Supporting Information

A Transtion-Metal Free Three-Component Coupling Approach to Quinap Derivates

Xin-Wei Guo,[b] Li-Xia Quan,*,[a] Xian-Hong Zhu,[a] Fa-Yun Chen,[a] An-Xi Zhou,[a] Liu-Liang Mao,*,[a] Jie-Ping Wan[c] and Shang-Dong Yang[b]

[a] College of Chemistry and Environment Science, Shangrao Normal University, Shangrao, Jiangxi 334001, China

[b] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, P. R. China

[c] College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, Jiangxi 330022, P. R. China

Contents:

1. General Information

Commercial reagents were purchased from commercial suppliers and used without further purification. All dry solvents were treated according to standard procedures prior to use unless otherwise noted. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Column chromatography was performed using silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker instrument 400(400 MHz for ^{1}H,100 MHz for ^{13}C and 162 MHz for ^{31}P) in $CDCl_3$ or Bruker instrument 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C and and 121 MHz for ^{31}P) using $CDCl_3$ as the solvent and tetramethyl silane (TMS) as internal reference. TMS Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal standard. The following abbreviations (or combinations there of) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signals. The ^{1}H NMR spectra are reported as follows: chemical shift δ in ppm relative to TMS (δ = 0 ppm), multiplicity, coupling constant *J*, are reported in hertz, number of protons. ^{13}C NMR spectra are reported as follows: chemical shift δ in ppm relative to $CDCl_3$ (δ = 77.0 ppm), multiplicity, coupling constant *J*, are reported in hertz. Mass spectroscopy data of the products were collected on a Bruker esquire 6000 instrument using ESI ionization.

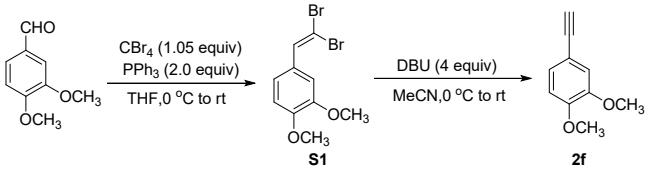
2. Preparation of starting materials

Substituted aniline **1a-1k**, were purchased from commercial source, and used without further purification.

Synthesis of substituted Alkyne

Substituted alkyne **2a-2e** and **2i-2m** were purchased from commercial source, and used without further purification. **2f**[1][2],**2g**[3] was prepared according to corresponding literatures.

Procedure to prepare **2f**[1][2]**:**

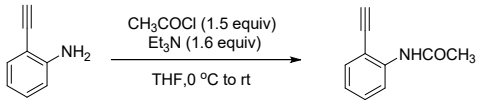


To a solution of the veratraldehyde (0.83 g, 5.0 mmol) in 10 ml dry DCM, carbon tetrabromide (1.74 g, 5.25 mmol) was added. The mixture was cooled to 0 °C, and a solution of triphenylphosphine (2.62 g, 10.0 mmol) in 10 mL dry DCM was added dropwise. The reaction mixture was allowed to gradually warm up to room temperature and stirred overnight at room temperature. The reaction mixture was quenched with water, and the organic layer was separated and washed with brine. The crude mixture concentrated under vacuum, and purified by flash column chromatography get the dibromoethane derivative S1, yellow oil (1.45g, 90%).

To a stirred solution of dibromoethane derivative S1 (1.45 g, 4.5 mmol) in anhydrous CH_3CN (10 mL) was added DBU (2.8 mL, 18.0 mmol) dropwise at 0 °C. The reaction mixture was warm to ambient temperature (25-30 °C) stir at for one day. After completion of reaction (monitored by TLC), reaction mixture quenched by dropwise addition of aqueous HCl then continued stirring for 5 mins. The reaction mixture was extracted three times with DCM; organic layers were washed with brine, solvent was evaporated under vacuum, and resulting residues were purified by flash

column chromatography to afford the **2f** as a yellow solid (0.47 g, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.99 (d, *J* = 1.6 Hz,1 H), 6.81 (d, *J* = 8.4 Hz, 1H), 3.89 (s, 3 H), 3.88 (s, 3 H), 3.01 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.8, 148.5, 125.4, 114.6, 114.1, 110.8, 83.7, 75.7, 55.8. **MS (ESI):** found $[M+H]^+$ 162.1. Spectral data for this compound is consistent with that previously reported.[2]

Procedure to prepare **2g[3]:**

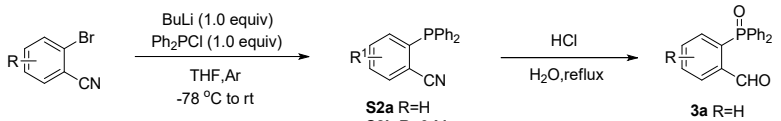


2g

To a solution of o-ethynyl aniline (0.227 mL, 2.0 mmol), Et_3N (0.42 mL, 3.2 mmol) in THF (4 mL) was added acetyl chloride (0.21 mL,3.0 mmol) dropwise at 0 °C. After the addition was complete, the reaction mixture was stirred at room temperature. The reaction was monitored by TLC, after completion of the reaction, the reaction was quenched by water and the resulting mixture was extracted three times with DCM. The combined extracts were washed with brine and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford *N*-acetyl-o-ethynyl aniline **2g** as a white solid (0.30g, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 1H), 7.92 (br, 1H), 7.46 (dd, *J* = 7.6 ,1.2 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 3.51 (s, 1H), 2.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 139.6, 132.1, 130.2, 123.3, 119.2, 110.4, 84.3, 79.2, 24.9. **MS (ESI):** found $[M+H]^+$ 159.9. Spectral data for this compound is consistent with that previously reported.[3]

Synthesis of substituted aldehyde

General Procedure A to prepare 3a-3d,3h[4][5]:



S2a R=H
S2b R=6-Me
S2c R=4-Me

3a R=H
3b R=6-Me
3c R=4-Me

To a solution of 2-bromobenzonitrile (1.0 equiv) in dry THF under Ar at -78 °C, n-butyllithium (2.4M in hexane, 1.0 equiv) was added dropwise, the mixture stirs at -78 °C for 1 hours. Then the solution of Ph_2PCl or Cy_2PCl (1.0 equiv) in dry THF was added dropwise to the solution, the mixture was stirred for further 30 min at -78 °C, and the reaction mixture allowed to warm to room temperature stir over night, and quenched by water. The resulting mixture was extracted three times with DCM. The combined extracts concentrated in vacuo, and the residue washed by methanol to give the rough product, use in next step without further purification.

A mixture of S2 in concerned hydrochloric acid (1 mmol S2~2 mL) was refluxed at 120 °C with vigorous stirring for overnight. During this period, after cooling down to room temperature, water was added and the mixture stirred for 30 min, and the resulting mixture was extracted three times with DCM. The combined extracts were washed with brine and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford product.

2-(diphenylphosphoryl)benzaldehyde (3a)

2-bromobenzonitrile (9.1 g, 50.0 mmol) was following the General Procedure A. The crude mixture was purified by column chromatography (petroleum ether /ethyl acetate = 1:1) to afford a white solid (8.9 g, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.75 (s, 1H), 8.21-8.10 (m, 1H), 7.74-7.46 (m, 12 H), 7.23 (dd, *J* = 13.6, 7.6Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.2 (d, J_{C-P} =

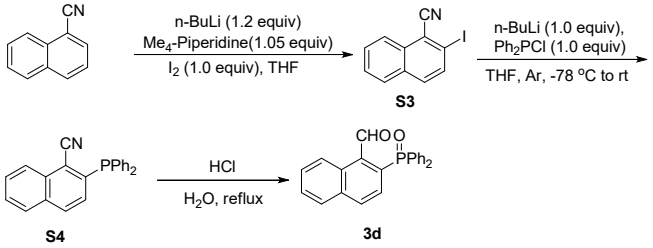
5.6 Hz), 139.4 (d, J_{C-P} = 6.5 Hz), 135.1 (d, J_{C-P} = 95.4 Hz), 133.6 (d, J_{C-P} = 11.0 Hz), 132.8, 132.7, 132.3 (d, J_{C-P} = 2.8 Hz), 131.8 (d, J_{C-P} = 10.0 Hz), 131.6 (d, J_{C-P} = 12.8 Hz), 129.0 (d, J_{C-P} = 8.7 Hz), 128.8 (d, J_{C-P} = 12.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.05. **MS (ESI):** found $[M+H]^+$ 307.0. Spectral data for this compound is consistent with that previously reported.[5]

2-(diphenylphosphoryl)-6-methylbenzaldehyde (3b)

2-bromo-6-methylbenzonitrile (3.6 g, 18.5 mmol) was following the General Procedure A. The crude mixture was purified by column chromatography (petroleum ether /ethyl acetate = 1:1) to afford a white solid (2.87 g, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.84 (s, 1H), 7.65 (dd, J = 12.2, 7.4 Hz, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.53-7.44 (m, 5H), 7.37 (td, J = 7.6, 2.4Hz, 1H), 7.10 (dd, J = 14.0, 7.6 Hz, 1H), 2.62 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.4 (d, J_{C-P} = 6.7 Hz), 141.5 (d, J_{C-P} = 8.7 Hz), 137.9 (d, J_{C-P} = 6.4 Hz), 136.1 (d, J_{C-P} = 2.5 Hz), 136.0, 135.1, 133.0, 132.2 (d, J_{C-P} = 2.8 Hz), 131.9 (d, J_{C-P} = 9.8 Hz), 131.1 (d, J_{C-P} = 13.2 Hz), 128.7 (d, J_{C-P} = 12.3 Hz), 21.7; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.38. **MS (ESI):** found $[M+H]^+$ 321.2. Spectral data for this compound is consistent with that previously reported.[5]

2-(diphenylphosphoryl)-4-methylbenzaldehyde (3c)

2-bromo-4-methylbenzonitrile (2.8 g, 14.4 mmol) was following the General Procedure A. The crude mixture was purified by column chromatography (petroleum ether/ethyl acetate = 1:1) to afford a white solid (2.1 g, 46 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.62 (s, 1 H), 8.07 (qt, J = 4.0, 1.6 Hz, 1H), 7.71-7.62 (m, 4 H), 7.61-7.55 (m, 2H), 7.54-7.45 (m, 5 H), 7.08 (d, J = 14.0 Hz, 1 H), 2.35 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.9 (d, J_{C-P} = 5.3 Hz), 143.9 (d, J_{C-P} = 11.8 Hz), 137.1 (d, J_{C-P} = 6.6 Hz), 135.4, 134.3 (d, J_{C-P} = 10.5 Hz), 133.0 (d, J_{C-P} = 2.3 Hz),132.3(d, J_{C-P} = 2.7 Hz), 131.9 (d, J_{C-P} = 9.9 Hz), 131.8, 129.4 (d, J_{C-P} = 9.3 Hz), 128.8 (d, J_{C-P} = 12.2 Hz), 21.9; **^{31}P NMR** (162MHz, $CDCl_3$) δ 30.86. **MS (ESI):** found $[M+H]^+$ 321.2. Spectral data for this compound is consistent with that previously reported.[5]

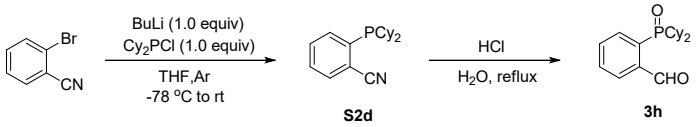


2-(diphenylphosphoryl)-1-naphthaldehyde (3d)

To obtain the substrate S3, n-BuLi (2.4 M in hexane, 23 mL, 1.2 equiv.) was slowly added to the 2,2,6,6-tetramethylpiperidine in THF solution at -5 °C - 0 °C. After the reaction for 1 h, the temperature was reduced to -78 °C, then add 1-naphthalenenitrile (45.7 mmol, 1.0 equiv.) in THF slowly to the solution, continue the reaction for 1h. Then add I_2 (45.7 mmol, 1.0 equiv.) solution in THF into reaction systems, continue stir at -78 °C for 2h, slowly raise to room temperature and stir overnight, the reaction was quenched with water, the reaction solution was washed with $NaHSO_3$ solution, and extracted three times with DCM. The organic phases were combined and the solvent was evaporated. 2-Iodo-1-naphthalenecarbonitrile was isolated by column chromatography.

1-iodo-2-naphthonitrile (9.7 g, 34.8 mmol) was following the General Procedure A. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 1:2) to provide a white solid **3d** (4.3 g, 35 %), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.22 (s, 1H), 8.91(d, J = 8.2 Hz, 1H), 7.96 (dd, J = 8.4, 2.2 Hz, 1H), 7.90-7.87 (m, 1H), 7.74-7.56 (m, 8H), 7.50 (td, J = 7.4, 3.0

Hz, 4H), 7.28 (dd, J = 12.3, 8.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.2 (d, J_{C-P} = 7.5 Hz), 135.1 (d, J_{C-P} = 2.2 Hz), 135.0, 134.0, 133.0, 132.4 (d, J_{C-P} = 2.7 Hz), 132.3, 132.0 (d, J_{C-P} = 10.0 Hz), 130.5 (d, J_{C-P} = 10.2 Hz), 129.4, 128.7 (d, J_{C-P} = 12.3 Hz), 128.6, 128.3, 127.9 (d, J_{C-P} = 11.5 Hz), 126.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.49. **MS (ESI):** found $[M+H]^+$ 357.0. Spectral data for this compound is consistent with that previously reported.[5]



2-(dicyclohexylphosphoryl)benzaldehyde (3h)

2-bromobenzonitrile (4.0 g, 21.9 mmol) was following the General Procedure A. The crude mixture was purified by column chromatography (petroleum ether /ethyl acetate = 1:1) to afford a white solid **3h** (2.5 g, 36 %), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.88 (br, 1H), 8.07 (s, 1H), 7.87-7.56 (m, 3H), 2.34-2.04 (m, 4H), 1.86 (d, J = 12.0 Hz, 2H) ,1.78-1.58 (m, 4H), 1.56-1.06 (m, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.9, 132.7, 132.6, 132.4, 131.6, 131.4, 131.4, 36.0 (d, J_{C-P} = 66.6 Hz), 26.3 (dd, J_{C-P} = 12.8, 10.3 Hz), 25.7 (d, J_{C-P} = 2.7 Hz), 25.6 (d, J_{C-P} = 0.8 Hz), 25.1 (d, J_{C-P} = 1.6 Hz); **^{31}P NMR** (162MHz, $CDCl_3$) δ 51.28. **MS (ESI):** found $[M+H]^+$ 319.2. Spectral data for this compound is consistent with that previously reported.[5]

Procedure for prepare 3e-3g[5][6][7]:

General Procedure B to prepare Cyclic acetal

A solution of the aldehyde (1.0 equiv), Ethylene glycol (5.0 equiv), and *p*-Toluenesulfonic acid (5.0 mol %) in toluene (10 mL/g) was heated at reflux for 24 h. After cooling to room temperature, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$. The mixture was extracted with DCM and the combined organic was washed with water and brine, filtered and concentrated in vacuo, the crude residue was then purified by column chromatography.

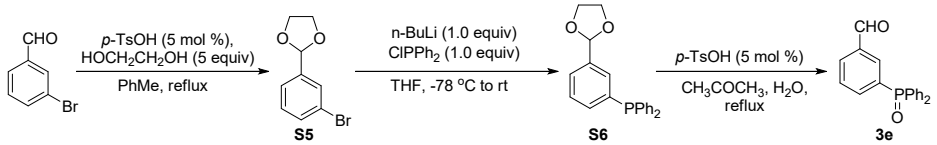
General Procedure C to prepare Cycloacetal phosphoxide

For the Synthesis of 1,3-dioxolanes diphenyl phosphine oxide, to a solution of cyclic acetal (1.0 eq) in anhydrous THF (10 mL/g), kept in an oven-dried Schlenk flask under an atmosphere of dry argon, was added dropwise a solution of n-BuLi in hexane (1.0 eq) at -78 °C. After stirring at -78 °C for 1 h, Ph_2PCl (1.0 eq) in anhydrous THF was added dropwise. Then the solution was stirred for 1 h at -78 °C, allowed to warm to room temperature and stirred for overnight. The reaction was quenched with a solution of NH_4Cl (aq.) and the product was extracted with DCM. The combined organic layer was washed with water and brine. Filtered and the residue was purified by column chromatography to afford the product.

General Procedure D to prepare Aldehyde phosphoxide[7]

p-Toluenesulfonic acid (5 mol %) was added to a solution of 1,3-dioxolanes diphenyl phosphine oxide (1.0 eq) in a mixture of acetone/water. The mixture was refluxed until completion. After the completion of the reaction, the mixture was cooled to room temperature, and the acetone was removed under vacuum. The residue was dissolved in DCM, washed with saturated aqueous $NaHCO_3$, water and brine, and concentrated under vacuum. The crude product was purified by silica gel column chromatography to afford the product.

Procedure for synthesis of 3e [7]:



2-(3-bromophenyl)-1,3-dioxolane (S5)

3-bromobenzaldehyde (3.7 g, 20 mmol) was following the General Procedure B. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 50:1) to afford a Colorless oily compound (3.04g, 67%).

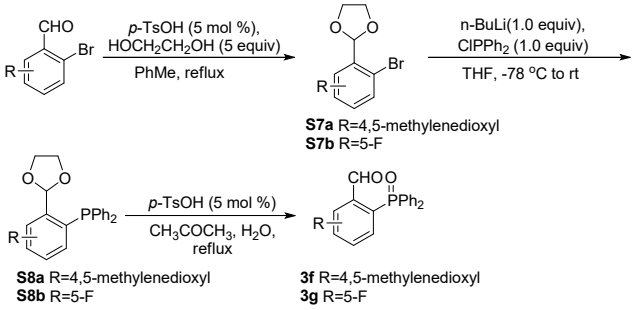
(3-(1,3-dioxolan-2-yl)phenyl)diphenylphosphine oxide (S6)

2-(3-bromophenyl)-1,3-dioxolane (3.04 g, 13.3 mmol) was following the General Procedure C. The residue was purified by column chromatography (petroleum ether /ethyl acetate = 1:3) to afford a white solid (1.42g, 31%).

3-(diphenylphosphoryl) benzaldehyde (3e)

(3-(1,3-dioxolan-2-yl)phenyl)diphenylphosphine oxide (1.42 g, 4.1 mmol) was following the General Procedure D. The residue was purified by column chromatography (petroleum ether /ethyl acetate = 1:2) to provide a white viscous substance **3e** (1.07g, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.21-8.15 (m, 1H), 8.11-8.05 (m, 1H), 8.02-7.94 (m, 1H), 7.73-7.64 (m, 5H), 7.63-7.56 (m, 2H), 7.54-7.46 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.4, 137.5 (d, $J_{C\text{-}P}$ = 9.9 Hz), 136.2 (d, $J_{C\text{-}P}$ = 10.9 Hz), 134.3 (d, $J_{C\text{-}P}$ = 101.5 Hz), 133.6 (d, $J_{C\text{-}P}$ = 10.1 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.5 Hz), 132.0 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.0, 129.4 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.28. **MS (ESI):** found $[M+H]^+$ 307.0. Spectral data for this compound is consistent with that previously reported.[7]

Procedure for synthesis of 3f-3g[5]:



5-bromo-6-(1,3-dioxolan-2-yl)benzo[d][1,3]dioxole (S7a)

6-bromobenzo[d][1,3]dioxole-5-carbaldehyde (3.43 g, 14.9 mmol) was following the General Procedure B. The residue was purified by column chromatography (petroleum ether /ethyl acetate = 30:1) to afford a white solid (3.63 g, 89 %).

(6-(1,3-dioxolan-2-yl)benzo[d][1,3]dioxol-5-yl)diphenylphosphine oxide (S8a)

5-bromo-6-(1,3-dioxolan-2-yl)benzo[d][1,3]dioxole (3.5 g, 12.9 mmol) was following the General Procedure C. The residue was purified by column chromatography (petroleum ether /ethyl acetate = 1:3) to afford a white solid (4.0 g, 79 %).

6-(diphenylphosphoryl)benzo[d][1,3]dioxole-5-carbaldehyde (3f)

(6-(1,3-dioxolan-2-yl)benzo[d][1,3]dioxol-5-yl)diphenylphosphine oxide (2.0 g, 5.07 mmol) was following the General Procedure D. The residue was purified by column chromatography (petroleum ether /ethyl acetate = 1:2) to provide a white solid **3f** (1.6 g, 90 %), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 7.77-7.56 (m, 7H), 7.50 (td, J = 7.4, 3.1 Hz, 4H), 6.59 (d, J = 13.2

Hz, 1H), 6.11 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.5 (d, J_{C-P} = 6.1 Hz), 151.2 (d, J_{C-P} = 17.8 Hz), 151.0 (d, J_{C-P} = 2.5 Hz), 136.1 (d, J_{C-P} = 7.1 Hz), 132.8, 132.4 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 10.0 Hz), 130.8, 128.9 (d, J_{C-P} = 12.3 Hz), 113.1 (d, J_{C-P} = 13.7 Hz), 108.7 (d, J_{C-P} = 11.2 Hz), 102.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.01. **MS (ESI):** found $[M+H]^+$ 351.0. Spectral data for this compound is consistent with that previously reported.[5]

2-(2-bromo-5-fluorophenyl)-1,3-dioxolane (S7b)

2-bromo-5-fluorobenzaldehyde (3.0 g, 14.8 mmol) was following the General Procedure B. The residue was purified by column chromatography (petroleum ether /ethyl acetate = 30:1) to afford a Colorless oily compound (3.4 g, 93 %).

(2-(1,3-dioxolan-2-yl)-4-fluorophenyl)diphenylphosphine oxide (S8b)

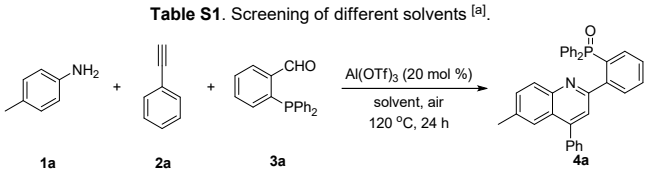
2-(2-bromo-5-fluorophenyl)-1,3-dioxolane (3.4 g, 13.8 mmol) was following the General Procedure C. The residue was purified by column chromatography (petroleum ether /ethyl acetate = 1:4) to afford a white solid (3.2 g, 78 %).

2-(diphenylphosphoryl)-5-fluorobenzaldehyde (3g)

(2-(1,3-dioxolan-2-yl)-4-fluorophenyl) diphenylphosphine oxide (1.1 g, 2.99 mmol) was following the General Procedure D. The residue was purified by column chromatography (petroleum ether /ethyl acetate = 1:4) to provide a white solid **3g** (0.86 g, 89 %), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.73 (d, J = 3.1 Hz, 1 H), 7.88-7.80 (m, 1 H), 7.70-7.58 (m, 6 H), 7.55-7.48 (m, 4 H), 7.26-7.17 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.8 (dd, J_{C-F} = 1.0 Hz, J_{C-P} = 5.2 Hz), 166.2 (d, J_{C-P} = 2.9 Hz), 163.7 (d, J_{C-P} = 2.8 Hz), 142.4 (t, J_{C-P} = 7.2 Hz), 136.2 (dd, J_{C-F} = 8.0 Hz, J_{C-P} = 12.4 Hz), 132.6 (d, J_{C-P} = 2.8 Hz), 132.5, 131.8 (d, J_{C-P} = 10.0 Hz), 131.4, 128.9 (d, J_{C-P} = 12.3 Hz), 119.5 (dd, J_{C-F} = 13.0 Hz, J_{C-P} = 21.2 Hz), 115.9 (dd, J_{C-F} = 9.8 Hz, J_{C-P} = 22.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.11. **MS (ESI):** found $[M+H]^+$ 325.1. Spectral data for this compound is consistent with that previously reported.[5]

3. Optimization of Reaction Condition

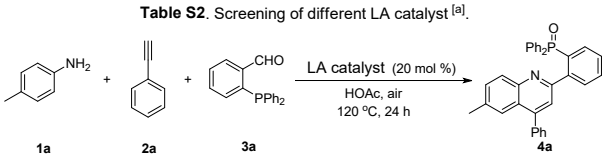
Table S1. Screening of different solvents [a].



Entry	solvent	Yield[%] [b]
1	PhMe	45
2	xylene	47
3	PhCl	61
4	1,4-dioxane	trace
5	DCE	41
6	H_2O	trace
7	DMF	N.R.
8	DMSO	N.R.
9	^{t}BuOH	34
10	Ethylene glycol	trace
11	neat	48
12	**HOAc**	**69**

[a] Reaction Conditions: $Al(OTf)_3$ (0.04 mmol,20 mol %), **1a** (0.22 mmol), **2a** (0.30 mmol), **3a**(0.20 mmol), solvent (2.0 mL), 120 °C under Air condition for 24 h. [b] Isolated yield.

Table S2. Screening of different LA catalyst [a].

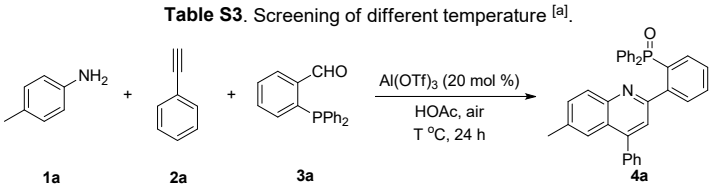


1a 2a 3a 4a

Entry	LA catalyst	yield [%][b]
1	AgOTf	55
2	$Cu(OTf)_2$	42
3	$Fe(OTf)_2$	58
4	$Mg(OTf)_2$	52
5	$Zn(OTf)_2$	64
6	$Sc(OTf)_2$	58
7	$Dy(OTf)_2$	56
8	$AlCl_3$	63
9	$FeCl_3$	57
10	$FeCl_2$	55
11	HOTf	47

[a] Reaction Conditions: LA catalyst (20 mol %), **1a** (0.22 mmol), **2a** (0.30 mmol), **3a**(0.20 mmol), HOAc (2.0 mL), 120 °C under Air condition for 24 h. [b] Isolated yield. [c] 0.40 mmol of **2a** were used.

Table S3. Screening of different temperature [a].

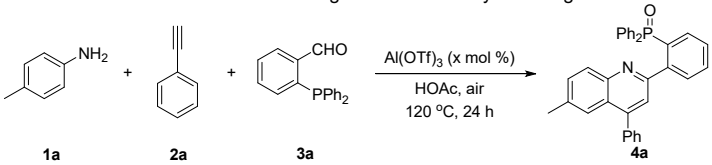


1a 2a 3a 4a

Entry	T [°C]	Yield [%][b]
1	rt	10
2	60	46
3	80	54
4	100	62
5	**120**	**69**
6	130	55

[a] Reaction Conditions: $Al(OTf)_3$ (0.04 mmol,20 mol %), **1a** (0.22 mmol), **2a** (0.30 mmol), **3a**(0.20 mmol), HOAc (2.0 mL), t °C under Air condition for 24 h. [b] Isolated yield.

Table S4. Screening of different catalyst loading [a].

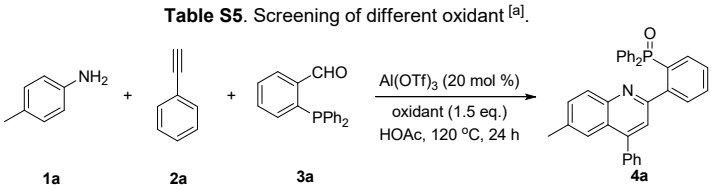


1a 2a 3a 4a

Entry	$Al(OTf)_3$ (mol %)	Yield [%][b]
1	20	69
2	10	55
3	5	50
4	0	34

[a] Reaction Conditions: $Al(OTf)_3$ (x mol %), **1a** (0.22 mmol), **2a** (0.30 mmol), **3a**(0.20 mmol), HOAc (2.0 mL), 120 °C under Air condition for 24 h. [b] Isolated yield. [c] 0.40 mmol of **2a** were used.

Table S5. Screening of different oxidant [a].



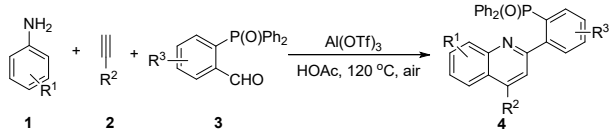
1a 2a 3a 4a

Entry	Oxidant	Yield [%] [b]
1	$Cu(OAc)_2 \cdot H_2O$	40
2	AgOAc	64
3	1,4-BQ	48
4	$PhI(OAc)_2$	24
5	$Ce(SO_4)_2$	45
6	$Mn(OAc)_3$	26

[a]Reaction Conditions: $Al(OTf)_3$ (0.04 mmol,20 mol %), **1a** (0.22 mmol), **2a** (0.30 mmol), **3a**(0.20 mmol), HOAc (2.0 mL), oxidant (0.30 mmol), 120 °C under Ar condition for 24 h. [b]Isolated yield.

4. The General Procedures

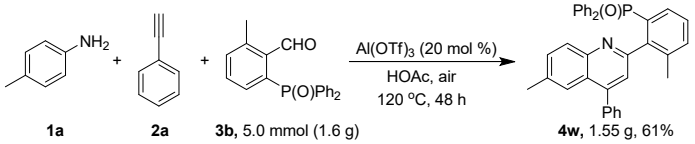
General procedure for reaction:



1 2 3 4

The mixture of amine **1a-1k** (1.1 equiv, 0.22 mmol), alkyne **2a-2l** (1.5 equiv, 0.30 mmol), aldehyde **3a-3h** (1.0 equiv, 0.20 mmol) and aluminium trifluromethanesulfonate (20 mol % ,0.04 mmol) was dissolved in acetic acid (2 mL). The reaction mixture was stirred at 120 °C in an oil bath for 24 hours under air atmosphere. After the starting material was consumed as indicated by TLC, acetic acid was evaporated concentrated. The crude product was extracted with dichloromethane, washed with saturated Na_2CO_3, and the organic solvent was evaporated concentrated in vacuo, purified by silica gel column chromatography (eluent: Petroleum ether: EtOAc = 1:1-1:3) affording the desired product.

General procedure for gram-scale reaction:

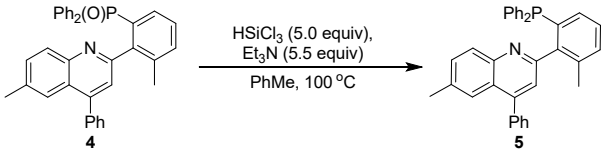


1a 2a **3b,** 5.0 mmol (1.6 g) **4w,** 1.55 g, 61%

The mixture of amine **1a** (1.1 equiv, 5.5 mmol), alkyne **2a** (1.5 equiv, 7.5 mmol), aldehyde **3b** or

3d (1.0 equiv, 5.0 mmol) and aluminium trifluromethanesulfonate (20 mol % ,1.0 mmol) was dissolved in acetic acid (50 mL) in a 100 mL flask. The reaction mixture was stirred at 120 °C in an oil bath for 24 hours under air atmosphere.After the starting material was consumed as indicated by TLC, acetic acid was evaporated concentrated. The crude product was extracted with dichloromethane, washed with saturated Na_2CO_3, and the organic solvent was evaporated concentrated in vacuo, purified by silica gel column chromatography (DCM: EtOAc = 10:1-2:1) affording the desired product.

General procedure for reduction 4 to 5:

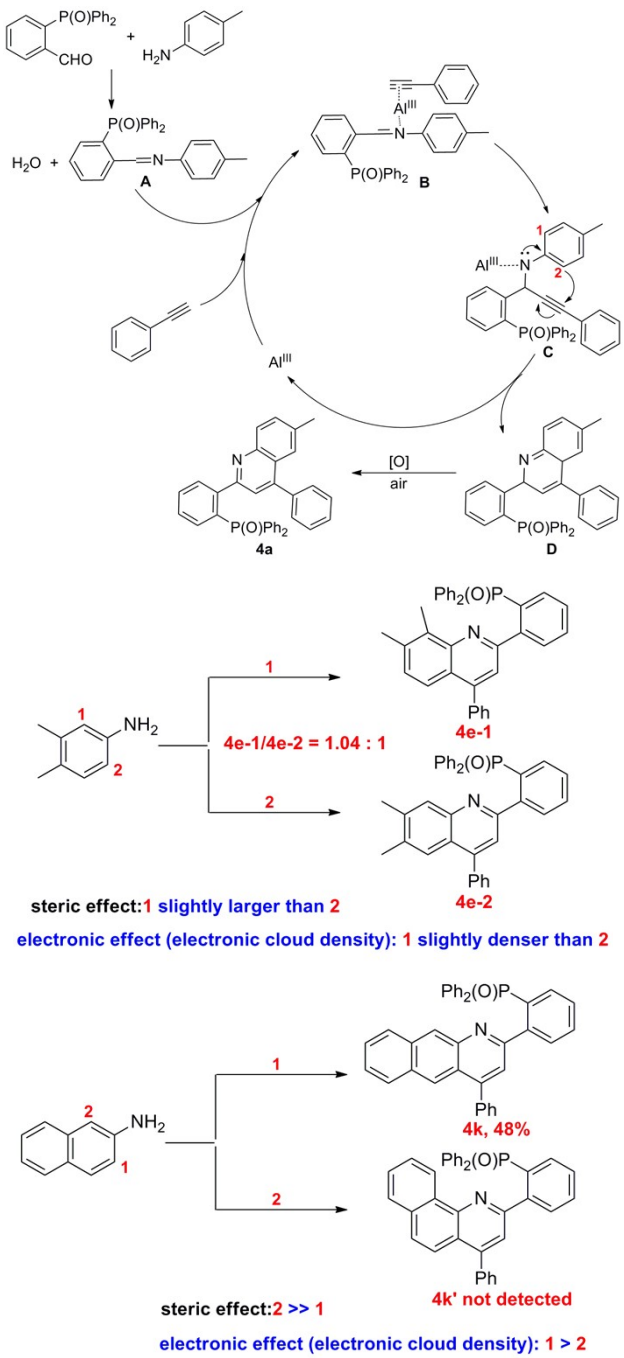


In a 25 mL of reaction tube under Ar atmosphere, **4** (1.0 equiv,0.6 mmol) was added to dry toluene(6 mL), trichlorosilane(5.0 equiv, 3.0 mmol)was add to solutions dropwise, then triethylamine (3.3 mmol, 5.5 equiv) was added dropwise to the solution and refluxed at 100 °C overnight, after which the reaction mixture was cooled, carefully quenching the reaction with saturated aqueous $NaHCO_3$ solution, and then extracting the solution three times with DCM, The organic phase are combined, and removed solvent, and then the flash column chromatography(eluent: Petroleum ether : EtOAc = 20:1-5:1) method is used to obtain the phosphorus-containing quinoline compound **5**.

5. Mechanism explaining the regioselectivity

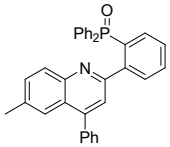
As show in the following figure, a tentative mechanism was proposed. Initially, Intermediate B was formed by coordination of imine A, which was generated in situ, and alkyne to $Al^{(III)}$, and then addition of alkyne to imine A forms the propargylamine intermediate C, which then undergoes an intramolecular hydroarylation of alkyne to give dihydroquinoline intermediate D. Subsequently, a oxidation of D by O_2 in air affords the quinoline product 4a.

For unsymmetrical aniline derivatives as substrate, the regioselectivity of the reaction mainly depends on the electronic and steric effects of the ortho position of amino on the propargylamine intermediate C. The greater the steric hindrance effect of the ortho position of amino on the propargylamine intermediate C, the worse the regioselectivity, and the higher the electron cloud density of the ortho position of amino on the propargylamine intermediate C,, the better the regioselectivity.



Scheme S1 Mechanism explaining the regioselectivity

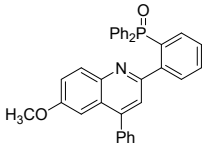
6. Characterization of product



4a

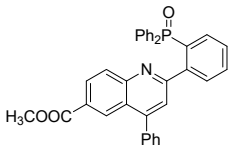
4a, Light yellow solid, 69 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77-7.44 (m, 16H), 7.40 (dd, J = 8.6, 1.8 Hz, 1H), 7.28-7.15 (m, 6 H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0 (d, $J_{C\text{-}P}$ = 3.8 Hz), 146.5 (d, $J_{C\text{-}P}$ = 41.8 Hz), 145.8 (d, $J_{C\text{-}P}$ = 8.1 Hz), 138.1, 136.3, 134.7 (d, $J_{C\text{-}P}$ =

10.9 Hz), 133.2 (d, J_{C-P} = 105.1 Hz), 132.3, 132.0 (d, J_{C-P} = 2.4 Hz), 131.7 (d, J_{C-P} = 9.7 Hz), 131.3, 131.3, 131.0, 130.9 (d, J_{C-P} = 2.5 Hz), 129.6, 129.2, 128.4, 128.1, 127.9 (d, J_{C-P} = 11.9 Hz), 127.7 (d, J_{C-P} = 12.2 Hz), 124.9, 124.0, 123.0, 21.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.79; **HRMS (ESI**, **m/z)**: calculated for $C_{34}H_{27}NOP^+$**:** 496.1825**,** found :496.1827 $[M+H]^+$.



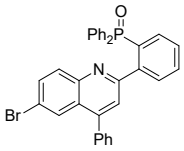
4b

4b, Light yellow solid, 63 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74-7.42 (m, 15H), 7.28-7.16 (m, 7H), 7.10 (d, *J*=2.8 Hz. 1H), 3.77 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 155.5 (d, J_{C-P} = 3.8 Hz), 146.0, 145.8 (d, J_{C-P} = 8.1 Hz), 143.8, 138.1, 134.6 (d, J_{C-P} = 10.9 Hz), 133.2 (d, J_{C-P} = 105.0 Hz), 132.3, 132.0 (d, J_{C-P} = 2.5 Hz), 131.6 (d, J_{C-P} = 9.6 Hz), 131.3, 130.9 (d, J_{C-P} = 3.0 Hz), 130.8 (d, J_{C-P} = 2.6 Hz), 128.9 (d, J_{C-P} = 79.1 Hz), 128.2, 127.8 (d, J_{C-P} = 12.1 Hz), 127.7 (d, J_{C-P} = 12.2 Hz), 127.7 (d, J_{C-P} = 3.0 Hz), 125.9, 123.3, 121.4, 103.2, 55.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.72; **HRMS (ESI**, **m/z)**: calculated for $C_{34}H_{27}NO_2P^+$**:** 512.1774, found: 512.1775 $[M+H]^+$.



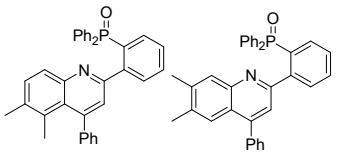
4c

4c, Light yellow solid, 47 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 1.7 Hz, 1H), 8.18 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.75-7.59 (m, 9H), 7.57-7.47 (m, 6H), 7.27-7.16 (m, 6H), 3.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 160.1 (d, J_{C-P} = 3.9 Hz), 149.3(d, J_{C-P} = 81.3 Hz), 145.3 (d, J_{C-P} = 7.7 Hz), 137.2, 134.7 (d, J_{C-P} = 11.0 Hz), 133.6, 132.5, 132.5, 132.1 (d, J_{C-P} = 2.4 Hz), 131.7 (d, J_{C-P} = 9.6 Hz), 131.5, 131.1 (d, J_{C-P} = 2.7 Hz), 130.9 (d, J_{C-P} = 9.2 Hz), 129.8, 129.7, 128.8, 128.7 (d, J_{C-P} = 0.8 Hz), 128.6, 128.3 (d, J_{C-P} = 12.1 Hz), 127.9, 127.8, 124.3, 123.9, 52.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.53; **HRMS (ESI**, **m/z)**: calculated for $C_{35}H_{27}NO_3P^+$**:** 540.1723, found: 540.1722 $[M+H]^+$.



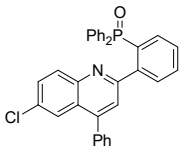
4d

4d, Light yellow solid, 61 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.1 Hz, 1H), 7.76-7.57 (m, 9H), 7.57-7.44 (m, 7H), 7.32-7.18 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.3(d, J_{C-P} = 3.8 Hz), 146.6, 146.3, 145.3 (d, J_{C-P} = 7.8 Hz), 137.1, 134.7 (d, J_{C-P} = 11.0 Hz), 133.6, 132.5, 132.5, 132.0 (d, J_{C-P} = 2.4 Hz), 132.4, 131.6 (d, J_{C-P} = 9.6 Hz), 131.4, 131.2, 131.0 (d, J_{C-P} = 2.6 Hz), 130.8 (d, J_{C-P} = 9.3Hz), 129.1 (d, J_{C-P} = 79.2 Hz), 128.6, 128.2 (d, J_{C-P} = 12.1 Hz), 127.8 (d, J_{C-P} = 12.2 Hz), 127.5, 126.2, 123.7, 120.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.62; **HRMS (ESI**, **m/z)**: calculated for $C_{33}H_{23}BrNOPNa^+$**:** 582.0593, found: 582.0591 $[M+Na]^+$.



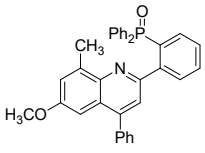
4e1 4e2

4e1, 4e2, Light yellow solid, 67 % yield (1:1.04),**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77-7.57 (m, 14H), 7.55-7.34 (m, 16H), 7.31-7.14 (m, 14H), 2.39 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8 (d, J_{C-P} = 3.7 Hz), 155.7 (d, J_{C-P} = 3.8 Hz), 147.6, 147.2, 146.9, 146.5, 146.0 (d, J_{C-P} = 8.0 Hz), 145.4 (d, J_{C-P} = 8.1 Hz), 142.8, 139.2, 138.2, 136.3, 135.9, 134.7 (d, J_{C-P} = 10.9 Hz), 133.8 (d, J_{C-P} = 7.5 Hz), 132.8 (d, J_{C-P} = 7.4 Hz), 132.3 (d, J_{C-P} = 4.4 Hz), 132.0, 132.0, 131.9 (d, J_{C-P} = 7.1 Hz), 131.9 (d, J_{C-P} = 2.0 Hz), 131.7 (d, J_{C-P} = 3.7 Hz), 131.6 (d, J_{C-P} = 3.8 Hz), 131.3 (d, J_{C-P} = 4.6 Hz), 130.9, 130.8, 130.8, 130.8, 130.8, 130.7, 129.5, 128.9, 128.5 (d, J_{C-P} = 17.9 Hz) ,128.1, 128.0, 128.0, 127.9. 127.7 (d, J_{C-P} = 1.6 Hz), 127.6 (d, J_{C-P} = 1.5 Hz), 127.4, 127.2, 125.2, 125.0, 124.4, 123.5, 122.1, 21.0, 20.2, 20.2, 20.2; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.90,29.77; **HRMS (ESI, m/z):** calculated for $C_{35}H_{28}NOPNa^+$**:** 532.1801, found: 532.1802 $[M+Na]^+$.



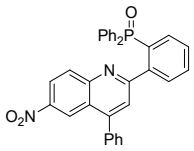
4f

4f, Light yellow solid, 63 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (*d*, J = 2.2 Hz, 1H), 7.73-7.57 (m, 9H), 7.56-7.45 (m, 7H), 7.31-7.17 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.2(d, J_{C-P} = 3.9 Hz), 146.7, 146.1, 145.4 (d, J_{C-P} = 7.8 Hz), 137.2, 134.7 (d, J_{C-P} = 11.0 Hz), 133.6, 132.5, 132.4, 132.3, 132.1 (d, J_{C-P} = 2.3 Hz), 131.6 (d, J_{C-P} = 9.6 Hz), 131.4, 131.1, 131.0 (d, J_{C-P} = 2.6 Hz), 130.8 (d, J_{C-P} = 9.3 Hz), 130.0, 129.1 (d, J_{C-P} = 79.3 Hz), 128.6, 128.2 (d, J_{C-P} = 12.0 Hz), 127.8 (d, J_{C-P} = 12.1 Hz), 125.7, 124.2, 123.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.62; **HRMS (ESI, m/z):** calculated for $C_{33}H_{23}ClNOPNa^+$**:** 538.1098, found: 538.1099 $[M+Na]^+$.



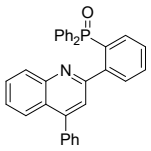
4g

4g, Light yellow solid, 44 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 13.6, 7.7 Hz, 1H), 7.68-7.62 (m, 2H), 7.62-7.54 (m, 4H), 7.53-7.41 (m, 6H), 7.37 (s, 1H) 7.26-7.09 (m, 7H), 6.91(d, *J* = 2.7 Hz ,1H), 3.74 (s, 3H), 2.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.2, 154.7 (d, J_{C-P} = 3.8 Hz), 146.3 (d, J_{C-P} = 8.7 Hz), 146.1, 143.3, 139.6, 138.6, 134.6 (d, J_{C-P} = 10.6 Hz), 133.7, 132.7, 131.9 (d, J_{C-P} = 2.5 Hz), 131.6 (d, J_{C-P} = 9.7 Hz), 131.1 (d, J_{C-P} = 9.6 Hz), 131.1, 130.7 (d, J_{C-P} = 2.7 Hz), 129.4, 128.5, 128.0, 127.7 (d, J_{C-P} = 11.8 Hz), 127.7 (d, J_{C-P} = 12.1 Hz), 126.0, 123.4, 121.4, 55.2, 18.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.34; **HRMS (ESI, m/z):** calculated for $C_{35}H_{29}NO_2P^+$**:** 526.1930, found: 526.1930 $[M+H]^+$.



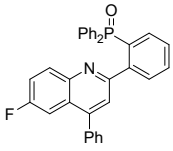
4h

4h, yellow solid, 25 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.8 Hz, 1H), 7.76-7.55 (m, 10H), 7.53-7.37 (m, 7H), 7.25-7.15 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.9 (d, J_{C-P} = 4.2 Hz), 147.6 (d, J_{C-P} = 29.4 Hz), 137.8, 134.7 (d, J_{C-P} = 11.0 Hz), 133.6, 132.5, 132.1 (d, J_{C-P} = 2.5 Hz), 131.9 (d, J_{C-P} = 100.9 Hz), 131.7 (d, J_{C-P} = 9.6 Hz), 131.4, 130.9, 130.9, 130.8, 129.7, 129.3 (d, J_{C-P} = 43.4 Hz), 128.5, 128.3, 128.1 (d, J_{C-P} = 11.9 Hz), 127.7 (d, J_{C-P} = 12.2 Hz), 126.4, 125.4, 125.0 ,123.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.69; **HRMS (ESI**, **m/z)**: calculated for $C_{33}H_{24}N_2O_3P^+$**:** 527.1519, found: 527.1516 $[M+H]^+$.



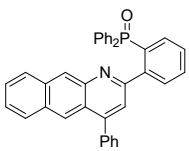
4i

4i, Light yellow solid, 12 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.81 (d, J= 2.5 Hz, 1H), 8.35 (dd, J = 9.2,2.5 Hz, 1H), 7.86 (s, 1H), 7.78-7.41 (m, 16H), 7.36-7.28 (m, 2H), 7.27-7.20 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.5(d, J_{C-P} = 3.8 Hz), 149.7 (d, J_{C-P} = 23.0 Hz), 145.4, 144.9 (d, J_{C-P} = 7.5 Hz), 136.4, 134.8 (d, J_{C-P} = 11.3 Hz), 133.5, 132.6, 132.5, 132.2 (d, J_{C-P} = 2.4 Hz), 131.6 (d, J_{C-P} = 9.6 Hz), 131.2, 131.2, 130.9 (d, J_{C-P} = 9.2 Hz), 129.3 (d, J_{C-P} = 55.1 Hz), 129.2, 128.7, 128.6 (d, J_{C-P} = 12.1 Hz), 128.4, 128.0 (d, J_{C-P} = 12.2 Hz), 124.7, 124.1, 122.6 (d, J_{C-P} = 18.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.74; **HRMS (ESI, m/z):** calculated for $C_{33}H_{25}NOPH^+$**:** 482.1668, found: 482.1666 $[M+H]^+$.



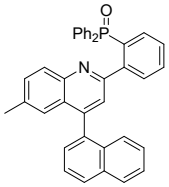
4j

4j, Light yellow solid, 67 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74-7.56 (m, 9H), 7.55-7.41 (m, 7H), 7.39-7.32 (td, J = 9.0, 2.8 Hz, 1H), 7.31-7.18 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.9, 159.4, 157.4 (t, J_{C-P} = 3.3 Hz), 147.0 (d, J_{C-P} = 5.5 Hz), 145.5 (d, J_{C-P} = 8.0 Hz), 144.8, 137.4, 134.7 (d, J_{C-P} = 11.0 Hz), 133.2 (d, J_{C-F} = 104.9 Hz), 132.1 (d, J_{C-P} = 2.5 Hz), 132.0 (d, J_{C-P} = 9.1 Hz), 131.9 (d, J_{C-P} = 100.7 Hz), 131.7 (d, J_{C-P} = 9.6 Hz), 131.0 (d, J_{C-P} = 2.8 Hz), 130.9 (d, J_{C-P} = 9.4 Hz), 129.1 (d, J_{C-F} = 73.3 Hz), 128.5, 128.1 (d, J_{C-F} = 12.0 Hz), 127.8 (d, J_{C-F} = 12.1 Hz), 125.9 (d, J_{C-P} = 9.6 Hz), 123.6, 119.3 (d, J_{C-F} = 25.5 Hz), 108.8 (d, J_{C-P} = 23.0 Hz) ; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.59; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -112.66. **HRMS (ESI, m/z):** calculated for $C_{33}H_{23}FNOPNa^+$**:** 522.1394, found: 522.1395 $[M+Na]^+$.



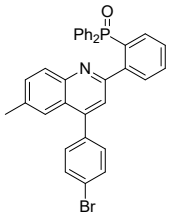
4k

4k, Light yellow solid, 48 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.76 (m, 3H), 7.75-7.57 (m, 8H), 7.55 (d, J = 9.0 Hz, 1H), 7.52-7.37 (m, 7H), 7.23-7.04 (m, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.4 (d, J_{C-P} = 3.8 Hz), 148.6, 147.4, 145.2 (d, J_{C-P} = 8.1 Hz), 142.2, 134.7 (d, J_{C-P} = 11.0 Hz), 133.6, 132.8, 132.6, 132.5, 132.1 (d, J_{C-P} = 2.3 Hz), 131.7, 131.6, 131.5, 131.1, 131.0 (d, J_{C-P} = 9.4 Hz), 130.9 (d, J_{C-P} = 2.8 Hz), 129.4, 129.1, 128.4, 128.2 (d, J_{C-P} = 12.5 Hz), 128.1 (d, J_{C-P} = 12.6 Hz), 127.8 (d, J_{C-P} = 12.2 Hz), 126.4, 125.7, 125.2, 122.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.67; **HRMS (ESI, m/z):** calculated for $C_{37}H_{26}NOPNa^+$**:** 554.1644, found: 554.1646 $[M+Na]^+$.



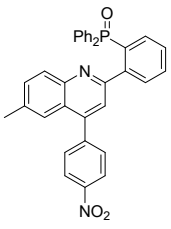
4l

4l, Light yellow solid, 69 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (t, J = 9.2 Hz, 2H), 7.81 (dd, J = 13.7, 7.7 Hz, 1H), 7.76-7.69 (m, 3H), 7.67-7.44 (m, 8H), 7.42-7.26 (m, 7H), 7.23-7.15 (m, 3H), 7.01 (s, 1H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8 (d, J_{C-P} = 3.4 Hz), 145.9 (d, J_{C-P} = 38.3 Hz), 145.5 (d, J_{C-P} = 7.6 Hz), 136.0 (d, J_{C-P} = 53.9 Hz), 135.1 (d, J_{C-P} = 10.8 Hz), 134.2 (d, J_{C-P} = 3.5 Hz), 133.3, 133.2 (d, J_{C-P} = 3.8 Hz), 132.1, 131.9, 131.9, 131.8 (d, J_{C-P} = 12.7 Hz), 131.7, 131.6 (d, J_{C-P} = 5.8 Hz), 131.1, 131.0, 131.0 (d, J_{C-P} = 2.6 Hz), 130.7 (d, J_{C-P} = 2.6 Hz), 128.8 (d, J_{C-P} = 58.8 Hz), 128.1, 128.0, 127.9, 127.7 (d, J_{C-P} = 6.0 Hz), 127.4 (d, J_{C-P} = 30.6 Hz), 126.3, 126.1 (d, J_{C-P} = 10.3 Hz), 125.6 (d, J_{C-P} = 69.4 Hz), 124.5, 123.3, 21.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.53; **HRMS (ESI, m/z):** calculated for $C_{38}H_{29}NOP^+$**:** 546.1981, found: 546.1918 $[M+H]^+$.



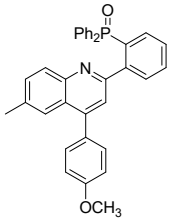
4m

4m, Light yellow solid, 64 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.57 (m, 11H), 7.51-7.38 (m, 5H), 7.27-7.15 (m, 6H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9 (d, J_{C-P} = 3.8 Hz), 145.8 (d, J_{C-P} = 100.1 Hz), 145.7 (d, J_{C-P} = 8.0 Hz), 136.9, 136.5, 134.6 (d, J_{C-P} = 11.1 Hz), 133.0 (d, J_{C-P} = 104.8 Hz), 132.2, 132.1 (d, J_{C-P} = 2.4 Hz), 131.6, 131.6, 131.5, 131.4, 131.2, 130.9 (d, J_{C-P} = 9.2 Hz), 130.9 (d, J_{C-P} = 2.6 Hz), 129.3, 128.0 (d, J_{C-P} = 12.0 Hz), 127.7 (d, J_{C-P} = 12.1 Hz), 124.6, 123.6 ,123.1, 122.5, 21.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.74; **HRMS (ESI, m/z):** calculated for $C_{34}H_{25}BrNOPNa^+$**:** 596.0749, found: 596.0750 $[M+Na]^+$.



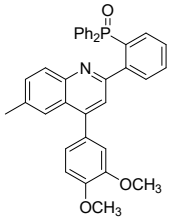
4n

4n, Light yellow solid, 42 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51-8.28 (m, 2H), 7.84-7.37 (m, 15H), 7.31-7.20 (m, 5H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9 (d, J_{C-P} = 4.0 Hz), 147.6, 146.4, 145.5 (d, J_{C-P} = 8.0 Hz), 144.3 (d, J_{C-P} = 97.8 Hz), 137.1, 134.5 (d, J_{C-P} = 11.4 Hz), 133.3, 132.2 (d, J_{C-P} = 4.3 Hz), 132.2 (d, J_{C-P} = 2.3 Hz), 131.7, 131.5 (d, J_{C-P} = 9.6 Hz), 131.2, 131.1, 131.1, 131.0, 130.6, 129.5, 128.1 (d, J_{C-P} = 12.1 Hz), 127.8 (d, J_{C-P} = 12.1 Hz), 124.1, 123.7, 123.3 (d, J_{C-P} = 31.3 Hz), 21.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.75; **HRMS (ESI, m/z):** calculated for $C_{34}H_{26}N_2O_3P^+$**:** 541.1676, found: 541.1674 $[M+H]^+$.



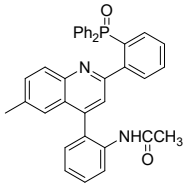
4o

4o, Light yellow solid, 65 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75-7.53 (m, 10H), 7.51-7.44 (m, 3H), 7.40 (dd, J = 8.6,1.7 Hz, 1H), 7.26-7.14 (m, 6H), 7.05 (d, J = 8.7 Hz, 2H), 3.89(s, 3H), 2.43(s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.6, 156.9 (d, J_{C-P} = 4.0 Hz), 146.4 (d, J_{C-P} = 2.8 Hz), 145.9 (d, J_{C-P} = 8.2 Hz), 136.1, 134.6 (d, J_{C-P} = 10.9 Hz), 133.1 (d, J_{C-P} = 105.1 Hz), 132.3, 132.3, 132.0 (d, J_{C-P} = 2.3 Hz), 131.6 (d, J_{C-P} = 9.6 Hz), 131.3, 131.2, 130.9, 130.9, 130.8 (d, J_{C-P} = 2.9 Hz), 130.3, 129.2, 127.9 (d, J_{C-P} = 12.0 Hz), 127.7 (d, J_{C-P} = 12.1 Hz), 125.1, 123.5 (d, J_{C-P} = 110.9 Hz), 113.9, 55.3, 21.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.73; **HRMS (ESI, m/z):** calculated for $C_{35}H_{29}NO_2P^+$**:** 526.1930, found: 526.1930 $[M+H]^+$.



4p

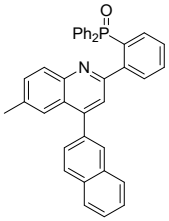
4p, Light yellow solid, 50 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74-7.53 (m, 10H), 7.51-7.45 (m, 1H), 7.41 (dd, J = 8.6,1.7 Hz, 1H), 7.27-7.15 (m, 6H), 7.12-7.00 (m, 3H), 3.98 (s, 3H), 3.96 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0 (d, J_{C-P} = 3.9 Hz), 148.9 (d, J_{C-P} = 25.1 Hz), 146.5 (d, J_{C-P} = 11.8 Hz), 145.8 (d, J_{C-P} = 8.1 Hz), 136.1, 134.7 (d, J_{C-P} = 10.9 Hz), 133.2 (d, J_{C-P} = 105.0 Hz), 132.3, 132.0 (d, J_{C-P} = 2.3 Hz), 131.6 (d, J_{C-P} = 9.7 Hz), 131.3, 131.2, 130.9, 130.8, 130.8, 130.6, 129.2, 127.9 (d, J_{C-P} = 11.9 Hz), 127.7 (d, J_{C-P} = 12.1 Hz), 125.1, 124.1, 122.9, 122.2, 112.9, 111.0, 56.0, 55.9, 21.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.71; **HRMS (ESI, m/z):** calculated for $C_{36}H_{31}NO_3P^+$**:** 556.2036, found: 556.2037 $[M+H]^+$.



4q

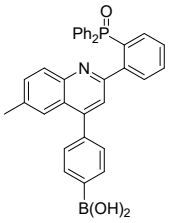
4q, Light yellow solid, 58 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.23 (d,

J=8.3 Hz, 1H), 7.75 (dd, *J* = 7.2,3.3 Hz,1H), 7.71-7.64 (m, 3H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.54-7.22 (m, 14H), 7.21-7.13 (m, 2H), 2.40 (s, 3H), 2.07 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 156.5 (d, J_{C-P} = 4.1 Hz), 146.6 (d, J_{C-P} = 7.3 Hz), 146.1, 142.3, 136.5 (d, J_{C-P} = 49.3 Hz), 133.4 (d, J_{C-P} = 2.2 Hz), 133.3, 132.6 (d, J_{C-P} = 41.2 Hz), 132.2 (d, J_{C-P} = 2.4 Hz), 131.9, 131.8, 131.7, 131.6, 131.5 (d, J_{C-P} = 2.8 Hz), 131.3 (d, J_{C-P} = 10.0 Hz), 130.9 (d, J_{C-P} = 9.4 Hz), 130.0, 129.1, 128.9 (d, J_{C-P} = 46.1 Hz), 128.5 (d, J_{C-P} = 12.0 Hz), 128.1 (d, J_{C-P} = 12.3 Hz), 127.6 (d, J_{C-P} = 12.5 Hz), 125.9, 124.9 (d, J_{C-P} = 93.8 Hz), 123.9 (d, J_{C-P} = 49.3 Hz), 24.0, 21.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.87; **HRMS (ESI, m/z):** calculated for $C_{36}H_{29}N_2O_2PNa^+$**:** 575.1859, found: 575.1860 $[M+Na]^+$.



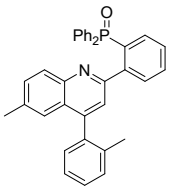
4r

4r, Light yellow solid, 69 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.95-7.89 (m, 3H), 7.81-7.69 (m, 2H), 7.69-7.39 (m, 13H), 7.30-7.17 (m, 6H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0(d, J_{C-P} = 3.8 Hz), 146.5 (d, J_{C-P} = 47.3 Hz), 145.7 (d, J_{C-P} = 8.1 Hz), 136.4, 135.5, 134.7 (d, J_{C-P} = 10.8 Hz), 133.8, 133.1, 132.8 (d, J_{C-P} = 12.1 Hz), 132.3, 132.0 (d, J_{C-P} = 2.3 Hz), 131.7 (d, J_{C-P} = 9.7 Hz), 131.4, 131.3, 130.9, 130.9 (d, J_{C-P} = 2.7 Hz), 129.2, 128.7, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 126.4 (d, J_{C-P} = 6.6 Hz), 125.1, 124.1, 123.1, 21.8 ; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.93; **HRMS (ESI, m/z):** calculated for $C_{38}H_{29}NOP^+$**:** 546.1981, found: 546.1981 $[M+H]^+$.



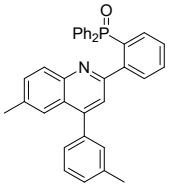
4s

4s, Light yellow solid, 37 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77-7.59 (m, 7H), 7.58-7.43 (m, 9H), 7.41 (dd, *J* = 8.5,1.9 Hz, 1H), 7.26-7.16 (m, 5H) , 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0 (d, J_{C-P} = 3.8 Hz), 146.5 (d, J_{C-P} = 41.5 Hz), 145.8 (d, J_{C-P} = 8.1 Hz), 138.1, 136.3, 134.7 (d, J_{C-P} = 11.0 Hz), 133.7, 132.7, 132.3, 132.0 (d, J_{C-P} = 2.5 Hz), 131.7 (d, J_{C-P} = 9.7 Hz), 131.1 (d, J_{C-P} = 42.0 Hz), 131.0, 130.9, 129.6, 129.2, 128.4, 128.1, 127.9 (d, J_{C-P} = 12.0 Hz), 127.7 (d, J_{C-P} = 12.2 Hz), 124.9, 124.1, 123.0, 21.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.80; **HRMS (ESI, m/z):** calculated for $C_{34}H_{28}BNO_3P^+$: 540.1894, found: 540.1897 $[M+H]^+$.



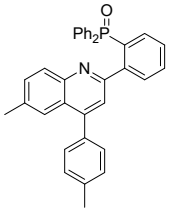
4t

4t, Light yellow solid, 68 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 13.9,7.4 Hz, 1H), 7.74-7.63 (m, 4H), 7.62-7.55 (m, 2H), 7.52-7.43 (m, 3H), 7.40-7.27 (m, 7H), 7.27-7.22 (m, 1H), 7.20-7.11 (m, 3H), 7.07(s, 1H), 2.36(s, 3H), 1.97(s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8 (d, J_{C-P} = 3.5 Hz), 146.5 (d, J_{C-P} = 157.3 Hz), 145.6 (d, J_{C-P} = 7.5 Hz), 137.6, 136.2 (d, J_{C-P} = 29.8 Hz), 135.0 (d, J_{C-P} = 10.8 Hz), 134.2 (d, J_{C-P} = 7.7 Hz), 133.1 (d, J_{C-P} = 7.7 Hz), 131.9 (d, J_{C-P} = 9.6 Hz), 131.9 (d, J_{C-P} = 2.5 Hz), 131.6 (d, J_{C-P} = 110.0 Hz), 131.6 (d, J_{C-P} = 9.7 Hz), 131.4, 131.1 (d, J_{C-P} = 13.6 Hz), 131.0 (d, J_{C-P} = 0.9 Hz) , 130.8 (d, J_{C-P} = 2.7 Hz), 129.7 (d, J_{C-P} = 48.1 Hz), 128.6 (d, J_{C-P} = 100.4 Hz), 128.0, 127.9, 127.7 (d, J_{C-P} = 3.8 Hz), 127.6, 125.6, 124.9 (d, J_{C-P} = 133.9 Hz), 124.2, 21.7, 20.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.51; **HRMS (ESI, m/z):** calculated for $C_{35}H_{29}NOP^+$: 510.1981, found: 510.1982 $[M+H]^+$.



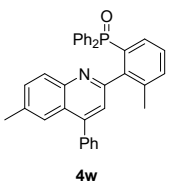
4u

4u, Light yellow solid, 68 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 13.5,8.0 Hz, 1H), 7.70-7.57 (m, 6H), 7.56-7.46 (m, 4H), 7.43-7.35 (m, 2H), 7.29-7.23 (m, 5H), 7.22-7.15 (m, 4H), 2.45 (s, 3H), 2.43(s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0 (d, J_{C-P} = 3.8 Hz), 146.6 (d, J_{C-P} = 79.4 Hz), 145.7 (d, J_{C-P} = 8.2 Hz), 138.1, 138.0, 136.2, 134.7 (d, J_{C-P} = 10.7 Hz), 133.8, 132.8, 132.3, 132.0 (d, J_{C-P} = 2.3 Hz), 131.7 (d, J_{C-P} = 9.7 Hz), 131.3, 131.1 (d, J_{C-P} = 42.2 Hz), 130.9, 130.8, 130.1, 129.0 (d, J_{C-P} = 27.6 Hz), 128.3, 127.9 (d, J_{C-P} = 12.0 Hz), 127.7 (d, J_{C-P} = 12.2 Hz), 126.7, 125.0, 124.1, 122.7, 21.8, 21.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.88; **HRMS (ESI, m/z):** calculated for $C_{35}H_{29}NOP^+$: 510.1981, found: 510.1982 $[M+H]^+$.



4v

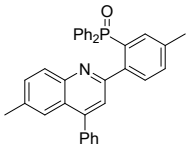
4v, Light yellow solid, 69 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 13.7,7.6 Hz, 1H), 7.70-7.53 (m, 8H), 7.52-7.45 (m, 2H), 7.41-7.36 (m, 3H), 7.32 (d, *J*=8.0 Hz, 2H), 7.27-7.14 (m, 6H), 2.45(s, 3H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9 (d, J_{C-P} = 3.8 Hz), 146.8, 146.3, 145.8 (d, J_{C-P} = 8.1 Hz), 138.0, 135.6 (d, J_{C-P} = 102.5 Hz), 134.7 (d, J_{C-P} = 10.7 Hz), 133.7, 132.7, 132.3, 132.0 (d, J_{C-P} = 2.4 Hz), 131.7 (d, J_{C-P} = 9.6 Hz), 131.3, 131.2, 130.9, 130.8, 130.8, 129.3 (d, J_{C-P} = 35.3 Hz), 129.2, 127.9 (d, J_{C-P} = 11.9 Hz), 127.6 (d, J_{C-P} = 12.1 Hz), 125.0, 123.5 (d, J_{C-P} = 126.2 Hz), 21.8, 21.2; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.78; **HRMS (ESI, m/z):** calculated for $C_{35}H_{29}NOP^+$: 510.1981, found: 510.1982 $[M+H]^+$.



4w

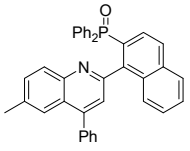
4w, Light yellow solid, 53 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.27 (m, 18H), 7.25-

6.84 (br, 4H), 2.46 (s, 3H), 2.15 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.1 (d, J_{C-P} = 4.8 Hz), 146.2 (d, J_{C-P} = 3.1 Hz), 144.5 (d, J_{C-P} = 8.9 Hz), 137.9, 137.8 (d, J_{C-P} = 9.7 Hz), 136.3, 134.4 (d, J_{C-P} = 2.5 Hz), 133.1, 132.5, 132.1, 131.8 (d, J_{C-P} = 9.8 Hz), 131.5 (d, J_{C-P} = 11.3 Hz), 131.5, 130.9, 129.8, 129.2, 128.4, 128.1, 127.8, 127.7, 124.8, 124.5, 124.0, 21.8, 20.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.91; **HRMS (ESI, m/z):** calculated for $C_{35}H_{29}NOP^+$: 510.1981, found: 510.1982 $[M+H]^+$.



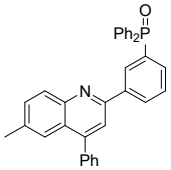
4x

4x, Light yellow solid, 65 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, J = 13.9 Hz, 1H), 7.67-7.59 (m, 4H), 7.56 (dd, J = 7.8, 4.6Hz, 1H), 7.53-7.36 (m, 10H), 7.27-7.21 (m, 2H), 7.20-7.12 (m, 4H), 2.42 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.1 (d, J_{C-P} = 3.6 Hz), 146.5 (d, J_{C-P} = 8.2 Hz), 142.7 (d, J_{C-P} = 8.2 Hz), 138.0, 137.9, 136.1, 135.2 (d, J_{C-P} = 10.2 Hz), 133.8, 132.8, 132.6 (d, J_{C-P} = 2.5 Hz),132.0, 131.8 (d, J_{C-P} = 9.8 Hz), 131.3, 131.0, 130.8, 130.8, 130.7, 129.0 (d, J_{C-P} = 110.8 Hz), 128.6 (d, J_{C-P} = 97.4 Hz), 127.6 (d, J_{C-P} = 12.2 Hz), 124.8, 124.0, 122.8, 21.8, 21.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.48; **HRMS (ESI, m/z):** calculated for $C_{35}H_{29}NOP^+$: 510.1981, found: 510.1982 $[M+H]^+$.



4y

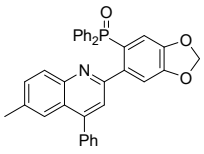
4y, Light brown solid, 50 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01-7.86 (m, 4H), 7.81(dd, J = 11.7, 8.6 Hz, 1H), 7.71-7.64 (m, 2H), 7.60-7.49 (m, 6H), 7.49-7.31 (m, 9H), 7.02-6.74 (m, 3H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3 (d, J_{C-P} = 5.5 Hz), 146.2 (d, J_{C-P} = 16.5 Hz), 144.3 (d, J_{C-P} = 8.9 Hz), 137.8, 136.6, 135.0 (d, J_{C-P} = 2.1 Hz), 132.3, 132.2, 131.4, 131.2, 131.1 (d, J_{C-P} = 8.6 Hz), 130.4, 129.8, 129.4, 128.8, 128.4, 128.3 (d, J_{C-P} = 5.7 Hz), 128.2, 128.1, 128.1, 128.0, 127.9, 127.2 (d, J_{C-P} = 12.8 Hz), 127.0 (d, J_{C-P} = 3.9 Hz), 125.3, 125.1, 124.1, 21.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.26; **HRMS (ESI, m/z):**calculated for $C_{38}H_{28}NOP\ Na^+$: 568.1801, found: 568.1801 $[M+Na]^+$.



4z

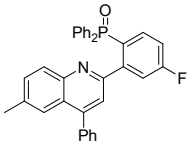
4z, Light yellow solid, 63 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (d, J = 12.8 Hz, 1H), 8.51-8.42 (m, 1H), 8.09 (d, J = 8.6 Hz, 1H), 7.79-7.68 (m, 5H), 7.64 (s, 1H), 7.62-7.57 (m, 2H), 7.56-7.43 (m, 12H), 2.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.6, 148.7, 147.2, 140.2 (d, J_{C-P} = 11.7 Hz), 138.2, 136.6, 133.4, 132.9, 132.5, 132.1 (d, J_{C-P} = 49.7 Hz), 132.1 (d, J_{C-P} = 9.9 Hz), 131.9 (d, J_{C-P} = 2.7 Hz), 131.8, 131.0 (d, J_{C-P} = 2.6 Hz), 130.9 (d, J_{C-P} = 9.8 Hz), 129.8, 129.0 (d, J_{C-P} = 89.7 Hz), 128.8 (d, J_{C-P} = 12.5 Hz), 128.4 (d, J_{C-P} = 6.7 Hz), 128.3, 125.8, 124.3, 119.2,

21.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.46; **HRMS (ESI, m/z):** calculated for $C_{34}H_{27}NOP^+$: 496.1825, found: 496.1827 $[M+H]^+$.



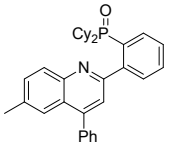
4aa

4aa, Light yellow solid, 58 % yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.55 (m, 5H), 7.55-7.42 (m, 7H),7.40 (dd, J = 8.6,1.7 Hz, 1H), 7.27-7.09 (m, 8H), 6.05 (s, 2H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5 (d, J_{C-P} = 4.1 Hz), 150.4 (d, J_{C-P} = 2.6 Hz), 147.4 (d, J_{C-P} = 17.7 Hz), 146.5 (d, J_{C-P} = 38.2 Hz), 141.7 (d, J_{C-P} = 9.0 Hz), 138.0, 136.2, 133.2 (d, J_{C-P} = 105.8 Hz), 131.6 (d, J_{C-P} = 9.6 Hz), 131.3, 130.8 (d, J_{C-P} = 2.7 Hz), 129.6, 129.1, 128.4, 128.1, 127.7 (d, J_{C-P} = 12.2 Hz), 125.7, 124.9, 124.7, 124.0, 123.1, 114.0 (d, J_{C-P} = 13.3 Hz), 111.5 (d, J_{C-P} = 12.1 Hz), 101.9, 21.7; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.45; **HRMS (ESI, m/z):** calculated for $C_{35}H_{27}NO_3P^+$: 540.1723, found: 540.1726 $[M+H]^+$.



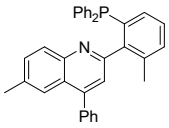
4ab

4ab, light yellow solid, 63% yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.68 (m, 1H), 7.66-7.37 (m, 14H), 7.29-7.14 (m, 7H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8 (d, J_{C-P} = 2.8 Hz), 163.3 (d, J_{C-P} = 3.0 Hz), 155.6 (dd, J_{C-F} = 1.7 Hz, J_{C-P} = 3.4 Hz), 148.6 (dd, J_{C-F} = 7.9 Hz, J_{C-P} = 9.6 Hz) , 146.9, 146.2, 137.8, 137.3 (dd, J_{C-F} = 8.9 Hz, J_{C-P} = 12.3 Hz) , 136.6, 133.3, 132.2, 131.6, 131.5, 131.0 (d, J_{C-P} = 2.6 Hz), 129.0 (d, J_{C-P} = 105.9 Hz), 128.7 (d, J_{C-P} = 89.1 Hz), 127.8 (d, J_{C-P} = 12.2 Hz), 127.4 (d, J_{C-P} = 3.3 Hz), 125.0, 124.0, 122.7, 118.3 (dd, J_{C-F} = 10.6 Hz, J_{C-P} = 21.9 Hz) , 115.0 (dd, J_{C-F} = 13.0 Hz, J_{C-P} = 20.4 Hz) , 21.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.92; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -106.54; **HRMS (ESI, m/z):** calculated for $C_{34}H_{26}FNOP^+$: 514.1731, found: 514.1731 $[M+H]^+$.



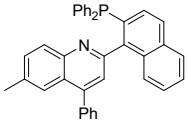
4ac

4ac, yellow solid, 37% yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (ddd, J = 10.7,5.6,3.5 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.75 (s, 1H), 7.65 (dd, J = 8.5,1.4 Hz, 1H), 7.61-7.50 (m, 8H), 7.47(s, 1H), 2.53 (s, 3H), 1.89-1.53 (m, 13H), 1.35-1.23 (m, 3H), 1.19-1.09 (m, 2H), 0.99-0.90 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5 (d, J_{C-P} = 2.0 Hz), 148.6, 146.1, 142.8 (d, J_{C-P} = 8.0 Hz), 137.9, 137.0, 132.4, 131.4, 130.7 (d, J_{C-P} = 2.3 Hz), 130.6, 130.2 (d, J_{C-P} = 8.8 Hz), 129.4, 129.0, 128.6, 128.5, 128.2 (d, J_{C-P} = 9.4 Hz), 125.3, 124.7, 122.4, 38.7, 38.0, 26.7 (dd, J_{C-P} = 12.9, 9.3 Hz), 26.4 (dd, J_{C-P} = 11.7,3.5 Hz), 25.7, 21.9; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 50.17; **HRMS (ESI, m/z):** calculated for $C_{34}H_{39}NOP^+$: 508.2764, found: 508.2763 $[M+H]^+$.



5w

5w, White solid, 73 % yield, **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.6 Hz, 1H), 7.61 (s, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.24 –7.08 (m, 14H), 6.92 – 6.83 (m, 2H), 2.38 (s, 3H), 2.10 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.3 (d, $J_{C\text{-}P}$ = 5.4 Hz), 146.9, 146.6, 146.4, 146.0, 138.1, 137.7, 137.5, 136.5, 136.4, 136.3, 134.1, 133.8, 131.5 (d, $J_{C\text{-}P}$ = 5.5 Hz), 131.0, 129.7, 129.6, 128.3, 128.2, 128.0, 125.1, 124.2, 123.9 (d, $J_{C\text{-}P}$ = 5.5 Hz), 21.8, 20.4; **^{31}P NMR** (121 MHz, $CDCl_3$) δ -12.15; **HRMS (ESI, m/z):** calculated for $C_{35}H_{29}NP^+$: 494.2032, found: 494.2032 $[M+H]^+$.



5y

5y, Light yellow solid, 80 % yield, **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.98–7.92 (m, 1H), 7.73 (dd, *J* = 16.2, 7.5 Hz, 3H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.10 (m, 19H), 2.41 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.5 (d, $J_{C\text{-}P}$ = 7.5 Hz), 147.0, 146.7, 145.6, 145.2, 138.1, 136.6, 133.9, 133.7, 133.6, 132.2, 132.1, 131.6, 129.9, 129.8, 129.6, 128.4, 128.3, 128.1, 127.9, 126.6, 126.5, 126.5, 126.5, 125.3, 124.8, 124.8, 21.8; **^{31}P NMR** (121 MHz, $CDCl_3$) δ -11.92; **HRMS (ESI, m/z):** calculated for $C_{38}H_{29}NP^+$: 530.2032, found: 530.2031 $[M+H]^+$.

7. References

[1] M. L. Abrams, F. Foarta and C. R. Landis, *J. Am. Chem. Soc.*, 2014, **136**, 14583.

[2] A. K. Morri, Y. Thummala and V. R. Doddi, *Org. Lett.*, 2015, **17**, 4640.

[3] X. Qi, H. Zhang, Z. Pan, R.-B. Liang, C. Zhu, J. Li, Q. Tong, X. Gao, L. Wu and J. Zhong, *Chem. Commun.*, 2019, **55**, 10848.

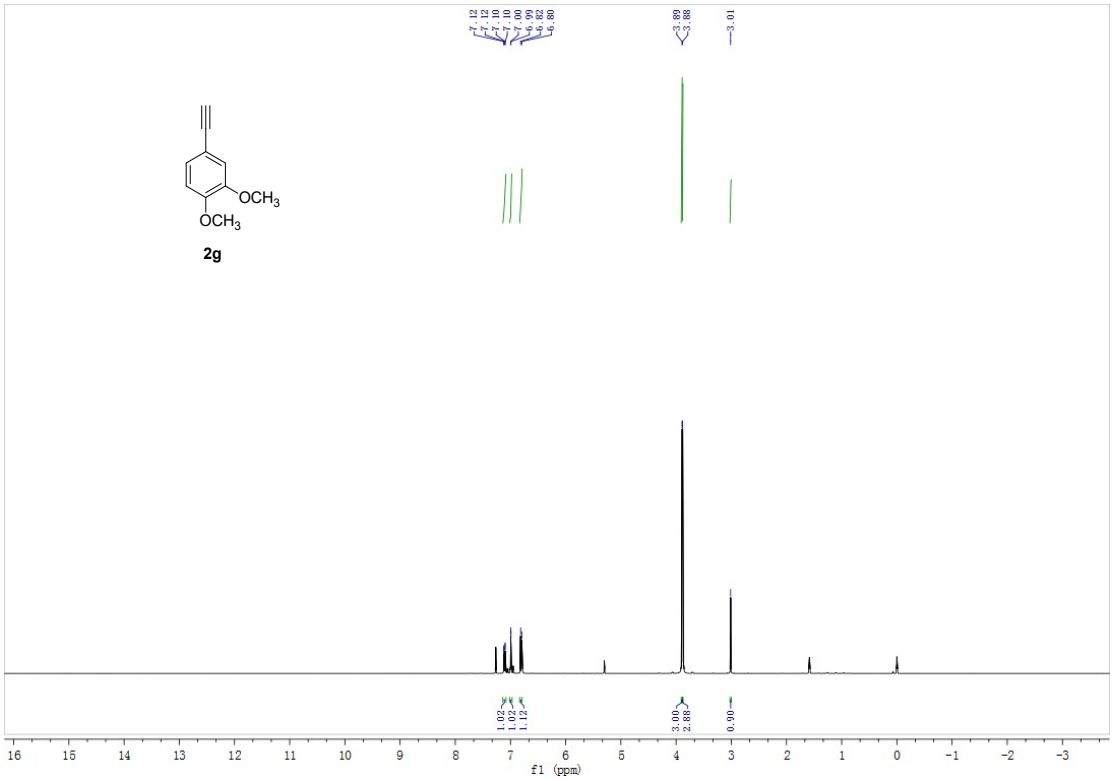
[4] V. Ravindar, H. Hemling, H. Schumann and J. Blum, *Synth. Commun.*, 1992, **22** ,1453.

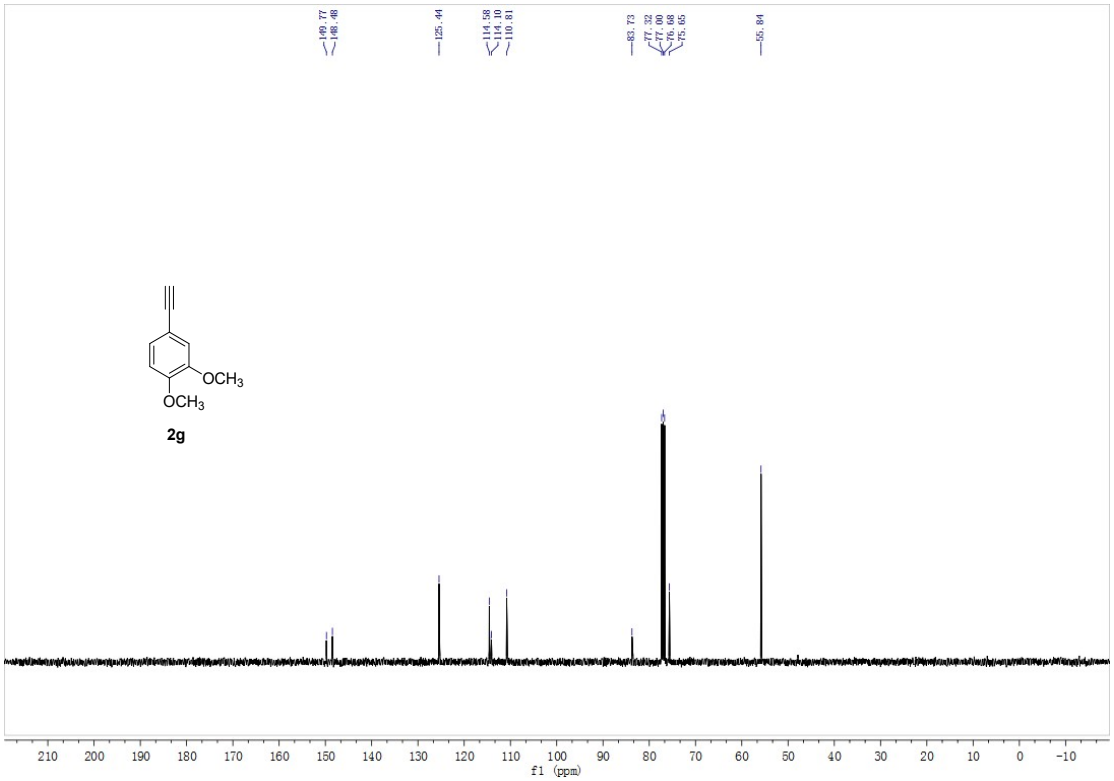
[5] W. Ren, Q.-M. Zuo and S.-D. Yang, *Synlett*, 2019, **30**, 1719.

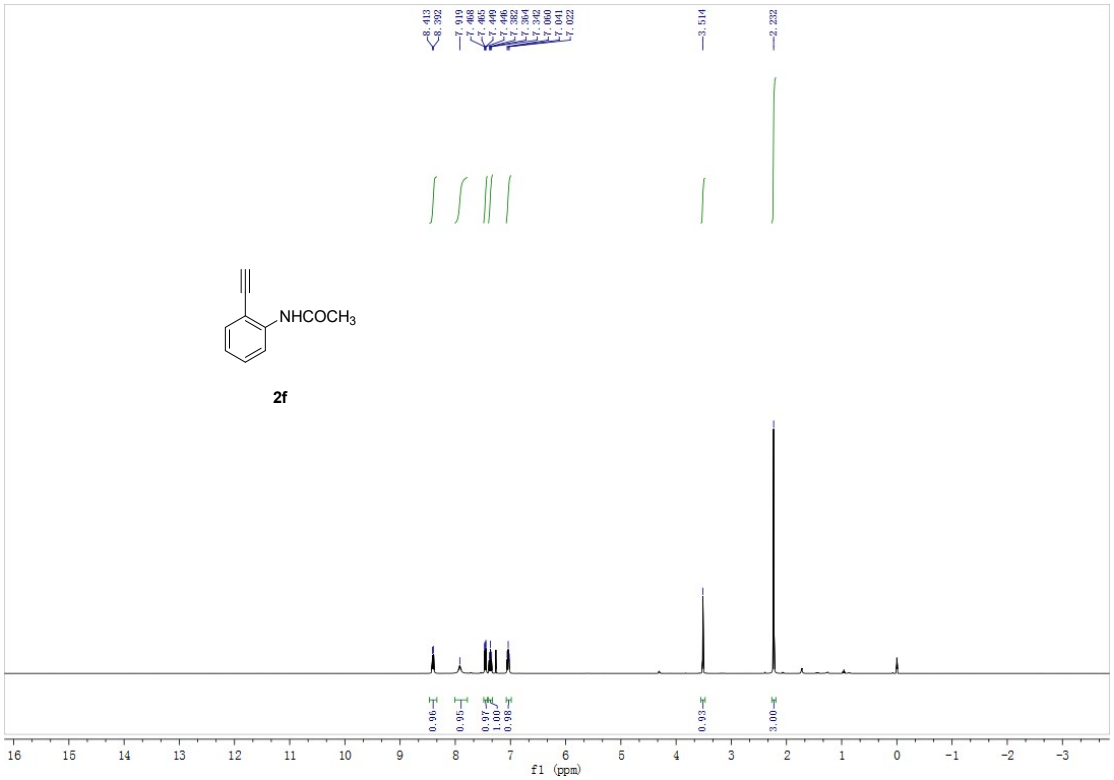
[6] G. London, M. Von, W. Rakowski, O. Dumile, W. B. Schweizer, J.-P. Gisselbrecht, C. Boudon and F. Diederich, *Chem. Sci.*, 2014, **5**, 965.

[7] F. Puls, N. Richter, O. Kataeva and H. J. Knolker, *Chem. Eur. J.*, 2017, **23**, 17576.

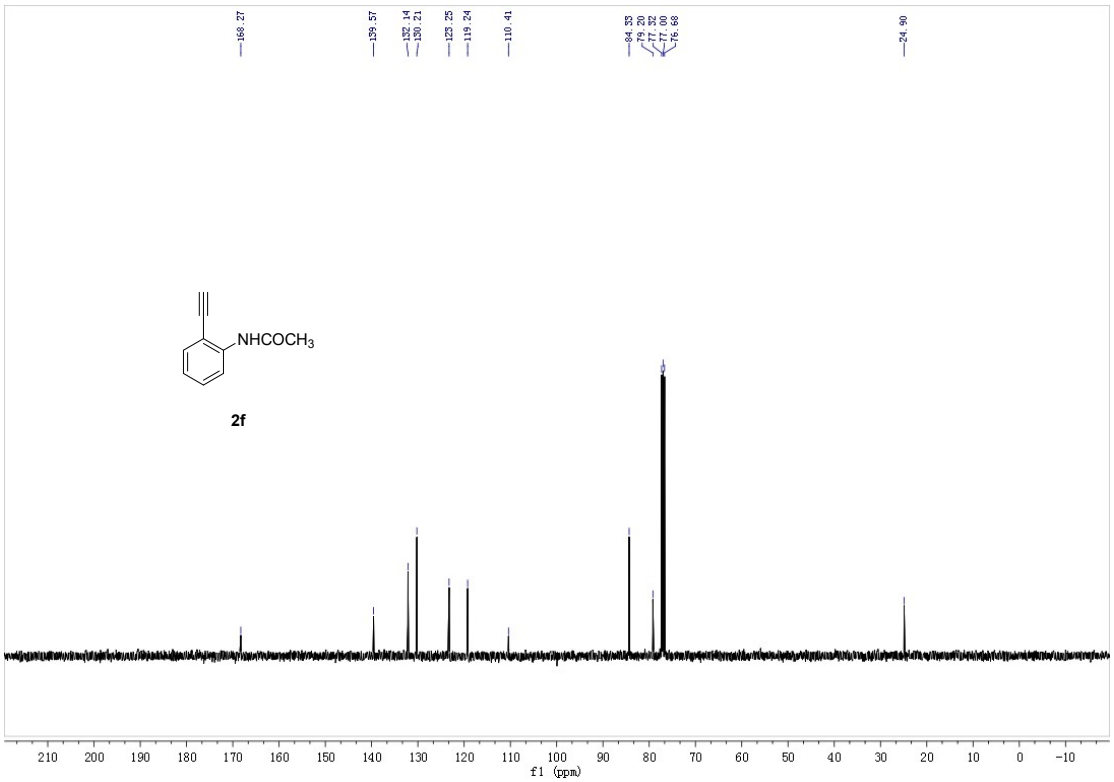
7. Copies of NMR spectra


7.12
7.12
7.10
7.10
7.00
6.99
6.82
6.80
3.89
3.88
3.01
OCH3
OCH3
2g
1.02
1.02
1.12
3.08
2.80
0.90
f1 (ppm)

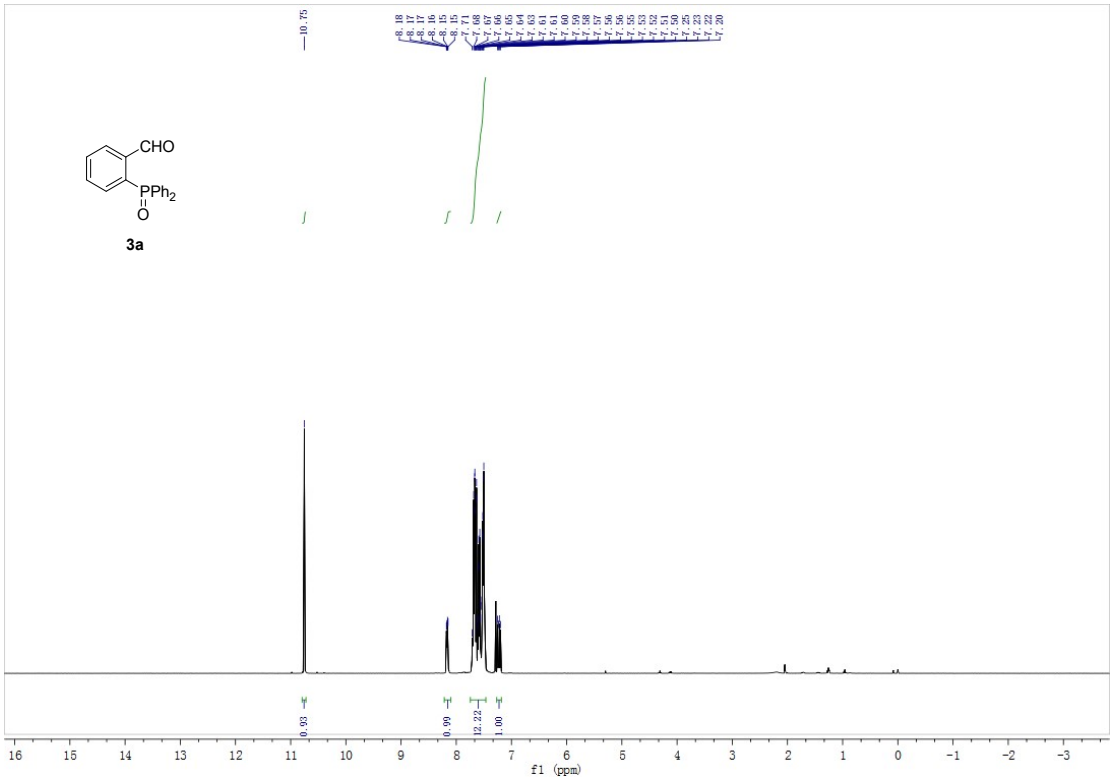

149.77
148.48
125.44
114.58
114.10
110.81
83.73
77.32
77.00
76.68
75.65
55.84
OCH3
OCH3
2g
f1 (ppm)

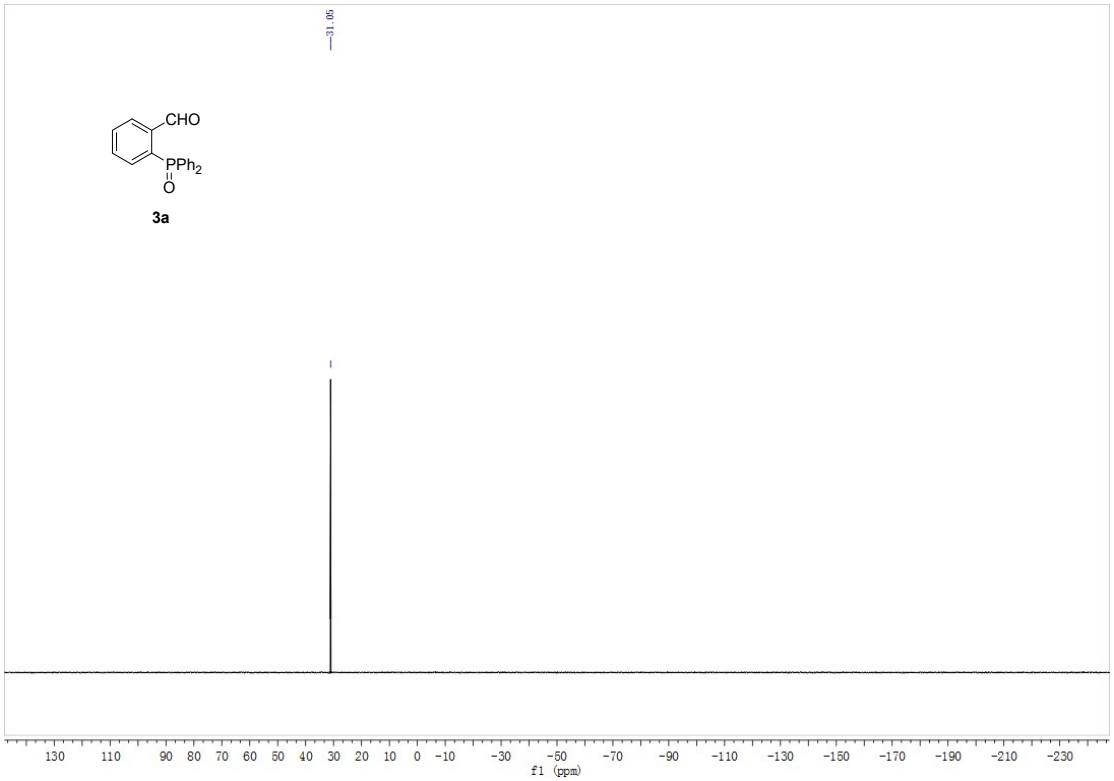

8.413
8.392
7.919
7.468
7.465
7.449
7.446
7.382
7.364
7.362
7.360
7.041
7.022
3.514
2.232
NHCOCH3
0.96
0.95
0.97
1.00
0.98
0.93
3.00
f1 (ppm)

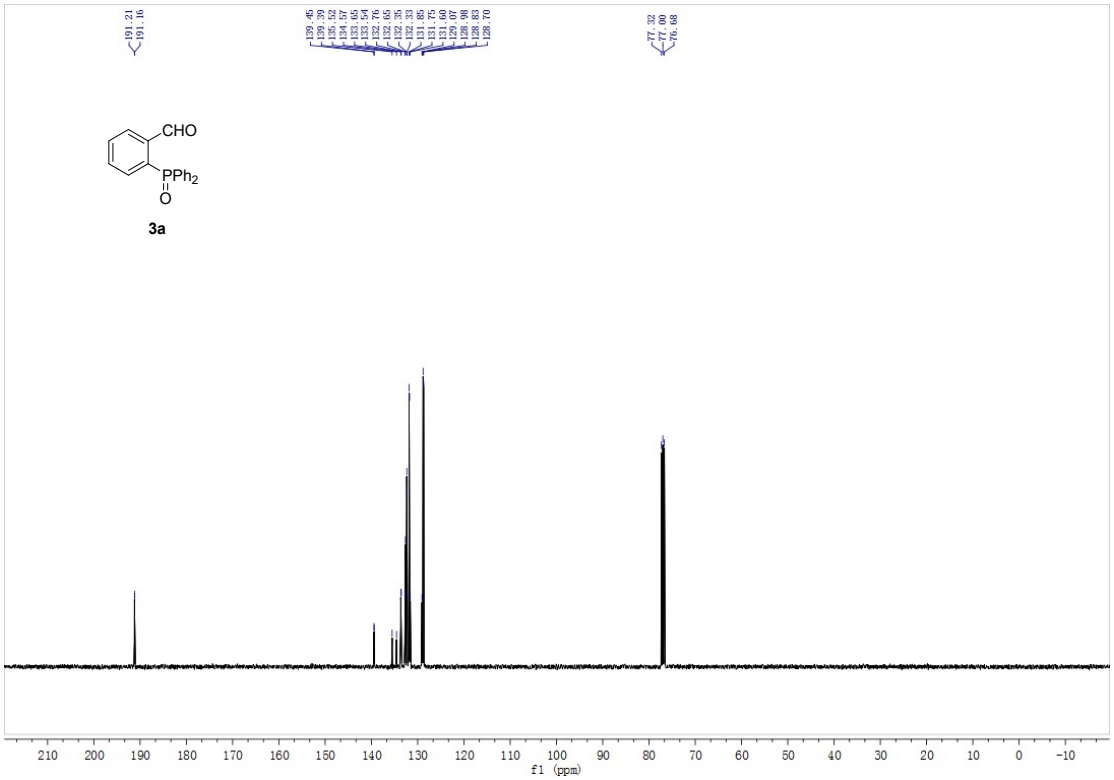
2f

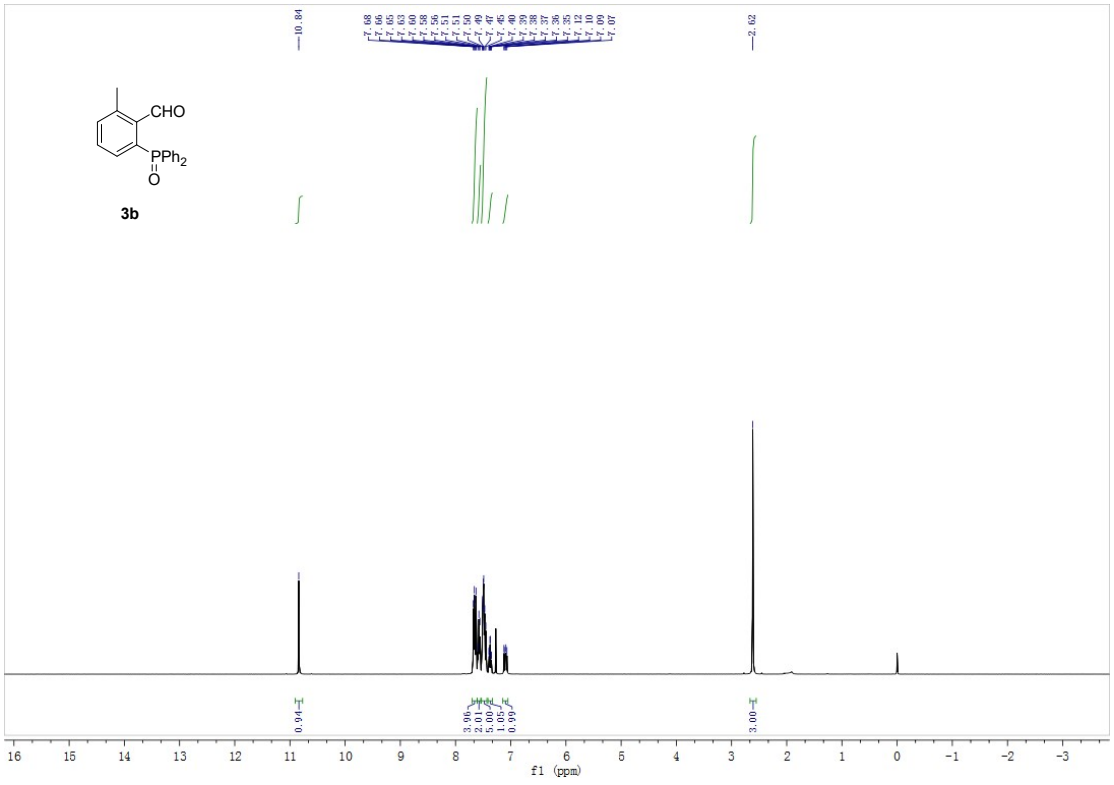

168.27
139.57
132.14
130.21
123.25
119.24
110.41
84.33
79.20
77.32
77.00
76.68
24.90
NHCOCH3
f1 (ppm)

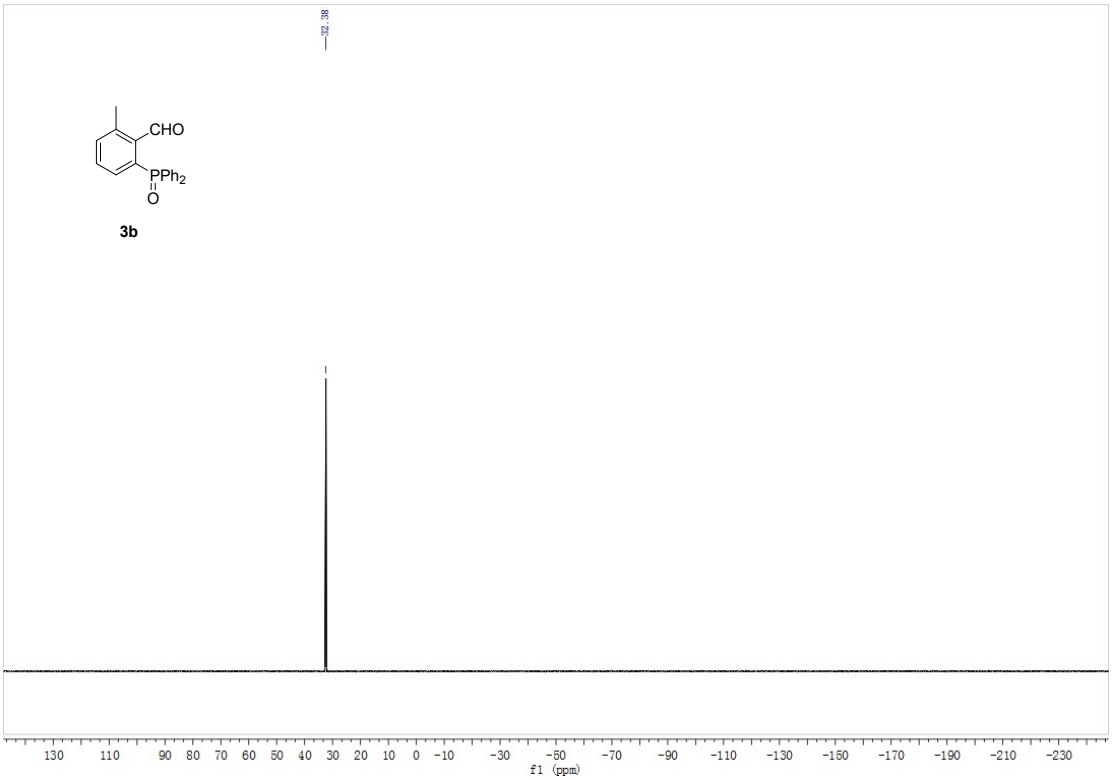
2f

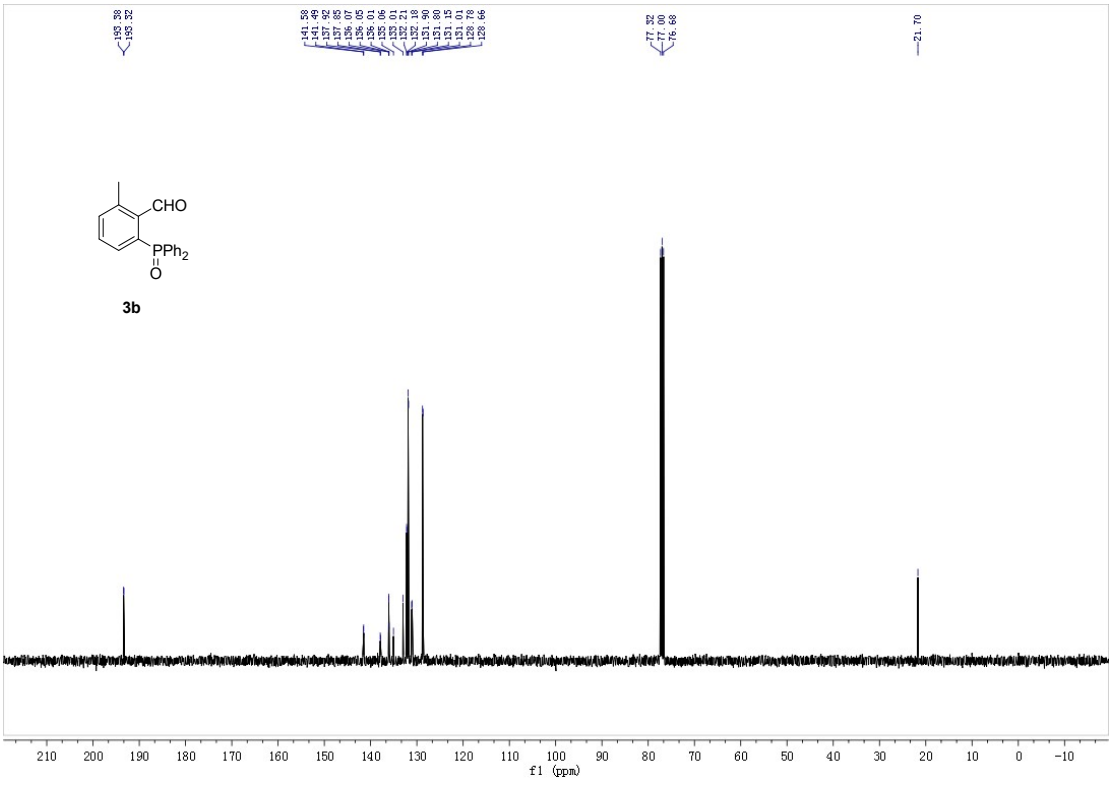

CHO
PPh2
O
3a
f1 (ppm)

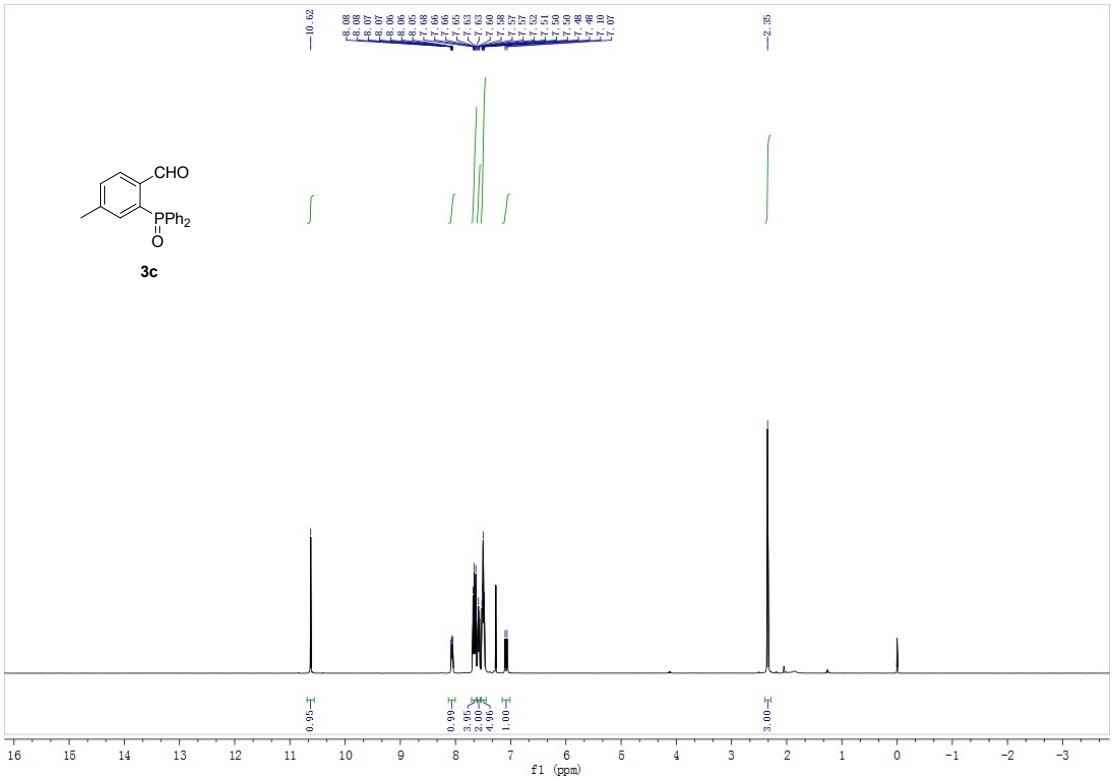

CHO
PPh2
O
3a
f1 (ppm)

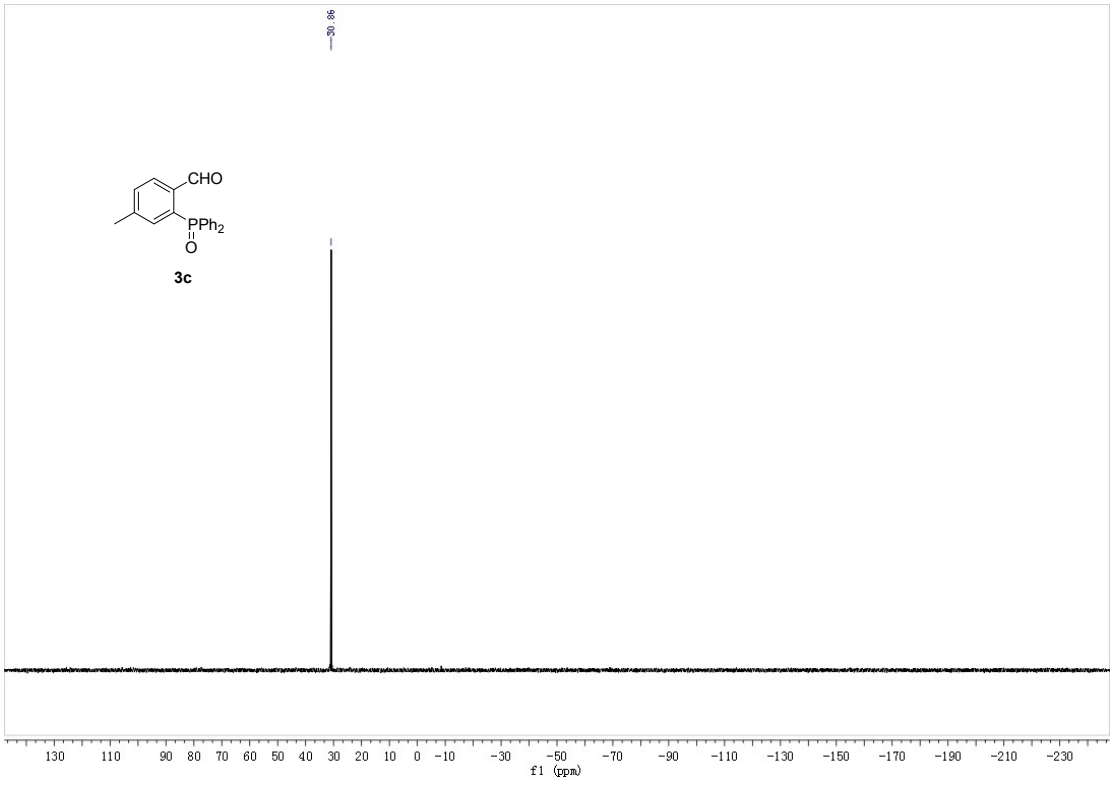

191.21
191.10
139.45
139.39
135.52
134.57
133.65
133.54
132.76
132.65
132.35
132.33
131.85
131.75
131.60
129.07
128.88
128.83
128.70
77.32
77.00
76.68
CHO
PPh2
O
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

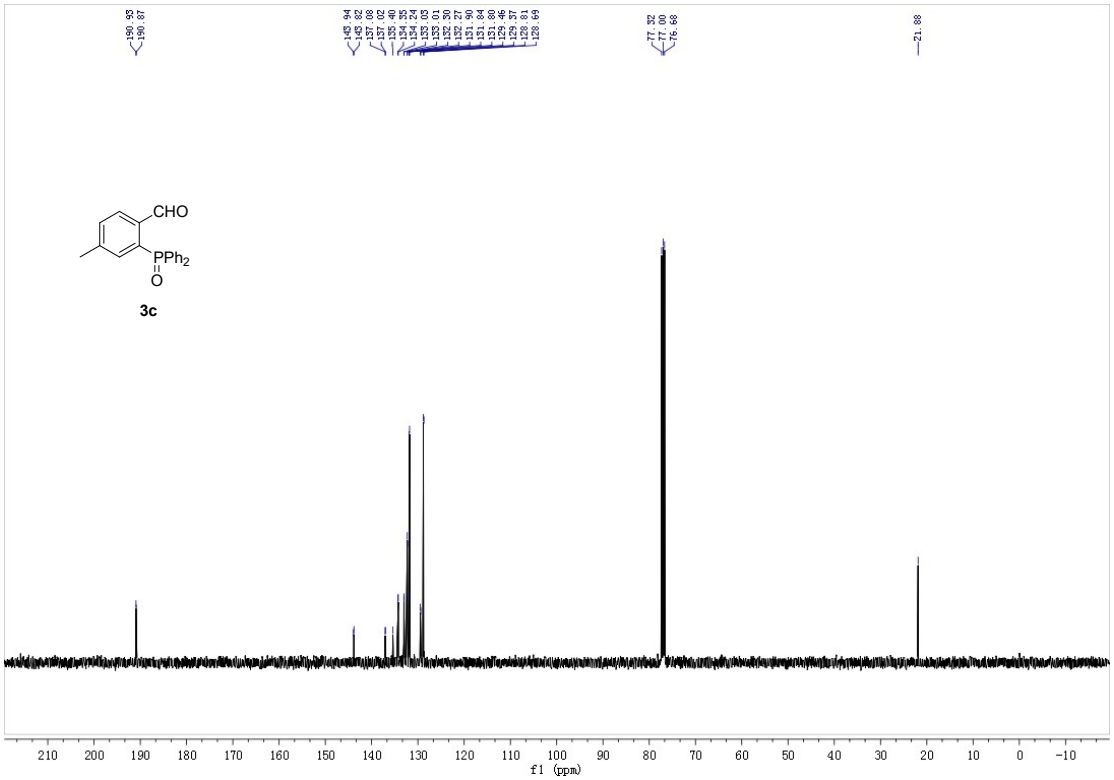

10.84
7.68
7.66
7.65
7.63
7.60
7.58
7.56
7.51
7.50
7.49
7.47
7.45
7.40
7.39
7.37
7.36
7.35
7.12
7.10
7.09
7.07
2.62
CHO
PPh2
O
3b
0.94
3.06
2.01
2.00
1.05
0.99
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

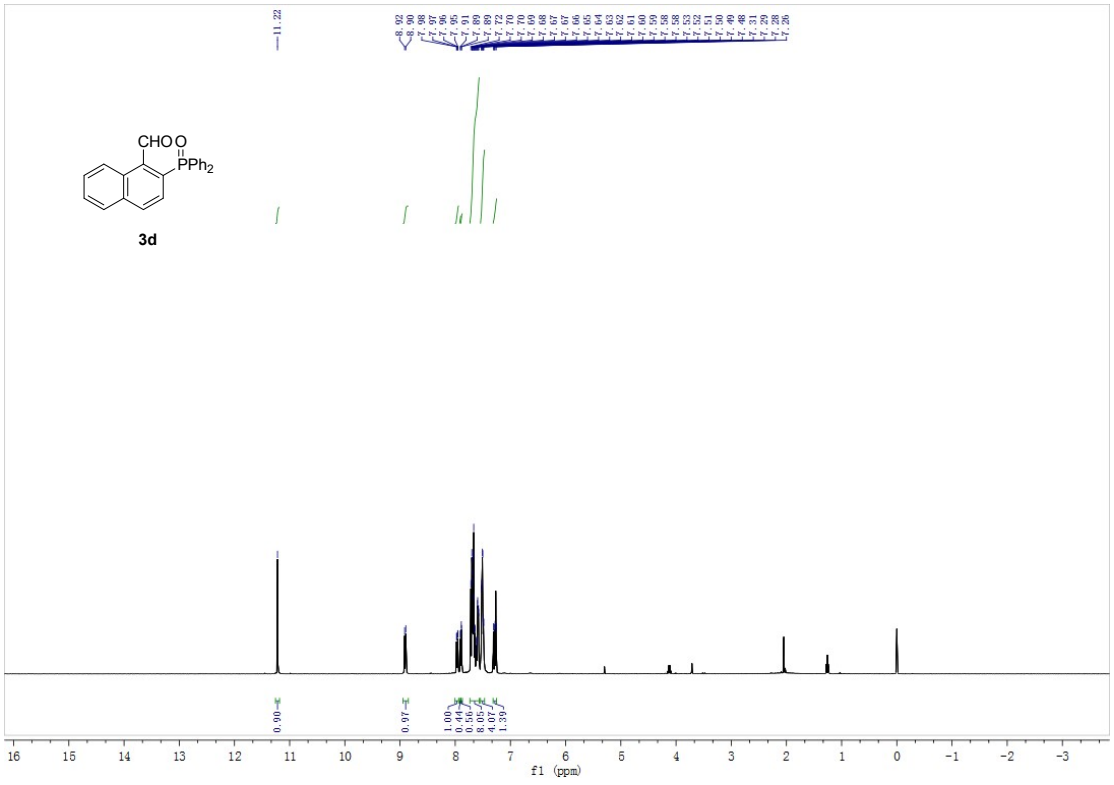

32.38
CHO
PPh2
O
3b
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

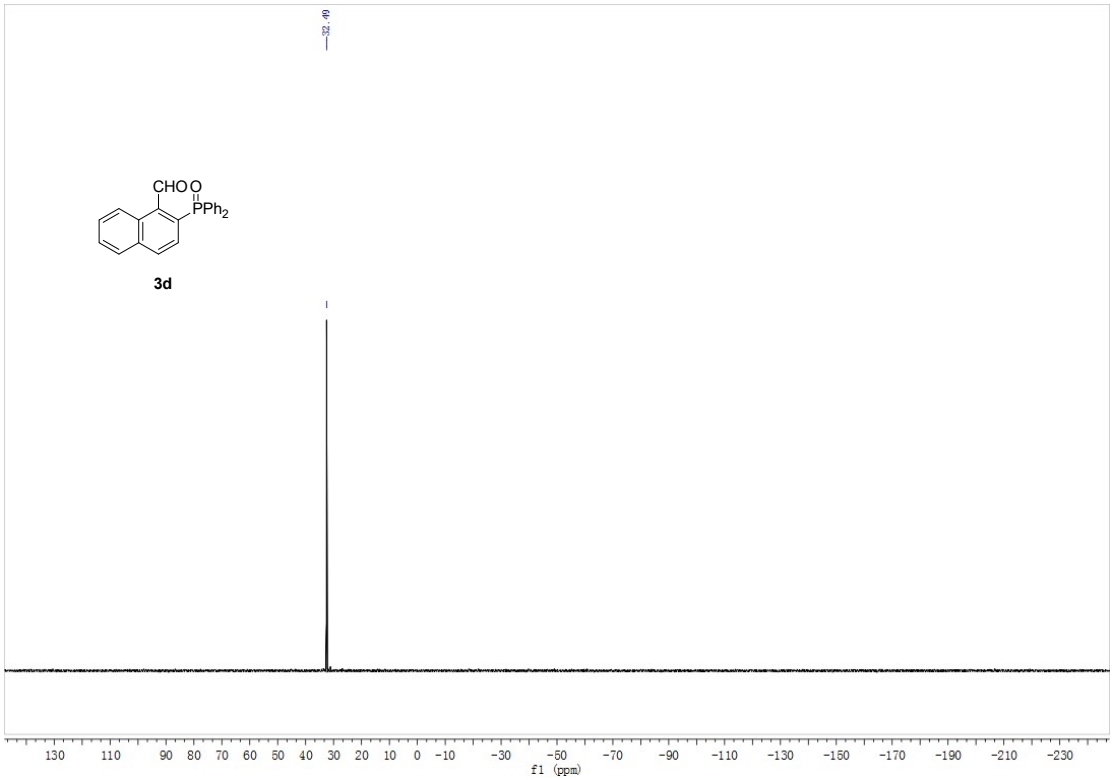

193.38
191.32
141.58
141.49
137.92
137.85
136.07
136.05
136.01
135.06
133.01
132.21
132.18
131.90
131.80
131.15
131.01
128.78
128.66
77.32
77.00
76.68
21.70
CHO
PPh2
O
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

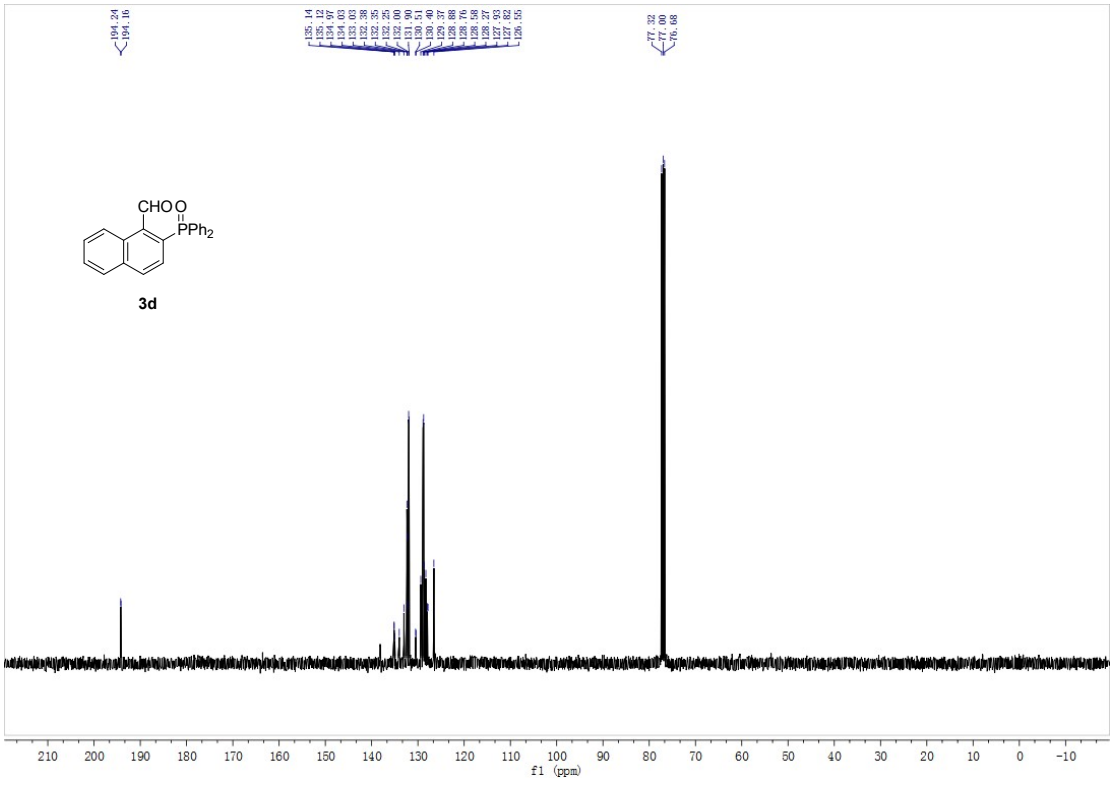

CHO
PPh2
O
3c
10.62
8.08
8.07
8.07
8.06
8.06
8.05
7.68
7.66
7.66
7.65
7.63
7.63
7.60
7.58
7.57
7.57
7.52
7.51
7.50
7.50
7.48
7.46
7.10
7.07
2.35
0.95
0.99
3.95
2.05
4.90
1.00
3.00
f1 (ppm)

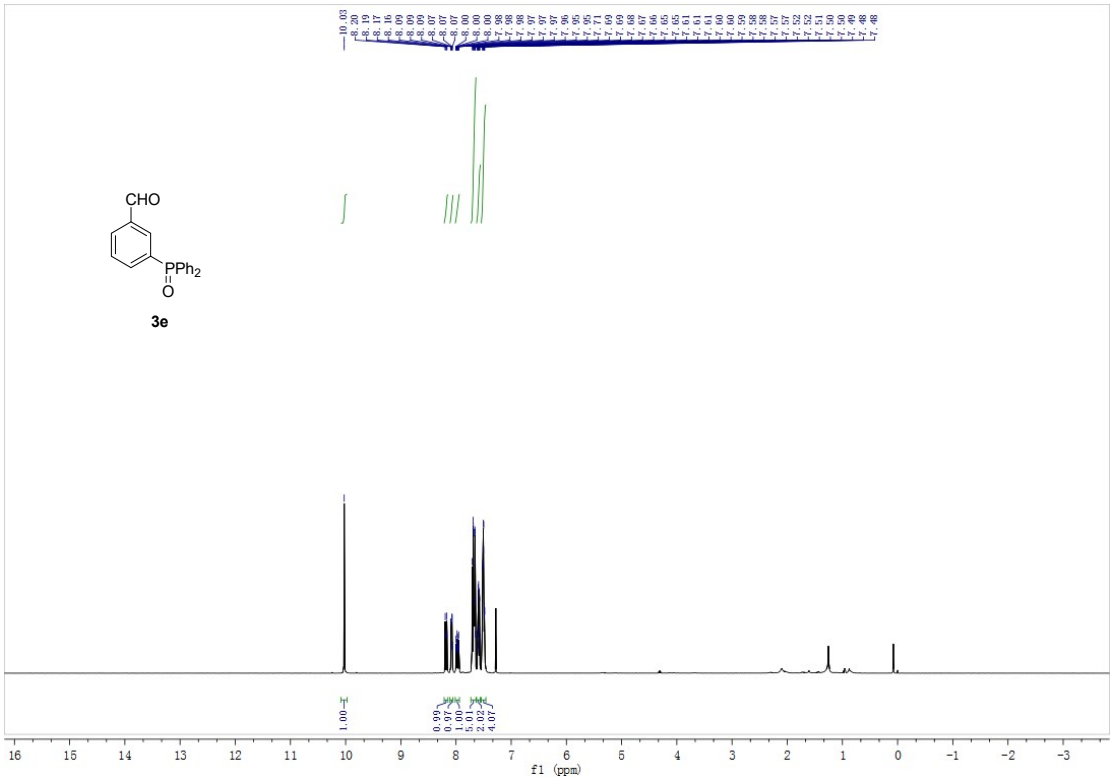

CHO
PPh2
O
3c
30.86
f1 (ppm)

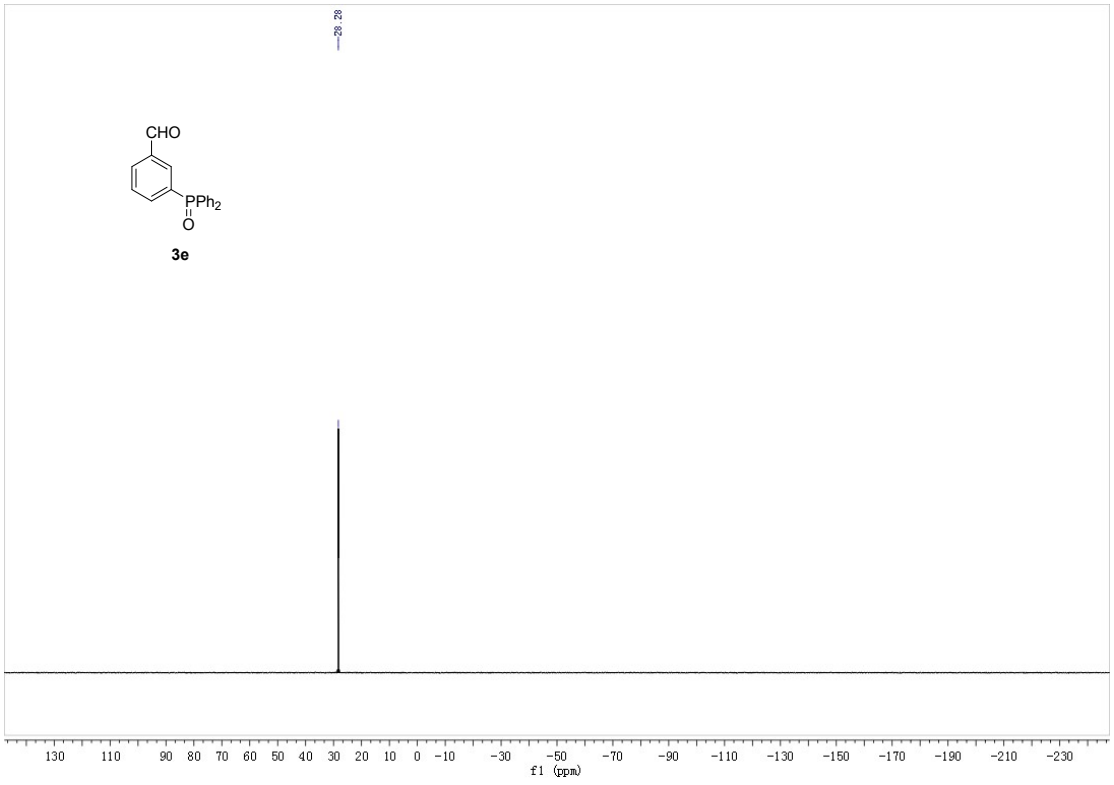

CHO
PPh2
O
3c
f1 (ppm)

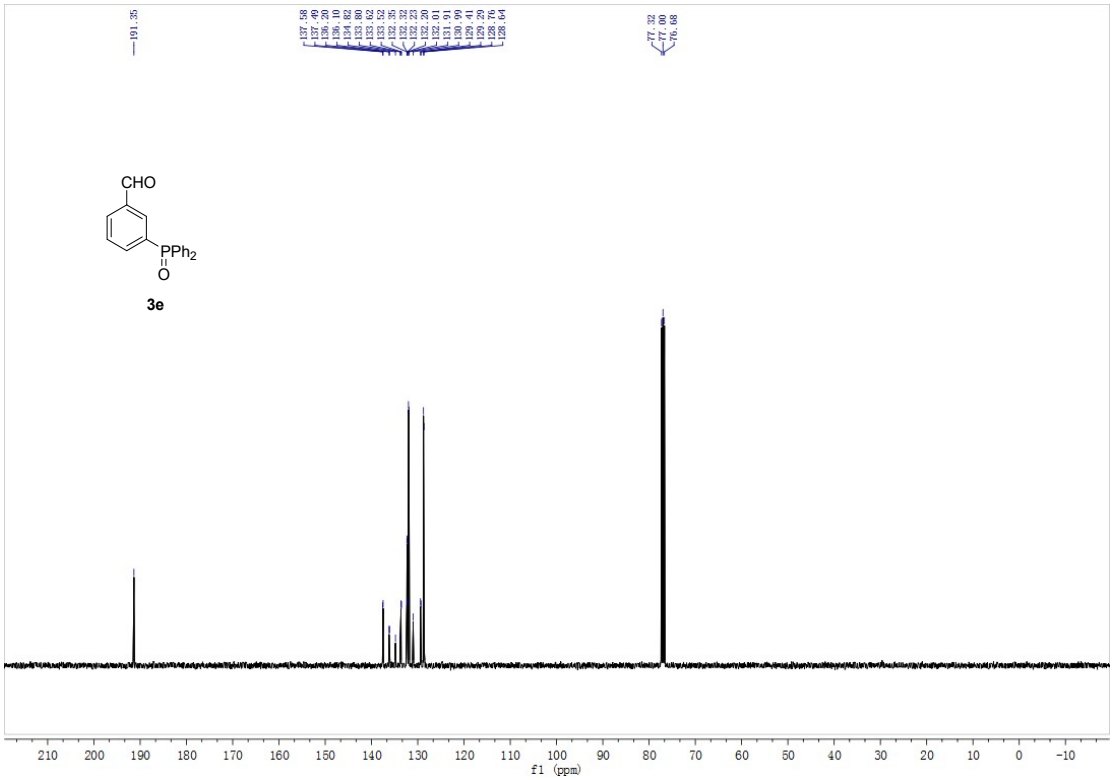

CHO O
PPh2
3d
f1 (ppm)

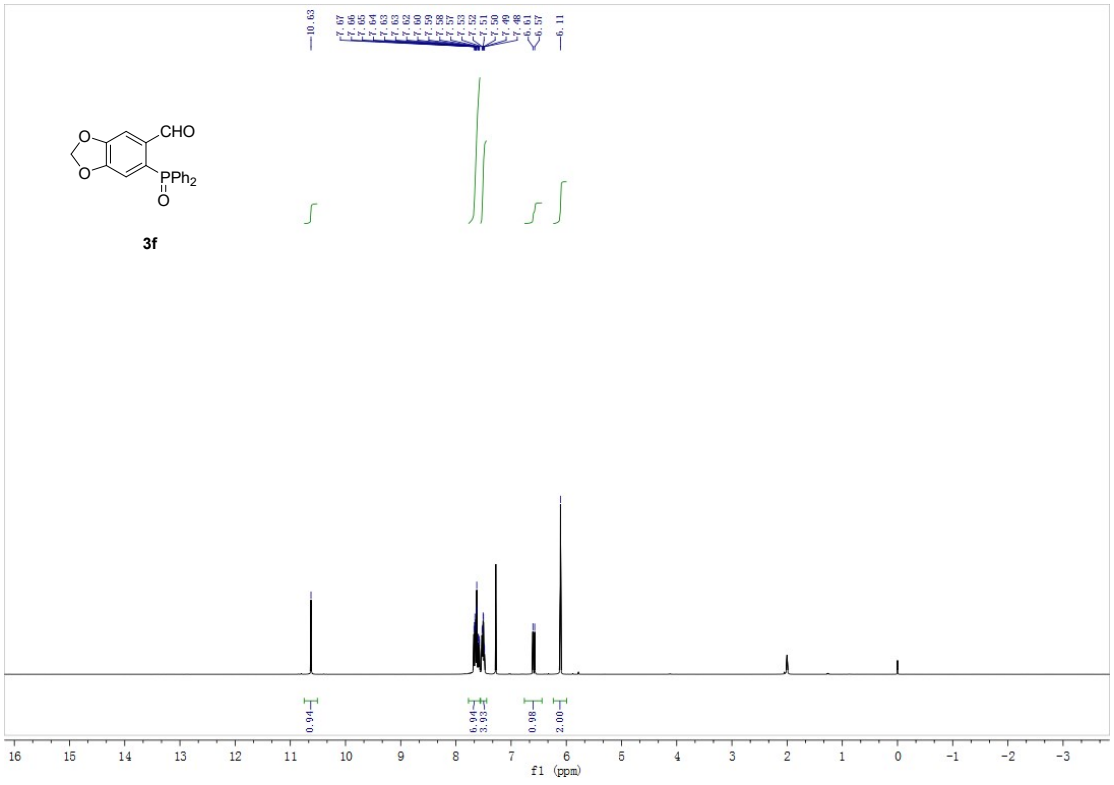

32.49
CHO O
PPh2
3d
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

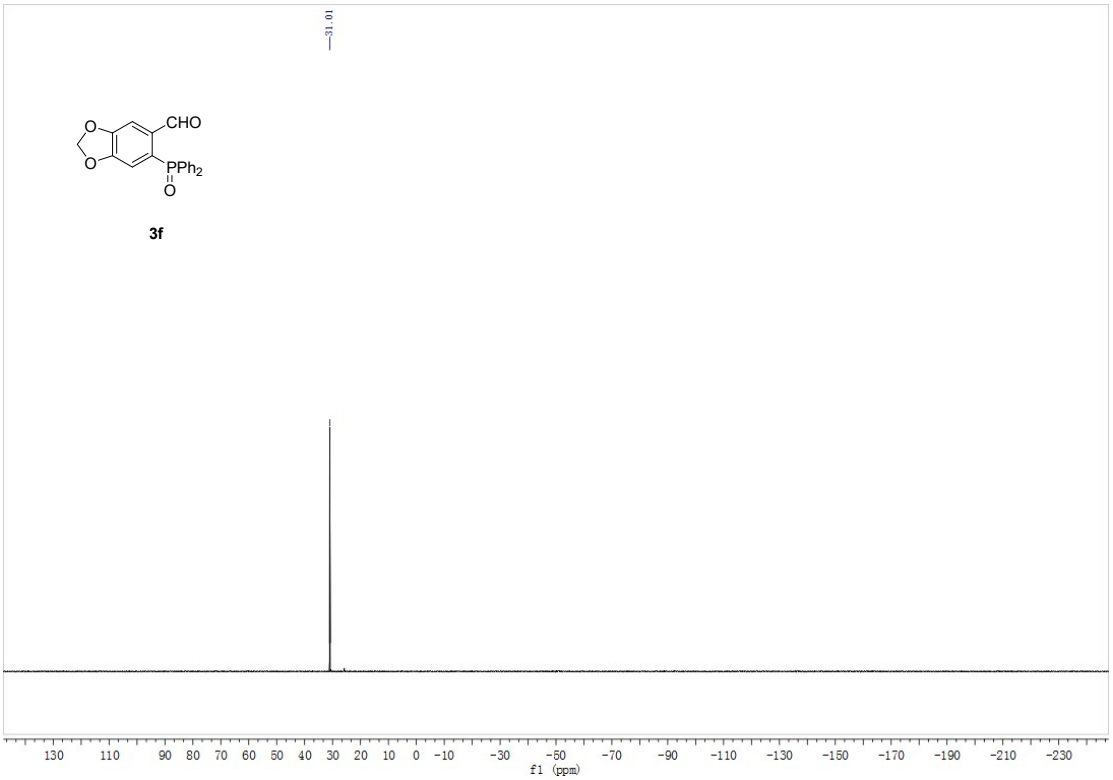

194.24
194.16
135.14
135.12
134.97
134.03
133.03
132.38
132.35
132.25
132.00
131.99
131.91
130.40
129.37
128.88
128.76
128.58
128.27
127.93
127.82
126.55
77.32
77.00
76.68
CHO O
PPh2
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

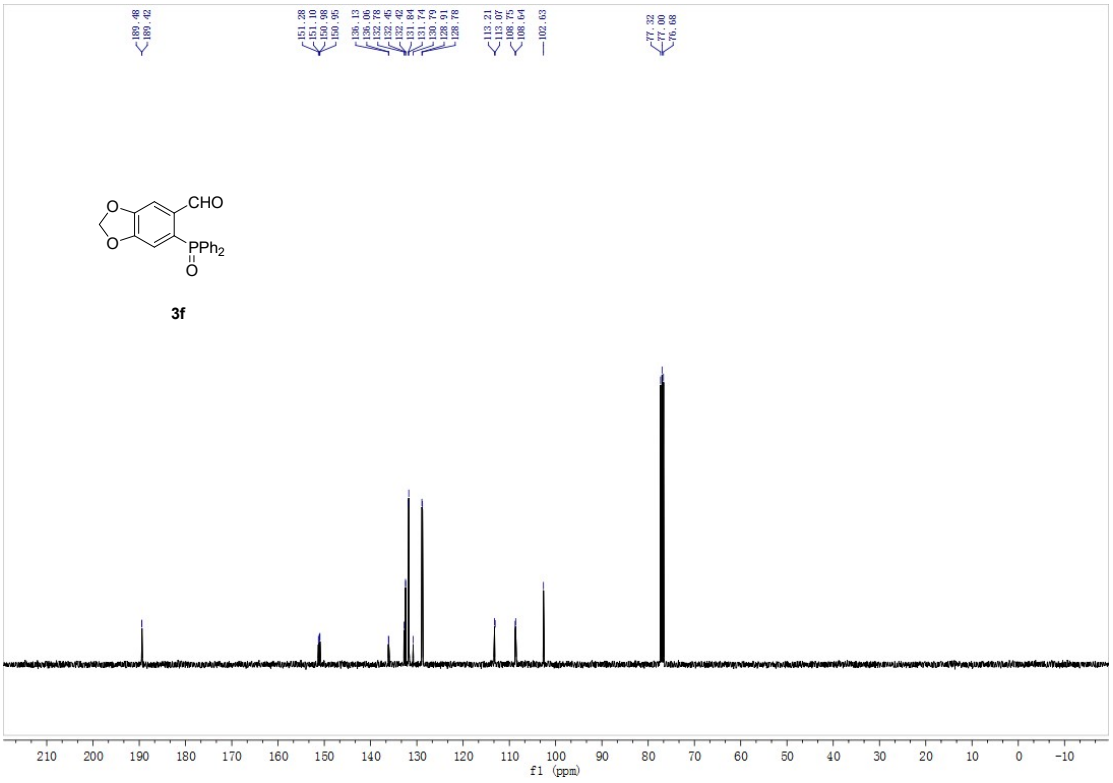

CHO
PPh2
O
3e
f1 (ppm)

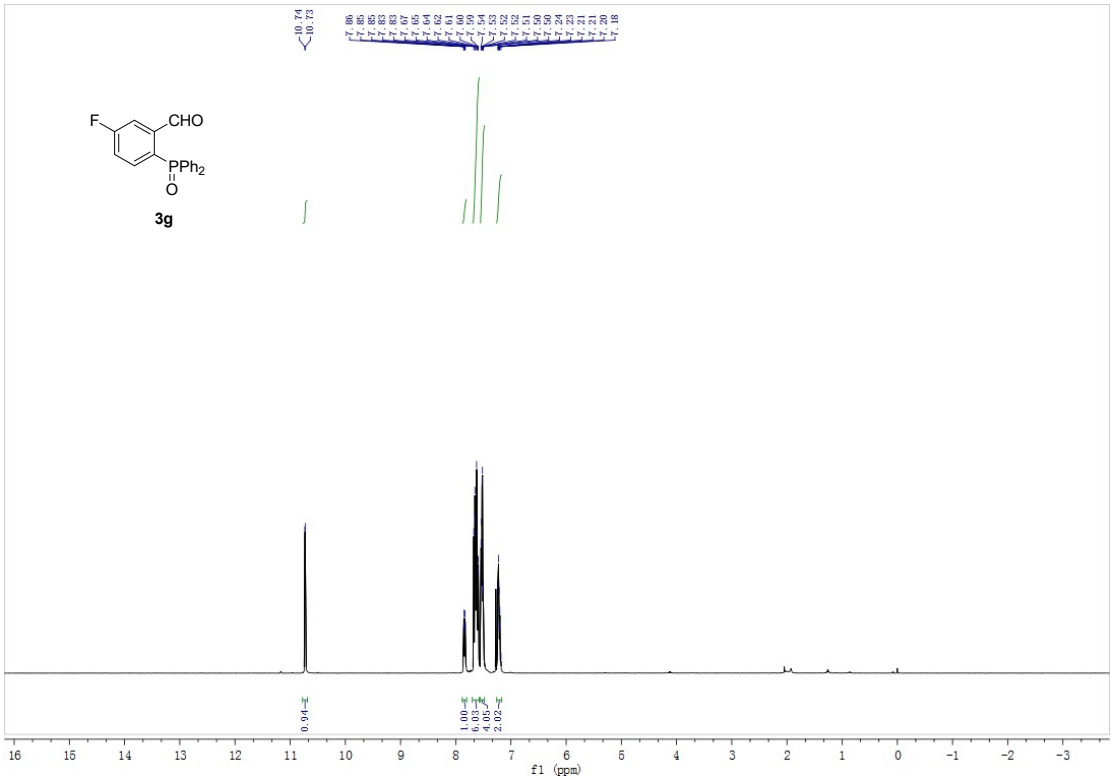

CHO
PPh2
O
3e
f1 (ppm)

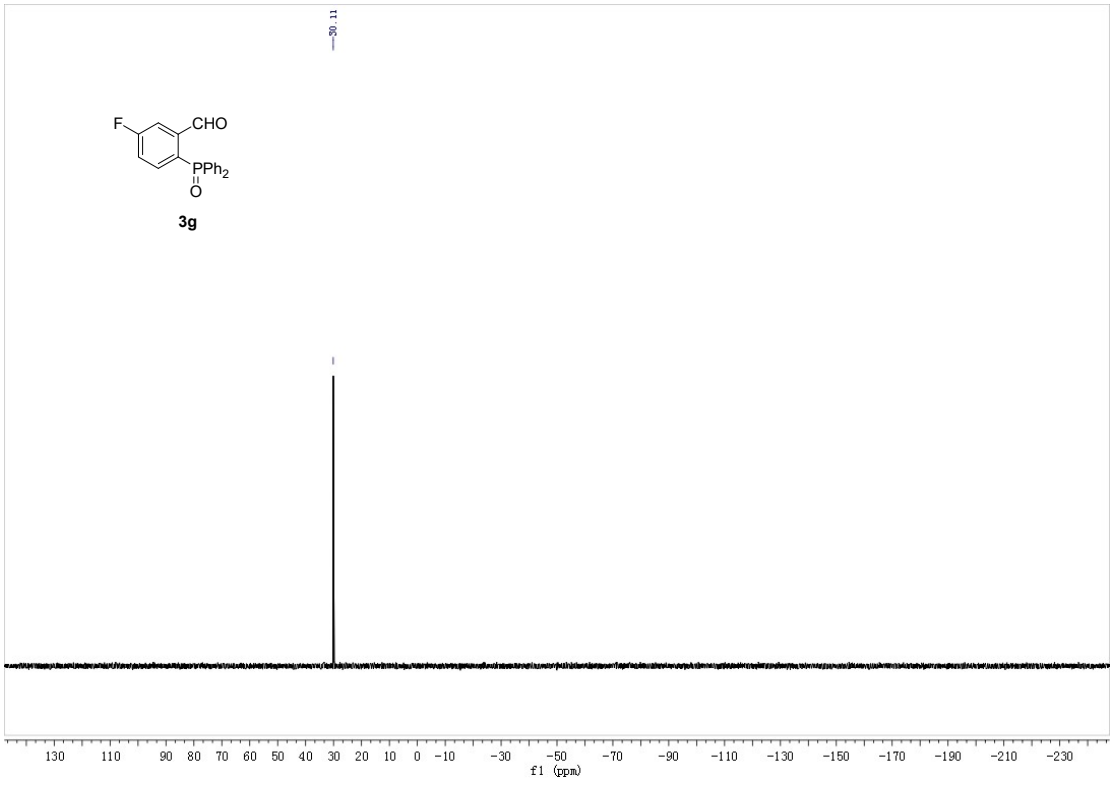

191.35
137.58
137.49
136.20
136.10
134.82
133.80
133.62
133.52
132.35
132.32
132.23
132.20
132.01
131.91
130.99
129.41
129.29
128.76
128.64
77.32
77.00
76.68
CHO
PPh2
O
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

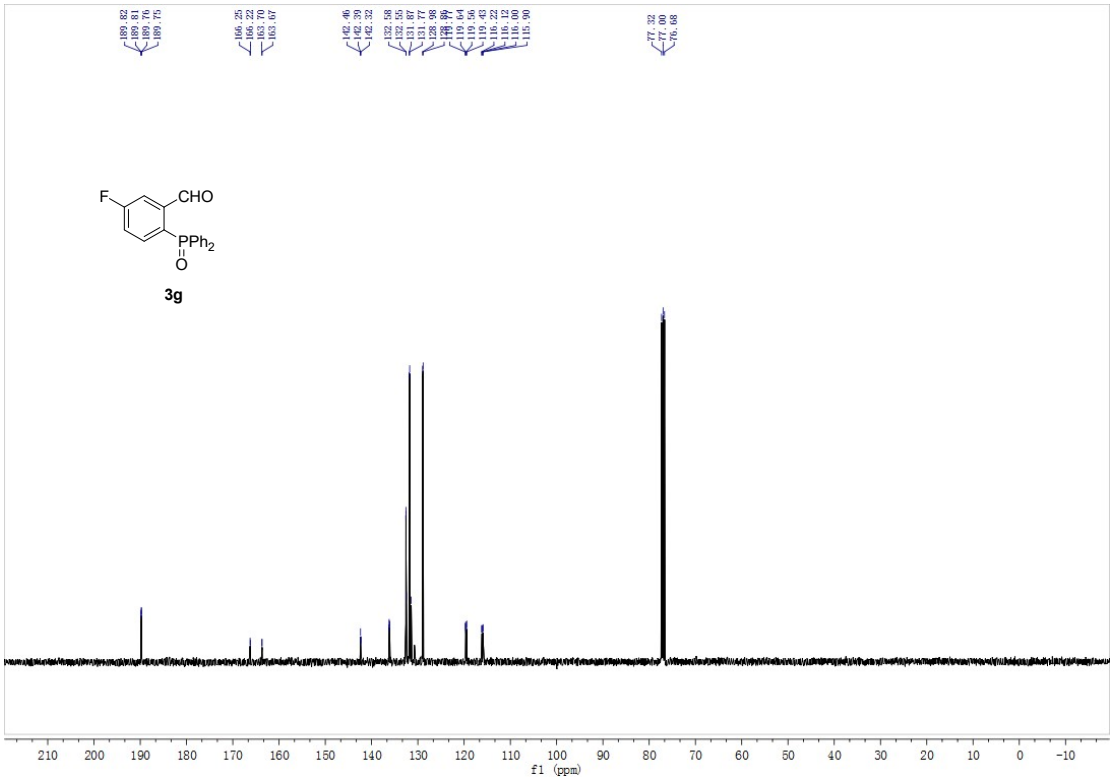

10.63
7.67
7.66
7.65
7.64
7.63
7.63
7.62
7.60
7.59
7.58
7.57
7.53
7.52
7.51
7.50
7.49
7.48
6.61
6.57
6.11
CHO
O
O
PPh2
O
3f
0.94
6.94
3.93
0.98
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


31.01
CHO
PPh2
O
3f
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

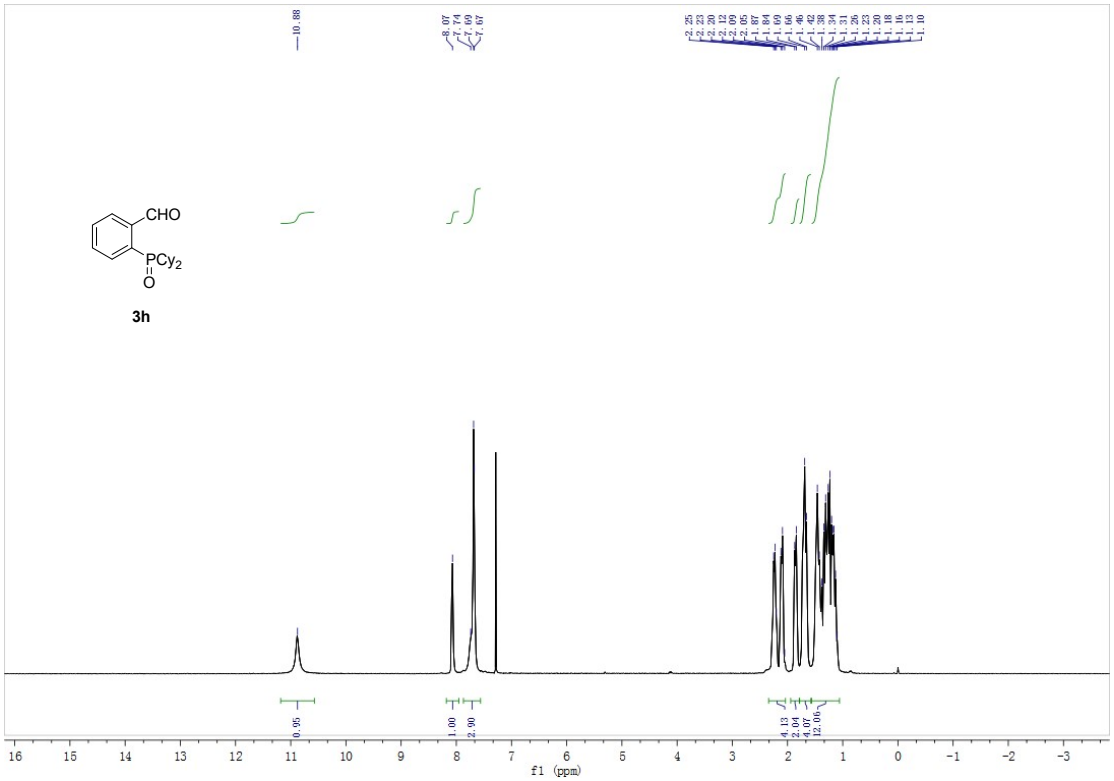

189.48
189.42
151.28
151.10
150.98
150.95
136.13
135.96
133.78
132.45
132.42
131.84
131.74
131.70
128.91
128.78
113.21
113.07
108.75
108.64
102.63
77.32
77.00
76.68
CHO
PPh2
O
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F
CHO
PPh2
O
3g
10.74
10.73
7.86
7.85
7.85
7.83
7.83
7.67
7.65
7.64
7.62
7.61
7.60
7.59
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.24
7.23
7.21
7.20
7.18
0.94
1.00
6.03
4.05
2.02
f1 (ppm)


F
CHO
PPh2
O
3g
30.11
f1 (ppm)



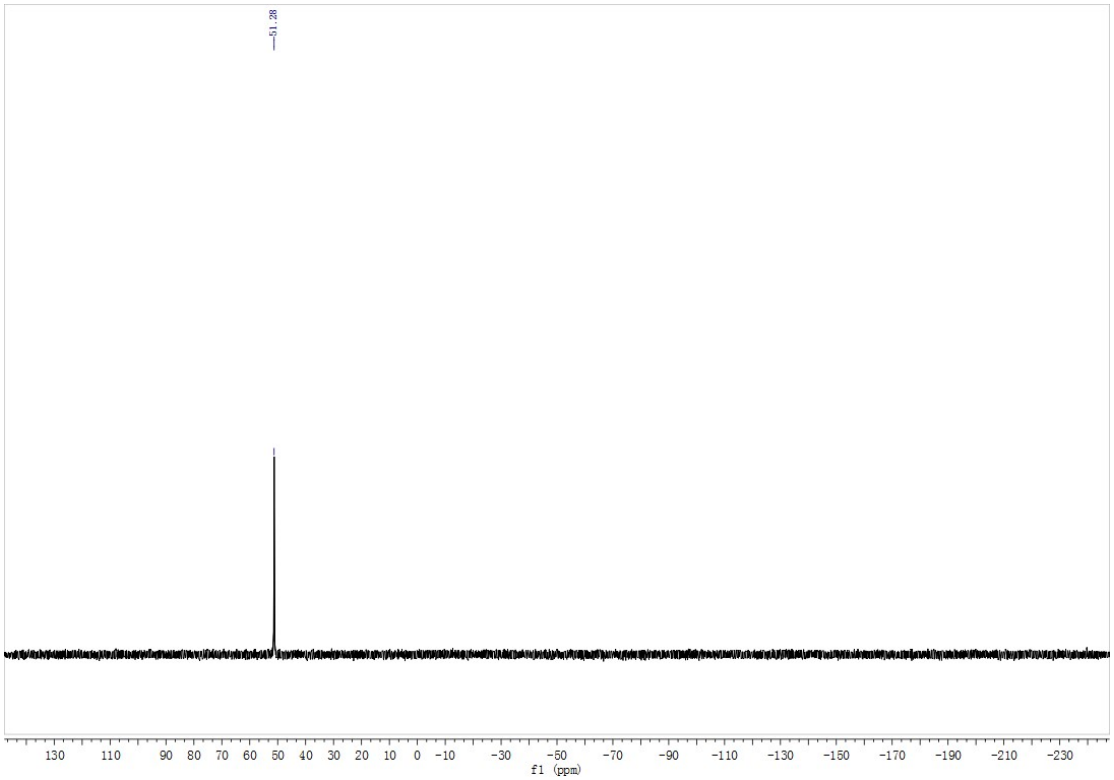
3g

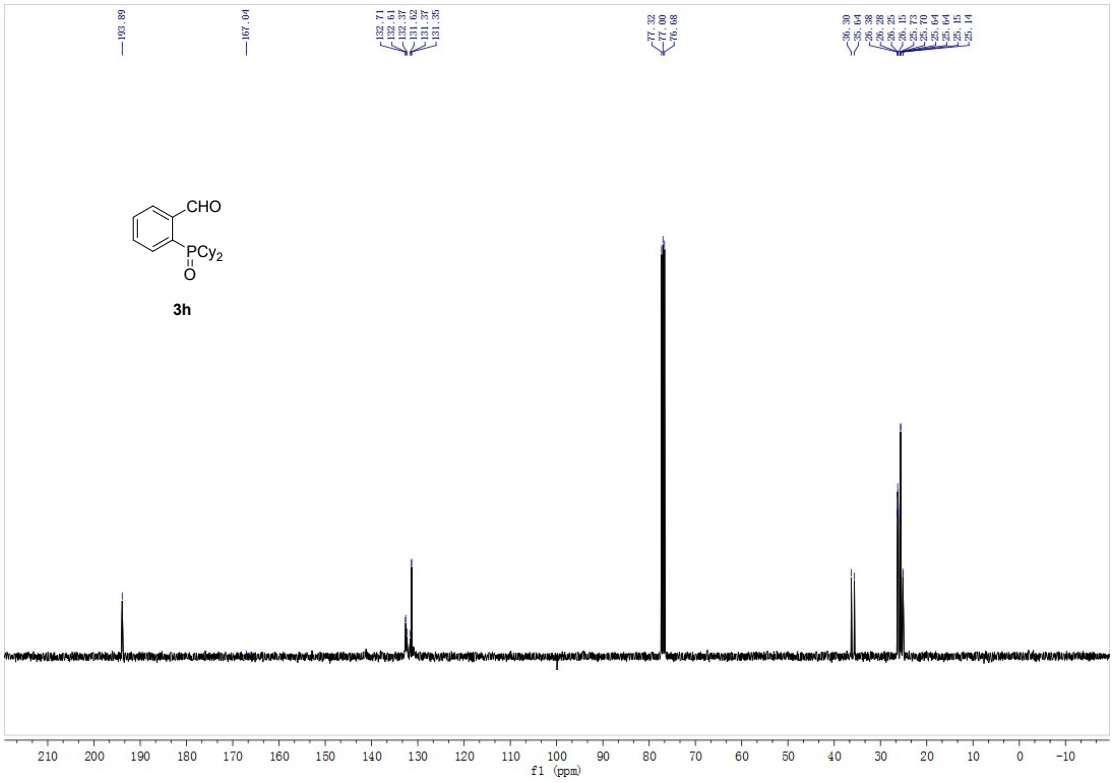


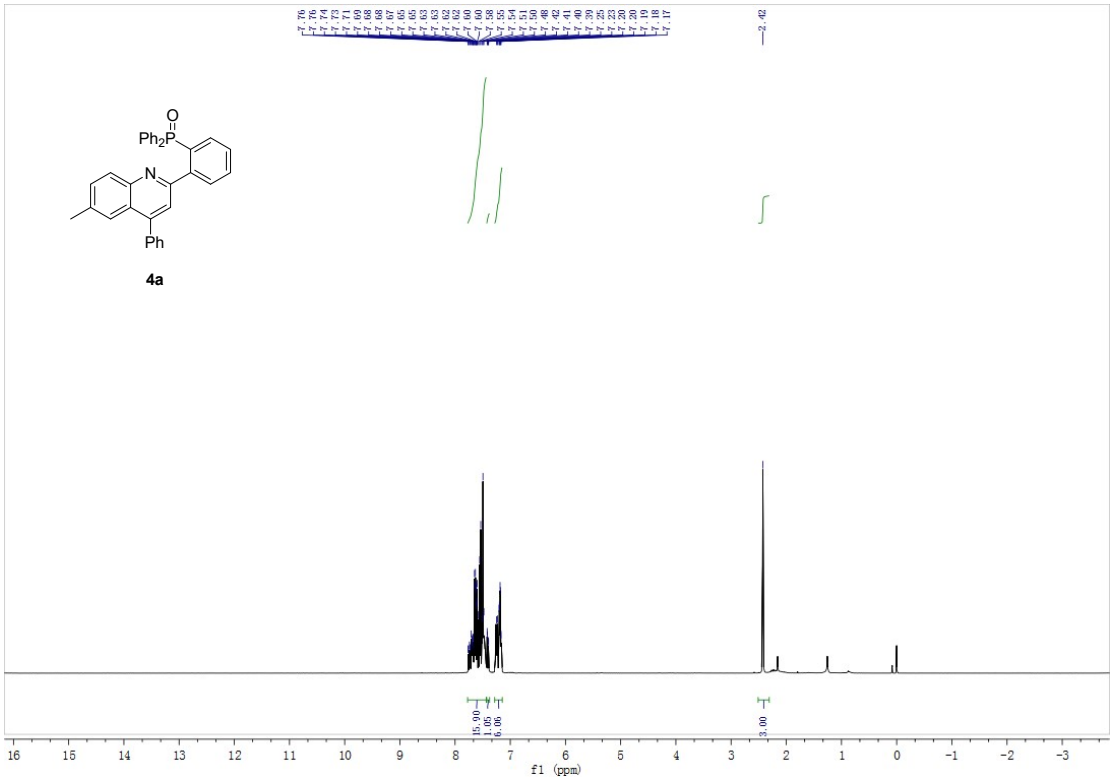
3h

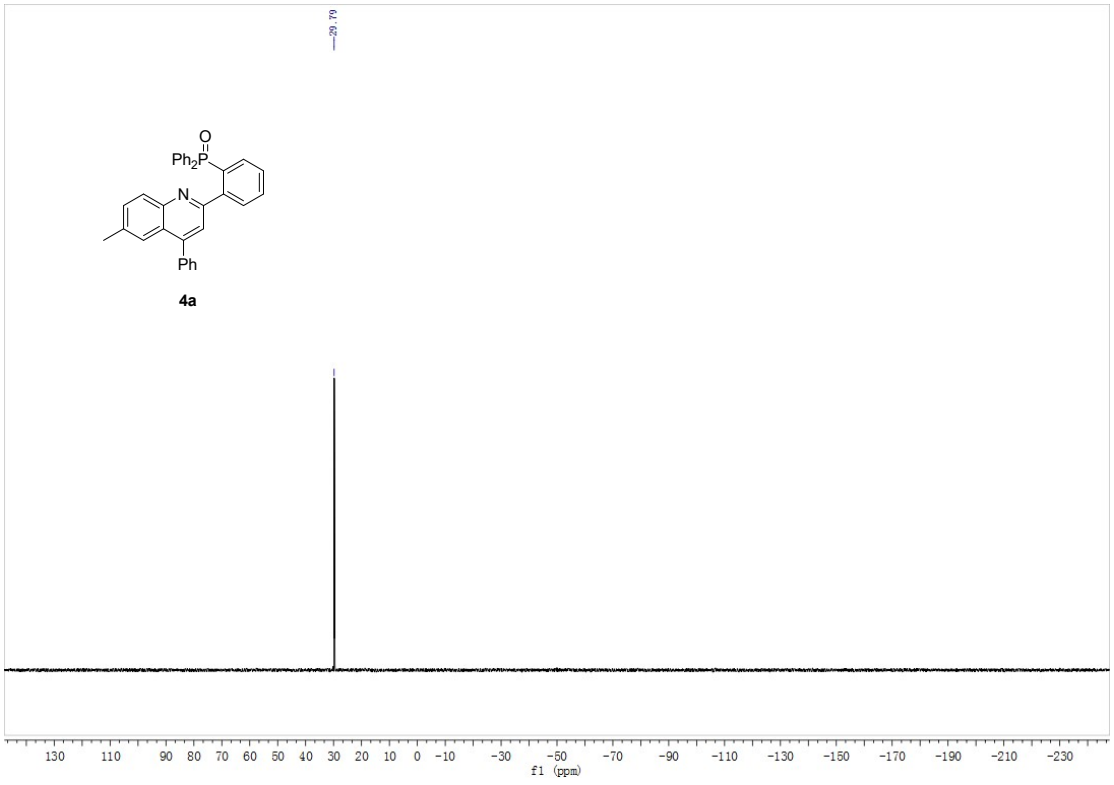
CHO
PCy2
O

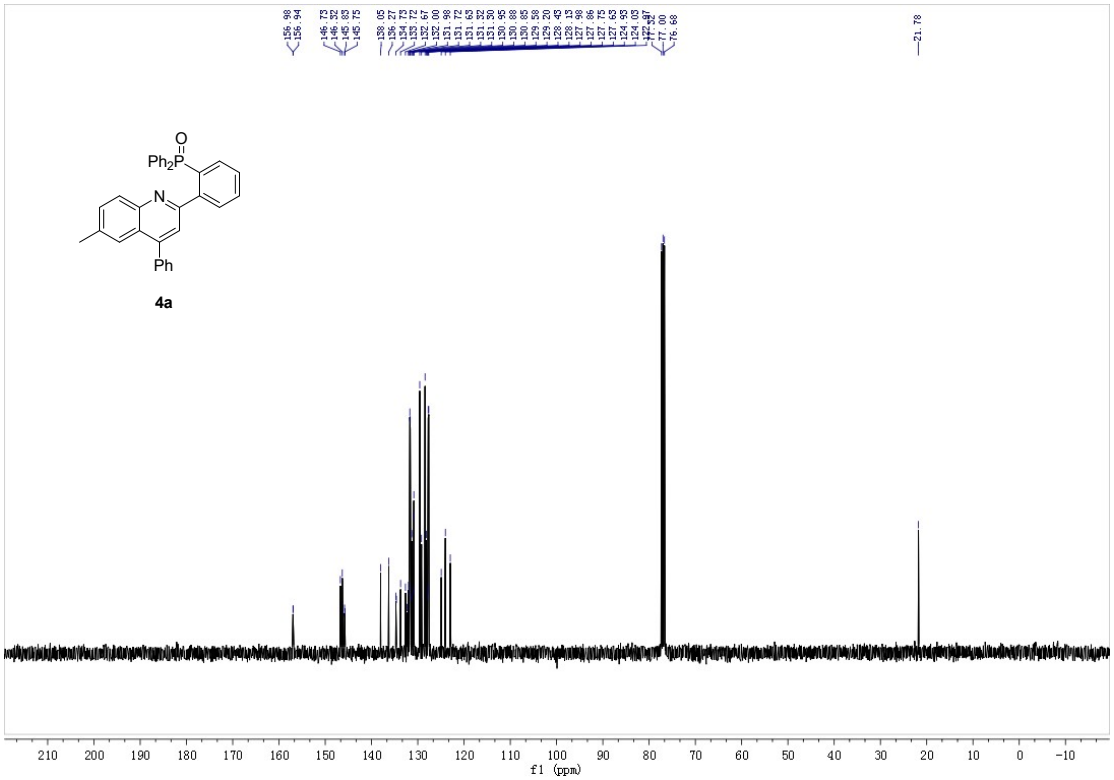
3h

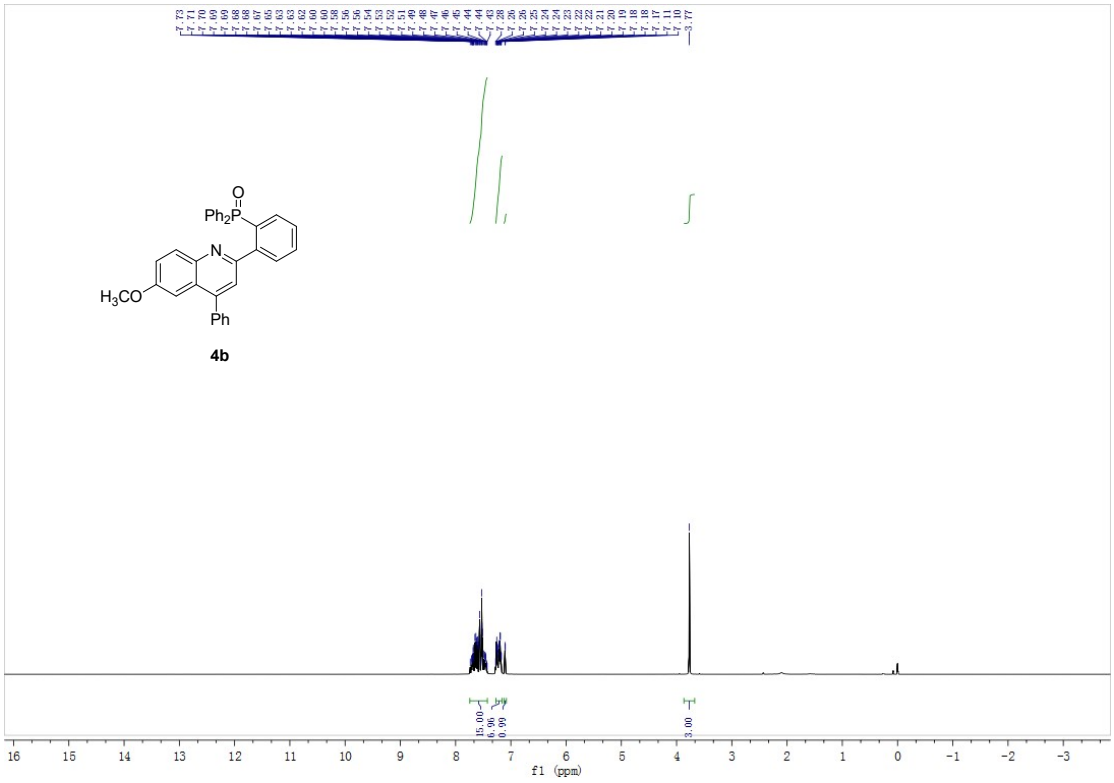

51.28
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

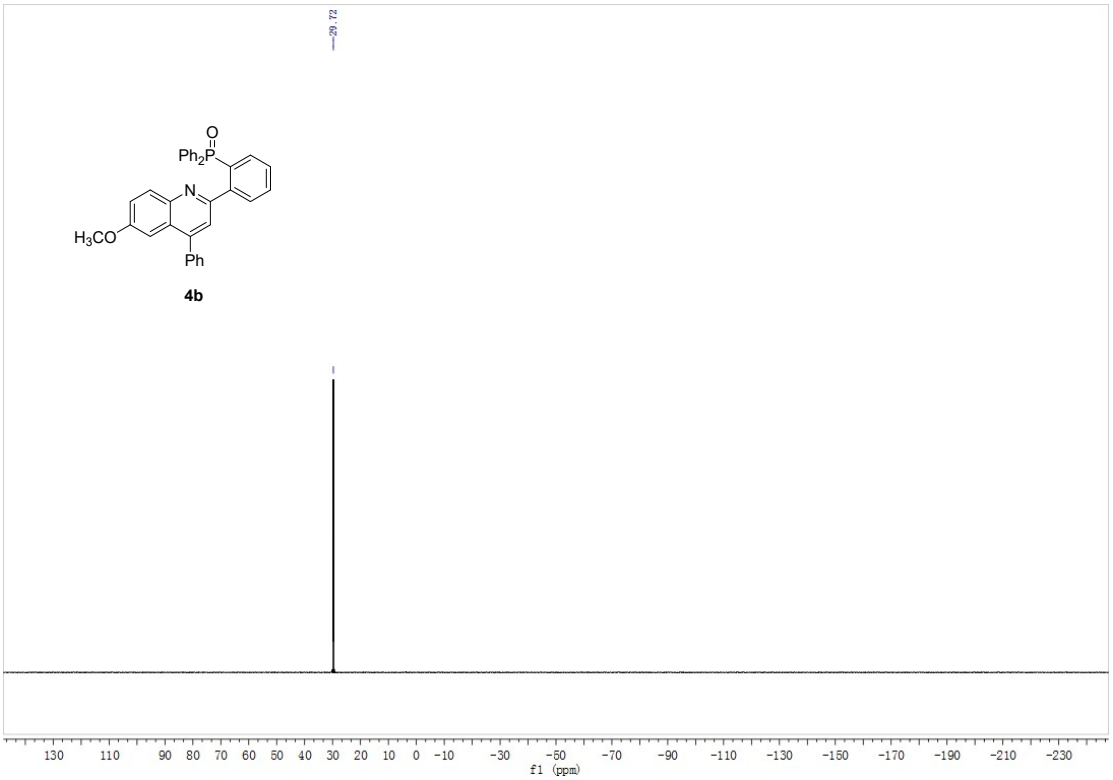

193.89
167.04
132.71
132.61
132.37
131.62
131.37
131.35
77.32
77.00
76.68
36.30
35.64
28.38
26.28
26.25
26.15
25.73
25.70
25.64
25.64
25.15
25.14
CHO
PCy2
O
3h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Ph2P
N
Ph
4a
f1 (ppm)

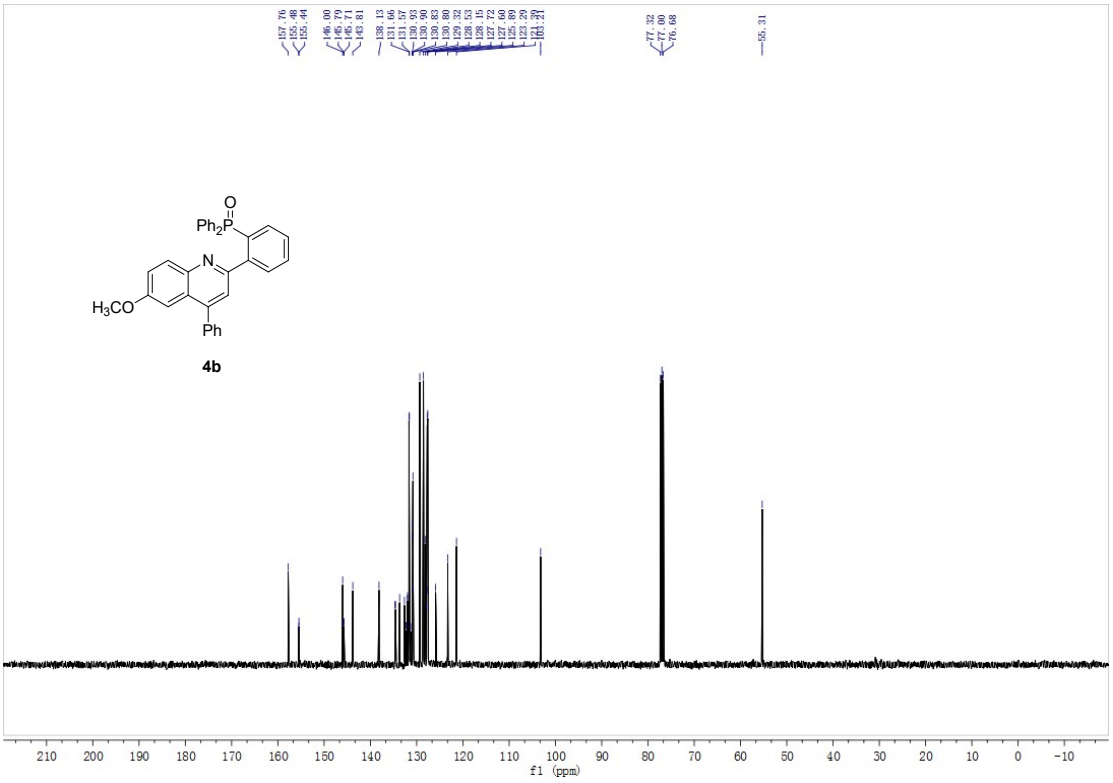

O
Ph2P
N
Ph
4a
f1 (ppm)


O
Ph2P
N
Ph
4a
f1 (ppm)

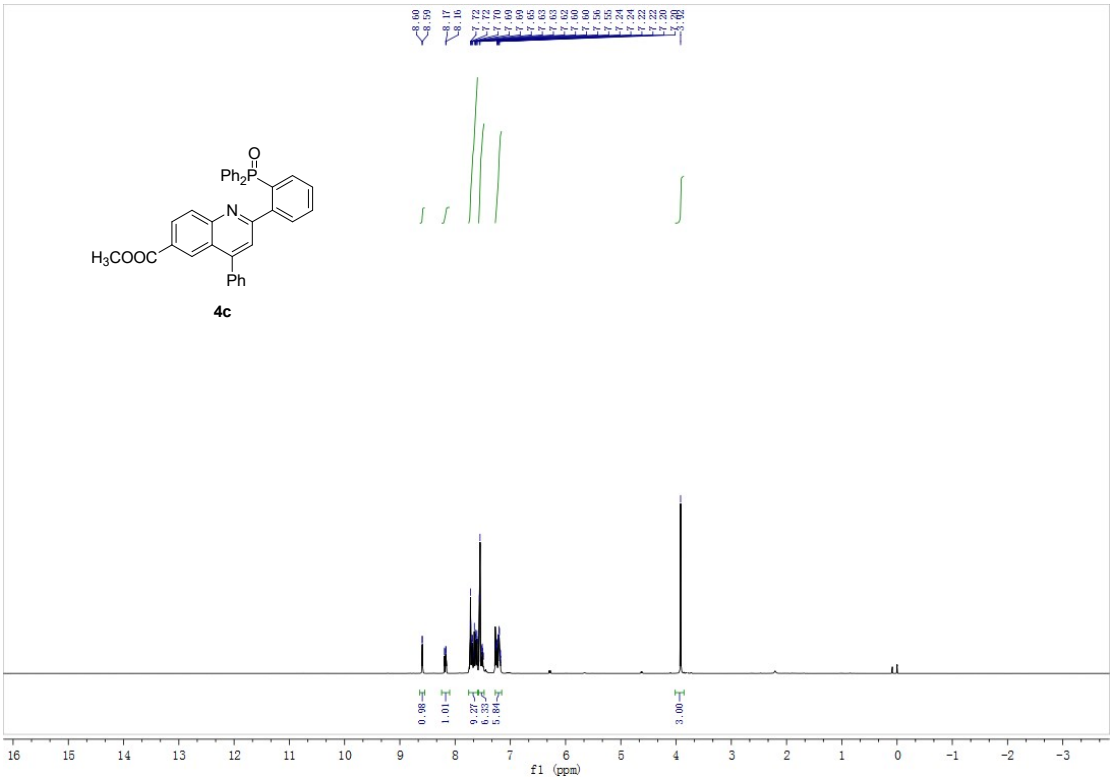

O
Ph2P
N
H3CO
Ph
4b
f1 (ppm)

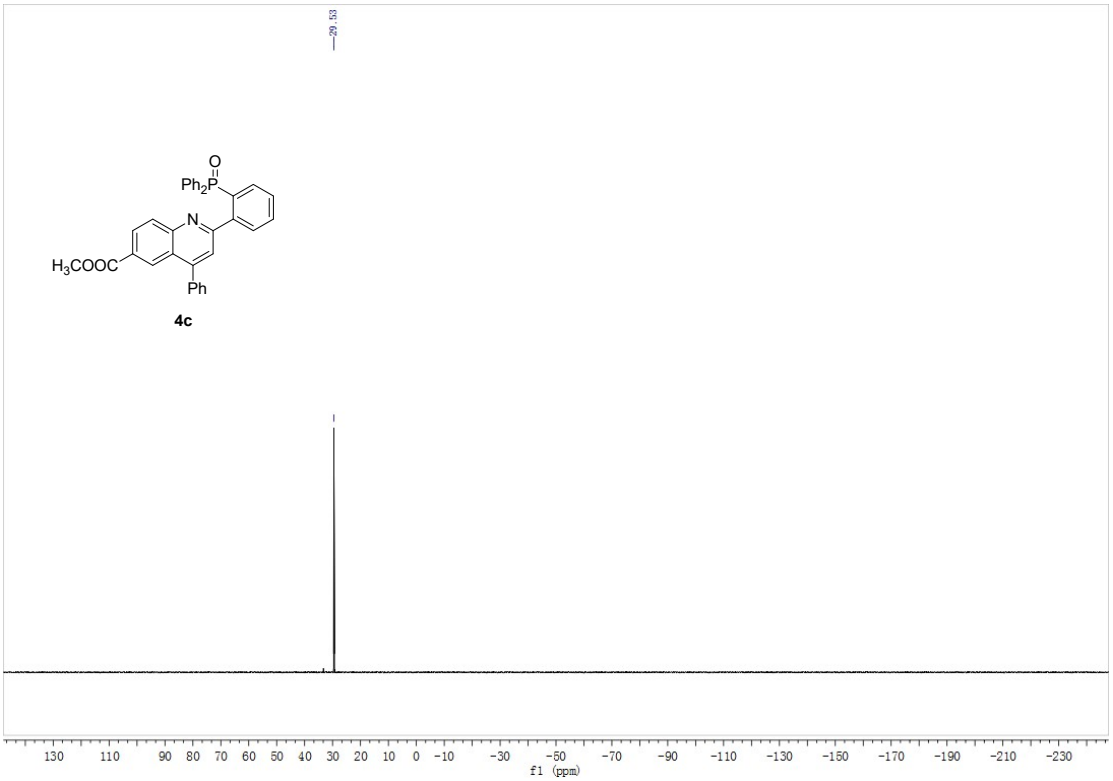

29.72
O
Ph2P
N
H3CO
Ph
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

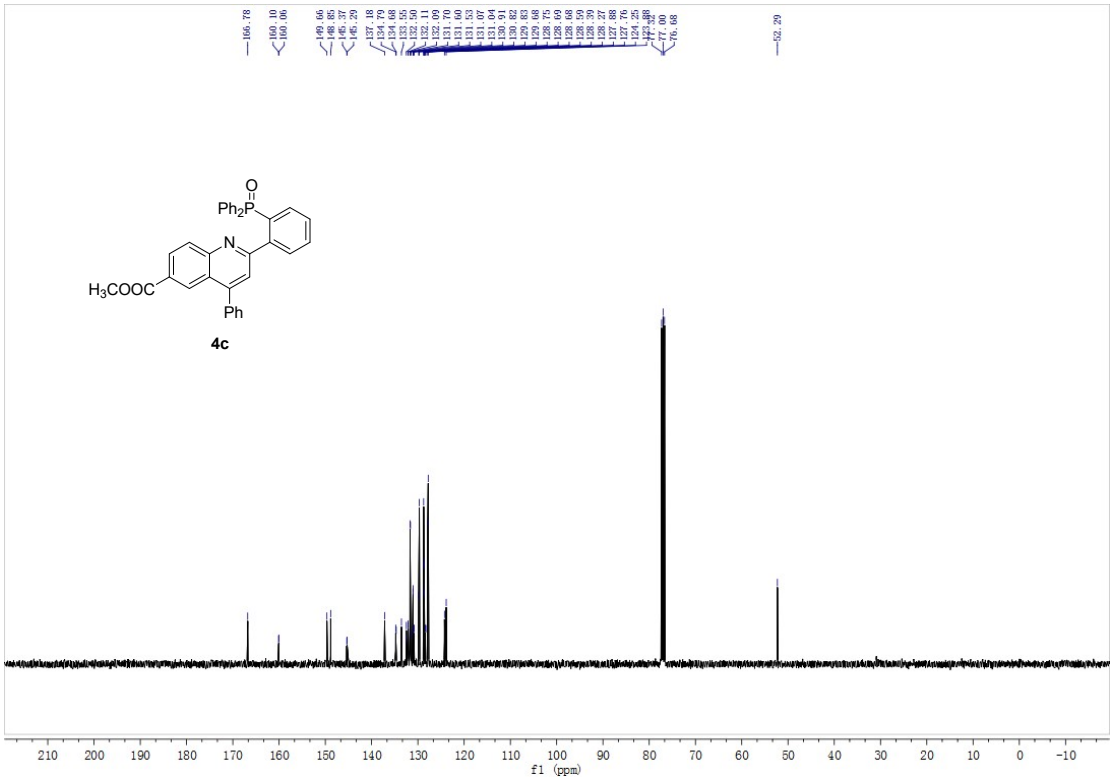
4b

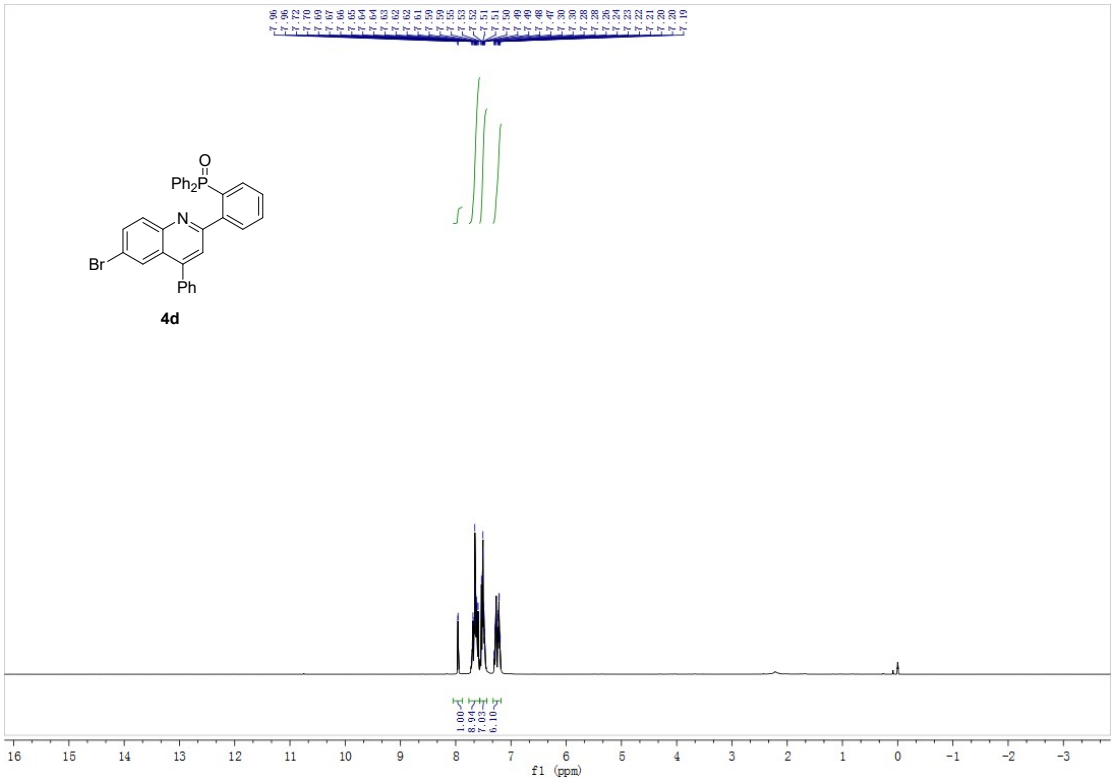

157.76
155.48
155.44
146.00
145.79
145.71
143.81
138.13
131.46
131.57
130.93
130.90
130.85
130.80
129.32
128.53
128.15
127.72
127.60
125.89
123.29
77.32
77.00
76.68
55.31
O
Ph2P
N
H3CO
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

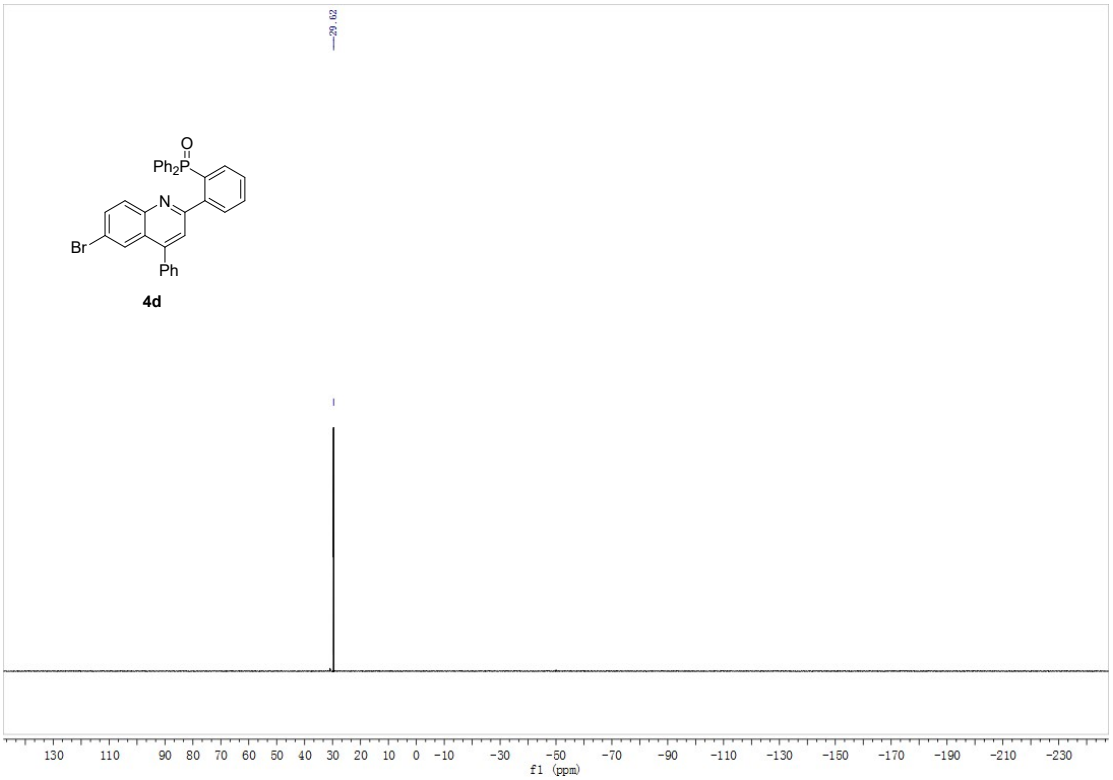
4b

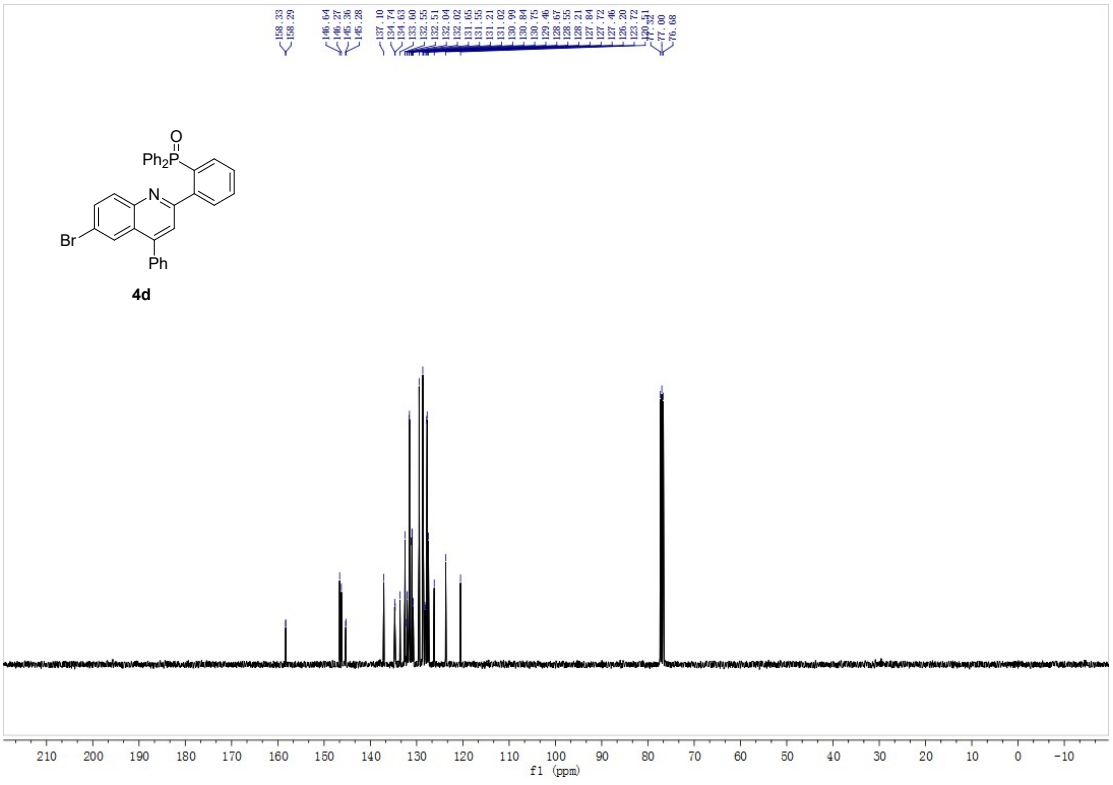

O
Ph2P
N
H3COOC
Ph
4c
f1 (ppm)

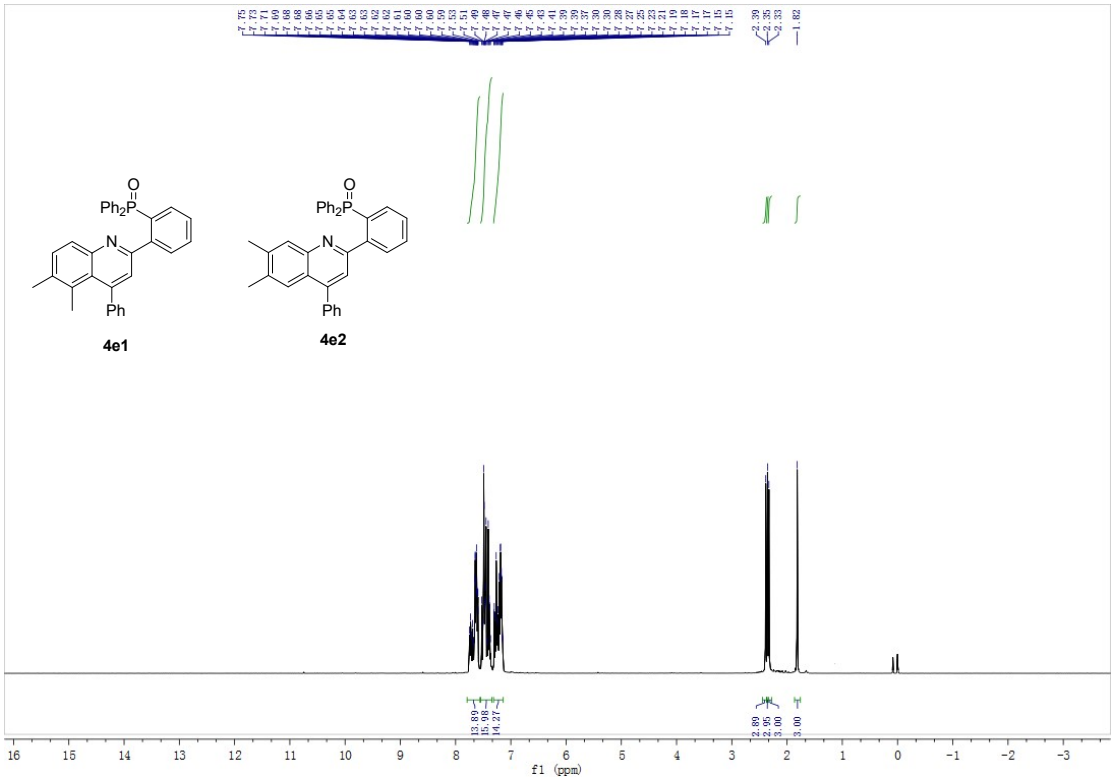

O
Ph2P
N
H3COOC
Ph
4c
f1 (ppm)

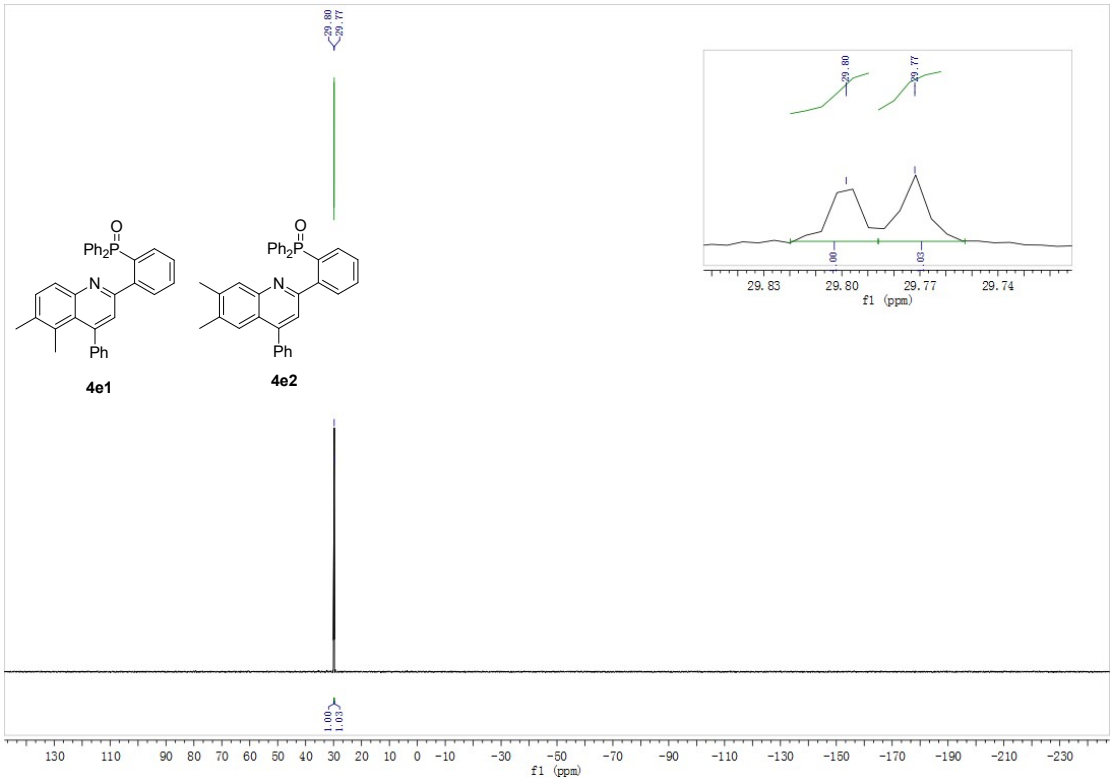

O
Ph2P
N
H3COOC
Ph
4c
f1 (ppm)

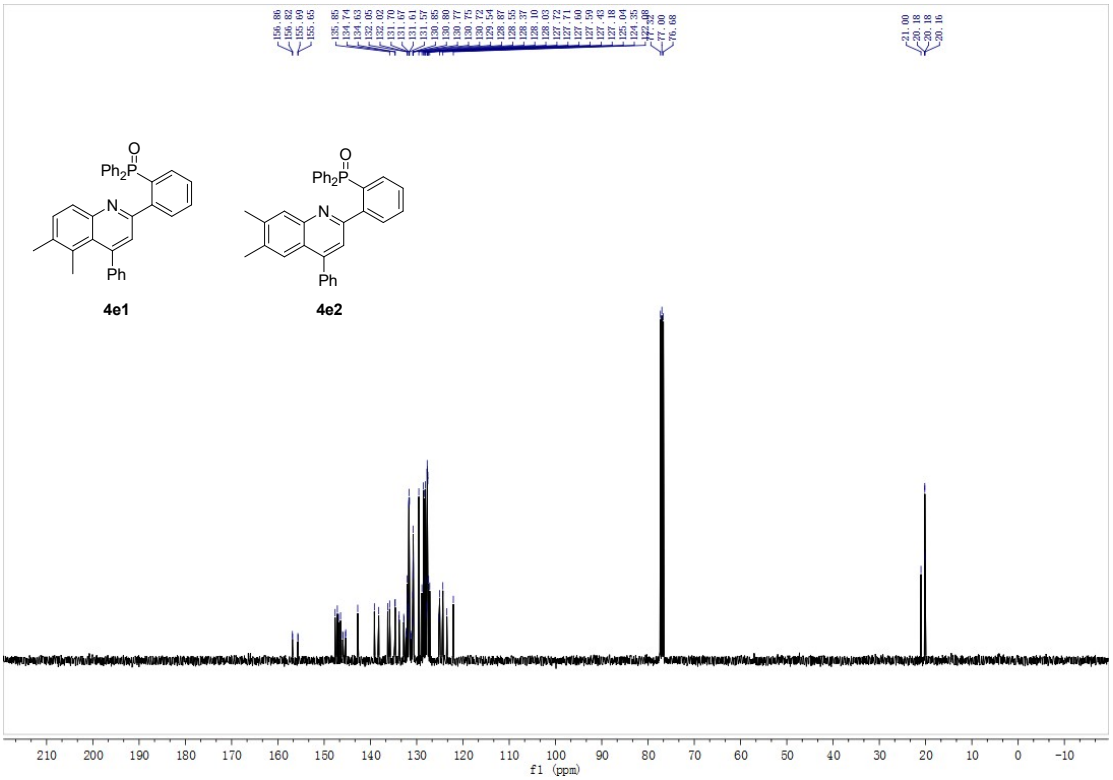

O
Ph2P
N
Br
Ph
4d
f1 (ppm)

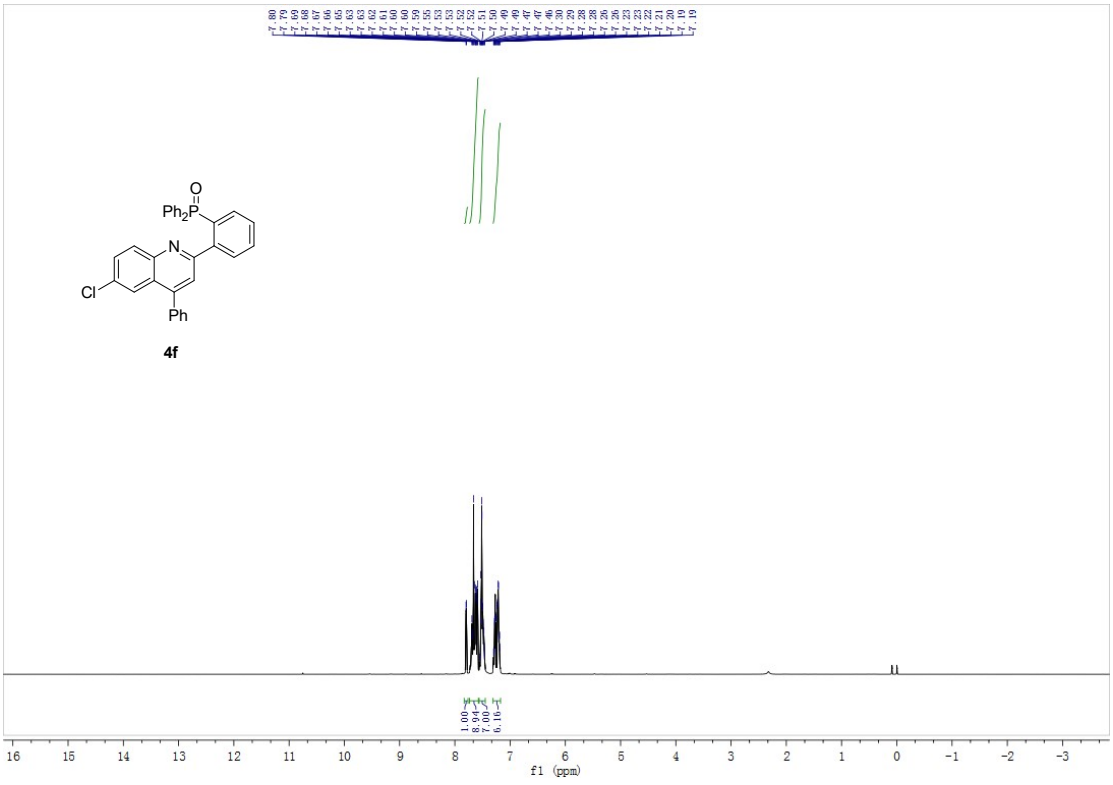

29.62
O
Ph2P
N
Br
Ph
4d
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

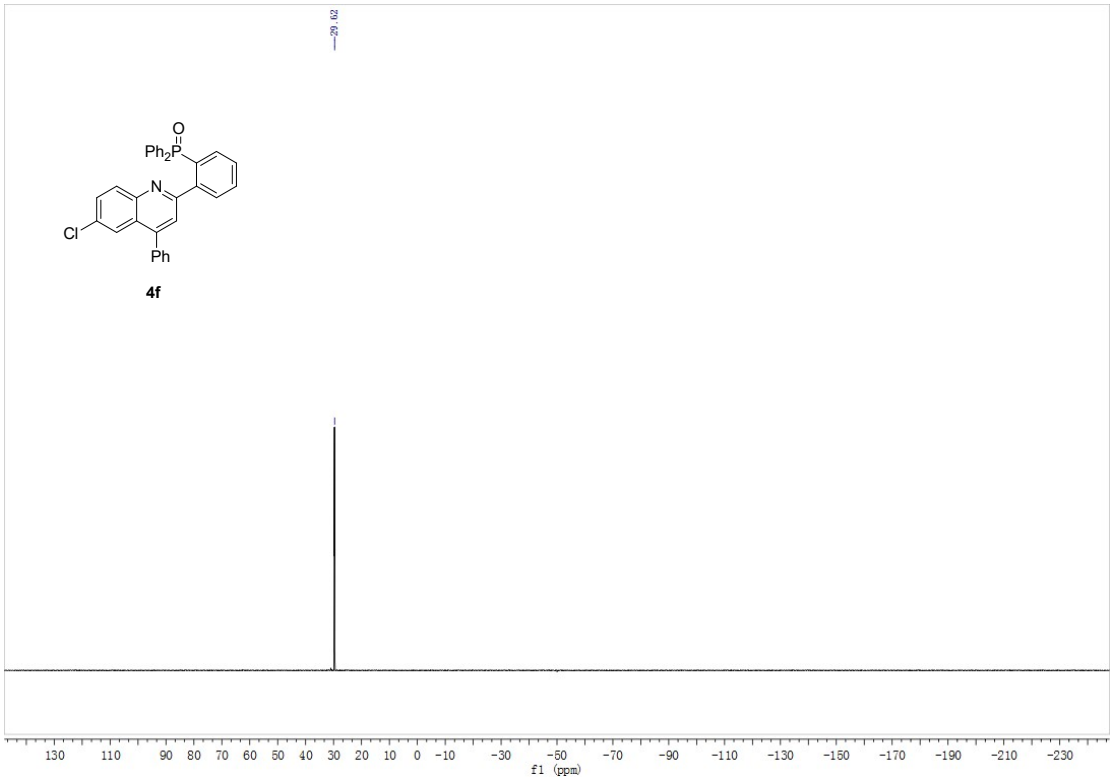

158.33
158.29
146.64
146.27
145.36
145.28
137.10
134.74
134.63
133.60
132.55
132.51
132.04
132.02
131.65
131.35
131.21
131.02
130.99
130.84
130.75
130.46
128.67
128.55
128.21
127.84
127.72
127.46
126.20
123.72
120.42
77.60
76.68
O
Ph2P
N
Br
Ph
4d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

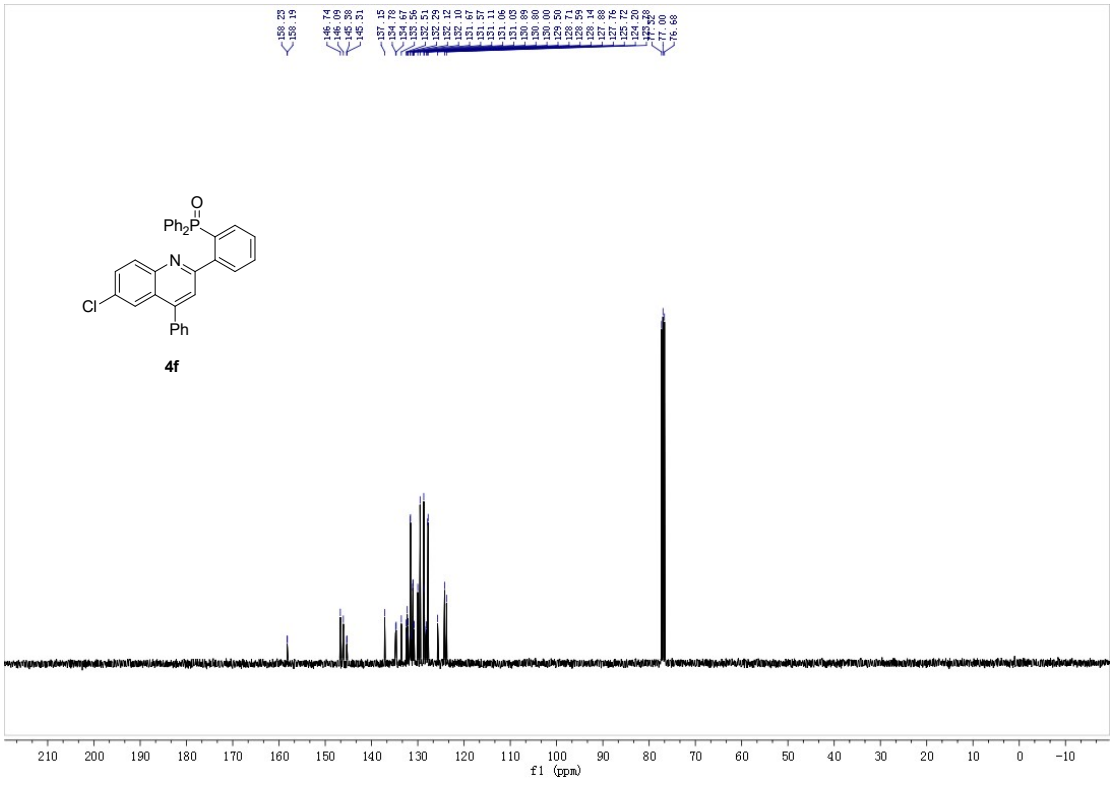

Ph2P
O
N
Ph
4e1
4e2
f1 (ppm)

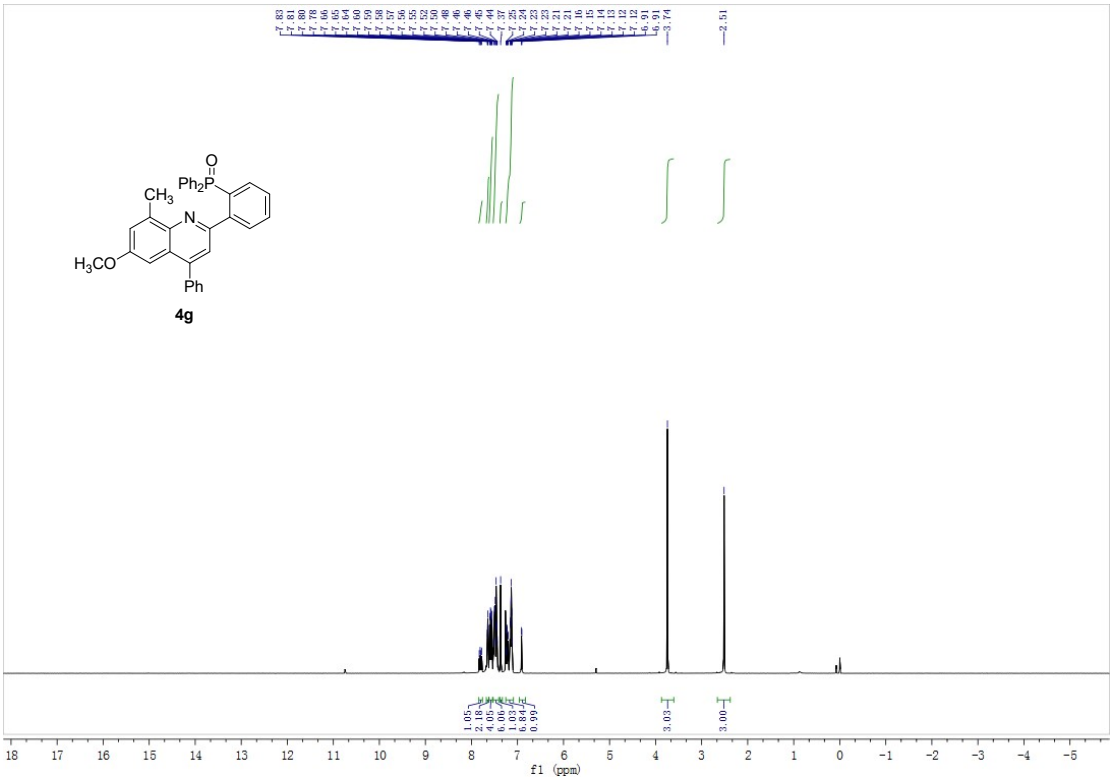

29.80
29.77
Ph2P
O
N
Ph
4e1
4e2
f1 (ppm)

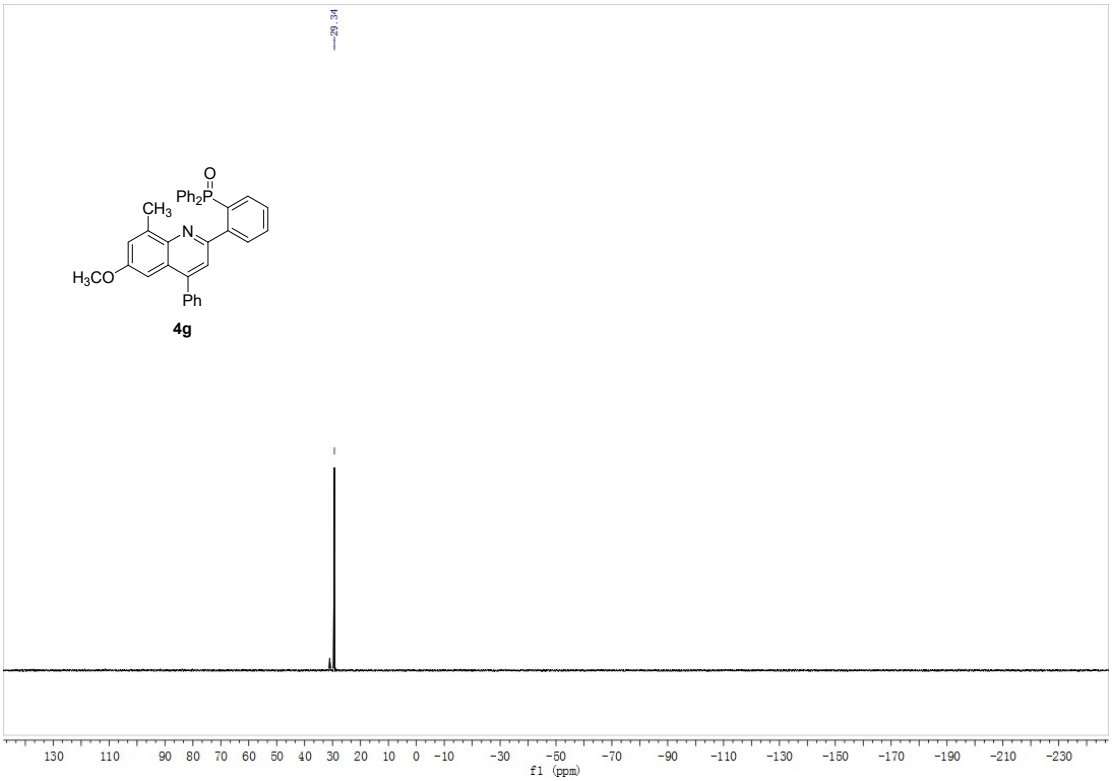

4e1
4e2
f1 (ppm)

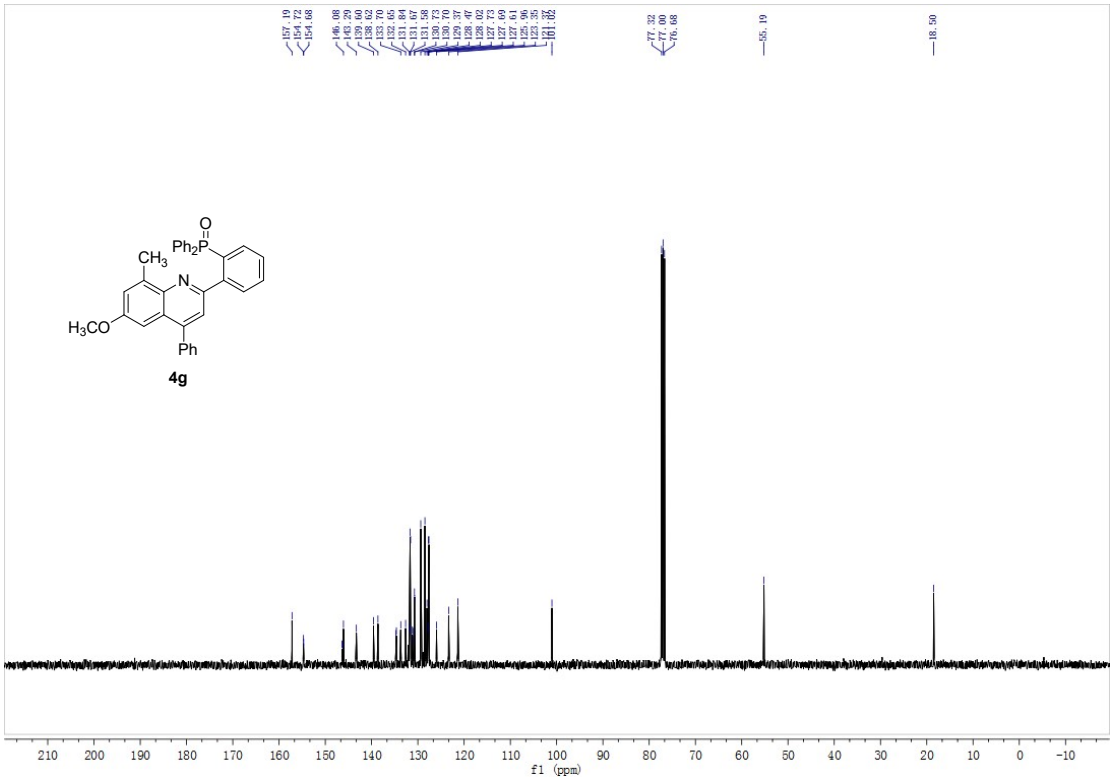

4f
f1 (ppm)

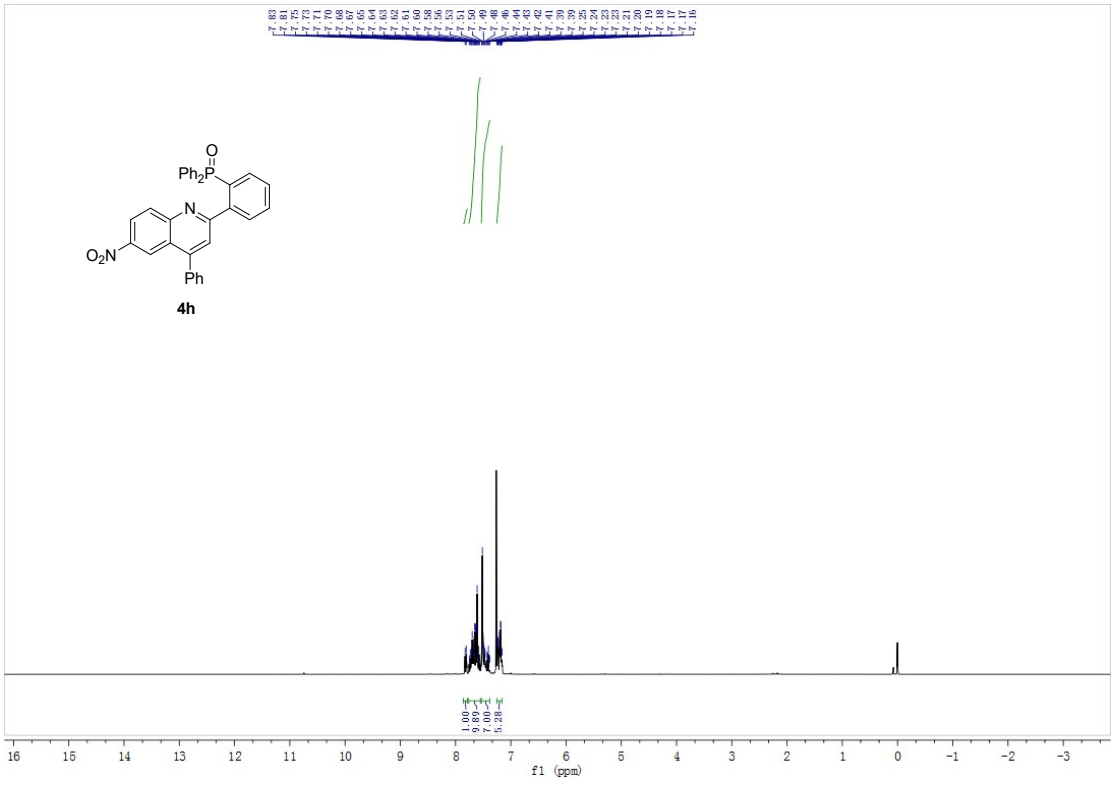

29.62
O
Ph2P
N
Cl
Ph
4f
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

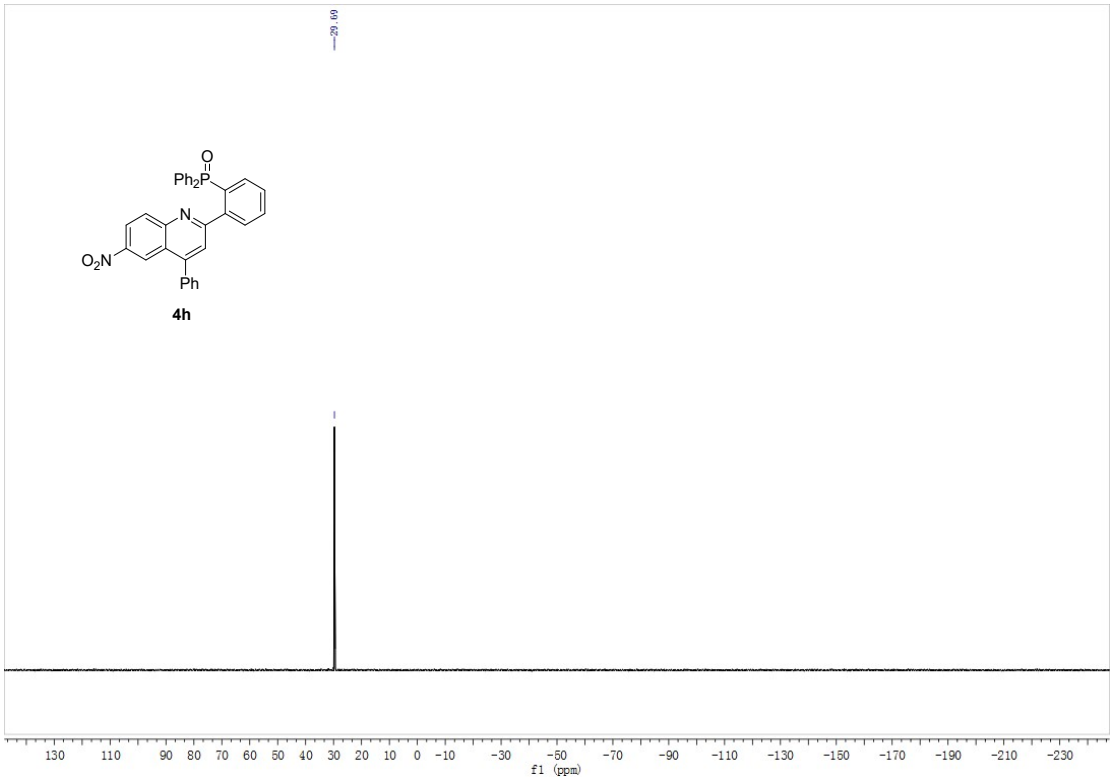

158.23
158.19
146.74
146.69
145.38
145.31
157.15
154.79
154.67
153.56
152.51
152.29
152.12
152.10
151.67
151.57
151.11
151.06
131.03
130.89
130.80
130.60
130.00
129.50
128.71
128.59
128.14
127.88
127.76
125.72
124.20
124.00
77.40
76.68
O
Ph2P
N
Cl
Ph
4f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

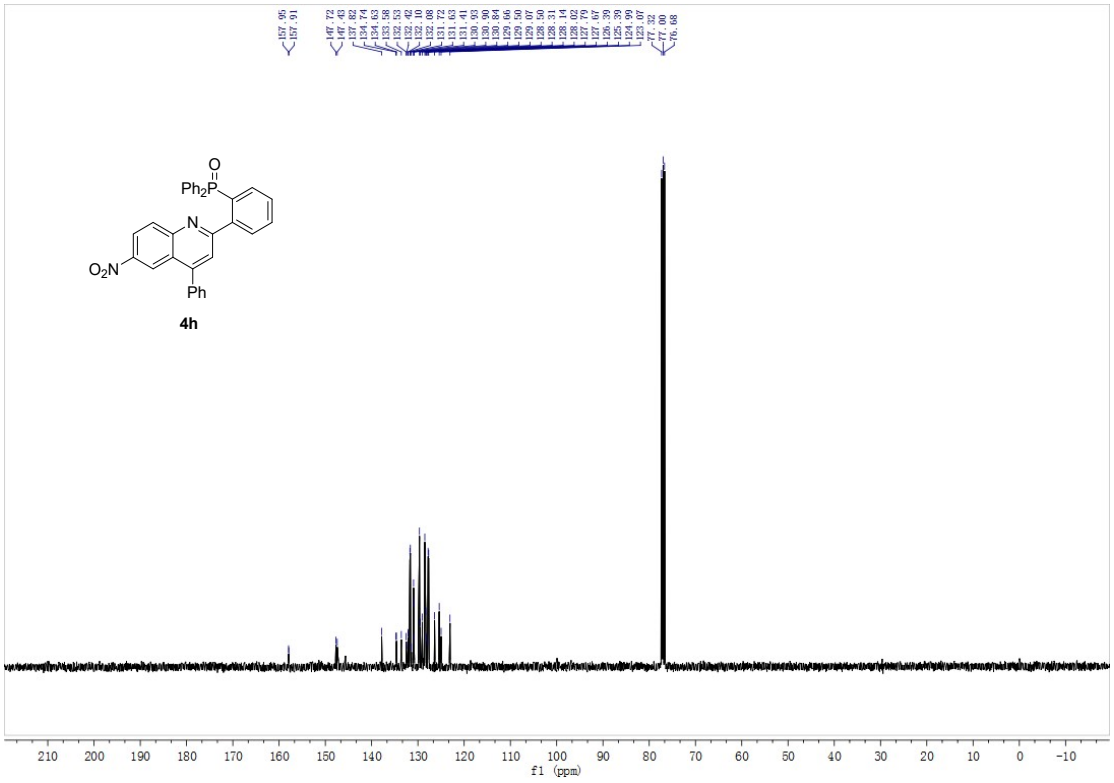

7.83
7.81
7.80
7.78
7.66
7.65
7.64
7.60
7.59
7.58
7.57
7.56
7.55
7.52
7.50
7.48
7.46
7.46
7.45
7.44
7.37
7.25
7.24
7.23
7.22
7.21
7.21
7.16
7.15
7.14
7.13
7.12
7.12
6.91
6.91
3.74
2.51
O
Ph2P
CH3
N
H3CO
Ph
4g
1.05
2.18
4.10
6.06
1.03
6.84
0.99
3.03
3.00
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
f1 (ppm)

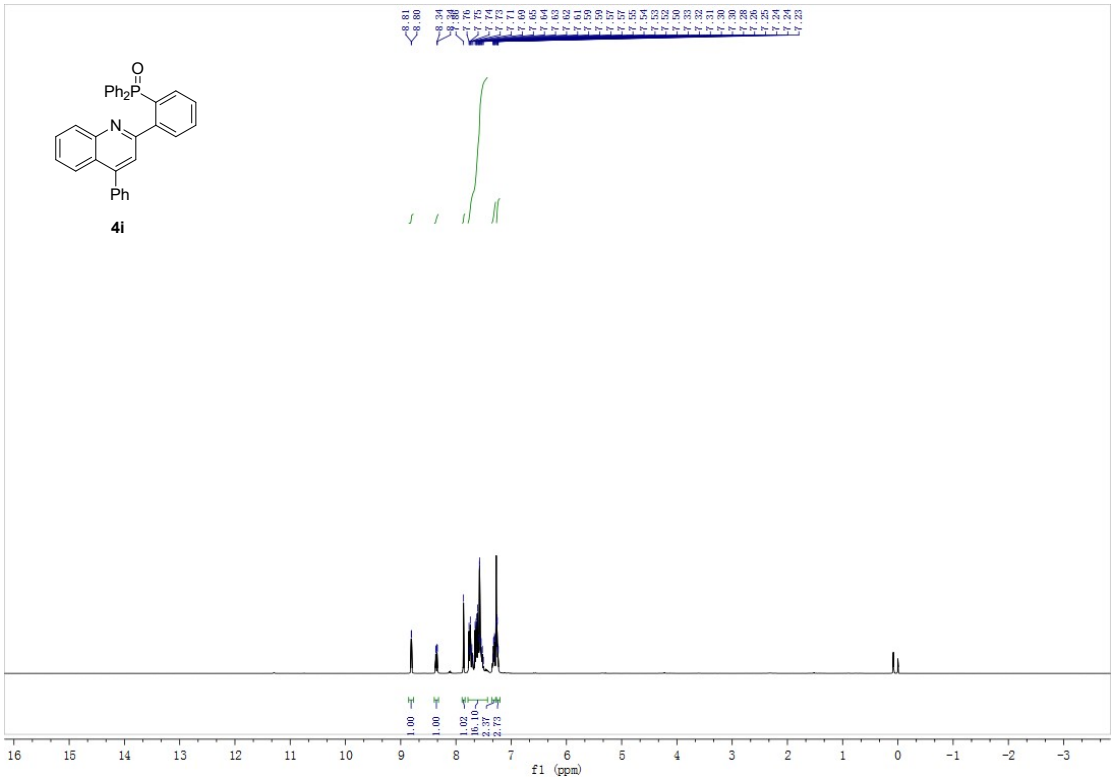

29.34
O
Ph2P
CH3
N
H3CO
Ph
4g
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

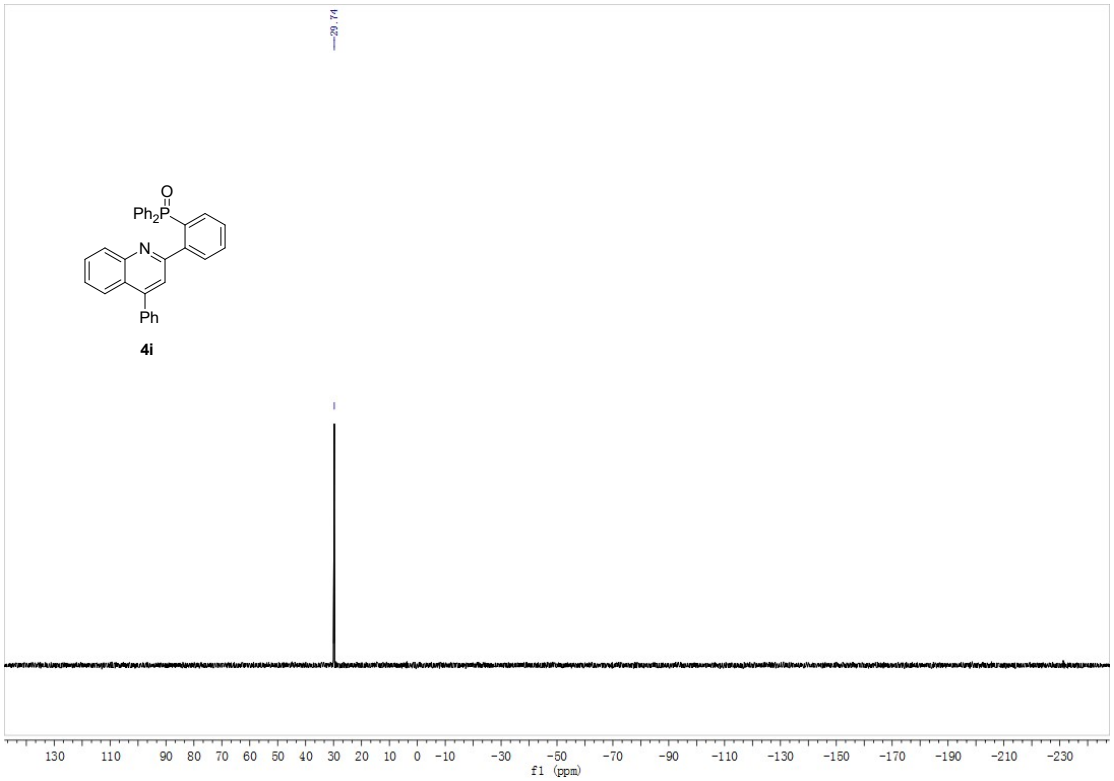

157.19
154.72
154.68
146.08
143.29
139.60
138.62
133.70
132.65
131.84
131.67
131.58
130.73
130.70
129.37
128.47
128.02
127.73
127.69
127.61
125.96
125.35
125.32
77.32
77.00
76.68
55.19
18.50
O
Ph2P
CH3
N
H3CO
Ph
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

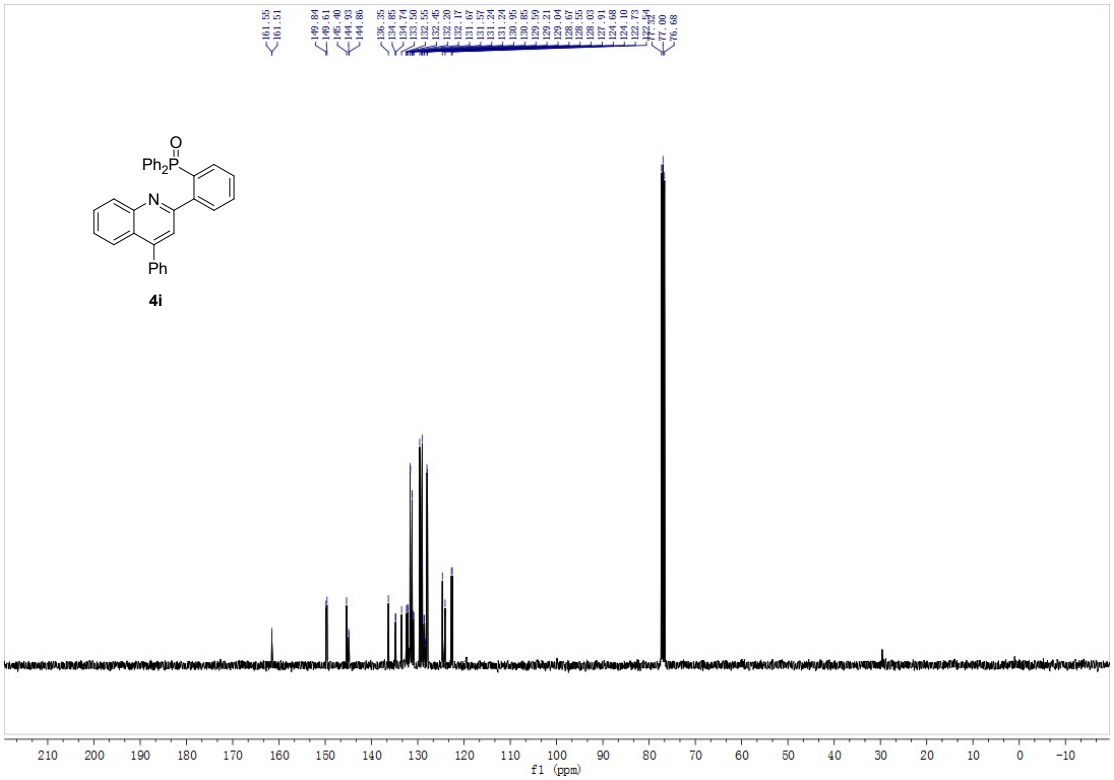

7.83
7.81
7.75
7.73
7.71
7.70
7.68
7.67
7.65
7.64
7.63
7.62
7.61
7.60
7.58
7.56
7.53
7.51
7.50
7.49
7.48
7.46
7.44
7.43
7.42
7.41
7.40
7.39
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.18
7.17
7.17
7.16
O
Ph2P
N
O2N
Ph
4h
1.00
0.93
7.10
5.28
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

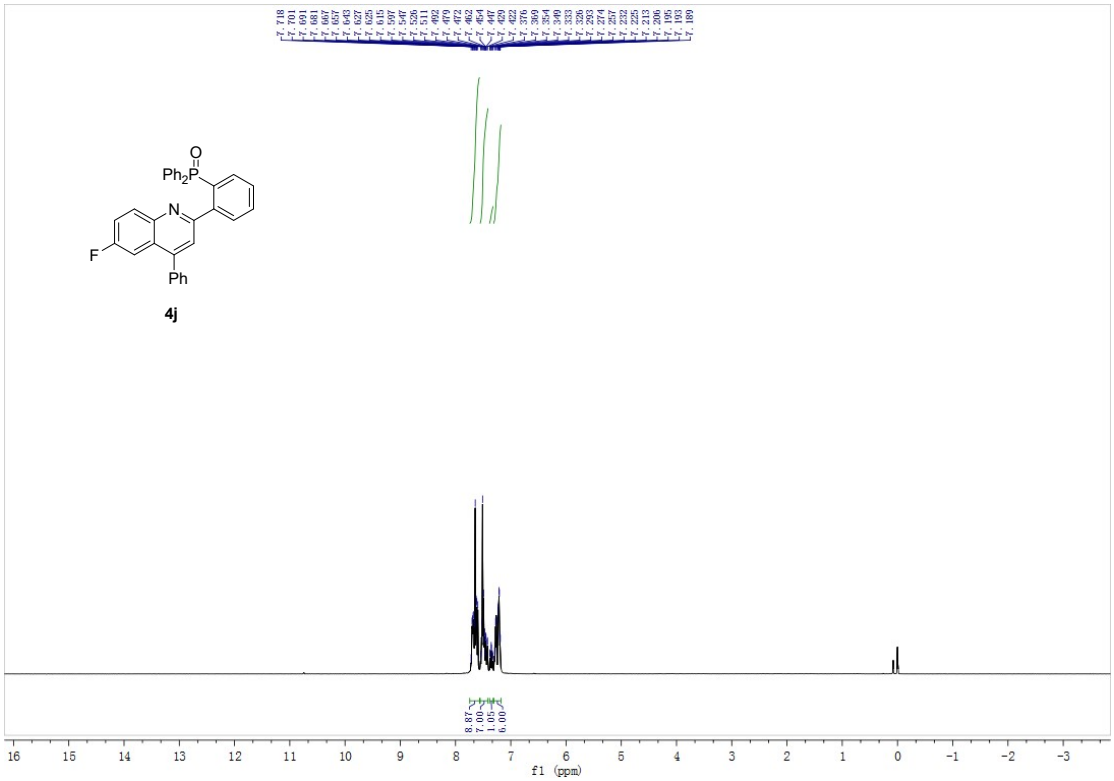

29.69
O
Ph2P
N
O2N
Ph
4h
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

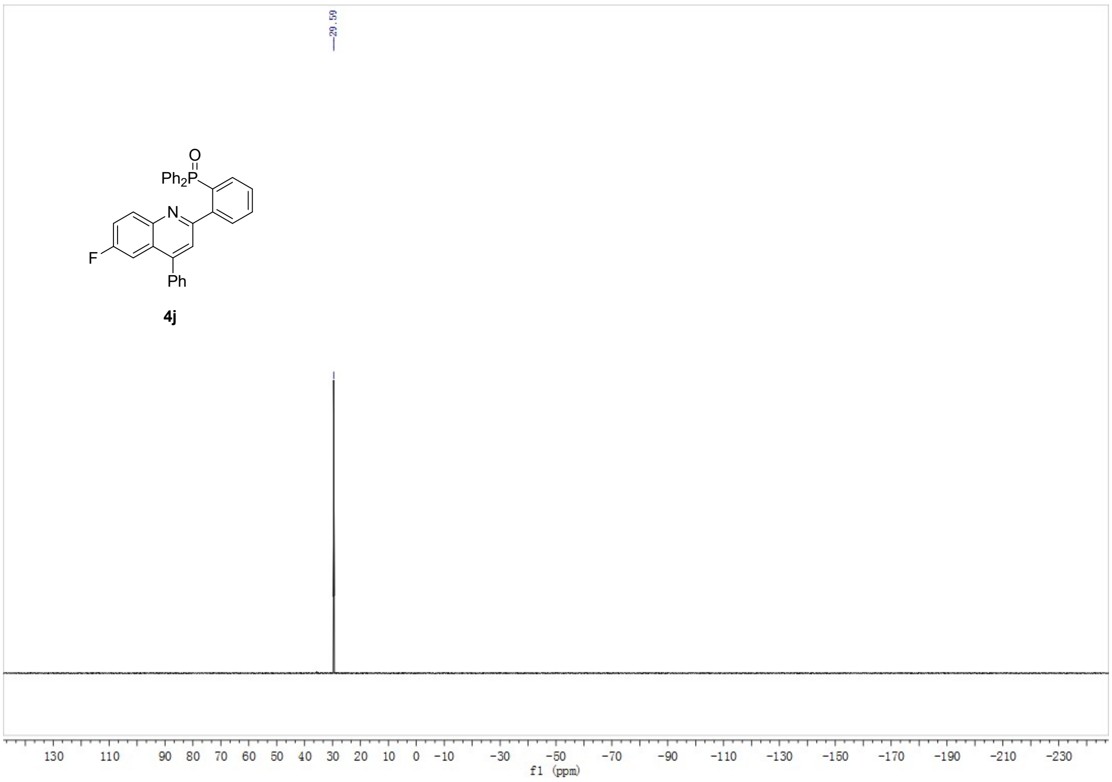

157.96
157.91
147.72
147.43
137.82
134.74
134.63
133.58
132.53
132.46
132.10
132.08
131.72
131.63
131.41
130.93
130.90
130.84
129.66
129.59
129.07
128.50
128.31
128.14
128.02
127.79
127.67
126.39
125.79
124.99
123.07
77.32
77.00
76.68
O
Ph2P
N
O2N
Ph
4h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

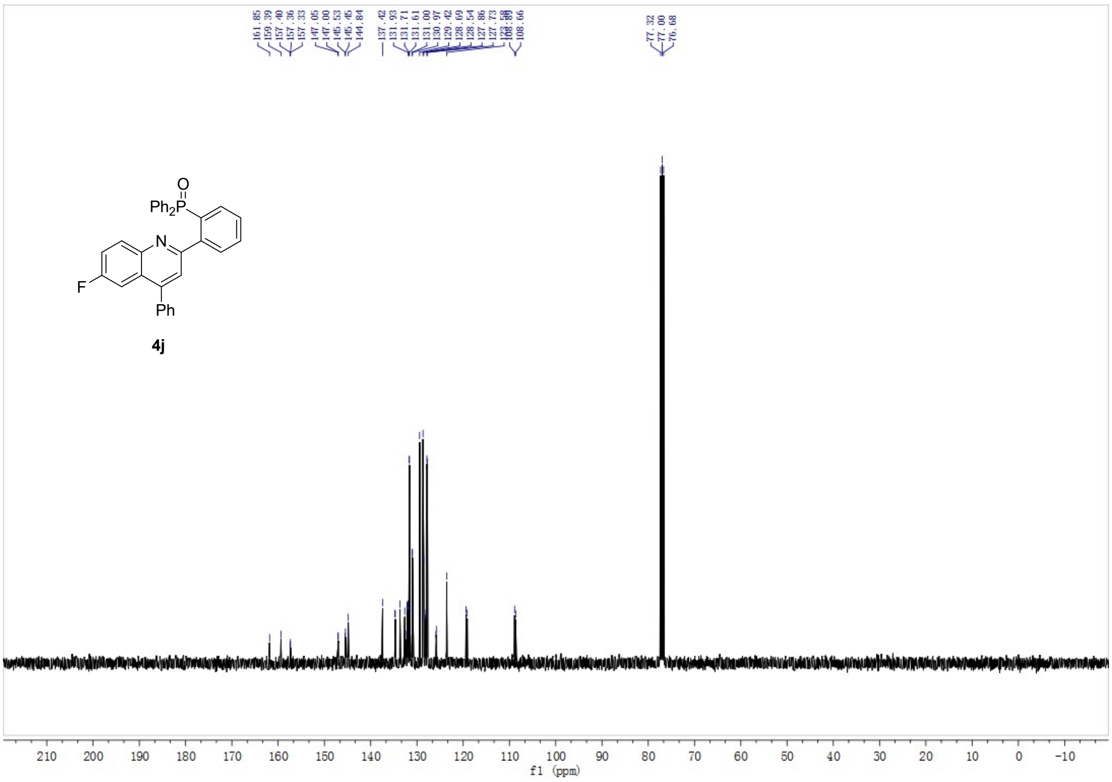

Ph2P
O
N
Ph
4i
f1 (ppm)

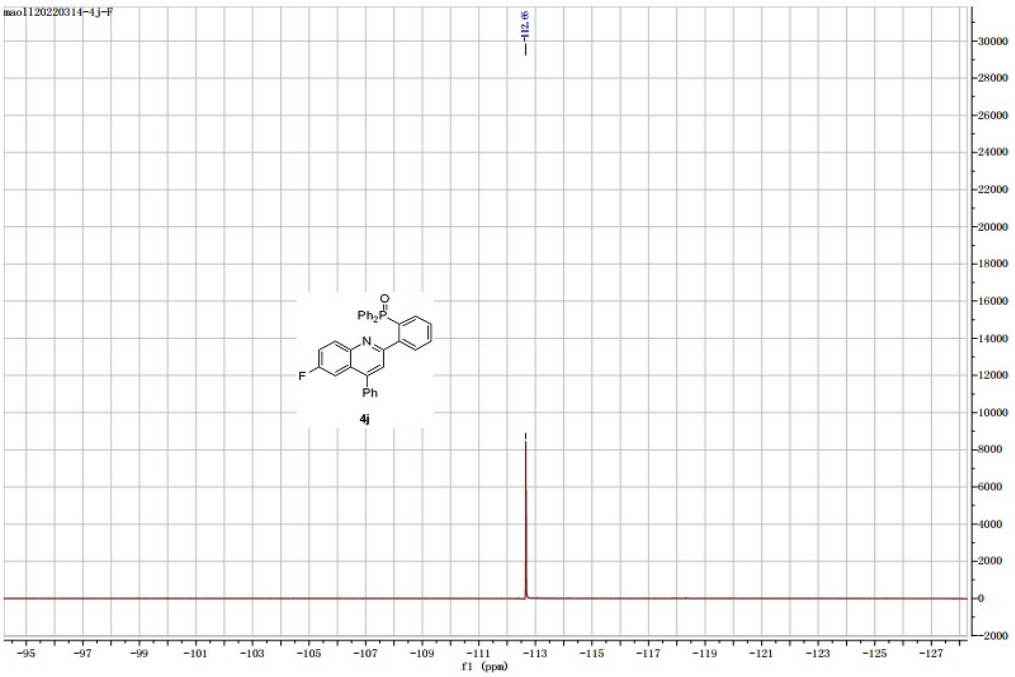

29.74
Ph2P
O
N
Ph
4i
f1 (ppm)


O
Ph2P
N
Ph
4i
f1 (ppm)

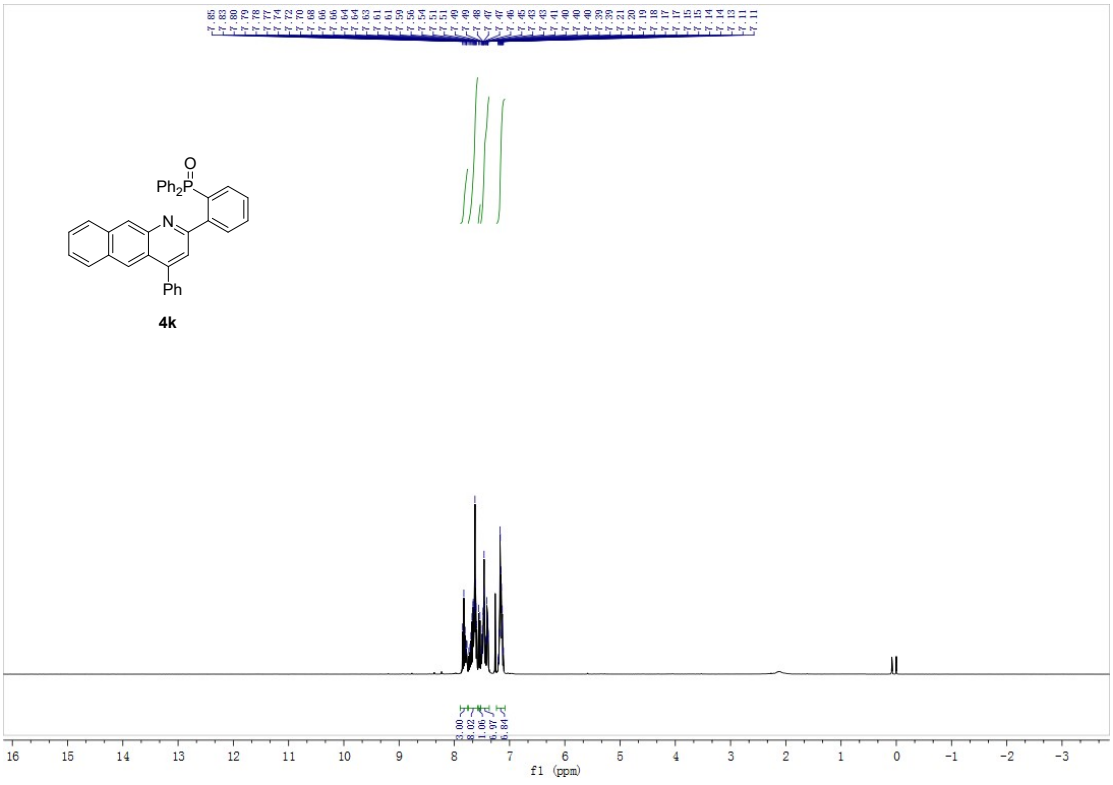

O
Ph2P
N
F
Ph
4j
f1 (ppm)


29.59
O
Ph2P
N
F
Ph
4j
130 110 90 80 70 60 50 40 30 20 10 0 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

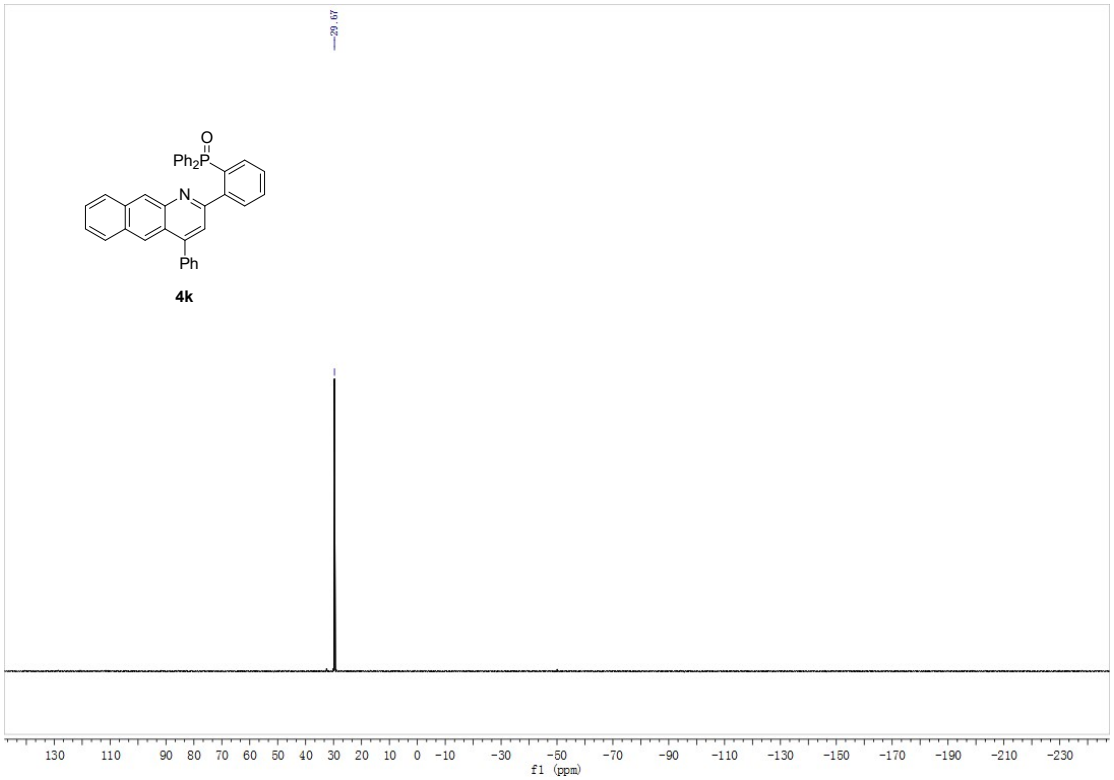

161.85
159.39
157.40
157.36
157.33
147.05
147.00
145.53
145.45
144.84
137.42
131.93
131.71
131.61
131.00
130.97
129.42
128.69
128.54
127.86
127.73
108.66
77.32
77.00
76.68
O
Ph2P
N
F
Ph
4j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



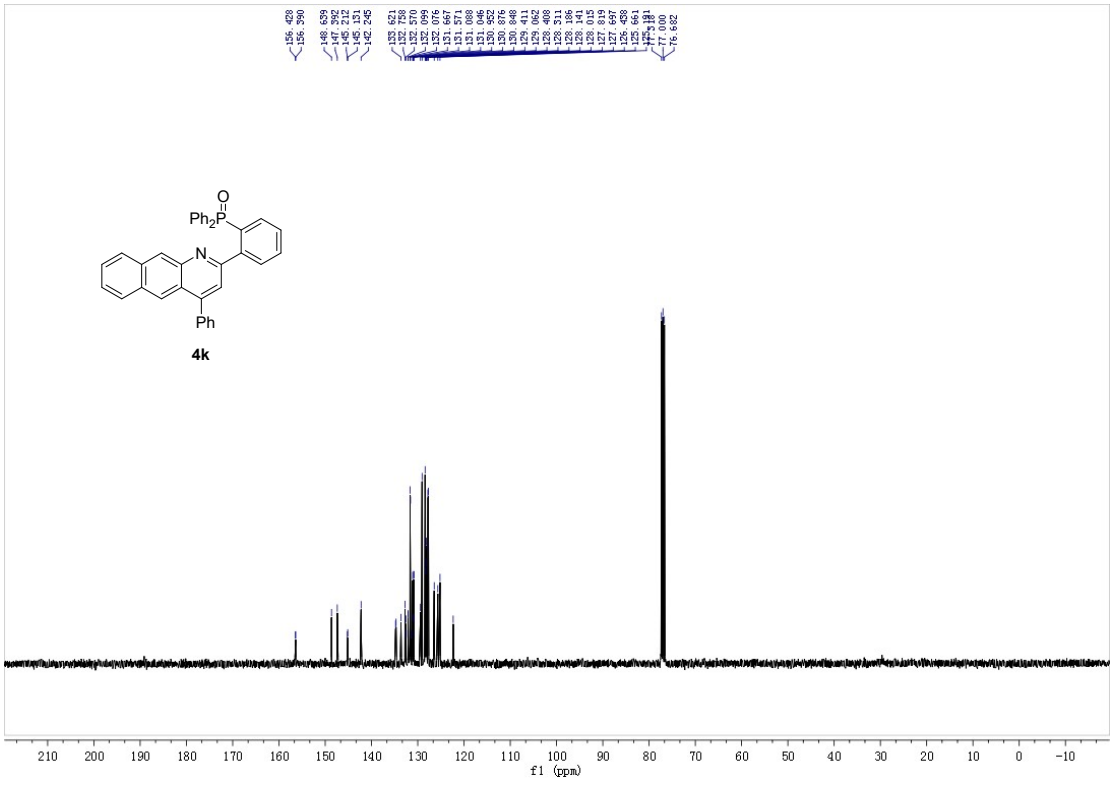
4j



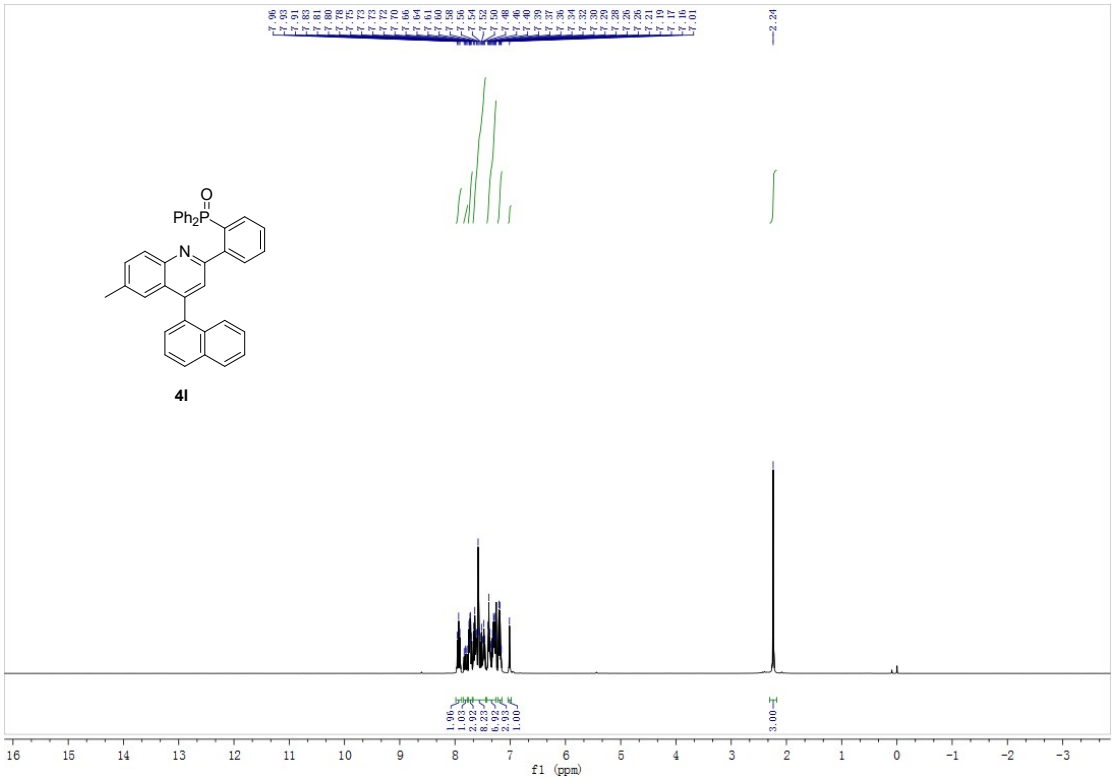
4k

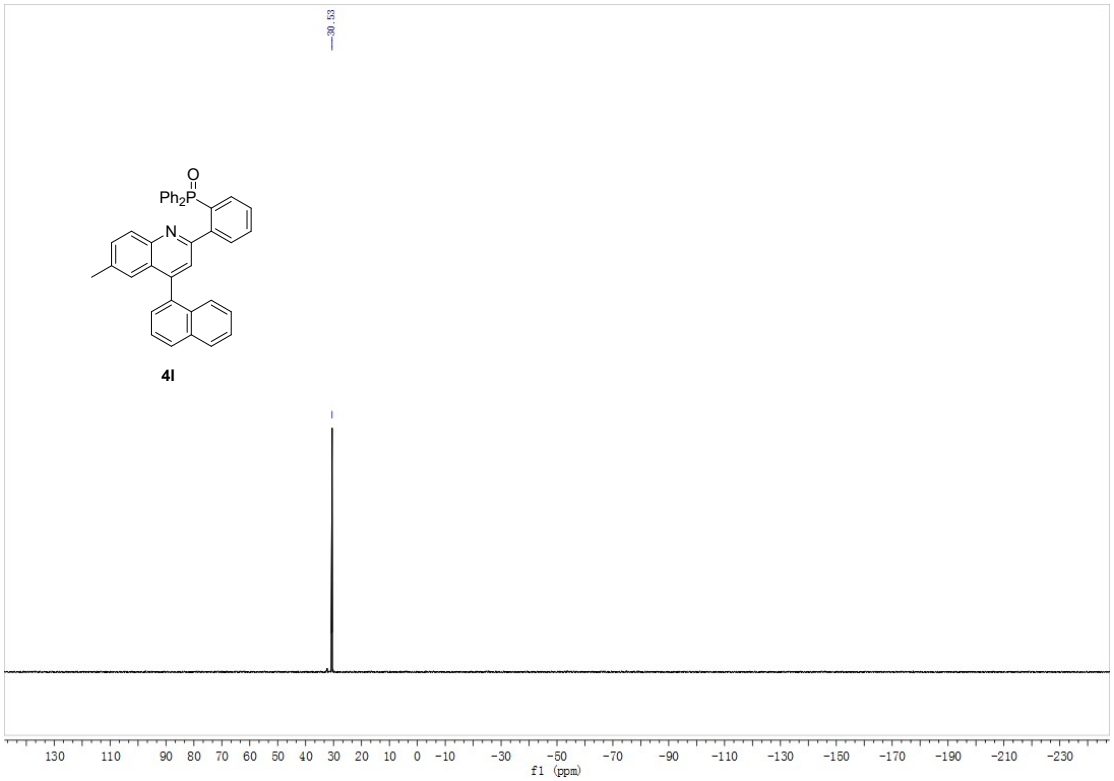

29.67
O
Ph2P
N
Ph
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

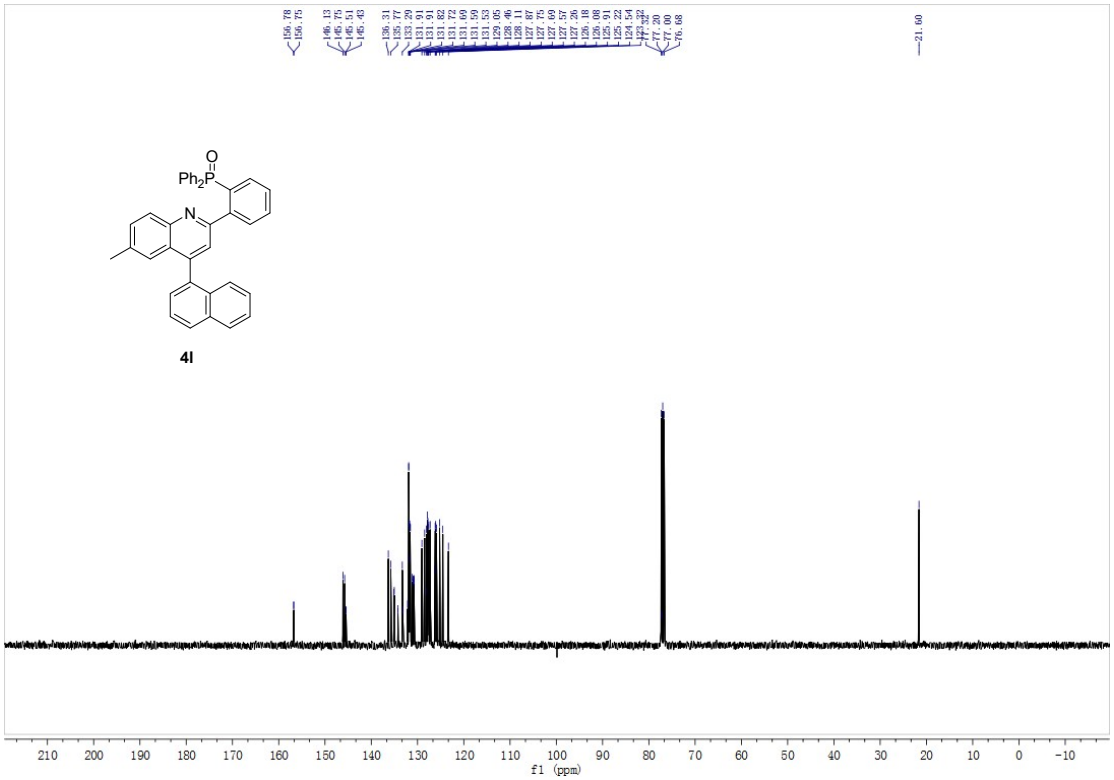
4k

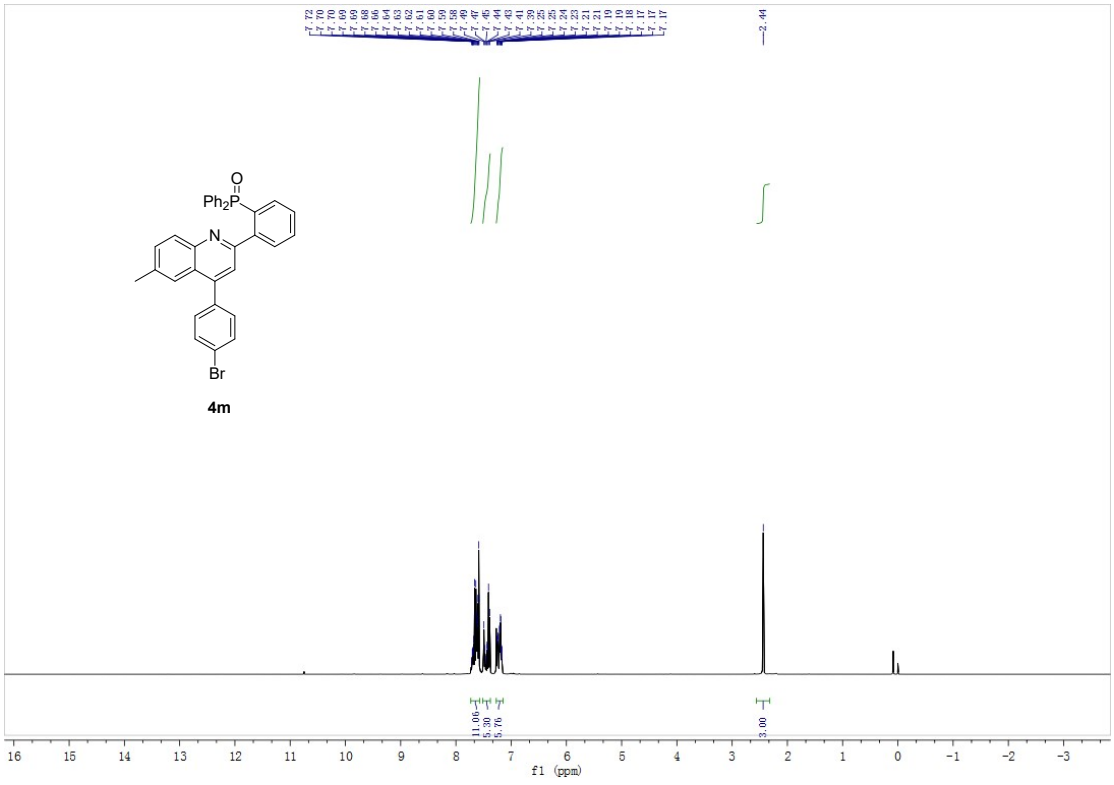

156.428
156.390
148.659
147.392
145.212
145.131
142.245
133.621
132.758
132.570
132.099
131.975
131.667
131.571
131.088
131.046
130.952
130.876
130.848
129.411
129.082
129.057
128.498
128.311
128.186
128.141
128.015
127.819
127.697
126.438
125.961
77.000
76.682
O
Ph2P
N
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

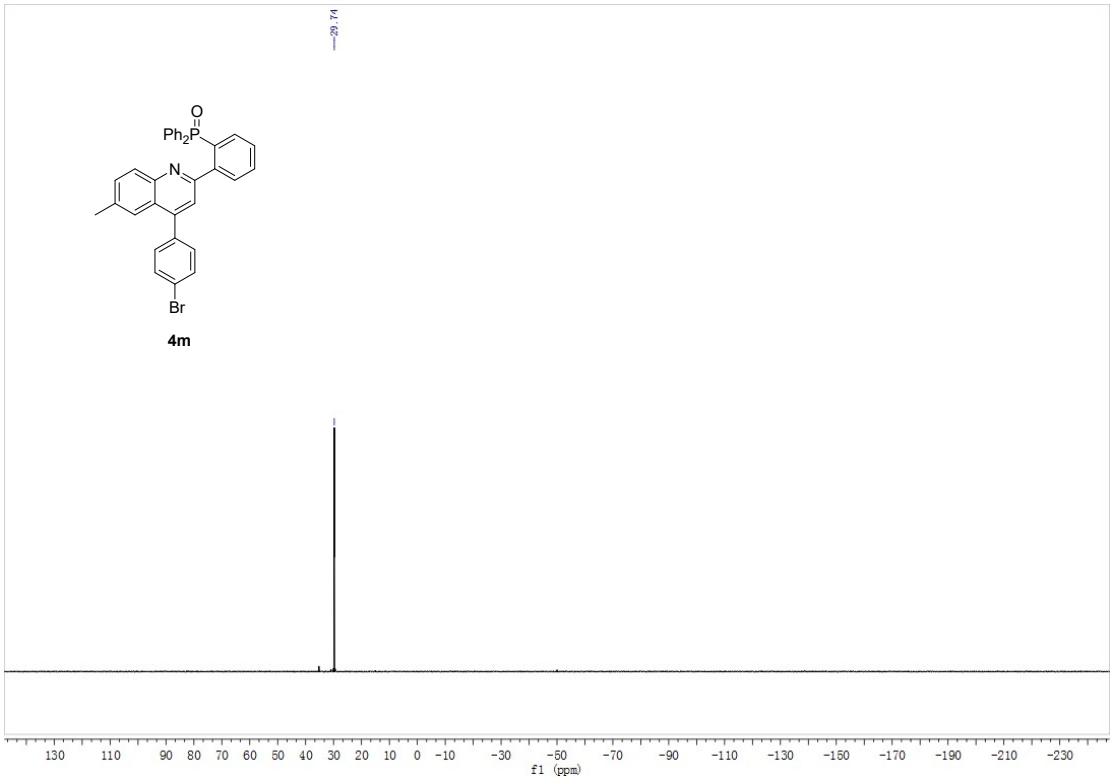
4k

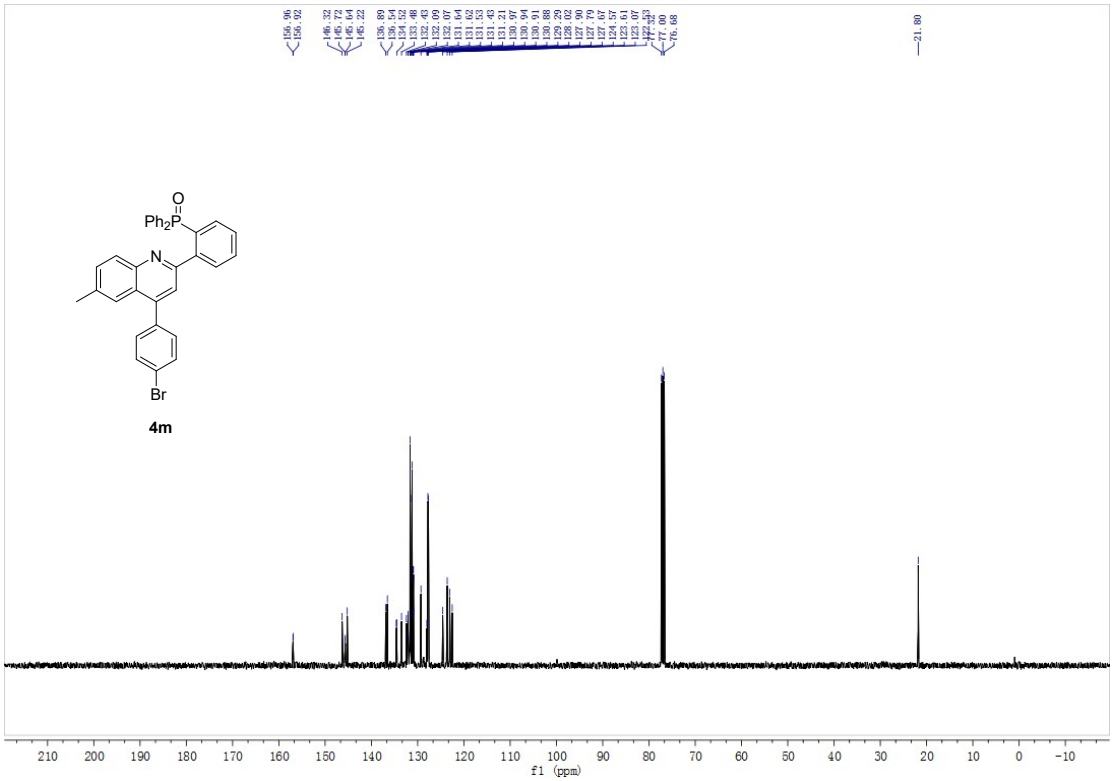

Ph2P
O
N
4l
f1 (ppm)

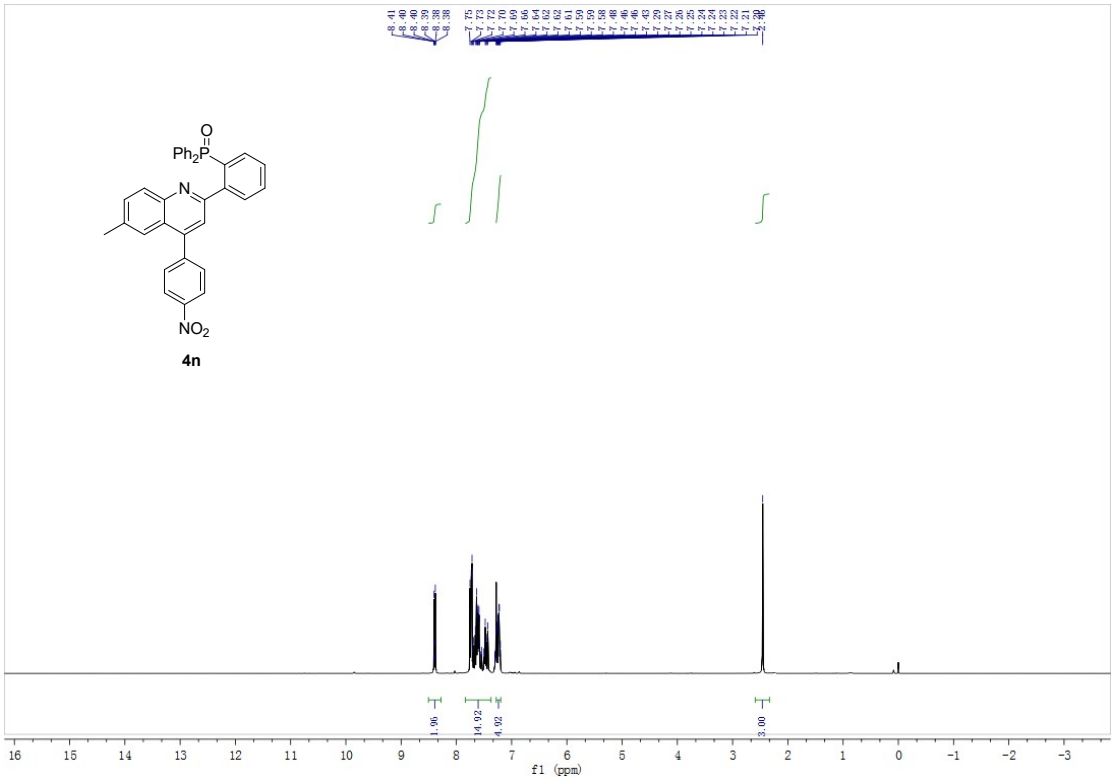

Ph2P
O
N
4l
f1 (ppm)

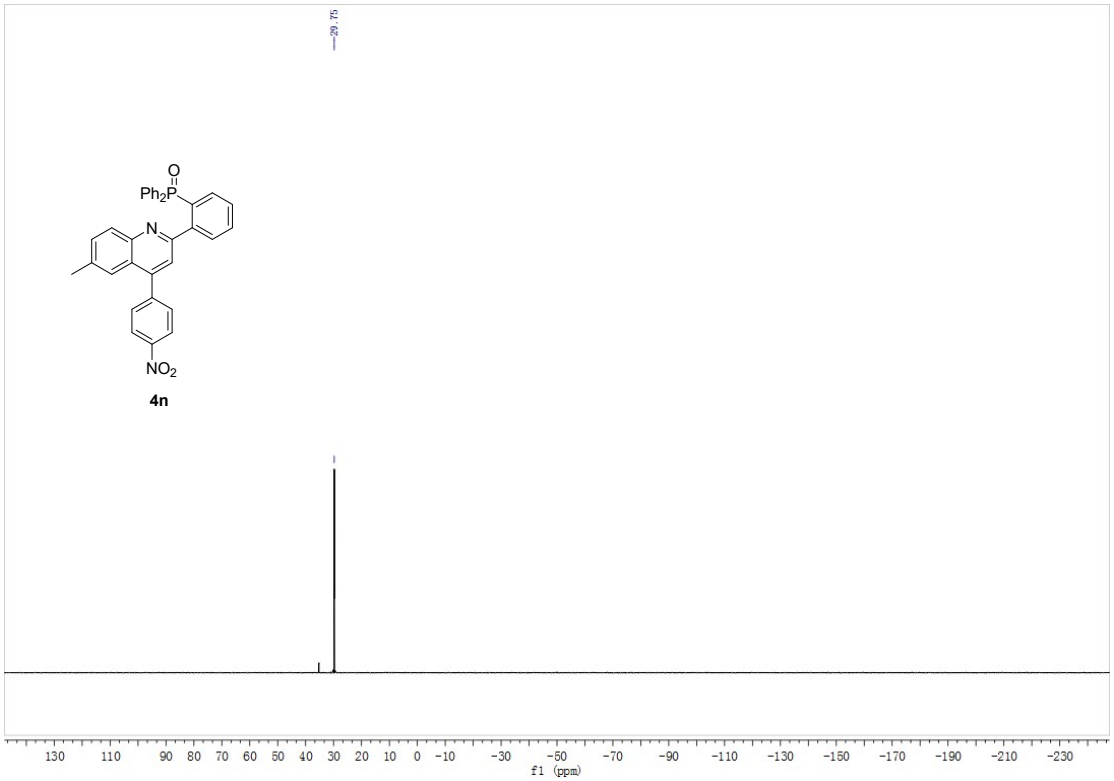

O
Ph2P
N
4l
f1 (ppm)

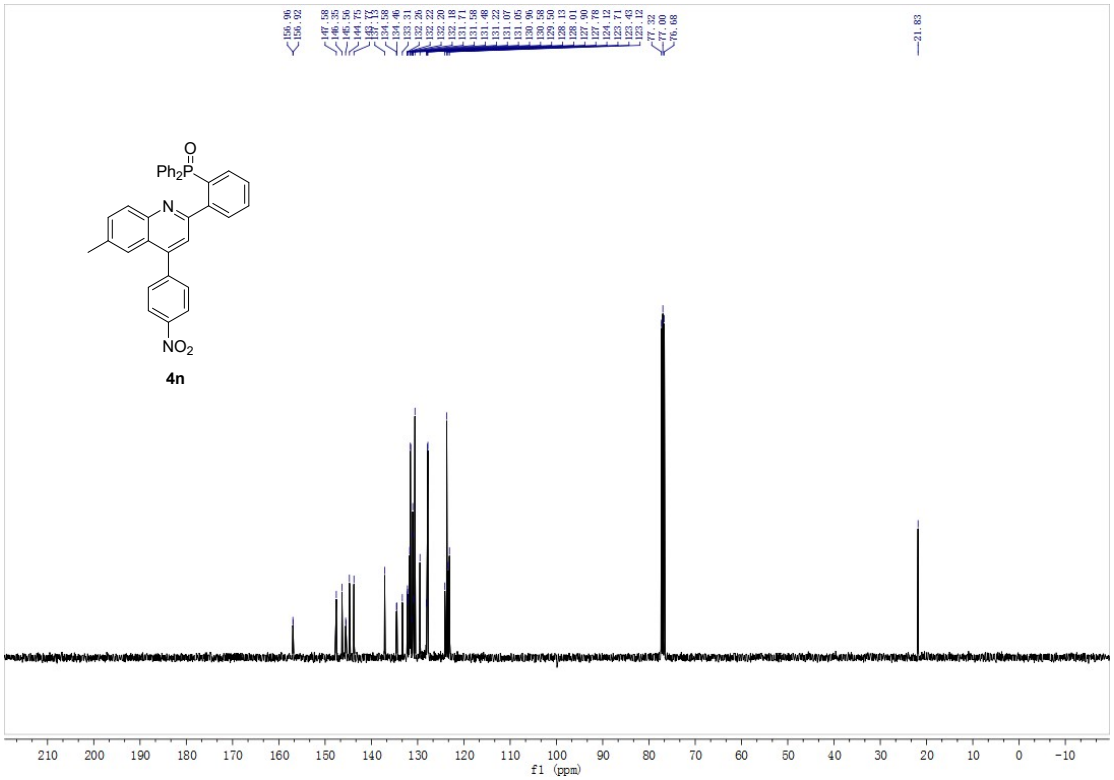

O
Ph2P
N
Br
4m
f1 (ppm)

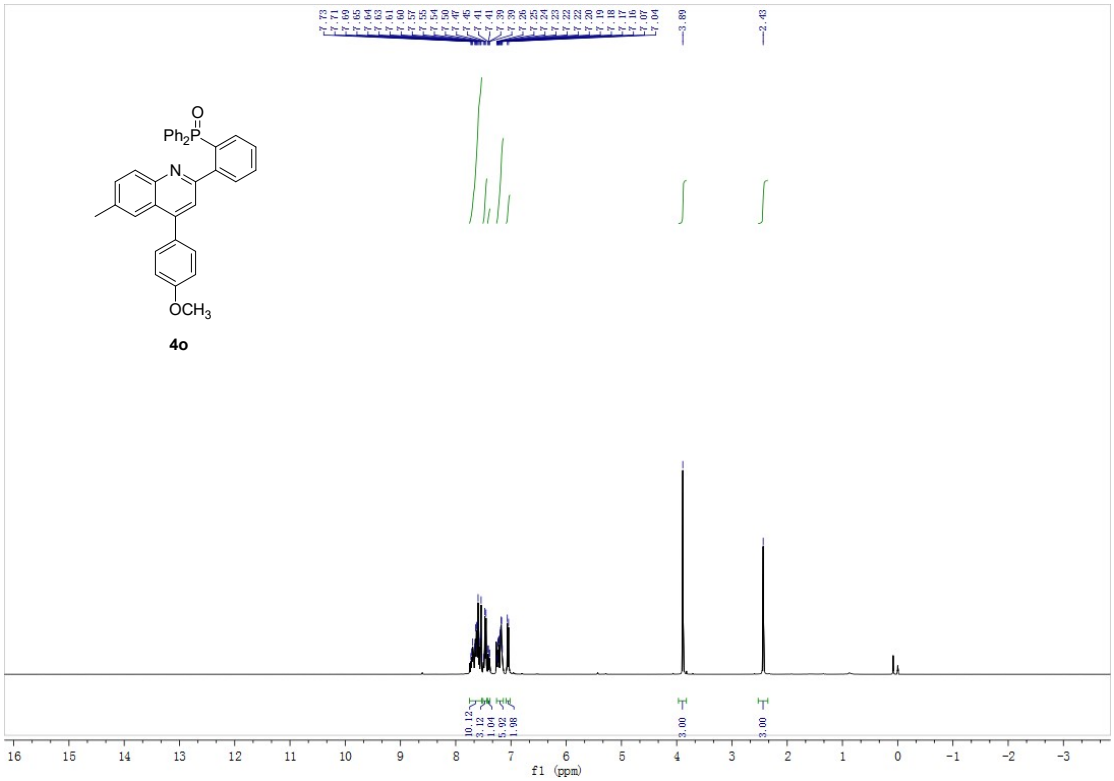

29.74
O
Ph2P
N
Br
4m
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

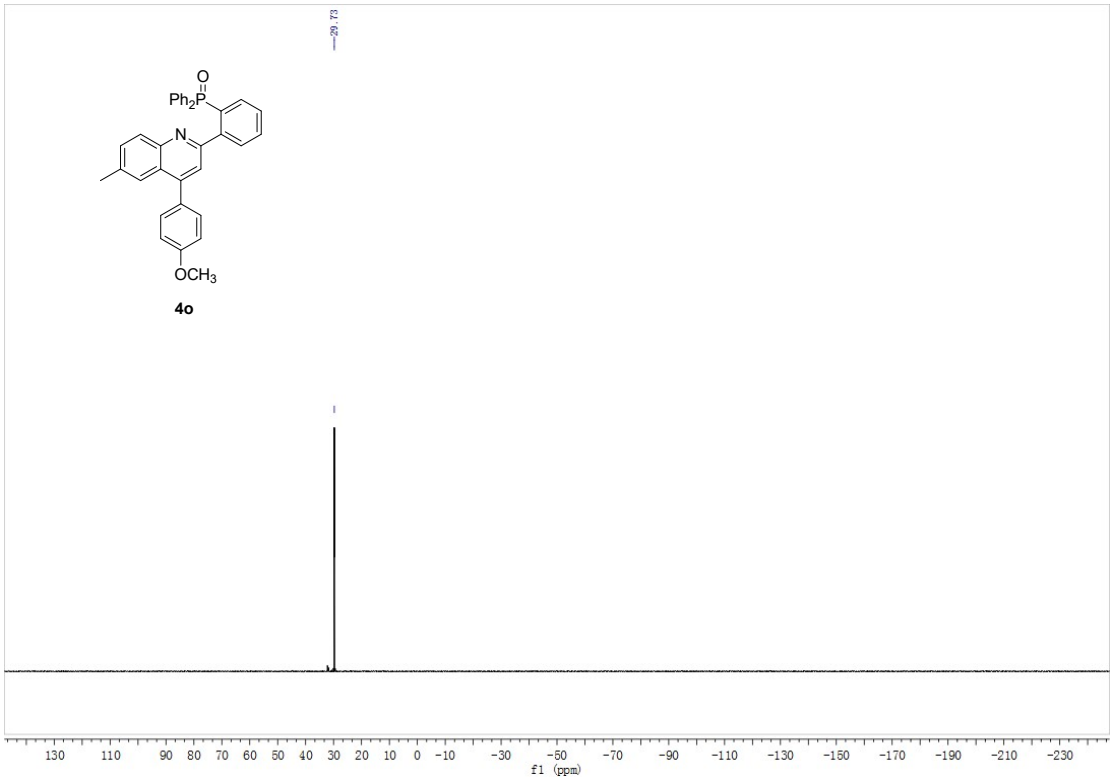

156.96
156.92
146.32
145.72
145.14
145.22
136.89
136.54
134.52
133.48
132.45
132.09
132.07
131.64
131.62
131.53
131.45
131.21
130.97
130.94
130.91
130.88
129.29
128.02
127.90
127.79
127.67
124.57
123.61
123.07
122.53
77.42
77.00
76.68
21.80
O
Ph2P
N
Br
4m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Ph2P
N
NO2
4n
1.00
14.92
4.92
3.00
f1 (ppm)

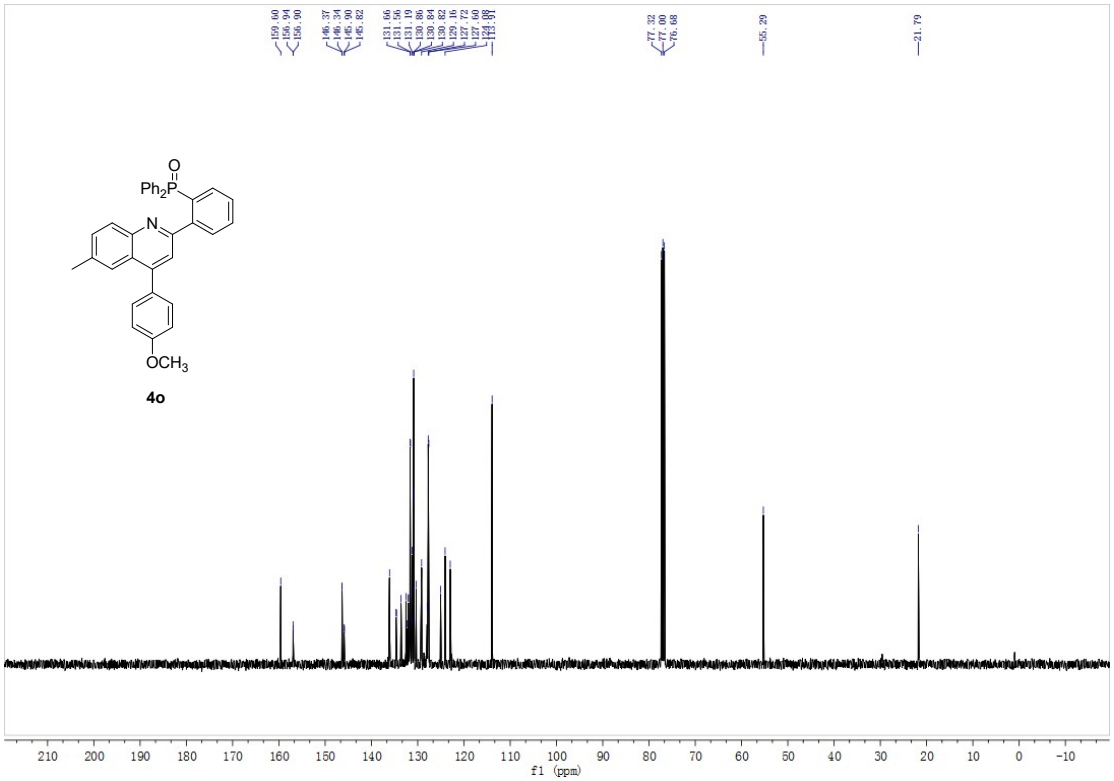

29.75
O
Ph2P
N
NO2
4n
f1 (ppm)


O
Ph2P
N
NO2
4n
f1 (ppm)

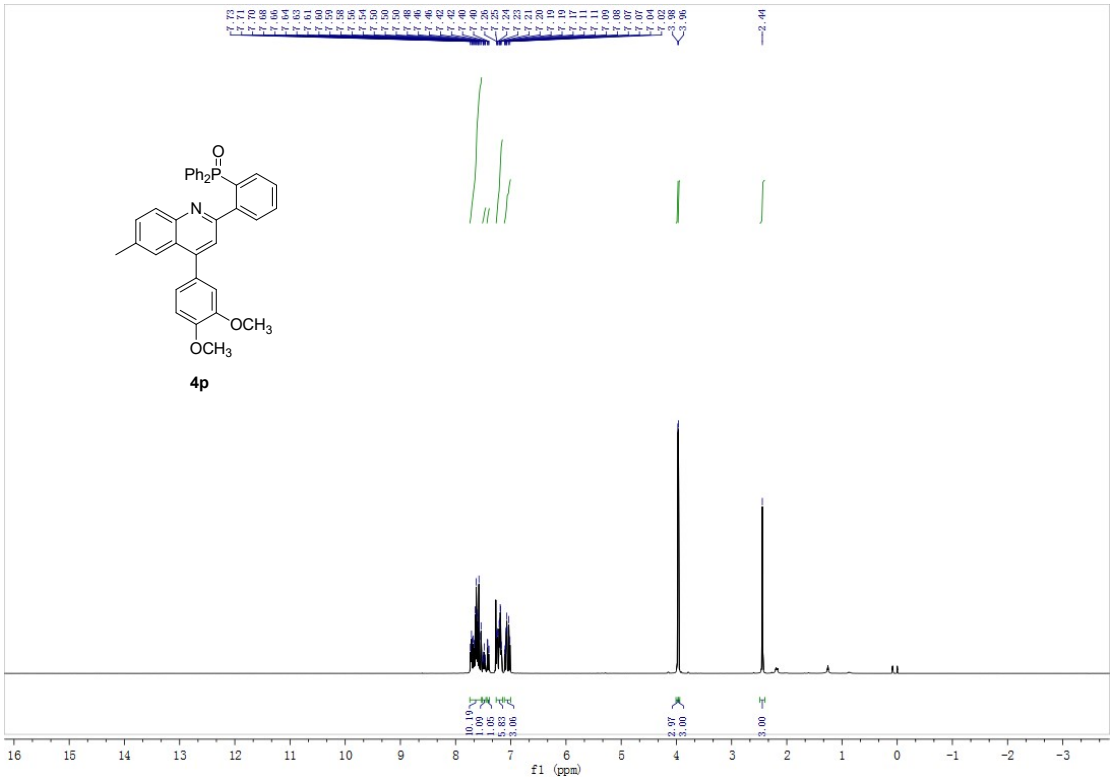

O
Ph2P
N
OCH3
4o
f1 (ppm)

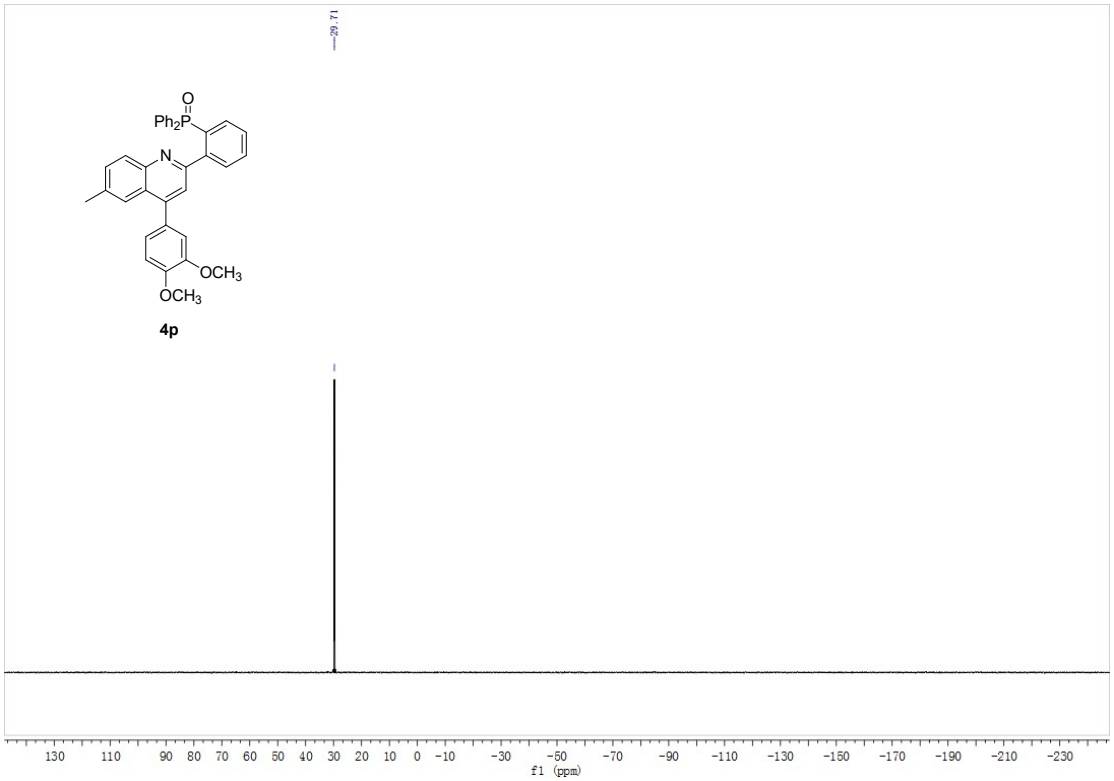

29.73
O
Ph2P
N
OCH3
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

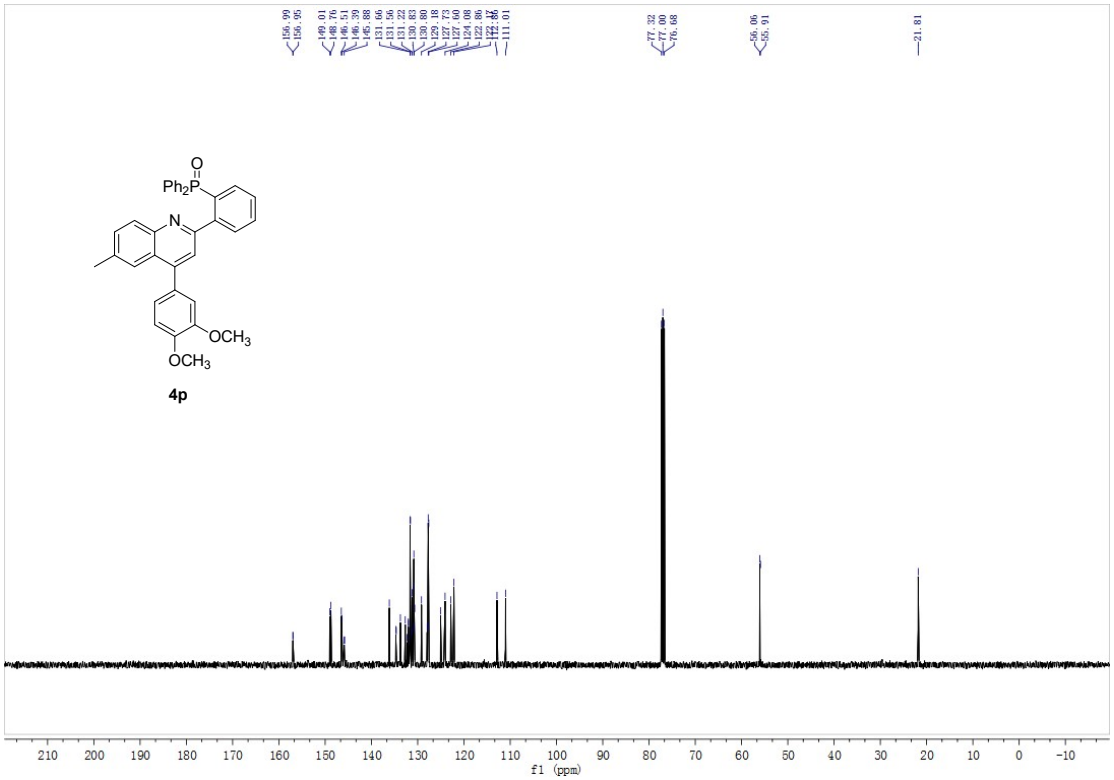
4o

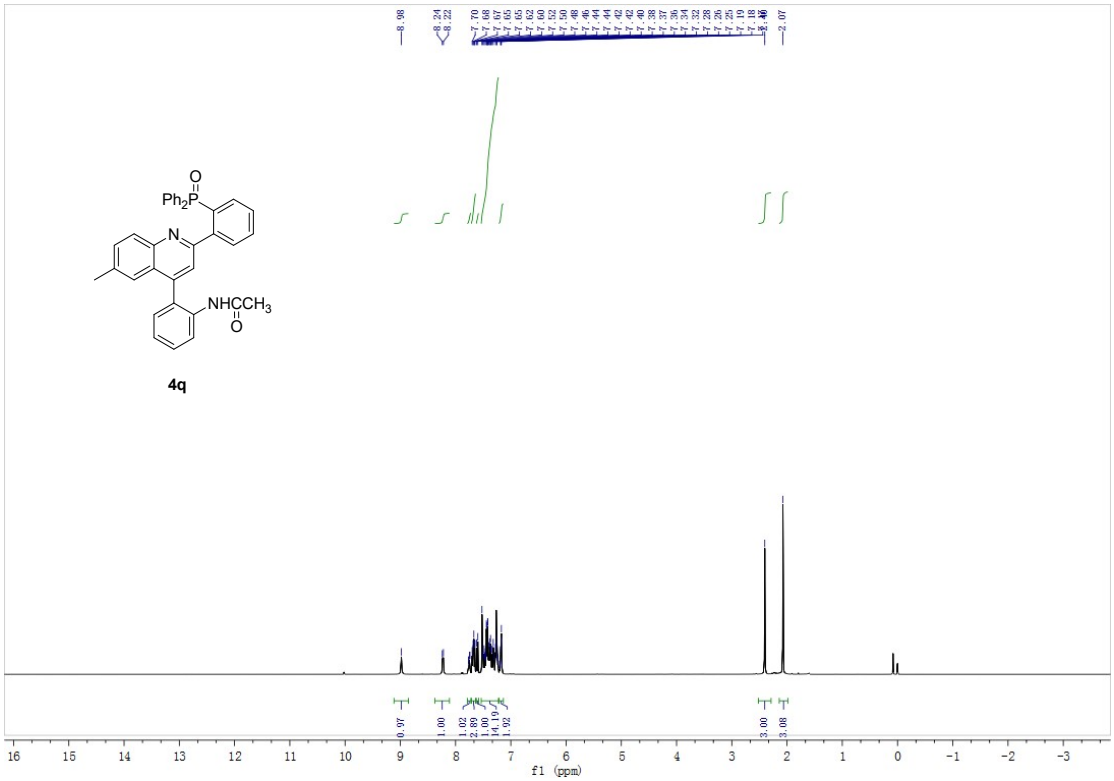

159.60
156.94
156.90
146.37
146.34
145.90
145.82
131.66
131.56
131.19
130.86
130.84
130.82
129.16
127.72
127.60
124.88
113.91
77.32
77.00
76.68
55.29
21.79
O
Ph2P
N
OCH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

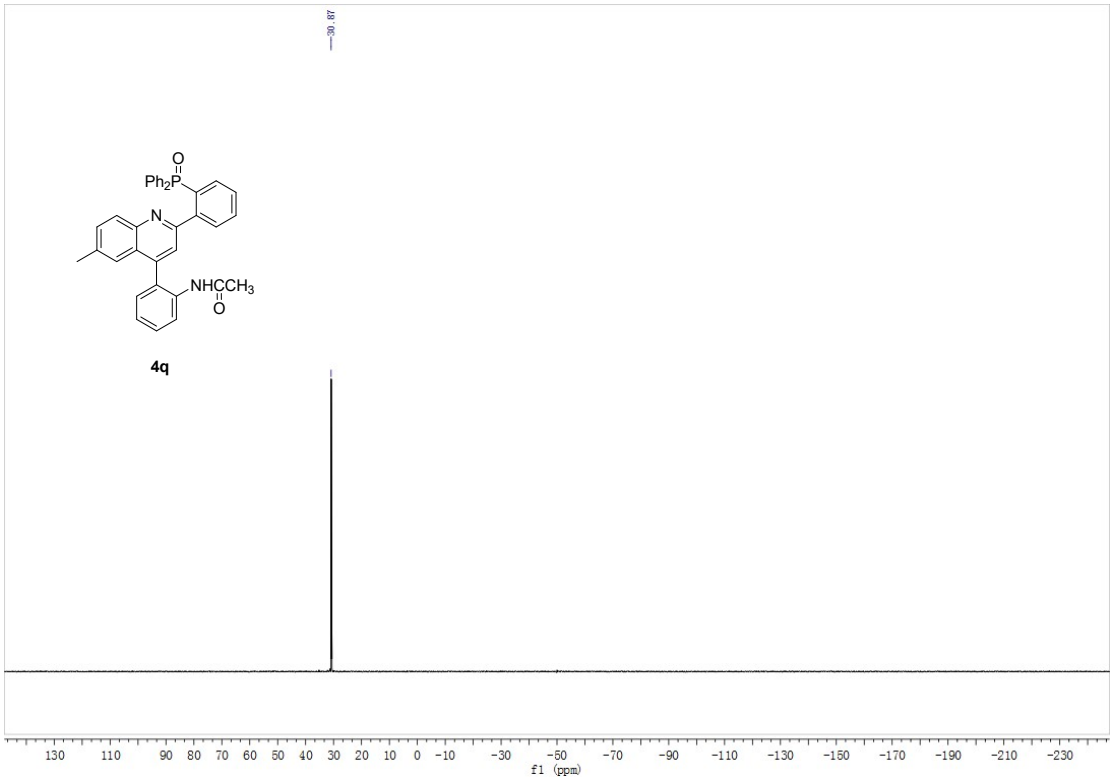
4o

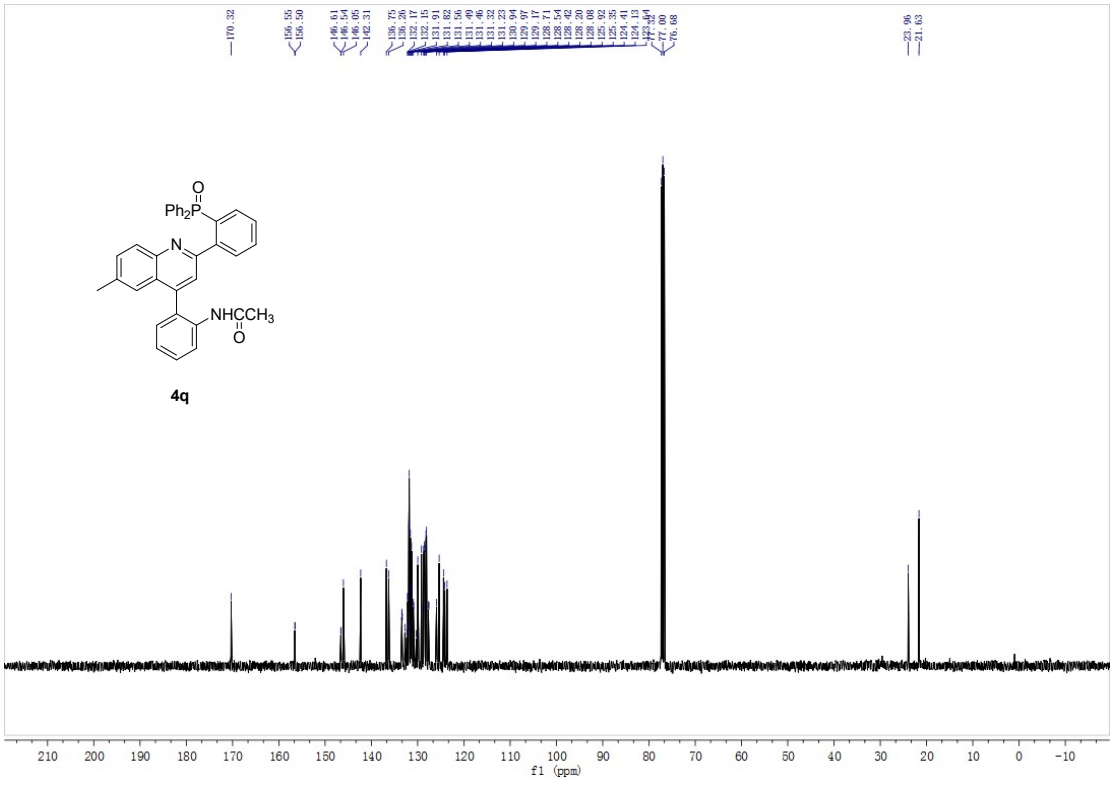

Ph2P
O
N
OCH3
OCH3
4p
f1 (ppm)

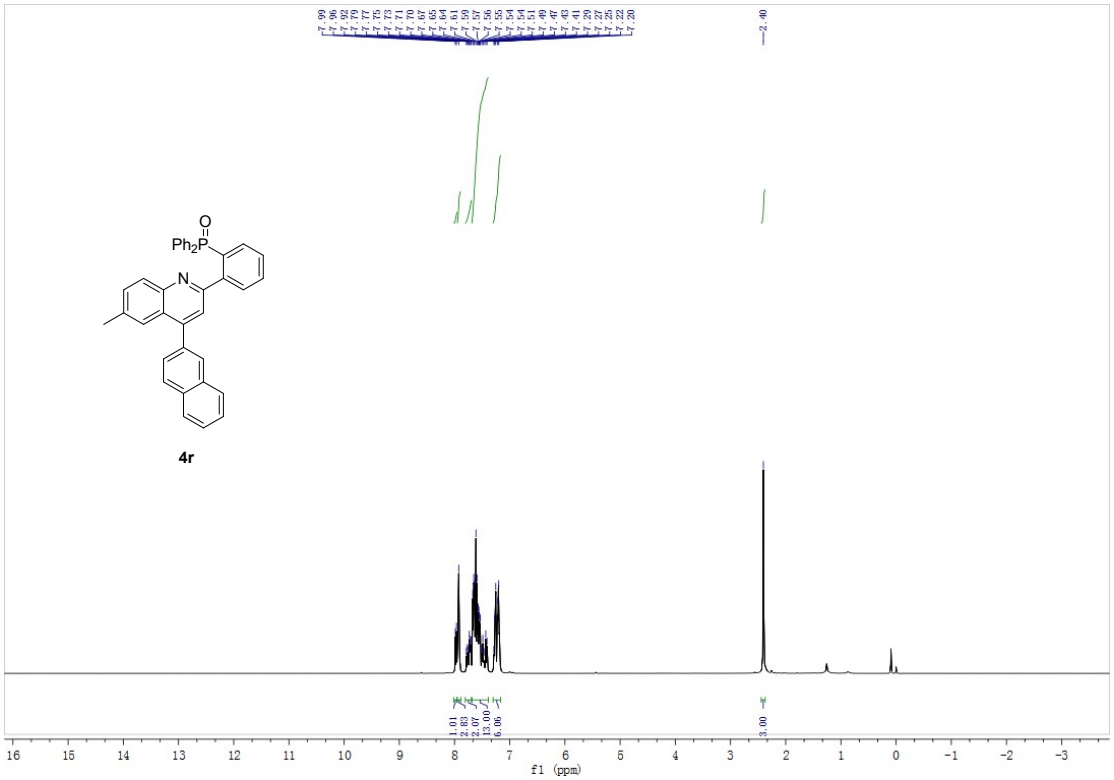

Ph2P
O
N
OCH3
OCH3
4p
f1 (ppm)


156.99
156.95
149.01
148.76
146.51
146.39
145.88
131.66
131.56
131.22
130.83
130.80
130.13
127.73
127.60
124.08
122.86
122.81
111.91
77.32
77.00
76.68
56.06
55.91
21.81
O
Ph2P
N
OCH3
OCH3
4p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

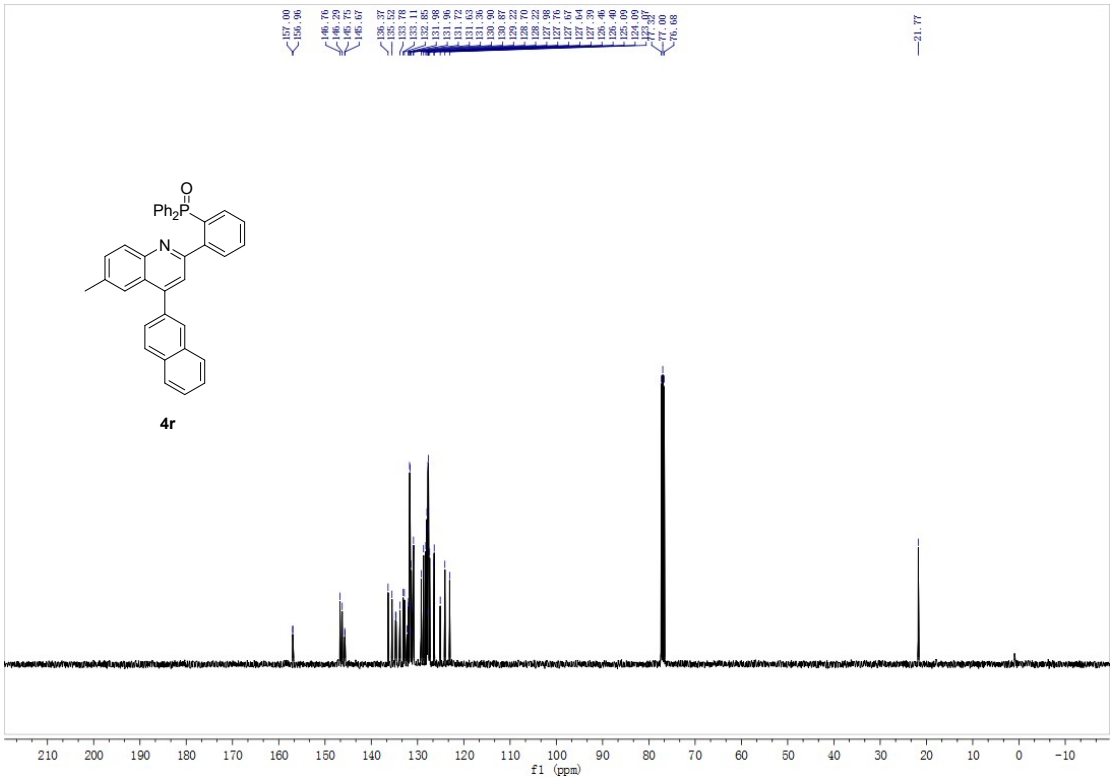

8.98
8.24
8.22
7.70
7.68
7.67
7.65
7.65
7.62
7.60
7.52
7.50
7.48
7.46
7.44
7.44
7.42
7.42
7.40
7.38
7.37
7.36
7.34
7.32
7.28
7.26
7.25
7.19
7.18
2.07
O
Ph2P
N
NHCCH3
O
4q
0.97
1.00
1.02
2.89
1.00
4.19
1.92
3.00
3.08
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

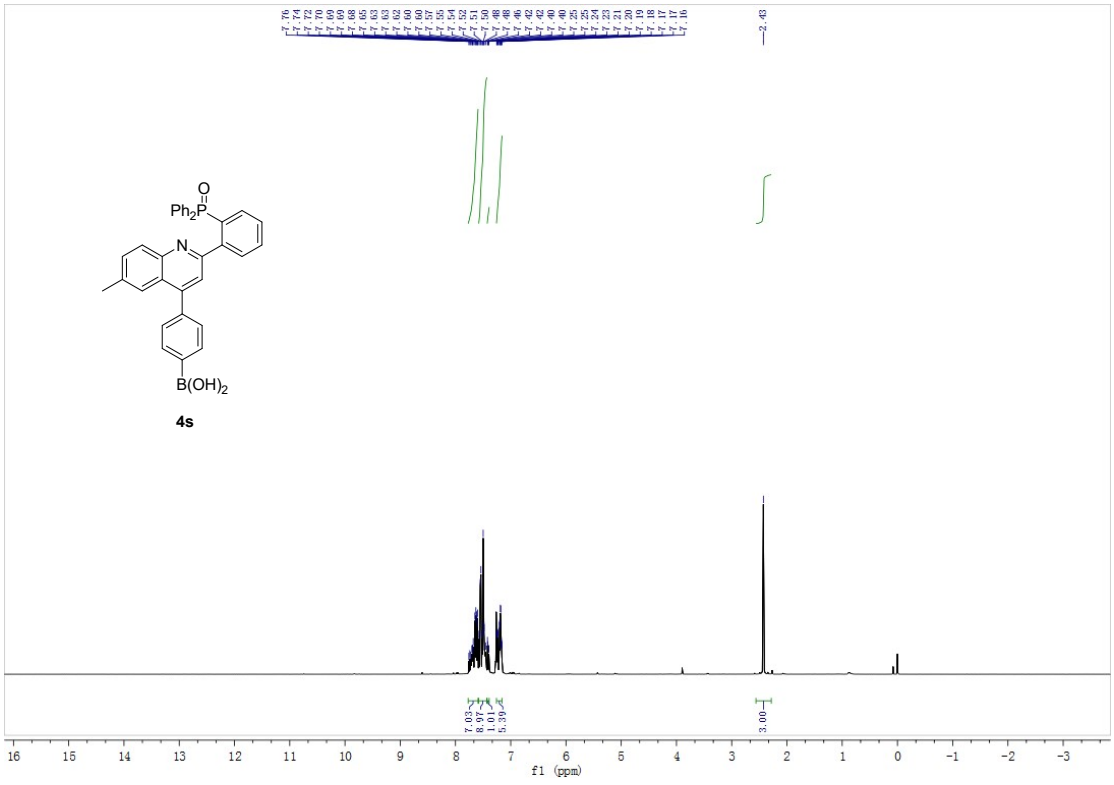

30.87
O
Ph2P
N
NHCCH3
O
4q
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

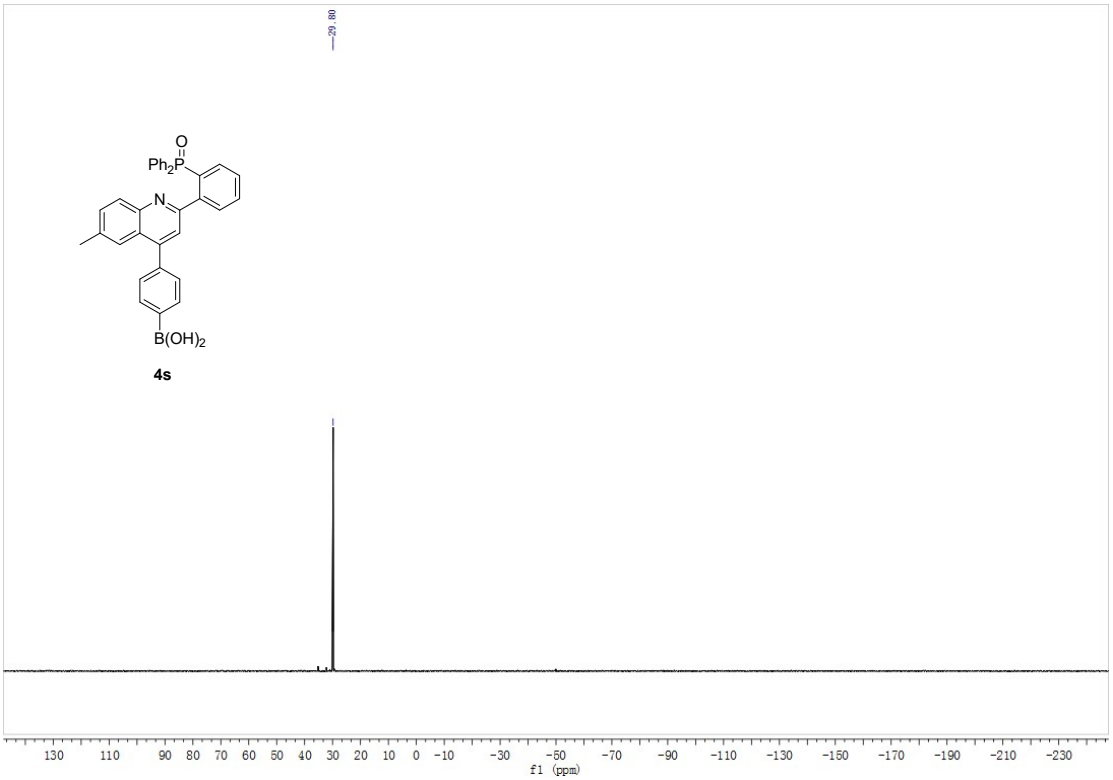

170.32
156.55
156.50
146.61
146.54
146.05
142.31
136.75
136.26
132.17
132.15
131.91
131.82
131.56
131.49
131.46
131.32
131.23
130.94
129.97
129.17
128.71
128.54
128.42
128.20
128.06
125.92
125.35
124.41
124.13
123.44
77.60
76.68
23.96
21.63
O
Ph2P
N
NHCCH3
O
4q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

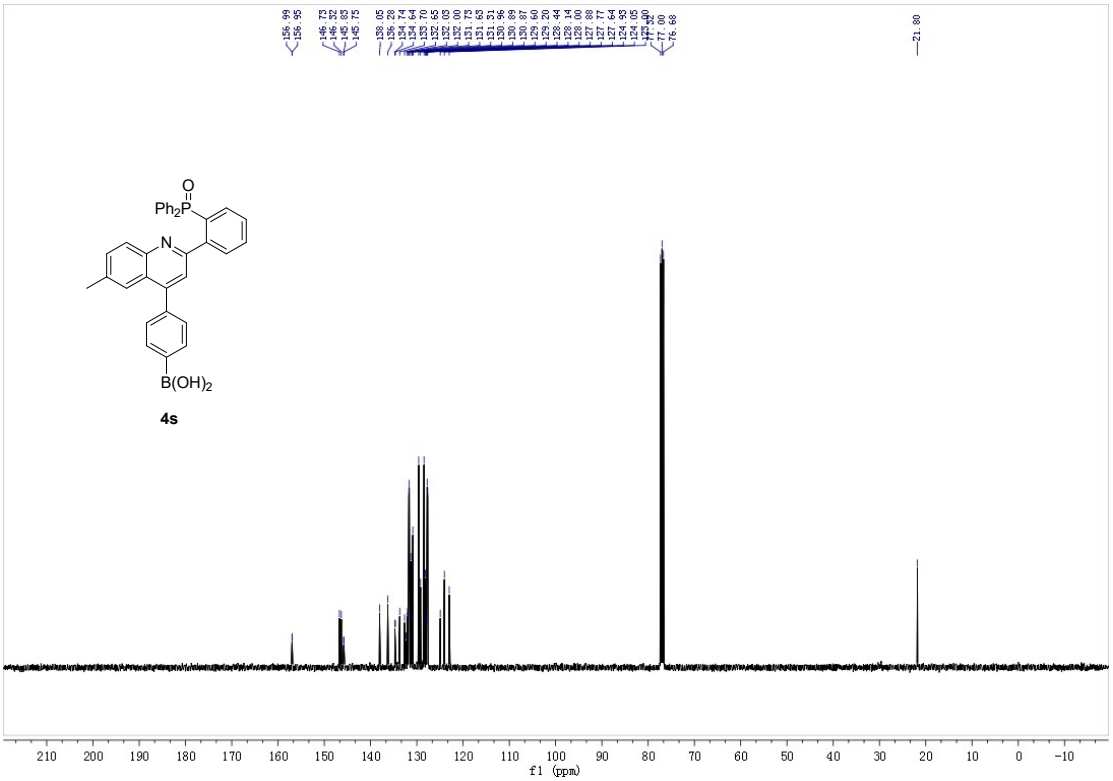

7.99
7.96
7.92
7.79
7.77
7.75
7.73
7.71
7.70
7.67
7.65
7.64
7.61
7.59
7.57
7.56
7.55
7.54
7.54
7.51
7.49
7.47
7.43
7.41
7.29
7.27
7.25
7.22
7.20
2.40
O
Ph2P
N
4r
1.01
2.07
2.07
13.00
6.06
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

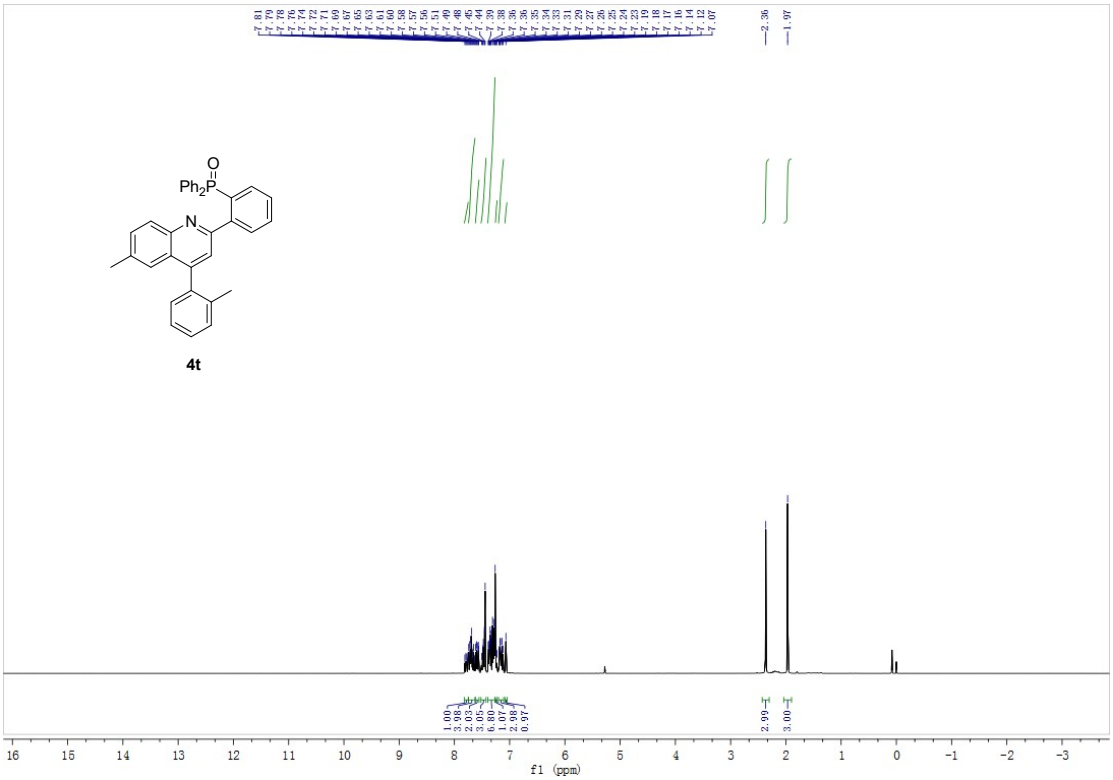

29.93
O
Ph2P
N
4r
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

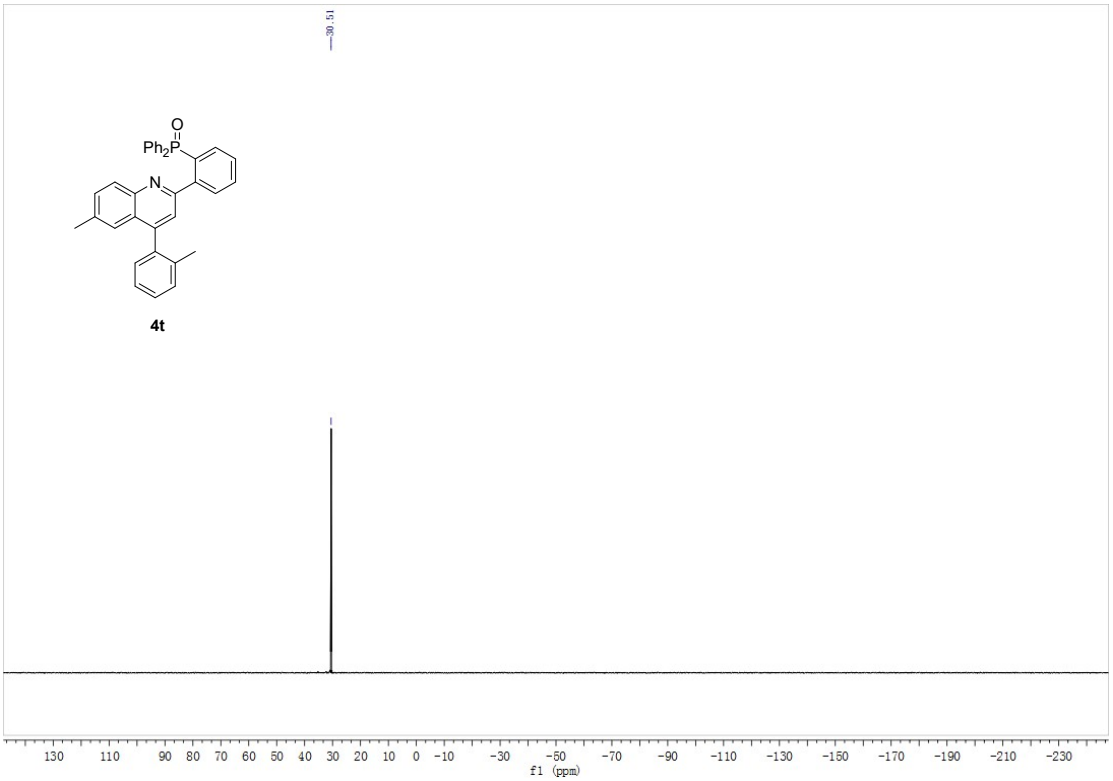

4r
f1 (ppm)

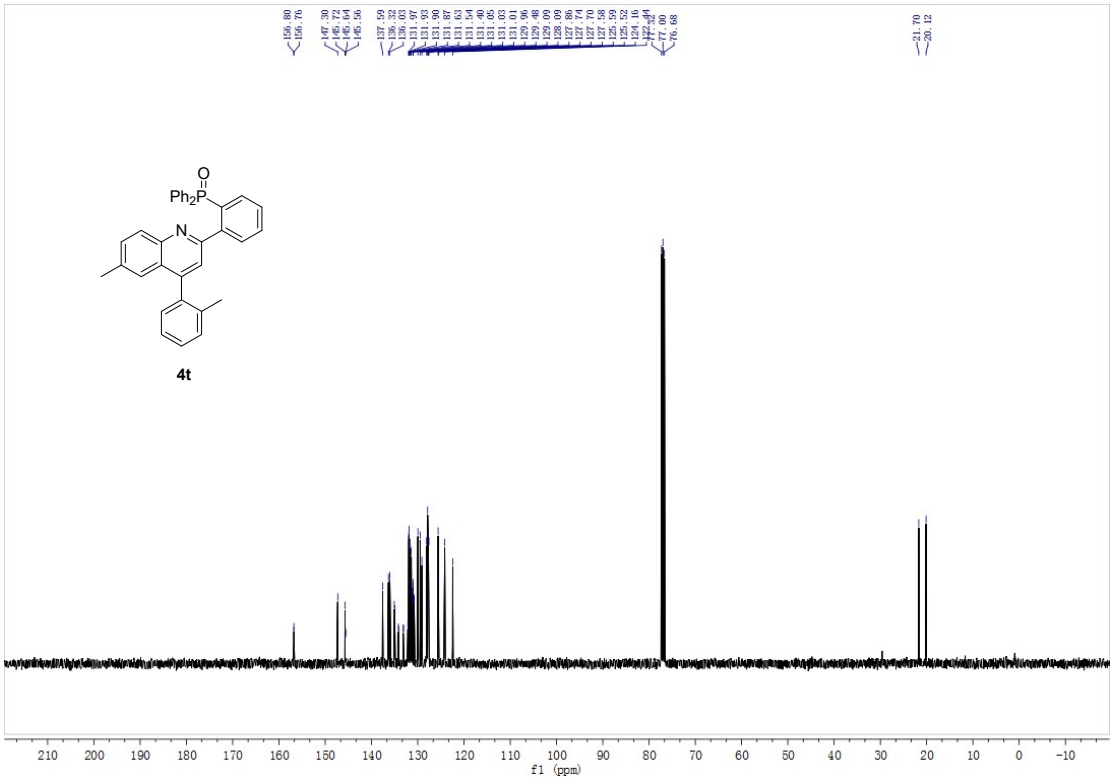

4s
f1 (ppm)

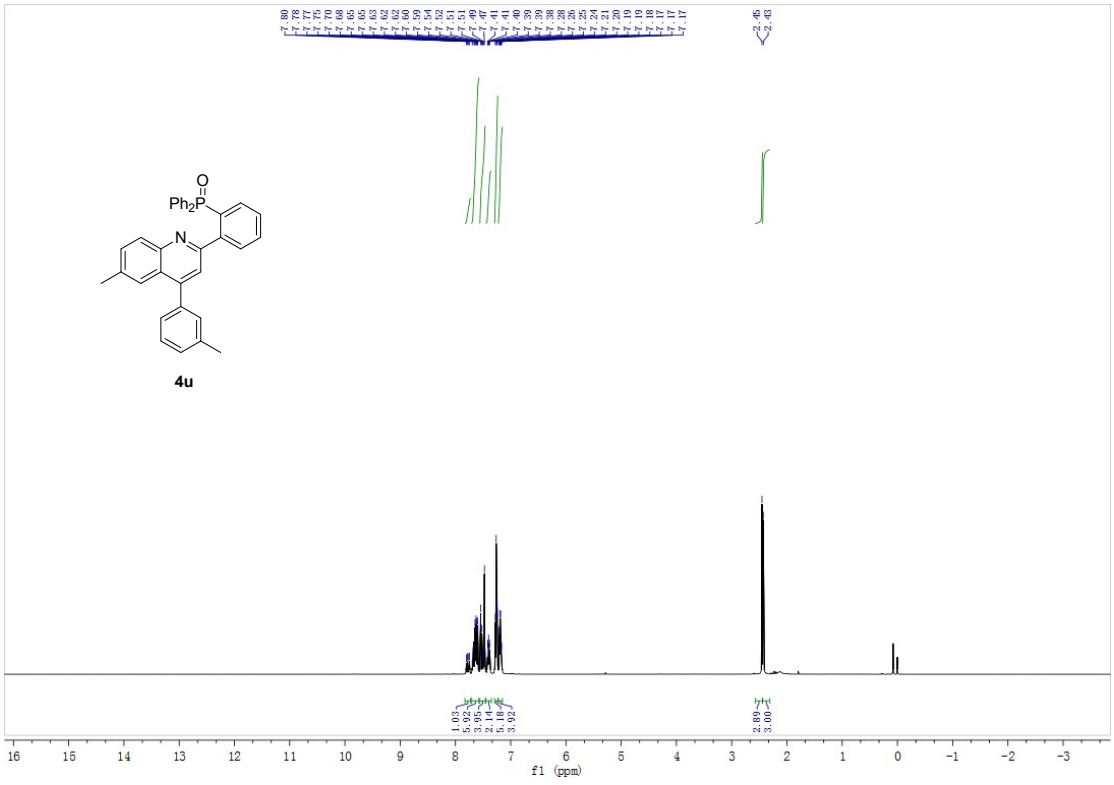

29.80
O
Ph2P
N
B(OH)2
4s
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

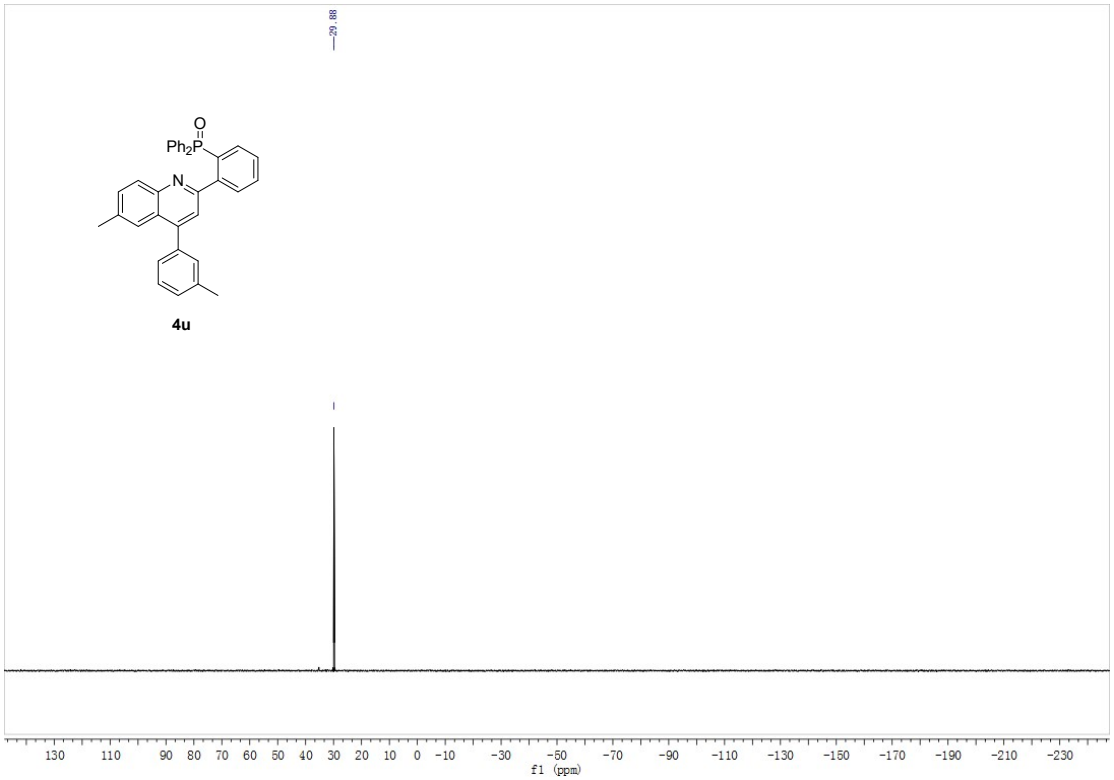

156.99
156.95
146.73
146.32
145.83
145.75
21.80
O
Ph2P
N
B(OH)2
4s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

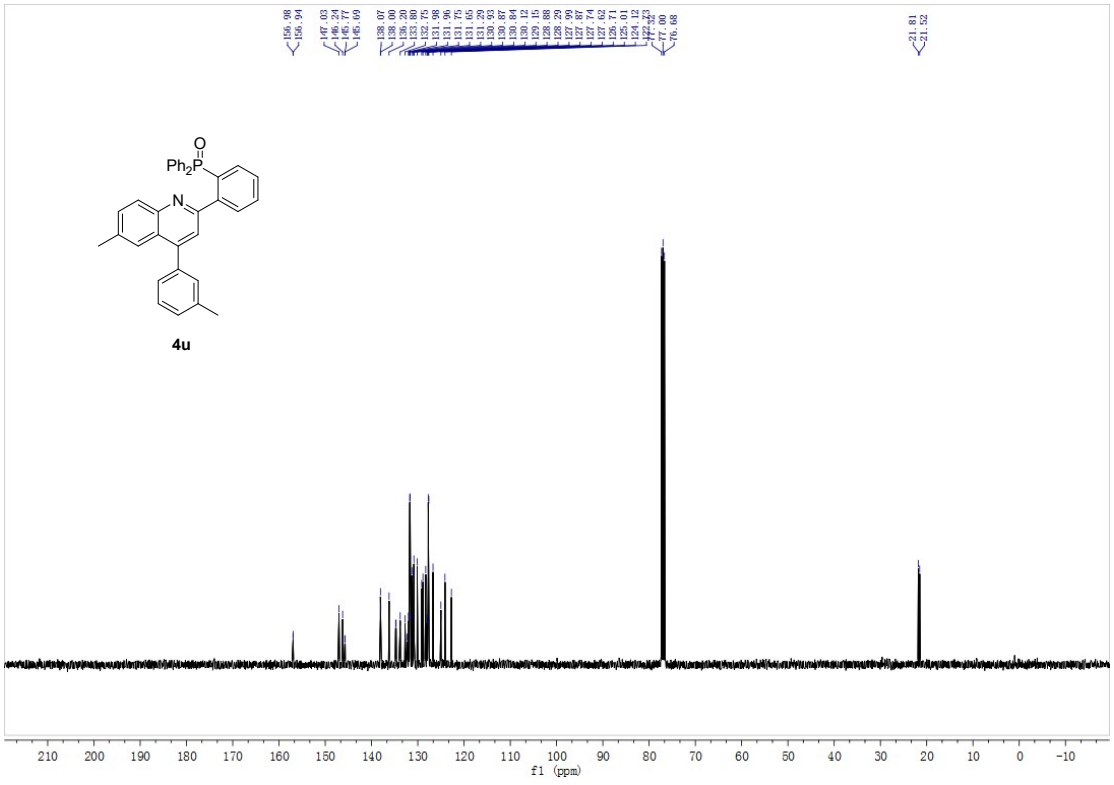

Ph2P
O
N
4t
f1 (ppm)

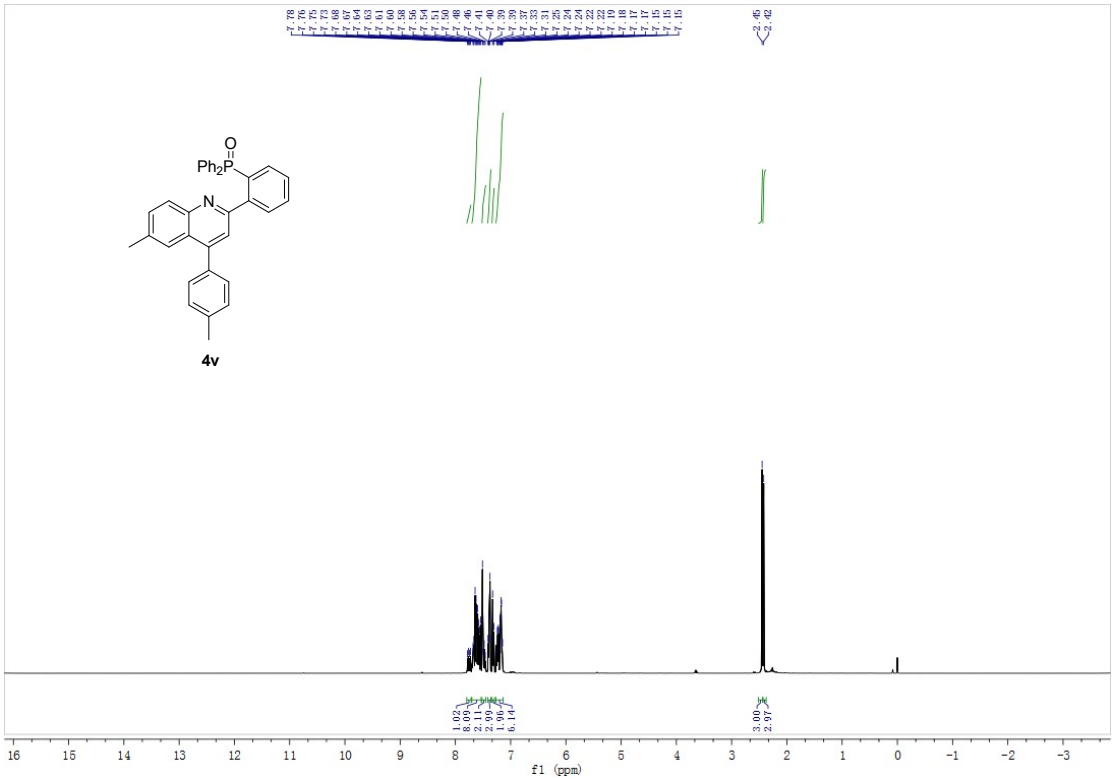

Ph2P
O
N
4t
f1 (ppm)

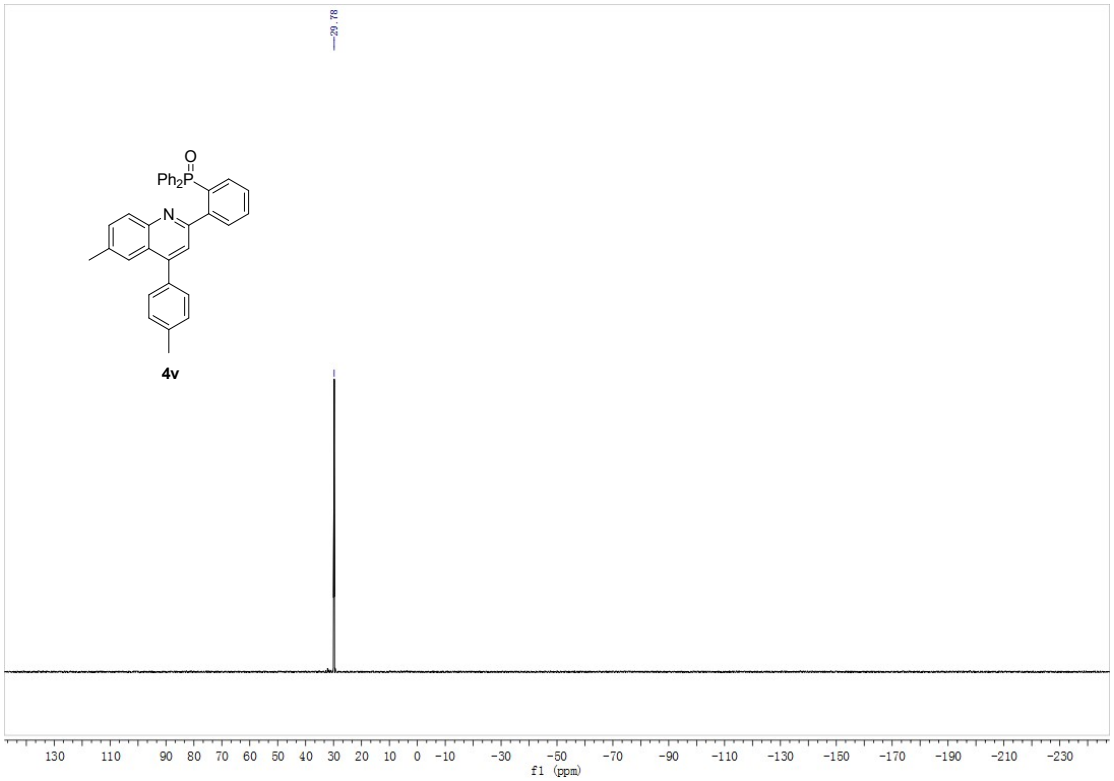

O
Ph2P
N
4t
f1 (ppm)

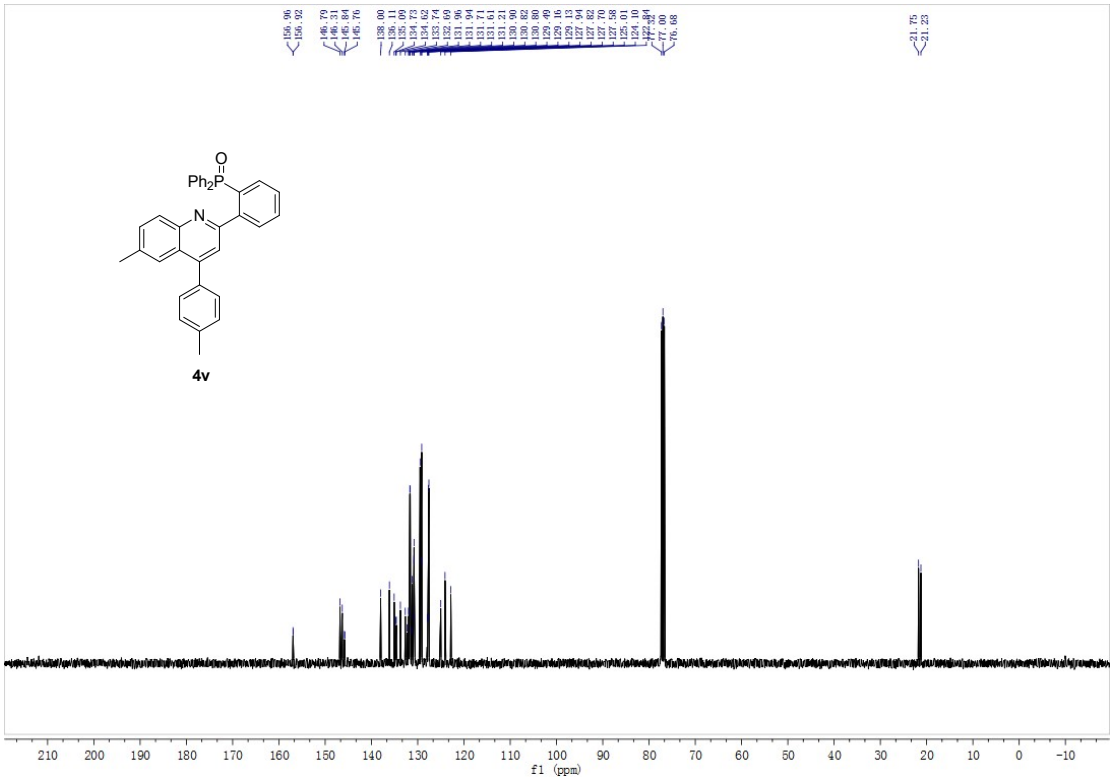

O
Ph2P
N
4u
f1 (ppm)

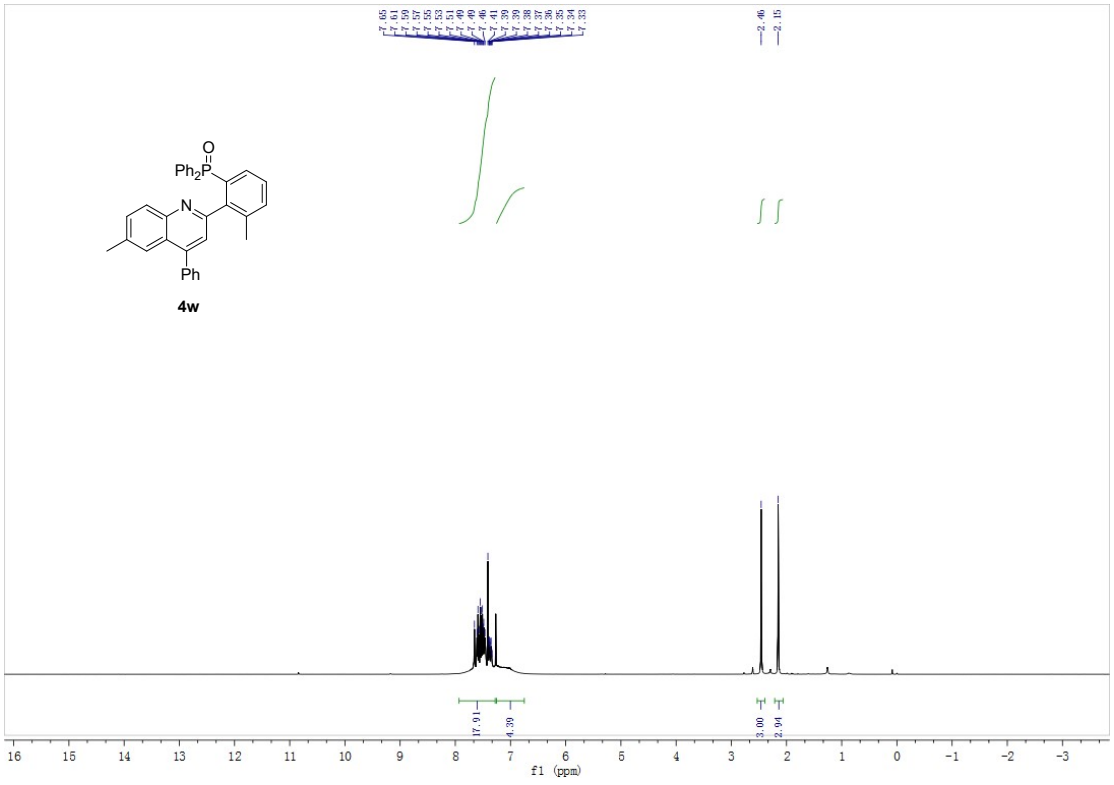

29.88
O
Ph2P
N
4u
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

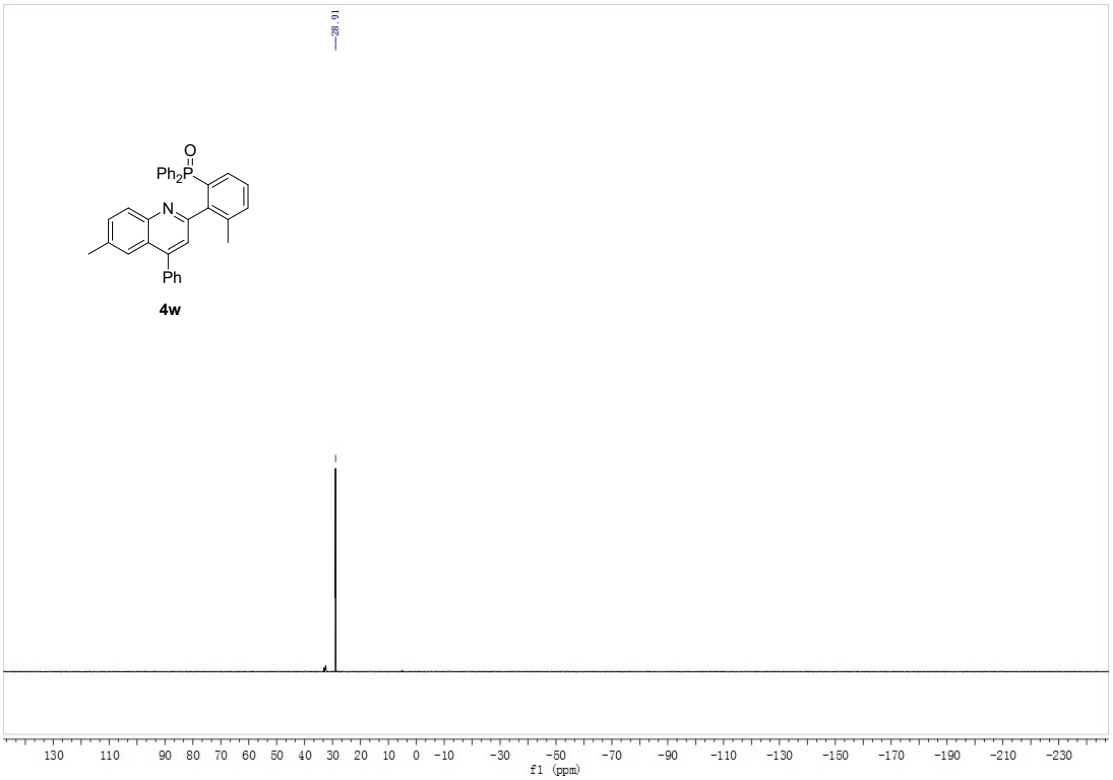

156.98
156.94
147.03
146.24
145.77
145.69
138.07
138.00
136.20
133.80
132.75
131.98
131.96
131.75
131.65
131.29
130.95
130.87
130.84
130.12
129.15
128.88
128.29
127.99
127.87
127.74
127.62
126.71
125.01
124.12
77.37
77.00
76.68
21.81
21.52
O
Ph2P
N
4u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph2P
O
N
4v
f1 (ppm)

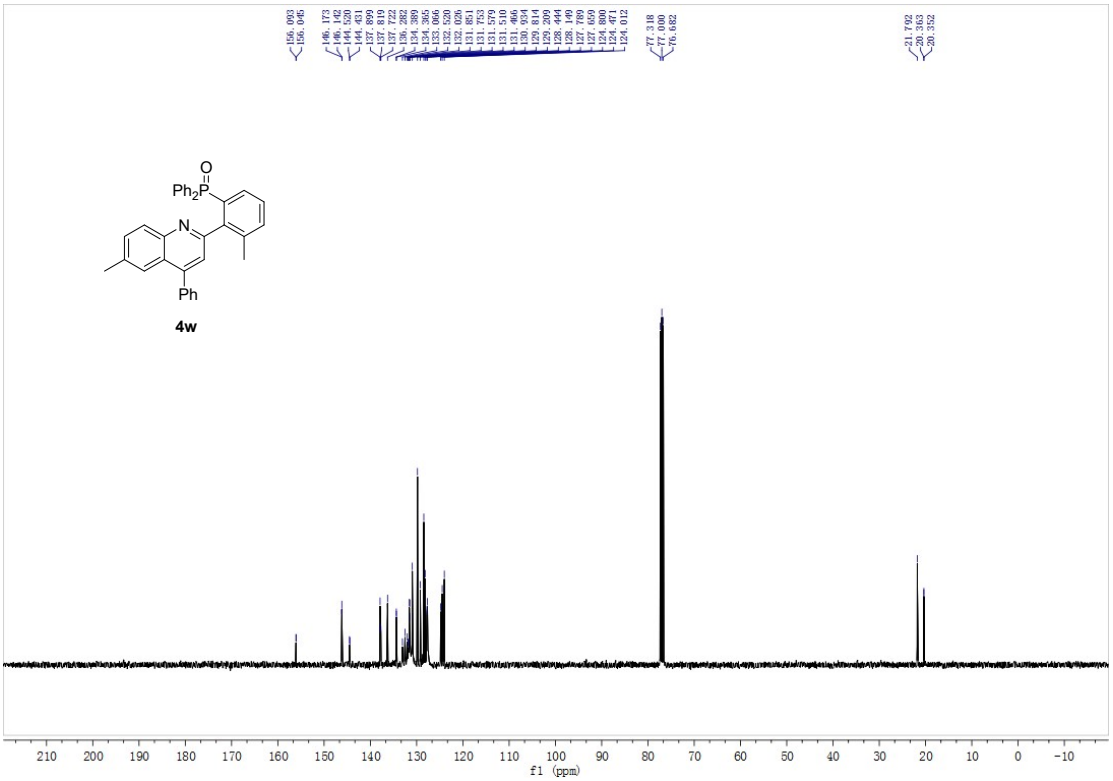

29.78
Ph2P
O
N
4v
f1 (ppm)


4v
f1 (ppm)

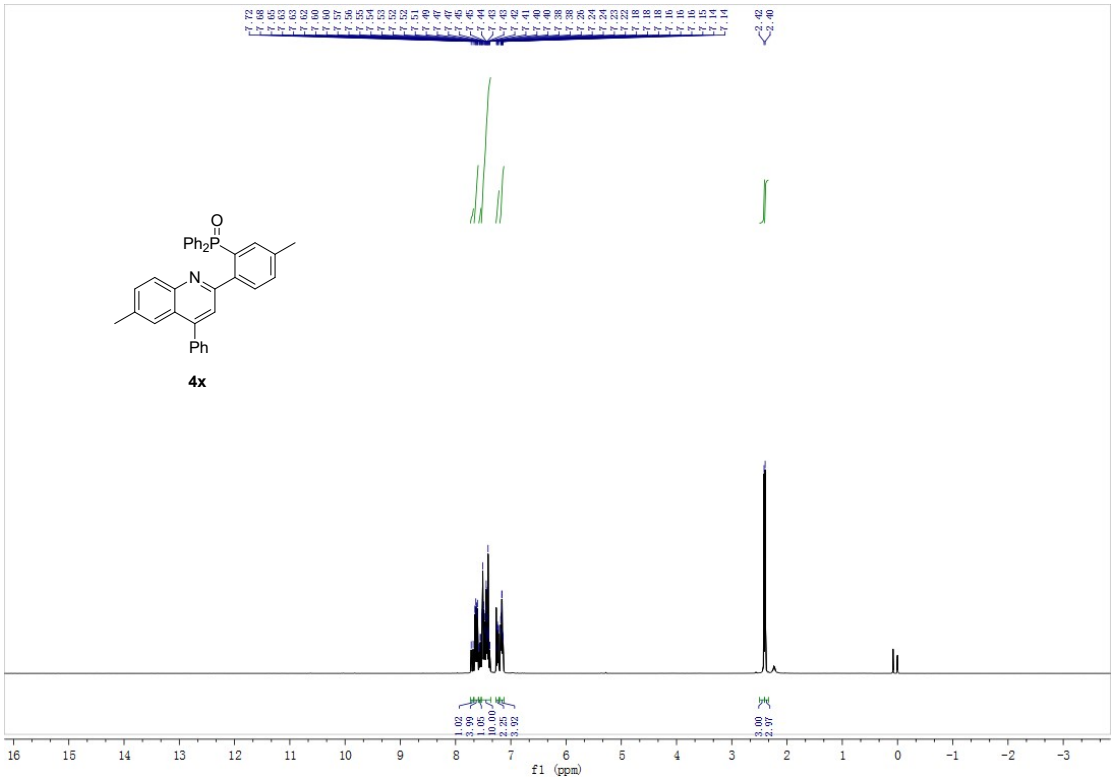

4w
f1 (ppm)

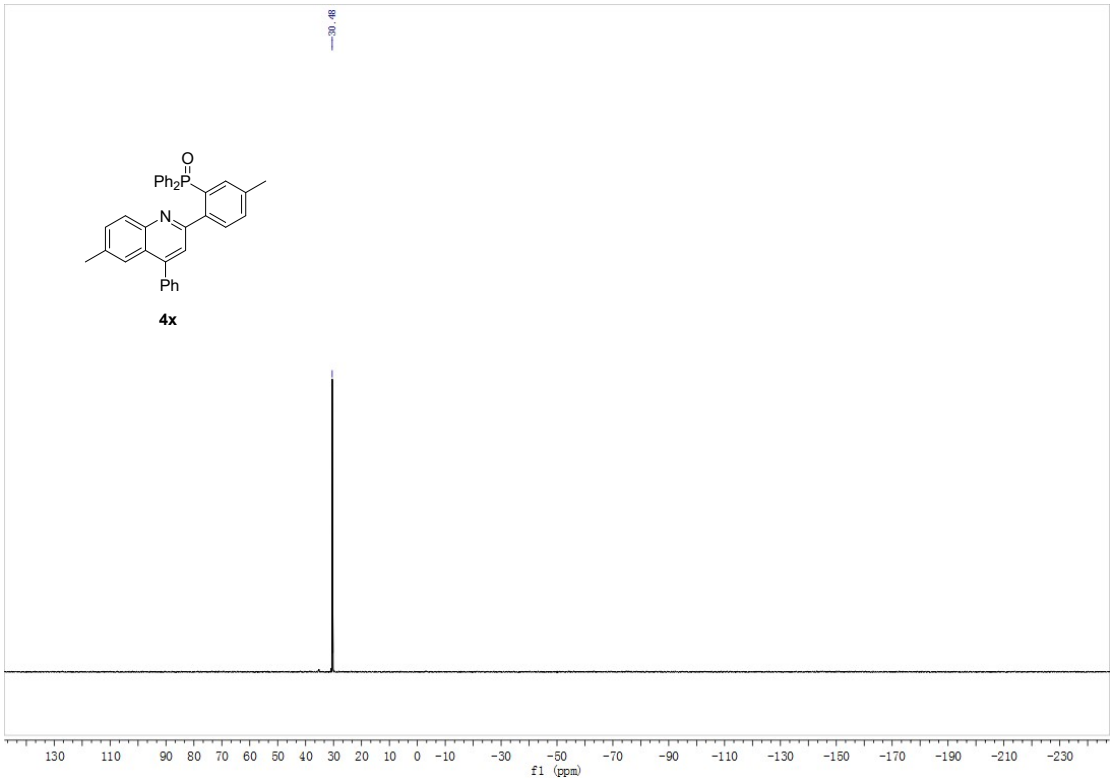

28.91
O
Ph2P
N
Ph
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

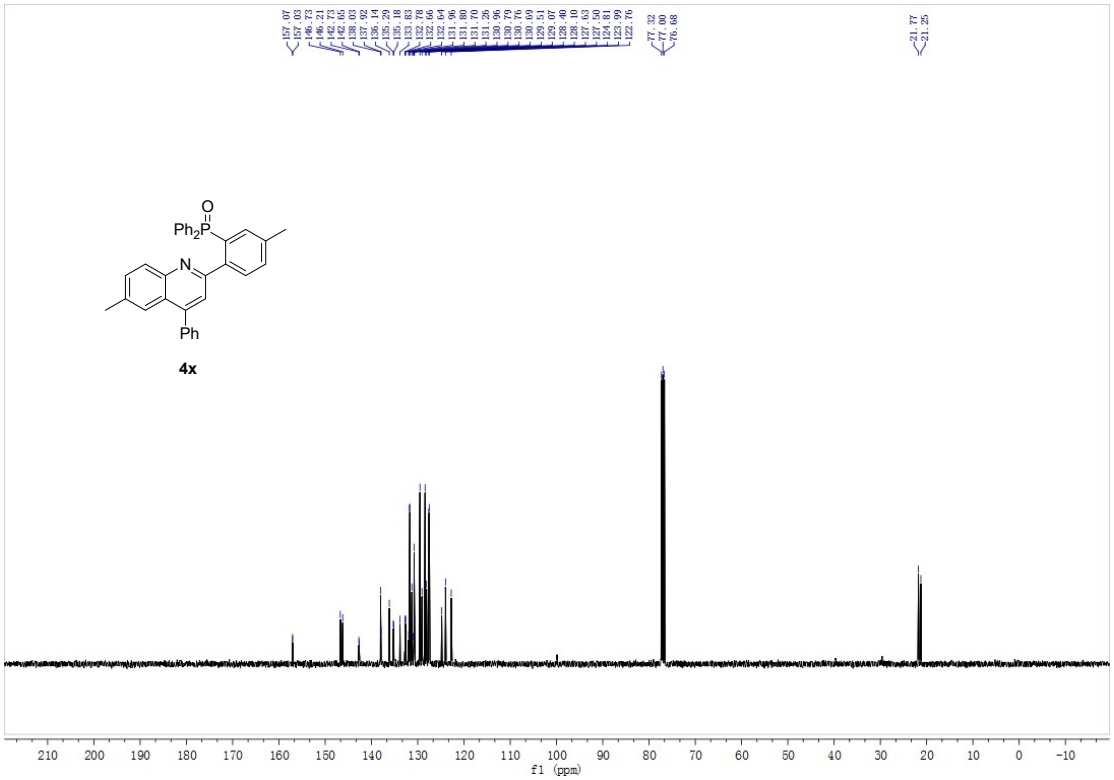
4w

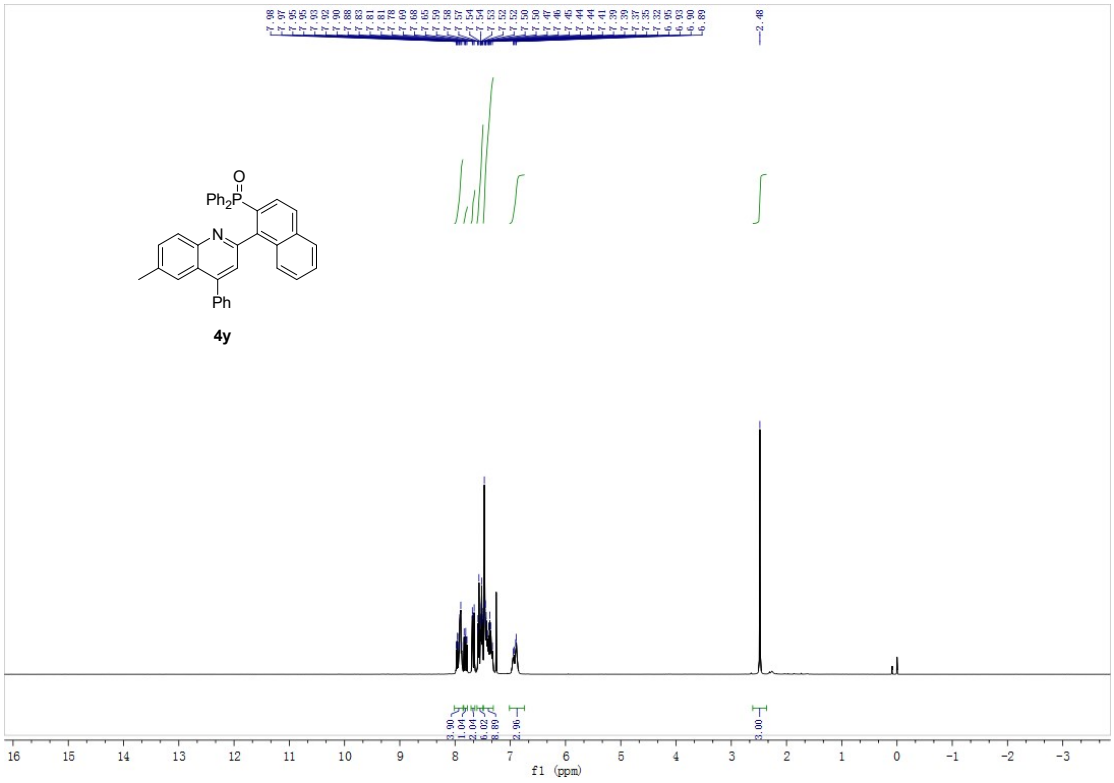

156.093
156.045
146.173
146.147
144.520
144.431
137.899
137.819
137.772
136.282
134.389
134.365
133.866
133.550
132.026
131.851
131.753
131.579
131.510
131.466
130.934
129.814
129.289
128.444
128.149
127.789
127.659
127.609
124.471
124.012
77.318
77.000
76.682
21.792
20.363
20.352
O
Ph2P
N
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

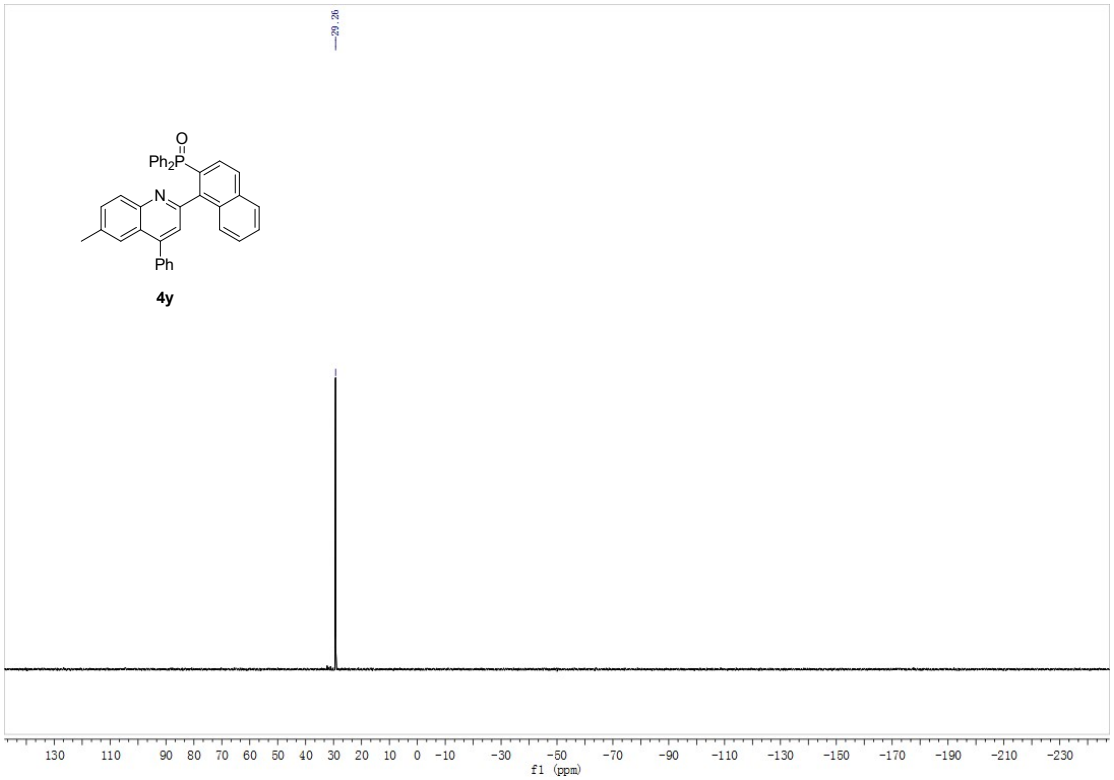
4w


Ph2P
O
N
Ph
4x
f1 (ppm)

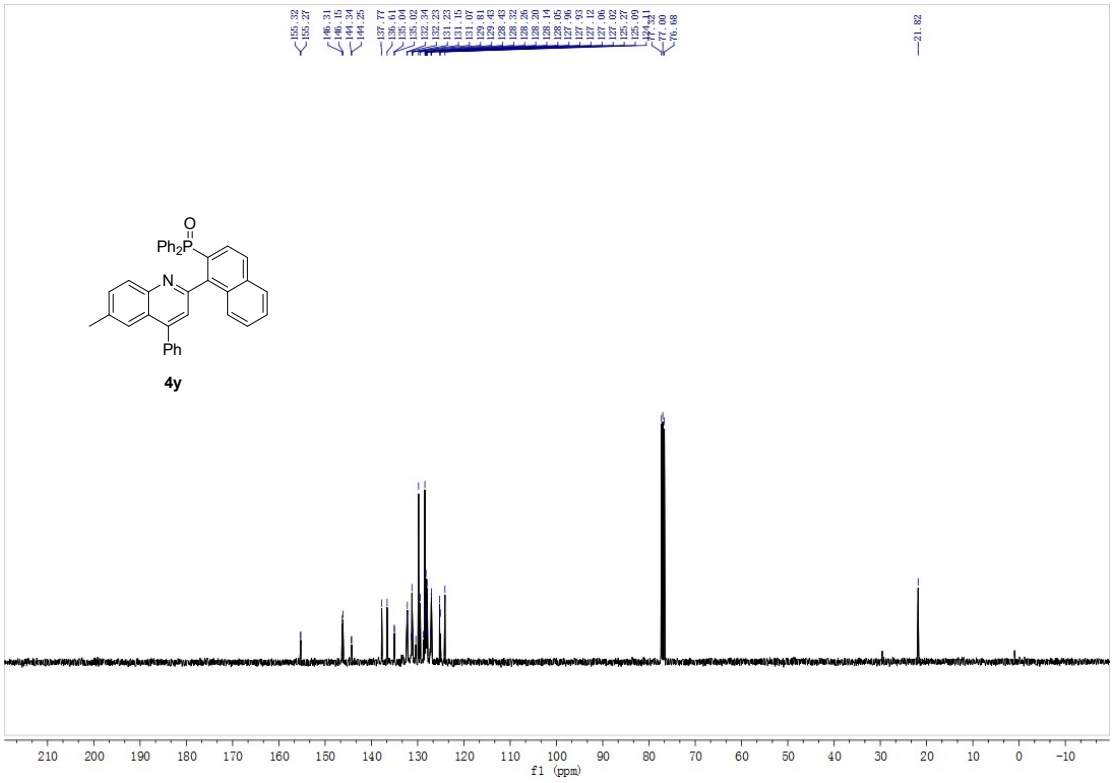

Ph2P
O
N
Ph
4x
f1 (ppm)


O
Ph2P
N
Ph
4x
f1 (ppm)

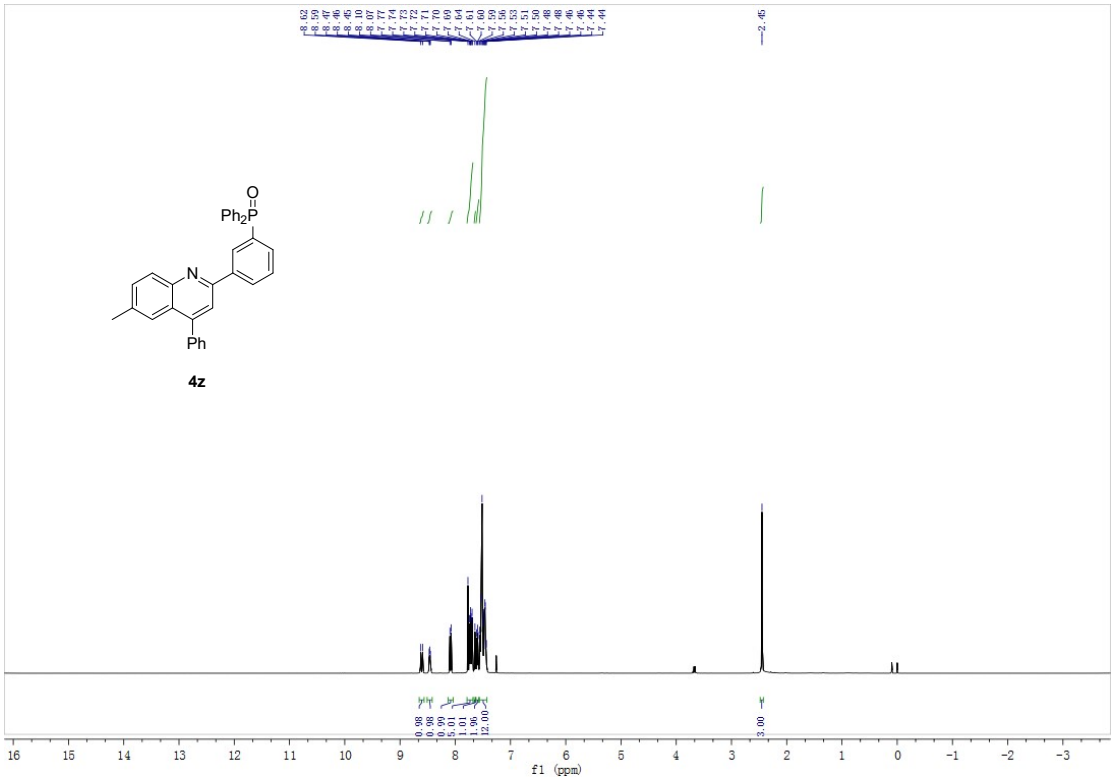

O
Ph2P
N
Ph
4y
f1 (ppm)


29.26
O
Ph2P
N
Ph
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

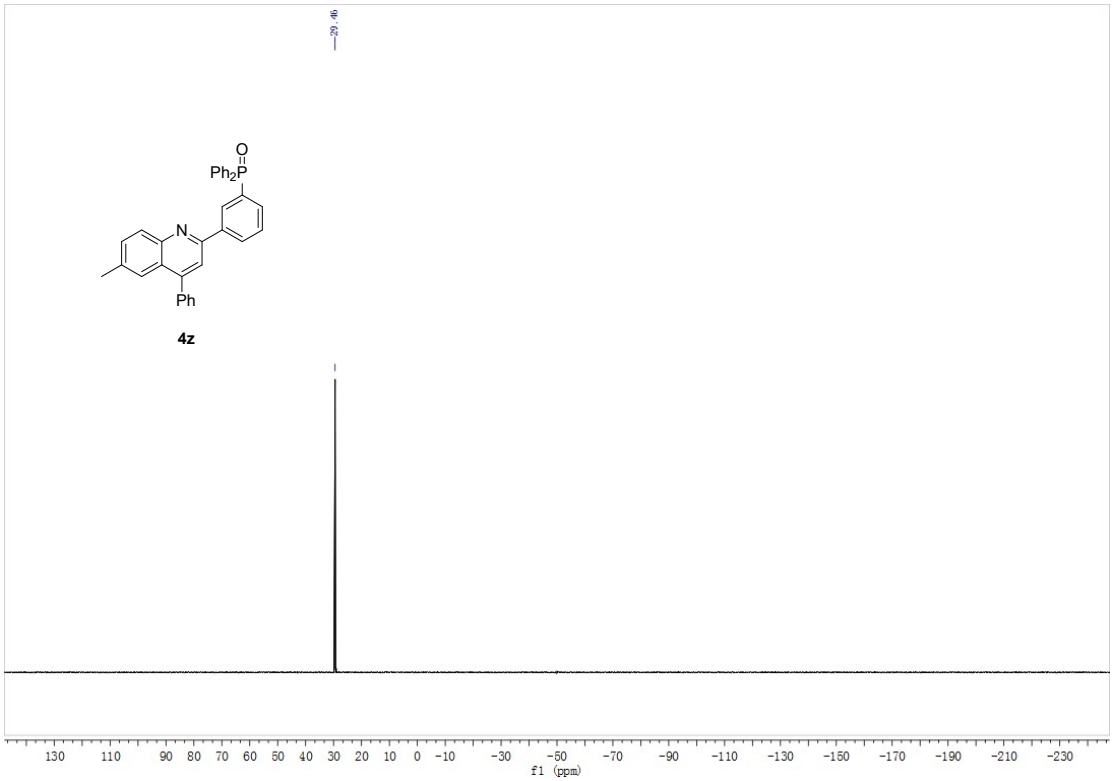
4y


155.32
155.27
146.31
146.15
144.34
144.25
137.77
136.41
135.04
135.02
132.34
132.23
131.23
131.15
131.07
129.81
129.45
128.43
128.32
128.26
128.20
128.14
128.05
127.93
127.72
127.16
127.02
125.27
125.09
77.41
77.00
76.68
21.82
O
Ph2P
N
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

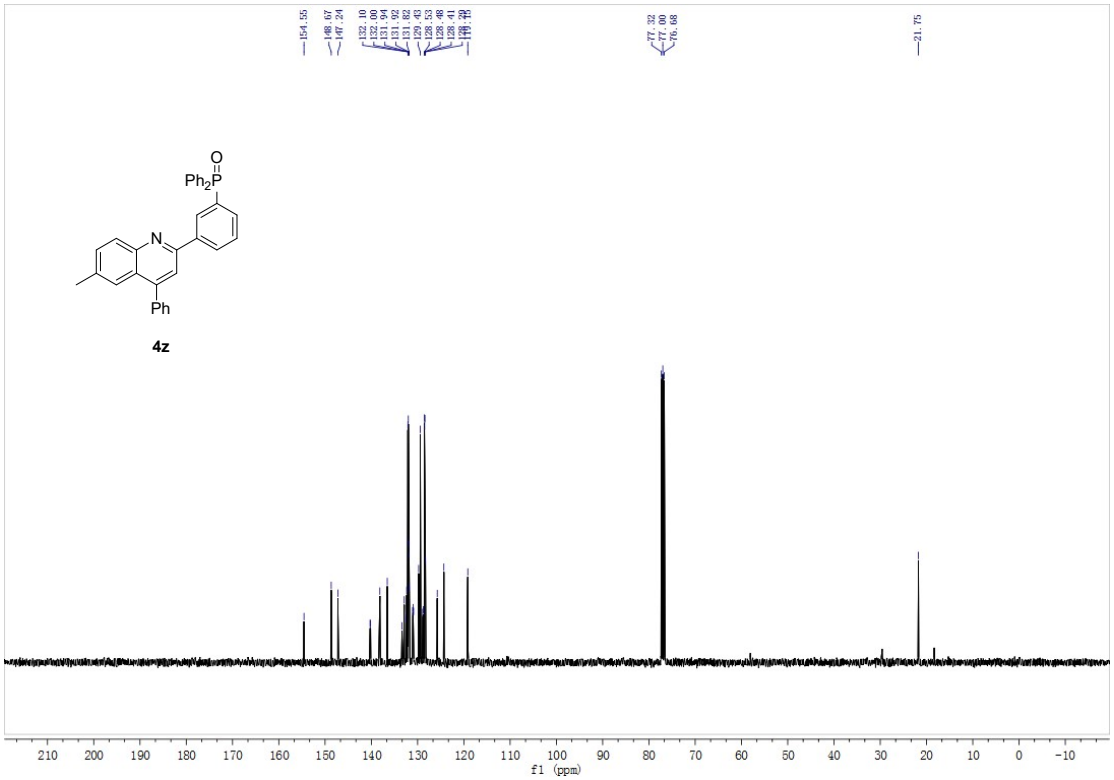
4y

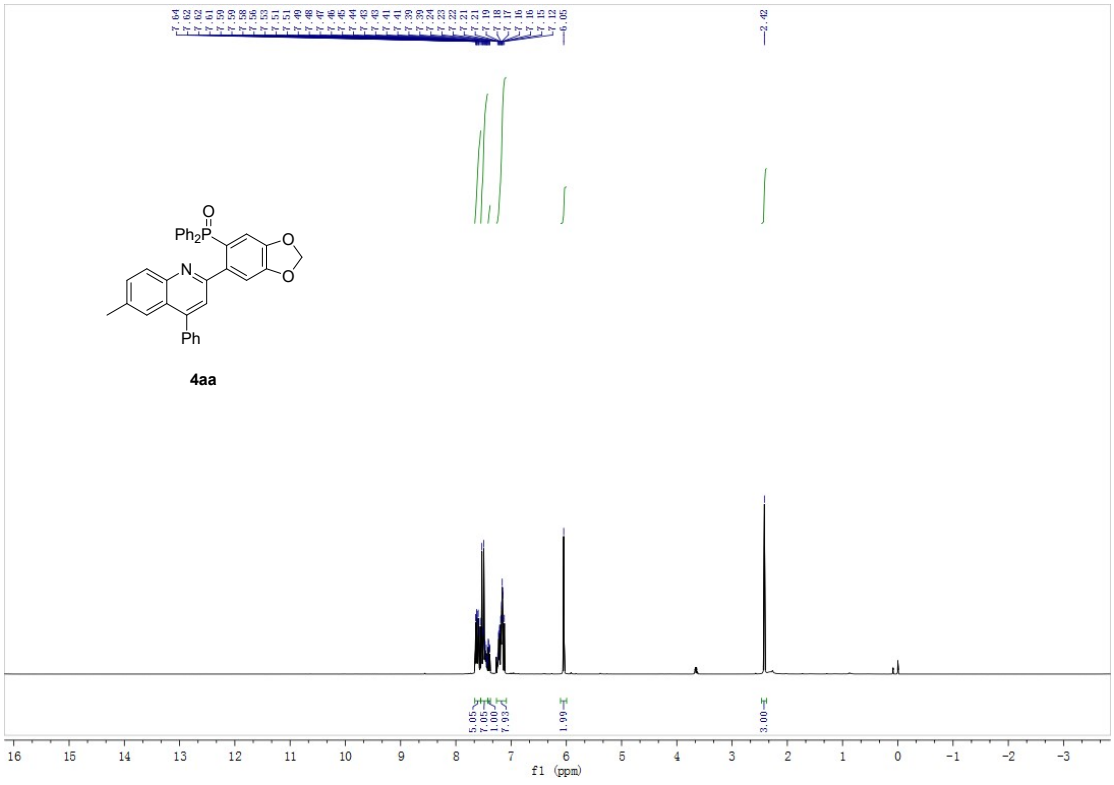

8.62
8.59
8.47
8.46
8.45
8.10
8.07
7.77
7.74
7.73
7.72
7.71
7.70
7.69
7.64
7.61
7.60
7.59
7.56
7.53
7.51
7.50
7.48
7.46
7.46
7.44
7.44
2.45
O
Ph2P
N
Ph
0.98
0.98
0.99
5.01
1.01
1.96
12.00
3.00
f1 (ppm)

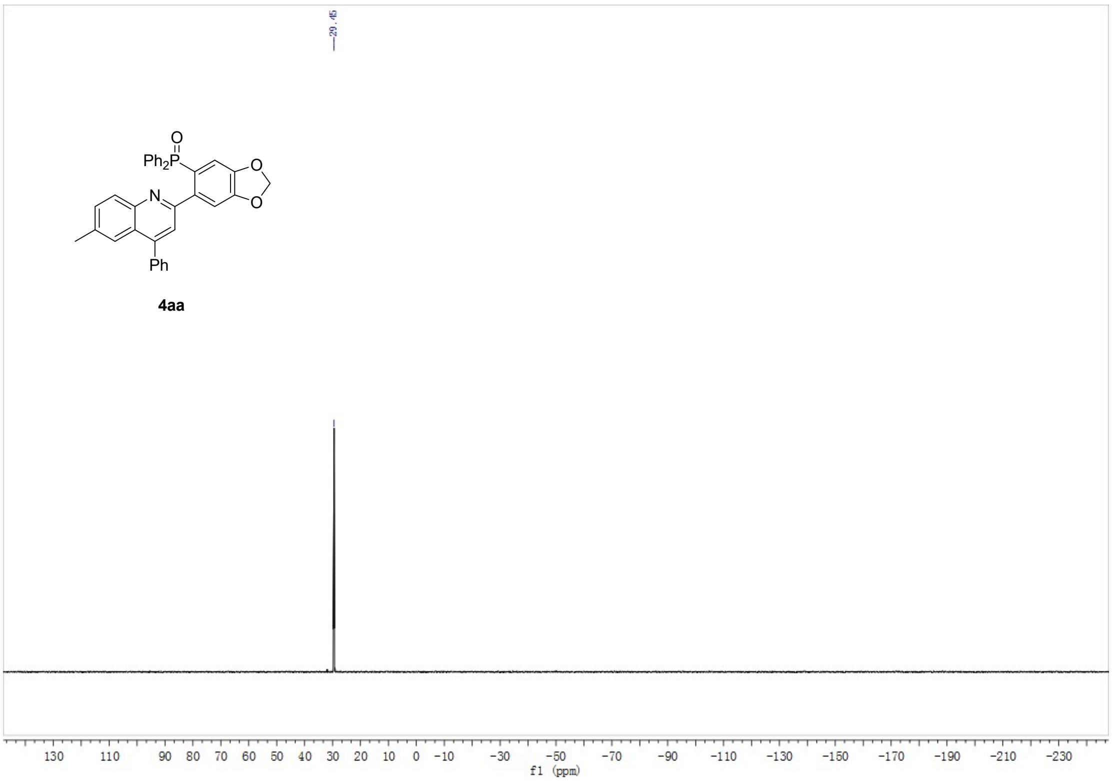
4z


29.46
O
Ph2P
N
Ph
f1 (ppm)

4z

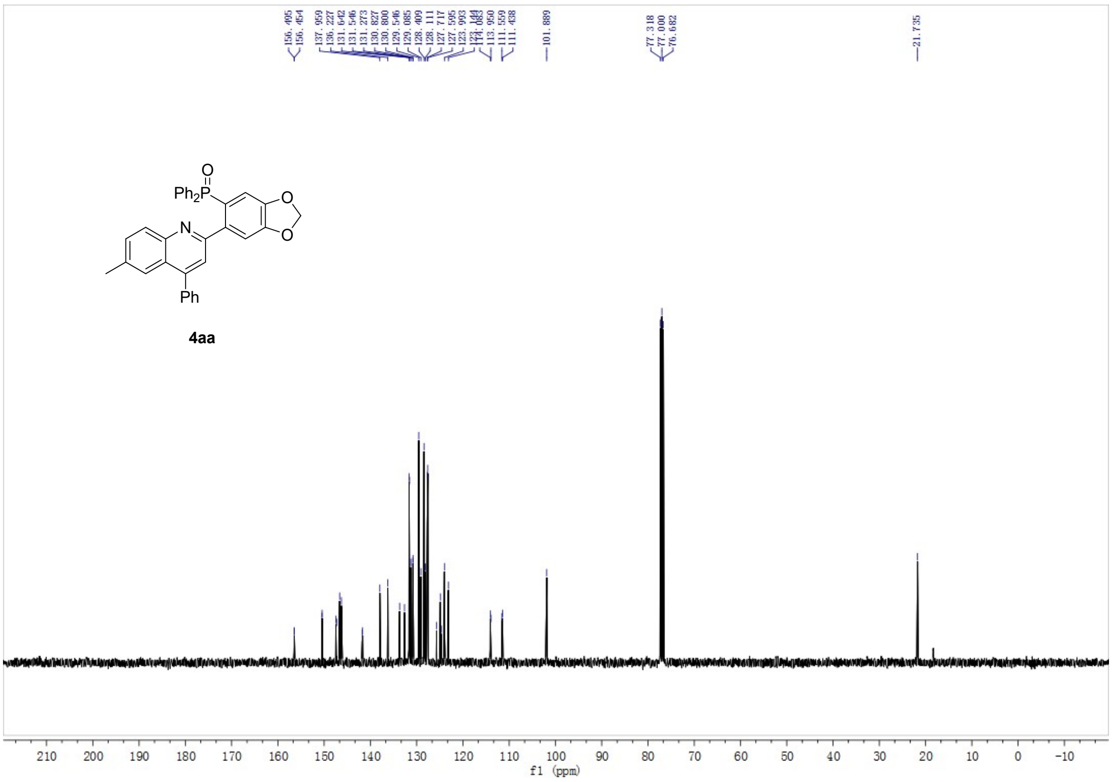

154.55
148.67
147.24
132.10
132.00
131.94
131.92
131.82
129.43
128.53
128.48
128.41
77.32
77.00
76.68
21.75
O
Ph2P
N
Ph
4z
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.64
7.62
7.62
7.61
7.59
7.59
7.58
7.56
7.53
7.51
7.51
7.49
7.48
7.47
7.46
7.45
7.44
7.43
7.41
7.41
7.39
7.39
7.24
7.23
7.22
7.21
7.21
7.19
7.18
7.17
7.16
7.16
7.15
7.12
6.05
2.42
O
Ph2P
N
O
O
Ph
4aa
5.05
7.05
1.00
7.93
1.09
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)



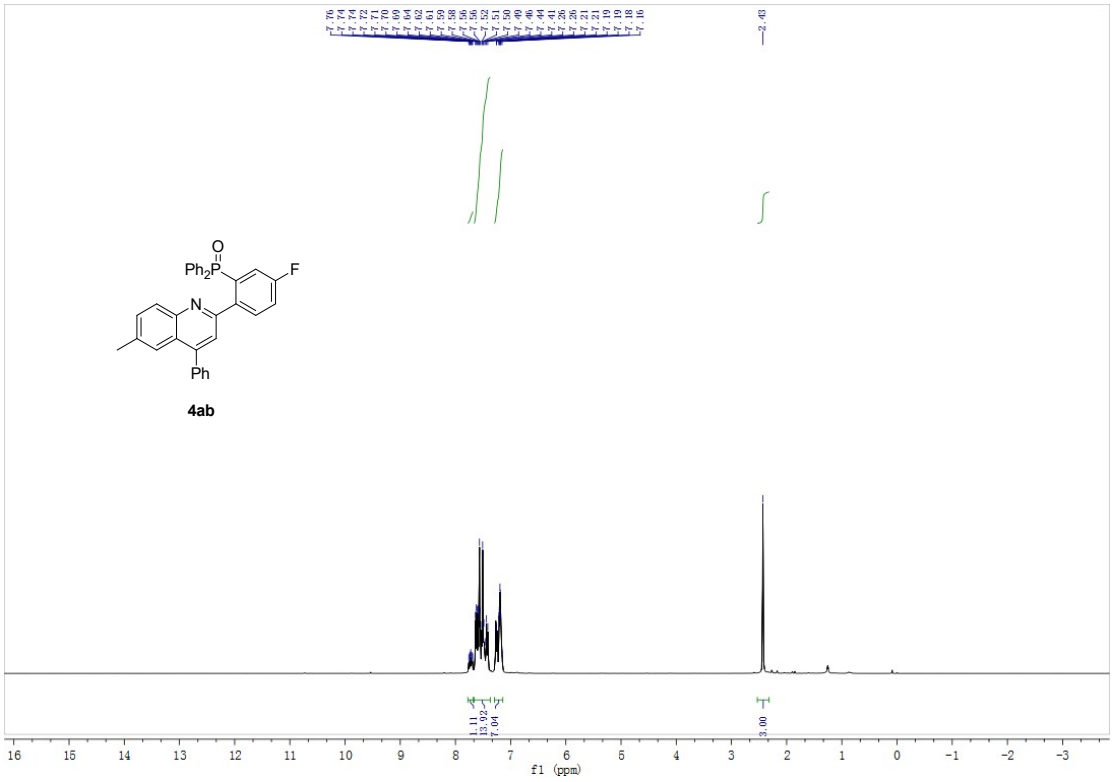
29.45
Ph2P
O
N
O
O
Ph
f1 (ppm)

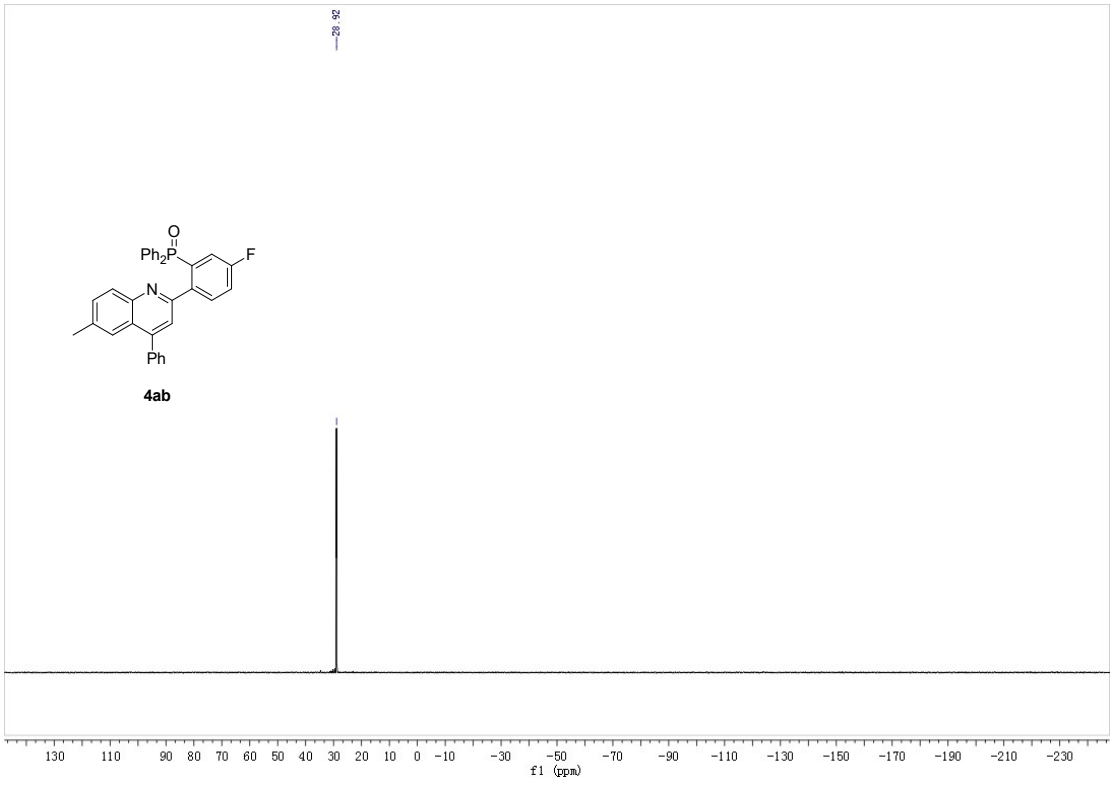
4aa

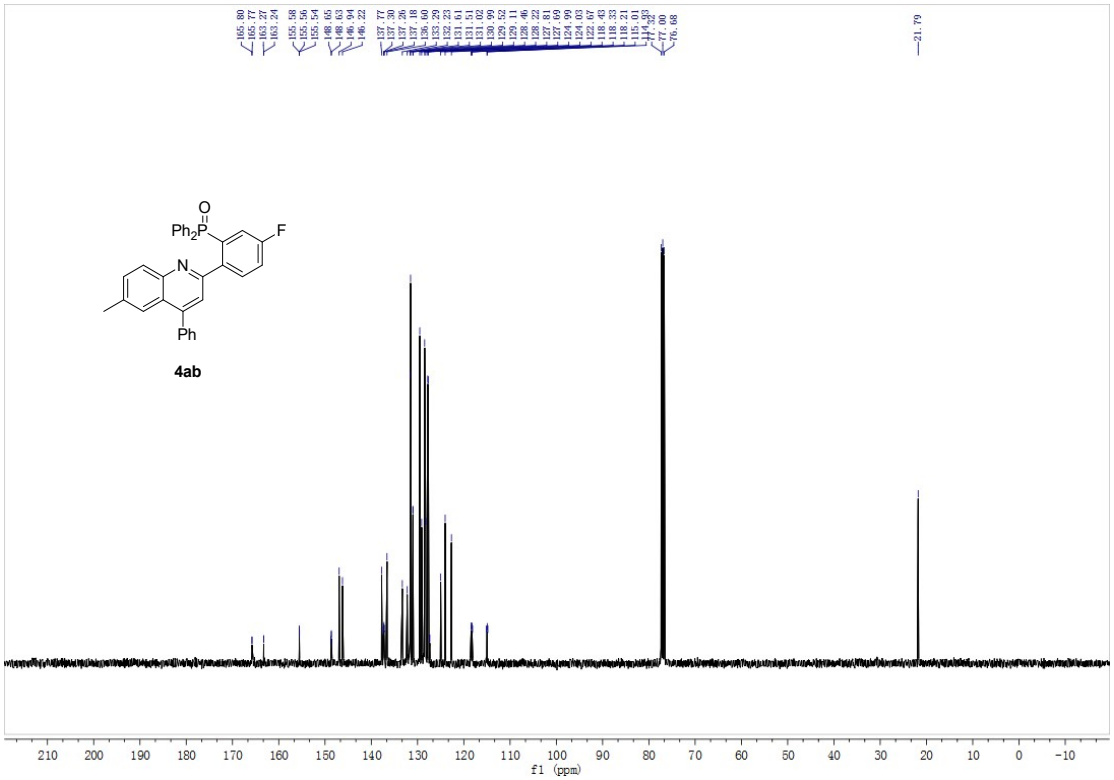


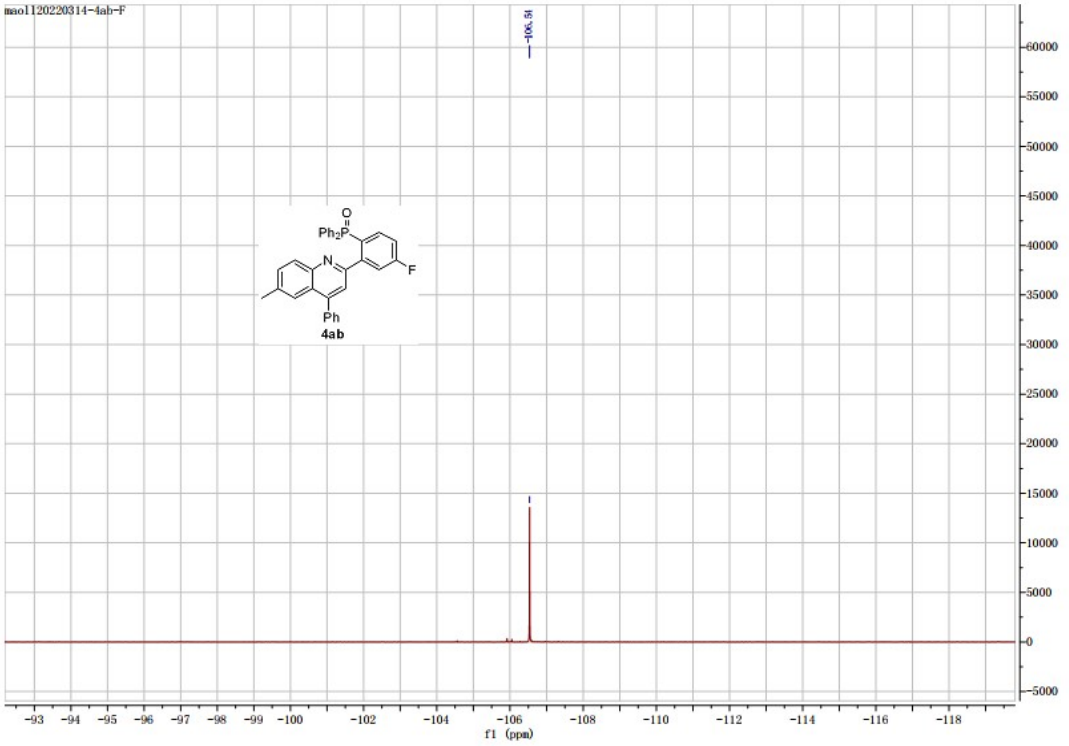
156.495
156.454
137.959
136.227
131.642
131.546
131.273
130.827
130.800
129.546
129.085
128.409
128.111
127.717
127.595
123.993
113.950
111.559
111.438
101.889
77.318
77.000
76.682
21.735
Ph2P
O
N
O
O
Ph
f1 (ppm)

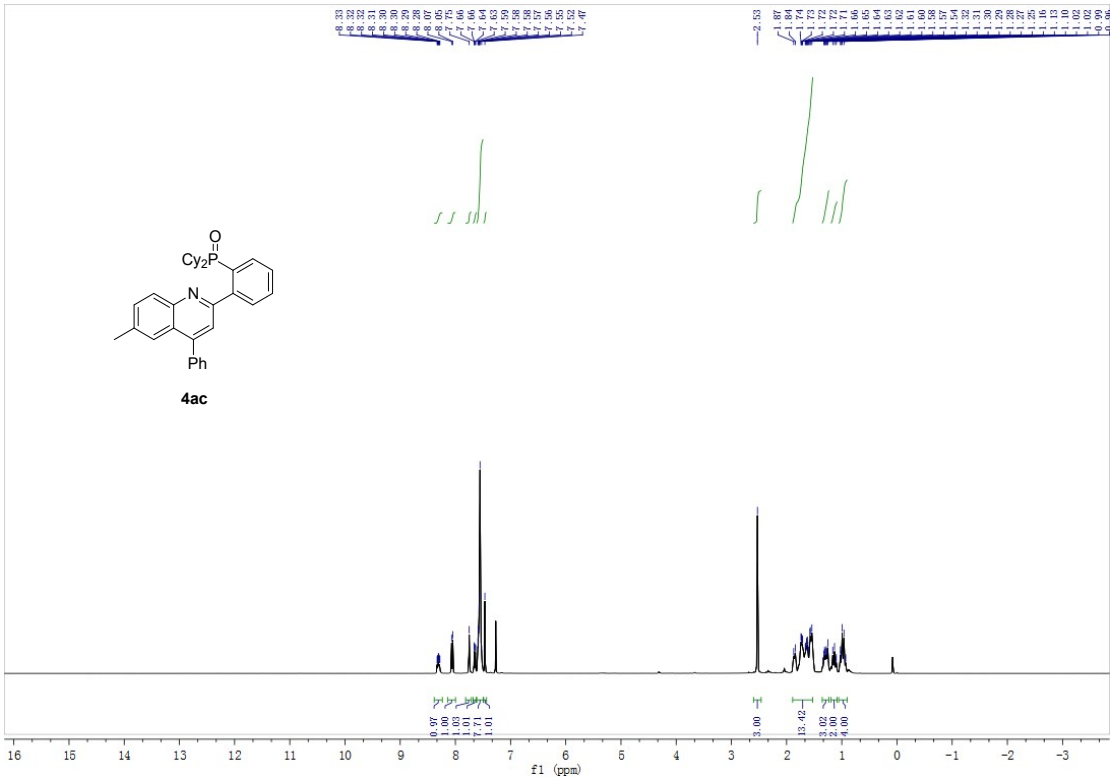
4aa

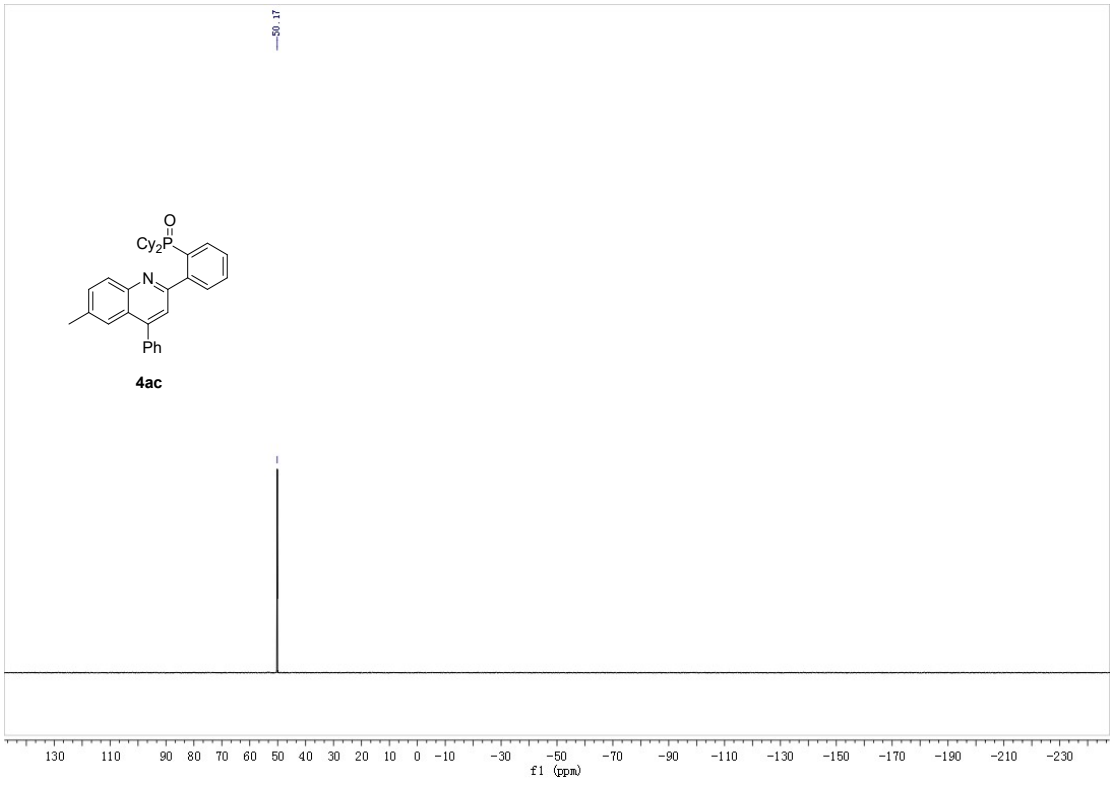

O
Ph2P
F
N
Ph
4ab
f1 (ppm)

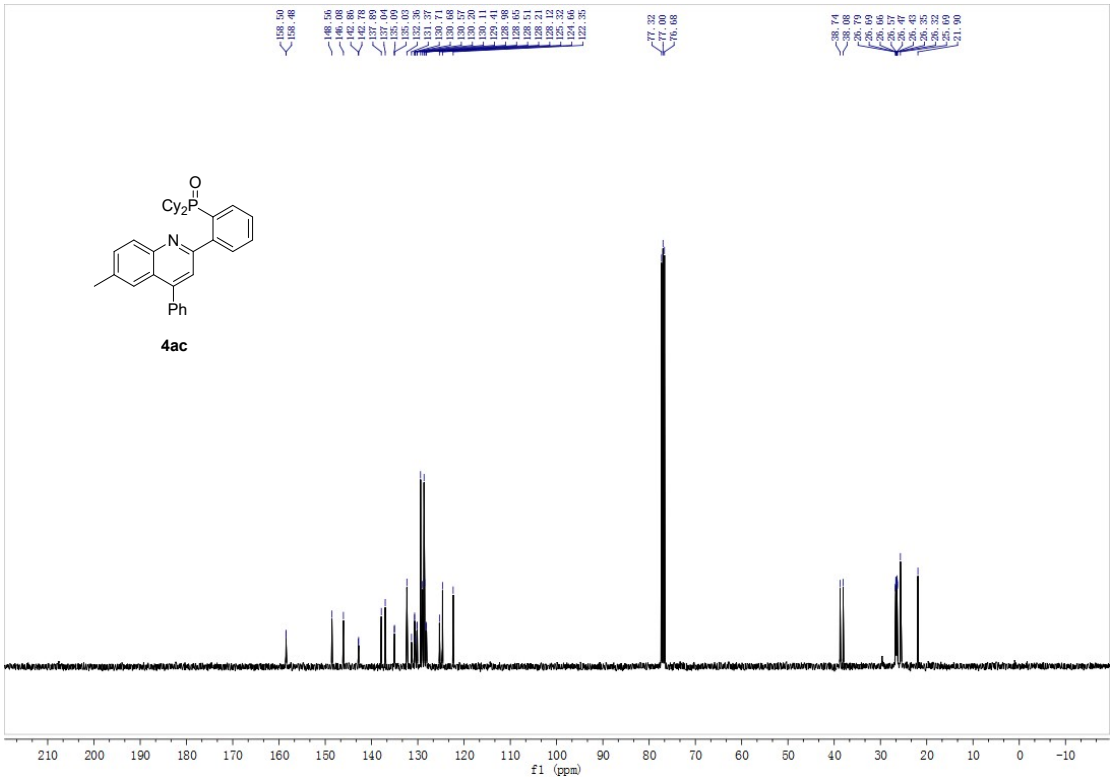

O
Ph2P
F
N
Ph
4ab
f1 (ppm)

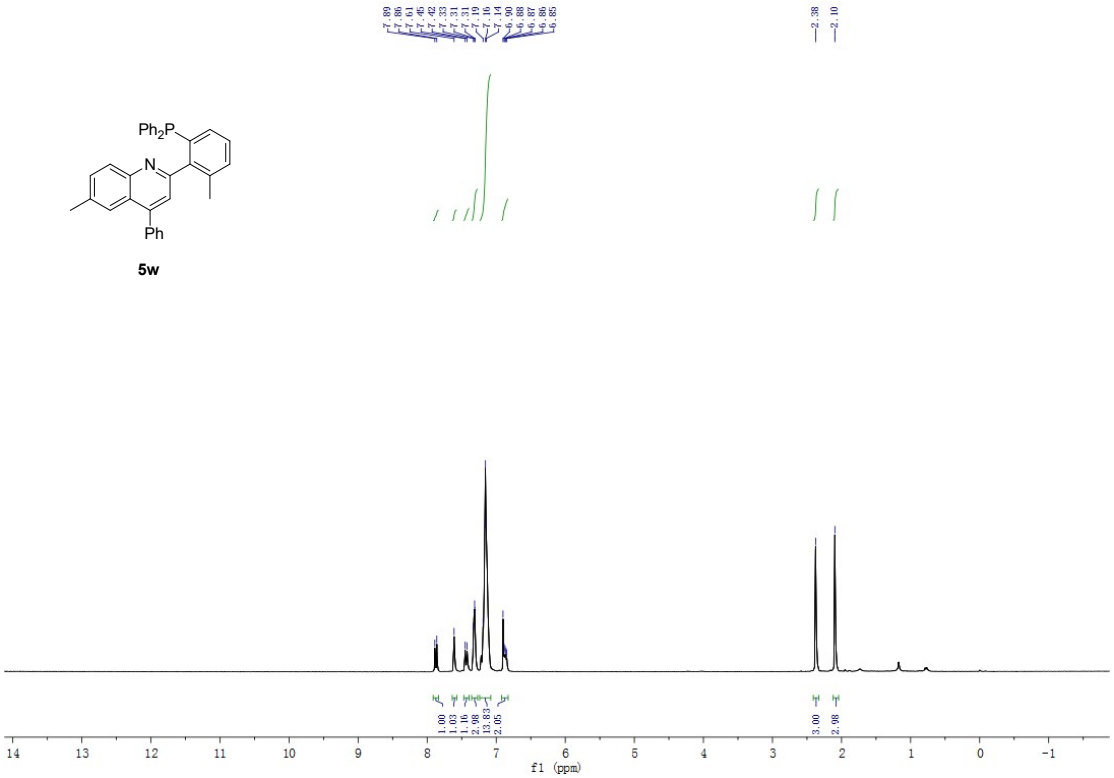

4ab
f1 (ppm)

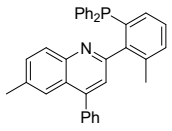

mao1120220314-4ab-F
4ab
f1 (ppm)


O
Cy2P
N
Ph
4ac
f1 (ppm)


O
Cy2P
N
Ph
4ac
f1 (ppm)

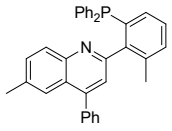

158.50
158.48
148.56
146.08
145.86
142.78
137.89
137.04
135.69
135.03
132.36
131.37
130.71
130.68
130.57
130.20
130.11
129.44
128.98
128.65
128.51
128.21
128.12
125.32
124.66
122.35
77.32
77.00
76.68
38.74
38.08
26.79
26.69
26.66
26.57
26.47
26.45
26.35
26.32
25.69
21.90
O
Cy2P
N
Ph
4ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.89
7.86
7.64
7.46
7.42
7.33
7.31
7.31
7.19
7.16
7.14
6.90
6.88
6.87
6.86
6.85
2.38
2.10
Ph2P
N
Ph
5w
1.00
1.03
1.16
2.98
13.83
2.05
3.00
2.98
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

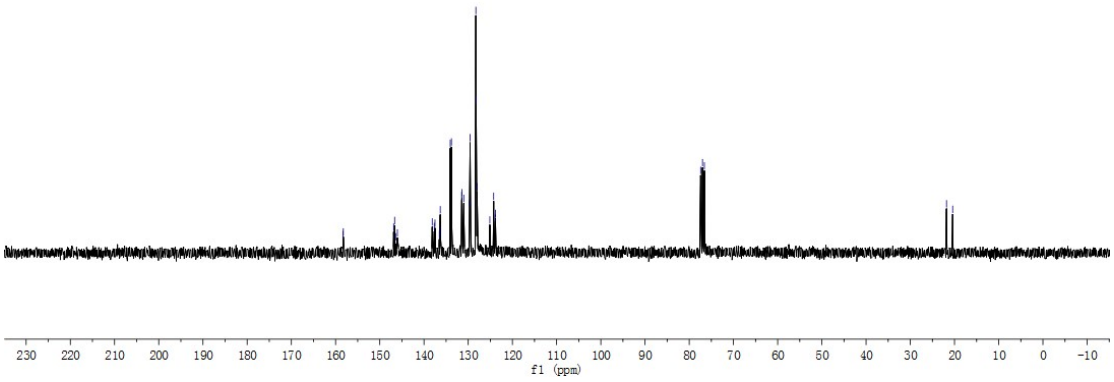

Ph2P
N
Ph

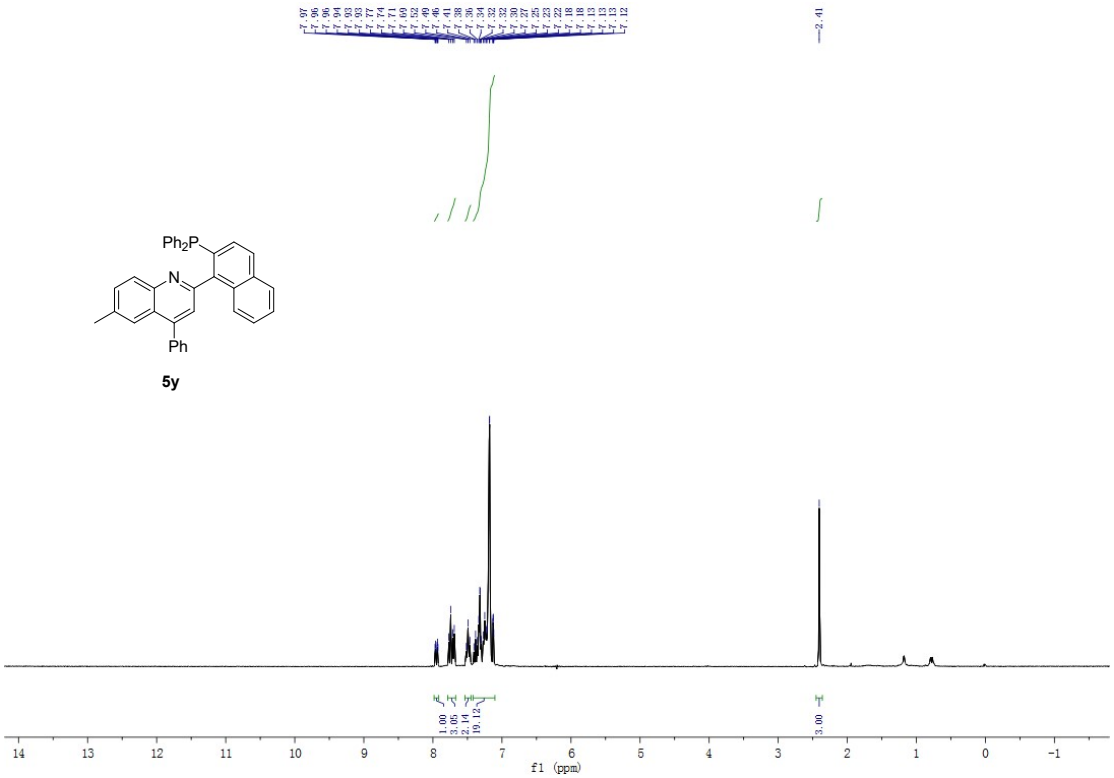
5w

12.15
40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
f1 (ppm)
158.32
158.25
146.87
146.64
146.41
146.02
138.14
137.68
137.51
136.53
136.45
136.32
134.06
133.79
131.49
131.42
131.00
129.70
129.57
128.37
128.18
127.99
125.11
124.24
123.88
123.84
77.42
77.00
76.58
21.80
20.41


Ph2P
N
Ph

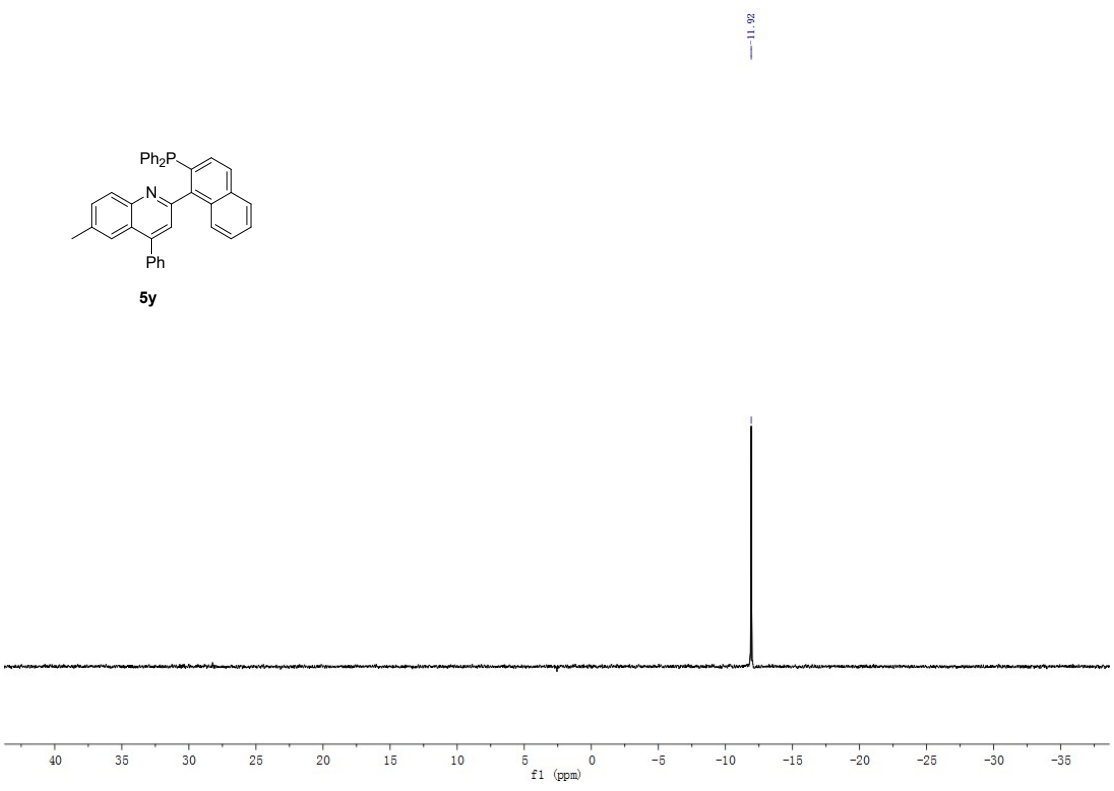
5w


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.97
7.96
7.96
7.94
7.93
7.77
7.74
7.71
7.69
7.52
7.49
7.46
7.41
7.38
7.36
7.34
7.32
7.32
7.30
7.27
7.25
7.22
7.22
7.18
7.13
7.13
7.13
7.12
2.41
1.00
3.05
2.14
10.18
3.00
f1 (ppm)

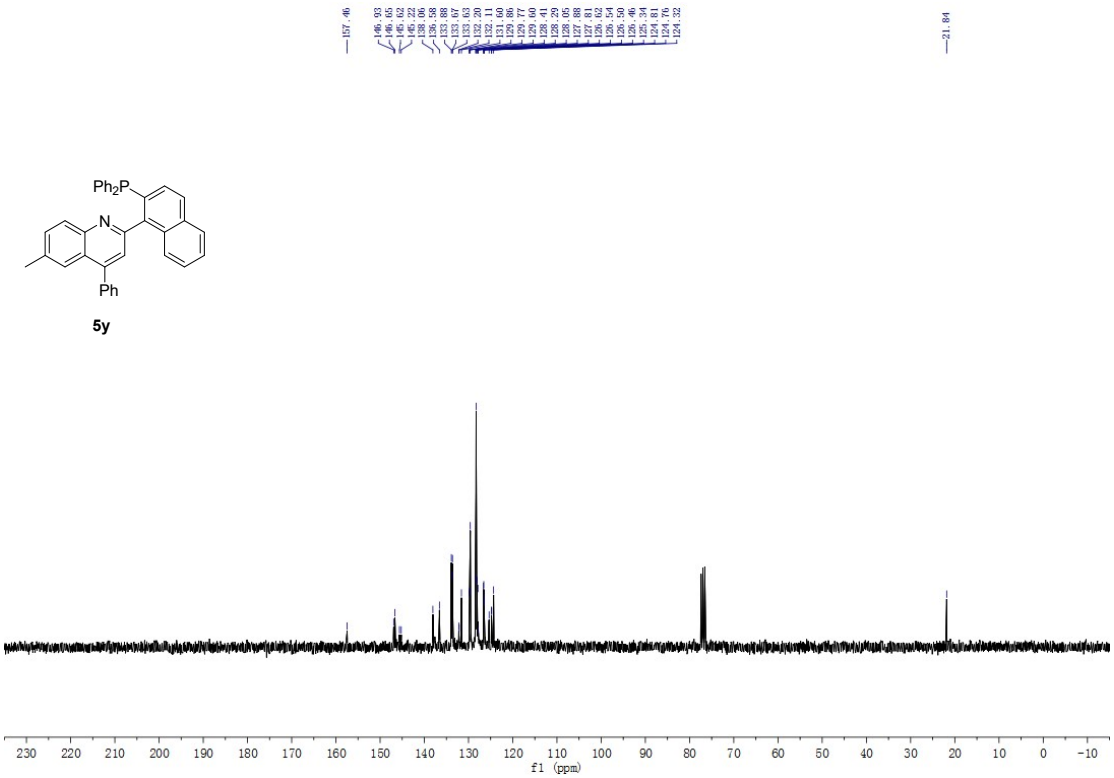
Ph2P
N
Ph

5y


11.92
f1 (ppm)

Ph2P
N
Ph

5y


157.46
146.93
146.65
145.62
145.22
138.06
136.58
133.88
133.67
133.63
132.20
132.11
131.60
129.86
129.77
129.60
128.41
128.29
128.05
127.88
127.81
126.62
126.54
126.50
126.46
125.34
124.81
124.76
124.32
21.84
Ph2P
N
Ph
5y
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)