Electronic Supplementary Information

Ruthenium/acid Co-catalyzed Reductive *α*-Phosphinoylation of 1,8-Naphthyridines with Diarylphosphine Oxides

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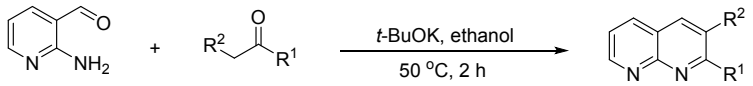
General Information

All the obtained products were characterized by melting points (m.p.), ^{1}H-NMR, ^{13}C-NMR, and mass spectra (MS), the NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. Additionally, all the new compounds were further characterized by high resolution mass spectra (HRMS). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; ^{1}H-NMR, ^{13}C-NMR spectra were obtained on Bruker-500 or 400; Mass spectra were recorded on Trace DSQ GC/MS，High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; All the reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC), and used without further purification.

Substrates preparation

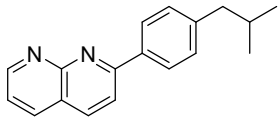
The preparation of 1,8-naphthyridines **1** was similar to the literature procedure[1,2]. 2-Amino-3-pyridinecarboxaldehyde (5 mmol), ketones (5 mmol), *t*-BuOK (20 mol %), and ethanol (10 mL) were introduced into a flask (50 mL). Then, it was stirred at 50 ^{o}C under atmosphere for 2 hours. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by column chromatography eluting with petroleum ether and ethyl acetate in a volume ratio of 2 : 1.

Table S1. Synthesis of substrates 1,8-naphthyridines



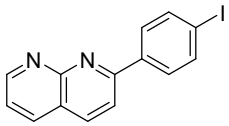
Entry	R^1	R^2	**1**
1	R^1=4-isobutyl-Ph	R^2=H	**1f**
2	R^1=4-IPh	R^2=H	**1l**
3	R^1=4-FPh	R^2=Et	**1t**

2-(4-isobutylphenyl)-1,8-naphthyridine (1f)



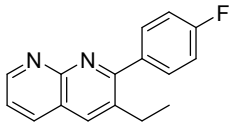
Unknown compound, white solid, m.p.: 105-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.22 (d, *J* = 7.2 Hz, 2H), 8.14 – 8.01 (m, 2H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.28 (d, *J* = 7.3 Hz, 2H), 2.53 (d, *J* = 6.8 Hz, 2H), 1.96 – 1.85 (m, 1H), 0.94 (s, 3H), 0.92 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 156.1, 153.6, 144.1, 137.6, 136.7, 135.9, 129.6, 127.7, 121.5, 119.4, 45.2, 30.1, 22.4. HRMS (ESI): Calcd. for $C_{18}H_{19}N_2$ $[M+H]^+$: 263.1543; found: 263.1537.

2-(4-iodophenyl)-1,8-naphthyridine (1l)



Unknown compound, brown solid, m.p.: 138.7-140.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.20 – 8.08 (m, 2H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.40 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 155.9, 153.9, 138.0, 137.9, 137.8, 136.8, 129.4, 121.9, 121.8, 119.1, 97.0. HRMS (ESI): Calcd. for $C_{14}H_{10}IN_2$ $[M+H]^+$: 332.9883; found: 332.9876.

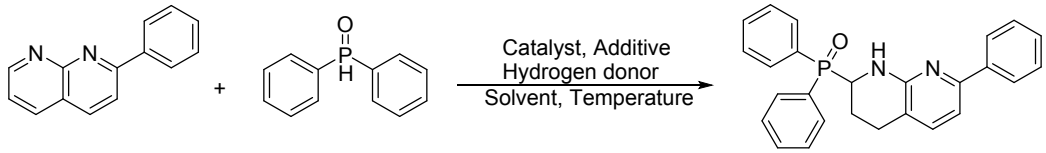
3-ethyl-2-(4-fluorophenyl)-1,8-naphthyridine (1t)



Unknown compound, white solid, m.p.: 138.0-138.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 – 9.00 (m, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 8.05 (s, 1H), 7.62 (dd, *J* = 8.1, 5.6 Hz, 2H), 7.43 (dd, *J* = 8.0, 4.2 Hz, 1H), 7.14 (t, *J* = 8.6 Hz, 2H), 2.85 (q, *J* = 7.4 Hz, 2H), 1.20 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, *J* = 249.5 Hz), 162.2, 154.4, 153.0, 136.4, 136.2, 136.2, 136.2, 136.0, 130.9 (d, *J* = 8.2 Hz), 121.9 (d, *J* = 4.6 Hz), 114.9 (d, *J* = 21.5 Hz), 25.8, 14.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.3. HRMS (ESI): Calcd. for $C_{16}H_{14}FN_2$ $[M+H]^+$: 253.1136; found: 253.1130.

Optimization of reaction conditions

Table S2 Screening of optimal reaction conditions. [a]

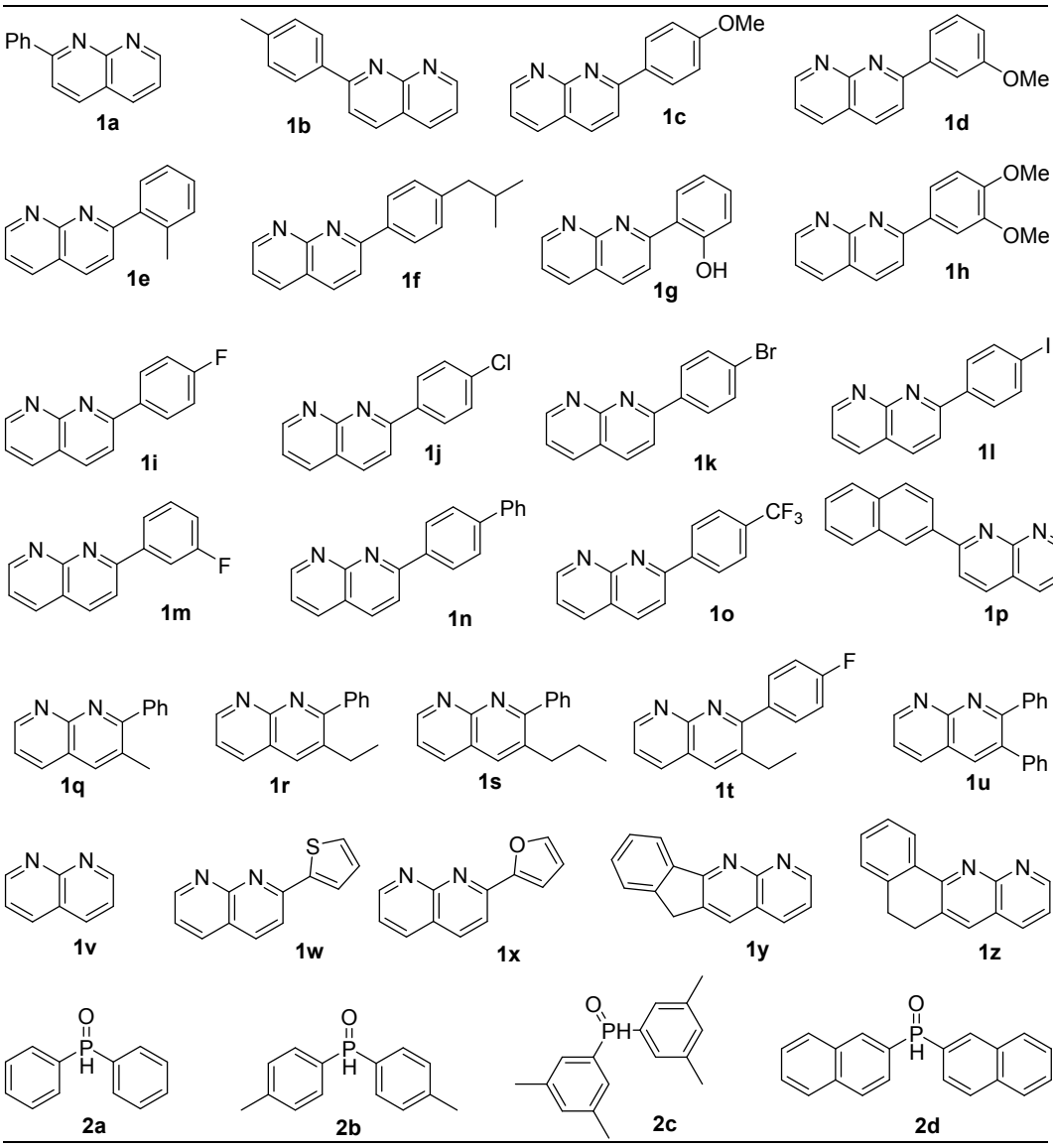


Entry	Catalyst	Hydrogen	Additive	Yield% of **3aa** [b]
1	$Pd(OAc)_2$	HCOOH	*p*-TSA	0
2	$[Cp^*IrCl_2]_2$	HCOOH	*p*-TSA	<10
3	$[Ru(p\text{-cymene})Cl_2]_2$	HCOOH	*p*-TSA	11
4	$Ru_3(CO)_{12}$	HCOOH	*p*-TSA	43
5	**$Ru_3(CO)_{12}$**	**HCOOH**	**CSA**	**75**
6	$Ru_3(CO)_{12}$	HCOOH	-	10
7	-	HCOOH	CSA	0
8	$Ru_3(CO)_{12}$	-	CSA	0
9	$Ru_3(CO)_{12}$	HCOOH	PhCOOH	21
10	$Ru_3(CO)_{12}$	HCOOH	CF_3COOH	15
11	$Ru_3(CO)_{12}$	HCOOH	$p\text{-}NO_2PhCOOH$	0
12	$Ru_3(CO)_{12}$	HCOOH	NaOTf	40
13	$Ru_3(CO)_{12}$	HCOOH	$NaSO_2CF_3$	32
14	$Ru_3(CO)_{12}$	HCOOH	$Zn(OTf)_2$	45
15	$Ru_3(CO)_{12}$	HCOOH	$Hf(OTf)_4$	26
16	$Ru_3(CO)_{12}$	*i*-Propanol	CSA	0
17	$Ru_3(CO)_{12}$	HCOONa	CSA	0
18	$Ru_3(CO)_{12}$	$(HCHO)_n$	CSA	0
19	$Ru_3(CO)_{12}$	Triethylsilane	CSA	10
20	$Ru_3(CO)_{12}$	HCOOH	CSA	(0,30,21,0,39)[c]
21	$Ru_3(CO)_{12}$	HCOOH	CSA	(58,63)[d]
22	$Ru_3(CO)_{12}$	HCOOH	CSA	(70,71)[e]
23	$Ru_3(CO)_{12}$	HCOOH	CSA	(66,67)[f]
24	$Ru_3(CO)_{12}$	HCOOH	CSA	(62,69,73)[g]

[a]Conditions: unless otherwise stated, all the reactions were performed with **1a** (0.25 mmol), **2a** (0.30 mmol), catalyst (2 mol %), hydrogen donor (4.0 equiv.), additive (0.1 equiv.), *p*-xylene (1.0 mL) at 120 °C for 16 h; [b]Separation yield by silica gel plate. [c]Yields obtained with DMSO, *t*-amyl alcohol, 1,4-dioxane, DMF, toluene as the solvents, respectively. [d]Yield obtained with 3 and 5 equiv. HCOOH, respectively. [e]Yields obtained with 0.25 and 0.375 mmol **2a**, respectively. [f] Yields obtained with 0.05 and 0.15 eq. CSA. Respectively. [g]Yields obtained at 100 °C, 110 °C, 130 °C.

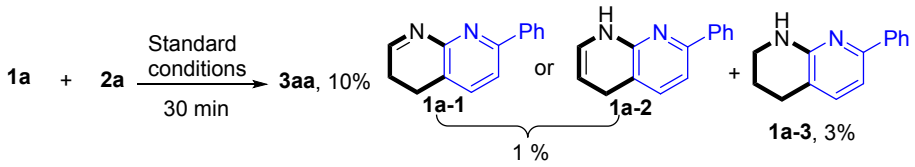
Typical Procedure for the Synthesis of product 3aa

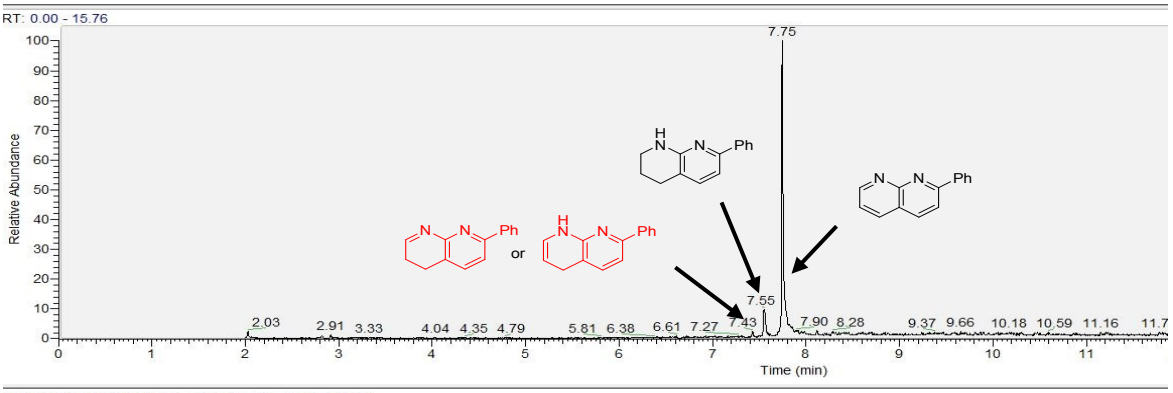
Under N_2 atmosphere, $Ru_3(CO)_{12}$ (2 mol%), CSA (10 mol%), formic acid (4 eq.), 1,8-naphthalidine **1a** (0.25 mmol), diarylphosphine oxide **2a** (0.30 mmol) and *p*-xylene (1 mL) were introduced in a Schlenk tube (50 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 120 °C for 16 h. After cooling down to room temperature, the reaction mixture was purified by preparative TLC on silica, eluting with petroleum ether (60-90 °C): ethyl acetate (1 : 1) to give product **3aa** as white solid.

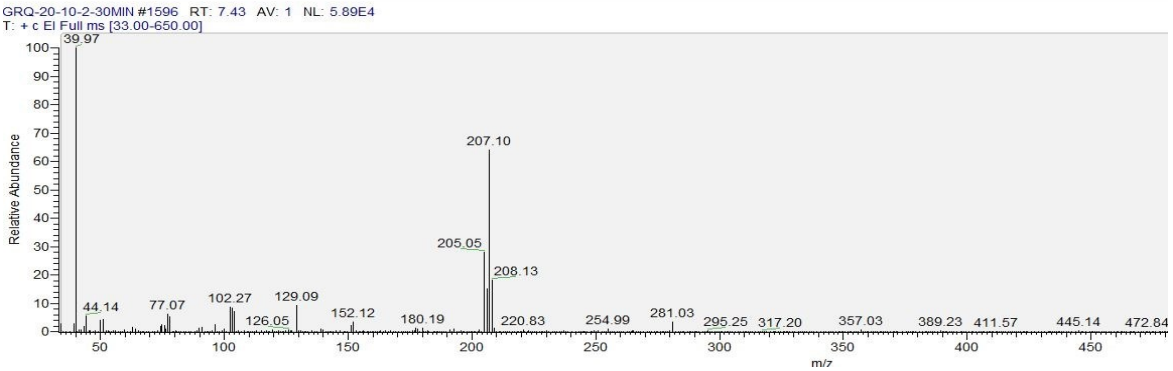


Scheme S1. Substrates employed for the transformation

Control experiment







Deuterium labeling experiment

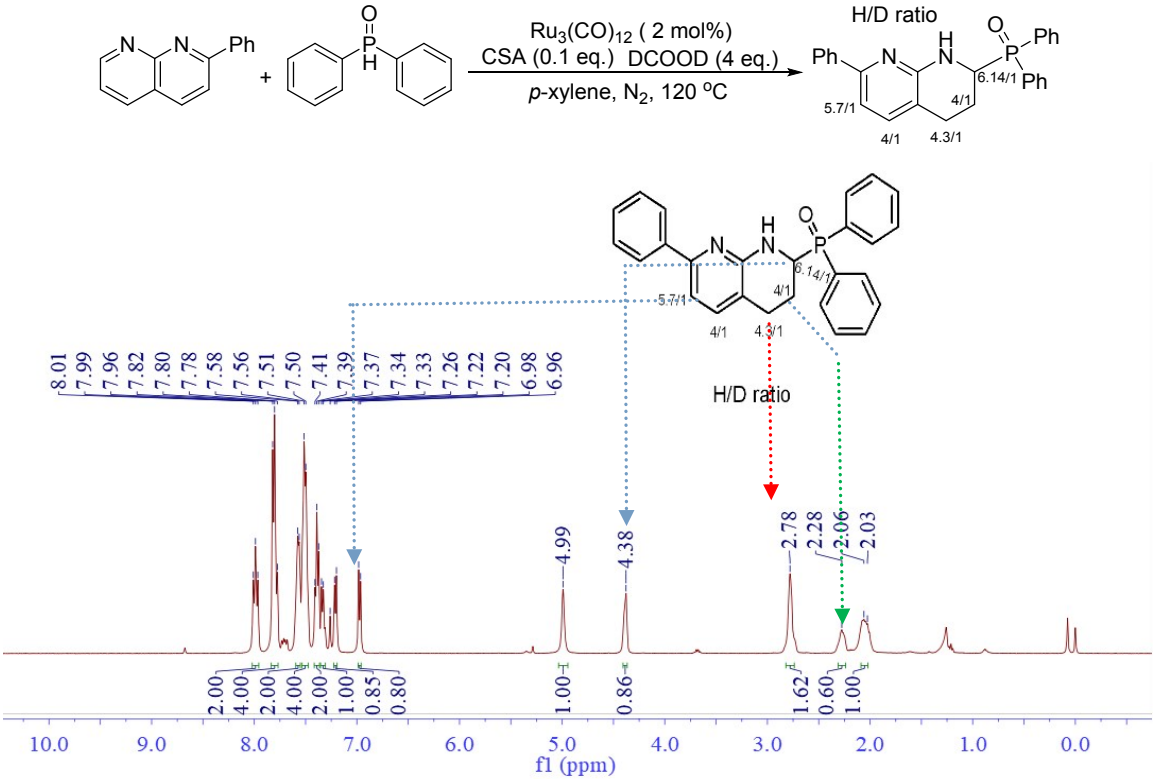


Figure S4. ^{1}H-NMR spectrum of deuterated **3aa**

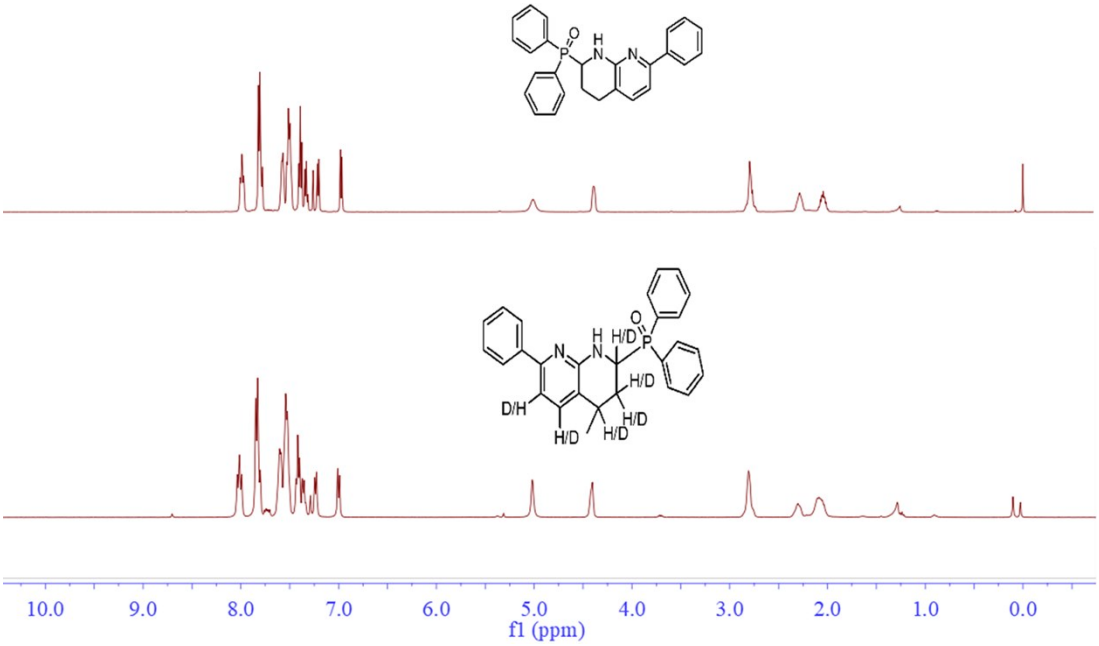


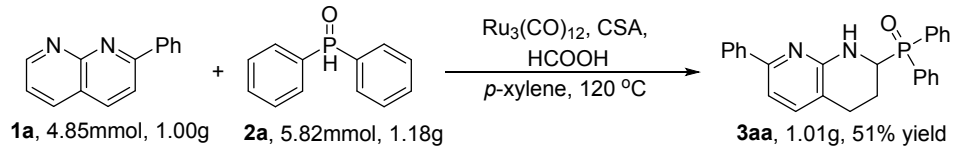
Figure S5. ^{1}H-NMR spectrum of compound **3aa** *vs* deuterated **3aa**

Confirmatory experiment

To confirm the product structure, synthesis of 2-methyl-7-phenyl-1,8-naphthyridine[3]: Under N_2 atmosphere, In a Schlenk tube of 50 mL, 2-phenyl-1,8-naphthyridine **1a** (41.2 mg, 0.2 mmol), *t*-BuONa (0.4 mmol, 2.0 equiv), and 1-phenylethanol (0.2 mmol, 1 equiv) were dissolved in DMSO (2 mL) under visible light irradiation (blue LEDs, 3W) and stirred at 100 °C for 8 h, irradiation was conducted in a photochemical reactor equipped with visible light irradiation (420 nm<λ<780 nm). After completion of the reaction, the resulting solution was cooled to room temperature; the solution was diluted with ethyl acetate (10 mL), washed with water (5 mL), extracted with ethyl acetate (3×5 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by preparative TLC on silica gel to give the desired product (**1a'**) (Known compound: CAS: 5174-96-9). Then, in a Schlenk tube of 50 mL ,**1a'**and **2a** were reacted under the standard conditions. After a series of post-treatment similar to standard reactions would less (2-methyl-7-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridin-4-yl)diphenylphosphine oxide (**1aa'**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, *J* = 8.7 Hz, 2H), 8.07 – 8.00 (m, 2H), 7.92 (d, *J* = 7.3 Hz, 2H), 7.75 – 7.67 (m, 1H), 7.59 – 7.54 (m, 1H), 7.53 – 7.45 (m, 5H), 7.44 – 7.36 (m, 5H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 5.20 (brs, 1H), 2.77 – 2.66 (m, 1H), 2.58 – 2.48 (m, 1H), 2.33 – 2.23 (m, 1H), 2.05 – 1.92 (m, 1H), 1.48 (d, *J* = 13.1 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.2. HRMS (ESI): Calcd. for $C_{27}H_{26}N_2OP$ $[M+H]^+$: 425.1777; found: 425.1767. The results were obtained by comparing hydrogen in high frequency region, the structure **3aa** is correct.

Derivatioztion

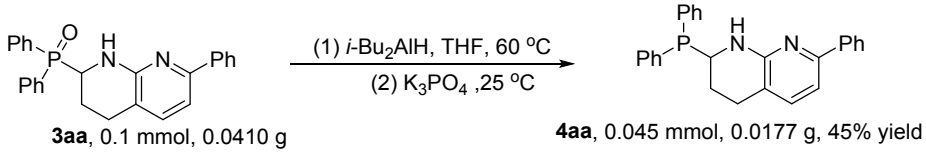
(1) Gram-scale synthesis of compound **3aa**



1a, 4.85mmol, 1.00g **2a**, 5.82mmol, 1.18g **3aa**, 1.01g, 51% yield

Under N_2 atmosphere, $Ru_3(CO)_{12}$ (2 mol%), CSA (0.1 eq.), methane acid (4 eq.), 1,8-naphthalidine **1a** (4.85 mmol), diarylphosphine oxide **2a** (5.82 mmol) and *p*-xylene (10 mL) were introduced in a Schlenk tube (100 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 120 ℃ for 16 h. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by flash column chromatography, eluting with petroleum ether (60-90 ℃): ethyl acetate (2 : 1) to give product **3aa** as white solid.

(2) Synthesis of compound 2-(diphenylphosphaneyl)-7-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridine **4aa**

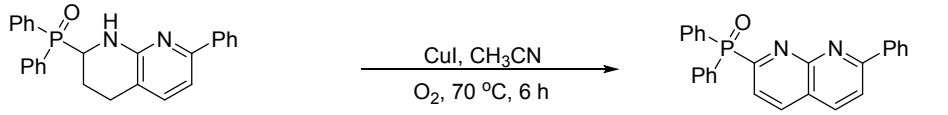


3aa, 0.1 mmol, 0.0410 g **4aa**, 0.045 mmol, 0.0177 g, 45% yield

Under N_2 atmosphere, the Schlenk tube (50 mL) was charged with **3aa** (0.0410 g, 0.10 mmol) in THF (1.0 mL) and diisobutyl hydroaluminium (0.0455 g, 0.32 mmol) was the dropped. After the resulting solution was heated at 60 ℃ for 12 h, After the end of the reaction which cooled to 25 ℃. Then drop the potassium phosphate solution (1.2 mmol, 0.2547g in 2.4 mL H_2O) into the schlenk tube. Next Stirring for 1 h fastly after mixing. After the reaction, the resulting mixture extract with aether, the combined organic layers were dried with anhydrous Na_2SO_4, then concentrated under vacuum. The residue was directly purified by preparative TLC on silica to give product **4aa** as a pale yellow solid. m.p.: 78.9-80.1 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.75 – 7.67 (m, 2H), 7.55 – 7.50 (m, 2H), 7.46 – 7.39 (m, 8H), 7.35 (d, *J* = 6.9 Hz, 1H), 7.29 – 7.23 (m, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 5.04 (s, 1H), 4.40 (d, *J* = 5.3 Hz, 1H), 3.04 – 2.95 (m, 1H), 2.84 – 2.70 (m, 1H), 2.18 – 2.10 (m, 1H), 1.96 – 1.86 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (d, *J* = 2.1 Hz), 154.4, 140.0, 136.9, 135.8 (d, *J* = 15.3 Hz), 134.5 (d, *J* = 19.9 Hz), 134.1 (d, *J* = 14.4 Hz), 133.2 (d, *J* = 18.6 Hz), 129.8, 129.1, 128.9, 128.9, 128.8, 128.7, 128.6, 128.5, 128.2, 126.7, 114.8, 110.4, 50.7 (d, *J* = 10.0 Hz), 25.9 (d, *J* = 13.0 Hz), 24.3 (d, *J* = 17.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -9.4. HRMS (ESI): Calcd. for $C_{26}H_{24}N_2P$ $[M+H]^+$: 395.1672; found: 395.1664.

(3) Synthesis of compound diphenyl(7-phenyl-1,8-naphthyridin-2-yl)phosphine oxide **5aa**



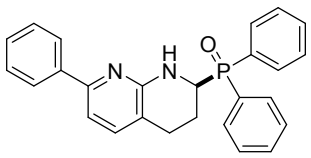
3aa, 0.1 mmol, 0.0410 g

5aa, 0.058 mmol, 0.0235 g, 60% yield

Under O_2 balloon atmosphere, CuI (0.0051 g, 30 mol%) and acetonitrile (1.0 mL) were introduced in a Schlenk tube (50 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 70 ℃ for 6 h. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with petroleum ether (60-90 ℃): ethyl acetate (1 : 1) to give product **5aa** as white solid. m.p.: 101-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 7.3, 4.7 Hz, 1H), 8.37 (dd, *J* = 7.8, 3.9 Hz, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 8.19 (d, *J* = 6.8 Hz, 2H), 8.07 (dd, *J* = 11.2, 7.9 Hz, 4H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.54 – 7.49 (m, 5H), 7.49 – 7.43 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 160.8, 155.7 (d, *J* = 22.7 Hz), 138.3 (d, *J* = 59.1 Hz), 137.3 (d, *J* = 9.5 Hz), 132.5, 132.4, 132.0 (d, *J* = 2.6 Hz), 131.3, 130.3, 129.0, 128.5, 128.4, 128.2, 124.3 (d, *J* = 20.4 Hz), 122.1 (d, *J* = 2.4 Hz), 121.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.6. HRMS (ESI): Calcd. for $C_{26}H_{20}N_2OP$ $[M+H]^+$: 407.1308; found: 407.1299.

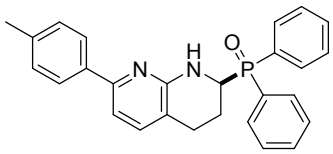
Analytical Data of the Obtained Compounds

(1) Diphenyl(7-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)phosphine oxide (3aa)



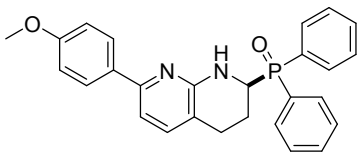
White solid (76.9 mg, 0.188 mmol, 75% yield); m.p.: 149.3-150.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.99 (t, *J* = 8.7 Hz, 2H), 7.80 (t, *J* = 10.1 Hz, 4H), 7.62 – 7.55 (m, 2H), 7.54 – 7.46 (m, 4H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 5.01 (s, 1H), 4.39 (d, *J* = 5.0 Hz , 1H), 2.90 – 2.68 (m, 2H), 2.34 – 2.23 (m, 1H), 2.12 – 1.95 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) : δ 154.6 (d, *J* = 6.7 Hz), 154.2, 139.7, 136.8, 132.2 (d, *J* = 7.0 Hz), 131.8 (d, *J* = 8.2 Hz), 131.3 (d, *J* = 8.9 Hz), 130.5 (d, *J* = 94.6 Hz), 129.1, 128.9, 128.8, 128.6, 128.5, 128.4, 128.1, 126.6, 114.7, 111.0, 77.3, 77.0, 76.8, 51.3 (d, *J* = 82.4 Hz), 25.3, 25.2, 20.8. ^{31}P NMR (202 MHz, $CDCl_3$) : δ 29.9. HRMS (ESI): Calcd. for $C_{26}H_{24}N_2OP$ $[M+H]^+$: 411.1621; found: 411.1609.

(2) Diphenyl(7-(p-tolyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)phosphine oxide (3ba)



White solid (55.1 mg, 0.130 mmol, 52% yield); m.p.: 202.5-203.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.98 – 7.92 (m, 2H), 7.80 – 7.75 (m, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.57 – 7.45 (m, 6H), 7.18 (t, *J* = 6.9 Hz, 3H), 6.94 (d, *J* = 7.5 Hz, 1H), 5.12 (s, 1H), 4.34 (d, *J* = 6.1 Hz, 1H), 2.84 – 2.71 (m, 2H), 2.35 (s, 3H), 2.29 – 2.19 (m, 1H), 2.07 – 1.98 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 154.8 (d, *J* = 7.1 Hz), 154.4, 138.2, 137.0, 132.6 (d, *J* = 2.8 Hz), 132.4 (dd, *J* = 6.2, 2.3 Hz), 132.1 (d, *J* = 8.4 Hz), 131.5 (d, *J* = 8.9 Hz), 130.9 (d, *J* = 97.0 Hz), 130.5 (d, *J* = 115.1 Hz), 129.3, 129.1, 129.0, 128.8, 128.7, 126.7, 114.6, 110.9, 51.5 (d, *J* = 82.1 Hz), 25.4 (d, *J* = 9.8 Hz), 21.3, 21.0.^{31}P NMR (162 MHz, $CDCl_3$) : δ 29.9. HRMS (ESI): Calcd. for $C_{27}H_{26}N_2OP$ $[M+H]^+$: 425.1777; found: 425.1765.

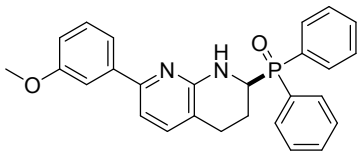
(3) (7-(4-methoxyphenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphos- phine oxide (3ca)



Kelly solid (67.1 mg, 0.153 mmol, 61% yield); m.p.: 184.8-185.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) : δ 8.02 – 7.96 (m, 2H), 7.82 – 7.76 (m, 4H), 7.60 – 7.55 (m, 2H), 7.53 – 7.47 (m, 4H), 7.18 (d, *J* = 7.6 Hz, 1H),

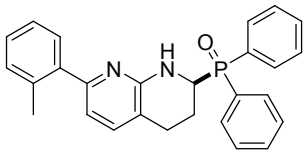
6.92 (d, *J* = 8.4 Hz, 3H), 4.99 (s, 1H), 4.38 (d, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 2.82 – 2.73 (m, 2H), 2.31 – 2.24 (m, 1H), 2.08 – 2.00 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) : δ 160.0, 154.6 (d, J = 7.8 Hz), 154.1, 137.1, 132.5 (dd, *J* = 5.5, 2.5 Hz), 132.2 (d, *J* = 8.3 Hz), 131.6 (d, *J* = 8.9 Hz), 130.7 (d, *J* = 95.1 Hz), 129.1, 129.0, 128.8, 128.7, 128.4, 127.9, 114.1, 113.9, 110.6, 55.3, 51.7 (d, *J* = 82.5 Hz), 25.5 (d, *J* = 10.7 Hz), 21.2. ^{31}P NMR (202 MHz, $CDCl_3$) : δ 30.0. HRMS (ESI): Calcd. for $C_{27}H_{26}N_2O_2P$ $[M+H]^+$: 441.1726; found: 441.1715.

(4) (7-(3-methoxyphenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphos phine oxide (3da)



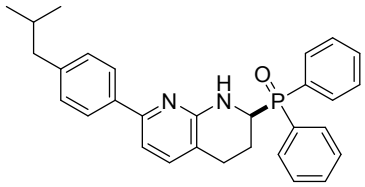
Yellow (59.4mg, 0.135 mmol, 54% yield); m.p.: 146.8-147.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 2H), 7.84 – 7.74 (m, 2H), 7.59 – 7.45 (m, 6H), 7.40 (d, *J* = 9.6 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 5.23 (s, 1H), 4.35 (d, *J* = 5.0 Hz, 1H), 3.83 (s, 3H), 2.91 – 2.63 (m, 2H), 2.31 – 2.16 (m, 1H), 2.11 – 1.97 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 159.9, 154.8 (d, *J* = 7.3 Hz), 154.2, 141.4, 137.1, 132.4 (dd, *J* = 6.2, 2.5 Hz), 132.1 (d, *J* = 8.5 Hz), 131.5 (d, *J* = 8.9 Hz), 130.6 (d, *J* = 95.0 Hz), 129.1, 129.0, 128.9, 128.7, 128.4, 119.2, 115.1, 114.1, 112.1, 111.3, 77.5, 77.2, 76.9, 55.3, 51.6 (d, *J* = 82.1 Hz), 25.5 (d, *J* = 10.2 Hz), 21.0. ^{31}P NMR (162 MHz, $CDCl_3$) : δ 29.9. HRMS (ESI): Calcd. for $C_{27}H_{26}N_2O_2P$ $[M+H]^+$: 441.1726; found: 441.1714.

(5) (S)-diphenyl(7-(o-tolyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)phosphine oxide (3ea)



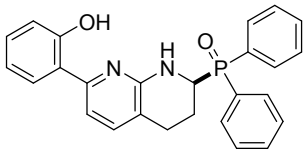
Yellow solid (66.8mg, 0.158 mmol, 63% yield); m.p.: 132.2-132.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.96 – 7.90 (m, 2H), 7.80 – 7.74 (m, 2H), 7.58 – 7.52 (m, 2H), 7.51 – 7.43 (m, 4H), 7.28 – 7.26 (m, 1H), 7.23 – 7.17 (m, 4H), 6.60 (d, *J* = 7.4 Hz, 1H), 5.17 (s, 1H), 4.34 – 4.29 (m, 1H), 2.89 – 2.73 (m, 2H), 2.29 (s, 3H), 2.28 – 2.20 (m, 1H), 2.09 – 1.99 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 156.6, 154.3 (d, *J* = 6.8 Hz), 140.7, 136.6, 135.6, 132.4 (d, *J* = 2.6 Hz), 132.4, 132.2 (d, *J* = 8.3 Hz), 131.5 (d, *J* = 8.9 Hz), 131.2, 130.6, 130.2, 129.2, 129.1, 129.0, 128.8, 128.7, 127.9, 125.8, 114.2, 51.4 (d, *J* = 81.9 Hz), 25.5 (d, *J* = 9.9 Hz), 20.9, 20.3. ^{31}P NMR (162 MHz, $CDCl_3$) : δ 30.0. HRMS (ESI): Calcd. for $C_{27}H_{26}N_2OP$ $[M+H]^+$: 425.1777; found: 425.1766.

(6) (S)-(7-(4-isobutylphenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphosphine oxide (3fa)



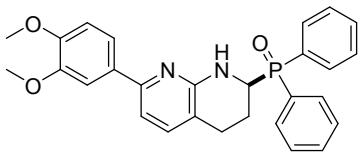
Kelly solid (53.6 mg, 0.115 mmol, 46% yield); m.p.: 165.0-165.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.00 – 7.95 (m, 2H), 7.79 (dd, *J* = 10.7, 7.6 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.52 – 7.47 (m, 4H), 7.17 (t, *J* = 7.1 Hz, 3H), 6.95 (d, *J* = 7.5 Hz, 1H), 5.03 (s, 1H), 4.36 (d, *J* = 5.6 Hz, 1H), 2.81 – 2.73 (m, 2H), 2.48 (d, *J* = 7.1 Hz, 2H), 2.31 – 2.22 (m, 1H), 2.08 – 1.99 (m, 1H), 1.90 – 1.82 (m, 1H), 0.90 (s, 3H), 0.88 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) : δ 154.74 (d, *J* = 7.3 Hz), 154.57, 142.00, 137.35, 137.04, 132.61 (d, *J* = 2.8 Hz), 132.42 (dd, *J* = 5.9, 2.5 Hz), 132.09 (d, *J* = 8.4 Hz), 131.52 (d, *J* = 8.9 Hz), 130.77, 130.65, 130.21, 129.35, 129.08, 128.99, 128.97, 128.87, 128.81, 128.70, 126.48, 114.52, 111.03, 51.59 (d, *J* = 82.3 Hz), 45.17, 30.25, 25.48 (d, *J* = 10.0 Hz), 22.40, 21.05. ^{31}P NMR (162 MHz, $CDCl_3$) : δ 30.0. HRMS (ESI): Calcd. for $C_{30}H_{32}N_2OP$ $[M+H]^+$: 467.2247; found: 467.2235.

(7) (S)-(7-(2-hydroxyphenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphos-phine oxide (3ga)



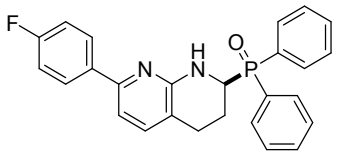
Yellow solid (68.2 mg, 0.1600 mmol, 64% yield); m.p.: 196.4-197.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.82 (s, 1H), 7.93 – 7.88 (m, 2H), 7.82 – 7.77 (m, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.52 – 7.47 (m, 4H), 7.21 (t, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 4.92 (s, 1H), 4.35 (d, *J* = 4.3 Hz, 1H), 2.83 – 2.76 (m, 1H), 2.72 – 2.65 (m, 1H), 2.24 – 2.15 (m, 1H), 2.07 – 1.99 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) : δ 159.0, 153.9, 151.9 (d, *J* = 6.1 Hz), 137.9, 132.6 (d, *J* = 3.7 Hz), 131.8 (d, *J* = 8.5 Hz), 131.5 (d, *J* = 8.8 Hz), 130.8, 130.6, 130.6, 129.1, 129.0, 128.9, 128.9, 126.2, 119.5, 118.8, 118.0, 114.5, 109.3, 51.2 (d, *J* = 80.6 Hz), 25.2 (d, *J* = 9.9 Hz), 20.9. ^{31}P NMR (162 MHz, $CDCl_3$) : δ 29.7. HRMS (ESI): Calcd. for $C_{26}H_{24}N_2O_2P$ $[M+H]^+$: 427.1570; found: 427.1557.

(8) (7-(3,4-dimethoxyphenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl) diphenylphos -phine oxide (3ha)



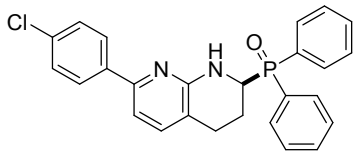
Yellow solid (62.3 mg, 0.133 mmol, 53% yield); m.p.: 146.8-147.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.02 – 7.96 (m, 2H), 7.84 – 7.77 (m, 2H), 7.60 – 7.55 (m, 2H), 7.54 – 7.48 (m, 4H), 7.44 (s, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 5.02 (s, 1H), 4.38 (d, *J* = 7.9 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 2.82 – 2.73 (m, 2H), 2.28 – 2.21 (m, 1H), 2.10 – 2.00 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6 (d, *J* = 7.5 Hz), 154.1, 149.4, 149.0, 137.1, 132.5 (dd, *J* = 8.4, 2.4 Hz), 132.1 (d, *J* = 8.4 Hz), 131.6 (d, *J* = 8.9 Hz), 130.6 (d, *J* = 95.4 Hz)., 129.4, 129.1, 129.0, 128.9, 128.8, 119.1, 114.3, 111.0, 110.7, 109.9, 56.0, 51.6 (d, *J* = 82.1 Hz), 25.5 (d, *J* = 10.4 Hz), 21.1. ^{31}P NMR (162 MHz, $CDCl_3$) : δ 29.9. HRMS (ESI): Calcd. for $C_{28}H_{28}N_2O_3P$ $[M+H]^+$: 471.1832; found:471.1821.

(9) (S)-(7-(4-fluorophenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphos-phine oxide (3ia)



Yellow solid (78.1 mg, 0.1825 mmol, 73% yield); m.p.: 169.3-170.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.02 – 7.96 (m, 2H), 7.83 – 7.77 (m, 4H), 7.60 – 7.55 (m, 2H), 7.54 – 7.48 (m, 4H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 7.5 Hz, 1H), 4.98 (s, 1H), 4.39 (d, *J* = 6.2 Hz, 1H), 2.83 – 2.72 (m, 2H), 2.32 – 2.23 (m, 1H), 2.09 – 1.99 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) : δ 163.1 (d, J_{C-F} = 247.4 Hz), 154.7 (d, J_{C-P} = 7.3 Hz), 153.3, 137.2, 135.9 (d, J_{C-F} = 2.8 Hz), 132.5 (dd, J_{C-P} = 6.3, 2.4 Hz), 132.0 (d, J_{C-P} = 8.4 Hz), 131.5 (d, J_{C-P} = 8.9 Hz), 130.5 (d, J_{C-P} = 95.1 Hz), 129.4, 129.1, 129.0, 128.9, 128.8, 128.5, 128.4, 115.4 (d, J_{C-F} = 21.5 Hz), 114.9, 110.9, 51.5 (d, J_{C-P} = 81.9 Hz), 25.5 (d, J_{C-P} = 10.3 Hz), 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) : δ -114.0. ^{31}P NMR (162 MHz, $CDCl_3$) : δ 29.8. HRMS (ESI): Calcd. for $C_{26}H_{23}FN_2OP$ $[M+H]^+$: 429.1527; found: 429.1514.

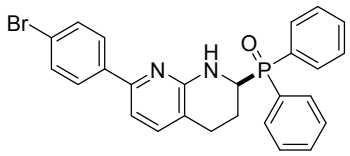
(10) (S)-(7-(4-chlorophenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphos-phine oxide (3ja)



White solid (66.6 mg, 0.1500 mmol, 60% yield); m.p.: 193.0-193.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.98 – 7.92 (m, 2H), 7.81 – 7.74 (m, 4H), 7.57 – 7.53 (m, 2H), 7.52 – 7.46 (m, 4H), 7.35 – 7.31 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 5.10 (s, 1H), 4.34 (dd, *J* = 8.4, 3.6 Hz, 1H), 2.86 – 2.79 (m, 1H), 2.77 – 2.69 (m, 1H), 2.26 – 2.18 (m, 1H), 2.09 – 2.00 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 154.8 (d, *J* = 7.1 Hz), 153.0, 138.2, 137.1, 134.3, 132.5 (dd, *J* = 6.5, 2.6 Hz), 132.0 (d, *J* = 8.4 Hz), 131.5 (d,

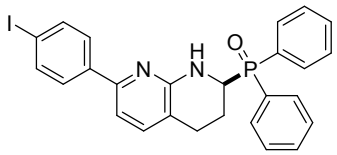
J = 8.9 Hz), 130.5 (d, *J* = 95.0 Hz), 131.0, 130.1, 129.4, 129.1, 129.0, 128.9, 128.8, 128.6, 128.4, 128.0, 115.3, 110.9, 51.5 (d, *J* = 81.7 Hz), 25.5 (d, *J* = 10.2 Hz), 21.0. ^{31}P NMR (162 MHz, $CDCl_3$) : δ 29.8. HRMS (ESI): Calcd. for $C_{26}H_{23}ClN_2OP$ $[M+H]^+$: 445.1231; found: 445.1219.

(11) (S)-(7-(4-bromophenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphos-phine oxide (3ka)



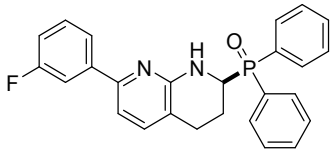
White solid (86.6 mg, 0.1775 mmol, 71% yield); m.p.: 206.5-206.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.00 – 7.94 (m, 2H), 7.83 – 7.77 (m, 2H), 7.72 – 7.68 (m, 2H), 7.59 – 7.55 (m, 2H), 7.54 – 7.48 (m, 6H), 7.19 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 5.05 (s, 1H), 4.38 (d, *J* = 6.1 Hz, 1H), 2.85 – 2.71 (m, 2H), 2.30 – 2.22 (m, 1H), 2.09 – 1.99 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 154.8 (d, *J* = 7.2 Hz), 153.1, 138.6, 137.1, 132.5 (dd, *J* = 6.1, 2.6 Hz), 132.1 (d, *J* = 8.4 Hz), 131.6, 131.5 (d, *J* = 9.0 Hz), 130.5 (d, *J* = 95.1 Hz), 129.4, 129.1, 129.0, 128.9, 128.8, 128.4, 128.3, 122.6, 115.3, 110.9, 51.6 (d, *J* = 81.7 Hz), 25.5 (d, *J* = 10.3 Hz), 21.0. ^{31}P NMR (162 MHz, $CDCl_3$) : δ 29.8. HRMS (ESI): Calcd. for $C_{26}H_{23}BrN_2OP$ $[M+H]^+$: 489.0726; found: 489.0710.

(12) (S)-(7-(4-iodophenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphosphine oxide (3la)



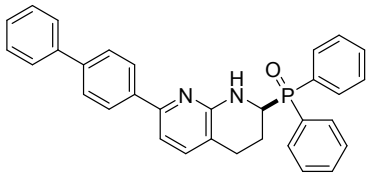
Yellow solid (111.2 mg, 0.2075 mmol, 83% yield); m.p.: 151.1-151.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.01 – 7.96 (m, 2H), 7.83 – 7.79 (m, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.56 (m, 4H), 7.54 – 7.50 (m, 4H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 4.91 (s, 1H), 4.42 – 4.38 (m, 1H), 2.81 – 2.75 (m, 2H), 2.31 – 2.24 (m, 1H), 2.07 – 2.02 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 154.8 (d, *J* = 6.7 Hz), 153.0, 139.2, 137.5, 137.1, 132.6, 132.6, 132.5 (d, *J* = 7.1 Hz), 131.9 (d, *J* = 7.9 Hz), 131.5 (d, *J* = 8.7 Hz), 130.9, 130.7, 130.6, 129.1, 129.0, 128.9, 128.8, 128.5, 115.4, 110.8, 94.3, 51.4 (d, *J* = 81.2 Hz), 25.4 (d, *J* = 10.1 Hz), 21.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.8. HRMS (ESI): Calcd. for $C_{26}H_{23}IN_2OP$ $[M+H]^+$: 537.0587; found: 537.0573.

(13) (S)-(7-(3-fluorophenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphos-phine oxide (3ma)



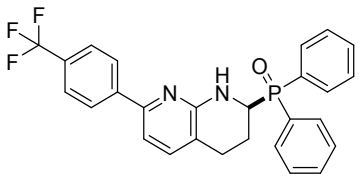
Yellow solid (64.2 mg, 0.1500 mmol, 60% yield); m.p.: 148.0-148.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.01 – 7.95 (m, 2H), 7.84 – 7.78 (m, 2H), 7.62 – 7.55 (m, 4H), 7.54 – 7.48 (m, 4H), 7.36 – 7.31 (m, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.01 (td, *J* = 8.3, 2.2 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 5.00 (s, 1H), 4.39 (d, *J* = 5.3 Hz, 1H), 2.85 – 2.73 (m, 2H), 2.32 – 2.24 (m, 1H), 2.10 – 2.01 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 163.2 (d, J_{C-F} = 244.9 Hz), 154.8 (d, J_{C-P} = 7.1 Hz), 152.9, 142.1 (d, J_{C-F} = 7.5 Hz), 137.1, 132.5 (dd, J_{C-P} = 5.5, 2.6 Hz), 132.5, 132.5, 132.0 (d, J_{C-P} = 8.4 Hz), 131.5 (d, J_{C-P} = 8.9 Hz), 131.0, 130.5 (d, J_{C-P} = 104.0 Hz), 130.0, 129.9, 129.3, 129.1, 129.0, 128.9, 128.8, 128.4, 122.2 (d, J_{C-F} = 2.6 Hz), 115.6, 115.1 (d, J_{C-F} = 21.3 Hz), 113.6 (d, J_{C-F} = 22.5 Hz), 111.2, 51.5 (d, J_{C-P} = 81.9 Hz), 25.5 (d, J_{C-P}= 10.3 Hz), 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) : δ -113.3. ^{31}P NMR (162 MHz, $CDCl_3$) : δ 29.8. HRMS (ESI): Calcd. for $C_{26}H_{23}FN_2OP$ $[M+H]^+$: 429.1527; found: 429.1513.

(14) (S)-(7-([1,1'-biphenyl]-4-yl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphosphine oxide (3na)



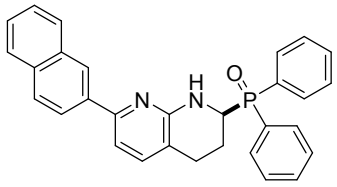
Yellow solid (85.1 mg, 0.1750 mmol, 70% yield); m.p.: 133.2-134.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.00 (t, *J* = 8.9 Hz, 2H), 7.90 (d, *J* = 7.4 Hz, 2H), 7.81 (t, *J* = 9.1 Hz, 2H), 7.65 – 7.57 (m, 6H), 7.53 – 7.49 (m, 4H), 7.44 (t, *J* = 7.1 Hz, 2H), 7.35 (t, *J* = 6.6 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 5.00 (s, 1H), 4.41 (d, *J* = 7.1 Hz, 1H), 2.83 – 2.76 (m, 2H), 2.35 – 2.26 (m, 1H), 2.04 – 1.94 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 154.8 (d, *J* = 6.5 Hz), 153.8, 141.0, 140.7, 138.7, 137.1, 132.6, 132.6, 132.4 (d, *J* = 7.1 Hz), 132.0 (d, *J* = 8.5 Hz), 131.5 (d, *J* = 8.6 Hz), 130.9, 130.8, 130.6, 129.1, 129.0, 129.0, 128.9, 128.8, 128.7, 127.4, 127.2, 127.2, 127.0, 115.0, 111.0, 51.5 (d, *J* = 83.0 Hz), 25.4 (d, *J* = 9.7 Hz), 21.0. ^{31}P NMR (162 MHz, $CDCl_3$) : δ 30.0. HRMS (ESI): Calcd. for $C_{32}H_{28}N_2OP$ $[M+H]^+$: 487.1934; found: 487.1918.

(15) (S)-diphenyl(7-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)phos-phine oxide (3oa)



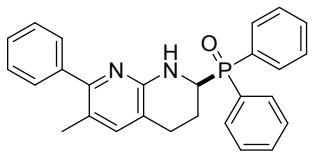
White solid (71.7 mg, 0.150 mmol, 60% yield); m.p.: 210.1-210.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.02 – 7.92 (m, 4H), 7.85 – 7.79 (m, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 7.1 Hz, 2H), 7.55 – 7.50 (m, 4H), 7.25 (d, 1H), 7.01 (d, J = 7.5 Hz, 1H), 5.01 (s, 1H), 4.40 (d, J = 6.3 Hz, 1H), 2.88 – 2.74 (m, 2H), 2.32 – 2.23 (m, 1H), 2.10 – 2.03 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 154.9 (d, J_{C-P} = 7.0 Hz), 152.6, 143.0, 137.2, 132.5 (dd, J_{C-P} = 5.9, 2.7 Hz), 132.0 (d, J_{C-P} = 8.4 Hz), 131.5 (d, J_{C-P} = 8.9 Hz), 130.5 (d, J_{C-P} = 96.0 Hz), 130.1 (q, J_{C-F} = 32.3 Hz), 130.0, 129.4, 129.1, 129.0, 128.9, 128.8, 128.4, 127.0, 125.5, 125.5 (q, J_{C-F} = 3.7 Hz), 125.4, 124.3 (q, J_{C-F} = 273.4 Hz), 116.0, 111.5, 51.5 (d, J_{C-P} = 81.5 Hz), 25.5 (d, J_{C-P} = 10.2 Hz), 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) : δ -62.5. ^{31}P NMR (162 MHz, $CDCl_3$) : δ 29.8. HRMS (ESI): Calcd. for $C_{27}H_{23}F_3N_2OP$ $[M+H]^+$: 479.1495; found: 479.1483.

(16) (S)-(7-(naphthalen-2-yl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphosphine oxide (3pa)



Yellow solid (82.8 mg, 0.1800 mmol, 72% yield); m.p.: 201.1-201.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.34 (s, 1H), 8.03 – 7.98 (m, 3H), 7.93 – 7.85 (m, 3H), 7.83 – 7.78 (m, 2H), 7.61 – 7.57 (m, 2H), 7.55 – 7.48 (m, 6H), 7.28 (d, J = 8.2 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H), 5.20 (s, 1H), 4.41 – 4.36 (m, 1H), 2.90 – 2.78 (m, 2H), 2.34 – 2.26 (m, 1H), 2.11 – 2.06 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 155.0 (d, J = 7.0 Hz), 154.2, 137.1, 133.5, 133.4, 132.4 (dd, J = 10.5, 2.3 Hz), 132.0 (d, J = 8.4 Hz), 131.5 (d, J = 8.8 Hz), 130.6 (d, J = 94.4 Hz), 129.5, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 128.2, 127.7, 126.2 (d, J = 2.4 Hz), 125.9, 124.9, 115.1, 111.5, 51.5 (d, J = 81.8 Hz), 25.5 (d, J = 9.4 Hz), 21.1. ^{31}P NMR (162 MHz, $CDCl_3$) : δ 29.9. HRMS (ESI): Calcd. for $C_{30}H_{26}N_2OP$ $[M+H]^+$: 461.1777; found: 461.1762.

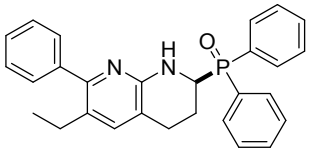
(17) (S)-(6-methyl-7-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphosphine oxide (3qa)



Kelly liquid (58.3 mg, 0.1375 mmol, 55% yield); m.p.: 105.8 -106.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ

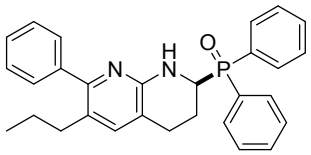
7.99 – 7.91 (m, 2H), 7.80 – 7.73 (m, 2H), 7.54 – 7.49 (m, 2H), 7.48 – 7.42 (m, 4H), 7.39 – 7.36 (m, 4H), 7.33 – 7.29 (m, 1H), 7.06 (s, 1H), 5.25 (brs, 1H), 4.33 (d, J = 4.3 Hz, 1H), 2.89 – 2.81 (m, 1H), 2.80 – 2.71 (m, 1H), 2.26 – 2.20 (m, 1H), 2.10 (s, 3H), 2.05 – 1.95 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6 (d, J = 7.4 Hz), 139.5, 132.4 (d, J = 1.8 Hz), 132.2 (d, J = 8.4 Hz), 131.5 (d, J = 9.0 Hz), 130.8 (d, J = 94.9 Hz), 130.8, 130.7, 129.2, 129.1, 129.0, 128.8, 128.8, 128.6, 128.1, 127.6, 120.3, 115.3, 51.5 (d, J = 82.7 Hz), 25.3 (d, J = 9.6 Hz), 21.0, 18.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.2. HRMS (ESI): Calcd. for $C_{27}H_{26}N_2OP$ $[M+H]^+$: 425.1777; found: 425.1764.

(18) (6-ethyl-7-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphosphine oxide (3ra)



Yellow solid (81.0 mg, 0.1850 mmol, 74% yield); m.p.: 151.7-152.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 2H), 7.80 – 7.72 (m, 2H), 7.59 – 7.52 (m, 2H), 7.51 – 7.45 (m, 4H), 7.40 – 7.30 (m, 5H), 7.11 (s, 1H), 4.83 (brs, 1H), 4.39 (d, J = 7.7 Hz, 1H), 2.87 – 2.78 (m, 2H), 2.42 (q, J = 7.5 Hz, 2H), 2.36 – 2.26 (m, 1H), 2.07 – 1.90 (m, 1H), 1.03 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 152.6 (d, J = 7.5 Hz), 140.8, 137.6, 132.4, 132.2 (d, J = 8.3 Hz), 131.5 (d, J = 9.0 Hz), 130.9, 130.8, 130.7, 130.5 (d, J = 94.9 Hz), 130.5, 129.1, 129.0, 128.7, 128.7, 128.6, 128.1, 127.5, 126.9, 115.4, 77.6, 77.3, 76.9, 51.5 (d, J = 82.6 Hz), 25.5 (d, J = 10.1 Hz), 24.6, 21.1, 15.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.3. HRMS (ESI): Calcd. for $C_{28}H_{28}N_2OP$ $[M+H]^+$: 439.1934; found: 439.1921.

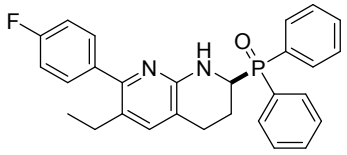
(19) Diphenyl(7-phenyl-6-propyl-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)phosphine oxide (3sa)



Kelly solid (46.3 mg, 0.1025 mmol, 41% yield); m.p.: 135.0-136.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 2H), 7.81 – 7.73 (m, 2H), 7.60 – 7.53 (m, 2H), 7.52 – 7.45 (m, 4H), 7.39 – 7.30 (m, 5H), 7.09 (s, 1H), 4.76 (brs, 1H), 4.42 (d, J = 8.3 Hz, 1H), 2.81 (t, J = 6.2 Hz, 2H), 2.37 (t, 3H), 2.11 – 1.93 (m, 1H), 1.41 (q, J = 15.2, 7.5 Hz, 2H), 0.78 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 152.5 (d, J = 7.7 Hz), 140.8, 138.2, 132.6 (d, J = 2.8 Hz), 132.4 (d, J = 1.3 Hz), 132.2 (d, J = 8.4 Hz), 131.5 (d, J = 9.0 Hz), 130.8 (d, J = 94.9 Hz), 130.8, 130.7, 129.1, 129.0 128.9, 128.7, 128.6, 128.1, 127.5, 125.4, 115.2, 51.5 (d, J = 82.8 Hz), 33.5, 25.5 (d, J = 10.4 Hz), 24.5, 21.0, 13.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.3. HRMS

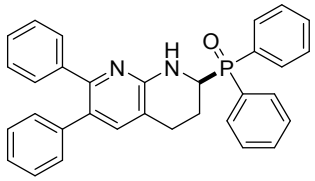
(ESI): Calcd. for $C_{29}H_{30}N_2OP$ $[M+H]^+$: 453.2090; found: 453.2078.

(20) (S)-(6-ethyl-7-(4-fluorophenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphosphine oxide (3ta)



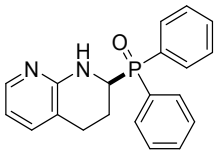
Yellow solid (51.3 mg, 0.1125 mmol, 45% yield); m.p.: 175.7-176.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.92 (m, 2H), 7.81 – 7.73 (m, 2H), 7.61 – 7.53 (m, 2H), 7.52 – 7.46 (m, 4H), 7.36 – 7.28 (m, 2H), 7.11 (s, 1H), 7.06 (t, J = 8.6 Hz, 2H), 4.74 (brs, 1H), 4.42 (d, J = 8.1 Hz, 1H), 2.98 – 2.70 (m, 2H), 2.40 (q, J = 7.5 Hz, 3H), 2.36 – 2.20 (m, 1H), 1.03 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, J_{C-F} = 246.3 Hz), 153.4, 152.5 (d, J_{C-P} = 7.7 Hz), 137.8, 136.8, 132.5, 132.2 (d, J_{C-P} = 8.4 Hz), 131.5 (d, J_{C-P} = 9.0 Hz), 131.1, 130.8 (d, J_{C-P} = 94.9 Hz), 130.7 (d, J_{C-P} = 11.4 Hz), 130.5, 130.4, 129.1, 129.0, 128.8, 128.7, 128.1, 127.0, 115.6, 115.0 (d, J_{C-F} = 21.4 Hz), 77.5, 77.2, 76.9, 51.5 (d, J_{C-P} = 82.3 Hz), 25.5 (d, J_{C-P} = 10.5 Hz), 24.5, 21.1, 15.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.2. HRMS (ESI): Calcd. for $C_{28}H_{27}FN_2OP$ $[M+H]^+$: 457.1840; found: 457.1827.

(21) (S)-(6,7-diphenyl-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphosphine oxide (3ua)



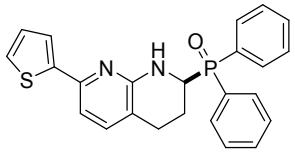
White solid (85.1 mg, 0.1750 mmol, 70% yield); m.p.: 122.8-123.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, J = 8.3 Hz, 2H), 7.80 – 7.74 (m, 2H), 7.60 – 7.53 (m, 2H), 7.53 – 7.46 (m, 4H), 7.24 – 7.21 (m, 3H), 7.20 – 7.14 (m, 6H), 7.04 (d, J = 6.9 Hz, 2H), 5.27 (s, 1H), 4.31 (d, 1H), 2.99 – 2.88 (m, 1H), 2.86 – 2.74 (m, 1H), 2.33 – 2.20 (m, 1H), 2.13 – 1.92 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0 (d, J = 6.0 Hz), 153.2, 140.4, 139.1, 132.6 (d, J = 2.9 Hz), 132.3 (dd, J = 6.5, 2.4 Hz), 132.0 (d, J = 8.5 Hz), 131.5 (d, J = 8.8 Hz), 130.8, 130.7, 130.6 (d, J = 93.9 Hz), 129.9, 129.6, 129.0, 128.9, 128.9, 128.8, 128.6, 128.1, 127.8, 127.4, 126.3, 126.2, 115.2, 51.3 (d, J = 82.0 Hz), 25.2 (d, J = 8.6 Hz), 21.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.0. HRMS (ESI): Calcd. for $C_{32}H_{28}N_2OP$ $[M+H]^+$: 487.1934; found: 487.1922.

(22) (S)-diphenyl(1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)phosphine oxide (3va)



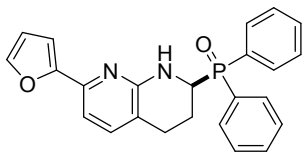
White solid (45.9 mg, 0.1375 mmol, 55% yield); m.p.: 181.1-182.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.92 (m, 2H), 7.86 (d, *J* = 4.7 Hz, 1H), 7.84 – 7.75 (m, 2H), 7.62 – 7.54 (m, 2H), 7.54 – 7.48 (m, 4H), 7.14 (d, *J* = 7.2 Hz, 1H), 6.55 (t, 1H), 4.78 (s, 1H), 4.37 (d, *J* = 8.9 Hz, 1H), 2.76 (t, *J* = 6.2 Hz, 2H), 2.38 – 2.22 (m, 1H), 2.06 – 1.87 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8 (d, *J* = 7.6 Hz), 146.0, 136.6, 132.5 (d, *J* = 2.2 Hz), 132.2 (d, *J* = 8.3 Hz), 131.5 (d, *J* = 9.0 Hz), 130.5 (d, *J* = 95.4 Hz), 129.2, 129.1, 128.9, 128.7, 128.0, 116.4, 114.2, 51.6 (d, *J* = 82.2 Hz), 25.8 (d, *J* = 11.0 Hz), 20.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.0. HRMS (ESI): Calcd. for $C_{20}H_{20}N_2OP$ $[M+H]^+$: 335.1308; found: 335.1298.

(23) (S)-diphenyl(7-(thiophen-2-yl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)phosphine oxide (3wa)



White solid (47.8 mg, 0.1150 mmol, 46% yield); m.p.: 189.5-190.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.84 – 7.76 (m, 2H), 7.60 – 7.53 (m, 2H), 7.53 – 7.46 (m, 4H), 7.45 – 7.41 (m, 1H), 7.26 (d, *J* = 5.1 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 4.0 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 4.96 (s, 1H), 4.38 (d, *J* = 6.2 Hz, 1H), 2.72 (s, 2H), 2.33 – 2.13 (m, 1H), 2.09 – 1.86 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5 (d, *J* = 7.3 Hz), 149.2, 145.0, 137.0, 132.5 (dd, *J* = 6.0, 2.4 Hz), 132.1 (d, *J* = 8.3 Hz), 131.6 (d, *J* = 8.9 Hz), 130.5 (d, *J* = 95.3 Hz), 129.1, 129.0, 128.9, 128.8, 128.4, 127.8, 126.3, 124.0, 114.8, 109.7, 77.5, 77.2, 76.9, 51.5 (d, *J* = 82.0 Hz), 25.5 (d, *J* = 10.4 Hz), 21.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.8. HRMS (ESI): Calcd. for $C_{24}H_{22}N_2OPS$ $[M+H]^+$: 417.1185; found: 417.1173.

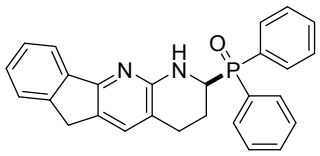
(24) (S)-(7-(furan-2-yl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)diphenylphosphine oxide (3xa)



White solid (42 mg, 0.105 mmol, 42% yield); m.p.: 168.3-169.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.94 (m, 2H), 7.84 – 7.73 (m, 2H), 7.61 – 7.53 (m, 2H), 7.53 – 7.47 (m, 4H), 7.44 (s, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 3.2 Hz, 1H), 6.43 (d, *J* = 1.3 Hz, 1H), 4.92 (s, 1H), 4.48 – 4.33 (m, 1H), 2.73 (t, *J* = 6.2 Hz, 2H), 2.36 – 2.16 (m, 1H), 2.11 – 1.90 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6 (d, *J* = 7.6 Hz), 153.7, 146.1, 142.7, 137.0, 132.5 (dd, *J* = 4.0, 2.0 Hz), 132.2 (d, *J* = 8.4

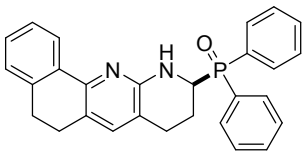
Hz), 131.5 (d, *J* = 9.0 Hz), 130.7 (d, *J* = 95.5 Hz), 129.2, 129.0, 128.9, 128.7, 128.1, 115.0, 111.7, 109.6, 107.6, 77.5, 77.1, 76.8, 51.6 (d, *J* = 82.2 Hz), 25.7 (d, *J* = 10.5 Hz), 21.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.9. HRMS (ESI): Calcd. for $C_{24}H_{22}N_2O_2P$ $[M+H]^+$: 401.1413; found: 401.1402.

(25) (S)-diphenyl(2,3,4,6-tetrahydro-1H-indeno[1,2-b][1,8]naphthyridin-2-yl)phosphine oxide (3ya)



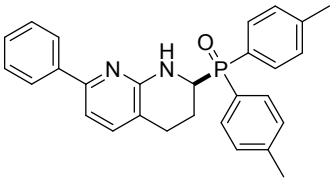
White solid (53.8 mg, 0.1275 mmol, 51% yield); m.p.: 148.0-148.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.99 (m, 2H), 7.88 – 7.76 (m, 3H), 7.60 – 7.56 (m, 2H), 7.55 – 7.46 (m, 5H), 7.39 – 7.28 (m, 3H), 4.91 (brs, 1H), 4.43 (d, *J* = 7.6 Hz, 1H), 3.66 (s, 2H), 2.80 (t, 2H), 2.39 – 2.26 (m, 1H), 2.14 – 1.98 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 154.5 (d, *J* = 7.7 Hz), 144.3, 141.0, 133.3, 132.5 (d, *J* = 2.4 Hz), 132.3 (d, *J* = 8.3 Hz), 131.6 (d, *J* = 9.0 Hz), 130.7 (d, *J* = 95.4 Hz), 129.2, 129.1, 128.8, 128.7, 127.6, 127.5, 126.9, 125.0, 120.1, 114.3, 51.9 (d, *J* = 82.8 Hz), 33.9, 26.3 (d, *J* = 10.8 Hz), 21.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.0. HRMS (ESI): Calcd. for $C_{27}H_{24}N_2OP$ $[M+H]^+$: 423.1621; found: 423.1606.

(26) (S)-(5,6,8,9,10,11-hexahydronaphtho[1,2-b][1,8]naphthyridin-10-yl)diphenylphosphine oxide (3za)



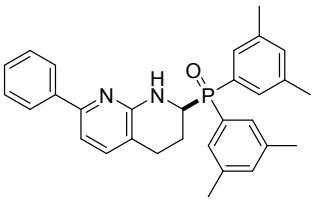
White solid (77.4 mg, 0.1775 mmol, 71% yield); m.p.: 142.5-143.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.97 (m, 3H), 7.85 – 7.77 (m, 2H), 7.63 – 7.56 (m, 2H), 7.55 – 7.48 (m, 4H), 7.24 (t, 1H), 7.21 (d, *J* = 7.1 Hz, 1H), 7.17 (d, *J* = 7.0 Hz, 1H), 7.01 (s, 1H), 4.78 (s, 1H), 4.38 (d, *J* = 8.7 Hz, 1H), 2.88 – 2.81 (m, 2H), 2.79 – 2.67 (m, 3H), 2.44 – 2.22 (m, 1H), 2.15 – 1.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6 (d, *J* = 8.0 Hz), 148.6, 138.1, 136.6, 134.7, 132.6 (d, *J* = 2.6 Hz), 132.5, 132.1 (d, *J* = 8.2 Hz), 131.6 (d, *J* = 8.8 Hz), 130.8, 130.7, 130.6 (d, *J* = 96.0 Hz), 129.1, 129.0, 128.9 (d, *J* = 2.9 Hz), 128.7, 128.3, 127.7, 126.9, 124.4, 122.4, 115.3, 51.8 (d, *J* = 82.8 Hz), 28.6, 27.0, 25.6 (d, *J* = 10.6 Hz), 21.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.1. HRMS (ESI): Calcd. for $C_{28}H_{26}N_2OP$ $[M+H]^+$: 437.1777; found: 437.1767.

(27) (S)-(7-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)di-p-tolylphosphine oxide (3ab)



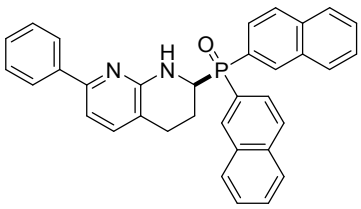
White solid (65.7 mg, 0.1500 mmol, 60% yield); m.p.: 178.0-178.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.73 (m, 4H), 7.66 – 7.60 (m, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.30 – 7.22 (m, 4H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 5.26 (s, 1H), 4.24 (d, *J* = 4.6 Hz, 1H), 2.89 – 2.78 (m, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 2.27 – 2.14 (m, 1H), 2.08 – 1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0 (d, *J* = 7.2 Hz), 154.4, 142.9, 139.9, 137.0, 132.0 (d, *J* = 8.7 Hz), 131.6 (d, *J* = 9.2 Hz), 130.7 (d, *J* = 11.8 Hz), 129.8, 129.7, 129.6, 129.4, 128.5, 128.3, 127.4 (d, *J* = 97.3 Hz), 126.9, 126.8, 126.1, 125.1, 114.9, 111.0, 51.6 (d, *J* = 82.5 Hz), 25.6 (d, *J* = 10.1 Hz), 21.7, 21.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.5. HRMS (ESI): Calcd. for $C_{28}H_{28}N_2OP$ $[M+H]^+$: 439.1934; found: 439.1920.

(28) (S)-bis(3,5-dimethylphenyl)(7-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)phosphine oxide (3ac)



White solid (67.6 mg, 0.1450 mmol, 58% yield); m.p.: 94.2-95.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 11.0 Hz, 2H), 7.42 (d, *J* = 11.5 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 3H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.18 (s, 3H), 6.94 (d, *J* = 7.5 Hz, 1H), 4.97 (s, 1H), 4.43 (d, *J* = 4.9 Hz, 1H), 2.80 – 2.72 (m, 2H), 2.35 (s, 6H), 2.33 (s, 6H), 2.26 – 2.20 (m, 1H), 2.15 – 2.07 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8 (d, *J* = 6.6 Hz), 154.5, 153.8, 140.0, 138.8, 138.7, 138.6, 138.5, 137.0, 134.2 (dd, *J* = 6.0, 2.7 Hz), 131.1, 130.1, 129.6 (d, *J* = 8.4 Hz), 128.9 (d, *J* = 8.9 Hz), 128.8, 128.6, 128.4 (d, *J* = 89.9 Hz), 128.2, 127.9, 126.7, 121.8, 119.7, 114.9, 111.1, 51.3 (d, *J* = 80.7 Hz), 25.5 (d, *J* = 9.9 Hz), 21.4, 20.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.3. HRMS (ESI): Calcd. for $C_{30}H_{32}N_2OP$ $[M+H]^+$: 467.2247; found: 467.2233.

(29) (S)-di(naphthalen-2-yl)(7-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)phosphine oxide (3ad)

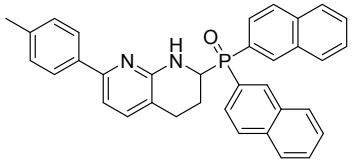


White solid (72.7 mg, 0.1425 mmol, 57% yield); m.p.: 195.2-195.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67

(d, *J* = 12.9 Hz, 1H), 8.41 (d, *J* = 12.9 Hz, 1H), 7.94 (dt, *J* = 19.9, 10.5 Hz, 6H), 7.87 – 7.84 (m, 2H), 7.82 – 7.77 (m, 2H), 7.55 (dt, *J* = 14.8, 7.0 Hz, 4H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 6.9 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 5.20 (brs, 1H), 4.56 (d, *J* = 5.1 Hz, 1H), 2.88 – 2.67 (m, 2H), 2.35 – 2.25 (m, 1H), 2.20 – 2.06 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8 (d, *J* = 7.5 Hz), 154.5, 139.8, 137.1, 135.0 (dd, *J* = 8.6, 2.2 Hz), 134.8 (d, *J* = 7.6 Hz), 133.9 (d, *J* = 8.6 Hz), 132.7 (d, *J* = 12.5 Hz), 129.1, 129.1 (dd, *J* = 8.0, 2.9 Hz), 129.0, 128.7, 128.6, 128.5, 128.3, 128.3, 127.9, 127.2 (d, *J* = 12.0 Hz), 126.7, 126.9 (d, *J* = 85.9 Hz), 126.6, 126.1, 126.0, 125.6, 114.9, 111.3, 77.5, 77.1, 76.8, 51.7 (d, *J* = 82.3 Hz), 25.6 (d, *J* = 10.5 Hz), 21.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.4.

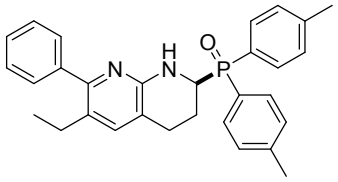
HRMS (ESI): Calcd. for $C_{34}H_{28}N_2OP$ $[M+H]^+$: 511.1934; found: 511.1928.

(30) (S)-di(naphthalen-1-yl)(7-(p-tolyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)phosphine oxide (3bd)



White solid (104.8 mg, 0.2000 mmol, 80% yield); m.p.: 198.1-198.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 12.8 Hz, 1H), 8.47 (d, *J* = 12.9 Hz, 1H), 8.06 – 7.95 (m, 4H), 7.94 – 7.86 (m, 4H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.65 – 7.54 (m, 4H), 7.21 (d, *J* = 7.3 Hz, 2H), 7.16 (d, *J* = 7.1 Hz, 1H), 6.94 (d, *J* = 7.1 Hz, 1H), 5.25 (s, 1H), 4.60 (d, *J* = 3.7 Hz, 1H), 2.89 – 2.71 (m, 2H), 2.38 (s, 3H), 2.35 – 2.30 (m, 1H), 2.24 – 2.13 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8 (d, *J* = 7.3 Hz), 154.4, 138.2, 137.0 (d, *J* = 4.3 Hz), 135.0 (dd, *J* = 9.1, 2.2 Hz), 134.8 (d, *J* = 7.4 Hz), 133.9 (d, *J* = 8.5 Hz), 132.7 (d, *J* = 12.4 Hz), 129.3, 129.1, 129.0, 129.0, 128.9, 128.7, 128.5, 128.5, 127.9, 127.2, 127.1, 126.8, 126.6, 126.5, 126.0 (d, *J* = 9.6 Hz), 125.3 (d, *J* = 12.5 Hz), 114.6, 111.0, 51.7 (d, *J* = 82.3 Hz), 25.6 (d, *J* = 10.1 Hz), 21.3, 21.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.4. HRMS (ESI): Calcd. for $C_{35}H_{30}N_2OP$ $[M+H]^+$: 525.2090; found: 525.2077.

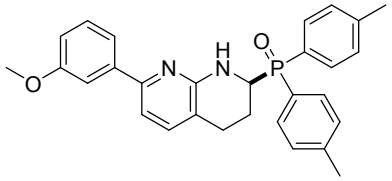
(31) (S)-(6-ethyl-7-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)di-p-tolylphosphine oxide (3rb)



White solid (75.7 mg, 0.1625 mmol, 65% yield); m.p.: 87.0-87.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 10.3, 8.2 Hz, 2H), 7.63 (dd, *J* = 10.8, 8.1 Hz, 2H), 7.41 – 7.33 (m, 4H), 7.33 – 7.30 (m, 1H), 7.29 – 7.22 (m, 4H), 7.09 (s, 1H), 4.82 (s, 1H), 4.32 (d, *J* = 9.1 Hz, 1H), 2.89 – 2.71 (m, 2H), 2.42 (q, 2H), 2.38 (s,

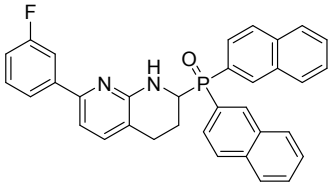
3H), 2.37 (s, 3H), 2.35 – 2.25 (m, 1H), 2.04 – 1.88 (m, 1H), 1.03 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 152.6 (d, J = 7.9 Hz), 142.9 (d, J = 5.1 Hz), 140.8, 137.6, 132.3 (d, J = 8.6 Hz), 131.5 (d, J = 9.3 Hz), 130.7 (d, J = 11.8 Hz), 129.8, 129.7, 129.5, 129.5, 129.4, 128.7, 128.1, 127.4, 127.1, 126.8, 125.3 (d, J = 98.4 Hz), 115.4, 51.6 (d, J = 83.0 Hz), 25.6 (d, J = 10.6 Hz), 24.6, 21.6, 21.1, 15.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.7. HRMS (ESI): Calcd. for $C_{30}H_{32}N_2OP$ $[M+H]^+$: 467.2247; found: 467.2234.

(32) (S)-(7-(3-methoxyphenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)di-p-tolylphosphine oxide (3db)



White solid (85.4 mg, 0.1825 mmol, 73% yield); m.p.: 92.8-93.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 13.5, 5.1 Hz, 2H), 7.68 – 7.61 (m, 2H), 7.42 – 7.36 (m, 2H), 7.32 – 7.24 (m, 5H), 7.18 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 6.90 – 6.85 (m, 1H), 5.11 (s, 1H), 4.29 (d, J = 7.5 Hz, 1H), 3.82 (s, 3H), 2.83 – 2.71 (m, 2H), 2.39 (s, 3H), 2.38 (s, 3H), 2.28 – 2.15 (m, 1H), 2.07 – 1.90 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 154.9 (d, J = 7.2 Hz), 154.1, 143.1 (d, J = 2.7 Hz), 142.9, 141.4, 136.9, 132.0 (d, J = 8.7 Hz), 131.5 (d, J = 9.2 Hz), 130.7 (d, J = 11.8 Hz), 129.8, 129.7, 129.6, 129.5, 127.4 (d, J = 97.4 Hz), 125.6 (d, J = 99.2 Hz), 119.2, 115.1, 114.0, 112.2, 111.1, 55.3 (d, J = 2.4 Hz), 51.6 (d, J = 82.2 Hz), 25.6 (d, J = 10.3 Hz), 21.6, 21.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.5. HRMS (ESI): Calcd. for $C_{27}H_{26}N_2OP$ $[M+H]^+$: 469.2039; found: 469.2027.

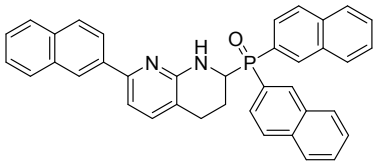
(33) (S)-(7-(3-fluorophenyl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)di(naphthalen-1-yl)phos-phine oxide (3md)



White solid (83.2 mg, 0.1575 mmol, 63% yield); m.p.: 86.1-86.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 12.9 Hz, 1H), 8.47 (d, J = 12.9 Hz, 1H), 8.06 – 7.93 (m, 4H), 7.94 – 7.82 (m, 4H), 7.64 – 7.53 (m, 6H), 7.31 (dt, J = 10.0, 5.0 Hz, 1H), 7.17 (d, J = 7.4 Hz, 1H), 7.02 (dd, J = 11.6, 4.8 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 5.21 (s, 1H), 4.62 (d, J = 4.6 Hz, 1H), 2.93 – 2.67 (m, 2H), 2.41 – 2.24 (m, 1H), 2.21 – 2.04 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (d, J_{C-F} = 244.8 Hz), 154.8 (d, J_{C-P} = 6.9 Hz), 152.9, 142.1 (d, J_{C-F} =

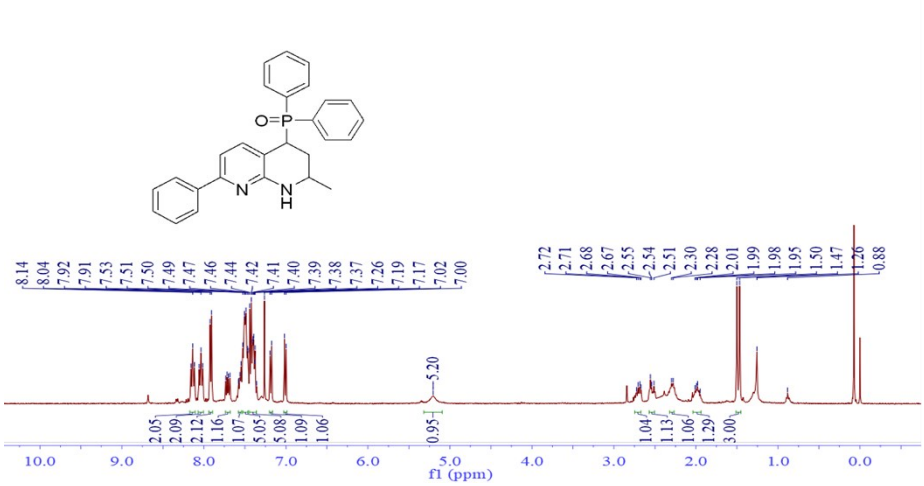
7.5 Hz), 137.1, 134.9 (dd, J_{C-P} = 24.8, 7.9 Hz), 133.9 (d, J_{C-P} = 8.4 Hz), 132.7 (d, J_{C-P} = 12.2 Hz), 129.9 (d, J_{C-P} = 8.2 Hz), 129.1, 129.1, 129.0, 128.7 (d, J_{C-P} = 11.2 Hz), 128.6 (d, J_{C-P} = 3.7 Hz), 128.2, 127.9, 127.3, 127.2, 126.7, 126.4 (d, J_{C-P} = 9.4 Hz), 125.9 (d, J_{C-P} = 9.7 Hz), 125.7, 122.2 (d, J_{C-F} = 2.5 Hz), 115.6, 115.2, 114.9, 113.6 (d, J_{C-F} = 22.5 Hz), 111.2, 51.6 (d, J_{C-P} = 82.0 Hz), 25.6 (d, J_{C-P} = 10.0 Hz), 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.3. HRMS (ESI): Calcd. for $C_{34}H_{27}FN_2OP$ $[M+H]^+$: 529.1840; found: 529.1830.

(34) (S)-di(naphthalen-1-yl)(7-(naphthalen-2-yl)-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)phos-phine oxide (3pd)

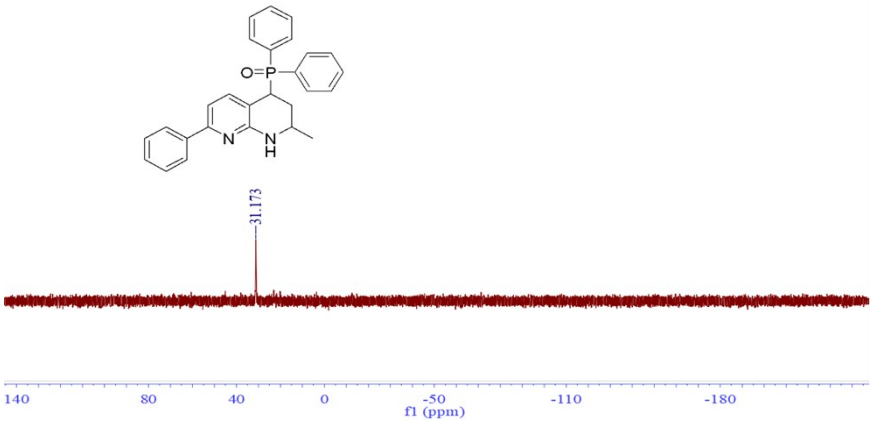


White solid (88.2 mg, 0.1575 mmol, 63% yield); m.p.: 111.2-111.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 12.9 Hz, 1H), 8.40 (d, *J* = 12.9 Hz, 1H), 8.27 (s, 1H), 8.02 – 7.90 (m, 5H), 7.89 – 7.79 (m, 6H), 7.75 (t, *J* = 8.7 Hz, 1H), 7.62 – 7.51 (m, 4H), 7.46 – 7.40 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 5.31 (s, 1H), 4.54 (d, 1H), 2.96 – 2.69 (m, 2H), 2.39 – 2.25 (m, 1H), 2.22 – 2.08 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (d, *J* = 7.8 Hz), 154.1, 137.1, 135.0 (dd, *J* = 10.8, 2.1 Hz), 134.7 (d, *J* = 7.7 Hz), 133.9 (d, *J* = 8.4 Hz), 133.4 (d, *J* = 14.5 Hz), 132.7 (dd, *J* = 12.5, 2.2 Hz), 129.1, 129.1, 129.0, 128.9, 128.7, 128.6, 128.6, 128.5, 128.1, 127.9, 127.7, 127.3, 127.2, 127.1, 126.6, 126.5, 126.2, 126.1, 126.0, 125.9, 125.8, 124.8, 115.1, 111.5, 51.7 (d, *J* = 82.3 Hz), 25.6 (d, *J* = 10.2 Hz), 21.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.6. HRMS (ESI): Calcd. for $C_{38}H_{30}N_2OP$ $[M+H]^+$: 561.2090; found: 561.2080.

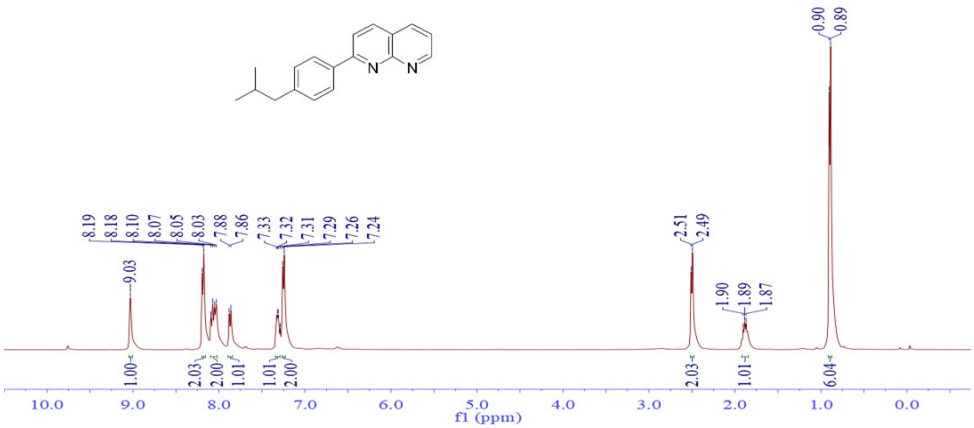
NMR Spectra of the Obtained Compounds



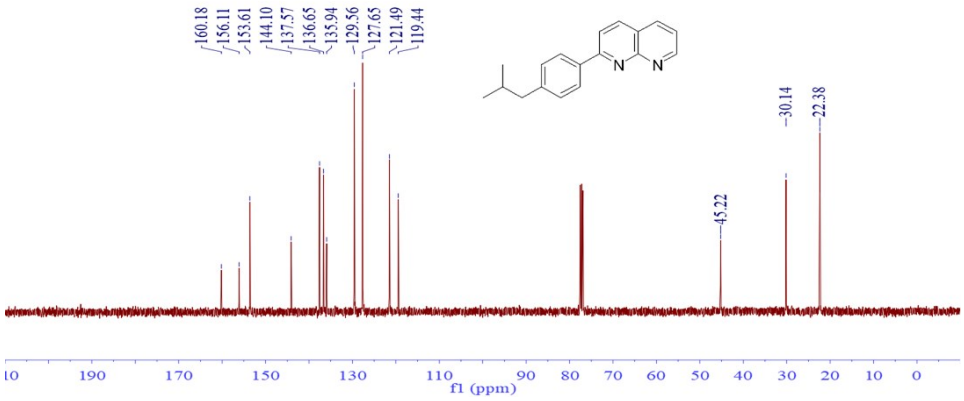
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 1aa'



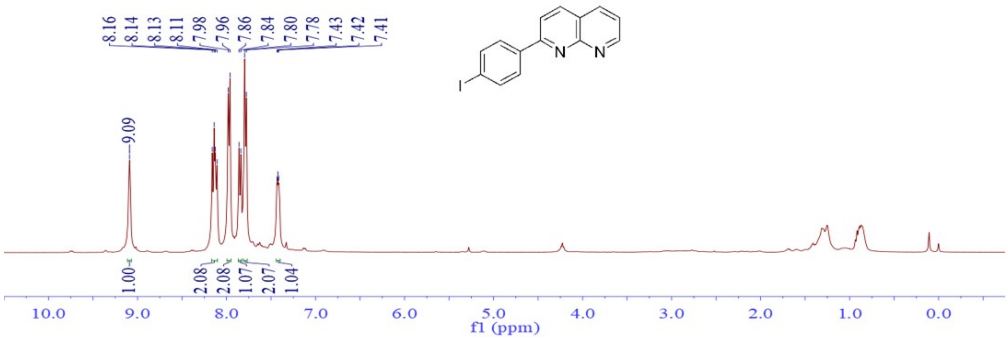
^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 1aa'



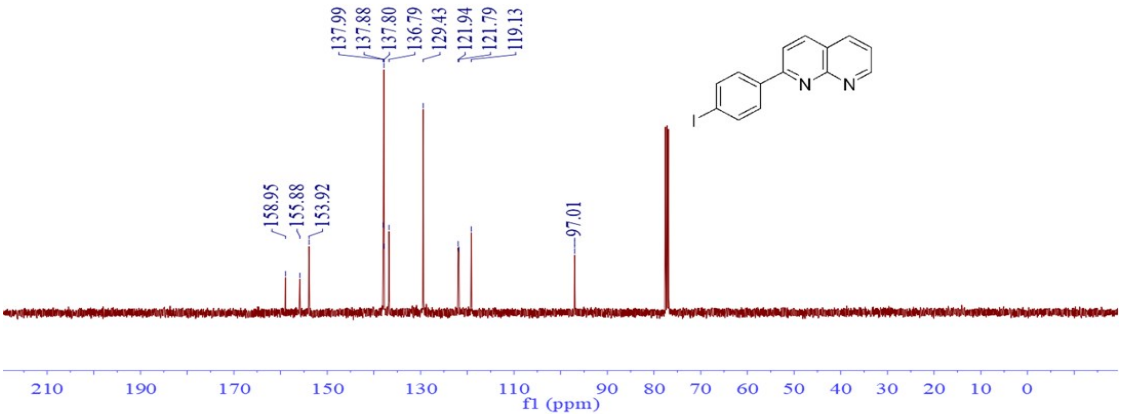
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 1f



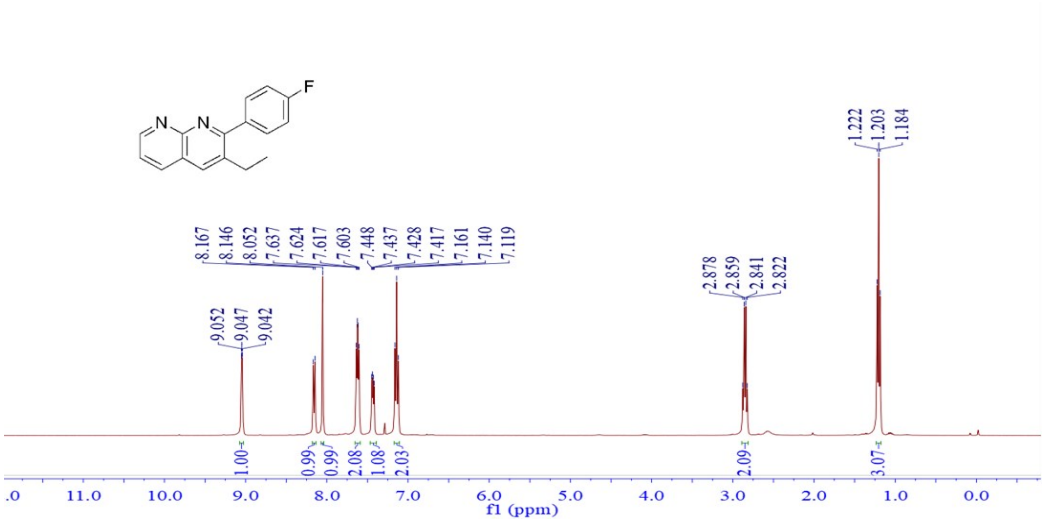
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 1f



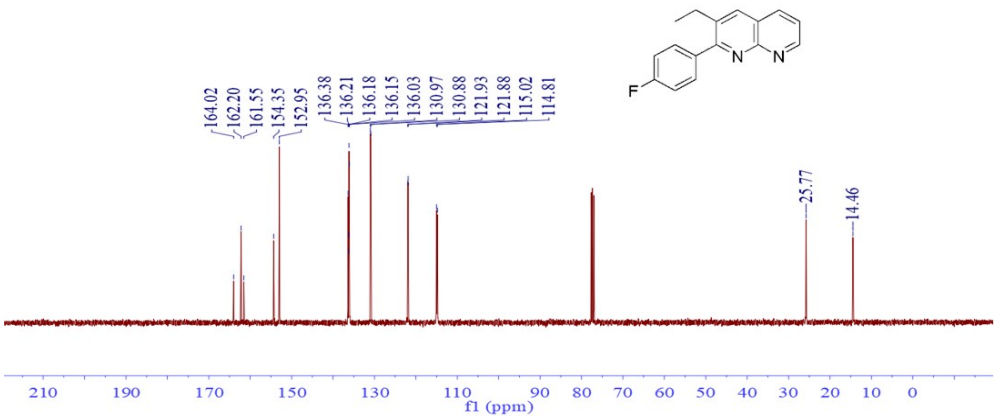
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 1l



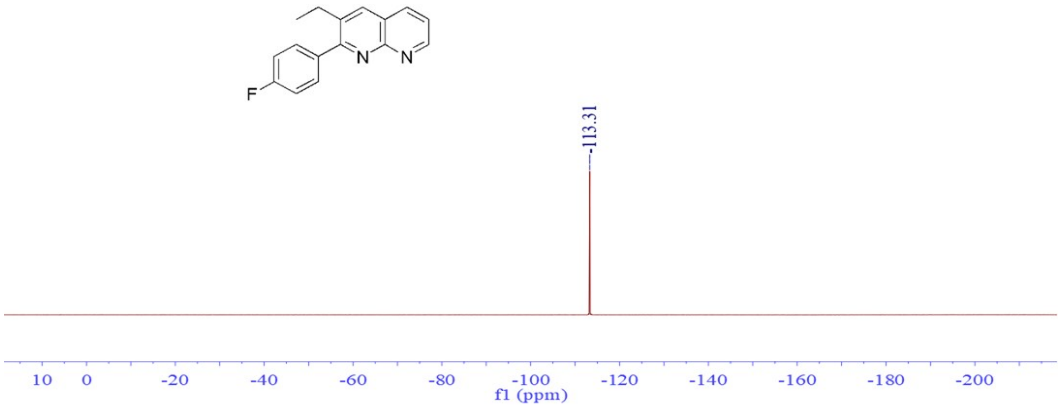
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 1l



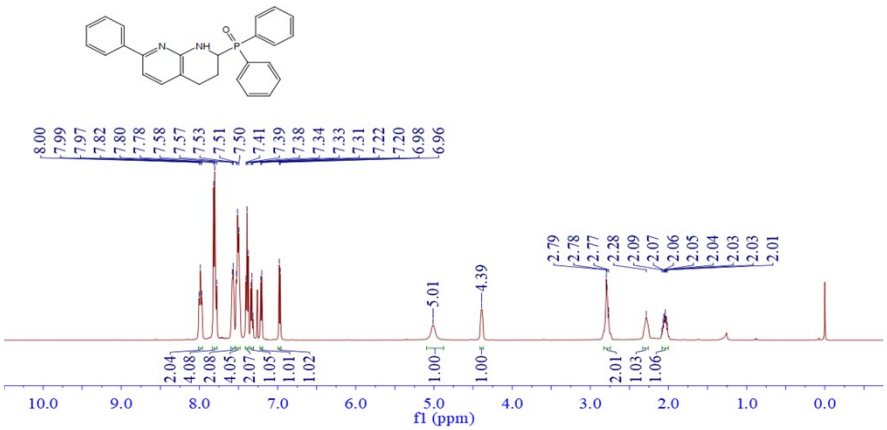
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 1t



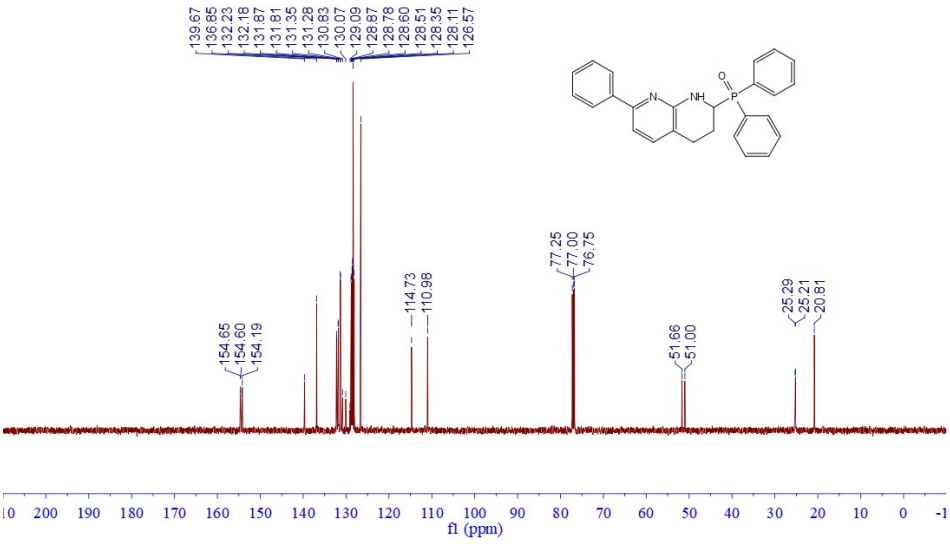
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 1t



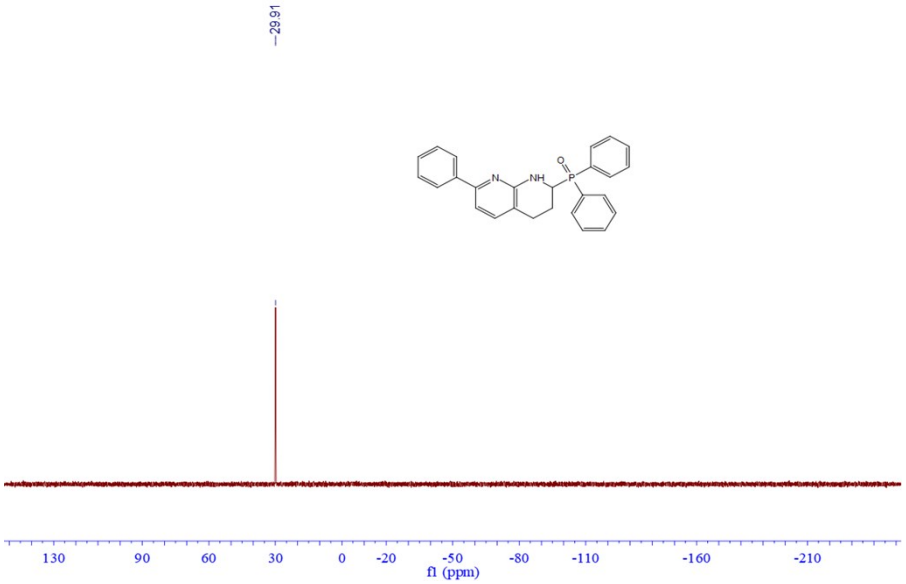
^{19}F-NMR (376 MHz, $CDCl_3$) spectrum of 1t



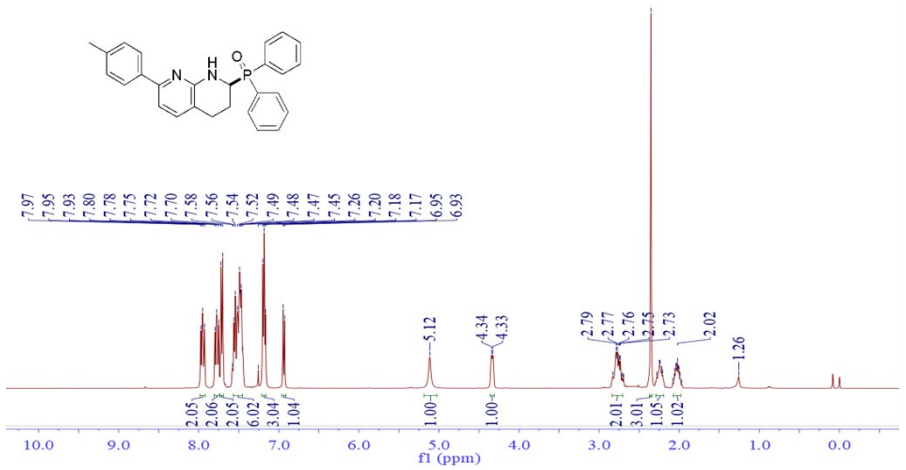
(1) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3aa



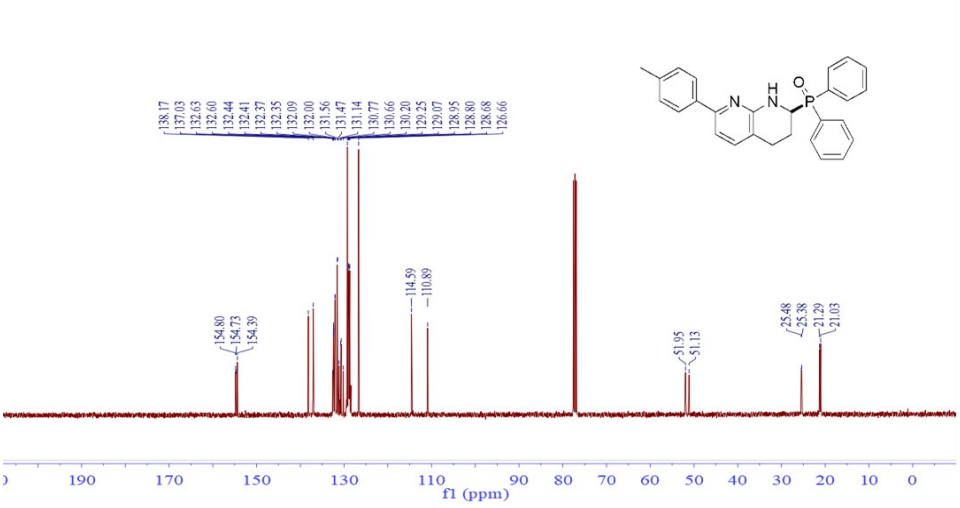
(1) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3aa



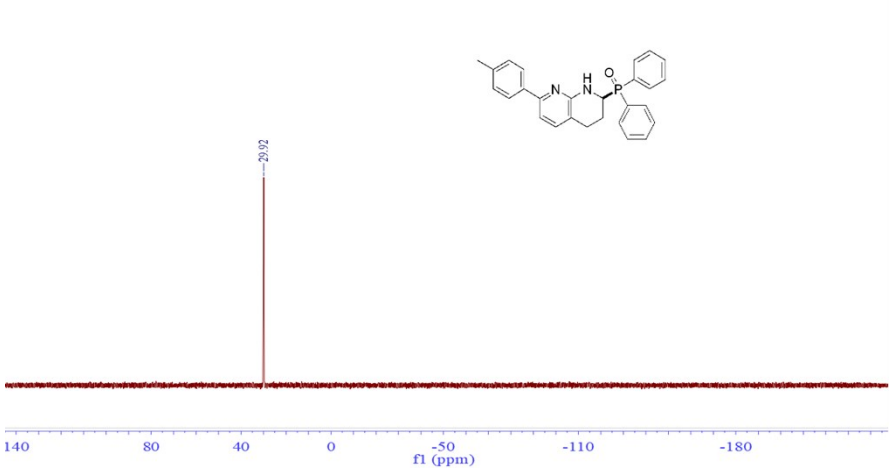
(1) ^{31}P-NMR (202 MHz, $CDCl_3$) spectrum of 3aa



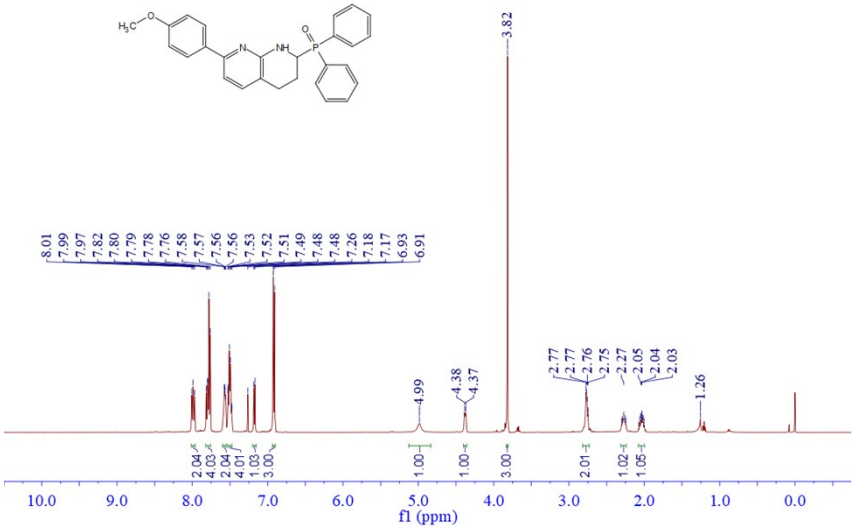
(2) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ba



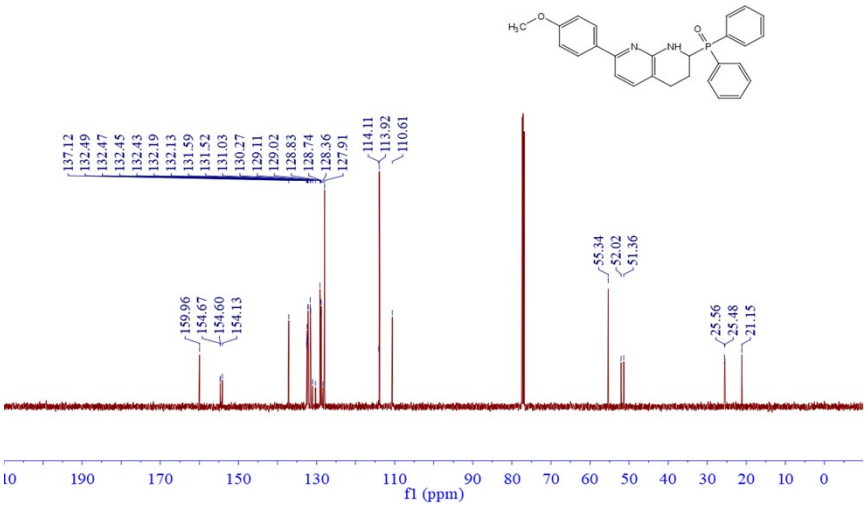
(2) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ba



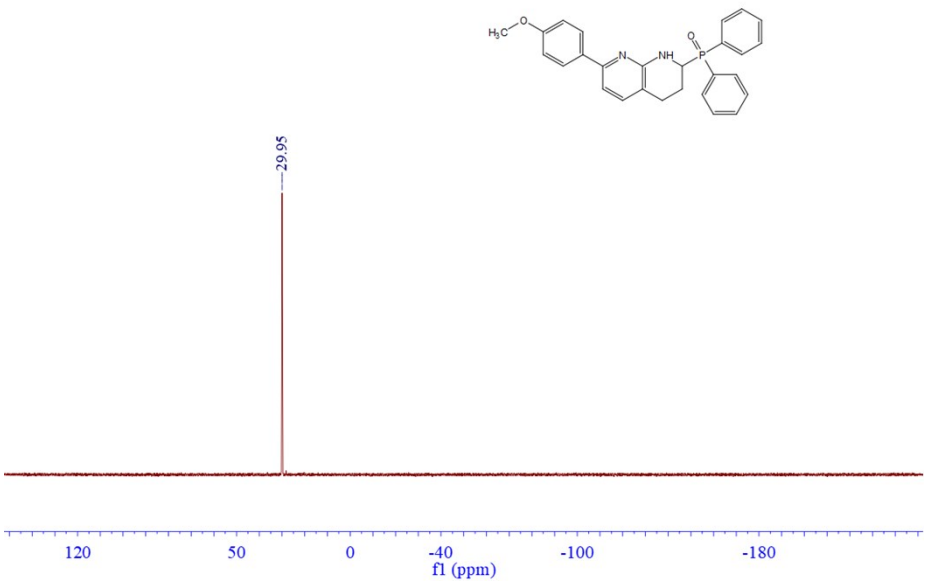
(2) ^{31}P-NMR(162 MHz, $CDCl_3$) spectrum of 3ba



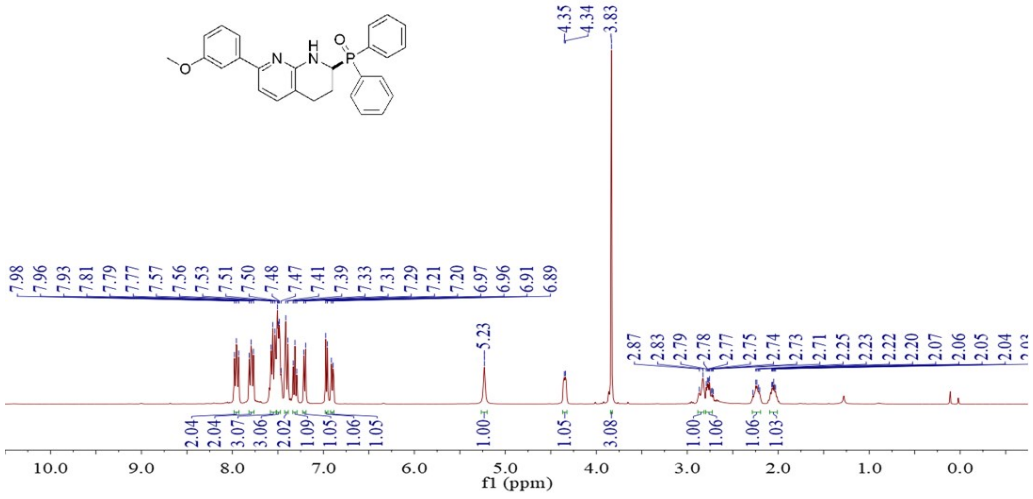
(3) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3ca



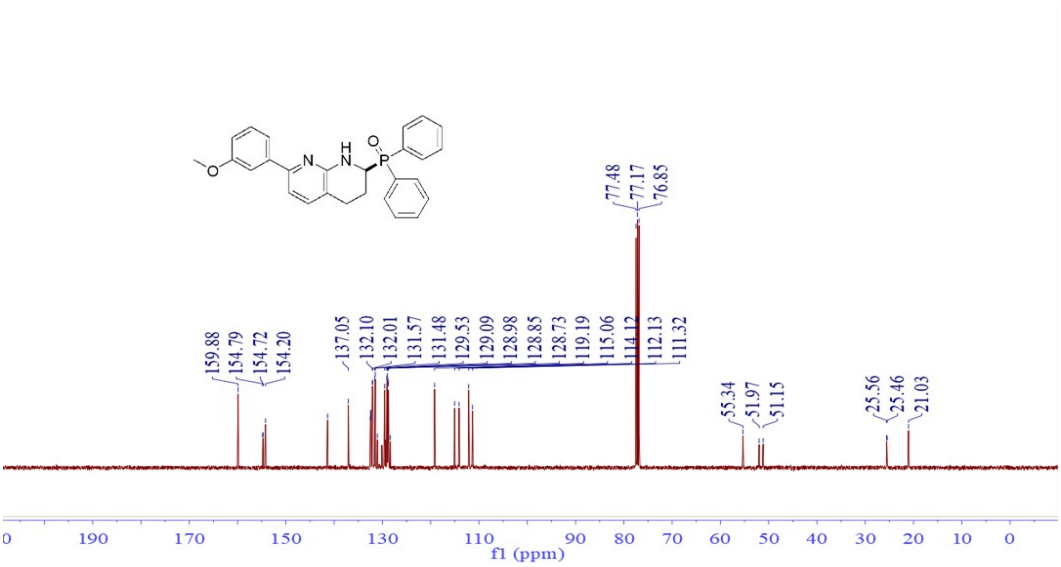
(3) ^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of 3ca



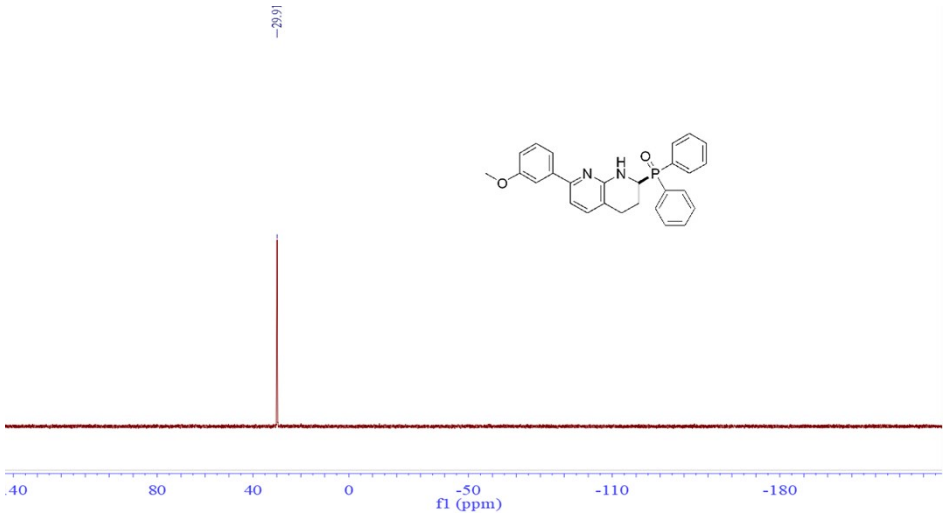
(3) ^{31}P-NMR (202 MHz, $CDCl_3$)spectrum of 3ca



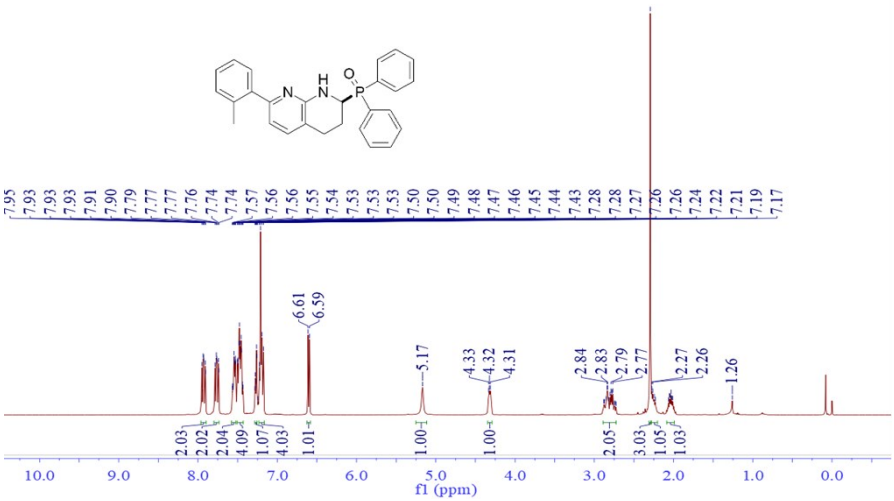
(4) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3da



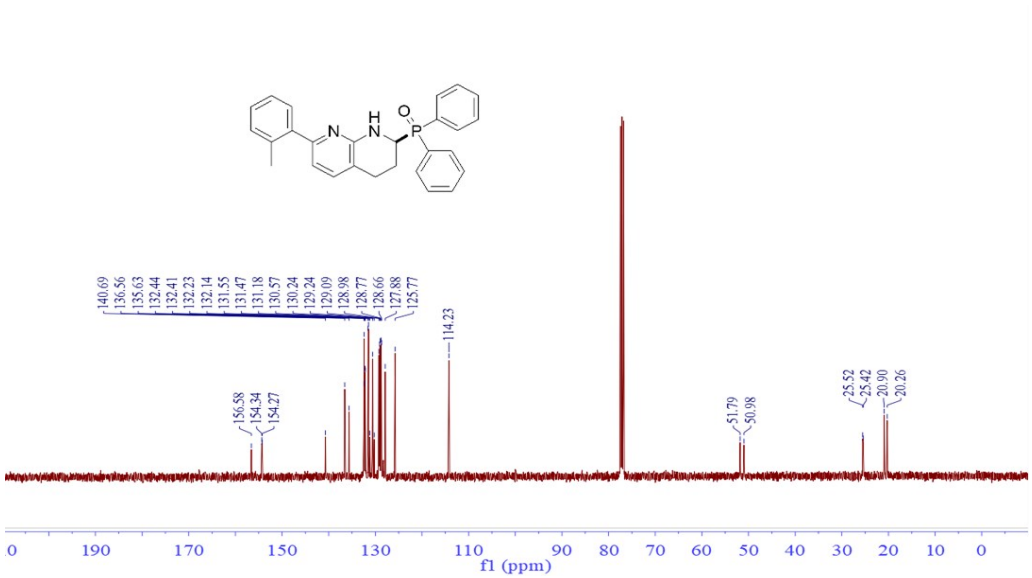
(4) ^{13}C-NMR(101 MHz, $CDCl_3$) spectrum of 3da



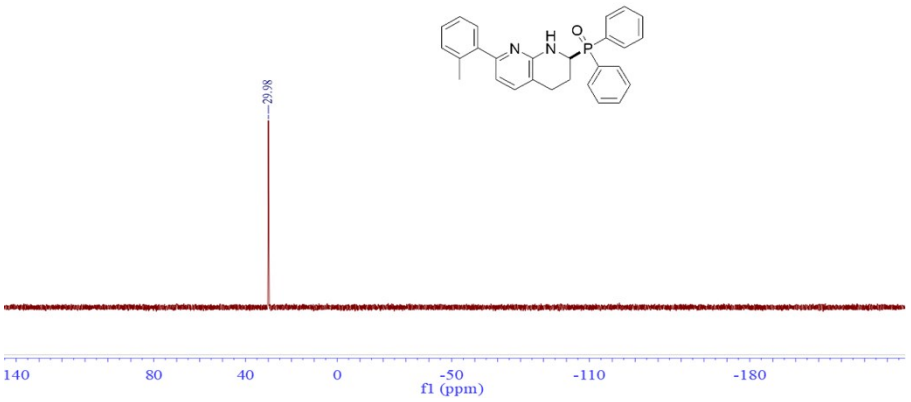
(4) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3da



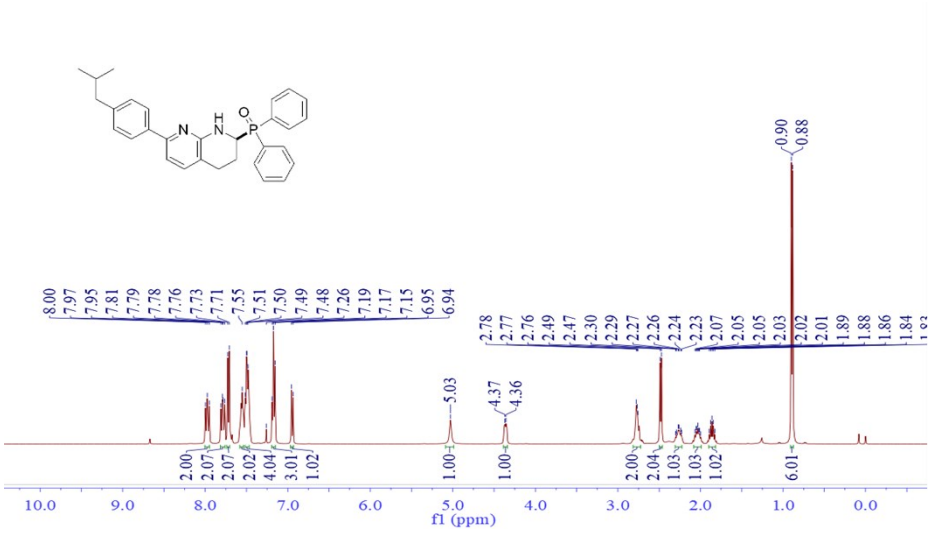
(5) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ea



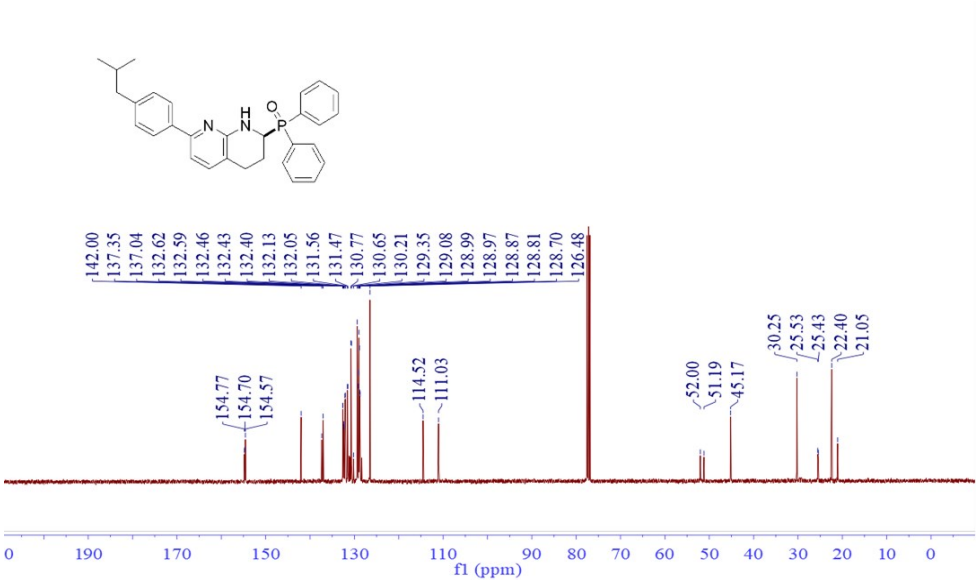
(5) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ea



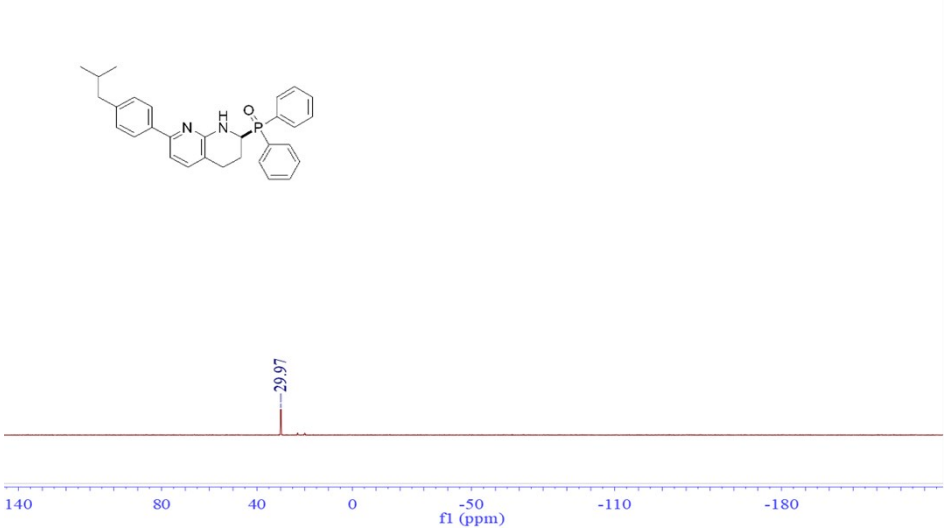
(5) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ea



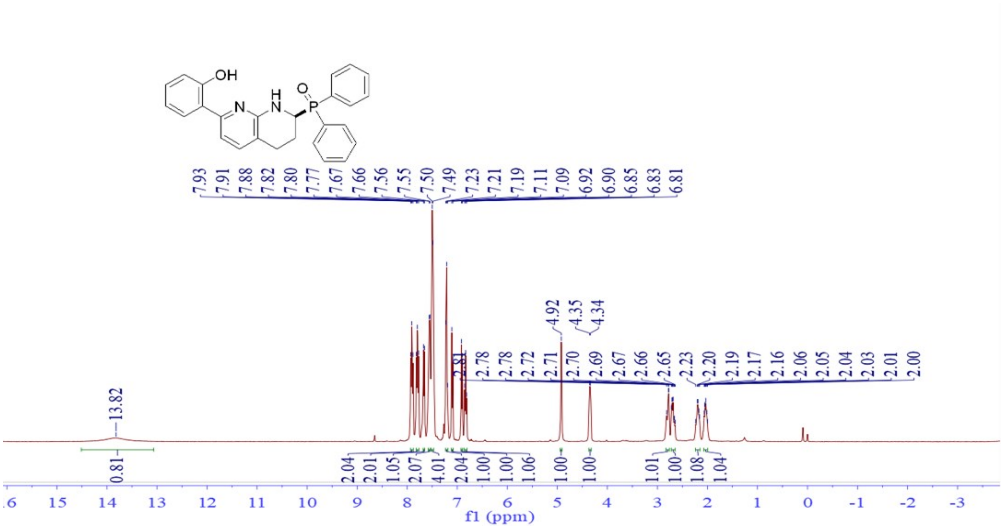
(6) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3fa



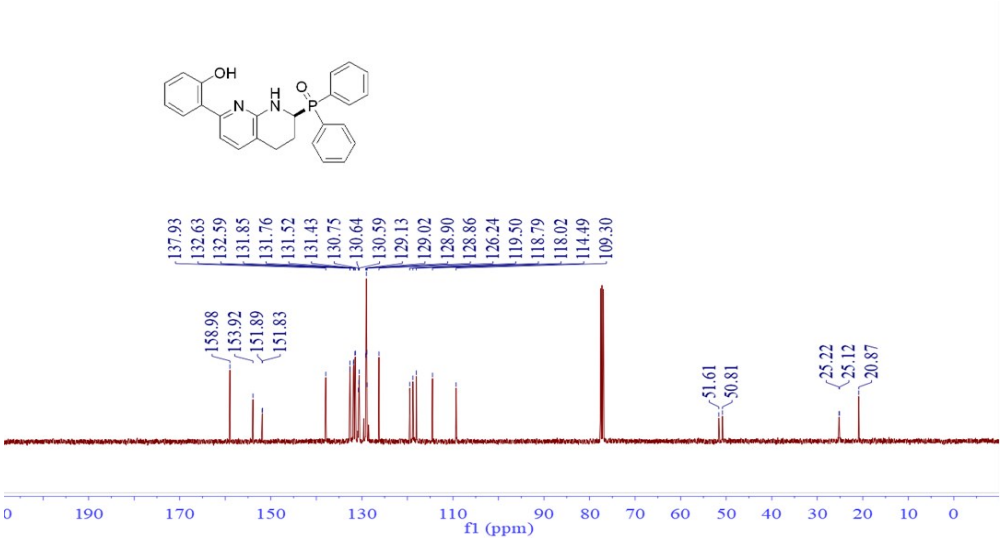
(6) ^{13}C-NMR (101 MHz, $CDCl_3$)spectrum of 3fa



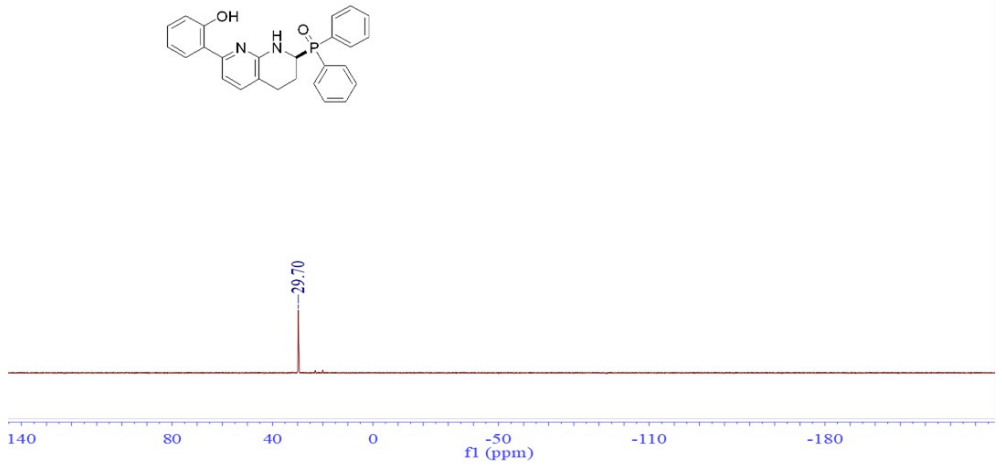
(6) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3fa



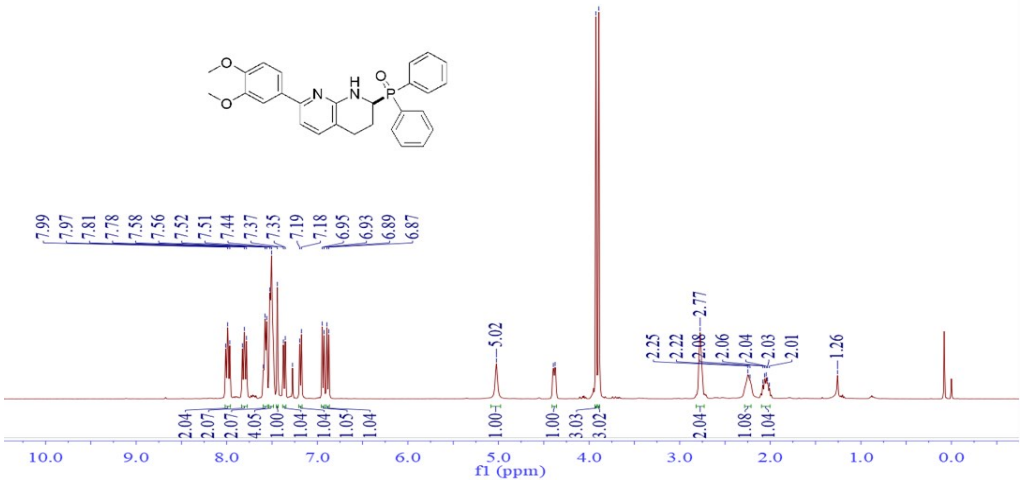
(7) ^{1}H-NMR (400 MHz, $CDCl_3$)spectrum of 3ga



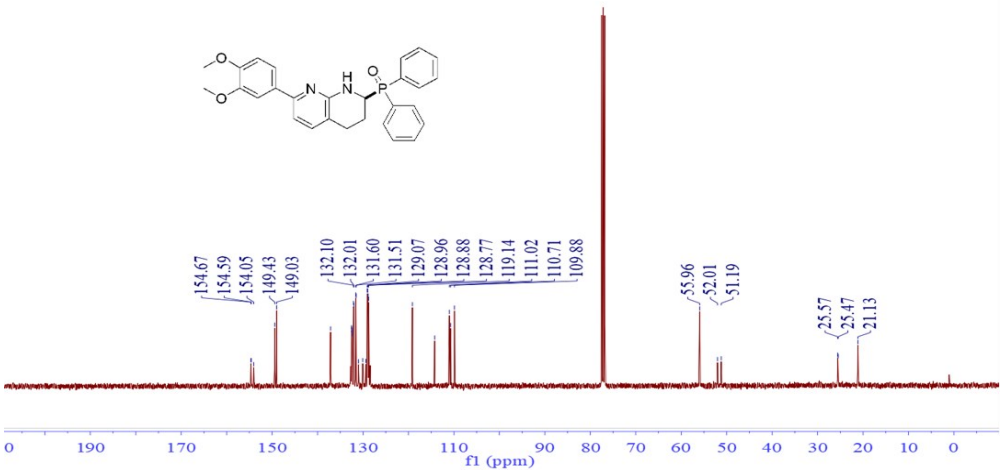
(7) ^{13}C-NMR(101 MHz, $CDCl_3$) spectrum of 3ga



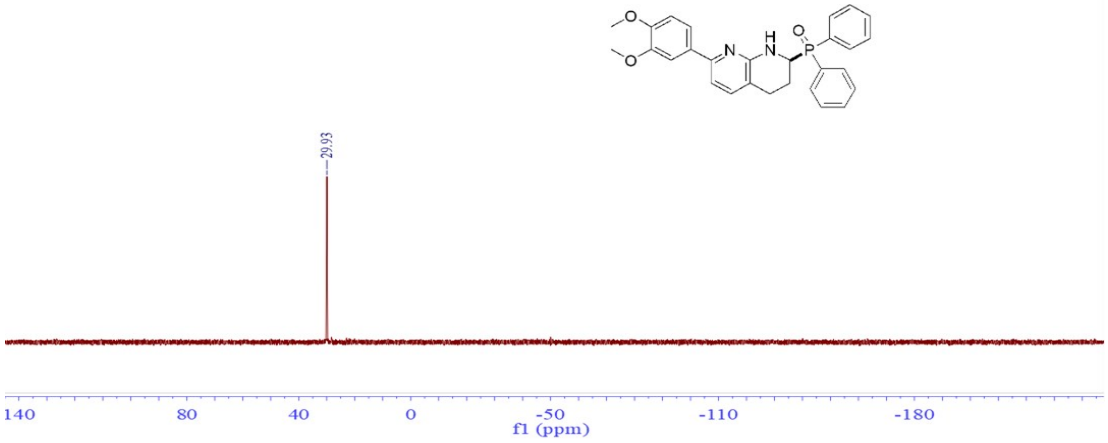
(7) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ga



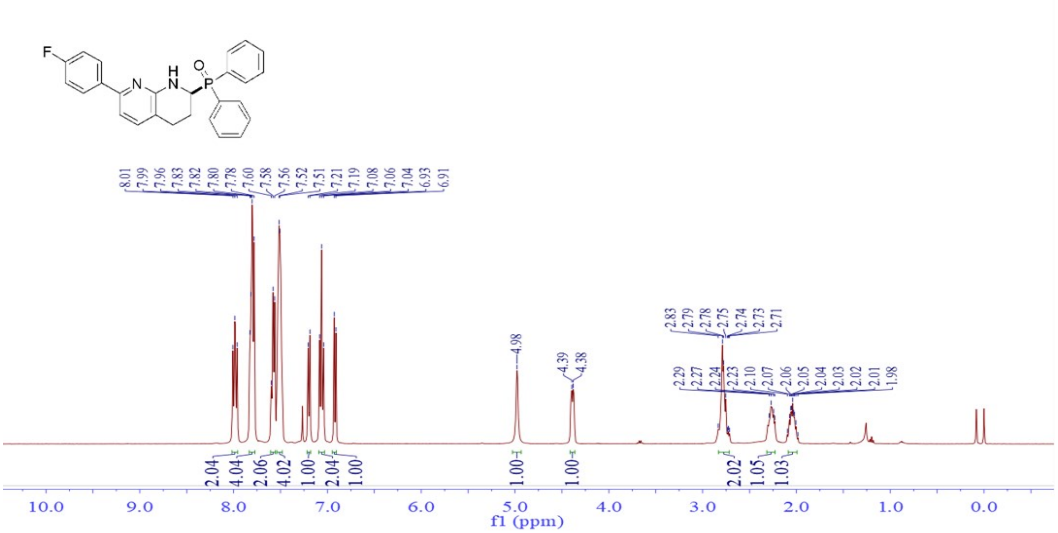
(8) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ha



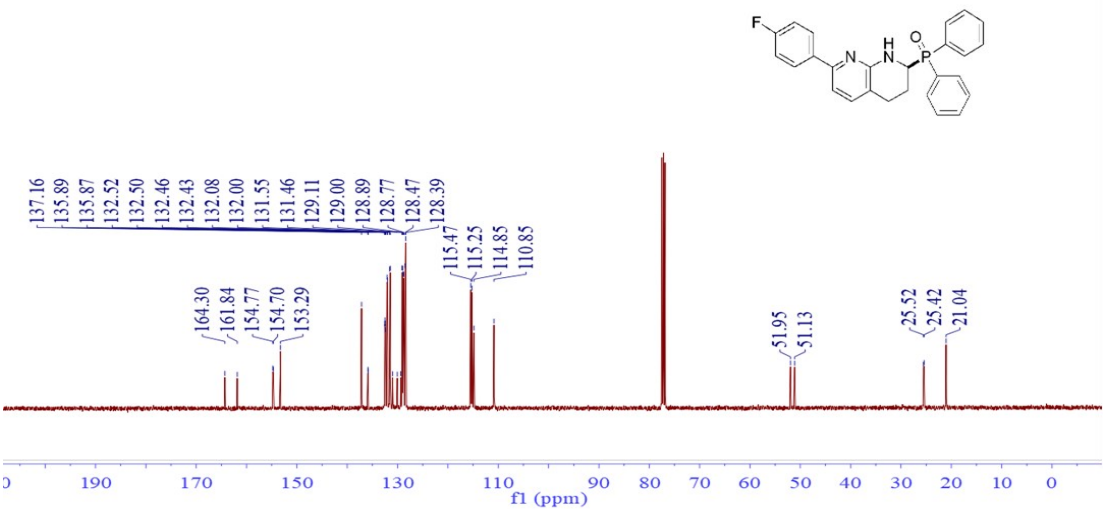
(8) ^{13}C-NMR (101 MHz, $CDCl_3$)spectrum of 3ha



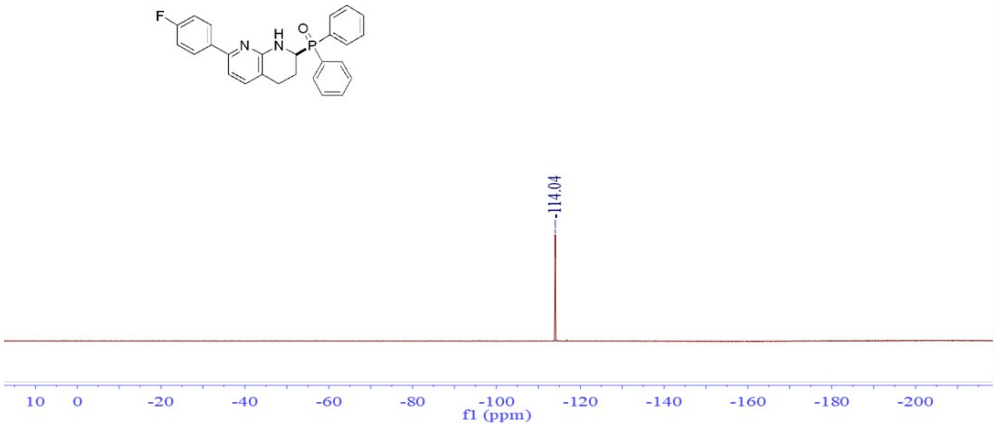
(8) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ha



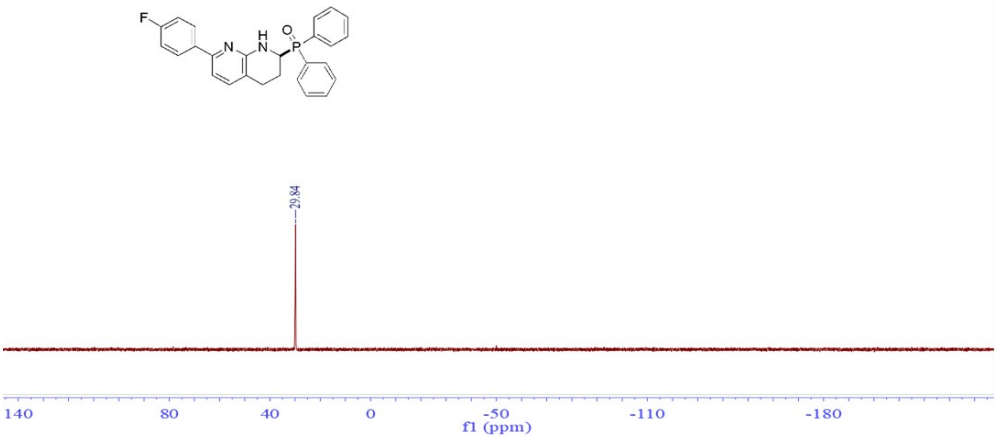
(9) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ia



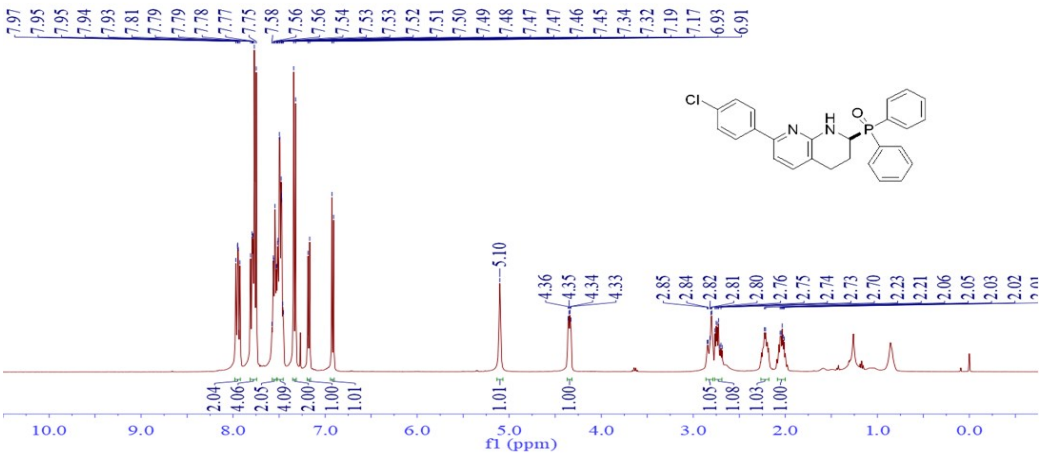
(9) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ia



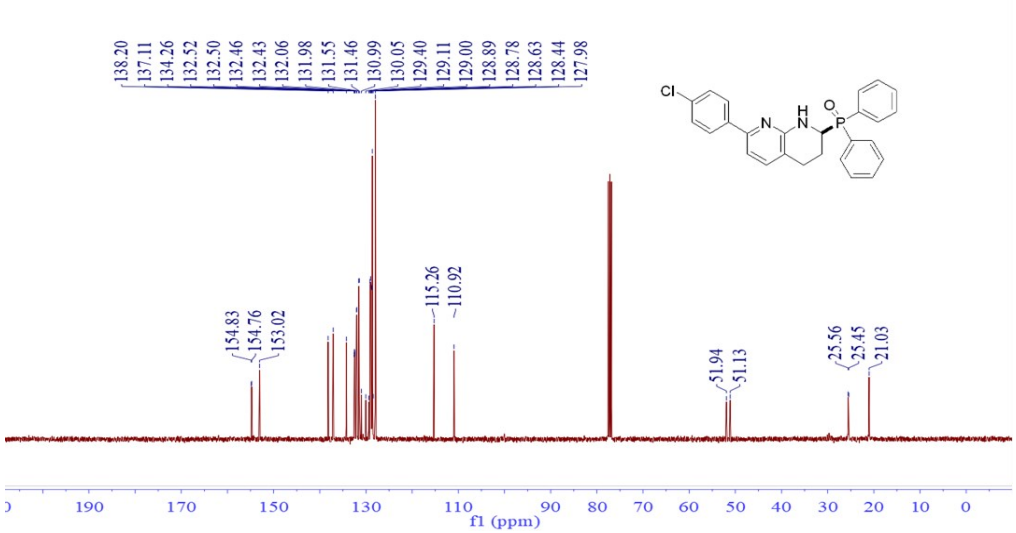
(9) ^{19}F-NMR (376 MHz, $CDCl_3$) spectrum of 3ia



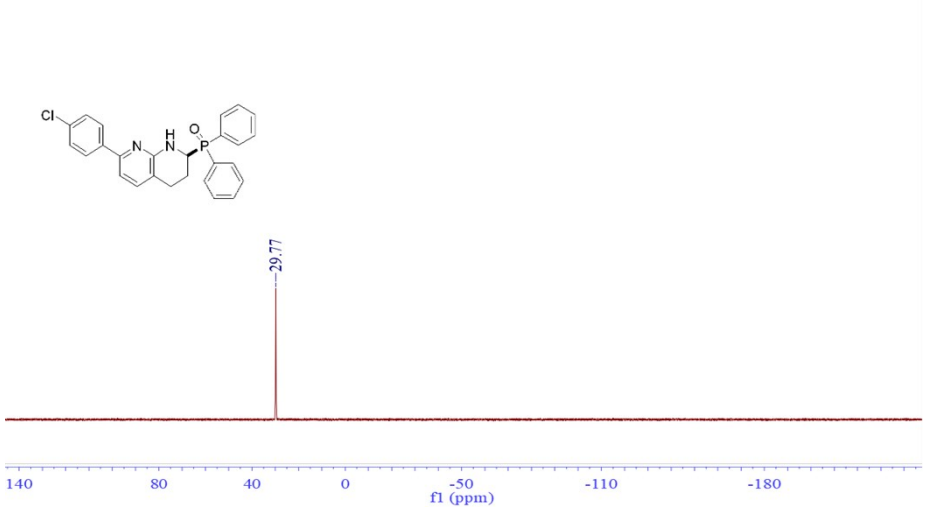
(9) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ia



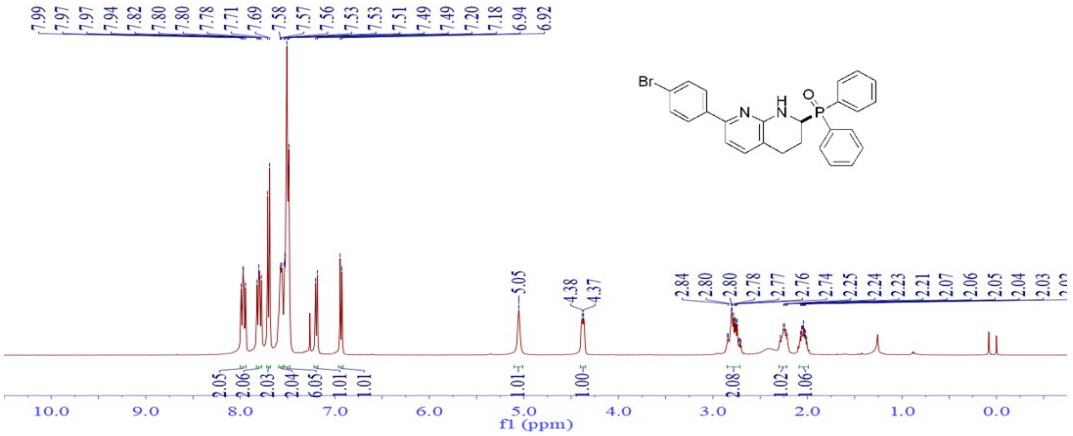
(10) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ja



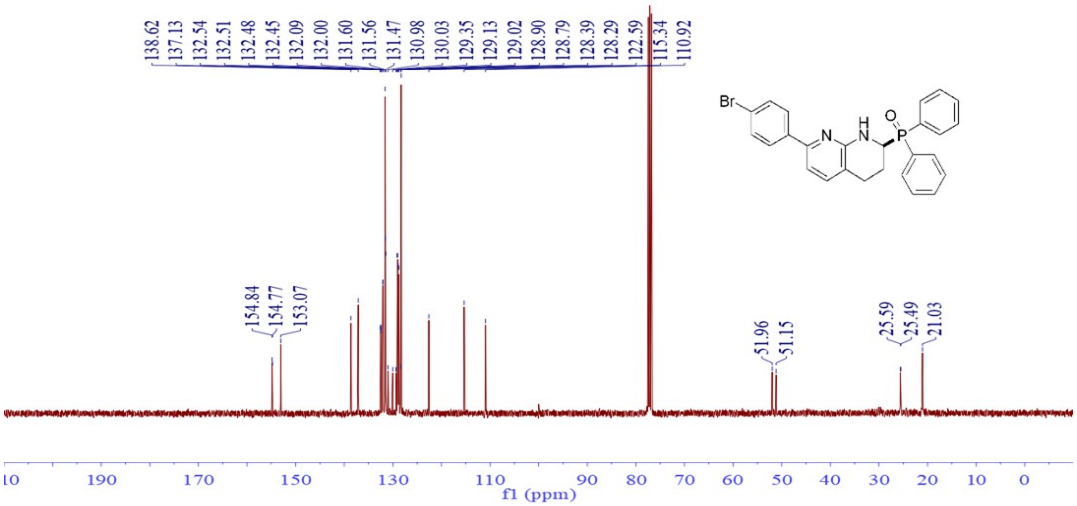
(10) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ja



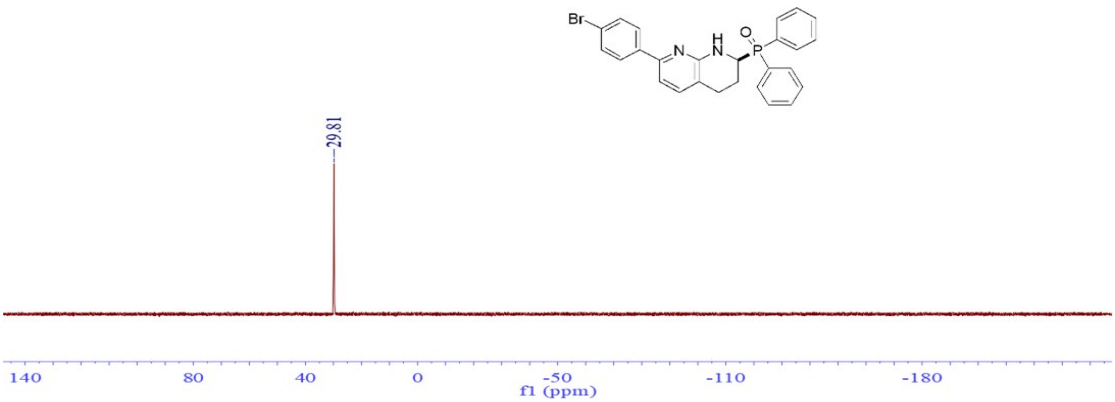
(10) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ja



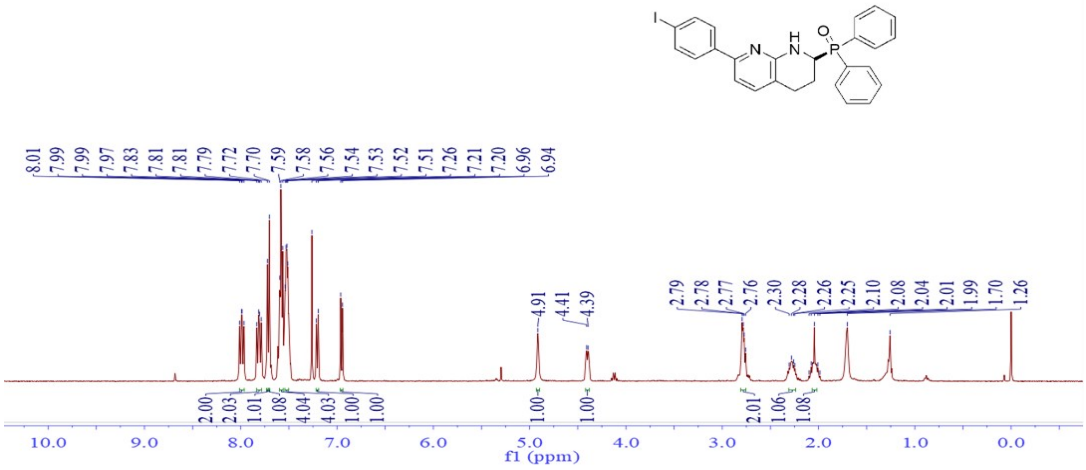
(11) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ka



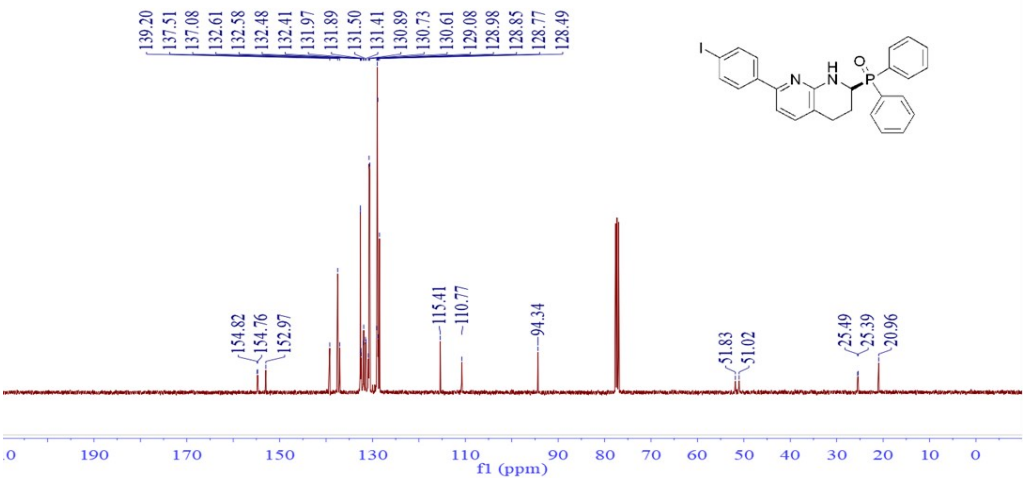
(11) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ka



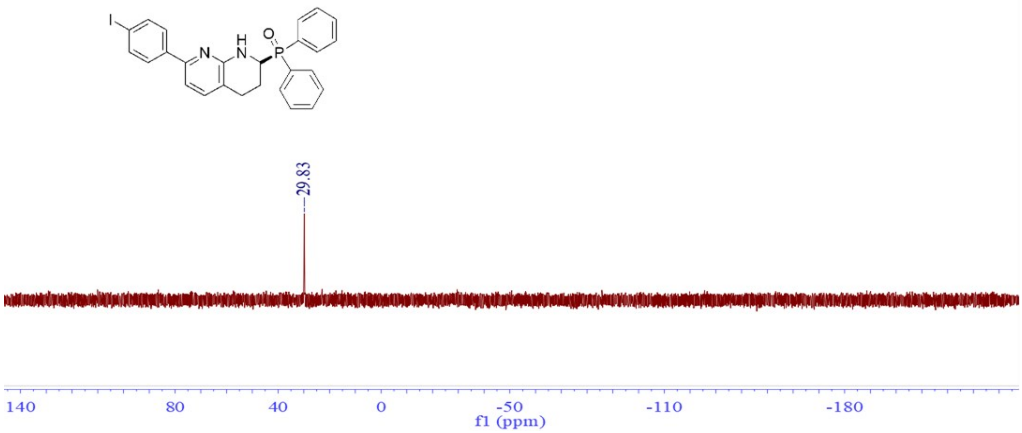
(11) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ka



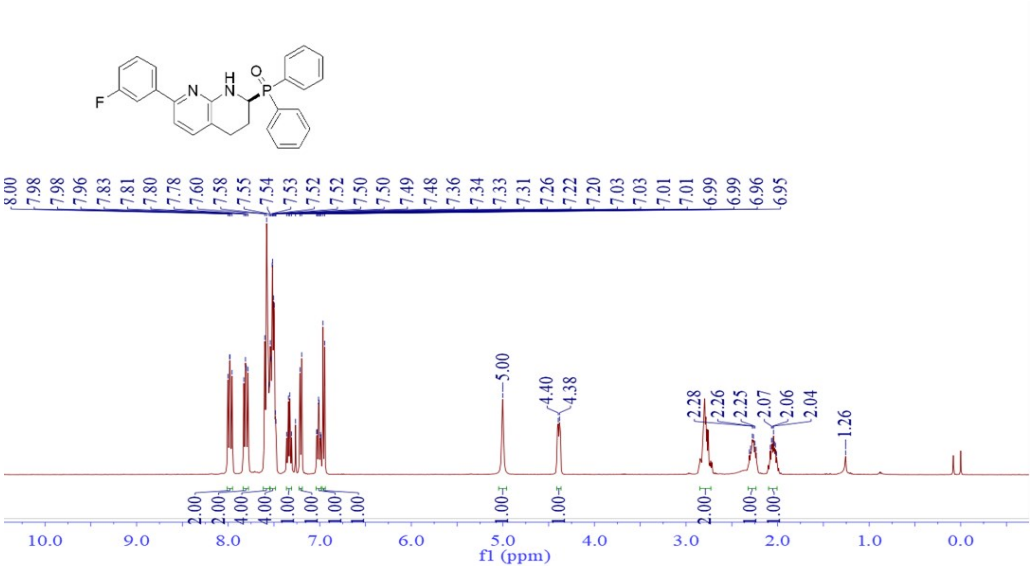
(12) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3la



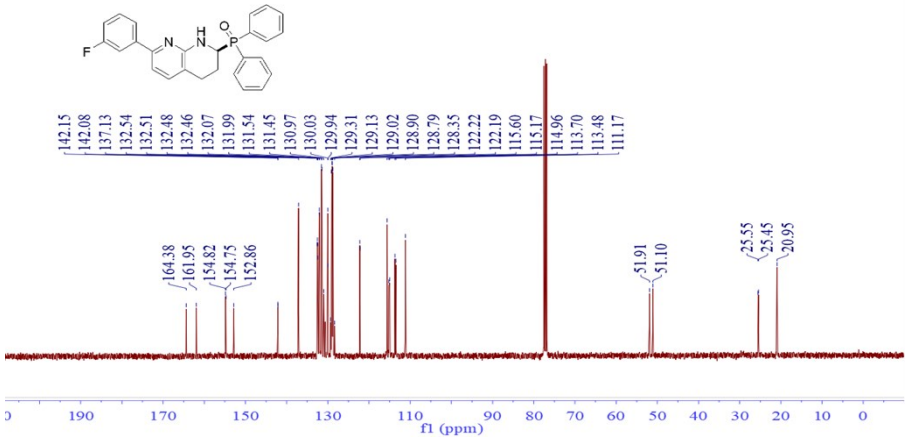
(12) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3la



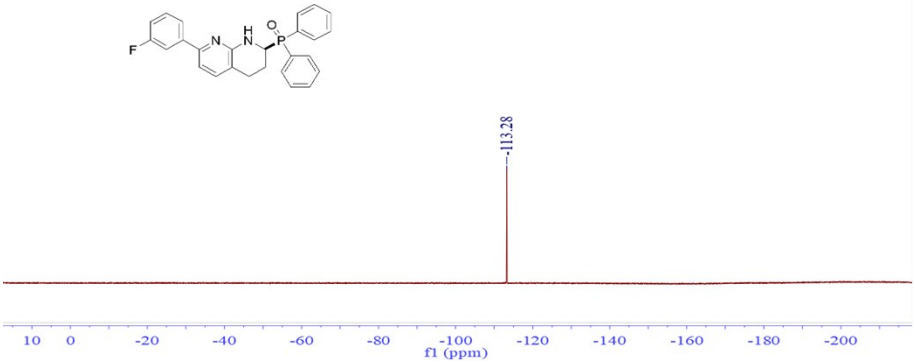
(12) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3la



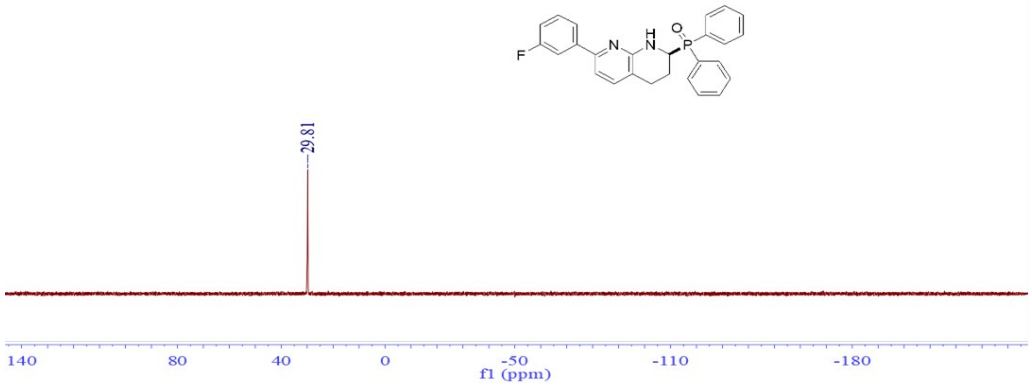
(13) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ma



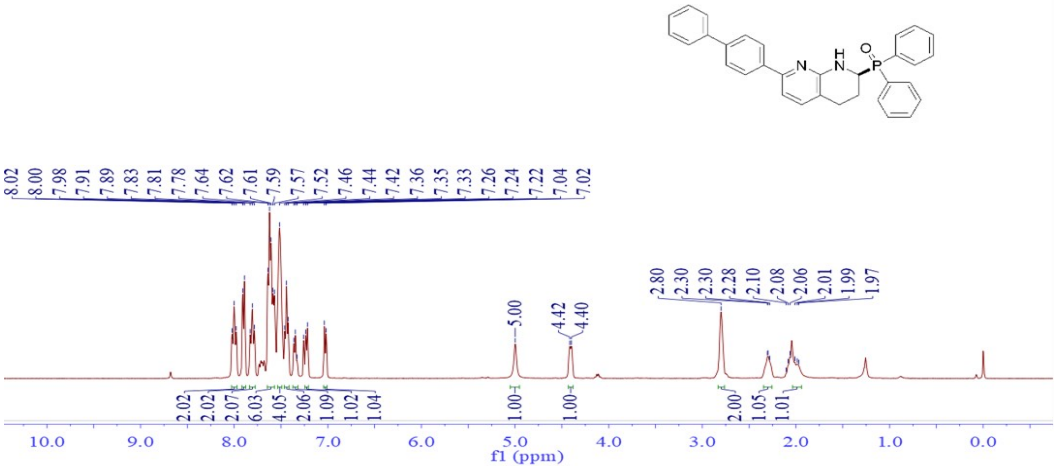
(13) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ma



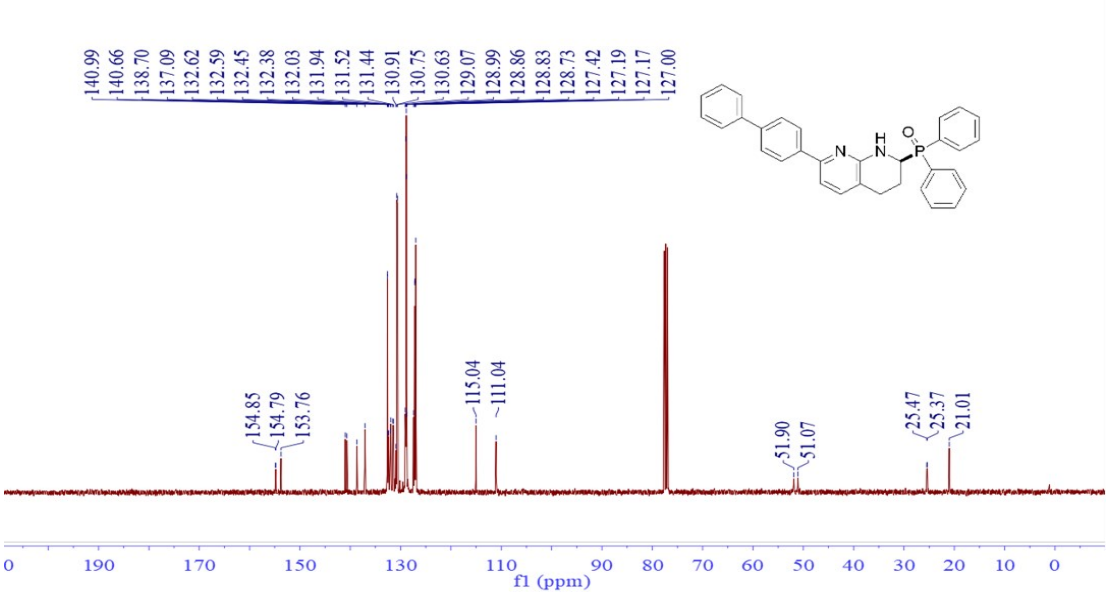
(13) ^{19}F-NMR (376 MHz, $CDCl_3$) spectrum of 3ma



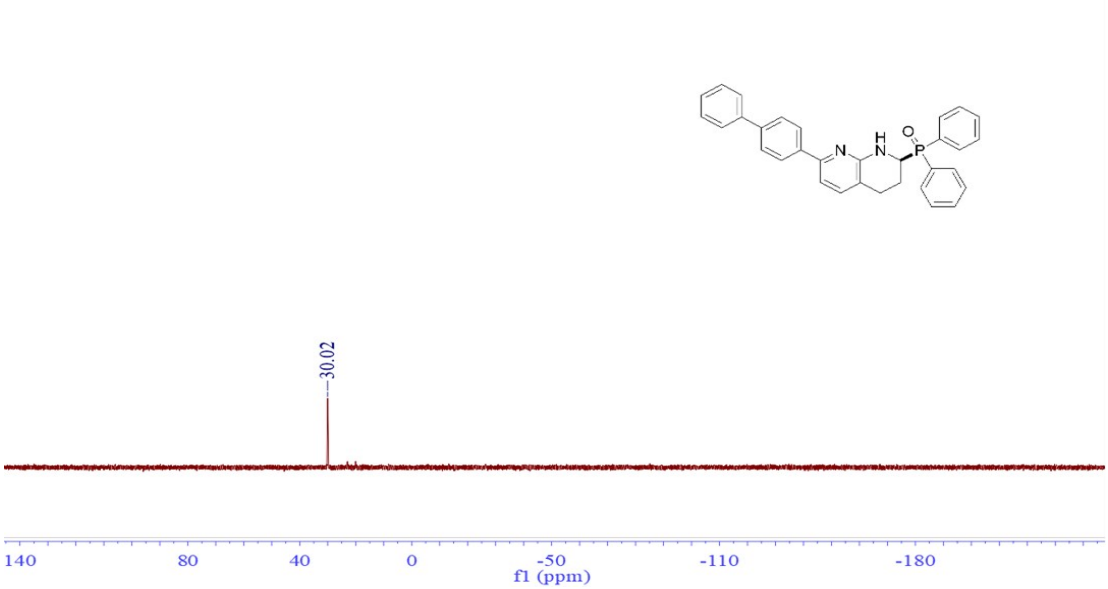
(13) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ma



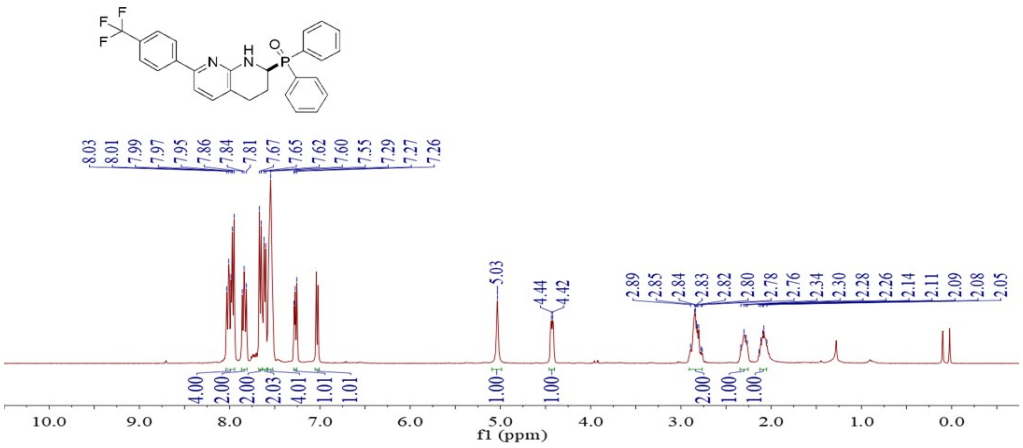
(14) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3na



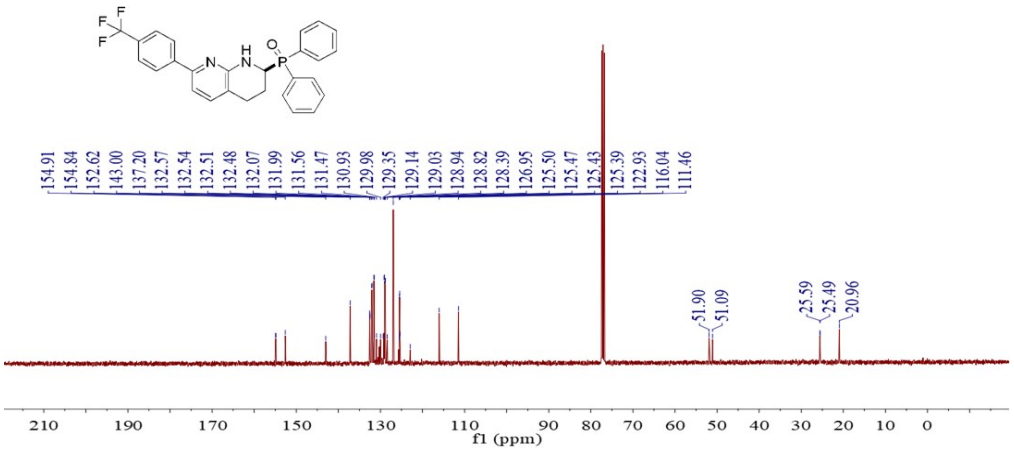
(14) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3na



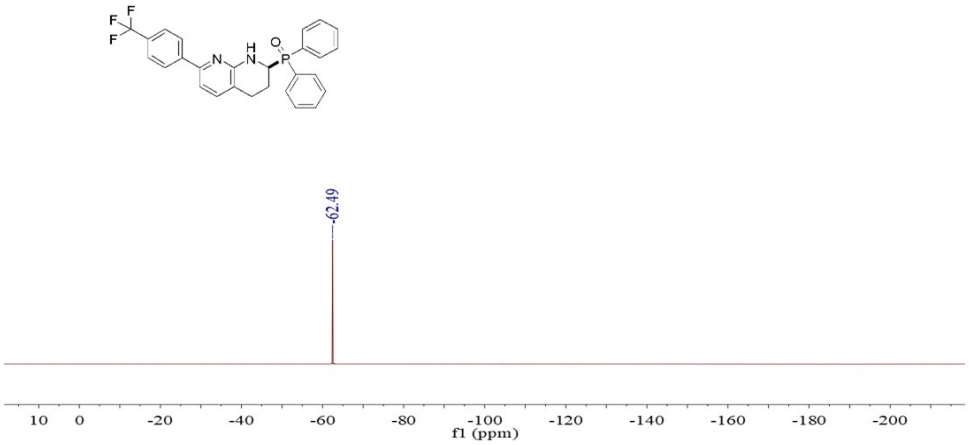
(14) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3na



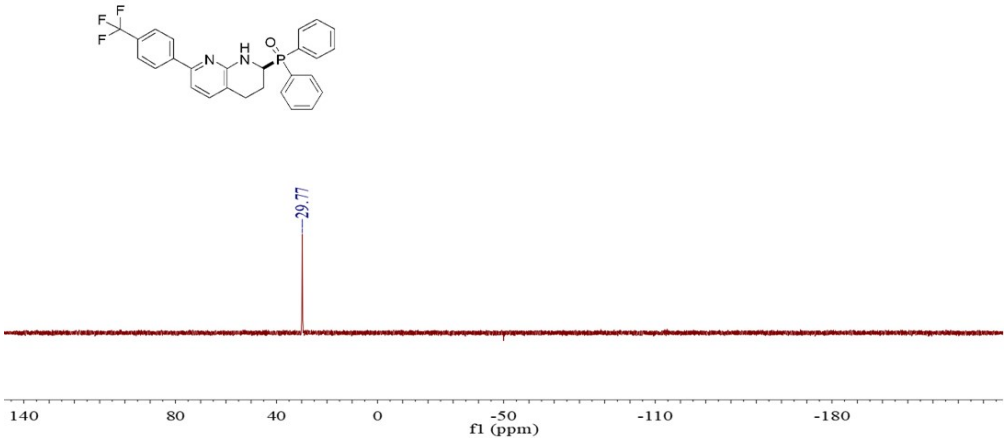
(15) ^{1}H-NMR(400 MHz, $CDCl_3$) spectrum of 3oa



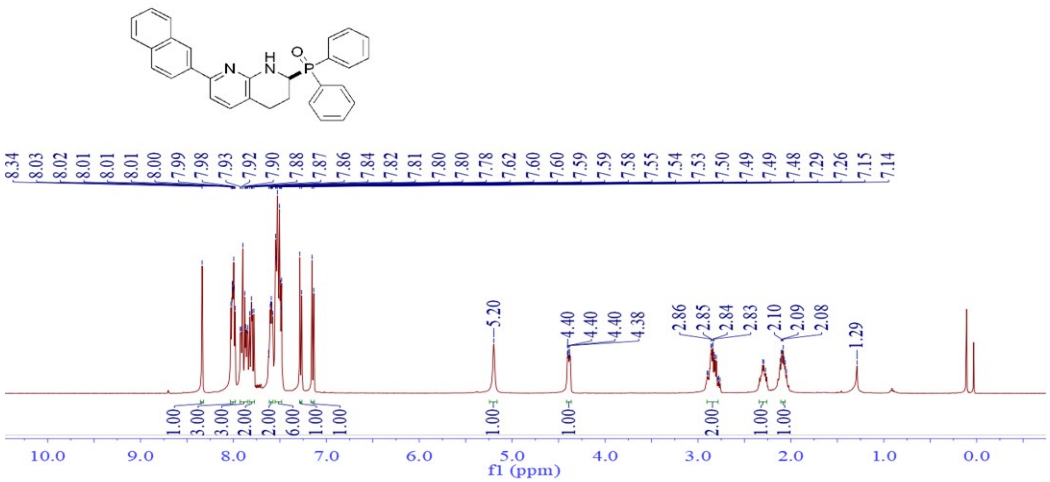
(15) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3oa



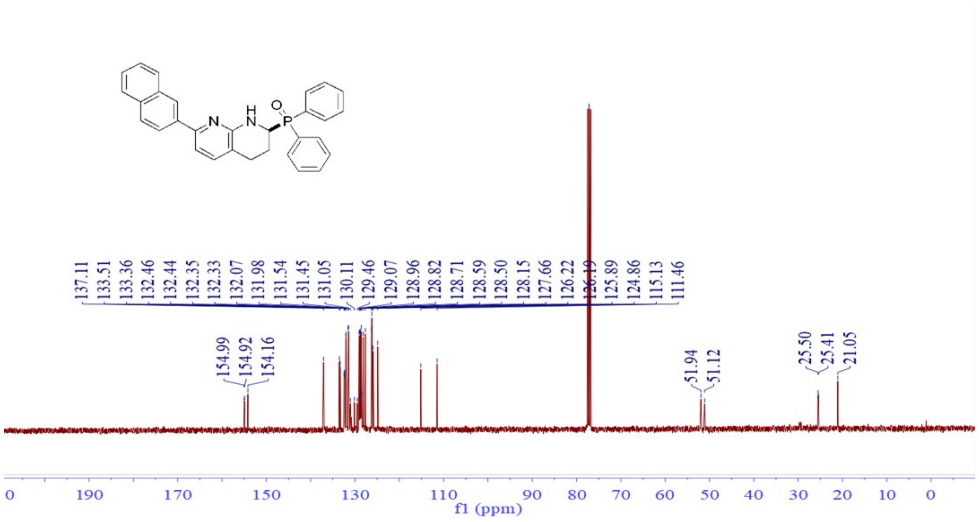
(15) ^{19}F-NMR (376 MHz, $CDCl_3$)spectrum of 3oa



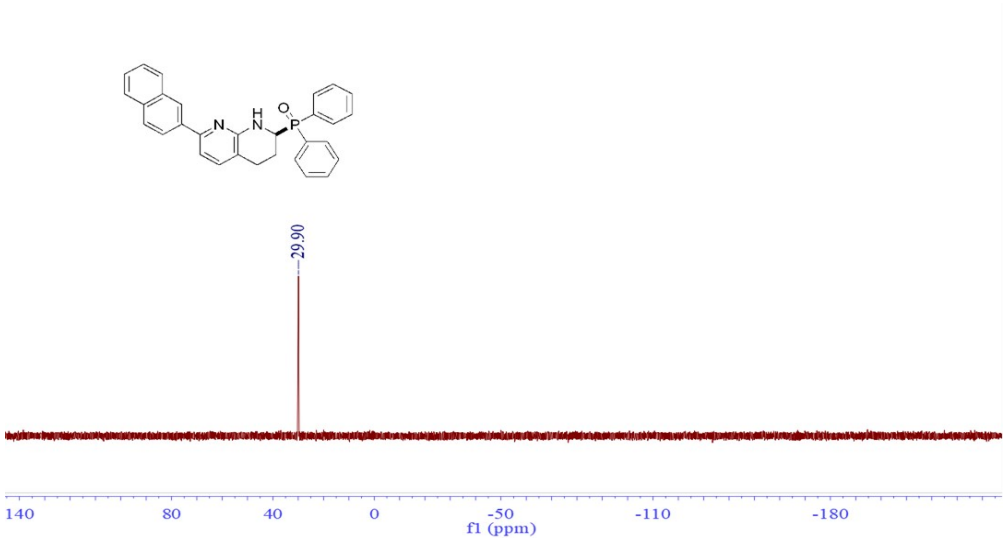
(15) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3oa



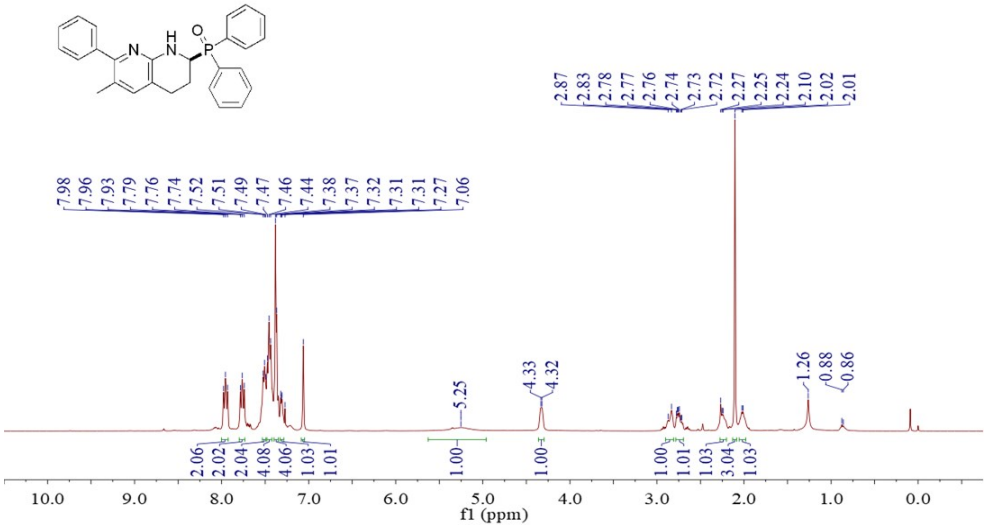
(16) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3pa



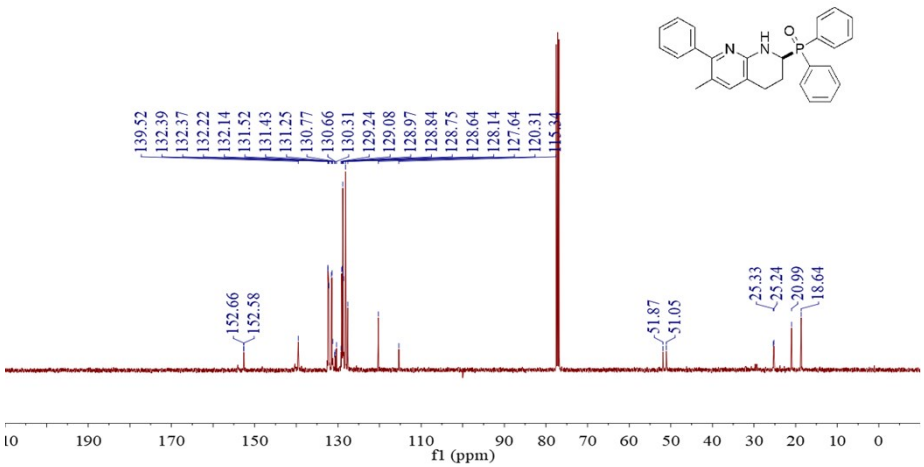
(16) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3pa



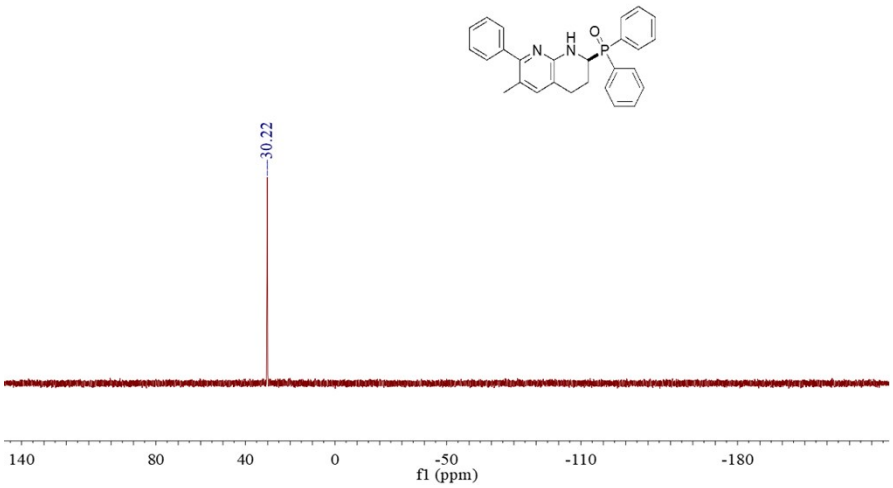
(16) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3pa



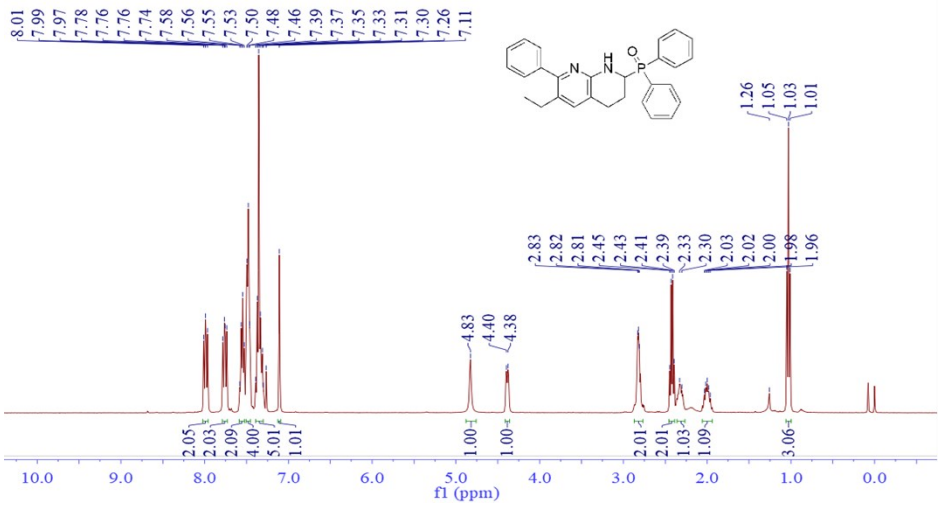
(17) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3qa



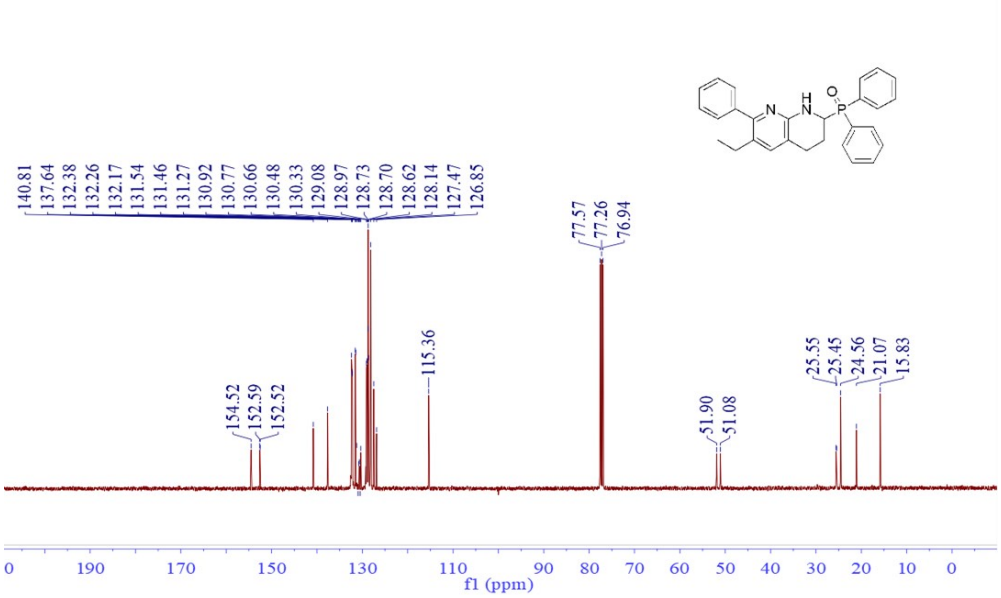
(17) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3qa



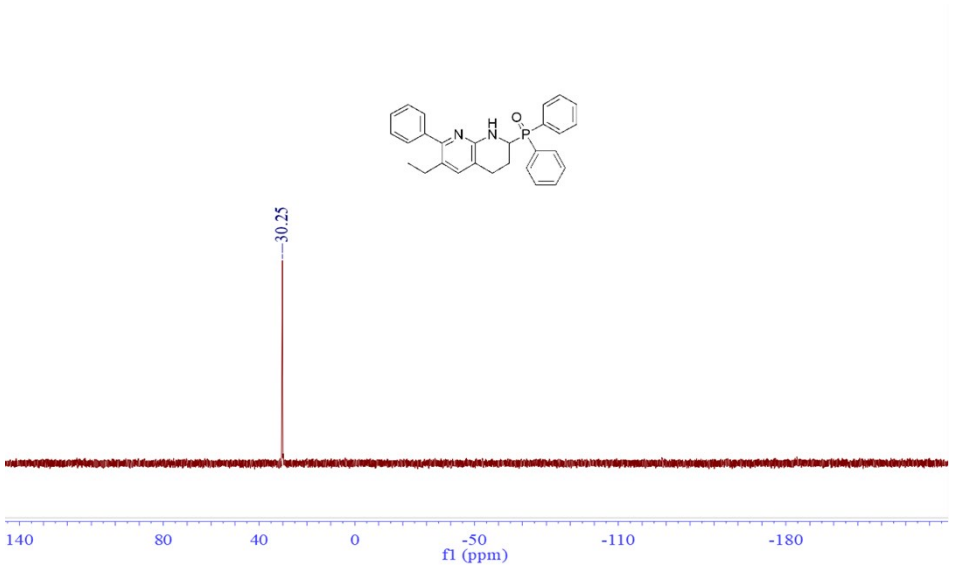
(17) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3qa



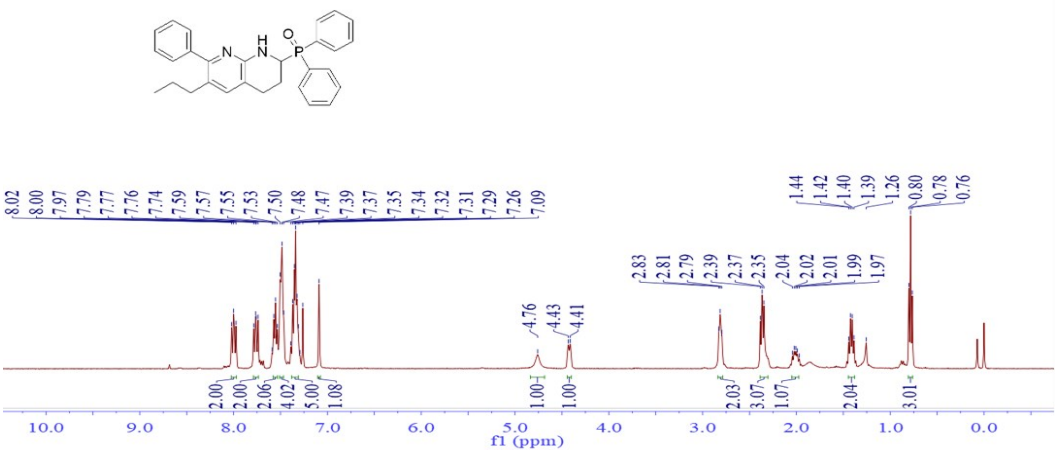
(18) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ra



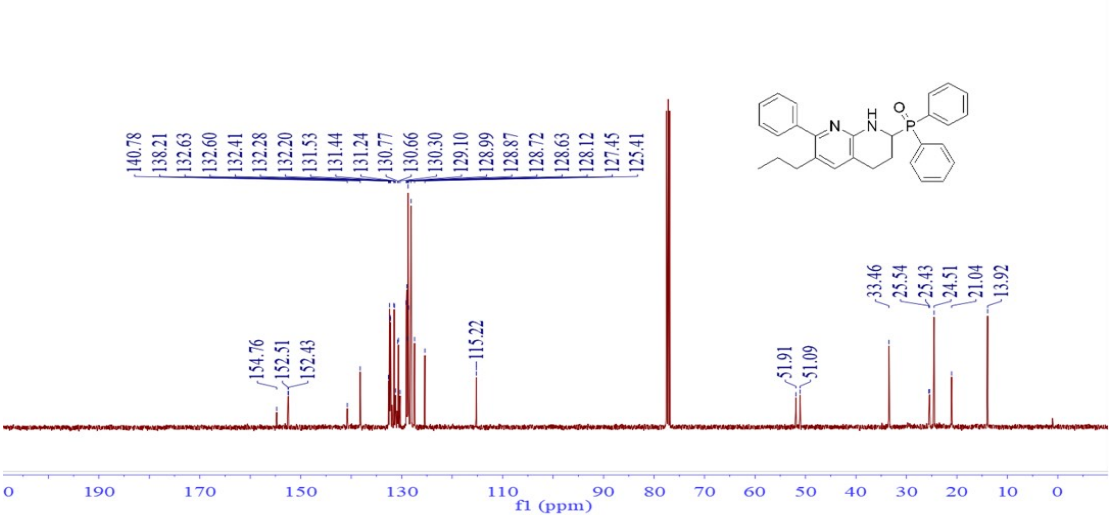
(18) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ra



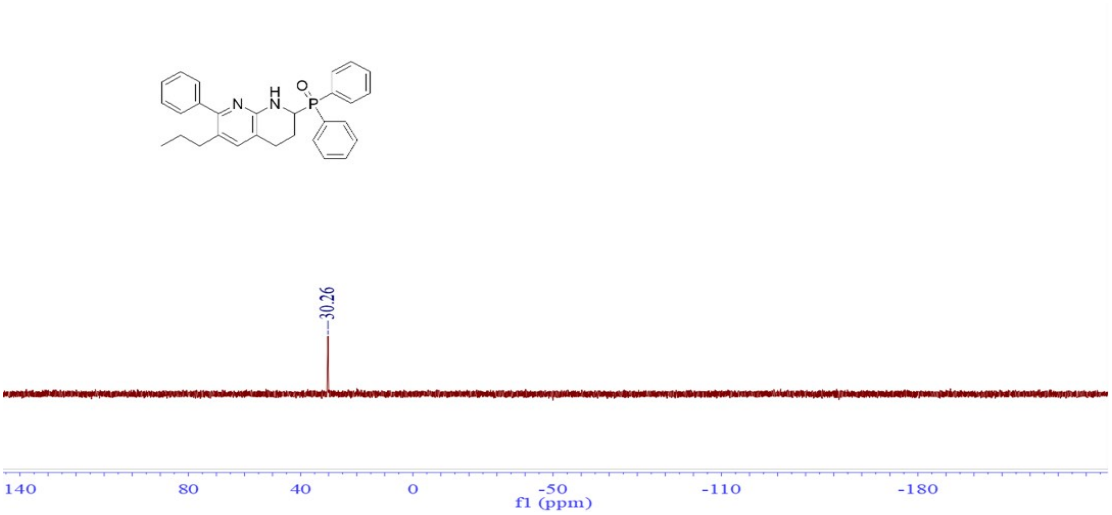
(18) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ra



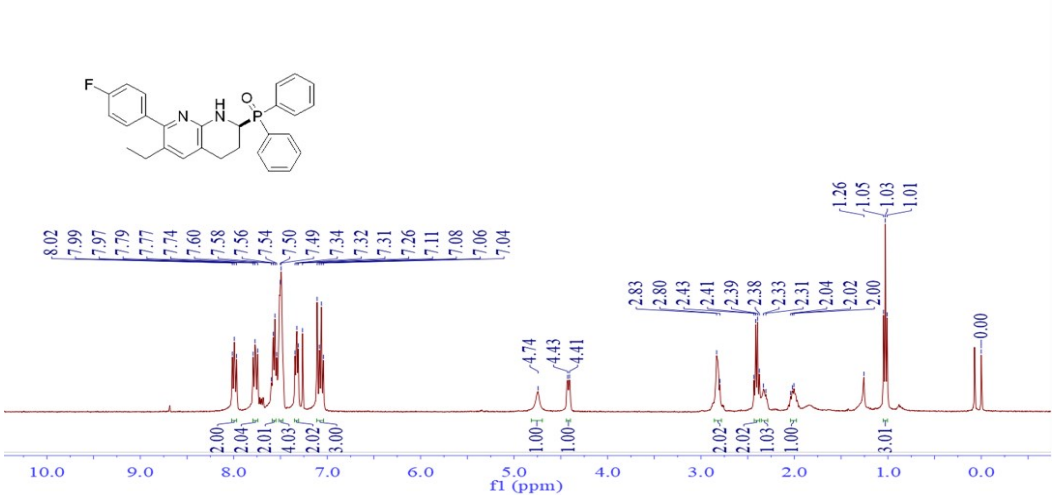
(19) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3sa



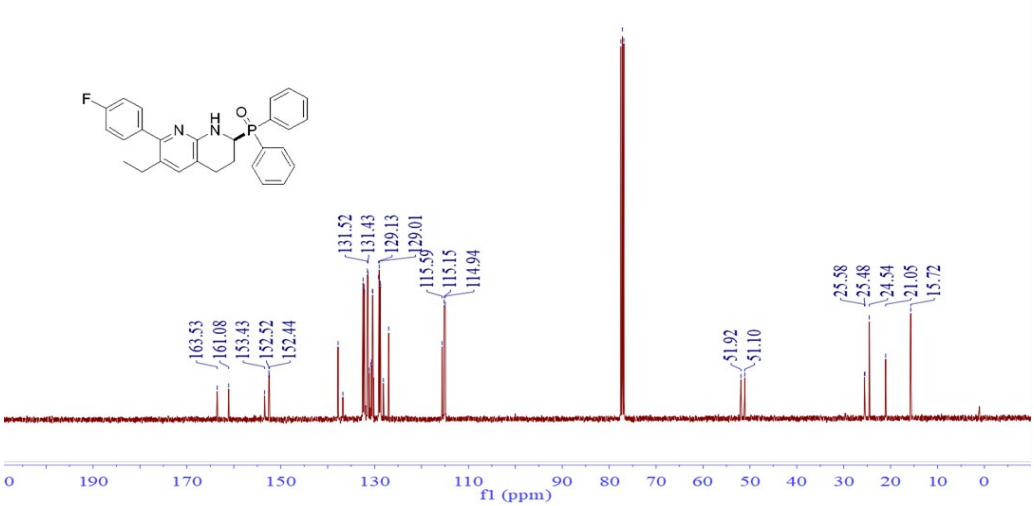
(19) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3sa



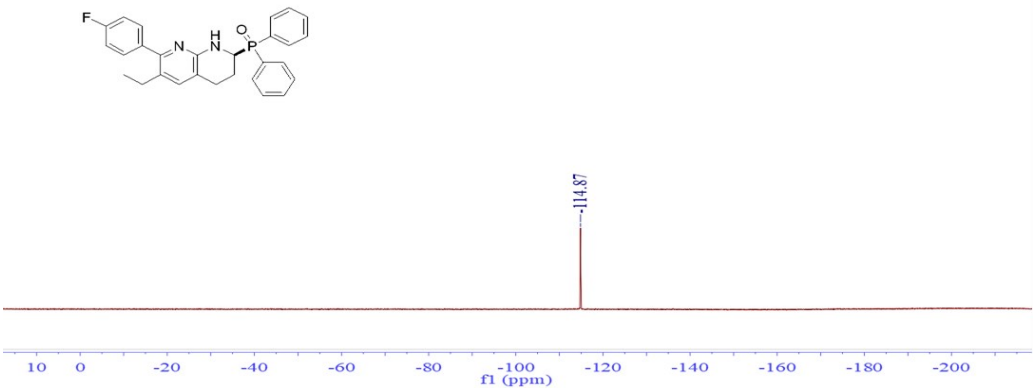
(19) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3sa



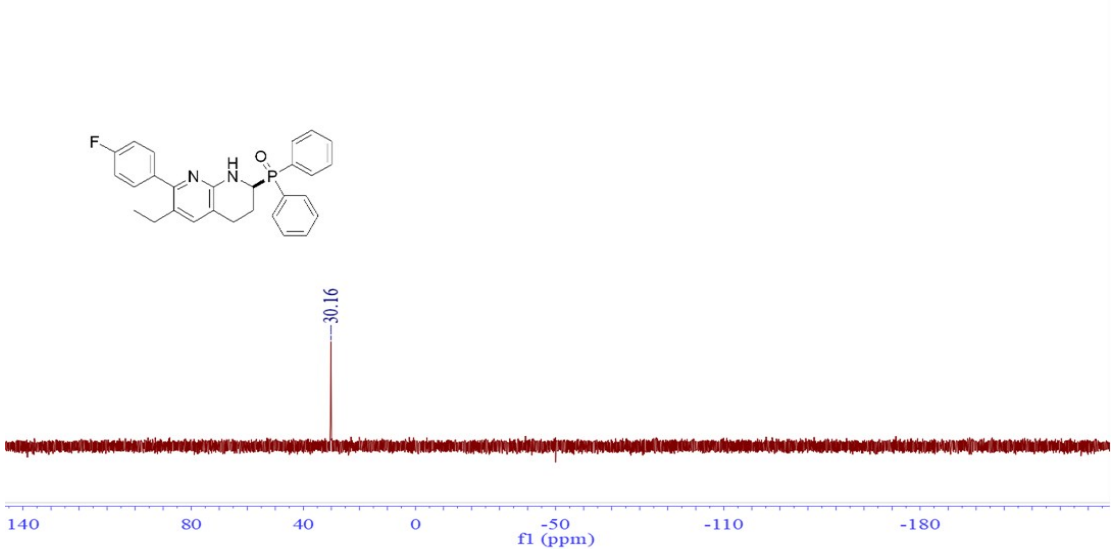
(20) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ta



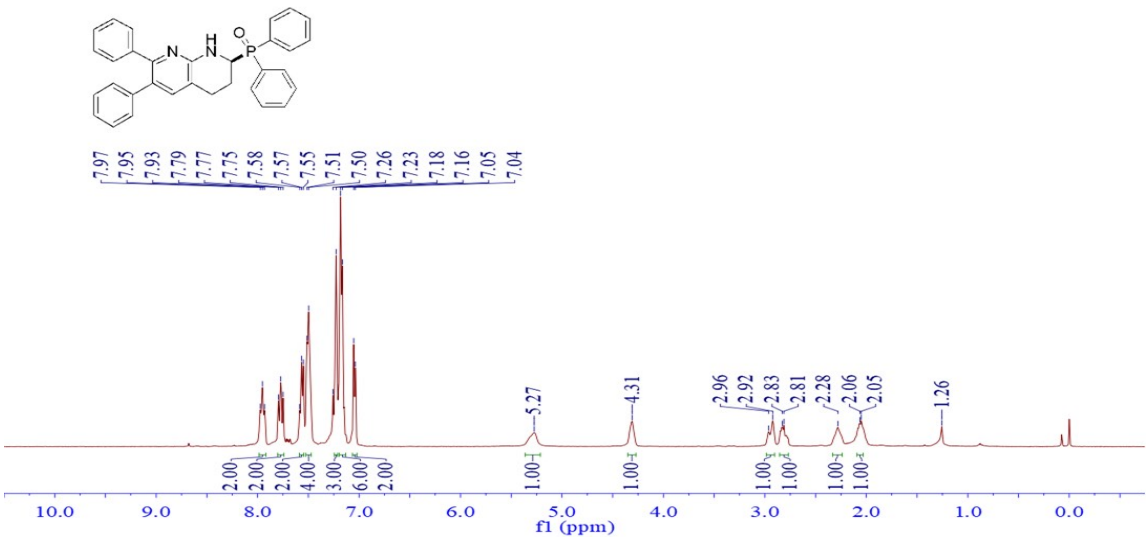
(20) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ta



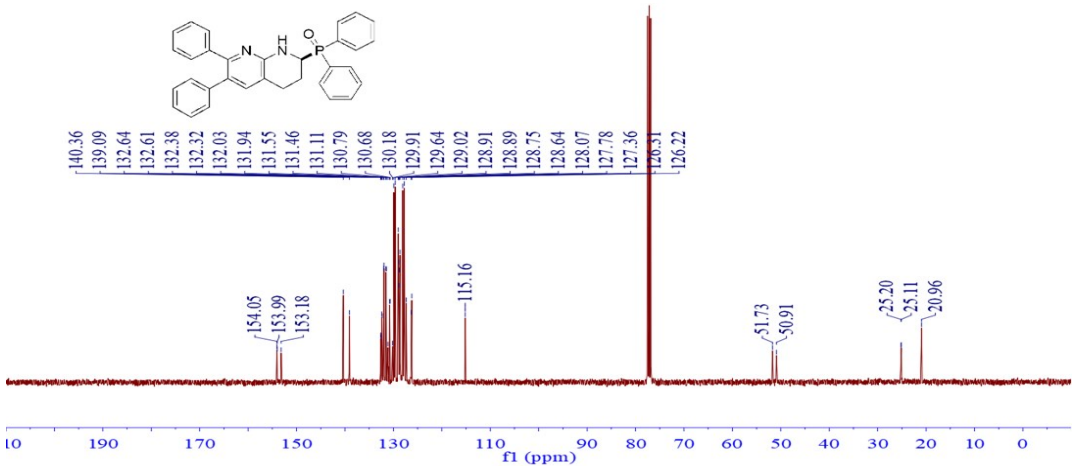
(20) ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3ta



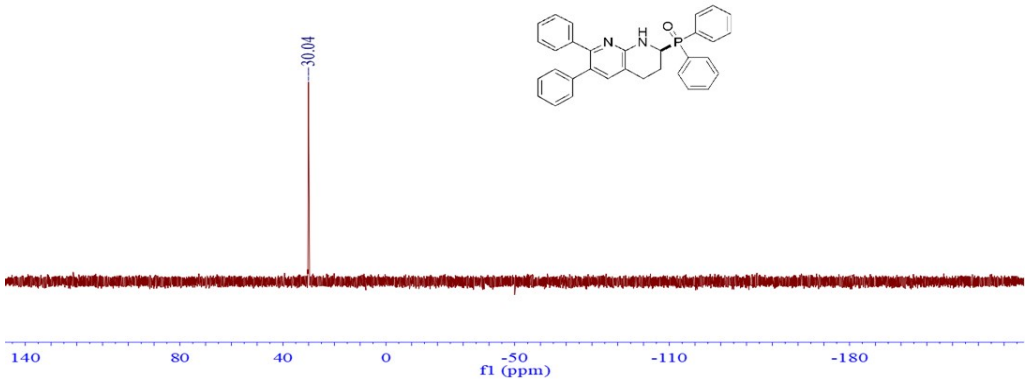
(20) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ta



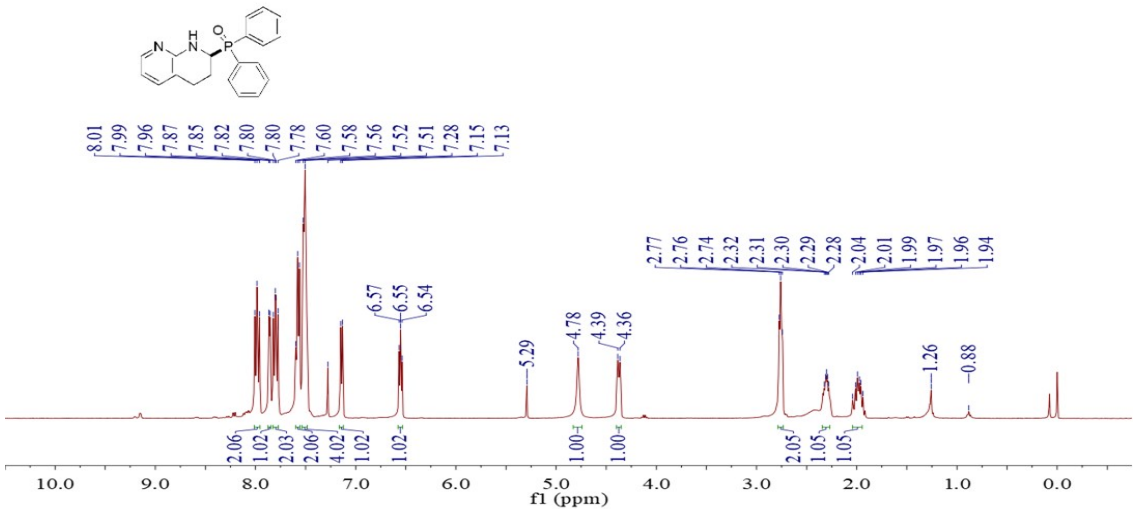
(21) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ua



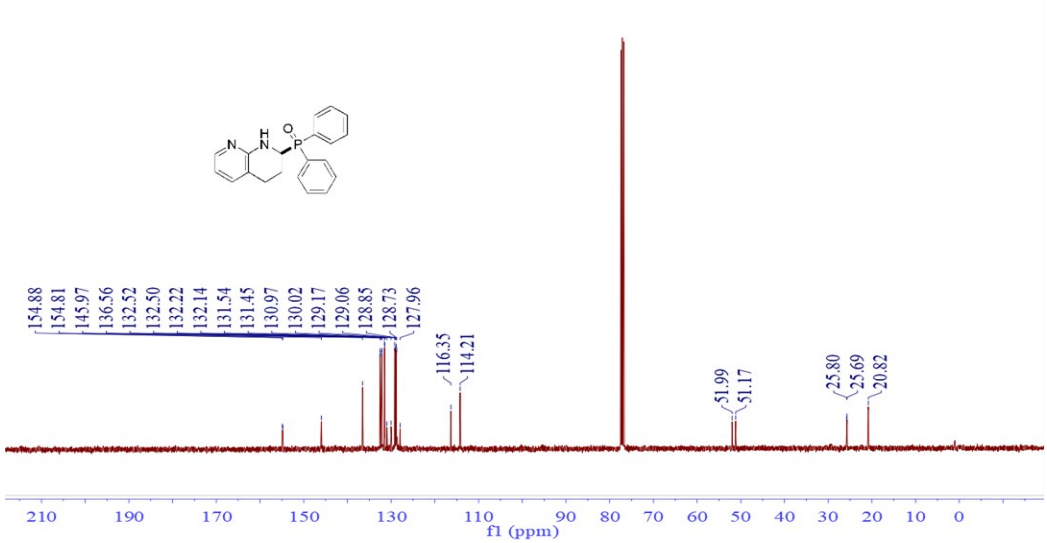
(21) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ua



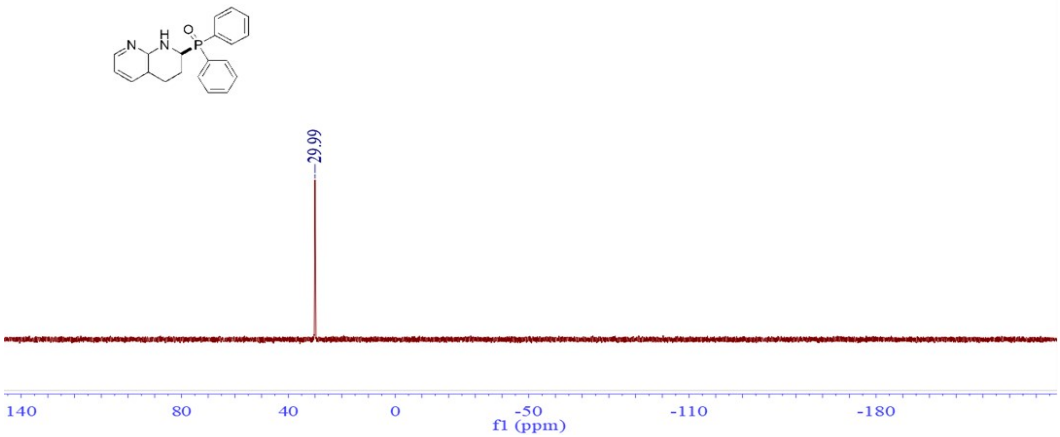
(21) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ua



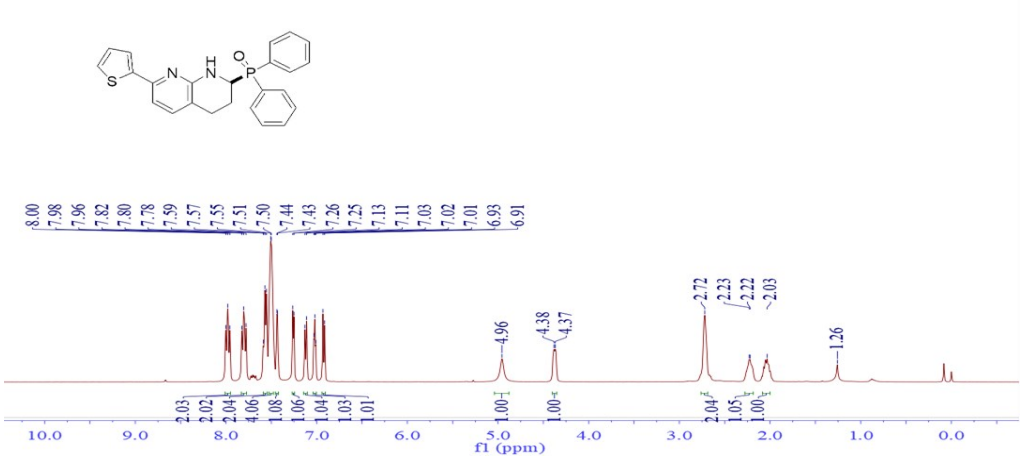
(22) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3va



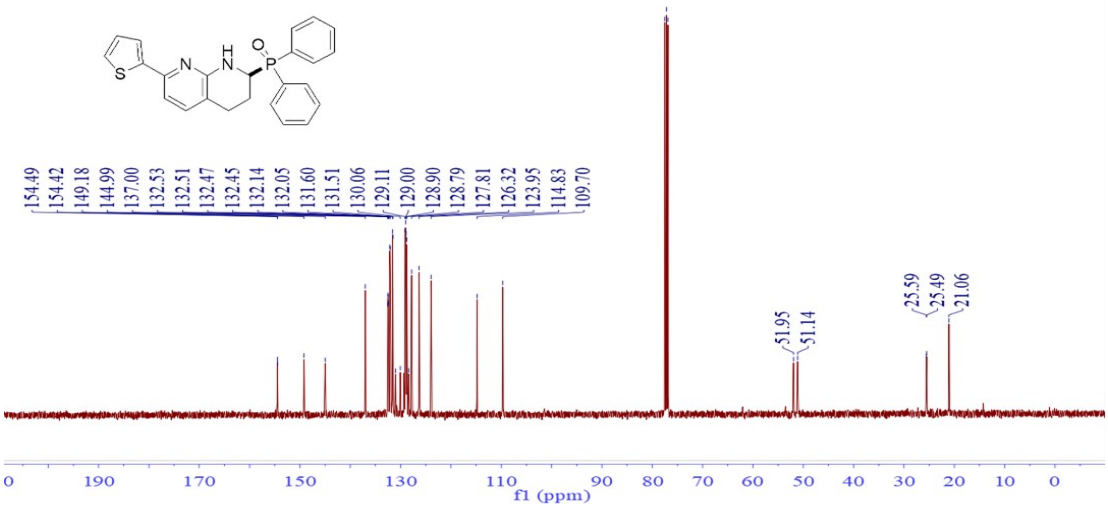
(22) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3va



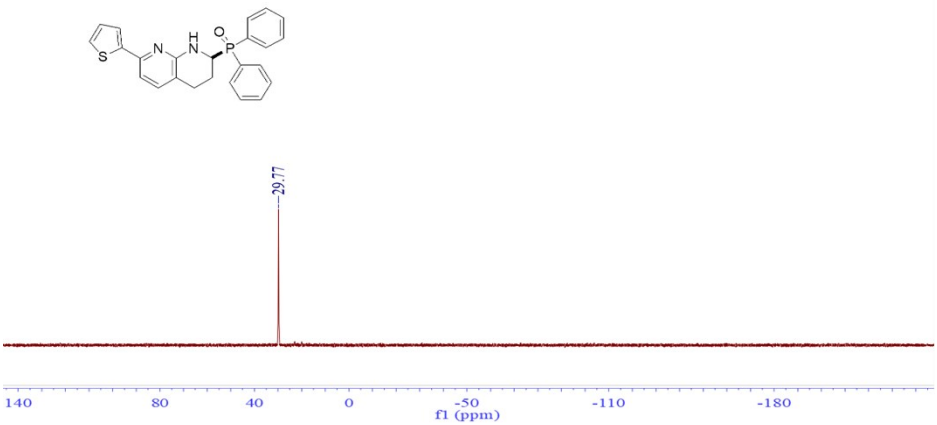
(22) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3va



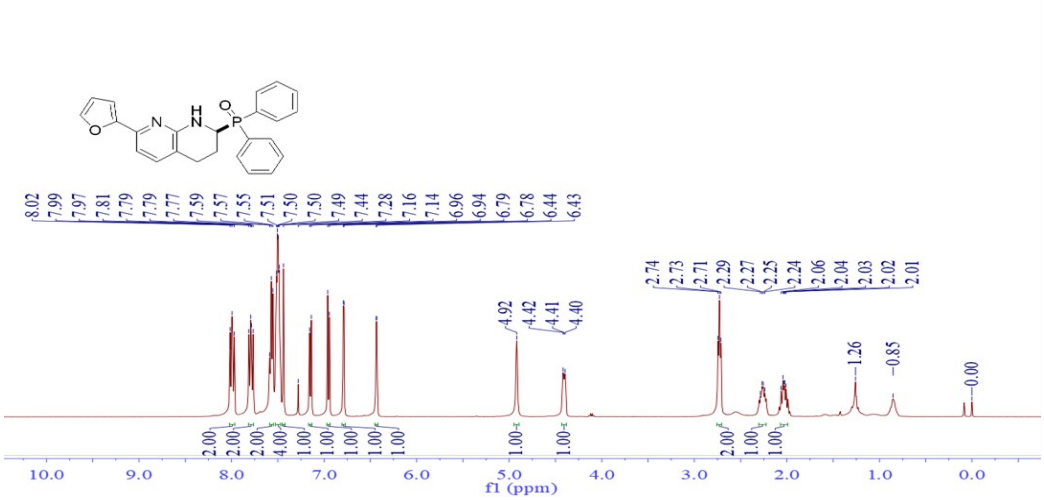
(23) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3wa



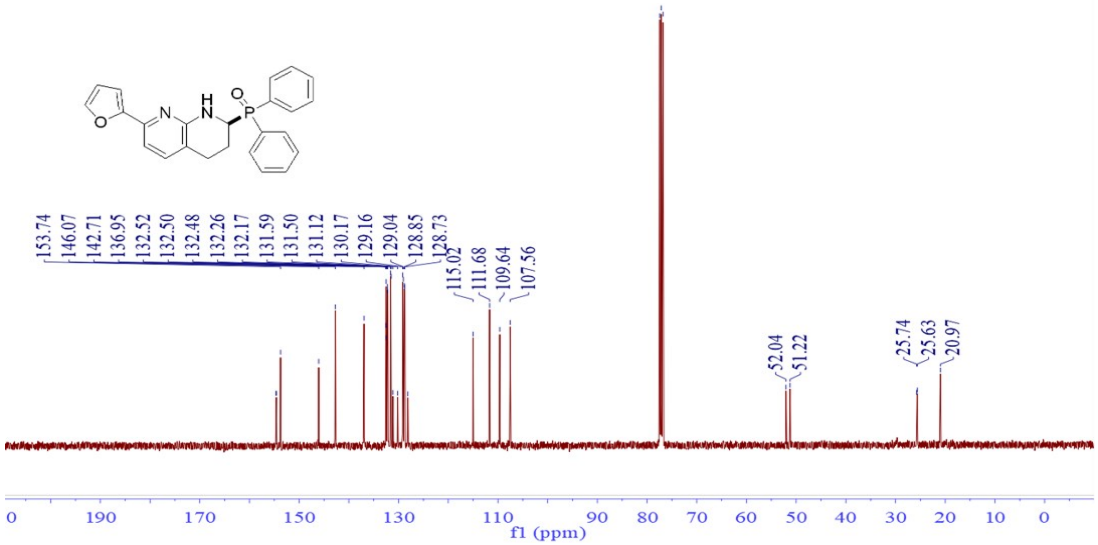
(23) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3wa



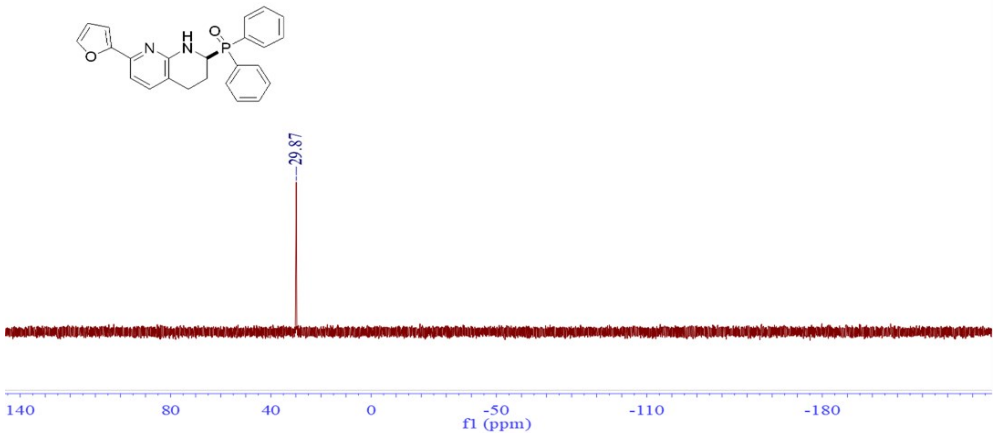
(23) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3wa



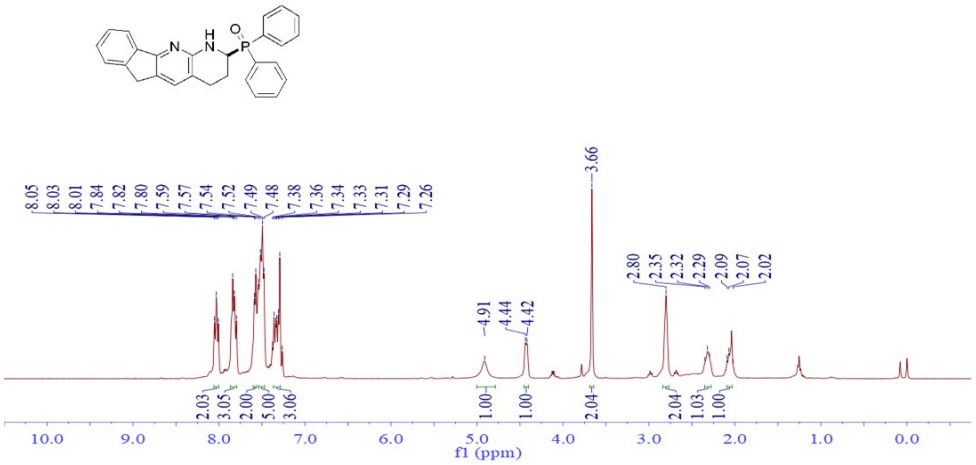
(24) ^{1}H-NMR (162 MHz, $CDCl_3$) spectrum of 3xa



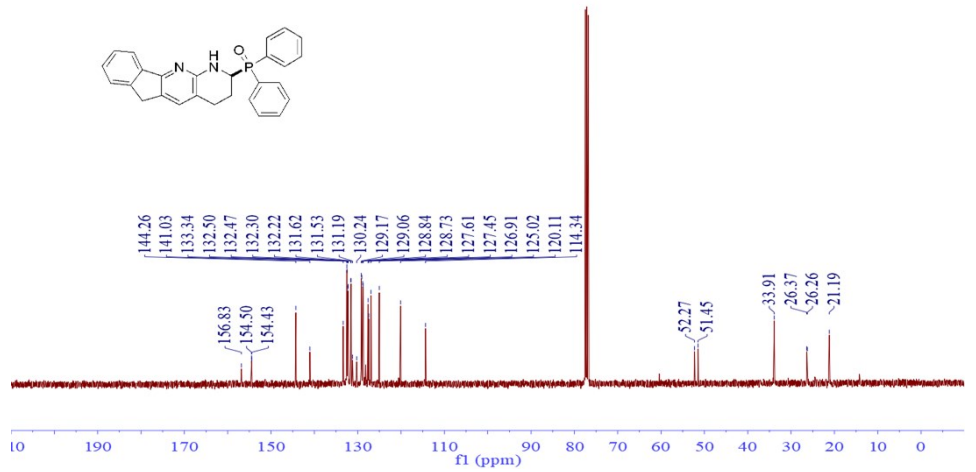
(24) ^{13}C-NMR (162 MHz, $CDCl_3$) spectrum of 3xa



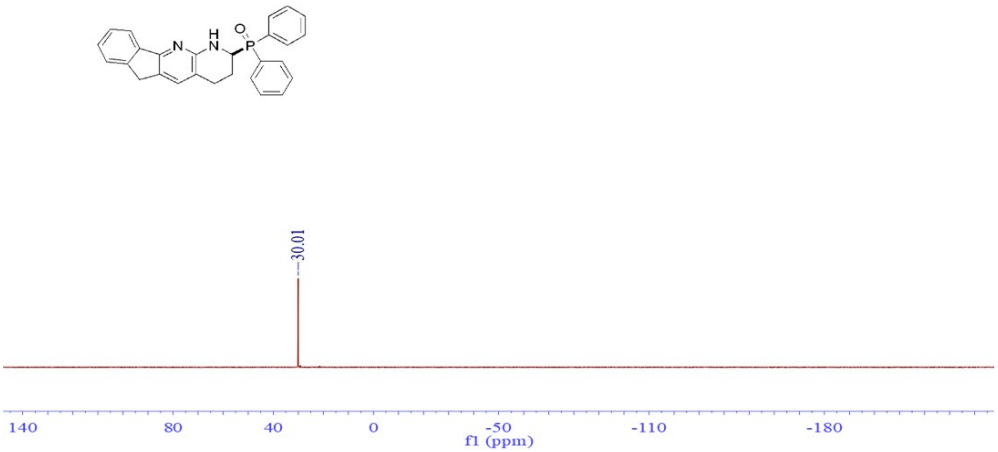
(24) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3xa



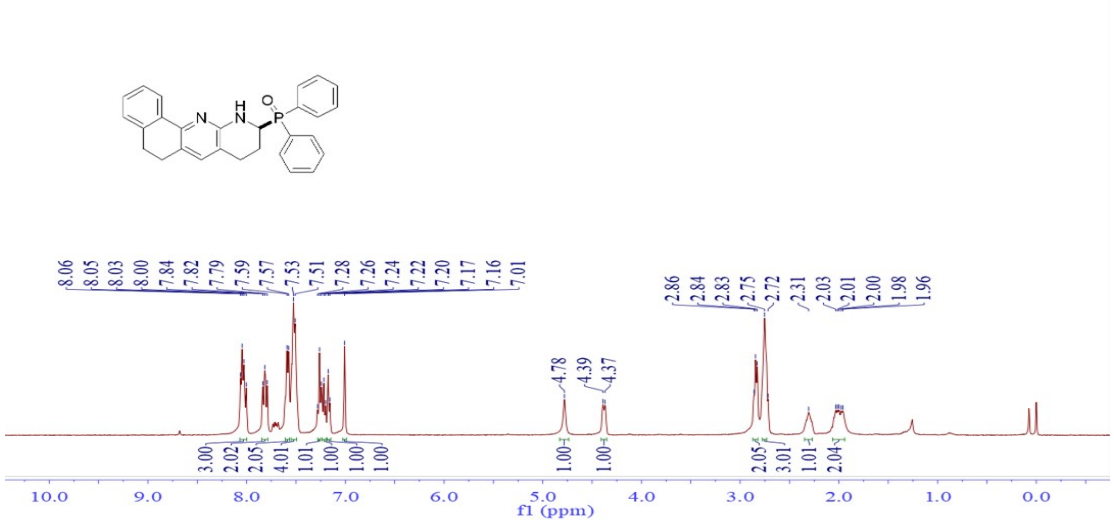
(25) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ya



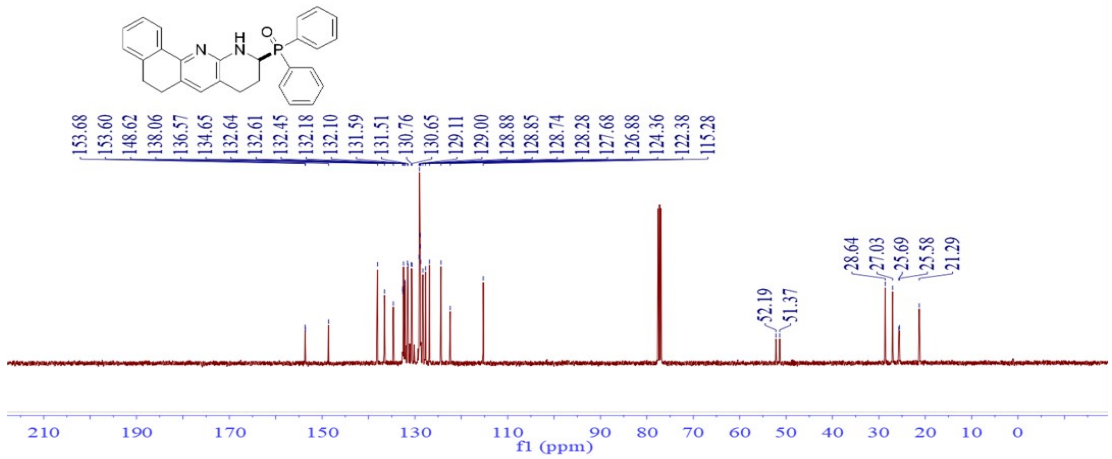
(25) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ya



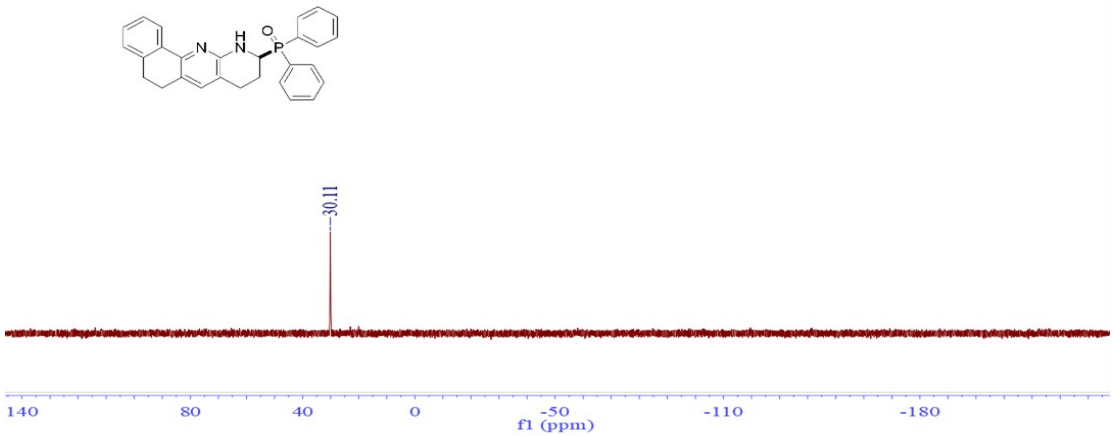
(25) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ya



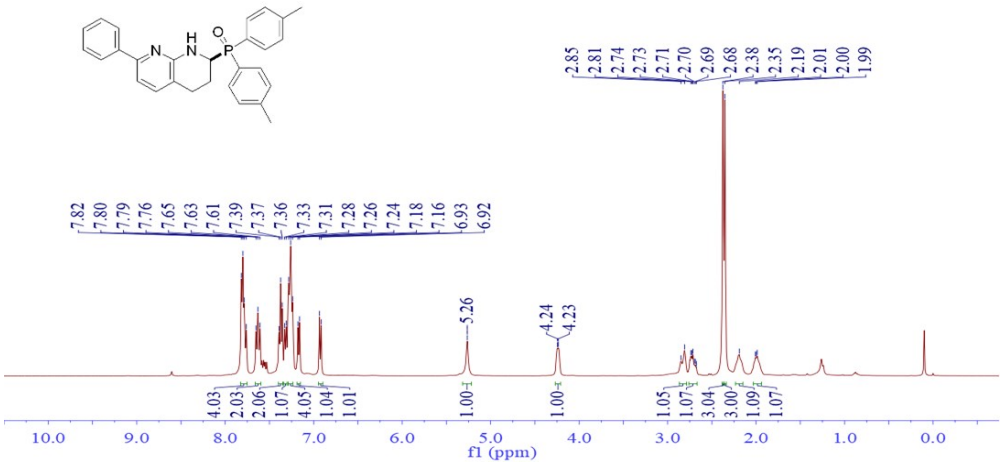
(26) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3za



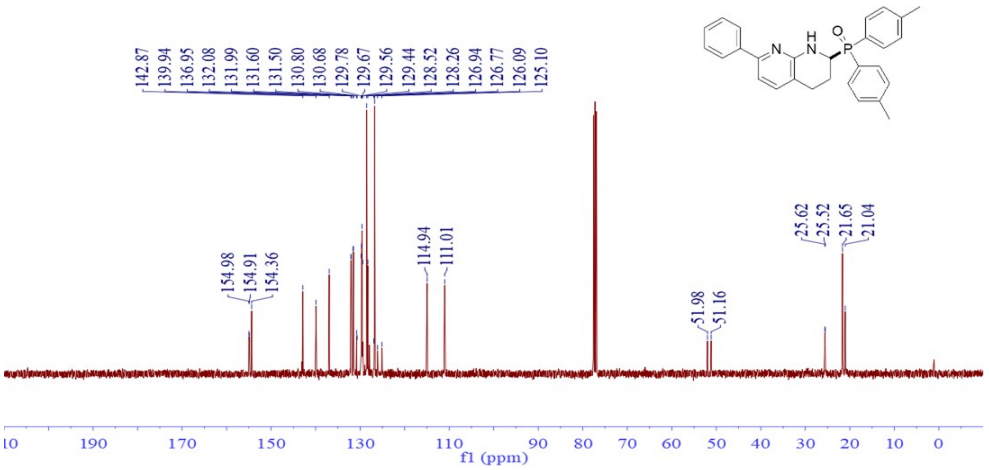
(26) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3za



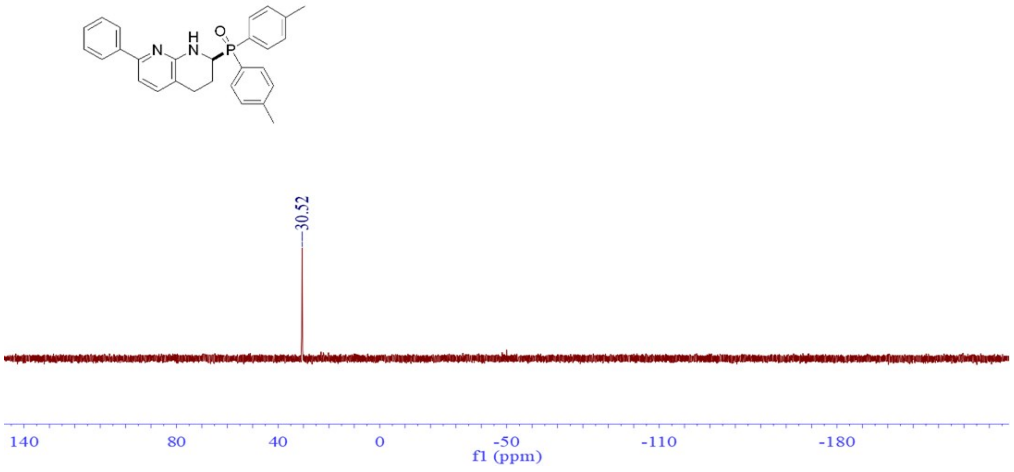
(26) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3za



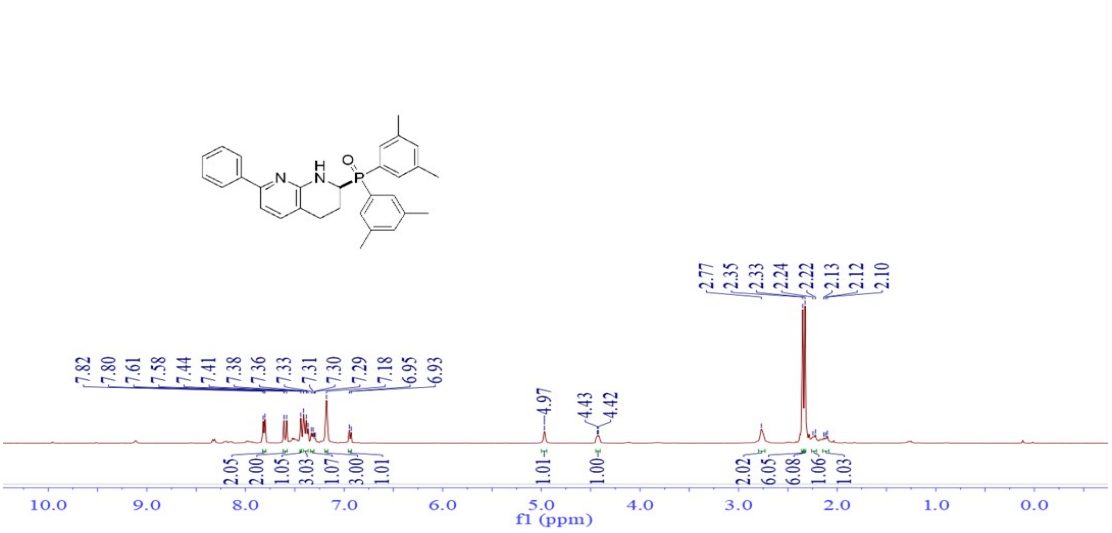
(27) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ab



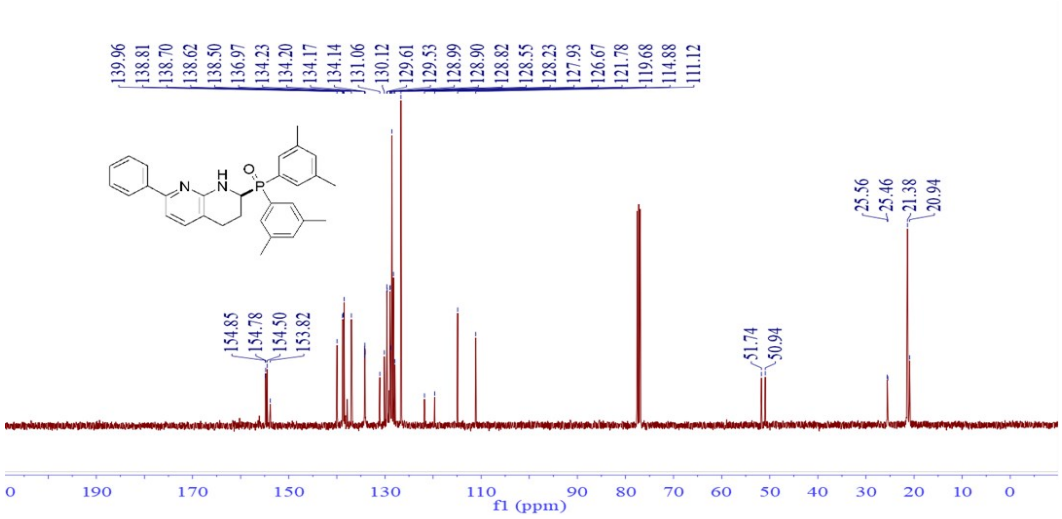
(27) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ab



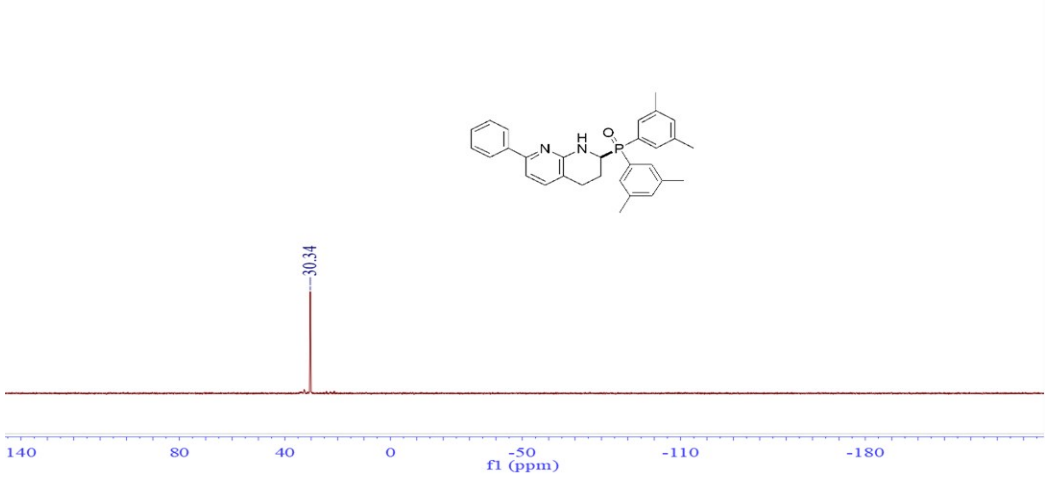
(27) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ab



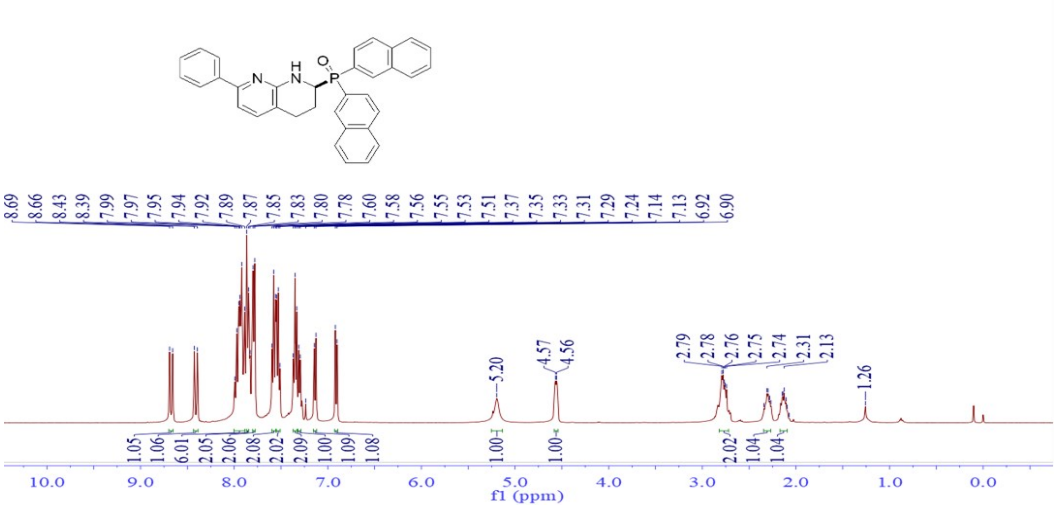
(28) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ac



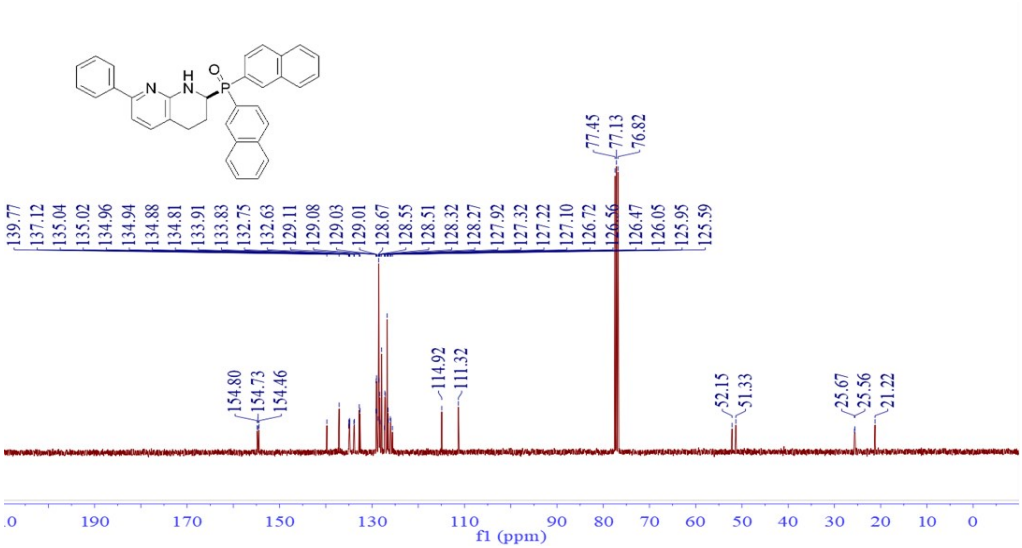
(28) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ac



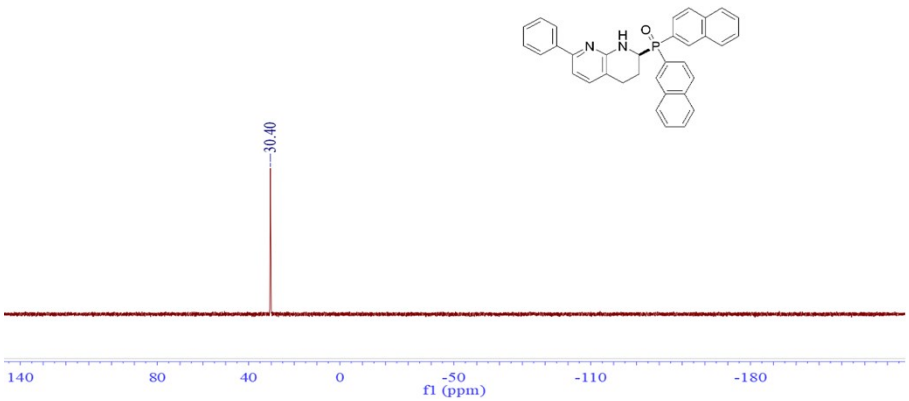
(28) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ac



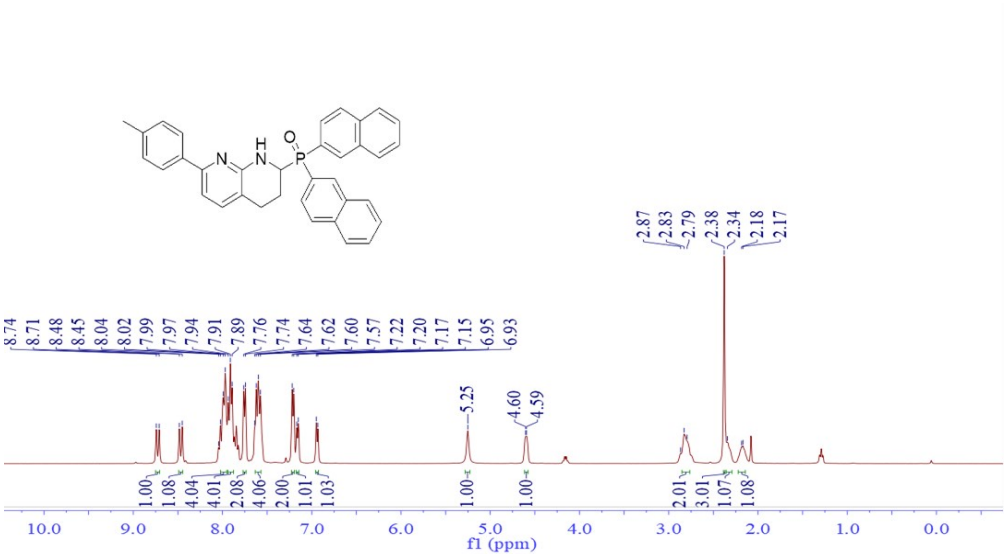
(29) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ad



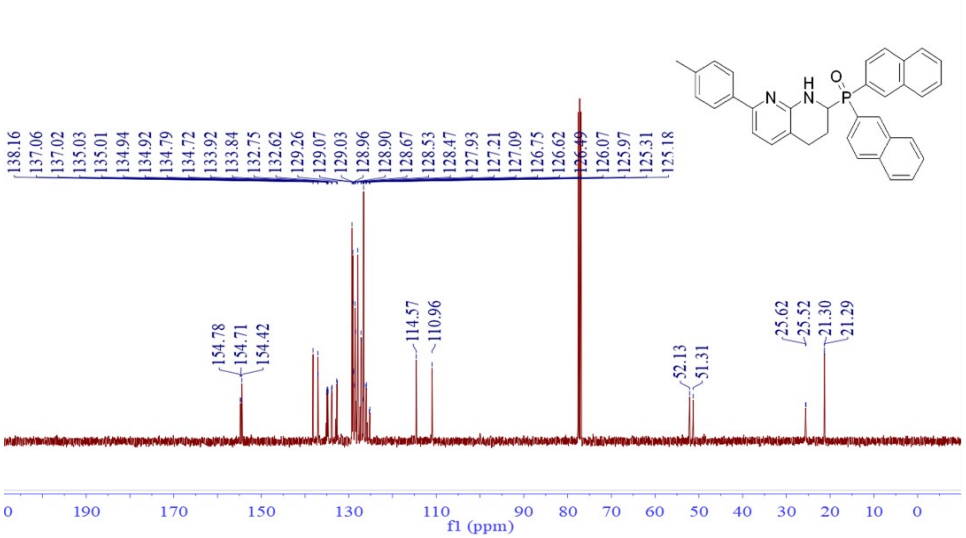
(29) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3ad



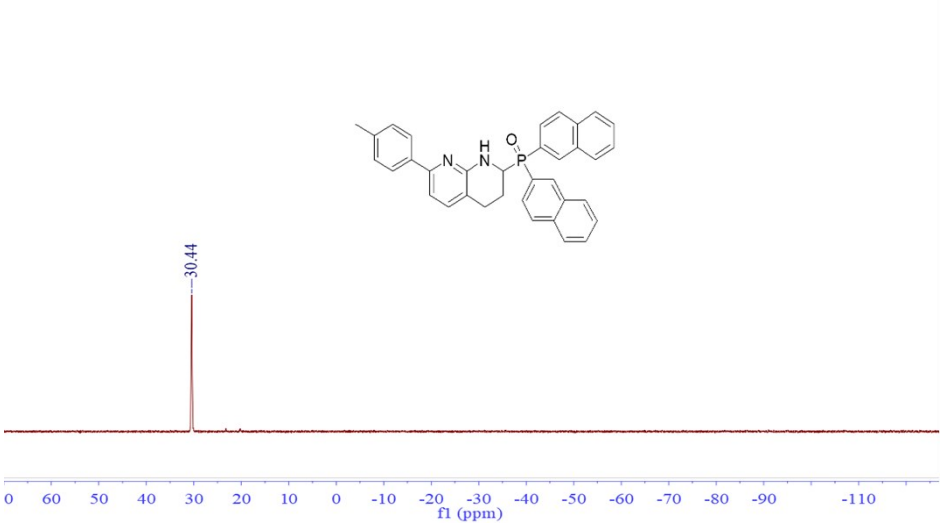
(29) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3ad



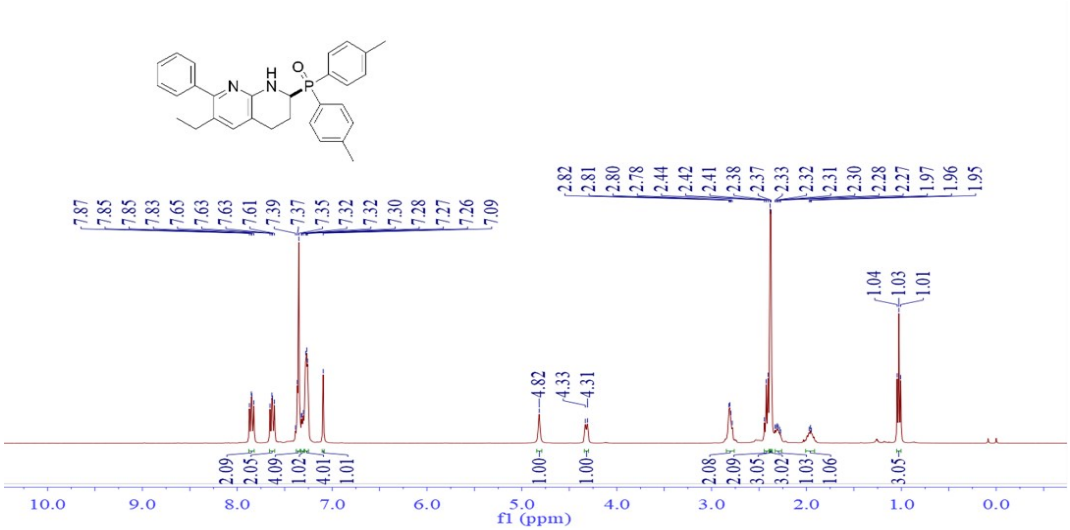
(30) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3bd



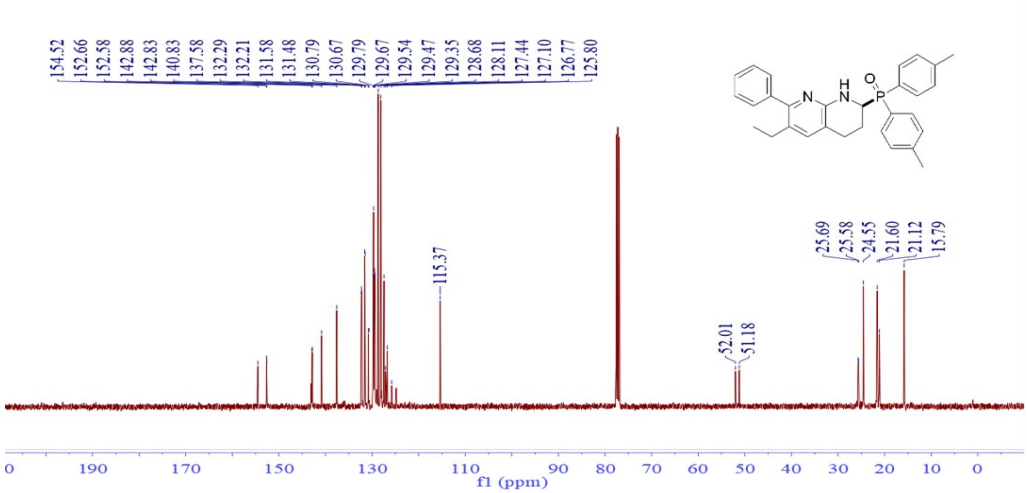
(30) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3bd



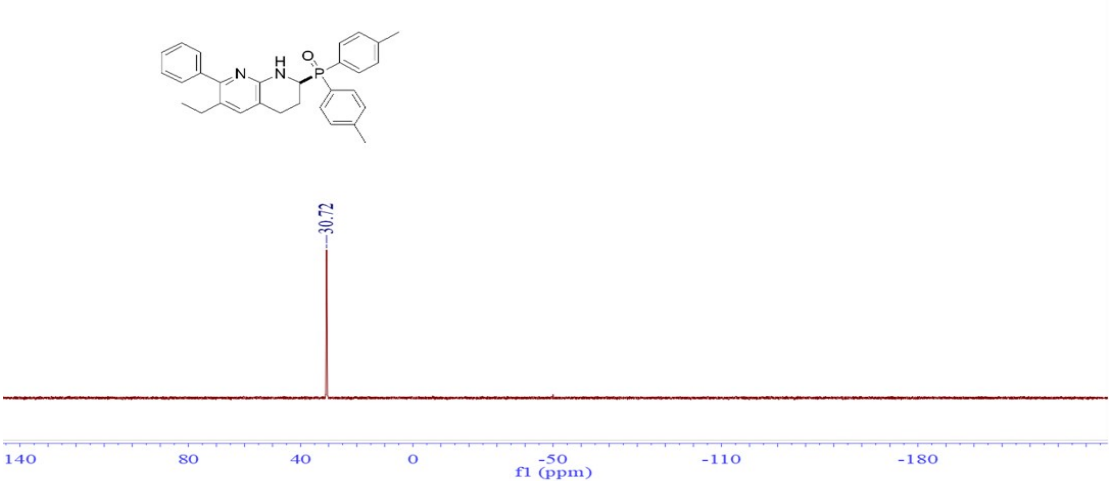
(30) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3bd



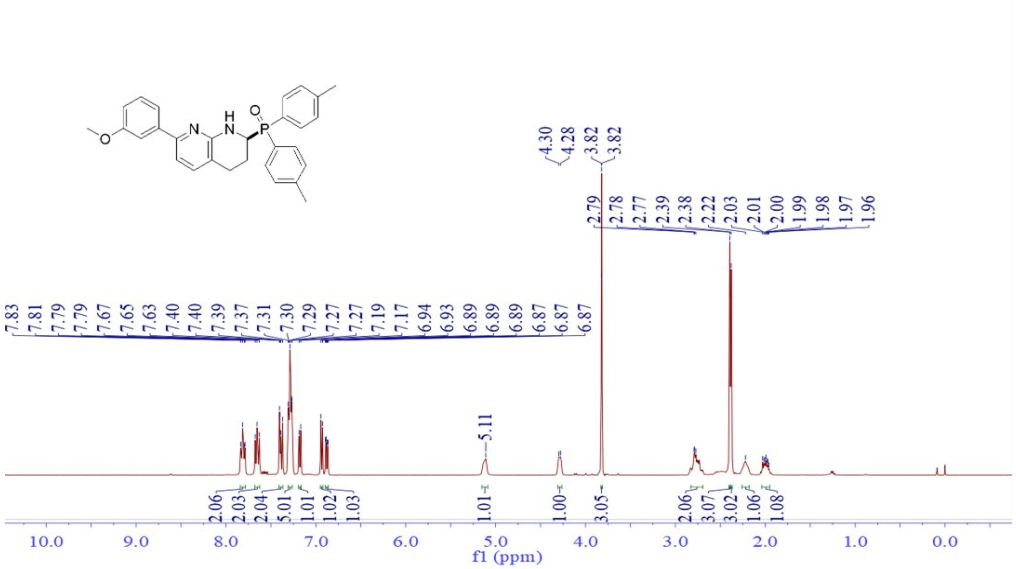
(31) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3rb



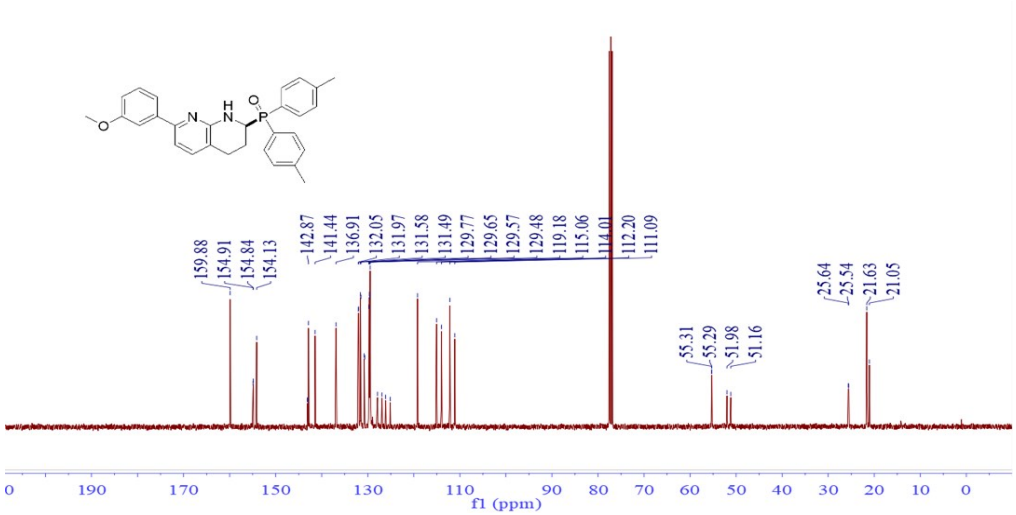
(31) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3rb



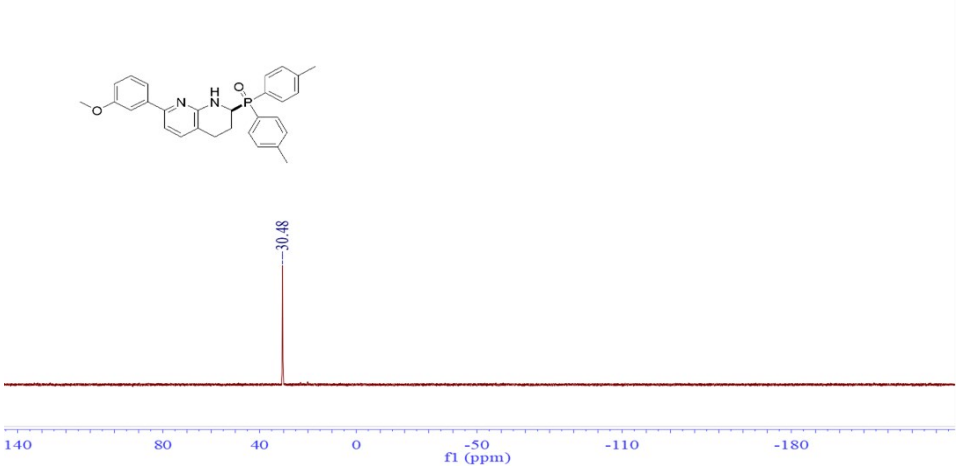
(31) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3rb



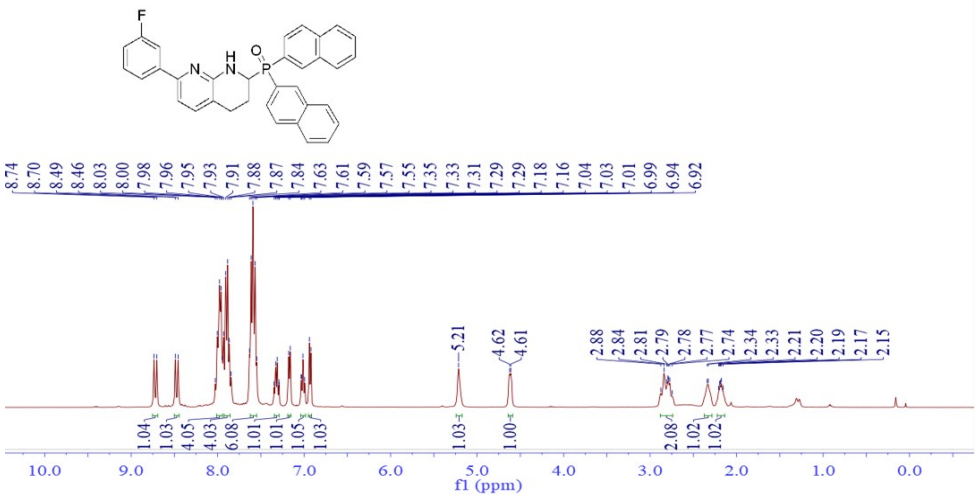
(32) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3db



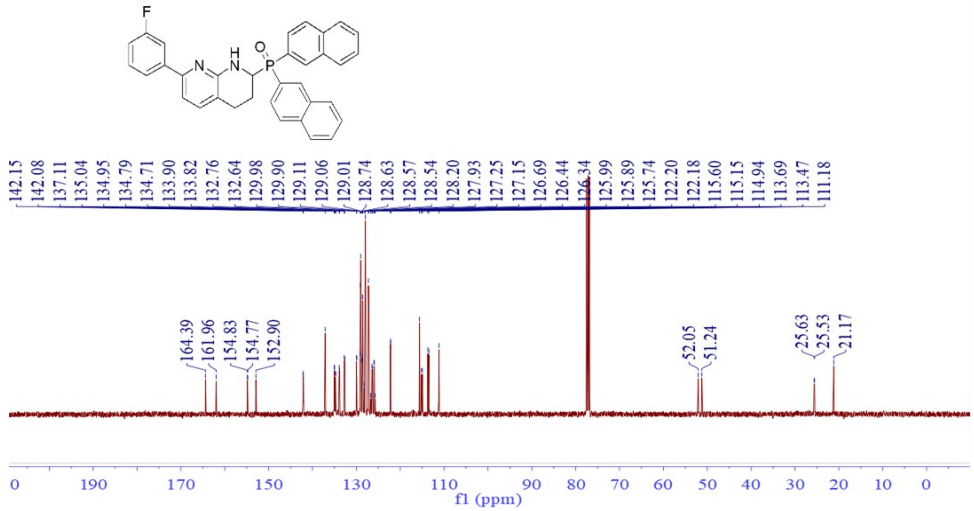
(32) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3db



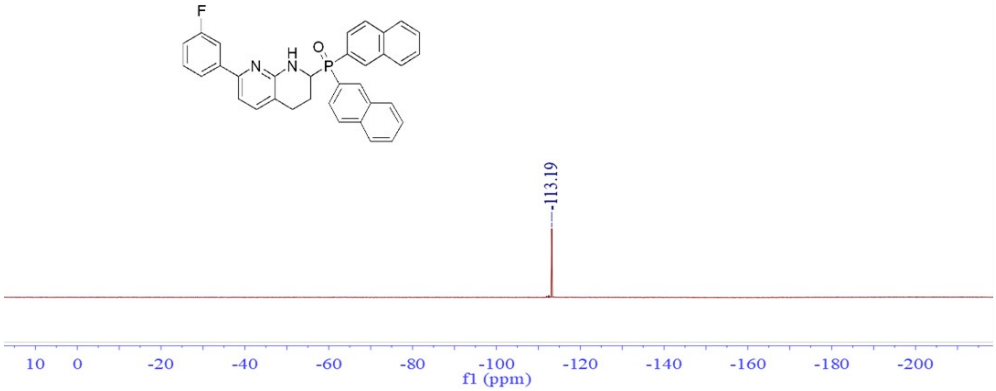
(32) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3db



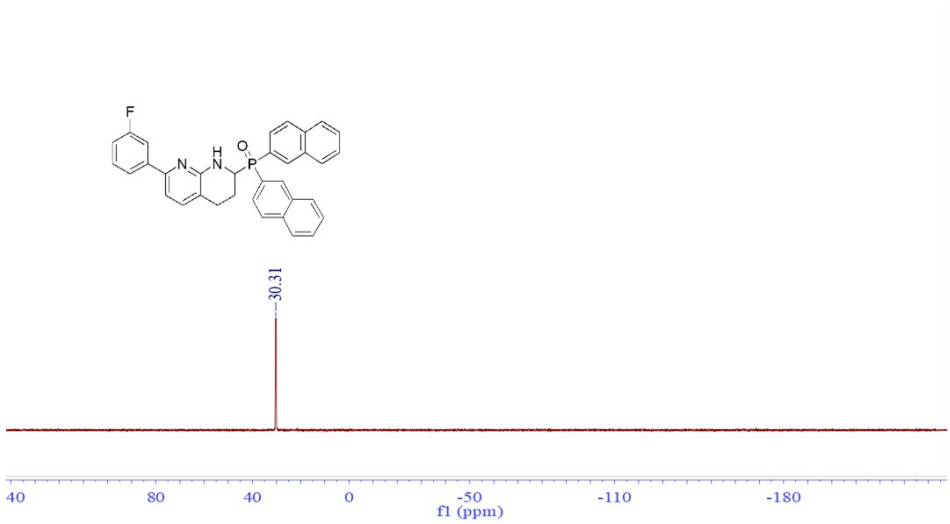
(33) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3md



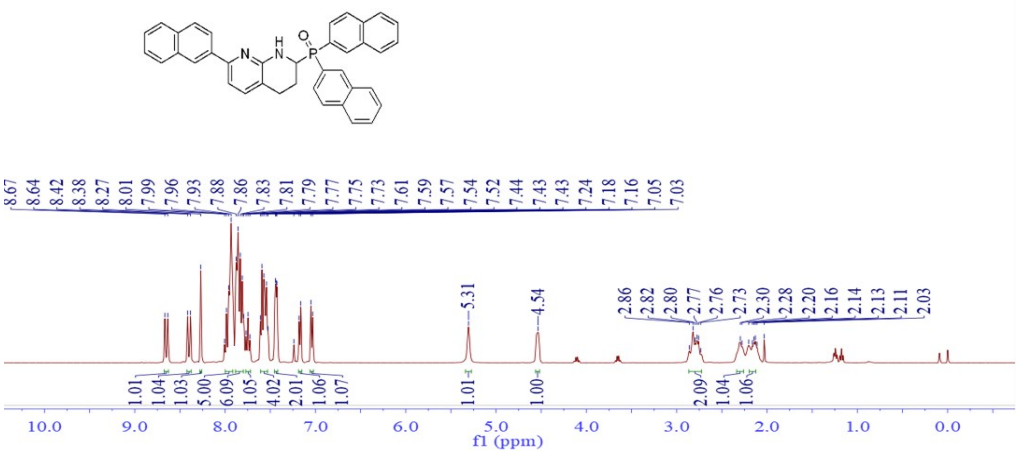
(33) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3md



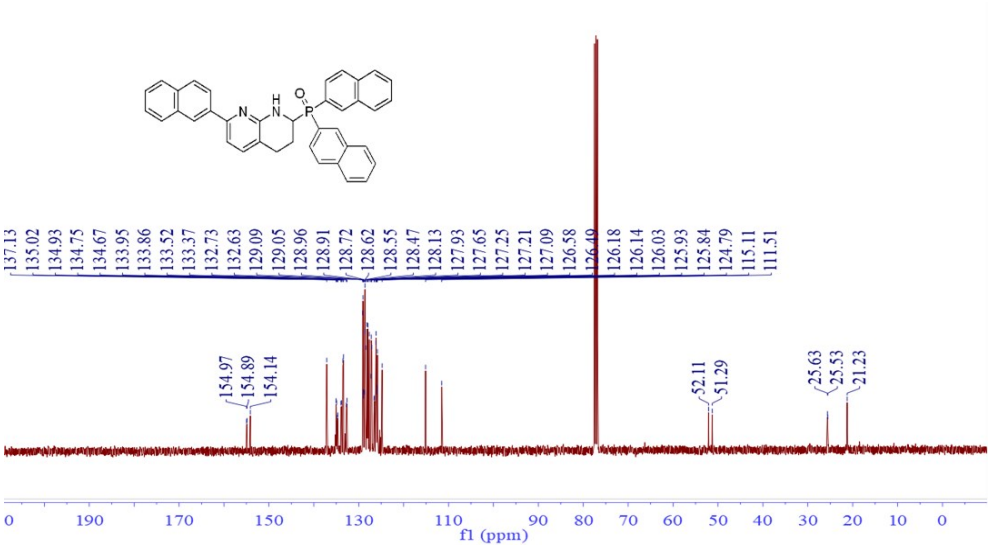
(33) ^{19}F-NMR (376 MHz, $CDCl_3$) spectrum of 3md



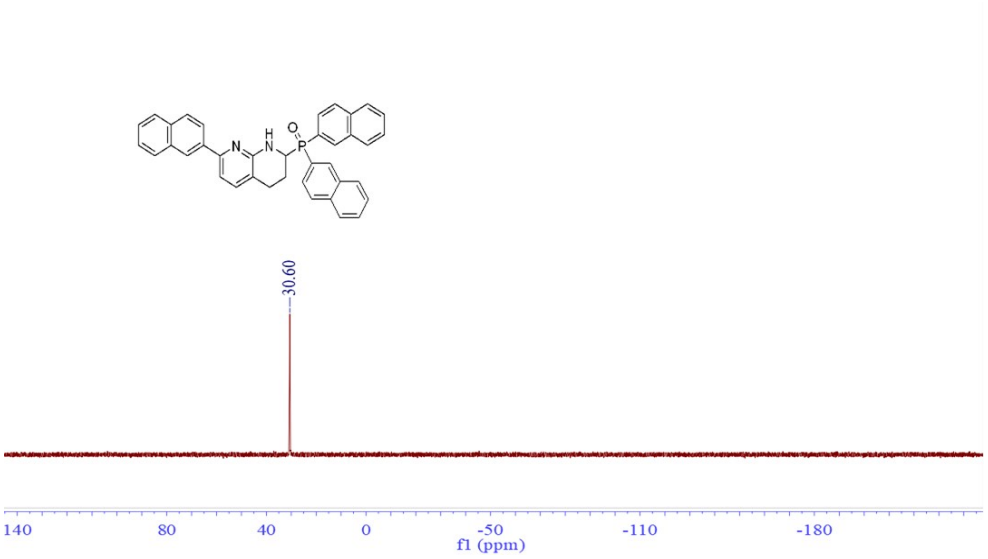
(33) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3md



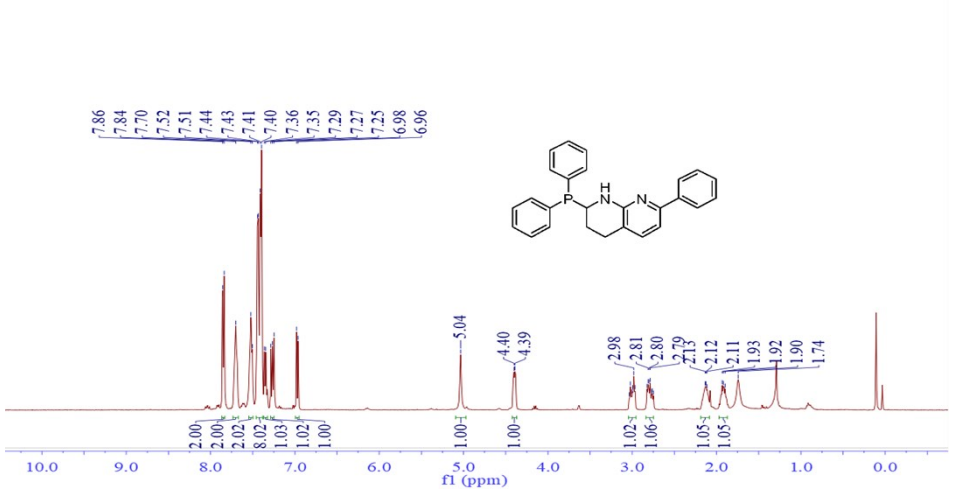
(34) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3pd



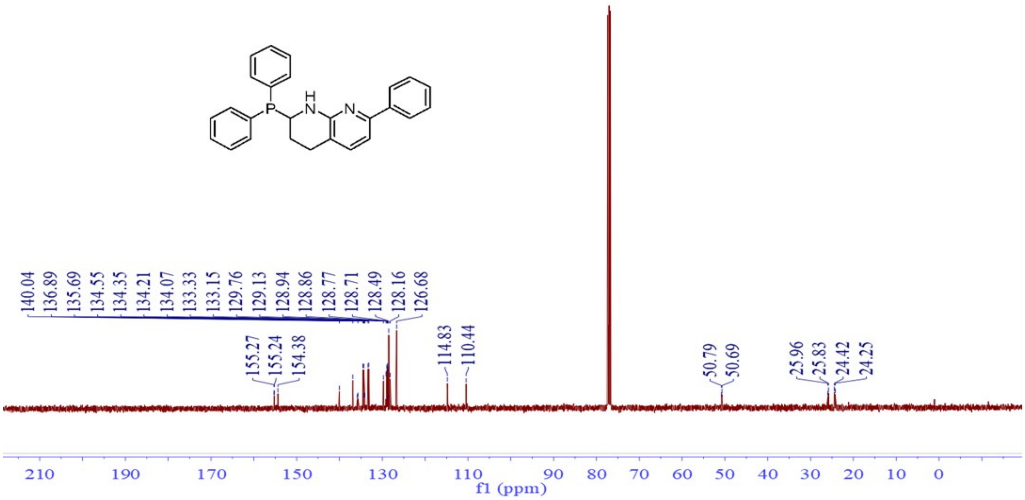
(34) ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 3pd



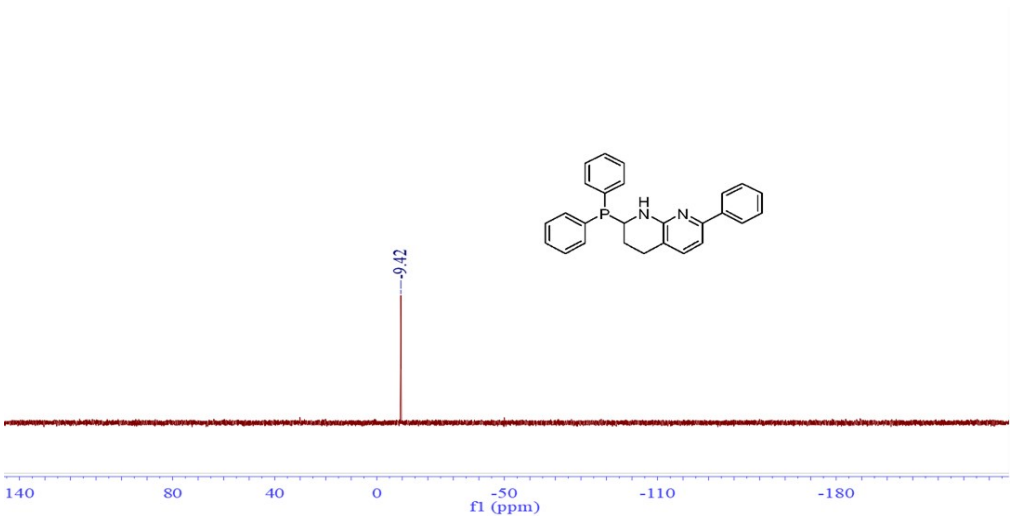
(34) ^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 3pd



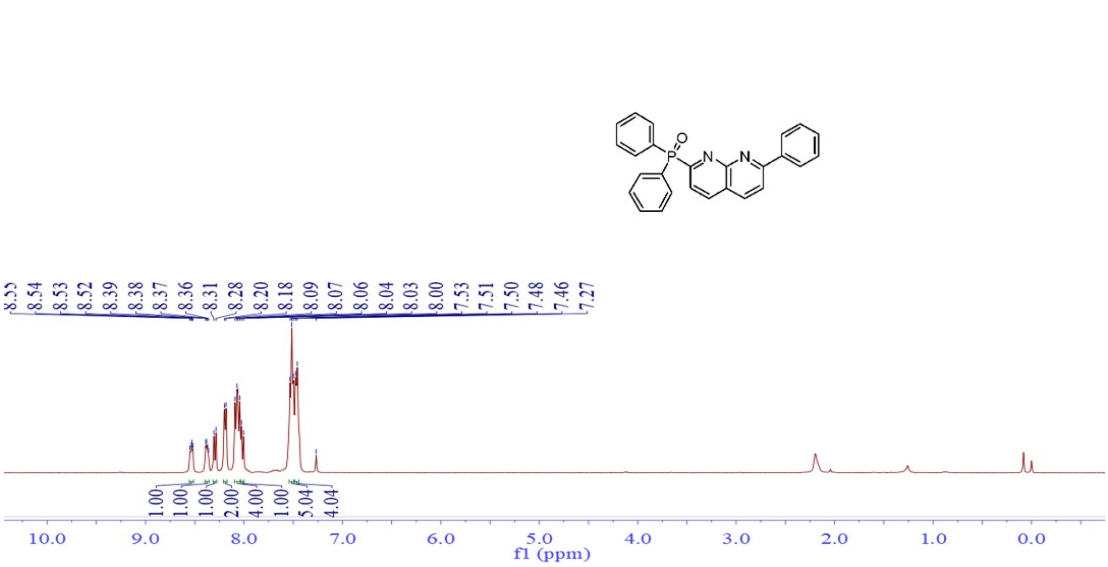
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 4aa



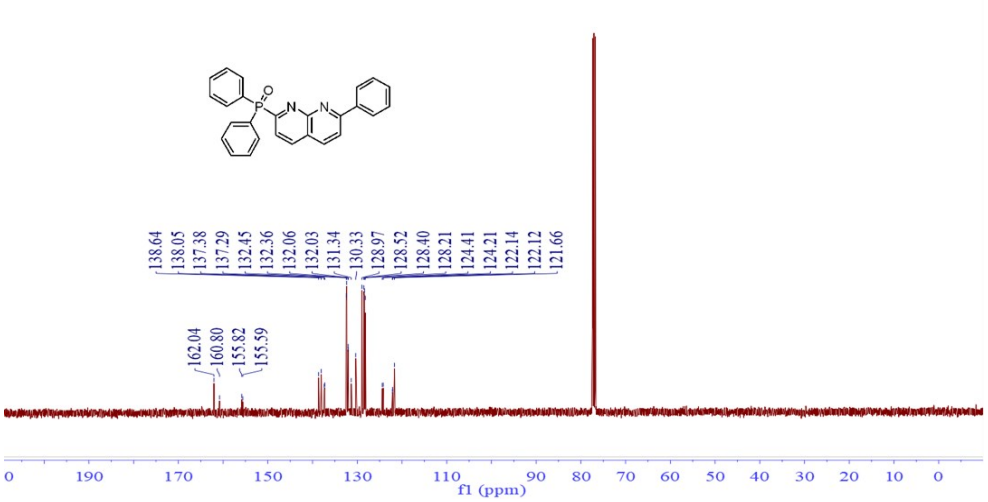
^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 4aa



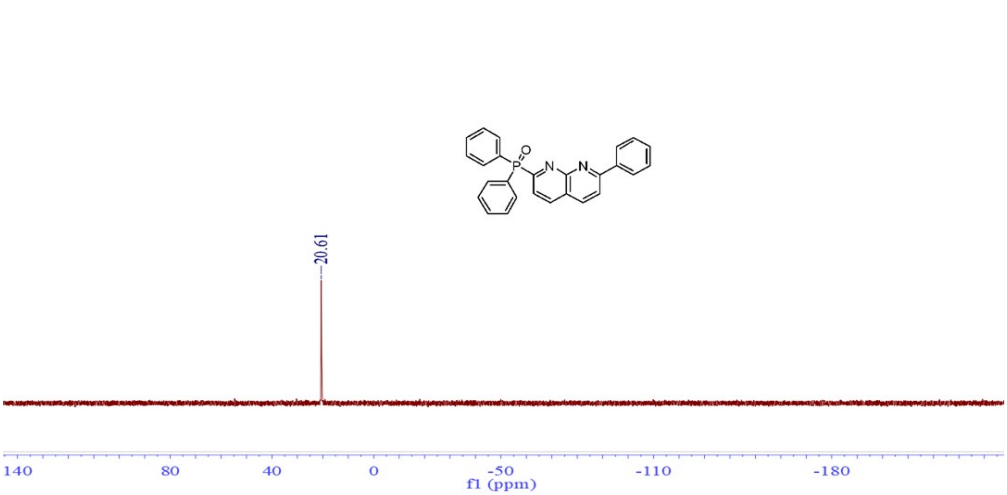
^{31}P-NMR (162 MHz, $CDCl_3$) spectrum of 4aa



^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 5aa



^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of 5aa



^{31}P-NMR (162 MHz, $CDCl_3$)spectrum of 5aa

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