*Supplementary information*

*for*

# Differentially Substituted Phosphines via Decarbonylation of Acylphosphines

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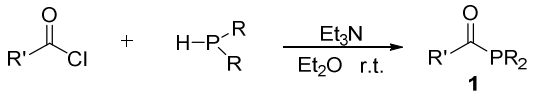
## General Information

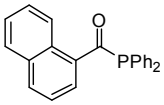
Unless otherwise noted, all commercial materials were purchased from Energy Chemical and used without further purification. Diethyl ether was freshly distilled over CaH and other solvents were used without further purification. Reaction temperatures are reported as the temperatures of the bath surrounding the vessel. Sensitive reagents and solvents were transferred under nitrogen in a glove-box using standard techniques. Proton nuclear magnetic resonance ($^{1}$H NMR) and carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were acquired in $CDCl_3$ unless otherwise noted. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm) and are referenced to residual solvent ($CDCl_3$, δ = 7.26 ppm (1H) and 77.16 ppm (13C)). Coupling constants (J) are reported in hertz (Hz) and the resonance multiplicity abbreviations used are: s, singlet; d, doublet; t, triplet; q, quartet; dt, doublet of triplets; td, triplet of doublets; dd, doublet of doublets; ddd, doublet of doublet of doublets; m, multiplet. Infrared (IR) spectra were obtained with a FT-IR series spectrometer as thin films on potassium bromide plates. Thin-layer chromatography (TLC) was performed on GF254 silica gel coated plates and were visualized using one or more of the following methods: UV light (254 nm) and staining with basic potassium permanganate ($KMnO_4$). Flash chromatography was performed using glass columns and carried out on $SiO_2$ (silica gel 200-300 mesh).

# Experimental Procedures and Compound Characterizations

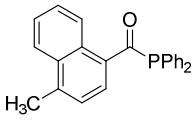
**General procedure A for preparation of acylphosphine[1]:**



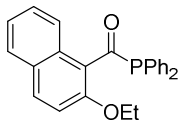

At room temperature, triethylamine (0.64 g, 6.3 mmol) was added to a solution of secondary phosphine (5.25 mmol) in 10 mL diethyl ether, followed by addition of acyl chloride (5.5 mmol). After the reaction completed (about 6 hours, monitored by TLC), the reaction mixture was filtrated through celite, the filtrate was evaporated under vacuum and the residue was recrystallized from 10 mL methol to afford the acylphosphine **1**.



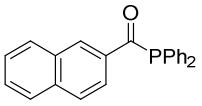

**1-naphthoyldiphenylphosphine (1a).** According to the general procedure A, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and 1-Naphthoyl chloride (1.05 g, 5.5 mmol) afforded **1a** (1.52 g) in a yield of 85% as a yellow solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 8.0 Hz, 1 H), 8.35-8.32 (m, 1 H), 7.87 (d, *J* = 8.0 Hz, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.56-7.37 (m, 8 H), 7.31-7.29 (m, 5 H); $^{31}$P NMR (162 MHz, $CDCl_3$): δ 18.27; MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{23}H_{18}OP$: 341, Found 341; IR (film): 1666, 1639, 1508, 1434, 1221, 1058, 900, 779, 742, 696 $cm^{-1}$.



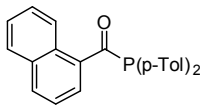

**(diphenylphosphanyl)(4-methylnaphthalen-1-yl)methanone (1b).** According to the general procedure A, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and 4-methyl-1-naphthoyl chloride (1.12 g, 5.5 mmol) afforded **1b** (1.62 g) in a yield of 87% as a yellow solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 8.0 Hz, 1 H), 8.32-8.29 (m, 1 H), 7.95 (d, *J* = 4.0 Hz, 1 H), 7.56-7.49 (m, 2 H), 7.45-7.41 (m, 4 H), 7.30-7.29 (m, 6 H), 7.23 (d, *J* = 8.0 Hz, 1 H), 2.63 (s, 3 H); $^{31}$P NMR (162 MHz, $CDCl_3$): δ 17.27. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 215.91 (d, *J* = 36.0 Hz), 140.20, 135.62 (d, *J* = 32 Hz), 134.73 (d, *J* = 18 Hz), 133.20 (d, *J* = 6 Hz), 132.94 (d, *J* = 3 Hz), 131.94 (d, *J* = 9 Hz), 130.28 (d, *J* = 21 Hz), 129.60 (d, *J* = 4 Hz), 129.30, 128.56 (d, *J* = 7 Hz), 127.73, 126.19 (d, *J* = 29 Hz), 125.25 (d, *J* = 1 Hz), 124.19, 20.10; HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{24}H_{20}OP$ 355.1252 Found 355.1252; IR (film): 3055, 2876, 1666, 1639, 1528, 1434, 1221, 1058, 920, 772, 742, 696 $cm^{-1}$.




**(diphenylphosphanyl)(2-ethoxynaphthalen-1-yl)methanone (1c).** According to the general procedure A, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and 2-ethoxy-1-naphthoyl chloride (1.28 g, 5.5 mmol) afforded **1c** (1.29 g) in a yield of 64% as a yellow solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.0 Hz, 1 H), 7.73-7.69 (m, 2 H), 7.46-7.42 (m, 1 H), 7.39-7.31 (m, 5 H), 7.28-7.18 (m, 6 H), 6.87 (d, *J* = 8.0 Hz, 1 H), 3.75 (q, *J* = 8 Hz, 2 H), 1.36 (t, *J* = 8 Hz, 3 H); $^{31}$P NMR (162 MHz, $CDCl_3$): δ 26.81. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 222.95 (d, *J* = 39.7 Hz), 153.07, 134.50 (d, *J* = 18.7 Hz), 133.23 (d, *J* = 8.6 Hz), 131.65, 130.34, 129.11, 128.47, 128.14, 128.07, 127.59, 124.52 (d, *J* = 24.2 Hz), 123.93, 123.83 (d, *J* = 2.7 Hz), 112.71, 64.35, 14.89. HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{25}H_{22}OP$ 385.1357 Found 385.1353; IR (film): 3051, 2981, 2930, 1644, 1433, 1247, 1081, 1050, 772, 743, 696 $cm^{-1}$.

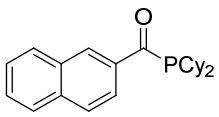



**2-naphthoyldiphenylphosphine (1d).** According to the general procedure A, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and 2-Naphthoyl chloride (1.05 g, 5.5 mmol) afforded **1d** (1.30 g) in a yield of 73% as a yellow solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1 H), 7.98 (d, *J* = 8 Hz, 1 H), 7.87 (d, *J* = 8.0 Hz, 1 H), 7.80-7.78 (m, 2 H), 7.57-7.43 (m, 6 H), 7.35-7.34 (m, 6 H); $^{31}$P NMR (162 MHz, $CDCl_3$): δ 12.83; MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{23}H_{18}OP$: 341, Found 341; IR (film): 3050, 2979, 1666, 1639, 1508, 1434, 1221, 1058, 900, 779, 742, 696 $cm^{-1}$.

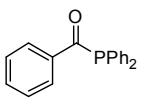



**(di-p-tolylphosphanyl)(naphthalen-1-yl)methanone (1e).** According to the general procedure A, reaction with di-p-tolylphosphane (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and 4-methyl-1-naphthoyl chloride (1.12 g, 5.5 mmol) afforded **1e** (1.68 g) in a yield of 87% as a yellow solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 8.0 Hz, 1 H), 8.35-8.33 (m, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.55-7.46 (m, 2 H), 7.39-7.30 (m, 5 H), 7.11-7.09 (m, 4 H), 2.28 (S, 6 H); $^{31}$P NMR (162 MHz, $CDCl_3$): δ 16.67. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 217.38 (d, *J* = 37.0 Hz), 139.46, 137.30 (d, *J* = 32 Hz), 134.69 (d, *J* = 18 Hz), 133.87 (d, *J* = 2 Hz), 132.73, 131.92 (d, *J* = 9 Hz), 129.82 (d, *J* = 20 Hz), 129.52 (d, *J* = 4 Hz), 129.48, 129.40, 128.12 (d, *J* = 27 Hz), 126.39, 125.51, 124.31 (d, *J* = 1 Hz), 21.33; HRMS

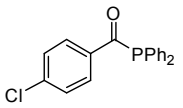
(ESI-QTOF) m/z: ([M+H]$^+$) Calcd for $C_{25}H_{22}OP$ 369.1408 Found 369.1402; IR (film): 3048, 2927, 1669, 1629, 1528, 1434, 1231, 1058, 920, 858, 772, 742, 696 cm$^{-1}$.



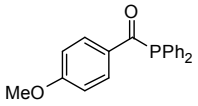
**(dicyclohexylphosphanyl)(naphthalen-2-yl)methanone (1f).** According to the general procedure A, reaction with dicyclohexylphosphane (1.04 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and 2-Naphthoyl chloride (1.05 g, 5.5 mmol) afforded **1f** (1.23 g) in a yield of 67% as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, $J$ = 8.4 Hz, 1 H), 8.36-8.28 (m, 1 H), 7.99 (d, $J$ = 8.2 Hz, 1 H), 7.91-7.84 (m, 1 H), 7.60-7.49 (m, 3 H), 2.09-2.02 (m, 2 H), 1.90-1.87 (m, 2 H), 1.77-1.58 (m, 8 H), 1.31-0.98 (m, 10 H); $^{31}$P NMR (162 MHz, $CDCl_3$): δ 28.34. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 221.92 (d, $J$ = 43.2 Hz), 139.68 (d, $J$ = 29.5 Hz), 134.02 (d, $J$ = 2.1 Hz), 132.79, 130.42 (d, $J$ = 21.3 Hz), 128.98 (d, $J$ = 3.5 Hz), 128.39, 127.95, 126.47, 125.45, 124.30 (d, $J$ = 1.3 Hz), 32.93 (d, $J$ = 12.9 Hz), 31.06 (d, $J$ = 10.0 Hz), 29.75 (d, $J$ = 9.4 Hz), 26.24 (d, $J$ = 0.7 Hz); HRMS (ESI-QTOF) m/z: ([M+H]$^+$) Calcd for $C_{23}H_{30}OP$ 353.2034 Found 353.2041; IR (film): 2924, 2849, 1630, 1507, 1446, 1220, 1171, 1058, 902, 805, 778 cm$^{-1}$.



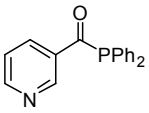
**benzoyldiphenylphosphine (1g).** According to the general procedure A, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and benzoyl chloride (0.77 g, 5.5 mmol) afforded **1g** (1.14 g) in a yield of 75% as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.98-7.96 (m, 2 H), 7.43-7.34 (m, 13 H); $^{31}$P (162 MHz, $CDCl_3$): $\delta$ 13.50; MS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{19}H_{16}OP$ 291 Found 291; IR (film): 1643, 1433, 1201, 1180, 1141, 1075, 740, 692 cm$^{-1}$.



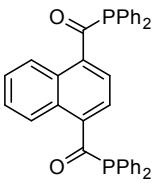
***p*-chlorobenzoyldiphenylphosphine (1h).** According to the general procedure A, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and 4-chlorobenzoyl chloride (0.96 g, 5.5 mmol) afforded **1h** (1.31 g) in a yield of 77% as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.09-8.06 (m, 1 H), 7.91-7.83 (m, 2 H), 7.58-7.56 (m, 1 H), 7.52-7.50 (m, 2 H), 7.46-7.35 (m, 7 H), 7.31 (d, $J$ = 8.0 Hz, 1 H); $^{31}$P (162 MHz, $CDCl_3$) $\delta$ 13.62; MS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{19}H_{15}ClOP$ 325 Found 325; IR (film): 1786, 1647, 1199, 1182, 1087, 1073, 901,742, 693 cm$^{-1}$.



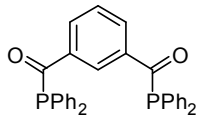
***p*-methoxylbenzoyldiphenylphosphine (1i).** According to the general procedure A, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.98 g, 5.25 mmol) and 4-methoxylbenzoyl chloride (0.93 g, 5.5 mmol) afforded **1i** (1.36 g) in a yield of 81% as a yellow solid. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.00-7.97 (m, 2 H), 7.43-7.33 (m, 10 H), 6.83 (d, $J$ = 8.0 Hz, 2 H), 3.81 (s, 3 H); $^{31}$P (162 MHz, $CDCl_3$): $\delta$ 11.36; MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{20}H_{18}O_2P$ 321 Found 321; IR(film): 1641, 1600, 1436, 1180, 1143, 1075, 901, 696 cm$^{-1}$.



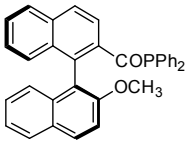
**(diphenylphosphanyl)(pyridin-3-yl)methanone (1j).** According to the general procedure A, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and 3-(chlorocarbonyl)pyridin-1-ium chloride (1.12 g, 5.5 mmol) afforded **1j** (1.16 g) in a yield of 76% as a dark yellow solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 9.16 (s, 1 H), 8.66 (d, $J$ = 4 Hz, 1 H), 8.16 (d, $J$ = 8 Hz, 1 H), 7.45-7.37 (m, 10 H), 7.31-7.26 (m, 1 H); $^{31}$P NMR (162 MHz, $CDCl_3$): δ 15.12. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 212.36 (d, $J$ = 39.0 Hz), 153.29 (d, $J$ = 2 Hz), 149.63 (d, $J$ = 10 Hz), 135.10 (d, $J$ = 8 Hz), 135.00 (d, $J$ = 19 Hz), 134.48 (d, $J$ = 34 Hz), 131.53 (d, $J$ = 5 Hz), 129.90, 128.92 (d, $J$ = 8 Hz), 123.52; HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{18}H_{15}NOP$ 292.0891. Found 292.0885; IR (film): 3055, 1720, 1646, 1436, 1284, 1208, 1129, 743, 695, 540 cm$^{-1}$.



**naphthalene-1,4-diylbis((diphenylphosphanyl)methanone) (1m).** According to the general procedure A, reaction with diphenylphosphine (1.95 g, 10.47 mmol), triethylamine (1.28 g, 12.56 mmol) and naphthalene-1,4-dicarbonyl dichloride (1.39 g, 5.5 mmol) afforded **1m** (2.17 g) in a yield of 75% as a orange solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.35-8.32 (m, 2 H), 8.03 (s, 1 H), 7.50-7.47 (m, 2 H), 7.39-7.35 (m, 8 H), 7.30-7.22 (m, 13 H); $^{31}$P NMR (162 MHz, $CDCl_3$): δ 21.01. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 217.77 (d, $J$ = 38.2 Hz), 140.74 (d, $J$ = 31.3 Hz), 134.78 (d, $J$ = 18 Hz), 134.71 (d, $J$ = 19 Hz), 131.99 (d, $J$ = 5.2 Hz), 129.65, 128.68 (d, $J$ = 7.9 Hz), 128.11, 126.56 (d, $J$ = 17.7 Hz), 125.35; HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{36}H_{27}O_2P_2$ 553.1486. Found 553.1485; IR (film): 3053, 1650, 1480, 1434, 1223, 1163, 1061, 874, 741, 492 cm$^{-1}$.

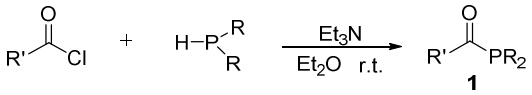


**1,3-phenylenebis((diphenylphosphanyl)methanone) (1n).** According to the general procedure A, reaction with diphenylphosphine (1.95 g, 10.47 mmol), triethylamine (1.28 g, 12.56 mmol) and isophthaloyl dichloride (1.11 g, 5.5 mmol) afforded **1n** (1.87 g) in a yield of 71% as a yellow solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1 H), 7.99 (d, *J* = 8 Hz, 2 H), 7.38-7.31 (m, 21 H); $^{31}$P NMR (162 MHz, $CDCl_3$): δ 14.08. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 212.50 (d, *J* = 38.2 Hz), 139.40 (d, *J* = 35.0 Hz), 134.91 (d, *J* = 18.8 Hz), 132.16, 132.12, 132.06, 129.64, 128.77 (d, *J* = 7.9 Hz), 128.12.; HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{32}H_{25}O_2P_2$ 503.1330. Found 503.1325; IR (film): 3058, 1715, 1650, 1435, 1157, 742, 695, 544, 526, 500 $cm^{-1}$.

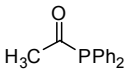


**(S)-(diphenylphosphanyl)(2'-methoxy-[1,1'-binaphthalen]-2-yl)methanone (1o).** According to the general procedure A, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and (S)-2'-methoxy-[1,1'-binaphthalene]-2-carbonyl chloride (1.64 g, 5.5 mmol) afforded **1o** (1.64 g) in a yield of 63% as a yellow solid. $[\alpha]_D^{20}$ -237° ($CHCl_3$, *c* 1). (literature rotation for **(S)-1o** $[\alpha]_D^{20}$ -238° ($CHCl_3$, *c* 1))[2]. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 9.0 Hz, 1 H), 7.88-7.84 (m, 3 H), 7.48-7.43 (m, 1 H), 7.39 (dd, *J* = 8.5, 2.8 Hz, 1 H), 7.30-7.06 (m, 15 H), 6.93 (d, *J* = 8.4 Hz, 1 H), 3.35 (s, 3 H); $^{31}$P NMR (162 MHz, $CDCl_3$): δ 20.64; MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{34}H_{26}O_2P$ 497 Found 497; IR (film): 2927, 1651, 1622, 1593, 1434, 1265, 1252, 1038, 1060, 740, 694 $cm^{-1}$.

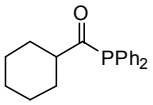
**General procedure B for preparation of acylphosphine[3]:**




At room temperature, triethylamine (0.64 g, 6.3 mmol) was added to a solution of secondary phosphine (5.25 mmol) in 10 mL diethyl ether, followed by addition of acyl chloride (5.5 mmol). After the reaction completed (about 6 hours, monitored by TLC), the mixture was filtrated through celite, the filtrate was evaporated under vacuum to afford crude acylphosphine **1**. The crude product was used in the following decarbonylation directly without further purification.

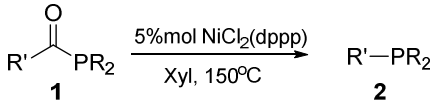


**1-(diphenylphosphanyl)ethan-1-one (1k).** According to the general procedure B, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and acetyl chloride (0.43 g, 5.5 mmol) afforded crude **1k** as a carlorless oil.

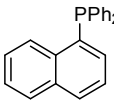


**cyclohexyl(diphenylphosphanyl)methanone (1l).** According to the general procedure B, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and cyclohexanecarbonyl chloride (0.80 g, 5.5 mmol) afforded crude **1l** as a carlorless oil.

**General procedure C for decarbonylation:**

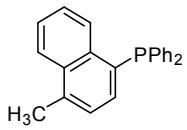



In a sealed vial, under nitrogen, acylphosphine (0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) were mixed and stirred at 150°C for 12 h. The reaction was allowed to cool down to room temperature. The solvent was removed under vacuum. The residue was purified by flash chromatography eluting with hexane/EtOAc (20:1 v/v) unless otherwise noted on silica gel to afford pure desired product.

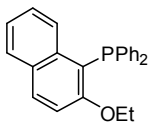


**naphthalen-1-yldiphenylphosphine (2a).** According to the general procedure C, reaction with 1-naphthoyldiphenylphosphine **(1a)** (68 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) afforded **2a** (51.8 mg) in a yield of 83% as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.41 (dd, $J$ = 8.0, 4.0 Hz, 1 H), 7.85 (t, $J$ = 8.0 Hz, 2 H), 7.50-7.41 (m, 2 H), 7.37-7.28 (m, 11 H), 7.02-6.98 (m, 1 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: -14.18. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{22}H_{18}P$: 313, Found 313. IR (film): 3051, 1433, 1265, 796, 774, 743, 696, 501, 446 $cm^{-1}$.

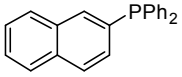
A large-scaled preparation of **2a** was carried out in Schlenk flask according to the general procedure C, with 1-naphthoyldiphenylphosphine **(1a)** (6.8 g, 20 mmol, 1.0 equiv), $NiCl_2$(dppp) (540 mg, 5% mol, 1.0 mmol) and xylene (50 mL) afforded **2a** (5.1 g) in a yield of 83% as a white solid with an extension of reacting time to 24h.



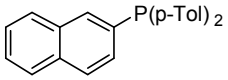

**(4-methylnaphthalen-1-yl)diphenylphosphane (2b).** According to the general procedure C, reaction with (diphenylphosphanyl)(4-methylnaphthalen-1-yl)-methanone **(1b)** (70.8 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) afforded **2b** (56.1 mg) in a yield of 86% as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.46 (dd, *J* = 8.2, 4.7 Hz, 1 H), 8.04 (d, *J* = 8.3 Hz, 1 H), 7.56-7.48 (m, 1 H), 7.48-7.40 (m, 1 H), 7.37-7.23 (m, 11 H), 7.20 (d, *J* = 7.2 Hz, 1 H), 2.69 (s, 3 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: -14.47. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{23}H_{20}P$: 327, Found 327. IR (film): 3058, 2930, 1736, 1481, 1436, 1273, 752, 723, 537 $cm^{-1}$.




**(2-ethoxynaphthalen-1-yl)diphenylphosphane (2c).** According to the general procedure C, reaction with (diphenylphosphanyl) (2-ethoxynaphthalen-1-yl) meth-anone **(1c)** (70.8 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) afforded **2c** (32.1 mg) in a yield of 45% as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.96-8.92 (m, 1 H), 7.86 (d, *J* = 9.0 Hz, 1 H), 7.72 (d, *J* = 8.1 Hz, 1 H), 7.45-7.23 (m, 6 H), 7.23-7.06 (m, 7 H), 3.75 (q, *J* = 7.0 Hz, 2 H), 0.73 (t, *J* = 7.0 Hz, 3 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: -24.16. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 158.74 (d, *J* = 1.8 Hz), 137.89 (d, *J* = 26.5 Hz), 137.89 (d, *J* = 26.5 Hz), 131.91, 131.33 (d, *J* = 19.4 Hz), 128.15 (d, *J* = 6.1 Hz), 127.25 (d, *J* = 1.6 Hz), 126.81 (d, *J* = 6.3 Hz), 126.35, 125.76 (d, *J* = 3.1 Hz), 125.76 (d, *J* = 3.1 Hz), 122.48 (d, *J* = 2.1 Hz), 114.70 (d, *J* = 19.2 Hz), 113.11, 63.06, 13.07. HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{24}H_{22}OP$: 357.1408, Found 357.1419 IR (film): 3048, 2978, 1503, 1263, 1239, 1113, 1026, 742, 695 $cm^{-1}$.

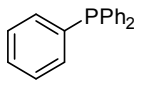



**naphthalen-2-yldiphenylphosphane (2d).** According to the general procedure C, reaction with (diphenylphosphanyl)(naphthalen-2-yl)methanone **(1d)** (68 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) afforded **2d** (56.2 mg) in a yield of 90% as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.83-7.78 (m, 3 H), 7.74-7.72 (m, 1 H), 7.51-7.44 (m, 2 H), 7.40-7.31 (m, 11 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: -4.84. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{22}H_{18}P$: 313, Found 313. IR (film): 3051, 1584, 1478, 1433, 1269, 1091, 1025, 817, 741, 695, 638, 475 $cm^{-1}$.

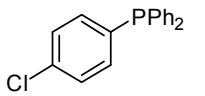



**naphthalen-2-yldi-p-tolylphosphane (2e).** According to the general procedure

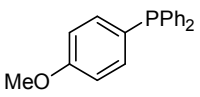
C, reaction with (di-p-tolylphosphanyl)(naphthalen-2-yl) methanone **(1e)** (73.6 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) afforded **2e** (56.5 mg) in a yield of 83% as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.42-8.34 (m, 1 H), 7.83 (dd, *J* = 12.6, 8.1 Hz, 2 H), 7.50-7.37 (m, 2 H), 7.38-7.29 (m, 1 H), 7.25-7.06 (m, 8 H), 7.04-6.95 (m, 1 H), 2.33 (s, 6 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: -15.90. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{24}H_{22}P$: 341, Found 341. IR (film): 3048, 2927, 2853, 1713, 1434, 1260, 1117, 1089, 743, 696, 544 $cm^{-1}$.



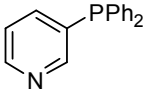

**triphenylphosphane (2g).** According to the general procedure C, reaction with (diphenylphosphanyl)(phenyl)methanone **(1g)** (58 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) afforded **2g** (21.5 mg) in a yield of 41% as a white solid; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.35-7.25 (m, 15 H). $^{31}$P NMR (162 MHz, $CDCl_3$): δ -5.37. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{18}H_{16}P$: 263, Found 263. IR (film): 3067, 1474, 1431, 1087, 1068, 1026, 741, 694, 510, 494 $cm^{-1}$.




**(4-chlorophenyl)diphenylphosphane (2h).** According to the general procedure C, reaction with (4-chlorophenyl)(diphenylphosphanyl)methanone **(1h)** (64.8 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) afforded **2h** (36.7 mg) in a yield of 62% as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 7.5 Hz, 2 H), 7.38-7.24 (m, 10 H), 7.19-7.10 (m, 2 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: -6.14. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{18}H_{15}ClP$: 297, Found 297. IR (film): 3069, 3053, 1584, 1478, 1433, 1384, 1070, 1013, 817, 738, 695, 506 $cm^{-1}$.

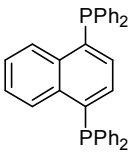



**(4-methoxyphenyl)diphenylphosphane (2i).** According to the general procedure C, reaction with (diphenylphosphanyl)(4-methoxyphenyl)methan- one **(1i)** (64 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) afforded **2i** (40.9 mg) in a yield of 70% as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.33-7.24 (m, 12 H), 6.89 (d, *J* = 8.0 Hz, 2 H), 3.81 (s, 3 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: -7.00. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{19}H_{18}OP$: 293, Found 293. IR (film): 3051, 3000, 1594, 1567, 1497, 1478, 1433, 1247, 1177, 1094, 1028, 826, 743, 696 $cm^{-1}$.

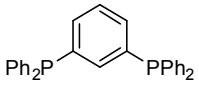



**3-(diphenylphosphanyl)pyridine (2j).** According to the general procedure C, reaction

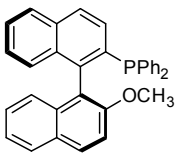
with (diphenylphosphanyl)(pyridin-3-yl)methanone **(1j)** (58.2 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) afforded **2j** (15.8 mg) in a yield of 30% as a white solid. The residue was purified by flash chromatography eluting with hexane/EtOAc (2:1 v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.56 (d, *J* = 4.6 Hz, 1 H), 8.52 (s, 1 H), 7.60-7.52 (m, 1 H), 7.41-7.28 (m, 10 H), 7.28-7.22 (m, 1 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: -11.76. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{17}H_{15}NP$: 264, Found 264. IR (film): 3069, 1557, 1478, 1433, 1399, 1089, 1021, 743, 698, 500 $cm^{-1}$.




**1,4-bis(diphenylphosphanyl)naphthalene (2m).** According to the general procedure C, reaction with naphthalene-1,4-diylbis((diphenylphosphanyl)methan- one) **(1m)** (110.4 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (10.8 mg, 10% mol, 0.02 mmol) and xylene (1.0 mL) afforded **2m** (54.6 mg) in a yield of 55% as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.39-8.30 (m, 2 H), 8.39-8.30 (m, 2 H), 7.29-7.14 (m, 20 H), 6.77-6.72 (m, 2 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: -13.39. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 136.19 (d, *J* = 14.6 Hz), 136.04 (d, *J* = 9.4 Hz), 135.03 (dd, *J* = 21.3, 4.0 Hz), 135.03 (dd, *J* = 21.3, 4.0 Hz), 131.42, 128.92, 128.59 (d, *J* = 7.3 Hz), 126.77 (dd, *J* = 26.8, 1.4 Hz), 126.33. HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{34}H_{27}P_2$: 497.1588, Found 497.1576 IR (film): 3095, 1479, 1433, 1088, 1018, 741, 694, 499 $cm^{-1}$.



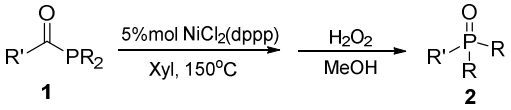

**1,3-bis(diphenylphosphanyl)benzene (2n).** According to the general procedure C, reaction with 1,3-phenylenebis((diphenylphosphanyl)methanone) **(1n)** (100.4 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (10.8 mg, 10% mol, 0.02 mmol) and xylene (1.0 mL) afforded **2n** (75.9 mg) in a yield of 85% as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.33-7.18 (m, 24 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: -5.33. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{30}H_{25}P_2$: 447, Found 447. IR (film): 3058, 1715, 1435, 1157, 742, 695, 544, 526 $cm^{-1}$.




**(S)-(2'-methoxy-[1,1'-binaphthalen]-2-yl)diphenylphosphane (2o).** According to the general procedure C, reaction with (S)-(diphenylphosphanyl)-(2'-methoxy-[1,1'-binaphthalen]-2-yl)methanone **(1o)** (99.2 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) afforded **2o** (64.5 mg) in a yield of 69% as a white solid; $[\alpha]_D^{20}$ -93.5° ($CHCl_3$, *c* 0.27). (literature rotation for **(S)-2o** $[\alpha]_D^{20}$ -94.5° ($CHCl_3$, *c* 0.27))[4]. $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 9.0 Hz, 1 H), 7.91-7.81 (m, 3 H),

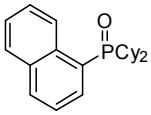
7.48-7.42 (m, 1 H), 7.39 (dd, $J$ = 8.5, 2.8 Hz, 1 H), 7.32-7.03 (m, 15 H), 6.93 (d, $J$ = 8.4 Hz, 1 H), 3.35 (s, 3 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: -13.71. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{33}H_{26}OP$: 469, Found 469. IR (film): 2927, 1622, 1593, 1434, 1265, 1252, 1038, 1060, 740, 694 $cm^{-1}$

**General procedure D for decarbonylation:**

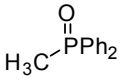



**1** **2**

For the consideration of stability, the desired product trivalent phosphine was separated and characterized by its corresponding phosphine oxide. In a sealed vial, under nitrogen, acylphosphine (0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) were stirred at 150°C for 12 h. The reaction was allowed to cool down to room temperature. After the removal of solvent, methol (1 mL) and $H_2O_2$ (30 wt% in $H_2O$, 0.2 mL) were added and the mixture was stirred at r.t. for 12 h. After that, the reaction mixture was dried under vacuum, and the residue was purified by flash chromatography eluting with hexane/EtOAc (1:1 v/v) on silica gel to afford desired product.

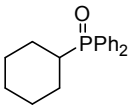



**dicyclohexyl(naphthalen-1-yl)phosphine oxide (2f°).** According to the general procedure D, reaction with (dicyclohexylphosphanyl)(naphthalen-1-yl)methanone **(1f)** (70.4 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol), xylene (0.5 mL), 1 mL methanol and 0.2 mL $H_2O_2$ (30 wt% in $H_2O$) afforded **2f°** (40.8 mg) in a yield of 60% as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.99 (s, 1 H), 7.98 (d, $J$ = 12.0 Hz,1 H), 7.89 (d, $J$ = 4.0 Hz, 1 H), 7.79-7.72 (m, 1 H), 7.59-7.50 (m, 3 H), 2.28-2.15 (m, 4 H), 1.85-1.82 (m, 2 H), 1.71-1.58 (m, 6 H), 1.50-1.07 (m, 10 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: 49.95. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{22}H_{30}OP$: 341, Found 341. IR (film): 2938, 2852, 1504, 1447, 1155, 917, 889, 805, 776, 739, 540 $cm^{-1}$.



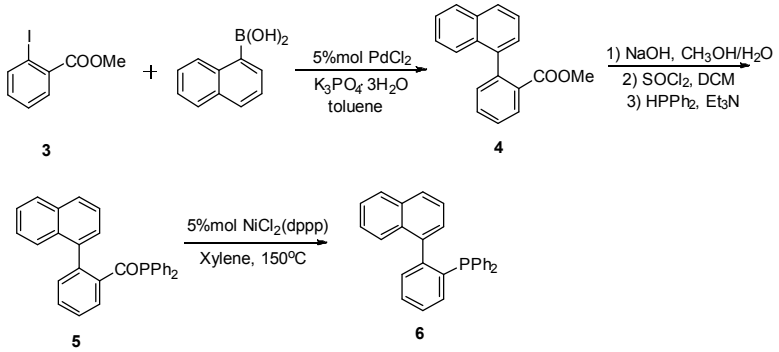

**methyldiphenylphosphine oxide (2k°).** According to the general procedure D, reaction with 1-(diphenylphosphanyl)ethan-1-one **(1k)** (45.6 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol), xylene (0.5 mL), 1 mL methanol and 0.2 mL $H_2O_2$ (30 wt%

in $H_2O$) afforded **2k$^o$** (12.5 mg) in a yield of 29% as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.77-7.68 (m, 4 H), 7.56-7.41 (m, 6 H), 2.02 (d, $J$ = 13.2 Hz, 3 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: 29.82. MS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{13}H_{14}OP$: 217, Found 217. IR (film): 3436, 3054, 1437, 1296, 1185, 1122, 1071, 884, 743, 504 cm$^{-1}$.



**cyclohexyldiphenylphosphine oxide (2l$^o$).** According to the general procedure D, reaction with cyclohexyl(diphenylphosphanyl)methanone **(1l)** (59.2 mg, 0.20 mmol, 1.0 equiv), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol), xylene (0.5 mL), 1 mL methanol and 0.2 mL $H_2O_2$ (30 wt% in $H_2O$) afforded **2l$^o$** (37.5 mg) in a yield of 66% as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.83-7.72 (m, 4 H), 7.53-7.41 (m, 6 H), 2.31-2.13 (m, 1 H), 1.88-1.63 (m, 5 H), 1.62-1.44 (m, 2 H), 1.36-1.15 (m, 3 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: 34.30 MS (ESI) m/z: ([M+H]$^+$) Calcd for $C_{18}H_{22}OP$: 285, Found 285. IR (film): 3053, 2929, 2853, 1437, 1176, 1118, 1071, 741, 698, 535 cm$^{-1}$.

**Procedure to synthesis the 6:**




**Methyl 2-(naphthalen-1-yl)benzoate (4)[5]:**

Under nitrogen, a 100 mL Schlenk flask was charged with methyl 2-iodobenzoate **3** (2.62 g, 10 mmol), naphthalen-1-ylboronic acid (2.58 g, 15 mmol), $K_3PO_4 \cdot 3H_2O$ (7.95 g, 30 mmol), $PdCl_2$ (87.9 mg, 5% mol, 0.5 mmol) and toluene (30 mL). After the mixture was heated at 100$^o$C for 12 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography eluting with hexane/EtOAc (20:1 v/v) on a silica gel to afford the **4** (2.14 g) in a yield of 82% as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.08-8.05 (m, 1 H), 7.91-7.86 (m,2 H), 7.65-7.59 (m, 1 H), 7.56-7.33

(m, 7 H), 3.64 (s, 3 H).

**(diphenylphosphanyl)(2-(naphthalen-1-yl)phenyl)methanone (5):**

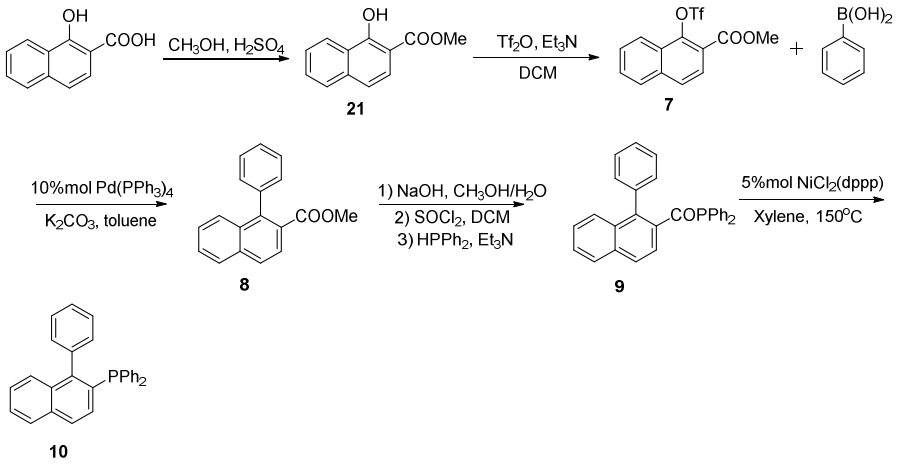
A 100 mL flask was charged with methyl 2-(naphthalen-1-yl)benzoate (**4**) (2.10 g, 8 mmol), NaOH (3.2 g, 80 mmol), methol (15 mL) and $H_2O$ (15 mL). The mixture was heated to reflux at 90$^oC$ for 12 h. The solvent was removed under vaccum and the reaction mixture was acidified with the addition of 6 N HCl (50 mL). The precipitation was filtrated and washed with water (3x15 mL) to afford the **19** (1.82 g) in a yield of 92% as a white solid. In a 50 mL flask, thionyl chloride (5 mL) was added to a solution of 2-(naphthalene- 1-yl)benzoic acid **19** (1.82 g, 7.2 mmol) in $CH_2Cl_2$ (20 mL). The mixture was heated to reflux for 5 h. The mixture was dried under vacuum to obtain 2-(naphthalen-1-yl)benzoyl chloride **20** (1.82 g) in a yield of 95% as a colorless solid. At room temperature, triethylamine (0.79 g, 7.8 mmol) was added to a solution of diphenylphosphine (1.22 g, 6.5 mmol) in 15 mL diethyl ether, followed by addition of 2-(naphthalen-1-yl)benzoyl chloride **20** (1.82 g, 6.8 mmol). After 6 h, the reaction mixture was filtrated through celite, the filtrate was evaporated under vacuum and the residue was recrystallized from 15 mL methol to afford **5** (1.52 g) in a yield of 54% as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.89-7.83 (m, 3 H), 7.48-7.08 (m, 16 H), 7.04-7.00 (m, 2 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: 19.24. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 217.67 (d, $J$ = 41.5 Hz), 141.85 (d, $J$ = 30.1 Hz), 138.63 (d, $J$ = 1.5 Hz), 137.80 (d, $J$ = 1.4 Hz), 134.80 (d, $J$ = 40 Hz), 134.79 (d, $J$ = 2.7 Hz), 133.50, 132.54, 131.91, 130.55, 129.17 (d, $J$ = 5.1 Hz), 128.64 (d, $J$ = 10.3 Hz), 128.34, 128.27, 128.24, 128.10 (d, $J$ = 2.3 Hz), 127.34, 126.25, 126.09, 125.66, 124.91. HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{29}H_{22}OP$: 417.1408, Found 497.1404 IR (film): 3055, 1651, 1480, 1434, 1193, 899, 801, 778, 648, 496 $cm^{-1}$.

**(2-(naphthalen-1-yl)phenyl)diphenylphosphane (6):**

In a sealed vial, under nitrogen, (diphenylphosphanyl)(2-(naphthalen-1-yl)phenyl)methanone **5** (83.2 mg, 0.20 mmol), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) were mixed and stirred at 150$^oC$ for 12 h. The reaction was allowed to cool down to room temperature. The solvent was removed under vacuum. The residue was purified by flash chromatography eluting with hexane/EtOAc (20:1 v/v) on silica gel to afford **6** (63.6 mg) in a yield of 82% as a white solid. $^1$H

NMR (400 MHz, $CDCl_3$) δ: 7.85-7.79 (m, 2 H), 7.46-7.27 (m, 10 H), 7.21-7.15 (m, 6 H), 7.11-7.05 (m, 3 H). $^{31}P$ NMR (162 MHz, $CDCl_3$) δ: -14.26. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{28}H_{22}P$: 389, Found 389. IR (film): 3436, 3011, 1437, 1296, 1185, 1132, 1071, 895, 743, 514 $cm^{-1}$.

**Procedure to synthesis the 10:**




**Methyl 1-hydroxy-2-naphthoate (21):**

In a 100 mL flask, 2mL $H_2SO_4$ was added slowly to a solution of 1-hydroxy-2-naphthoic acid (4.0 g, 21.2 mmol) in 40 mL methol under continuous stirring. The reaction mixture was heated to refluxed at 100°C for 24 h. The reaction mixture was dried under vacuum and the residue was purified by flash chromatography eluting with hexane/EtOAc (2:1 v/v)on a silica gel to afford **21** (3.4 g) in a yield of 80% as a white solid. $^1H$ NMR (400 MHz, $CDCl_3$) δ: 11.99 (s, 1 H), 8.42 (d, $J$ = 8.6 Hz, 1 H), 7.77 (d, $J$ = 8.9 Hz, 2 H), 7.61 (m, 1 H), 7.53 (m, 1 H), 7.29 (d, $J$ = 8.9 Hz, 1 H), 3.87 (s, 3 H).

**Methyl 1-(((trifluoromethyl)sulfonyl)oxy)-2-naphthoate (7):**

In a 100 mL flask, 3.5 mL $Tf_2O$ (5.7 g, 20.4 mmol) was added slowly to a solution of 1-hydroxy-2-naphthoate **21** (3.4 g, 17.0 mmol), $Et_3N$ (2.58 g, 25.5 mmol) in $CH_2Cl_2$ (30 mL) under continuous stirring. After 6 h, the reaction mixture was poured into 30 mL water and extracted with ethyl acetate (3 x 40 mL). The combined organic phase was dried under vacuum and the residue was purified by flash chromatography eluting with hexane/EtOAc (20:1 v/v)on a silica gel to afford **7** (5.2 g) in a yield of 92% as a white solid. $^1H$ NMR (400 MHz, $CDCl_3$) δ: 8.23-8.20 (m, 1 H), 8.04-8.02 (m,

1 H), 7.97-7.92 (m, 2 H), 7.73-7.70 (m, 2 H), 4.04 (s, 3 H).

**Methyl 1-phenyl-2-naphthoate (8)[6]:**

Under nitrogen, a 100 mL Schlenk flask was charged with methyl 1-(((trifluoromethyl)-sulfonyl)oxy)-2-naphthoate **7** (5.2 g, 15.64 mmol), phenylboronic acid (2.9 g, 24 mmol), $K_2CO_3$ (3.45 g, 25 mmol), $Pd(PPh_3)_4$ (1.8 g, 10% mol, 1.56 mmol) and toluene (40 mL). After the mixture was heated at 100°C for 12 h, the solvent was evaporated under vacuum and the residue was purified by flash chromatography eluting with hexane/EtOAc (20:1 v/v) on a silica gel to afford the **8** (3.77 g) in a yield of 92% as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.97-7.86 (m, 3 H), 7.60 (d, *J* = 8.6 Hz, 1 H), 7.56 (dd, *J* = 7.5, 1.0 Hz, 1 H), 7.52-7.39 (m, 4 H), 7.31 (dd, *J* = 7.7, 1.5 Hz, 2 H), 3.62 (s, 3 H).

**(diphenylphosphanyl)(1-phenylnaphthalen-2-yl)methanone (9):**

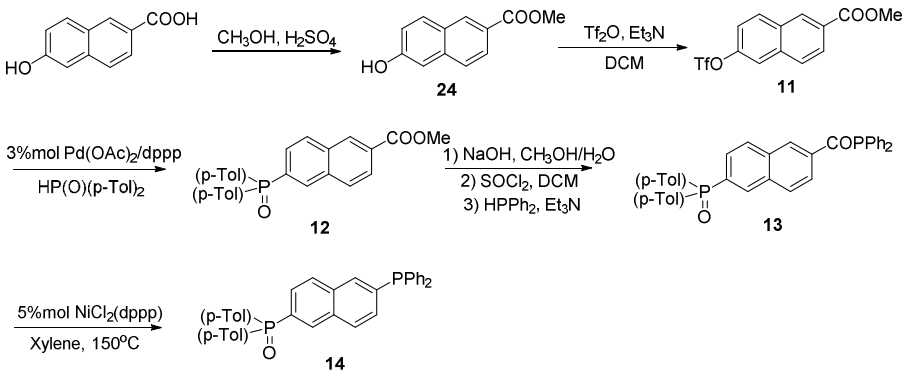
A 250 mL flask was charged with Methyl 1-phenyl-2-naphthoate **8** (3.77 g, 14.39 mmol), NaOH (5.6 g, 140 mmol), methol (40 mL) and $H_2O$ (40 mL). The mixture was heated to reflux at 90°C for 12 h. The solvent was removed under vaccum and the reaction mixture was acidified with the addition of 6N HCl (100 mL). The precipitation was filtrated and washed with water (3 x 30 mL) to afford 1-phenyl-2-naphthoic acid **22** in a yield of 79% as a white solid. In a 50 mL flask, thionyl chloride (5 mL) was added to a solution of 1-phenyl-2-naphthoic acid **22** (2.82 g, 11.36 mmol) in $CH_2Cl_2$ (30 mL). The mixture was heated to reflux for 5 h. The mixture was dried under vacuum to obtain 1-phenyl-2-naphthoyl chloride **23** (2.92 g) in a yield of 96% as a colorless solid. At room temperature, triethylamine (1.26 g, 12.5 mmol) was added to a solution of diphenylphosphine (1.93 g, 10.39 mmol) in 30 mL diethyl ether, followed by addition of 1-phenyl-2-naphthoyl chloride **23** (2.92 g, 10.91 mmol). After 6 h, the reaction mixture was filtrated through celite, the filtrate was evaporated under vacuum and the residue was recrystallized from 30 mL methol to afford **9** (2.85 g) in a yield of 66% as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.85-7.77 (m, 2 H), 7.69 (d, *J* = 8.5 Hz, 1 H), 7.54 (d, *J* = 8.5 Hz, 1 H), 7.50-7.38 (m, 4 H), 7.38-7.31 (m, 1 H), 7.29-7.14 (m, 10 H), 7.14-7.07 (m, 2 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: 21.37. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 219.98 (d, *J* = 41.8 Hz), 138.68 (d, *J* = 29.0 Hz), 137.73, 137.02, 134.87 (d, *J* = 18.8 Hz), 134.14, 132.32 (d, *J* = 8.4 Hz), 132.19, 131.83 (d, *J* = 9.2 Hz), 131.48 (d, *J* = 2.0 Hz), 130.86, 129.24, 128.35 (d, *J* = 7.6 Hz), 127.92 (d, *J* = 3.2 Hz),

127.81, 127.53, 127.35, 127.04, 126.59. HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{29}H_{22}OP$: 417.1408, Found 417.1413 IR (film): 3054, 1655, 1481, 1434, 1196, 1028, 951, 783, 696, 505, 490 $cm^{-1}$.

**Diphenyl(1-phenylnaphthalen-2-yl)phosphane (10):**

In a sealed vial, under nitrogen, (diphenylphosphanyl)(1-phenylnaphthalen-2-yl)methanone **9** (83.2 mg, 0.20 mmol), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) were mixed and stirred at 150°C for 12 h. The reaction was allowed to cool down to room temperature. The solvent was removed under vacuum. The residue was purified by flash chromatography eluting with hexane/EtOAc (20:1 v/v) on silica gel to afford **10** (67.5 mg) in a yield of 87% as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1 H), 7.51-7.43 (m, 2 H), 7.42-7.32 (m, 4 H), 7.31-7.17 (m, 11 H), 7.17-7.11 (m, 2 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: -13.71. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 146.87 (d, *J* = 31.6 Hz), 139.42 (d, *J* = 8.5 Hz), 139.42 (d, *J* = 8.5 Hz), 133.75 (d, *J* = 19 Hz), 133.75, 133.46, 132.83 (d, *J* = 6.3 Hz), 132.83 (d, *J* = 6.3 Hz), 129.73, 128.34 (d, *J* = 1.7 Hz), 128.29, 127.81, 127.76, 127.61, 127.43, 127.01 (d, *J* = 2.8 Hz), 126.54, 126.19. HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{28}H_{22}P$: 389.1459, Found 389.1455. IR (film): 3045, 2917, 1496, 1185, 1092, 1020, 806, 796, 774, 507, 497 $cm^{-1}$.

**Procedure to synthesis the 14:**




**Methyl 6-hydroxy-2-naphthoate (24):**

In a 100 mL flask, 2 mL $H_2SO_4$ was added slowly to a solution of 6-hydroxy-2-naphthoic acid (4.0 g, 21.2 mmol) in 40 mL methol under continuous stirring. The reaction mixture was heated to

refluxed at 100°C for 24 h. The reaction mixture was dried under vacuum and the residue was purified by flash chromatography eluting with hexane/EtOAc (2:1 v/v)on a silica gel to afford **24** (3.4 g) in a yield of 75% as a white solid. $^1$H NMR (400 MHz, DMSO-$d_6$) δ: 10.20 (s, 1 H), 8.50 (s, 1 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.89-7.86 (m, 1 H), 7.79-7.77 (m, 1 H), 7.20-7.17 (m, 2 H), 3.89 (s, 3 H).

**Methyl 6-(((trifluoromethyl)sulfonyl)oxy)-2-naphthoate (11):**

In a 100 mL flask, 3.3 mL $Tf_2O$ (5.4 g, 19.1 mmol) was added slowly to a solution of 6-hydroxy-2-naphthoate **24** (3.2 g, 15.9 mmol), $Et_3N$ (2.42 g, 24.0 mmol) in $CH_2Cl_2$ (30 mL) under continuous stirring. After 6 h, the reaction mixture was poured into 30 mL water and extracted with ethyl acetate (3 x 30 mL). The combined organic phase was dried under vacuum and the residue was purified by flash chromatography eluting with hexane/EtOAc (20:1 v/v)on a silica gel to afford **11** (4.4 g) in a yield of 83% as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.65 (s, 1 H), 8.17 (dd, *J* = 8.6, 1.6 Hz, 1 H), 8.05 (d, *J* = 9.0 Hz, 1 H), 7.93 (d, *J* = 8.7 Hz, 1 H), 7.80 (d, *J* = 2.4 Hz, 1 H), 7.45 (dd, *J* = 9.0, 2.5 Hz, 1 H), 4.00 (s, 3 H).

**Methyl 6-(di-p-tolylphosphoryl)-2-naphthoate (12)[7]:**

In a 100 mL Schlenk flask, under nitrogen, a mixture of $Pd(OAc)_2$ (90.0 mg, 0.4 mmol), dppp (165 mg, 0.4 mmol) and DMSO (30 mL) at room temperature was stirred for 30 minutes. Methyl 6-(((trifluoromethyl)sulfonyl)oxy)-2-naphthoate **11** (4.4 g, 13.2 mmol), di-p-tolylphosphine oxide (6.07 g, 26.4 mmol), and $EtN(i\text{-}Pr)_2$ (8.53 g, 66 mmol) was added to the mixture. And then, the mixture was stirred at 100°C for 20 h. After cooling to room temperature, 50 mL diethyl ether was added to the reaction mixture. The organic phase was washed with water (3 x 50 mL) and dried by $Na_2SO_4$. The solvent was dried under vacuum and the residue was purified by flash chromatograghy eluting with hexane/EtOAc (1:1 v/v)on silica gel to afford **12** (4.86 g) in a yield of 89% as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.62 (s, 1 H), 8.31 (d, *J* = 13.6 Hz, 1 H), 8.10 (d, *J* = 1.5 Hz, 1 H), 7.99 (dd, *J* = 8.5, 2.6 Hz, 1 H), 7.92 (d, *J* = 8.6 Hz, 1 H), 7.76 – 7.65 (m, 1 H), 7.64 – 7.53 (m, 4 H), 7.33 – 7.21 (m, 4 H), 3.99 (s, 3 H), 2.41 (s, 6 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: 28.77. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 166.82, 142.61 (d, *J* = 2.8 Hz), 134.44 (d, *J* = 13.1 Hz), 133.74 (d, *J* = 2.4 Hz), 133.49 (d, *J* = 9.2 Hz), 133.16 (d, *J* = 100 Hz), 132.16 (d, *J* = 10.3 Hz), 130.74, 129.55, 129.42,

129.29, 129.23, 129,11 (d, $J$ = 106 Hz), 127.77 (d, $J$ = 10.5 Hz), 126.24, 52.42, 21.63. HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{26}H_{24}O_3P$: 415.1463, Found 415.1466. IR (film): 3043, 2918, 1496, 1185, 1092, 1020, 806, 799, 771, 507, 491 $cm^{-1}$.

**(6-(di-p-tolylphosphoryl)naphthalen-2-yl)(diphenylphosphanyl)methanone (13):**

A 250 mL flask was charge with methyl 6-(di-p-tolylphosphoryl)-2-naphthoate **12** (4.86 g, 11.75 mmol), NaOH (4.8 g, 120 mmol), methol (40 mL) and $H_2O$ (40 mL). The mixture was heated to reflux at 90$^o$C for 12 h. The solvent was removed under vaccum and the reaction mixture was acidified with the addition of 6N HCl (100 mL). The precipitation was filtrated and washed with water (3 x 30 mL) to afford 6-(di-p-tolylphosphoryl)-2-naphthoic acid **25** (3.76 g) in a yield of 80% as a white solid. In a 50 mL flask, thionyl chloride (5 mL) was added to a solution of 6-(di-p-tolylphosphoryl)-2-naphthoic acid (3.76 g, 9.4 mmol) **25** in toluene (30 mL). The mixture was heated to 100$^o$C for 5 h. The mixture was dried under vacuum to obtain 6-(di-p-tolylphosphoryl)-2-naphthoyl chloride **26** (3.85 g) in a yield of 98% as a colorless solid. At room temperature, triethylamine (1.06 g, 10.51 mmol) was added to a solution of diphenylphosphine (1.63 g, 8.76 mmol) in 30 mL diethyl ether, followed by addition of 6-(di-p-tolylphosphoryl)-2-naphthoyl chloride (3.85 g, 9.2 mmol) **26**. After 6 h, the reaction mixture was filtrated through celite, the filtrate was evaporated under vacuum and the residue was recrystallized from 30 mL PE/EtOAc (2:1 v/v) to afford **13** (4.38 g) in a yield of 88% as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.59 (s, 1 H), 8.23 (d, $J$ = 13.5 Hz, 1 H), 8.01 (d, $J$ = 8.5 Hz, 1 H), 7.90 (d, $J$ = 7.0 Hz, 1 H), 7.82 (d, $J$ = 8.6 Hz, 1 H), 7.69-7.61 (m, 1 H), 7.61-7.50 (m, 4 H), 7.49-7.39 (m, 4 H), 7.39-7.31 (m, 6 H), 7.30-7.20 (m, 4 H), 2.40 (s, 6 H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ: 28.61, 13.79. $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 212.82 (d, $J$ = 37.7 Hz), 142.63 (d, $J$ = 2.7 Hz), 138.33 (d, $J$ = 34.6 Hz), 134.91 (d, $J$ = 18.7 Hz), 134.50 (d, $J$ = 13.1 Hz), 133.37 (d, $J$ = 101 Hz), 133.74, 133.40 (d, $J$ = 9.2 Hz), 132.42 (d, $J$ = 5.3 Hz), 132.13 (d, $J$ = 10.3 Hz), 129.99 (d, $J$ = 11.8 Hz), 129.81 (d, $J$ = 11.7 Hz), 129.65, 129.04 (d, $J$ = 106 Hz), 129.50, 129.35 (d, $J$ = 12.6 Hz), 128.79 (d, $J$ = 7.9 Hz), 127.82 (d, $J$ = 10 Hz), 124.63 (d, $J$ = 6.8 Hz), 21.63. HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{37}H_{31}O_2P_2$: 569.1799, Found 569.1790 IR (film): 3051, 2920, 1639, 1434, 1186, 1116, 1102, 695, 663, 534 $cm^{-1}$.

**(6-(diphenylphosphanyl)naphthalen-2-yl)di-p-tolylphosphine oxide (14):**

In a sealed vial, under nitrogen, (6-(di-p-tolylphosphoryl)naphthalen-2-yl) (diphenylphospha-nyl)methanone **13** (113.62 mg, 0.20 mmol), $NiCl_2$(dppp) (5.4 mg, 5% mol, 0.01 mmol) and xylene (0.5 mL) were mixed and stirred at 150$^oC$ for 12 h. The reaction was allowed to cool down to room temperature. The solvent was removed under vacuum. The residue was purified by flash chromatography eluting with hexane/EtOAc (1:1 v/v) on silica gel to afford **14** (67.0 mg) in a yield of 62% as a white solid. $^1H$ NMR (400 MHz, $CDCl_3$) δ: 8.25 (d, *J* = 13.6 Hz, 1 H), 7.83-7.72 (m, 3 H), 7.66-7.52 (m, 5 H), 7.47-7.40 (m, 1 H), 7.39-7.29 (m, 10 H), 7.29-7.21 (m, 4 H), 2.40 (s, 6 H). $^{31}P$ NMR (162 MHz, $CDCl_3$) δ: 28.93, -4.55. $^{13}C$ NMR (100 MHz, $CDCl_3$) δ: 142.43 (d, *J* = 2.8 Hz), 138.10 (d, *J* = 12.8 Hz), 136.52 (d, *J* = 10.8 Hz), 136.52 (d, *J* = 10.8 Hz), 133.60, 133.45 (d, *J* = 12.1 Hz), 132.16 (d, *J* = 10.2 Hz), 131.96 (d, *J* = 72 Hz), 130.93 (d, *J* = 18.4 Hz), 130.58, 129.97, 129.27 (d, *J* = 12.5 Hz), 129.03, 128.91, 128.78 (d, *J* = 6.9 Hz), 128.66 (d, *J* = 7.1 Hz), 128.24 (d, *J* = 11.8 Hz), 127.47 (d, *J* = 10.5 Hz), 21.63. HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd for $C_{36}H_{31}OP_2$: 541.1850, Found 541.1852 IR (film): 3048, 1607, 1431, 1193, 1116, 1103, 808, 697, 667, 535 $cm^{-1}$.

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(2) Yang, J.; Chen, X.; Wang, Z. *Tetrahedron Lett*. **2015**, *56*, 5673.

(3) Hayashi, M.; Ishitobi, H.; Matsuura, Y.; Matsuura, T.; Watanabe, Y. *Org. Lett*. **2014**, *16*, 5830.

(4) Uozumi, Y.; Tanahashi, A.; Lee, S.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945.

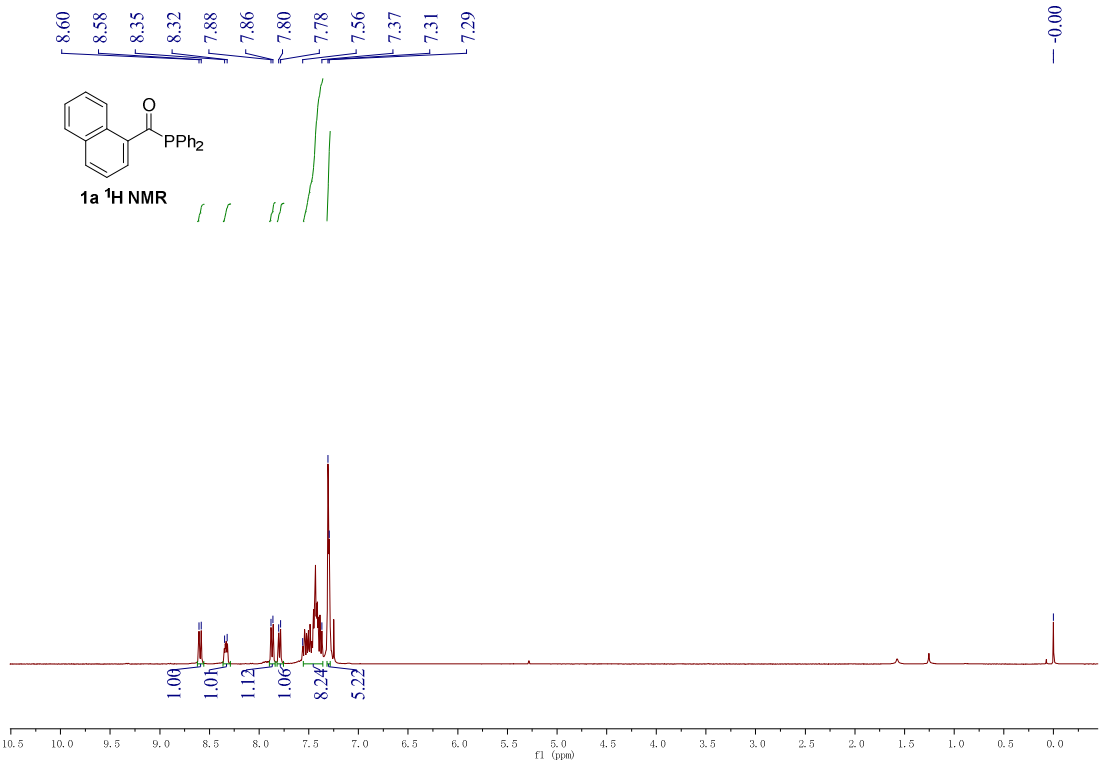
(5) Pan, C.; Liu, M.; Zhang, L.; Wu, H.; Ding, J.; Cheng, J. *Catal. Commun*. **2008**, *9*, 508.

(6) Peng, S.; Wang, L.; Wang, J. *Chem. Eur. J*. **2013**, *19*, 13322.

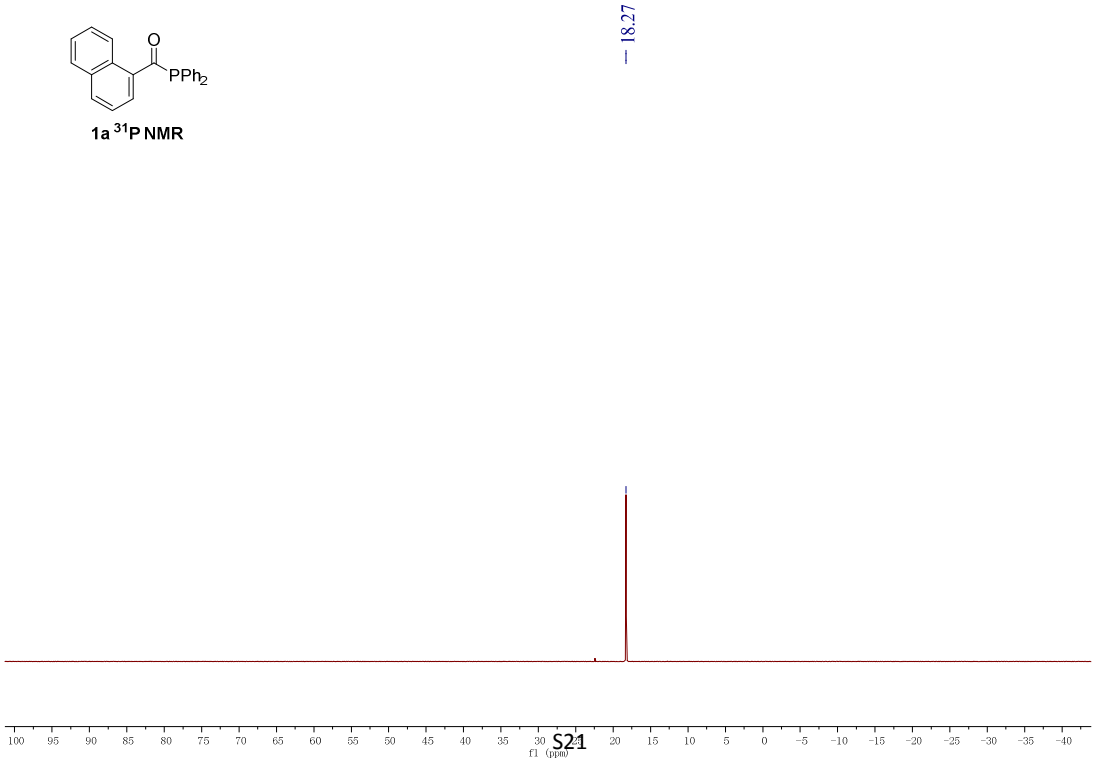
(7) Feng, J.; Li, B.; He, Y.; Gu, Z. *Angew. Chem. Int. Ed*. **2016**, *55*, 2186.

# NMR Spectra:

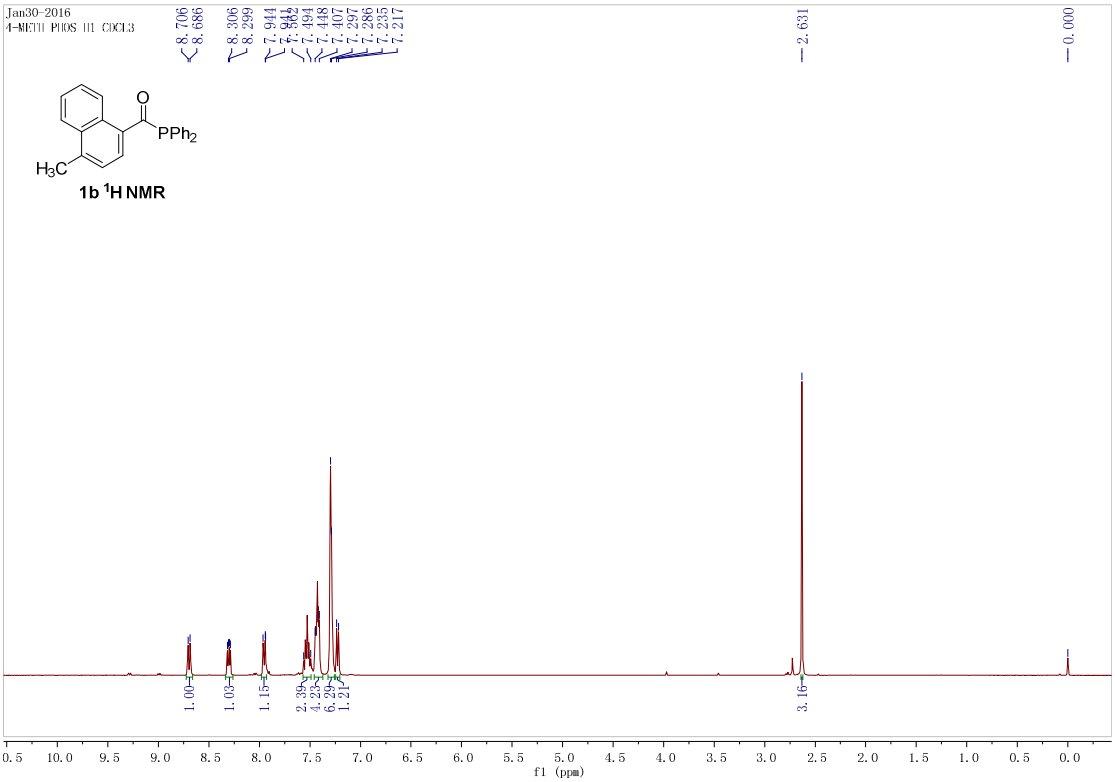
$^{1}$H NMR spectra of **1a** in $CDCl_3$:



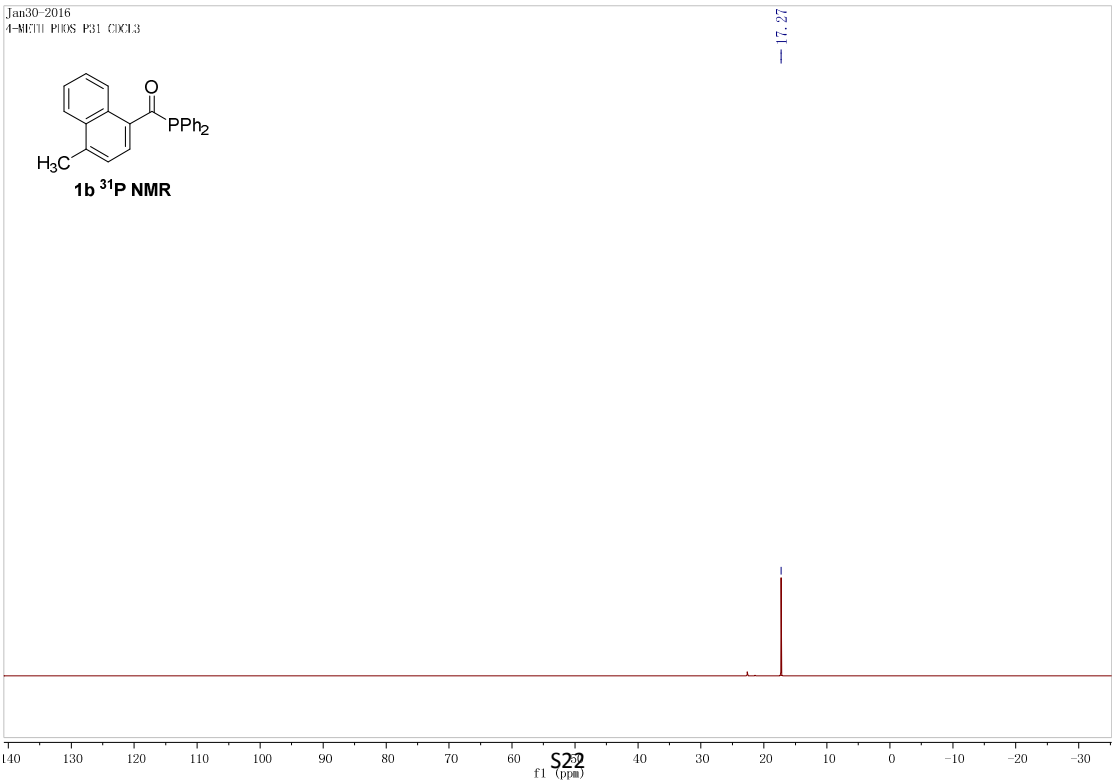

$^{31}$P NMR spectra of **1a** in $CDCl_3$:



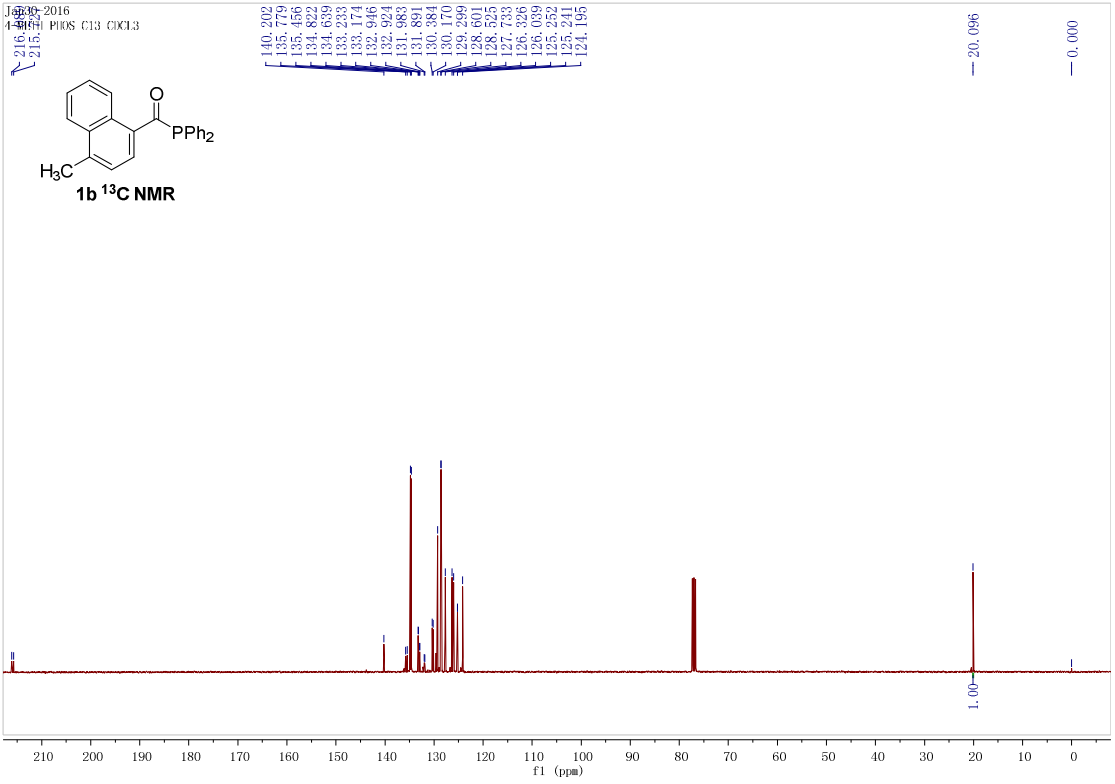
$^{1}$H NMR, spectra of **1b** in $CDCl_3$:



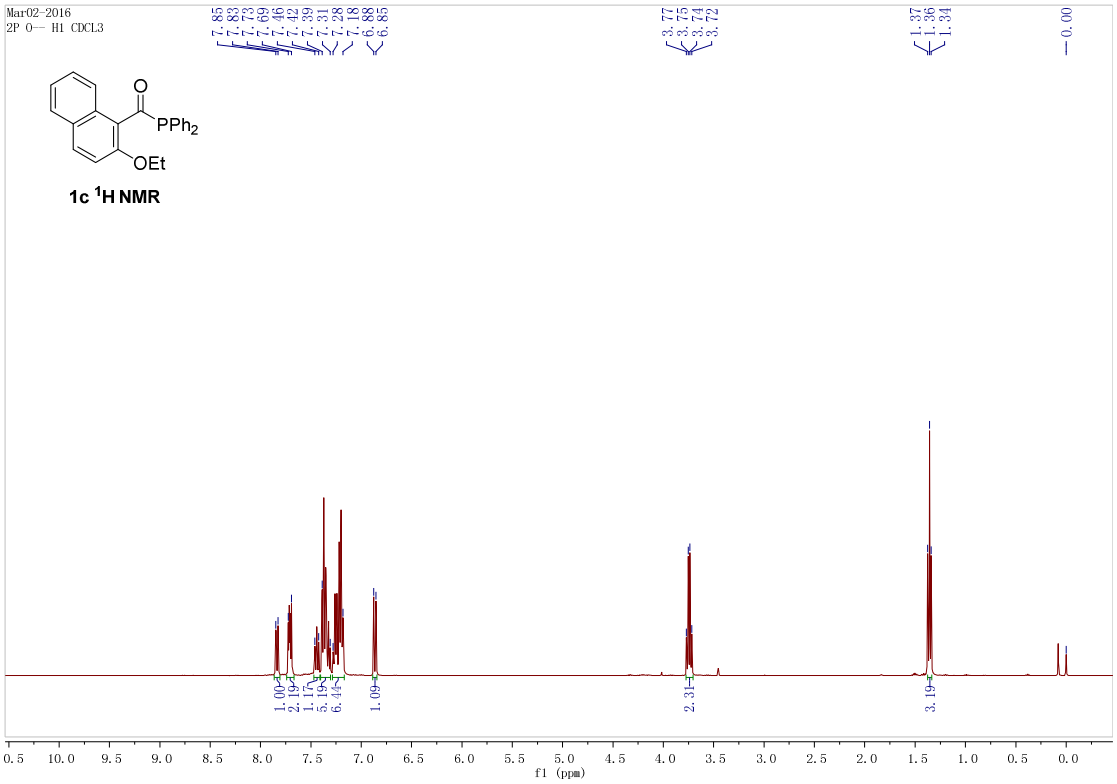

$^{31}$P NMR spectra of **1b** in $CDCl_3$:



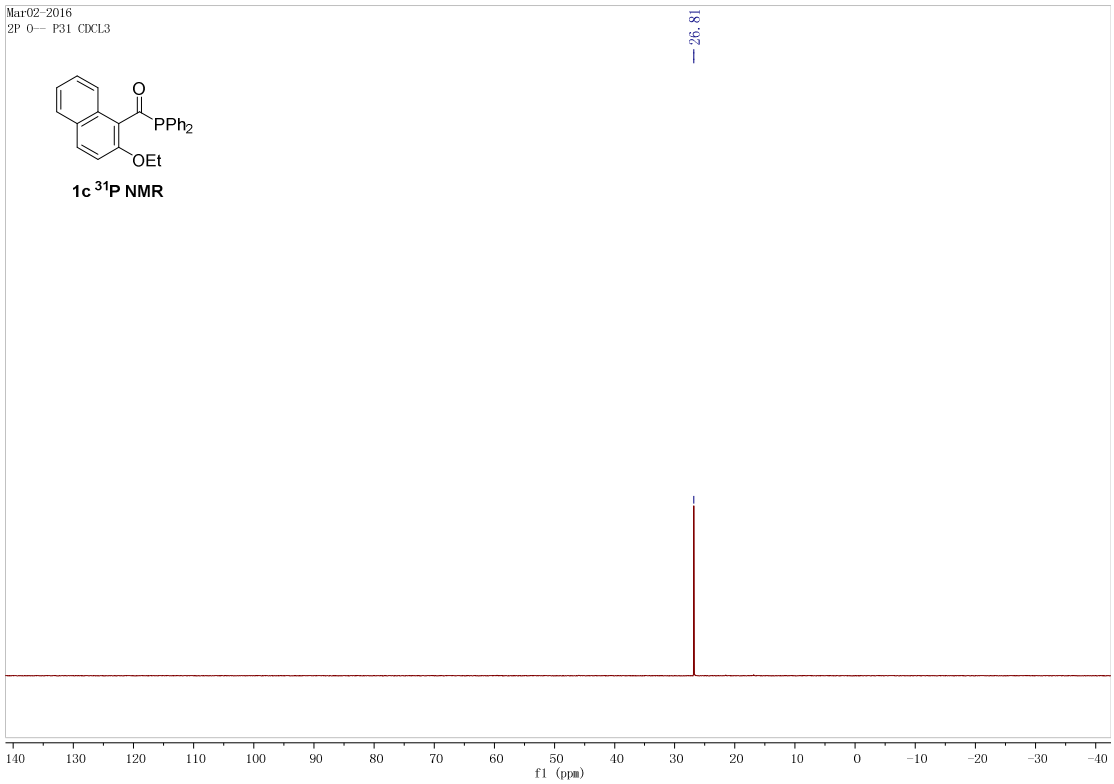
$^{13}C$ NMR spectra of **1b** in $CDCl_3$:



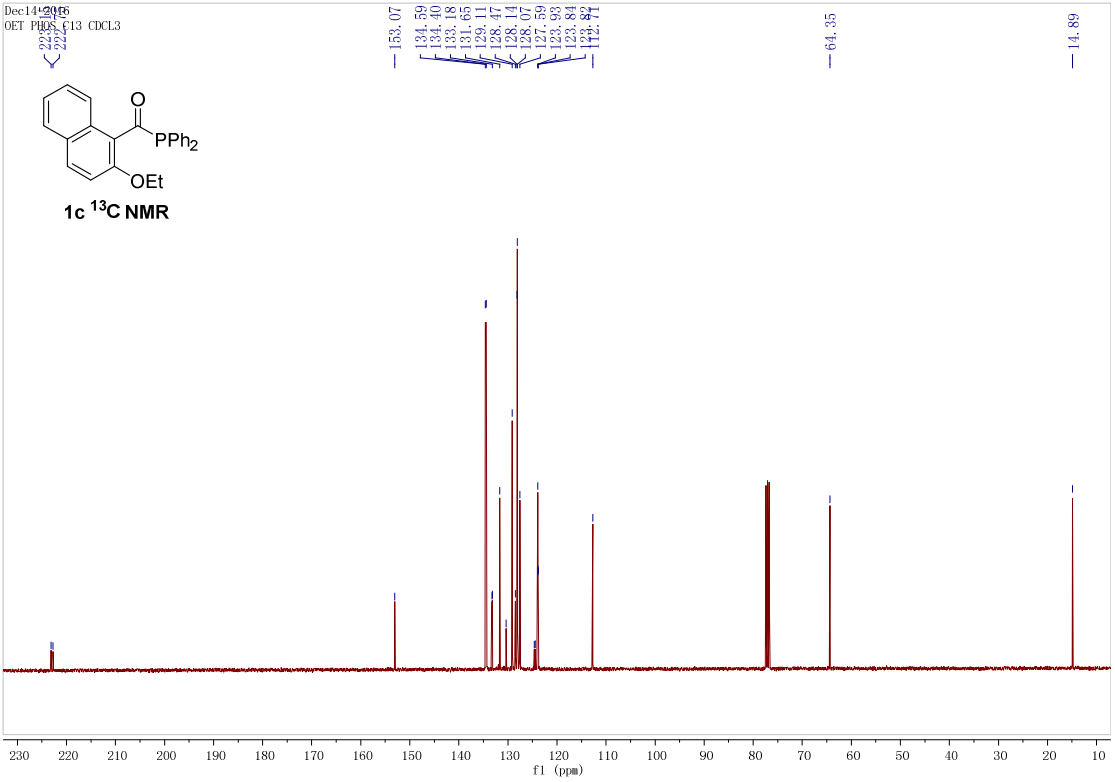
$^{1}$H NMR spectra of **1c** in $CDCl_3$:



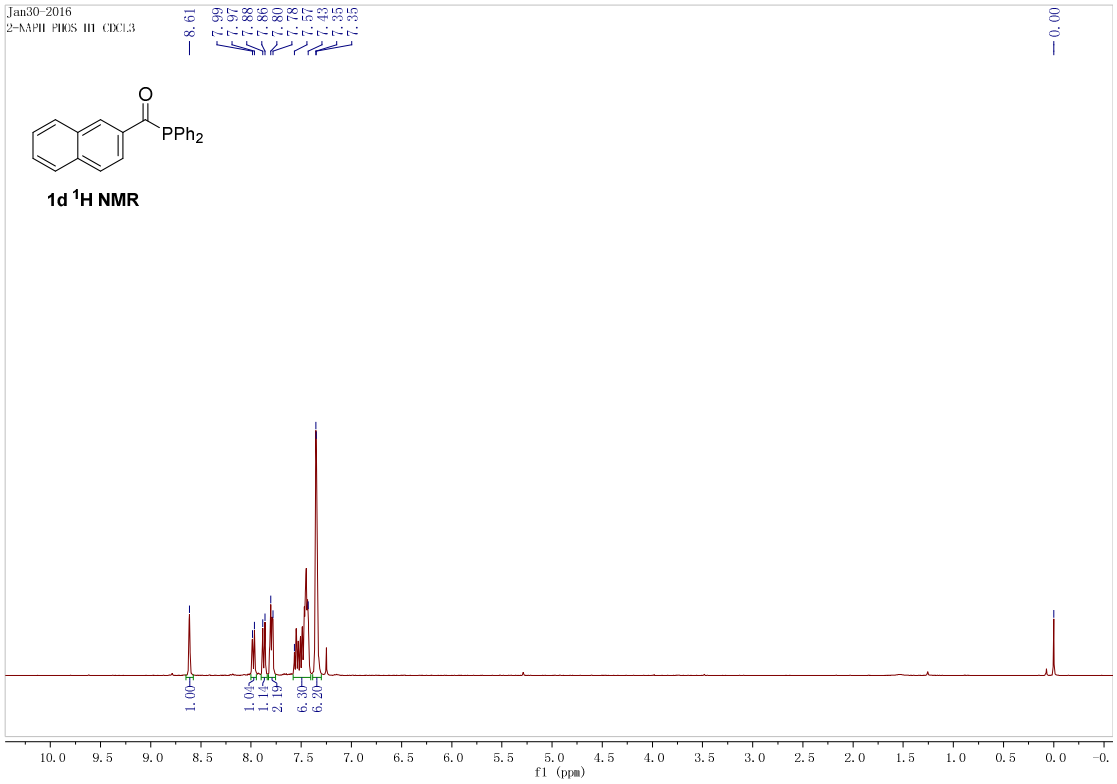

$^{31}$P NMR spectra of **1c** in $CDCl_3$:



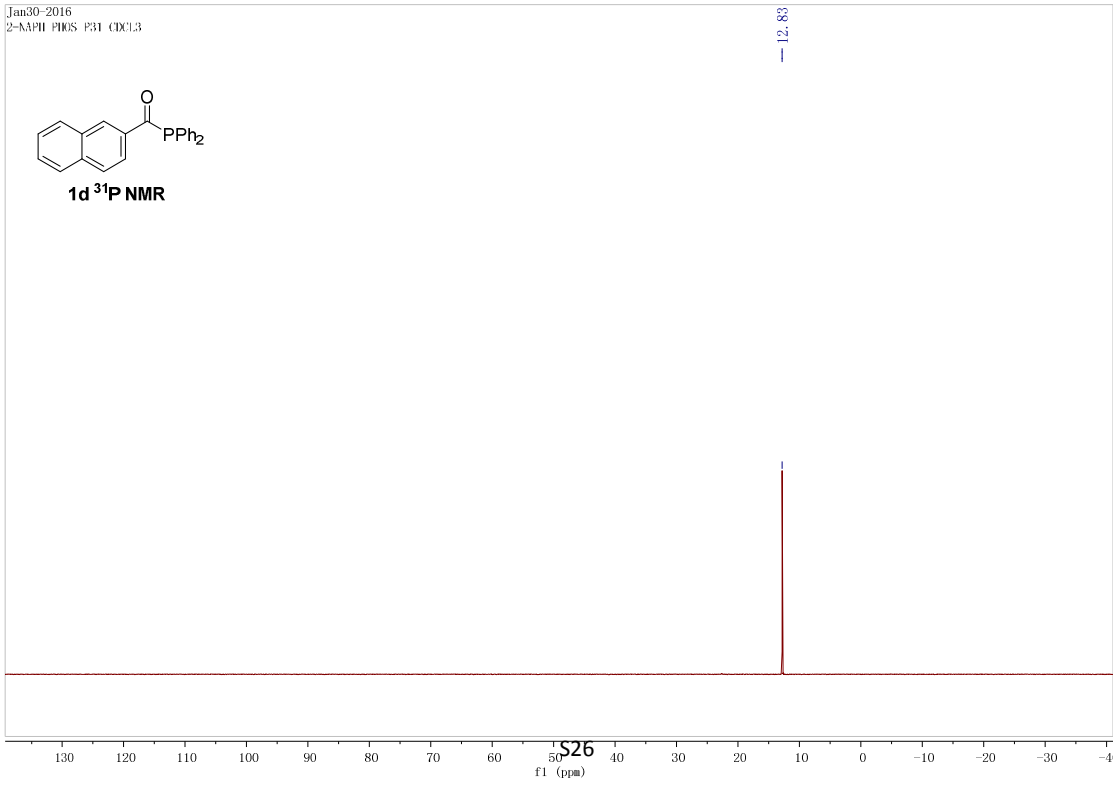
$^{13}C$ NMR spectra of **1c** in $CDCl_3$:



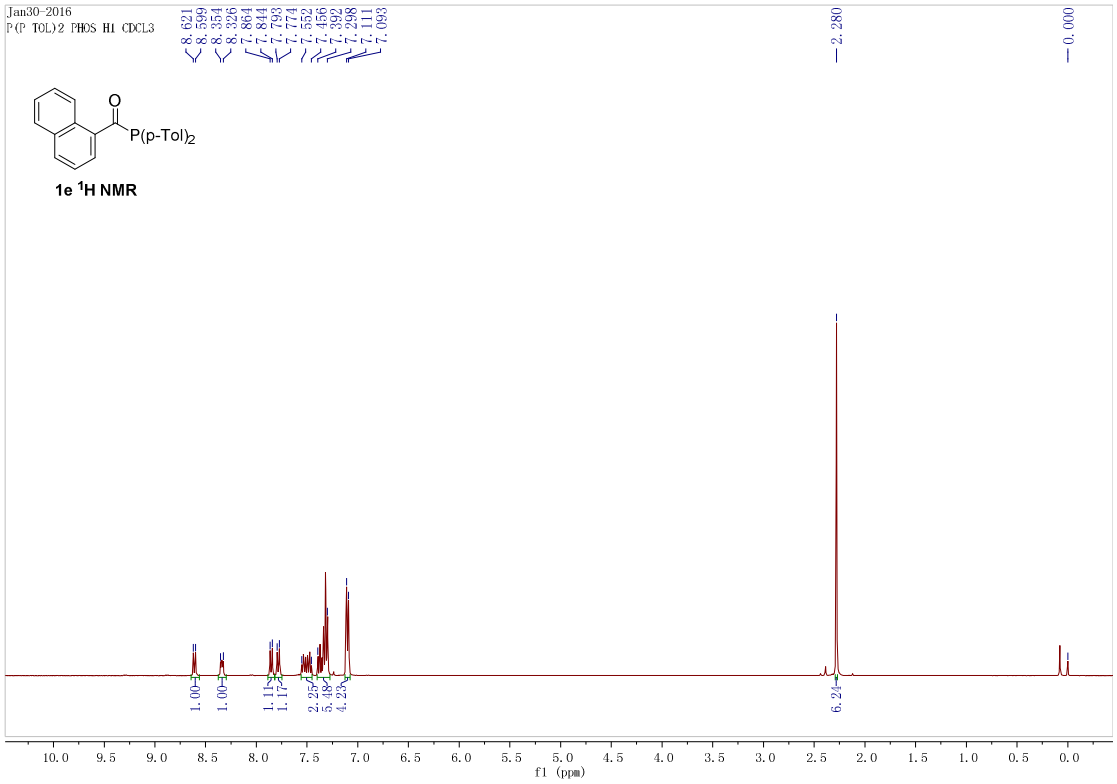
$^{1}$H NMR spectra of **1d** in $CDCl_3$:



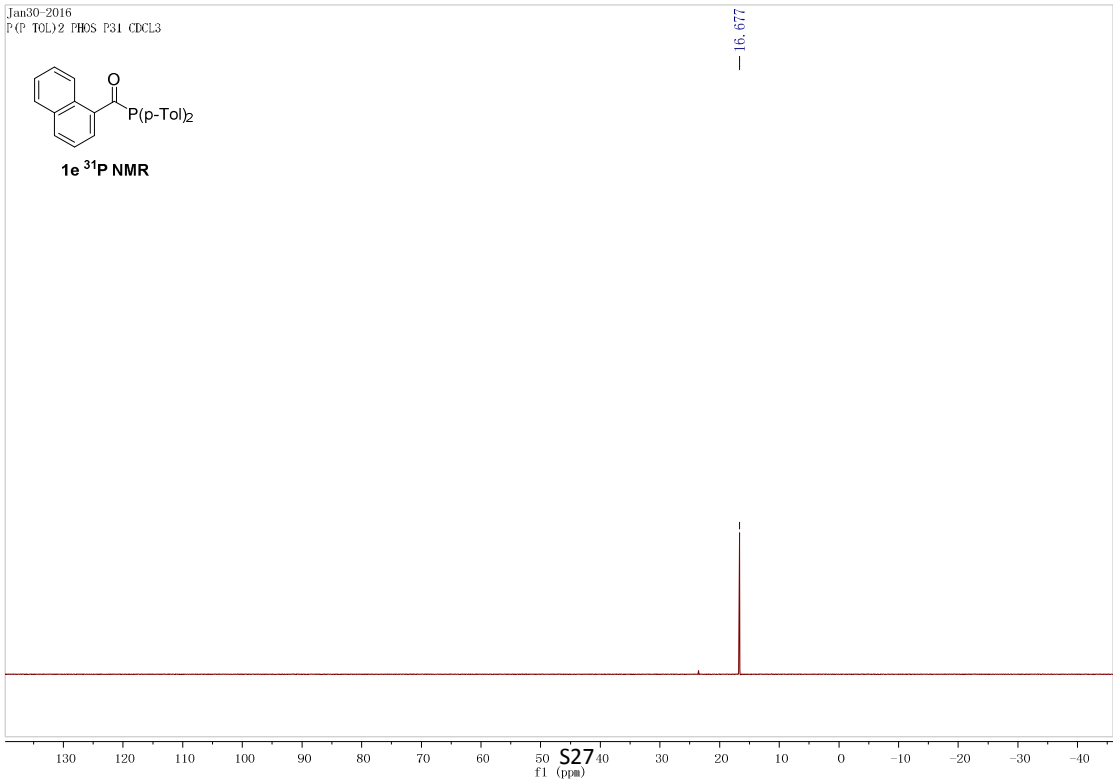

$^{31}$P NMR spectra of **1d** in $CDCl_3$:



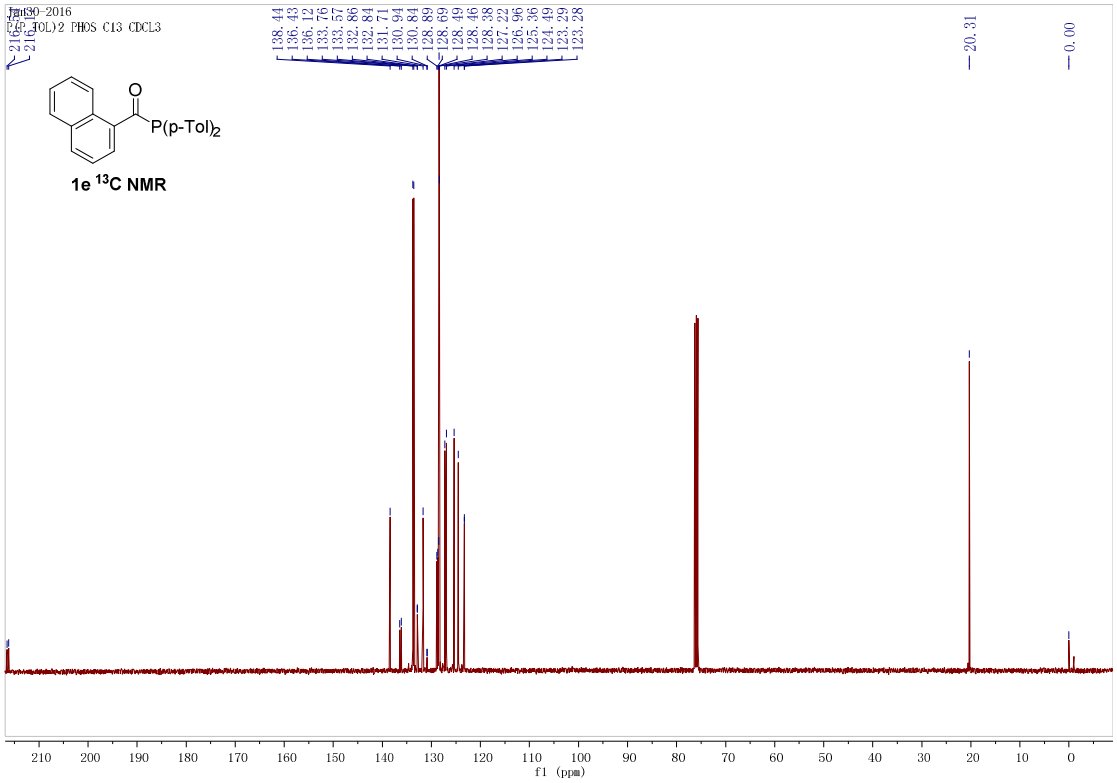
$^{1}$H NMR spectra of **1e** in $CDCl_3$:



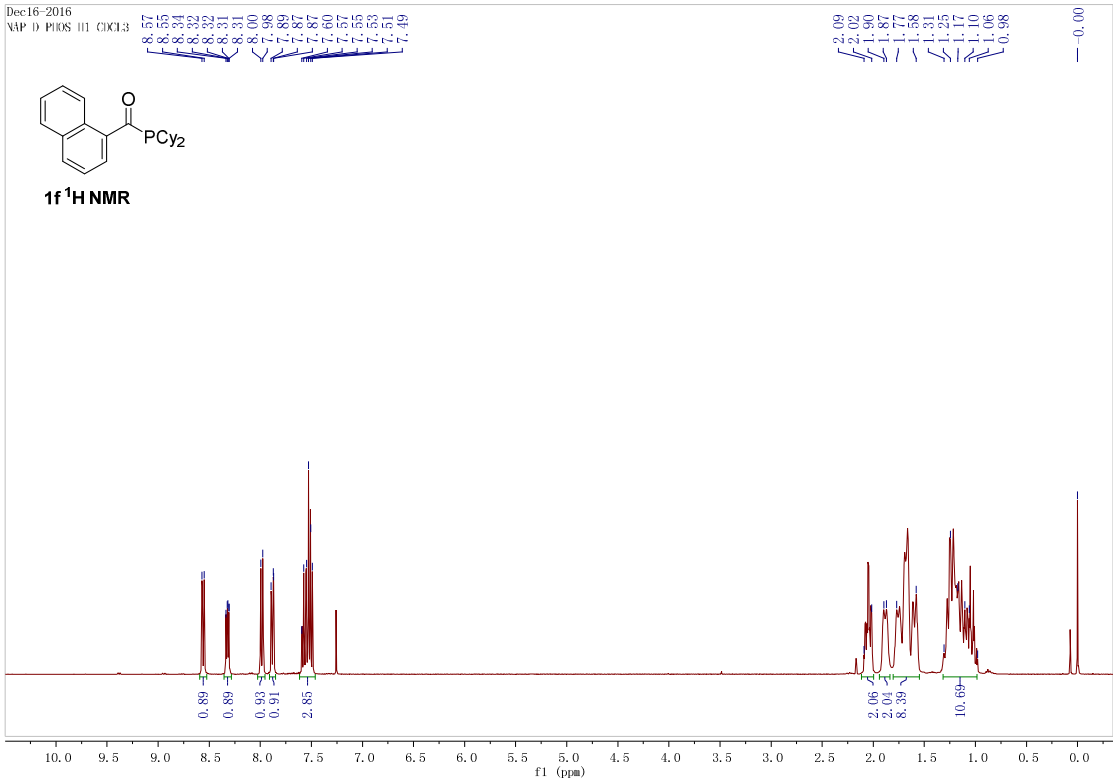

$^{31}$P NMR spectra of **1e** in $CDCl_3$:



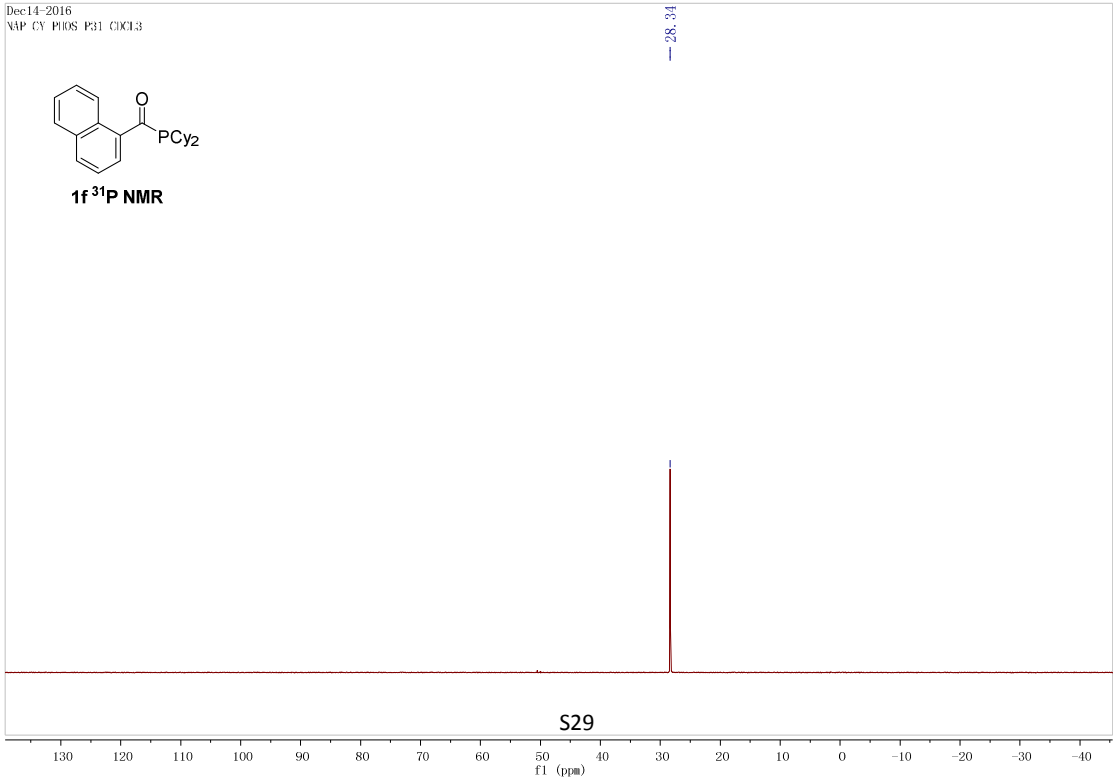
$^{13}C$ NMR spectra of **1e** in $CDCl_3$:



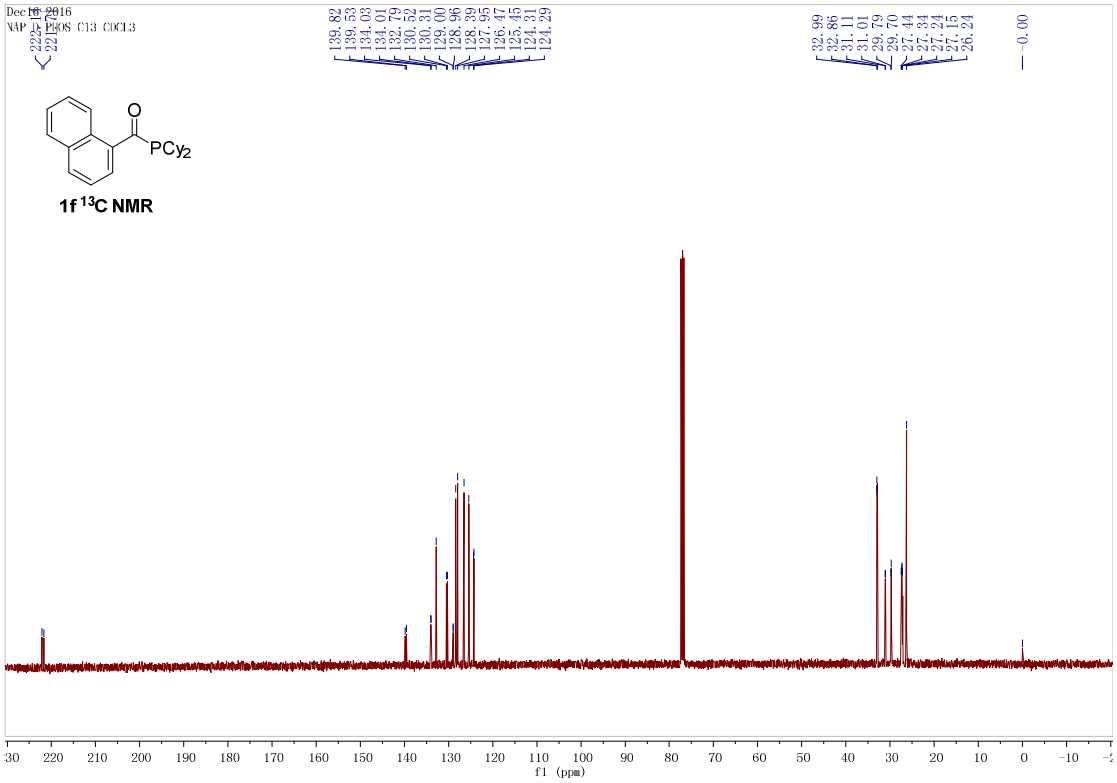
$^{1}$H NMR spectra of **1f** in $CDCl_3$:



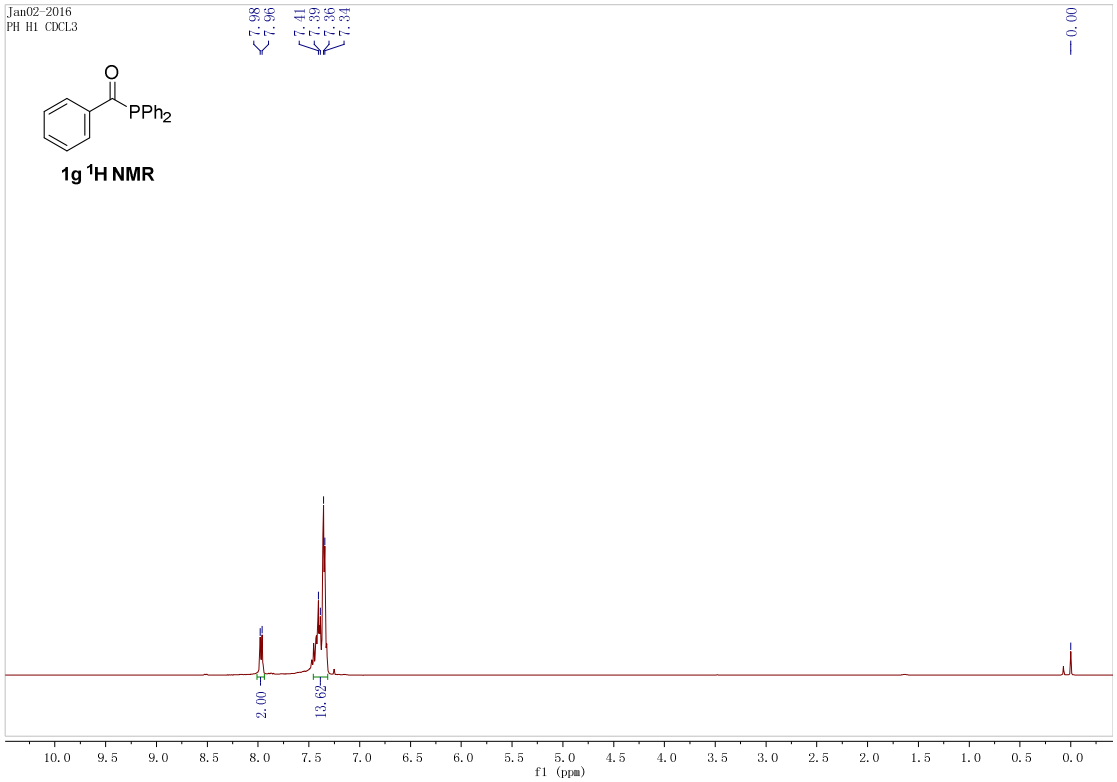

$^{31}$P NMR spectra of **1f** in $CDCl_3$:



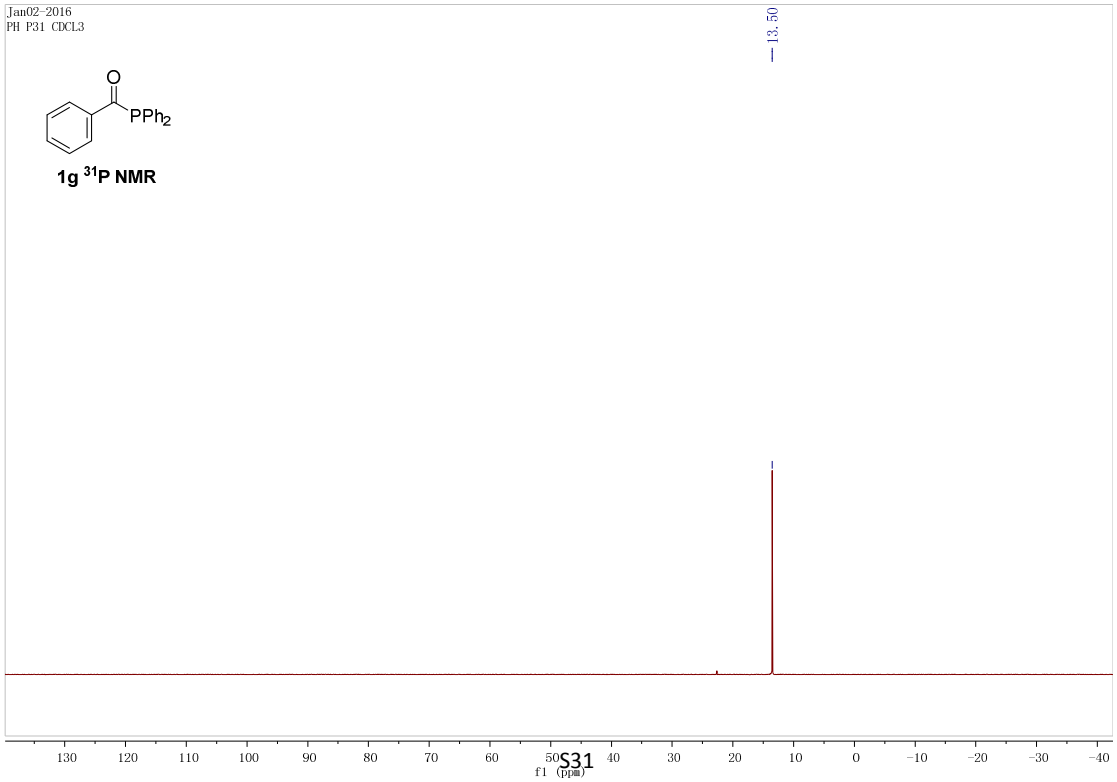
$^{13}C$ NMR spectra of **1f** in $CDCl_3$:



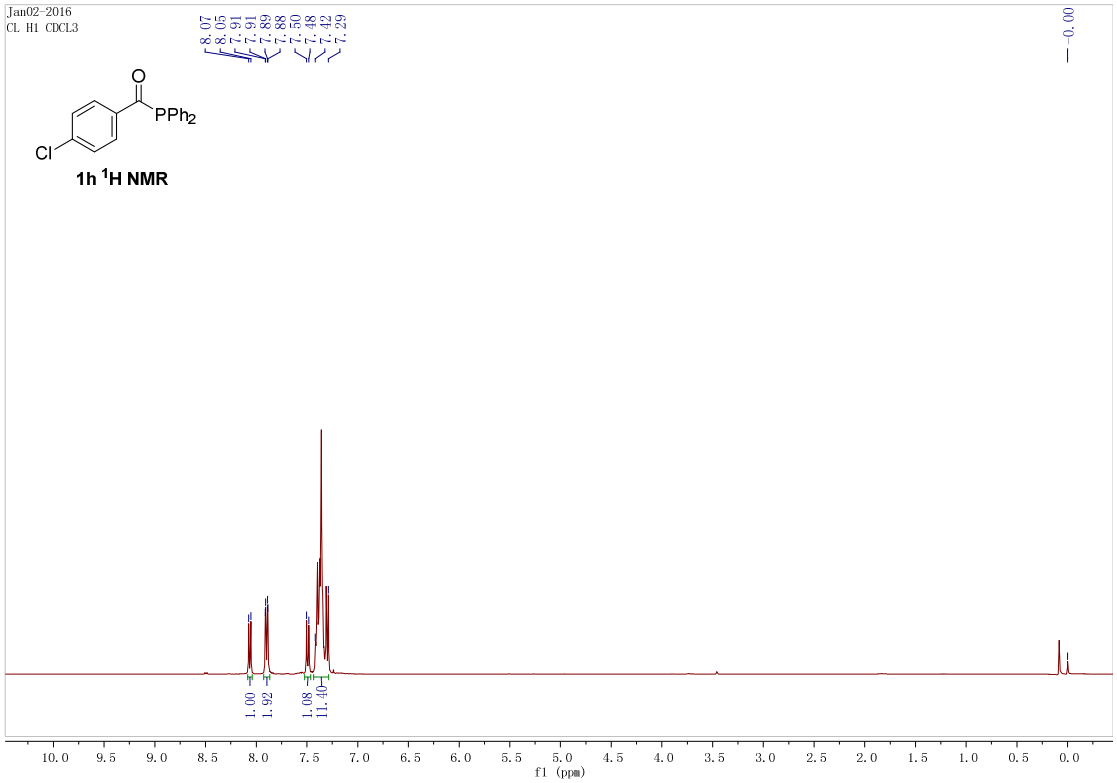
$^{1}$H NMR spectra of **1g** in $CDCl_3$:



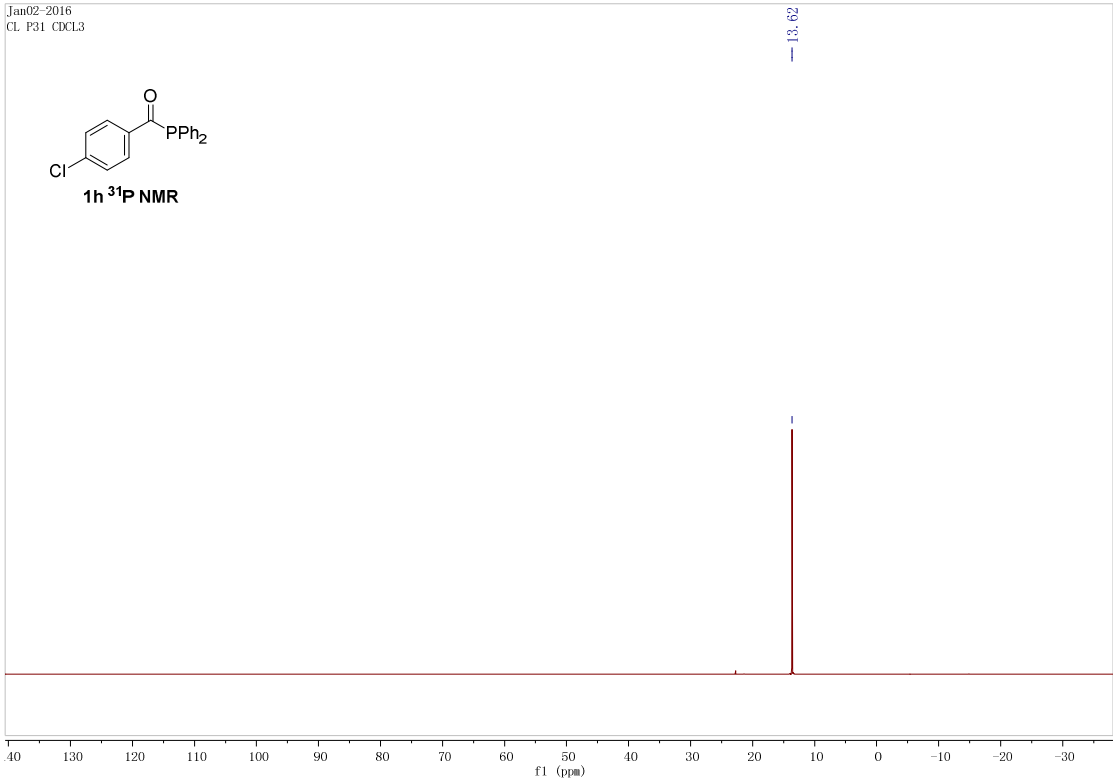

$^{31}$P NMR spectra of **1g** in $CDCl_3$:



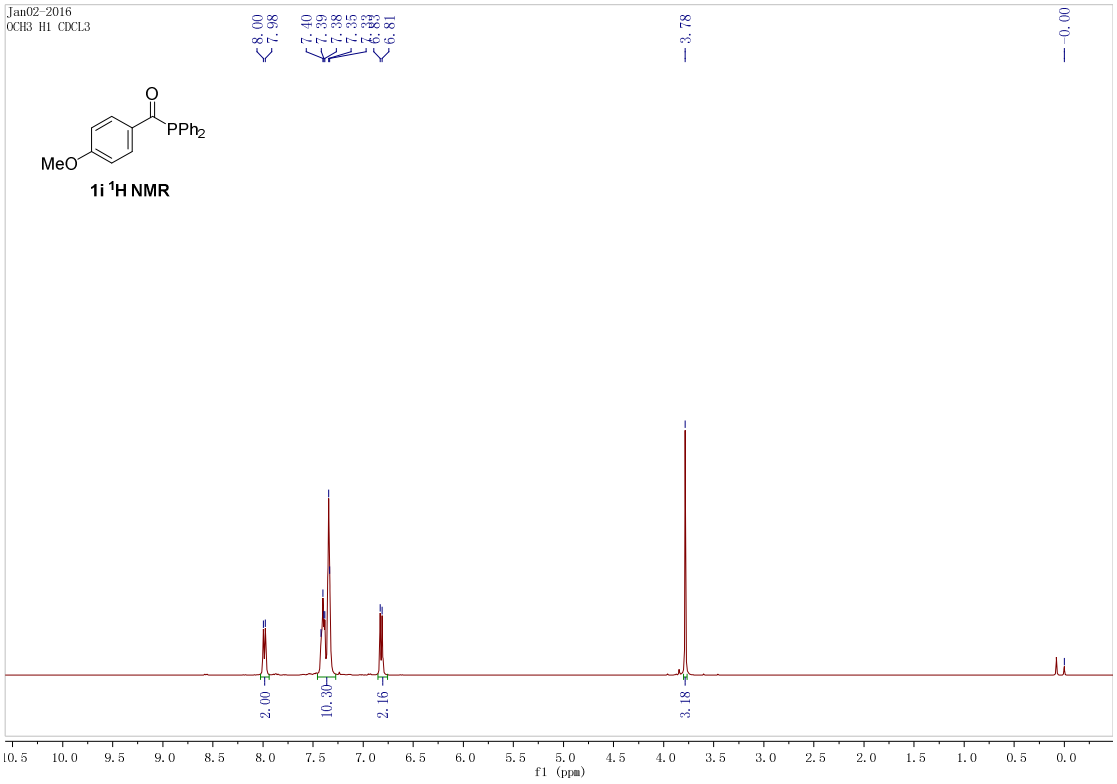
$^{1}$H NMR spectra of **1h** in $CDCl_3$:



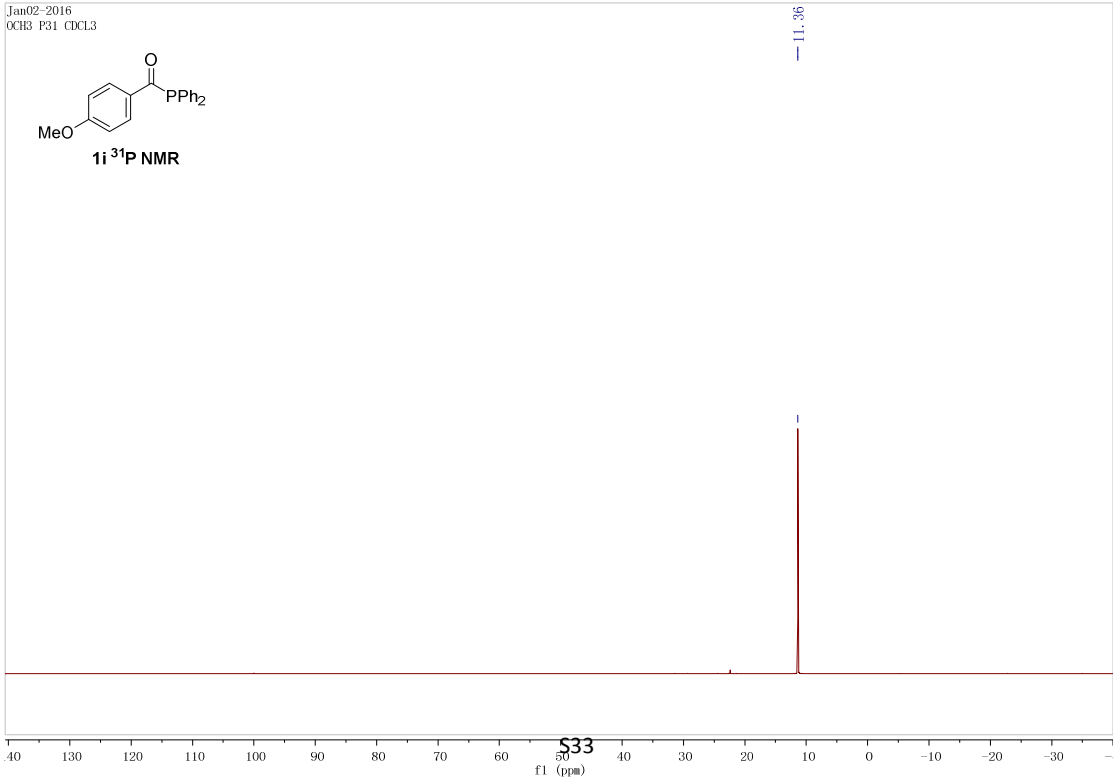

$^{31}$P NMR spectra of **1h** in $CDCl_3$:



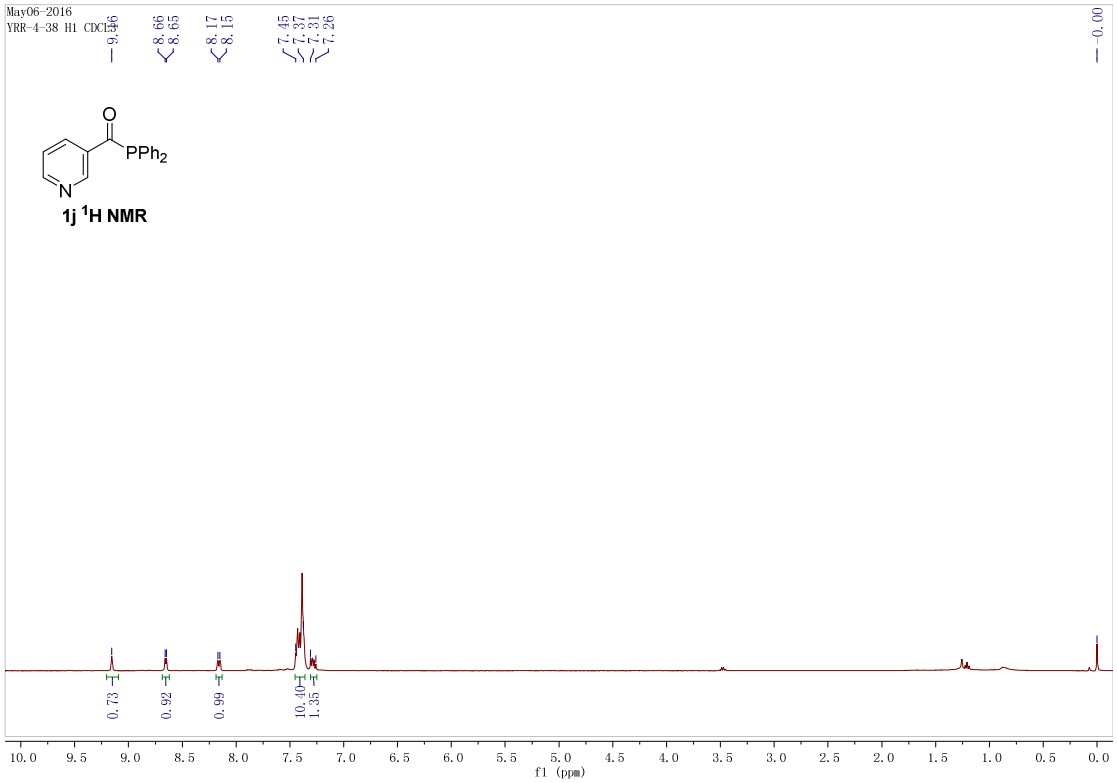
$^{1}$H NMR spectra of **1i** in $CDCl_3$:



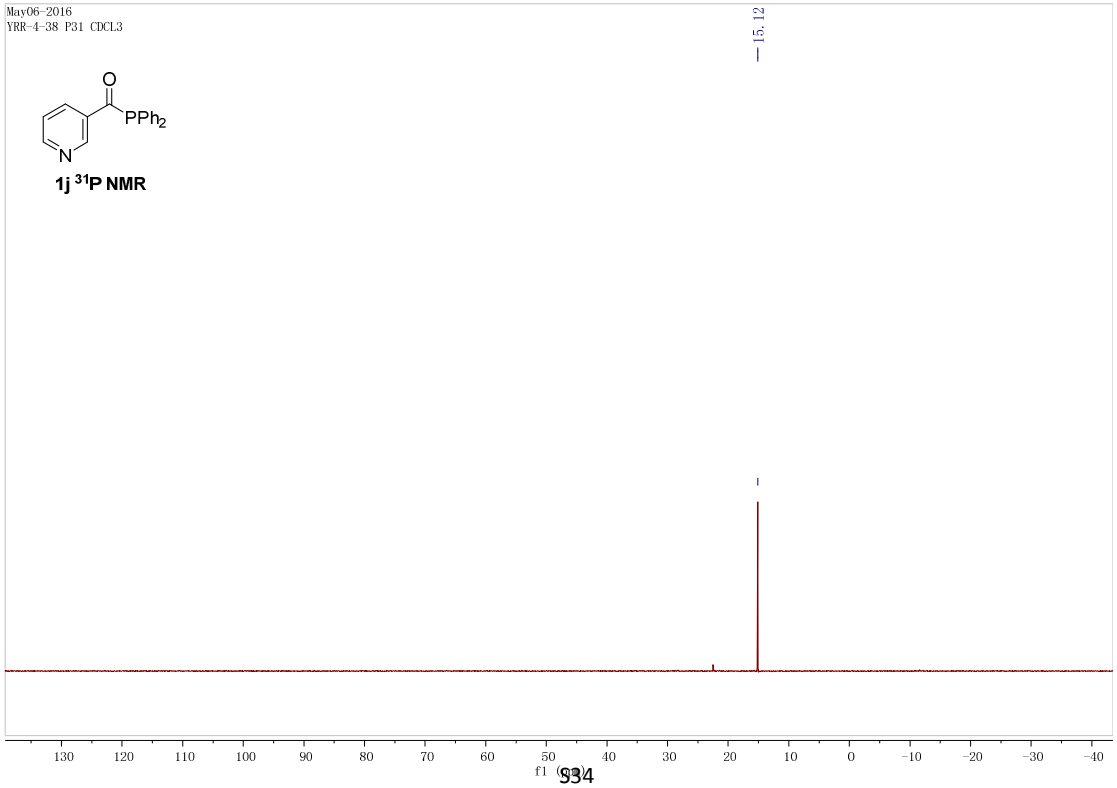

$^{31}$P NMR spectra of **1i** in $CDCl_3$:



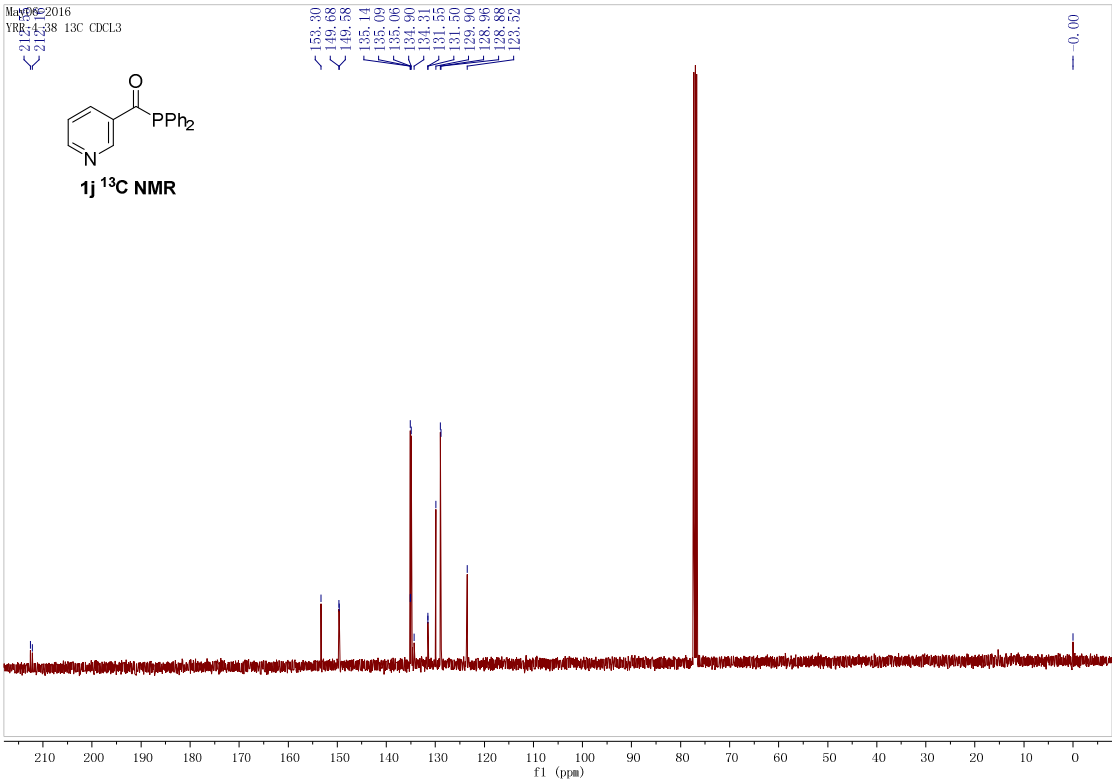
$^{1}$H NMR spectra of **1j** in $CDCl_3$:



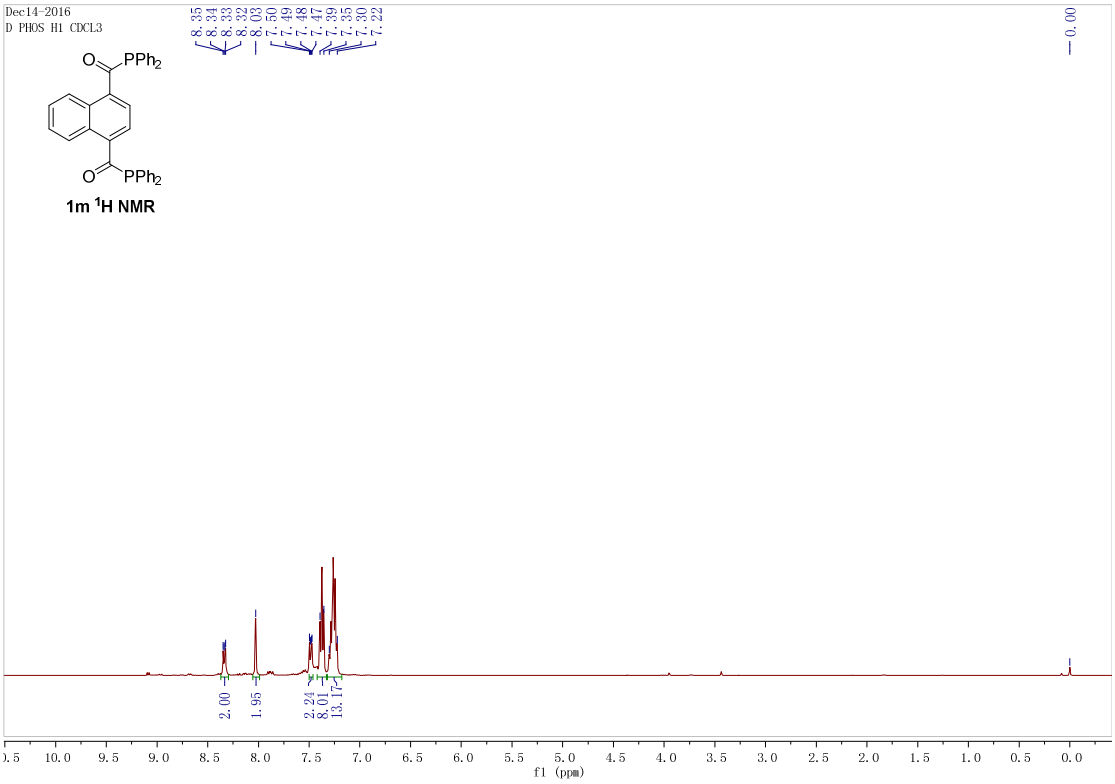

$^{31}$P NMR spectra of **1j** in $CDCl_3$:



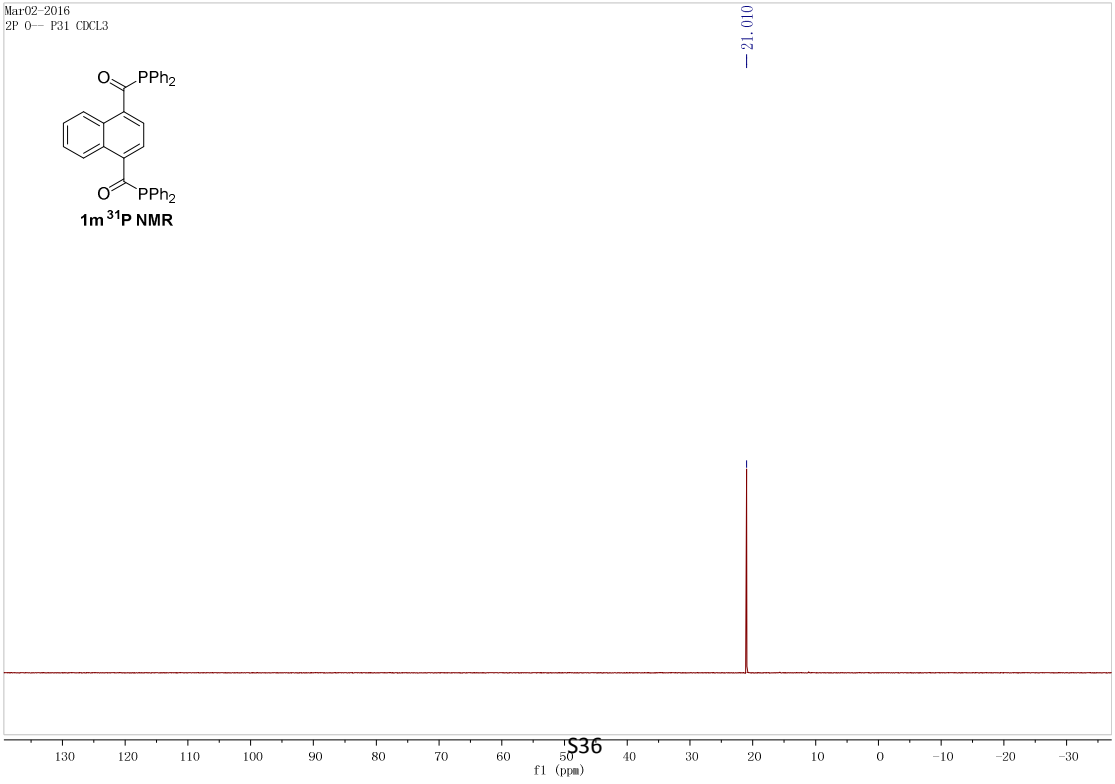
$^{13}C$ NMR spectra of **1j** in $CDCl_3$:



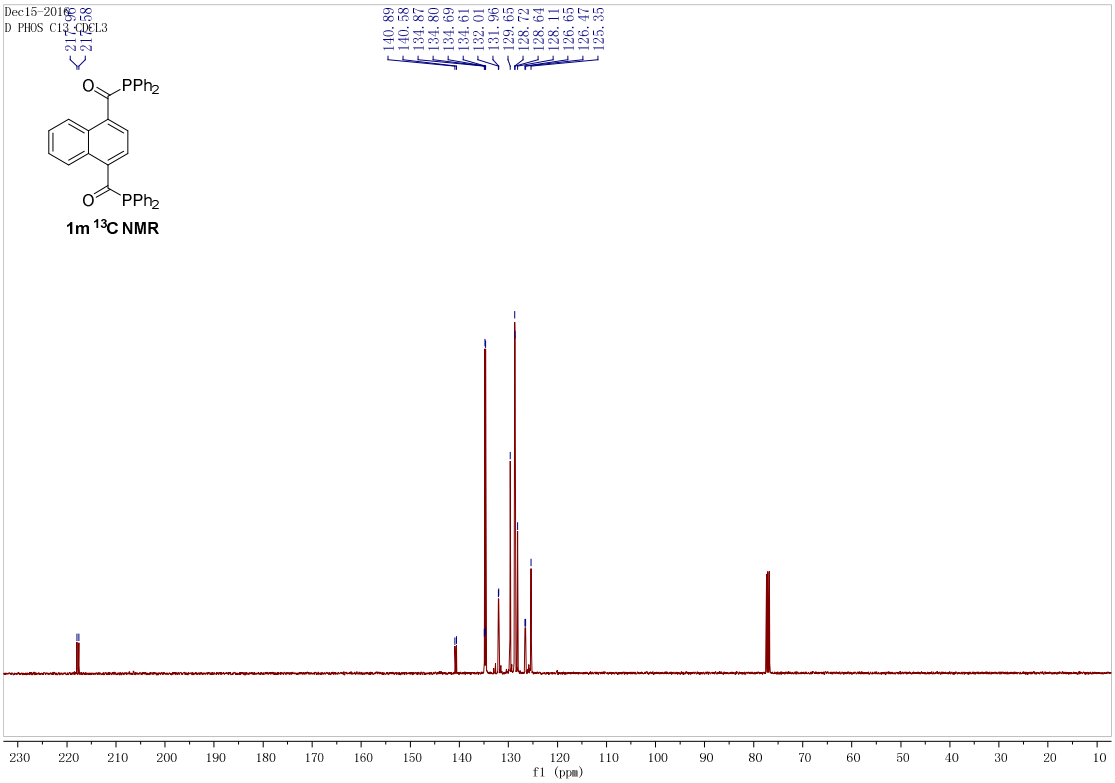
$^{1}$H NMR spectra of **1m** in $CDCl_3$:



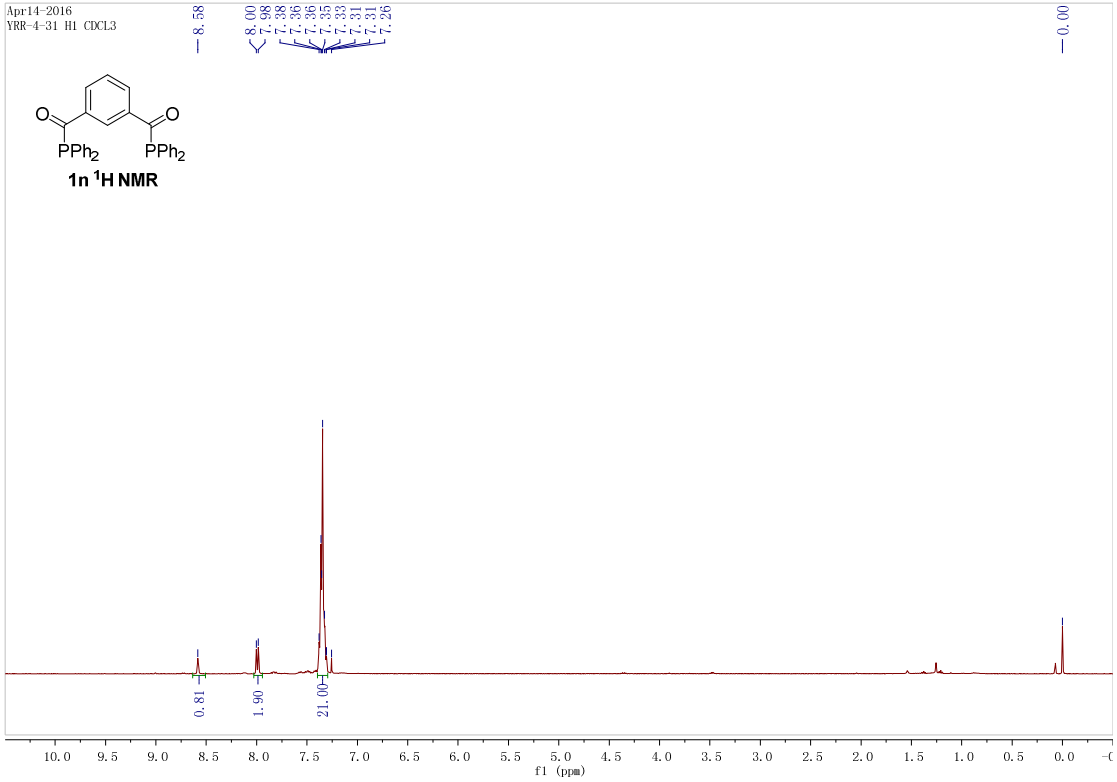

$^{31}$P NMR spectra of **1m** in $CDCl_3$:



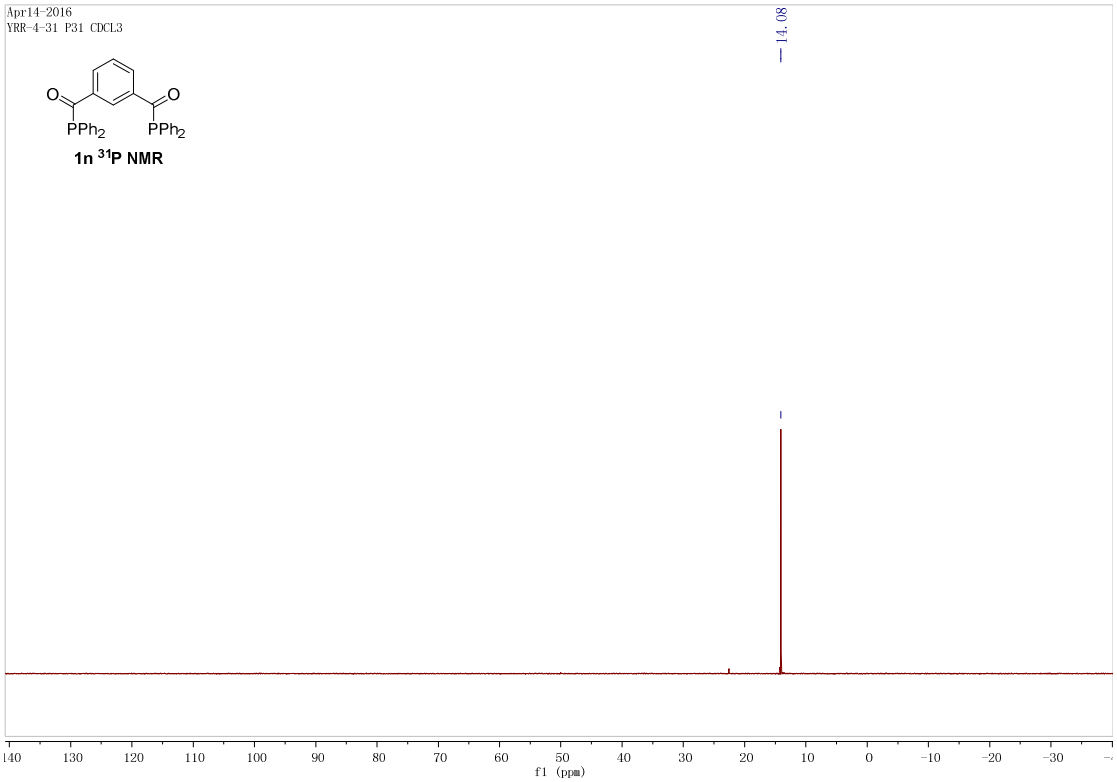
$^{13}C$ NMR spectra of **1m** in $CDCl_3$:



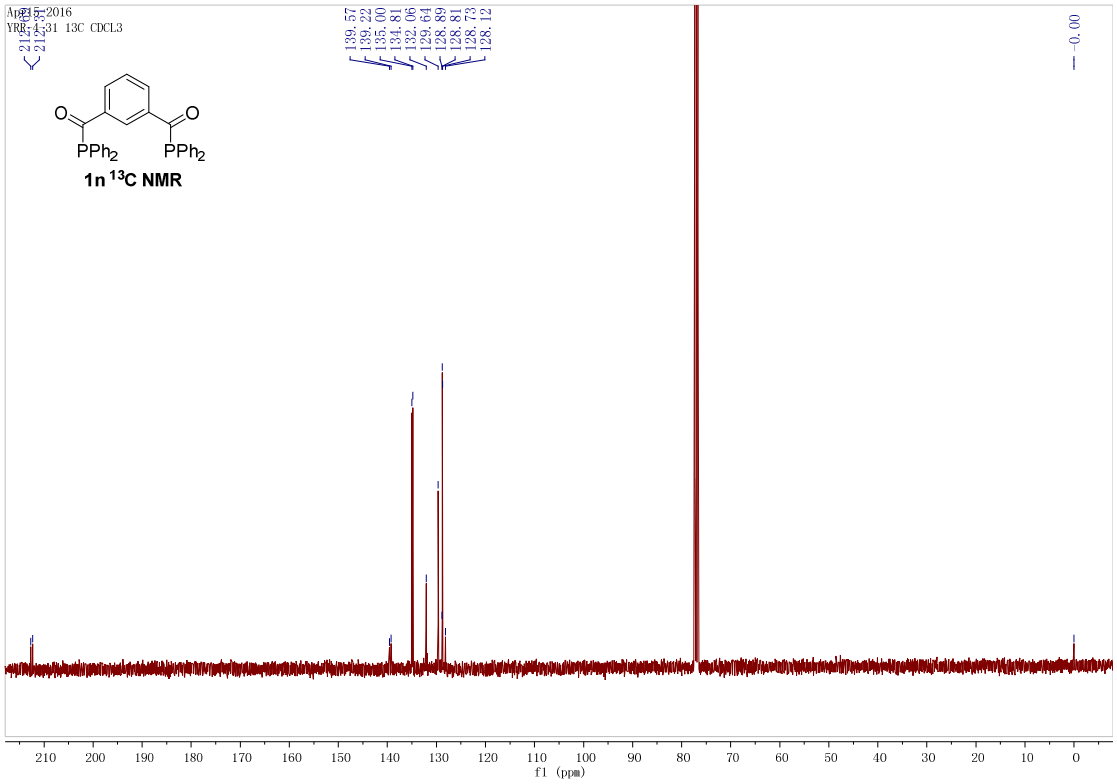
$^{1}$H NMR spectra of **1n** in $CDCl_3$:



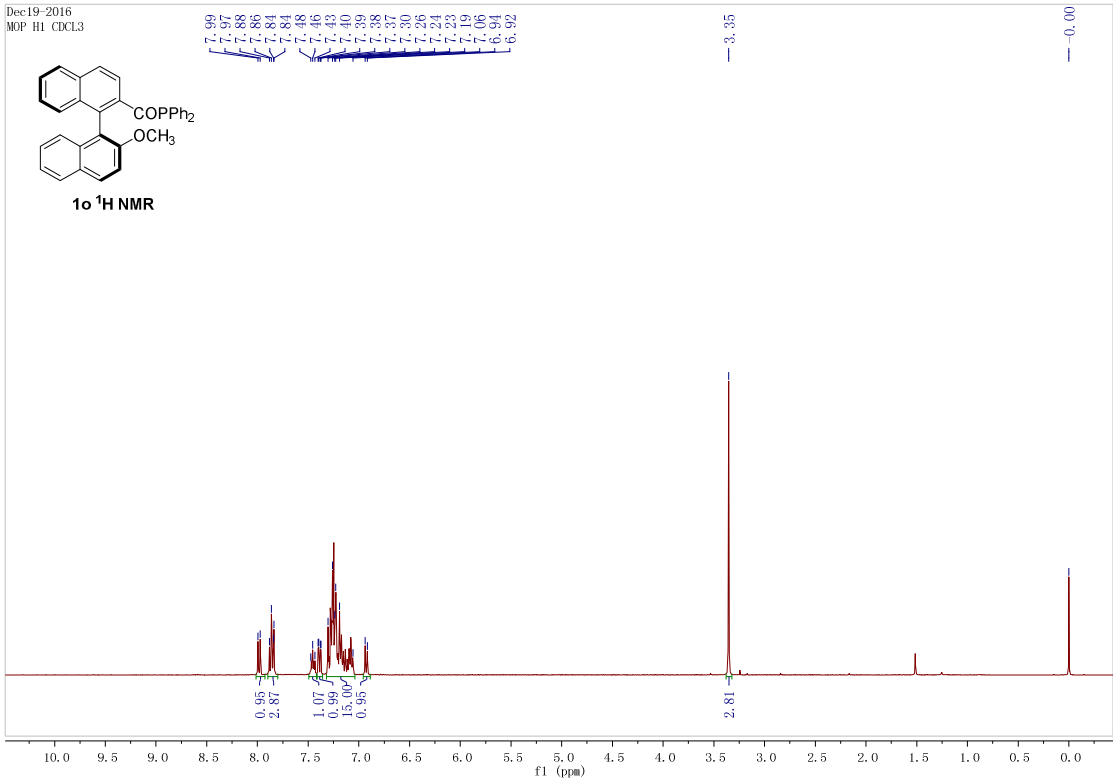

$^{31}$P NMR spectra of **1n** in $CDCl_3$:



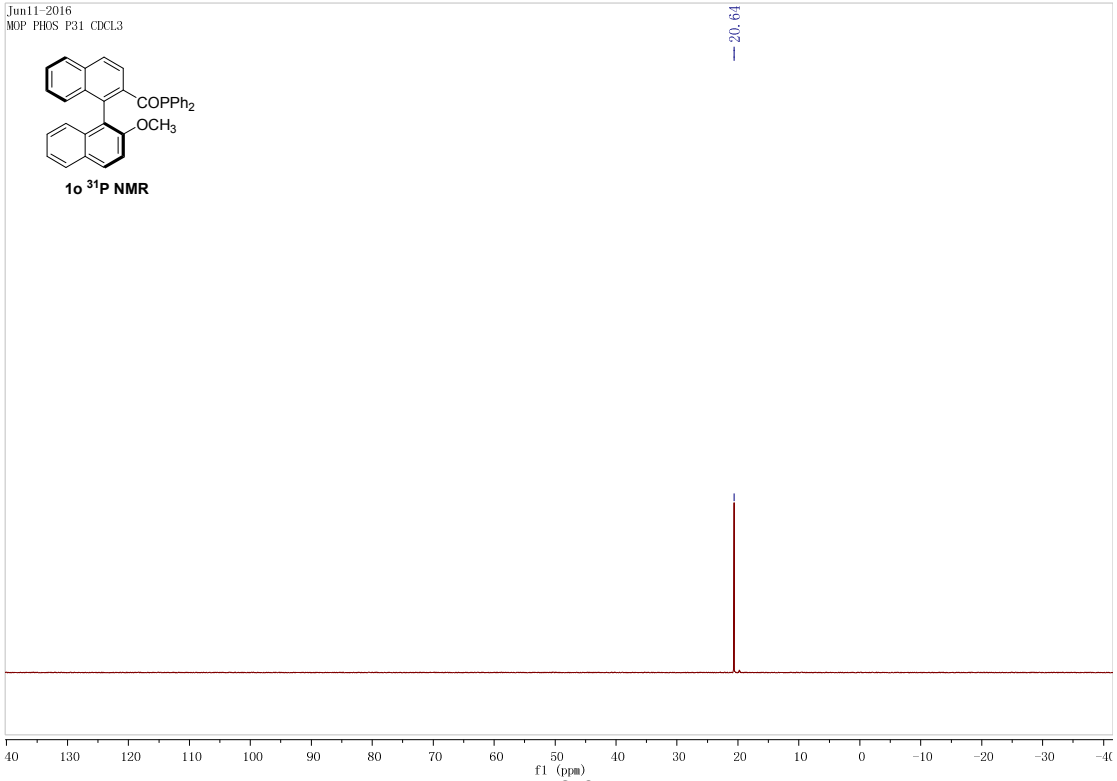
$^{13}C$ NMR spectra of **1n** in $CDCl_3$:



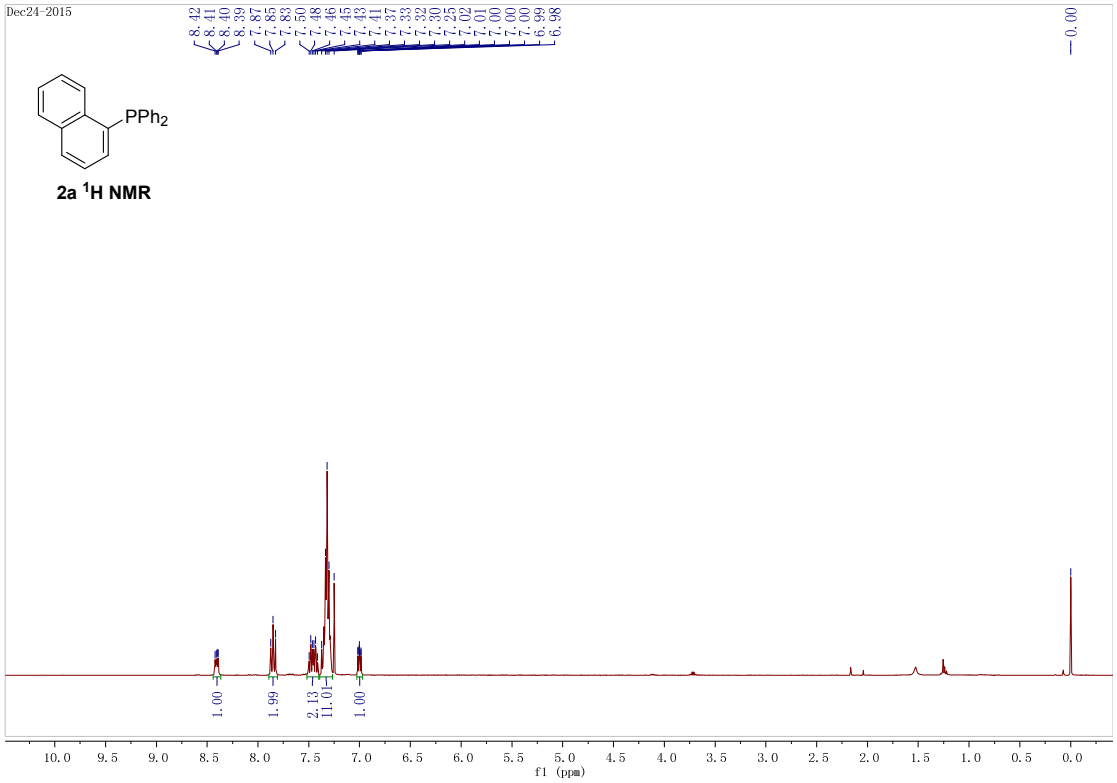
$^{1}$H NMR spectra of **1o** in $CDCl_3$:



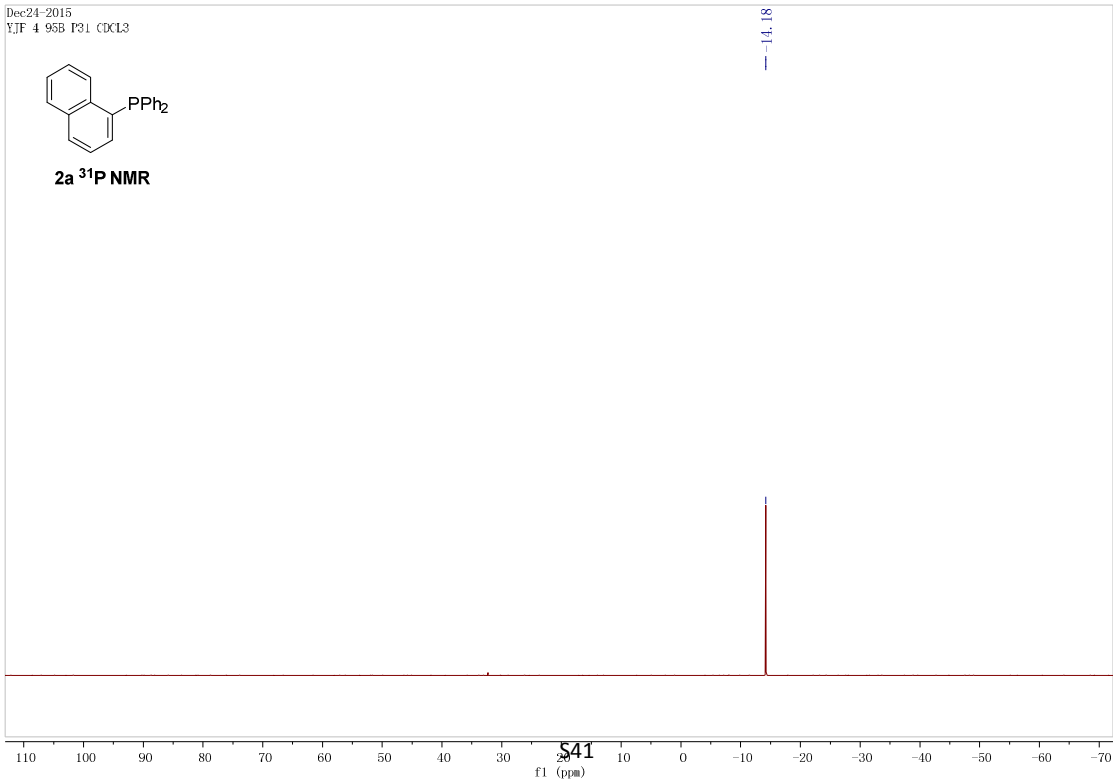

$^{31}$P NMR spectra of **1o** in $CDCl_3$:



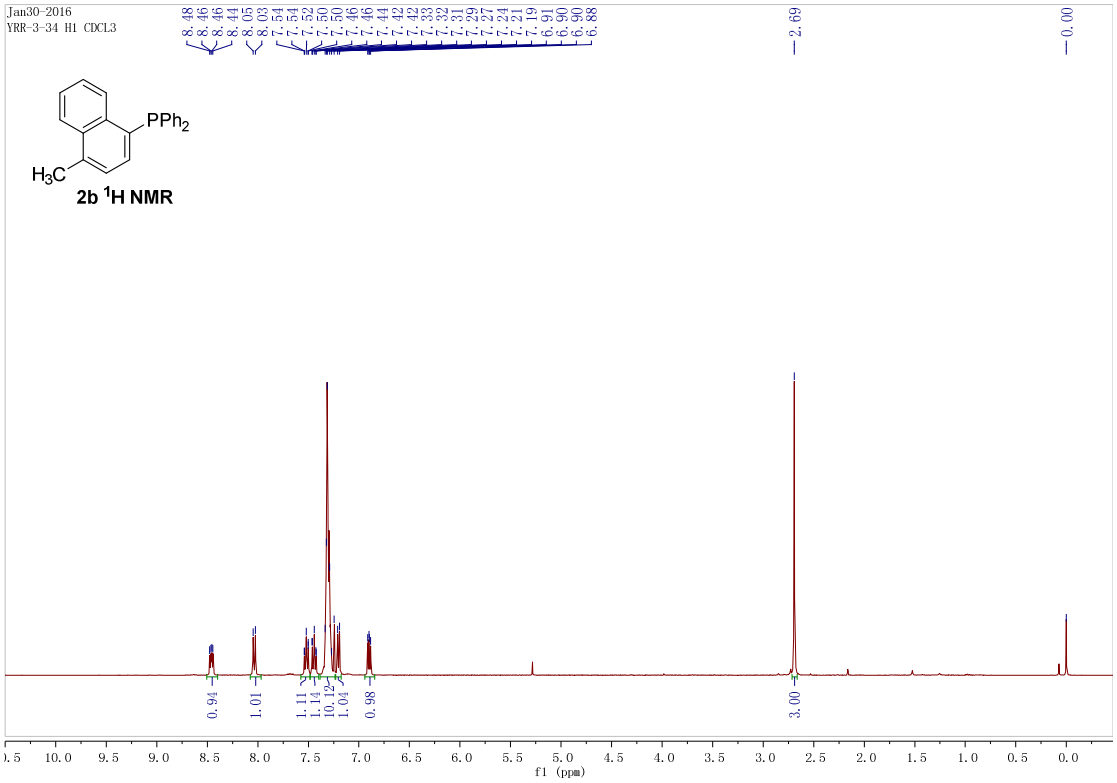
$^{1}$H NMR spectra of **2a** in $CDCl_3$:



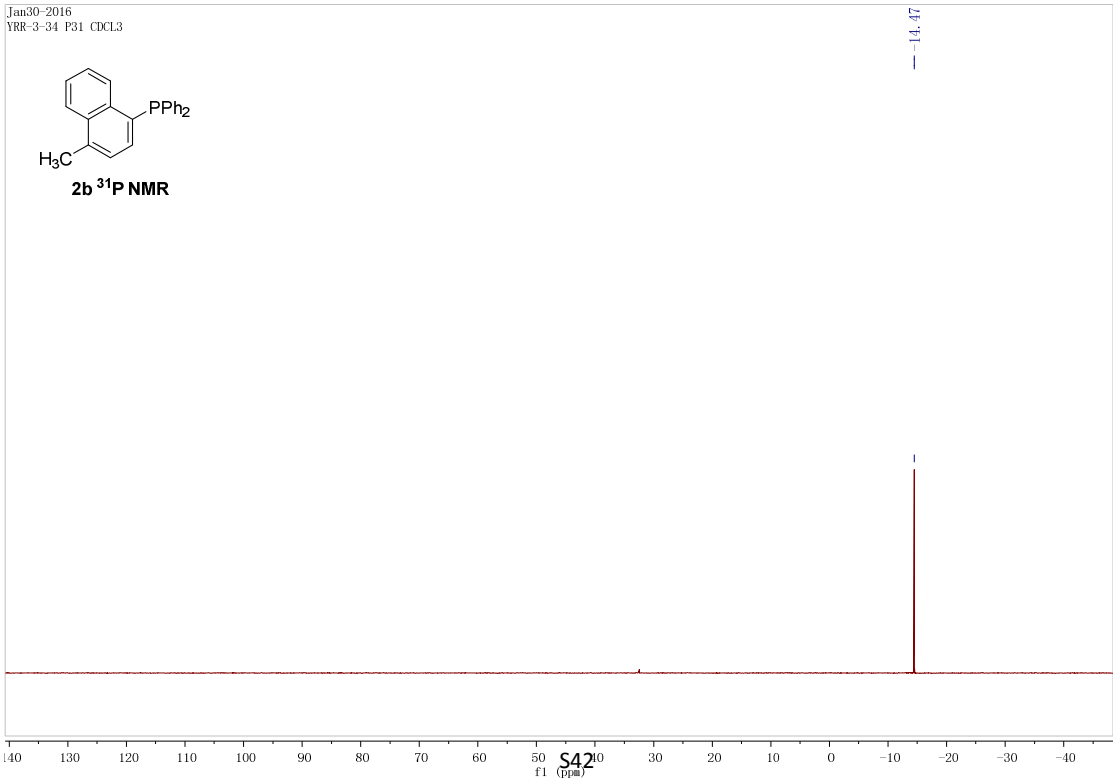

$^{31}$P NMR spectra of **2a** in $CDCl_3$:



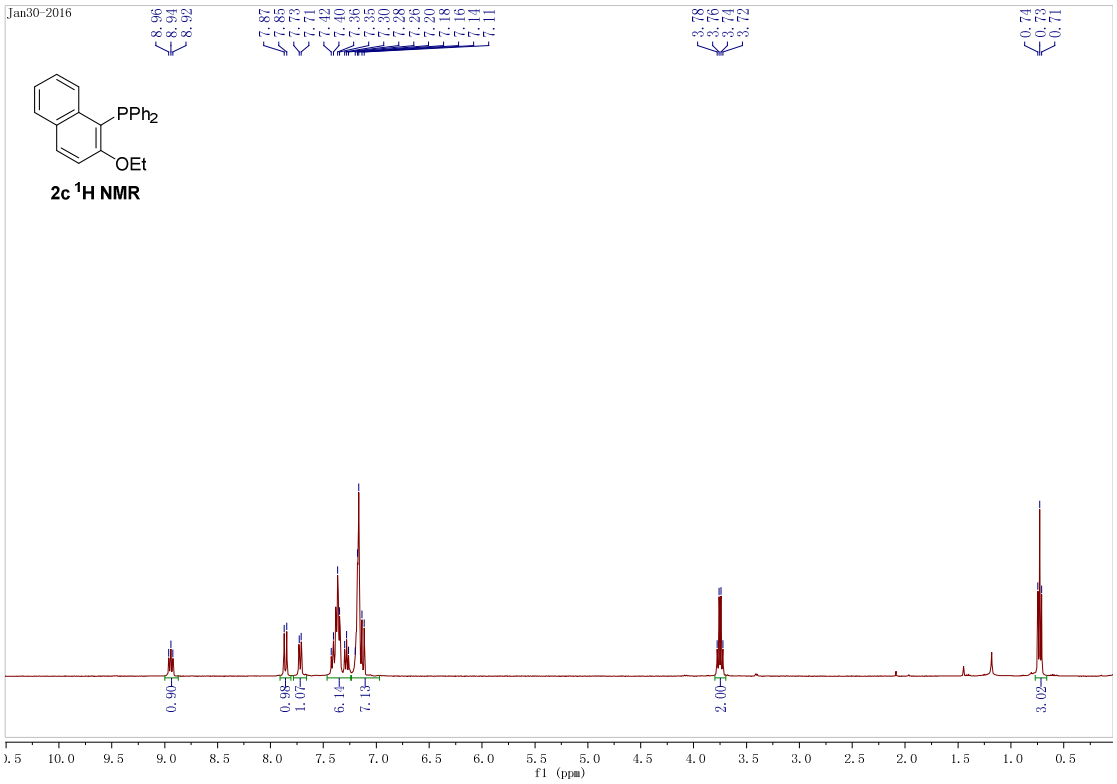
$^{1}$H NMR spectra of **2b** in $CDCl_3$:



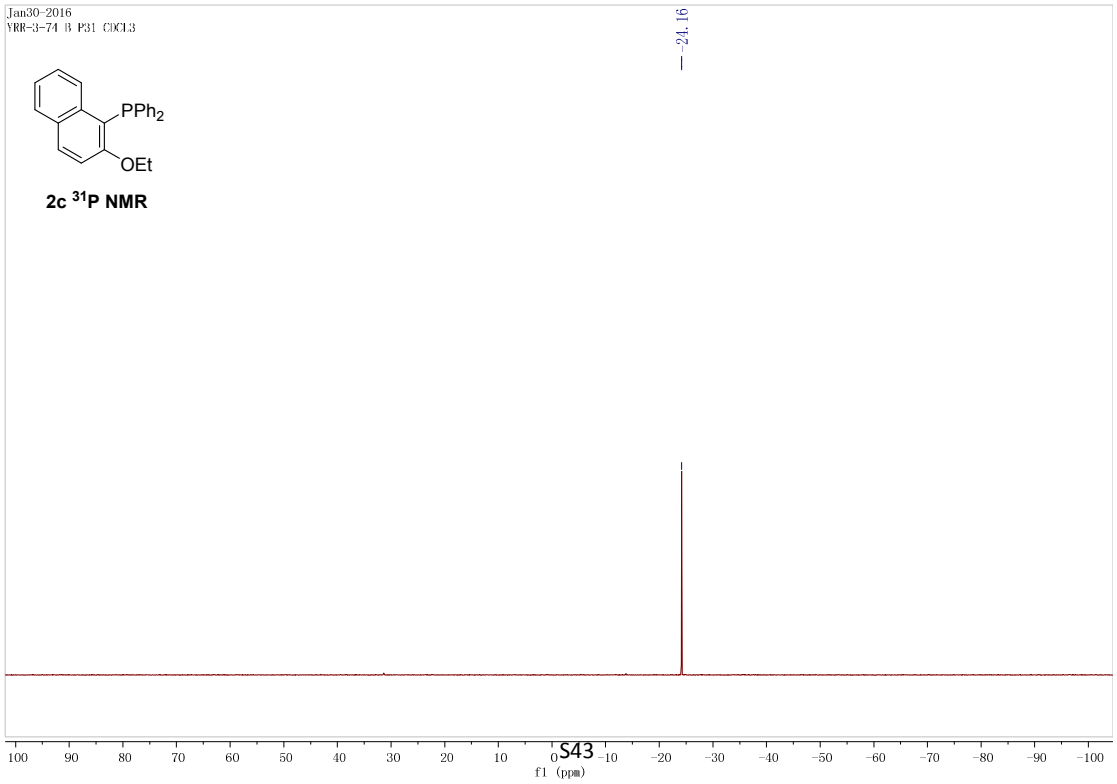

$^{31}$P NMR spectra of **2b** in $CDCl_3$:



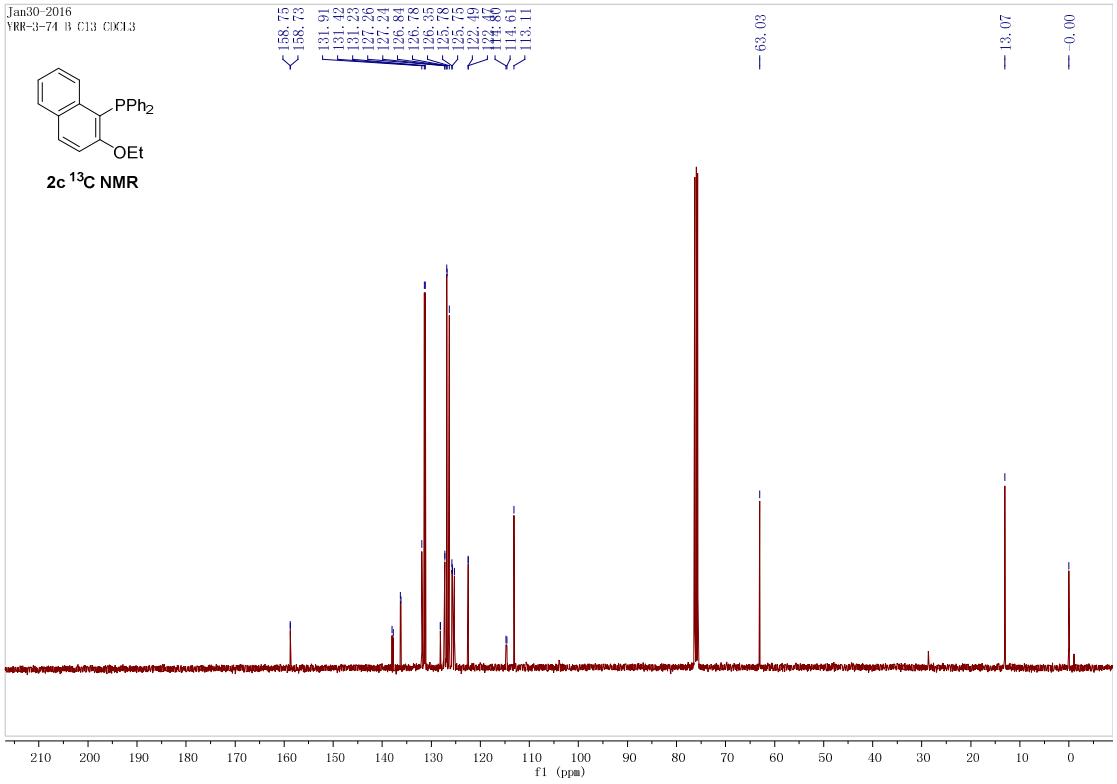
$^{1}$H NMR spectra of **2c** in $CDCl_3$:



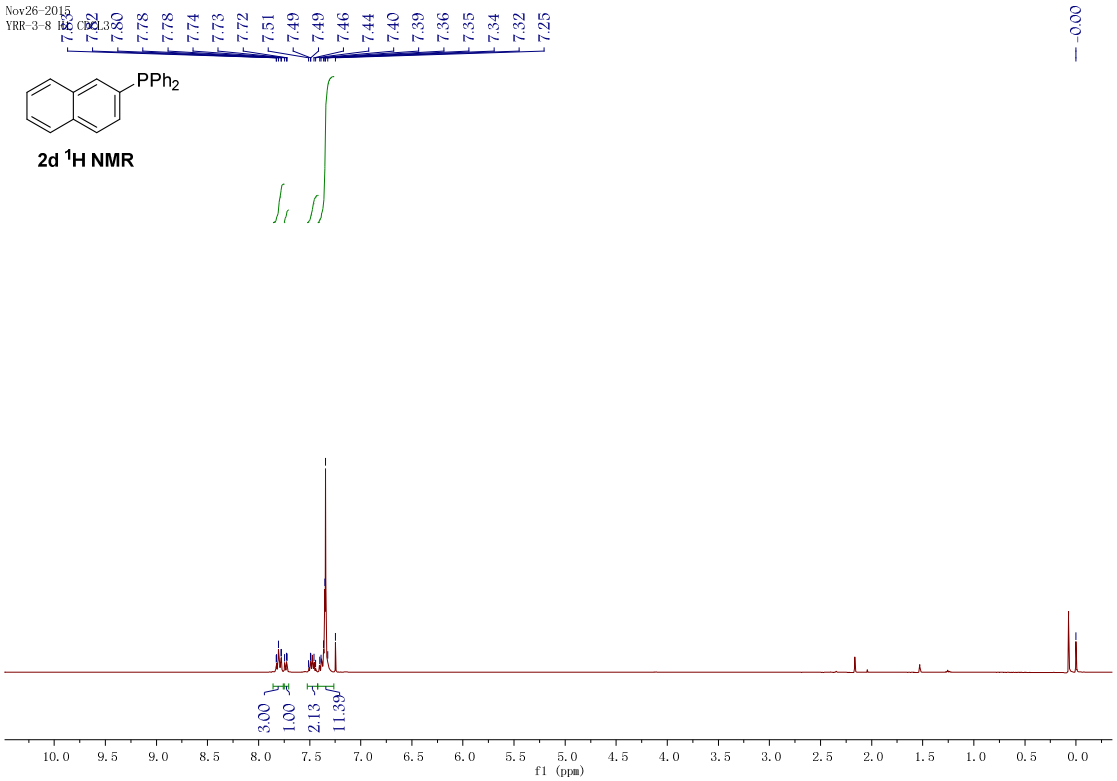

$^{31}$P NMR spectra of **2c** in $CDCl_3$:



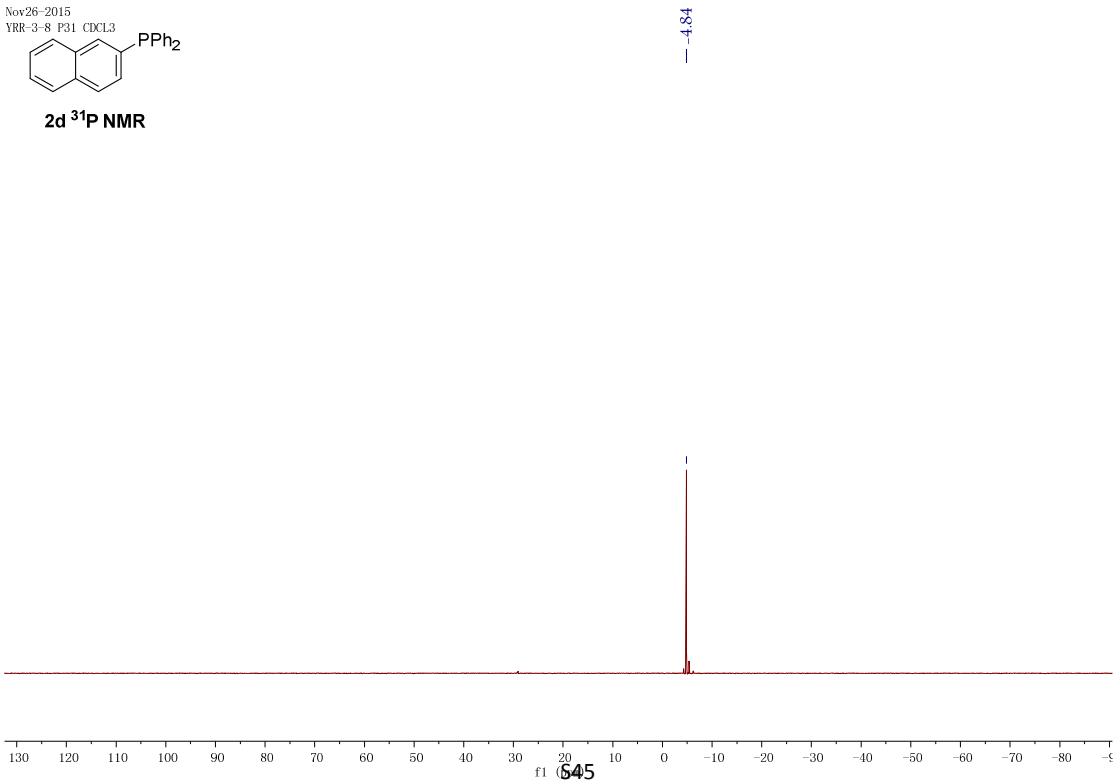
$^{13}C$ NMR spectra of **2c** in $CDCl_3$:



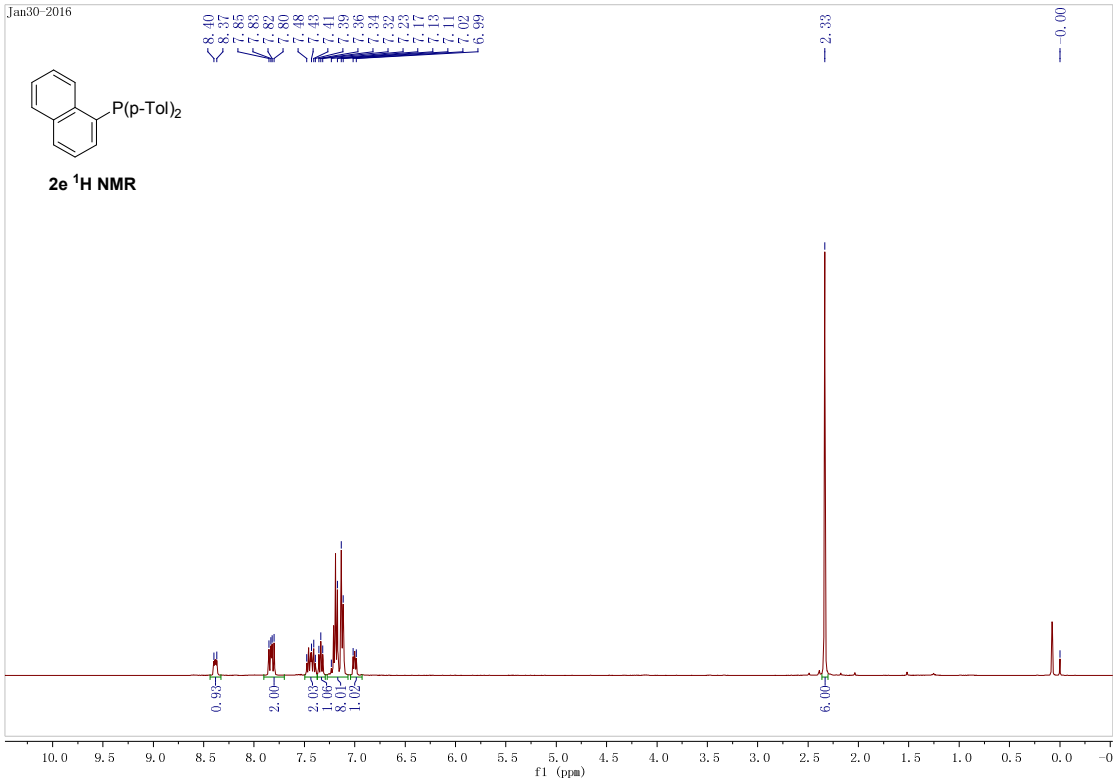
$^{1}$H NMR spectra of **2d** in $CDCl_3$:



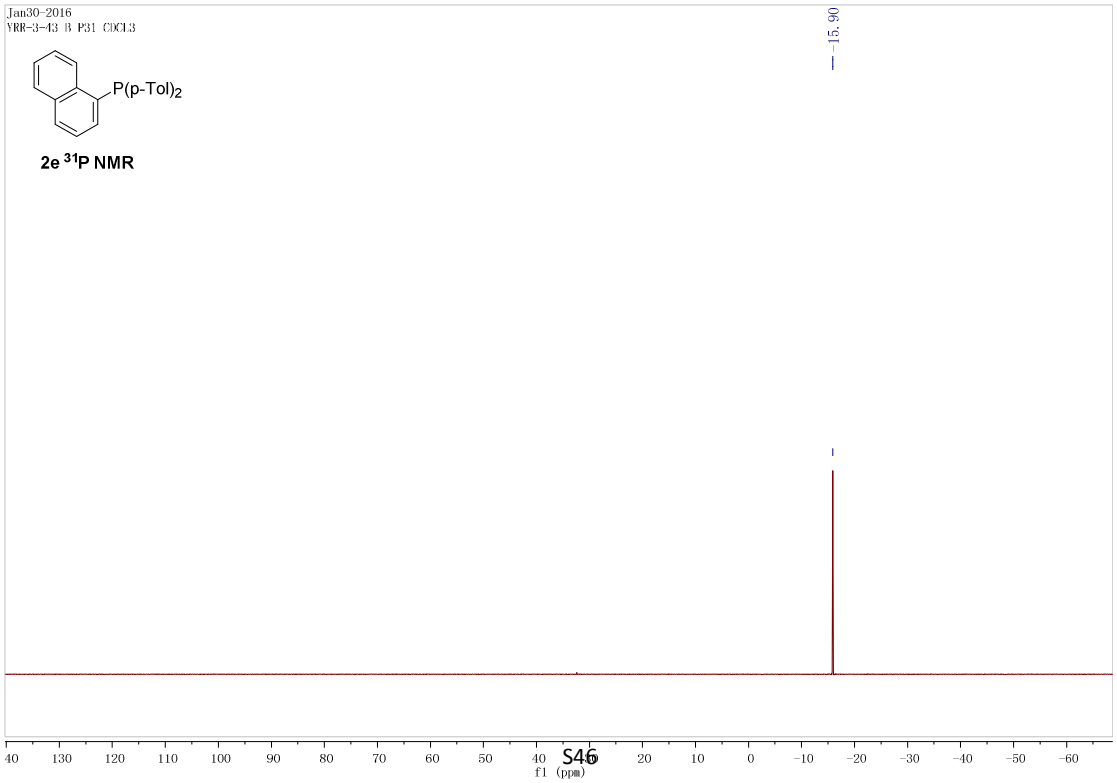

$^{31}$P NMR spectra of **2d** in $CDCl_3$:



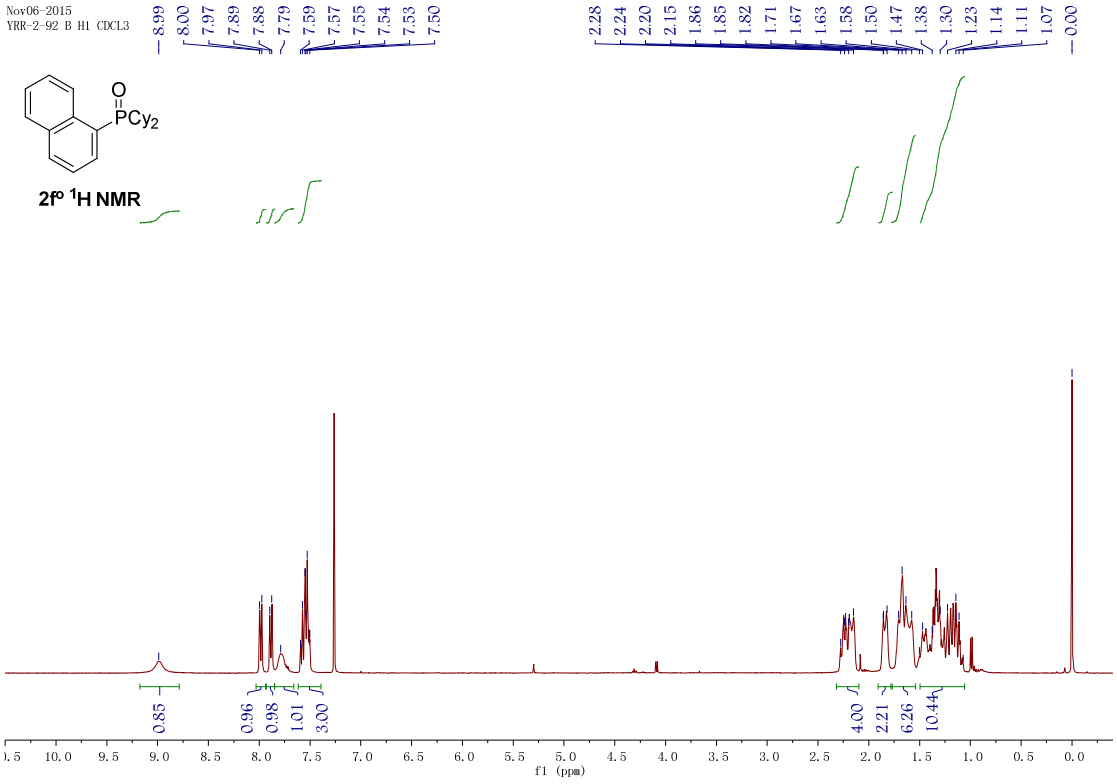
$^{1}$H NMR spectra of **2e** in $CDCl_3$:



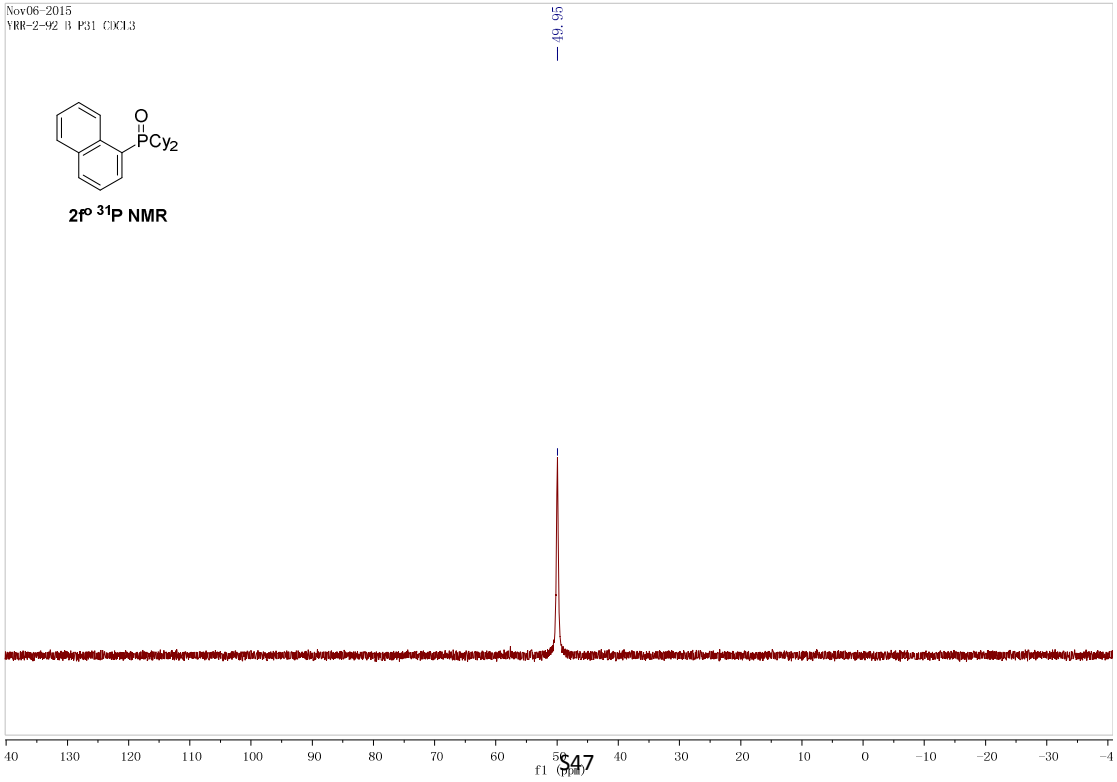

$^{31}$P NMR spectra of **2e** in $CDCl_3$:



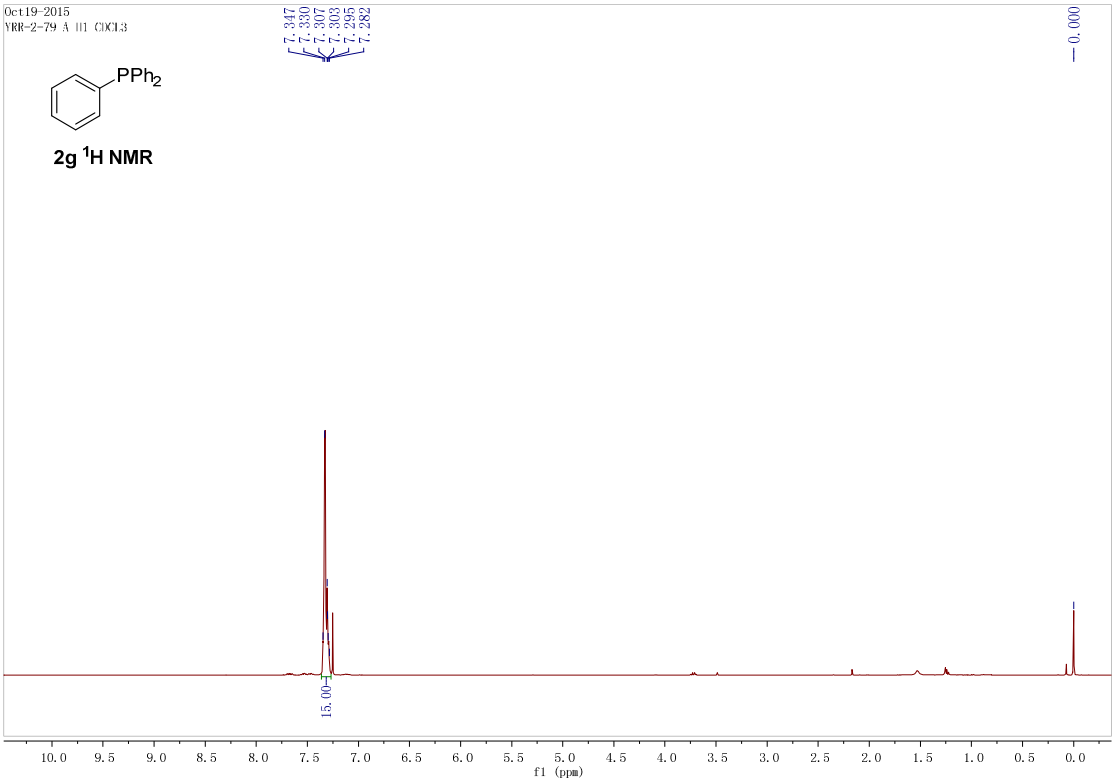
$^{1}$H NMR spectra of **2f$^{o}$** in $CDCl_3$:



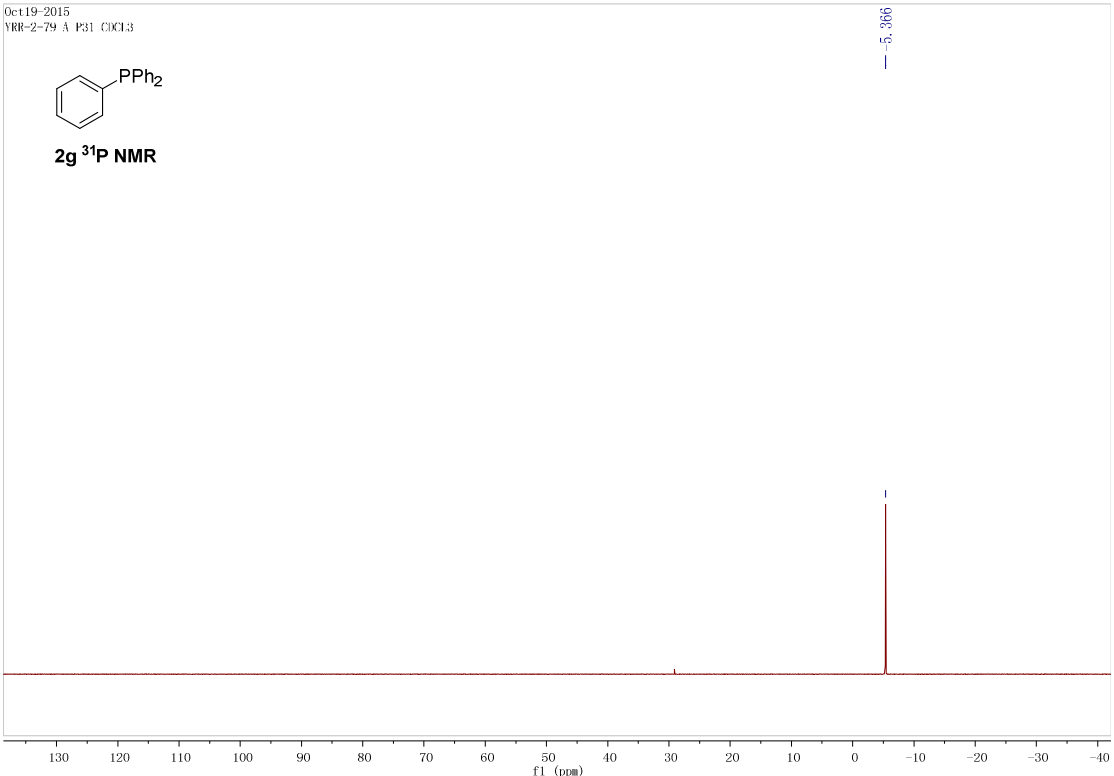

$^{31}$P NMR spectra of **2f$^{o}$** in $CDCl_3$:



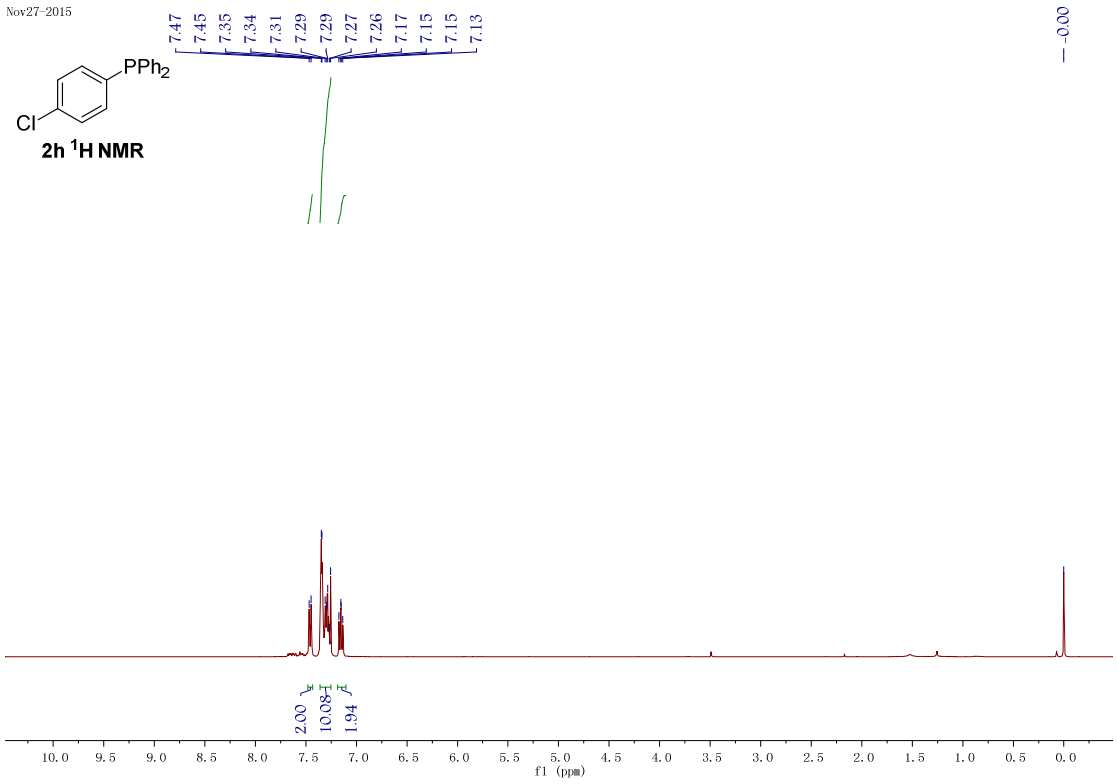
$^{1}$H NMR spectra of **2g** in $CDCl_3$:



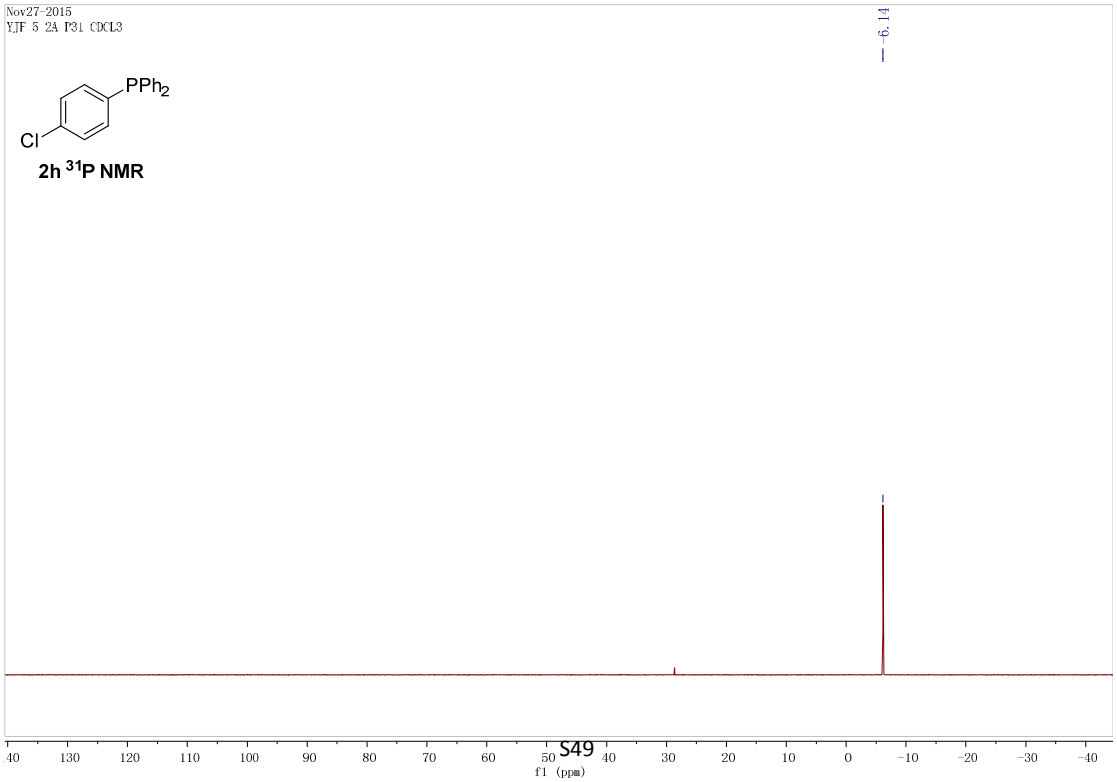

$^{31}$P NMR spectra of **2g** in $CDCl_3$:



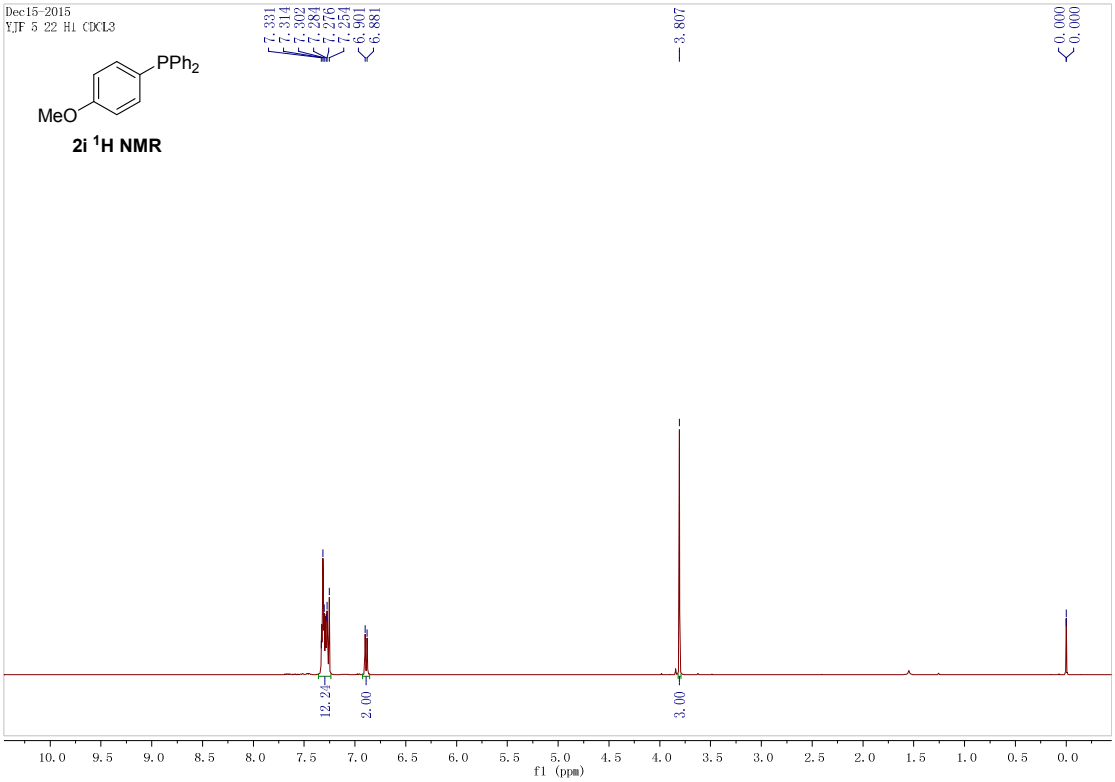
$^{1}$H NMR spectra of **2h** in $CDCl_3$:



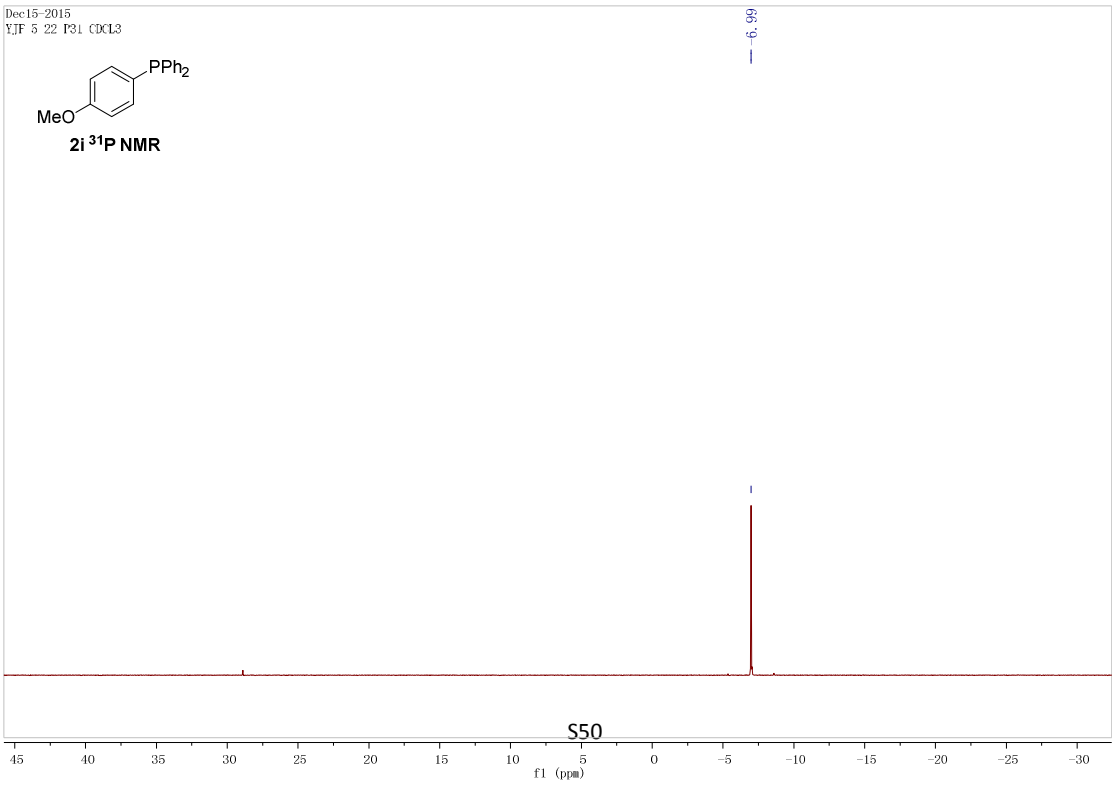

$^{31}$P NMR spectra of **2h** in $CDCl_3$:



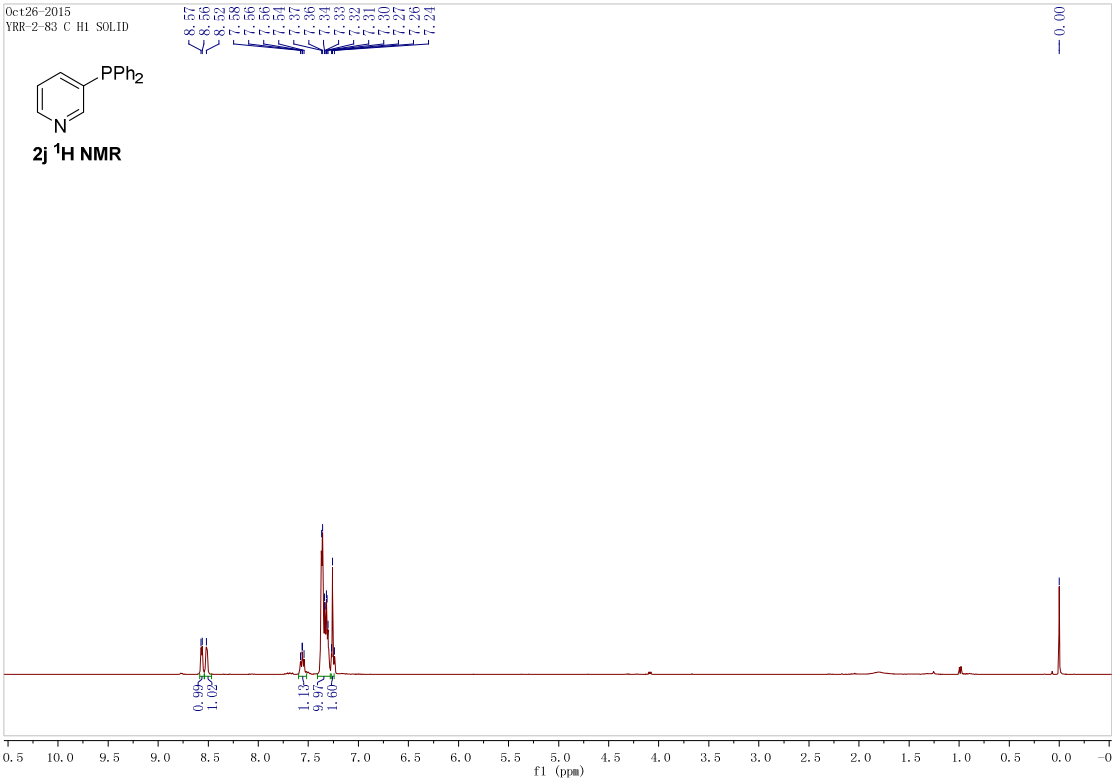
$^{1}$H NMR spectra of **2i** in $CDCl_3$:



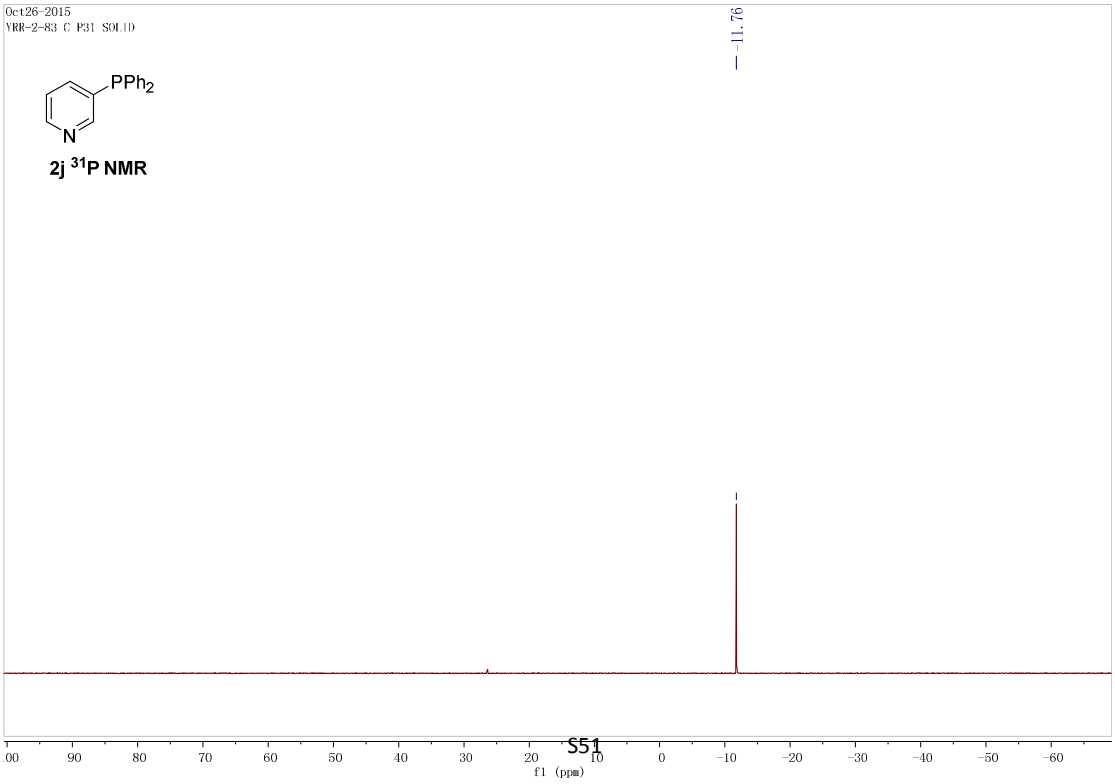

$^{31}$P NMR spectra of **2i** in $CDCl_3$:



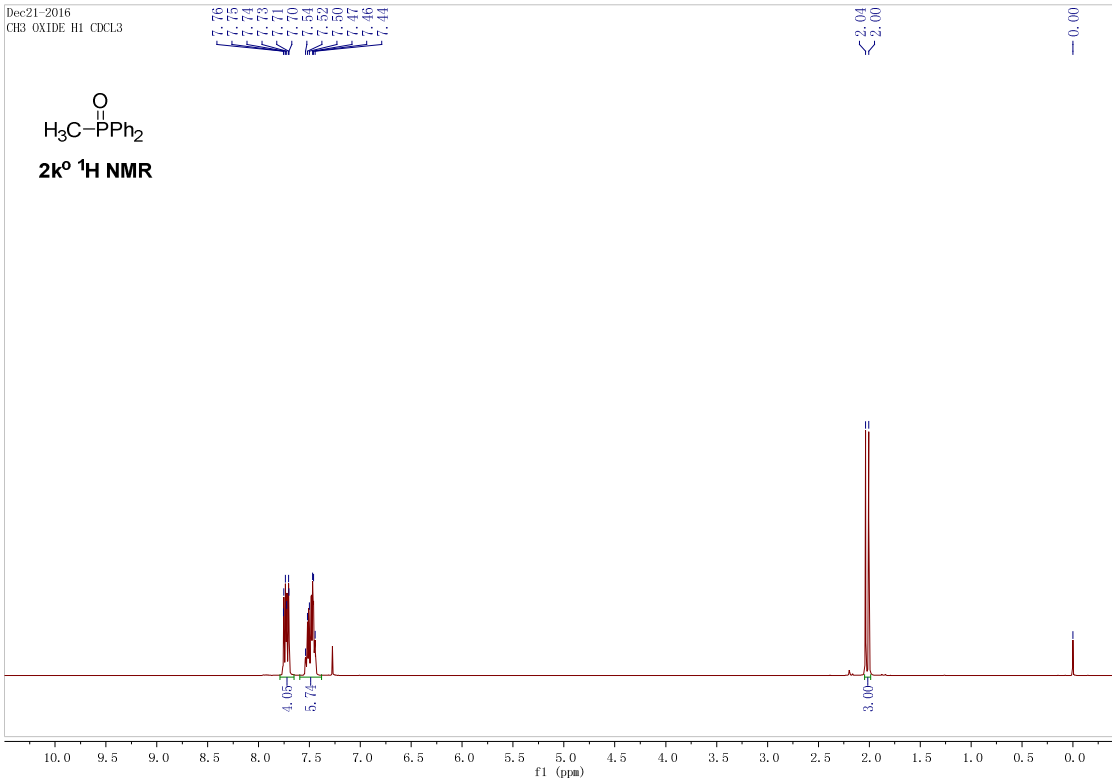
$^{1}$H NMR spectra of **2j** in $CDCl_3$:



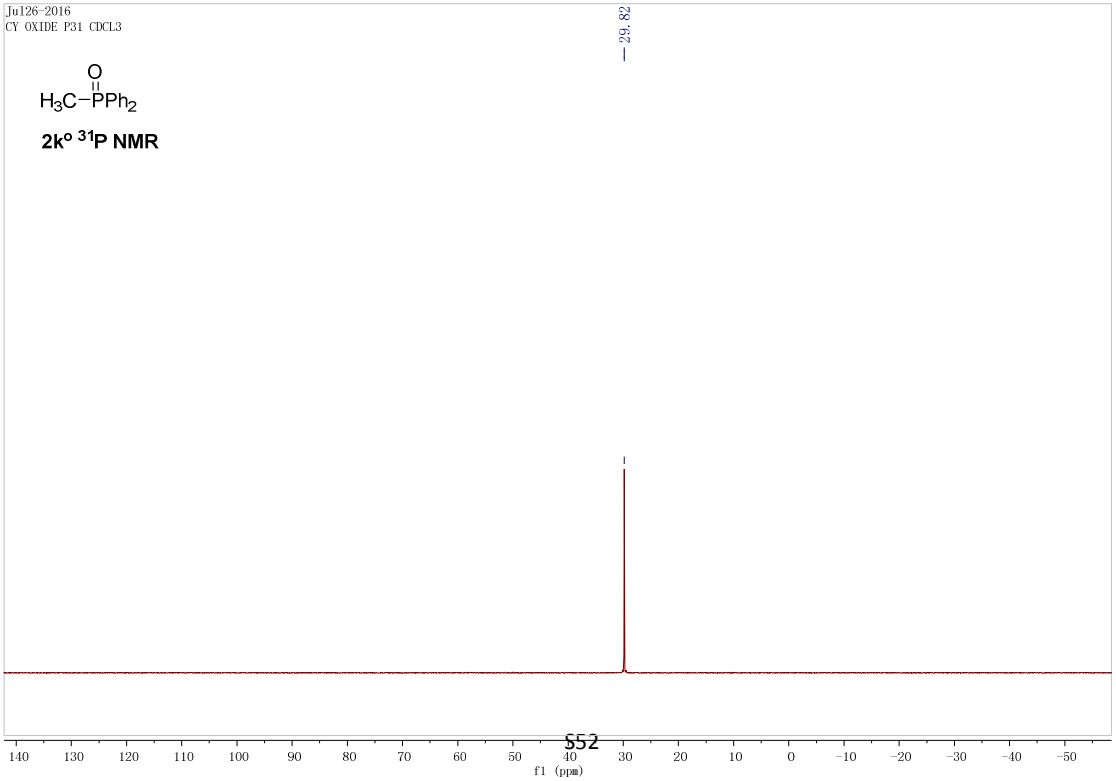

$^{31}$P NMR spectra of **2j** in $CDCl_3$:



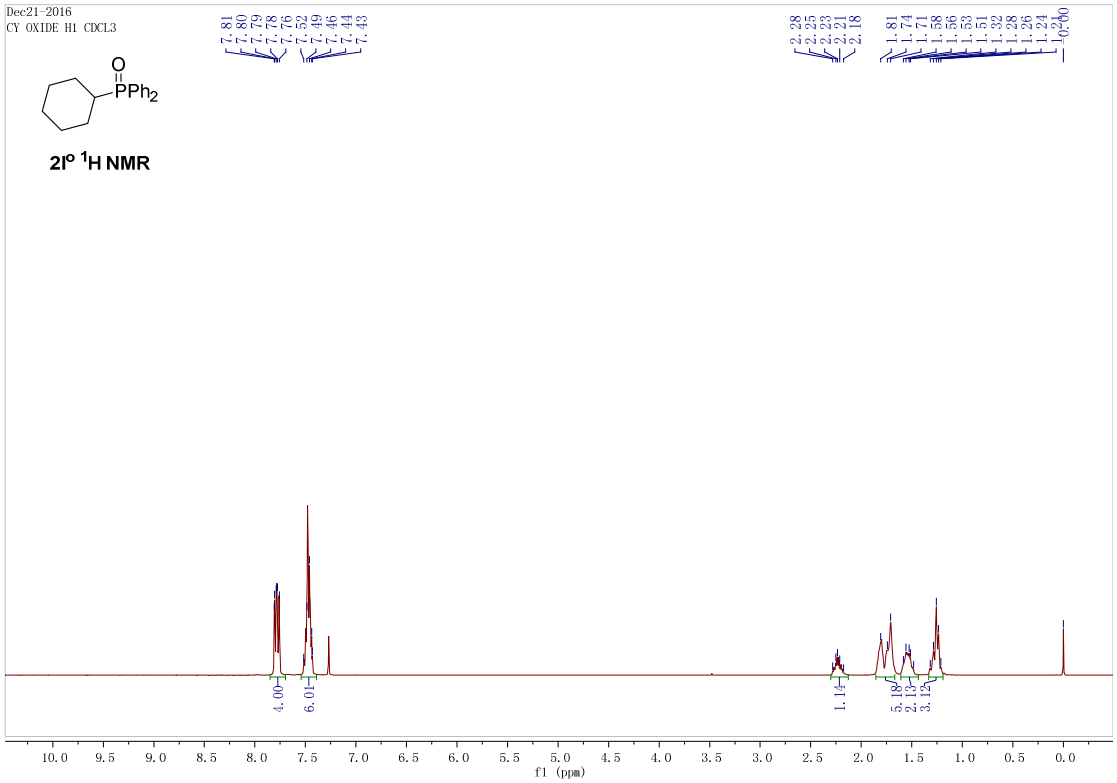
$^{1}$H NMR spectra of **2k$^{o}$** in $CDCl_3$:



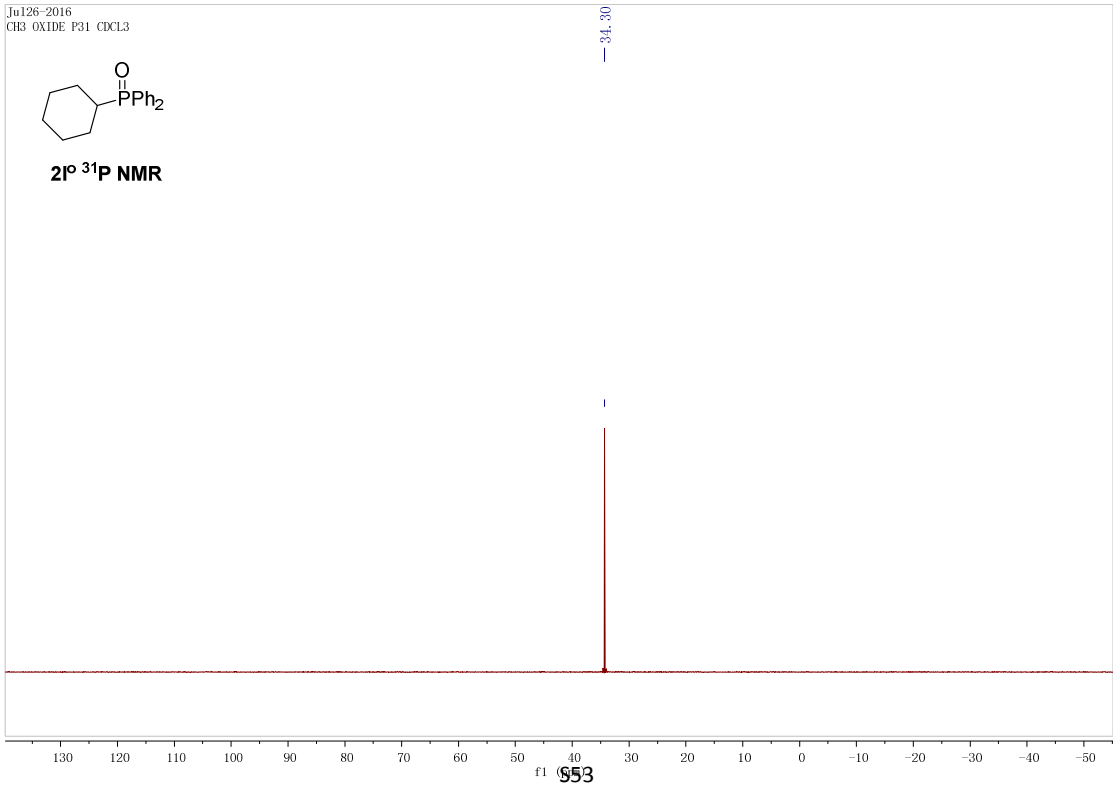

$^{31}$P NMR spectra of **2k$^{o}$** in $CDCl_3$:



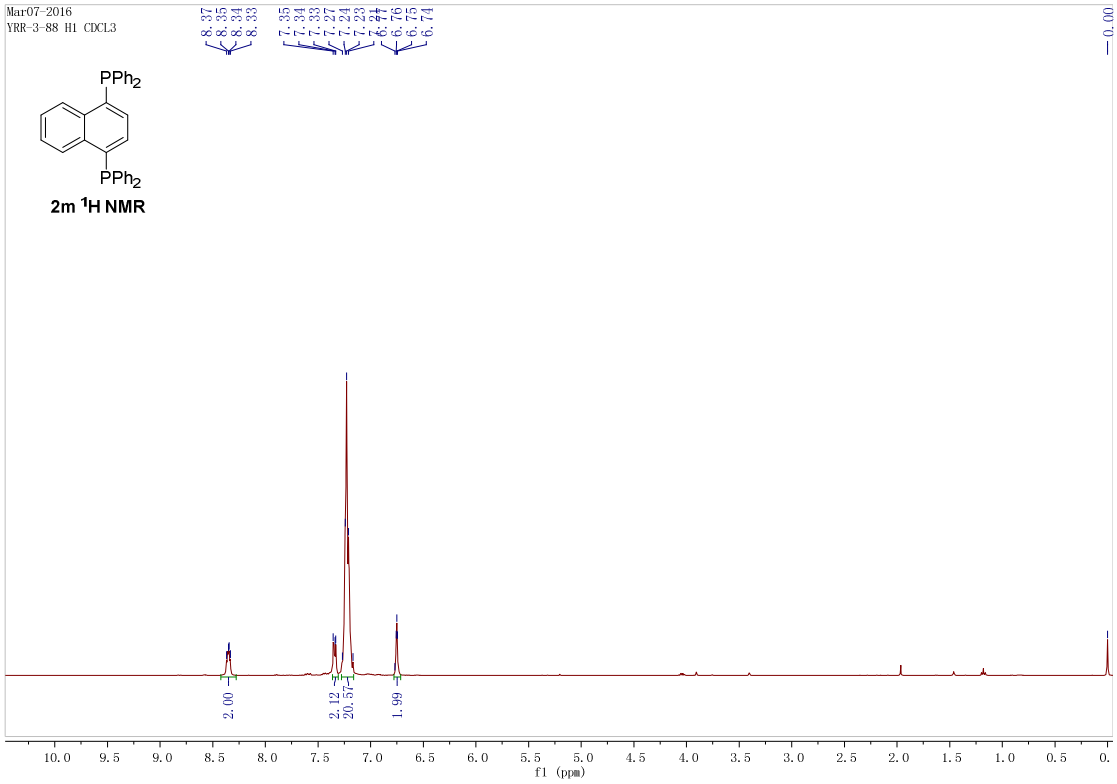
$^{1}$H NMR spectra of **2l$^{o}$** in $CDCl_3$:



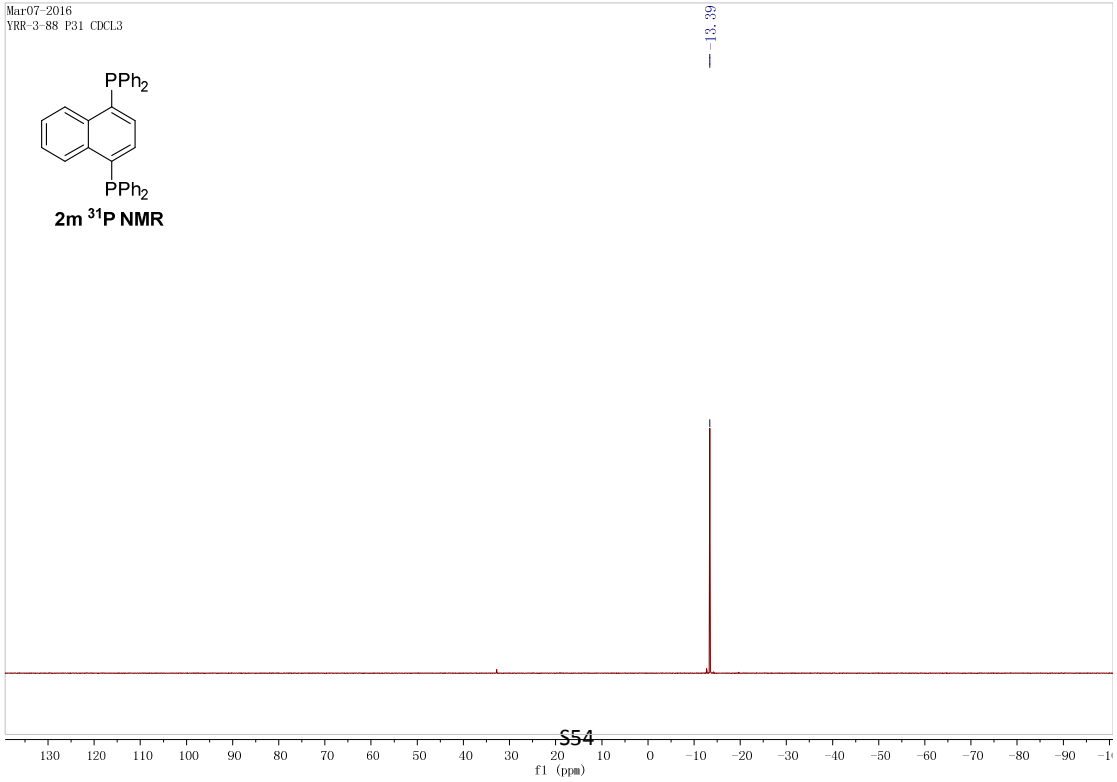

$^{31}$P NMR spectra of **2l$^{o}$** in $CDCl_3$:



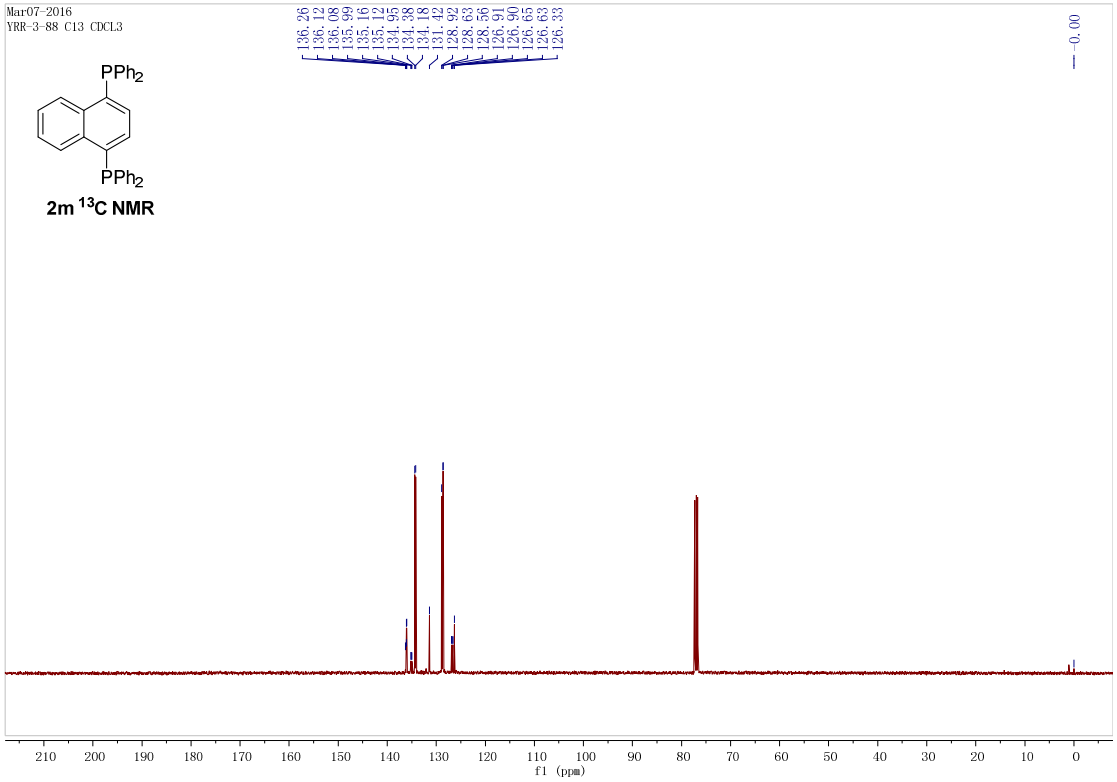
$^{1}$H NMR spectra of **2m** in $CDCl_3$:



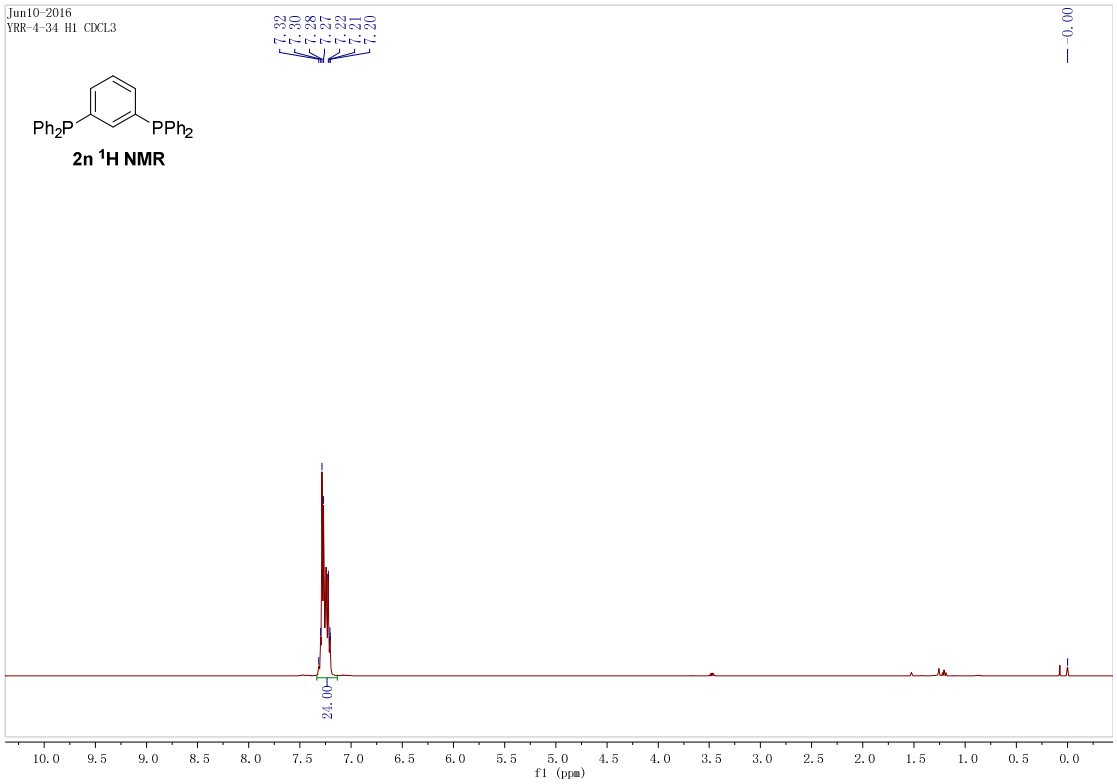

$^{31}$P NMR spectra of **2m** in $CDCl_3$:



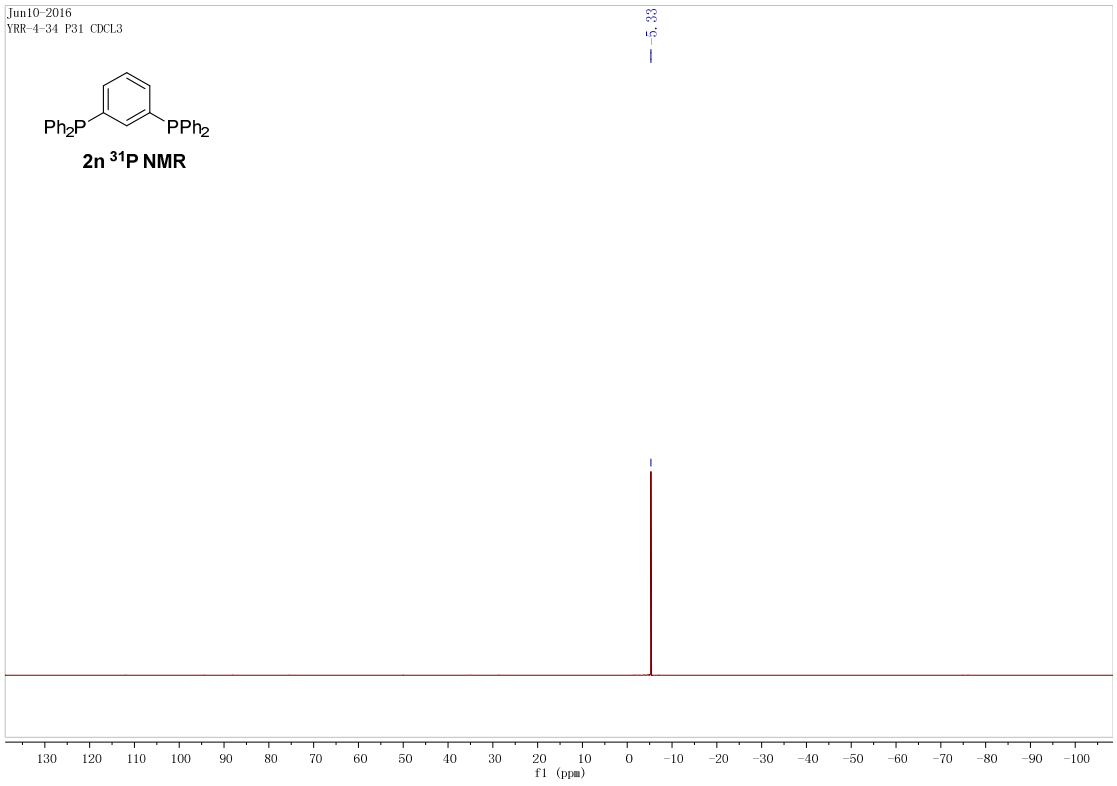
$^{13}C$ NMR spectra of **2m** in $CDCl_3$:



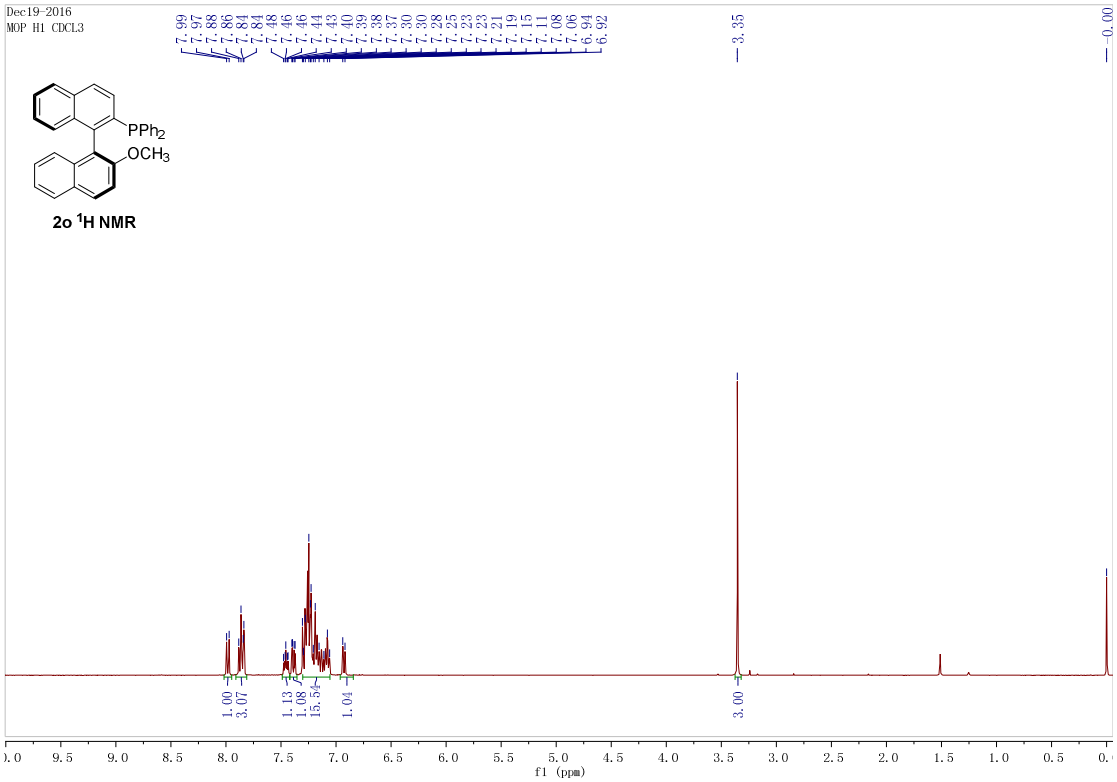
$^{1}$H NMR spectra of **2n** in $CDCl_3$:



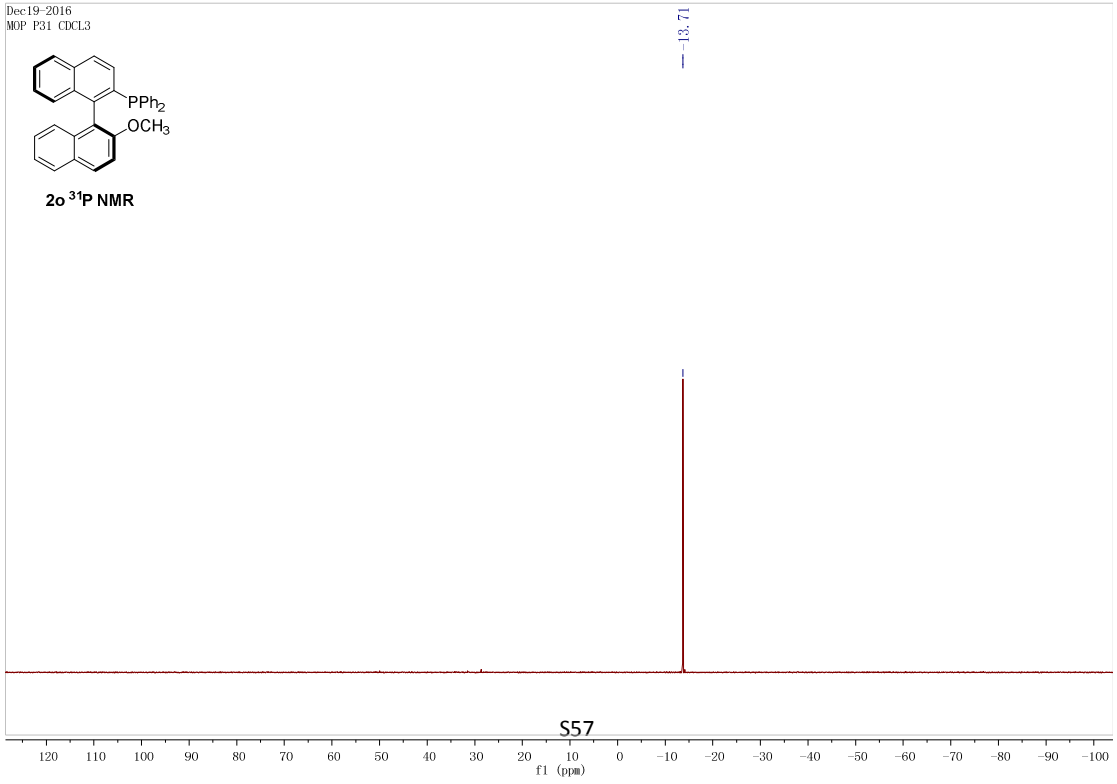

$^{31}$P NMR spectra of **2n** in $CDCl_3$:



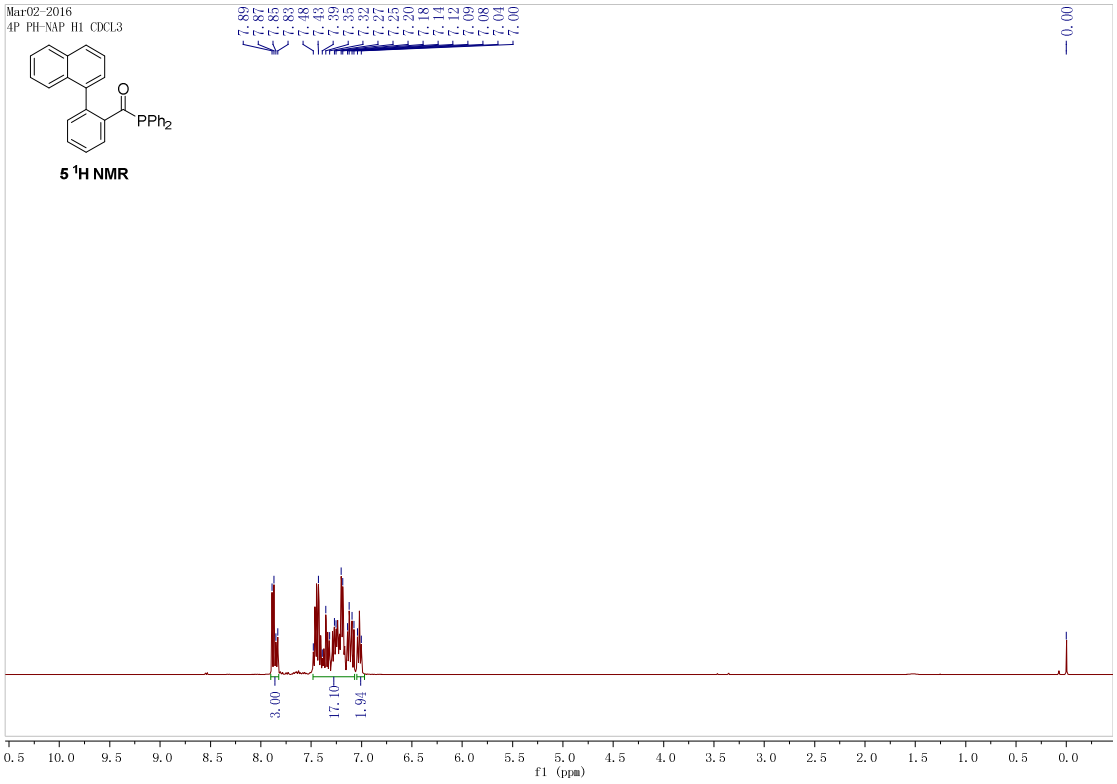
$^{1}$H NMR spectra of **2o** in $CDCl_3$:



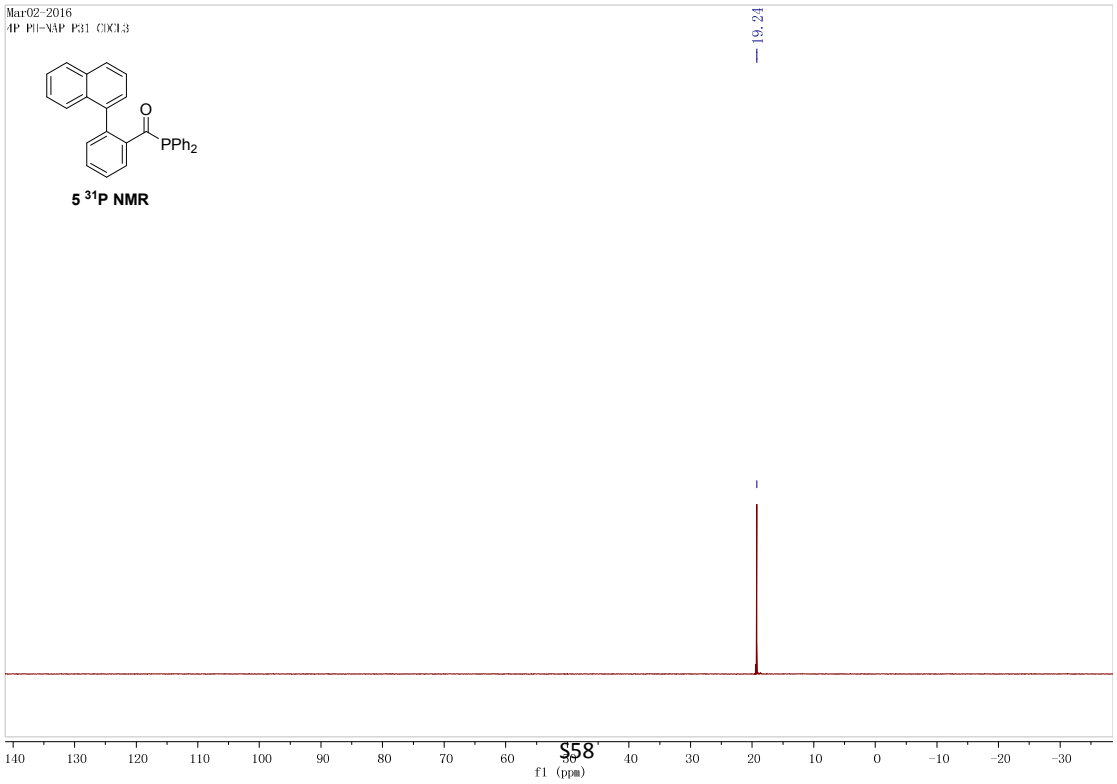

$^{31}$P NMR spectra of **2o** in $CDCl_3$:



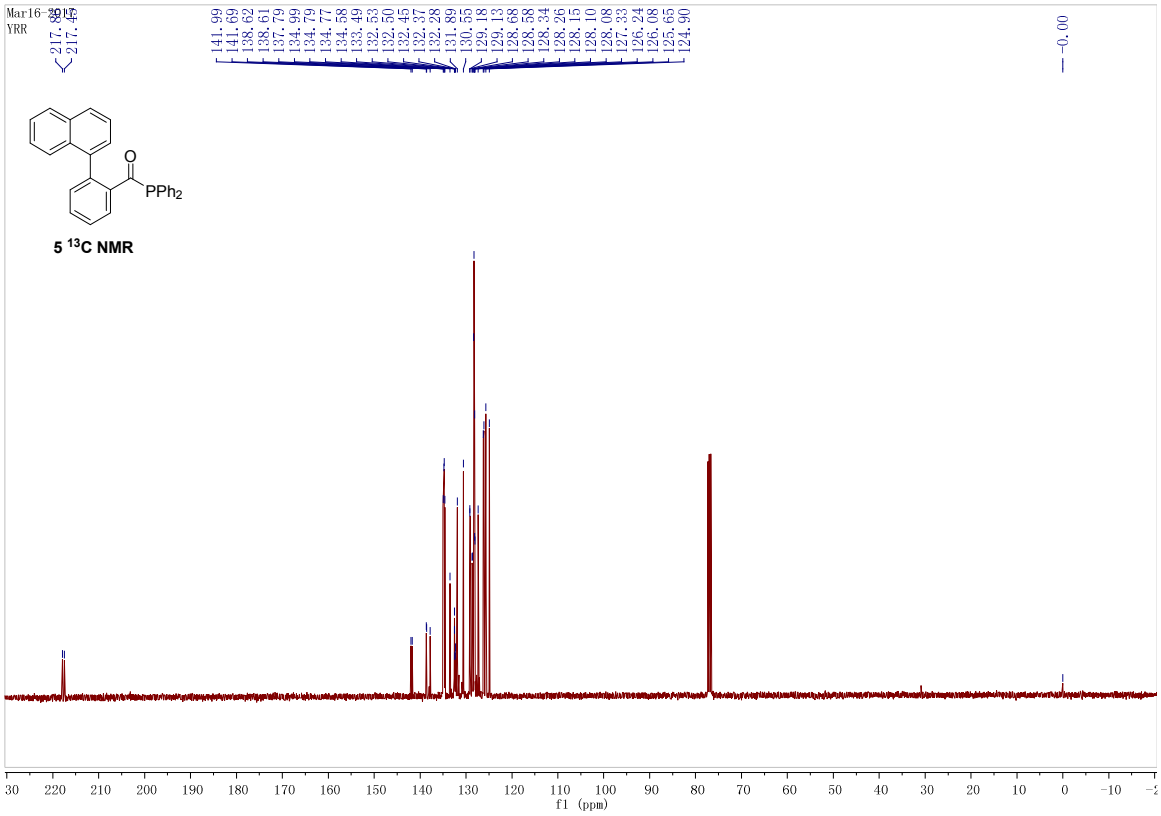
$^{1}$H NMR spectra of **5** in $CDCl_3$:



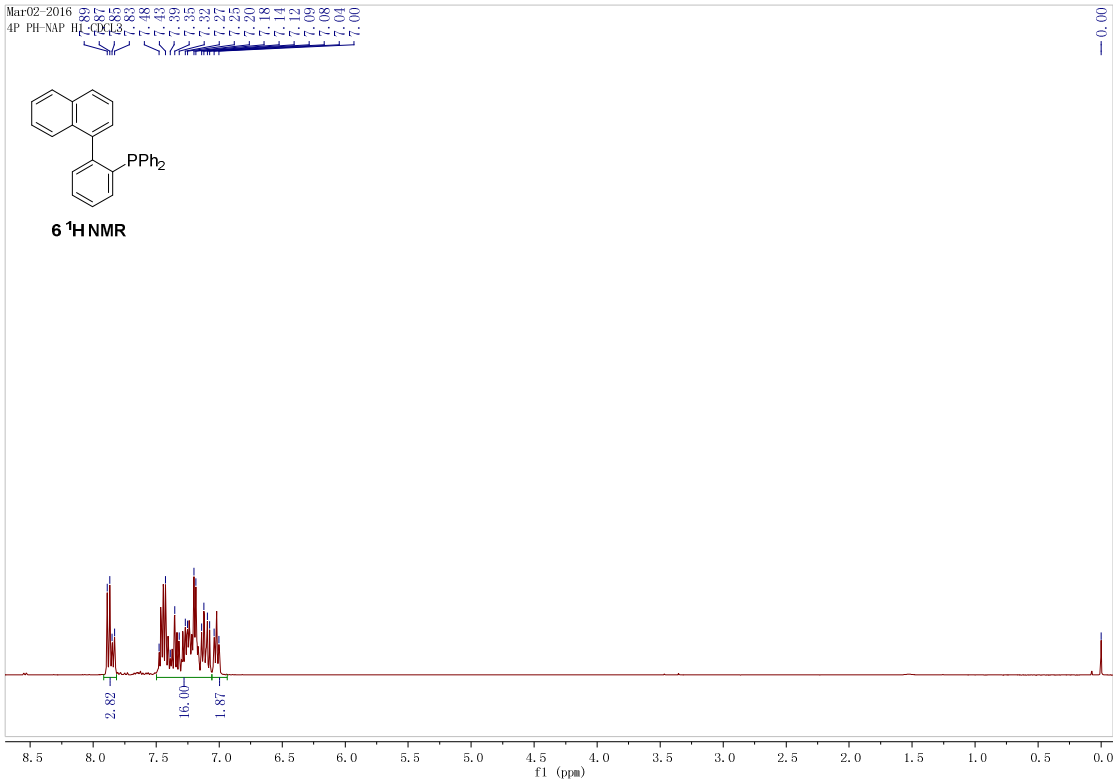

$^{31}$P NMR spectra of **5** in $CDCl_3$:



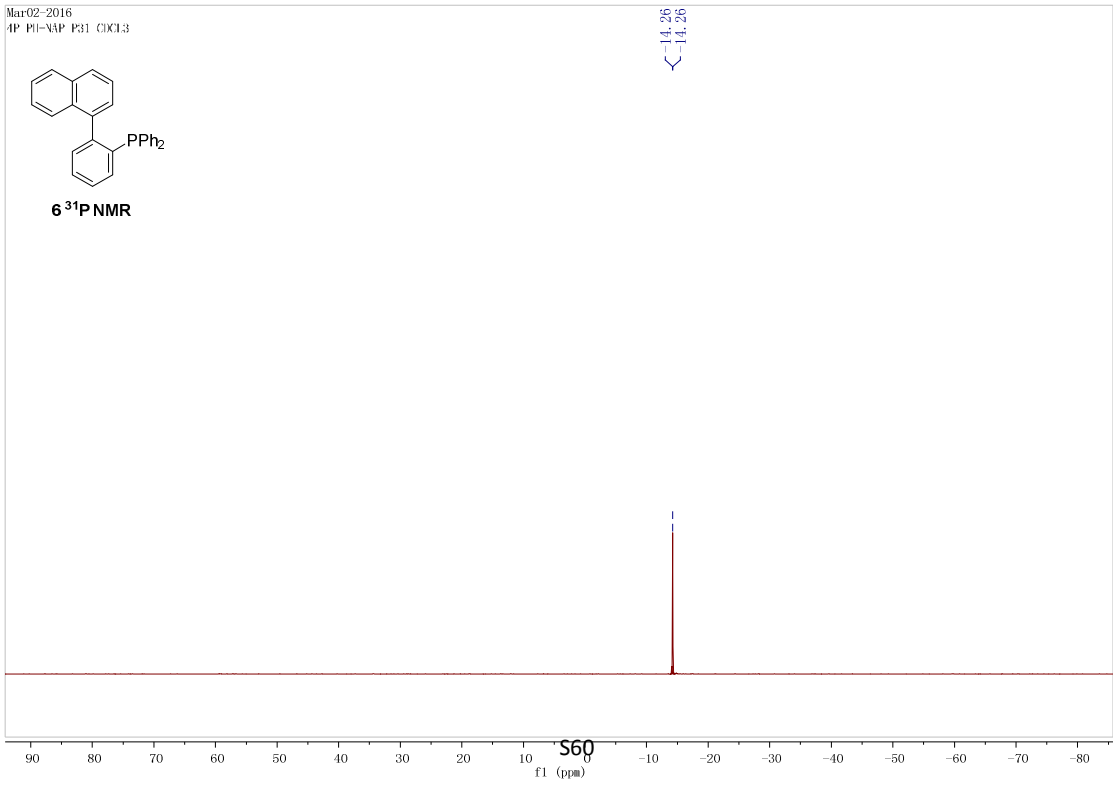
$^{13}C$ NMR spectra of **5** in $CDCl_3$:



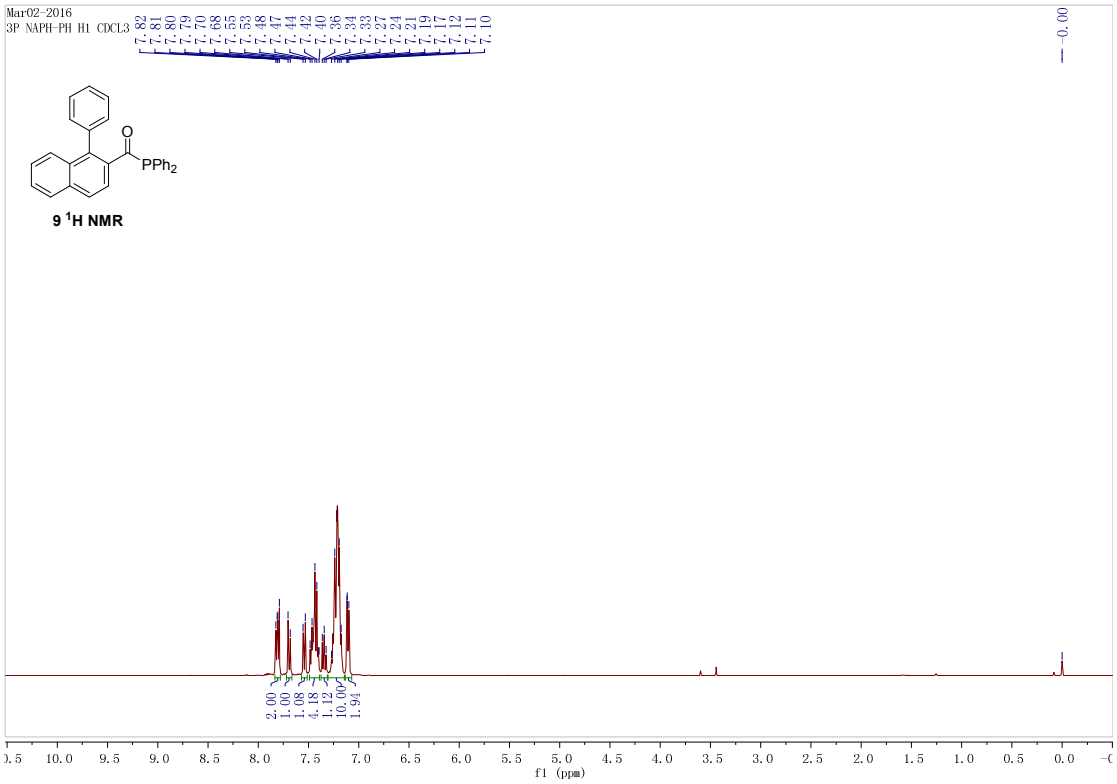
$^{1}$H NMR spectra of **6** in $CDCl_3$:



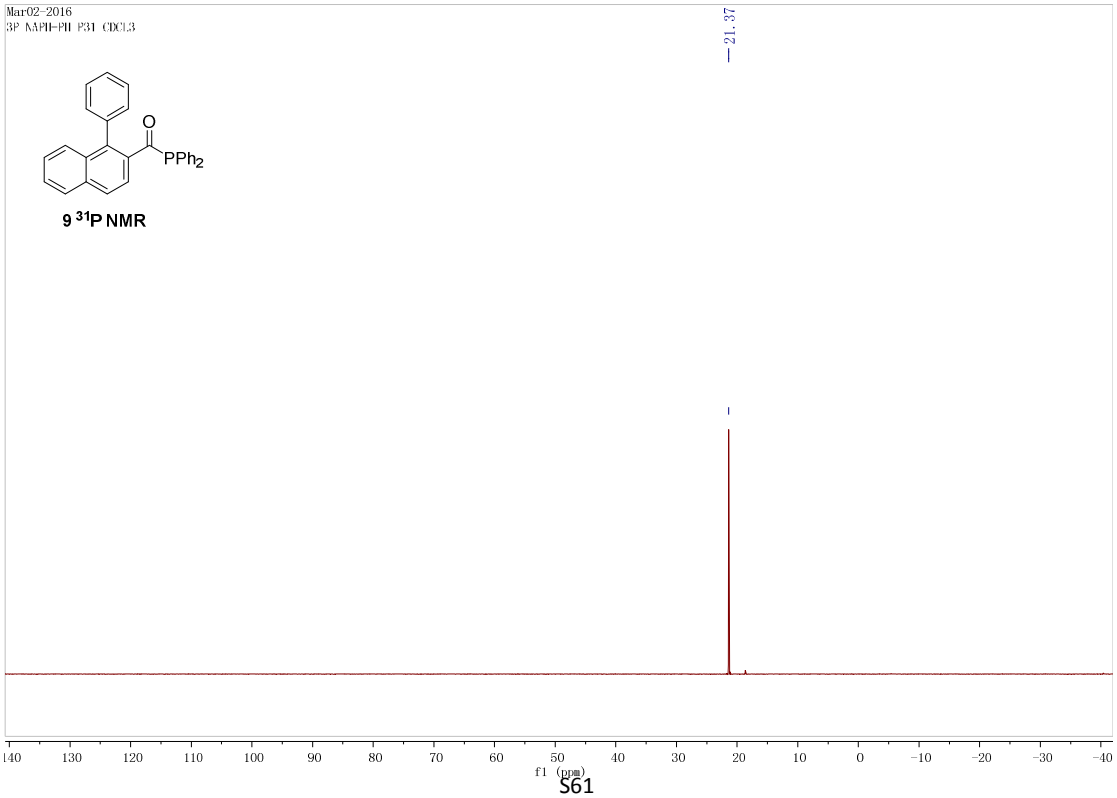

$^{31}$P NMR spectra of **6** in $CDCl_3$:



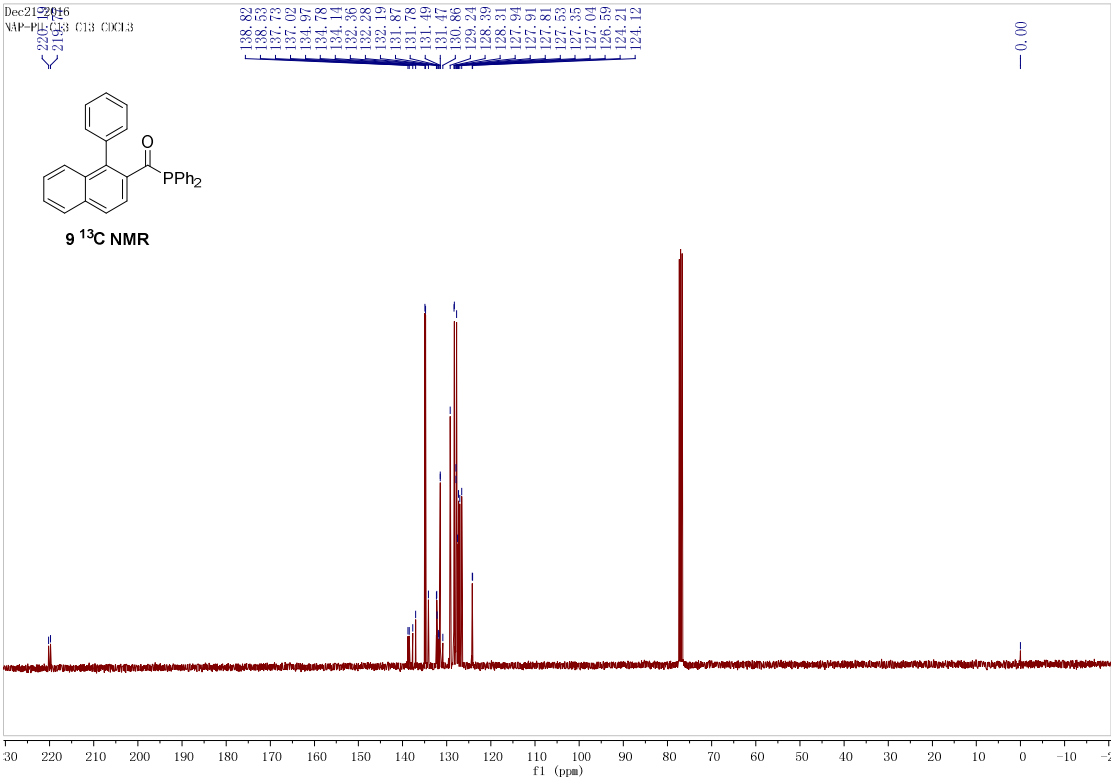
$^{1}$H NMR spectra of **9** in $CDCl_3$:



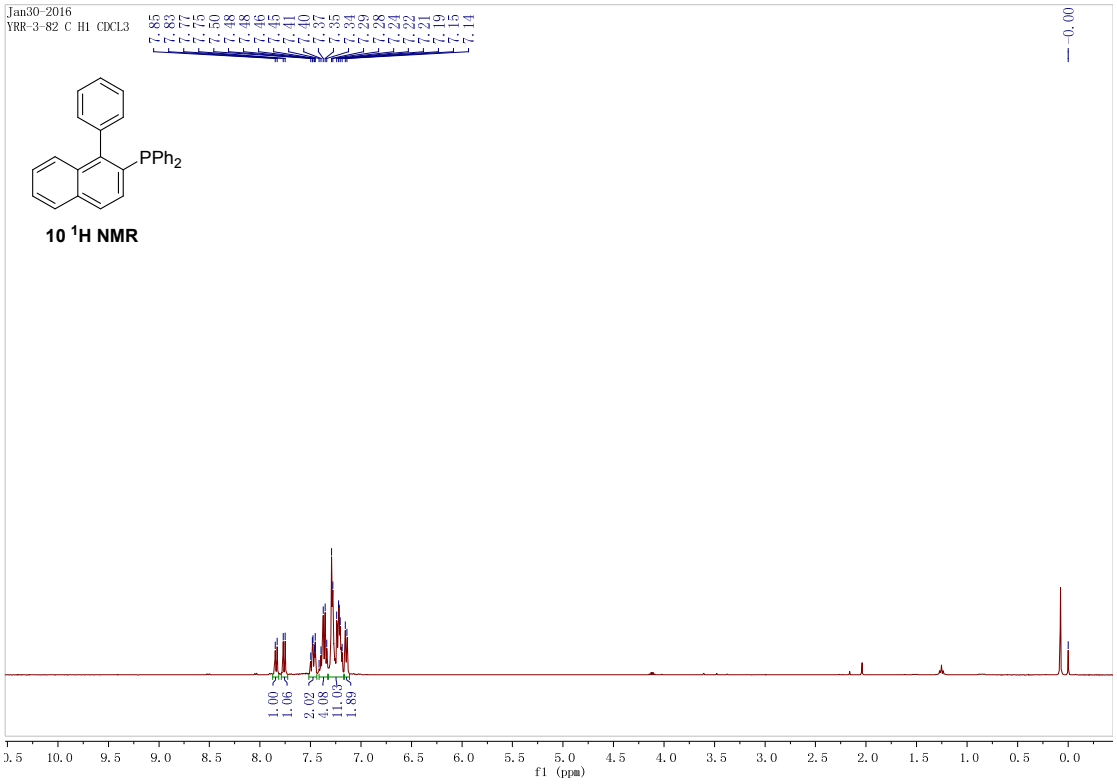

$^{31}$P NMR spectra of **9** in $CDCl_3$:



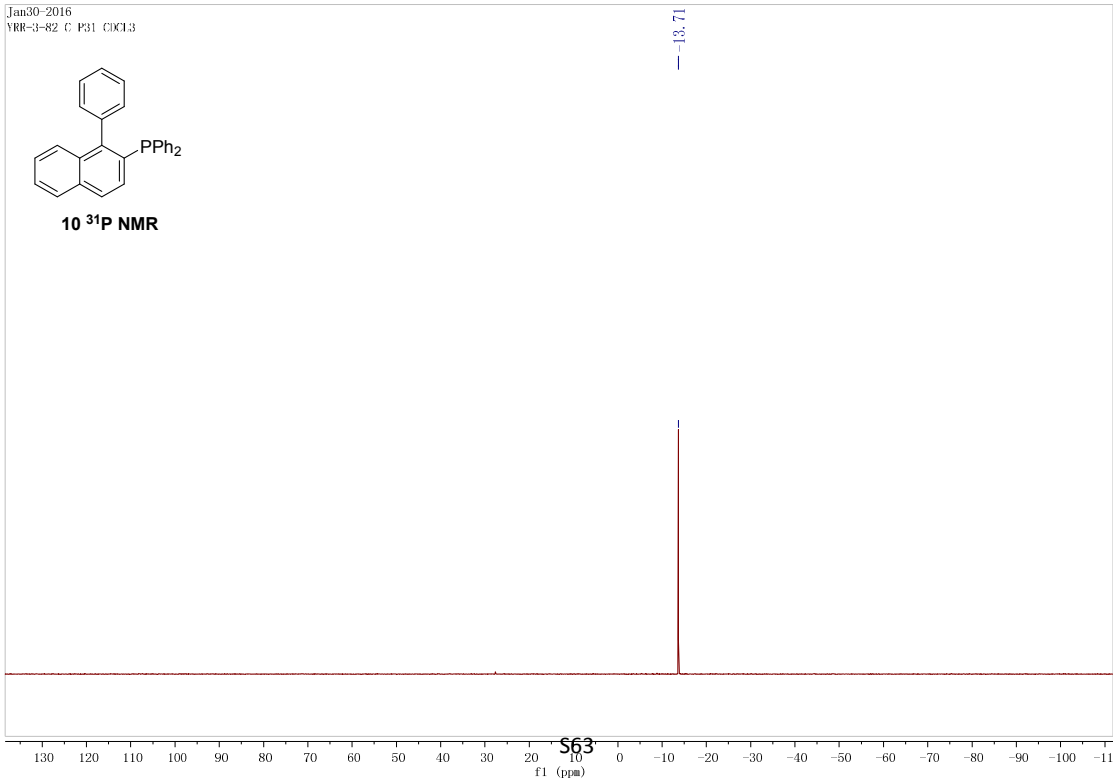
$^{13}C$ NMR spectra of **9** in $CDCl_3$:



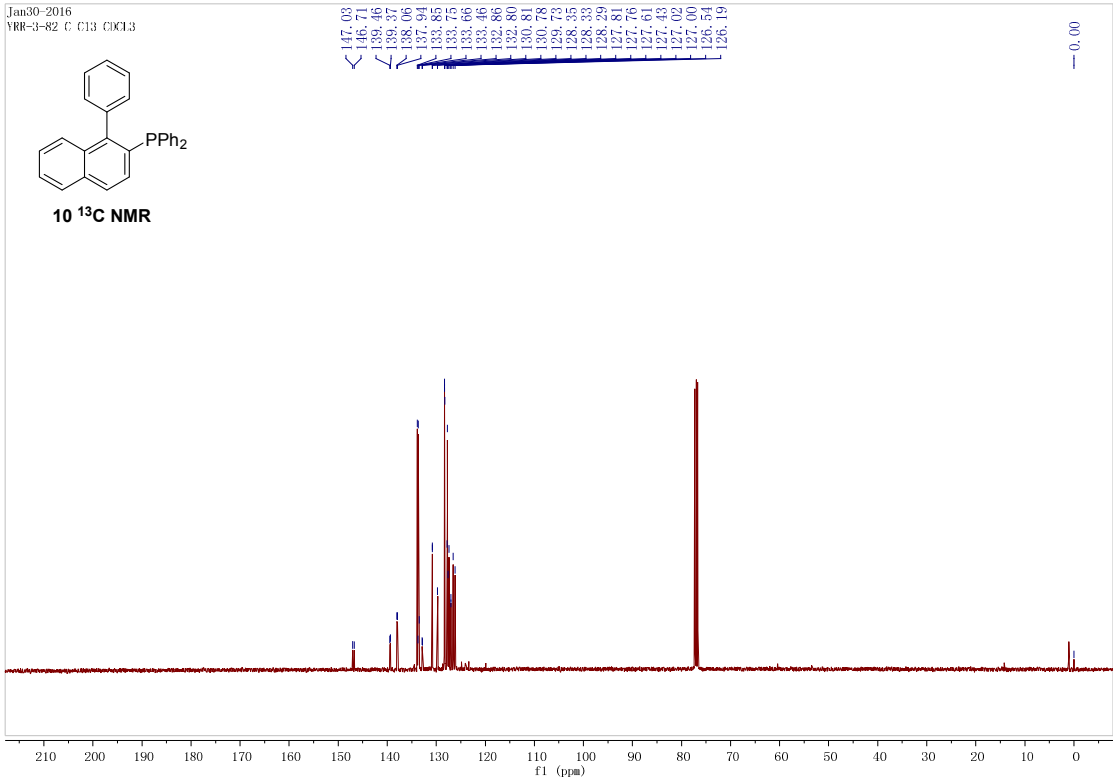
$^{1}$H NMR spectra of **10** in $CDCl_3$:



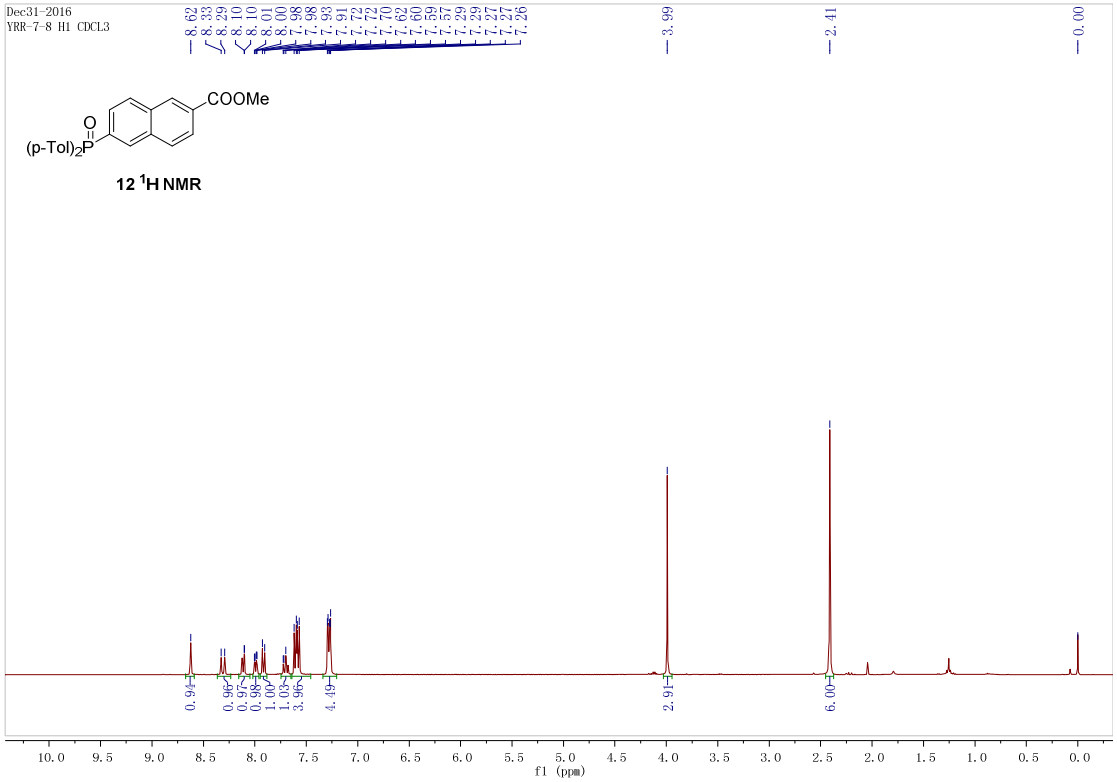

$^{31}$P NMR spectra of **10** in $CDCl_3$:



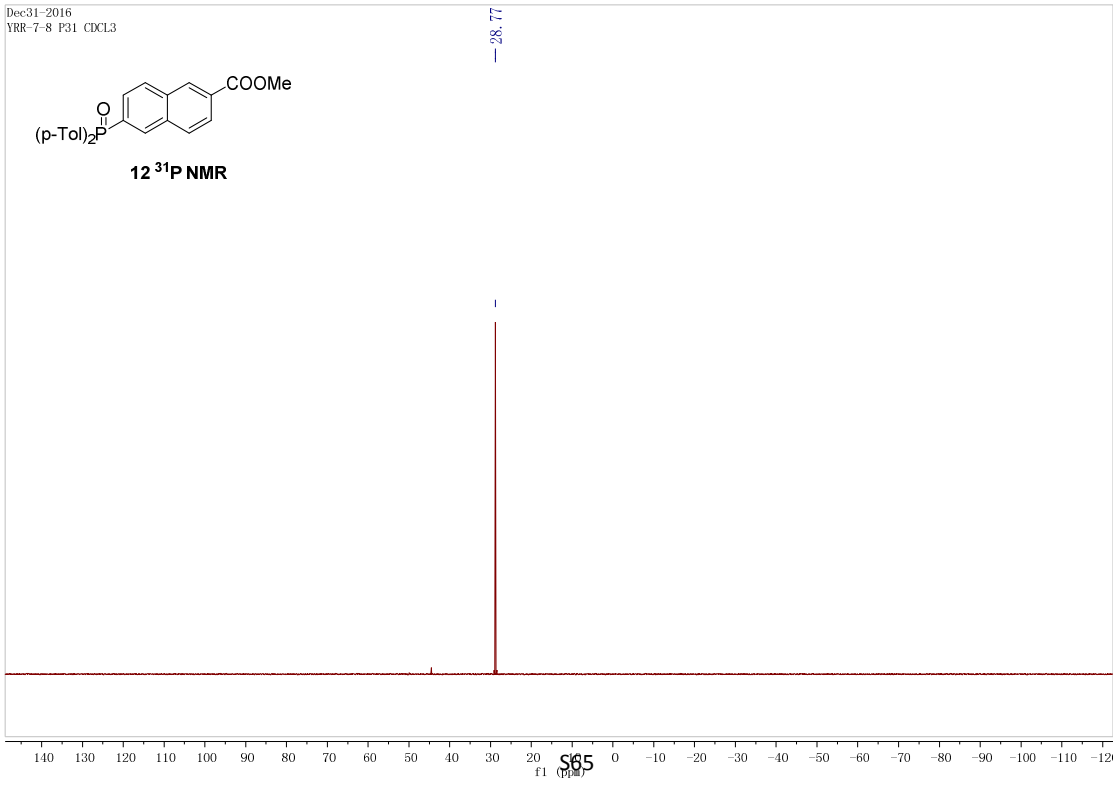
$^{13}C$ NMR spectra of **10** in $CDCl_3$:



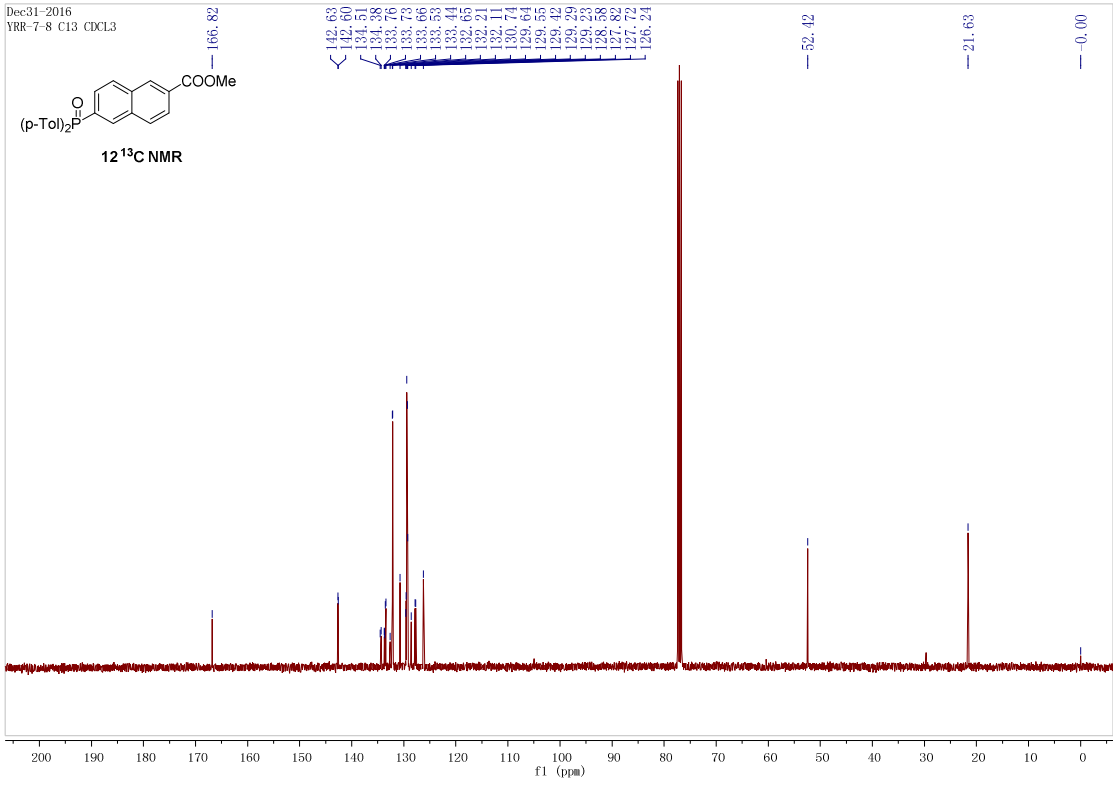
H NMR spectra of **12** in $CDCl_3$:



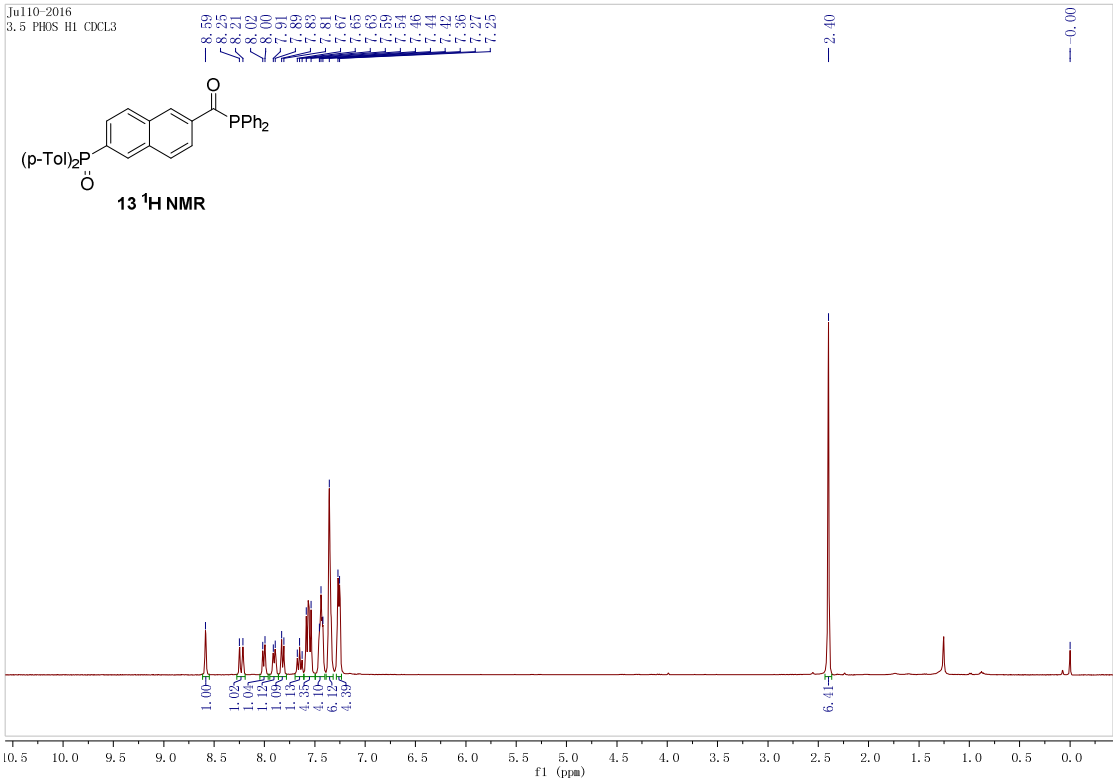

$^{31}P$ NMR spectra of **12** in $CDCl_3$:



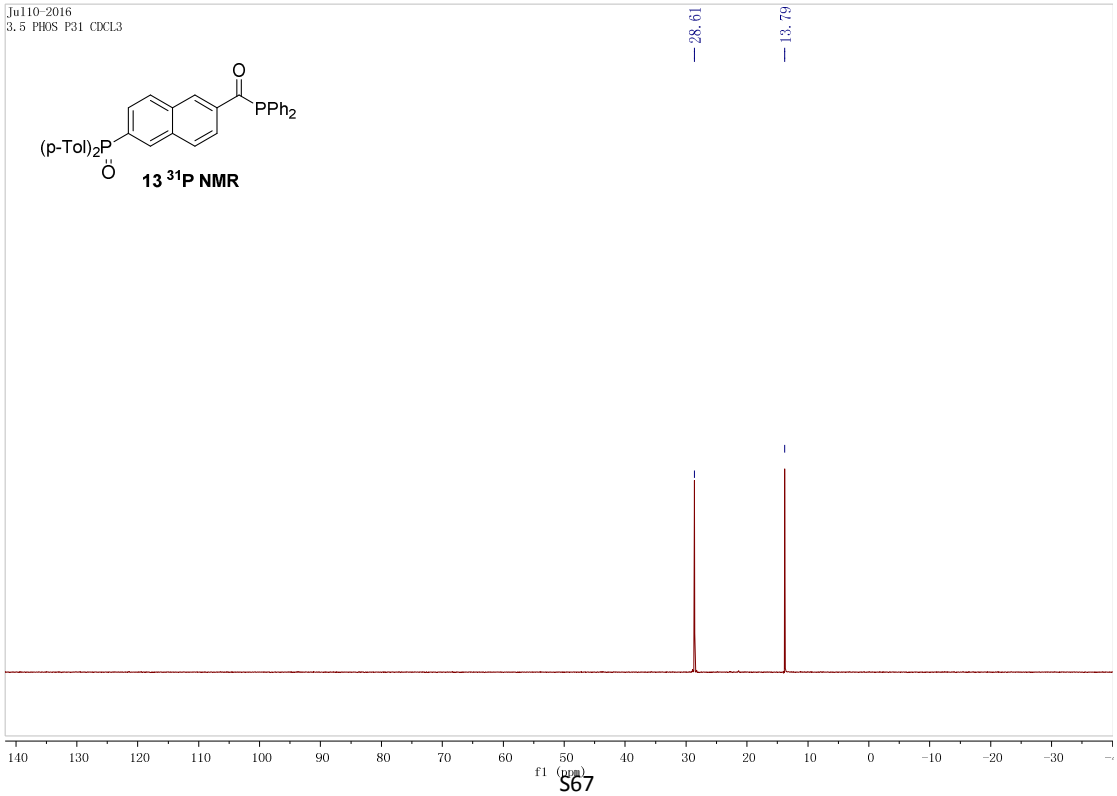
$^{13}C$ NMR spectra of **12** in $CDCl_3$:



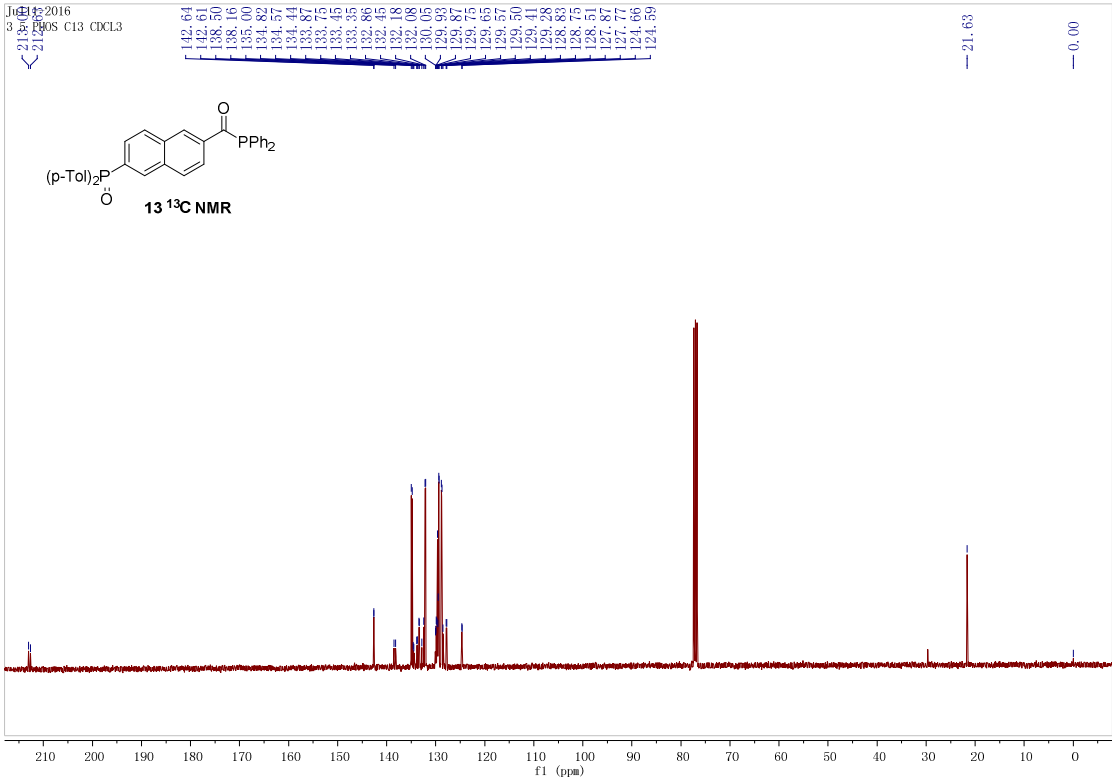
$^{1}$H NMR spectra of **13** in $CDCl_3$:



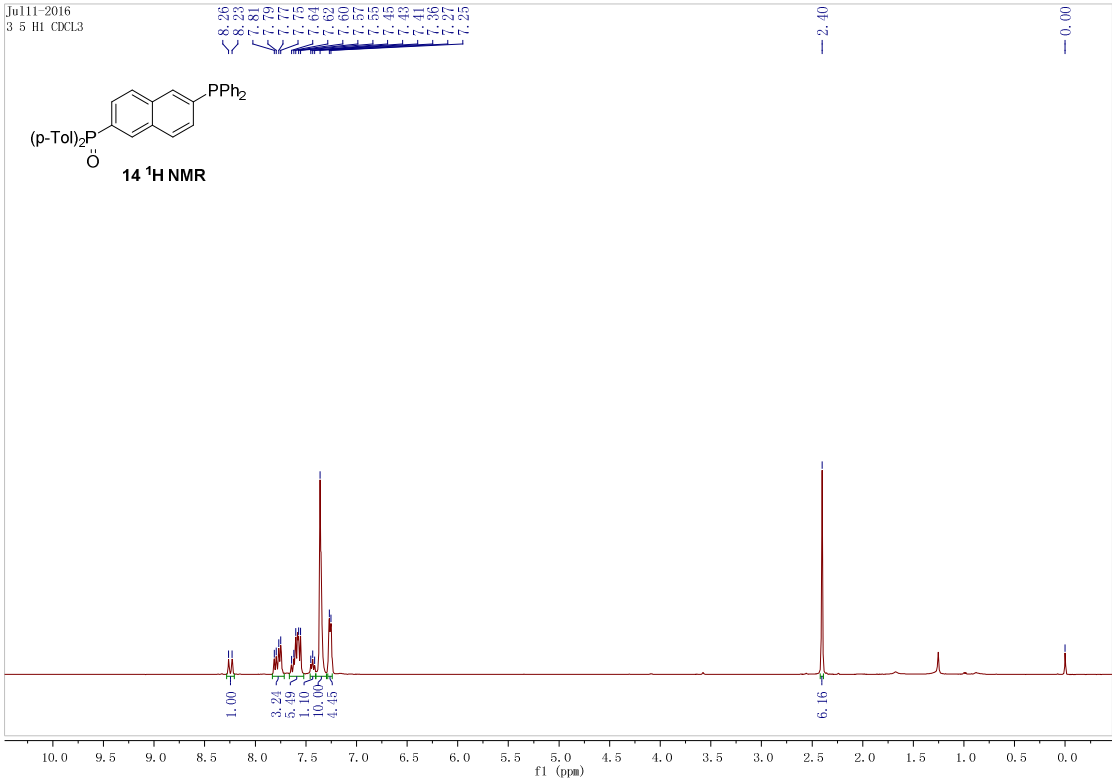

$^{31}$P NMR spectra of **13** in $CDCl_3$:



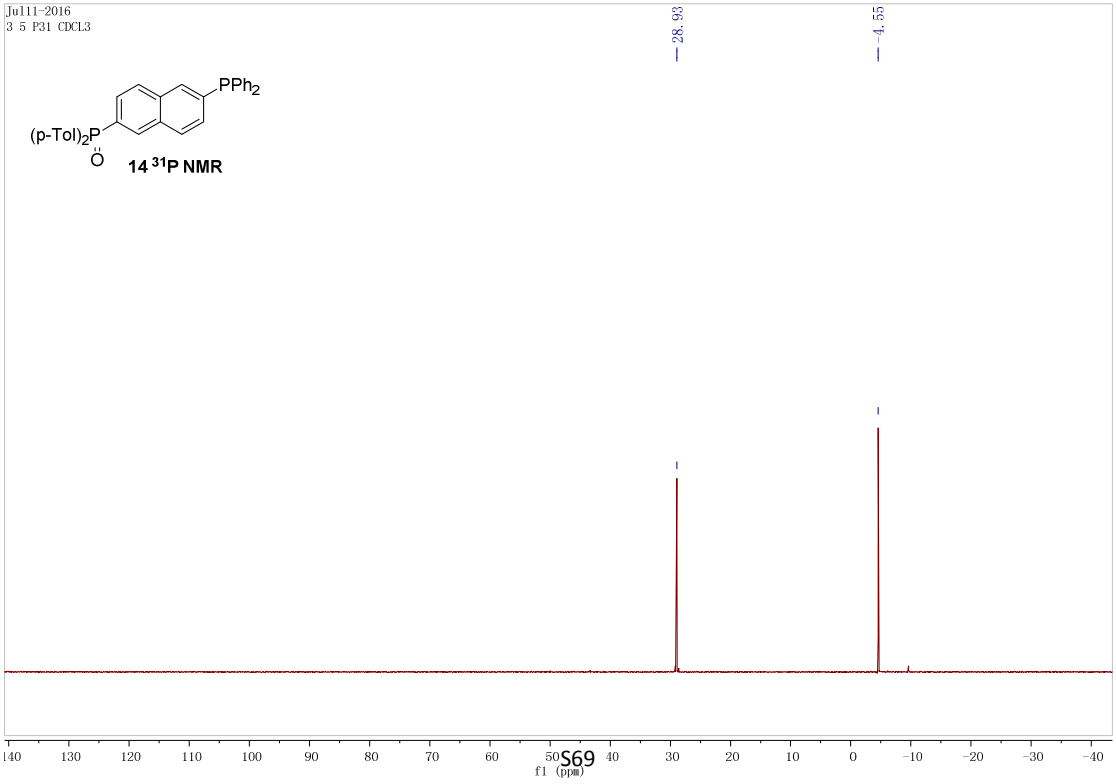
$^{13}C$ NMR spectra of **13** in $CDCl_3$:



$^{1}$H NMR spectra of **14** in $CDCl_3$:




$^{31}$P NMR spectra of **14** in $CDCl_3$:



$^{13}C$ NMR spectra of **14** in $CDCl_3$: