

Electronic Supplementary Information (ESI)

**Palladium-catalyzed phosphorylation of of arylsulfonium salts with
P(O)H compounds via C-S bond cleavage**

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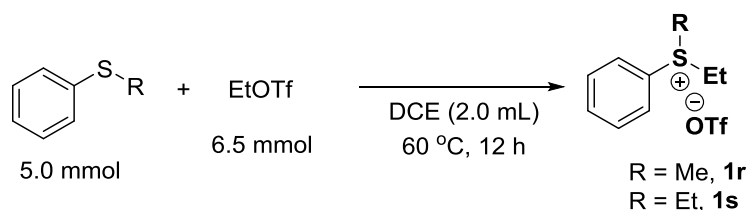
1. General information:

All the palladium-catalyzed phosphonation reactions were carried out in oven-dried glassware sealed with rubber septa under N₂ atmosphere. Column chromatography was performed on silica gel 200 - 300 mesh. All the compounds were known and characterized by ¹H NMR, ¹³C NMR and ³¹P NMR with 400 MHz Bruker AVANCE spectrometers (400 MHz, 100 MHz and 162 MHz, respectively). Chemical shifts are reported relative to tetramethylsilane (TMS, δ 0.0 ppm) for ¹H NMR and CDCl₃ (δ 77.0 ppm) for ¹³C NMR.

Materials: Unless otherwise noted, all reagents were purchased energy chemistry, Ouhe and J&K and used without further purification. Solvents were purified according to standard operation procedure. The arylsulfonium salts **1r** to **1q** were prepared in accordance with references.^[1]

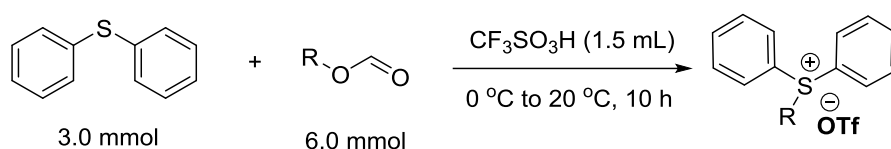
2. General procedures for the synthesis of arylsulfonium triflates **1r-w**^[1-2].

GP A (Arylsulfonium salts **1r** and **1s**)^[1]: To a stirred solution of methyl(phenyl)sulfane or ethyl(phenyl)sulfane (5.0 mmol) and EtOTf (6.5 mmol) in DCE (2.0 mL) was treated with EtOTf (6.5 mL) at 0 °C. The resulting solution was stirred at 60 °C for 12 h, poured into distilled water (20 mL), and extracted with dichloromethane (3 × 30 mL). The crude product was purified by column chromatography on silica gel using a mixture of dichloromethane/methanol = 10/1 (v/v) as eluents to give the desired arylsulfonium triflates **1r** and **1s**.

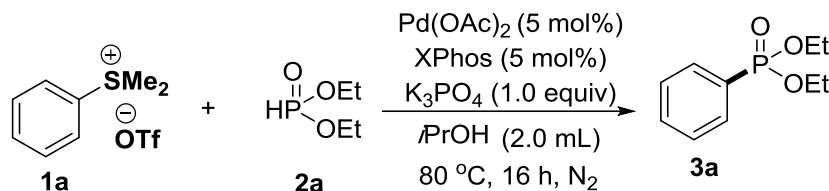


GP B (Arylsulfonium salts **1t-w**)^[2]: To a stirred mixture of diaryl sulfide (3.0 mmol) and alkyl formate (6.0 mmol) was added trifluoromethanesulfonic acid (1.5 mL) at

0 °C. The mixture was warmed to 20 °C for 10 h, poured into distilled water (20 mL), and extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from dichloromethane/diethyl ether system to give the desired alkyl(diaryl)sulfonium triflates **1t-w**.



3. General procedure for palladium-catalyzed phosphonation of arylsulfonium salts with P(O)H compounds.



The phosphonation of **1a** to synthesize **3a** (Table 1, entry 22) is representative.

To a 10 mL of a flame-dried seal tube equipped with a magnetic bar were added Pd(PPh₃)₂Cl₂ (0.015 mmol, 3.4 mg), XPhos (0.015 mmol, 7.3 mg), [PhSMe₂][OTf] (**1a**, 0.36 mmol, 103.8 mg) and H₃PO₄ (0.3 mmol, 63.7 mg). The reaction flask was degassed three times with nitrogen and dry *i*PrOH (2.0 mL) was added using a syringe. Note that the H-phosphonate diester **2a** in a liquid form was added to the reaction tube by syringe after being added in the solvent. The reaction was heated at 80 °C with stirring for 16 h, then cooled to room temperature. After completion of the reaction, the reaction was quenched with water and extracted with EA (25 ml × 3). The organic layers were combined and washed with brine twice. It was dried over anhydrous Na₂SO₄ and solvent was then removed in vacuo to leave a crude mixture, which is purified by silica gel column chromatography to afford the pure desired product **3a**.

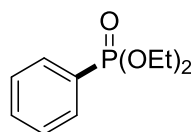
4. One-pot phosphonation of aryl sulfide.

A 10 mL of a flame-dried seal tube equipped with a magnetic bar was charged with methyl phenyl sulfide (44.7 mg, 0.40 mmol) and CH₂Cl₂ (2.0 mL). To this solution, methyl triflate (48 μL, 0.44 mmol) was added, and the resulting mixture was

stirred for 10 h at room temperature. All volatiles were removed under reduced pressure to afford the corresponding sulfonium salt **1a**. To the tube, Pd(PPh₃)₂Cl₂ (0.015 mmol, 3.4 mg), XPhos (0.015 mmol, 7.3 mg), and H₃PO₄ (0.3 mmol, 63.7 mg). The reaction flask was degassed three times with nitrogen and dry *i*PrOH (2.0 mL) was added using a syringe. Note that the H-phosphonate diester **2a** in a liquid form was added to the reaction tube by syringe after being added in the solvent. The reaction was heated at 80 °C with stirring for 16 h, then cooled to room temperature. After completion of the reaction, the reaction was quenched with water and extracted with EA (25 ml × 3). The organic layers were combined and washed with brine twice. It was dried over anhydrous Na₂SO₄ and solvent was then removed in vacuo to leave a crude mixture, which is purified by silica gel column chromatography to afford the pure desired product **3a**.

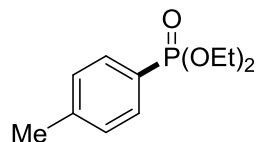
5. Characterization data for the products.

Diethyl phenylphosphonate (**3a**).



Colorless oil (phenyltriethoxysilane, 38.5 mg, 72 % yield), ¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.73 (m, 2H), 7.55 – 7.47 (m, 1H), 7.45 – 7.38 (m, 2H), 4.16 – 3.97 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 132.3 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 9.9 Hz), 128.4 (d, *J* = 15.0 Hz), 128.2 (d, *J* = 186.8 Hz), 62.0 (d, *J* = 5.4 Hz), 16.2 (d, *J* = 6.5 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 18.82. This compound is known^[3].

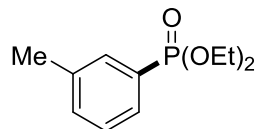
Diethyl *p*-tolylphosphonate (**3b**).



Colorless oil (37.1 mg, 65 % yield): ¹H NMR (400 MHz, CDCl₃) δ 7.66 (dd, *J* = 13.1, 8.0 Hz, 2H), 7.24 (dt, *J* = 7.8, 4.0 Hz, 2H), 4.23 – 3.91 (m, 4H), 2.36 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 142.8 (d, *J* = 3.1 Hz), 131.7 (d, *J* = 10.3 Hz), 129.1 (d, *J* = 15.4 Hz), 124.8 (d, *J* = 190.0 Hz), 61.8 (d, *J* = 5.3 Hz), 21.5 (d,

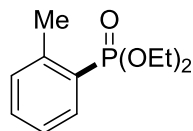
$J = 1.2$ Hz), 16.2 (d, $J = 6.6$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 19.57. This compound is known^[3].

Diethyl *m*-tolylphosphonate (3c).



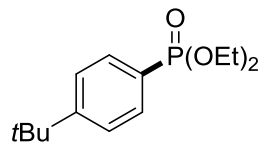
Colorless oil (38.8 mg, 68 % yield): ^1H NMR (400 MHz, CDCl_3) δ 7.70 – 7.49 (m, 2H), 7.31 (t, $J = 4.1$ Hz, 2H), 4.22 – 3.93 (m, 4H), 2.35 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.2 (d, $J = 15.0$ Hz), 133.1 (d, $J = 3.2$ Hz), 132.1 (d, $J = 10.0$ Hz), 128.6 (d, $J = 9.7$ Hz), 128.3 (d, $J = 15.8$ Hz), 127.9 (d, $J = 185.7$ Hz), 61.9 (d, $J = 5.4$ Hz), 21.2, 16.2 (d, $J = 6.5$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 19.36. This compound is known^[3].

Diethyl *o*-tolylphosphonate (3d).



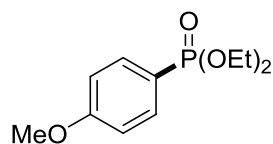
Colorless oil (18.8 mg, 50 % yield): ^1H NMR (400 MHz, CDCl_3) δ 7.91 (ddd, $J = 14.4, 7.9, 1.3$ Hz, 1H), 7.42 (dd, $J = 10.6, 4.5$ Hz, 1H), 7.30 – 7.19 (m, 2H), 4.25 – 3.98 (m, 4H), 2.57 (d, $J = 1.3$ Hz, 3H), 1.32 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.8 (d, $J = 10.2$ Hz), 133.9 (d, $J = 10.3$ Hz), 132.4 (d, $J = 3.0$ Hz), 131.2 (d, $J = 14.9$ Hz), 126.7 (d, $J = 183.8$ Hz), 125.4 (d, $J = 14.8$ Hz), 61.9 (d, $J = 5.5$ Hz), 21.2 (d, $J = 3.6$ Hz), 16.3 (d, $J = 6.6$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 19.50. This compound is known^[3].

Diethyl (4-(*tert*-butyl)phenyl)phosphonate (3e).



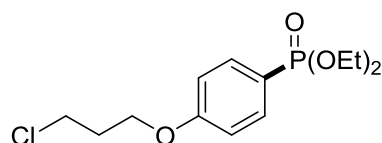
Colorless oil (47.9 mg, 63 % yield): ^1H NMR (400 MHz, CDCl_3) δ 7.69 (dd, $J = 13.0, 8.4$ Hz, 2H), 7.49 – 7.32 (m, 2H), 4.27 – 3.95 (m, 4H), 1.49 – 1.08 (m, 15H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.7 (d, $J = 3.1$ Hz), 131.5 (d, $J = 10.3$ Hz), 125.3 (d, $J = 15.2$ Hz), 124.7 (d, $J = 189.0$ Hz), 61.8 (d, $J = 5.3$ Hz), 34.9, 30.9, 16.2 (d, $J = 6.6$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 19.51. This compound is known^[4].

Diethyl (4-methoxyphenyl)phosphonate (3f)



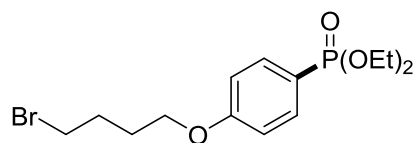
Colorless oil (51.2 mg, 84 % yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 – 7.65 (m, 2H), 6.98 – 6.85 (m, 2H), 4.17 – 3.91 (m, 4H), 3.81 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 162.8 (d, $J = 3.4$ Hz), 133.7 (d, $J = 11.4$ Hz), 119.3 (d, $J = 194.9$ Hz), 113.9 (d, $J = 16.0$ Hz), 61.8 (d, $J = 5.3$ Hz), 55.2, 16.2 (d, $J = 6.6$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 19.77. This compound is known^[3].

diethyl (4-(3-chloropropoxy)phenyl)phosphonate (3g).



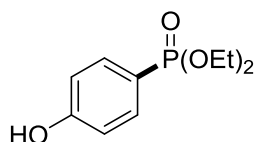
Colorless oil (66 % yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 – 7.63 (m, 2H), 7.02 – 6.90 (m, 2H), 4.13 (t, $J = 5.7$ Hz, 2H), 4.11 – 3.96 (m, 4H), 3.72 (t, $J = 6.3$ Hz, 2H), 2.22 (p, $J = 6.0$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.9 (d, $J = 3.4$ Hz), 133.7 (d, $J = 11.3$ Hz), 119.6 (d, $J = 194.7$ Hz), 114.4 (d, $J = 16.0$ Hz), 64.2, 61.8 (d, $J = 5.3$ Hz), 41.2, 31.9, 16.2 (d, $J = 6.6$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 19.62. **HRMS (ESI) m/z:** $[\text{M}+\text{K}]^+$ Calcd for $\text{C}_{13}\text{H}_{20}\text{ClO}_4\text{PK}^+$ 345.0419; found 345.0396.

diethyl (4-(4-bromobutoxy)phenyl)phosphonate (3h).



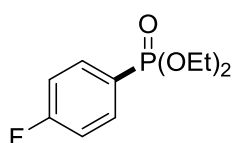
Colorless oil (68 % yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 – 7.63 (m, 2H), 6.97 – 6.87 (m, 2H), 4.08 (ddd, $J = 14.5, 7.2, 2.8$ Hz, 2H), 4.02 – 3.96 (m, 4H), 3.45 (t, $J = 6.5$ Hz, 2H), 2.08 – 1.98 (m, 2H), 1.97 – 1.88 (m, 2H), 1.27 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 162.0 (d, $J = 3.4$ Hz), 133.7 (d, $J = 11.3$ Hz), 119.4 (d, $J = 194.9$ Hz), 114.3 (d, $J = 16.0$ Hz), 66.8, 61.8 (d, $J = 5.3$ Hz), 33.2, 29.2, 27.6, 16.2 (d, $J = 6.6$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 19.69. **HRMS (ESI) m/z:** $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{23}\text{BrO}_4\text{P}^+$ 365.0512; found 365.0492.

diethyl (4-hydroxyphenyl)phosphonate (3-3i).



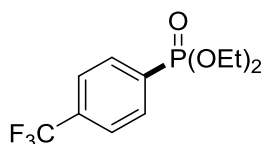
Colorless oil (67 % yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.95 (s, 1H), 7.65-7.60 (m, 2H), 7.08 – 6.92 (m, 2H), 4.23 – 3.91 (m, 4H), 1.30 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.8 (d, $J = 3.3$ Hz), 133.7 (d, $J = 11.7$ Hz), 116.1 (d, $J = 196.2$ Hz), 116.0 (d, $J = 16.4$ Hz), 62.3 (d, $J = 5.4$ Hz), 16.2 (d, $J = 6.6$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 21.10. This compound is known^[5].

Diethyl (4-fluorophenyl)phosphonate (3j).



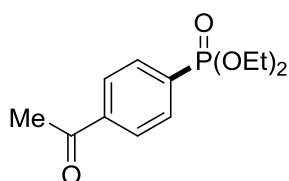
Colorless oil (37.2 mg, 64 % yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 – 7.71 (m, 2H), 7.11 (td, $J = 8.7, 3.1$ Hz, 2H), 4.26 – 3.92 (m, 4H), 1.28 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.2 (dd, $J = 253.5, 3.9$ Hz), 134.3 (dd, $J = 11.3, 8.9$ Hz), 124.3 (dd, $J = 192.7, 3.4$ Hz), 115.7 (dd, $J = 21.4, 16.3$ Hz), 62.1 (d, $J = 5.4$ Hz), 16.2 (d, $J = 6.5$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 17.84. This compound is known^[3].

Diethyl (4-(trifluoromethyl)phenyl)phosphonate (3k).



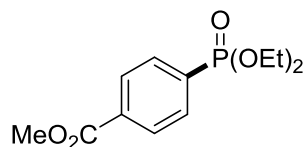
Colorless oil (49.5 mg, 70 % yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 (dd, $J = 13.0, 8.0$ Hz, 2H), 7.68 (dd, $J = 8.1, 3.5$ Hz, 2H), 4.23 – 3.96 (m, 4H), 1.29 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 133.9 (dd, $J = 32.7, 3.3$ Hz), 132.7 (d, $J = 185.7$ Hz), 132.1 (d, $J = 10.2$ Hz), 125.2 (dq, $J = 15.1, 3.7$ Hz), 123.4 (d, $J = 272.7$ Hz), 62.4 (d, $J = 5.5$ Hz), 16.2 (d, $J = 6.4$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 16.29. This compound is known^[3].

diethyl (4-acetylphenyl)phosphonate (3l).



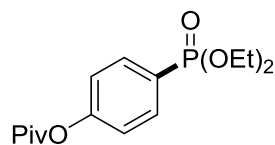
Colorless oil (46 % yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.08 – 7.94 (m, 2H), 7.90-7.85 (m, 2H), 4.22 – 3.97 (m, 4H), 2.60 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 197.4, 139.7 (d, $J = 3.2$ Hz), 133.2 (d, $J = 186.5$ Hz), 132.0 (d, $J = 10.0$ Hz), 128.0 (d, $J = 15.1$ Hz), 62.3 (d, $J = 5.5$ Hz), 26.7, 16.2 (d, $J = 6.4$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 16.87. This compound is known^[5].

methyl 4-(diethoxyphosphoryl)benzoate (3m).



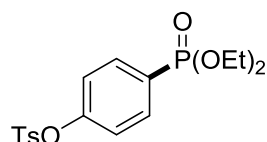
Colorless oil (57 % yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10-8.07 (m, 2H), 7.92 – 7.77 (m, 2H), 4.21 – 3.98 (m, 4H), 3.91 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.1, 133.4 (d, $J = 3.3$ Hz), 133.1 (d, $J = 185.3$ Hz), 131.7 (d, $J = 10.1$ Hz), 129.3 (d, $J = 15.0$ Hz), 62.3 (d, $J = 5.5$ Hz), 52.4, 16.2 (d, $J = 6.4$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 17.02. This compound is known^[6].

4-(diethoxyphosphoryl)phenyl pivalate (3n).



Colorless oil (70 % yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 – 7.74 (m, 2H), 7.18 – 7.06 (m, 2H), 4.21 – 3.94 (m, 4H), 1.32 (s, 9H), 1.28 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 176.4, 154.3 (d, $J = 3.8$ Hz), 133.3 (d, $J = 11.0$ Hz), 125.5 (d, $J = 190.9$ Hz), 121.7 (d, $J = 15.9$ Hz), 62.1 (d, $J = 5.4$ Hz), 39.1, 26.9, 16.2 (d, $J = 6.5$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 18.06. **HRMS (ESI) m/z:** $[\text{M}+\text{K}]^+$ Calcd for $\text{C}_{15}\text{H}_{23}\text{O}_5\text{PK}^+$ 353.0915; found 353.0892.

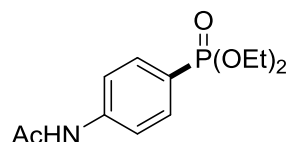
4-(diethoxyphosphoryl)phenyl 4-methylbenzenesulfonate (3o).



Colorless oil (66 % yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 – 7.70 (m, 2H), 7.69-7.66 (m, 2H), 7.30-7.28 (m, 2H), 7.11 – 7.00 (m, 2H), 4.19 – 3.96 (m, 4H), 2.42 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.4 (d, $J = 4.0$ Hz),

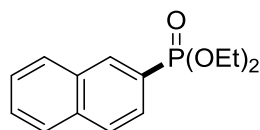
145.7, 133.4 (d, $J = 11.0$ Hz), 131.9, 129.8, 128.4, 126.5, 122.4 (d, $J = 15.9$ Hz), 62.3 (d, $J = 5.6$ Hz), 21.6, 16.2 (d, $J = 6.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 17.12. This compound is known^[6].

diethyl (4-acetamidophenyl)phosphonate (3p).



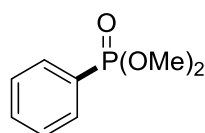
White solid (50 % yield): ^1H NMR (400 MHz, CDCl_3) δ 9.26 (s, 1H), 7.71 (dd, $J = 9.6, 5.2$ Hz, 3H), 7.65 (d, $J = 8.6$ Hz, 1H), 4.12 – 3.97 (m, 4H), 2.17 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.5, 142.7 (d, $J = 3.4$ Hz), 132.6 (d, $J = 10.8$ Hz), 121.8 (d, $J = 193.3$ Hz), 119.2 (d, $J = 15.3$ Hz), 62.2 (d, $J = 5.5$ Hz), 24.4, 16.2 (d, $J = 6.6$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 18.91. This compound is known^[6].

diethyl naphthalen-2-ylphosphonate (3q).



Colorless oil (70 % yield): ^1H NMR (400 MHz, CDCl_3) δ 8.42 (d, $J = 15.5$ Hz, 1H), 7.90 (dd, $J = 11.2, 6.6$ Hz, 2H), 7.85 (d, $J = 7.9$ Hz, 1H), 7.78 – 7.71 (m, 1H), 7.61 – 7.50 (m, 2H), 4.35 – 3.88 (m, 4H), 1.32 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.9 (d, $J = 2.7$ Hz), 134.0 (d, $J = 10.2$ Hz), 132.2 (d, $J = 16.7$ Hz), 128.8, 128.3 (d, $J = 14.3$ Hz), 128.2, 127.7, 126.8 (d, $J = 1.0$ Hz), 126.3 (d, $J = 9.8$ Hz), 125.2 (d, $J = 187.9$ Hz), 62.1 (d, $J = 5.3$ Hz), 16.3 (d, $J = 6.5$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 19.17. This compound is known^[3].

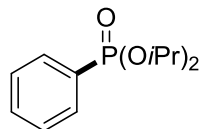
Dimethyl phenylphosphonate (4a).



Colorless oil (53.1 mg, 95 % yield): ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.71 (m, 2H), 7.56-7.52 (m, 1H), 7.47-7.42 (m, 2H), 3.72 (d, $J = 11.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.6 (d, $J = 3.0$ Hz), 131.8 (d, $J = 9.9$ Hz), 128.5 (d, $J = 15.1$ Hz),

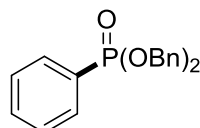
126.7 (d, $J = 188.6$ Hz), 52.6 (d, $J = 5.5$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 21.66. This compound is known^[3].

Diisopropyl phenylphosphonate (4b).



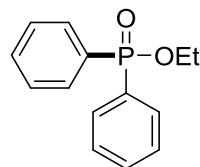
Colorless oil (34.2 mg, 47 % yield): ^1H NMR (400 MHz, CDCl_3) δ 7.81-7.76 (m, 2H), 7.51-7.47 (m, 1H), 7.44-7.39 (m, 2H), 4.65 (dq, $J = 18.8, 6.2$ Hz, 2H), 1.32 (dd, $J = 9.5, 4.4$ Hz, 6H), 1.19 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.0 (d, $J = 3.0$ Hz), 131.6 (d, $J = 9.8$ Hz), 129.8 (d, $J = 188.4$ Hz), 128.2 (d, $J = 15.0$ Hz), 70.6 (d, $J = 5.5$ Hz), 24.0 (d, $J = 4.0$ Hz), 23.7 (d, $J = 4.8$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 16.69. This compound is known^[3].

dibenzyl phenylphosphonate (4c).



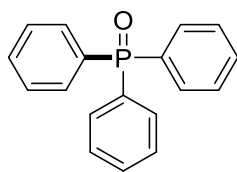
Colorless oil (65.1 mg, 64 % yield): ^1H NMR (400 MHz, CDCl_3) δ 7.82 (ddd, $J = 13.5, 8.2, 1.4$ Hz, 2H), 7.55 (td, $J = 7.4, 1.5$ Hz, 1H), 7.44 (ddd, $J = 8.5, 6.9, 4.3$ Hz, 2H), 7.35 – 7.29 (m, 10H), 5.20 – 4.93 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.1 (d, $J_{\text{C-P}} = 6.8$ Hz), 132.5 (d, $J_{\text{C-P}} = 3.1$ Hz), 131.8 (d, $J_{\text{C-P}} = 10.0$ Hz), 128.5, 128.5, 128.4, 128.3, 127.8, 67.6. ^{31}P NMR (162 MHz, CDCl_3) δ 19.7. This compound is known^[3].

ethyl diphenylphosphinate (4d).



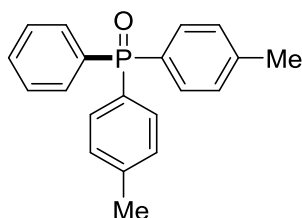
Colorless oil (60.7 mg, 82 % yield): ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.78 (m, 4H), 7.54 – 7.47 (m, 2H), 7.44 (tdd, $J = 8.2, 3.4, 1.3$ Hz, 4H), 4.10 (p, $J = 7.1$ Hz, 2H), 1.36 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.0 (d, $J = 2.7$ Hz), 131.5 (d, $J = 136.2$ Hz), 131.5 (d, $J = 10.1$ Hz), 128.4 (d, $J = 13.1$ Hz), 61.0 (d, $J = 5.9$ Hz), 16.4 (d, $J = 6.7$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 31.39. This compound is known^[7].

triphenylphosphine oxide (4e).



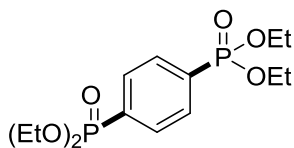
White solid (19.2 mg, 23% yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 – 7.61 (m, 6H), 7.55-7.51 (m, 3H), 7.47-7.42 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 132.95, 132.03 (d, $J = 9.9$ Hz), 131.89 (d, $J = 2.8$ Hz), 128.45 (d, $J = 12.1$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 29.25. This compound is known^[7].

phenyldi-*p*-tolylphosphine oxide (4f).



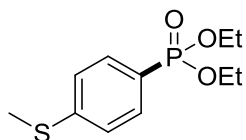
Colorless oil (58.8 mg, 64% yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 – 7.61 (m, 2H), 7.58 – 7.48 (m, 5H), 7.43 (ddd, $J = 8.4, 6.6, 2.9$ Hz, 2H), 7.28 – 7.21 (m, 4H), 2.38 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.3 (d, $J_{\text{C-P}} = 2.9$ Hz), 132.5, 132.0 (d, $J_{\text{C-P}} = 10.3$ Hz), 132.0 (d, $J_{\text{C-P}} = 9.9$ Hz), 131.7 (d, $J_{\text{C-P}} = 2.8$ Hz), 129.4 (d, $J_{\text{C-P}} = 106.4$ Hz), 129.2 (d, $J_{\text{C-P}} = 12.5$ Hz), 128.3 (d, $J_{\text{C-P}} = 12.1$ Hz), 21.6. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 29.4. This compound is known^[7].

tetraethyl 1,4-phenylenebis(phosphonate) (5).



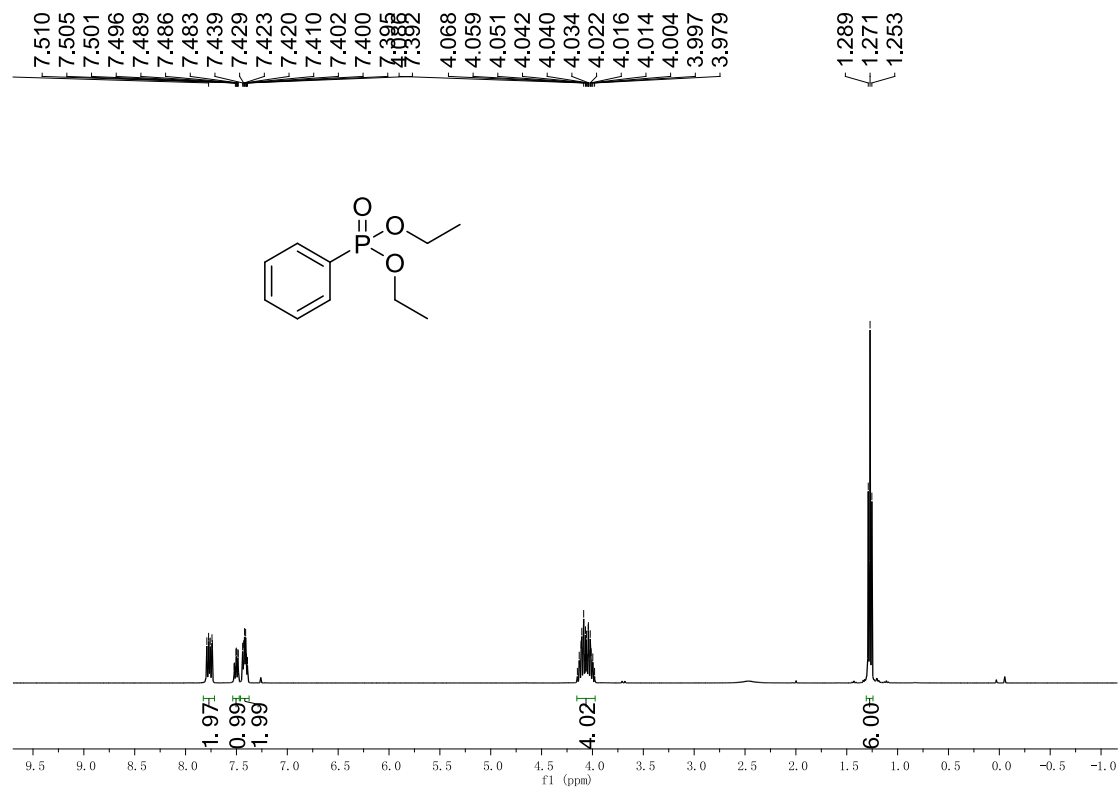
Colorless oil (23.1 mg, 22 % yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 – 7.76 (m, 4H), 4.36 – 3.88 (m, 8H), 1.33 (t, $J = 7.1$ Hz, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 132.9 (dd, $J = 186.9, 3.1$ Hz), 131.75 – 131.37 (m), 62.5 (d, $J = 5.6$ Hz), 16.3 (d, $J = 6.4$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 16.84. This compound is known^[8].

diethyl (4-(methylthio)phenyl)phosphonate (6).

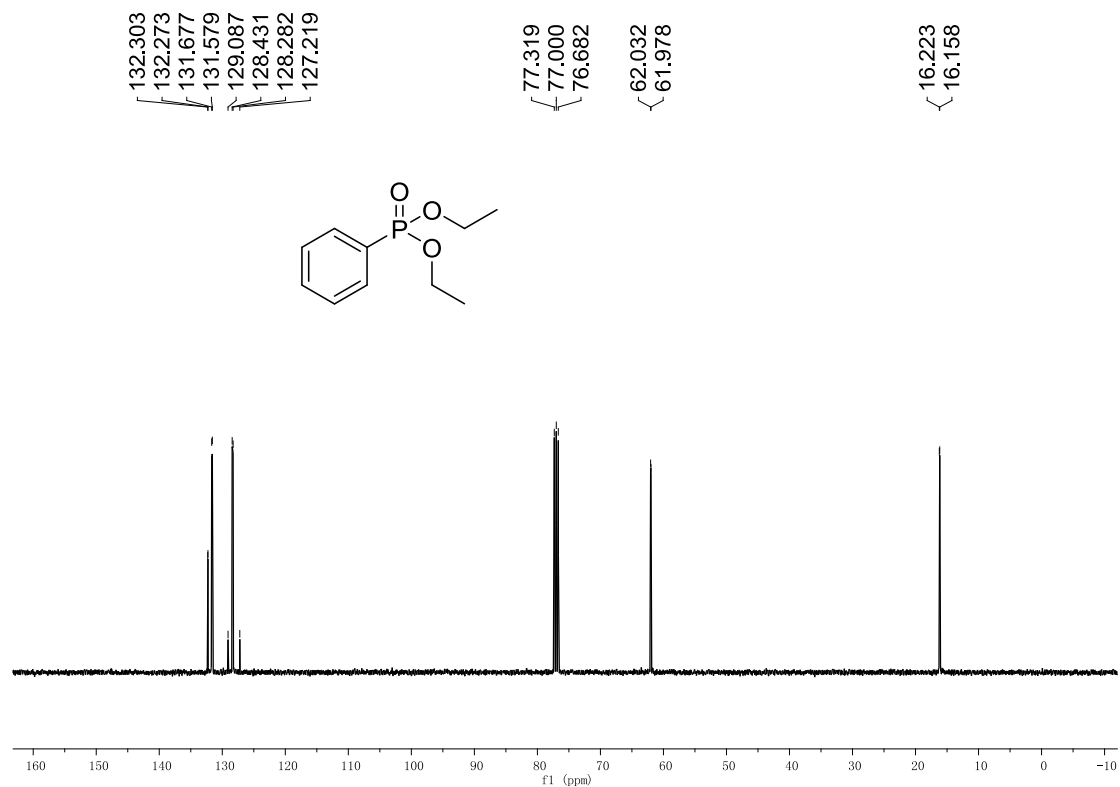


Yellow oil (27.3 mg, 35 % yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 – 7.55 (m, 2H), 7.38 – 7.11 (m, 2H), 4.21 – 3.96 (m, 4H), 2.48 (s, 3H), 1.29 (dd, $J = 8.9, 5.3$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 144.8 (d, $J = 3.5$ Hz), 132.0 (d, $J = 10.6$ Hz), 125.0 (d, $J = 15.4$ Hz), 123.6 (d, $J = 192.1$ Hz), 62.0 (d, $J = 5.3$ Hz), 16.2 (d, $J = 6.6$ Hz), 14.6 (s). $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 19.12. This compound is known ^[5].

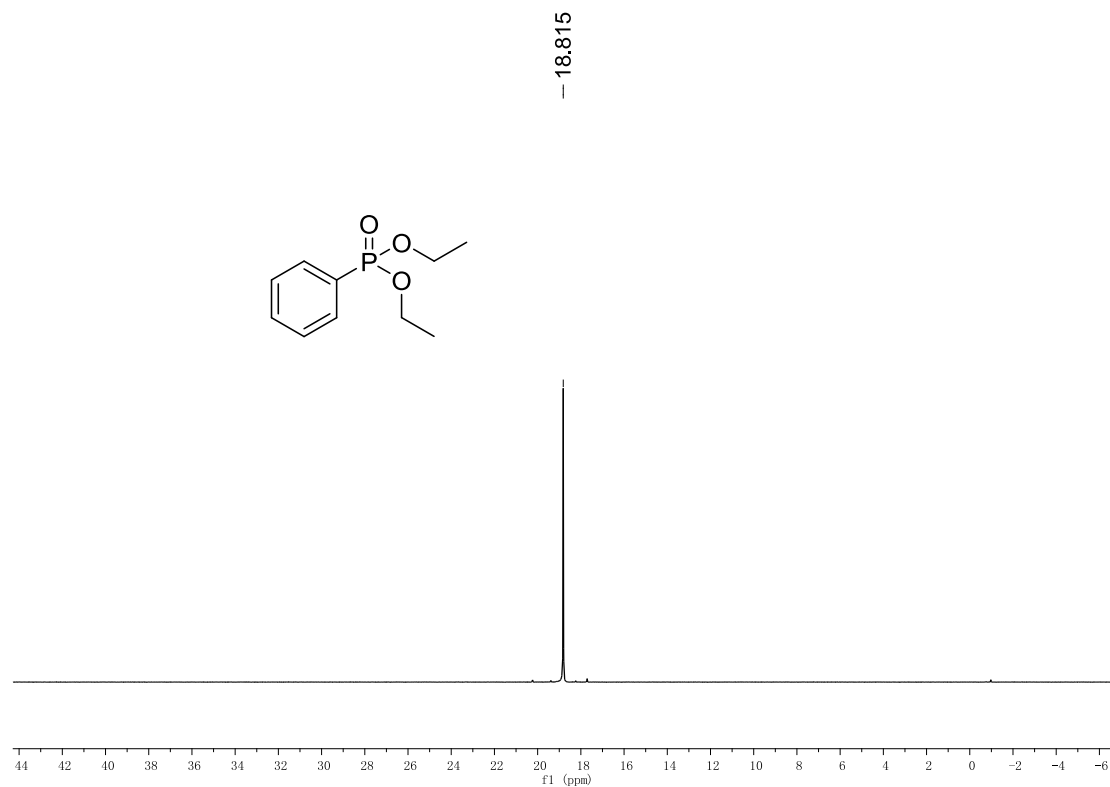
5. ^1H , ^{13}C and ^{31}P NMR spectra of the products.



^1H NMR of 3a

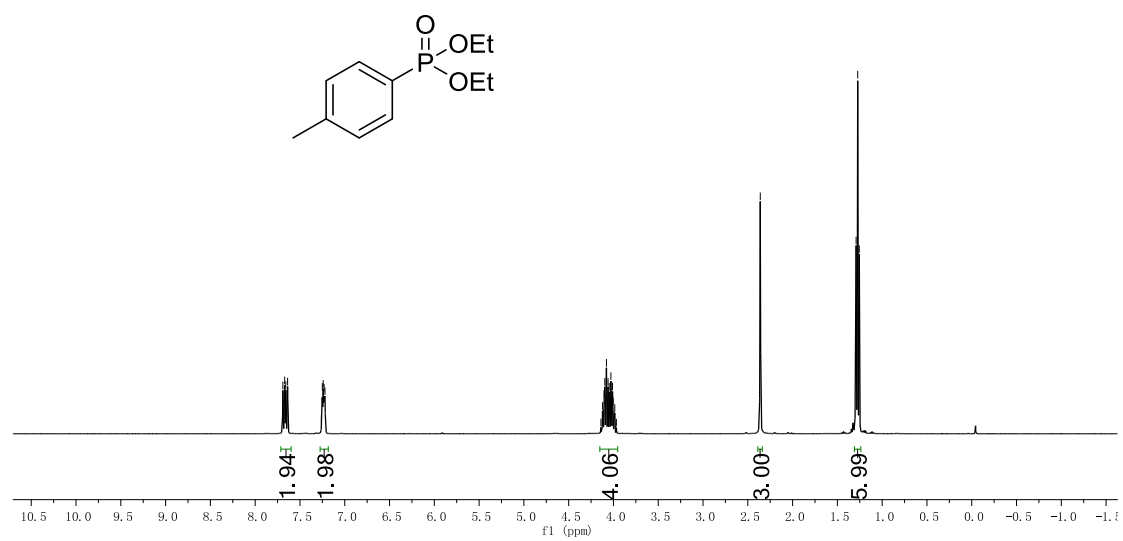


^{13}C NMR of 3a



^{31}P NMR of 3a

7.691
7.671
7.658
7.638
7.260
7.250
7.240
7.231
7.221
4.078
4.048
4.043
4.029
4.022
4.011
4.003
3.993
3.985
3.967
- 2.361
1.291
1.273
1.256



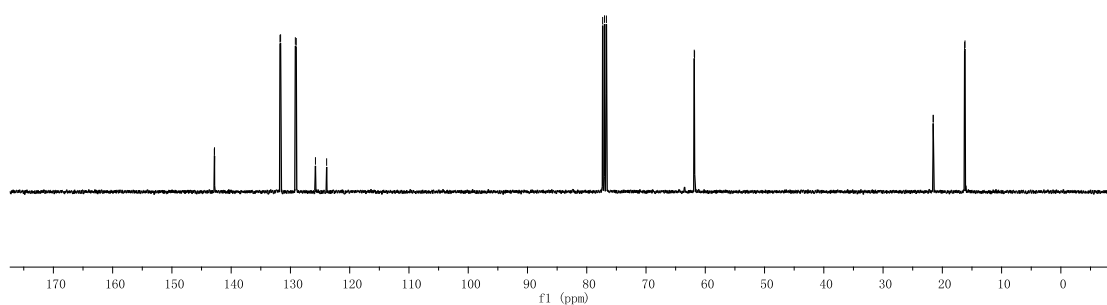
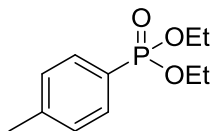
^1H NMR of 3b

142.842
142.811
131.761
131.659
129.173
129.020
125.779
123.891

77.319
77.000
76.682

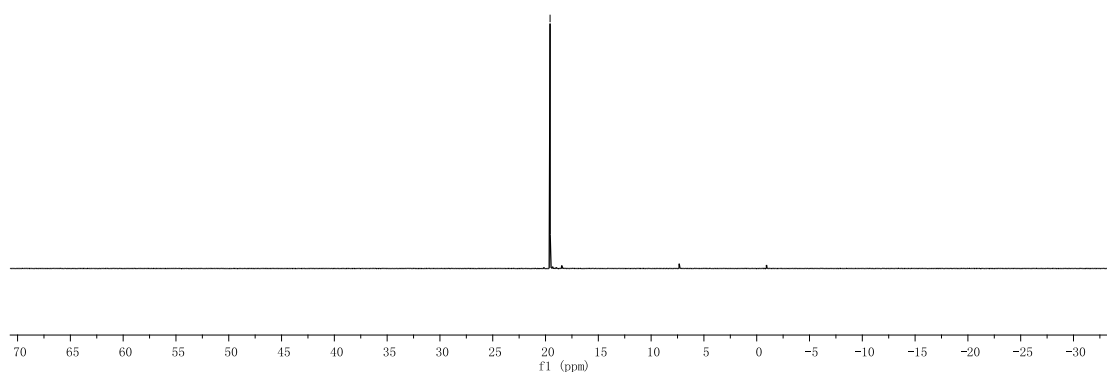
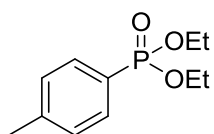
61.861
61.808

21.543
21.531
16.239
16.173

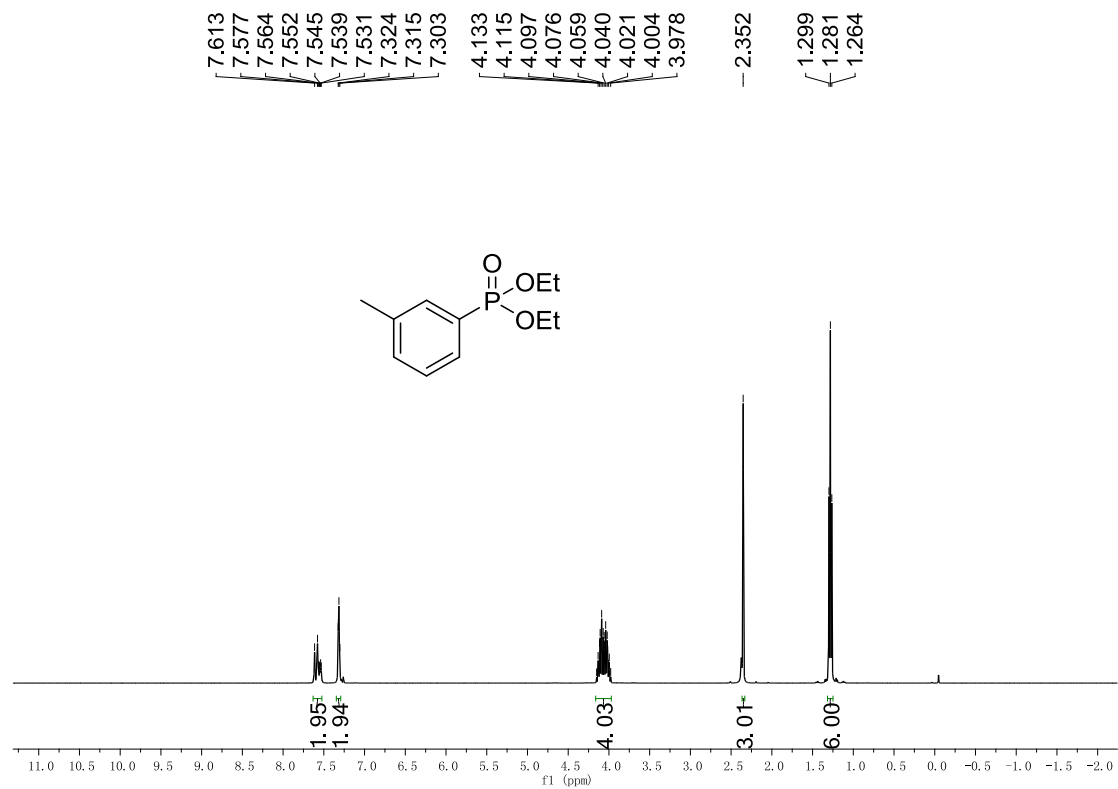


¹³C NMR of 3b

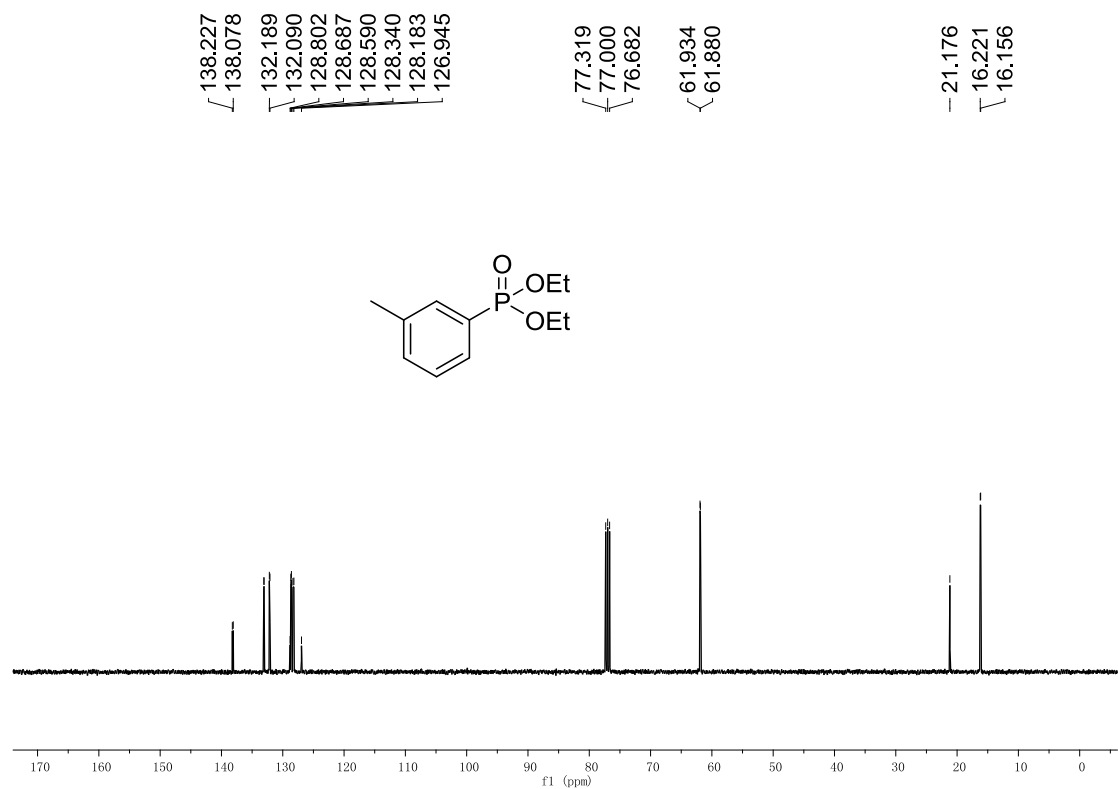
19.570



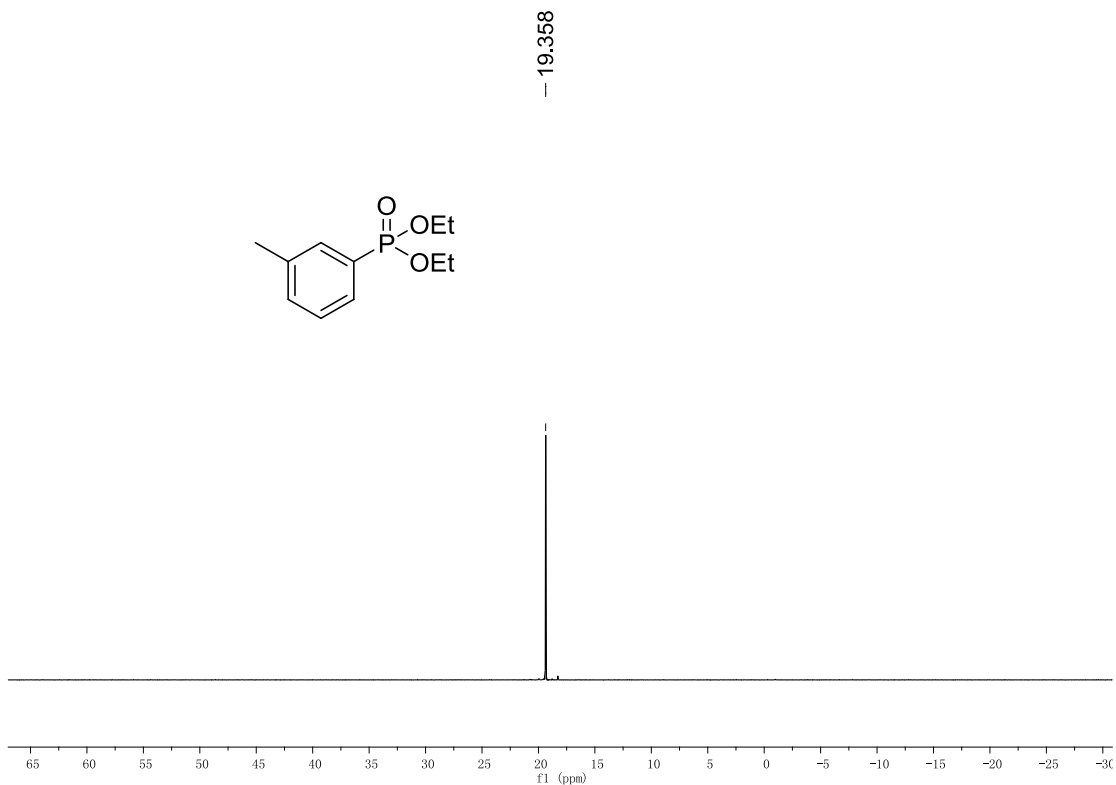
³¹P NMR of 3b



¹H NMR of **3c**

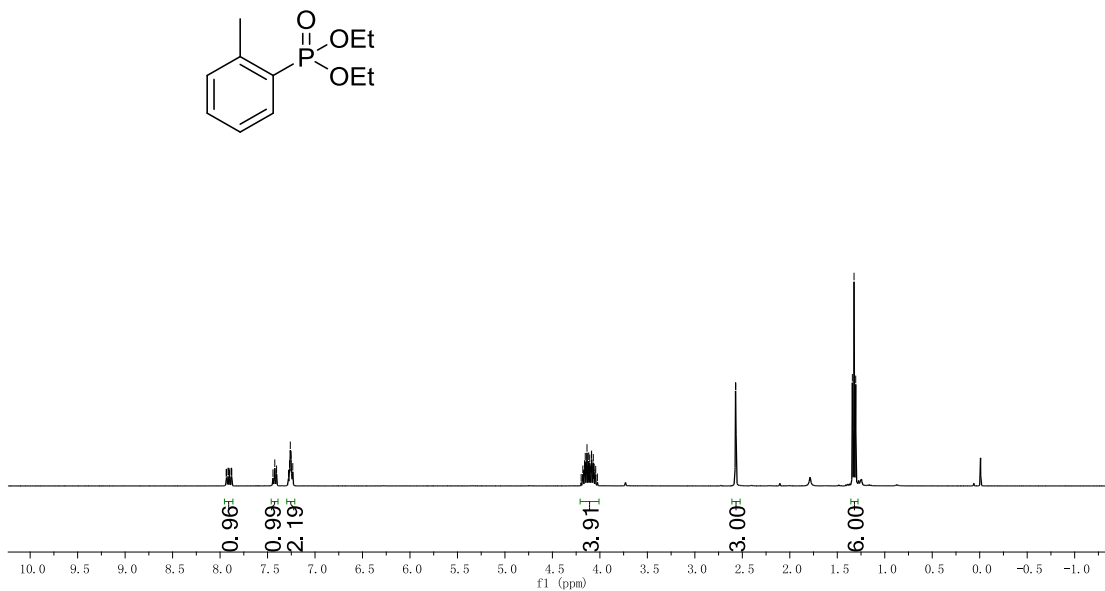


¹³C NMR of **3c**

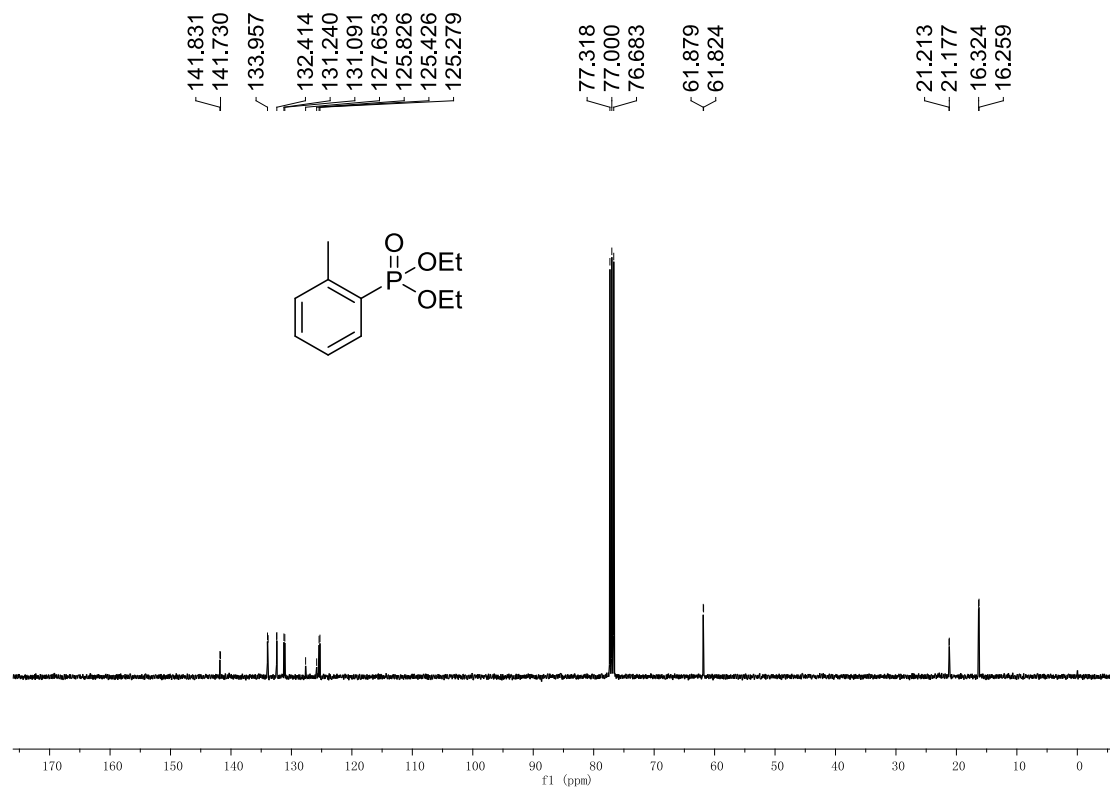


³¹P NMR of 3c

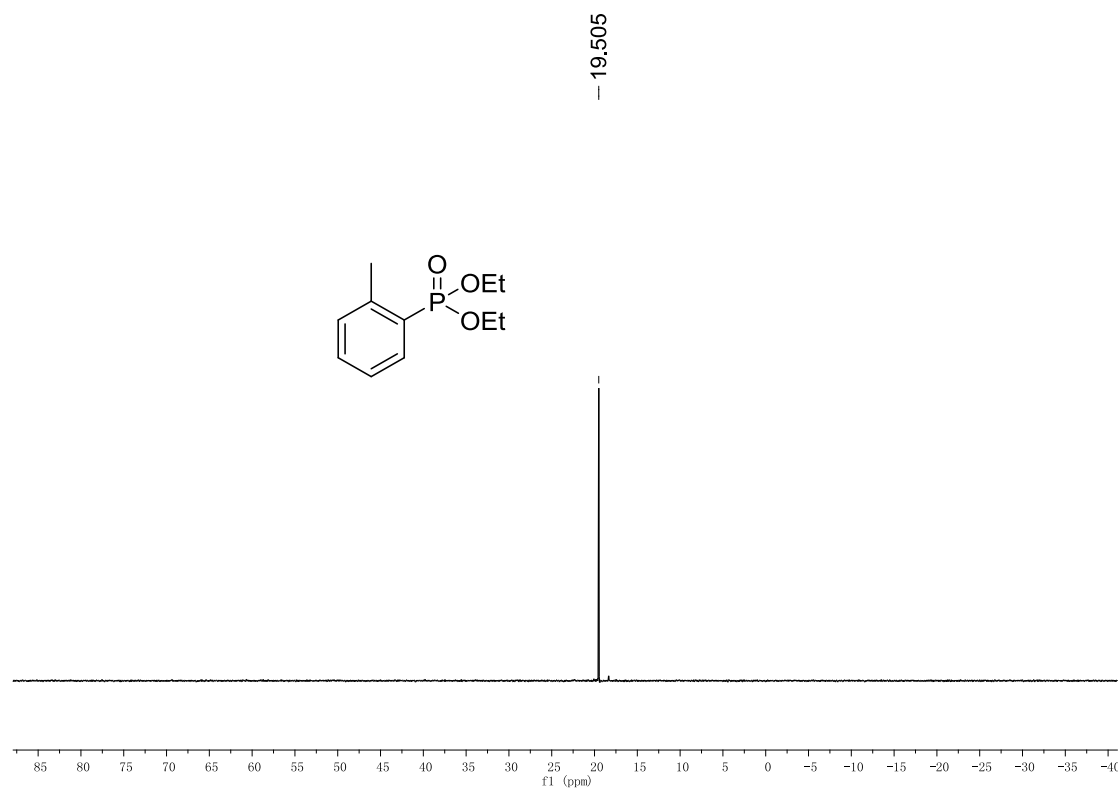
7.936
7.932
7.916
7.913
7.900
7.896
7.880
7.877
7.424
7.405
7.280
7.269
7.260
7.252
4.279
4.161
4.143
4.125
4.107
4.089
4.082
4.064
4.052
4.026
2.572
2.568
1.341
1.323
1.306



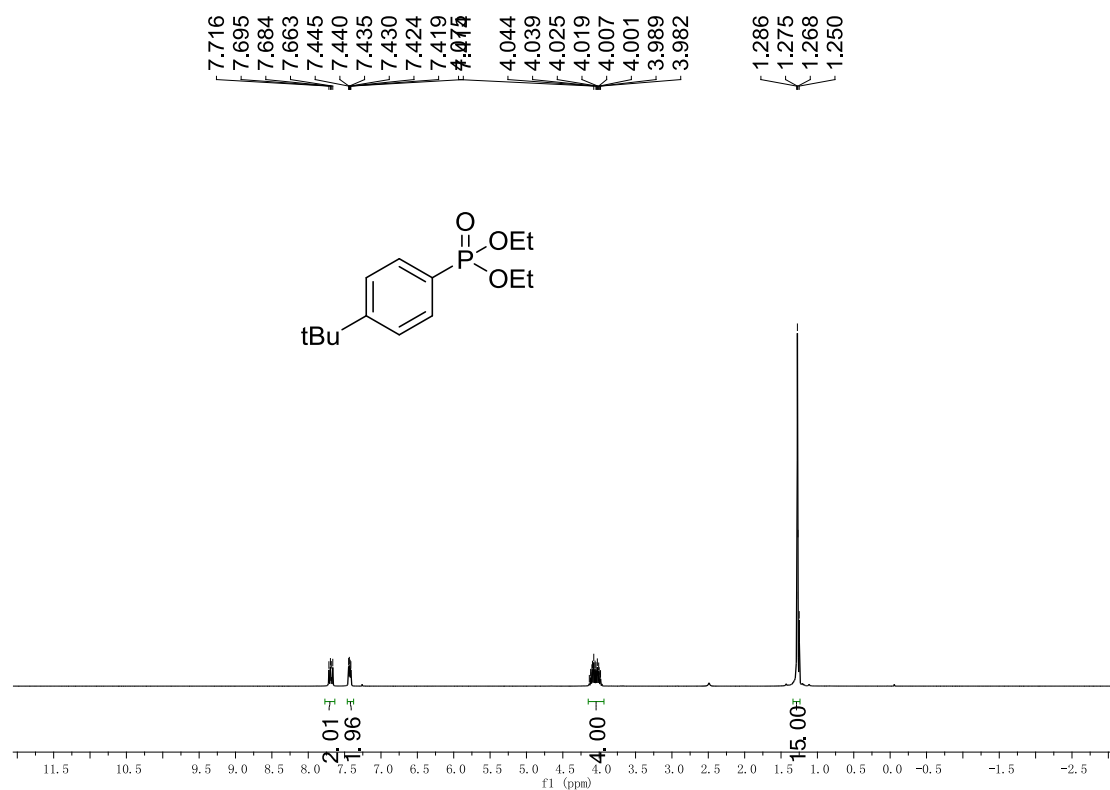
¹H NMR of 3d



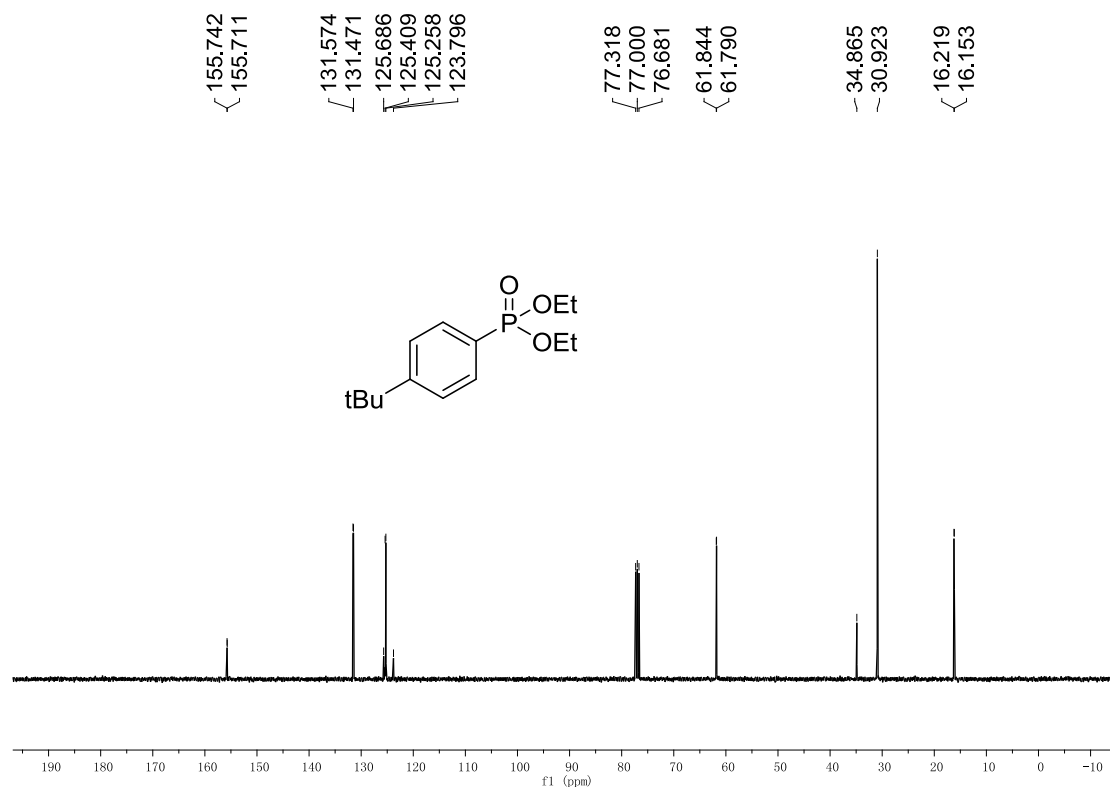
¹³C NMR of 3d



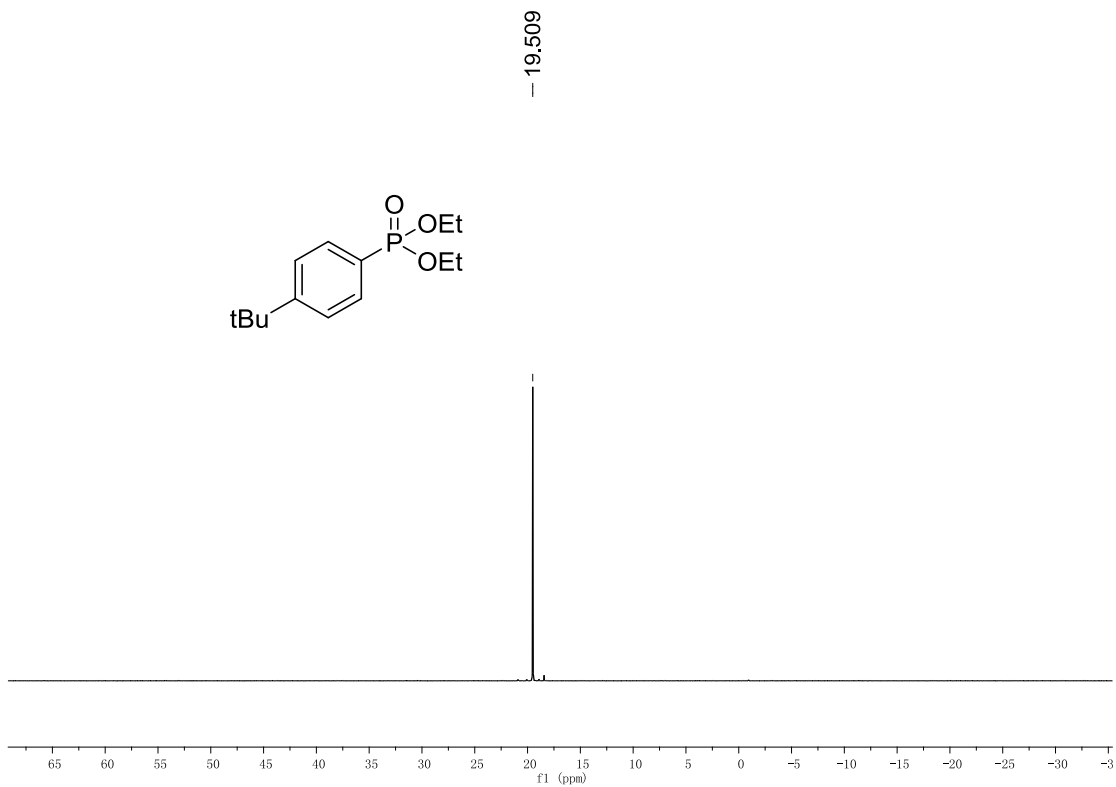
³¹P NMR of 3d



^1H NMR of **3e**

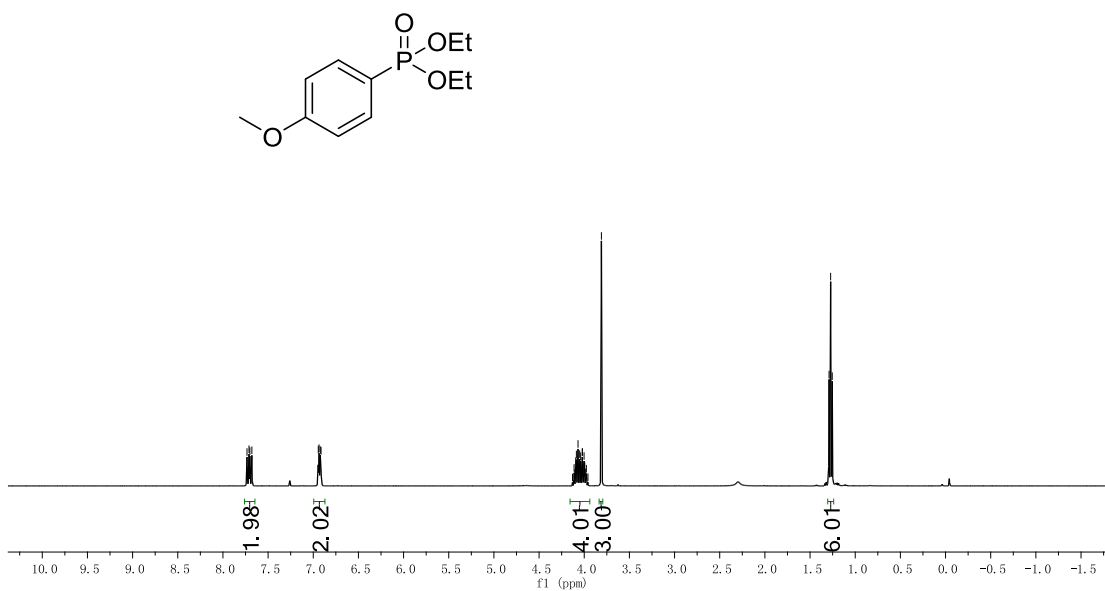


^{13}C NMR of **3e**



³¹P NMR of **3e**

7.734 7.729 7.716 7.712 7.702 7.697 7.685 7.680
 6.944 6.936 6.931 6.927 6.922 6.914 6.909
 4.022 4.020 4.014 4.002 3.996 3.995 3.984 3.977 3.959 3.810
 1.290 1.272 1.254



¹H NMR of **3f**

162.770
162.736

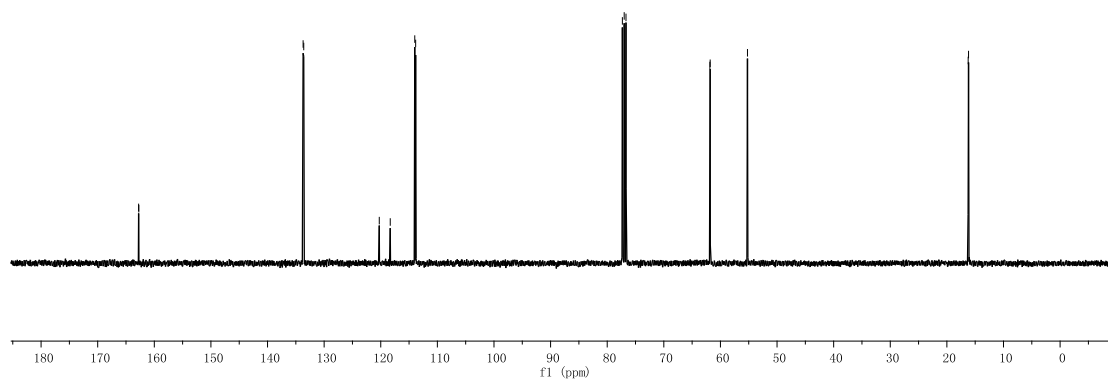
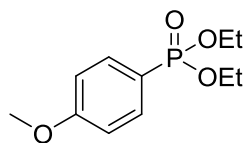
133.716
133.603

120.262
118.325
113.993
113.834

77.319
77.000
76.682

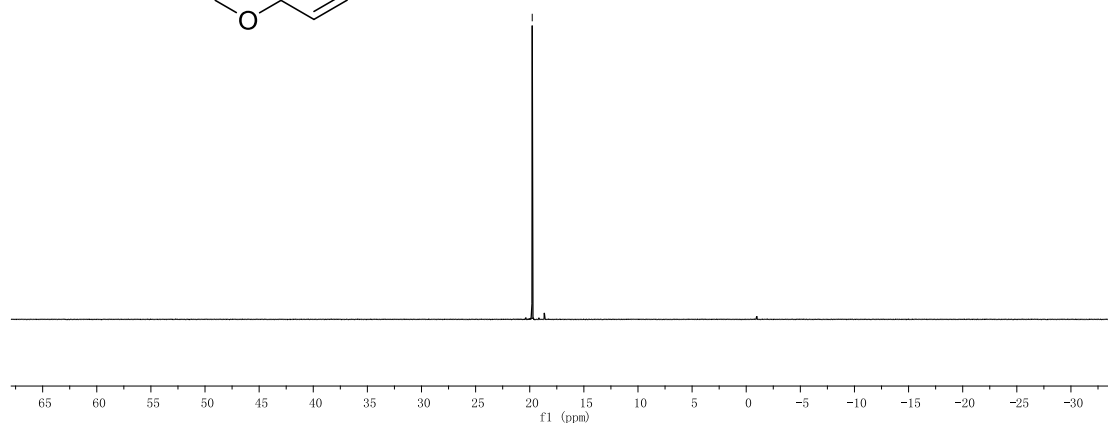
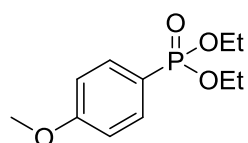
61.863
61.810
55.224

16.239
16.173



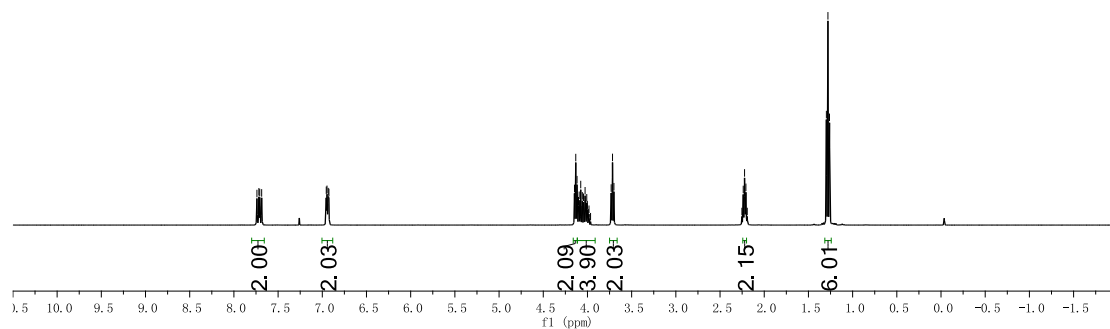
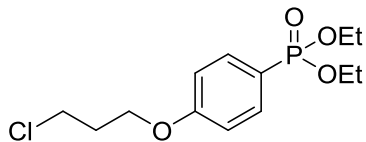
¹³C NMR of **3f**

19.770



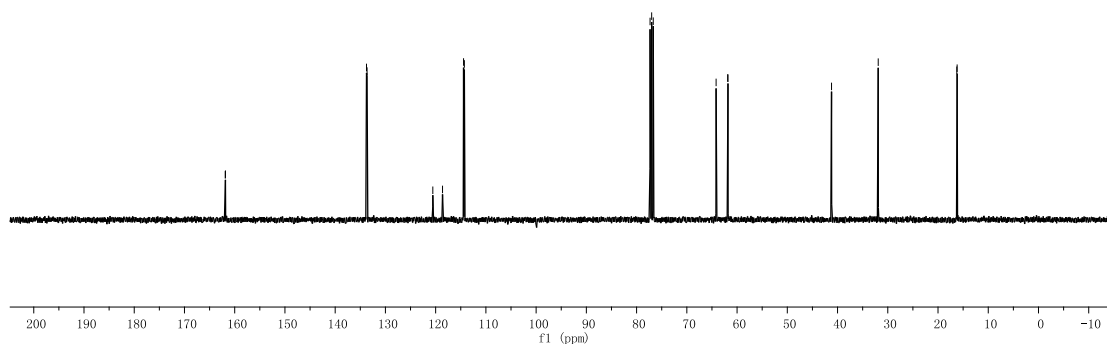
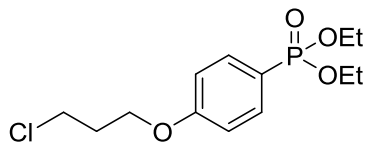
³¹P NMR of **3f**

7.739
7.722
7.718
7.707
7.690
7.686
6.955
6.947
6.938
6.933
6.925
4.132
4.101
4.083
4.063
4.045
4.020
4.002
3.983
3.732
3.701
2.238
2.223
2.207
2.192
1.297
1.279
1.262

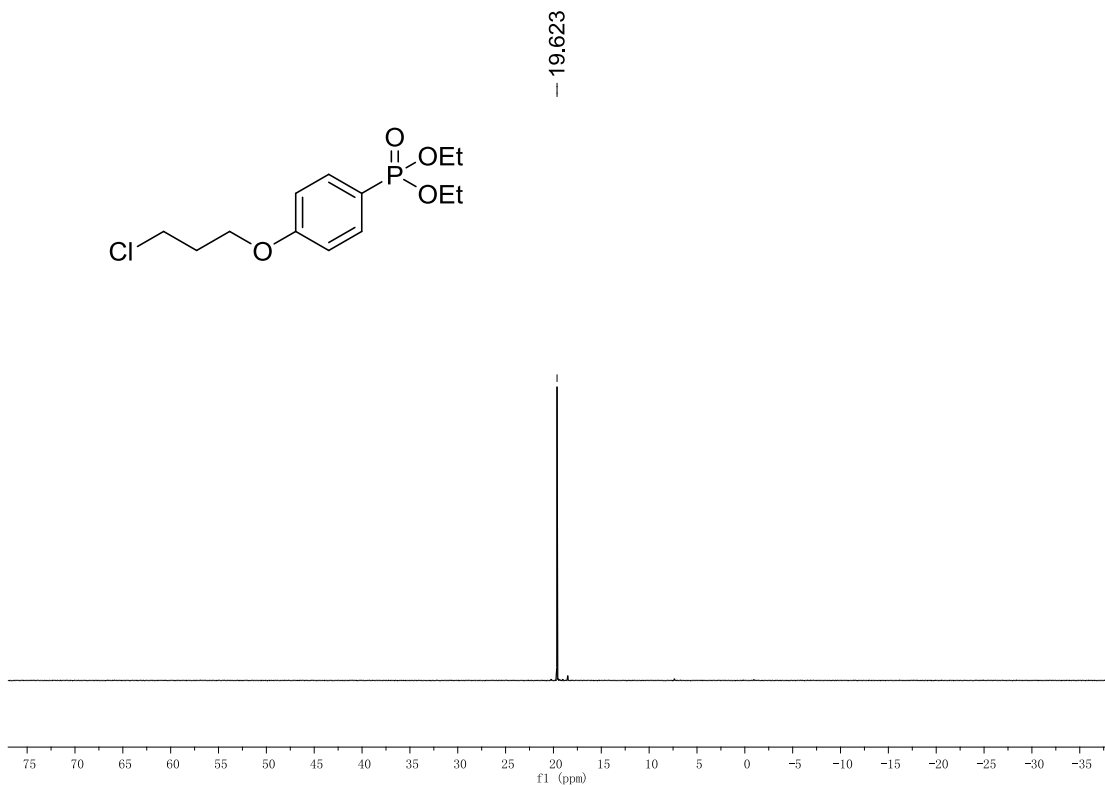


¹H NMR of **3g**

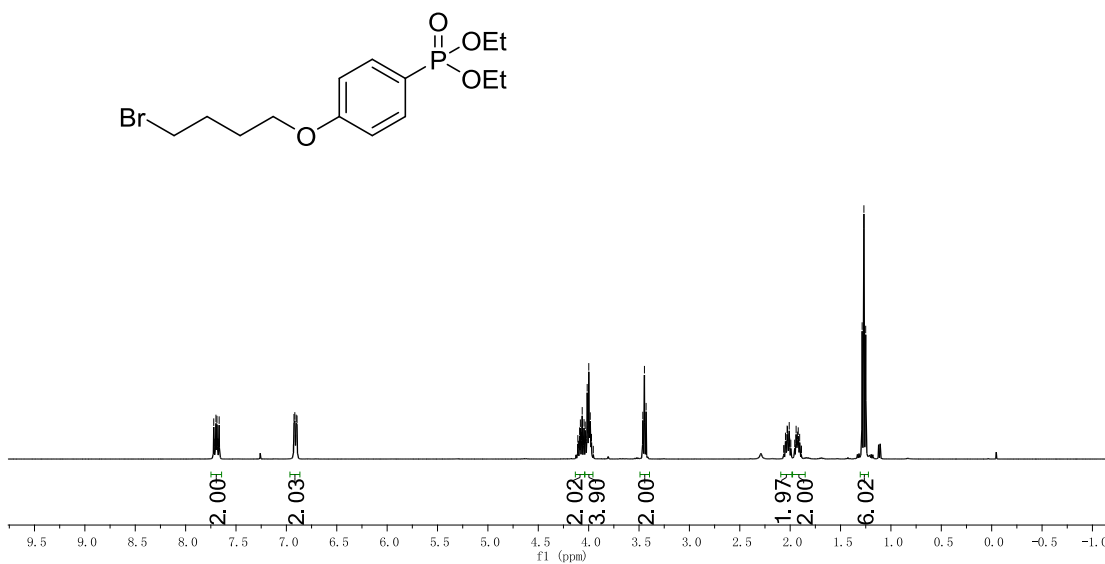
161.880
161.846
133.766
133.653
120.565
118.630
114.444
114.284
77.318
77.000
76.682
64.173
61.864
61.812
-41.194
-31.903
16.259
16.193



¹³C NMR of **3g**



^{31}P NMR of 3g



^1H NMR of 3h

\swarrow 162.014
 \swarrow 161.981

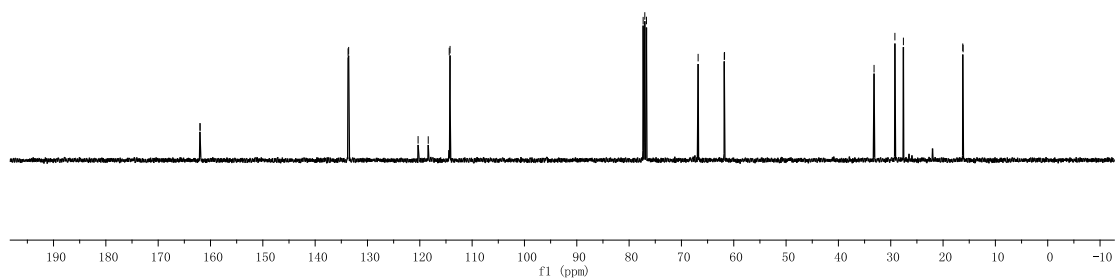
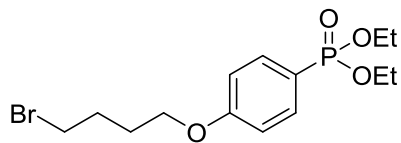
 \swarrow 133.709
 \swarrow 133.597

 \swarrow 120.328
 \swarrow 118.391
 \swarrow 114.378
 \swarrow 114.219

 \swarrow 77.319
 \swarrow 77.000
 \swarrow 76.682
 \swarrow 66.810
 \swarrow 61.816
 \swarrow 61.764

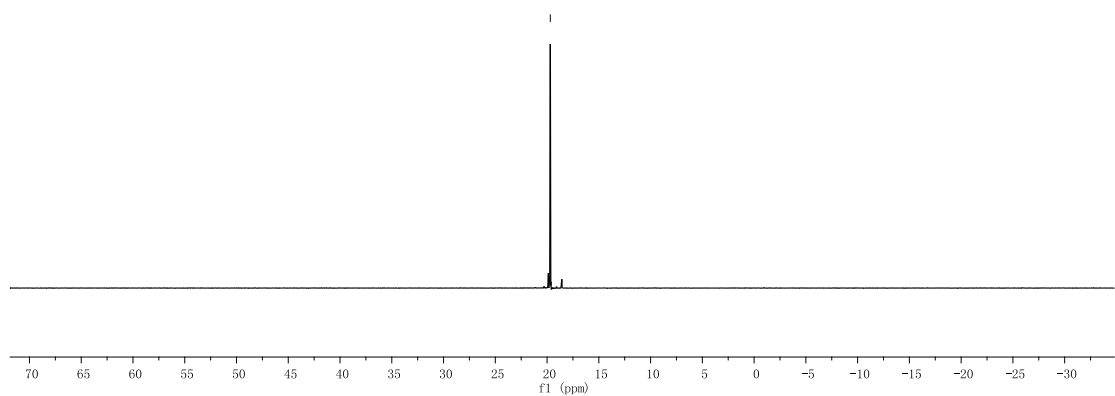
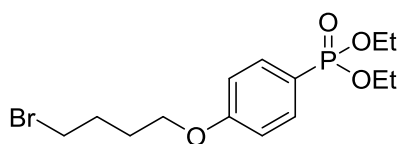
 \swarrow 33.187
 \swarrow 29.205
 \swarrow 27.579

 \swarrow 16.236
 \swarrow 16.171

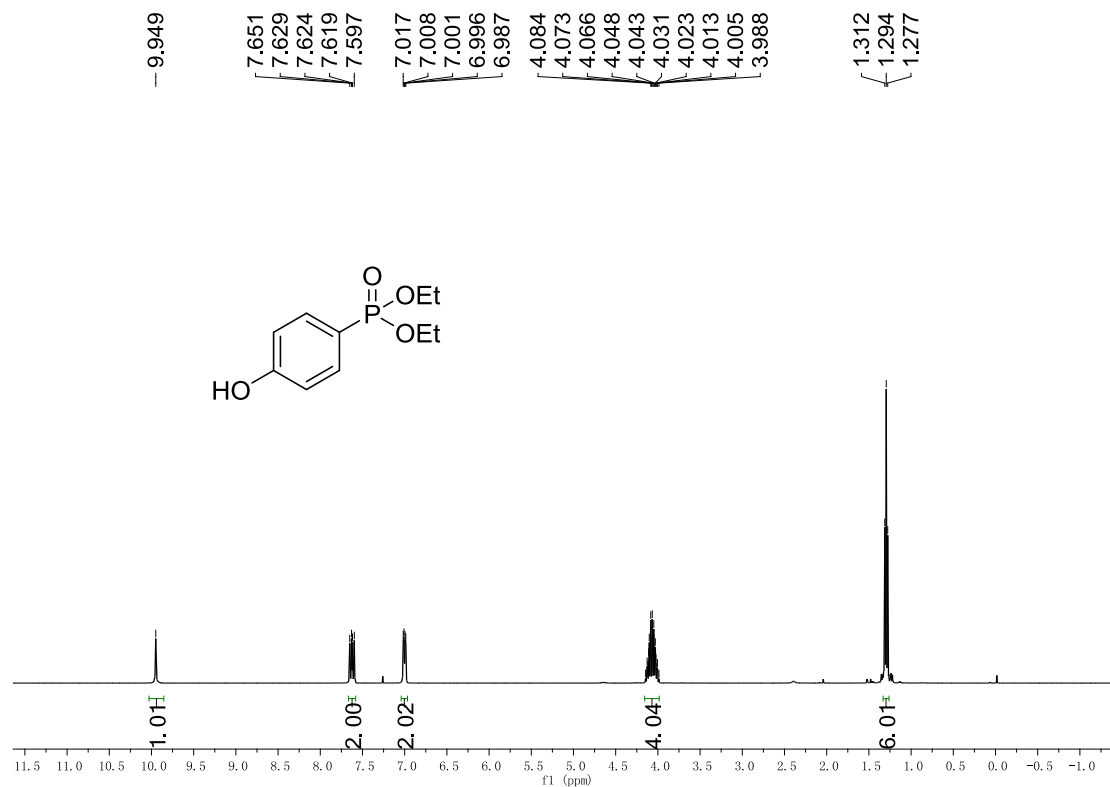


^{13}C NMR of **3h**

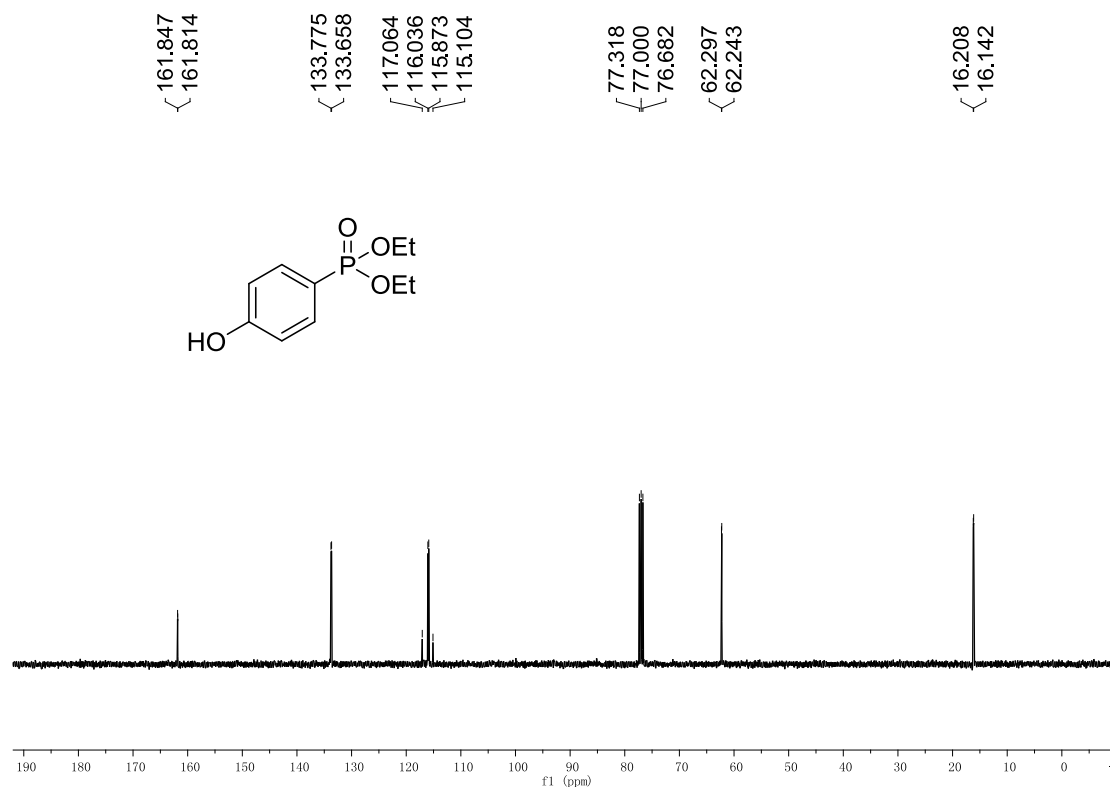
\swarrow 19.688



^{31}P NMR of **3h**

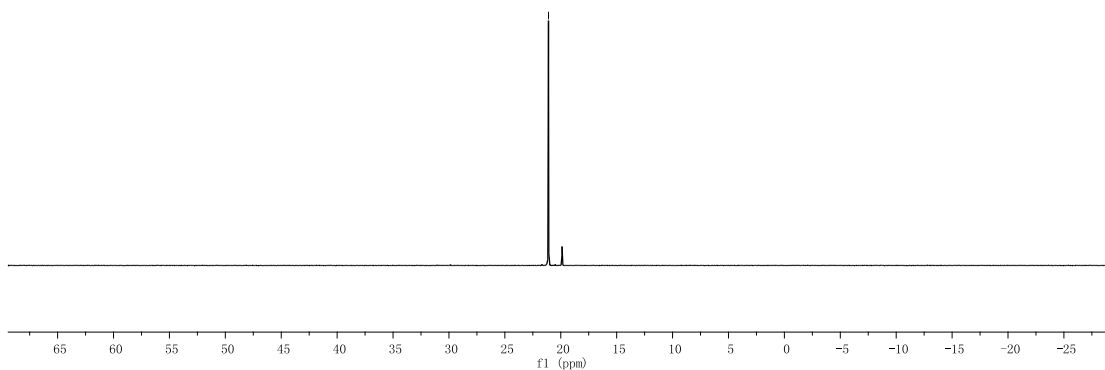
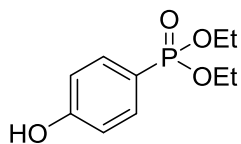


^1H NMR of 3i



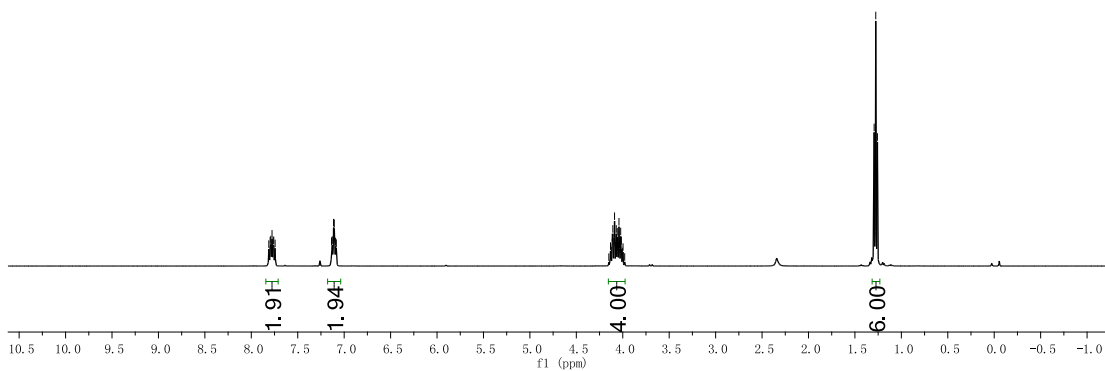
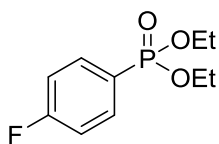
^{13}C NMR of 3i

-21.098



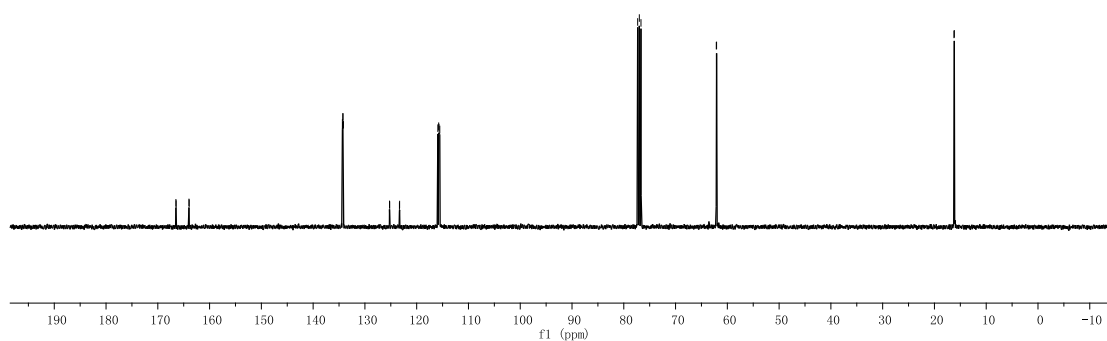
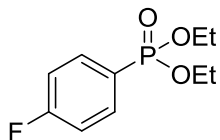
³¹P NMR of 3i

7.811
7.797
7.790
7.777
7.765
7.758
7.744
7.136
7.128
7.114
7.106
7.093
7.085
4.088
4.070
4.059
4.052
4.041
4.034
4.022
4.016
4.004
3.997
3.979
1.293
1.276
1.258



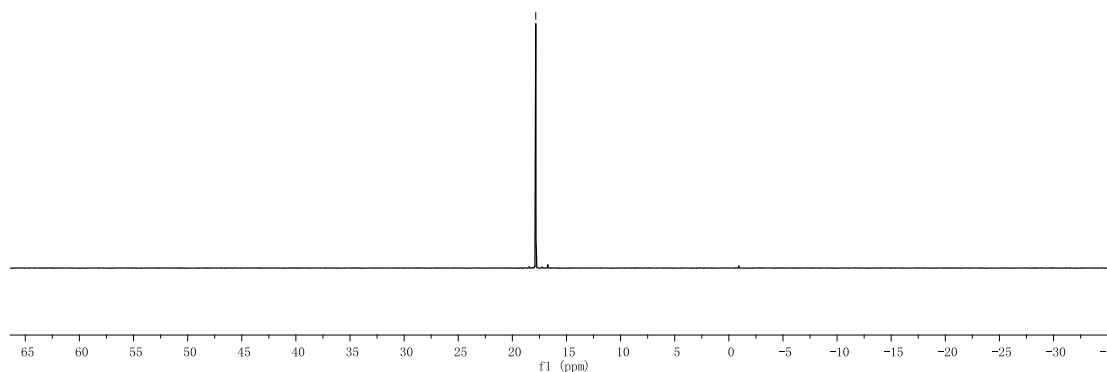
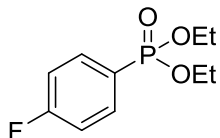
¹H NMR of 3j

166.503
166.464
163.983
163.945
134.349
134.261
134.237
134.148
- 123.299
115.915
115.752
115.701
115.540
77.318
77.000
76.681
62.132
62.078
16.226
16.161

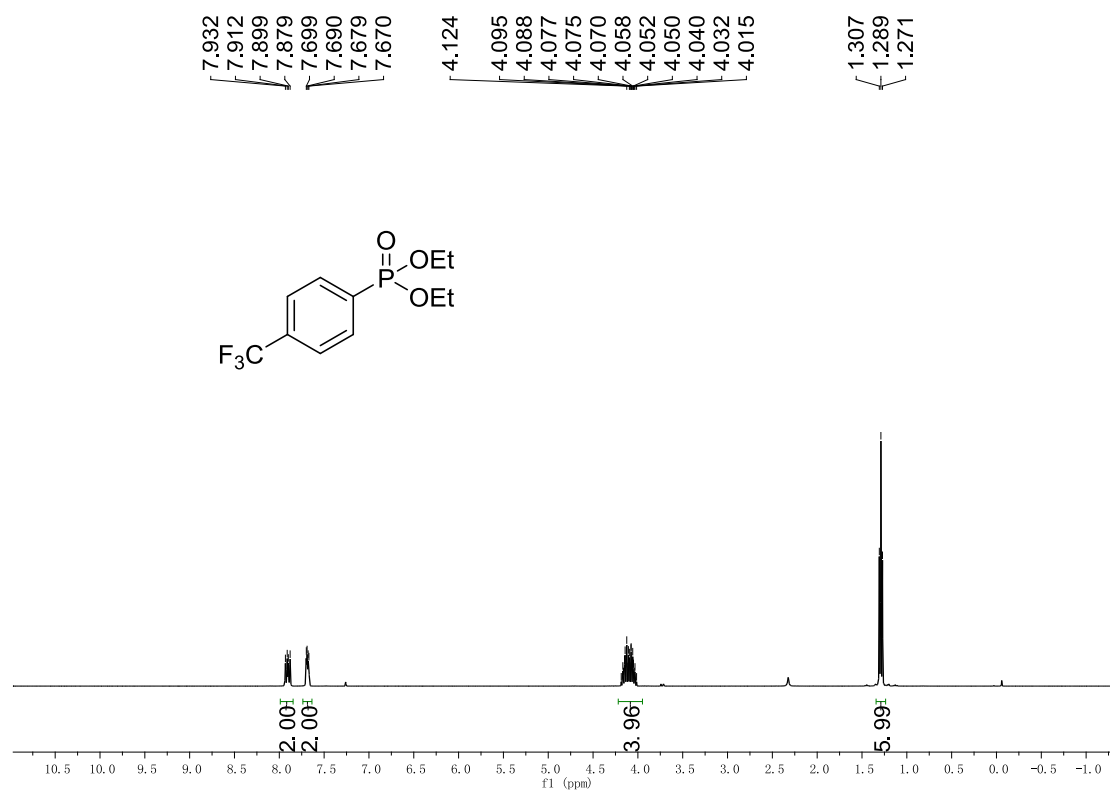


¹³C NMR of **3j**

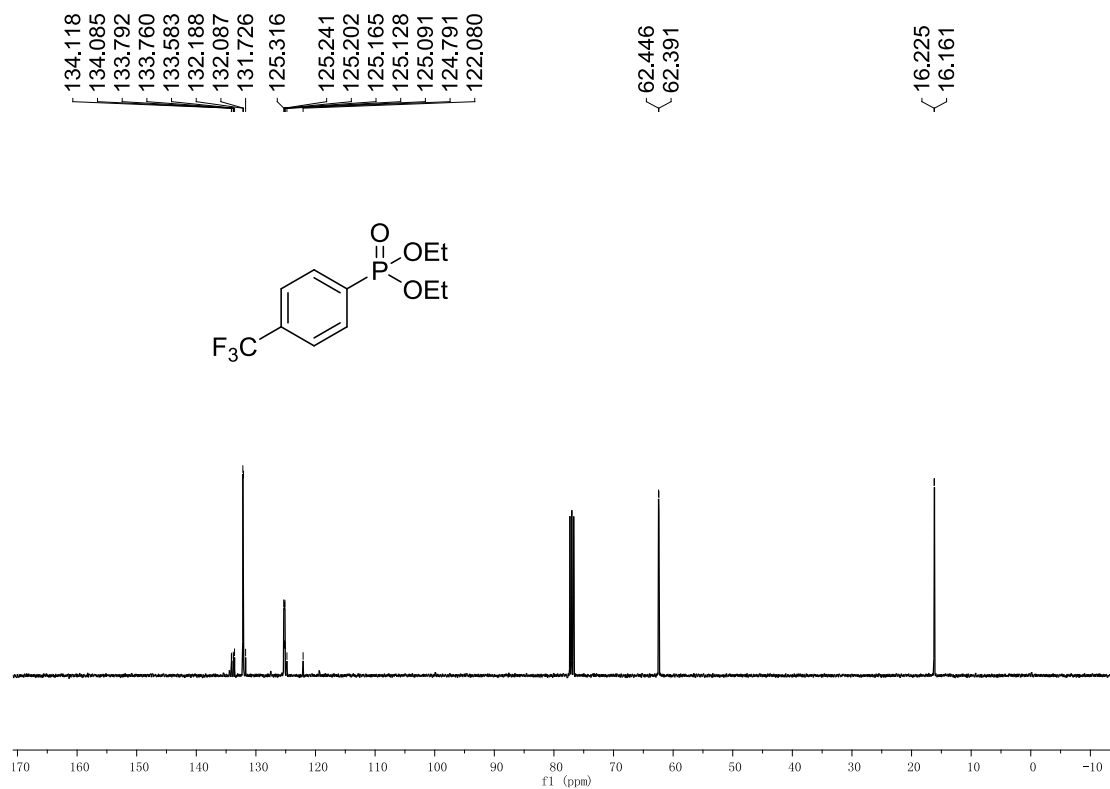
17.838
-



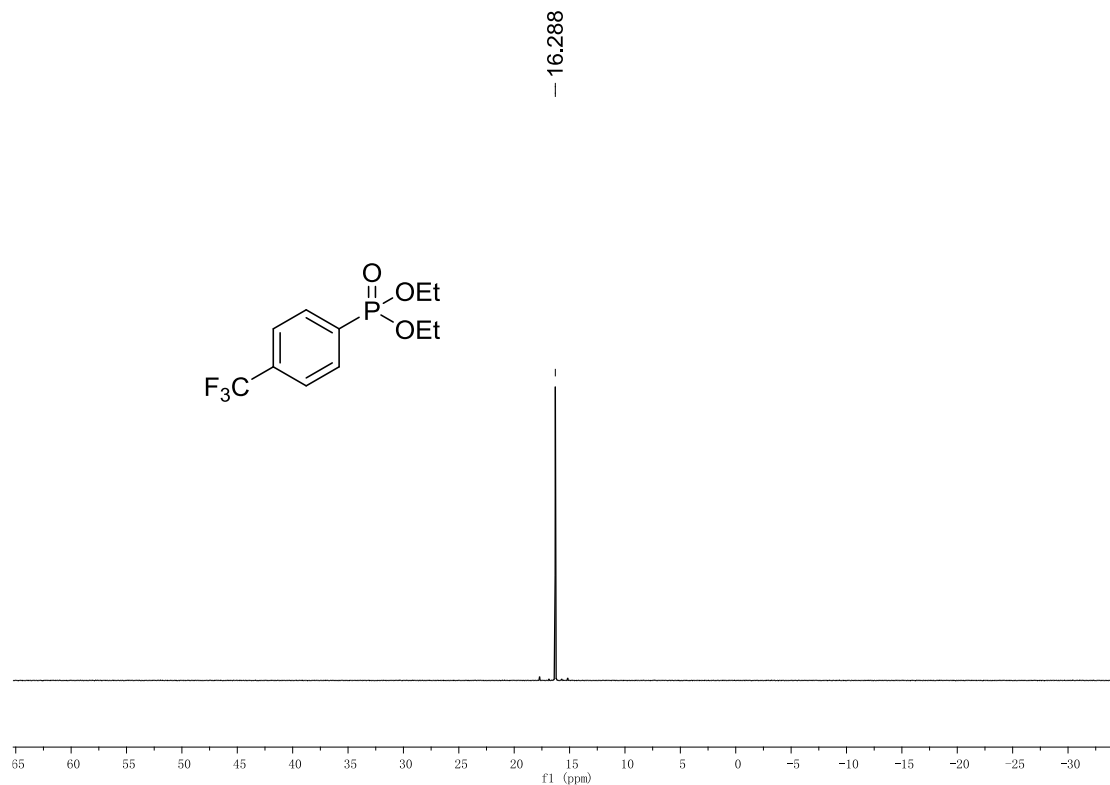
³¹P NMR of **3j**



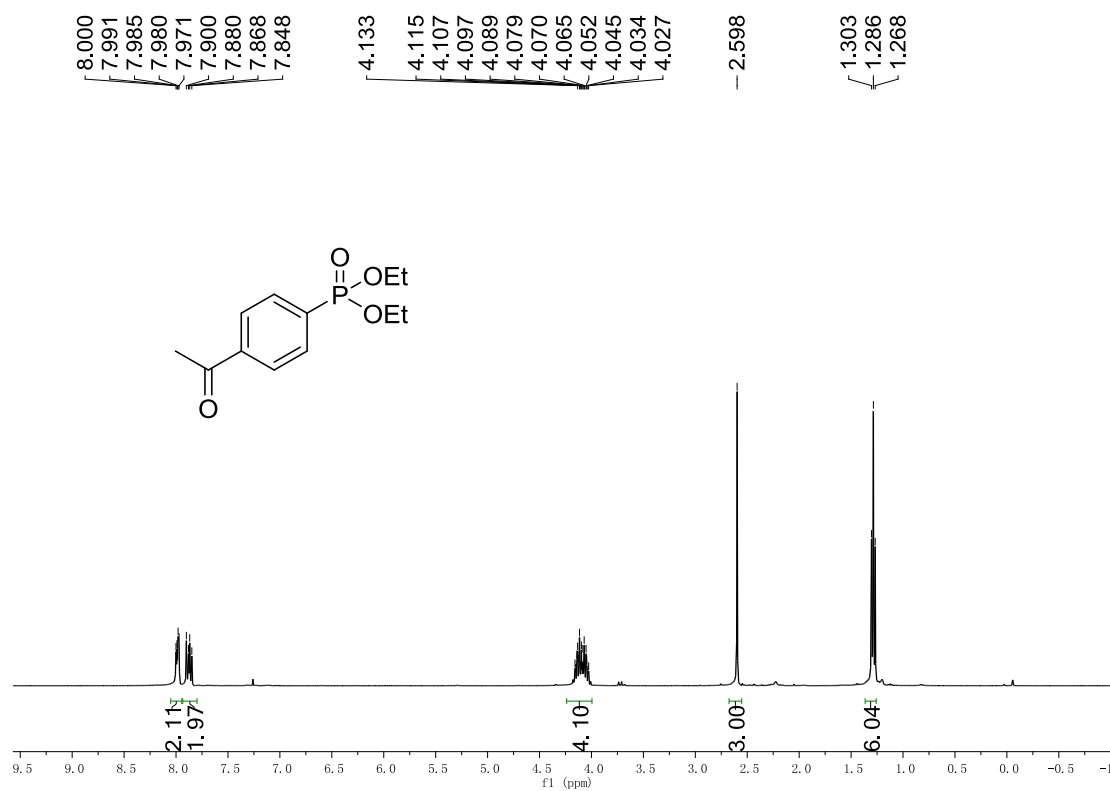
¹H NMR of 3k



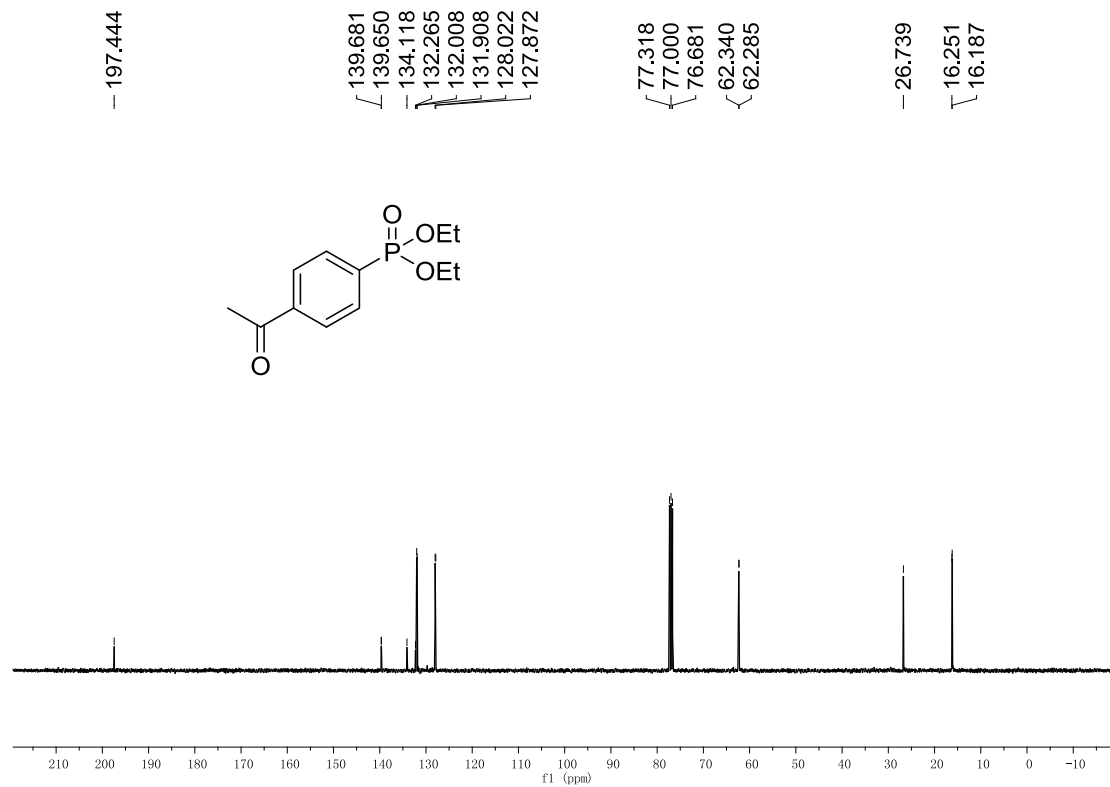
¹³C NMR of 3k



^{31}P NMR of 3k



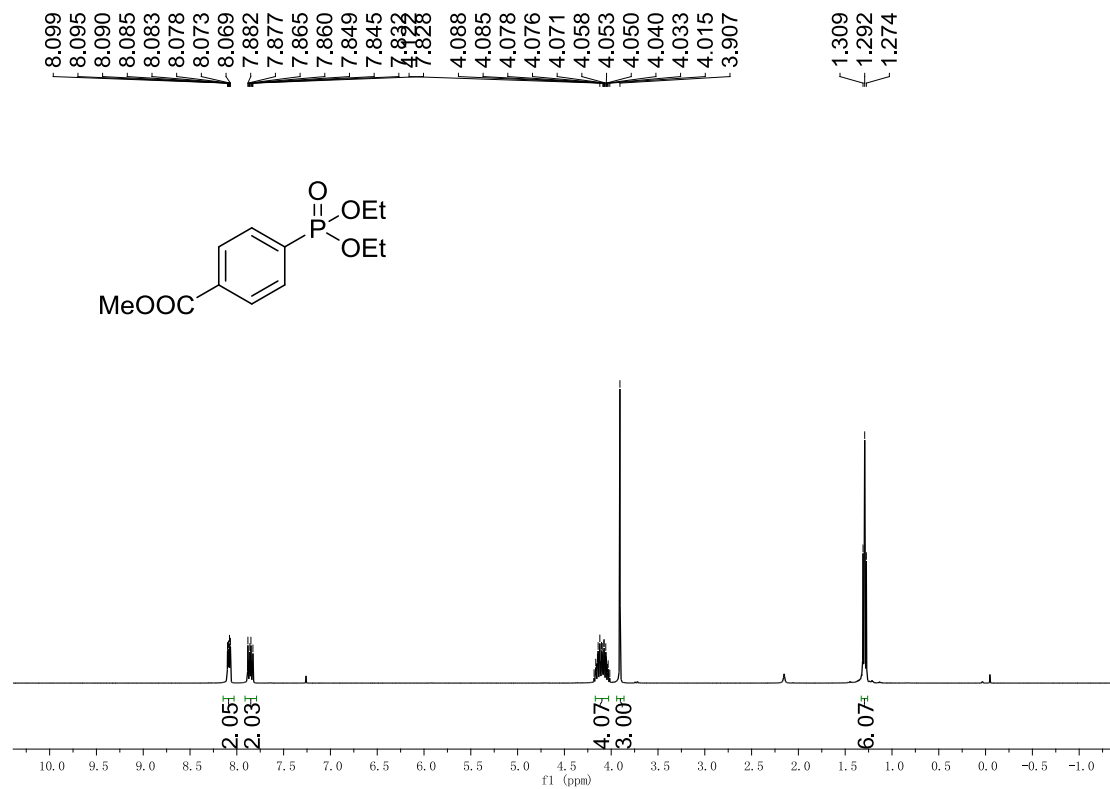
^1H NMR of 3l



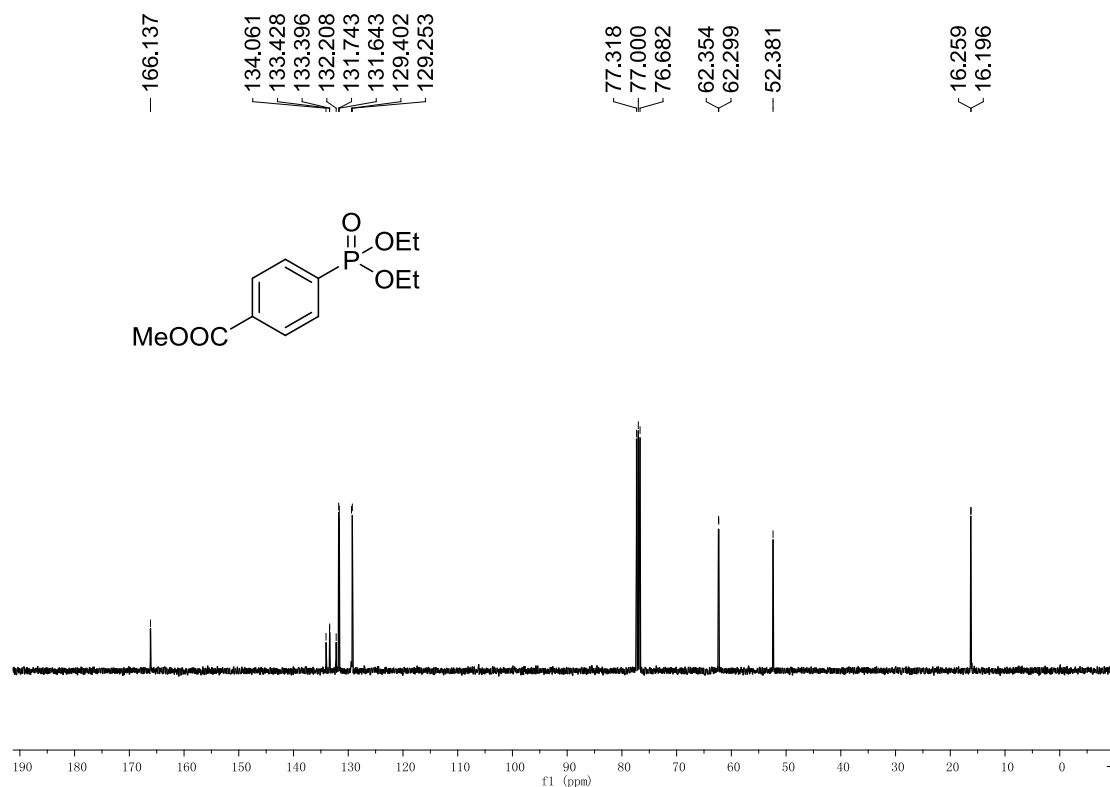
^{13}C NMR of **31**



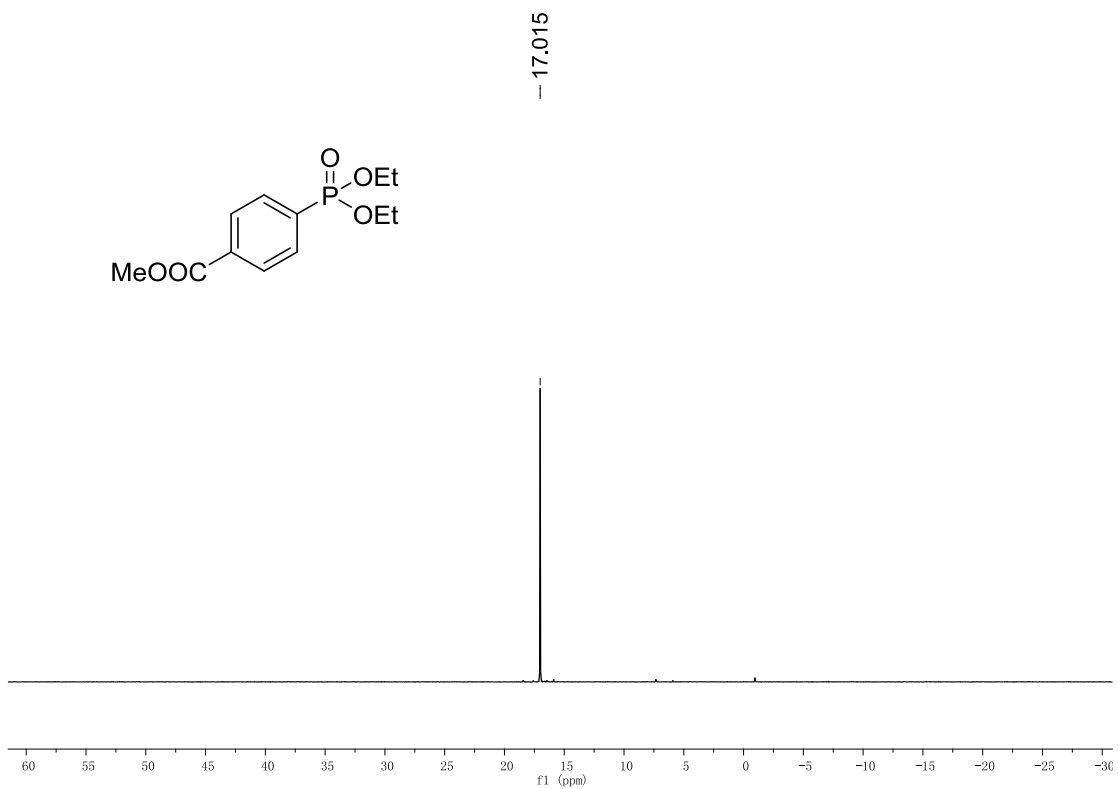
^{31}P NMR of **31**



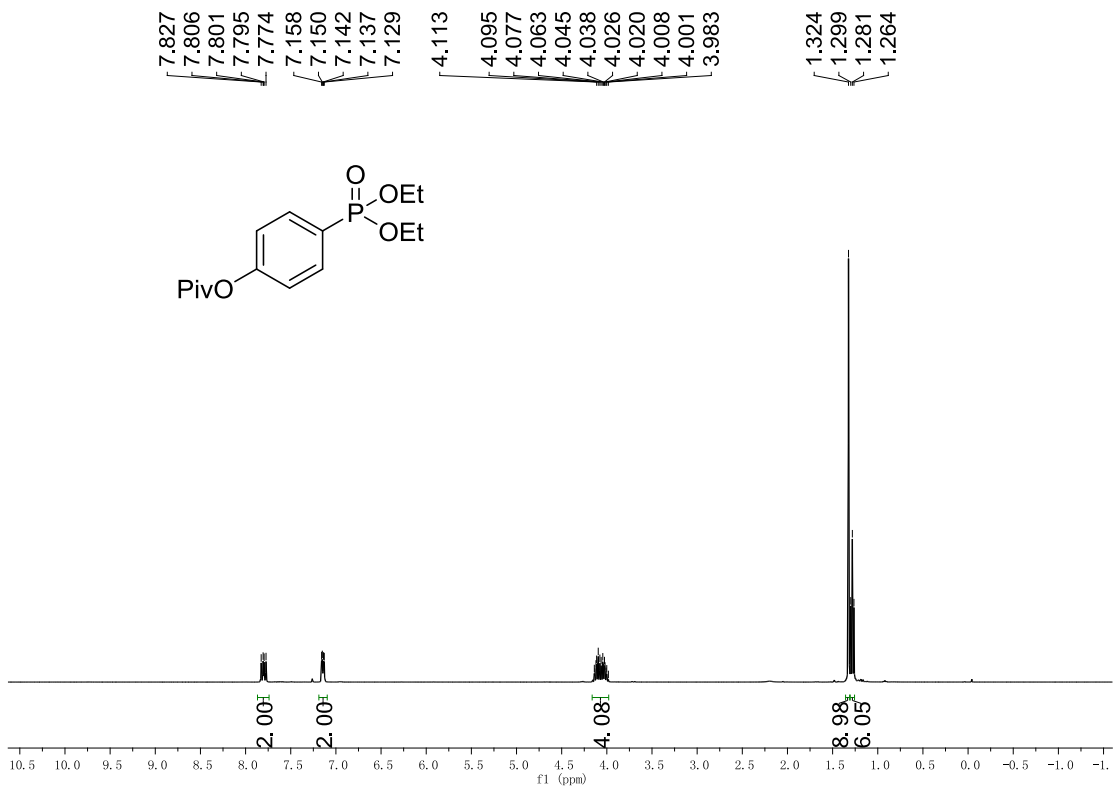
¹H NMR of **3m**



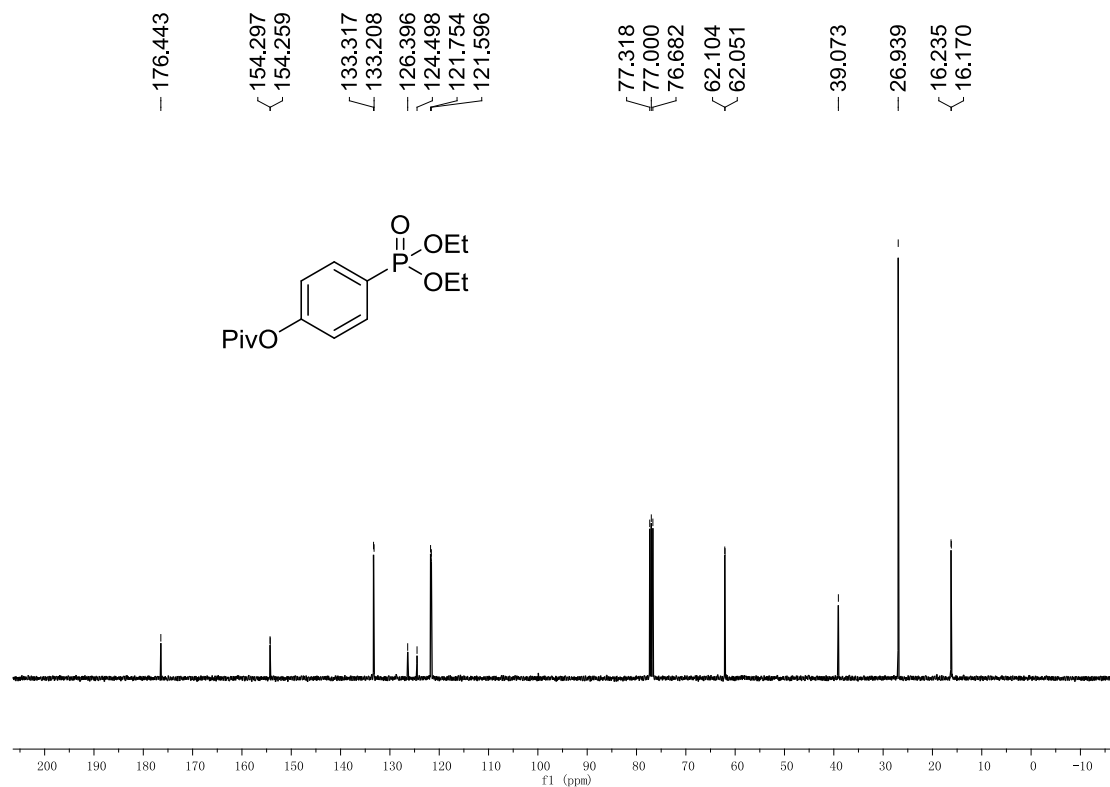
¹³C NMR of **3m**



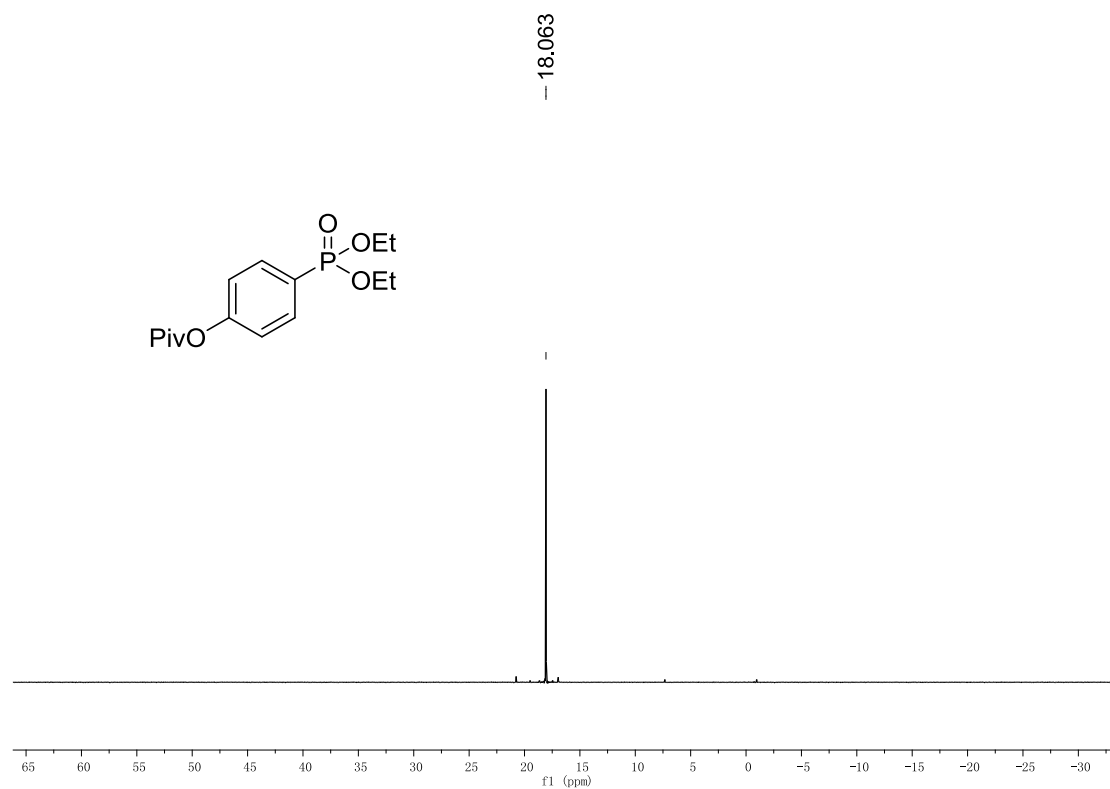
^{31}P NMR of **3m**



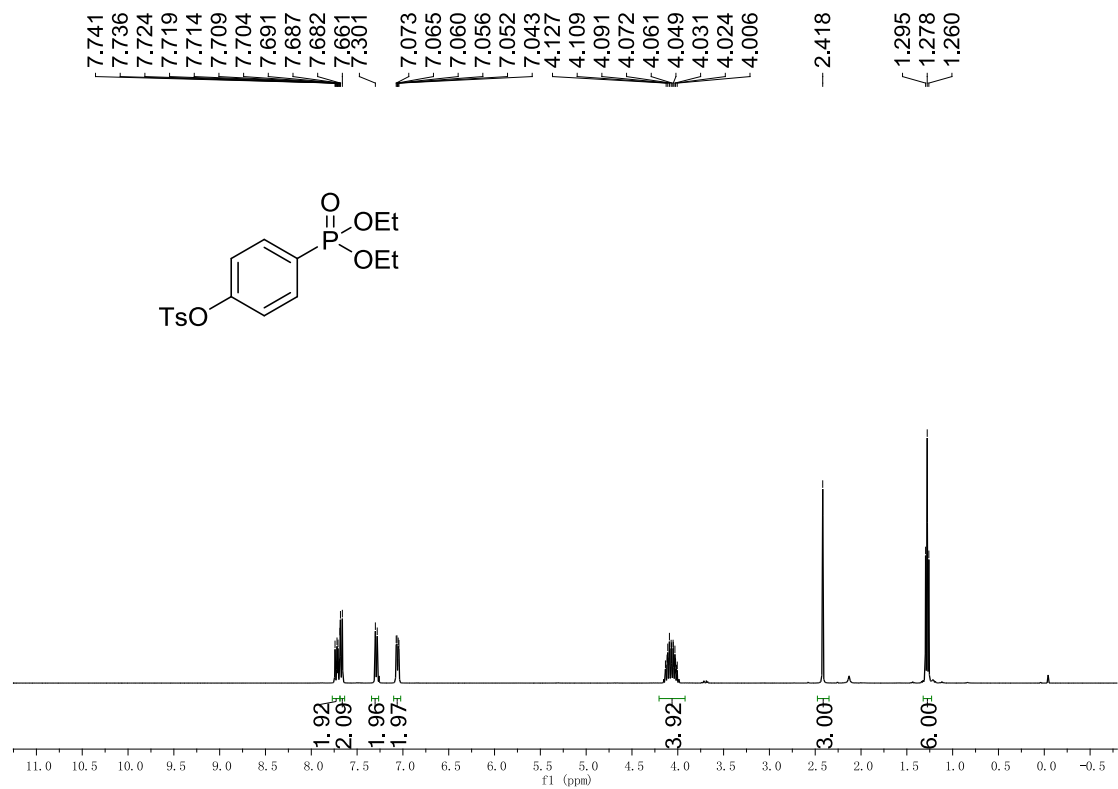
^1H NMR of **3m**



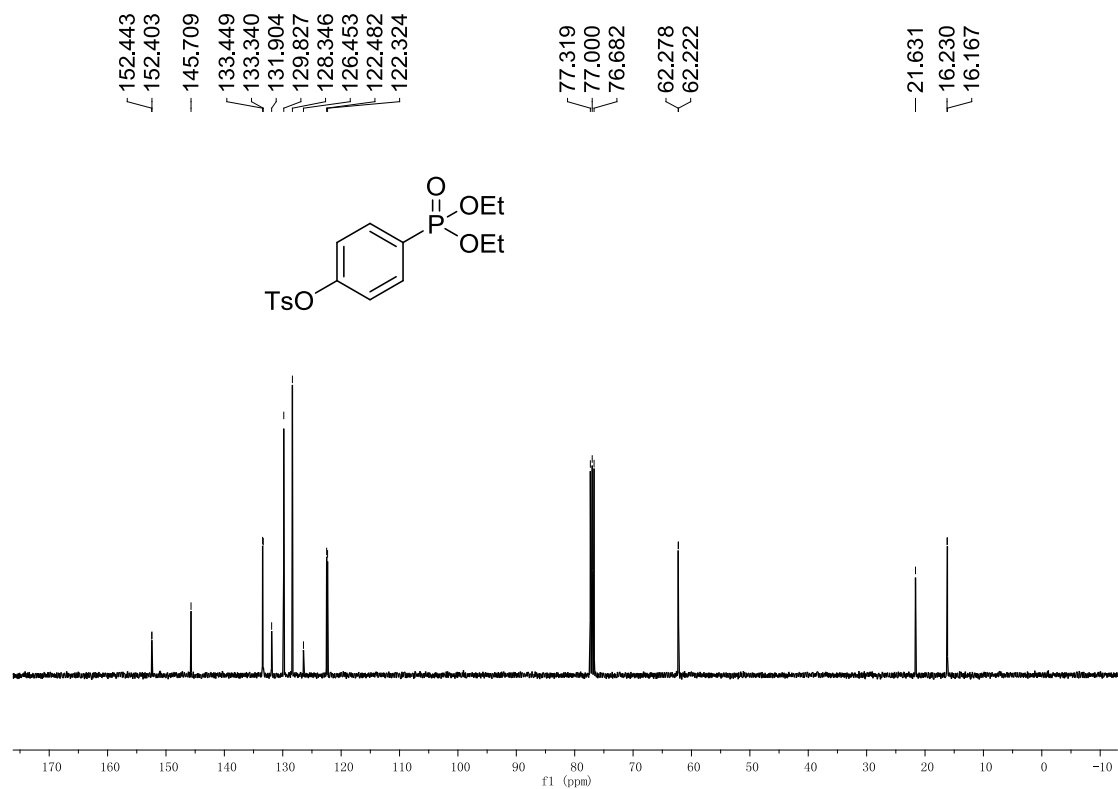
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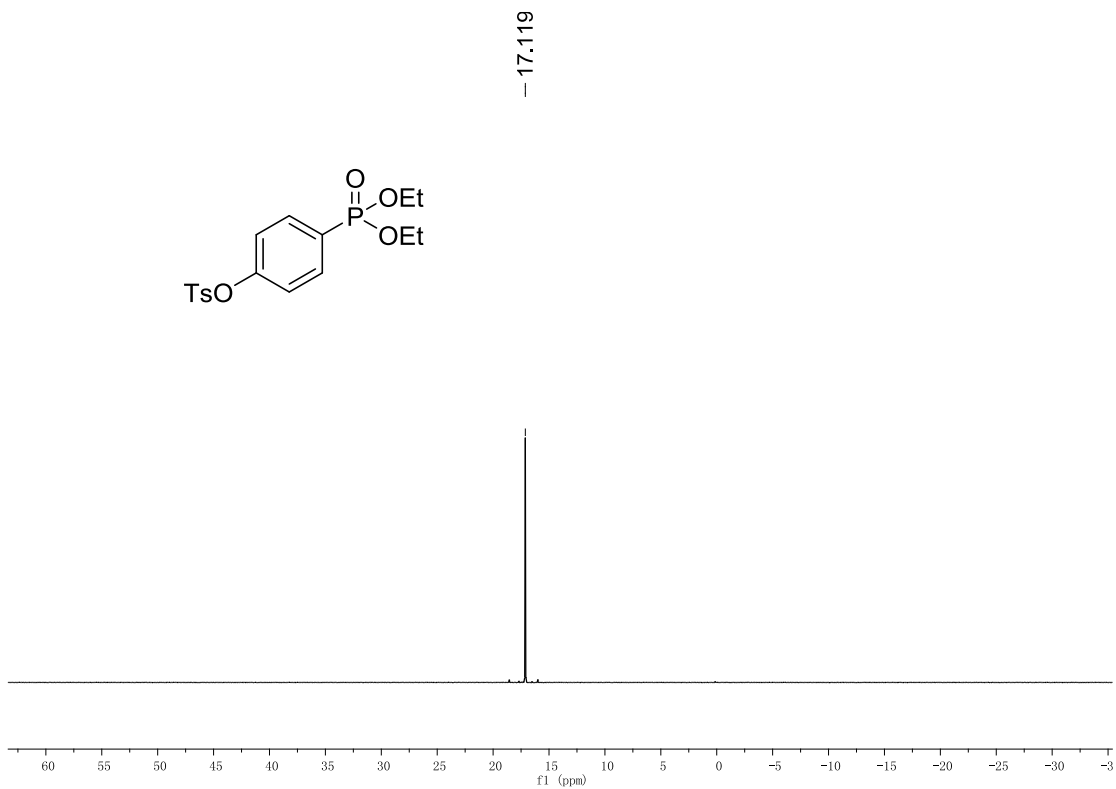
³¹P NMR of 3n



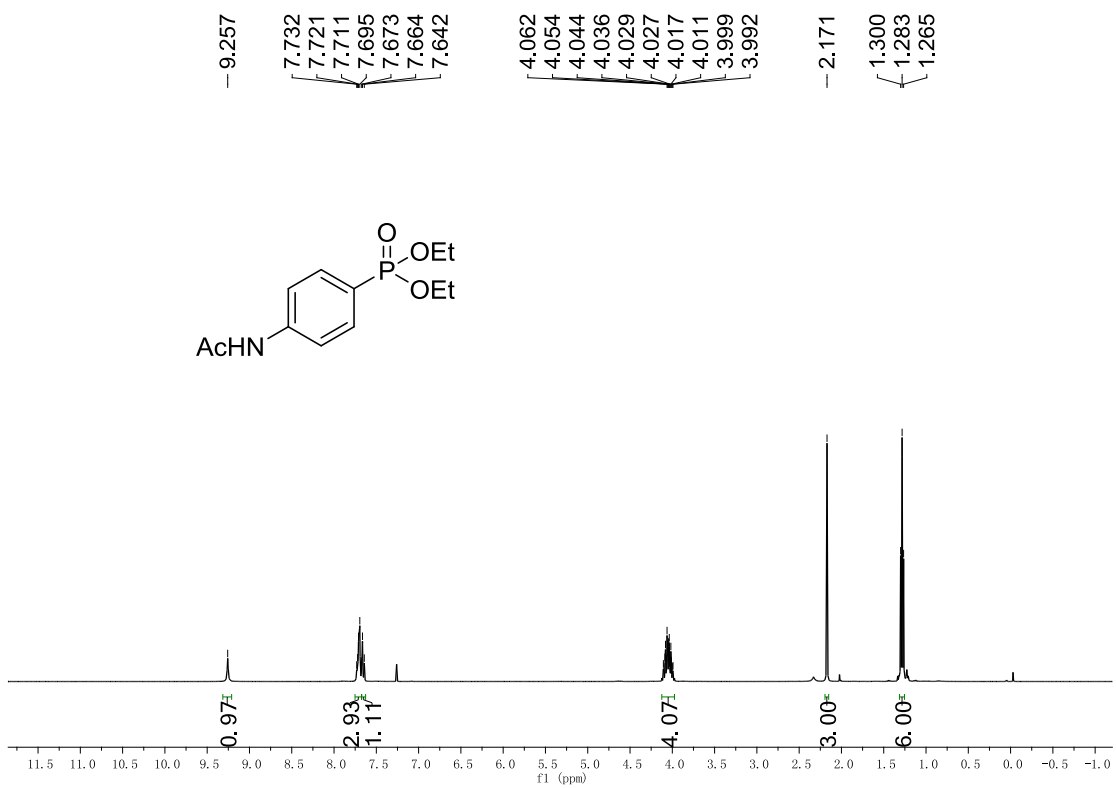
¹H NMR of **30**



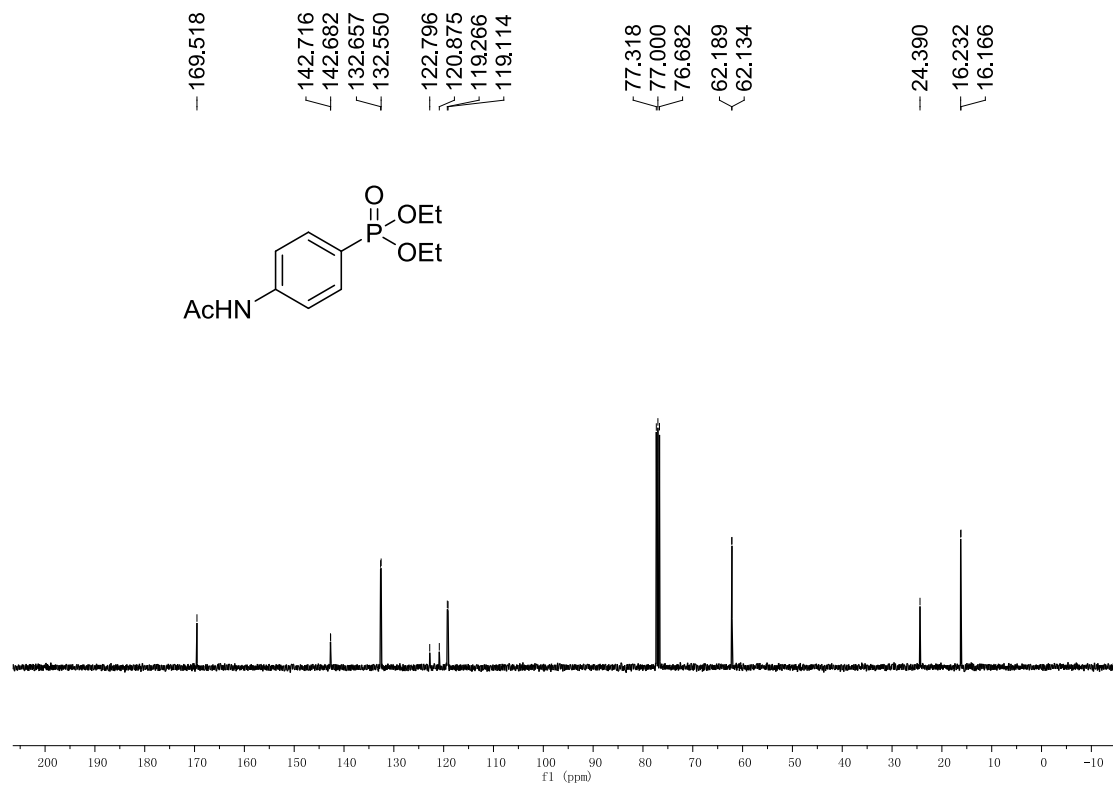
¹³C NMR of **30**



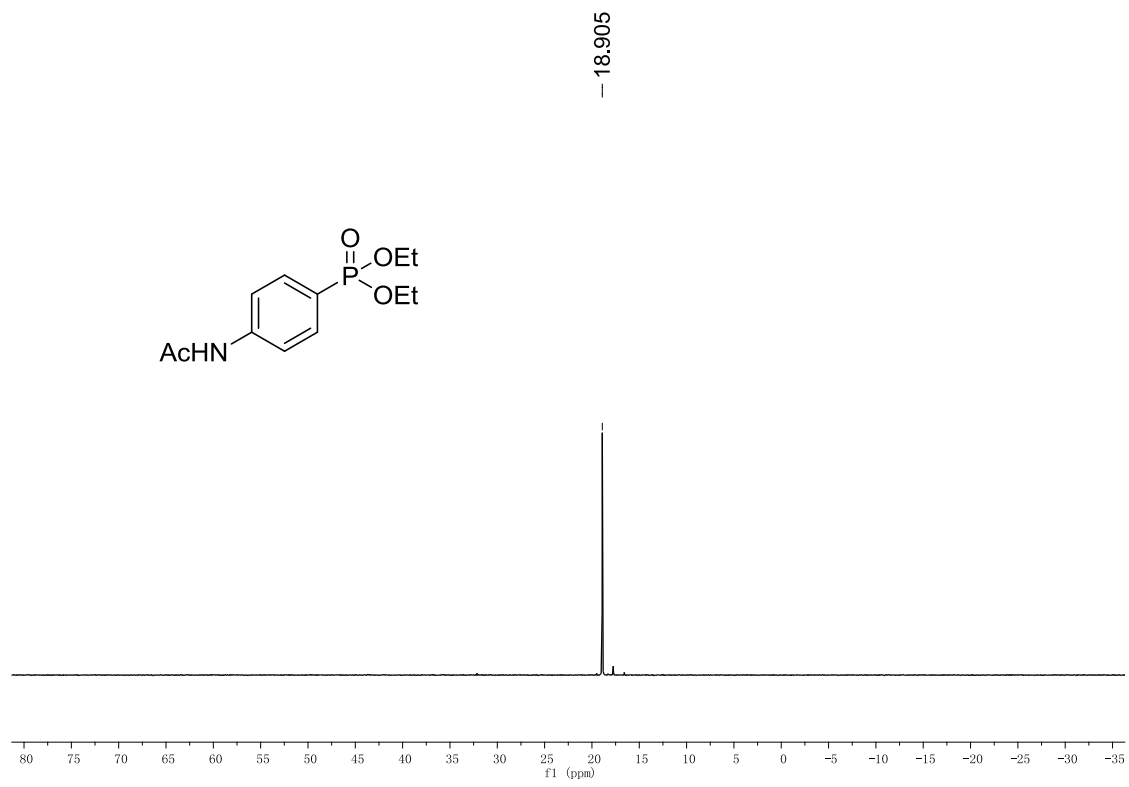
³¹P NMR of **3o**



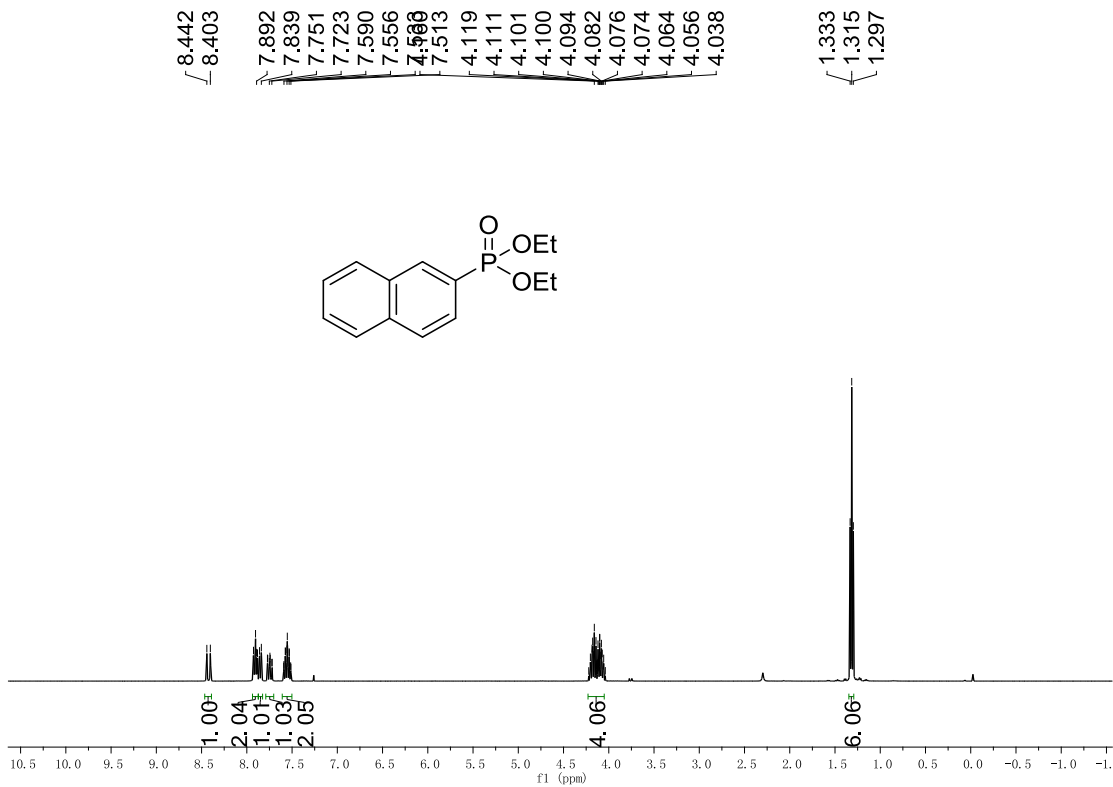
¹H NMR of **3p**



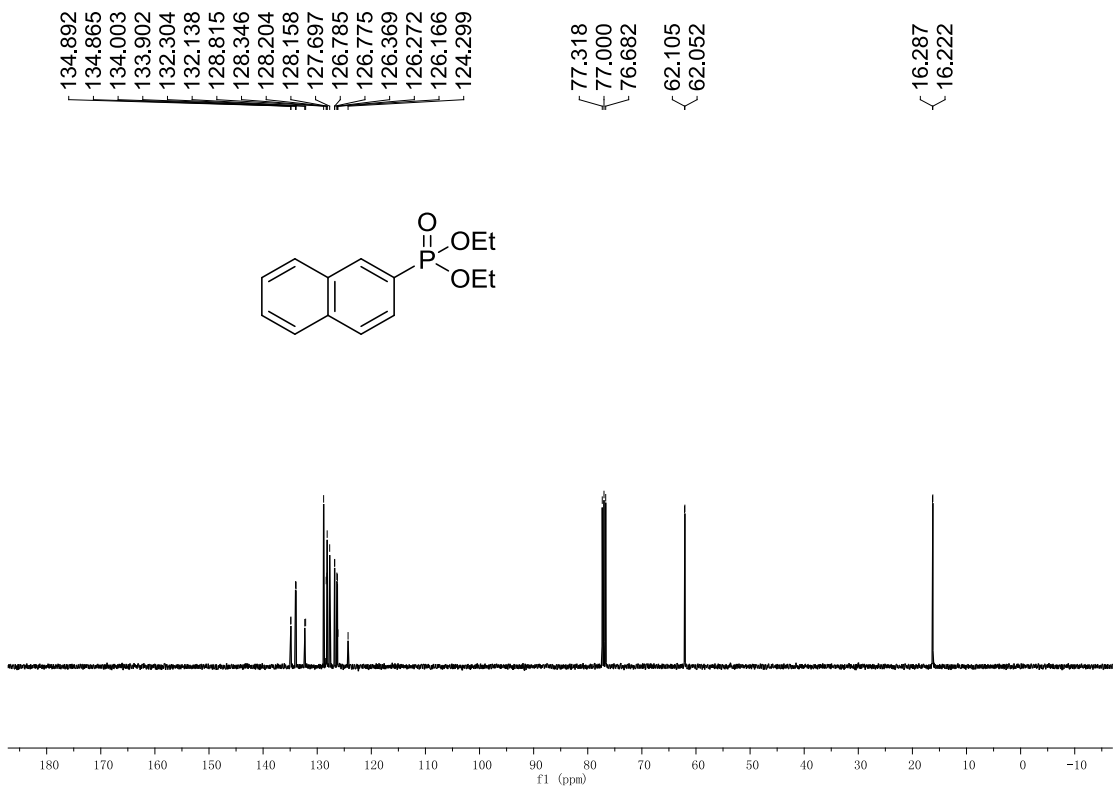
¹³C NMR of 3p



³¹P NMR of 3p



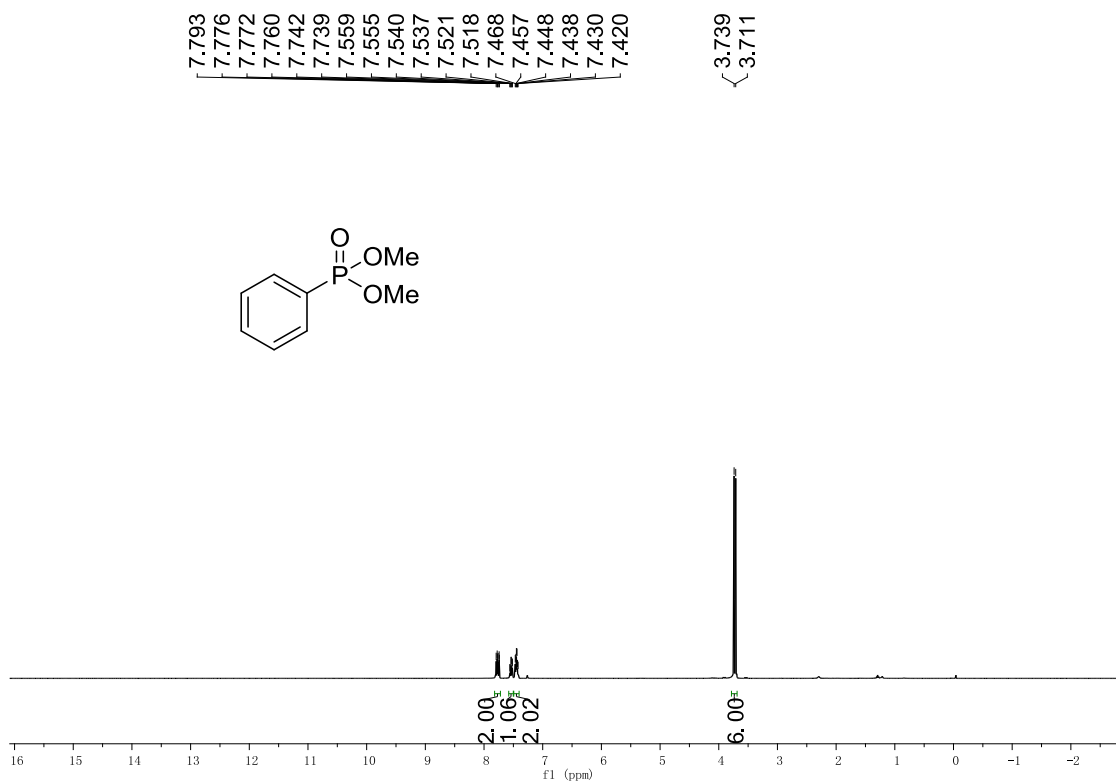
¹H NMR of 3q



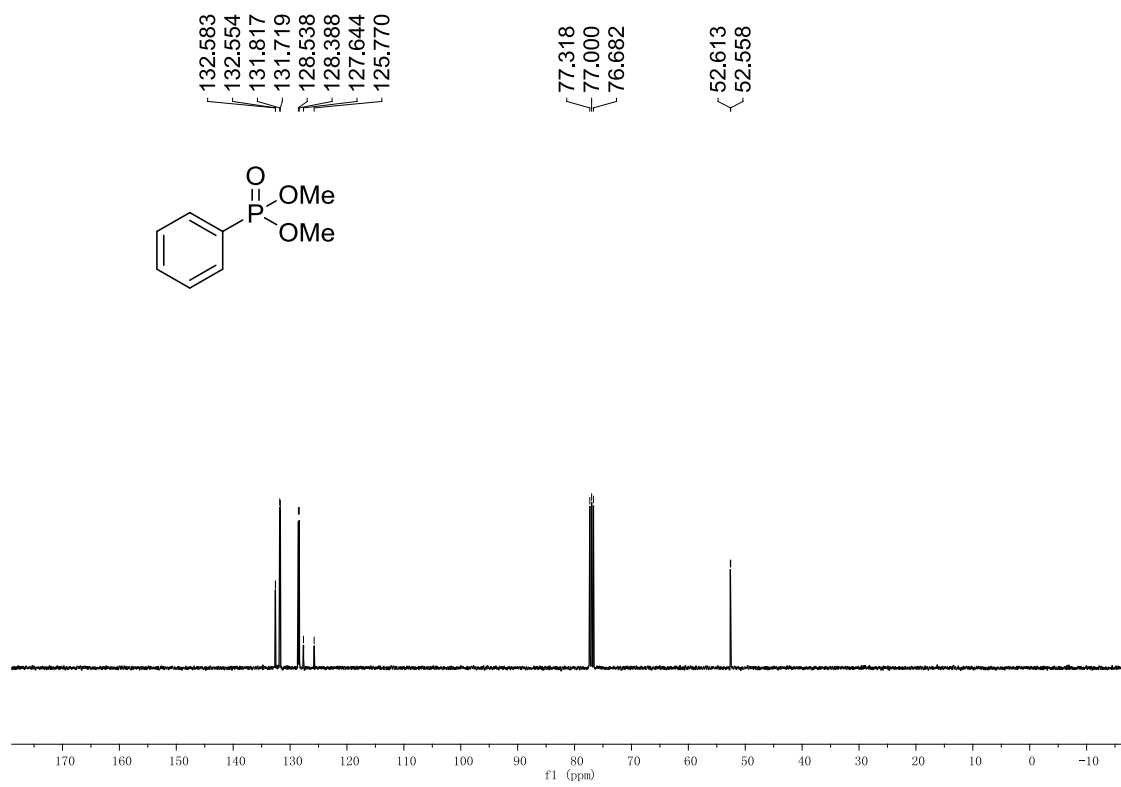
¹³C NMR of 3q



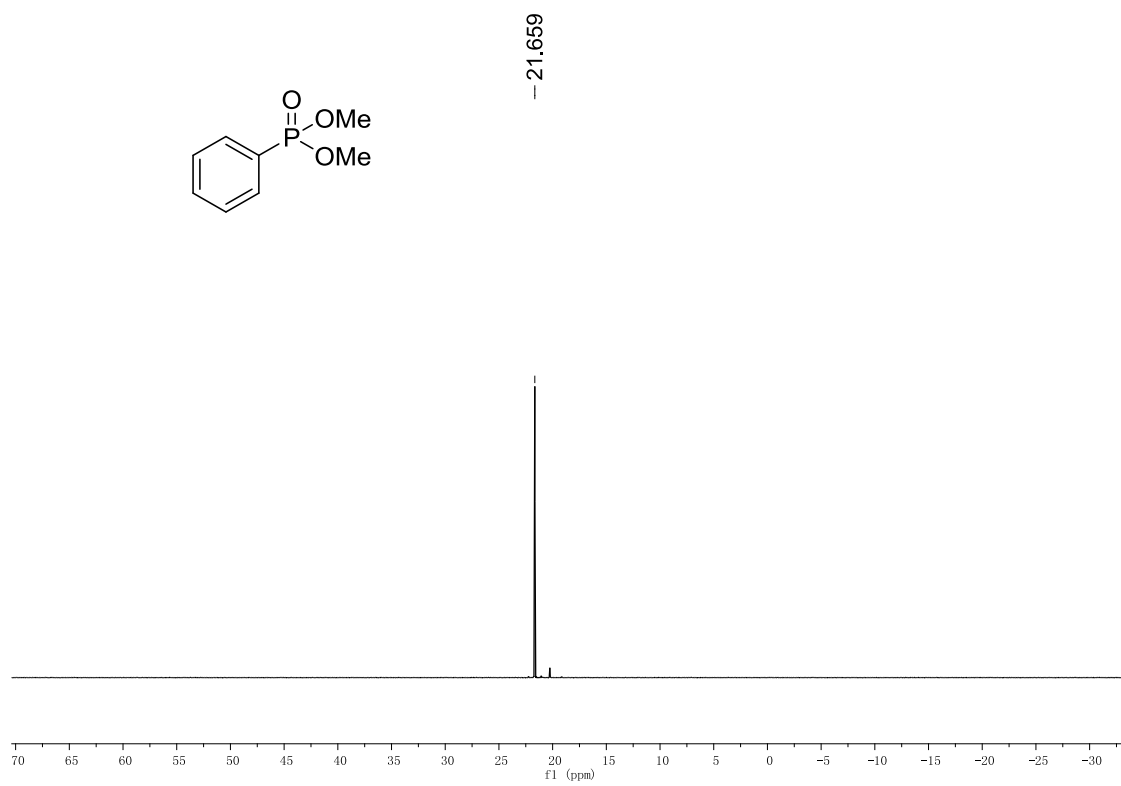
^{31}P NMR of 3q



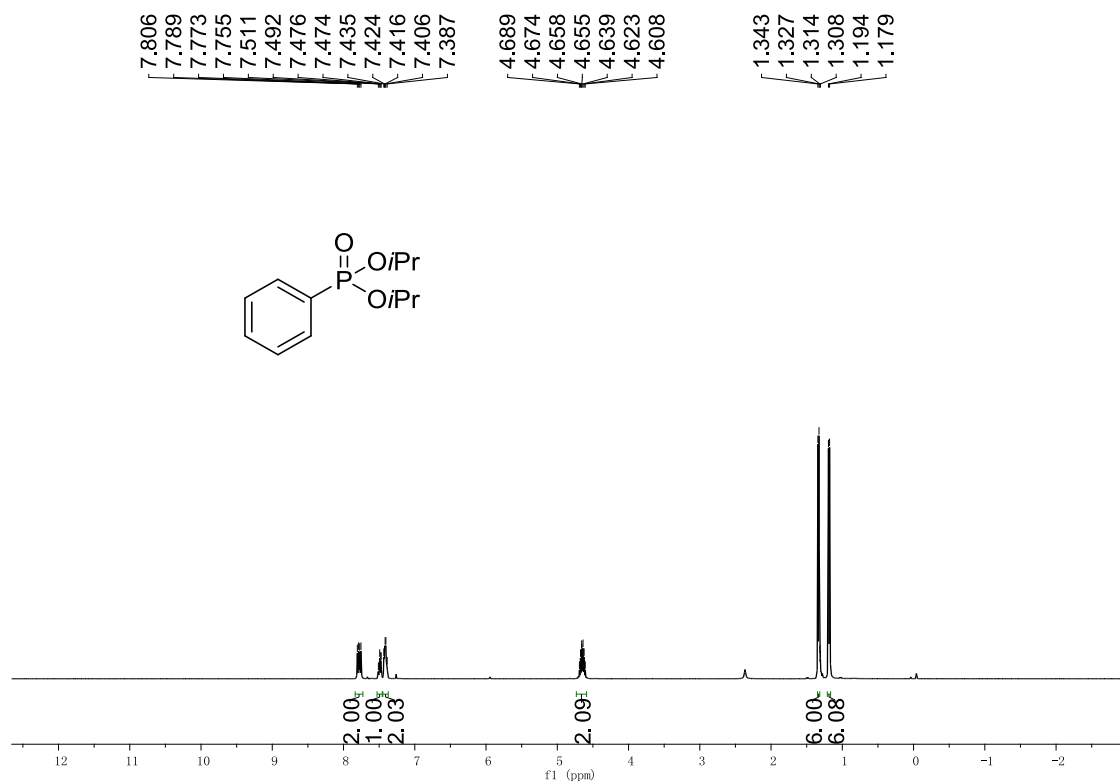
^1H NMR of 4a



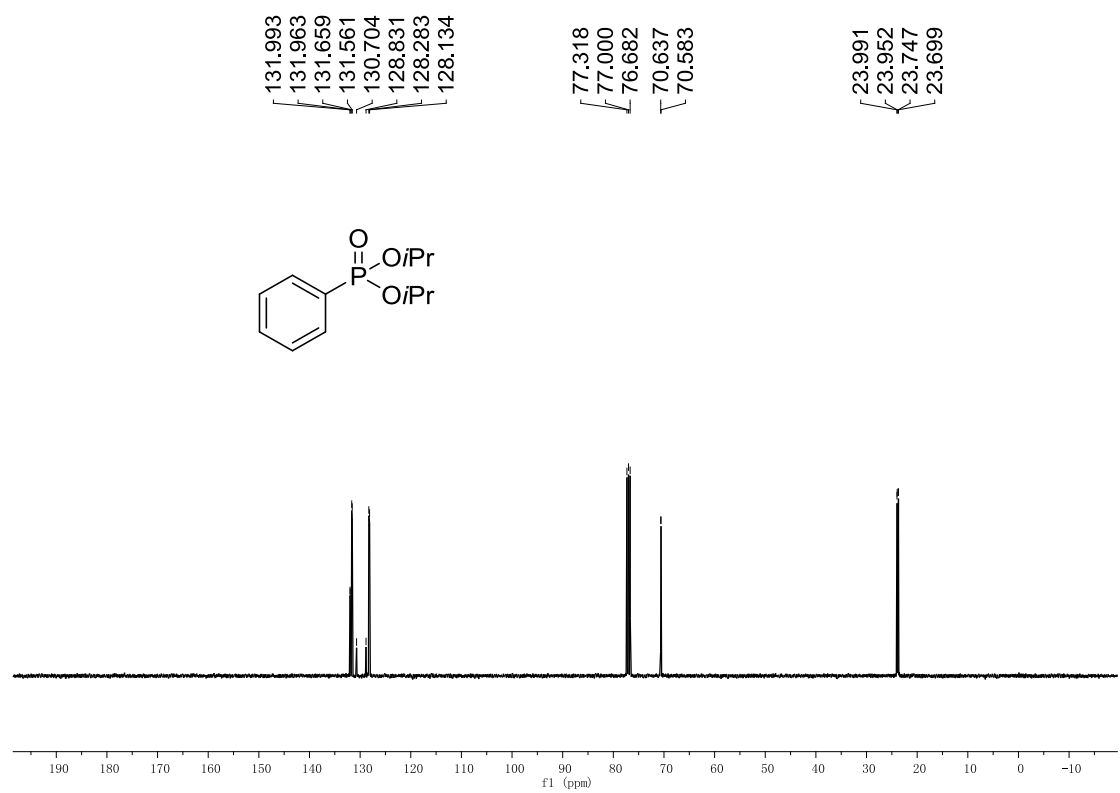
¹³C NMR of **4a**



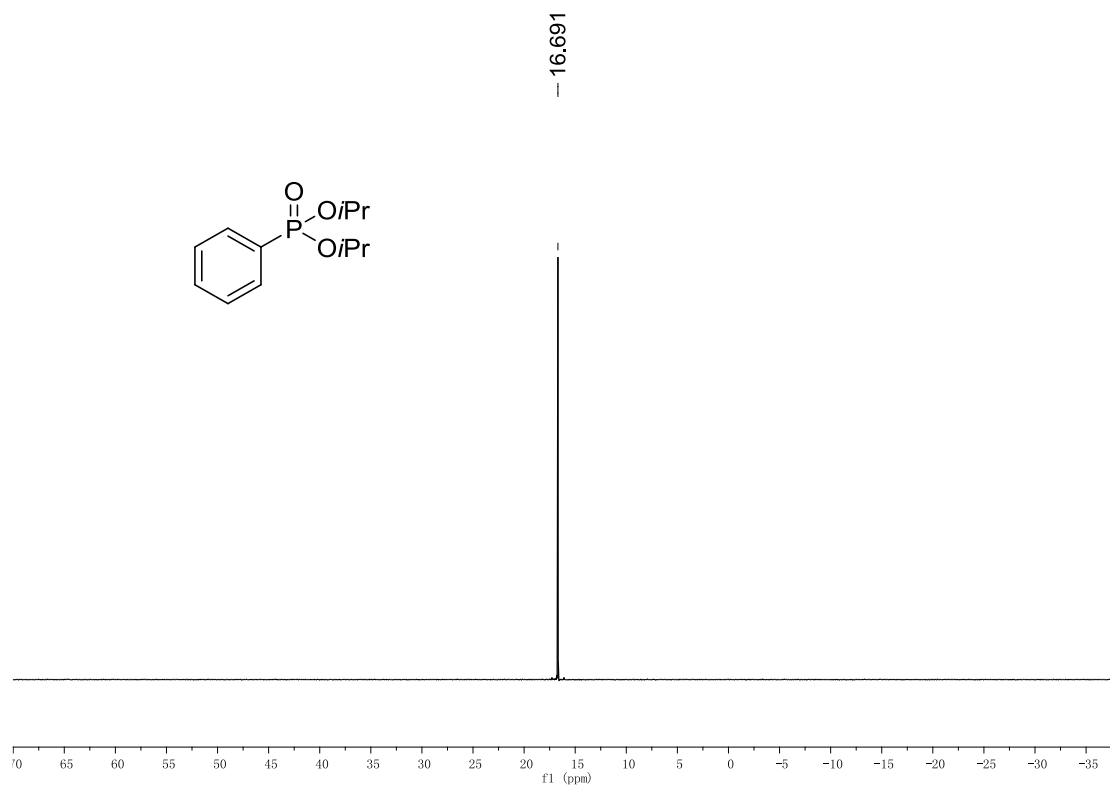
³¹P NMR of **4a**



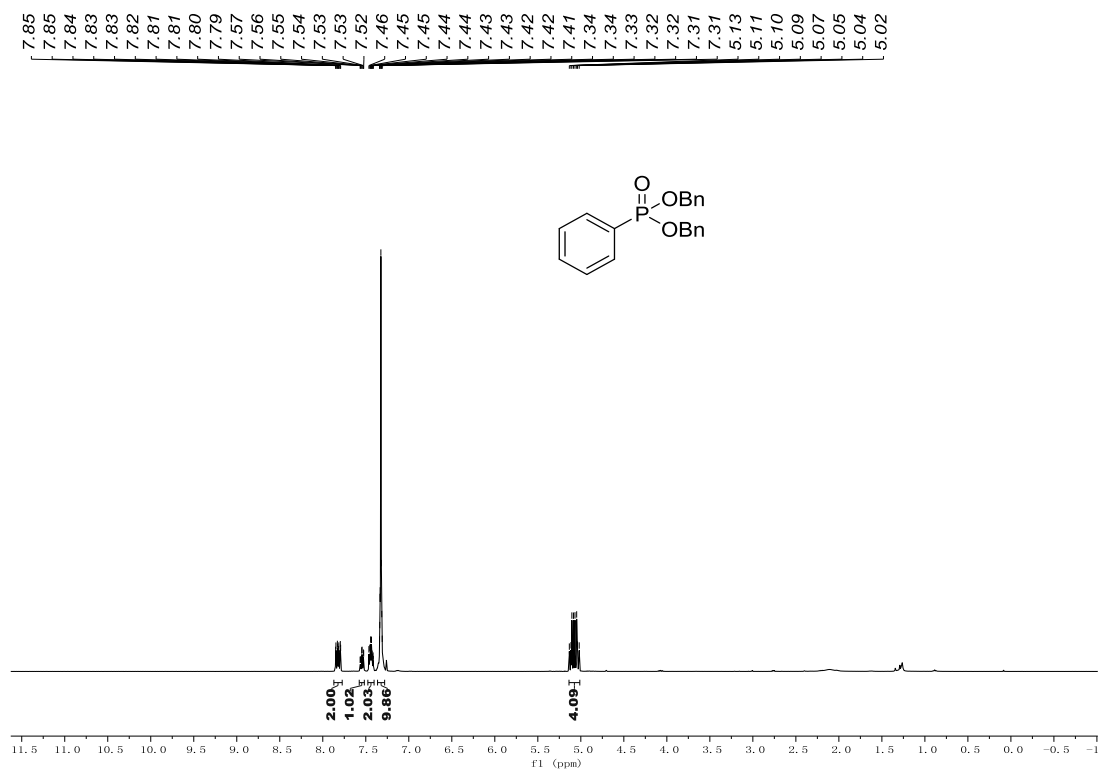
¹H NMR of **4b**



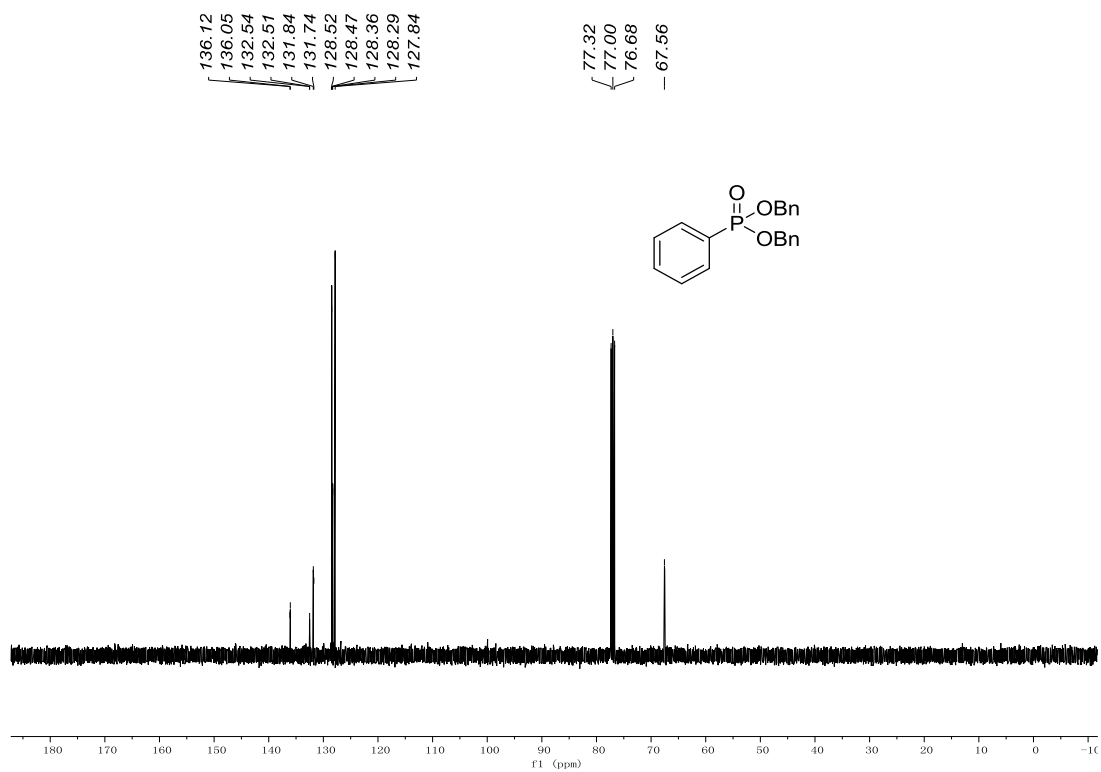
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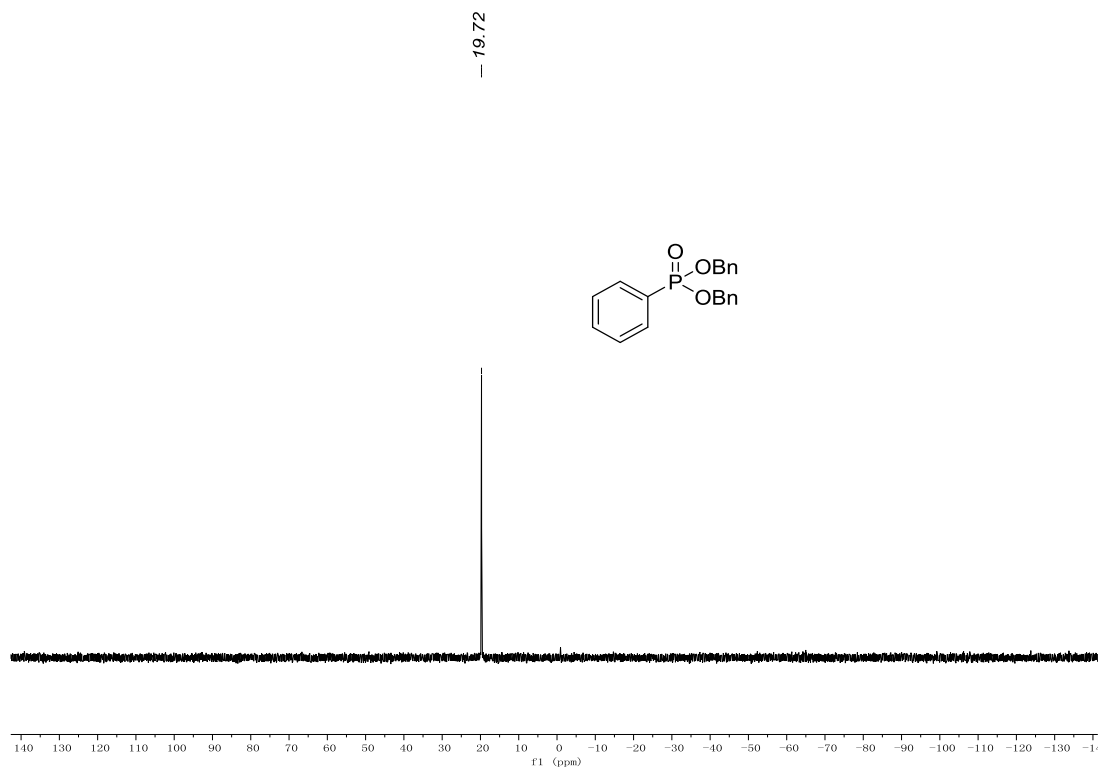
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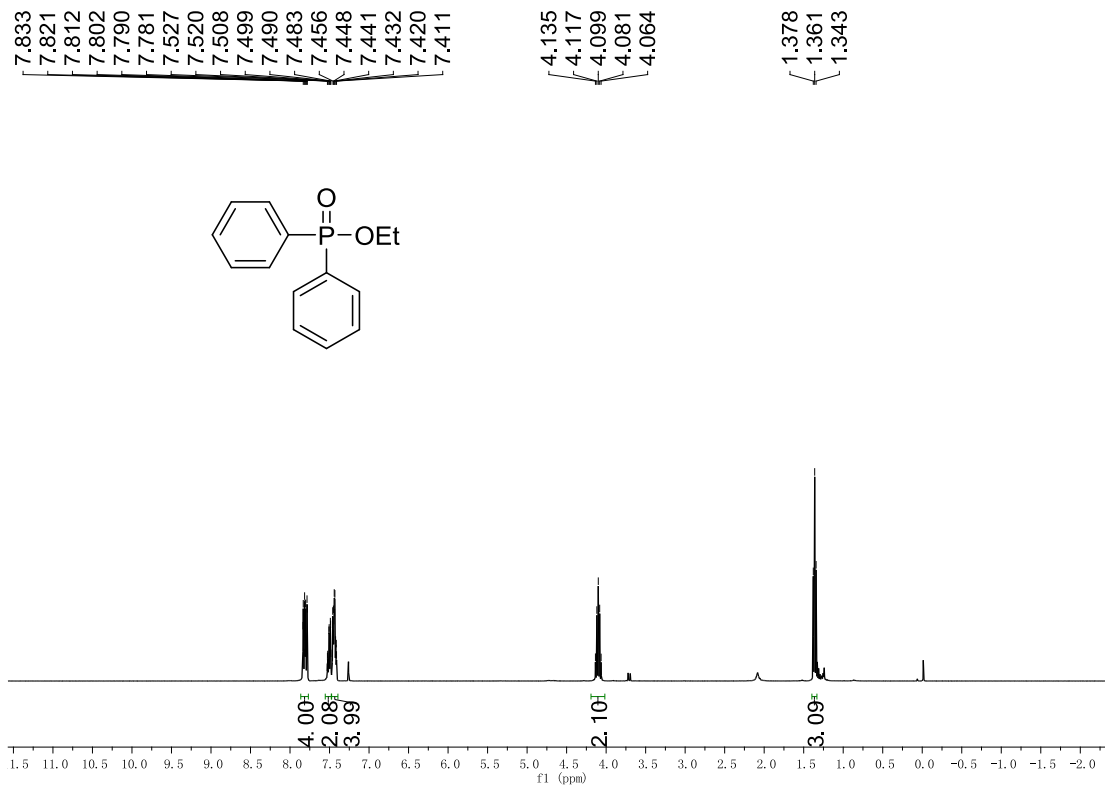
^1H NMR of 4c



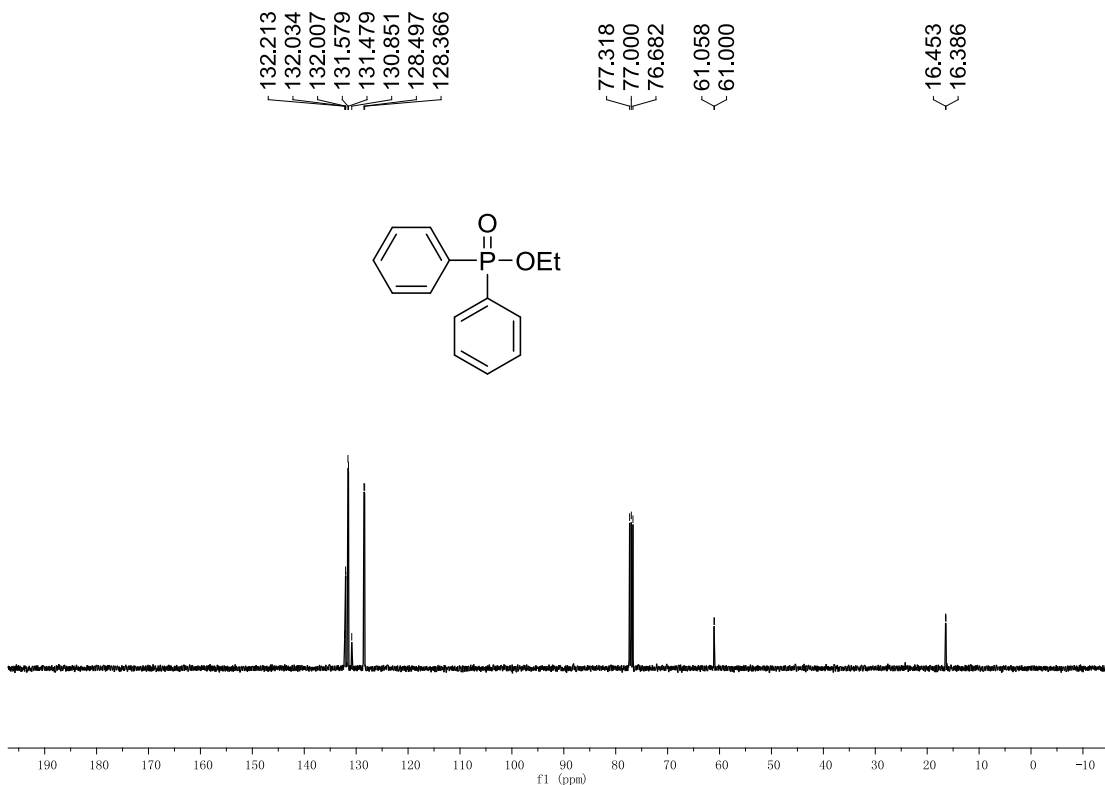
^{13}C NMR of 4c



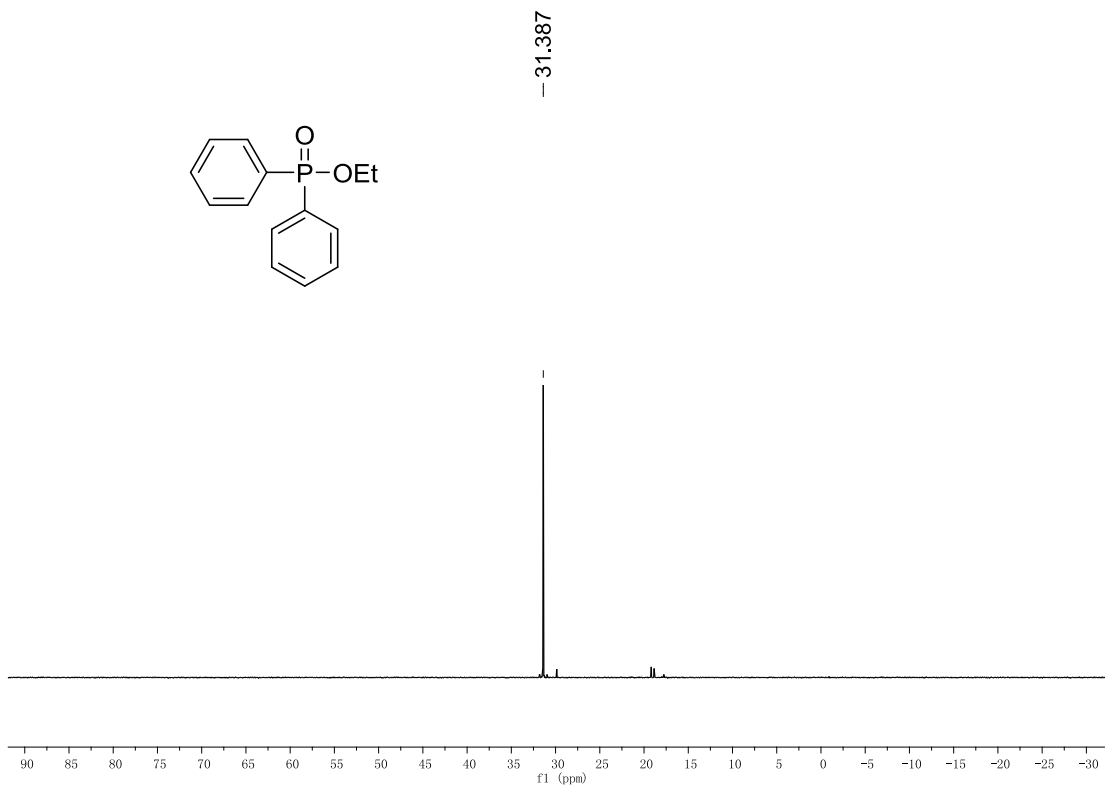
^{31}P NMR of 4c



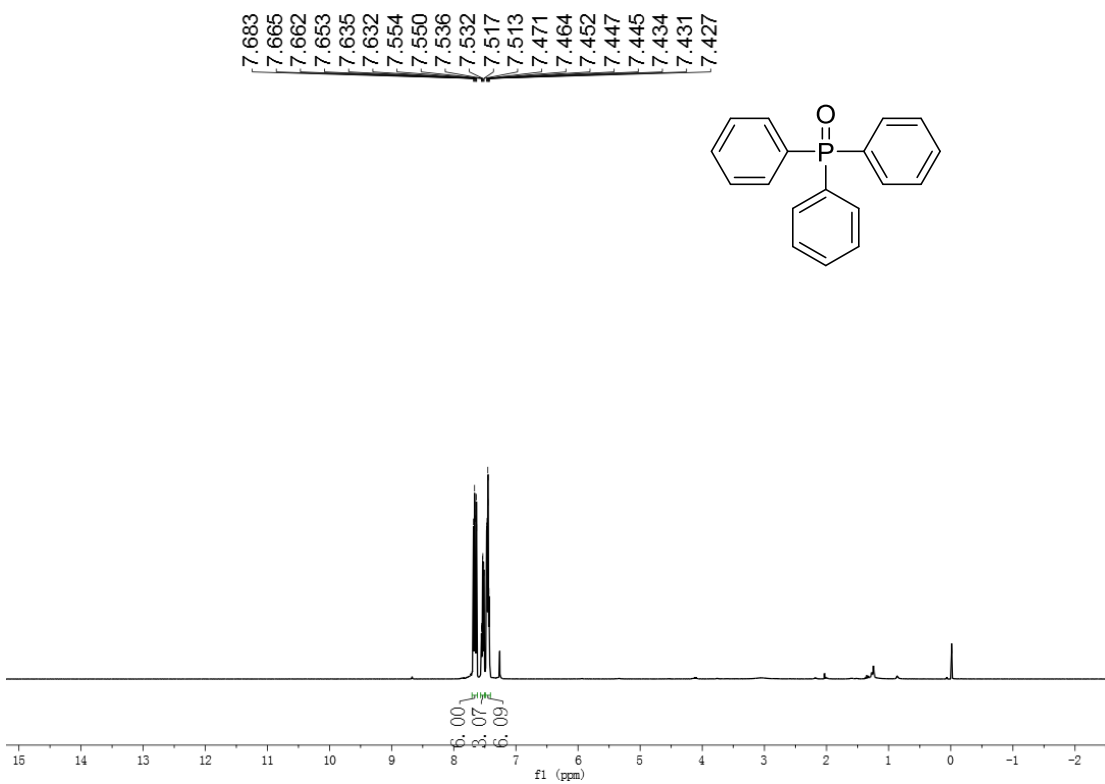
¹H NMR of 4d



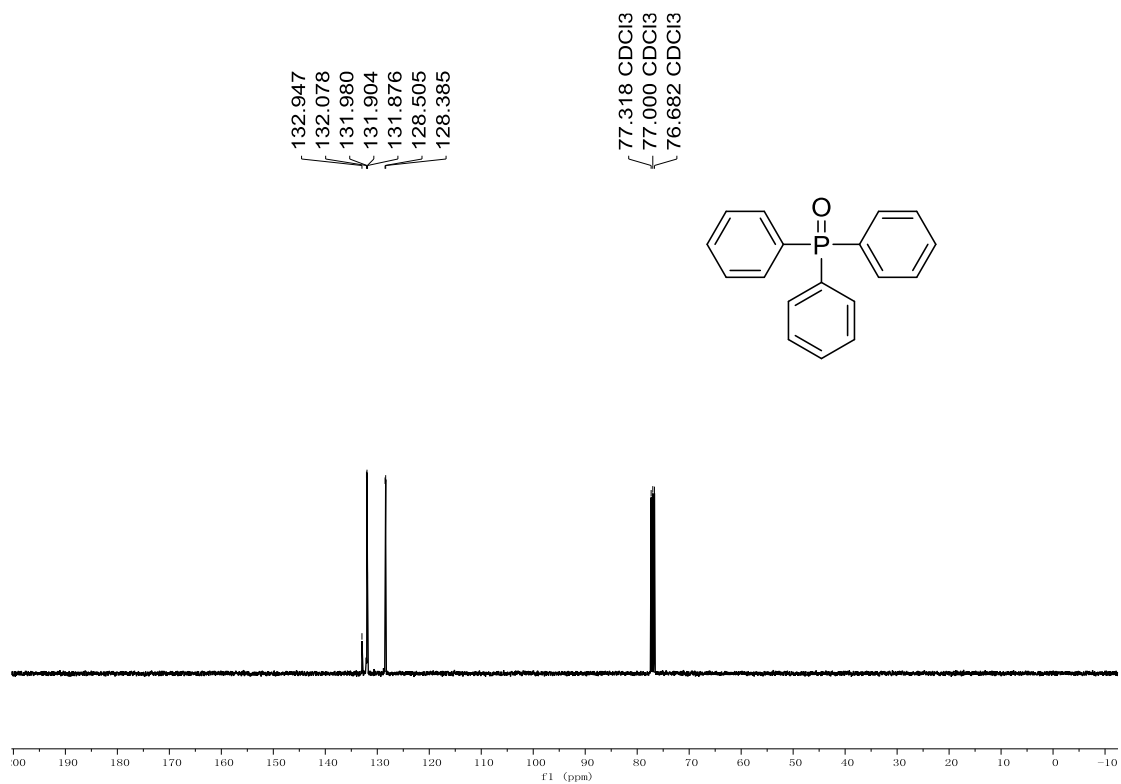
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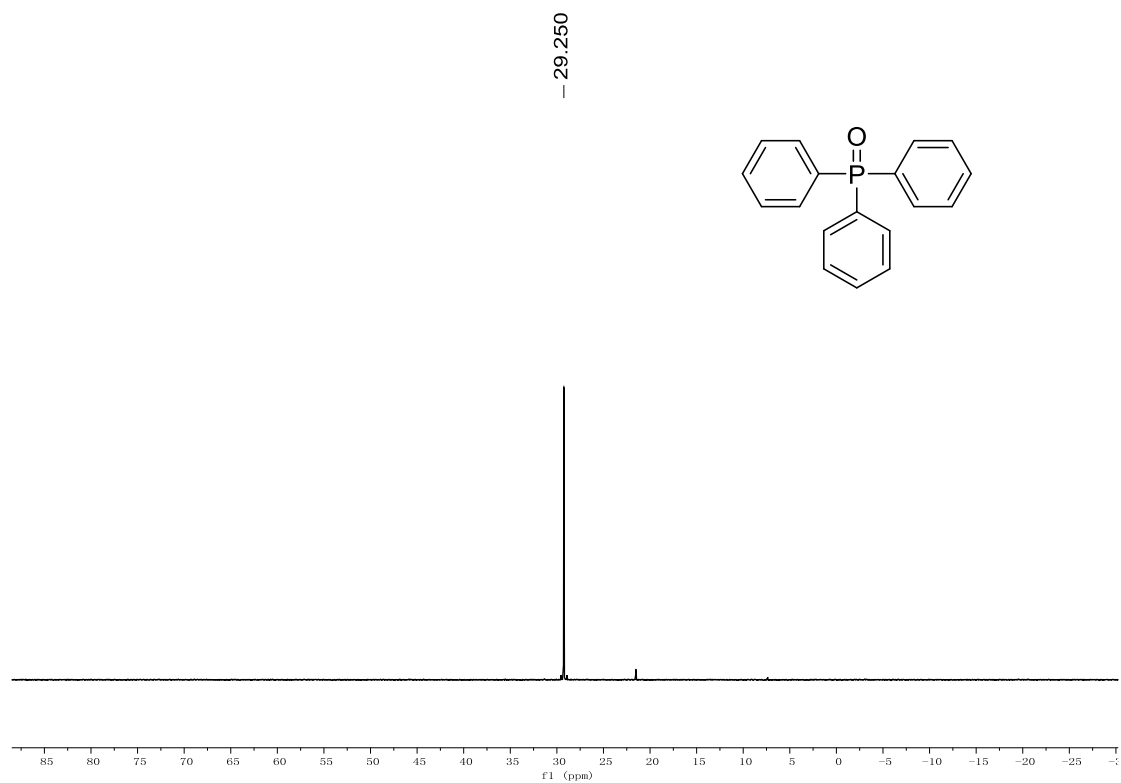
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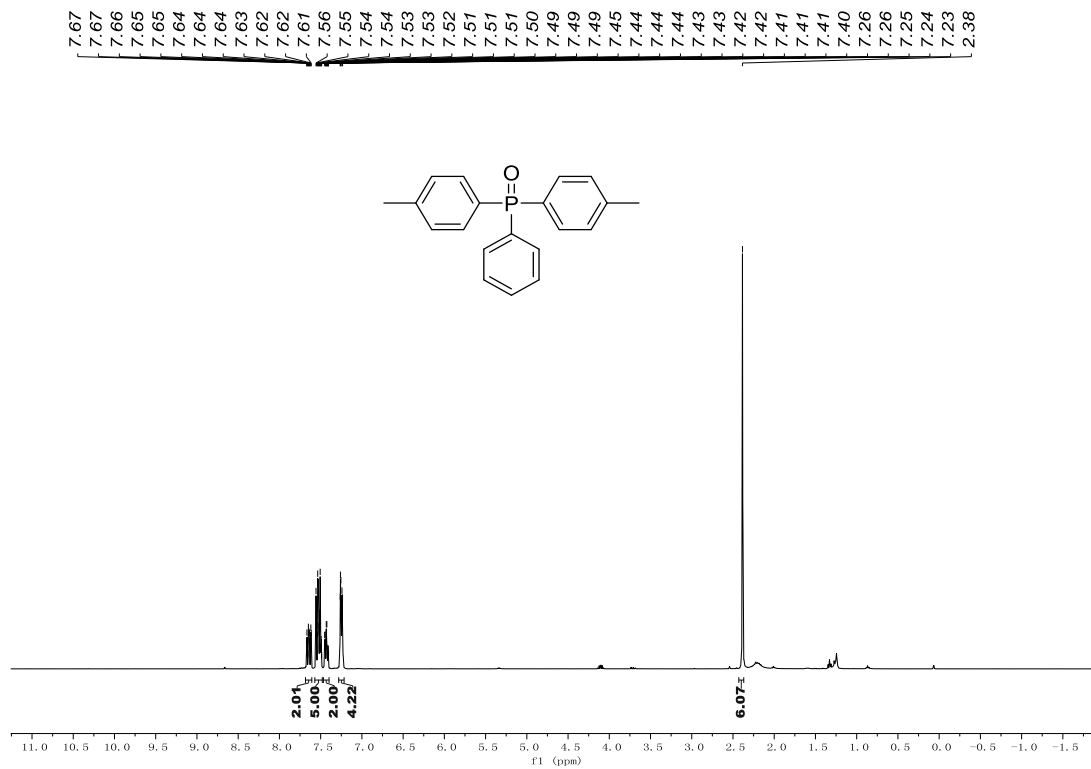
^1H NMR of **4e**



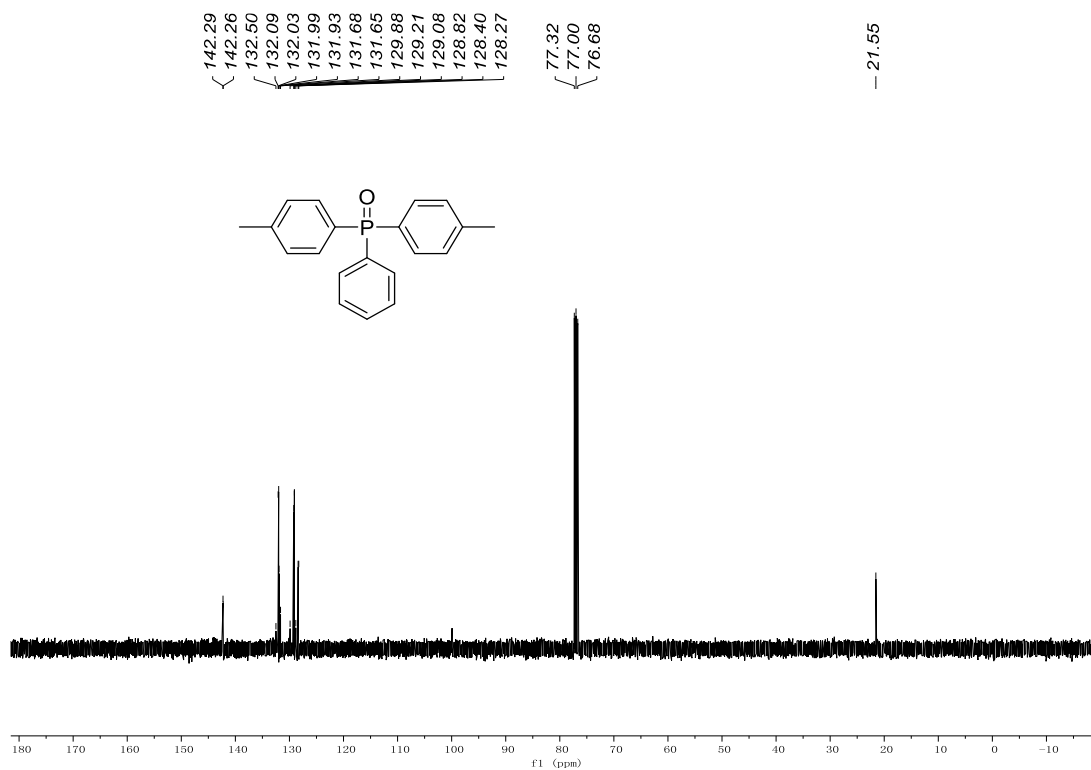
¹³C NMR of **4e**



³¹P NMR of **4e**



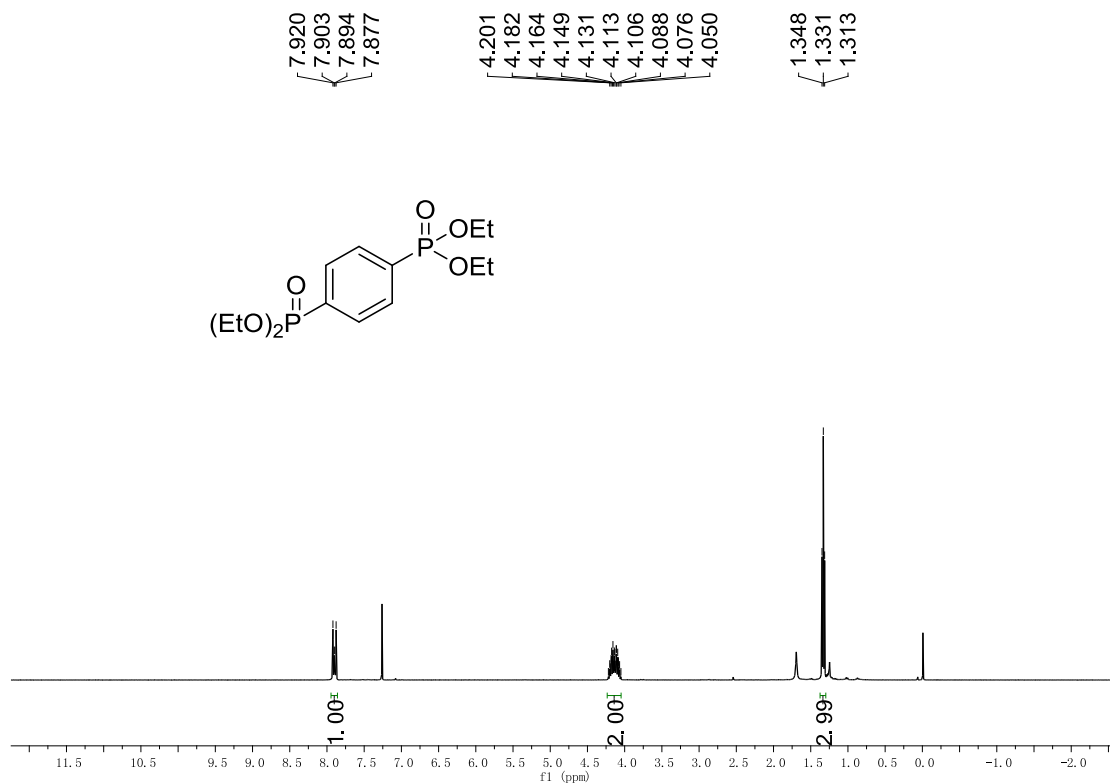
¹H NMR of 4f



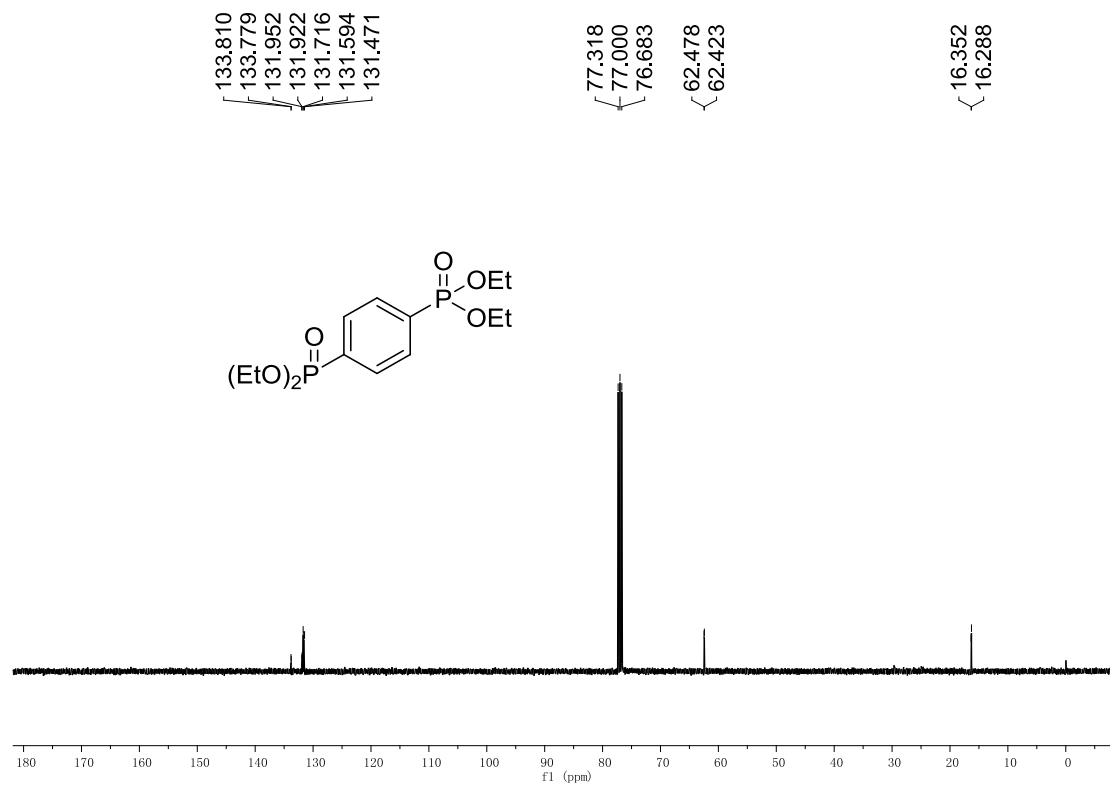
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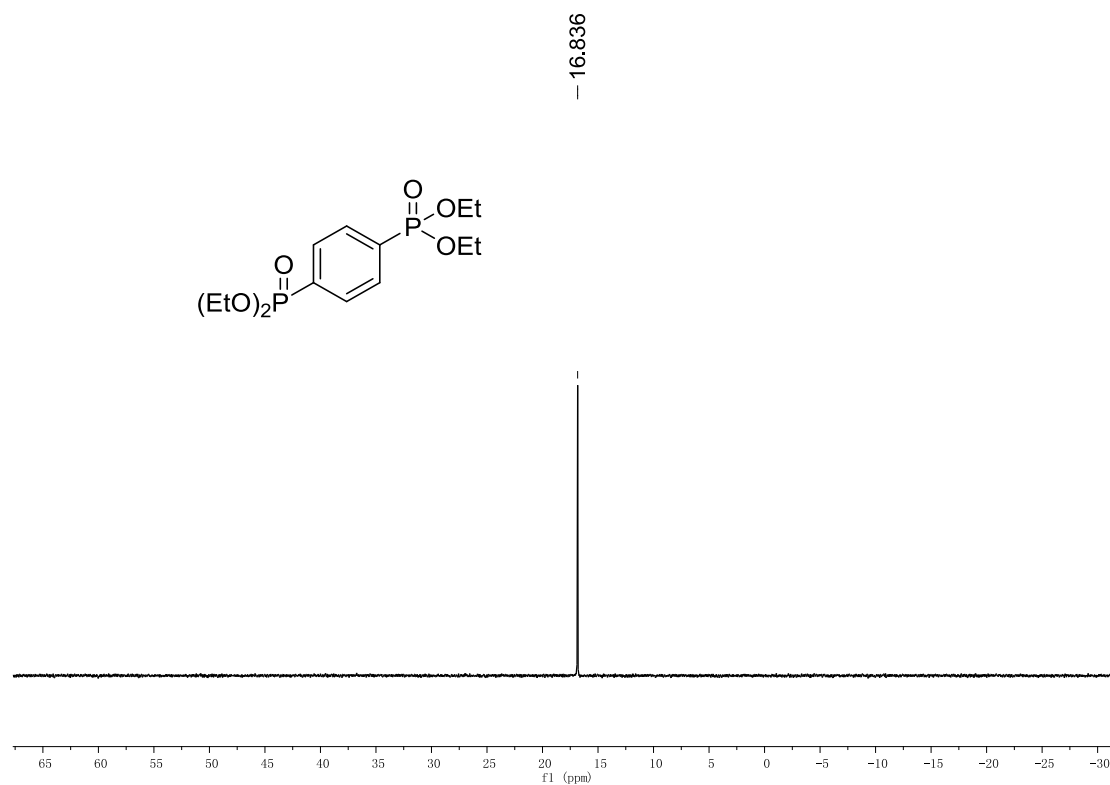
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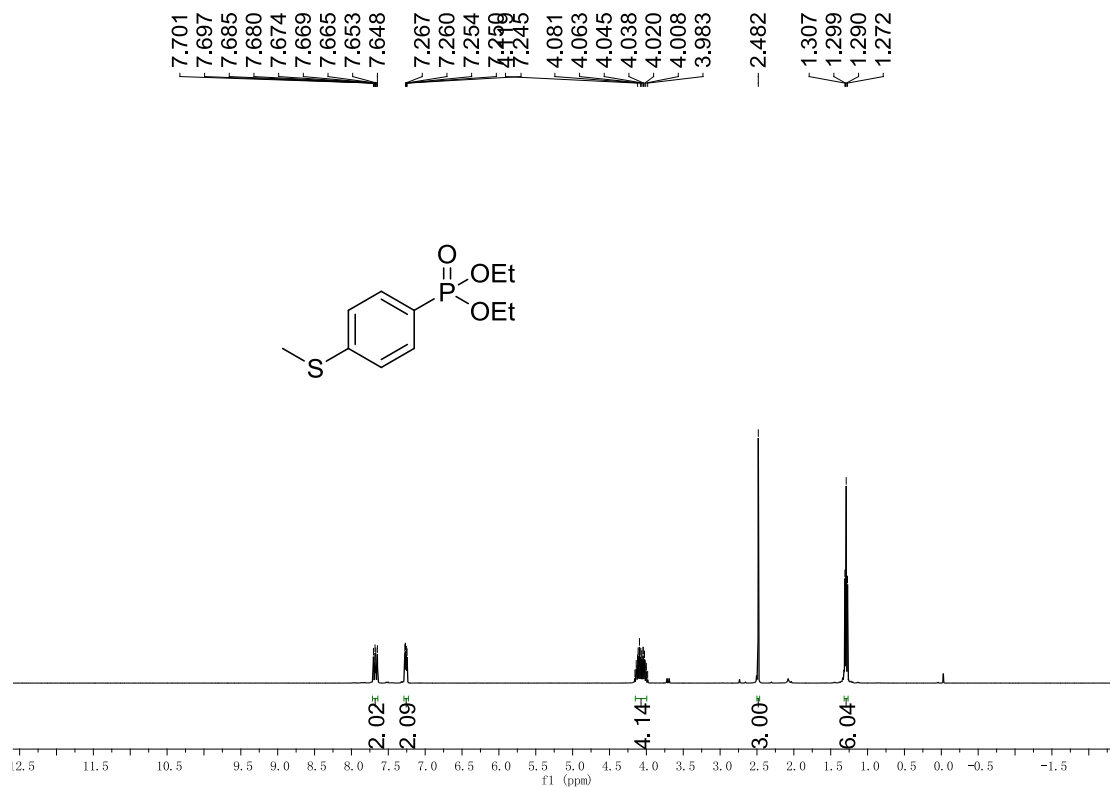
^1H NMR of 5



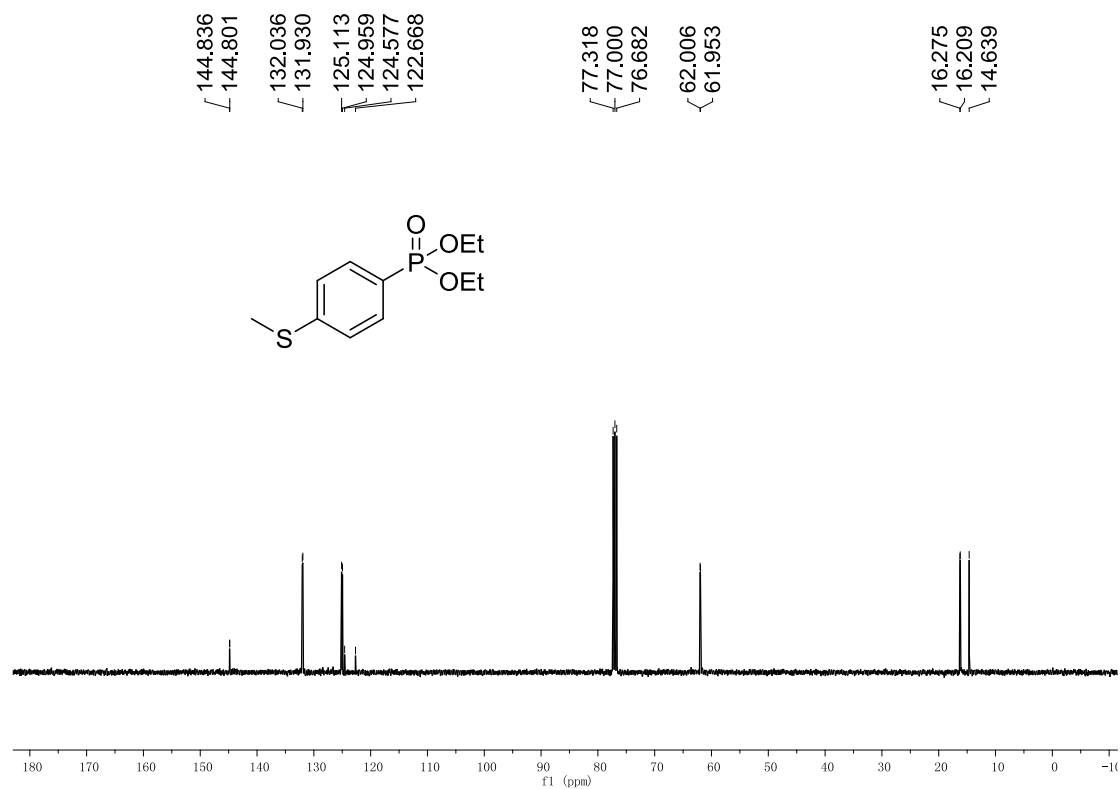
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³¹P NMR of 5

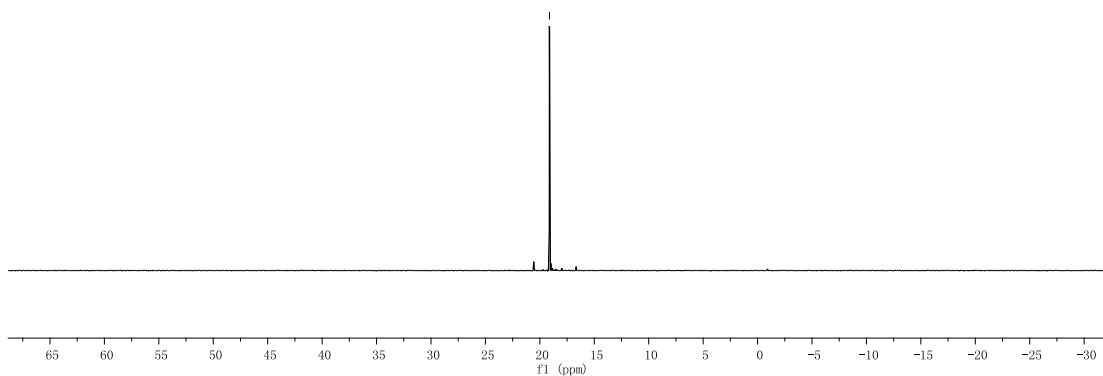
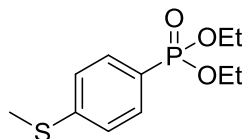


¹H NMR of 6



¹³C NMR of 6

- 19.116



³¹P NMR of **6**

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