

## Supplementary Information

### Synthesis of Triarylphosphines from Arylammonium Salts via One-Pot Transition-Metal-Free C–P Coupling

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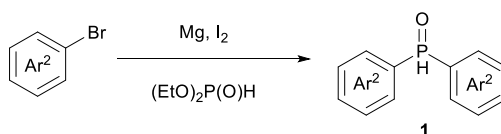
## I. General remarks

$^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were recorded on Bruker ADVANCE III 400 spectrometer or Bruker Ascend 600 spectrometer. Chemical shifts ( $\delta$ ) for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual solvent peak. Chemical shifts ( $\delta$ ) for carbon are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent. Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, q = quartet, quint = quintet, m = multiplet), coupling constants ( $J$ ) in Hertz (Hz), integration; “app” is used to denote the apparent splitting of a signal. High resolution mass spectrometry (HRMS) was carried out using MicroMass GCT CA 055 instrument and recorded on a MicroMass LCTTM spectrometer.

Anhydrous THF was distilled from calcium hydride. Anhydrous DMF was dried by 4 Å molecular sieve.

## II. General procedure for the synthesis of starting materials

### General procedure for the synthesis of diarylphosphine oxides<sup>1</sup>

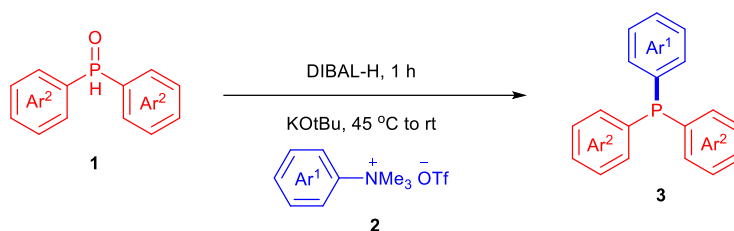


To the three-necked flask was charged with magnesium turnings (607.75 mg, 25 mmol) and iodine (10 mg), then 5 mL of solution of the aryl bromide (25 mmol) in THF (25 mL) was added via dropping funnel under nitrogen atmosphere. The mixture was heated to trigger the reaction, then the residual solution was added dropwise at room temperature. After the completion of dropping, the reaction was warmed to 45 °C for 2 h. The diethyl phosphite (7.6 mmol) in THF (7.6 mL) was dropped slowly at 0 °C. After the completion of dropping, the mixture was warmed to 45 °C again and stirred for 30 min. Then 1 M HCl (20 mL) was poured at 0 °C, and the mixture was stirred for 15 min. The mixture was extracted with ethyl acetate (3 × 20 mL), and the organic phase was washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, then concentrated in vacuo. The crude product was purified by silica gel column chromatography (eluent; hexane:EtOAc = 3:1 to 1:1), to give the desired product 1.

### General procedure for the synthesis of aryltrimethylammonium triflates<sup>2</sup>

To a stirred solution of *N,N*-dimethylaniline (10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added dropwise methyl trifluoromethanesulfonate (1.24 mL, 11.0 mmol, 1.1 equiv.) at 25 °C. The resulting solution was stirred for 4 h or 12 h at 25 °C. Solvent was then removed in vacuum and the residue was washed with Et<sub>2</sub>O, dried under vacuum to give the solid product **2**.

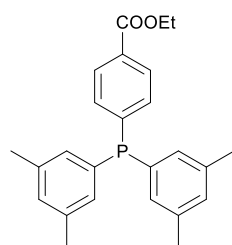
### III. General procedure for the synthesis of triarylphosphines



To the schlenk tube, were added the diarylphosphine oxide (0.5 mmol) and anhydrous THF (2.5 mL) under nitrogen atmosphere. Then the DIBAL-H (1 M, 1 mL) was added dropwise using the syringe to the mixture at room temperature and stirred for 1 h. KO<sup>t</sup>Bu (1 mmol) in anhydrous THF (4 mL) was added to the system, and the mixture was heated to 45 °C for 1 h. Then the reaction was transferred to the room temperature, and the aryltrimethylammonium triflate (0.25 mmol) in DMF (1 mL) was added. The mixture was stirred at room temperature for 3 h, then water (20 mL) was added to the mixture and stirred 30 min. The solution was extracted by dichloromethane (3 × 20 mL), and the combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, then concentrated in vacuo. The residue was further purified by column chromatography on silica gel to give the corresponding product **3**.

### IV. Characterization data for products

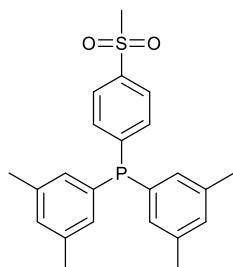
#### ethyl 4-(bis(3,5-dimethylphenyl)phosphanyl)benzoate (**3aa**)



Colorless oil, 69% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 – 7.91 (m, 2H), 7.41 – 7.30 (m, 2H), 7.05 – 6.90 (m, 6H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 12H), 1.40 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.67, 144.67 (d, *J* = 14.3 Hz), 138.18 (d, *J* = 7.7 Hz), 136.05 (d, *J* = 9.9 Hz), 133.23 (d, *J* = 18.5 Hz), 131.80 (d, *J* = 20.2 Hz),

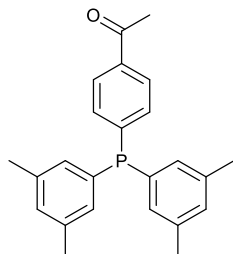
131.04, 130.18, 129.24 (d,  $J = 6.4$  Hz), 61.10, 21.42, 14.44. HRMS (EI): exact mass calculated for  $C_{25}H_{27}O_2P$   $[M]^+$  require  $m/z = 390.1749$ , found  $m/z = 390.1752$ .

**bis(3,5-dimethylphenyl)(4-(methylsulfonyl)phenyl)phosphane (3ab)**



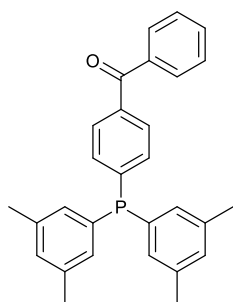
White solid, 56% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.84 (d,  $J = 7.9$  Hz, 2H), 7.42 (t,  $J = 6.9$  Hz, 2H), 7.02 (s, 2H), 6.95 (d,  $J = 8.6$  Hz, 4H), 3.05 (s, 3H), 2.28 (s, 12H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  146.98 (d,  $J = 16.9$  Hz), 139.92, 138.42 (d,  $J = 7.9$  Hz), 135.25 (d,  $J = 9.7$  Hz), 133.82 (d,  $J = 18.3$  Hz), 131.87 (d,  $J = 20.7$  Hz), 131.41, 126.95 (d,  $J = 5.9$  Hz), 44.56, 21.42. HRMS (EI): exact mass calculated for  $C_{23}H_{25}O_2PS$   $[M]^+$  require  $m/z = 396.1313$ , found  $m/z = 396.1315$ .

**1-(4-(bis(3,5-dimethylphenyl)phosphanyl)phenyl)ethan-1-one (3ac)**



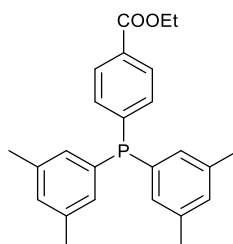
Colorless oil, 50% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.88 (dt,  $J = 8.4, 1.4$  Hz, 2H), 7.39 – 7.32 (m, 2H), 7.04 – 6.99 (m, 2H), 6.95 (dd,  $J = 8.5, 1.6$  Hz, 4H), 2.59 (s, 3H), 2.27 (s, 12H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  198.13, 145.28 (d,  $J = 14.6$  Hz), 138.25 (d,  $J = 7.7$  Hz), 136.69, 135.92 (d,  $J = 9.8$  Hz), 133.40 (d,  $J = 18.4$  Hz), 131.84 (d,  $J = 20.3$  Hz), 131.13, 128.04 (d,  $J = 6.2$  Hz), 26.78, 21.44. HRMS (EI): exact mass calculated for  $C_{24}H_{25}OP$   $[M]^+$  require  $m/z = 360.1643$ , found  $m/z = 360.1645$ .

**(4-(bis(3,5-dimethylphenyl)phosphanyl)phenyl)(phenyl)methanone (3ad)**



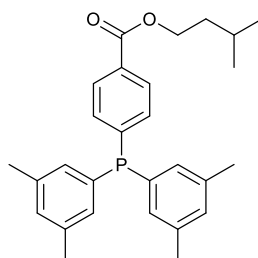
White solid, 76% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 – 7.80 (m, 2H), 7.78 – 7.73 (m, 2H), 7.63 – 7.56 (m, 1H), 7.52 – 7.44 (m, 2H), 7.43 – 7.36 (m, 2H), 7.06 – 6.96 (m, 6H), 2.30 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.64, 144.40 (d,  $J = 14.6$  Hz), 138.23 (d,  $J = 7.7$  Hz), 137.63, 137.13, 135.95 (d,  $J = 9.9$  Hz), 133.12 (d,  $J = 18.4$  Hz), 132.56, 131.84 (d,  $J = 20.3$  Hz), 131.11, 130.14, 129.86 (d,  $J = 6.3$  Hz), 128.40, 21.44. HRMS (EI): exact mass calculated for  $\text{C}_{29}\text{H}_{27}\text{OP}$   $[\text{M}]^+$  require  $m/z = 422.1800$ , found  $m/z = 422.1803$ .

#### 4-(bis(3,5-dimethylphenyl)phosphanyl)benzonitrile (3ae)



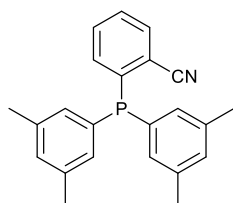
Colorless oil, 41% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.53 (m, 2H), 7.37 – 7.29 (m, 2H), 7.05 – 7.00 (m, 2H), 6.93 (dd,  $J = 8.7, 1.6$  Hz, 4H), 2.28 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.94 (d,  $J = 17.0$  Hz), 138.43 (d,  $J = 7.8$  Hz), 135.23 (d,  $J = 9.8$  Hz), 133.55 (d,  $J = 18.4$  Hz), 131.88 (d,  $J = 20.6$  Hz), 131.70 (d,  $J = 6.0$  Hz), 131.40, 119.04, 111.65, 21.43. HRMS (EI): exact mass calculated for  $\text{C}_{23}\text{H}_{22}\text{NP}$   $[\text{M}]^+$  require  $m/z = 343.1490$ , found  $m/z = 343.1492$ .

#### isopentyl 4-(bis(3,5-dimethylphenyl)phosphanyl)benzoate (3af)



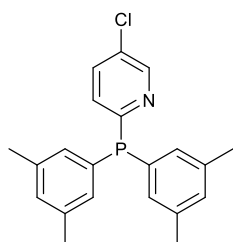
Colorless oil, 37% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 – 7.93 (m, 2H), 7.37 – 7.30 (m, 2H), 7.00 (s, 2H), 6.95 (dd,  $J = 8.5, 1.6$  Hz, 4H), 4.35 (t,  $J = 6.7$  Hz, 2H), 2.27 (s, 12H), 1.80 (dp,  $J = 13.3, 6.7$  Hz, 1H), 1.66 (q,  $J = 6.8$  Hz, 2H), 0.97 (d,  $J = 6.6$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.75, 144.68 (d,  $J = 14.2$  Hz), 138.20 (d,  $J = 7.7$  Hz), 136.05 (d,  $J = 9.8$  Hz), 133.25 (d,  $J = 18.6$  Hz), 131.81 (d,  $J = 20.1$  Hz), 131.06, 130.21, 129.25 (d,  $J = 6.3$  Hz), 63.79, 37.55, 25.34, 22.64, 21.44. HRMS (EI): exact mass calculated for  $\text{C}_{28}\text{H}_{33}\text{O}_2\text{P}$   $[\text{M}]^+$  require  $m/z = 432.2218$ , found  $m/z = 432.2215$ .

### 2-(bis(3,5-dimethylphenyl)phosphanyl)benzonitrile (3ag)



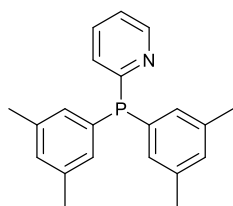
Colorless oil, 47% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (ddd,  $J = 7.5, 3.0, 1.4$  Hz, 1H), 7.48 (td,  $J = 7.7, 1.5$  Hz, 1H), 7.40 (td,  $J = 7.5, 1.3$  Hz, 1H), 7.07 (ddd,  $J = 7.7, 3.4, 1.3$  Hz, 1H), 7.01 (s, 2H), 6.91 (dd,  $J = 8.6, 1.7$  Hz, 4H), 2.27 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.72 (d,  $J = 20.1$  Hz), 138.29 (d,  $J = 7.8$  Hz), 134.55 (d,  $J = 9.6$  Hz), 133.72 (d,  $J = 4.9$  Hz), 133.67, 132.40, 131.80 (d,  $J = 20.5$  Hz), 131.31, 128.73, 118.20, 117.89 (d,  $J = 3.9$  Hz), 21.45. HRMS (EI): exact mass calculated for  $\text{C}_{23}\text{H}_{22}\text{NP}$   $[\text{M}]^+$  require  $m/z = 343.1490$ , found  $m/z = 343.1493$ .

### 2-(bis(3,5-dimethylphenyl)phosphanyl)-5-chloropyridine (3ah)



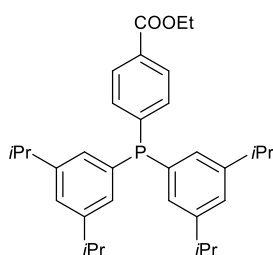
Colorless oil, 49% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J = 2.5$  Hz, 1H), 7.52 (ddd,  $J = 8.3, 2.5, 1.5$  Hz, 1H), 7.05 (d,  $J = 8.3$  Hz, 1H), 6.99 (d,  $J = 7.5$  Hz, 6H), 2.27 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.98, 149.23 (d,  $J = 12.4$  Hz), 138.26 (d,  $J = 7.8$  Hz), 135.53 (d,  $J = 9.7$  Hz), 135.43 (d,  $J = 2.8$  Hz), 131.97 (d,  $J = 20.3$  Hz), 131.25, 130.97, 128.67 (d,  $J = 16.8$  Hz), 21.46. HRMS (EI): exact mass calculated for  $\text{C}_{21}\text{H}_{21}\text{ClNP}$   $[\text{M}]^+$  require  $m/z = 353.1100$ , found  $m/z = 353.1103$ .

### 2-(bis(3,5-dimethylphenyl)phosphanyl)pyridine (3ai)



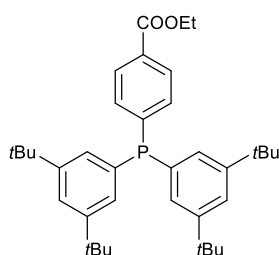
Colorless oil, 60% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.70 (ddd,  $J = 4.7, 1.7, 1.0$  Hz, 1H), 7.53 (tt,  $J = 7.7, 1.9$  Hz, 1H), 7.13 (ddt,  $J = 7.4, 4.8, 1.1$  Hz, 1H), 7.09 (dq,  $J = 7.8, 1.1$  Hz, 1H), 7.04 – 6.95 (m, 6H), 2.26 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.74 (d,  $J = 3.9$  Hz), 150.31 (d,  $J = 12.6$  Hz), 138.05 (d,  $J = 7.7$  Hz), 135.95 (d,  $J = 9.9$  Hz), 135.68 (d,  $J = 2.3$  Hz), 132.01 (d,  $J = 20.0$  Hz), 130.98, 127.89 (d,  $J = 15.6$  Hz), 122.02, 21.44. HRMS (EI): exact mass calculated for  $\text{C}_{21}\text{H}_{22}\text{NP}$   $[\text{M}]^+$  require  $m/z = 319.1490$ , found  $m/z = 319.1488$ .

#### ethyl 4-(bis(3,5-diisopropylphenyl)phosphanyl)benzoate (3ba)



Colorless oil, 40% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 7.7$  Hz, 2H), 7.35 (t,  $J = 7.5$  Hz, 2H), 7.07 (s, 2H), 7.02 (d,  $J = 8.3$  Hz, 4H), 4.42 – 4.34 (m, 2H), 3.10 – 2.69 (m, 4H), 1.45 – 1.35 (m, 3H), 1.19 (dd,  $J = 6.9, 2.3$  Hz, 24H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.75, 149.10 (d,  $J = 7.2$  Hz), 145.32 (d,  $J = 14.4$  Hz), 136.06 (d,  $J = 9.4$  Hz), 133.14 (d,  $J = 18.2$  Hz), 130.07, 129.71 (d,  $J = 20.2$  Hz), 129.15 (d,  $J = 6.2$  Hz), 125.79, 61.10, 34.25, 24.11 (d,  $J = 8.8$  Hz), 14.46. HRMS (EI): exact mass calculated for  $\text{C}_{33}\text{H}_{43}\text{O}_2\text{P}$   $[\text{M}]^+$  require  $m/z = 502.3001$ , found  $m/z = 502.3003$ .

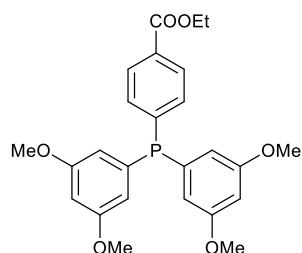
#### ethyl 4-(bis(3,5-di-tert-butylphenyl)phosphanyl)benzoate (3ca)



White solid, 50% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (dd,  $J = 8.3, 1.5$  Hz, 2H),

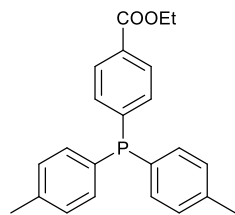
7.40 (d,  $J = 2.0$  Hz, 2H), 7.32 (dd,  $J = 8.3, 6.6$  Hz, 2H), 7.17 (dd,  $J = 8.5, 1.8$  Hz, 4H), 4.37 (q,  $J = 7.1$  Hz, 2H), 1.39 (t,  $J = 7.1$  Hz, 3H), 1.24 (s, 36H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.79, 150.92 (d,  $J = 7.2$  Hz), 145.69 (d,  $J = 14.5$  Hz), 135.39 (d,  $J = 8.8$  Hz), 133.02 (d,  $J = 18.0$  Hz), 129.95, 129.10 (d,  $J = 6.2$  Hz), 128.47 (d,  $J = 20.5$  Hz), 123.13, 61.11, 35.05, 31.51, 14.45. HRMS (EI): exact mass calculated for  $\text{C}_{37}\text{H}_{51}\text{O}_2\text{P}$   $[\text{M}]^+$  require  $m/z = 558.3627$ , found  $m/z = 558.3624$ .

#### ethyl 4-(bis(3,5-dimethoxyphenyl)phosphanyl)benzoate (3da)



White solid, 62% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.93 (m, 2H), 7.41 – 7.33 (m, 2H), 6.51 – 6.42 (m, 6H), 4.37 (q,  $J = 7.1$  Hz, 2H), 3.72 (s, 12H), 1.38 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.51, 160.95 (d,  $J = 9.9$  Hz), 143.31 (d,  $J = 14.0$  Hz), 138.30 (d,  $J = 11.1$  Hz), 133.42 (d,  $J = 19.1$  Hz), 130.66, 129.38 (d,  $J = 6.6$  Hz), 111.75 (d,  $J = 21.4$  Hz), 101.37, 61.16, 55.44, 14.42. HRMS (EI): exact mass calculated for  $\text{C}_{25}\text{H}_{27}\text{O}_6\text{P}$   $[\text{M}]^+$  require  $m/z = 454.1545$ , found  $m/z = 454.1543$ .

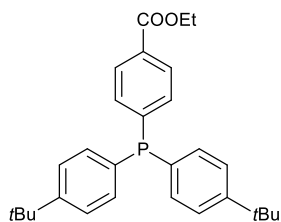
#### ethyl 4-(di-*p*-tolylphosphanyl)benzoate (3ea)



Colorless oil, 50% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (dd,  $J = 8.3, 1.6$  Hz, 2H), 7.31 (dd,  $J = 8.1, 6.6$  Hz, 2H), 7.22 (t,  $J = 7.8$  Hz, 4H), 7.15 (d,  $J = 7.6$  Hz, 4H), 4.36 (q,  $J = 7.1$  Hz, 2H), 2.35 (s, 6H), 1.37 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.60, 144.84 (d,  $J = 13.9$  Hz), 139.29, 134.11 (d,  $J = 20.2$  Hz), 133.01 (d,  $J = 18.4$  Hz), 132.99 (d,  $J = 9.3$  Hz), 130.23, 129.60 (d,  $J = 7.5$  Hz), 129.28 (d,  $J = 6.2$  Hz), 61.10, 21.46, 14.45. HRMS (EI): exact mass calculated for  $\text{C}_{23}\text{H}_{23}\text{O}_2\text{P}$   $[\text{M}]^+$  require  $m/z = 362.1436$ , found  $m/z = 362.1438$ .

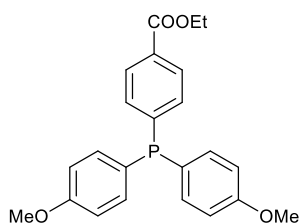
#### ethyl 4-(bis(4-(tert-butyl)phenyl)phosphanyl)benzoate (3fa)





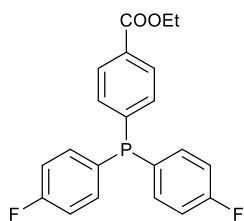
White solid, 63% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (dd,  $J = 8.2, 1.6$  Hz, 2H), 7.31 – 7.22 (m, 6H), 7.18 (t,  $J = 8.0$  Hz, 4H), 4.28 (q,  $J = 7.1$  Hz, 2H), 1.29 (t,  $J = 7.1$  Hz, 3H), 1.23 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.61, 152.33, 144.91 (d,  $J = 13.8$  Hz), 133.92 (d,  $J = 20.1$  Hz), 133.15 (d,  $J = 18.5$  Hz), 132.93 (d,  $J = 8.8$  Hz), 130.21, 129.26 (d,  $J = 6.3$  Hz), 125.78 (d,  $J = 7.4$  Hz), 61.08, 34.81, 31.36, 14.45. HRMS (EI): exact mass calculated for  $\text{C}_{29}\text{H}_{35}\text{O}_2\text{P}$   $[\text{M}]^+$  require  $m/z = 446.2375$ , found  $m/z = 446.2373$ .

#### ethyl 4-(bis(4-methoxyphenyl)phosphanyl)benzoate (3ga)



White solid, 47% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (dd,  $J = 8.2, 1.6$  Hz, 2H), 7.32 – 7.23 (m, 6H), 6.90 (d,  $J = 8.3$  Hz, 4H), 4.36 (q,  $J = 7.1$  Hz, 2H), 3.81 (s, 6H), 1.37 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.61, 160.65, 145.62 (d,  $J = 13.5$  Hz), 135.67 (d,  $J = 21.6$  Hz), 132.66 (d,  $J = 18.1$  Hz), 130.06, 129.25 (d,  $J = 6.0$  Hz), 127.47 (d,  $J = 7.6$  Hz), 114.49 (d,  $J = 8.2$  Hz), 61.10, 55.35, 14.45. HRMS (EI): exact mass calculated for  $\text{C}_{23}\text{H}_{23}\text{O}_4\text{P}$   $[\text{M}]^+$  require  $m/z = 394.1334$ , found  $m/z = 394.1333$ .

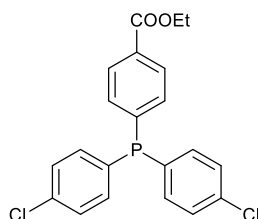
#### ethyl 4-(bis(4-fluorophenyl)phosphanyl)benzoate (3ha)



Colorless oil, 50% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (dd,  $J = 8.4, 1.6$  Hz, 2H), 7.34 – 7.24 (m, 6H), 7.11 – 7.02 (m, 4H), 4.37 (q,  $J = 7.1$  Hz, 2H), 1.38 (t,  $J = 7.1$  Hz,

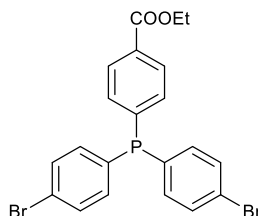
3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.40, 164.99, 162.50, 143.71 (d,  $J = 13.6$  Hz), 136.11 (d,  $J = 8.1$  Hz), 135.90 (d,  $J = 8.1$  Hz), 132.94 (d,  $J = 18.7$  Hz), 131.79 (d,  $J = 3.5$  Hz), 131.69 (d,  $J = 3.5$  Hz), 130.75, 129.54 (d,  $J = 6.5$  Hz), 116.28 (d,  $J = 8.0$  Hz), 116.07 (d,  $J = 8.0$  Hz), 61.24, 14.44. HRMS (EI): exact mass calculated for  $\text{C}_{21}\text{H}_{17}\text{F}_2\text{O}_2\text{P}$   $[\text{M}]^+$  require  $m/z = 370.0934$ , found  $m/z = 370.0936$ .

#### ethyl 4-(bis(4-chlorophenyl)phosphanyl)benzoate (3ia)



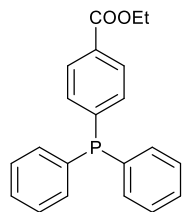
Colorless oil, 63% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (dd,  $J = 8.2, 1.6$  Hz, 2H), 7.38 – 7.27 (m, 6H), 7.25 – 7.17 (m, 4H), 4.38 (q,  $J = 7.1$  Hz, 2H), 1.38 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  166.34, 142.75 (d,  $J = 13.9$  Hz), 135.90, 135.24 (d,  $J = 21.1$  Hz), 134.55 (d,  $J = 11.8$  Hz), 133.19 (d,  $J = 19.3$  Hz), 131.01, 129.64 (d,  $J = 7.0$  Hz), 129.21 (d,  $J = 7.6$  Hz), 61.29, 14.45. HRMS (EI): exact mass calculated for  $\text{C}_{21}\text{H}_{17}\text{Cl}_2\text{O}_2\text{P}$   $[\text{M}]^+$  require  $m/z = 402.0343$ , found  $m/z = 402.0345$ .

#### ethyl 4-(bis(4-bromophenyl)phosphanyl)benzoate (3ja)



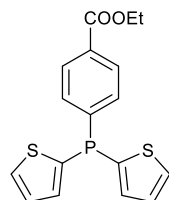
Colorless oil, 47% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (dd,  $J = 8.2, 1.6$  Hz, 2H), 7.55 – 7.44 (m, 4H), 7.30 (dd,  $J = 8.3, 7.1$  Hz, 2H), 7.19 – 7.09 (m, 4H), 4.38 (q,  $J = 7.1$  Hz, 2H), 1.38 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.32, 142.49 (d,  $J = 13.7$  Hz), 135.45 (d,  $J = 20.7$  Hz), 135.04 (d,  $J = 12.2$  Hz), 133.23 (d,  $J = 19.2$  Hz), 132.13 (d,  $J = 7.3$  Hz), 131.05, 129.65 (d,  $J = 6.6$  Hz), 124.28, 61.29, 14.44. HRMS (EI): exact mass calculated for  $\text{C}_{21}\text{H}_{17}\text{Br}_2\text{O}_2\text{P}$   $[\text{M}]^+$  require  $m/z = 489.9333$ , found  $m/z = 489.9335$ .

#### ethyl 4-(diphenylphosphanyl)benzoate (3ka)



Colorless oil, 50% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (dd,  $J = 8.3, 1.6$  Hz, 2H), 7.43 – 7.29 (m, 12H), 4.38 (q,  $J = 7.1$  Hz, 2H), 1.39 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.50, 143.97 (d,  $J = 14.0$  Hz), 136.32 (d,  $J = 10.6$  Hz), 134.05 (d,  $J = 20.0$  Hz), 133.27 (d,  $J = 18.7$  Hz), 130.49, 129.37 (d,  $J = 6.4$  Hz), 129.23, 128.78 (d,  $J = 7.2$  Hz), 61.13, 14.43. HRMS (EI): exact mass calculated for  $\text{C}_{21}\text{H}_{19}\text{O}_2\text{P}$   $[\text{M}]^+$  require  $m/z = 334.1123$ , found  $m/z = 334.1120$ .

#### ethyl 4-(di(thiophen-2-yl)phosphanyl)benzoate (3la)



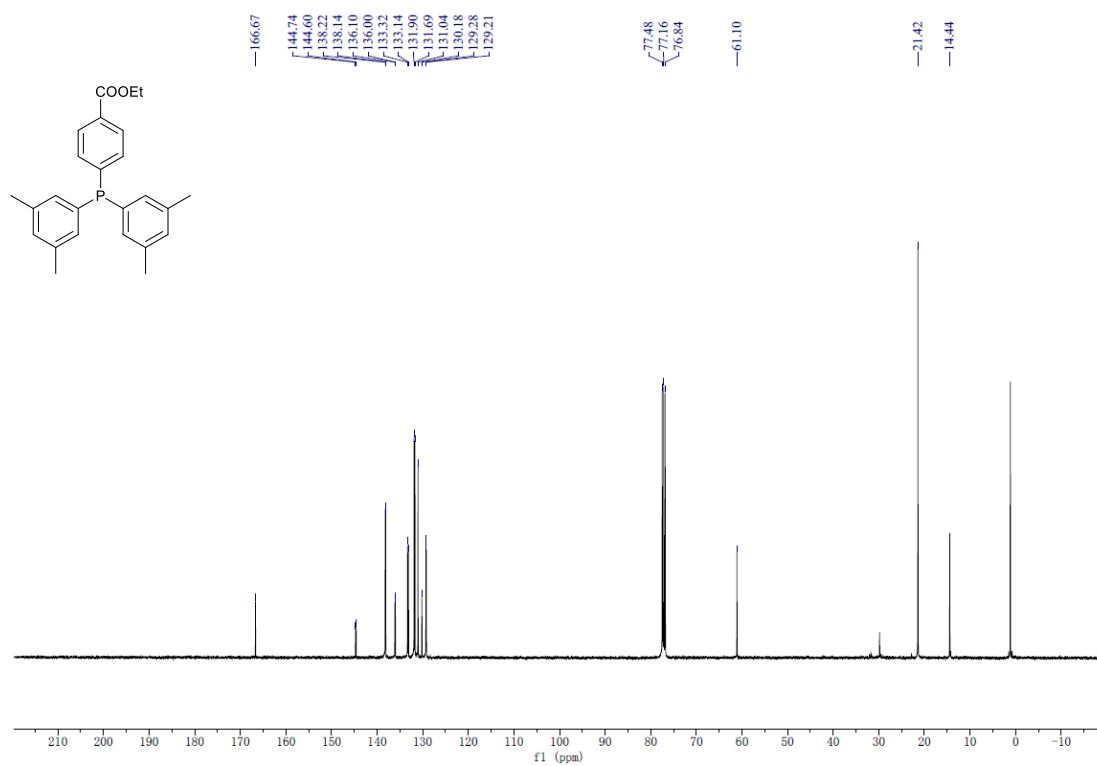
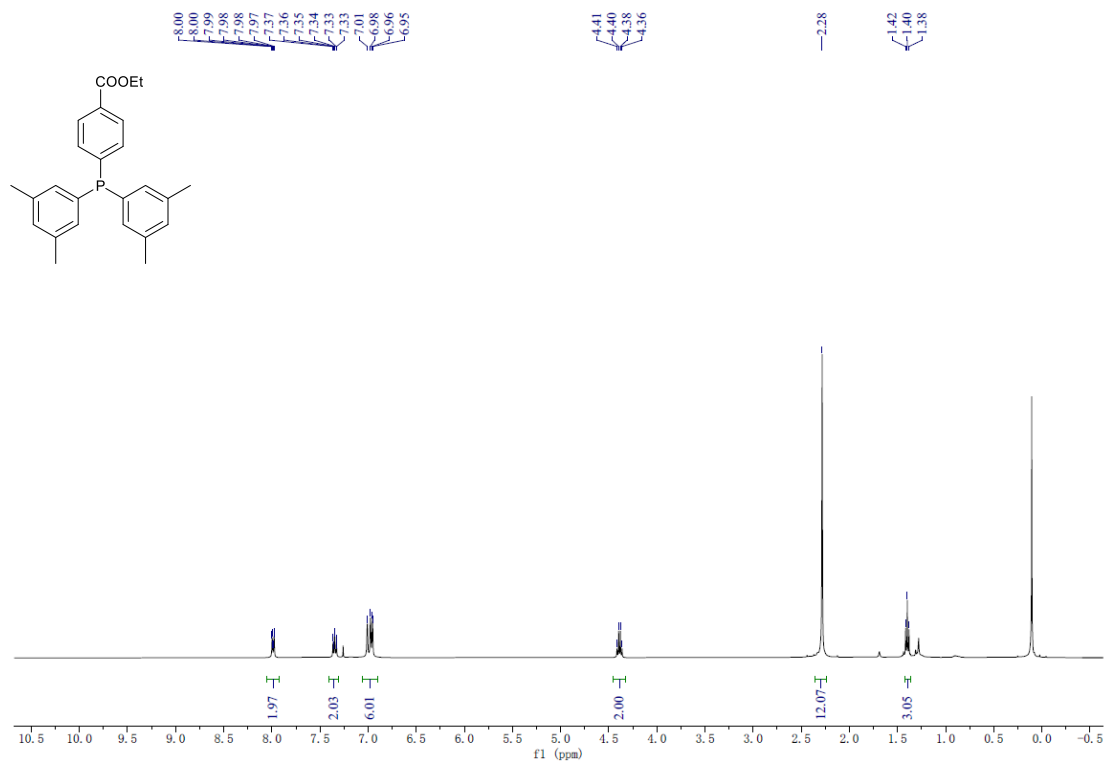
Colorless oil, 69% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (dd,  $J = 8.3, 1.8$  Hz, 2H), 7.63 (dd,  $J = 4.9, 1.1$  Hz, 2H), 7.43 (ddd,  $J = 6.7, 3.6, 1.1$  Hz, 2H), 7.40 – 7.35 (m, 2H), 7.16 – 7.09 (m, 2H), 4.37 (q,  $J = 7.1$  Hz, 2H), 1.38 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.41, 145.46 (d,  $J = 8.8$  Hz), 137.16 (d,  $J = 24.2$  Hz), 137.09 (d,  $J = 29.4$  Hz), 132.85, 131.51 (d,  $J = 18.4$  Hz), 130.44, 129.21 (d,  $J = 6.3$  Hz), 128.12 (d,  $J = 9.1$  Hz), 61.13, 14.41. HRMS (EI): exact mass calculated for  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{PS}_2$   $[\text{M}]^+$  require  $m/z = 346.0251$ , found  $m/z = 346.0252$ .

## V. References

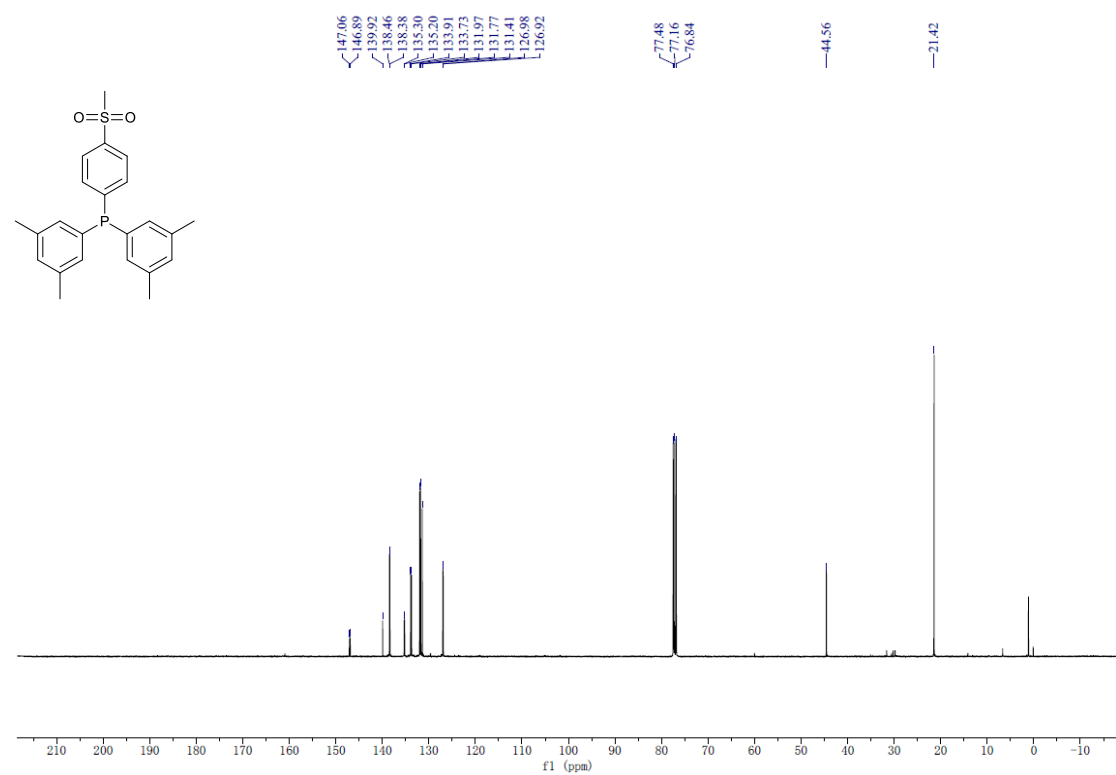
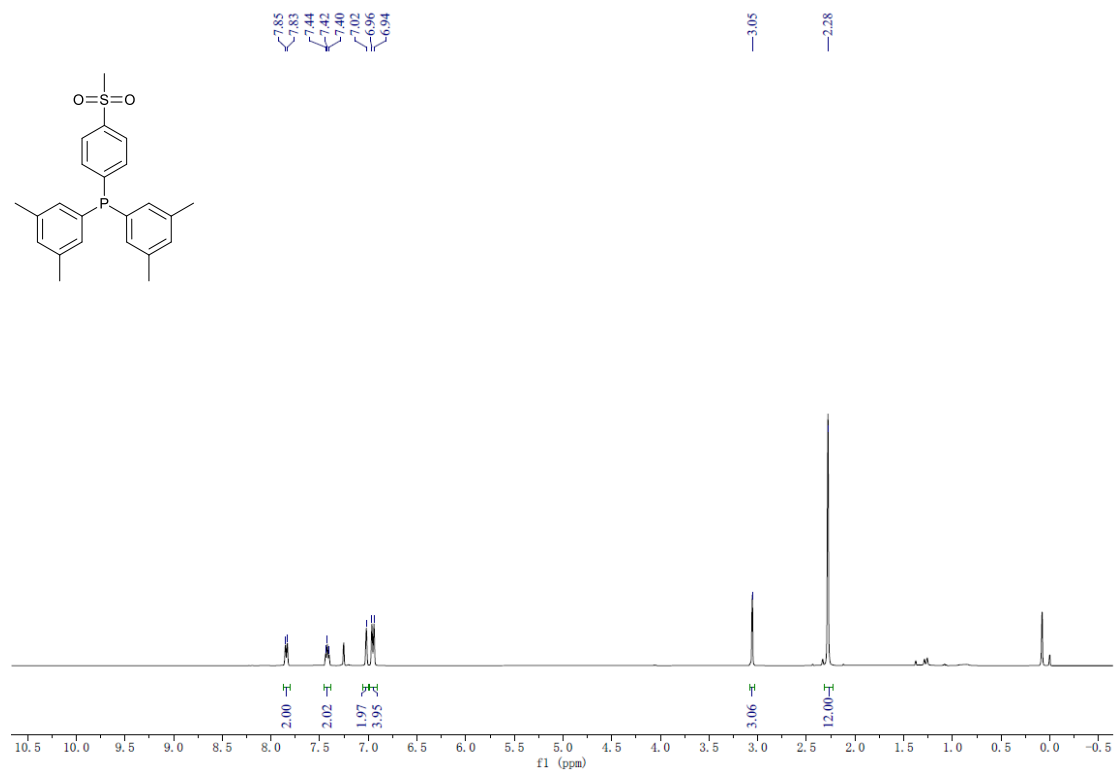
- 1 R. Shen, B. Luo, J. Yang, L. Zhang and L.-B. Han, *Chem. Commun.*, 2016, **52**, 6451-6454.
- 2 D.-Y. Wang, M. Kawahata, Z.-K. Yang, K. Miyamoto, S. Komagawa, K. Yamaguchi, C. Wang and M. Uchiyama, *Nat. Commun.*, 2016, **7**, 12937.

## VI. NMR spectra

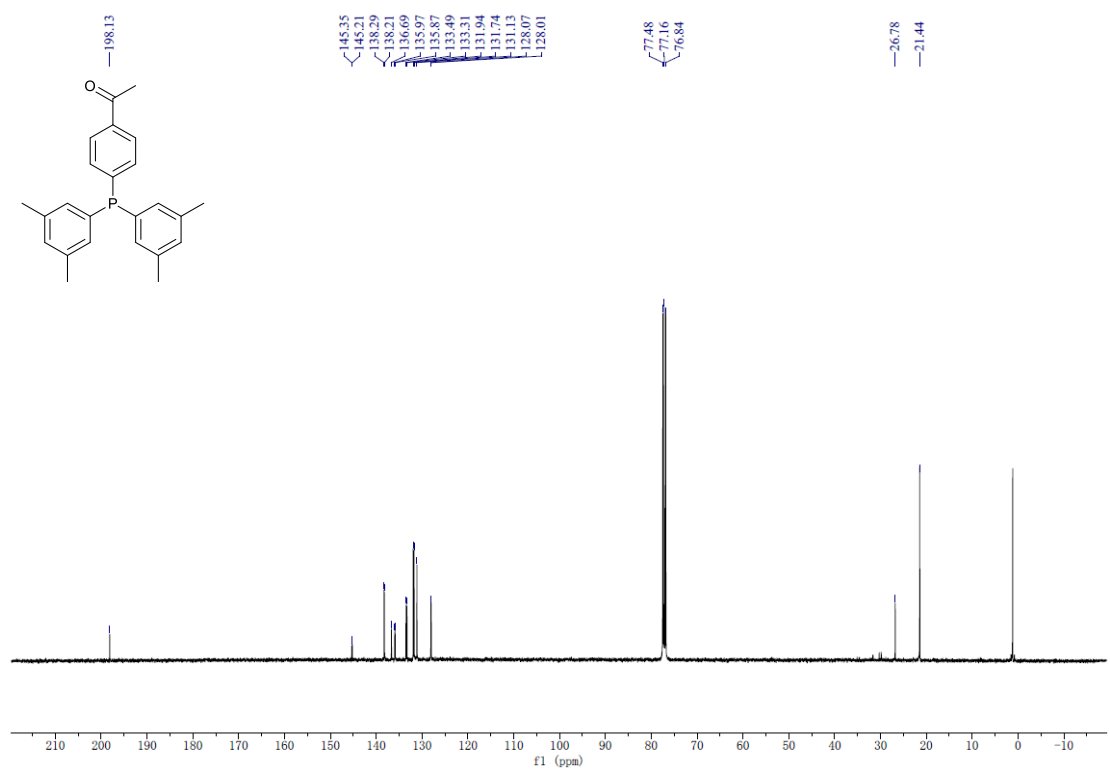
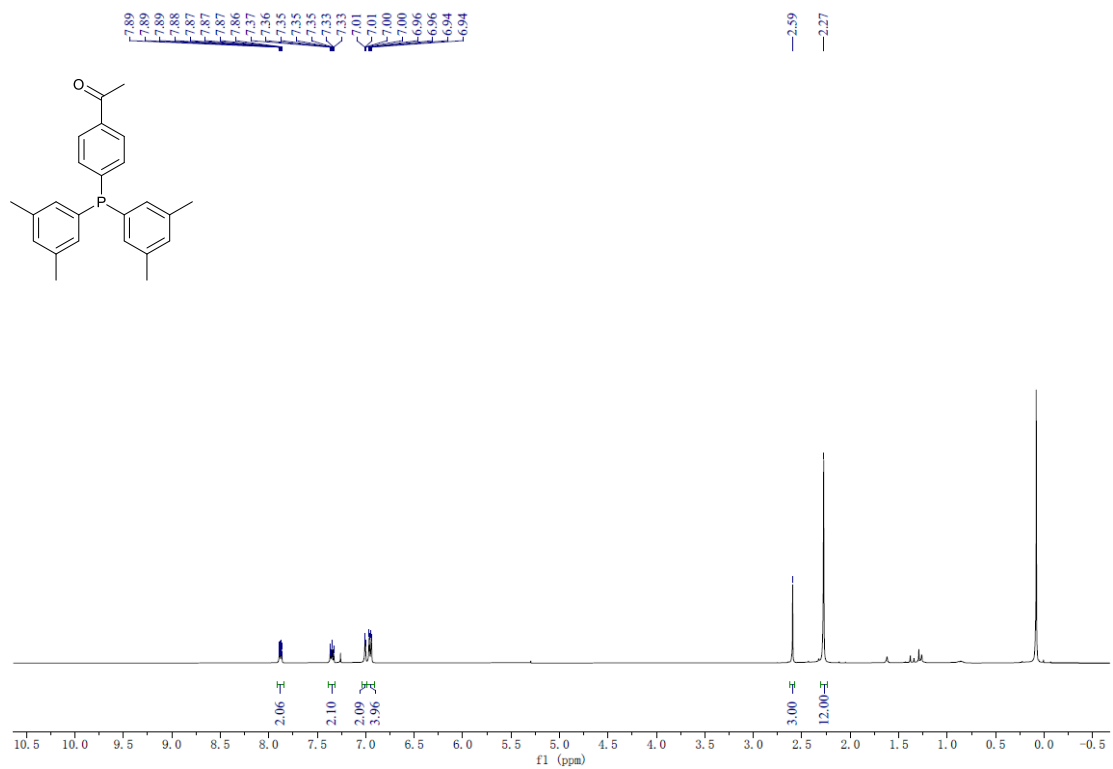
### ethyl 4-(bis(3,5-dimethylphenyl)phosphanyl)benzoate (3aa)



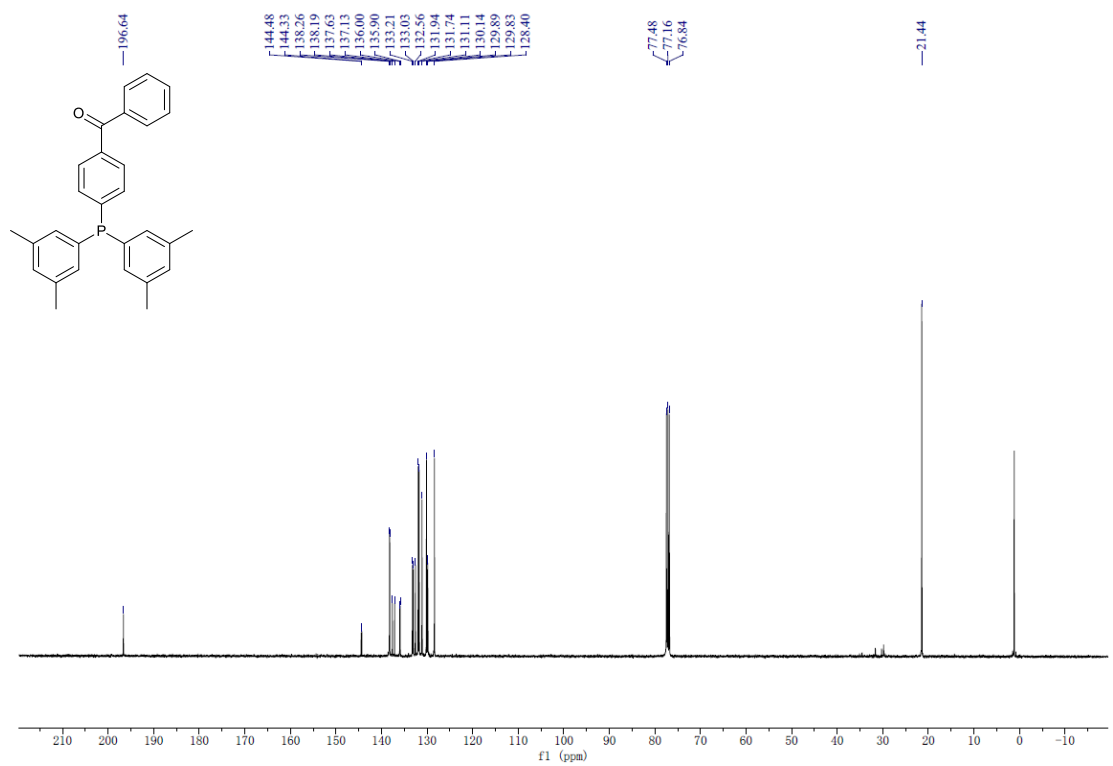
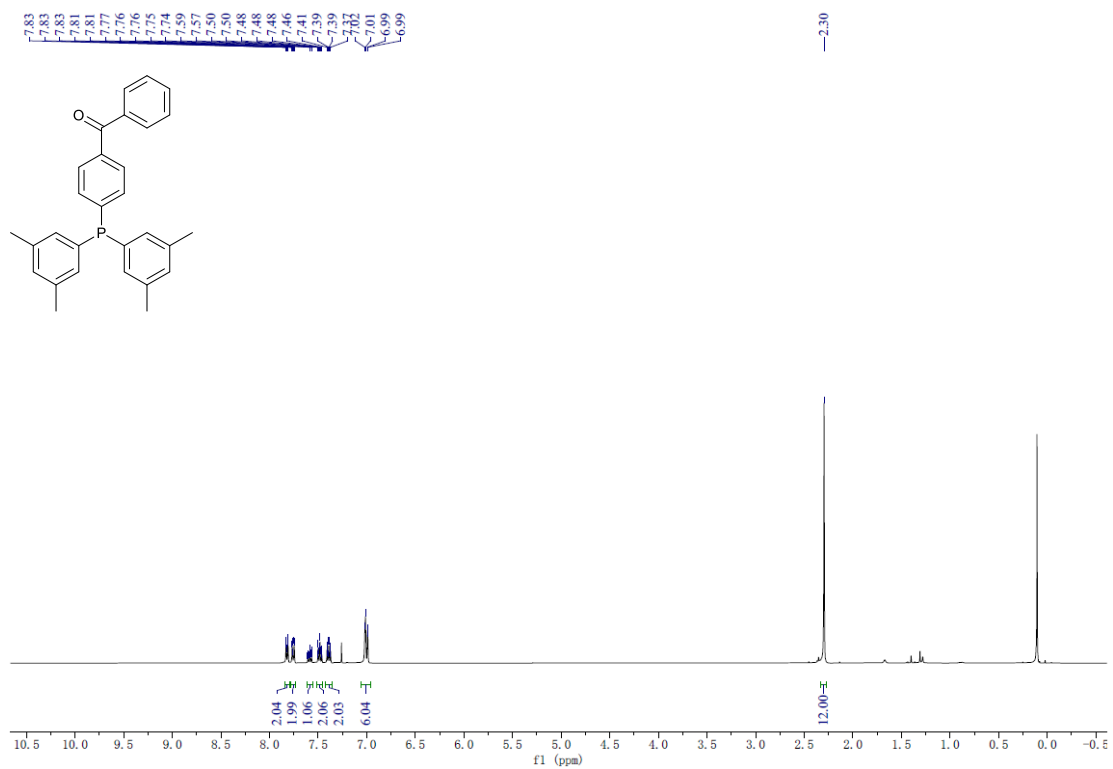
# bis(3,5-dimethylphenyl)(4-(methylsulfonyl)phenyl)phosphane (3ab)



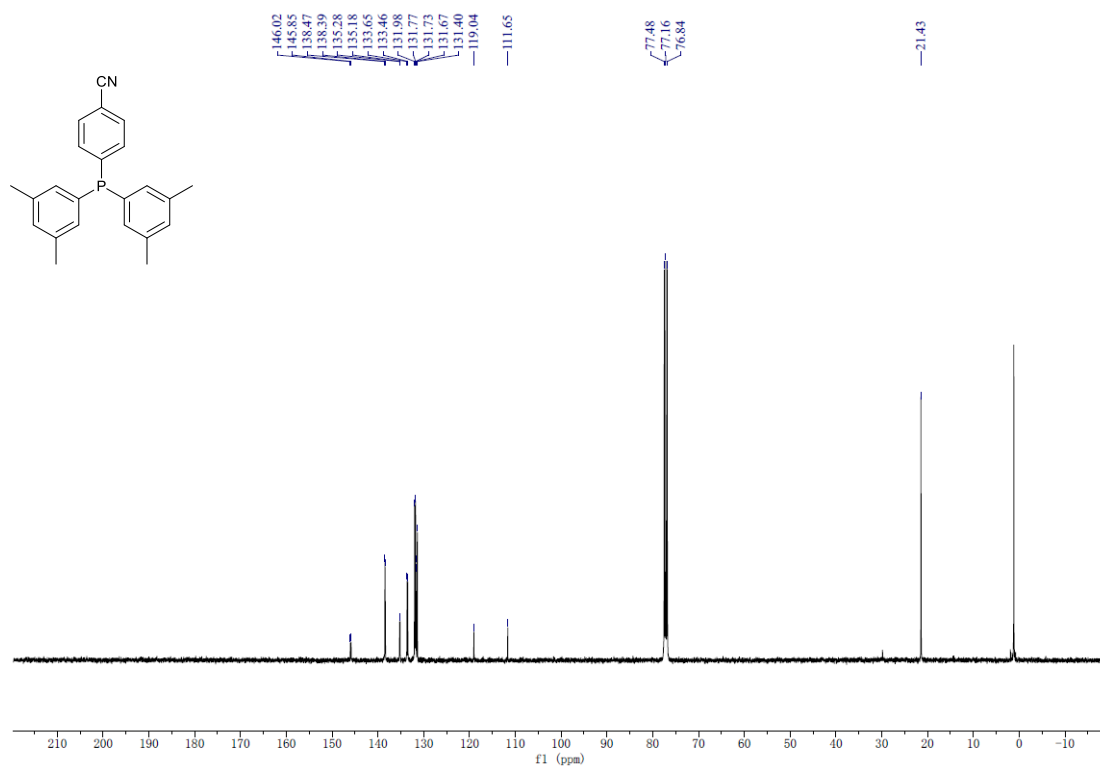
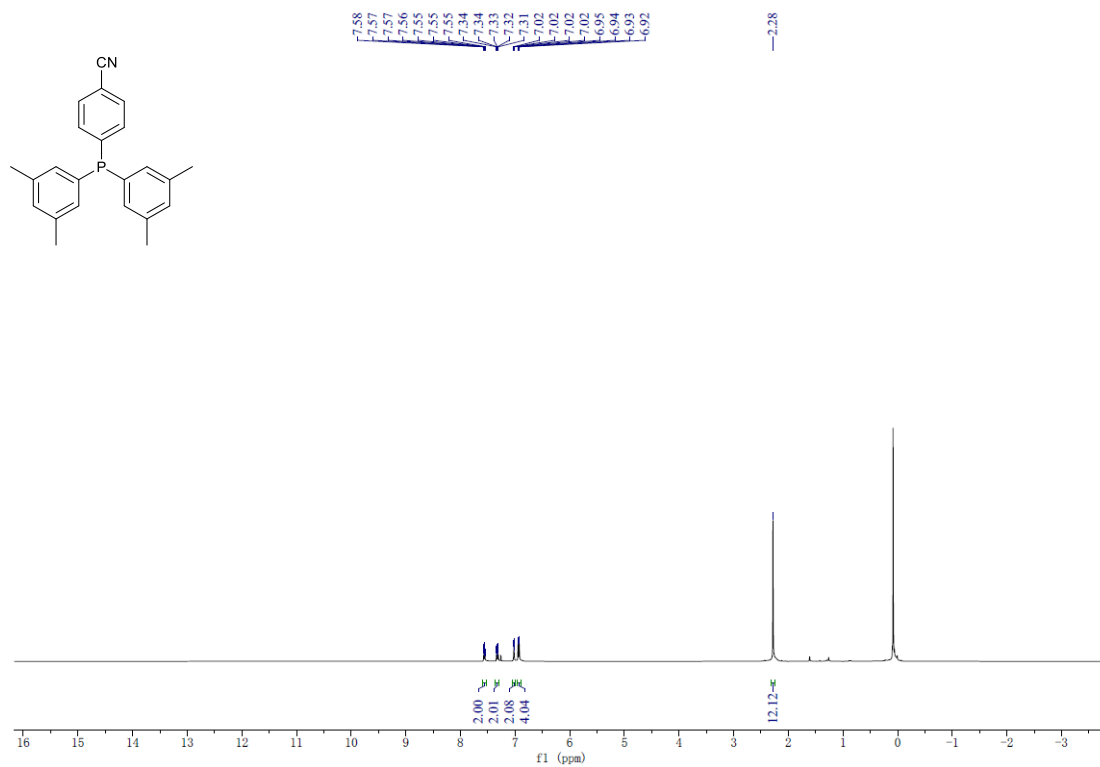
# 1-(4-(bis(3,5-dimethylphenyl)phosphanyl)phenyl)ethan-1-one (3ac)



# (4-(bis(3,5-dimethylphenyl)phosphanyl)phenyl)(phenyl)methanone (3ad)

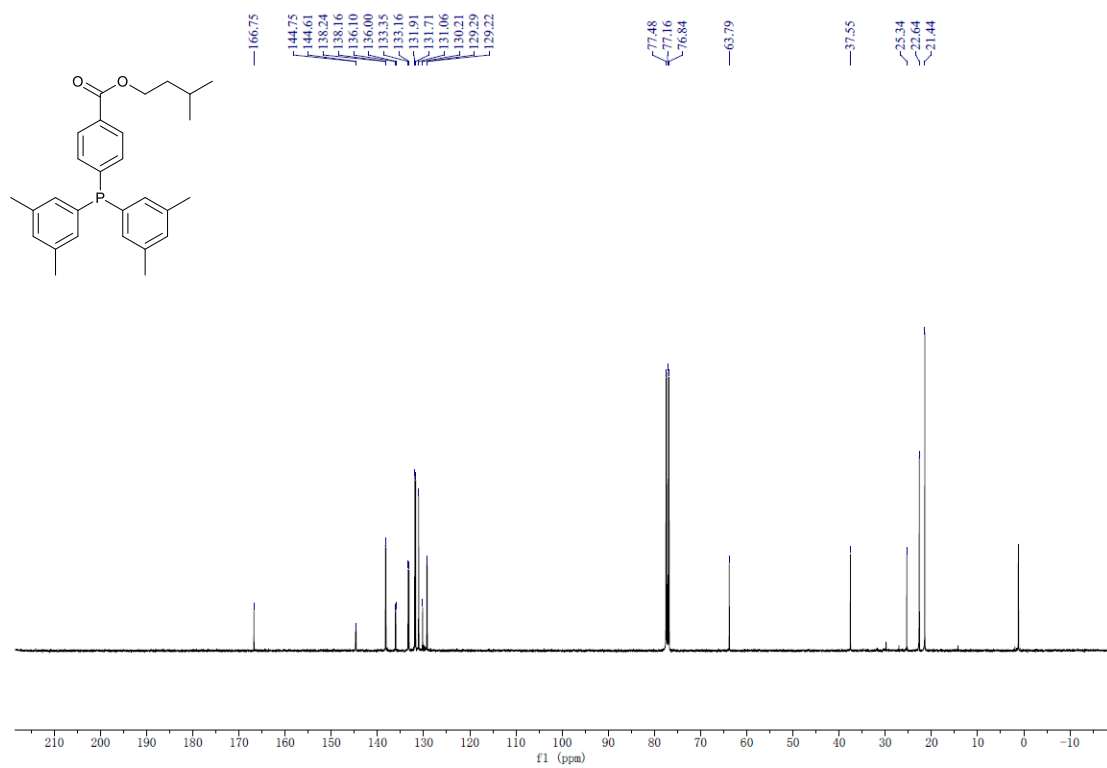
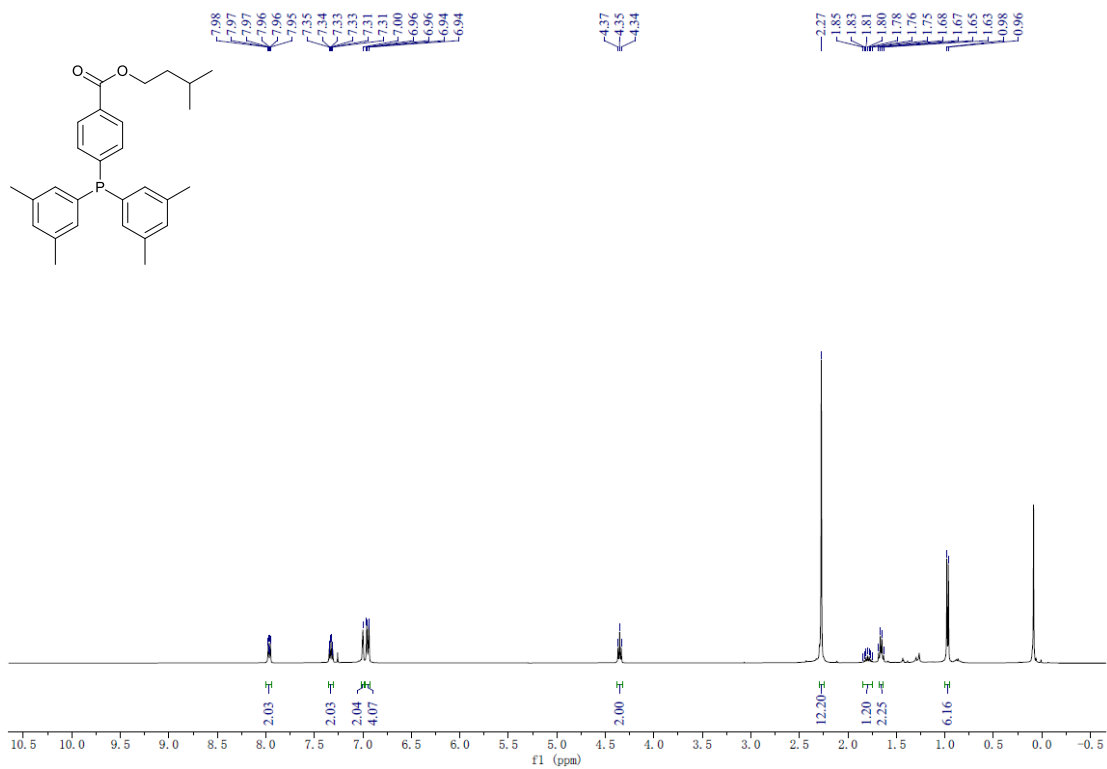


# 4-(bis(3,5-dimethylphenyl)phosphanyl)benzonitrile (3ae)

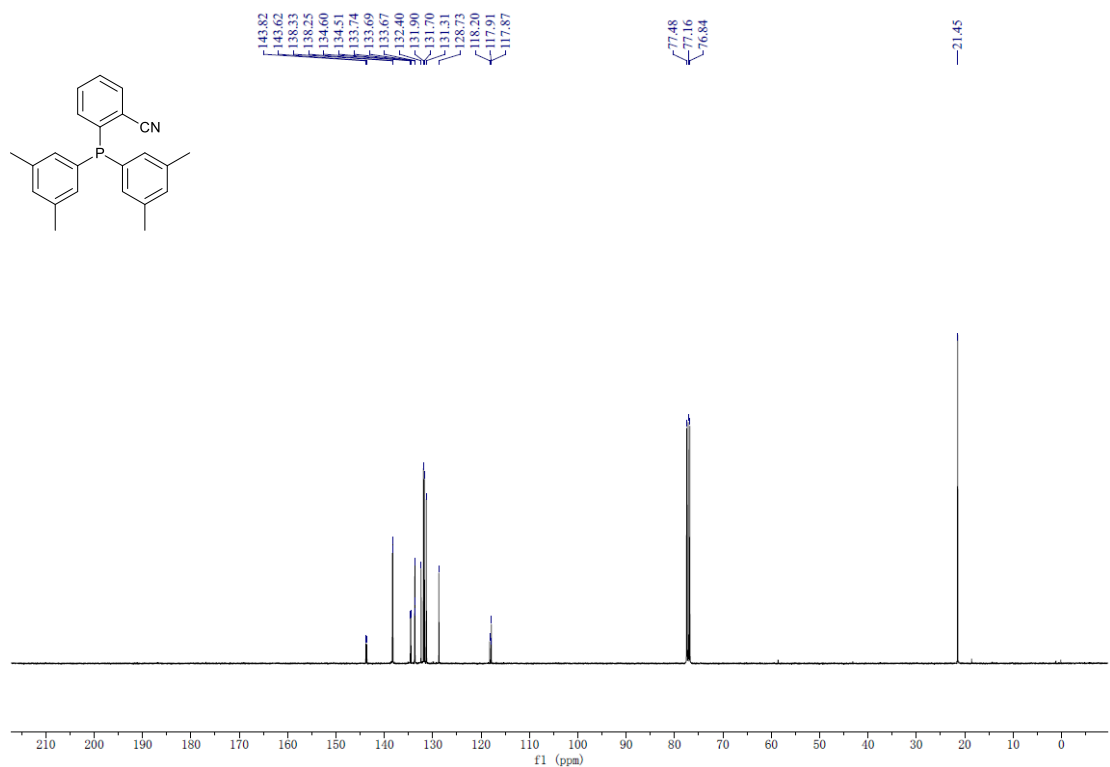
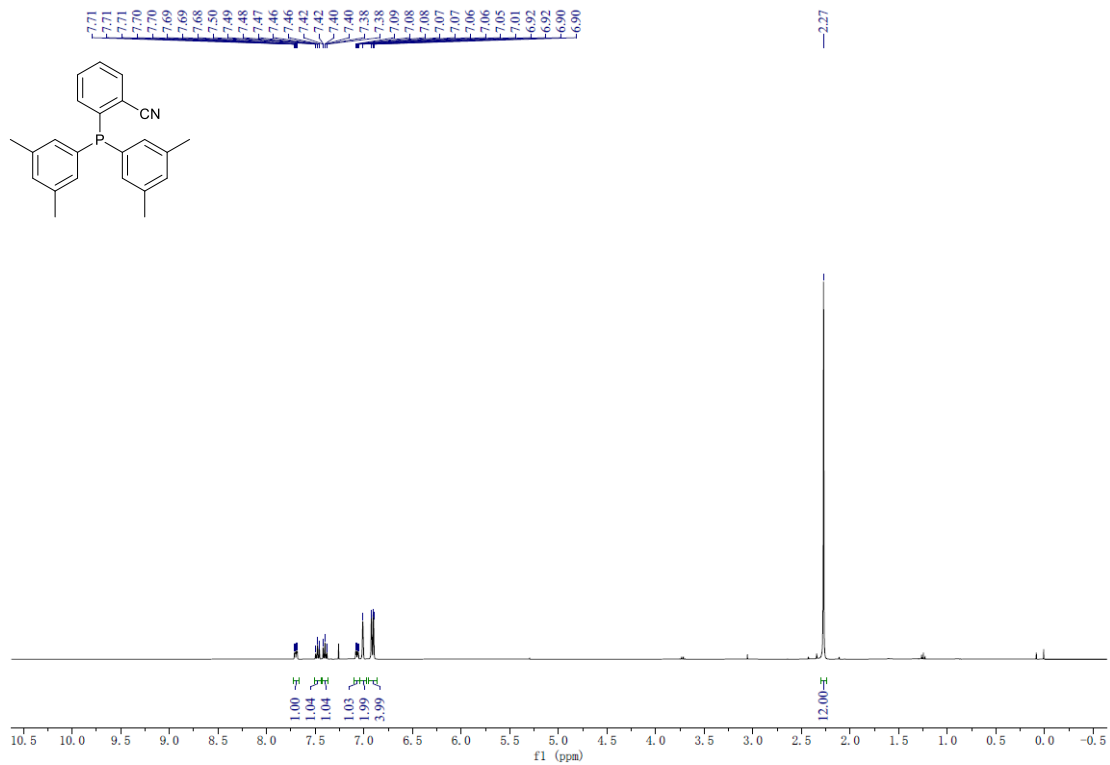




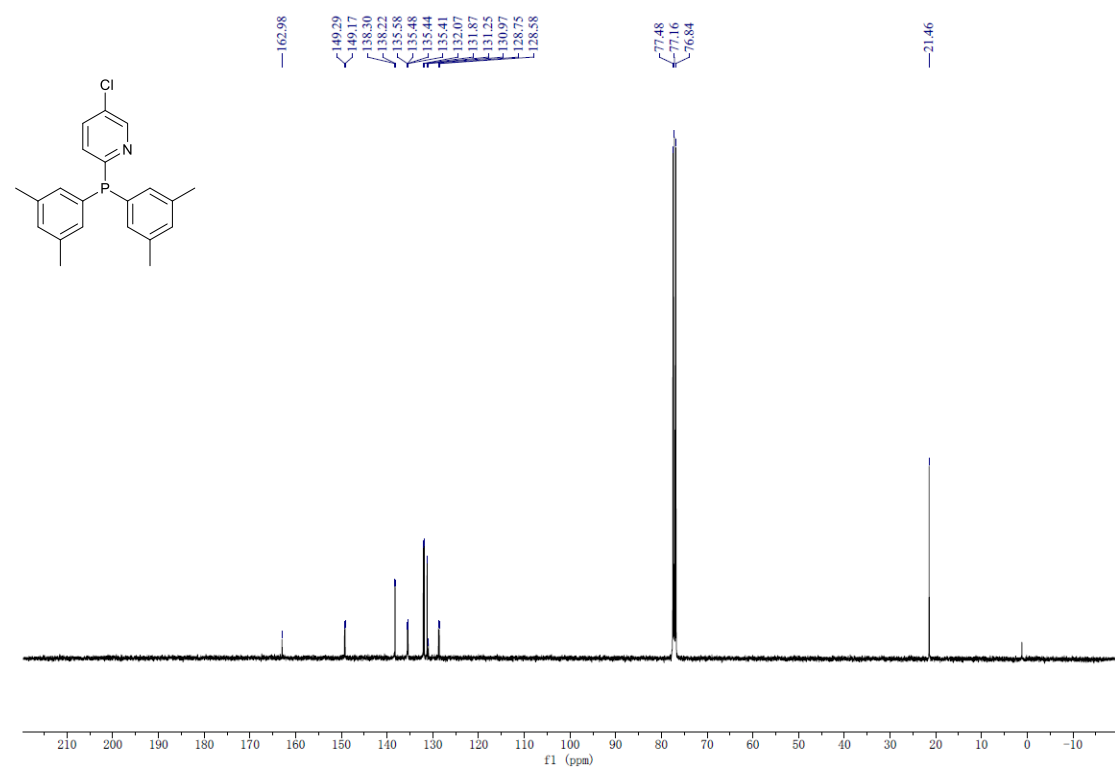
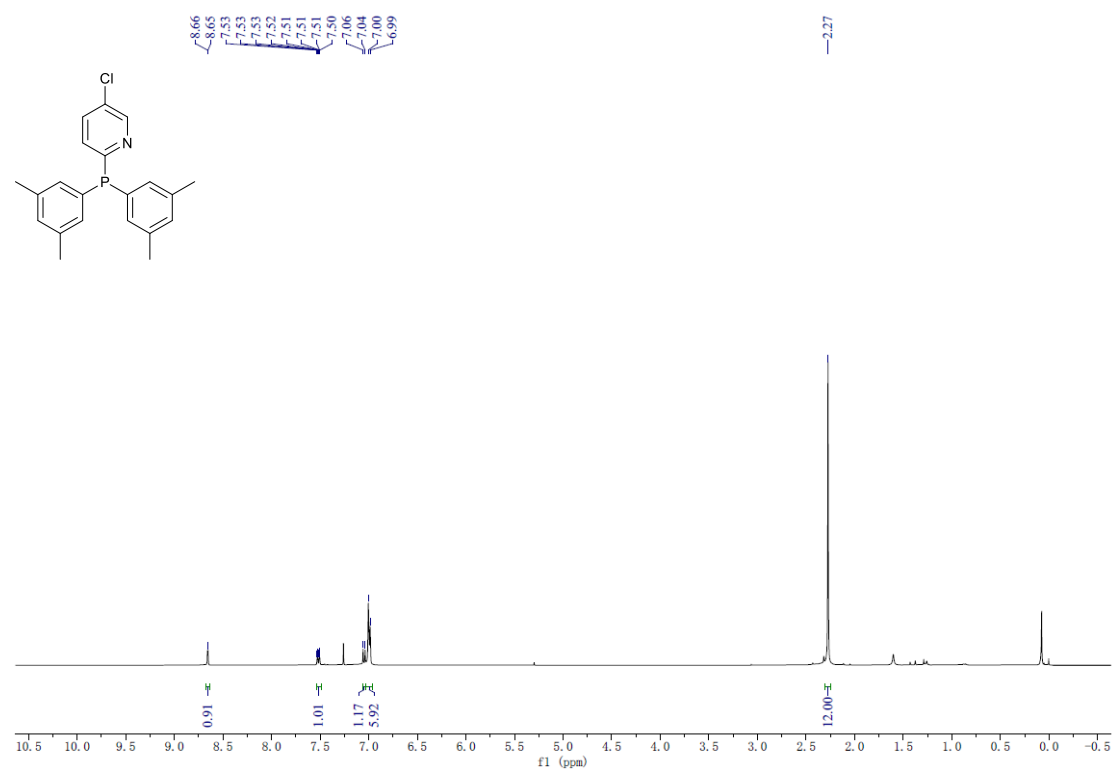
isopentyl 4-(bis(3,5-dimethylphenyl)phosphanyl)benzoate (3af)



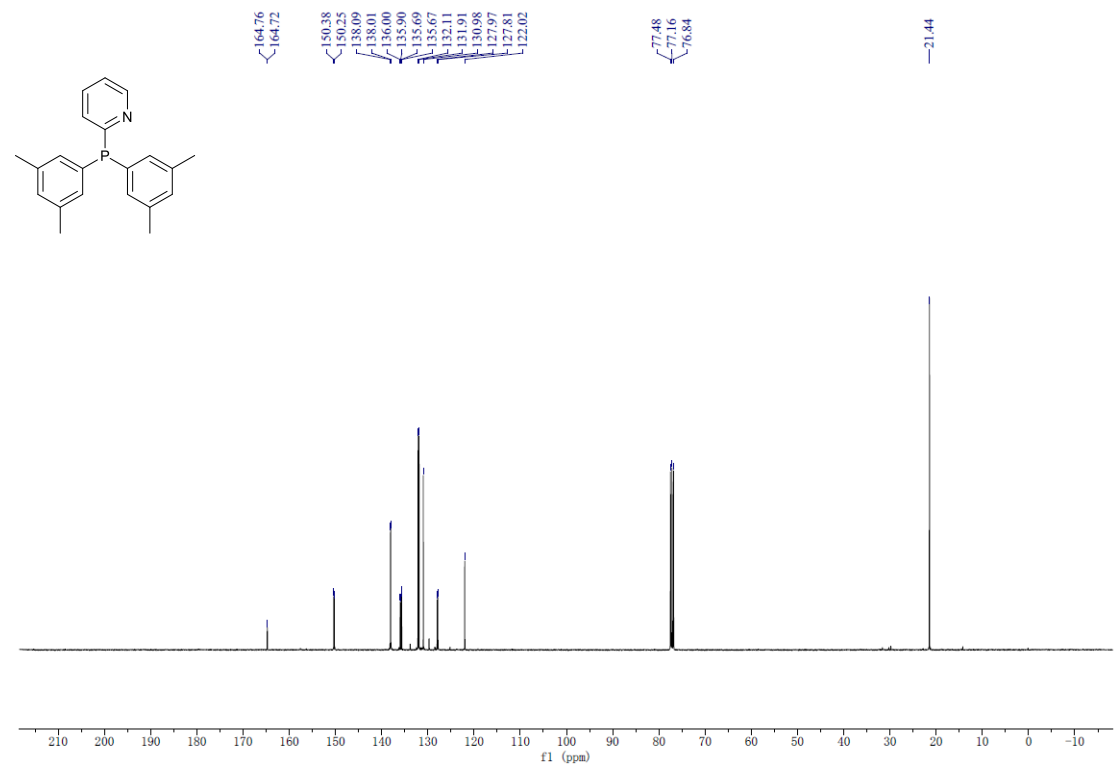
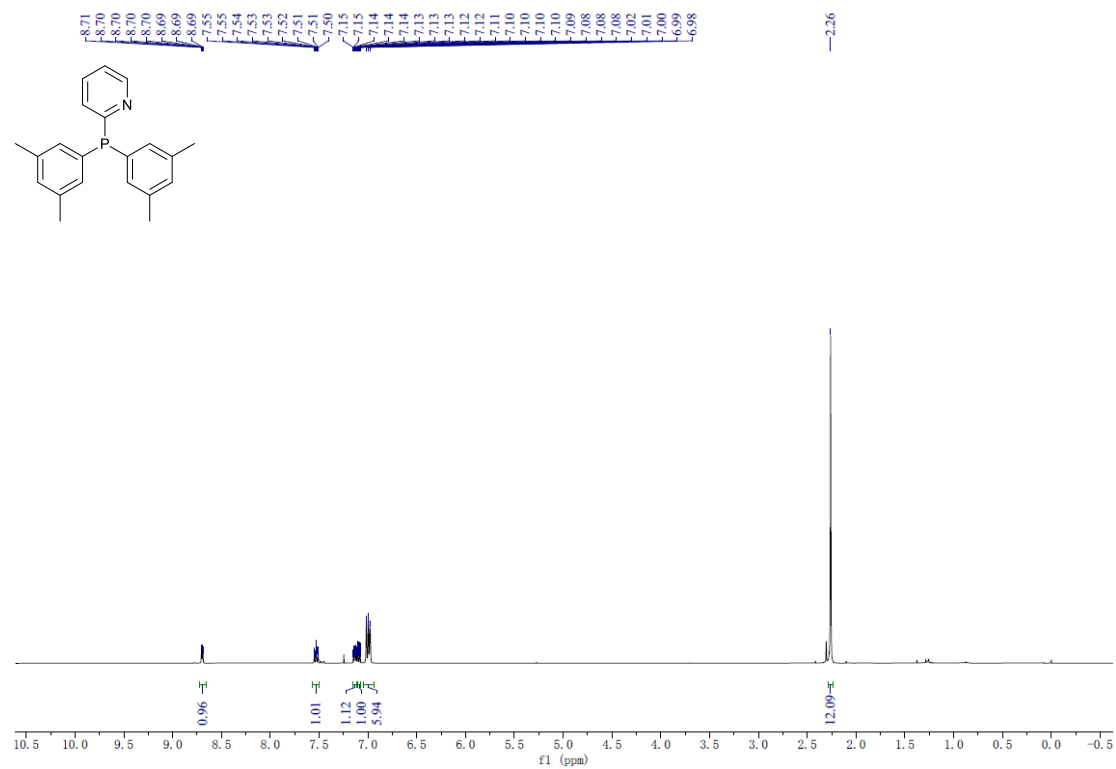
## 2-(bis(3,5-dimethylphenyl)phosphanyl)benzonitrile (3ag)



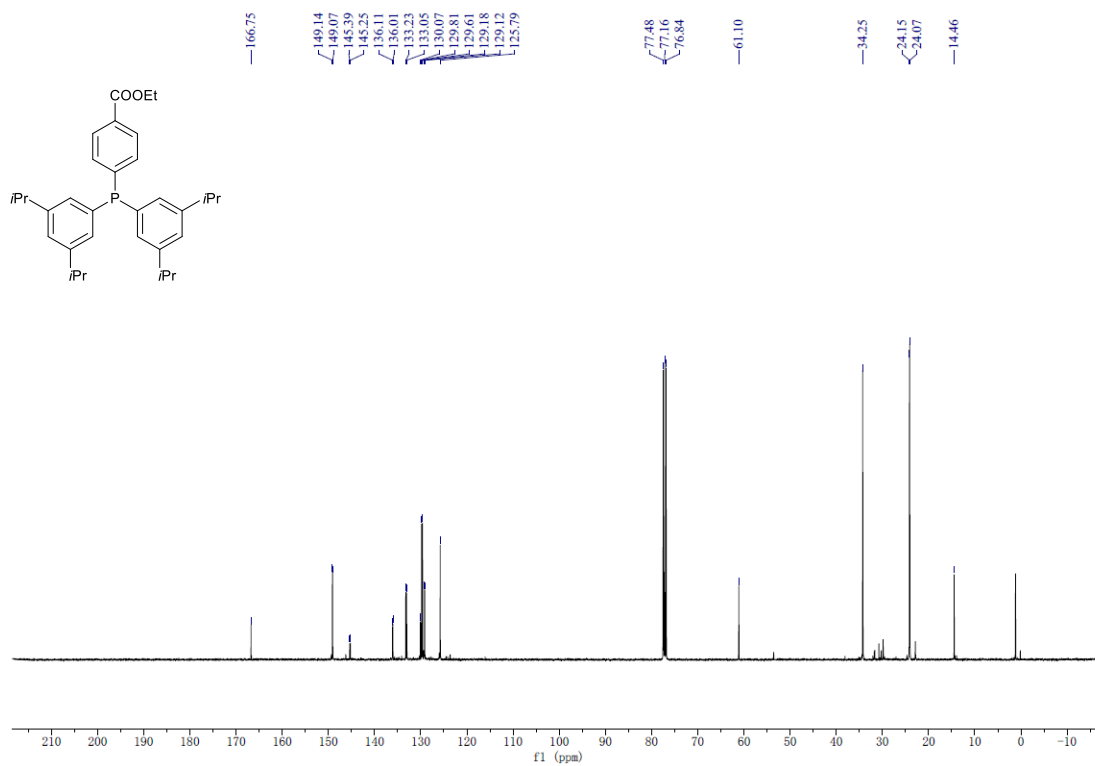
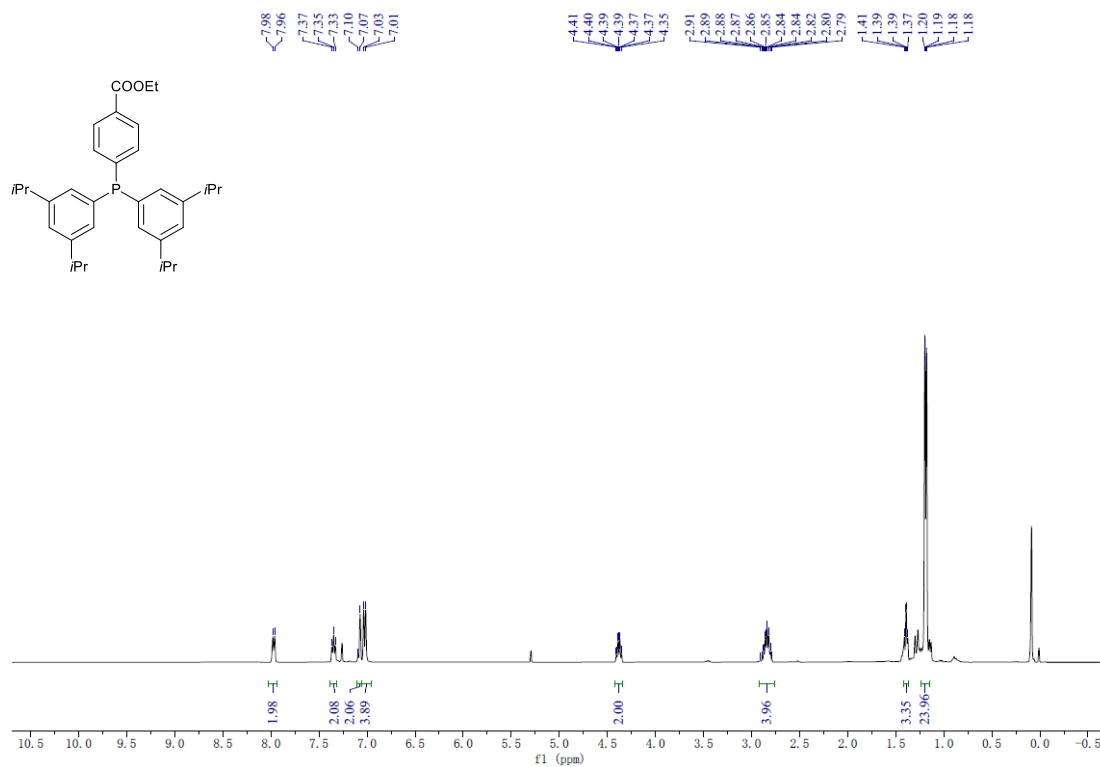
## 2-(bis(3,5-dimethylphenyl)phosphanyl)-5-chloropyridine (3ah)



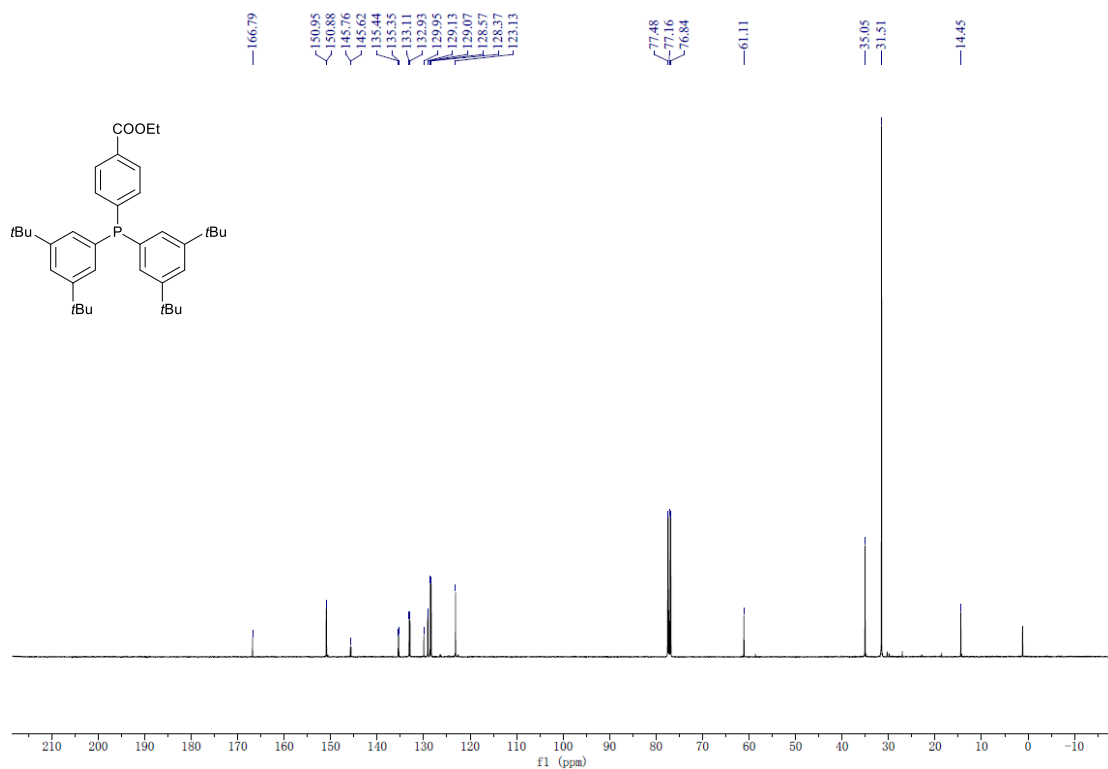
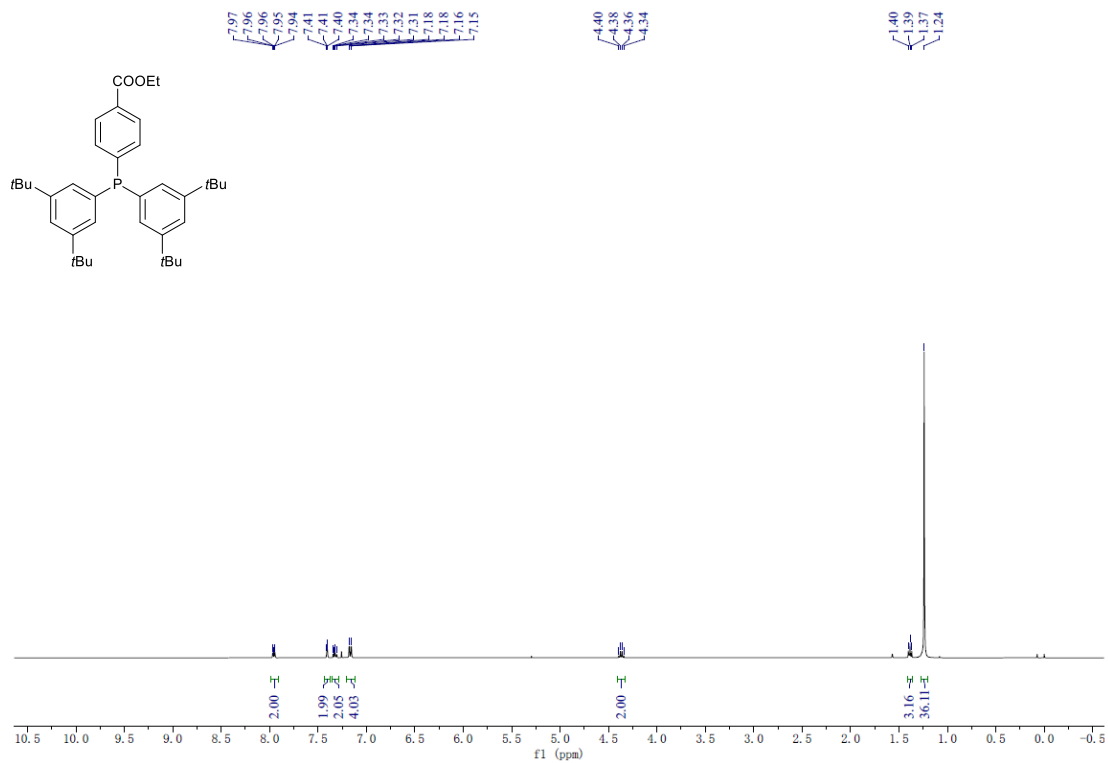
## 2-(bis(3,5-dimethylphenyl)phosphanyl)pyridine (3ai)



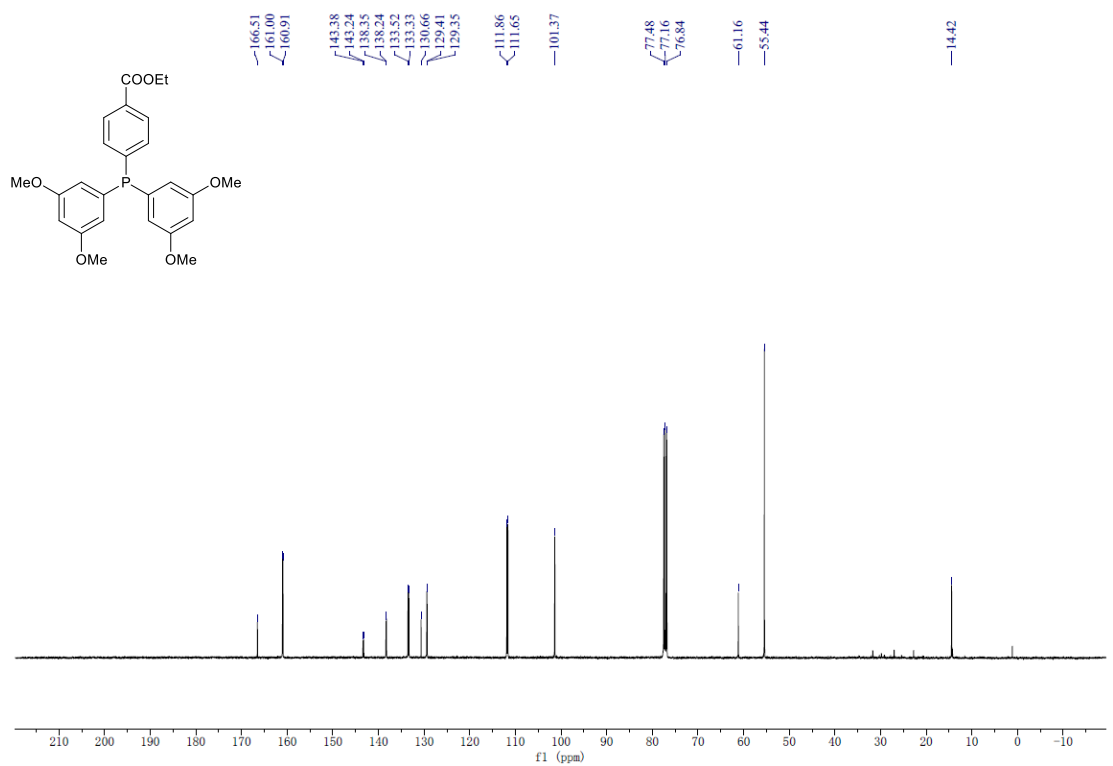
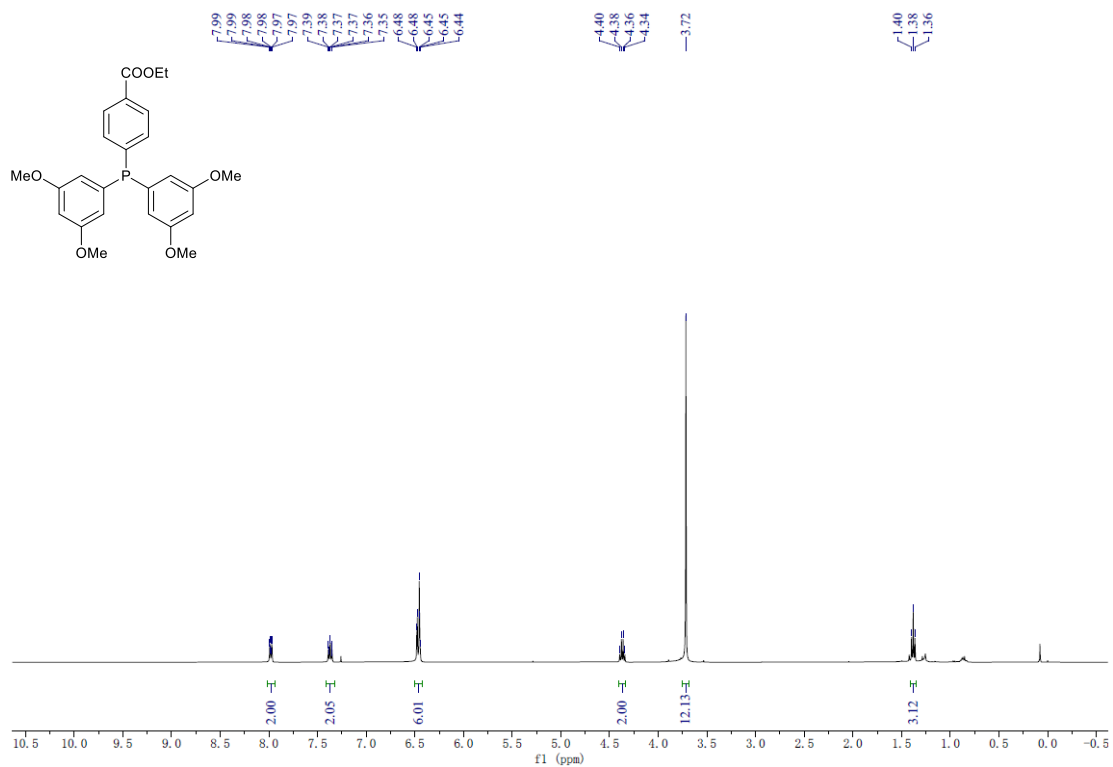
ethyl 4-(bis(3,5-diisopropylphenyl)phosphanyl)benzoate (3ba)



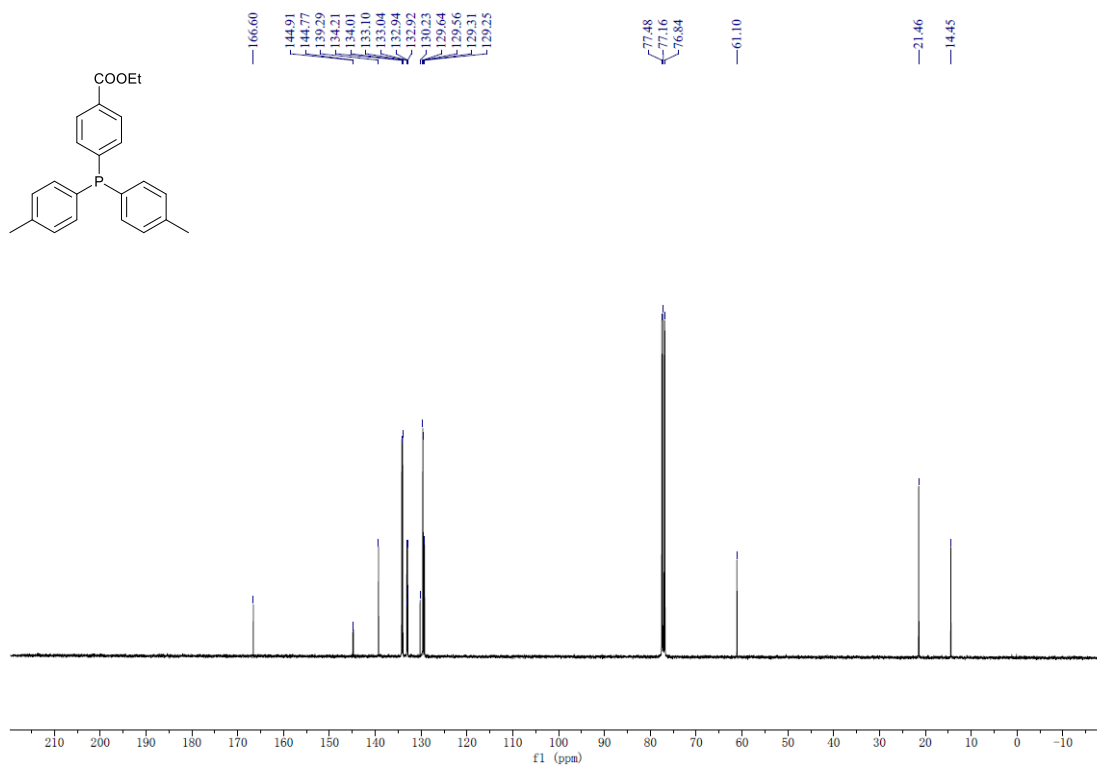
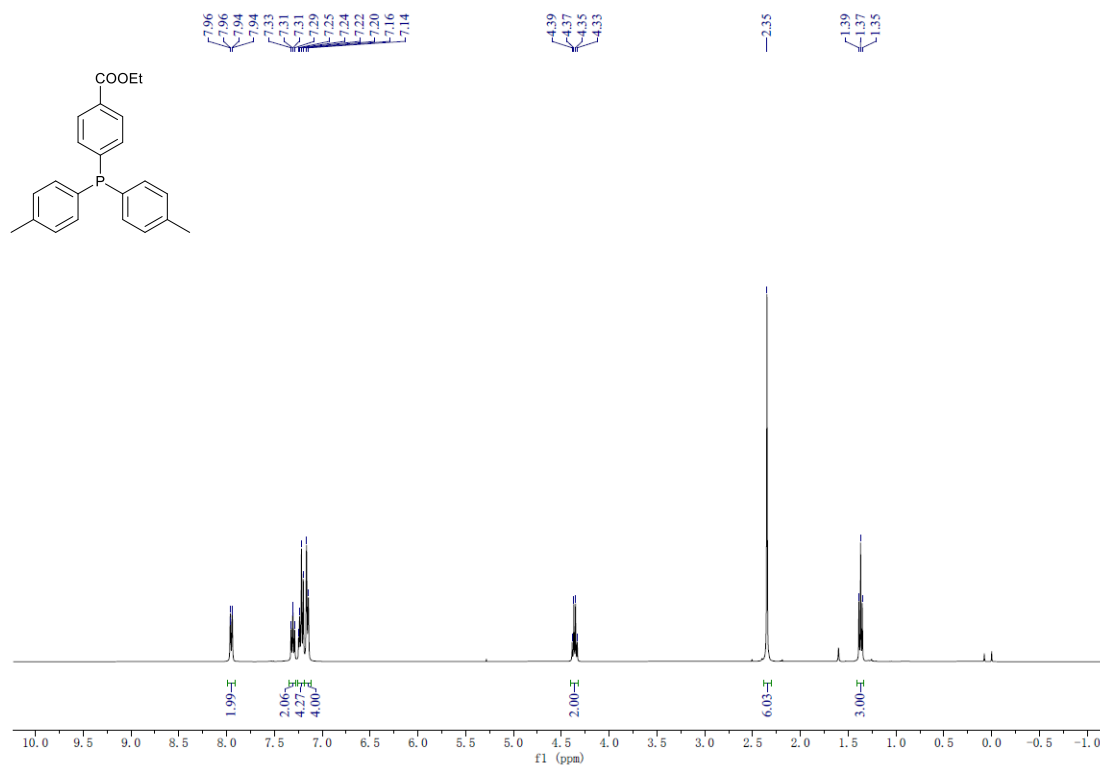
ethyl 4-(bis(3,5-di-tert-butylphenyl)phosphanyl)benzoate (3ca)



ethyl 4-(bis(3,5-dimethoxyphenyl)phosphanyl)benzoate (3da)

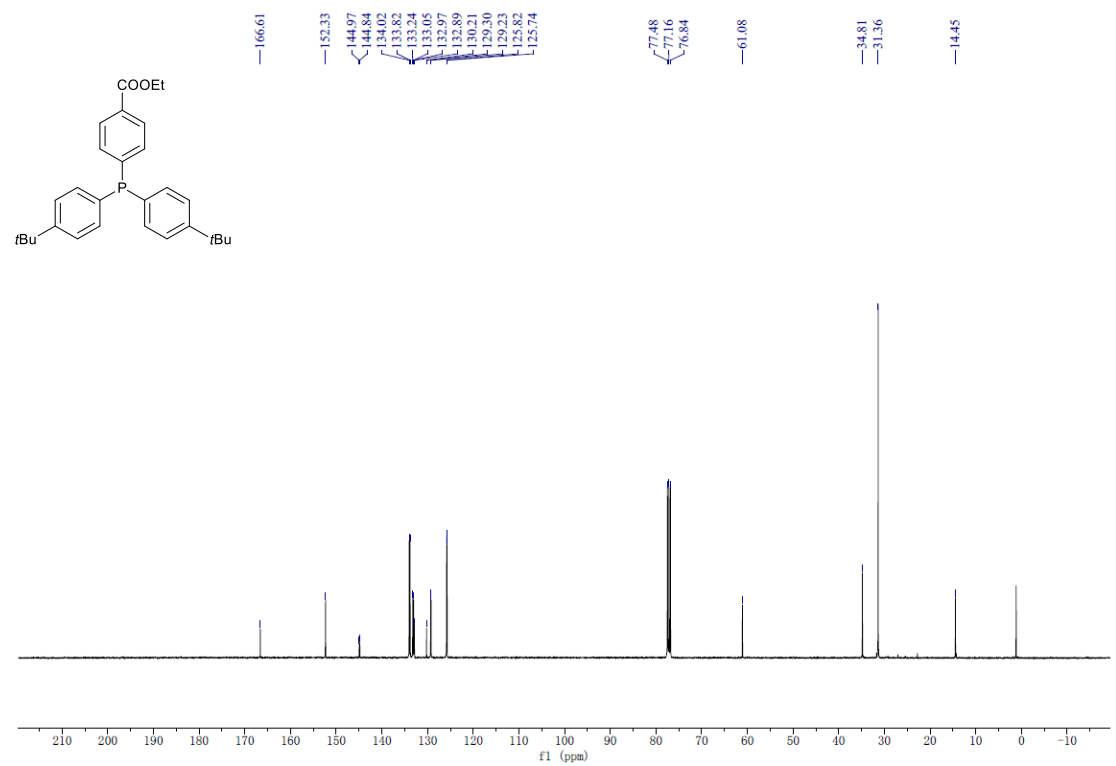
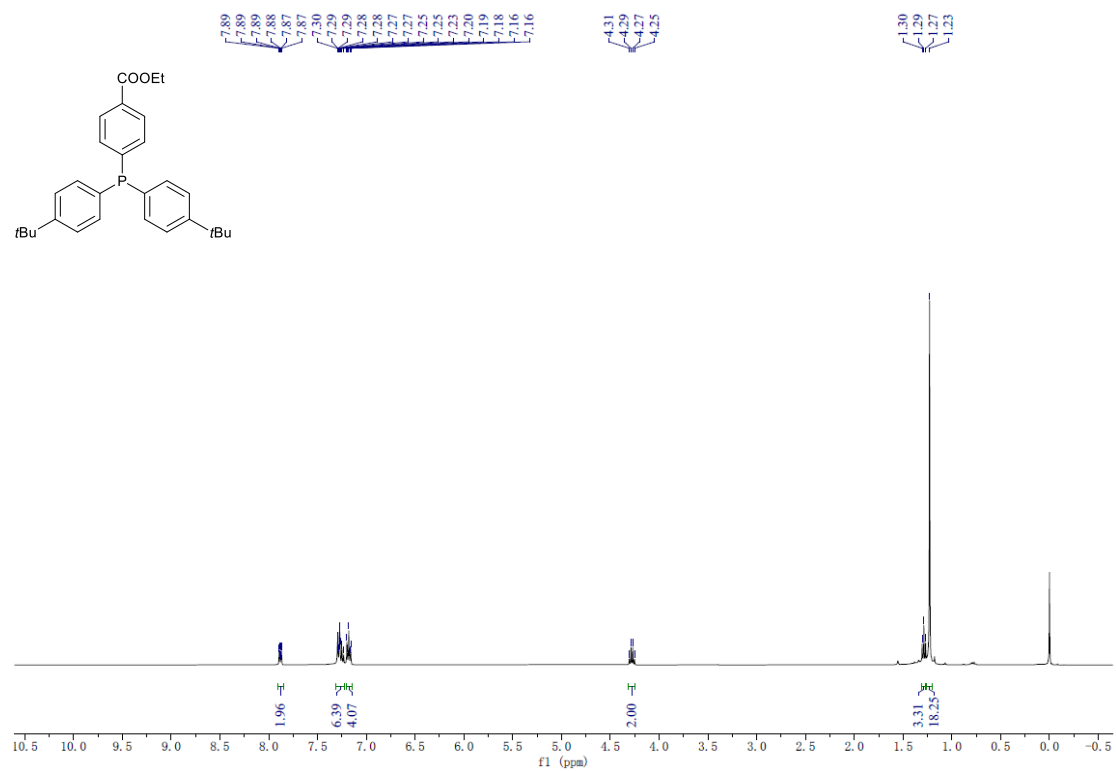


# ethyl 4-(di-p-tolylphosphanyl)benzoate (3ea)

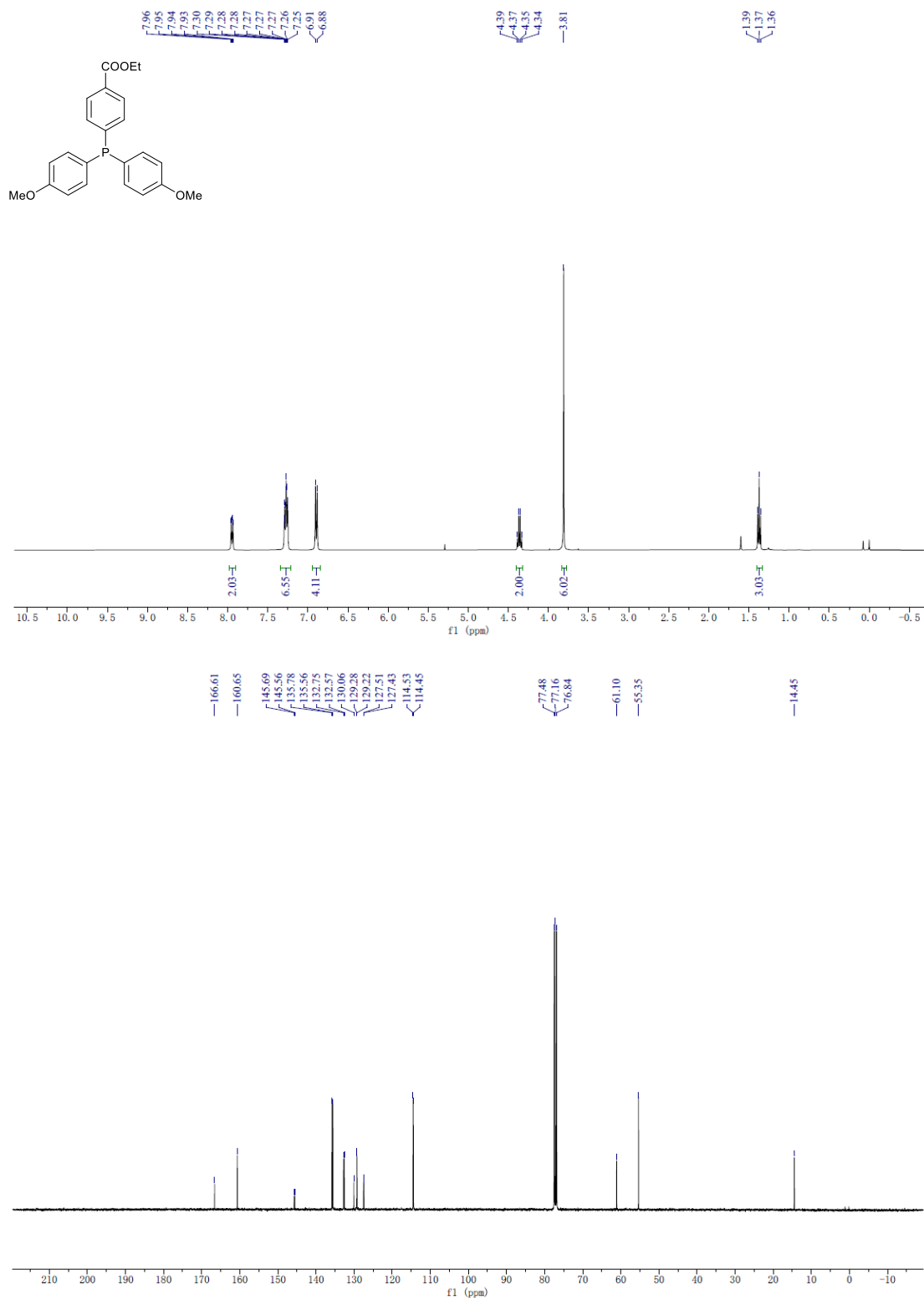




ethyl 4-(bis(4-(tert-butyl)phenyl)phosphanyl)benzoate (3fa)

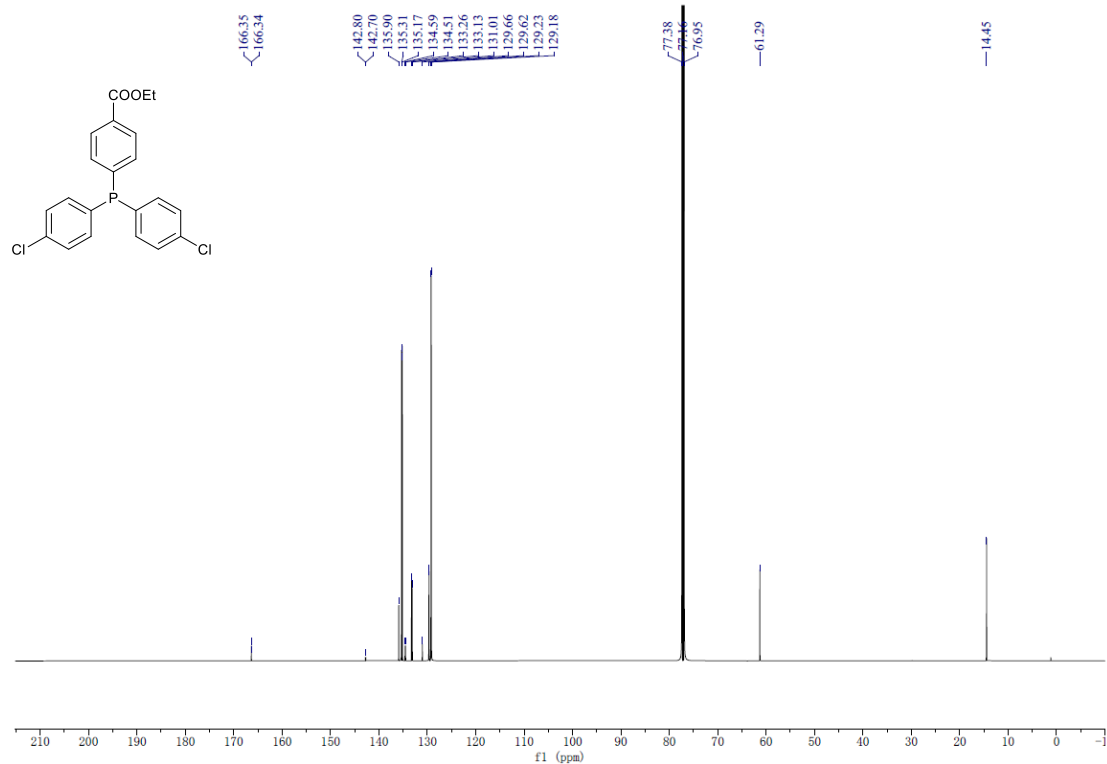
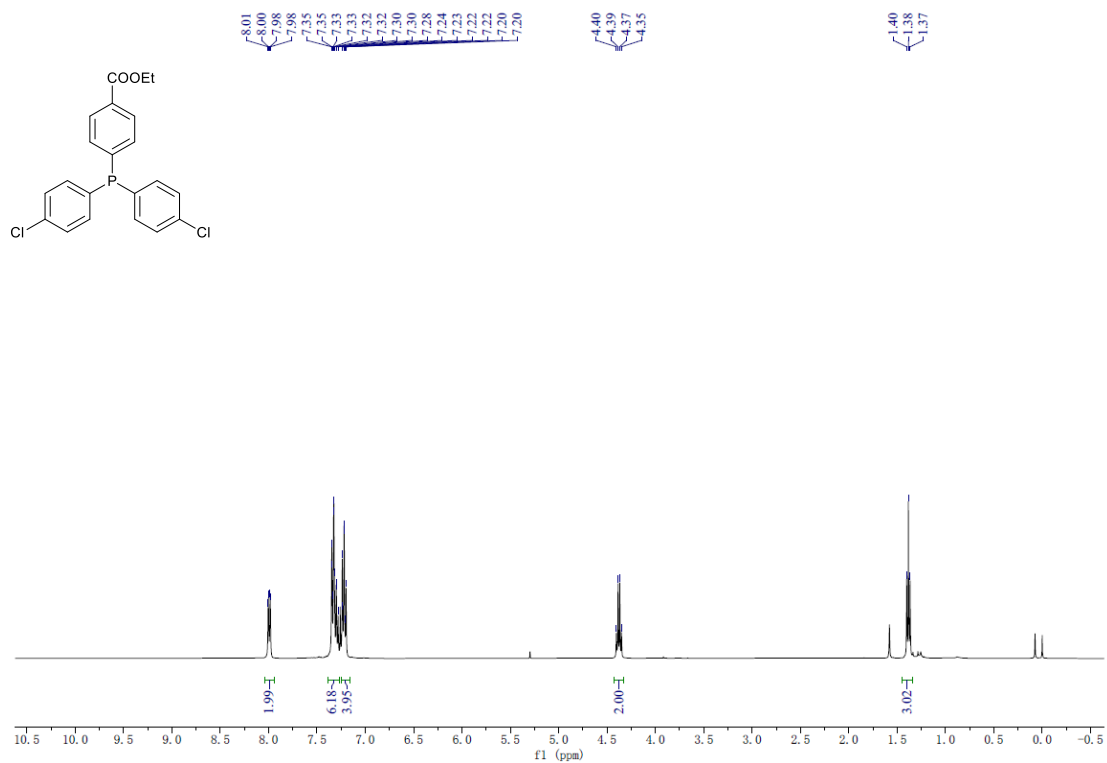


# ethyl 4-(bis(4-methoxyphenyl)phosphanyl)benzoate (3ga)

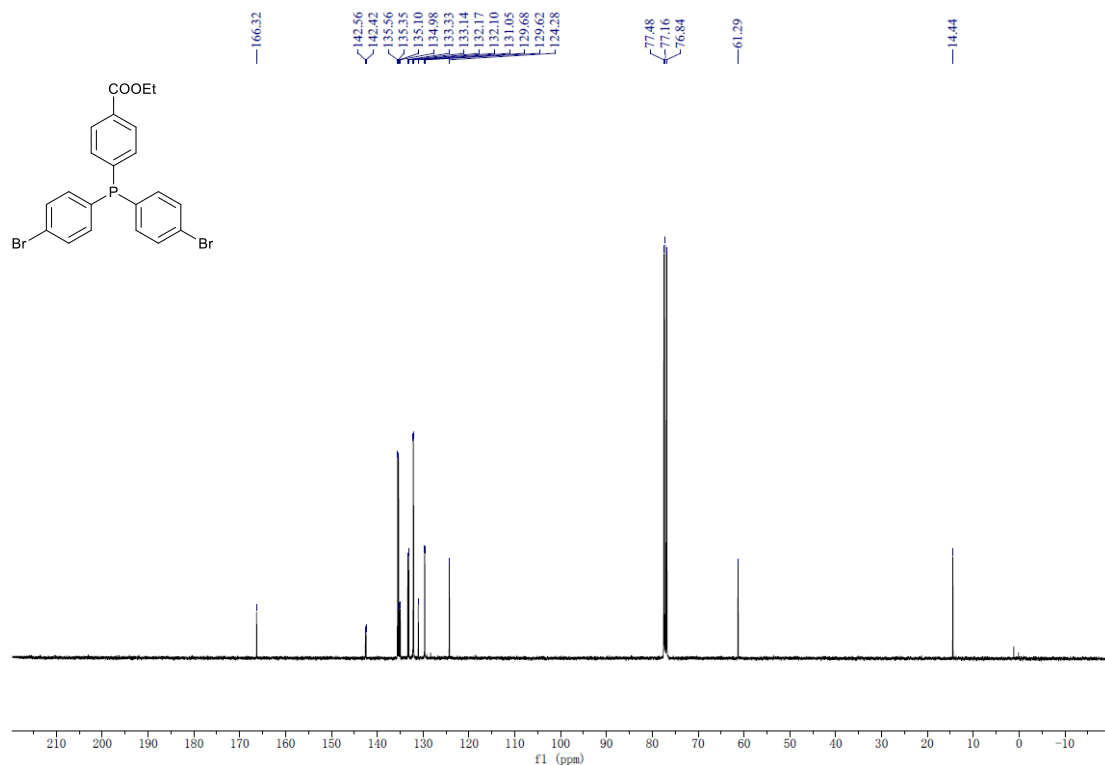
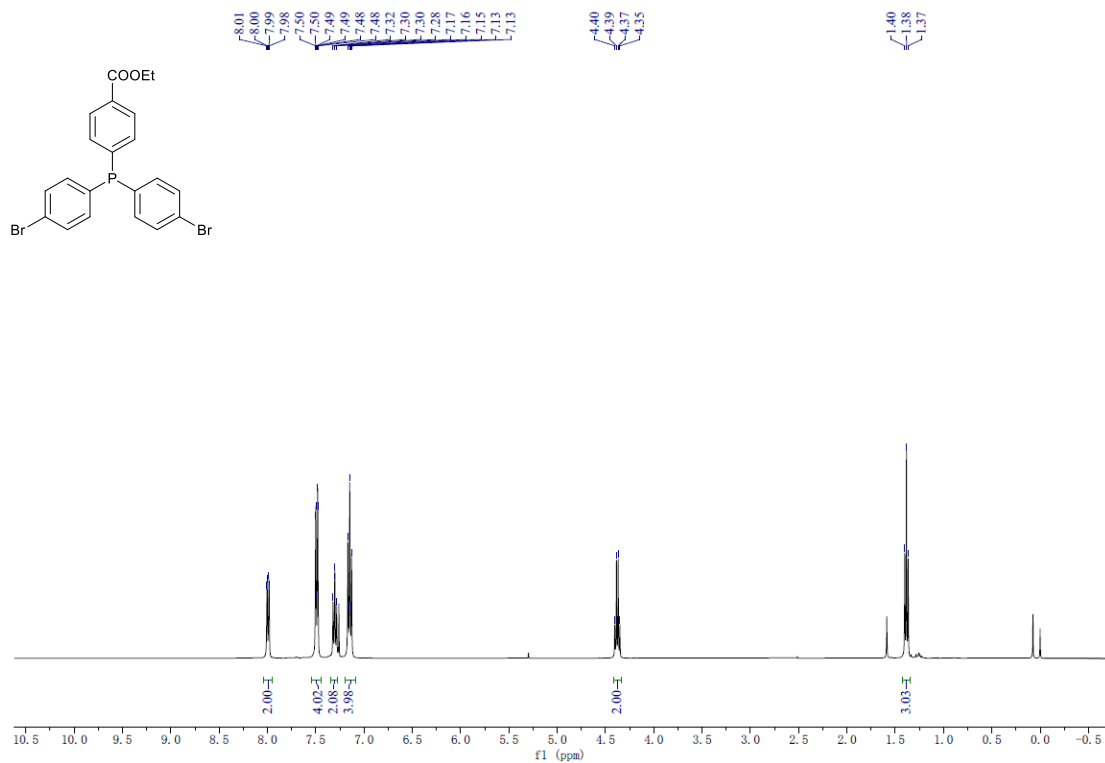




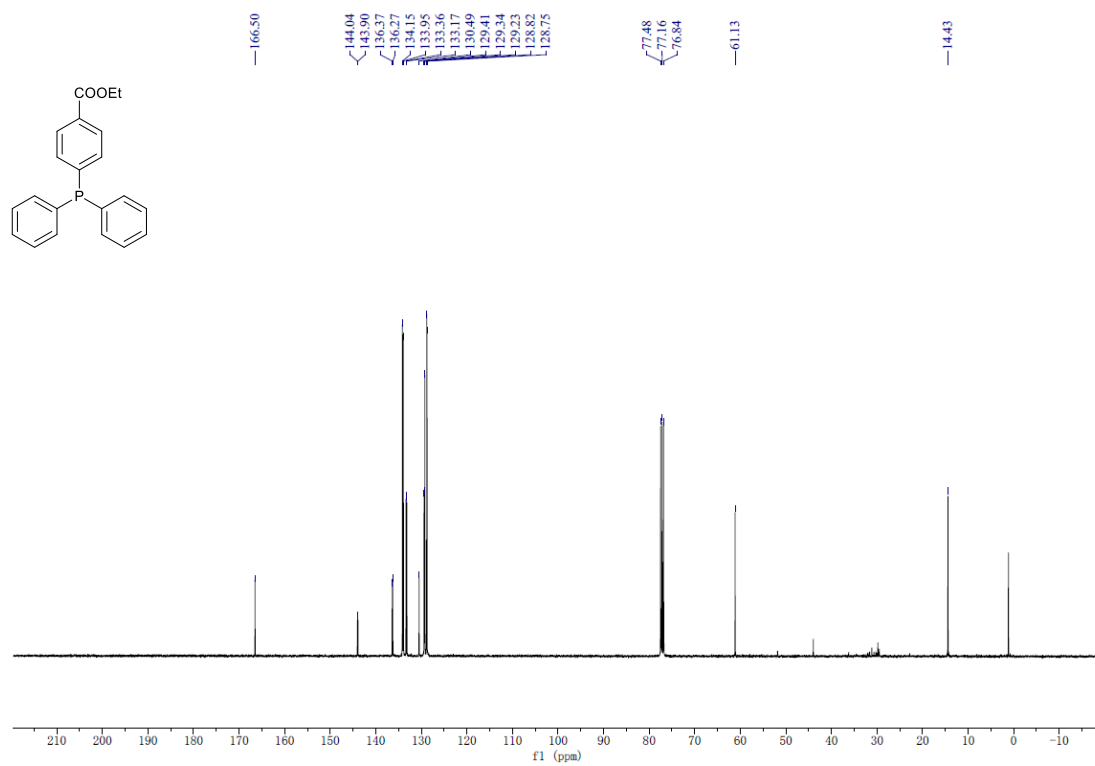
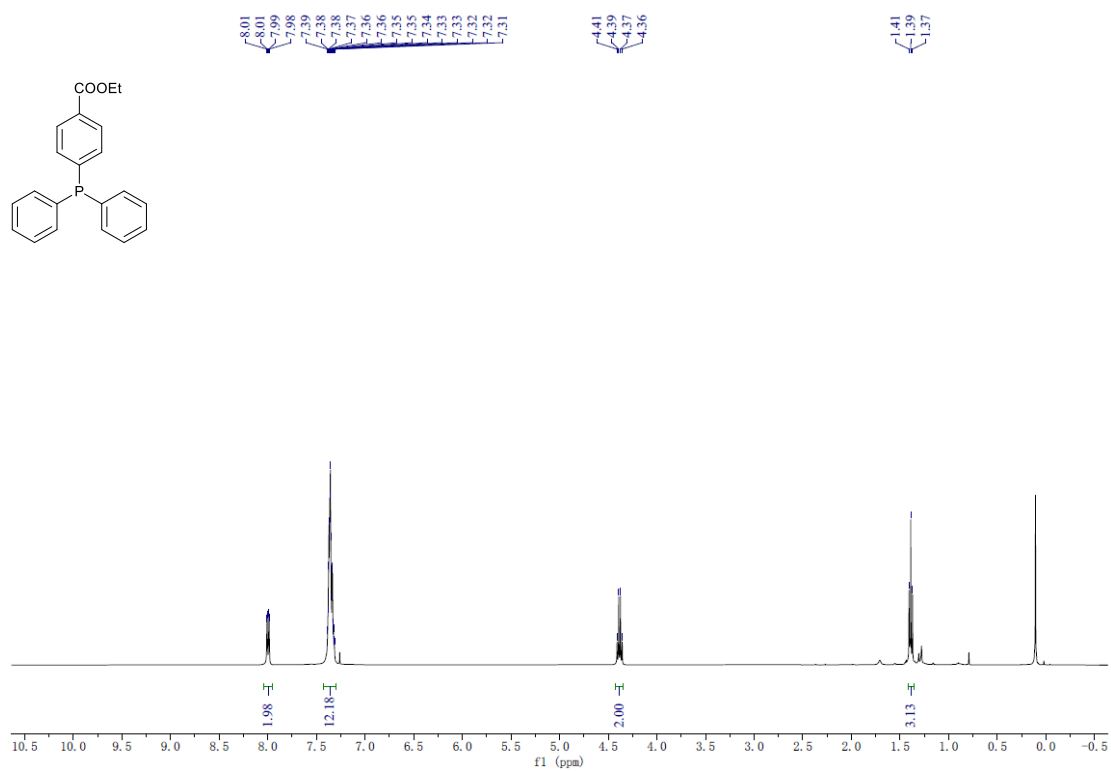
ethyl 4-(bis(4-chlorophenyl)phosphanyl)benzoate (3ia)



# ethyl 4-(bis(4-bromophenyl)phosphanyl)benzoate (3ja)



ethyl 4-(diphenylphosphanyl)benzoate (3ka)



ethyl 4-(di(thiophen-2-yl)phosphanyl)benzoate (3la)

