

# Supporting Information

## Visible Light-Induced External Oxidant-Free Oxidative Phosphonylation of C(sp<sup>2</sup>)-H Bonds

Linbin Niu,<sup>1</sup> Jiamei Liu,<sup>1</sup> Hong Yi,<sup>1</sup> Shengchun Wang,<sup>1</sup> Xing-An Liang,<sup>1</sup> Atul K. Singh,<sup>1</sup>

Chien-Wei Chiang,<sup>1</sup> and Aiwen Lei<sup>1,2\*</sup>

1. College of Chemistry and Molecular Sciences, the Institute for Advanced Studies (IAS), Wuhan University, Wuhan, Hubei 430072, People's Republic of China
2. State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

**\*corresponding author,**

**E-mail: aiwenlei@whu.edu.cn**

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## 1. General information:

All manipulations were carried out by standard schlenk techniques. Unless otherwise stated, analytical grade solvents and commercially available reagents were used to conduct the reactions. LED irradiation was accomplished using the photochemical reactors (Figure S1). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in dichloromethane (bp. 39.8 °C). Gradient flash chromatography was conducted and eluted with a continuous gradient from dichloromethane to the methanol. All the new compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and HRMS. The known compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR. The  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. The chemical shifts ( $\delta$ ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for  $^1\text{H}$  NMR),  $\text{CDCl}_3$  (77.30 ppm for  $^{13}\text{C}$  NMR). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion + Hydrogen (M+H). Hydrogen gas content was analyzed by gas chromatography (7890-II, Tianmei, China, TCD, nitrogen as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector).



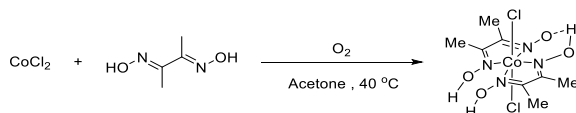
**Figure S1** The photochemical reactor (containing 24 small blue LEDs).

## 2. Experiment procedure

A solution of *p*-xylene **1a** (0.4 mmol, 2 equiv., 42.5 mg), triethyl phosphite **2a** (0.2 mmol, 33.3 mg), ammonium acetate (0.1 mmol, 0.5 equiv., 7.7 mg), photocatalyst (0.014 mmol, 7 mol%, 5.8 mg) and  $\text{Co}^{\text{III}}(\text{dmgH})(\text{dmgH}_2)\text{Cl}_2$  (0.016 mmol, 8 mol%, 5.9 mg) or oxidants ( $\text{O}_2$ , 95.3 mg  $\text{Na}_2\text{S}_2\text{O}_8$  or 90.8 mg DDQ) in degassed dry  $\text{CH}_3\text{CN}$  (3.0 mL) were stirred under nitrogen atmosphere and irradiated by 3 W blue LEDs at 25 °C for 24 h. After completion of



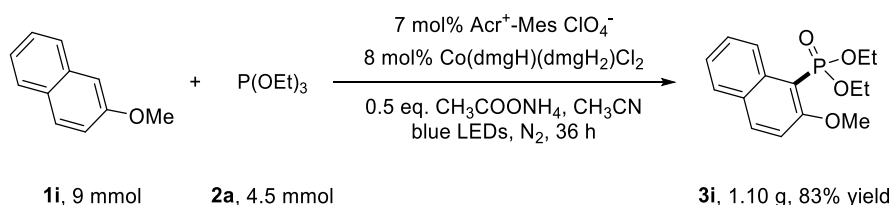
(10 mL), and diethyl ether (10 mL) to give  $\text{Co}(\text{dmgH})(\text{dmgH}_2)\text{Cl}_2$  (Figure S2).



**Figure S2** Preparation method of  $\text{Co}(\text{dmgH})(\text{dmgH}_2)\text{Cl}_2$ .<sup>1</sup>

### 3. Procedure for gram-scale reaction

A solution of 2-methoxynaphthalene **1i** (9 mmol, 2 equiv., 1.42 g), triethyl phosphite **2a** (4.5 mmol, 0.748 g),  $\text{Acr}^+\text{-Mes ClO}_4^-$  (0.315 mmol, 7 mol%, 130.5 mg),  $\text{Co}^{\text{III}}(\text{dmgH})(\text{dmgH}_2)\text{Cl}_2$  (0.36 mmol, 8 mol%, 132.8 mg) and ammonium acetate (2.25 mmol, 0.5 equiv., 173.3 mg) in degassed  $\text{CH}_3\text{CN}$  (30.0 mL) were stirred under a nitrogen atmosphere and irradiated by 3 W blue LEDs at 25 °C for 36 h. The aqueous solution was extracted with ethyl acetate ( $3 \times 30$  mL) and the combined extracts were dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained by flash column chromatography on silica gel (eluent: dichloromethane/methanol=100:1) in 83% yield (Figure S3).

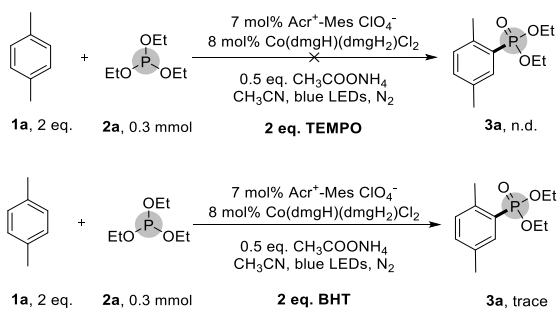


**Figure S3** Gram scale reaction of the oxidative phosphorylation of 2-methoxynaphthalene.

## 4. Mechanistic studies

### 4.1 Procedure for the radical inhibition experiments

A solution of *p*-xylene **1a** (0.4 mmol, 2 equiv., 42.5 mg), triethyl phosphite **2a** (0.2 mmol, 33.3 mg), ammonium acetate (0.1 mmol, 0.5 equiv., 7.7 mg), TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy, 0.4 mmol, 2 equiv., 62.5 mg) or BHT (Butylated hydroxytoluene, 0.4 mmol, 2 equiv., 88.4 mg),  $\text{Acr}^+\text{-Mes ClO}_4^-$  (0.014 mmol, 7 mol%, 5.8 mg) and  $\text{Co}^{\text{III}}(\text{dmgH})(\text{dmgH}_2)\text{Cl}_2$  (0.016 mmol, 8 mol%, 5.9 mg) in degassed dry  $\text{CH}_3\text{CN}$  were stirred under nitrogen atmosphere and irradiated by 3 W blue LEDs at 25 °C for 24 h. After completion of the reaction, the reaction results were monitored by TLC and GC-MS (Figure S4).



**Figure S4** The radical inhibition experiments.

## 4.2 Procedure for kinetic isotope effect (KIE) experiment

A solution of biphenyl **4d** (0.2 mmol, 30.8 mg) and 1,1'-biphenyl- $d_{10}$  **4d- $d_{10}$**  (0.2 mmol, 32.9 mg), triethyl phosphite **2a** (0.2 mmol, 33.3 mg), ammonium acetate (0.1 mmol, 0.5 equiv., 7.7 mg),  $\text{Acr}^+\text{-Mes ClO}_4^-$  (0.014 mmol, 7 mol%, 5.8 mg) and  $\text{Co}^{\text{III}}(\text{dmgh})(\text{dmgh}_2)\text{Cl}_2$  (0.016 mmol, 8 mol%, 5.9 mg) in degassed dry  $\text{CH}_3\text{CN}$  (3.0 mL) were stirred under nitrogen atmosphere and irradiated by 3 W blue LEDs at 25 °C for 0.5 h. After completion of the reaction,  $\text{H}_2$  was detected by GC-TCD. The aqueous solution was extracted with ethyl acetate ( $3 \times 10$  mL) and the combined extracts were dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product was obtained by flash column chromatography on silica gel (eluent: dichloromethane/methanol= 100:1) to afford 15% combined phosphonylation products. The ratio was  $K_{\text{H}}:K_{\text{D}} = 1.25$  determined by  $^1\text{H}$  NMR spectrum (Figure S5 and S6).

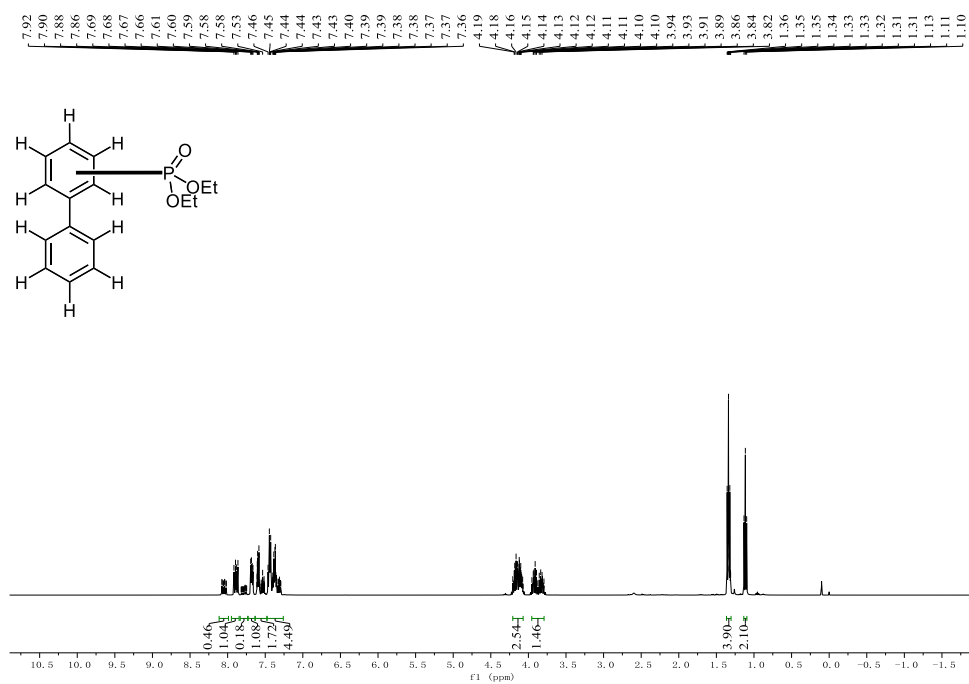


Figure S5 <sup>1</sup>H NMR spectrum of desired product of biphenyl.

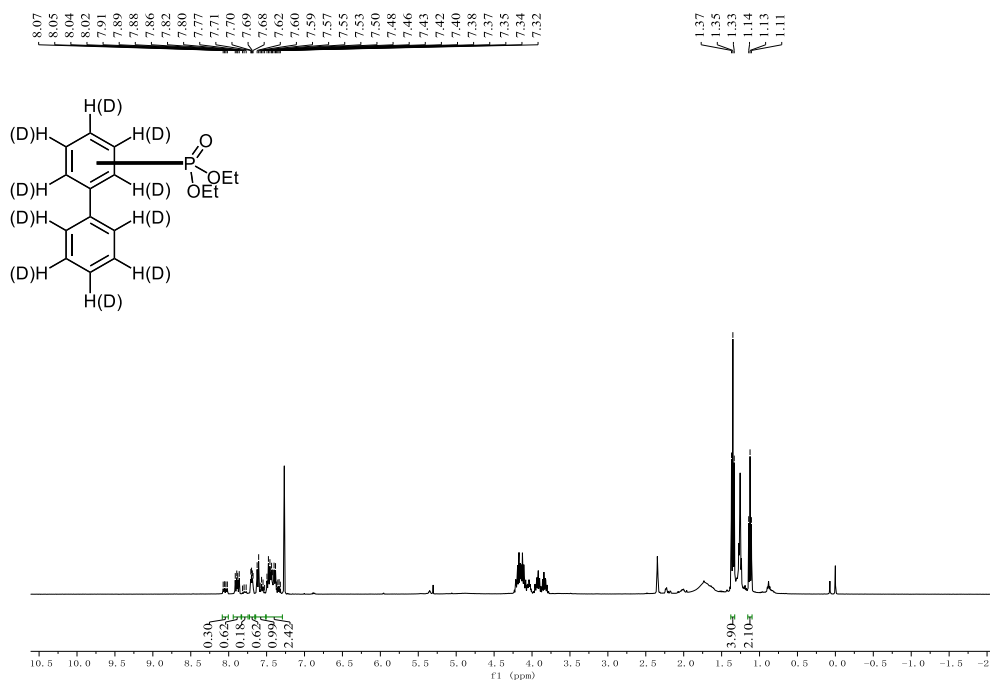
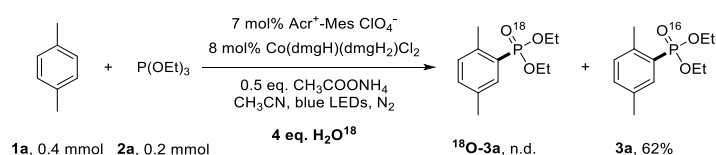


Figure S6 <sup>1</sup>H NMR spectrum of desired product from KIE experiment.

### 4.3 Procedure for H<sub>2</sub>O<sup>18</sup> labeling experiment

A solution of *p*-xylene **1a** (0.4 mmol, 2 equiv., 42.5 mg), triethyl phosphite **2a** (0.2 mmol, 33.3 mg), ammonium acetate (0.1 mmol, 0.5 equiv., 7.7 mg), H<sub>2</sub>O<sup>18</sup> (0.8 mmol, 4 equiv., 16.0 mg), Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> (0.014 mmol, 7 mol%, 5.8 mg) and Co<sup>III</sup>(dmgH)(dmgH<sub>2</sub>)Cl<sub>2</sub> (0.016 mmol,

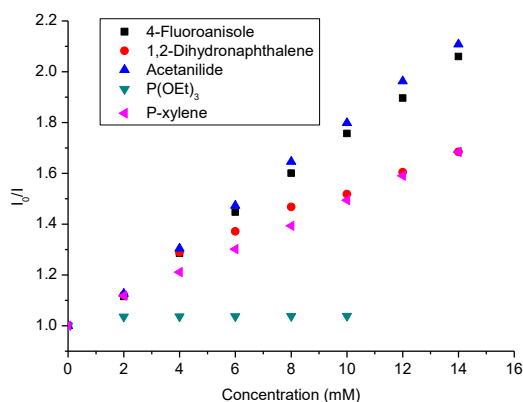
8 mol%, 5.9 mg) in degassed dry CH<sub>3</sub>CN (3.0 mL) were stirred under nitrogen atmosphere and irradiated by 3 W blue LEDs at 25 °C for 24 h. After completion of the reaction, GC-MS was used to monitor whether the desirable product marked by O<sup>18</sup> had been yielded. Then the reaction system was quenched by water. The aqueous solution was extracted with ethyl acetate (3 × 10 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **3a** was obtained by flash column chromatography on silica gel (eluent: dichloromethane/methanol= 100:1) in 62% yield (Figure S7).



**Figure S7** The result of H<sub>2</sub>O<sup>18</sup> labeling experiment.

#### 4.4 Procedure for emission quenching experiments for Acr<sup>+</sup>-MesClO<sub>4</sub><sup>-</sup>

Emission intensities were recorded using a HITACHI F-4500 Fluorescence Spectrometer. All the Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> solutions were excited at 450 nm and the emission intensity was observed at 500 nm. CH<sub>3</sub>CN was degassed with a stream of N<sub>2</sub> for 30 min. All the solutions were prepared under N<sub>2</sub> atmosphere. In a typical experiment, the emission spectrum of a 2 × 10<sup>-5</sup> M solution of Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> in CH<sub>3</sub>CN was collected (Figure S8).

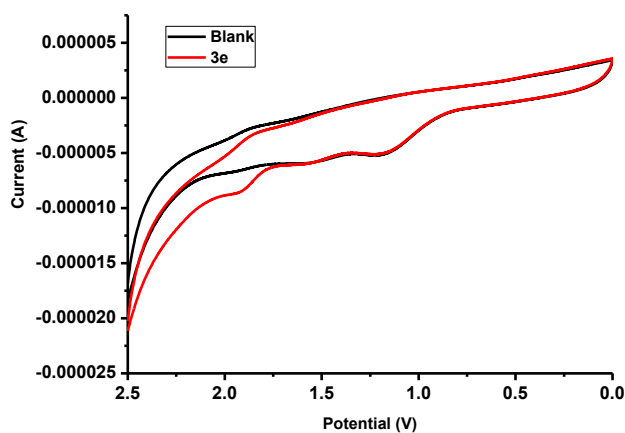


**Figure S8** Photoluminescence quenching of the photocatalyst Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> (2.00 × 10<sup>-5</sup> M) in anaerobic CH<sub>3</sub>CN.

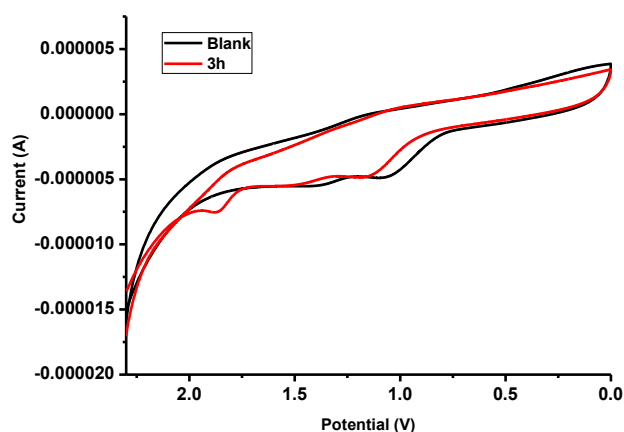
#### 4.5 The cyclic voltammetry experiments of representative products

The cyclic voltammograms were recorded in an electrolyte solution of *n*Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M)

in CH<sub>3</sub>CN using a glassy carbon disk working electrode (diameter, 1 mm), a Pt wire auxiliary electrode and a silver chloride electrode as reference electrode. The scan rate was 20 mV/s.



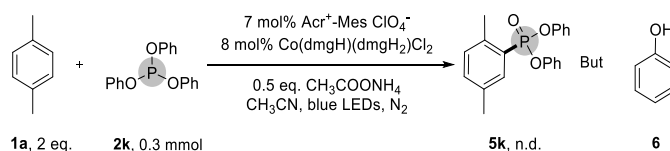
**Figure S9.** Cyclic voltammograms of **3e** ( $E_{1/2 \text{ ox}} = +1.85 \text{ V}$  vs Ag/AgCl;  $E_{1/2 \text{ ox}} = +1.82 \text{ V}$  vs SCE).



**Figure S10.** Cyclic voltammograms of **3h** ( $E_{1/2 \text{ ox}} = +1.81 \text{ V}$  vs Ag/AgCl;  $E_{1/2 \text{ ox}} = +1.78 \text{ V}$  vs SCE).

#### 4.6 Procedure for phosphorylation of *p*-xylene using P(OPh)<sub>3</sub> as phosphorylation reagent

A solution of *p*-xylene **1a** (0.4 mmol, 2 equiv., 42.5 mg), triphenyl phosphite **2k** (0.2 mmol, 62.1 mg), ammonium acetate (0.1 mmol, 0.5 equiv., 7.7 mg), Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> (0.014 mmol, 7 mol%, 5.8 mg) and Co<sup>III</sup>(dmgH)(dmgH<sub>2</sub>)Cl<sub>2</sub> (0.016 mmol, 8 mol%, 5.9 mg) in degassed dry CH<sub>3</sub>CN (3.0 mL) were stirred under nitrogen atmosphere and irradiated by 3 W blue LEDs at 25 °C for 24 h. After completion of the reaction, GC-MS was used to monitor whether the desirable product had been yielded (Figure S11).

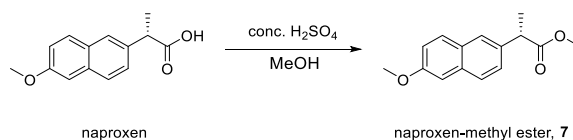


**Figure S11** P(OPh)<sub>3</sub> as as phosphonylation reagent.

## 5. Synthesis of substrate

### 5.1 Synthesis of Methyl (RS)-2-(6-methoxynaphthalen-2-yl)propanoate (methyl ester of naproxen)

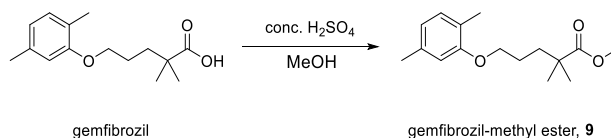
To a methanol solution (30 mL) of (RS)-2-(6-methoxynaphthalen-2-yl)propanoic acid (naproxen, 0.5 g, 2.2 mmol) was added 0.1 mL of conc. H<sub>2</sub>SO<sub>4</sub> and the reaction mixture was stirred for overnight before it was diluted with CH<sub>2</sub>Cl<sub>2</sub> (ca. 50 mL), washed with sat. NaHCO<sub>3</sub> aq. solution and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent evaporation gave the title methyl ester quantitatively (Figure S12).



**Figure S12** The synthesis of methyl ester of naproxen 7.<sup>2</sup>

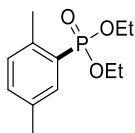
### 5.2 Synthesis of Methyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (methyl ester of gemfibrozil)

To a methanol solution (30 mL) of 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid (gemfibrozil, 0.5 g, 2.0 mmol) was added 0.1 mL conc. H<sub>2</sub>SO<sub>4</sub> and the reaction mixture was stirred for overnight before it was diluted with CH<sub>2</sub>Cl<sub>2</sub> (ca. 50 mL), washed with sat. NaHCO<sub>3</sub> aq. solution and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent evaporation gave the title methyl ester quantitatively (Figure S13).



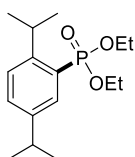
**Figure S13** The synthesis of methyl ester of gemfibrozil 9.<sup>2</sup>

## 6. Characterization of products



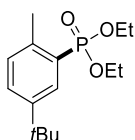
3a

**Diethyl (2,5-dimethylphenyl)phosphonate (3a):** 44.6 mg pale yellow liquid was obtained in 92% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 14.2$  Hz, 1H), 7.24 (d,  $J = 7.7$  Hz, 1H), 7.18 – 7.10 (m, 1H), 4.21 – 3.99 (m, 4H), 2.52 (s, 3H), 2.34 (s, 3H), 1.33 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.79 (d,  $J = 9.9$  Hz), 135.21 (d,  $J = 15.0$  Hz), 134.84 (d,  $J = 10.5$  Hz), 133.45 (d,  $J = 3.2$  Hz), 131.42 (d,  $J = 15.7$  Hz), 126.56 (d,  $J = 182.4$  Hz), 62.06 (d,  $J = 5.3$  Hz), 21.04, 20.94 (d,  $J = 3.4$  Hz), 16.58 (d,  $J = 6.5$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.07. **HRMS (ESI)** calcd for  $\text{C}_{12}\text{H}_{20}\text{O}_3\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 243.1145, found 243.1136.



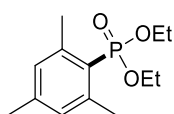
3b

**Diethyl (2,5-diisopropylphenyl)phosphonate (3b):** 37.0 mg pale yellow liquid was obtained in 62% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 – 7.72 (m, 1H), 7.41 – 7.32 (m, 2H), 4.21 – 4.06 (m, 4H), 3.62 (hept,  $J = 6.7$  Hz, 1H), 2.92 (hept,  $J = 6.9$  Hz, 1H), 1.34 (t,  $J = 7.1$  Hz, 6H), 1.25 (dd,  $J = 6.9$ , 1.7 Hz, 12H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.64 (d,  $J = 11.3$  Hz), 146.03 (d,  $J = 14.0$  Hz), 132.12 (d,  $J = 11.0$  Hz), 131.10 (d,  $J = 3.3$  Hz), 126.81 (d,  $J = 15.6$  Hz), 125.46 (d,  $J = 182.9$  Hz), 62.09 (d,  $J = 5.6$  Hz), 33.85, 30.87 (d,  $J = 3.9$  Hz), 24.49, 24.09, 16.56 (d,  $J = 6.9$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.85. **HRMS (ESI)** calcd for  $\text{C}_{16}\text{H}_{28}\text{O}_3\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 299.1771, found 299.1759.



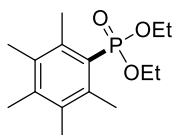
3c

**Diethyl (5-(tert-butyl)-2-methylphenyl)phosphonate (3c):** 27.3 mg pale yellow liquid was obtained in 48% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (dd,  $J = 15.5$ , 2.3 Hz, 1H), 7.45 (d,  $J = 8.1$  Hz, 1H), 7.22 – 7.14 (m, 1H), 4.21 – 4.05 (m, 4H), 2.53 (s, 3H), 1.38 – 1.30 (m, 15H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.49 (d,  $J = 13.9$  Hz), 138.86 (d,  $J = 10.2$  Hz), 131.26 (d,  $J = 15.8$  Hz), 131.00 (d,  $J = 11.3$  Hz), 129.75 (d,  $J = 3.1$  Hz), 126.36 (d,  $J = 183.2$  Hz), 62.03 (d,  $J = 5.5$  Hz), 34.71, 31.48, 20.87 (d,  $J = 3.5$  Hz), 16.57 (d,  $J = 6.6$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.38. **HRMS (ESI)** calcd for  $\text{C}_{15}\text{H}_{26}\text{O}_3\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 285.1614, found 285.1605.



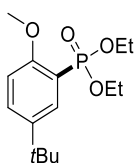
3d

**Diethyl mesitylphosphonate (3d):** 47.7 mg pale yellow liquid was obtained in 93% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.90 (d,  $J = 4.6$  Hz, 2H), 4.21 – 3.96 (m, 4H), 2.60 (d,  $J = 1.6$  Hz, 6H), 2.28 (s, 3H), 1.31 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.99 (d,  $J = 12.1$  Hz), 142.10 (d,  $J = 3.0$  Hz), 130.59 (d,  $J = 15.8$  Hz), 122.29 (d,  $J = 181.9$  Hz), 61.41 (d,  $J = 5.3$  Hz), 23.37 (d,  $J = 2.8$  Hz), 21.31 (d,  $J = 1.5$  Hz), 16.52 (d,  $J = 6.7$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.52. **HRMS (ESI)** calcd for  $\text{C}_{13}\text{H}_{22}\text{O}_3\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 257.1301, found 257.1293.



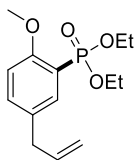
3e

**Diethyl (2,3,4,5,6-pentamethylphenyl)phosphonate (3e):** 46.1 mg pale yellow liquid was obtained in 81% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.19 – 3.99 (m, 4H), 2.58 (s, 6H), 2.26 (s, 3H), 2.22 (s, 6H), 1.31 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.53 (d,  $J = 3.4$  Hz), 139.17 (d,  $J = 11.7$  Hz), 134.02 (d,  $J = 16.1$  Hz), 123.70 (d,  $J = 181.2$  Hz), 61.39 (d,  $J = 5.5$  Hz), 20.01 (d,  $J = 3.7$  Hz), 17.70, 16.92 (d,  $J = 1.9$  Hz), 16.52 (d,  $J = 6.8$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  22.16. **HRMS (ESI)** calcd for  $\text{C}_{15}\text{H}_{26}\text{O}_3\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 285.1614, found 285.1604.



3f

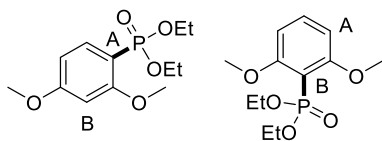
**Diethyl (5-(tert-butyl)-2-methoxyphenyl)phosphonate (3f):** 42.0 mg pale yellow liquid was obtained in 70% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (dd,  $J = 15.8, 2.6$  Hz, 1H), 7.52 (dd,  $J = 8.6, 2.6$  Hz, 1H), 6.89 (t,  $J = 7.9$  Hz, 1H), 4.26 – 4.03 (m, 4H), 3.88 (s, 3H), 1.38 – 1.28 (m, 15H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.35, 143.33 (d,  $J = 13.1$  Hz), 132.13 (d,  $J = 7.7$  Hz), 131.41, 129.17, 111.12 (d,  $J = 10.3$  Hz), 62.37 (d,  $J = 5.4$  Hz), 56.11, 34.46, 31.65, 16.66 (d,  $J = 6.3$  Hz).  $^{31}\text{P NMR}$  (162 MHz, DMSO)  $\delta$  16.75. **HRMS (ESI)** calcd for  $\text{C}_{15}\text{H}_{26}\text{O}_4\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 301.1563, found 301.1557.



3g

**Diethyl (5-allyl-2-methoxyphenyl)phosphonate (3g):** 51.7 mg pale yellow liquid was obtained in 91% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (dd,  $J = 15.2, 2.3$  Hz, 1H), 7.35 – 7.29 (m, 1H), 6.89 (dd,  $J = 8.4, 7.0$  Hz, 1H), 5.93 (ddt,  $J = 18.1, 9.4, 6.7$  Hz, 1H), 5.07 (d,  $J = 1.3$  Hz, 1H), 5.04 (dq,  $J = 6.3, 1.6$  Hz, 1H), 4.25 – 4.05 (m, 4H), 3.88 (s, 3H), 3.35 (d,  $J = 6.6$  Hz, 2H), 1.33 (t,  $J = 7.0$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.89 (d,  $J = 2.6$  Hz), 137.37, 135.35 (d,  $J = 7.2$  Hz), 134.55 (d,  $J = 2.4$  Hz), 132.11 (d,  $J = 14.1$  Hz), 116.36 (d,  $J = 186.1$  Hz), 116.20, 111.49 (d,  $J = 10.0$  Hz), 62.34, 56.09, 39.26,

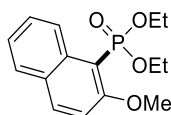
16.57 (d,  $J = 6.5$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.51. HRMS (ESI) calcd for  $\text{C}_{14}\text{H}_{22}\text{O}_4\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 285.1250, found 285.1243.



3h

**Diethyl (2,4-dimethoxyphenyl)phosphonate and Diethyl (2,6-dimethoxyphenyl)phosphonate (3h):**

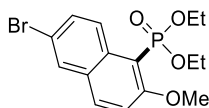
33.5 mg pale yellow liquid was obtained in 61% isolated yield. The ratio of the mixture was 25:1 (A: B) determined by  $^{31}\text{P}$  NMR.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (dd,  $J = 14.5, 8.5$  Hz, 1H), 6.53 (dt,  $J = 8.5, 2.4$  Hz, 1H), 6.47 (dd,  $J = 5.9, 2.1$  Hz, 1H), 4.18 – 4.04 (m, 4H), 3.89 – 3.81 (m, 6H), 1.32 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.07 (d,  $J = 2.8$  Hz), 163.00 (d,  $J = 3.7$  Hz), 137.05 (d,  $J = 8.4$  Hz), 108.29 (d,  $J = 194.0$  Hz), 104.71 (d,  $J = 15.2$  Hz), 98.85 (d,  $J = 10.1$  Hz), 62.14 (d,  $J = 5.4$  Hz), 56.40, 55.94, 55.71, 16.57 (d,  $J = 6.6$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  18.12, 15.66. HRMS (ESI) calcd for  $\text{C}_{12}\text{H}_{20}\text{O}_5\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 275.1043, found 275.1041.



3i

**Diethyl (2-methoxynaphthalen-1-yl)phosphonate (3i):**

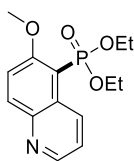
50.6 mg pale yellow liquid was obtained in 86% isolated yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.18 (d,  $J = 8.6$  Hz, 1H), 8.00 (d,  $J = 8.9$  Hz, 1H), 7.77 (d,  $J = 7.6$  Hz, 1H), 7.56 (t,  $J = 7.5$  Hz, 1H), 7.38 (t,  $J = 7.2$  Hz, 1H), 7.28 (t,  $J = 7.0$  Hz, 1H), 4.28 – 4.05 (m, 4H), 4.01 (s, 3H), 1.32 (t,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.11, 135.89 (d,  $J = 2.6$  Hz), 135.60 (d,  $J = 10.3$  Hz), 129.25 (d,  $J = 13.3$  Hz), 128.58, 128.14, 126.61 (d,  $J = 3.2$  Hz), 124.26, 113.57 (d,  $J = 10.6$  Hz), 108.94 (d,  $J = 178.9$  Hz), 61.99 (d,  $J = 5.2$  Hz), 57.23, 16.58 (d,  $J = 6.7$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  18.04. HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{20}\text{O}_4\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 295.1094, found 295.1090.



3j

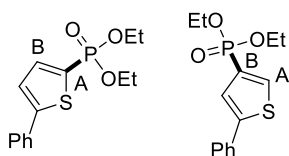
**Diethyl (6-bromo-2-methoxynaphthalen-1-yl)phosphonate (3j):**

70.9 mg pale yellow liquid was obtained in 95% isolated yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.14 (d,  $J = 9.4$  Hz, 1H), 7.91 (d,  $J = 8.6$  Hz, 2H), 7.60 (dd,  $J = 9.4, 2.2$  Hz, 1H), 7.31 (dd,  $J = 9.2, 5.5$  Hz, 1H), 4.25 – 4.07 (m, 4H), 4.01 (s, 3H), 1.32 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.20, 134.85 (d,  $J = 2.6$  Hz), 134.28 (d,  $J = 10.7$  Hz), 131.35, 130.53 (d,  $J = 13.5$  Hz), 130.37 (d,  $J = 1.3$  Hz), 128.72 (d,  $J = 2.9$  Hz), 118.25, 114.65 (d,  $J = 10.4$  Hz), 109.51 (d,  $J = 182.2$  Hz), 62.23 (d,  $J = 5.3$  Hz), 57.30, 16.64 (d,  $J = 6.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.25. HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{19}\text{BrO}_4\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 373.0199, found 373.0191.



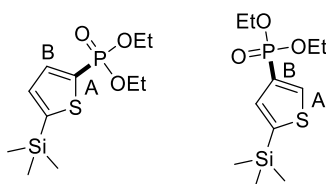
5a

**Diethyl (6-methoxyquinolin-5-yl)phosphonate (5a):** 41.9 mg pale yellow liquid was obtained in 71% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.64 (d,  $J = 8.7$  Hz, 1H), 8.81 (s, 1H), 8.30 (d,  $J = 9.3$  Hz, 1H), 7.53 (dd,  $J = 9.4, 6.4$  Hz, 1H), 7.46 (dd,  $J = 8.5, 3.6$  Hz, 1H), 4.28 – 4.08 (m, 4H), 4.06 (s, 3H), 1.33 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.91, 148.68, 143.94 (d,  $J = 12.0$  Hz), 137.23, 135.15 (d,  $J = 3.0$  Hz), 131.34 (d,  $J = 10.5$  Hz), 122.64, 116.82, 109.00 (d,  $J = 180.3$  Hz), 62.29 (d,  $J = 5.4$  Hz), 57.29, 16.60 (d,  $J = 6.7$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  16.29. **HRMS (ESI)** calcd for  $\text{C}_{14}\text{H}_{19}\text{NO}_4\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 296.1046, found 296.1038.



5b

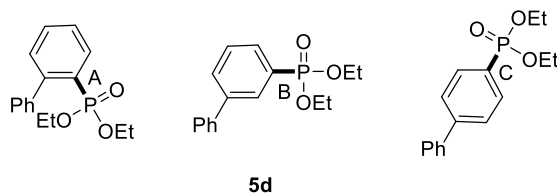
**Diethyl (5-phenylthiophen-2-yl)phosphonate and Diethyl (5-phenylthiophen-3-yl)phosphonate (5b):** 40.9 mg pale yellow liquid was obtained in 69% isolated yield. The ratio of the mixture was 3.4:1 (A: B) determined by  $^{31}\text{P NMR}$ .  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.68 – 7.56 (m, 2.75H), 7.46 – 7.38 (m, 2.50H), 7.37 – 7.30 (m, 1.75H), 4.28 – 4.07 (m, 3H), 4.07 – 3.86 (m, 1H), 1.36 (t,  $J = 7.1$  Hz, 4.60H), 1.14 (t,  $J = 7.1$  Hz, 1.40H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.88 (d,  $J = 7.5$  Hz), 137.94 (d,  $J = 11.3$  Hz), 133.36 (d,  $J = 2.0$  Hz), 132.76 (d,  $J = 16.6$  Hz), 129.93, 129.31, 128.94 (d,  $J = 2.5$  Hz), 128.34, 126.62 (d,  $J = 210.1$  Hz), 126.48, 125.21 (d,  $J = 19.6$  Hz), 124.17 (d,  $J = 17.0$  Hz), 62.93 (d,  $J = 5.3$  Hz), 62.24 (d,  $J = 5.7$  Hz), 16.52 (d,  $J = 6.8$  Hz), 16.25 (d,  $J = 6.9$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  13.22, 11.66. **HRMS (ESI)** calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_3\text{PS}^+$ ,  $[\text{M}+\text{H}]^+$ , 297.0709, found 297.0697.



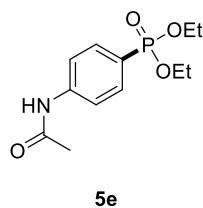
5c

**Diethyl (5-(trimethylsilyl)thiophen-2-yl)phosphonate and Diethyl (5-(trimethylsilyl)thiophen-3-yl)phosphonate (5c):** 34.5 mg pale yellow liquid was obtained in 59% isolated yield. The ratio of the mixture was 8:1 (A: B) determined by  $^1\text{H NMR}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (dd,  $J = 7.4, 3.4$  Hz, 1H), 7.58 (dd,  $J = 4.8, 2.5$  Hz, 0.10H), 7.32 – 7.24 (m, 0.90H), 4.21 – 4.05 (m, 4H), 1.37 – 1.30 (m, 6H), 0.45 (s, 1H), 0.34 (s, 8H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.37 (d,  $J = 3.6$  Hz), 137.68 (d,  $J = 13.6$  Hz), 136.93 (d,  $J = 12.4$  Hz), 134.68 (d,  $J = 20.3$  Hz), 133.53 (d,  $J = 28.9$  Hz), 132.53 (d,  $J = 206.6$  Hz), 130.19 (d,  $J = 18.8$  Hz), 128.28 (d,  $J = 18.4$  Hz), 62.80 (d,  $J = 5.4$  Hz), 61.99 (d,  $J = 5.3$  Hz), 16.51

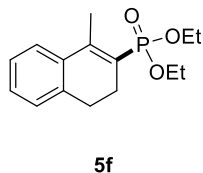
(d,  $J = 6.8$  Hz), 0.55, 0.02.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  14.56, 12.24. **HRMS (ESI)** calcd for  $\text{C}_{11}\text{H}_{22}\text{O}_3\text{PSSi}^+$ ,  $[\text{M}+\text{H}]^+$ , 293.0791, found 293.0781.



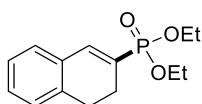
**Diethyl [1,1'-biphenyl]-ylphosphonate (5d):** 46.4 mg pale yellow liquid was obtained in 80% isolated yield. The ratio of the mixture was 5.7:1:7.3 (A: B: C) determined by **GC** and  $^1\text{H}$  NMR.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.05 (ddd,  $J = 14.3, 7.7, 1.5$  Hz, 0.46H), 7.89 (dd,  $J = 13.0, 8.3$  Hz, 1H), 7.83 – 7.74 (m, 0.18H), 7.71 – 7.64 (m, 1H), 7.62 – 7.51 (m, 1.72H), 7.49 – 7.26 (m, 4.49H), 4.22 – 4.06 (m, 2.54H), 3.96 – 3.79 (m, 1.46H), 1.39 – 1.29 (m, 3.90H), 1.11 (t,  $J = 7.1$  Hz, 2.10H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.16 (d,  $J = 9.7$  Hz), 145.31 (d,  $J = 3.2$  Hz), 141.56 (d,  $J = 4.1$  Hz), 140.05, 133.93 (d,  $J = 9.7$  Hz), 132.44 (d,  $J = 10.2$  Hz), 132.09 (d,  $J = 2.8$  Hz), 131.49 (d,  $J = 14.1$  Hz), 131.21 (d,  $J = 3.1$  Hz), 130.58 (d,  $J = 2.2$  Hz), 130.58 (d,  $J = 17.9$  Hz), 129.45, 129.08, 128.30, 127.98, 127.62, 127.57, 127.40, 127.32, 127.23, 127.01 (d,  $J = 14.6$  Hz), 62.28 (d,  $J = 5.4$  Hz), 61.92 (d,  $J = 6.1$  Hz), 16.52 (d,  $J = 6.4$  Hz), 16.20 (d,  $J = 6.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  19.01, 18.77, 18.15. **HRMS (ESI)** calcd for  $\text{C}_{16}\text{H}_{20}\text{O}_3\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 291.1145, found 291.1139.



**Diethyl (4-acetamidophenyl)phosphonate (5e):** 32.0 mg pale yellow liquid was obtained in 59% isolated yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.57 (s, 1H), 7.75 – 7.67 (m, 4H), 4.17 – 3.99 (m, 4H), 2.21 (s, 3H), 1.31 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.46, 142.60 (d,  $J = 3.1$  Hz), 133.06 (d,  $J = 10.8$  Hz), 122.52 (d,  $J = 197.7$  Hz), 119.46 (d,  $J = 15.1$  Hz), 62.48 (d,  $J = 5.4$  Hz), 24.90, 16.56 (d,  $J = 6.5$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  18.78. **HRMS (ESI)** calcd for  $\text{C}_{12}\text{H}_{19}\text{NO}_4\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 272.1046, found 272.1041.

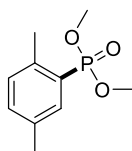


**Diethyl (1-methyl-3,4-dihydronaphthalen-2-yl)phosphonate (5f):** 25.2 mg pale yellow liquid was obtained in 45% isolated yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 – 7.42 (m, 1H), 7.28 – 7.24 (m, 2H), 7.18 – 7.15 (m, 1H), 4.19 – 4.02 (m, 4H), 2.74 (t,  $J = 7.7$  Hz, 2H), 2.53 – 2.44 (m, 5H), 1.34 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.76 (d,  $J = 12.1$  Hz), 137.57 (d,  $J = 2.8$  Hz), 135.73 (d,  $J = 20.2$  Hz), 129.03, 127.57, 126.86, 124.84, 122.64 (d,  $J = 181.5$  Hz), 61.65 (d,  $J = 5.3$  Hz), 28.28 (d,  $J = 7.3$  Hz), 25.50 (d,  $J = 9.9$  Hz), 17.62 (d,  $J = 6.9$  Hz), 16.63 (d,  $J = 6.5$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.74. **HRMS (ESI)** calcd for  $\text{C}_{15}\text{H}_{22}\text{O}_3\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 281.1301, found 281.1313.



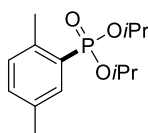
5g

**Diethyl (3,4-dihydronaphthalen-2-yl)phosphonate (5g):** 23.9 mg pale yellow liquid was obtained in 45% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 19.9$  Hz, 1H), 7.30 – 7.11 (m, 4H), 4.20 – 4.04 (m, 4H), 2.86 (t,  $J = 8.2$  Hz, 2H), 2.47 (q,  $J = 8.1$  Hz, 2H), 1.35 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.62 (d,  $J = 10.5$  Hz), 136.44 (d,  $J = 2.9$  Hz), 132.26 (d,  $J = 19.5$  Hz), 129.69, 128.25, 127.95, 127.10 (d,  $J = 1.5$  Hz), 126.69 (d,  $J = 185.2$  Hz), 62.07 (d,  $J = 5.3$  Hz), 27.42 (d,  $J = 8.3$  Hz), 22.98 (d,  $J = 9.1$  Hz), 16.67 (d,  $J = 6.3$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  19.93. **HRMS (ESI)** calcd for  $\text{C}_{14}\text{H}_{20}\text{O}_3\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 267.1145, found 267.1137.



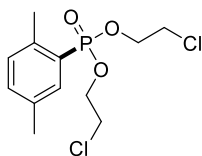
5h

**Dimethyl (2,5-dimethylphenyl)phosphonate (5h):** 21.4 mg pale yellow liquid was obtained in 50% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 14.5$  Hz, 1H), 7.31 – 7.23 (m, 1H), 7.16 (t,  $J = 6.7$  Hz, 1H), 3.76 (d,  $J = 10.8$  Hz, 6H), 2.50 (s, 3H), 2.35 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.94 (d,  $J = 10.0$  Hz), 135.32 (d,  $J = 15.0$  Hz), 134.95 (d,  $J = 10.5$  Hz), 133.71 (d,  $J = 3.1$  Hz), 131.50 (d,  $J = 15.9$  Hz), 125.24 (d,  $J = 183.7$  Hz), 52.66 (d,  $J = 5.6$  Hz), 21.03, 20.87 (d,  $J = 3.6$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  23.07. **HRMS (ESI)** calcd for  $\text{C}_{10}\text{H}_{16}\text{O}_3\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 215.0832, found 215.0836.



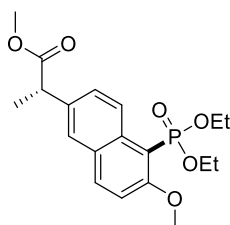
5i

**Diisopropyl (2,5-dimethylphenyl)phosphonate (5i):** 38.9 mg pale yellow liquid was obtained in 72% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 14.9$  Hz, 1H), 7.21 (d,  $J = 7.8$  Hz, 1H), 7.15 – 7.10 (m, 1H), 4.75 – 4.62 (m, 2H), 2.51 (s, 3H), 2.34 (s, 3H), 1.38 (d,  $J = 6.2$  Hz, 6H), 1.33 (d,  $J = 6.2$  Hz, 0.8H), 1.22 (d,  $J = 6.2$  Hz, 5.2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.52 (d,  $J = 9.7$  Hz), 134.96 (d,  $J = 15.0$  Hz), 134.67 (d,  $J = 10.7$  Hz), 133.12 (d,  $J = 3.1$  Hz), 131.26 (d,  $J = 15.5$  Hz), 127.91 (d,  $J = 183.4$  Hz), 70.70 (d,  $J = 5.7$  Hz), 24.29 (d,  $J = 4.0$  Hz), 23.95 (d,  $J = 4.7$  Hz), 20.98, 20.93 (d,  $J = 3.3$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.79. **HRMS (ESI)** calcd for  $\text{C}_{14}\text{H}_{24}\text{O}_3\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 271.1458, found 271.1456.



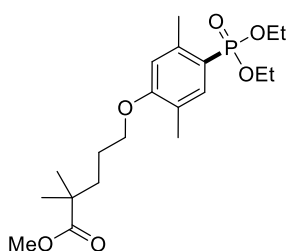
5j

**Bis(2-chloroethyl) (2,5-dimethylphenyl)phosphonate (5j):** 59.1 mg pale yellow liquid was obtained in 95% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 15.1$  Hz, 1H), 7.27 (d,  $J = 7.9$  Hz, 1H), 7.22 – 7.05 (m, 1H), 4.45 – 4.10 (m, 4H), 3.79 – 3.65 (m, 4H), 2.55 (s, 3H), 2.35 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.13 (d,  $J = 10.2$  Hz), 135.36 (d,  $J = 15.4$  Hz), 134.68 (d,  $J = 11.0$  Hz), 134.07 (d,  $J = 3.3$  Hz), 131.61 (d,  $J = 16.3$  Hz), 124.99 (d,  $J = 184.9$  Hz), 65.62 (d,  $J = 5.4$  Hz), 43.00 (d,  $J = 7.2$  Hz), 20.98 (d,  $J = 3.1$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  21.52. **HRMS** (ESI) calcd for  $\text{C}_{12}\text{H}_{18}\text{Cl}_2\text{O}_3\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 311.0365, found 311.0361.



8

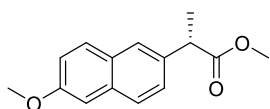
**Methyl (S)-2-(5-(diethoxyphosphoryl)-6-methoxynaphthalen-2-yl)propanoate (8):** 69.2 mg pale yellow liquid was obtained in 91% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.14 (d,  $J = 9.1$  Hz, 1H), 7.99 (d,  $J = 9.1$  Hz, 1H), 7.68 (s, 1H), 7.51 (dd,  $J = 9.1, 1.9$  Hz, 1H), 7.29 (dd,  $J = 8.8, 5.6$  Hz, 1H), 4.29 – 4.06 (m, 4H), 4.01 (s, 3H), 3.87 (q,  $J = 7.1$  Hz, 1H), 3.67 (s, 3H), 1.58 (d,  $J = 7.2$  Hz, 3H), 1.32 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.16, 162.09, 136.35, 135.79 (d,  $J = 2.7$  Hz), 134.81 (d,  $J = 10.4$  Hz), 129.41 (d,  $J = 13.5$  Hz), 128.17, 127.18 (d,  $J = 3.2$  Hz), 126.65 (d,  $J = 1.5$  Hz), 113.91 (d,  $J = 10.6$  Hz), 108.96 (d,  $J = 182.6$  Hz), 62.07 (d,  $J = 5.3$  Hz), 57.31, 52.36, 45.27, 18.66, 16.64 (d,  $J = 6.7$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.95. **HRMS** (ESI) calcd for  $\text{C}_{19}\text{H}_{26}\text{O}_6\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 381.1462, found 381.1450.



10

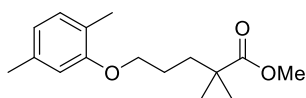
**Methyl 5-(4-(diethoxyphosphoryl)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (10):** 48.1 mg pale yellow liquid was obtained in 60% isolated yield.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 13.7$  Hz, 1H), 6.65 (d,  $J = 4.4$  Hz, 1H), 4.19 – 4.00 (m, 4H), 3.96 (t,  $J = 5.4$  Hz, 2H), 3.67 (s, 3H), 2.51 (s, 3H), 2.19 (s, 3H), 1.73 (s, 4H), 1.31 (t,  $J = 7.0$  Hz, 6H), 1.22 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.42, 160.40 (d,  $J = 3.5$  Hz), 141.64 (d,  $J = 11.4$  Hz), 136.60 (d,  $J = 11.7$  Hz), 123.85 (d,  $J = 15.4$  Hz), 113.63 (d,  $J = 17.2$  Hz), 68.12, 61.85, 51.98, 42.27, 37.17, 25.39, 25.22, 21.46 (d,  $J = 3.3$  Hz), 16.52 (d,

$J = 6.6$  Hz), 15.71.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.98. HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{34}\text{O}_6\text{P}^+$ ,  $[\text{M}+\text{H}]^+$ , 401.2088, found 401.2083.



7

**Methyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (7):** white solide was obtained in previous report.<sup>2</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.64 (m, 3H), 7.39 (d,  $J = 8.4$  Hz, 1H), 7.15 – 7.08 (m, 2H), 3.89 (s, 3H), 3.86 – 3.81 (m, 1H), 3.65 (s, 3H), 1.57 (d,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.38, 157.85, 135.88, 133.92, 129.50, 129.14, 127.41, 126.40, 126.16, 119.23, 105.78, 55.51, 52.28, 45.56, 18.83.



9

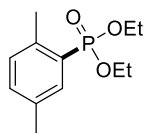
**Methyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (9):** pale yellow liquid was obtained in previous report.<sup>2</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.97 (d,  $J = 7.5$  Hz, 1H), 6.63 (d,  $J = 7.5$  Hz, 1H), 6.58 (s, 1H), 3.91 – 3.84 (m, 2H), 3.64 (s, 3H), 2.29 (s, 3H), 2.17 (s, 3H), 1.70 (d,  $J = 3.1$  Hz, 4H), 1.21 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.32, 157.04, 136.48, 130.40, 123.60, 120.78, 111.95, 67.89, 51.80, 42.20, 37.25, 25.33, 25.31, 21.53, 15.90.

## 7. References

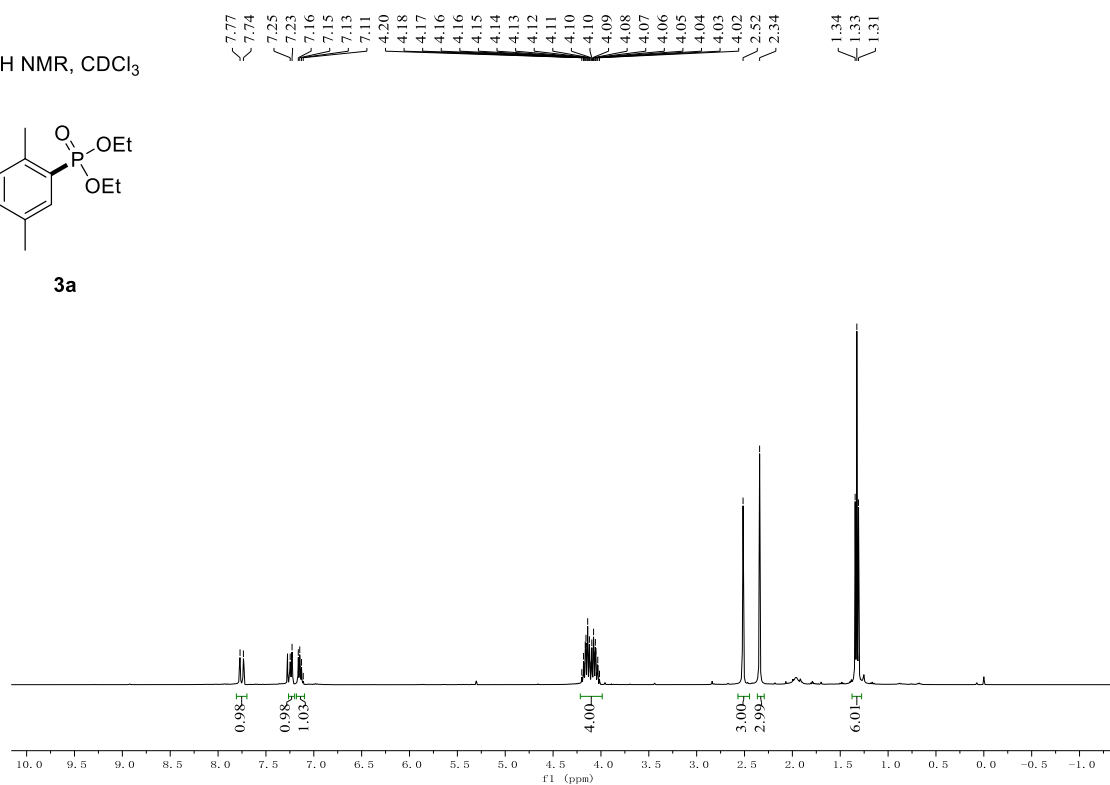
- [1] Wu, C. J.; Zhong, J. J.; Meng, Q. Y.; Lei, T.; Gao, X. W.; Tung, C. H.; Wu, L. Z. *Org. Lett.* **2015**, *17*, 884-887.
- [2] Noorduin, W. L.; Kaptein, B.; Meekes, H.; van Enkevort, W. J.; Kellogg, R. M.; Vlieg, E. *Angew. Chem., Int. Ed.* **2009**, *48*, 4581-4583.
- [3] (a) Momiyama, N.; Narumi, T.; Terada, M. *Chem. Commun.* **2015**, *51*, 16976-16979; (b) Andaloussi, M.; Lindh, J.; Sävmarker, J.; JR Sjöberg, P.; Larhed, M. *Chem. - Eur. J.* **2009**, *15*, 13069-13074; (c) Luo, H.; Liu, H.; Chen, X.; Wang, K.; Luo, X.; Wang, K. *Chem. Commun.* **2017**, *53*, 956-958.

## 8. NMR Spectra of Products

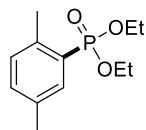
$^1\text{H}$  NMR,  $\text{CDCl}_3$



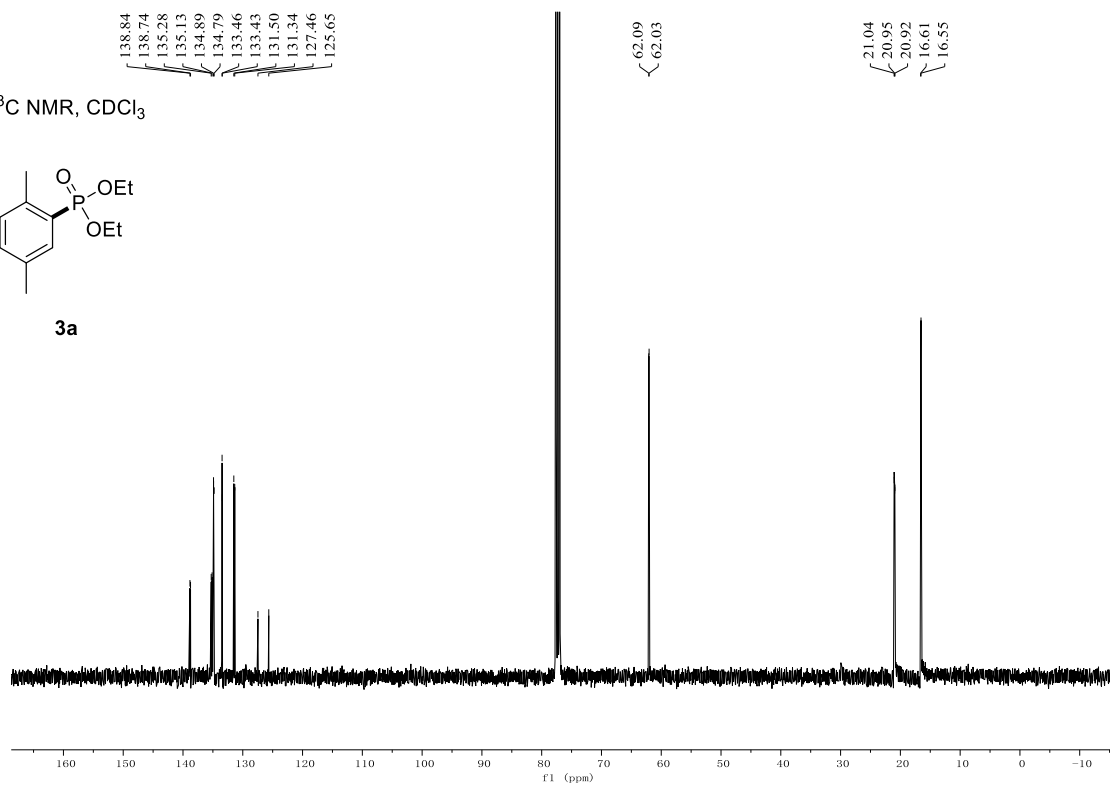
**3a**



$^{13}\text{C}$  NMR,  $\text{CDCl}_3$

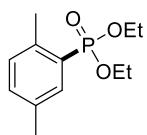


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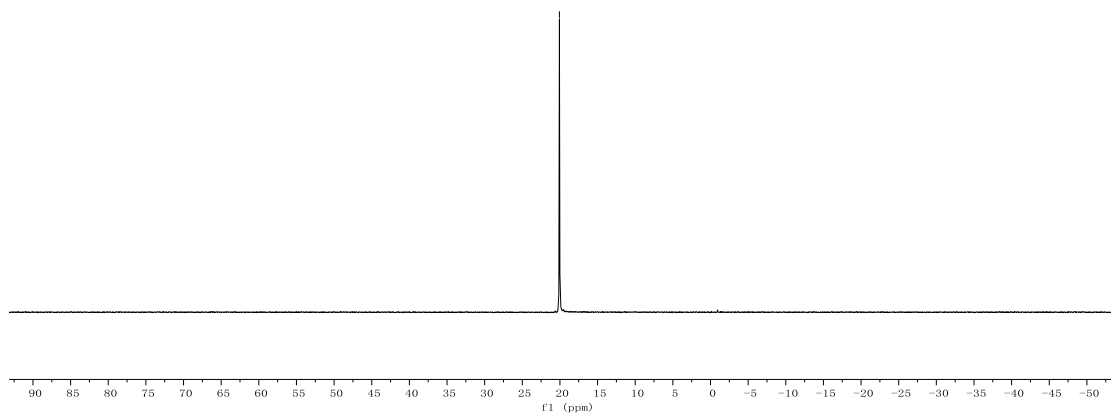


<sup>31</sup>P NMR, CDCl<sub>3</sub>

— 20.07

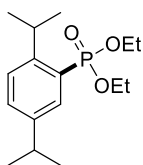


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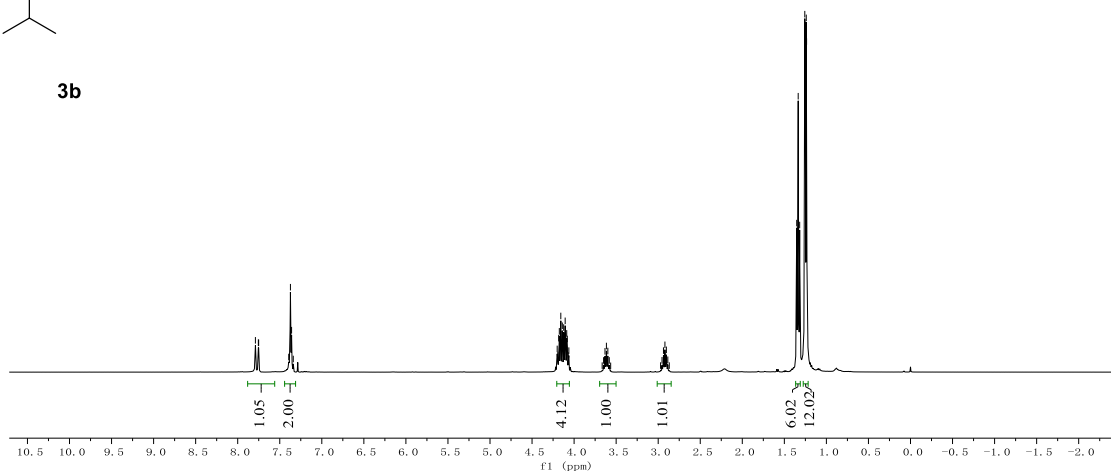


7.79  
7.75  
7.75  
7.39  
7.37  
7.36  
7.34  
4.20  
4.19  
4.18  
4.18  
4.17  
4.16  
4.14  
4.14  
4.12  
4.12  
4.11  
4.10  
4.10  
4.09  
4.08  
4.07  
4.06  
3.67  
3.65  
3.63  
3.62  
3.60  
3.58  
3.57  
2.97  
2.95  
2.94  
2.92  
2.90  
2.89  
2.87  
1.35  
1.34  
1.32  
1.26  
1.25  
1.24  
1.24

<sup>1</sup>H NMR, CDCl<sub>3</sub>



**3b**

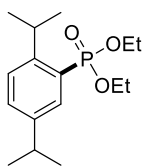


150.70  
150.59  
146.10  
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132.18  
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126.37  
124.55

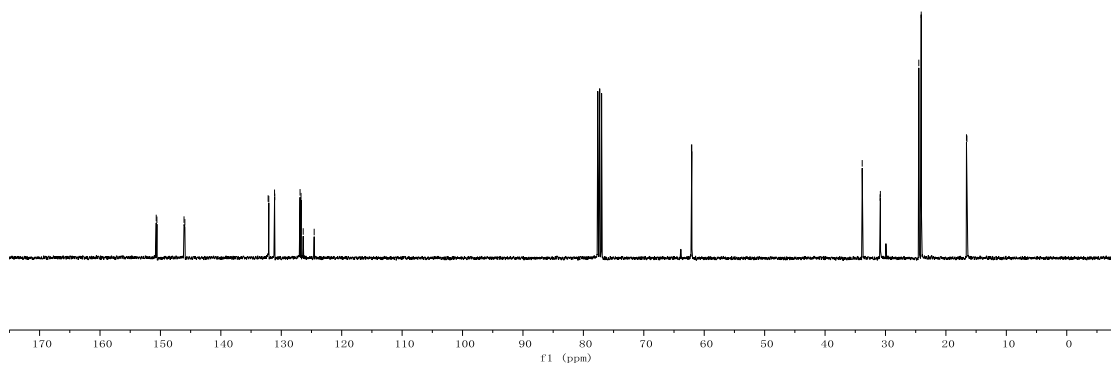
62.11  
62.06

33.85  
30.89  
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16.53

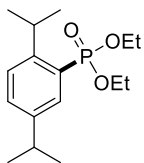
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$



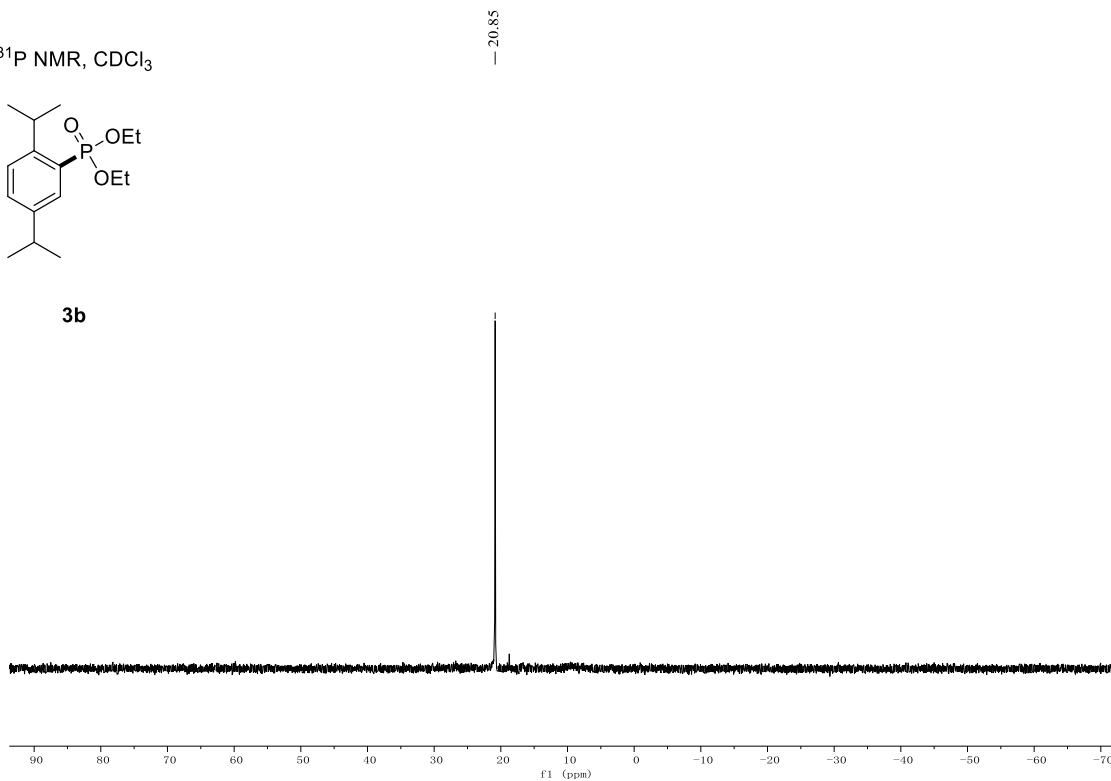
**3b**



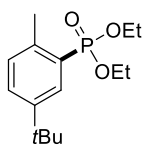
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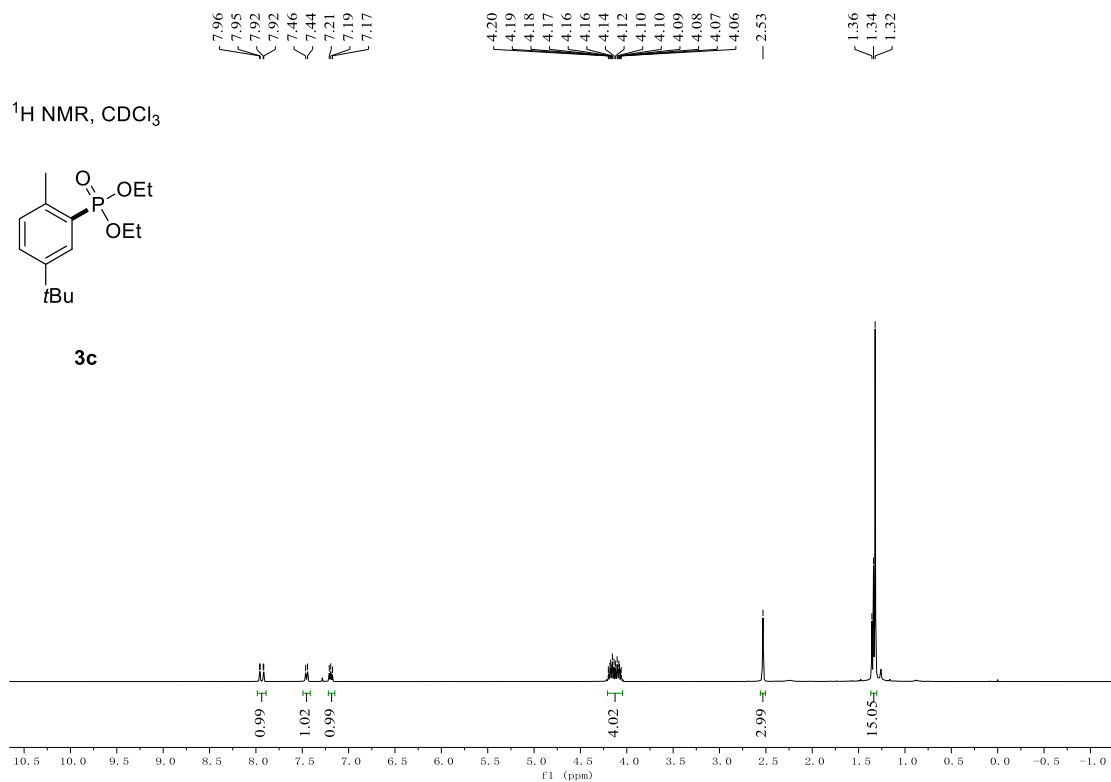
**3b**



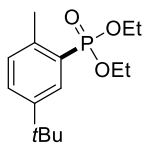
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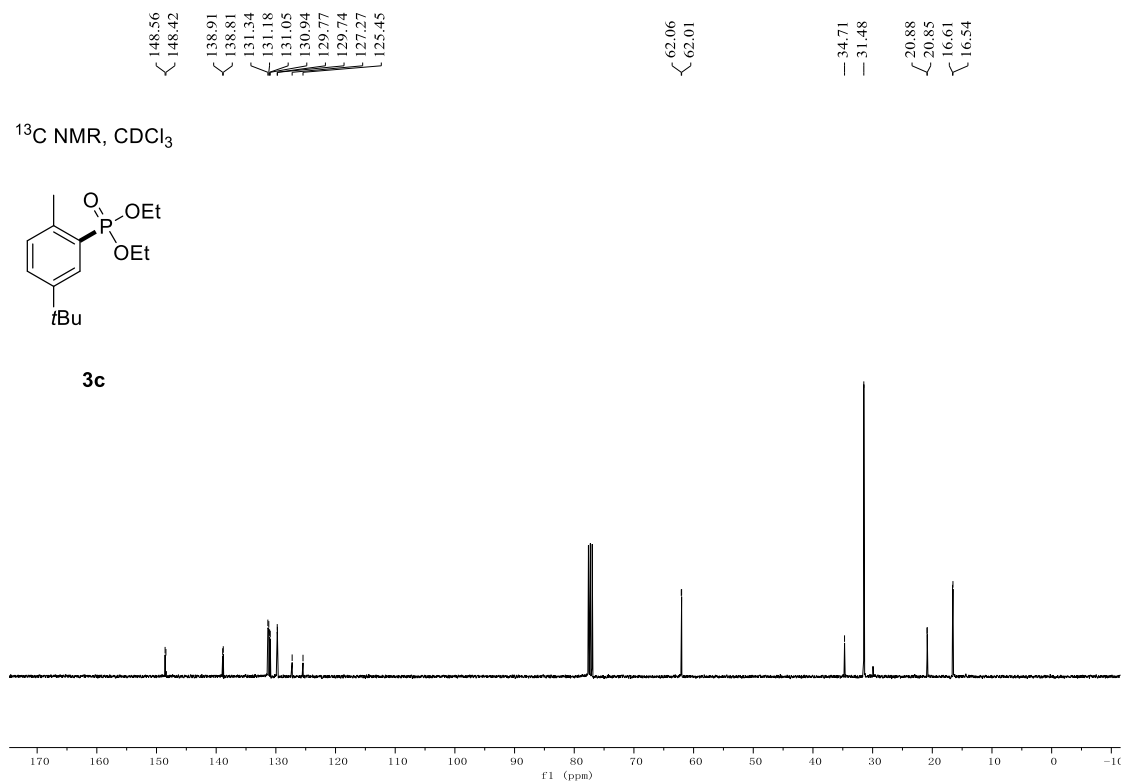
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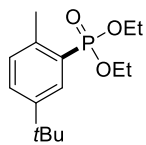
$^{13}\text{C NMR}$ ,  $\text{CDCl}_3$



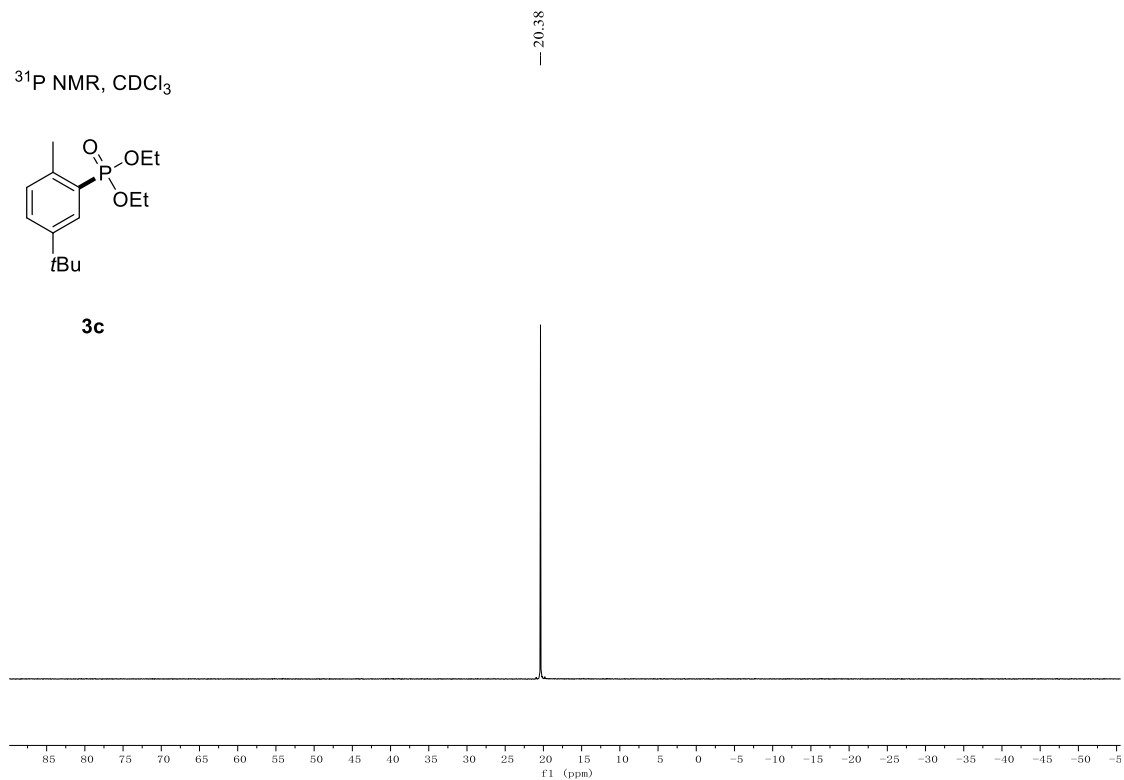
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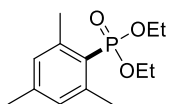
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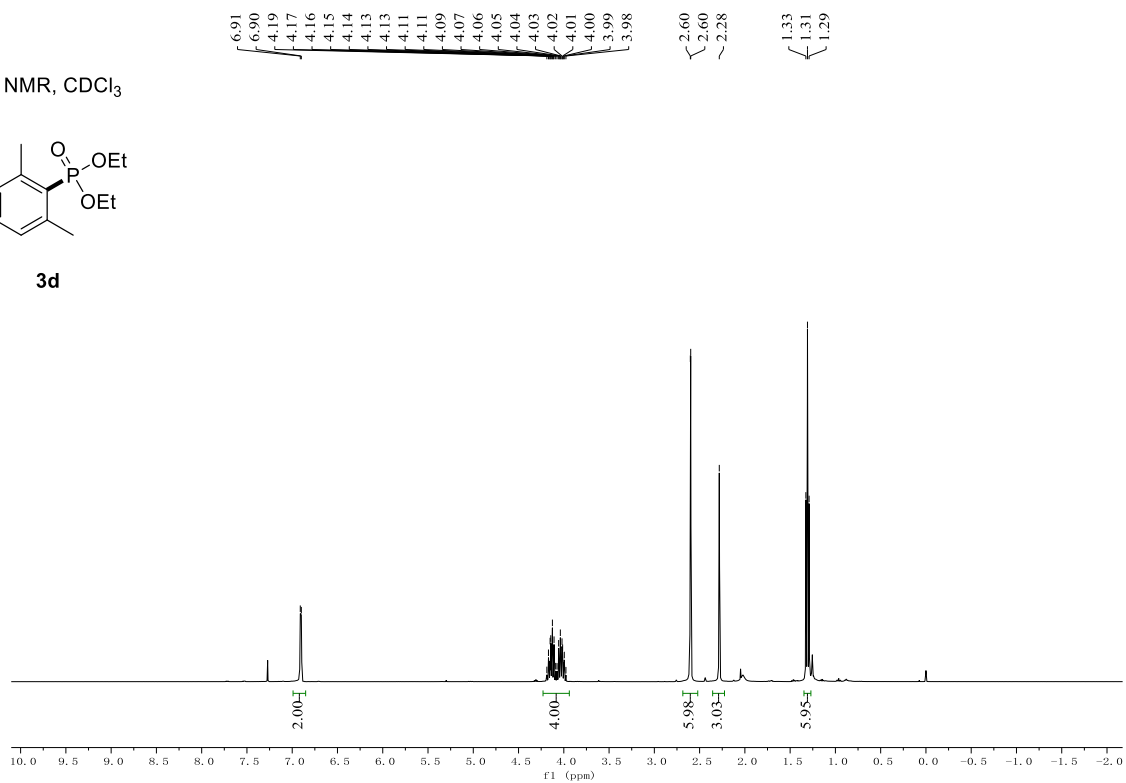
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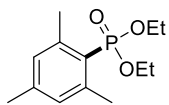
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**3d**

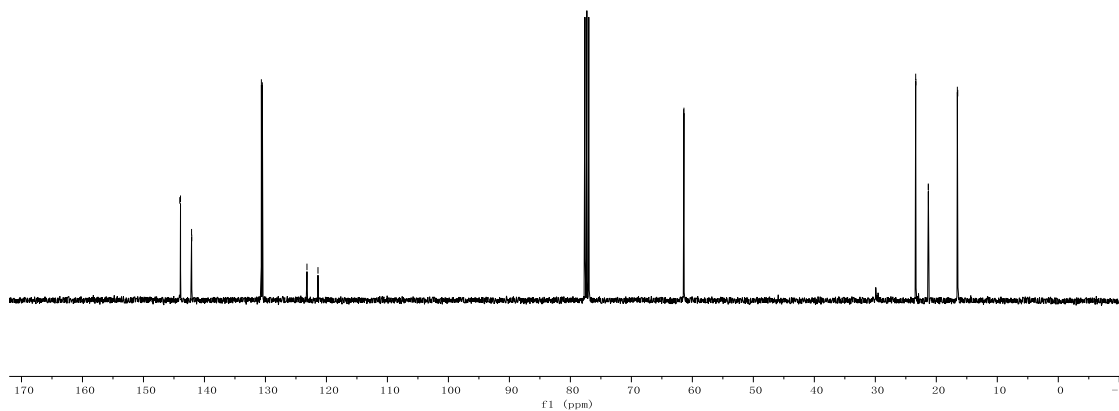


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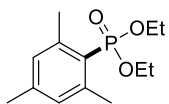


**3d**

144.05  
143.93  
142.11  
142.09  
130.67  
130.51  
123.19  
121.39  
61.43  
61.38  
23.38  
23.35  
21.32  
21.30  
16.55  
16.49

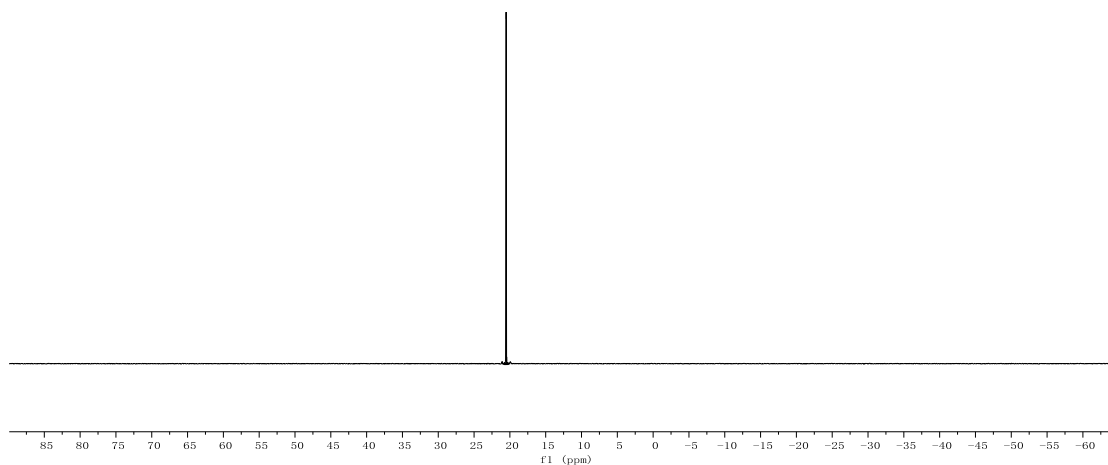


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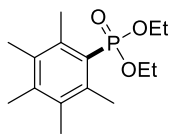


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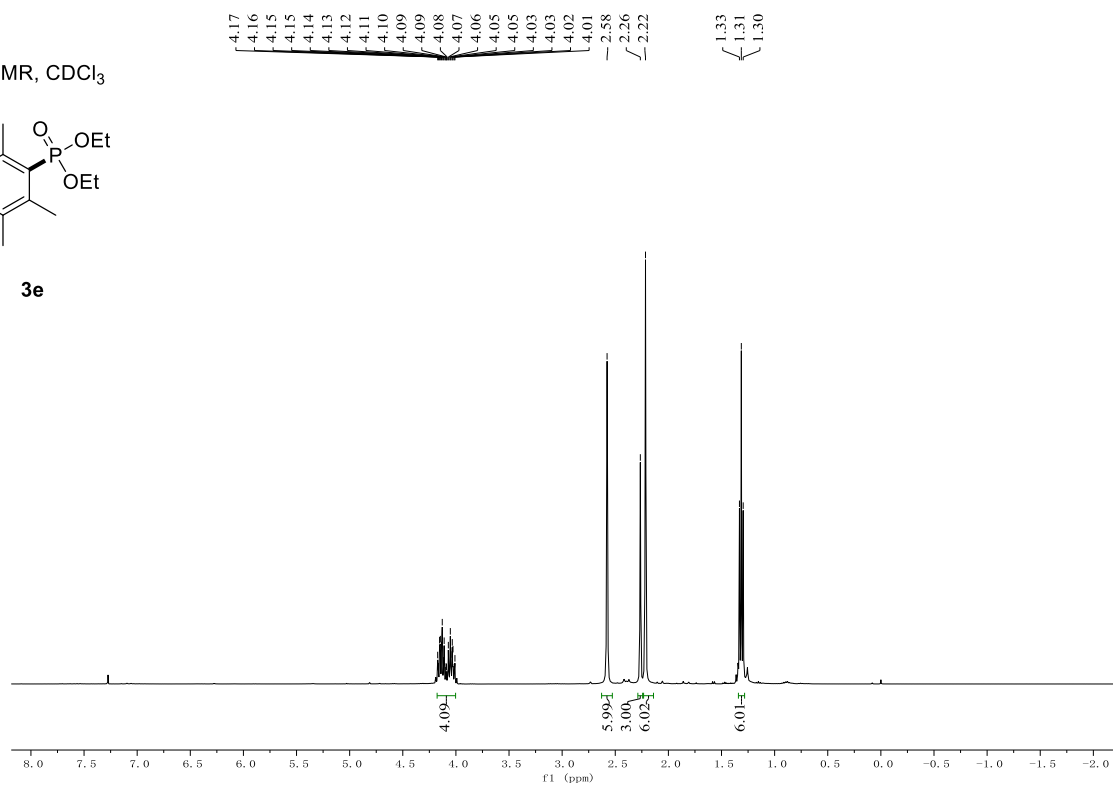
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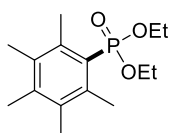
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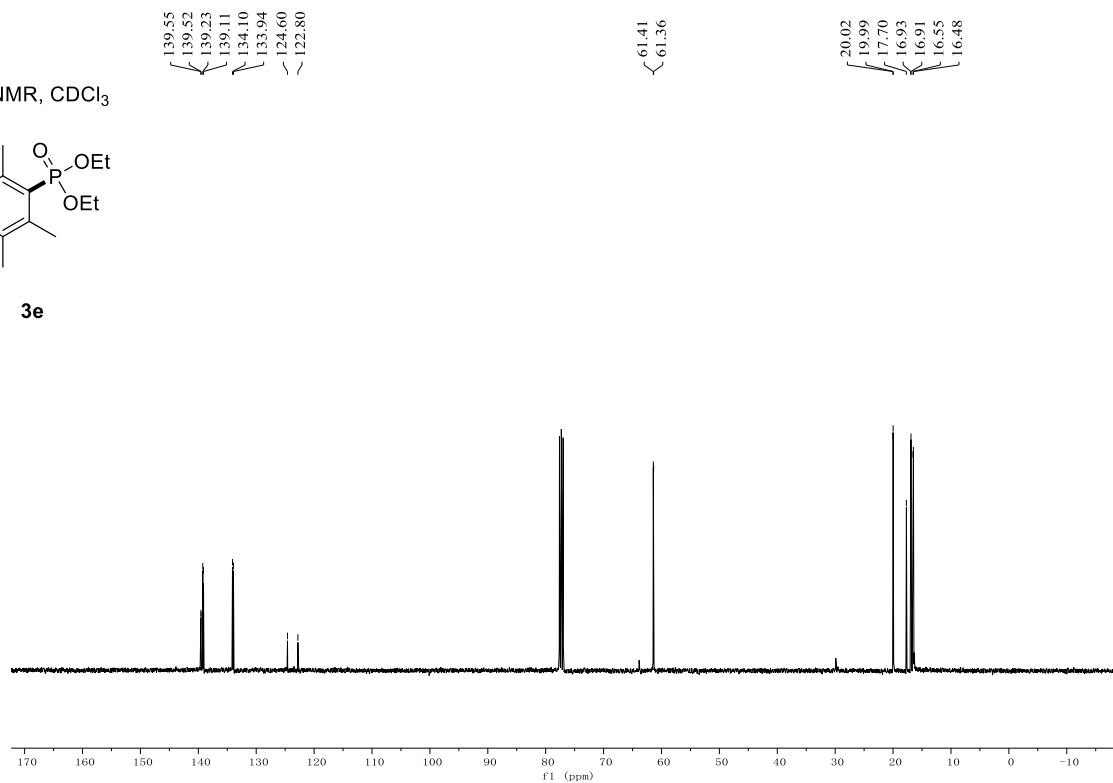
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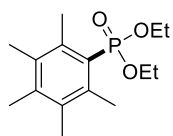
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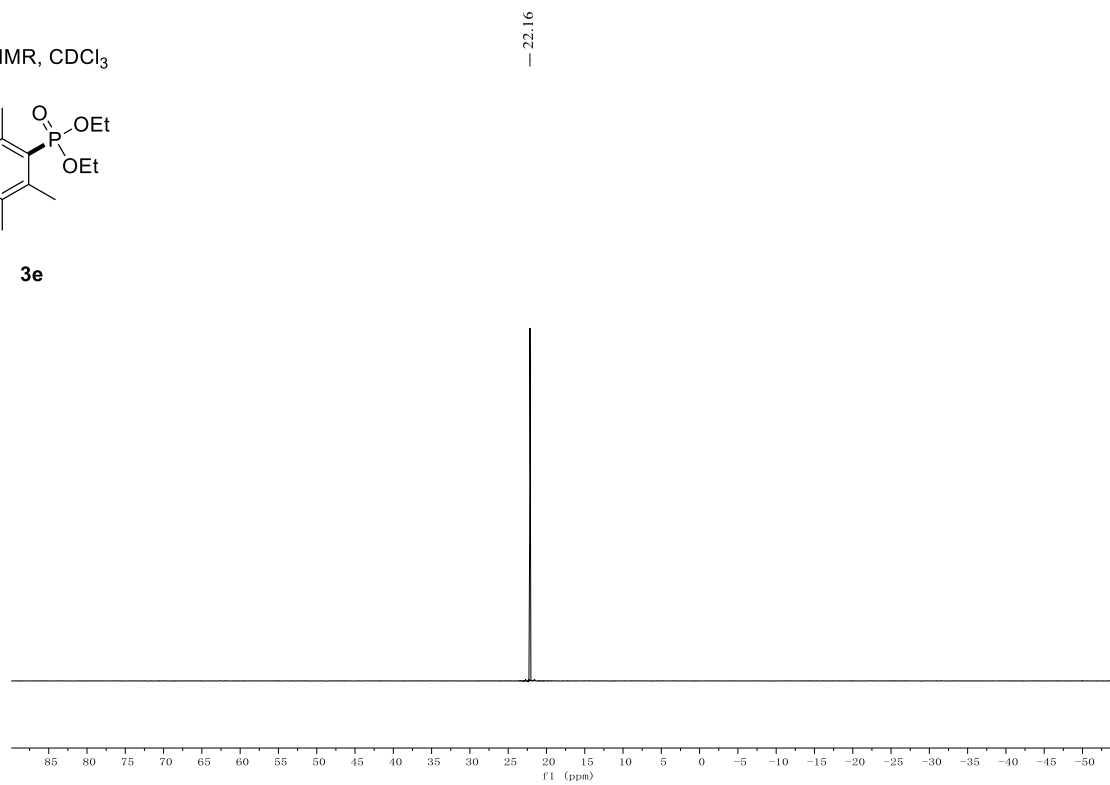
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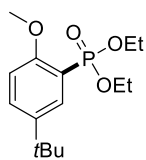
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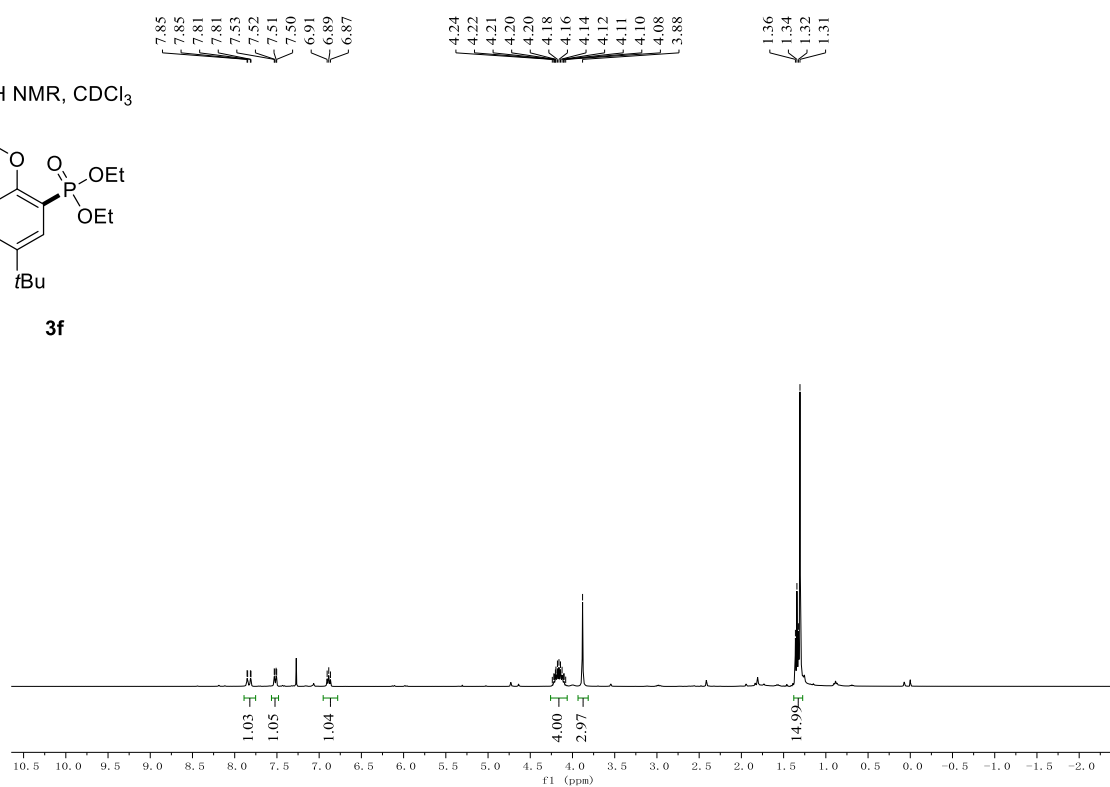
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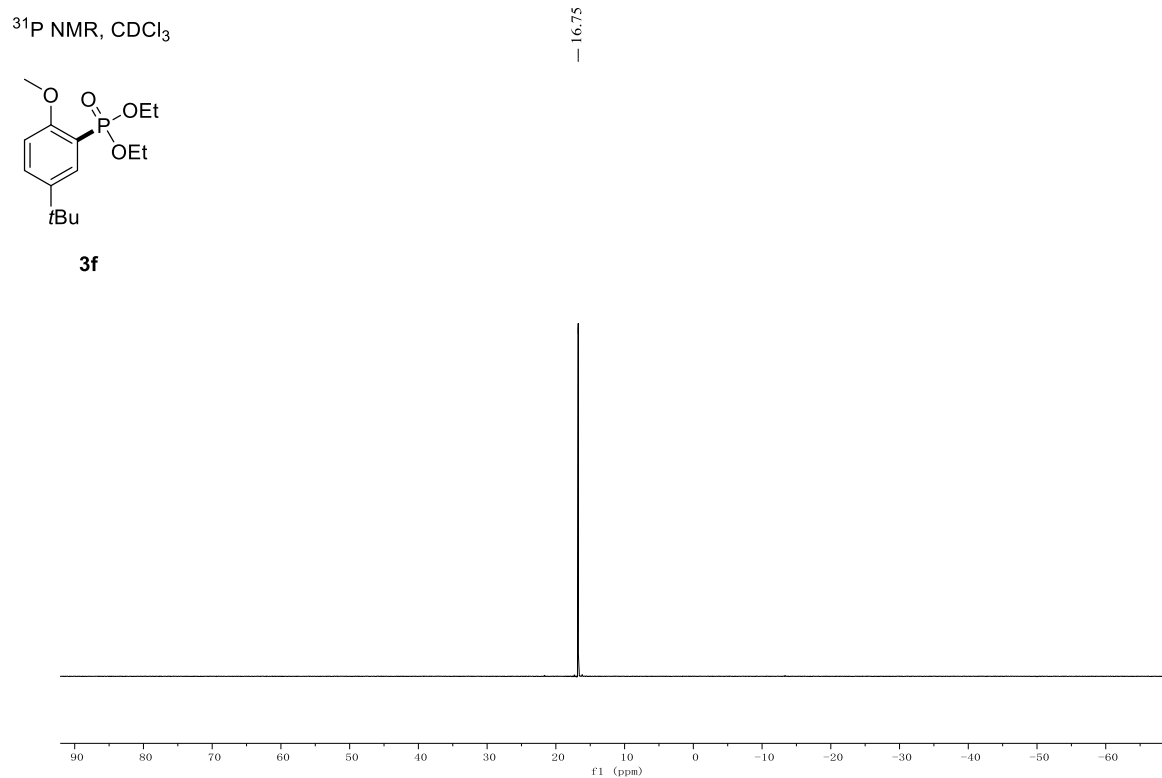
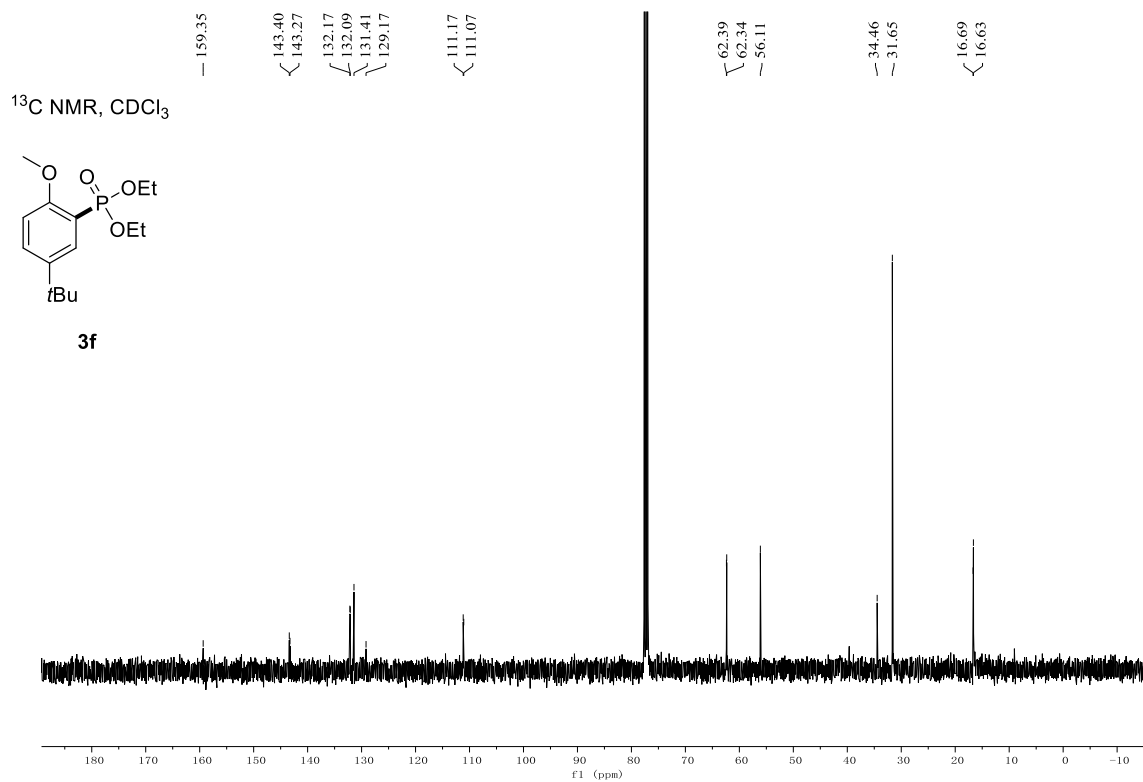


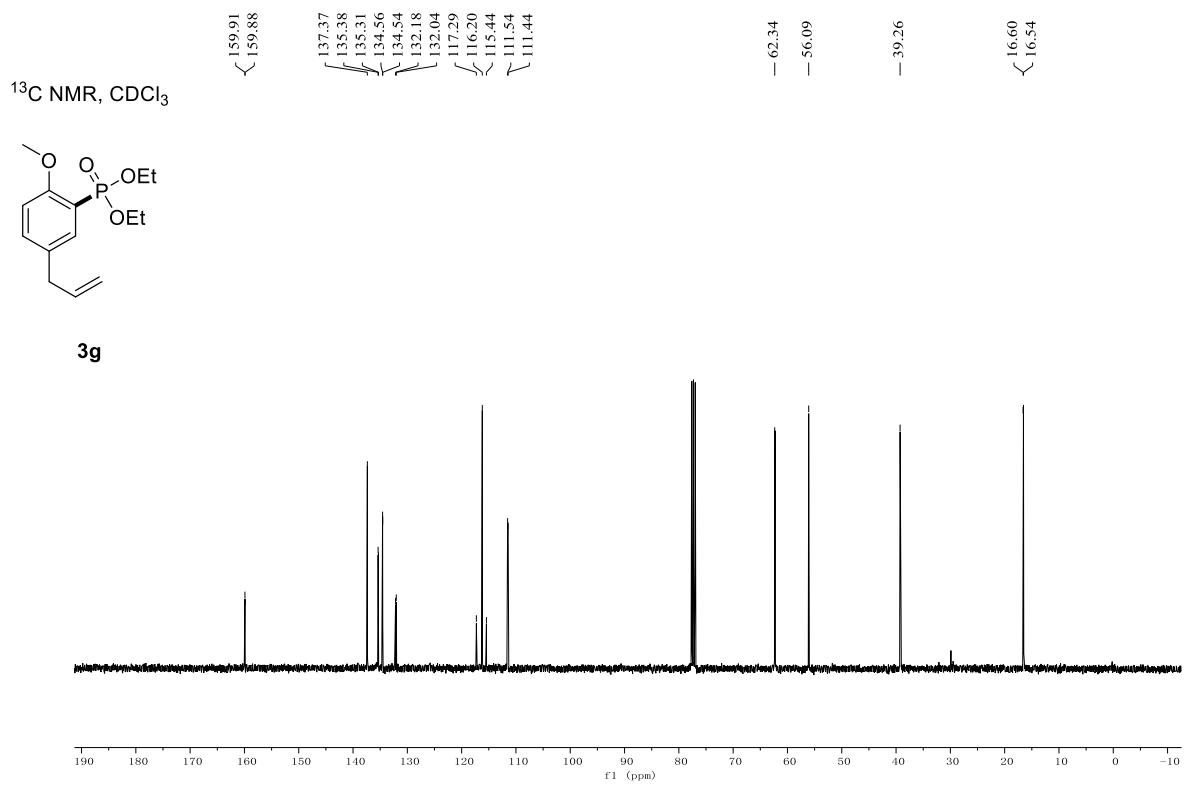
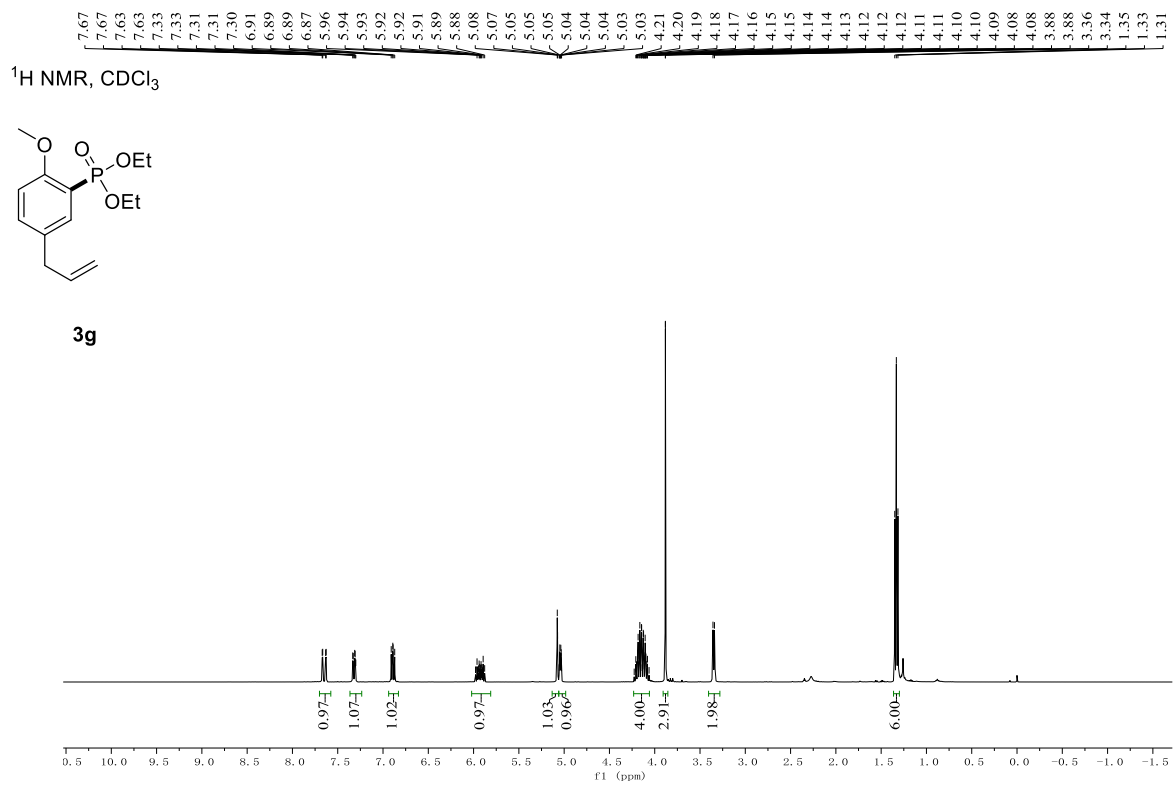
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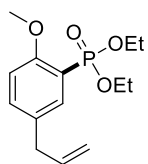
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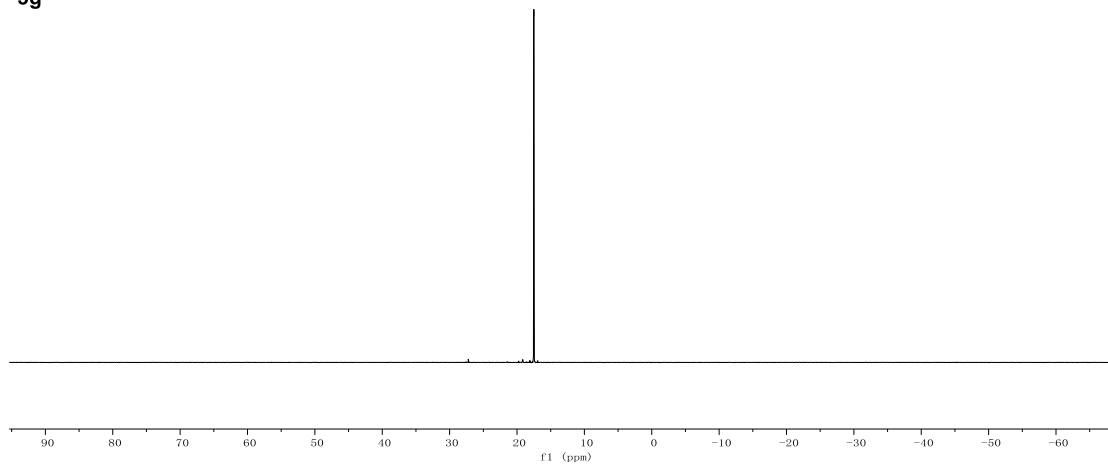




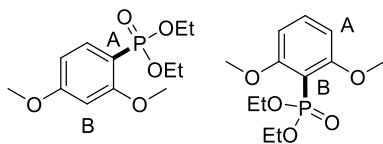
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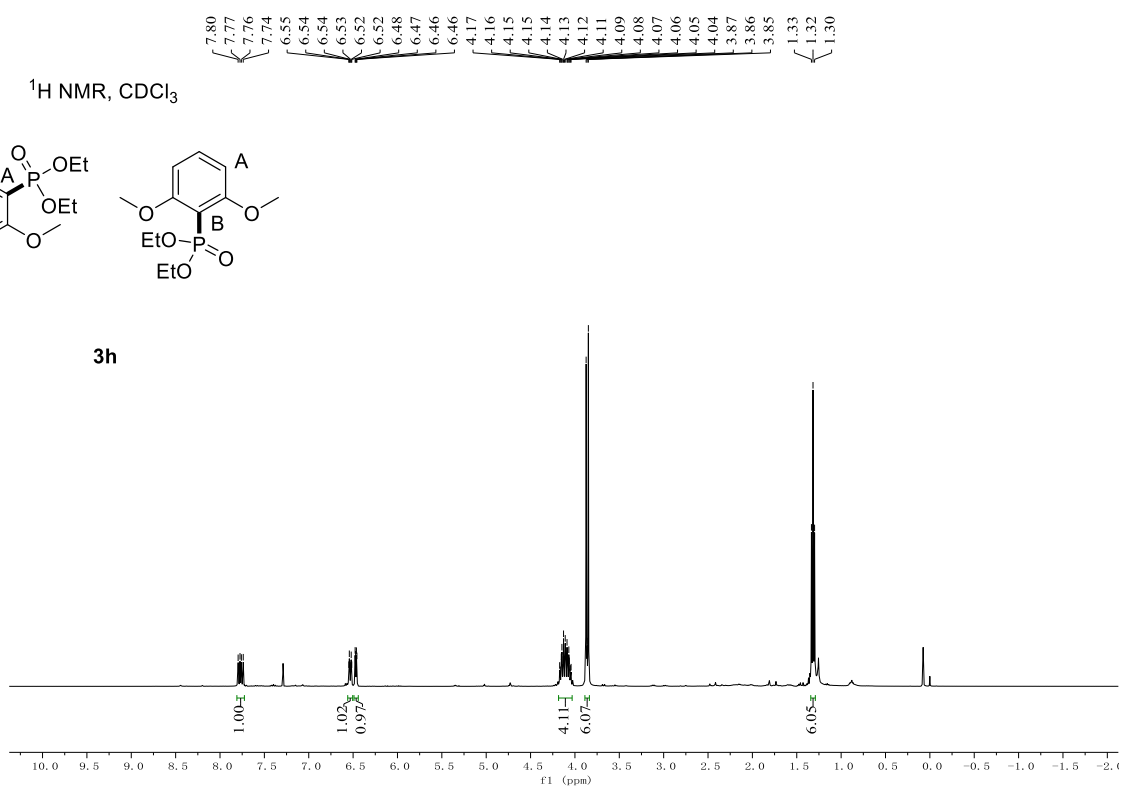
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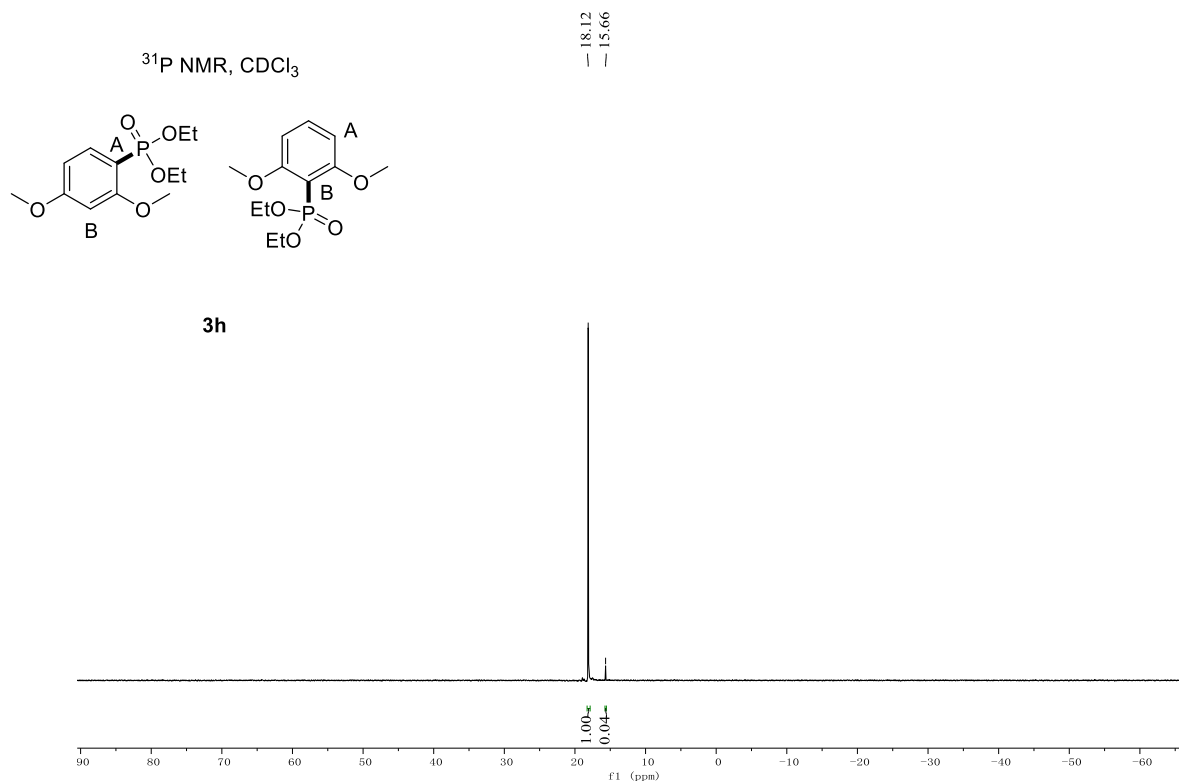
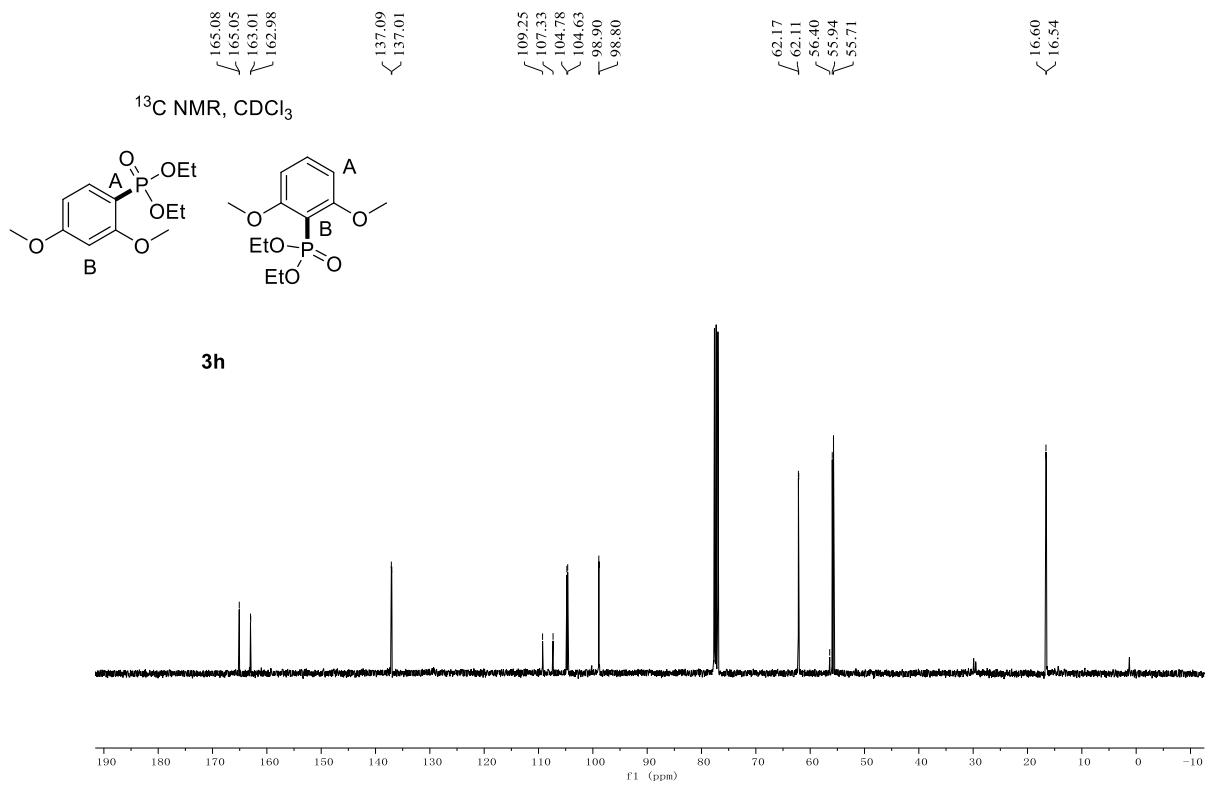


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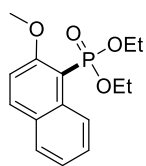


**3h**

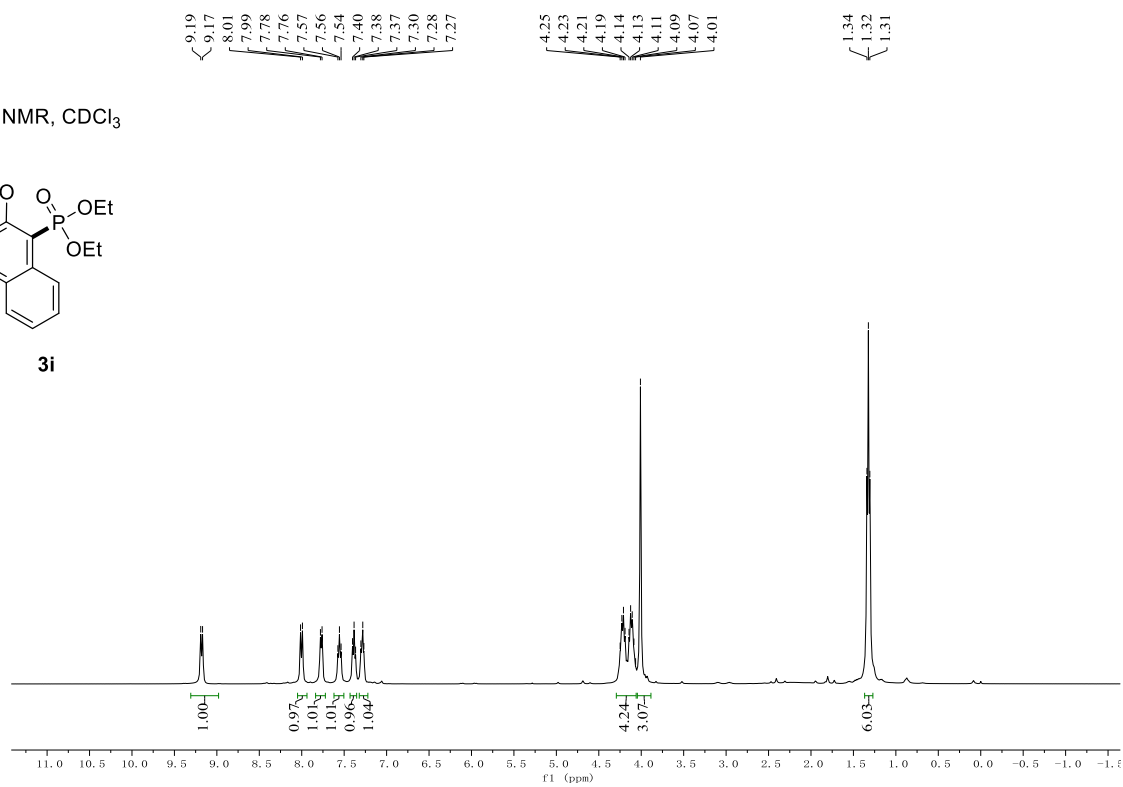




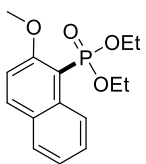
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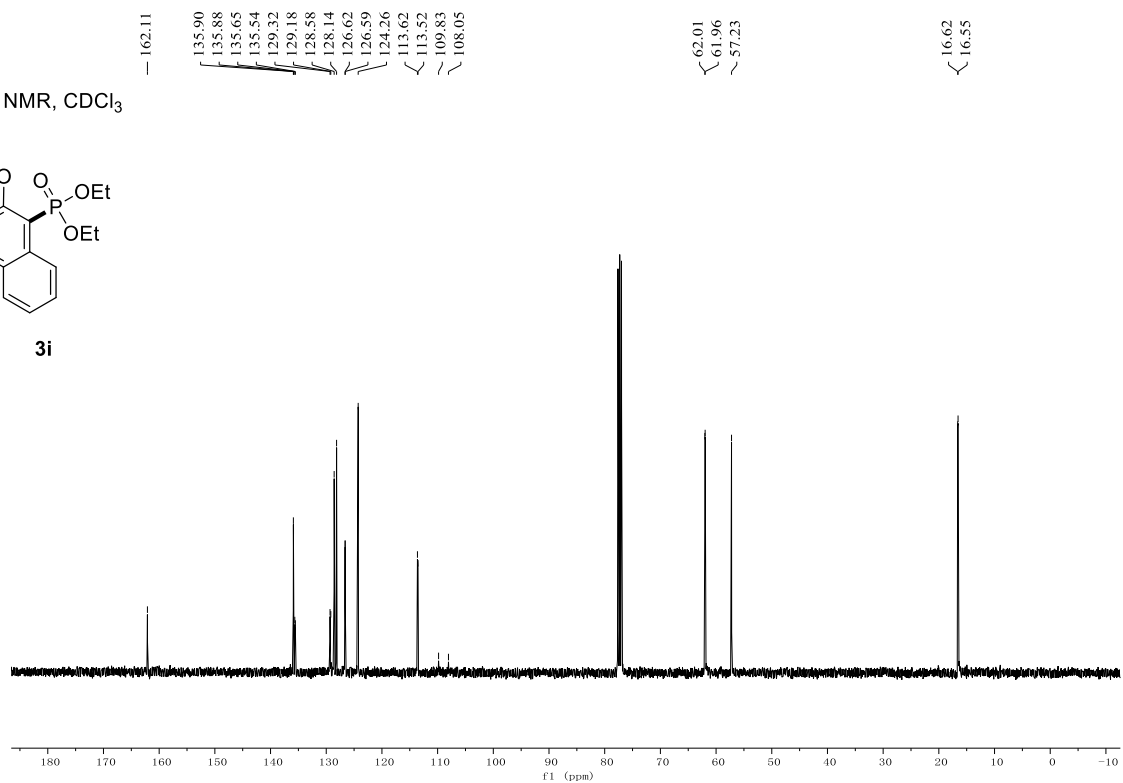
**3i**



<sup>13</sup>C NMR, CDCl<sub>3</sub>

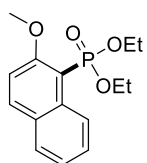


**3i**

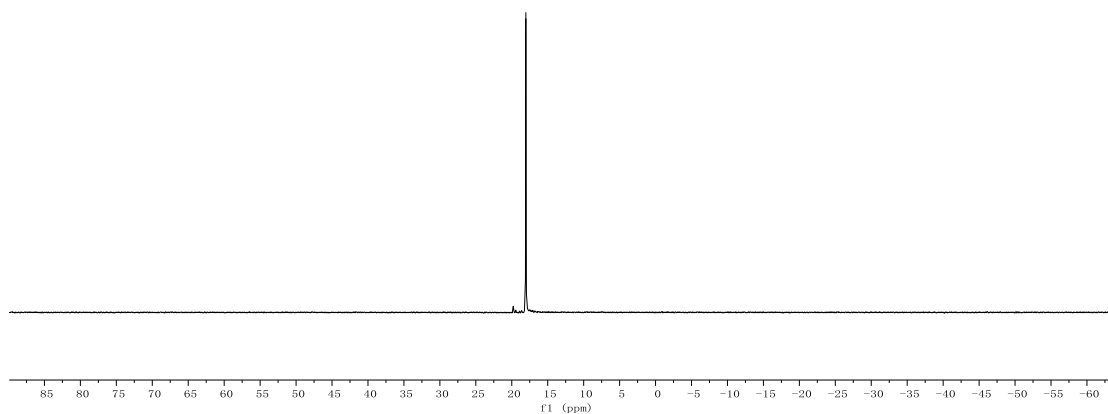


$^{31}\text{P}$  NMR,  $\text{CDCl}_3$

-18.04

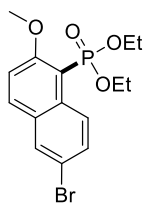


**3i**

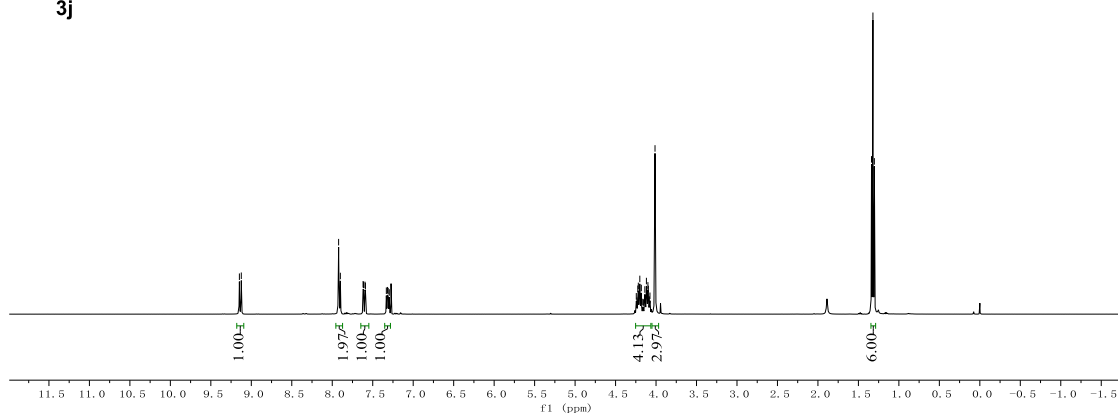


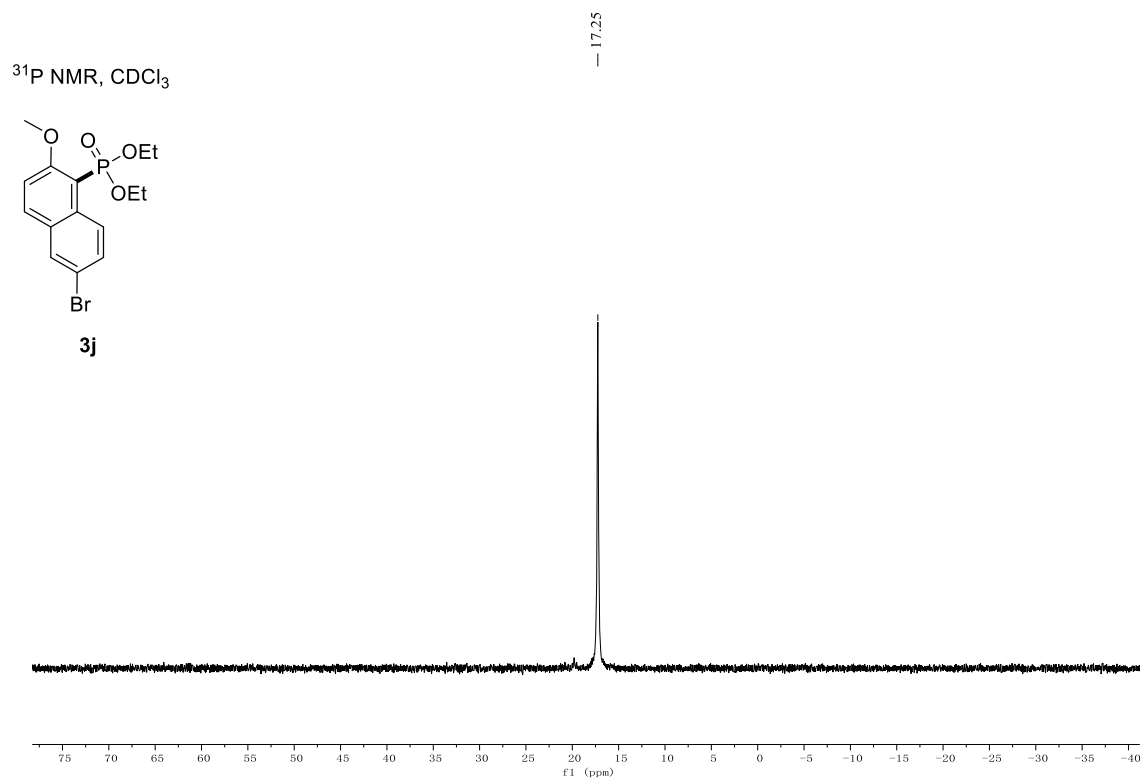
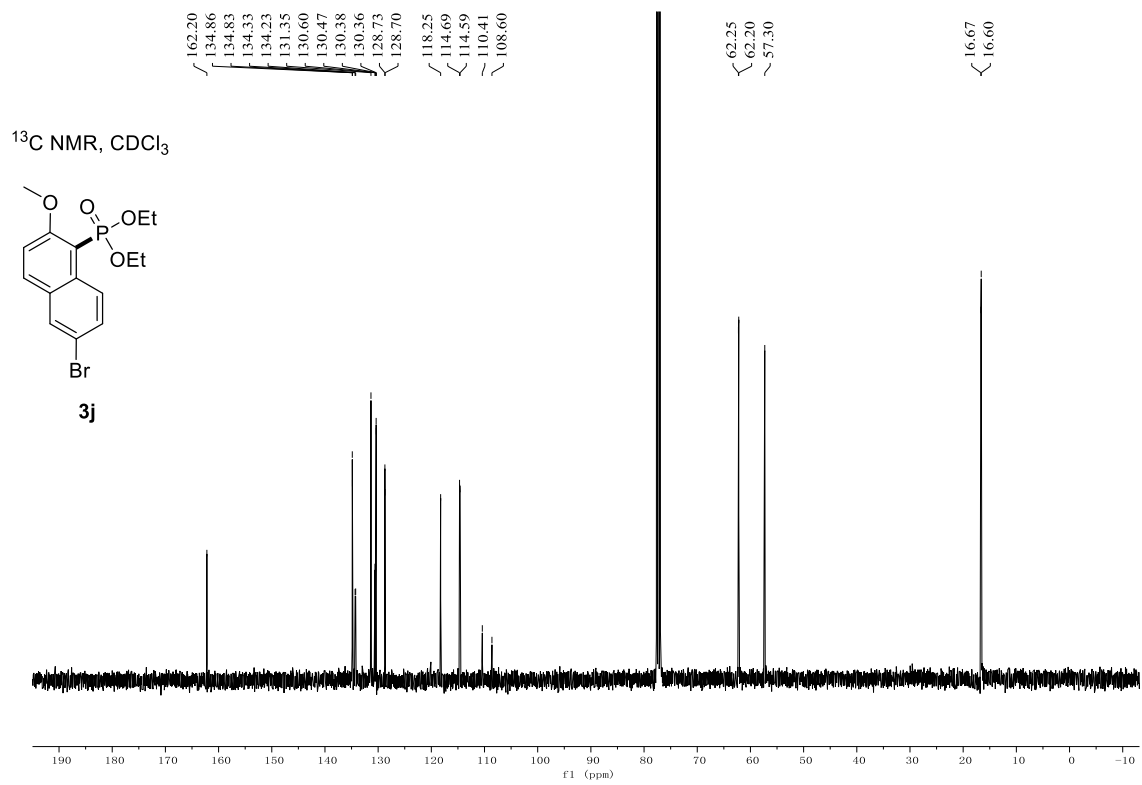
9.15  
9.12  
7.92  
7.90  
7.62  
7.61  
7.60  
7.59  
7.33  
7.32  
7.31  
7.30  
4.24  
4.24  
4.23  
4.22  
4.21  
4.20  
4.19  
4.18  
4.16  
4.16  
4.14  
4.12  
4.11  
4.10  
4.10  
4.08  
4.08  
4.01  
1.34  
1.32  
1.30

$^1\text{H}$  NMR,  $\text{CDCl}_3$

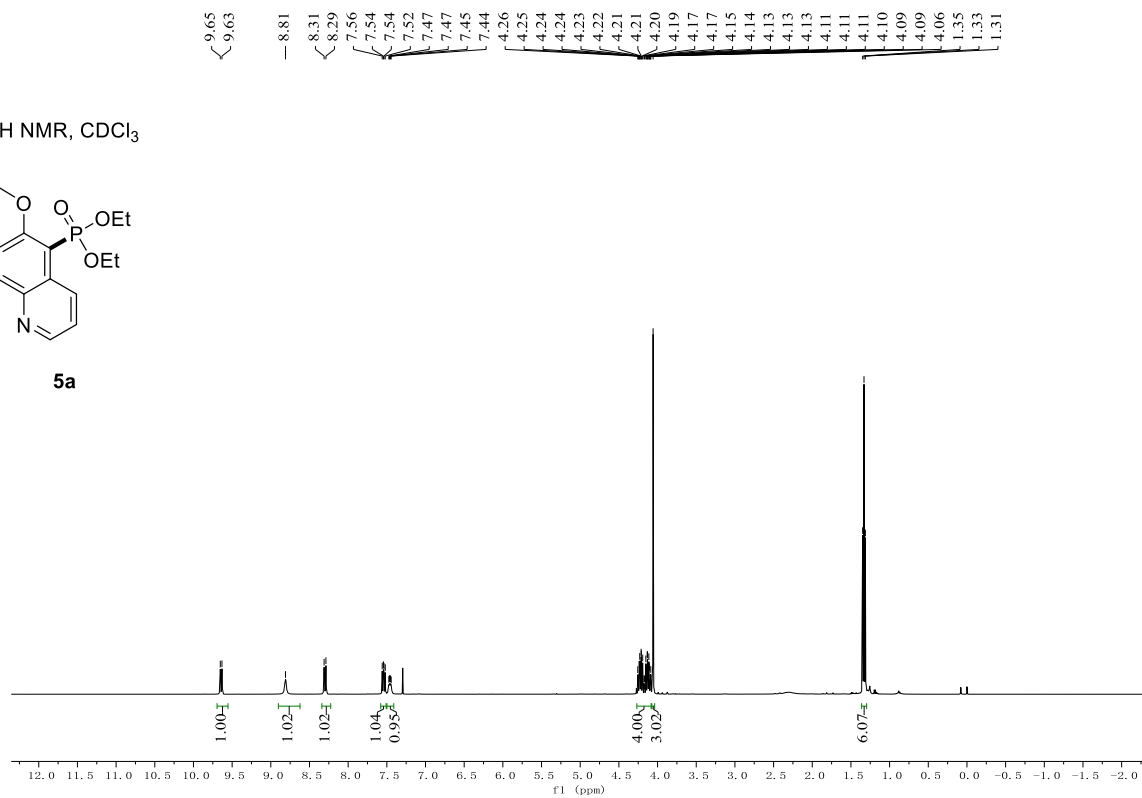
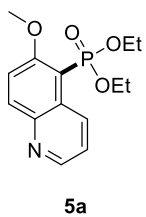


**3j**

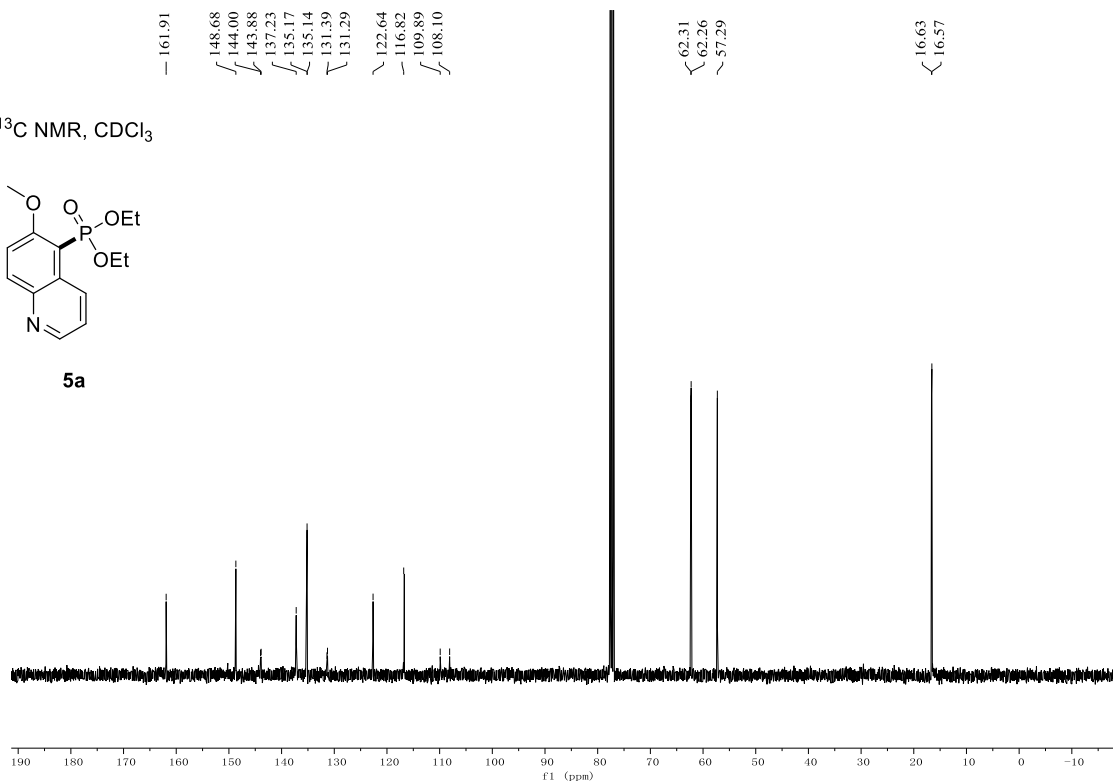
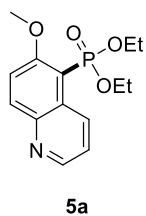




<sup>1</sup>H NMR, CDCl<sub>3</sub>

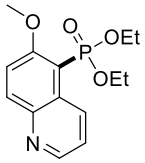


<sup>13</sup>C NMR, CDCl<sub>3</sub>

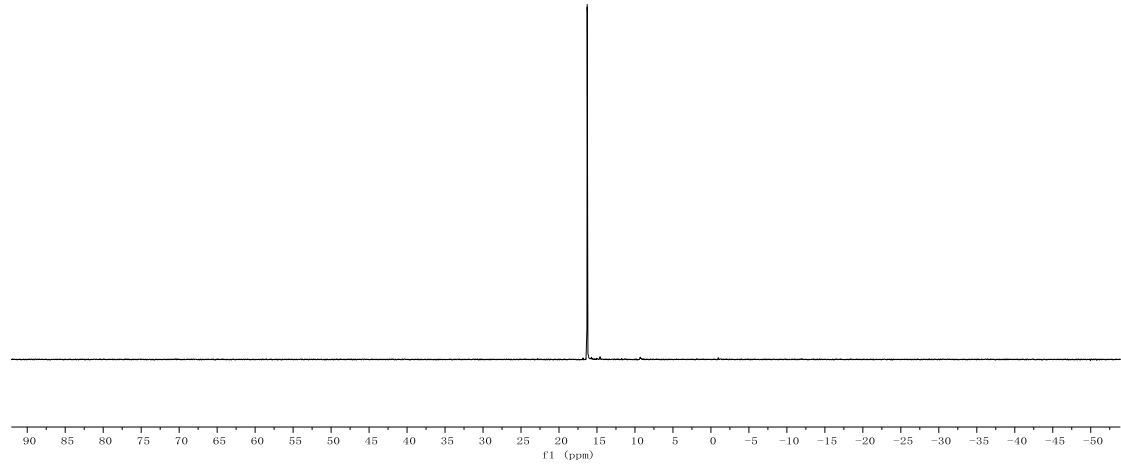


$^{31}\text{P}$  NMR,  $\text{CDCl}_3$

— 16.29

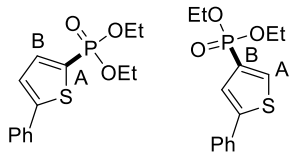


**5a**

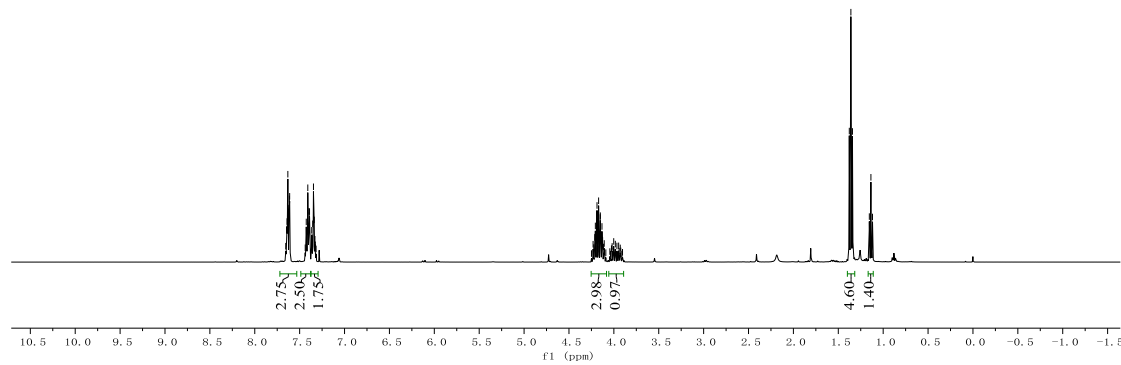


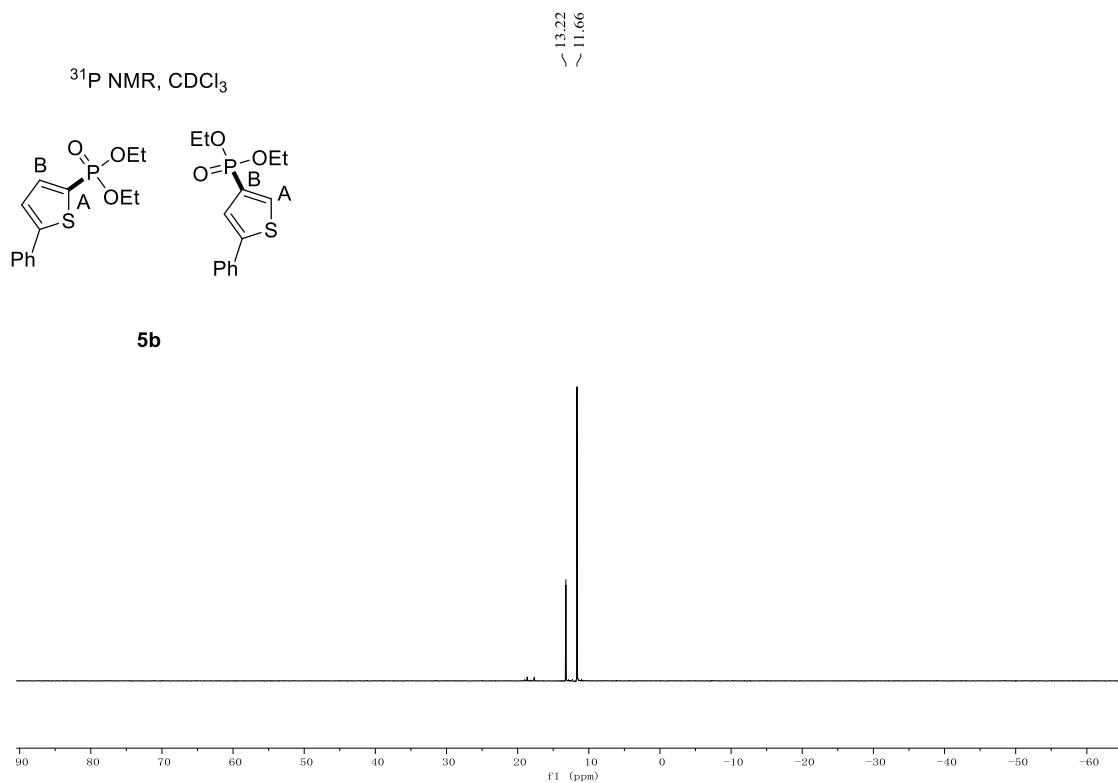
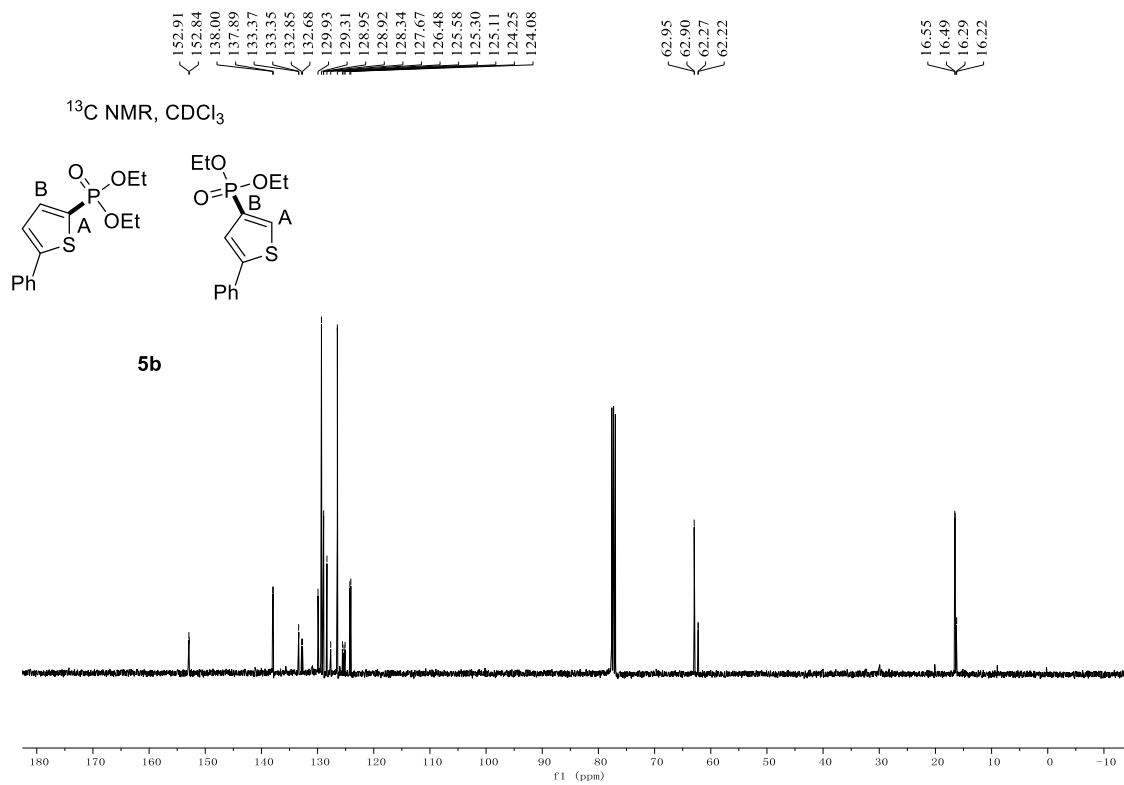
7.65  
7.64  
7.64  
7.63  
7.62  
7.61  
7.61  
7.44  
7.43  
7.41  
7.41  
7.40  
7.39  
7.39  
7.37  
7.36  
7.35  
7.35  
7.34  
7.33  
7.33  
7.32  
7.32  
4.25  
4.23  
4.23  
4.22  
4.21  
4.21  
4.21  
4.19  
4.19  
4.18  
4.17  
4.17  
4.15  
4.15  
4.15  
4.13  
4.13  
4.13  
4.13  
4.11  
4.11  
4.09  
4.04  
4.04  
4.04  
4.03  
4.02  
4.01  
4.01  
4.00  
3.98  
3.97  
3.95  
3.94  
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3.92  
3.90  
1.38  
1.36  
1.34  
1.15  
1.14  
1.12

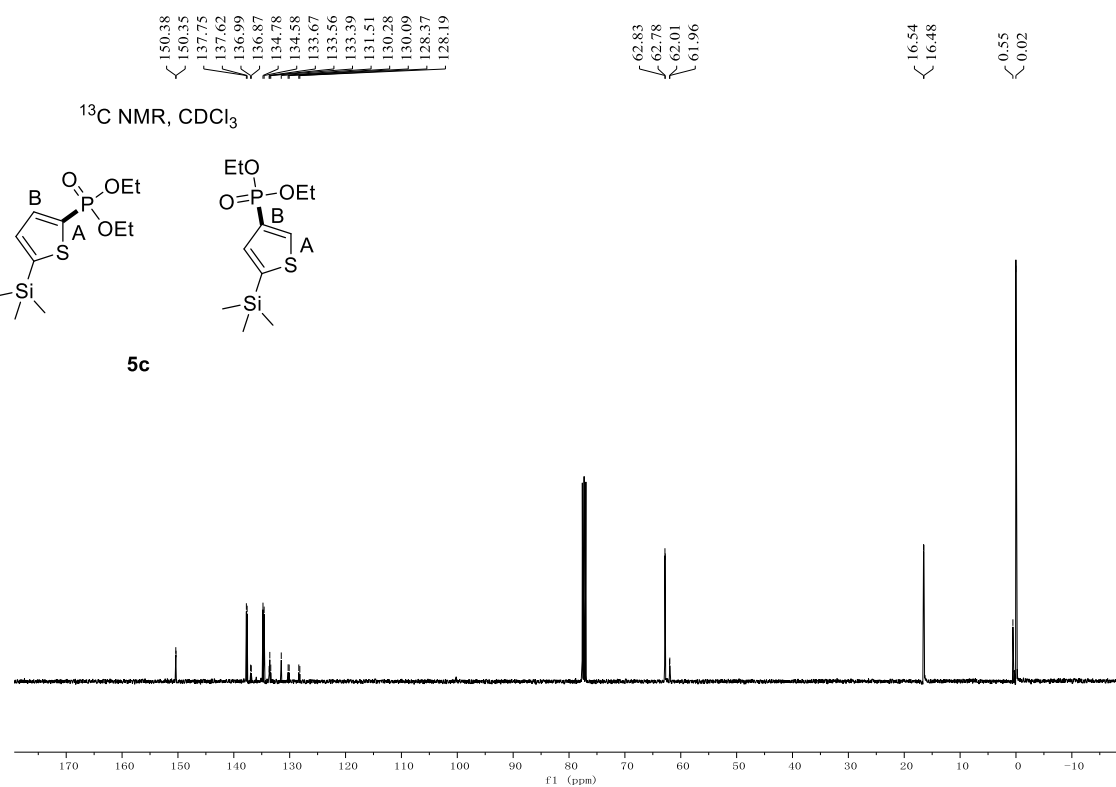
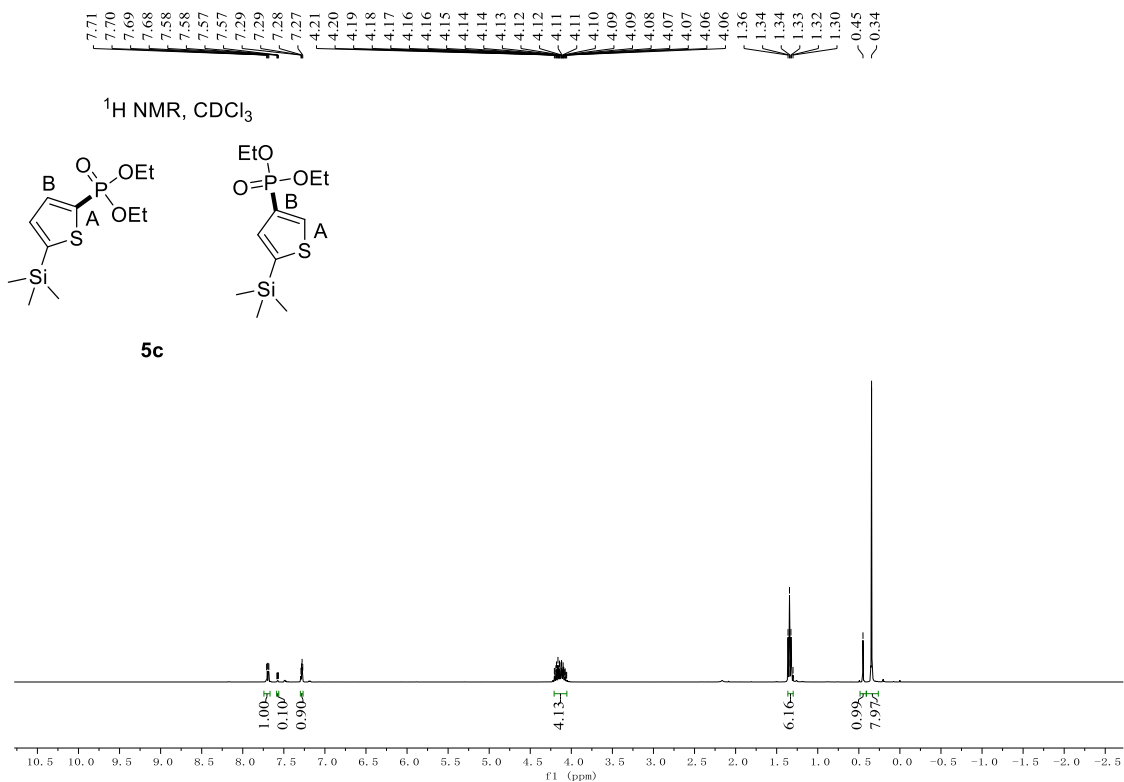
$^1\text{H}$  NMR,  $\text{CDCl}_3$

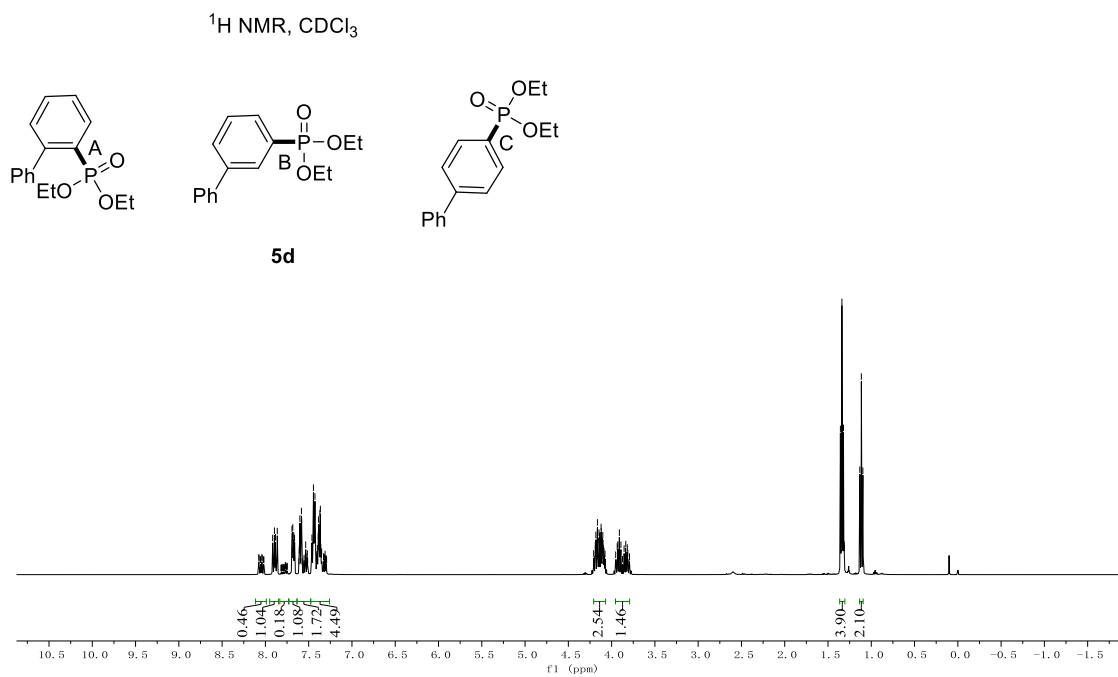
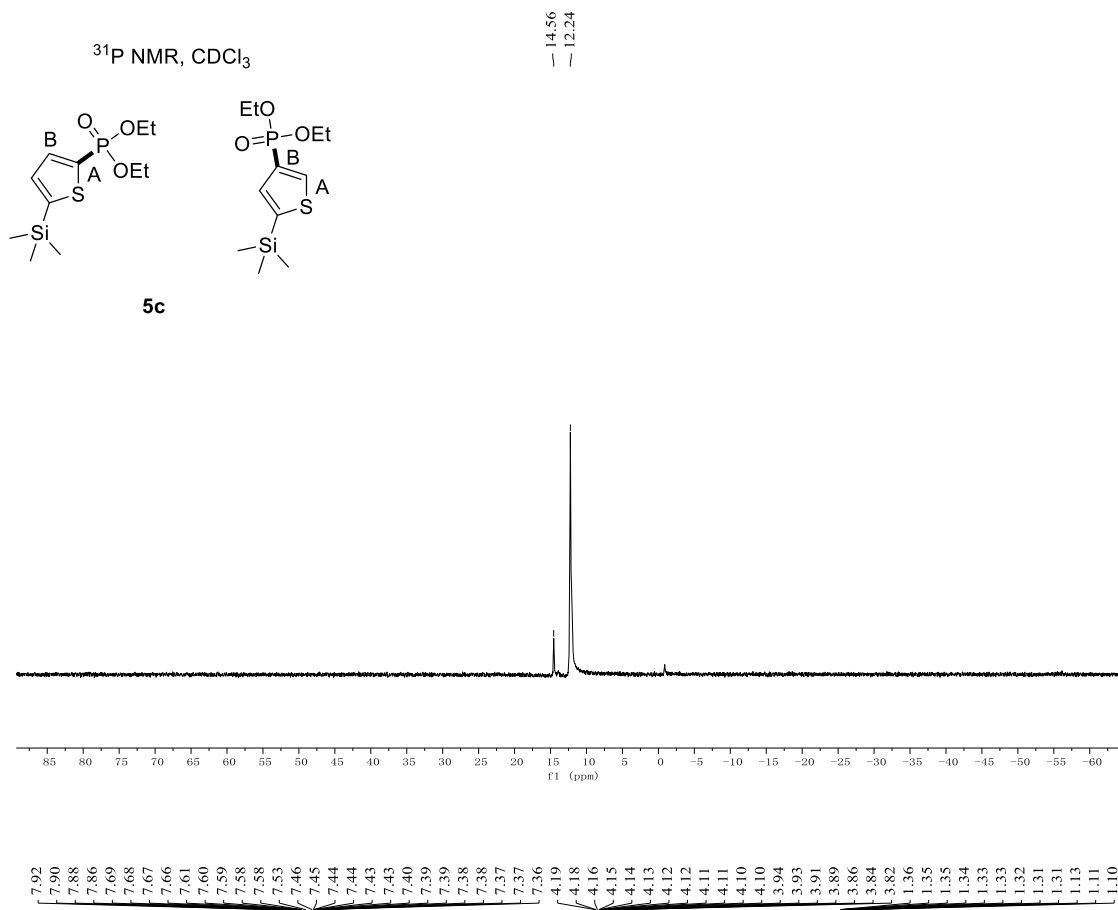


**5b**







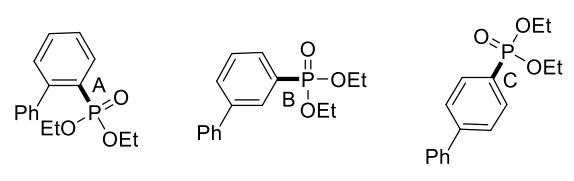


146.21  
146.11  
145.32  
145.29  
141.58  
141.54  
140.05  
133.98  
133.88  
132.49  
132.39  
132.11  
132.08  
131.56  
131.42  
131.23  
131.19  
130.67  
130.59  
130.57  
130.49  
129.45  
129.08  
128.30  
127.98  
127.62  
127.57  
127.40  
127.32  
127.23  
127.08  
126.94

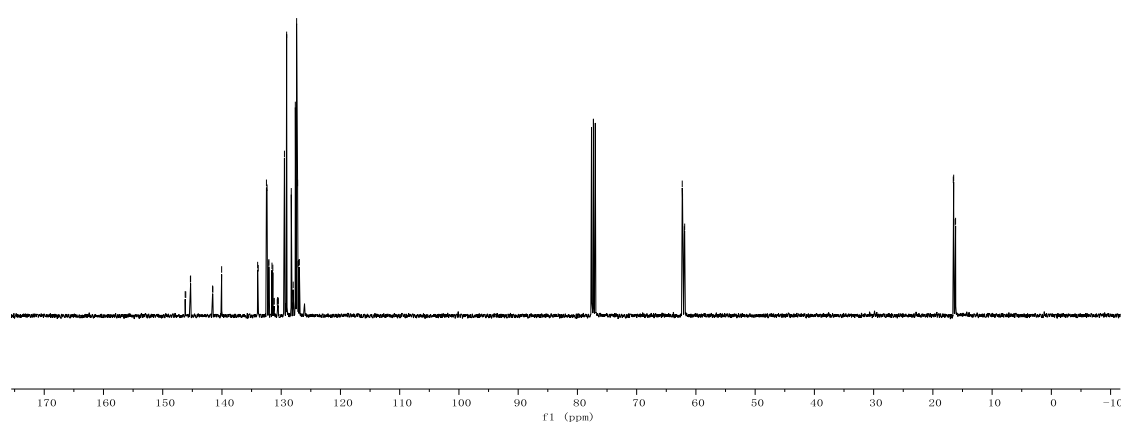
62.31  
62.25  
61.96  
61.89

16.55  
16.49  
16.23  
16.17

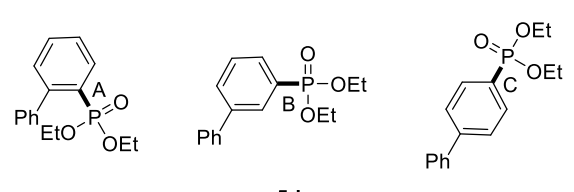
<sup>13</sup>C NMR, CDCl<sub>3</sub>



5d

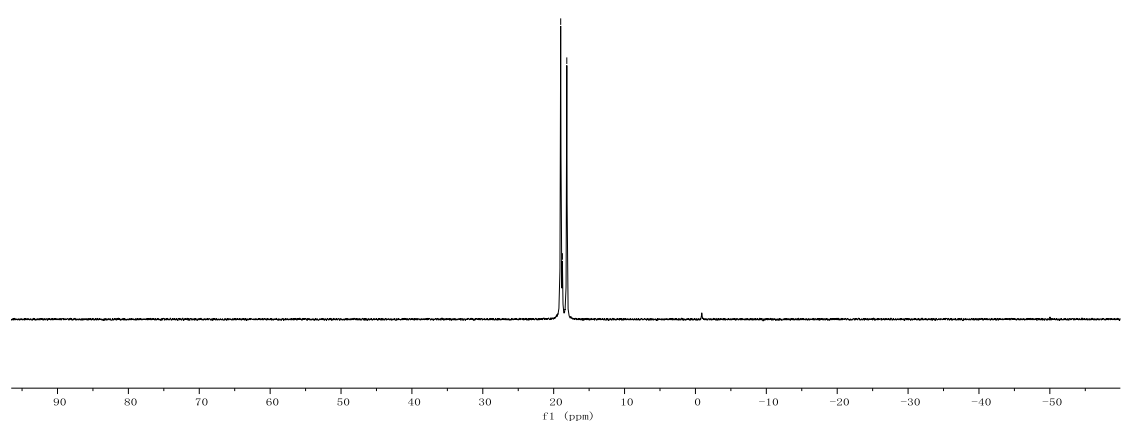


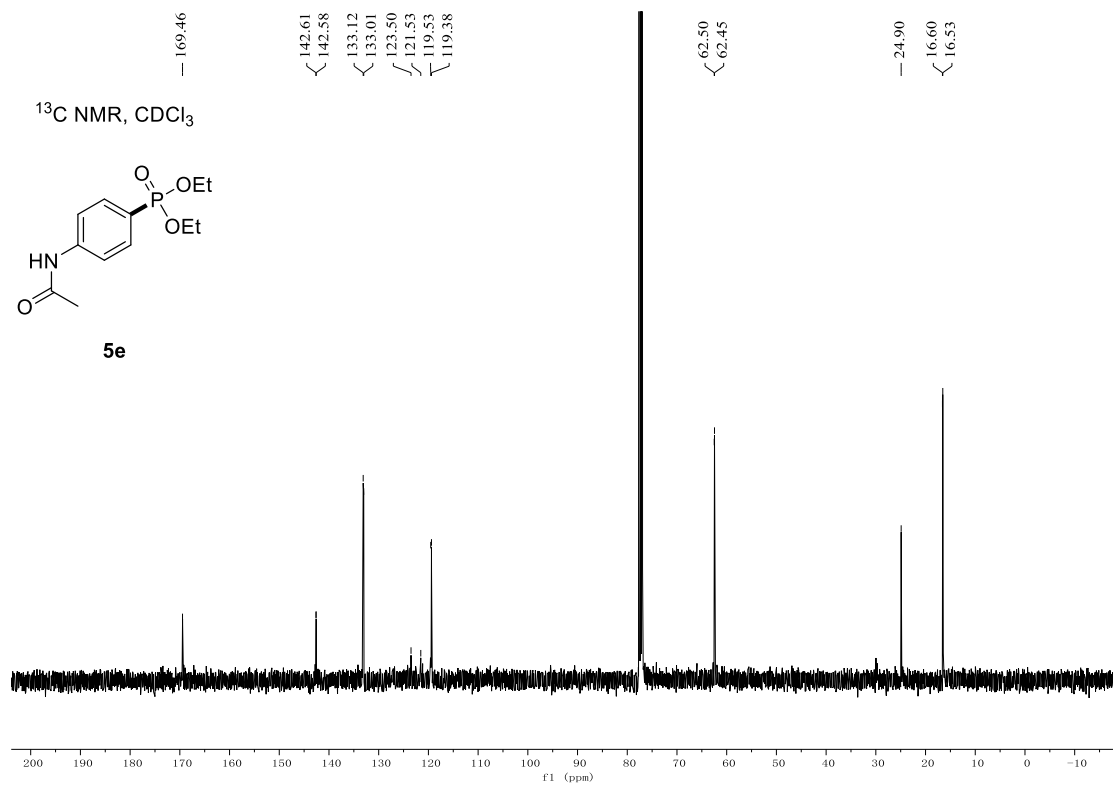
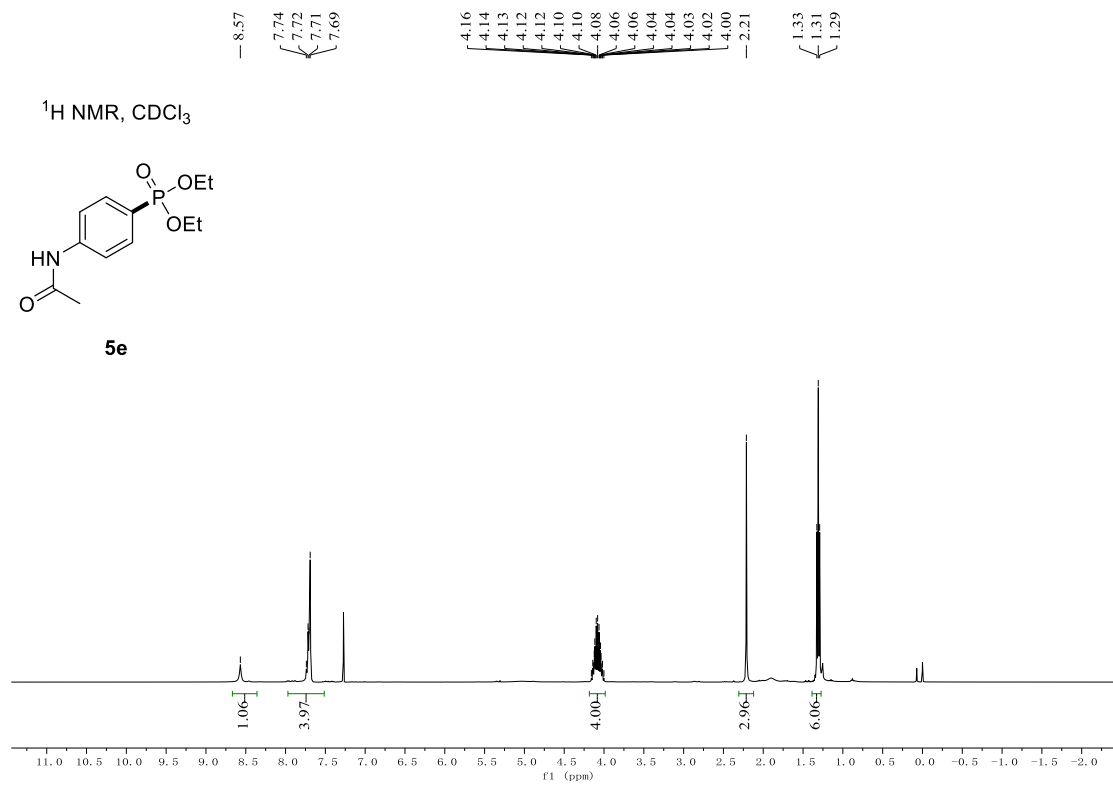
<sup>31</sup>P NMR, CDCl<sub>3</sub>



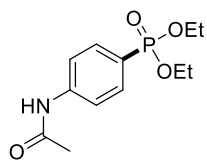
5d

19.01  
18.77  
18.15

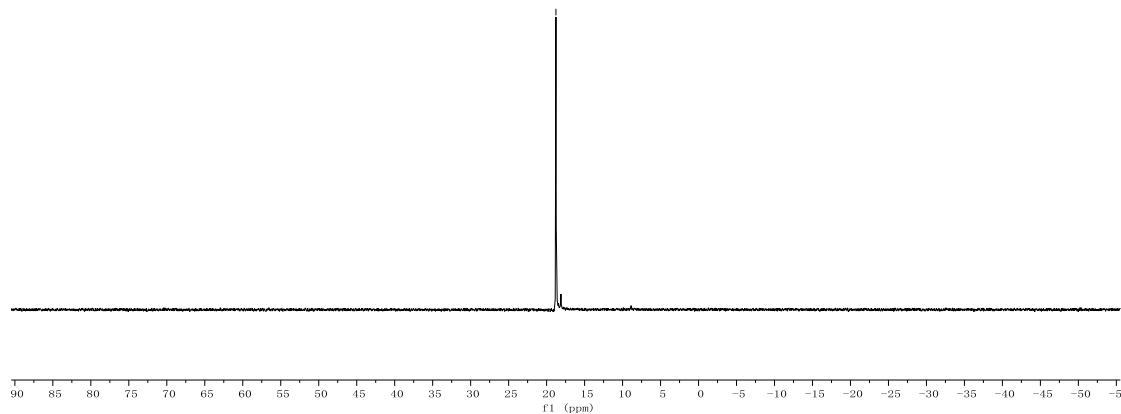




$^{31}\text{P}$  NMR,  $\text{CDCl}_3$

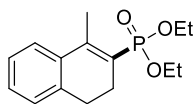


**5e**

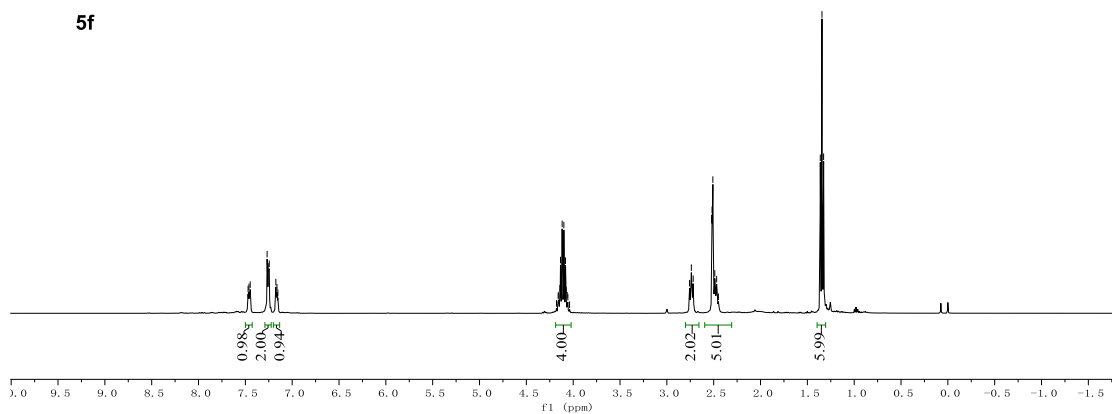


7.47  
7.46  
7.45  
7.27  
7.26  
7.24  
7.17  
7.16  
7.15  
4.18  
4.16  
4.15  
4.14  
4.14  
4.12  
4.10  
4.08  
4.06  
4.06  
4.04  
2.76  
2.74  
2.72  
2.52  
2.51  
2.51  
2.49  
2.47  
2.45  
1.36  
1.34  
1.33

$^1\text{H}$  NMR,  $\text{CDCl}_3$



**5f**

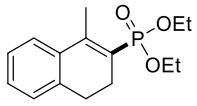


146.82  
146.70  
137.59  
137.56  
135.83  
135.63  
129.03  
127.57  
126.87  
124.84  
123.54  
121.74

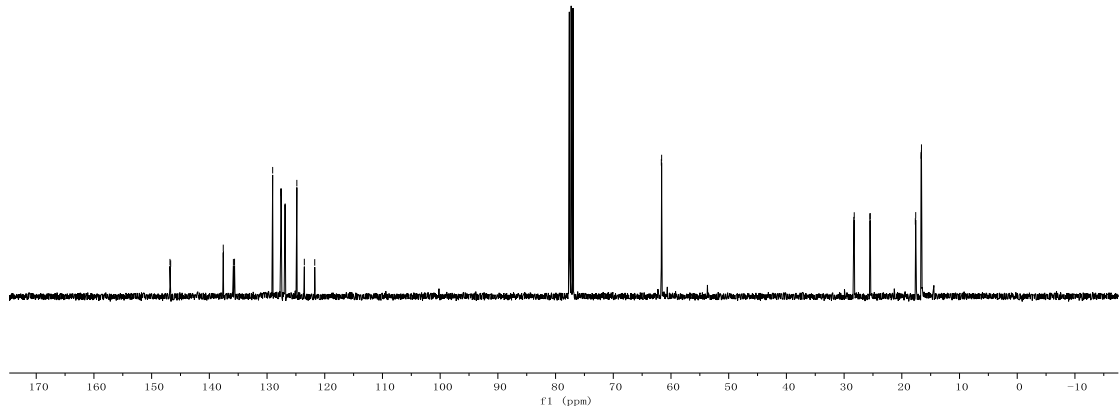
61.67  
61.62

28.32  
28.24  
25.55  
25.45  
17.66  
17.59  
16.66  
16.60

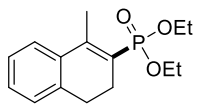
<sup>13</sup>C NMR, CDCl<sub>3</sub>



5f

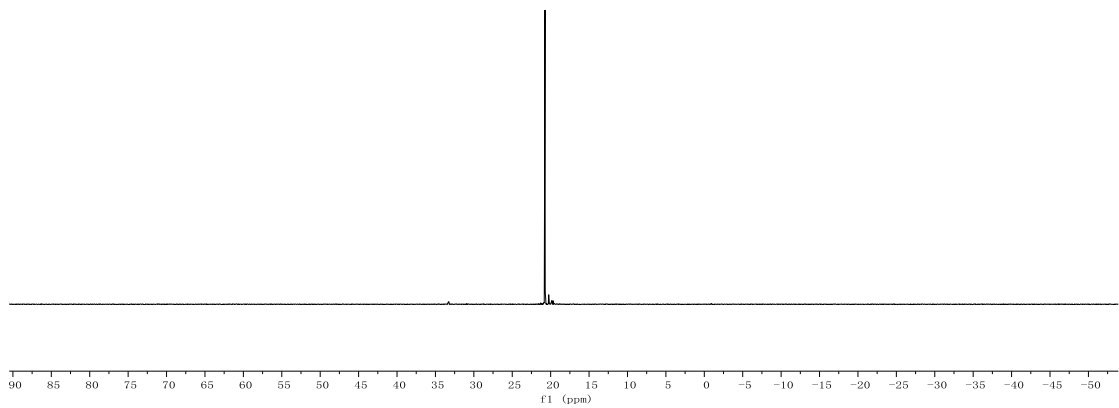


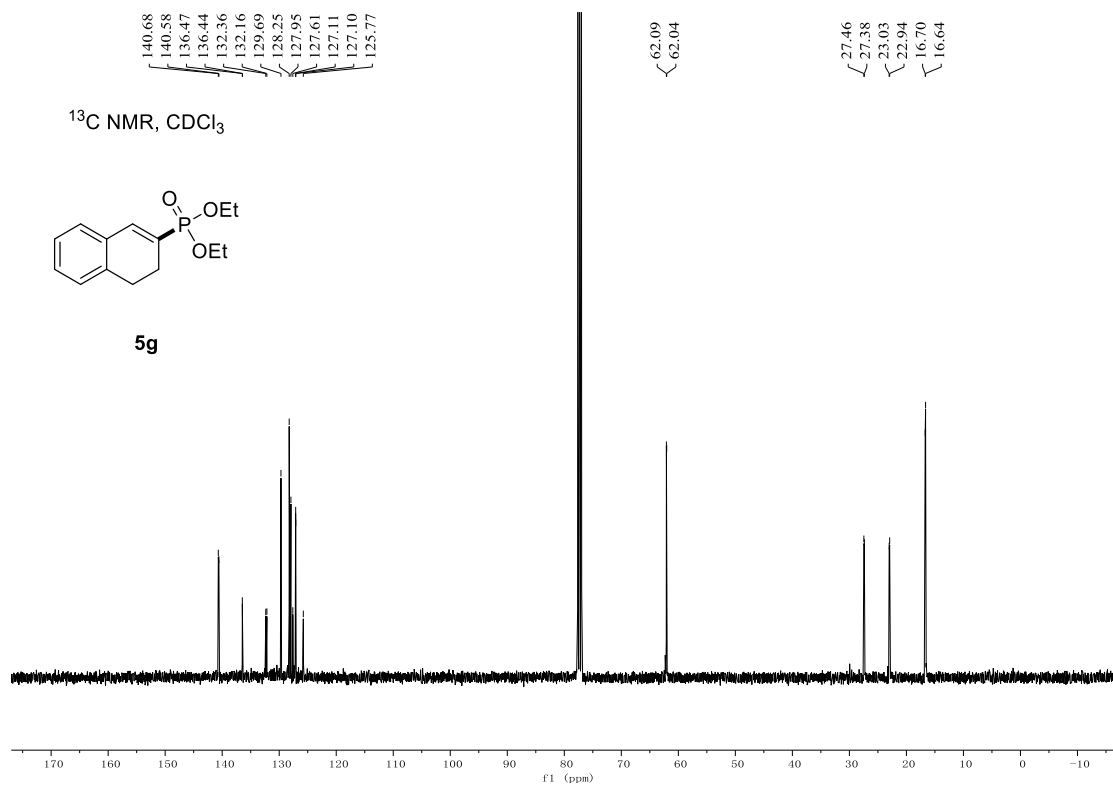
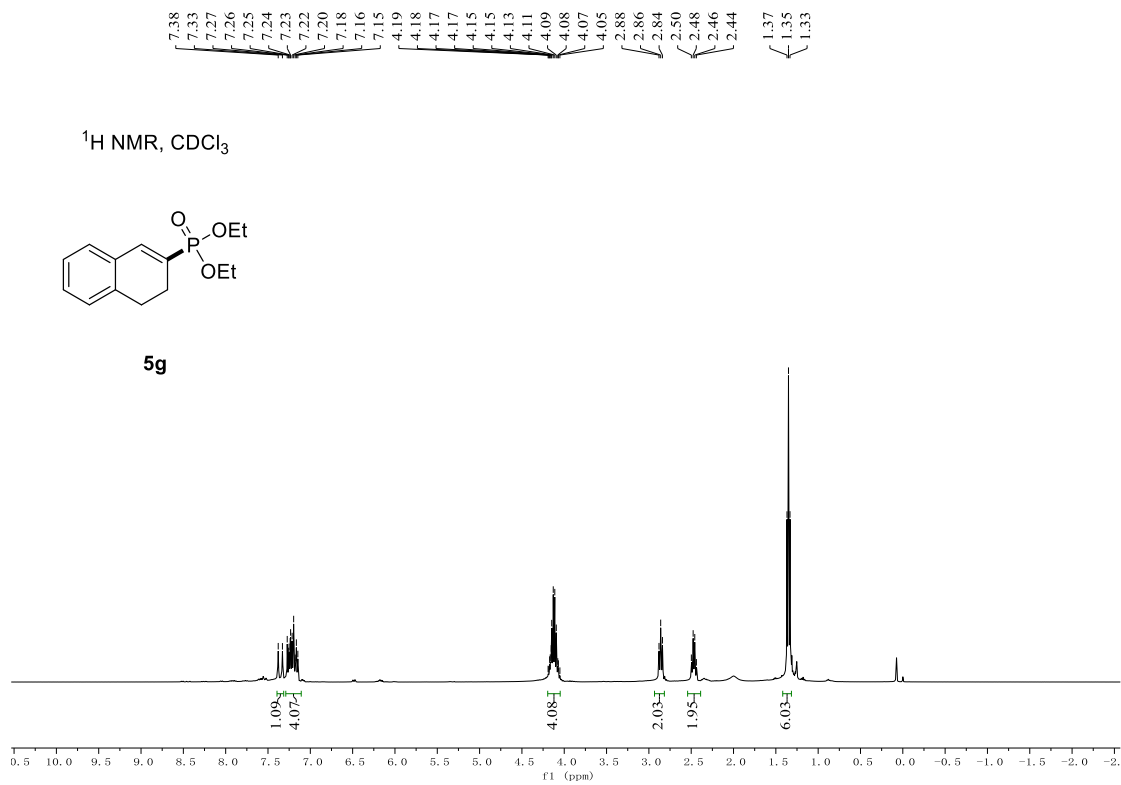
<sup>31</sup>P NMR, CDCl<sub>3</sub>



5f

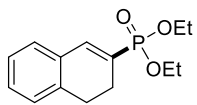
20.74



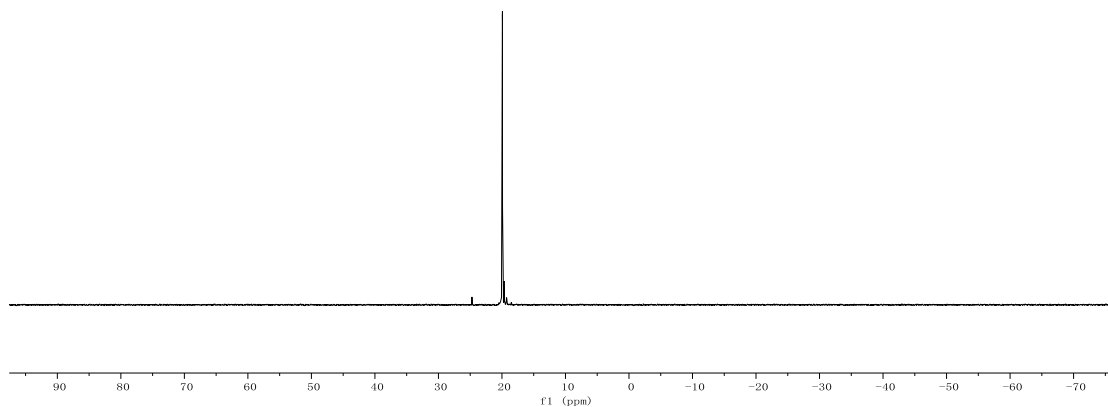


$^{31}\text{P}$  NMR,  $\text{CDCl}_3$

— 19.93



**5g**

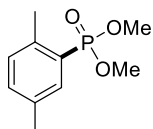


7.74  
7.70  
7.29  
7.26  
7.24  
7.17  
7.16  
7.14

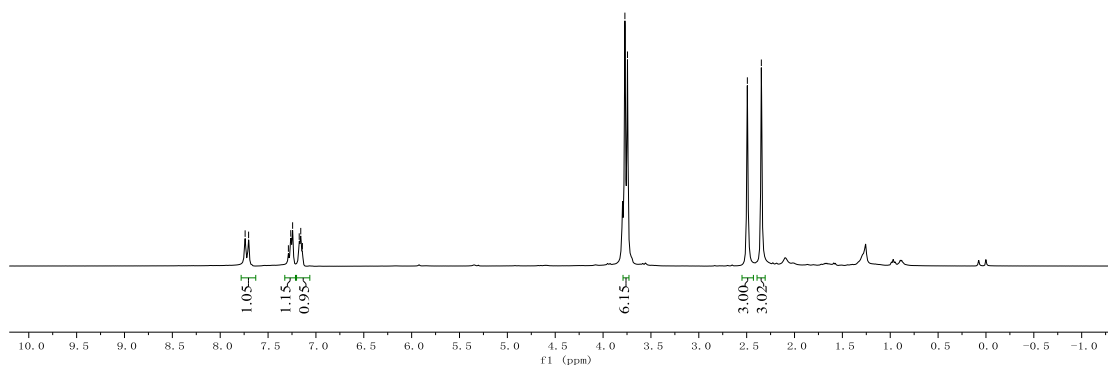
3.77  
3.75

2.49  
2.35

$^1\text{H}$  NMR,  $\text{CDCl}_3$



**5h**

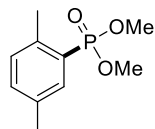


138.99  
138.89  
135.39  
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135.00  
134.90  
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133.69  
131.58  
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126.15  
124.33

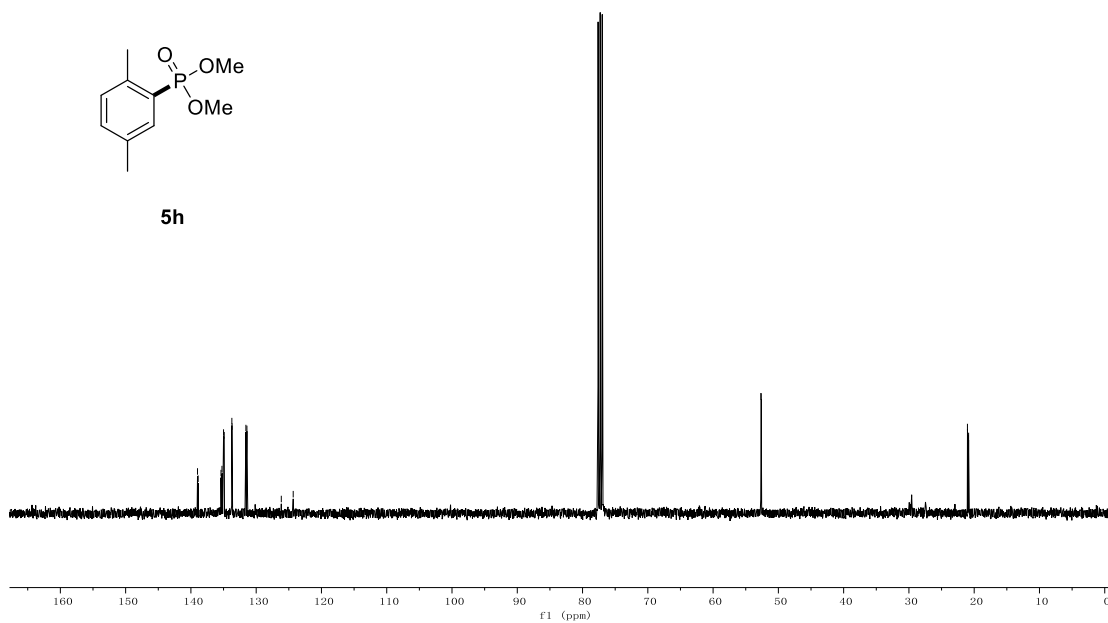
52.68  
52.63

21.03  
20.89  
20.86

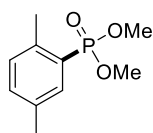
<sup>13</sup>C NMR, CDCl<sub>3</sub>



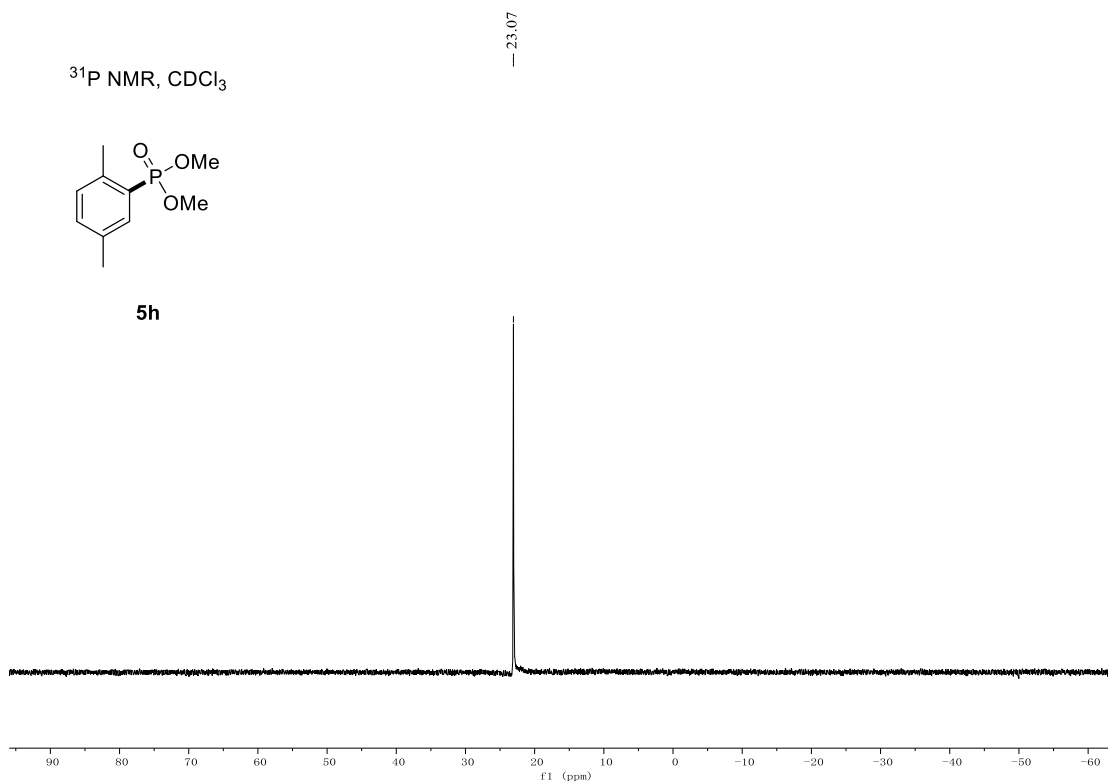
5h



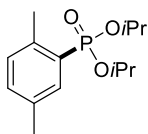
<sup>31</sup>P NMR, CDCl<sub>3</sub>



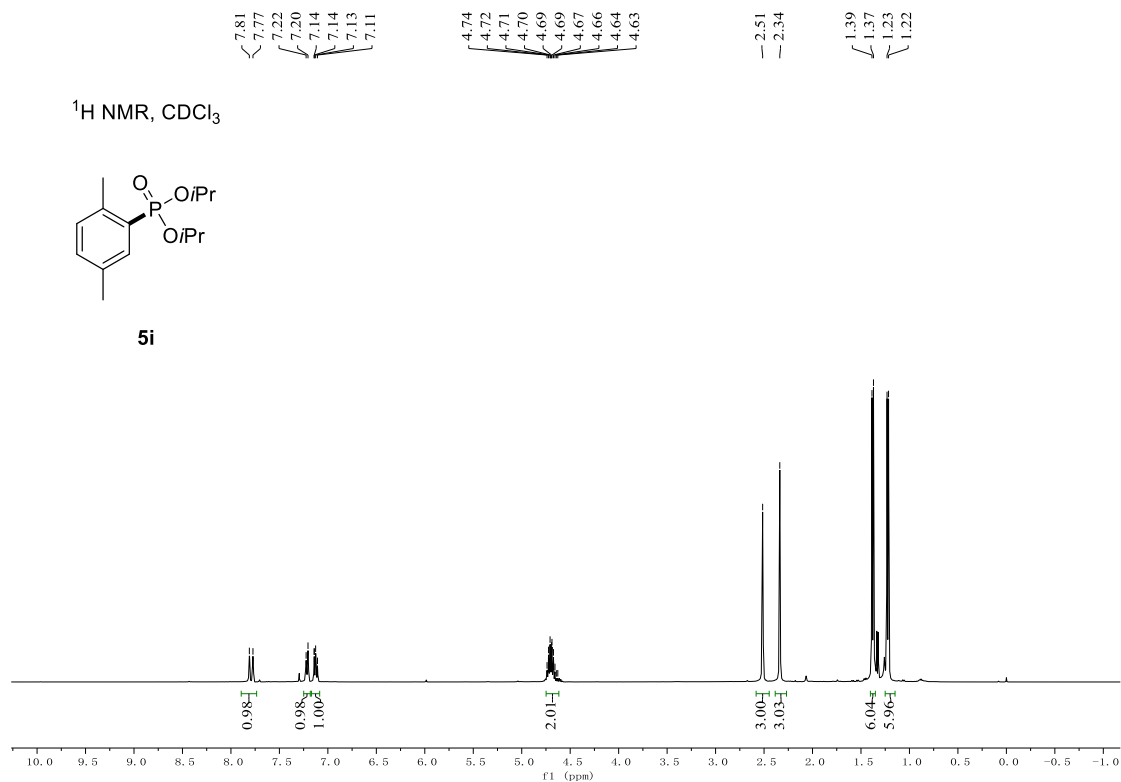
5h



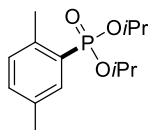
<sup>1</sup>H NMR, CDCl<sub>3</sub>



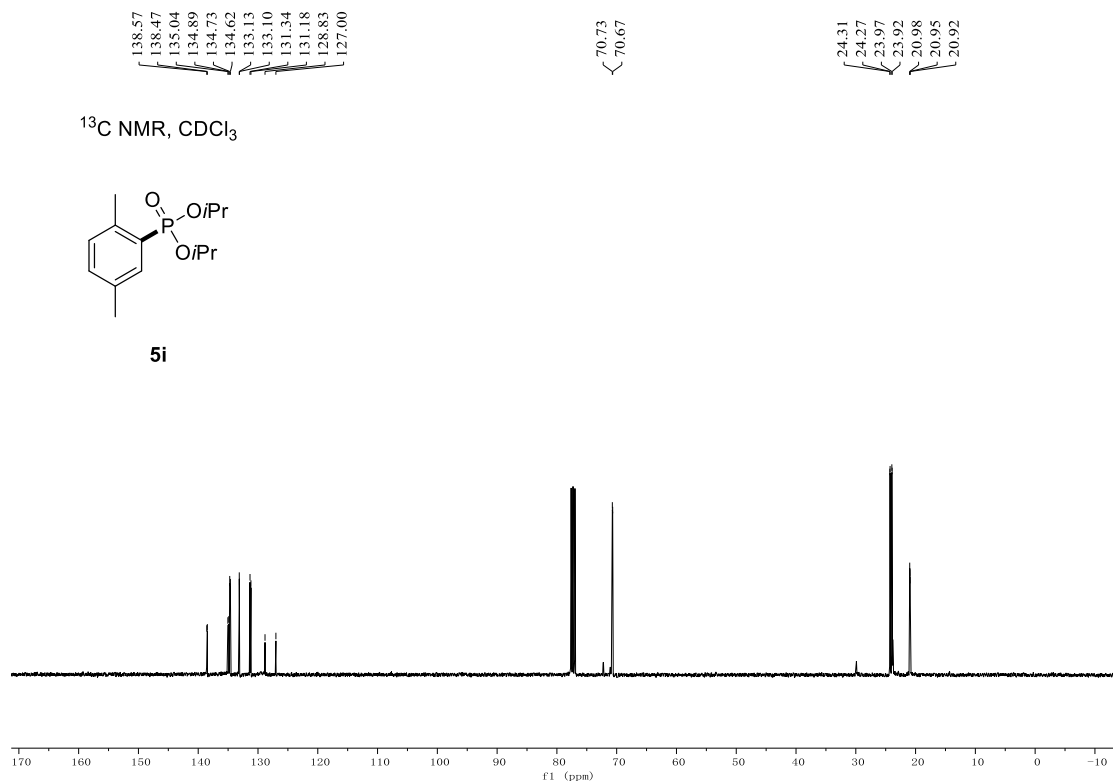
**5i**



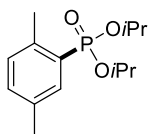
<sup>13</sup>C NMR, CDCl<sub>3</sub>



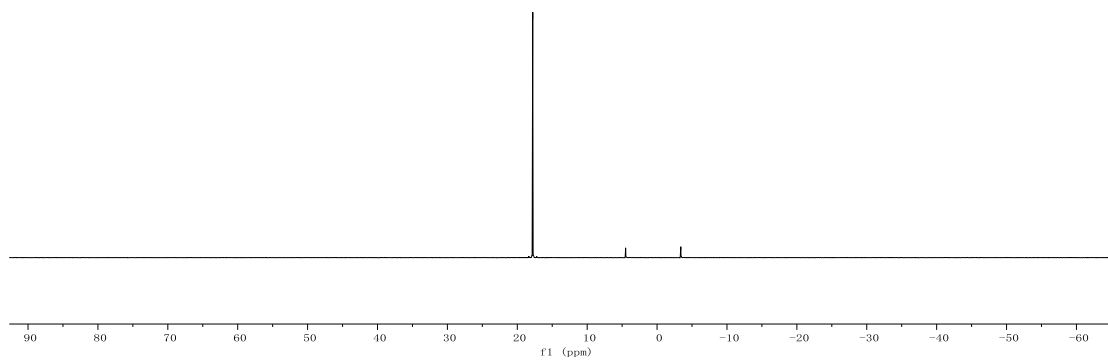
**5i**



$^{31}\text{P}$  NMR,  $\text{CDCl}_3$

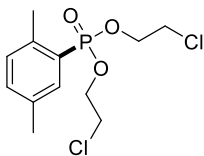


**5i**

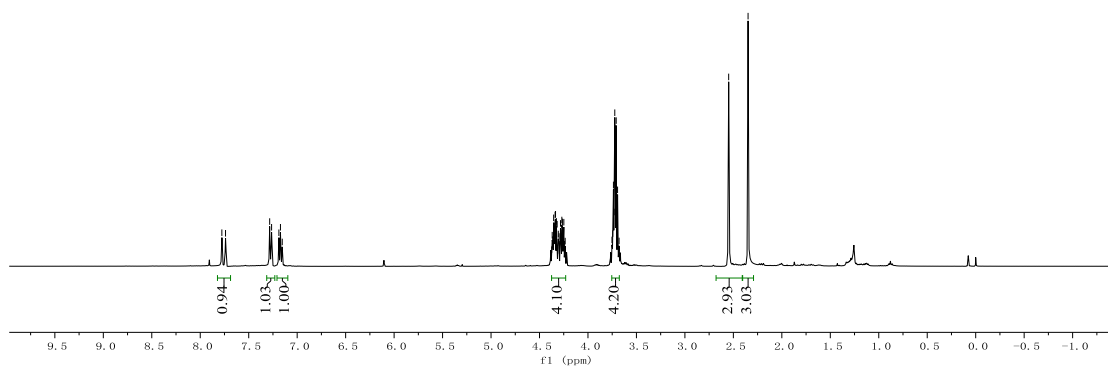


7.78  
7.74  
7.28  
7.26  
7.19  
7.17  
7.15  
4.37  
4.37  
4.36  
4.36  
4.35  
4.35  
4.34  
4.34  
4.33  
4.33  
4.32  
4.32  
4.31  
4.31  
4.30  
4.30  
4.28  
4.28  
4.27  
4.26  
4.26  
4.25  
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3.75  
3.74  
3.74  
3.73  
3.72  
3.72  
3.71  
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3.68  
2.55  
2.35

$^1\text{H}$  NMR,  $\text{CDCl}_3$



**5j**



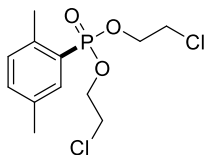
139.18  
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135.29  
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134.09  
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125.91  
124.07

65.65  
65.59

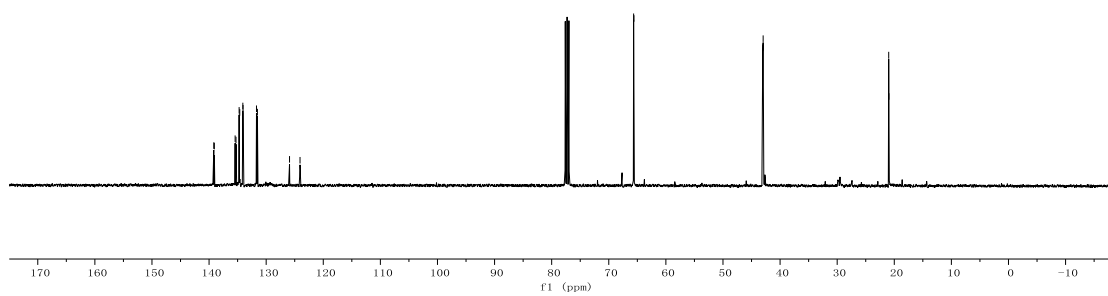
43.04  
42.97

20.98  
20.95

$^{13}\text{C}$  NMR,  $\text{CDCl}_3$

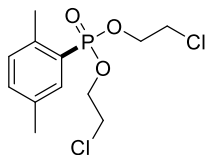


**5j**

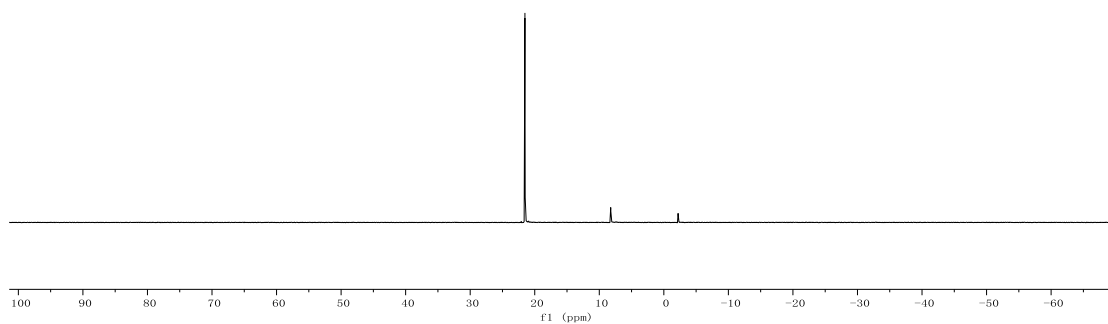


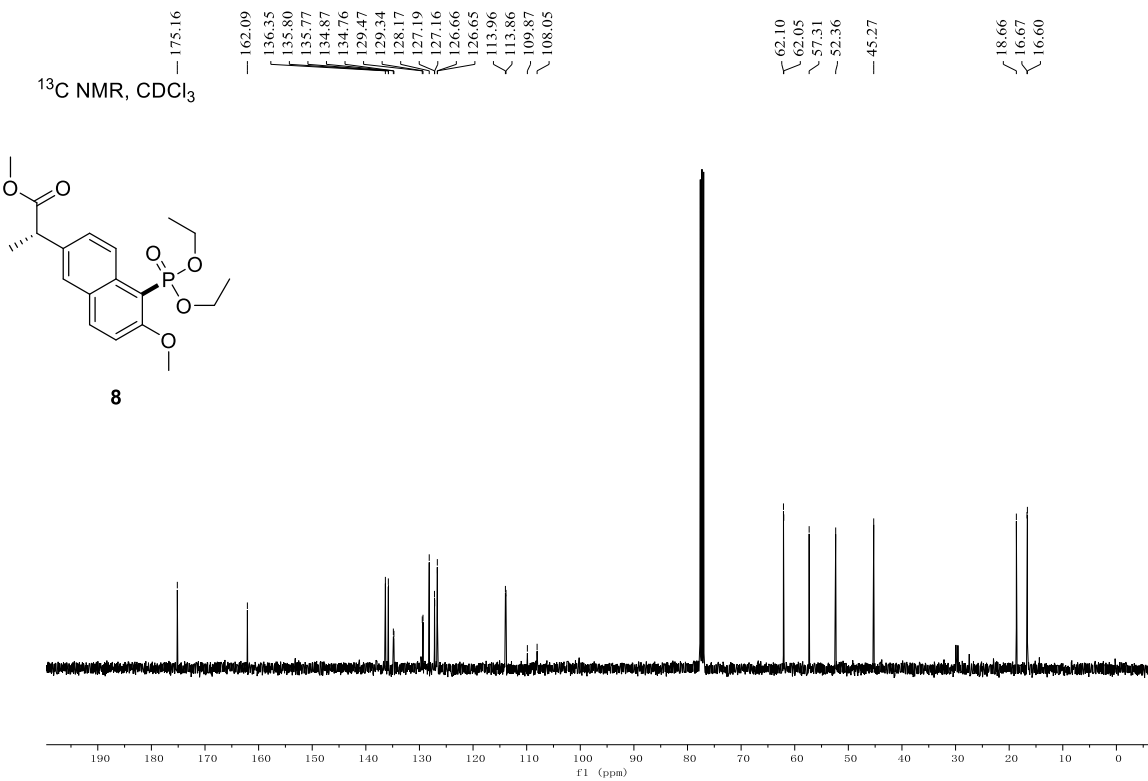
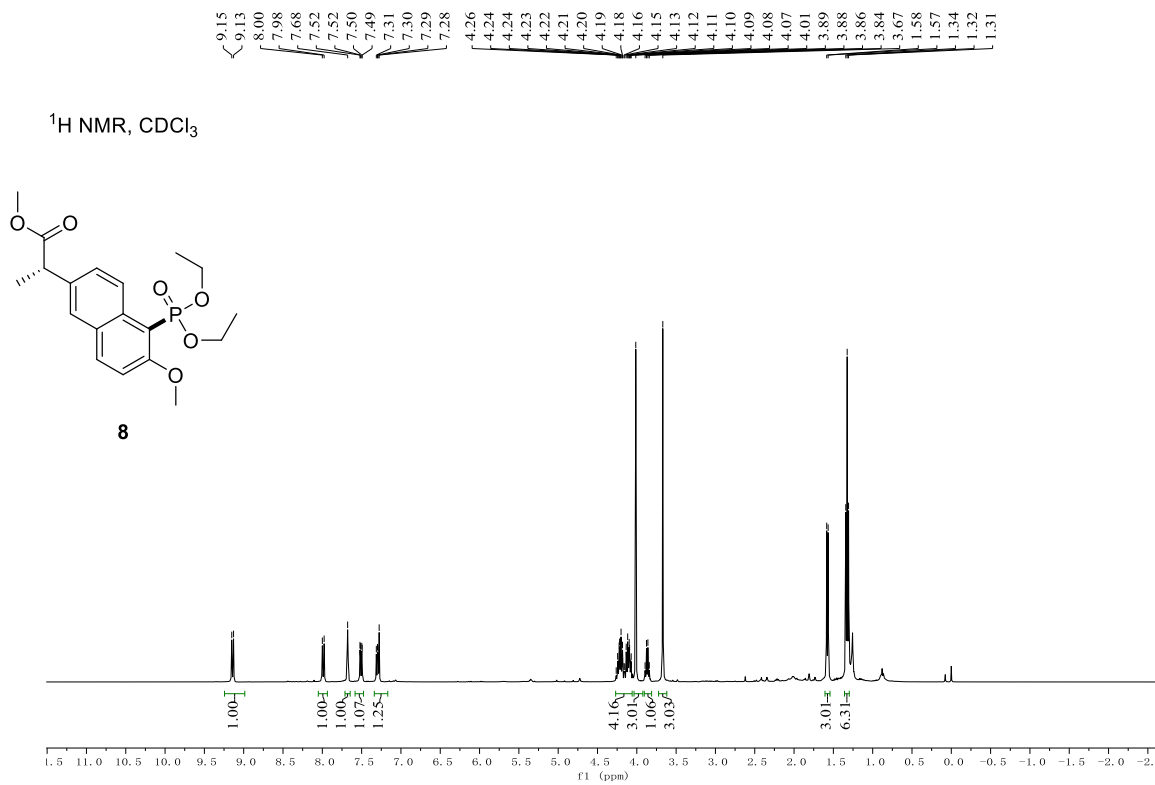
21.52

$^{31}\text{P}$  NMR,  $\text{CDCl}_3$



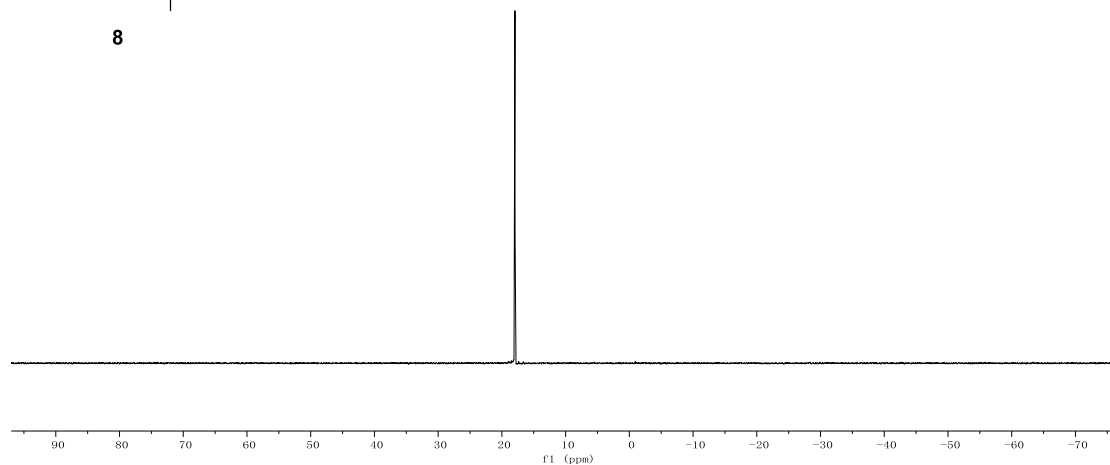
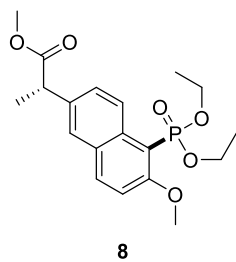
**5j**





$^{31}\text{P}$  NMR,  $\text{CDCl}_3$

— 17.95



7.69  
7.66  
6.66  
6.64  
4.17  
4.15  
4.13  
4.13  
4.11  
4.09  
4.07  
4.05  
4.03  
4.01  
4.00  
3.98  
3.96  
3.95  
2.97  
2.51  
2.19  
1.73  
1.33  
1.31  
1.30  
1.22

$^1\text{H}$  NMR,  $\text{CDCl}_3$

