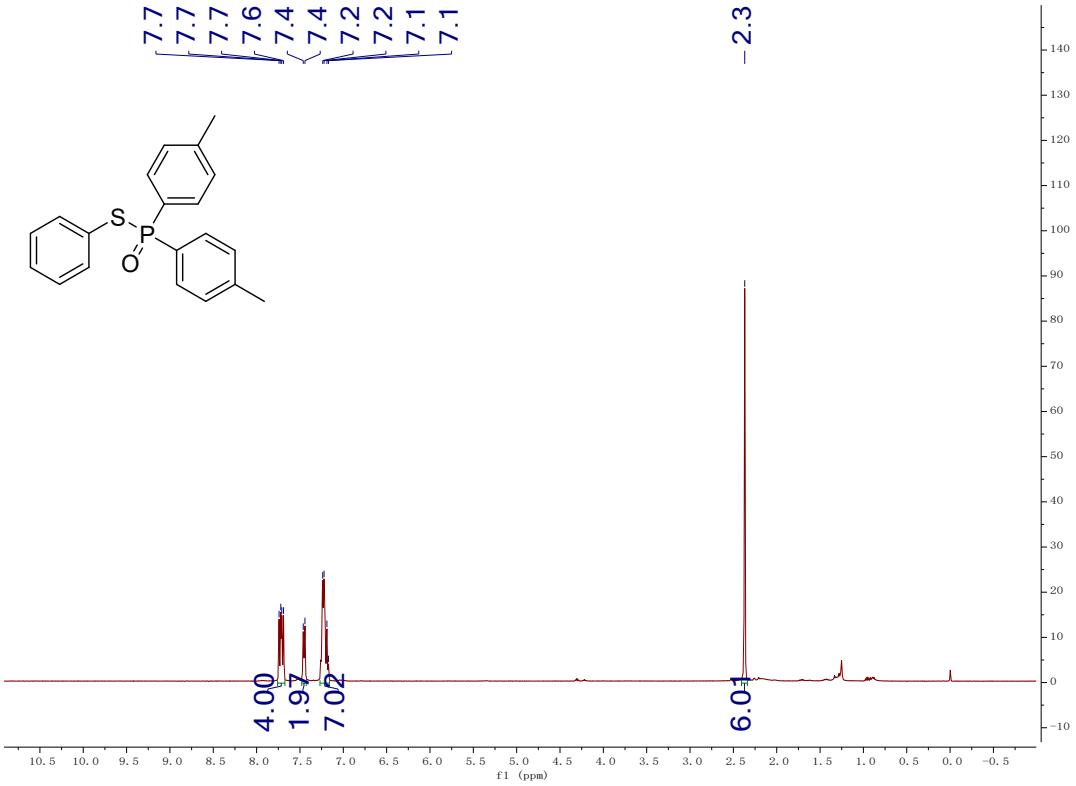
S-(naphthalen-2-yl) diphenylphosphinothioate (3p)

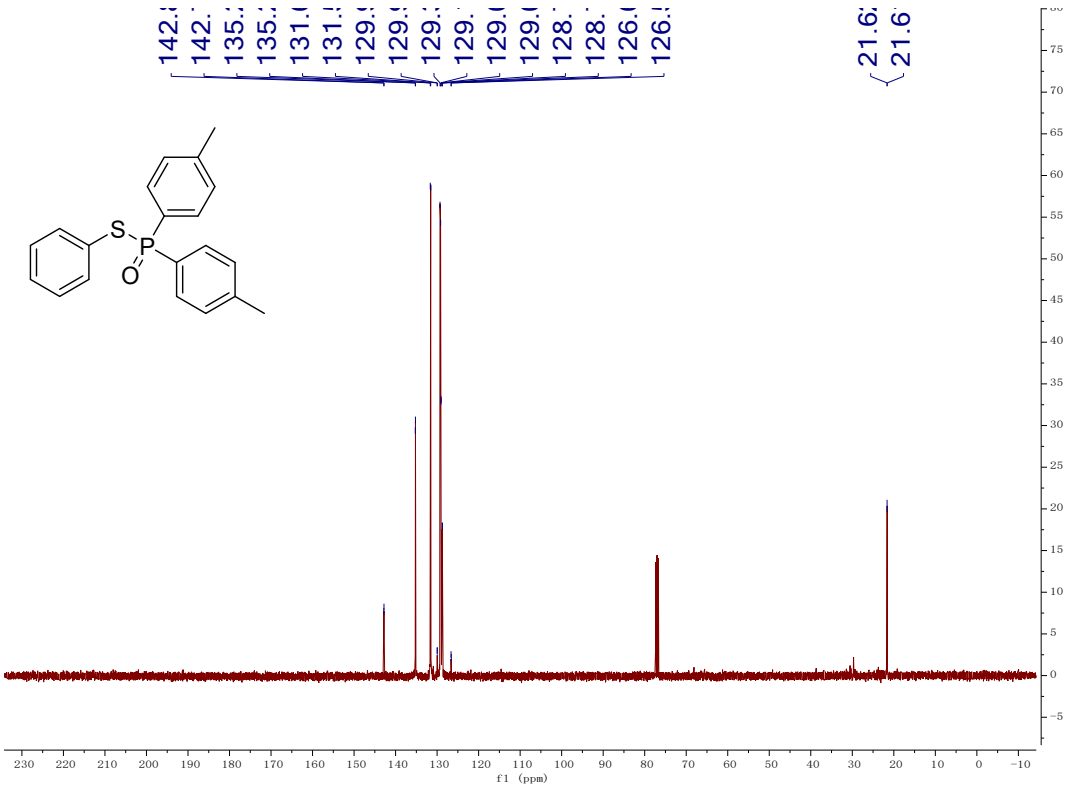


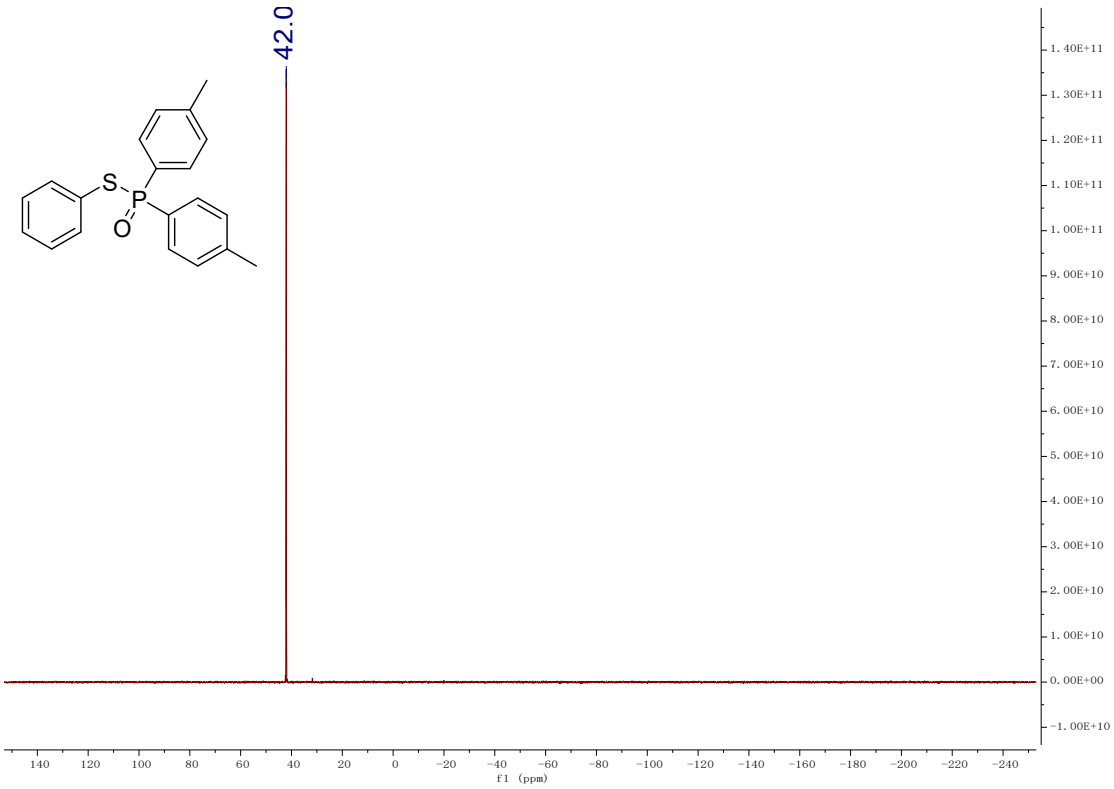

135.4
135.4
133.1
133.1
133.
133.0
133.0
132.4
132.1
132.0
131.
131.0
131.0
131.1
128.
128.
128.0
128.1
127.8
127.0
126.9
126.4
123.1
123.4
S
P
O
1. 10E+11
1. 00E+11
9. 00E+10
8. 00E+10
7. 00E+10
6. 00E+10
5. 00E+10
4. 00E+10
3. 00E+10
2. 00E+10
1. 00E+10
0. 00E+00
-1. 00E+10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


41.
S
P
O
3. 8E+11
3. 6E+11
3. 4E+11
3. 2E+11
3. 0E+11
2. 8E+11
2. 6E+11
2. 4E+11
2. 2E+11
2. 0E+11
1. 8E+11
1. 6E+11
1. 4E+11
1. 2E+11
1. 0E+11
8. 0E+10
6. 0E+10
4. 0E+10
2. 0E+10
0. 0E+00
-2. 0E+10
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

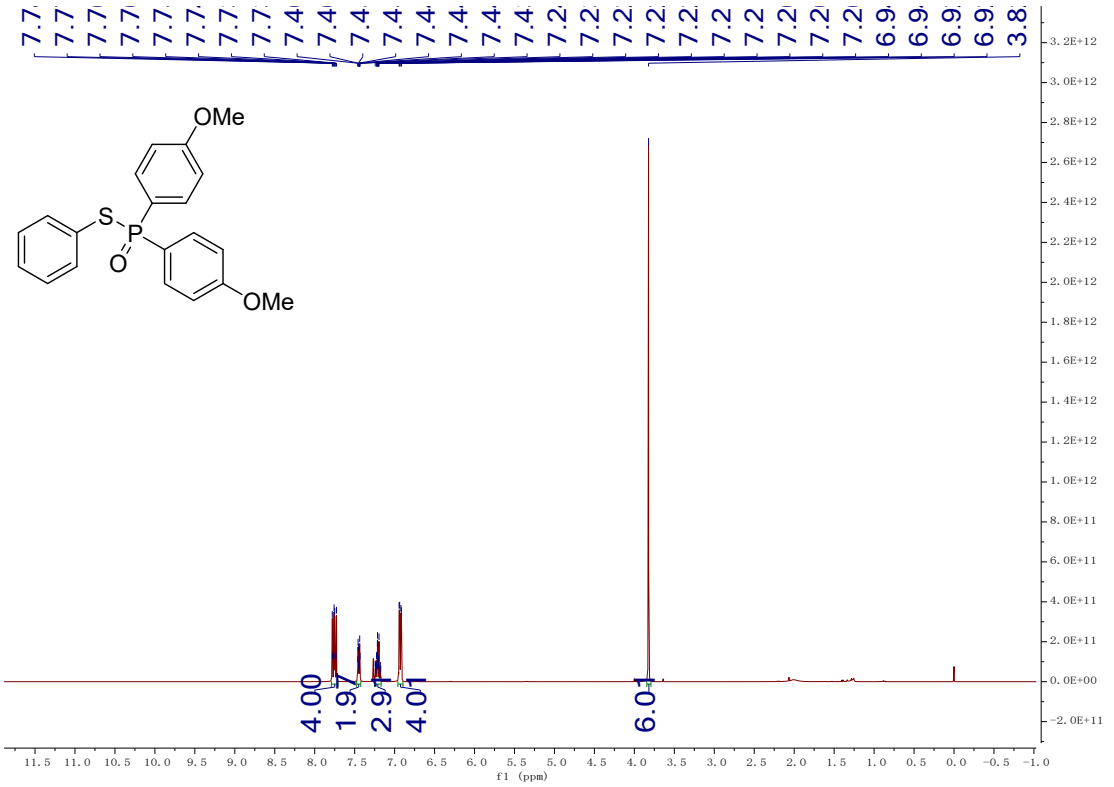
S-phenyl di-p-tolylphosphinothioate (3r)

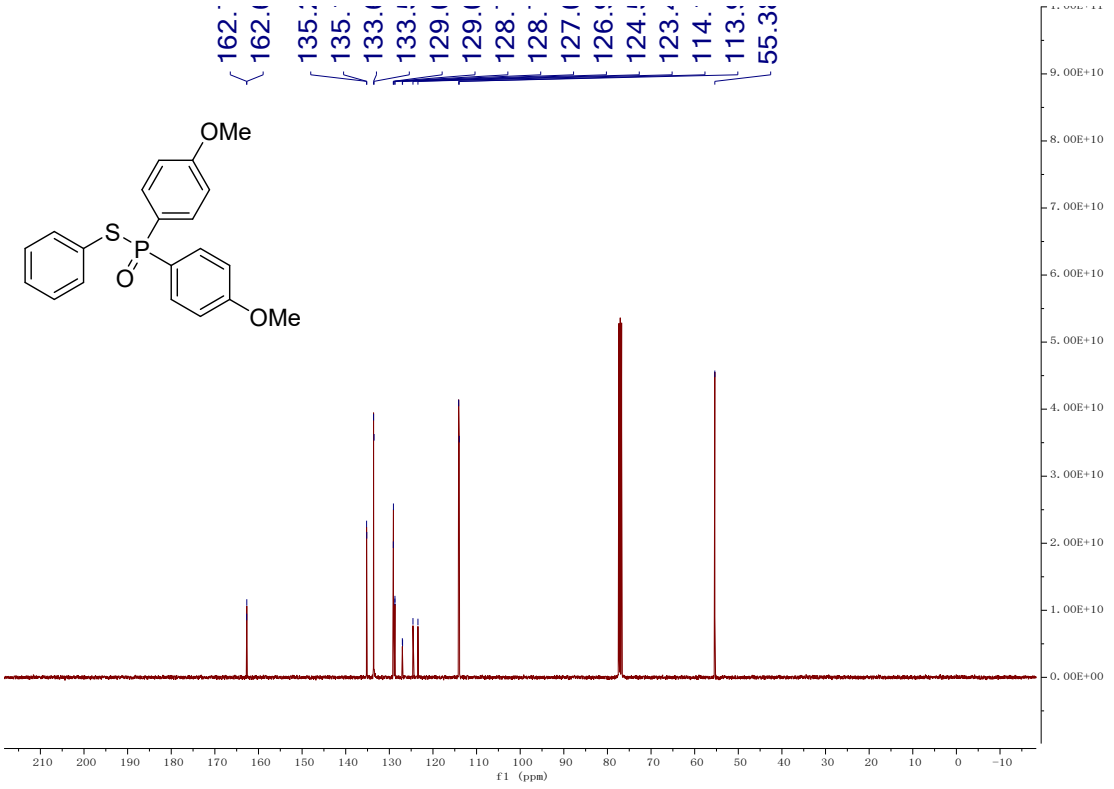


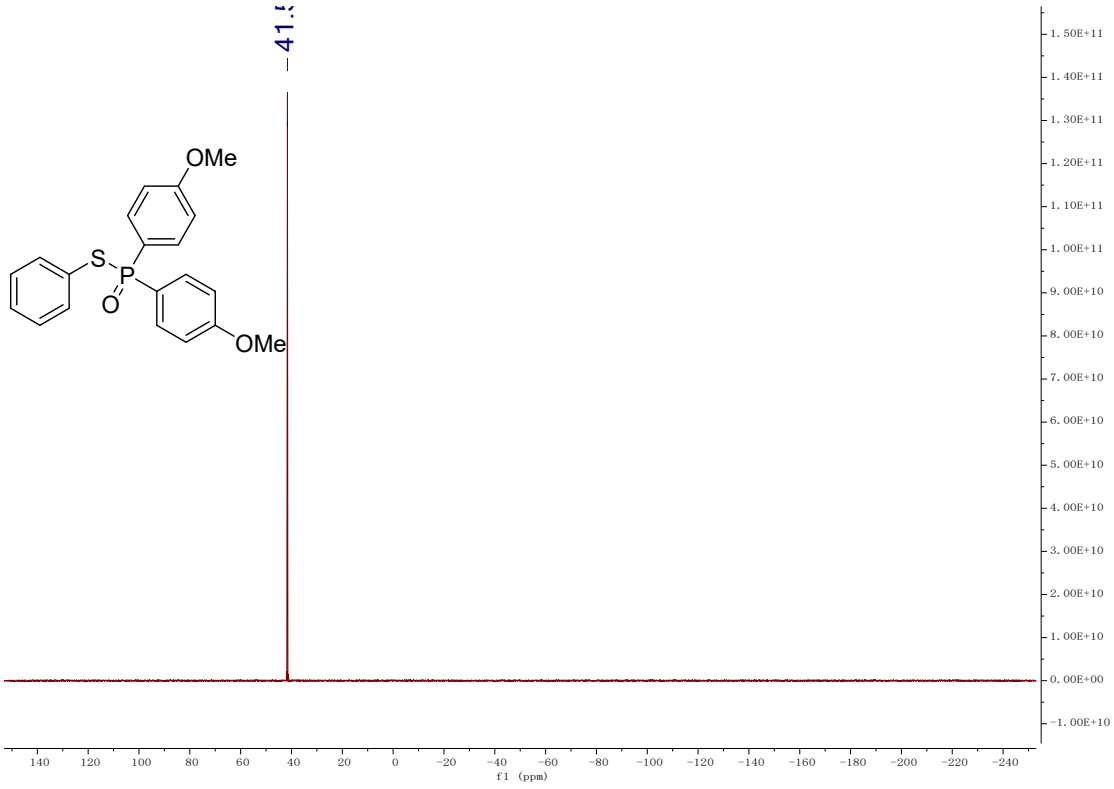




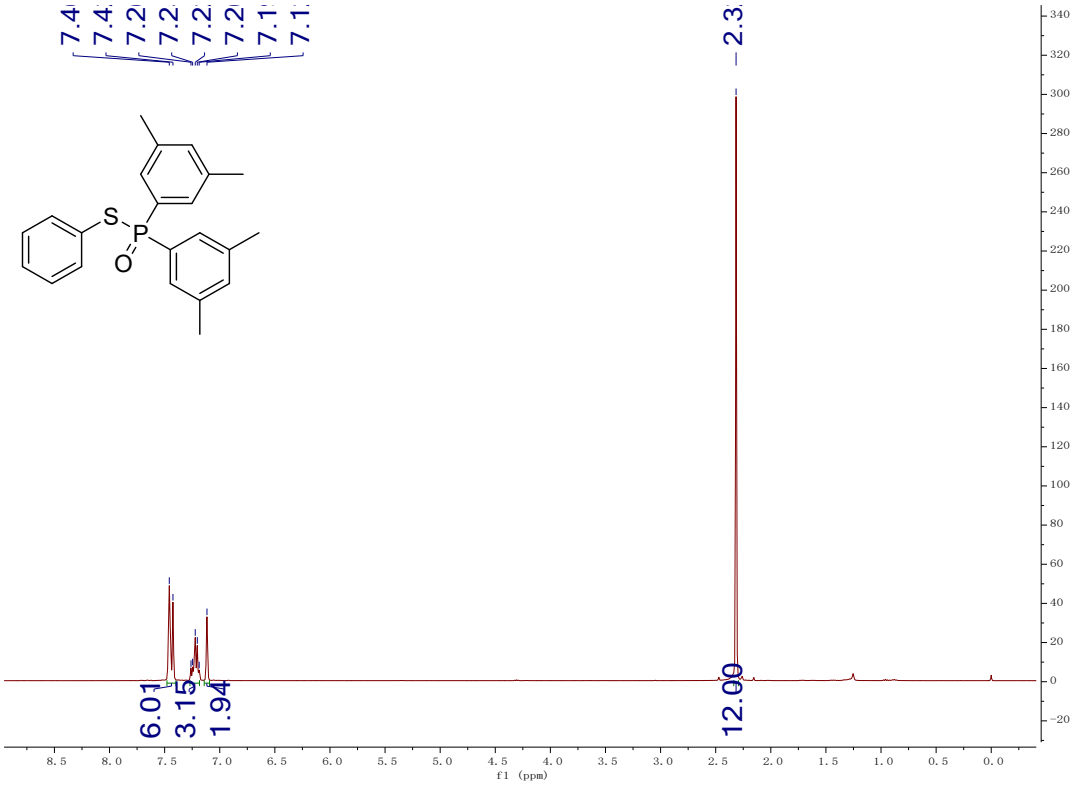
S-phenyl bis(4-methoxyphenyl)phosphinothioate (3s)

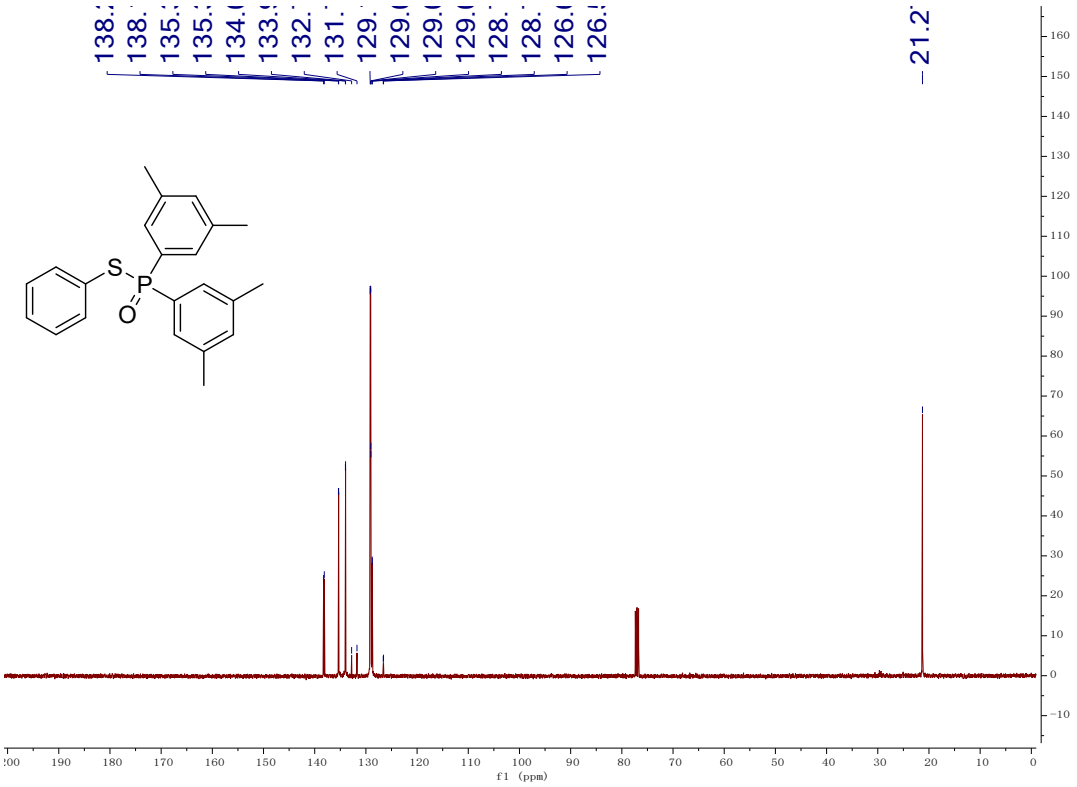


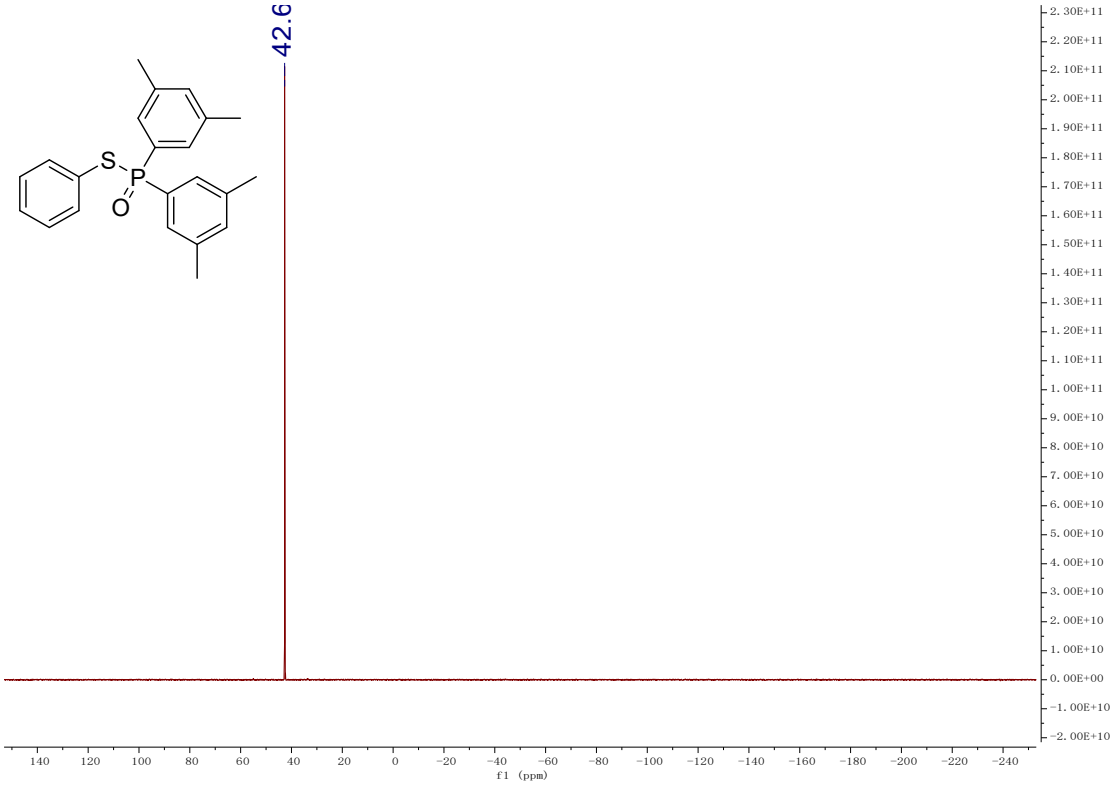

55.3
OMe
OMe
S
P
O
f1 (ppm)


OMe
OMe
S
P
O
f1 (ppm)

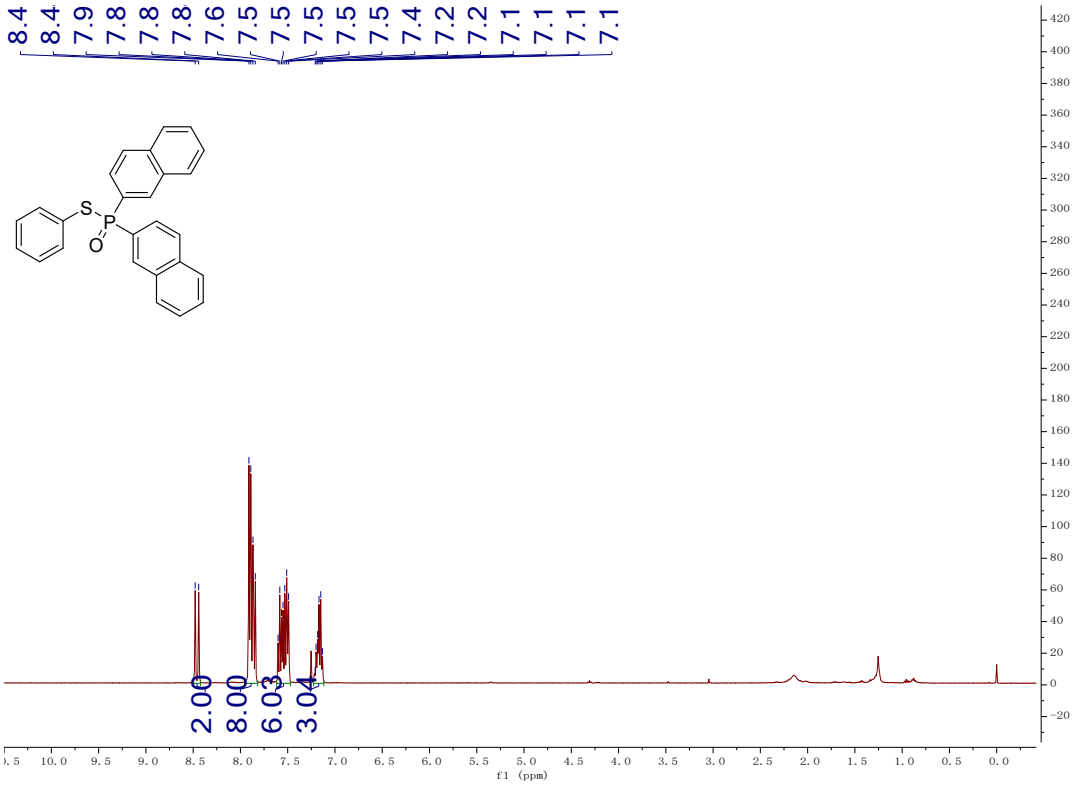
S-phenyl bis(3,5-dimethylphenyl)phosphinothioate (3t)

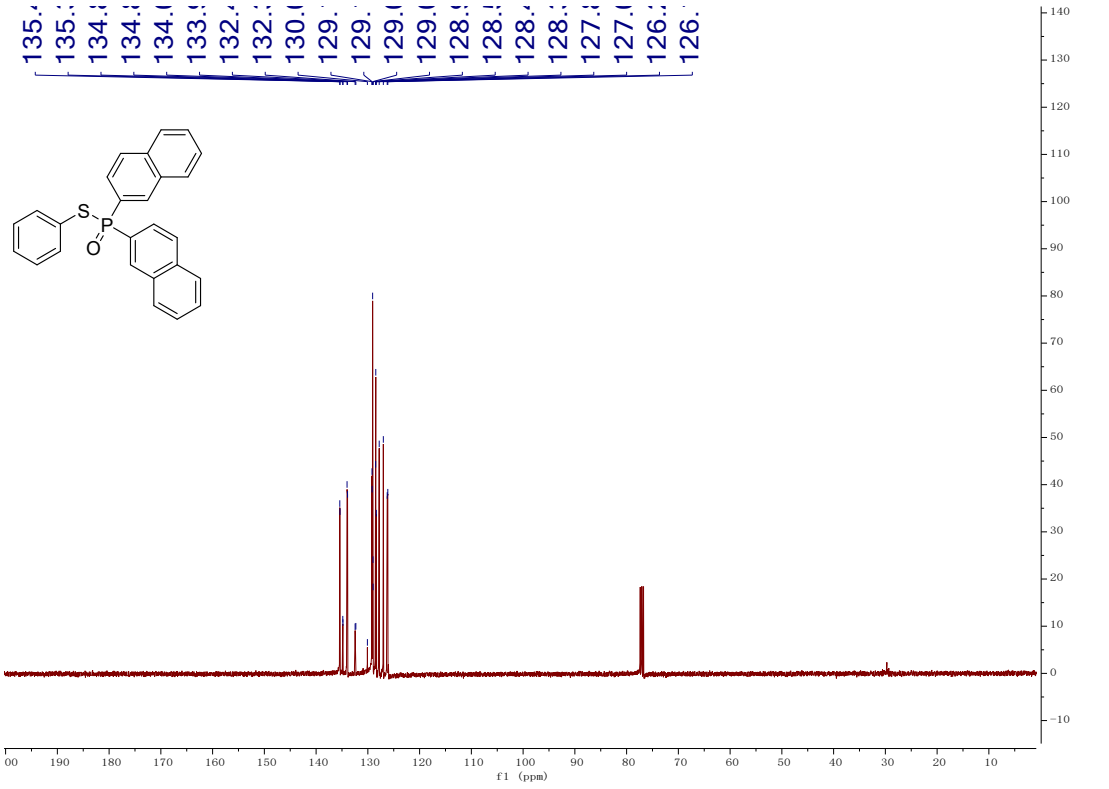


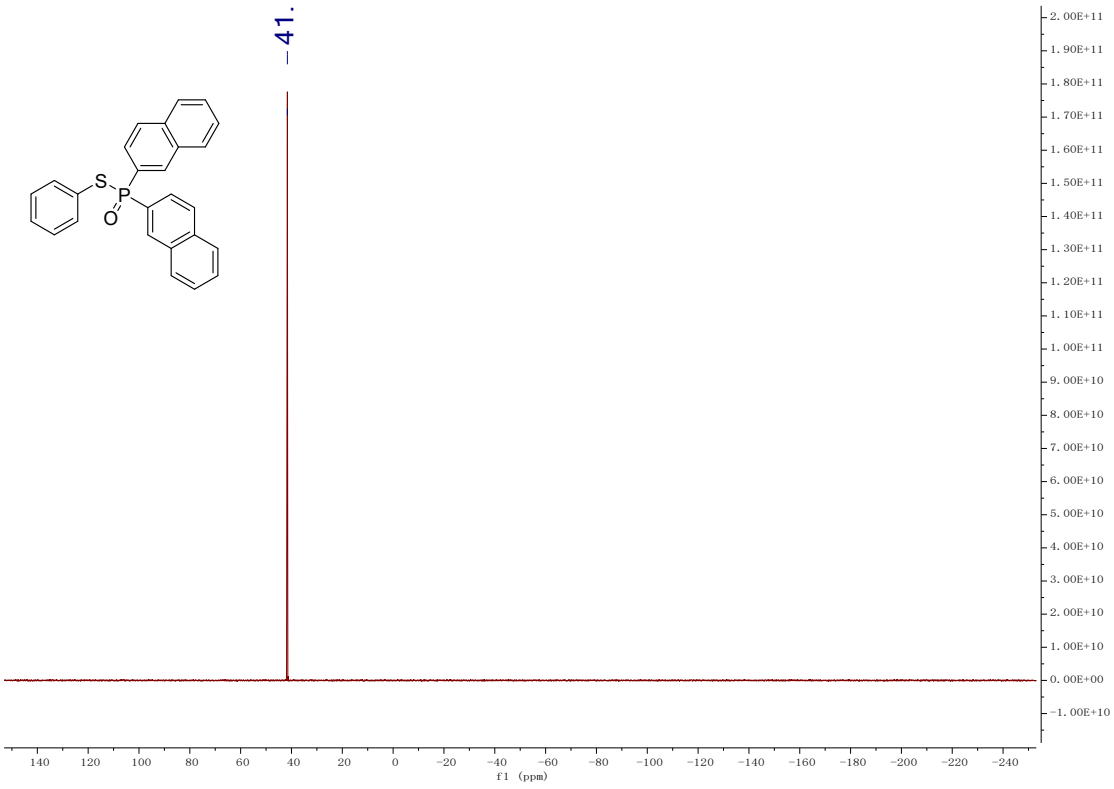




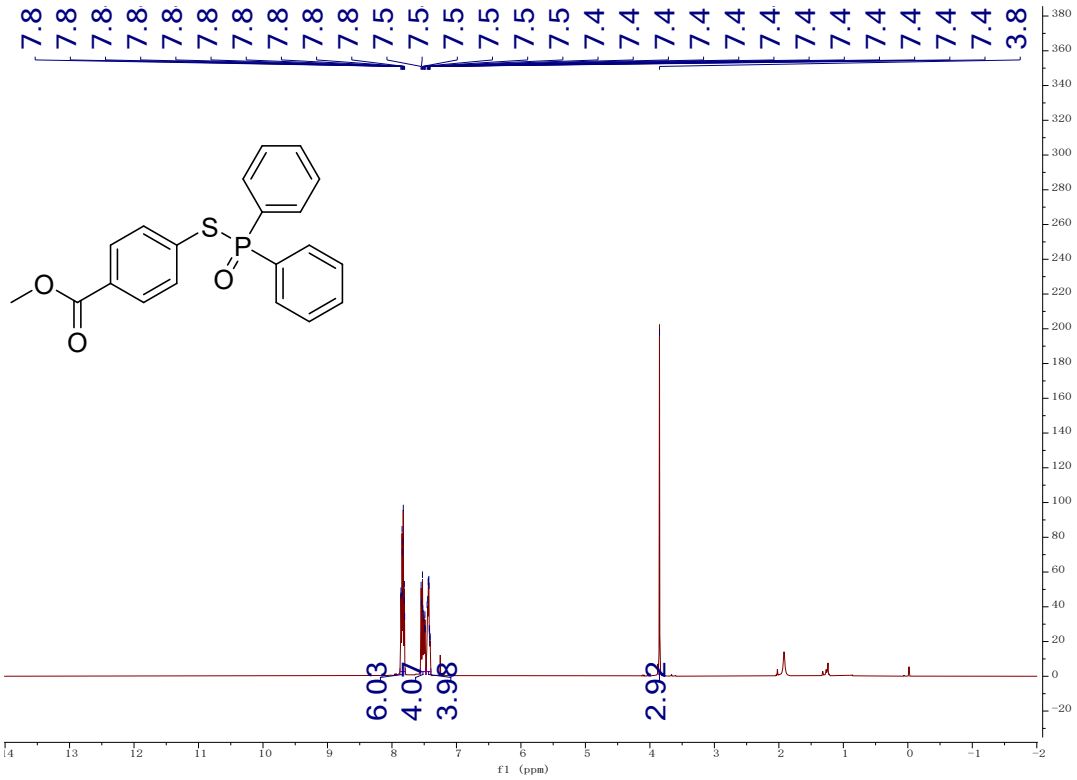
S-phenyl di(naphthalen-2-yl)phosphinothioate (3u)

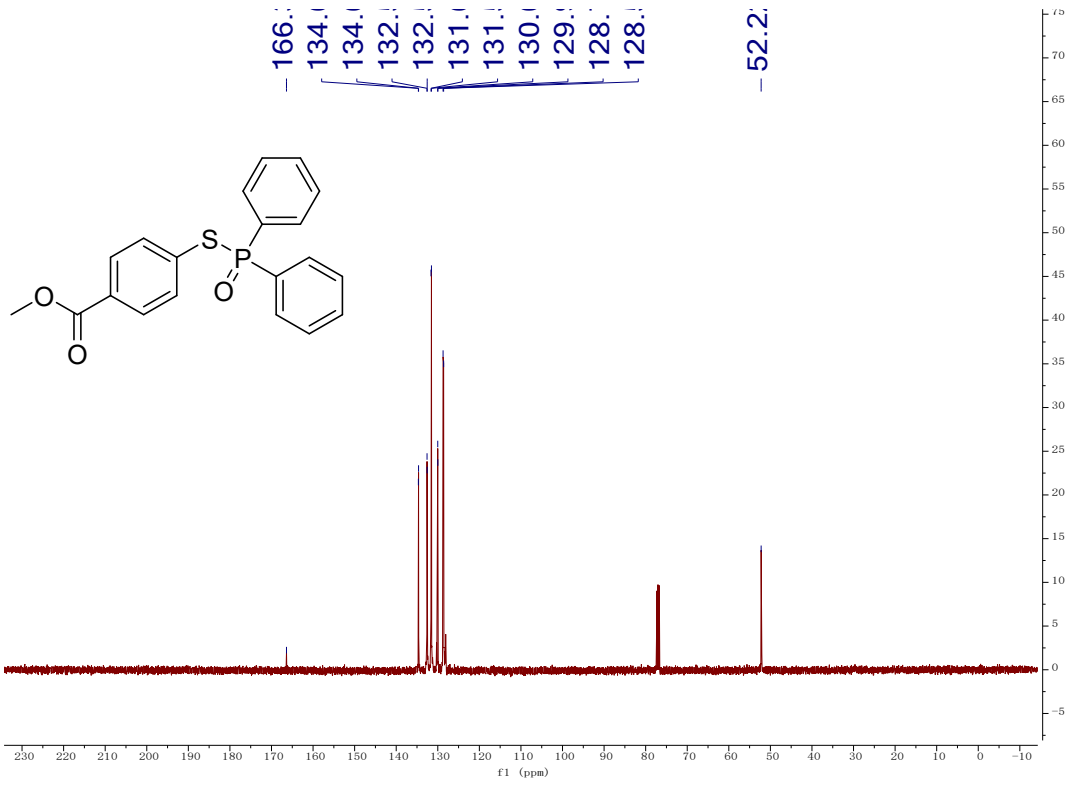


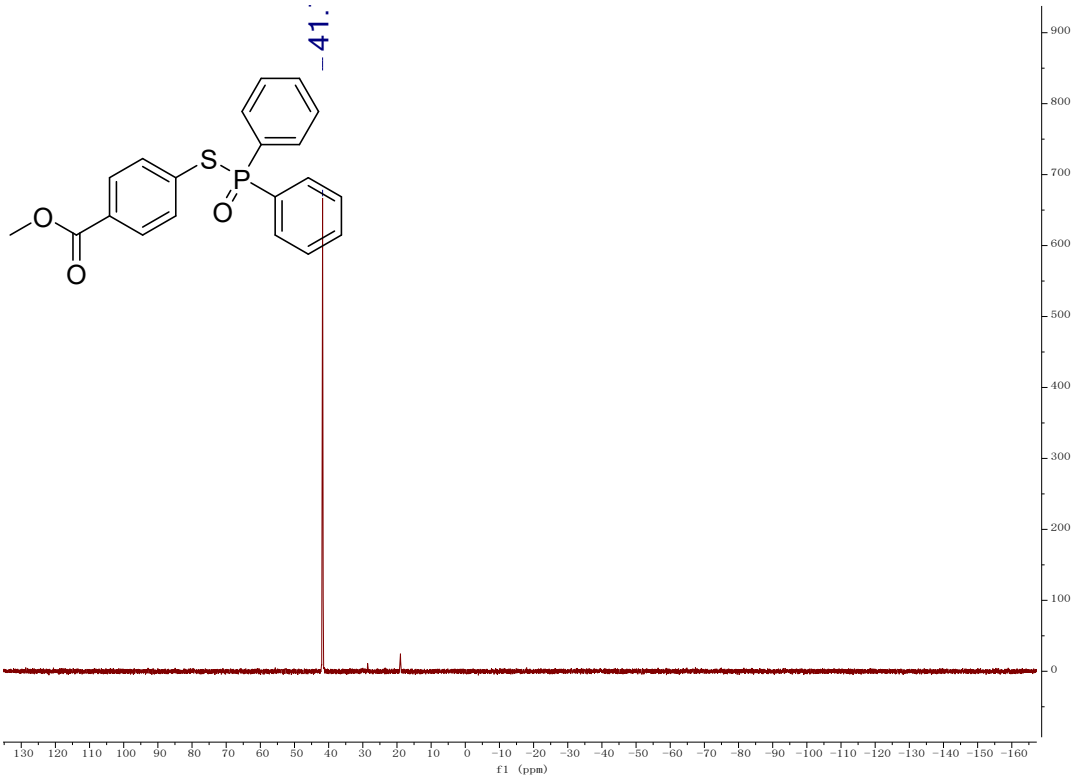

135.
135.
134.
134.
134.
133.
132.
132.
130.
129.
129.
129.
129.
128.
128.
128.
128.
127.
127.
126.
126.
S
P
O
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


41.
S
P
O
2.00E+11
1.90E+11
1.80E+11
1.70E+11
1.60E+11
1.50E+11
1.40E+11
1.30E+11
1.20E+11
1.10E+11
1.00E+11
9.00E+10
8.00E+10
7.00E+10
6.00E+10
5.00E+10
4.00E+10
3.00E+10
2.00E+10
1.00E+10
0.00E+00
−1.00E+10
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240
f1 (ppm)

methyl 4-((diphenylphosphoryl)thio)benzoate (3w)

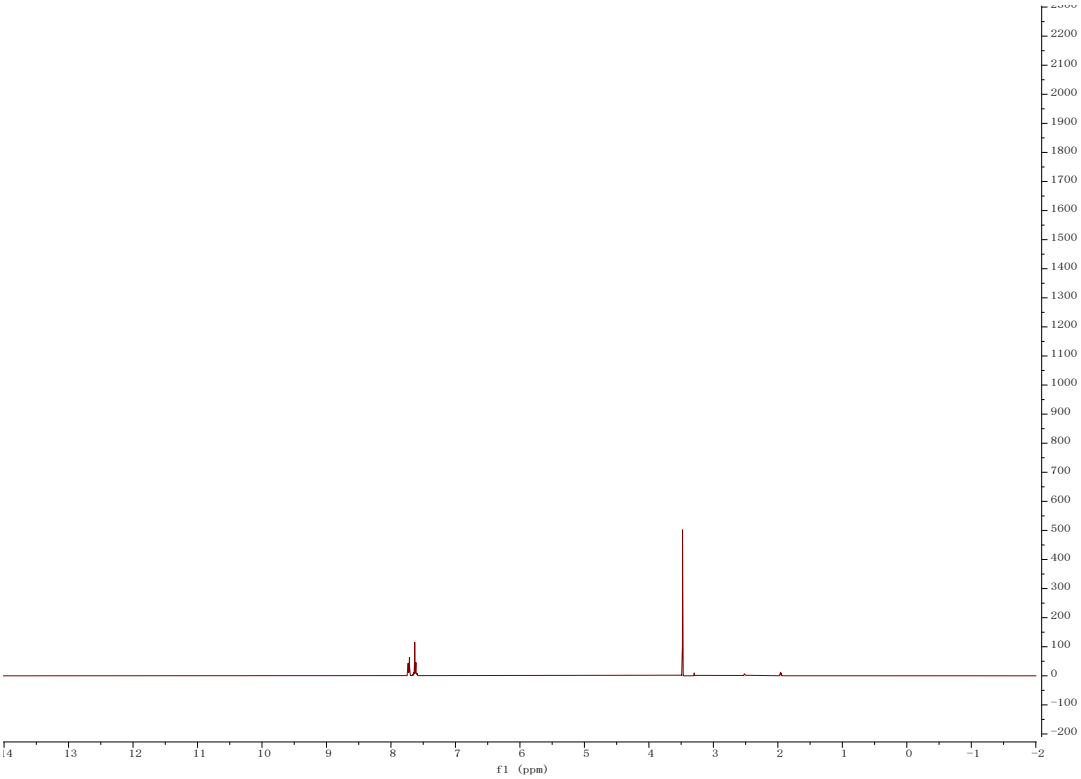




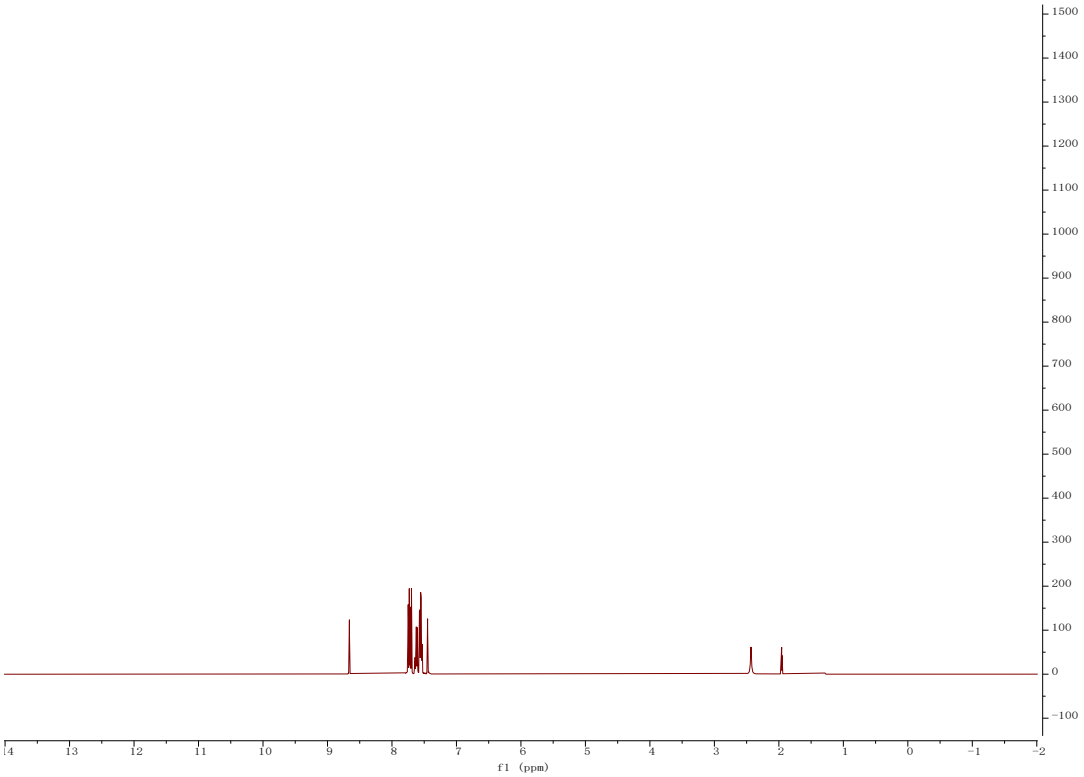


^{1}H NMR track experiments (CD_3CN)

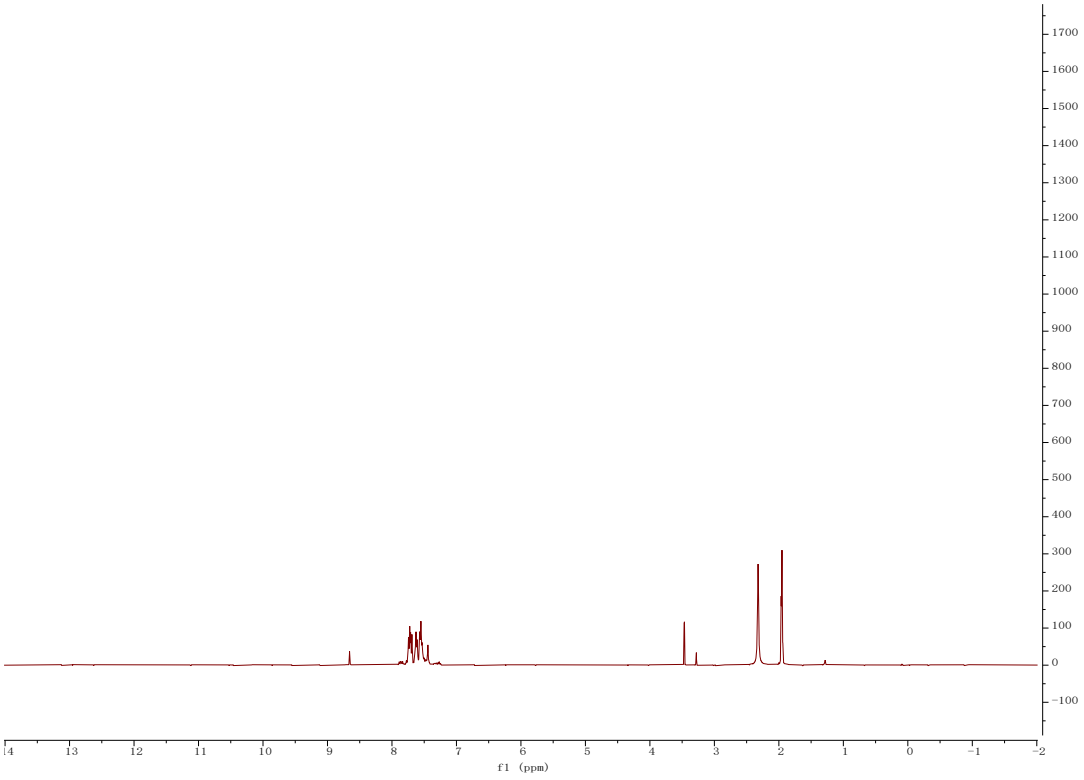
^{1}H NMR of 1a



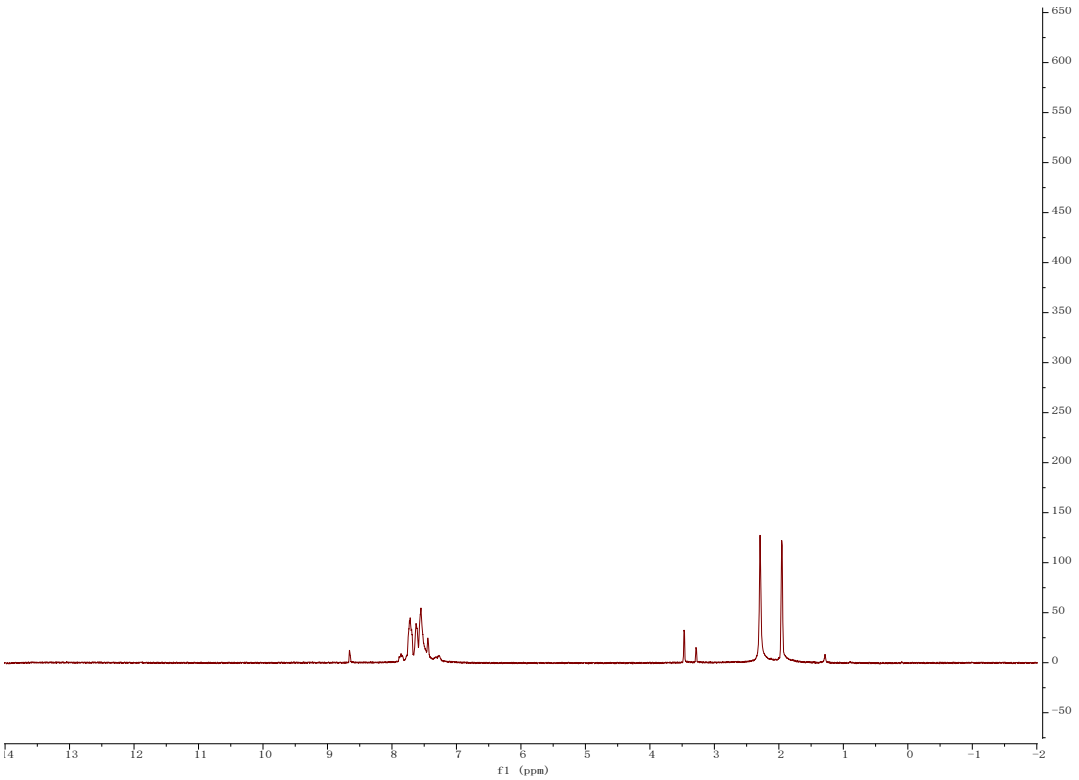
^{1}H NMR of 2a



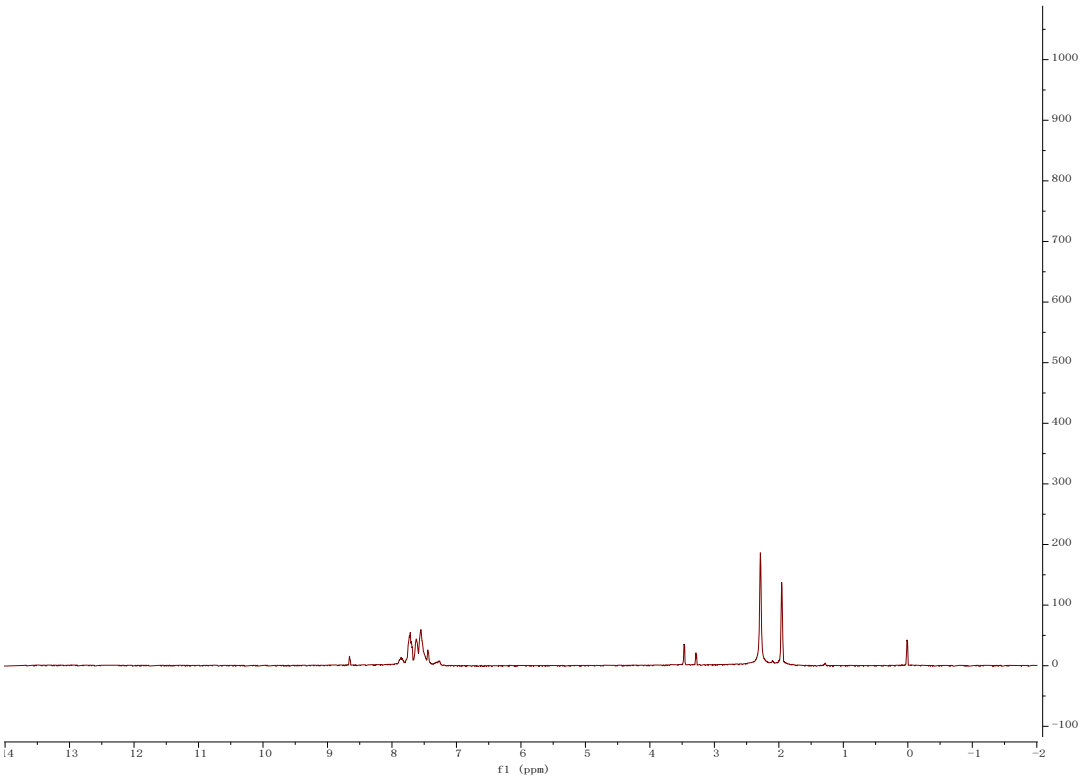
^{1}H NMR of 1a+2a 10min



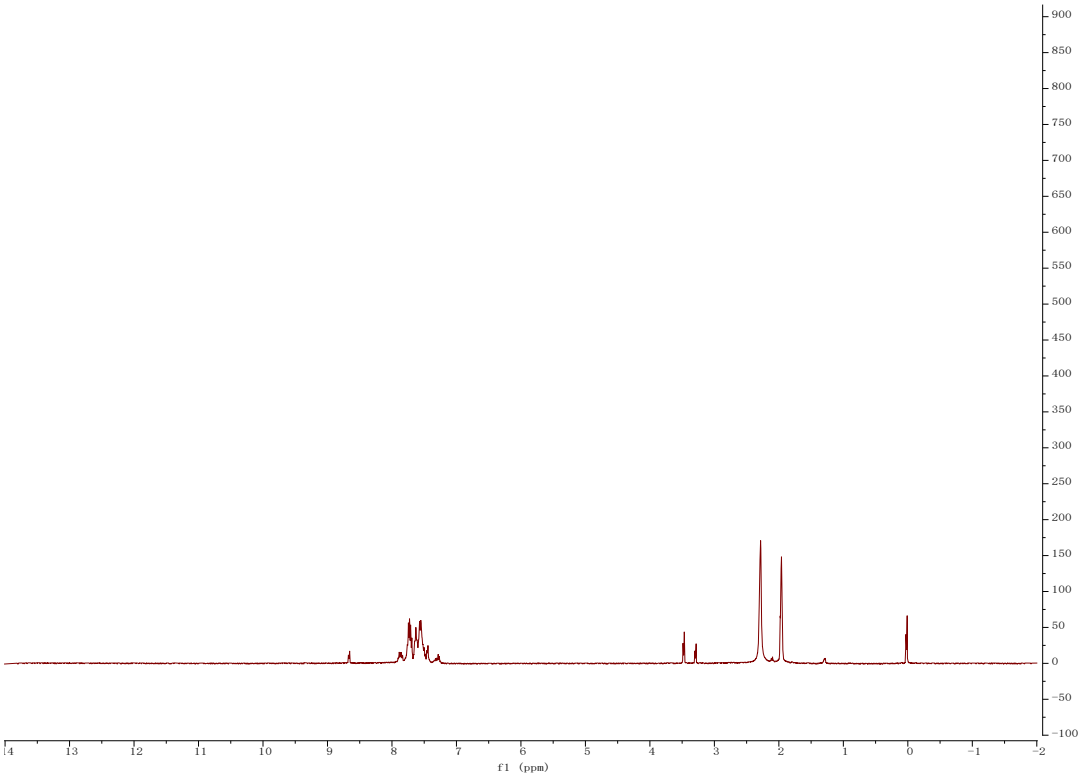
^{1}H NMR of 1a+2a 20min



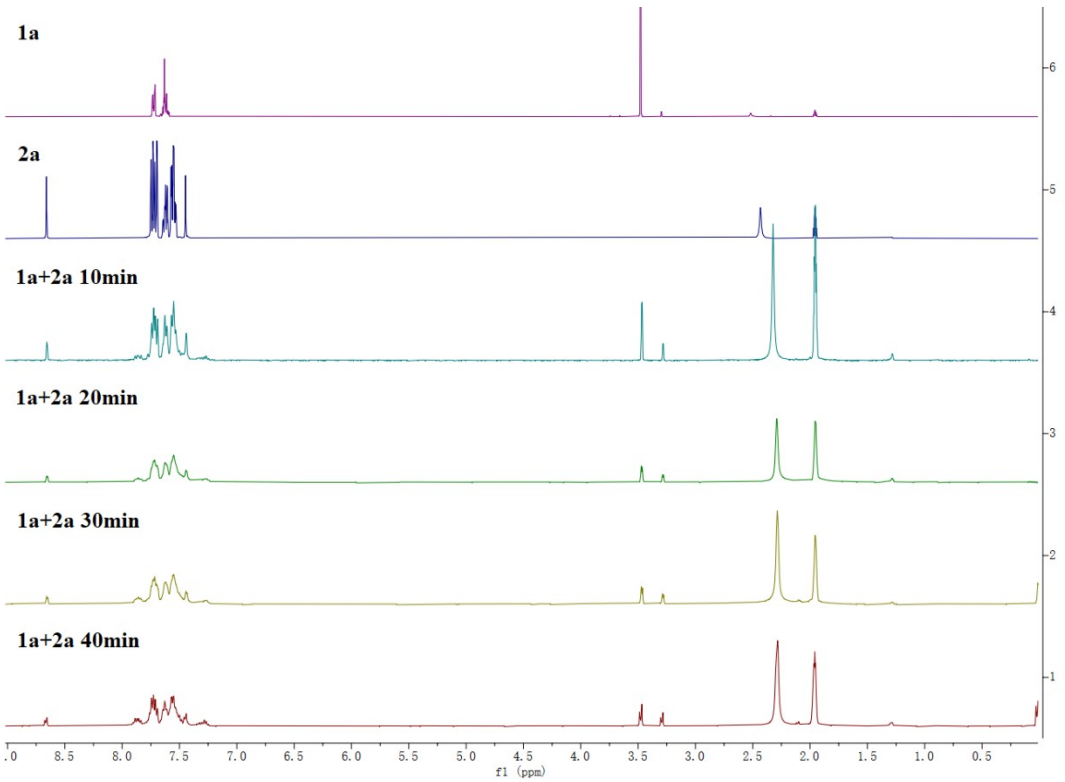
^{1}H NMR of 1a+2a 30 min



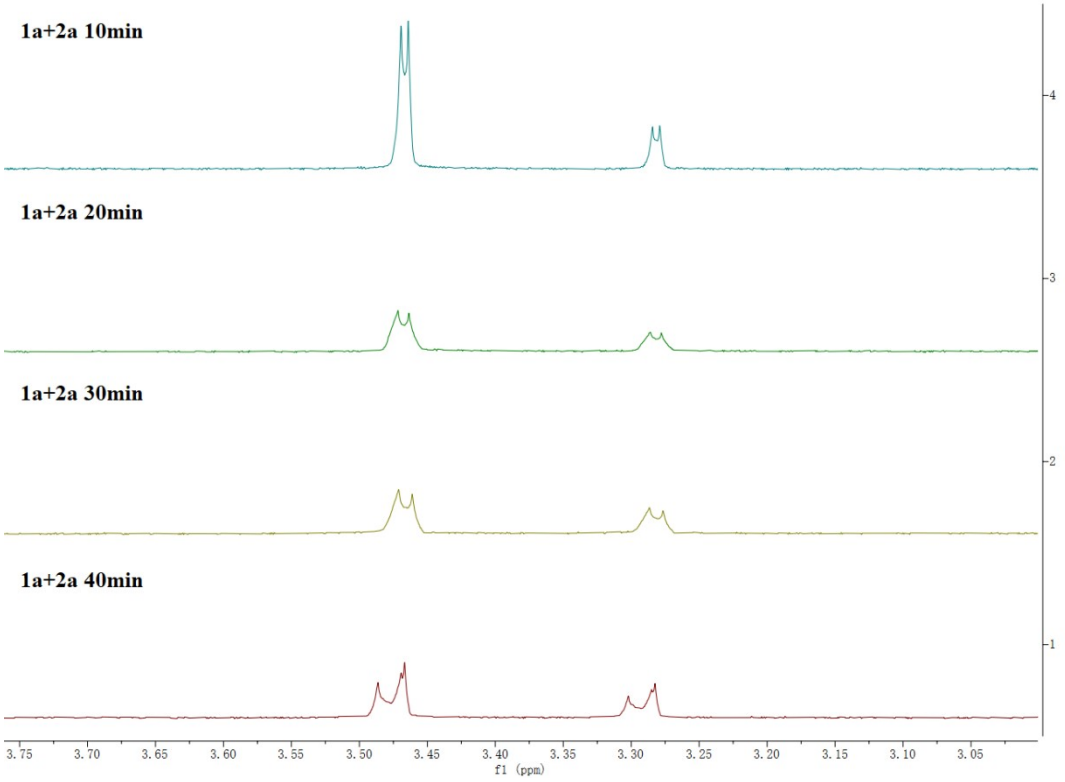
^{1}H NMR of 1a+2a 40 min



^{1}H NMR



^{1}H NMR (3.0-3.75 ppm)



5. Crystal data

Crystal data of 3a

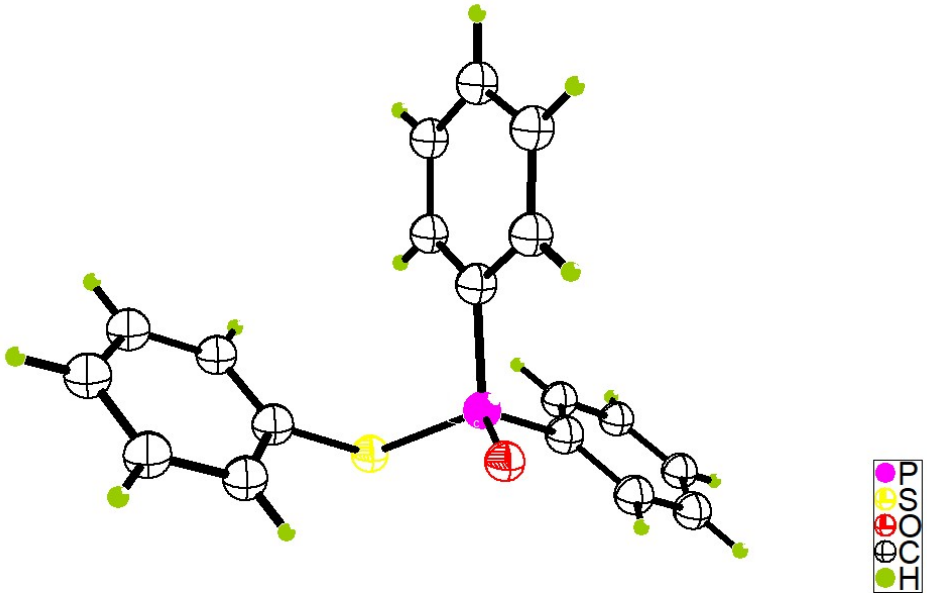


Table 1 Crystal data and structure refinement for 3a.

Identification code	3aa
Empirical formula	$C_{18}H_{15}OPS$
Formula weight	310.33
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	6.190(2)
b/Å	8.426(3)
c/Å	16.517(5)
α/°	100.248(5)
β/°	96.034(5)
γ/°	108.478(5)
Volume/Å^3	791.9(4)
Z	2
ρ_{calc}g/cm^3	1.302
μ/mm^{-1}	0.301
F(000)	324.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.09 to 54.926
Index ranges	-6 ≤ h ≤ 7, -10 ≤ k ≤ 10, -15 ≤ l ≤ 21
Reflections collected	4768
Independent reflections	3428 [R_{int} = 0.0181, R_{sigma} = 0.0341]
Data/restraints/parameters	3428/0/190
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.1047
Final R indexes [all data]	R_1 = 0.0581, wR_2 = 0.1128
Largest diff. peak/hole / e Å^{-3}	0.24/-0.33

CCDC-number: 2184647

Crystal data of Diphenylphosphinic acid

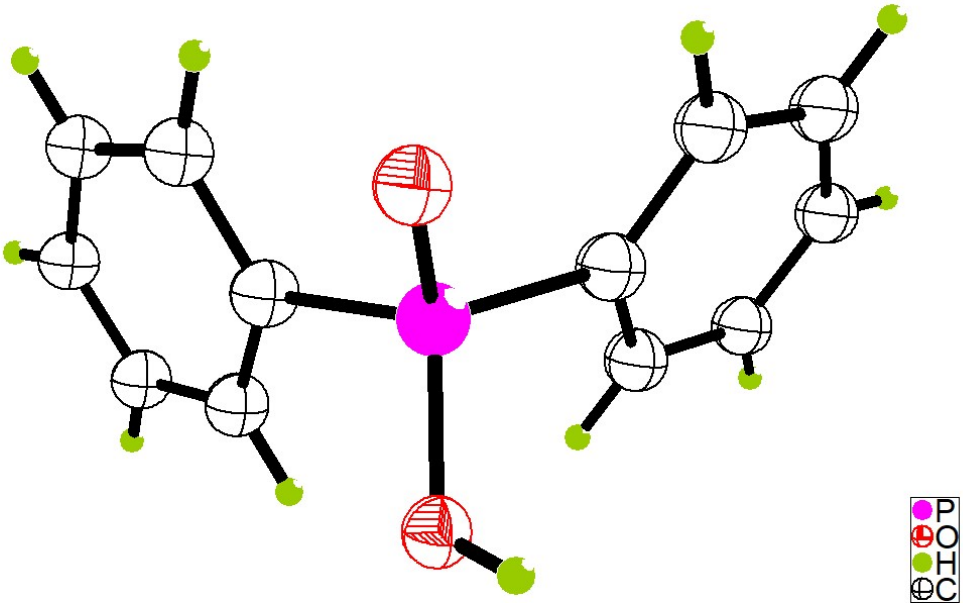


Table 2 Crystal data and structure refinement for Diphenylphosphinic acid.

Identification code	Diphenylphosphinic acid
Empirical formula	$C_{12}H_{11}O_2P$
Formula weight	218.18
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.482(3)
b/Å	6.0814(17)
c/Å	15.777(5)
α/°	90
β/°	99.883(5)
γ/°	90
Volume/Å^3	1085.3(5)
Z	4
ρ_{calc}g/cm^3	1.335
μ/mm^{-1}	0.228
F(000)	456.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.6 to 55.272
Index ranges	$-14 \le h \le 14, 0 \le k \le 7, 0 \le l \le 20$
Reflections collected	2459
Independent reflections	2459 [R_{int} = ?, R_{sigma} = 0.0349]
Data/restraints/parameters	2459/0/138
Goodness-of-fit on F^2	1.083

Final R indexes [I>=2σ (I)]	R_1 = 0.0705, wR_2 = 0.2407
Final R indexes [all data]	R_1 = 0.0841, wR_2 = 0.2568
Largest diff. peak/hole / e Å^{-3}	0.72/-0.35

CCDC-number: 2184646