Supporting Information

Deoxygenative Phosphonation of Ketones by Titanium

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Table of Contents

1. General Information

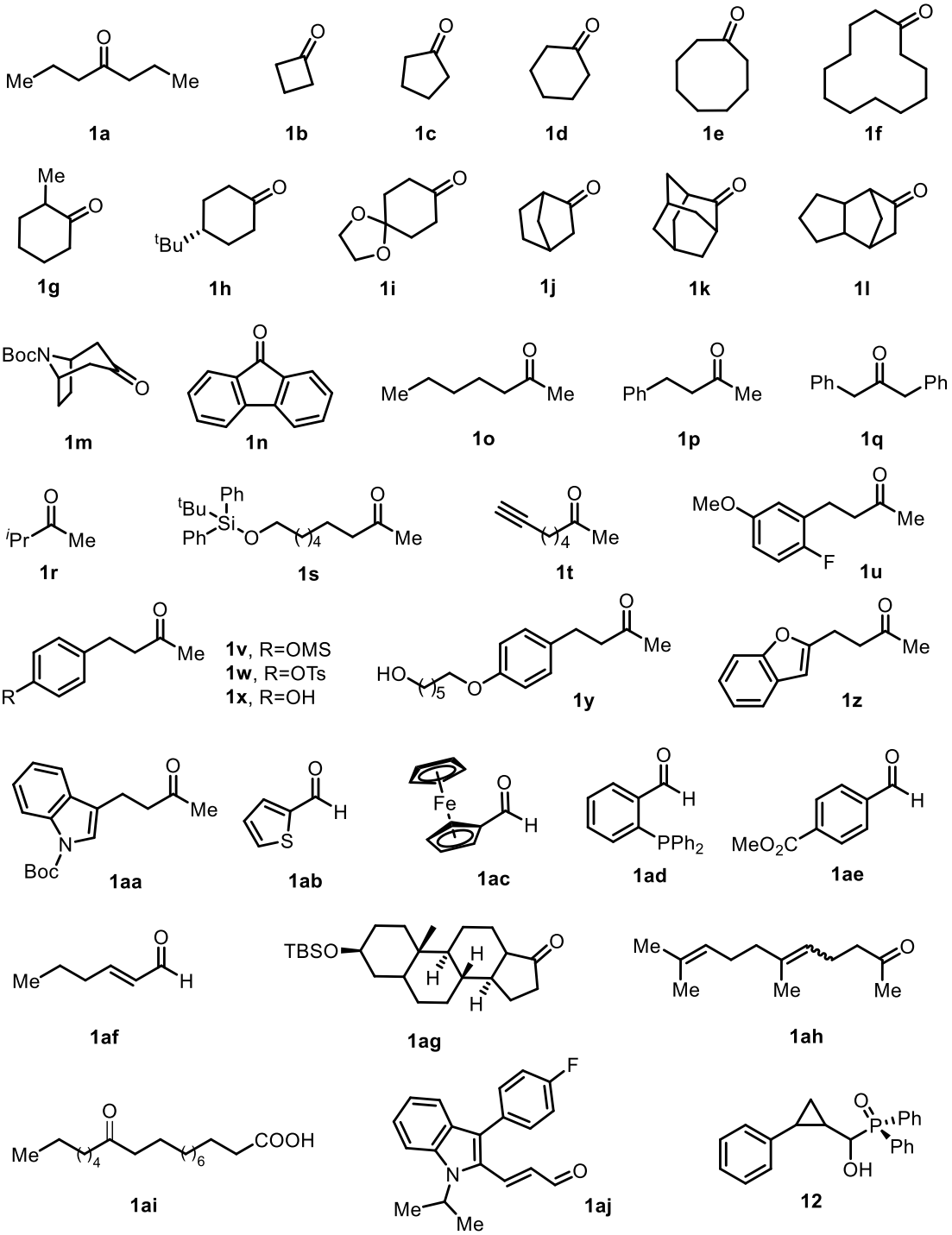
All reactions were carried out under an atmosphere of argon in sealed tube with magnetic stirring. Dry DMF were purified using a solvent-purification system that contained activated alumina and molecular sieves. DMPU and Other solvents were dried and purified according to the procedure from ‘‘Purification of Laboratory Chemicals’’.[1]

Unless otherwise specified, all chemicals used in the preparation of starting materials were commercially available and used as received without further purification. The catalysts, reductants, additives, and other chemicals were purchased from *Acros*, *Alfa Aesar*, *Aldrich*, *Ark Pharm*, *Strem, Adamas*, *TCI* and *Energy chemicals*, and were used directly without further purification.

^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were collected on a Bruker AVANCE III 400MHz, JEOL JNM-ECS 400M and Agilent-NMR-inova 600 MHz spectrometer at room temperature. ^{1}H NMR spectra were reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and were referenced to the signal of TMS (0 ppm). ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.16 ppm). Coupling constants, *J*, are reported in hertz (Hz). Melting points were determined on a microscopic apparatus. IR spectra were collected using Bruker-TENSOR 27 spectrometer and Agilent Technologies Cary 630 FTIR, and only major peaks were reported in cm^{-1}. HRMS was performed on Bruker Apex II FT-ICR mass instrument (ESI) and waters GCT Premier TOFMS (EI). GC analysis was performed on Thermo Scientific TRACE 1300. GC-MS data was collected on Thermo Scientific TRACE DSQ GC-MS. Contact angle of glass surface was analyzed by Contact angle meter SZ-CAMB_3. Thin layer chromatography was carried out using XINNUO SGF254 TLC plates. Flash chromatography was performed using XINNUO silica gel (200-300 mesh).

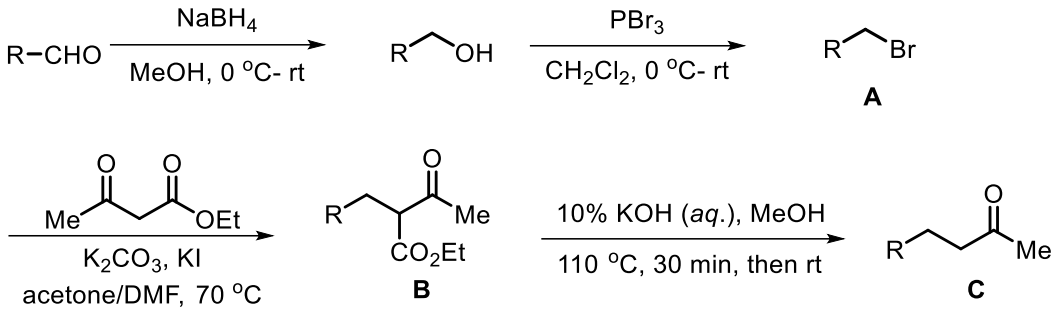
2. Synthesis of Substrates and Ti-Complexes

2.1 Ketones and aldehydes



Ketones **1a-r**, **1t**, **1x**, **1ab-1ah** and **1aj** are commercially available. Ketones **1s**,[2] **1t**,[3] **1w**,[4] **1af**,[5] and **1ai**[6] are known compounds and were prepared according to the literature procedure. The preparation of other compounds, and their characterization data are provided as follows.

General procedure for the preparation of compounds 1u, 1z and 1aa:



Step 1: To a dried round-bottom flask equipped with a magnetic stir bar were added the aldehyde (1.0 equiv) and anhydrous MeOH (50 mL). $NaBH_4$ (0.4 equiv) was then added slowly at 0 °C. After the addition was complete, the mixture was stirred for 30 min, concentrated under reduced pressure, quenched with water, and extracted with ethyl acetate. The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was used directly in the next step without further purification.

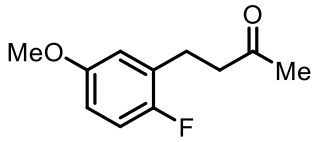
Step 2: The residue obtained from the previous step was dissolved in dichloromethane (DCM, 50 mL). PBr_3 (1.1 equiv) was added dropwise at 0 °C with continuous stirring. The reaction mixture was stirred for 2 h, then quenched with water and extracted with DCM. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford **A**.

Step 3: To a dried round-bottom flask equipped with a magnetic stir bar were added the compound **A** (1.0 equiv), ethyl acetoacetate (1.2 equiv), K_2CO_3 (2.2 equiv), KI (1.0 equiv), DMF (3.75 mL), and acetone (50.0 mL). The reaction mixture was stirred at 70 °C for 16 h, then concentrated under reduced pressure. Water was added to dissolve the solid residues, and the mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by a short silica gel column chromatography to afford crude compound **B**.

Step 4: To a solution of methanol (4.0 mL) and 10% aqueous KOH (4.0 mL) in a dried

round-bottom flask was added compound B. The mixture was refluxed for 30 min, then cooled to room temperature and stirred overnight. The solvent was removed under reduced pressure, the residue was dissolved in water, and the mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by silica gel column chromatography afforded ketone C.

4-(2-Fluoro-5-methoxyphenyl)butan-2-one (1u)



This compound was prepared from 2-fluoro-5-methoxybenzaldehyde (1.54 g, 10.0 mmol) according to General procedure. 1.02 g, 5.2 mmol, 52% yield for four steps, yellow oil, R_f = 0.3 (silica gel, petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.86-6.83 (m, 2 H), 6.75-6.73 (m, 1 H), 3.79 (s, 3 H), 2.85 (t, *J* = 7.2 Hz, 2 H), 2.71 (t, *J* = 7.2 Hz, 2 H), 2.14 (s, 3 H).

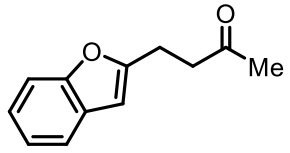
^{13}C NMR (150 MHz, $CDCl_3$) δ 208.2, 157.0 (d, *J* = 237.0 Hz), 153.7, 131.2 (d, J = 7.5 Hz), 116.8 (d, *J* = 22.5 Hz), 113.1 (d, *J* = 24.0 Hz), 111.1 (d, *J* = 7.5 Hz), 55.9, 43.4, 30.0, 24.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -124.3.

IR (neat, cm^{-1}): 2946, 2839, 1717, 1499, 1364, 1217, 1033, 749.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{11}H_{14}FO_2$ 197.0972, found 197.0966.

4-(Benzofuran-2-yl)butan-2-one (1z, known compound)



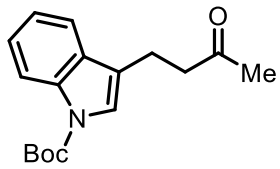
This compound was prepared from benzofuran-2-carbaldehyde (1.46 g, 10.0 mmol) according to General procedure. 0.94 g, 5.0 mmol, 50% yield for four steps, colorless oil, R_f = 0.3 (silica gel, petroleum ether/ethyl acetate = 10:1). ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 7.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.8 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 7.22-7.16 (m, 2 H), 6.39 (s, 1 H), 3.05 (t, *J* = 7.2 Hz, 2 H), 2.88 (t, *J* = 7.2 Hz, 2 H), 2.18 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 206.9, 157.8, 154.8, 128.9, 123.5, 122.7, 120.5, 110.8,

102.5, 41.4, 30.0, 22.7

***tert*-Butyl 3-(3-oxobutyl)-1H-indole-1-carboxylate (1aa, known compound)**

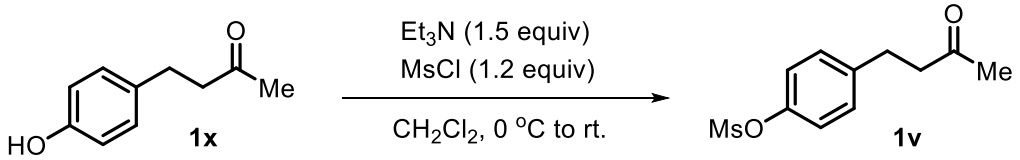


This compound was prepared from *tert*-butyl 3-formyl-1H-indole-1-carboxylate (2.45 g, 10.0 mmol) according to General procedure. 1.18 g, 4.1 mmol, 41% yield for four steps, yellow oil, R_f = 0.3 (silica gel, petroleum ether/ethyl acetate = 5:1). ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 8.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14-8.11 (m, 1 H), 7.52-7.51 (m, 1 H), 7.35-7.30 (m, 2 H), 7.26-7.23 (1 H), 2.97 (t, *J* = 7.8 Hz, 2 H), 2.85 (t, *J* = 7.8 Hz, 2 H), 2.18 (s, 3 H), 1.66 (s, 9 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 208.0, 149.9, 135.7, 130.5, 124.6, 122.6, 122.55, 119.9, 118.9, 115.5, 83.6, 43.2, 30.2, 28.4, 19.0.

4-(3-Oxobutyl)phenyl methanesulfonate (1v)



General procedure: To a 50 mL oven-dried round-bottom flask equipped with a magnetic stir bar were added compound **1x** (0.82 g, 5 mmol), Et_3N (1.1 mL, 1.5 equiv), and anhydrous DCM (20 mL). MsCl (0.5 mL, 1.2 equiv) was introduced dropwise at 0 °C. The reaction was allowed to warm to room temperature and stirred for 12 h. The mixture was quenched with water, extracted with ethyl acetate (3 × 30 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was roughly purified by column chromatography on silica gel to afford **1v** in 91% (1.1 g, white solid, mp: 57.6-58.4 °C) for one step. R_f = 0.5 (silica gel, petroleum ether/ethyl acetate = 10:1).

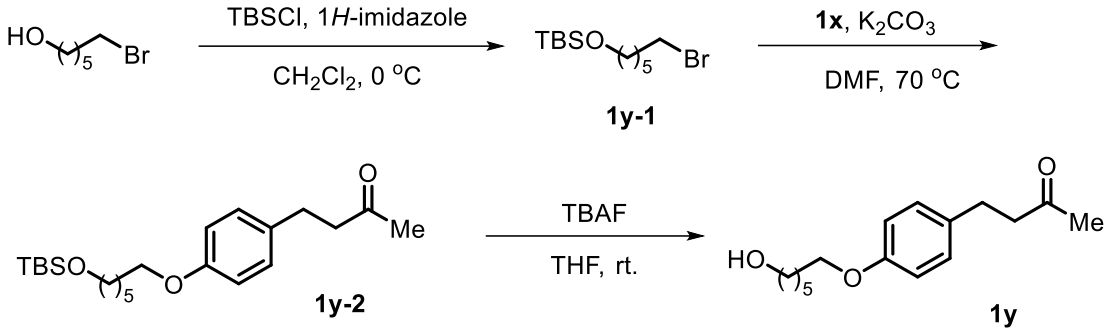
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.18 (m, 4 H), 3.12 (s, 3 H), 2.90 (t, *J* = 7.2 Hz, 2 H), 2.77 (t, *J* = 7.2 Hz, 2 H), 2.15 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 147.6, 140.6, 130.0, 122.1, 44.9, 37.3, 30.2, 29.0.

IR (neat, cm^{-1}): 3025, 1704, 1364, 1174, 1148, 985, 881, 528.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{11}H_{15}O_4S$ 243.0686, found 243.0676.

4-(4-((6-Hydroxyhexyl)oxy)phenyl)butan-2-one (1y)



Step 1: To a dried round-bottom flask equipped with a magnetic stir bar were added 6-bromohexan-1-ol (1.8 g, 10 mmol) and anhydrous THF (20 mL). Imidazole (1.0 g, 15 mmol, 1.5 equiv) in DCM (30 mL) was added dropwise at 0 °C, and the solution was stirred for 30 min. TBSCl (1.7 g, 11 mmol, 1.1 equiv) was then introduced dropwise over 15 min at 0 °C. The reaction was maintained at 0 °C for an additional 30 min, quenched with ice-cold H_2O (50 mL), and extracted with DCM (3 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was roughly purified by column chromatography on silica gel to afford **1y-1** (99% yeild). R_f = 0.6 (silica gel, petroleum ether).

Step 2: To a dried round-bottom flask equipped with a magnetic stir bar were added **1y-1** (1.6 g, 10.0 mmol, 1.0 equiv), K_2CO_3 (1.7 g, 12.0 mmol, 1.2 equiv), and anhydrous DMF (20 mL). The suspension was heated to 70 °C and stirred overnight. Upon completion, the reaction was cooled to room temperature, quenched with water (50 mL), and the mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield **1y-2** (90% yeild). R_f = 0.5 (silica gel, petroleum ether/ethyl acetate = 20:1).

Step 3: To a 50 mL oven-dried round-bottom flask equipped with a magnetic stir bar

was added **1y-2** (2.1 g, 9.0 mmol, 1.0 equiv). The flask was cooled to 0 ºC, and TBAF (2.3 g, 9.0 mmol, 1.0 equiv) was added slowly in one portion. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was then quenched with water (30 mL) at 0 ºC and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield **1y** (2.1g, 80% yield for three steps). R_f = 0.3 (silica gel, petroleum ether/ethyl acetate = 3:1).

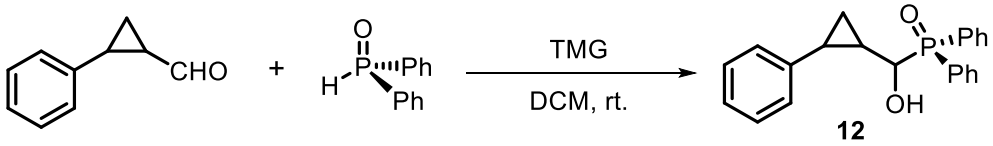
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 2 H), 6.80 (d, *J* = 8.4 Hz, 2 H), 3.93 (t, *J* = 6.4 Hz, 2 H), 3.65 (t, *J* = 6.4 Hz, 2 H), 2.85-2.81 (m, 2 H), 2.74-2.70 (m, 2 H), 2.13 (s, 3 H), 1.80-1.75 (m, 2 H), 1.62-1.58 (m, 2 H), 1.51-1.39 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 157.6, 133.0, 129.3, 114.6, 68.0, 63.0, 45.6, 32.8, 30.2, 29.4, 29.0, 26.0, 25.7.

IR (neat, cm^{-1}): 3411, 2936, 1714, 1513, 1246, 1045, 751.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{16}H_{25}O_3$ 265.1798, found 265.1790.

(Hydroxy(2-phenylcyclopropyl)methyl)diphenylphosphine oxide (12)



12

General procedure: To a solution of 2-phenylcyclopropane-1-carbaldehyde (1.5 g, 10 mmol) and diphenylphosphine oxide (1.0 g, 5.0 mmol) in DCM (20.0 mL) at 0 ºC was dropwise added TMG (1,1,3,3-Tetramethylguanidine, 28.8 mg, 0.25 mmol). The reaction mixture was stirred at room temperature for 0.5–6 h, and concentrated in vacuum. The residue was roughly purified by column chromatography on silica gel to afford **12** in 92% (1.6 g, white solid, mp: 57.6-60.2 ºC). R_f = 0.3 (silica gel, petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94-7.72 (m, 4 H), 7.56-7.35 (m, 6 H), 7.21-7.10 (m, 3 H), 6.96-6.95 (m, 2 H), 4.04-4.02 (m, 1 H), 2.03-1.73 (m, 1 H), 1.48-1.43 (m, 1 H), 1.12-0.99 (m, 1 H), 0.93-0.91 (m, 1 H).

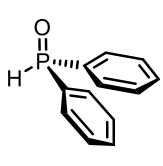
^{13}C NMR (150 MHz, $CDCl_3$) δ 141.8, 141.2, 132.3, 132.2, 132.1, 132.0, 131.9, 131.8, 130.9, 130.1, 128.7, 128.67, 128.6, 128.4, 128.2, 126.3, 126.0, 125.9, 125.8, 74.4, 74.0, 73.8, 73.5, 23.6, 23.5, 23.48., 21.5, 21.4, 14.0.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 31.1.

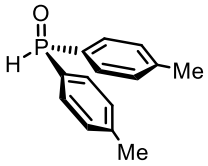
IR (neat, cm^{-1}): 3223, 1604, 1438, 1161, 1120, 722, 695.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{22}O_2P$ 349.1352, found 349.1360.

2.2 Secondary phosphine oxides



2a



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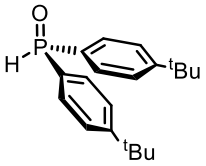

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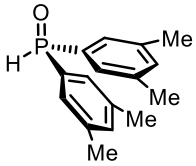

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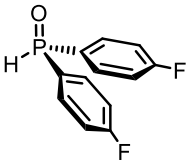

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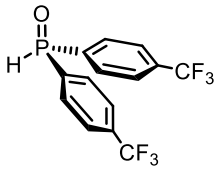
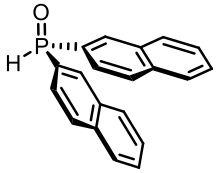


2f



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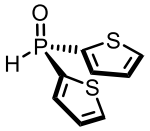
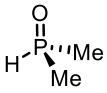
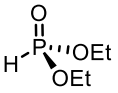


2h



2i

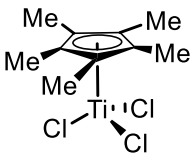


2j

Compounds **2a-2d**, **2f**, **2g, 2i** and **2j** is commercially available. Compounds **2e**[9] and **2h**[10] are known compounds and were prepared according the literature procedure.

2.3 Titanium complexes

3a



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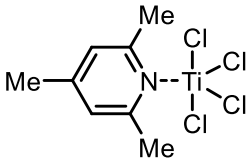

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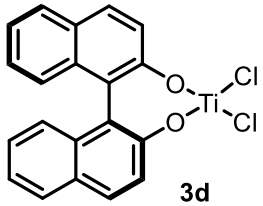
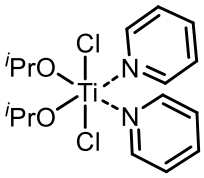


3d



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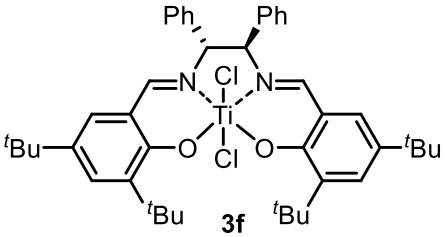

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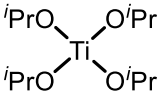
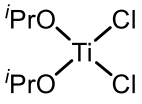


3g



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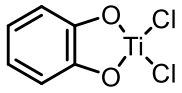

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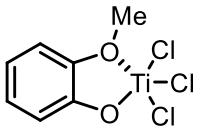
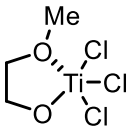
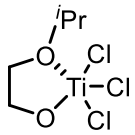


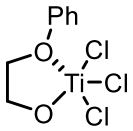
3j



3k



3l

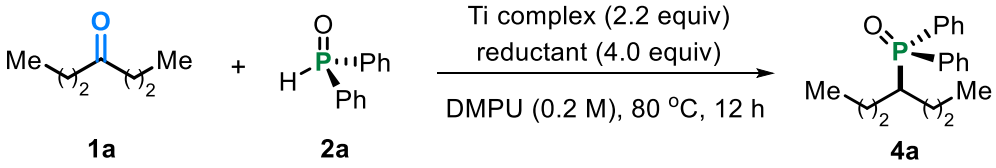


3m

Compounds **3a**, **3b**, **3e**, and **3f** are commercially available. Compounds **3c**[11], **3d**[12], **3g**[13], **3h**[14], **3i**[15], **3j**[16], **3k**[17], **3l**[17] and **3m**[17] are known compounds and were prepared according the literature procedure.

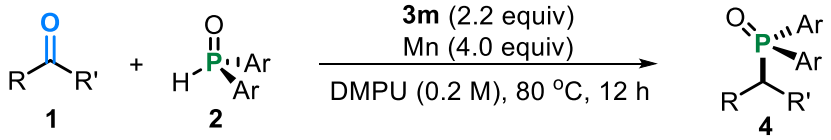
3. Deoxygenative Phosphonation of Ketones by Titanium

3.1 Optimization of reaction parameters



General Procedure I. The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with **1a** (0.1 mmol), **2a** (0.15 mmol, 1.5 equiv), Ti complex (0.22 mmol, 2.2 equiv), reductant (0.4 mmol, 4.0 equiv), and solution (0.5 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short plug of silica gel with EtOAc as an eluent. The solvent was removed under reduced pressure. The residue was applied for ^{1}H HMR analysis to determine the yield by using CH_2Br_2 as an internal standard.

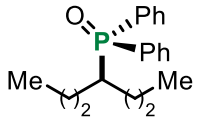
3.2 Reductive Deoxygenative Phosphonation of Ketones



General Procedure II. The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv), **3m** (0.44 mmol, 2.2 equiv), Mn (0.8 mmol, 4.0 equiv), and DMPU (1.0 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 80 °C for 12 h. The reaction was quenched with aqueous HCl (15.0 mL, 2.0 M), and the mixture solution was extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford product **4**.

3.3 Characterization data of products

Heptan-4-yldiphenylphosphine oxide (4a, known compound)



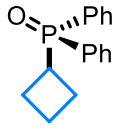
This compound was prepared according to General procedure II from the reaction of **1a** (22.8 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol).48.0 mg, 80% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 18.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.82-7.78 (m, 4 H), 7.49-7.44 (m, 6 H), 7.27-7.23 (m, 1 H), 1.67-1.63 (m, 2 H), 1.55-1.44 (m, 4 H), 1.27-1.22 (m, 2 H), 0.81-0.78 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (150 MHz, CDCl$_3$) δ 133.2 (d, *J* = 93.2 Hz), 131.5 (d, *J* = 2.7 Hz), 131.1 (d, *J* = 8.6 Hz), 128.6 (d, *J* = 11.0 Hz), 37.0 (d, *J* = 70.4 Hz), 29.9, 21.4 (d, *J* = 9.5 Hz), 14.3.

^{31}P NMR (242.9 MHz, CDCl$_3$) δ 36.7.

Cyclobutyldiphenylphosphine oxide (4b, known compound)



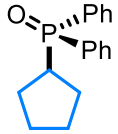
This compound was prepared according to General procedure II from the reaction of **1b** (14.0 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 41.5 mg, 81% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 19.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70-7.65 (m, 4 H), 7.52-7.42 (m, 6 H), 3.36-3.24 (m, 1 H), 2.59-2.46 (m, 2 H), 2.20-2.09 (m, 3 H), 2.07-2.01 (m, 1 H).

^{13}C NMR (150 MHz, CDCl$_3$) δ 132.7 (d, *J* = 96.0 Hz), 131.7 (d, *J* = 3.0 Hz), 131.1 (d, *J* = 9.0 Hz), 128.7 (d, *J* = 12.0 Hz), 32.8 (d, *J* = 76.5 Hz), 21.4, 21.4 (d, *J* = 4.5 Hz), 20.3 (d, *J* = 15.0 Hz).

^{31}P NMR (161.9 MHz, CDCl$_3$) δ 32.3.

Cyclopentyldiphenylphosphine oxide (4c, known compound)



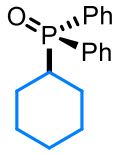
This compound was prepared according to General procedure II from the reaction of **1c** (16.8 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol).48.0 mg, 90% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 19.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.76 (m, 4 H), 7.51-7.44 (m, 6 H), 2.77-2.71 (m, 1 H), 1.98-1.89 (m, 2 H), 1.83-1.71 (m, 4 H), 1.65-1.60 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 133.7 (d, *J* = 94.5 Hz), 131.5 (d, *J* = 3.0 Hz), 131.1 (d, *J* = 9.0 Hz), 128.6 (d, *J* = 12.0 Hz), 37.3 (d, *J* = 76.5 Hz), 27.0 (d, *J* = 9.0 Hz), 26.6.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 35.1.

Cyclohexyldiphenylphosphine oxide (4d, known compound)



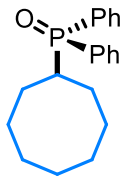
This compound was prepared according to General procedure II from the reaction of **1d** (19.6 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol).43.7 mg, 77% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 19.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80-7.76 (m, 4 H), 7.51-7.45 (m, 6 H), 2.26-2.21 (m, 1 H), 1.82-1.80 (m, 2 H), 1.74-1.70 (m, 3 H), 1.55-1.52 (m, 2 H), 1.30-1.22 (m, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 132.2 (d, *J* = 94.5 Hz), 131.6 (d, *J* = 1.5 Hz), 131.2 (d, *J* = 9.0 Hz), 128.7 (d, *J* = 10.5 Hz), 37.3 (d, *J* = 72.0 Hz), 26.5 (d, *J* = 13.5 Hz), 25.9, 24.9 (d, *J* = 1.5 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 34.5.

Cyclooctyldiphenylphosphine oxide (4e, known compound)



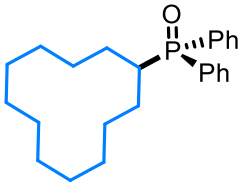
This compound was prepared according to General procedure II from the reaction of **1e** (25.2 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 58.1 mg, 93% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 20.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.77 (m, 4 H), 7.49-7.44 (m, 6 H), 2.50-2.43 (m, 1 H), 1.86-1.79 (m, 2 H), 1.74-1.66 (m, 4 H), 1.64-1.55 (m, 6 H), 1.45-1.38 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 132.8 (d, *J* = 93.0 Hz), 131.5 (d, *J* = 1.5 Hz), 131.1 (d, *J* = 9.0 Hz), 128.6 (d, *J* = 10.5 Hz), 35.7 (d, *J* = 69.0 Hz), 27.1, 26.4 (d, *J* = 13.5 Hz), 26.1, 25.9.

^{31}P NMR (161.9 MHz, $CDCl_3$) δ 38.7.

Cyclododecyldiphenylphosphine oxide (4f)



This compound was prepared according to General procedure II from the reaction of **1f** (36.4 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 62.6 mg, 85% yield, white solid, mp: 167.9-168.4 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83-7.80 (m, 4 H), 7.49-7.44 (m, 6 H), 2.43-2.38 (m, 1 H), 1.71-1.62 (m, 4 H), 1.43-1.19 (m, 18 H).

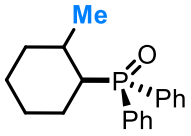
^{13}C NMR (150 MHz, $CDCl_3$) δ 133.4 (d, J = 93.0 Hz), 131.5 (d, J = 3.0 Hz), 131.0 (d, J = 9.0 Hz), 128.6 (d, J = 10.5 Hz), 33.8 (d, J = 70.5 Hz), 24.7, 24.1, 23.8, 23.6, 23.5, 23.04, 23.0.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 36.2.

IR (neat, cm^{-1}): 2930, 2864, 1471, 1438, 1178, 1117, 913, 744, 718, 697, 593, 541.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{24}H_{34}OP$ 369.2342, found 369.2342.

(2-Methylcyclohexyl)diphenylphosphine oxide (4g)



This compound was prepared according to General procedure II from the reaction of **1g** (33.6 mg, 0.3 mmol) and **2a** (40.4 mg, 0.2 mmol). 54.3 mg, 91% yield, dr = 1:1, white solid, mp: 150.2-151.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89-7.14 (m, 4 H), 7.49-7.42 (m, 6 H), 2.40-1.65 (m, 5 H), 1.56-1.45 (m, 3 H), 1.35-1.17 (m, 2 H), [1.13 (d, J = 7.2 Hz), 0.79 (d, J = 6.6 Hz), 3 H].

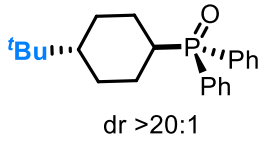
^{13}C NMR (150 MHz, $CDCl_3$) δ 134.5 (dd, J_1 = 268.5 Hz, J_2 = 91.5 Hz), 133.2 (dd, J_1 = 94.5 Hz, J_2 = 85.5 Hz), 131.4 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz), 131.2 (dd, J_1 = 24.0 Hz, J_2 = 3.0 Hz), 131.0 (dd, J_1 = 8.3 Hz, J_2 = 3.0 Hz), 130.8 (dd, J_1 = 55.5 Hz, J_2 = 8.0 Hz), 128.6 (t, J = 12.0 Hz), 42.9 (d, J = 70.4 Hz), 41.0 (d, J = 71.6 Hz), 36.1 (d, J = 10.5 Hz), 34.4 (d, J = 12.0 Hz), 32.6 (d, J = 3.0 Hz), 28.1, 26.9 (d, J = 13.5 Hz), 26.5, 26.4 (d, J = 13.5 Hz), 25.5, 22.8 (d, J = 4.5 Hz), 20.2, 19.7, 14.7.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 34.0, 32.9.

IR (neat, cm^{-1}): 3056, 2927, 2855, 1438, 1276, 1182, 1115, 913, 748, 559.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{19}H_{24}OP$ 299.1559, found 299.1559.

(Trans-4-(*tert*-Butyl)cyclohexyl)diphenylphosphine oxide (4h, known compound)



dr >20:1

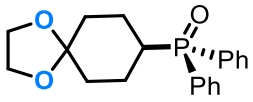
This compound was prepared according to General procedure II from the reaction of **1h** (30.8 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 32.7 mg, 48% yield, dr >20:1, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 21.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.75 (m, 4 H), 7.50-7.46 (m, 6 H), 2.21-2.14 (m, 1 H), 1.87-1.80 (m, 4 H), 1.54-1.52 (m, 2 H), 1.02-1.00 (m, 3 H), 0.82 (s, 9 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 132.2 (d, J = 93.0 Hz), 131.6 (d, J = 1.5 Hz), 131.2 (d, J = 9.0 Hz), 128.7 (d, J = 10.5 Hz), 47.4, 37.3 (d, J = 72.0 Hz), 32.5, 27.5, 27.4 (d, J = 13.5 Hz), 25.4 (d, J = 3.0 Hz).

^{31}P NMR (161.9 MHz, $CDCl_3$) δ 34.4.

Diphenyl(1,4-dioxaspiro[4.5]decan-8-yl)phosphine oxide (4i)



This compound was prepared according to General procedure II from the reaction of **1i** (31.2 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol).51.3 mg, 75% yield, white solid, mp: 202.5-204.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80-7.77 (m, 4 H), 7.53-7.46 (m, 6 H), 3.92-3.88 (m, 4 H), 2.25-2.22 (m, 1 H), 1.86-1.79 (m, 6 H), 1.56-1.51 (m, 2 H).

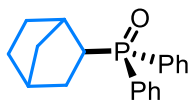
^{13}C NMR (150 MHz, $CDCl_3$) δ 132.4, 131.8 (d, J = 3.0 Hz), 131.3 (d, J = 9.0 Hz), 128.8 (d, J = 10.5 Hz), 108.0, 64.5 (d, J = 10.5 Hz), 36.4 (d, J = 72.0 Hz), 35.0 (d, J = 13.5 Hz), 23.0.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 34.0.

IR (neat, cm^{-1}): 3444, 1620, 1276, 1261, 764, 750.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{20}H_{24}O_3P$ 343.1458, found 343.1458.

Bicyclo[2.2.1]heptan-2-yldiphenylphosphine oxide (4j, known compound)



This compound was prepared according to General procedure II from the reaction of **1j** (22.0 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 48.6 mg, 82% yield, dr = 1:1, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 20.

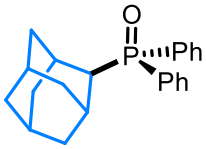
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2 H), 7.73-7.70 (m, 2 H), 7.51-7.41 (m,

6 H), 2.60-2.58 (m, 1 H), 2.39-2.36 (m, 2 H), 2.34-2.29 (m, 1 H), 1.86-1.80 (m, 1 H), 1.77-1.71 (m, 1 H), 1.55-1.47 (m, 2 H), 1.39-1.35 (m, 2 H), 1.29-1.25 (m, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 134.5 (dd, J_1 = 132.0 Hz, J_2 = 96.0 Hz), 131.4 (dd, J_1 = 6.0 Hz, J_2 = 3.0 Hz), 130.9 (dd, J_1 = 52.5 Hz, J_2 = 9.0 Hz), 128.6 (dd, J_1 = 10.5 Hz, J_2 = 3.0 Hz), 41.5 (d, J = 13.5 Hz), 39.7 (dd, J_1 = 39.0 Hz, J_2 = 37.5 Hz), 37.7 (d, J = 4.5 Hz), 30.3, 29.3, 25.4 (d, J = 4.5 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 32.7.

Adamantan-2-yldiphenylphosphine oxide (4k, known compound)



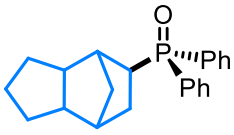
This compound was prepared according to General procedure II from the reaction of **1k** (30.0 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol).45.7 mg, 68% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 22.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81-7.78 (m, 4 H), 7.49-7.44 (m, 6 H), 2.66 (d, J = 12.0 Hz, 2 H), 2.51 (d, J = 6.0 Hz, 1 H), 2.11-2.10 (m, 2 H), 1.97-1.95 (m, 2 H), 1.86-1.82 (m, 2 H), 1.75-1.73 (m, 4 H), 1.56 (d, J = 12.6 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 133.6 (d, J = 93.0 Hz), 131.3 (d, J = 3.0 Hz), 131.0 (d, J = 7.5 Hz), 128.7 (d, J = 10.5 Hz), 44.0 (d, J = 70.5 Hz), 40.1 (d, J = 13.5 Hz), 37.5, 33.2, 28.6 (d, J = 3.0 Hz), 28.2, 27.3.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 33.8.

(Octahydro-1H-4,7-methanoinden-5-yl)diphenylphosphine oxide (4l)



This compound was prepared according to General procedure II from the reaction of **1l** (30.0 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol).45.0 mg, 67% yield, dr =1:1, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82-7.70 (m, 4 H), 7.50-7.42 (m, 6 H), [2.93 (q, J = 9.0 Hz), 2.55-2.52 (m), 1 H], 2.25-2.06 (m, 3 H), 1.96-1.53 (m, 6 H), 1.36-1.04 (m, 3 H), 0.95-0.72 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 135.0 (d, J = 94.5 Hz), 134.3, 134.1, 133.6, 133.4, 131.5, 131.46, 131.4, 131.3, 131.1, 131.07, 131.0, 130.98, 130.8, 130.7, 128.7, 128.7, 128.6, 128.57, 128.5, 50.8, 50.7, 47.9, 47.8, 43.8, 42.6, 42.56, 42.0, 41.98, 41.0, 40.95,

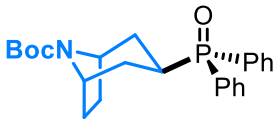
40.2, 39.7, 39.4, 38.9, 35.0, 34.9, 32.52, 32.5, 32.4, 31.9, 31.8, 31.1, 30.5, 30.48, 29.5, 27.3, 27.0.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 34.3, 33.1.

IR (neat, cm^{-1}): 2944, 1592, 1427, 1183, 1118, 913, 702, 540.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{26}OP$ 337.1716, found 337.1707.

***tert*-Butyl-(1R,5S)-3-(diphenylphosphoryl)-8-azabicyclo[3.2.1]octane-8-carboxylate (4m)**



This compound was prepared according to General procedure II from the reaction of **1m** (45.0 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol).66.6 mg, 81% yield, dr = 6:1, white solid, mp: 202.2-203.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.75 (m, 4 H), 7.51-7.45 (m, 6 H), 4.25-4.14 (m, 2 H), 2.41-2.34 (m, 1 H), 2.23-2.11 (m, 2 H), 1.95-1.64 (6 H), 1.48 (s, 9 H).

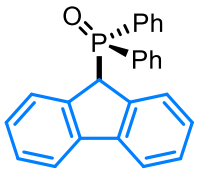
^{13}C NMR (150 MHz, $CDCl_3$) δ 154.7,131.7, 131.0 (d, *J* = 9.0 Hz), 128.8 (d, J = 9.0 Hz), 79.4, 51.3 (d, *J* = 94.5 Hz), 30.8, 30.4, 29.7, 28.9, 28.6, 27.4, 26.9.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 34.0.

IR (neat, cm^{-1}): 2974, 2929, 1690, 1392, 1333, 1249, 1181, 1103, 1033703, 540.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{24}H_{31}NO_3P$ 412.2036, found 412.2036.

(9H-Fluoren-9-yl)diphenylphosphine oxide (4n, known compound)



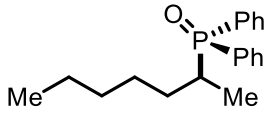
This compound was prepared according to General procedure II from the reaction of **1n** (36.0 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 32.2 mg, 44% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 24.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 2 H), 7.46-7.40 (m, 6 H), 7.33-7.31 (m, 6 H), 7.26-7.25 (m, 2 H), 7.16-7.14 (m, 2 H), 5.13 (d, *J* = 23.4 Hz, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 142.0 (d, *J* = 4.5 Hz), 139.2 (d, *J* = 4.5 Hz), 132.6 (d, *J* = 3.0 Hz), 131.8 (d, *J* = 9.0 Hz), 130.1 (d, *J* = 97.5 Hz), 128.3 (d, *J* = 12 Hz), 127.9, 127.0, 126.3 (d, *J* = 3.0 Hz), 120.0, 50.8 (d, *J* = 61.5 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 33.6.

Heptan-2-yldiphenylphosphine oxide (4o, known compound)



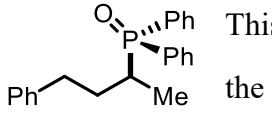
This compound was prepared according to General procedure II from the reaction of **1o** (22.8 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 54.0 mg, 90% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 23.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81-7.76 (m, 4 H), 7.52-7.44 (m, 6 H), 2.2-2.33 (m, 1 H), 1.66-1.60 (m, 1 H), 1.51-1.44 (m, 2 H), 1.25-1.14 (m, 8 H), 0.83 (t, *J* = 6.6 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 132.5 (d, *J* = 93.0 Hz), 132.4 (d, J = 94.5 Hz), 131.6 (d, *J* = 3.0 Hz), 131.5 (d, *J* = 3.0 Hz), 131.1 (d, *J* = 9.0 Hz), 128.7 (d, *J* = 10.5 Hz), 128.6 (d, *J* = 12.0 Hz),, 32.1 (d, *J* = 72.0 Hz), 31.6, 28.8, 27.2 (d, *J* = 13.5 Hz), 22.6, 14.1, 12.1 (d, *J* = 1.5 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 37.4.

Diphenyl(4-phenylbutan-2-yl)phosphine oxide (4p, known compound)



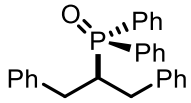
This compound was prepared according to General procedure II from the reaction of **1p** (29.6 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 44.8 mg, 67% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 19.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70-7.62 (m, 4 H), 7.48-7.47 (m, 2 H), 7.43-7.41 (m, 4 H), 7.28-7.25 (m, 2 H), 7.22-7.19 (m, 1 H), 7.06 (d, *J* = 7.2 Hz, 2 H), 2.88-2.84 (m, 1 H), 2.58-2.53 (m, 1 H), 2.35-2.31 (m, 1 H), 2.00-1.95 (m, 1 H), 1.83-1.76 (m, 1 H), 1.22 (dd, J_1 = 16.8 Hz, J_2 = 7.2 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 141.1, 132.3 (d, J_1 = 94.5 Hz, J_2 = 57.0 Hz), 131.6 (d, *J* = 3.0 Hz), 131.5 (d, *J* = 3.0 Hz), 131.2, 131.1, 131.06, 128.7, 128.69, 128.6, 128.5, 126.2, 33.2 (d, *J* = 12.0 Hz), 31.0, 31.5, 11.9 (d, *J* = 3.0 Hz)

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 36.9.

(1,3-diphenylpropan-2-yl)diphenylphosphine oxide (**4q**)



This compound was prepared according to General procedure II from the reaction of **1q** (42.0 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 53.9 mg, 68% yield, white solid, mp: 203.1-203.4 ºC.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.75 (m, 4 H), 7.42--7.39 (m, 2 H), 7.36-7.34 (m, 4 H), 7.06-7.02 (m, 6 H), 6.80-6.79 (m, 4 H), 3.09-3.04 (m, 2 H), 2.94-2.90 (m, 1 H), 2.87-2.81 (m, 2 H).

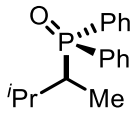
^{13}C NMR (150 MHz, $CDCl_3$) δ 139.9 (d, *J* = 9.0 Hz), 132.8 (d, *J* = 94.5 Hz), 131.5, 131.47, 130.9 (d, J = 7.5 Hz), 129.1, 128.7, 128.6, 128.3, 126.2, 42.3 (d, J = 69.0 Hz), 33.9.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 34.4.

IR (neat, cm^{-1}): 3058, 3027, 2923, 1604, 1438, 1178, 1118, 700, 545.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{27}H_{26}OP$ 397.1716, found 397.1717.

(3-Methylbutan-2-yl)diphenylphosphine oxide (**4r**)



This compound was prepared according to General procedure II from the reaction of **1r** (17.2 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 32.1 mg, 59% yield, white solid, mp: 158.8-159.4 ºC.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83-7.79 (m, 4 H), 7.49-7.45 (m, 6 H), 2.34-2.29 (m, 1 H), 2.18-2.12 (m, 1 H), 1.14-1.09 (m, 3 H), 1.02-0.97 (m, 6 H).

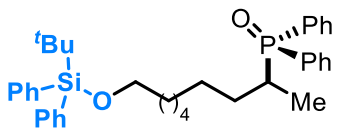
^{13}C NMR (150 MHz, $CDCl_3$) δ 133.7 (d, J = 93.0 Hz), 133.3 (d, J = 94.5 Hz), 131.4 (d, J = 1.5 Hz), 131.4 (d, J = 3.0 Hz), 131.0 (d, J = 1.5 Hz), 131.0, 128.7 (d, J = 105 Hz), 128.6 (d, J = 10.5 Hz), 37.8, 37.3, 26.8, 23.0, 22.9, 6.6 (d, J = 1.5 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 36.1.

IR (neat, cm^{-1}): 2960, 1592, 1438, 1182, 1117, 707, 537.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{17}H_{22}OP$ 273.1403, found 273.1394.

(9-((*tert*-Butyldiphenylsilyl)oxy)nonan-2-yl)diphenylphosphine oxide (4s)



This compound was prepared according to General procedure II from the reaction of **1s** (79.2 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 96.7 mg, 83% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80-7.77 (m, 4 H), 7.67-7.65 (m, 4 H), 7.49-7.43 (m, 6 H), 7.42-7.35 (m, 6 H), 3.63 (t, J = 6.6 Hz, 2 H), 2.36-2.31 (m, 1 H), 1.65-1.59 (m, 1 H), 1.53-1.43 (m, 4 H), 1.29-1.14 (m, 10 H), 1.04 (s, 9 H).

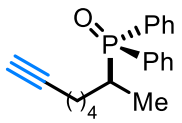
^{13}C NMR (150 MHz, $CDCl_3$) δ 135.7, 134.3, 132.9 (d, J = 13.5 Hz), 132.3 (d, J = 13.5 Hz), 131.5 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz), 131.1 (d, J = 9.0 Hz), 129.6, 128.6 (dd, J_1 = 10.5 Hz, J_2 = 4.5 Hz), 127.7, 64.0, 32.6, 32.1 (d, J = 72.0 Hz), 29.3 (d, J = 18.0 Hz), 28.8, 27.5 (d, J = 12.0 Hz), 27.0, 25.8, 19.3, 12.2 (d, J = 3.0 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 37.0.

IR (neat, cm^{-1}): 3054, 2932, 2858, 1428, 1186, 1113, 702, 542.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{37}H_{48}O_2PSi$ 583.3156, found 583.3135.

Oct-7-yn-2-yldiphenylphosphine oxide (4t)



This compound was prepared according to General procedure II from the reaction of **1t** (24.8 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 31.6 mg, 51% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81-7.77 (m, 4 H), 7.51-7.47 (m, 6 H), 2.38-2.34 (m, 1 H), 2.14-2.10 (m, 2 H), 1.91 (t, J = 3.0 Hz, 1 H), 1.65-1.60 (m, 2 H), 1.51-1.37 (m, 4 H), 1.17 (dd, J_1 = 16.8 Hz, J_2 = 7.2 Hz, 3 H).

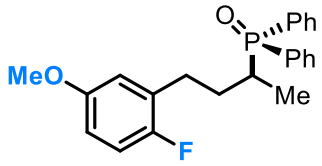
^{13}C NMR (150 MHz, $CDCl_3$) δ 132.5 (d, J = 94.5 Hz), 131.7 (d, J = 1.5 Hz), 131.6 (d, J = 3.0 Hz), 131.2,131.18,131.17,131.1, 128.8, 128.74, 128.7, 128.67, 84.4, 68.5, 32.1 (d, J = 72.0 Hz), 28.4, 28.2, 26.7, 26.6, 18.3, 12.2.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 36.8.

IR (neat, cm^{-1}): 2925, 1592, 1270, 1119, 697.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{20}H_{24}OP$ 311.1559, found 311.1550.

(4-(2-Fluoro-5-methoxyphenyl)butan-2-yl)diphenylphosphine oxide (4u)



This compound was prepared according to General procedure II from the reaction of **1u** (39.2 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 61.9 mg, 81% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71-7.64 (m, 4 H), 7.49-7.40 (m, 6 H), 6.88-6.85 (m, 1 H), 6.74-6.70 (m, 2 H), 3.64 (s, 3 H), 2.82-2.77 (m, 1 H), 2.61-2.57 (m, 1 H), 2.33-2.71 (m, 1 H), 1.99-1.94 (m, 1 H), 1.72-1.67 (m, 1 H), 1.24 (dd, J_1 = 16.8 Hz, J_2 = 6.6 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.9 (d, J = 235.5 Hz), 153.7 (d, J = 1.5 Hz), 132.4 (dd, J_1 = 93.0 Hz, J_2 = 63.0 Hz), 131.6,131.5, 131.3 (d, J = 7.5 Hz), 131.2, 131.15, 131.1, 131.07, 116.9 (d, J = 22.5 Hz), 113.0 (d, J = 22.5 Hz), 111.0 (d, J = 7.5 Hz), 55.7, 31.4 (d, J = 72.0 Hz), 28.9, 28.0 (d, J = 13.5 Hz), 11.9 (d, J = 3.0 Hz).

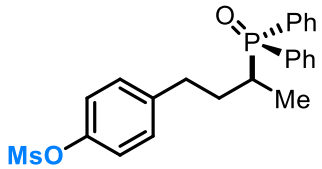
^{19}F NMR (376 MHz, $CDCl_3$) δ -124.4.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 37.0.

IR (neat, cm^{-1}): 2931, 1592, 1498, 1438, 1219, 1181, 1118, 1031, 721.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{25}FO_2P$ 383.1571, found 383.1561.

4-(3-(Diphenylphosphoryl)butyl)phenyl methanesulfonate (4v)



This compound was prepared according to General procedure II from the reaction of **1v** (48.4 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 77.9 mg, 91% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.65 (m, 4 H), 7.51-7.43 (m, 6 H), 7.18-7.08 (m, 4 H), 3.14 (s, 3 H), 2.89-2.84 (m, 1 H), 2.60-2.55 (m, 1 H), 2.35-2.31 (m, 1 H), 1.98-1.94 (m, 1 H), 1.82-1.77 (m, 1 H), 1.23 (dd, J_1 = 16.2 Hz, J_2 = 6.6 Hz, 3 H).

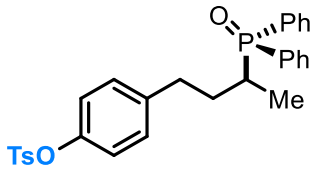
^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 140.7, 132.1 (dd, J_1 = 94.5 Hz, J_2 = 21.0 Hz), 131.7 (dd, J_1 = 12.0 Hz, J_2 = 3.0 Hz), 131.1 (dd, J_1 = 9.0 Hz, J_2 = 7.5 Hz), 130.1, 128.8 (dd, J_1 = 9.8 Hz, J_2 = 8.9 Hz), 122.1, 37.5, 32.6 (d, J = 12.0 Hz), 31.0 (d, J = 72.0 Hz), 30.6, 12.13, 12.0.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 36.7.

IR (neat, cm^{-1}): 3056, 2931, 1619, 1503, 1438, 1366, 1175, 1149, 1118, 970, 870, 721, 543.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{26}O_4PS$ 429.1284, found 429.1283.

4-(3-(Diphenylphosphoryl)butyl)phenyl 4-methylbenzenesulfonate (4w)



This compound was prepared according to General procedure II from the reaction of **1w** (63.6 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol).70.6 mg, 70% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.61 (m, 6 H), 7.52-7.40 (m, 6 H), 7.32-7.30 (m, 2 H), 6.97-6.95 (m, 2 H), 6.88-6.86 (m, 2 H), 2.83-2.77 (m, 1 H), 2.56-2.48 (m, 1 H), 2.44 (s, 3 H), 2.30-2.25 (m, 1 H), 1.98-1.87 (m, 1 H), 1.79-1.71 (m, 1 H), 1.20 (dd, J_1 = 16.8 Hz, J_2 = 7.2 Hz, 3 H).

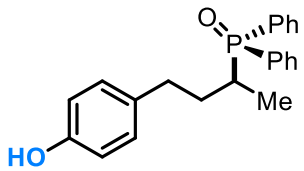
^{13}C NMR (150 MHz, $CDCl_3$) δ 148.0, 145.5, 140.2, 132.6, 132.1 (d, J = 63.0 Hz), 131.7 (dd, J_1 = 12.0 Hz, J_2 = 3.0 Hz), 131.1 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz), 129.9, 129.7, 128.7 (dd, J_1 = 12.0 Hz, J_2 = 9.0 Hz), 128.6, 122.4, 32.6 (d, J = 12.0 Hz), 30.9 (d, J = 72.0 Hz), 30.5, 21.9, 12.0 (d, J = 3.0 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 36.8.

IR (neat, cm^{-1}): 3441, 3056, 2930, 1598, 1438, 1372, 1197, 1177, 1152, 1117, 1094, 913, 867, 748, 539.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{29}H_{30}O_4PS$ 505.1597, found 505.1595.

(4-(4-Hydroxyphenyl)butan-2-yl)diphenylphosphine oxide (4x)



This compound was prepared according to General procedure II from the reaction of **1x** (32.8 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol).56.0 mg, 80% yield, white solid, mp: 177.9-179.2 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (s, 1 H), 7.71-7.67 (m, 4 H), 7.47-7.41 (m, 6 H), 6.86-6.86 (m, 4 H), 2.77-2.73 (m, 1 H), 2.46-2.38 (m, 2 H), 2.00-1.93 (m, 1 H), 1.76-

1.71 (m, 1 H), 1.23-1.90 (dd, J_1 = 16.8 Hz, J_2 = 6.6 Hz, 3 H).

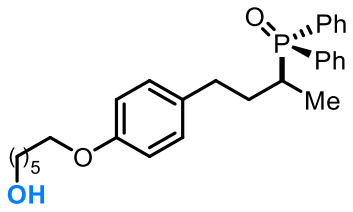
^{13}C NMR (150 MHz, CDCl$_3$) δ 155.8 (d, J = 4.5 Hz), 131.8 (dd, J_1 = 16.5 Hz, J_2 = 3.0 Hz), 131.7 (d, J = 94.5 Hz), 131.5 (d, J = 6.0 Hz), 131.1 (dd, J_1 = 9.0 Hz, J_2 = 1.5 Hz), 115.7, 32.5 (dd, J_1 = 13.5 Hz, J_2 = 1.5 Hz), 31.0, 30.9 (dd, J_1 = 72.0 Hz, J_2 = 6.0 Hz), 12.0.

^{31}P NMR (242.9 MHz, CDCl$_3$) δ 39.4.

IR (neat, cm^{-1}): 3146, 1593, 1516, 1438, 1275, 1262, 1164, 1119, 764, 751, 722, 696, 546.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{24}O_2P$ 351.1508, found 351.1505.

(4-(4-((6-Hydroxyhexyl)oxy)phenyl)butan-2-yl)diphenylphosphine oxide (4y)



This compound was prepared according to General procedure II from the reaction of **1y** (52.8 mg, 0.2 mmol) and **2a** (60.6, 0.3 mmol).67.5 mg, 75% yield, colorless oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.70-7.62 (m, 4 H), 7.49-7.45 (m, 2 H), 7.43-7.40 (m, 4 H), 6.96-6.95 (m, 2 H), 6.81-6.79 (m, 2 H), 3.94 (t, J = 6.6 Hz, 2 H), 3.66 (t, J = 6.6 Hz, 2 H), 2.81-2.77 (m, 1 H), 2.52-2.47 (m, 1 H), 2.34-2.39 (m, 1 H), 1.96-1.91 (m, 2 H), 1.81-1.72 (m, 3 H), 1.63-1.59 (m, 2 H), 1.53-1.41 (m, 4 H), 1.20 (dd, J_1 = 16.8 Hz, J_2 = 7.2 Hz, 3 H).

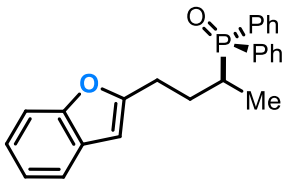
^{13}C NMR (150 MHz, CDCl$_3$) δ 157.6, 132.9, 132.3 (dd, J_1 = 94.5 Hz, J_2 = 57.0 Hz), 131.6 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz), 131.1 (t, J = 9.0 Hz), 129.6, 128.6 (dd, J_1 = 12.0 Hz, J_2 = 3.0 Hz), 114.6, 68.0, 62.9, 32.8, 32.2 (d, J = 13.5 Hz), 30.8, 30.6, 30.4, 29.4, 26.0, 25.7, 11.8 (d, J = 3.0 Hz).

^{31}P NMR (242.9 MHz, CDCl$_3$) δ 37.3.

IR (neat, cm^{-1}): 3356, 2934, 2861, 1612, 1512, 1438, 1245, 1177, 1118, 1071, 913, 748, 722.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{28}H_{36}O_3P$ 451.2397, found 451.2395.

(4-(Benzofuran-2-yl)butan-2-yl)diphenylphosphine oxide (4z)



This compound was prepared according to General procedure II from the reaction of **1z** (37.6 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 51.6 mg, 69% yield, white solid, mp: 143.4-144.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73-7.68 (m, 4 H), 7.49-7.46 (m, 3 H), 7.43-7.38 (m, 5 H), 7.25-7.19 (m, 2 H), 6.34 (s, 1 H), 2.99-2.94 (m, *J* = 1 H), 2.82-2.76 (m, 1 H), 2.44-2.37 (m, 1 H), 2.19-2.15 (m, 1 H), 1.91-1.84 (m, 1 H), 1.23 (dd, J_1 = 16.8 Hz, J_2 = 7.2 Hz, 3 H).

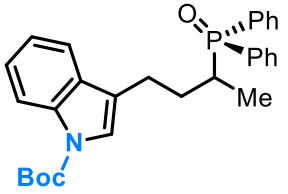
^{13}C NMR (150 MHz, $CDCl_3$) δ 157.9, 154.8, 132.6, 132.4, 132.0, 131.7, 131.72, 131.6 (d, *J* = 1.5 Hz), 131.2 (d, J = 1.5 Hz), 131.1 (d, J = 1.5 Hz), 128.9, 128.8 (d, 6.0 Hz), 128.7 (d, J = 4.5 Hz), 123.5, 122.7, 120.5, 110.9, 103.0, 31.0 (d, J = 72.0 Hz), 27.3, 26.0 (d, J = 12.0 Hz), 12.0 (d, J = 3.0 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 36.8.

IR (neat, cm^{-1}): 2932, 1600, 1455, 1438, 1252, 1182, 1118, 721.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{24}H_{24}O_2P$ 375.1508, found 375.1499.

***tert*-Butyl 3-(3-(diphenylphosphoryl)butyl)-1H-indole-1-carboxylate (4aa)**



This compound was prepared according to General procedure II from the reaction of **1aa** (57.4 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 61.5 mg, 65% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (s, 1 H), 7.71-7.63 (m, 4 H), 7.48-7.44 (m, 2 H), 7.42-7.39 (m, 2 H), 7.36-7.33 (m, 2 H), 7.32-7.26 (m, 3 H), 7.16-7.14 (m, 1 H), 2.93-2.89 (m, 1 H), 2.71-2.66 (m, 1 H), 2.42-2.38 (m, 1 H), 2.13-2.10 (m, 1 H), 1.88-1.84 (m, 1 H), 1.68 (s, 9 H), 1.26 (dd, J_1 = 16.8 Hz, J_2 = 7.2 Hz, 3 H).

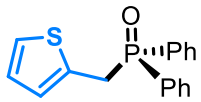
^{13}C NMR (150 MHz, $CDCl_3$) δ 132.5 (d, *J* = 93.0 Hz), 132.1 (d, *J* = 94.5 Hz), , 131.8,131.61,131.6, 131.58, 131.56, 131.1 (d, *J* = 9.0 Hz), 130.5, 128.7 (d, *J* = 1.5 Hz), 128.6 (d, *J* = 3.0 Hz), 124.5, 122.9, 122.5, 119.7, 119.1, 115.4, 83.7, 31.3 (d, *J* = 72.0 Hz), 28.6, 28.4, 22.7 (d, *J* = 13.5 Hz), 12.0 (d, *J* = 3.0 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 36.9.

IR (neat, cm^{-1}): 2084, 1728, 1638, 1453, 137, 1258, 1158, 748.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{29}H_{33}NO_3P$ 474.2193, found 474.2183.

Diphenyl(thiophen-2-ylmethyl)phosphine oxide (4ab, known compound)



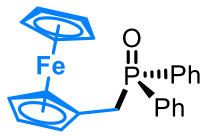
This compound was prepared according to General procedure II from the reaction of **1ab** (22.4 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 39.9 mg, 67% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 25.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74-7.71 (m, 4 H), 7.53-7.45 (m, 6 H), 7.08-7.07 (m, 1 H), 6.85-6.84 (m, 2 H), 3.89-3.87 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1 (d, J = 1.0 Hz), 131.3 (d, J = 9.0 Hz), 130.8 (d, J = 11.0 Hz), 129.0 (d, J = 12.0 Hz), 128.7 (d, J = 11.0 Hz), 127.9 (d, J = 6.0 Hz), 127.1 (d, J = 2.0 Hz), 125.0 (d, J = 3.0 Hz), 32.7.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 28.6.

(Ferrocenylmethyl)diphenylphosphine oxide (4ac, known compound)



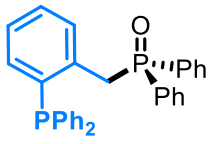
This compound was prepared according to General procedure II from the reaction of **1ac** (42.8 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 47.2 mg, 59% yield, yellow solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 26.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.65 (m, 4 H), 7.50-7.48 (m, 2 H), 7.43-7.41 (m, 4 H), 4.08 (s, 5 H), 4.01 (d, J = 7.2 Hz, 4 H), 3.42 (d, J = 12.6 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 132.4 (d, J = 97.5 Hz), 131.8 (d, J = 1.5 Hz), 131.3 (d, J = 9.0 Hz), 128.3 (d, J = 10.5 Hz), 69.9 (d, J = 1.5 Hz), 68.9, 68.1, 33.4 (d, J = 67.5 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 28.3.

Cyclohexylbis(3,5-dimethylphenyl)phosphine oxide (4ad, known compound)



This compound was prepared according to General procedure II from the reaction of **1ad** (58.0 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3

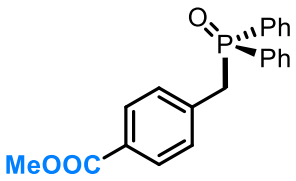
mmol). 30.5 mg, 32% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 27.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.84-7.82 (m, 1 H), 7.76-7.72 (m, 4 H), 7.48-7.46 (m, 2 H), 7.40-7.37 (m, 4 H), 7.32-7.26 (m, 7 H), 7.12-7.05 (m, 5 H), 6.82-6.80 (m, 1 H), 4.11-4.08 (m, 2 H).

^{13}C NMR (150 MHz, CDCl$_3$) δ 137.2 (dd, J_1 = 27.0 Hz, J_2 = 7.5 Hz), 136.4 (d, J = 10.5 Hz), 136.3 (dd, J_1 = 9.0 Hz, J_2 = 6.0 Hz), 134.4, 133.8, 133.6, 133.0, 132.4, 131.8, 131.76, 131.5, 131.4, 131.0 (t, J = 4.5 Hz), 129.4, 128.8 (d, J = 18.0 Hz), 128.6, 128.5 (d, J = 12.0 Hz), 127.4 (d, J = 1.5 Hz), 35.2 (dd, J_1 = 64.5 Hz, J_2 = 35.5 Hz).

^{31}P NMR (242.9 MHz, CDCl$_3$) δ 30.2, -15.9, -16.0.

Methyl 4-((diphenylphosphoryl)methyl)benzoate (4ae, known compound)



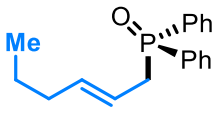
This compound was prepared according to General procedure II from the reaction of **1ae** (32.8 mg, 0.2 mmol) and **2b** (69.0 mg, 0.3 mmol). 30.8 mg, 44% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 34.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.86-7.85 (m, 2 H), 7.70-7.67 (m, 4 H), 7.54-7.51 (m, 2 H), 7.47-7.43 (m, 4 H), 7.19-7.17 (m, 2 H), 3.88 (s, 3 H), 3.70 (d, J = 13.8 Hz, 2 H).

^{13}C NMR (150 MHz, CDCl$_3$) δ 167.1, 136.9 (d, J = 6.0 Hz), 132.2, 131.3, 131.2, 130.3, 129.9, 129.7, 129.68, 128.8, 128.7, 52.2, 38.6 (d, J = 67.5 Hz).

^{31}P NMR (242.9 MHz, CDCl$_3$) δ 29.0.

(*E*)-Hex-2-en-1-yldiphenylphosphine oxide (4af, known compound)



This compound was prepared according to General procedure II from the reaction of **1af** (19.6 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 36.4 mg, 64% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 28.

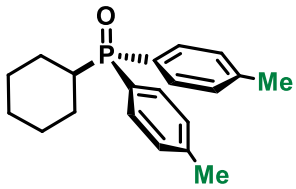
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.75-7.20 (m, 4 H), 7.53-7.47 (m, 6 H), 5.48-5.41 (m, 2 H), 3.09 (dd, J_1 = 13.8 Hz, J_2 = 6.6 Hz, 2 H), 1.92-1.916 (m, 2 H), 1.27-1.21 (m, 2 H), 0.75 (t, J = 7.2 Hz, 3 H).

^{13}C NMR (150 MHz, CDCl$_3$) δ 137.4 (d, J = 10.5 Hz), 132.7 (d, J = 97.5 Hz), 131,8,

131.2 (d, J = 9.0 Hz), 128.6 (d, J = 10.5 Hz), 35.0 (d, J = 67.5 Hz), 34.8, 22.4, 13,6.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 30.6.

Cyclohexyldi-p-tolylphosphine oxide (4ag, known compound)



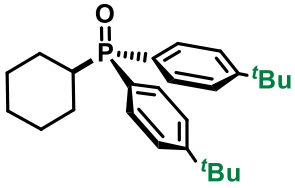
This compound was prepared according to General procedure II from the reaction of **1d** (19.6 mg, 0.2 mmol) and **2b** (69.0 mg, 0.3 mmol).53.1 mg, 85% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 29.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (dd, J_1 = 10.8 Hz, J_2 = 8.4 Hz, 4 H), 7.26 (m, 4 H), 2.38 (s, 6 H), 2.21-2.16 (m, 1 H), 1.80-1.79 (m, 2 H), 1.74-1.70 (m, 3 H), 1.54-1.46 (m, 2 H), 1.29-1.21 (m, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 141.8 (d, J = 1.5 Hz), 131.2 (d, J = 9.0 Hz), 129.4 (d, J = 12.0 Hz), 128.7, 37.5 (d, J = 72.0 Hz), 26.5 (d, J = 12.0 Hz), 25.9, 25.0 (d, J = 3.0 Hz), 21.6.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 34.9.

bis(4-(*tert*-butyl)phenyl)(cyclohexyl)phosphine oxide (4ah)



This compound was prepared according to General procedure II from the reaction of **1d** (19.6 mg, 0.2 mmol) and **2c** (94.2 mg, 0.3 mmol).51.5 mg, 65% yield, white solid, mp: 238.1-238.6 ºC.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71-7.68 (m, 4 H), 7.47-7.45 (m, 4 H), 2.22-2.16 (m, 1 H), 1.82-1.68 (m, 5 H), 1.56-1.49 (m, 2 H), 1.31 (s, 18 H), 1.28-1.21 (m, 3 H)

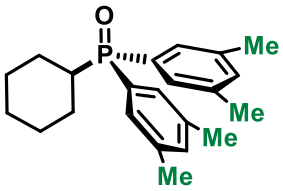
^{13}C NMR (150 MHz, $CDCl_3$) δ 154.7 (d, J = 1.5 Hz), 131.1 (d, J = 7.5 Hz), 129.1 (d, J = 96.0 Hz), 125.6 (d, J = 10.5 Hz), 37.6 (d, J = 72.0 Hz), 35.0, 31.3, 26.6 (d, J = 12.0 Hz), 26.0, 25.0 (d, J = 3.0 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 34.3.

IR (neat, cm^{-1}): 2964, 2933, 2856, 2213, 1600, 1449, 1393, 1182, 1094, 755, 600.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{26}H_{38}OP$ 397.2655, found 397.2646.

Cyclohexylbis(3,5-dimethylphenyl)phosphine oxide (4ai)



This compound was prepared according to General procedure II from the reaction of **1d** (19.6 mg, 0.2 mmol) and **2d** (77.4 mg, 0.3 mmol). 61.2 mg, 90% yield, white solid, mp: 185.0-186.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 10.8 Hz, 4 H), 7.10 (s, 2 H), 2.34 (s, 12 H), 2.24-2.16 (m, 1 H), 1.81-1.70 (m, 6 H), 1.54-1.50 (m, 2 H), 1.29-1.24 (m, 2 H).

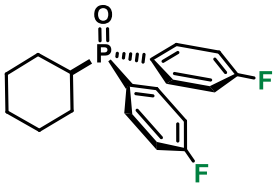
^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3 (d, *J* = 12.0 Hz), 133.2 (d, *J* = 3.0 Hz), 132.2 (d, *J* = 93.0 Hz), 128.7 (d, *J* = 9.0 Hz), 37.2 (d, *J* = 72.0 Hz), 26.6 (d, *J* = 13.5 Hz), 26.0, 24.9 (d, *J* = 3.0 Hz), 21.5.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 34.6.

IR (neat, cm^{-1}): 2928, 2854, 1600, 1272, 1178, 1126, 851, 699.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{30}OP$ 341.2029, found 341.2027.

Cyclohexylbis(4-fluorophenyl)phosphine oxide (4aj)



This compound was prepared according to General procedure II from the reaction of **1d** (19.6 mg, 0.2 mmol) and **2e** (71.4 mg, 0.3 mmol). 38.4 mg, 60% yield, white solid, mp: 144.8-146.9 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.74 (m, 4 H), 7.19-7.15 (m, 4 H), 2.21-2.16 (m, 1 H), 1.83-1.82 (m, 2 H), 1.72-1.70 (m, 3 H), 1.53-1.48 (m, 2 H), 1.30-1.22 (m, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.0 (dd, J_1 = 250.5 Hz, J_2 = 1.5 Hz), 133.6 (t, *J* = 9.0 Hz), 127.9 (dd, J_1 = 96.0 Hz, J_2 = 3.0 Hz), 116.2 (dd, J_1 = 22.5 Hz, J_2 = 13.5 Hz), 37.5 (d, *J* = 73.5 Hz), 26.4 (d, *J* = 13.5 Hz), 25.8, 24.9 (d, *J* = 3.0 Hz).

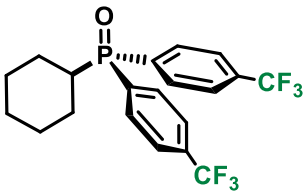
^{19}F NMR (376 MHz, $CDCl_3$) δ -107.3.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 33.5.

IR (neat, cm^{-1}): 3445, 2933, 2857, 1593, 1499, 1398, 1231, 1161, 1115, 913, 830, 748, 547.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{20}F_2OP$ 321.1214, found 321.1211.

Cyclohexylbis(4-(trifluoromethyl)phenyl)phosphine oxide (4ak)



This compound was prepared according to General procedure II from the reaction of **1d** (19.6 mg, 0.2 mmol) and **2f** (101.4 mg, 0.3 mmol).58.8 mg, 70% yield, white solid, mp: 226.4-227.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94-7.91 (m, 4 H), 7.76-7.71 (m, 4 H), 2.33-2.27 (m, 1 H), 1.87-1.81 (m, 2 H), 1.74-1.67 (m, 3 H), 1.63-1.55 (m, 2 H), 1.33-1.25 (m, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 136.1 (d, J = 91.5 Hz), 133.8 (qd, J_1 = 33.0 Hz, J_2 = 3.0 Hz), 131.6 (d, J = 9.0 Hz), 125.8 (q, J = 45.0 Hz), 125.7 (q, J = 45.0 Hz), 123.6 (q, J = 270.0 Hz), 37.1 (d, J = 73.5 Hz), 26.3 (d, J = 13.5 Hz), 25.7, 24.7 (d, J = 3.0 Hz)

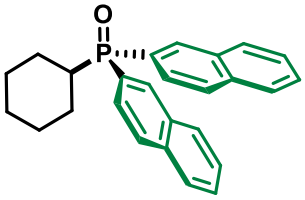
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 32.6.

IR (neat, cm^{-1}): 2935, 2856, 1959, 1400, 1327, 1319, 1118, 1063, 1017, 842, 711, 562.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{20}H_{20}F_6OP$ 421.1150, found 421.1143.

Cyclohexyldi(naphthalen-2-yl)phosphine oxide (4al, known compound)



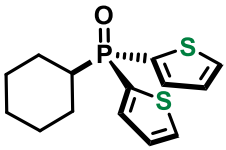
This compound was prepared according to General procedure II from the reaction of **1d** (19.6 mg, 0.2 mmol) and **2g** (90.6 mg, 0.3 mmol).35.3 mg, 46% yield, white solid. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref 30.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, J = 12.6 Hz, 2 H), 7.94-7.90 (m, 4 H), 7.85 (d, J = 7.8 Hz, 2 H), 7.80-7.77 (m, 2 H), 7.57-7.52 (m, 4 H), 2.49-2.44 (m, 1 H), 1.82-1.81 (m, 4 H), 1.72-1.60 (m, 3 H), 1.34-1.24 (m, 3 H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 134.6 (d, J = 1.5 Hz), 133.3 (d, J = 7.5 Hz), 132.8 (d, J = 13.5 Hz), 129.3 (d, J = 94.5 Hz), 129.0, 128.5 (d, J = 12.0 Hz), 128.1, 127.9, 127.0, 126.0 (d, J = 9.0 Hz), 37.2 (d, J = 72.0 Hz), 26.5 (d, J = 13.5 Hz), 25.9, 25.0 (d, J = 3.0 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 35.0.

Cyclohexyldi(thiophen-2-yl)phosphine oxide (4am)



This compound was prepared according to General procedure II from the reaction of **1d** (19.6 mg, 0.2 mmol) and **2h** (64.2 mg, 0.3 mmol).27.8 mg, 47% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73-7.72 (m, 2 H), 7.64-7.63 (m, 2 H), 7.22-7.20 (m, 2 H), 2.12-2.06 (m, 1 H), 1.93-1.89 (m, 2 H), 1.85-1.81 (m, 2 H), 1.72-1.69 (m, 1 H), 1.53-1.45 (m, 2 H), 1.31-1.20 (m, 3 H).

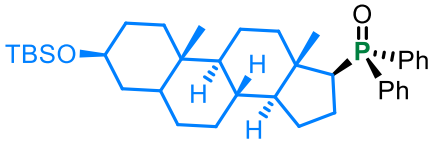
^{13}C NMR (150 MHz, $CDCl_3$) δ 135.9 (d, J = 9.0 Hz)135.2 (d, J = 4.5 Hz), 132.9 (d, J = 106.5 Hz), 128.3 (d, J = 13.5 Hz), 41.9 (d, J = 81.0 Hz), 26.4 (d, J = 13.5 Hz), 25.9 (d, J = 1.5 Hz), 25.2 (d, J = 3.0 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 27.1.

IR (neat, cm^{-1}): 3061, 2930, 2853, 1598, 1449, 1406, 1092, 1016, 852, 716.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{14}H_{18}OPS_2$ 297.0531, found 297.0525.

((*3S*,*8R*,*9S*,*10S*,*13S*,*14S*)-3-((*tert*-Butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)diphenylphosphine oxide (4ap)



This compound was prepared according to General procedure II from the reaction of **1ag** (80.8 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 92.1 mg, 78% yield, dr > 20:1, white solid, mp: 285.7-286.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.80 (m, 4 H), 7.47-7.41 (m, 6 H), 3.55-3.47 (m, 1 H), 2.29-2.19 (m, 2 H), 1.71-1.62 (m, 4 H),1.58-1.54 (m, 1 H), 1.43-1.21 (m, 8 H), 1.16-1.02 (m, 3 H), 1.00 (s, 3 H), 0.97-0.96 (m, 1 H), 0.87-0.80 (m, 12 H), 0.73 (s, 3H), 0.57-50 (m, 1 H), 0.03(s, 6 H).

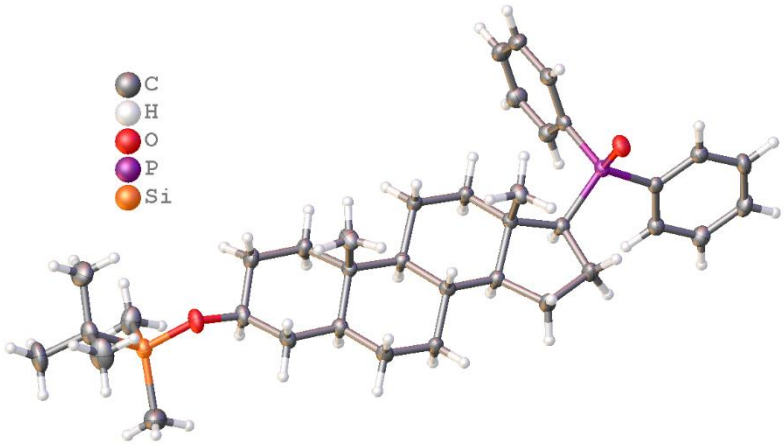
^{13}C NMR (150 MHz, $CDCl_3$) δ 134.6 (dd, J_1 = 141.0 Hz, J_2 = 94.5 Hz), 131.2 (dd, J_1 = 28.5 Hz, J_2 = 1.5 Hz), 130.9 (dd, J_1 = 87.0 Hz, J_2 = 9.0 Hz), 128.4 (dd, J_1 = 33.0 Hz, J_2 = 10.5 Hz), 72.1, 57.9, 57.8, 54.3, 49.1, 48.6, 45.0, 44.9, 39.3, 38.6, 37.2, 35.5, 35.0, 32.2, 31.9, 28.7, 26.0, 24.5, 24.46, 22.9, 21.0, 18.3, 14.92, 14.9, 12.3, -4.5.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 28.3.

IR (neat, cm^{-1}): 2929, 2856, 1438, 1388, 1258, 1101, 1071, 913, 836, 748, 548.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{37}H_{56}O_2PSi$ 591.3782, found 591.3778.

X-ray Single Crystal Data of 4ap

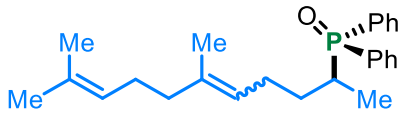


X-ray of 4ap, CCDC: 2467845

Identification code	wangyuq_0626_auto
Empirical formula	$C_{37}H_{55}O_2PSi$
Formula weight	590.87
Temperature/K	149.99(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.16070(10)
b/Å	16.4581(2)
c/Å	33.3457(4)
α /°	90
β /°	90
γ /°	90
Volume/$Å^3$	3381.03(8)
Z	4
ρ_{calc}g/cm^3	1.161
μ /mm^{-1}	1.280
F(000)	1288.0
Crystal size/mm^3	0.25 × 0.15 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.3 to 152.244
Index ranges	-7 ⩽ h ⩽ 2, -19 ⩽ k ⩽ 20, -41 ⩽ l ⩽ 38
Reflections collected	17022

Independent reflections	6611 [R_{int} = 0.0336, R_{sigma} = 0.0390]
Data/restraints/parameters	6611/0/377
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2 σ (I)]	R_1 = 0.0299, wR_2 = 0.0753
Final R indexes [all data]	R_1 = 0.0313, wR_2 = 0.0763
Largest diff. peak/hole / e Å^{-3}	0.18/-0.20
Flack parameter	-0.007(8)

(6,10-Dimethylundeca-5,9-dien-2-yl)diphenylphosphine oxide (4aq)



This compound was prepared according to General procedure II from the reaction of **1ah** (38.8 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol). 60.1 mg, 79% yield, colorless oil, a *E/Z* mixture of 1.3:1 isomers.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81-7.76 (m, 4 H), 7.51-7.44 (m, 6 H), 5.10-5.06 (m, 1 H), 5.02-4.98 (m, 1 H), 2.40-2.36 (m, 1 H), 2.17-2.13 (m, 1 H), 2.08-1.95 (m, 5 H), 1.72-1.66 (m, 5 H), 1.60-1.54 (m, 5 H), 1.50-1.47 (m, 1H), 1.19-1.15 (m, 3 H).

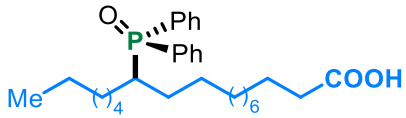
^{13}C NMR (150 MHz, $CDCl_3$) δ 136.6, 136.58, 132.6 (dd, J_1 = 94.5 Hz, J_2 = 42.0 Hz), 132.5 (dd, J_1 = 94.5 Hz, J_2 = 42.0 Hz), 131.8, 131.6, 131.6 (dd, J_1 = 12.0 Hz, J_2 = 1.5 Hz), 131.2 (t, J = 9.0 Hz), 128.6 (dd, J_1 = 12.0 Hz, J_2 = 3.0 Hz), 124.3, 124.2, 124.1, 39.8, 32.1, 31.4 (d, J = 72.0 Hz), 31.3 (d, J = 72.0 Hz), 26.8, 26.7, 25.8, 25.5 (dd, J_1 = 13.5 Hz, J_2 = 7.5 Hz), 23.5, 17.8, 17.76, 16.2, 12.1 (d, J = 3.0 Hz), 12.0 (d, J = 3.0 Hz).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 37.2, 37.1.

IR (neat, cm^{-1}): 3449, 2968, 1619, 1438, 1276, 1261, 1188, 1118, 764, 721, 541..

HRMS (ESI): $[M+H]^+$ calcd. for $C_{25}H_{34}OP$ 381.2342, found 381.2340.

12-(Diphenylphosphoryl)octadecanoic acid (4ar)



This compound was prepared according to General procedure II from the reaction of **1ai** (59.7 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol).68.8 mg, 71% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.80 (m, 4 H), 7.51-7.45 (m, 6 H), 2.35 (t, J = 7.2 Hz, 2 H), 2.23-2.22 (m, 1 H), 1.67-1.62 (m, 4 H), 1.56-1.51 (m, 2 H), 1.46-1.38 (m, 2 H), 1.34-1.14 (m, 21 H), 0.82 (t, J = 7.2 Hz, 3 H).

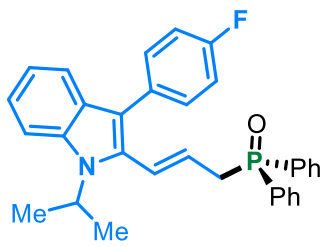
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.1, 132.6 (dd, J_1 = 94.5 Hz, J_2 = 24.0 Hz), 131.7, 131.2 (t, J = 9.0 Hz), 128.7 (dd, J_1 = 10.5 Hz, J_2 = 4.5 Hz), 37.4 (d, J = 70.5 Hz), 34.3, 34.26, 31.6, 29.5, 29.3, 28.9, 28.8, 28.7, 28.6, 28.59, 28.2, 28.1, 27.6, 27.58, 27.5, 24.9, 22.6, 14.2.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 38.4.

IR (neat, cm^{-1}): 3444, 2928, 2855, 1722, 1593, 1438, 1276, 1262, 1118, 913, 748,545.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{30}H_{46}O_3P$ 485.3179, found 485.3178.

(*E*)-(3-(3-(4-fluorophenyl)-1-isopropyl-1H-indol-2-yl)allyl)diphenylphosphine oxide (4as)



This compound was prepared according to General procedure II from the reaction of **1aj** (61.4 mg, 0.2 mmol) and **2a** (60.6 mg, 0.3 mmol).44.4 mg, 45% yield, white solid, mp: 186.2-188.0 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72-7.69 (m, 4 H), 7.55-7.53 (m, 2 H), 7.49-7.45 (m, 6 H), 7.28-7.26 (m, 2 H), 7.17-7.14 (m, 1 H), 7.06-7.03 (m, 1 H), 7.01-6.98 (m, 2 H), 6.53-6.50 (m, 1 H), 5.76-5.70 (m, 1 H), 4.59-4.54 (m, 1 H), 3.26 (dd, J_1 = 14.4 Hz, J_2 = 1.8 Hz, 2 H), 1.51 (d, J = 6.6 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 160.6, 135.2, 133.5, 132.9, 132.3, 132.1 (d, J = 3.0 Hz), 131.8 (d, J = 7.5 Hz), 131.4 (d, J = 3.0 Hz), 131.3 (d, J = 9.0 Hz), 128.8 (d, J = 12.0 Hz), 128.4, 125.7 (d, J = 9.0 Hz), 125.2 (d, J = 12.0 Hz), 121.9, 119.7 (d, J = 22.5 Hz), 115.4 (d, J = 21.0 Hz), 114.8, 112.0, 47.8, 36.1 (d, J = 67.5 Hz), 21.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.8.

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 38.4.

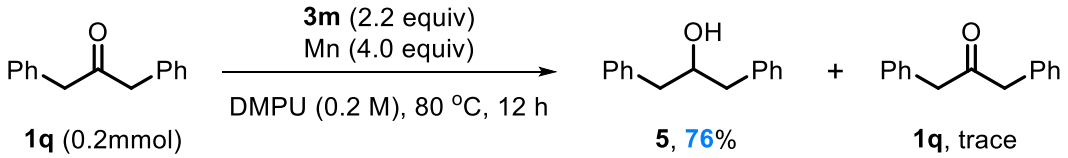
IR (neat, cm^{-1}): 2967, 2932, 1959, 1720, 1592, 1546, 1438, 1347, 1193, 1120, 914, 743.

HRMS (ESI): $[M+K]^+$ calcd. for $C_{32}H_{29}FKNOP$ 532.1602, found 532.1592.

4. Mechanistic Investigation

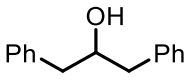
4.1 Reactivity of ketones and H(O)PAr$_2$ under the standard conditions

4.1.1 Reactivity of ketones



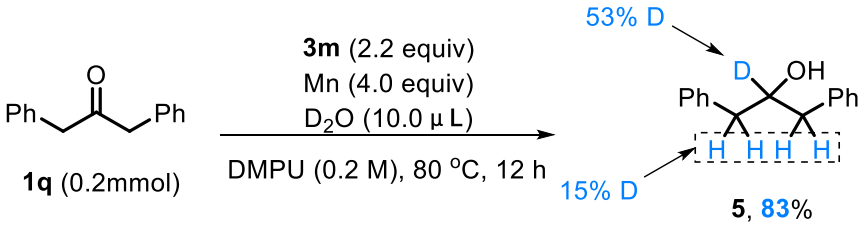
The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with **1q** (42.0 mg, 0.2 mmol), **3m** (127.6 mg, 0.44 mmol), Mn (44.0 mg, 0.8 mmol) and DMPU (1.0 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 80 °C for 12 h. The reaction was quenched with aqueous HCl (20.0 mL, 2.0 M), and the mixture solution was extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford product **5.** [31]

1,3-Diphenylpropan-2-ol (5, known compound)



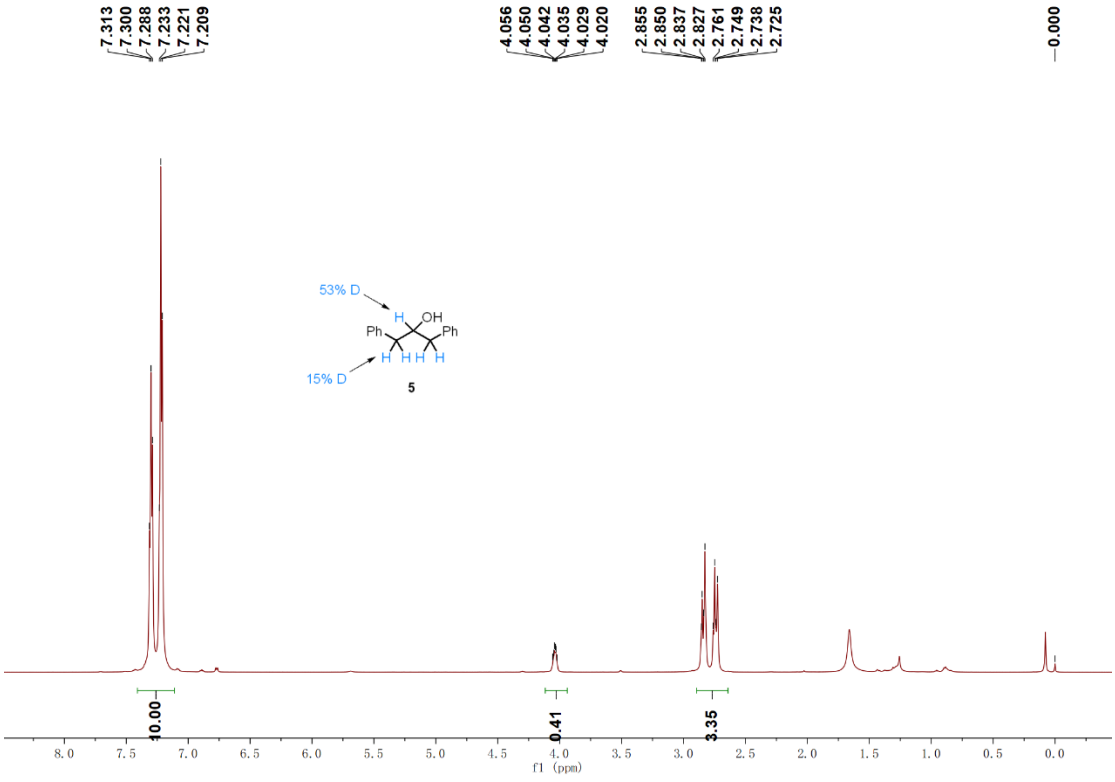
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.29 (m, 4 H), 7.23-7.21 (m, 6 H), 4.08-4.02 (m, 1 H), 2.88-2.72 (m, 4 H).

■ **Isotope-labeling Experiment**

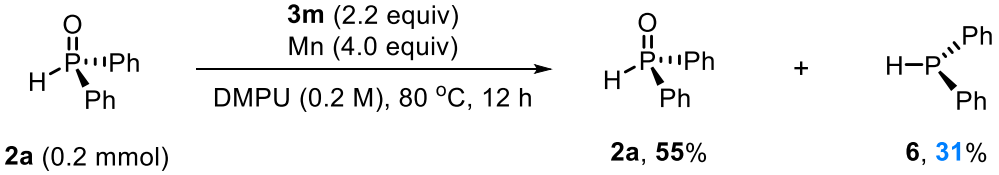


The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with **1q** (42.0 mg, 0.2 mmol), **3m** (127.6 mg, 0.44 mmol), Mn (44.0 mg, 0.8 mmol) D_2O (10.0 μL) and DMPU (1.0 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 80 °C for 12 h. The reaction was quenched with aqueous HCl (20.0 mL, 2.0 M), and the

mixture solution was extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford product **5.**



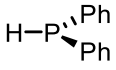
4.1.2 Reactivity of H(O)PAr$_2$



The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with **2a** (60.6 mg, 0.3 mmol), **3m** (127.6 mg, 0.44 mmol), Mn (44.0 mg, 0.8 mmol) and DMPU (1.0 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 80 °C for 12 h. The reaction was quenched with aqueous HCl (20.0 mL, 2.0 M), and the mixture solution was extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under

reduced pressure. The residue was purified by flash chromatography on silica gel to afford **2a** and **6**[32].

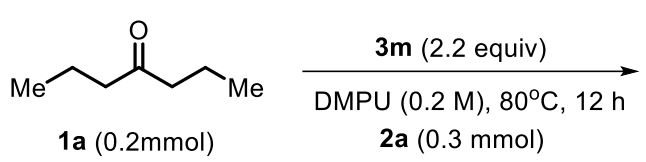
Diphenylphosphane (6, known compound)

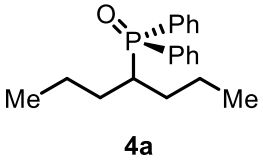


^{1}H NMR (600 MHz, $CDCl_3$) δ7.50-7.46 (m, 4 H), 7.33–7.31 (m, 6 H), 5.25 (d, J = 219.0 Hz, 1 H).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ -40.4.

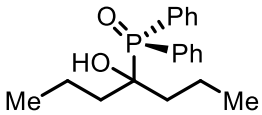
4.2 Effect of Mn on the reaction of 1a with 2a



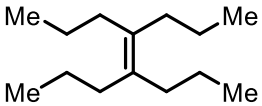


4a

entry	conditions	**4a**	**10**	**11**
1	without Mn	0%	0%	0%
2	with Mn	80%	0%	0%
3	with Mn[a]	33%	trace	6%



10



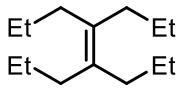
11

General procedure III: The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with **1a** (22.8 mg, 0.2 mmol), **3m** (127.6 mg, 0.44 mmol) and DMPU (1.0 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 80 °C for 12 h. The reaction was quenched with aqueous HCl (20.0 mL, 2.0 M), and the mixture solution was extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica.

General procedure IV: The reaction tube was sealed and removed from the glove box. To a stirred reaction tube equipped with a magnetic stir bar was added **3m** (127.6 mg, 0.44 mmol, 2.2 equiv), Mn (44.0 mg, 0.80 mmol, 4.0 equiv), and anhydrous DMPU (1.0 mL). The mixture was stirred at room temperature for 12 h, then filtered to remove Mn. To the resulting filtrate was added **1a** (30.0 mg, 0.20 mmol) and **2a** (60.6 mg, 0.30 mmol). The tube was sealed and removed from the glove box again. The reaction

mixture was stirred at 80 °C for 12 h, then quenched with 2.0 M aqueous HCl (20.0 mL) and extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel. The yields of **4a** and **10** were determined by ^{1}H NMR and ^{31}P NMR analysis.

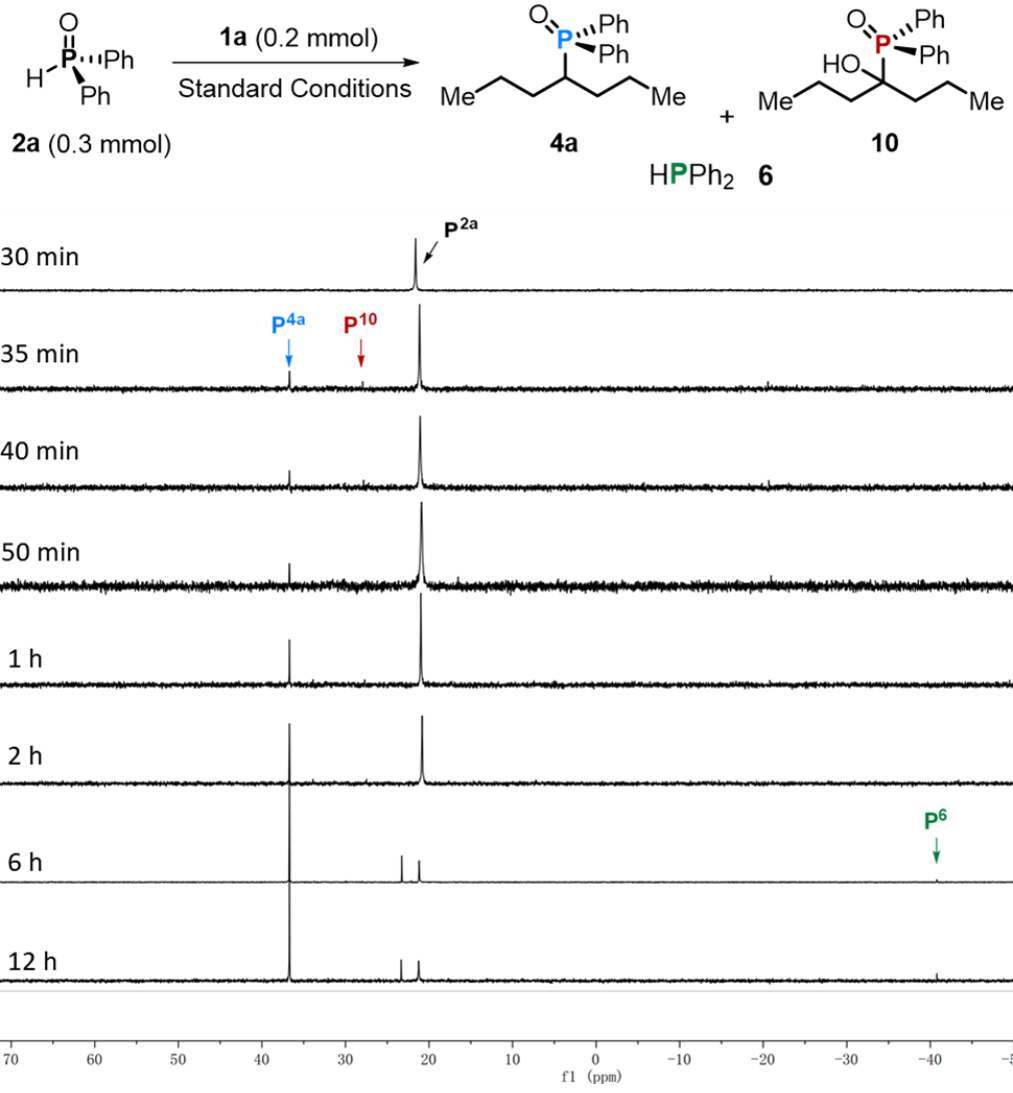
4,5-Dipropyloct-4-ene (11, known compound)



^{1}H NMR (600 MHz, $CDCl_3$) δ 1.95 (t, *J* = 7.8 Hz, 8 H), 1.38-1.32 (m, 8 H), 0.88 (t, *J* = 7.2 Hz, 12 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 133.6, 33.8, 22.5, 14.5.

4.3 Real-time ^{31}P NMR monitoring of the coupling of 1a and 2a

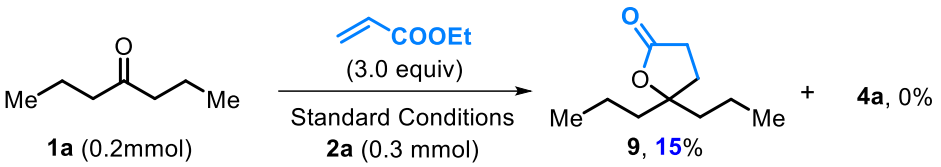


The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with **1a** (22.8 mg, 0.2 mmol), **3m** (127.6 mg, 0.44

mmol) and DMPU (1.0 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 80 °C. A 60 μL aliquot of the reaction solution was collected by pipette every 5–10 min. Each sample was quenched with 50 μL of 2.0 M aqueous HCl, diluted with ethyl acetate (1.0 mL), filtered through a syringe filter, concentrated under reduced pressure, and analyzed by ^{31}P NMR without further purification.

4.4 Radical verification studies

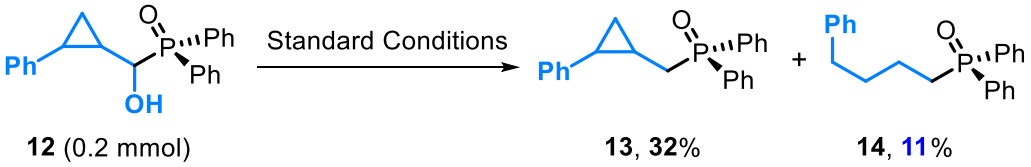
4.4.1 Radical trapping experiment using ethyl acrylate



The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with **1a** (22.8 mg, 0.2 mmol), **2a** (60.6 mg, 0.3 mmol), **3m** (127.6 mg, 0.44 mmol), Mn (44.0 mg, 0.8 mmol), ethyl acrylate (60.0 mg, 0.6 mmol) and DMPU (1.0 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 80 °C for 12 h. The reaction was quenched with aqueous HCl (20.0 mL, 2.0 M), and the mixture solution was extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford product **9**. ^{1}H NMR data are consistent with those reported in ref 33.

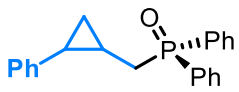
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (t, J = 8.4 Hz, 2 H), 2.02 (t, J = 8.0 Hz, 2 H), 1.65-1.60 (m, 4 H), 1.40-1.35 (m, 4 H), 0.94 (t, J = 7.2 Hz, 6 H).

4.4.2 Radical clock experiment of *α*-hydroxyphosphonates



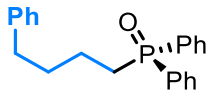
The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with **12** (65.6 mg, 0.2 mmol), **3m** (127.6 mg, 0.44

mmol), Mn (44.0 mg, 0.8 mmol) and DMPU (1.0 mL). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 80 °C for 12 h. The reaction was quenched with aqueous HCl (20.0 mL, 2.0 M), and the mixture solution was extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica. The yield of **13** and **14** were determined by ^{1}H NMR analysis.



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77-73.72 (m, 4 H), 7.53-7.44 (m, 6 H), 7.19-7.16 (m, 2 H), 7.11-1.09 (m, 1 H), 6.87-6.86 (m, 2 H), 2.53-2.48 (m, 1 H), 2.40-2.34 (m, 1 H), 1.68-1.65 (m, 1 H), 1.32-1.28 (m, 1 H), 0.99-0.96 (m, 1 H), 0.84-0.81 (m, 1 H).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 31.2.



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74-7.71 (m, 4 H), 7.53-7.51 (m, 2 H), 7.48-7.45 (m, 4 H), 7.24-7.23 (m, 2 H), 7.17-7.15 (m, 1 H), 7.12-7.10 (m, 2 H), 2.59 (t, J = 7.2 Hz, 2 H), 2.31-2.26 (m, 2 H), 1.76-1.66 (m, 4 H).

^{31}P NMR (242.9 MHz, $CDCl_3$) δ 32.4.

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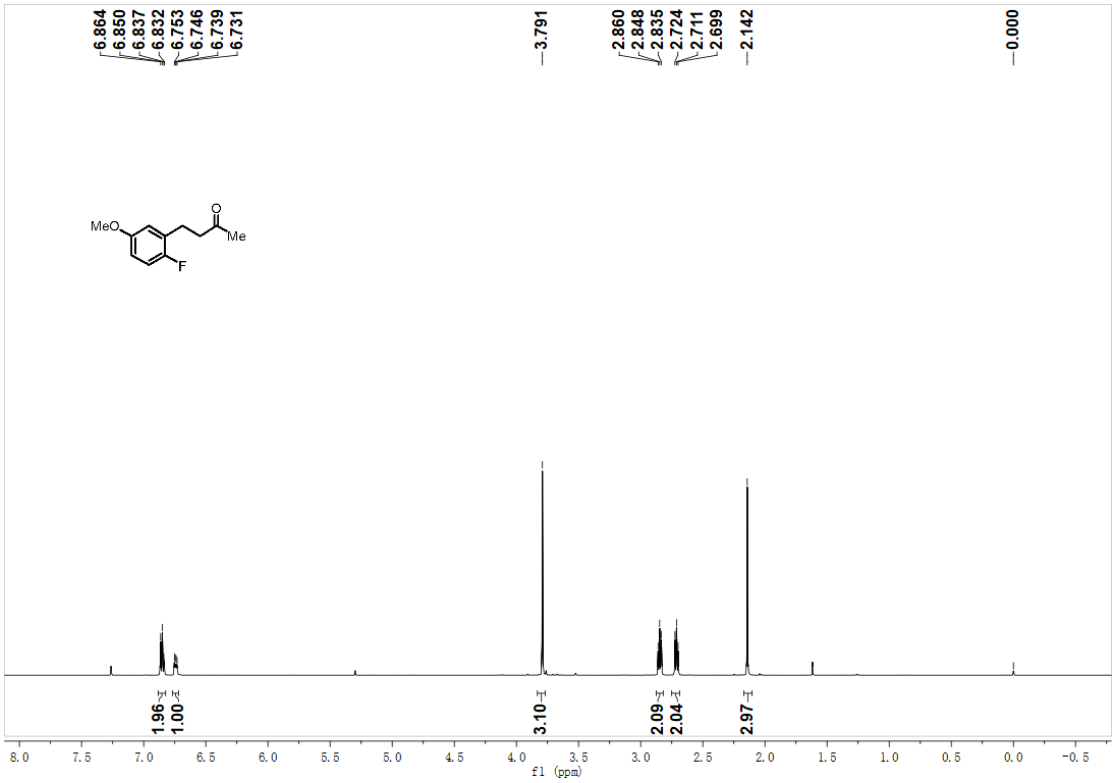
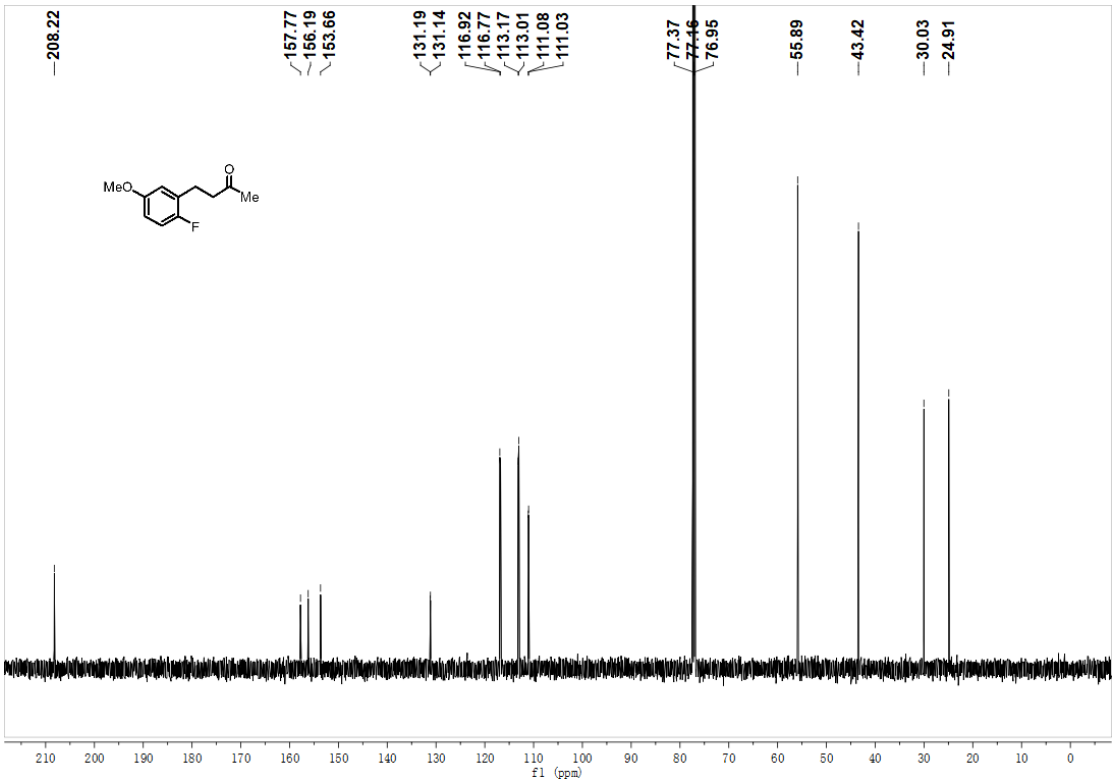
6. Copies of NMR Spectra

1u; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)





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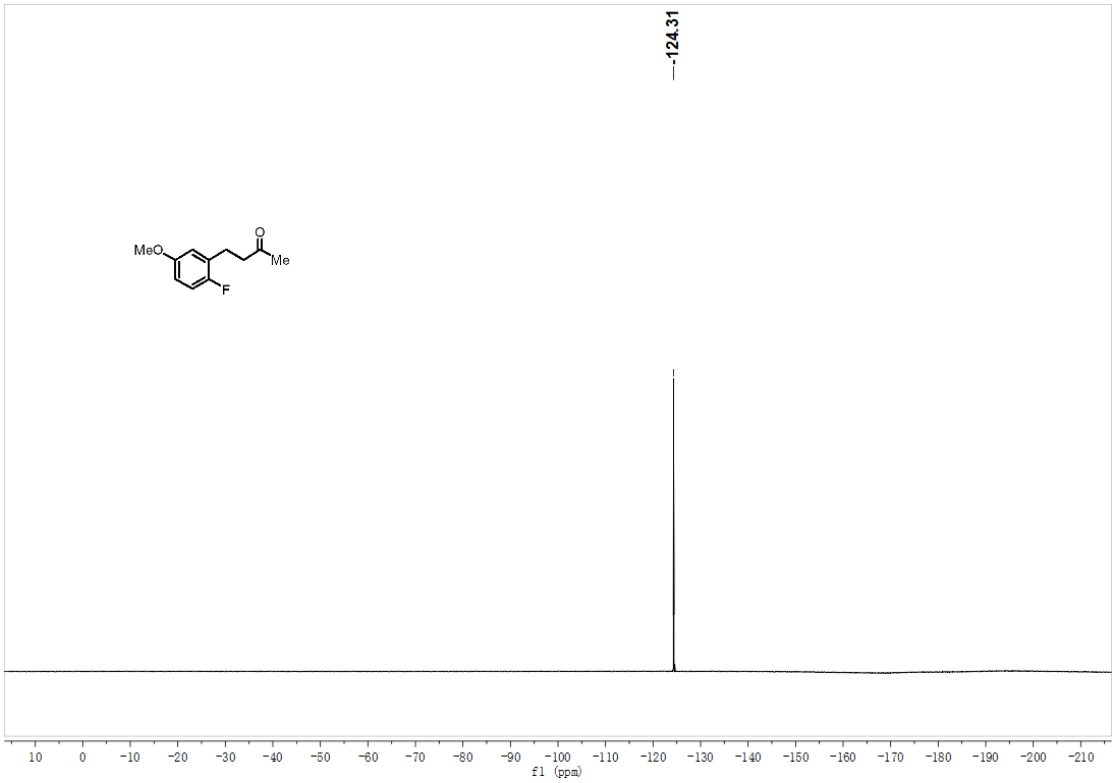
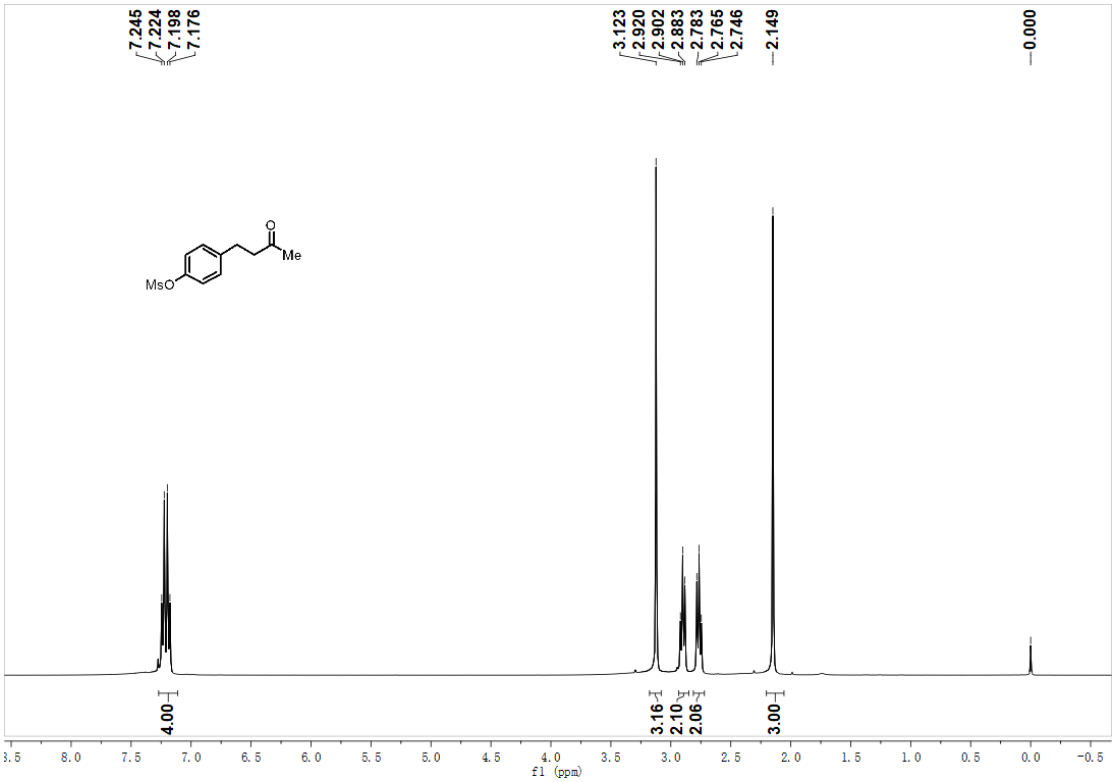
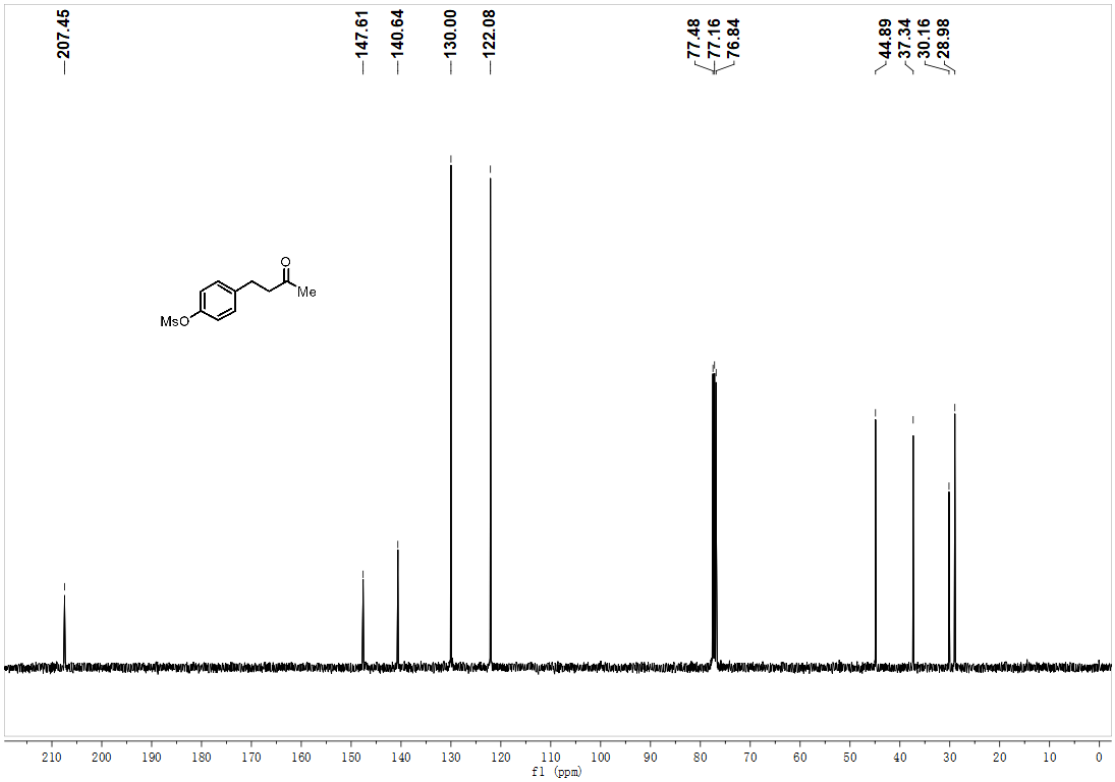


1v; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)





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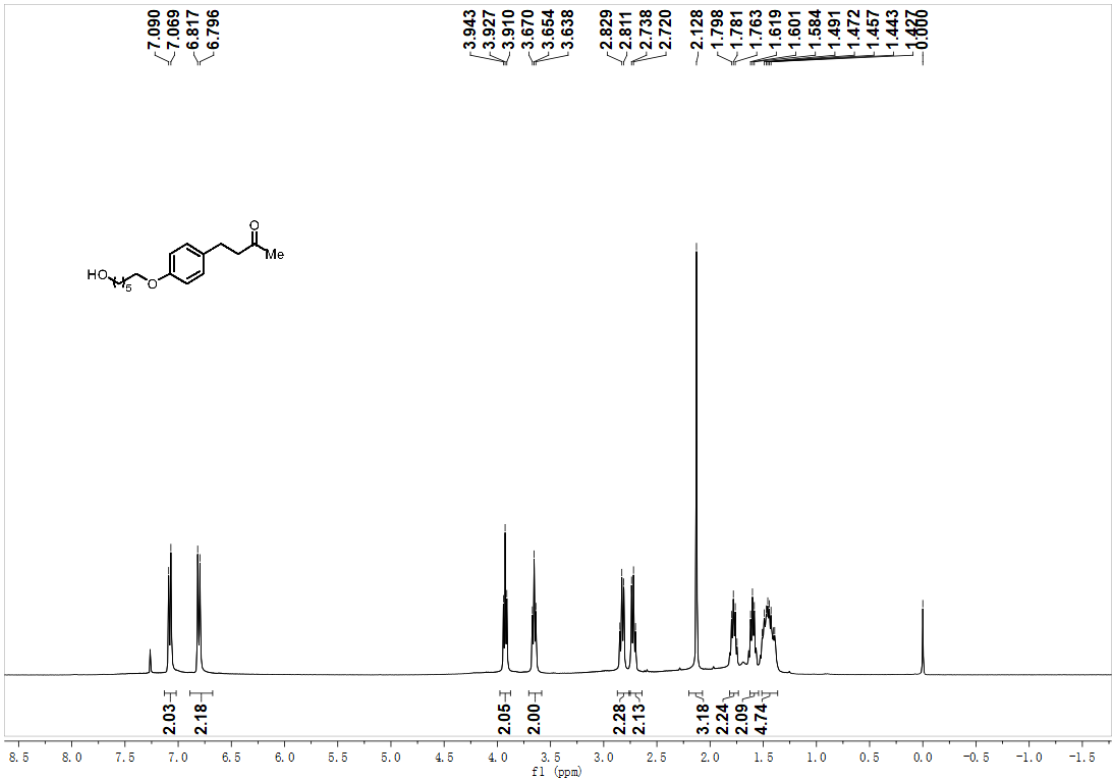
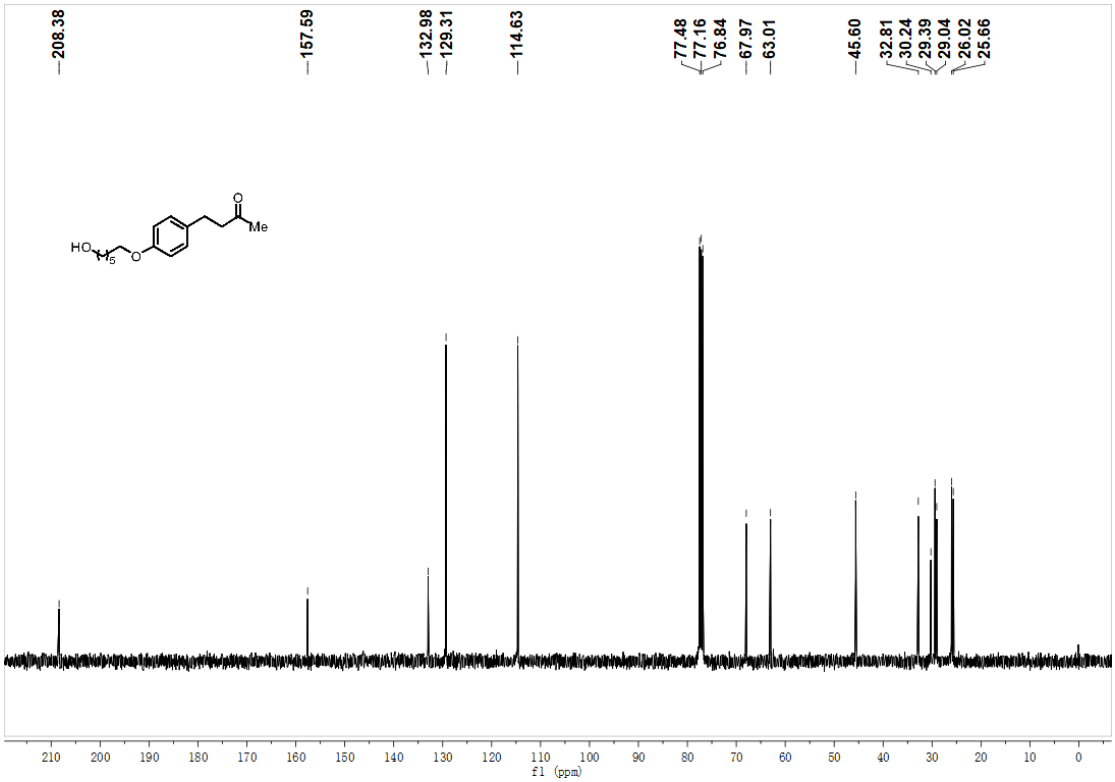
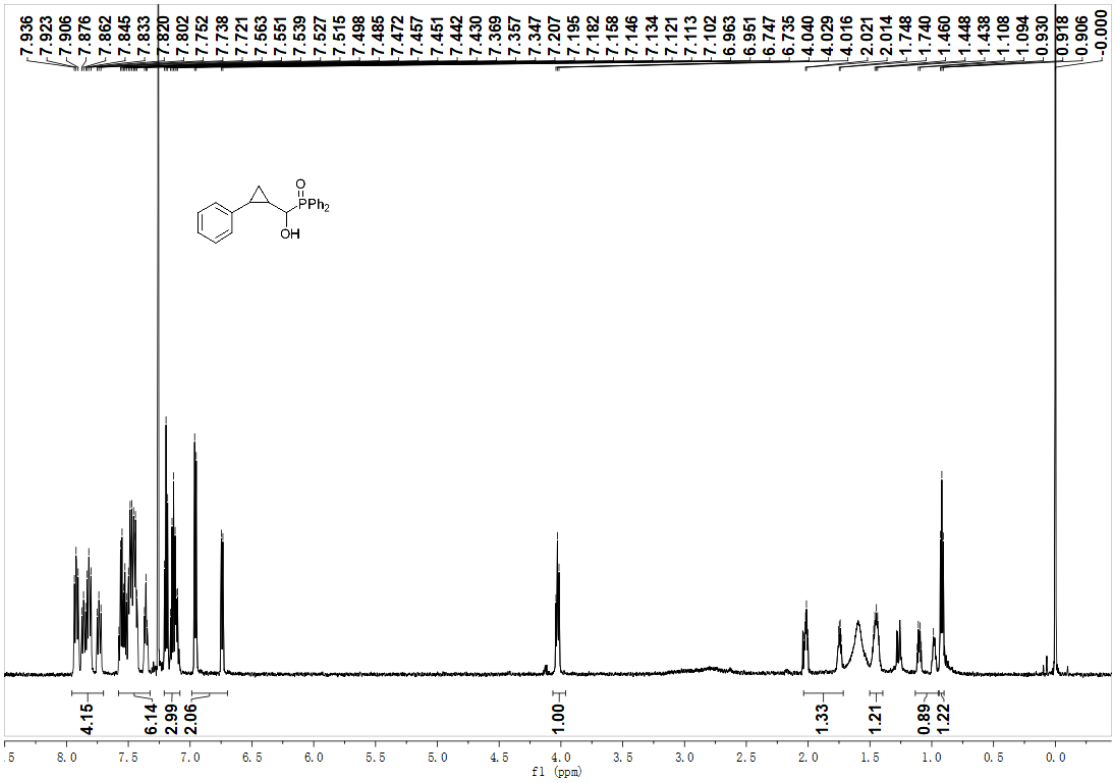
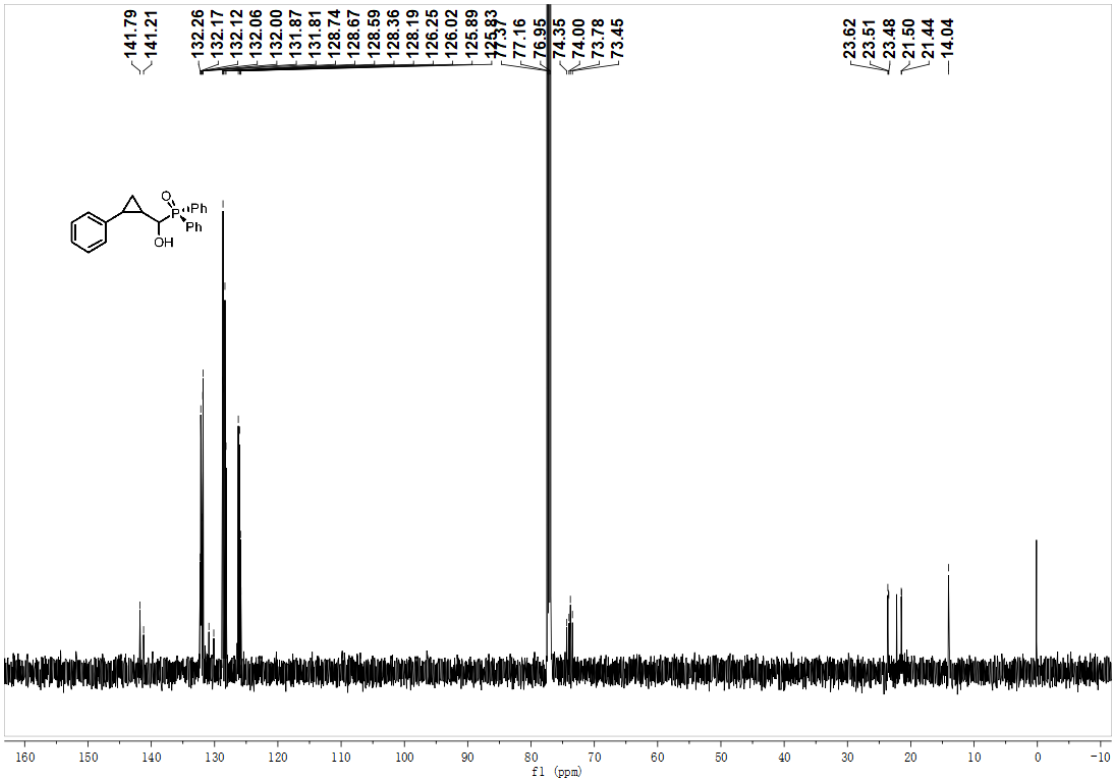


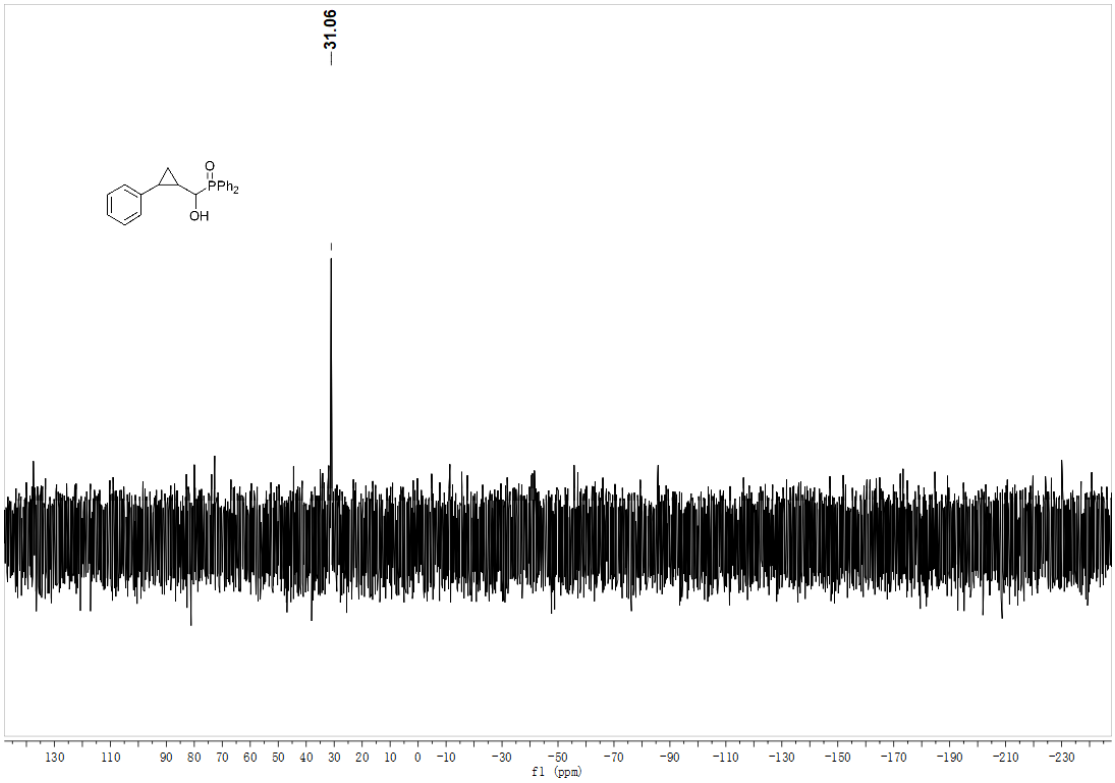


12; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)





12; ^{31}P NMR (242.9 MHz, $CDCl_3$)



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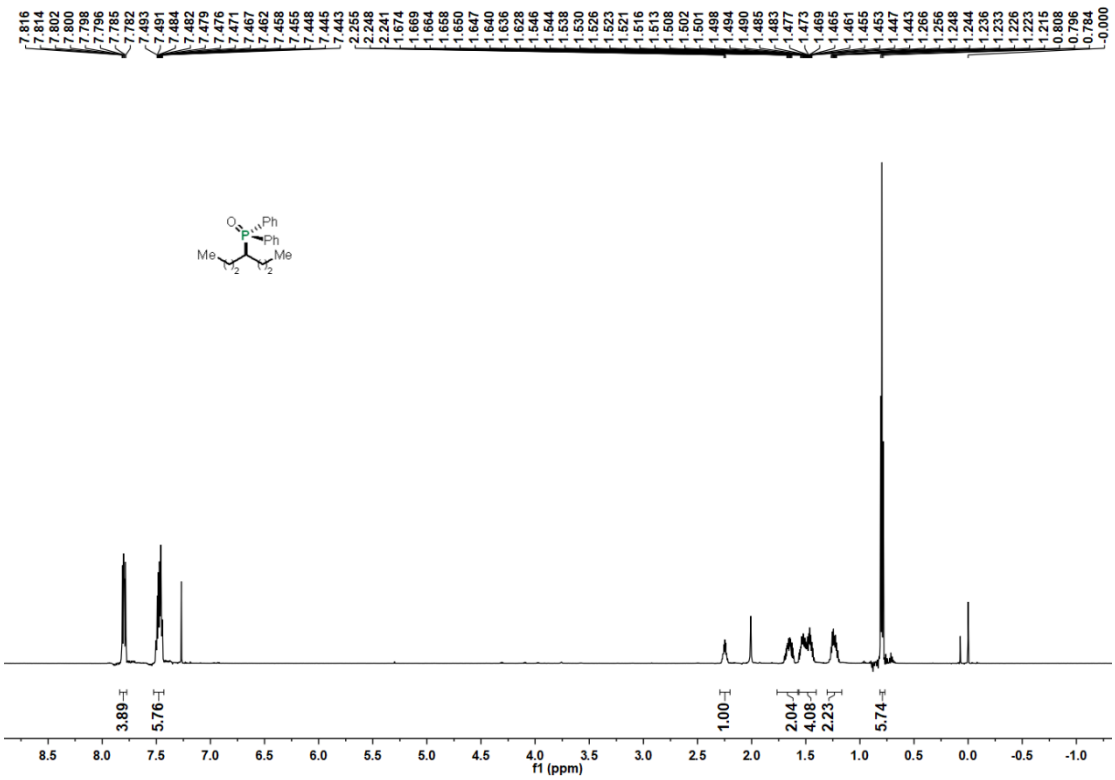
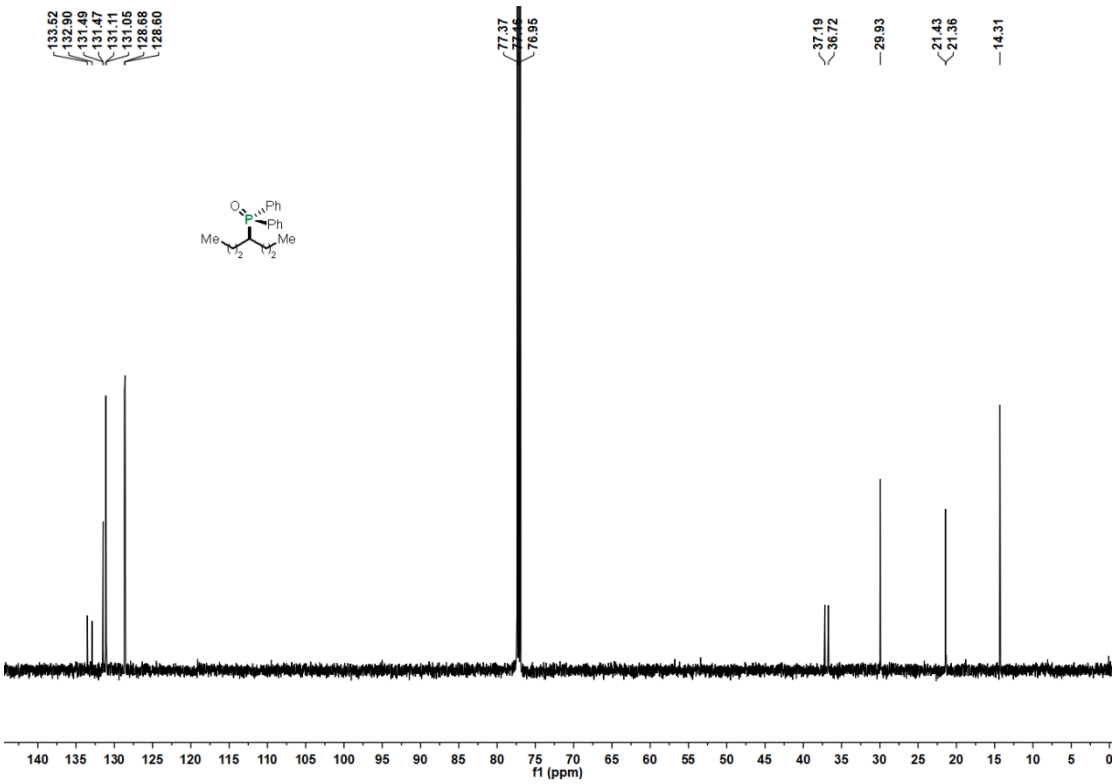
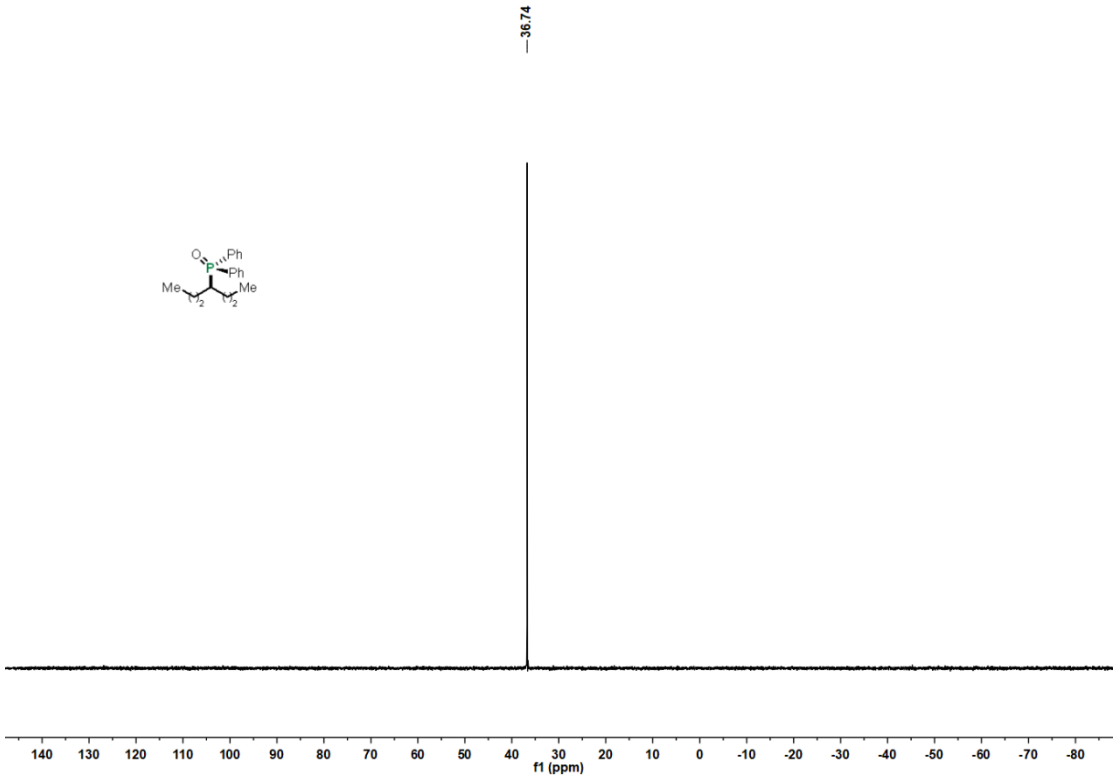




4a; ^{31}P NMR (242.9 MHz, $CDCl_3$)



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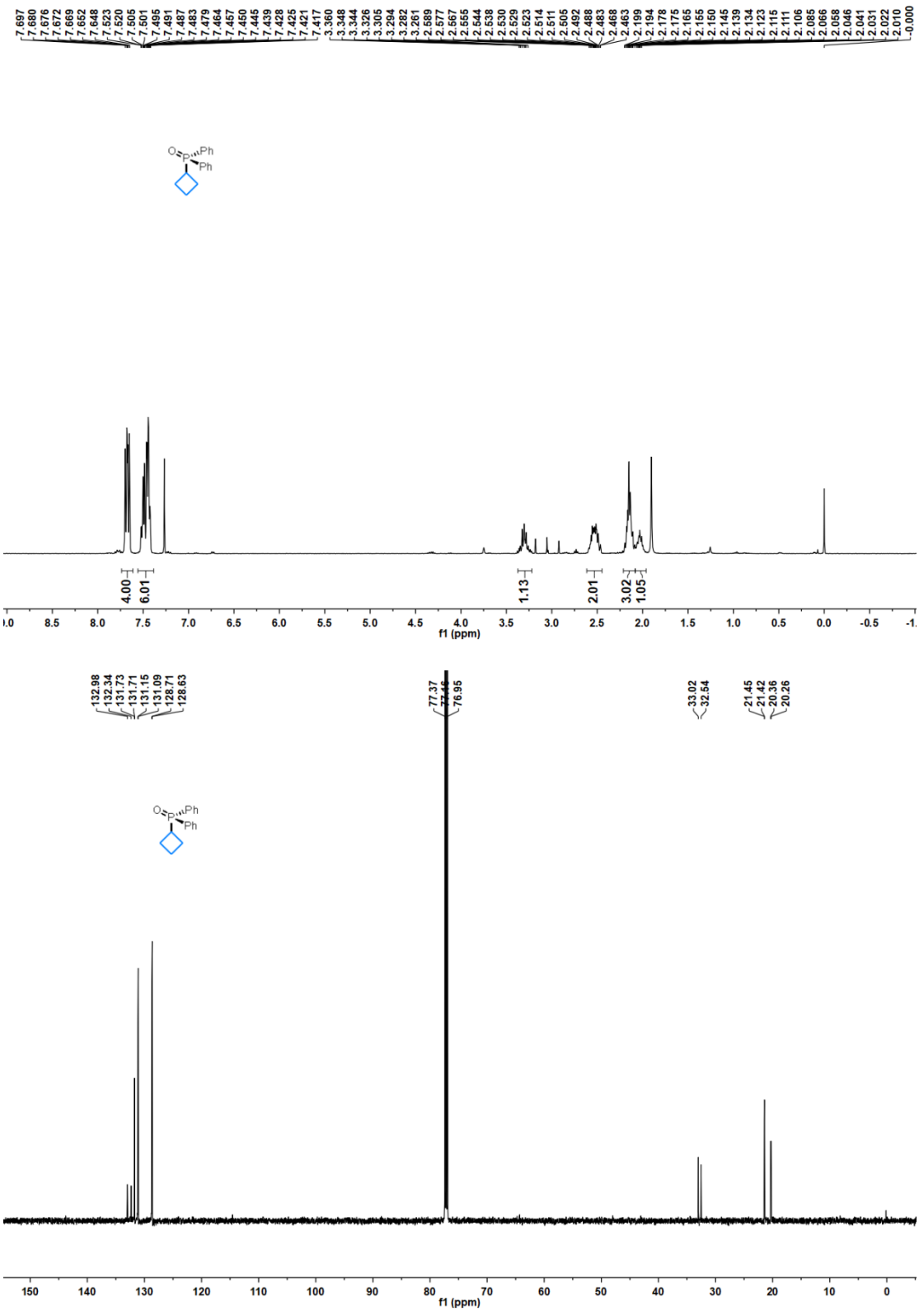
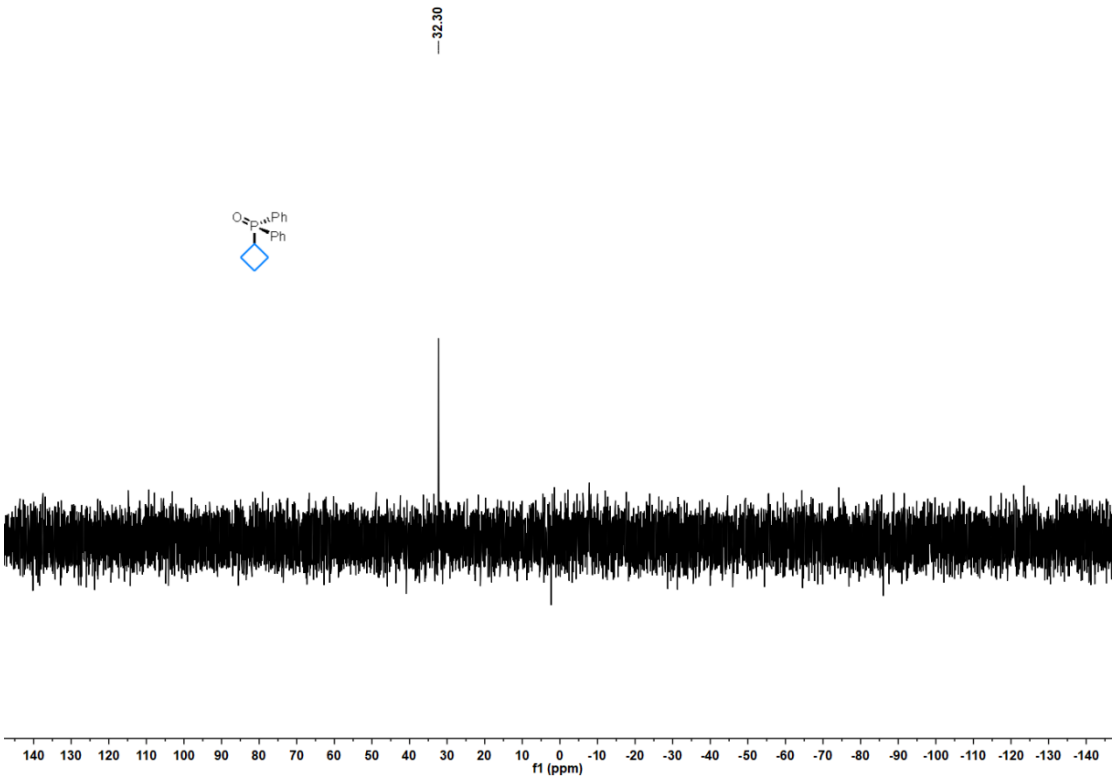


4b; ^{31}P NMR (242.9 MHz, $CDCl_3$)



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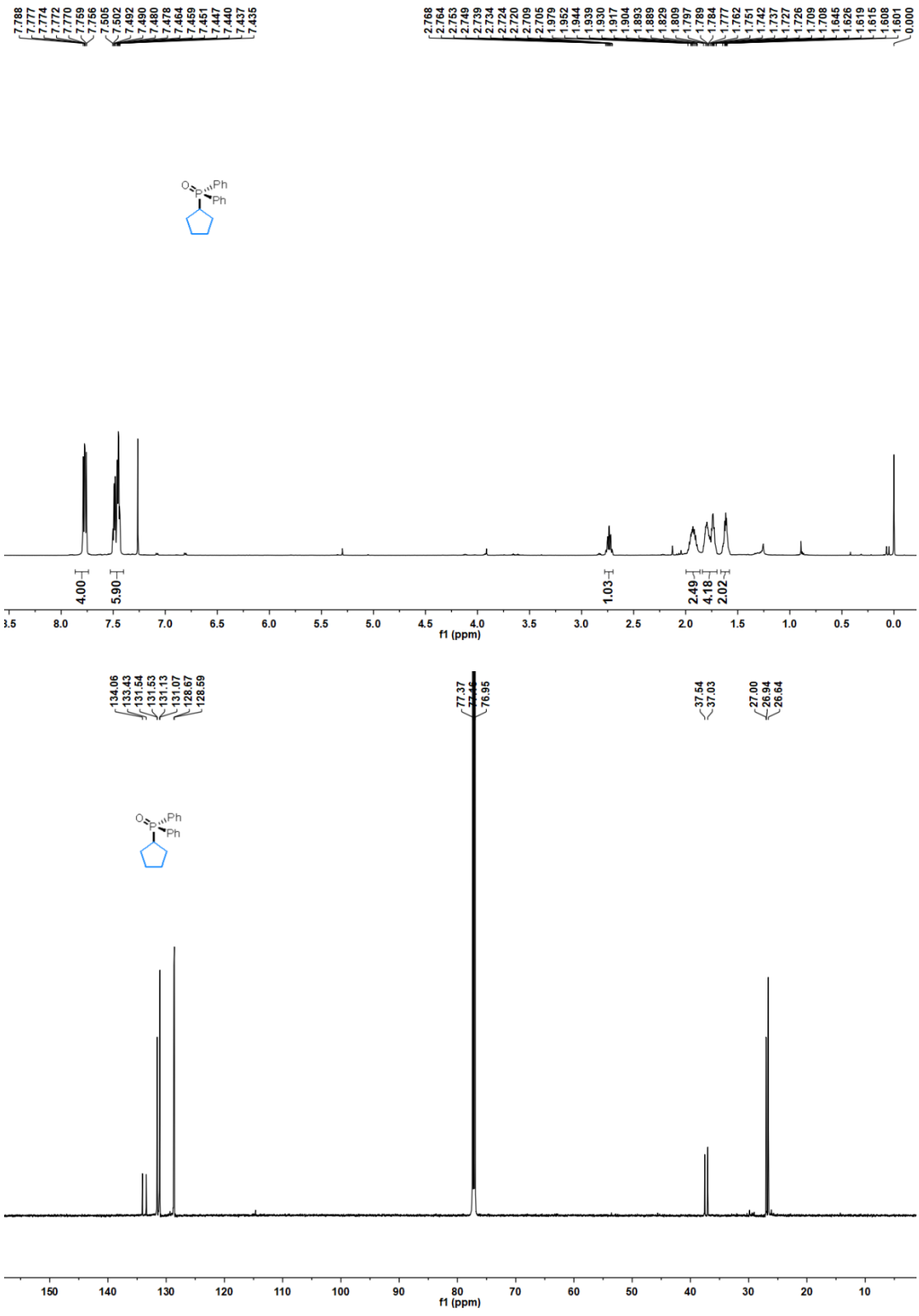
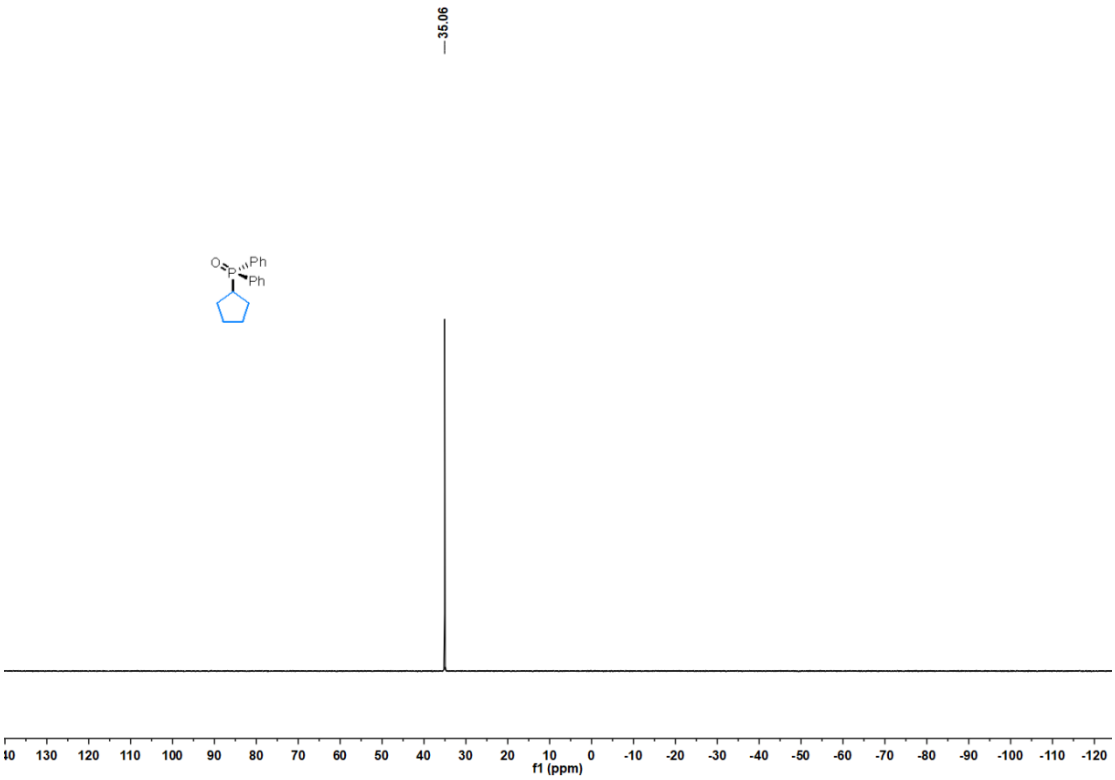
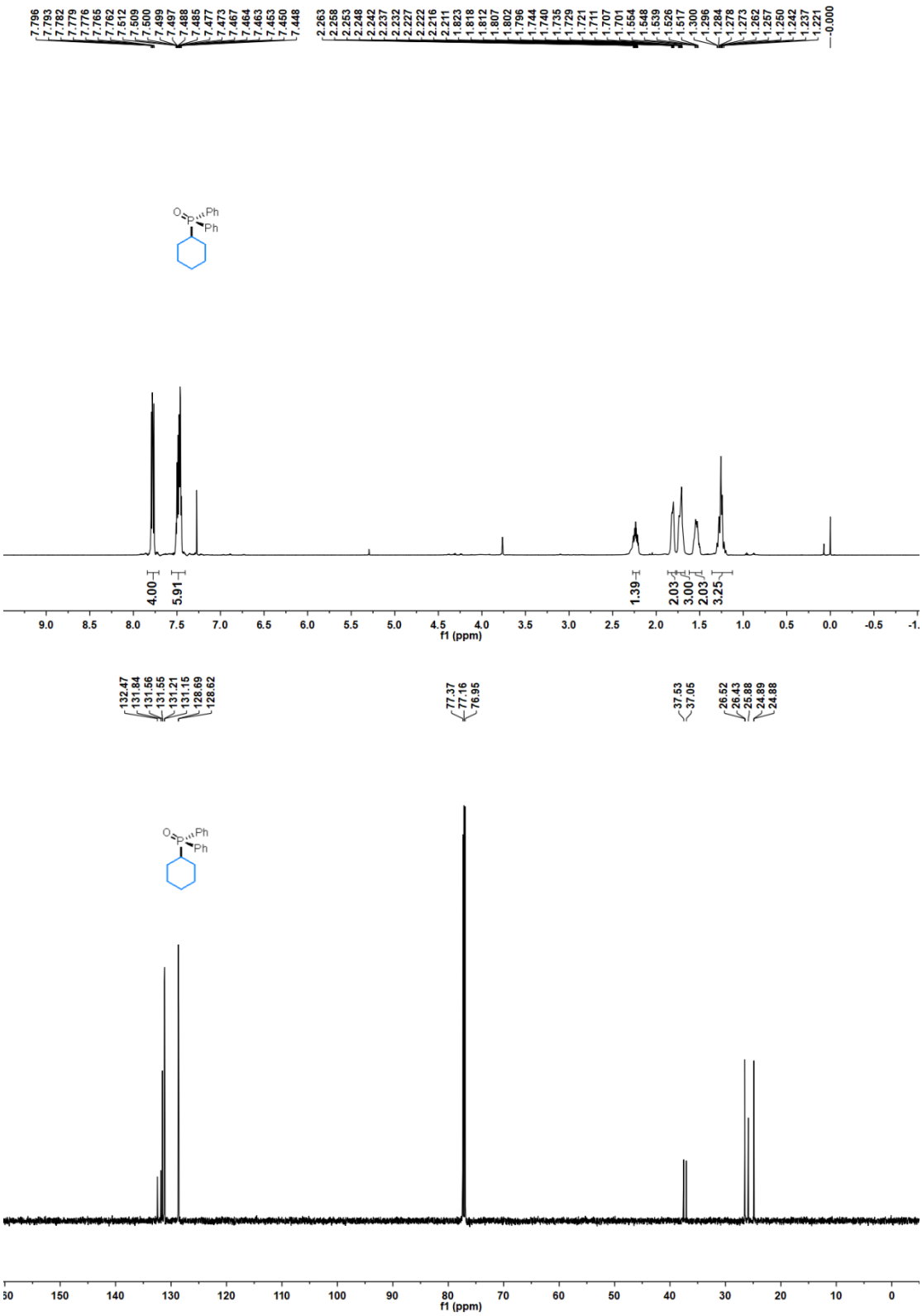


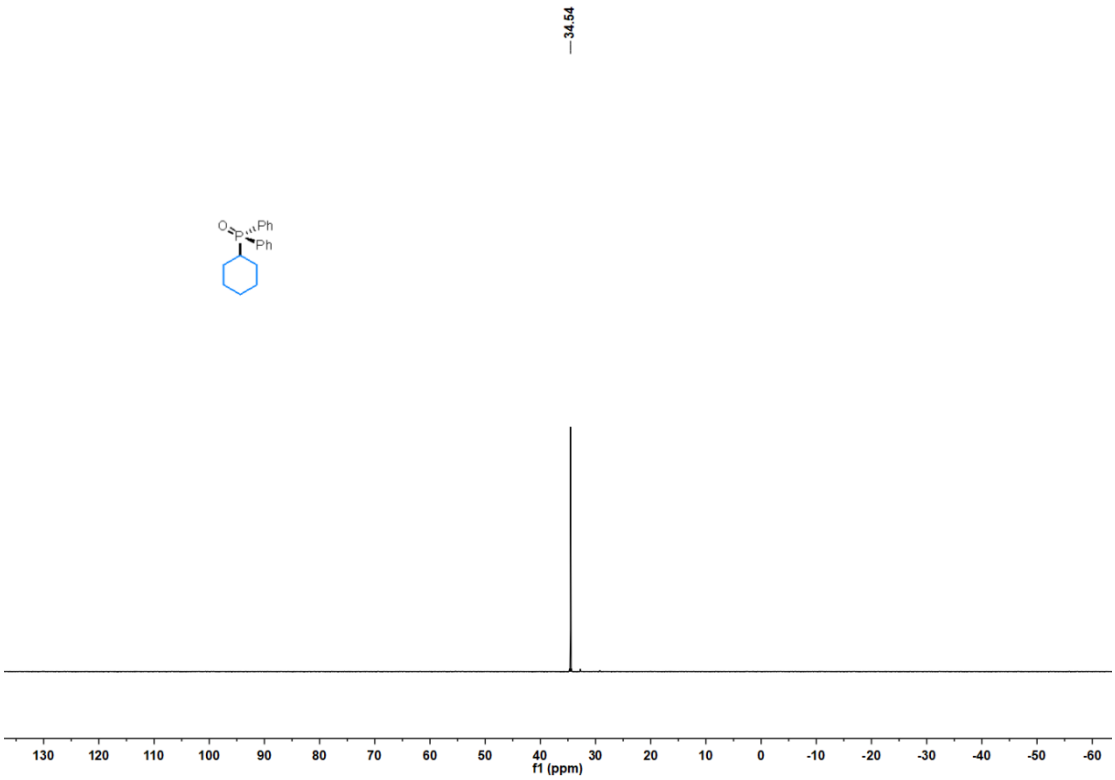
4c; ^{31}P NMR (242.9 MHz, $CDCl_3$)



4d; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



4d; ^{31}P NMR (242.9 MHz, $CDCl_3$)



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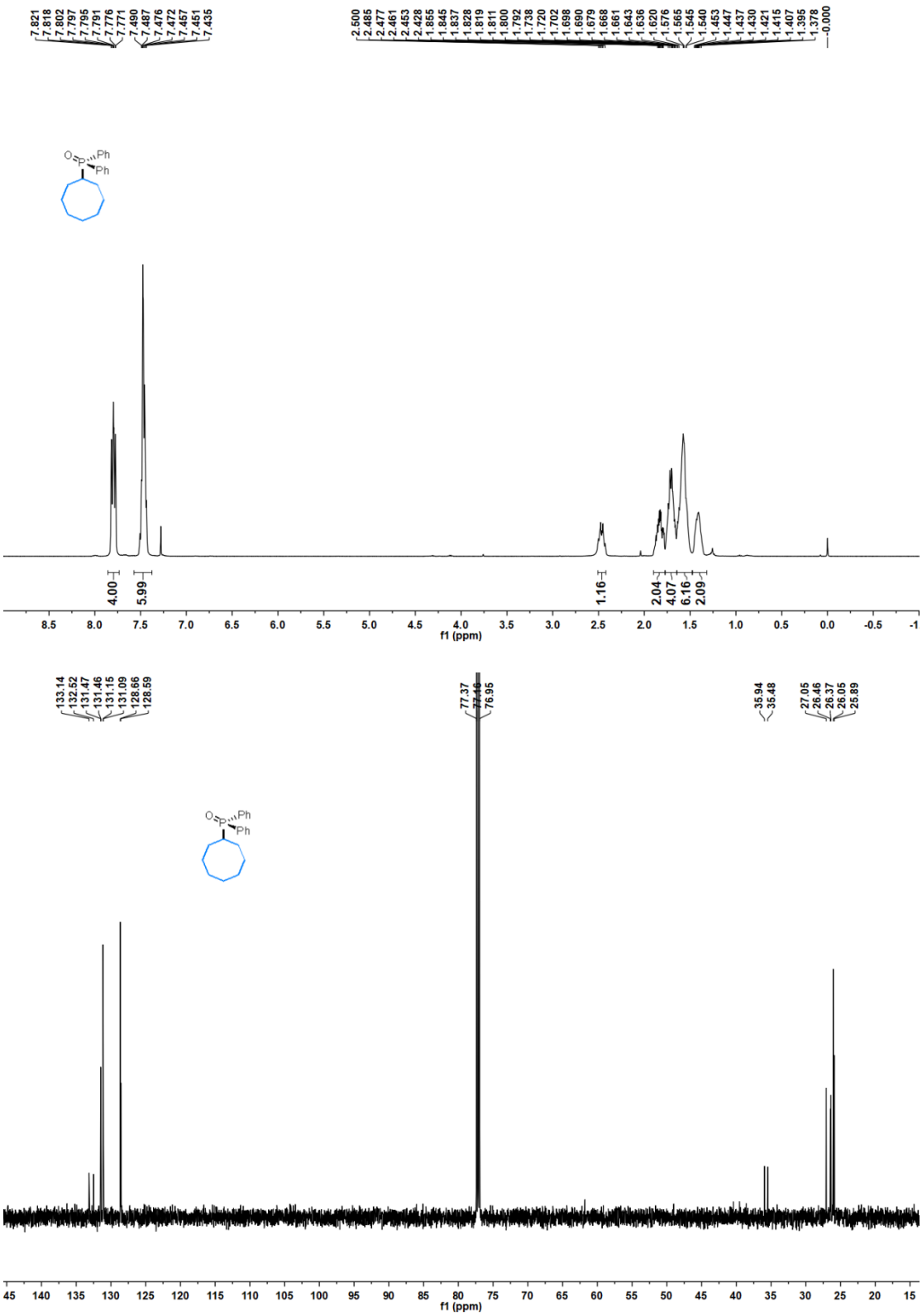
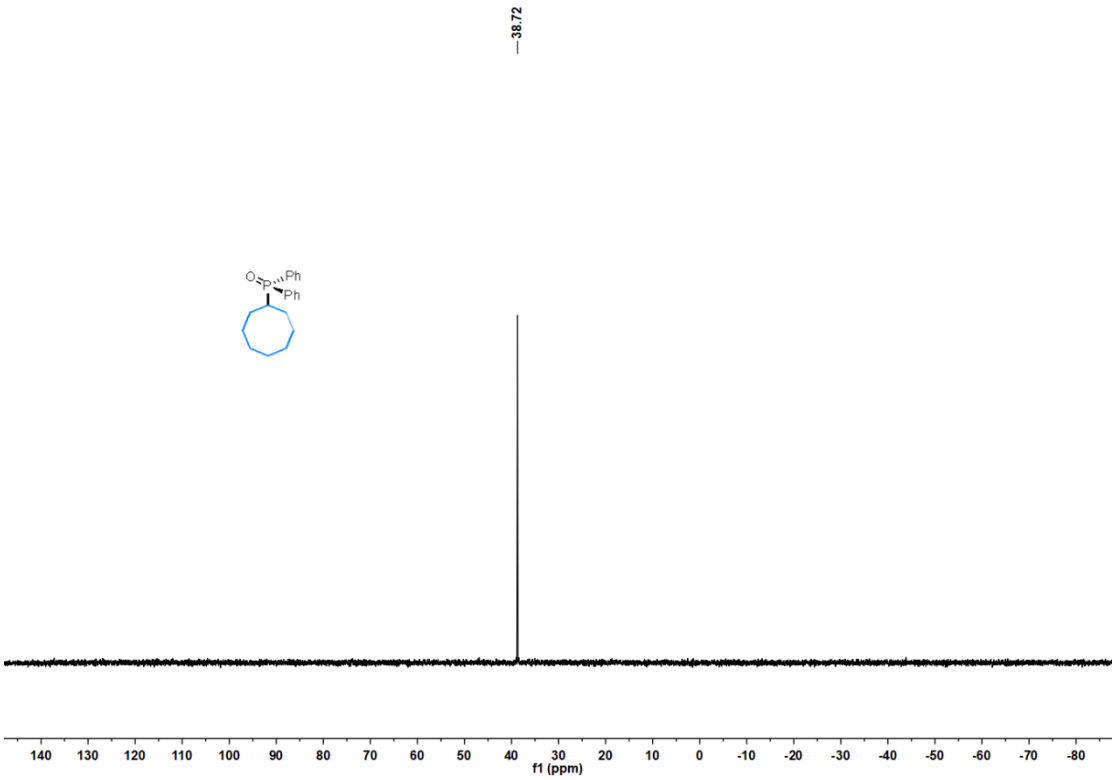
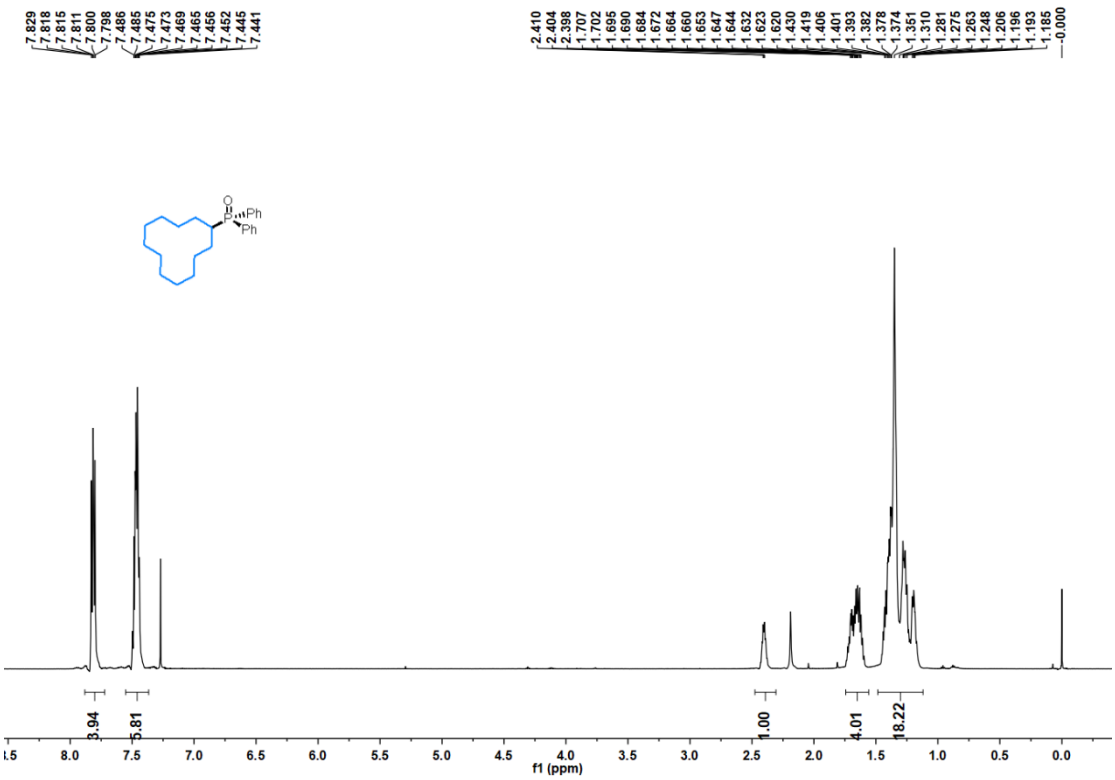
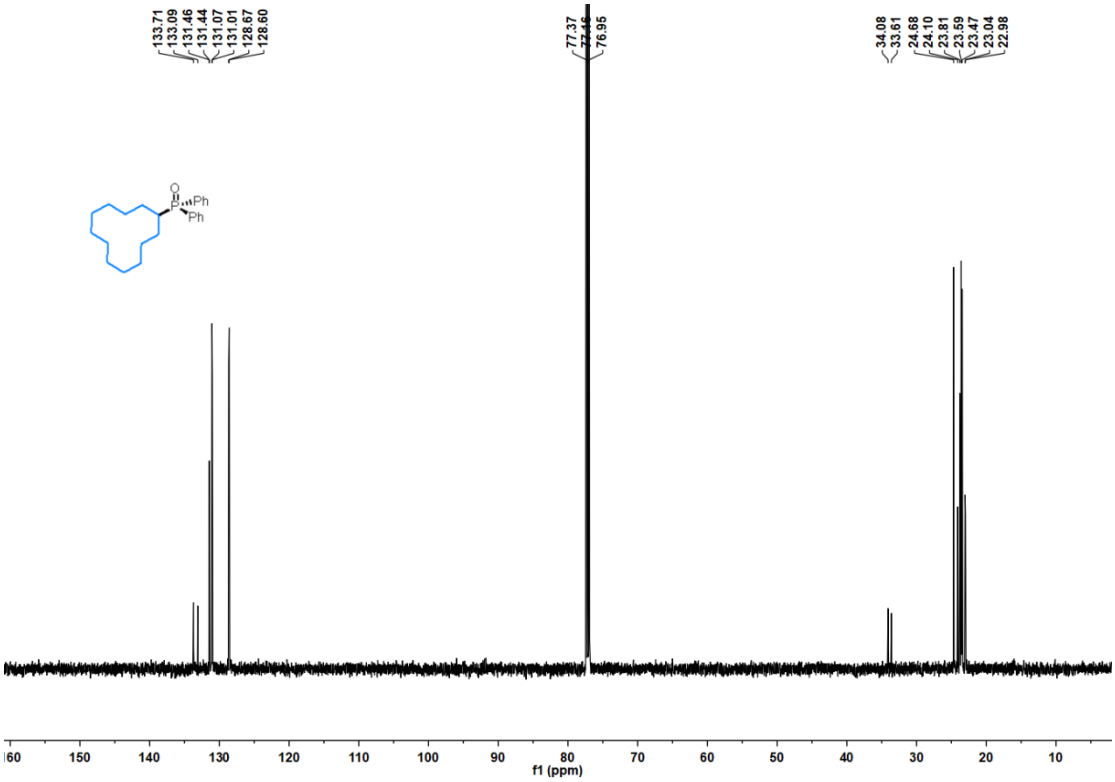


4e; ^{31}P NMR (161.9 MHz, $CDCl_3$)

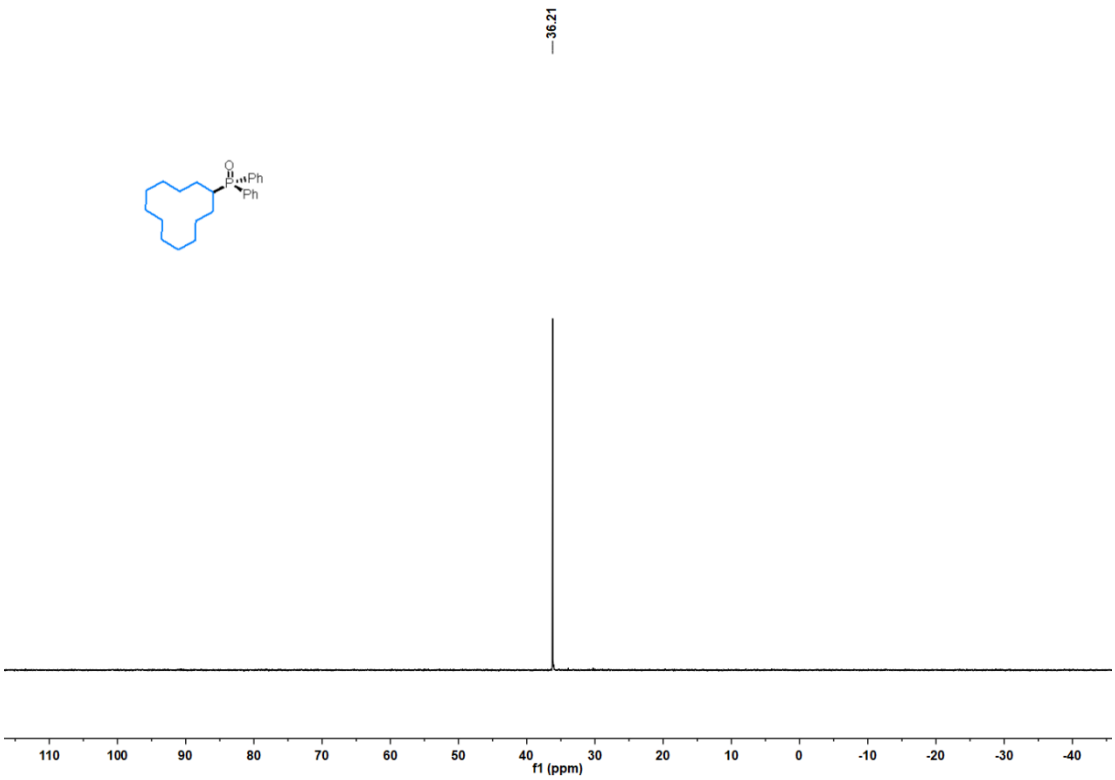


4f; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)





4f; ^{31}P NMR (242.9 MHz, $CDCl_3$)



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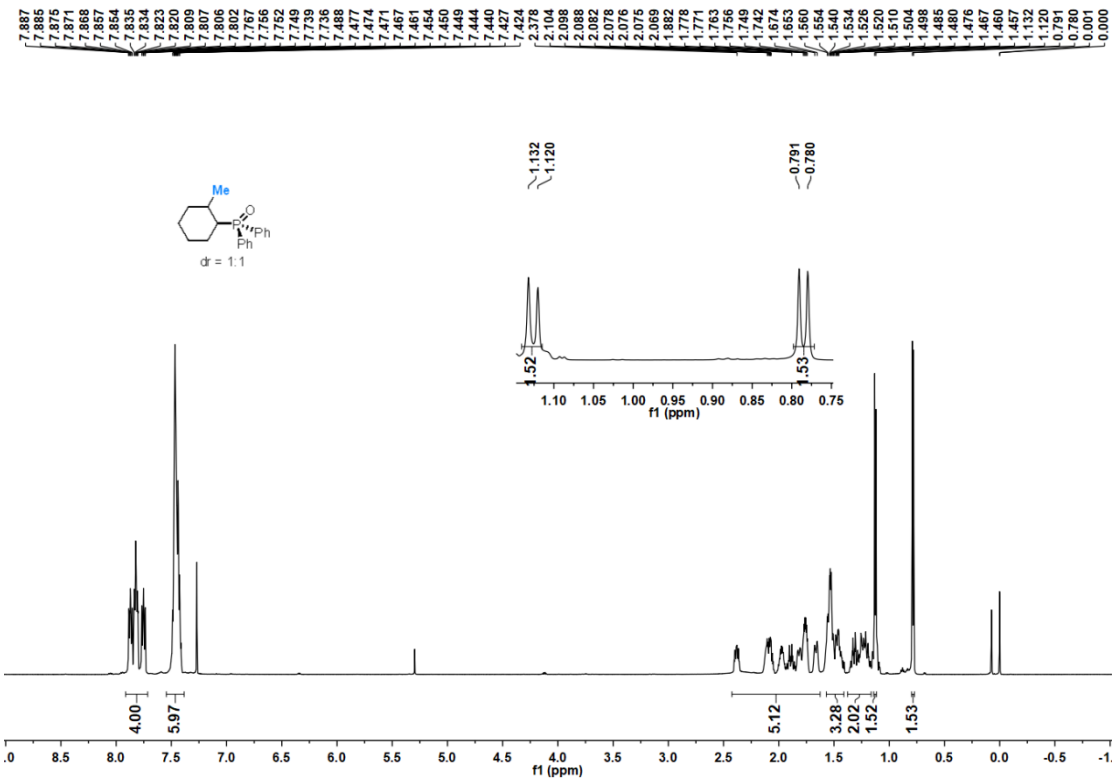
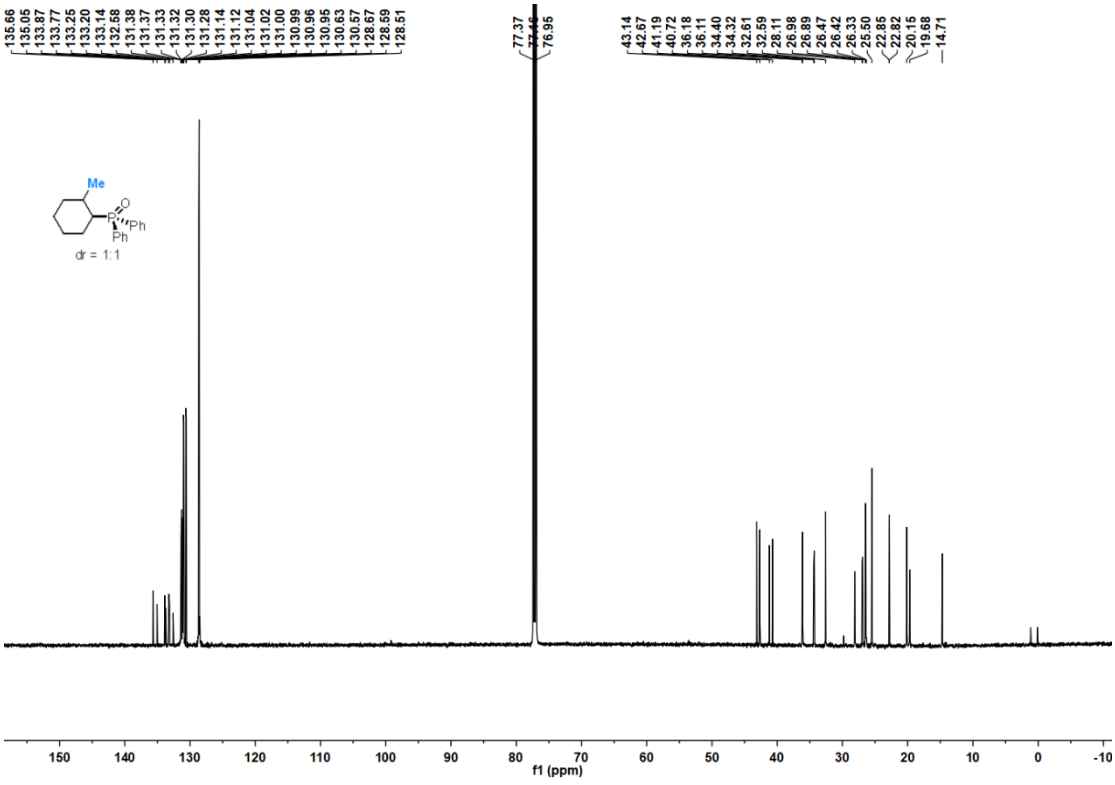
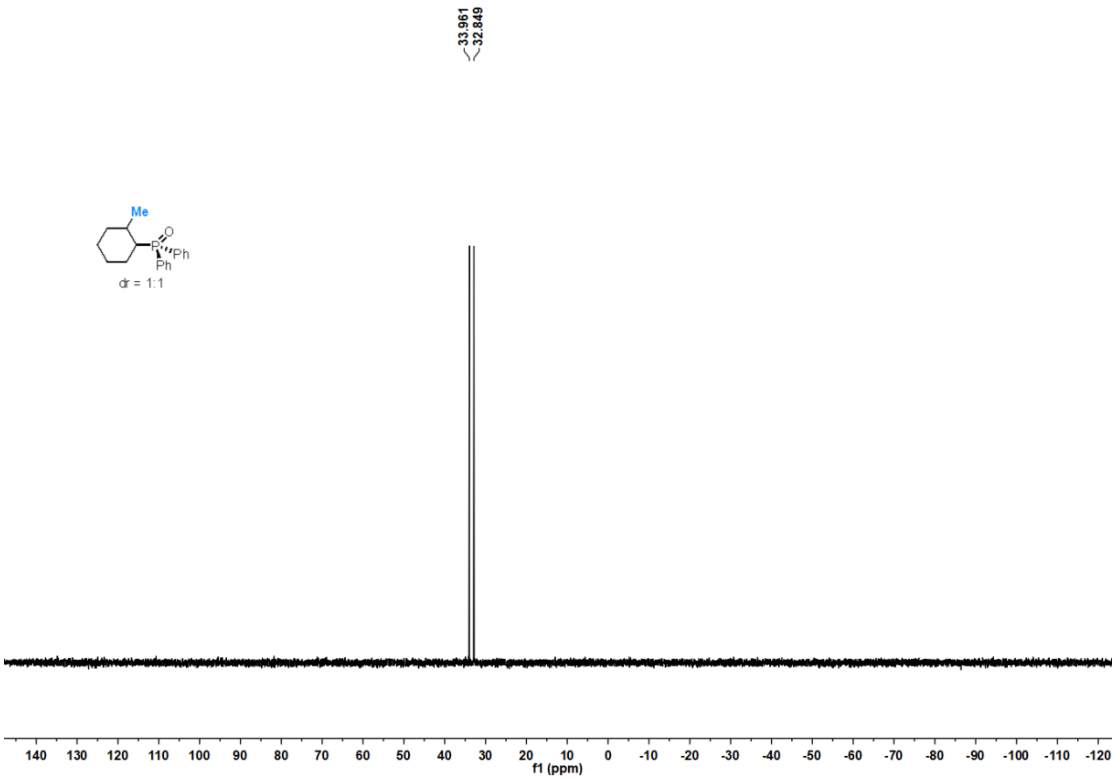




4g; ^{31}P NMR (242.9 MHz, $CDCl_3$)



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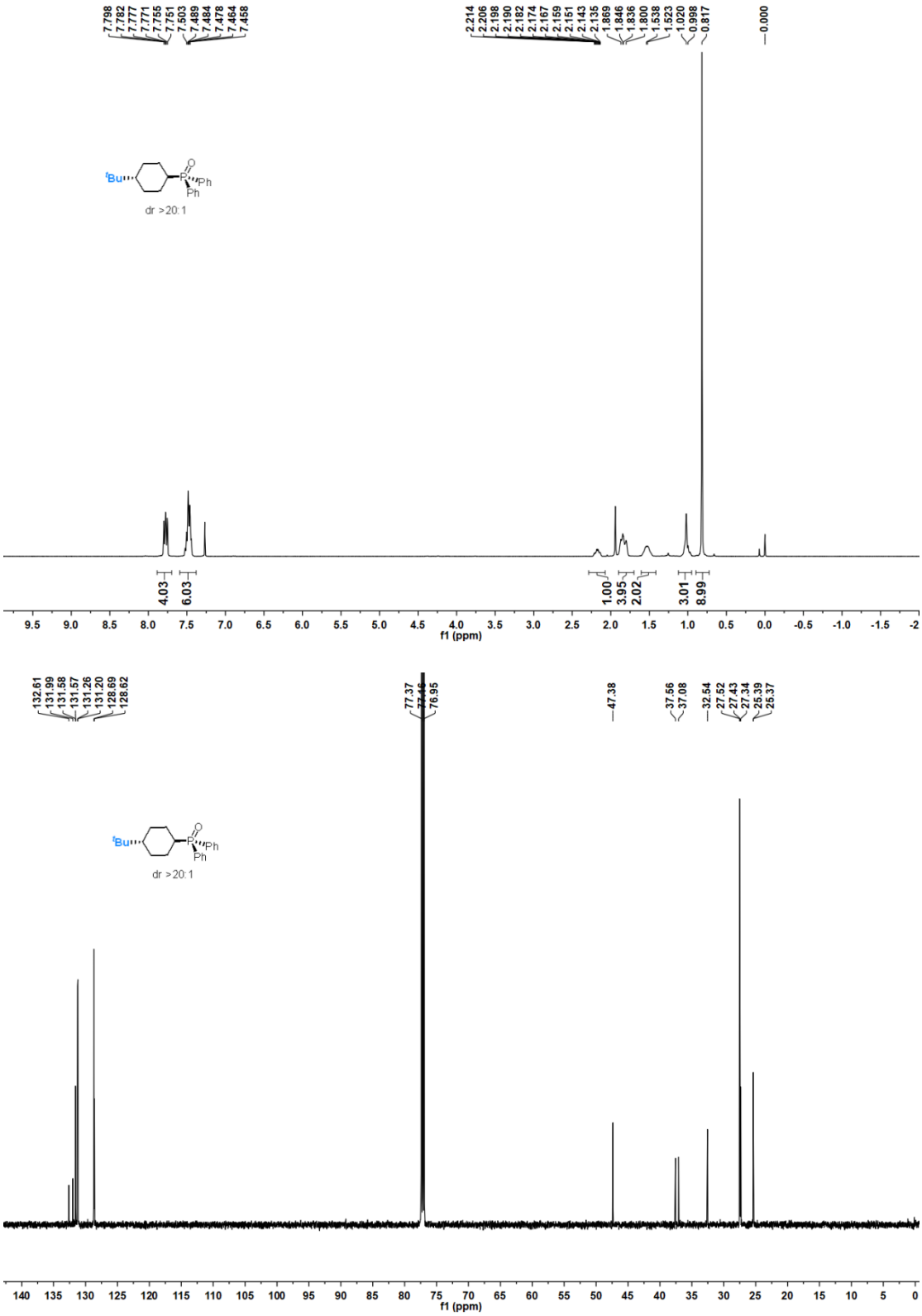
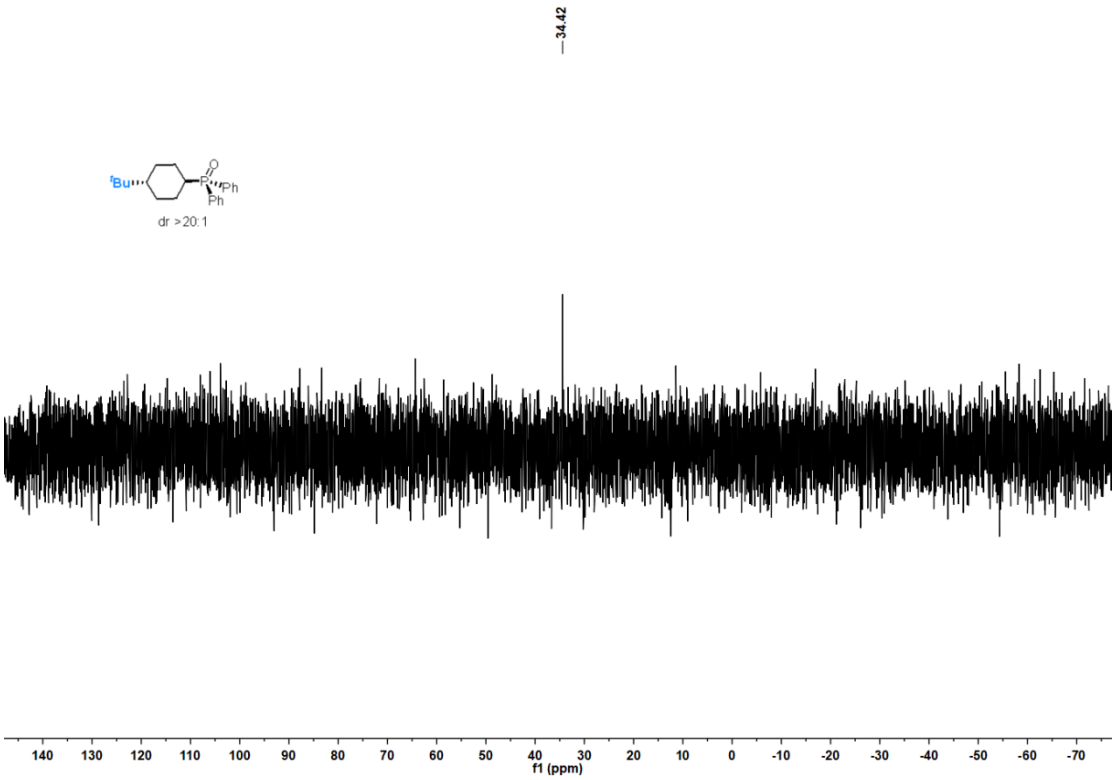


4h; ^{31}P NMR (161.9 MHz, $CDCl_3$)



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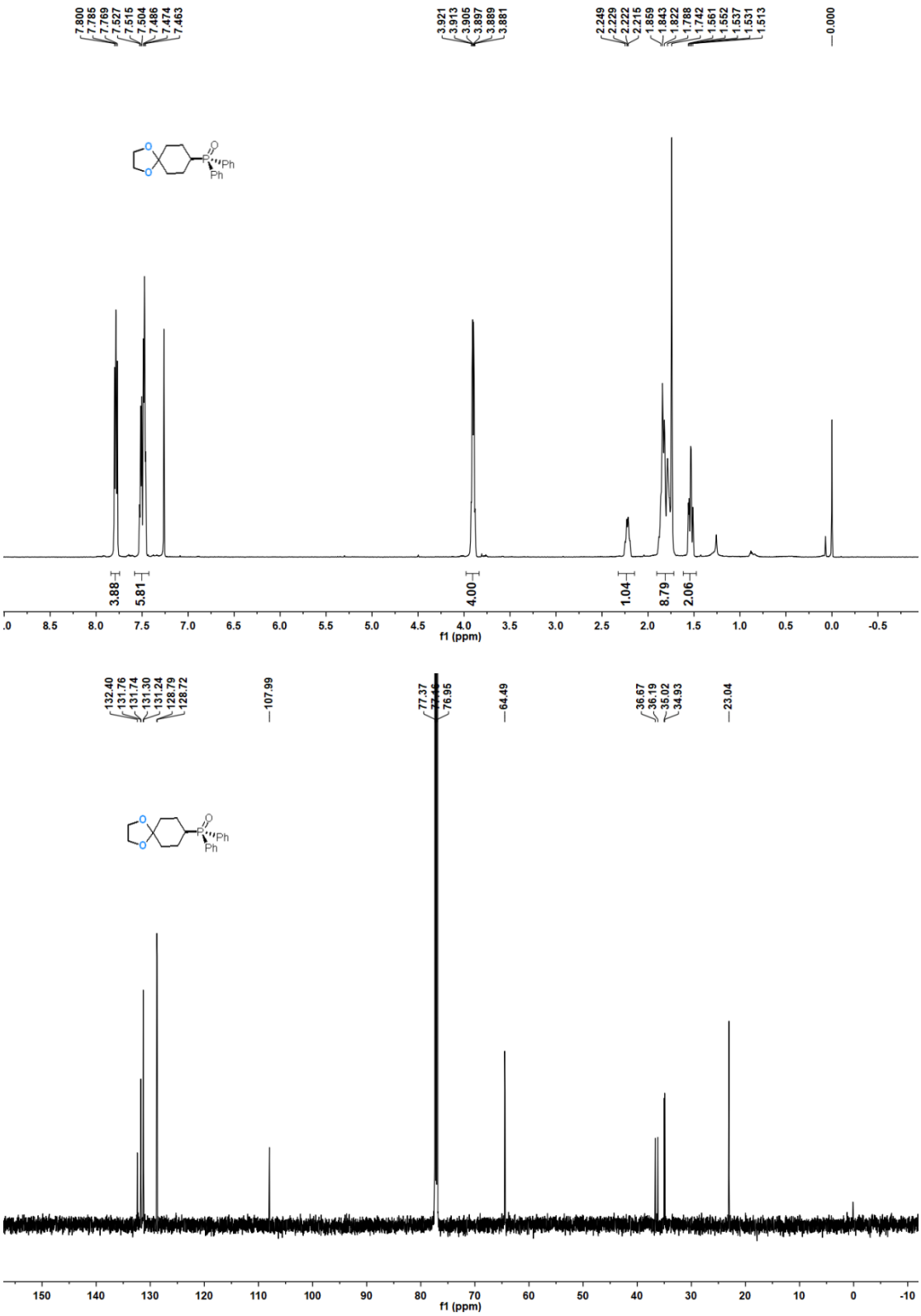
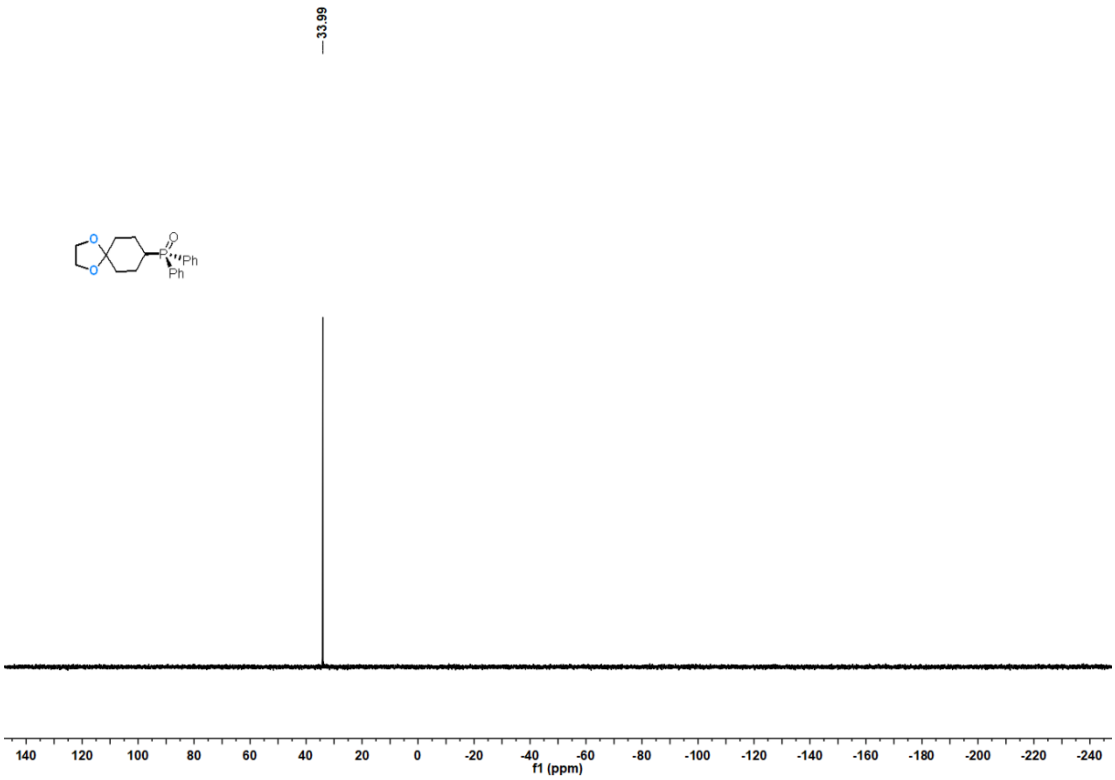


4i; ^{31}P NMR (242.9 MHz, $CDCl_3$)



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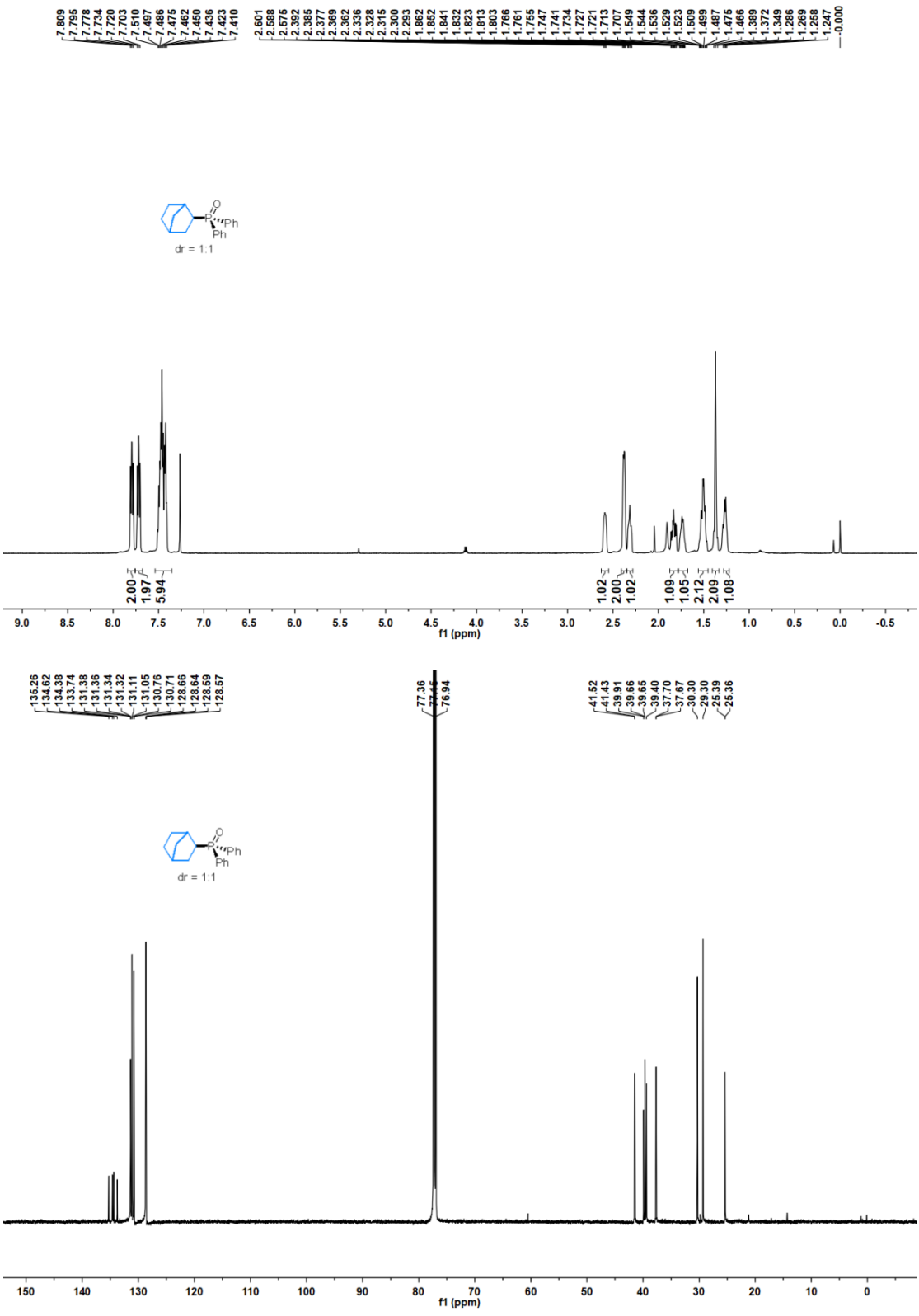

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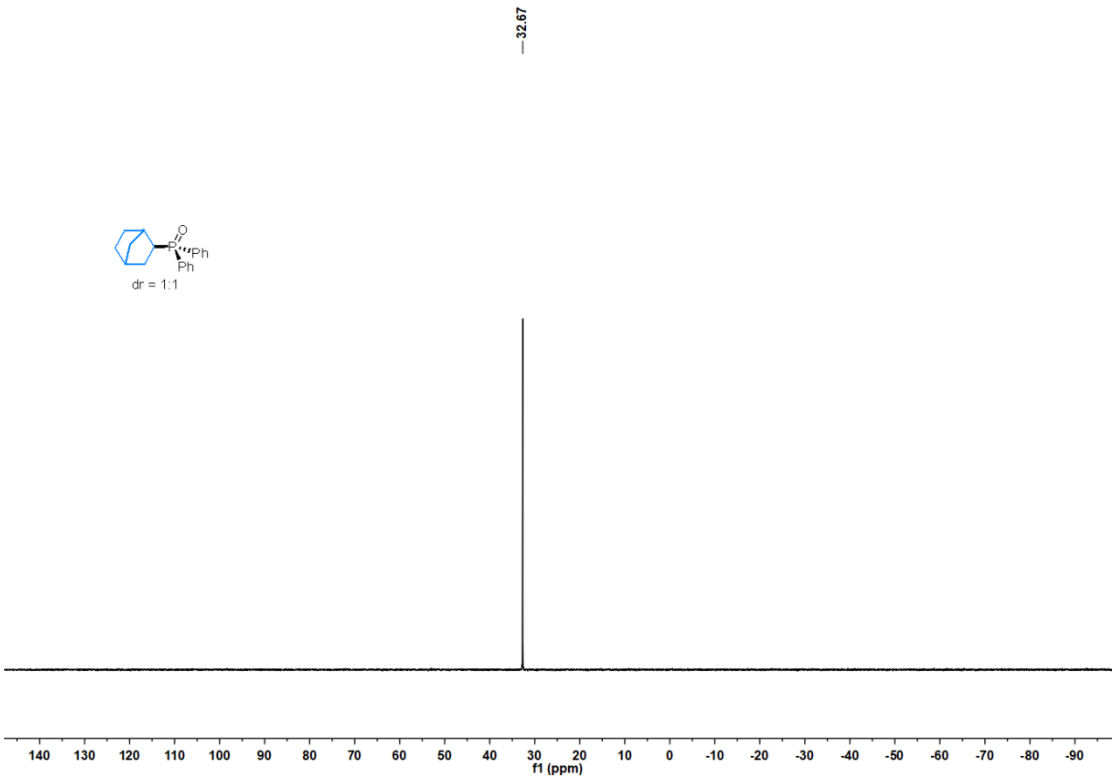
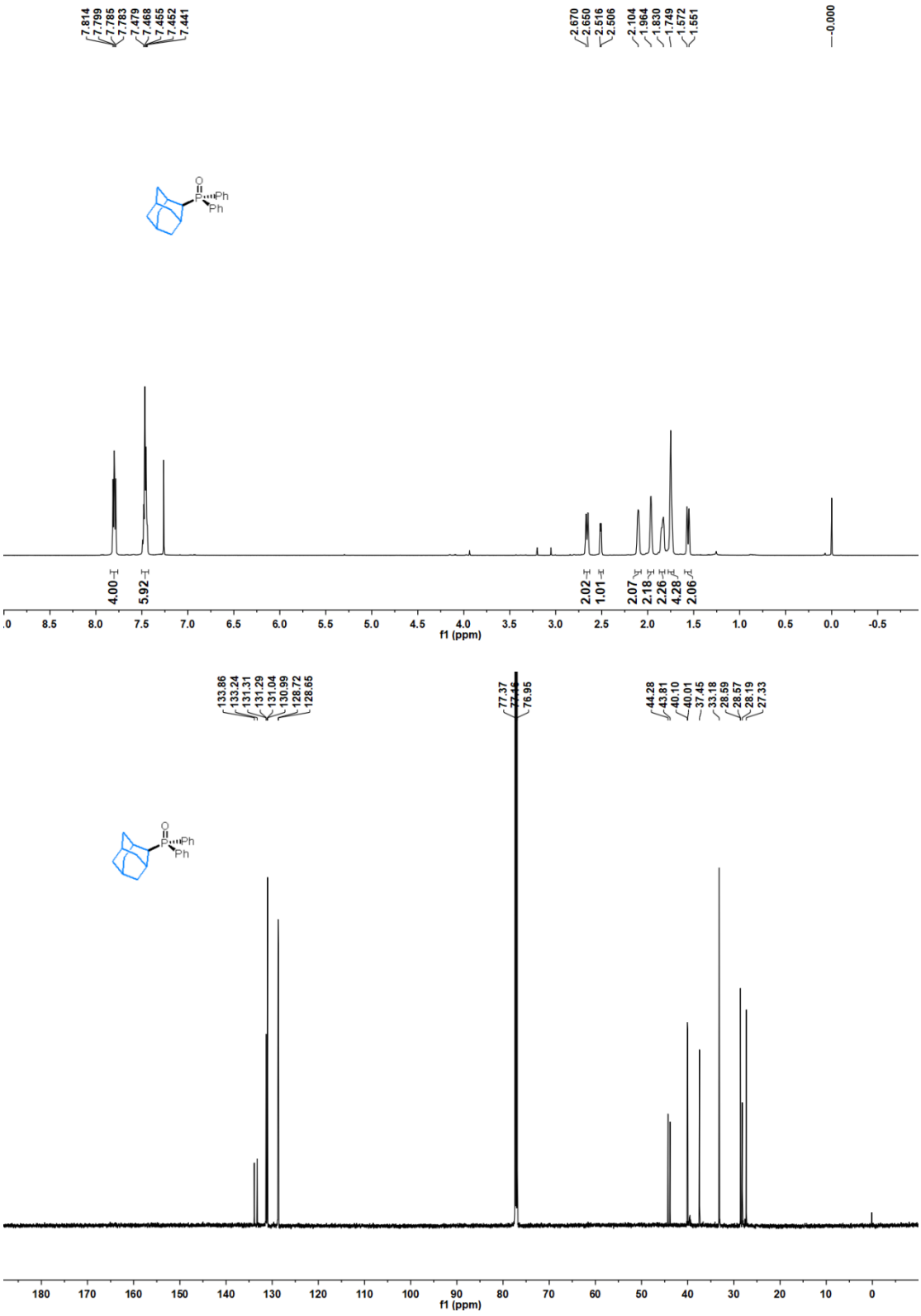
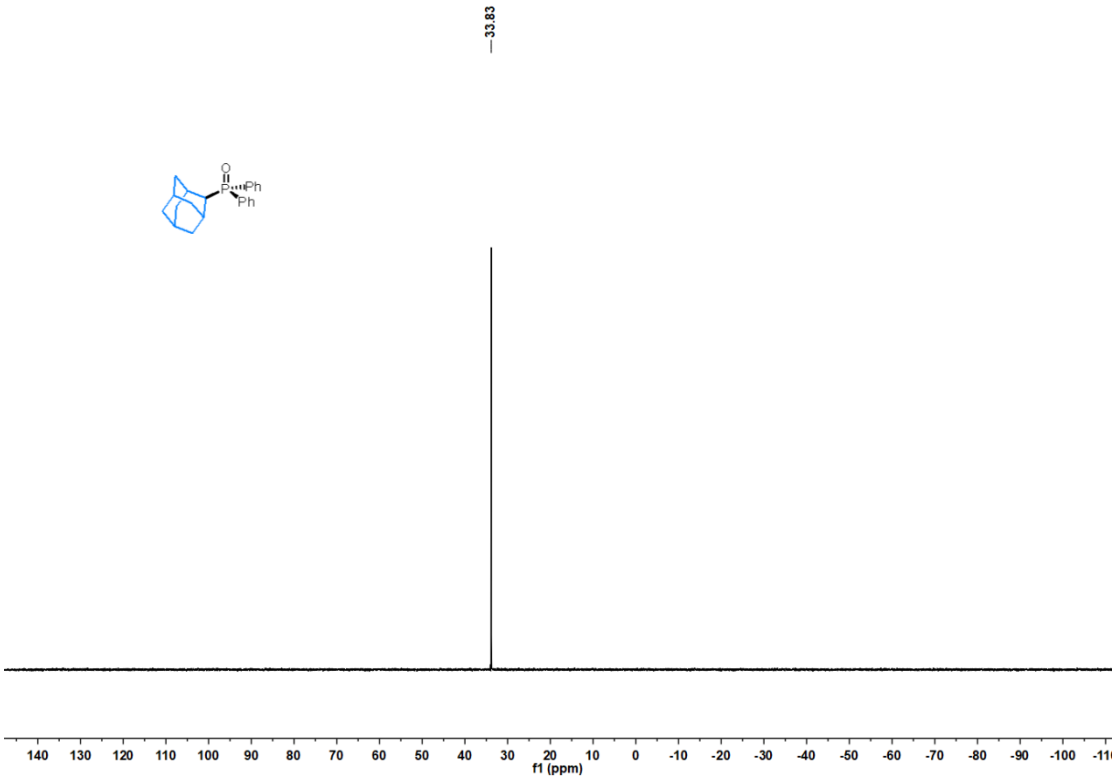


4k; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



4k; ^{31}P NMR (242.9 MHz, $CDCl_3$)



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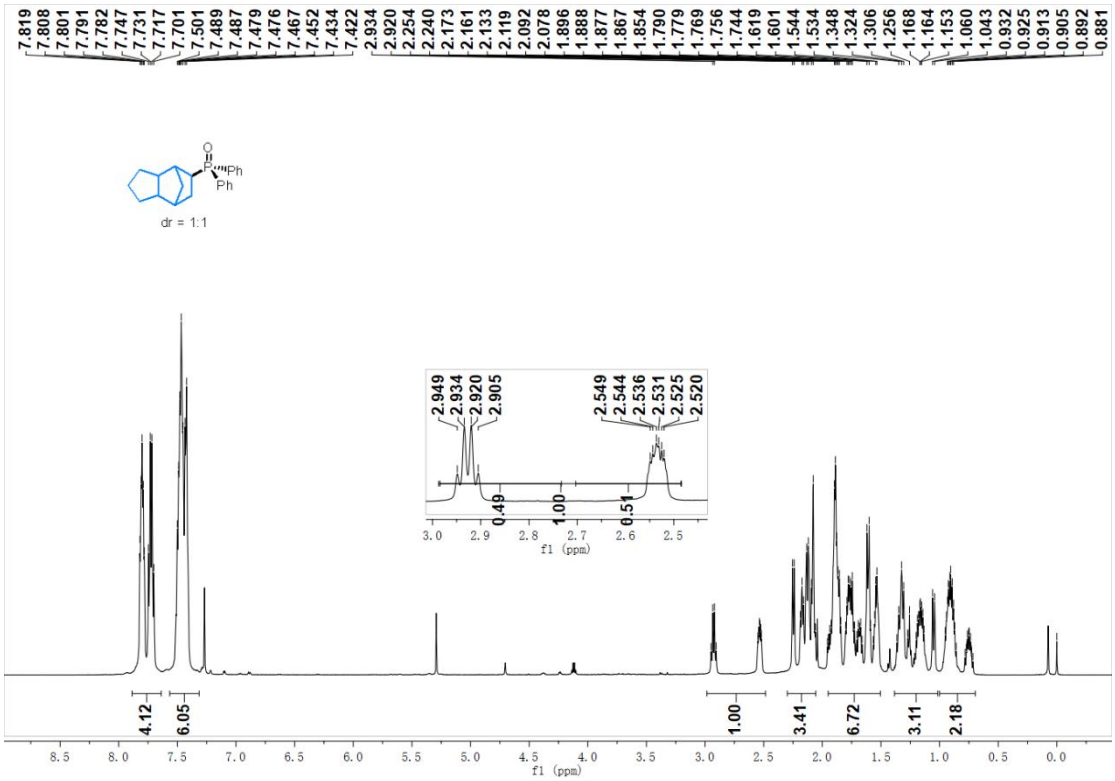
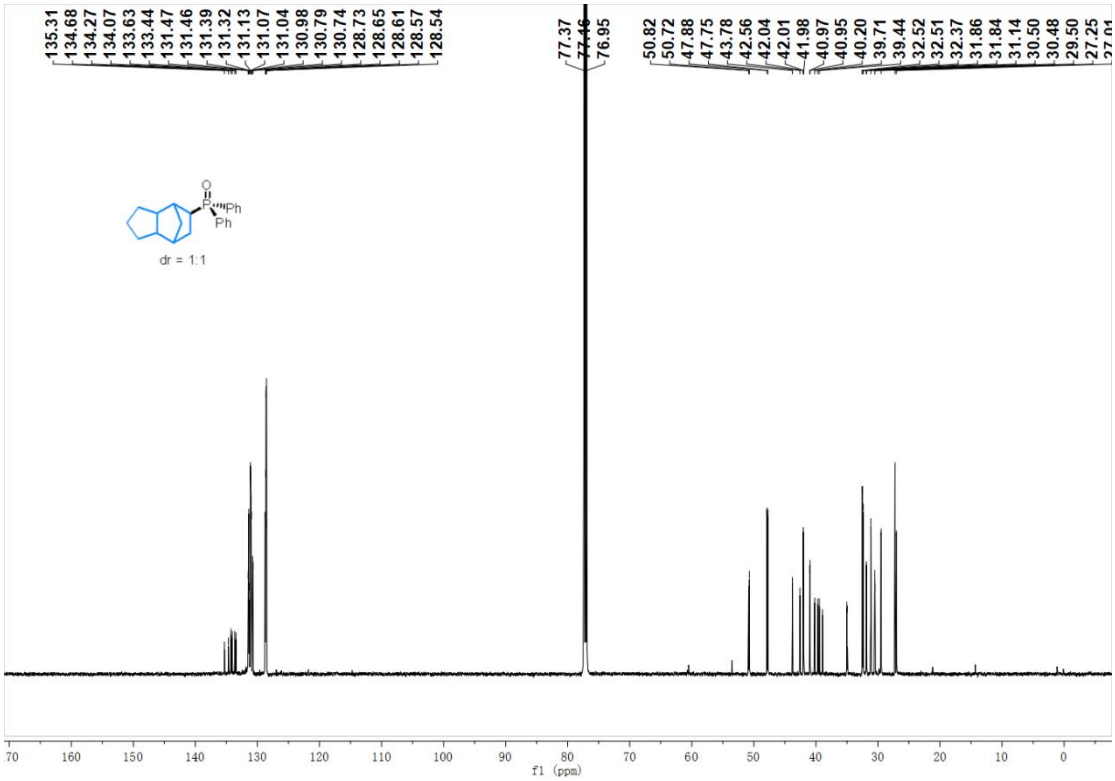
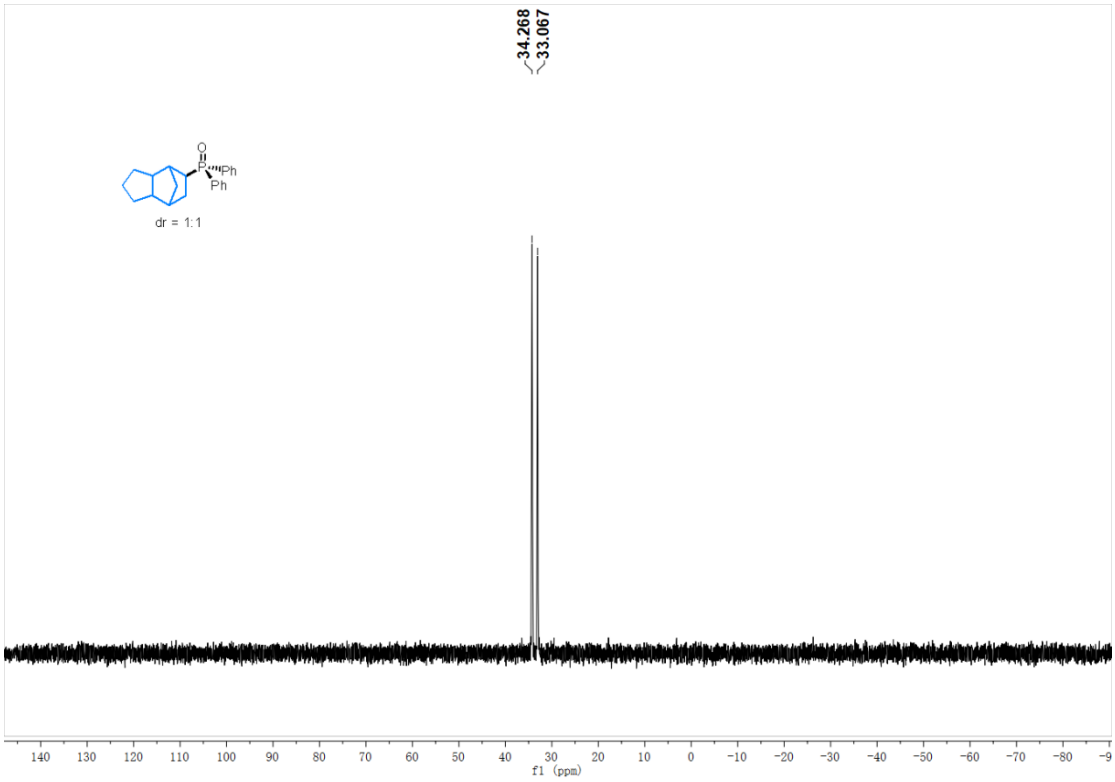
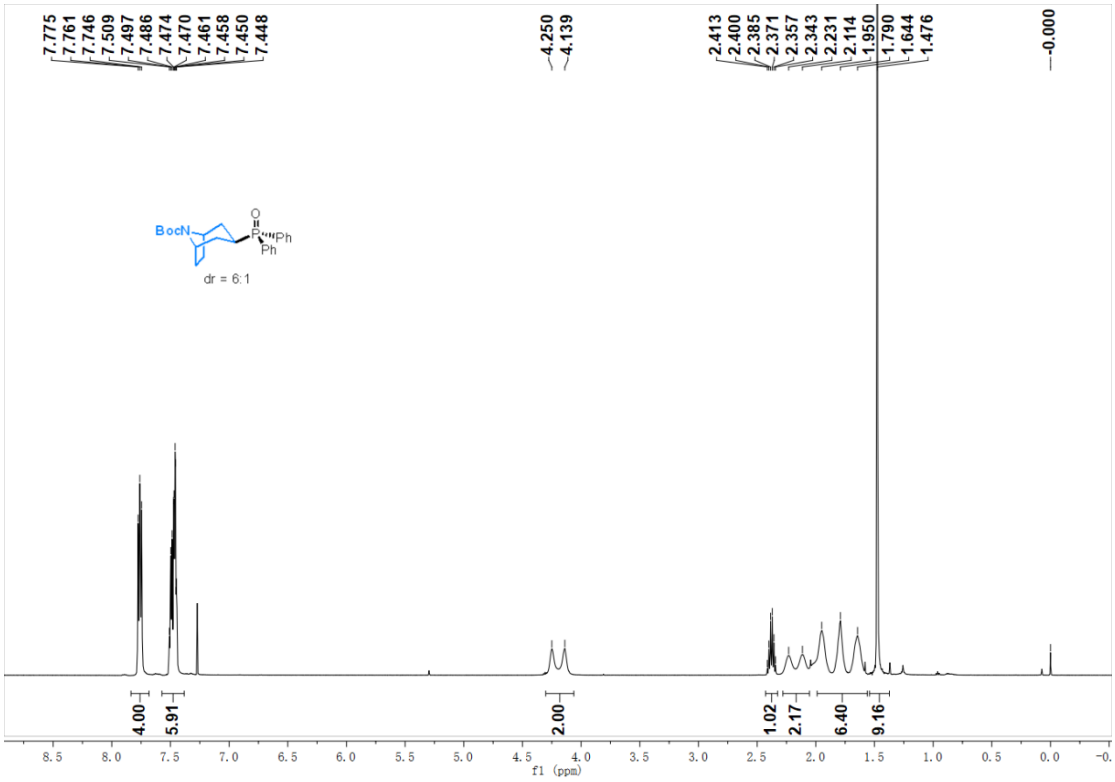


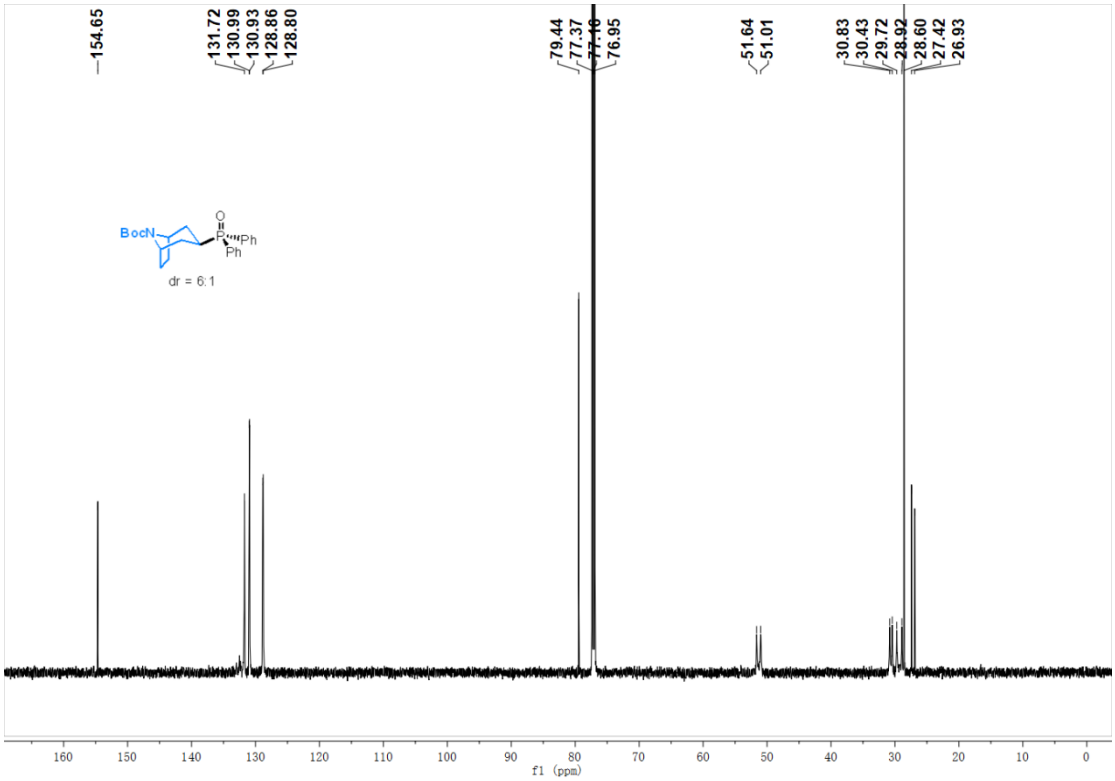


4l; ^{31}P NMR (242.9 MHz, $CDCl_3$)

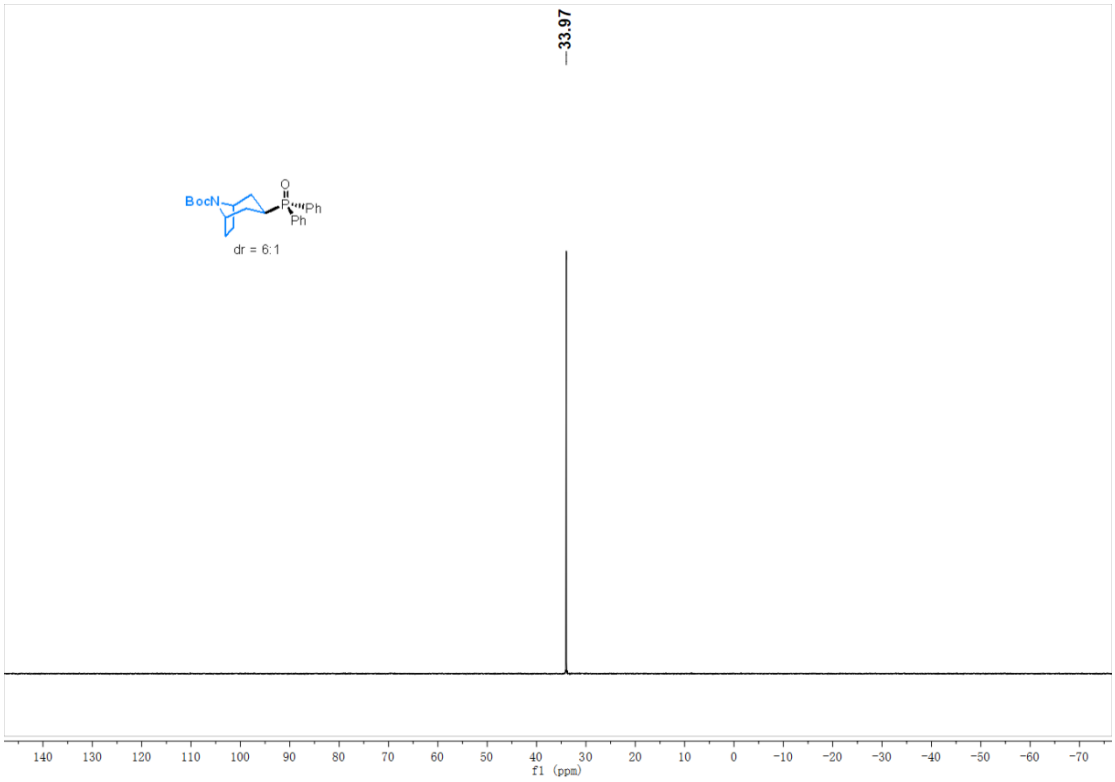


4m; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

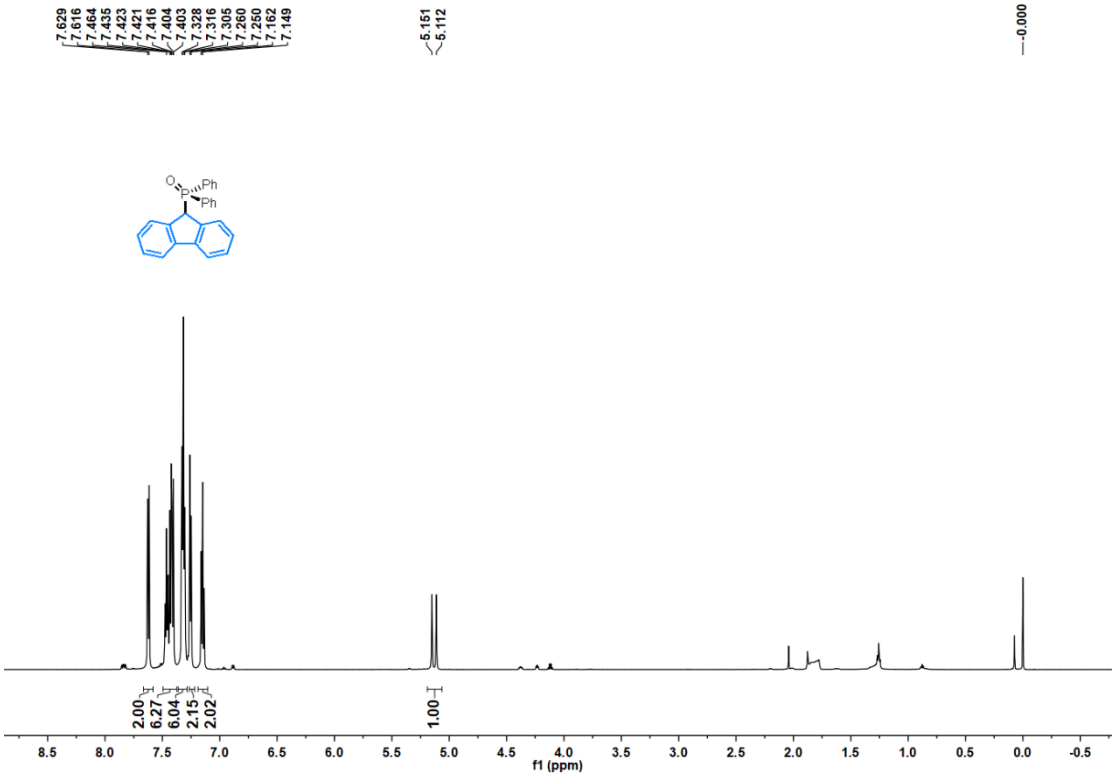


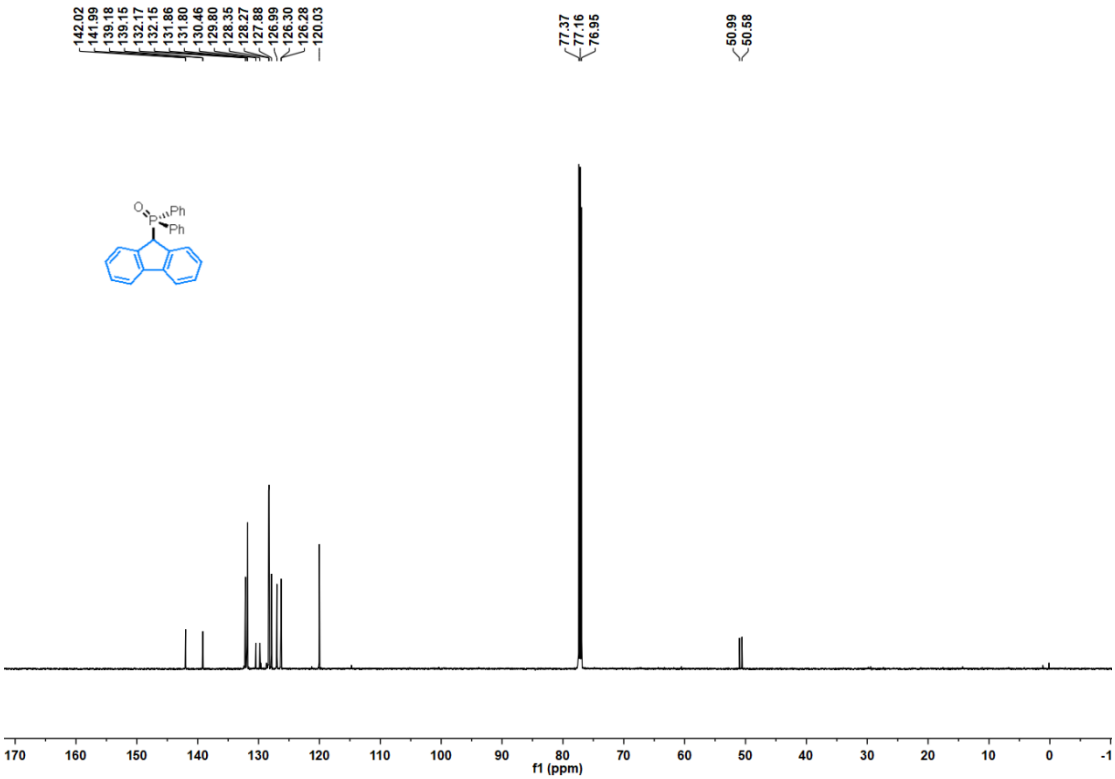


4m; ^{31}P NMR (242.9 MHz, $CDCl_3$)

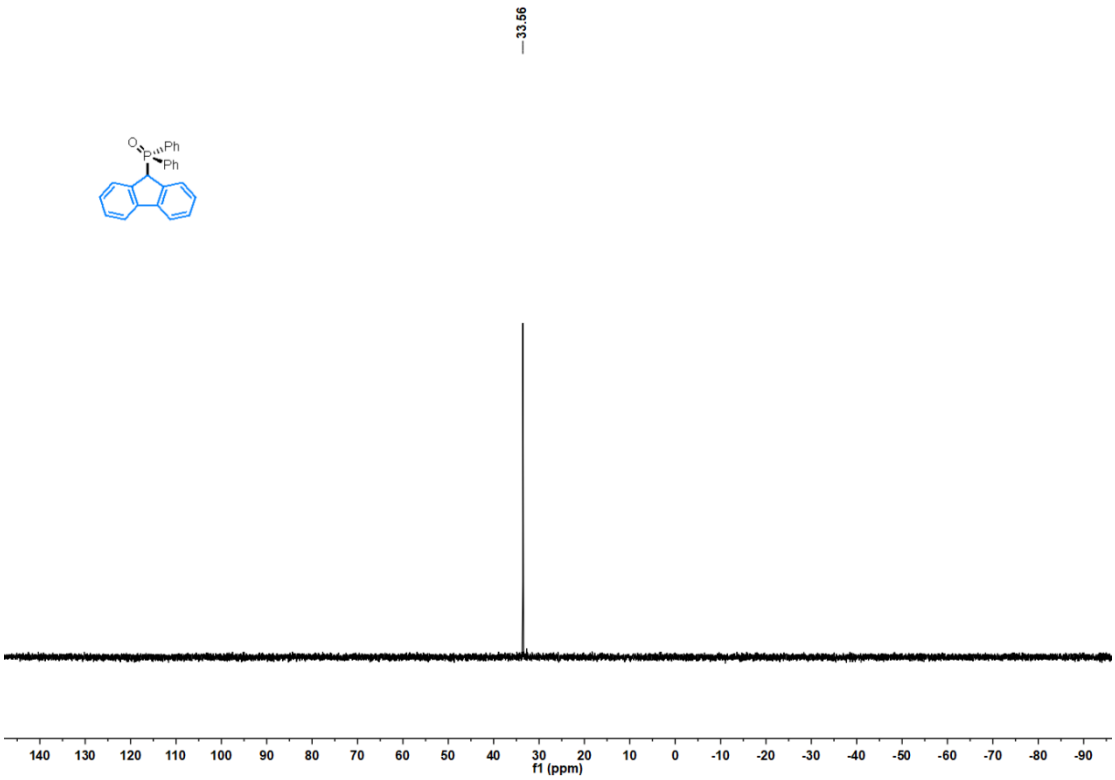


4n; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

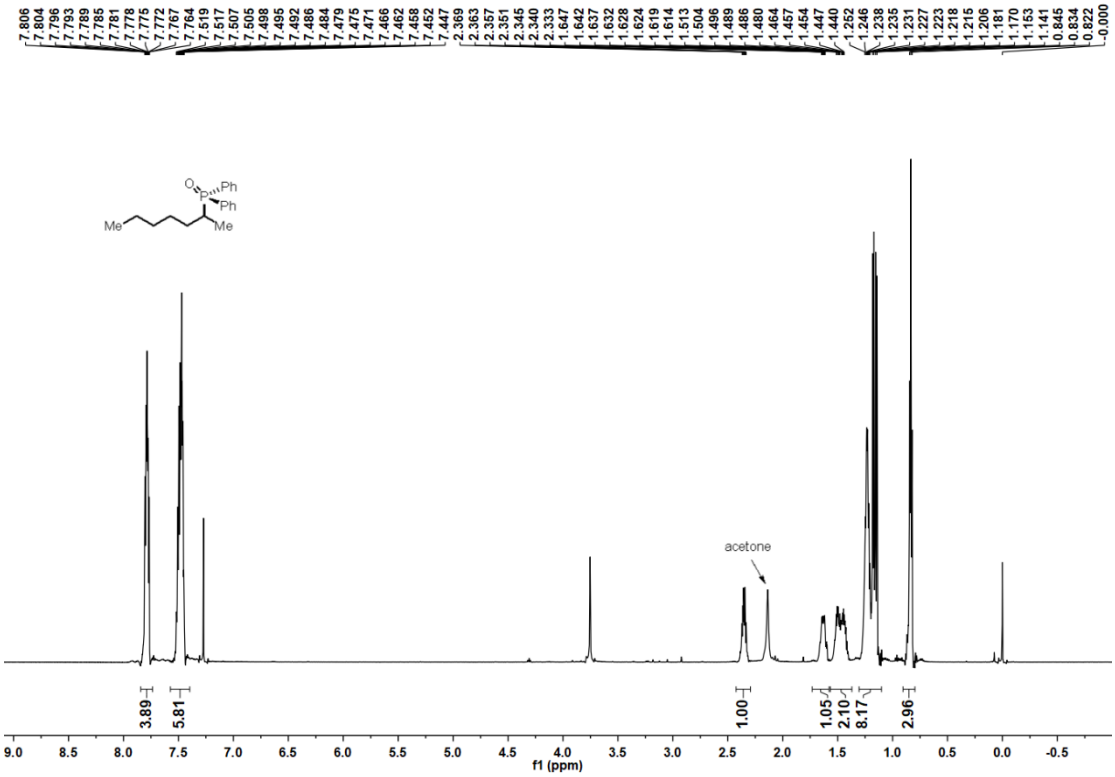


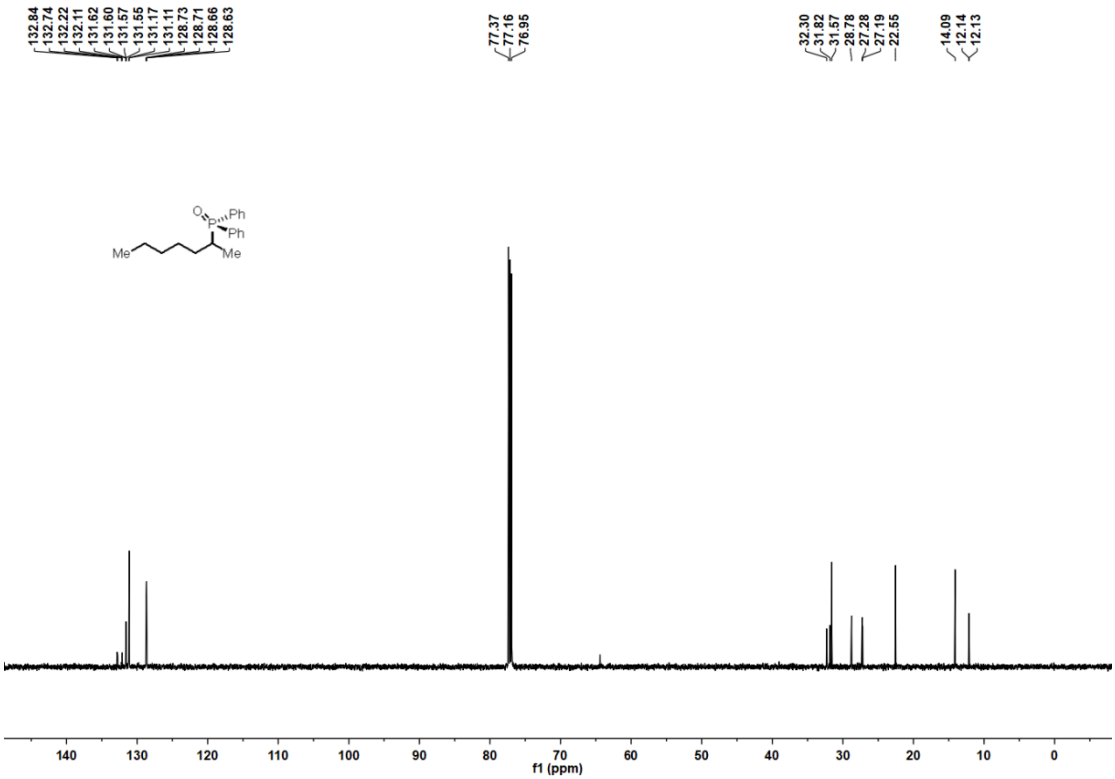


4n; ^{31}P NMR (242.9 MHz, $CDCl_3$)

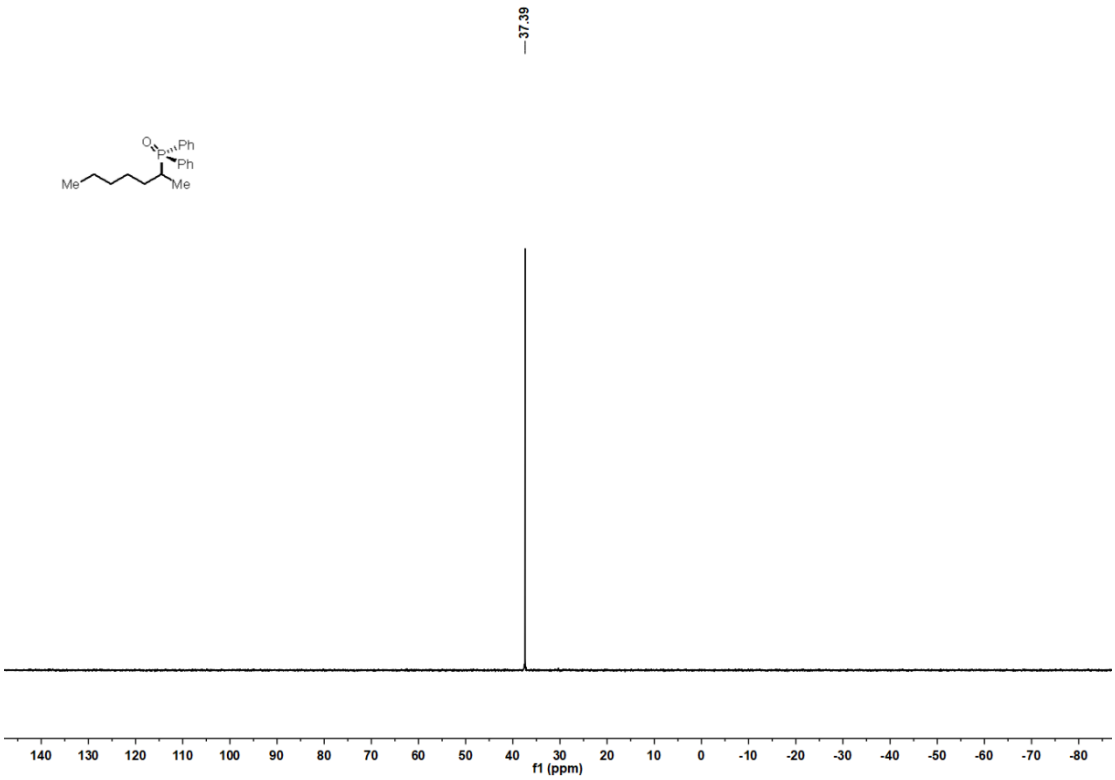


4o; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

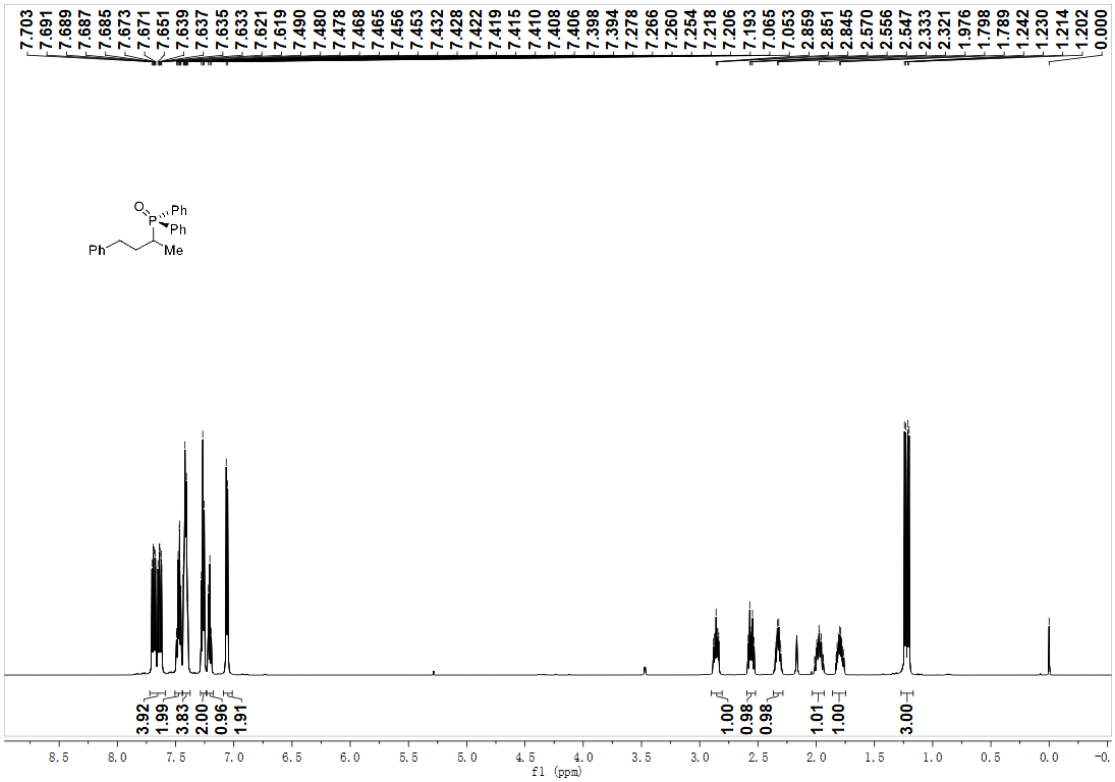


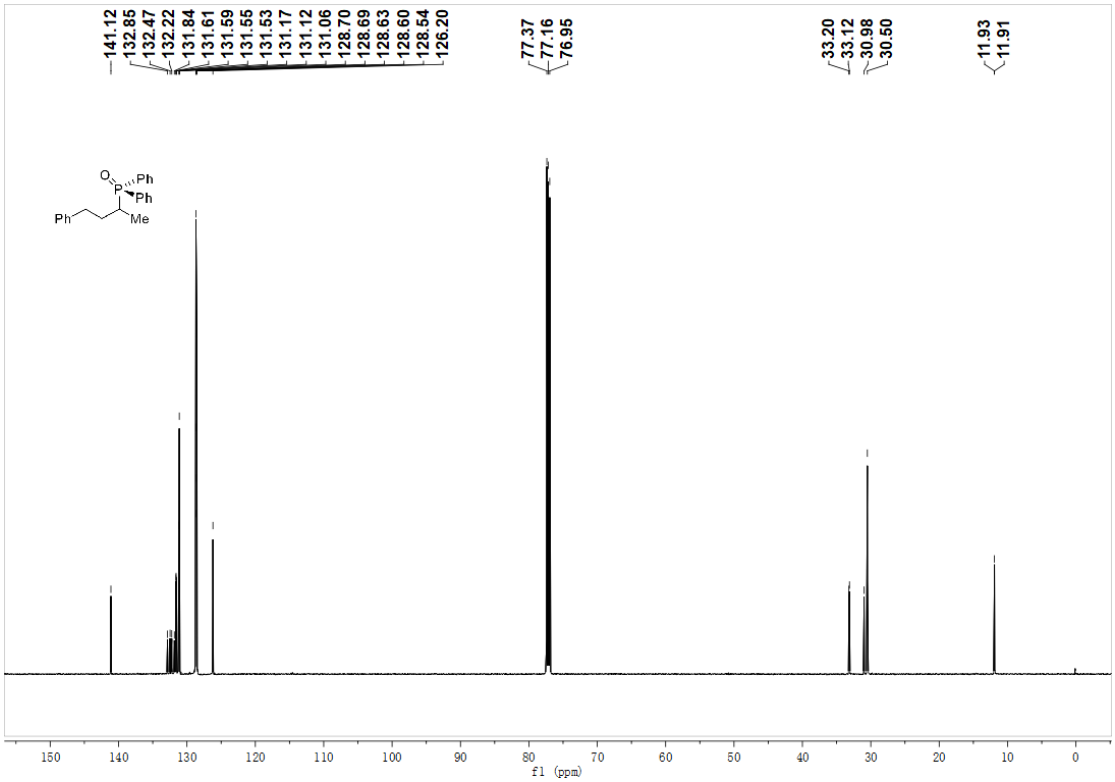


4o; ^{31}P NMR (242.9 MHz, $CDCl_3$)

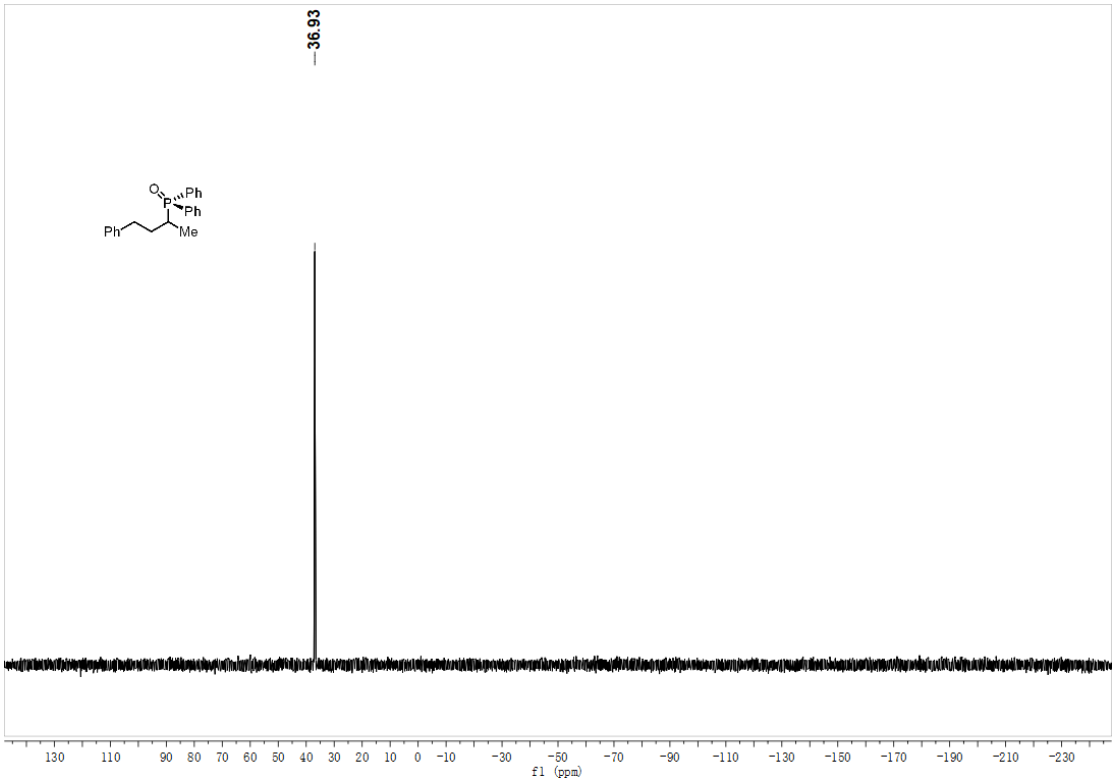


4p; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

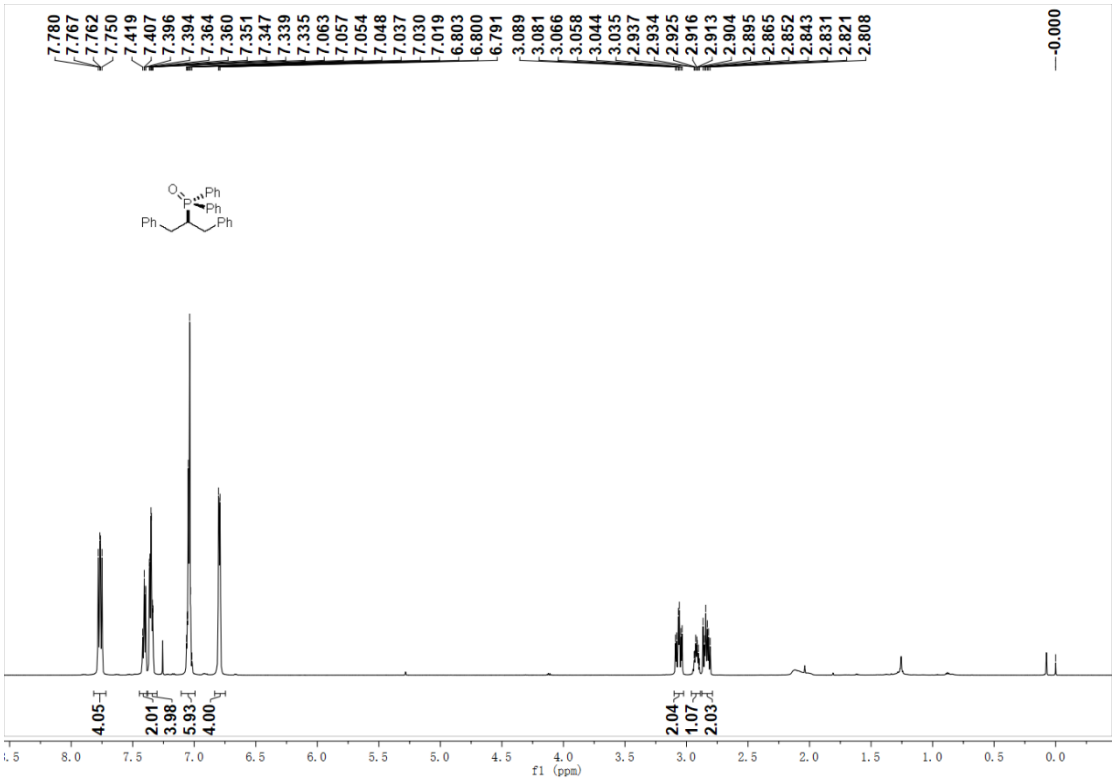


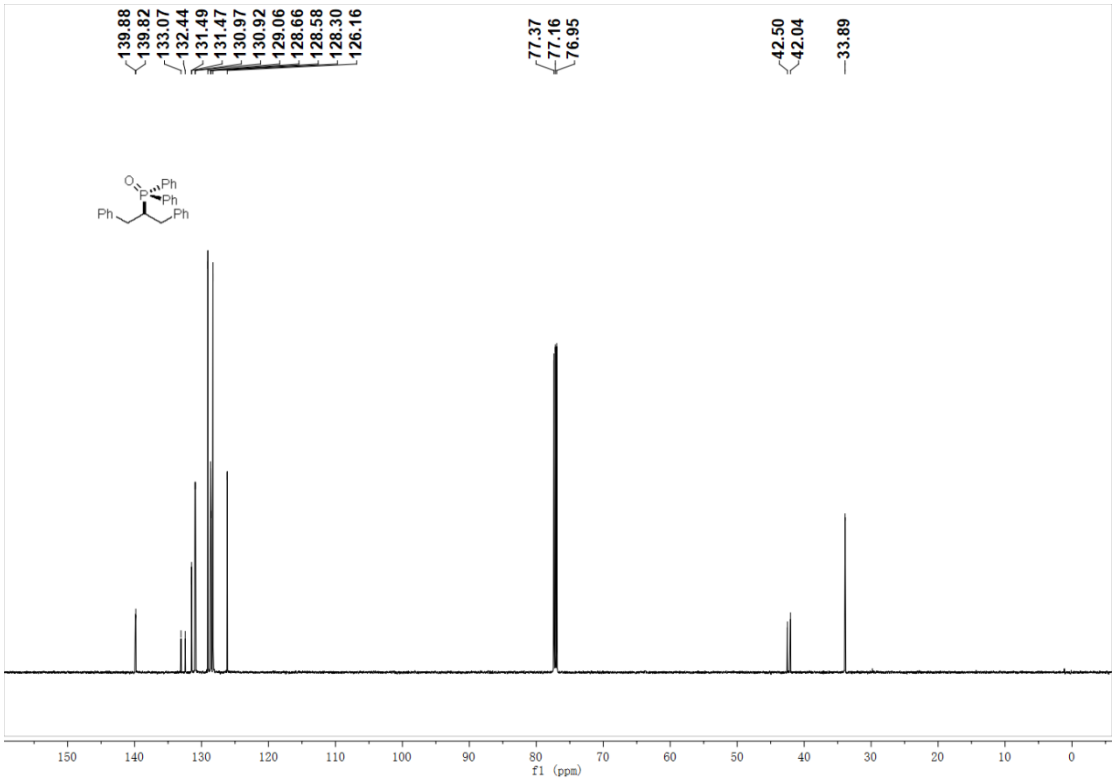


4p; ^{31}P NMR (242.9 MHz, $CDCl_3$)

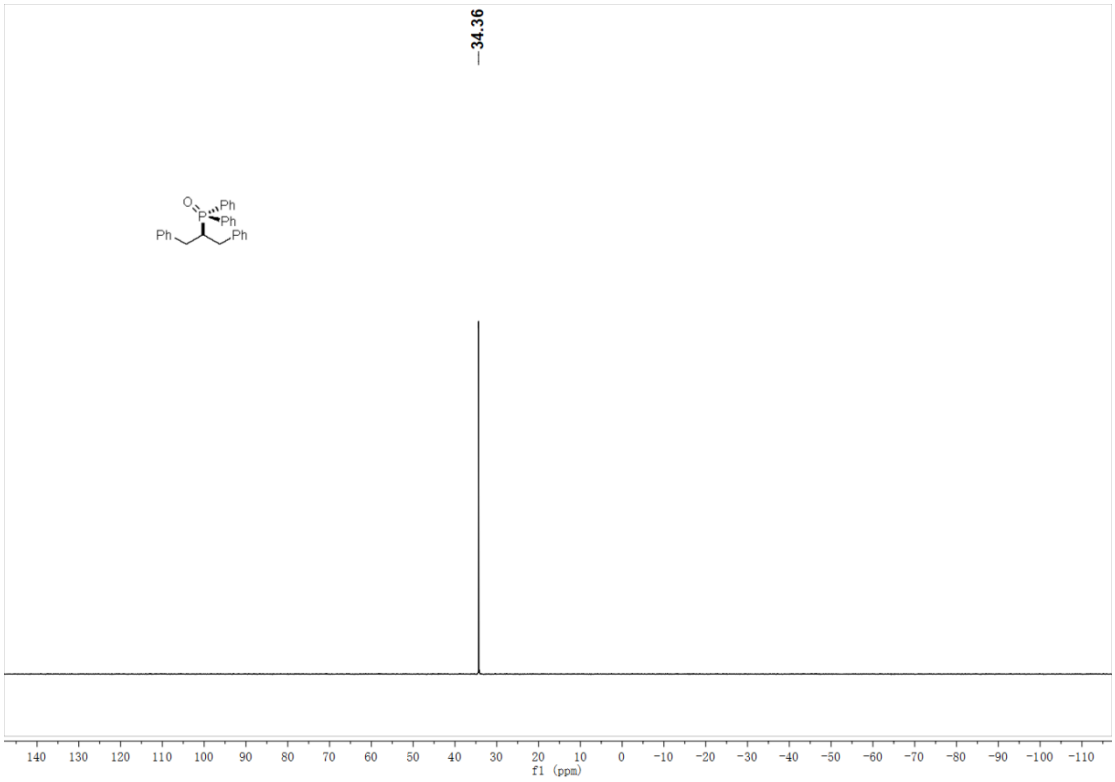


4q; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

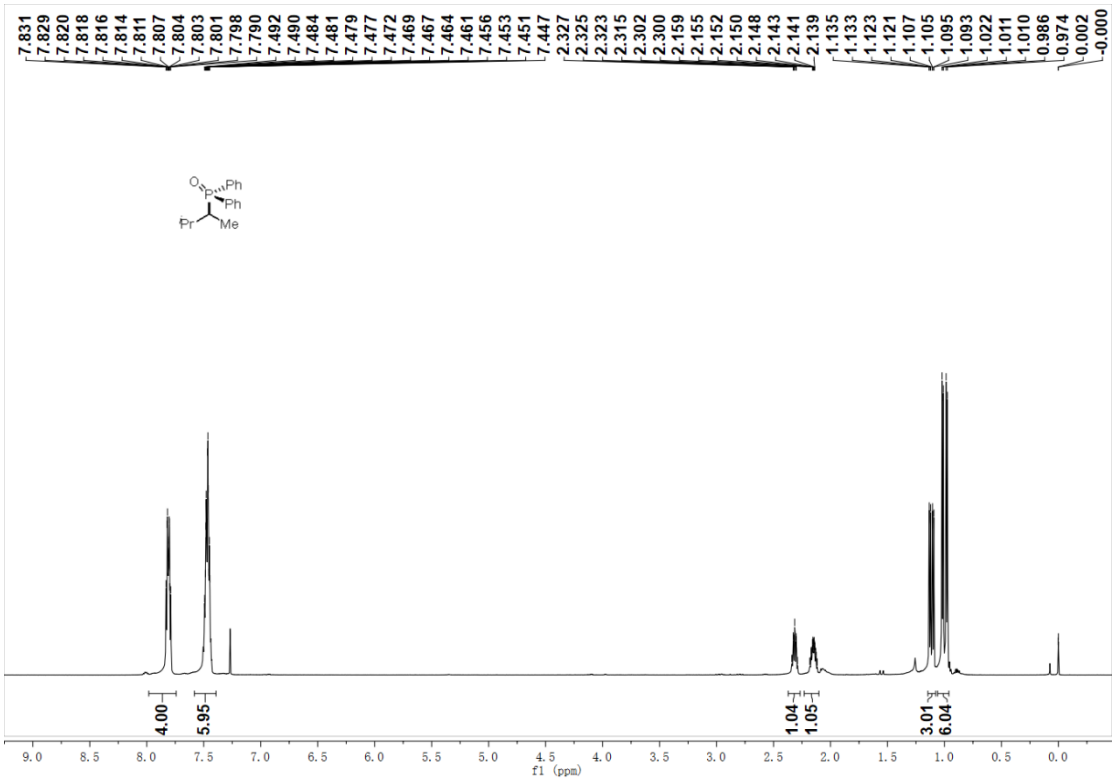


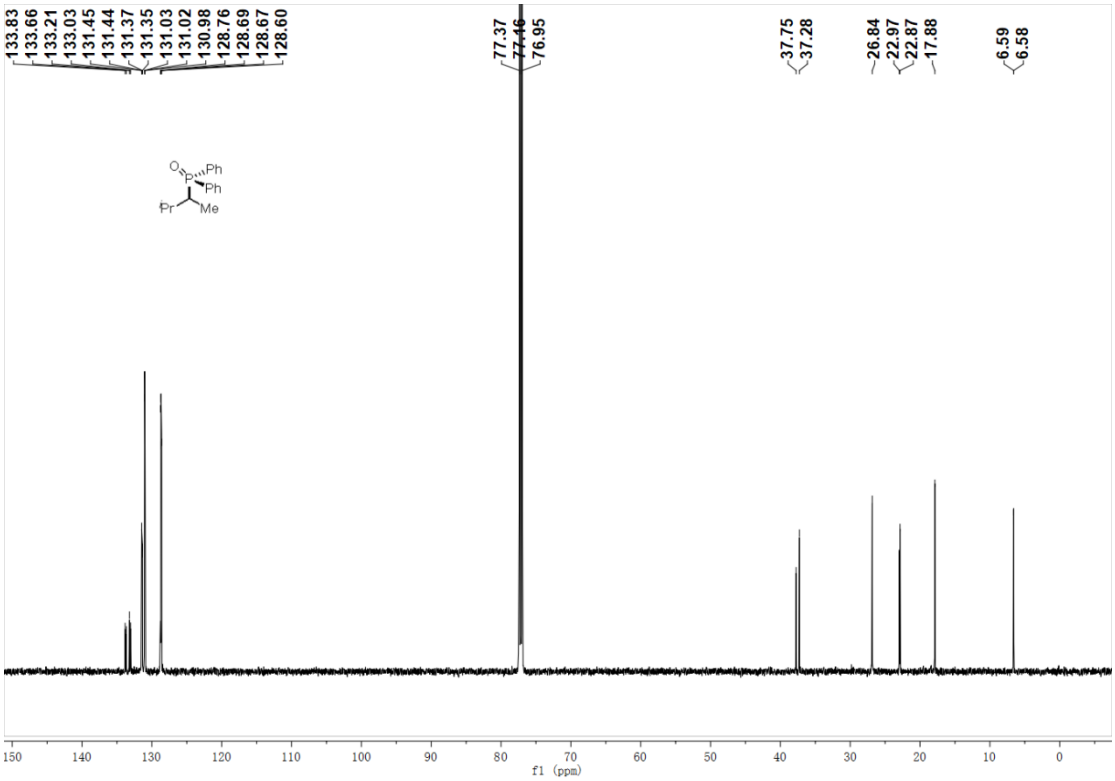


4q; ^{31}P NMR (242.9 MHz, $CDCl_3$)

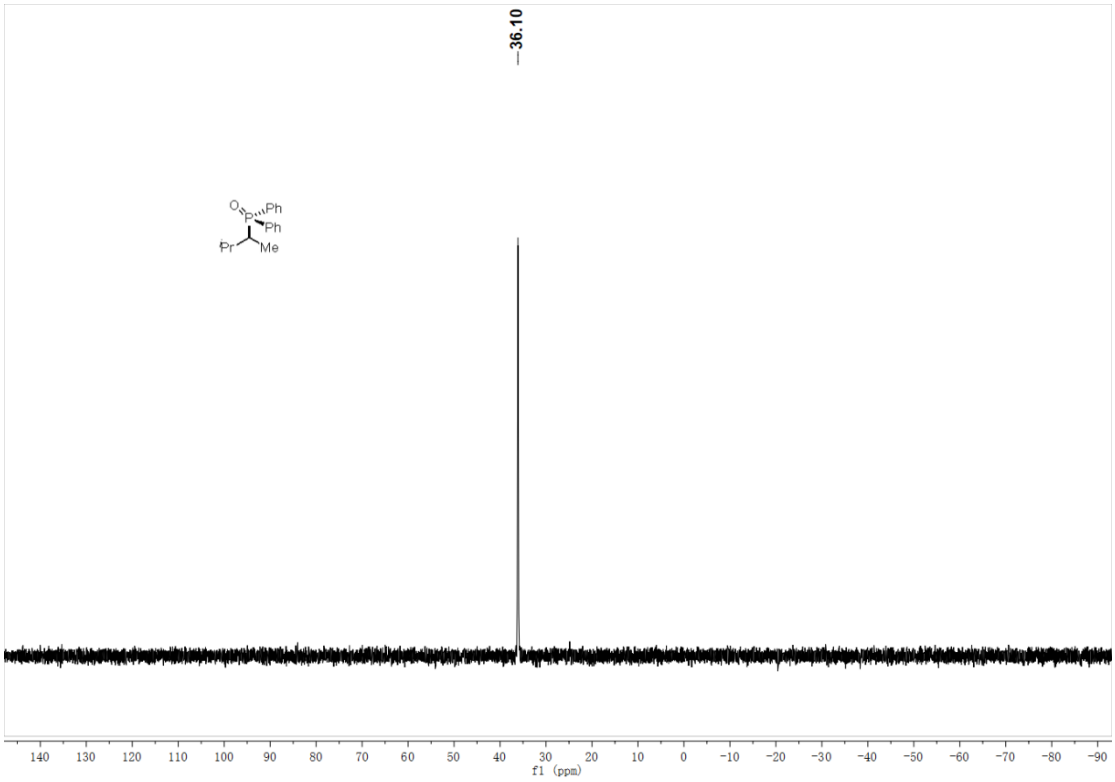


4r; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

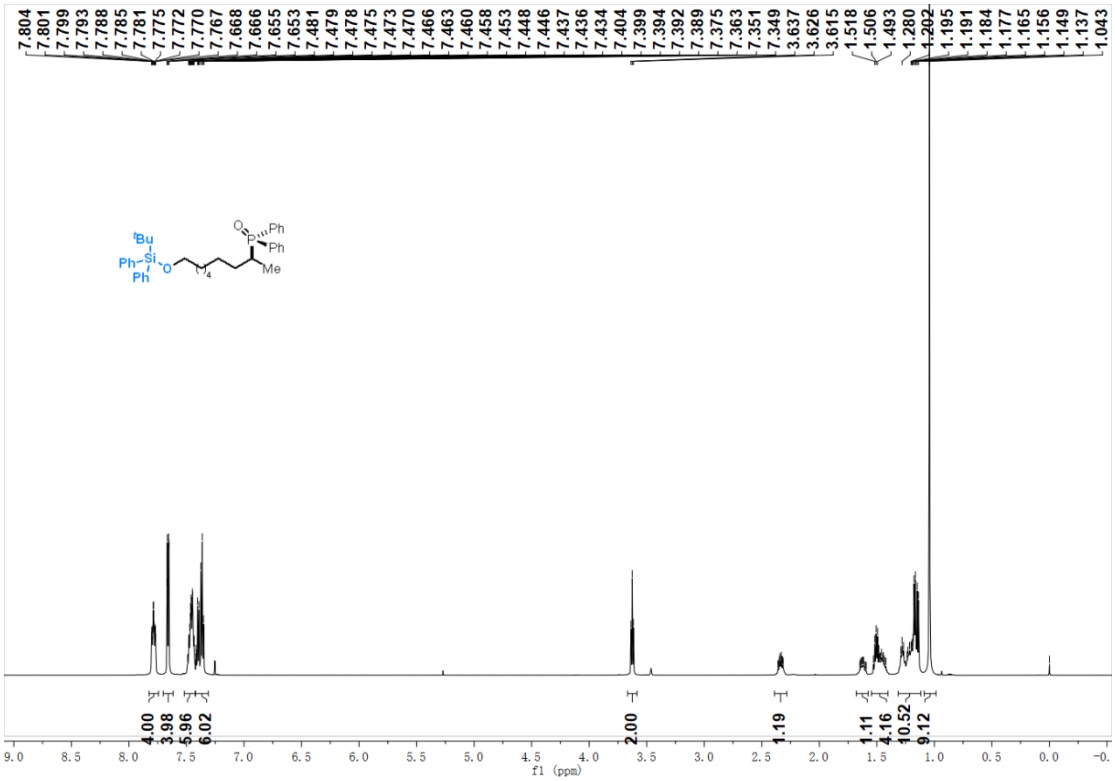


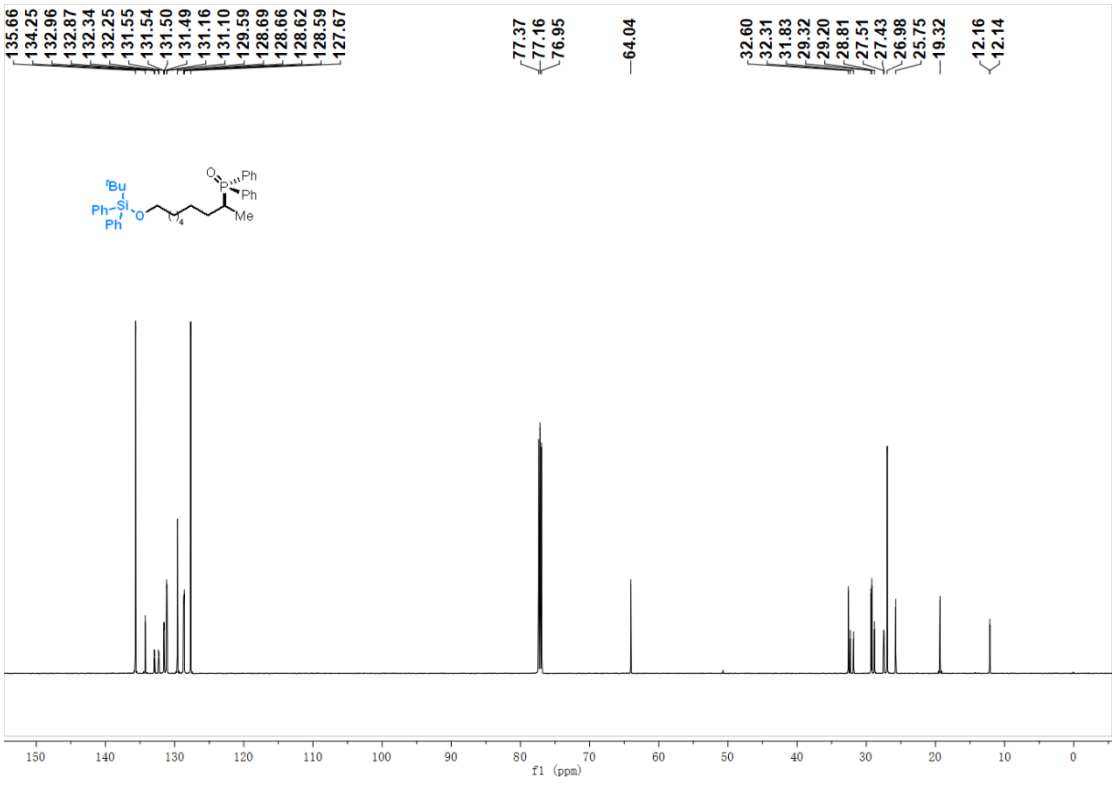


4r; ^{31}P NMR (242.9 MHz, $CDCl_3$)

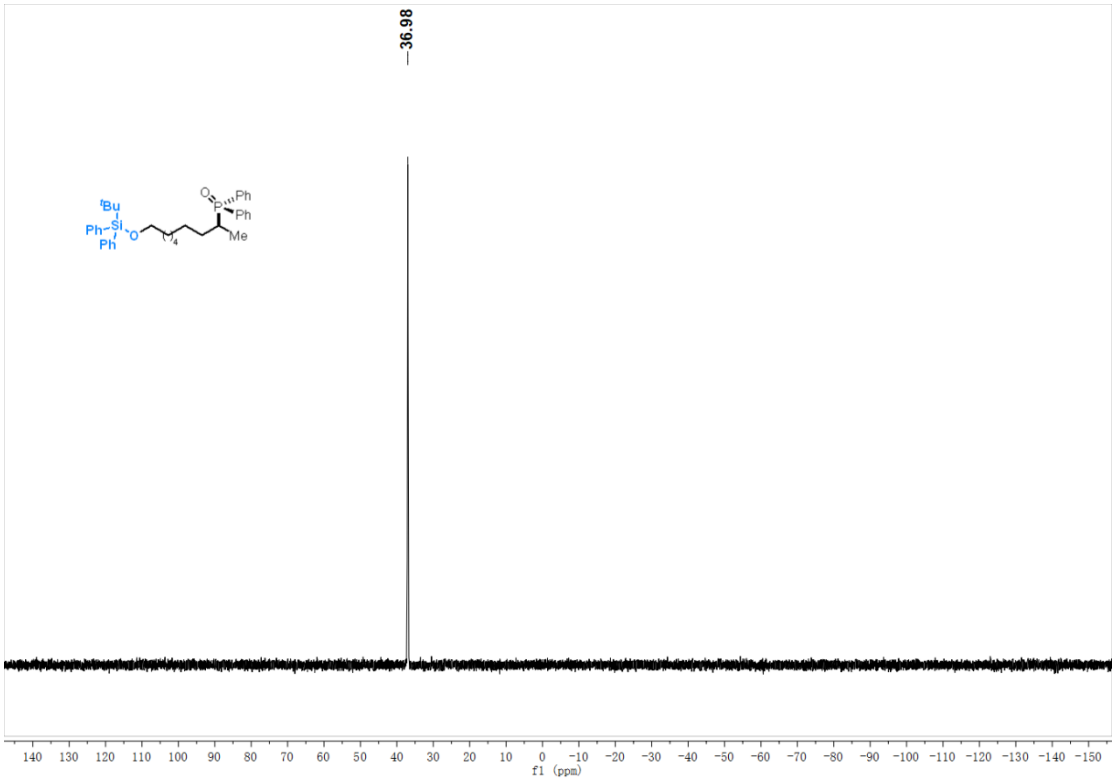


4s; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

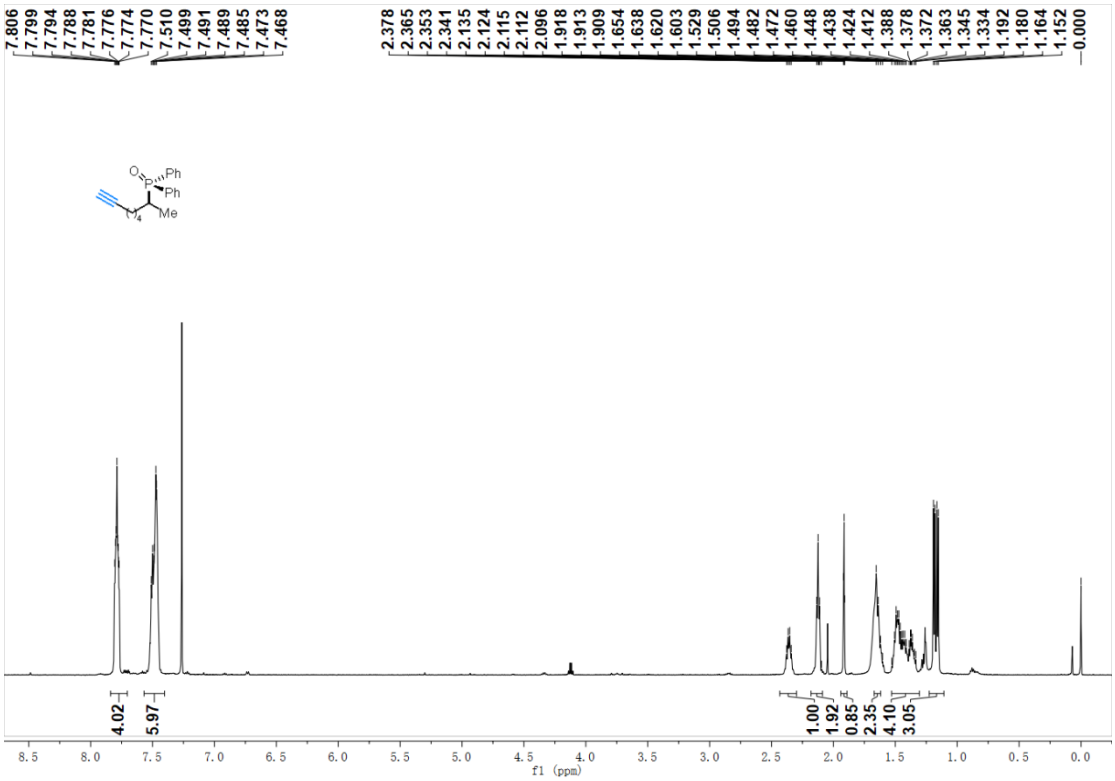


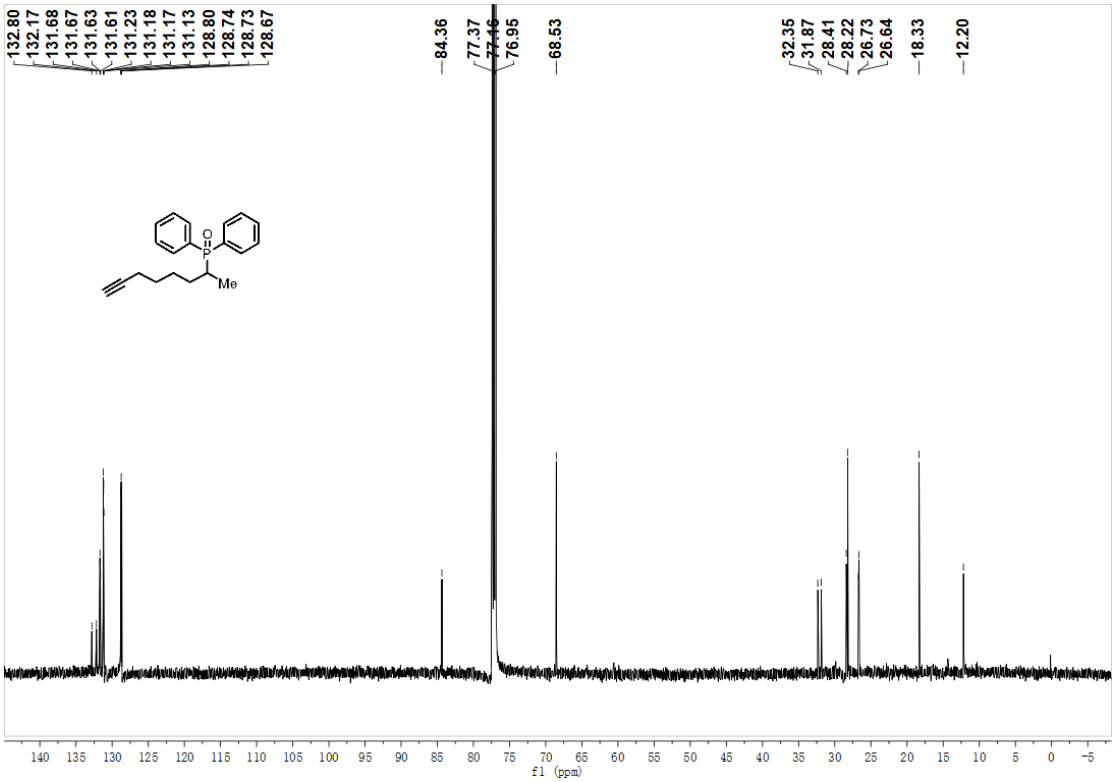


4s; ^{31}P NMR (242.9 MHz, $CDCl_3$)

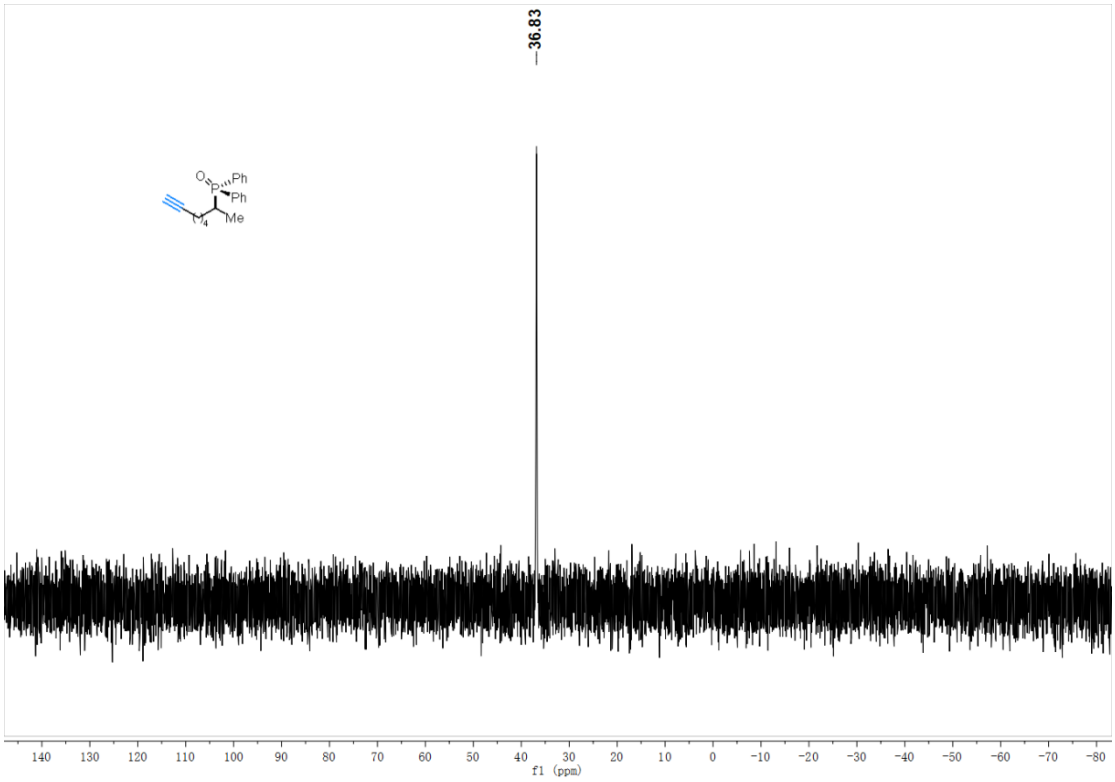


4t; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

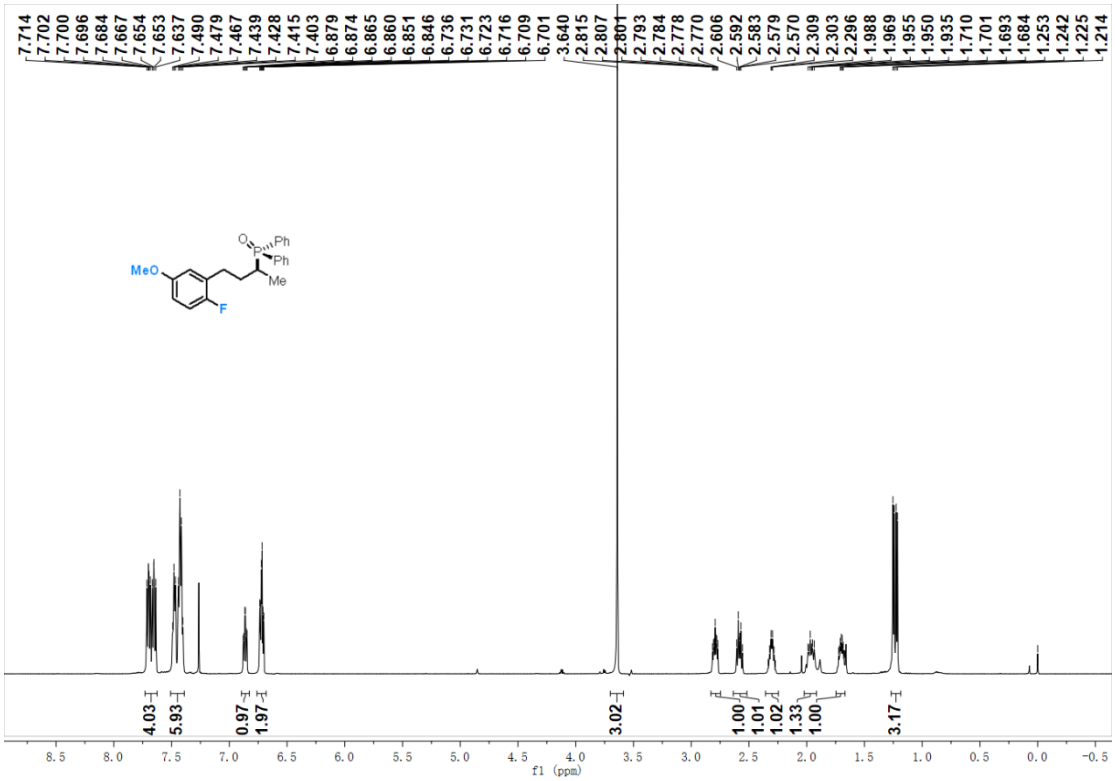


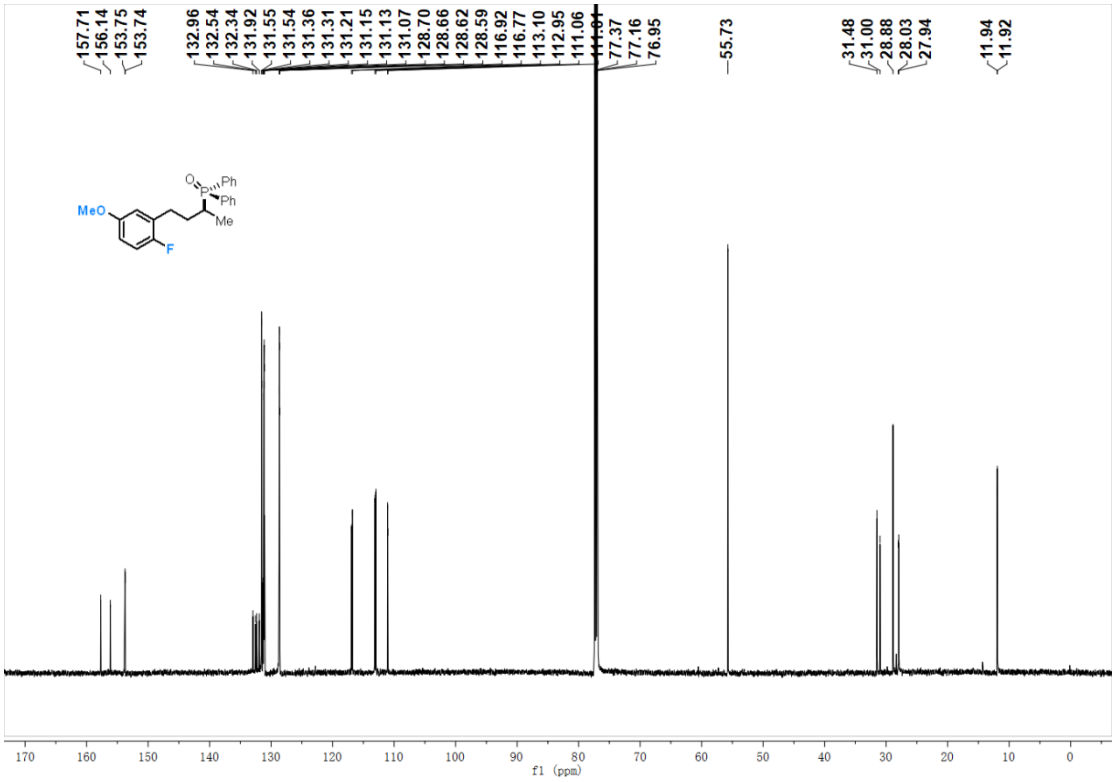


4t; ^{31}P NMR (242.9 MHz, $CDCl_3$)

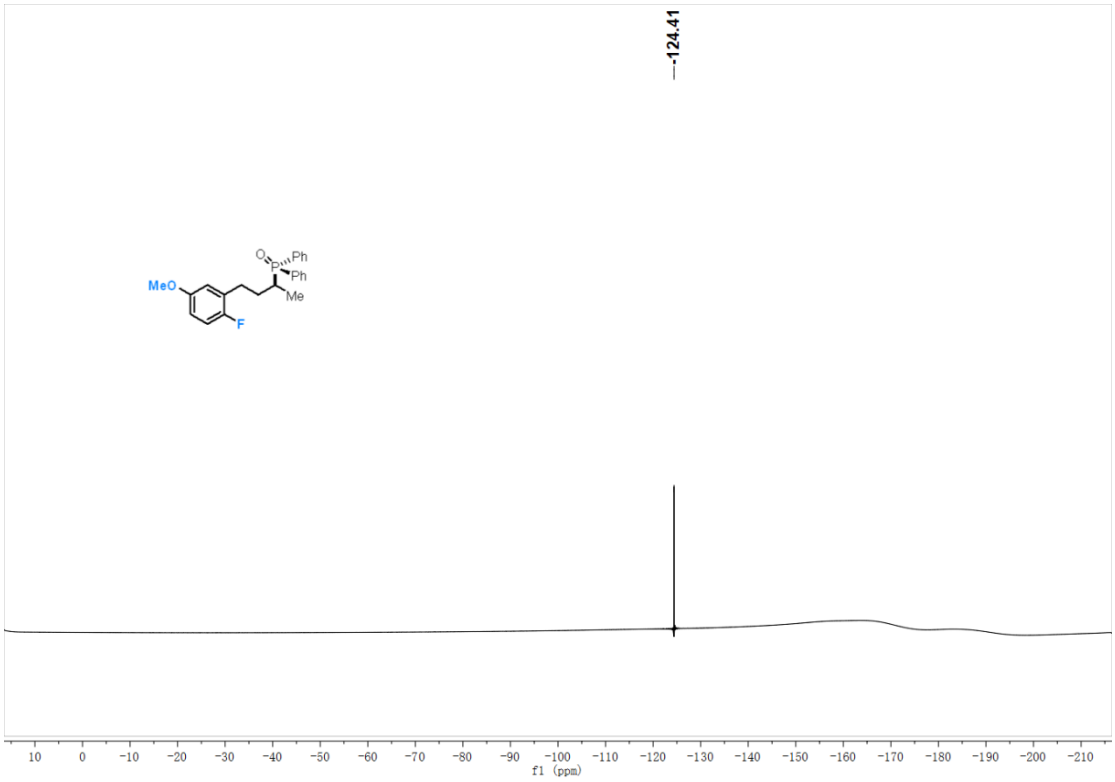


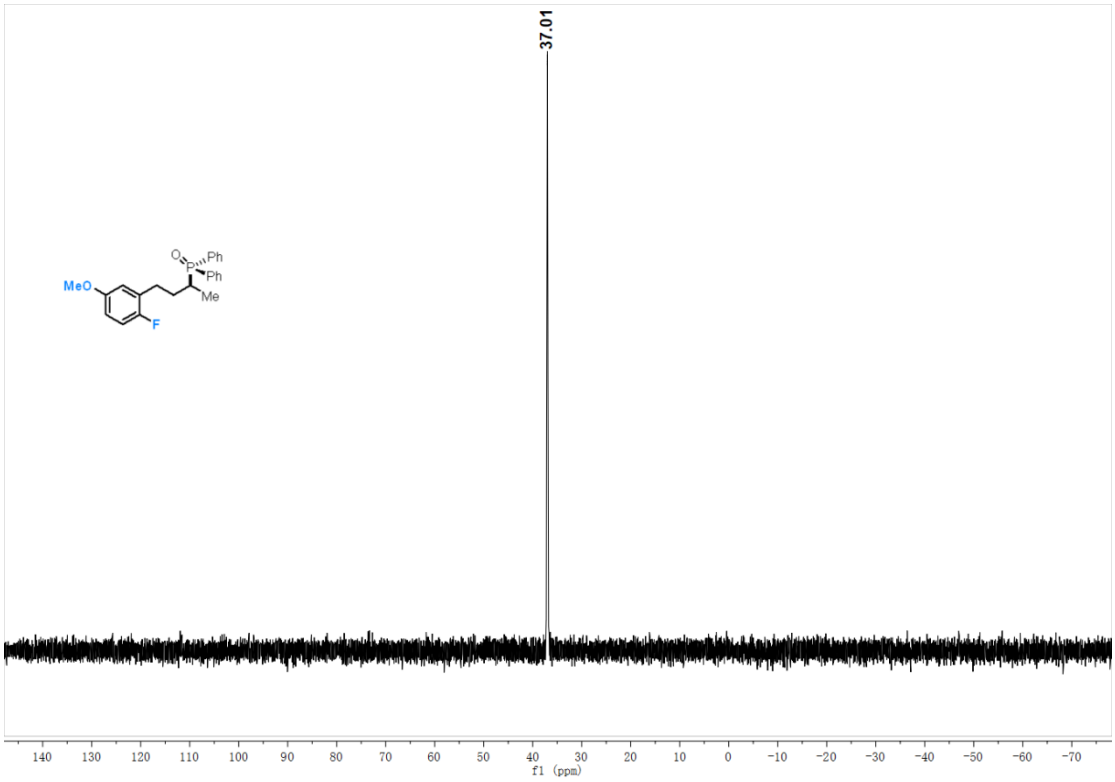
4u; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



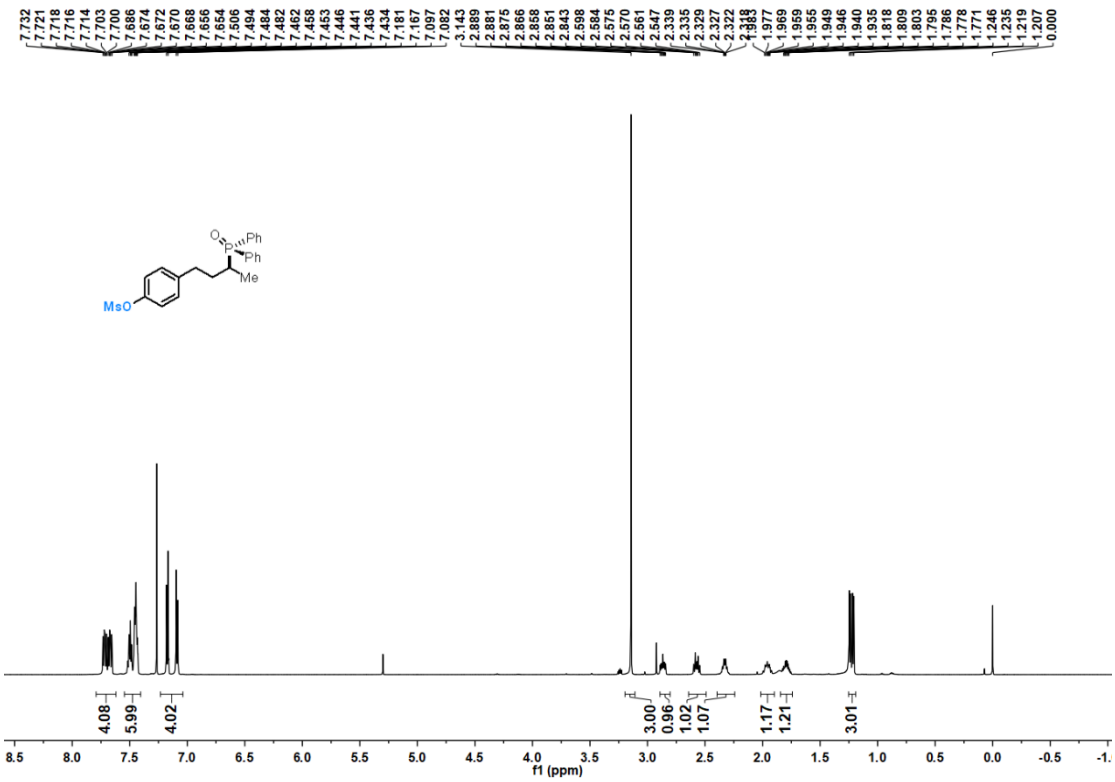


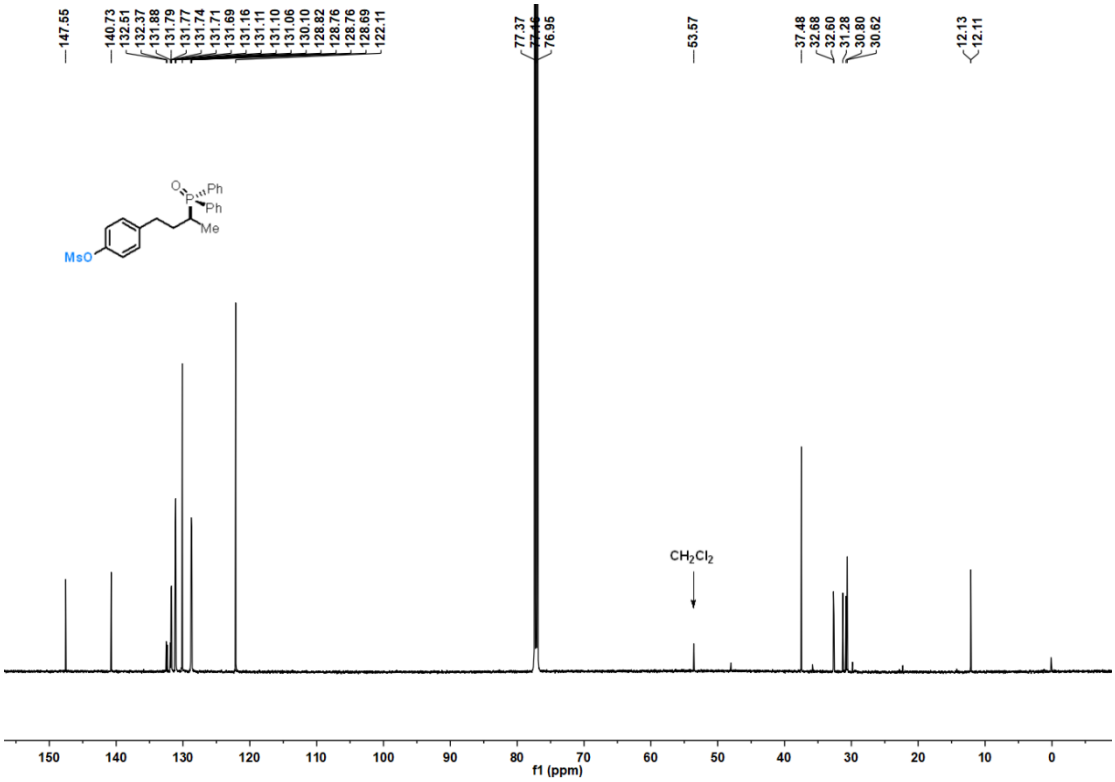
4u; ^{19}F NMR (376 MHz, $CDCl_3$); ^{31}P NMR (242.9 MHz, $CDCl_3$)



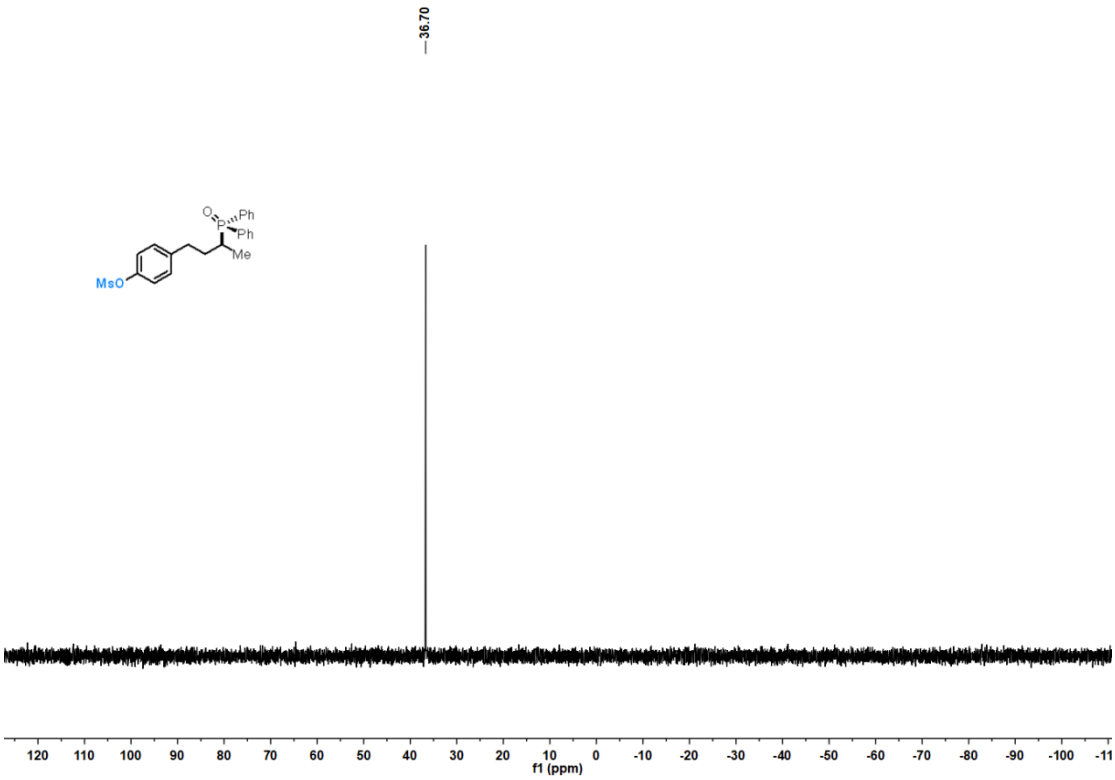


4v; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

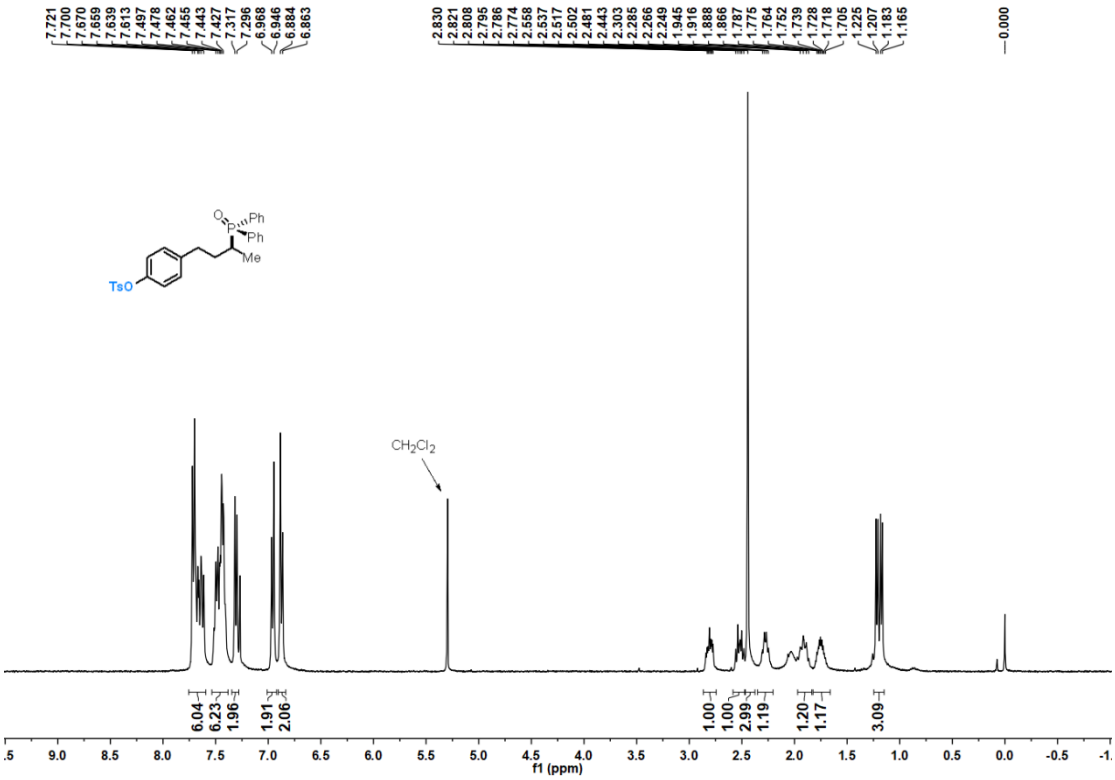


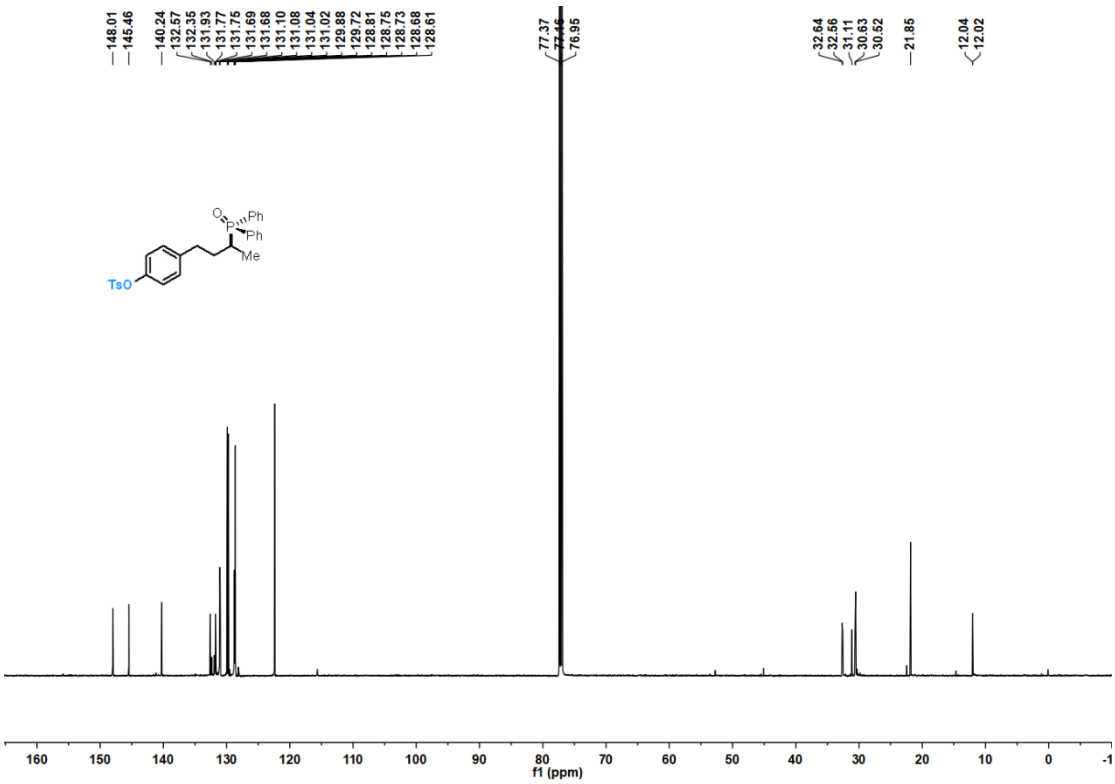


4v; ^{31}P NMR (242.9 MHz, $CDCl_3$)

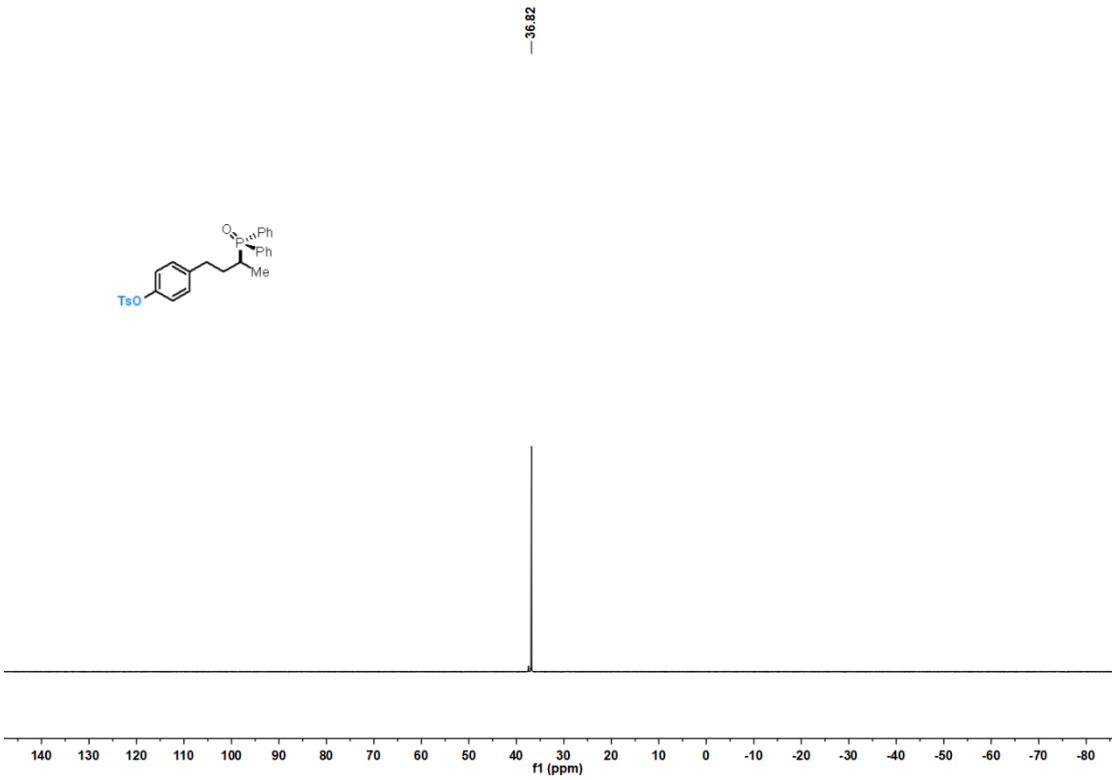


4w; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

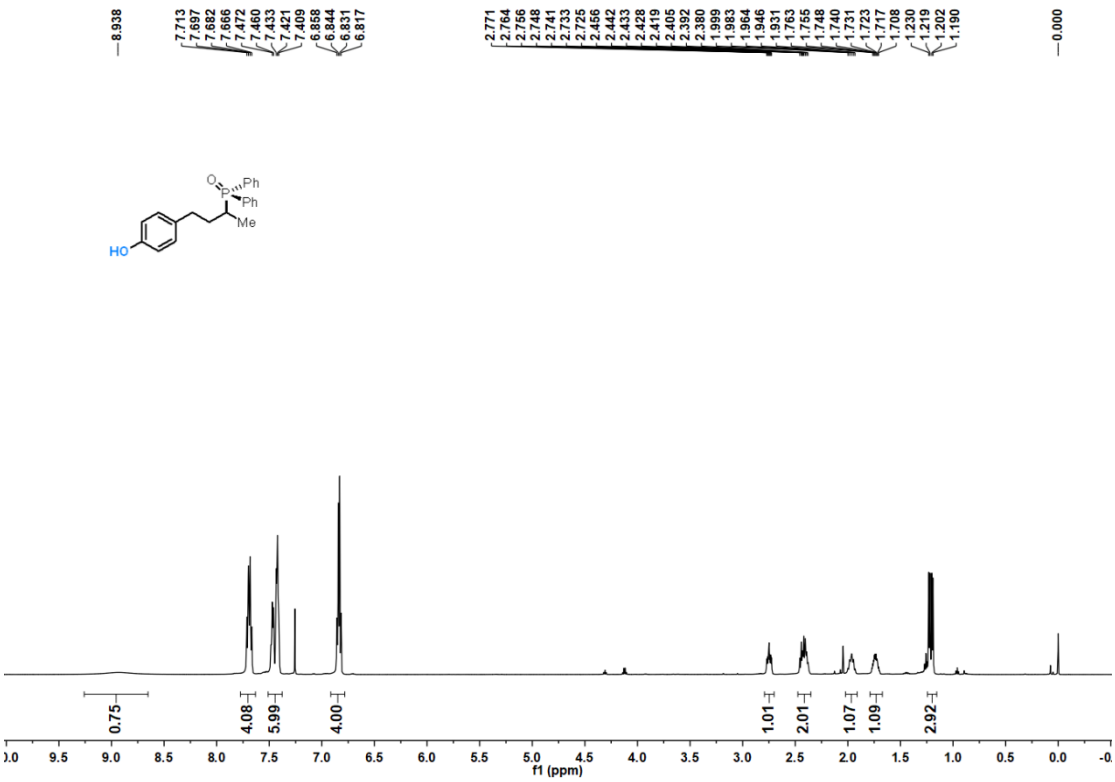


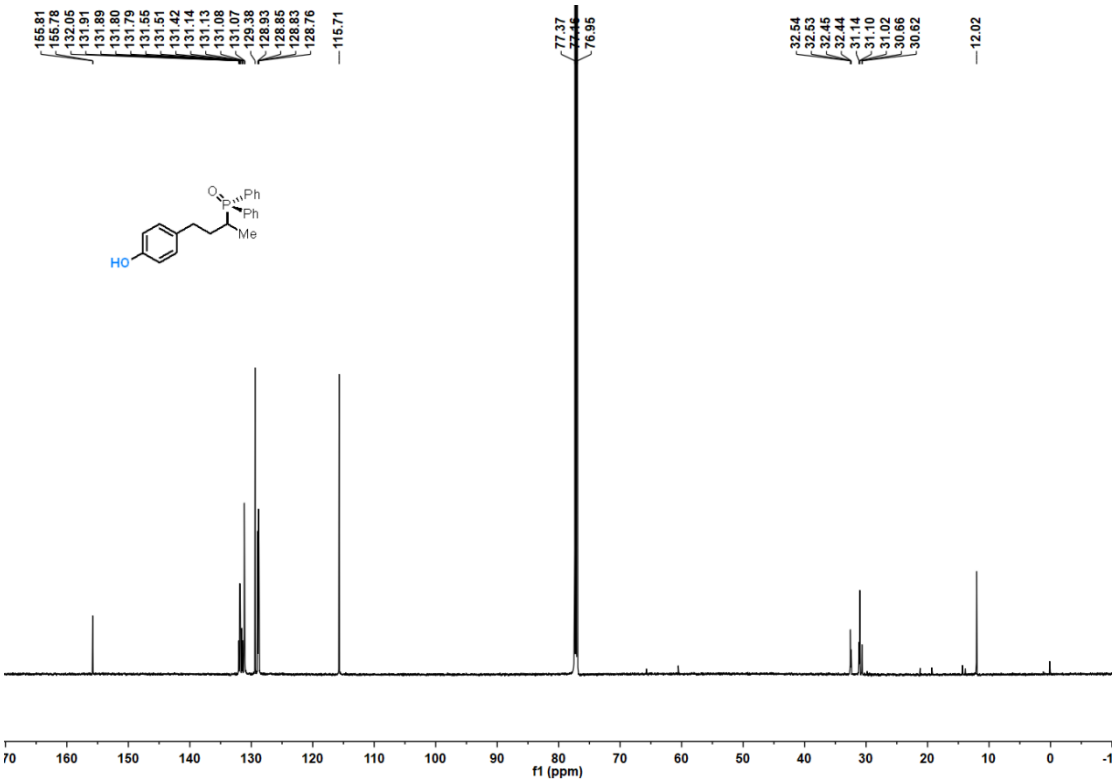


4w; ^{31}P NMR (242.9 MHz, $CDCl_3$)

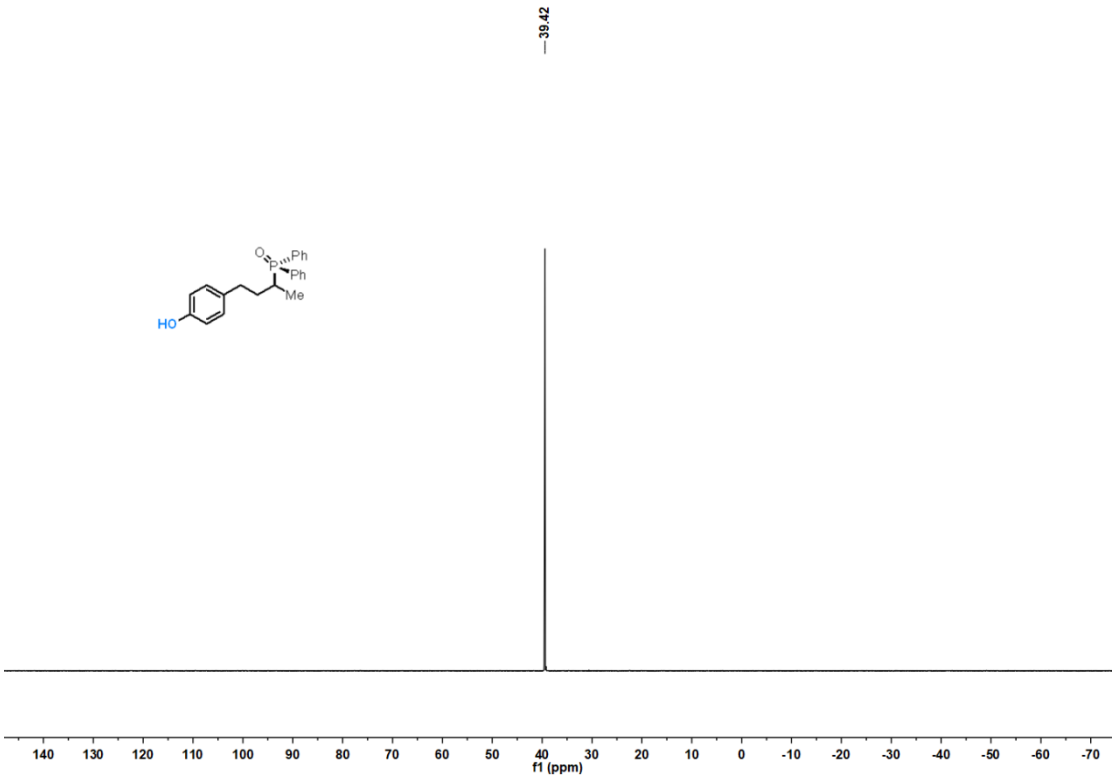


4x; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

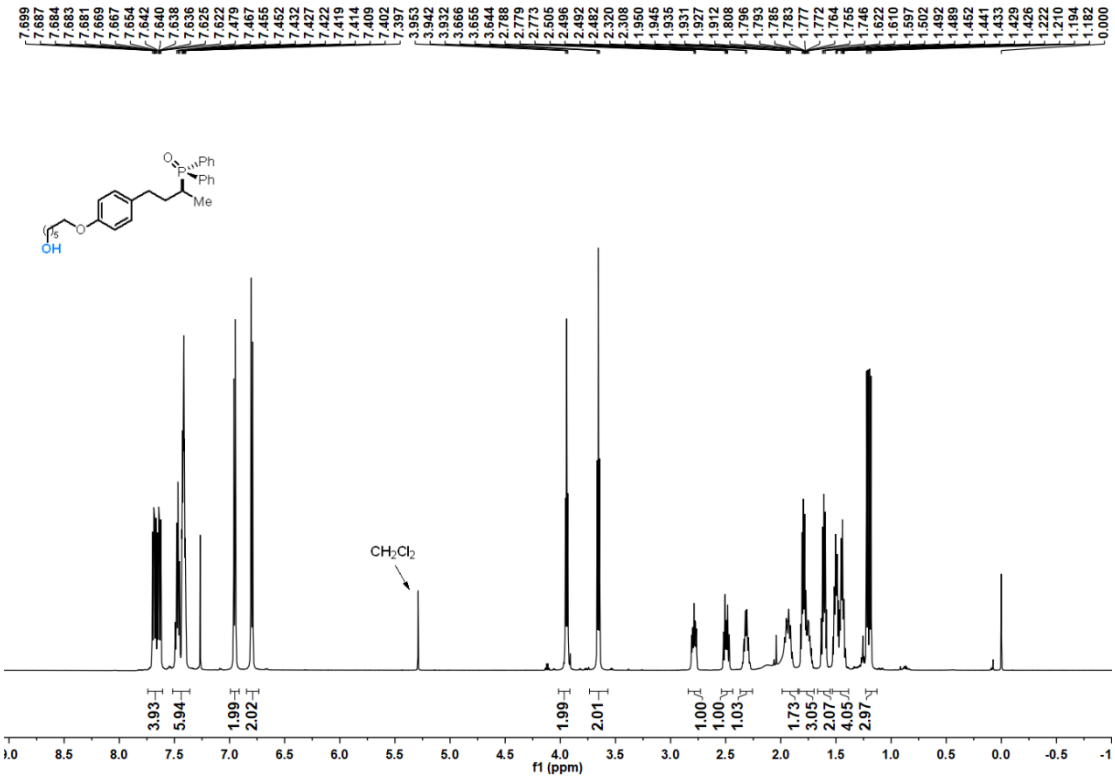


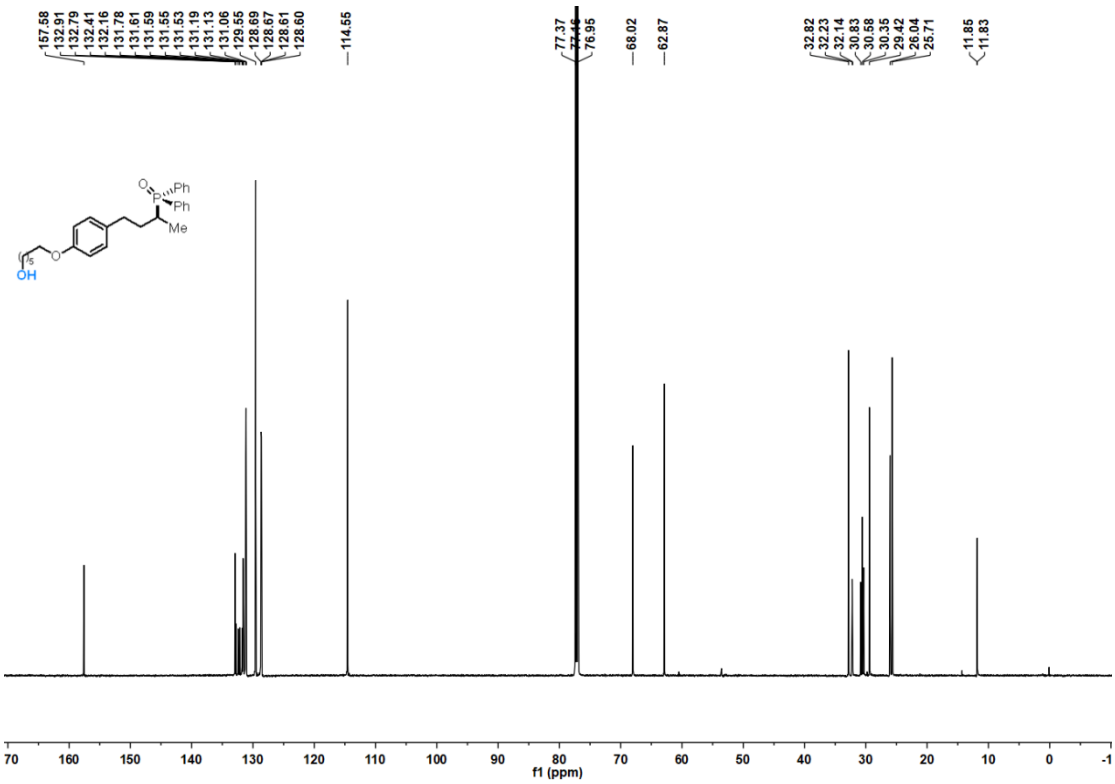


4x; ^{31}P NMR (242.9 MHz, $CDCl_3$)

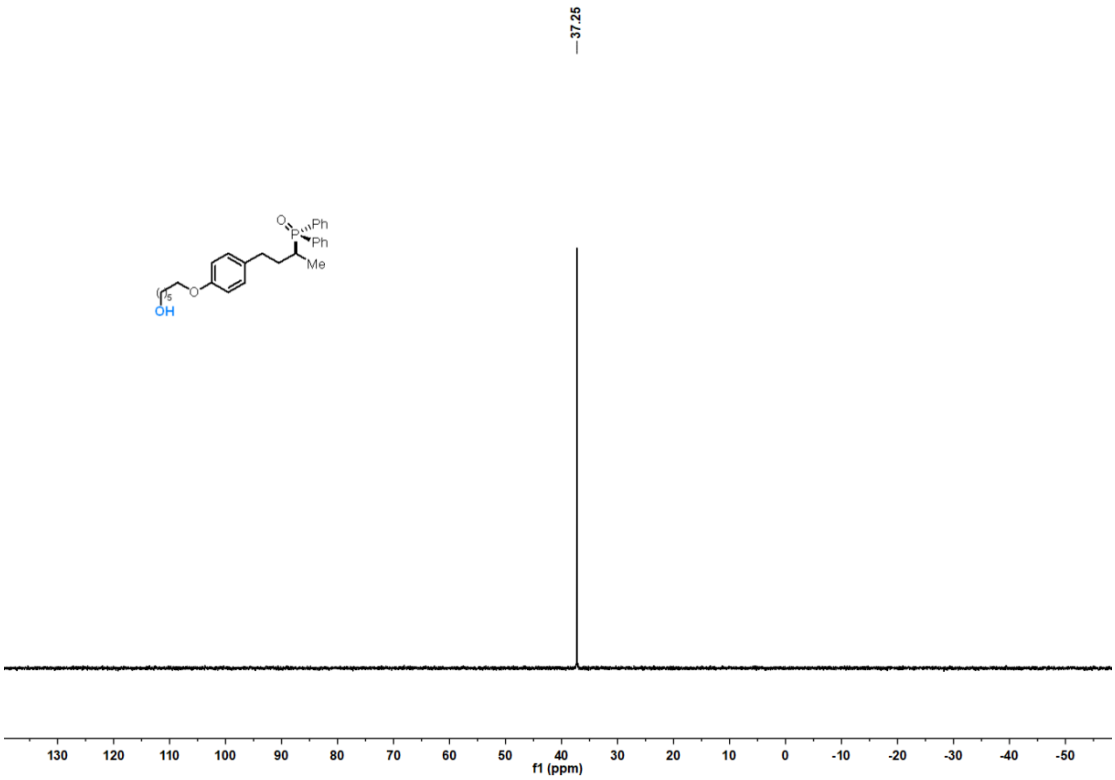


4y; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

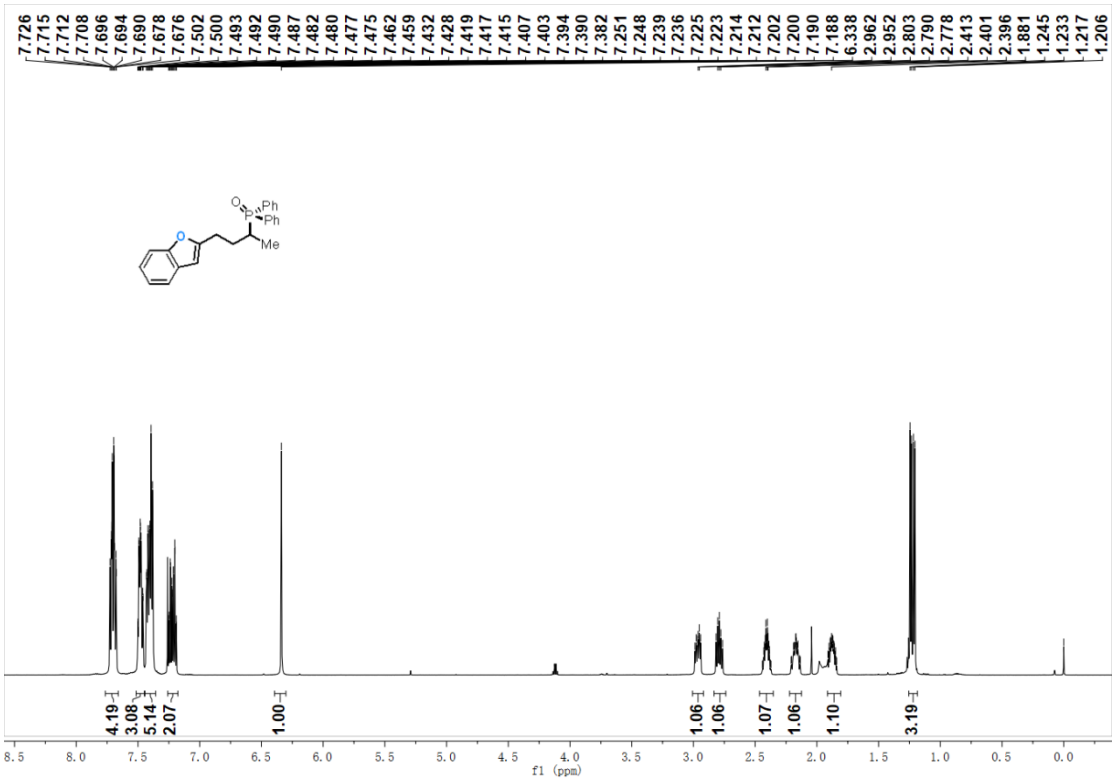


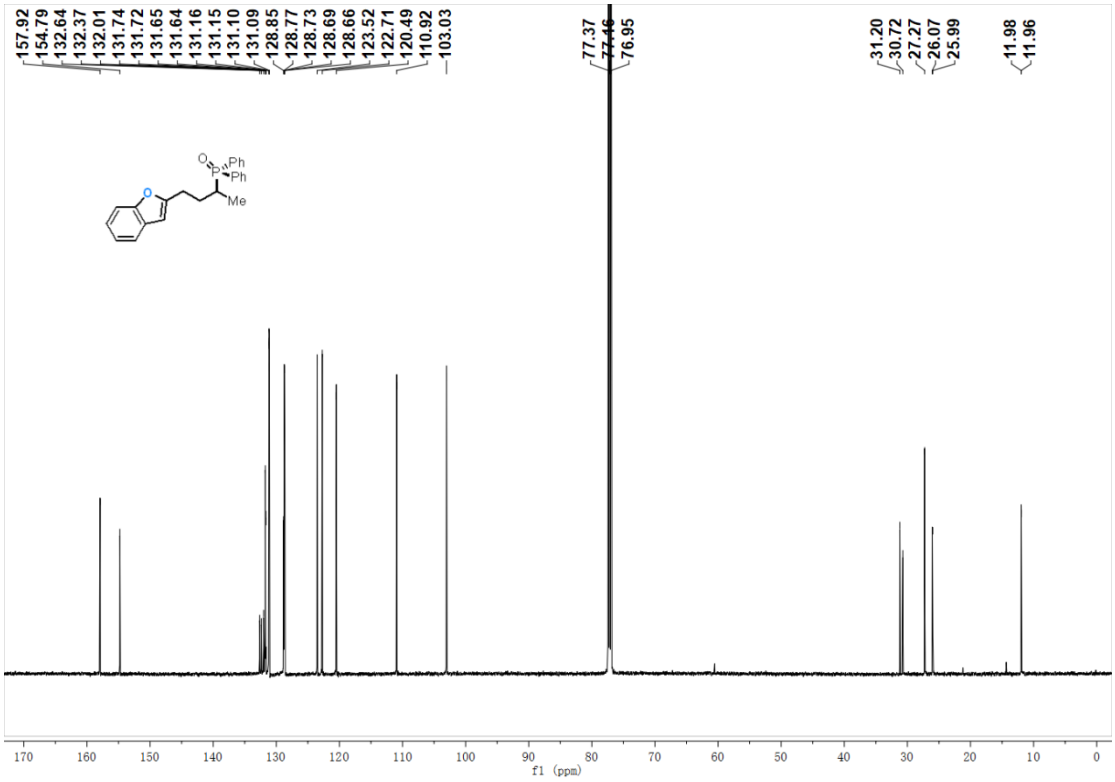


4y; ^{31}P NMR (242.9 MHz, $CDCl_3$)

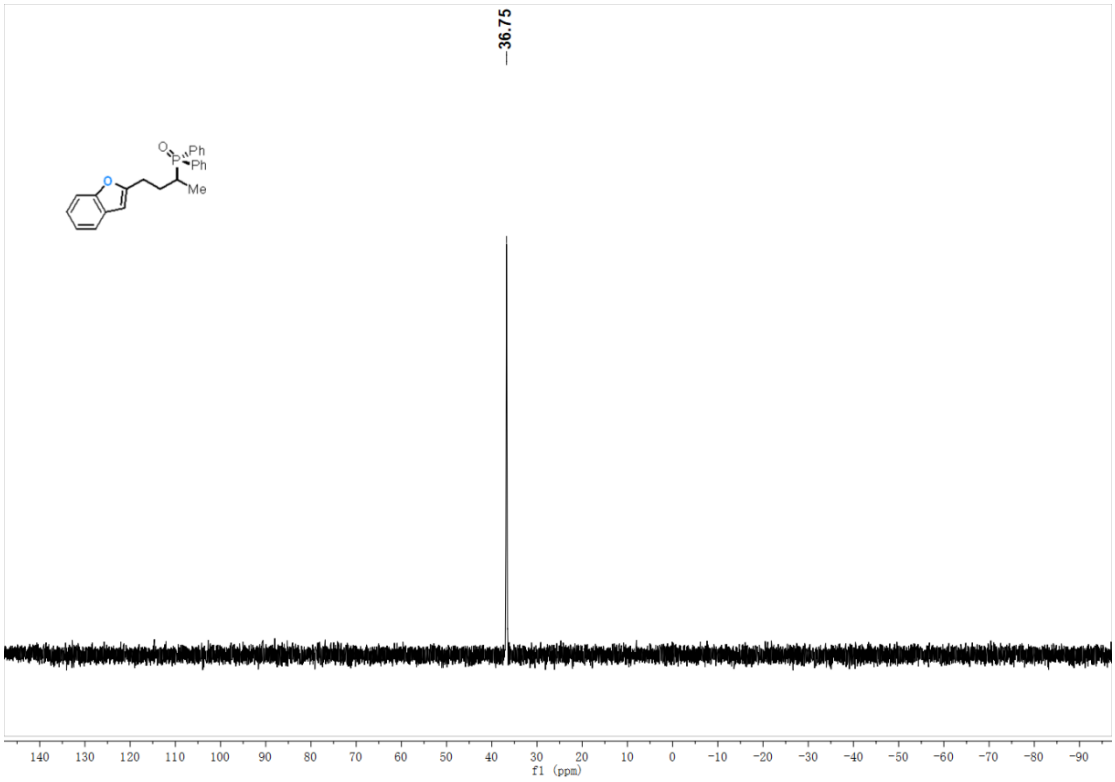


4z; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

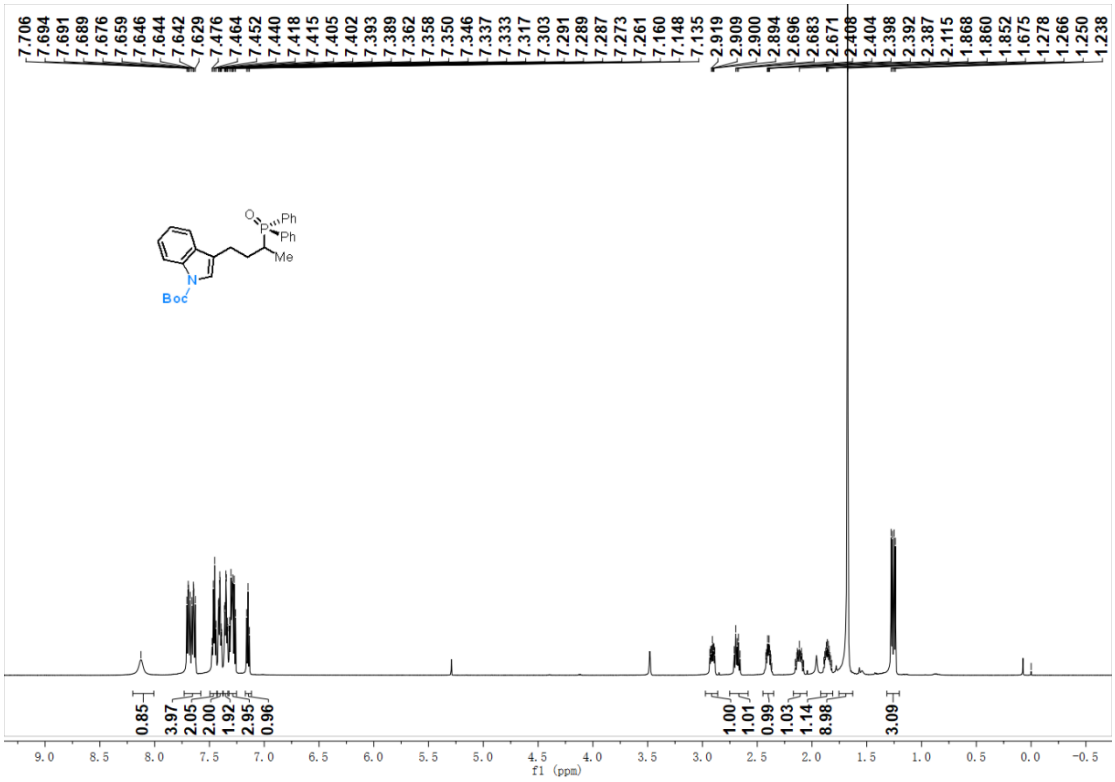


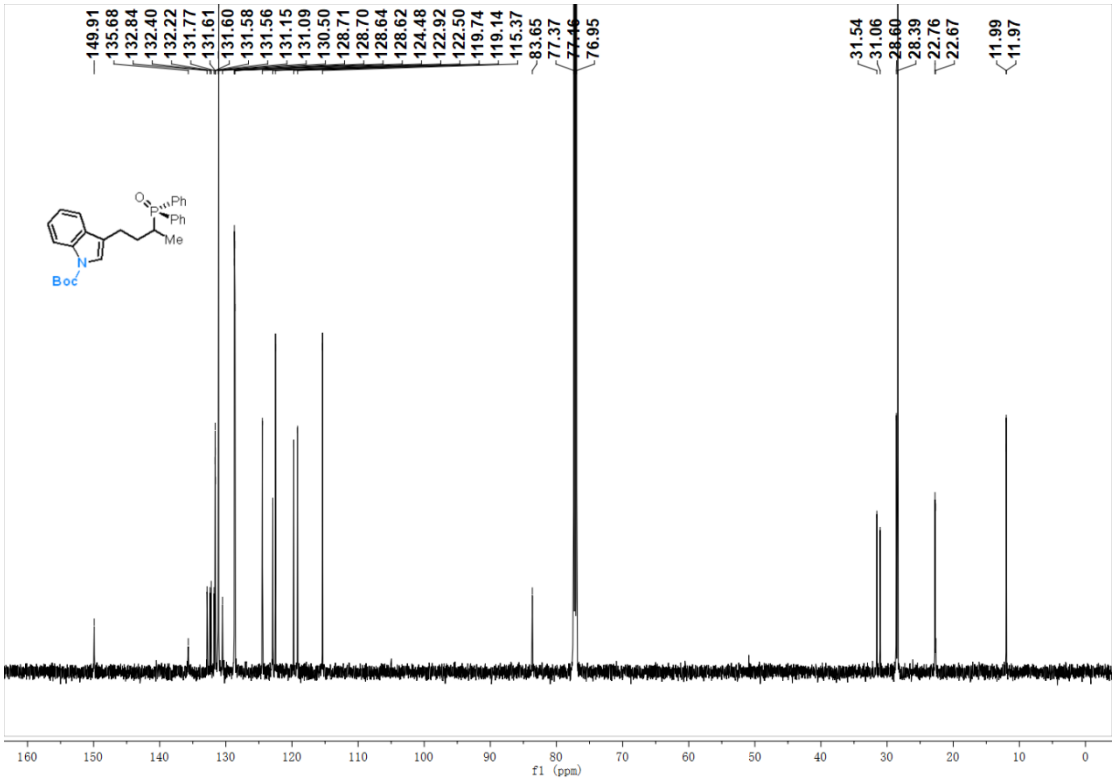


4z; ^{31}P NMR (242.9 MHz, $CDCl_3$)

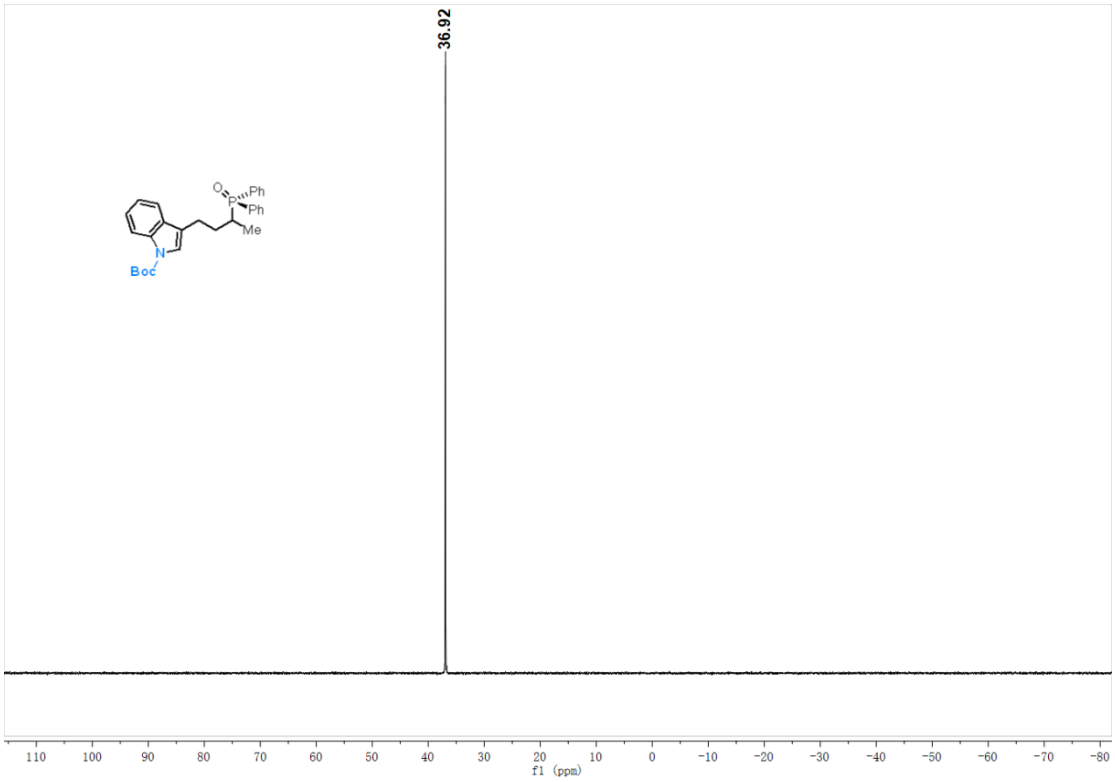


4aa; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

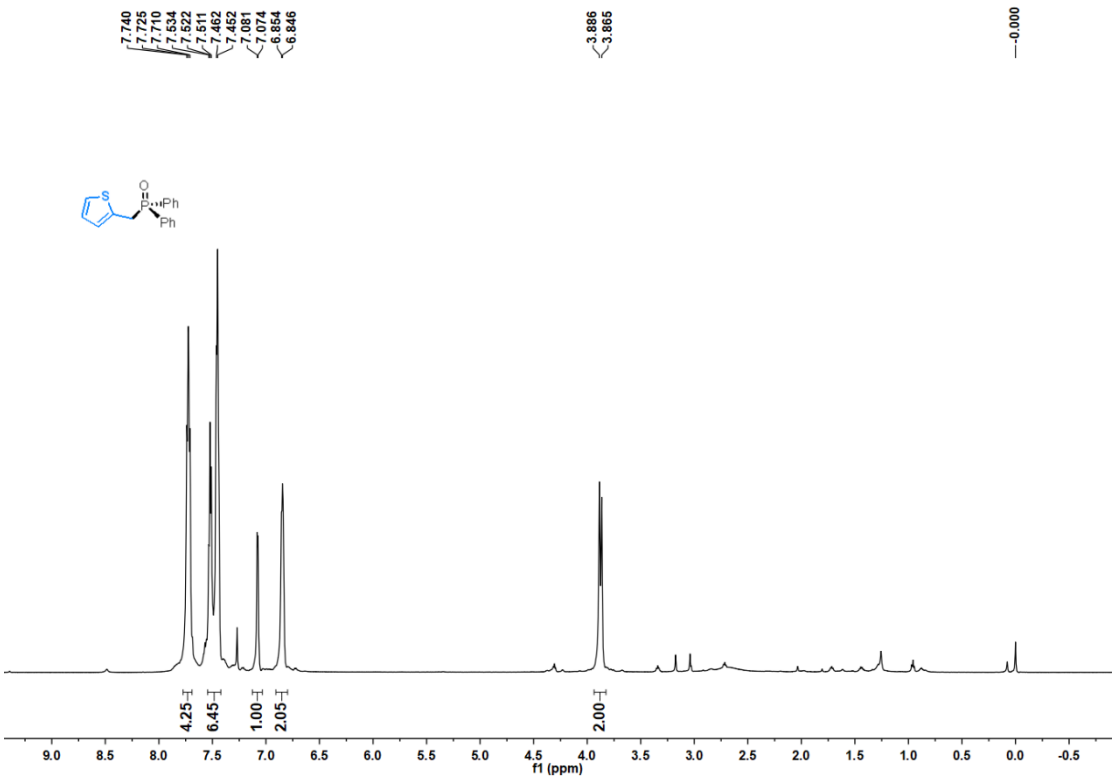


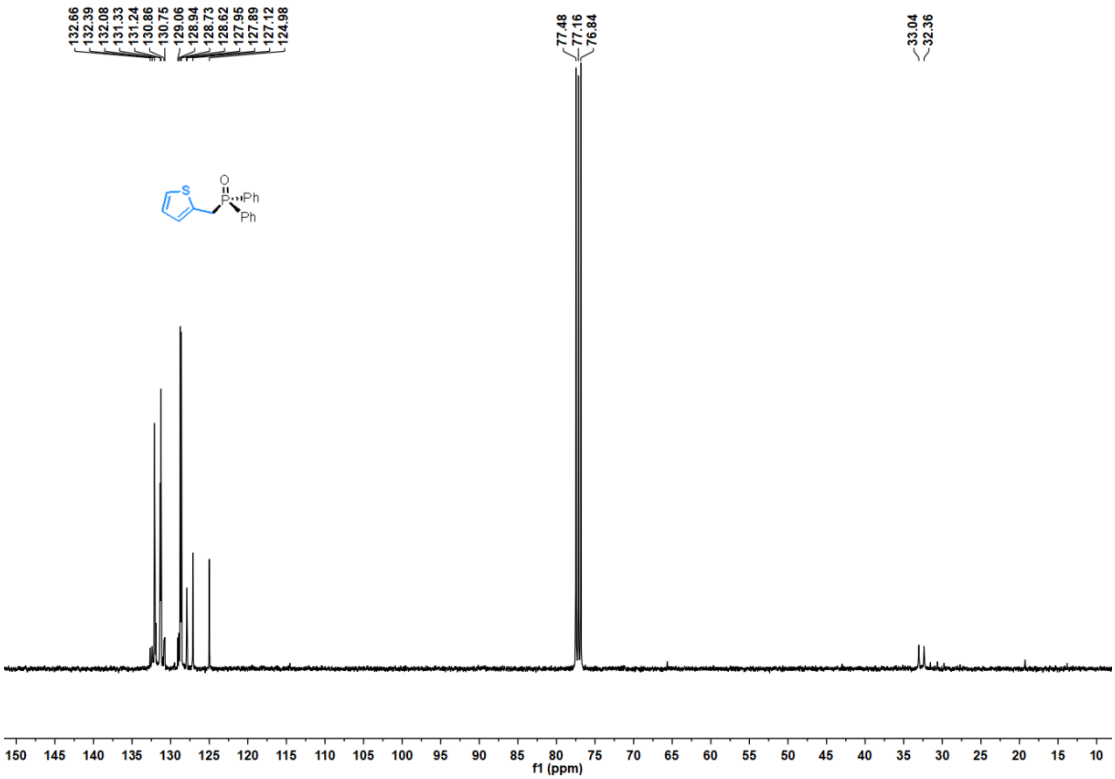


4aa; ^{31}P NMR (242.9 MHz, $CDCl_3$)

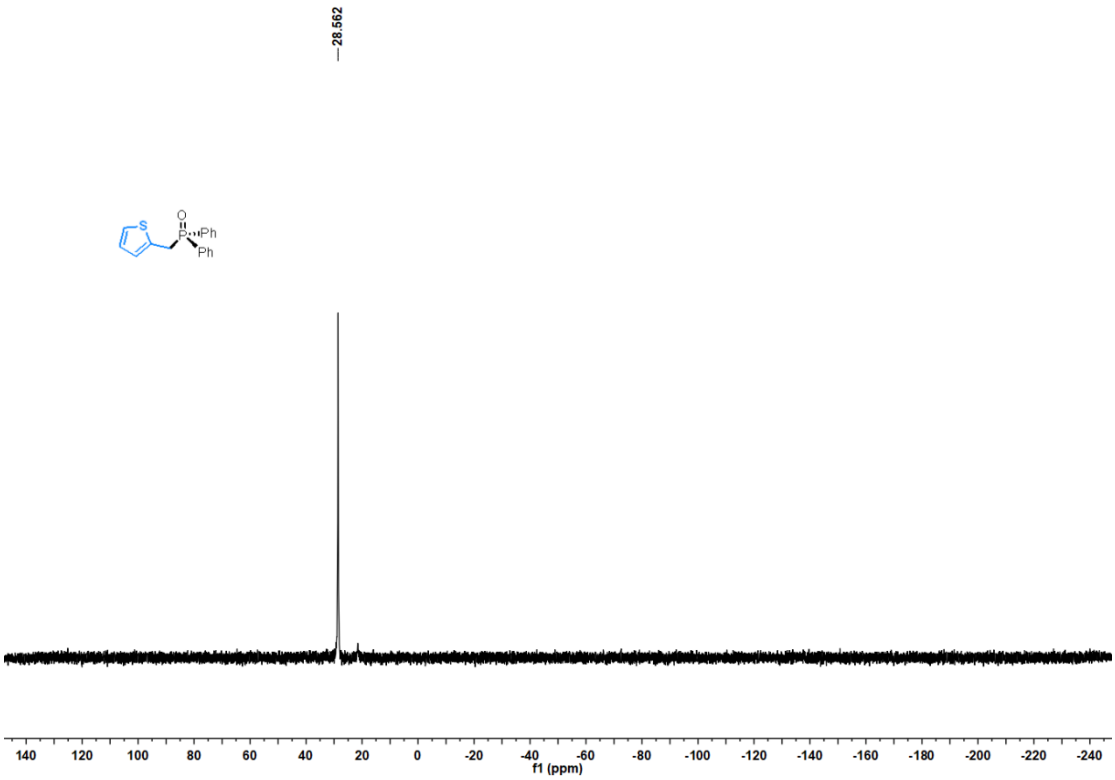


4ab; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

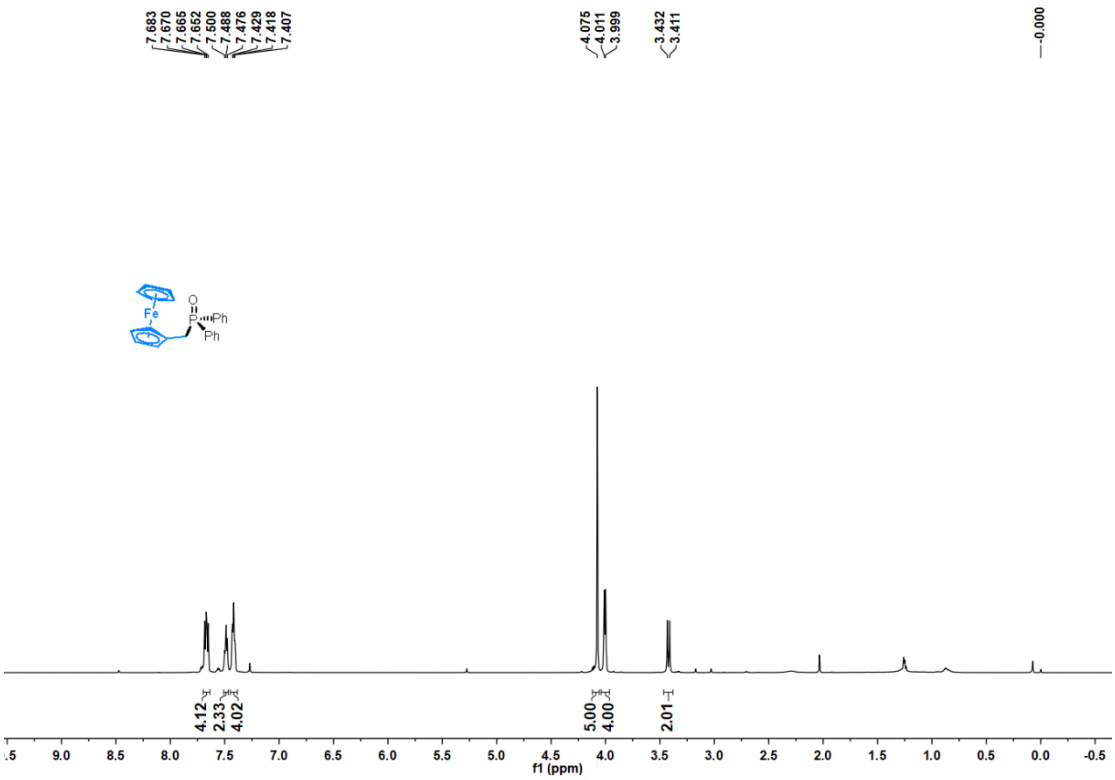


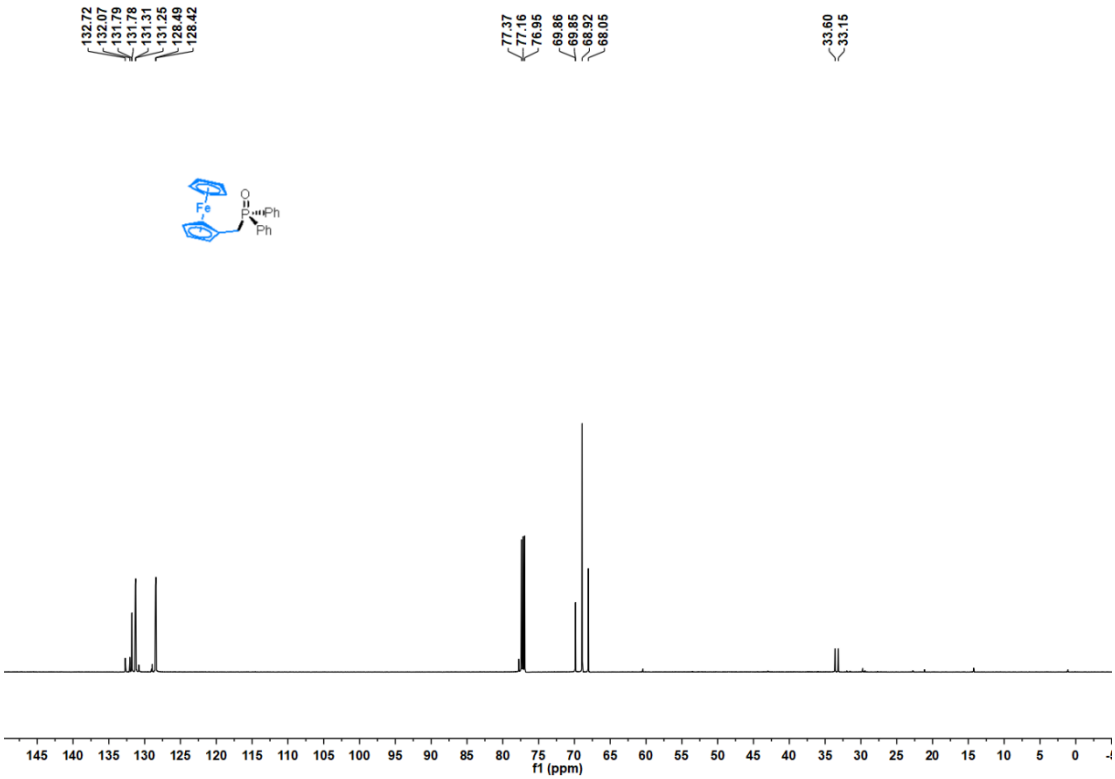


4ab; ^{31}P NMR (242.9 MHz, $CDCl_3$)

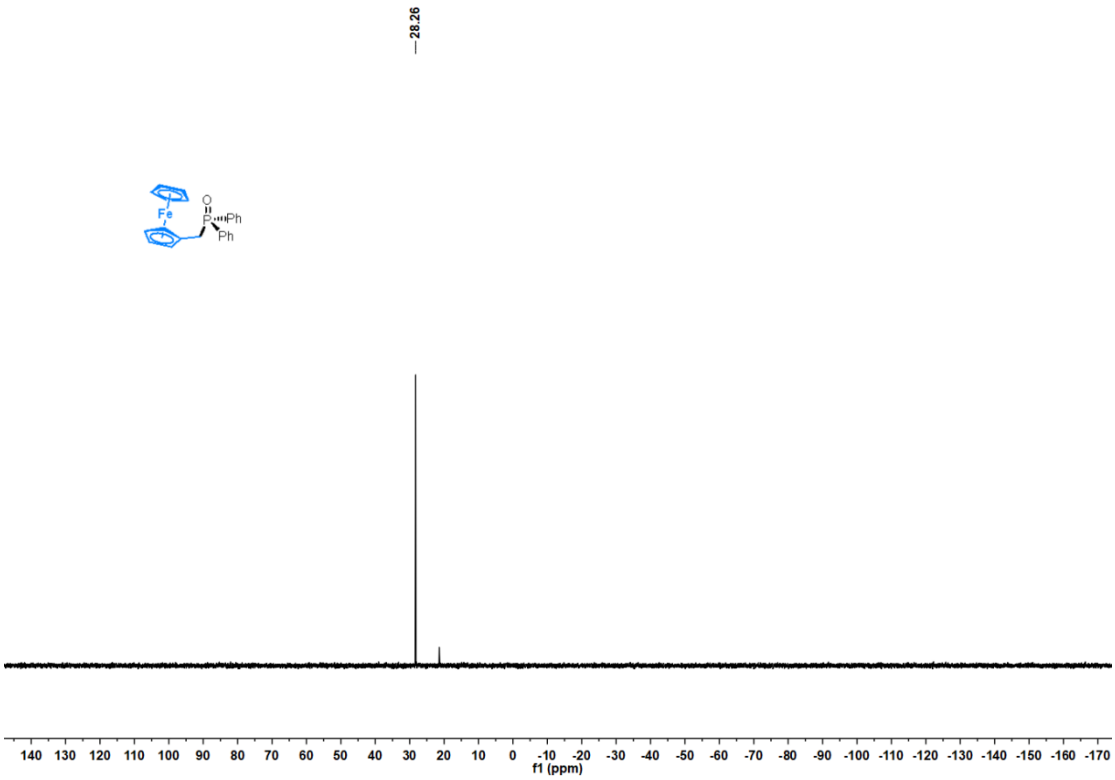


4ac; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

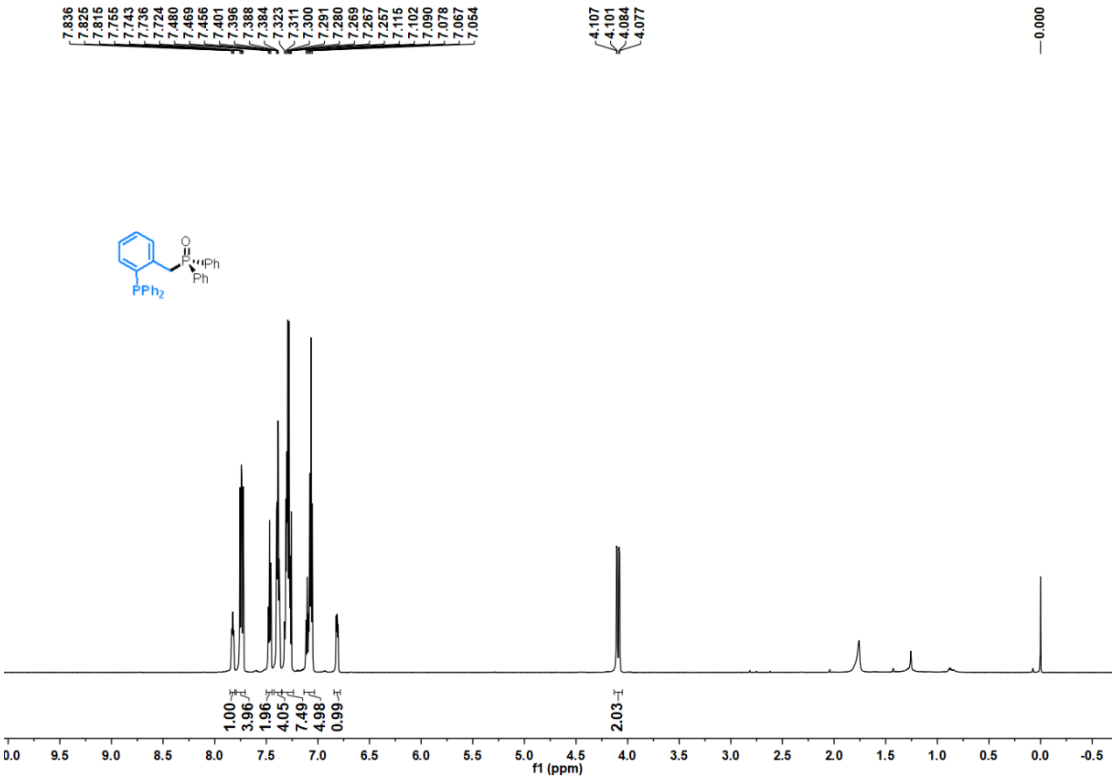


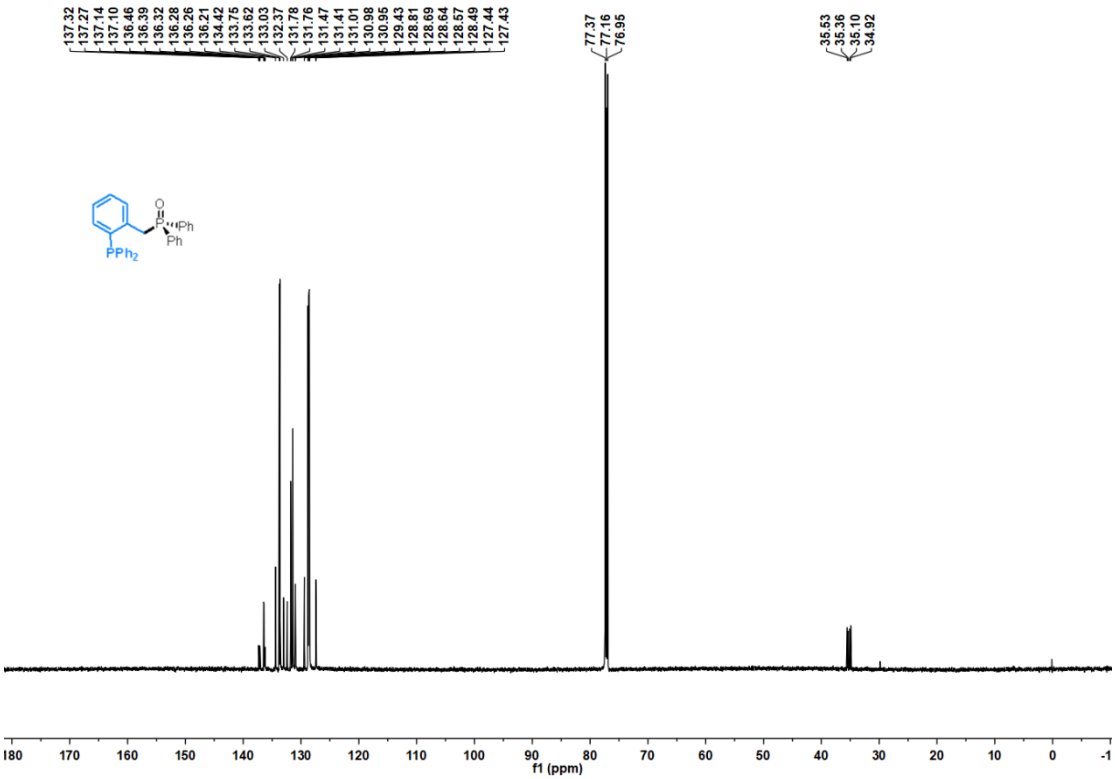


4ac; ^{31}P NMR (242.9 MHz, $CDCl_3$)

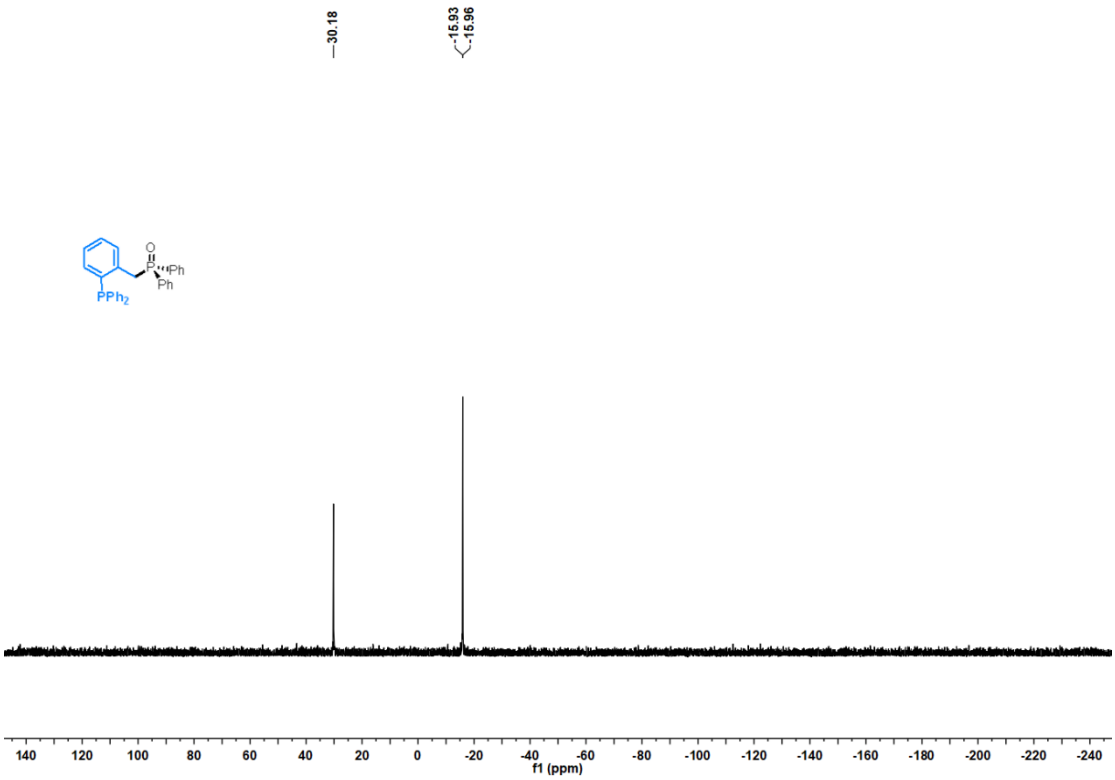


4ad; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

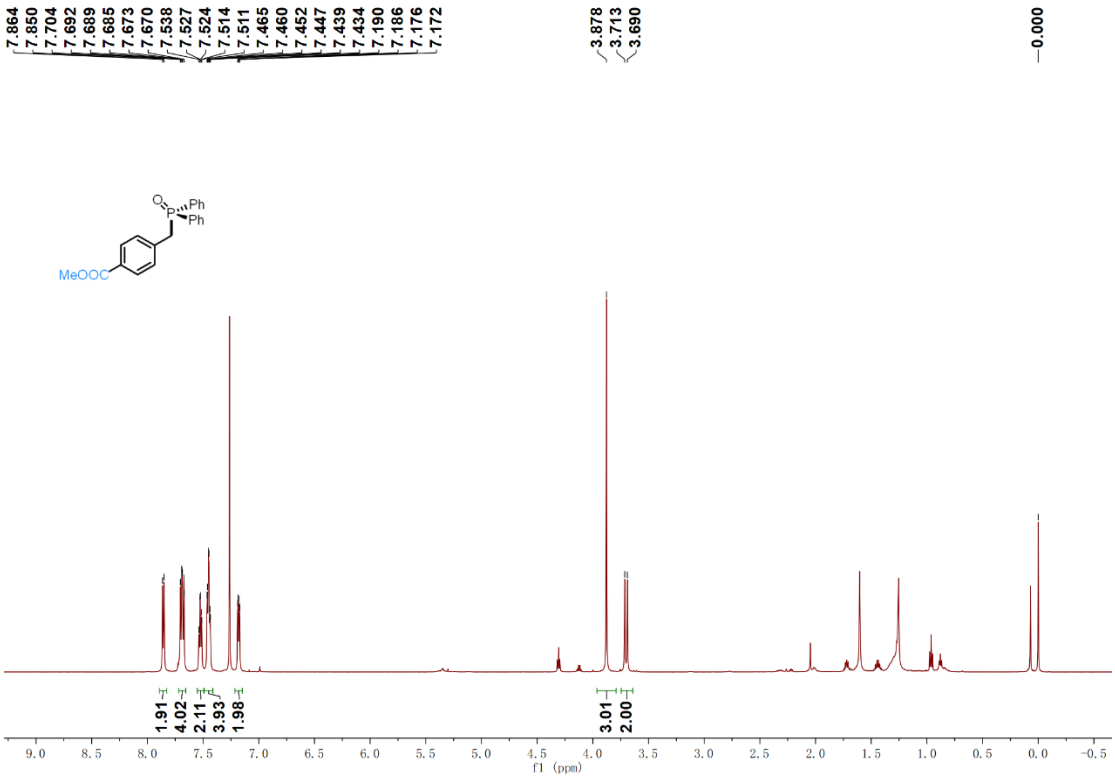


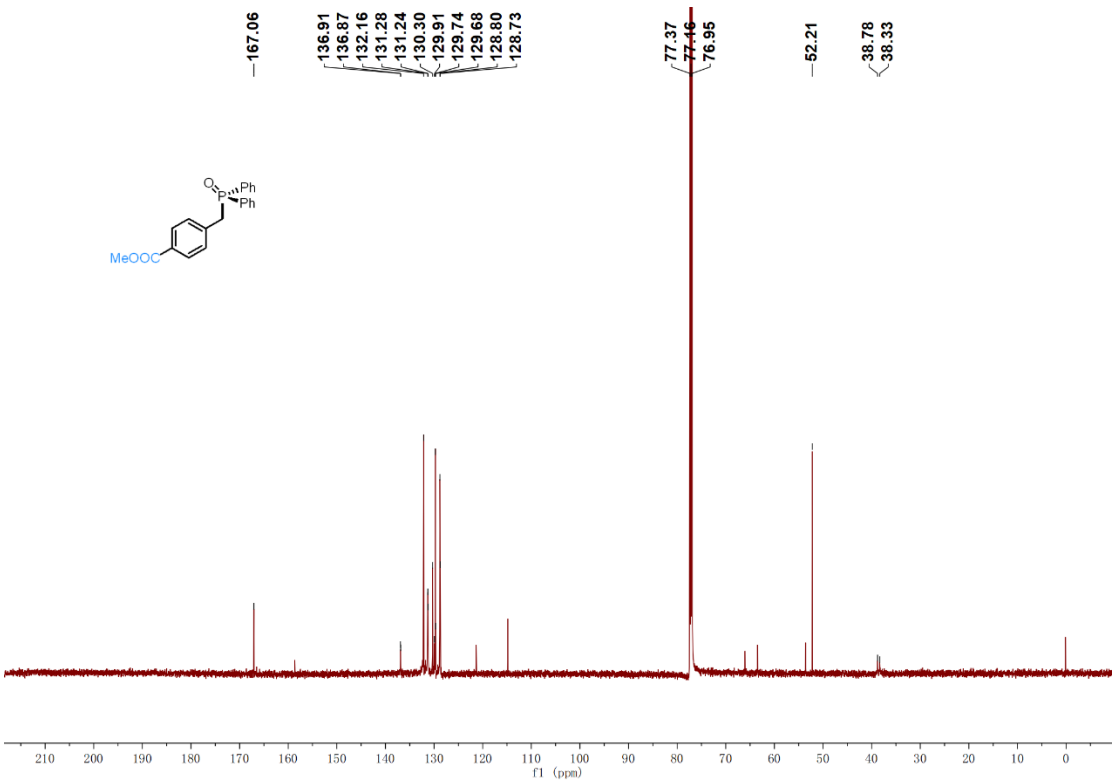


4ad; ^{31}P NMR (242.9 MHz, $CDCl_3$)

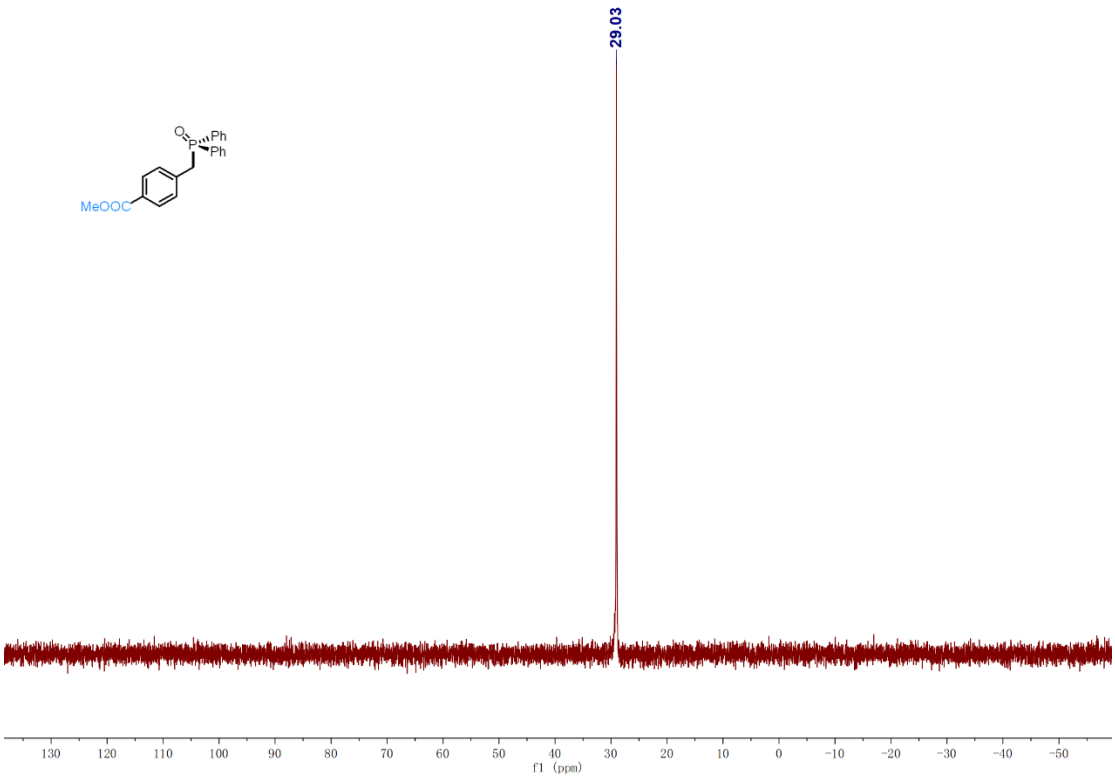


4ae; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

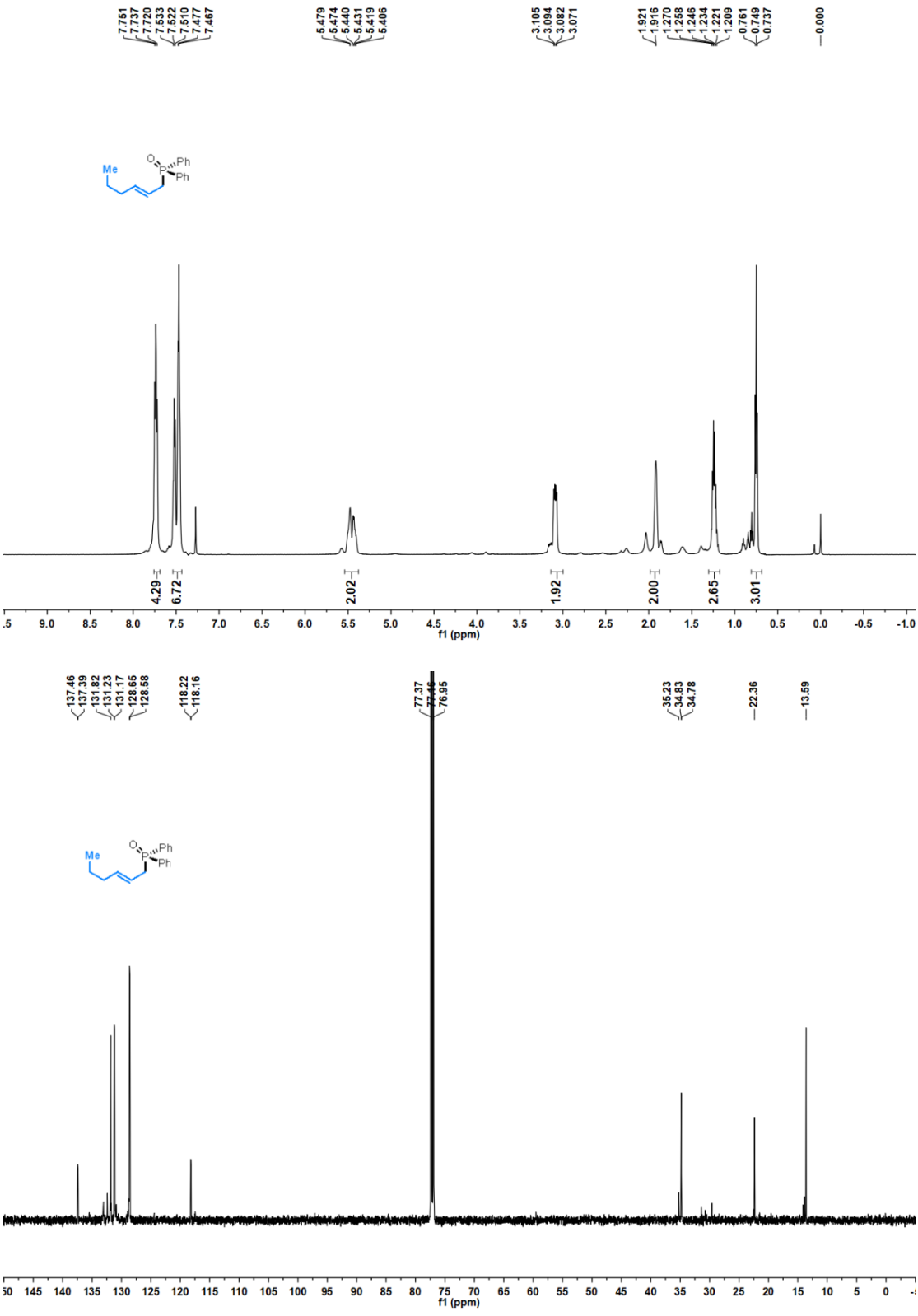




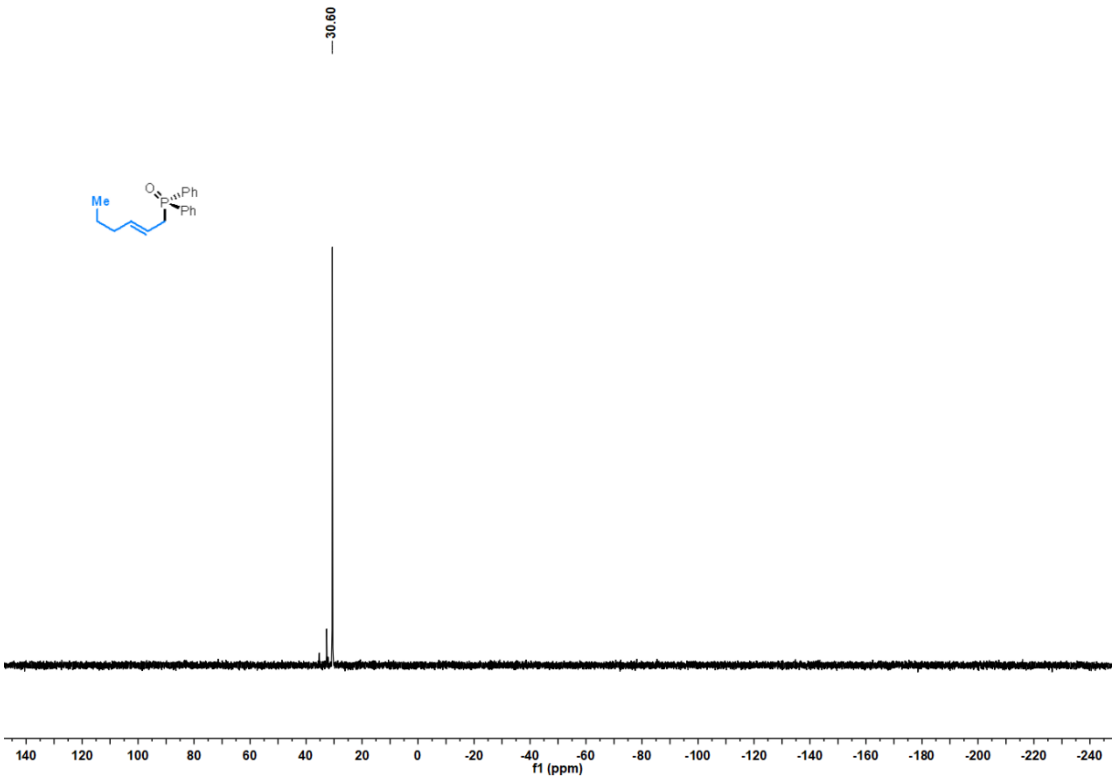
4ae; ^{31}P NMR (242.9 MHz, $CDCl_3$)



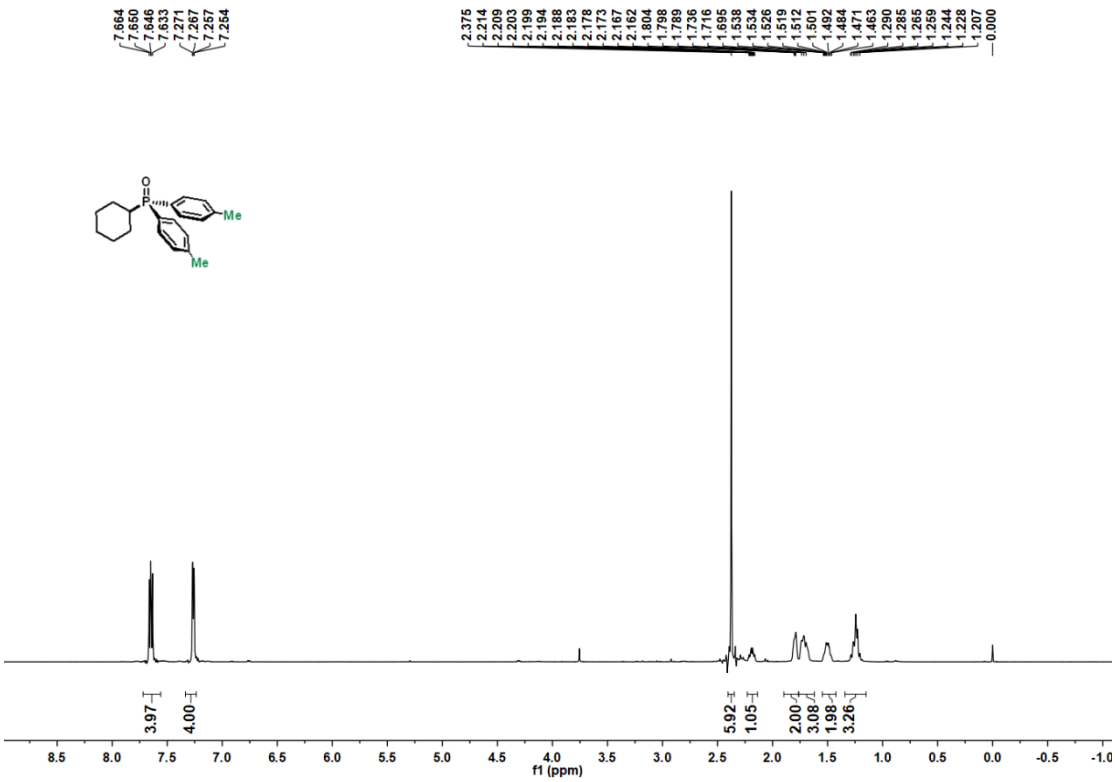
4af; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

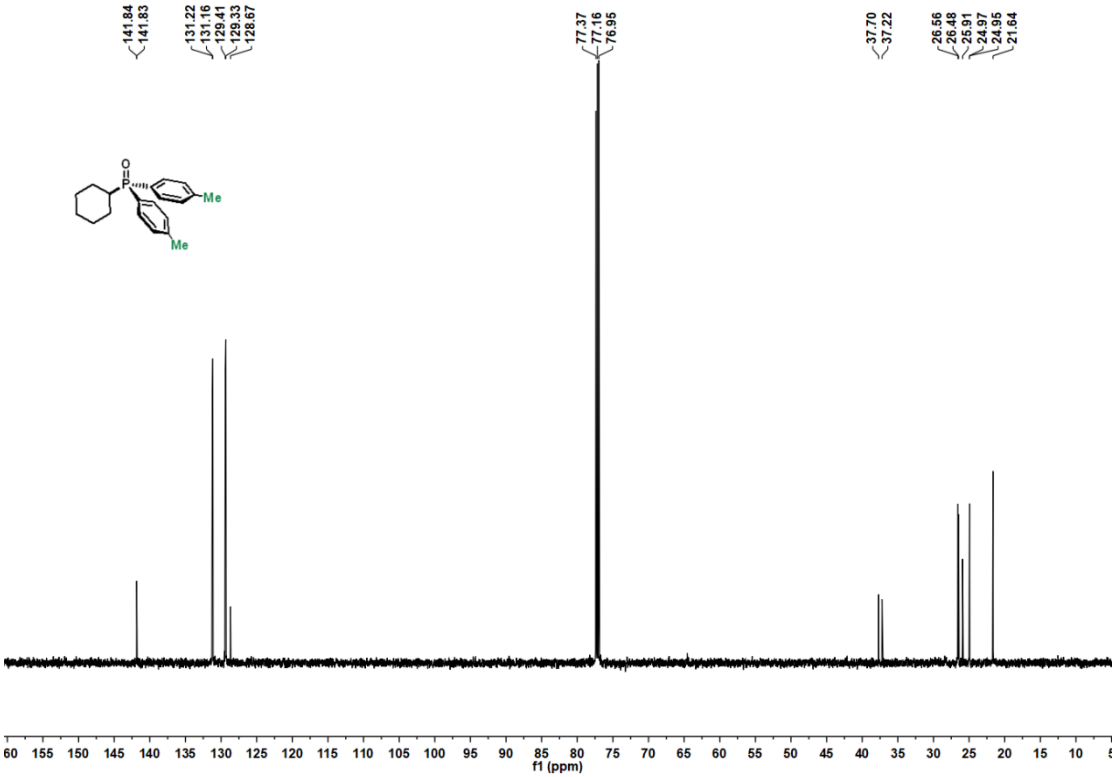


4af; ^{31}P NMR (242.9 MHz, $CDCl_3$)

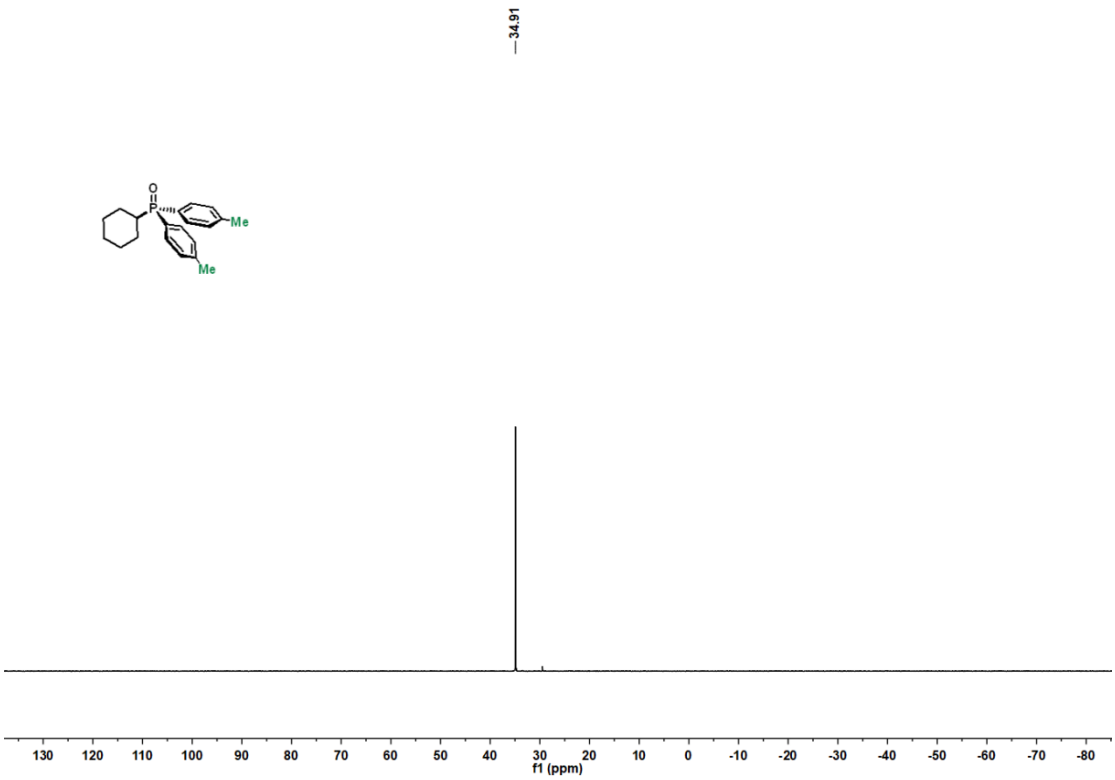


4ag; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

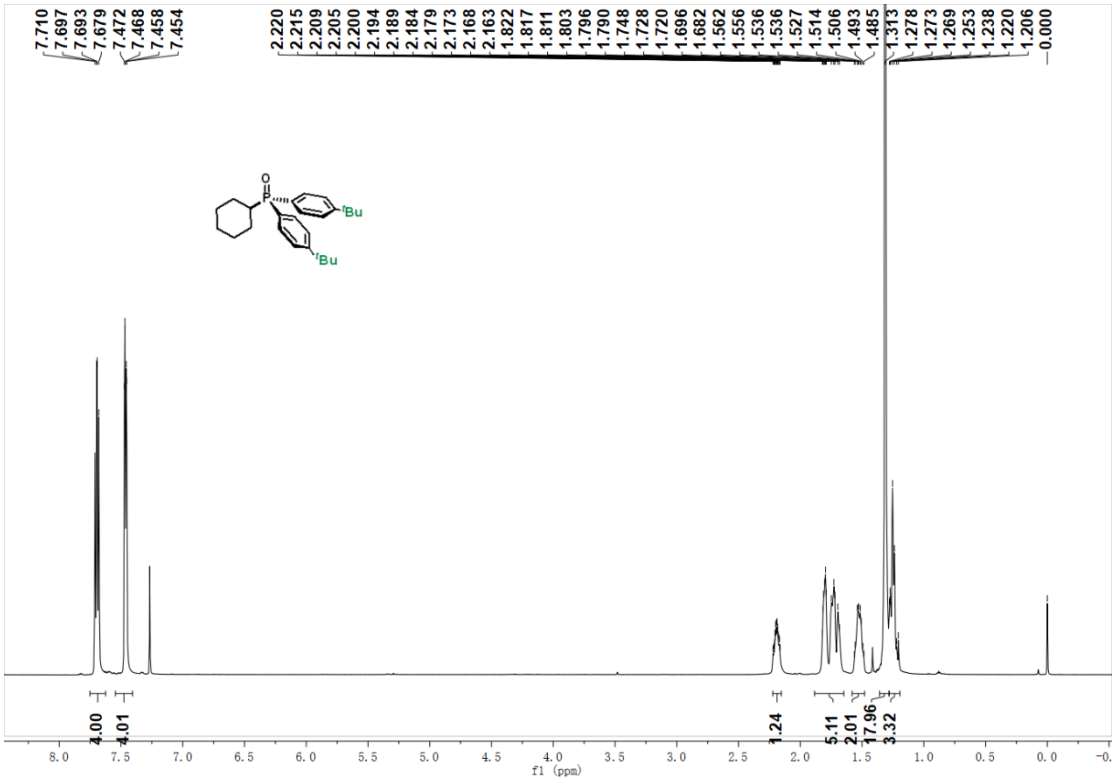


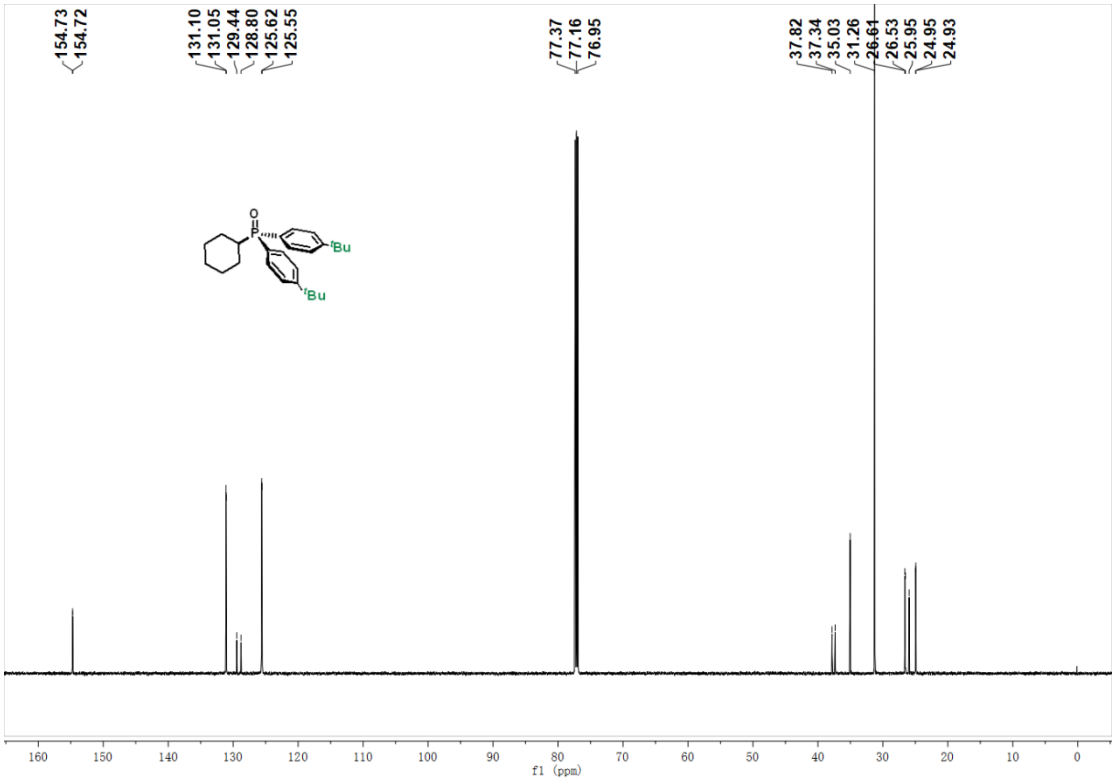


4ag; ^{31}P NMR (242.9 MHz, $CDCl_3$)

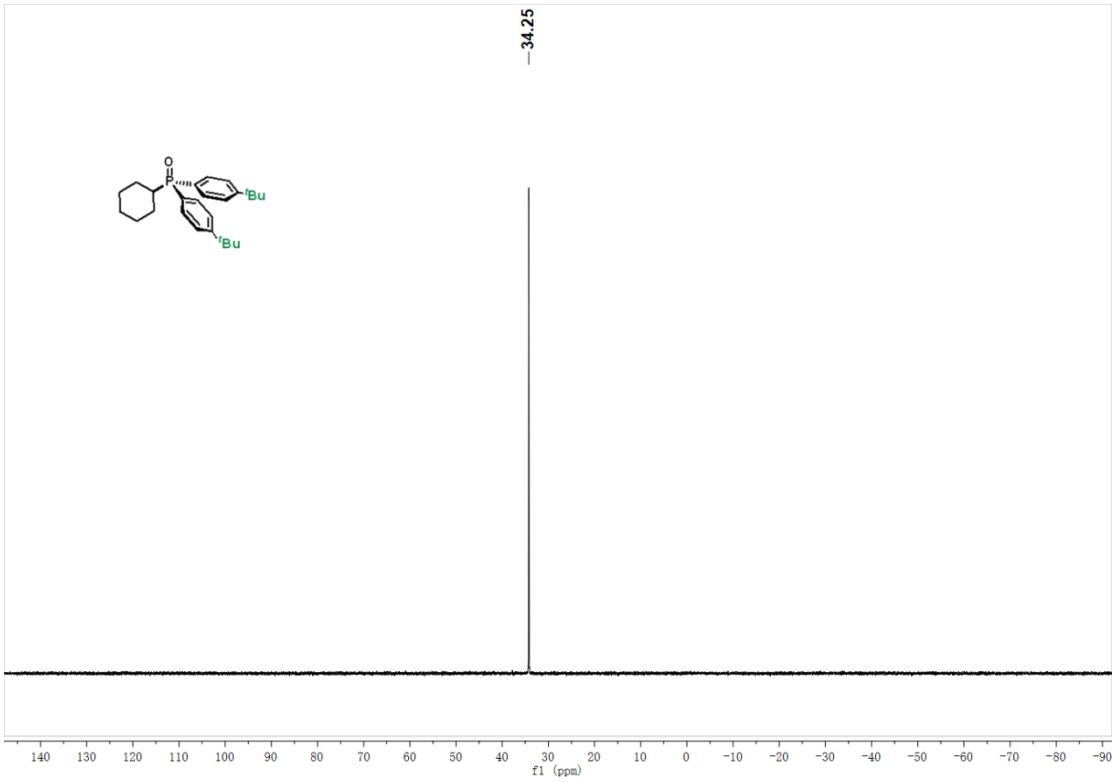


4ah; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

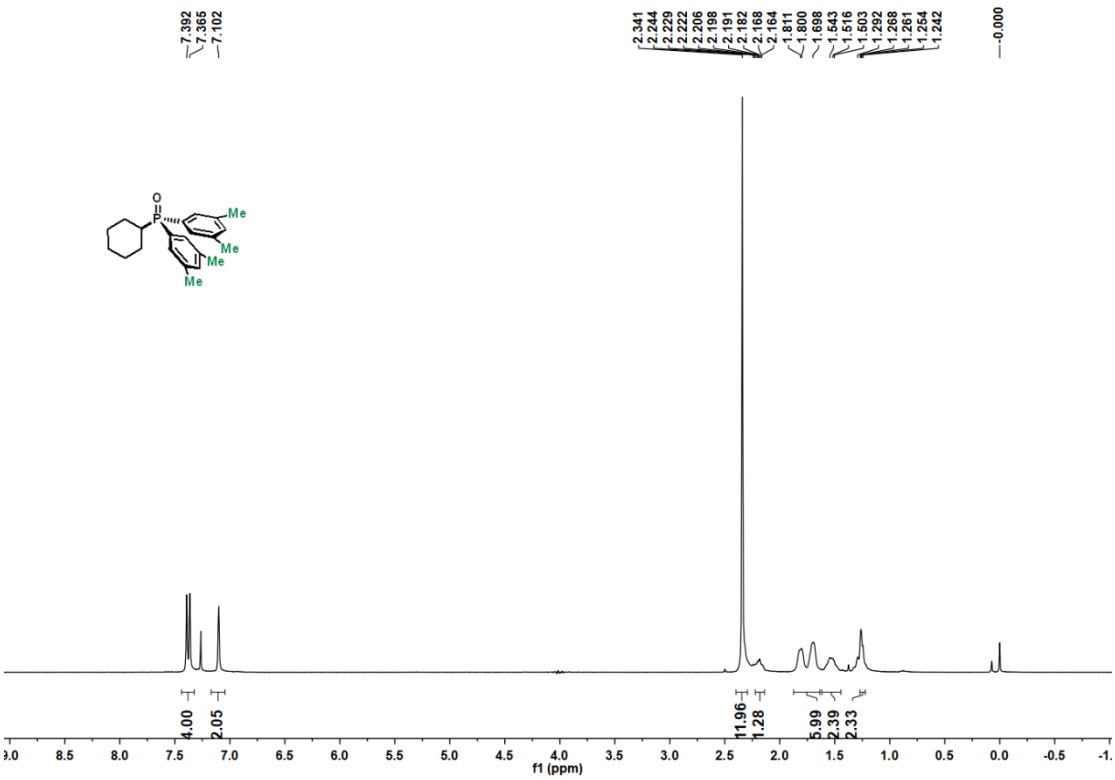


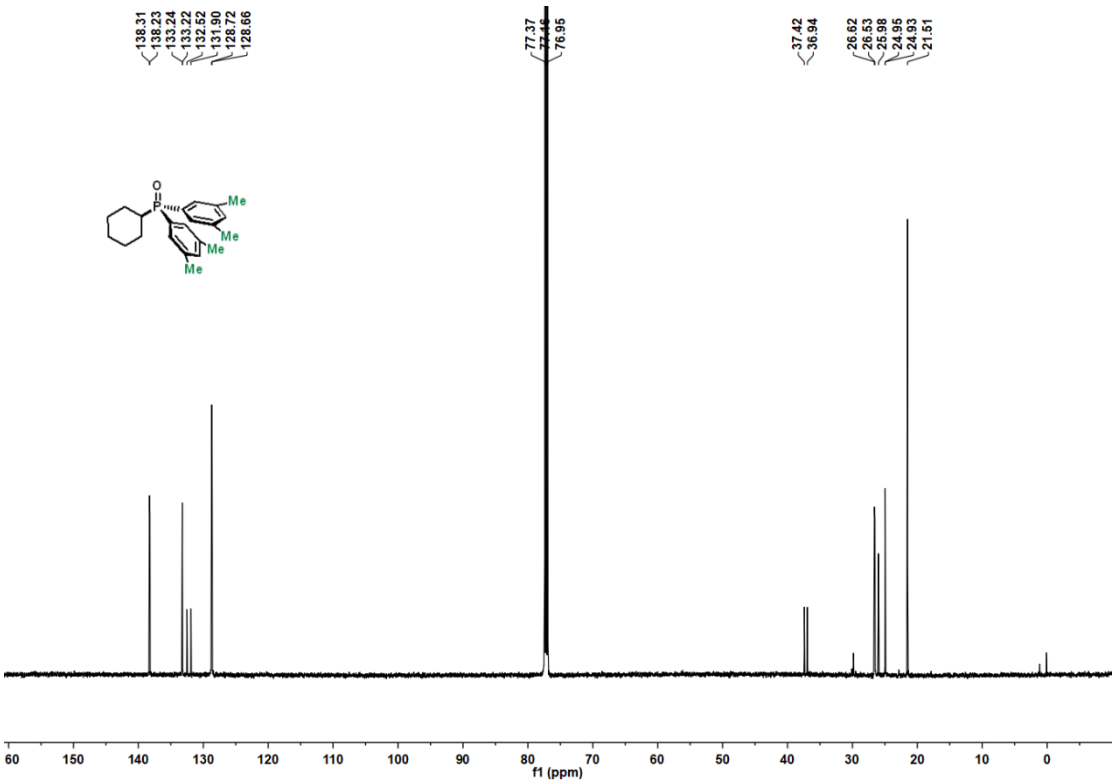


4ah; ^{31}P NMR (242.9 MHz, $CDCl_3$)

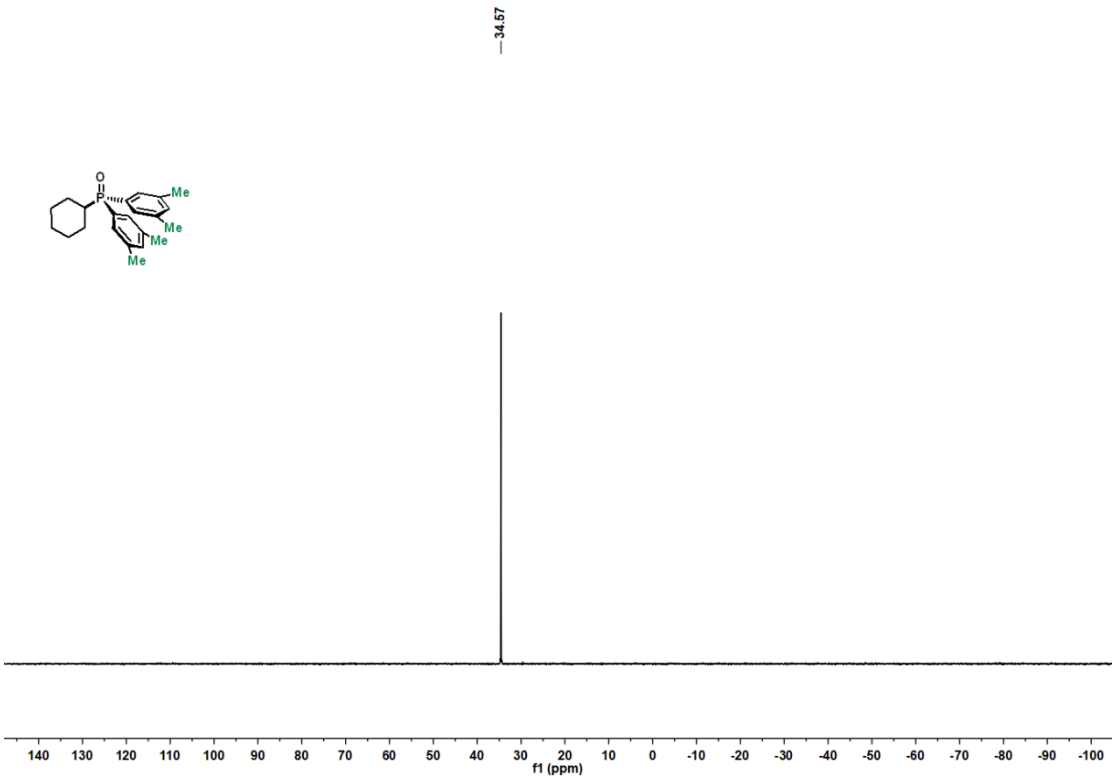


4ai; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

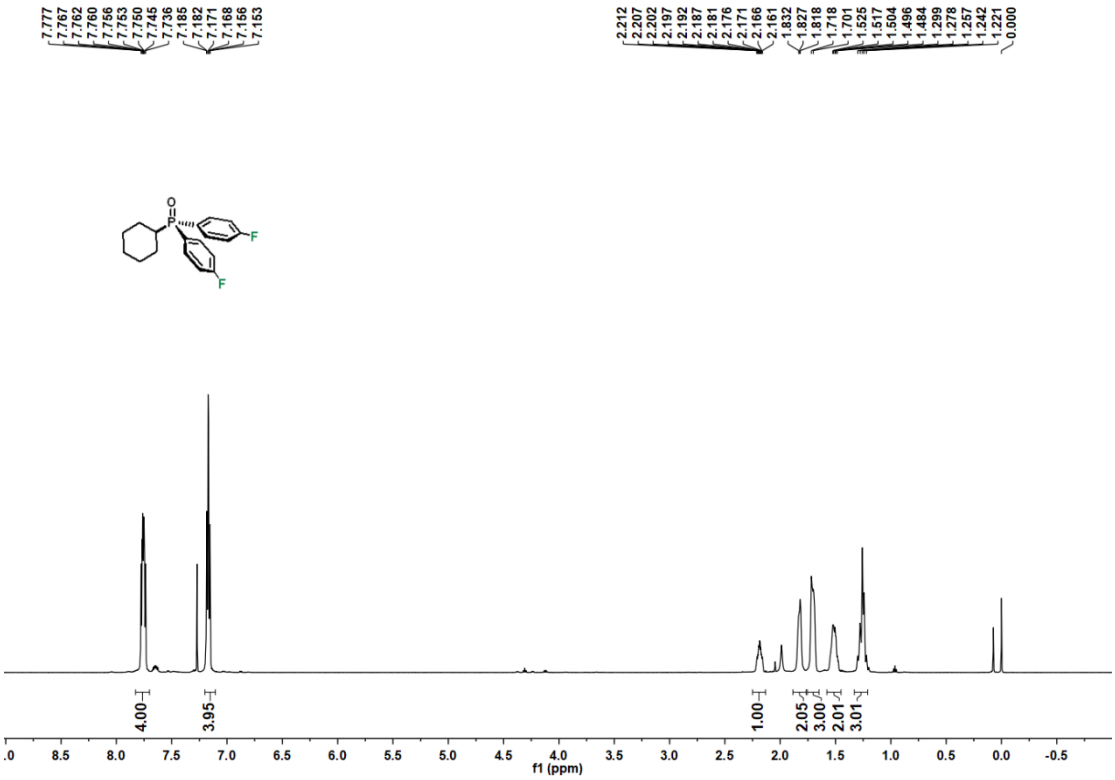


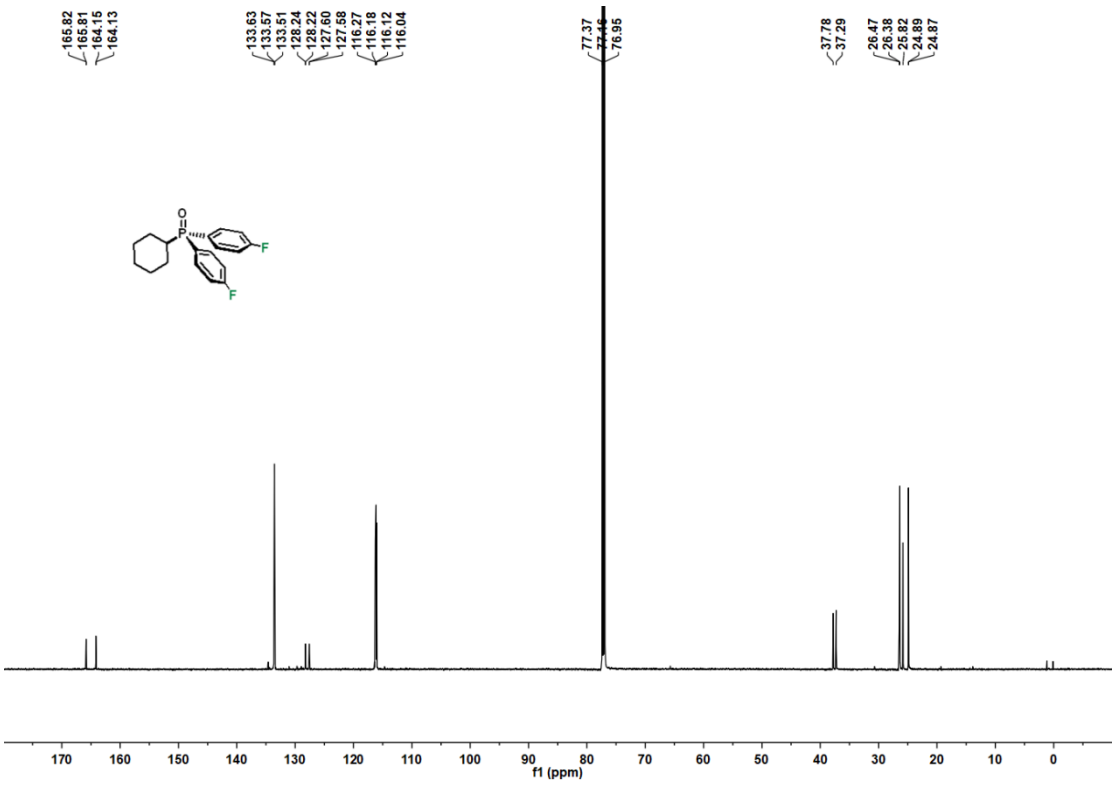


4ai; ^{31}P NMR (242.9 MHz, $CDCl_3$)

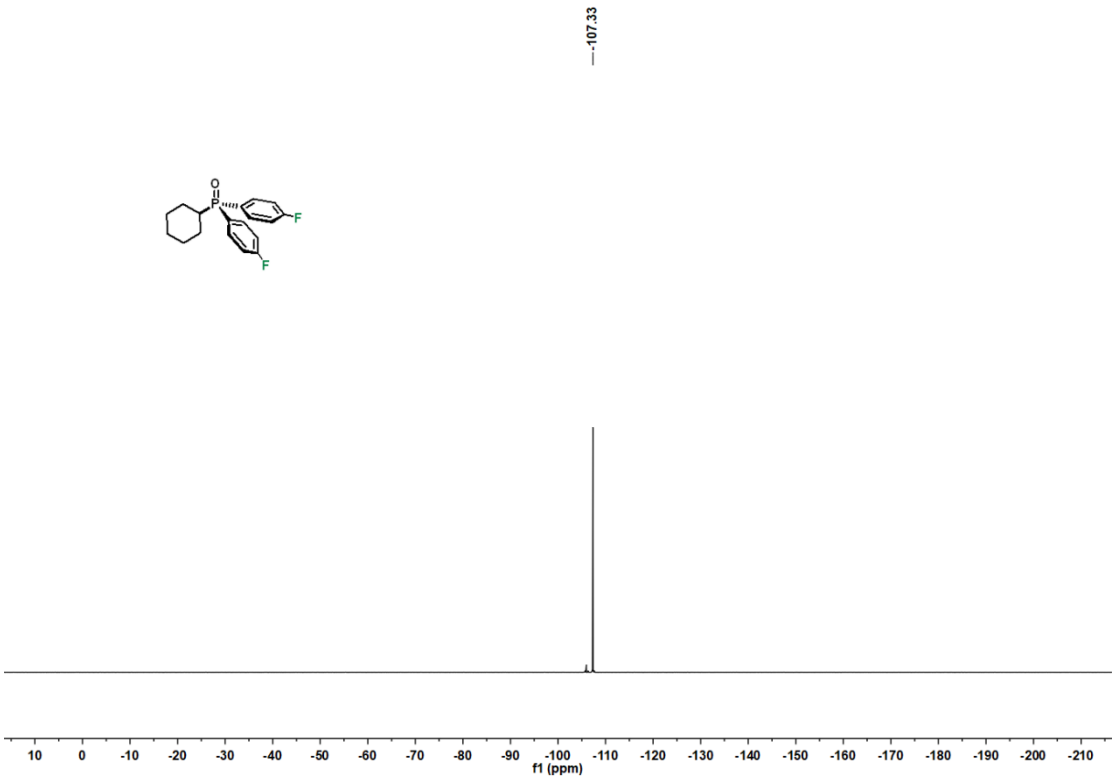


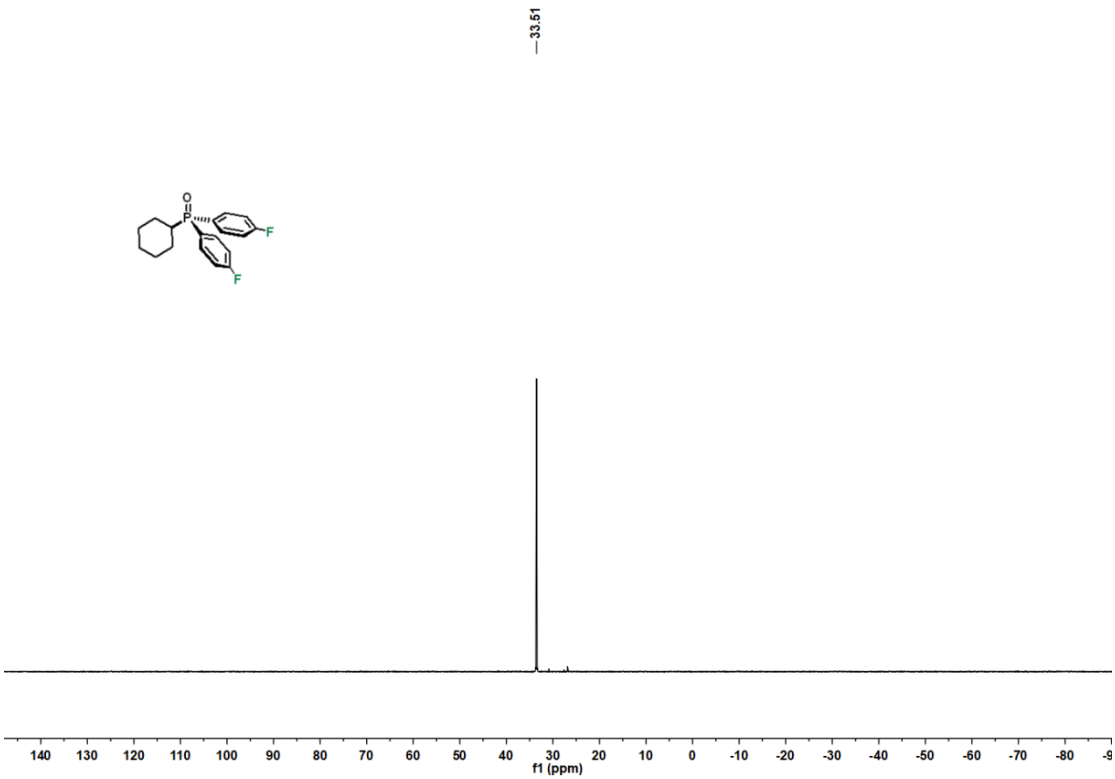
4aj; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



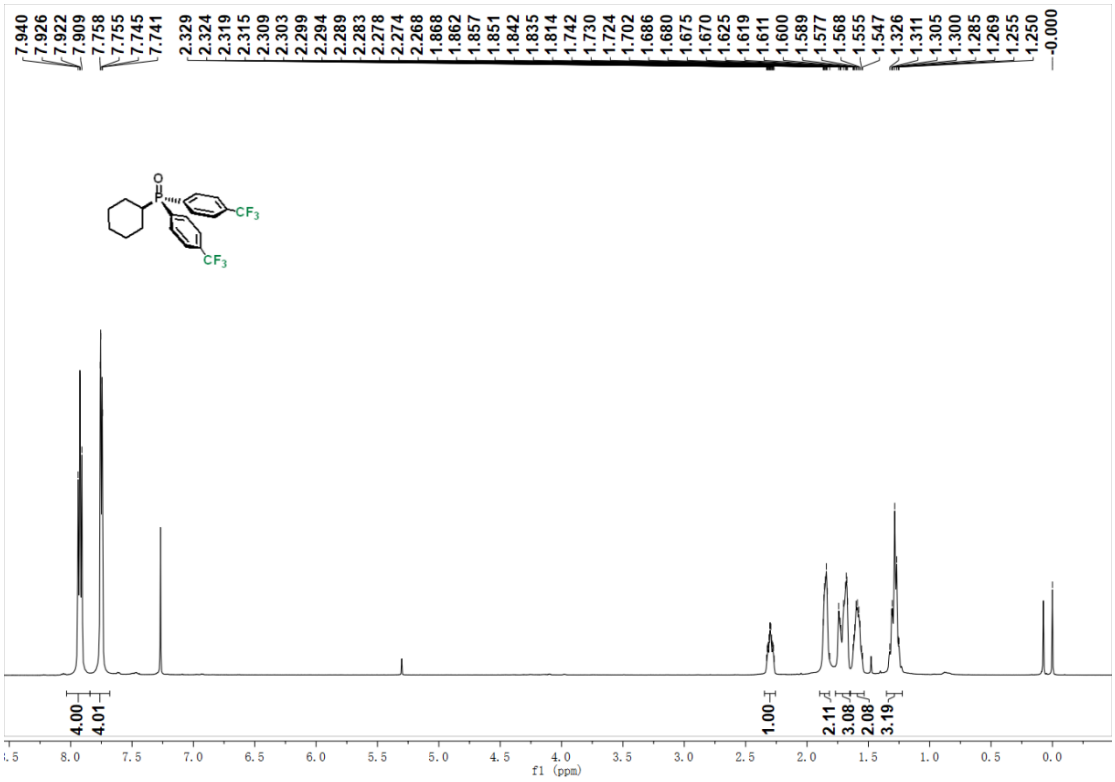


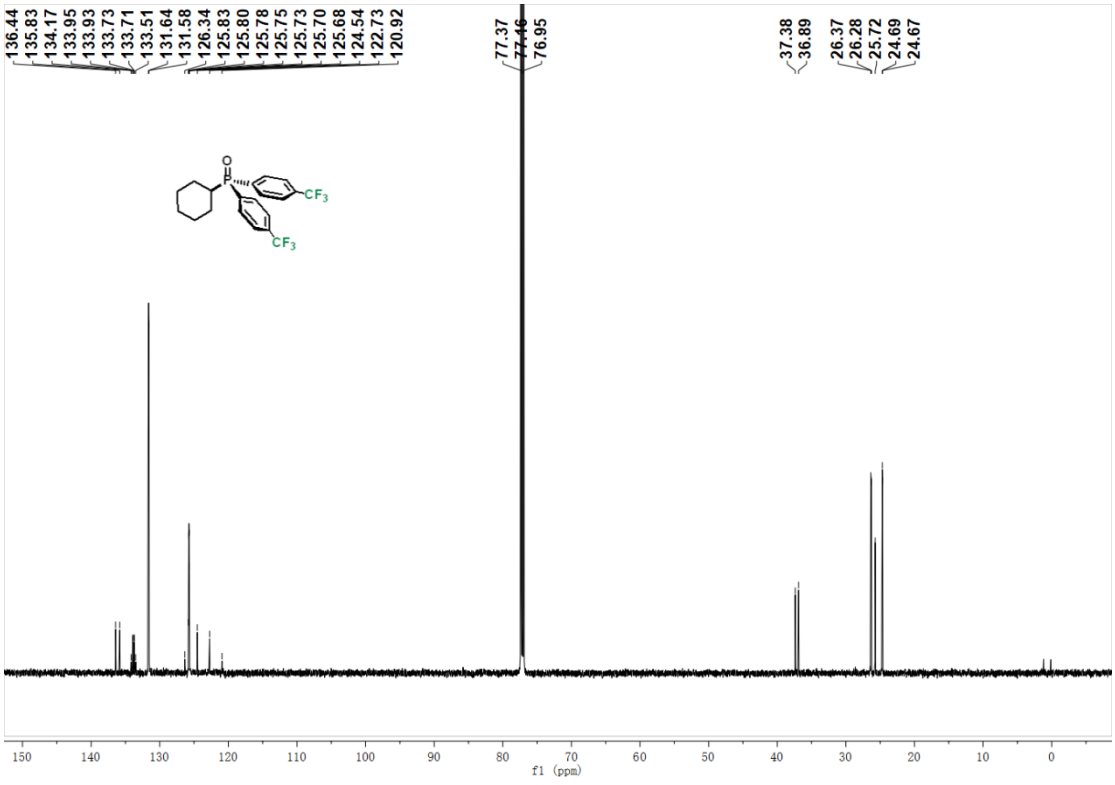
4aj; ^{19}F NMR (376 MHz, $CDCl_3$); ^{31}P NMR (242.9 MHz, $CDCl_3$)



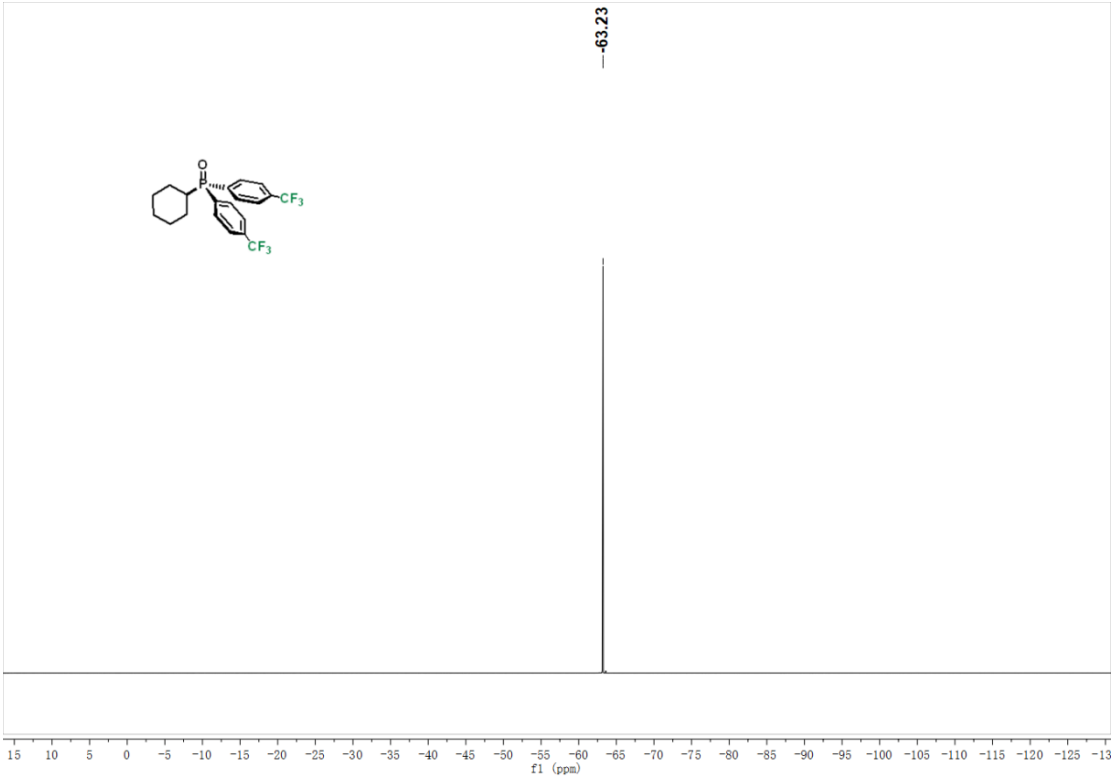


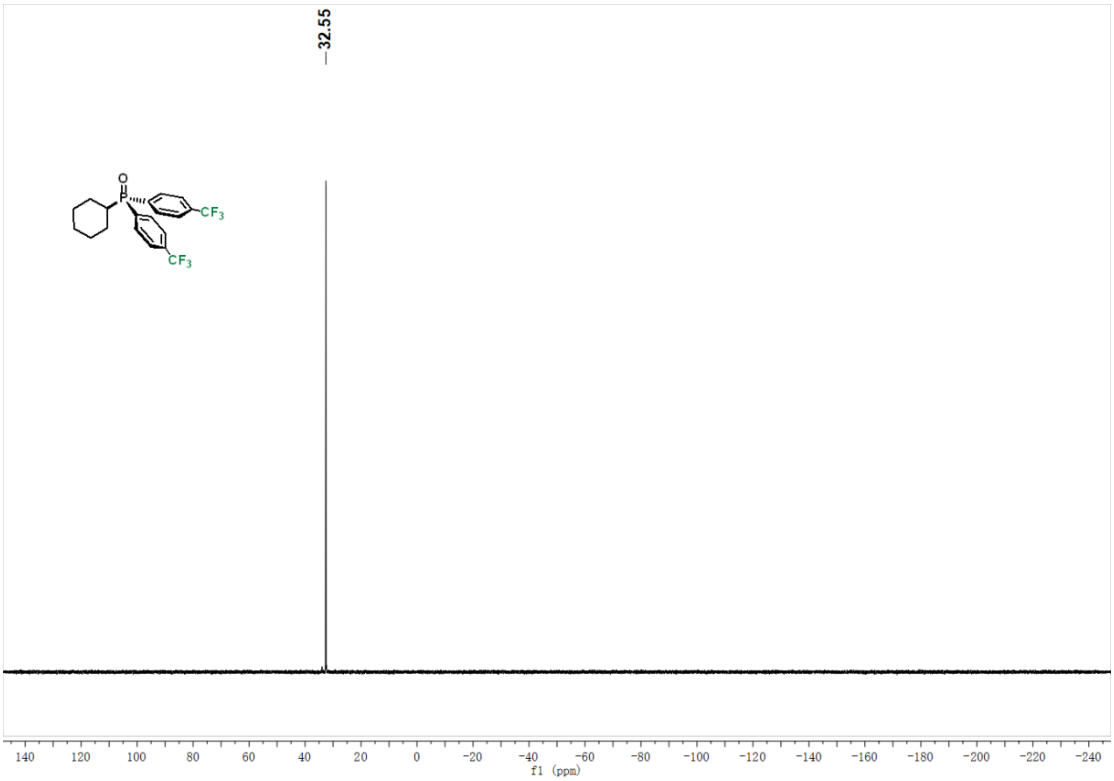
4ak; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



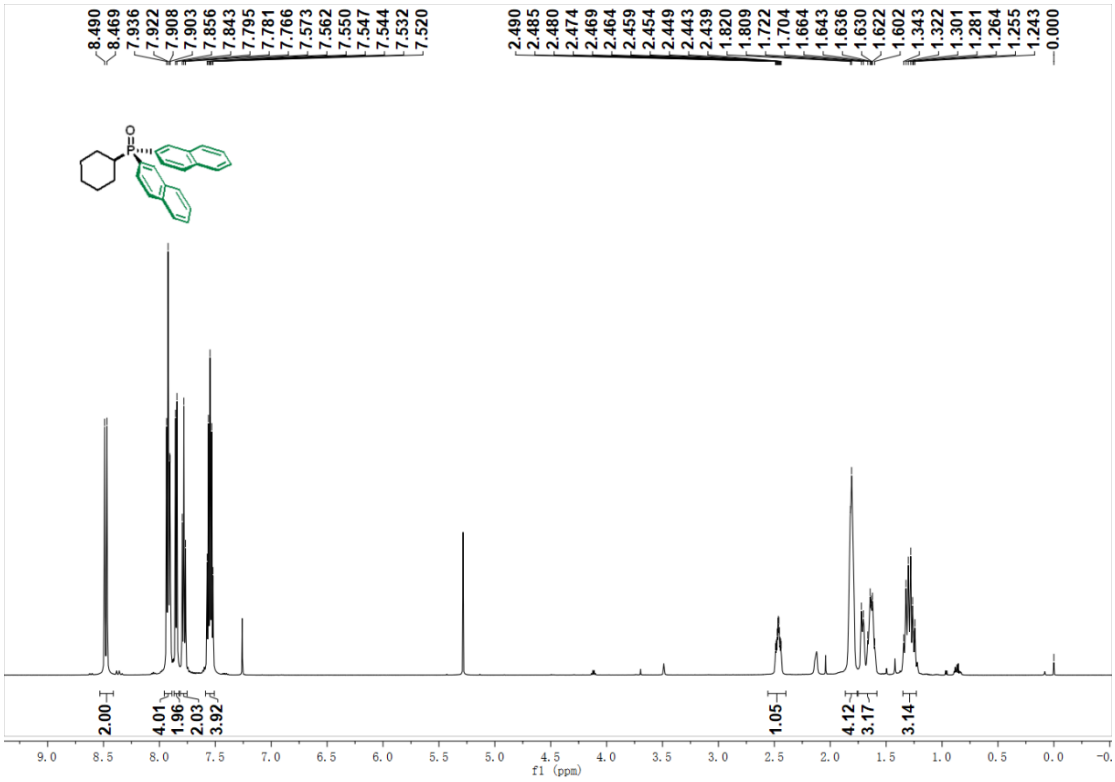


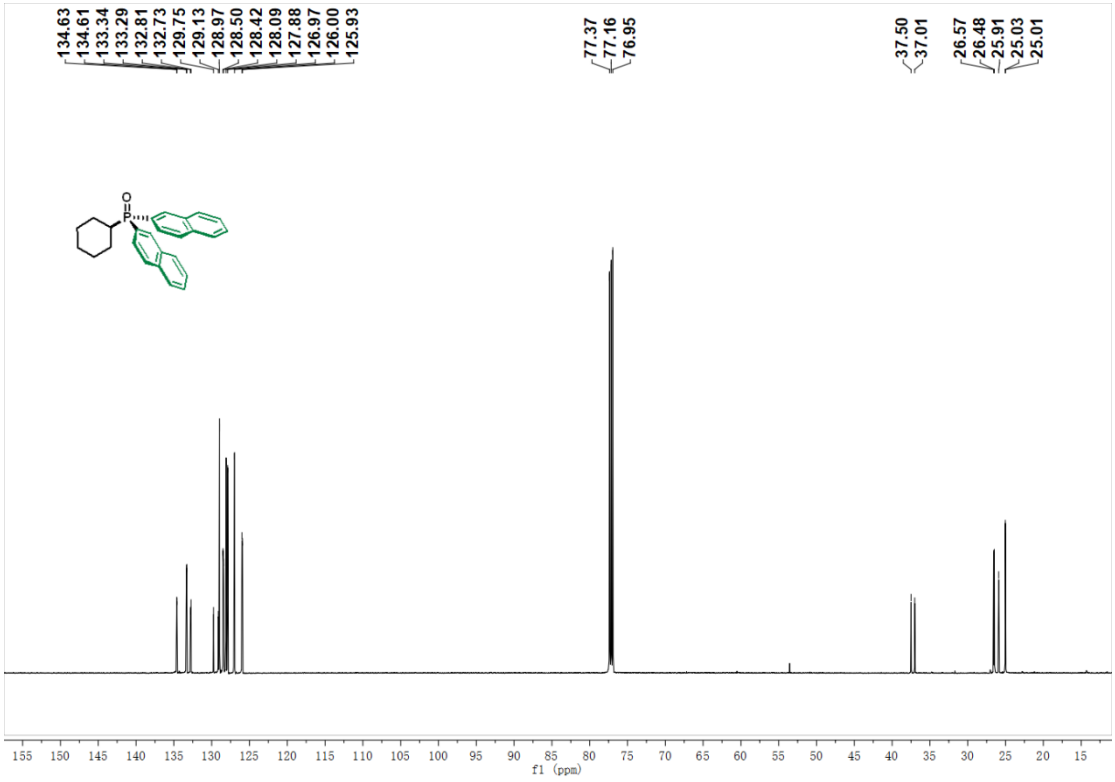
4ak; ^{19}F NMR (376 MHz, $CDCl_3$); ^{31}P NMR (242.9 MHz, $CDCl_3$)



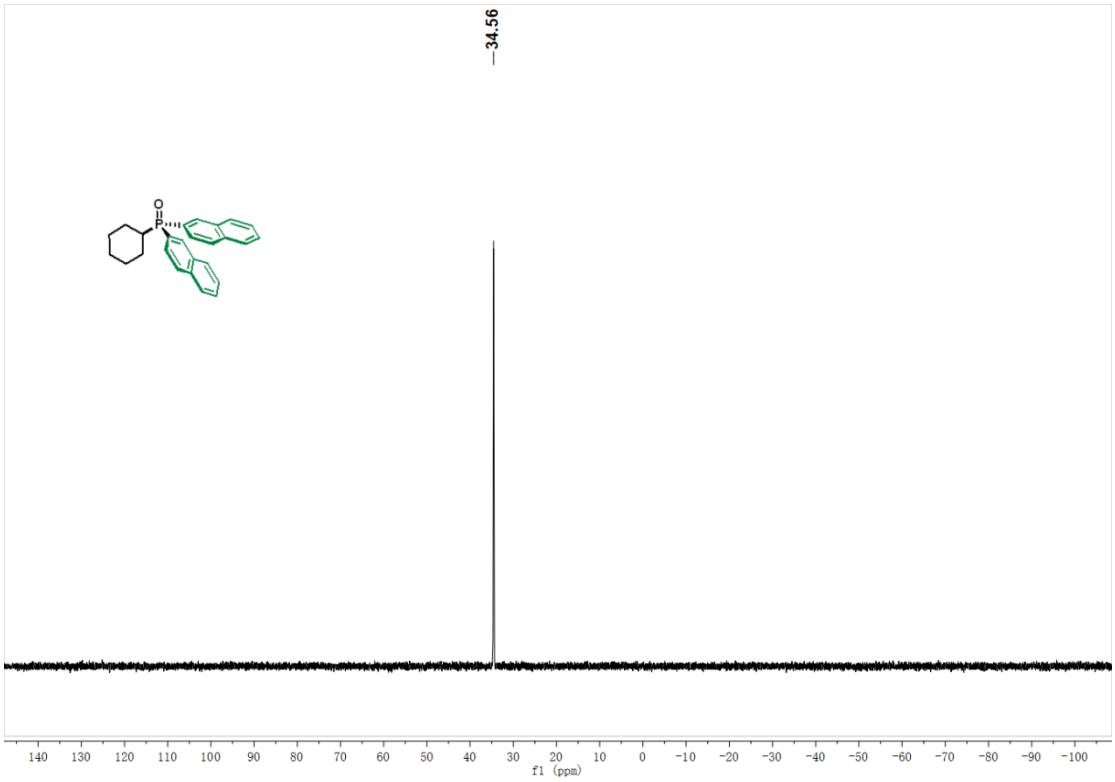


4al; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

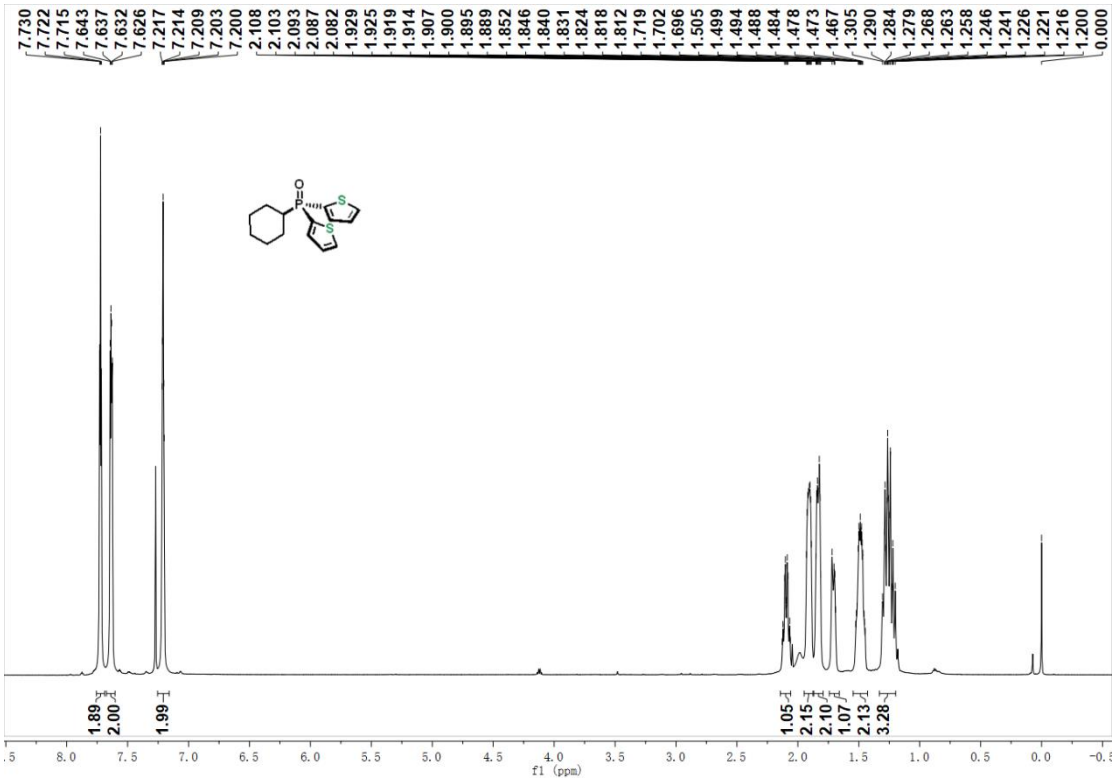


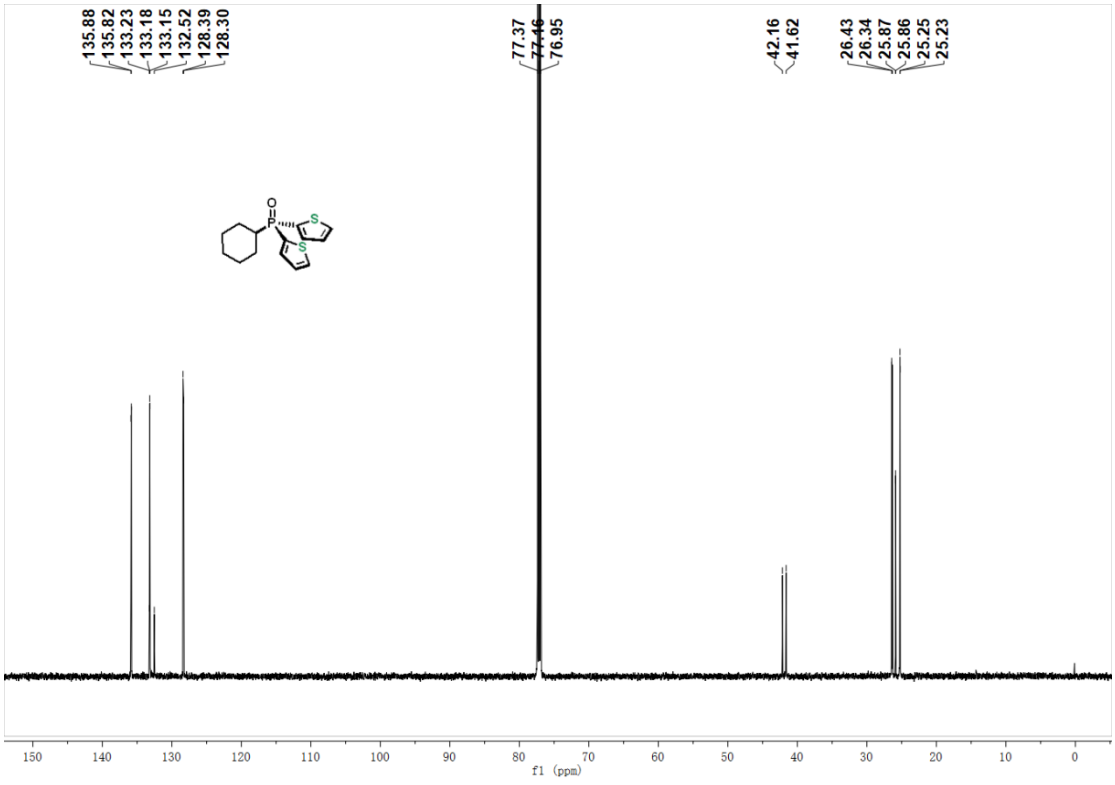


4al; ^{31}P NMR (242.9 MHz, $CDCl_3$)

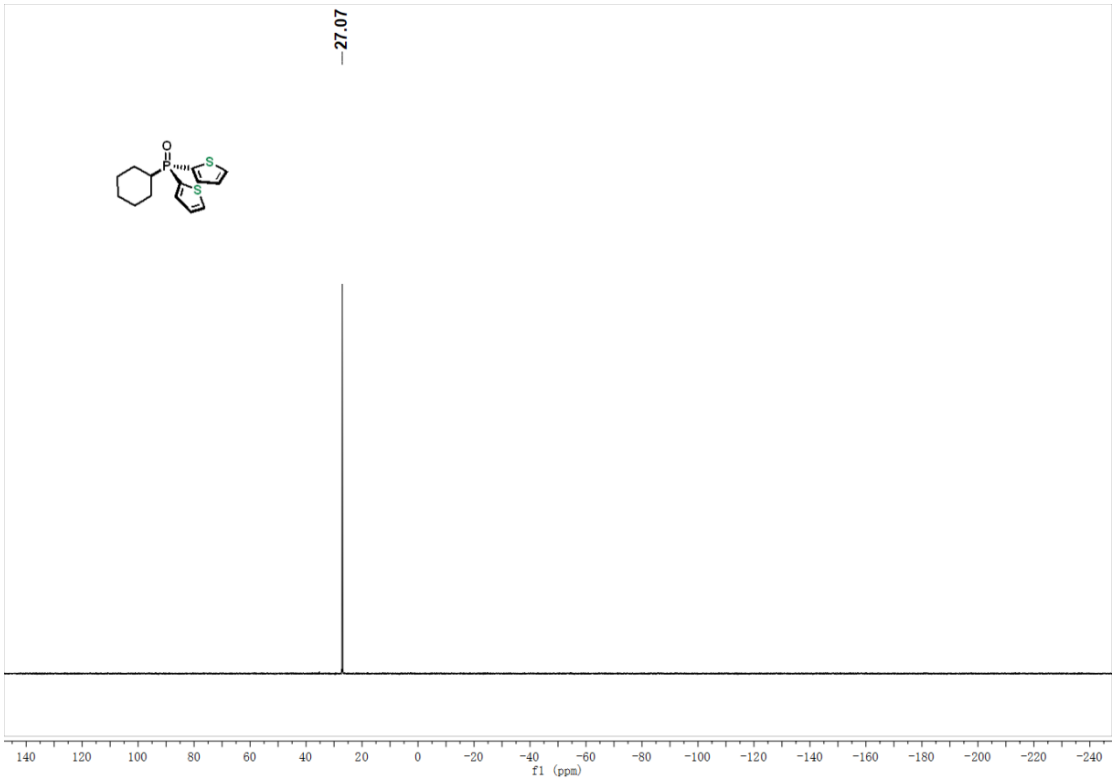


4am; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

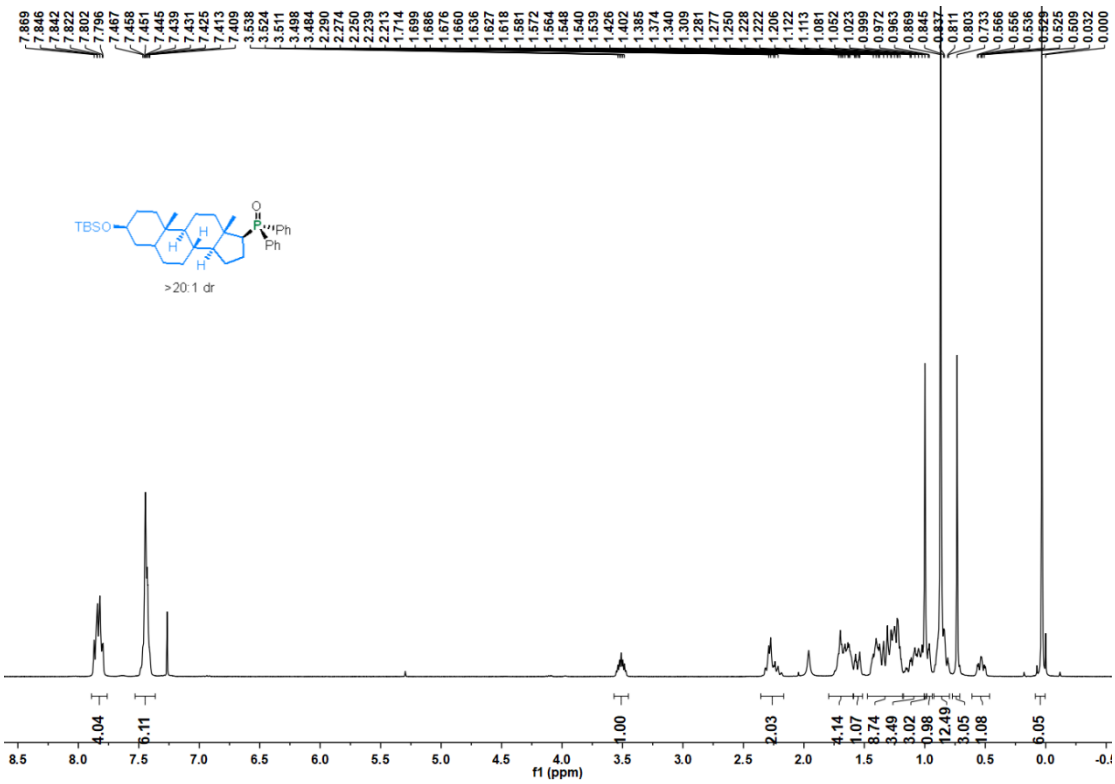


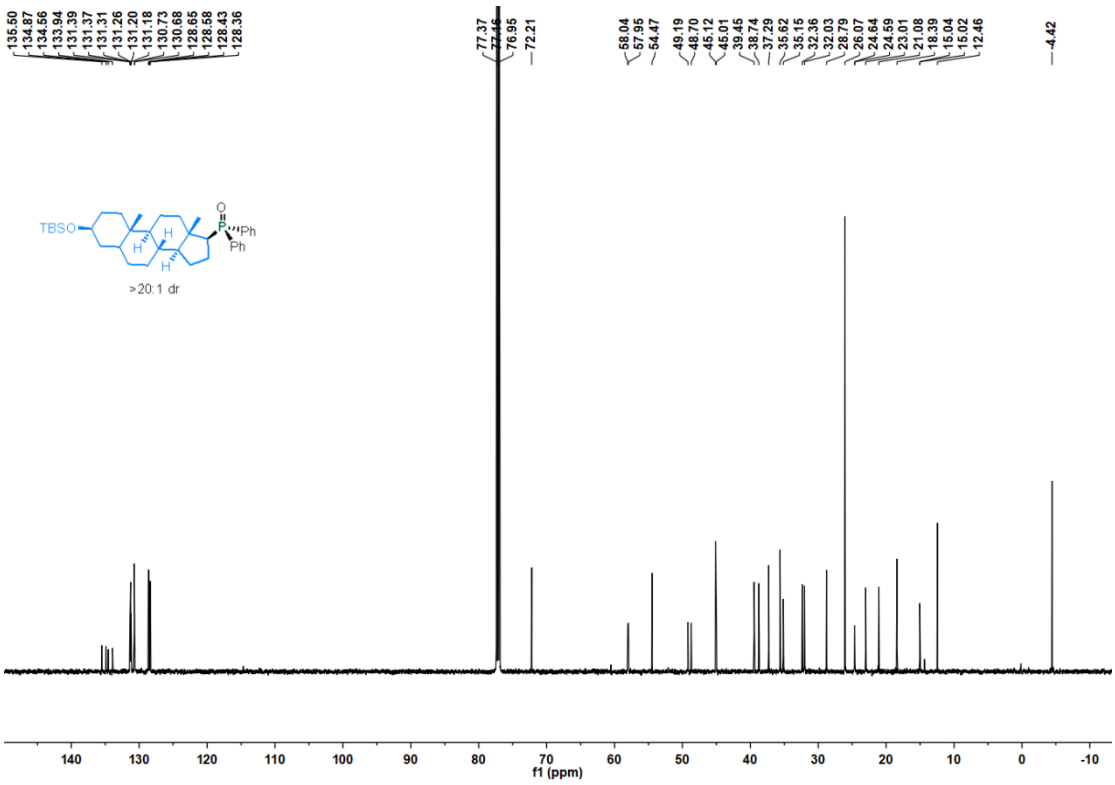


4am; ^{31}P NMR (242.9 MHz, $CDCl_3$)

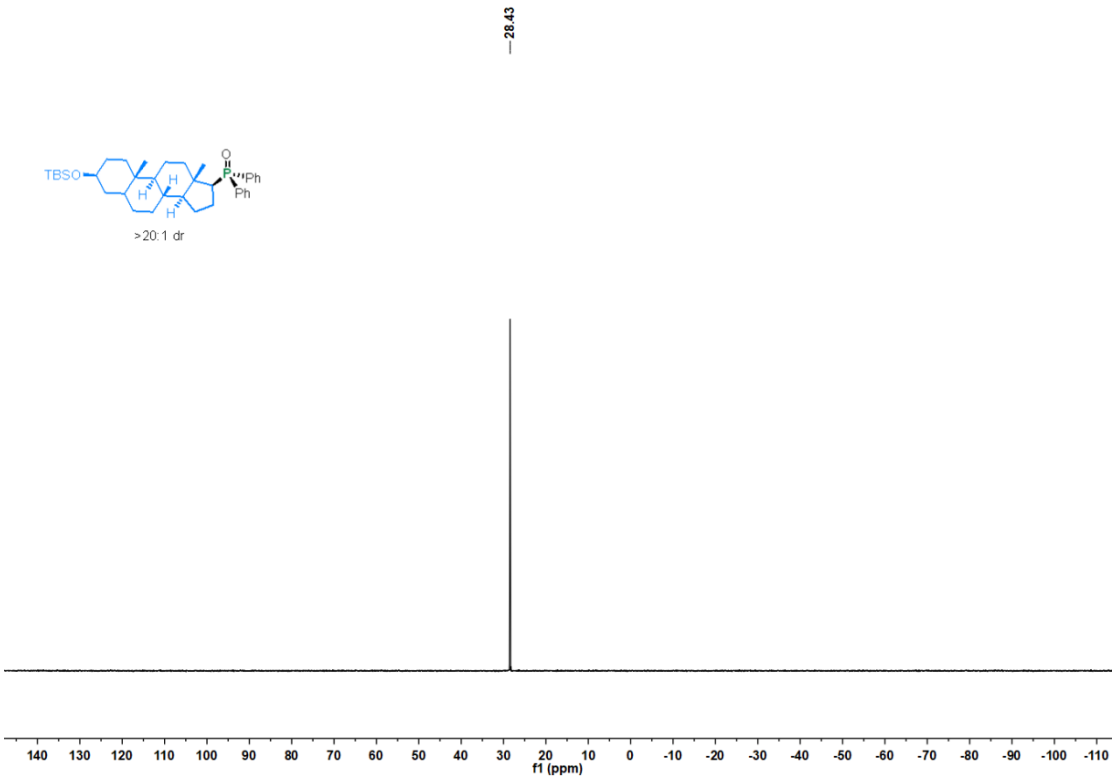


4ap; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

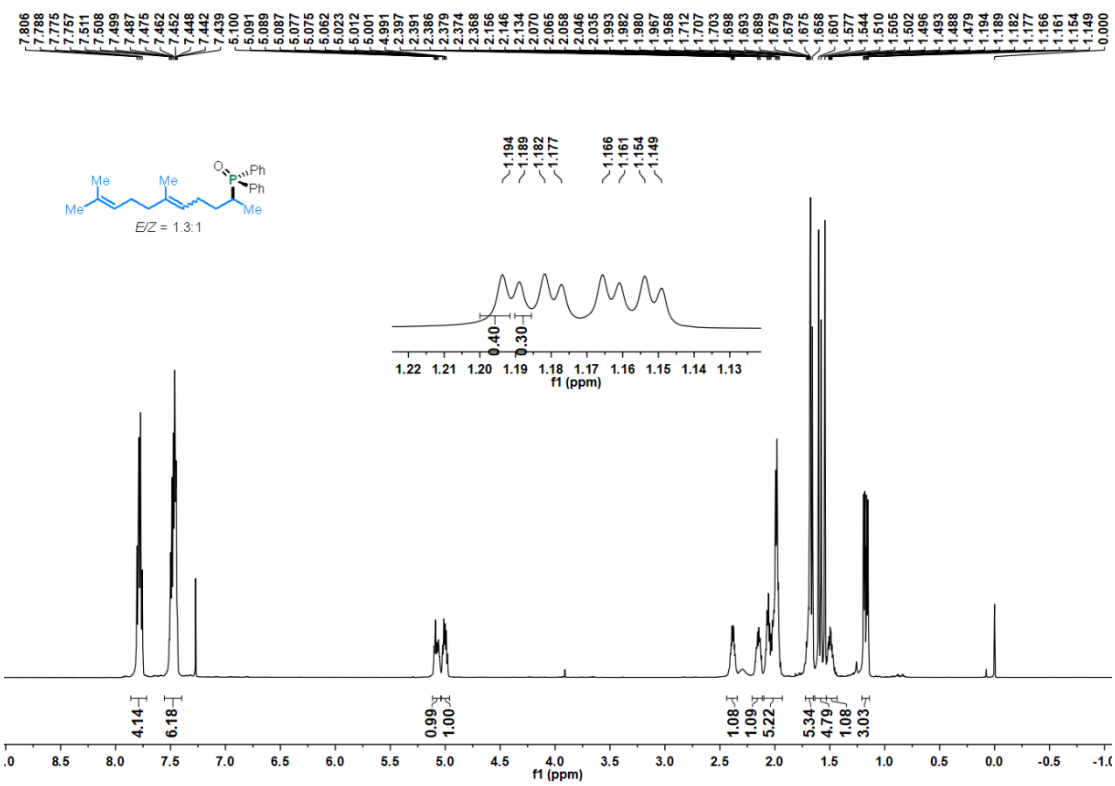


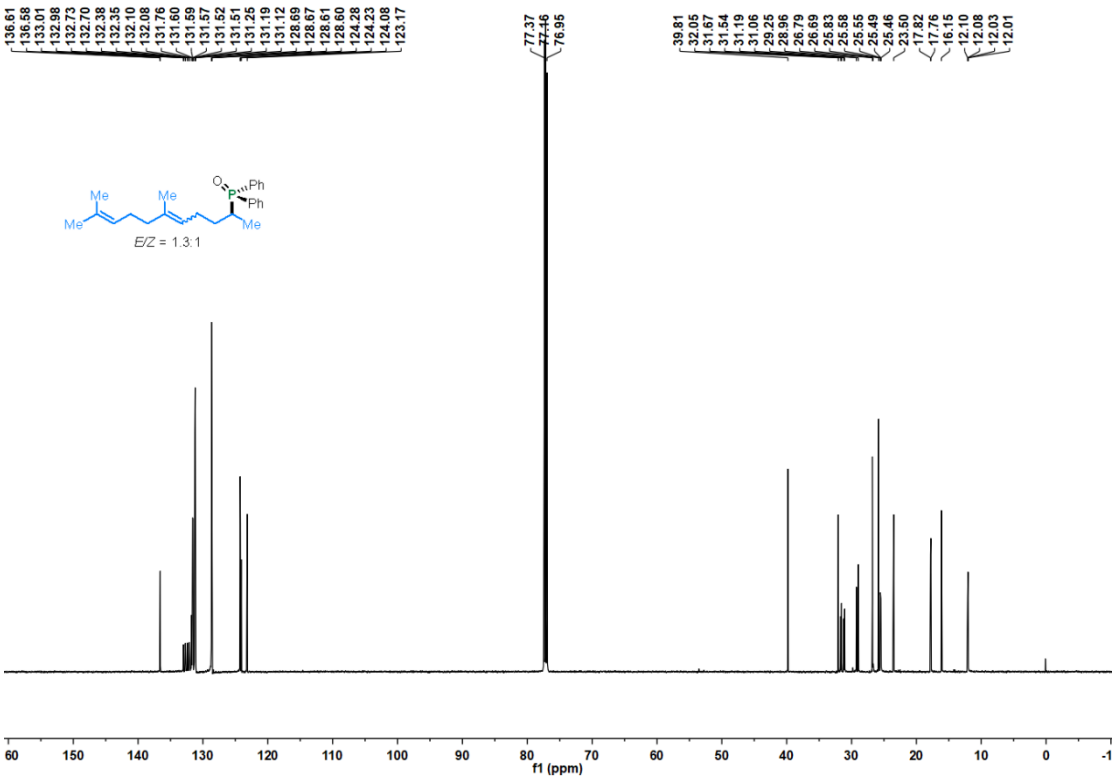


4ap; ^{31}P NMR (242.9 MHz, $CDCl_3$)

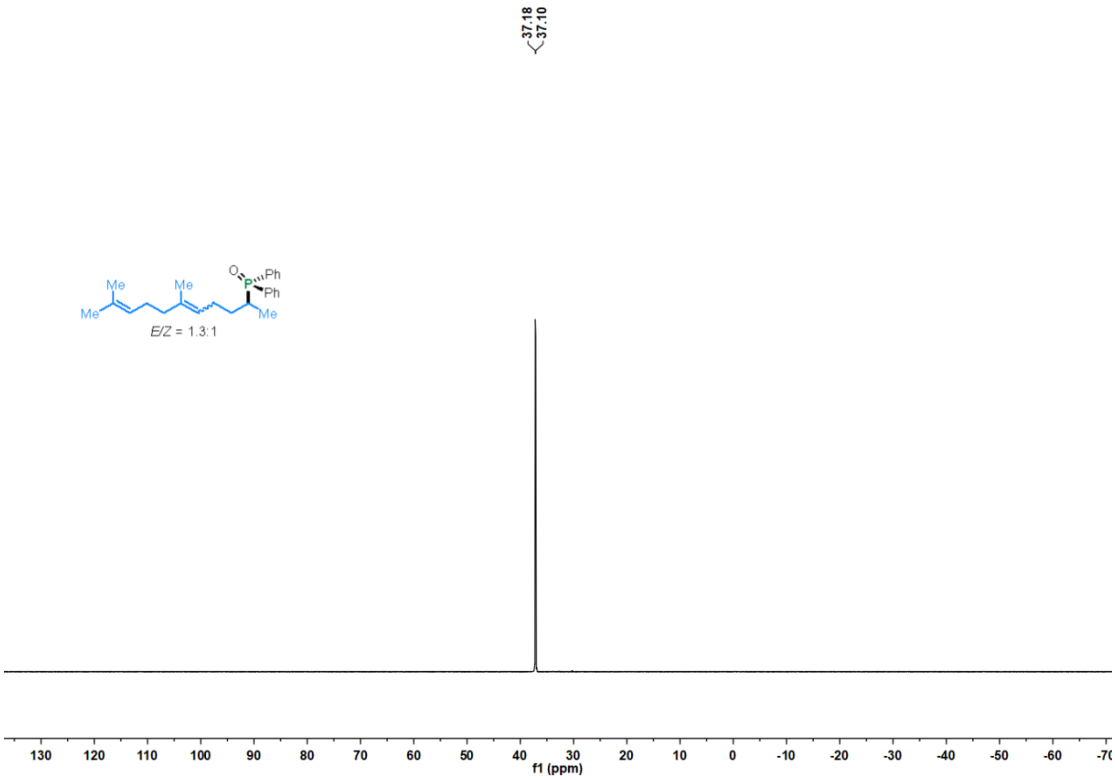


4aq; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

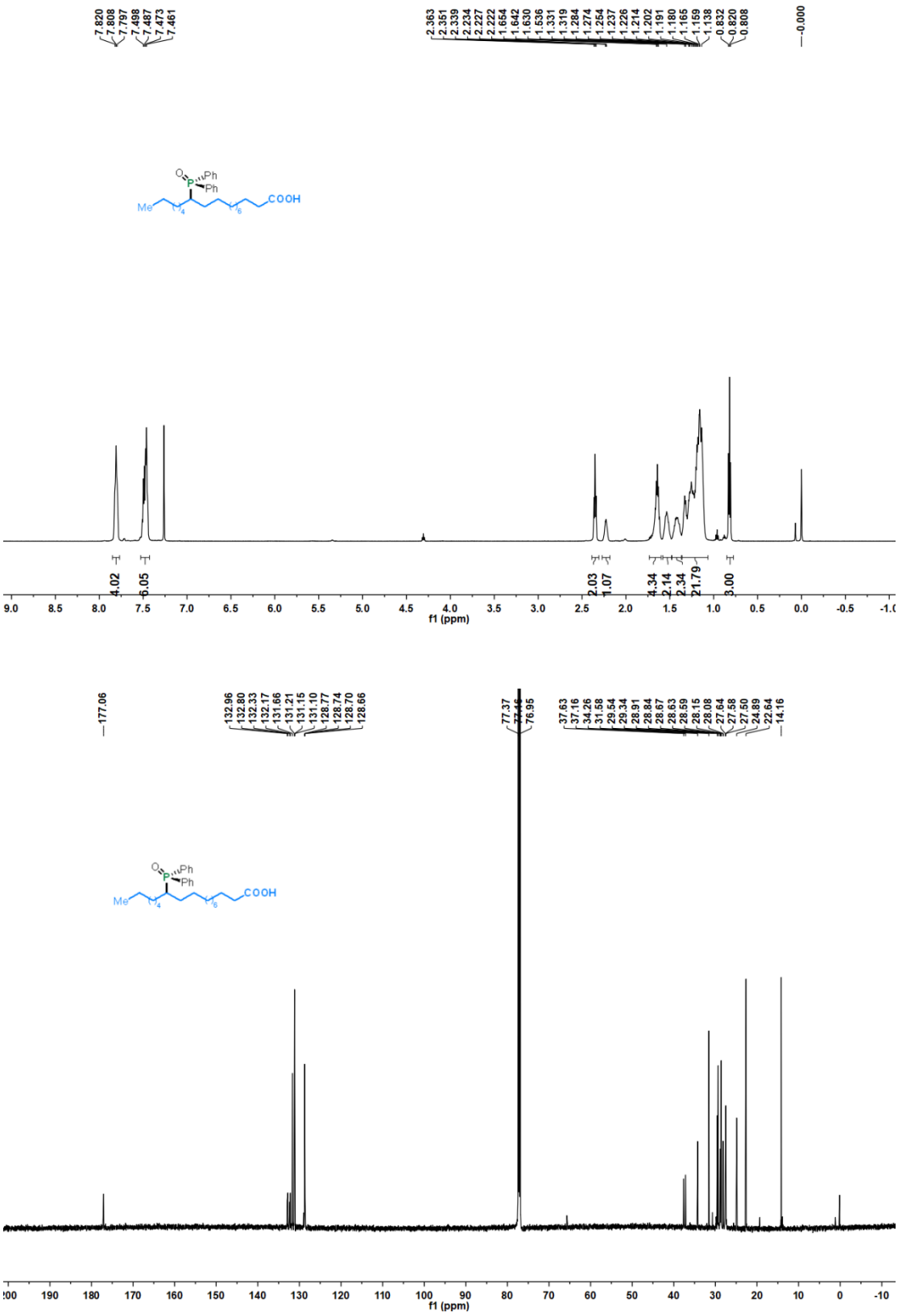




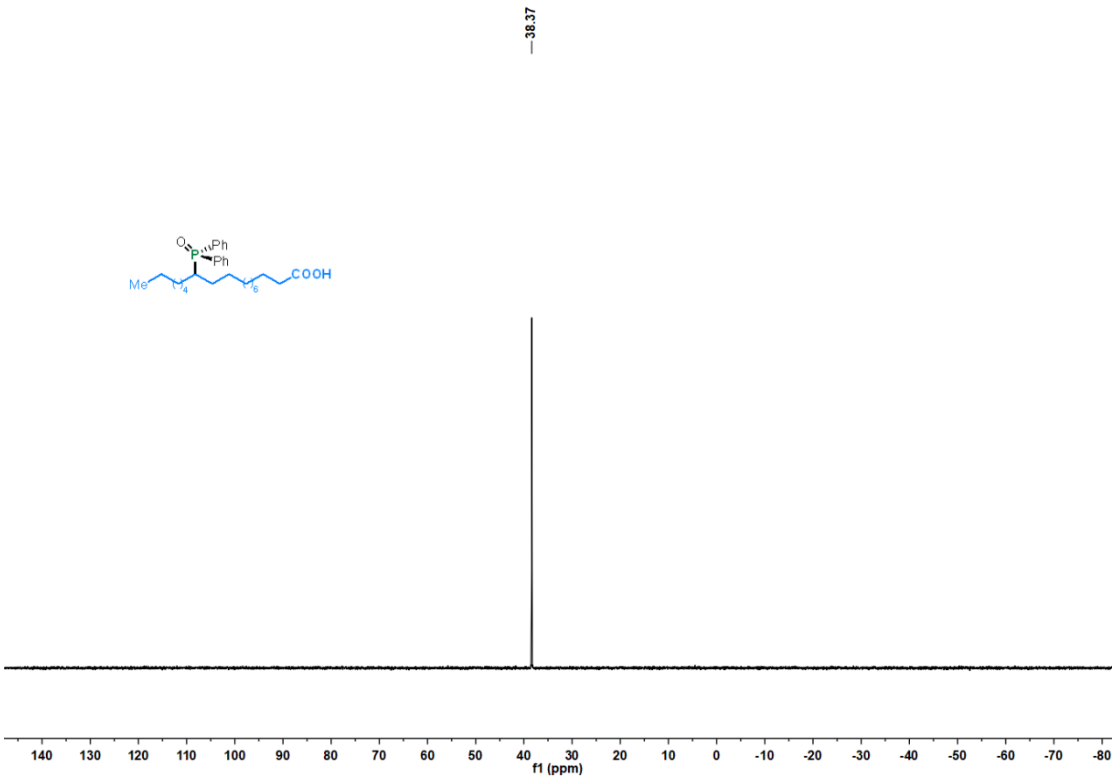
4aq; ^{31}P NMR (242.9 MHz, $CDCl_3$)



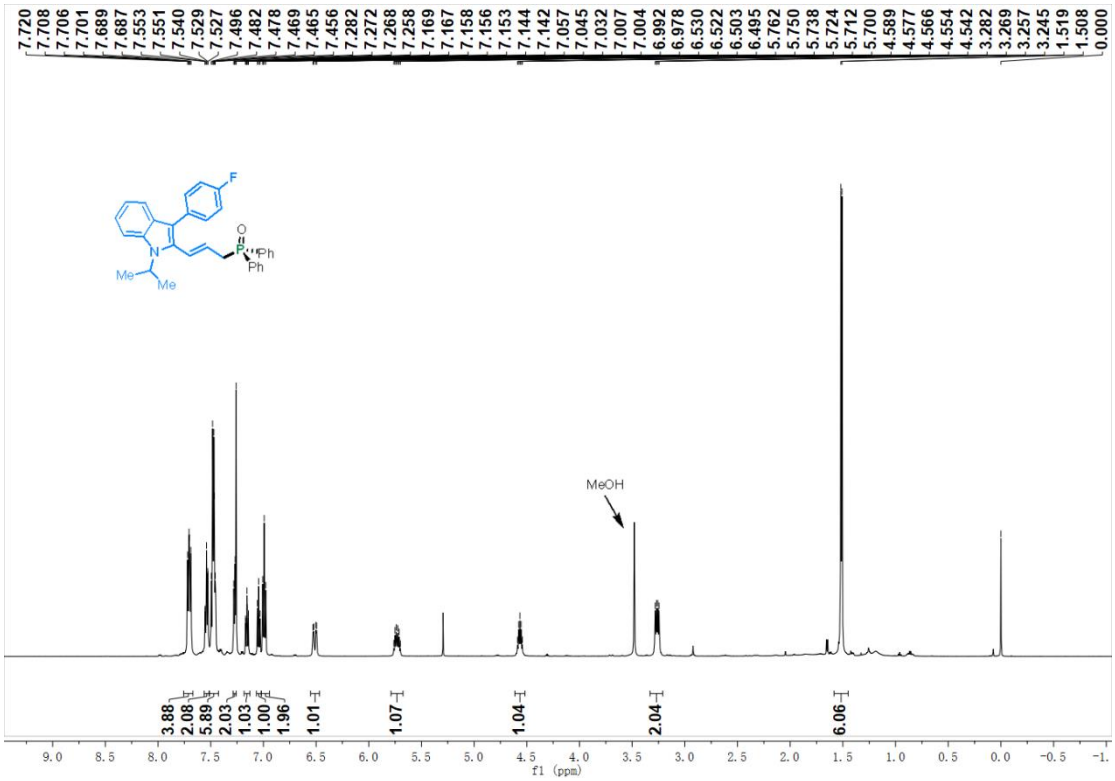
4ar; ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

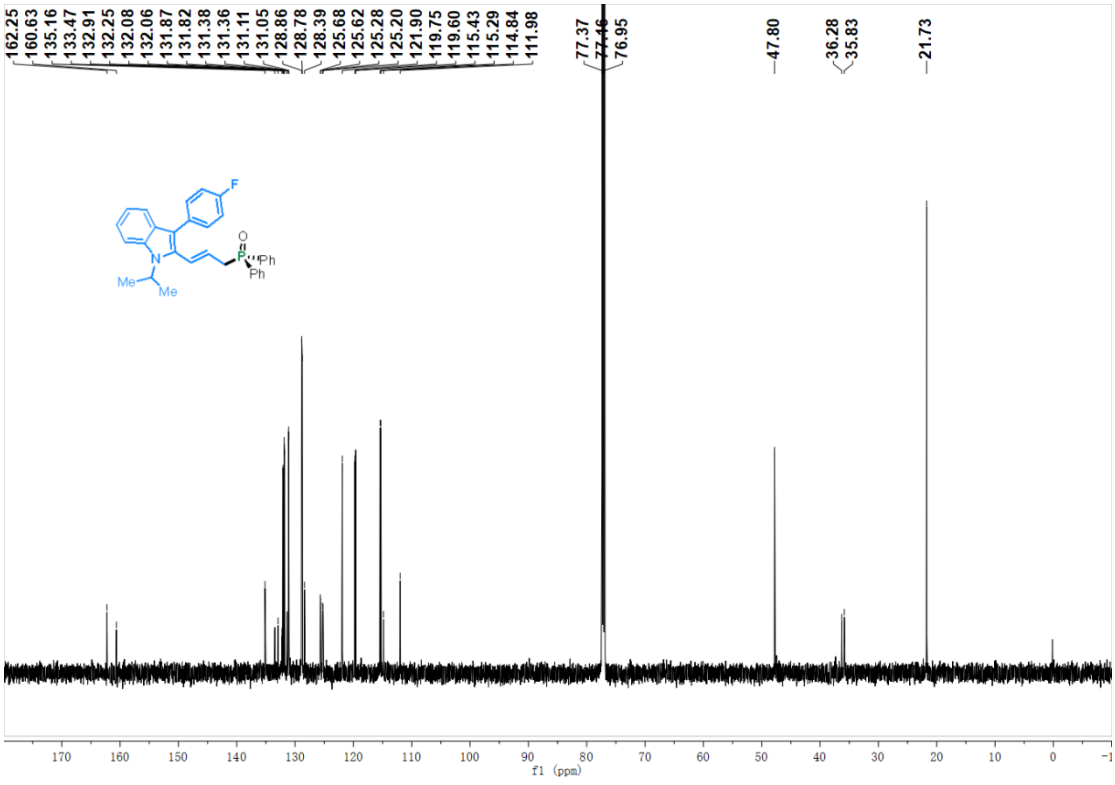


4ar; ^{31}P NMR (242.9 MHz, $CDCl_3$)

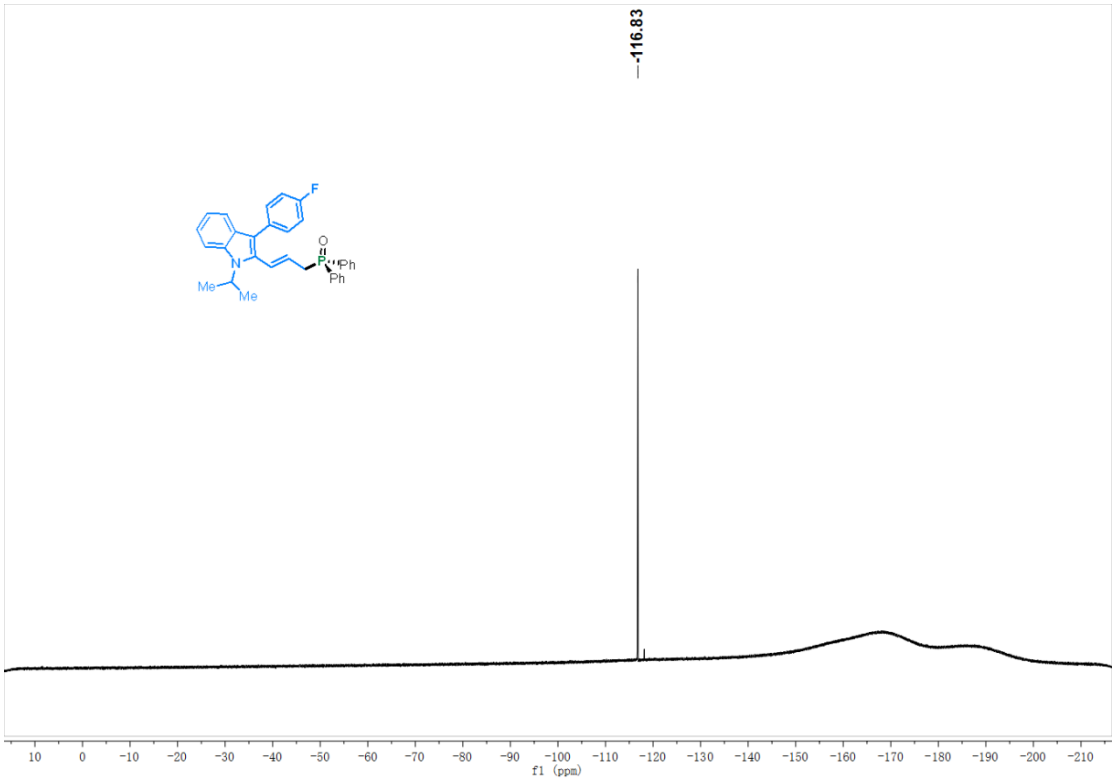


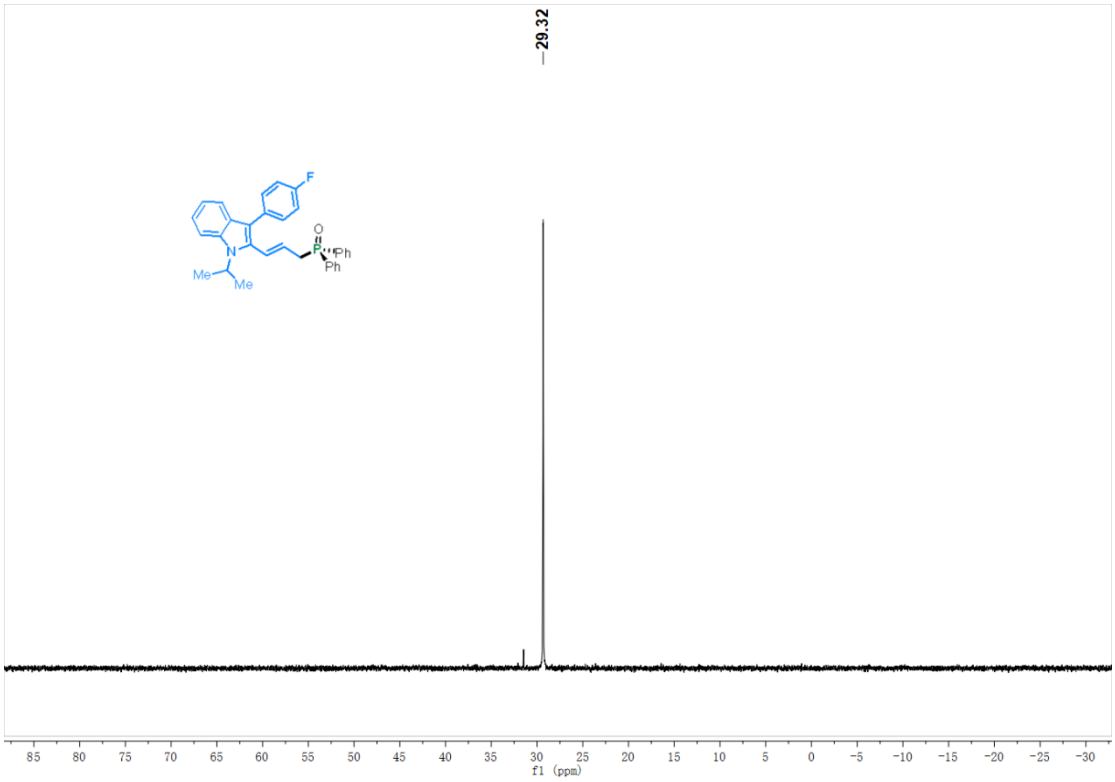
4as; ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



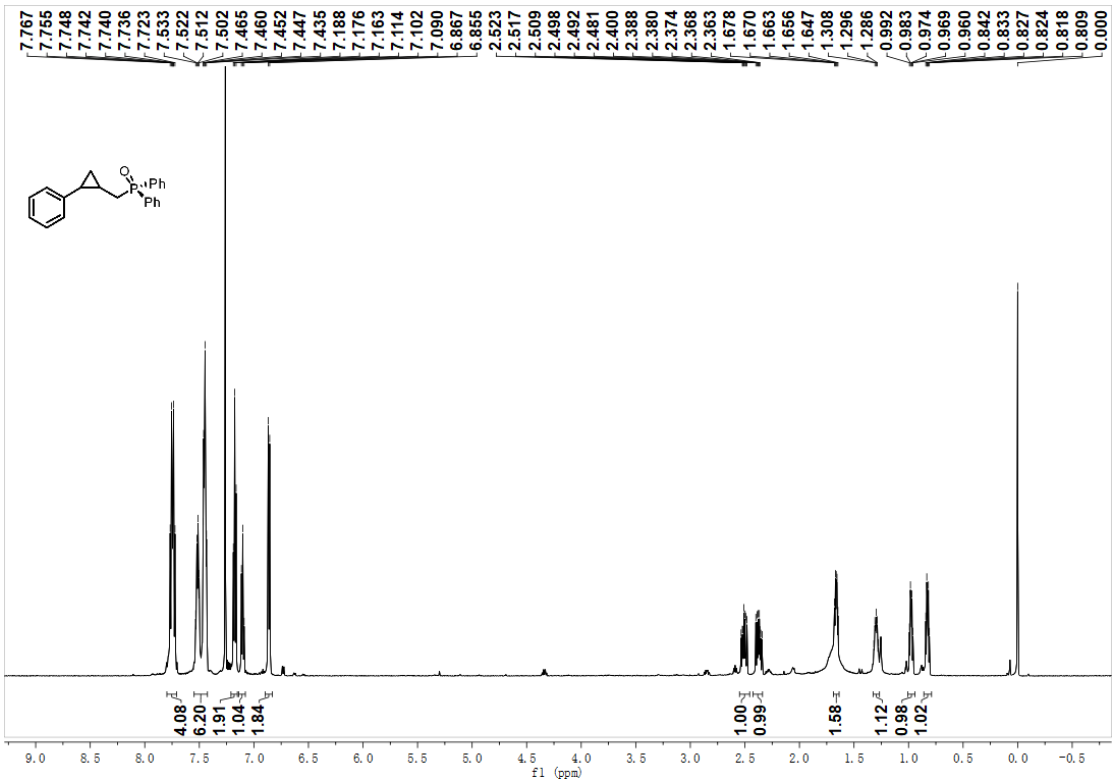


4as; ^{19}F NMR (376 MHz, $CDCl_3$); ^{31}P NMR (242.9 MHz, $CDCl_3$)

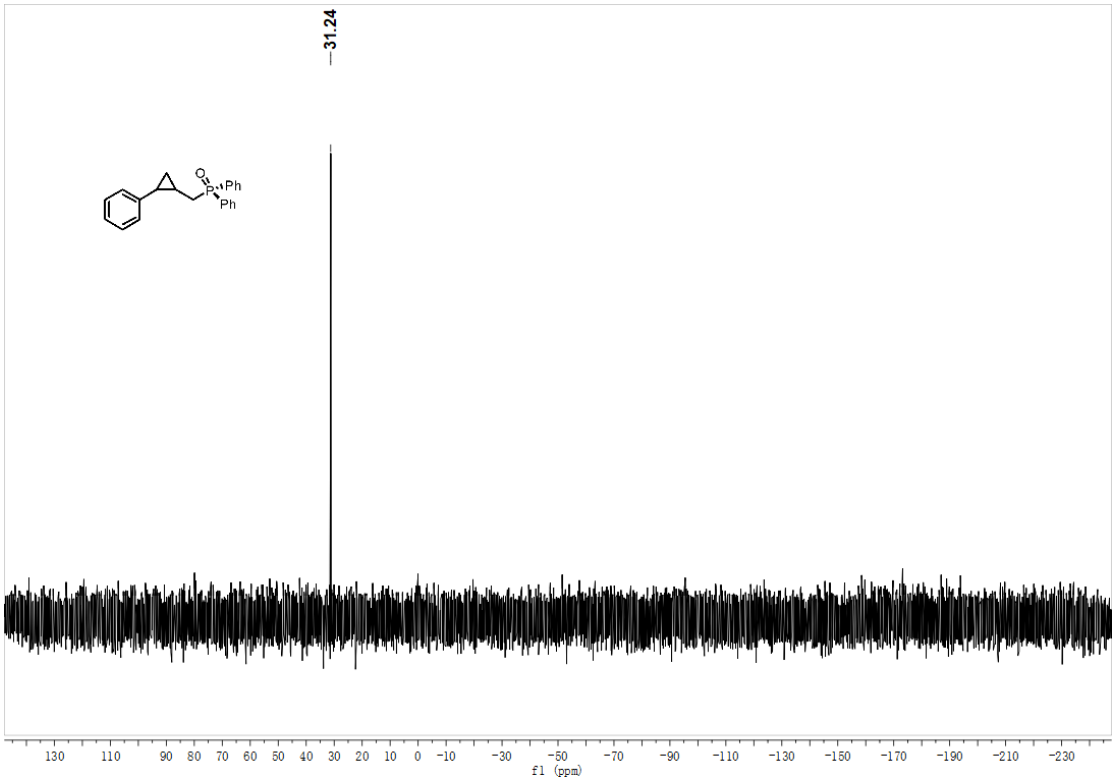




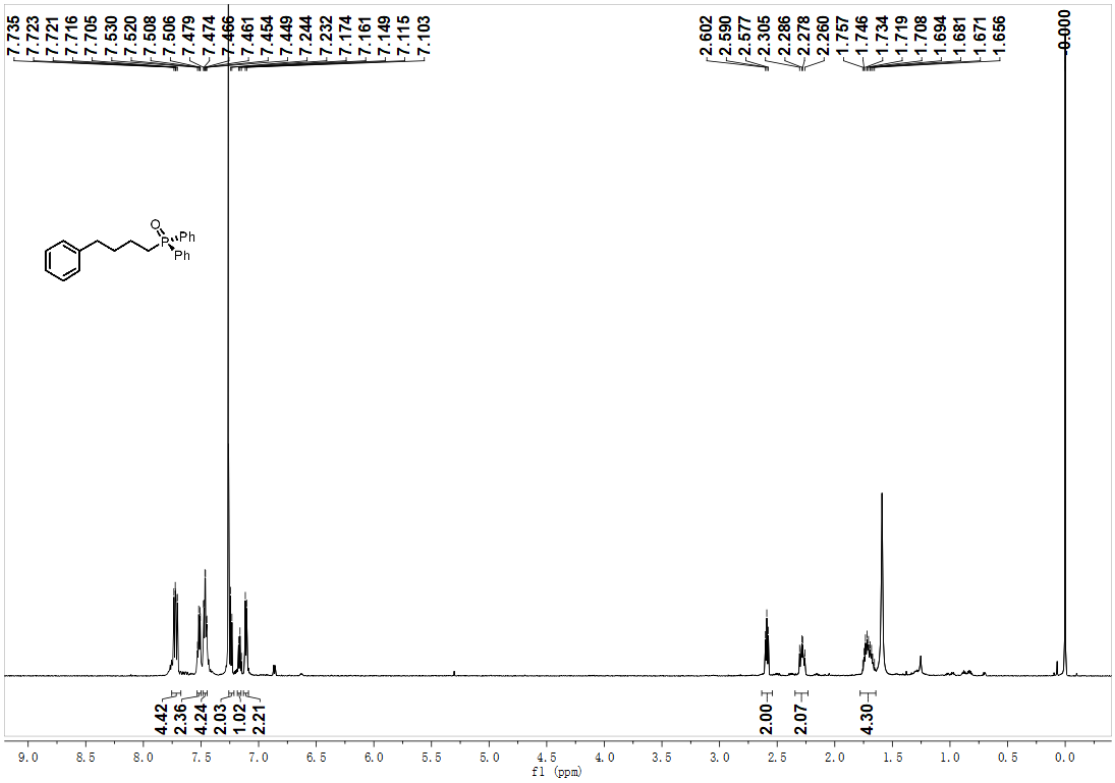
13; ^{1}H NMR (600 MHz, $CDCl_3$);



13; ^{31}P NMR (242.9 MHz, $CDCl_3$)



14; ^{1}H NMR (600 MHz, $CDCl_3$);



14; ^{31}P NMR (242.9 MHz, $CDCl_3$)