Supporting Information

A Metal-Free Visible-Light-Promoted Phosphorylation/Cyclization Reaction in Water towards 3-Phosphorylated Benzothiophenes

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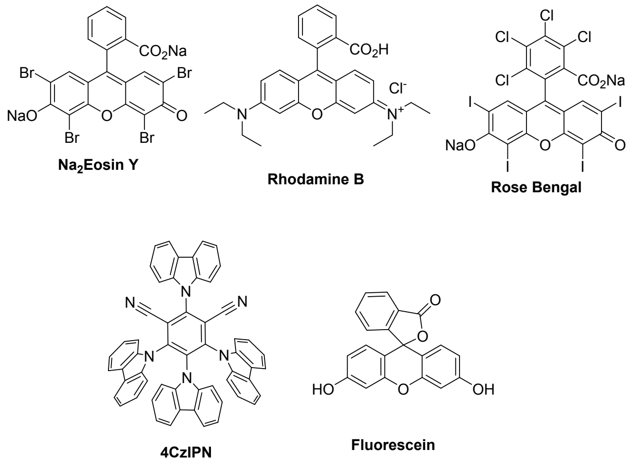
1. General Information

All reagents were purchased from Zhengzhou Alfa chem Co., Ltd. Unless otherwise stated, all commercially available reagents were directly used without further purification. All reactions were monitored by thin layer chromatography (TLC), and column chromatography was carried out on 200-300 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co. All nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz in $CDCl_3$ at room temperature (20 ± 3 °C), using tetramethylsilane as internal standard. High resolution mass spectra (HRMS) were conducted on a 3000-mass spectrometer, using Waters Q-Tof MS/MS system with the ESI technique.

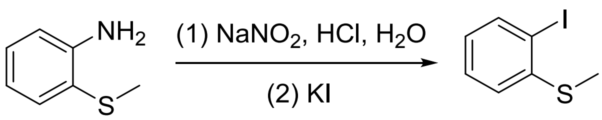


Scheme S1. The structures of photocatalysts used in this work

2. Experimental procedures

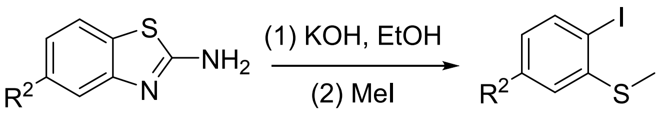
2.1. Preparation of Starting Materials

General experimental procedures for substrates 1a-m[1]



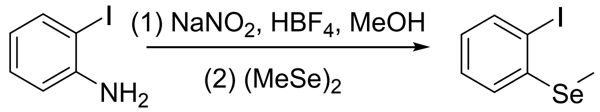
A mixture of 2-(methylthio)aniline (149 mg, 1.5 mmol), aqueous HCl (37%, 0.3 mL) and water (1.3 mL) was cooled to 0 °C. A solution of $NaNO_2$ (113 mg, 1.6 mmol) in water (0.3 mL) was added dropwise and stirred for 10 min. The resulting diazonium salt was treated with a solution of KI (285 mg, 1.7 mmol) in water (0.3 mL). The resulting brown foamy mixture was stirred for 30 min at room temperature and heated at reflux for 15 min. After cooling to ambient temperature, the reaction was diluted with water (10 mL) and neutralized by slow addition of aqueous $Na_2S_2O_3$. The mixture was extracted with dichloromethane (10 mL×2). The combined organic layer was dried over Na_2SO_4, filtered and evaporated in vacuo. The residue was purified by silica gel column chromatography to afford (2-iodophenyl)(methyl)sulfane as colorless oil (260 mg, 81%).

General experimental procedures for substrates 1n-p[1]

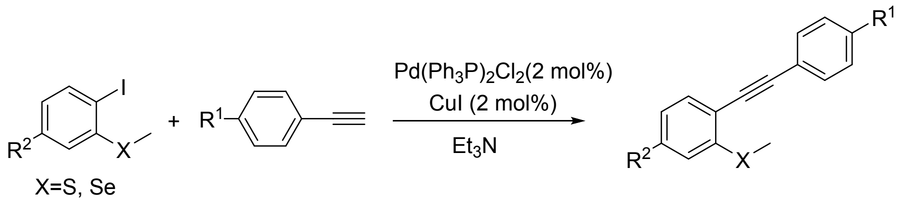


To the stirred solution of KOH (6 g) in 24 mL of water, benzothioazole (3 mmol) was added and refluxed for 17 h. After cooling to room temperature, MeI (3 mmol) was added drop wise and stirring was continued for an additional 1 h. The resultant reaction mixture extracted with diethyl ether (3×25 mL) combined organic layers dried over Na_2SO_4, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate (15:1) as eluent.

General experimental procedures for substrates 1t[1]

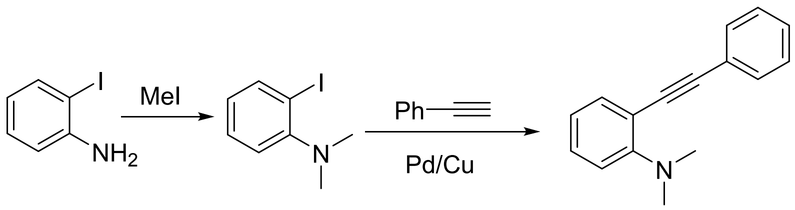


To a stirred solution of methanol (30 mL) and 10 mmol of the 2-iodoaniline, 20 mmol of HBF_4 (3.6 mL, 48% solution) was added dropwise. After the addition was complete, the solution was allowed to cool to 0 °C. To this solution an aqueous solution of $NaNO_2$ (12 mmol in 5 mL of water) was added dropwise to the reaction mixture, which turned a pale yellow to red brown. The mixture was allowed to warm to room temperature and methanol was removed under vacuum at room temperature. The mixture was filtered and washed with cold methanol. The diazonium salt was dried under vacuum and used for the next step without purification. A suspension of 8 mmol of the crude diazonium salt in 25 mL of $CHCl_3$ containing 10 mol% of 18-crown-6 and 9 mmol of dimethyl diselenide was stirred at 0 °C. To this mixture, 16 mmol of KOAc was added in small portions over a period of 10 min and the resulting solution was allowed to stir for 4 h and then filtered. The solid residue was washed with chloroform and the resulting filtrate was washed with water (2×5 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product obtained was then purified by flash chromatography on silica gel using ethyl acetate/hexanes as the eluent.



To a solution of (2-iodophenyl)(methyl)sulfane (5 mmol), CuI (2 mol %), and $Pd(Ph_3P)_2Cl_2$ (2 mol%) in triethylamine (100 mL) was added drop-wise an alkyne (6 mmol) under N_2. The reaction mixture was stirred for 5-10 h at room temperature. Upon completion, the mixture was diluted with diethyl ether and then washed with water and brine successively. The organic phase was dried with anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified through silica gel flash chromatography to give the desired product in mostly > 90% yield.

Synthesis of N,N-dimethyl-2-iodoaniline[2]

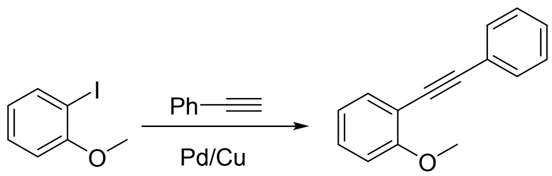


2-Iodoaniline (2.19 g, 10 mmol), K_2CO_3 (3.45 g, 25 mmol) and iodomethane (1.87 mL, 30 mmol) in 10 mL CH_3CN were stirred under reflux for 12 h. When the reaction was done, the mixture was treated with water (50 mL), extracted with DCM (2×30 mL). The organic phase was dried over anhydrous magnesium sulfate and filtered. The solvents were evaporated and the residue purified by silica gel column chromatography eluting with Hexane/EtOAc (19:1) yielding *N*,*N*-dimethyl-2-iodoaniline (2.37 g, 96%).

Synthesis of N,*N*-dimethyl-2-((trimethylsilyl)ethynyl)aniline[2]

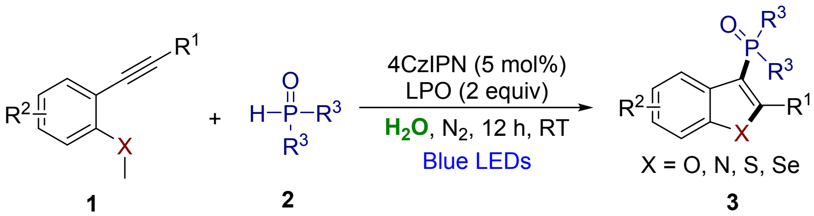
To a stirred solution of N,*N*-dimethyl-2-iodoaniline (2.47 g, 10 mmol) in 5 mL DMF were added triethylamine (1.4 mL, 10 mmol), bis(triphenylphosphine)palladium(II) dichloride (70.1 mg, 0.1 mmol), CuI (57 mg, 0.3 mmol), and (trimethylsilyl)acetylene (11-15 mmol), under N_2 atmosphere. When the reaction was done, the mixture treated with saturated aqueous ammonium chloride solution (50 mL) and extracted with diethyl ether (50 mL). The organic phase was dried over anhydrous magnesium sulfate and filtered. The solvents were evaporated and the residue purified by silica gel column chromatography eluting with Hexane/Diethyl ether (100:1) yielding *N*,*N*-dimethyl-2-((trimethylsilyl)ethynyl)aniline (1.96 g, 90%).

General procedure for synthesis of 1-methoxy-2-(phenylethynyl)benzene[3]



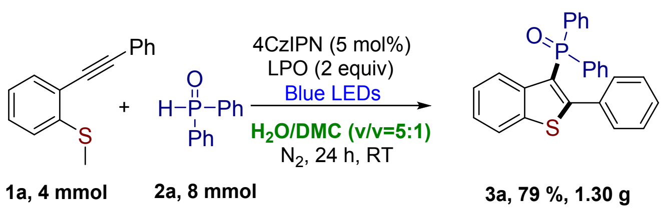
To a solution of *2*-iodothioanisole (5.0 mmol, 1.3 g), $PdCl_2(PPh_3)_2$ (2.0 mol%, 70 mg), and CuI (1.0 mol%, 10 mg) in Et_3N (20 mL) (stirring for 5 min) was added dropwise terminal alkyne (1.2 equiv) in 5.0 mL of Et_3N over 10 min. The reaction flask was flushed with Ar and the mixture was stirred at room temperature for 2 h. The resulting solution was diluted with EtOAc, filtered through a pad of celite. The solution was washed with brine. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to give 1-methoxy-2-(phenylethynyl)benzene (1.04g, 100%).

2.2. General Procedures for the Synthesis of 3-Phosphorylated Benzothiophenes



The mixture of **1** (0.4 mmol), diarylphosphine oxide **2** (0.8 mmol), LPO (2 equiv) and 4CzIPN (5 mol%) were combined in H_2O (3 mL) at room temperature for 12 h in a nitrogen atmosphere. After the reaction, the solution was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1 to 5/1) to give the desired products **3**.

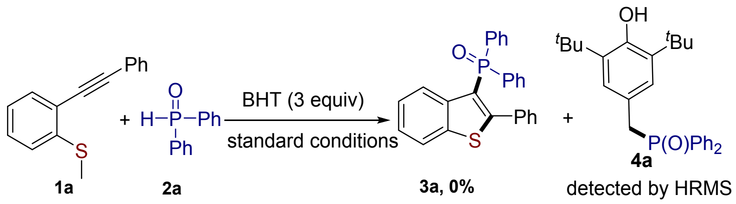
2.3. Gram scale synthesis



Dimethyl carbonate (DMC) was used as the cosolvent to enhance the solubility of reactants.

The mixture of methyl(2-(phenylethynyl) phenyl) sulfane **1a** (4 mmol), diphenylphosphine oxide **2a** (8 mmol), LPO (2 equiv) and 4CzIPN (5 mol%) were combined in H_2O/DMC (v/v = 5:1) (60 mL) under the irradiation of blue light at room temperature for 24 h in a nitrogen atmosphere. After the reaction, the solution was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1 to 5/1) to give the desired product **3a**.

3. Control experiment performed with BHT



A mixture of **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2 equiv), LPO (2 equiv), 4CzIPN (5 mol%) and BHT (3 equiv) were sequentially added in a 10-mL reaction vial. Then, H_2O (3 mL) was added into this reaction system. The reaction vial was sealed under N_2 and stirred under the irradiation of blue LEDs at room temperature for 12 h. After the reaction, the reaction mixture was analyzed by HRMS, and product **4a** was successfully detected (Figure S1). HRMS calc. for $C_{27}H_{34}O_2P^+$ (**4a**) m/z = 421.2291 found 421.2288

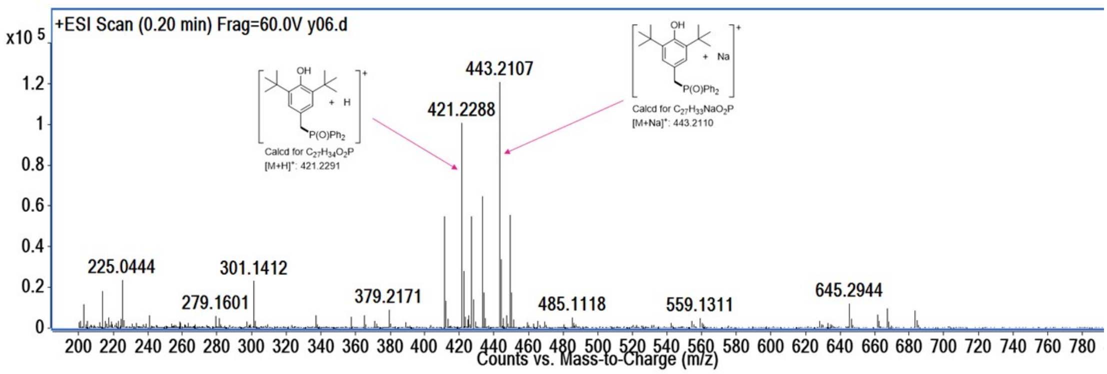
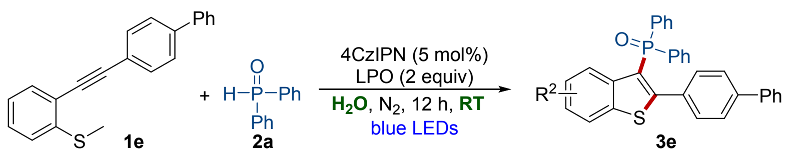


Figure S1. HRMS spectrum of compound **4a**

4. ^{31}P NMR monitored reaction

The reaction of **1e** and **2a** was conducted under the standard conditions, which was monitored by ^{31}P NMR every 2 h. The results showed that with the increase of time, the peak area of **2a** gradually decreased along with the product **3a** peak gradually increased (Figure S2a). Then the yield/time profile of the generation of **3e** was calculated based on area normalization as shown in Figure S2b. Unfortunately, the signals of P-containing intermediates were not observed.



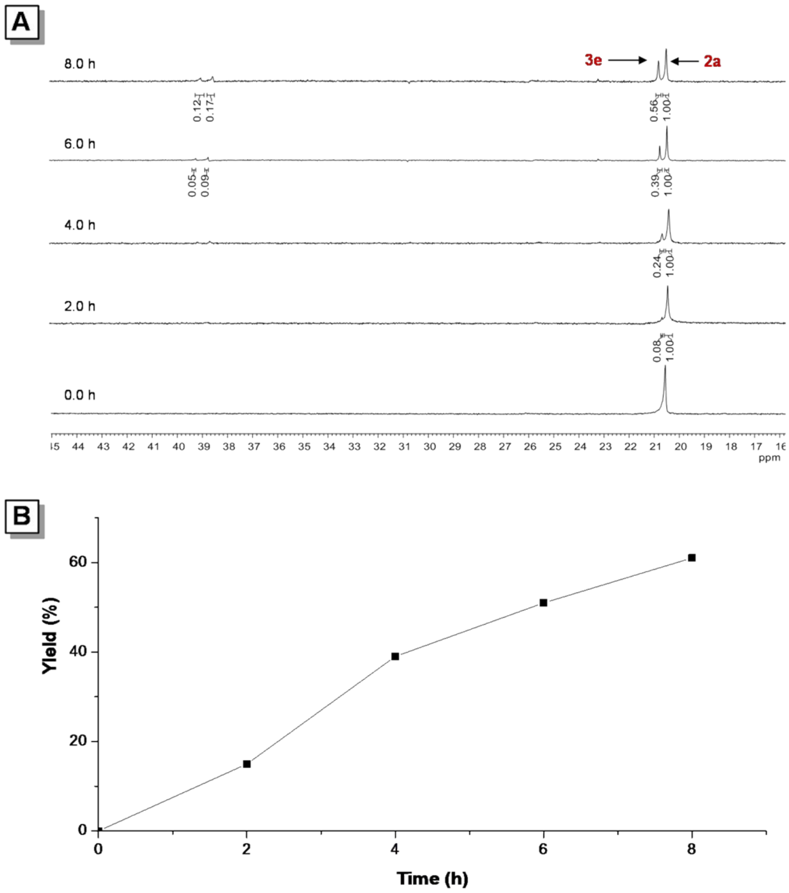


Figure S2. (a) The reaction time course monitored by ^{31}P NMR; (b) The yield/time profile of the generation of **3e**

5. Procedure for emission quenching experiments

Emission intensities were recorded using a F-4600 FL Spectrophotometer. First, the emission intensity of 4CzIPN solutions was observed at 550 nm. The solutions were irradiated at 378 nm and fluorescence was measured from 530 nm to 700 nm. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of 4CzIPN and different concentration of methyl(2-(phenylethynyl) phenyl)sulfane **1a**, phosphine oxides **2a** and LPO in degassed anhydrous CH_3CN in 10 mm path length quartz cuvette was collected.

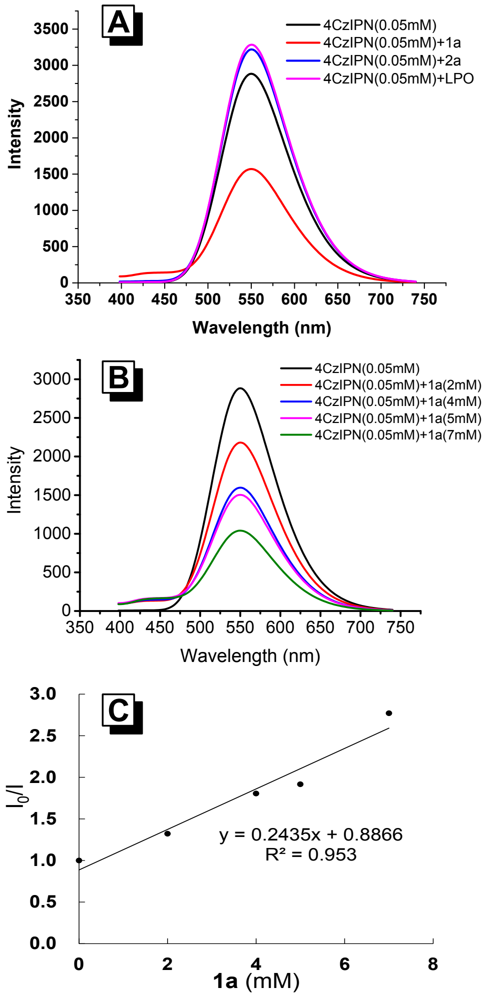
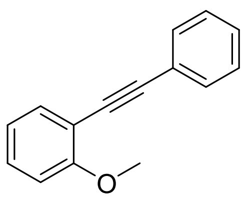


Figure S3. (a) The emission spectra of a 5 × 10^{-5} M solution of 4CzIPN with various reactants in degassed anhydrous CH_3CN excited at 550 nm; (b) The emission spectra of a 5 × 10^{-5} M solution of 4CzIPN with various concentrations of **1a** in degassed anhydrous CH_3CN excited at 550 nm; (c) The linear relationship between I_0/I (I_0 and I are the fluorescence intensities before and after the increasing the concentration of **1a**, respectively) and the increasing concentration of **1a**.

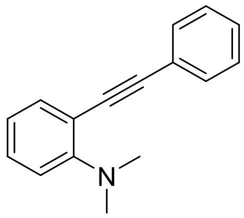
6. Characterization Data for Products

1-methoxy-2-(phenylethynyl)benzene[3]



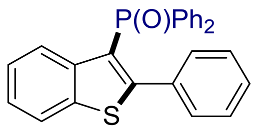
984 mg; 94% yield; yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.6 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.5 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.4 (t, *J* = 7.2 Hz, 4H), 7.0 – 6.9 (m, 2H), 3.9 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 133.6, 131.7, 129.9, 128.4, 128.2, 123.7, 120.6, 112.5, 110.8, 93.5, 85.9, 55.9.

N,N-dimethyl-2-(phenylethynyl)aniline[2]



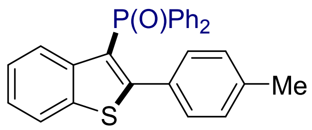
964 mg; 88% yield; yellow liquid;^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.6 – 7.5 (m, 3H), 7.4 – 7.2 (m, 4H), 7.0 – 6.9 (m, 2H), 3.0 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.8, 134.4, 131.4, 129.3, 128.4, 128.1, 124.0, 120.5, 117.0, 115.1, 94.8, 89.1, 43.6.

Diphenyl(2-phenylbenzo[b]thiophen-3-yl) phosphine oxide ***(3a)***[4]



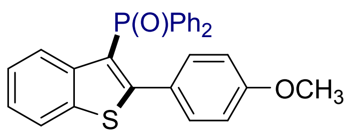
148 mg, 90%; white solid, m. p. 169.4-171.9 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.58 (m, 4H), 7.36 (m, 3H), 7.26 (m, 5H), 7.16 (d, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.7 Hz, 2H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.9 (d, *J* = 12.9 Hz), 141.4 (d, *J* = 13.0 Hz), 139.4 (d, *J* = 12.7 Hz), 133.9, 132.9, 132.9 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 10.1 Hz), 131.5 (d, *J* = 2.9 Hz), 129.9, 128.4, 128.3 (d, *J* = 12.5 Hz), 127.6, 126.0, 124.9 (d, *J* = 4.4 Hz), 122.8 (d, *J* = 105.4 Hz), 121.5.^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.5.

Diphenyl(2-(p-tolyl) benzo[b]thiophen-3-yl)phosphine oxide ***(3b)***[4]



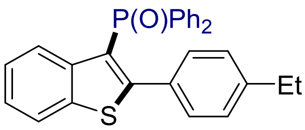
156 mg, 94%; white solid, m. p. 198.2-200.7 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.9 (d, *J* = 8.3 Hz, 1H), 7.9 (d, *J* = 8.0 Hz, 1H), 7.6 – 7.5 (m, 4H), 7.4 – 7.3 (m, 3H), 7.2 (m, 5H), 7.0 (d, *J* = 8.0 Hz, 2H), 6.8 (d, *J* = 7.8 Hz, 2H), 2.2 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.1 (d, *J* = 12.8 Hz), 141.5 (d, *J* = 12.9 Hz), 139.4 (d, *J* = 12.6 Hz), 138.4, 134.1, 133.1, 131.7 (d, *J* = 10.2 Hz), 131.2 (d, *J* = 2.9 Hz), 129.9 (d, *J* = 2.9 Hz), 129.8, 128.3, 128.2 (d, *J* = 4.1 Hz), 125.9, 124.8 (d, *J* = 8.3 Hz), 122.8 (d, *J* = 104.5 Hz), 121.5 21.2. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.7.

(2-(4-methoxyphenyl)benzo[b]thiophen-3-yl)diphenylphosphine oxide ***(3c)***[4]



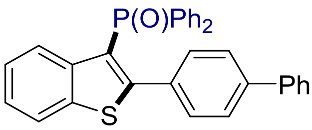
111 mg; 63%; white solid; m. p. 159.4-162.7 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (t, *J* = 7.1 Hz, 2H), 7.61 – 7.54 (m, 4H), 7.37 (m, 3H), 7.27 (m, 5H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.51 (d, *J* = 8.7 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.7, 155.1 (d, *J* = 13.0 Hz), 141.5 (d, *J* = 13.0 Hz), 139.3 (d, *J* = 12.8 Hz), 134.2, 133.2, 131.7, 131.6, 131.3 (d, *J* = 2.9 Hz), 131.2, 128.3 (d, *J* = 12.4 Hz), 125.8, 125.1 (d, *J* = 3.0 Hz), 124.8 (d, *J* = 9.1 Hz), 122.5 (d, *J* = 104.9 Hz), 121.5, 55.3.^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.5.

*(2-(4-ethylphenyl)benzo[b]thiophen-3-yl)diphenylphosphine oxide (**3d**)*[4]



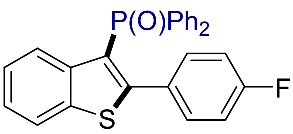
128 mg; 73%; white solid; m. p. 203.1-204.0 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.51 (m, 4H), 7.38 – 7.31 (m, 3H), 7.27 – 7.19 (m, 5H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 8.1 Hz, 2H), 2.52 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.1 (d, *J* = 13.1 Hz), 144.5, 141.5 (d, *J* = 12.8 Hz), 139.4 (d, *J* = 12.6 Hz), 134.1, 133.0, 131.7 (d, *J* = 10.2 Hz), 131.3 (d, *J* = 2.8 Hz), 130.1 (d, *J* = 2.8 Hz), 129.9, 128.2 (d, *J* = 12.5 Hz), 127.1, 125.9, 124.8 (d, *J* = 7.5 Hz), 122.6 (d, *J* = 104.6 Hz), 121.4, 28.6, 15.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.7.

*(2-(4-ethylphenyl)benzo[b]thiophen-3-yl)diphenylphosphine oxide (**3e**)*[4]



163 mg; 84%; yellow solid; m. p. 210.6-211.4 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.60 (dd, *J* = 12.3, 7.5 Hz, 4H), 7.48 (d, *J* = 3.4 Hz, 4H), 7.38 (m, 4H), 7.32 – 7.13 (m, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.4 (d, *J* = 12.8 Hz), 141.4 (d, *J* = 12.8 Hz), 141.2, 140.4, 139.4 (d, *J* = 12.7 Hz), 134.0, 132.9, 131.8, 131.7, 131.4 (d, *J* = 2.9 Hz), 130.4, 128.9, 128.3 (d, *J* = 12.5 Hz), 127.6, 127.0, 126.3, 126.0, 125.0 (d, *J* = 2.7 Hz), 123.2 (d, *J* = 104.5 Hz), 121.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.7.

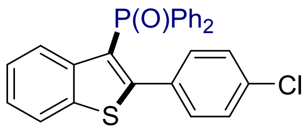
*(2-(4-fluorophenyl)benzo[b]thiophen-3-yl)diphenylphosphine oxide (**3f**)*[4]



153 mg; 89%; white solid; m. p. 186.7-187.8 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (t, *J* = 7.8 Hz, 2H), 7.57 (dd, *J* = 12.4, 8.3 Hz, 4H), 7.43 – 7.32 (m, 3H), 7.27 (m, 5H), 7.16 (m, 2H), 6.68 (t, *J* = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.7 (d, *J* = 249.1 Hz), 153.6 (d, *J* = 12.8 Hz), 141.3 (d, *J* = 12.8 Hz), 139.3 (d, *J* = 12.5 Hz), 133.9, 132.9, 131.7 (d, *J* = 24.5 Hz), 131.6 (d, *J* = 10.9

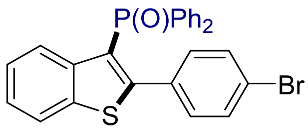
Hz), 128.9, 128.4 (d, *J* = 12.5 Hz), 125.9, 125.0, 123.5 (d, *J* = 103.7 Hz), 121.5, 114.6 (d, *J* = 22.0 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.29. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.6.

*(2-(4-chlorophenyl)benzo[b]thiophen-3-yl)diphenylphosphine oxide (**3g**)*[4]



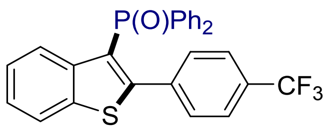
144 mg; 81%; white solid; m. p.216.9-218.1 ℃ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 12.9, 8.2 Hz, 2H), 7.60 – 7.52 (m, 4H), 7.47 – 7.41 (m, 2H), 7.36 (t, 1H), 7.25 (m,5 H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.2 (d, *J* = 12.5 Hz), 141.2 (d, *J* = 12.6 Hz), 139.4 (d, *J* = 12.6 Hz), 134.8, 133.8, 132.8, 131.7 (d, *J* = 10.2 Hz), 131.6 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 2.9 Hz), 131.2, 128.4 (d, *J* = 12.5 Hz), 127.7, 126.0, 125.1 (d, *J* = 2.5 Hz), 123.8 (d, *J* = 103.6 Hz), 121.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.4.

*(2-(4-bromophenyl)benzo[b]thiophen-3-yl)diphenylphosphine oxide (**3h**)*[4]



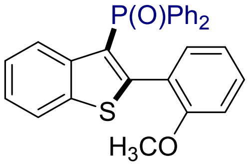
159 mg; 81%; white solid; m. p. 240.6-241.9 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.56 (dd, *J* = 12.5, 7.5 Hz, 4H), 7.48 – 7.40 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.28 (m, 5H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.1 (d, *J* = 12.5 Hz), 141.2 (d, *J* = 12.7 Hz), 139.4 (d, *J* = 12.6 Hz), 133.8, 132.7, 131.8 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 10.2 Hz), 131.6 (d, *J* = 2.9 Hz), 131.4, 130.7, 128.4 (d, *J* = 12.5 Hz), 126.0, 125.1 (d, *J* = 2.9 Hz), 123.8 (d, *J* = 103.4 Hz), 123.1, 121.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.5.

*Diphenyl(2-(4-(trifluoromethyl)phenyl)benzo[b]thiophen-3-yl)phosphine oxide (**3i**)*[4]



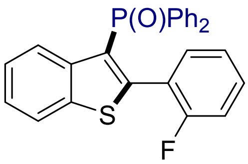
115 mg; 60%; white solid; m. p. 210.2-212.5 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.52 (m, 4H), 7.43 – 7.36 (m, 3H), 7.32 – 7.22 (m, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.3 (d, *J* = 12.4 Hz), 141.2 (d, *J* = 12.5 Hz), 139.4 (d, *J* = 12.4 Hz), 136.6, 133.6, 132.6, 131.8 (d, *J* = 2.9 Hz),130.1 (q, *J* = 325.22). 130.3, 130.1 (d, *J* = 32.32). 128.4 (d, *J* = 12.5 Hz), 126.2, 125.3 (d, *J* = 9.8 Hz), 125.0 (d, *J* = 21.5 Hz), 124.3 (q, *J* = 8.08), 123.1 (d, *J* = 147.9 Hz), 121.6.^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.2.

*(2-(2-methoxyphenyl)benzo[b]thiophen-3-yl)diphenylphosphine oxide (**3j**)*



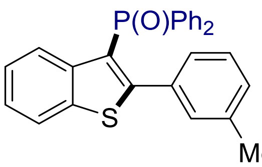
106 mg; 60%; white solid; m. p. 190.0-191.9 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.57 (s, 4H), 7.43 – 7.19 (m, 8H), 7.17 – 7.01 (m,2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 8.2 Hz, 1H), 3.52 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.0, 150.1 (d, *J* = 13.1 Hz), 141.3 (d, *J* = 12.8 Hz), 139.7 (d, *J* = 12.5 Hz), 133.5, 132.4, 131.8 (d, *J* = 10.4 Hz), 131.6, 131.5 (d, *J* = 2.9 Hz), 130.5, 127.9 (d, *J* = 12.5 Hz), 125.8 (d, *J* = 1.5 Hz), 124.7 (d, *J* = 9.8 Hz), 123.9 (d, *J* = 106.1 Hz), 121.7 (d, *J* = 2.7 Hz), 121.4, 119.7, 109.9, 54.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 23.1. HRMS Calcd for $C_{27}H_{22}O_2PS$ $[M + H]^+$: m/z 441.1073, found: 441.1077.

*(2-(2-fluorophenyl)benzo[b]thiophen-3-yl)diphenylphosphine oxide (**3k**)*



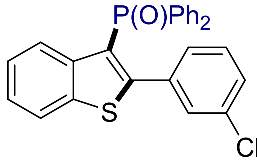
110 mg; 64%; white solid; m. p. 191.3-193.6 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.61 (dd, *J* = 12.5, 7.4 Hz, 4H), 7.32 (m, 8H), 7.10 (m, 2H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.64 (t, *J* = 8.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.9 (d, *J* = 247.2 Hz), 146.5 (d, *J* = 13.4 Hz), 141.0 (d, *J* = 12.6 Hz), 139.8 (d, *J* = 11.8 Hz), 133.2, 132.1, 131.9, 131.8, 131.8, 130.9 (d, *J* = 7.9 Hz), 128.2 (d, *J* = 12.6 Hz), 126.1, 125.4 (d, *J* = 103.9 Hz), 125.1 (d, *J* = 11.9 Hz), 123.5, 121.5, 120.9 (d, *J* = 16.3 Hz), 115.3 (d, *J* = 21.5 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ 21.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.8. HRMS Calcd for $C_{26}H_{19}FOPS$ $[M + H]^+$: m/z 429.0873, found: 429.0874.

*Diphenyl(2-(m-tolyl)benzo[b]thiophen-3-yl)phosphine oxide (**3l**)*[4]



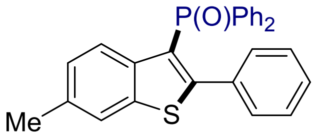
124 mg; 73%; yellow solid; m. p. 176.5-179.1 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 12.4, 7.3 Hz, 4H), 7.42 – 7.33 (m, 3H), 7.26 (m, 5H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.97 – 6.84 (m, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.0 (d, *J* = 13.0 Hz), 141.5 (d, *J* = 13.0 Hz), 139.3 (d, *J* = 12.6 Hz), 137.1, 134.1, 133.0, 132.7 (d, *J* = 2.7 Hz), 131.6 (d, *J* = 10.2 Hz), 131.4 (d, *J* = 2.9 Hz), 130.9, 129.3, 128.2 (d, *J* = 12.5 Hz), 127.6, 126.9, 126.0, 124.8 (d, *J* = 5.9 Hz), 122.7 (d, *J* = 104.8 Hz), 121.4, 21.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.6.

*(2-(3-chlorophenyl)benzo[b]thiophen-3-yl)diphenylphosphine oxide (**3m**)*



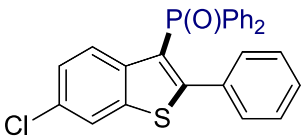
160 mg; 90%; white solid; m. p. 193.1-195.2 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 12.4, 7.4 Hz, 4H), 7.38 (q, *J* = 8.4, 8.0 Hz, 3H), 7.29 (m, 5H), 7.14 – 7.01 (m, 3H), 7.00 – 6.92 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.5 (d, *J* = 12.6 Hz), 141.2 (d, *J* = 12.5 Hz), 139.3 (d, *J* = 12.5 Hz), 134.6 (d, *J* = 2.9 Hz), 133.6, 133.4, 132.6, 131.8 (d, *J* = 2.9 Hz), 131.6 (d, *J* = 10.2 Hz), 130.1, 128.8, 128.7, 128.4 (d, *J* = 12.6 Hz), 128.1, 126.1, 125.1 (d, *J* = 8.5 Hz), 123.8 (d, *J* = 103.3 Hz), 121.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.4. HRMS Calcd for $C_{26}H_{18}ClNaOPS$ $[M + Na]^+$: m/z 467.0397, found: 467.0400.

*(6-methyl-2-phenylbenzo[b]thiophen-3-yl)diphenylphosphine oxide (**3n**)*



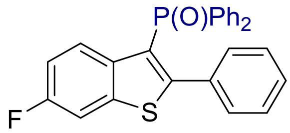
117 mg; 69%; white solid; m. p. 207.6-209.6 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.5 Hz, 1H), 7.65 (s, 1H), 7.62 – 7.53 (m, 4H), 7.40 – 7.33 (m, 2H), 7.25 (m, 4H), 7.19 – 7.14 (m, 2H), 7.08 (t, 2H), 6.97 (t,2 H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.8 (d, *J* = 12.8 Hz), 139.7 (d, *J* = 12.6 Hz), 139.2 (d, *J* = 12.9 Hz), 134.9, 134.1, 133.0, 133.0 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 10.1 Hz), 131.4 (d, *J* = 2.9 Hz), 130.0, 128.3 (d, *J* = 12.7 Hz), 127.5, 126.6, 125.5 (d, *J* = 1.4 Hz), 122.5 (d, *J* = 104.4 Hz), 121.2, 21.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.5. HRMS Calcd for $C_{27}H_{21}OPS$ $[M + H]^+$: m/z 425.1123, found: 425.1122.

*(6-chloro-2-phenylbenzo[b]thiophen-3-yl)diphenylphosphine oxide (**3o**)*



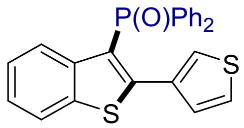
76 mg; 43%; white solid; m. p. 209.2-211.1 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.9 Hz, 1H), 7.84 (s, 1H), 7.55 (dd, *J* = 12.4, 7.4 Hz, 4H), 7.37 (t, *J* = 7.0 Hz, 2H), 7.30 – 7.19 (m, 5H), 7.11 (dd, *J* = 16.2, 7.4 Hz, 3H), 6.98 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.0 (d, *J* = 12.7 Hz), 140.4 (d, *J* = 12.4 Hz), 140.0 (d, *J* = 12.6 Hz), 133.7, 132.6, 132.4 (d, *J* = 2.7 Hz), 131.6 (d, *J* = 10.0 Hz), 131.1, 129.8, 128.6, 128.4 (d, *J* = 12.5 Hz), 127.7, 126.9, 125.7, 122.8 (d, *J* = 103.5 Hz), 121.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.1. HRMS Calcd for $C_{26}H_{19}ClOPS$ $[M + H]^+$: m/z 445.0577, found: 445.0579.

*(6-fluoro-2-phenylbenzo[b]thiophen-3-yl)diphenylphosphine oxide (**3p**)*



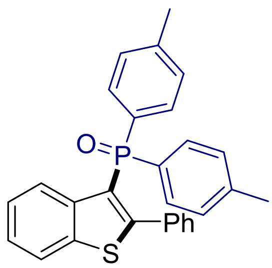
68 mg; 40%; white solid; m. p. 188.3-190.7 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.0 (dd, *J* = 9.1, 5.2 Hz, 1H), 7.6 – 7.5 (m, 5H), 7.4 (m, 2H), 7.3 (m, 4H), 7.1 – 7.1 (m, 3H), 7.1 – 6.9 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.5 (d, *J* = 246.4 Hz), 154.3, 140.4 (dd, *J* = 12.4, 10.0 Hz), 137.9 (d, *J* = 11.2 Hz), 133.7, 132.6, 132.5 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 10.0 Hz), 129.9, 128.5, 128.3 (d, *J* = 12.5 Hz), 127.6, 127.3 (d, *J* = 9.3 Hz), 122.6 (d, *J* = 104.0 Hz), 113.9 (d, *J* = 23.7 Hz), 107.6 (d, *J* = 25.3 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.2. HRMS Calcd for $[M + H]^+$: $C_{27}H_{19}FOPS$ m/z 429.0873, found: 429.0871.

Diphenyl(2-(thiophen-3-yl)benzo[b]thiophen-3-yl)phosphine oxide ***(3q)***[4]



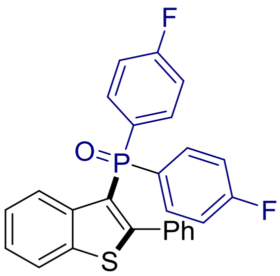
120 mg; 72%; yellow solid; m. p. 185.9-186.1 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.63 (dd, *J* = 12.5, 7.6 Hz, 4H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.17 (m, 7H), 6.94 (t, *J* = 3.9 Hz, 1H), 6.84 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.6 (d, *J* = 12.5 Hz), 141.3 (d, *J* = 12.9 Hz), 139.3 (d, *J* = 12.7 Hz), 134.1, 133.1 (d, *J* = 3.2 Hz), 133.0, 131.5, 131.5 (d, *J* = 10.0 Hz), 129.0, 128.4 (d, *J* = 12.4 Hz), 126.7, 125.7, 125.1, 124.8, 123.2 (d, *J* = 104.3 Hz), 121.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.0.

(2-phenylbenzo[b]thiophen-3-yl)di-p-tolylphosphine oxide ***(3r)***[4]



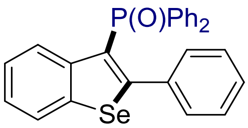
132 mg; 75%; white solid; m. p. 176.5-178.1 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.43 (dd, *J* = 12.3, 8.1 Hz, 4H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.12 (d, *J* = 12.7 Hz, 3H), 7.04 (dd, *J* = 8.0, 2.5 Hz, 4H), 7.00 – 6.95 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.3 (d, *J* = 12.8 Hz), 141.8 (d, *J* = 2.9 Hz), 141.5 (d, *J* = 12.6 Hz), 139.3 (d, *J* = 12.4 Hz), 133.1 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 10.6 Hz), 130.8, 129.9, 129.7, 129.0 (d, *J* = 12.9 Hz), 127.8, 127.4, 126.2 (d, *J* = 1.3 Hz), 124.8 (d, *J* = 7.8 Hz), 123.5 (d, *J* = 103.9 Hz), 121.3, 21.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 22.2.

Bis(4-fluorophenyl)(2-phenylbenzo[b]thiophen-3-yl)phosphine oxide ***(3s)***



118 mg; 66%; white solid; m. p. 149.1-152.6 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.54 (m, 4H), 7.42 – 7.35 (m, 1H), 7.33 – 7.26 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.94 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.8 (dd, *J* = 253.5, 3.4 Hz), 154.9 (d, *J* = 13.3 Hz), 141.1 (d, *J* = 12.9 Hz), 139.4 (d, *J* = 12.8 Hz), 134.1 (dd, *J* = 11.7, 8.8 Hz), 132.7 (d, *J* = 2.8 Hz), 129.9, 129.8 (d, *J* = 3.3 Hz), 128.7 (d, *J* = 3.4 Hz), 128.6, 127.7, 125.8 (d, *J* = 1.7 Hz), 125.1 (d, *J* = 1.8 Hz), 122.5 (d, *J* = 106.6 Hz), 121.6, 115.8 (dd, *J* = 21.5, 13.7 Hz).^{31}P NMR (162 MHz, Chloroform-*d*) δ 19.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.6. HRMS Calcd for $C_{26}H_{18}F_2PS$ [M + H]$^+$: m/z 447.0779, found: 447.0780.

*diphenyl(2-phenylbenzo[b]selenophen-3-yl)phosphine oxide (**3t**)*[4]



174 mg; 95%; white solid; m. p. 207.5-208.9 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.2 (d, *J* = 7.3 Hz, 1H), 7.9 (d, *J* = 7.5 Hz, 1H), 7.6 (dd, *J* = 12.5, 7.6 Hz, 4H), 7.4 – 7.2 (m, 8H), 7.1 (m, 3H), 6.9 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8 (d, *J* = 10.6 Hz), 143.6 (d, *J* = 13.7 Hz), 141.8 (d, *J* = 12.2 Hz), 135.0 (d, *J* = 3.5 Hz), 134.2, 133.2, 131.7 (d, *J* = 10.1 Hz), 131.4 (d, *J* = 2.7 Hz), 129.3, 128.3, 128.2, 128.1, 127.5, 126.1 (d, *J* = 99.0 Hz), 125.0 (d, *J* = 5.5 Hz), 124.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 23.2.

Reference

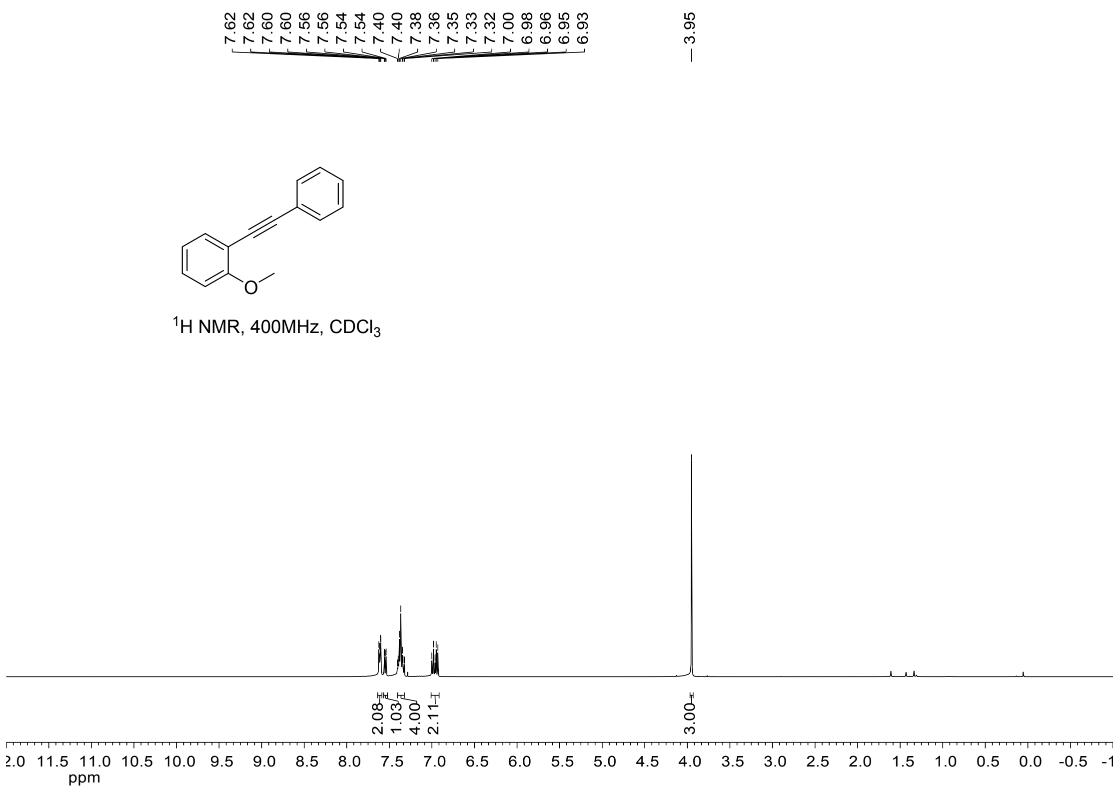
[1] J. Yan, J. Xu, Y. Zhou, J. Chen, Q. Song, *Org. Chem. Front.* **2018**, *5*, 1483.

[2] B. Yao, Q. Wang, J. Zhu, **2012**, *51*, 5170.

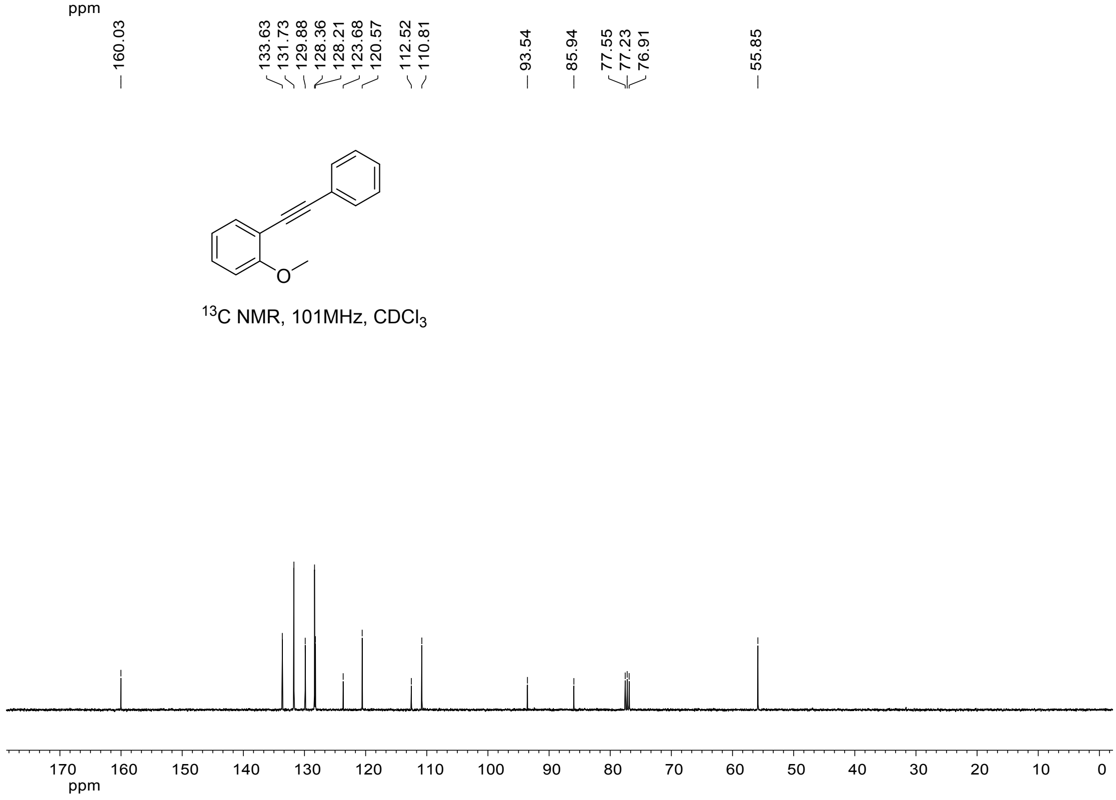
[3] T. Yamauchi, F. Shibahara, T. Murai, *Tetrahedron Lett.* **2016**, *57*, 2945.

[4] T. Cai, J. Liu, H. Zhang, X. Wang, J. Feng, R. Shen, Y. Gao, *Org. Lett.* **2019**, *21*, 4605.

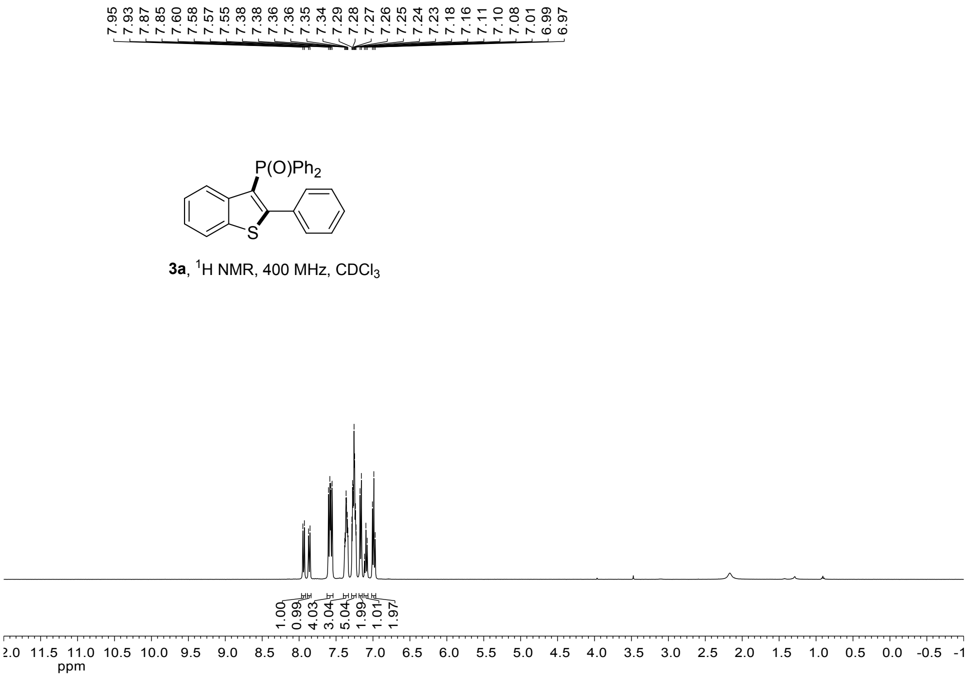
7. NMR Spectra for Products



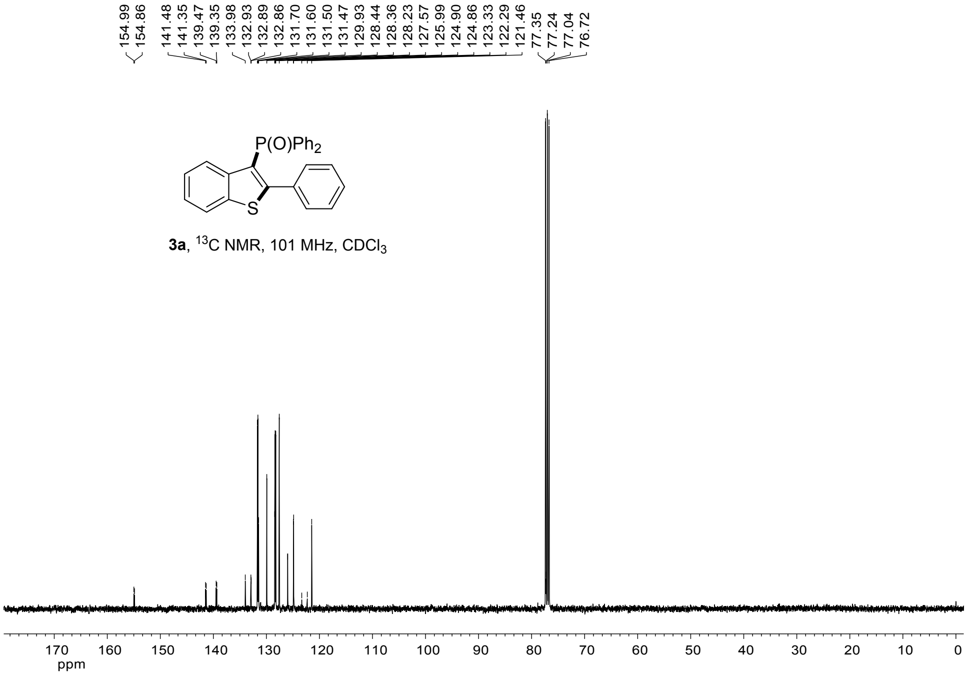
^{1}H NMR, 400MHz, $CDCl_3$



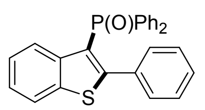
^{13}C NMR, 101MHz, $CDCl_3$



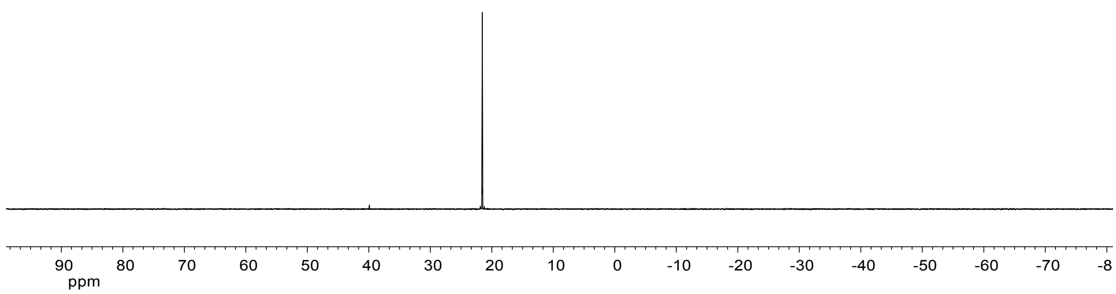
3a, ^{1}H NMR, 400 MHz, $CDCl_3$

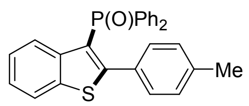


3a, ^{13}C NMR, 101 MHz, $CDCl_3$

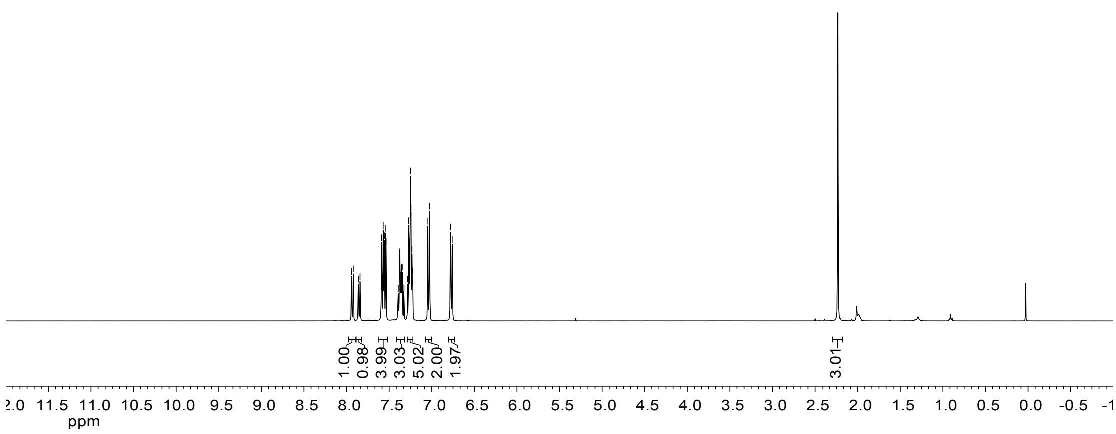


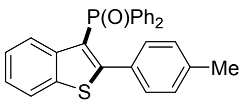
3a, ^{31}P NMR, 162 MHz, $CDCl_3$



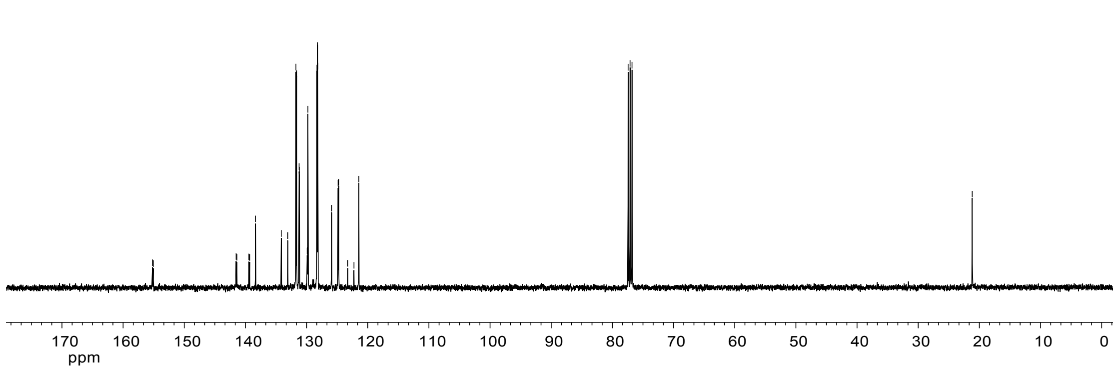


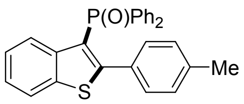
3b, ^{1}H NMR, 400 MHz, $CDCl_3$



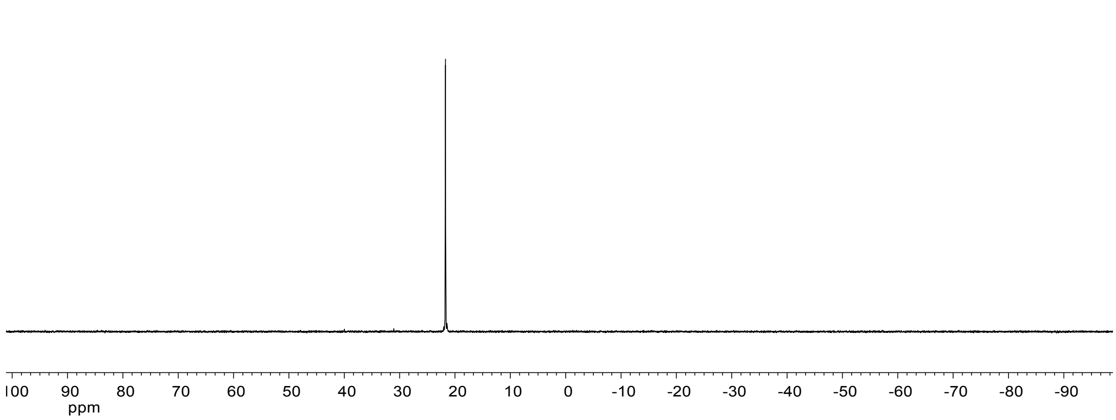


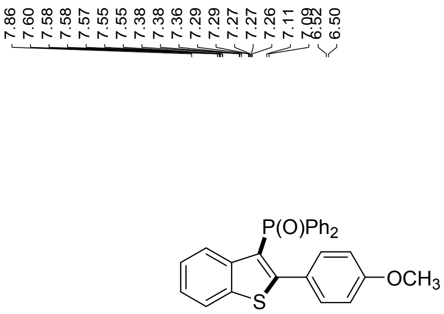
3b, ^{13}C NMR, 101 MHz, $CDCl_3$



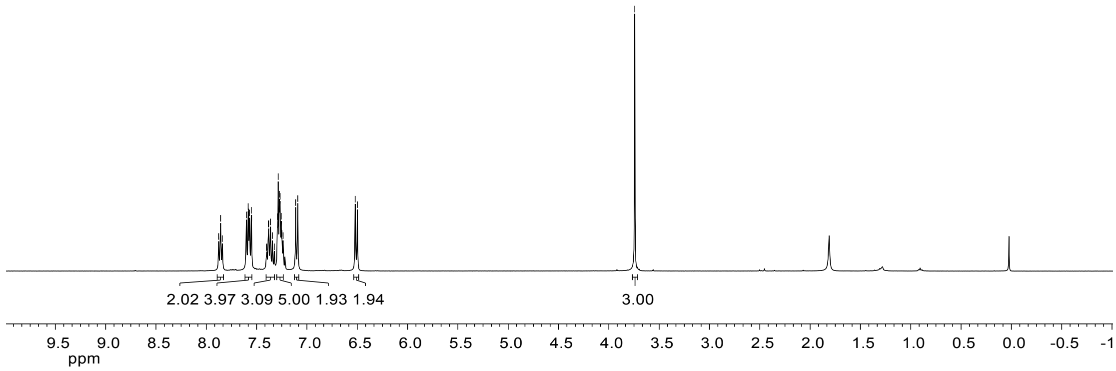


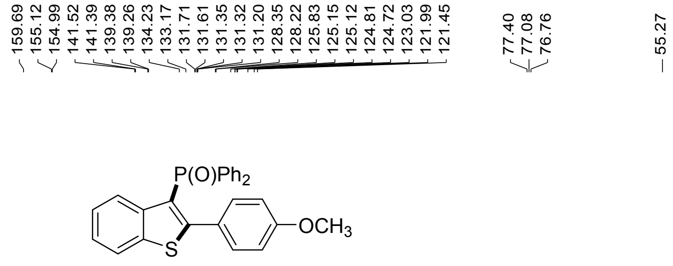
3b, ^{31}P NMR, 162 MHz, $CDCl_3$



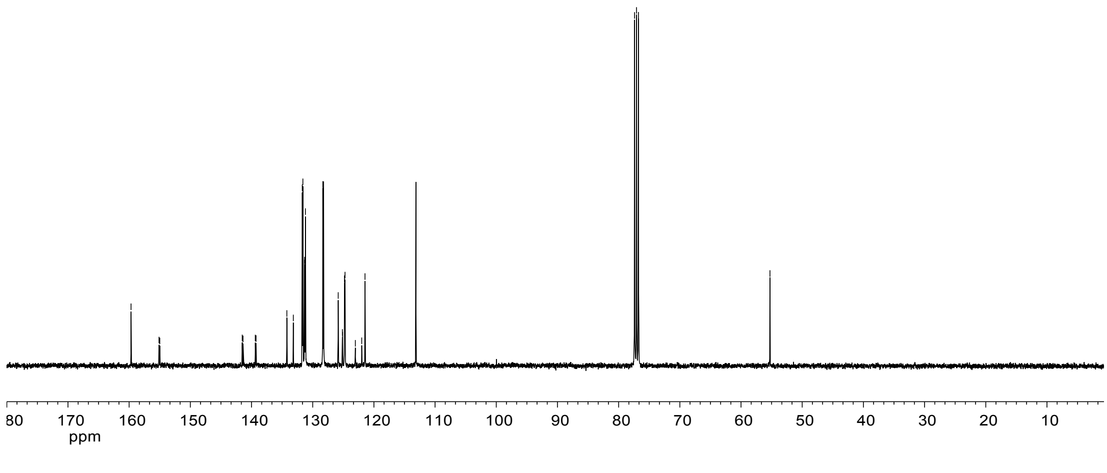


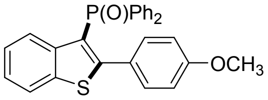
3c, ^{1}H NMR, 400 MHz, CDCl$_3$



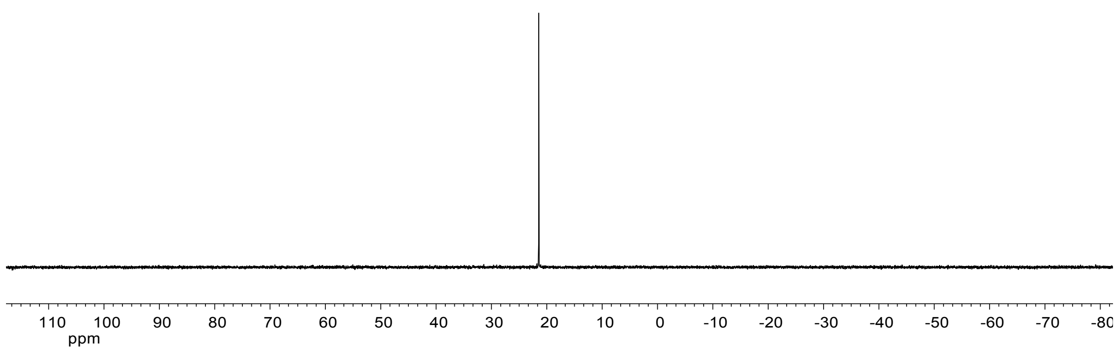


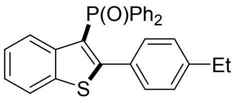
3c, ^{13}C NMR, 101 MHz, CDCl$_3$



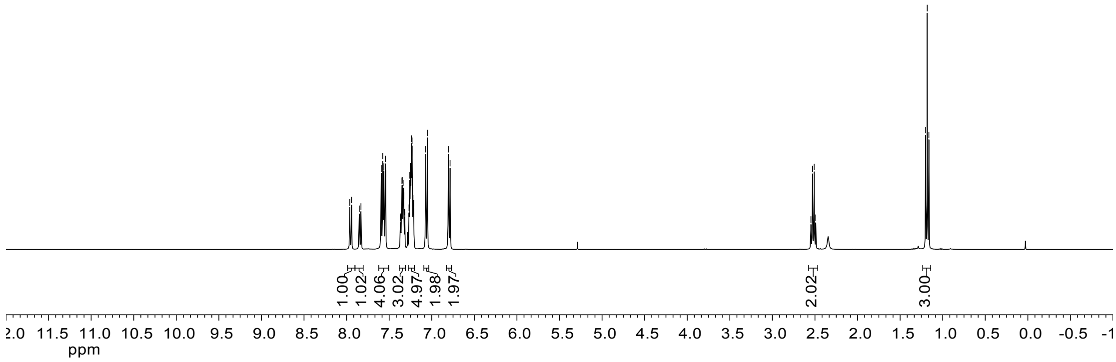


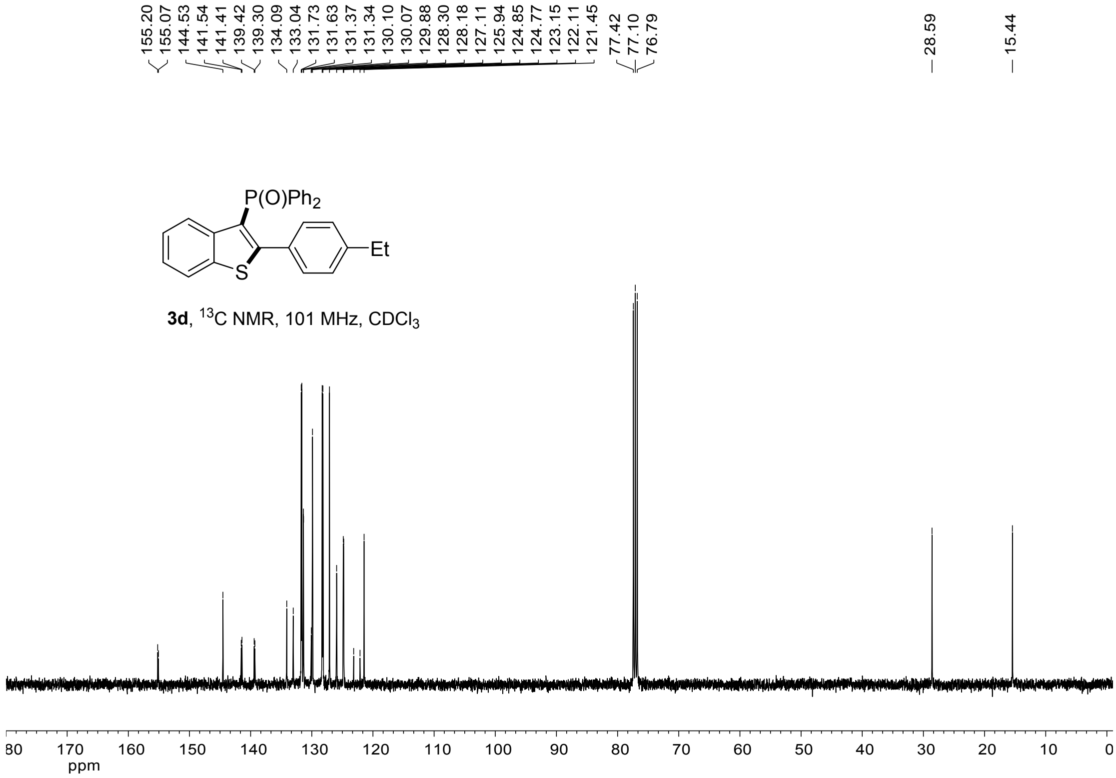
3c, ^{31}P NMR, 162 MHz, CDCl$_3$





3d, ^{1}H NMR, 400 MHz, CDCl$_3$

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122.11
121.45
77.42
77.10
76.79
28.59
15.44
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Et
S
3d, 13C NMR, 101 MHz, CDCl3
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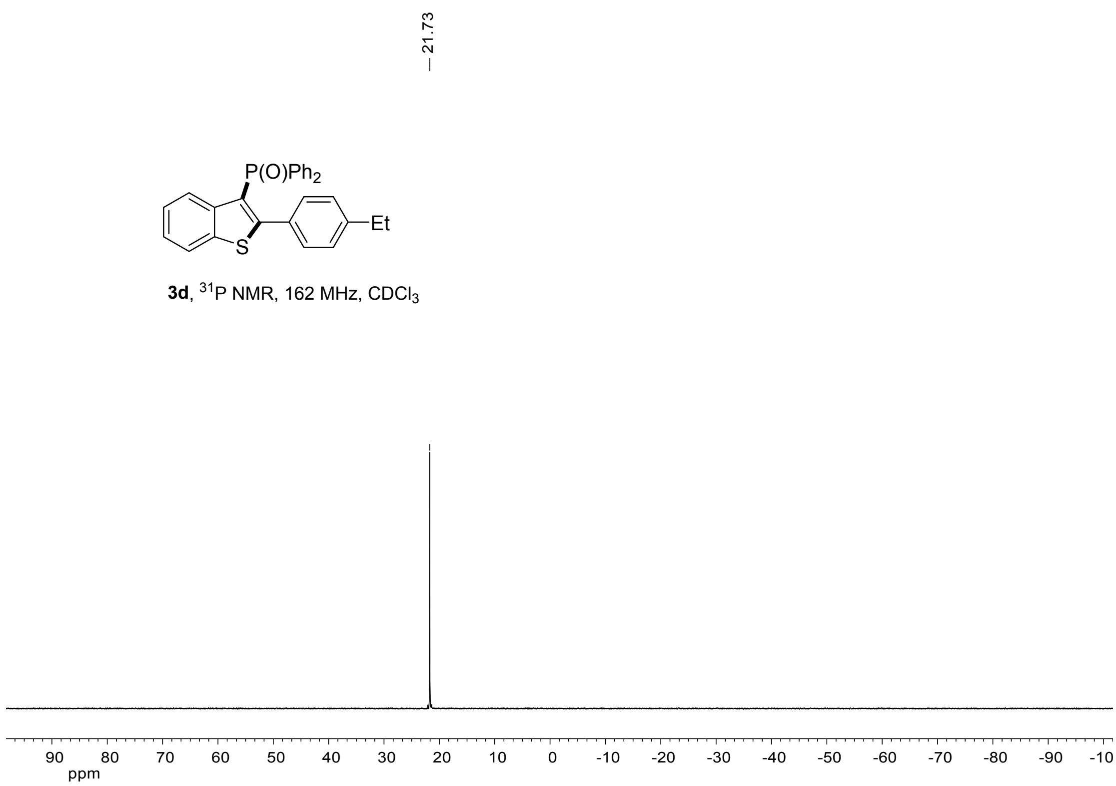
ppm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P(O)Ph2
Et
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3d, 31P NMR, 162 MHz, CDCl3
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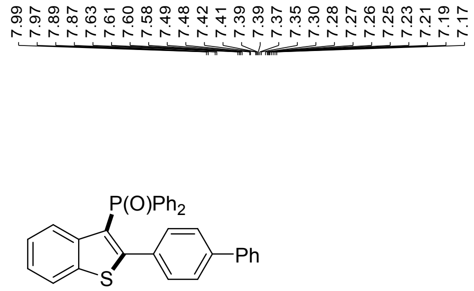
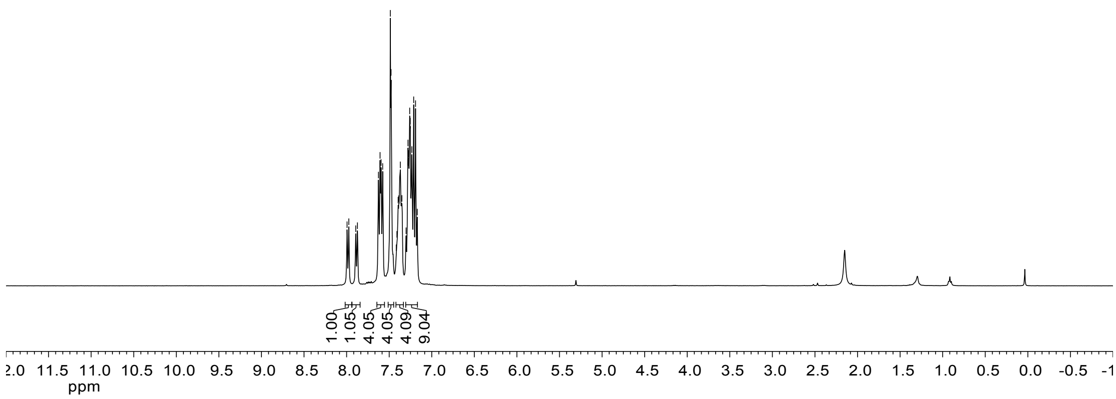
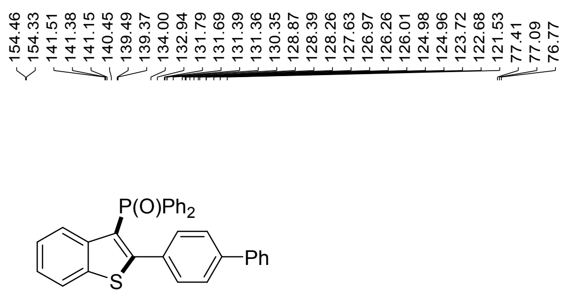
ppm

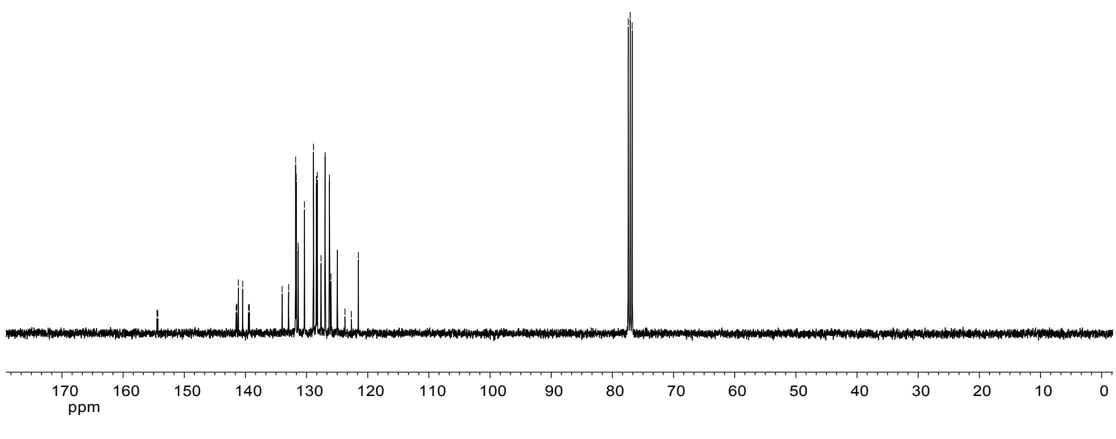


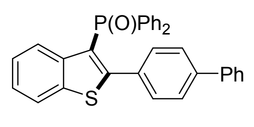
3e, ^{1}H NMR, 400 MHz, $CDCl_3$



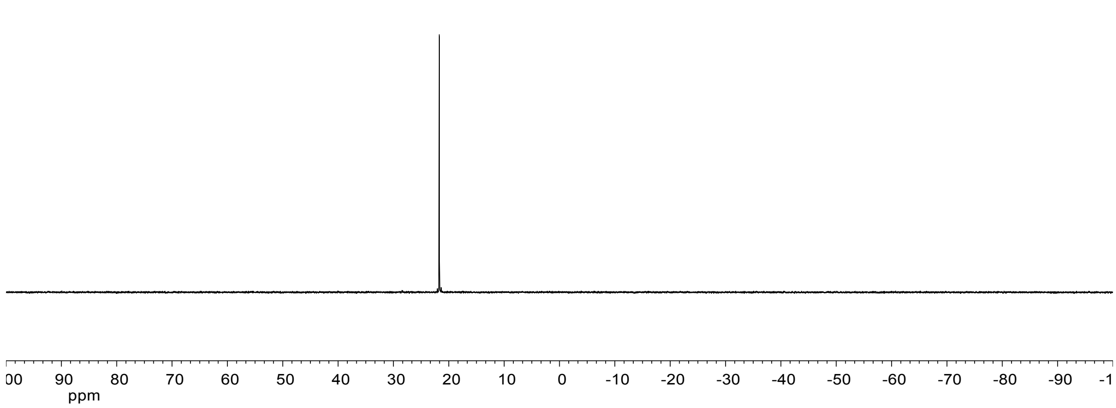


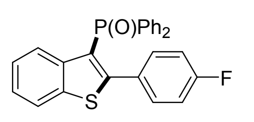
3e, ^{13}C NMR, 101 MHz, $CDCl_3$



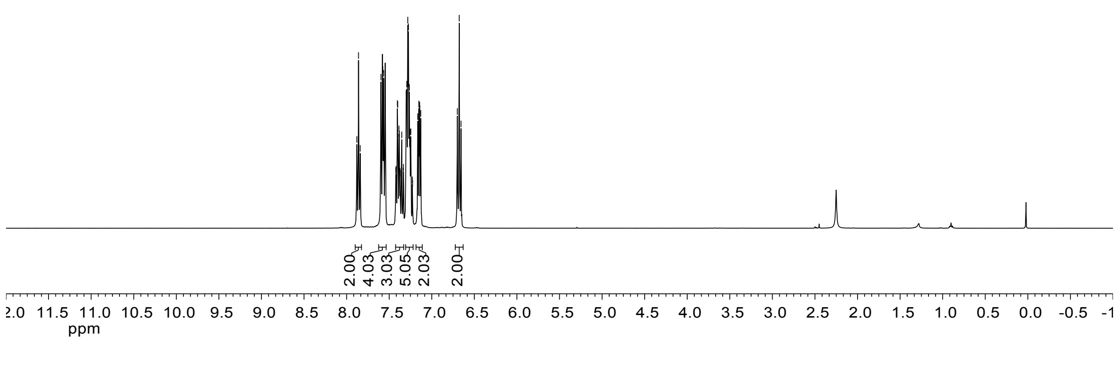


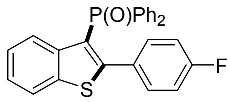
3e, ^{31}P NMR, 162 MHz, $CDCl_3$



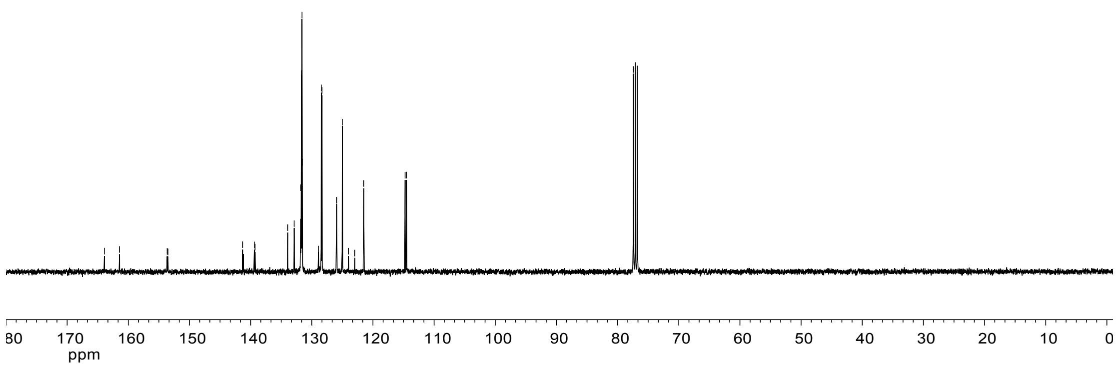


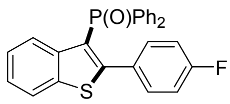
3f, ^{1}H NMR, 400 MHz, $CDCl_3$



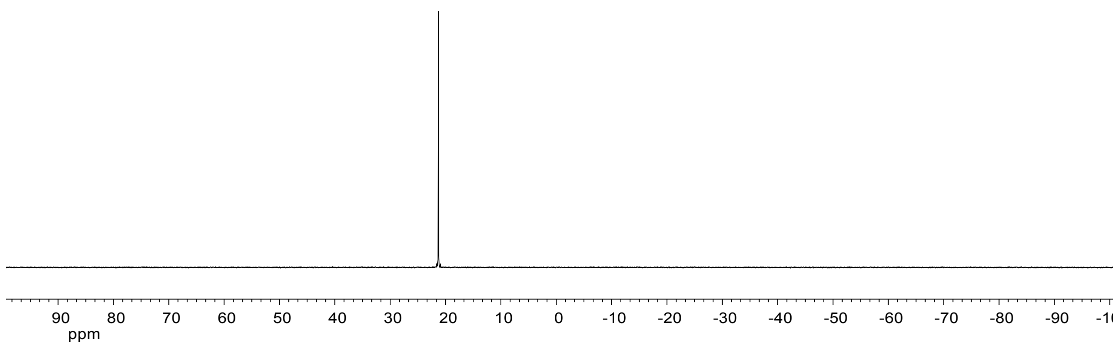


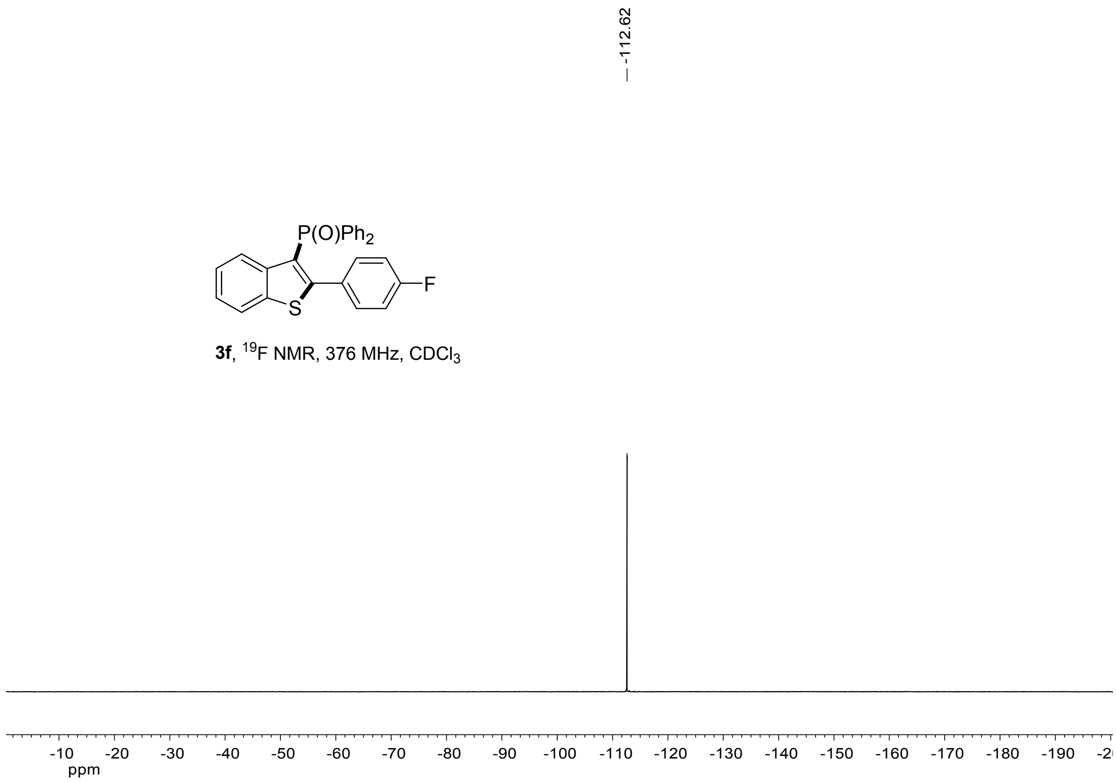
3f, ^{13}C NMR, 101 MHz, CDCl$_3$



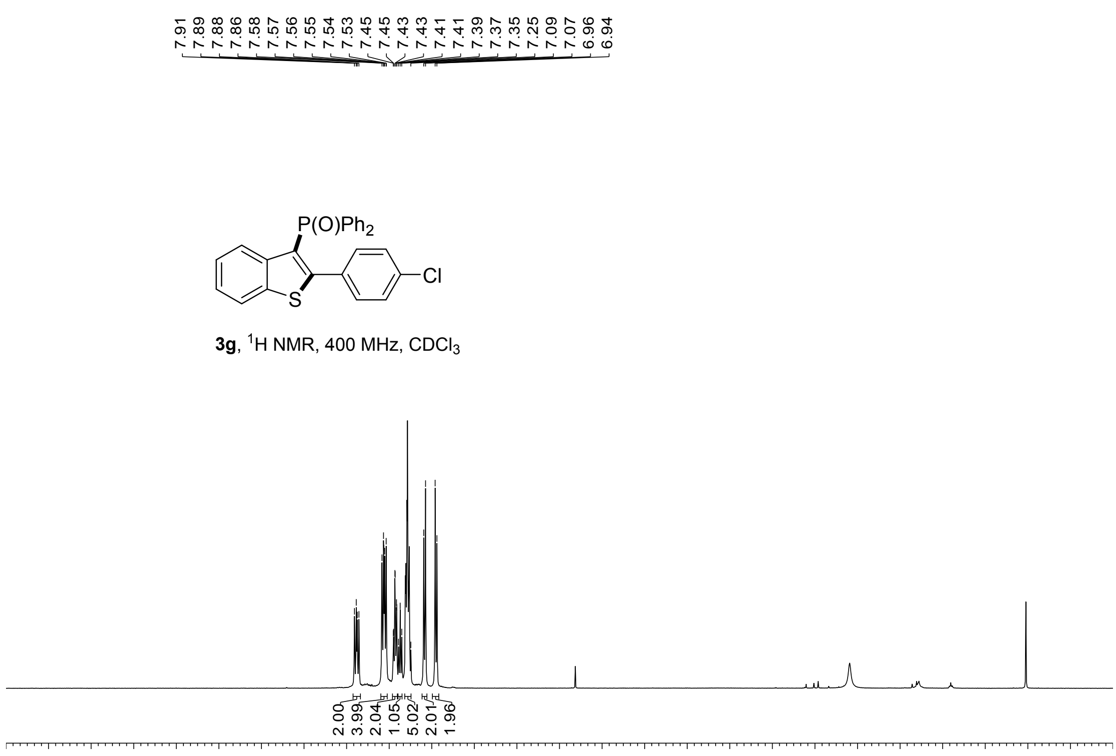


3f, ^{31}P NMR, 162 MHz, CDCl$_3$

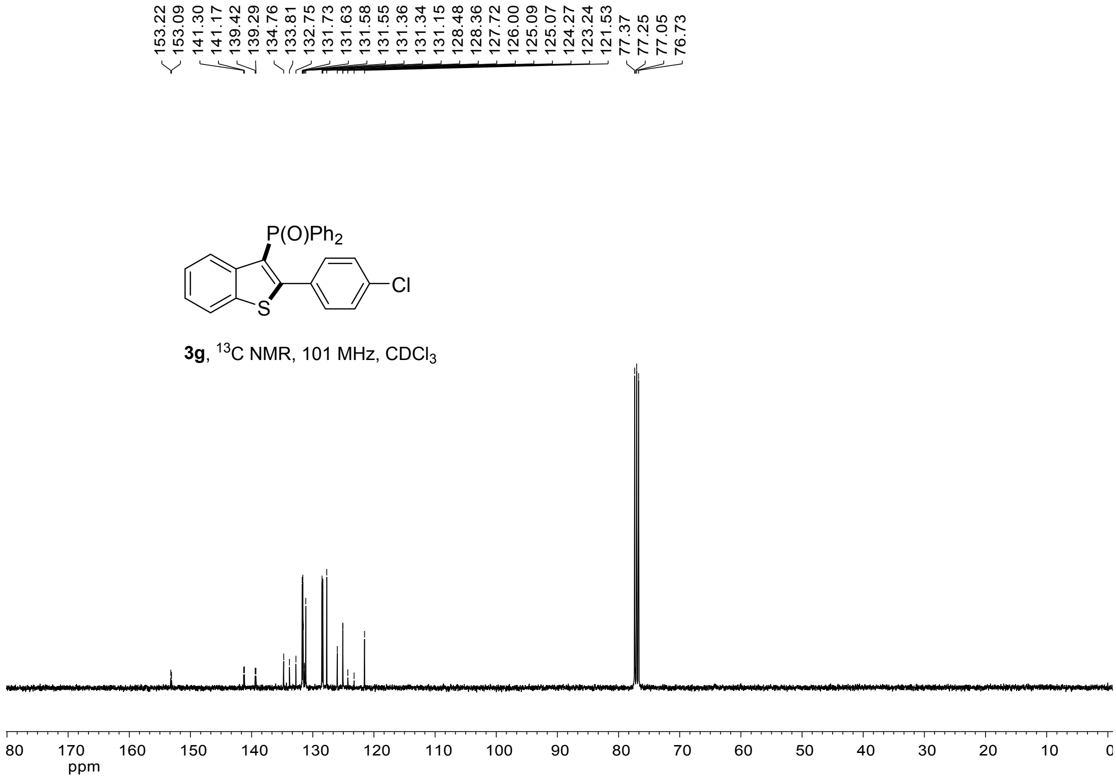




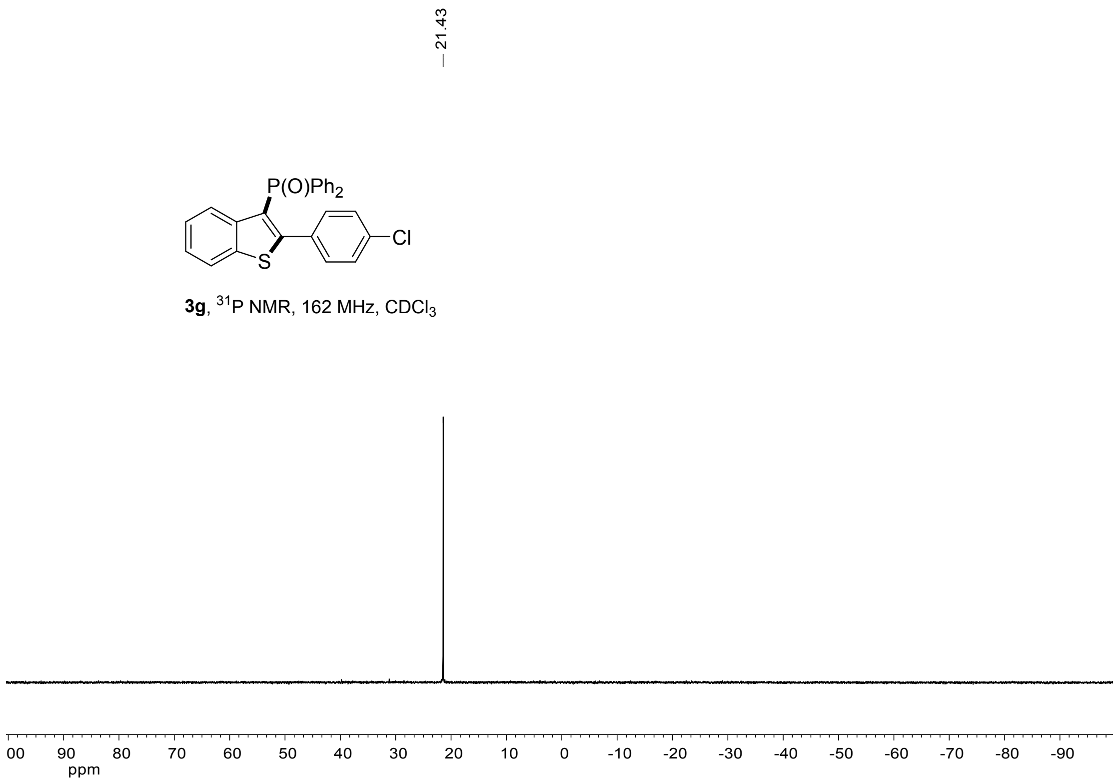
3f, ^{19}F NMR, 376 MHz, $CDCl_3$



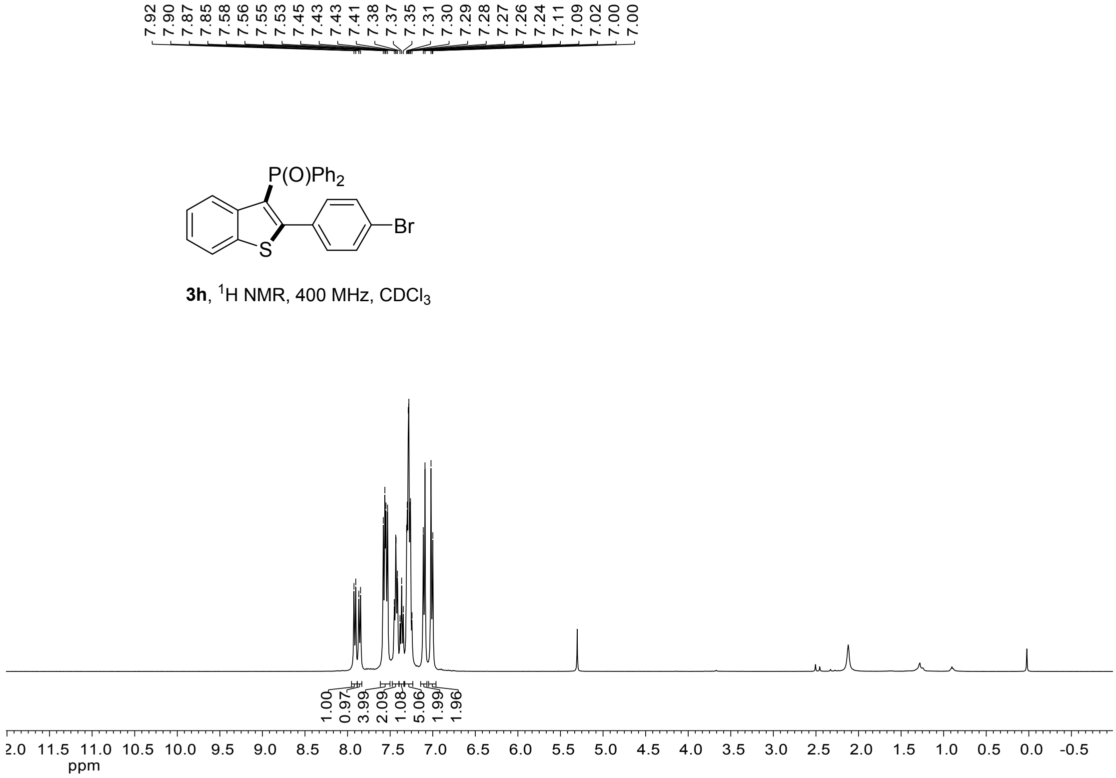
3g, ^{1}H NMR, 400 MHz, $CDCl_3$



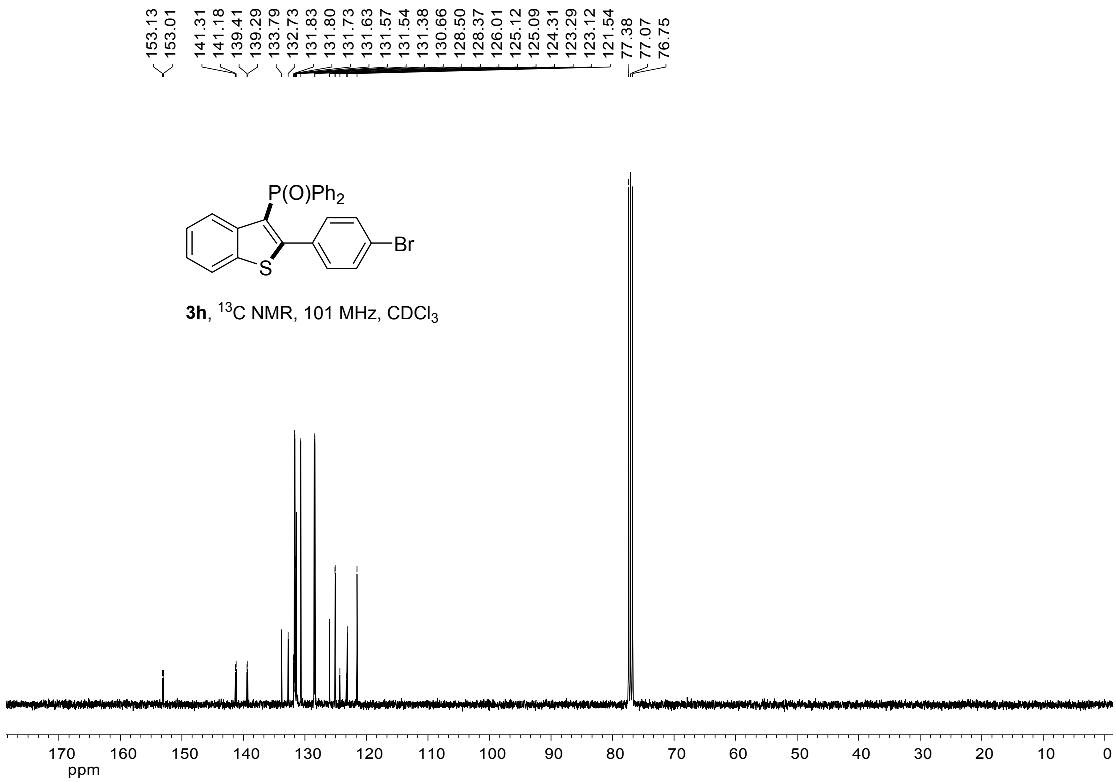
3g, ^{13}C NMR, 101 MHz, $CDCl_3$



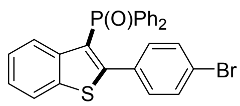
3g, ^{31}P NMR, 162 MHz, $CDCl_3$



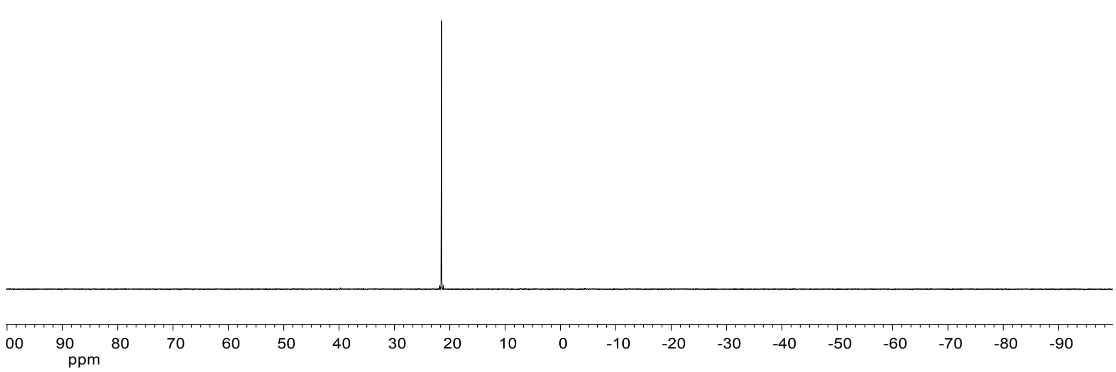
3h, ^{1}H NMR, 400 MHz, $CDCl_3$

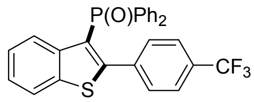


3h, ^{13}C NMR, 101 MHz, $CDCl_3$

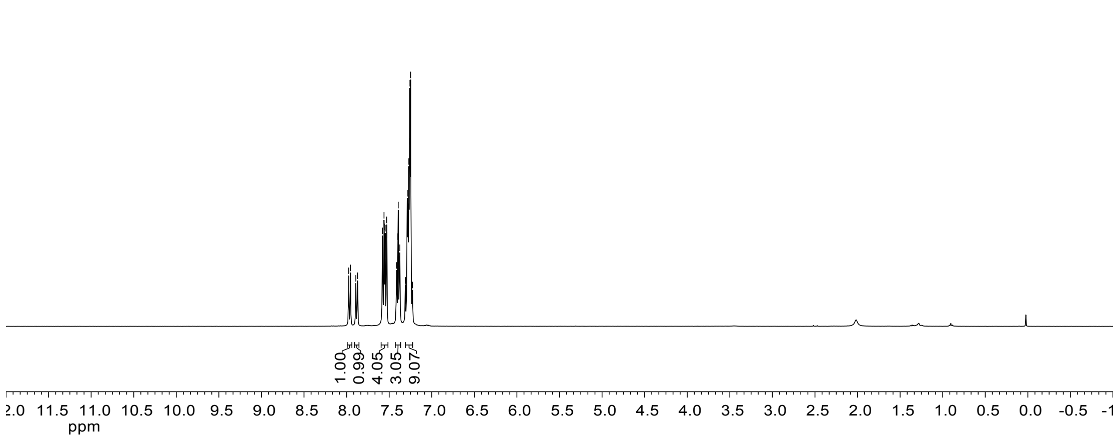


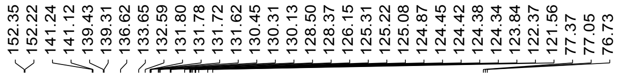
3h, ^{31}P NMR, 162 MHz, $CDCl_3$

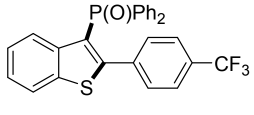




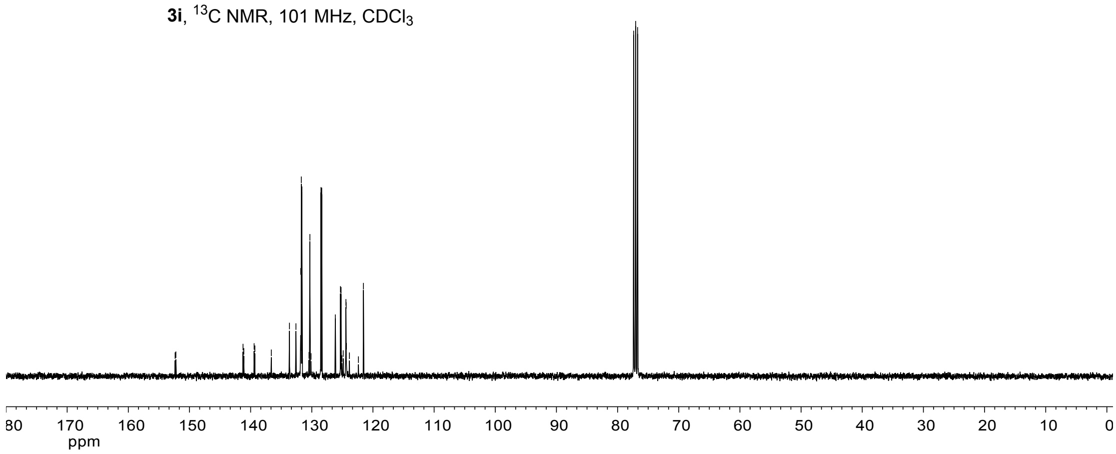
3i, ^{1}H NMR, 400 MHz, $CDCl_3$

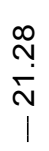


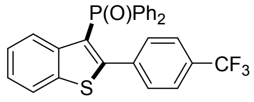




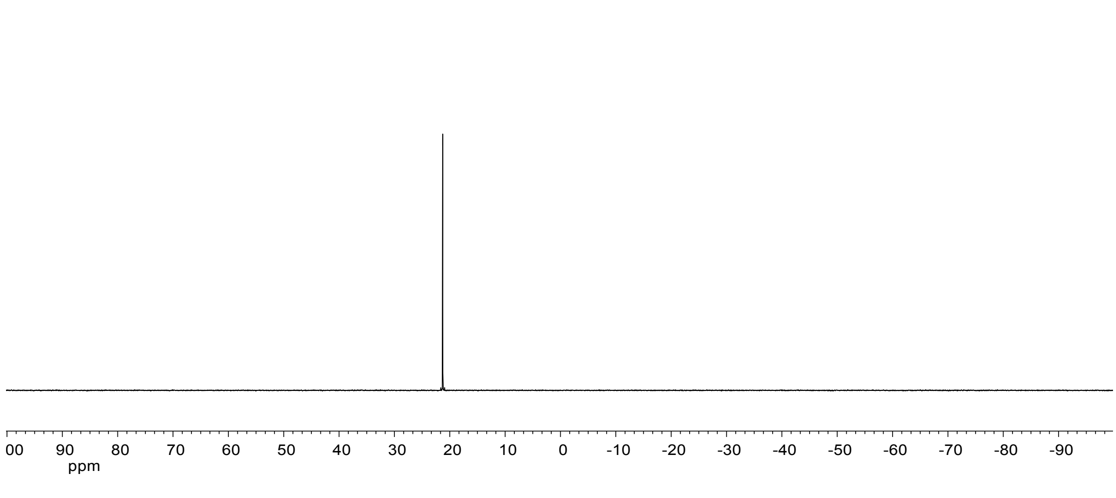
3i, ^{13}C NMR, 101 MHz, $CDCl_3$

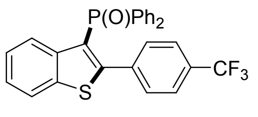




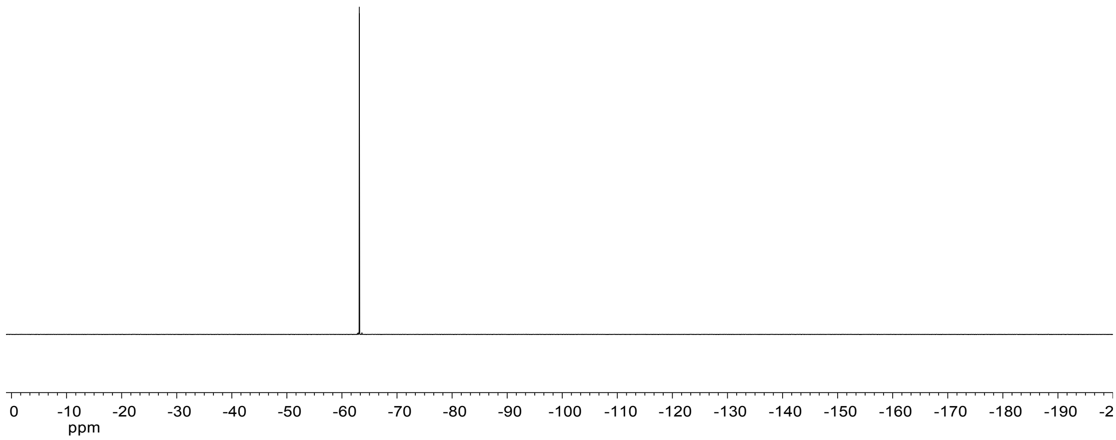


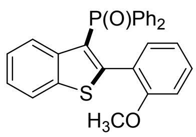
3i, ^{31}P NMR, 162 MHz, $CDCl_3$



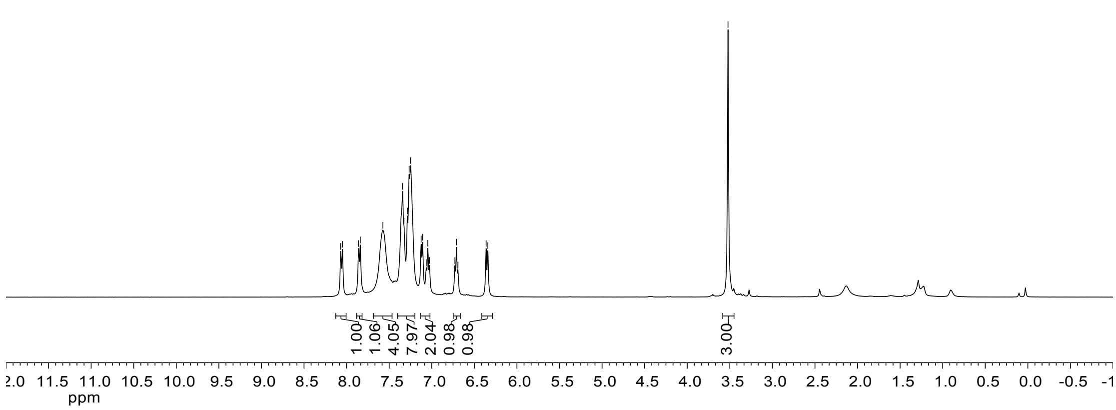


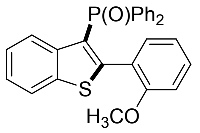
3i, ^{19}F NMR, 376 MHz, $CDCl_3$



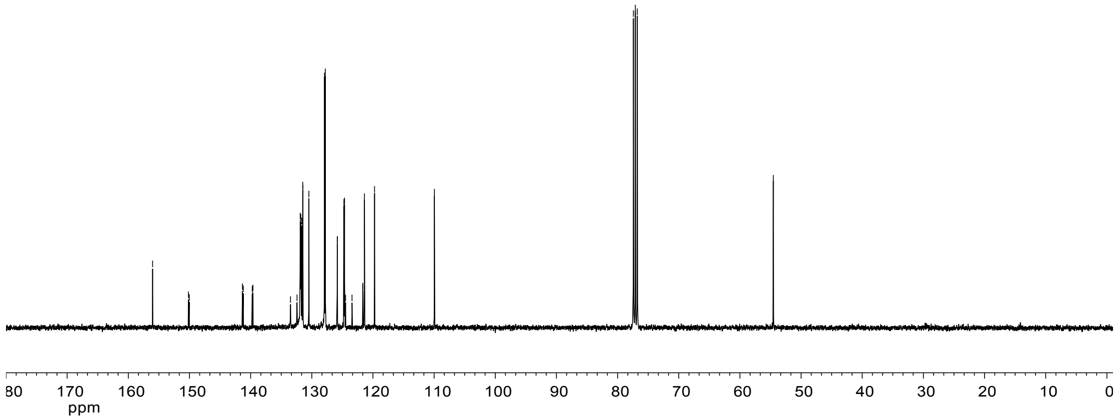


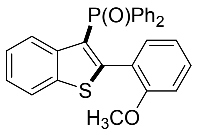
3j, ^{1}H NMR, 400 MHz, $CDCl_3$



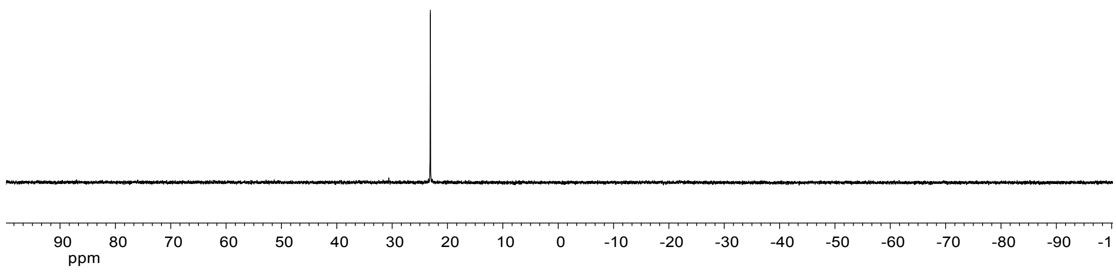


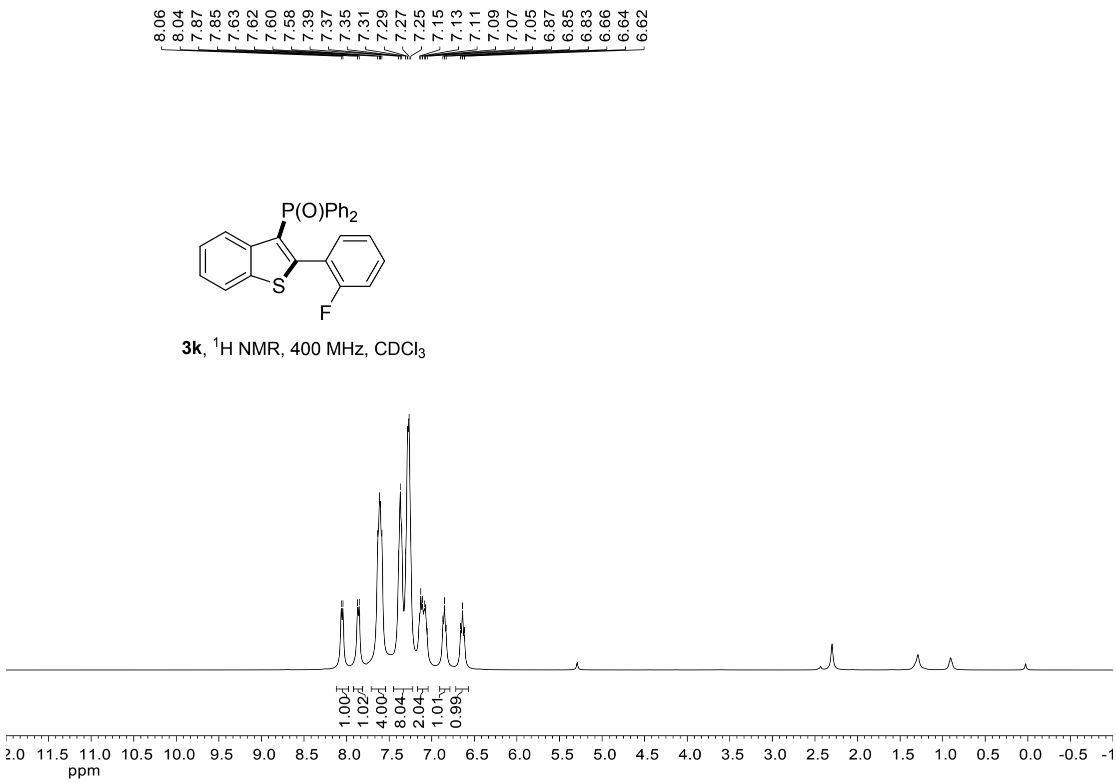
3j, ^{13}C NMR, 101 MHz, $CDCl_3$



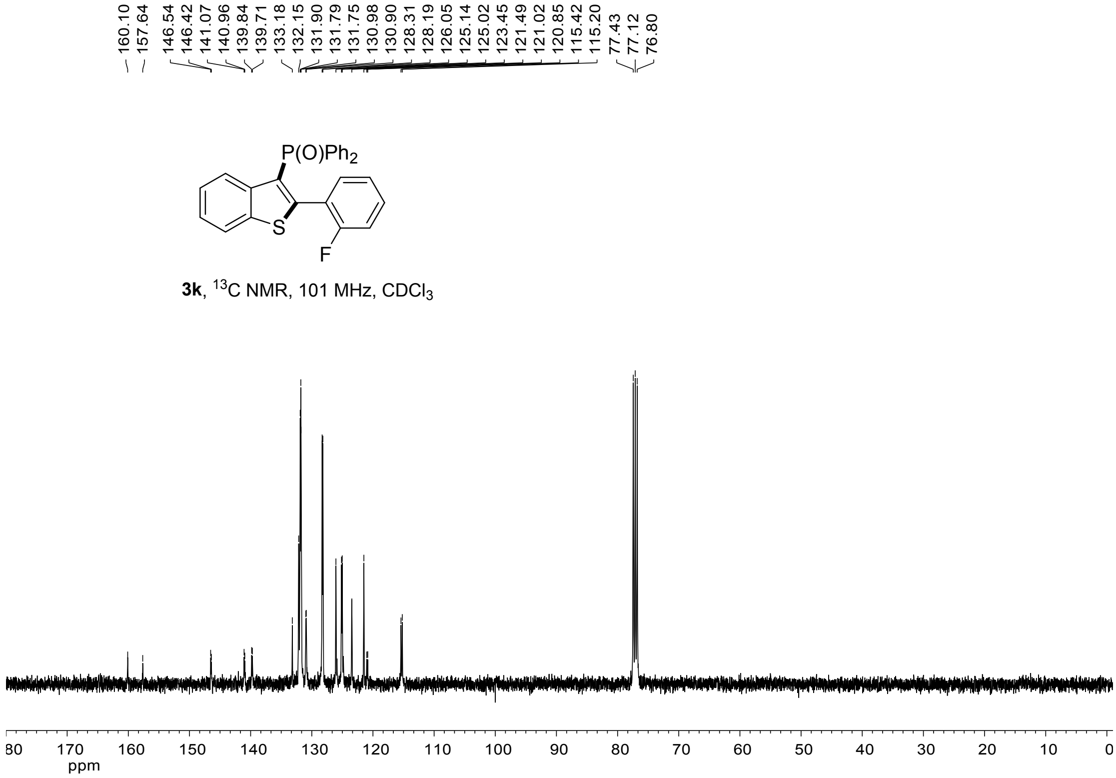


3j, ^{31}P NMR, 162 MHz, $CDCl_3$

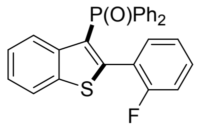




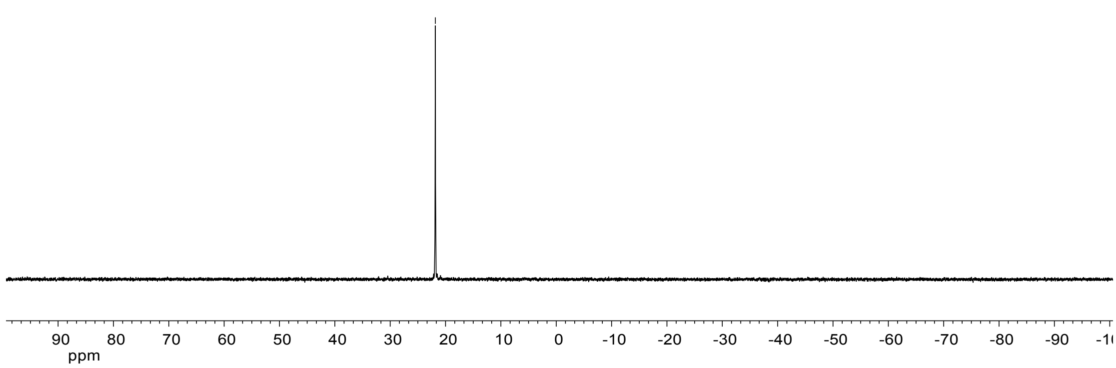
3k, ^{1}H NMR, 400 MHz, $CDCl_3$

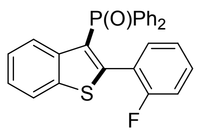


3k, ^{13}C NMR, 101 MHz, $CDCl_3$

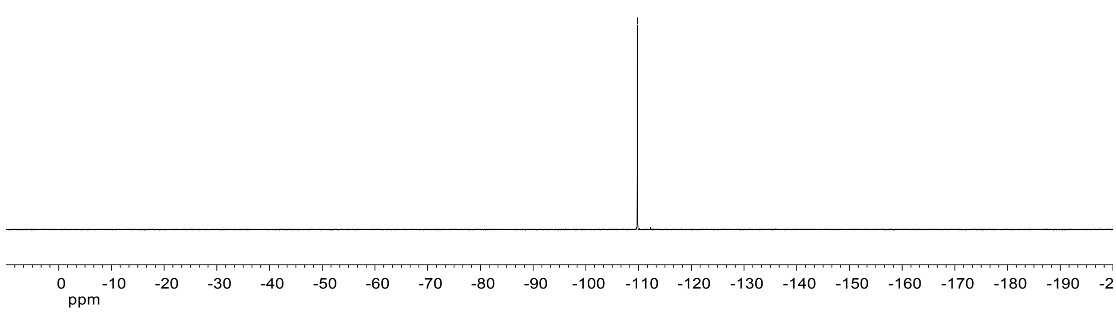


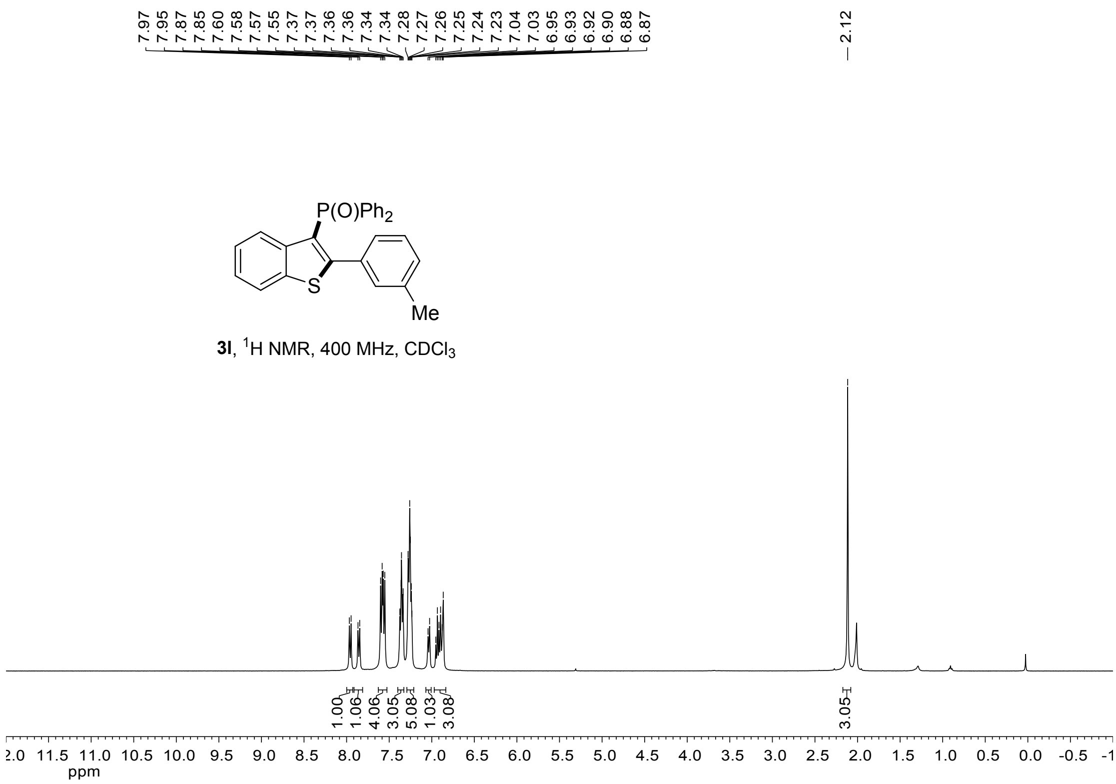
3k, ^{31}P NMR, 162 MHz, $CDCl_3$





3k, ^{19}F NMR, 376 MHz, $CDCl_3$

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S
Me
3l, 1H NMR, 400 MHz, CDCl3
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4.06
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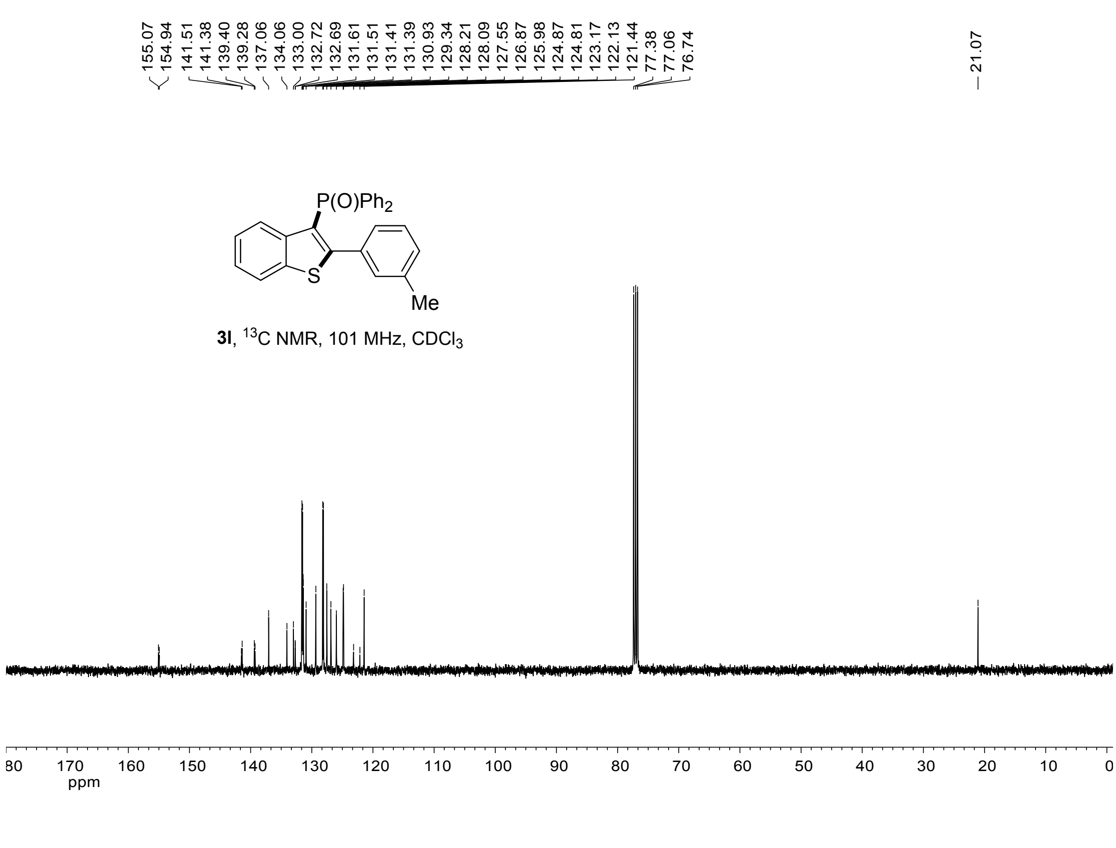
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77.06
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S
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3l, 13C NMR, 101 MHz, CDCl3
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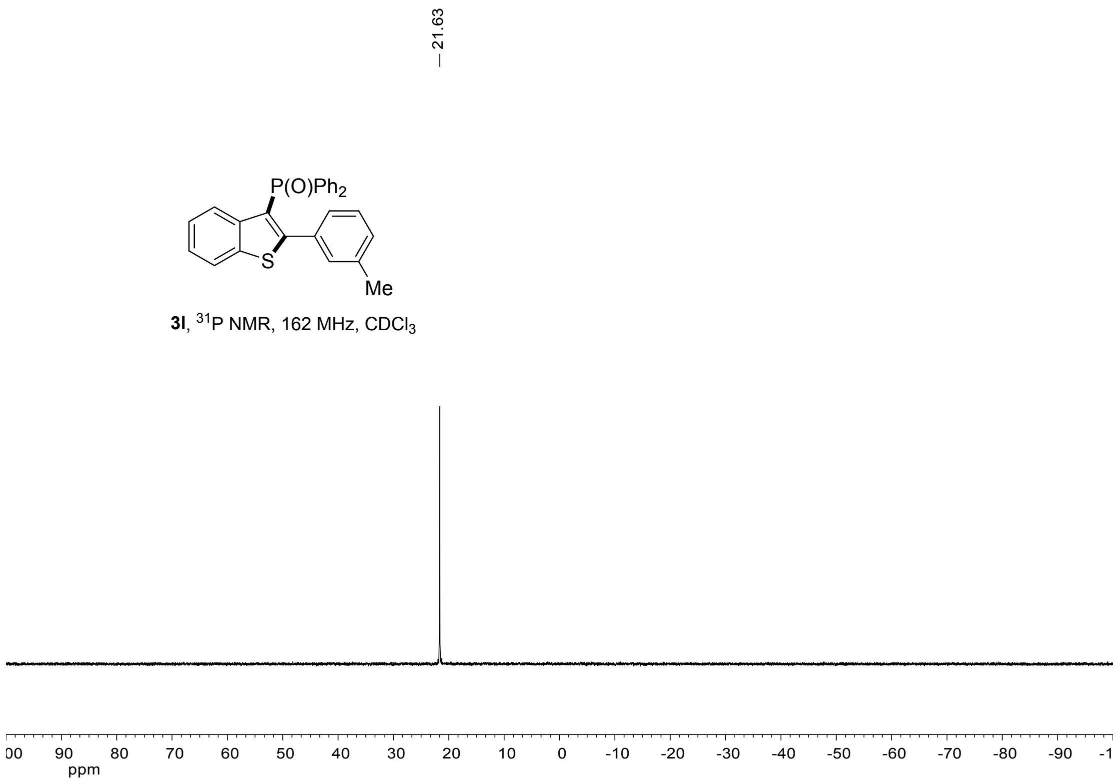
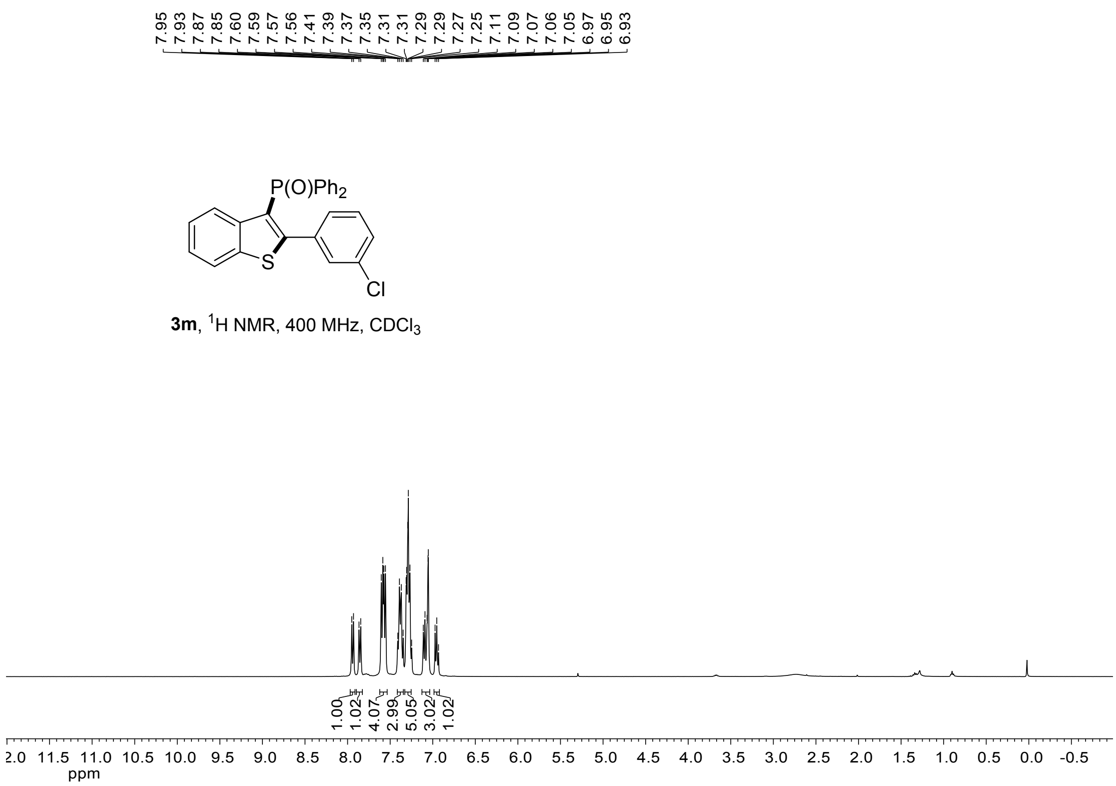
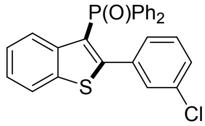
ppm



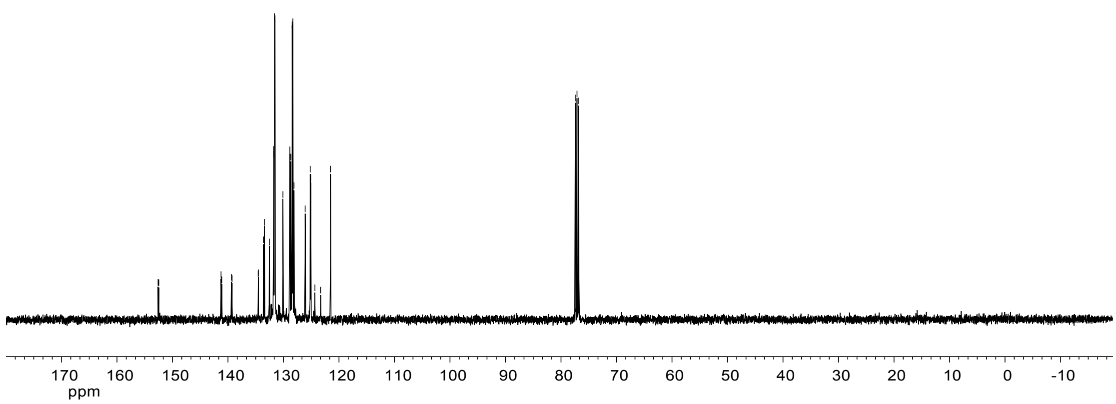
3l, ^{31}P NMR, 162 MHz, $CDCl_3$

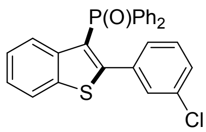


3m, ^{1}H NMR, 400 MHz, $CDCl_3$

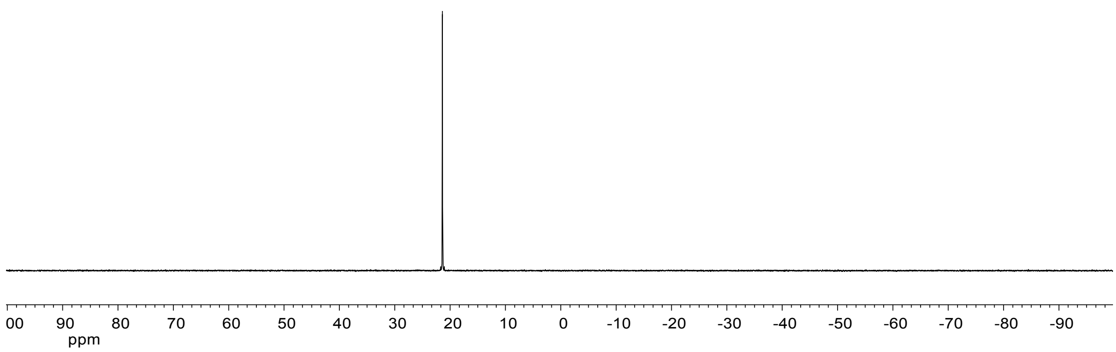


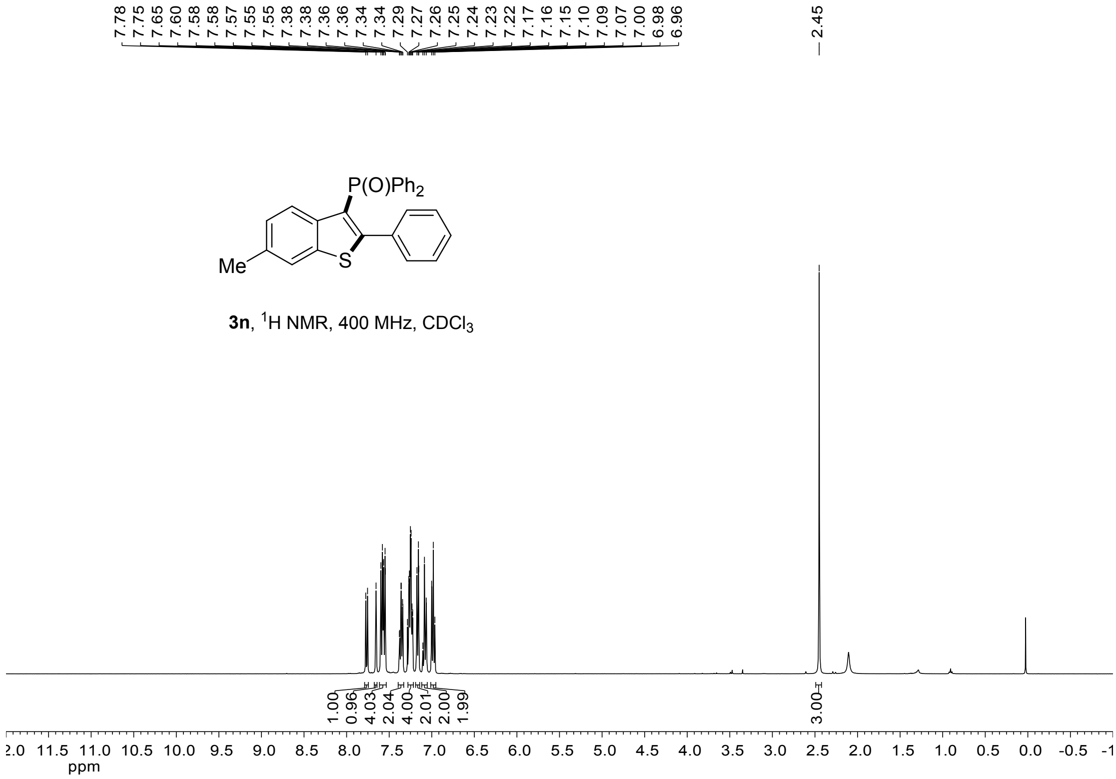
3m, ^{13}C NMR, 101 MHz, $CDCl_3$





3m, ^{31}P NMR, 162 MHz, $CDCl_3$

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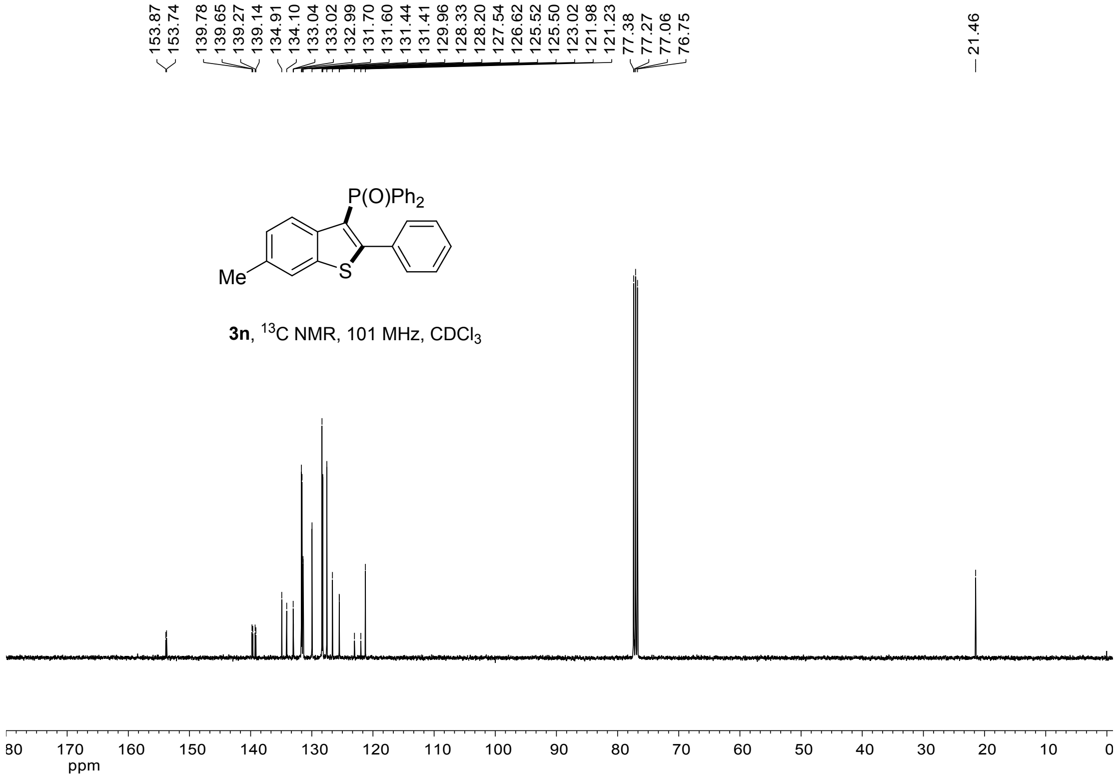
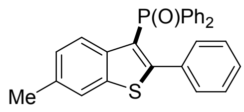
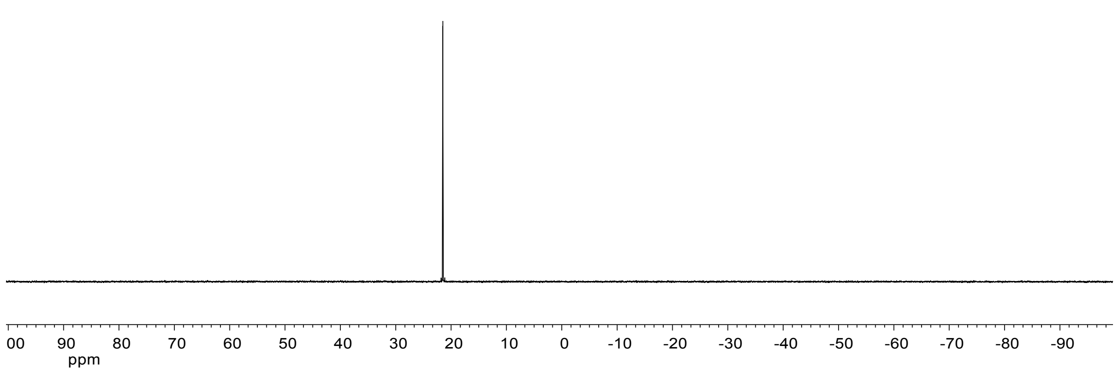
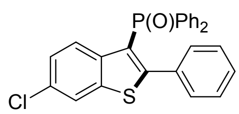
2.45
P(O)Ph2
Me
S
3n, 1H NMR, 400 MHz, CDCl3
1.00 0.96 4.03 2.04 4.00 2.01 2.00 1.99
3.00
ppm


153.87 153.74 139.78 139.65 139.27 139.14 134.91 134.10 133.04 133.02 132.99 131.70 131.60 131.44 131.41 129.96 128.33 128.20 127.54 126.62 125.52 125.50 123.02 121.98 121.23 77.38 77.27 77.06 76.75
21.46
P(O)Ph2
Me
S
3n, 13C NMR, 101 MHz, CDCl3
ppm

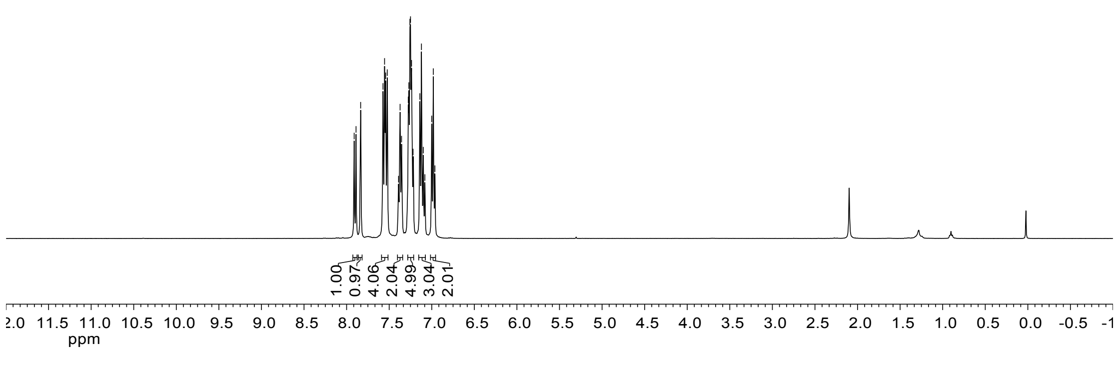


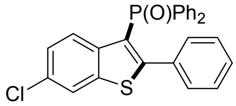
3n, ^{31}P NMR, 162 MHz, $CDCl_3$



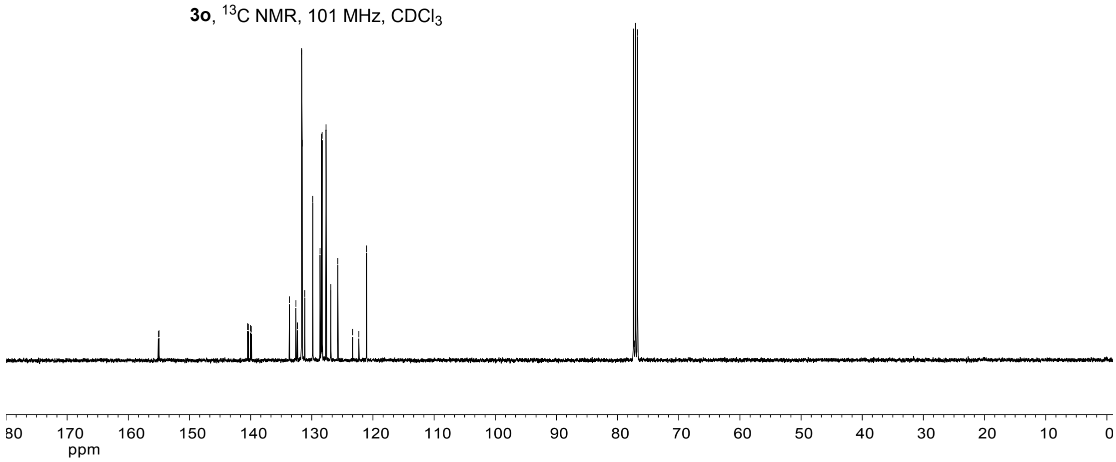


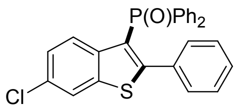
3o, ^{1}H NMR, 400 MHz, $CDCl_3$



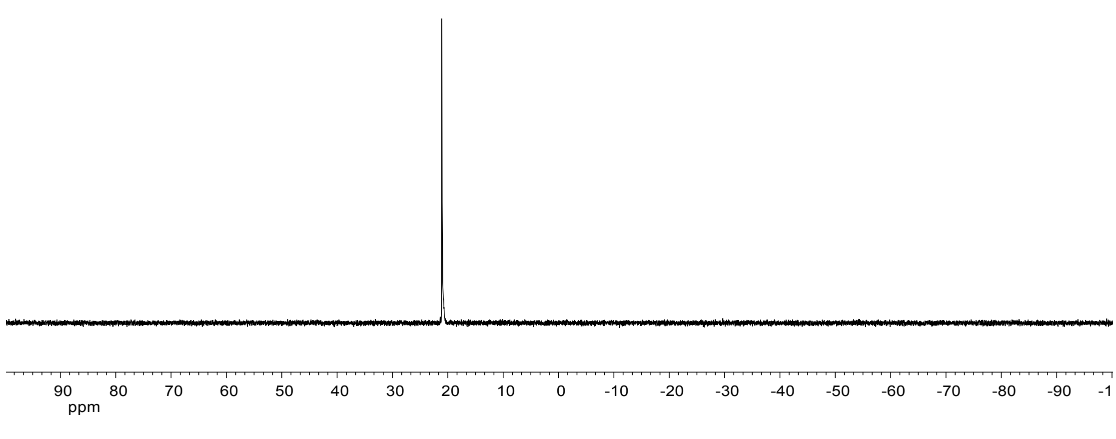


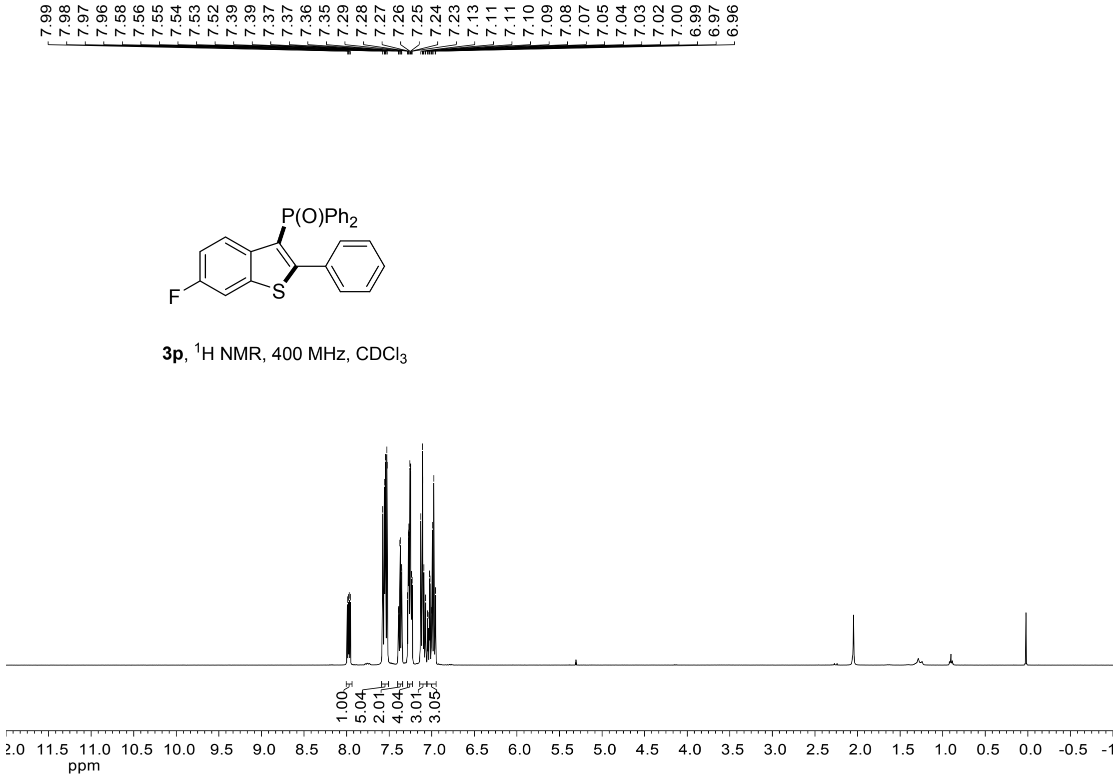
3o, ^{13}C NMR, 101 MHz, $CDCl_3$



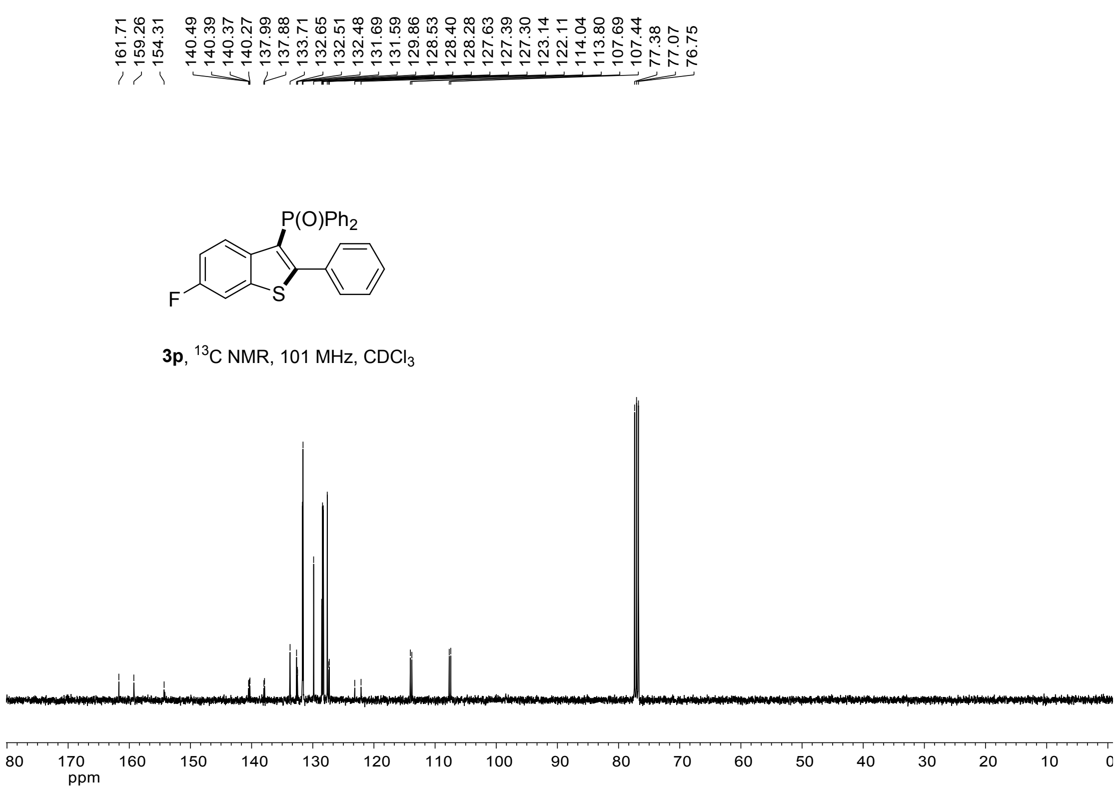


3o, ^{31}P NMR, 162 MHz, $CDCl_3$

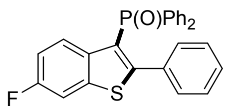




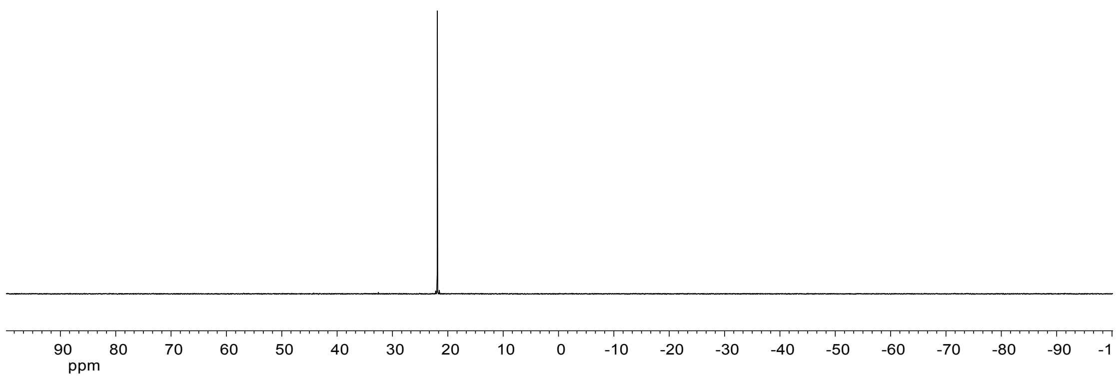
3p, ^{1}H NMR, 400 MHz, $CDCl_3$

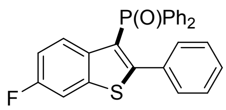


3p, ^{13}C NMR, 101 MHz, $CDCl_3$

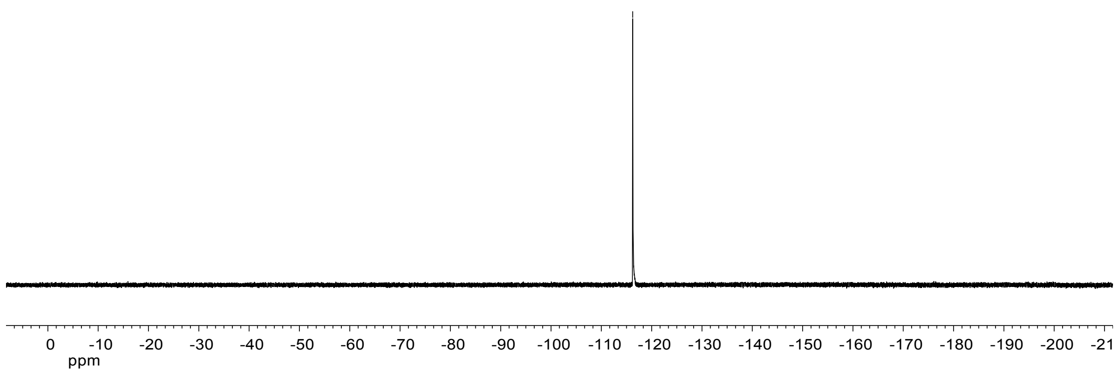


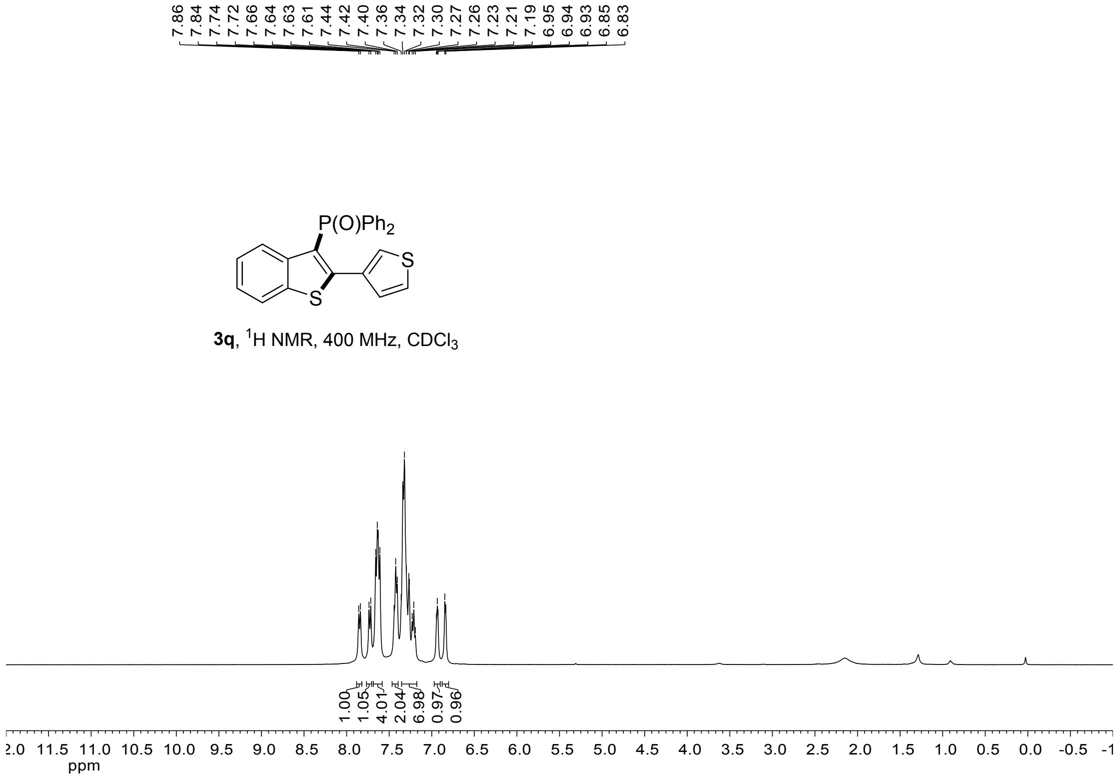
3p, ^{31}P NMR, 162 MHz, $CDCl_3$



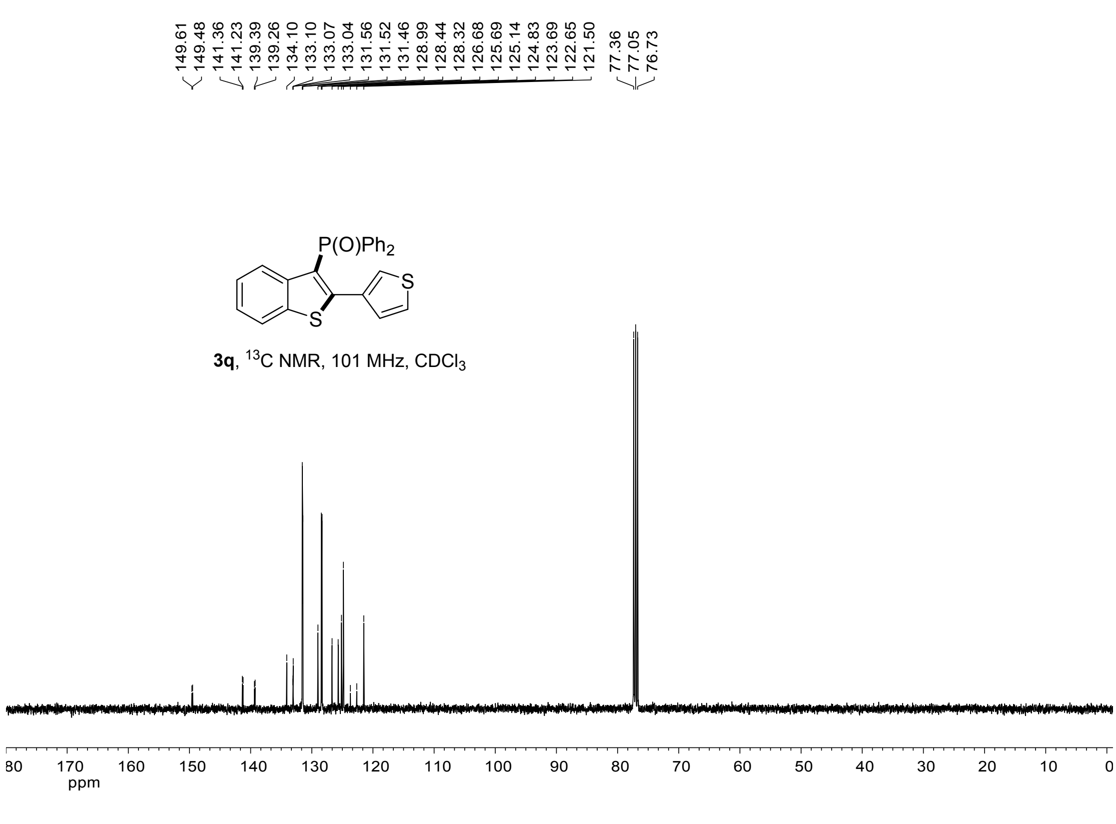


3p, ^{19}F NMR, 376 MHz, $CDCl_3$

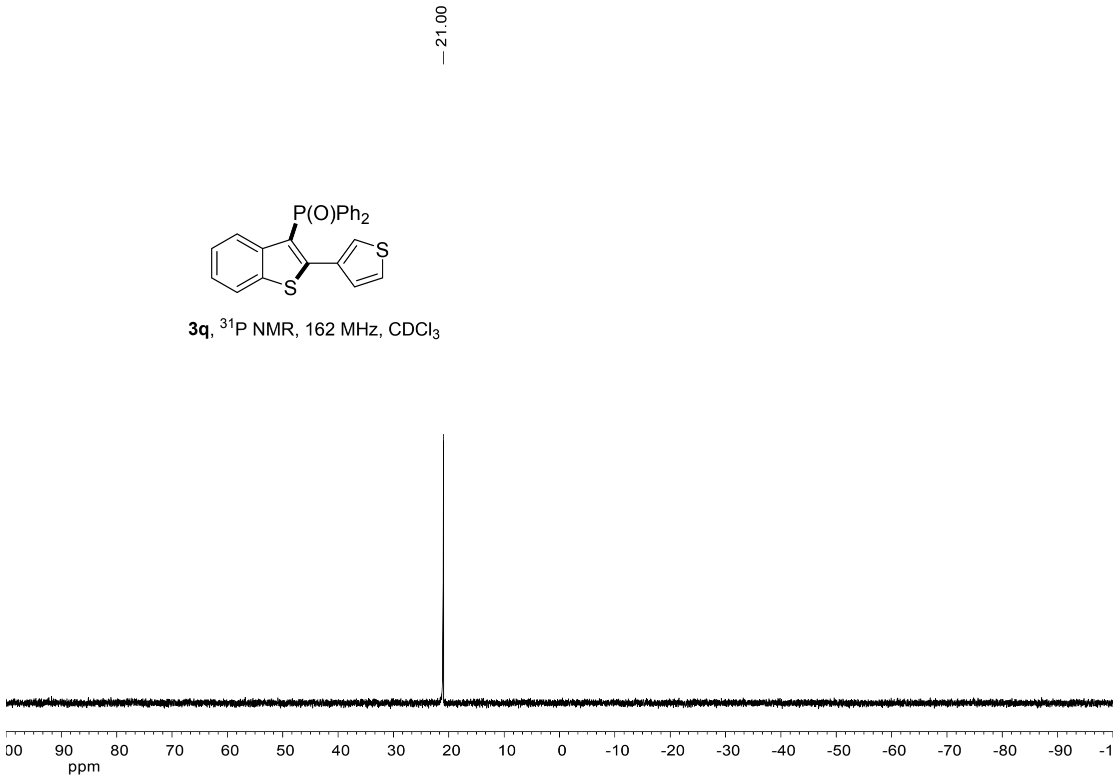




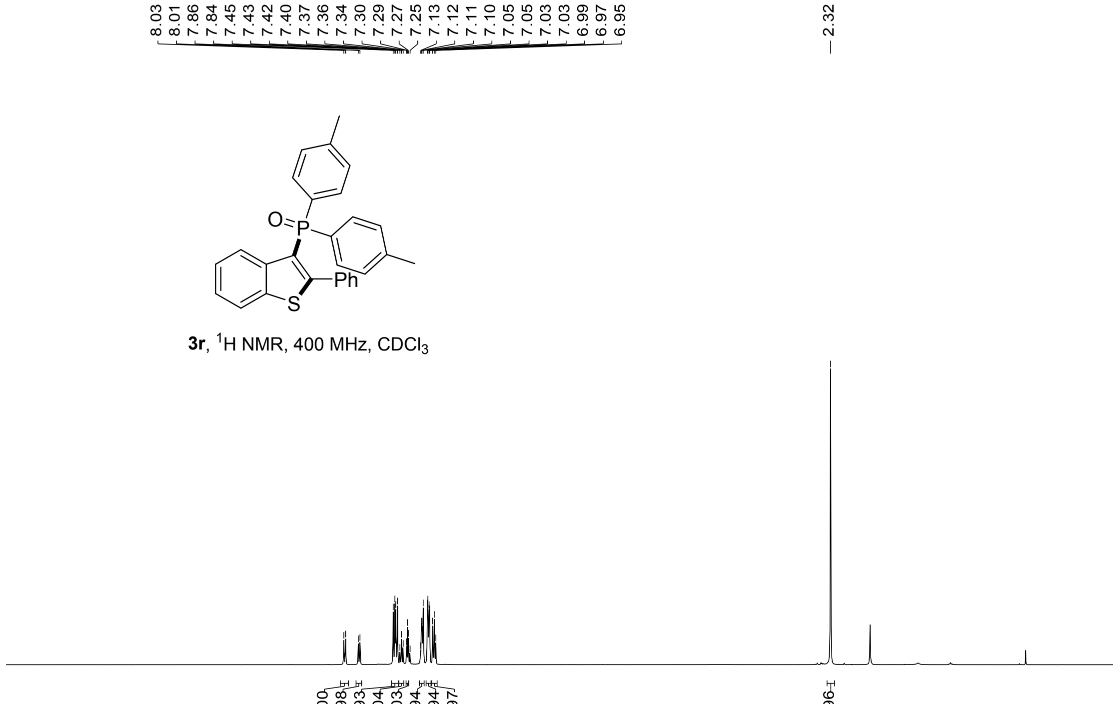
3q, ^{1}H NMR, 400 MHz, $CDCl_3$



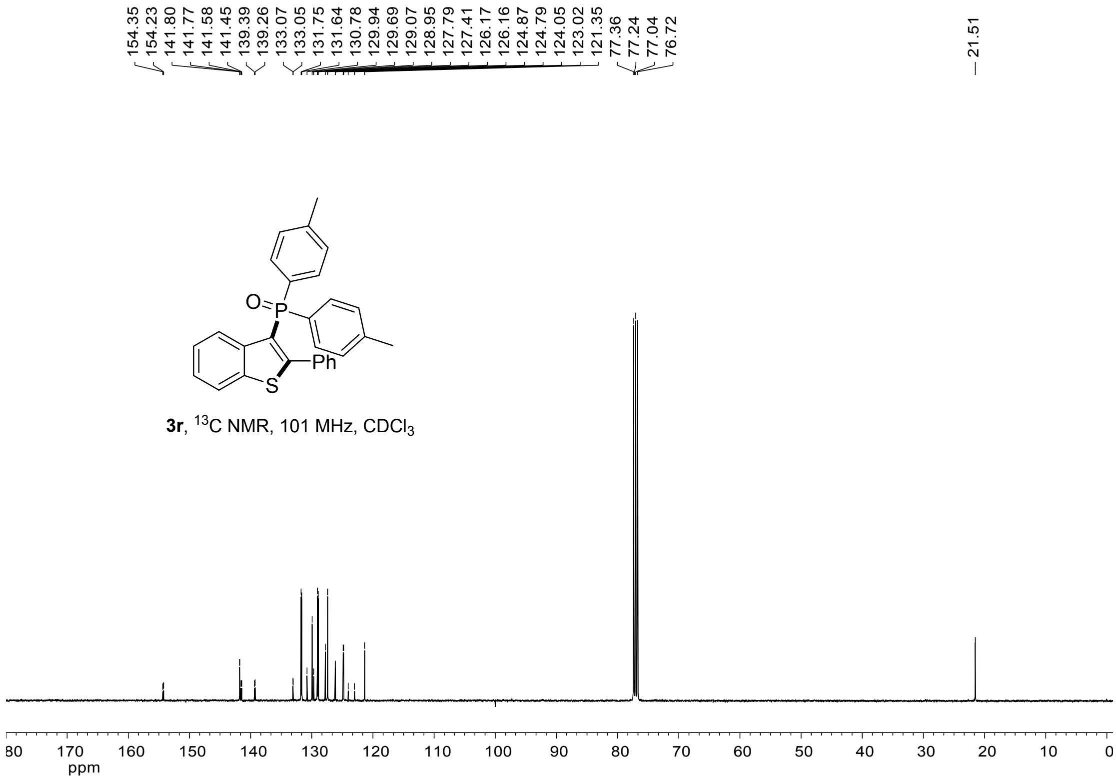
3q, ^{13}C NMR, 101 MHz, $CDCl_3$



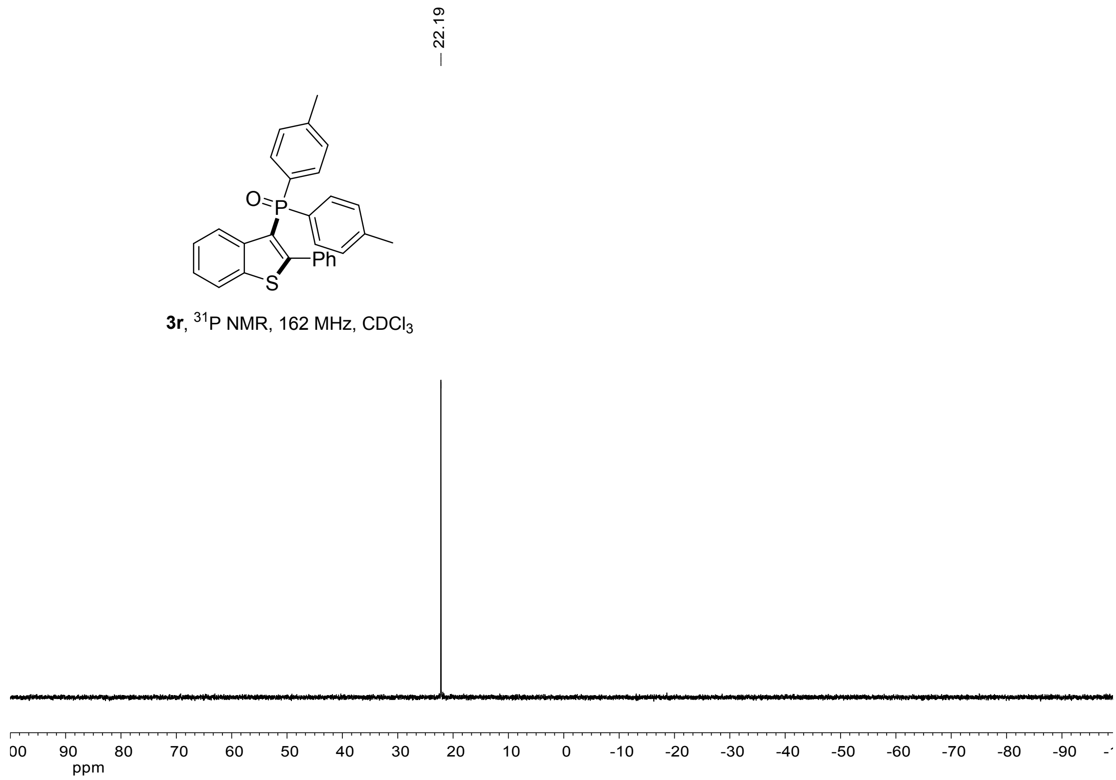
3q, ^{31}P NMR, 162 MHz, $CDCl_3$



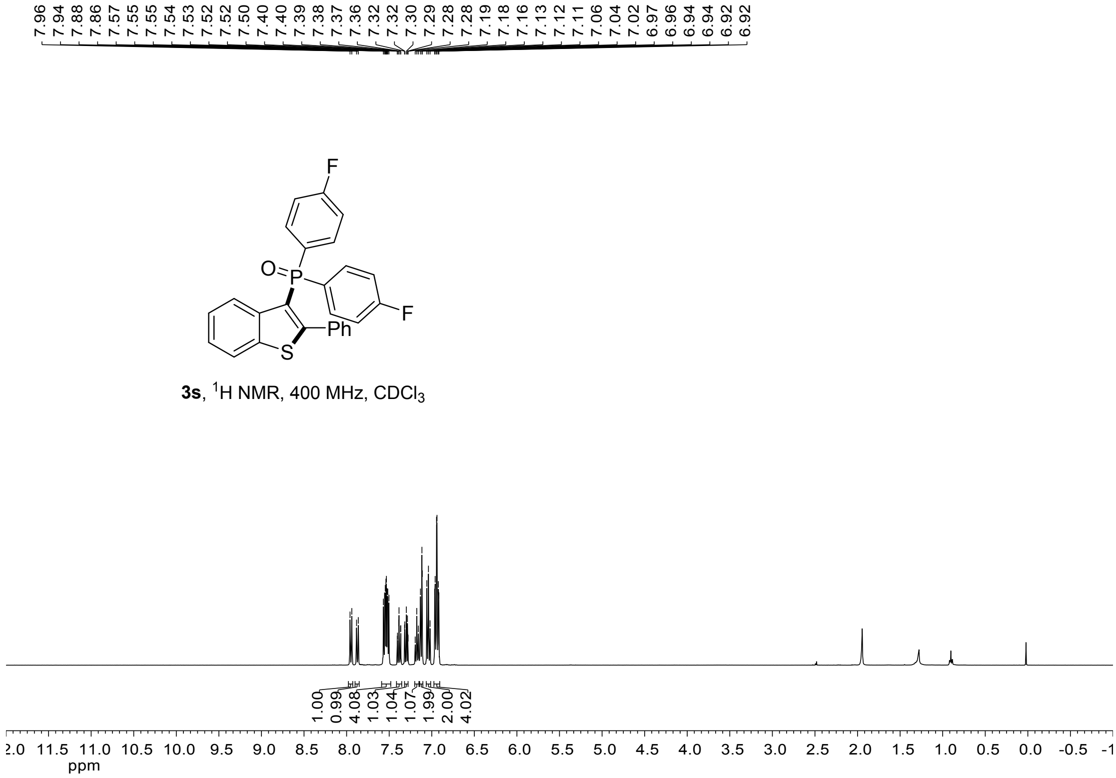
3r, ^{1}H NMR, 400 MHz, $CDCl_3$



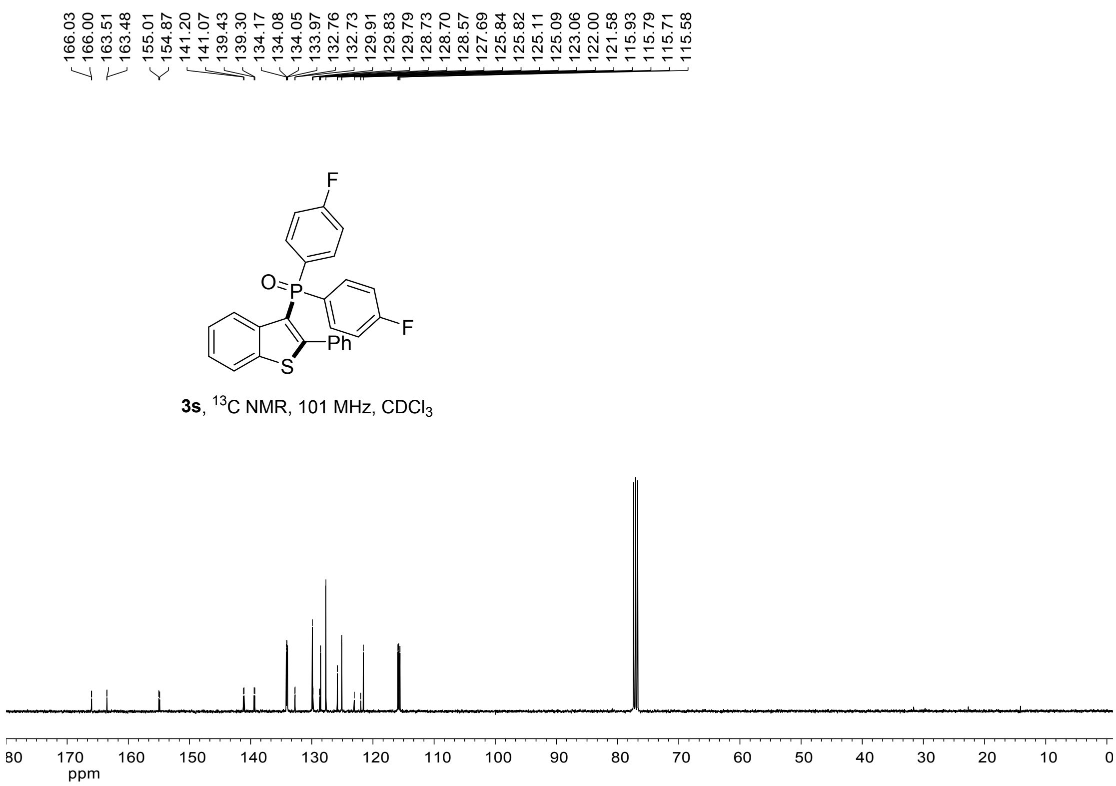
3r, ^{13}C NMR, 101 MHz, $CDCl_3$



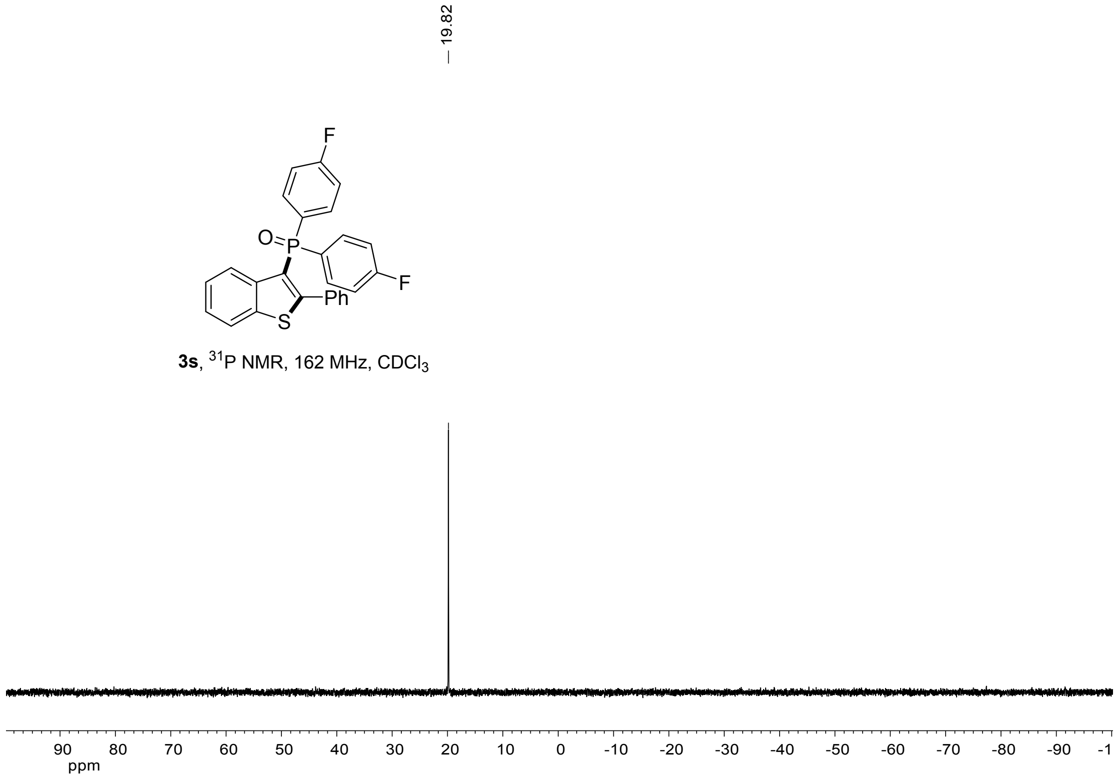
3r, ^{31}P NMR, 162 MHz, $CDCl_3$



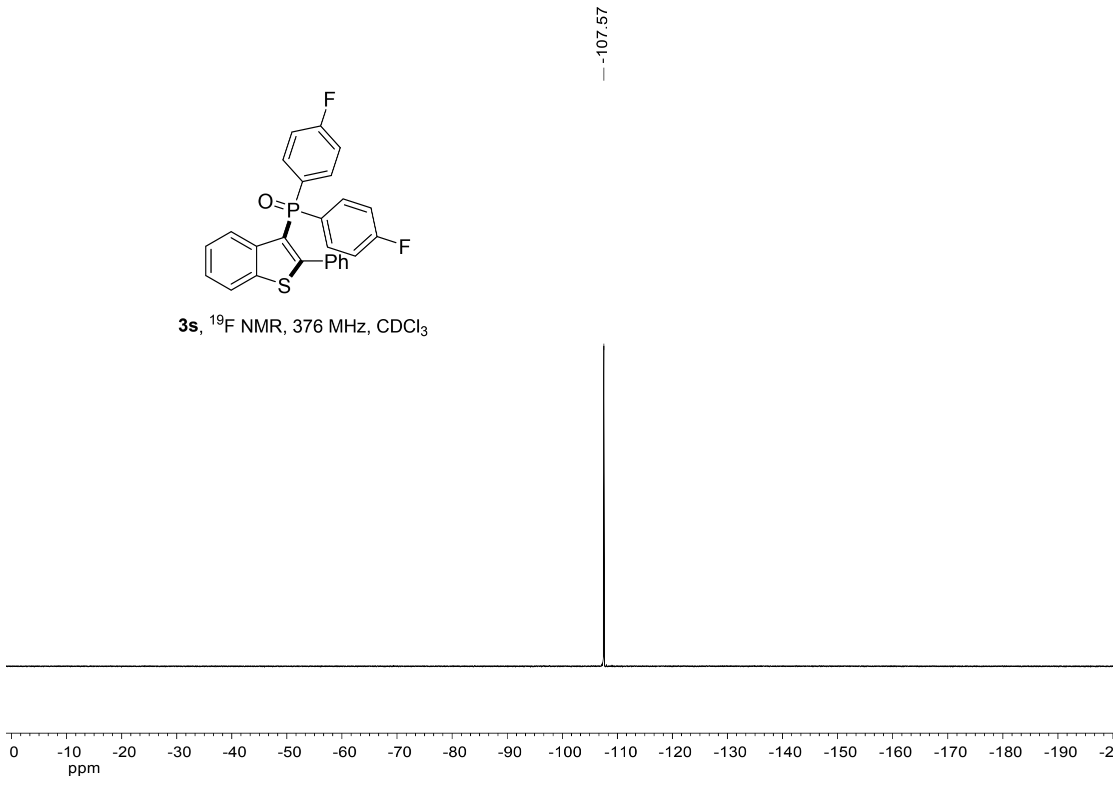
3s, ^{1}H NMR, 400 MHz, $CDCl_3$



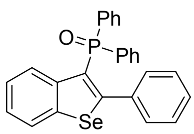
3s, ^{13}C NMR, 101 MHz, $CDCl_3$



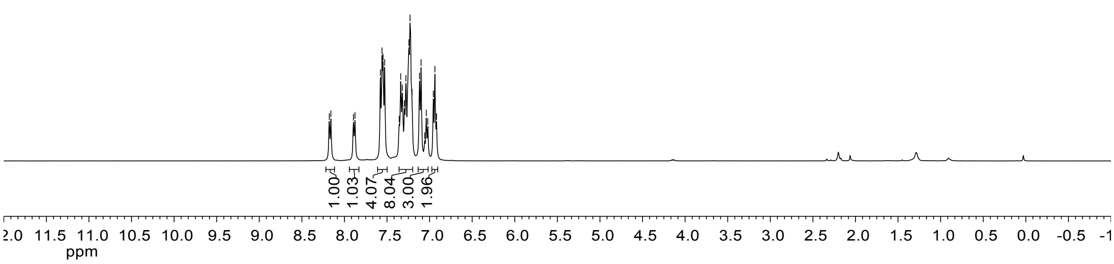
3s, ^{31}P NMR, 162 MHz, $CDCl_3$

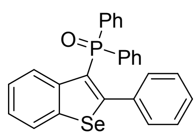


3s, ^{19}F NMR, 376 MHz, $CDCl_3$

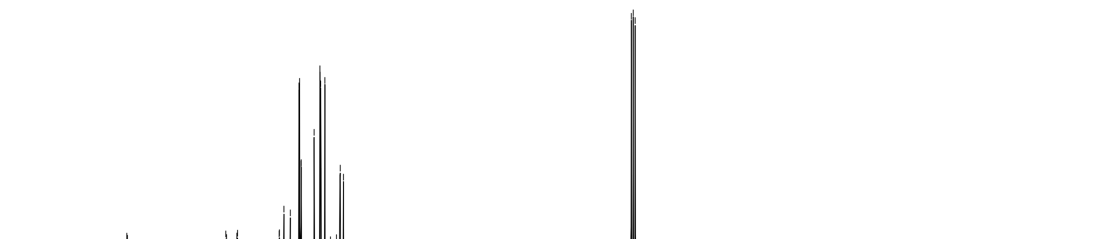


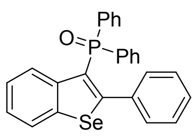
3t, ^{1}H NMR, 400 MHz, $CDCl_3$





3t, ^{13}C NMR, 101 MHz, $CDCl_3$





3t, ^{31}P NMR, 162 MHz, $CDCl_3$