Supporting Information

for

Copper(I)-Catalyzed Asymmetric Addition of Diarylthiophosphines to Aldimines

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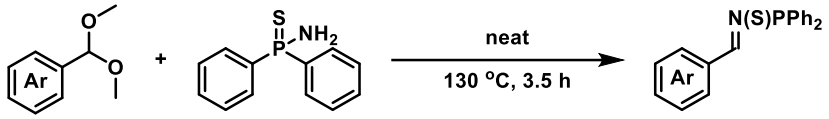
1. General Information

All reagents were obtained commercially unless otherwise noted. Nuclear Magnetic Resonance (NMR) spectra were acquired on an Agilent 400, Bruker 400 or Bruker 500 spectrometer. For ^{1}H NMR, chemical shifts were reported in δ ppm referenced to an internal $SiMe_4$ standard. For ^{19}F NMR, $CFCl_3$ was used as the reference with chemical shift at 0 ppm. For ^{13}C NMR, chemical shifts were reported in the scale relative to NMR solvent ($CDCl_3$: δ 77.0 ppm) as an internal reference. ^{31}P NMR spectra were referenced externally to phosphoric acid. Multiplicities are reported using the following abbreviations: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet. High-resolution mass spectra (ESI) were measured on Thermo Scientific LTQ FT Ultra FT-MS. Infrared (IR) spectra were recorded on Thermo Scientific Nicolet iS5 FT-IR. Melting point was measured on BUCHI M-565. Optical rotation was measured using a 1 mL cell with 1.0 dm path length on an Anton Paar MCP 5500 polarimeter. HPLC analysis was conducted on a Shimadzu HPLC system equipped with Daicel chiral-stationary-phase columns (ϕ 4.6 mm×250 mm).

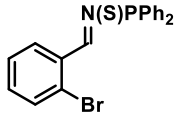
2. Substrate Synthesis

2.1. Preparation of *N*-thiophosphonoaldehyde imines

1a-1c, **1e-1j**, and **1l-1s** are known compounds. [1-3]



N-thiophosphonoaldehyde imines were synthesized starting from the corresponding acetals[4] and diphenylphosphinothioic amide[5] by following reported literatures with modifications. Accordingly, diphenylphosphinothioic amide (1.0 equiv) and acetals (1.2 equiv) were mixed and allowed to warm up to 130 °C for 3.5 h. After cooling to room temperature, the mixture was diluted with petroleum ether and triethylamine. The crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to afford the desired *N*-thiophosphonoaldehyde imines.



1d

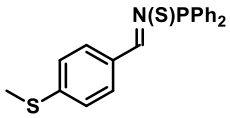
1d: amorphous white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (d, *J* = 38.7 Hz, 1H), 8.30 (d, *J* = 7.2 Hz, 1H), 8.02 (dd, *J* = 12.9, 7.5 Hz, 4H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.39 (m, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.08, 134.54, 133.84, 131.66, 131.39 (d, *J* = 10.3 Hz), 130.39, 128.48 (d, *J* = 12.9 Hz), 128.37, 127.75.

^{31}P NMR (162 MHz, $CDCl_3$) δ 91.90.

HRMS (ESI) m/z [M+Na]$^+$: calcd. 421.9738, found 421.9738.



1k

1k: amorphous white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.31 (d, *J* = 39.4 Hz, 1H), 8.01 (dd, *J* = 12.8, 7.7 Hz, 4H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.51 – 7.37 (m, 6H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.54 (s, 3H).

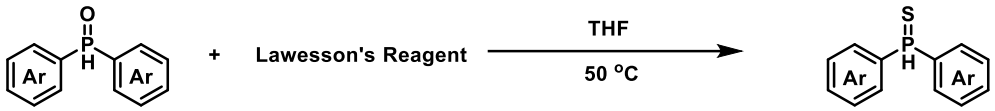
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.85, 146.90, 135.43, 131.41 (d, *J* = 20.7 Hz), 131.24, 130.86, 128.40 (d, *J* = 12.9 Hz), 125.32, 14.82.

^{31}P NMR (162 MHz, $CDCl_3$) δ 90.83.

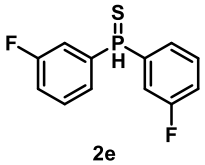
HRMS (ESI) [M+Na]$^+$: calcd. 368.0691, found 368.0693.

2.2. Preparation of diarylthiophosphines

2a-**2d**, and **2g** are known compounds. [6,7]



In a reaction vessel equipped with a magnetic stir bar, commercially available diarylphosphine oxide (10.0 mmol, 1.0 equiv) was charged. Tetrahydrofuran (THF, 20 mL) was added as the solvent and after complete dissolution of the solid, Lawesson's Reagent (5.0 mmol, 2.02 g, 0.5 equiv) was introduced into the mixture. The reaction mixture was heated to 50 °C and stirred overnight. After removal of volatiles under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40/1) to afford the desired diarylthiophosphines.



2e

2e: amorphous white solid.

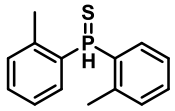
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 488.5 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.47 – 7.52 (m, 4H), 7.24 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.68 (d, *J* = 18.1 Hz), 178.18 (d, *J* = 18.2 Hz), 150.29 (d, *J* = 5.7 Hz), 149.47 (d, *J* = 5.8 Hz), 147.76 (dd, *J* = 15.3, 7.6 Hz), 143.44 (dd, *J* = 11.2, 3.1 Hz), 136.50, 136.29, 134.74 (dd, *J* = 23.0, 13.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 51.12 (t, *J* = 5.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -79.82.

HRMS (ESI) [M+H]$^{+}$: calcd. 255.0242, found 255.0233.



2f

2f: amorphous white solid.

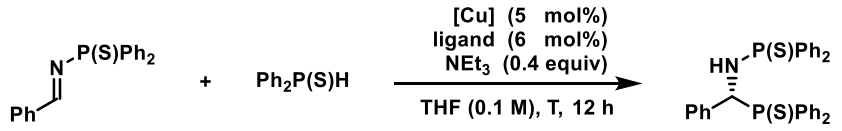
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 465 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.37 – 7.32 (m, 2H), 7.25 – 7.19 (m, 2H), 2.35 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.19, 132.94 (d, *J* = 13.3 Hz), 132.21, 131.23 (d, *J* = 10.0 Hz), 126.53 (d, *J* = 13.5 Hz), 128.27, 20.17 (d, *J* = 7.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 40.96.

HRMS (ESI) [M+Na]$^{+}$: calcd. 269.0524, found 269.0535.

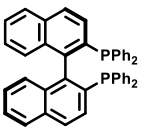
3. Optimization of the Reaction Conditions[a]



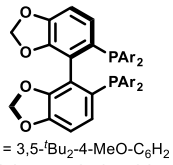
1a 2a 3aa

entry	[Cu]	ligand	T/ °C	yield (%)[b]	ee (%)[c]
1	$Cu(CH_3CN)_4PF_6$	(*R*)-BINAP	RT	94	-33
2	$Cu(CH_3CN)_4PF_6$	(*R*)-DTBMSEGPHOS	RT	82	-83
3	$Cu(CH_3CN)_4PF_6$	(*R*,*R*)-Ph-BPE	RT	91	92
4	$Cu(CH_3CN)_4PF_6$	(R,R)-BDPP	RT	76	-31
5	$Cu(CH_3CN)_4PF_6$	(*R*,R_P)-TANIAPHOS	RT	97	5
6	$Cu(CH_3CN)_4PF_6$	(*R*,*R*)-QUINOXP*	RT	85	-80
7	$Cu(CH_3CN)_4PF_6$	(*R*,S_P)-JOSIPHOS	RT	83	-14
8	$Cu(CH_3CN)_4PF_6$	(*R*,R_P)-Ph-FOXAP	RT	83	31
9	$Cu(CH_3CN)_4BF_4$	(*R*,*R*)-Ph-BPE	RT	99	87
10	$Cu(CH_3CN)_4ClO_4$	(*R*,*R*)-Ph-BPE	RT	41	61
11	CuCl	(*R*,*R*)-Ph-BPE	RT	85	23
12	CuOTf	(*R*,*R*)-Ph-BPE	RT	>99	52
13	$Cu(CH_3CN)_4PF_6$	(*R*,*R*)-Ph-BPE	0	81	96
14	$Cu(CH_3CN)_4PF_6$	(*R*,*R*)-Ph-BPE	-20	72	97

[a]**1a**: 0.10 mmol, **2a**: 0.12 mmol. [b]Determined by ^1H NMR analysis of reaction crude mixture using CH_2Br_2 as an internal standard. [c]Determined by chiral-stationary-phase HPLC analysis.

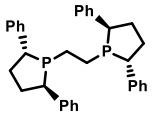


(*R*)-BINAP

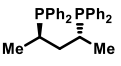


Ar = 3,5-^{t}Bu$_2$-4-MeO-C$_6$H$_2$

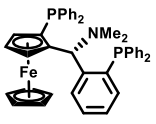
(*R*)-DTBM-SEGPHOS



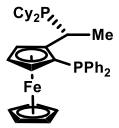
(*R*,*R*)-Ph-BPE



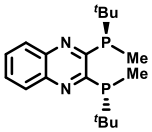
(*R*,*R*)-BDPP



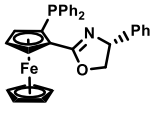
(*R*,R_P)-TANIAPHOS



(*R*,S_P)-JOSIPHOS



(*R*,*R*)-QUINOXP*



(*R*,R_P)-Ph-FOXAP

Table S1. Optimization of reaction conditions

4. Copper(I)-Catalyzed Asymmetric Addition of Diarylthiophosphines to Aldimines

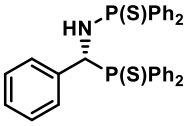
General Procedures for Copper(I)-Catalyzed Asymmetric Addition of Diarylthiophosphines to Aldimines.

Procedure for the synthesis of chiral products：

A dried 10 ml test tube equipped with a magnetic stirring bar was charged with $Cu(CH_3CN)_4PF_6$ (1.8 mg, 0.005 mmol, 0.05 equiv) and (*R,R*)-Ph-BPE (3.0 mg, 0.006 mmol, 0.06 equiv) in a glove box under Ar atmosphere. Anhydrous THF (1.0 mL, 0.1 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. **1** (0.10 mmol, 1.0 equiv) and **2** (0.12 mmol, 1.2 equiv) were added sequentially. After the tube was taken out of the glove box, the reaction mixture was stirred at 0 °C for 10 minutes. Then NEt_3 (6.0 uL, 0.04 mmol, 0.4 equiv) was added. The resulting reaction mixture was stirred at 0 °C for 12 hours and quenched by acetic acid (10 uL). After volatiles were removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to give the desired product.

Procedure for the synthesis of racemic products

A dried 10 ml test tube equipped with a magnetic stirring bar was charged with $Cu(CH_3CN)_4PF_6$ (1.8 mg, 0.005 mmol, 0.05 equiv) and *rac*-BINAP (3.7 mg, 0.006 mmol, 0.06 equiv) in a glove box under Ar atmosphere. Anhydrous THF (1.0 mL, 0.1 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. **1** (0.10 mmol, 1.0 equiv) and **2** (0.12 mmol, 1.2 equiv) were added sequentially. After the tube was taken out of the glove box, NEt_3 (6.0 uL, 0.04 mmol, 0.4 equiv) was added. The resulting reaction mixture was stirred at rt for 12 hours and quenched by acetic acid (10 uL). After volatiles were removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to give the desired product.



3aa

3aa: 43.9 mg, 81% yield, white solid.

IR (film): ν_{max} **(cm^{-1})** 3054, 1480, 1435, 1391, 1215, 1158, 1102, 1027, 998, 874, 797, 721, 689.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 11.3, 7.9 Hz, 2H), 7.51 – 7.47 (m, 5H), 7.43 – 7.33 (m, 5H), 7.33 – 7.26 (m, 2H), 7.23 (d, *J* = 7.1 Hz, 2H), 7.21 – 7.12 (m, 4H), 7.08 (d, *J* = 6.7 Hz, 2H), 7.00 (d, *J* = 7.1 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.10 – 6.03 (m, 1H), 4.54 (dd, *J* = 18.7, 9.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.34, 132.45 (d, *J* = 9.7 Hz), 132.13 – 131.66 (m), 131.43 (dd, *J* = 27.3, 11.3 Hz), 130.93 (d, *J* = 11.4 Hz), 130.37, 128.98 – 128.40 (m), 128.33, 127.88 (dd, *J* = 22.5, 18.4 Hz), 127.61 – 127.49 (m), 127.40, 53.42 (d, *J* = 59.2 Hz).

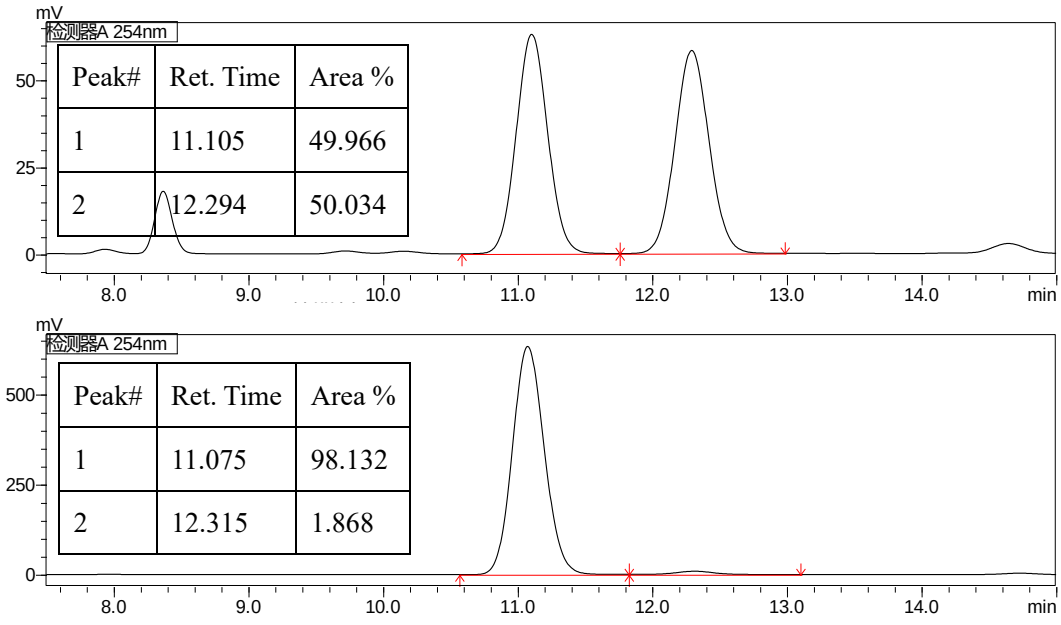
^{31}P NMR (162 MHz, $CDCl_3$) δ 89.40 (d, *J* = 33.8 Hz), 83.96 (d, *J* = 33.8 Hz).

HRMS (ESI) [M+Na]$^{+}$: calcd. 562.0952, found 562.0960.

Optical rotation: $[\alpha]_D^{25}$ = -117.03 (c = 1.12, $CHCl_3$, 96% ee).

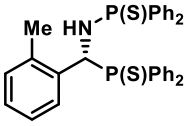
M.P.: 44-45 ℃.

HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 11.1 min, t_R(minor) = 12.3 min, 96% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	11.105	49.966
2	12.294	50.034

Peak#	Ret. Time	Area %
1	11.075	98.132
2	12.315	1.868



3ba

3ba: 49.3 mg, 89% yield, yellow oil.

IR (film): ν_{max} **(cm^{-1})** 3055, 1436, 1397, 1183, 1103, 1070, 799, 746, 719, 690.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 12.3, 7.1 Hz, 2H), 7.77 (d, *J* = 9.4 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.47 (dd, *J* = 14.0, 7.4 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.31 – 7.25 (m, 2H), 7.22 – 7.16 (m, 4H), 7.12 – 7.06 (m, 5H), 7.04 – 7.00 (m, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 6.32 – 6.24 (m, 1H), 4.58 (dd, *J* = 19.4, 10.3 Hz, 1H), 1.81 (s, 3H).

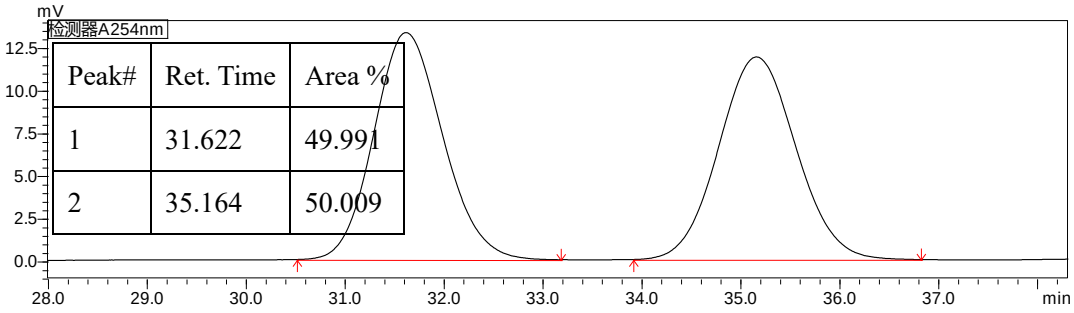
^{13}C NMR (126 MHz, $CDCl_3$) δ 134.03, 133.00 (d, *J* = 9.6 Hz), 132.23, 131.93 (d, *J* = 9.9 Hz), 131.62, 131.56 – 131.15 (m), 130.93 (d, *J* = 11.4 Hz), 129.51, 129.08, 128.75 (d, *J* = 11.9 Hz), 128.31 (d, *J* = 13.2 Hz), 127.83 (dd, *J* = 31.9, 12.7 Hz), 125.46, 48.71 (d, *J* = 58.7 Hz), 19.29.

^{31}P NMR (162 MHz, $CDCl_3$) δ 89.38 (d, *J* = 33.2 Hz), 84.00 (d, *J* = 33.2 Hz).

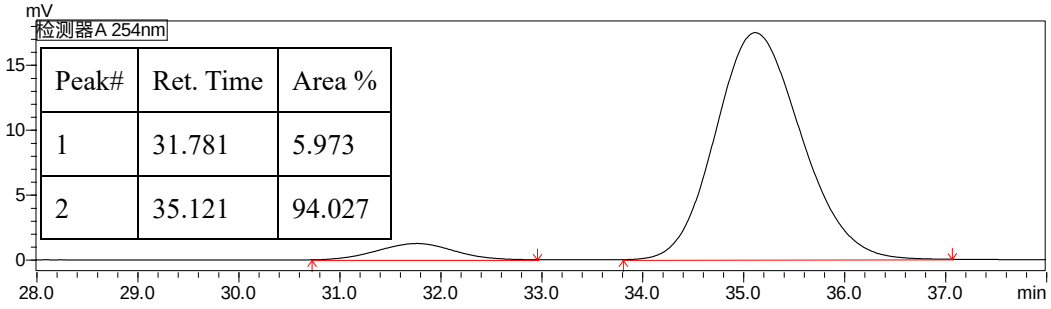
HRMS (ESI) [M+Na]$^{+}$: calcd. 576.1109, found 576.1116.

Optical rotation: $[\alpha]_D^{25}$ = -92.03 (c = 0.96, $CHCl_3$, 88% ee).

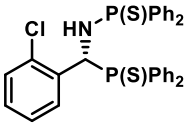
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 99/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 35.1 min, t_R(minor) = 31.8 min, 88% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	31.622	49.991
2	35.164	50.009



Peak#	Ret. Time	Area %
1	31.781	5.973
2	35.121	94.027



3ca

3ca: 56.7 mg, 99% yield, yellow oil.

IR (film): ν_{max} **(cm^{-1})** 3055, 1472, 1435, 1397, 1102, 1035, 785, 746, 721, 690, 641.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 12.5, 7.3 Hz, 2H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.52 (m, 5H), 7.47 (dd, *J* = 13.6, 7.5 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.30 (dd, *J* = 13.0, 5.6 Hz, 1H), 7.24 – 7.19 (m, 6H), 7.18 – 7.14 (m, 1H), 7.09 – 7.02 (m, 3H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.52 – 6.41 (m, 1H), 4.81 (dd, *J* = 10.2 Hz, 1H).

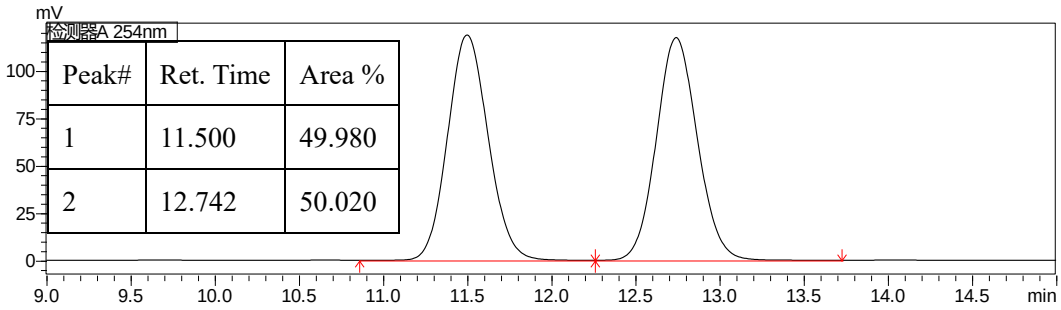
^{13}C NMR (126 MHz, $CDCl_3$) δ 134.65, 134.42, 133.96, 133.83, 133.57 (d, *J* = 6.2 Hz), 132.84 (d, *J* = 9.8 Hz), 132.38, 132.14 (d, *J* = 10.1 Hz), 131.69, 131.23 (dd, *J* = 28.8, 11.5 Hz), 130.28, 129.17 – 128.72 (m), 128.72 – 128.62 (m), 128.62 – 127.85 (m), 127.60 (d, *J* = 12.4 Hz), 126.32, 49.28 (d, *J* = 57.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 88.80 (d, *J* = 31.1 Hz), 85.38 (d, *J* = 31.1 Hz).

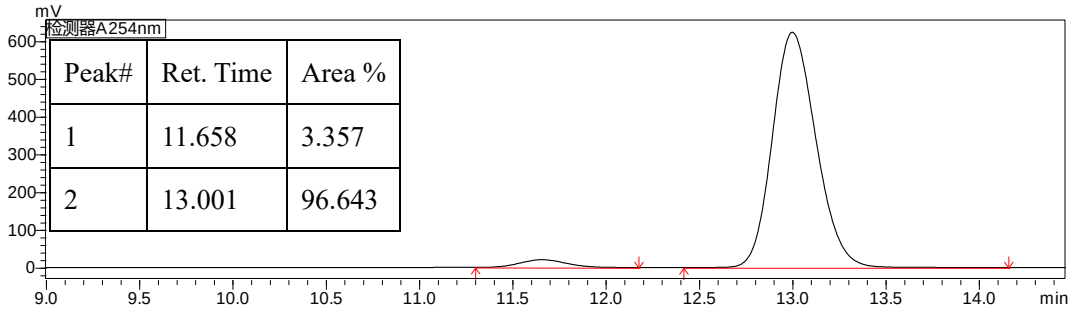
HRMS (ESI) [M+Na]$^{+}$: calcd. 596.0563, found 596.0570.

Optical rotation: $[\alpha]_D^{25}$ = -72.92 (c = 1.02, $CHCl_3$, 93% ee).

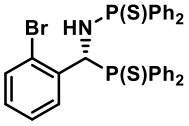
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 13.0 min, t_R(minor) = 11.7 min, 93% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	11.500	49.980
2	12.742	50.020



Peak#	Ret. Time	Area %
1	11.658	3.357
2	13.001	96.643



3da

3da: 58.3 mg, 94% yield, yellow oil.

IR (film): ν_{max} **(cm^{-1})** 3055, 1467, 1436, 1394, 1102, 1025, 880, 784, 746, 721, 690.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 12.5, 7.4 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.54 (m, 5H), 7.42 (dd, *J* = 13.6, 7.6 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 7.26 – 7.16 (m, 7H), 7.08– 7.04 (m, 3H), 7.01 – 6.95 (m, 1H), 6.47 – 6.34 (m, 1H), 4.82 (dd, *J* = 10.2 Hz, 1H).

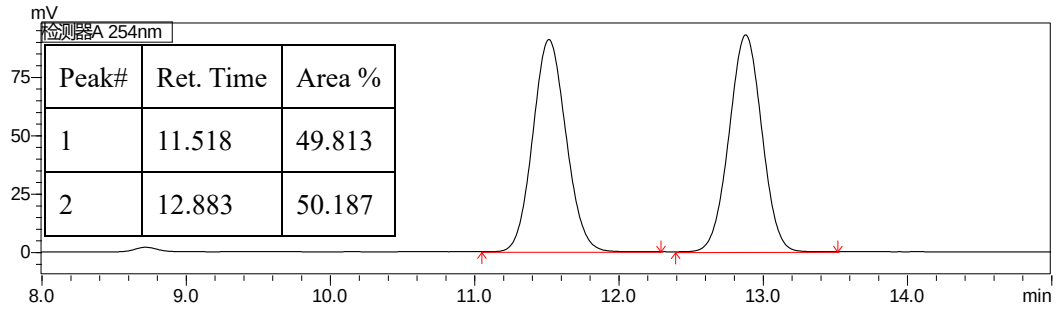
^{13}C NMR (126 MHz, $CDCl_3$) δ 132.96 (d, *J* = 9.7 Hz), 132.72 – 132.19 (m), 131.91, 131.73, 131.25 (dd, *J* = 31.5, 11.5 Hz), 130.59, 129.85 , 129.39, 128.82 (d, *J* = 12.1 Hz), 128.21 (dd, *J* = 30.9, 13.3 Hz), 127.60 (d, *J* = 12.4 Hz), 126.96, 124.73, 52.01 (d, *J* = 57.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 88.71 (d, *J* = 30.9 Hz), 85.65 (d, *J* = 30.9 Hz).

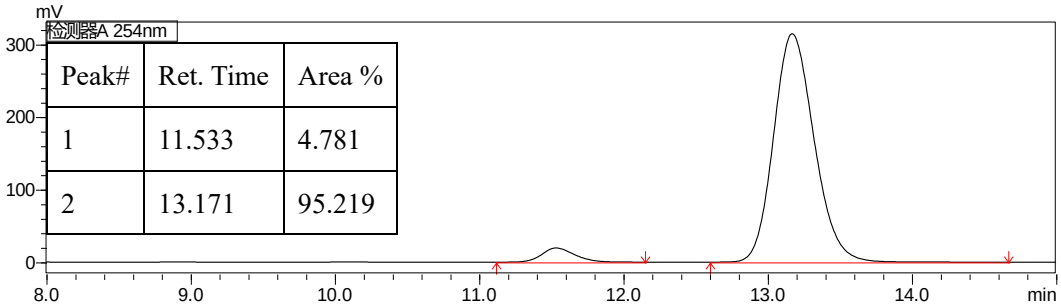
HRMS (ESI) $[M+H]^+$: calcd. 618.0238, found 618.0230.

Optical rotation: $[\alpha]_D^{25}$ = -74.22 (c = 1.03, $CHCl_3$, 90% ee).

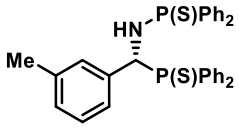
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 13.2 min, t_R(minor) = 11.5 min, 90% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	11.518	49.813
2	12.883	50.187



Peak#	Ret. Time	Area %
1	11.533	4.781
2	13.171	95.219



3ea

3ea: 54.8 mg, 99% yield, yellow oil.

IR (film): ν_{max} **(cm^{-1})** 3054, 1436, 1393, 1103, 805, 746, 720, 691, 642, 626, 613.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 12.2, 7.1 Hz, 2H), 7.56 – 7.47 (m, 6H), 7.42 – 7.34 (m, 5H), 7.26 – 7.15 (m, 7H), 6.87 – 6.80 (m, 3H), 6.75 – 6.73 (m, 1H), 6.08 – 6.00 (m, 1H), 4.51 (dd, *J* = 18.9, 10.4 Hz, 1H), 2.01 (s, 3H).

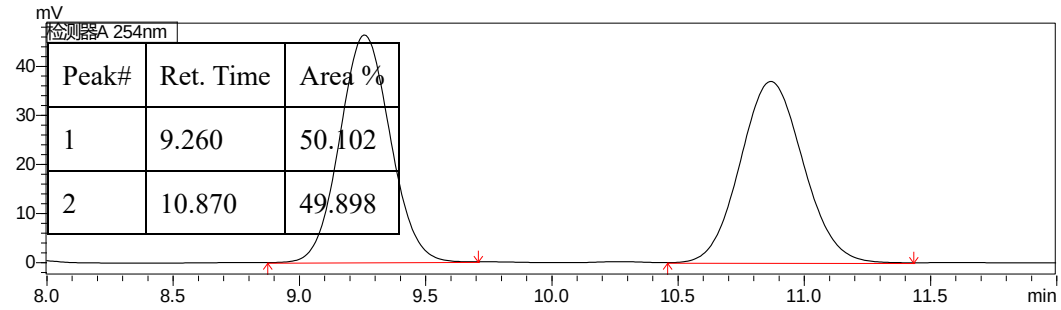
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.79, 134.95, 132.49 (d, *J* = 9.6 Hz), 131.97 (d, *J* = 9.7 Hz), 131.66 – 131.19 (m), 130.91 (d, *J* = 11.5 Hz), 129.72 (d, *J* = 4.9 Hz), 128.96, 128.71 (d, *J* = 11.9 Hz), 128.38 (d, *J* = 13.3 Hz), 128.17 – 127.73 (m), 127.23, 125.95 (d, *J* = 4.8 Hz), 53.48 (d, *J* = 58.7 Hz), 21.12.

^{31}P NMR (162 MHz, $CDCl_3$) δ 89.28 (d, *J* = 34.4 Hz), 83.99 (d, *J* = 34.4 Hz).

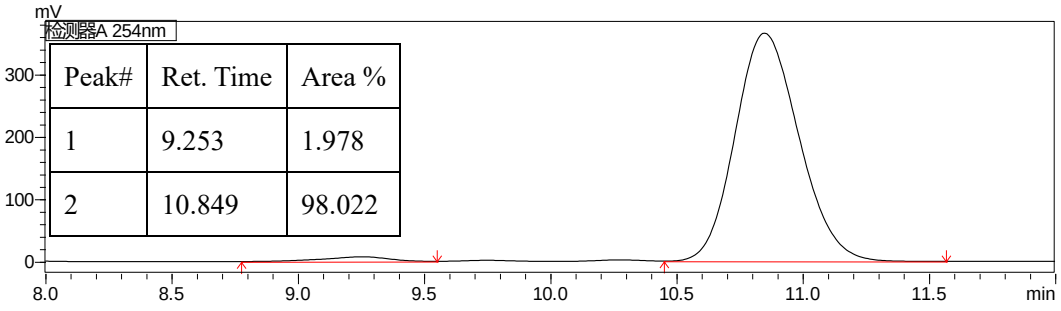
HRMS (ESI) [M+Na]$^{+}$: calcd. 576.1109, found 576.1115.

Optical rotation: $[\alpha]_D^{25}$ = -91.60 (c = 0.98, $CHCl_3$, 96% ee).

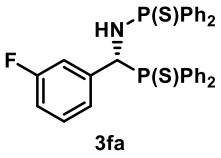
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 10.8 min, t_R(minor) = 9.3 min, 96% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	9.260	50.102
2	10.870	49.898



Peak#	Ret. Time	Area %
1	9.253	1.978
2	10.849	98.022



3fa

3fa: 53.8 mg, 97% yield, white solid.

IR (film): ν_{max} **(cm^{-1})** 3055, 1590, 1485, 1447, 1435, 1393, 1259, 1244, 1141, 1102, 1027, 868, 798, 746, 721, 689, 642, 627, 523.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 12.4, 7.3 Hz, 2H), 7.56 – 7.49 (m, 5H), 7.45 – 7.37 (m, 5H), 7.35 – 7.30 (m, 2H), 7.25 – 7.18 (m, 6H), 6.89 – 6.83 (m, 2H), 6.79 (d, *J* = 7.4 Hz, 1H), 6.73 – 6.66 (m, 1H), 6.11 – 6.00 (m, 1H), 4.53 (dd, *J* = 19.3, 10.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.87 (dd, *J* = 246.0, 2.3 Hz), 138.12 (dd, *J* = 7.0, 2.7 Hz), 135.34 (d, *J* = 1.5 Hz), 135.17, 134.36 (d, *J* = 1.6 Hz), 134.13, 132.32 (d, *J* = 9.6 Hz), 132.06 (d, *J* = 2.9 Hz), 131.82 (d, *J* = 10.0 Hz), 131.53 (d, *J* = 3.1 Hz), 131.27 (d, *J* = 11.8 Hz), 128.38 (d, *J* = 13.3 Hz), 127.99 (d, J = 24.8 Hz), 124.61 (dd, *J* = 5.1, 2.9 Hz), 115.84 (dd, *J* = 22.6, 4.7 Hz), 114.55 (dd, *J* = 21.2, 2.7 Hz), 52.96 (d, J = 58.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 89.40 (d, *J* = 33.2 Hz), 83.80 (d, *J* = 33.2 Hz).

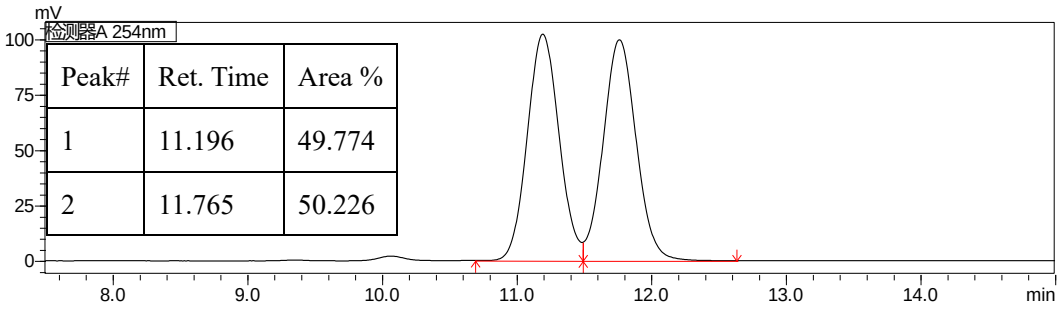
^{19}F NMR (376 MHz, $CDCl_3$) δ -83.57 (d, *J* = 6.5 Hz).

HRMS (ESI) [M+Na]$^{+}$:calcd. 580.0858, found 580.0865.

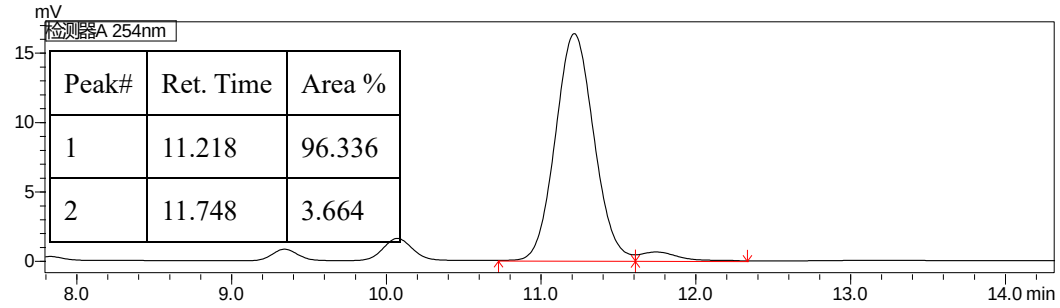
Optical rotation: $[\alpha]_D^{25}$ = -131.95 (c = 1.00, $CHCl_3$, 93% ee).

M.P.: 102-106 ℃.

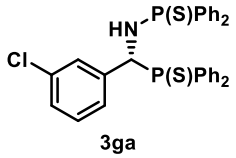
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 11.2 min, t_R(minor) = 11.7 min, 93% ee.The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	11.196	49.774
2	11.765	50.226



Peak#	Ret. Time	Area %
1	11.218	96.336
2	11.748	3.664



3ga

3ga: 53.9 mg, 94% yield, colorless oil.

IR (film): ν_{max} (cm^{-1}) 3055, 1478, 1436, 1392, 1196, 1103, 1027, 998, 876, 746, 721, 689.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 12.4, 7.1 Hz, 2H), 7.56 – 7.49 (m, 5H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.38 (m, 3H), 7.35 – 7.31 (m, 3H), 7.25 – 7.19 (m, 6H), 7.02 – 6.99 (m, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.86 – 6.80 (m, 1H), 6.09 – 5.97 (m, 1H), 4.52 (dd, *J* = 19.3, 10.2 Hz, 1H).

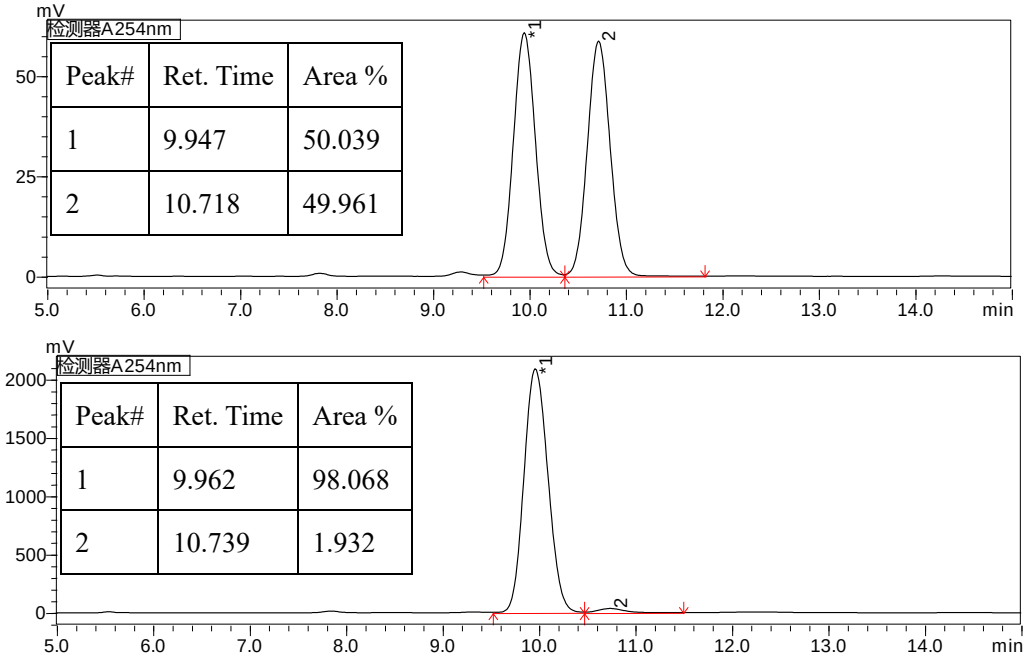
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.33, 133.25, 132.38 (d, *J* = 9.7 Hz), 132.19, 131.96 (t, *J* = 21.7 Hz), 131.46 (dd, *J* = 28.8, 14.9 Hz), 130.87 (d, *J* = 11.5 Hz), 128.93 (dd, *J* = 23.1, 8.4 Hz), 128.61 – 128.33 (m), 128.08 (dd, *J* = 17.0, 12.9 Hz), 127.75, 126.98 (d, *J* = 4.9 Hz), 52.96 (d, *J* = 58.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 89.35 (d, *J* = 33.4 Hz), 83.97 (d, *J* = 33.4 Hz).

HRMS (ESI) $[M+Na]^+$: calcd. 596.0563, found 596.0571.

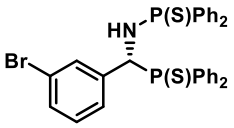
Optical rotation: $[\alpha]_D^{25}$ = -115.40 (c = 1.03, $CHCl_3$, 96% ee).

HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 10.0 min, t_R(minor) = 10.7 min, 96% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	9.947	50.039
2	10.718	49.961

Peak#	Ret. Time	Area %
1	9.962	98.068
2	10.739	1.932



3ha

3ha: 61.2 mg, 99% yield, yellow oil.

IR (film): ν_{max} (cm^{-1}) 3055, 1474, 1435, 1393, 1102, 873, 798, 746, 721, 689, 641, 613, 554, 511.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 12.2, 7.5 Hz, 2H), 7.56 – 7.52 (m, 5H), 7.43 – 7.37 (m, 5H), 7.37 – 7.31 (m, 3H), 7.25 – 7.16 (m, 5H), 7.13 – 7.10 (m, 2H), 6.92 (d, *J* = 7.3 Hz, 1H), 6.80 – 6.74 (m, 1H), 6.06 – 5.97 (m, 1H), 4.52 (dd, *J* = 19.3, 10.0 Hz, 1H).

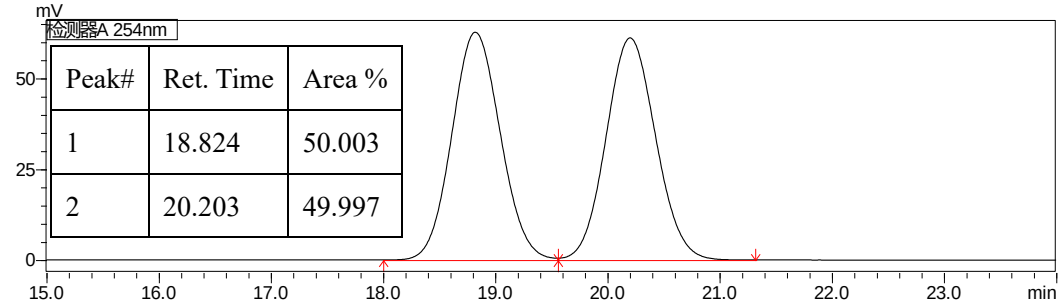
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.55, 134.98, 132.53 – 132.17 (m), 132.17 – 132.01 (m), 132.01 – 131.43 (m), 131.35 (d, *J* = 11.8 Hz), 130.87 (d, *J* = 11.5 Hz), 130.65, 128.85 (d, *J* = 12.2 Hz), 128.49 (d, *J* = 13.4 Hz), 128.30 – 127.88 (m), 127.41 (d, *J* = 4.8 Hz), 121.45, 52.95 (d, *J* = 58.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 89.35 (d, *J* = 33.5 Hz), 84.06 (d, *J* = 33.5 Hz).

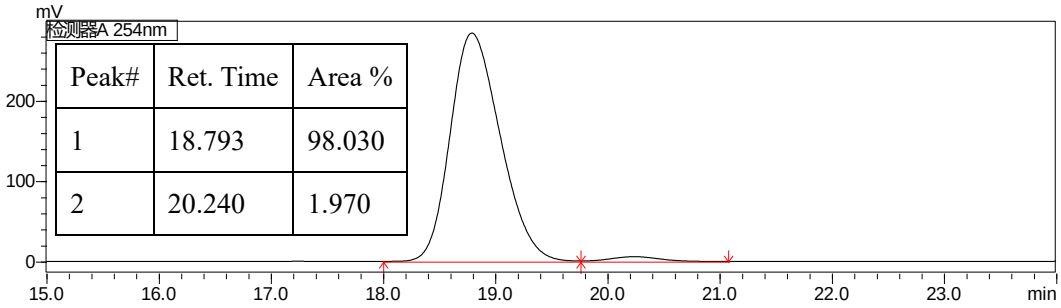
HRMS (ESI) [M+H]$^{+}$: calcd. 618.0238, found 618.0243.

Optical rotation: $[\alpha]_D^{25}$ = -101.15 (c = 1.01, $CHCl_3$, 96% ee).

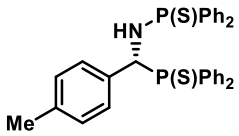
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 39/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 18.8 min, t_R(minor) = 20.2 min, 96% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	18.824	50.003
2	20.203	49.997



Peak#	Ret. Time	Area %
1	18.793	98.030
2	20.240	1.970



3ia

3ia: 42.8 mg, 77% yield, white solid.

IR (film): ν_{max} **(cm^{-1})** 3054, 1435, 1393, 1102, 826, 746, 720, 690, 637.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 12.2, 7.4 Hz, 2H), 7.53 – 7.45 (m, 5H), 7.43 (d, *J* = 5.0 Hz, 1H), 7.40 (d, *J* = 6.1 Hz, 1H), 7.37 (d, *J* = 6.1 Hz, 2H), 7.36 – 7.34 (m, 1H), 7.33 – 7.28 (m, 2H), 7.23 – 7.16 (m, 6H), 6.96 (d, *J* = 6.8 Hz, 2H), 6.75 (d, *J* = 7.7 Hz, 2H), 6.10 – 6.00 (m, 1H), 4.47 (dd, *J* = 18.7, 10.4 Hz, 1H), 2.16 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.36, 135.20, 134.37, 132.43 (d, *J* = 9.5 Hz), 131.93 (d, *J* = 9.7 Hz), 131.70 – 131.03 (m), 130.94 (d, *J* = 11.4 Hz), 130.49, 129.87, 128.72 (dd, *J* = 13.7, 8.4 Hz), 128.33 (d, *J* = 13.3 Hz), 128.21 – 127.74 (m), 53.26 (d, *J* = 59.4 Hz), 21.10.

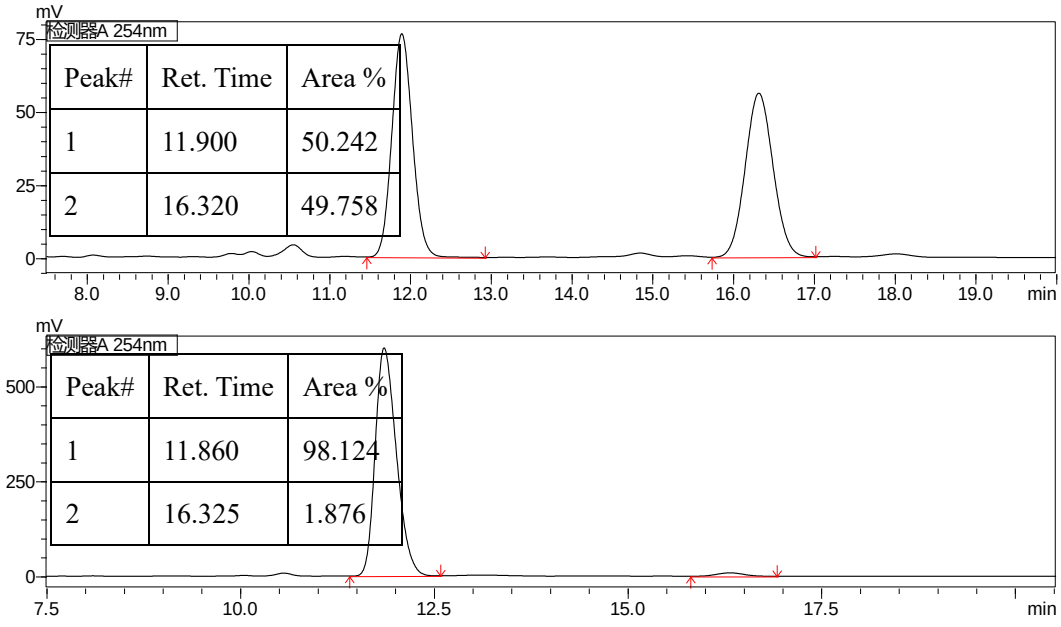
^{31}P NMR (162 MHz, $CDCl_3$) δ 89.42 (d, *J* = 34.3 Hz), 83.69 (d, *J* = 34.3 Hz).

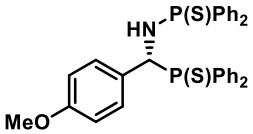
HRMS (ESI) [M+Na]$^{+}$:calcd. 576.1109, found 576.1115.

Optical rotation: $[\alpha]_D^{25}$ = -135.76 (c = 1.10, $CHCl_3$, 96% ee).

M.P.: 145-147 °C.

HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 11.9 min, t_R(minor) = 16.3 min, 96% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.





3ja

3ja: 45.5 mg, 80% yield, white solid.

IR (film): ν_{max} **(cm^{-1})** 3054, 1608, 1510, 1480, 1435, 1393, 1305, 1249, 1177, 1102, 1028, 834, 746, 719, 690, 636, 543.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 12.1, 7.3 Hz, 2H), 7.54 – 7.45 (m, 5H), 7.43 (dd, *J* = 12.6, 7.5 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.33 – 7.28 (m, 2H), 7.24 – 7.19 (m, 6H), 7.02 (d, *J* = 7.3 Hz, 2H), 6.48 (d, *J* = 8.4 Hz, 2H), 6.08 – 5.98 (m, 1H), 4.45 (dd, *J* = 18.8, 10.2 Hz, 1H), 3.66 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.08, 135.20, 134.37, 132.42 (d, *J* = 9.5 Hz), 131.90 (d, *J* = 9.8 Hz), 131.75 – 131.08 (m), 130.91 (d, *J* = 11.4 Hz), 130.53, 130.01 (t, *J* = 11.8 Hz), 128.69 (d, *J* = 11.9 Hz), 128.37 (d, *J* = 13.3 Hz), 127.99 (dd, *J* = 12.7, 8.1 Hz), 127.49, 112.90, 55.17, 52.85 (d, *J* = 60.1 Hz).

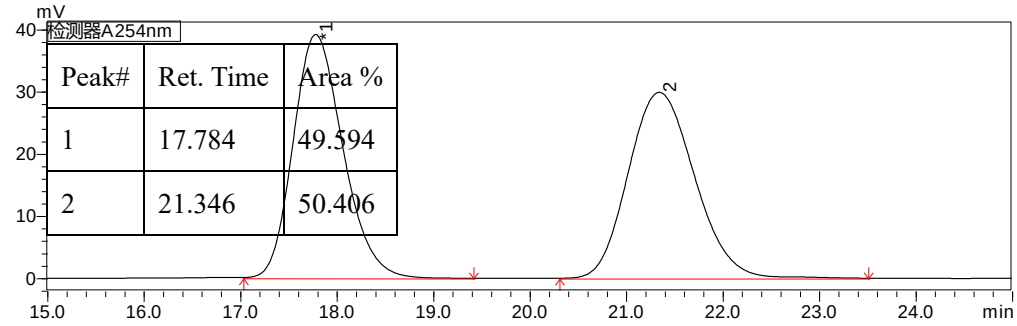
^{31}P NMR (162 MHz, $CDCl_3$) δ 89.31 (d, *J* = 35.1 Hz), 83.54 (d, *J* = 35.1 Hz).

HRMS (ESI) [M+Na]$^{+}$: calcd. 592.1058, found 592.1068.

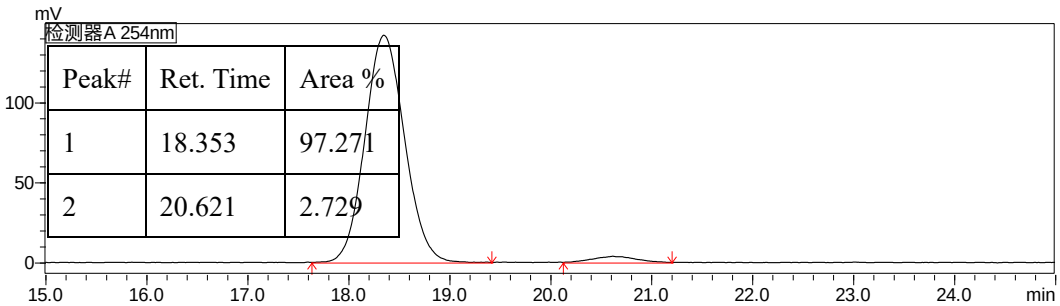
Optical rotation: $[\alpha]_D^{25}$ = -133,46 (c = 0.98, $CHCl_3$, 95% ee).

M.P.: 153-156 ℃.

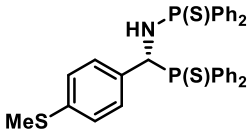
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 18.4 min, t_R(minor) = 20.6 min, 95% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	17.784	49.594
2	21.346	50.406



Peak#	Ret. Time	Area %
1	18.353	97.271
2	20.621	2.729



3ka

3ka: 45.0 mg, 74% yield, white solid.

IR (film): ν_{max} (cm^{-1}) 3054, 1493, 1481, 1435, 1409, 1391, 1260, 1102, 1027, 1015, 998, 877, 824, 746, 720, 690, 534.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 12.3, 7.2 Hz, 2H), 7.54 – 7.45 (m, 6H), 7.43 (d, *J* = 5.2 Hz, 1H), 7.40 – 7.35 (m, 3H), 7.34 – 7.29 (m, 2H), 7.26 – 7.18 (m, 6H), 6.99 (dd, *J* = 7.4, 1.4 Hz, 2H), 6.81 (d, *J* = 8.2 Hz, 2H), 6.08 – 6.00 (m, 1H), 4.48 (dd, *J* = 18.7, 10.3 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.98, 135.42, 135.08, 134.25, 132.52 – 132.14 (m), 131.88 (dd, *J* = 25.5, 15.7 Hz), 131.52, 131.30 (d, *J* = 11.7 Hz), 130.91 (d, *J* = 11.4 Hz), 130.34 (d, *J* = 11.0 Hz), 129.71 (d, *J* = 14.0 Hz), 129.27 (d, *J* = 4.9 Hz), 128.73 (d, *J* = 11.9 Hz), 128.40 (d, *J* = 13.4 Hz), 128.23 – 127.80 (m), 125.43, 53.05 (d, *J* = 59.2 Hz), 15.73.

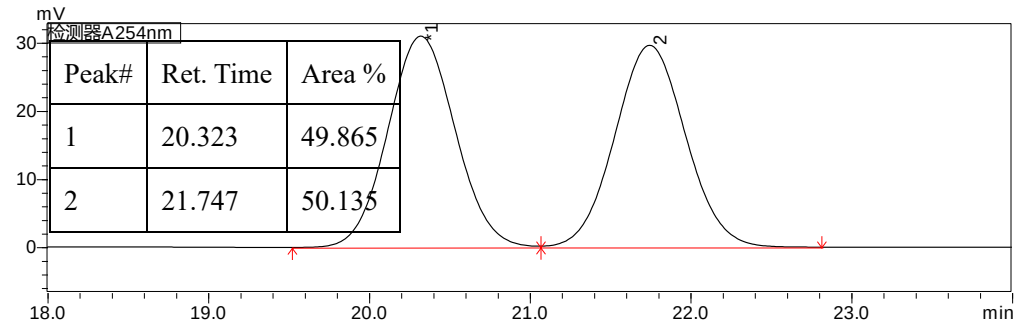
^{31}P NMR (162 MHz, $CDCl_3$) δ 89.39 (d, *J* = 34.2 Hz), 83.58 (d, *J* = 34.2 Hz).

HRMS (ESI) [M+Na]$^{+}$: calcd. 608.0830, found 608.0836.

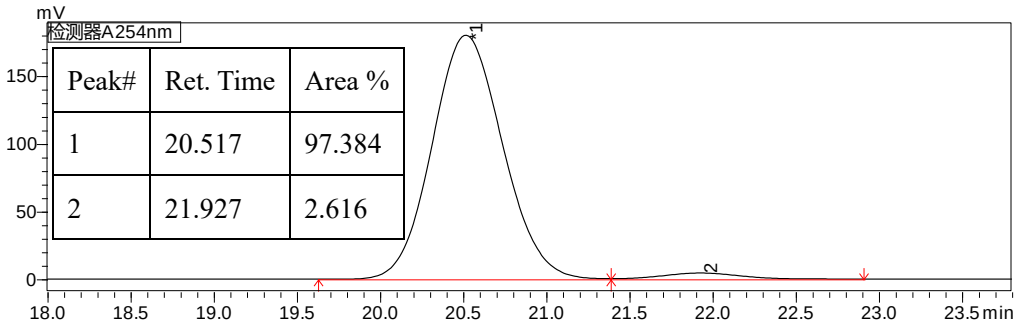
Optical rotation: $[\alpha]_D^{25}$ = -169.56 (c = 1.03, $CHCl_3$, 95% ee).

M.P.: 158-160 ℃.

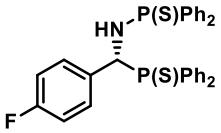
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 20.5 min, t_R(minor) = 21.9 min, 95% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	20.323	49.865
2	21.747	50.135



Peak#	Ret. Time	Area %
1	20.517	97.384
2	21.927	2.616



3la

3la: 48.2 mg, 86% yield, white solid.

IR (film): ν_{max} **(cm^{-1})** 3055, 1601, 1507, 1435, 1392, 1225, 1160, 1102, 1027, 998, 877, 840, 746, 721, 690, 540.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 12.3, 7.3 Hz, 2H), 7.56 – 7.48 (m, 5H), 7.44 – 7.35 (m, 5H), 7.33 – 7.32 (m, 2H), 7.25 – 7.19 (m, 6H), 7.06 – 7.04 (m, 2H), 6.68 – 6.56 (m, 2H), 6.12 – 6.01 (m, 1H), 4.49 (dd, *J* = 19.1, 10.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.04, 132.37 (d, *J* = 9.7 Hz), 132.12, 131.82 (d, *J* = 10.0 Hz), 131.48 (d, *J* = 31.8 Hz), 131.26, 130.88 (d, *J* = 11.5 Hz), 130.65 – 129.77 (m), 129.67, 128.79 (d, *J* = 12.0 Hz), 128.45 (d, *J* = 13.3 Hz), 128.06 (dd, *J* = 16.0, 12.8 Hz), 114.41, 114.24, 52.60 (d, *J* = 59.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 89.31 (d, *J* = 34.3 Hz), 83.74 (d, *J* = 34.3 Hz).

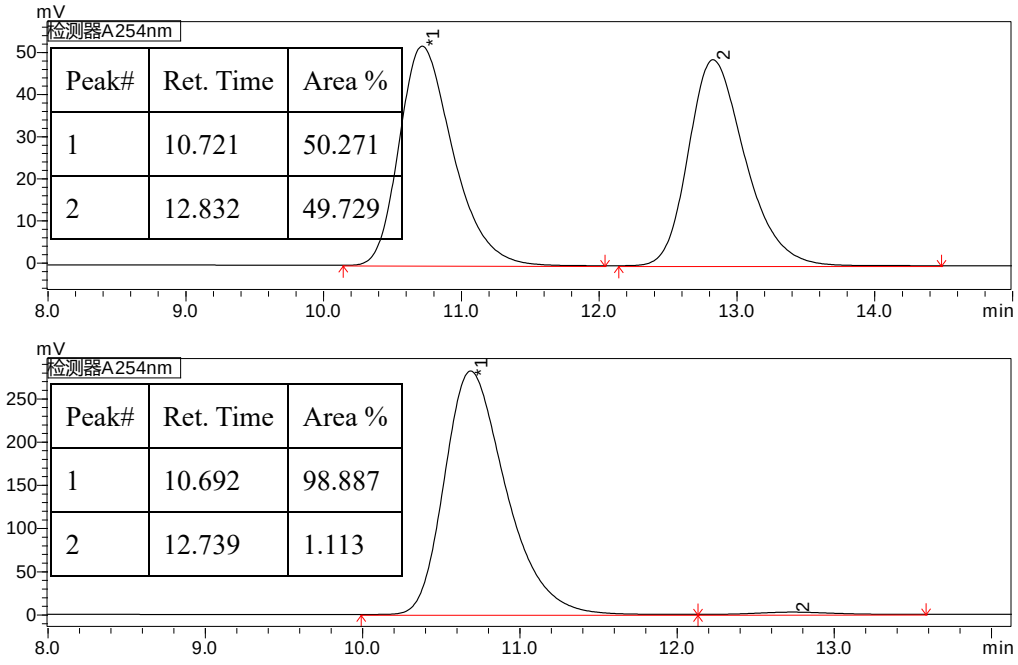
^{19}F NMR (376 MHz, $CDCl_3$) δ -84.13 (d, *J* = 4.0 Hz).

HRMS (ESI) [M+Na]$^{+}$:calcd. 580.0858, found 580.0865.

Optical rotation: $[\alpha]_D^{25}$ = -134.18 (c = 1.06, $CHCl_3$, 98% ee).

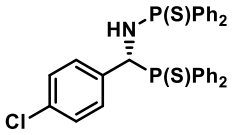
M.P.: 115-117 ℃.

HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 10.7 min, t_R(minor) = 12.7 min, 98% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	10.721	50.271
2	12.832	49.729

Peak#	Ret. Time	Area %
1	10.692	98.887
2	12.739	1.113



3ma

3ma: 55.9 mg, 78% yield, white solid.

IR (film): ν_{max} (cm^{-1}) 3054, 1490, 1436, 1102, 1027, 1014, 998, 877, 831, 746, 721, 689.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 12.3, 7.5 Hz, 2H), 7.53 (dd, *J* = 12.1, 5.8 Hz, 1H), 7.51 – 7.47 (m, 4H), 7.43 (dd, *J* = 12.8, 7.8 Hz, 2H), 7.40 – 7.36 (m, 3H), 7.35 – 7.32 (m, 2H), 7.25 – 7.20 (m, 6H), 7.00 (d, *J* = 7.0 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.09 – 6.01 (m, 1H), 4.48 (dd, *J* = 19.0, 10.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.07, 133.62, 132.35 (d, *J* = 9.6 Hz), 132.12, 131.96 – 131.58 (m), 131.58 – 131.47 (m), 131.47 – 131.08 (m), 130.89 (d, *J* = 11.5 Hz), 130.15 (d, *J* = 4.8 Hz), 128.81 (d, *J* = 12.1 Hz), 128.45 (d, *J* = 13.3 Hz), 128.12 (dd, *J* = 16.8, 12.8 Hz), 127.53, 52.79 (d, *J* = 59.1 Hz).

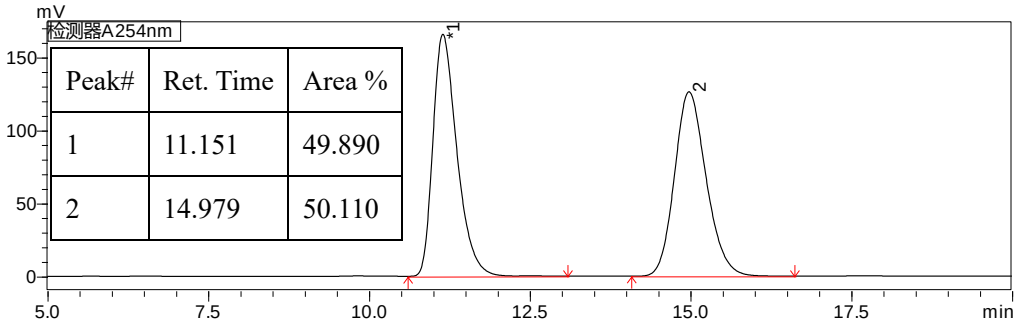
^{31}P NMR (162 MHz, $CDCl_3$) δ 89.39 (d, *J* = 33.8 Hz), 83.67 (d, *J* = 33.8 Hz).

HRMS (ESI) [M+Na]$^+$ calcd.: 596.0563, found 596.0570.

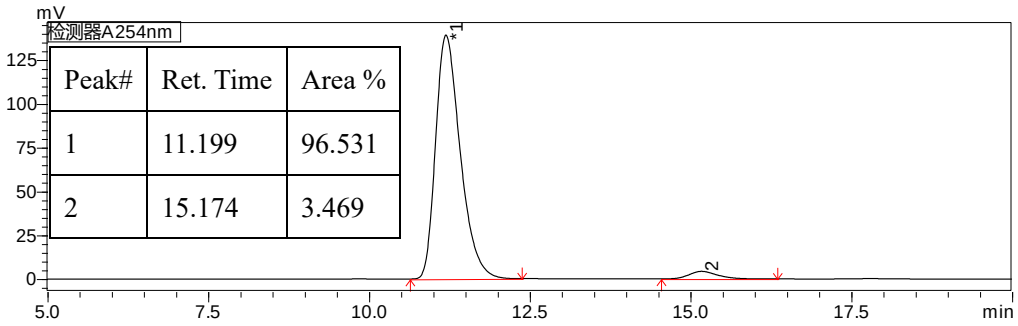
Optical rotation: $[\alpha]_D^{25}$ = -155.01 (c = 0.96, $CHCl_3$, 93% ee).

M.P.: 160-163 ℃.

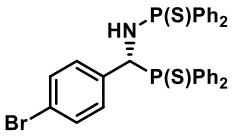
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 11.2 min, t_R(minor) = 15.2 min, 93% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	11.151	49.890
2	14.979	50.110



Peak#	Ret. Time	Area %
1	11.199	96.531
2	15.174	3.469



3na

3na: 61.1 mg, 99% yield, white solid.

IR (film): ν_{max} (cm^{-1}) 3054, 1486, 1436, 1409, 1387, 1103, 1010, 827, 745, 721, 690.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 12.4, 7.2 Hz, 2H), 7.57 (dd, *J* = 7.5, 5.8 Hz, 1H), 7.54 – 7.49 (m, 5H), 7.47 – 7.45 (m, 2H), 7.43 – 7.36 (m, 5H), 7.29 – 7.23 (m, 5H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.97 – 6.96 (m, 2H), 6.08 – 6.00 (m, 1H), 4.51 (dd, *J* = 19.0, 10.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.59, 132.46 – 132.10 (m), 131.84 (d, *J* = 9.9 Hz), 131.61, 131.43 – 131.02 (m), 130.89 (d, *J* = 11.4 Hz), 130.48, 128.81 (d, *J* = 12.0 Hz), 128.57 – 127.65 (m), 121.95, 52.88 (d, *J* = 58.8 Hz).

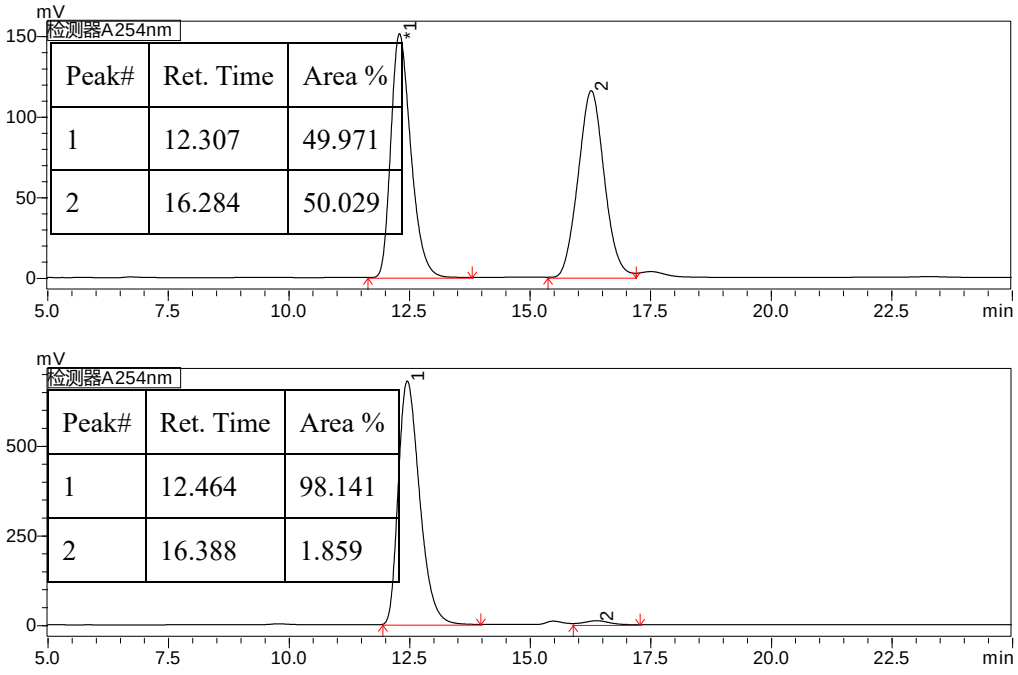
^{31}P NMR (162 MHz, $CDCl_3$) δ 89.41 (d, *J* = 33.7 Hz), 83.54 (d, *J* = 33.7 Hz).

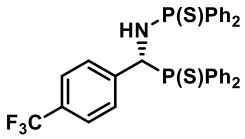
HRMS (ESI) [M+Na]$^{+}$:calcd. 640.0057, found 640.0064.

Optical rotation: $[\alpha]_D^{25}$ = -139.31 (c = 1.02, $CHCl_3$, 96% ee).

M.P.: 167-168 ℃.

HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 12.5 min, t_R(minor) = 16.4 min, 96% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.





3oa

3oa: 60.2 mg, 99% yield, white solid.

IR (film): ν_{max} (cm^{-1}) 3055, 1436, 1420, 1393, 1324, 1166, 1110, 1067, 1017, 852, 746, 720, 690, 654, 638, 624, 614, 529.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 12.5, 7.2 Hz, 2H), 7.56 (dd, *J* = 7.5, 5.9 Hz, 1H), 7.53 – 7.49 (m, 3H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.43 – 7.38 (m, 5H), 7.32 (dd, *J* = 12.5, 5.8 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.21 – 7.16 (m, 4H), 7.16 – 7.13 (m, 4H), 6.17 – 6.09 (m, 1H), 4.55 (dd, *J* = 19.1, 10.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.49, 134.79, 134.22, 133.96, 132.45 – 132.00 (m), 132.00 – 131.51 (m), 131.51 – 131.18 (m), 131.18 – 130.97 (m), 130.89 (d, *J* = 11.5 Hz), 130.07, 129.44 129.16 (d, *J* = 4.6 Hz), 128.88 (d, *J* = 12.1 Hz), 128.51 (d, *J* = 13.3 Hz), 128.12 (dd, *J* = 19.3, 12.9 Hz), 124.19, 53.05 (d, *J* = 58.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 89.42 (d, *J* = 33.3 Hz), 83.81 (d, *J* = 33.3 Hz).

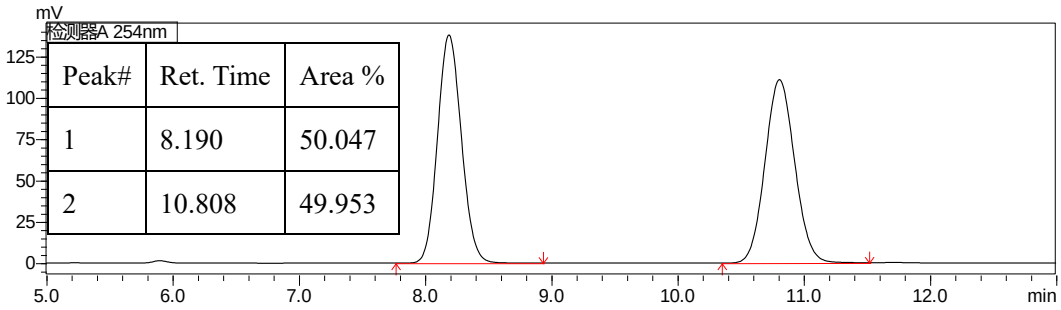
^{19}F NMR (376 MHz, $CDCl_3$) δ -32.62.

HRMS (ESI) [M+Na]$^+$:calcd. 630.0826, found 630.0836.

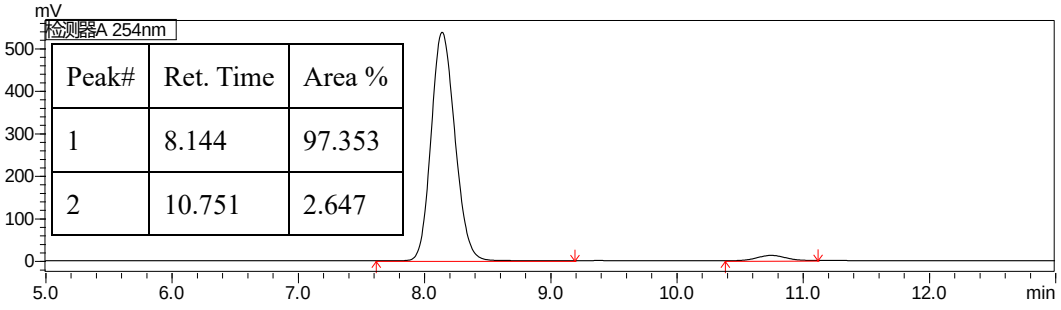
Optical rotation: $[\alpha]_D^{25}$ = -127.56 (c = 1.08, $CHCl_3$, 95% ee).

M.P.: 136-139 ℃.

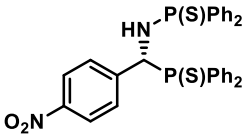
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 8.1 min, t_R(minor) = 10.8 min, 95% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	8.190	50.047
2	10.808	49.953



Peak#	Ret. Time	Area %
1	8.144	97.353
2	10.751	2.647



3pa

3pa: 52.9 mg, 91% yield, golden solid.

IR (film): ν_{max} (cm^{-1}) 3055, 1520, 1480, 1436, 1345, 1260, 1102, 1026, 998, 859, 748, 721, 690.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 12.5, 7.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.53 – 7.49 (m, 4H), 7.48 – 7.42 (m, 3H), 7.41 – 7.33 (m, 5H), 7.25 – 7.23 (m, 2H), 7.22 (d, *J* = 2.6 Hz, 2H), 7.21 – 7.18 (m, 3H), 6.23 – 6.14 (m, 1H), 4.58 (dd, *J* = 19.4, 10.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.07, 143.13, 134.93, 134.65, 134.14, 133.82, 132.51 – 132.17 (m), 131.91 – 131.32 (m), 131.24 (d, *J* = 11.8 Hz), 130.88 (d, *J* = 11.6 Hz), 129.88 – 129.51 (m), 129.45, 128.97 (d, *J* = 12.2 Hz), 128.70 – 127.82 (m), 122.33, 53.10 (d, *J* = 57.1 Hz).

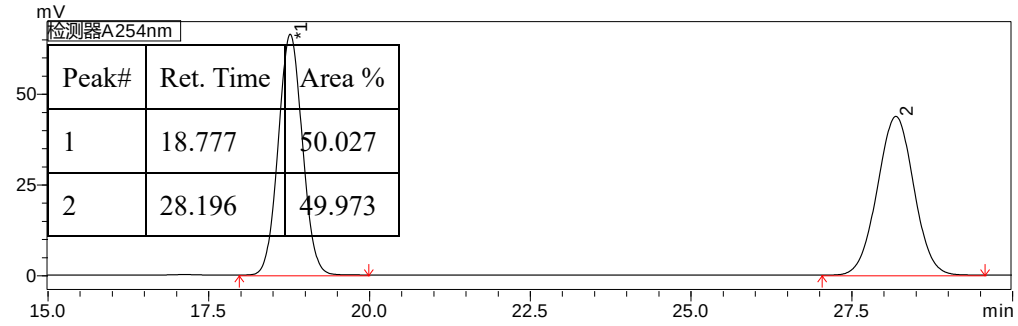
^{31}P NMR (162 MHz, $CDCl_3$) δ 89.45 (d, *J* = 32.3 Hz), 83.94 (d, *J* = 32.3 Hz).

HRMS (ESI) [M+H]$^+$:calcd. 585.0984, found 585.0990.

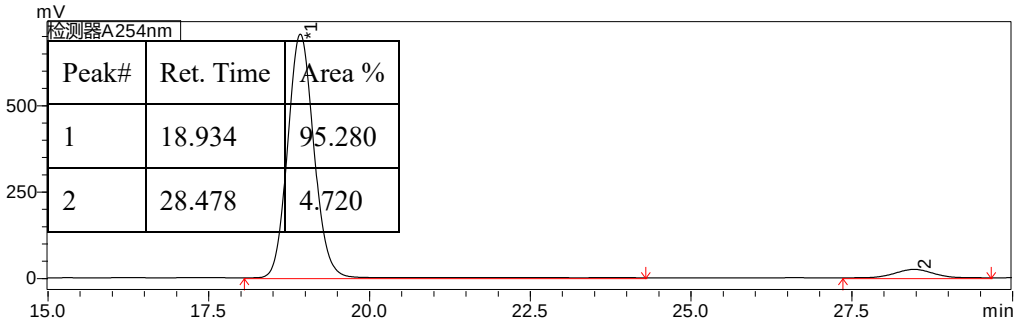
Optical rotation: $[\alpha]_D^{25}$ = -157.95 (c = 0.94, $CHCl_3$, 91% ee).

M.P.: 174-177 ℃.

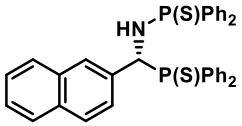
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 18.9 min, t_R(minor) = 28.5 min, 91% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	18.777	50.027
2	28.196	49.973



Peak#	Ret. Time	Area %
1	18.934	95.280
2	28.478	4.720



3qa

3qa: 52.2 mg, 87% yield, yellow oil.

IR (film): ν_{max} (cm^{-1}) 3054, 1436, 1396, 1102, 803, 780, 744, 720, 690, 647, 608, 502.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 11.7, 7.4 Hz, 2H), 7.90 (d, *J* = 5.3 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.60 – 7.54 (m, 5H), 7.47 – 7.42 (m, 4H), 7.40 – 7.35 (m, 1H), 7.34 – 7.29 (m, 1H), 7.25 – 7.19 (m, 4H), 7.14 – 7.07 (m, 3H), 7.05 – 7.01 (m, 3H), 6.94 – 6.87 (m, 1H), 6.78 – 6.68 (m, 2H), 4.79 (dd, *J* = 19.5, 10.1 Hz, 1H).

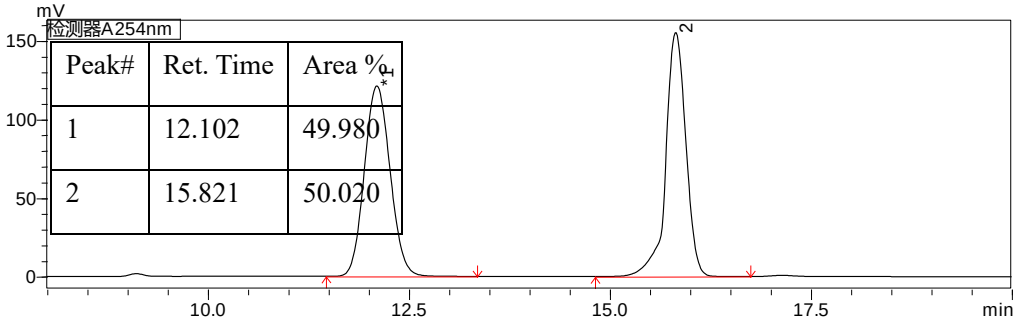
^{13}C NMR (126 MHz, $CDCl_3$) δ 135.41, 135.17, 134.63, 134.34, 132.85 (d, *J* = 9.6 Hz), 132.20, 131.79 – 131.15 (m), 130.98 (d, *J* = 11.4 Hz), 128.82 (d, *J* = 11.9 Hz), 128.52 – 128.04 (m), 127.83 (d, *J* = 13.3 Hz), 127.54, 127.32 (d, *J* = 12.2 Hz), 125.65, 124.83, 124.55, 122.47, 47.50 (d, *J* = 58.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 89.58 (d, *J* = 32.5 Hz), 85.12 (d, *J* = 32.5 Hz).

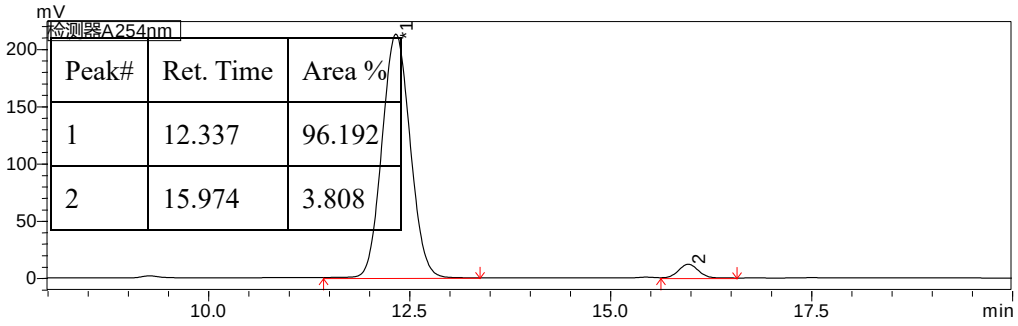
HRMS (ESI) $[M+H]^+$:calcd. 590.1289, found 590.1281.

Optical rotation: $[\alpha]_D^{25}$ = -98.20 (c = 1.02, $CHCl_3$, 92% ee).

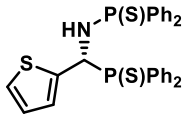
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 12.3 min, t_R(minor) = 16.0 min, 92% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	12.102	49.980
2	15.821	50.020



Peak#	Ret. Time	Area %
1	12.337	96.192
2	15.974	3.808



3ra

3ra: 54.0 mg, 99% yield, white solid.

IR (film): ν_{max} (cm^{-1}) 3054, 1480, 1435, 1391, 1215, 1158, 1102, 1027, 998, 874, 797, 721, 689.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 12.5, 7.2 Hz, 2H), 7.61 (dd, *J* = 12.7, 7.5 Hz, 2H), 7.55 – 7.50 (m, 3H), 7.48 – 7.45 (m, 2H), 7.38 – 7.29 (m, 5H), 7.27 – 7.19 (m, 6H), 6.97 (d, *J* = 4.9 Hz, 1H), 6.80 – 6.77 (m, 1H), 6.61 – 6.55 (m, 1H), 6.51 – 6.43 (m, 1H), 4.38 (dd, *J* = 17.5, 7.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.67, 135.17, 134.34, 132.33 (d, *J* = 9.7 Hz), 131.93 (d, *J* = 20.4 Hz), 131.77, 131.55 – 131.09 (m), 130.84 (d, *J* = 11.5 Hz), 130.27, 129.64, 128.68 (d, *J* = 12.0 Hz), 128.46 – 127.75 (m), 126.04, 125.80, 49.91 (d, *J* = 64.8 Hz).

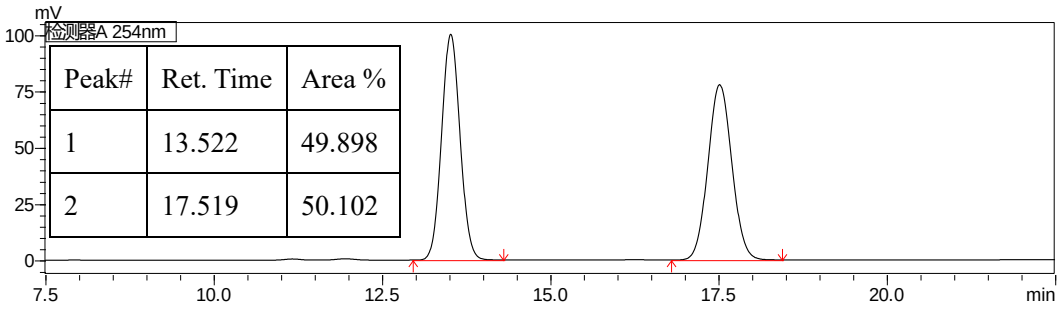
^{31}P NMR (162 MHz, $CDCl_3$) δ 89.77 (d, *J* = 32.5 Hz), 82.87 (d, *J* = 32.5 Hz).

HRMS (ESI) $[M+H]^+$: calcd. 546.0697, found 546.0704.

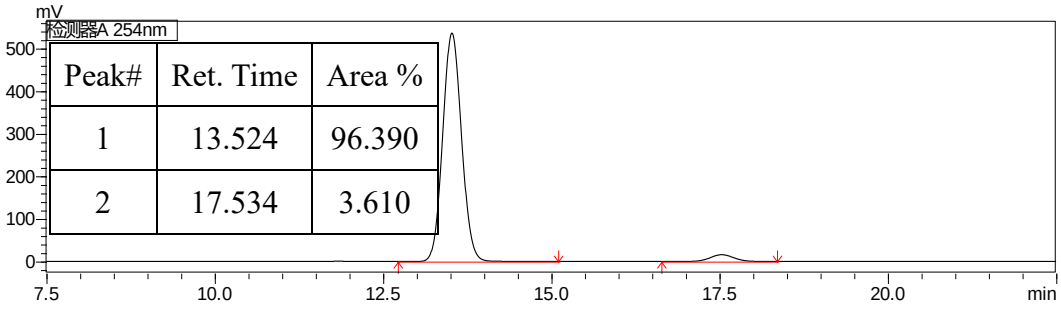
Optical rotation: $[\alpha]_D^{25}$ = -73.75 (c = 1.00, $CHCl_3$, 93% ee).

M.P.: 141-144 ℃.

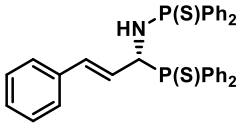
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 13.5 min, t_R(minor) = 17.5 min, 93% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	13.522	49.898
2	17.519	50.102



Peak#	Ret. Time	Area %
1	13.524	96.390
2	17.534	3.610



3sa

3sa: 55.9 mg, 70% yield, white solid.

IR (film): ν_{max} (cm^{-1}) 3055, 1435, 1102, 962, 720, 690, 636, 614, 527.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 12.4, 7.0 Hz, 2H), 7.90 – 7.69 (m, 4H), 7.52 – 7.45 (m, 3H), 7.44 – 7.42 (m, 1H), 7.40 – 7.34 (m, 4H), 7.34 – 7.29 (m, 4H), 7.25 – 7.19 (m, 2H), 7.14 – 7.13 (m, 3H), 6.86 – 6.85 (m, 2H), 6.16 (dd, *J* = 15.6, 4.1 Hz, 1H), 5.88 – 5.81 (m, 1H), 5.79 – 5.72 (m, 1H), 4.00 (dd, *J* = 16.1, 9.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.11, 135.26, 132.28 (d, *J* = 9.7 Hz), 131.98 (d, *J* = 9.8 Hz), 131.80 – 131.30 (m), 130.87 (d, *J* = 11.5 Hz), 128.44 (m), 127.75, 126.47, 123.47, 52.90 (d, *J* = 63.3 Hz).

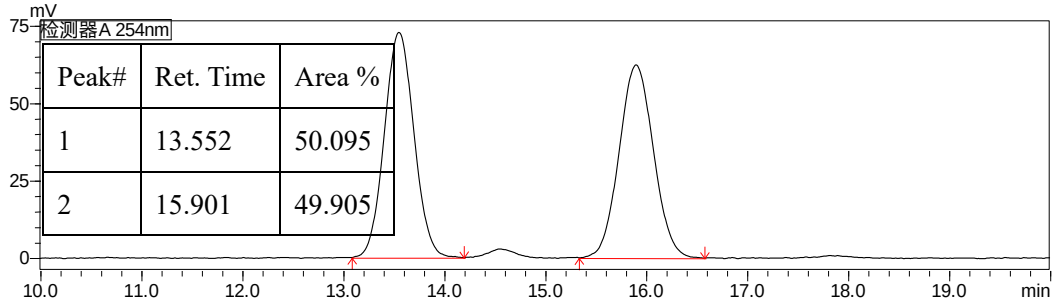
^{31}P NMR (162 MHz, $CDCl_3$) δ 89.37 (d, *J* = 34.3 Hz), 81.52 (d, *J* = 34.3 Hz).

HRMS (ESI) [M+H]$^+$:calcd. 566.1289, found 566.1291.

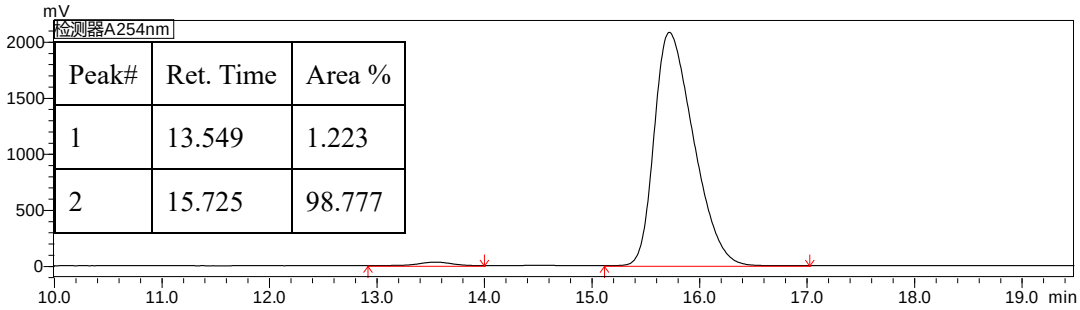
Optical rotation: $[\alpha]_D^{25}$ = -74.47 (c = 1.03, $CHCl_3$, 98% ee).

M.P.: 87-90 ℃.

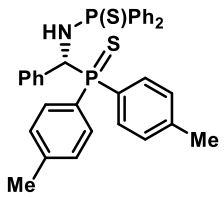
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 15.7 min, t_R(minor) = 13.5 min, 98% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	13.552	50.095
2	15.901	49.905



Peak#	Ret. Time	Area %
1	13.549	1.223
2	15.725	98.777



3ab

3ab: 51.6 mg, 91% yield, white solid.

IR (film): ν_{max} (cm^{-1}) 3054, 2920, 1599, 1494, 1453, 1436, 1397, 1187, 1102, 1069, 880, 718.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 12.2, 8.0 Hz, 2H), 7.52 (dd, *J* = 14.0, 7.4 Hz, 2H), 7.41 – 7.34 (m, 3H), 7.32 – 7.23 (m, 6H), 7.22 – 7.16 (m, 3H), 7.14 (d, *J* = 7.4 Hz, 2H), 7.06 – 7.01 (m, 1H), 7.05 – 7.02 (m, 4H), 6.06 – 5.96 (m, 1H), 4.57 (dd, *J* = 19.0, 10.5 Hz, 1H), 2.42 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.40, 142.05, 135.66, 132.43 (d, *J* = 10.0 Hz), 131.90 (d, *J* = 10.2 Hz), 131.28 (d, *J* = 11.7 Hz), 131.00 (d, *J* = 11.5 Hz), 129.40 (d, *J* = 12.3 Hz), 128.81 (dd, *J* = 26.1, 8.8 Hz), 128.24 (d, *J* = 13.3 Hz), 127.96 (d, *J* = 13.3 Hz), 127.48 (d, *J* = 27.7 Hz), 127.35 – 127.05 (m), 53.60 (d, *J* = 58.8 Hz), 21.51 (d, *J* = 18.2 Hz).

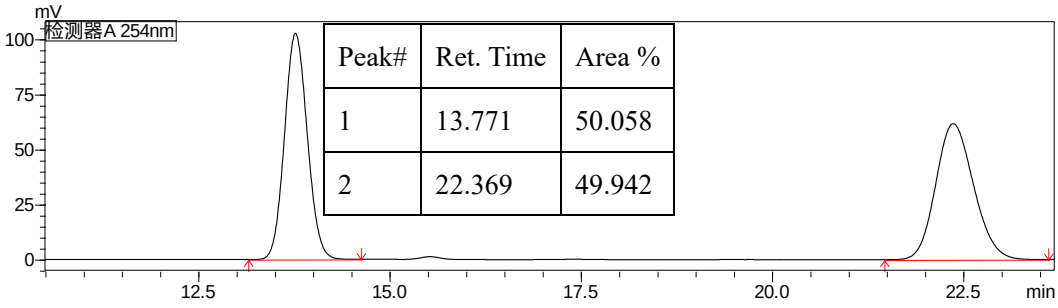
^{31}P NMR (162 MHz, $CDCl_3$) δ 89.31 (d, *J* = 32.8 Hz), 83.63 (d, *J* = 32.8 Hz).

HRMS (ESI) $[M+H]^+$: calcd. 568.1446, found 568.1453.

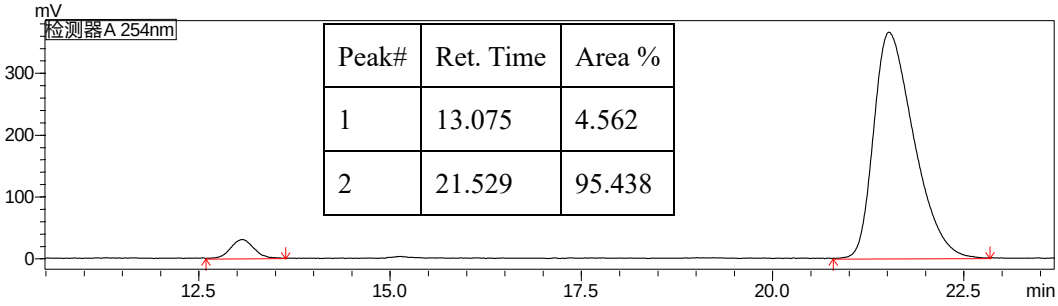
Optical rotation: $[\alpha]_D^{25}$ = -102.55 (c = 0.93, $CHCl_3$, 91% ee).

M.P.: 165-169 ℃.

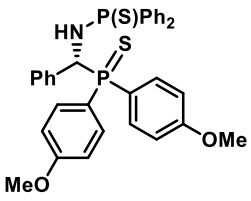
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 21.5 min, t_R(minor) = 13.1 min, 91% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	13.771	50.058
2	22.369	49.942



Peak#	Ret. Time	Area %
1	13.075	4.562
2	21.529	95.438



3ac

3ac: 47.9 mg, 80% yield, white solid.

IR (film): ν_{max} (cm^{-1}) 2962, 2929, 1593, 1568, 1499, 1454, 1436, 1405, 1293, 1257, 1179, 1158, 1103, 1069, 1026, 880, 827, 800, 748, 719, 693, 637.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 11.7, 8.7 Hz, 2H), 7.48 (dd, *J* = 14.0, 7.5 Hz, 2H), 7.44 – 7.36 (m, 3H), 7.33 – 7.28 (m, 1H), 7.28 – 7.22 (m, 4H), 7.21 – 7.16 (m, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.06 – 7.03 (m, 1H), 6.99 – 6.94 (m, 4H), 6.65 (dd, *J* = 8.7, 1.9 Hz, 2H), 6.01 – 5.92 (m, 1H), 4.54 (dd, *J* = 19.2, 10.4 Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.48 (d, *J* = 3.3 Hz), 162.13 (d, *J* = 3.1 Hz), 135.75, 135.22, 134.91, 134.25 (d, *J* = 11.0 Hz), 133.75 (d, *J* = 11.3 Hz), 132.97 (d, *J* = 13.5 Hz), 131.27 (d, *J* = 11.7 Hz), 131.01 (d, *J* = 11.4 Hz), 128.87 (d, *J* = 4.8 Hz), 128.30 (d, *J* = 13.3 Hz), 127.97 (d, *J* = 13.3 Hz), 127.84 – 127.62 (m), 127.51 (d, *J* = 25.7 Hz), 114.19 (d, *J* = 13.1 Hz), 113.47 (d, *J* = 13.5 Hz), 55.38 (d, *J* = 16.0 Hz), 53.84 (d, *J* = 59.0 Hz).

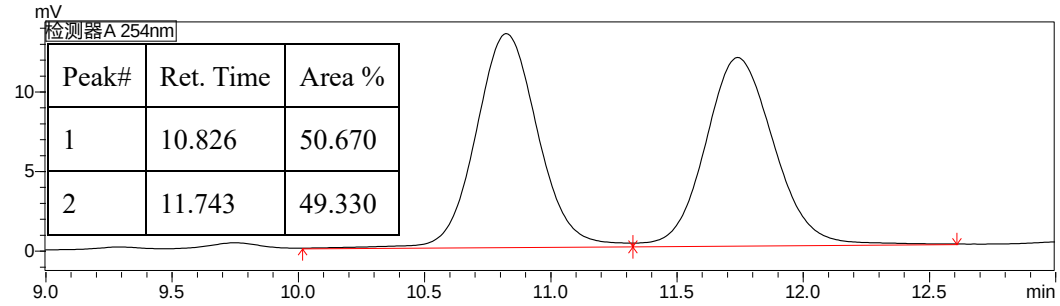
^{31}P NMR (162 MHz, $CDCl_3$) δ 89.31 (d, *J* = 32.3 Hz), 82.69 (d, *J* = 32.3 Hz).

HRMS (ESI) $[M+H]^+$: calcd. 600.1344, found 600.1352.

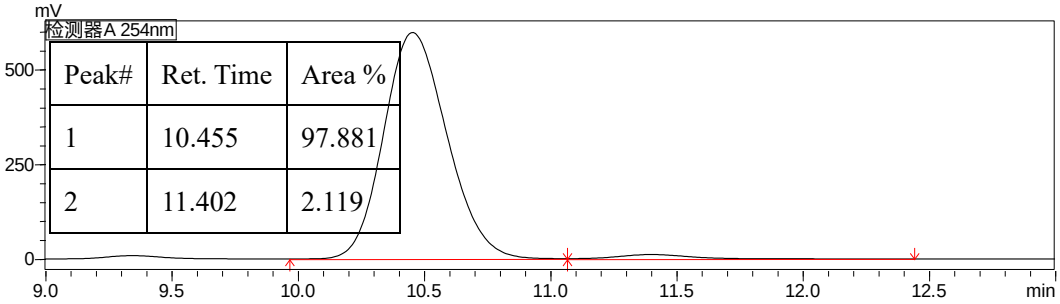
Optical rotation: $[\alpha]_D^{25}$ = -111.65 (c = 1.06, $CHCl_3$, 96% ee).

M.P.: 168-172 ℃.

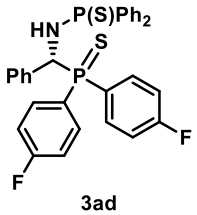
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 10.5 min, t_R(minor) = 11.4 min, 96% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	10.826	50.670
2	11.743	49.330



Peak#	Ret. Time	Area %
1	10.455	97.881
2	11.402	2.119



3ad

3ad: 56.93 mg, 99% yield, yellow oil.

IR (film): ν_{max} (cm^{-1}) 3057, 1590, 1495, 1453, 1396, 1300, 1234, 1197, 1159, 1102, 1069, 1028, 1013, 880, 828, 747, 719, 637, 530.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 – 8.12 (m, 2H), 7.50 – 7.39 (m, 5H), 7.39 – 7.31 (m, 2H), 7.31 – 7.23 (m, 3H), 7.21 – 7.13 (m, 4H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 7.1 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.90 – 6.82 (m, 2H), 6.11 – 6.01 (m, 1H), 4.50 (dd, *J* = 18.7, 10.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.23 (dd, *J* = 246.9, 3.0 Hz), 135.41 (d, *J* = 1.7 Hz), 135.19, 134.43 (d, *J* = 1.8 Hz), 134.15, 132.33 (d, *J* = 9.7 Hz), 132.00 (d, *J* = 3.0 Hz), 131.79 (d, *J* = 9.9 Hz), 131.66 (d, *J* = 3.0 Hz), 131.50 (d, *J* = 3.1 Hz), 131.25 (d, *J* = 11.7 Hz), 130.83 (d, *J* = 11.4 Hz), 130.49 (dd, *J* = 8.2, 4.9 Hz), 128.53 (dd, *J* = 33.9, 12.7 Hz), 128.11, 127.98, 127.85, 114.27 (dd, *J* = 21.6, 2.0 Hz), 52.60 (d, *J* = 59.6 Hz).

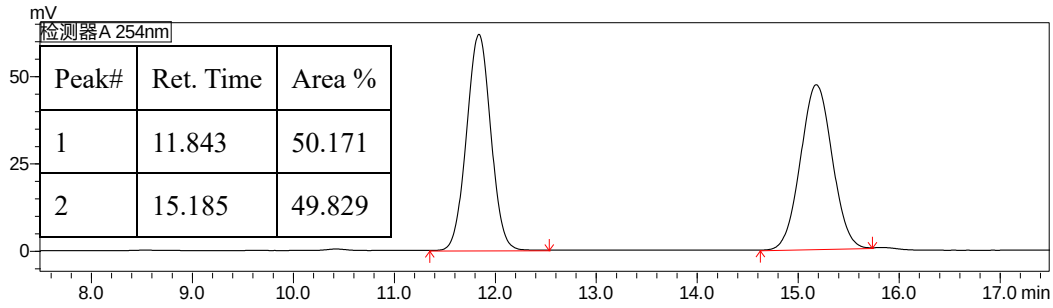
^{31}P NMR (162 MHz, $CDCl_3$) δ 89.79 (d, *J* = 32.1 Hz), 82.25 (d, *J* = 32.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -76.48, -76.74.

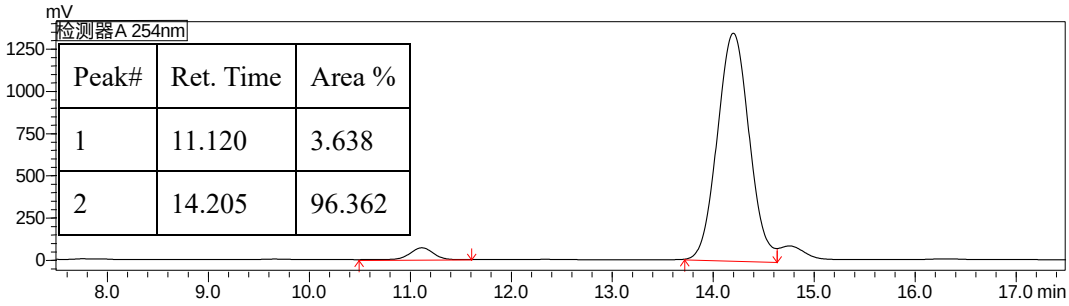
HRMS (ESI) [M+H]$^{+}$:calcd. 576.0945, found 576.0949.

Optical rotation: $[\alpha]_D^{25}$ = -90.15 (c = 1.03, $CHCl_3$, 93% ee).

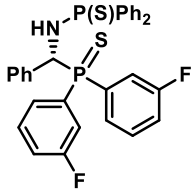
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 14.2 min, t_R(minor) = 11.1 min, 93% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	11.843	50.171
2	15.185	49.829



Peak#	Ret. Time	Area %
1	11.120	3.638
2	14.205	96.362



3ae

3ae: 49.1 mg, 85% yield, white solid.

IR (film): ν_{max} (cm^{-1}) 3057, 1581, 1476, 1454, 1436, 1422, 1266, 1223, 1094, 885, 787, 719, 690, 640, 626, 615, 576.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 11.2, 7.8 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.48 – 7.39 (m, 5H), 7.32 – 7.25 (m, 3H), 7.23 – 7.17 (m, 5H), 7.14 – 7.13 (m, 3H), 7.11 – 7.06 (m, 2H), 7.03 – 6.97 (m, 3H), 6.14 – 6.04 (m, 1H), 4.47 (dd, *J* = 18.4, 10.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.57 (dd, *J* = 54.1, 17.1 Hz), 161.08 (dd, *J* = 53.8, 17.0 Hz), 135.57 (d, *J* = 1.9 Hz), 135.12 (d, *J* = 3.1 Hz), 135.00, 134.58 (d, *J* = 2.1 Hz), 133.97, 132.94 (dd, *J* = 21.6, 5.8 Hz), 132.16 (dd, *J* = 19.6, 5.8 Hz), 131.57 – 131.26 (m), 131.36 – 130.70 (m), 130.49 (dd, *J* = 13.8, 7.4 Hz), 129.83 (dd, *J* = 14.2, 7.4 Hz), 128.78 (d, *J* = 5.2 Hz), 128.15 (dd, *J* = 36.1, 13.4 Hz), 127.64 (d, *J* = 2.1 Hz), 127.30 (dd, *J* = 9.1, 3.2 Hz), 119.79 (dd, *J* = 23.5, 11.2 Hz), 119.35 (dd, *J* = 21.2, 2.6 Hz), 119.16 – 118.83 (m), 118.76 (d, *J* = 3.1 Hz), 53.56 (d, *J* = 59.8 Hz).

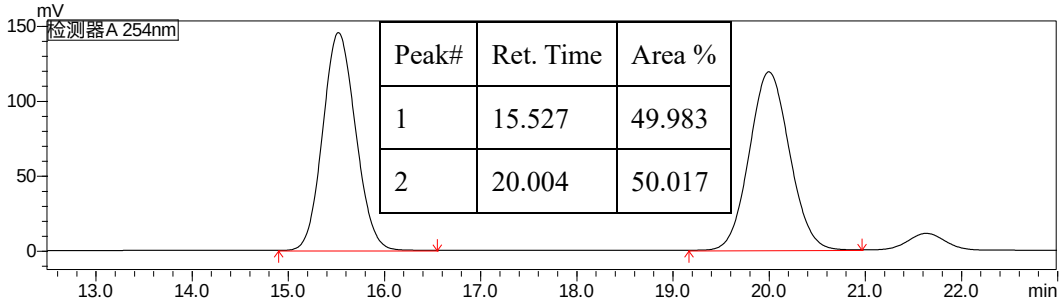
^{19}F NMR (376 MHz, $CDCl_3$) δ -80.06, -81.04.

HRMS (ESI) [M+H]$^{+}$: calcd. 576.0945, found 576.0951.

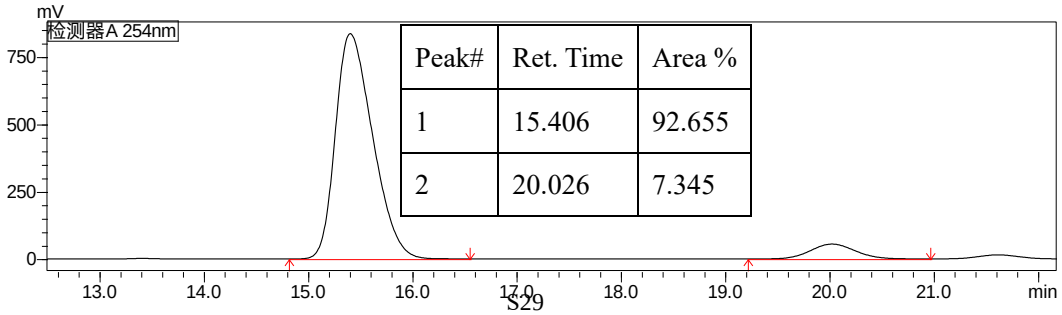
Optical rotation: $[\alpha]_D^{25}$ = -79.51 (c = 1.01, $CHCl_3$, 85% ee).

M.P.: 124-127 ℃.

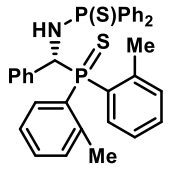
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 39/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 15.4 min, t_R(minor) = 20.0 min, 85% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	15.527	49.983
2	20.004	50.017



Peak#	Ret. Time	Area %
1	15.406	92.655
2	20.026	7.345



3af

3af: 42.5 mg, 75% yield, white solid.

IR (film): ν_{max} (cm^{-1}) 3055, 1453, 1436, 1394, 1133, 1103, 1070, 804, 788, 751, 716, 691, 640, 610, 548.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 12.5, 7.4 Hz, 1H), 7.76 (dd, *J* = 13.6, 7.4 Hz, 2H), 7.54 (dd, *J* = 14.2, 7.4 Hz, 2H), 7.47 (dd, *J* = 7.7, 6.4 Hz, 1H), 7.43 – 7.38 (m, 5H), 7.25 – 7.22 (m, 1H), 7.19 – 7.16 (m, 1H), 7.14 – 7.09 (m, 3H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.00 – 6.95 (m, 1H), 6.91 – 6.86 (m, 1H), 6.82 – 6.77 (m, 1H), 6.74 – 6.68 (m, 2H), 6.31 – 6.22 (m, 1H), 5.26 (dd, *J* = 20.9, 10.2 Hz, 1H), 2.11 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.08 (d, *J* = 5.9 Hz), 135.70, 135.33, 134.71, 134.30, 134.09 (d, *J* = 2.4 Hz), 132.95 (d, *J* = 9.5 Hz), 132.12 (d, *J* = 3.0 Hz), 131.90 (d, *J* = 9.9 Hz), 131.52 (d, *J* = 3.0 Hz), 131.37 – 131.06 (m), 130.89 (d, *J* = 11.4 Hz), 129.45 (d, *J* = 1.7 Hz), 129.09 (d, *J* = 3.5 Hz), 128.67 (d, *J* = 12.0 Hz), 128.23 (d, *J* = 13.3 Hz), 128.01 – 127.51 (m), 125.40 (d, *J* = 2.7 Hz), 48.68 (d, *J* = 58.5 Hz), 19.22.

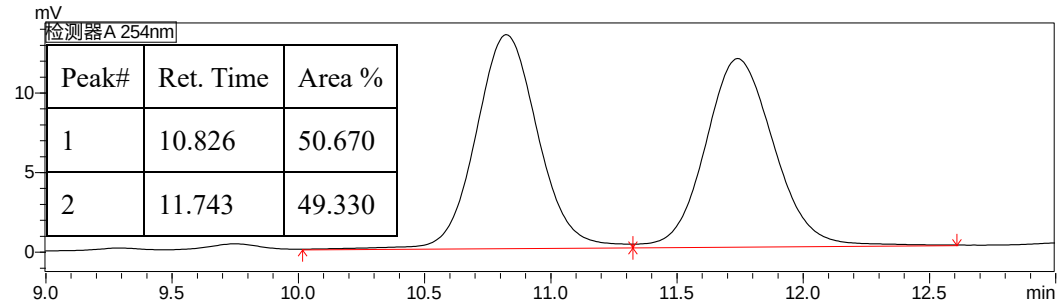
^{31}P NMR (162 MHz, $CDCl_3$) δ 87.30 (d, *J* = 38.7 Hz), 80.85 (d, *J* = 38.7 Hz).

HRMS (ESI) $[M+H]^+$:calcd. 568.1446, found 568.1448.

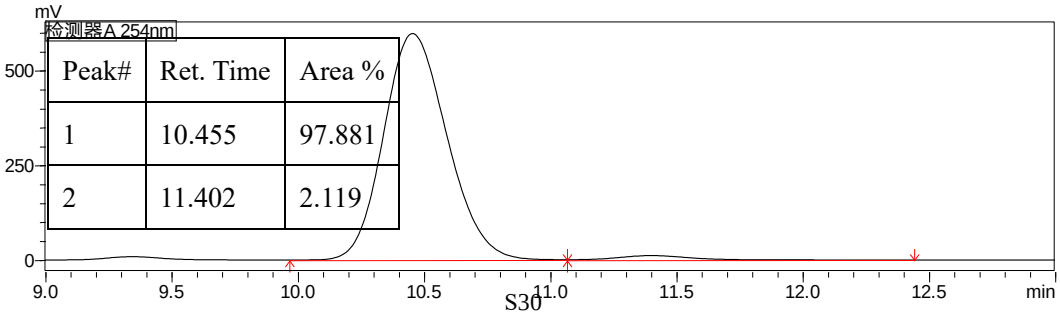
Optical rotation: $[\alpha]_D^{25}$ = -178.38 (c = 1.03, $CHCl_3$, 96% ee).

M.P.: 50-52 ℃.

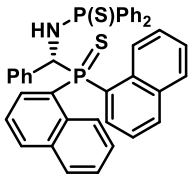
HPLC: DAICEL CHIRALPAK ADH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 10.5 min, t_R(minor) = 11.4 min, 96% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



Peak#	Ret. Time	Area %
1	10.826	50.670
2	11.743	49.330



Peak#	Ret. Time	Area %
1	10.455	97.881
2	11.402	2.119



3ag

3ag: 63.3 mg, 99% yield, yellow solid.

IR (film): ν_{max} (cm^{-1}) 3056, 1506, 1436, 1146, 1103, 823, 798, 770, 752, 714, 692.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.21 (dd, *J* = 14.4, 7.2 Hz, 1H), 8.56 – 8.52 (m, 1H), 8.18 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.82 (dd, *J* = 13.5, 7.5 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.48 – 7.45 (m, 2H), 7.42 – 7.35 (m, 2H), 7.30 – 7.25 (m, 3H), 7.21 (dd, *J* = 15.0, 7.7 Hz, 2H), 7.11 – 7.06 (m, 2H), 6.77 – 6.69 (m, 2H), 6.67 – 6.62 (m, 1H), 6.62 – 6.54 (m, 1H), 6.52 – 6.44 (m, 2H), 5.43 (dd, *J* = 20.8, 10.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.26 (d, *J* = 18.5 Hz), 131.91, 131.56 (d, *J* = 11.9 Hz), 131.16 – 130.71 (m), 130.64, 130.25, 129.23, 128.88 (d, *J* = 13.2 Hz), 128.19 (d, *J* = 5.2 Hz), 127.67 (d, *J* = 13.4 Hz), 127.33 (d, *J* = 17.9 Hz), 126.90 – 126.30 (m), 126.30 – 125.96 (m), 125.91 (d, *J* = 7.9 Hz), 125.39 (d, *J* = 13.5 Hz), 124.61 (d, *J* = 14.9 Hz), 124.29, 53.01 (d, *J* = 57.6 Hz).

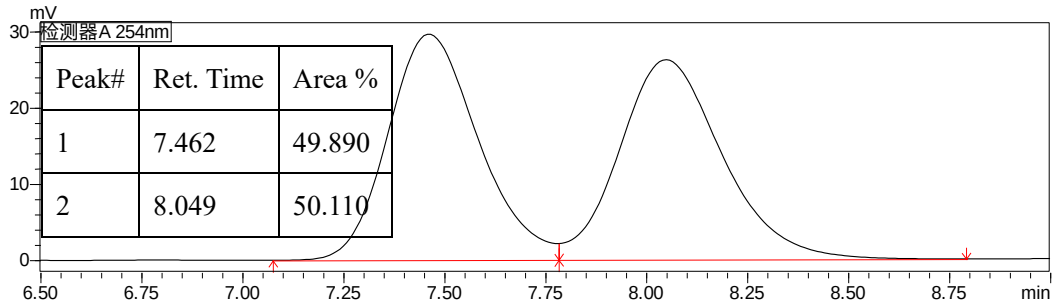
^{31}P NMR (162 MHz, $CDCl_3$) δ 87.51 (d, *J* = 38.9 Hz), 79.99 (d, *J* = 38.9 Hz).

HRMS (ESI) [M+H]$^{+}$: calcd. 640.1446, found 640.1449.

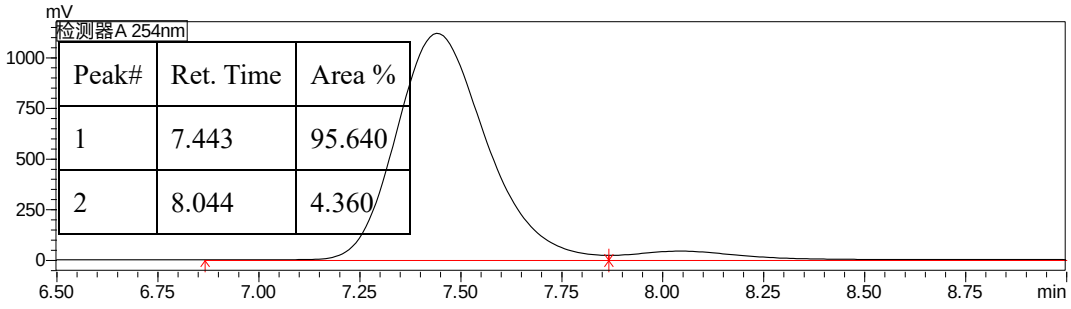
Optical rotation: $[\alpha]_D^{25}$ = -270.76 (c = 1.06, $CHCl_3$, 91% ee).

M.P.: 69-72 ℃.

HPLC: DAICEL CHIRALPAK ODH, hexane/i-PrOH = 19/1, flow rate: 1.0 mL/min, λ = 254 nm, t_R(major) = 7.4 min, t_R(minor) = 8.0 min, 91% ee. The racemic sample was prepared by using *rac*-BINAP as the ligand.



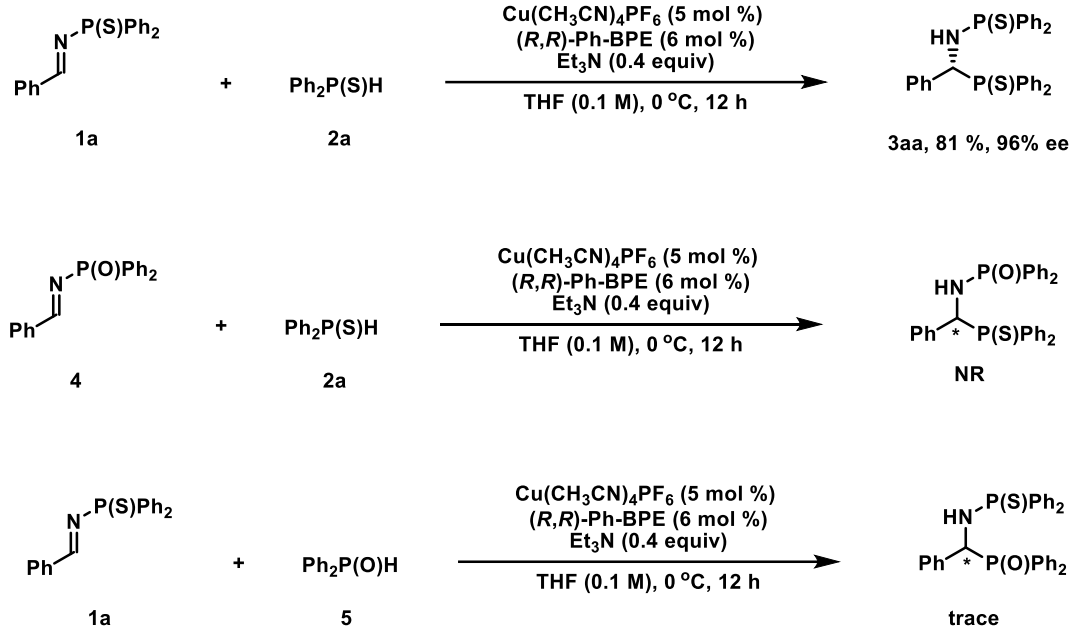
Peak#	Ret. Time	Area %
1	7.462	49.890
2	8.049	50.110



Peak#	Ret. Time	Area %
1	7.443	95.640
2	8.044	4.360

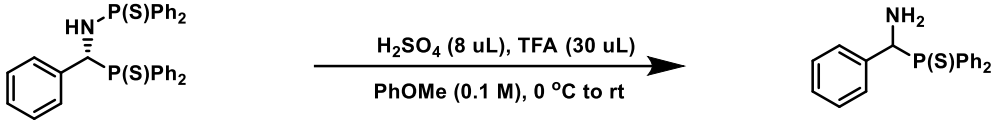
5. Mechanism Investigation

In order to shed light on the mechanism of these reactions, some control experiments were done.



Three dried 10 ml test tubes equipped with magnetic stirring bars were charged with $Cu(CH_3CN)_4PF_6$ (1.8 mg, 0.005 mmol, 0.05 equiv) and (*R,R*)-Ph-BPE (3 mg, 0.006 mmol, 0.06 equiv) in a glove box under Ar atmosphere. Anhydrous THF (1.0 mL, 0.1 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a coloress catalyst solution. Corresponding aldehyde imines (0.10 mmol, 1.0 equiv) and diarylphosphines (0.12 mmol, 1.2 equiv) were added sequentially. After the tubes were taken out of the glove box, the reaction mixture were stirred at 0 °C for 10 minutes. Then NEt_3 (6.0 uL, 0.04 mmol, 0.4 equiv) was added. The resulting reaction mixture were stirred at 0 °C for 12 hours and quenched by acetic acid (10 uL). After volatiles were removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to give the desired product.

6. Transformation of 3aa



3aa, 97% ee

47%, 0% ee

A dried 10 mL test tube equipped with a magnetic stirring bar was charged with **3aa** (53.9 mg, 0.1 mmol, 1.0 equiv) and anisole (1.0 mL, 0.1 M). The reaction mixture was stirred at 0 °C for 10 minutes. Then H_2SO_4 (8 uL) and Trifluoroacetic acid (30 uL) was added sequentially. The reaction mixture was stirred at room temperature for 18 hours. After removal of volatiles were removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1 to 1/1) to give the product (15.3 mg, 47% yield, 0% ee, colorless oil).

7. References

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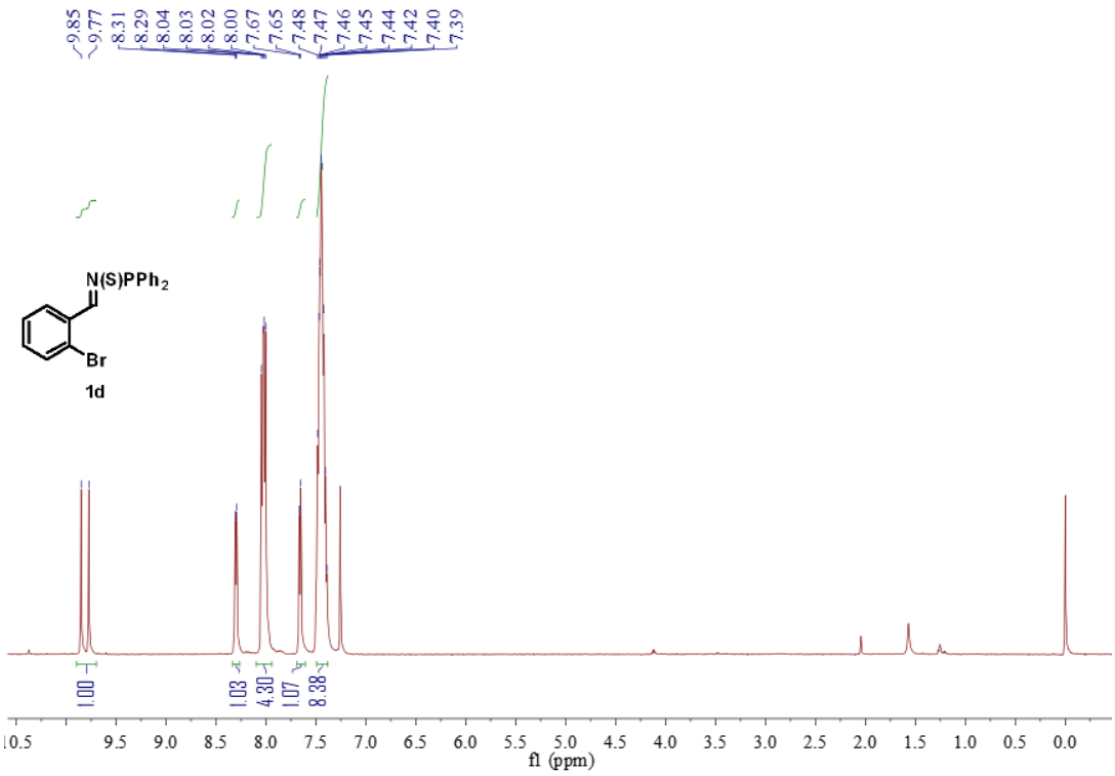
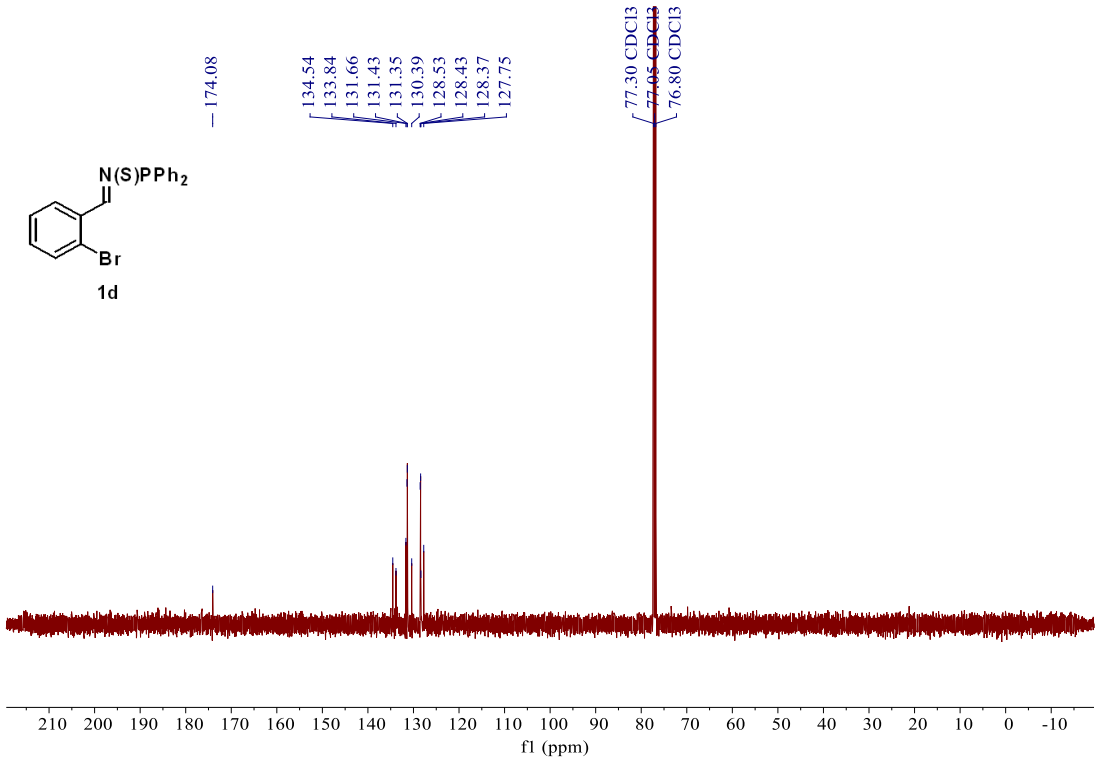
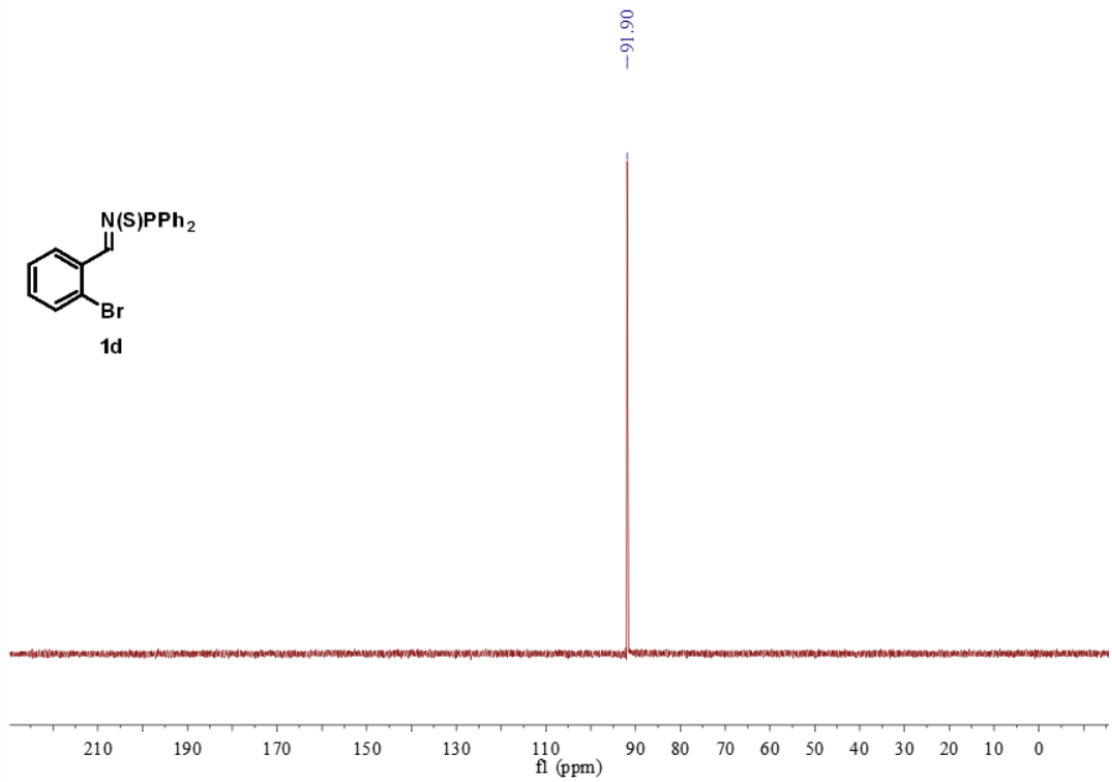
8. NMR Spectra



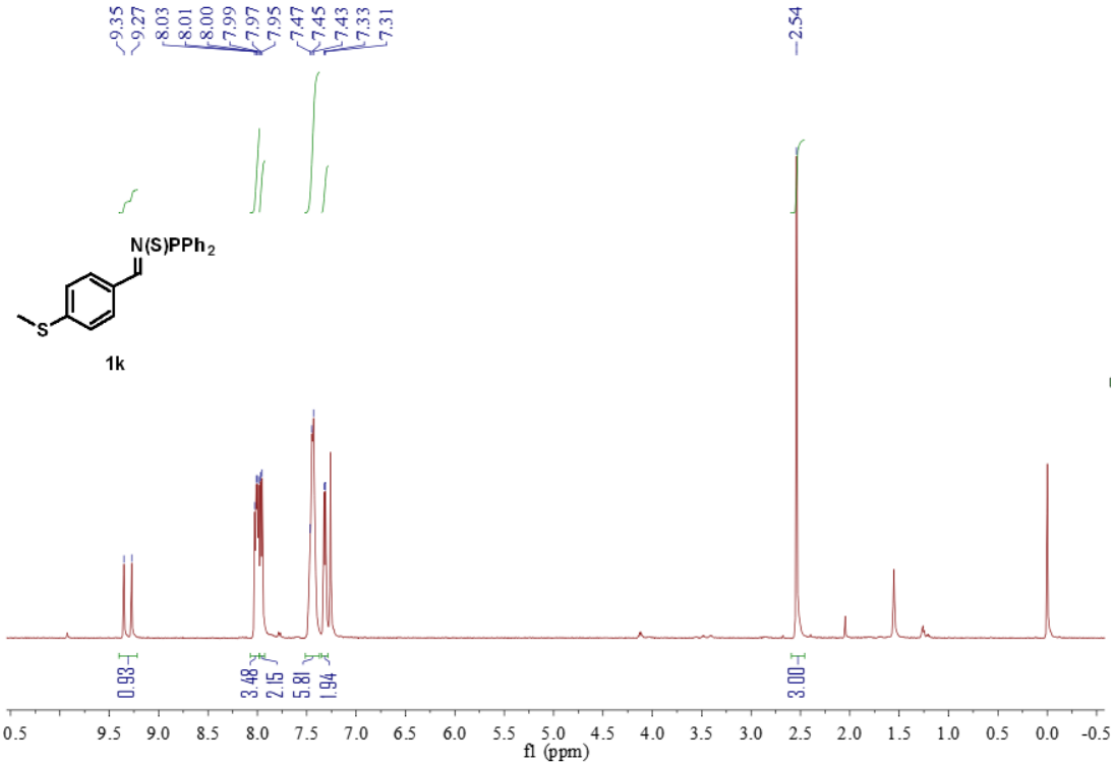
^{1}H NMR of **1d**



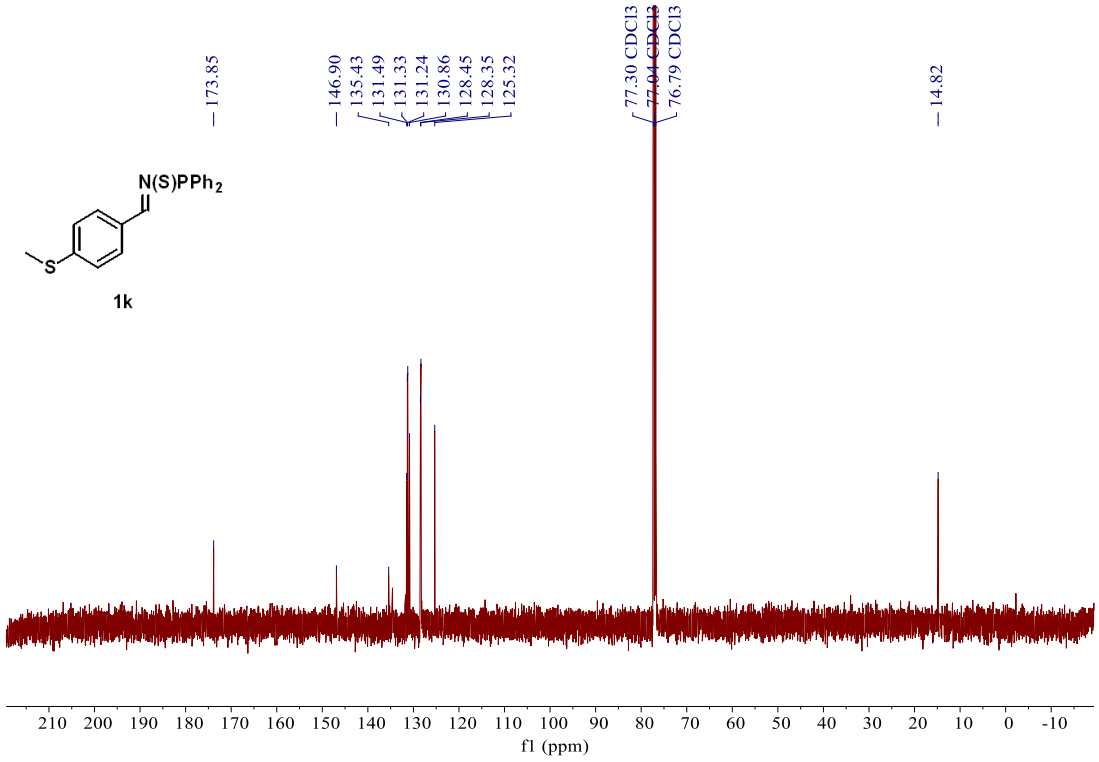
^{13}C NMR of **1d**



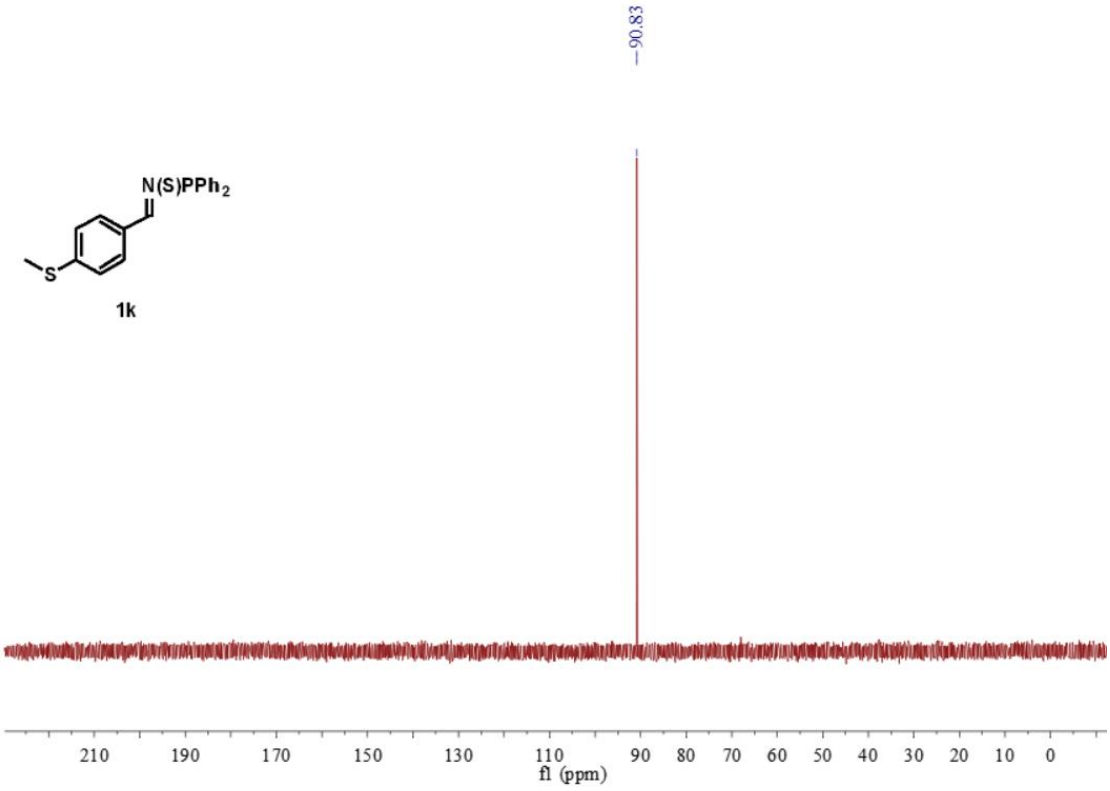
^{31}P NMR of **1d**



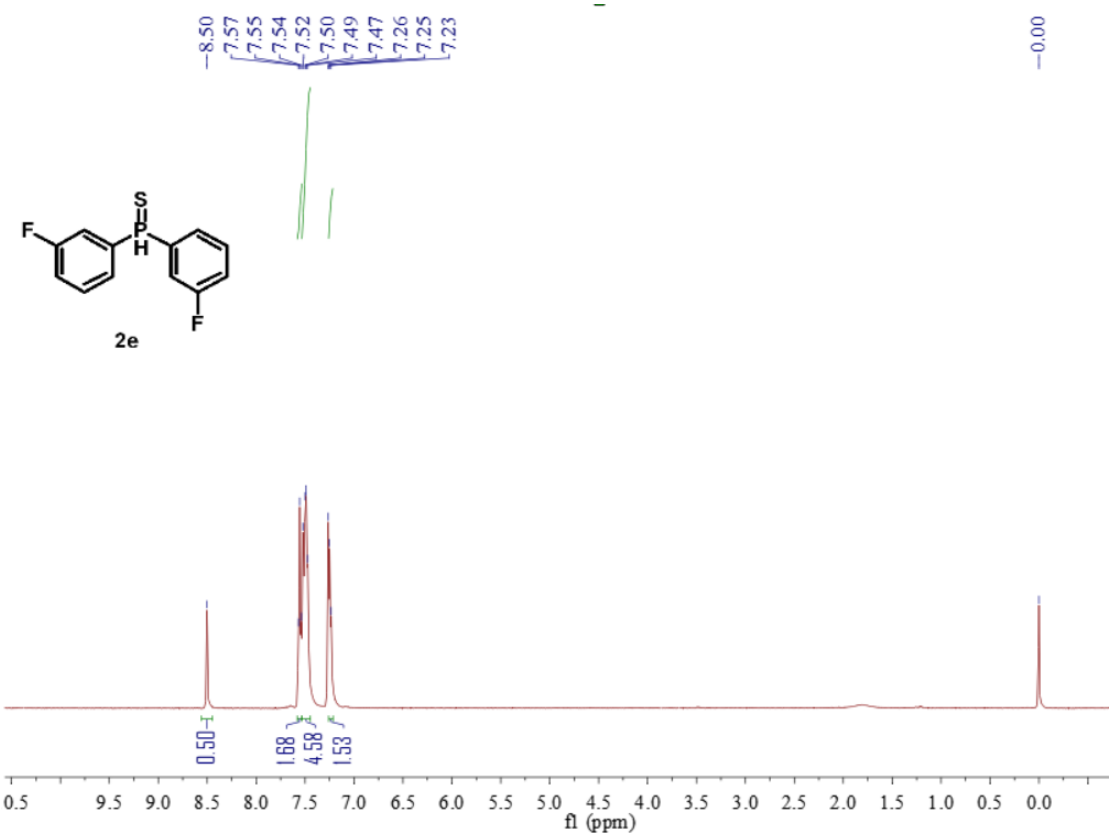
^{1}H NMR of **1k**



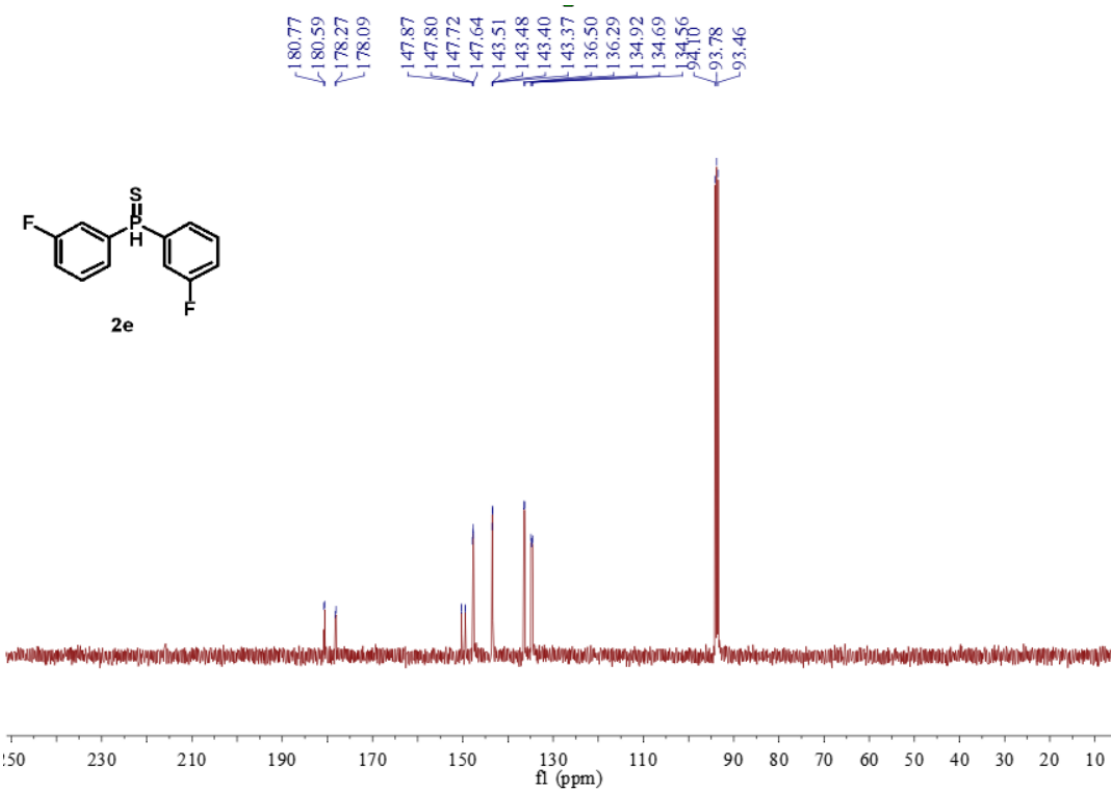
^{13}C NMR of **1k**



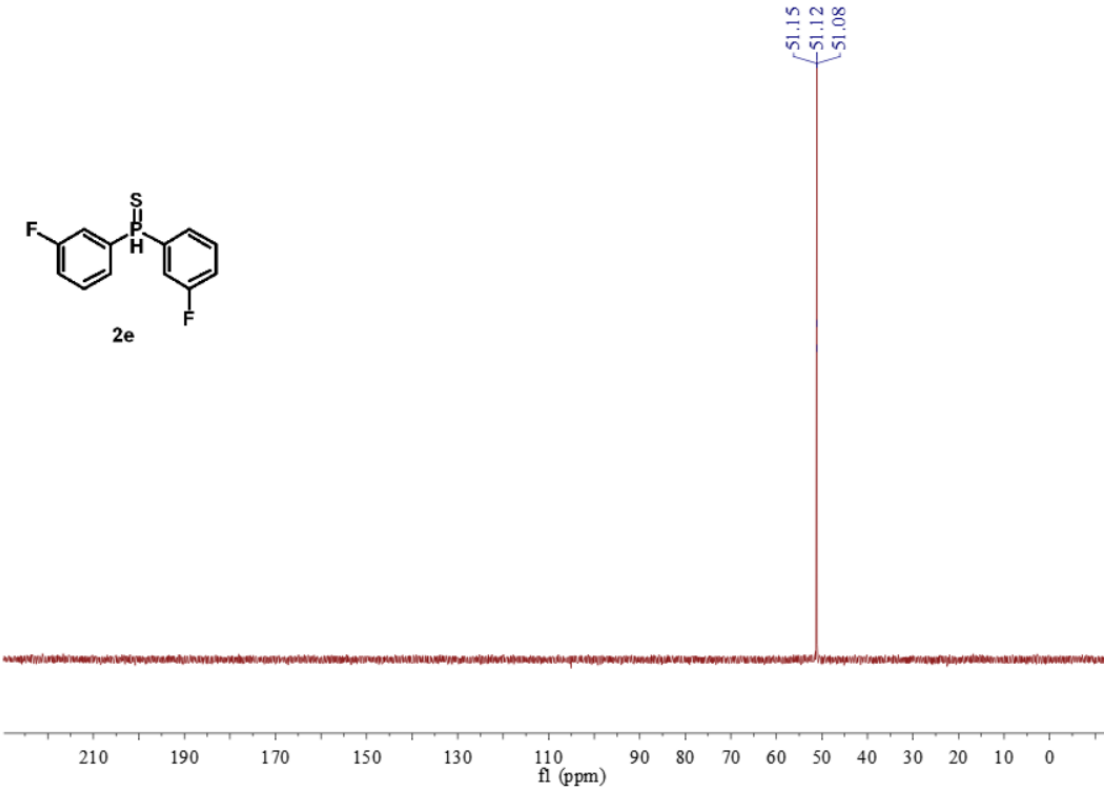
^{31}P NMR of **1k**



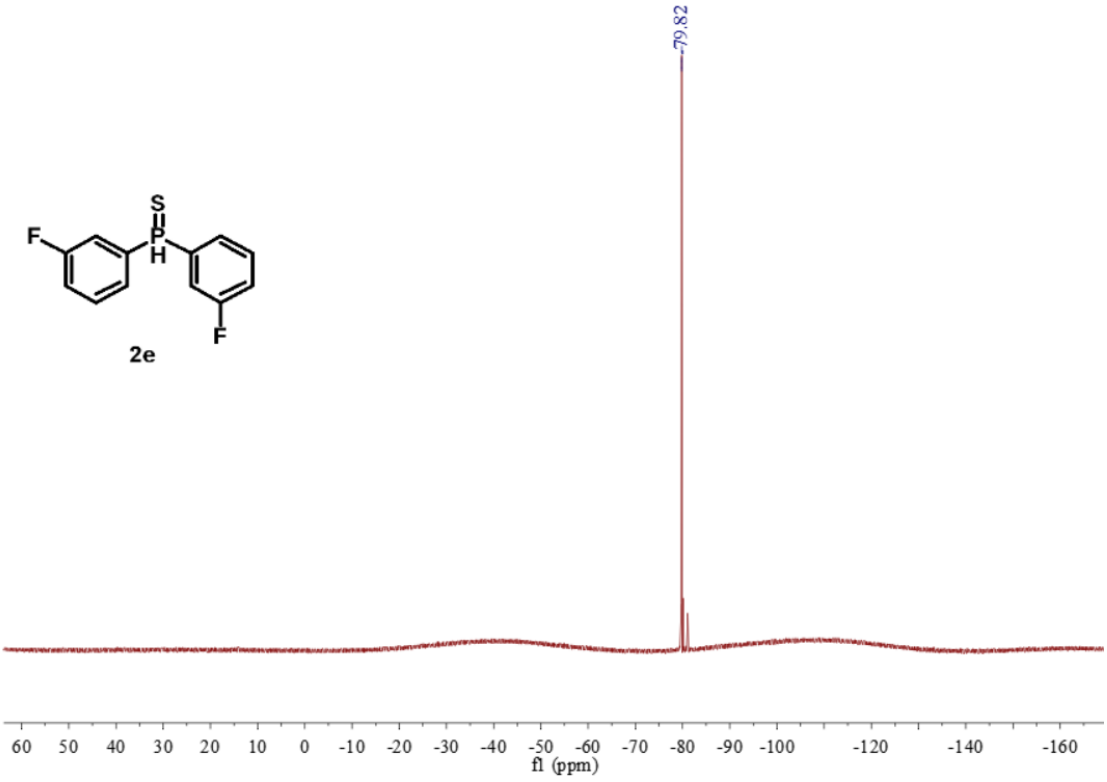
^{1}H NMR of **2e**



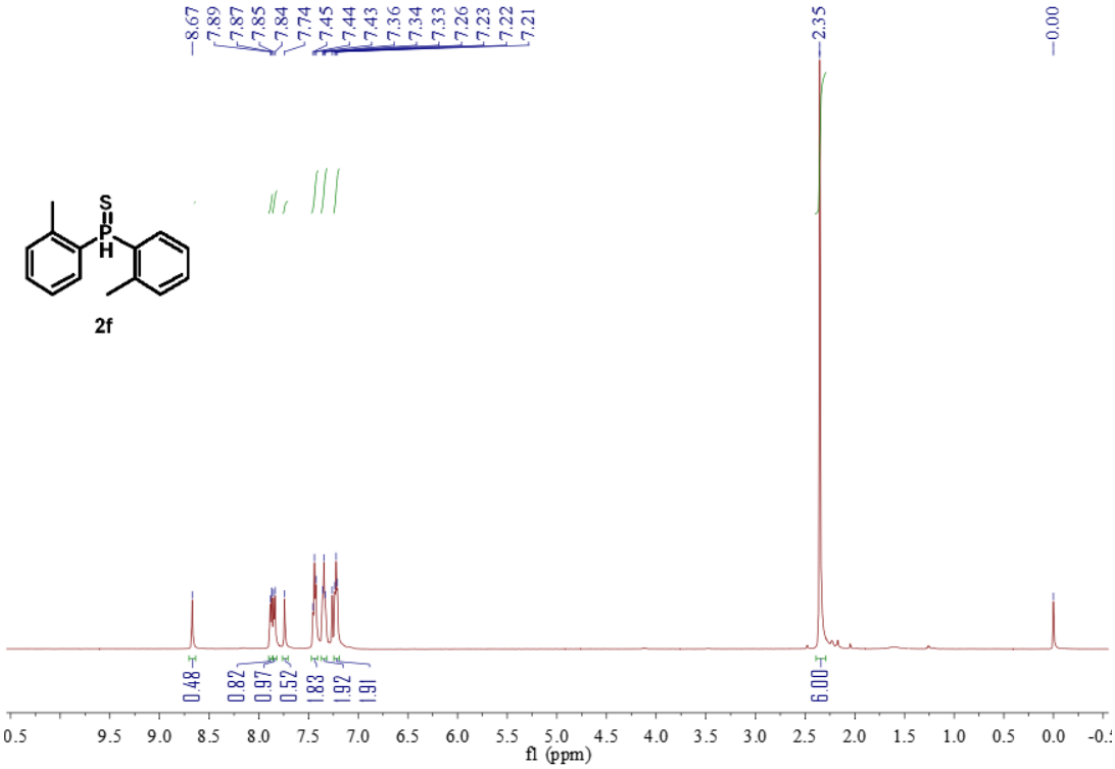
^{13}C NMR of **2e**



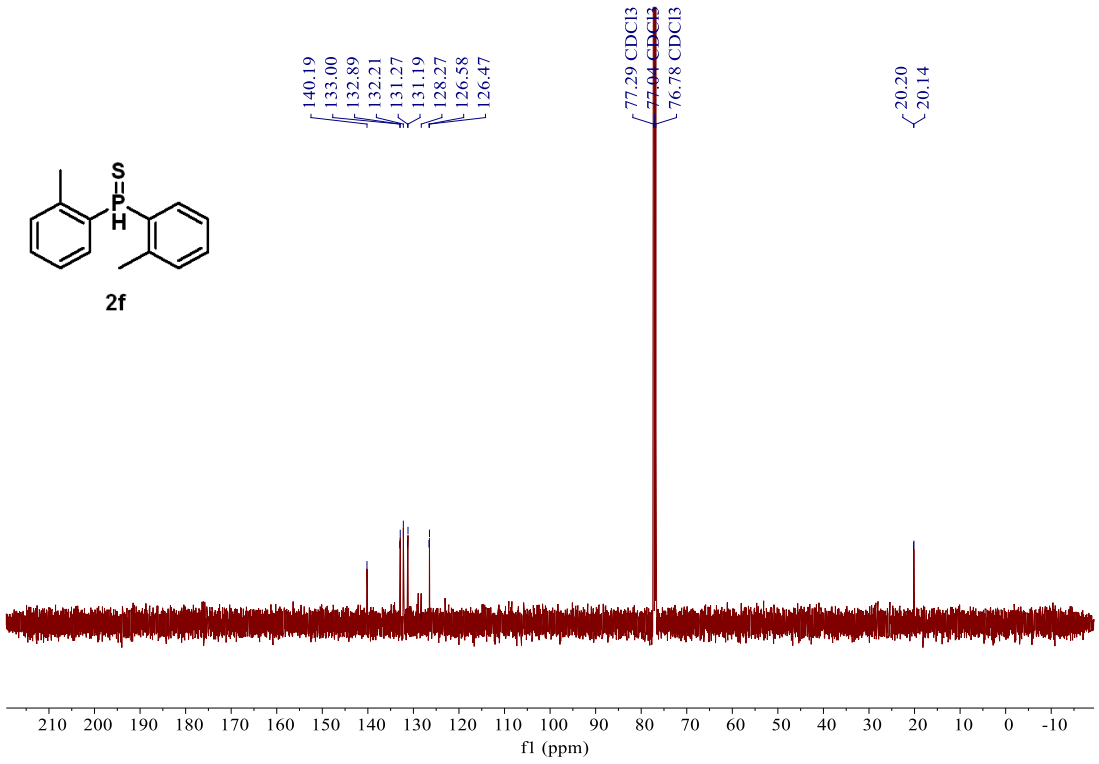
^{31}P NMR of **2e**



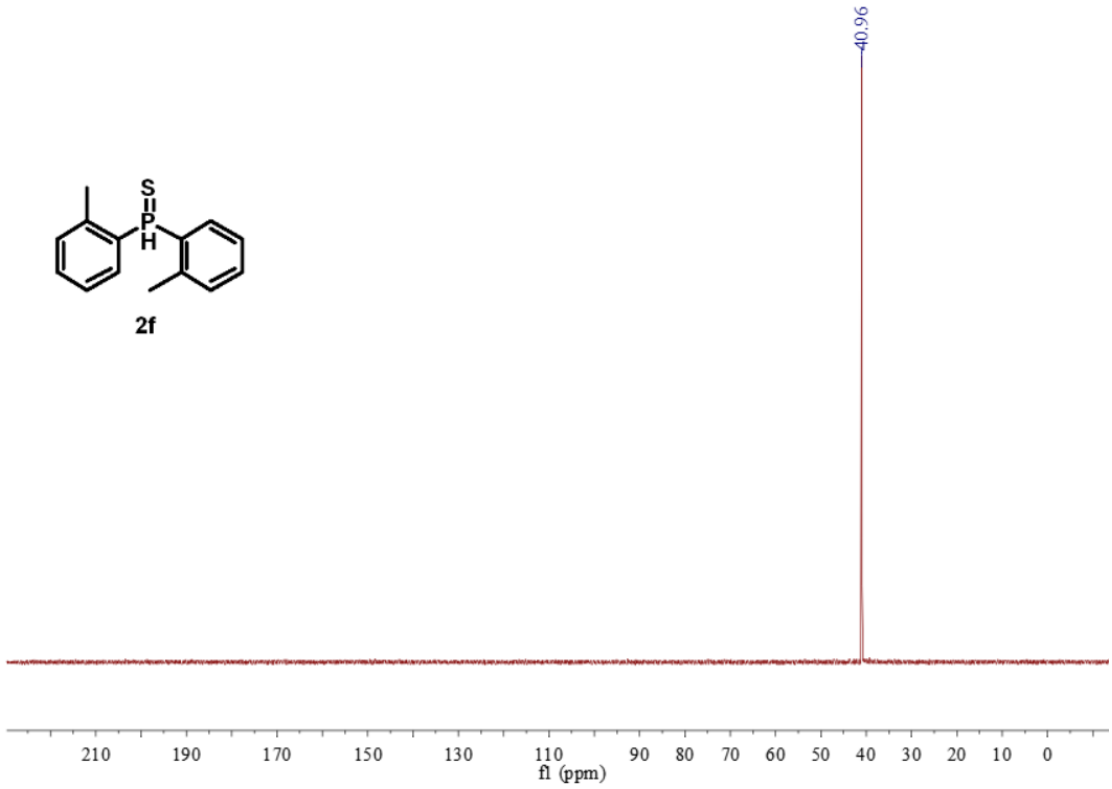
^{19}F NMR of **2e**



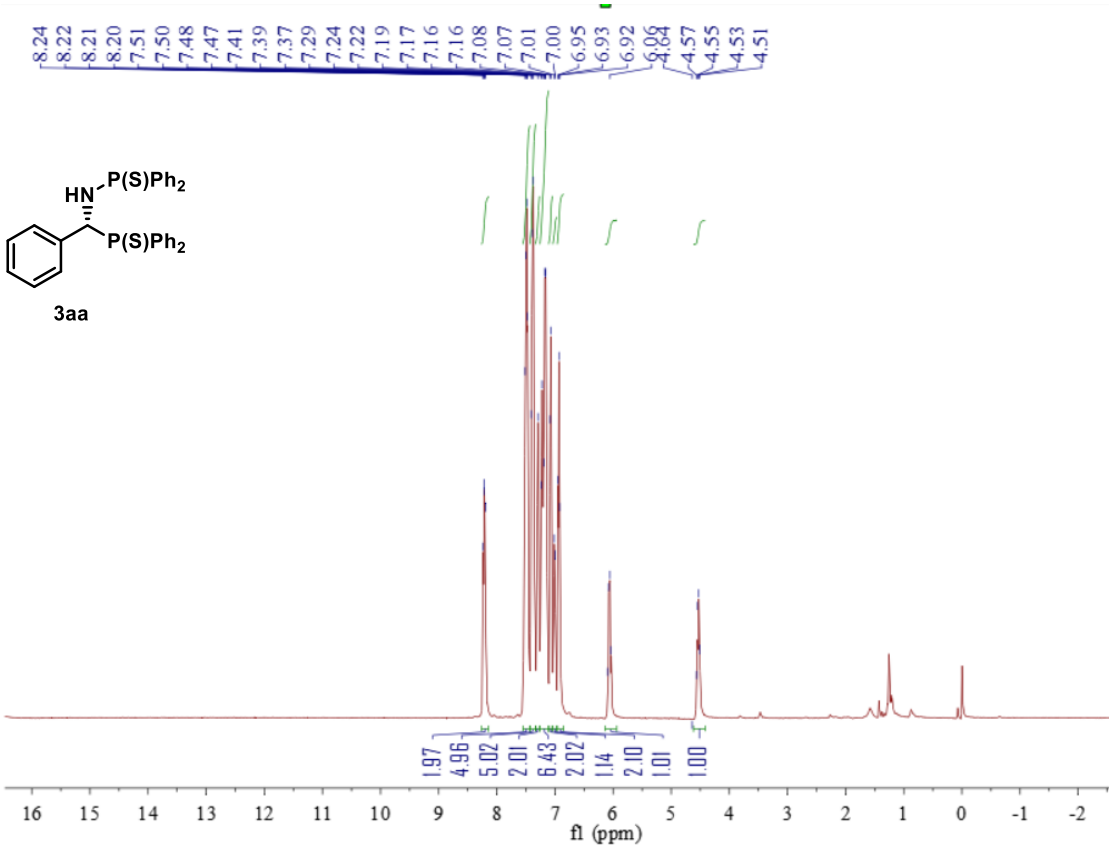
^{1}H NMR of **2f**



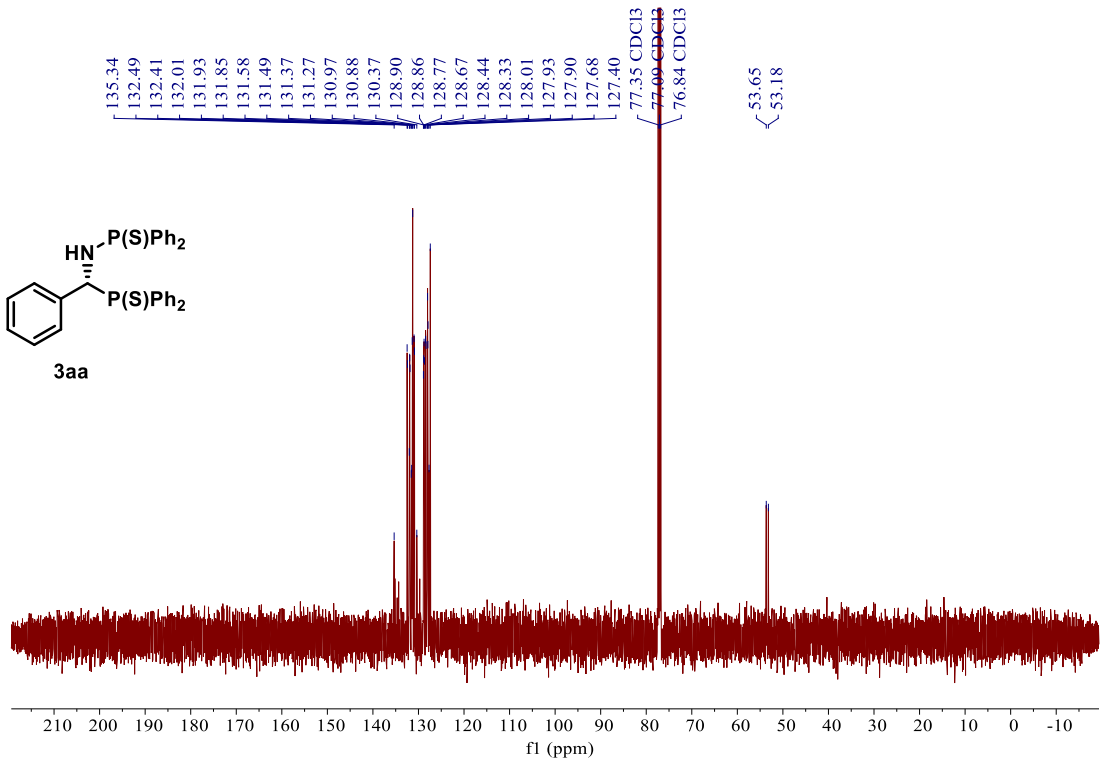
^{13}C NMR of **2f**


40.96
S
P
H
2f
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

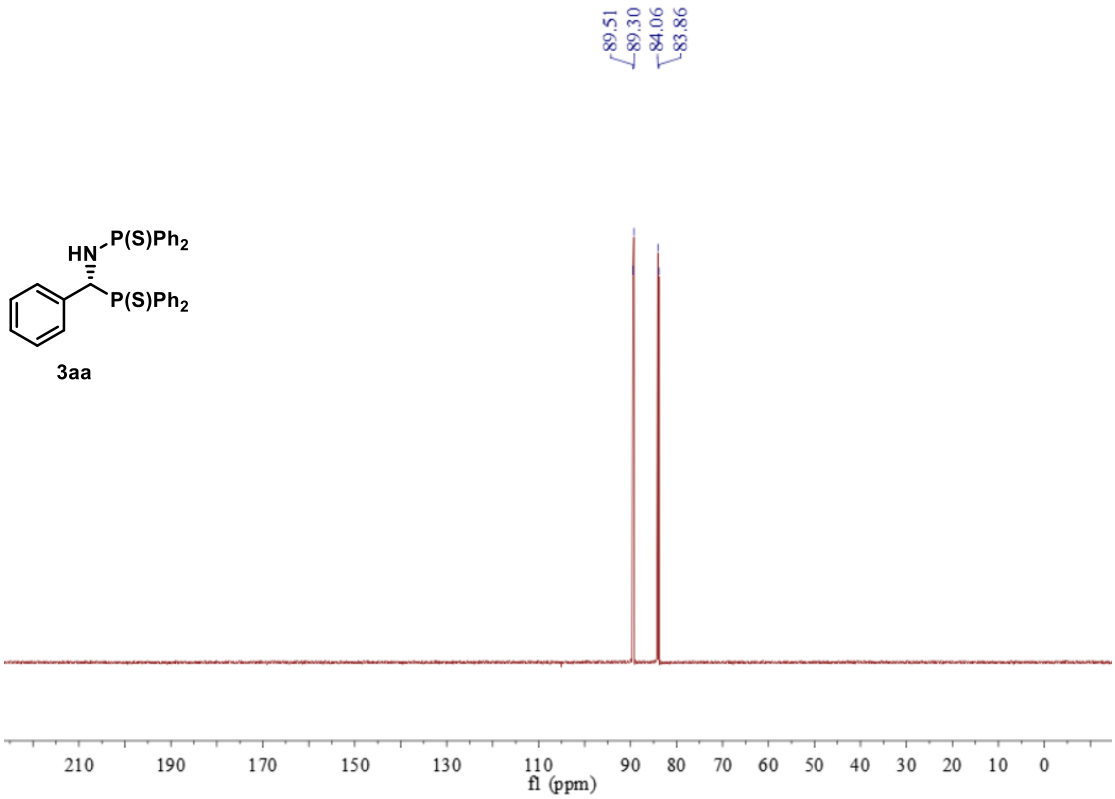
^{31}P NMR of **2f**



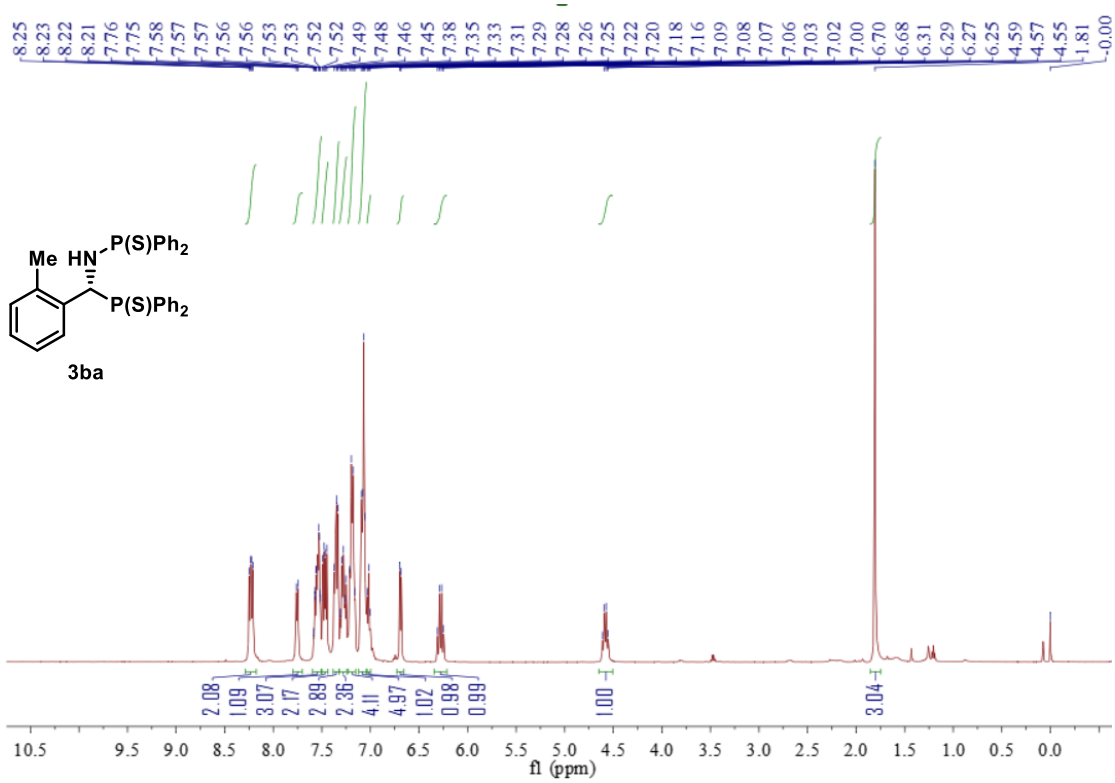
^{1}H NMR of 3aa



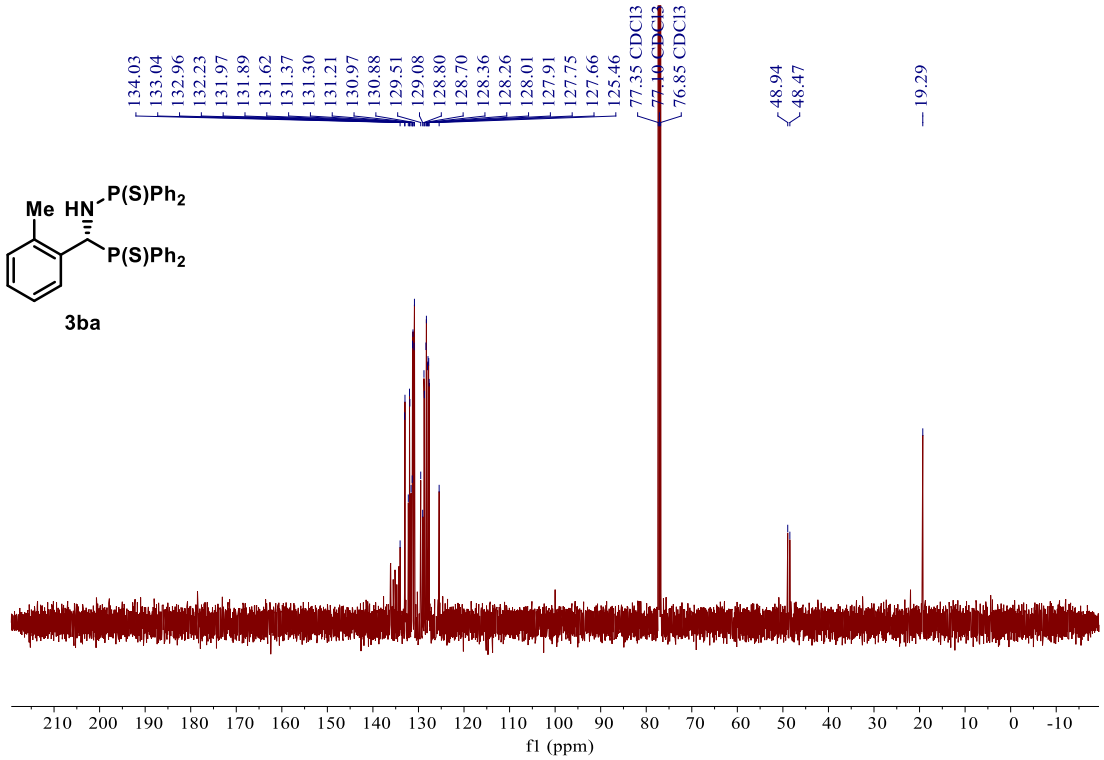
^{13}C NMR of 3aa



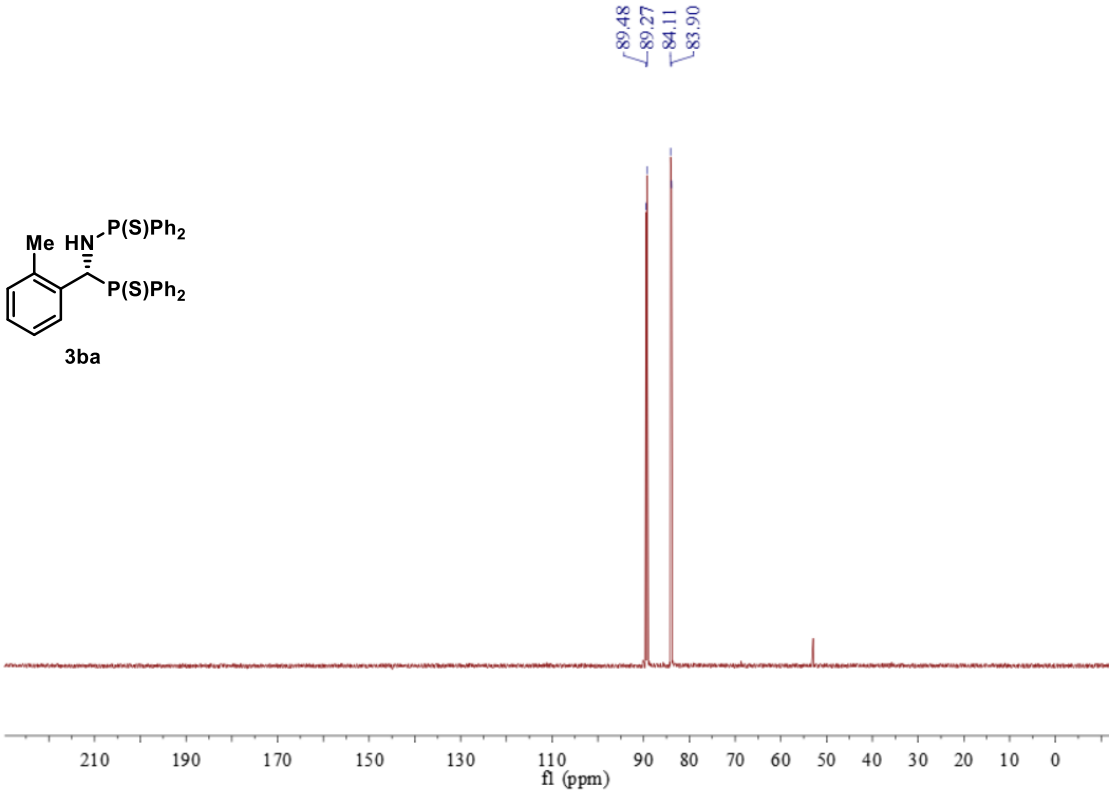
^{31}P NMR of 3aa



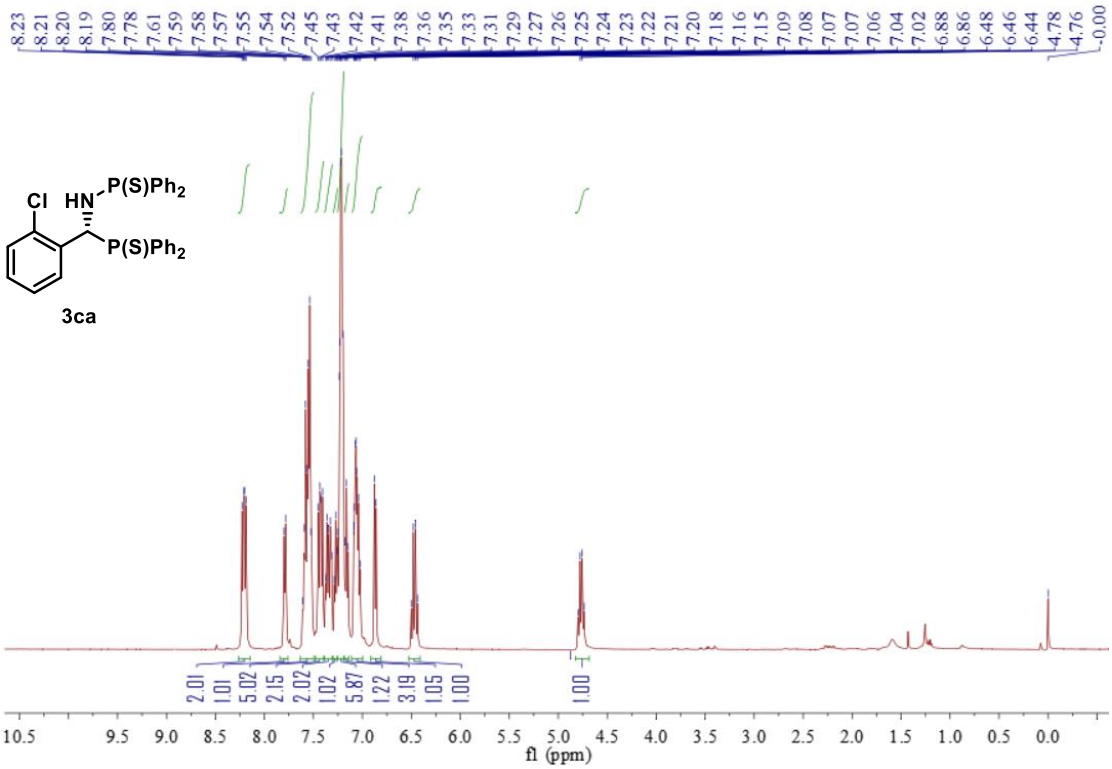
^{1}H NMR of 3ba



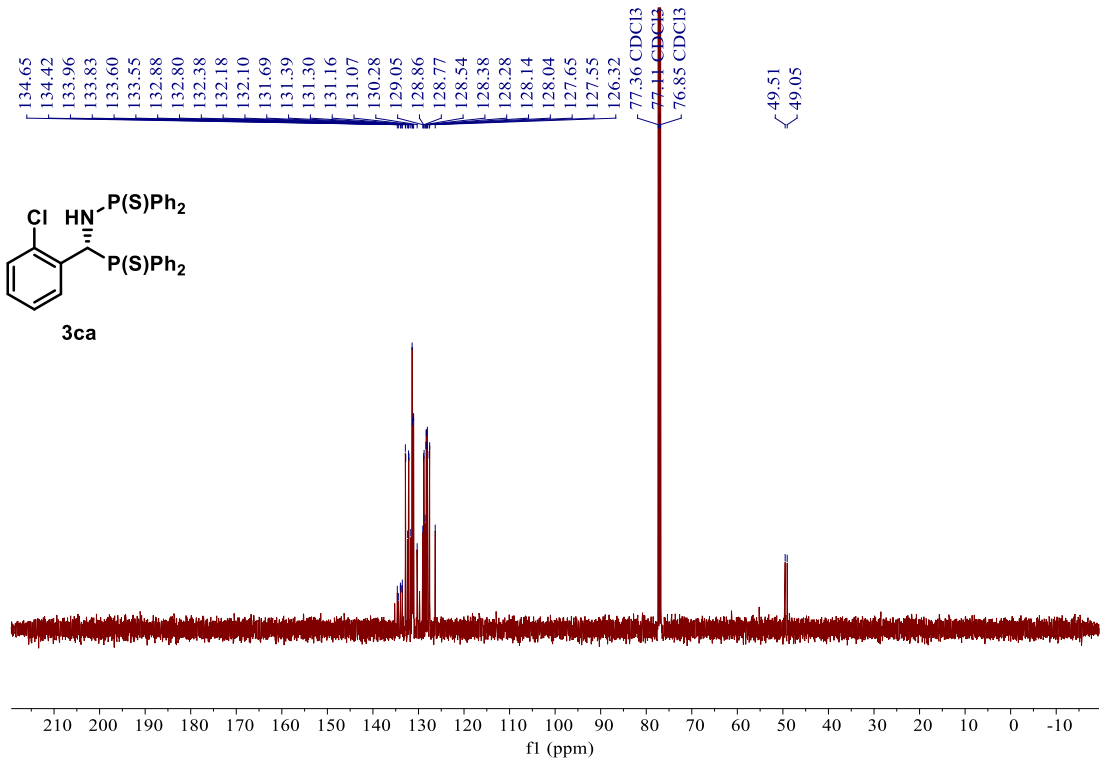
^{13}C NMR of 3ba



^{31}P NMR of 3ba



^{1}H NMR of 3ca



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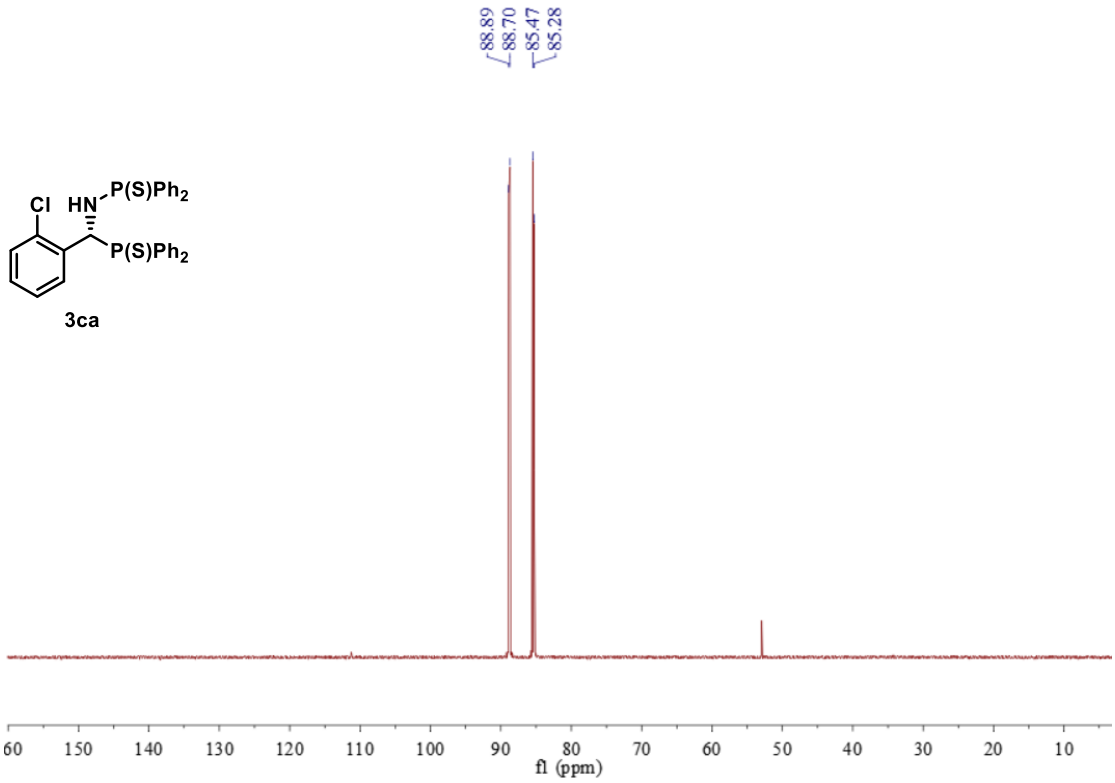

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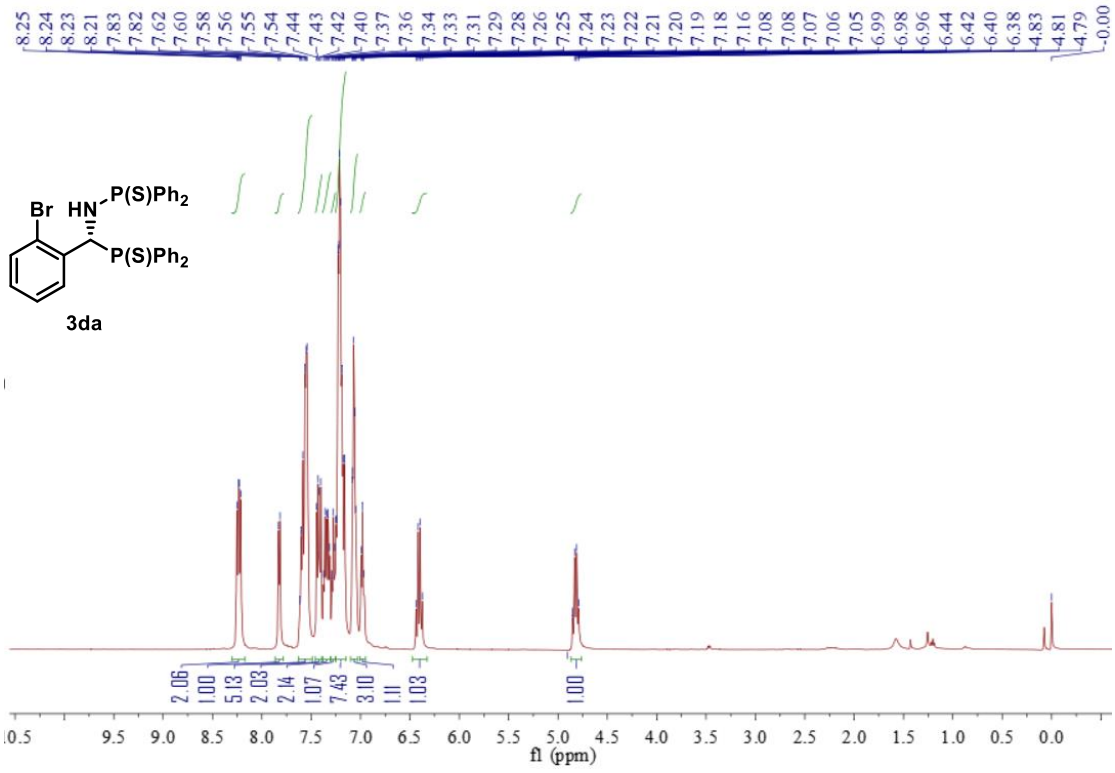

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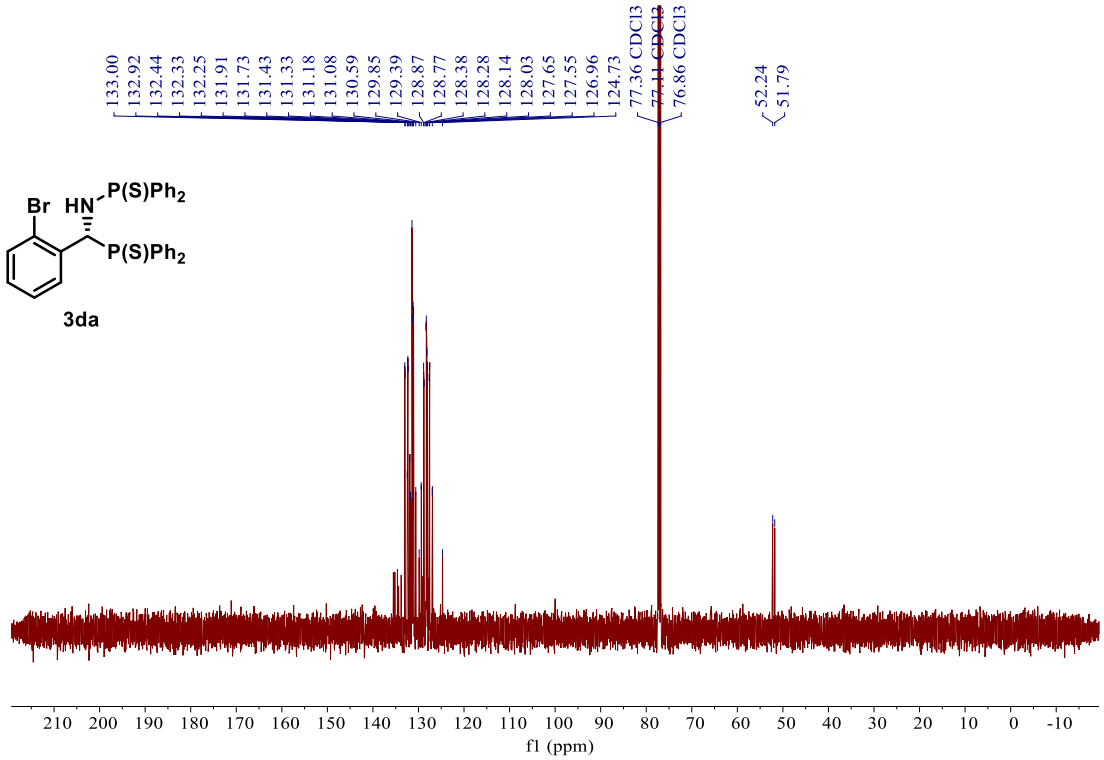
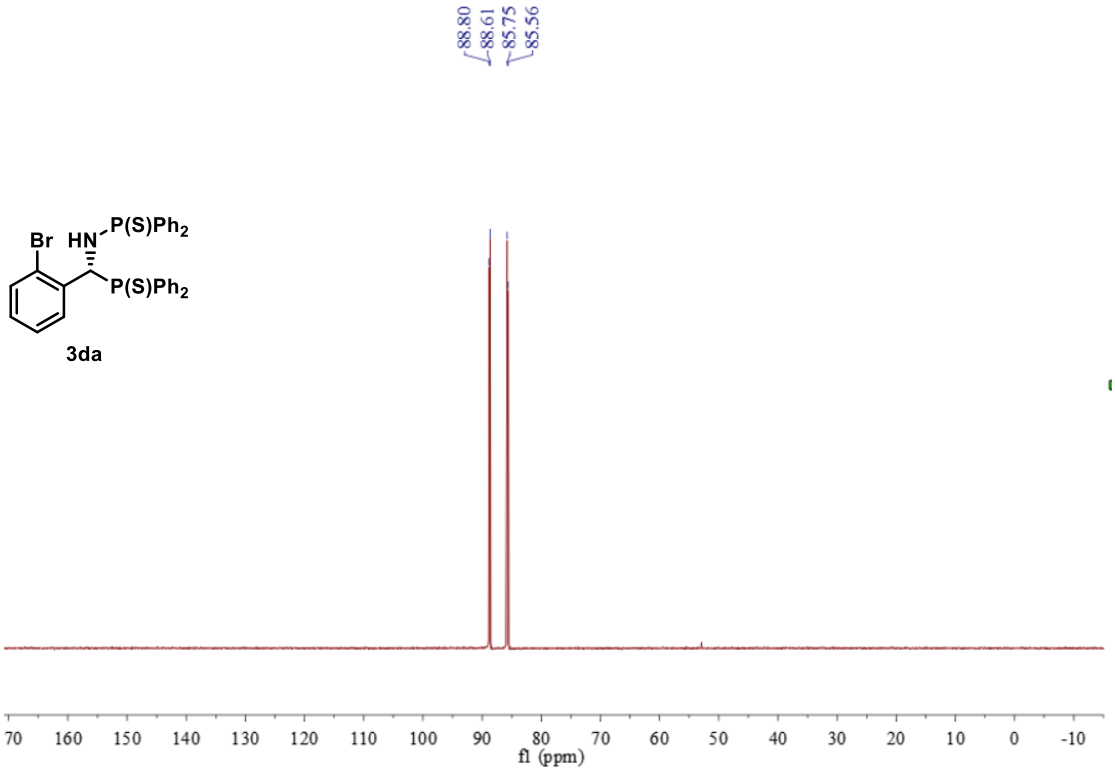


^{13}C NMR of 3da



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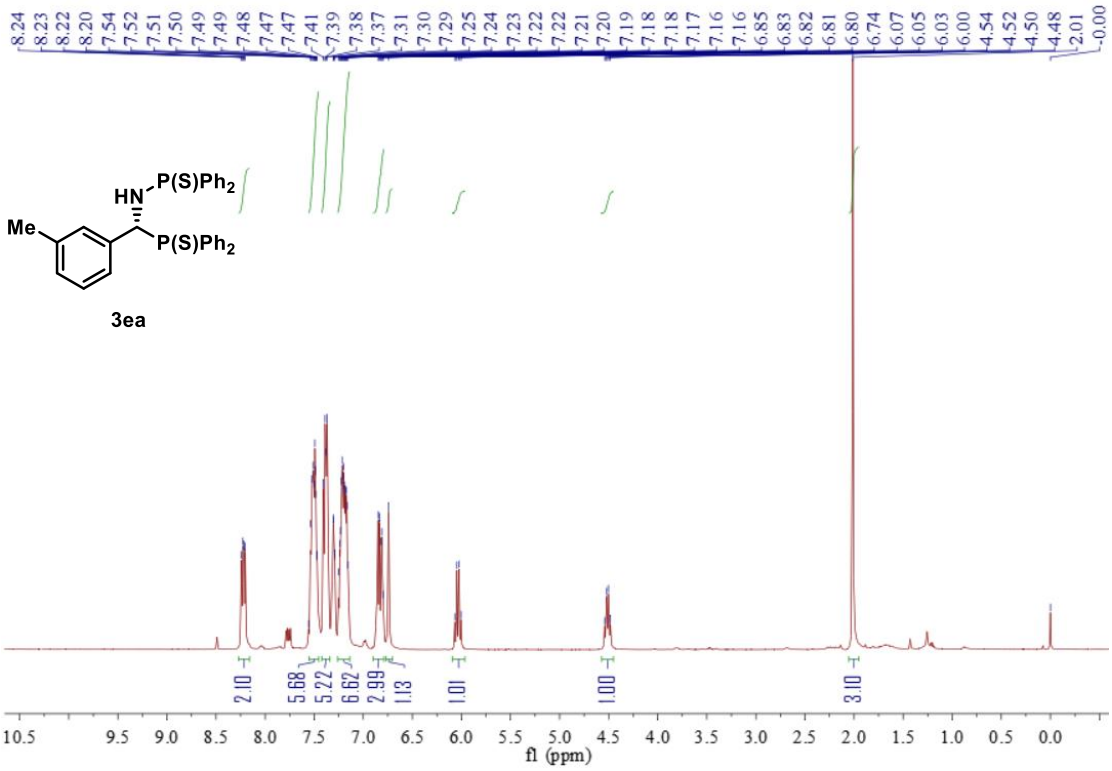

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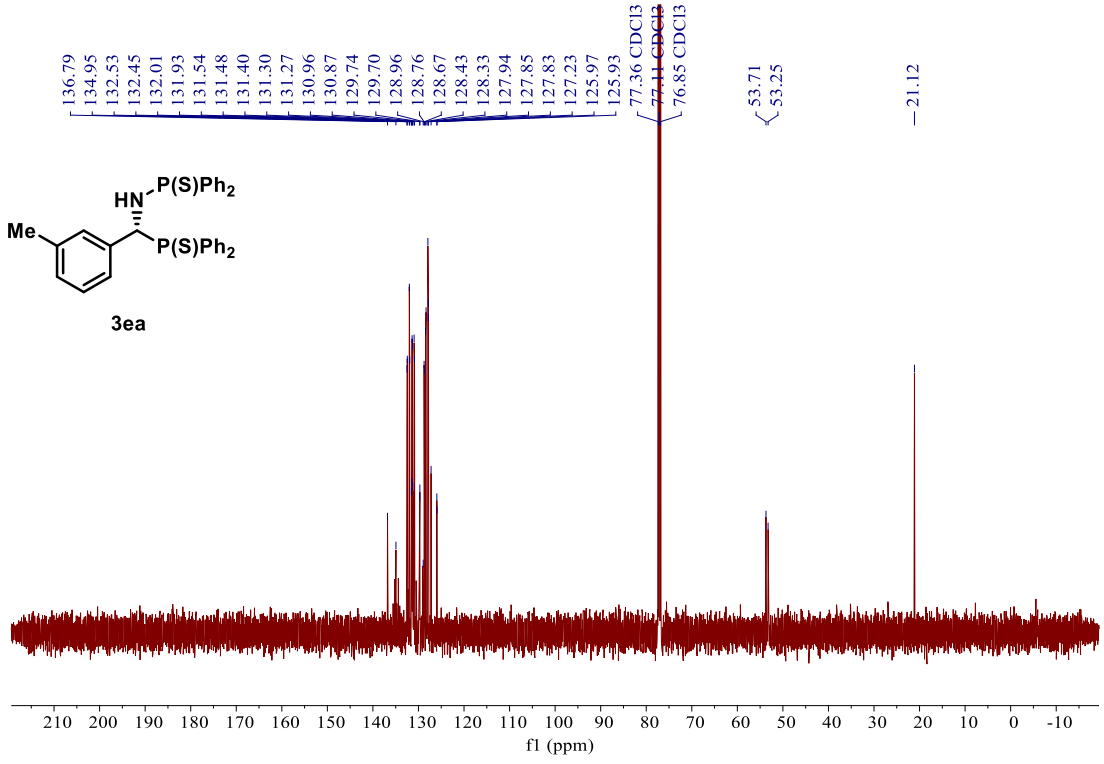
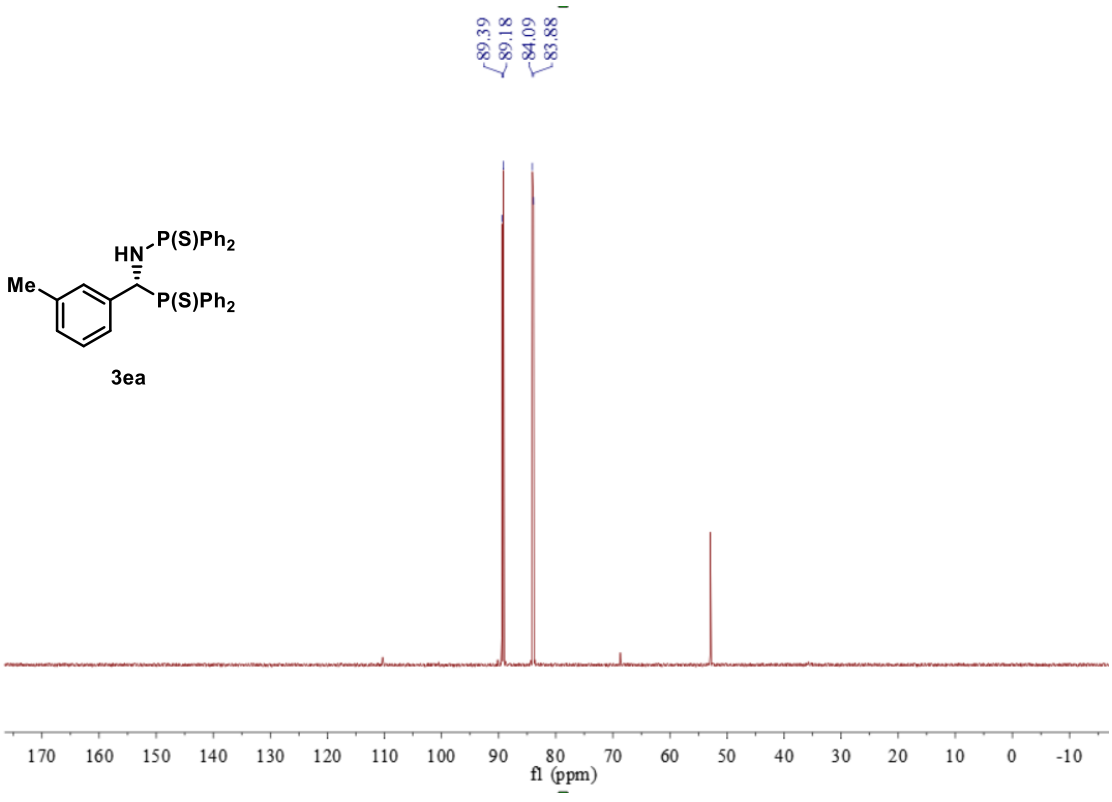
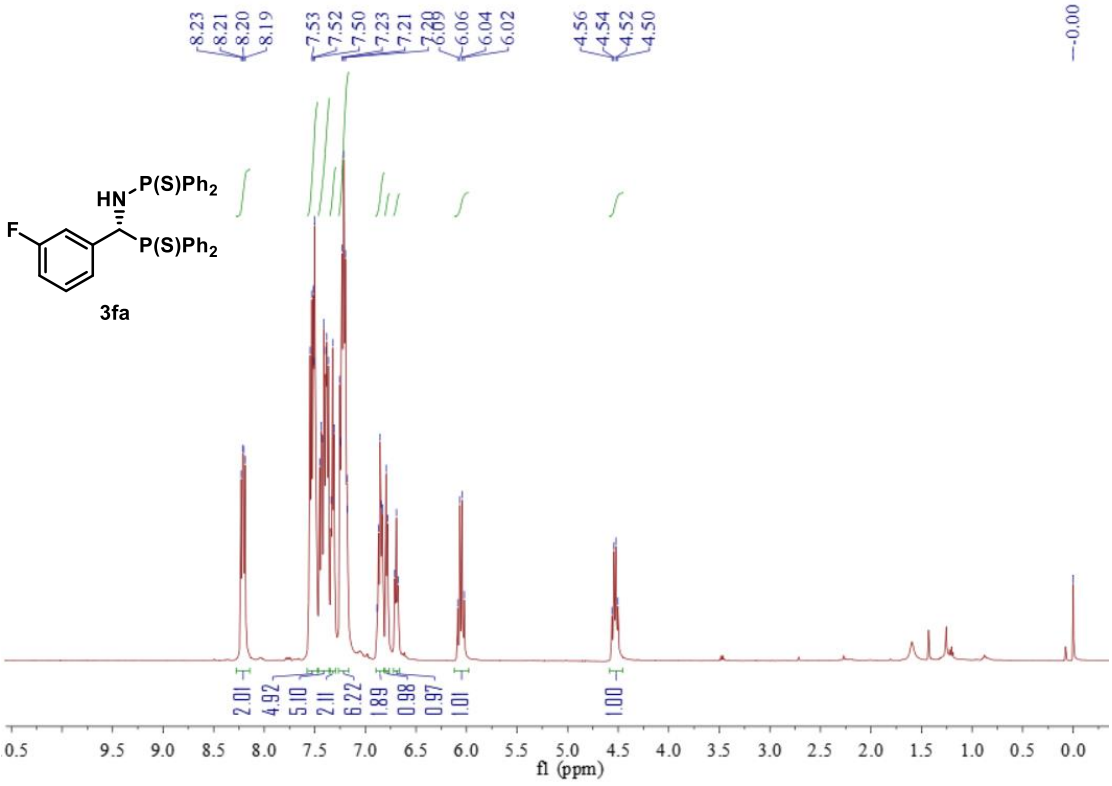


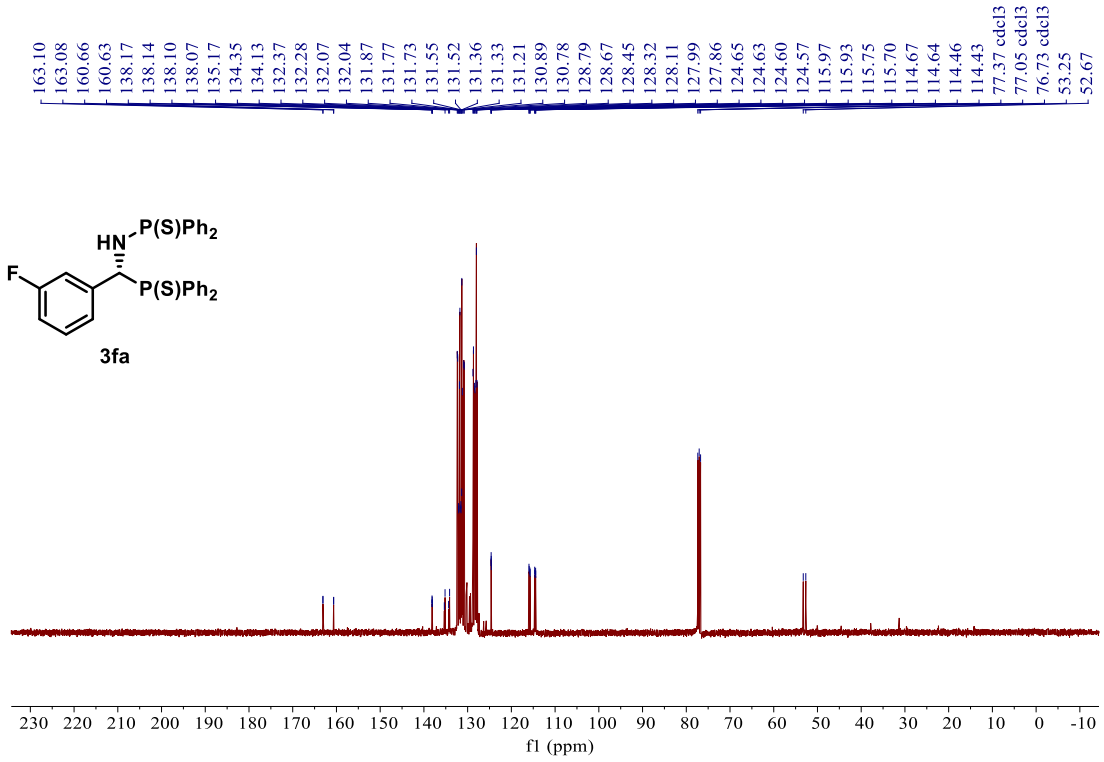
^{13}C NMR of 3ea



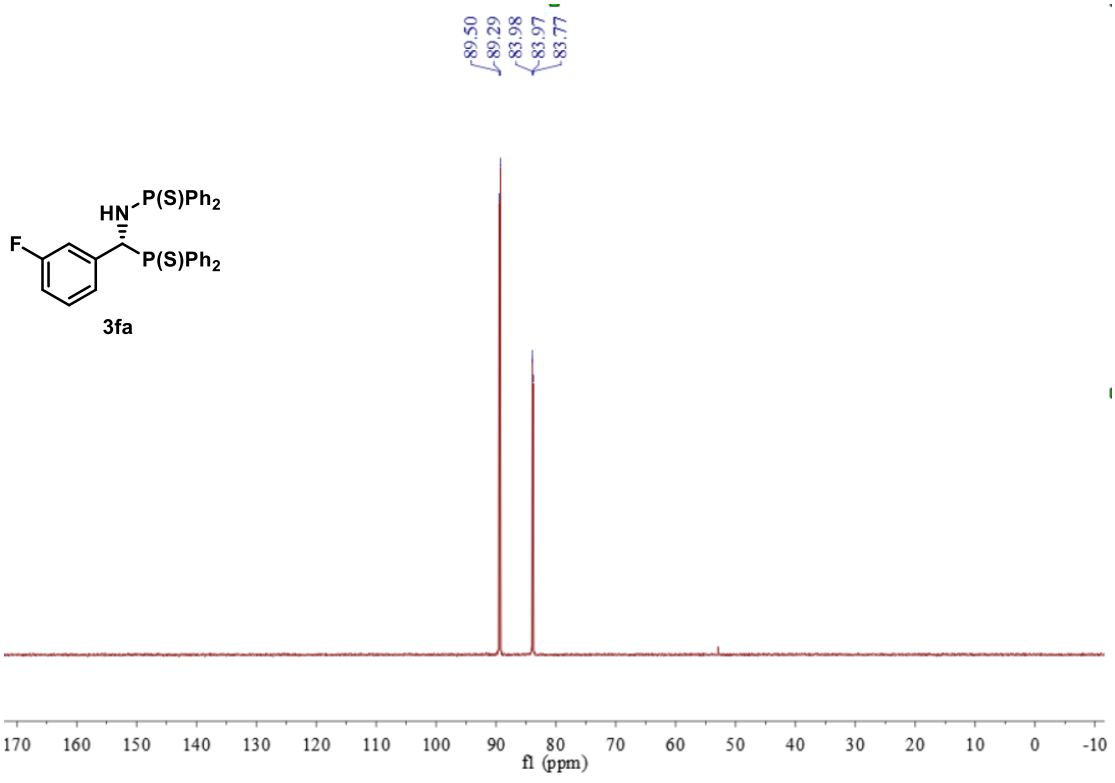
^{31}P NMR of 3ea



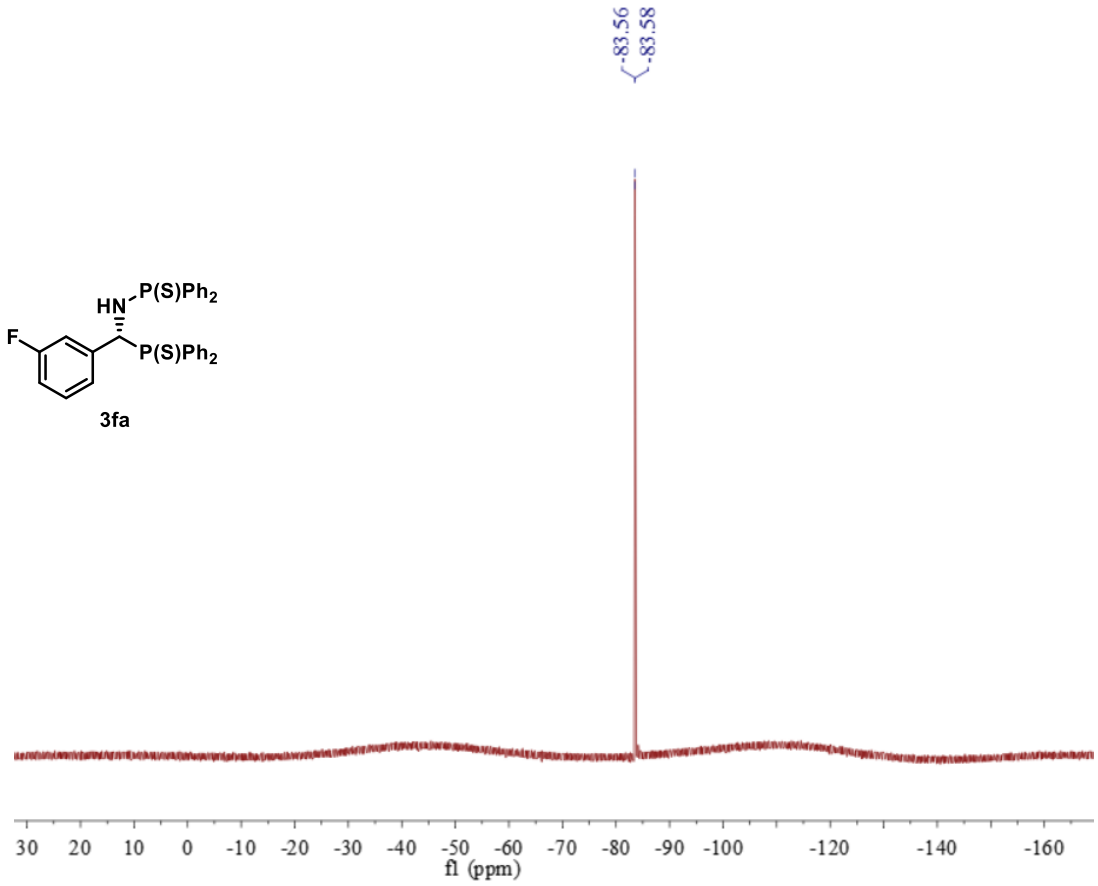
^{1}H NMR of 3fa



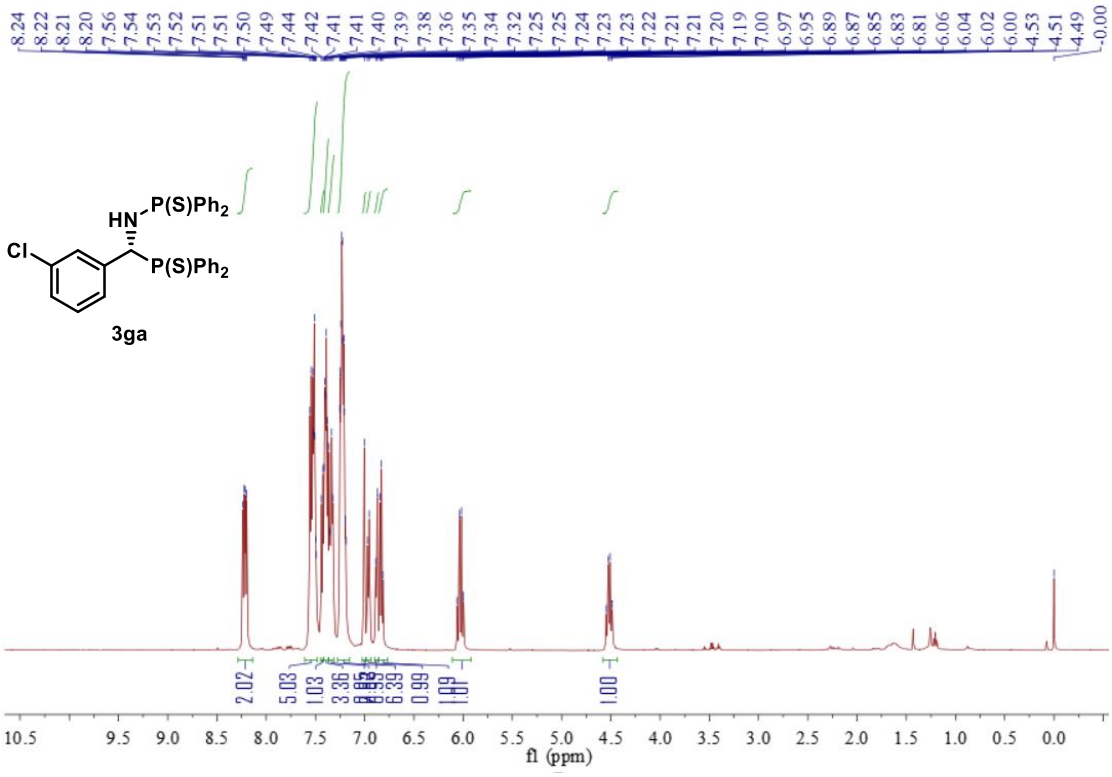
^{13}C NMR of 3fa



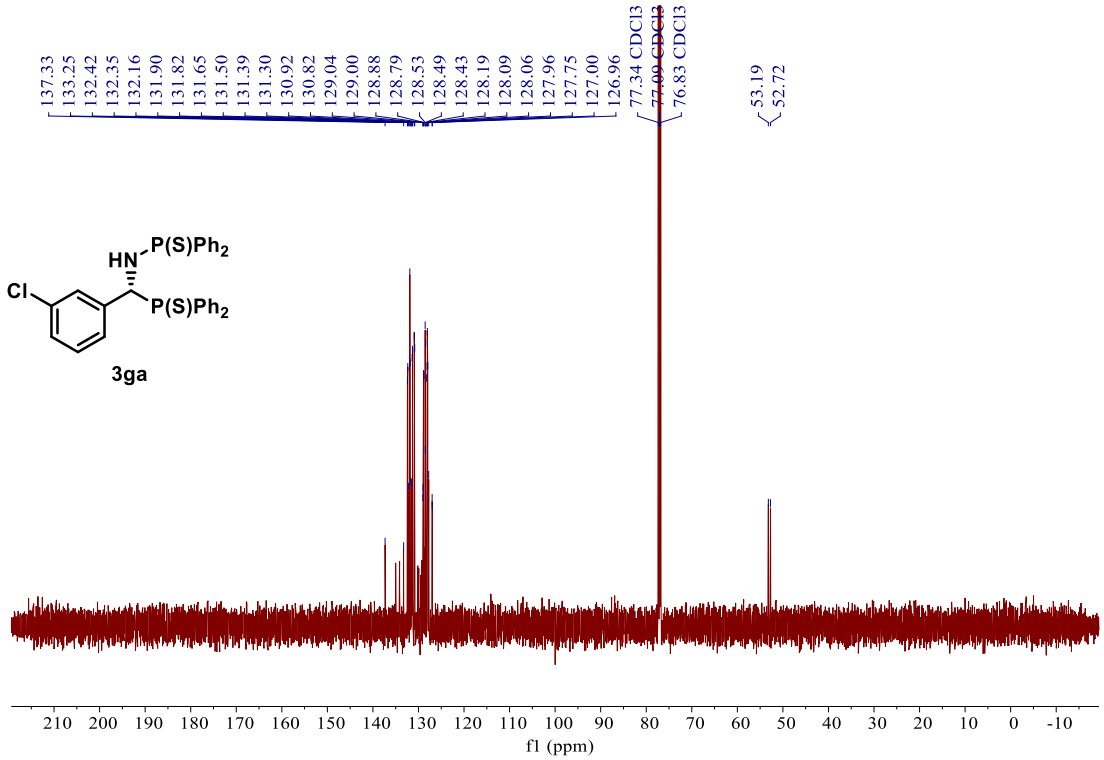
^{31}P NMR of 3fa



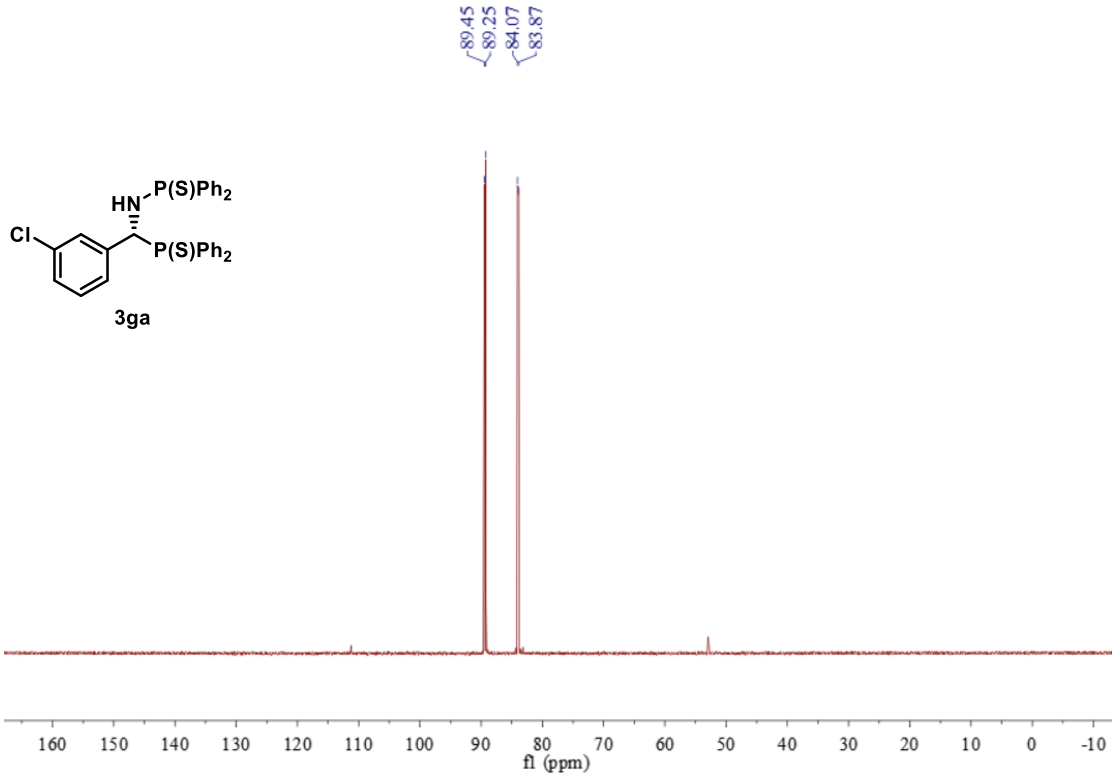
^{19}F NMR of 3fa



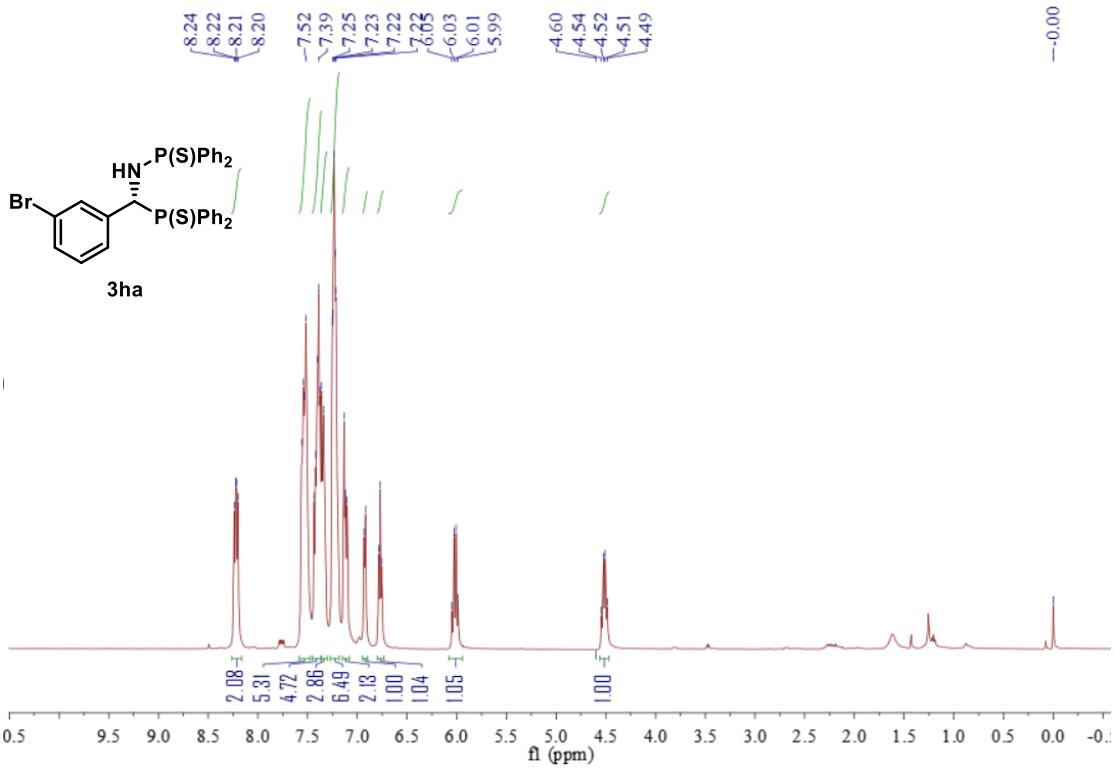
^{1}H NMR of 3ga



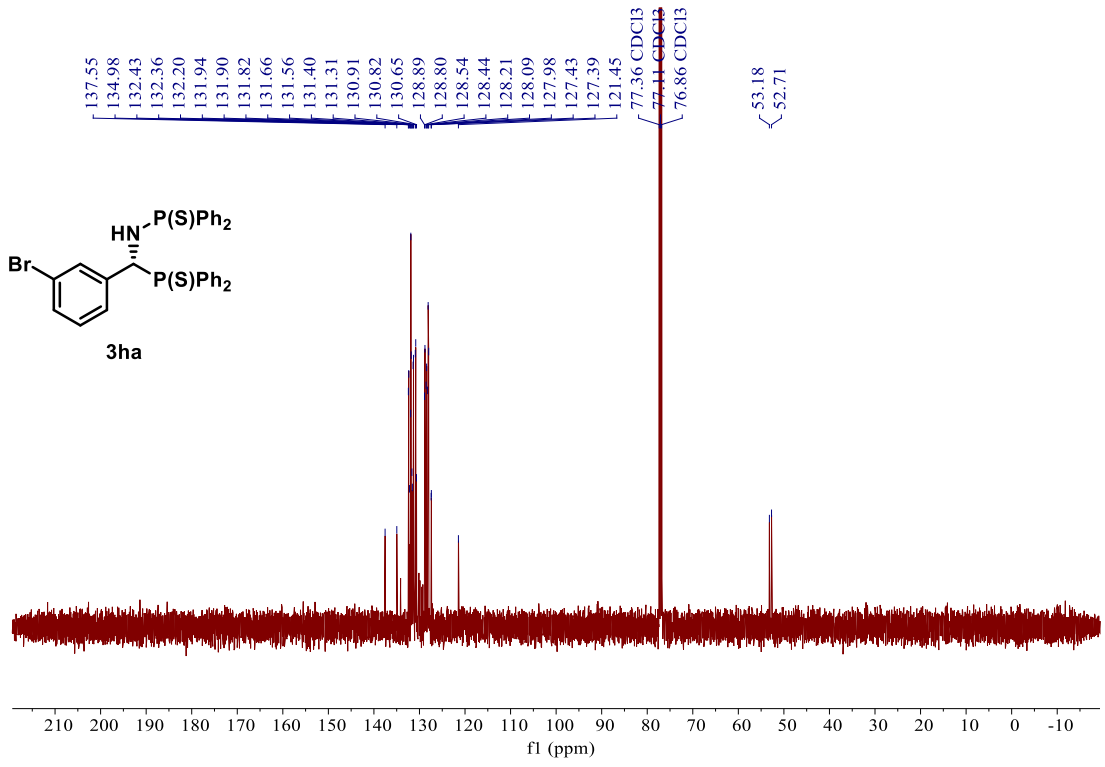
^{13}CNMR of 3ga



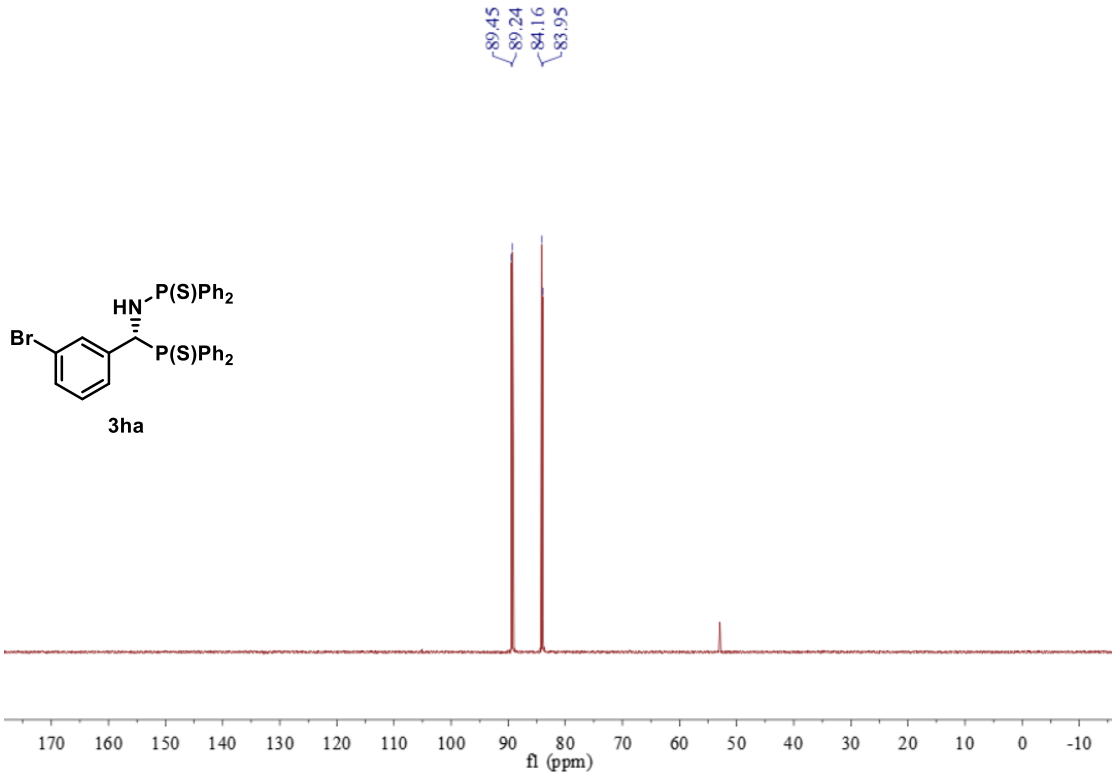
^{31}P NMR of 3ga



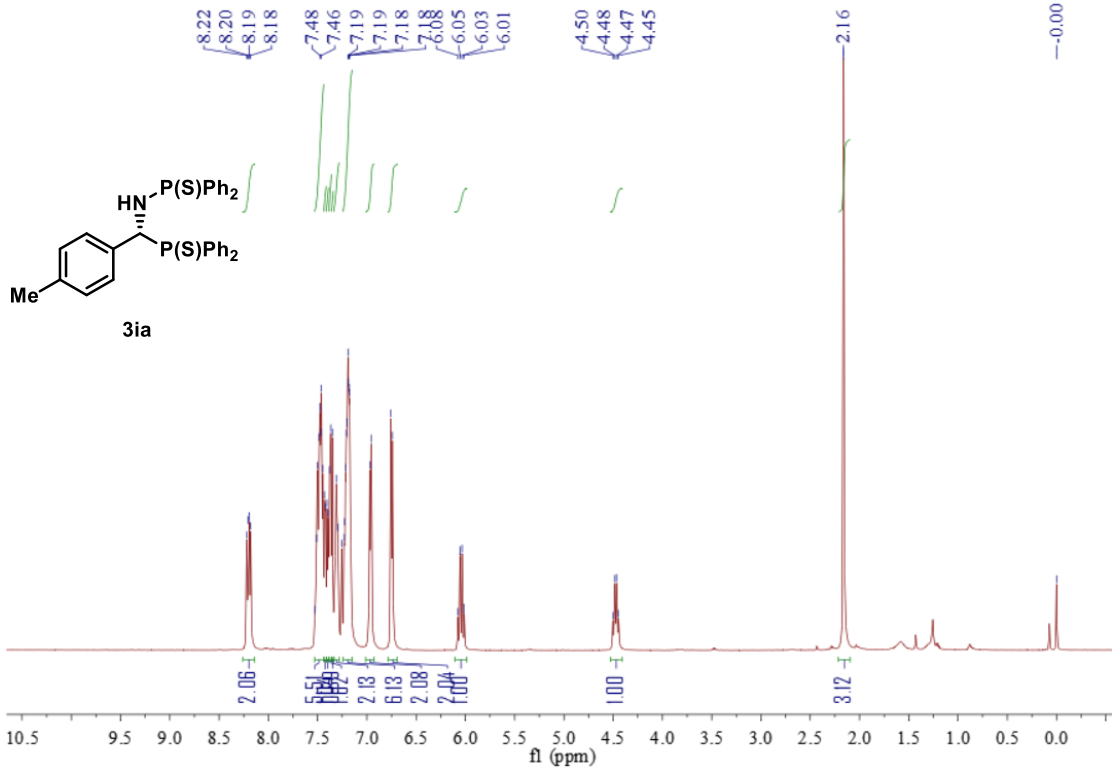
^{1}H NMR of 3ha



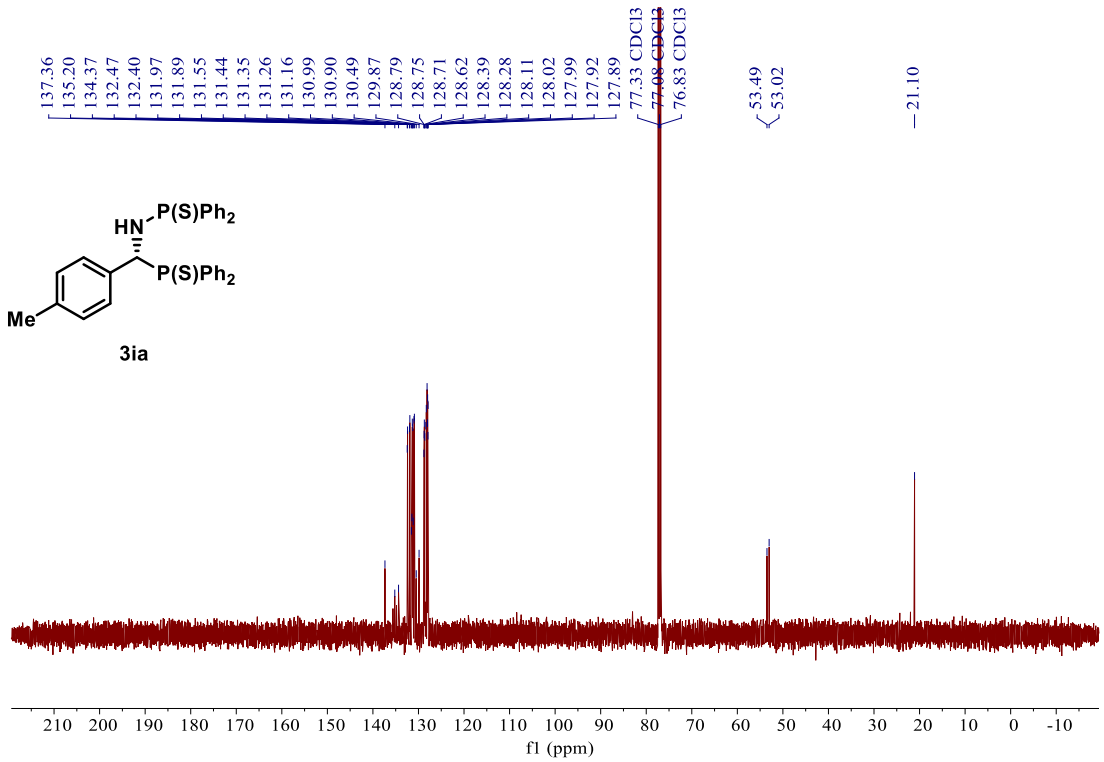
^{13}C NMR of 3ha



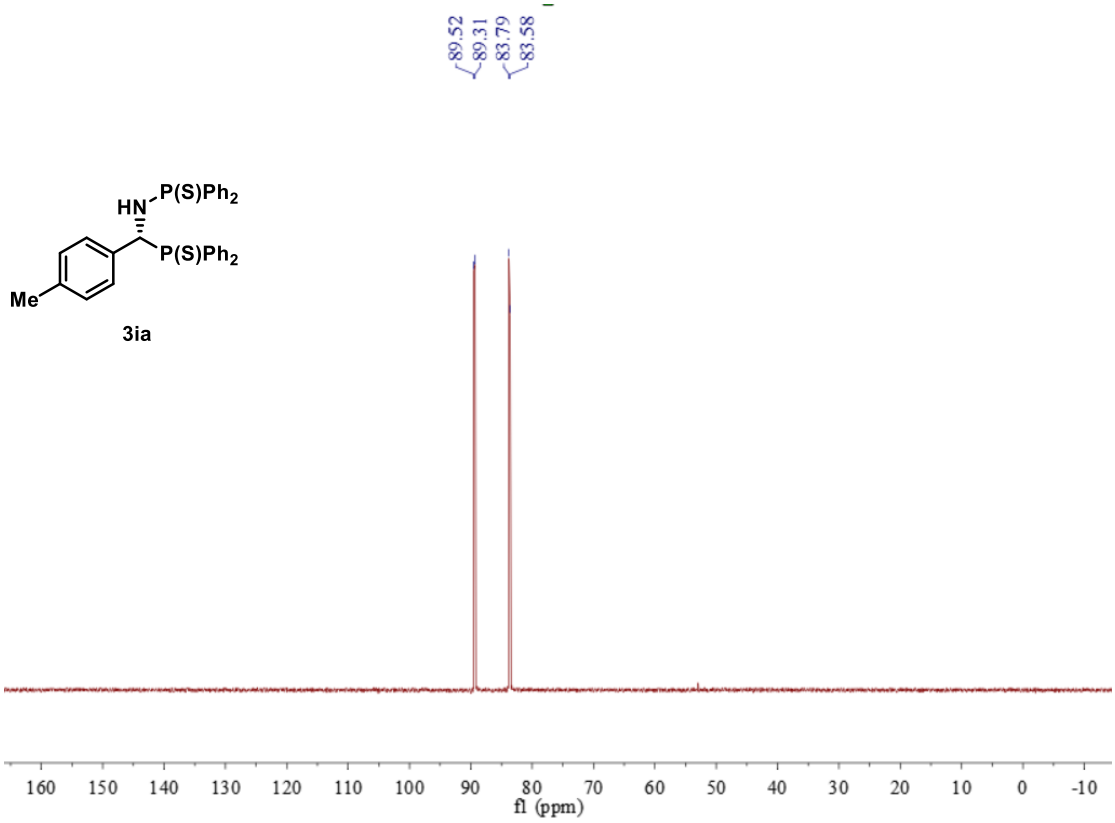
^{31}P NMR of 3ha



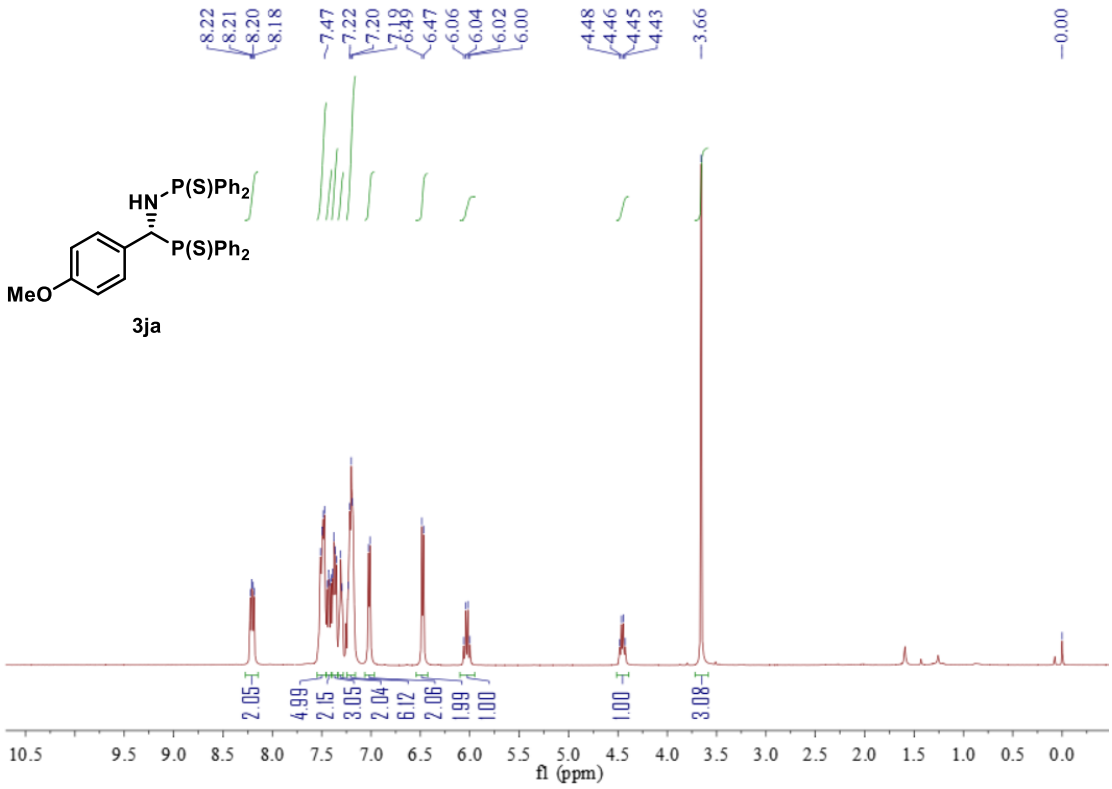
^{1}H NMR of 3ia



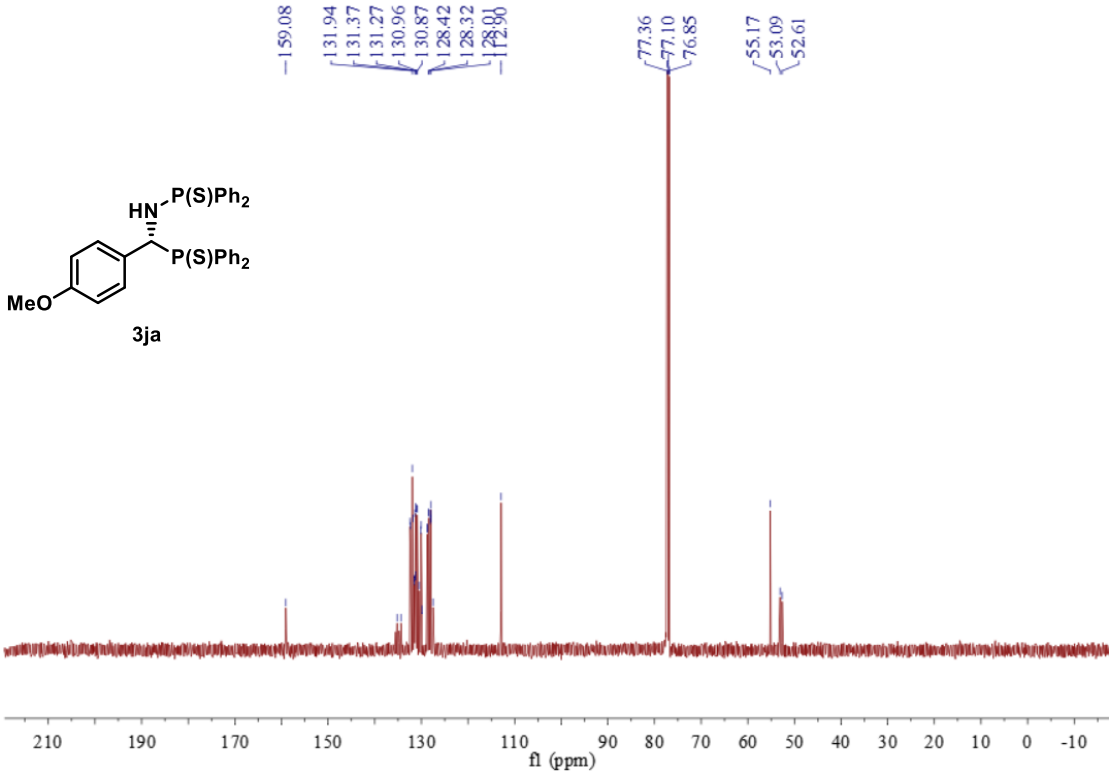
^{13}CNMR of 3ia



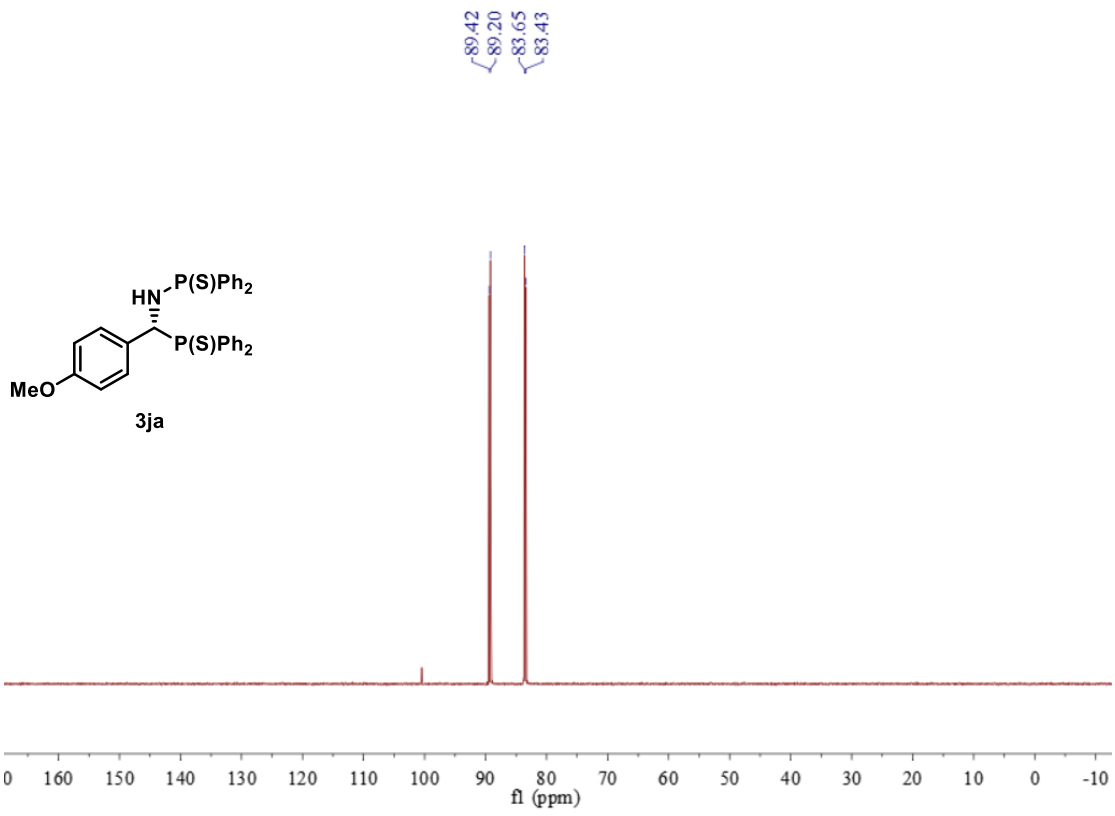
^{31}P NMR of 3ia



^{1}H NMR of 3ja



^{13}C NMR of 3ja



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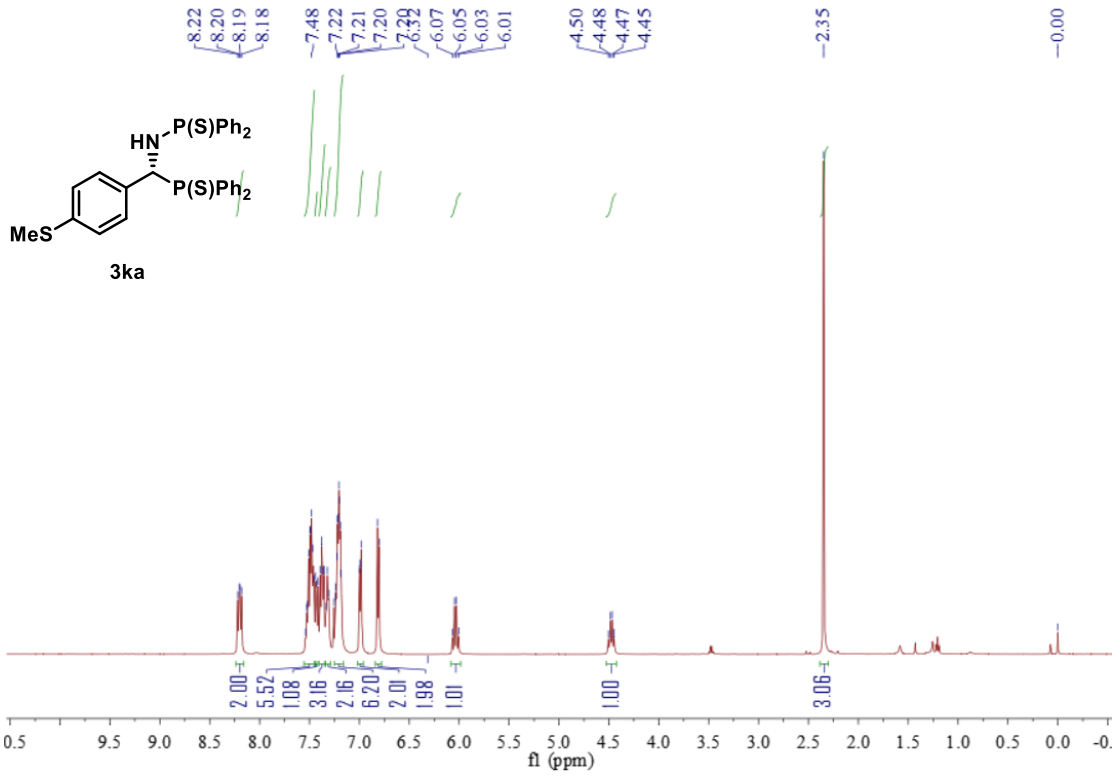
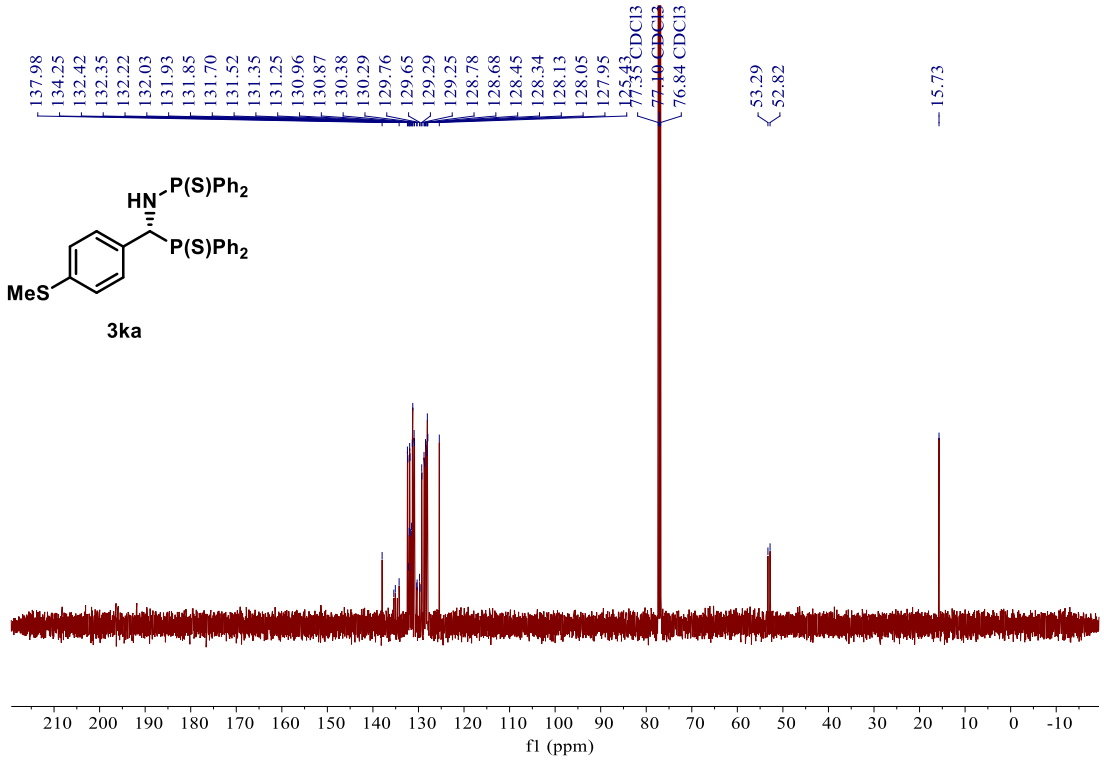
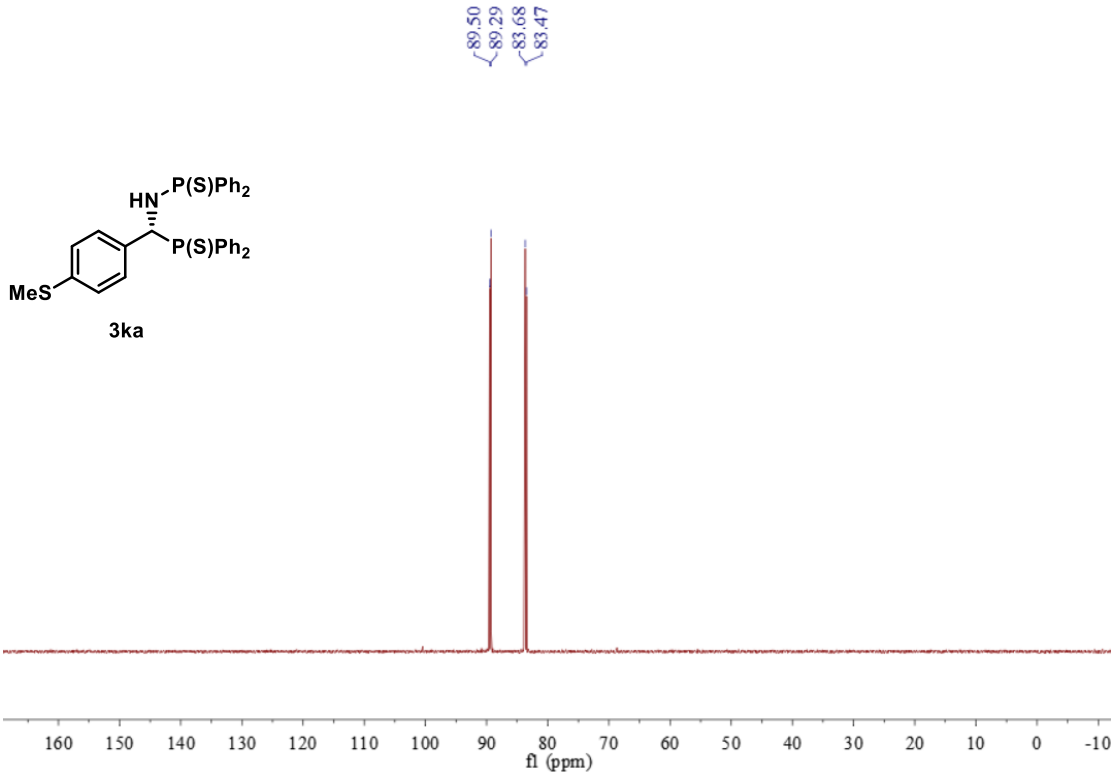


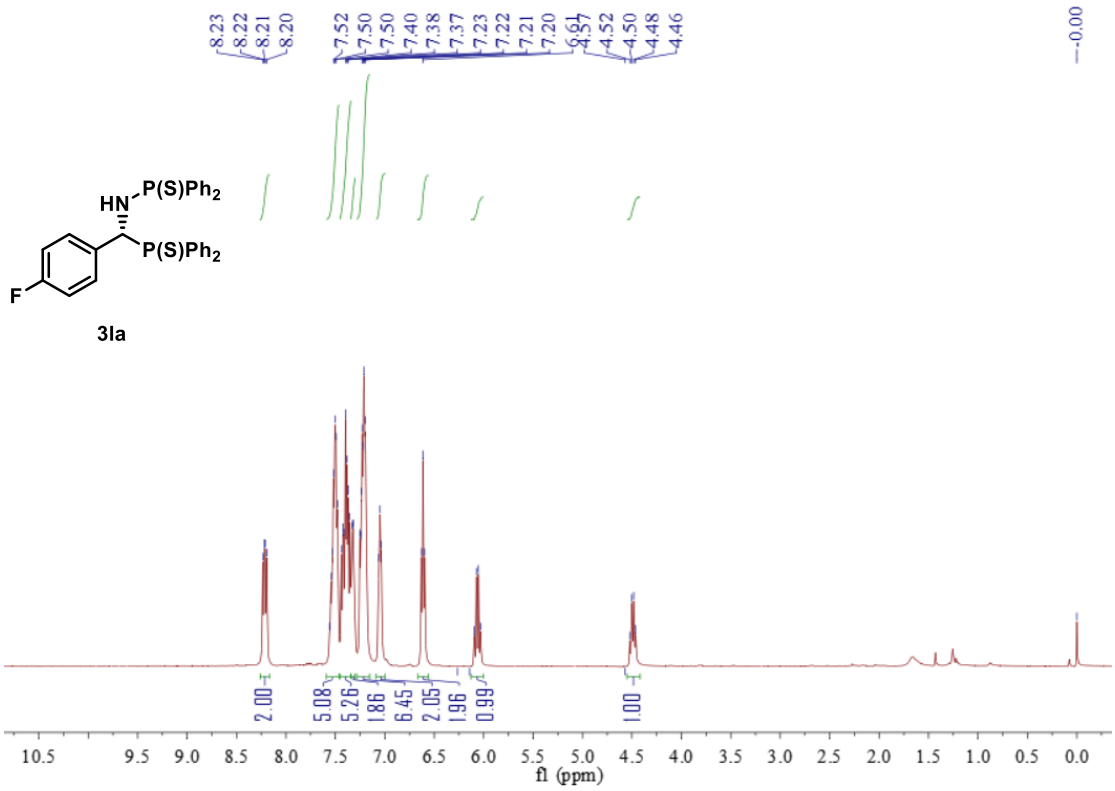
^{1}H NMR of 3ka



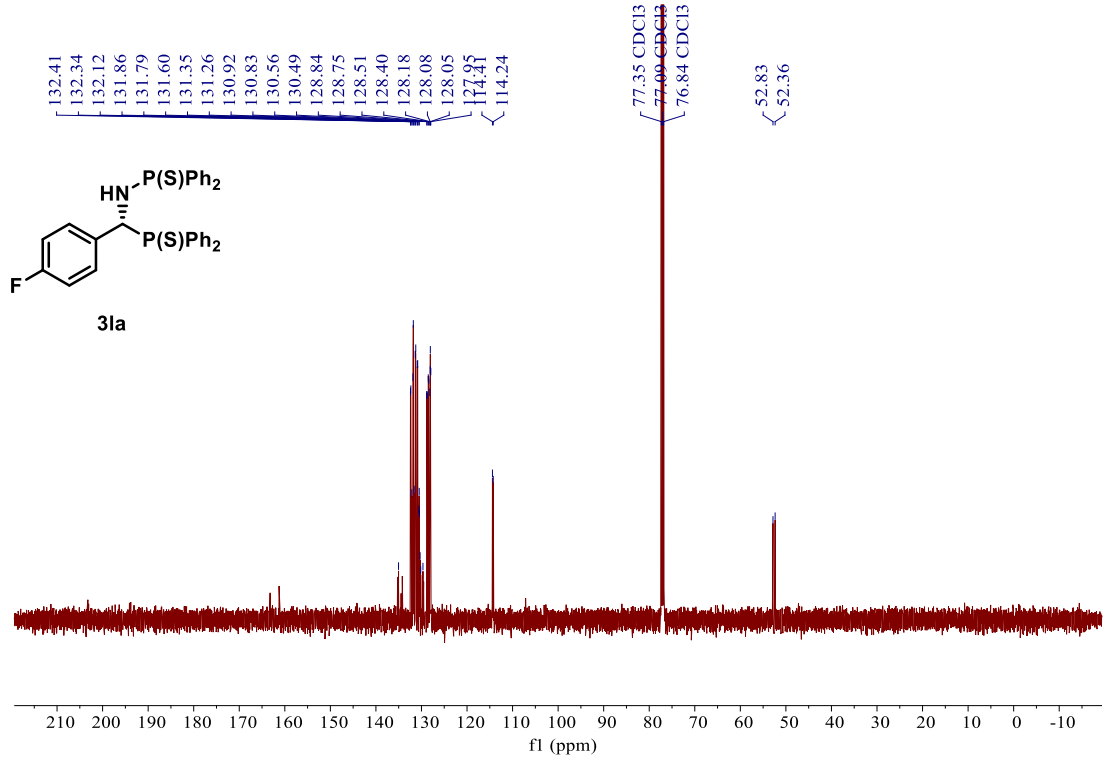
^{13}C NMR of 3ka



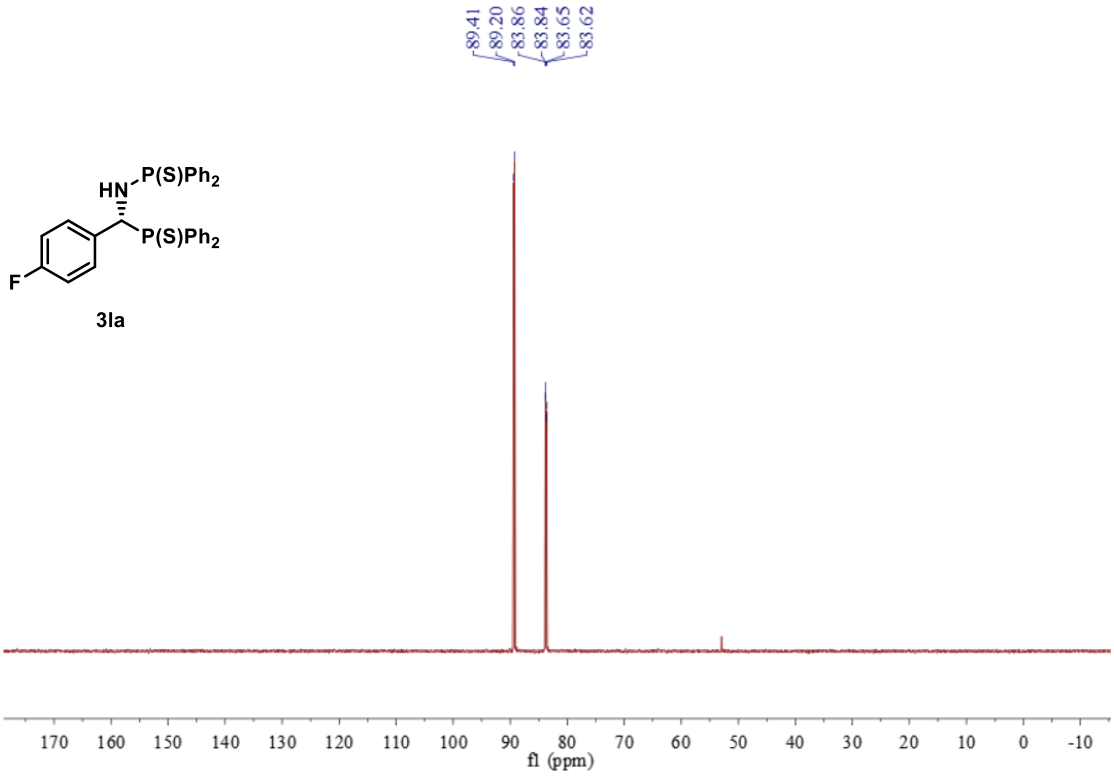
^{31}P NMR of 3ka



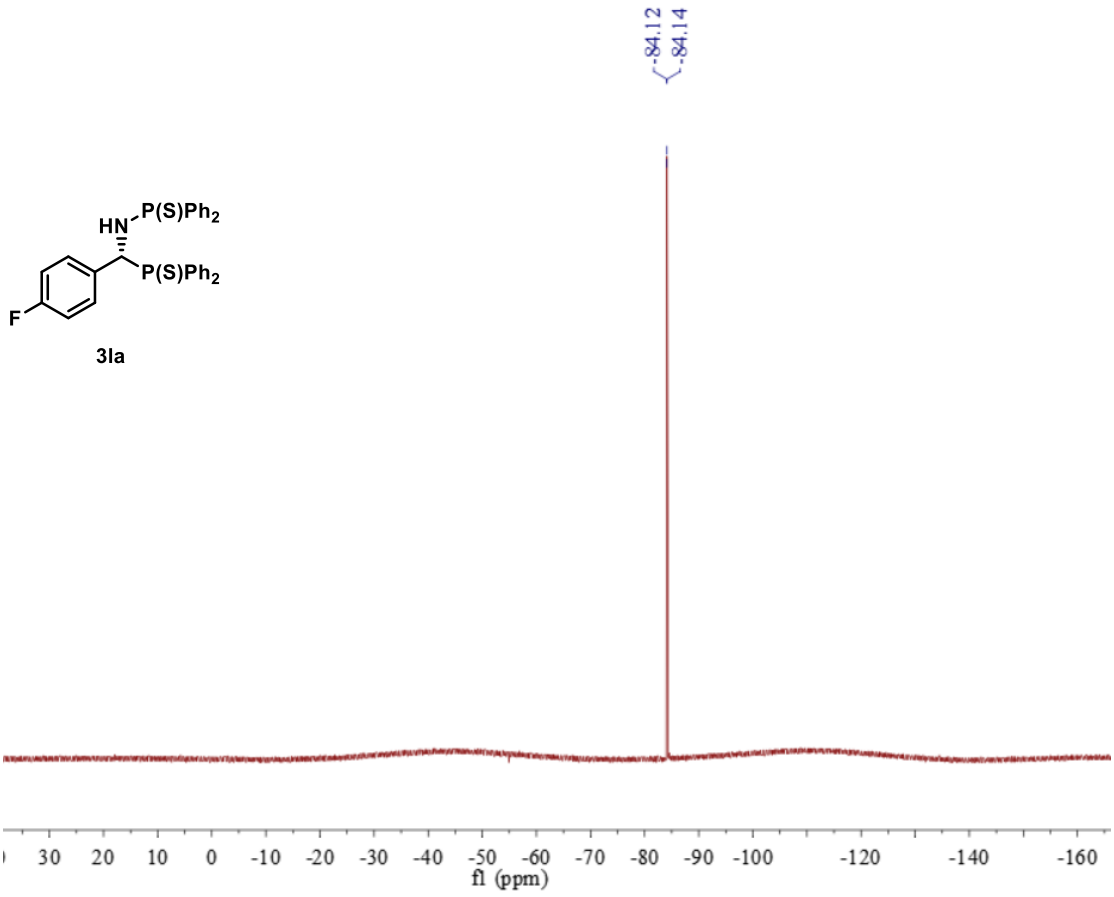
^{1}H NMR of 3la



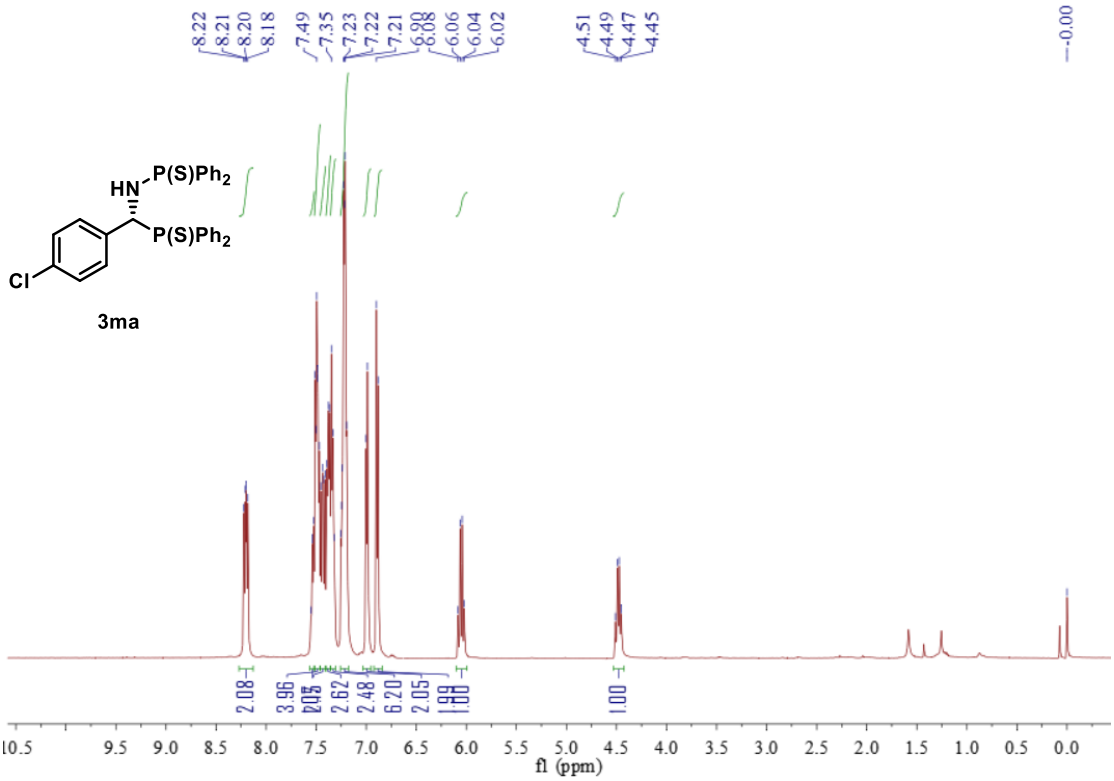
^{13}C NMR of 3la



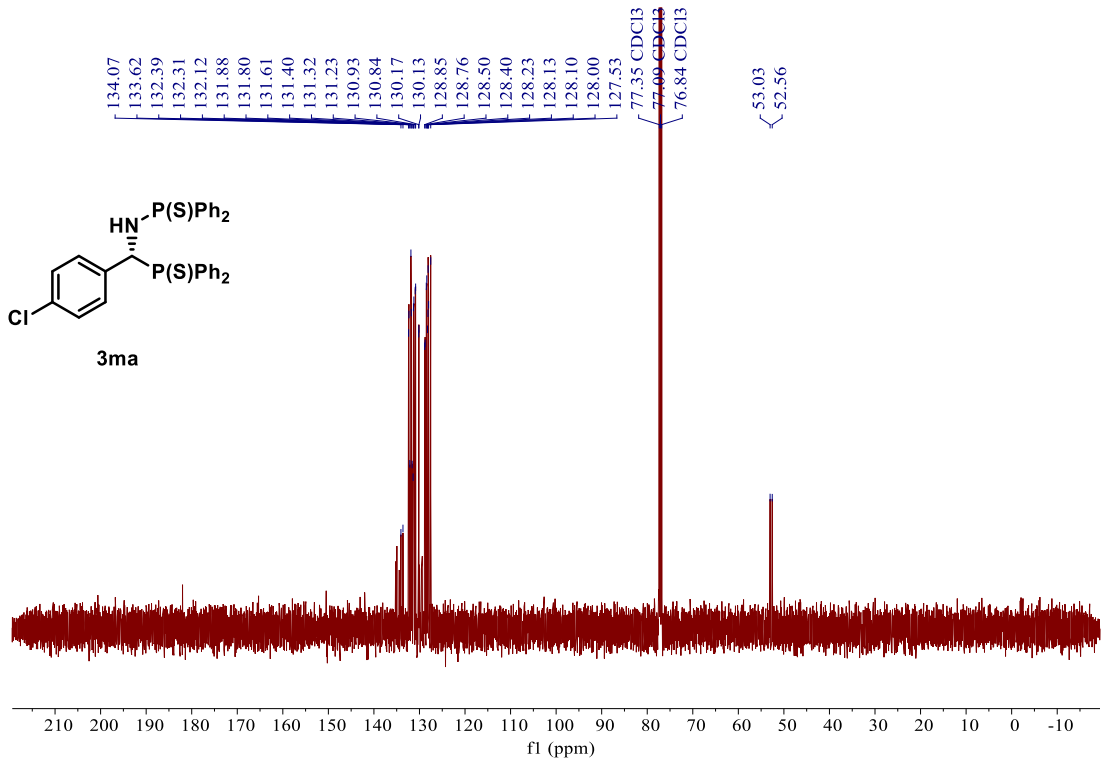
^{31}P NMR of 3la



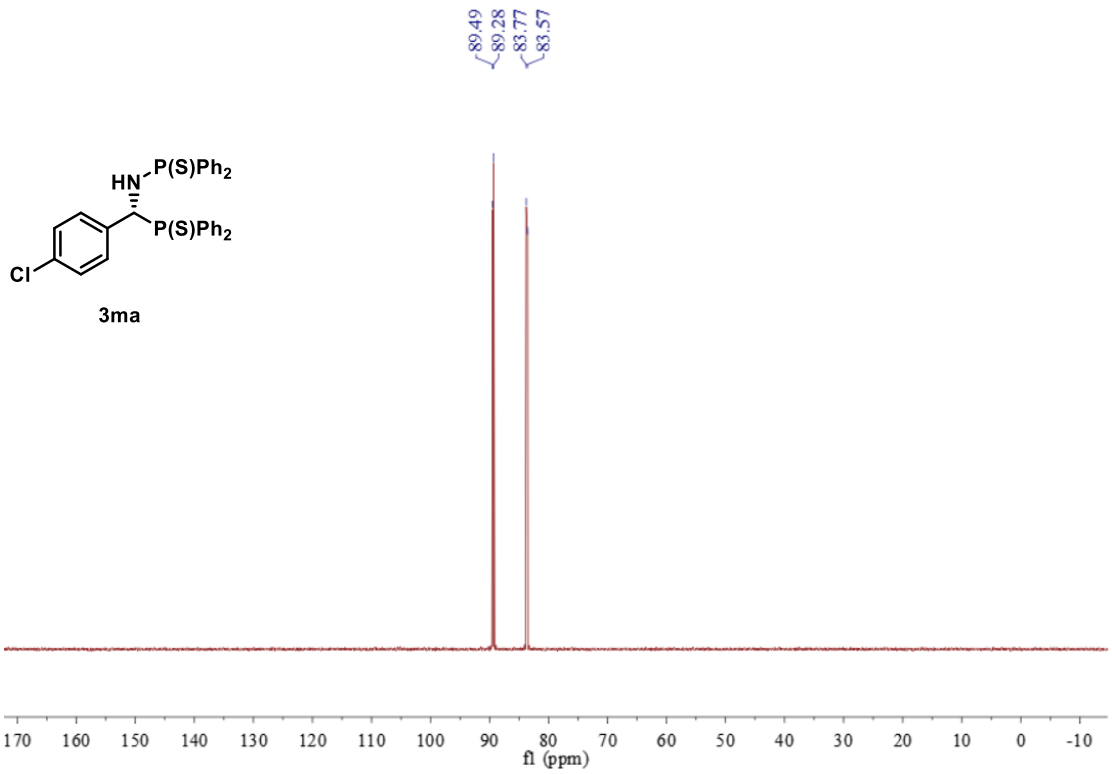
^{19}F NMR of 3la



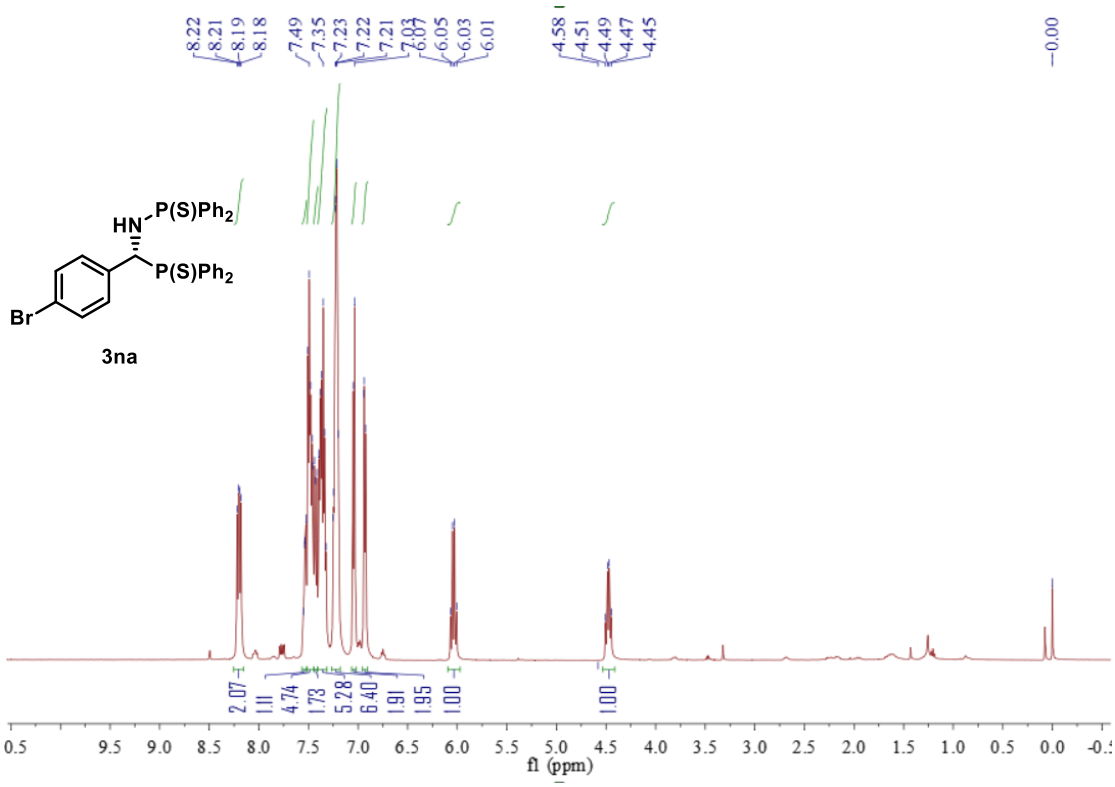
^{1}H NMR of 3ma



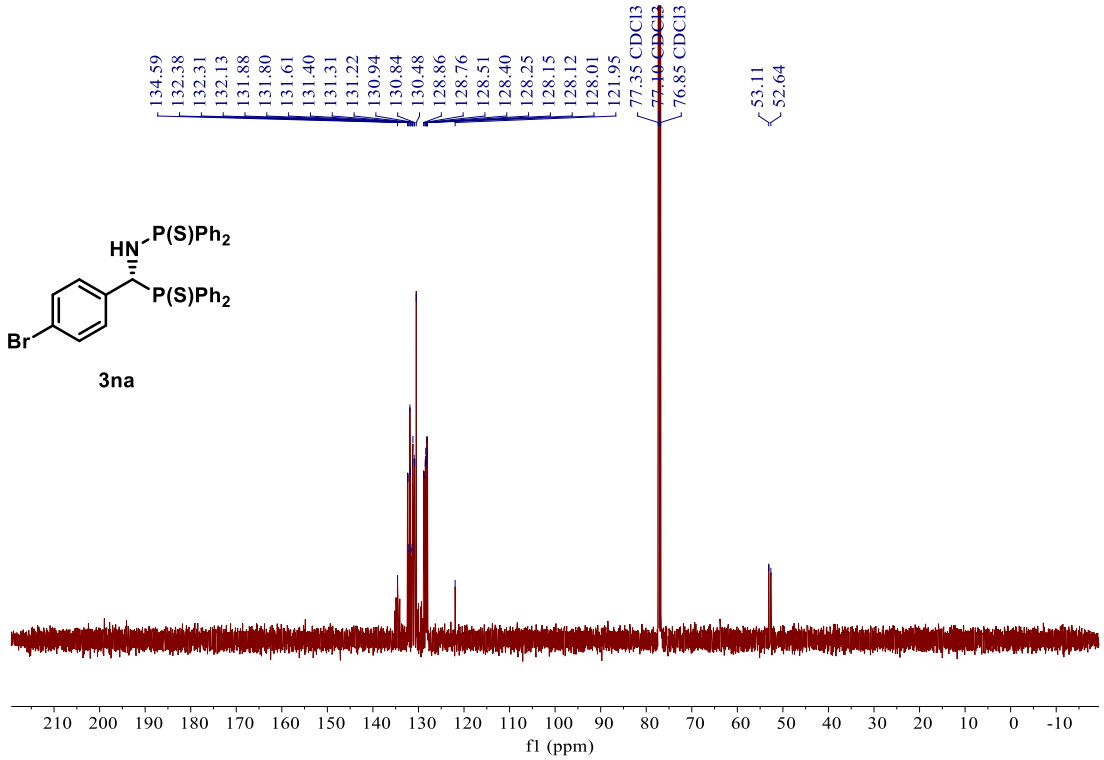
^{13}C NMR of 3ma



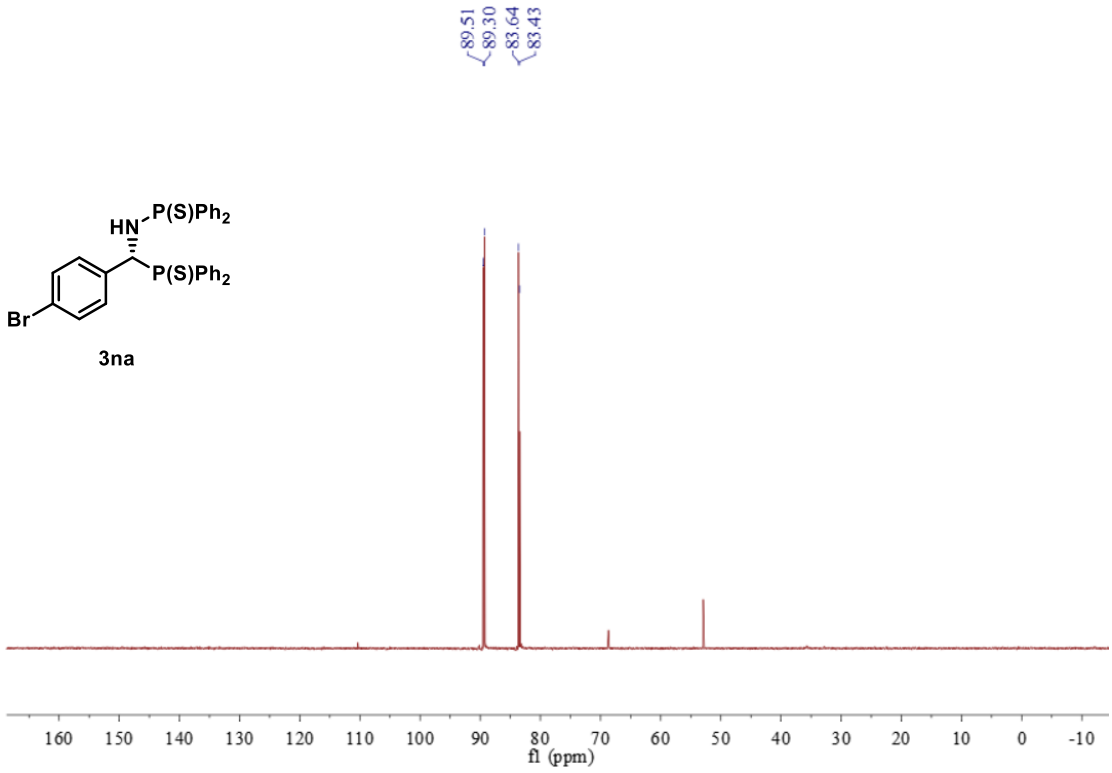
^{31}P NMR of 3ma



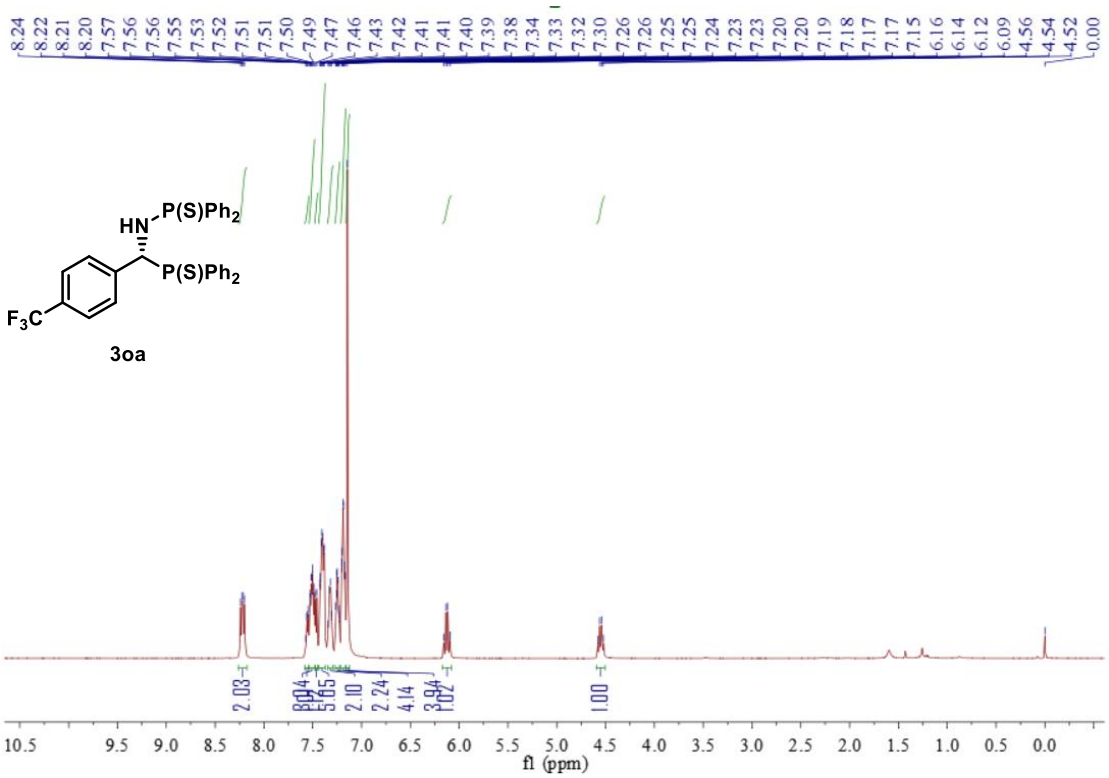
^{1}H NMR of 3na



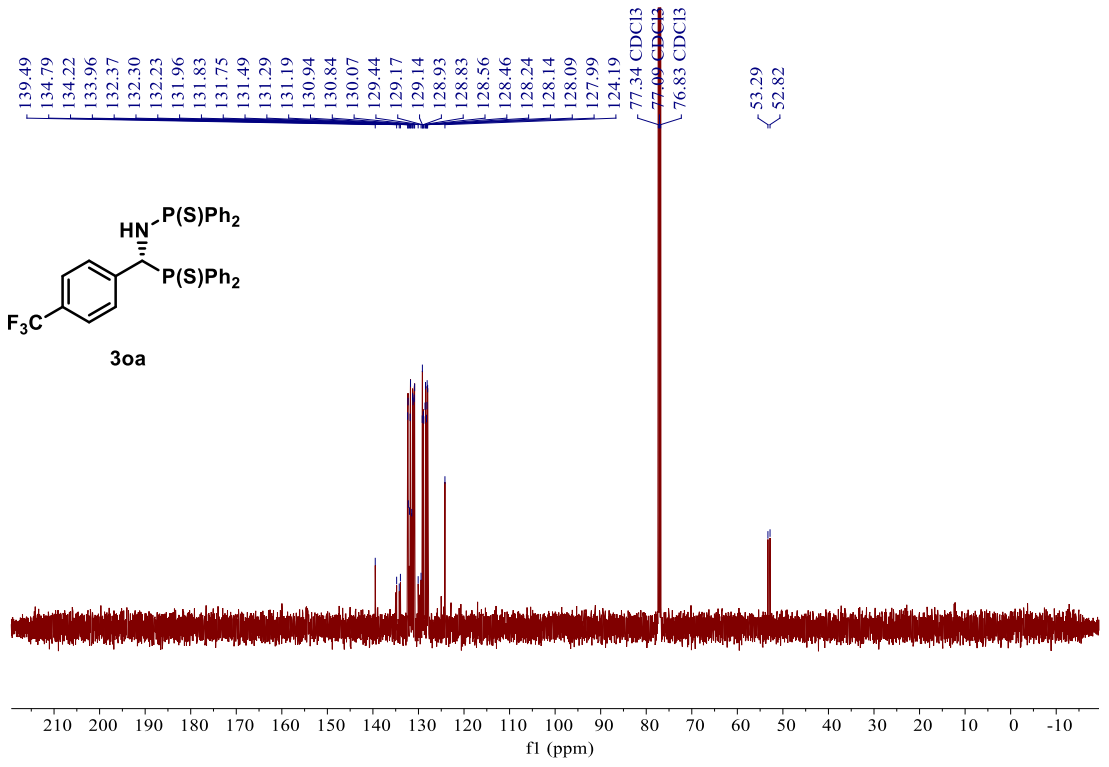
^{13}C NMR of 3na



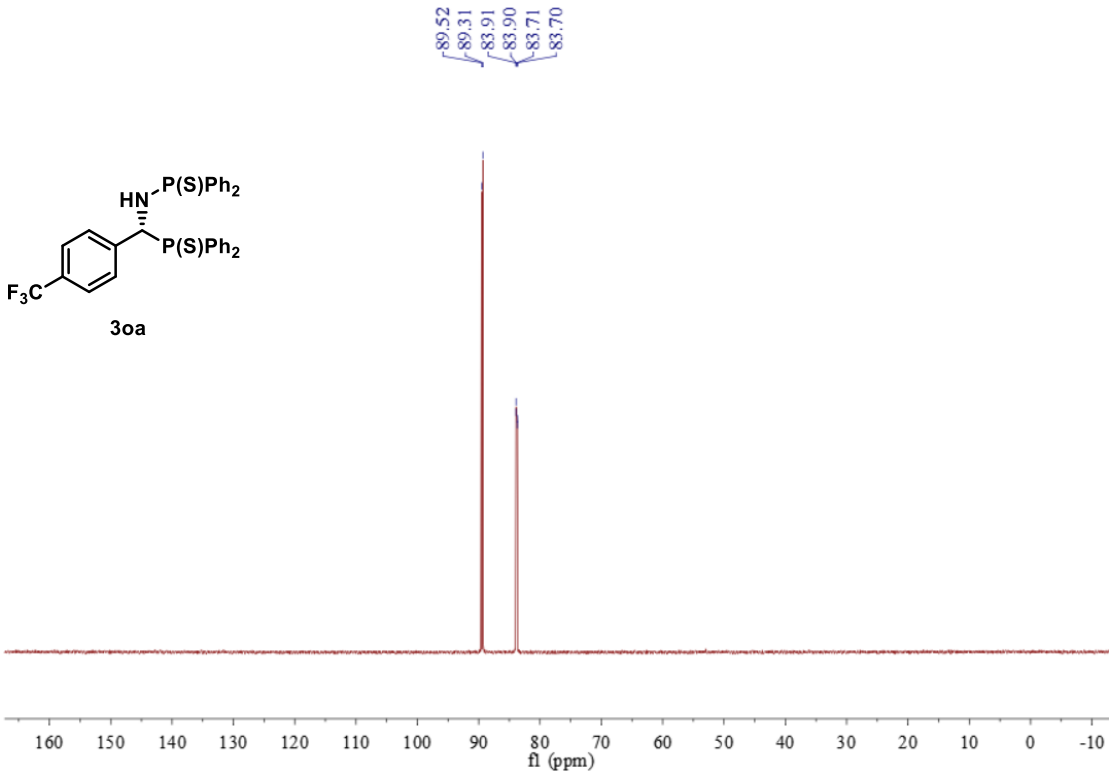
^{31}P NMR of 3na



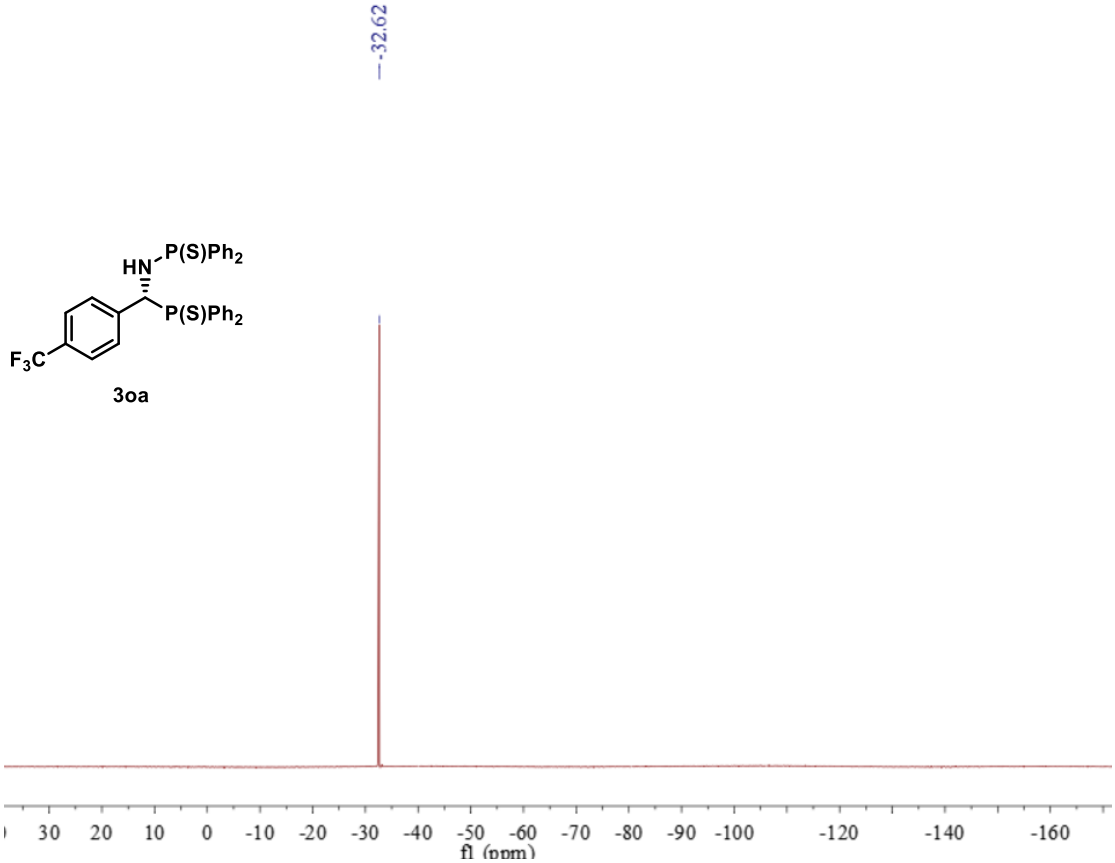
^{1}H NMR of 3oa



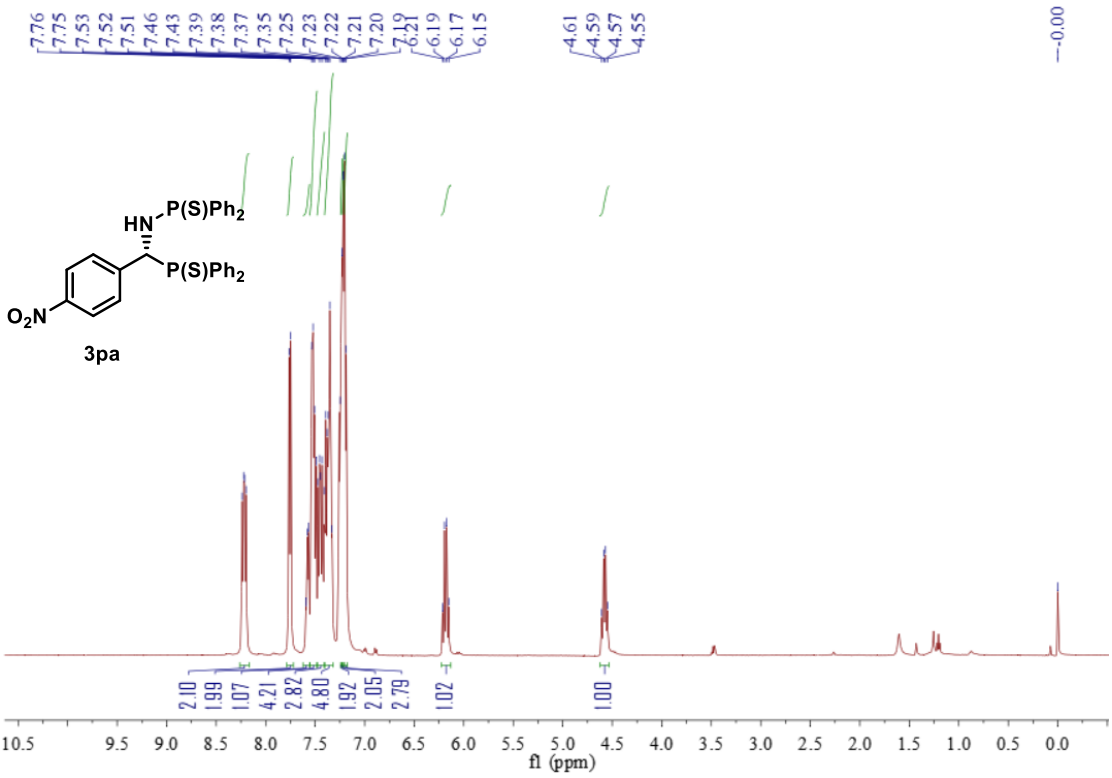
^{13}C NMR of 3oa



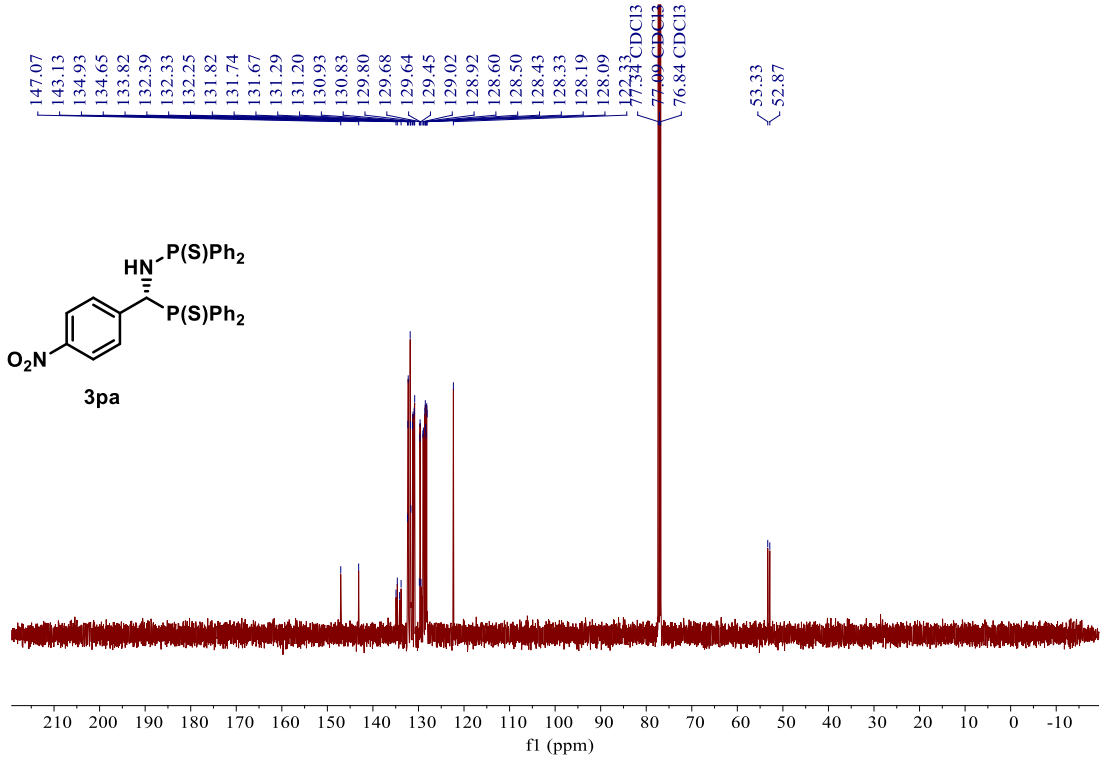
^{31}P NMR of 3oa



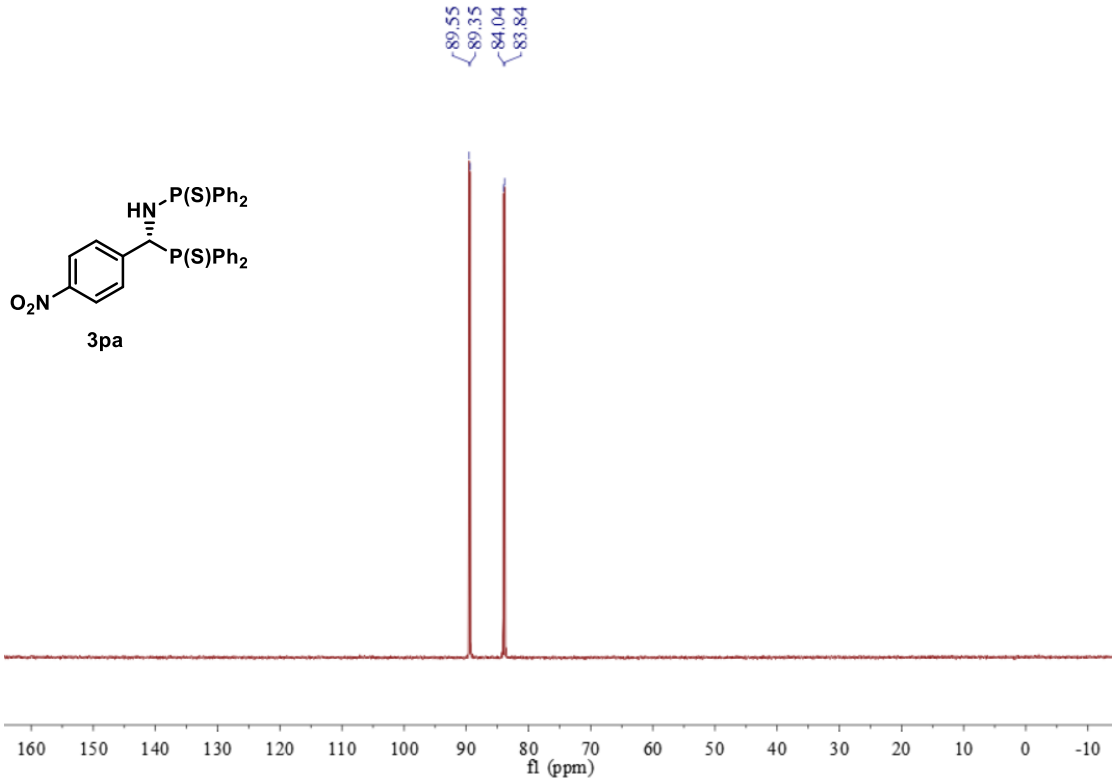
^{19}F NMR of 3oa



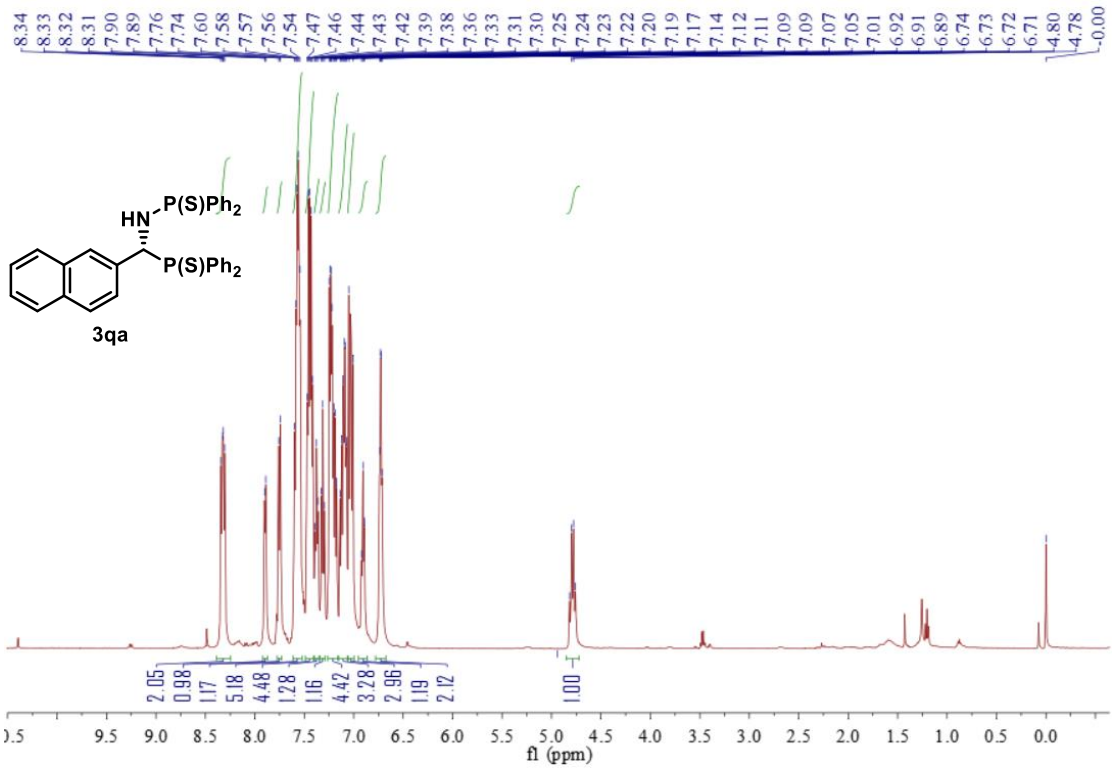
^{1}H NMR of 3pa



^{13}C NMR of 3pa



^{31}P NMR of 3pa



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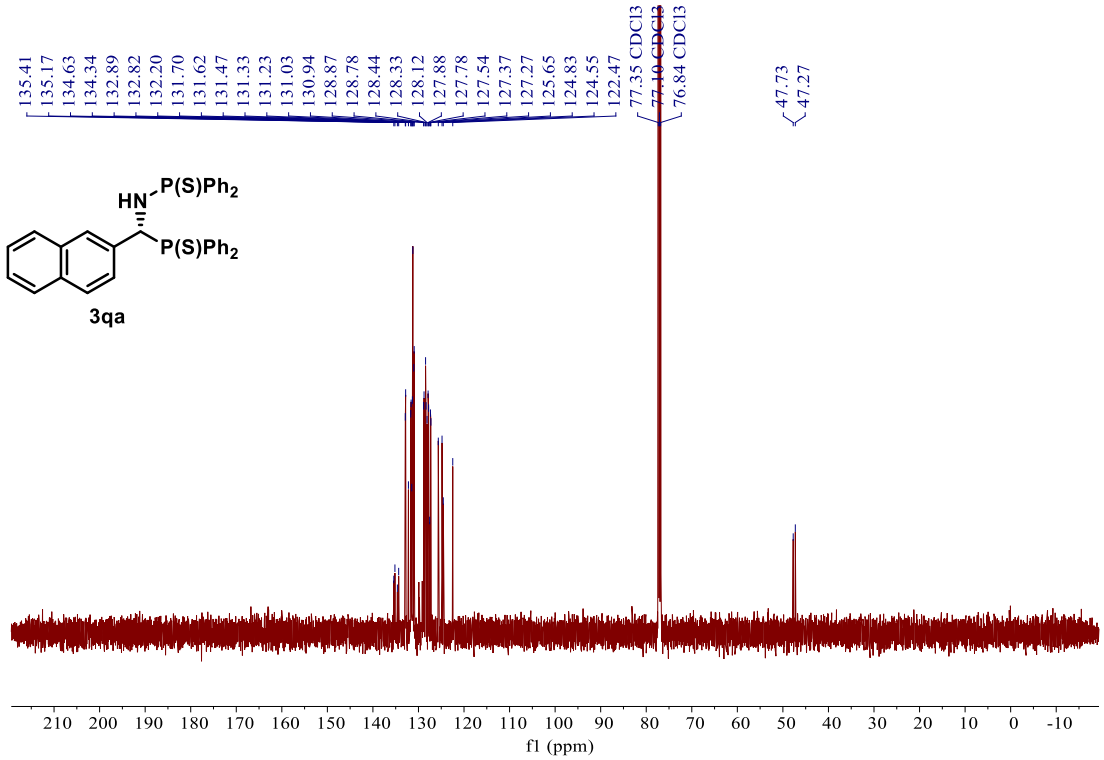

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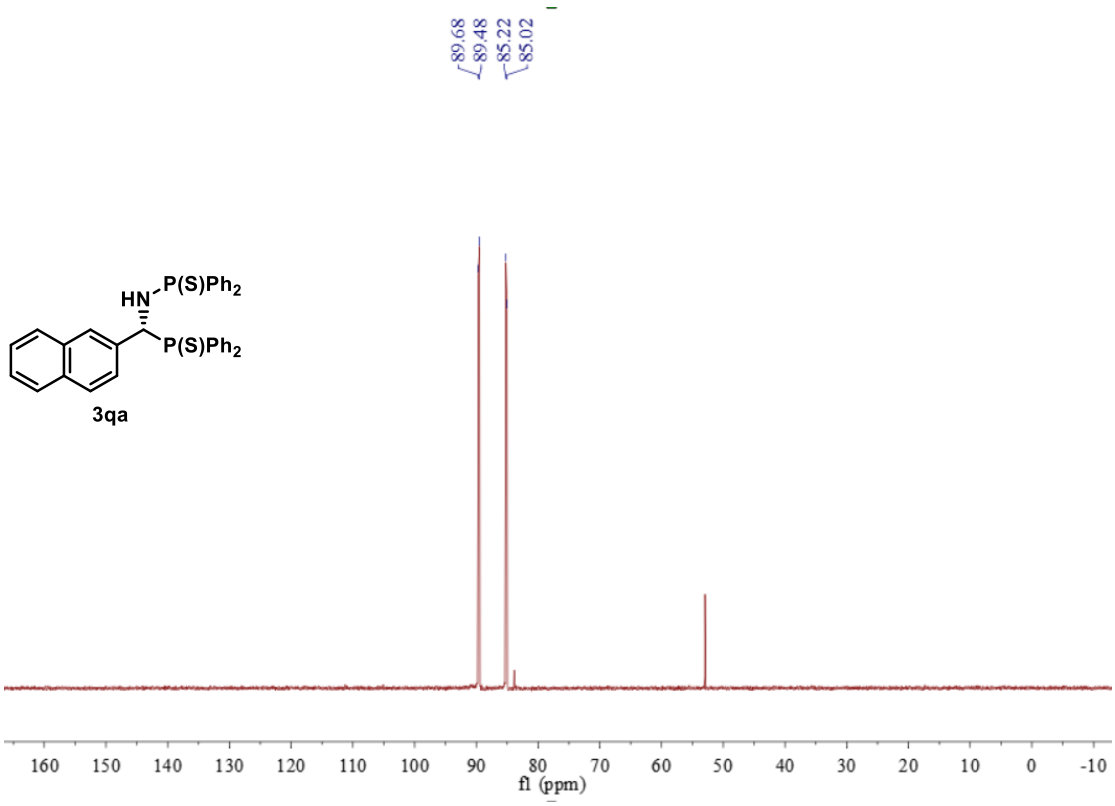

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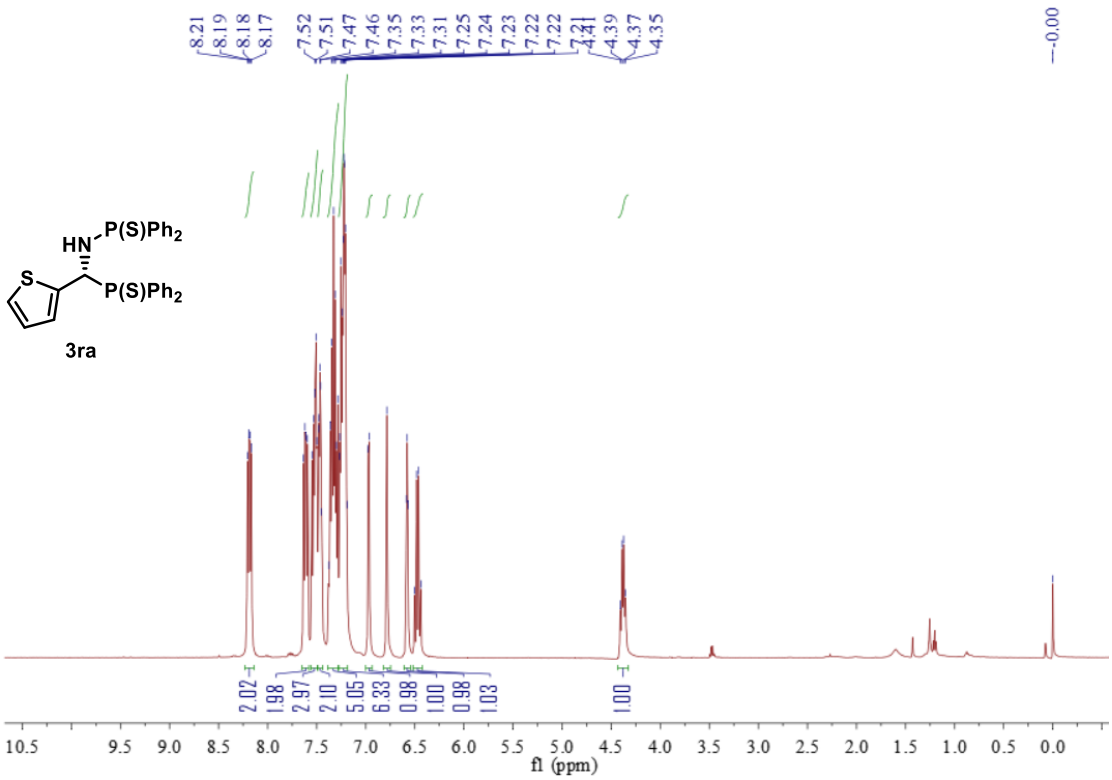
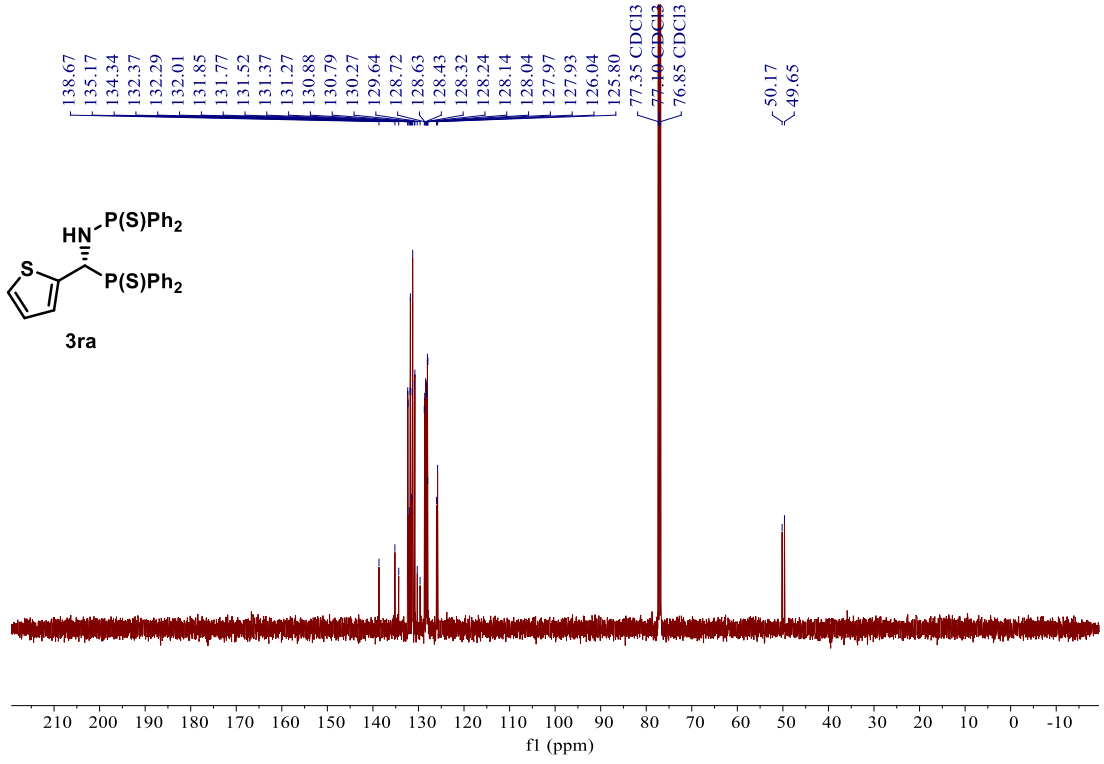


^{1}H NMR of 3ra



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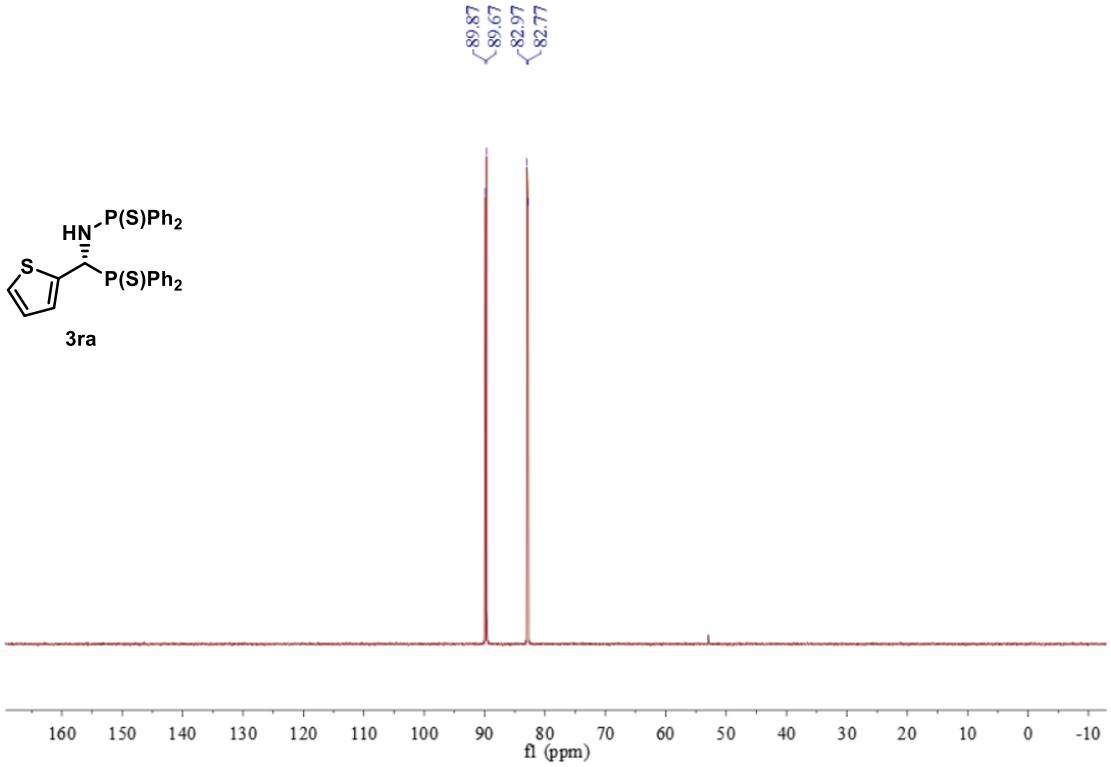

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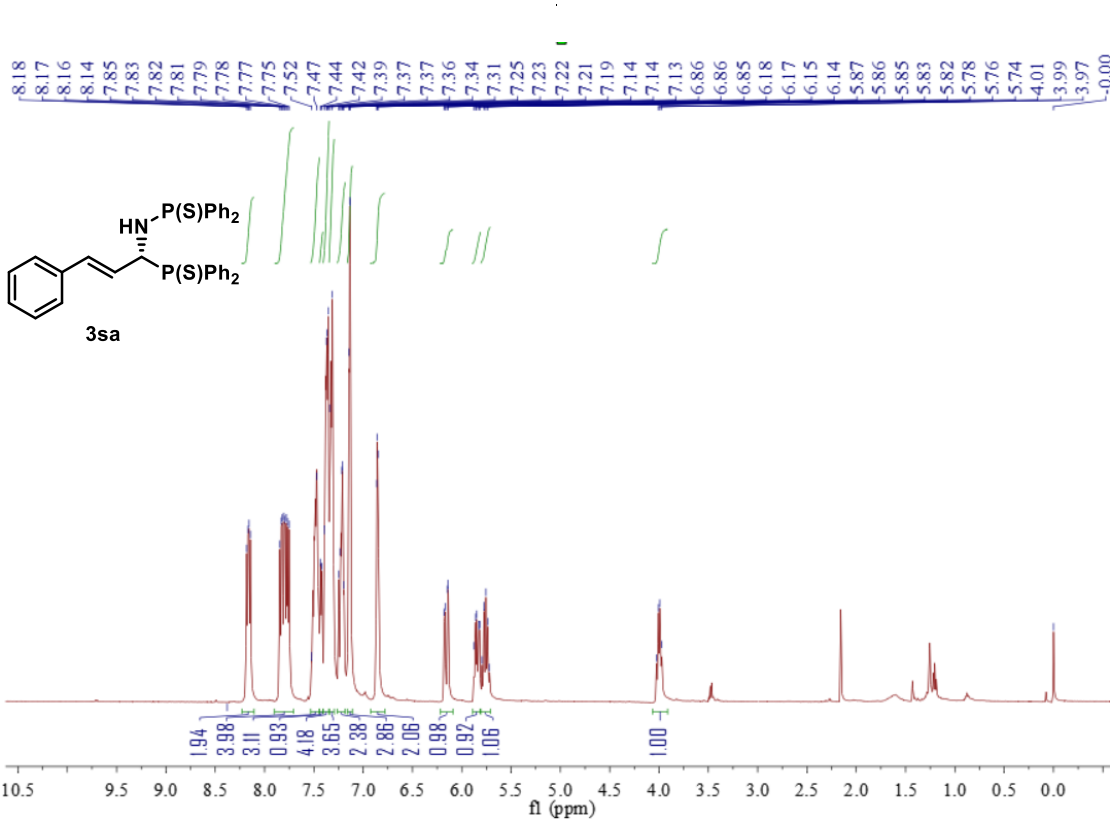

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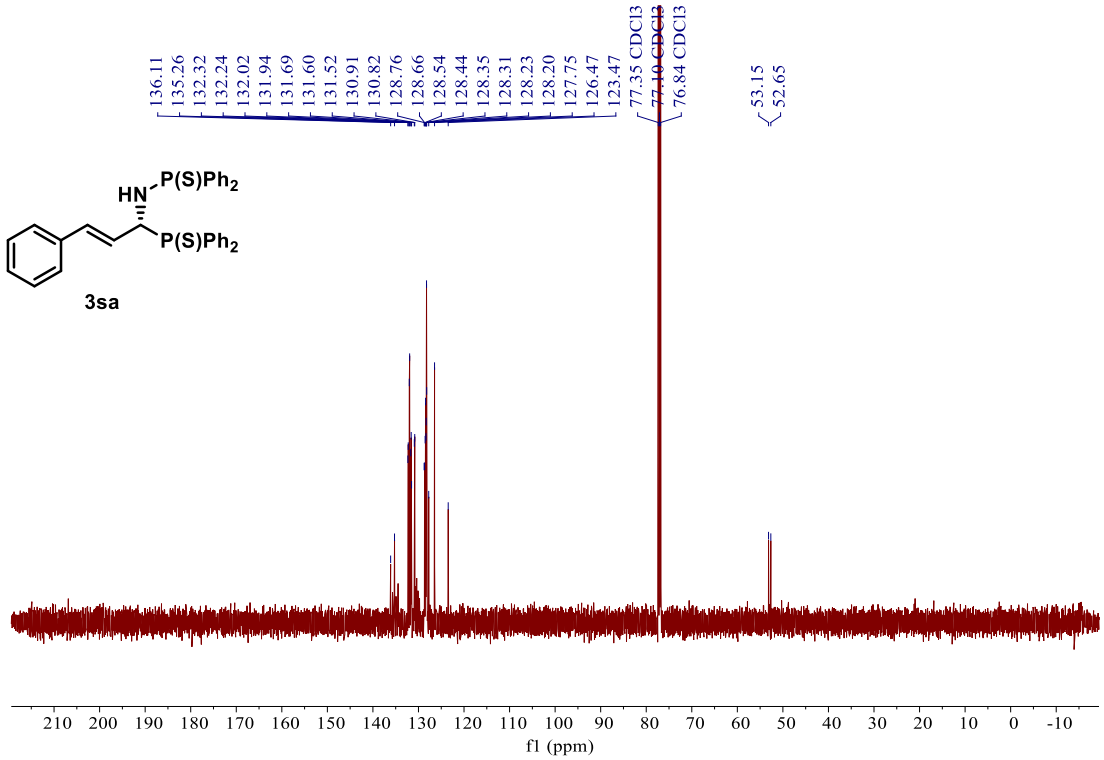

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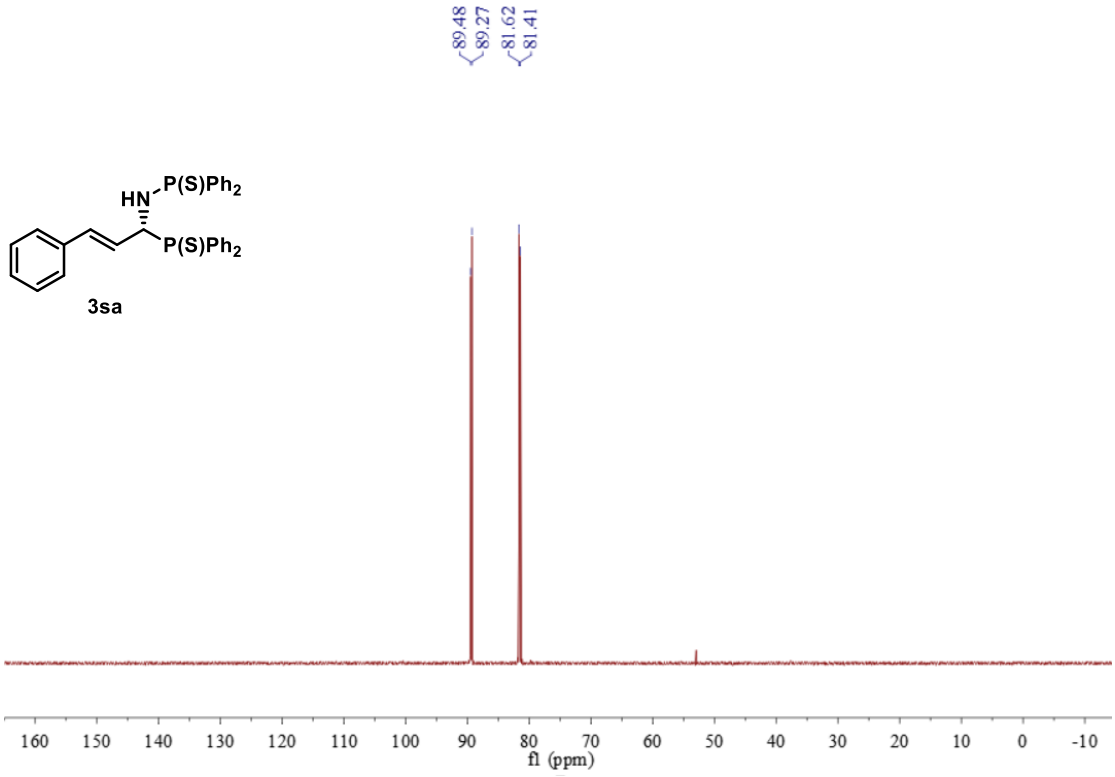
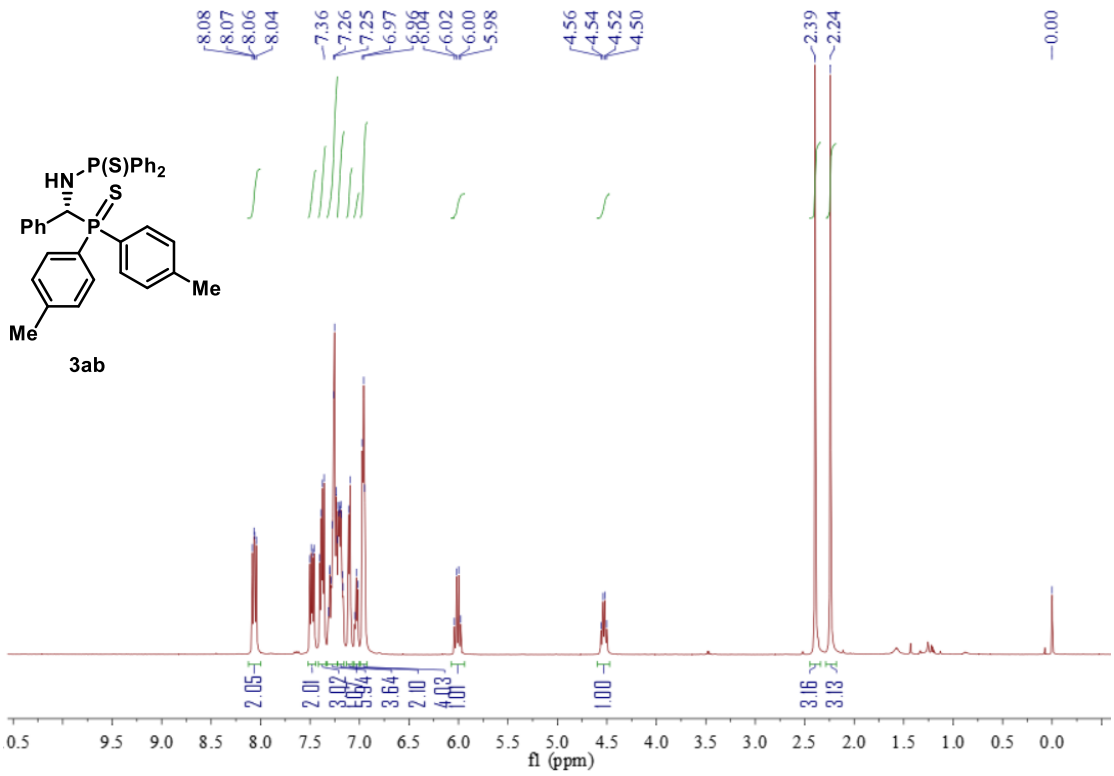
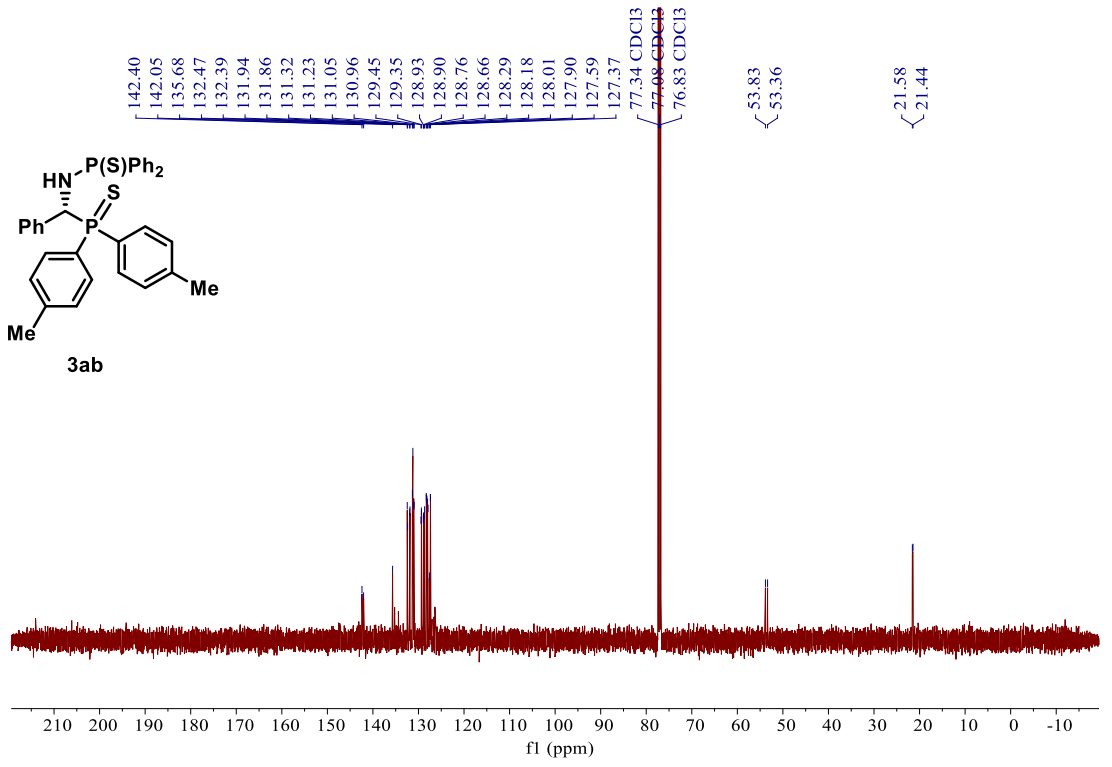


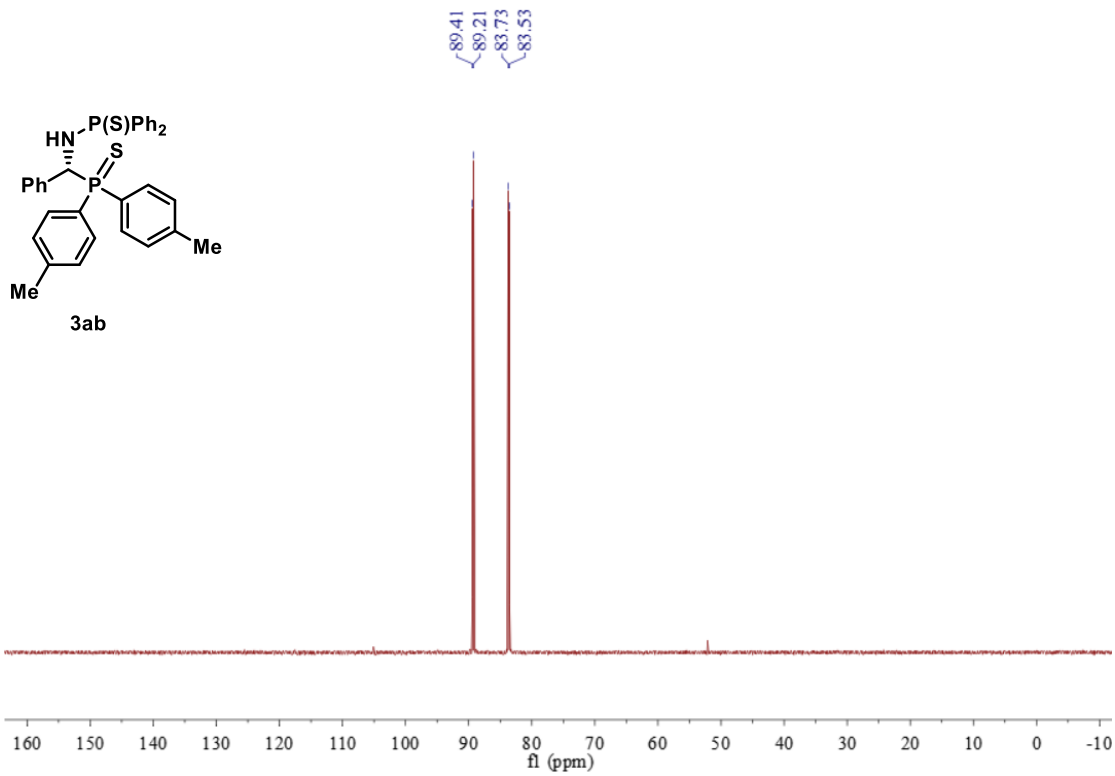
^{31}P NMR of 3sa



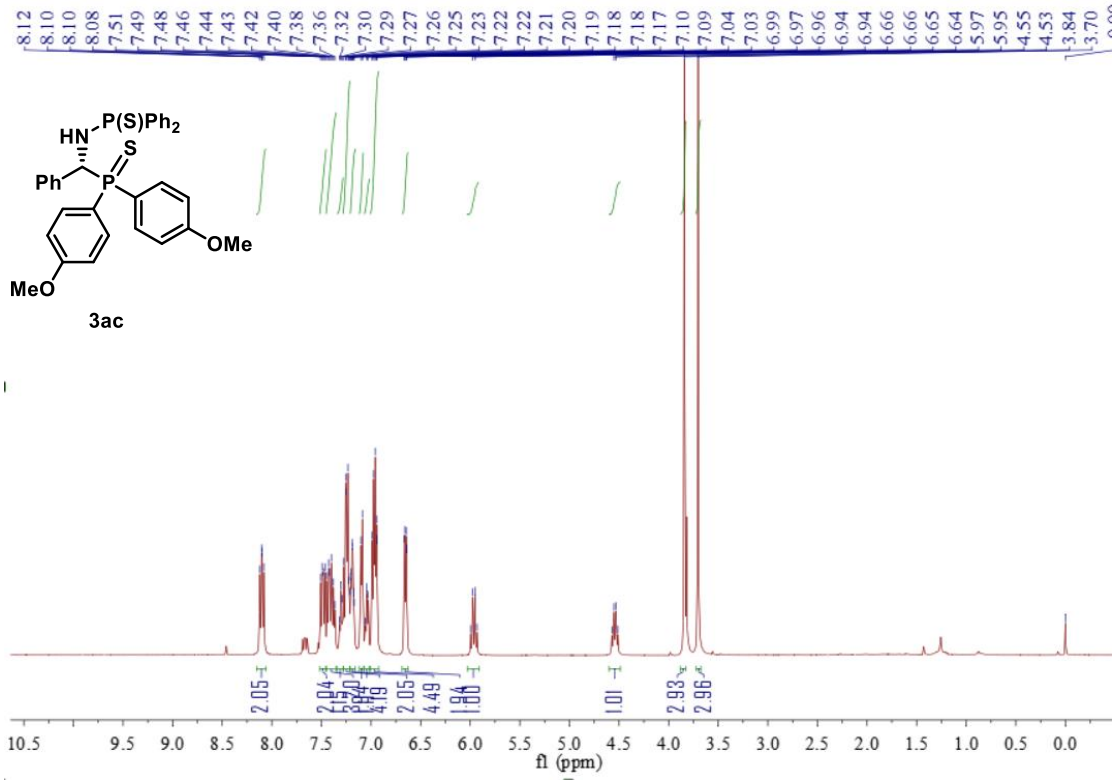
^{1}H NMR of 3ab



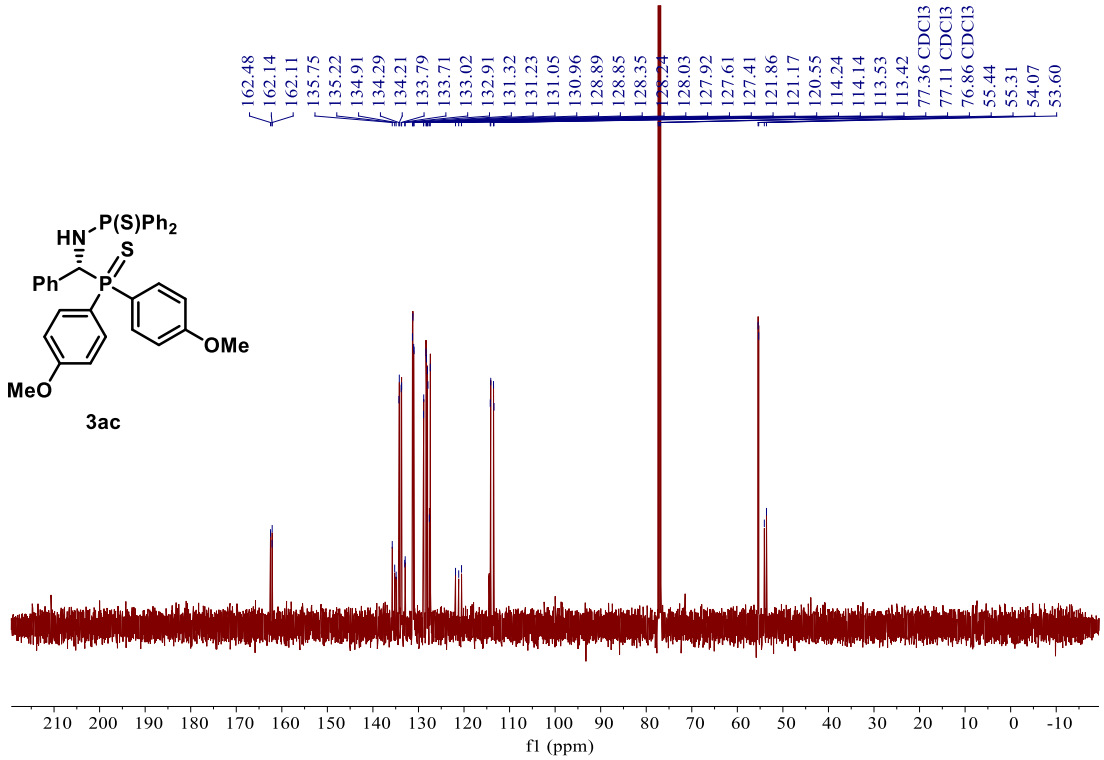
^{13}C NMR of 3ab



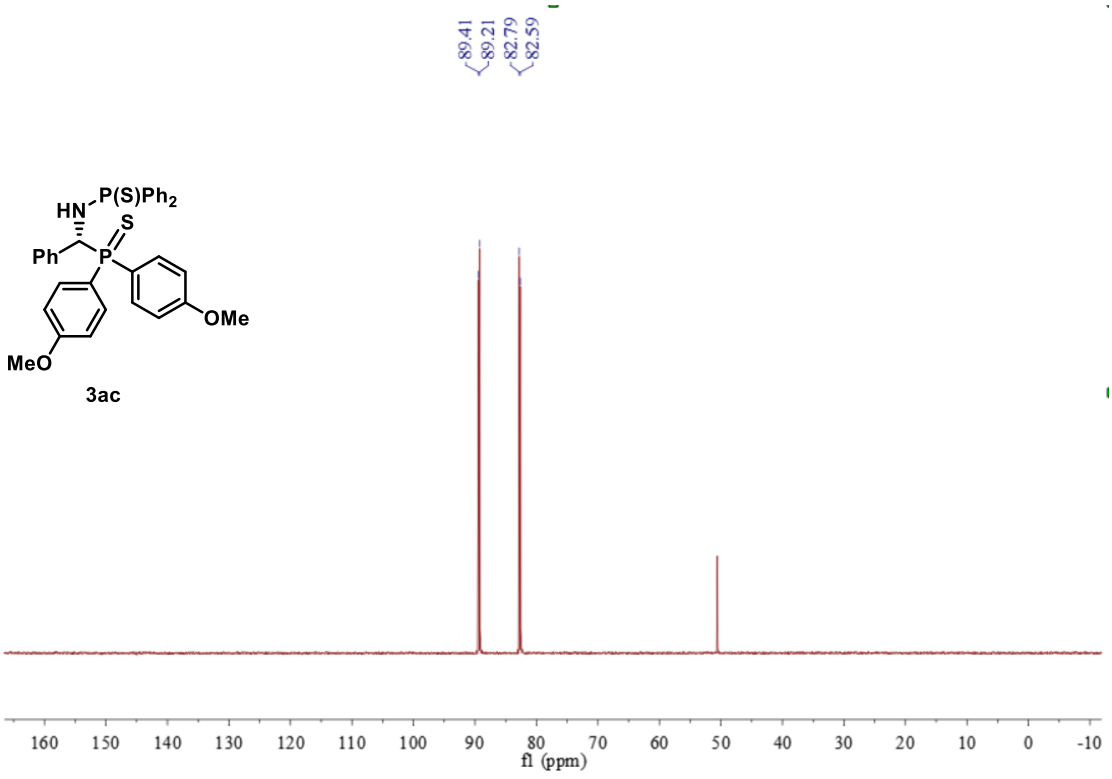
^{31}P NMR of 3ab



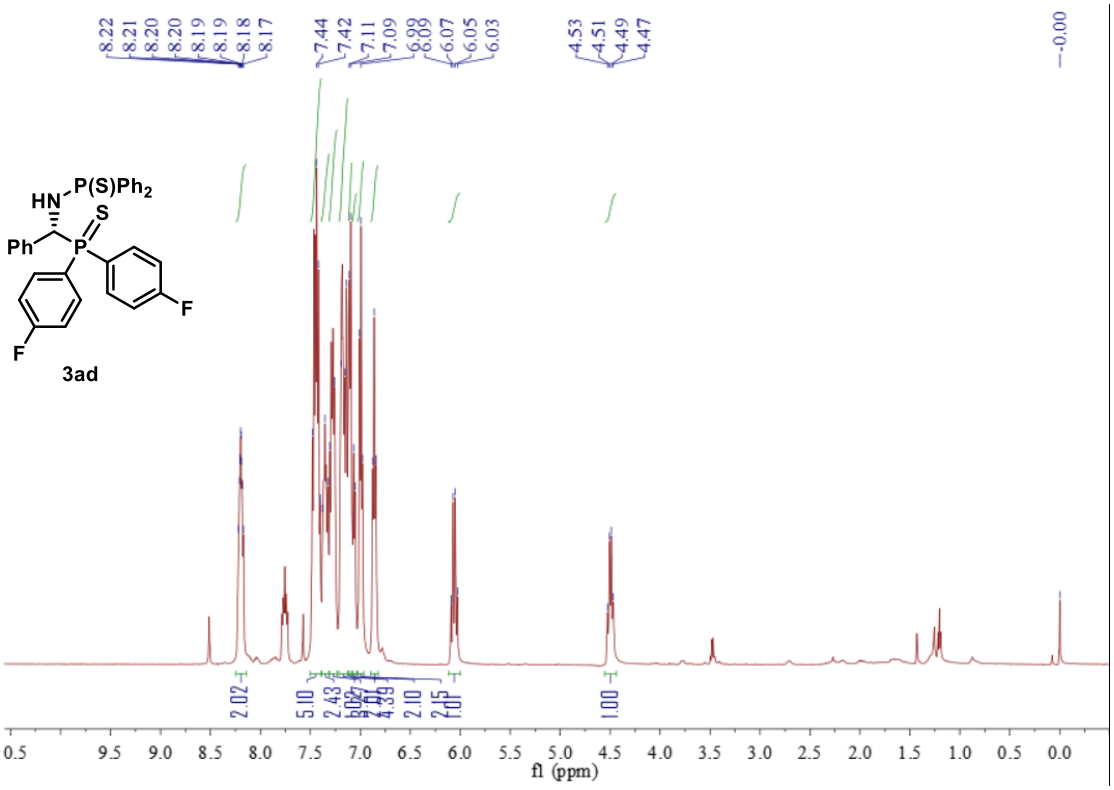
^{1}H NMR of 3ac



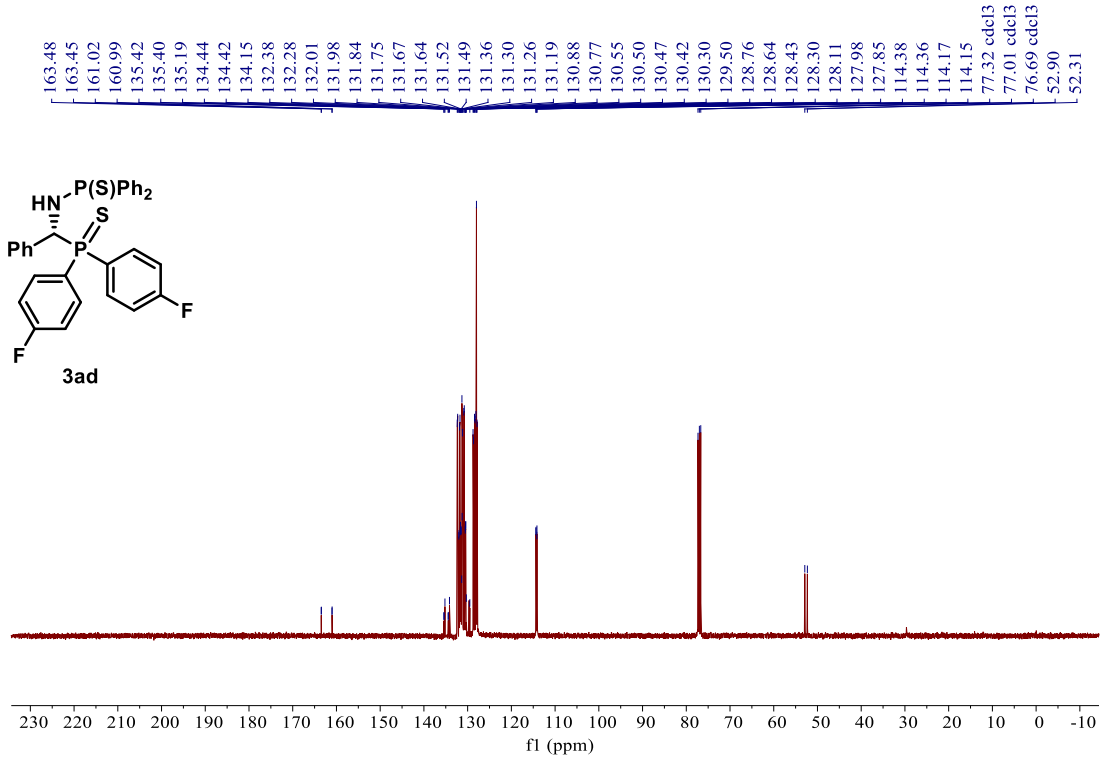
^{13}C NMR of 3ac



^{31}P NMR of 3ac



^{1}H NMR of 3ad



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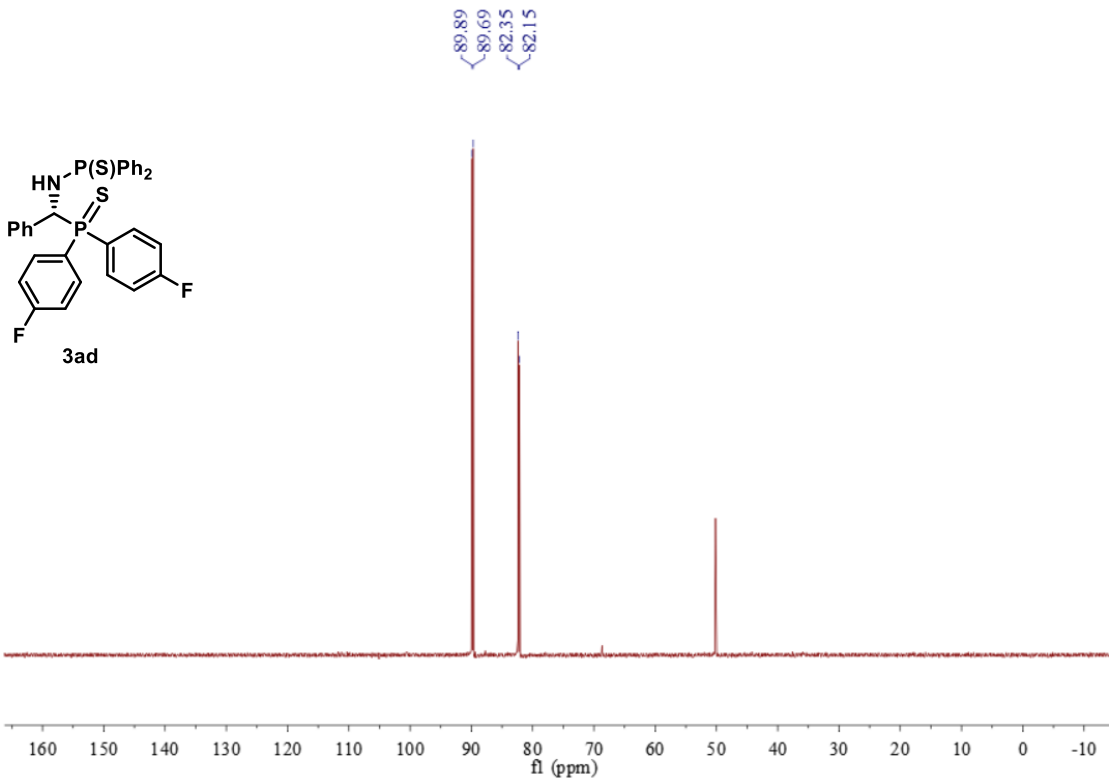
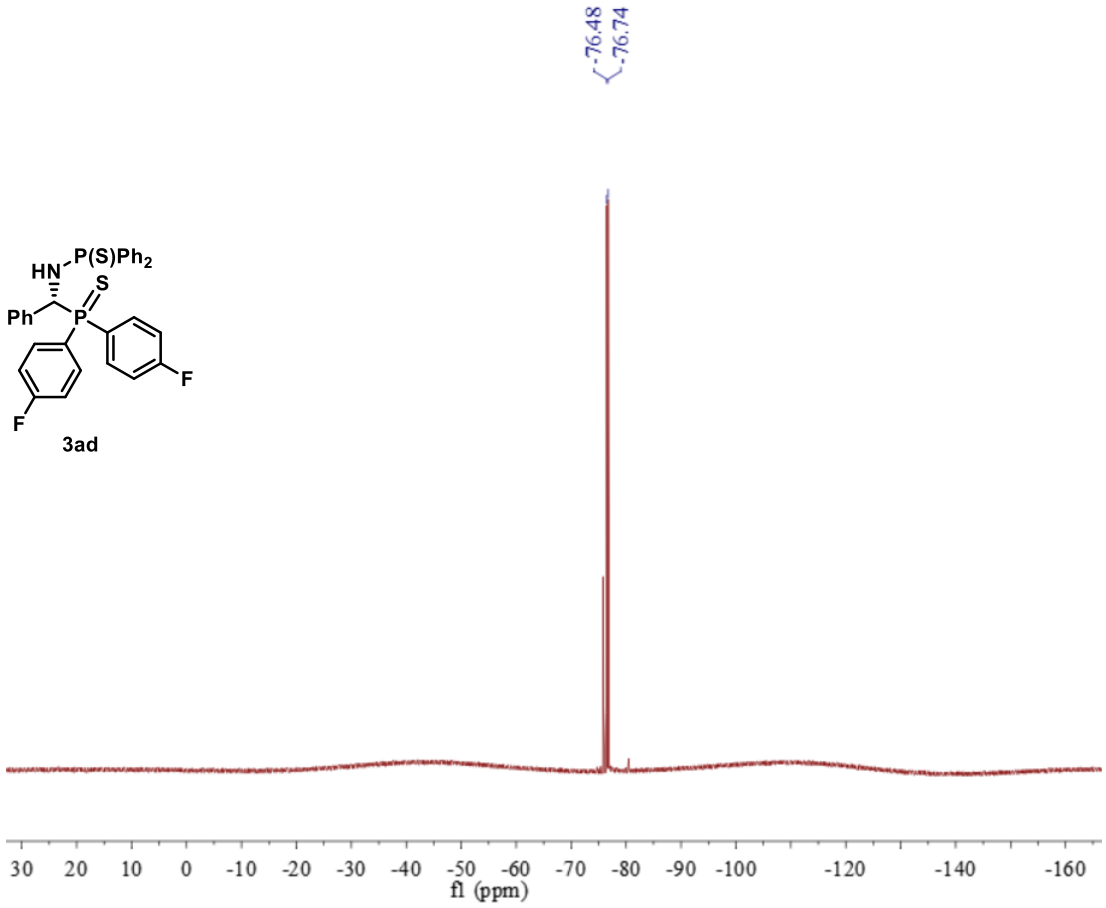


^{31}P NMR of 3ad



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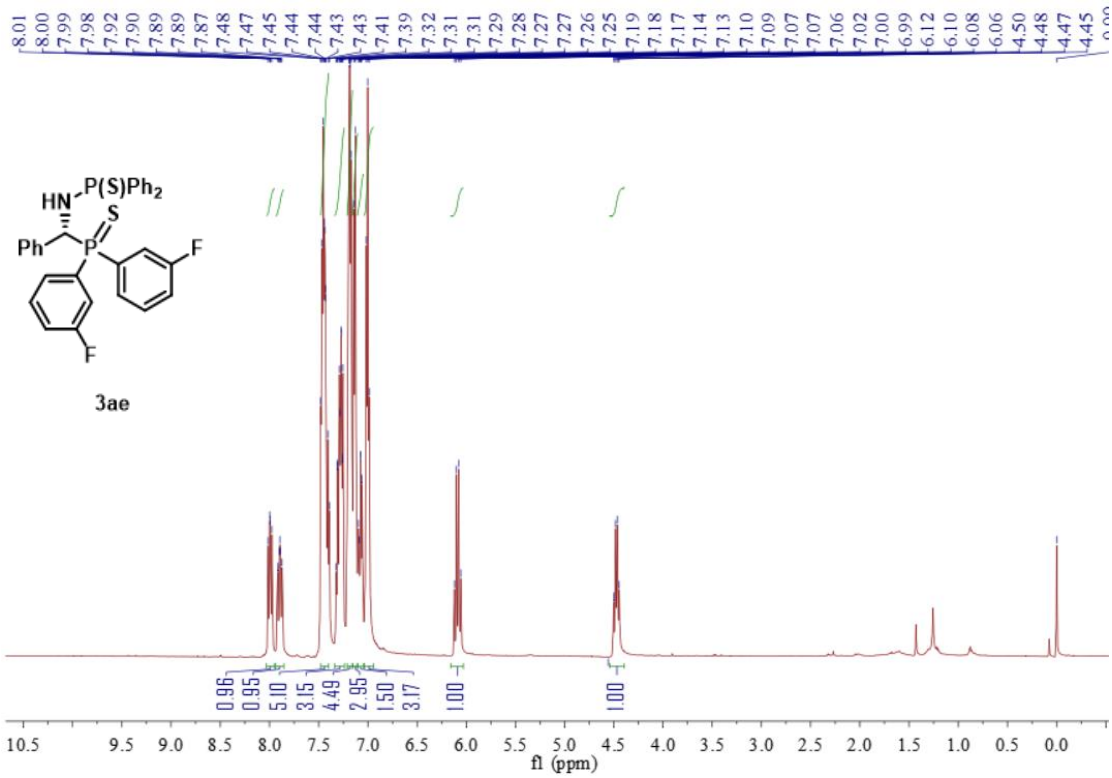
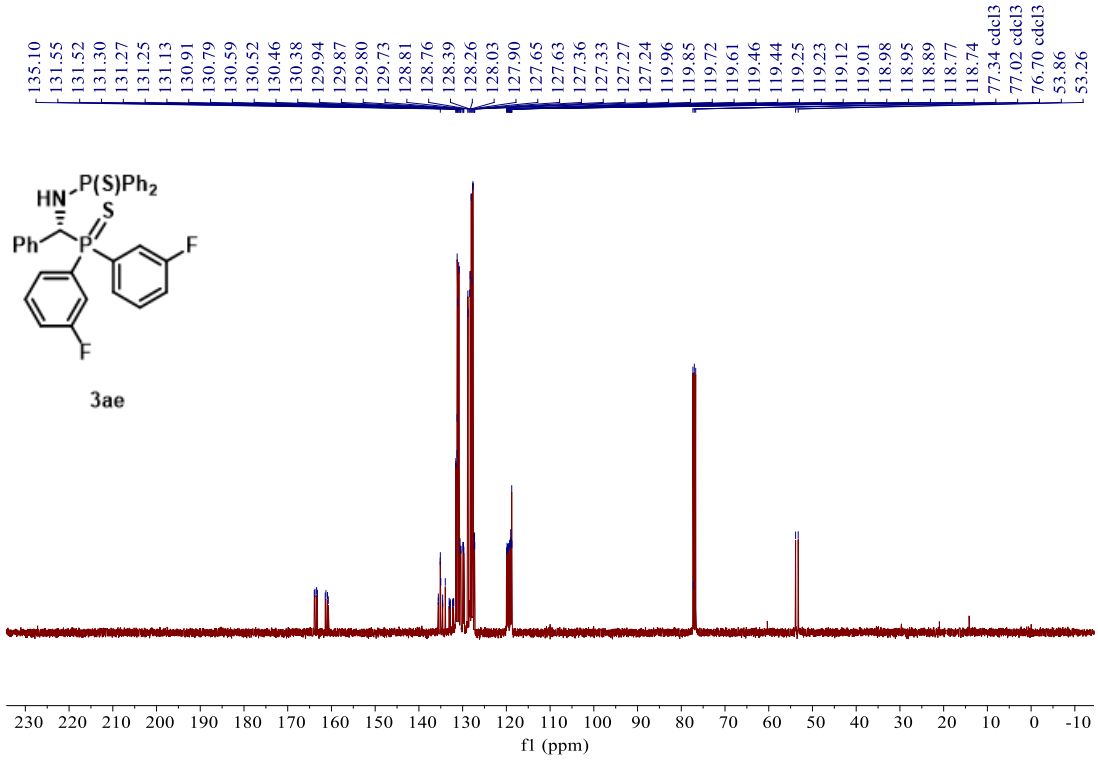


^{1}H NMR of 3ae



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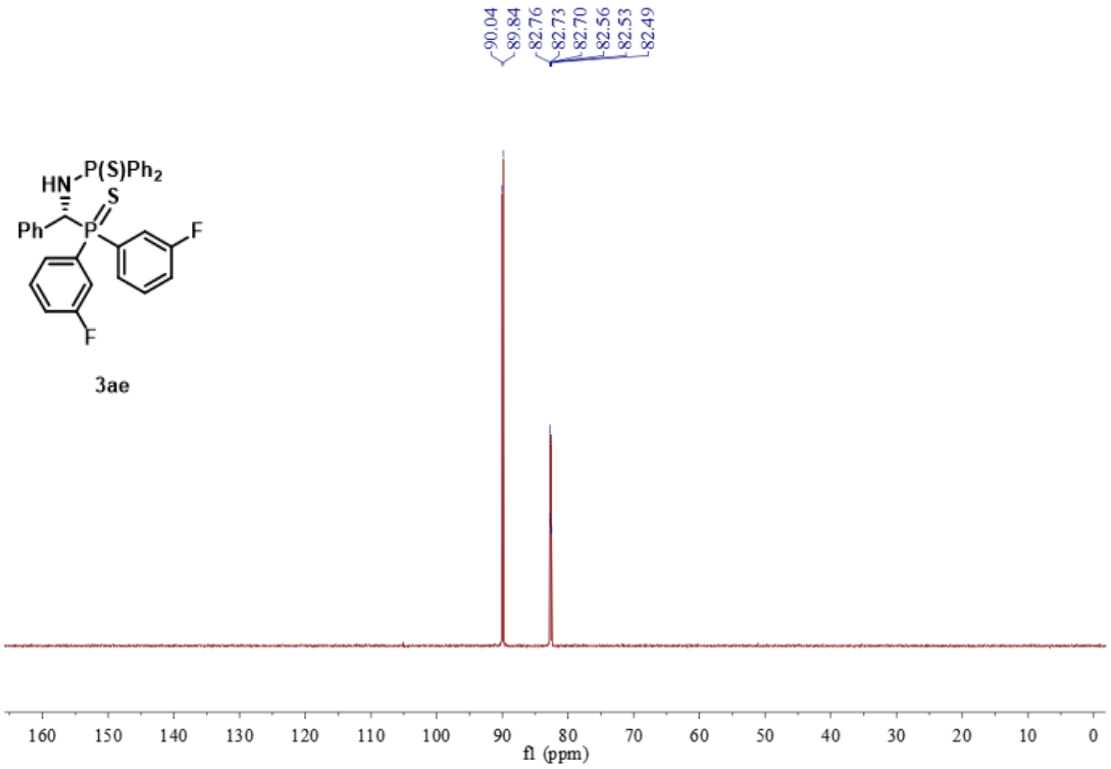

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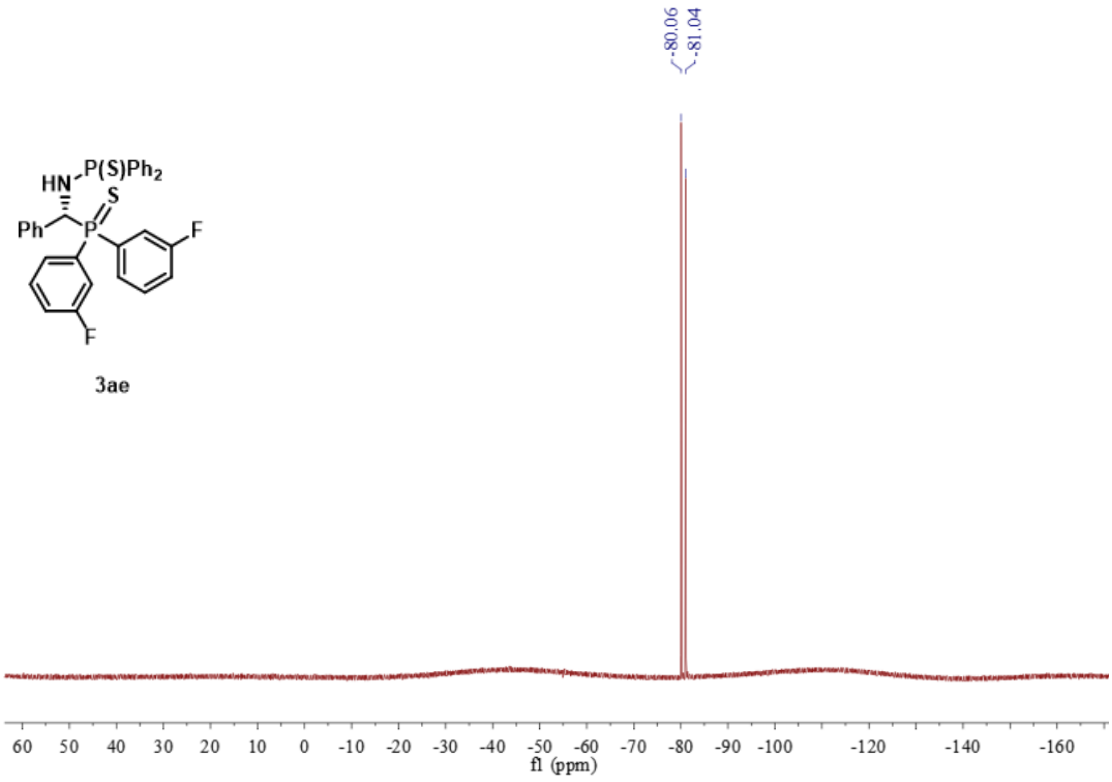
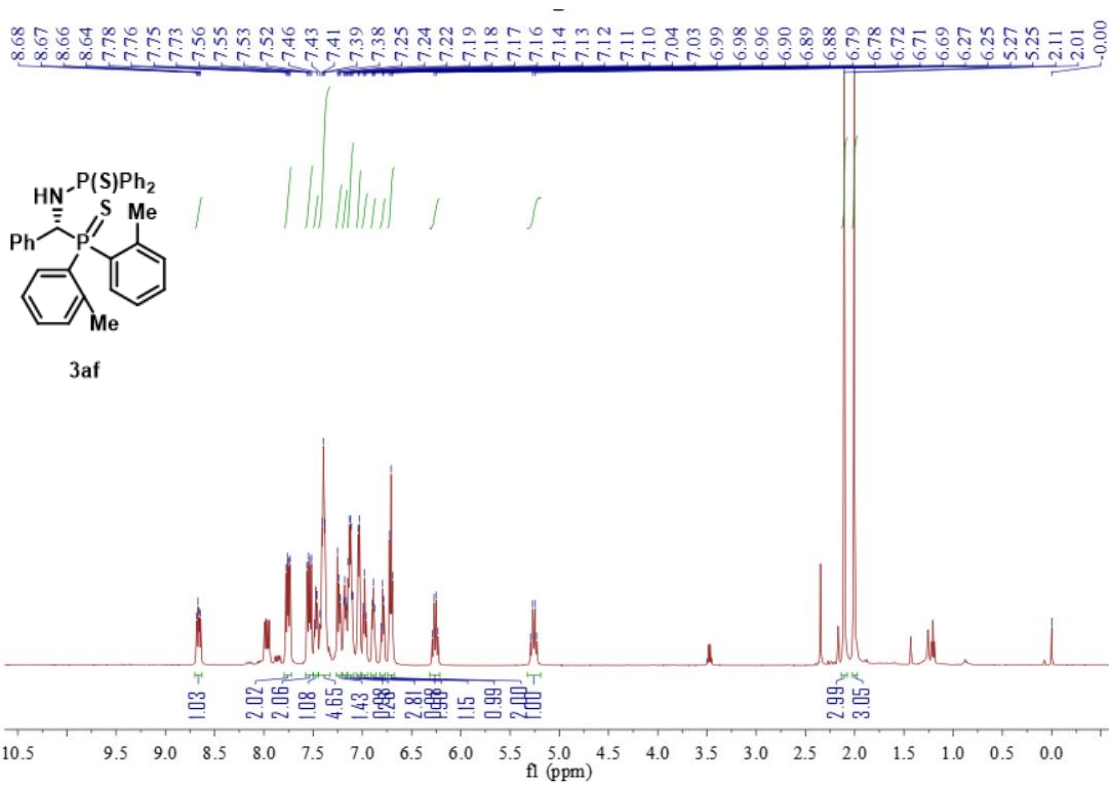
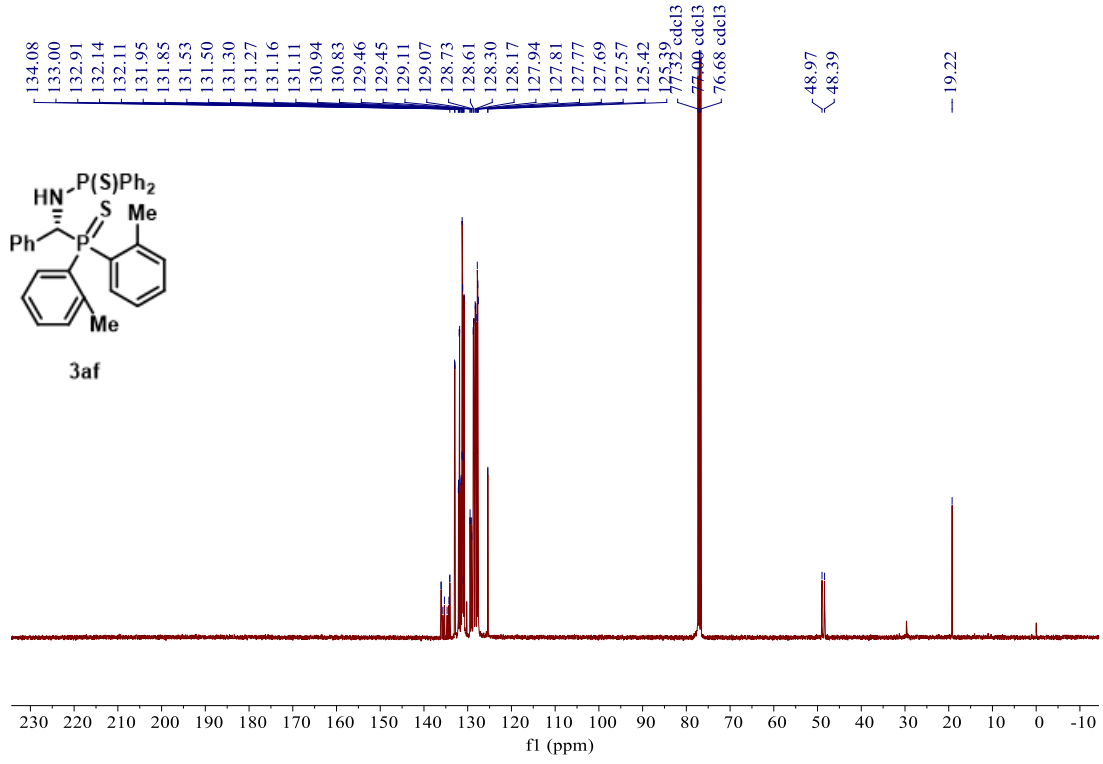


^{19}F NMR of 3ae



^{1}H NMR of 3af



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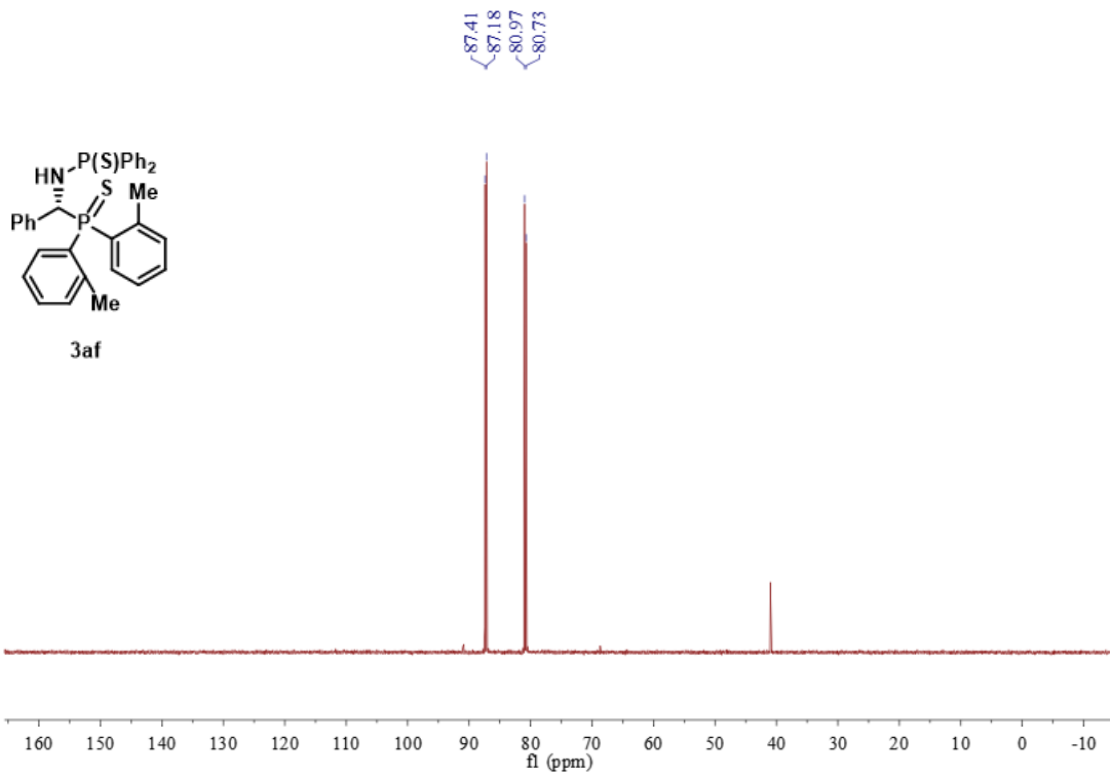
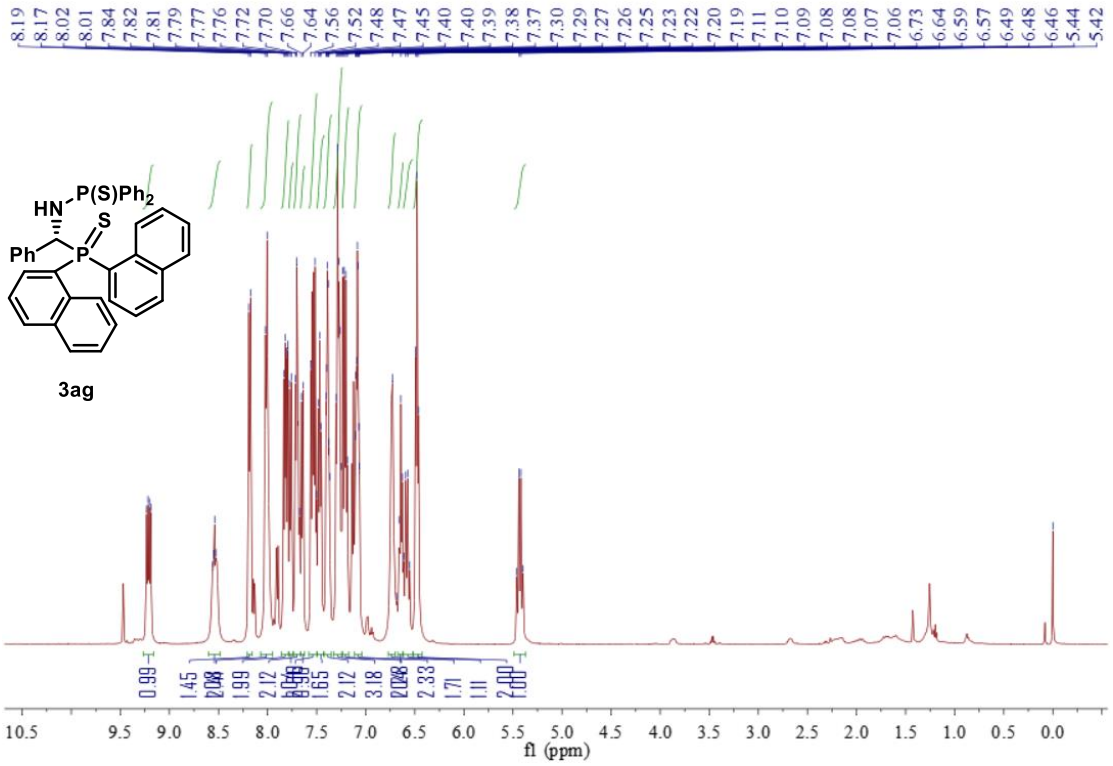
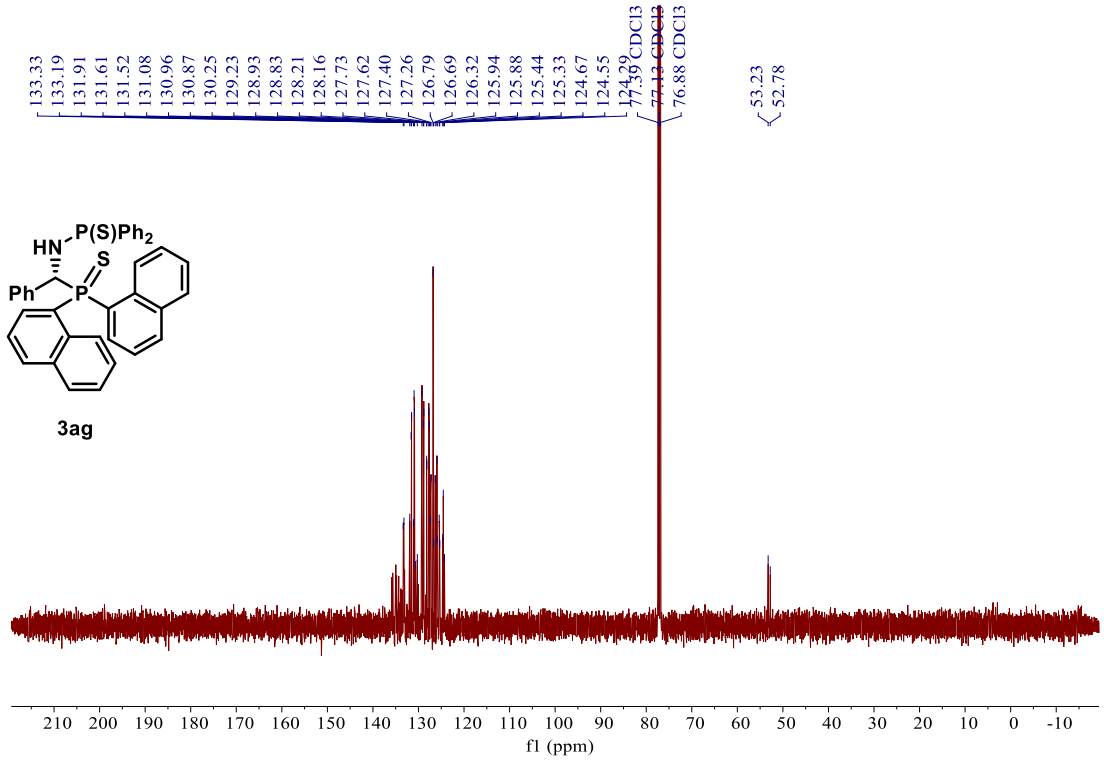


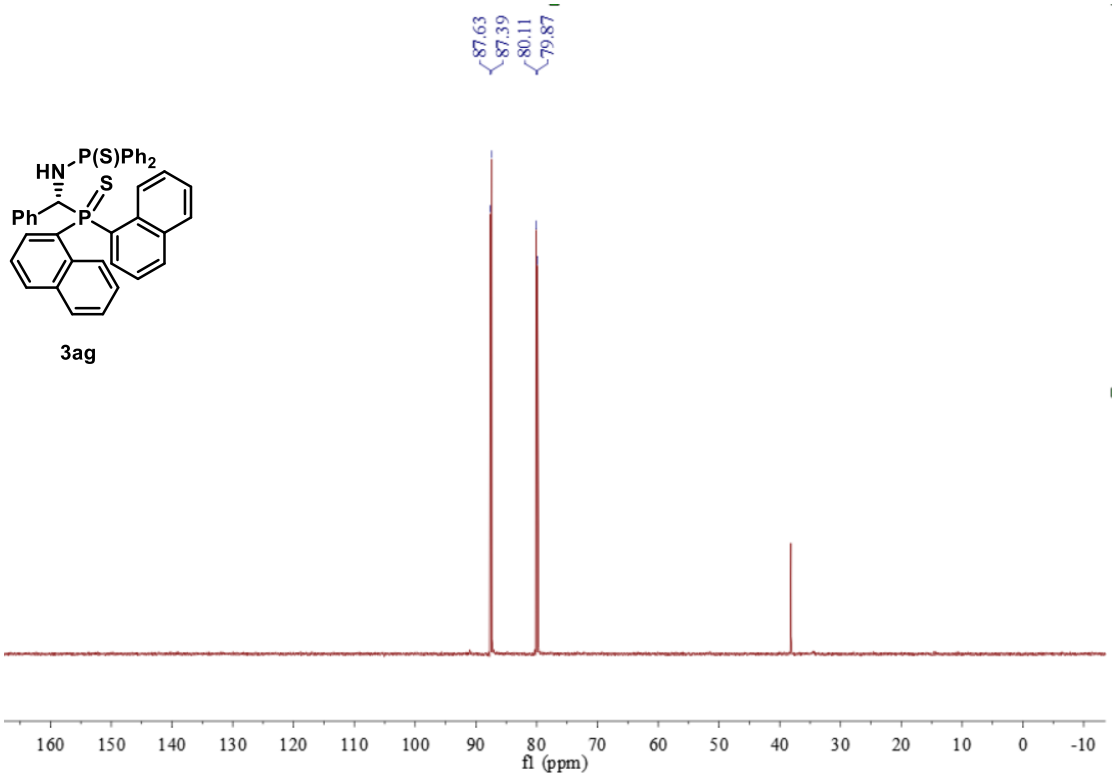
^{31}P NMR of 3af



^{1}H NMR of 3ag



^{13}C NMR of 3ag



^{31}P NMR of 3ag