The Conversion of Ether Bond to Hydroxyl via Base-Promoted Rearrangement of Cyclic Phosphine Oxides

Zhan-Cai Li,‡ Yu Zhang,‡ Bing-Xia Yan, Xiao-Ning Wang, De-Hua Zhai, Hong-Xing Zheng*, Qiang Li* and Chang-Qiu Zhao*

College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, Shandong 252059, China

List of Contents

General Chemistry:

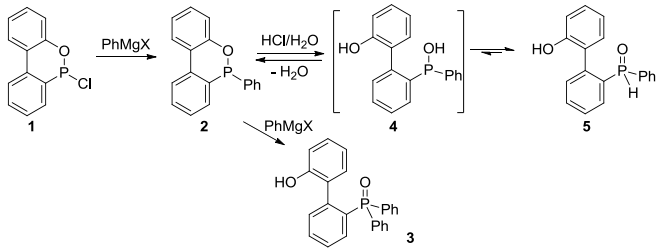
^{1}H NMR spectrum were recorded on a 500 MHz spectrometer. Chemical shift for ^{1}H NMR spectrum (in parts per million) relative to internal tetramethylsilane (Me_4Si, δ = 0.00 ppm) with $CDCl_3$. ^{13}C NMR spectrum were recorded at 126 MHz. Chemical shifts for ^{13}C NMR spectrum are reported (in parts per million) relative to $CDCl_3$ (δ = 77.0 ppm). ^{31}P NMR spectrum were recorded at 202 MHz, and chemical shifts reported (in parts per million) relative to external 85% phosphoric acid (δ = 0.0 ppm). TLC plates were visualized by UV. All products were further characterized by HRMS (high resolution mass spectrum) or Elemental Analysis. Copies of their ^{1}H, ^{31}P and ^{13}C NMR spectrum were provided. Melting points were determined on a Reichert Thermovar melting point apparatus and are uncorrected.

Reagent and solvents:

All the solvents used were dried and freshly distilled prior to use. Toluene, chloroform and dichloromethane distilled under calcium hydride. THF, ether and hexane were distilled under sodium and benzophenone. Unless otherwise stated, the commercially available reagents were used without further purification. Some of the Grignard reagent was prepared according standard procedure in ca. 1 M solution in ether or THF. All reactions were carried out under N_2 atmosphere in dry glassware using Schlenk-line techniques. Air and moisture sensitive liquids and solutions were transferred via syringe.

Part 1. The preparation of 5.

The optimization of the preparation of 2/5 from CDOP, via Method A:



Entry 1 of Table 1: To the solution of **1** (0.76 g, 3.25 mmol) in THF (4 ml), was added phenyl magnesium bromide (1.6 eq, 6.5 ml, 0.8 M solution in THF) under ice bath. After the mixture was stirred under ice bath for 1h, the reaction was quenched with water. The crude product was analyzed with ^{31}P NMR spectrum, and four peaks were observed to located at 83.6 (4%, **2**), 30.9 (2%, unconfirmed), 18.2 (2%, unconfirmed), -13.2 (91%, **3**) ppm.

Entry 2 of Table 1: To the solution of **1** (0.66 g, 2.82 mmol) in THF (4 ml), was added phenyl magnesium bromide (1.3 eq, 4.6 ml, 0.8 M solution in THF) under ice bath. After the mixture was stirred under ice bath for 1 h, the reaction was quenched with water. The crude product was analyzed with ^{31}P NMR spectrum, and three peaks were observed to located at 127.2 (7%; **1**), 83.7 (57%; **2**), -13.2 (36%; **3**) ppm.

Entry 3 of Table 1: To the solution of **1** (0.5 g, 2.14 mmol) in THF (2.5 ml), was added phenyl magnesium bromide (1.3 eq, 3.5 ml, 0.8 M solution in THF) at -80 ℃. After the mixture was stirred at -80 ℃ for 1h, the reaction was quenched with dilute hydrochloric acid (8%). The crude product was analyzed with ^{31}P NMR spectrum, and four peaks were observed to located at 83.6 (9%, **2**), 26.2 (35%, **5**), 20.7 (46%, **5**), 14.3 (9%, **6**) ppm.

Entry 4 of Table 1: To the solution of **1** (0.58 g, 2.48 mmol) in THF (3 ml), was added phenyl magnesium bromide (1.1 eq, 3.4 ml, 0.8 M solution in THF) at -80 ℃ and the mixture was warmed to room temperature with stirring. The reaction was quenched with water. The crude product was analyzed with ^{31}P NMR spectrum, and three peaks were observed to located at 127.2 (1%; **1**), 83.8 (46%; **2**), -13.2 (53%, **3**) ppm.

Entry 5 of Table 1: To the solution of **1** (313 mg, 1.34 mmol) in THF (2 ml), was added phenyl magnesium bromide (1.1 eq, 1.8 ml, 0.8 M solution in THF) at -30 ℃. After the mixture was stirred under -30 ℃ for 1h, the reaction was quenched with water. The crude product was

analyzed with ^{31}P NMR spectrum, and three peaks were observed to located at 127.1 (4%; **1**), 83.6 (90%, **2**), 23.3 (1%, **5**), 19.7 (3%, **5**), -13.3 ppm (2%, **3**).

The preparation of dibenzo[*c*,*e*][1,2]-oxaphosphinine-6-oxide (6).

To the solution of CDOP (5.00 g, 21.31 mmol) in THF (5 mL), equal molar of water was added dropwise and the mixture was stirred at room temperature for 10 hours. After the reaction was completed, as monitored with TLC, the solvent was removed in vacuo, and the residue was extracted with dichloromethane (3×20 ml), washed with water (3×20 ml), dried over magnesium sulfate. After removing solvent, the crude product was recrystallized from ether at room temperature to afford **6** as white solid (weighted 4.6 g, 82 %; NMR spectrum was seen as in Fig. S1. N. V. Dubrovina and A. Borner, *Angew. Chem. Int. Ed.*, 2004, **43**, 5883 – 5886).

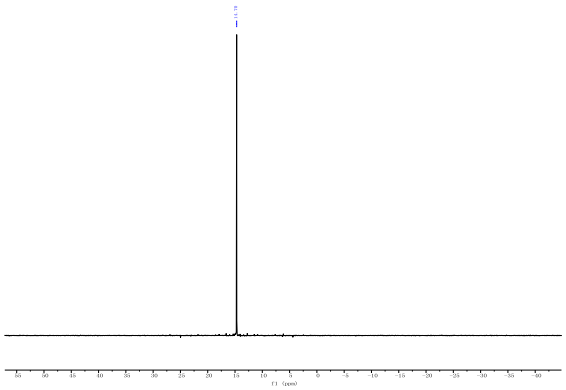


Fig. S1-A. The ^{31}P NMR spectrum of **6**.

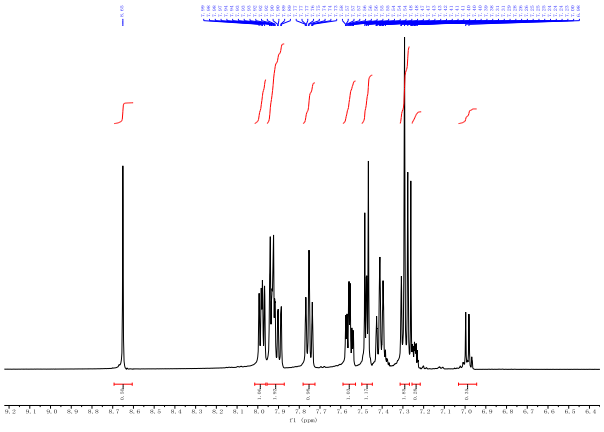
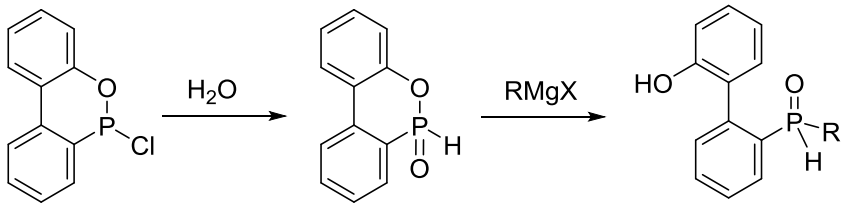


Fig. S1-B. The ^{1}H NMR spectrum of **6**.

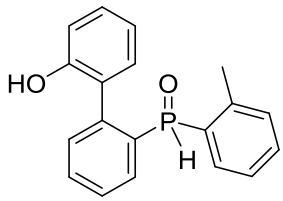
The preparation of hydroxyl substituted secondary phosphine oxide 5 via Method B, typical procedure (for entry 3 of Table 2):



1 **6** **5**

To the solution of **6** (500 mg, 2.31 mmol) in diethyl ether (2.5 ml), was added *o*-tolyl magnesium bromide (4 eq, 12 ml, 0.8 M solution in ether) at 0 ℃. The mixture was stirred at 25 ℃ for 12 days. The reaction was quenched with dilute hydrochloric acid (8%) and the solvent was removed. The mixture was extracted with dichloromethane (3×10 mL), washed with water (3×10 mL), dried over magnesium sulfate. After removing solvent, the residue was purified with recrystallization from dichloromethane/methanol (10/1) to afford **5c** (467 mg, 65%).

(2'-Hydroxy-biphenyl-2-yl)(*o*-tolyl)phosphine oxide (5c)



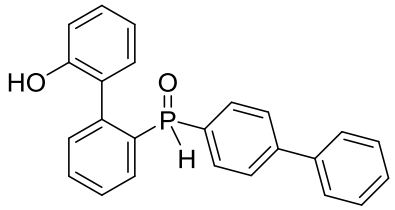
The pure compound **5c** was obtained as white solid, m.p. 157.5 - 160.1 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 81.71 (s, 1%), 21.50 (s, 33%), 16.19 (s, 66%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.33 (s, 0.65H), 8.42 (d, *J* = 45.9 Hz, 0.56H), 7.91 (dd, *J* = 15.9, 7.3 Hz, 0.46H), 7.74 (dd, *J* = 13.4, 7.5 Hz, 0.79H), 7.60 (t, *J* = 5.5 Hz, 0.50H), 7.51 (dq, *J* = 25.8, 9.1, 8.5 Hz, 2.25H), 7.41 (d, *J* = 7.7 Hz, 0.80H), 7.37 – 7.32 (m, 1.03H), 7.29 (dd, *J* = 7.6, 4.8 Hz, 1.13H), 7.19 (t, *J* = 7.6 Hz, 1.69H), 7.13 (d, *J* = 8.2 Hz, 1.15H), 7.07 (t, *J* = 6.2 Hz, 0.80H), 7.04 – 6.94 (m, 0.75H), 6.91 (d, *J* = 7.8 Hz, 0.40H), 6.82 (d, *J* = 7.5 Hz, 0.70H), 6.73 (dt, *J* = 22.1, 7.5 Hz, 1.31H), 2.79 (s, 0.06H), 2.05 (d, *J* = 5.2 Hz, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 154.1 (d, *J* = 49.2 Hz), 142.1 (d, *J* = 11.1 Hz), 140.3 (d, *J* = 10.7 Hz), 132.9 (s), 132.6 (s), 132.3 (d, *J* = 11.2 Hz), 132.2 (s), 131.7 (d, *J* = 9.4 Hz), 131.3 (d, *J* = 9.5 Hz), 130.8 (d, *J* = 10.5 Hz), 130.6 (s), 130.3 (s), 130.1 (d, *J* = 14.8 Hz), 129.9 (s), 129.5 (s), 128.7 (s), 127.8 (d, *J* = 13.2 Hz), 127.6 (d, *J* = 11.7 Hz), 127.3 (d, *J* = 13.8 Hz), 126.7 (s), 125.9 (d, *J* = 12.7 Hz), 125.7 (d, *J* = 13.2 Hz), 125.0 (s), 124.4 (s), 123.1 (s), 120.8 (s), 120.0 (d, *J* = 6.4 Hz), 119.4 (s), 117.4 (s), 20.9 (d, *J* = 16.4 Hz), 19.8 (d, *J* = 7.5 Hz); **HRMS (ESI^{+})** Calcd. for $C_{16}H_{19}O_2P$ [M+Na^{+}]: 331.0864, Found: 331.0885.

The preparation of hydroxyl substituted secondary phosphine oxide 5 via Method A, typical

procedure (for entry 6 of Table 2):

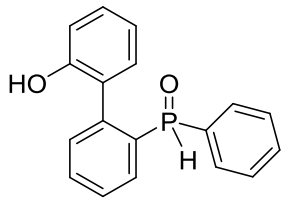
To the solution of **1** (1.0 g, 4.26 mmol) in toluene (5 ml), was added biphenyl-4-yl magnesium bromide (1 eq, 5.4 ml, 0.8 M solution in THF) at -30 ℃. After the mixture was stirred at -30 ℃ for 1 h, the reaction was quenched with dilute hydrochloric acid (8%) and the solvent was removed. The mixture was extracted with dichloromethane (3×10 mL), washed with water (3×10 mL), dried over magnesium sulfate. After removing solvent, the residue was purified from recrystallization with dichloromethane/methanol (10/1) to afford **5e** (0.96 g, 61%).

(Biphenyl-4-yl)(2'-hydroxy-biphenyl-2-yl)phosphine oxide (5e)



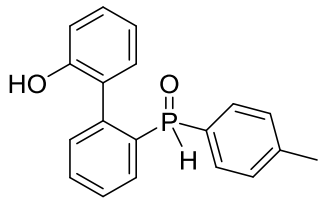
The pure compound **5e** was obtained as white solid, m.p. 151.7 – 153.2 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 24.37(s, 38%), 18.95(s, 62%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.08 (d, *J* = 138.4 Hz, 0.56H), 8.43 (d, *J* = 29.7 Hz, 0.52H), 7.89 (dd, *J* = 14.3, 7.5 Hz, 1.15H), 7.64 (s, 0.50H), 7.60 – 7.48 (m, 4.41H), 7.43 (t, *J* = 7.6 Hz, 4.42H), 7.37 (d, *J* = 7.2 Hz, 1.44H), 7.35 (s, 0.22H), 7.32 (dd, *J* = 7.6, 4.6 Hz, 1.27H), 7.27 (d, *J* = 13.0 Hz, 0.62H), 7.23 (d, *J* = 6.0 Hz, 0.42H), 7.18 (d, *J* = 7.5 Hz, 0.43H), 7.14 (d, *J* = 8.1 Hz, 0.58H), 7.07 – 6.90 (m, 1H), 6.84 (d, *J* = 7.8 Hz, 0.63H), 6.71 (s, 0.81H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 154.1 (s), 144.8 (s), 139.9 (s), 133.1 (s), 132.7 (s), 132.0 (s), 131.5 (s), 131.3 (s), 130.9 (s), 130.9 (s), 130.0 (s), 129.0 (s), 128.2 (s), 127.7 (d, *J* = 12.1 Hz), 127.2 (s), 127.1 (s), 120.0 (d, *J* = 182.9 Hz), 118.5 (d, *J* = 367.3 Hz); **HRMS (ESI^{+})** Calcd. for $C_{24}H_{19}O_2P$ [M+Na^{+}]: 393.1020, Found: 393.1031.

(2'-Hydroxy-biphenyl-2-yl)(phenyl)phosphine oxide (5a)



The crude **5a** was obtained from phenyl magnesium bromide via method B, as white solid, weighted 584 mg, yield 86%.^{31}P NMR spectrum of crude **5a** gave three single peaks at 84.1 (s, 24%, **2a**), 20.3 (s, 23%) and 19.3 ppm (s, 40%).

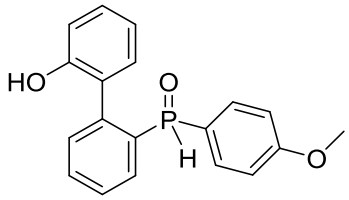
(2'-Hydroxy-biphenyl-2-yl)(*p*-tolyl)phosphine oxide (5b)



The crude **5b** was obtained from *p*-tolyl magnesium bromide via method B as white solid, weighted 1.3 g, yield 93%.^{31}P NMR spectrum of crude **5b** gave three single peaks at 83.5 (s, 8%, **2b**),

26.4 (s, 30%) and 19.1 ppm (s, 44%).

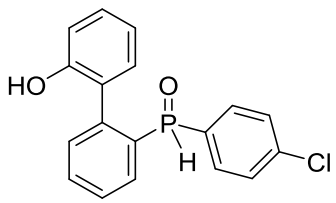
(2'-Hydroxy-biphenyl-2-yl)(4-methoxyphenyl)phosphine oxide (5d)



The crude **5d** was obtained from (4-methoxyphenyl) magnesium bromide via Method B. The pure **5d** was obtained as white solid (811 mg, 54%) from recrystallization with dichloromethane/methanol (10/1), m.p. 133.1 – 135 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 81.88 (s, 1%), 24.38 (s, 37%), 18.83 (s, 62%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.36 (s, 0.58H), 8.32 (d, *J* = 24.0 Hz, 0.64H), 8.07 (s, 0.51H), 7.94 (s, 0.19H), 7.82 (dt, *J* = 17.9, 8.4 Hz, 1.19H), 7.56 (dt, *J* = 16.1, 6.8 Hz, 1.36H), 7.50 – 7.35 (m, 1.65H), 7.29 (d, *J* = 6.5 Hz, 1.64H), 7.21 (ddd, *J* = 24.6, 14.2, 7.5 Hz, 3.25H), 7.11 (t, *J* = 10.9 Hz, 1.09H), 7.03 – 6.91 (m, 0.84H), 6.91 – 6.64 (m, 4.51H), 3.75 (d, *J* = 19.6 Hz, 3H), 3.68 (s, 0.15H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 162.6 (d, *J* = 3.2 Hz), 161.0 (s), 154.1 (s), 151.1 (d, *J* = 10.1 Hz), 141.9 (s), 133.7 (s), 133.6 (d, *J* = 21.8 Hz), 132.7 (d, *J* = 38.0 Hz), 132.3 (d, *J* = 13.2 Hz), 132.0 (s), 131.6 (s), 131.5 – 131.1 (m), 130.8 (s), 129.9 (s), 129.6 (s), 127.6 (d, *J* = 11.9 Hz), 127.4 (s), 126.6 (s), 124.9 (s), 124.3 (d, *J* = 6.2 Hz), 124.0 (s), 123.0 (s), 122.5 (d, *J* = 109.7 Hz), 120.8 (s), 120.6 (s), 119.9 (s), 119.2 (s), 117.1 (s), 114.2 (d, *J* = 13.7 Hz), 113.8 (d, *J* = 6.4 Hz), 55.3 (s), 55.1 (s); **HRMS (ESI^{+})** Calcd. for $C_{19}H_{17}O_3P$ [M+Na^{+}]: 347.0813, Found: 347.0828.

5d was obtained from Method A as white solid (580 mg, 42%), which had the same spectrum data to that obtained from Method B.

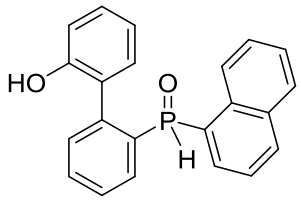
(4-Chlorophenyl)(2'-hydroxy-biphenyl-2-yl)phosphine oxide (5f)



The crude **5f** was obtained from 4-chlorophenyl magnesium bromide via Method A, and the pure **5f** was obtained as white solid (406 mg, 57%) from recrystallization with dichloromethane/methanol (10/1), m.p. 117.4 - 118.9 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 21.29 (s, 38%), 18.36 (s, 62%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.07 (s, 0.51H), 8.37 (d, *J* = 23.9 Hz, 0.50H), 7.84 (td, *J* = 14.0, 13.0, 7.9 Hz, 1H), 7.63 (t, *J* = 6.9 Hz, 0.76H), 7.61 – 7.55 (m, 0.66H), 7.52 (d, *J* = 13.3 Hz, 0.41H), 7.45 (td, *J* = 9.6, 7.4, 3.7 Hz, 0.66H), 7.40 (s, 0.28H), 7.31 (dt, *J* = 9.6, 4.7 Hz, 2.35H), 7.28 – 7.12 (m, 4H), 7.09 (d, *J* = 8.1 Hz, 0.59H), 6.97 (d, *J* = 8.1 Hz, 0.43H), 6.92 (d, *J* = 7.5 Hz, 0.53H), 6.84 (t, *J* =

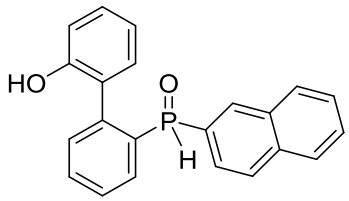
7.5 Hz, 0.61H), 6.75 (t, *J* = 7.6 Hz, 0.43H), 6.69 (d, *J* = 7.7 Hz, 0.34H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 154.0 (s), 142.1 (d, *J* = 82.9 Hz), 138.6 (s), 132.9 (s), 132.1 (s), 131.5 (s), 131.3 (s), 130.9 (s), 130.6 (s), 130.3 (s), 130.0 (s), 129.8 (s), 129.6 (s), 129.5 (s), 128.8 (d, *J* = 13.5 Hz), 127.7 (d, *J* = 12.0 Hz), 120.2 (d, *J* = 58.0 Hz), 117.4 (d, *J* = 206.8 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{18}H_{14}ClO_2P$ [M+Na^+]: 351.0318, Found: 351.0328.

(2'-Hydroxy-biphenyl-2-yl)(naphthalen-1-yl)phosphine oxide (5g)



The crude **5g** was obtained from naphthalen-1-yl magnesium bromide via Method A. The pure **5g** was obtained as white solid (606 mg, 43%) from recrystallization with dichloromethane/methanol (10/1), m.p. 109.5 – 111.1 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 20.33 (s, 33%), 18.19 (s, 67%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.41 (s, 0.57H), 8.76 (d, *J* = 26.1 Hz, 0.48H), 7.88 (ttd, *J* = 29.5, 21.2, 8.0 Hz, 4.14H), 7.71 (s, 0.34H), 7.64 (tt, *J* = 10.8, 6.2 Hz, 0.83H), 7.55 (s, 0.60H), 7.49 (t, *J* = 7.6 Hz, 1.09H), 7.43 (t, *J* = 7.4 Hz, 0.81H), 7.36 (q, *J* = 7.3 Hz, 2.32H), 7.26 (d, *J* = 5.5 Hz, 1.29H), 7.19 (d, *J* = 12.8 Hz, 1.36H), 7.11 (t, *J* = 7.5 Hz, 0.61H), 6.95 – 6.54 (m, 2.55H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 154.1 (d, *J* = 52.4 Hz), 141.9 (d, *J* = 12.1 Hz), 133.2 (s), 133.1 (s), 132.6 (s), 132.4 (d, *J* = 11.1 Hz), 132.2 (s), 131.8 (d, *J* = 9.4 Hz), 131.4 (d, *J* = 10.1 Hz), 131.0 (s), 130.6 (s), 130.2 (s), 130.0 (s), 129.9 (s), 129.0 (s), 128.1 – 127.8 (m), 127.6 (d, *J* = 11.6 Hz), 127.3 (s), 126.8 (s), 126.3 (d, *J* = 16.5 Hz), 124.9 (d, *J* = 14.4 Hz), 124.7 (d, *J* = 8.4 Hz), 124.2 (s), 120.5 (s), 120.0 (s), 118.5 (s), 117.4; **HRMS (ESI$^+$)** Calcd. for $C_{22}H_{17}O_2P$ [M+Na^+]: 367.0864, Found: 361.0887.

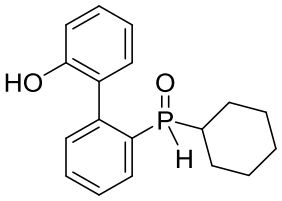
(2'-Hydroxy-biphenyl-2-yl)(naphthalen-2-yl)phosphine oxide (5h)



The crude **5h** was obtained from naphthalen-2-yl magnesium bromide via Method A, and the pure **5h** was obtained as white solid (795 mg, 87%) from recrystallization with dichloromethane/methanol (10/1), m.p. 129.7 – 132.6 ℃. **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 23.15 (s, 36%), 19.54 (s, 64%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.57 (s, 0.53H), 8.49 (s, 0.52H), 8.30 (s, 0.39H), 7.91 (dt, *J* = 13.6, 6.9 Hz, 0.82H), 7.88 – 7.78 (m, 1.16H), 7.78 – 7.61 (m, 2.65H), 7.61 – 7.34 (m, 4.64H), 7.28 (dd, *J* = 12.3, 6.2 Hz, 1.28H), 7.25 – 7.21 (m, 0.92H), 7.21 – 7.05 (m, 1.57H), 6.96 (d, *J* = 8.2 Hz, 0.50H), 6.82

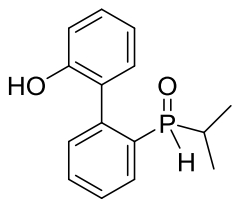
(t, *J* = 11.3 Hz, 0.97H), 6.76 – 6.48 (m, 1H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 154.1 (s), 142.3 (d, *J* = 80.3 Hz), 134.8 (s), 132.7 (s), 132.4 (s), 132.3 (s), 132.1 (d, *J* = 11.1 Hz), 131.9 (d, *J* = 7.6 Hz), 131.5 (s), 131.2 (d, *J* = 9.5 Hz), 130.9 (s), 130.0 (s), 128.8 (s), 128.4 (d, *J* = 12.3 Hz), 128.1 (s), 127.8 (s), 127.7 (s), 127.6 (s), 126.9 (s), 126.4 (s), 124.9 (d, *J* = 12.7 Hz), 119.5 (d, *J* = 231.6 Hz), 118.4 (d, *J* = 367.6 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{22}H_{17}O_2P$ [M+Na$^+$]: 367.0864, Found: 367.0879.

Cyclohexyl(2'-hydroxy-biphenyl-2-yl)phosphine oxide (5i)



The crude **5i** was obtained from cyclohexyl magnesium bromide via Method A, the pure **5i** was obtained as white solid (896 mg, 70%) from recrystallization with dichloromethane, m.p. 118.4 - 120.2 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 44.58 (s, 32%), 34.82 (s, 68%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.78 (s, 0.62H), 8.37 (s, 0.33H), 7.89 (t, *J* = 9.7 Hz, 0.70H), 7.75 (dd, *J* = 15.4, 7.7 Hz, 0.38H), 7.59 (dt, *J* = 16.2, 8.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1.49H), 7.39 – 7.33 (m, 0.33H), 7.28 (q, *J* = 8.3, 7.3 Hz, 1H), 7.22 (t, *J* = 8.1 Hz, 0.75H), 7.08 (q, *J* = 7.1, 5.8 Hz, 1.89H), 6.97 (d, *J* = 7.9 Hz, 0.34H), 6.88 (t, *J* = 7.6 Hz, 0.64H), 6.50 (s, 0.47H), 1.77 (s, 1H), 1.70 (s, 1H), 1.61 (d, *J* = 19.5 Hz, 2.60H), 1.45 – 1.29 (m, 1H), 1.25 (s, 0.37H), 1.09 (dqd, *J* = 41.1, 25.0, 21.4, 9.1 Hz, 5H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 154.1 (s), 141.6 (s), 132.6 (s), 132.3 (s), 132.0 (s), 131.1 (s), 130.7 (s), 130.2 (s), 129.9 (s), 129.1 (s), 127.4 (s), 126.3 (s), 120.4 (d, *J* = 100.9 Hz), 119.5 (s), 116.3 (s), 37.1 (dd, *J* = 201.7, 69.7 Hz), 25.9 (s), 25.9 (s), 25.6 (s), 25.2 (d, *J* = 12.3 Hz), 25.0 (s), 24.9 (s); **HRMS (ESI$^+$)** Calcd. for $C_{18}H_{21}O_2P$ [M+Na$^+$]: 323.1177, Found: 323.1197.

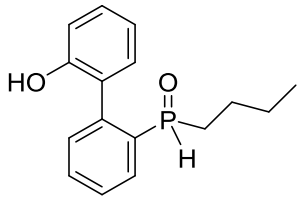
(2'-Hydroxy-biphenyl-2-yl)(isopropyl)phosphine oxide (5j)



The crude **5j** was obtained from isopropyl magnesium bromide via Method A, and the pure **5j** was obtained as white solid (688 mg, 62%) from recrystallization with dichloromethane, m.p. 134.8 - 136.4 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 52.43 (s, 44%), 37.77 (s, 56%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.30 (s, 0.52H), 8.06 (s, 0.41H), 7.96 – 7.86 (m, 0.53H), 7.73 (dd, *J* = 16.3, 7.6 Hz, 0.43H), 7.66 (t, *J* = 7.6 Hz, 0.44H), 7.60 (t, *J* = 7.6 Hz, 0.52H), 7.54 – 7.46 (m, 1H), 7.45 (d, *J* = 4.0 Hz, 0.25H), 7.41 – 7.36 (m, 0.56H), 7.36 – 7.29 (m, 1H), 7.25 (d, *J* = 8.0 Hz,

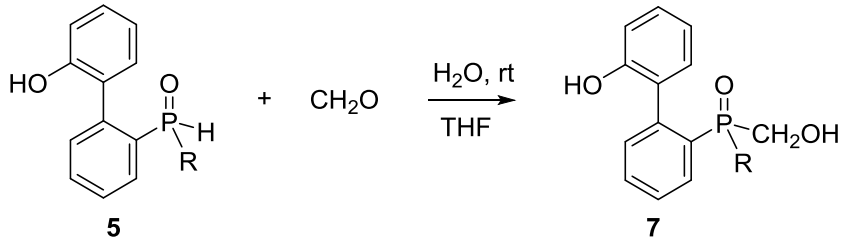
0.93H), 7.16 – 7.10 (m, 0.90H), 7.08 (d, *J* = 8.1 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 0.43H), 6.90 (t, *J* = 7.5 Hz, 0.53H), 6.47 (dd, *J* = 9.4, 5.0 Hz, 0.47H), 1.94 – 1.81 (m, 0.56H), 1.60 (dd, *J* = 14.0, 7.0 Hz, 0.43H), 1.07 (ddd, *J* = 36.2, 17.8, 7.2 Hz, 3H), 0.81 (ddd, *J* = 50.4, 20.6, 7.2 Hz, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*/Methanol-*d* = 3/1)** δ 157.7 (d, *J* = 96.8 Hz), 145.5 (d, *J* = 69.2 Hz), 136.5 (s), 136.2 (s), 135.5 (s), 135.3 (s), 135.0 (s), 134.7 (s), 134.5 (s), 133.6 (s), 132.5 (s), 131.5 (d, *J* = 10.9 Hz), 130.1 (s), 127.0 (s), 124.4 (s), 123.9 (s), 120.6 (s), 119.7 (s), 31.8 (d, *J* = 68.7 Hz), 30.7 (d, *J* = 69.2 Hz), 19.4 (d, *J* = 46.6 Hz), 18.0 (d, *J* = 17.5 Hz) ; **HRMS (ESI$^+$)** Calcd. for $C_{15}H_{17}O_2P$ [M+Na$^+$]: 283.0864, Found: 283.0882.

Butyl(2'-hydroxy-biphenyl-2-yl)phosphine oxide (5k)



The crude **5k** was obtained from butyl magnesium bromide via Method A, and the pure **5k** was obtained as white solid (0.94 g, 81%) from recrystallization with dichloromethane, m.p. 117.6 - 119.6 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 34.64 (s, 38%), 27.10(s, 64%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.99 – 7.78 (m, 1H), 7.75 (t, *J* = 3.7 Hz, 0.5H), 7.65 – 7.54 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 6.5 Hz, 0.38H), 7.33 – 7.27 (m, 0.86H), 7.22 (d, *J* = 7.8 Hz, 0.61H), 7.15 – 7.02 (m, 2H), 7.00 – 6.93 (m, 0.39H), 6.89 (t, *J* = 7.5 Hz, 0.63H), 6.78 (t, *J* = 3.6 Hz, 0.53H), 1.76 – 1.46 (m, 2H), 1.39 – 1.12 (m, 4H), 0.74 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 154.2 (d, *J* = 39.9 Hz), 141.5 (d, *J* = 47.3 Hz), 132.4 (s), 131.7 (s), 131.3 (s), 131.1 (s), 130.7 (s), 130.0 (s), 129.0 (s), 127.6 (s), 126.3 (s), 119.9 (d, *J* = 65.3 Hz), 117.4 (d, *J* = 205.4 Hz), 28.7 (dd, *J* = 131.8, 68.2 Hz), 23.5 (s), 23.3 (s), 13.4 (s); **HRMS (ESI$^+$)** Calcd. for $C_{16}H_{19}O_2P$ [M+Na$^+$]: 297.1020, Found: 297.1042.

Part 2. The preparation of hydroxymethyl phosphine oxide 7.

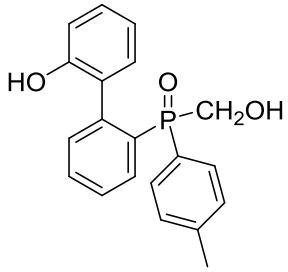


5 **7**

Typical procedure:

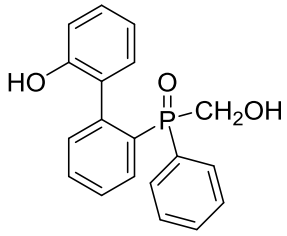
To the solution of crude **5b** (336 mg, 0.89 mmol) in THF (5 ml), was added Formalin solution (5 ml, 37-40%) at room temperature with stirring. After the reaction was completed, as monitored with TLC, the solvent was removed in vacuo, and the residue was extracted with dichloromethane (3×10 ml), washed with water (3×10 ml), dried over magnesium sulfate. After removing solvent, the residue was purified with preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent) to afford **7b** as white solid (weighted 209 mg, 57%).

(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(*p*-tolyl)phosphine oxide (7b)



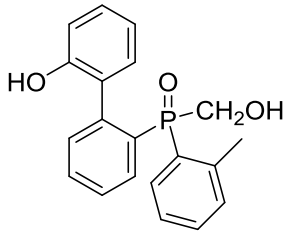
The pure **7b** was obtained as white solid, m.p. 100.1 - 101.4 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 36.98 (s, 43%), 34.05 (s, 57%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.09 – 7.96 (m, 0.54H), 7.64 – 7.53 (m, 1.84H), 7.52 – 7.40 (m, 1H), 7.39 – 7.32 (m, 0.52H), 7.32 – 7.26 (m, 1.42H), 7.25 – 7.20 (m, 0.94H), 7.06 (td, *J* = 8.3, 2.1 Hz, 1.78H), 7.03 – 7.00 (m, 0.49H), 6.98 (dd, *J* = 8.1, 2.8 Hz, 1.35H), 6.94 (dd, *J* = 8.2, 1.4 Hz, 0.63H), 6.92 – 6.84 (m, 0.41H), 6.55 – 6.33 (m, 1H), 4.41 (dt, *J* = 14.7, 1.8 Hz, 0.56H), 4.25 – 4.09 (m, 0.54H), 3.88 (dd, *J* = 14.5, 3.4 Hz, 0.43H), 3.76 (d, *J* = 14.5 Hz, 0.4 H), 2.35 (d, *J* = 66.1 Hz, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 154.0 (d, *J* = 25.6 Hz), 143.9 – 142.9 (m), 142.8 – 142.0 (m), 133.2 (d, *J* = 10.8 Hz), 132.7 (d, *J* = 8.9 Hz), 132.5 (s), 132.4 (d, *J* = 10.2 Hz), 131.7 (d, *J* = 9.7 Hz), 131.4 (d, *J* = 11.2 Hz), 131.0 (d, *J* = 16.7 Hz), 130.4 (d, *J* = 10.3 Hz), 130.2 (s), 129.7 (d, *J* = 12.1 Hz), 129.5 (d, *J* = 12.5 Hz), 129.3 (s), 128.9 (d, *J* = 12.6 Hz), 127.4 (dd, *J* = 24.0, 11.8 Hz), 126.6 – 124.9 (m), 120.9 (d, *J* = 35.0 Hz), 120.4 (s), 60.6 (dd, *J* = 95.1, 82.3 Hz), 21.6 (d, *J* = 21.0 Hz); **HRMS (ESI^{+})** Calcd. for $C_{20}H_{19}O_3P$ [M+Na^{+}]: 361.0970, Found: 361.0977.

(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(phenyl)phosphine oxide (7a)



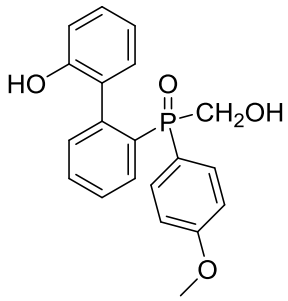
The pure **7a** was obtained as colorless oil (107 mg, 53%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent); **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 36.07 (s, 39%), 33.87 (s, 61%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.04 (dd, *J* = 12.4, 7.7 Hz, 0.58H), 7.67 – 7.52 (m, 0.24H), 7.52 – 7.46 (m, 0.77H), 7.45 – 7.39 (m, 0.79H), 7.37 (s, 0.33H), 7.36 – 7.27 (m, 1.2H), 7.23 (dd, *J* = 7.6, 3.8 Hz, 0.64H), 7.21 – 7.14 (m, 2.8H), 7.05 (t, *J* = 7.8 Hz, 0.64H), 6.94 (t, *J* = 5.9 Hz, 0.97H), 6.88 (s, 0.40H), 6.82 (s, 0.40H), 6.49 (t, *J* = 7.4 Hz, 0.59H), 6.37 (d, *J* = 7.5 Hz, 0.56H), 4.13 (dd, *J* = 290 Hz, 1H), 4.08 (dd, *J* = 130 Hz, 1H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 154.2 – 142.3 (m), 133.0 (dd, *J* = 66.8, 9.6 Hz), 132.7 – 132.2 (m), 131.7 – 131.4 (m), 131.3 – 130.8 (m), 130.3 (dd, *J* = 23.9, 11.0 Hz), 130.0 – 129.2 (m), 128.9 (dd, *J* = 58.9, 11.9 Hz), 128.2 (d, *J* = 11.9 Hz), 127.5 (dd, *J* = 24.3, 11.6 Hz), 120.9 (d, *J* = 13.8 Hz), 120.1 (d, *J* = 89.9 Hz), 60.6 (dd, *J* = 87.8, 82.3 Hz); **HRMS (ESI^{+})** Calcd. for $C_{19}H_{17}O_3P$ [M+Na^{+}]: 347.0813, Found: 347.0831.

(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(*o*-tolyl)phosphine oxide (7c)



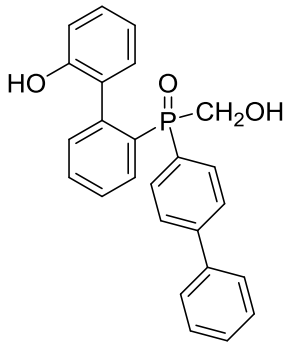
The pure **7c** was obtained as white solid (324 mg, 74%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent), m.p. 128.0 - 129.5 ℃; **^{31}P NMR (202 MHz, CD_3OD)** δ 39.50 (s, 47%), 37.11 (s, 53%); **^{1}H NMR (500 MHz, CD_3OD)** δ 8.20 (dd, *J* = 12.1, 7.6 Hz, 0.49H), 7.92 (dd, *J* = 12.5, 7.8 Hz, 0.43H), 7.58 (dq, *J* = 12.7, 7.7 Hz, 1.54H), 7.50 (t, *J* = 7.8 Hz, 0.43H), 7.41 – 7.18 (m, 3H), 7.18 – 7.09 (m, 1.13H), 7.09 – 6.92 (m, 2.41H), 6.76 (t, *J* = 7.4 Hz, 0.49H), 6.61 (d, *J* = 8.2 Hz, 0.53H), 6.46 (dd, *J* = 25.0, 7.8 Hz, 1H), 6.35 (t, *J* = 7.5 Hz, 0.49H), 4.38 (dd, *J* = 22.7, 14.2 Hz, 1H), 4.24 (dd, *J* = 14.6, 2.8 Hz, 0.52H), 4.12 – 4.00 (m, 0.45H), 2.21 (s, 3H); **^{13}C NMR (126 MHz, Methanol-d_4)** δ 154.2 (d, *J* = 73.8 Hz), 142.7 (s), 142.2 (s), 141.3 (s), 132.6 (d, *J* = 8.5 Hz), 132.1 (dd, *J* = 20.4, 10.1 Hz), 131.5 (s), 131.3 (s), 130.9 (s), 130.7 (s), 129.9 (s), 129.1 (d, *J* = 35.2 Hz), 128.6 (s), 127.7 (s), 127.0 (d, *J* = 9.9 Hz), 125.1 (dd, *J* = 26.8, 12.3 Hz), 118.5 (d, *J* = 3.2 Hz), 115.1 (d, *J* = 82.9 Hz), 60.6 (dd, *J* = 85.0, 61.1 Hz), 20.0 (s); **HRMS (ESI^{+})** Calcd. for $C_{20}H_{19}O_3P$ [M+Na^{+}]: 361.0970, Found: 361.0983.

(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(4-methoxyphenyl)phosphine oxide (7d)



The pure **7d** was obtained as white solid (399 mg, 90%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent), m.p. 81.0 - 82.6 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 35.31 (s, 43%), 34.73(s, 57%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.84 (dd, *J* = 12.5, 7.7 Hz, 0.63H), 7.71 (dd, *J* = 12.7, 7.8 Hz, 0.44H), 7.50 (dt, *J* = 12.3, 7.6 Hz, 1H), 7.38 (ddt, *J* = 26.9, 15.9, 8.0 Hz, 2H), 7.23 – 7.14 (m, 2H), 7.04 (dddd, *J* = 14.2, 8.7, 6.9, 2.5 Hz, 1H), 6.87 (dd, *J* = 12.4, 8.1 Hz, 1H), 6.81 (dd, *J* = 8.8, 2.3 Hz, 0.84H), 6.69 (ddd, *J* = 9.2, 7.2, 4.0 Hz, 2H), 6.60 – 6.50 (m, 1.16H), 4.21 – 4.13 (m, 0.56H), 4.05 (dd, *J* = 14.6, 3.0 Hz, 0.56H), 3.90 (dd, *J* = 14.5, 2.4 Hz, 0.42H), 3.81 (d, *J* = 14.5 Hz, 0.44H), 3.73 (d, *J* = 22.5 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 162.4 (dd, *J* = 32.2, 2.8 Hz), 154.0 (d, *J* = 30.5 Hz), 143.0 (dd, *J* = 141.0, 8.7 Hz), 133.3 (t, *J* = 9.1 Hz), 132.6 (dd, *J* = 10.5, 7.0 Hz), 132.4 – 132.1 (m), 132.0 (d, *J* = 11.2 Hz), 131.1 (d, *J* = 12.1 Hz), 130.6 (d, *J* = 3.8 Hz), 130.1 (dd, *J* = 95.8, 15.5 Hz), 129.6 (d, *J* = 60.6 Hz), 121.3 (d, *J* = 51.0 Hz), 120.6 (d, *J* = 9.2 Hz), 120.2 (d, *J* = 10.7 Hz), 119.0 (d, *J* = 102.2 Hz), 114.2 (d, *J* = 12.9 Hz), 113.9 (d, *J* = 12.9 Hz), 60.5 (dd, *J* = 99.0, 83.8 Hz), 55.3 (d, *J* = 6.2 Hz); **HRMS (ESI^{+})** Calcd. for $C_{20}H_{19}O_4P$ [M+Na^{+}]: 377.0919, Found: 377.0926.

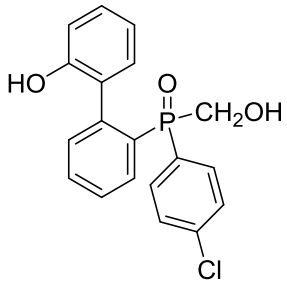
(Biphenyl-4-yl)(2'-hydroxy-biphenyl-2-yl)(hydroxymethyl)phosphine oxide (7e)



The pure **7e** was obtained as white solid (344 mg, 86%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent), m.p. 113.1 - 114.5 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 36.29(s, 40%), 33.80(s, 60%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.07 (dd, *J* = 12.3, 7.6 Hz, 0.6H), 7.70 (dd, *J* = 11.1, 8.1 Hz, 0.8H), 7.66 – 7.54 (m, 3.12H), 7.53 – 7.41 (m, 4.23H), 7.37 (ddt, *J* = 14.8, 8.2, 3.8 Hz, 2.51H), 7.32 – 7.28 (m, 0.47H), 7.25 – 7.15 (m, 1.74H), 7.06 (td, *J* = 7.7, 1.8 Hz, 0.61H), 6.97 (ddd, *J* = 7.9, 6.5, 1.1 Hz, 1.01H), 6.92 (dd, *J* = 7.5, 1.8 Hz, 0.4H), 6.83 (td, *J* = 7.5, 1.1 Hz, 0.4H), 6.47 (td, *J* = 7.4, 1.2 Hz, 0.6H), 6.37 (dd, *J* = 7.5, 1.7 Hz, 0.6H), 4.48 (d, *J* = 14.6 Hz, 0.6H), 4.27 (dd, *J* = 14.5, 2.6 Hz, 0.6H), 3.99 (dd, *J* = 14.5, 2.9 Hz, 0.4H), 3.88 (d, *J* = 14.5 Hz, 0.39H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 154.0 (d, *J* = 28.8 Hz), 144.7 (dd, *J* = 78.1, 2.5 Hz), 143.1 (dd, *J* = 145.2, 8.1 Hz), 140.0 (d, *J* = 21.2 Hz), 133.3 (d, *J* = 10.0 Hz), 132.8 (s),

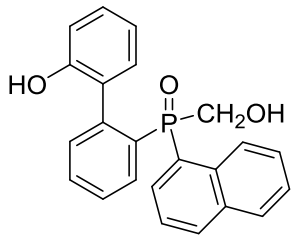
132.5 (dd, *J* = 29.5, 9.8 Hz), 132.0 (d, *J* = 9.3 Hz), 131.5 – 131.3 (m), 130.9 (d, *J* = 10.2 Hz), 130.4 (d, *J* = 9.3 Hz), 130.2 (d, *J* = 13.8 Hz), 129.6 (d, *J* = 21.3 Hz), 129.3 (s), 129.0 (d, *J* = 6.6 Hz), 128.4 (d, *J* = 14.2 Hz), 128.2 (d, *J* = 17.7 Hz), 127.7 (d, *J* = 5.5 Hz), 127.5 (d, *J* = 11.7 Hz), 127.4 (s), 127.2 (d, *J* = 12.0 Hz), 126.9 (d, *J* = 12.1 Hz), 120.8 (d, *J* = 16.0 Hz), 120.1 (d, *J* = 90.3 Hz), 60.6 (dd, *J* = 82.6, 73.3 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{25}H_{21}O_3P$ [M+Na$^+$]: 423.1126, Found: 423.1127.

(4-Chlorophenyl)(2'-hydroxy-biphenyl-2-yl)(hydroxymethyl)phosphine oxide (7f)



The pure **7f** was obtained as white solid (329 mg, 75%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent), m.p. 94.8 - 96.2 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 34.74 (d, *J* = 26.7 Hz, 39%), 33.43 (d, *J* = 12.2 Hz, 61%).**^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.01 (dd, *J* = 11.8, 7.5 Hz, 0.65H), 7.68 – 7.55 (m, 1.54H), 7.51 (dddd, *J* = 14.4, 7.9, 4.3, 2.0 Hz, 1.31H), 7.42 – 7.33 (m, 1.14H), 7.29 (dq, *J* = 7.6, 4.1, 3.5 Hz, 0.43H), 7.25 – 7.22 (m, 0.47H), 7.21 – 7.12 (m, 2.21H), 7.12 – 7.06 (m, 1.32H), 6.96 – 6.86 (m, 1.20H), 6.83 (q, *J* = 7.5 Hz, 0.56H), 6.57 (td, *J* = 7.5, 1.2 Hz, 0.63H), 6.43 – 6.31 (m, 0.63H), 4.46 – 4.34 (m, 0.63H), 4.26 – 4.16 (m, 0.62H), 3.95 (dt, *J* = 14.6, 2.8 Hz, 0.38H), 3.83 (dd, *J* = 14.4, 7.6 Hz, 0.37H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 153.8 (s), 143.0 (dd, *J* = 154.5, 8.4 Hz), 138.6 (dd, *J* = 71.8, 3.4 Hz), 133.2 (d, *J* = 10.0 Hz), 133.0 (s), 132.9 – 132.8 (m), 132.6 (s), 132.4 (d, *J* = 10.2 Hz), 131.8 (d, *J* = 10.1 Hz), 131.4 (d, *J* = 11.5 Hz), 131.0 (d, *J* = 9.1 Hz), 130.8 (s), 130.2 (s), 129.9 (d, *J* = 3.4 Hz), 129.6 (s), 129.1 (d, *J* = 5.6 Hz), 128.9 (d, *J* = 12.2 Hz), 128.6 (s), 128.5 (s), 127.8 – 127.6 (m), 127.5 (d, *J* = 11.9 Hz), 120.9 (d, *J* = 32.6 Hz), 120.6 – 119.1 (m), 60.5 (dd, *J* = 83.2, 61.1 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{19}H_{16}ClO_3P$ [M+Na$^+$]: 381.0423, Found: 381.0432.

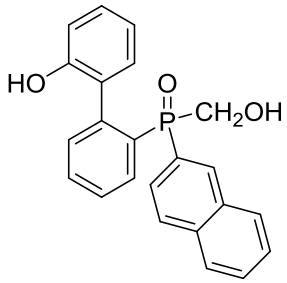
(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(naphthalen-1-yl)phosphine oxide (7g)



The pure **7g** was obtained as white solid (223 mg, 51%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent), m.p. 197.2 – 199.0 ℃; **^{31}P NMR (202 MHz, DMSO-d_6)** δ 32.74 (s, 44%), 30.35 (s, 56%); **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.37 (d, *J* = 8.9 Hz, 0.7H), 8.16 (s, 1H), 8.06 (d, *J* = 20.1 Hz, 1H),

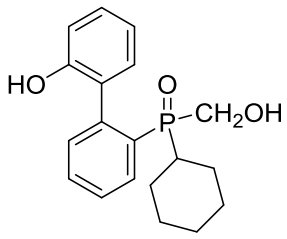
7.98 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 24.4 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 2H), 7.47 (dt, *J* = 46.7, 7.4 Hz, 3H), 7.36 (t, *J* = 7.2 Hz, 0.48H), 7.17 (d, *J* = 41.9 Hz, 1.47H), 6.92 (d, *J* = 27.3 Hz, 1H), 6.83 – 6.62 (m, 1.4H), 6.18 (d, *J* = 41.4 Hz, 1H), 4.34 (t, *J* = 16.4 Hz, 1H), 4.19 – 3.90 (m, 1H); **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 154.8 (d, *J* = 61.4 Hz), 142.9 (s), 133.6 (d, *J* = 8.4 Hz), 133.2 (d, *J* = 7.4 Hz), 133.0 (s), 132.5 (d, *J* = 9.7 Hz), 131.7 (s), 131.0 (s), 129.2 (s), 129.1 (s), 127.8 (s), 127.5 (d, *J* = 10.8 Hz), 126.9 (s), 126.3 (s), 125.1 (d, *J* = 12.9 Hz), 118.3 (s), 115.8 (s), 61.0 (d, *J* = 86.1 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{23}H_{19}O_3P$ [M+Na$^+$]: 397.0970, Found: 397.0984.

(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(naphthalen-2-yl)phosphine oxide (7h)



The pure **7h** was obtained as white solid (413 mg, 95%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent), m.p. 84.3 - 85.9 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 35.58 (s, 42%), 34.46 (s, 58%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.07 (d, *J* = 12.9 Hz, 0.43H), 7.94 – 7.56 (m, 4.63H), 7.45 (ddq, *J* = 42.3, 18.1, 9.9, 8.9 Hz, 3.99H), 7.31 – 7.16 (m, 2.1H), 6.95 (t, *J* = 7.7 Hz, 0.40H), 6.87 (d, *J* = 5.7 Hz, 1.19H), 6.82 (d, *J* = 7.7 Hz, 0.40H), 6.67 (t, *J* = 6.1 Hz, 0.42H), 6.52 (d, *J* = 7.3 Hz, 0.43H), 6.39 (t, *J* = 8.5 Hz, 0.57H), 6.22 (d, *J* = 7.6 Hz, 0.58H), 4.32 (d, *J* = 14.1 Hz, 0.59H), 4.17 (d, *J* = 14.6 Hz, 0.58H), 4.06 (d, *J* = 14.7 Hz, 0.42H), 4.02 – 3.91 (d, J = 14.8 Hz 0.39H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 154.3 – 142.0 (m), 134.7 (d, *J* = 29.5 Hz), 133.7 – 133.3 (m), 133.1 (d, *J* = 8.2 Hz), 132.6 (s), 132.5 (d, *J* = 7.3 Hz), 132.3 (d, *J* = 12.5 Hz), 132.1 (d, *J* = 11.0 Hz), 131.1 (d, *J* = 9.7 Hz), 130.4 – 129.9 (m), 129.6 – 129.3 (m), 128.9 (d, *J* = 27.4 Hz), 128.3 (d, *J* = 10.1 Hz), 128.0 (d, *J* = 4.1 Hz), 127.9 (d, *J* = 7.2 Hz), 127.7 (d, *J* = 13.9 Hz), 127.5 – 127.2 (m), 126.8 (d, *J* = 11.1 Hz), 126.6 (d, *J* = 18.4 Hz), 125.7 (dd, *J* = 88.6, 10.7 Hz), 120.3 (d, *J* = 34.0 Hz), 119.0 (d, *J* = 105.2 Hz), 60.5 (t, *J* = 82.4 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{23}H_{19}O_3P$ [M+Na$^+$]: 397.0970, Found: 397.0975.

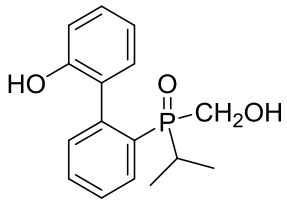
Cyclohexyl (2'-hydroxy-biphenyl-2-yl)(hydroxymethyl)phosphine oxide (7i)



The pure **7i** was obtained as colorless oil (345 mg, 77%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent); **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 46.80 (s, 36%), 45.92 (s, 64%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.09 (dd, *J* = 11.4, 7.6 Hz, 0.64H), 7.85 (dd, *J* = 11.6, 7.7 Hz, 0.36H), 7.54 (dt, *J* = 15.0, 7.5 Hz, 1H), 7.45 (t, *J* = 7.1

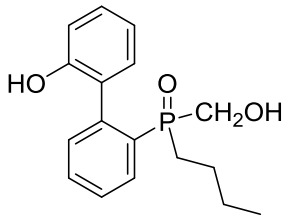
Hz, 1H), 7.32 – 7.21 (m, 2.29H), 7.08 (dd, *J* = 8.6, 3.6 Hz, 1H), 7.02 – 6.94 (m, 1.37H), 6.90 (t, *J* = 7.4 Hz, 0.64H), 4.13 (s, 0.73H), 3.76 (dd, *J* = 14.4, 4.0 Hz, 0.63H), 3.68 (dd, *J* = 14.4, 3.5 Hz, 0.63H), 1.73 – 1.57 (m, 3.63H), 1.47 (ddd, *J* = 36.7, 19.1, 12.1 Hz, 3H), 1.35 (dd, *J* = 12.6, 5.0 Hz, 0.50H), 1.28 – 0.84 (m, 4H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 154.8 (s), 154.2 (s), 142.3 (d, *J* = 8.0 Hz), 140.8 (d, *J* = 10.9 Hz), 134.5 (d, *J* = 5.7 Hz), 132.4 (dd, *J* = 9.1, 3.8 Hz), 131.8 (d, *J* = 10.1 Hz), 130.6 (d, *J* = 63.6 Hz), 130.0 (d, *J* = 29.3 Hz), 128.4 (d, *J* = 86.5 Hz), 128.2 (d, *J* = 85.9 Hz), 127.5 (dd, *J* = 22.4, 10.4 Hz), 119.5 (d, *J* = 177.1 Hz), 118.4 (d, *J* = 246.2 Hz), 60.1 (d, *J* = 73.4 Hz), 58.9 (d, *J* = 75.7 Hz), 36.7 (d, *J* = 66.0 Hz), 36.6 (d, *J* = 65.8 Hz), 26.5 – 26.2 (m), 26.2 – 25.9 (m), 25.7 (d, *J* = 9.4 Hz), 25.0 (d, *J* = 3.6 Hz), 24.6 (d, *J* = 3.8 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{19}H_{23}O_3P$ [M+Na$^+$]: 353.1283, Found: 353.1293.

(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(isopropyl)phosphine oxide (7j)



The pure **7j** was obtained as white solid (348 mg, 78%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent), m.p. 84.0 - 85.3 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 49.64 (s, 36%), 48.83 (s, 64%); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.09 (dd, *J* = 11.4, 7.7 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.40 (dt, *J* = 16.5, 7.7 Hz, 1H), 7.25 – 7.14 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.85 (t, *J* = 7.3 Hz, 1H), 4.05 – 3.85 (m, 1H), 3.73 (dq, *J* = 6.6, 3.4 Hz, 1H), 1.66 (ddt, *J* = 11.4, 7.4, 4.0 Hz, 1H), 1.03 (dd, *J* = 15.7, 7.0 Hz, 2H), 0.93 (ddd, *J* = 15.7, 11.2, 7.9 Hz, 4H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 155.7 – 153.4 (m), 141.7 (dd, *J* = 181.7, 9.7 Hz), 134.4 (d, *J* = 5.8 Hz), 132.5 (d, *J* = 9.3 Hz), 131.9 (d, *J* = 11.9 Hz), 131.0 (s), 130.3 (d, *J* = 21.9 Hz), 129.9 (s), 129.2 (d, *J* = 110.3 Hz), 128.6 – 127.7 (m), 127.4 (dd, *J* = 32.7, 10.3 Hz), 121.0 – 116.0 (m), 59.6 (dd, *J* = 150.3, 75.1 Hz), 26.6 (dd, *J* = 65.3, 30.4 Hz), 15.7 – 14.8 (m); **HRMS (ESI$^+$)** Calcd. for $C_{16}H_{19}O_3P$ [M+Na$^+$]: 313.0970, Found: 313.0981.

Butyl (2'-hydroxy-biphenyl-2-yl)(hydroxymethyl)phosphine oxide (7k)

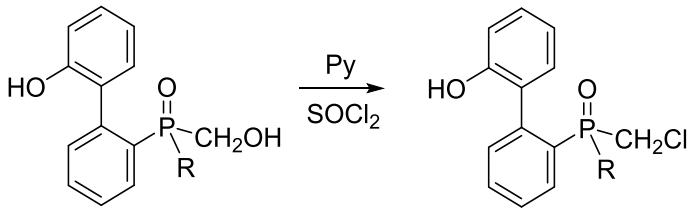


The pure **7k** was obtained as white solid (361 mg, 79%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent), m.p. 53.3 - 55.1 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 45.36 (s, 38%), 44.29 (s, 62%); **^{1}H NMR (500 MHz, Chloroform-*d*)**

δ 8.05 (dd, *J* = 11.8, 7.7 Hz, 0.63H), 7.84 (dd, *J* = 11.8, 7.8 Hz, 0.41H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.39 (dt, *J* = 15.6, 7.7 Hz, 1H), 7.20 (dp, *J* = 26.8, 6.5, 5.7 Hz, 2.24H), 7.05 (d, *J* = 7.6 Hz, 0.49H), 6.98 (t, *J* = 6.2 Hz, 1.63H), 6.85 (dt, *J* = 14.5, 7.5 Hz, 1H), 3.79 (ddd, *J* = 77.2, 40.7, 14.4 Hz, 2H), 1.88 – 1.56 (m, 1.43H), 1.40 (q, *J* = 11.0, 8.4 Hz, 1.3H), 1.33 – 1.06 (m, 3.4H), 0.72 (dt, *J* = 35.1, 7.4 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 154.5 (d, *J* = 57.5 Hz), 141.8 (dd, *J* = 110.2, 9.9 Hz), 133.9 (d, *J* = 6.5 Hz), 132.3 (dd, *J* = 15.7, 9.2 Hz), 131.9 (d, *J* = 16.2 Hz), 130.9 (d, *J* = 58.8 Hz), 130.1 (d, *J* = 18.8 Hz), 129.1 (d, *J* = 52.5 Hz), 128.6 (s), 128.3 (d, *J* = 18.3 Hz), 127.5 (dd, *J* = 19.2, 10.3 Hz), 120.6 – 116.7 (m), 60.5 (dd, *J* = 118.7, 78.2 Hz), 26.2 (dd, *J* = 91.8, 65.8 Hz), 23.9 (d, *J* = 14.9 Hz), 23.1 (dd, *J* = 35.9, 4.4 Hz), 13.5 (d, *J* = 4.7 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{21}O_3P$ [M+Na$^+$]: 327.1126, Found: 327.1136.

Part 3. The chlorination and cyclization of 7 to afford 9.

3-1. The preparation of chloromethyl substituted 8.

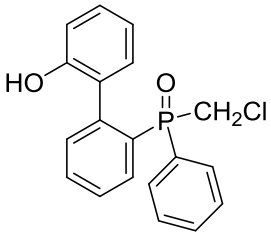


7 **8**

Typical procedure:

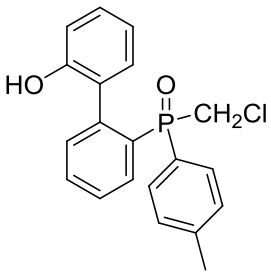
Pyridine (1.2 eq, 32 ul, 31.64 mg 0.40 mmol) was added to the solution of **7a** (107 mg, 0.33 mmol) in THF (2.4 ml). After the solution was cooled to -5 ℃, thionyl chloride (48 ul, 78.52 mg, 2 eq, 0.66 mmol) was added dropwise, then the solution was warmed to room temperature. After the reaction was completed, as monitored with TLC, the reaction was quenched with water and the solvent was removed in vacuo. The mixture was extracted with dichloromethane (3×10 ml), washed with water (3×10 ml) and dried over magnesium sulfate.

(Chloromethyl)(2'-hydroxy-biphenyl-2-yl)(phenyl)phosphine oxide (8a)



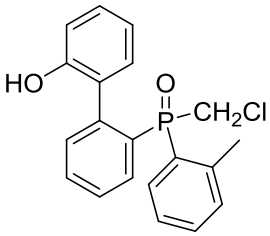
The crude **8a** was obtained as white solid, weighted 95 mg, yield 84%. ^{31}P NMR spectrum of crude **8a** gave two single peaks at 36.2 (s, 62%) and 31.8 ppm (s, 36%). ^{1}H NMR spectrum of crude **8a** gave two peaks of chloromethyl at 4.02 and 3.37 ppm.

(Chloromethyl)(2'-hydroxy-biphenyl-2-yl)(*p*-tolyl)phosphine oxide (8b)



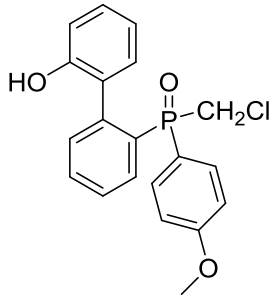
The crude **8b** was obtained as white solid, weighted 207 mg, yield 95%. ^{31}P NMR spectrum of crude **8b** gave two single peaks at 35.5 (s, 57%) and 32.5 ppm (s, 32%). ^{1}H NMR spectrum of crude **8b** gave two peaks of chloromethyl at 3.81 and 3.43 ppm.

(Chloromethyl)(2'-hydroxy-biphenyl-2-yl)(*o*-tolyl)phosphine oxide (8c)



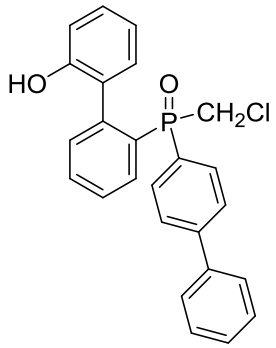
The crude **8c** was obtained as white solid, weighted 192 mg, yield 85%. ^{31}P NMR spectrum of crude **8c** gave two single peaks at 35.1 (s, 57%) and 32.7 ppm (s, 43%). ^{1}H NMR spectrum of crude **8c** gave two peaks of chloromethyl at 3.98 and 3.74 ppm.

(Chloromethyl)(2'-hydroxy-biphenyl-2-yl)(4-methoxyphenyl)phosphine oxide (8d)



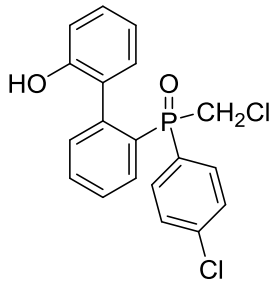
The crude **8d** was obtained as white solid, weighted 339 mg, yield >99%. ^{31}P NMR spectrum of crude **8d** gave two single peaks at 34.4 (s, 58%) and 32.8 ppm (s, 38%). ^{1}H NMR spectrum of crude **8d** gave two peaks of chloromethyl at 3.76 and 3.50 ppm.

(Biphenyl-4-yl)(chloromethyl)(2'-hydroxy-biphenyl-2-yl)phosphine oxide (8e)



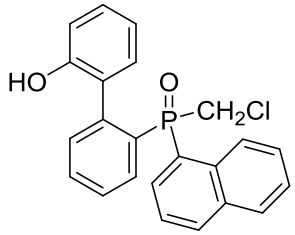
The crude **8e** was obtained as white solid, weighted 333 mg, yield >99%. ^{31}P NMR spectrum of crude **8e** gave two single peaks at 35.1 (s, 60%) and 32.1 ppm (s, 39%). ^{1}H NMR spectrum of crude **8e** gave two peaks of chloromethyl at 3.83 and 3.40 ppm.

(Chloromethyl)(4-chlorophenyl)(2'-hydroxy-biphenyl-2-yl)phosphine oxide (8f)



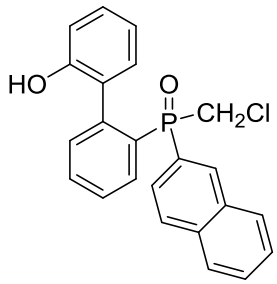
The crude **8f** was obtained as white solid, weighted 368 mg, yield 97%. ^{31}P NMR spectrum of crude **8f** gave two single peaks at 34.2 (s, 54%) and 31.3 ppm (s, 42%). ^{1}H NMR spectrum of crude **8f** gave two peaks of chloromethyl at 3.92and 3.47 ppm.

(Chloromethyl)(2'-hydroxy-biphenyl-2-yl)(naphthalen-1-yl)phosphine oxide (8g)



The crude **8g** was obtained as white solid, weighted 227 mg, yield 98%. ^{31}P NMR spectrum of crude **8g** gave two single peaks at 34.5 (s, 51%) and 31.8 ppm (s, 40%). ^{1}H NMR spectrum of crude **8g** gave two peaks of chloromethyl at 4.06 and 3.88 ppm.

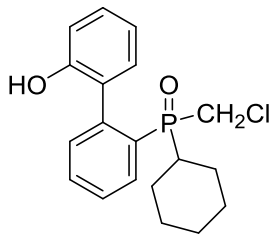
(Chloromethyl)(2'-hydroxy-biphenyl-2-yl)(naphthalen-2-yl)phosphine oxide (8h)



The crude **8h** was obtained as white solid, weighted 376 mg, yield >99%. ^{31}P NMR spectrum of crude **8h** gave two single peaks at 36.4 (s, 58%) and 31.8 ppm (s, 31%). ^{1}H NMR spectrum of crude **8h**

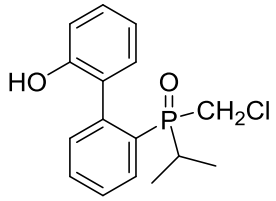
gave two peaks of chloromethyl at 4.04 and 3.45 ppm.

(Chloromethyl)(cyclohexyl)(2'-hydroxy-biphenyl-2-yl)phosphine oxide (8i)



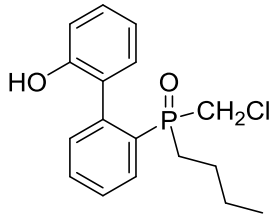
The crude **8i** was obtained as white solid, weighted 224 mg, yield >99%. ^{31}P NMR spectrum of crude **8i** gave two single peaks at 43.8 (s, 46%) and 43.1 ppm (s, 54%). ^{1}H NMR spectrum of crude **8i** gave two peaks of chloromethyl at 3.68 and 3.38 ppm.

(Chloromethyl)(2'-hydroxy-biphenyl-2-yl)(isopropyl)phosphine oxide (8j)



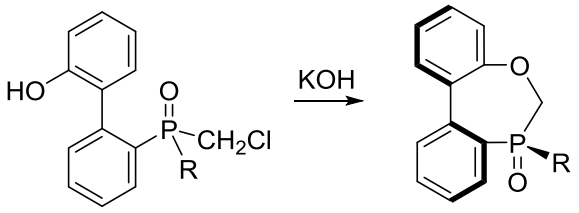
The crude **8g** was obtained as white solid, weighted 242 mg, yield 94%. ^{31}P NMR spectrum of crude **8j** gave two single peaks at 36.2 46.8 (s, 48%) and 46.2 ppm (s, 52%). ^{1}H NMR spectrum of crude **8j** gave two peaks of chloromethyl at 3.66 and 3.31 ppm.

Butyl(chloromethyl)(2'-hydroxy-biphenyl-2-yl)phosphine oxide (8k)



The crude **8k** was obtained as white solid, weighted 350 mg, yield >99%. ^{31}P NMR spectrum of crude **8k** gave two single peaks at 43.1 (s, 66%) and 42.0 ppm (s, 34%). ^{1}H NMR spectrum of crude **8k** gave two peaks of chloromethyl at 3.44 and 3.20 ppm.

3-2. The cyclization of 8 to afford compound *u*-9.

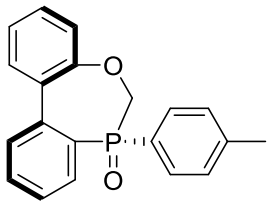


8 *u*-**9**

Typical procedure:

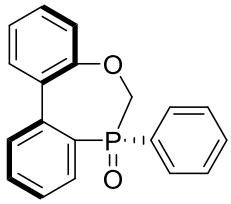
Potassium hydroxide (68 mg, 1.22 mmol) was added to the solution of crude **8b** (200 mg) in DMSO (2 ml). After the reaction was completed, as monitored with TLC, the reaction was quenched with diluted hydrochloric acid (7%) and the mixture was extracted with dichloromethane (3×10 mL). The combined organic phase was washed with water (8×10 mL), dried over magnesium sulfate. After removing solvent, the residue was purified with preparative TLC (silica gel, petroleum ether/ethyl acetate = 1/3 as eluent) to afford *u*-**9b** (123 mg, 70%).

***u*-7-(*p*-Tolyl)-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9b)**



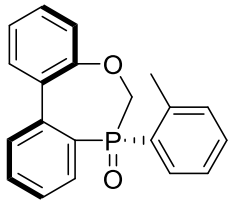
The pure *u*-**9b** was obtained as a colorless oil. **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 30.95 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.19 (dd, *J* = 12.4, 7.6 Hz, 1H), 7.64 (td, *J* = 7.7, 4.6 Hz, 1H), 7.51 (q, *J* = 7.9, 5.8 Hz, 1H), 7.40 (dq, *J* = 7.4, 3.6 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.19 (dd, *J* = 7.5, 2.8 Hz, 2H), 7.17 – 7.12 (m, 1H), 7.09 (dd, *J* = 11.5, 8.1 Hz, 2H), 6.98 (dd, *J* = 8.0, 3.2 Hz, 2H), 5.25 – 5.17 (m, 1H), 5.09 – 4.98 (m, 1H), 2.22 (t, *J* = 3.2 Hz, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 156.3 (s), 142.2 (d, *J* = 3.3 Hz), 140.1 (d, *J* = 9.2 Hz), 134.9 (s), 133.0 (d, *J* = 2.5 Hz), 132.2 (d, *J* = 7.5 Hz), 130.8 (s), 130.3 (d, *J* = 10.1 Hz), 130.2 (s), 130.2 (d, *J* = 96.6 Hz), 129.8 (d, *J* = 10.2 Hz), 129.1 (d, *J* = 99.2 Hz), 129.0 (d, *J* = 12.7 Hz), 127.7 (d, *J* = 11.0 Hz), 126.5 (s), 122.6 (s), 79.9 (d, *J* = 75.2 Hz), 21.4 (s); **HRMS (ESI^{+})** Calcd. for $C_{20}H_{17}O_2P$ [M+Na^{+}]: 343.0864, Found: 343.0873.

***u*-7-Phenyl-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9a)**



The crude *u*-**9a** was obtained with DMSO as solvent, and the pure *u*-**9a** was obtained as a colorless oil (42 mg, 43%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 1/3 as eluent); **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 31.01 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.22 (dd, *J* = 12.4, 7.6 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.43 (dd, *J* = 7.7, 4.7 Hz, 1H), 7.29 (td, *J* = 7.7, 6.6, 4.0 Hz, 2H), 7.23 – 7.10 (m, 7H), 5.25 (dd, *J* = 14.3, 4.7 Hz, 1H), 5.05 (dd, *J* = 14.3, 11.7 Hz, 1H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 156.2 (s), 140.2 (d, *J* = 9.2 Hz), 134.9 (s), 133.2 (d, *J* = 2.7 Hz), 132.5 (d, *J* = 96.7 Hz), 132.3 (d, *J* = 7.4 Hz), 131.7 (d, *J* = 3.1 Hz), 130.8 (s), 130.3 (s), 130.2 (s), 129.9 (d, *J* = 10.5 Hz), 129.7 (d, *J* = 97.0 Hz), 128.2 (d, *J* = 11.9 Hz), 127.8 (d, *J* = 11.0 Hz), 126.5 (s), 122.6 (s), 79.6 (d, *J* = 74.9 Hz); **HRMS (ESI^{+})** Calcd. for $C_{19}H_{15}O_2P$ [M+Na^{+}]: 329.0707, Found: 329.0718.

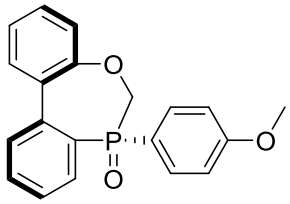
***u*-7-(*o*-Tolyl)-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9c)**



The crude *u*-**9c** was obtained with DMSO as solvent, and the pure *u*-**9c** was obtained as white solid (151 mg, 76%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 1/3 as eluent), m.p. 190.0 - 191.1 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 32.97 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.18 (dd, *J* = 12.5, 7.6 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.56 (tt, *J* = 7.5, 1.5 Hz,

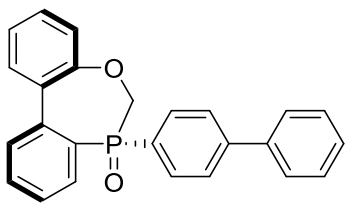
1H), 7.42 (dd, *J* = 7.8, 4.5 Hz, 1H), 7.27 (td, *J* = 7.7, 1.8 Hz, 1H), 7.24 – 7.14 (m, 3H), 7.14 – 7.05 (m, 2H), 7.01 (dd, *J* = 13.3, 7.7 Hz, 1H), 6.89 (ddd, *J* = 9.1, 7.3, 2.6 Hz, 1H), 5.35 (dd, *J* = 14.3, 4.5 Hz, 1H), 4.99 (dd, *J* = 14.3, 11.1 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 156.1 (s), 141.2 (d, *J* = 8.3 Hz), 140.4 (s), 134.8 (s), 133.0 (d, *J* = 2.5 Hz), 132.9 (d, *J* = 7.7 Hz), 131.7 (d, *J* = 3.1 Hz), 131.5 (d, *J* = 10.2 Hz), 131.4 (d, *J* = 11.8 Hz), 130.5 (s), 130.3 (d, *J* = 3.7 Hz), 130.1 (s), 129.9 (d, *J* = 10.1 Hz), 129.5 (d, *J* = 4.0 Hz), 127.6 (d, *J* = 11.0 Hz), 126.4 (s), 124.9 (d, *J* = 12.0 Hz), 122.4 (s), 79.7 (d, *J* = 74.3 Hz), 21.5 (d, *J* = 3.9 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{20}H_{17}O_2P$ [M+Na$^+$]: 343.0864, Found: 343.0873.

***u*-7-(4-Methoxyphenyl)-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9d)**



The crude *u*-**9d** was obtained with DMF as solvent, and the pure *u*-**9d** was obtained as a colorless oil (273 mg, 93%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 1/3 as eluent); **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 30.39 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.19 (ddd, *J* = 12.3, 7.6, 1.5 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.55 – 7.49 (m, 1H), 7.41 (ddd, *J* = 7.8, 4.6, 1.2 Hz, 1H), 7.30 (ddd, *J* = 8.9, 6.0, 1.9 Hz, 1H), 7.19 (dt, *J* = 8.0, 2.1 Hz, 2H), 7.17 – 7.08 (m, 3H), 6.73 – 6.63 (m, 2H), 5.19 (dd, *J* = 14.3, 4.7 Hz, 1H), 5.02 (dd, *J* = 14.3, 11.6 Hz, 1H), 3.68 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 162.2 (d, *J* = 2.7 Hz), 156.2 (s), 140.1 (d, *J* = 9.2 Hz), 135.0 (s), 133.0 (d, *J* = 2.7 Hz), 132.2 (d, *J* = 11.2 Hz), 132.1 (d, *J* = 7.6 Hz), 130.8 (s), 130.3 (d, *J* = 97.0 Hz), 130.2 (s), 129.8 (d, *J* = 10.2 Hz), 127.7 (d, *J* = 11.0 Hz), 126.5 (s), 123.6 (d, *J* = 102.8 Hz), 122.5 (s), 113.8 (d, *J* = 13.1 Hz), 79.9 (d, *J* = 75.3 Hz), 55.21 (s); **HRMS (ESI$^+$)** Calcd. for $C_{20}H_{17}O_3P$ [M+Na$^+$]: 359.0813, Found: 359.0825.

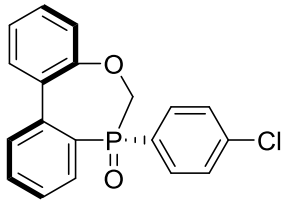
***u*-7-(Biphenyl-4-yl)-6*H*-dibenzo-[*d,f*][1,3]-oxaphosphepine 7-oxide (*u*-9e)**



The crude *u*-**9e** was obtained with DMF as solvent, and the pure *u*-**9e** was obtained as white solid (241 mg, 85%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 1/4 as eluent), m.p. 184.6-185.9; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 30.96 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.26 (dd, *J* = 12.4, 7.6 Hz, 1H), 7.66 (q, *J* = 7.8, 7.3 Hz, 1H), 7.56 (q, *J* = 7.6, 7.0 Hz, 1H), 7.48 – 7.35 (m, 7H), 7.31 (dd, *J* = 11.5, 6.7 Hz, 2H), 7.23 (ddd, *J* = 21.8, 12.3, 7.3 Hz, 4H), 7.15 (q, *J* = 7.5, 6.1 Hz, 1H), 5.26 (dd, *J* = 14.3, 5.0 Hz, 1H),

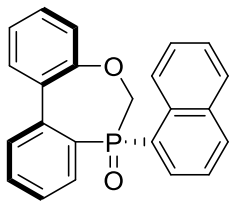
5.08 (t, *J* = 13.1 Hz, 1H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 156.3 (s), 144.4 (d, *J* = 2.8 Hz), 140.2 (d, *J* = 9.2 Hz), 139.7 (s), 134.9 (s), 133.3 (d, *J* = 2.7 Hz), 132.3 (d, *J* = 7.8 Hz), 131.1 (d, *J* = 97.6 Hz), 130.9 (d, *J* = 6.5 Hz), 130.8 (s), 130.3 (s), 123.0 (d, *J* = 10.7 Hz), 129.9 (d, *J* = 97.1 Hz), 129.0 (s), 128.2 (s), 127.8 (d, *J* = 11.0 Hz), 127.2 (s), 126.9 (d, *J* = 12.0 Hz), 126.6 (s), 122.7 (s), 79.9 (d, *J* = 75.1 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{25}H_{19}O_2P$ [M+Na$^+$]: 405.1020, Found: 405.1029.

***u*-7-(4-Chlorophenyl)-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9f)**



The crude ***u*-9f** was obtained with DMF as solvent, and the pure ***u*-9f** was obtained as a colorless oil (131 mg, 40%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 1/4 as eluent); **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 30.43 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.22 (ddd, *J* = 12.4, 7.6, 1.6 Hz, 1H), 7.69 (dddd, *J* = 7.6, 5.8, 2.9, 1.5 Hz, 1H), 7.62 – 7.53 (m, 1H), 7.44 (ddd, *J* = 7.8, 4.7, 1.3 Hz, 1H), 7.33 (ddd, *J* = 8.0, 5.3, 3.7 Hz, 1H), 7.24 – 7.18 (m, 3H), 7.16 (dq, *J* = 8.5, 2.4 Hz, 2H), 7.10 (ddd, *J* = 11.0, 8.5, 2.0 Hz, 2H), 5.24 – 5.15 (m, 1H), 5.11 – 5.01 (m, 1H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 156.2 (s), 140.0 (d, *J* = 9.2 Hz), 138.2 (d, *J* = 3.5 Hz), 134.7 (s), 133.4 (d, *J* = 2.7 Hz), 132.3 (d, *J* = 7.3 Hz), 131.6 (d, *J* = 11.0 Hz), 130.9 (s), 130.9 (s), 130.4 (s), 129.9 (d, *J* = 10.1 Hz), 129.3 (d, *J* = 97.5 Hz), 128.6 (d, *J* = 12.3 Hz), 127.9 (d, *J* = 10.4 Hz), 126.7 (s), 122.7 (s), 79.6 (d, *J* = 75.4 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{19}H_{14}ClO_2P$ [M+Na$^+$]: 363.0318, Found: 363.0328.

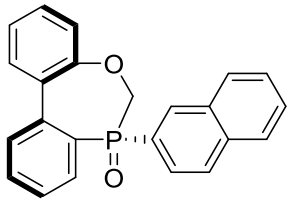
***u*-7-(Naphthalen-1-yl)-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9g)**



The crude ***u*-9g** was obtained with DMF as solvent, and the pure ***u*-9g** was obtained as colorless oil (348 mg, 71%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 1/4 as eluent); **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 33.77 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.32 (d, *J* = 8.3 Hz, 1H), 8.15 – 7.98 (m, 1H), 7.82 (dd, *J* = 21.8, 8.1 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.46 (ddt, *J* = 16.7, 8.3, 5.1 Hz, 5H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.18 – 7.09 (m, 2H), 5.37 (dd, *J* = 14.1, 4.6 Hz, 1H), 5.07 (dd, *J* = 14.2, 10.0 Hz, 1H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 156.2 (s), 140.8 (d, *J* = 8.3 Hz), 134.9 (s), 133.6 (d, *J* = 9.1 Hz), 133.3 (d, *J* = 3.7 Hz), 133.3 (s), 133.2 (d, *J* = 8.5 Hz), 132.8 (d, *J* = 9.2 Hz), 132.4 (d, *J* = 8.6 Hz), 130.7 (s),

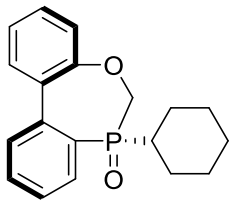
130.3 (d, *J* = 3.3 Hz), 130.2 (s), 129.5 (s), 129.3 (s), 127.8 (d, *J* = 11.2 Hz), 127.5 (s), 127.3 (d, *J* = 93.6 Hz), 126.6 (s), 126.4 (s), 126.2 (d, *J* = 4.8 Hz), 124.3 (d, *J* = 13.6 Hz), 122.4 (s), 81.1 (d, *J* = 74.7 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{23}H_{17}O_2P$ [M+Na$^+$]: 379.0864, Found: 379.0873.

***u*-7-(Naphthalen-2-yl)-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9h)**



The crude *u*-**9h** was obtained with DMF as solvent, and the pure *u*-**9h** was obtained as colorless oil (192 mg, 65%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 1/4 as eluent); **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 31.11 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.28 (dd, *J* = 12.4, 7.6 Hz, 1H), 7.61 (dd, *J* = 10.3, 6.3 Hz, 3H), 7.54 (dd, *J* = 12.0, 7.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.33 – 7.30 (m, 1H), 7.30 – 7.24 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 6.8 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 5.30 (dd, *J* = 14.4, 5.2 Hz, 1H), 5.13 (dd, *J* = 14.4, 11.6 Hz, 1H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 156.4 (s), 140.0 (d, *J* = 9.2 Hz), 134.9 (s), 134.3 (d, *J* = 2.6 Hz), 133.2 (d, *J* = 2.6 Hz), 132.1 (d, *J* = 2.6 Hz), 132.1 (s), 132.0 (d, *J* = 8.2 Hz), 130.9 (s), 130.3 (s), 130.6 – 129.8 (m), 130.0 (s), 129.5 (d, *J* = 75.3 Hz), 128.7 (s), 128.2 (d, *J* = 11.5 Hz), 128.2 (s), 127.8 (d, *J* = 11.0 Hz), 127.6 (s), 126.8 (s), 126.6 (s), 125.2 (d, *J* = 10.1 Hz), 122.8 (s), 80.3 (d, *J* = 74.4 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{23}H_{17}O_2P$ [M+Na$^+$]: 379.0864, Found: 379.0876.

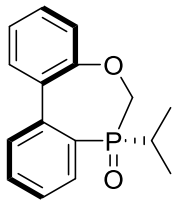
***u*-7-Cyclohexyl-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9i)**



The crude *u*-**9i** was obtained with DMF as solvent, and the pure *u*-**9i** was obtained as colorless oil (164 mg, 88%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 1/4 as eluent); **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 41.58 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.16 (dt, *J* = 11.6, 5.8 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.55 (q, *J* = 7.5, 6.8 Hz, 1H), 7.46 (dd, *J* = 7.7, 4.5 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.34 (dd, *J* = 10.5, 3.9 Hz, 1H), 7.22 (t, *J* = 6.5 Hz, 1H), 4.91 (dt, *J* = 14.0, 5.4 Hz, 1H), 4.74 (td, *J* = 13.4, 4.8 Hz, 1H), 1.81 – 1.65 (m, 2H), 1.60 – 1.39 (m, 3H), 1.26 – 1.14 (m, 1H), 1.13 – 0.95 (m, 2H), 0.86 (qt, *J* = 12.7, 3.7 Hz, 1H), 0.71 (ddddd, *J* = 18.9, 12.4, 9.6, 7.1, 3.4 Hz, 2H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 155.8 (s), 139.2 (d, *J* = 9.2 Hz), 135.2 (s), 132.8 (d, *J* = 2.6 Hz), 132.7 (d, *J* = 6.2 Hz), 130.3 (s), 130.2 (s), 129.2 (d, *J* = 10.0 Hz), 128.7 (d, *J* = 87.9 Hz), 127.6 (d, *J* = 10.7 Hz), 126.6 (s), 122.5 (s), 76.7 (d, *J* = 66.2 Hz), 38.1

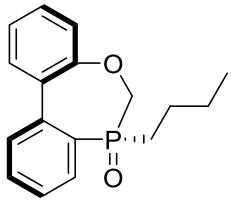
(d, *J* = 66.4 Hz), 26.1 (s), 26.1 (d, *J* = 25.8 Hz), 25.4 (s), 24.6 (d, *J* = 3.3 Hz), 24.1 (d, *J* = 3.9 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{19}H_{21}O_2P$ [M+Na$^+$]: 335.1177, Found: 335.1186.

***u*-7-Isopropyl-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9j)**



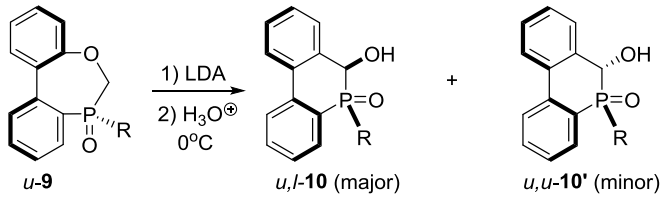
The crude *u*-**9j** was obtained with DMF as solvent, and the pure *u*-**9j** was obtained as white solid (234 mg, 80%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 1/4 as eluent), m.p. 134.1-135.8 ℃;**^{31}P NMR (202 MHz, Chloroform-*d*)** δ 44.11 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.19 (dd, *J* = 11.5, 7.4 Hz, 1H), 7.66 (q, *J* = 7.5, 6.6 Hz, 1H), 7.55 (dt, *J* = 14.9, 7.3 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.40 (dq, *J* = 13.8, 6.7, 5.4 Hz, 2H), 7.33 (dd, *J* = 12.1, 7.1 Hz, 1H), 7.22 (t, *J* = 9.2 Hz, 1H), 5.12 – 4.60 (m, 2H), 1.08 (qd, *J* = 14.5, 12.7, 6.5 Hz, 4H), 0.71 (ddd, *J* = 16.5, 10.6, 6.4 Hz, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 155.7 (s), 139.0 (d, *J* = 9.9 Hz), 135.0 (d, *J* = 4.1 Hz), 132.8 (s), 132.6 (t, *J* = 5.1 Hz), 130.4 (s), 130.1 (s), 129.3 (d, *J* = 10.1 Hz), 128.8 (d, *J* = 88.0 Hz), 127.6 (dd, *J* = 10.1, 4.1 Hz), 126.7 (s), 122.4 (s), 77.2 (d, *J* = 66.9 Hz), 27.9 (dd, *J* = 66.0, 3.0 Hz), 15.0 (d, *J* = 3.7 Hz), 14.4 (d, *J* = 3.8 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{16}H_{17}O_2P$ [M+Na$^+$]: 295.0864, Found: 295.0879.

***u*-7-Butyl-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9k)**



The crude *u*-**9k** was obtained with DMF as solvent, and the pure *u*-**9k** was obtained as a colorless oil (258 mg, 85%) from preparative TLC (silica gel, petroleum ether/ethyl acetate = 1/4 as eluent); **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 38.60; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.19 (dd, *J* = 11.8, 7.0 Hz, 1H), 7.67 (t, *J* = 7.9 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.47 (h, *J* = 4.3 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.26 – 7.17 (m, 1H), 4.96 – 4.62 (m, 2H), 1.56 – 1.33 (m, 2H), 1.11 (ddq, *J* = 29.1, 13.5, 6.6, 5.9 Hz, 4H), 0.64 (dd, *J* = 8.4, 6.1 Hz, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 155.7 (s), 139.2 (d, *J* = 9.5 Hz), 135.0 (s), 132.9 (d, *J* = 2.6 Hz), 132.3 (d, *J* = 6.3 Hz), 130.4 (s), 130.2 (s), 129.3 (d, *J* = 10.2 Hz), 129.2 (d, *J* = 90.1 Hz), 127.7 (d, *J* = 10.3 Hz), 126.6 (s), 122.5 (s), 79.2 (d, *J* = 69.8 Hz), 30.2 (d, *J* = 65.3 Hz), 23.4 (d, *J* = 13.9 Hz), 23.2 (d, *J* = 4.6 Hz), 13.2 (s); **HRMS (ESI$^+$)** Calcd. for $C_{17}H_{19}O_2P$ [M+Na$^+$]: 309.1020, Found: 309.1040.

Part 4. The rearrangement of *u*-9 to afford 10.

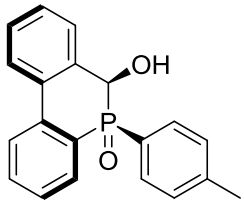


u-**9** *u,l*-**10** (major) *u,u*-**10'** (minor)

Typical procedure:

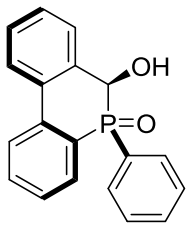
The solution of LDA (3 eq, 370 μl, 0.75 mmol, 2 mol/L) in THF was added to the solution of *u*-**9b** (79 mg, 0.25 mmol) in THF (2 ml) at -30 °C, then the solution was stirred with warming to room temperature. After the reaction was completed, as monitored with TLC, the mixture was cooled with ice bath and quenched with saturated ammonium chloride. The solvent was removed and the mixture was extracted with dichloromethane (3×10 mL), washed with water (3×10 mL), dried over magnesium sulfate. After removing solvent, the residue was purified with preparative TLC (silica gel, petroleum ether/ethyl acetate = 1/3 as eluent) to afford *u,l*-**10b** (51 mg, 65%).

***u,l*-6-Hydroxy-5-(*p*-tolyl)-6*H*-phosphanthridine 5-oxide (*u,l*-10b)**



The pure *u,l*-**10b** was obtained as white solid, m.p. 226.4 – 228.1 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 25.01 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.05 (ddd, *J* = 11.5, 7.5, 1.4 Hz, 1H), 7.84 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.80 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.71 – 7.61 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.33 (td, *J* = 8.2, 2.5 Hz, 4H), 7.24 (s, 1H), 7.00 (dd, *J* = 8.1, 2.8 Hz, 2H), 5.88 (d, *J* = 13.4 Hz, 1H), 2.22 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 142.5 (d, *J* = 2.7 Hz), 140.3 (d, *J* = 8.1 Hz), 135.2 (s), 133.4 (d, *J* = 2.3 Hz), 132.7 (d, *J* = 6.5 Hz), 131.9 (d, *J* = 9.2 Hz), 131.6 (d, *J* = 4.7 Hz), 129.2 (s), 129.0 (d, *J* = 12.1 Hz), 128.5 (d, *J* = 10.1 Hz), 128.1 (d, *J* = 3.0 Hz), 126.7 (d, *J* = 93.1 Hz), 126.3 (d, *J* = 3.0 Hz), 126.0 (s), 125.9 (d, *J* = 3.3 Hz), 124.5 (d, *J* = 101.2 Hz), 70.4 (d, *J* = 84.4 Hz), 21.5 (s); **HRMS (ESI^{+})** Calcd. for $C_{20}H_{17}O_2P$ [M+Na^{+}]: 343.0864, Found: 343.0874.

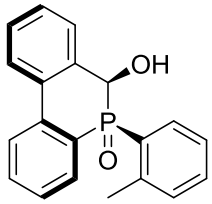
***u,l*-6-Hydroxy-5-phenyl-6*H*-phosphanthridine 5-oxide (*u,l*-10a)**



The pure *u,l*-**10a** was obtained as colorless oil (17 mg, 42%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent); **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 25.01 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.07 (ddd, *J* = 11.6, 7.5, 1.5 Hz, 1H), 7.82 (td, *J* = 8.0, 3.4 Hz, 2H), 7.73 – 7.62 (m,

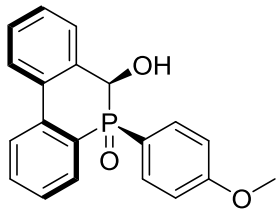
2H), 7.52 – 7.42 (m, 3H), 7.37 – 7.29 (m, 3H), 7.19 (td, *J* = 7.8, 3.1 Hz, 3H), 5.90 (d, *J* = 13.3 Hz, 1H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 140.4 (d, *J* = 7.8 Hz), 135.0 (s), 133.6 (d, *J* = 2.7 Hz), 132.6 (d, *J* = 6.6 Hz), 132.0 (d, *J* = 2.7 Hz), 131.9 (s), 131.8 (s), 131.6 (d, *J* = 4.9 Hz), 129.3 (s), 128.5 (d, *J* = 10.2 Hz), 128.3 (d, *J* = 4.0 Hz), 128.1 (d, *J* = 3.6 Hz), 127.1 (d, *J* = 94.7 Hz), 126.3 (d, *J* = 3.6 Hz), 126.0 (d, *J* = 8.9 Hz), 125.9 (d, *J* = 6.3 Hz), 70.4 (d, *J* = 83.8 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{19}H_{15}O_2P$ [M+Na$^+$]: 329.0707, Found: 329.0724.

***u,l*-6-Hydroxy-5-(*o*-tolyl)-6*H*-phosphanthridine 5-oxide (*u,l*-10c)**



The pure *u,l*-**10c** was obtained as white solid (47 mg, 59%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent), m.p. 233.5 – 234.7 ℃; **^{31}P NMR (202 MHz, Methanol-d_4)** δ 30.75 (s); **^{1}H NMR (500 MHz, Methanol-d_4)** δ 7.99 (ddd, *J* = 11.5, 7.5, 1.5 Hz, 1H), 7.91 (dd, *J* = 8.0, 4.9 Hz, 1H), 7.83 – 7.76 (m, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.37 – 7.32 (m, 1H), 7.29 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.21 (dd, *J* = 7.5, 3.9 Hz, 1H), 6.91 (ddd, *J* = 13.5, 7.9, 1.4 Hz, 1H), 6.82 (dq, *J* = 7.2, 5.1, 3.8 Hz, 1H), 5.64 (d, *J* = 14.2 Hz, 1H), 2.77 (d, *J* = 1.4 Hz, 3H); **^{13}C NMR (126 MHz, Methanol-d_4)** δ 144.0 (d, *J* = 7.5 Hz), 140.4 (d, *J* = 6.6 Hz), 134.9 (s), 133.6 (d, *J* = 2.7 Hz), 132.8 (d, *J* = 13.0 Hz), 132.7 (s), 132.0 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 11.1 Hz), 131.3 (d, *J* = 5.5 Hz), 128.9 (s), 128.3 (d, *J* = 10.8 Hz), 128.1 (d, *J* = 2.8 Hz), 126.7 (d, *J* = 94.5 Hz), 126.3 (d, *J* = 3.6 Hz), 126.0 (d, *J* = 9.0 Hz), 125.3 (d, *J* = 96.6 Hz), 124.8 (d, *J* = 6.3 Hz), 124.4 (d, *J* = 13.2 Hz), 72.2 (s), 21.4 (d, *J* = 3.3 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{20}H_{17}O_2P$ [M+Na$^+$]: 343.0864, Found: 343.0886.

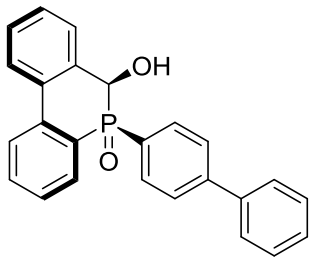
***u,l*-6-Hydroxy-5-(4-methoxyphenyl)-6*H*-phosphanthridine 5-oxide (*u,l*-10d)**



The pure *u,l*-**10d** was obtained as white solid (103 mg, 71%) from preparative TLC (silica gel, dichloromethane/methanol = 30/2 as eluent), m.p. 242.1 – 243.9 ℃; **^{31}P NMR (202 MHz, DMSO-d_6)** δ 20.29 (s); **^{1}H NMR (500 MHz, DMSO-d_6)** δ 7.92 (dd, *J* = 8.0, 4.6 Hz, 1H), 7.82 (ddd, *J* = 11.4, 7.5, 1.5 Hz, 1H), 7.78 – 7.75 (m, 1H), 7.75 – 7.70 (m, 1H), 7.61 – 7.56 (m, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.28 (m, 3H), 6.82 (dt, *J* = 8.7, 2.1 Hz, 2H), 6.71 (dd, *J* = 7.2, 5.5 Hz, 1H), 5.40 (dd, *J* = 14.0, 5.5 Hz, 1H), 3.71 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d_6)** δ 162.4 (s), 139.9 (d, *J* = 7.1 Hz), 136.3 (s), 133.9 (d, *J* = 9.6 Hz),

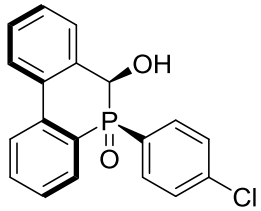
133.6 (s), 133.0 (d, *J* = 6.6 Hz), 131.4 (d, *J* = 5.5 Hz), 129.2 (s), 128.7 (s), 128.6 (s), 128.3 (d, *J* = 87.6 Hz), 126.9 (s), 126.5 (d, *J* = 6.2 Hz), 126.4 (d, *J* = 8.9 Hz), 120.5 (d, *J* = 102.8 Hz), 114.1 (d, *J* = 12.5 Hz), 70.1 (d, *J* = 87.4 Hz), 55.5 (s); **HRMS (ESI$^+$)** Calcd. for $C_{20}H_{17}O_3P$ [M+Na$^+$]: 359.0813, Found: 359.0823.

***u,l*-5-(Biphenyl-4-yl)-6-hydroxy-6*H*-phosphanthridine 5-oxide (*u,l*-10e)**



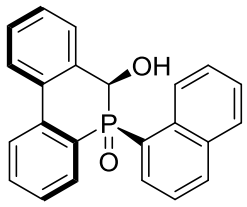
The pure *u,l*-**10e** was obtained as white solid (47 mg, 47%) from preparative TLC (silica gel, trichloromethane/isopropanol = 20/1 as eluent), m.p. 230.5 – 232.0 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 24.76 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.10 (ddd, *J* = 11.5, 7.5, 1.5 Hz, 1H), 7.92 – 7.86 (m, 1H), 7.84 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.56 – 7.48 (m, 3H), 7.48 – 7.41 (m, 4H), 7.40 – 7.34 (m, 4H), 7.34 – 7.29 (m, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 5.94 (dd, *J* = 13.4, 3.7 Hz, 1H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 144.7 (d, *J* = 2.6 Hz), 140.3 (d, *J* = 8.2 Hz), 140.0 (s), 134.9 (s), 133.6 (s), 132.7 (d, *J* = 6.6 Hz), 132.4 (d, *J* = 9.2 Hz), 131.6 (d, *J* = 5.3 Hz), 129.3 (s), 128.8 (s), 128.6 (d, *J* = 10.3 Hz), 128.3 (s), 128.0 (s), 127.2 (s), 127.0 (d, *J* = 12.0 Hz), 126.8 (d, *J* = 3.3 Hz), 126.4 (d, *J* = 3.5 Hz), 126.1 (s), 126.0 (s), 125.9 (s), 70.5 (d, *J* = 83.9 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{25}H_{19}O_2P$ [M+Na$^+$]: 405.1020, Found: 405.1023.

***u,l*-5-(4-Chlorophenyl)-6-hydroxy-6*H*-phosphanthridine 5-oxide (*u,l*-10f)**



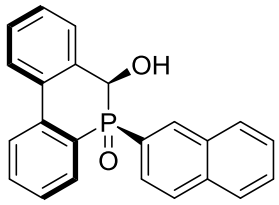
The pure *u,l*-**10f** was obtained as white solid (54 mg, 41%) from preparative TLC (silica gel, dichloromethane/methanol = 20/1 as eluent), m.p. 134.2 – 135.8 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 24.47 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.06 (dd, *J* = 11.6, 7.5 Hz, 1H), 7.82 (dd, *J* = 8.0, 5.5 Hz, 2H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.31 (m, 4H), 7.24 – 7.11 (m, 3H), 5.88 (dd, *J* = 13.1, 4.9 Hz, 1H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 140.4 (d, *J* = 7.4 Hz), 138.7 (d, *J* = 3.6 Hz), 134.6 (s), 133.8 (s), 133.2 (d, *J* = 9.4 Hz), 132.5 (d, *J* = 7.3 Hz), 131.6 (d, *J* = 4.9 Hz), 129.4 (s), 128.6 (d, *J* = 11.9 Hz), 128.3 (s), 126.9 (s), 126.4 (d, *J* = 3.6 Hz), 126.2 (s), 126.1 (s), 125.9 (d, *J* = 6.3 Hz), 125.4 (s), 70.3 (d, *J* = 84.5 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{19}H_{14}ClO_2P$ [M+Na$^+$]: 363.0318, Found: 363.0328.

***u,l*-6-Hydroxy-5-(naphthalen-1-yl)-6*H*-phosphanthridine 5-oxide (*u,l*-10g)**



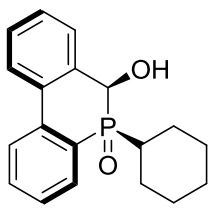
The pure *u,l*-**10g** was obtained as white solid (48 mg, 62%) from preparative TLC (silica gel, dichloromethane/methanol = 10/1 as eluent), m.p. 206.0 – 207.3 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 26.65 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.81 (d, *J* = 8.2 Hz, 1H), 8.02 (ddd, *J* = 12.4, 7.5, 1.5 Hz, 1H), 7.92 – 7.85 (m, 3H), 7.76 – 7.69 (m, 2H), 7.61 – 7.52 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.40 (ddd, *J* = 15.4, 7.2, 1.3 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 5.46 (d, *J* = 2.1 Hz, 1H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 140.3 (d, *J* = 6.8 Hz), 133.8 (d, *J* = 9.2 Hz), 133.6 (d, *J* = 1.6 Hz), 133.6 (d, *J* = 20.3 Hz), 133.5 (d, *J* = 2.9 Hz), 133.4 (s), 133.3 (d, *J* = 3.7 Hz), 133.2 (s), 133.2 (s), 131.5 (d, *J* = 9.7 Hz), 130.1 (s), 129.2 (s), 129.0 (s), 128.8 (d, *J* = 11.0 Hz), 127.7 (s), 127.0 (s), 126.5 (s), 126.4 (d, *J* = 4.7 Hz), 125.99 (d, *J* = 9.1 Hz), 125.0 (d, *J* = 91.3 Hz), 124.4 (d, *J* = 13.7 Hz), 124.3 (d, *J* = 92.0 Hz), 68.9 (d, *J* = 79.1 Hz); **HRMS (ESI^{+})** Calcd. for $C_{23}H_{17}O_2P$ [M+Na^{+}]: 379.0864, Found: 379.0862.

***u,l*-6-Hydroxy-5-(naphthalen-2-yl)-6*H*-phosphanthridine 5-oxide (*u,l*-10h)**



The pure *u,l*-**10h** was obtained as white solid (48 mg, 45%) from preparative TLC (silica gel, dichloromethane/methanol = 30/2 as eluent), m.p. 240.3 – 241.6 ℃; **^{31}P NMR (202 MHz, DMSO-d_6)** δ 20.38 (s) (s); **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.09 (d, *J* = 12.8 Hz, 1H), 8.02 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.86 (q, *J* = 7.5, 7.1 Hz, 4H), 7.83 – 7.77 (m, 2H), 7.58 (dq, *J* = 7.3, 4.5 Hz, 3H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.30 (m, 2H), 6.84 (dd, *J* = 7.7, 5.5 Hz, 1H), 5.51 (dd, *J* = 13.9, 5.5 Hz, 1H); **^{13}C NMR (126 MHz, DMSO-d_6)** δ 140.1(d, *J* = 7.1 Hz), 136.3 (s), 134.6 (s), 134.1 (s), 133.9 (d, *J* = 8.3 Hz), 133.1 (d, *J* = 7.2 Hz), 132.2 (d, *J* = 12.7 Hz), 131.7 (d, *J* = 5.6 Hz), 129.4 (s), 129.0 (s), 128.9 (s), 128.6 (s), 128.2 (s), 128.1 (s), 128.0 (s), 127.9 (s), 127.6 (d, *J* = 24.8 Hz), 127.4 (s), 127.2 (s), 127.0 (d, *J* = 27.6 Hz), 126.8 (s), 126.7 (s), 70.1 (d, *J* = 87.2 Hz); **HRMS (ESI^{+})** Calcd. for $C_{23}H_{17}O_2P$ [M+Na^{+}]: 379.0864, Found: 379.0876.

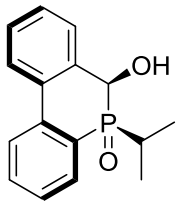
***u,l*-5-Cyclohexyl-6-hydroxy-6*H*-phosphanthridine 5-oxide (*u,l*-10i)**



The pure *u,l*-**10i** was obtained as white solid (47 mg, 55%) from preparative TLC (silica gel, trichloromethane/isopropanol = 30/2 as eluent), m.p. 163.1 – 164.5 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 35.75 (s); **^{1}H NMR (500**

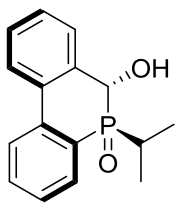
MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.92 (dd, *J* = 10.4, 7.3 Hz, 1H), 7.71 (dd, *J* = 8.0, 4.7 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 2H), 7.52 – 7.33 (m, 4H), 5.71 (dd, *J* = 14.4, 3.5 Hz, 1H), 2.16 (dt, *J* = 13.5, 4.0 Hz, 1H), 1.77 (dq, *J* = 12.4, 4.3 Hz, 1H), 1.66 (dt, *J* = 8.7, 4.2 Hz, 1H), 1.49 (dt, *J* = 25.5, 10.9 Hz, 3H), 1.35 – 1.22 (m, 2H), 1.06 (qd, *J* = 12.8, 6.5 Hz, 2H), 1.00 – 0.88 (m, 1H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 139.6 (d, *J* = 7.4 Hz), 135.6 (s), 132.9 (d, *J* = 2.5 Hz), 132.6 (d, *J* = 6.2 Hz), 131.8 (d, *J* = 4.5 Hz), 129.2 (s), 128.0 (d, *J* = 13.2 Hz), 127.9 (s), 126.5 (d, *J* = 424.1 Hz), 126.2 (d, *J* = 2.8 Hz), 125.9 (d, *J* = 8.4 Hz), 125.4 (d, *J* = 5.6 Hz), 70.5 (d, *J* = 78.2 Hz), 33.8 (d, *J* = 66.2 Hz), 26.1 (dd, *J* = 12.6, 5.8 Hz), 25.6 (s), 25.3 (d, *J* = 3.3 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{19}H_{21}O_2P$ [M+Na$^+$]: 335.1177, Found: 335.1190.

***u,l*-6-Hydroxy-5-isopropyl-6*H*-phosphanthridine 5-oxide (*u,l*-10j)**



The pure *u,l*-**10j** was obtained as white solid (90 mg, 51%) from preparative TLC (silica gel, trichloromethane/isopropanol = 30/2 as eluent, R_f = 0.6), m.p. 223.5 – 226.1 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 38.35 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.03 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.94 (ddd, *J* = 10.4, 7.4, 1.4 Hz, 1H), 7.71 (dd, *J* = 7.9, 4.7 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.51 – 7.34 (m, 4H), 5.72 (d, *J* = 14.2 Hz, 1H), 2.00 – 1.87 (m, 1H), 1.26 (dd, *J* = 15.2, 7.1 Hz, 3H), 0.85 (dd, *J* = 16.4, 7.3 Hz, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 139.6 (d, *J* = 8.0 Hz), 135.6 (s), 133.0 (d, *J* = 2.4 Hz), 132.6 (d, *J* = 5.7 Hz), 131.7 (d, *J* = 4.3 Hz), 129.2 (s), 128.0 (d, *J* = 9.9 Hz), 127.9 (d, *J* = 2.7 Hz), 126.5 (d, *J* = 84.2 Hz), 126.3 (d, *J* = 2.9 Hz), 125.9 (d, *J* = 8.5 Hz), 125.3 (d, *J* = 5.6 Hz), 70.4 (d, *J* = 78.0 Hz), 23.7 (d, *J* = 66.9 Hz), 16.1 (d, *J* = 2.9 Hz), 15.7 (d, *J* = 4.4 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{16}H_{17}O_2P$ [M+Na$^+$]: 295.0864, Found: 295.0878.

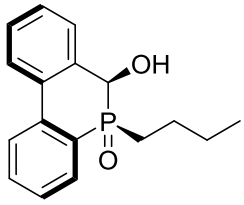
***u,u*-6-Hydroxy-5-isopropyl-6*H*-phosphanthridine 5-oxide (*u,u*-10j')**



The pure *u,u*-**10j'** was obtained from the same reaction to *u,u*-**10j**, as white solid (32 mg, 18%) from preparative TLC (silica gel, trichloromethane/isopropanol = 30/2 as eluent, R_f = 0.4), m.p. 203.5 – 205.3 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 37.63 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.92 (ddd, *J* = 11.1, 7.4, 1.8 Hz, 1H), 7.79 – 7.69 (m, 2H), 7.63 – 7.56 (m, 1H), 7.44 (dd, *J* = 10.0, 7.6 Hz, 3H), 7.33 (t, *J* = 7.5 Hz, 1H), 5.93 – 5.48 (m, 1H), 4.95 (d, *J* = 2.8 Hz, 1H), 1.68 (ddq, *J* = 6.8, 4.4, 2.1 Hz, 1H), 1.17 – 1.05 (m, 3H), 1.04 – 0.92 (m, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 138.3

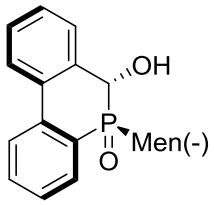
(d, *J* = 7.7 Hz), 133.4 (d, *J* = 9.1 Hz), 132.4 (d, *J* = 6.9 Hz), 131.7 (s), 131.7 (s), 131.2 (d, *J* = 10.6 Hz), 129.5 (s), 128.1 (s), 127.2 (d, *J* = 10.1 Hz), 126.2 (s), 125.0 (d, *J* = 8.5 Hz), 123.5 (d, *J* = 87.2 Hz), 65.5 (d, *J* = 73.3 Hz), 24.1 (d, *J* = 66.3 Hz), 14.4 (d, *J* = 3.7 Hz), 14.2 (d, *J* = 3.8 Hz); **HRMS (ESI$^+$)** Calcd. for $C_{16}H_{17}O_2P$ [M+Na^+]: 295.0864, Found: 295.0881.

***u,l*-5-Butyl-6-hydroxy-6*H*-phosphanthridine 5-oxide (*u,l*-10k)**



The pure *u,l*-**10k** was obtained as white solid (45 mg, 39%) from preparative TLC (silica gel, trichloromethane/isopropanol = 30/2 as eluent), m.p. 180.0 – 181.3 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 35.36 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.06 – 7.93 (m, 2H), 7.71 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.62 (td, *J* = 7.7, 1.5 Hz, 2H), 7.49 – 7.32 (m, 4H), 5.59 (d, *J* = 13.4 Hz, 1H), 2.03 – 1.90 (m, 1H), 1.60 (dddd, *J* = 11.0, 6.5, 4.2, 1.9 Hz, 1H), 1.47 – 1.37 (m, 1H), 1.34 – 1.25 (m, 1H), 1.23 – 1.13 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 139.5 (d, *J* = 7.9 Hz), 135.5 (s), 133.1 (d, *J* = 2.6 Hz), 132.3 (d, *J* = 6.5 Hz), 131.5 (d, *J* = 4.8 Hz), 129.2 (s), 128.1 (d, *J* = 10.0 Hz), 128.0 (d, *J* = 2.3 Hz), 126.8 (d, *J* = 86.8 Hz), 126.3 (d, *J* = 2.9 Hz), 126.0 (d, *J* = 9.1 Hz), 125.6 (d, *J* = 5.6 Hz), 69.4 (d, *J* = 80.9 Hz), 24.0 (d, *J* = 13.8 Hz), 23.1 (d, *J* = 4.5 Hz), 21.7 (d, *J* = 67.5 Hz), 13.4 (s); **HRMS (ESI$^+$)** Calcd. for for $C_{17}H_{19}O_2P$ [M+Na^+]: 309.1020, Found: 309.1035.

(R_P,S_A,R_C)-6-Hydroxy-5-(-)-menthyl-6*H*-phosphanthridine 5-oxide (R_P,S_A,R_C -10l')



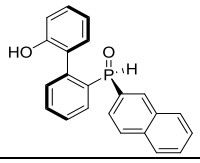
The preparation of R_P,S_A,R_C-**10l'** was performed with **9l**, via to quench the reaction at -80^{o}C. The pure compound was obtained as white solid (41 mg, 73%) from preparative TLC (silica gel, trichloromethane /isopropanol = 30/2 as eluent), m.p. 124.1 – 125.3 ℃; **^{31}P NMR (202 MHz, Chloroform-*d*)** δ 36.02 (s); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.81 (ddd, *J* = 11.5, 7.4, 1.7 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.60 (dd, *J* = 7.8, 5.0 Hz, 1H), 7.52 – 7.40 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 5.89 (d, *J* = 25.6 Hz, 1H), 5.04 (s, 1H), 2.20 (dt, *J* = 6.9, 3.4 Hz, 1H), 1.73 – 1.66 (m, 1H), 1.66 – 1.53 (m, 4H), 1.12 (qd, *J* = 13.1, 12.5, 6.2 Hz, 1H), 1.05 – 0.98 (m, 1H), 0.79 (dd, *J* = 16.8, 6.6 Hz, 8H), 0.19 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 139.4 (d, *J* = 8.1 Hz), 135.3 (d, *J* = 9.0 Hz), 133.3 (s), 132.9 (d, *J* = 5.2 Hz), 132.1 (d, *J* = 2.3 Hz), 131.9 (d, *J* = 10.8 Hz), 130.6 (s), 129.0 (s), 128.1 (d, *J* = 10.4 Hz), 127.4 (d, *J* = 84.8 Hz), 126.9 (s), 125.8

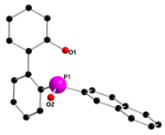
(d, *J* = 8.5 Hz), 67.4 (d, *J* = 71.9 Hz), 42.8 (d, *J* = 3.6 Hz), 38.8 (d, *J* = 63.5 Hz), 35.0 (d, *J* = 3.1 Hz), 34.1 (s), 32.9 (d, *J* = 12.8 Hz), 28.7 (d, *J* = 2.7 Hz), 24.4 (d, *J* = 11.9 Hz), 22.5 (s), 21.4 (s), 14.7 (s); **HRMS (ESI$^+$)** Calcd. for $C_{23}H_{29}O_2P$ [M+Na^+]: 391.1803, Found: 391.1813.

Part 5. Crystallographic information *l*-5h, *u*-7c, *u*-9c, *u,l*-10d and R_P,S_A,R_C-10l'.

Table S2. Crystallography data of *l*-5h.

The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of **5h** in dichloromethane at rt.

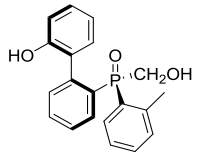




Empirical formula	C22 H16 O2 P
Crystal system	monoclinic
space group	P 1 21/n 1
Formula weight	343.32
a, Å	10.572(14)
b, Å	11.144(14)
c, Å	15.98(2)
α, deg	90
β, deg	107.132(19)
γ, deg	90
V, Å3	1799(4)
Z	4
T, K	298(2)
λ, Å	0.71073
ρ, Mg m-3	1.267
Rint	0.0439
R1 [I N 2σ(I)]	0.1503
R1 (all data)	0.2350
wR2 [I N 2σ(I)]	0.3947
wR2 (all data)	0.4322
Flack	
CCDC	2070968

Table S3. Crystallography data of *u*-7c.

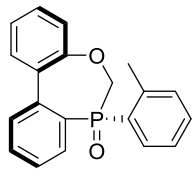
The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of **7c** in dichloromethane at rt.

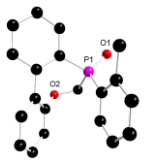


Empirical formula	C20 H19 O3 P
Crystal system	Triclinic
space group	P -1
Formula weight	338.32
a, Å	9.0317(9)
b, Å	9.3941(9)
c, Å	11.3045(11)
α, deg	75.041(2)
β, deg	74.257(2)
γ, deg	63.6620(10)
V, Å3	816.70(14)
Z	2
T, K	298.15
λ, Å	0.71073
ρ, Mg m-3	1.376
Rint	0.0590
R1 [I N 2σ(I)]	0.1035
R1 (all data)	0.1661
wR2 [I N 2σ(I)]	0.2153
wR2 (all data)	0.2317
Flack	
CCDC	2070973

Table S4. Crystallography data of *u*-9c

The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of ***u*-9c** in dichloromethane at rt.

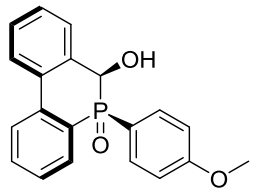


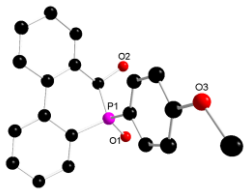


Empirical formula	C20 H17 O2 P1
Crystal system	orthorhombic
space group	P b c a
Formula weight	320.30
a, Å	9.8615(8)
b, Å	14.7818(12)
c, Å	21.4475(17)
α, deg	90
β, deg	90
γ, deg	90
V, Å3	3126.4(4)
Z	8
T, K	298(2)
λ, Å	0.71073
ρ, Mg m-3	1.361
Rint	0.0818
R1 [I N 2σ(I)]	0.0627
R1 (all data)	0.1013
wR2 [I N 2σ(I)]	0.1623
wR2 (all data)	0.1842
Flack	
CCDC	2070977

Table S5. Crystallography data of *u,l*-10d

The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of *u,l*-**10d** in methanol at rt.

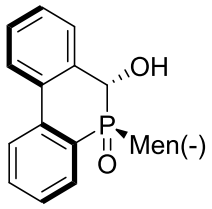


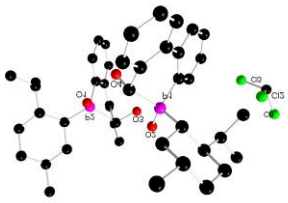


Empirical formula	C20 H16 O3 P1
Crystal system	monoclinic
space group	P 1 21/c 1
Formula weight	336.30
a, Å	8.2777(9)
b, Å	21.057(2)
c, Å	20.145(2)
α, deg	90
β, deg	95.107(2)
γ, deg	90
V, Å3	3497.4(6)
Z	8
T, K	293(2)
λ, Å	0.71073
ρ, Mg m-3	1.277
R1 [I N 2σ(I)]	0.1688
R1 (all data)	0.3667
wR2 [I N 2σ(I)]	0.4229
wR2 (all data)	0.3427
Flack	
CCDC	2080531

Table S6. Crystallography data of R_P,S_A,R_C-10l'

The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of R_P,S_A,R_C-**10l'** in trichloromethane at rt.

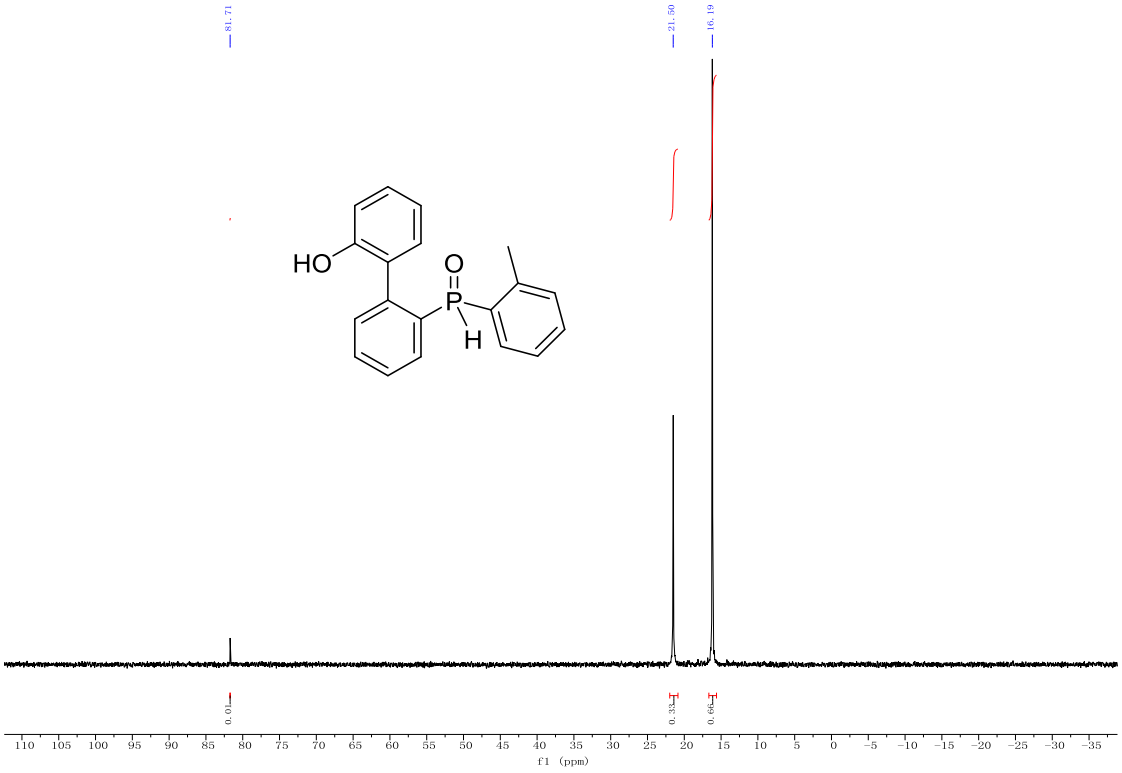


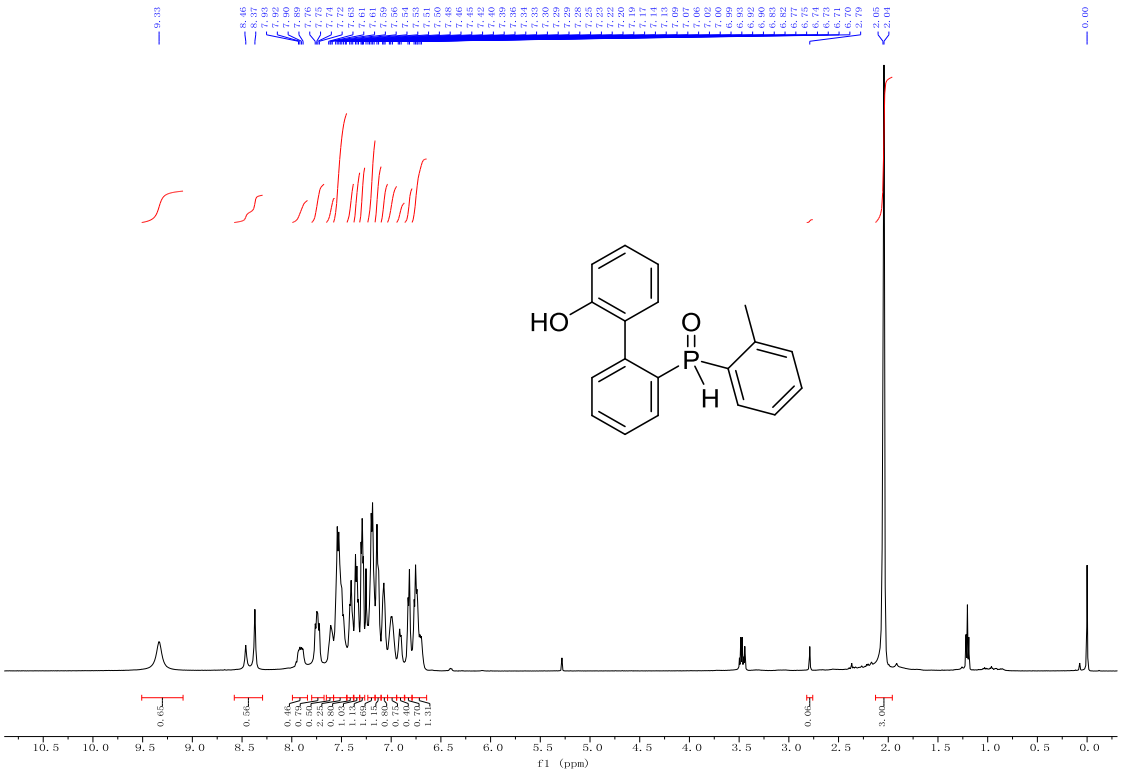


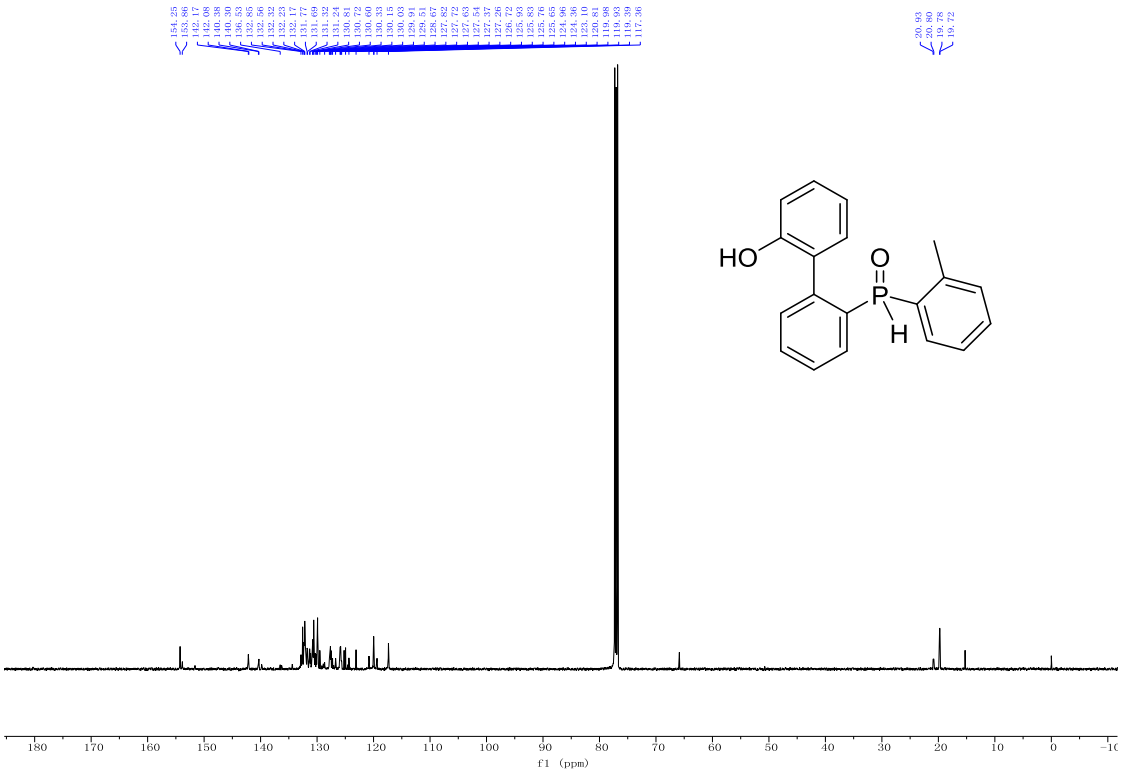
Empirical formula	2(C23 H29 O2 P), C H Cl3
Crystal system	orthorhombic
space group	P 21 21 21
Formula weight	854.21
a, Å	9.4585(8)
b, Å	15.8220(16)
c, Å	15.8220(16)
α, deg	90
β, deg	90
γ, deg	90
V, Å3	4574.2(7)
Z	4
T, K	298(2)
λ, Å	0.71073
ρ, Mg m-3	1.240
Rint	0.0984
R1 [I N 2σ(I)]	0.1309
R1 (all data)	0.2241
wR2 [I N 2σ(I)]	0.3201
wR2 (all data)	0.3735
Flack	0.05(8)
CCDC	2072520

Part 6. Selected photocopies of ^{1}H, ^{31}P and ^{13}C NMR spectrum.

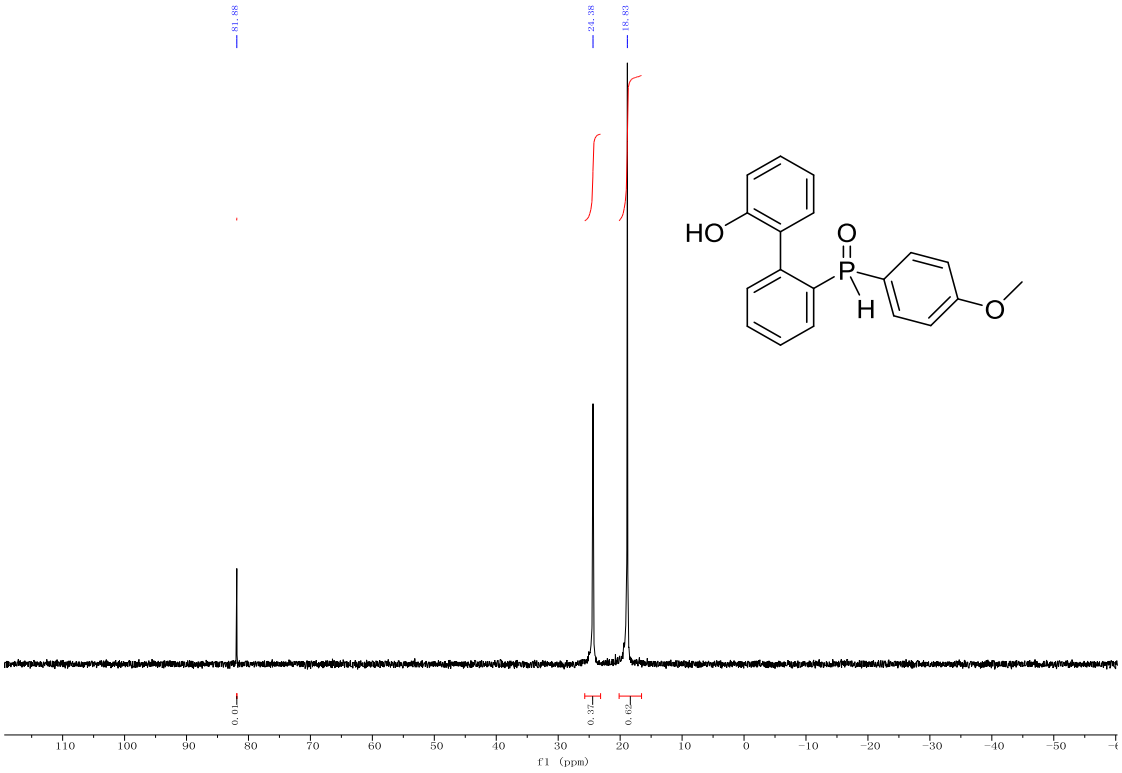
(2'-Hydroxy-biphenyl-2-yl)(*o*-tolyl)phosphine oxide (5c)

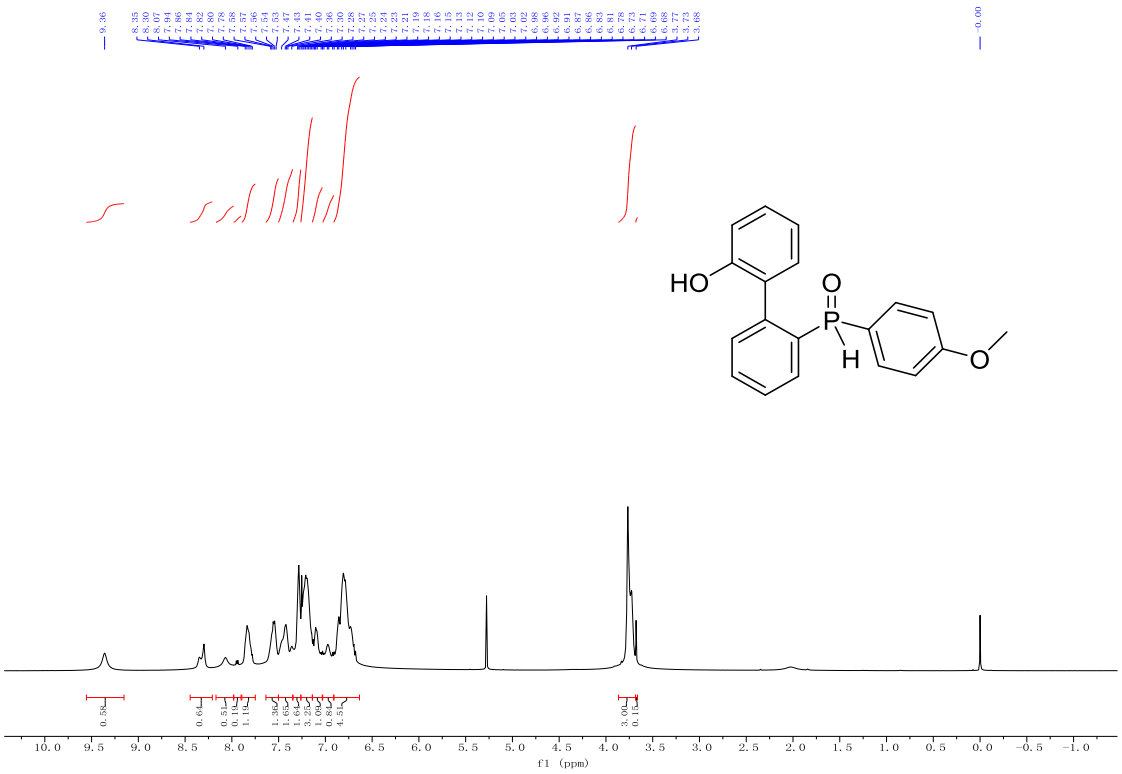


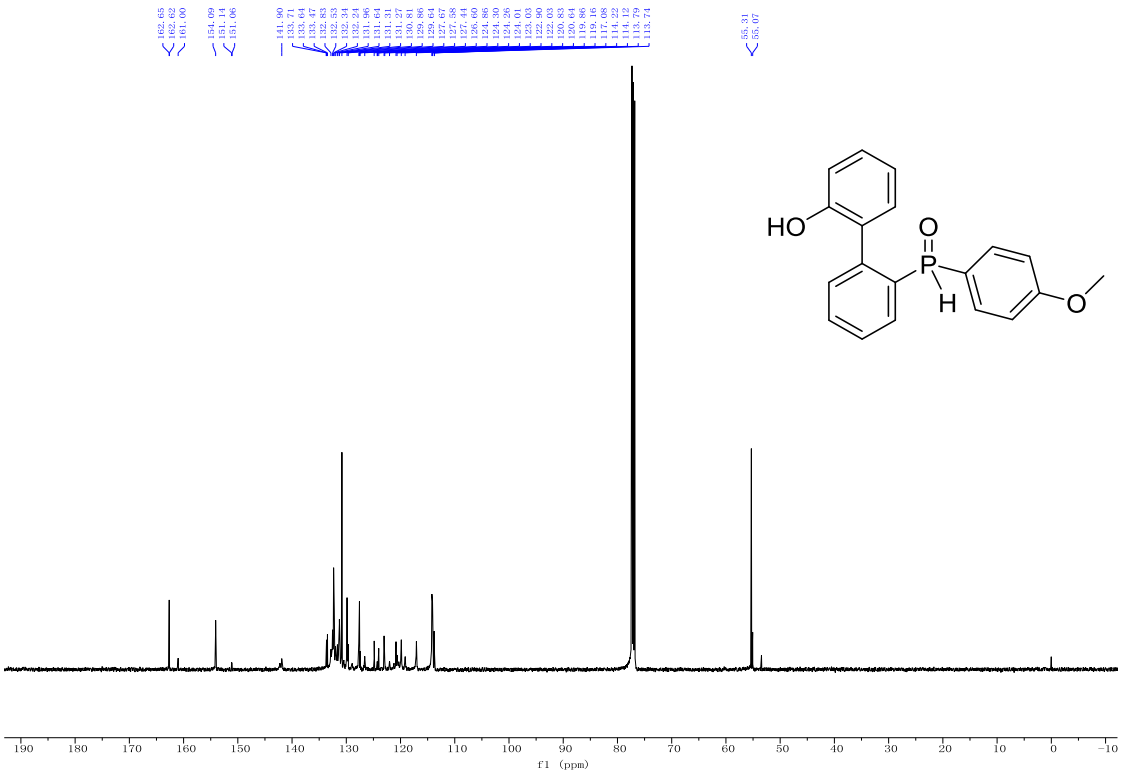




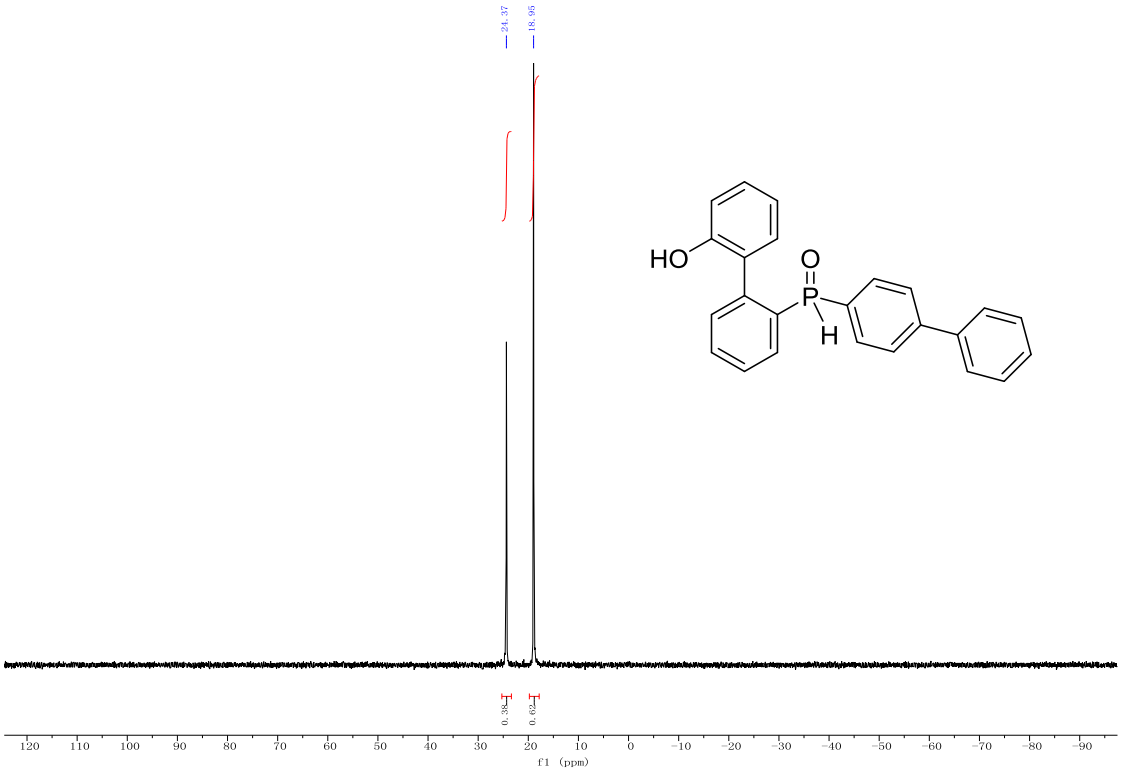
(2'-Hydroxy-biphenyl-2-yl)(4-methoxyphenyl)phosphine oxide (5d)

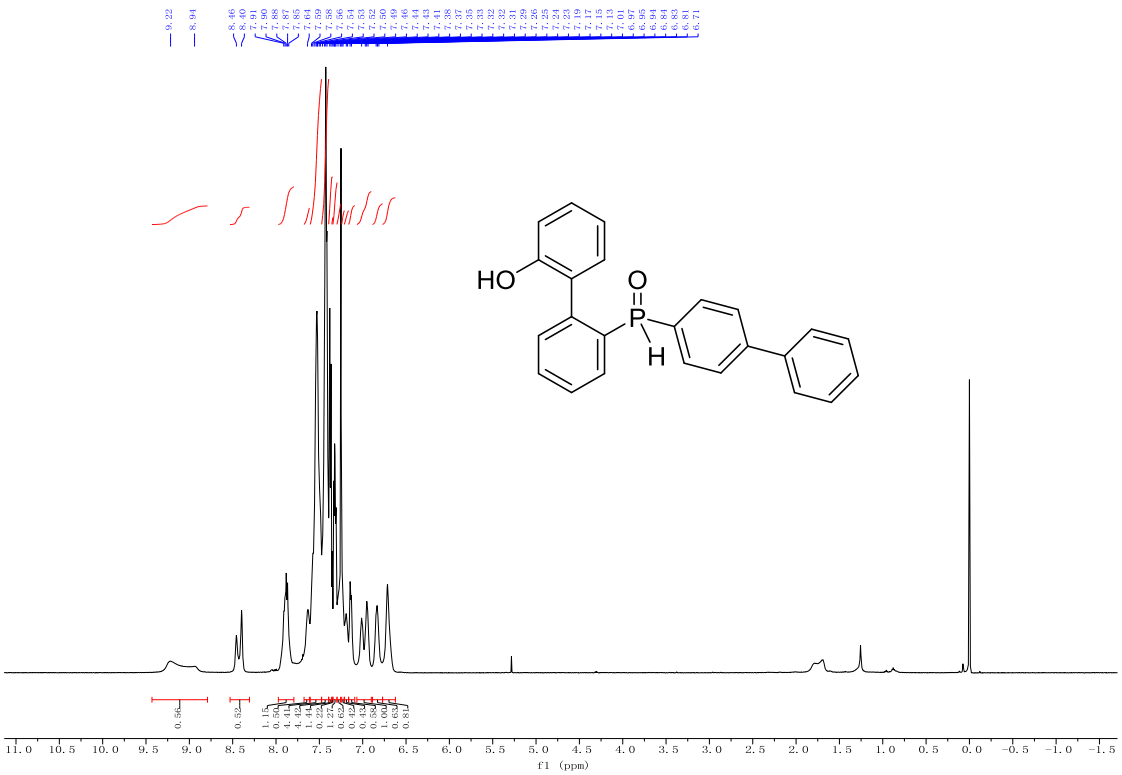


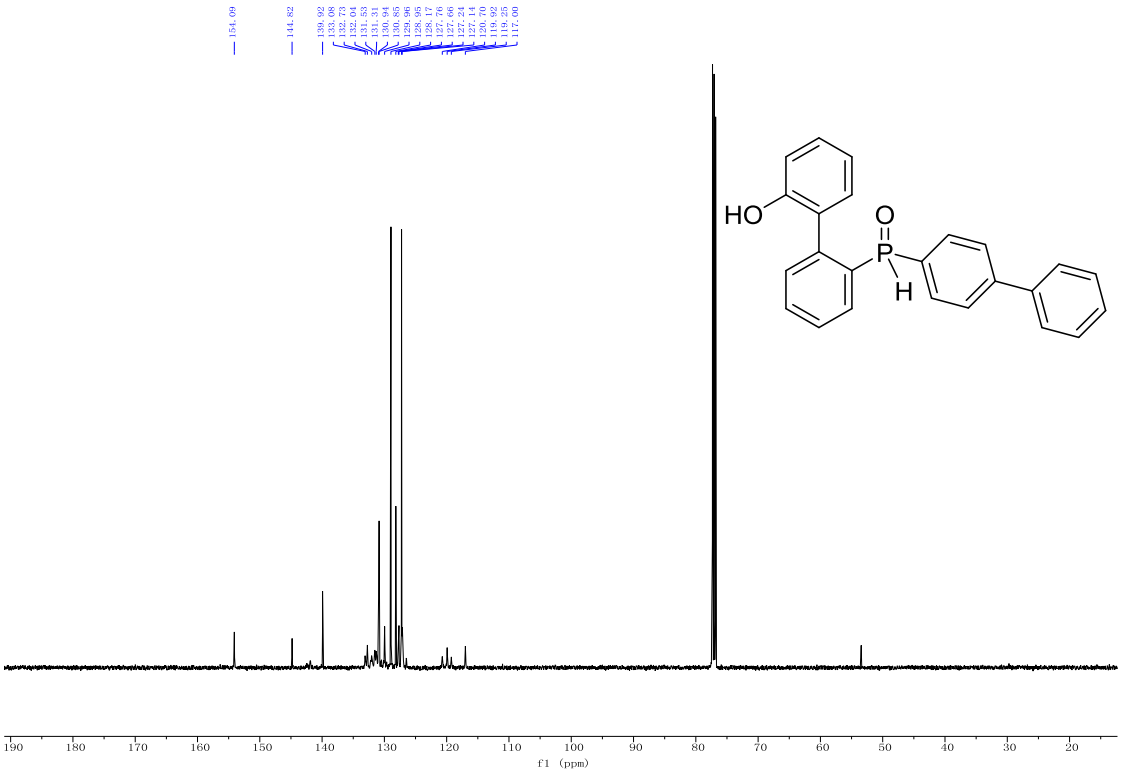

HO
O
P
H
O
f1 (ppm)


HO
O
P
H
O
f1 (ppm)

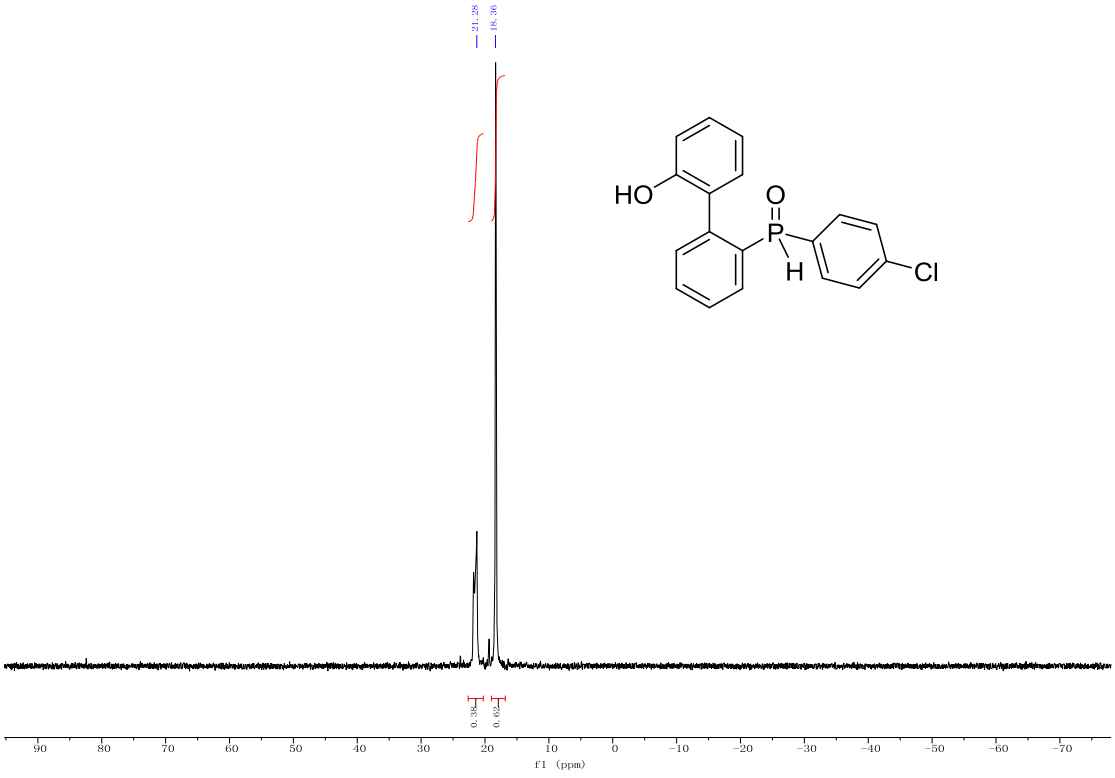
(Biphenyl-4-yl)(2'-hydroxy-biphenyl-2-yl)phosphine oxide (5e)

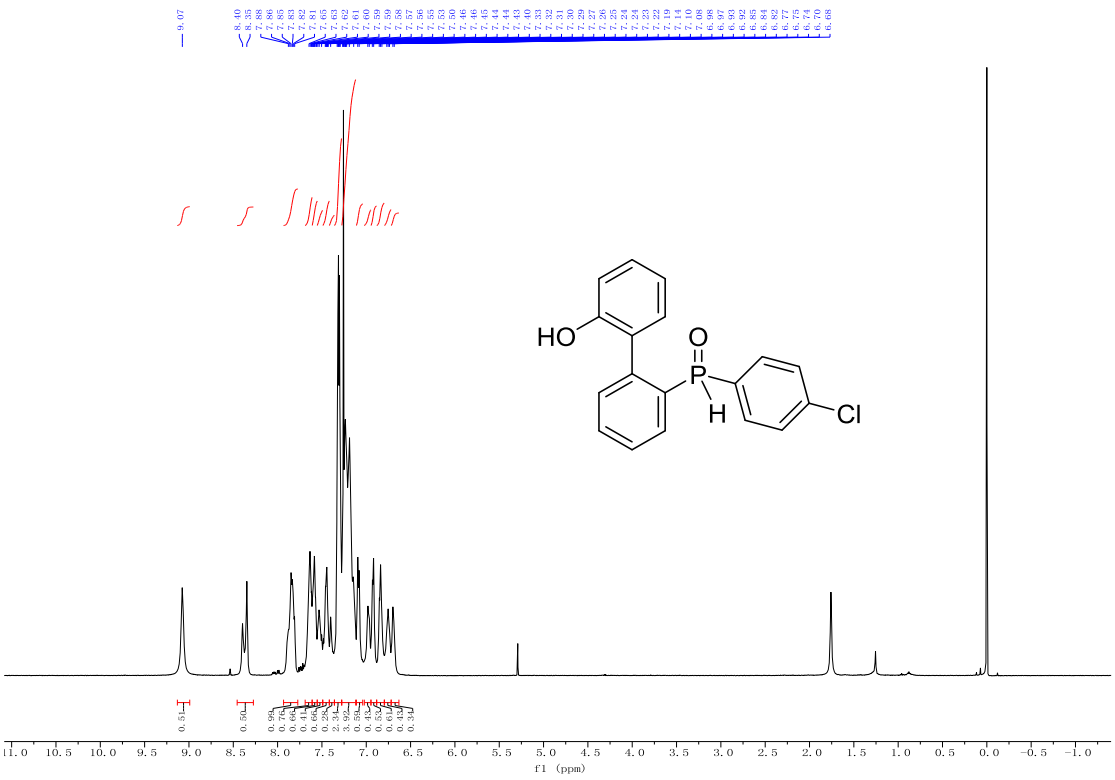


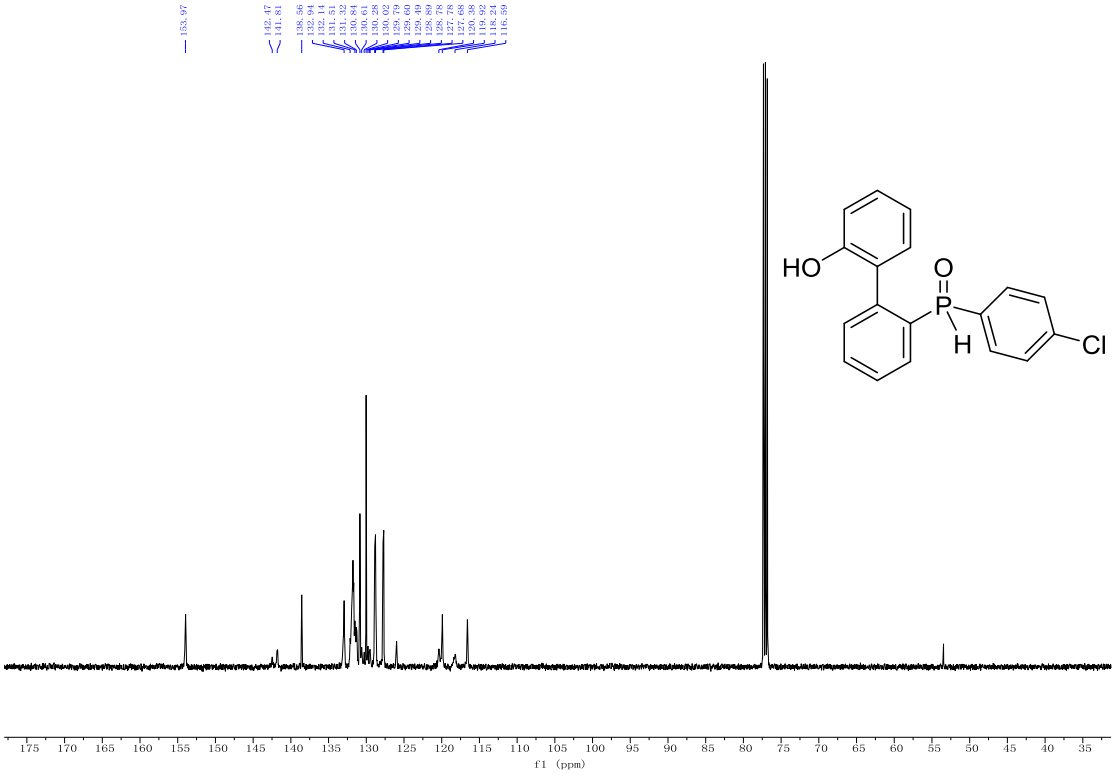




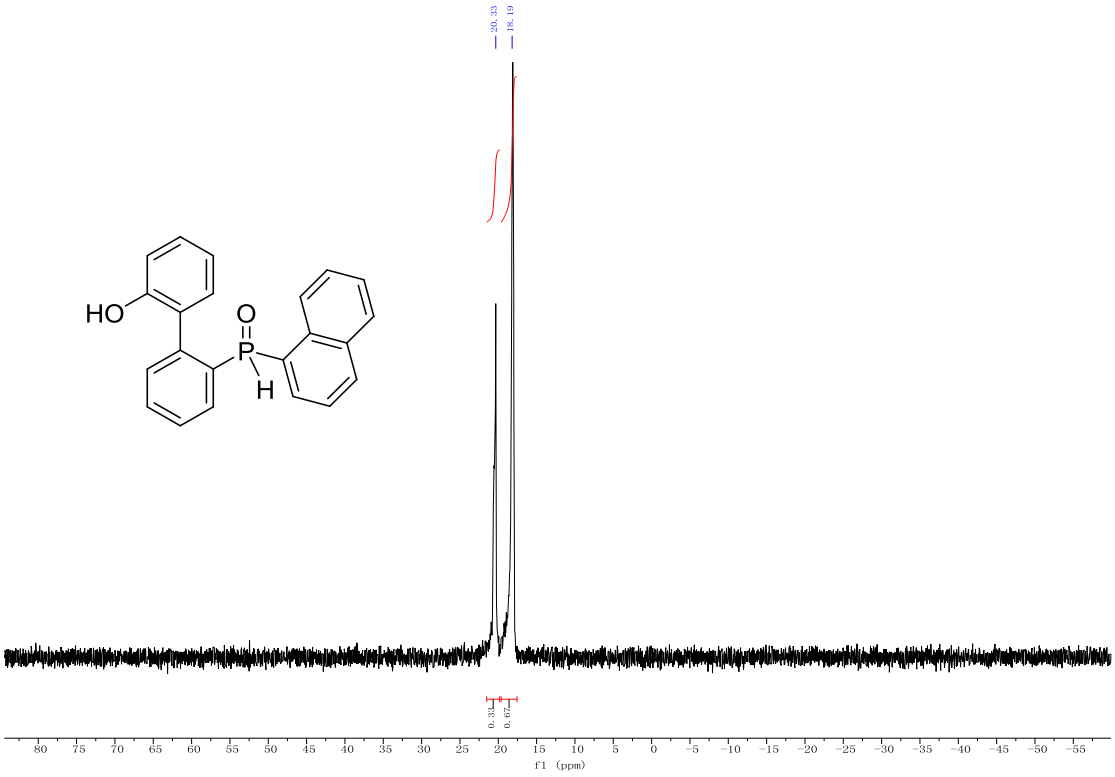
(4-Chlorophenyl)(2'-hydroxy-biphenyl-2-yl)phosphine oxide (5f)

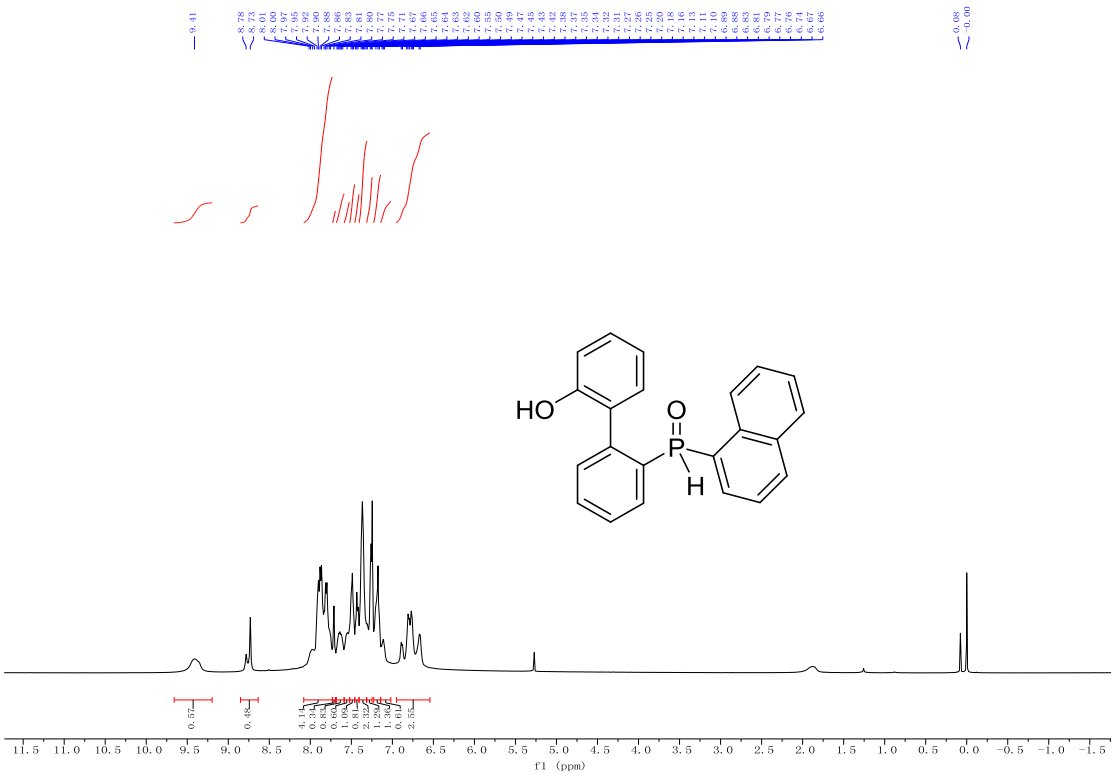


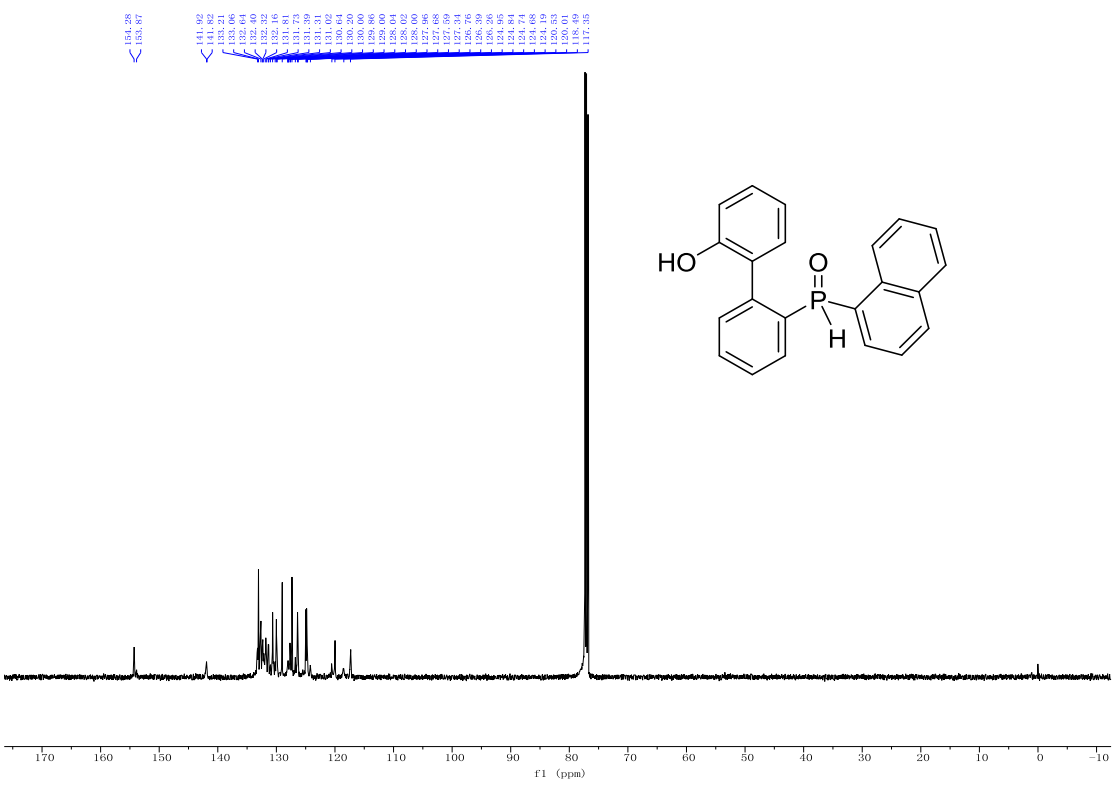

HO
O
P
H
Cl
f1 (ppm)


HO
O
P
H
Cl
f1 (ppm)

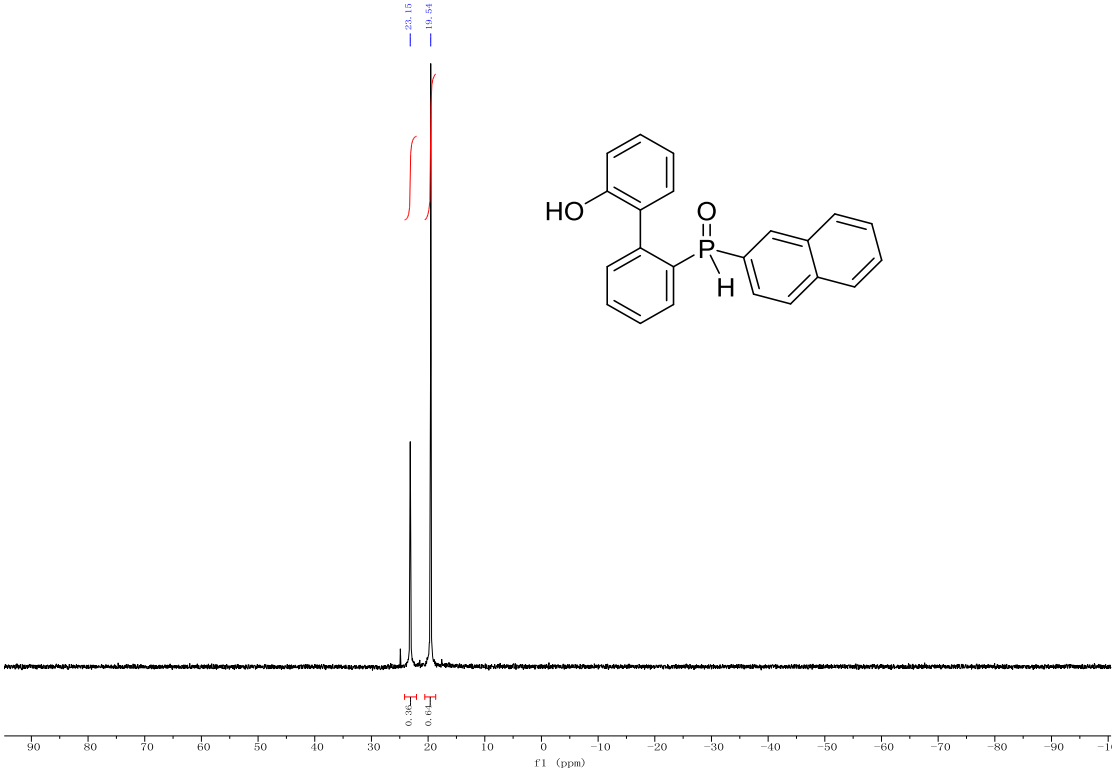
(2'-Hydroxy-biphenyl-2-yl)(naphthalen-1-yl)phosphine oxide (5g)

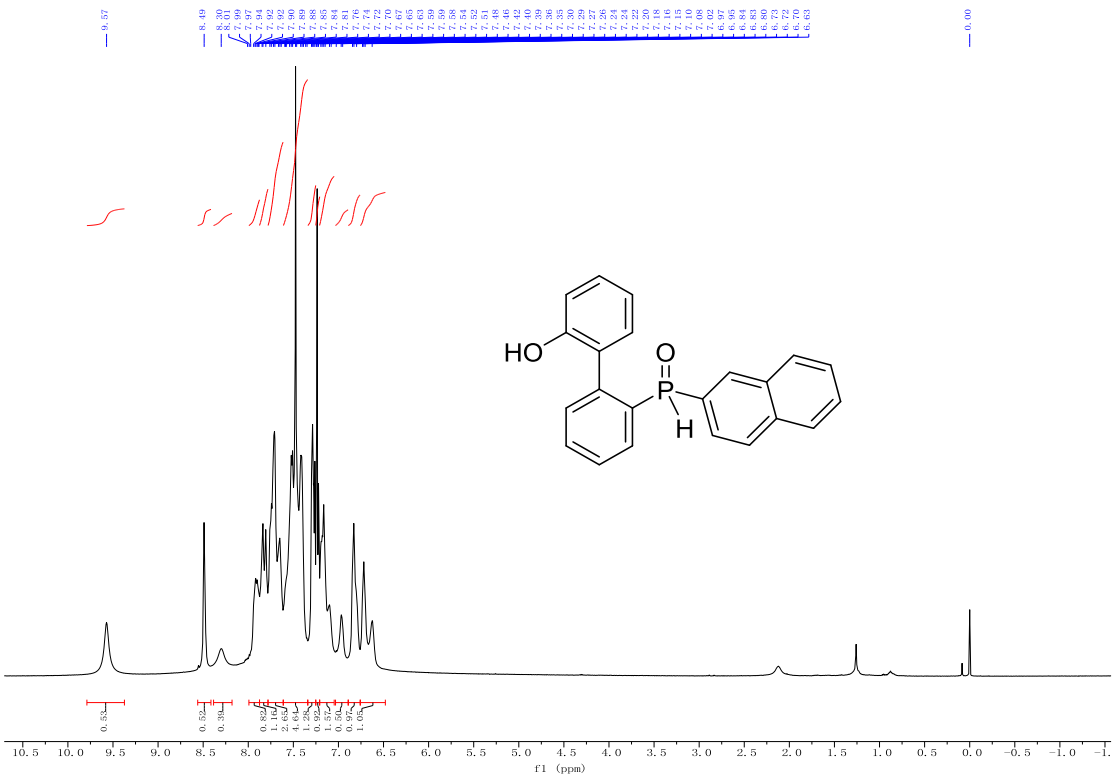


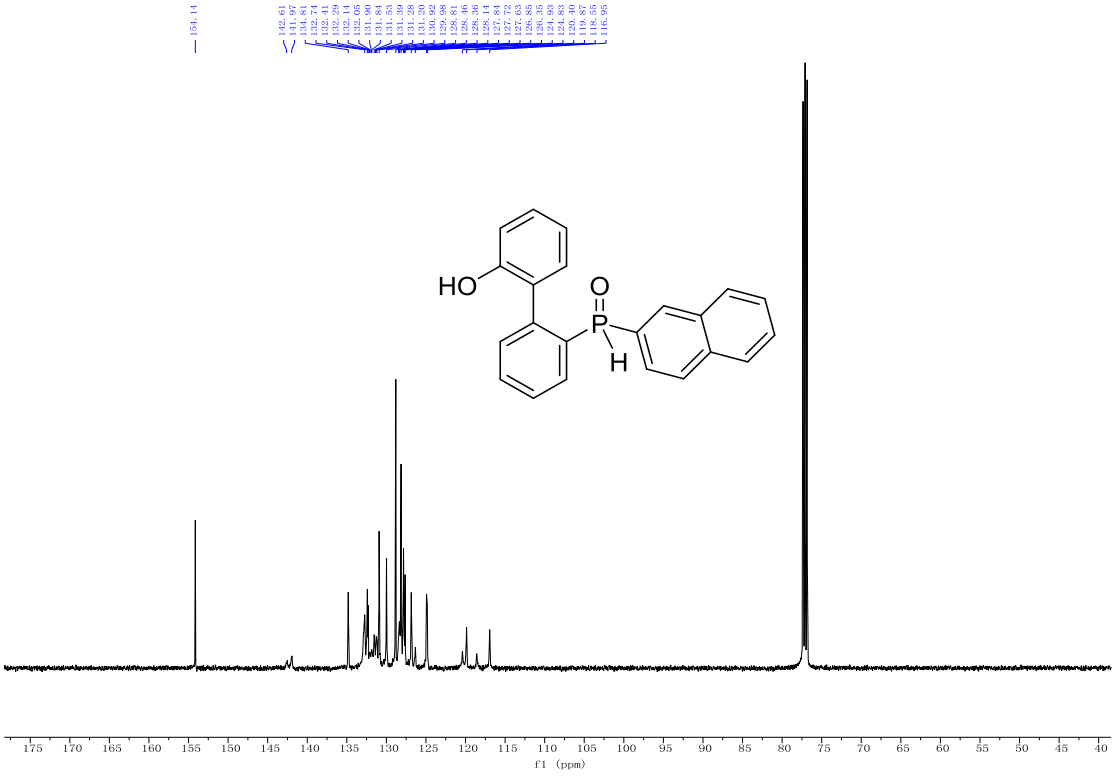




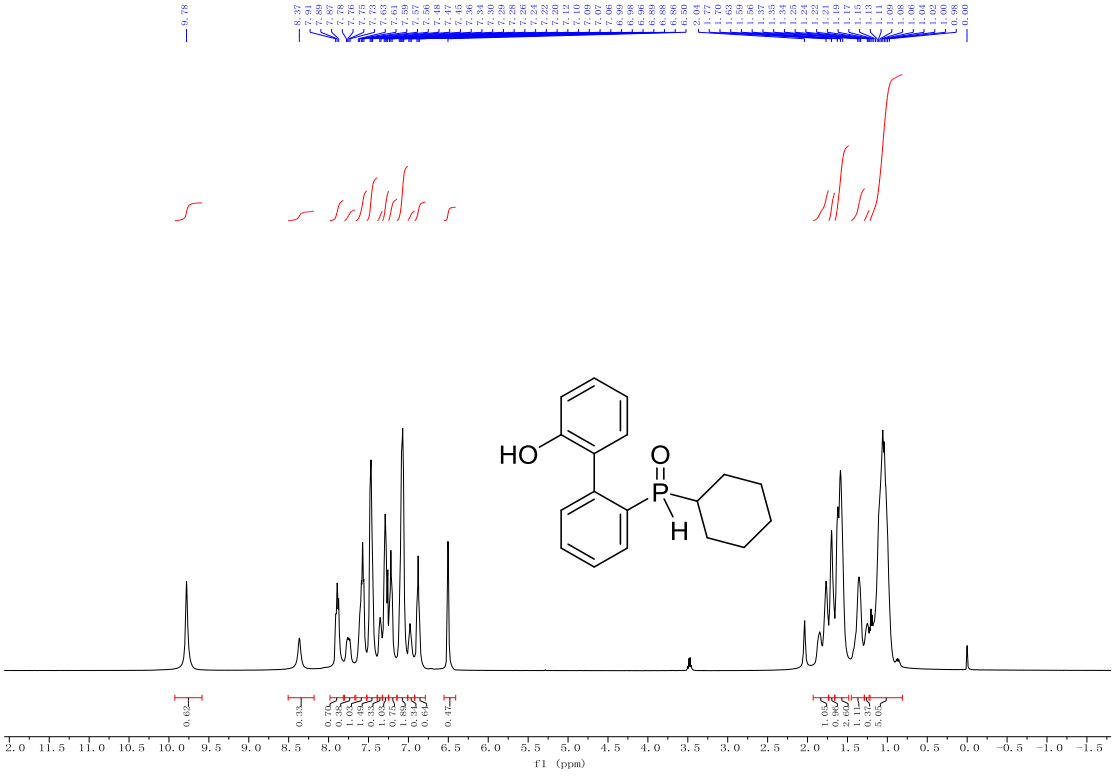
(2'-Hydroxy-biphenyl-2-yl)(naphthalen-2-yl)phosphine oxide (5h)

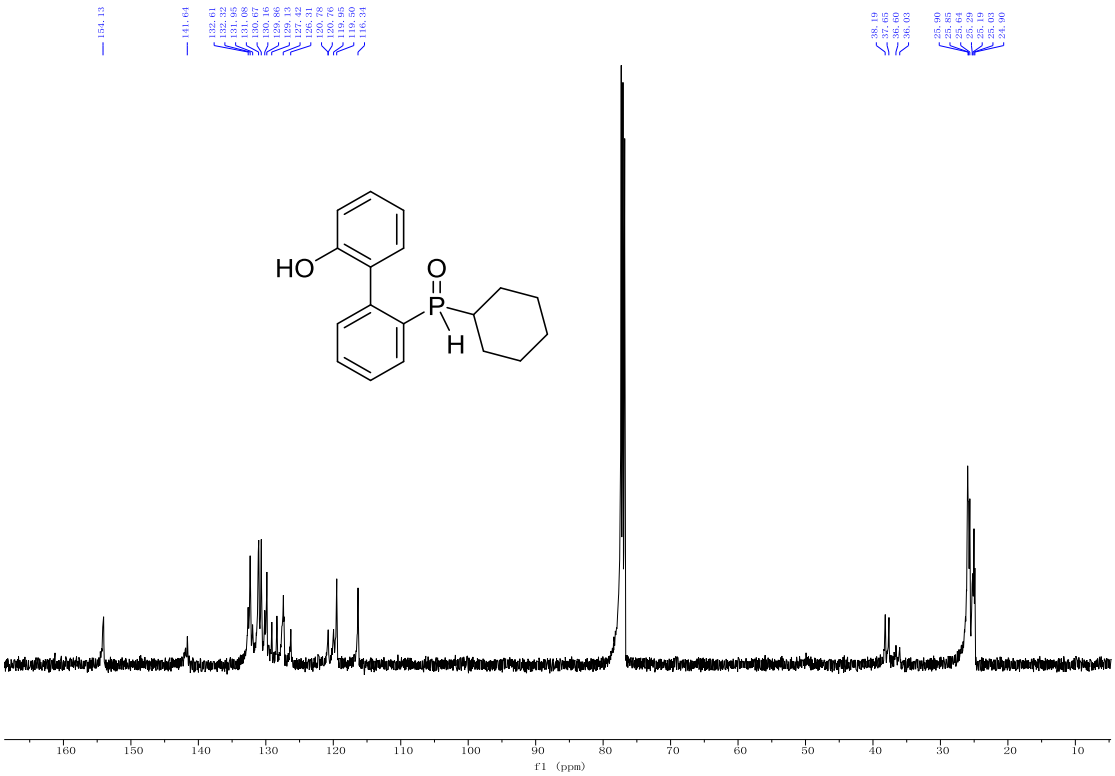



HO
O
P
H
f1 (ppm)

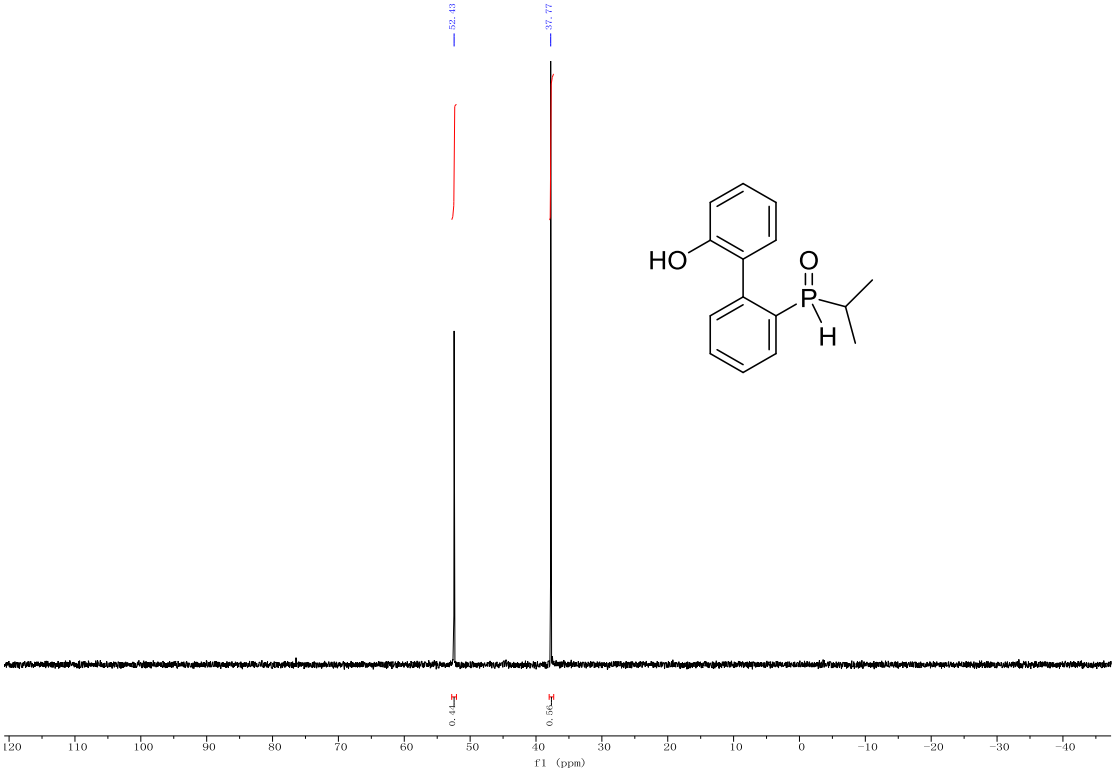

HO
O
P
H
f1 (ppm)

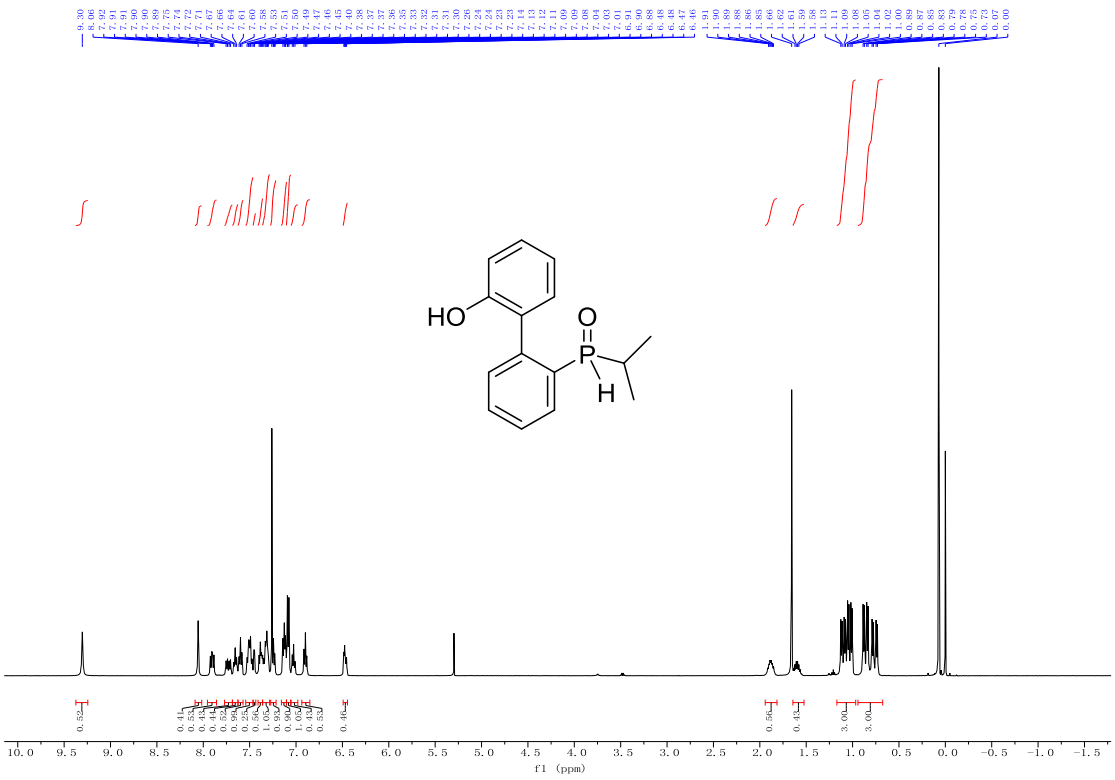
Cyclohexyl(2'-hydroxy-biphenyl-2-yl)phosphine oxide (5i)

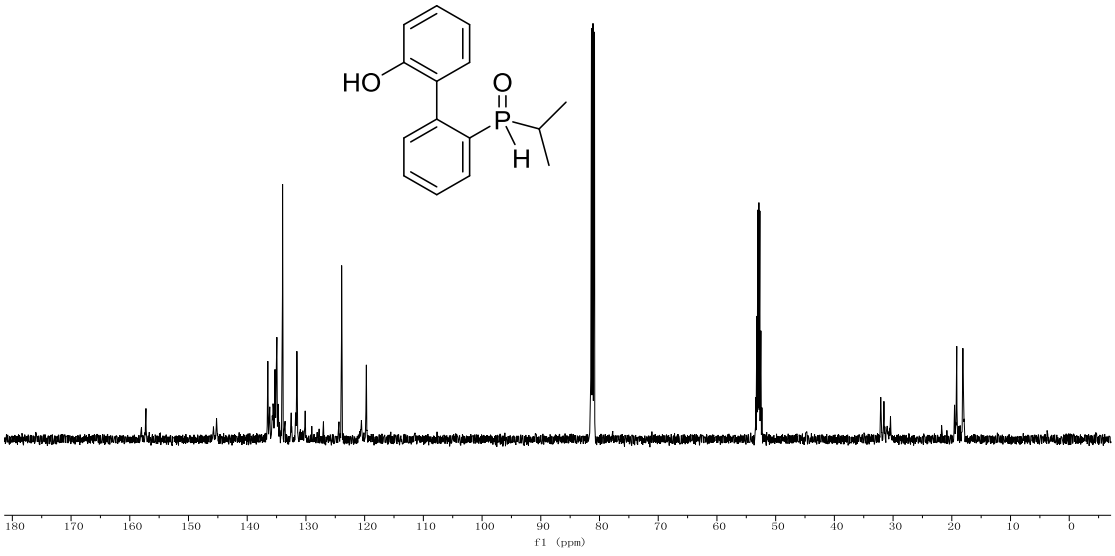




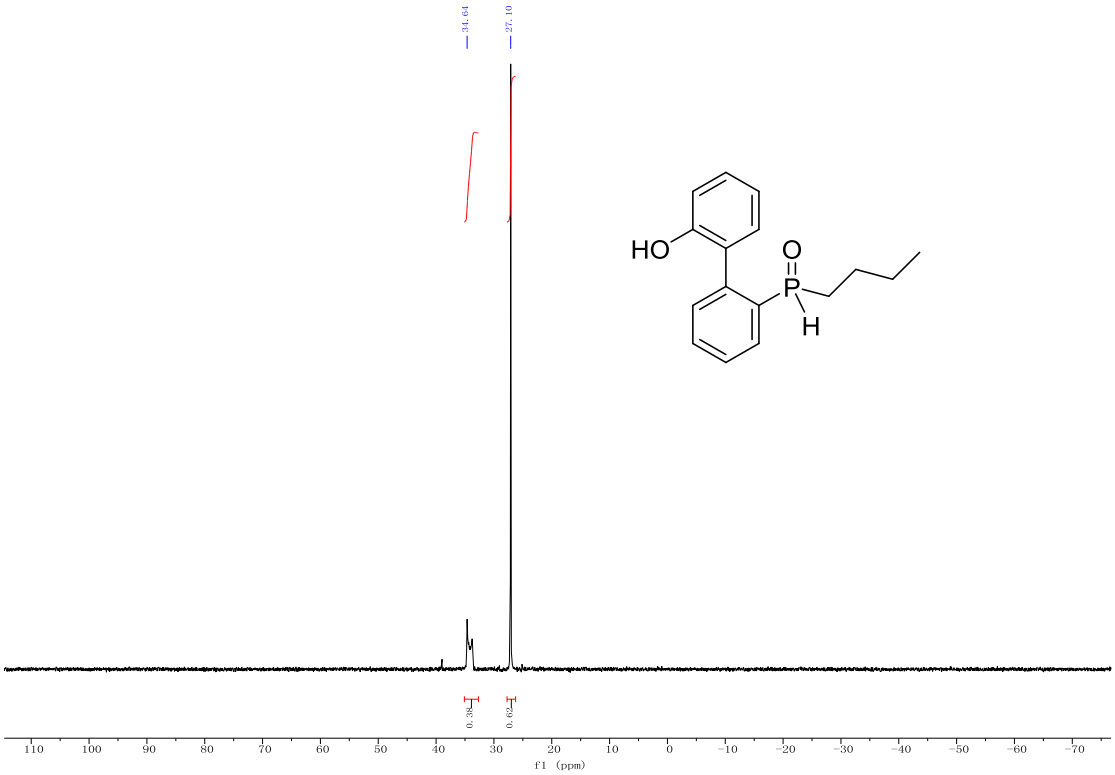
(2'-Hydroxy-biphenyl-2-yl)(isopropyl)phosphine oxide (5j)

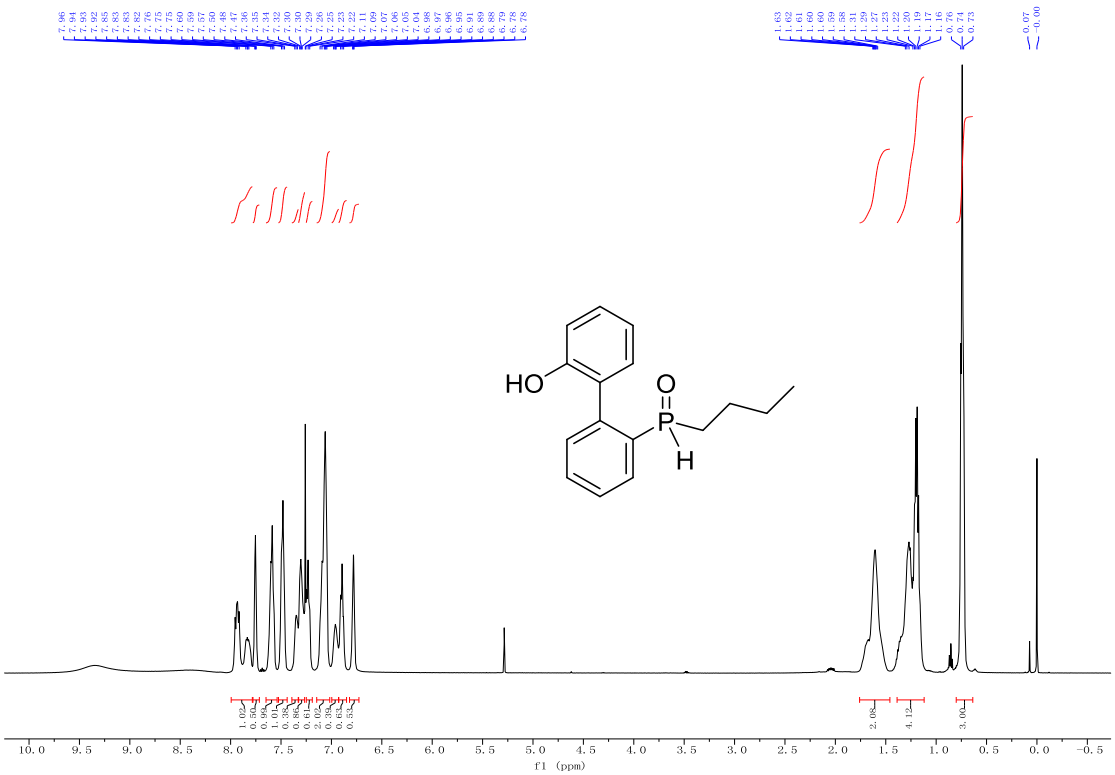


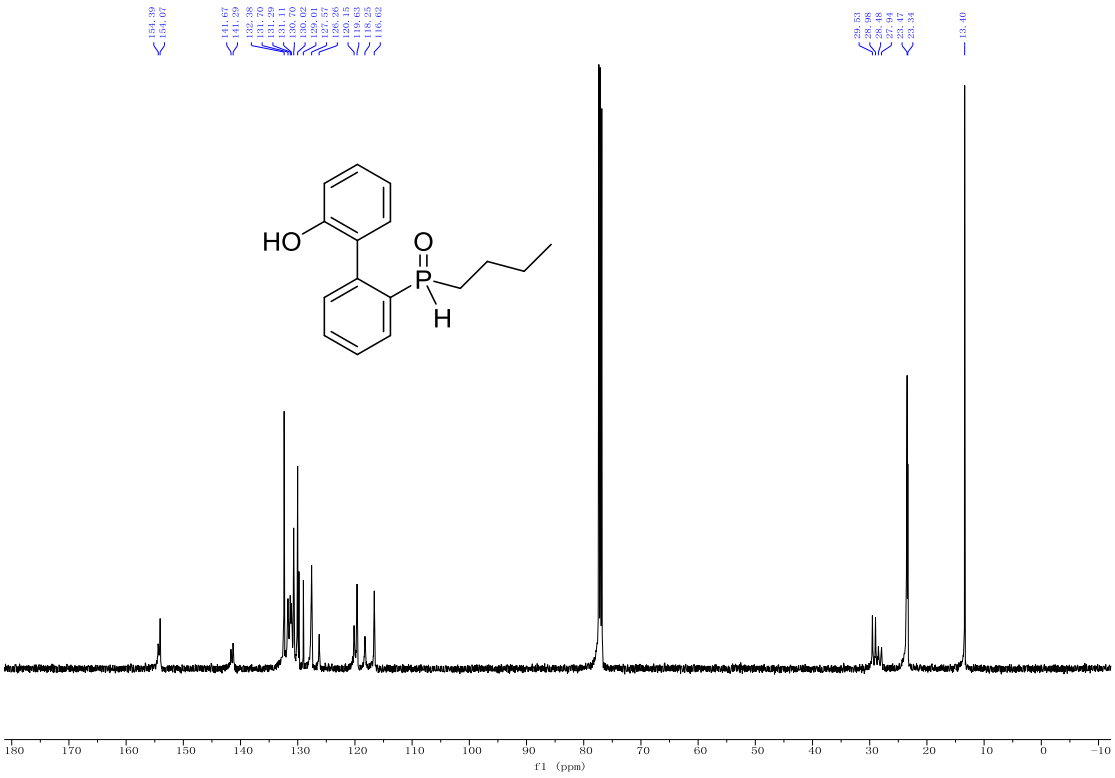

HO
O
P
H
f1 (ppm)


HO
O
P
H
f1 (ppm)

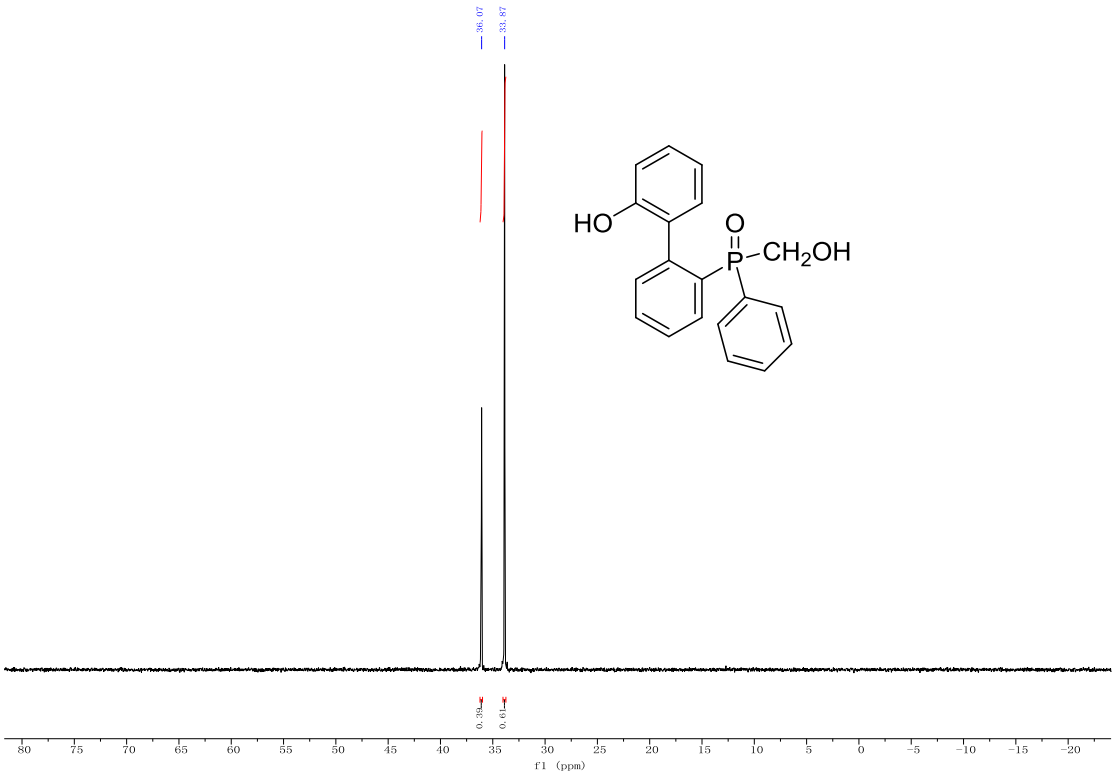
Butyl(2'-hydroxy-biphenyl-2-yl)phosphine oxide (5k)

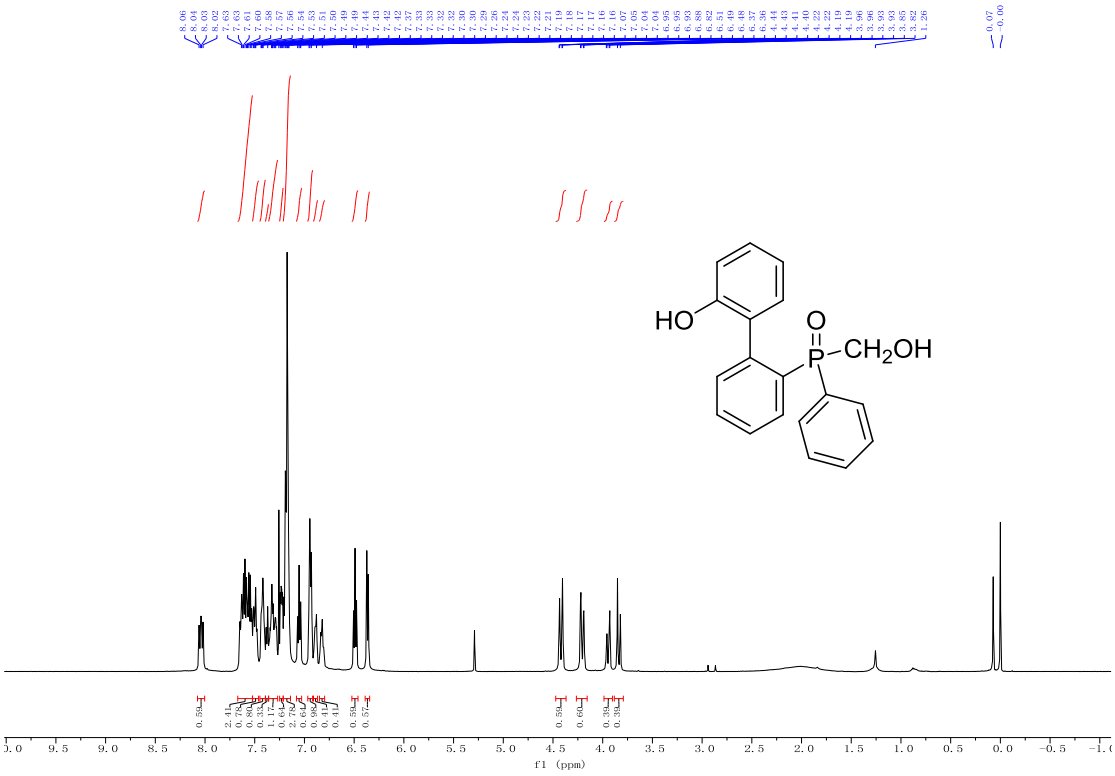


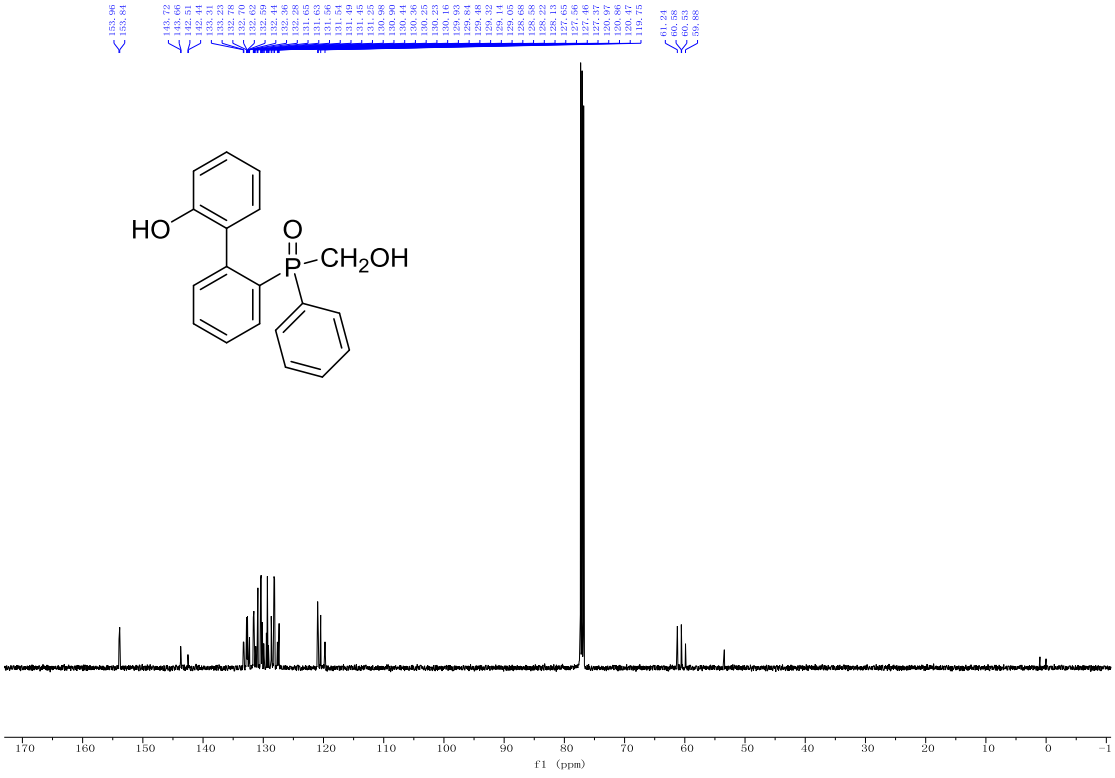




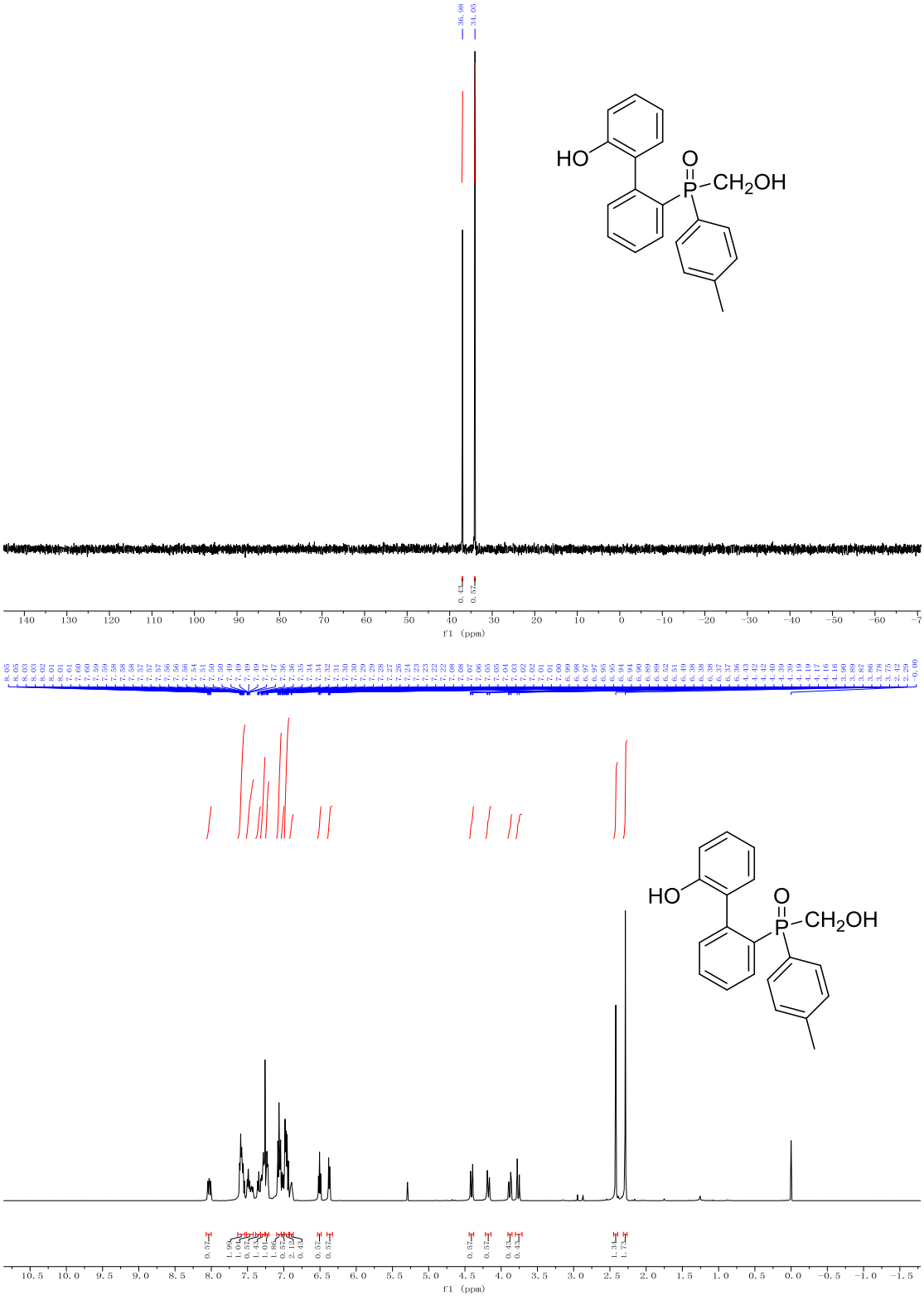
(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(phenyl)phosphine oxide (7a)

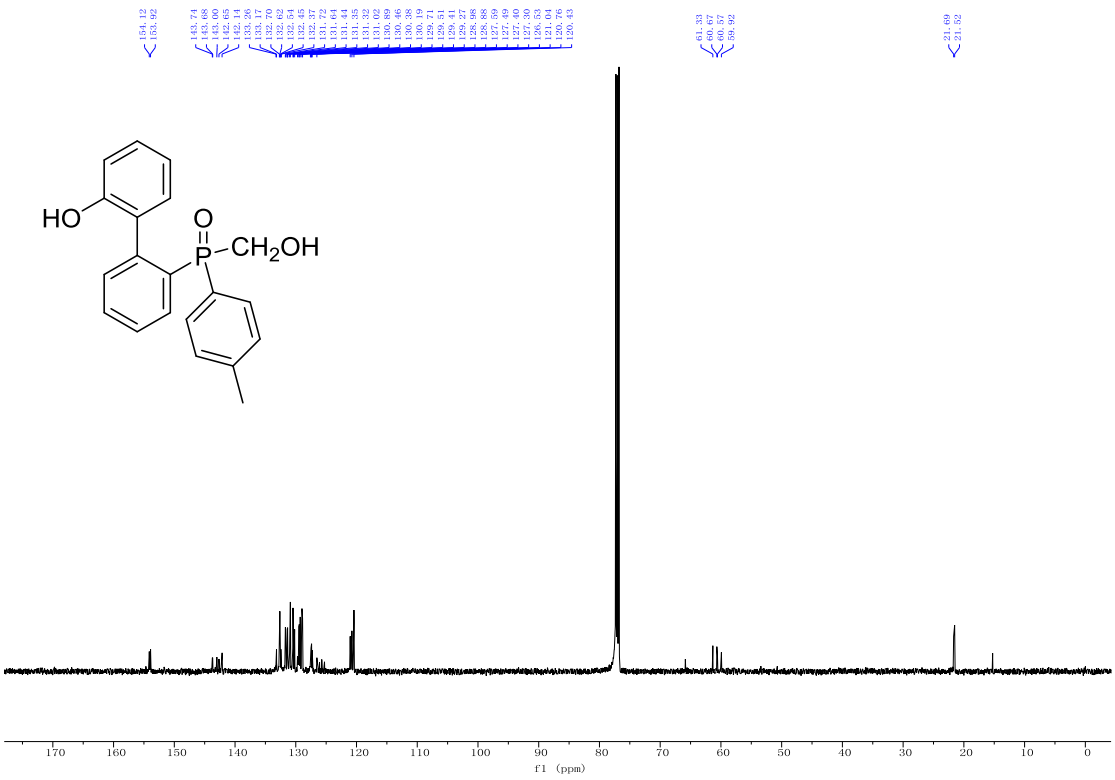



HO
O
P
CH2OH
f1 (ppm)

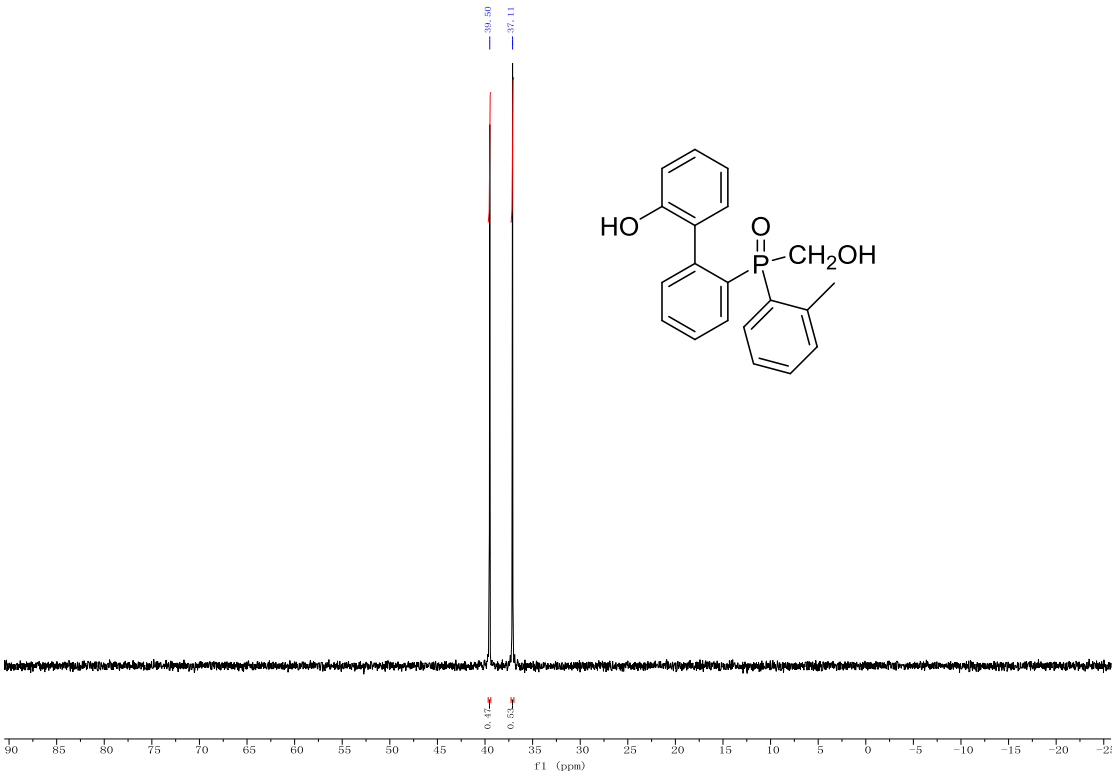

HO
O
P
CH2OH
f1 (ppm)

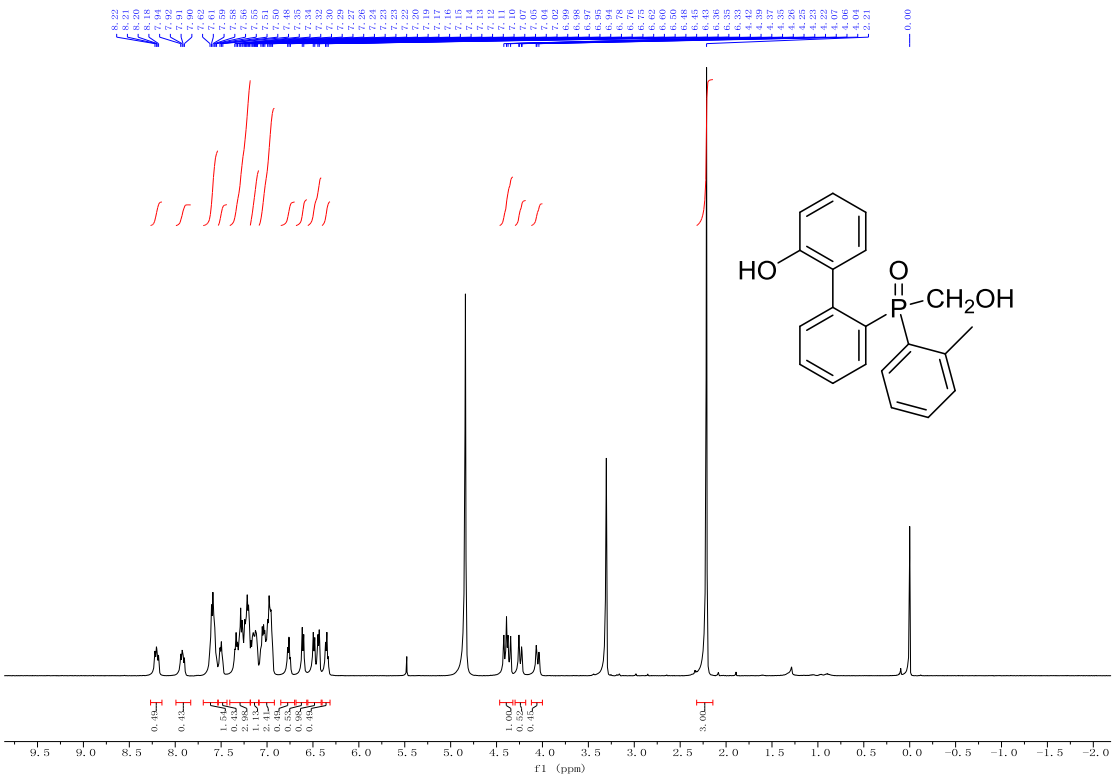
(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(*p*-tolyl)phosphine oxide (7b)

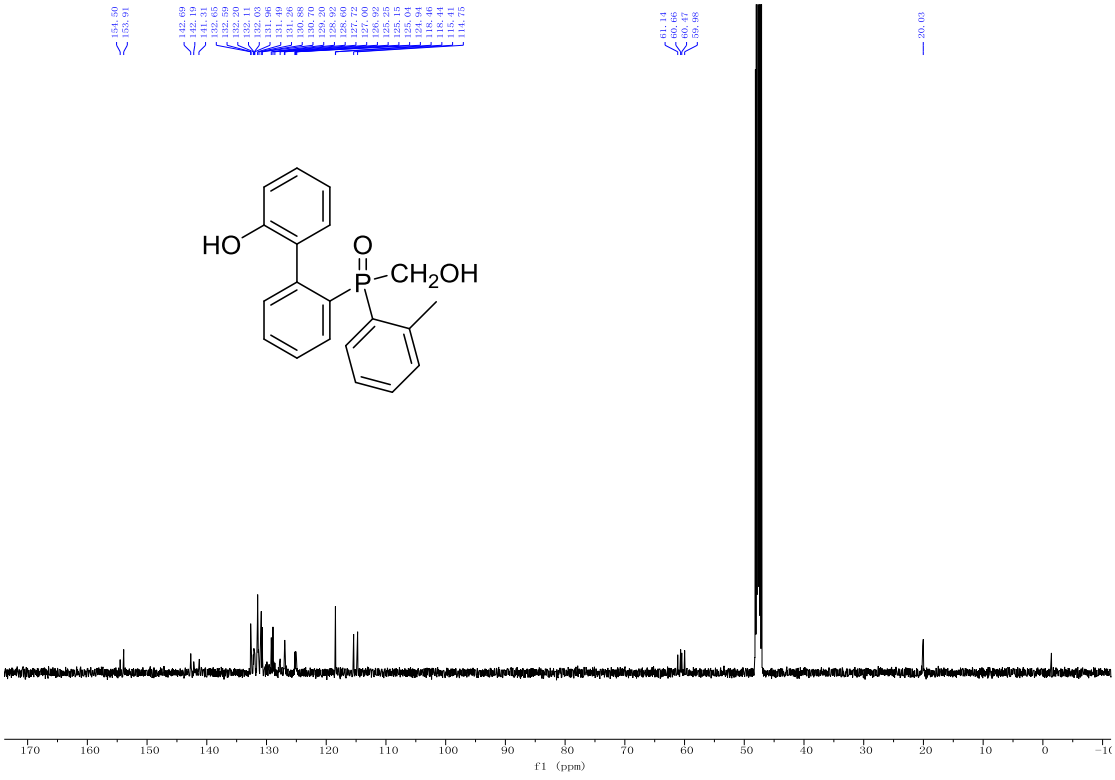




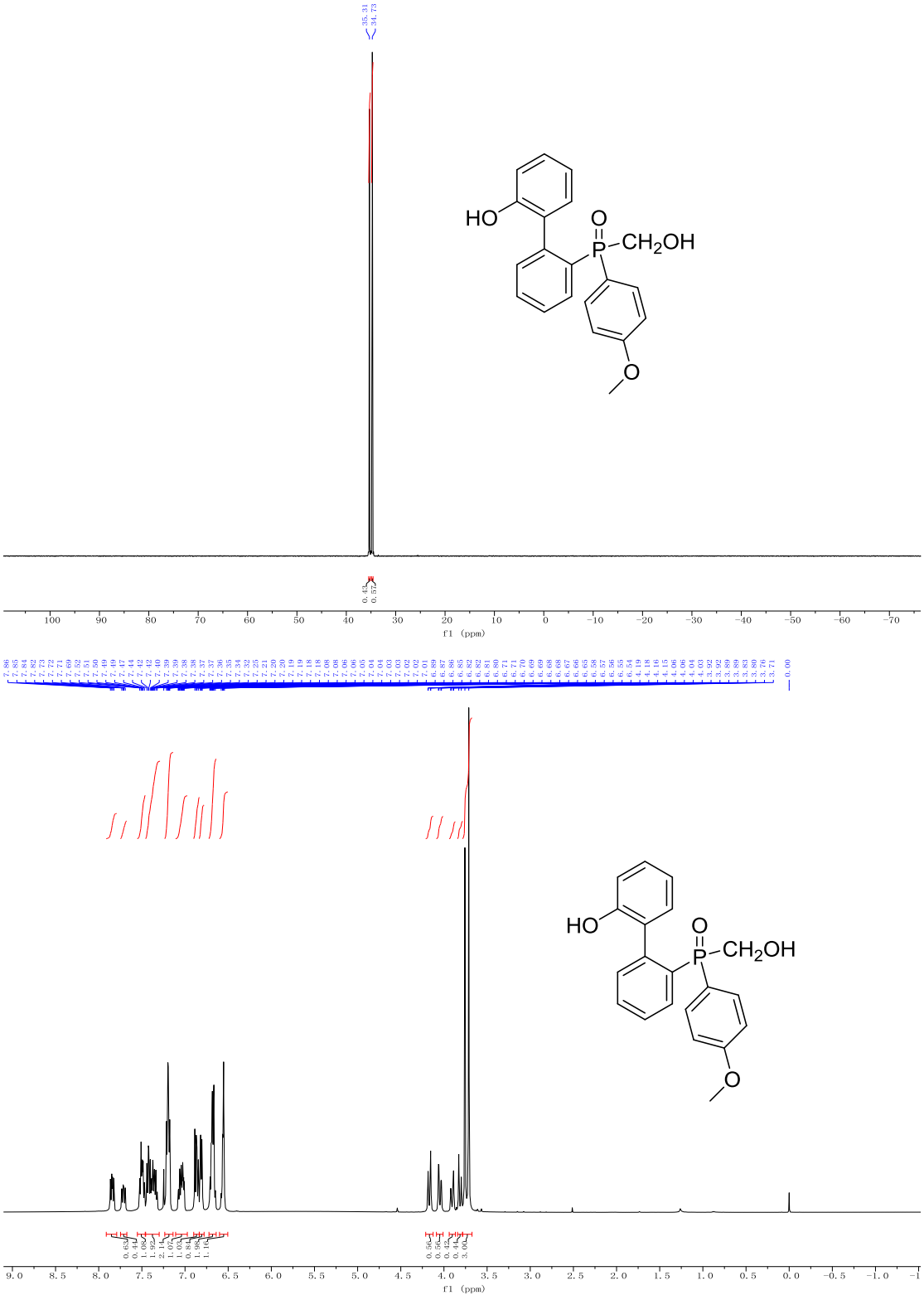
(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(*o*-tolyl)phosphine-oxide (7c)

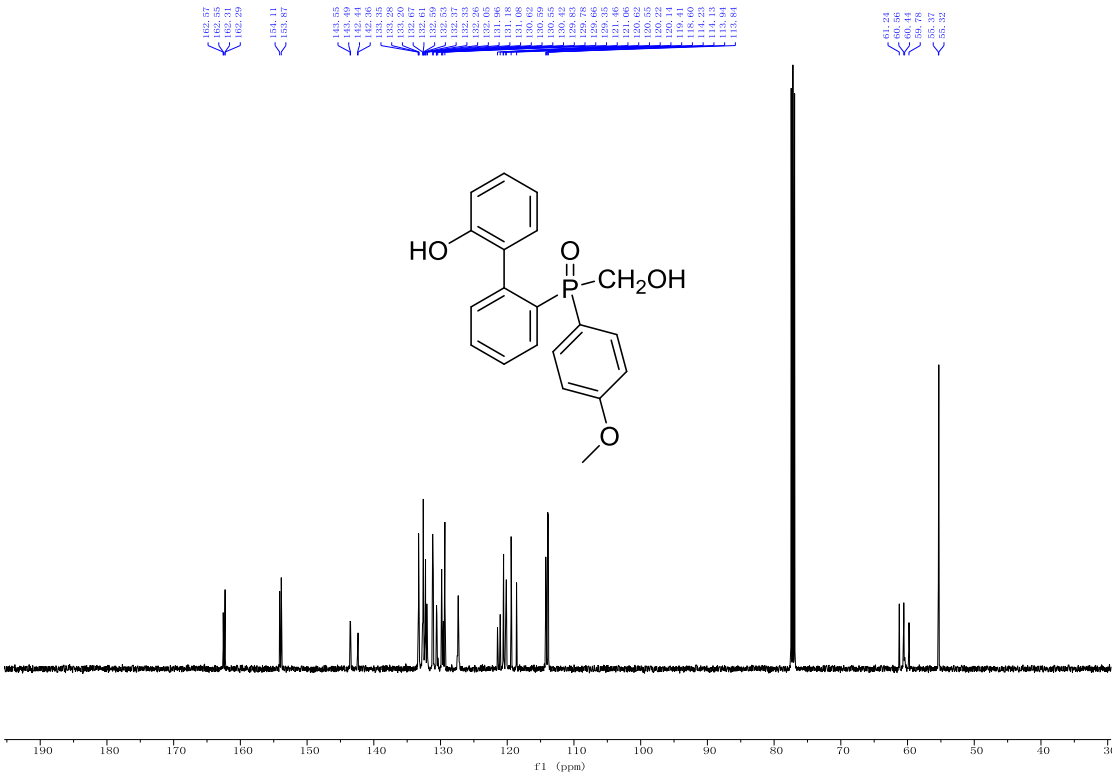



HO
O
P
CH2OH
f1 (ppm)

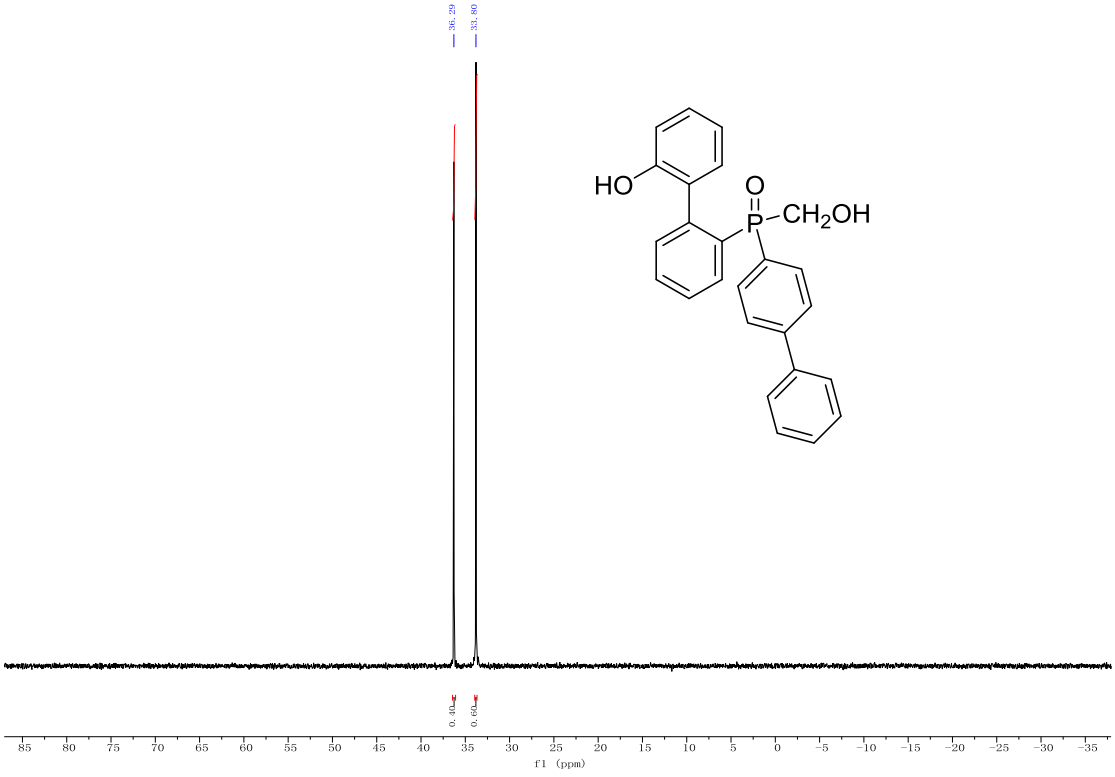

HO
O
P
CH2OH
f1 (ppm)

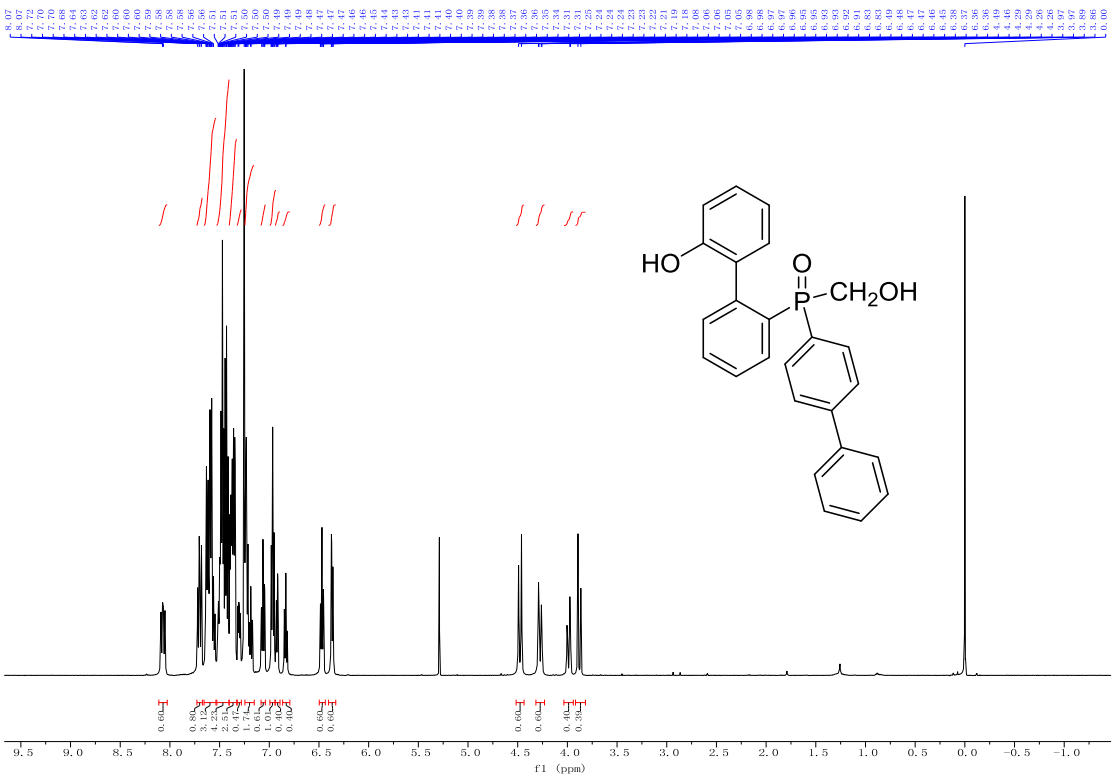
(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(4-methoxyphenyl)phosphine oxide (7d)

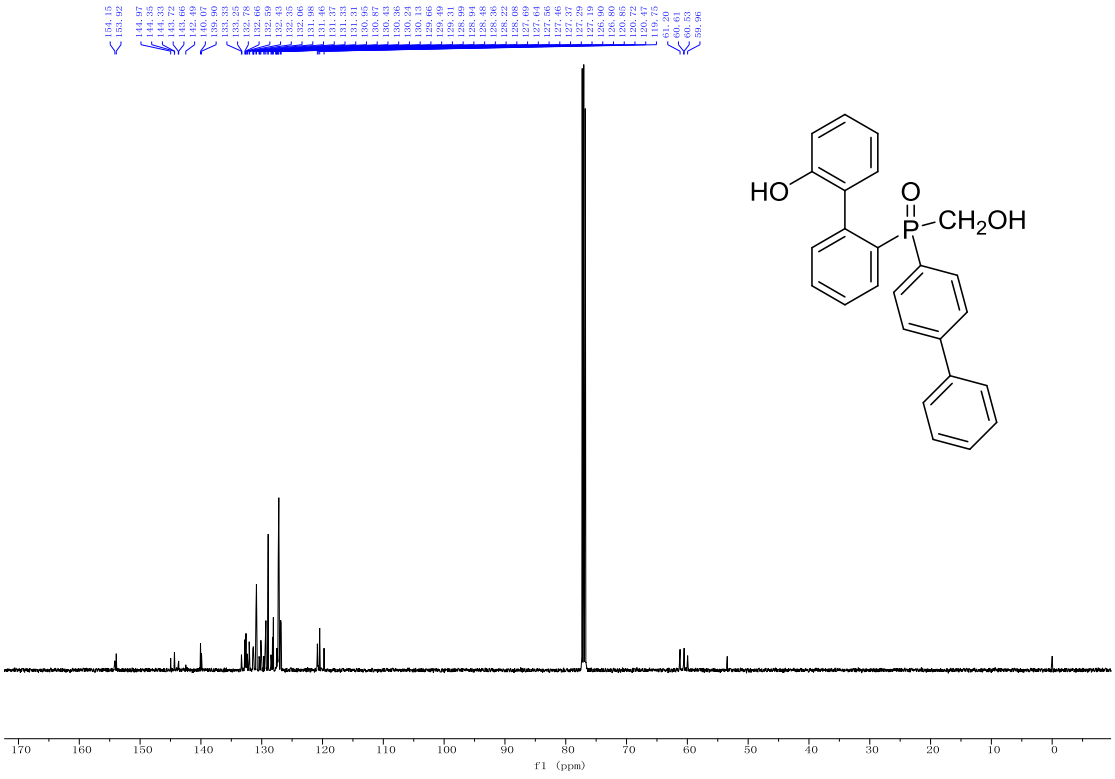




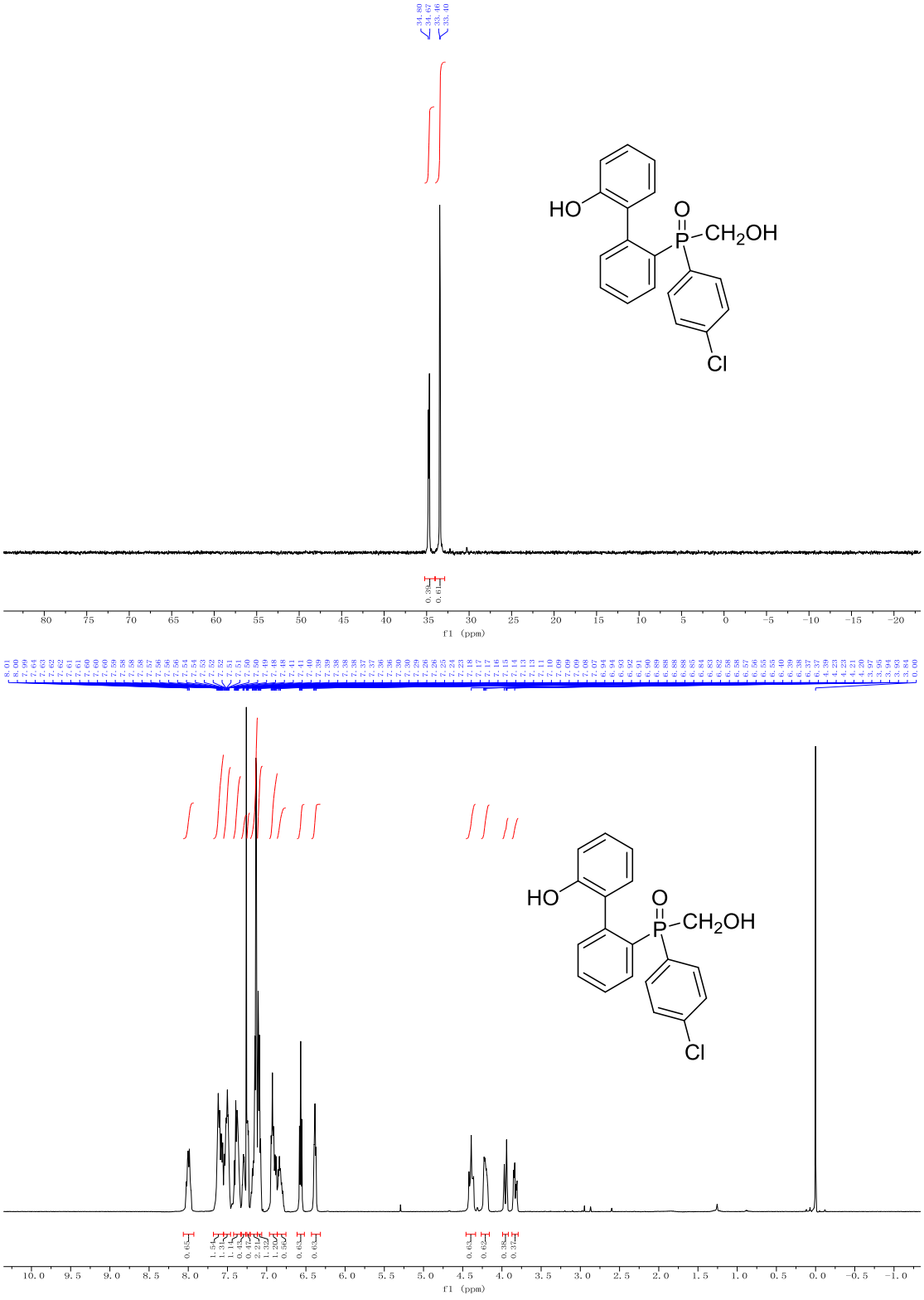
(Biphenyl-4-yl)(2'-hydroxy-biphenyl-2-yl)(hydroxymethyl)phosphine oxide (7e)

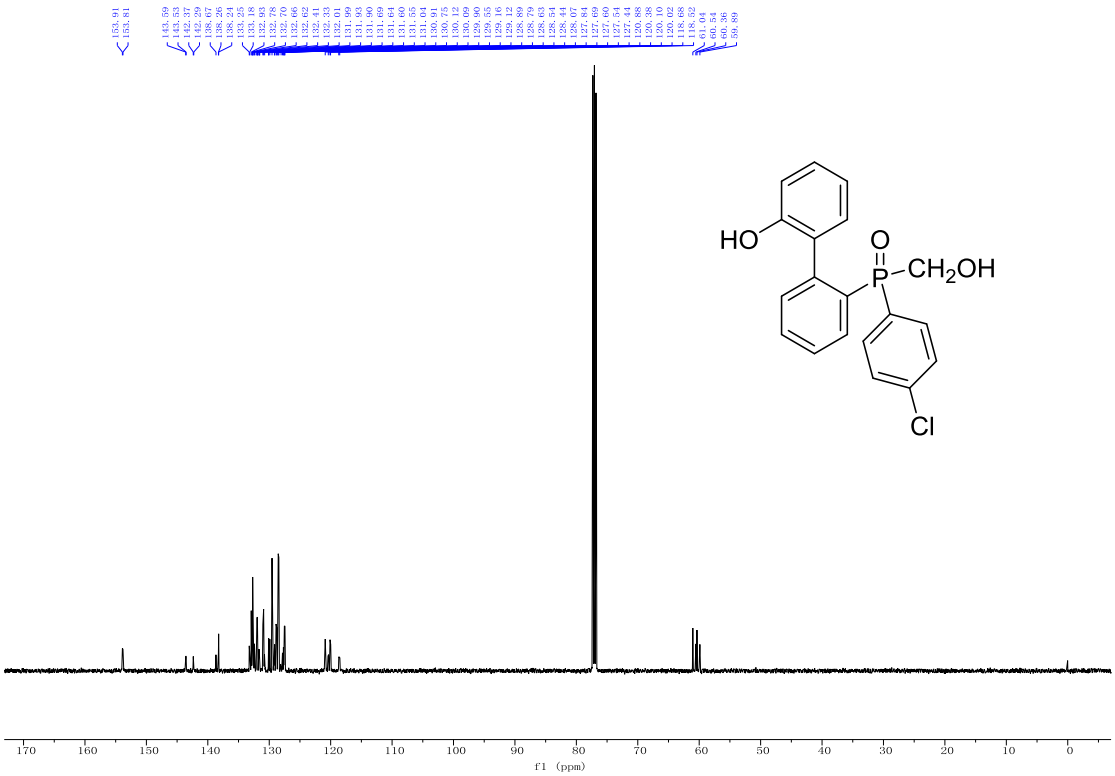



HO
O
P
CH2OH
f1 (ppm)

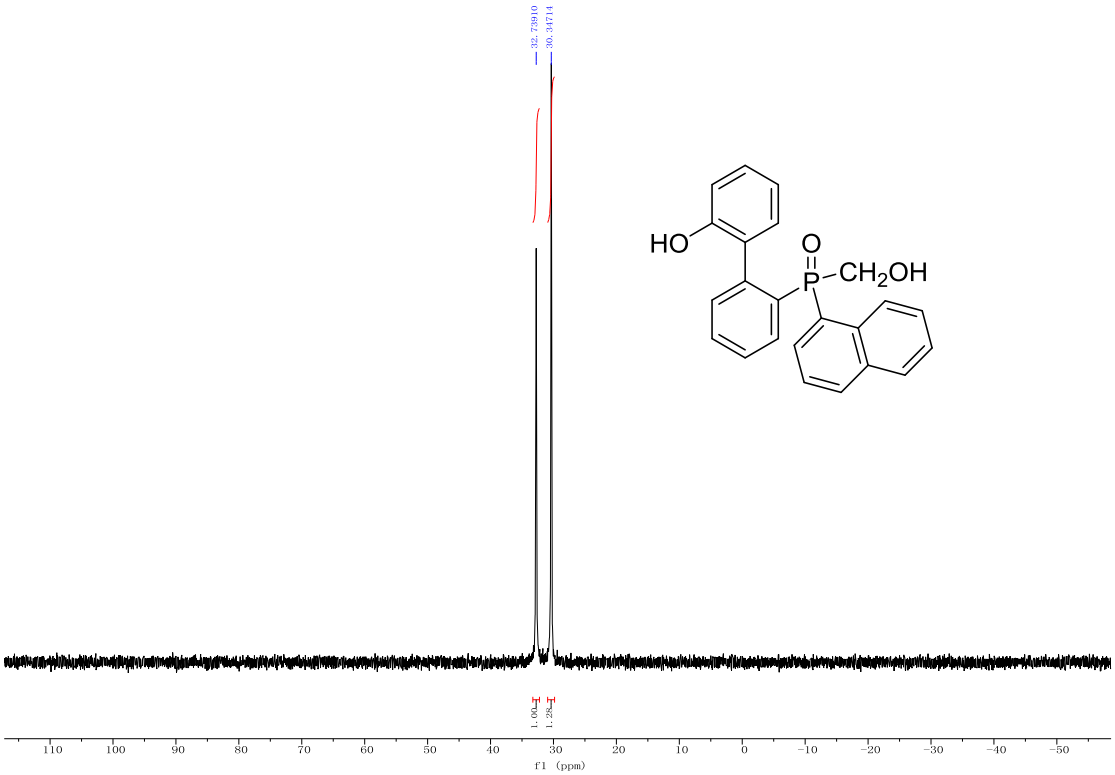

HO
O
P
CH2OH
f1 (ppm)

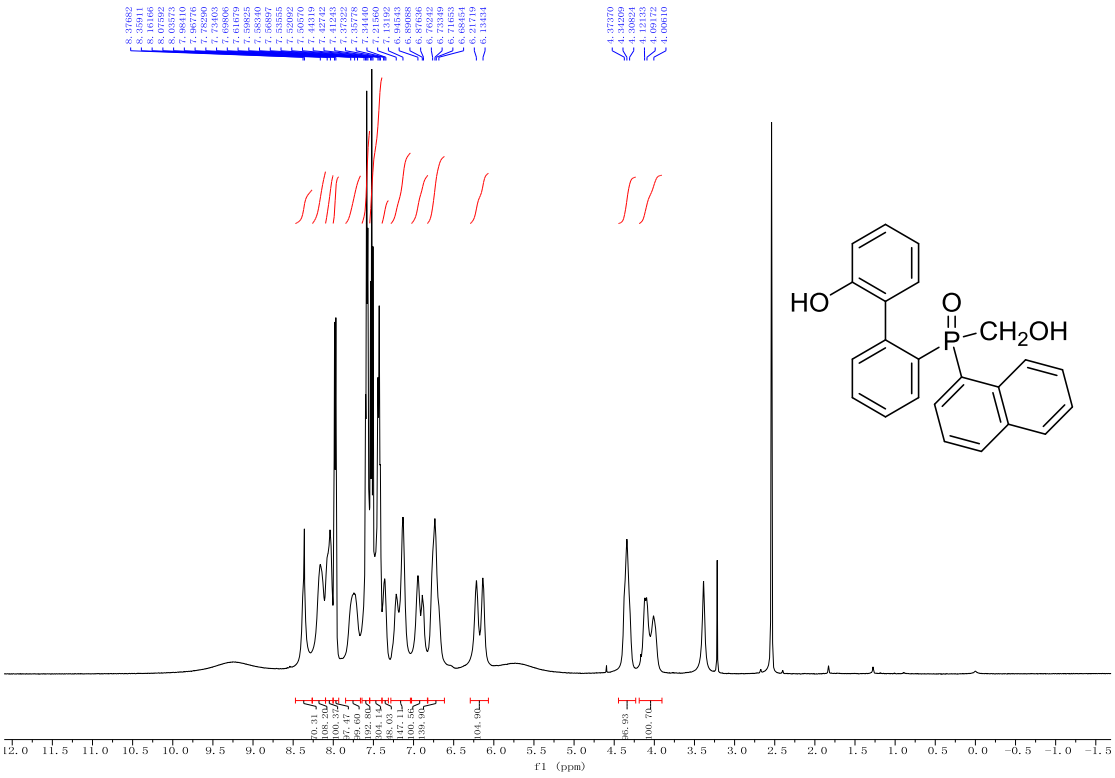
(4-Chlorophenyl)(2'-hydroxy-biphenyl-2-yl)(hydroxymethyl)phosphine-oxide (7f)

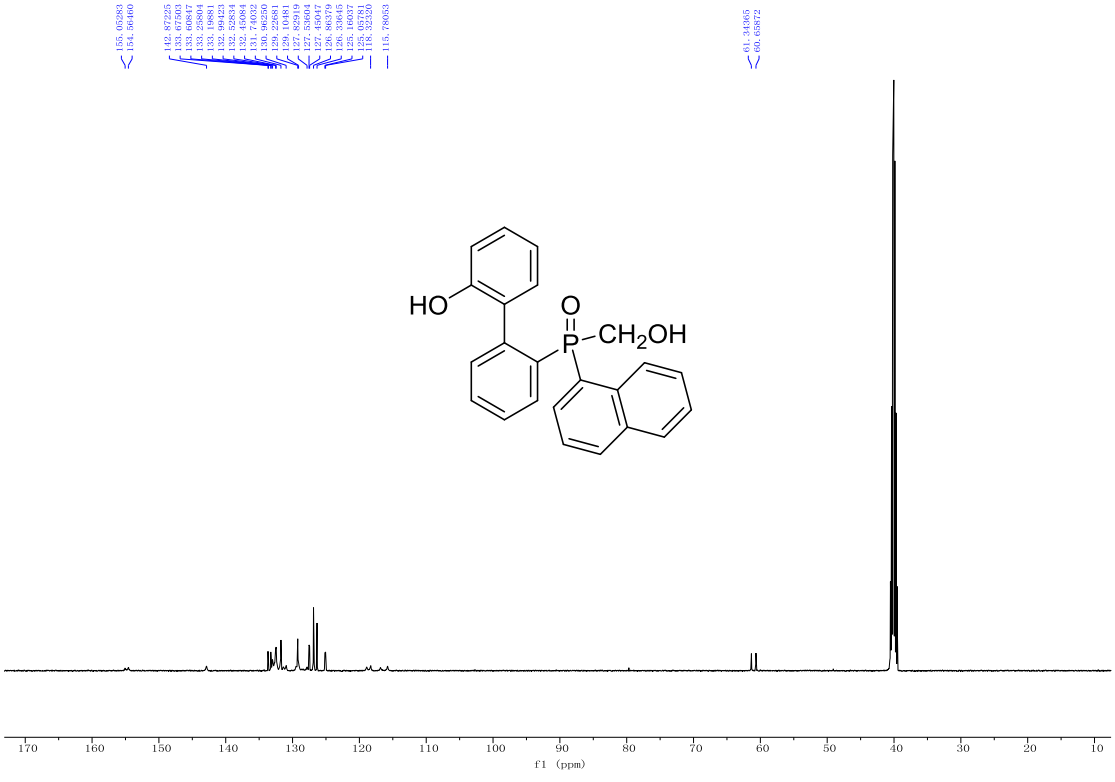




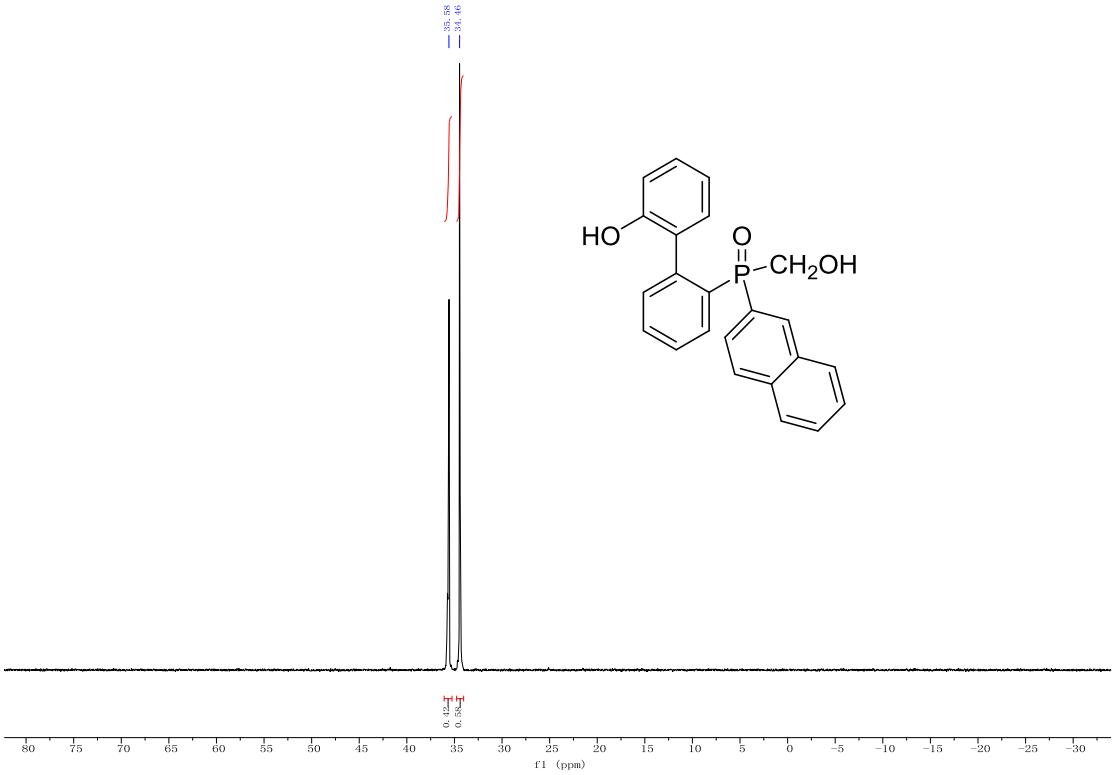
(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(naphthalen-1-yl)phosphine oxide (7g)

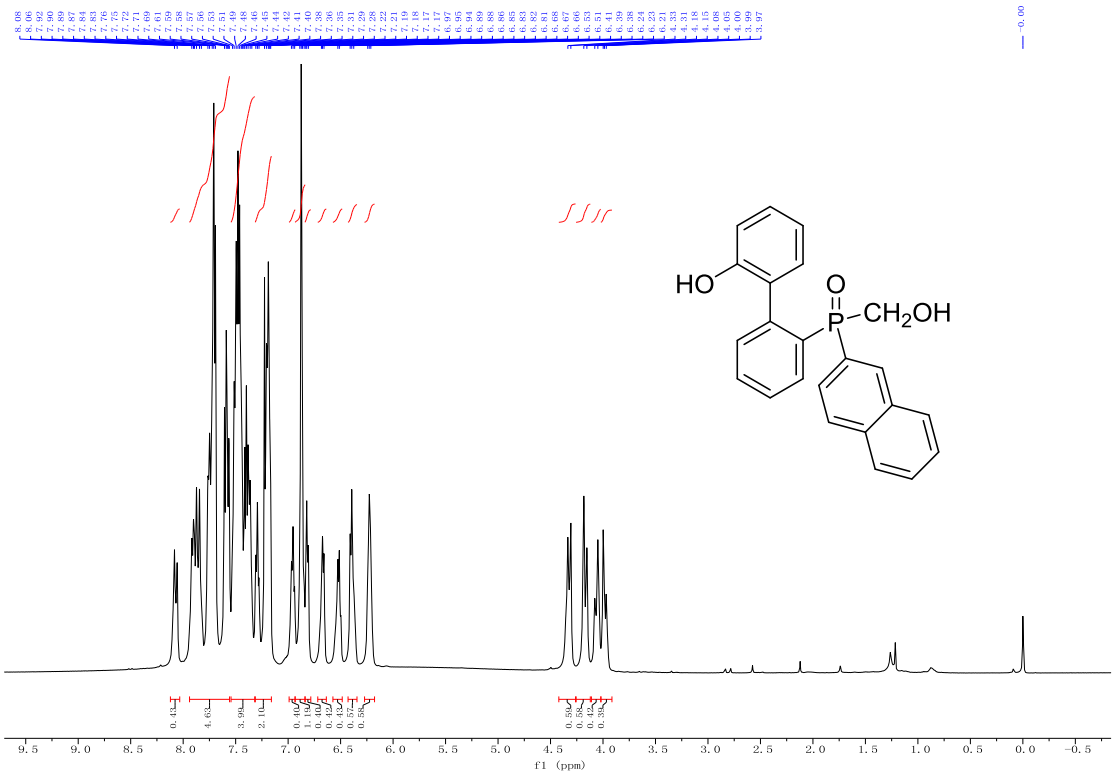


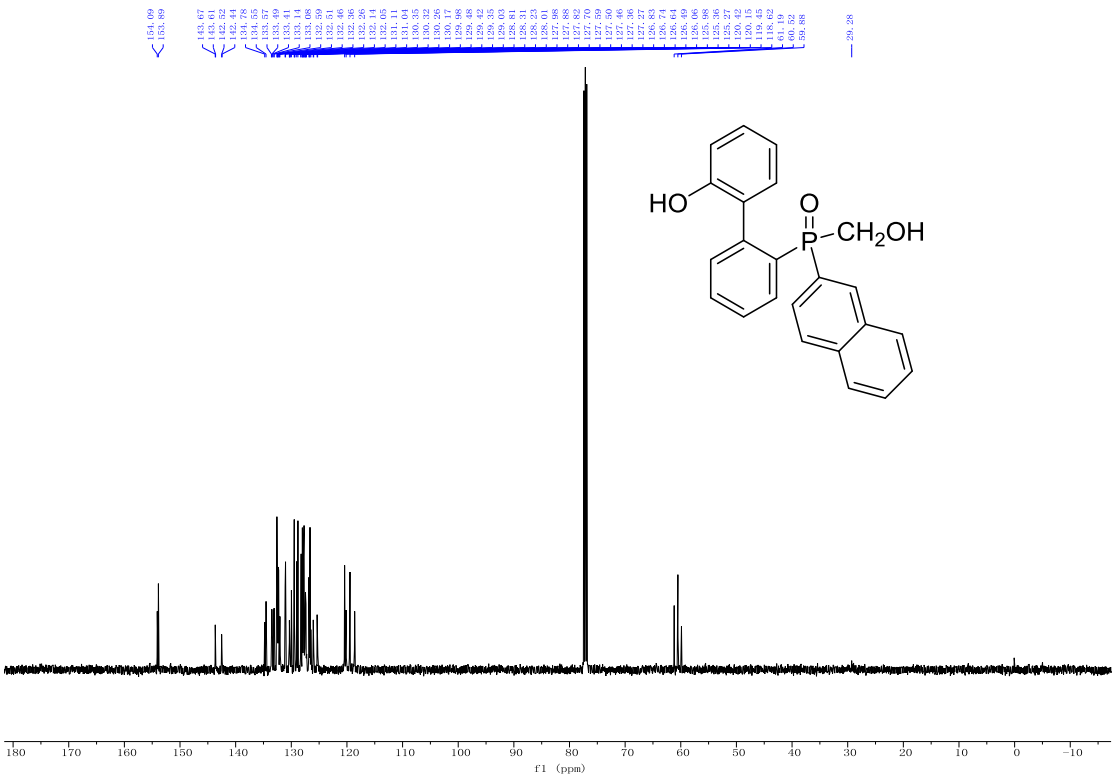

HO
O
P
CH2OH
f1 (ppm)


HO
O
P
CH2OH
f1 (ppm)

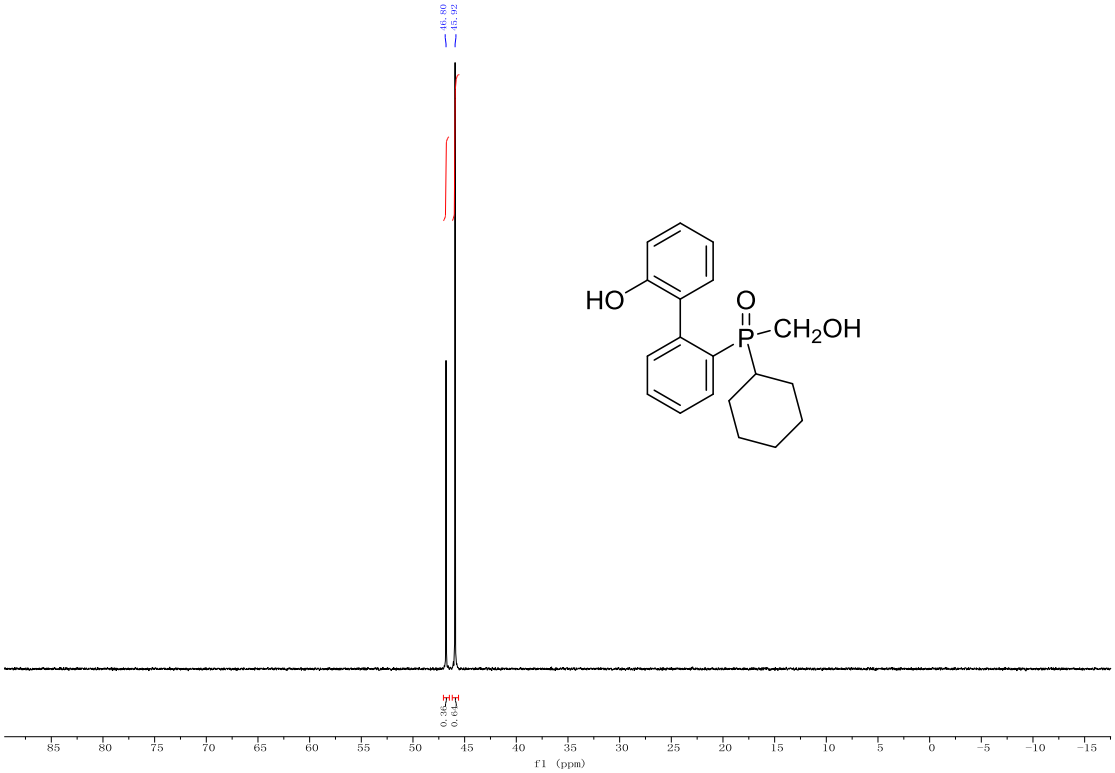
(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(naphthalen-2-yl)phosphine oxide (7h)

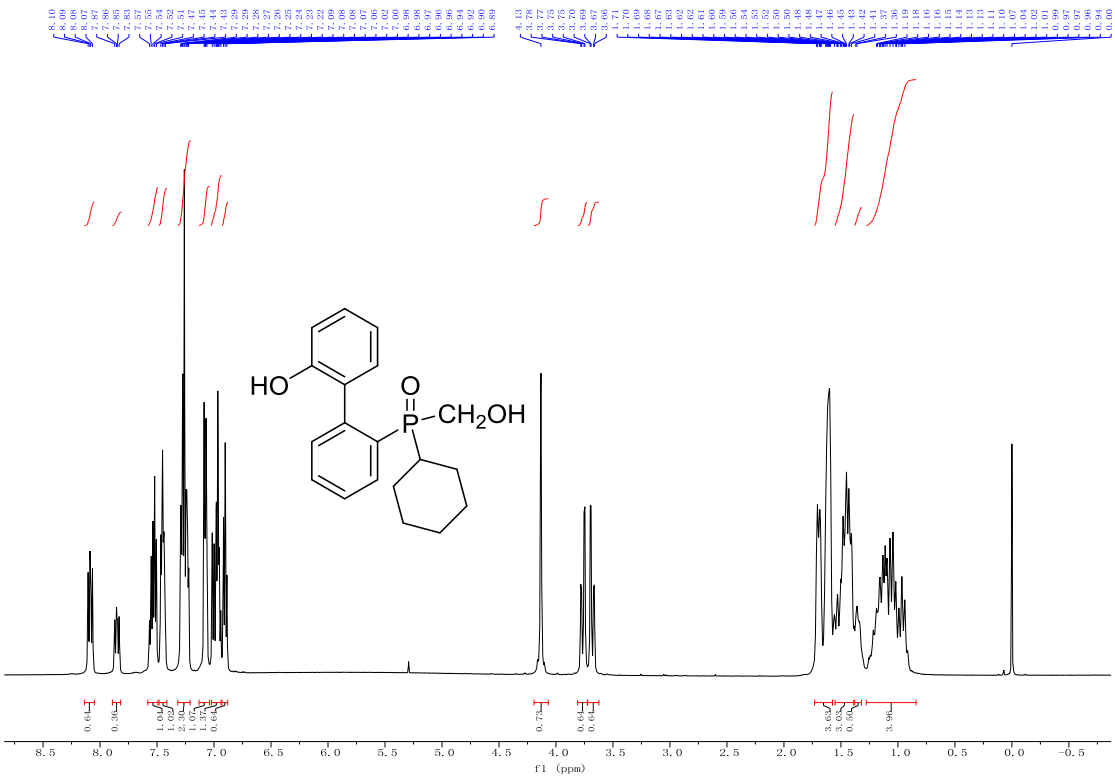


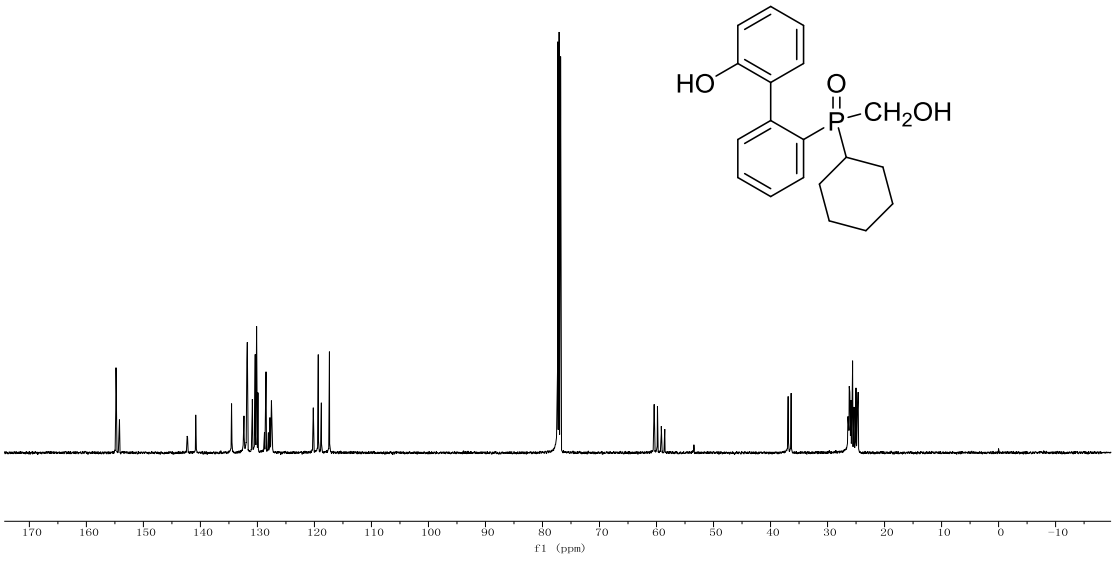




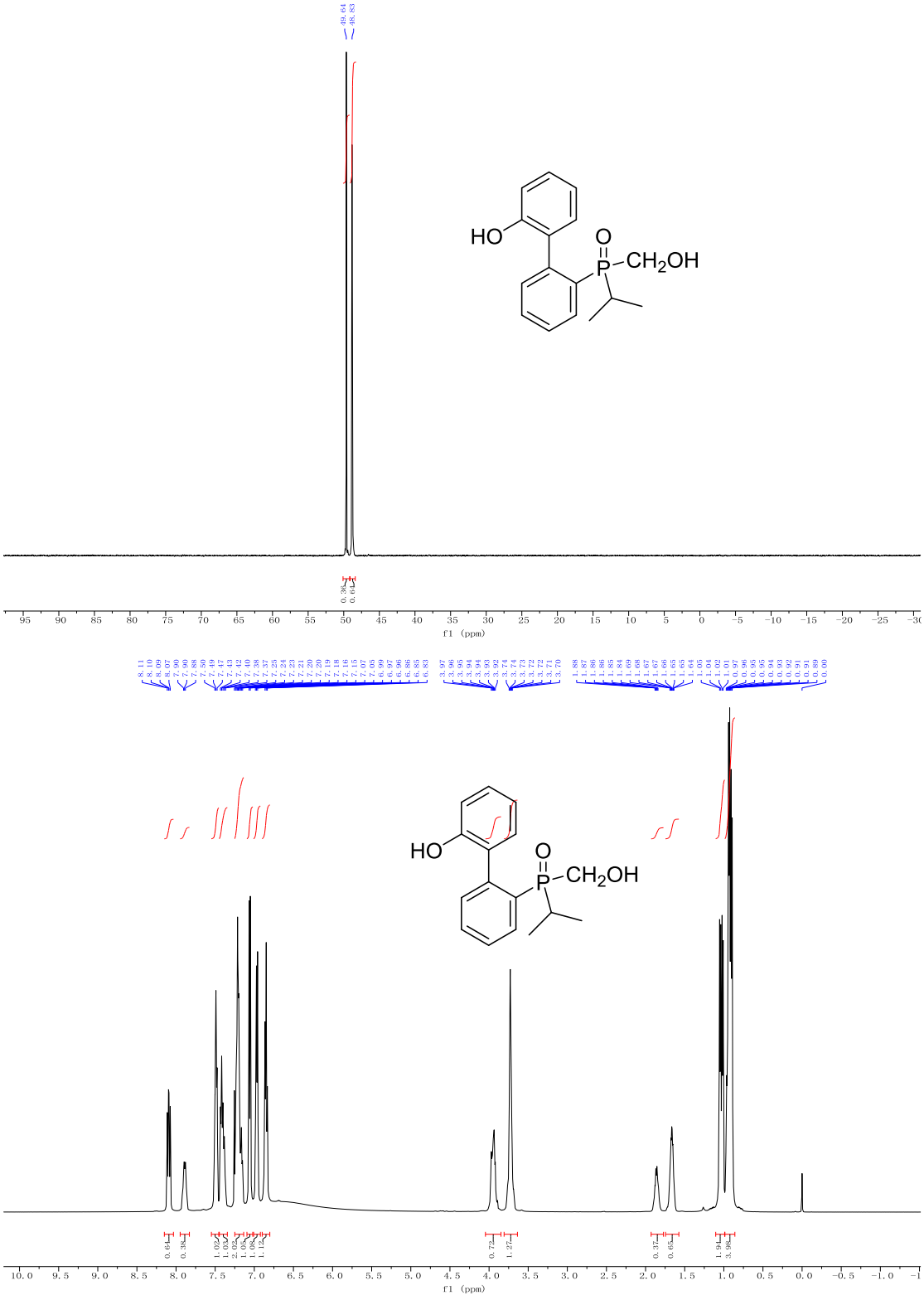
Cyclohexyl(2'-hydroxy-biphenyl-2-yl)(hydroxymethyl)phosphine oxide (7i)

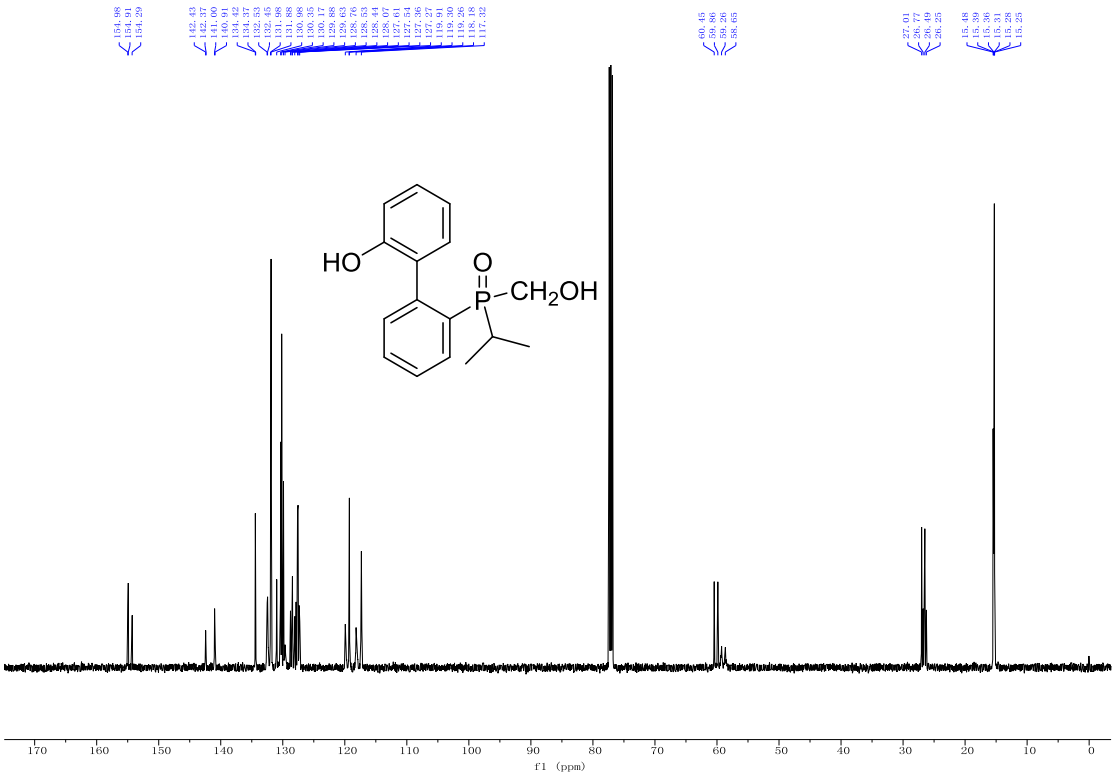



HO
O
P
CH2OH
f1 (ppm)

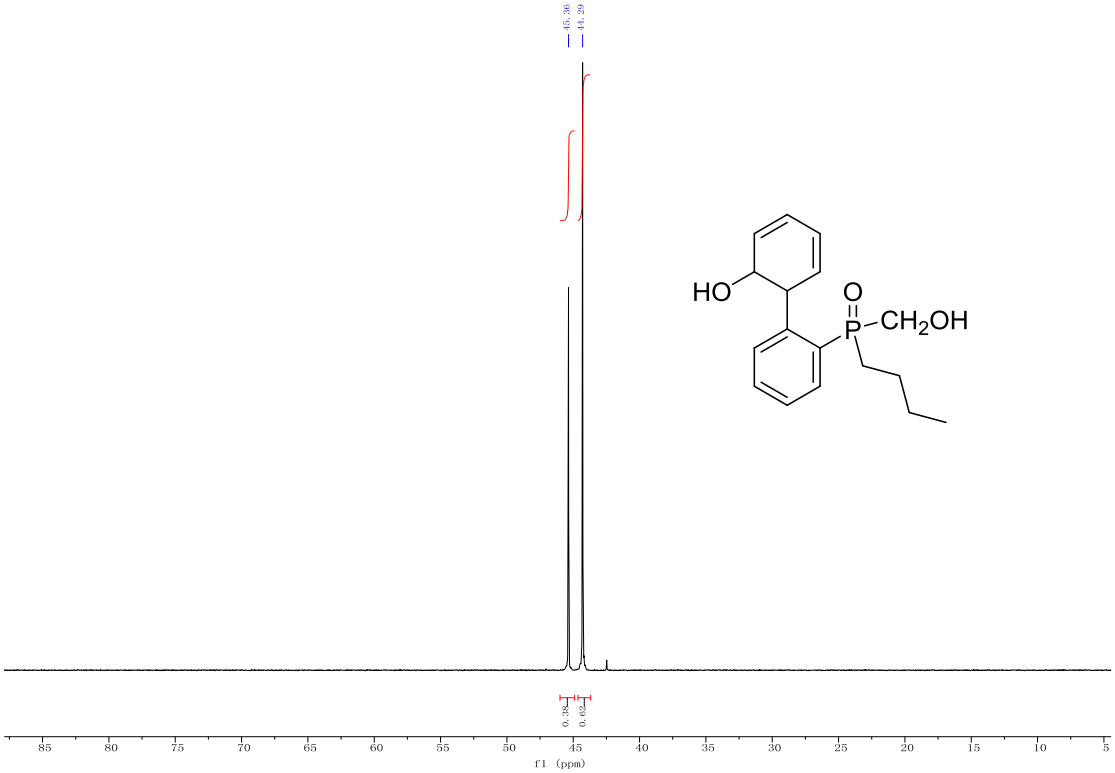

HO
O
P
CH2OH
f1 (ppm)

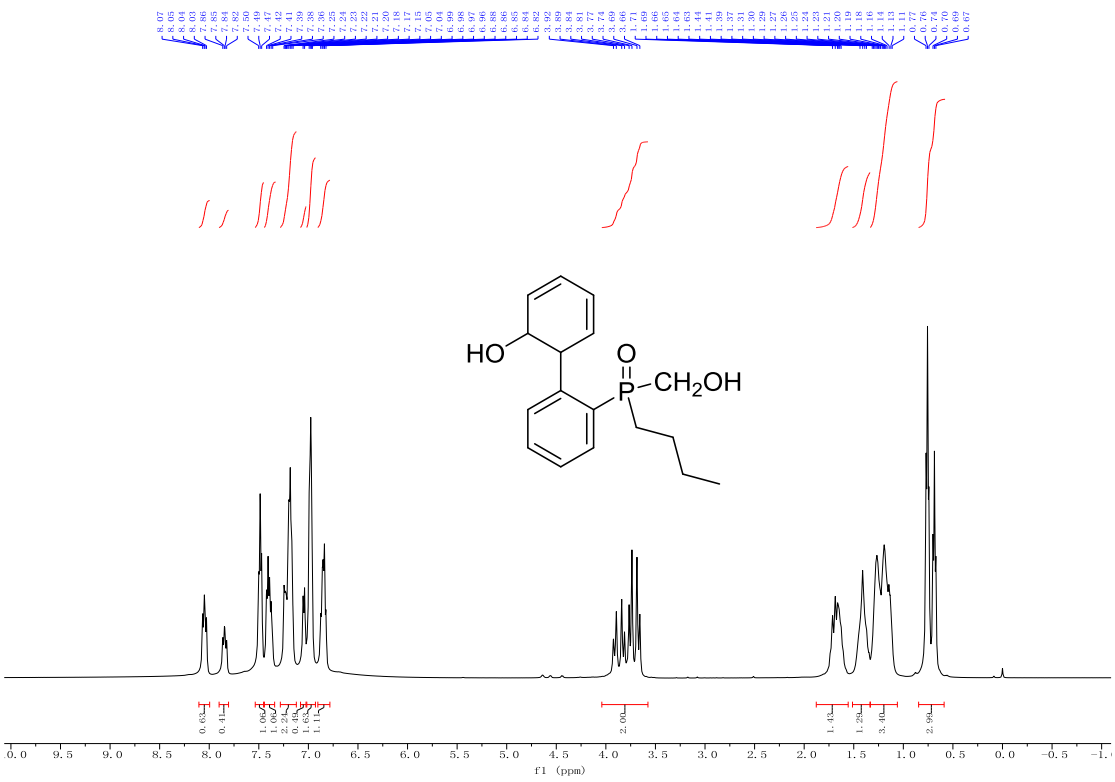
(2'-Hydroxy-biphenyl-2-yl)(hydroxymethyl)(isopropyl)phosphine oxide (7j)

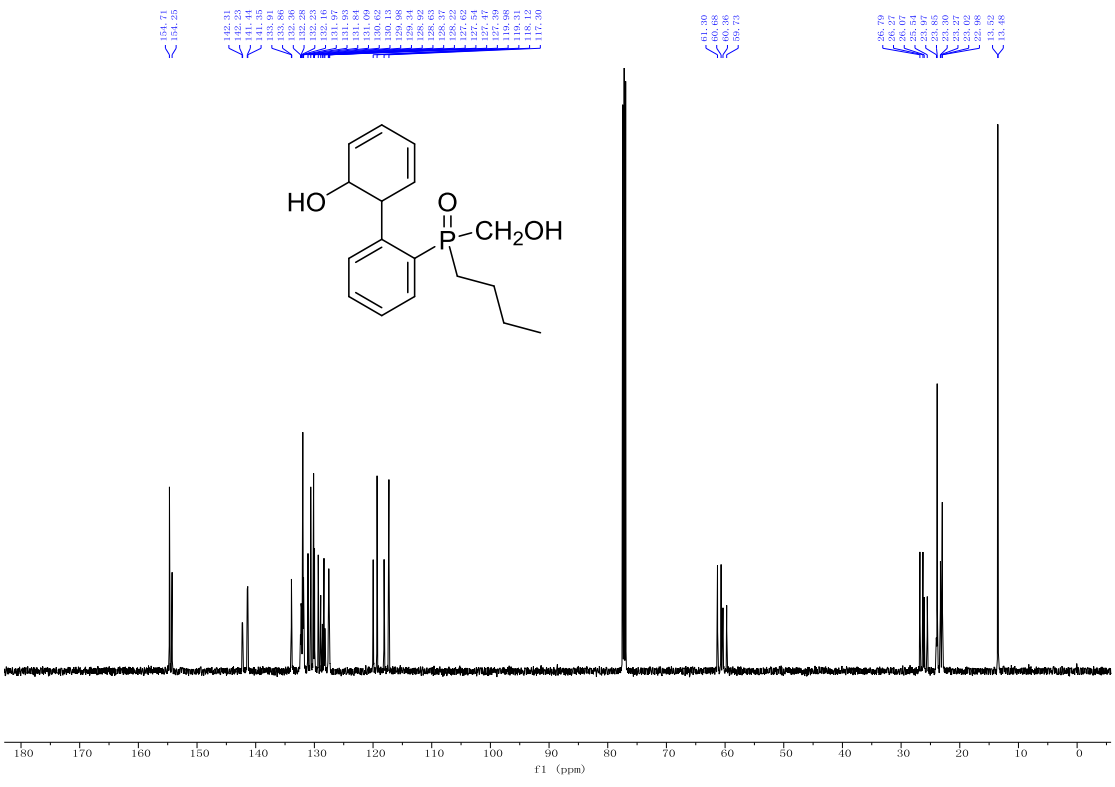




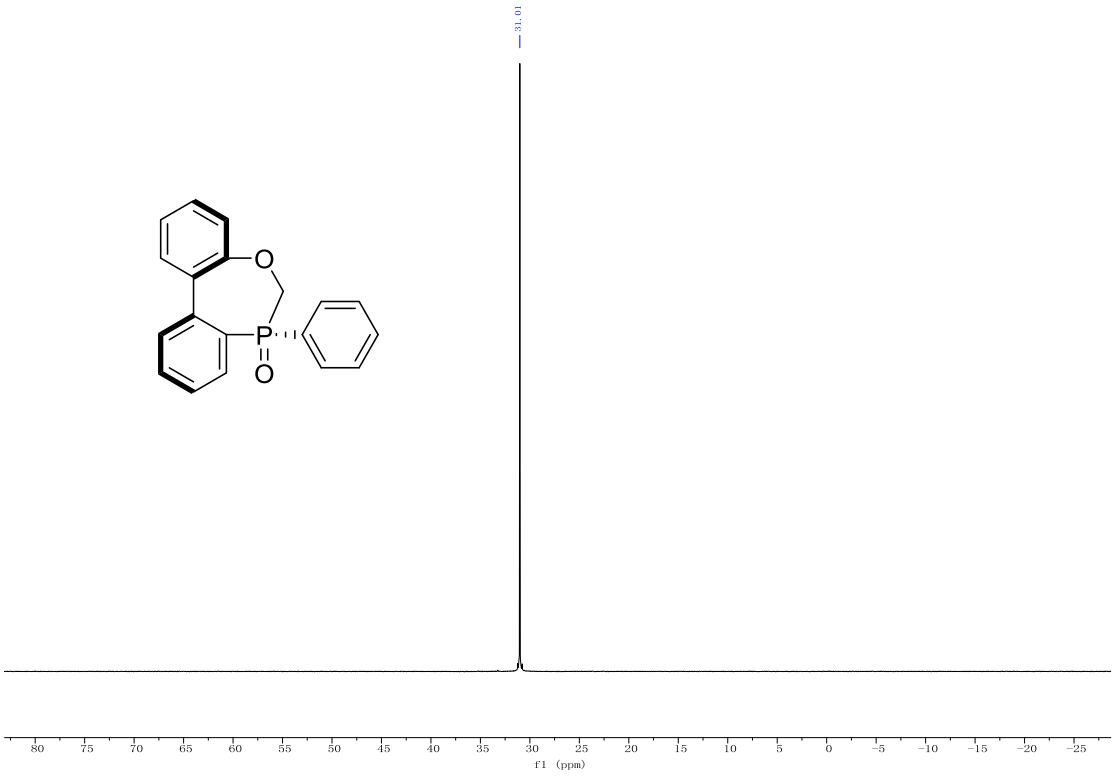
Butyl(2'-hydroxy-biphenyl-2-yl)(hydroxymethyl)phosphine oxide (7k)

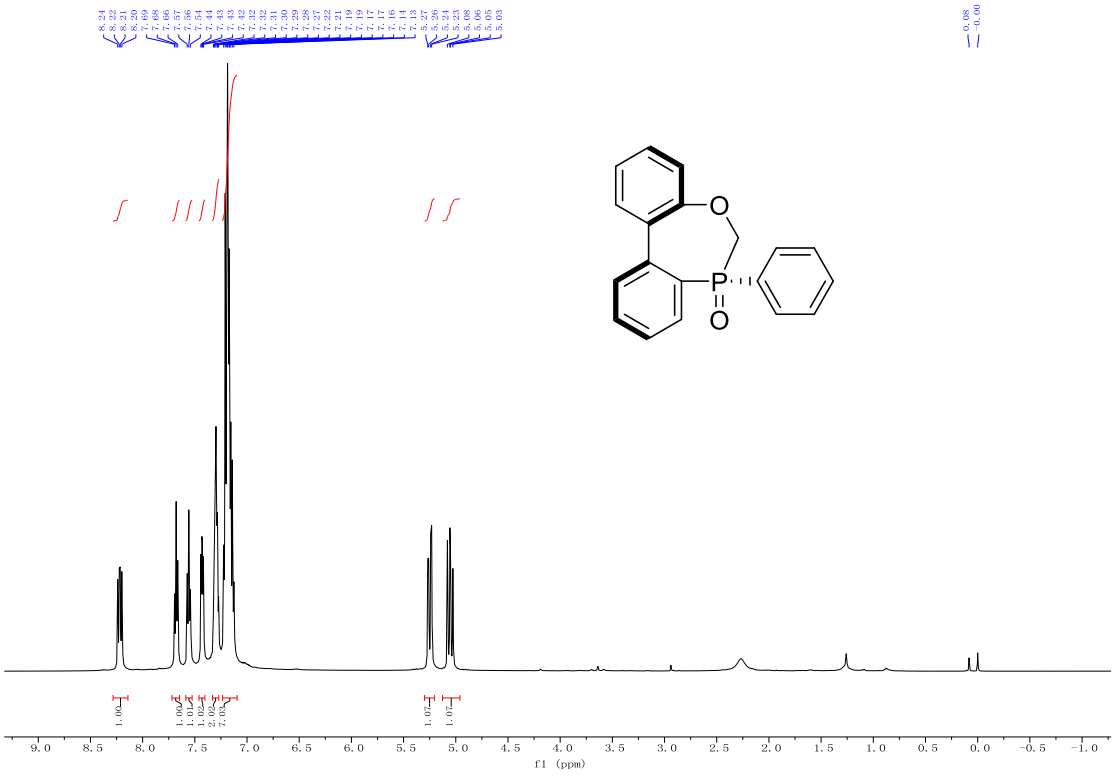


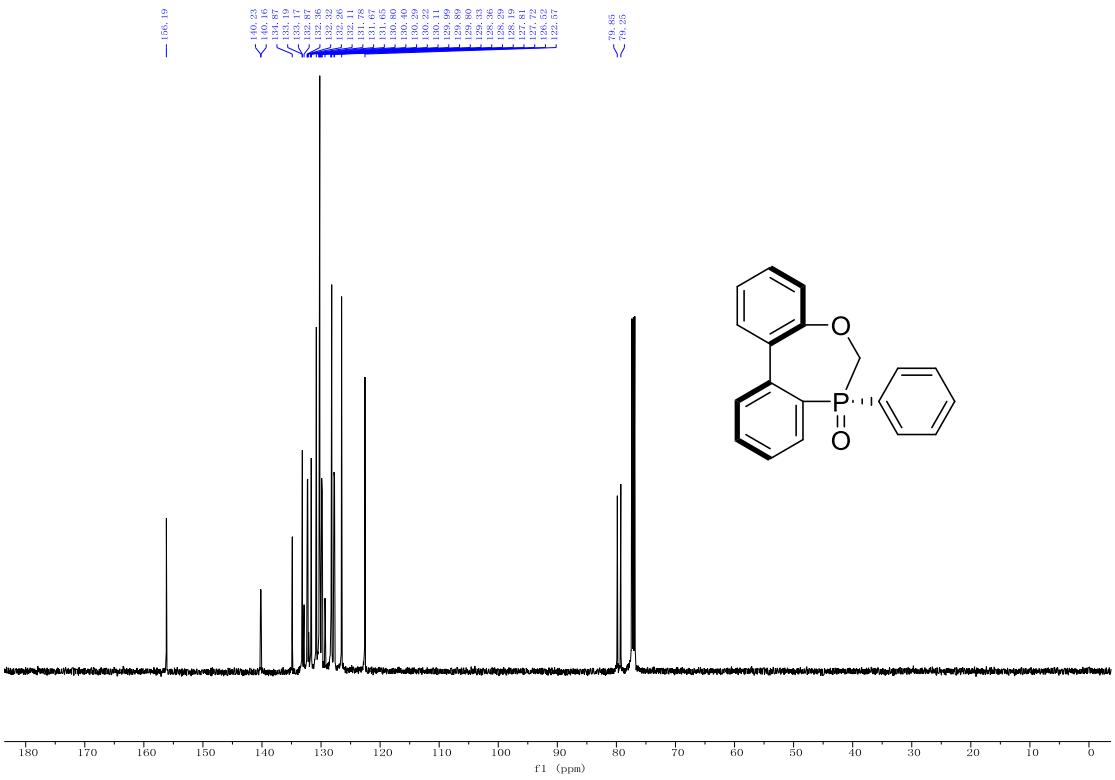

HO
O
P
CH2OH
f1 (ppm)


HO
O
P
CH2OH
f1 (ppm)

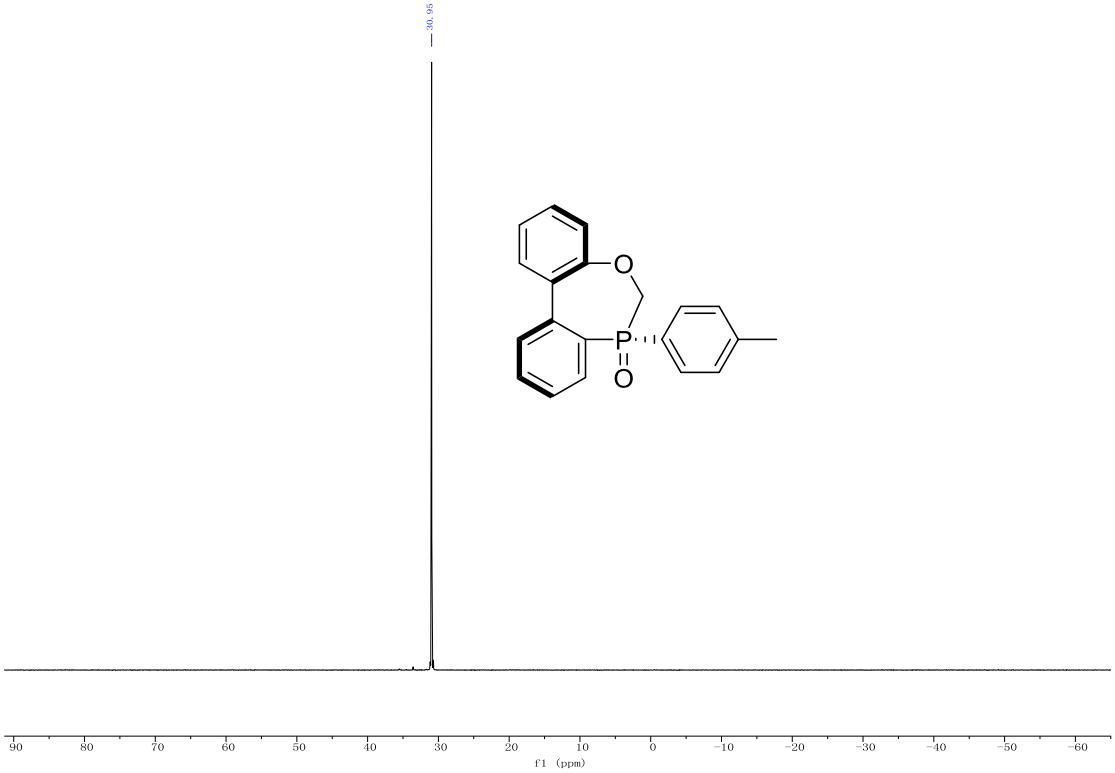
***u*-7-Phenyl-6*H*-dibenzo[*d*,*f*][1,3]oxaphosphepine 7-oxide (*u*-9a)**

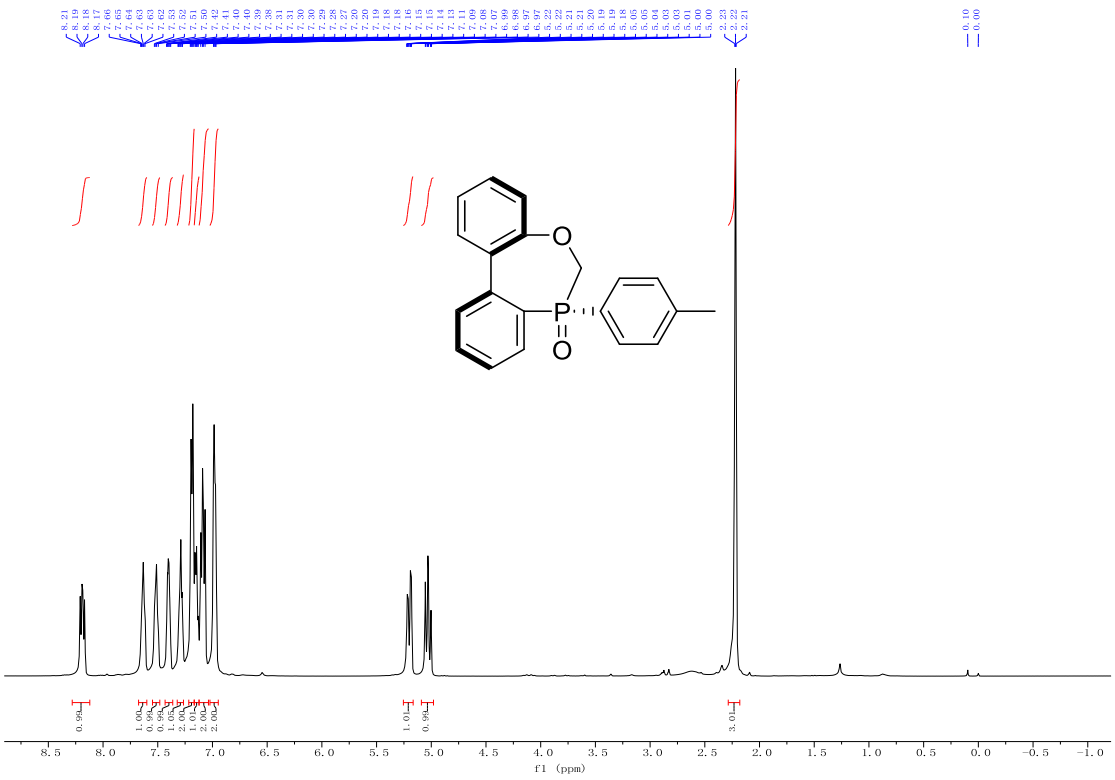


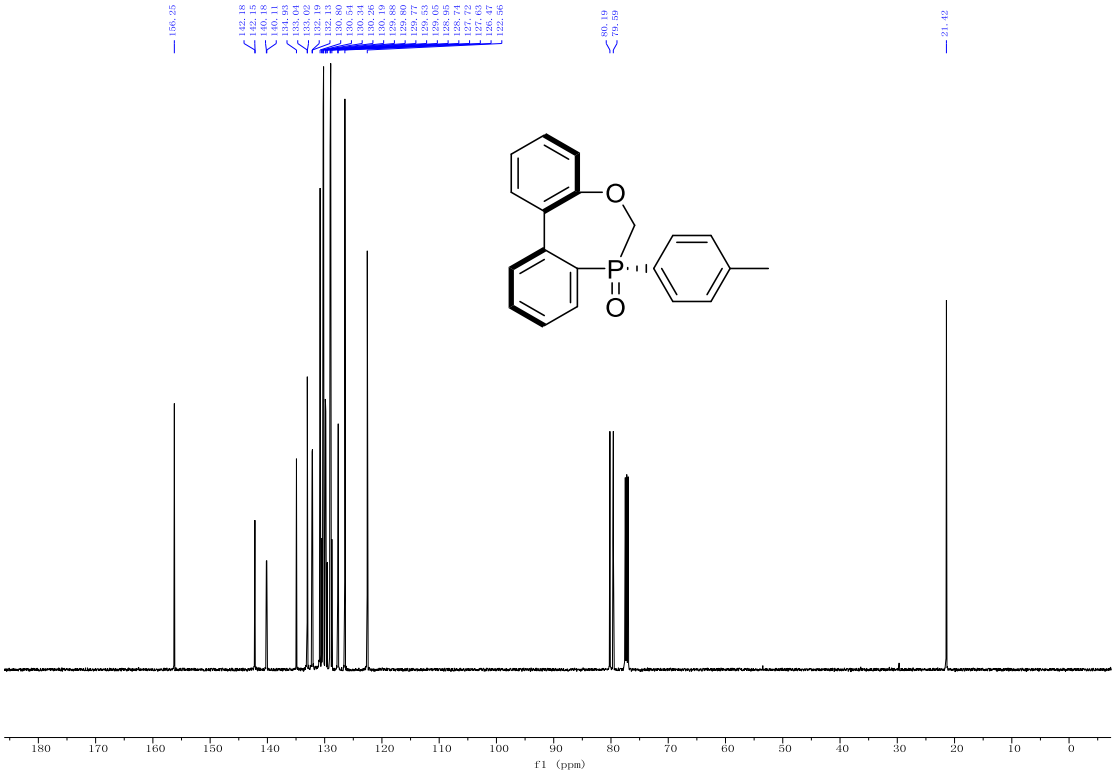




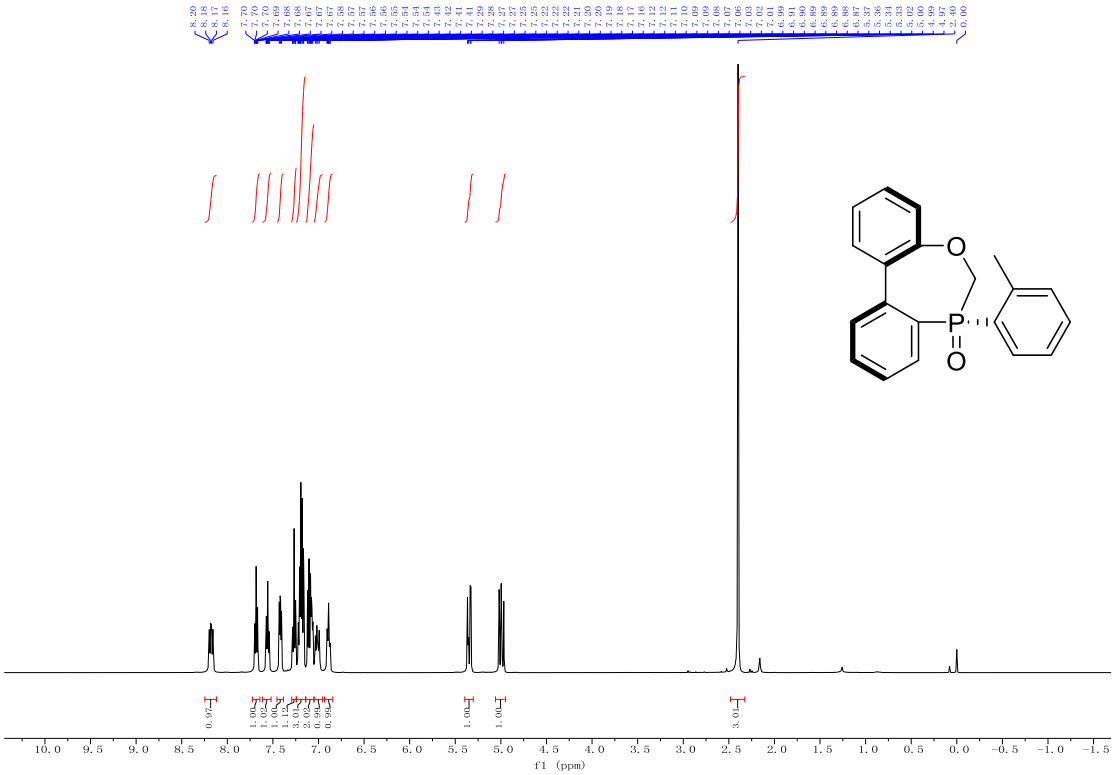
***u*-7-(*p*-Tolyl)-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9b)**

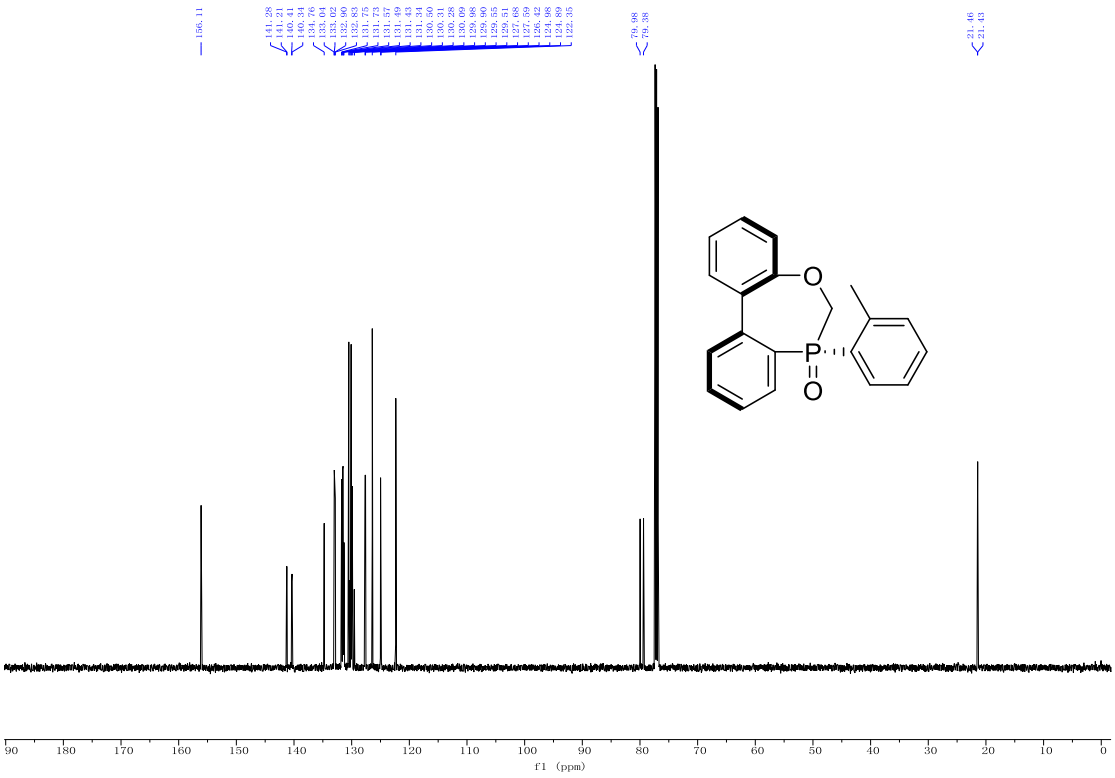



O
P
O
f1 (ppm)

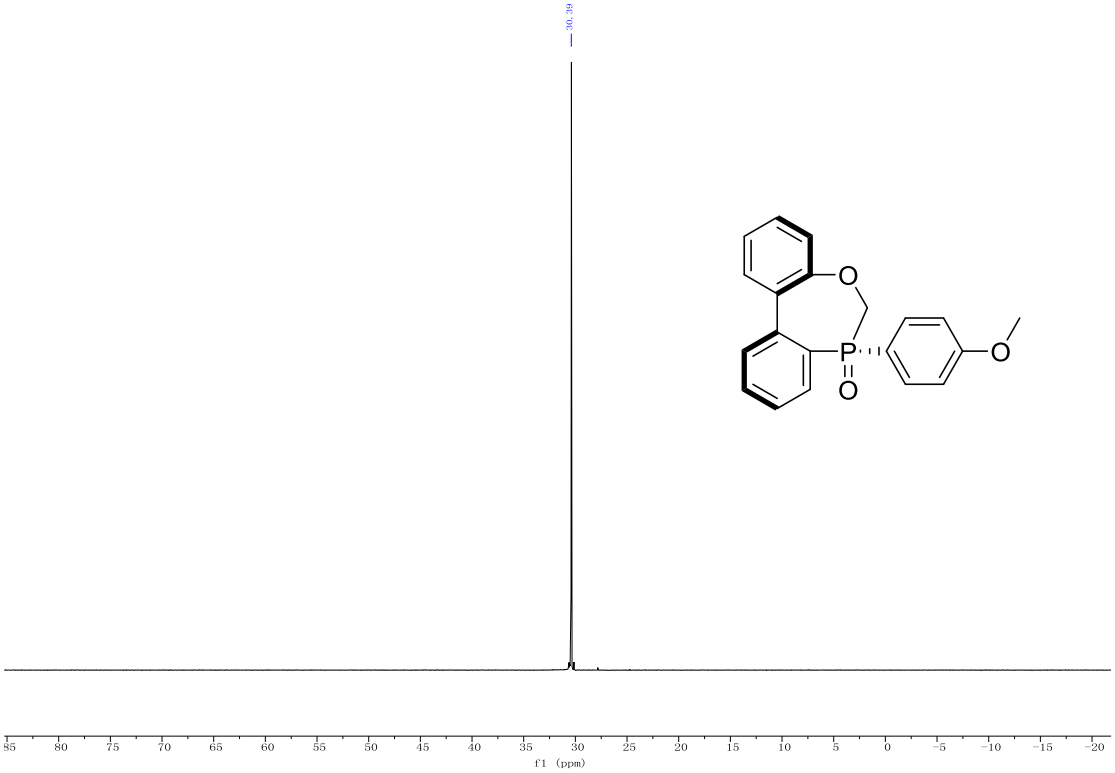

O
P
O
f1 (ppm)

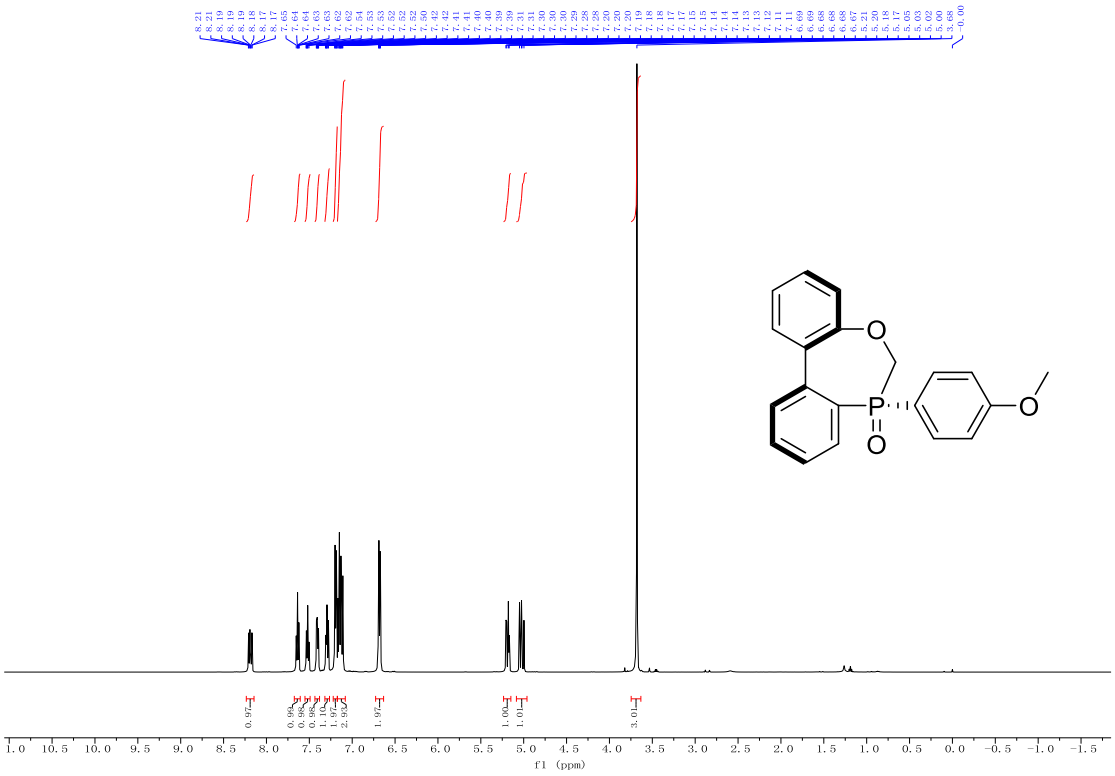
***u*-7-(*o*-Tolyl)-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9c)**

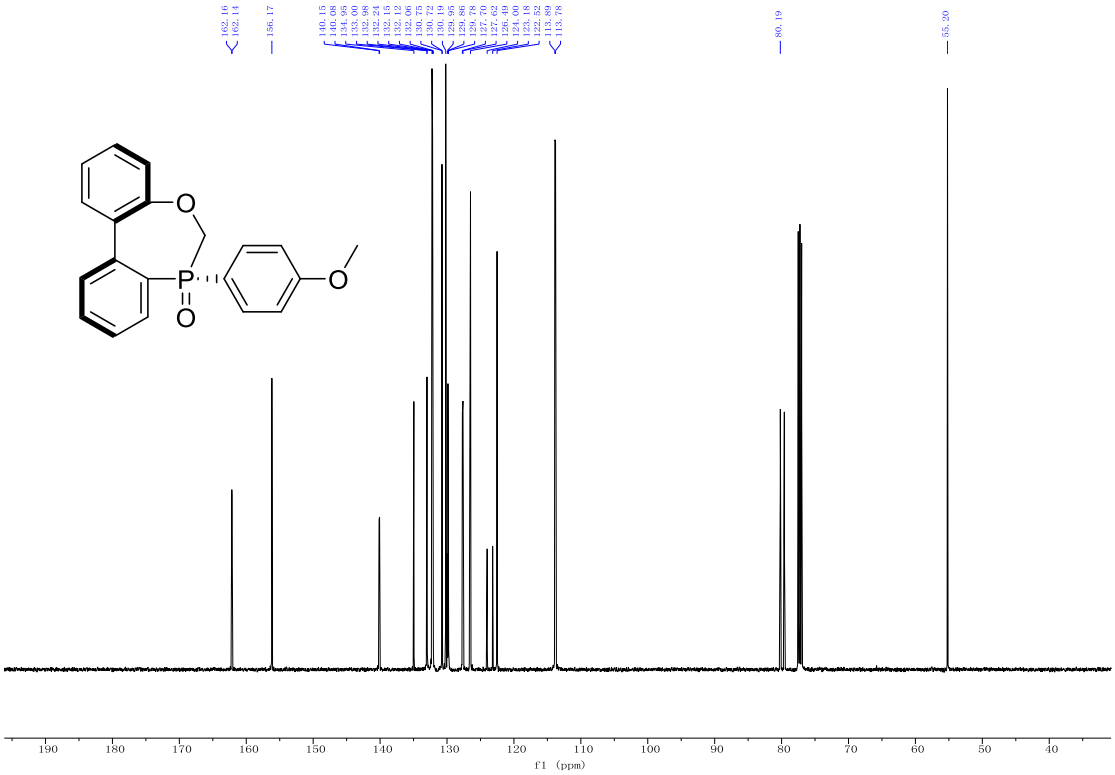




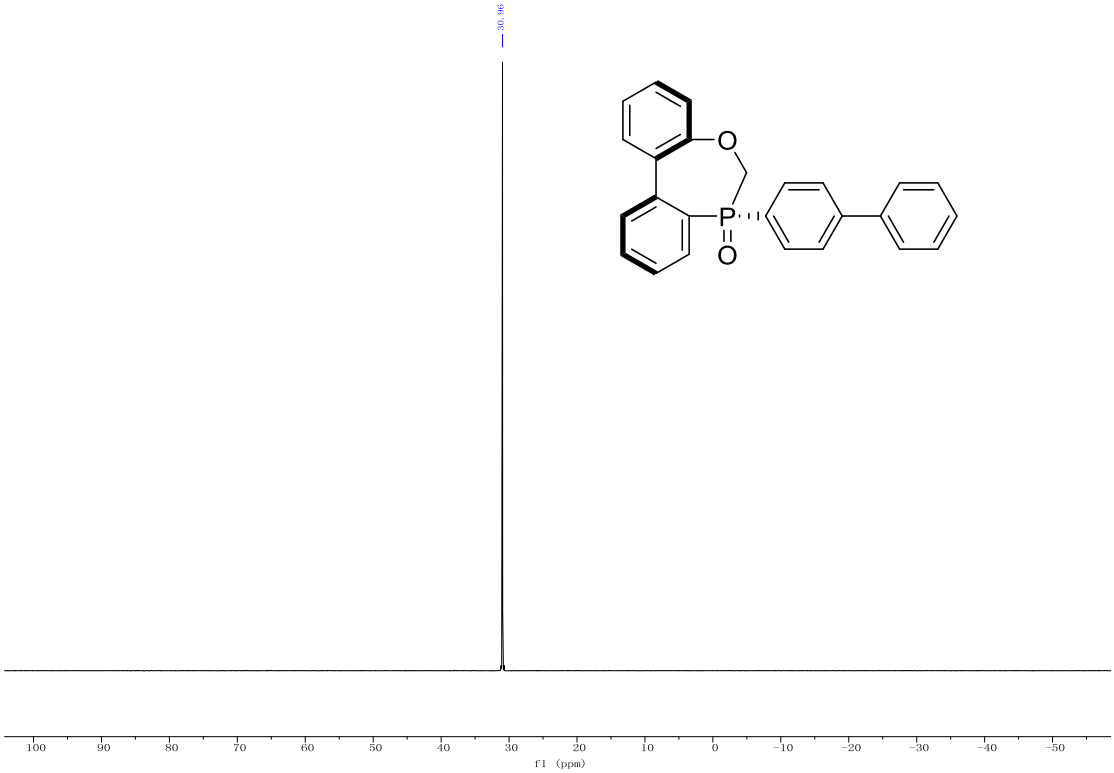
***u*-7-(4-Methoxyphenyl)-6*H*-dibenzo[*d*,*f*][1,3]oxaphosphepine 7-oxide (*u*-9d)**

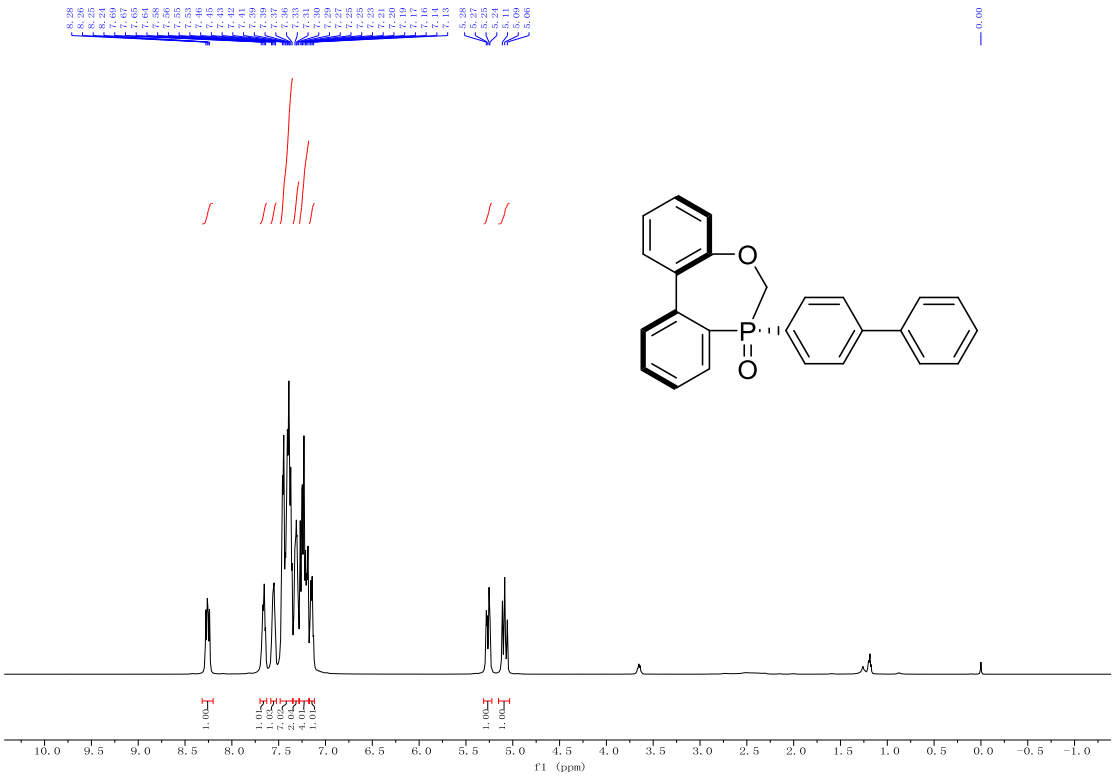


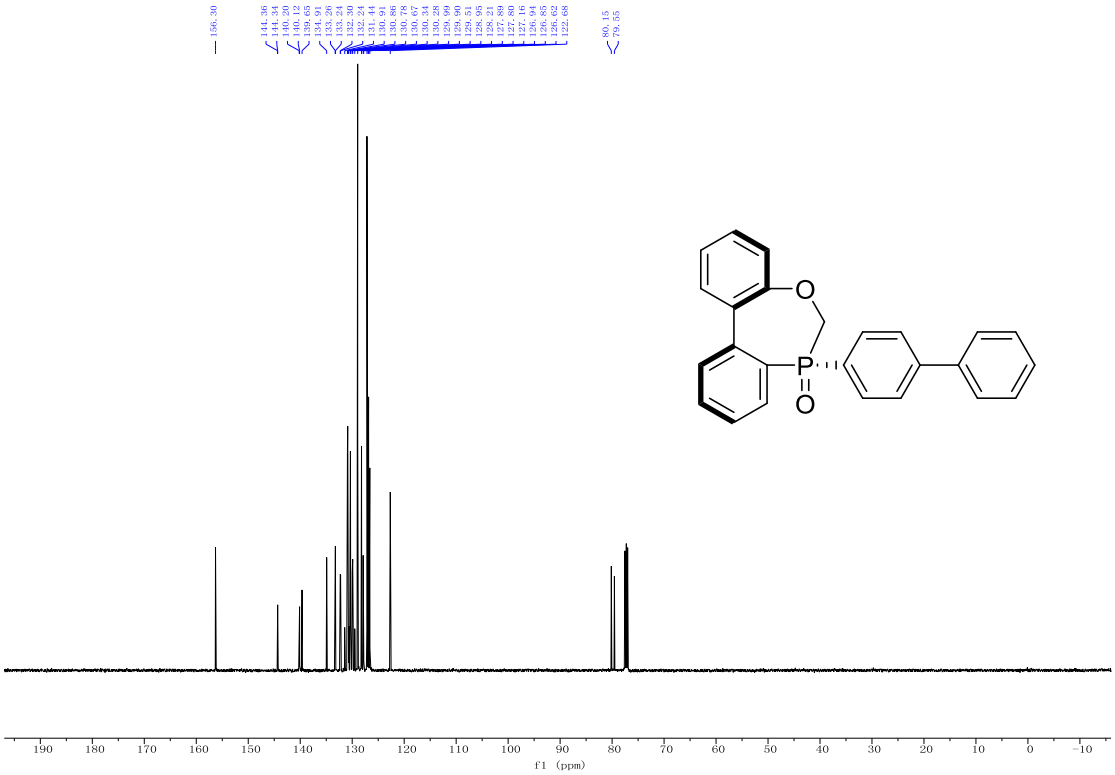

f1 (ppm)


f1 (ppm)

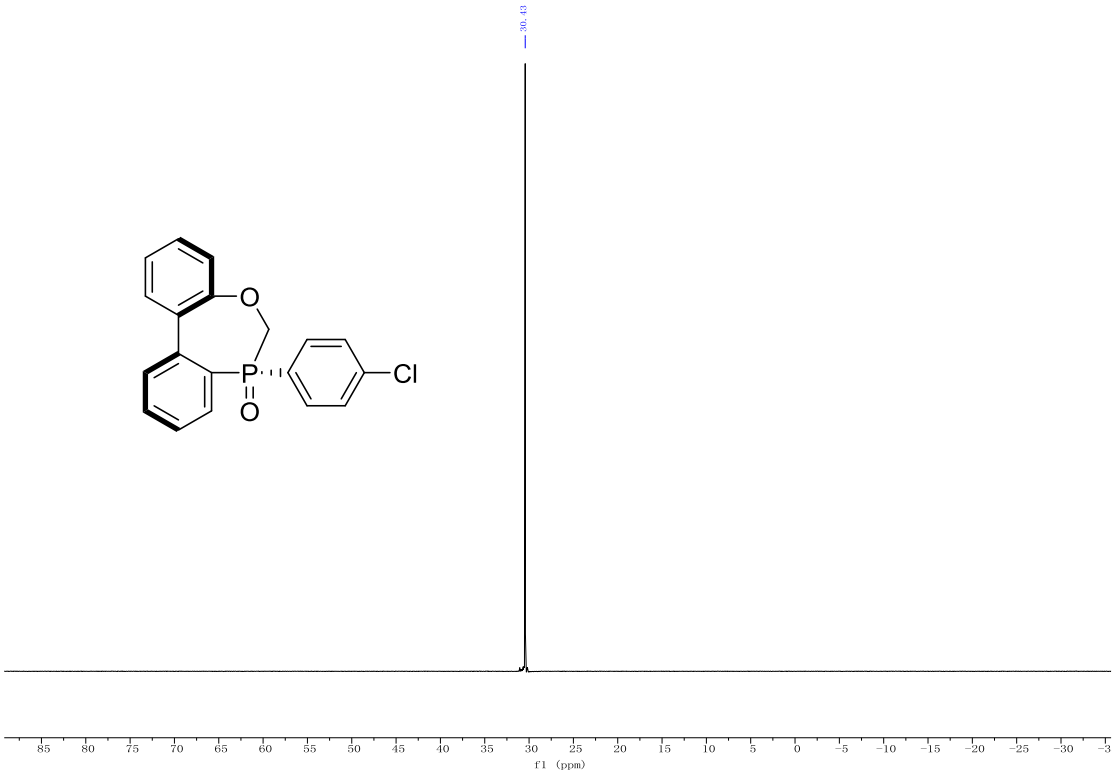
_u_-7-(Biphenyl-4-yl)-6*H*-dibenzo[*d*,*f*][1,3]oxaphosphepine 7-oxide (_u_-9e)

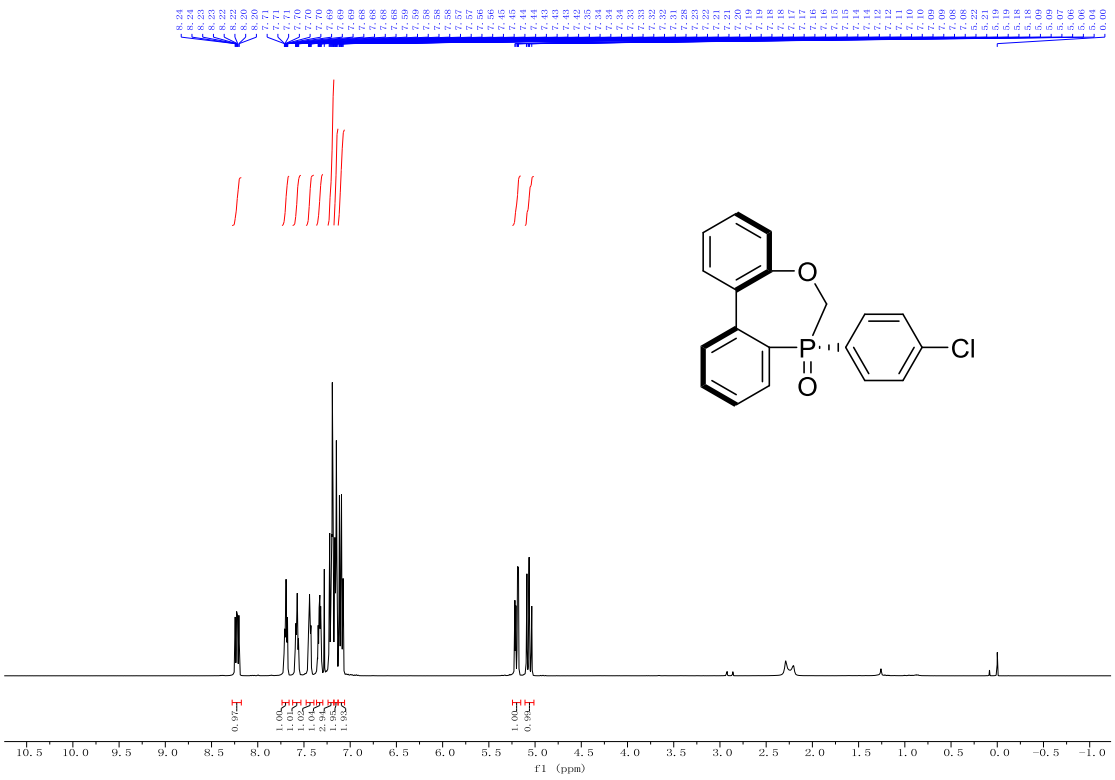


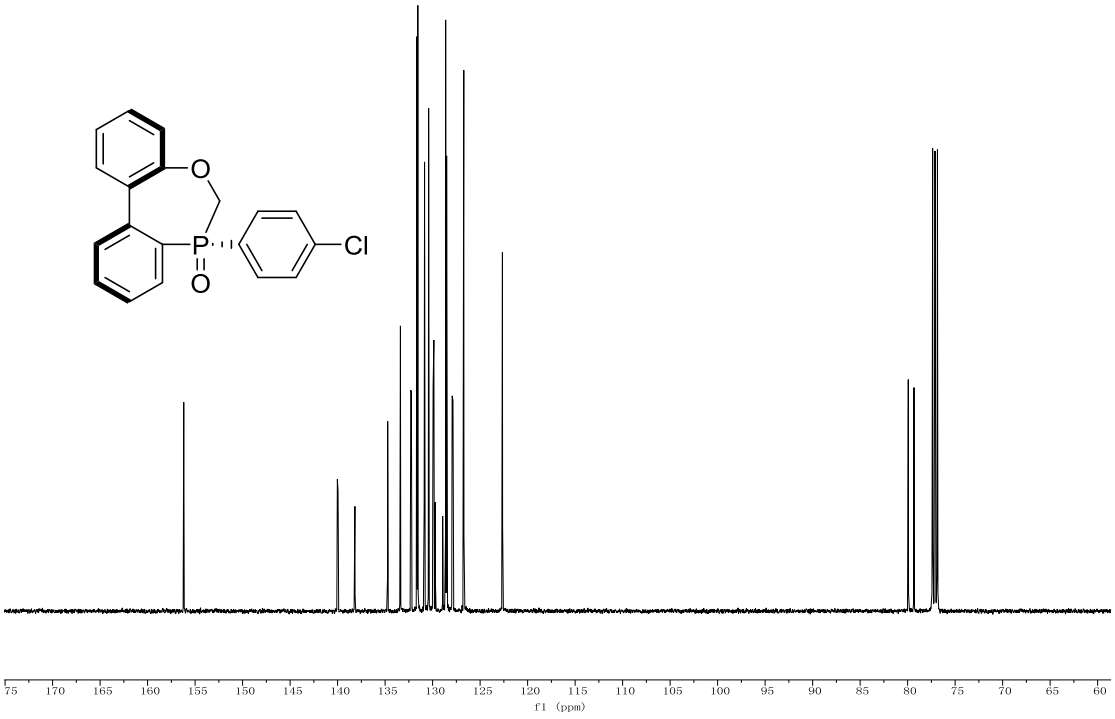




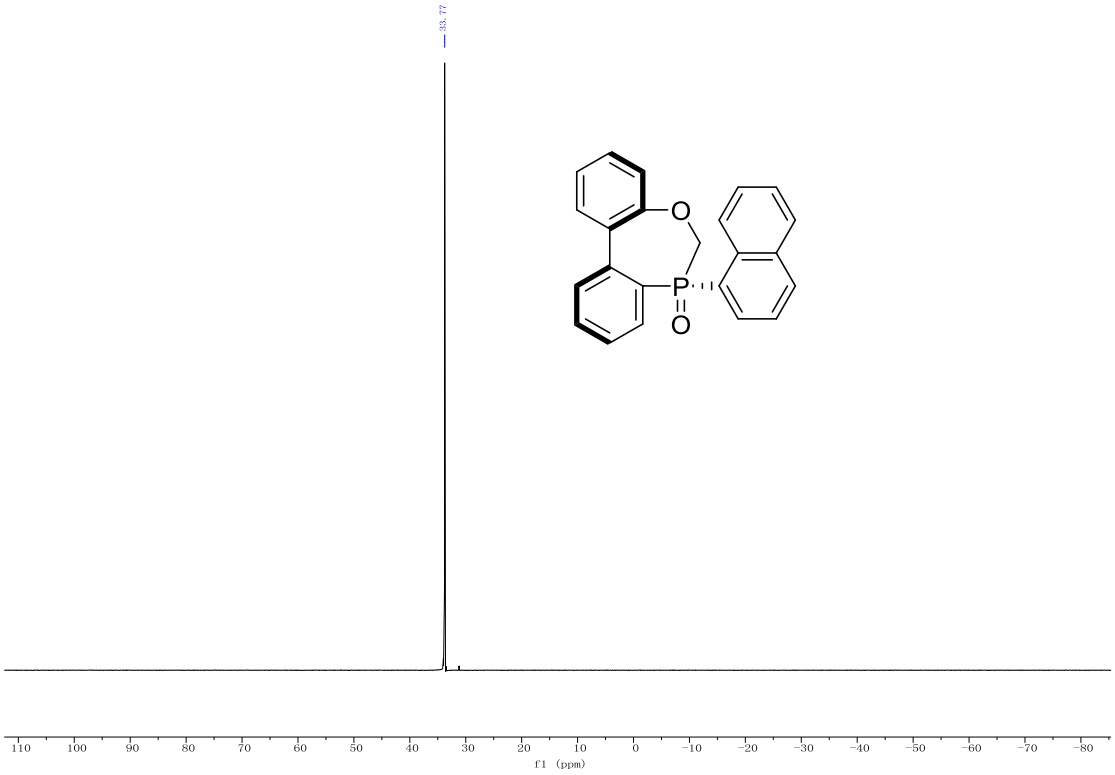
***u*-7-(4-Chlorophenyl)-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9f)**

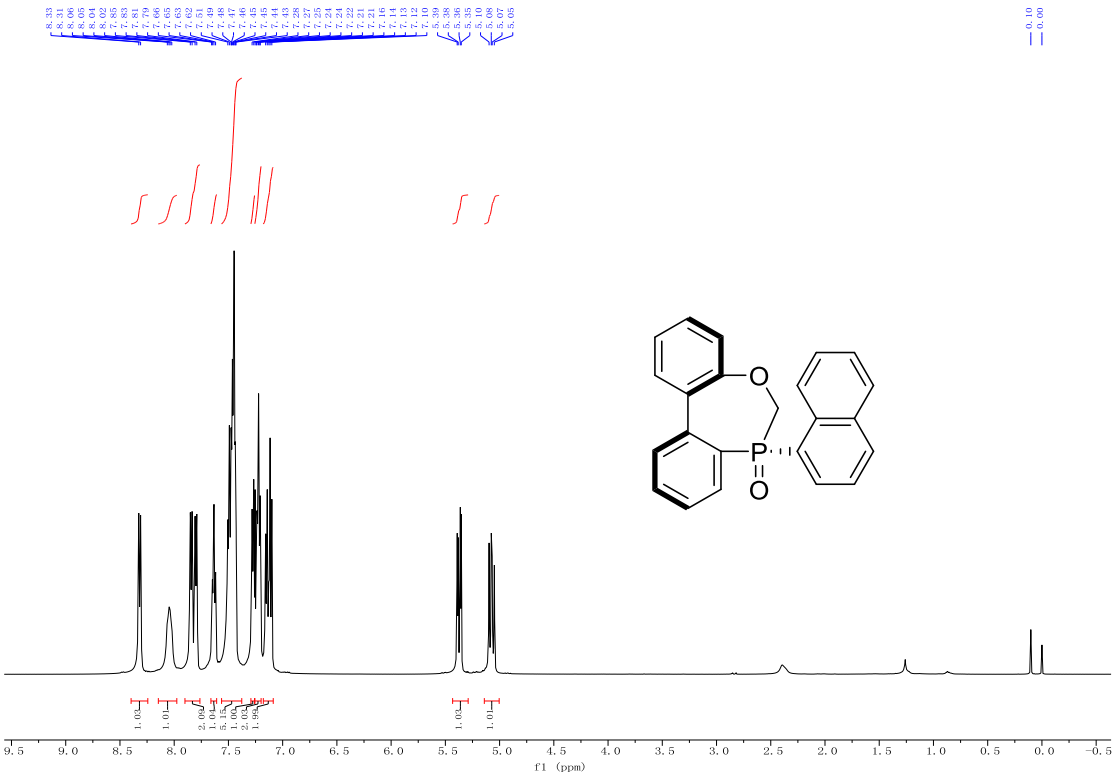


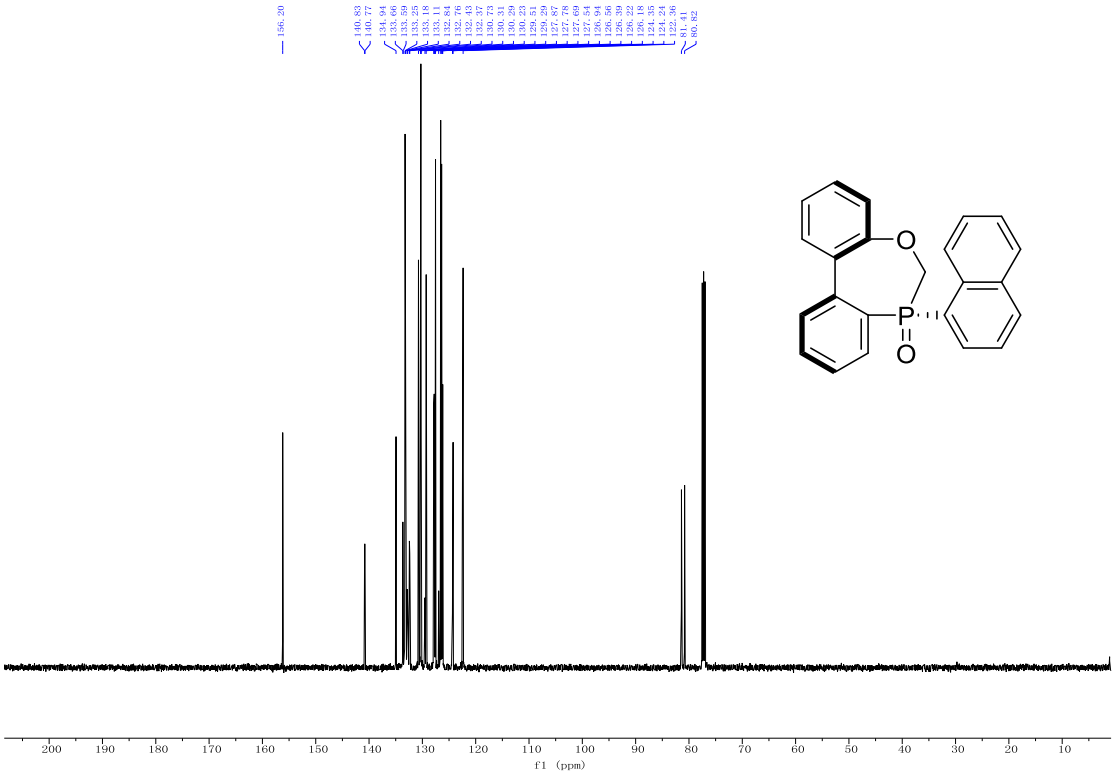

O
P
O
Cl
f1 (ppm)


O
P
O
Cl
f1 (ppm)

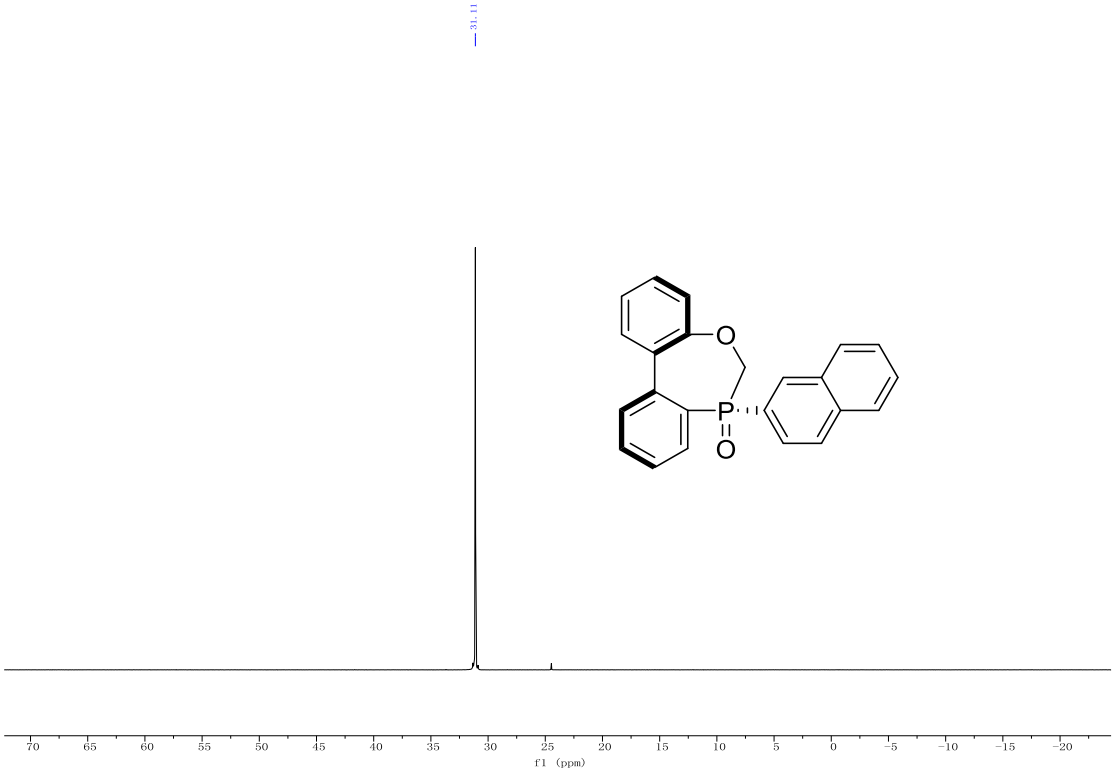
***u*-7-(Naphthalen-1-yl)-6*H*-dibenzo[*d,f*][1,3]oxaphosphepine 7-oxide (*u*-9g)**

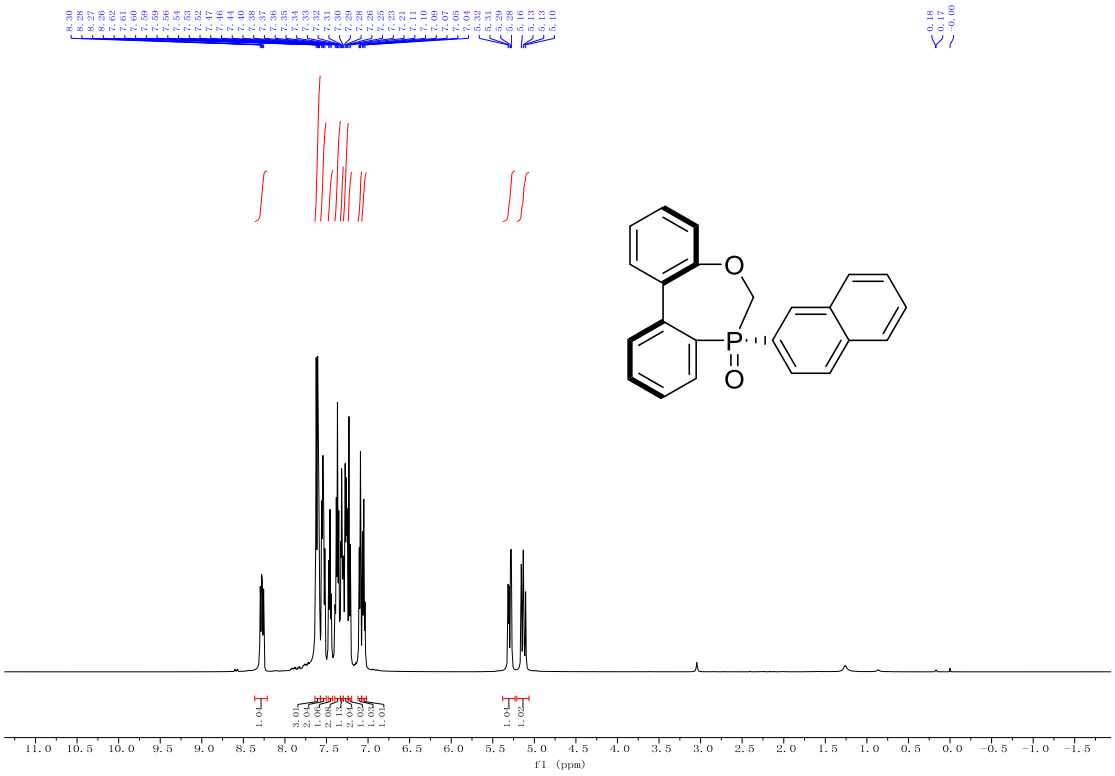


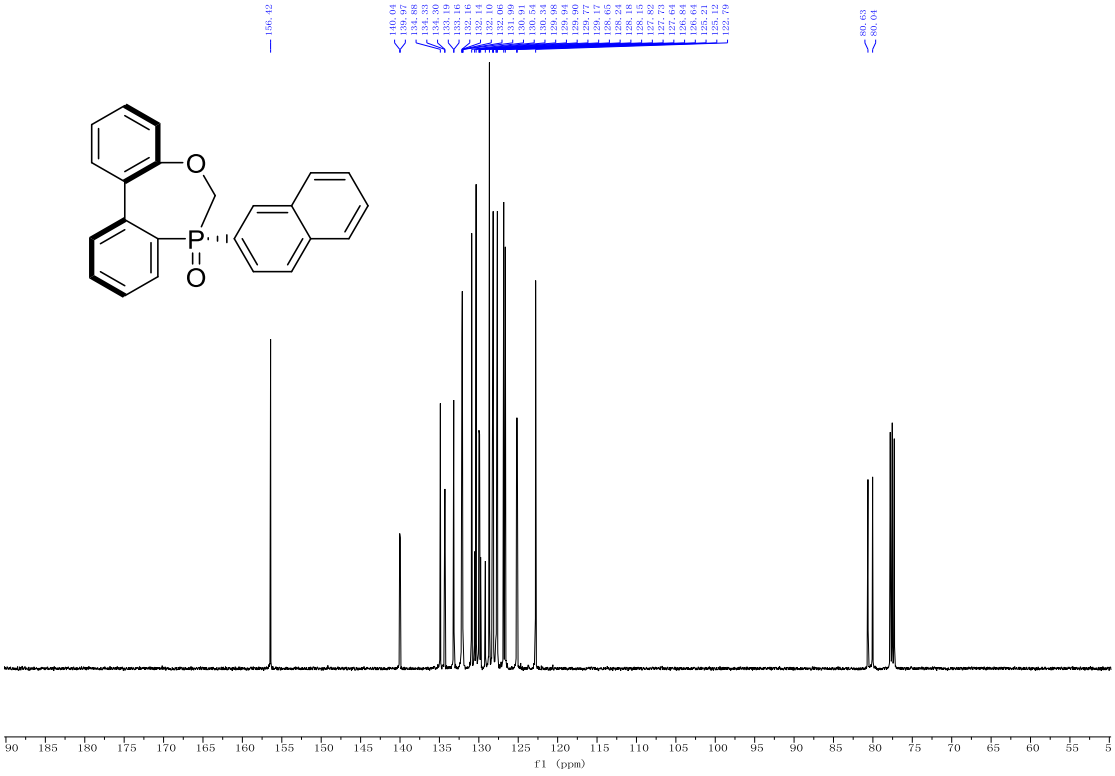




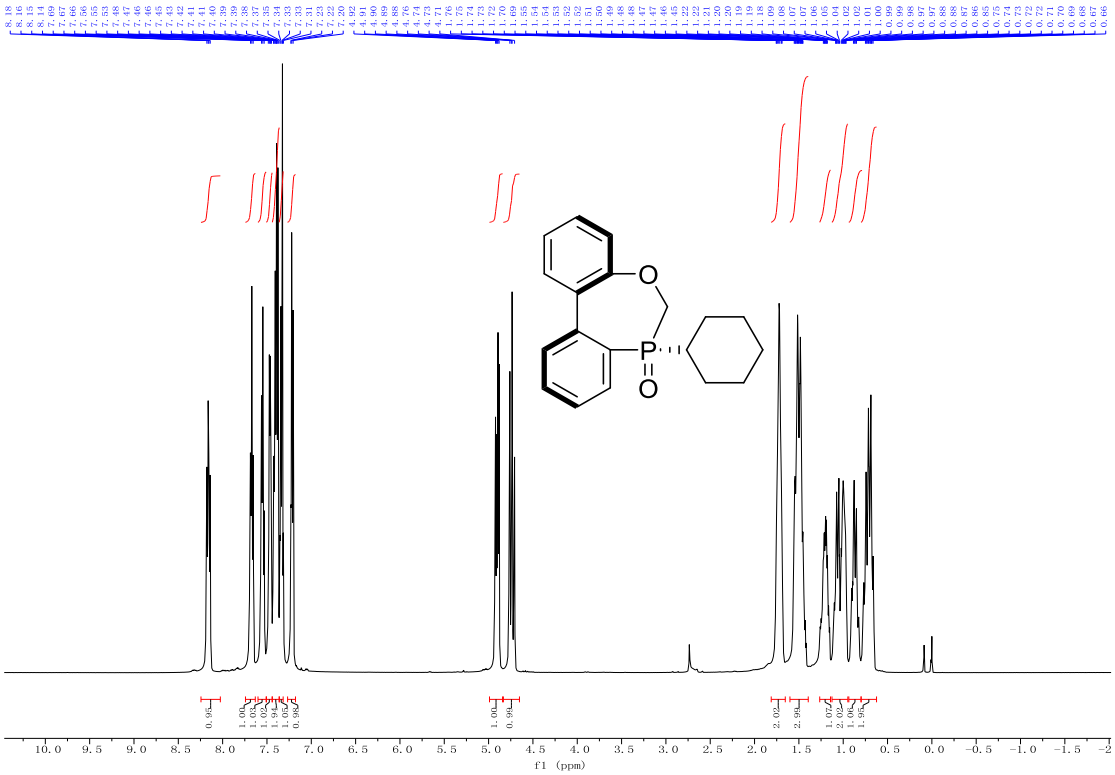
***u*-7-(Naphthalen-2-yl)-6*H*-dibenzo[*d*,*f*][1,3]oxaphosphepine 7-oxide (*u*-9h)**

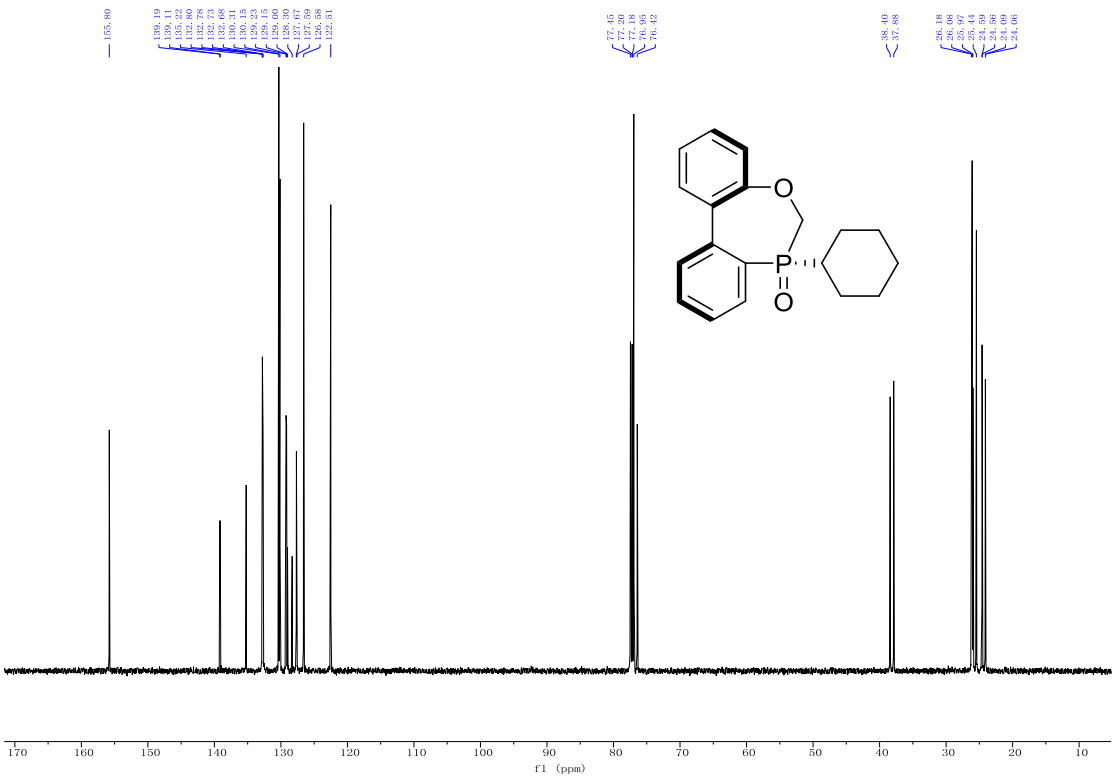



f1 (ppm)

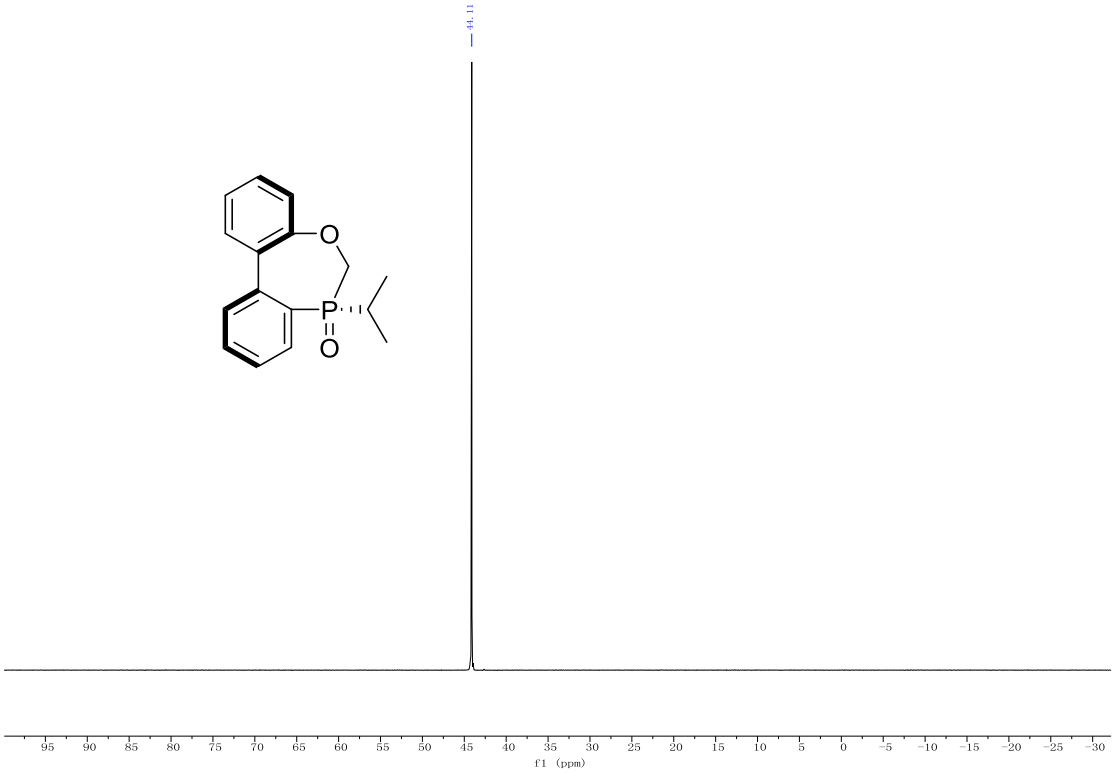

f1 (ppm)

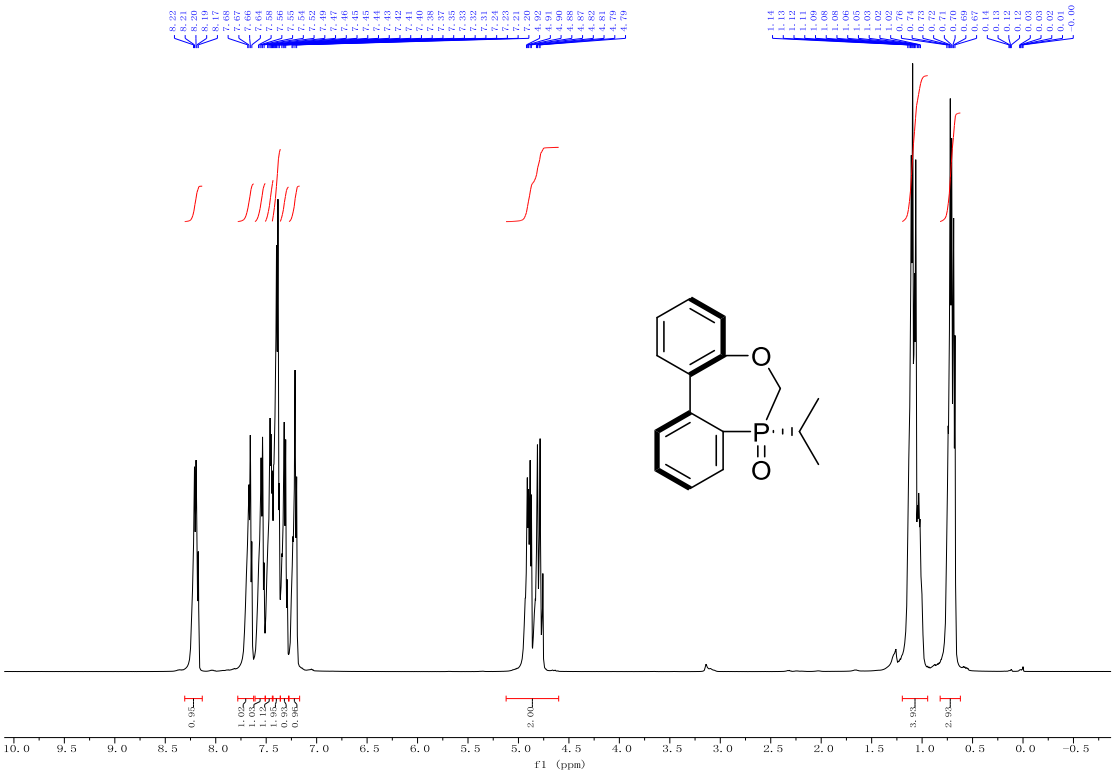
***u*-7-Cyclohexyl-6*H*-dibenzo[*d*,*f*][1,3]oxaphosphepine 7-oxide (*u*-9i)**

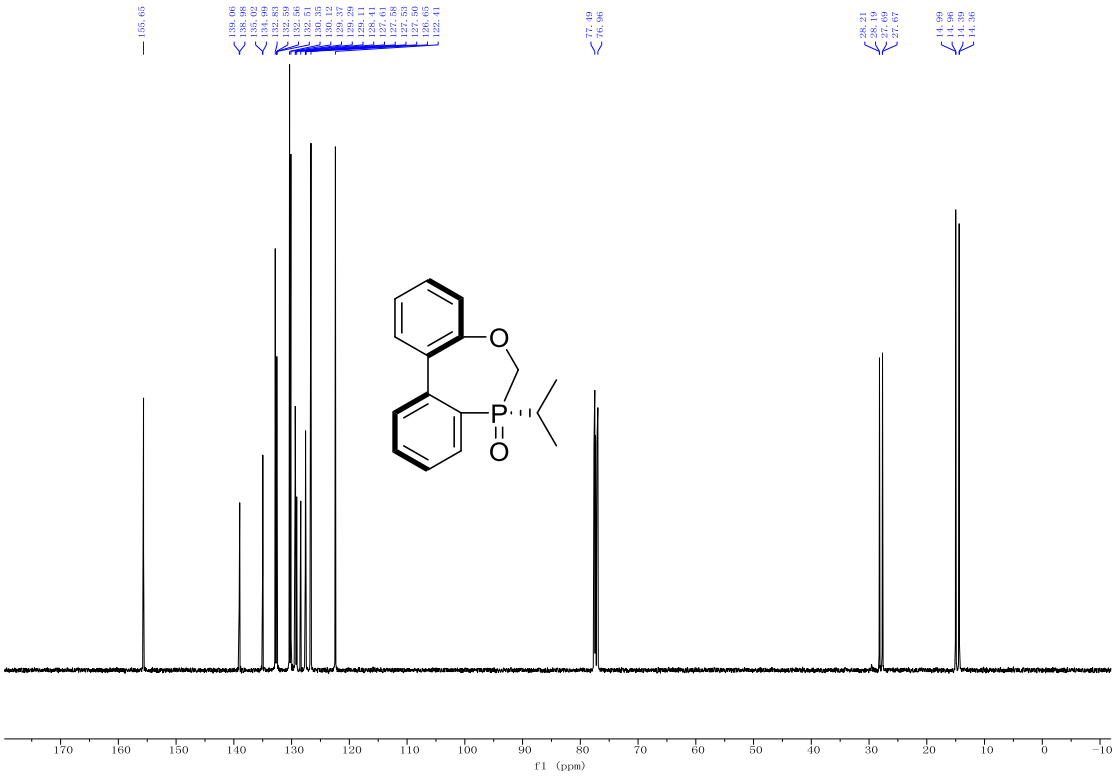




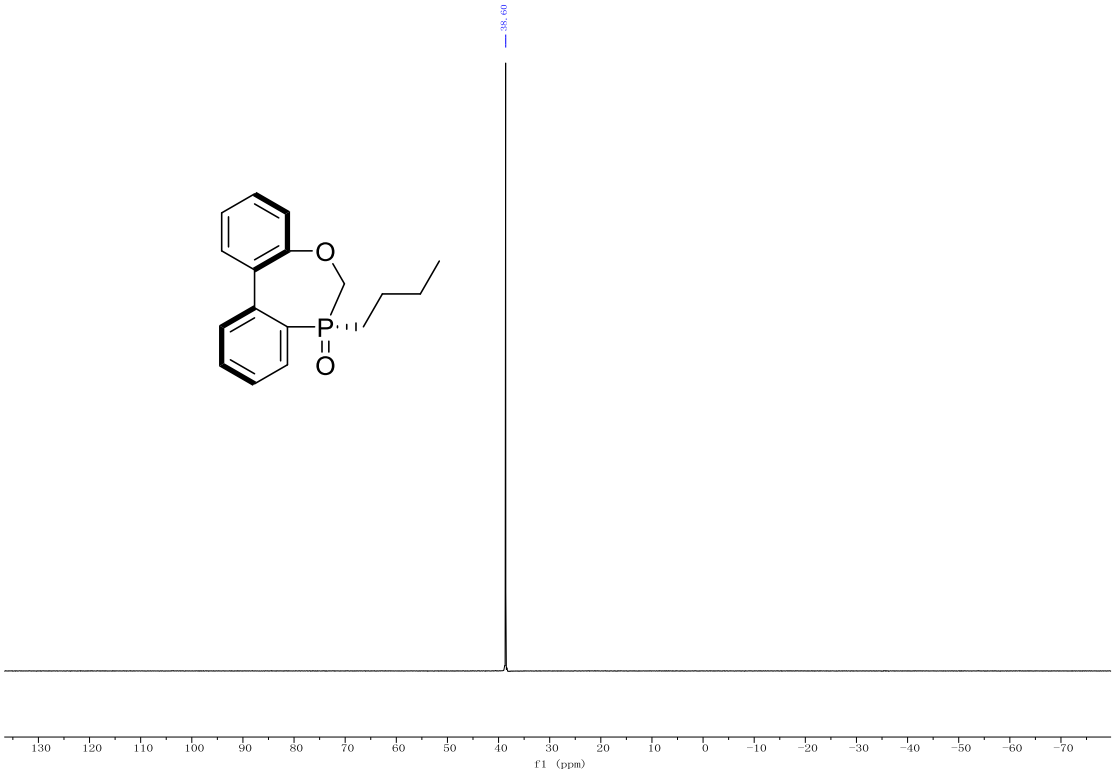
_u_-7-Isopropyl-6_H_-dibenzo[_d,f_][1,3]oxaphosphepine 7-oxide (_u_-9j)

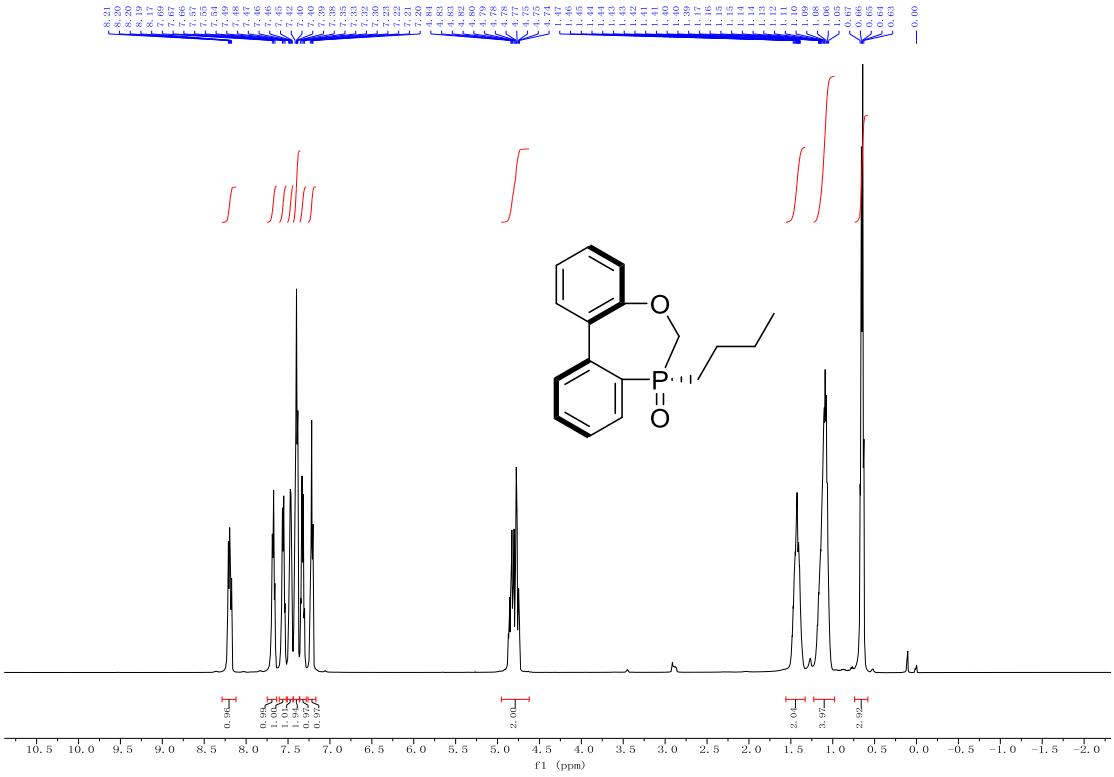


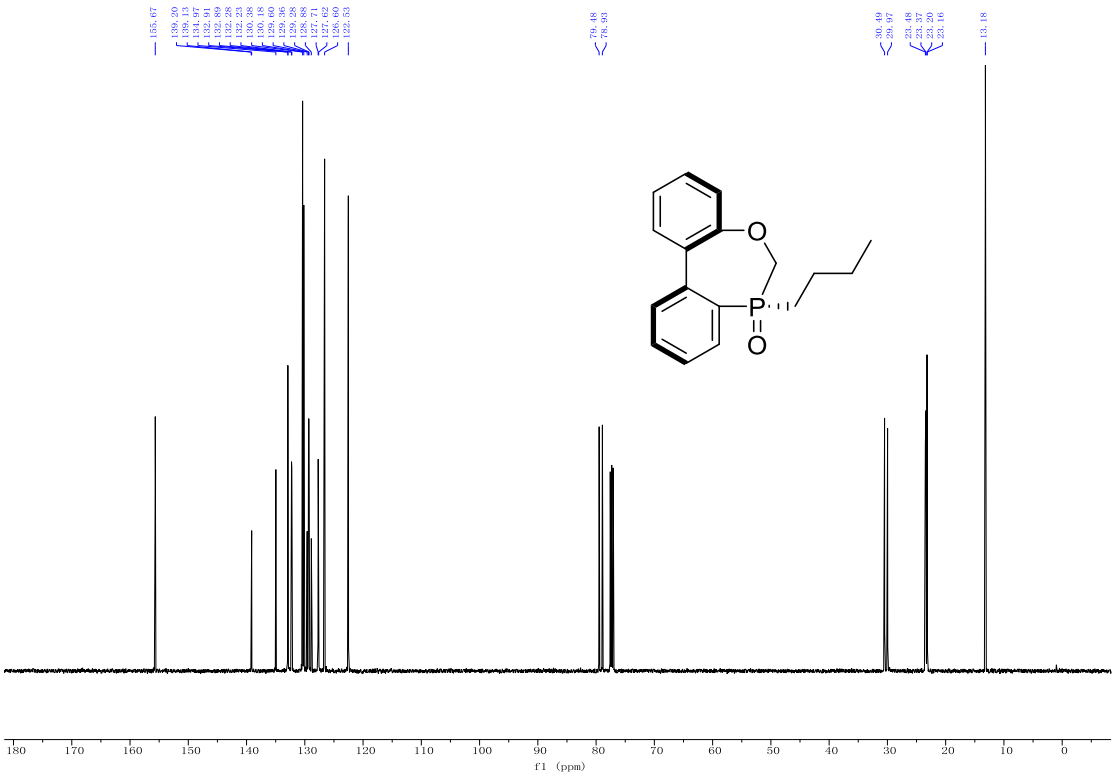

f1 (ppm)


f1 (ppm)

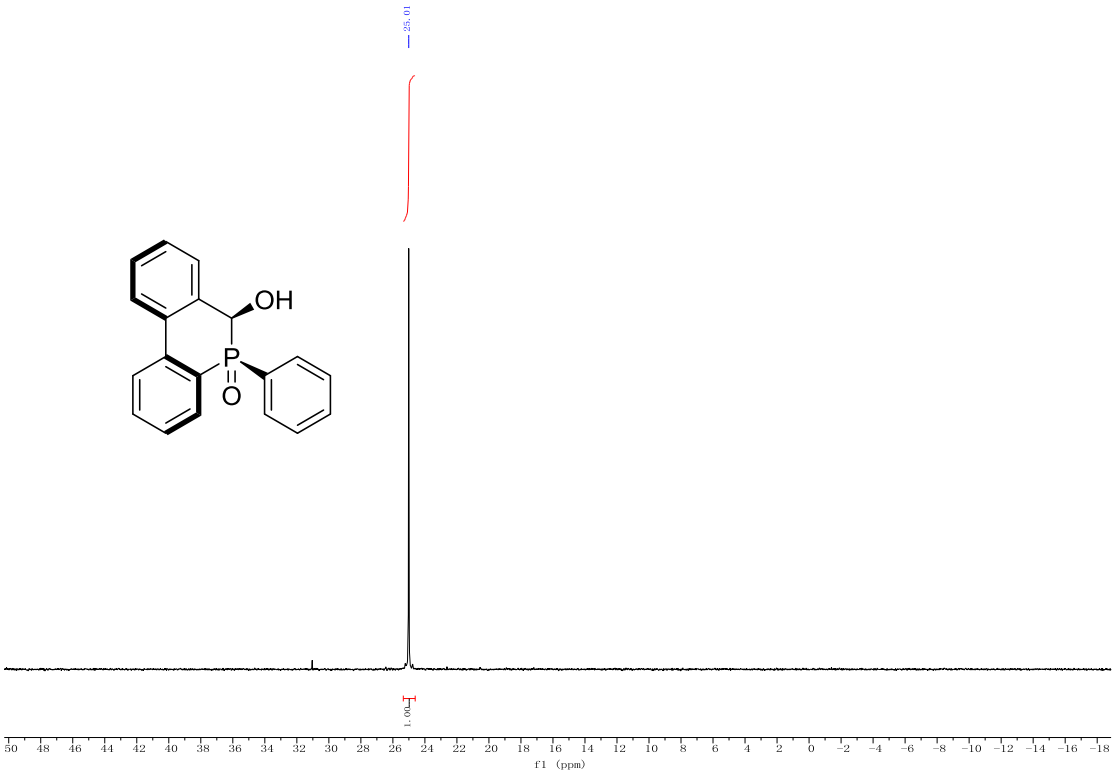
***u*-7-Butyl-6*H*-dibenzo[*d*,*f*][1,3]oxaphosphepine 7-oxide (*u*-9k)**

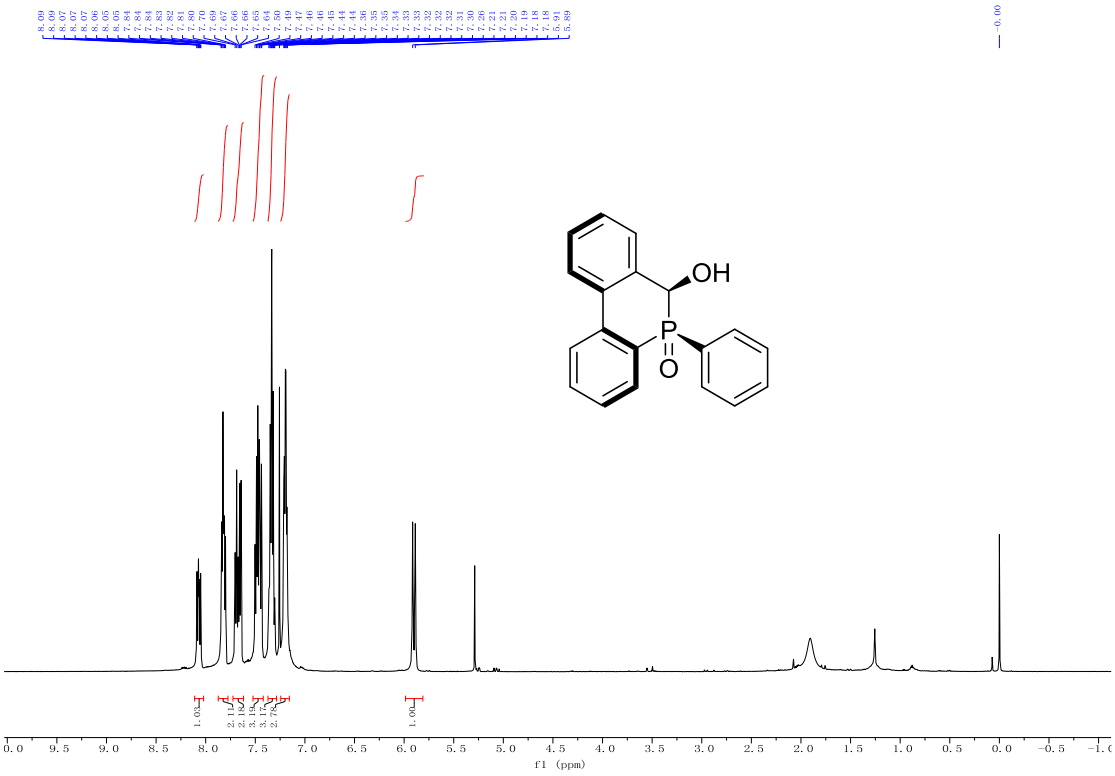


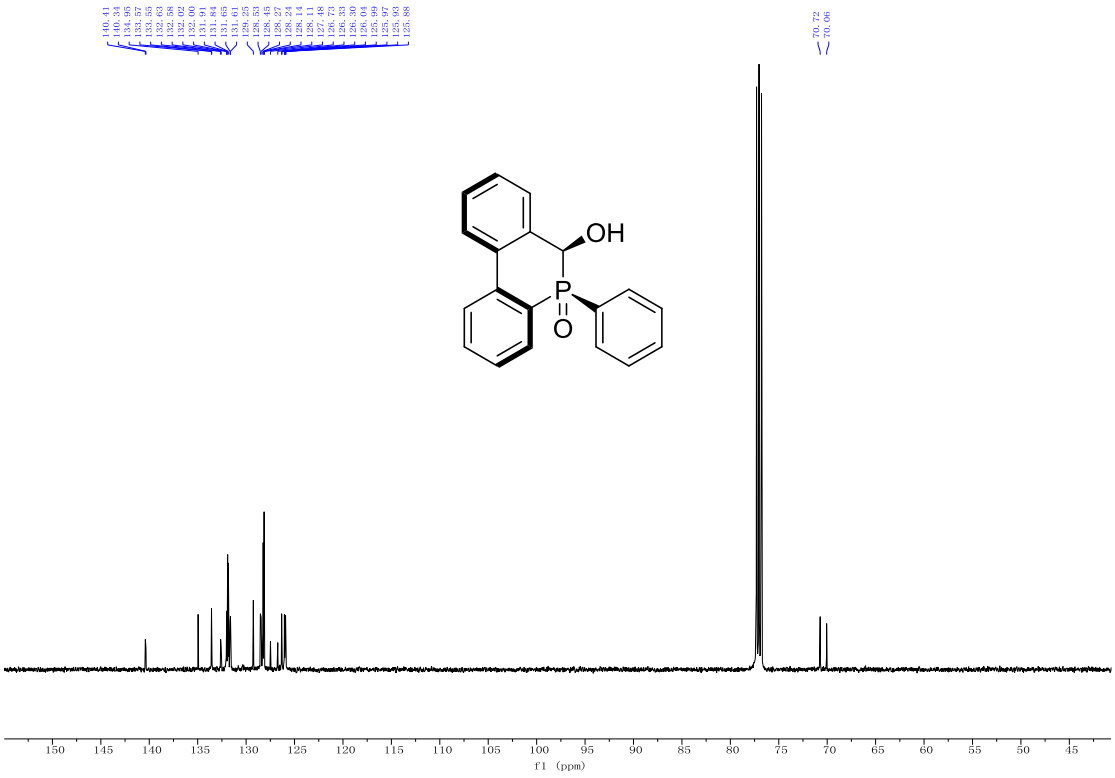




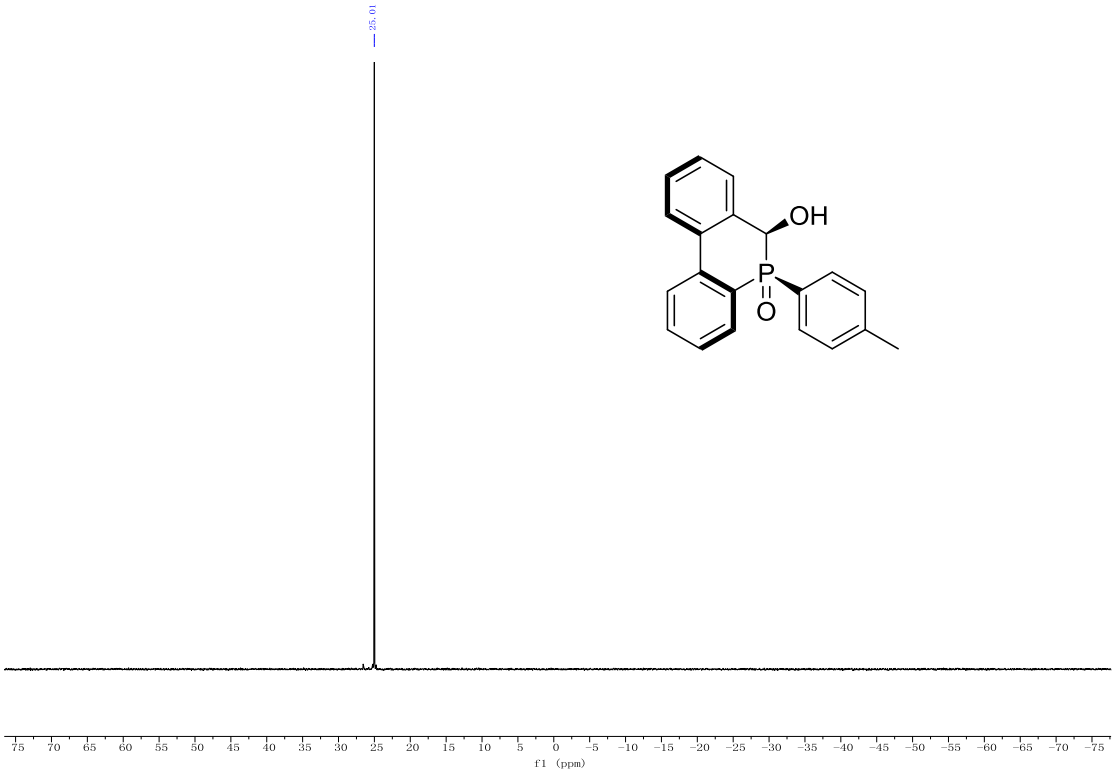
_u,l_-6-Hydroxy-5-phenyl-6_H_-phosphanthridine 5-oxide (_u,l_-10a)

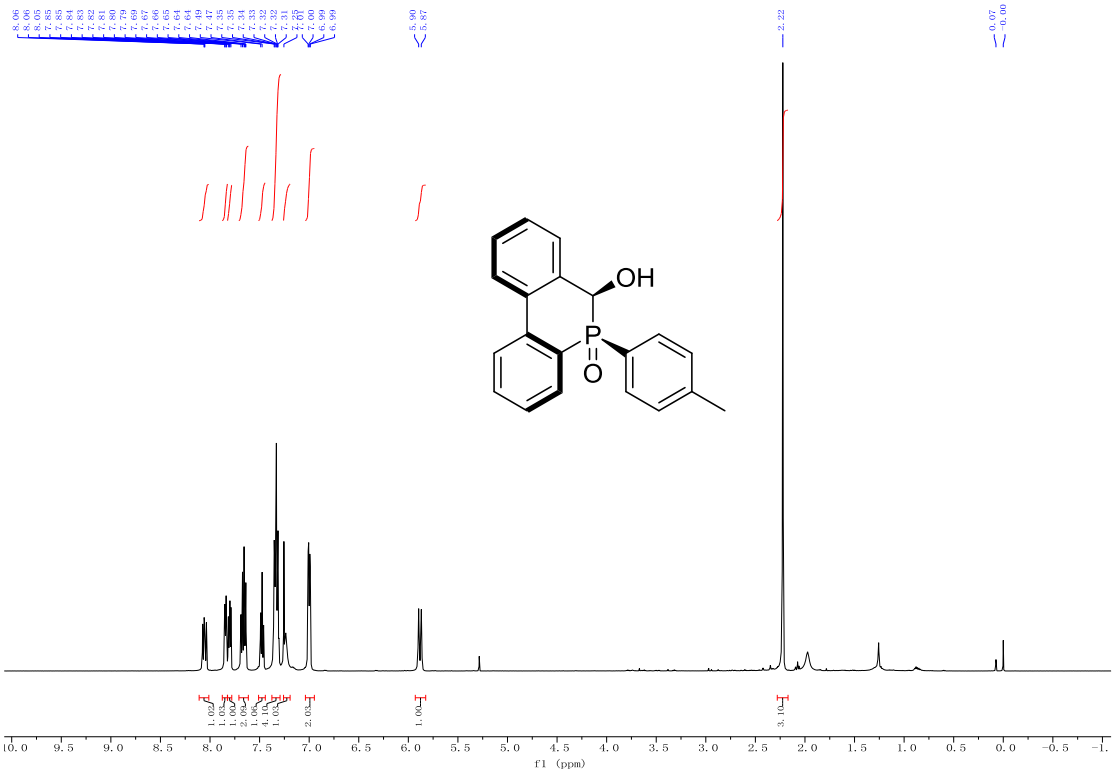


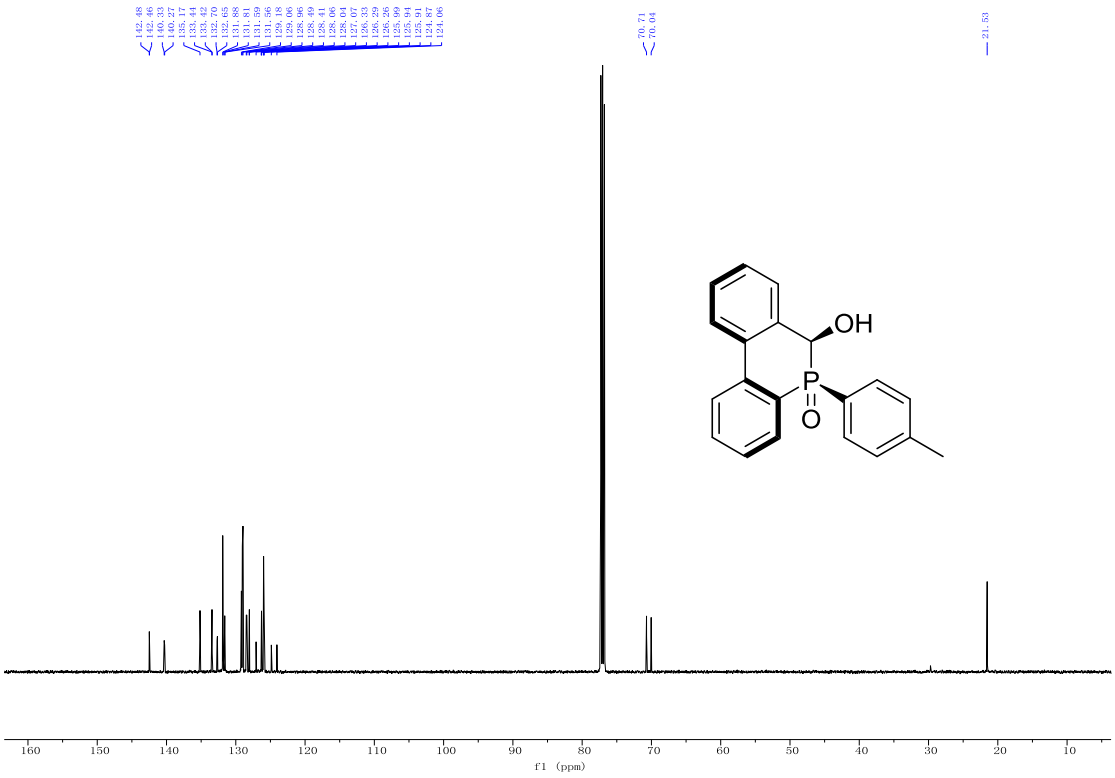

OH
P
O
f1 (ppm)


OH
P
O
f1 (ppm)

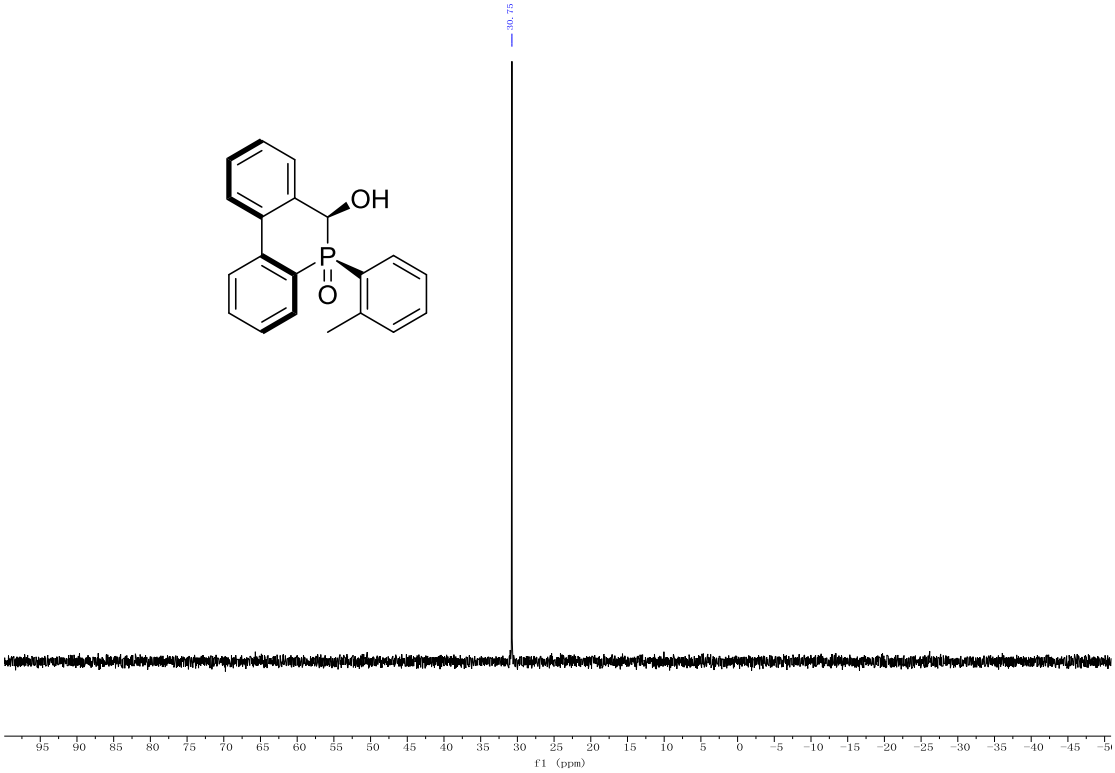
_u,l_-6-Hydroxy-5-(_p_-tolyl)-6_H_-phosphanthridine 5-oxide (_u,l_-10b)



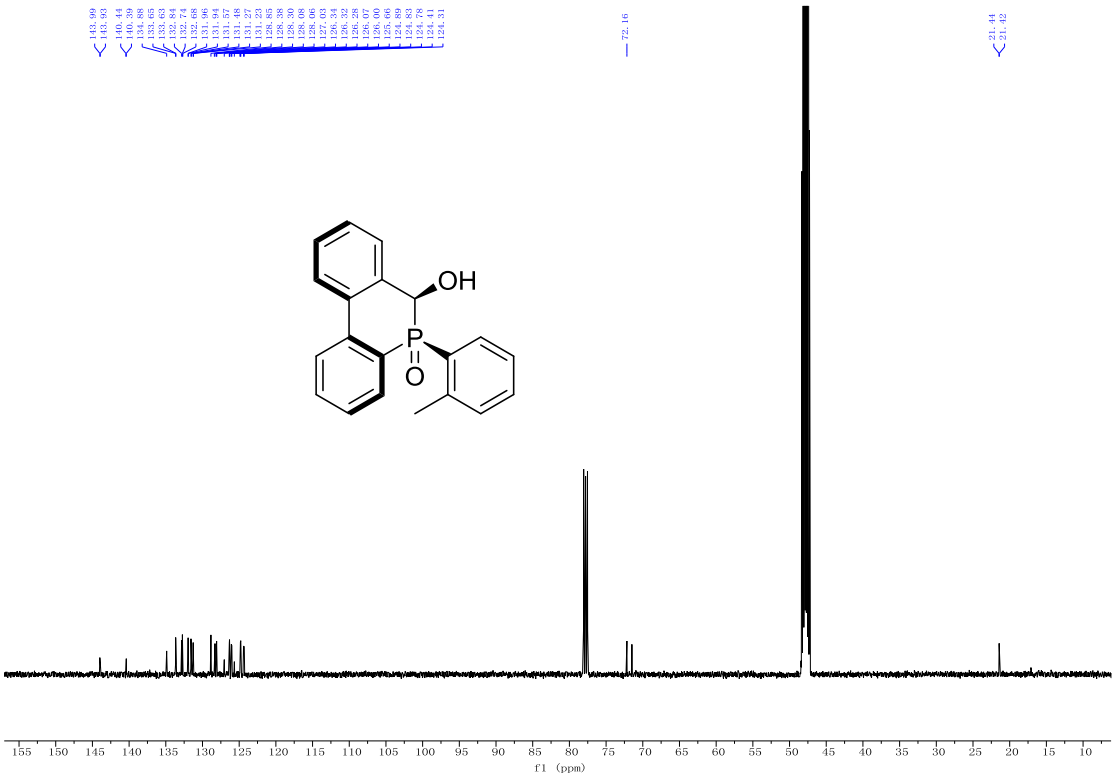




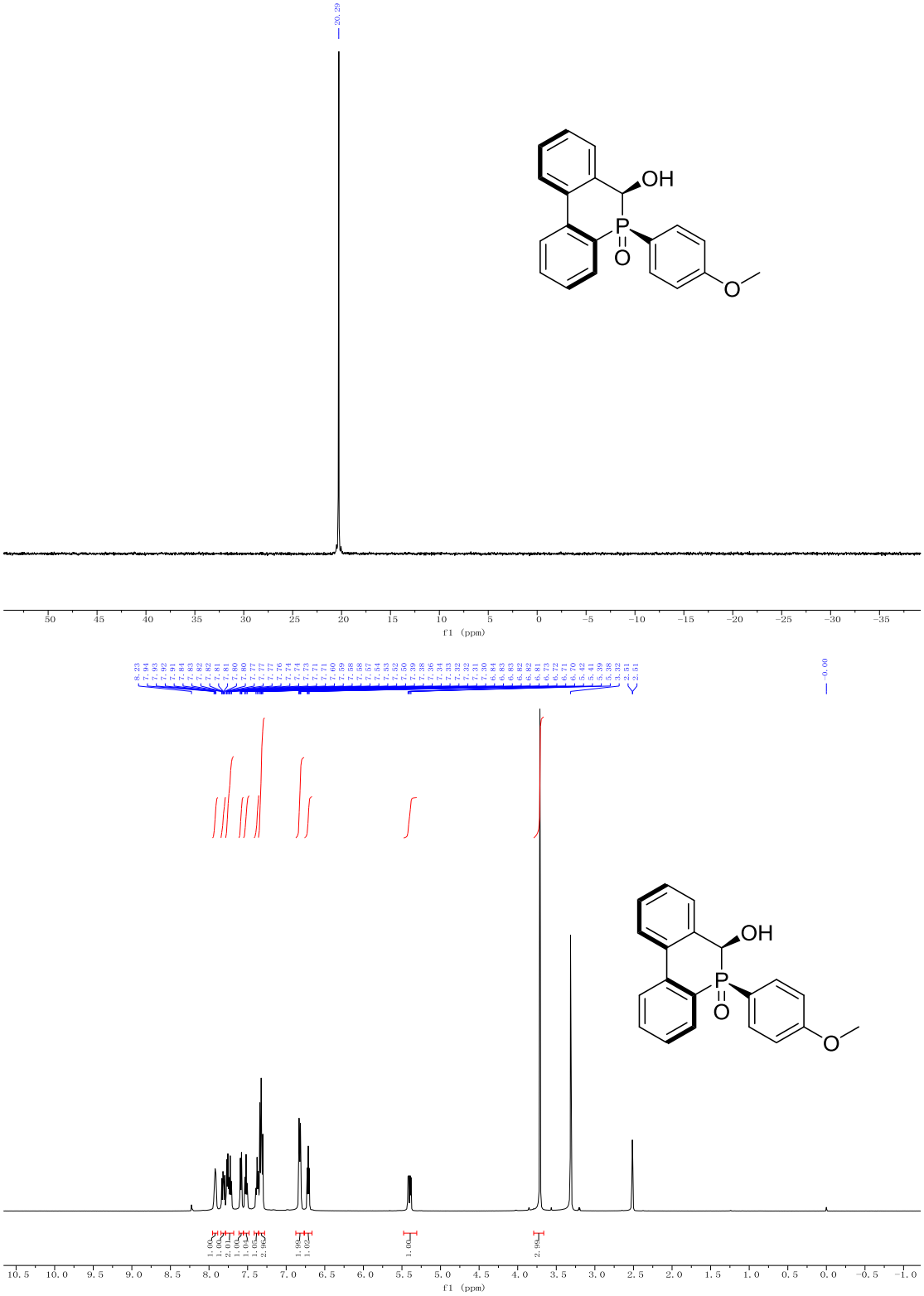
_u,l_-6-Hydroxy-5-(_o_-tolyl)-6_H_-phosphanthridine 5-oxide (_u,l_-10c)

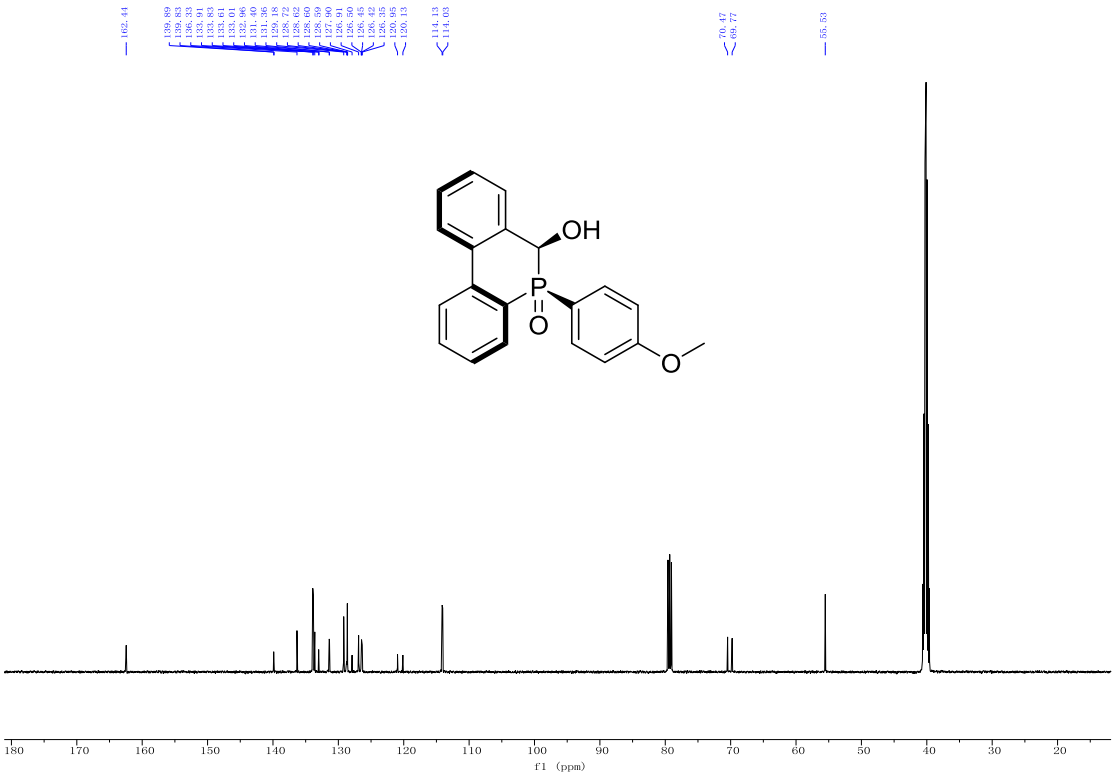



OH
P
O
f1 (ppm)

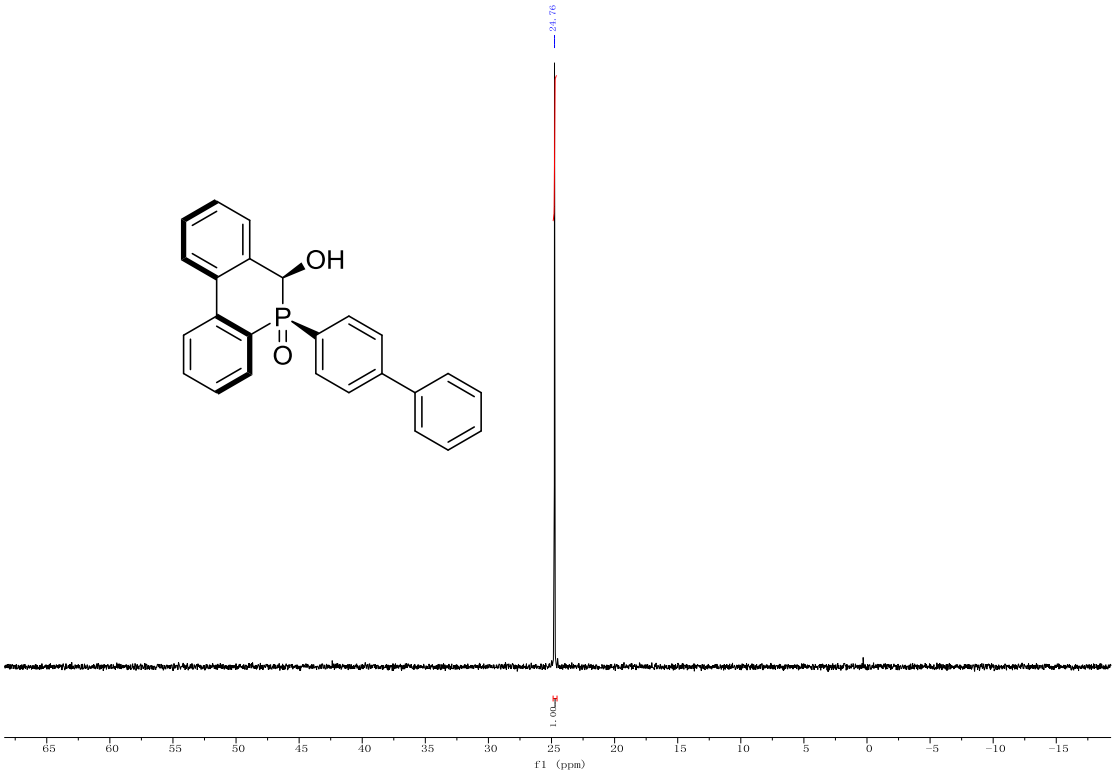

OH
P
O
f1 (ppm)

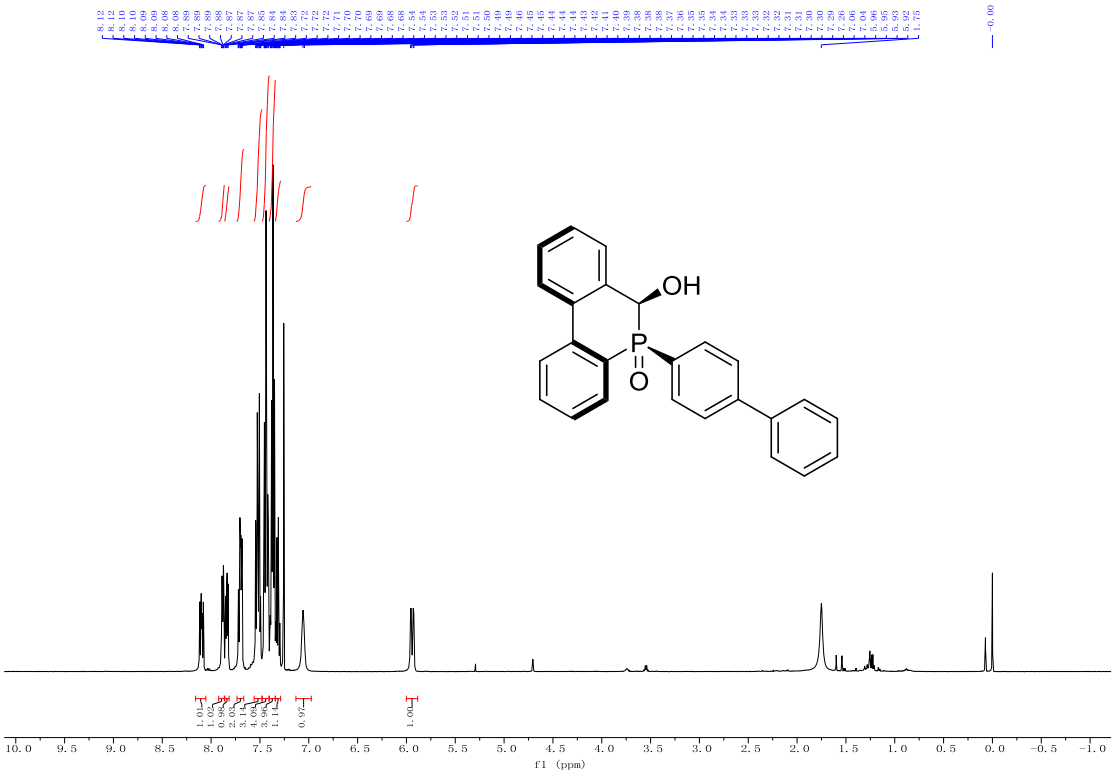
***u,l*-6-Hydroxy-5-(4-methoxyphenyl)-6*H*-phosphanthridine 5-oxide (*u,l*-10d)**

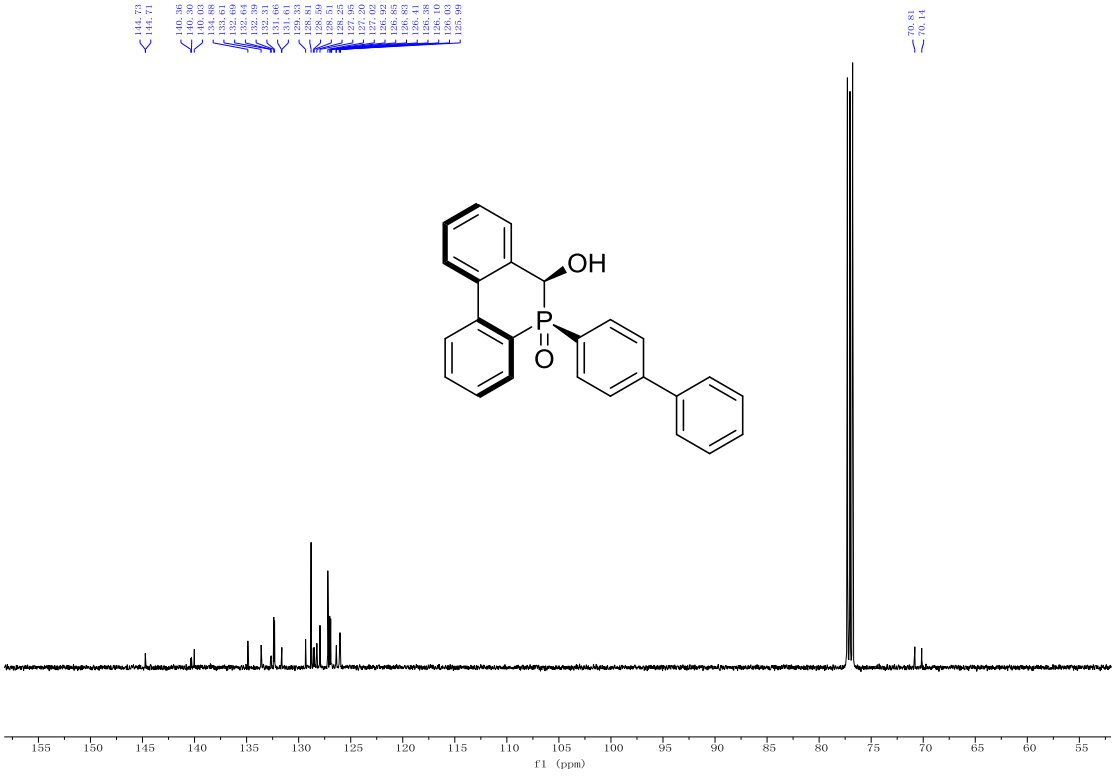




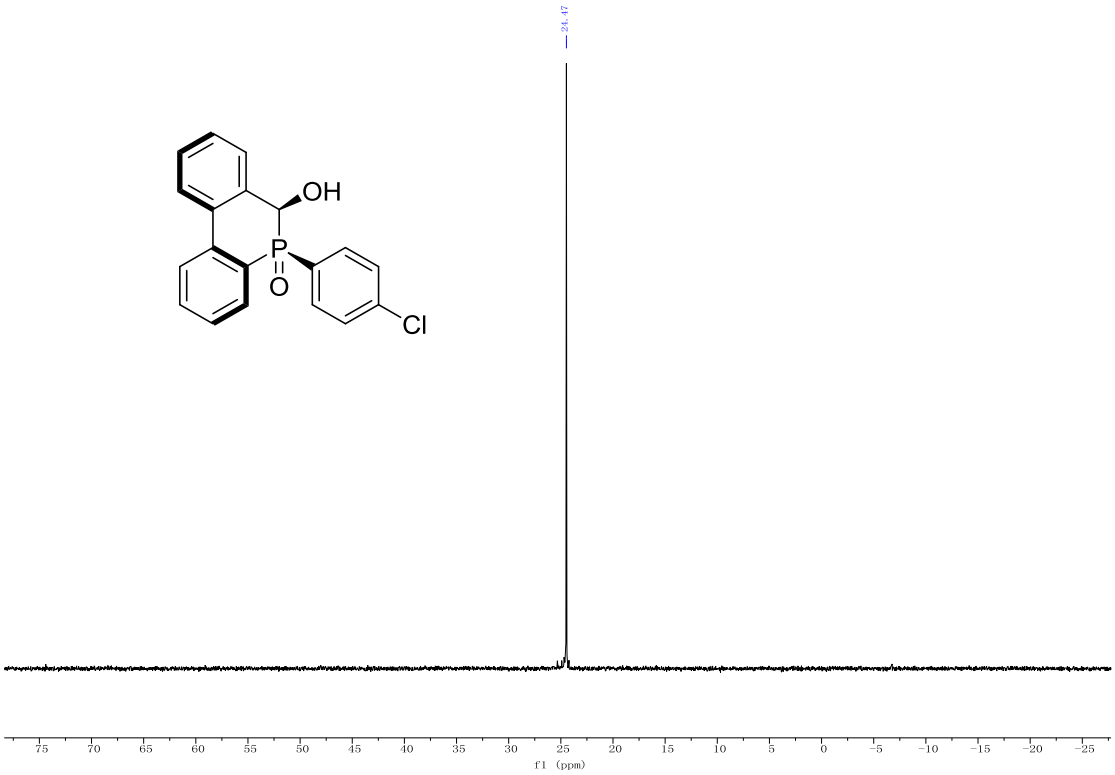
_u,l_-5-(Biphenyl-4-yl)-6-hydroxy-6*H*-phosphanthridine 5-oxide (_u,l_-10e)

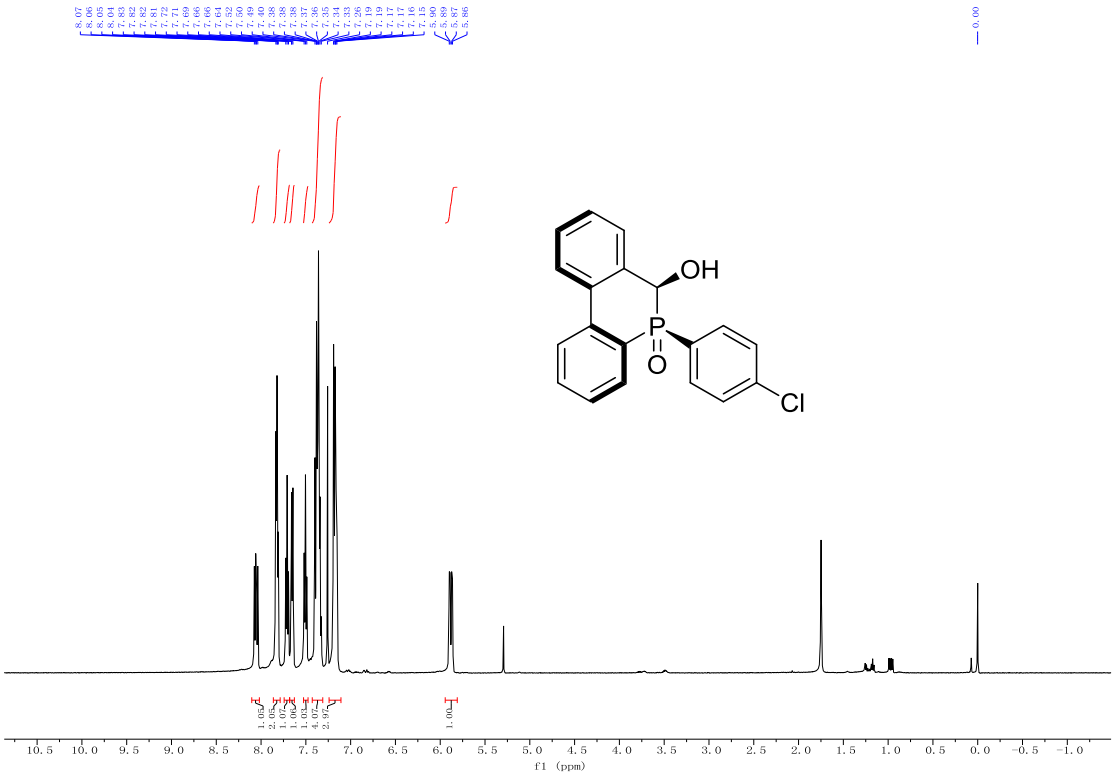


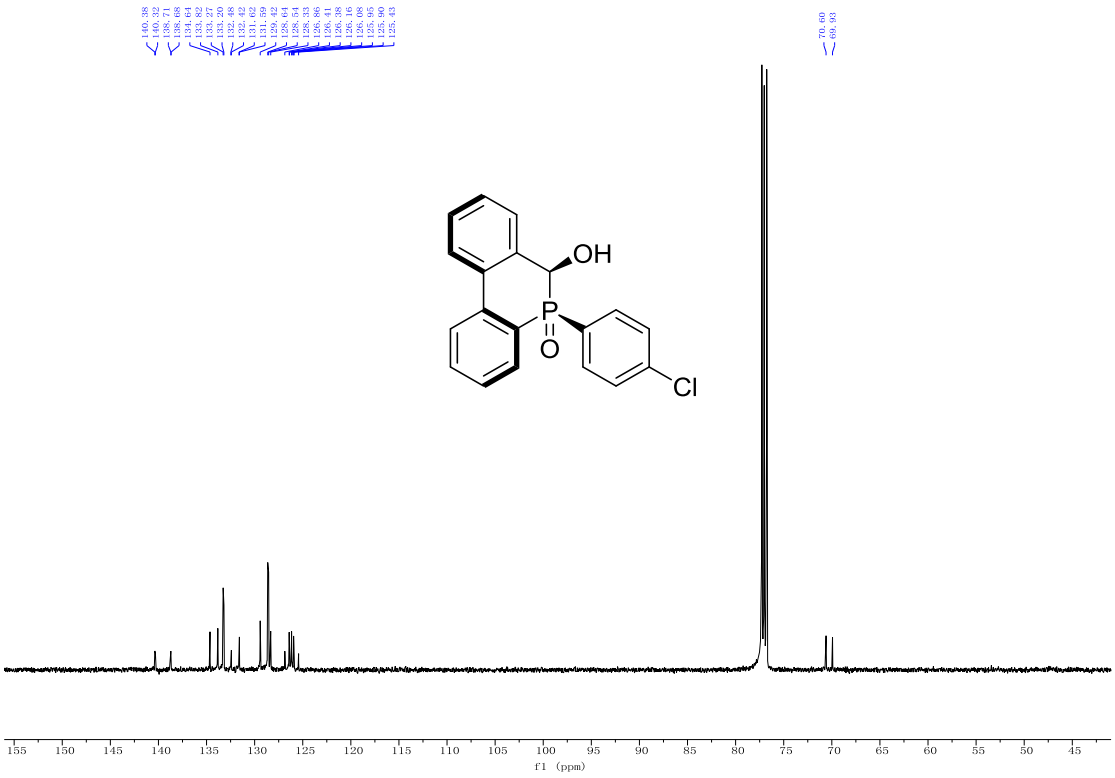

OH
P
O
f1 (ppm)


OH
P
O
f1 (ppm)

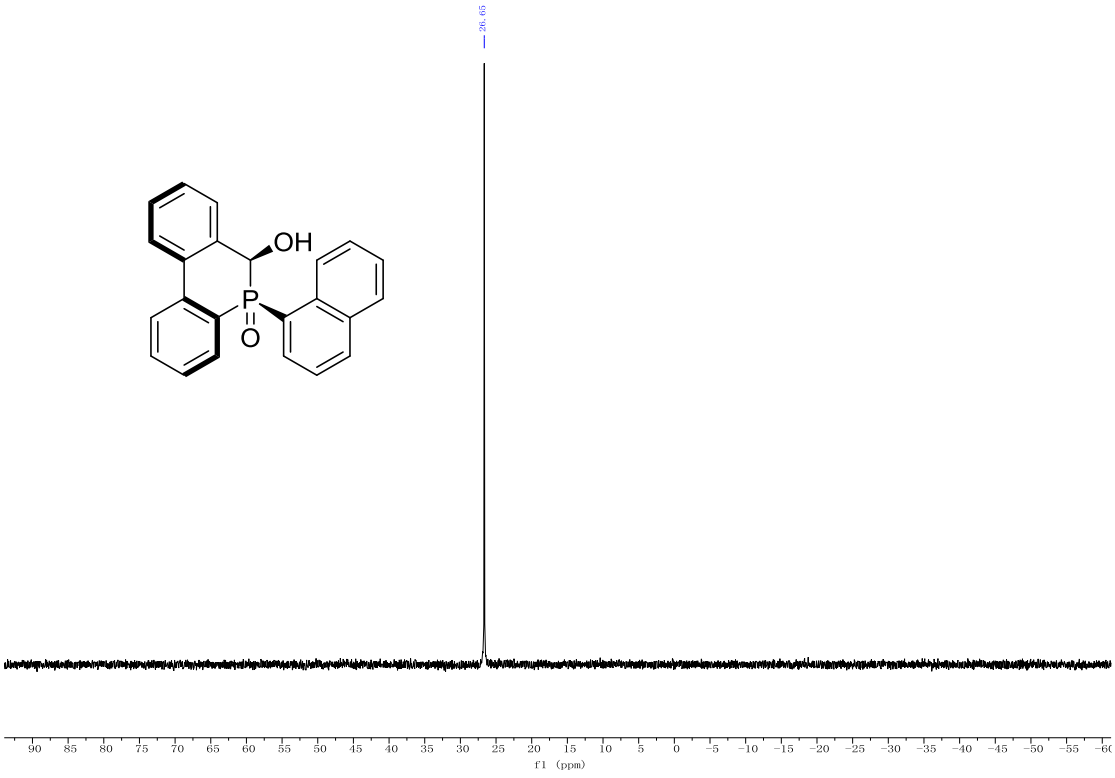
***u,l*-5-(4-Chlorophenyl)-6-hydroxy-6*H*-phosphanthridine 5-oxide (*u,l*-10f)**

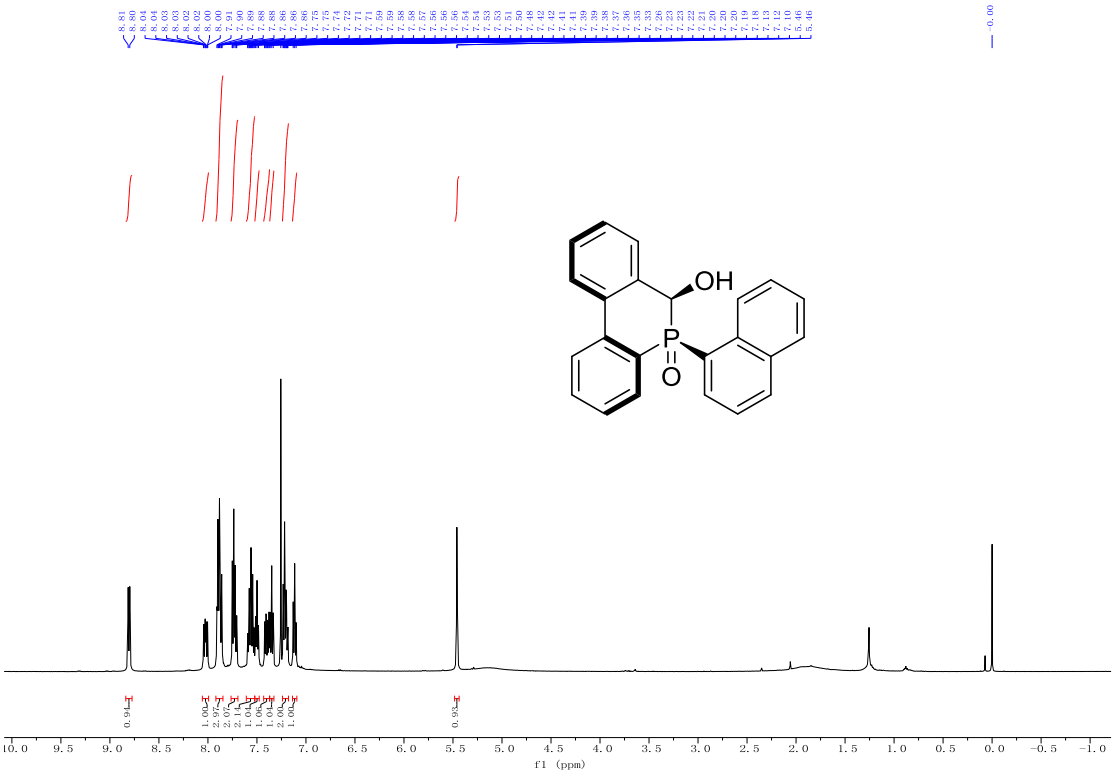


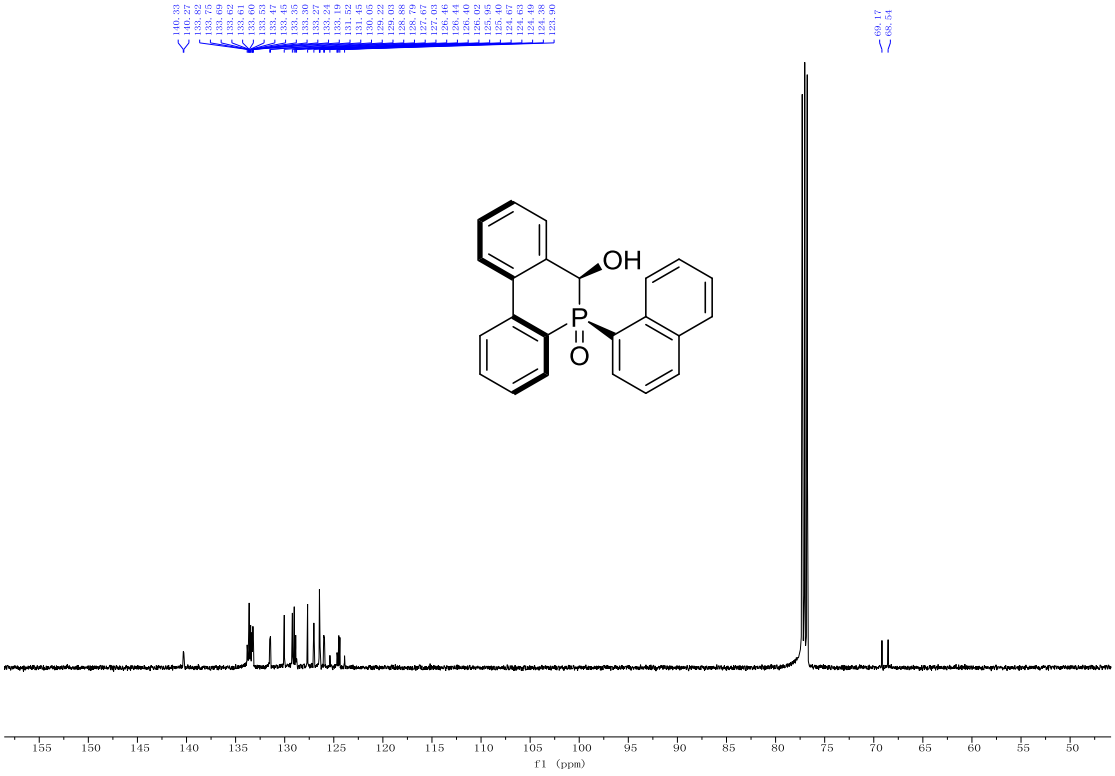




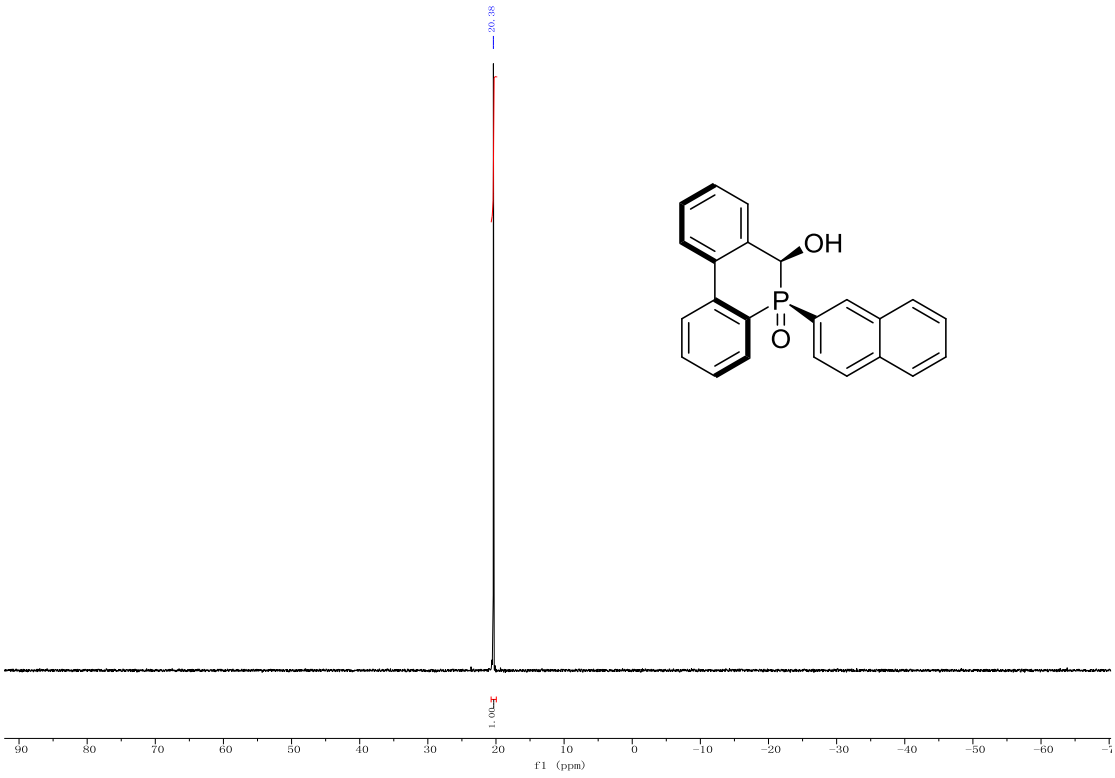
_u,l_-6-Hydroxy-5-(naphthalen-1-yl)-6_H_-phosphanthridine 5-oxide (_u,l_-10g)

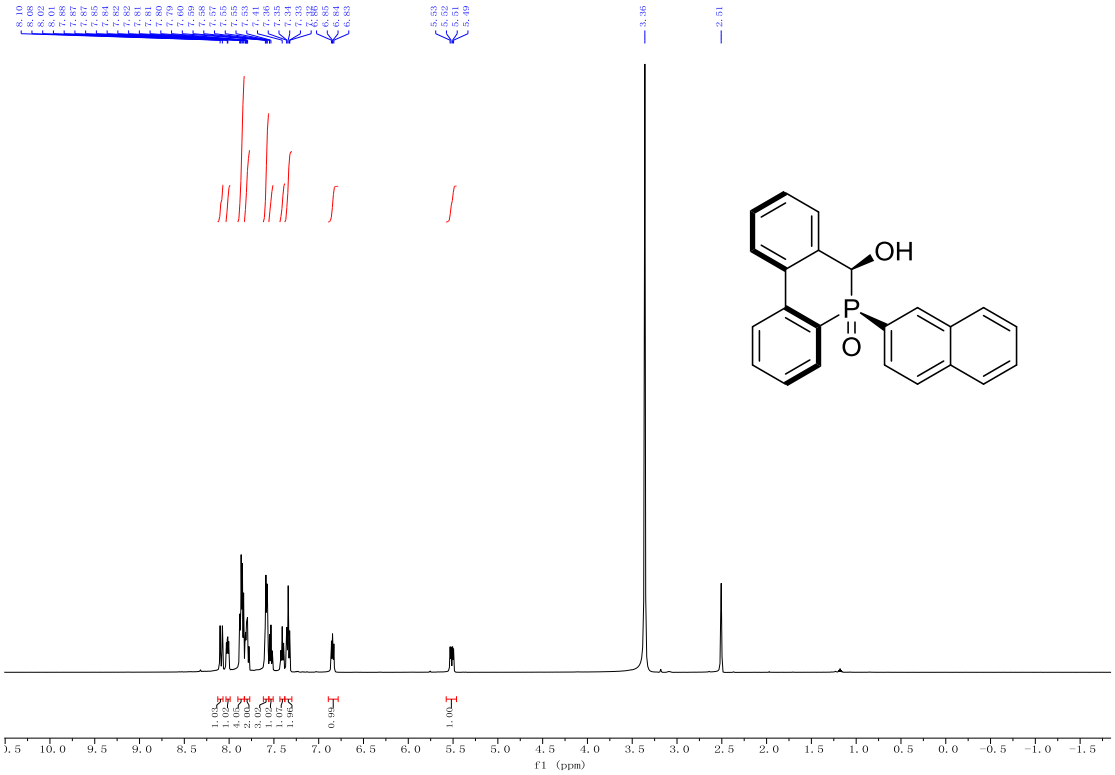


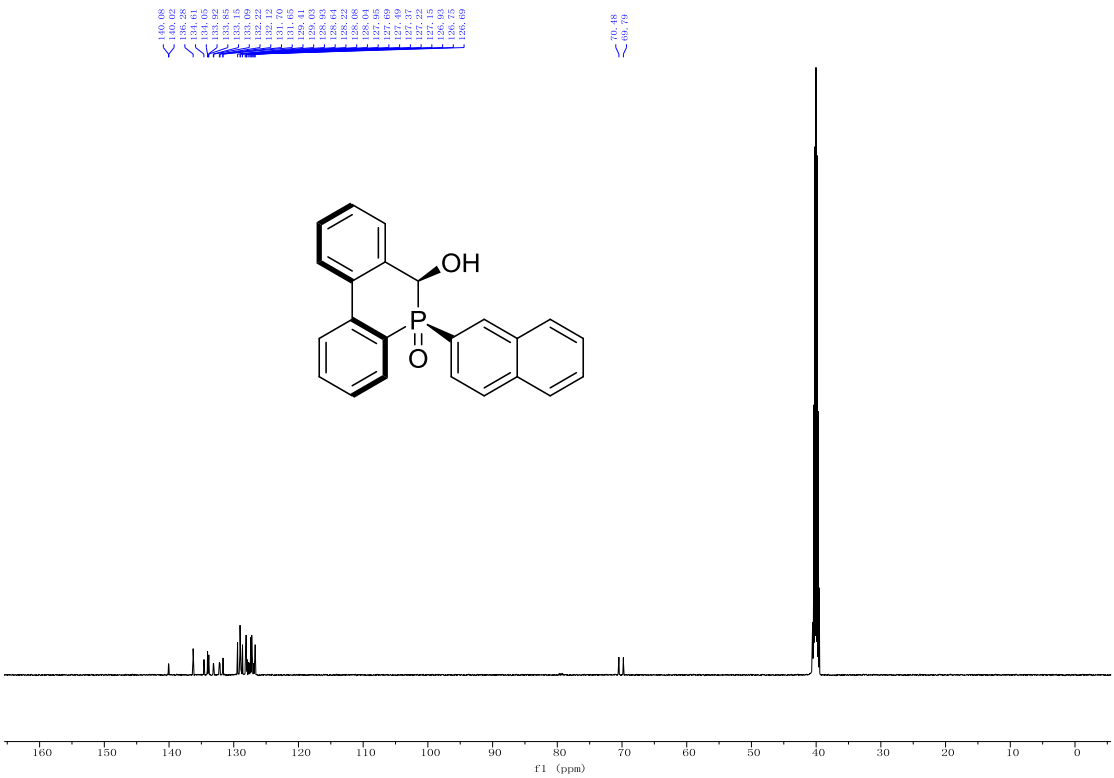

OH
P
O
f1 (ppm)


OH
P
O
f1 (ppm)

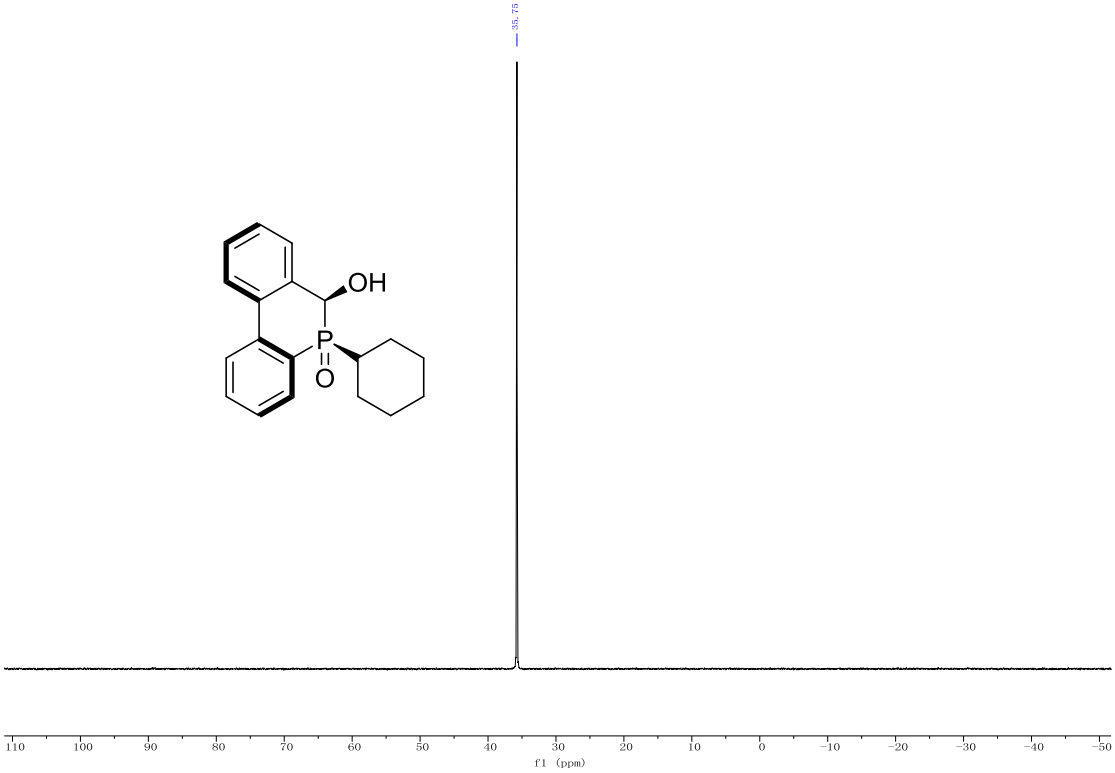
_u,l_-6-Hydroxy-5-(naphthalen-2-yl)-6_H_-phosphanthridine 5-oxide (_u,l_-10h)

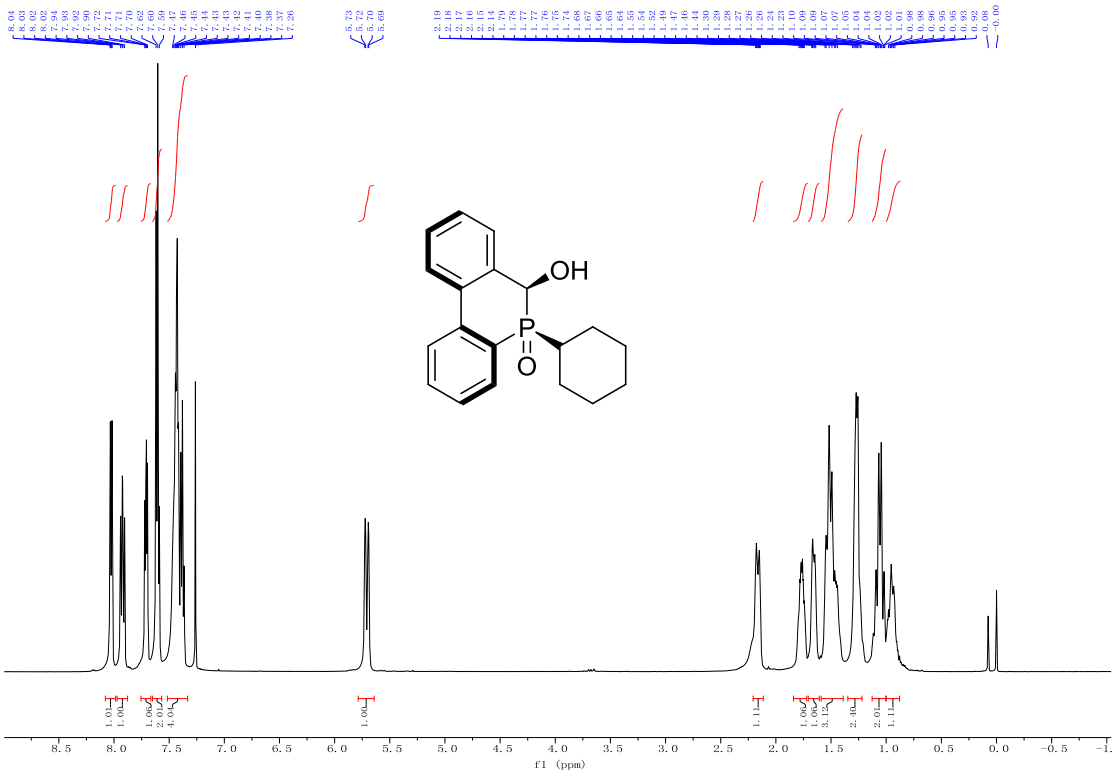


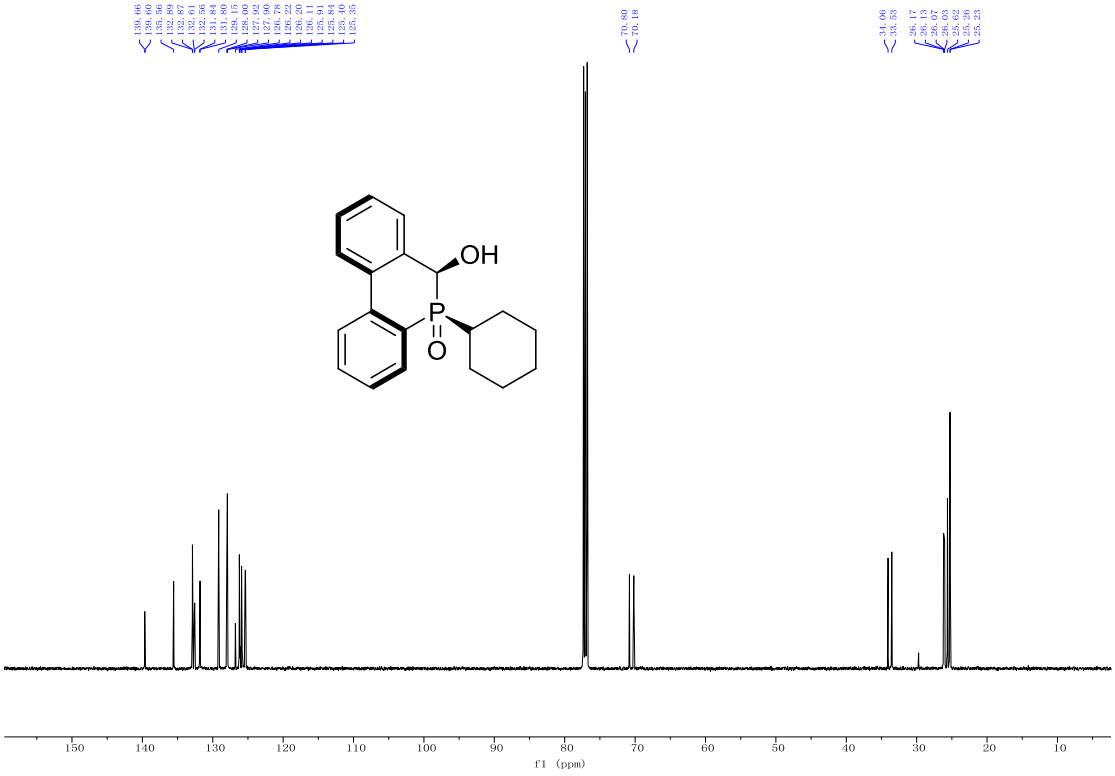




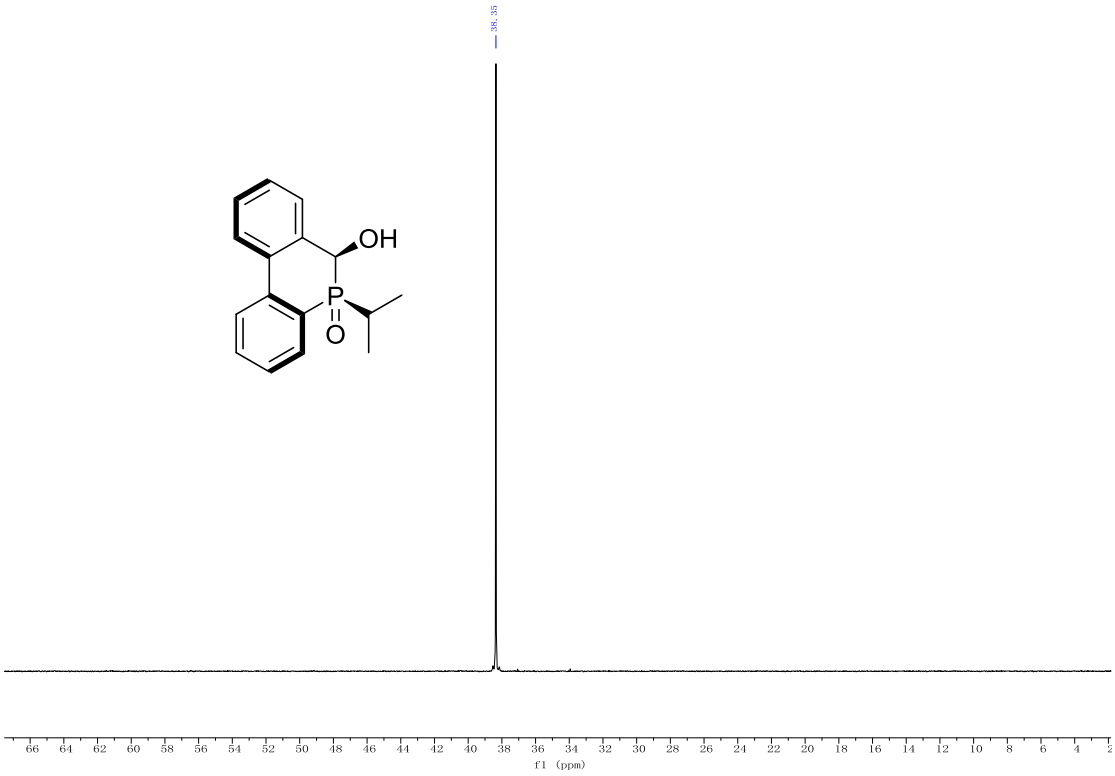
***u,l*-5-Cyclohexyl-6-hydroxy-6*H*-phosphanthridine 5-oxide (*u,l*-10i)**

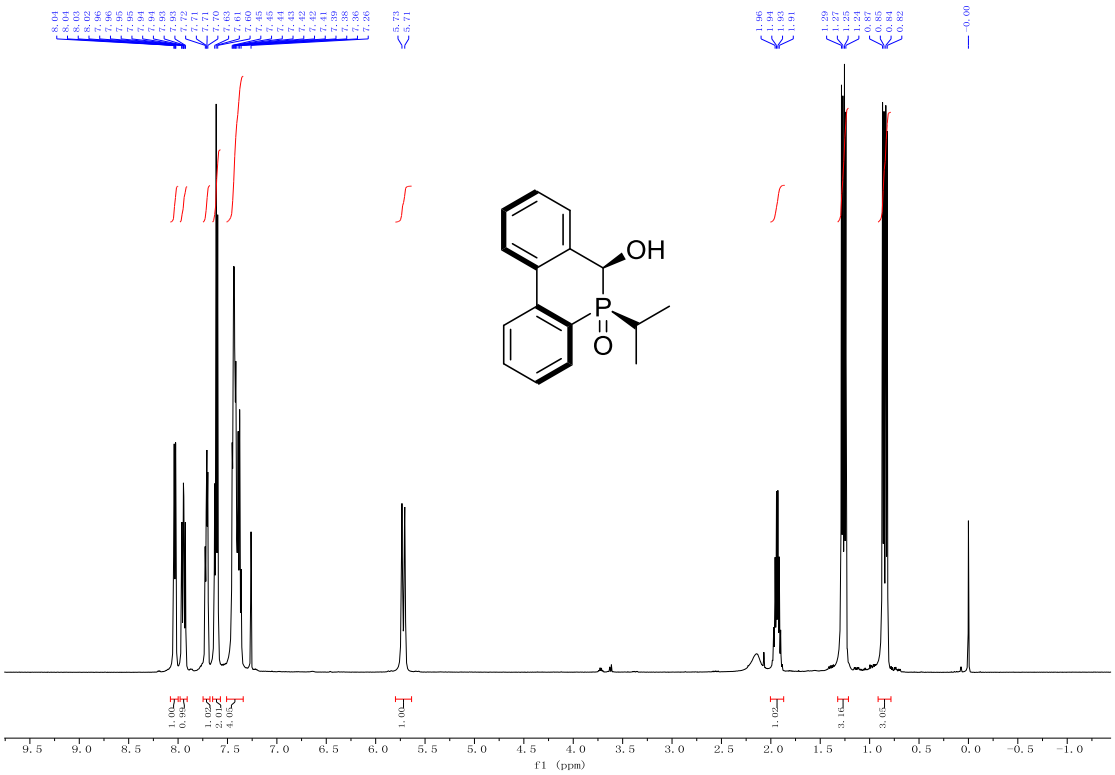


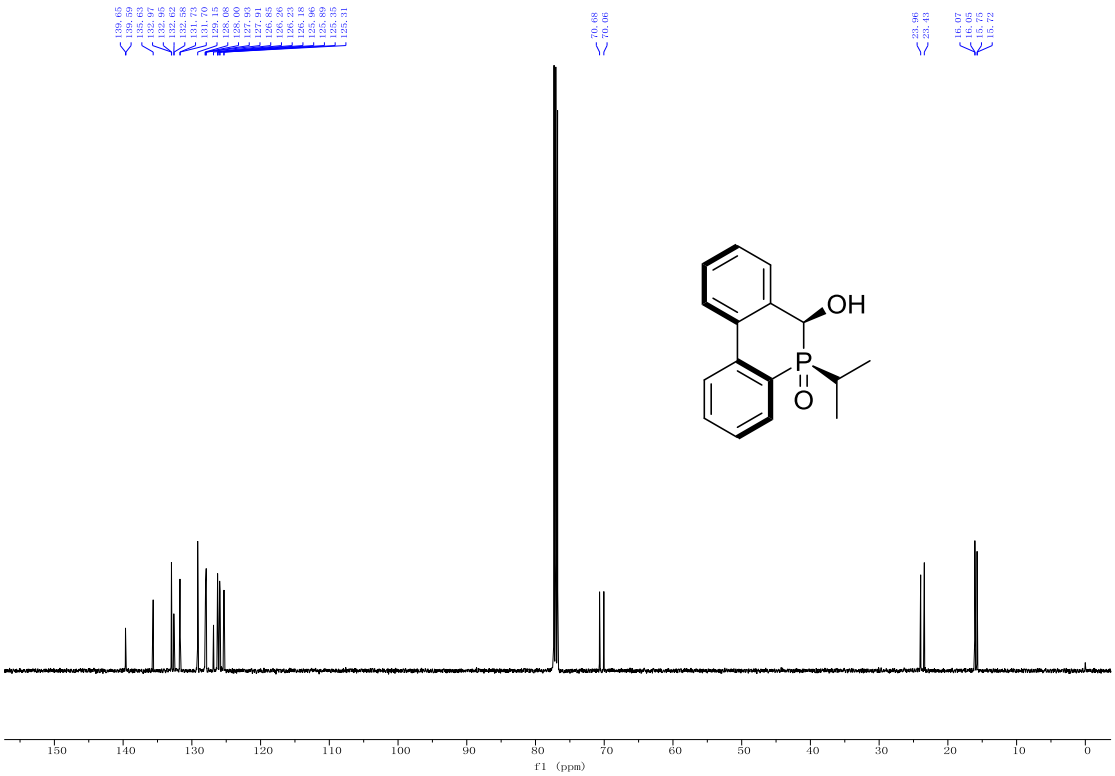

OH
P
O
f1 (ppm)


OH
P
O
f1 (ppm)

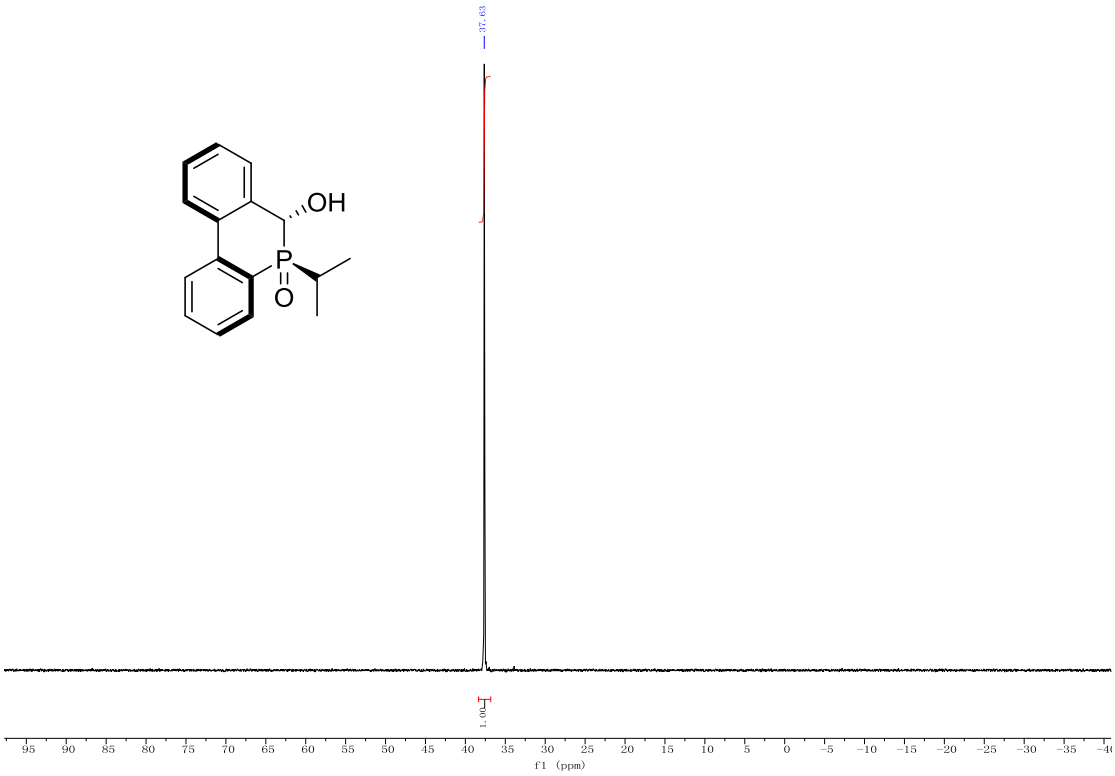
_u,l_-6-Hydroxy-5-isopropyl-6_H_-phosphanthridine 5-oxide (_u,l_-10j)

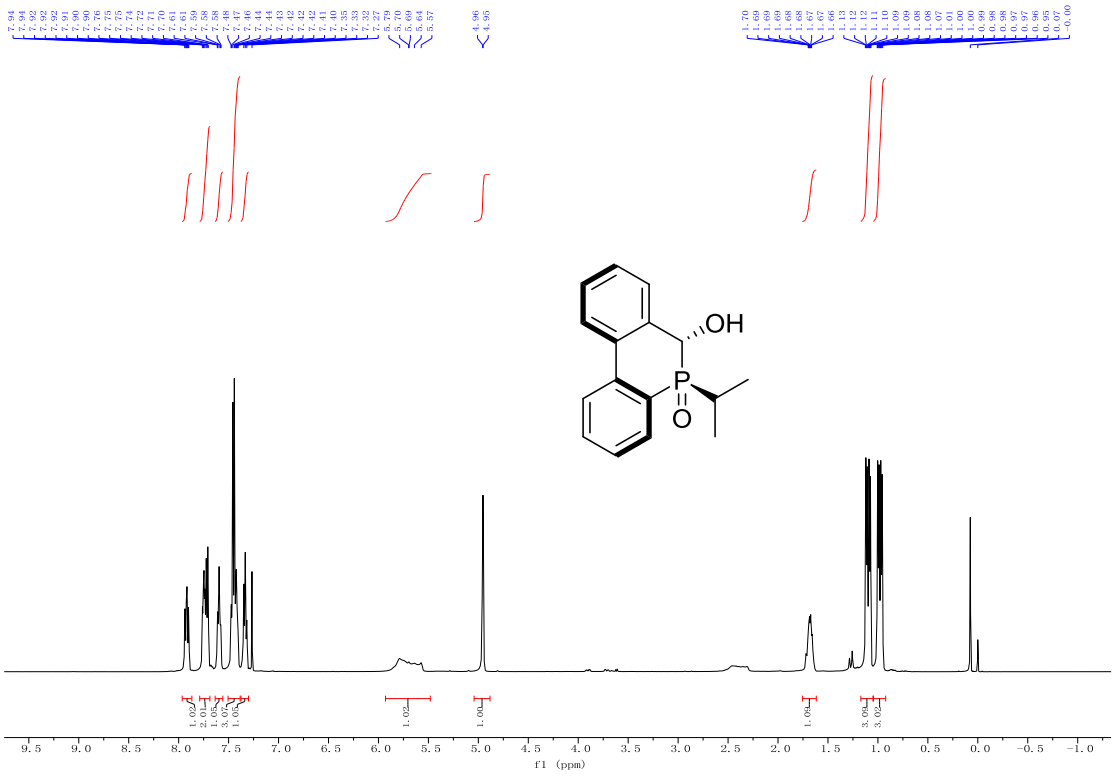


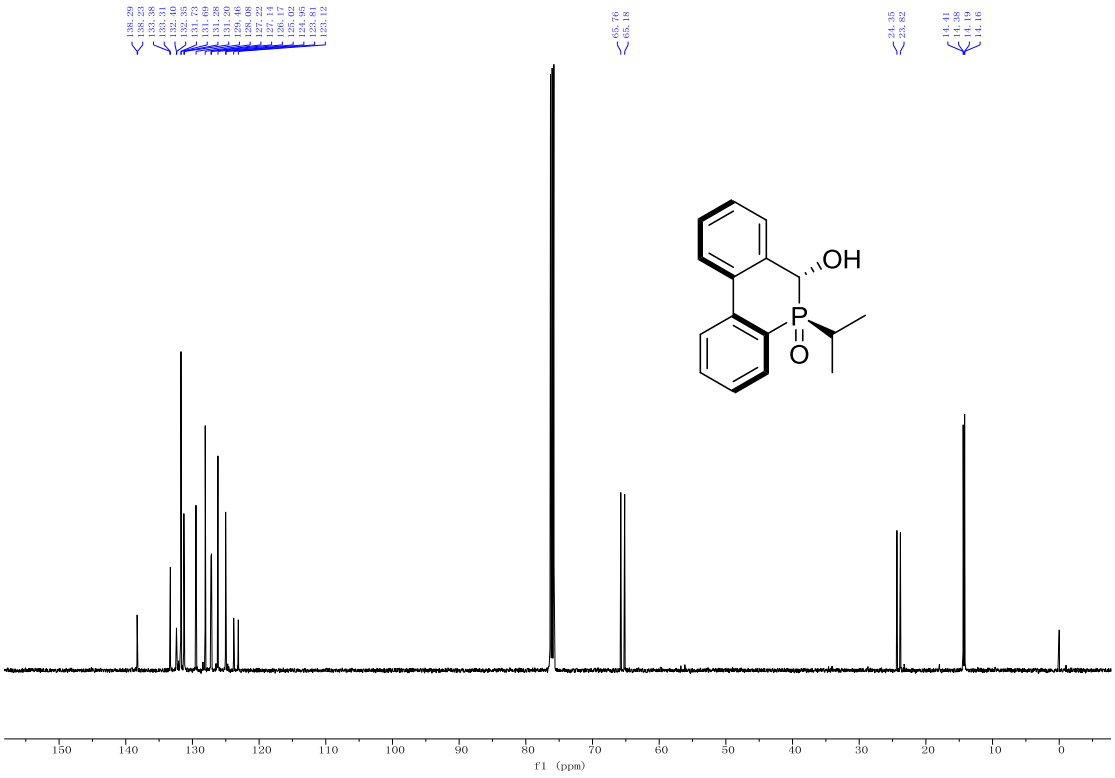




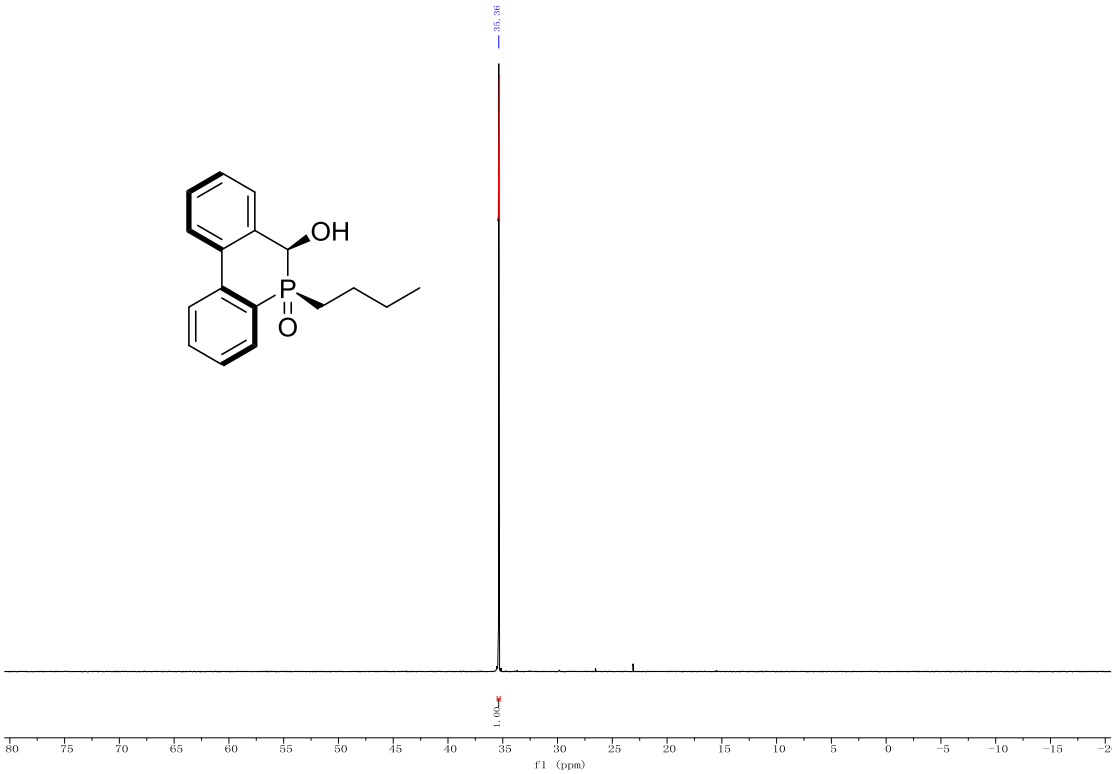
***u,u*-6-Hydroxy-5-isopropyl-6H-phosphanthridine-5-oxide (*u,u*-10j')**

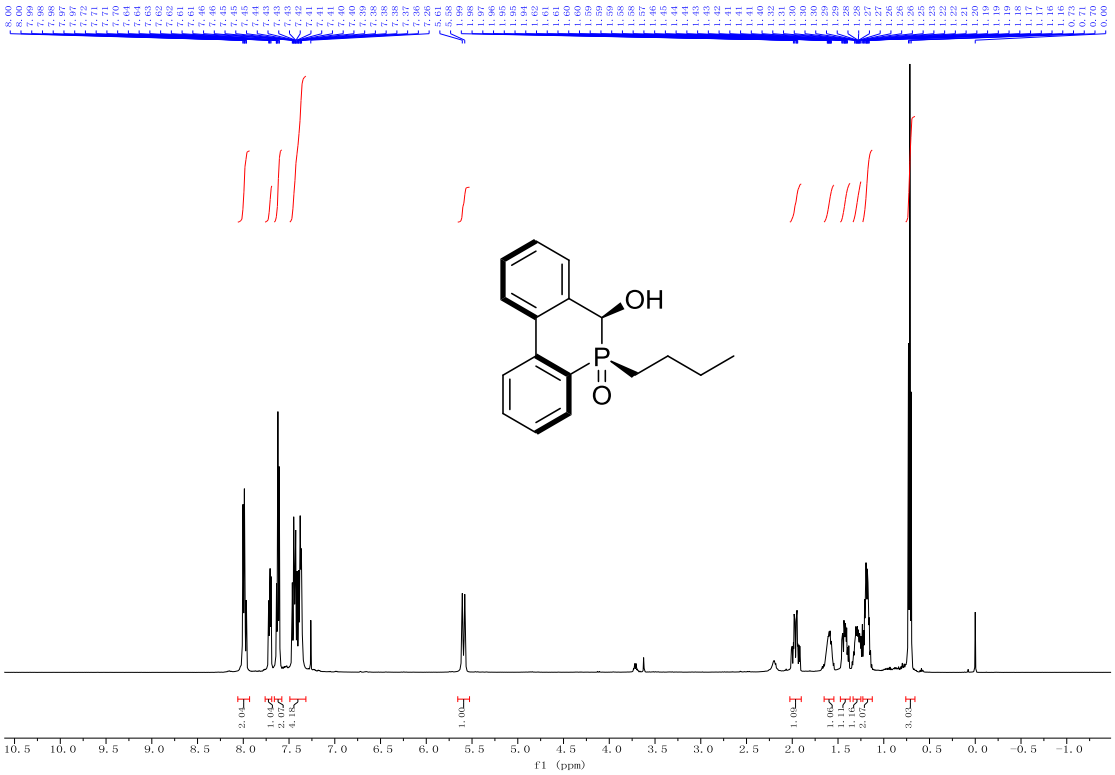


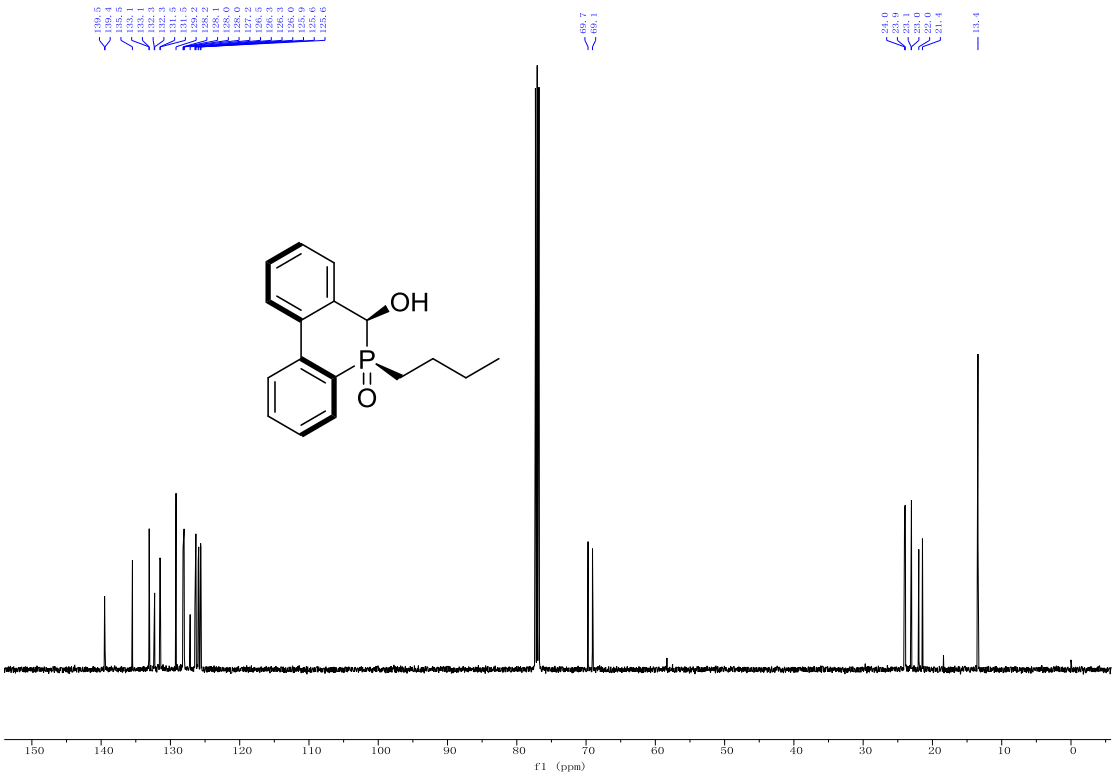

OH
P
O
f1 (ppm)


OH
P
O
f1 (ppm)

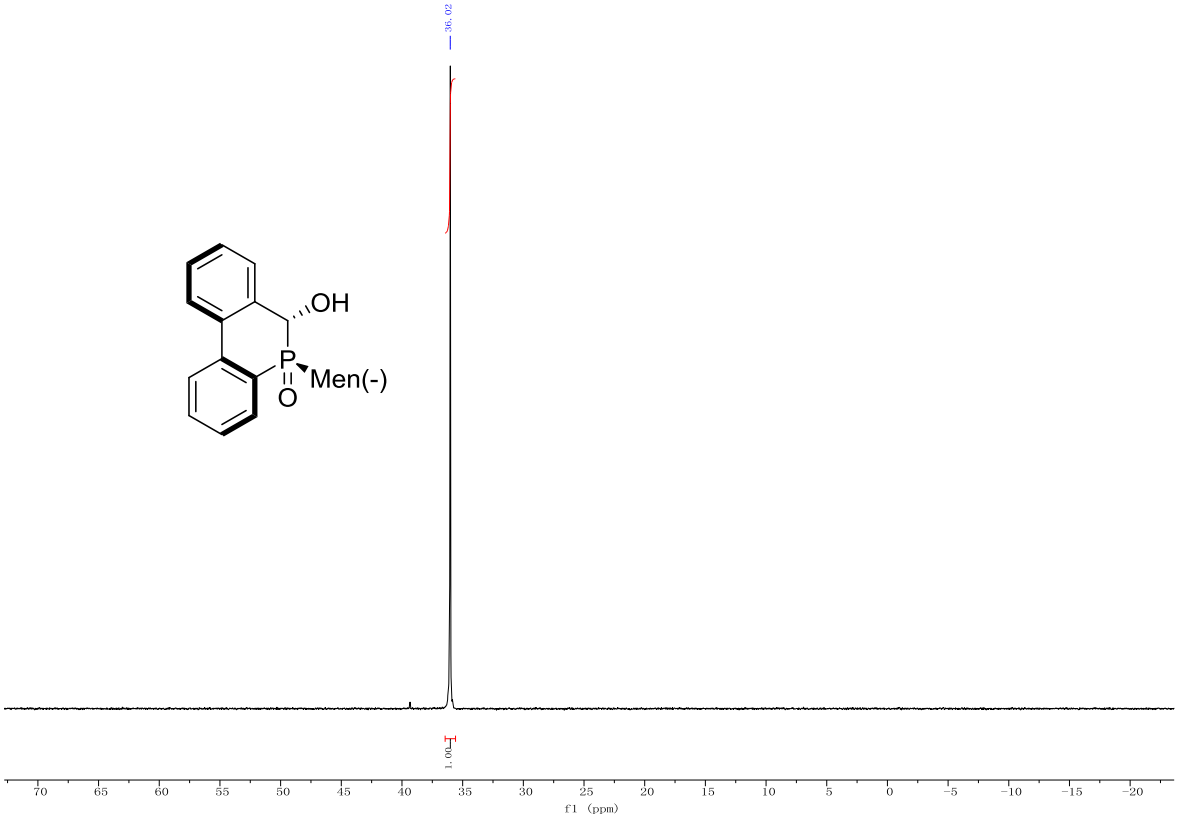
***u,l*-5-Butyl-6-hydroxy-6*H*-phosphanthridine 5-oxide (*u,l*-10k)**

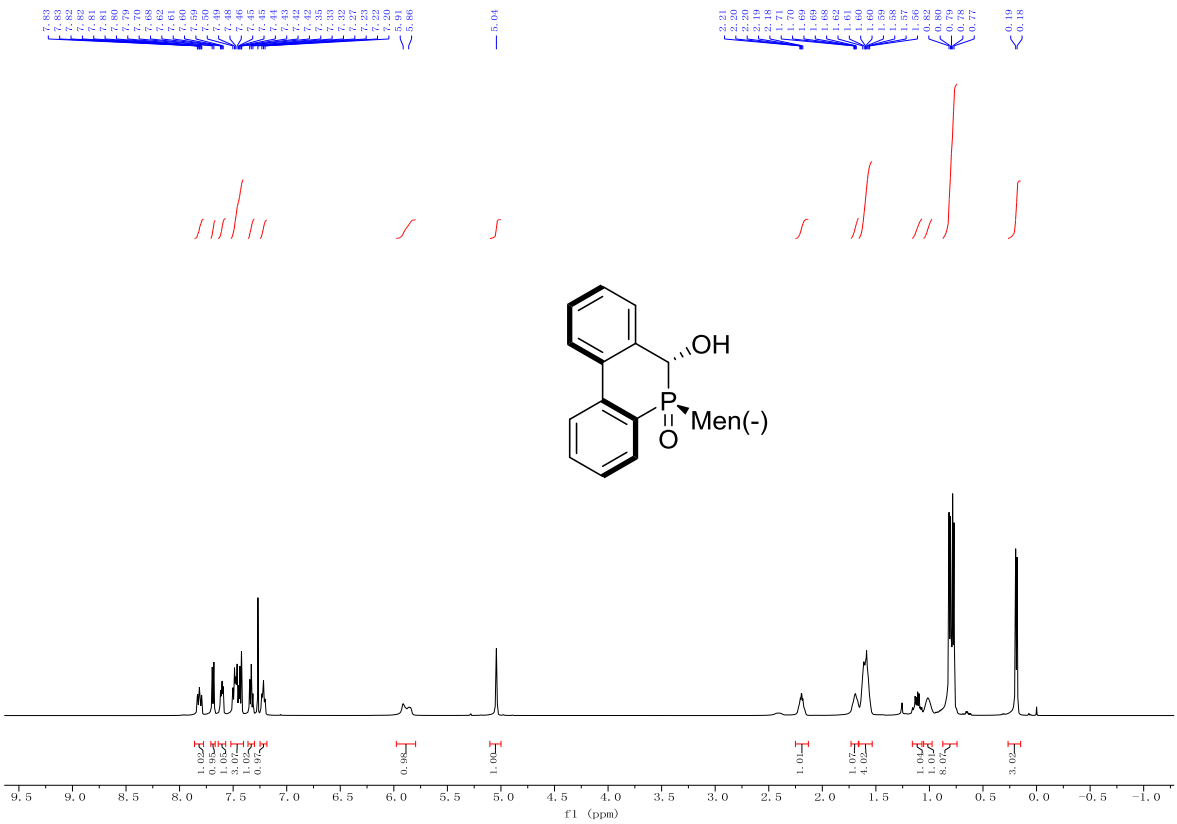


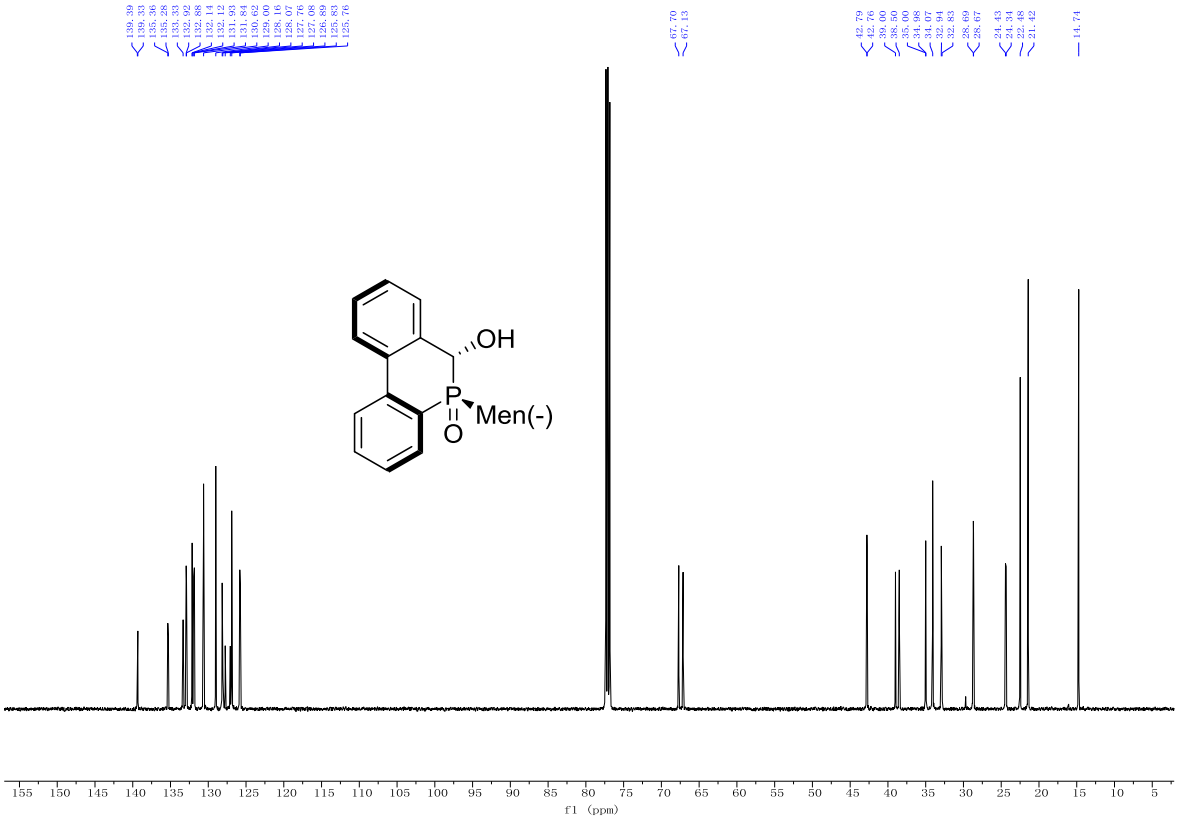




(R_P,S_A,R_C)-6-Hydroxy-5-(-)-menthyl-6*H*-phosphanthridine 5-oxide (R_P,S_A,R_C-10l')




OH
P
O
Men(-)
f1 (ppm)


OH
P
O
Men(-)
f1 (ppm)