

## *Supporting Information*

### **Direct C-OH/P(O)-H Dehydration Coupling Forming Phosphine**

#### **Oxides**

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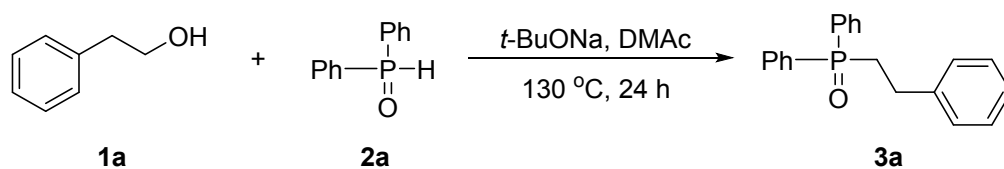
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## 1. General information

All reactions were carried out in dry Schlenk tubes under N<sub>2</sub> atmosphere. Dry solvents were obtained by purification according to standard methods. Reagents were used as received unless otherwise noted. Column chromatography was performed using Silica Gel 60 (particle size 37–54 μm). The pure products were obtained by means of column chromatography. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR data were acquired on a Bruker-400 spectrometer (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C, and 162 MHz for <sup>31</sup>P NMR spectroscopy). Chemical shifts for <sup>1</sup>H NMR are referred to internal Me<sub>4</sub>Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration.

## 2. Procedures for the base-promoted dehydration coupling of P(O)-H compounds with phenylethanol

1) A Typical procedure.

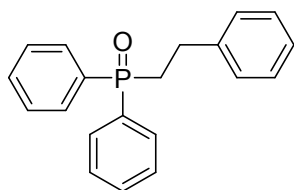


Under the Nitrogen atmosphere, 0.5 mmol phenylethanol **1a**, 0.2 mmol diphenylphosphine oxide **2a**, 0.2 mmol sodium *tert*-butoxide and 1 mL DMAc were charged into a 25 mL Schleck tube, and the mixture was heated at 130 °C for 24 h. After being cooled to room temperature, the mixture was added to 10 mL CH<sub>2</sub>Cl<sub>2</sub> and washed by 10 mL water for three times. After removal of the volatiles in vacuum, the residues were passed through a short silica chromatography (particle size 37–54 μm, ethyl acetate/petroleum ether as eluent) to afford analytically pure **3a** in 80% isolated yield.

2) 10 mmol scale experiment

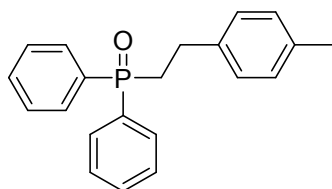
Under the Nitrogen atmosphere, 25 mmol phenylethanol **1a** (3.0541 g), 10 mmol diphenylphosphine oxide **2a** (2.0220 g), 10 mmol sodium *tert*-butoxide and 40 mL DMAc were charged into a 100 mL Schleck tube, and the mixture was heated at 130 °C for 24 h. After being cooled to room temperature, the mixture was added to 200 mL CH<sub>2</sub>Cl<sub>2</sub> and washed by 100 mL water for three times. After removal of the volatiles in vacuum, the residues were passed through a silica chromatography (particle size 37–54 μm, ethyl acetate/petroleum ether as eluent) to afford analytically pure **3a** in 85% isolated yield (2.6041 g). When the experiment was conducted in the absence of solvent DMAc, **3a** was obtained in 76% isolated yield according to a similar procedure (2.3281 g).

### 3.Characterization and analytical data of products 3



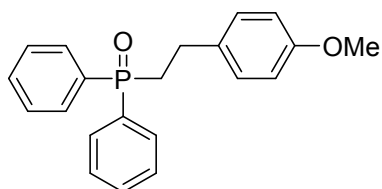
**3a**

**phenethyldiphenylphosphine oxide (3a).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/2) afforded **3a** (49.0 mg, 80% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79–7.74 (m, 4H), 7.56–7.44 (m, 6H), 7.28–7.24 (m, 2H), 7.19–7.15 (m, 3H), 2.98–2.88 (m, 2H), 2.63–2.54 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.2 (d,  $J_{\text{C-P}} = 15.3$  Hz), 132.7 (d,  $J_{\text{C-P}} = 97.8$  Hz), 131.9 (d,  $J_{\text{C-P}} = 2.6$  Hz), 130.8 (d,  $J_{\text{C-P}} = 9.2$  Hz), 128.8, 128.7 (d,  $J_{\text{C-P}} = 6.5$  Hz), 128.1, 126.4, 31.9 (d,  $J_{\text{C-P}} = 69.6$  Hz), 27.5 (d,  $J_{\text{C-P}} = 3.0$  Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.69. This compound is known.<sup>1</sup>



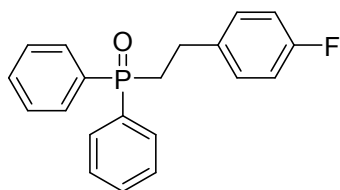
**3b**

**(4-methylphenethyl)diphenylphosphine oxide (3b).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/2) afforded **3b** (46.8 mg, 73% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81–7.71 (m, 4H), 7.55–7.43 (m, 6H), 7.05 (m, 4H), 2.92–2.86 (m, 2H), 2.60–2.53 (m, 2H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  138.1 (d,  $J_{\text{C-P}} = 15.3$  Hz), 135.9, 132.8 (d,  $J_{\text{C-P}} = 97.6$  Hz), 131.8 (d,  $J_{\text{C-P}} = 2.6$  Hz), 130.8 (d,  $J_{\text{C-P}} = 9.3$  Hz), 129.3, 128.7 (d,  $J_{\text{C-P}} = 11.5$  Hz), 128.0, 32.0 (d,  $J_{\text{C-P}} = 69.3$  Hz), 27.1 (d,  $J_{\text{C-P}} = 3.1$  Hz), 21.0;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.66. This compound is known.<sup>1</sup>



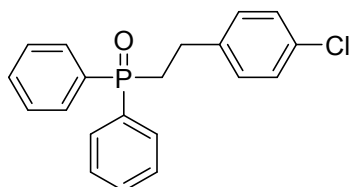
**3c**

**(4-methoxyphenethyl)diphenylphosphine oxide (3c).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/2) afforded **3c** (47.1 mg, 70% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.82–7.71 (m, 4H), 7.55–7.48 (m, 6H), 7.09–7.07 (m, 2H), 6.81–6.79 (m, 2H), 3.77 (s, 3H), 2.91–2.85 (m, 2H), 2.59–2.52 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.1, 133.2 (d,  $J_{\text{C-P}} = 15.6$  Hz), 132.8 (d,  $J_{\text{C-P}} = 97.5$  Hz), 131.8 (d,  $J_{\text{C-P}} = 2.6$  Hz), 130.8 (d,  $J_{\text{C-P}} = 9.3$  Hz), 129.0, 128.7 (d,  $J_{\text{C-P}} = 11.5$  Hz), 114.0, 55.3, 32.1 (d,  $J_{\text{C-P}} = 69.2$  Hz), 26.7 (d,  $J_{\text{C-P}} = 3.1$  Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.62. This compound is known.<sup>2</sup>



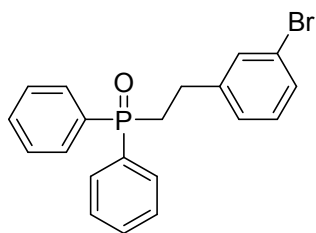
**3d**

**(4-fluorophenethyl)diphenylphosphine oxide(3d).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (2/1) afforded **3d** (38.3 mg, 59% yield) as a white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.72–7.64 (m, 4H), 7.48–7.36 (m, 6H), 7.06–7.00 (m, 2H), 6.84 (m, 2H), 2.83 (m, 2H), 2.47 (m, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.5 (d,  $J_{\text{F-C}} = 244.4$  Hz), 136.7 (dd,  $J_{\text{C-P}} = 15.0$  Hz,  $J_{\text{C-F}} = 3.1$  Hz), 132.7 (d,  $J_{\text{C-P}} = 98.3$  Hz), 131.9 (d,  $J_{\text{C-P}} = 2.6$  Hz), 130.8 (d,  $J_{\text{C-P}} = 9.3$  Hz), 129.5 (d,  $J_{\text{C-F}} = 7.9$  Hz), 128.8 (d,  $J_{\text{C-P}} = 11.6$  Hz), 115.4 (d,  $J_{\text{C-F}} = 21.3$  Hz), 32.0 (d,  $J_{\text{C-P}} = 69.8$  Hz), 26.8 (d,  $J_{\text{C-P}} = 2.9$  Hz);  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.43. This compound is known.<sup>2</sup>



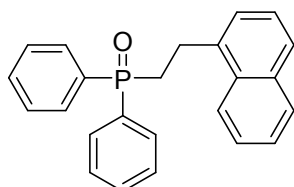
**3e**

**(4-chlorophenethyl)diphenylphosphine oxide (3e).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/2) afforded **3e** (60.7 mg, 89% yield) as a white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80–7.70 (m, 4H), 7.53–7.48 (m, 6H), 7.21–7.20 (m, 2H), 7.09–7.07 (m, 2H), 2.94–2.88 (m, 2H), 2.58–2.52 (m, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.6 (d,  $J_{\text{C-P}} = 15.0$  Hz), 132.6 (d,  $J_{\text{C-P}} = 98.4$  Hz), 132.1, 131.9 (d,  $J_{\text{C-P}} = 2.6$  Hz), 130.8 (d,  $J_{\text{C-P}} = 9.3$  Hz), 129.5, 128.8 (d,  $J_{\text{C-P}} = 11.6$  Hz), 128.7, 31.8 (d,  $J_{\text{C-P}} = 69.5$  Hz), 27.0 (d,  $J_{\text{C-P}} = 2.9$  Hz);  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.30. This compound is known.<sup>2</sup>



**3f**

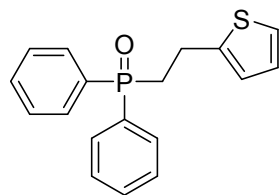
**(3-bromophenethyl)diphenylphosphine oxide (3f).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/2) afforded **3f** (67.8 mg, 88% yield) as a white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.78–7.74 (m, 4H), 7.55–7.46 (m, 6H), 7.29–7.27 (m, 2H), 7.13–7.08 (m, 2H), 2.94–2.88 (m, 2H), 2.59–2.52 (m, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.4 (d,  $J_{\text{C-P}} = 14.9$  Hz), 132.5 (d,  $J_{\text{C-P}} = 98.1$  Hz), 131.9 (d,  $J_{\text{C-P}} = 2.7$  Hz), 131.1, 130.8 (d,  $J_{\text{C-P}} = 9.3$  Hz), 130.2, 129.5, 128.8 (d,  $J_{\text{C-P}} = 11.6$  Hz), 126.9, 122.6, 31.6 (d,  $J_{\text{C-P}} = 69.5$  Hz), 27.3 (d,  $J_{\text{C-P}} = 2.9$  Hz);  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.20. This compound is known.



**3g**

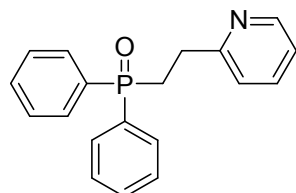
**(2-(naphthalen-1-yl)ethyl)diphenylphosphine oxide(3g).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/2) afforded **3g** (64.9 mg, 91% yield) as a pale yellow solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89–7.80 (m, 6H), 7.73–7.71 (m, 1H), 7.58–7.48 (m, 8H), 7.39–7.32 (m, 2H), 3.45–3.39 (m, 2H), 2.75–2.68 (m, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.3 (d,  $J_{\text{C-P}} = 14.6$  Hz), 133.9, 132.8 (d,  $J_{\text{C-P}} = 97.7$  Hz), 131.9 (d,  $J_{\text{C-P}} = 2.7$  Hz), 131.3, 130.8 (d,  $J_{\text{C-P}} = 9.3$  Hz), 128.9, 128.7 (d,  $J_{\text{C-P}} = 11.5$  Hz), 127.2, 126.2,

125.8, 125.7, 125.6, 123.3, 31.2 (d,  $J_{C-P}$  = 69.1 Hz), 24.8 (d,  $J_{C-P}$  = 2.8 Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.69. This compound is known.<sup>1</sup>



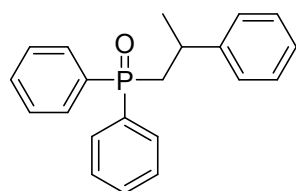
**3h**

**diphenyl(2-(thiophen-2-yl)ethyl)phosphine oxide(3h).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/2) afforded **3h** (48.7 mg, 78% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79–7.74 (m, 4H), 7.54–7.49 (m, 6H), 7.11 (s, 1H), 6.88 (s, 1H), 6.79 (s, 1H), 3.18–3.13 (m, 2H), 2.89–2.63 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.9 (d,  $J_{C-P}$  = 17.5 Hz), 132.5 (d,  $J$  = 99.3 Hz), 132.0 (d,  $J_{C-P}$  = 2.7 Hz), 130.8 (d,  $J_{C-P}$  = 9.3 Hz), 128.8 (d,  $J_{C-P}$  = 11.6 Hz), 126.9, 124.6, 123.6, 32.2 (d,  $J_{C-P}$  = 69.2 Hz), 22.2 (d,  $J_{C-P}$  = 2.1 Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.07. This compound is known.<sup>1</sup>



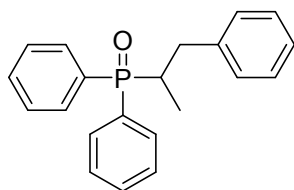
**3i**

**diphenyl(2-(pyridin-2-yl)ethyl)phosphine oxide(3i).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/1) afforded **3i** (40.0 mg, 65% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.49–8.48 (m, 1H), 7.81–7.78 (m, 4H), 7.55–7.44 (m, 7H), 7.14–7.12 (m, 1H), 7.10–7.07 (m, 1H), 3.15–3.09 (m, 2H), 2.82–2.78 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.2 (d,  $J_{C-P}$  = 14.4 Hz), 149.3, 136.5, 132.8 (d,  $J_{C-P}$  = 98.2 Hz), 131.8 (d,  $J$  = 2.7 Hz), 130.8 (d,  $J_{C-P}$  = 9.4 Hz), 128.7 (d,  $J_{C-P}$  = 11.7 Hz), 123.11, 121.51, 29.7 (d,  $J_{C-P}$  = 2.7 Hz), 29.2 (d,  $J_{C-P}$  = 71.2 Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  32.39. This compound is known.<sup>2</sup>



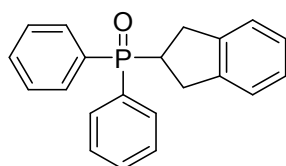
**3j**

**diphenyl(2-phenylpropyl)phosphine oxide (3j).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/2) afforded **3j** (48.7 mg, 76% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.77–7.72 (m, 2H), 7.68–7.63 (m, 2H), 7.49–7.35 (m, 6H), 7.21–7.17 (m, 2H), 7.13–7.09 (m, 3H), 3.38–3.27 (m, 1H), 2.63–2.54 (m, 2H), 1.38–1.37 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.0 (d,  $J_{C-P}$  = 10.2 Hz), 134.4 (d,  $J_{C-P}$  = 97.2 Hz), 132.8 (d,  $J_{C-P}$  = 97.6 Hz), 131.6 (d,  $J_{C-P}$  = 2.7 Hz), 131.5 (d,  $J_{C-P}$  = 2.7 Hz), 130.8 (d,  $J_{C-P}$  = 9.1 Hz), 130.5 (d,  $J_{C-P}$  = 9.2 Hz), 128.6 (d,  $J_{C-P}$  = 23.9 Hz), 128.55 (d,  $J_{C-P}$  = 1.6 Hz), 128.5, 126.6, 126.4, 38.4 (d,  $J_{C-P}$  = 69.0 Hz), 34.3 (d,  $J_{C-P}$  = 3.1 Hz), 23.5 (d,  $J_{C-P}$  = 5.2 Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  30.30. This compound is known.<sup>2</sup>



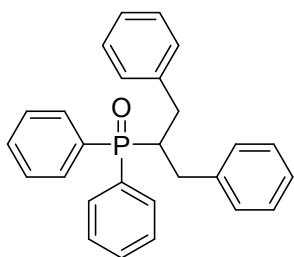
**3k**

**diphenyl(1-phenylpropan-2-yl)phosphine oxide (3k).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/2) afforded **3k** (36.5 mg, 57% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.91–7.81 (m, 4H), 7.55–7.45 (m, 6H), 7.28–7.24 (m, 2H), 7.20–7.17 (m, 1H), 7.12–7.10 (m, 2H), 3.09–3.02 (m, 1H), 2.87–2.59 (m, 2H), 1.09–1.04 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.6 (d,  $J_{\text{C-P}} = 14.7$  Hz), 132.2 (d,  $J_{\text{C-P}} = 94.1$  Hz), 132.2 (d,  $J_{\text{C-P}} = 96.2$  Hz), 131.7 (d,  $J_{\text{C-P}} = 2.8$  Hz), 131.6 (d,  $J_{\text{C-P}} = 2.6$  Hz), 131.1, 131.0 (d,  $J_{\text{C-P}} = 8.6$  Hz), 129.0, 128.70, 128.7 (d,  $J_{\text{C-P}} = 23.5$  Hz), 128.5, 126.4, 35.0, 34.5 (d,  $J_{\text{C-P}} = 70.6$  Hz), 11.7 (d,  $J_{\text{C-P}} = 2.5$  Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  36.16. This compound is known.<sup>4</sup>



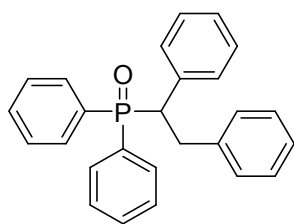
**3l**

**(2,3-dihydro-1H-inden-2-yl)diphenylphosphine oxide(3l).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/1) afforded **3l** (45.2 mg, 71% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.84–7.80 (m, 4H), 7.54–7.46 (m, 6H), 7.12 (s, 4H), 3.46–3.10 (m, 3H), 3.06–3.01 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.7 (d,  $J_{\text{C-P}} = 9.9$  Hz), 132.8 (d,  $J_{\text{C-P}} = 96.8$  Hz), 131.8 (d,  $J_{\text{C-P}} = 2.6$  Hz), 131.0 (d,  $J_{\text{C-P}} = 8.9$  Hz), 128.7 (d,  $J_{\text{C-P}} = 11.3$  Hz), 126.7, 124.3, 37.8 (d,  $J_{\text{C-P}} = 75.7$  Hz), 33.1;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 33.38. Melting point: 170.8–176.3 °C. HRMS: Cal. for  $\text{C}_{21}\text{H}_{19}\text{OP}$  318.1174. Found 318.1182. IR: 3021, 1435, 1183, 1118, 746, 722, 695  $\text{cm}^{-1}$ .



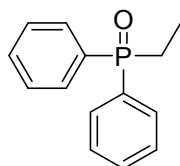
**3m**

**(1,3-diphenylpropan-2-yl)diphenylphosphine oxide(3m).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/1) afforded **3m** (36.5 mg, 46% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79–7.74 (m, 4H), 7.43–7.34 (m, 6H), 7.05–7.04 (m, 6H), 6.81–6.79 (m, 4H), 3.10–3.02 (m, 2H), 2.93–2.79 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.7 (d,  $J_{\text{C-P}} = 9.1$  Hz), 132.6 (d,  $J_{\text{C-P}} = 93.9$  Hz), 131.4 (d,  $J_{\text{C-P}} = 2.6$  Hz), 130.8 (d,  $J_{\text{C-P}} = 8.7$  Hz), 129.0, 128.5 (d,  $J_{\text{C-P}} = 11.3$  Hz), 128.2, 126.1, 42.2 (d,  $J_{\text{C-P}} = 68.9$  Hz), 33.8;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  34.59. This compound is known.<sup>7</sup>



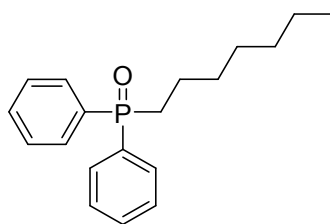
**3n**

**(1,2-diphenylethyl)diphenylphosphine oxide(3n).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/1) afforded **3n** (24.7 mg, 32% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.01–7.97 (m, 2H), 7.59 (s, 3H), 7.46–7.42 (m, 2H), 7.33–7.30 (m, 1H), 7.24–7.17 (m, 4H), 7.12–7.07 (m, 6H), 6.83–6.81 (m, 2H), 3.68–3.63 (m, 1H), 3.37–3.24 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.4 (d,  $J_{\text{C-P}} = 14.1$  Hz), 135.4 (d,  $J_{\text{C-P}} = 5.3$  Hz), 132.1 (d,  $J_{\text{C-P}} = 98.7$  Hz), 132.0 (d,  $J_{\text{C-P}} = 94.1$  Hz), 131.6 (d,  $J_{\text{C-P}} = 59.1$  Hz), 131.7 (d,  $J_{\text{C-P}} = 59.1$  Hz), 131.2 (d,  $J_{\text{C-P}} = 39.7$  Hz), 131.1 (d,  $J_{\text{C-P}} = 40.1$  Hz), 130.0 (d,  $J_{\text{C-P}} = 5.9$  Hz), 128.9 (d,  $J_{\text{C-P}} = 11.2$  Hz), 128.4 (d,  $J_{\text{C-P}} = 53.9$  Hz), 128.2, 128.2, 128.0 (d,  $J_{\text{C-P}} = 11.6$  Hz), 127.0 (d,  $J_{\text{C-P}} = 2.4$  Hz), 126.2, 49.2 (d,  $J_{\text{C-P}} = 66.1$  Hz), 36.0;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  32.86. This compound is known.<sup>8</sup>



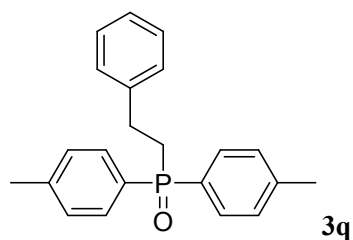
**3o**

**ethyldiphenylphosphine oxide(3o).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/1) afforded **3o** (16.1 mg, 35% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.76–7.72 (m, 4H), 7.54–7.45 (m, 6H), 2.33–2.24 (m, 2H), 1.26–1.24 (m, 1H), 1.20–1.16 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  132.9 (d,  $J_{\text{C-P}} = 97.5$  Hz), 131.7 (d,  $J_{\text{C-P}} = 2.8$  Hz), 130.9 (d,  $J_{\text{C-P}} = 9.1$  Hz), 128.6 (d,  $J_{\text{C-P}} = 11.5$  Hz), 22.7 (d,  $J_{\text{C-P}} = 72.5$  Hz), 5.6 (d,  $J_{\text{C-P}} = 5.1$  Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  34.06. This compound is known.<sup>3</sup>

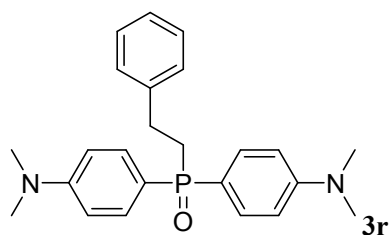


**3p**

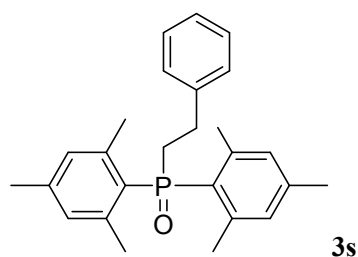
**heptyldiphenylphosphine oxide(3p).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/1) afforded **3p** (22.8 mg, 38% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.68–7.63 (m, 4H), 7.45–7.36 (m, 6H), 2.21–2.14 (m, 2H), 1.59–1.49 (m, 2H), 1.32–1.27 (m, 2H), 1.18–1.15 (m, 6H), 0.78–0.75 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  133.2 (d,  $J_{\text{C-P}} = 97.2$  Hz), 131.6 (d,  $J_{\text{C-P}} = 2.6$  Hz), 130.8 (d,  $J_{\text{C-P}} = 9.2$  Hz), 128.6 (d,  $J_{\text{C-P}} = 9.4$  Hz), 31.6, 31.0 (d,  $J_{\text{C-P}} = 14.6$  Hz), 29.7 (d,  $J_{\text{C-P}} = 76.9$  Hz), 28.7, 22.6, 21.4 (d,  $J_{\text{C-P}} = 3.8$  Hz), 14.0;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  32.66. This compound is known.<sup>5</sup>



**phenethyldi-p-tolylphosphine oxide(3q).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/2) afforded **3q** (50.8 mg, 76% yield) as a whitesolid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59–7.54 (m, 4H), 7.21–7.17 (m, 6H), 7.12–7.08 (m, 3H), 2.86–2.80 (m, 2H), 2.50–2.43 (m, 2H), 2.32 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.2 (d,  $J_{\text{C-P}} = 2.6$  Hz), 141.4 (d,  $J_{\text{C-P}} = 15.2$  Hz), 130.8 (d,  $J_{\text{C-P}} = 9.6$  Hz), 129.6 (d,  $J_{\text{C-P}} = 100.2$  Hz), 129.5 (d,  $J_{\text{C-P}} = 12.0$  Hz), 128.6, 128.1, 126.3, 32.1 (d,  $J_{\text{C-P}} = 70.1$  Hz), 27.6 (d,  $J_{\text{C-P}} = 2.9$  Hz), 21.6.;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  32.01. This compound is known.<sup>1</sup>

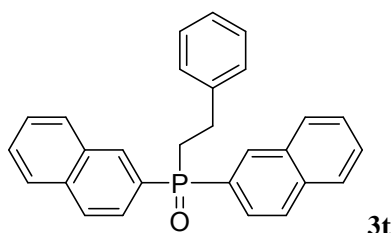


**bis(4-(dimethylamino)phenyl)(phenethyl)phosphine oxide(3r).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/1) afforded **3r** (65.9 mg, 84% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59–7.54 (m, 4H), 7.27–7.24 (m, 2H), 7.18–7.15 (m, 3H), 6.73–6.70 (m, 4H), 3.00 (s, 12H), 2.93–2.87 (m, 2H), 2.50–2.43 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.2 (d,  $J_{\text{C-P}} = 2.3$  Hz), 142.1 (d,  $J_{\text{C-P}} = 15.5$  Hz), 132.2 (d,  $J_{\text{C-P}} = 10.4$  Hz), 128.3 (d,  $J_{\text{C-P}} = 39.0$  Hz), 126.0, 118.9, 117.8, 111.5 (d,  $J_{\text{C-P}} = 12.3$  Hz), 40.0, 32.6 (d,  $J_{\text{C-P}} = 70.8$  Hz), 29.0 (d,  $J_{\text{C-P}} = 2.7$  Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  32.84. Melting point: 177.5–179.1 °C. HRMS: Cal. for  $\text{C}_{24}\text{H}_{29}\text{N}_2\text{OP}$  392.2018. Found 392.2025. IR: 2943, 2861, 1452, 1400, 1165, 1118, 817, 740  $\text{cm}^{-1}$ .

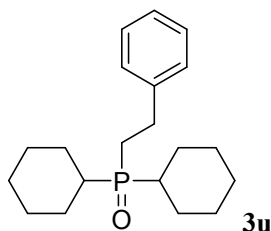


**dimesityl(phenethyl)phosphine oxide(3s).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/2) afforded **3s** (55.5 mg, 71% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.19–7.16 (m, 2H), 7.11–7.04 (m, 3H), 6.75 (s, 4H), 2.79–2.73 (m, 2H), 2.64–2.58 (m, 2H), 2.30 (s, 12H), 2.19 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.0 (d,  $J_{\text{C-P}} = 16.8$  Hz), 141.2 (d,  $J_{\text{C-P}} = 10.0$  Hz), 140.7 (d,  $J_{\text{C-P}} = 2.6$  Hz), 131.1 (d,  $J_{\text{C-P}} = 11.0$  Hz), 130.0 (d,  $J_{\text{C-P}} = 94.1$  Hz), 128.4 (d,  $J_{\text{C-P}} = 28.2$  Hz), 126.1, 38.2 (d,  $J_{\text{C-P}} = 64.7$  Hz), 28.8 (d,  $J_{\text{C-P}} = 2.5$  Hz), 22.9 (d,  $J_{\text{C-P}} = 4.1$  Hz), 20.9;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  40.39. Melting point: 219.8–223.5 °C. HRMS: Cal. for  $\text{C}_{26}\text{H}_{31}\text{OP}$  390.2113. Found 390.2116. IR: 2918, 1400, 1200, 1169, 764, 735, 699, 646  $\text{cm}^{-1}$ .

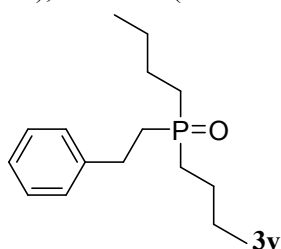




**di(naphthalen-2-yl)(phenethyl)phosphine oxide(3t).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/2) afforded **3t** (56.1 mg, 69% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.37–8.34 (m, 2H), 7.81–7.79 (m, 4H), 7.74–7.72 (m, 2H), 7.64–7.59 (m, 2H), 7.47–7.40 (m, 4H), 7.15–7.11 (m, 2H), 7.08–7.02 (m, 3H), 2.93–2.87 (m, 2H), 2.70–2.63 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.2 (d,  $J_{\text{C-P}} = 15.2$  Hz), 134.7 (d,  $J_{\text{C-P}} = 2.3$  Hz), 132.9 (d,  $J_{\text{C-P}} = 8.5$  Hz), 132.7 (d,  $J_{\text{C-P}} = 12.5$  Hz), 129.9 (d,  $J_{\text{C-P}} = 98.2$  Hz), 128.9, 128.8, 128.7, 128.3, 128.2, 127.9, 127.1, 126.4, 125.6 (d,  $J_{\text{C-P}} = 10.5$  Hz), 31.8 (d,  $J_{\text{C-P}} = 69.5$  Hz), 27.7 (d,  $J_{\text{C-P}} = 3.0$  Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.99. Melting point: 233.4–236.1 °C. HRMS: Cal. for  $\text{C}_{28}\text{H}_{23}\text{OP}$  406.1487. Found 406.1482. IR: 3094, 1452, 1440, 1167, 1094, 700, 653  $\text{cm}^{-1}$ .



**dicyclohexyl(phenethyl)phosphine oxide(3u).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (2/1) afforded **3u** (38.2 mg, 60% yield) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32–7.28 (m, 2H), 7.23–7.19 (m, 3H), 2.97–2.91 (m, 2H), 1.98–1.93 (m, 5H), 1.85–1.75 (m, 9H), 1.42–1.39 (m, 4H), 1.28–1.24 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.8 (d,  $J_{\text{C-P}} = 12.5$  Hz), 128.6, 128.0, 126.3, 36.4 (d,  $J_{\text{C-P}} = 63.8$  Hz), 28.1 (d,  $J_{\text{C-P}} = 3.6$  Hz), 26.6 (dd,  $J_{\text{C-P}} = 12.1, 2.9$  Hz), 26.0, 25.7 (d,  $J_{\text{C-P}} = 3.1$  Hz), 25.6 (d,  $J_{\text{C-P}} = 58.4$  Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  50.24. This compound is known.<sup>6</sup>

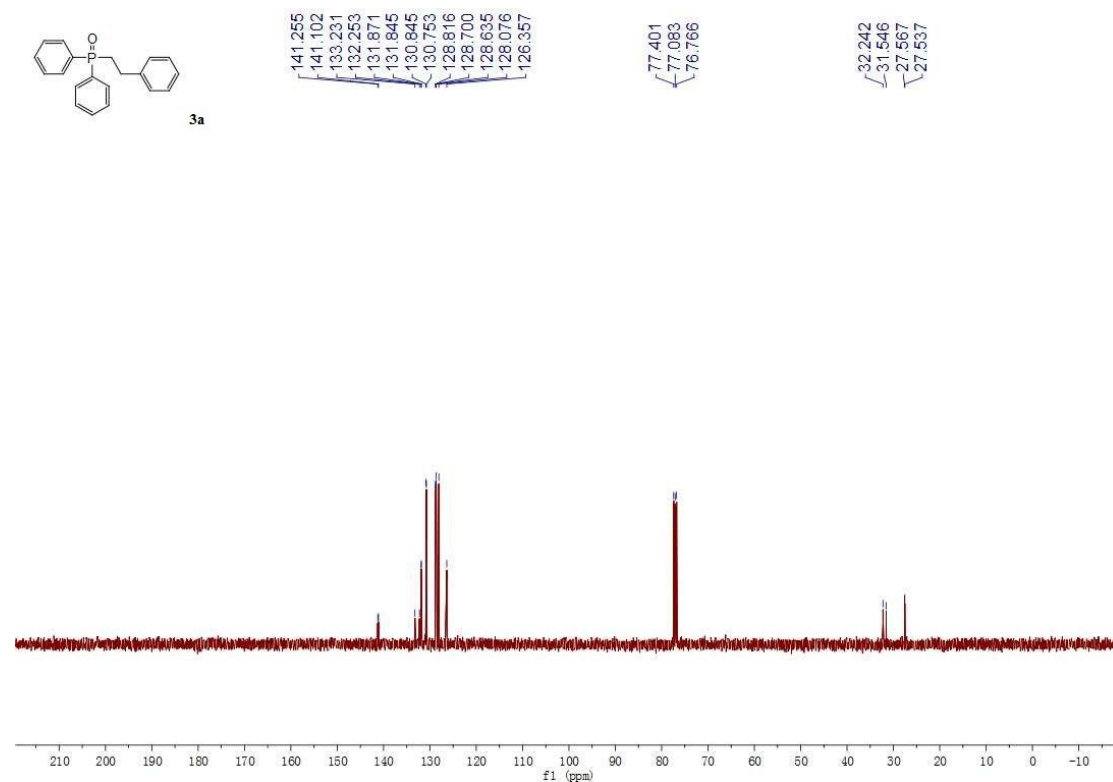
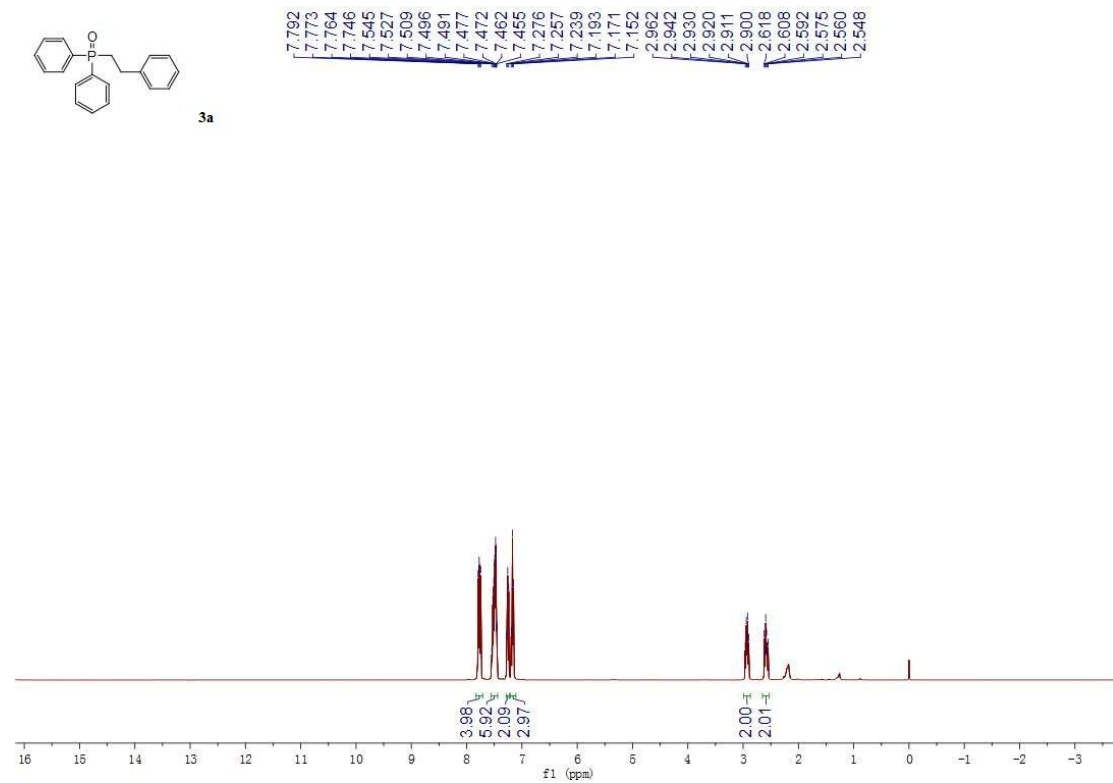


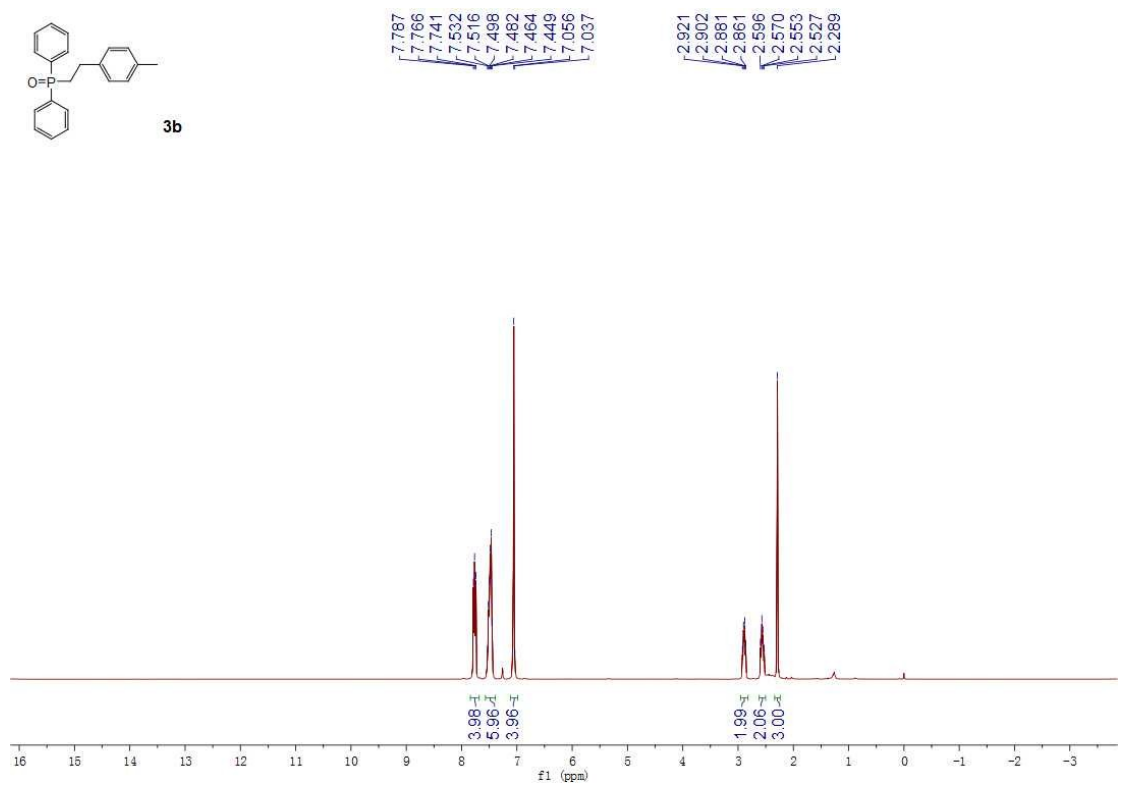
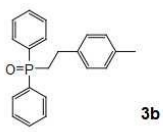
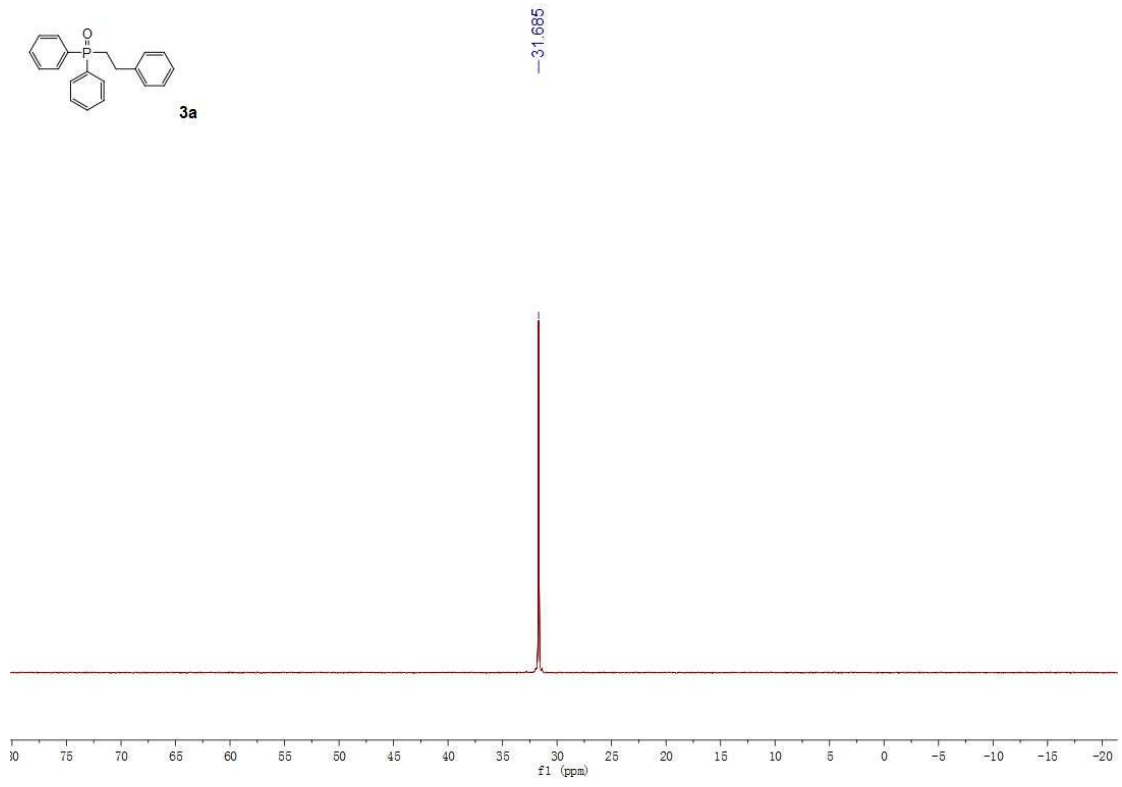
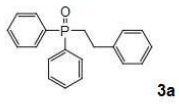
**dibutyl(phenethyl)phosphine oxide(3v).** Purification by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (2/1) afforded **3v** (34.6 mg, 65% yield) as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32–7.28 (m, 2H), 7.24–7.20 (m, 3H), 2.96–2.90 (m, 2H), 2.05–1.99 (m, 2H), 1.75–1.68 (m, 4H), 1.60–1.50 (m, 4H), 1.46–1.37 (m, 4H), 0.946–0.910 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.2 (d,  $J_{\text{C-P}} = 13.2$  Hz), 128.7, 128.1, 126.4, 29.7 (d,  $J_{\text{C-P}} = 62.6$  Hz), 27.8 (d,  $J_{\text{C-P}} = 64.5$  Hz), 27.7 (d,  $J_{\text{C-P}} = 3.1$  Hz), 24.3 (d,  $J_{\text{C-P}} = 14.3$  Hz), 23.8 (d,  $J_{\text{C-P}} = 3.7$  Hz), 13.6;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  48.17. This compound is known.<sup>1</sup>

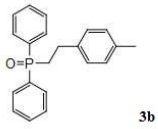
#### 4. References:

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## 5. Copies of $^1\text{H}$ NMR, $^{31}\text{P}$ NMR and $^{13}\text{C}$ NMR spectroscopies



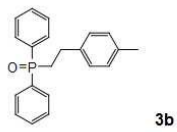
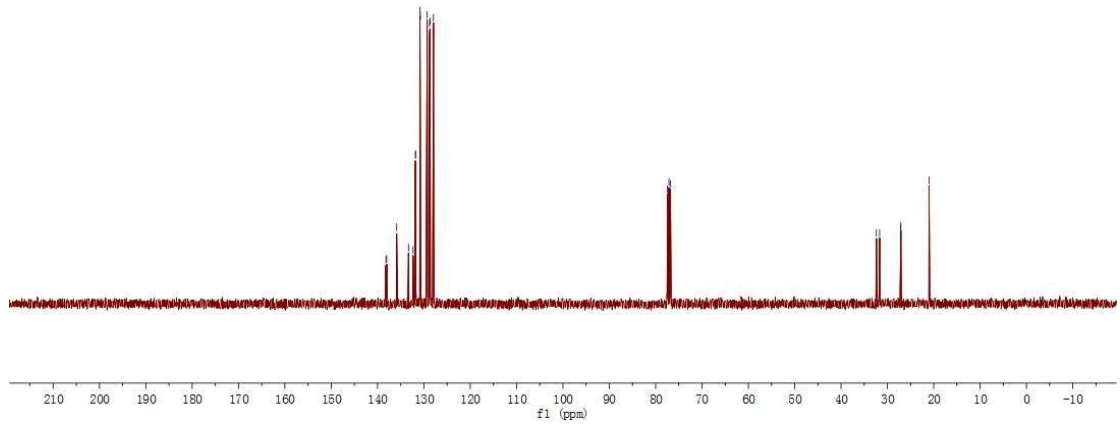




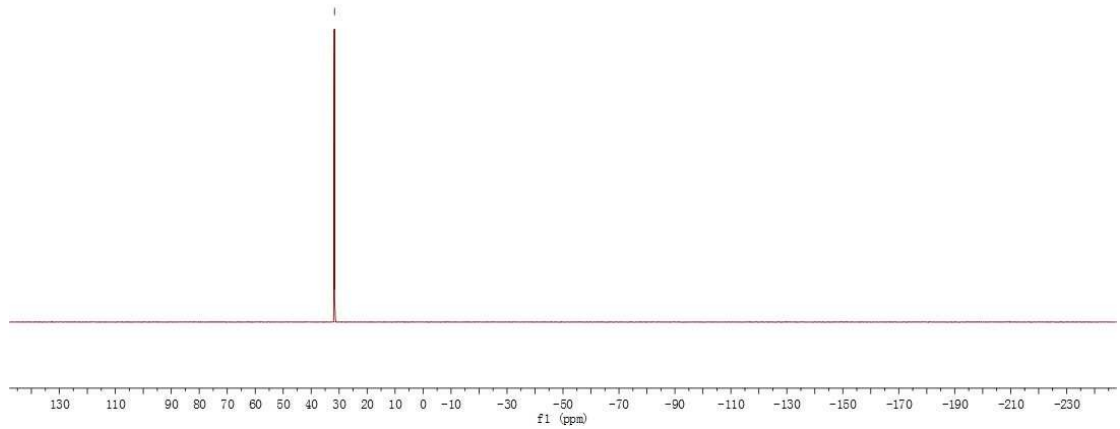
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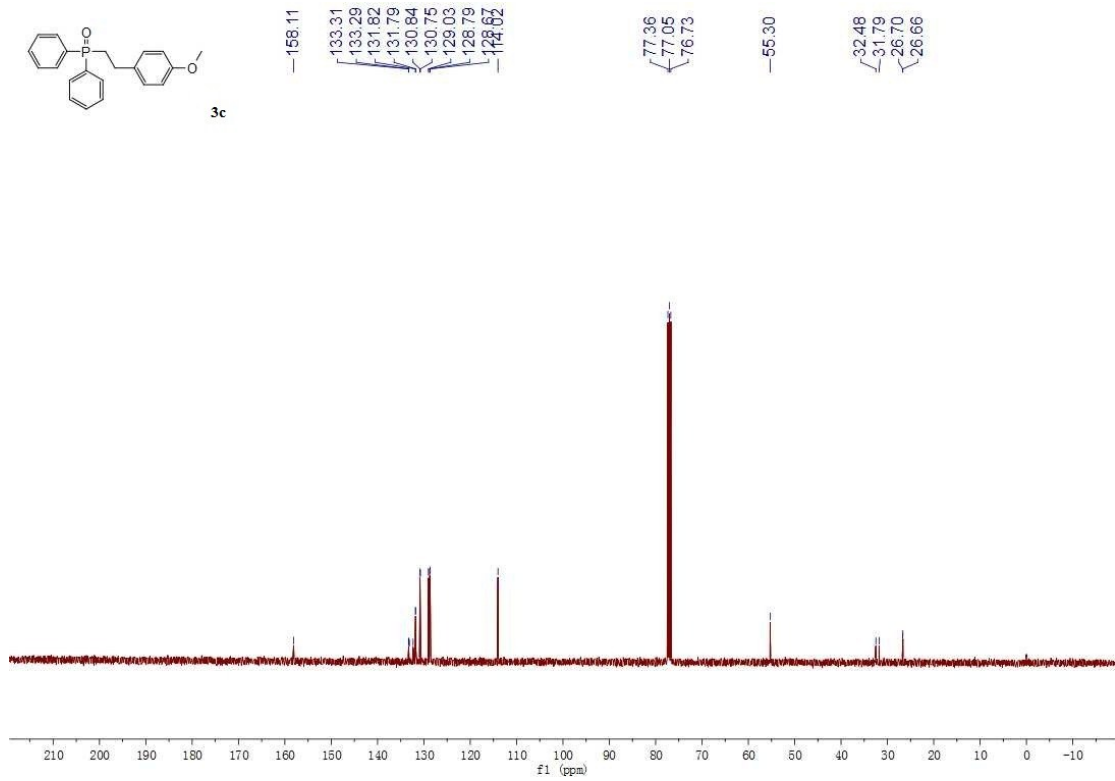
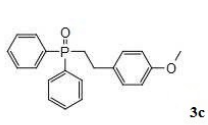
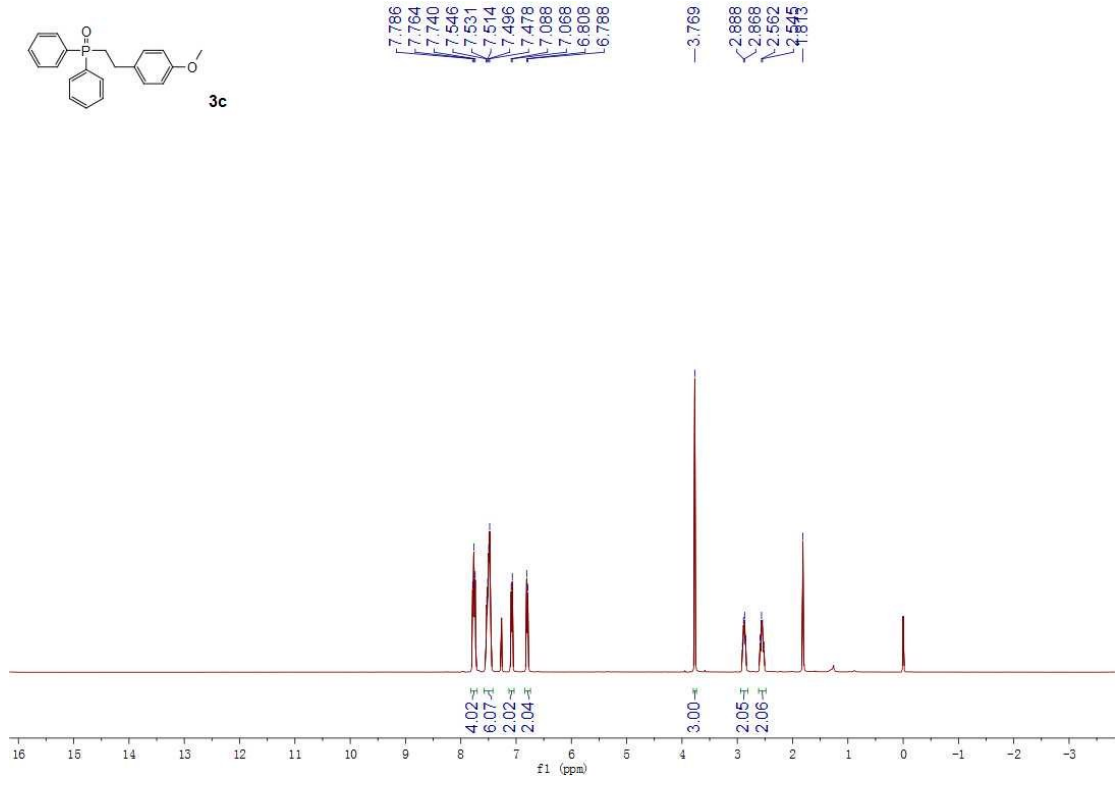
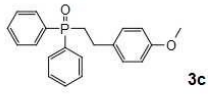
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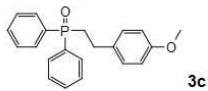
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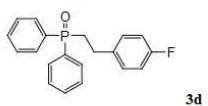
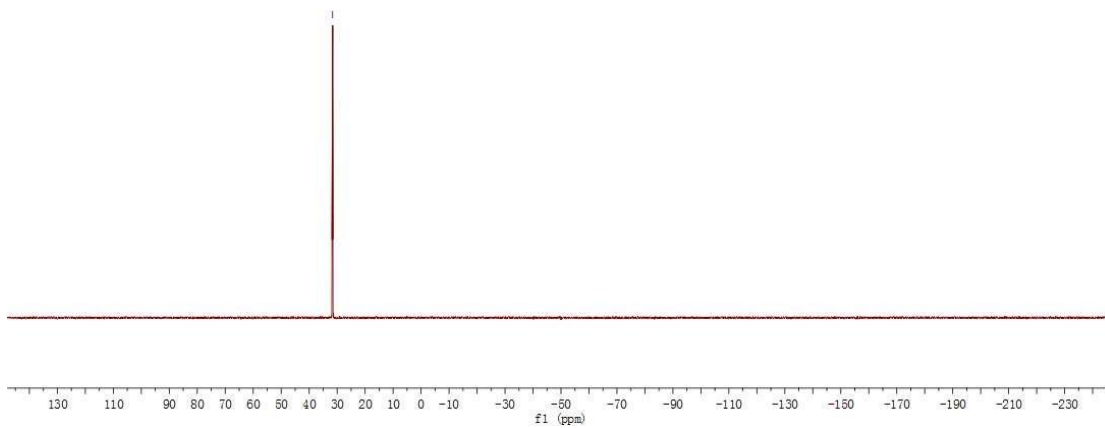
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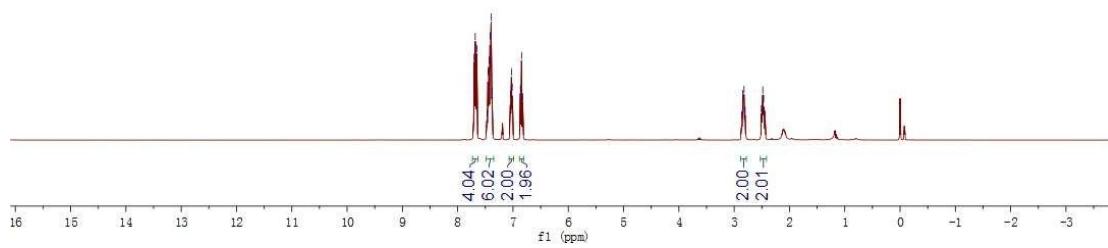


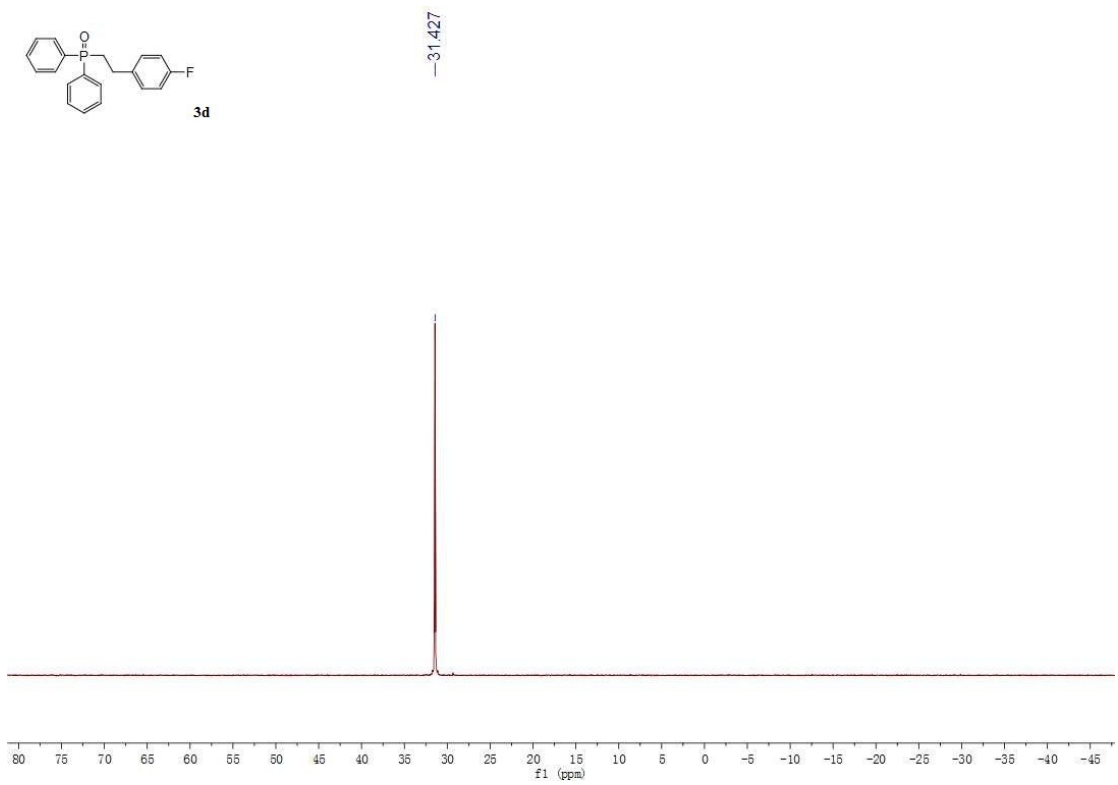
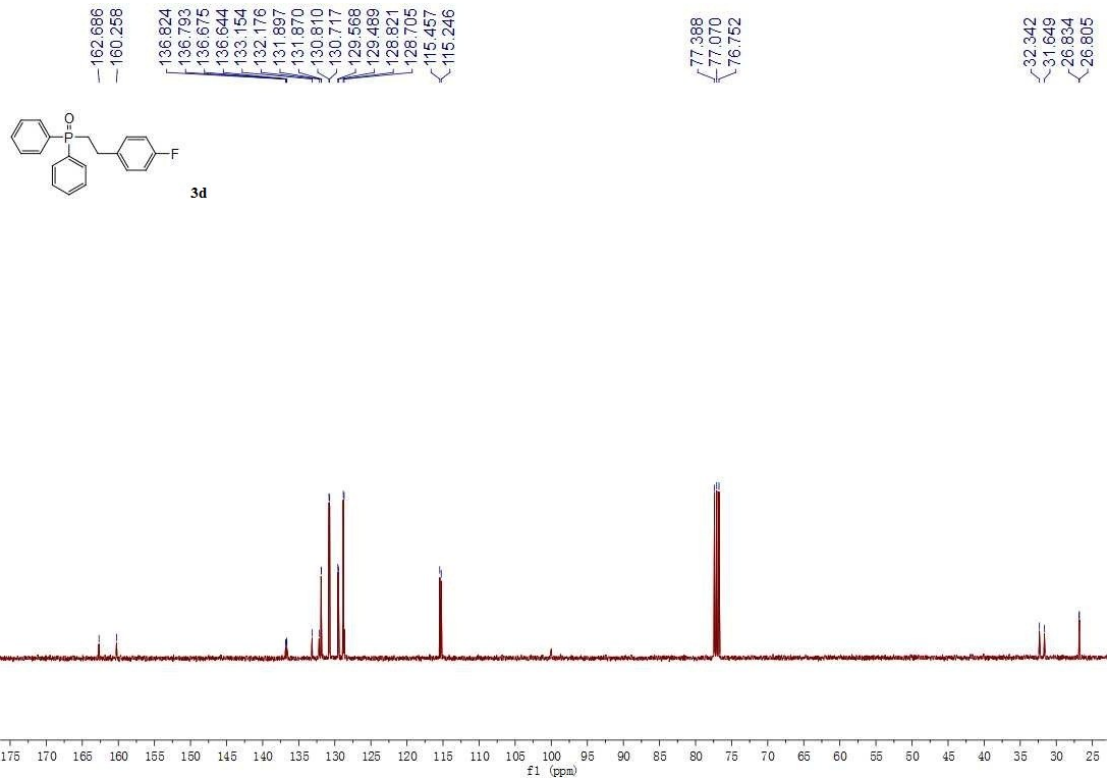


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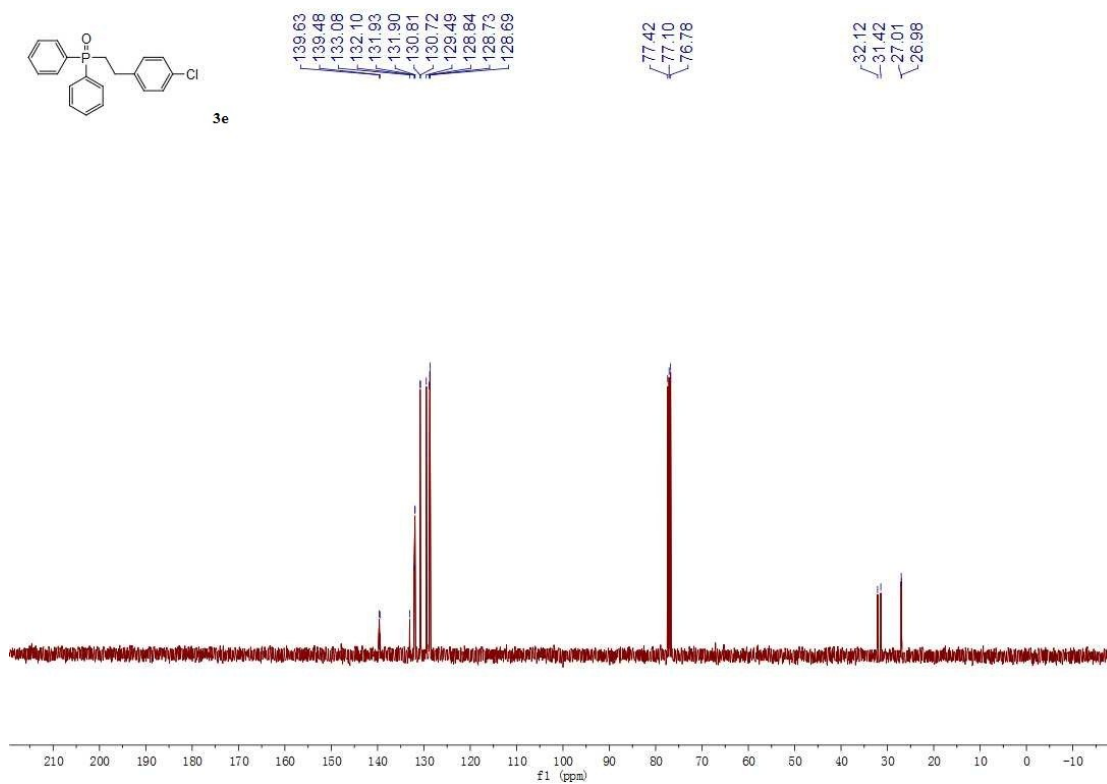
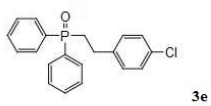
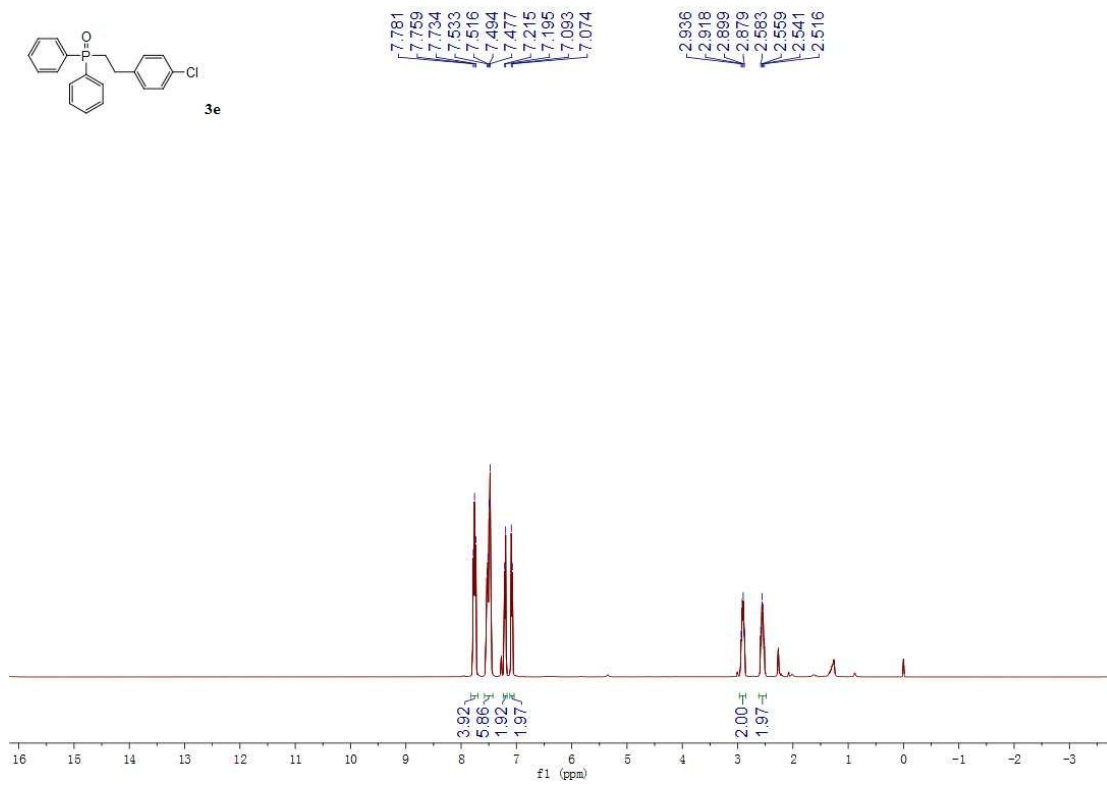
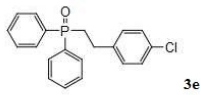


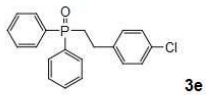
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7.013  
6.865  
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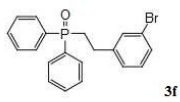
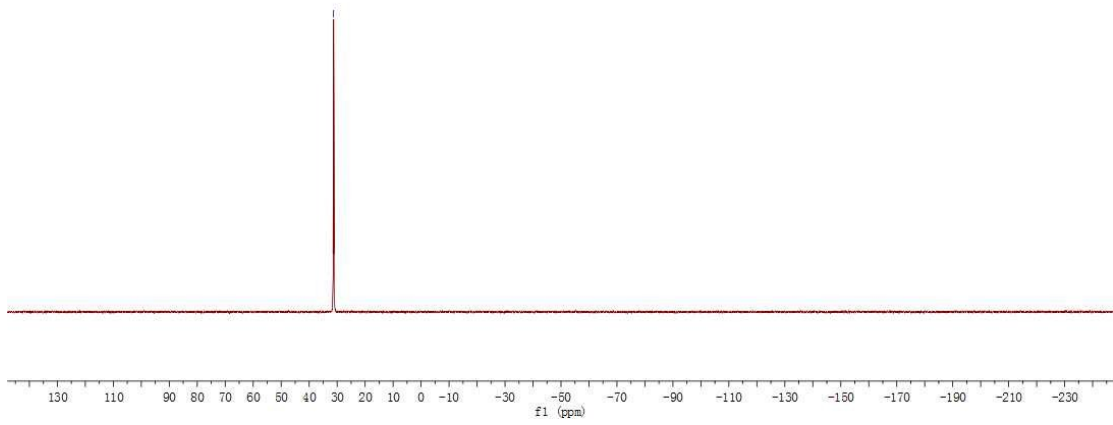




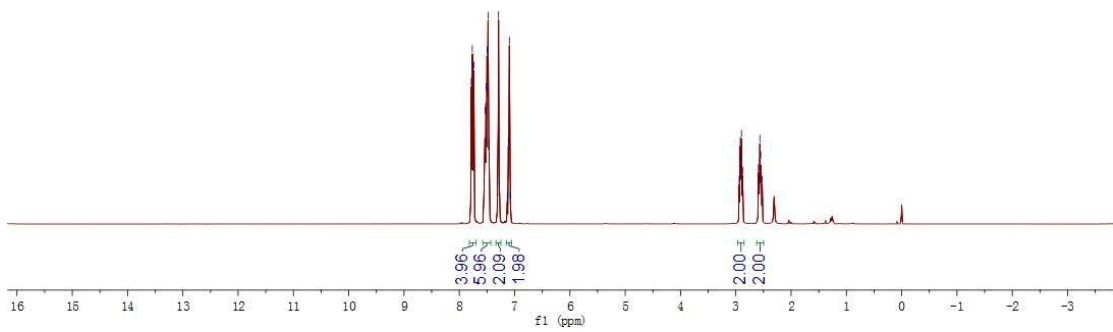


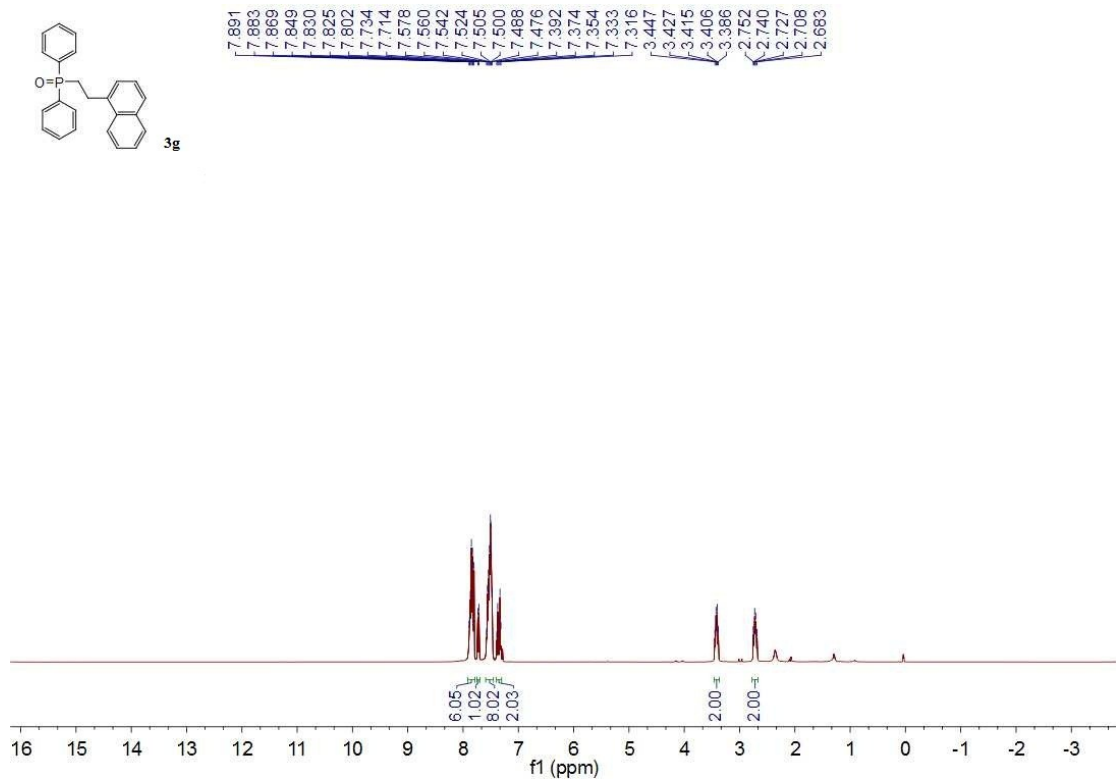
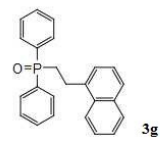
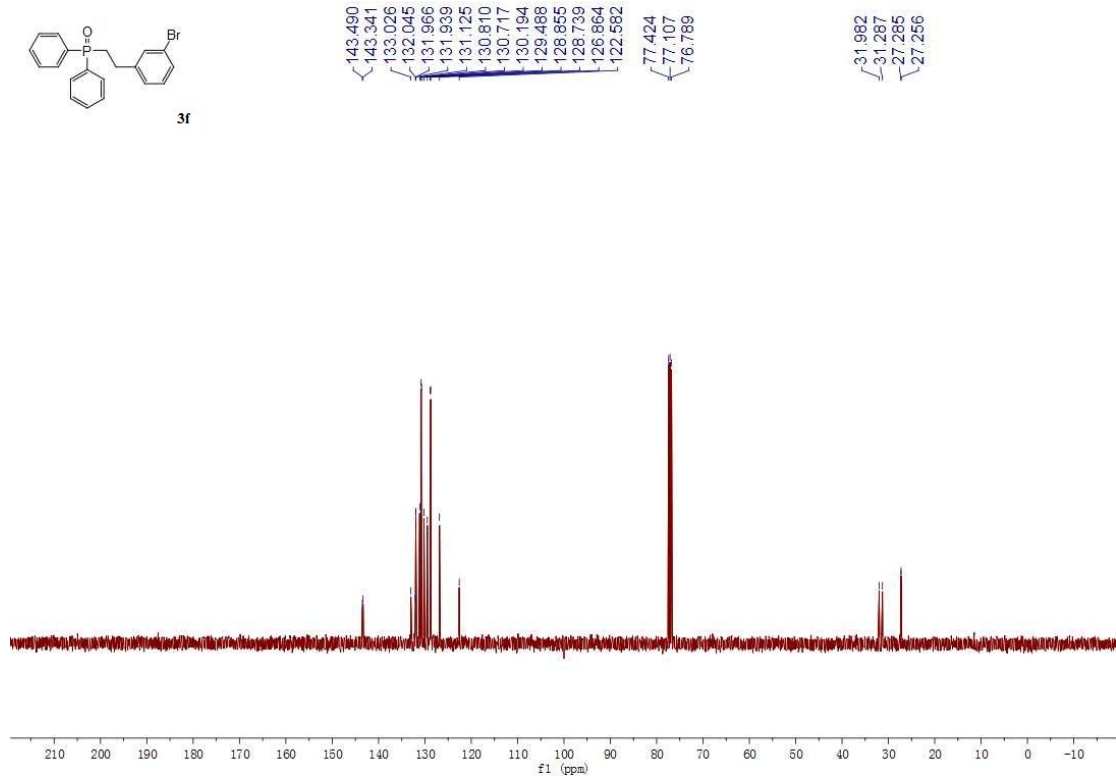
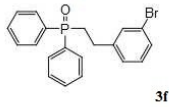


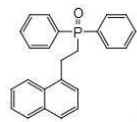
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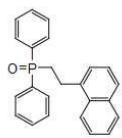
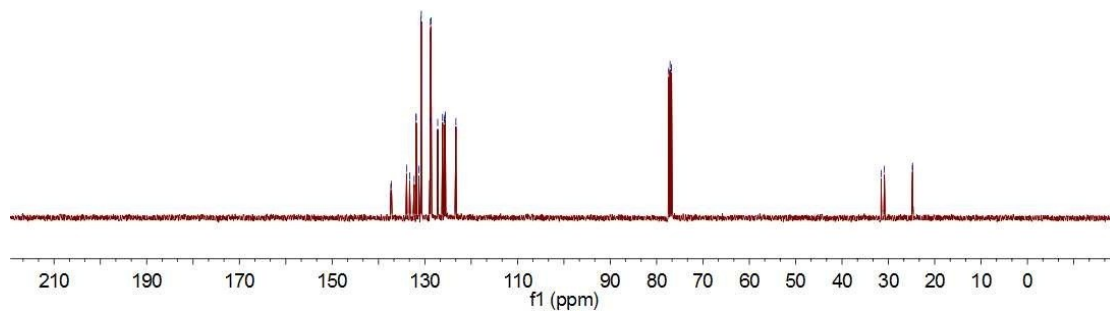


3g

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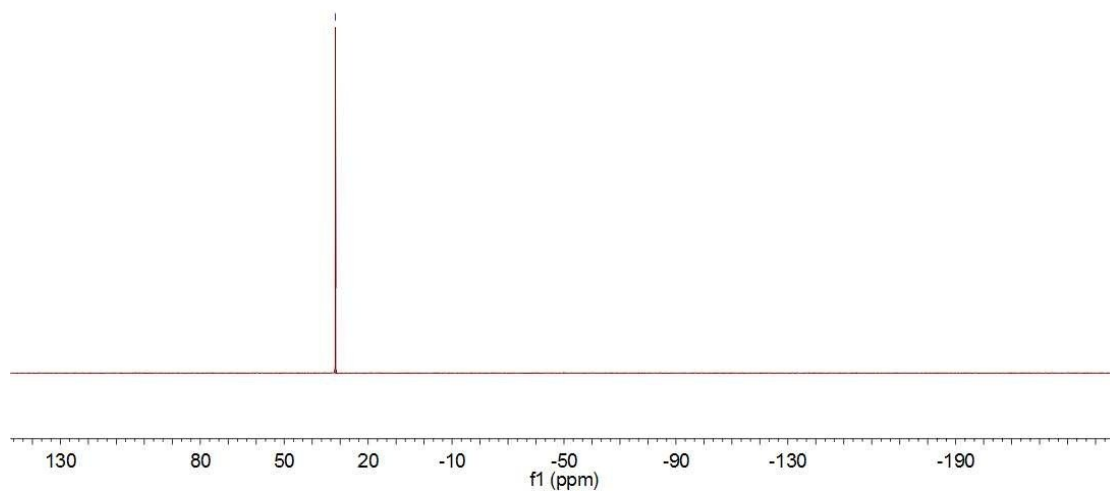
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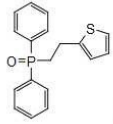
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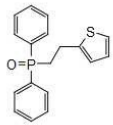
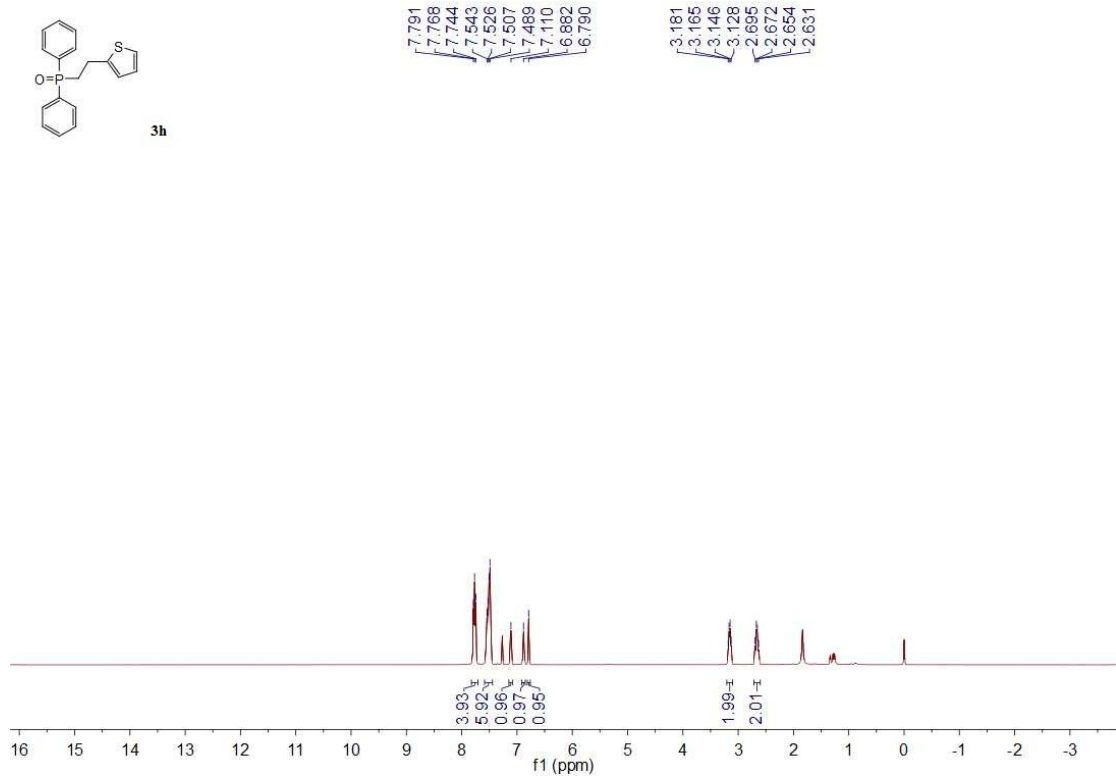
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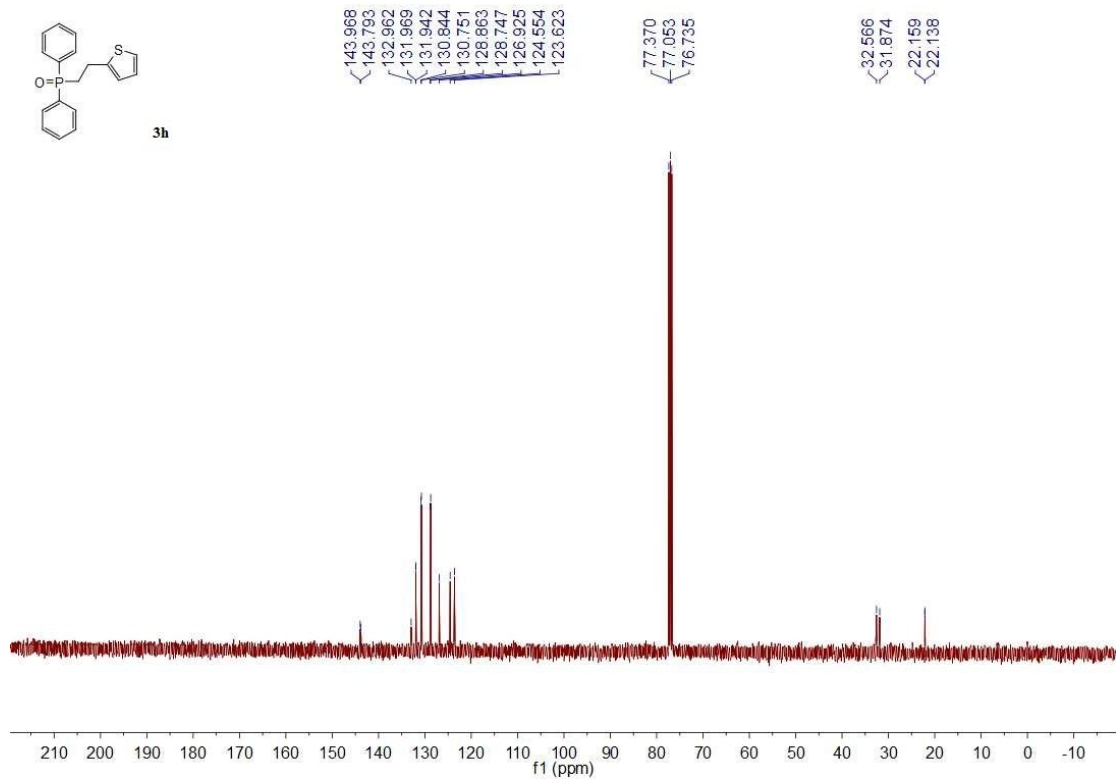


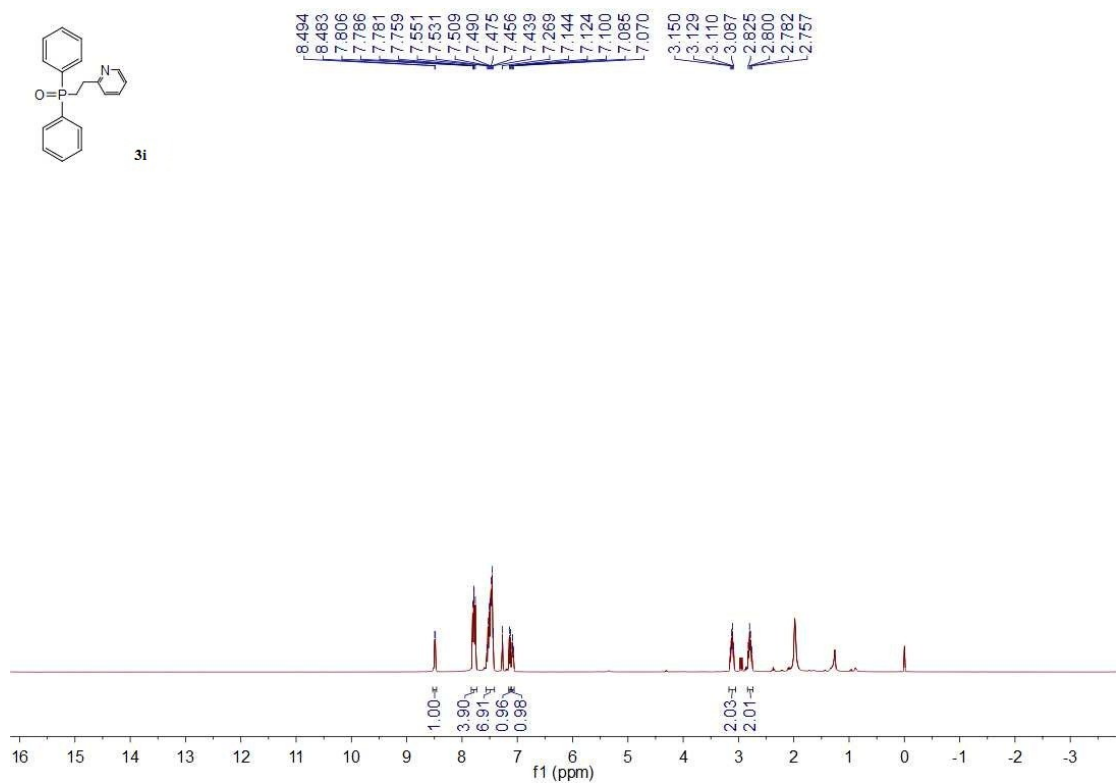
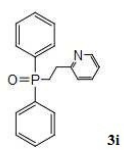
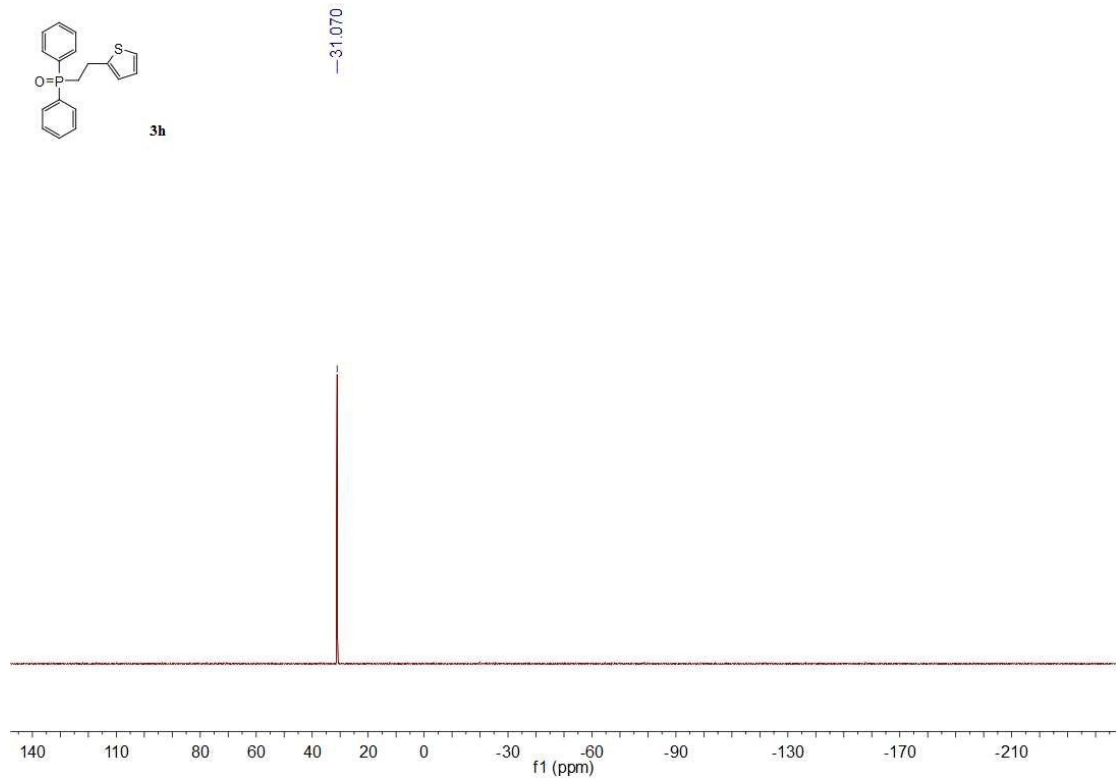
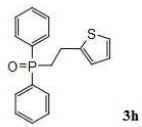


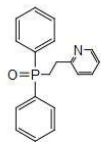
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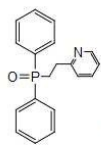
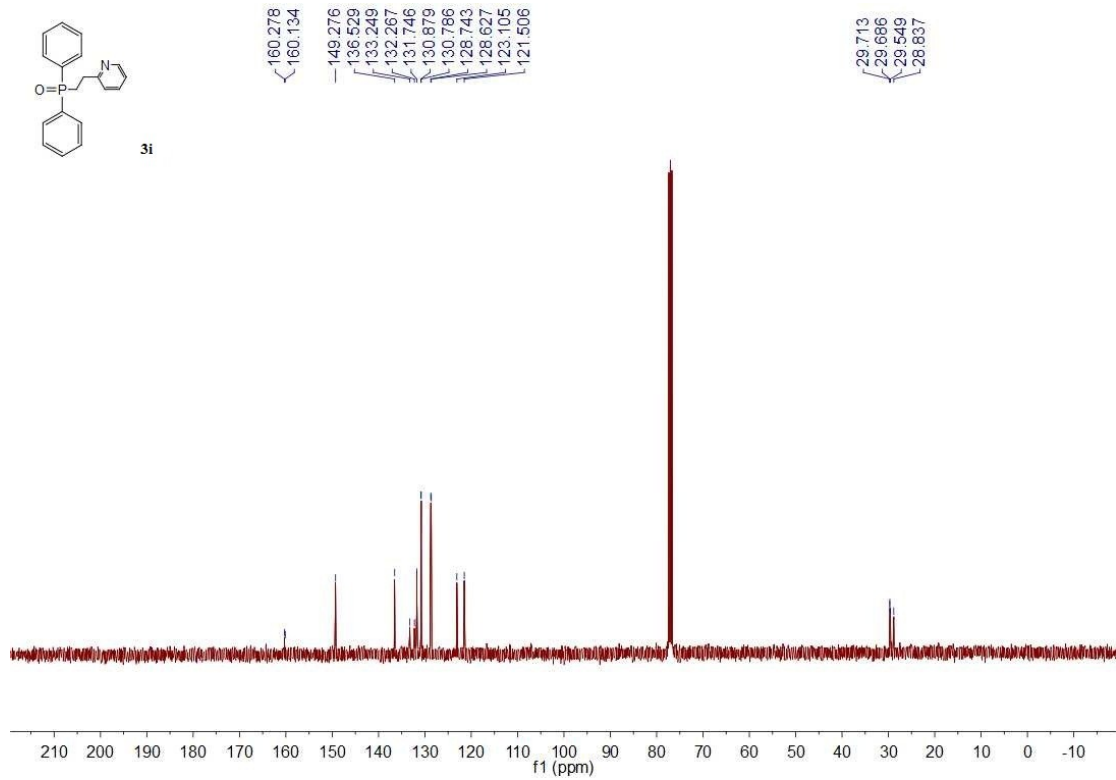
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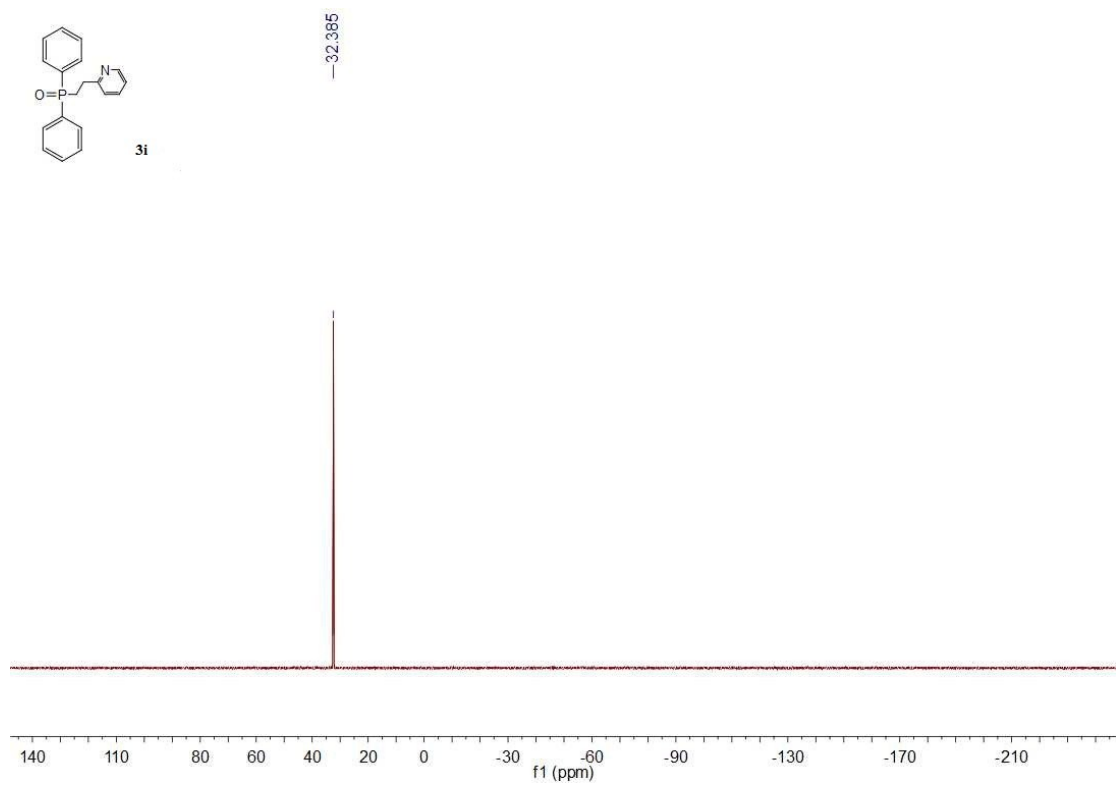


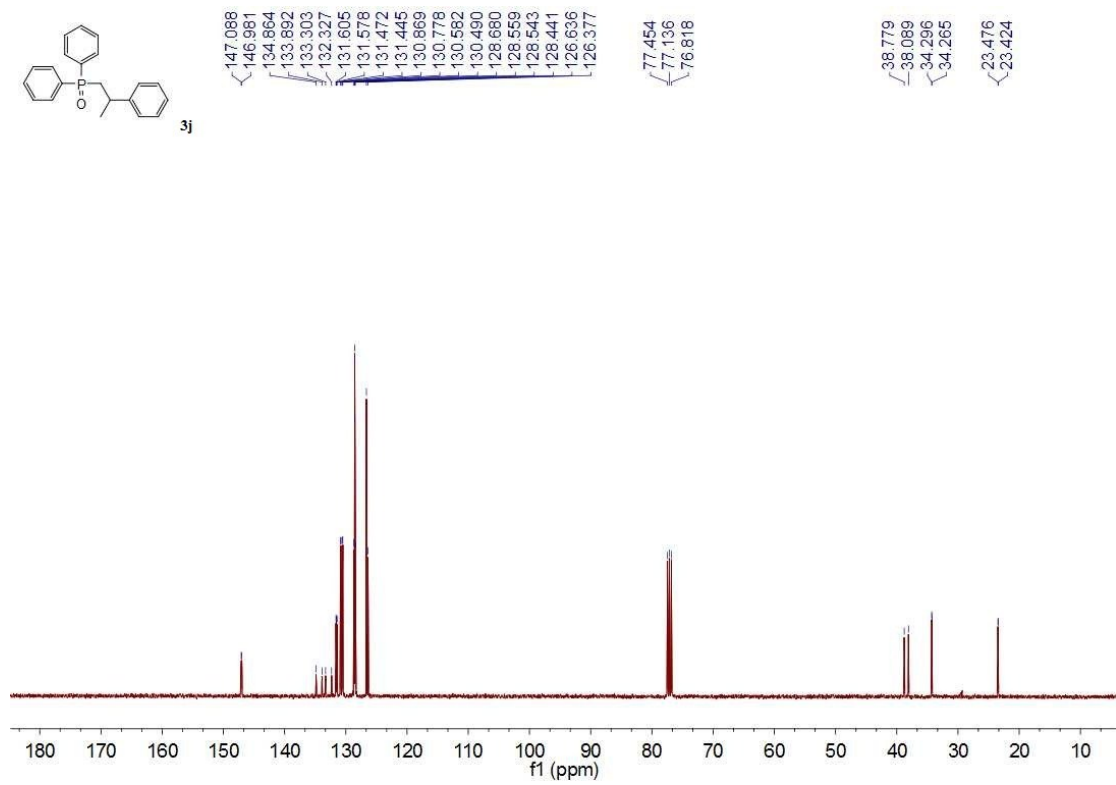
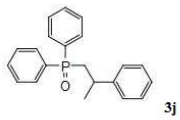
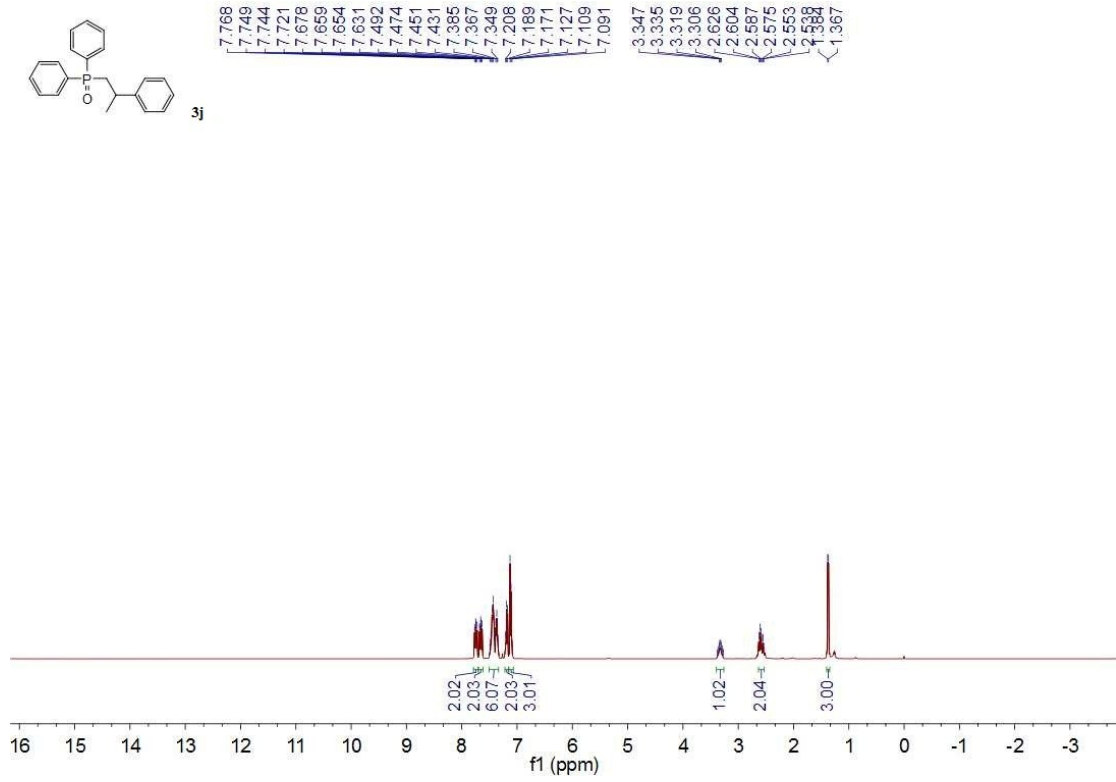
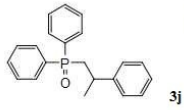


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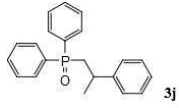


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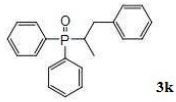
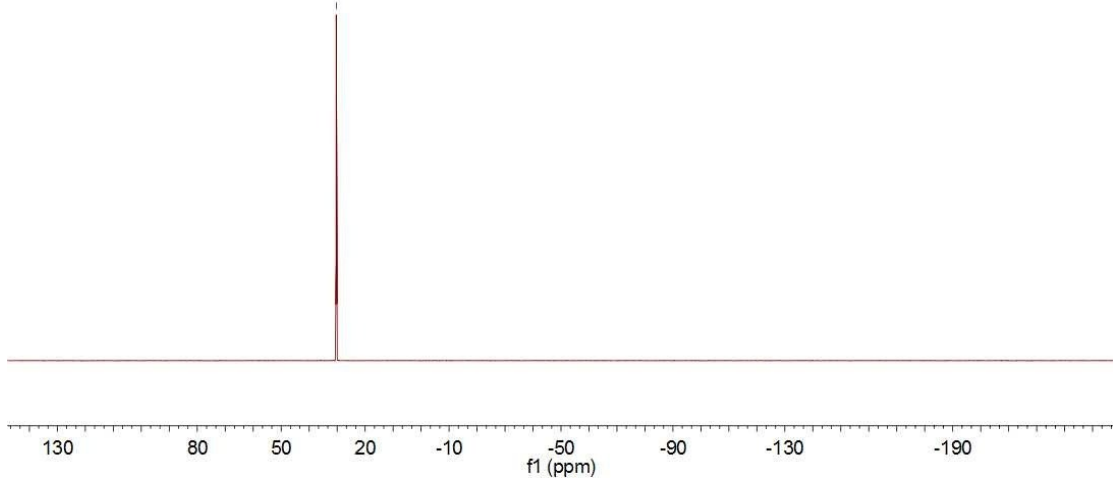






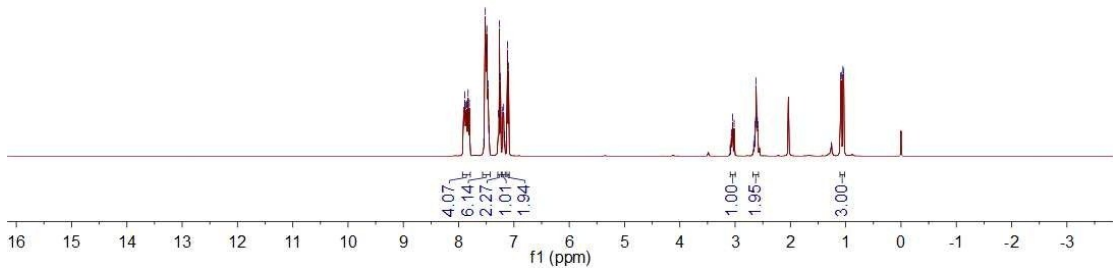


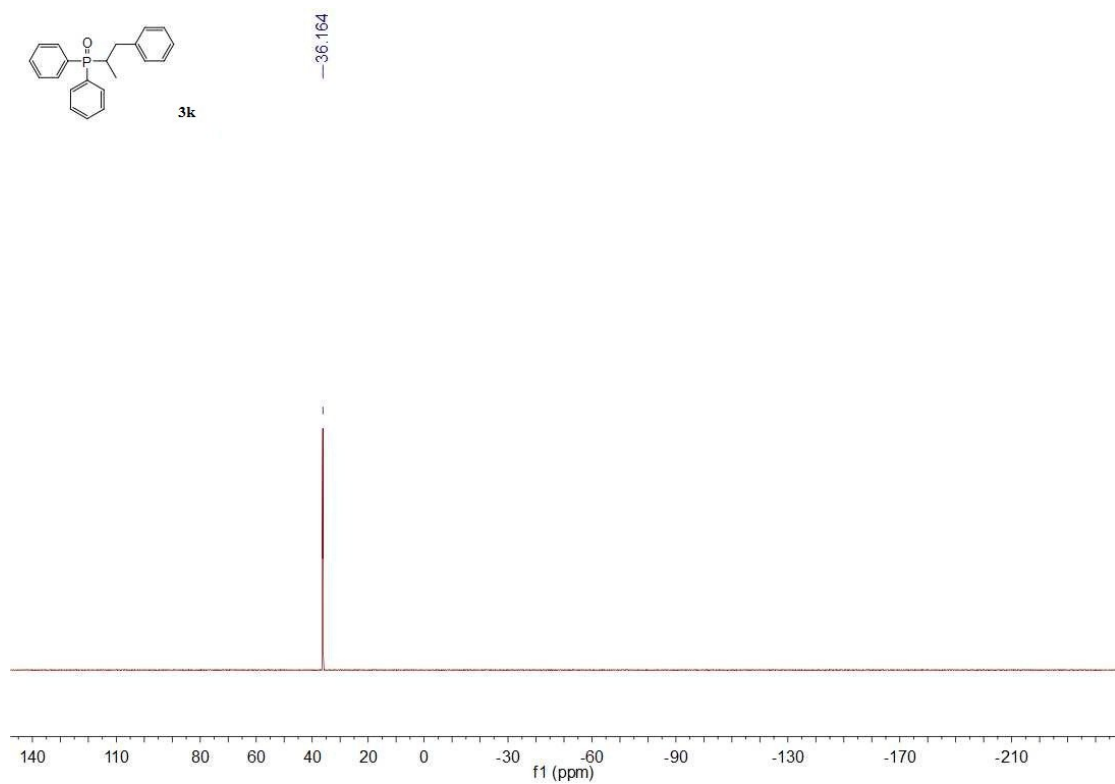
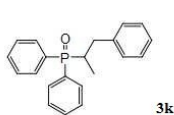
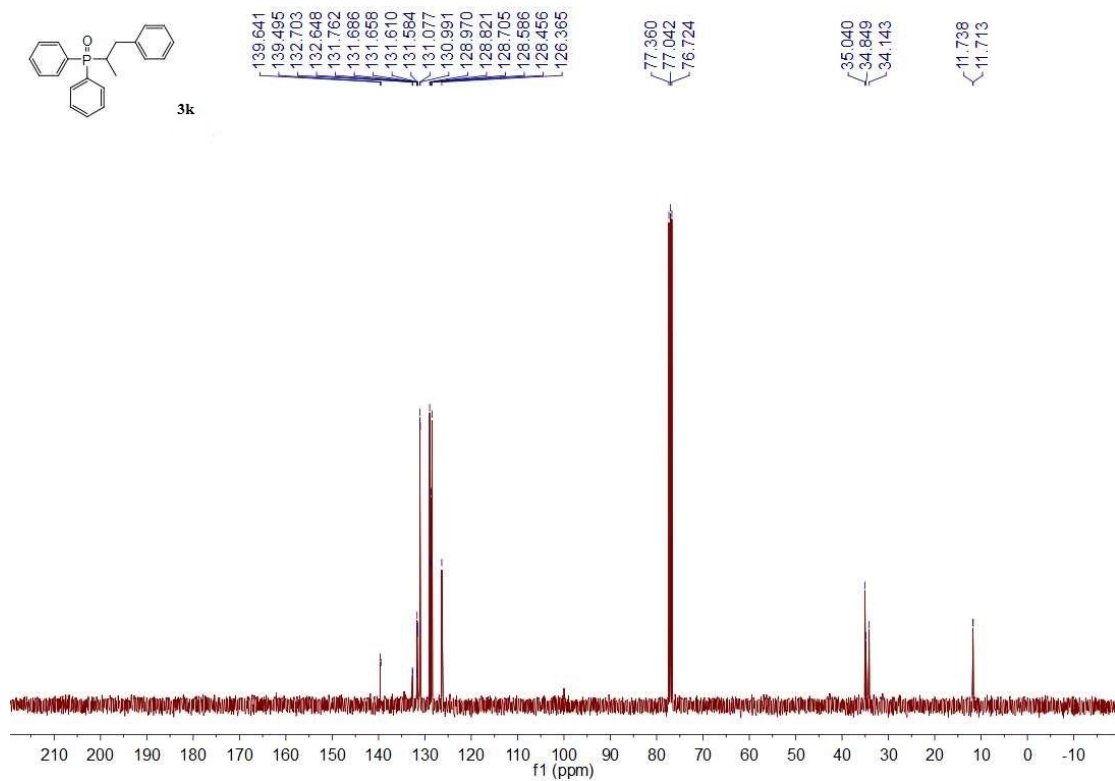
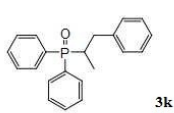
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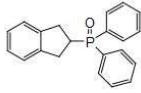


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7.547  
7.520  
7.508  
7.490  
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7.098

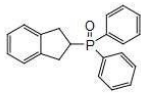
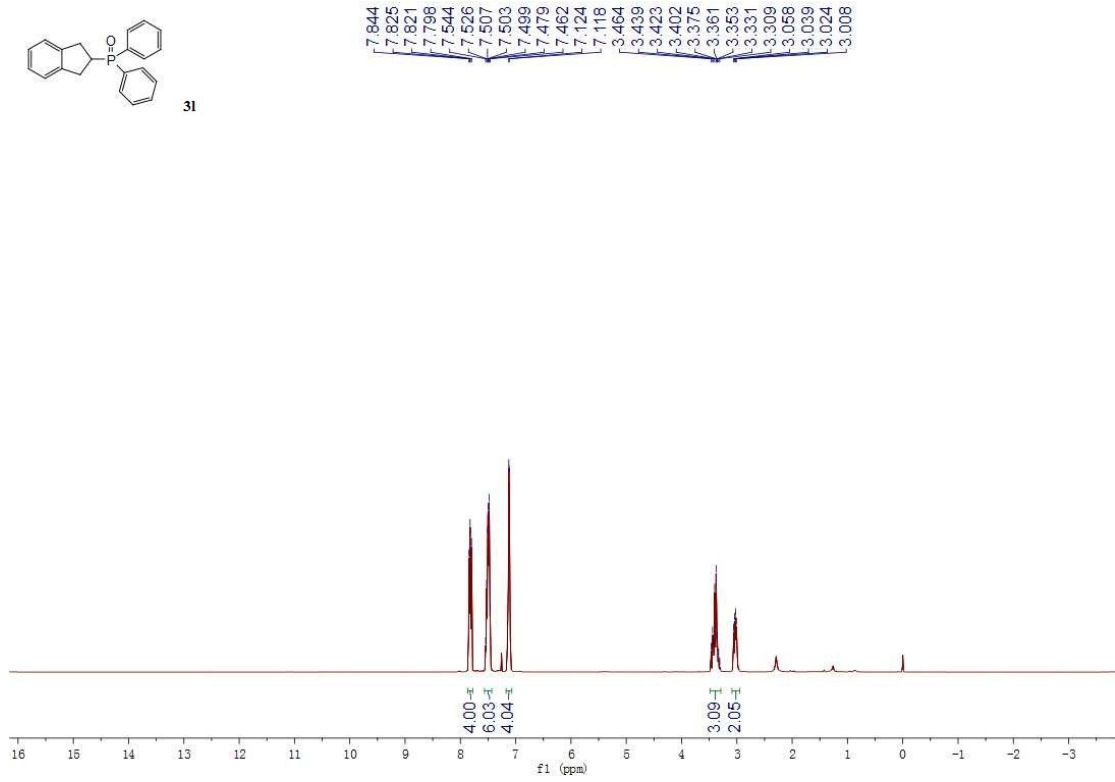
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2.620  
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2.589  
1.078  
1.051  
1.036



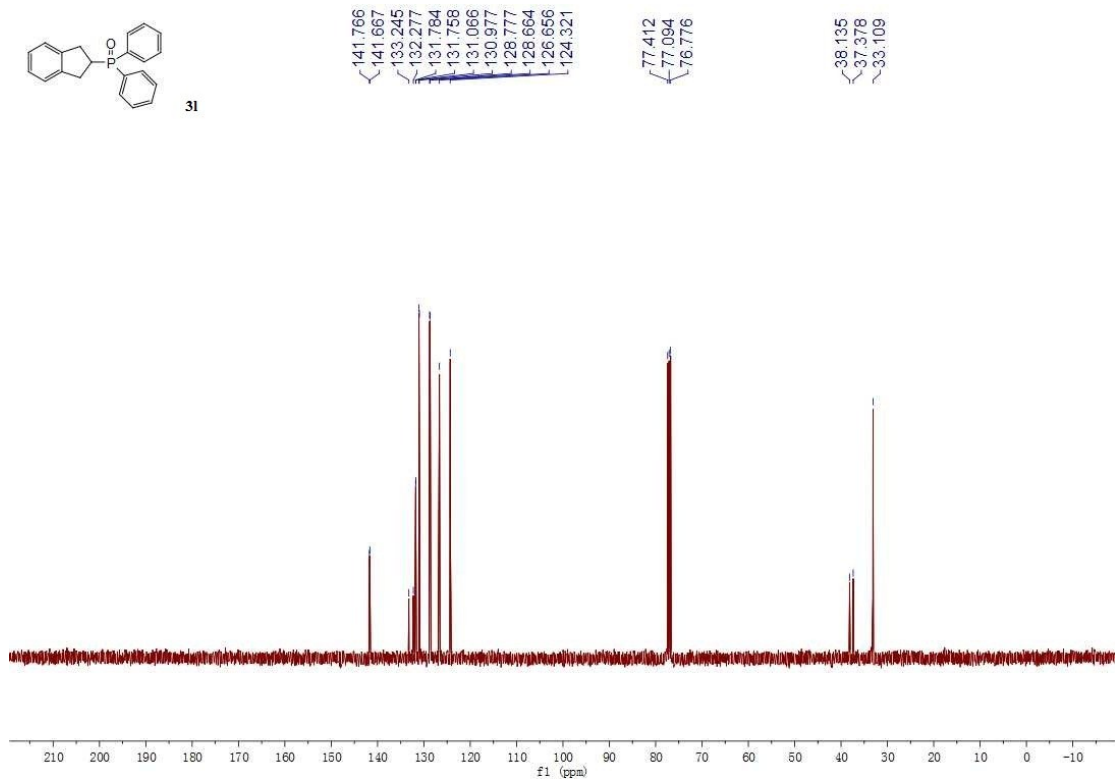


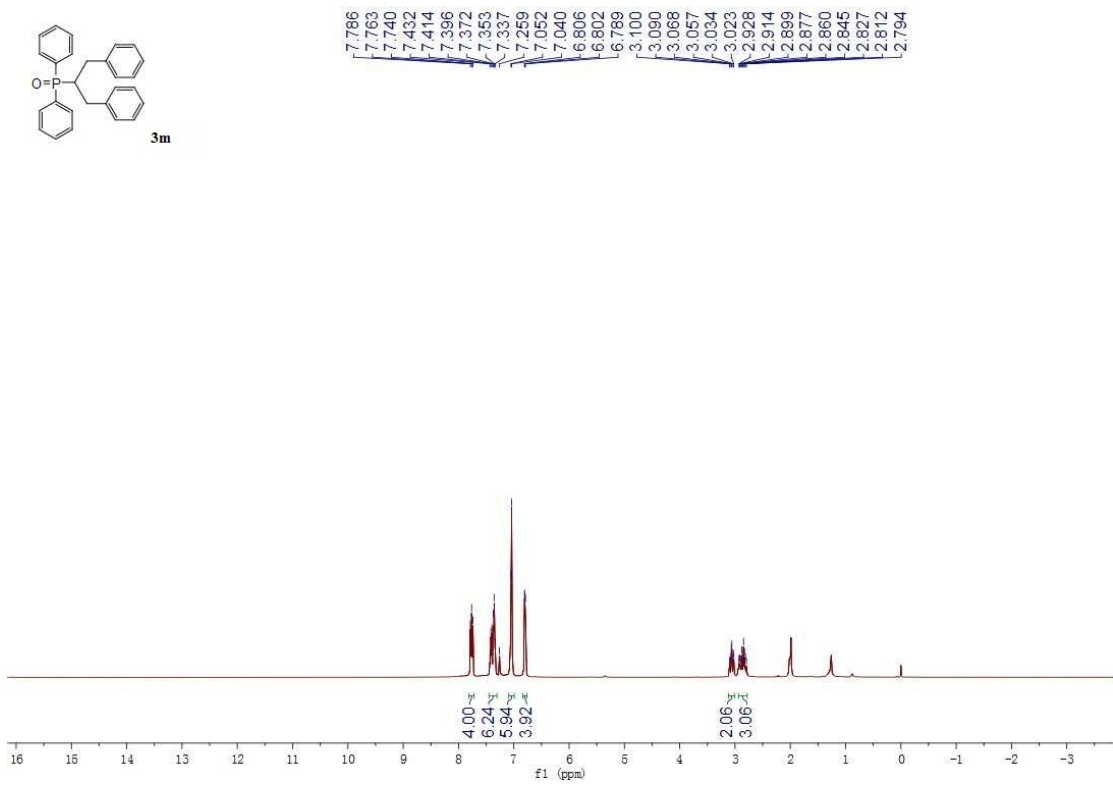
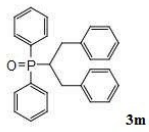
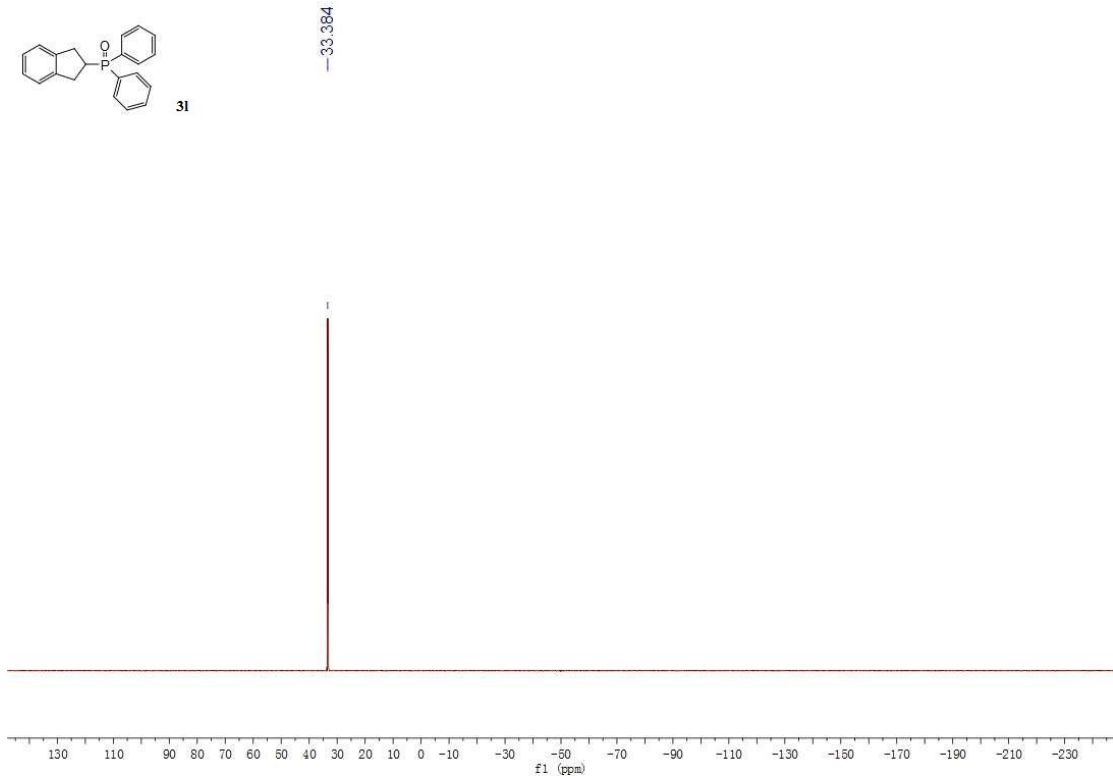
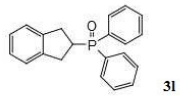


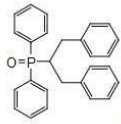
31



31



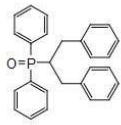
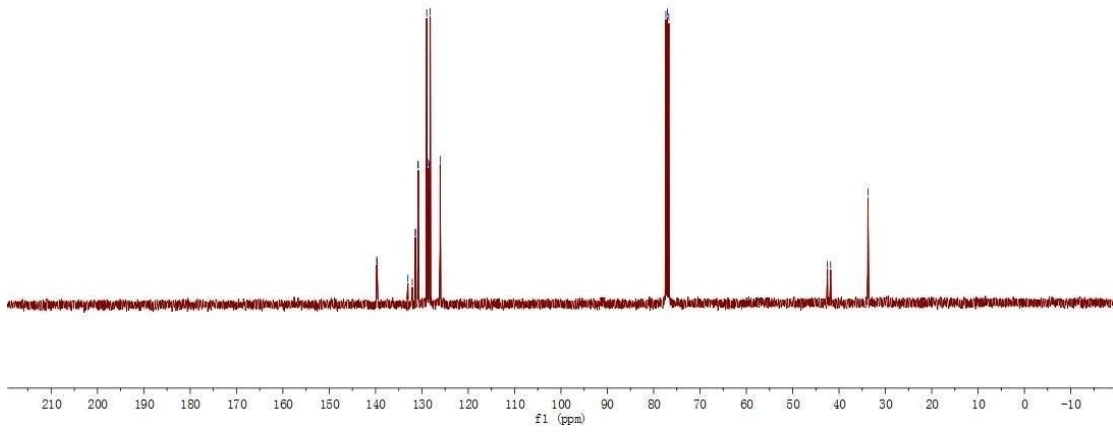




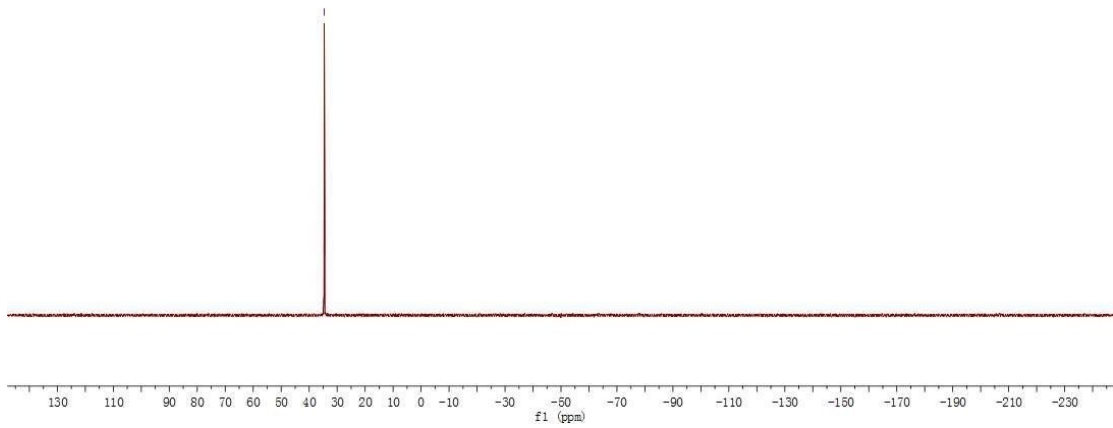
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128.197  
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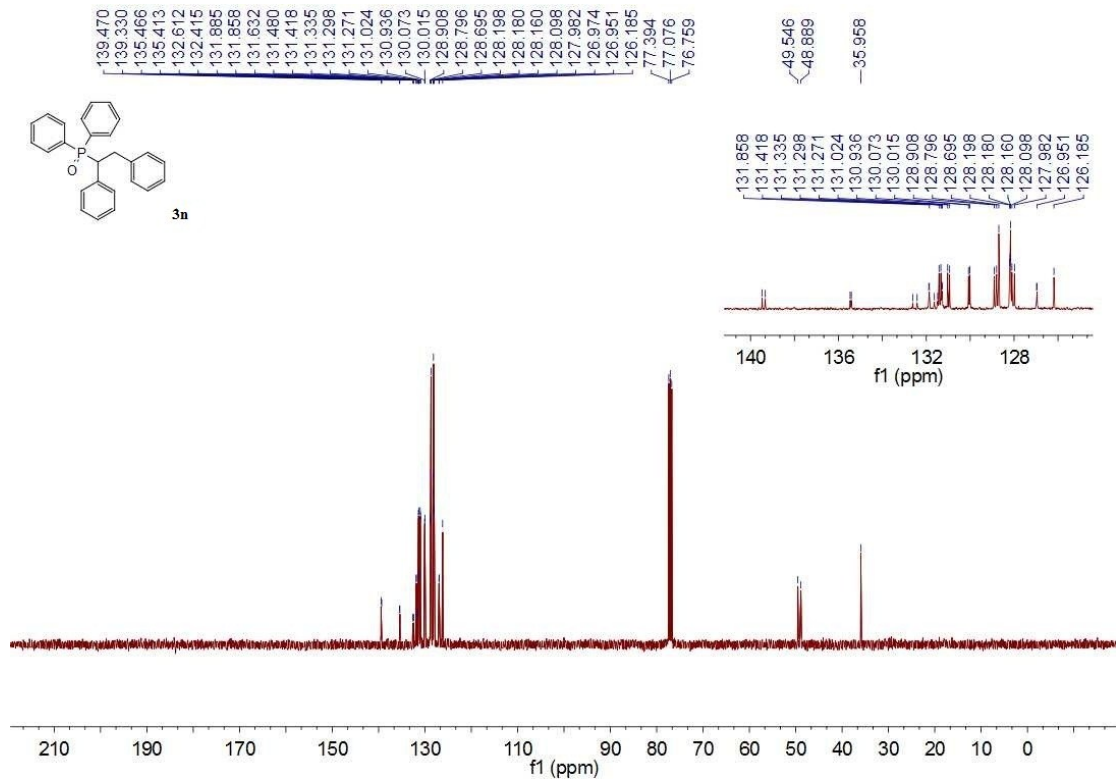
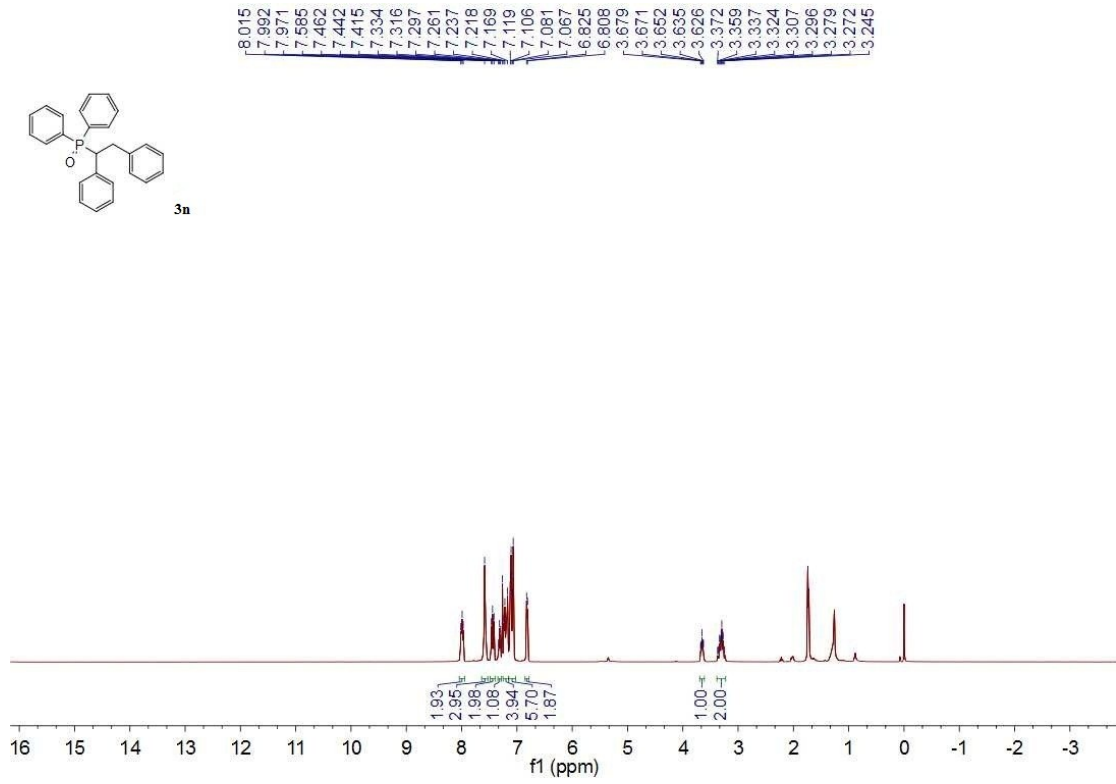
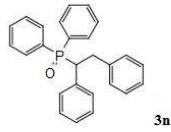
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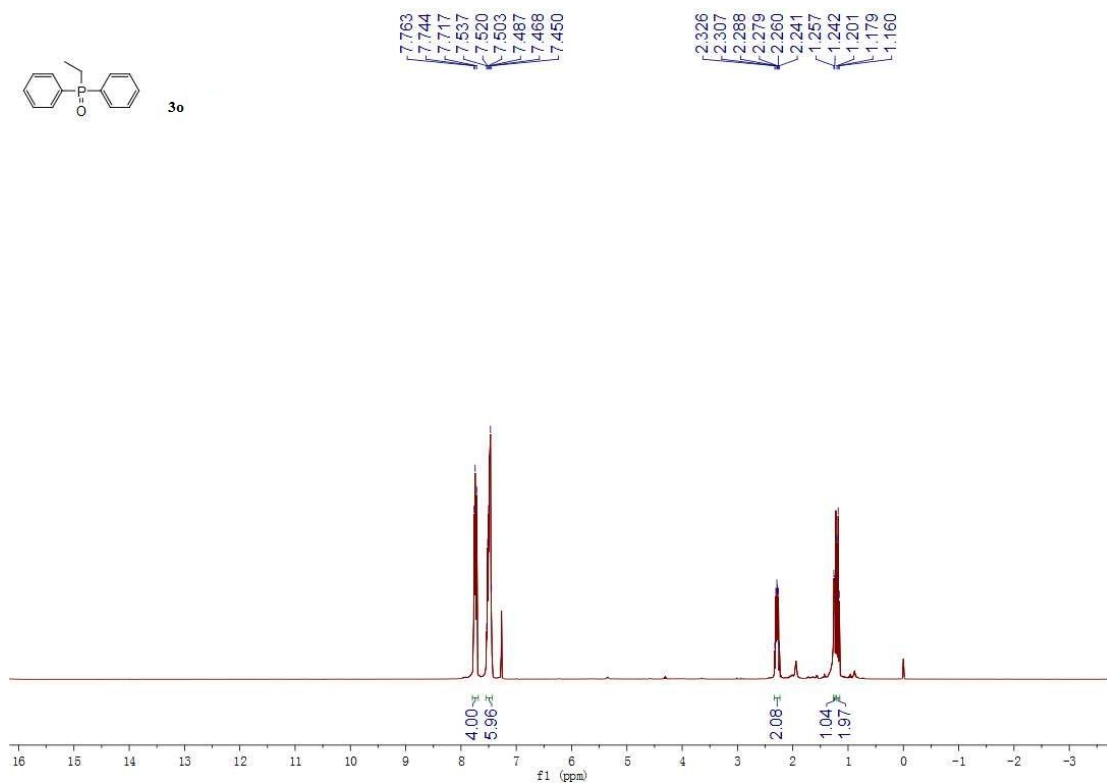
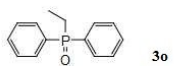
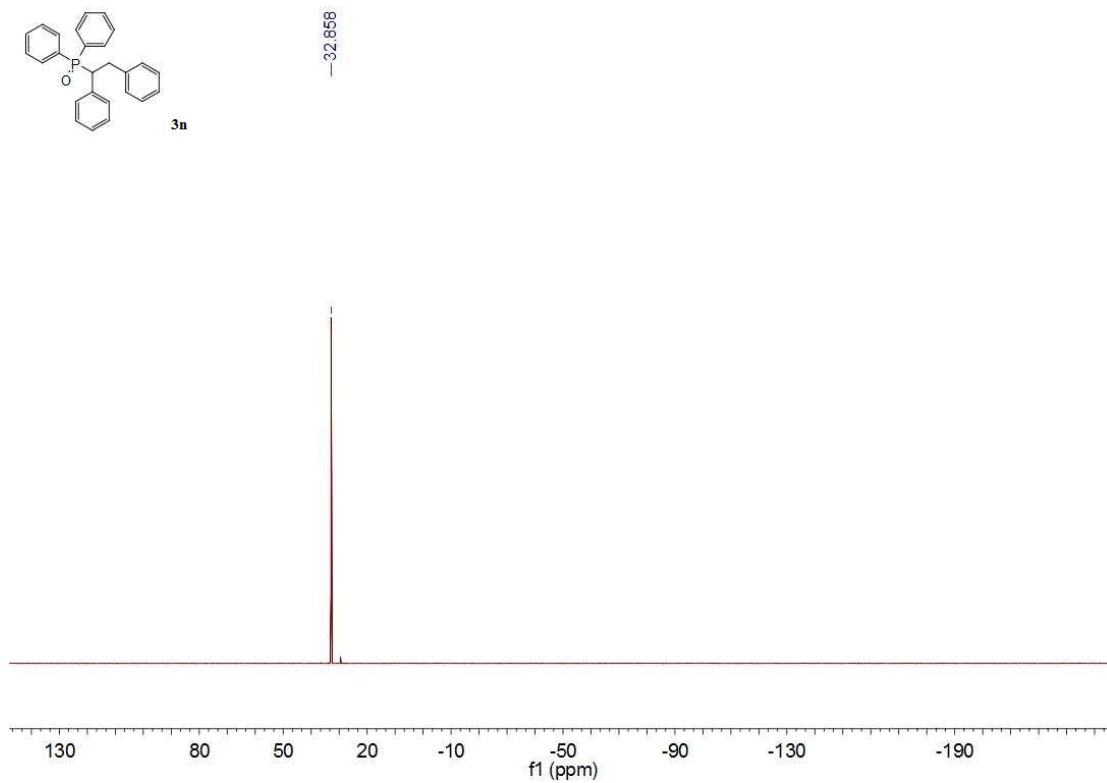
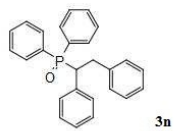
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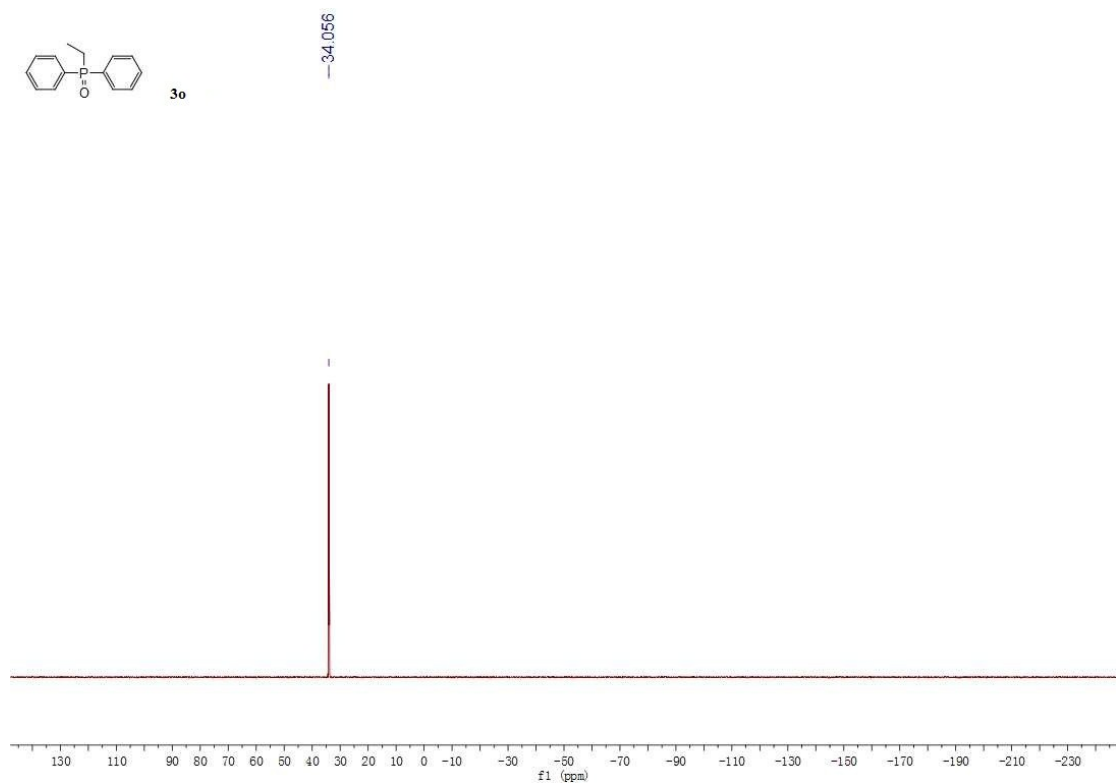
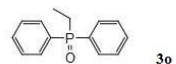
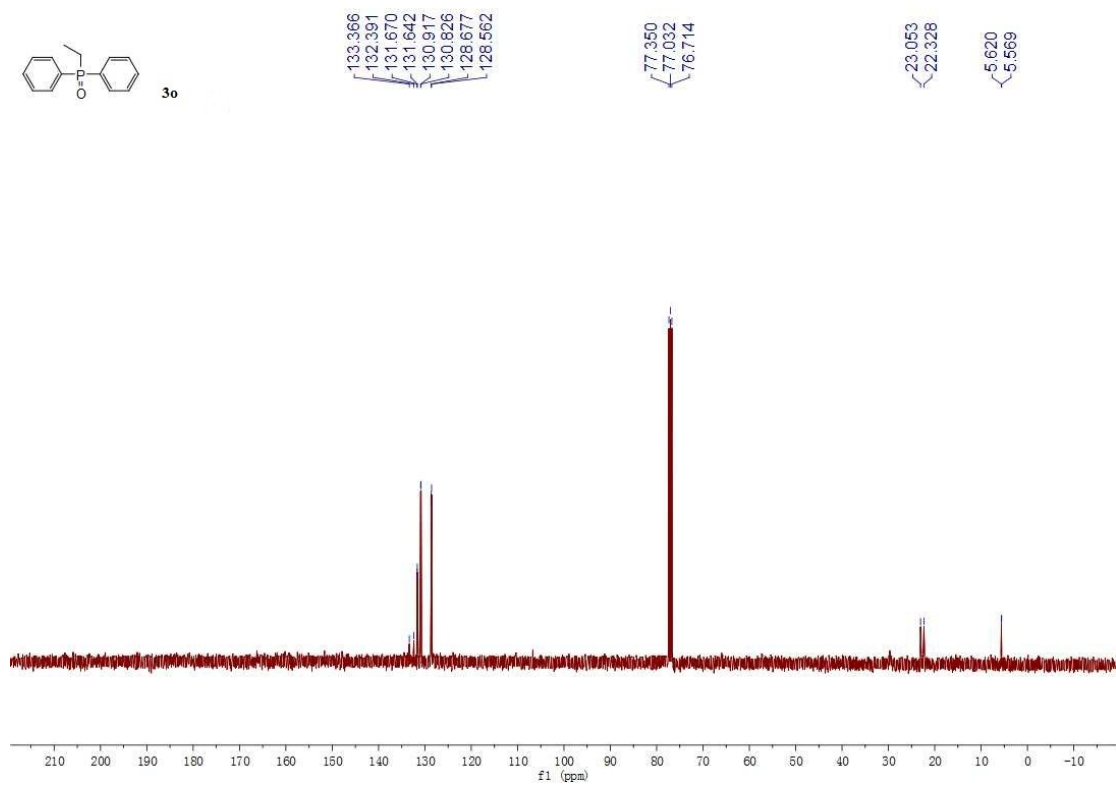
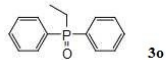


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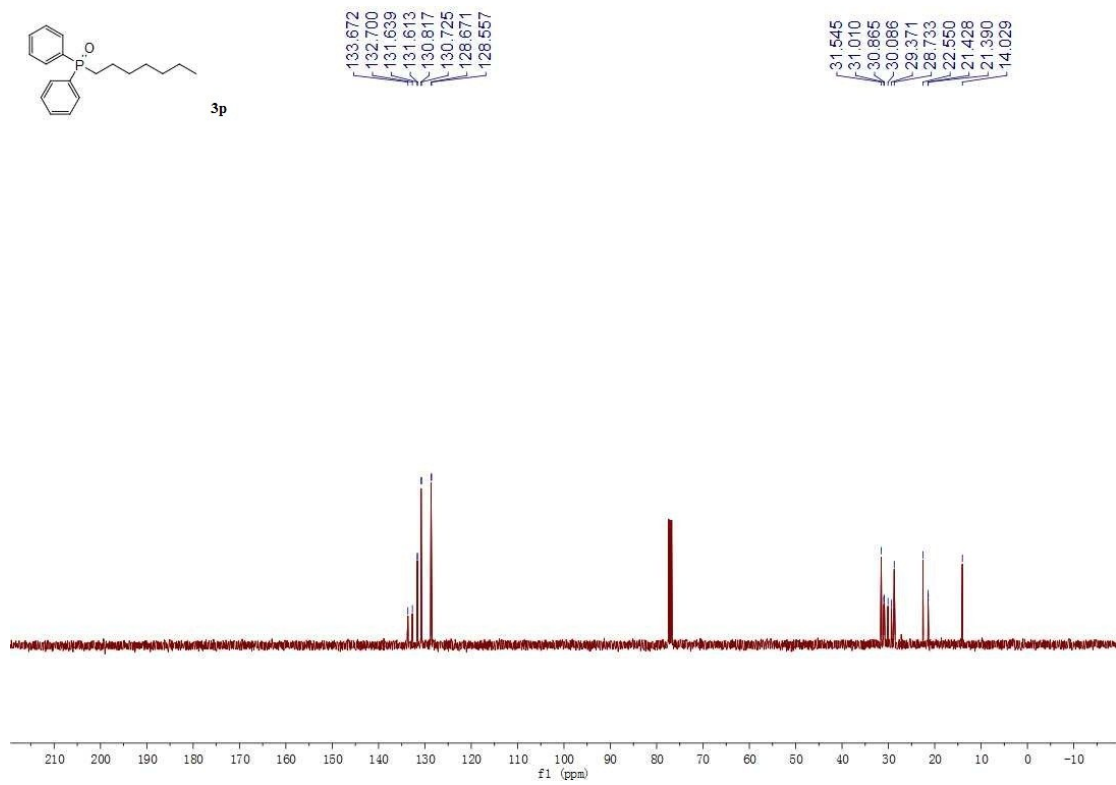
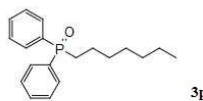
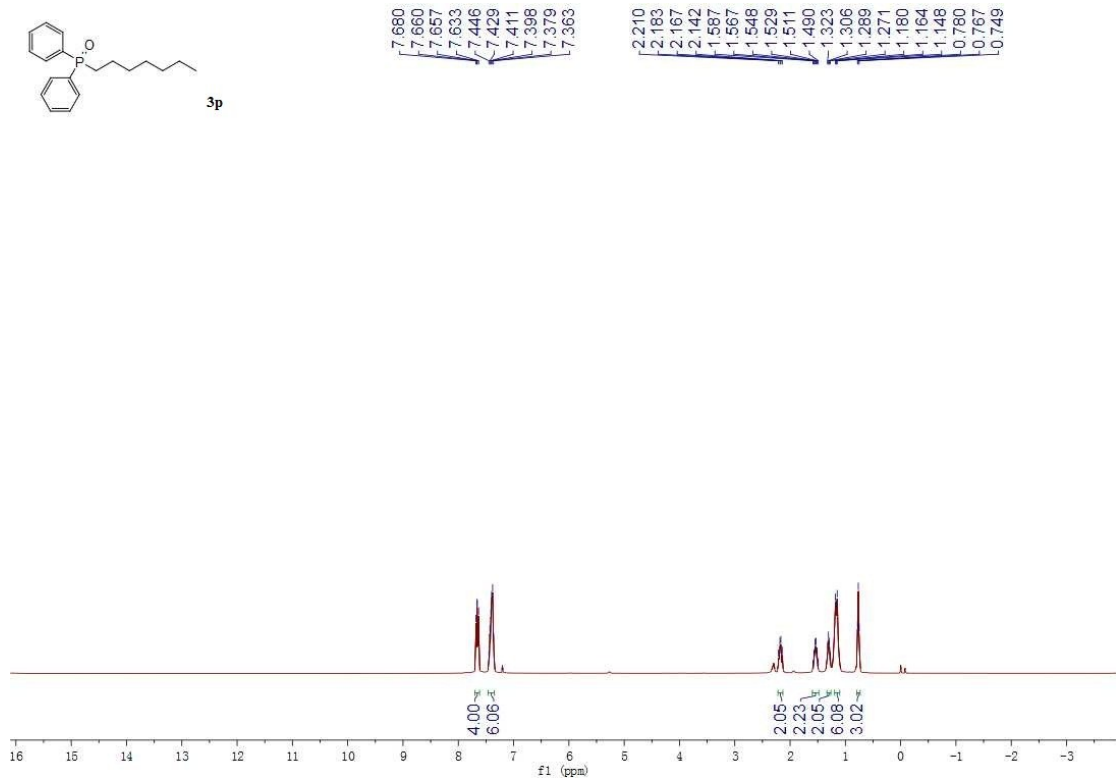
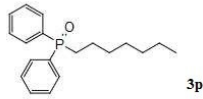


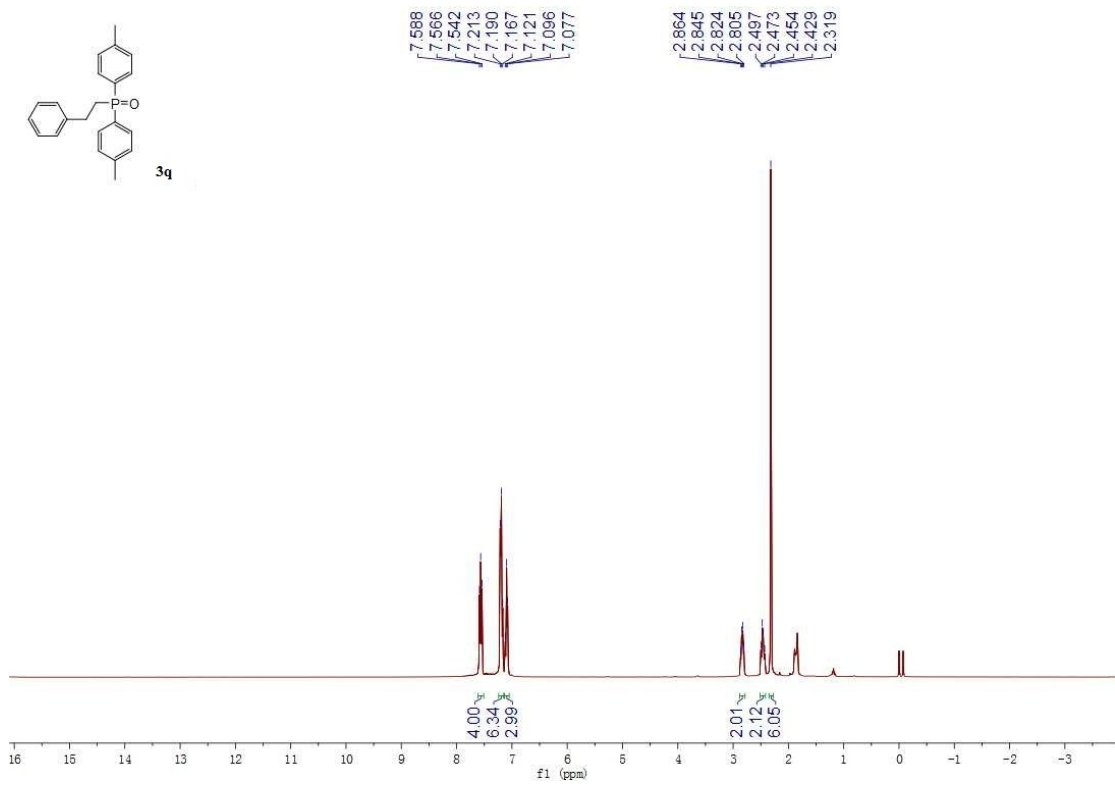
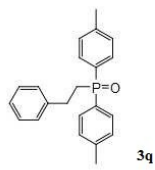
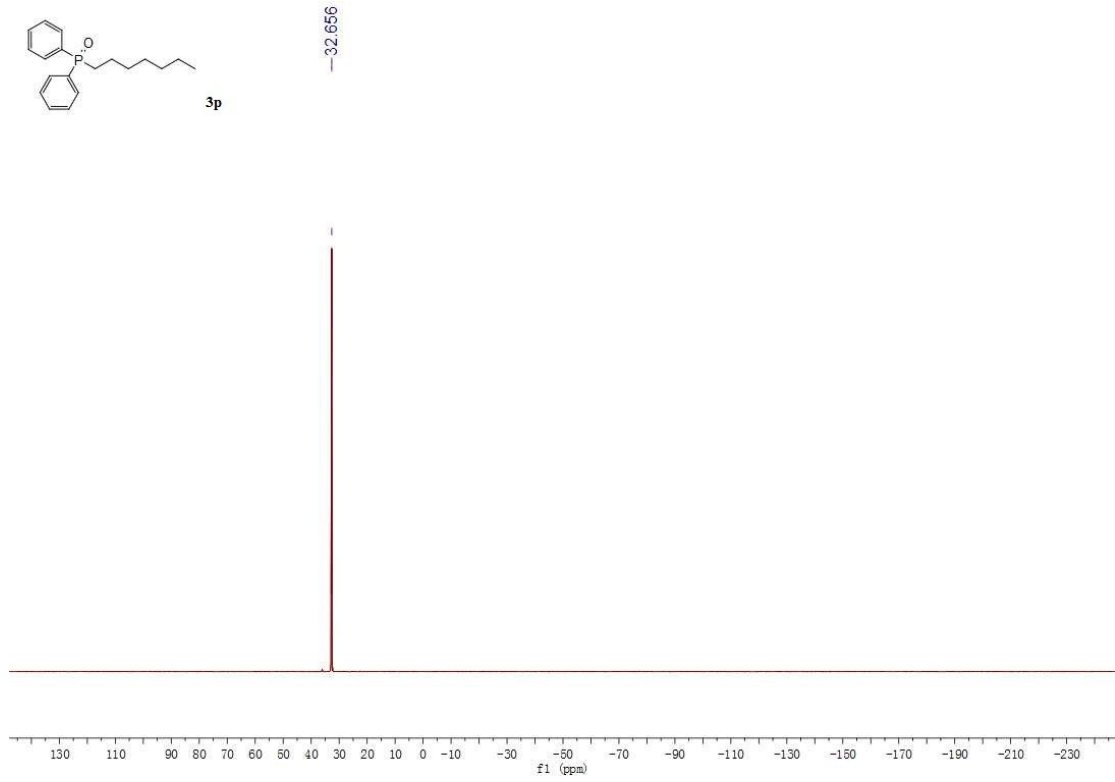
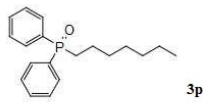


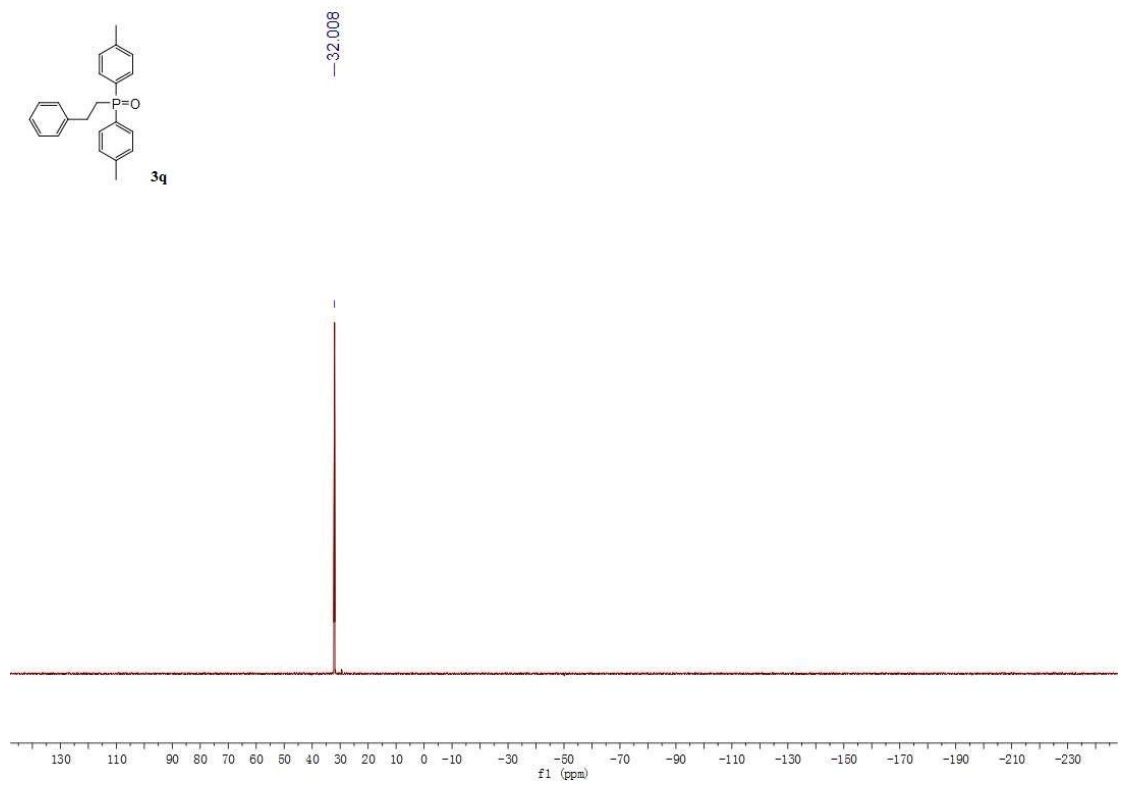
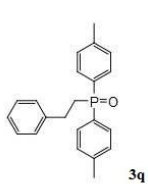
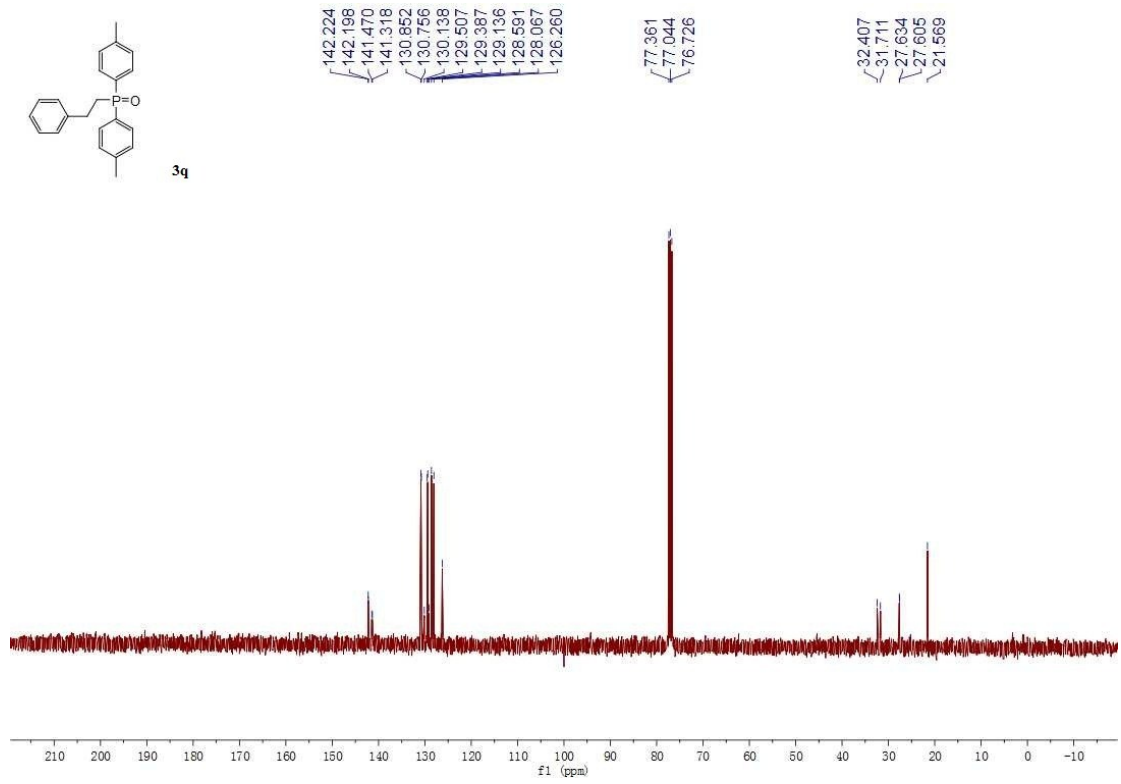
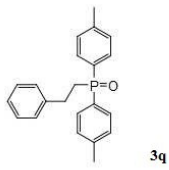


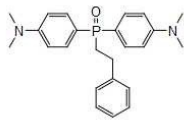




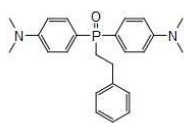
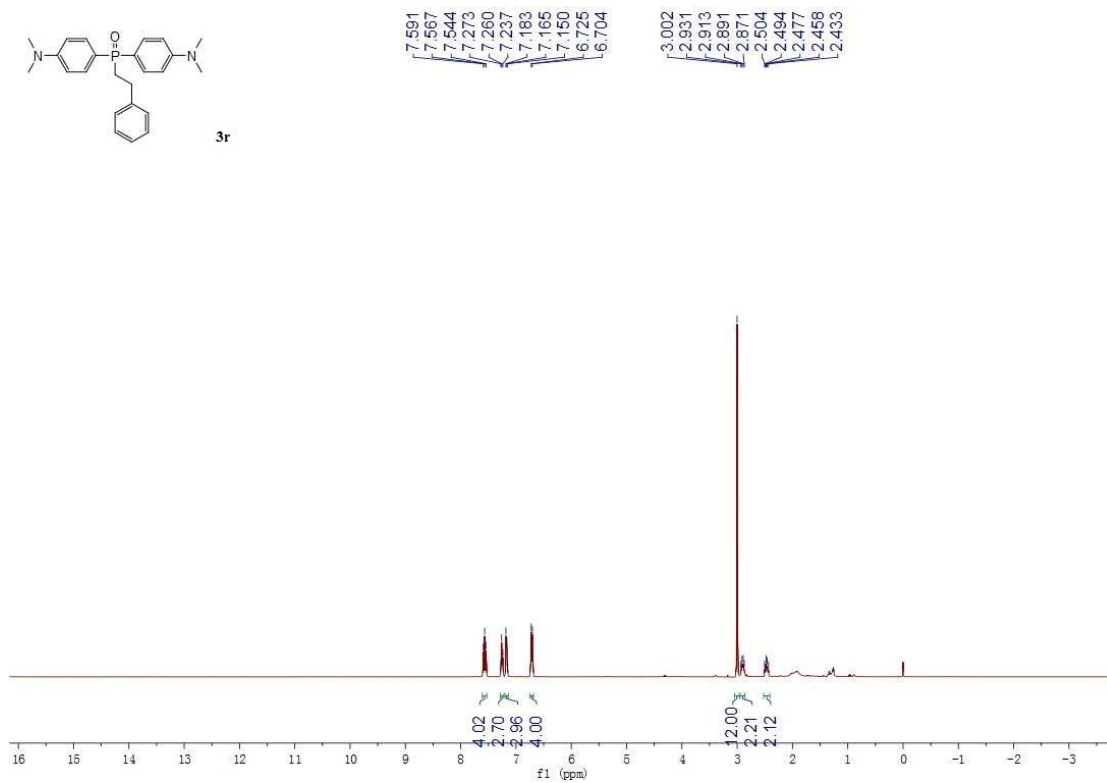




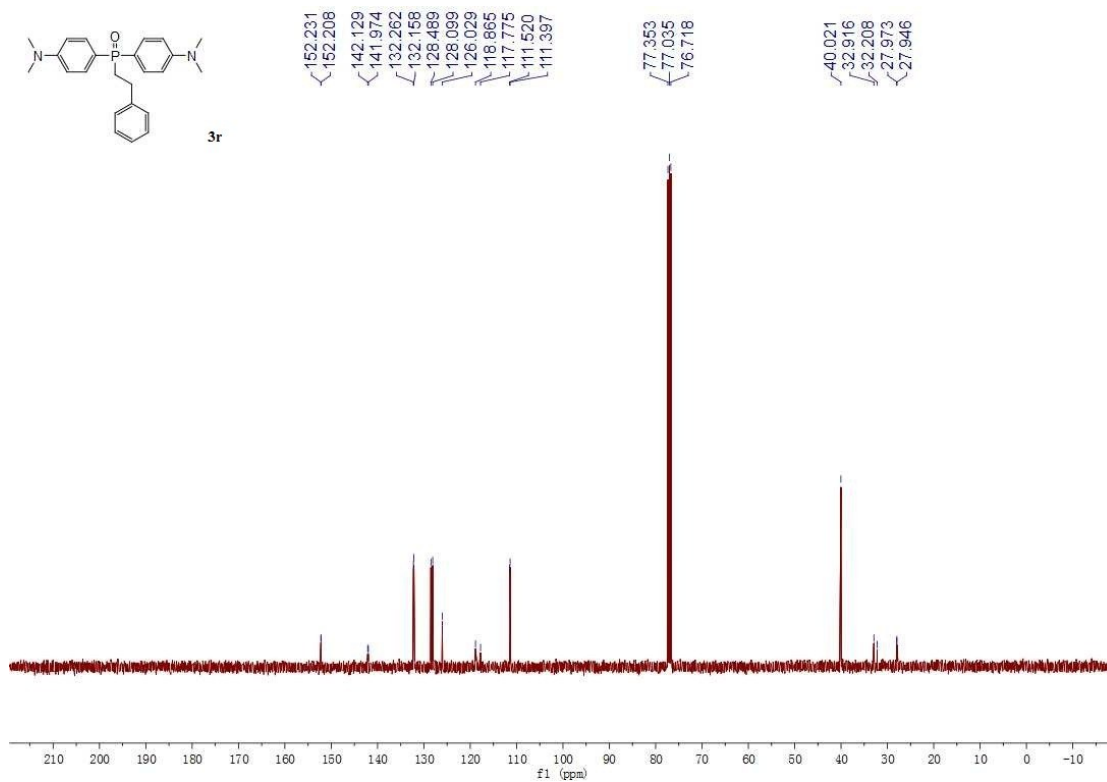


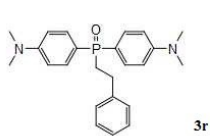


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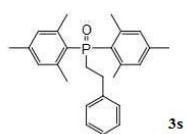
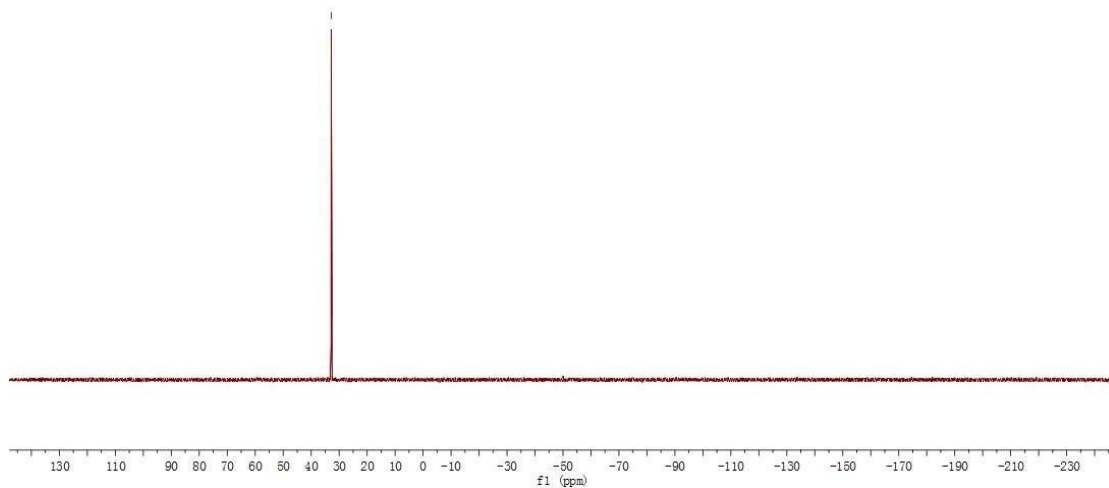


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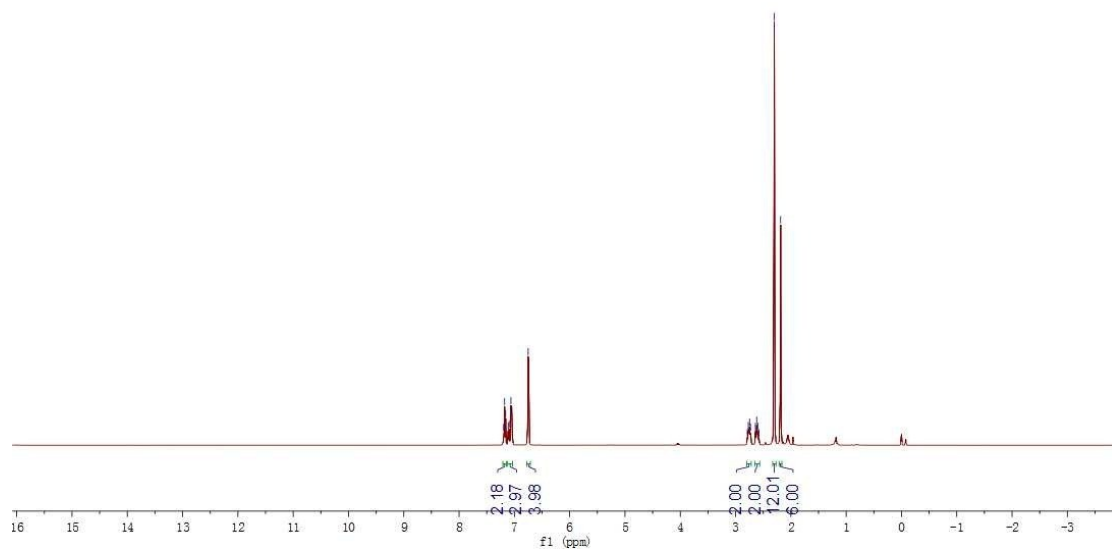


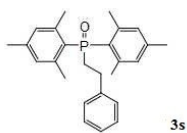
—32.841



7.194  
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7.062  
7.044  
6.750

2.787  
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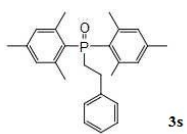
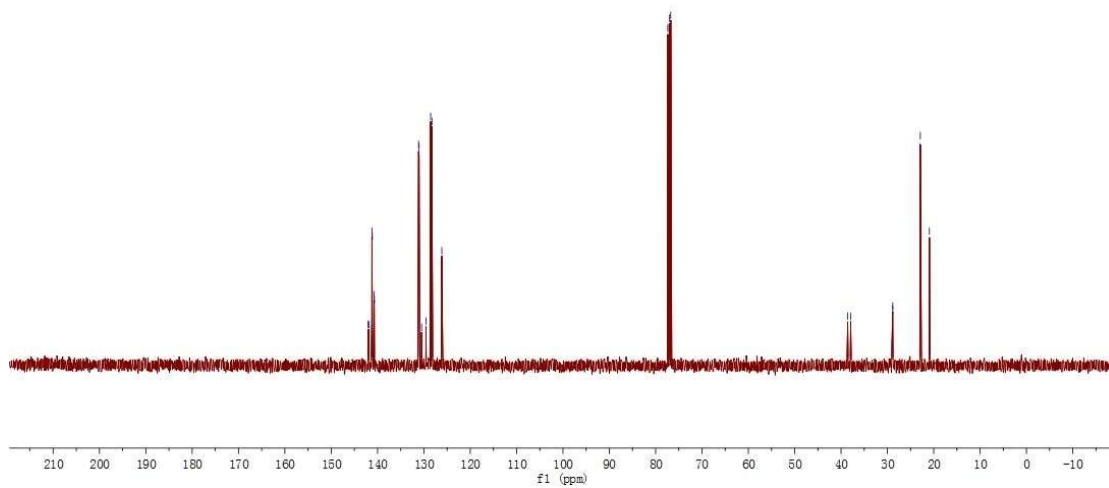




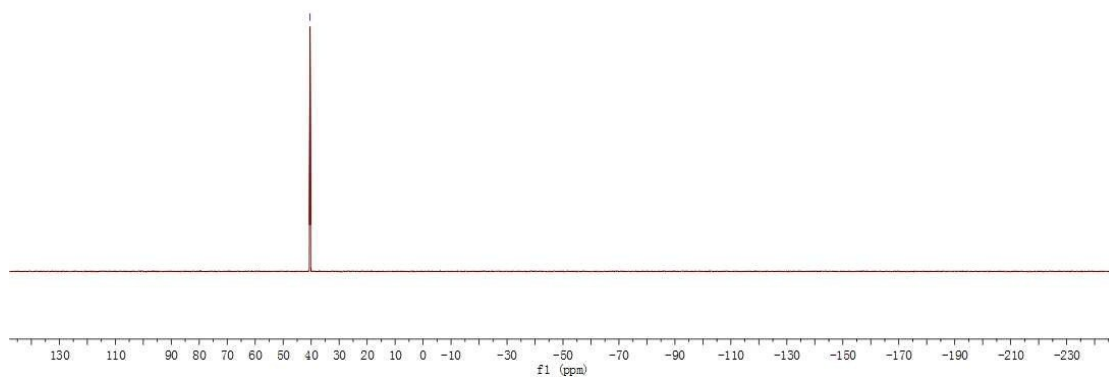
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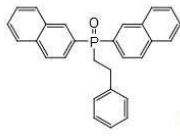
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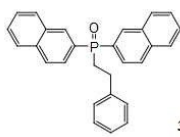
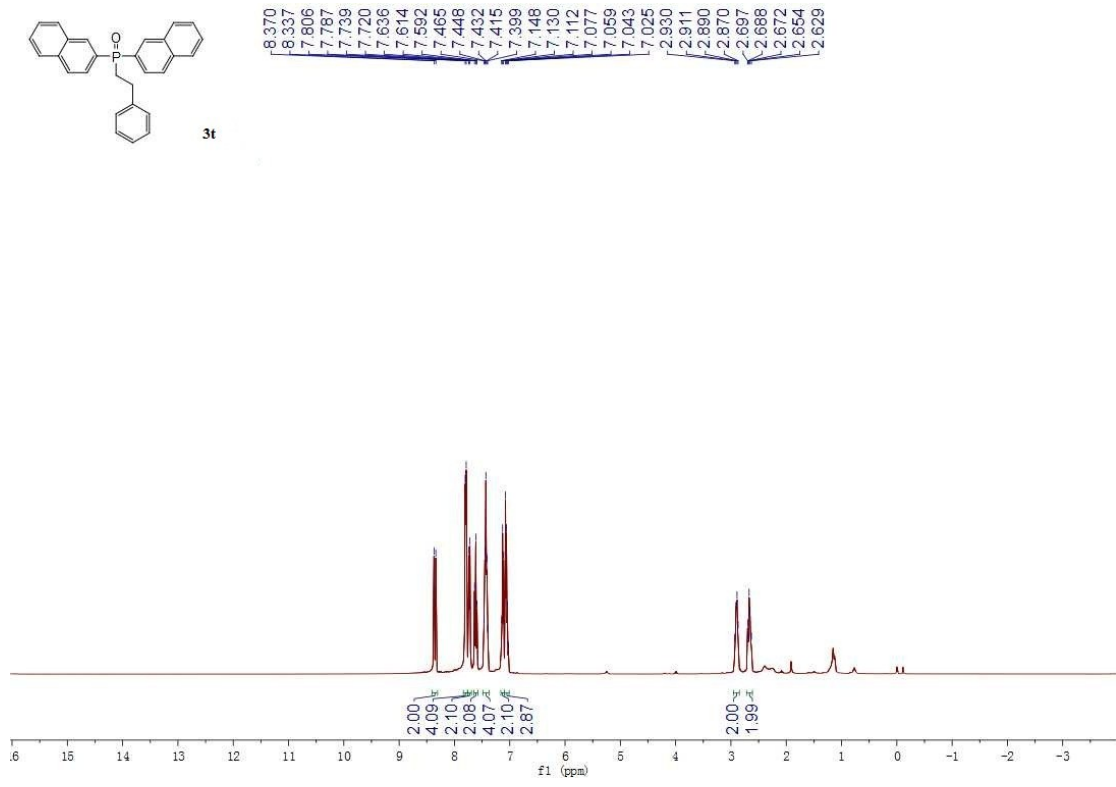


40.391

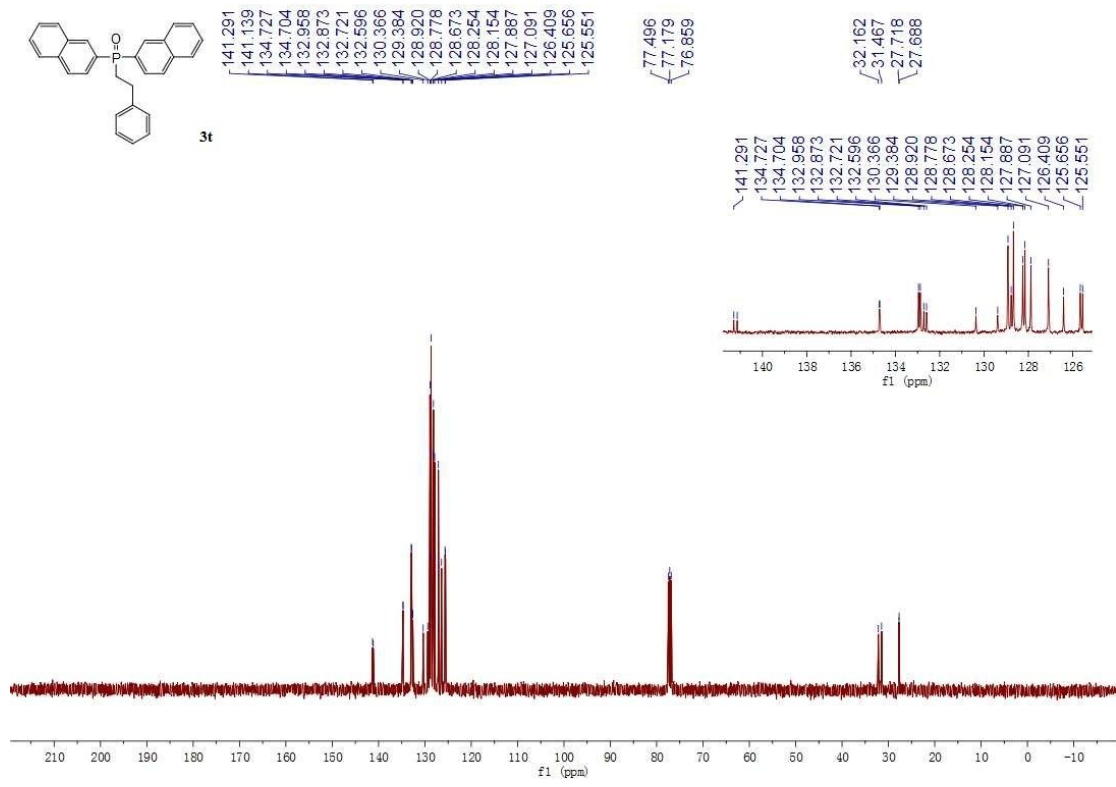


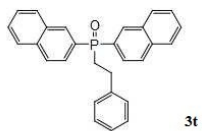


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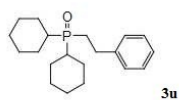
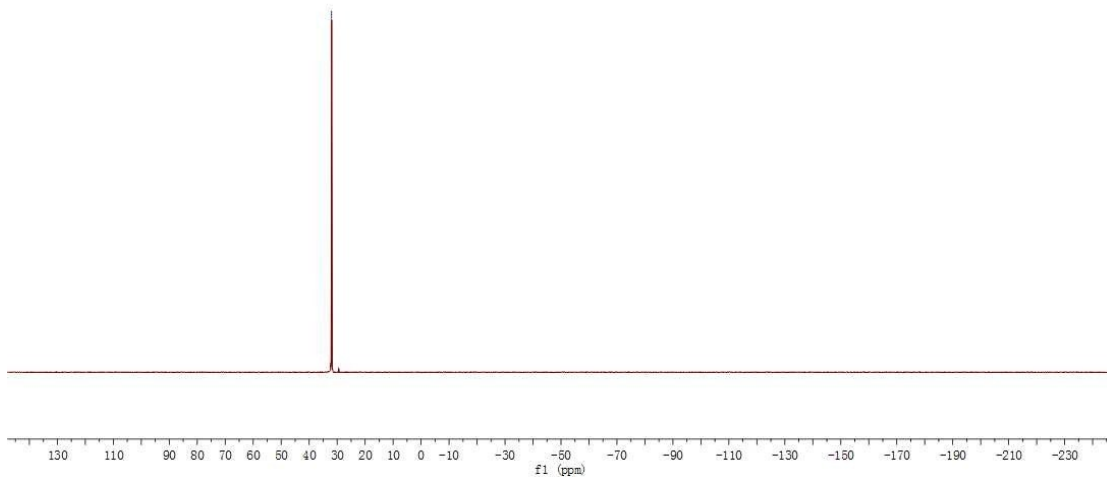


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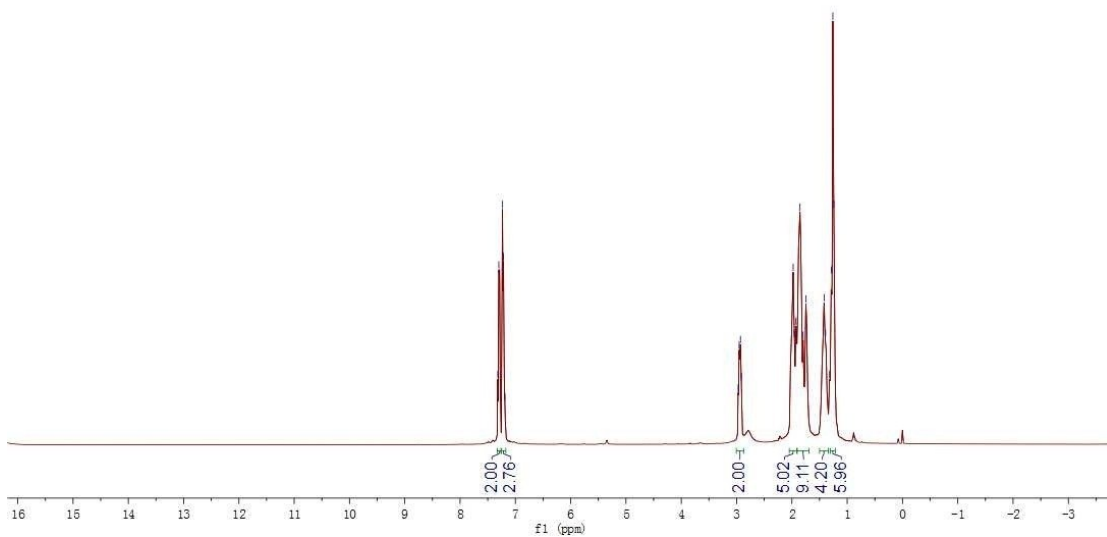




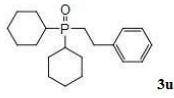
-31.993



7.318  
7.300  
7.284  
7.234  
7.216  
7.190  
2.972  
2.954  
2.930  
2.914  
1.977  
1.956  
1.926  
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1.797  
1.746  
1.417  
1.391  
1.318  
1.284  
1.259  
1.240



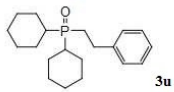
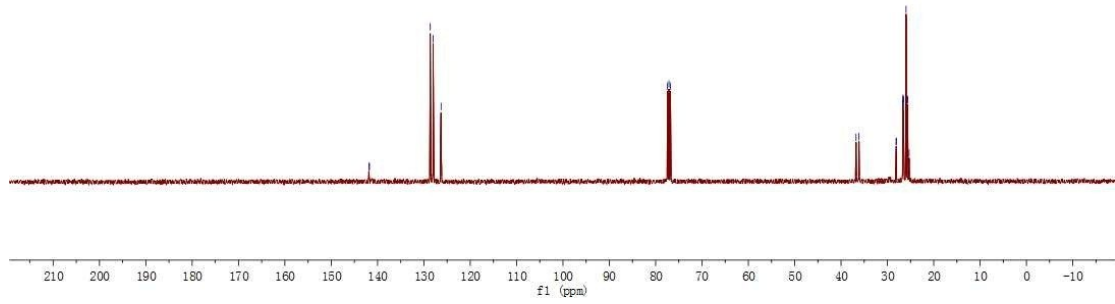




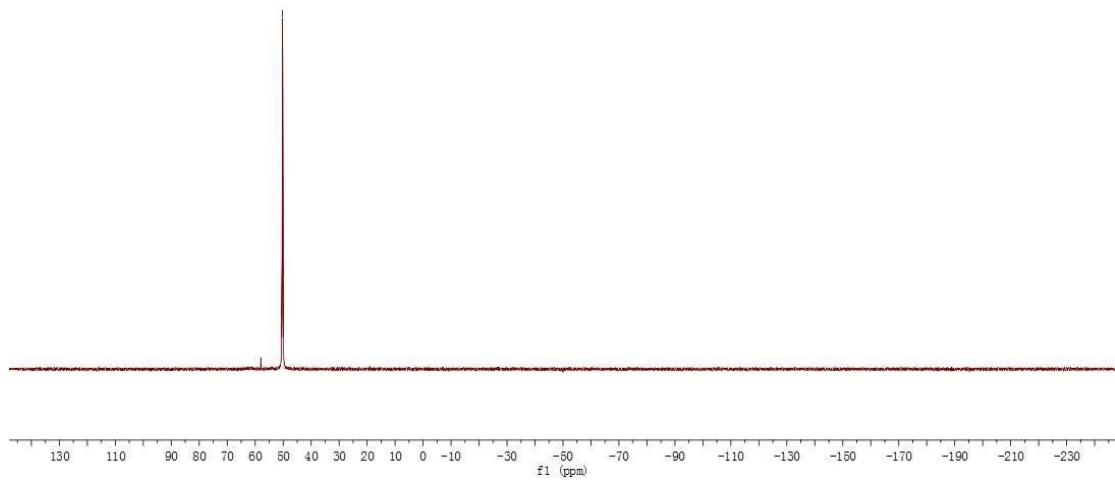
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141.754  
128.630  
128.011  
126.296

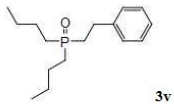
77.444  
77.126  
76.807

36.761  
36.127  
28.115  
28.080  
26.690  
26.659  
26.568  
26.541  
25.973  
25.683  
25.653  
25.312



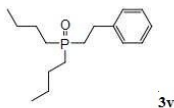
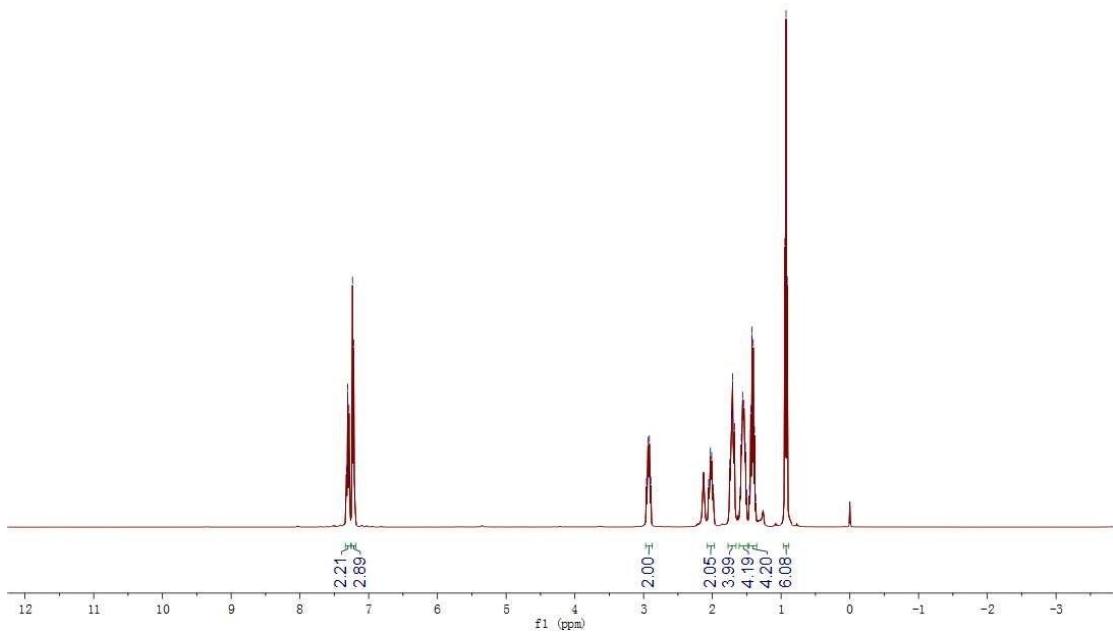
-60.244





7.324  
7.305  
7.287  
7.275  
7.235  
7.217  
7.200

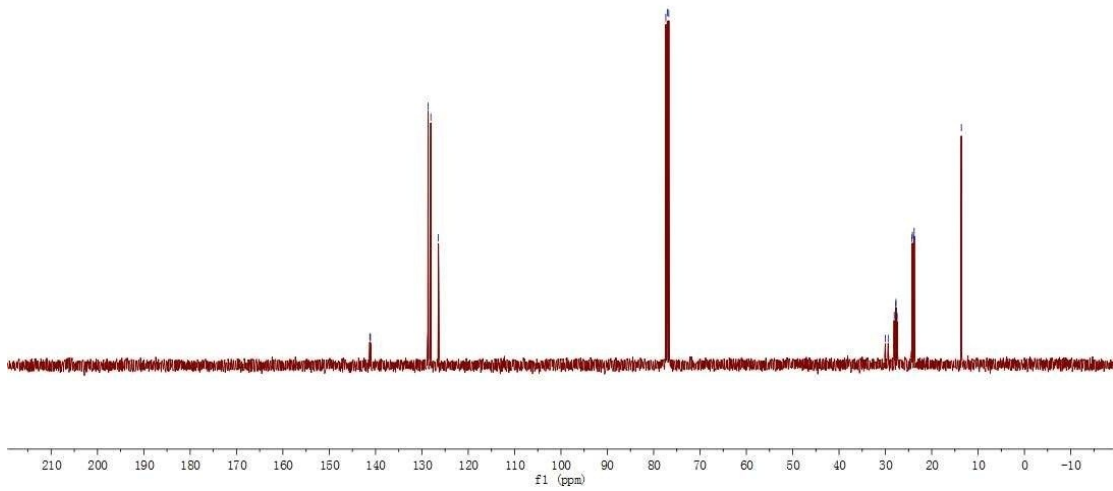
2.958  
2.937  
2.916  
2.895  
2.054  
2.029  
2.011  
1.985  
1.747  
1.719  
1.706  
1.678  
1.595  
1.578  
1.560  
1.540  
1.520  
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0.928  
0.910

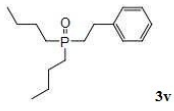


141.232  
141.100  
128.665  
128.060  
126.441

77.379  
77.062  
76.744

30.015  
29.389  
28.098  
27.748  
27.717  
27.454  
24.321  
24.178  
23.823  
23.786  
13.609





—48.166

