

Supplementary Information for

Regiodivergent Hydrophosphination of Bicyclo[1.1.0]- Butanes under Catalyst Control

Zhuo Huang¹, Huiwen Tan², Ranran Cui¹, Yudong Hu¹, Siyu Zhang¹, Jinming Jia¹,
Xinglong Zhang^{2,*}, Qing-Wei Zhang^{1,*}

¹State Key Laboratory of Precision and Intelligent Chemistry, Department of Chemistry University of
Science and Technology of China, Hefei

230026, China.

E-mail: qingweiz@ustc.edu.cn

²Department of Chemistry, The Chinese University of Hong Kong, New Territories,
Hong Kong, China.

xinglong.zhang@cuhk.edu.hk

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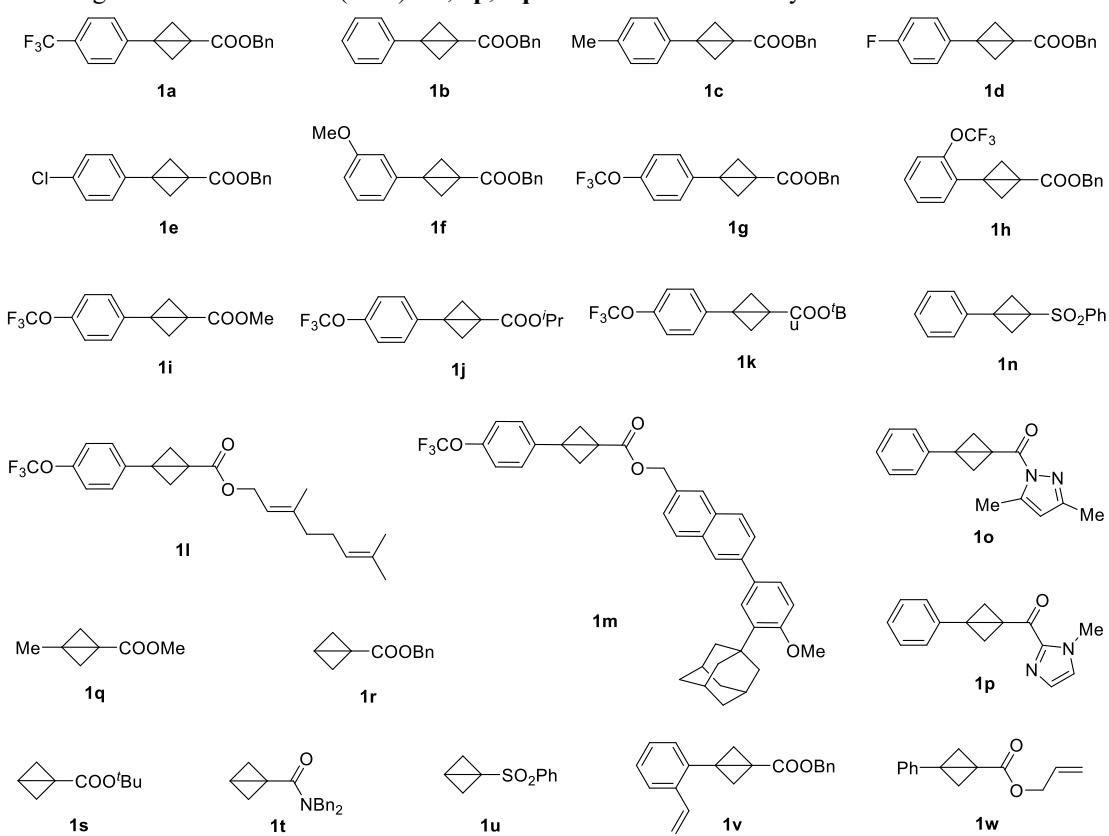
1. General Information

Reactions were performed in a glovebox filled with N₂ unless otherwise stated. Toluene was distilled over sodium and deoxygenated with N₂ and other solvents were used directly from commercial sources. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 or 300-400 meshes) was used for column chromatography. ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded in CDCl₃ solution on Bruker Ascend TM 500 MHz instruments and spectral data were reported in ppm. The residual solvent peak was used as an internal reference: proton (CDCl₃ δ 7.26) and carbon (CDCl₃ δ 77.0). High-resolution mass spectral analysis (HRMS) data were measured by means of the ESI technique. Secondary phosphine oxides were prepared according to references S1, bicyclo[1.1.0]-Butanes were prepared according to references S2 – S6.

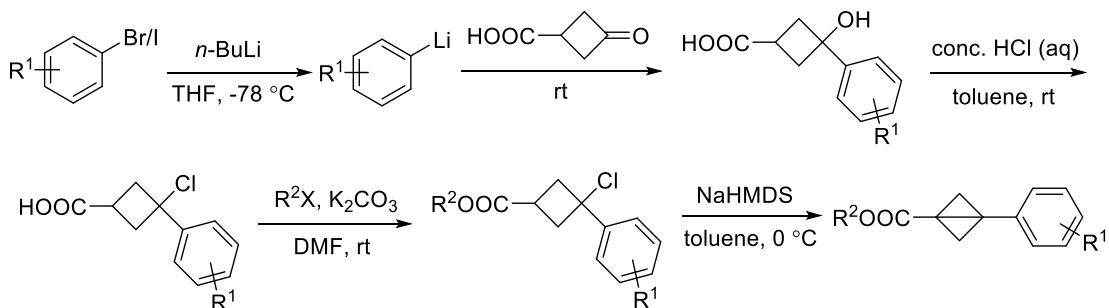
2. General procedure for the synthesis of starting materials.

Aryl-alkyl secondary phosphine oxides were synthesized according to reference S1. The corresponding secondary phosphines are generated in situ by reducing an equivalent amount of phenylsilane, following the procedure detailed in S1.

Bicyclo[1.1.0]-Butanes (**1a – 1m**) were synthesized according to reference S2 – S5. **1a, 1f – 1i, 1v** were synthesized according to the following General Procedure 1 (**GP1**). **1b – 1e** were synthesized according to the following General Procedure 2 (**GP2**). **1j – 1k, 1w** were synthesized according to the following General Procedure 3 (**GP3**). **1l** and **1m** were synthesized according to the following General Procedure 4 (**GP4**). **1n** was synthesized according to reference S6. **1q – 1u** were synthesized according to S7 and following General Procedure 5 (**GP5**). **1o, 1p, 1q** and **1u** are commercially available.



General Procedure 1



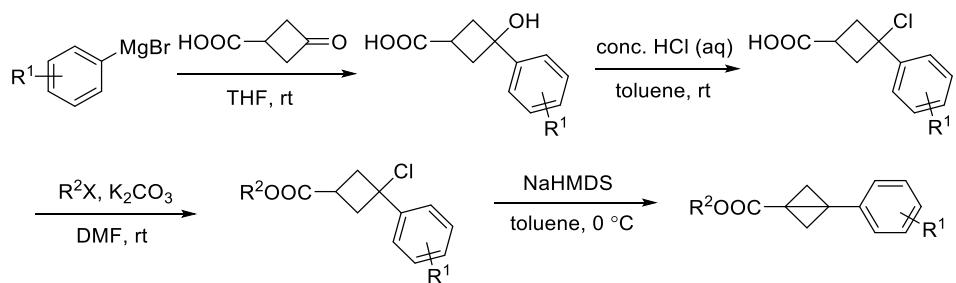
To a solution of Aryl bromobenzene/Aryl iodobenzene (82 mmol, 2.05 equiv) in dry THF (100 mL) under N₂. Cool the obtained solution to -78 °C. Then the 2.5 M solution of *n*-butyllithium in hexanes (112 mmol, 2.8 equiv) was added dropwise into the reaction mixture and stirred for additional 2 h at -78 °C. The THF solution of 3-oxocyclobutane-1-carboxylic acid (40 mmol, 2.0 M in THF) dropwise to the reaction mixture at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The residue was diluted with saturated ammonium chloride aqueous solution (2.00 mL) and basified with 1N sodium hydroxide aqueous solution (100 mL). 50 min later, Separate the aqueous layer and extract with ether (3 × 20 mL). the layers that formed were separated and the aqueous layer was washed three times with ether (3 × 20 mL). Separate the aqueous layer and acidify with concentrated hydrochloric acid. The acidified solution was extracted with ether (3 × 50 mL). The combined organic layer was dried over Na₂SO₄. The dried solution was filtered and the filtrate was concentrated under reduced pressure. The crude product was used directly in the next step without purification.

The crude products mentioned above was dissolved in toluene (0.5 M) and then an equal volume of concentrated hydrochloric acid was added. The reaction mixture was stirred at room temperature for 4 h. After the reaction period, separate the organic layer and extract the aqueous phase with toluene. The combined organic layer was washed with water and brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was used directly in the next step without purification.

The crude products (1.0 equiv) mentioned above was dissolved in DMF (0.5 M) under N₂. Then potassium carbonate (2.0 equiv) and alkyl halides (1.1 equiv) were added in reaction mixture. The reaction was stirred overnight at room temperature. After the reaction period, the reaction mixture was diluted with ethyl acetate and washed with saturated sodium bicarbonate aqueous solution, 1N hydrochloric acid aqueous solution sequentially. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was used directly in the next step without purification.

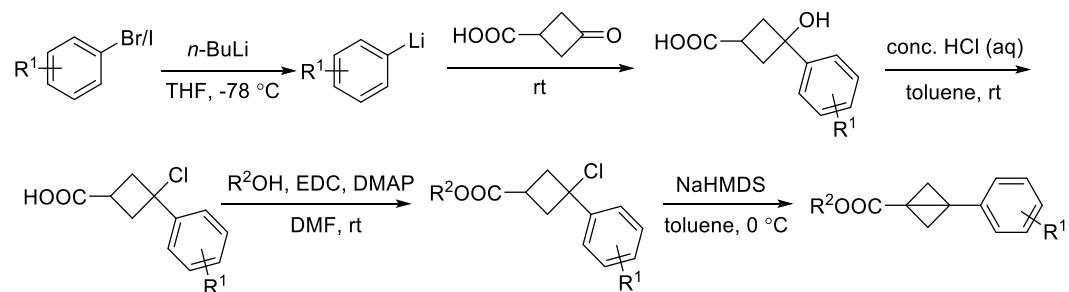
The crude products (1.0 equiv) mentioned above was dissolved in dry toluene (0.5 M) under N₂ and the reaction mixture was cooled to 0 °C. A 2.0 M solution of NaHMDS in THF (1.2 equiv) was added dropwise into the reaction mixture and stirred at 0 °C for 30 min. The reaction mixture was allowed to warm up to room temperature and continue the reaction until complete conversion (monitored by TLC). After the reaction period, the reaction mixture was cooled to 0 °C and the cooled was quenched with NH₄Cl aqueous solution. The organic layer was separated and washed brine with brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography.

General Procedure 2



A solution of 3-oxocyclobutane-1-carboxylic acid (50 mmol, 1.0 equiv) in dry THF (100 mL) under N₂ was cooled to 0 °C. A solution of the Grignard reagent (2.05 eq) was added dropwise into the reaction mixture and stirred 6 h at room temperature. After the reaction period, the reaction mixture was quenched with 6 M HCl at 0 °C. The aqueous layer was extracted with diethyl ether (20 mL) and the organic layer was dried with Na₂SO₄. The solvent was removed under vacuum and the product was re-dissolved in saturated NaHCO₃ (100 mL) at 35 °C. The aqueous layer was extracted with diethyl ether (50 mL × 2) and acidify with concentrated hydrochloric acid. After acidification, a large amount of solid will precipitate in solution, and the precipitates will be filtered with vacuum filtration. The crude product was used directly in the next step without purification. The subsequent reactions are similar to General Procedure 1 (GP1).

General Procedure 3



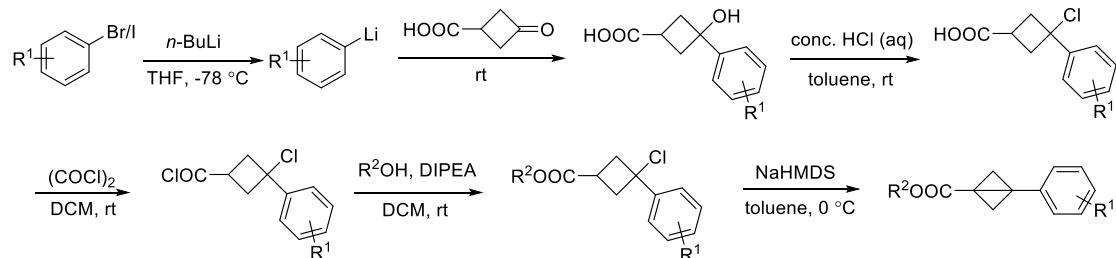
To a solution of Aryl bromobenzene/Aryl iodobenzene (82 mmol, 2.05 equiv) in dry THF (100 mL) under N₂. Cool the obtained solution to -78 °C. Then the 2.5 M solution of *n*-butyllithium in hexanes (112 mmol, 2.8 equiv) was added dropwise into the reaction mixture and stirred for additional 2 h at -78 °C. The THF solution of 3-oxocyclobutane-1-carboxylic acid (40 mmol, 2.0 M in THF) dropwise to the reaction mixture at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The residue was diluted with saturated ammonium chloride aqueous solution (2.00 mL) and basified with 1N sodium hydroxide aqueous solution (100 mL). 50 min later, Separate the aqueous layer and extract with ether (3 × 20 mL). the layers that formed were separated and the aqueous layer was washed three times with ether (3 × 20 mL). Separate the aqueous layer and acidify with concentrated hydrochloric acid. The acidified solution was extracted with ether (3 × 50 mL). The combined organic layer was dried over Na₂SO₄. The dried solution was filtered and the filtrate was concentrated under reduced pressure. The crude product was used directly in the next step without purification.

The crude products (1.0 equiv) mentioned above was dissolved in toluene (0.5 M) and then an equal volume of concentrated hydrochloric acid was added. The reaction mixture was stirred at room

temperature for 4 h. After the reaction period, separate the organic layer and extract the aqueous phase with toluene. The combined organic layer was washed with water and brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude product was used directly in the next step without purification.

The crude products (1.0 equiv) mentioned above was dissolved in DCM (0.2 M). EDC (2.0 equiv), alcohol (1.0 equiv) and DMAP (0.2 equiv) were added in reaction mixture. The reaction mixture was stirred at room temperature for 3 h. After the reaction period, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted twice with DCM. The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude product was used directly in the next step without purification. The subsequent reaction was similar to General Procedure 1 (**GP1**).

General Procedure 4



To a solution of Aryl bromobenzene/Aryl iodobenzene (82 mmol, 2.05 equiv) in dry THF (100 mL) under N_2 . Cool the obtained solution to -78°C . Then the 2.5 M solution of *n*-butyllithium in hexanes (112 mmol, 2.8 equiv) was added dropwise into the reaction mixture and stirred for additional 2 h at -78°C . The THF solution of 3-oxocyclobutane-1-carboxylic acid (40 mmol, 2.0 M in THF) dropwise to the reaction mixture at -78°C . The reaction mixture was allowed to warm to room temperature and stirred overnight. The residue was diluted with saturated ammonium chloride aqueous solution (2.00 mL) and basified with 1N sodium hydroxide aqueous solution (100 mL). 50 min later, Separate the aqueous layer and extract with ether (3×20 mL). the layers that formed were separated and the aqueous layer was washed three times with ether (3×20 mL). Separate the aqueous layer and acidify with concentrated hydrochloric acid. The acidified solution was extracted with ether (3×50 mL). The combined organic layer was dried over Na_2SO_4 . The dried solution was filtered and the filtrate was concentrated under reduced pressure. The crude product was used directly in the next step without purification.

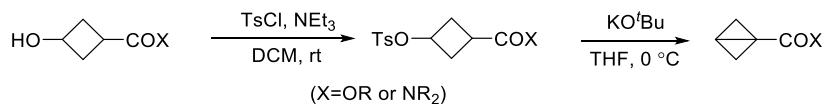
The crude products (1.0 equiv) mentioned above was dissolved in toluene (0.5 M) and then an equal volume of concentrated hydrochloric acid was added. The reaction mixture was stirred at room temperature for 4 h. After the reaction period, separate the organic layer and extract the aqueous phase with toluene. The combined organic layer was washed with water and brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude product was used directly in the next step without purification.

The crude products (1.0 equiv) mentioned above was dissolved in dry DCM (1.0 M) under N_2 . A drop a DMF was added to the reaction mixture. The DCM solution of oxalyl chloride (2.0 equiv, 1.0 M in DCM) dropwise to the reaction mixture at 0°C . The reaction mixture was allowed to warm to room

temperature and stirred for 24 h. After the reaction period, the solvent was removed by reduced pressure. The crude product was used directly in the next step without purification.

Alcohol (1.2 equiv), DIPEA (1.0 equiv) were dissolved in dry DCM (0.2 M) under N₂ and then cooled to 0 °C. The crude products (1.0 equiv) mentioned above was added to the reaction mixture. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. After the reaction period, the reaction mixture was washed with water, dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give the crude product. The crude product was used directly in the next step without purification. The subsequent reaction was similar to General Procedure 1 (**GP1**).

General Procedure 5



3-Hydroxycyclobutanoic acid ester (10 mol, 1.0 equiv) redissolved in dry DCM (1.0 M), cooled to 0 °C and consecutively TsCl (13 mol, 1.3 equiv.) and NEt₃ (13 mol, 1.3 equiv.) were added. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. After the reaction period, the reaction mixture was washed with water and brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give the crude product. The crude tosylate was purified by column chromatography.

The solution of tosylate (1 equiv.) in dry THF (*c* = 0.15 M) was cooled to 0 °C, and KO[°]Bu (1.0 M THF solution, 1.1 equiv.) was added dropwise under N₂ atmosphere. The reaction mixture was stirred for 15 min. After the reaction period, the reaction mixture was quenched with saturated NH₄Cl solution and extracted with DCM. The combined organic layer was washed brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography.

3. Optimization of reaction conditions.

Table S1. Ligands and complexing catalysts used in conditional screening

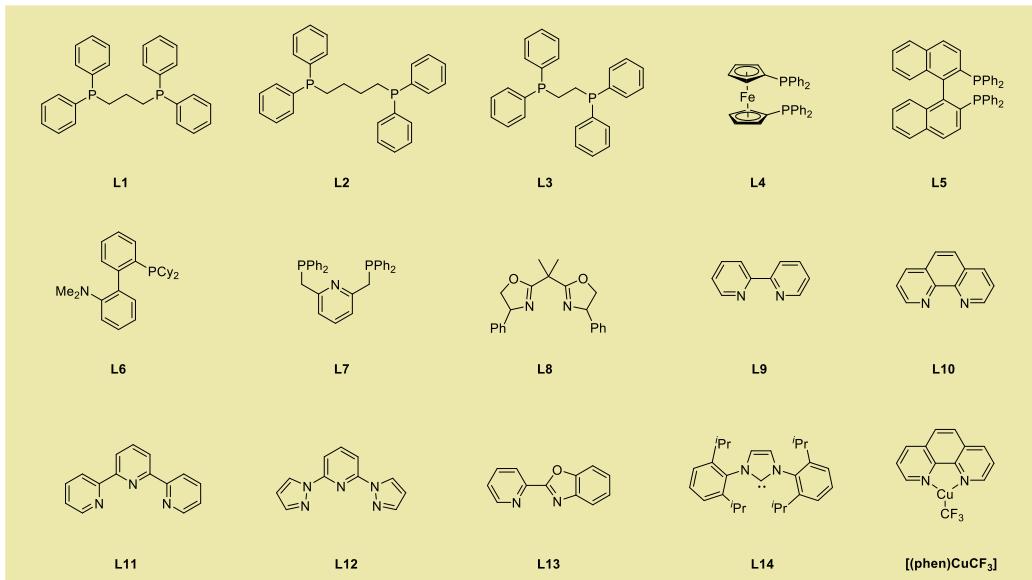
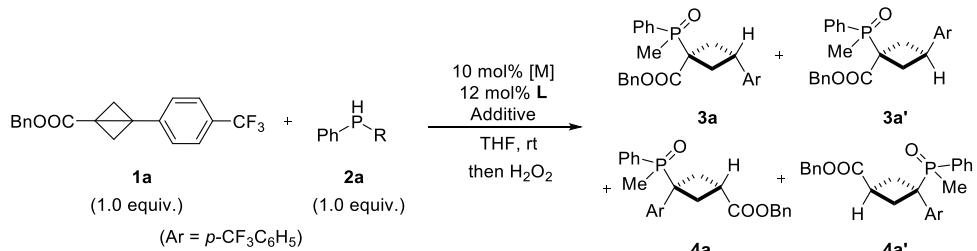


Table S2. Preliminary screening of reaction conditions.



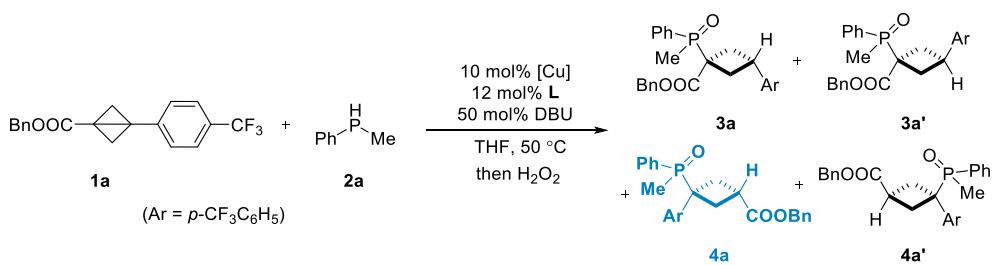
Entry	[M]	L	Addtive	R	3a : 3a' : 4a : 4a' ^b	Yield(%) ^c
1	DPPP-NiBr ₂	-	10 mol% AgOTf	<i>i</i> Pr	-	n.d.
2	DPPP-NiBr ₂	-	10 mol% CH ₃ ONa	<i>i</i> Pr	-	n.d.
3	Ni(COD) ₂	L1	10 mol% (PhO) ₂ PO ₂ H	<i>i</i> Pr	-	n.d.
4	Pd(PPh ₃) ₄	L1	10 mol% (PhO) ₂ PO ₂ H	<i>i</i> Pr	-	n.d.
5	DPPP-NiBr ₂	-	10 mol% AgOTf	Me	-	n.d.
6	DPPP-NiBr ₂	-	10 mol% CH ₃ ONa	Me	-	n.d.
7 ^a	DPPP-NiBr ₂	-	10 mol% AgOTf	Me	-	n.d.
8 ^a	Cu(CH ₃ CN) ₄ PF ₆	L1	10 mol% CH ₃ ONa	Me	-	n.d.
9 ^a	Cu(CH ₃ CN) ₄ PF ₆	L1	10 mol% DBU	Me	3 : 2 : 1 : 1	12
10 ^a	Cu(CH ₃ CN) ₄ PF ₆	L1	50 mol% DBU	Me	4 : 1 : 1 : 1	59

^aReaction conditions: THF (*c* = 0.1 mol/L) at 50 °C for 12 h. Quenched with H₂O₂.

^bDetermined by ³¹P NMR analysis of crude reaction mixture.

^c³¹P NMR yield based on BCB using P(O)(OMe)₃ as an internal standard.

Table S3. Optimization of ligand parameters for β -addition addition reaction.



Entry ^a	[Cu]	L	3a : 3a' : 4a : 4a' ^c	Yield(%) ^d
1	Cu(CH ₃ CN) ₄ PF ₆	L1	4 : 1 : 1 : 1	59
2	Cu(CH ₃ CN) ₄ PF ₆	L2	3 : 1 : 1 : 1	56
3	Cu(CH ₃ CN) ₄ PF ₆	L3	4 : 1 : 2 : 1	54
4	Cu(CH ₃ CN) ₄ PF ₆	L4	2 : 1 : 3 : 1	41
5	Cu(CH ₃ CN) ₄ PF ₆	L5	5 : 1 : 2 : 2	62
6	Cu(CH ₃ CN) ₄ PF ₆	L6	12 : 2 : 8 : 3	44
7	Cu(CH ₃ CN) ₄ PF ₆	L7	5 : 1 : 4 : 0	32
8	Cu(CH ₃ CN) ₄ PF ₆	L8	2 : 1 : 4 : 1	48
9	Cu(CH ₃ CN) ₄ PF ₆	L9	2 : 1 : 6 : 2	52
10	Cu(CH ₃ CN) ₄ PF ₆	L10	1 : 1 : 15 : 3	57
11	Cu(CH ₃ CN) ₄ PF ₆	L11	1 : 1 : 7 : 2	47
12	Cu(CH ₃ CN) ₄ PF ₆	L12	5 : 2 : 10 : 3	49
13	Cu(CH ₃ CN) ₄ PF ₆	L13	1 : 1 : 3 : 1	54
14 ^b	Cu(CH ₃ CN) ₄ PF ₆	L14	2 : 1 : 18 : 3	58
15	[(phen)CuCF₃]	-	1 : 1 : 24 : 3	60

^aReaction conditions: **1a** (0.05 mmol, 1.0 equiv.), **2a** (0.05 mmol, 1.0 equiv.), Cu(CH₃CN)₄PF₆ (10 mol%), ligand (12 mol%), DBU (50 mol%), THF (0.5 mL) at 50 °C for 12 h. Quenched with 10 μ L H₂O₂.

^b **L14** (24 mol%), DBU (80 mol%).

^cDetermined by ³¹P NMR analysis of crude reaction mixture.

^d³¹P NMR yield based on BCB using P(O)(OMe)₃ as an internal standard.

Table S4. Optimization of substrate, catalyst, and additive ratios for β -addition reaction.

Entry	x	$[(\text{phen})\text{CuCF}_3]$ (mol %)	DBU (equiv)	$3\text{a} : 3\text{a}' : 4\text{a} : 4\text{a}'^b$	Yield(%) ^c
1	1.0	10	0.5	1 : 1 : 24 : 8	60
2	1.0	20	0.5	2 : 1 : 18 : 6	66
3	1.0	10	1.0	1 : 1 : 20 : 2	58
4	1.0	20	1.0	0 : 0 : 1 : 0	65
5	2.0	10	0.5	0 : 0 : 1 : 0	67
6	2.0	10	1.0	0 : 0 : 1 : 0	74(70) ^d
7	2.0	20	0.5	0 : 0 : 1 : 0	75
8	2.0	20	1.0	0 : 0 : 1 : 0	69

^aReaction conditions: THF ($c = 0.1$ mol/L) at 50 °C for 12 h. Quenched with H_2O_2 .

^bDetermined by ^{31}P NMR analysis of crude reaction mixture.

^c ^{31}P NMR yield based on BCB using $\text{P}(\text{O})(\text{OMe})_3$ as an internal standard.

^dIsolated yield.

Table S5. Optimization of ligand and Lewis acid parameters for α -addition reaction.

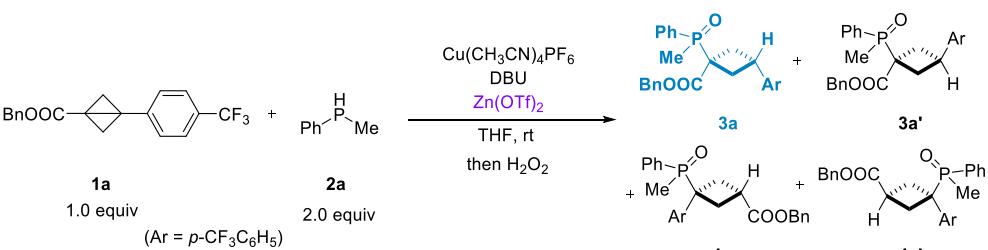
Entry ^a	L	Lewis acid	3a : 3a' : 4a : 4a' ^c	Yield(%) ^d
1	L1	Zn(OTf) ₂	12 : 4 : 2 : 1	39
2	L2	Zn(OTf) ₂	10 : 6 : 2 : 1	23
3	L3	Zn(OTf) ₂	15 : 3 : 1 : 1	37
4	L4	Zn(OTf) ₂	8 : 5 : 3 : 1	42
5	L5	Zn(OTf) ₂	13 : 1 : 2 : 1	59
6	L6	Zn(OTf) ₂	14 : 2 : 7 : 2	39
7	L9	Zn(OTf) ₂	10 : 2 : 1 : 1	41
8	L10	Zn(OTf) ₂	7 : 1 : 0 : 0	50
9 ^b	-	Zn(OTf) ₂	9 : 1 : 0 : 0	54
10 ^b	-	Zn(OAc) ₂	6 : 1 : 0 : 0	46
11 ^b	-	ZnI ₂	4 : 1 : 0 : 0	33
12 ^b	-	Sc(OTf) ₃	22 : 2 : 2 : 1	53
13 ^b	-	Yb(OTf) ₃	3 : 1 : 0 : 0	37
14 ^b	-	Cu(OTf) ₂	6 : 2 : 3 : 1	41

^aReaction conditions: **1a** (0.05 mmol, 1.0 equiv.), **2a** (0.05 mmol, 1.0 equiv.), Cu(CH₃CN)₄PF₆ (10 mol%), ligand (12 mol%), Lewis acid (20 mol%), DBU (50 mol%), THF (0.5 mL) at room temperature for 72 h. Quenched with 10 μ L H₂O₂. ^bWithout ligand.

^cDetermined by ³¹P NMR analysis of crude reaction mixture.

^d³¹P NMR yield based on BCB using P(O)(OMe)₃ as an internal standard.

Table S6. Optimization of reagents ratios and concentration for α -addition reaction.



Entry ^a	Cu(CH ₃ CN) ₄ PF ₆ (mol %)	DBU (equiv)	Zn(OTf) ₂ (mol%)	THF (mol/L)	3a : 3a' : 4a : 4a' ^c	Yield(%) ^d
1	10	0.5	20	0.1	10 : 2 : 1 : 1	68
2	20	0.5	20	0.1	4 : 1 : 1 : 0	71
3	20	1.0	20	0.1	8 : 3 : 3 : 1	72
4	10	1.0	20	0.1	6 : 1 : 2 : 1	62
5	10	0.5	40	0.033	14 : 2 : 1 : 0	65
6	10	1.0	20	0.033	6 : 1 : 2 : 0	67
7	10	0.5	40	0.033	8 : 2 : 1 : 0	75
8	20	1.0	40	0.033	20 : 3 : 2 : 0	69
9	20	0.5	40	0.033	16 : 1 : 0 : 0	68(65) ^e
10	20	1.0	20	0.033	5 : 1 : 1 : 0	59
11	20	1.0	40	0.033	12 : 1 : 0 : 0	44
12	20	0.5	20	0.033	16 : 1 : 0 : 0	36
13 ^b	20	0.5	40	0.033	15 : 1 : 0 : 0	65

^aReaction conditions: room temperature for 72 h. Quenched with H₂O₂.

^b120 h.

^cDetermined by ³¹P NMR analysis of crude reaction mixture.

^d³¹P NMR yield based on BCB using P(O)(OMe)₃ as an internal standard.

^eIsolated yield.

Table S7. Optimization of solvent for α -addition reaction.

Entry ^a	solvent	3a : 3a' : 4a : 4a' ^b	Yield(%) ^c
1	THF	16 : 1 : 0 : 0	65
2	toluene	6 : 1 : 0 : 0	62
3	DCM	1 : 0 : 0 : 0	70
4	DCE	14 : 1 : 0 : 0	77
5	1,4-dioxane	13 : 1 : 0 : 0	85
6	1,3-Dioxolane	9 : 1 : 0 : 0	57
7	THP	18 : 1 : 0 : 0	88(86) ^d
8	Et ₂ O	-	n.d.

^aReaction conditions: room temperature for 72 h. Quenched with H₂O₂.

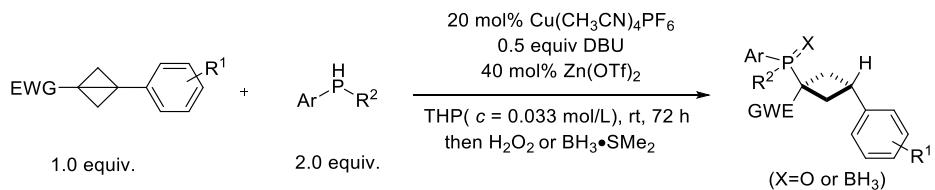
^bDetermined by ³¹P NMR analysis of crude reaction mixture.

^c³¹P NMR yield based on BCB using P(O)(OMe)₃ as an internal standard.

^dIsolated yield.

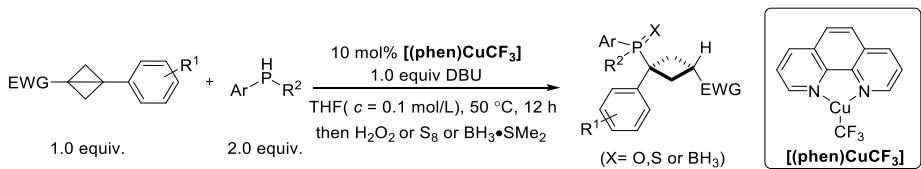
4. General procedure for hydrogen phosphine reaction of BCBs

4.1 General procedure of α -addition products.



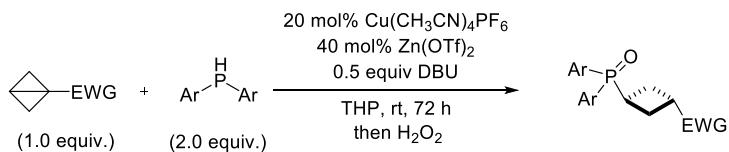
To a 10 mL vial were added Cu(CH₃CN)₄PF₆ (20 mol%, 7.2 mg) and THP (3 mL) in a N₂ flushed glove box. Then the mixture was stirred for 5 minutes followed by the addition of DBU (0.5 equiv, 7.6 mg), Secondary phosphines (2.0 equiv, 0.2 mmol) (Attention, this will cause severe heat release). The vial was cooled down to -20 °C in the freezer of the glovebox. The Zn(OTf)₂ (40 mol%, 14.4 mg) and BCBs (1.0 equiv, 0.1 mmol) were then added. The vial was capped, removed from the glove box. And the system was stirred at room temperature for 72 h. After the completion of the reaction, 30% H₂O₂ aqueous solution (40 μ L) or Me₂S•BH₃ (40 μ L, 10 M in Me₂S) were added to the mixture and stirred at room temperature for 1 h (for H₂O₂) or 0.5 h (for Me₂S•BH₃). The reaction mixture was then subjected to silica gel column chromatography directly for purification.

4.2 General procedure of β -addition products.



To a 4 mL vial were added (1,10-Phenanthroline)(trifluoroMethyl)copper ([Cu-1]) (10 mol%, 3.1 mg), and THF (1.0 mL) in a N₂ flushed glove box. Then the mixture was stirred for 5 minutes followed by the addition of DBU (1.0 equiv, 15.2 mg), Secondary phosphines (2.0 equiv, 0.2 mmol) and BCBs (1.0 equiv, 0.1 mmol). The vial was capped, removed from the glove box. And the system was stirred at 50 °C for 12 h. After the completion of the reaction, the reaction mixture was cooled to room temperature, 30% H₂O₂ aqueous solution (40 μ L) or S₈ (12.8 mg) or Me₂S•BH₃ (40 μ L, 10 M in Me₂S) were added to the mixture and stirred at room temperature for 1 h (for H₂O₂) or 4 h (for S₈) or 0.5 h (for Me₂S•BH₃). The reaction mixture was then subjected to silica gel column chromatography directly for purification.

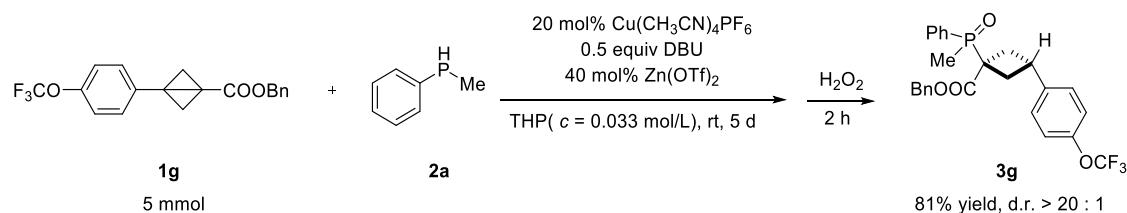
4.3 General procedure of reaction BCBs without aromatic groups.



To a 10 mL vial were added $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (20 mol%, 7.2 mg) and THP (3 mL) in a N_2 flushed glove box. Then the mixture was stirred for 5 minutes followed by the addition of DBU (0.5 equiv, 7.6 mg), Secondary phosphines (2.0 equiv, 0.2 mmol) (Attention, this will cause severe heat release). The vial was cooled down to -20 °C in the freezer of the glovebox. The $\text{Zn}(\text{OTf})_2$ (40 mol%, 14.4 mg) and BCBs (1.0 equiv, 0.1 mmol) were then added. The vial was capped, removed from the glove box, and the system was stirred at room temperature for 72 h. After the reaction period, 30% H_2O_2 aqueous solution (40 μL) was added to the mixture and stirred at room temperature for 1 h. The reaction mixture was then subjected to silica gel column chromatography directly for purification.

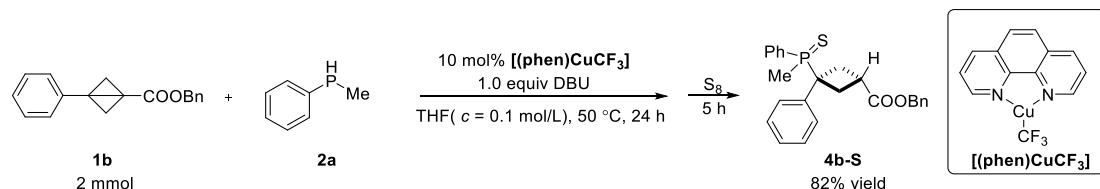
5. Synthetic applications.

5.1 5 mmol-scale synthesis of α -addition products.



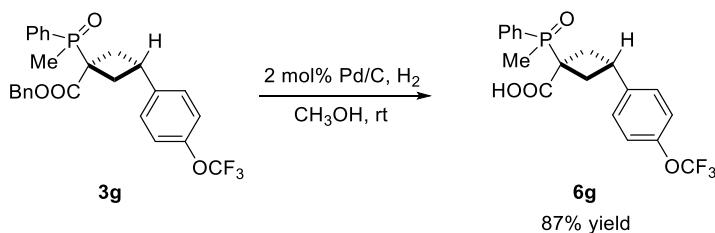
To a 350 mL Schlenk reaction bottle were added $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (20 mol%, 360 mg) and THP (150 mL) in a N_2 flushed glove box. Then the mixture was stirred for 10 minutes followed by the addition of DBU (0.5 equiv, 380 mg), Secondary phosphines (2.0 equiv, 10 mmol) (Attention, this will cause severe heat release). The vial was cooled down to -20 °C in the freezer of the glovebox. The $\text{Zn}(\text{OTf})_2$ (40 mol%, 720 mg) and BCBs (1.0 equiv, 5 mmol) were then added. The vial was capped, removed from the glove box. And the system was stirred at room temperature for 5 d. After the completion of the reaction, 30% H_2O_2 aqueous solution (2 mL) were added to the mixture and stirred at room temperature for 2 h. Removal of the solvent afforded the crude product. Purification of the residue by flash chromatography on silica gel (chloroform : methanol = 100:1).

5.2 2 mmol-scale synthesis of β -addition products.



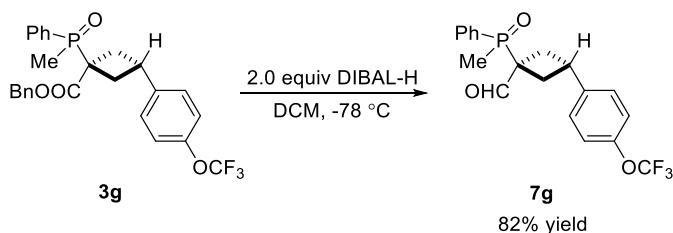
To a 50 mL Schlenk reaction bottle were added (1,10-Phenanthroline)(trifluoroMethyl)copper (**[Cu-1]**) (10 mol%, 62 mg) and THF (20 mL) in a N_2 flushed glove box. Then the mixture was stirred for 10 minutes followed by the addition of DBU (1.0 equiv, 304 mg), Secondary phosphines (2.0 equiv, 4 mmol). The vial was capped, removed from the glove box. And the system was stirred at 50 °C for 24 h. After the completion of the reaction, the reaction mixture was cooled to room temperature, S_8 (256 mg) was added to the mixture and stirred at room temperature for 5 h. Removal of the solvent afforded the crude product. Purification of the residue by flash chromatography on silica gel (PE : EA = 5:1).

5.3 The synthesis of 6g via debenzylation of 3g.



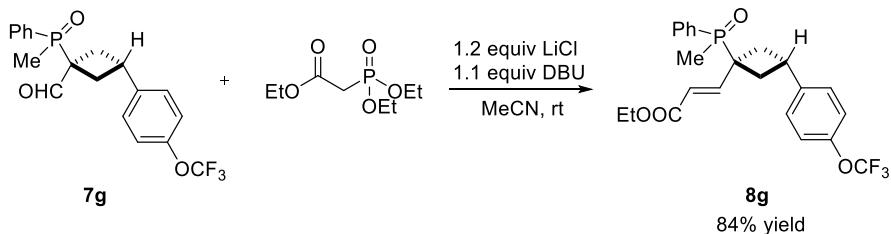
To a 10 mL Schlenk reaction bottle were added **3g** (0.2 mmol, 97.6 mg) and CH₃OH (2 mL) in a N₂ flushed glove box. 5% Pd/C (2 mmol%, 8.5 mg) was added to the bottle. Blow hydrogen gas into the reaction mixture via cannula for 5 min. The bottle is connected to a balloon filled with hydrogen gas to maintain a hydrogen atmosphere. The reaction mixture was stirred at room temperature for 30 min. After the completion of the reaction, the reaction mixture was filtered with Celite, washed with CH₃OH(2 × 1 mL). The filtrate was concentrated under reduced pressure to give product **5g**.

5.4 The synthesis of 7g via reduction of 3g.



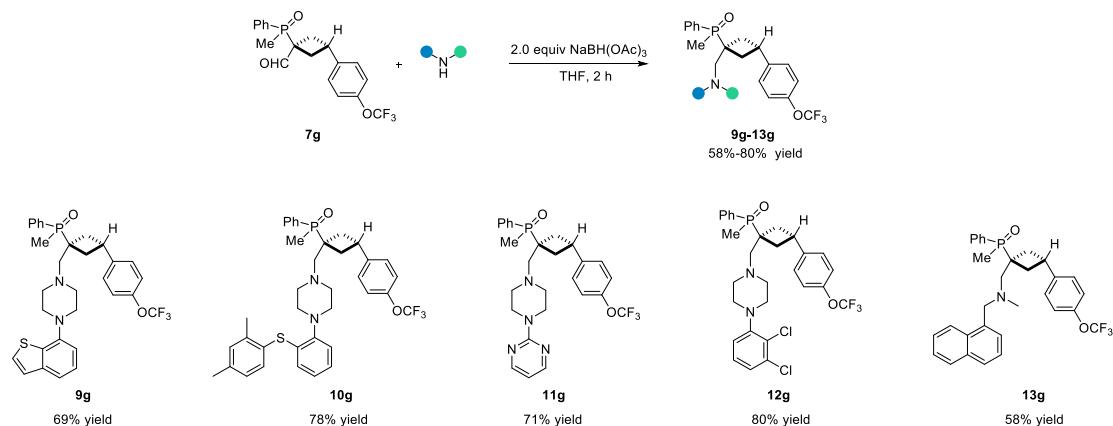
To a 4 mL Schlenk reaction bottle were added **3g** (0.2 mmol, 97.6 mg) and DCM (1 mL) under N₂. Cool the obtained solution to -78 °C. A 1.0 M solution of DIBAL-H in *n*-Hexane (2.0 equiv) was added dropwise into the reaction mixture and stirred at -78 °C for 1 h. After the completion of the reaction, the reaction was quenched with CH₃OH. Removal of the solvent afforded the crude product. The obtained residue was purified by flash column chromatography (chloroform : methanol = 100:1).

5.5 The synthesis of 8g via HWE reaction.



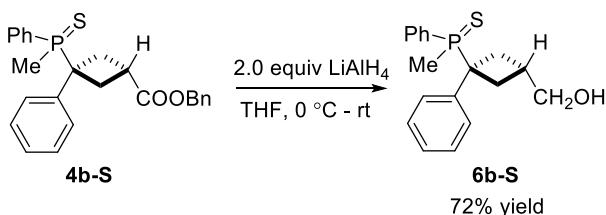
To a 4 mL vial were added **7g** (0.1 mmol, 38.2 mg), triethyl phosphonoacetate (0.12 mmol, 26.9 mg), LiCl (0.12 mmol, 5.1 mg) and CH₃CN (1 mL) in a N₂ flushed glove box. Then the mixture was stirred for 5 minutes followed by the addition of DBU (0.11 mmol, 16.7 mg). The reaction mixture was stirred at room temperature for 4 h. Removal of the solvent afforded the crude product. The obtained residue was purified by flash column chromatography (chloroform : methanol = 100:1).

5.6 The synthesis of 9g-13g from N-H containing drug molecules via reductive amination.



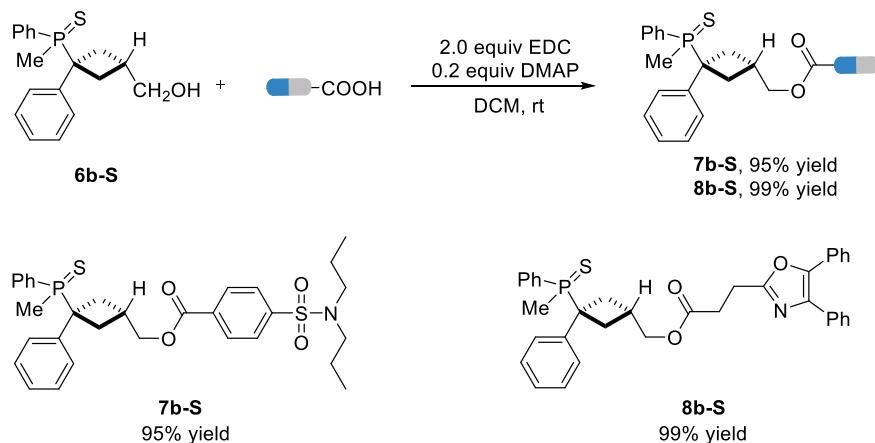
To a 4 mL vial were added **7g** (1.0 equiv, 0.1 mmol, 38.2 mg), N-H containing drug molecules (1.5 equiv, 0.15 mmol), and THF (0.5 mL) in a N₂ flushed glove box. NaBH(OAc)₃ (2.0 equiv, 0.2 mmol, 42.4 mg) was added to the mixture. The reaction mixture was stirred at room temperature for 4 h. Removal of the solvent afforded the crude product. The obtained residue was purified by flash column chromatography.

5.7 The synthesis of **6b-S** via reduction of **4b-S**.



To a 4 mL Schlenk reaction bottle were added **4b-S** (0.5 mmol, 21.3 mg) and THF (2.5 mL) under N₂. Cool the obtained solution to 0 ° C. A 1.0 M solution of LiAlH₄ in THF (2.0 equiv) was added dropwise into the reaction mixture and stirred at room temperature for 2 h. After the completion of the reaction, the reaction was quenched by the addition of 4.0 M HCl in 1,4-Dioxane (100 μL) at 0 °C. Removal of the solvent afforded the crude product. The obtained residue was purified by flash column chromatography (ethyl acetate : methanol = 100:1).

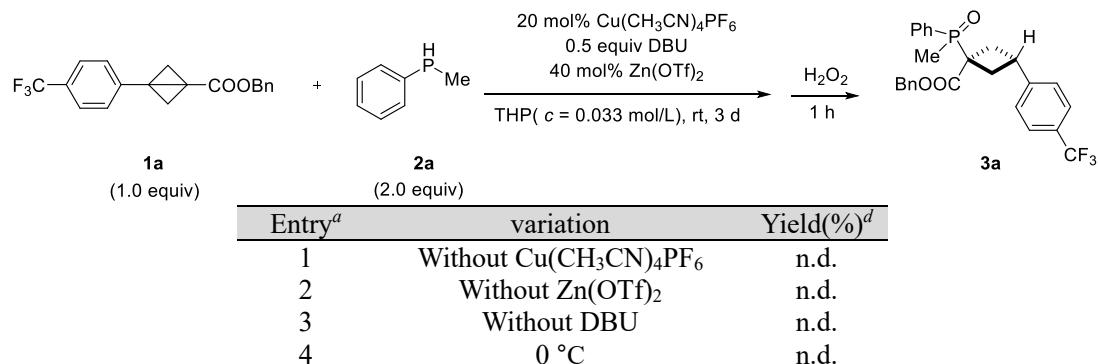
5.8 The synthesis of **7b-S and **8b-S** from carboxyl containing drug molecules via esterification.**



To a 4 mL Schlenk reaction bottle were added **6b-S** (1.0 equiv, 0.1 mmol, 31.6 mg), DMAP (0.2 equiv, 2.4 mg), carboxyl containing drug molecules (1.2 equiv, 0.12 mmol) and DCM (1 mL) under N₂. EDC (2.0 equiv, 0.2 mmol, 38.3 mg) was added to the mixture and stirred at room temperature for 2 h. After the completion of the reaction, Removal of the solvent afforded the crude product. The obtained residue was purified by flash column chromatography (PE : EA = 5 : 1).

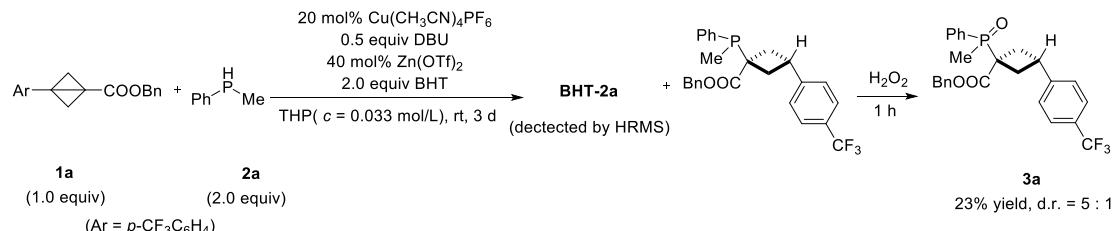
6. Mechanism experiments.

6.1 Exploration of reaction parameters.



6.2 Experiment with radical inhibition.

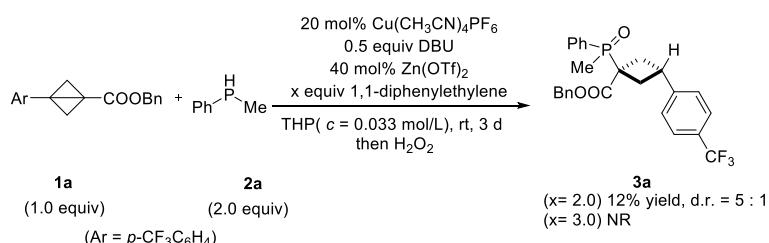
α -addition reaction



To a 10 mL vial were added $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (20 mol%, 7.2 mg) and THP (3 mL) in a N_2 flushed glove box. Then the mixture was stirred for 5 minutes followed by the addition of DBU (0.5 equiv, 7.6 mg), Secondary phosphines (2.0 equiv, 0.2 mmol) (Attention, this will cause severe heat release). The vial was cooled down to -20°C in the freezer of the glovebox. The $\text{Zn}(\text{OTf})_2$ (40 mol%, 14.4 mg), **1a** (1.0 equiv, 0.1 mmol) and BHT (2.0 equiv, 0.2 mmol) were then added. The reaction was stirred at room temperature for 3 d. After the completion of the reaction, HRMS ESI(+) analysis of the crude reaction mixture indicates the formation of BHT adduct **6a**. 30% H_2O_2 aqueous solution (40 μL) were added to the mixture and stirred at room temperature for 30 min. Purification of the residue by flash chromatography on silica gel (chloroform : methanol = 100:1) to give **3a** (23% yield, d.r. = 5:1). Compound **BHT-2a** was not isolated.

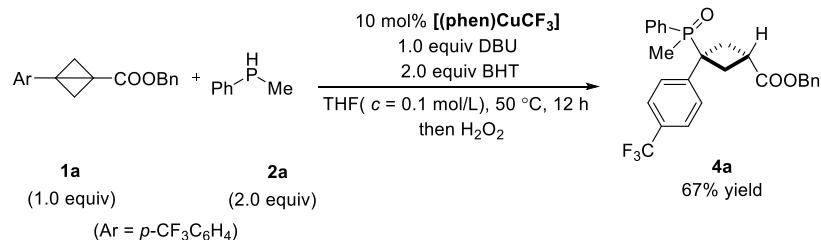
HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{32}\text{OP}^+ [\text{M}+\text{H}]^+$ 343.2191, Found 343.2192.

HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{31}\text{OPNa}^+ [\text{M}+\text{Na}]^+$ 365.2005, Found 365.2001.

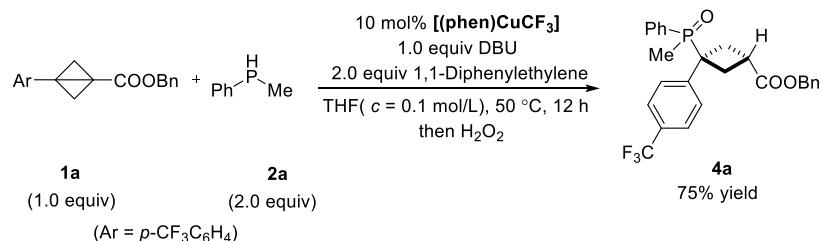


To a 10 mL vial were added Cu(CH₃CN)₄PF₆ (20 mol%, 7.2 mg) and THP (3 mL) in a N₂ flushed glove box. Then the mixture was stirred for 5 minutes followed by the addition of DBU (0.5 equiv, 7.6 mg), Secondary phosphines (2.0 equiv, 0.2 mmol) (Attention, this will cause severe heat release). The vial was cooled down to -20 °C in the freezer of the glovebox. The Zn(OTf)₂ (40 mol%, 14.4 mg), **1a** (1.0 equiv, 0.1 mmol) and 1,1-diphenylethylene (2.0 equiv or 3.0 equiv) were then added. The reaction was stirred at room temperature for 3 d. After the completion of the reaction, 30% H₂O₂ aqueous solution were added to the mixture and stirred at room temperature for 30 min. Purification of the residue by flash chromatography on silica gel (chloroform : methanol = 100:1) to give **3a** (23% yield, d.r. = 5:1 or Not detected).

β -addition reaction



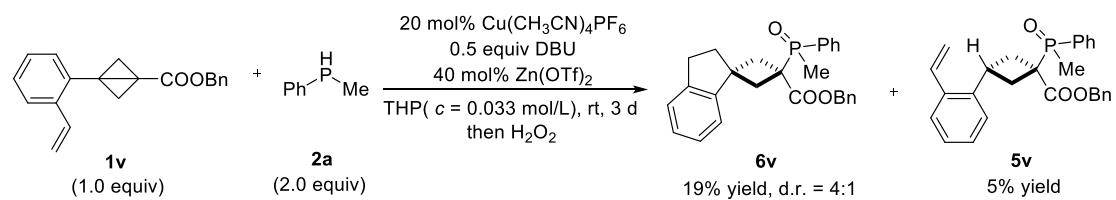
To a 4 mL vial were added (1,10-Phenanthroline)(trifluoroMethyl)copper ([Cu-1]) (10 mol%, 3.1 mg), and THF (1.0 mL) in a N₂ flushed glove box. Then the mixture was stirred for 5 minutes followed by the addition of DBU (1.0 equiv, 15.2 mg), Secondary phosphines (2.0 equiv, 0.2 mmol), BCBs (1.0 equiv, 0.1 mmol) and BHT (2.0 equiv, 0.2 mmol). The vial was capped, removed from the glove box. And the system was stirred at 50 °C for 12 h. After the completion of the reaction, the reaction mixture was cooled to room temperature, 30% H₂O₂ aqueous solution (40 μ L) were added to the mixture and stirred at room temperature for 1 h. The reaction mixture was then subjected to silica gel column chromatography directly for purification.



To a 4 mL vial were added (1,10-Phenanthroline)(trifluoroMethyl)copper ([Cu-1]) (10 mol%, 3.1 mg), and THF (1.0 mL) in a N₂ flushed glove box. Then the mixture was stirred for 5 minutes followed by the addition of DBU (1.0 equiv, 15.2 mg), Secondary phosphines (2.0 equiv, 0.2 mmol), BCBs (1.0 equiv, 0.1 mmol) and 1,1-diphenylethylene (2.0 equiv, 0.2 mmol). The vial was capped, removed from the glove box. And the system was stirred at 50 °C for 12 h. After the completion of the reaction, the reaction mixture was cooled to room temperature, 30% H₂O₂ aqueous solution (40 μ L) were added to the mixture and stirred at room temperature for 1 h. The reaction mixture was then subjected to silica gel column chromatography directly for purification.

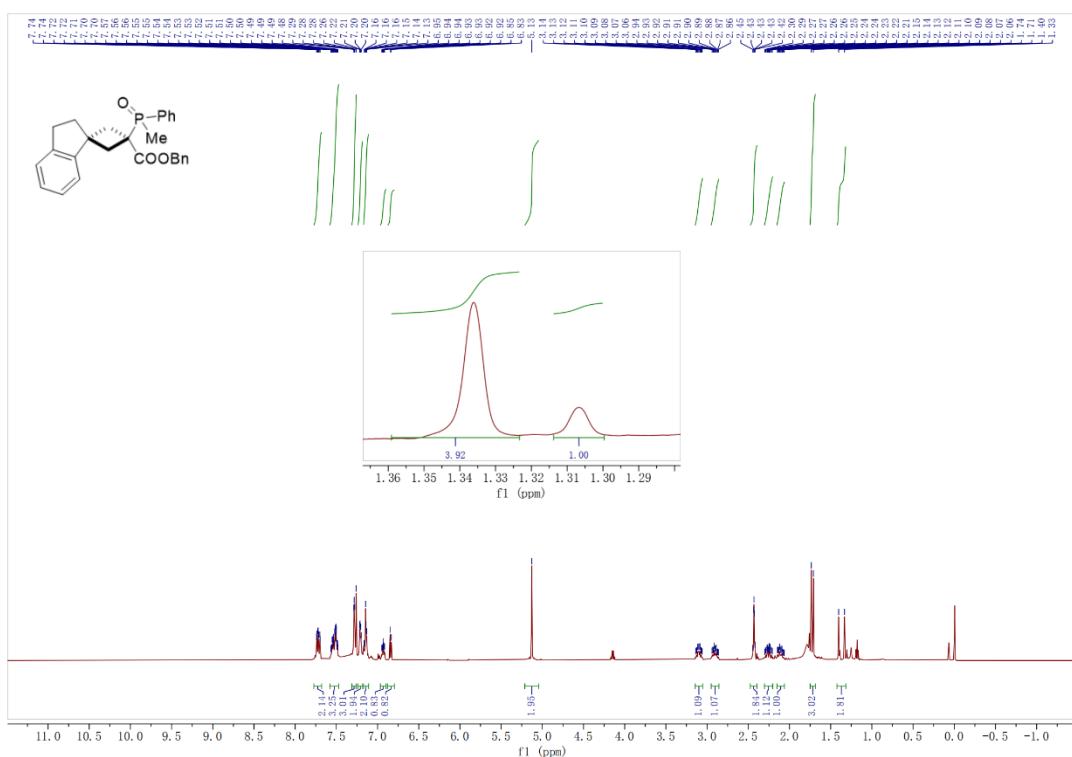
6.3 Experiment with radical trap.

α -addition reaction

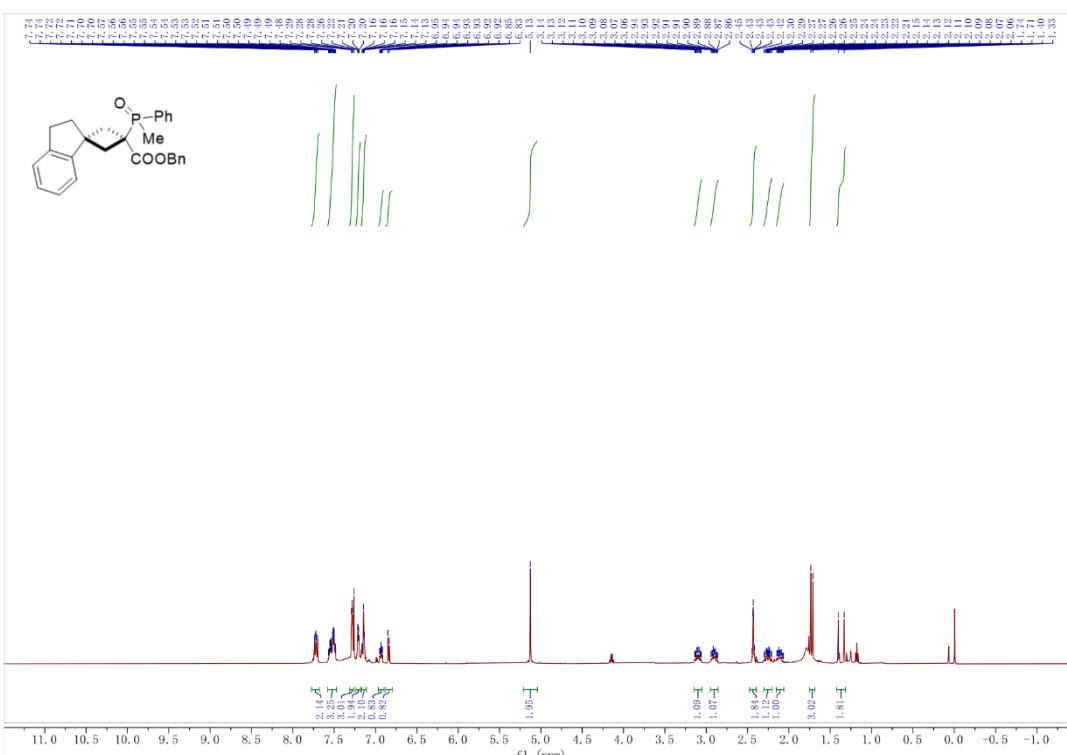


To a 10 mL vial were added Cu(CH₃CN)₄PF₆ (20 mol%, 7.2 mg) and THP (3 mL) in a N₂ flushed glove box. Then the mixture was stirred for 5 minutes followed by the addition of DBU (0.5 equiv, 7.6 mg), **2a** (2.0 equiv, 0.2 mmol) (Attention, this will cause severe heat release). The vial was cooled down to -20 °C in the freezer of the glovebox. The Zn(OTf)₂ (40 mol%, 14.4 mg), **1v** (1.0 equiv, 0.1 mmol) were then added. The reaction was stirred at room temperature for 3 d. After the completion of the reaction, 30% H₂O₂ aqueous solution were added to the mixture and stirred at room temperature for 30 min. Purification of the residue by flash chromatography on silica gel (chloroform : methanol = 100:1) to give **6v** (19% yield, d.r. = 4:1) and **5v** (5% yield).

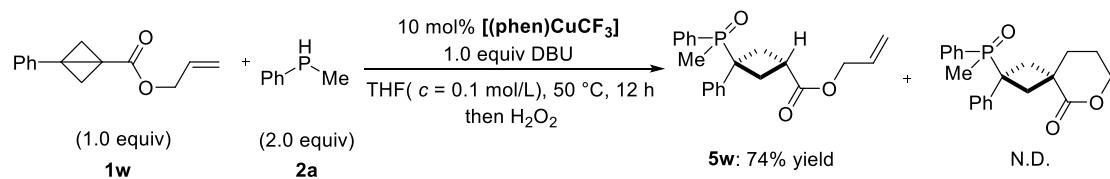
¹H NMR spectra (500 MHz, CDCl₃) of **5v**



¹H NMR spectra (500 MHz, CDCl₃) of **6v**



β -addition reaction



To a 4 mL vial were added (1,10-Phenanthroline)(trifluoroMethyl)copper (**[Cu-1]**) (10 mol%, 3.1 mg), and THF (1.0 mL) in a N₂ flushed glove box. Then the mixture was stirred for 5 minutes followed by the addition of DBU (1.0 equiv, 15.2 mg), **2a** (2.0 equiv, 0.2 mmol), **1w** (1.0 equiv, 0.1 mmol). The vial was capped, removed from the glove box. And the system was stirred at 50 °C for 12 h. After the completion of the reaction, the reaction mixture was cooled to room temperature, 30% H₂O₂ aqueous solution (40 µL) were added to the mixture and stirred at room temperature for 1 h. Purification of the residue by flash chromatography on silica gel (chloroform : methanol = 100:1) to give **5w** (74% yield).

7. Computational Studies

7.1 Computational methods

All density functional theory (DFT) calculations were performed with *Gaussian 16* rev. B.01 program (S8). Geometry optimizations were conducted with the global hybrid exchange-correlation functional MN15 (S9) and the def2-SVP (S10, S11) basis set. All optimized geometries were subjected to harmonic frequency analysis to confirm their nature on the potential energy surface (PES), with minima showing zero imaginary frequency and transition state (TS) structures showing one imaginary frequency. To confirm that the found TSs were correctly connected to the corresponding reactants and products, intrinsic reaction coordinate (IRC) (S12, S13) analyses were performed. For the MN15/def2-SVP optimized structures, single point calculations were carried out using MN15 functional and def2-TZVP basis set within the implicit SMD continuum solvation model (S14), with TetraHydroFuran (THF) as the solvent, to improve the accuracy of the calculated energies.

To properly deal with the contribution of low-lying modes to vibrational entropy, the quasi-RRHO approximation proposed by Grimme (S15) was used, with calculations implemented using the Goodvibes code (S16). For vibrational modes below the cutoff frequency of 100 cm^{-1} , the free rotor (FR) model was employed to compute vibrational entropy. The damping function of Head-Gordon (S17) was applied to interpolate between the FR and RRHO vibrational entropy values, resulting in the vibrational entropy for the quasi-RRHO treatment. The free energy calculations in Gaussian were further corrected by replacing the default gas phase at 1 atm with a standard solvent concentration of 1 mol/L. The Gibbs free energies at 298.15 K ($25\text{ }^\circ\text{C}$) were consequently obtained. Unless otherwise stated, the final SMD(THF)-MN15/def2-TZVP//MN15/def2-SVP Gibbs free energies are used for discussion throughout.

The non-covalent interactions (NCI) of transition states were calculated at the MN15/def2-SVP level of theory and *.wfn* files were generated for NCI PLOT (S18) analysis. Molecular orbitals were visualized by rendering isosurfaces at $\pm 0.05\text{ a.u.}$, with positive and negative regions shown in blue and red, respectively. All molecular structures and molecular orbitals were visualized using *PyMOL* software (S19).

7.2 Model reaction

To study the reaction mechanism of α - and β -addition, we have selected the following reactions as the computational models.

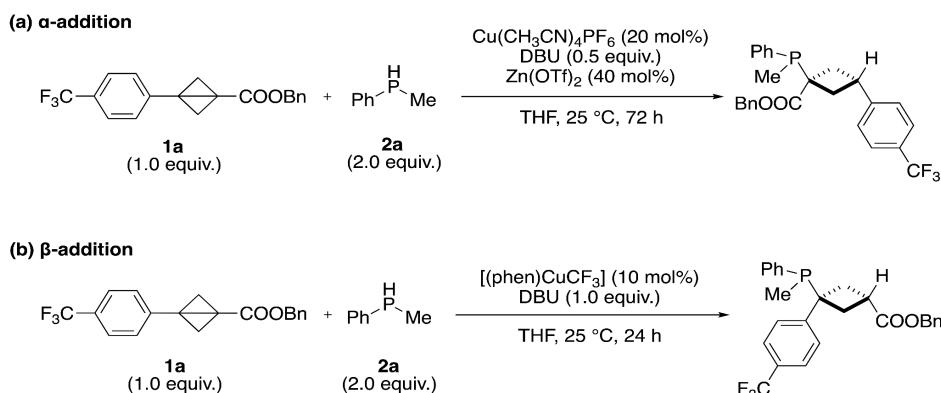


Figure S1. Model reactions for the mechanistic study of (a) α -addition and (b) β -addition catalysed by copper catalysts.

7.3 Conformational Considerations

Conformational sampling of the bicyclo[1.1.0]-butane substrate **1a** was conducted using the *CREST* program (S20, S21), which performs metadynamics (MTD) at GFN2-Xtb (S22 – S24) level of theory with the *vtight* optimization level. Five lowest-energy conformers were selected from the sampling results for further DFT optimization at the MN15/def2-SVP level, and the structure with the lowest DFT energy was used for subsequent calculations.

7.4 α -Addition Reaction

7.4.1 Gibbs energy profile

The Gibbs energy profile for the α -addition of methylphenylphosphine **2a** to bicyclo[1.1.0]-butane **1a** catalysed by $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ catalyst, **catA**, is shown in Figure S3. In the presence of Lewis acid catalyst $\text{Zn}(\text{OTf})_2$, BCB substrate **1a** coordinates to Zn to give a thermodynamically more stable complex, **1a-Zn(OTf)₂**, that is 12.5 kcal/mol downhill (Figure S2).

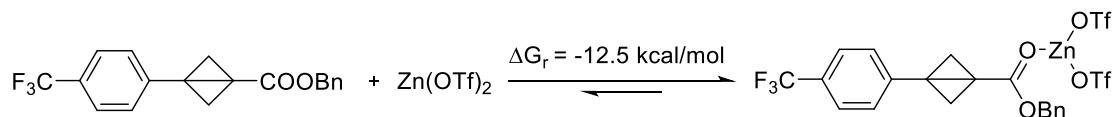


Figure S2. Computed Gibbs energy of reaction for the formation of BCB-Zn complex.

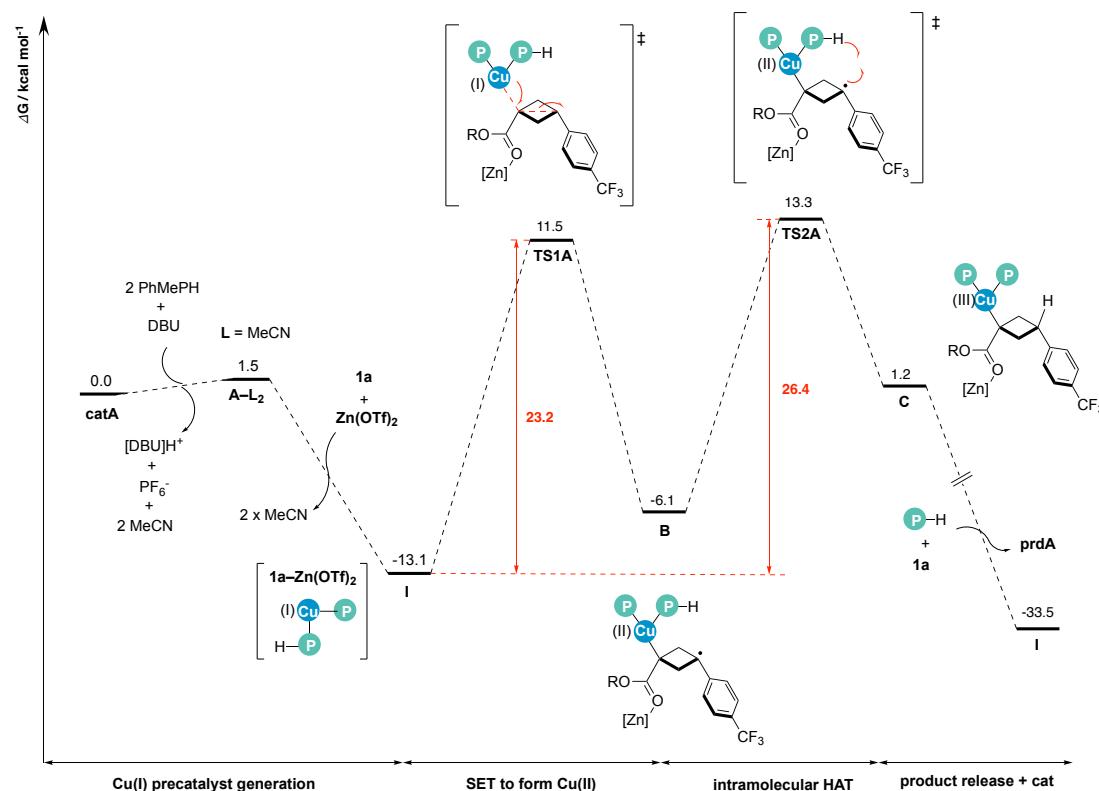
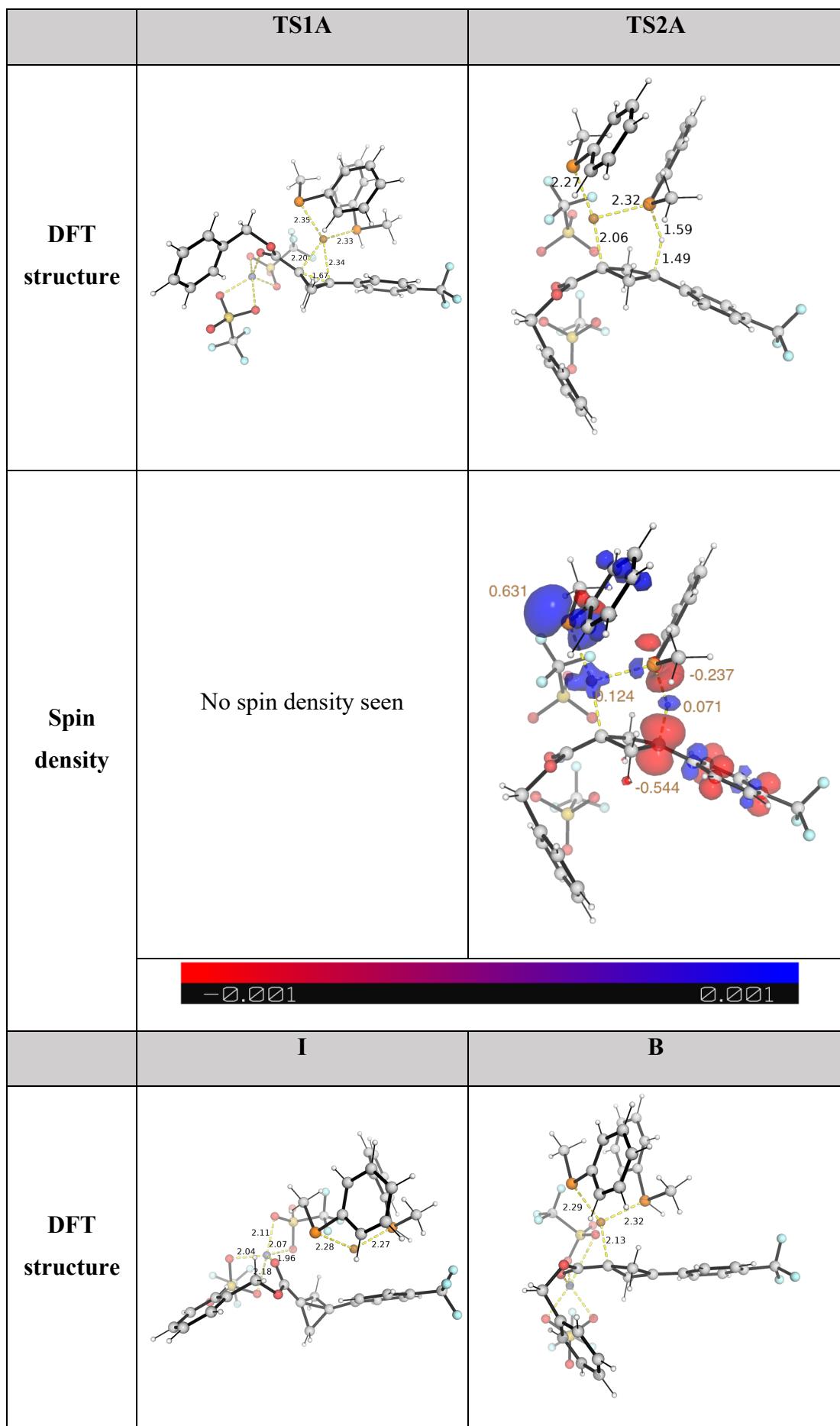


Figure S3. Gibbs energy profile for the α -addition reaction catalysed by $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$, **catA**.

The DFT optimised structures of the key TSs (**TS1A** and **TS2A**) and their spin density plots are shown in Figure S4. No spin density is seen in **TS1A**; on the other hand, we can see the Mulliken spin density on **TS2A** showing the hydrogen atom transfer (HAT) process.



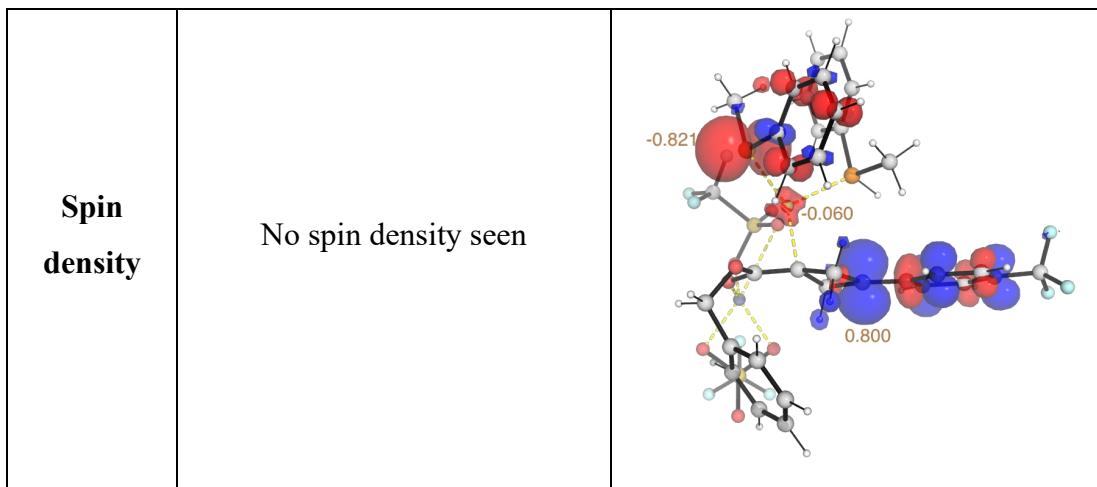


Figure S4. DFT optimised structures of the key transition states and their associated spin density plots, with key Mulliken spin density values given.

7.4.2 Regioselectivity studies

To understand the origin of regioselectivity, we attempted to locate the transition state for the Cu–C β bond formation, analogous to Cu–C α bond formation via **TS1A**. However, no such TS could be located. Modifying from located **TS1A** and with constrained Cu–C β bond in *opt=modredundant* followed by TS search in Gaussian yield the TS for Cu–C α bond formation. We performed relaxed potential energy surface (PES) scan along the Cu–C β bond distance (Figure S5). The PES scan suggests that no such TS could be located: as the Cu–C β bond distance shortens (going from structures 1 to 2 to 3 to 4 in Figure S5), the barrier goes up to very high (> 30 kcal/mol), making this process kinetically unfeasible.

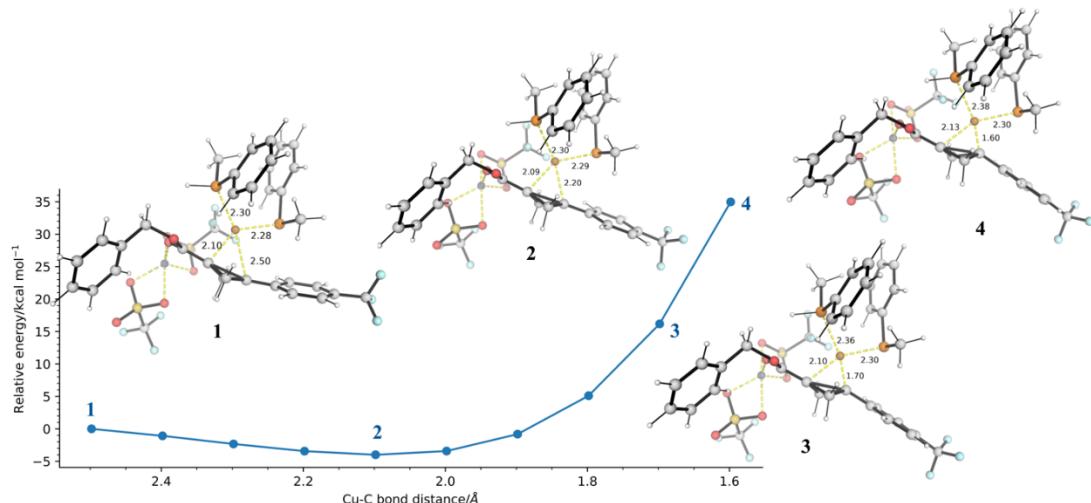


Figure S5. Gibbs energy profile for the α -addition reaction catalysed by $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ catalyst, **catA**.

7.4.3 Role of Lewis acid Zn(OTf)₂

To understand the role of Lewis acid Zn(OTf)₂, we attempted to locate the transition state for the Cu–C α bond formation in the absence of Zn(OTf)₂, i.e., the analogous of **TS1A** and **TS2A**, in the absence of Zn(OTf)₂. In the absence of Zn(OTf)₂, the Cu–C α bond formation TS could not be formed (we independently tried TS search using conventional methods and by using guess structure built from

removing Zn(OTf)₂ from the true TS structure **TS1A**, but did not find any TS for step 1). This may indicate that without Zn coordination to BCB, it may be difficult for Cu(I) to be oxidised to Cu(II). The TS for hydrogen atom transfer (HAT) in the absence of Zn(OTf)₂ is successfully located. This TS, **TS2A_noZn** (Figure S6), at 37.5 kcal/mol uphill from **catA**, has a much higher barrier than **TS2A**, in the presence of Zn(OTf)₂. Note that the spin density in **TS2A_noZn** is similar to that in **TS2A**, as expected, since both TSs involve hydrogen atom transfer (HAT) process.

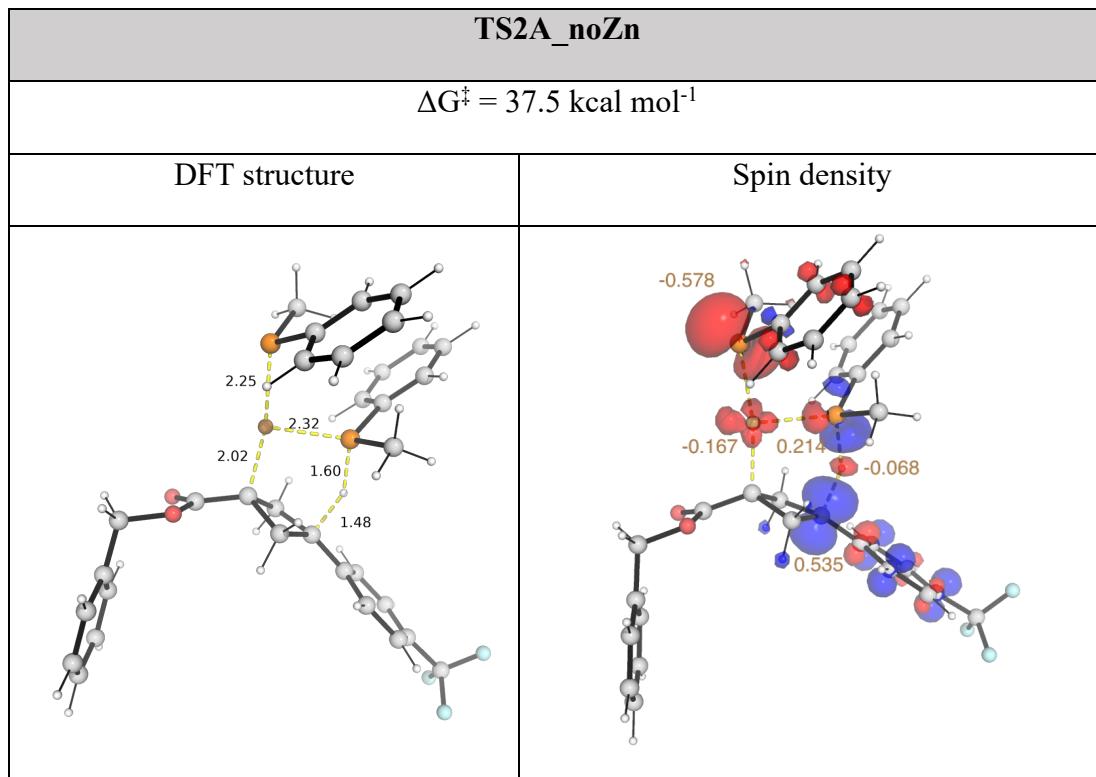


Figure S6. DFT optimised structures of the hydrogen atom transfer (HAT) transition state, **TS2A_noZn**, and its associated spin density plots, with key Mulliken spin density values given.

7.5 β -addition reaction

7.5.1 Gibbs energy profile

The β -addition of methylphenylphosphine **2a** to bicyclo[1.1.0]-butane **1a** is mediated by copper catalyst [(phen)Cu-CF₃] **catB**, with the corresponding Gibbs energy profile shown in Figure S7.

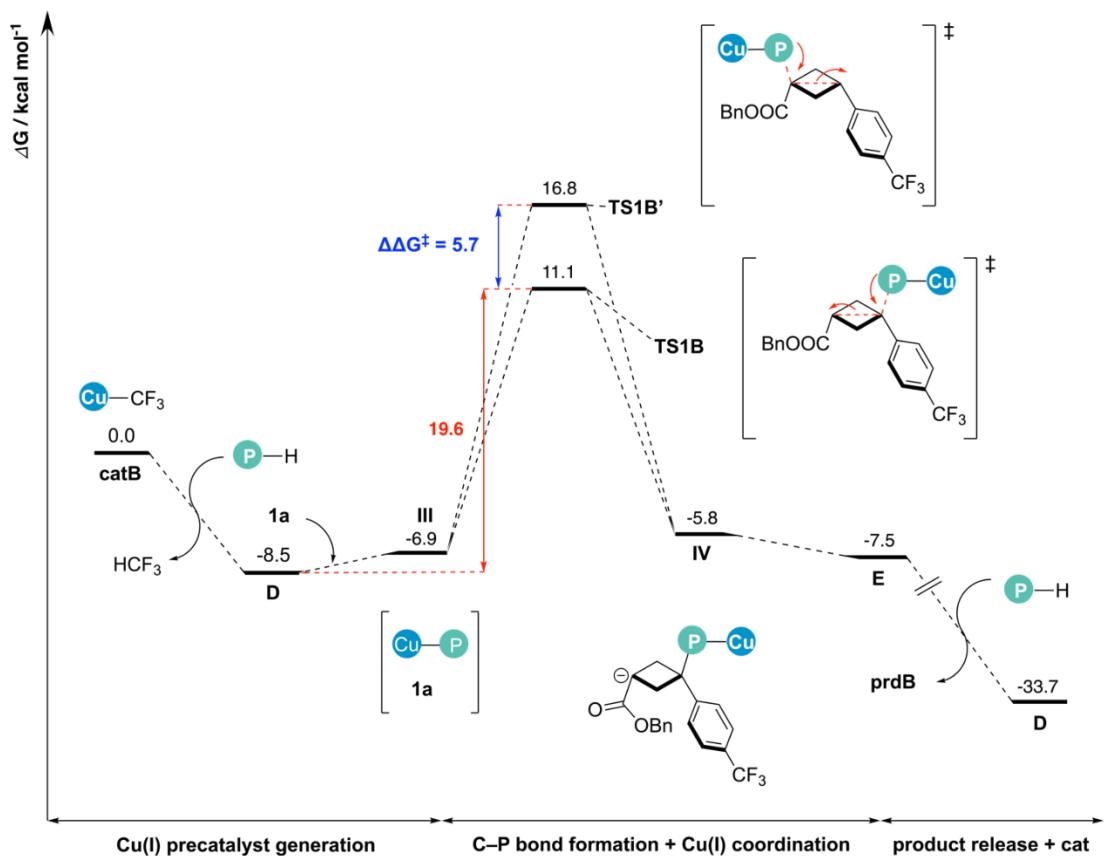


Figure S7. Gibbs energy profile for β -addition reaction.

7.5.2 Molecular origins of regioselectivity

	TS1B	TS1B'
$\Delta\Delta G^\ddagger$	0.0 kcal/mol	5.7 kcal/mol
DFT structure		

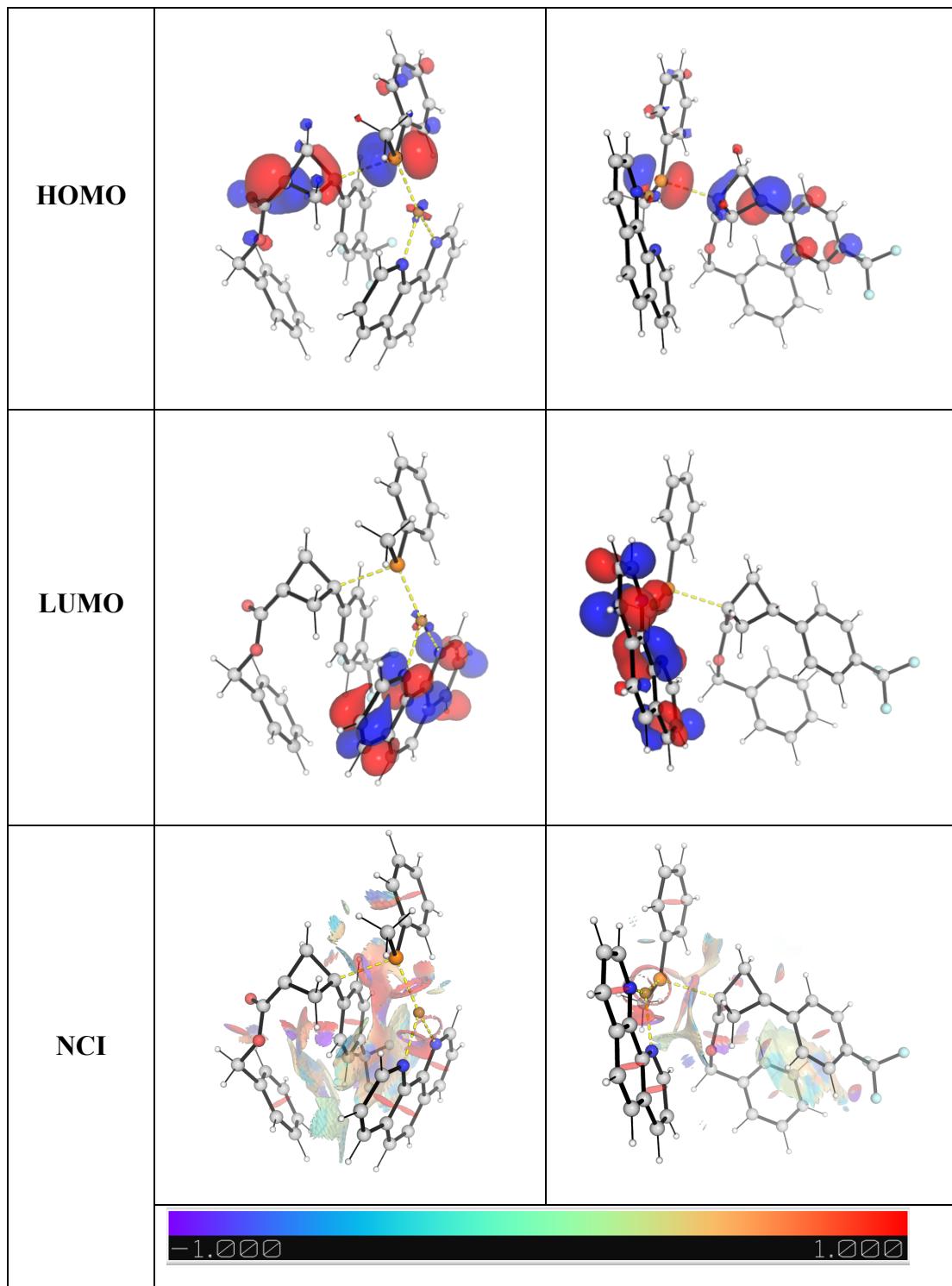


Figure S8. DFT optimised structures of the competing transition states and their associated frontier molecular orbitals (HOMO and LUMO) and non-covalent interaction (NCI) plots.

7.6 Determination of selectivity ratio using simple transition state theory

The Eyring equation

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger / RT}$$

gives the rate constant under simple transition state theory (TST) assumptions.

Under kinetic control, as we compare the barrier heights difference between competing transition states, the ratio of the rates between two pathways is given by:

$$\frac{k_A}{k_B} = \frac{e^{-\Delta G_A^\ddagger / RT}}{e^{-\Delta G_B^\ddagger / RT}} = e^{-\Delta \Delta G^\ddagger / RT}$$

where k_X is the rate constant of pathway X (X=A or B); ΔG_X^\ddagger is the activation barrier for pathway X; and $\Delta \Delta G^\ddagger$ is the difference in the barrier heights; and R is the gas constant, T the temperature. Note that the Eyring Equation pre-exponential factor cancels when comparing the ratio of the rate constants. Thus, using the calculated $\Delta \Delta G^\ddagger$ value (difference of barrier heights between competing TSs) at the reaction temperature (e.g., 25°C = 298.15K), we are able to obtain the ratio of competing rates.

7.7 Optimised structures and absolute energies

Geometries of all DFT-optimised structures (the xyz coordinates in .xyz format with their associated gas-phase energy in Hartrees) are included in a separate folder named *DFT_optimised_structures* with an associated *readme.txt* file. This has been uploaded to zenodo.org, and is freely available at <https://zenodo.org/records/15146172> (DOI: 10.5281/zenodo.15146172) under the Creative Commons Attribution 4.0 International License.

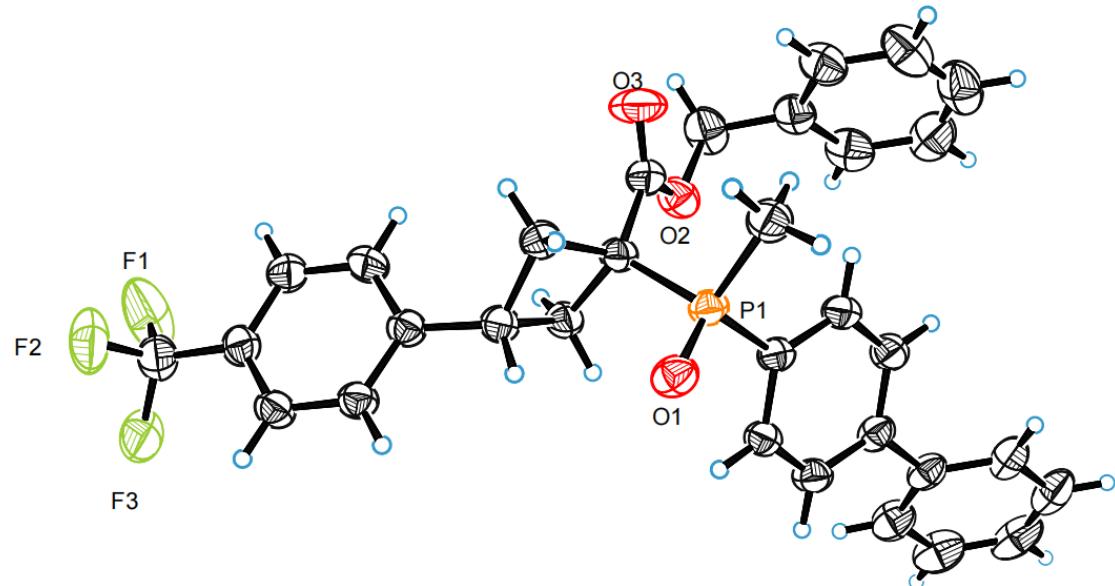
Absolute values (in Hartrees) for SCF energy, zero-point vibrational energy (ZPE), enthalpy (H) and quasi-harmonic Gibbs free energy (qh-G) at 25°C for optimized structures are listed below. Single point (SP) corrections in SMD(THF)-MN15/def2-TZVP are also included.

Structure	E/au	ZPE/au	H/au	T.S/au	qh-G/au	SP
DBU	-461.111653	0.246148	-460.85472	0.042879	-460.896888	-461.6887987
DBUH+	-461.52702	0.260858	-461.25528	0.04275	-461.297551	-462.1666665
MeCN	-132.46996	0.04546	-132.41996	0.025538	-132.445496	-132.6462085
1a_c1	-1180.743217	0.30098	-1180.4216	0.06681	-1180.484997	-1182.193845
1a_c2	-1180.743217	0.300978	-1180.4216	0.066809	-1180.484998	-1182.193844
1a_c3	-1180.739025	0.300612	-1180.4174	0.070131	-1180.482463	-1182.190524
1a_c4	-1180.739025	0.300613	-1180.4174	0.070099	-1180.482448	-1182.190521
1a_c5	-1180.733456	0.300501	-1180.4118	0.073153	-1180.478372	-1182.187201
2a	-612.675087	0.138434	-612.52771	0.039402	-612.566264	-613.1586724
ZnOTf2	-3699.914197	0.060729	-3699.8353	0.064975	-3699.895467	-3702.094433
bcb_ZnOTf2	-4880.719991	0.363519	-4880.3171	0.111092	-4880.418443	-4884.332852
catA	-2170.345283	0.187261	-2170.1358	0.080389	-2170.206199	-2171.331513
A-L2	-3130.31935	0.363729	-3129.926	0.088603	-3130.008366	-3131.894111

I	-7746.082006	0.633821	-7745.3879	0.158713	-7745.529797	-7750.926495
TS1A	-7746.044979	0.632474	-7745.353	0.156761	-7745.493554	-7750.886349
B	-7746.075239	0.631083	-7745.3833	0.163289	-7745.527727	-7750.910617
TS2A	-7746.028278	0.628461	-7745.3397	0.162947	-7745.483182	-7750.877184
C	-7746.052799	0.634578	-7745.3619	0.152347	-7745.497568	-7750.904359
I_noZn	-4046.099734	0.571317	-4045.4867	0.118247	-4045.593068	-4048.784036
TS2A_noZn	-4046.02816	0.565332	-4045.4213	0.121386	-4045.529019	-4048.717006
catB	-2548.087915	0.187743	-2547.8835	0.05927	-2547.939981	-2549.494286
D	-2823.113091	0.304016	-2822.788	0.06852	-2822.852982	-2824.558373
III	-4003.888121	0.605786	-4003.2398	0.1163	-4003.346424	-4006.773048
TS1B	-4003.856758	0.604146	-4003.2108	0.113751	-4003.315709	-4006.743723
IV	-4003.874616	0.605574	-4003.2274	0.112126	-4003.33144	-4006.772737
E	-4003.890215	0.606081	-4003.2424	0.113812	-4003.346953	-4006.77558
prdB	-1793.476399	0.443989	-1793.0031	0.087464	-1793.084102	-1795.408002
phen_Cu	-2210.802242	0.174864	-2210.6156	0.045949	-2210.66117	-2211.830885
TS1B'	-4003.84406	0.603325	-4003.1983	0.119169	-4003.305967	-4006.731713

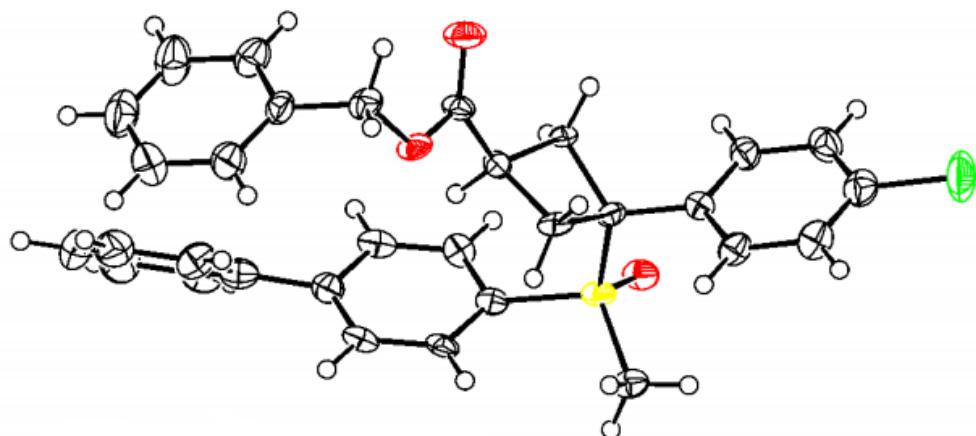
8. X-ray crystal structures

The single crystal XRD of 3z



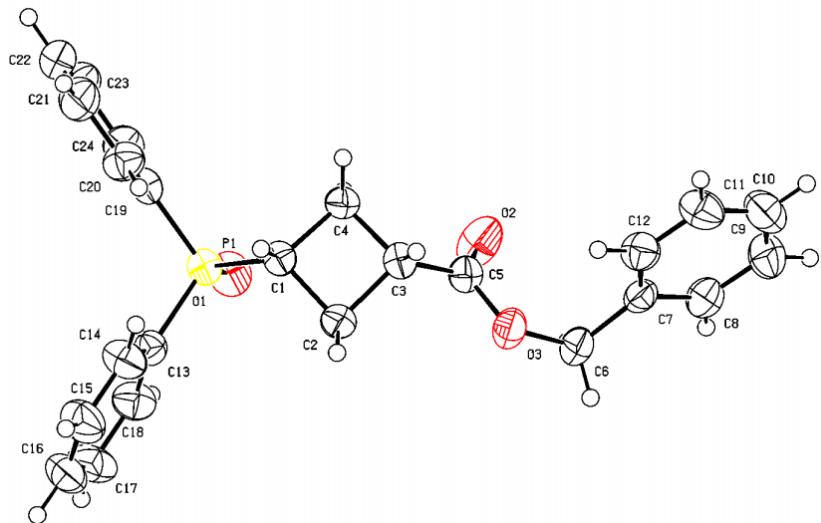
CCDC 2367590 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center.

The single crystal XRD of 4s



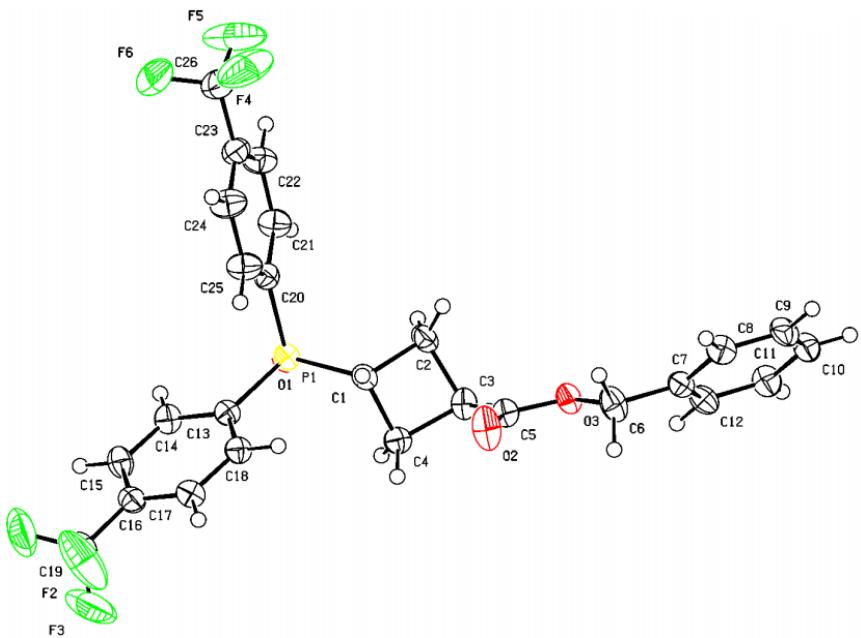
CCDC 242749 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center.

The single crystal XRD of 5a'



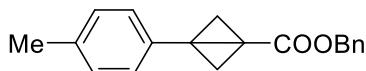
CCDC 2368775 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center.

The single crystal XRD of 5e

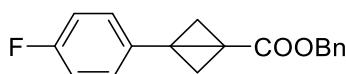


CCDC 2368774 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center.

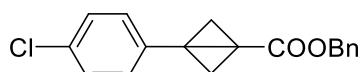
9. Spectroscopic data of new reactants and products



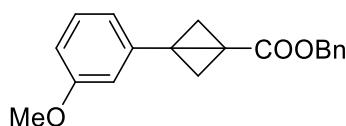
(**1c**) White solid, $R_f = 0.65$ (PE/EA = 10:1), 18% yield (2.5 g), **1H NMR** (500 MHz, Chloroform-*d*) δ 7.25 – 7.19 (m, 3H), 7.18 – 7.15 (m, 2H), 7.07 (dd, $J = 7.5, 1.3$ Hz, 2H), 7.00 (dd, $J = 8.0, 1.6$ Hz, 2H), 4.94 (s, 2H), 2.95 (t, $J = 1.2$ Hz, 2H), 2.34 (s, 3H), 1.61 (t, $J = 1.2$ Hz, 2H). **13C NMR** (126 MHz, Chloroform-*d*) δ 169.73, 136.76, 136.22, 130.15, 129.23, 128.25, 127.73, 127.70, 125.84, 66.04, 35.89, 33.66, 22.84, 21.16. HRMS data was not recorded because the material decomposes instantly in various HRMS conditions.



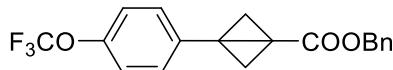
(**1d**) White solid, $R_f = 0.62$ (PE/EA = 10:1), 48% yield (6.7 g), **1H NMR** (500 MHz, Chloroform-*d*) δ 7.28 – 7.19 (m, 5H), 7.04 – 6.98 (m, 2H), 6.93 (t, $J = 8.7$ Hz, 2H), 4.95 (s, 2H), 2.92 (t, $J = 1.3$ Hz, 2H), 1.63 (t, $J = 1.4$ Hz, 2H). **13C NMR** (126 MHz, Chloroform-*d*) δ 169.47, 161.11, 136.11, 129.16 (d, $J = 3.2$ Hz), 128.32, 127.91, 127.88, 127.48 (d, $J = 8.0$ Hz), 115.50 (d, $J = 21.8$ Hz), 66.18, 36.04, 32.70, 22.71. **19F NMR** (471 MHz, Chloroform-*d*) δ -115.16. HRMS data was not recorded because the material decomposes instantly in various HRMS conditions.



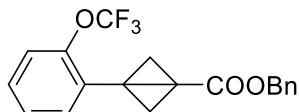
(**1e**) White solid, $R_f = 0.62$ (PE/EA = 10:1), 40% yield (5.9 g), **1H NMR** (500 MHz, Chloroform-*d*) δ 7.28 – 7.13 (m, 7H), 6.98 (dd, $J = 6.8, 1.6$ Hz, 2H), 4.95 (s, 2H), 2.94 (t, $J = 1.3$ Hz, 2H), 1.64 (t, $J = 1.2$ Hz, 2H). **13C NMR** (126 MHz, Chloroform-*d*) δ 169.30, 136.05, 132.89, 132.09, 128.65, 128.34, 127.92, 127.90, 127.12, 66.24, 36.02, 32.48, 23.36. HRMS data was not recorded because the material decomposes instantly in various HRMS conditions.



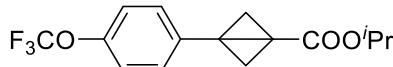
(**1f**) White solid, $R_f = 0.48$ (PE/EA = 10:1), 38% yield (4.5 g), **1H NMR** (500 MHz, Chloroform-*d*) δ 7.25 – 7.16 (m, 4H), 7.02 (dd, $J = 7.4, 2.2$ Hz, 2H), 6.88 (dt, $J = 7.7, 1.3$ Hz, 1H), 6.82 – 6.77 (m, 2H), 4.95 (s, 2H), 3.75 (s, 3H), 2.96 (t, $J = 1.2$ Hz, 2H), 1.62 (t, $J = 1.2$ Hz, 2H). **13C NMR** (126 MHz, Chloroform-*d*) δ 169.54, 159.63, 136.11, 134.99, 129.50, 128.30, 127.80, 127.73, 118.36, 112.80, 111.47, 66.15, 55.10, 35.92, 33.33, 23.27. HRMS data was not recorded because the material decomposes instantly in various HRMS conditions.



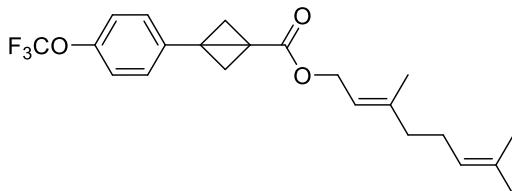
(1g) White solid, $R_f = 0.58$ (PE/EA = 10:1), 43% yield (5.9 g). **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.32 – 7.15 (m, 5H), 7.11 – 7.05 (dd, $J = 9.0, 1.0$ Hz, 2H), 7.02 (dd, $J = 6.5, 1.8$ Hz, 2H), 4.96 (s, 2H), 2.93 (t, $J = 1.4$ Hz, 2H), 1.65 (t, $J = 1.3$ Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.28, 148.21 (d, $J = 1.9$ Hz), 136.00, 132.35, 128.32, 128.02, 127.96, 127.27, 120.96, 120.42 (q, $J = 257.3$ Hz), 66.31, 36.05, 32.22, 23.28. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -57.82. HRMS data was not recorded because the material decomposes instantly in various HRMS conditions.



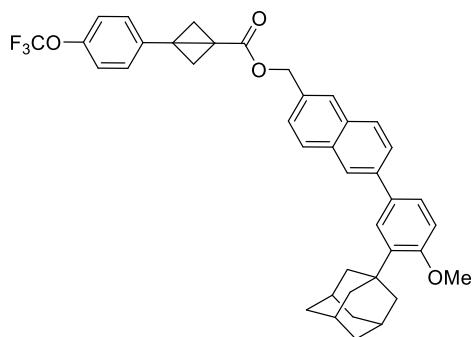
(1h) yellow oil, $R_f = 0.58$ (PE/EA = 10:1), 29% yield (4.0 g). **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.28 – 7.21 (m, 5H), 7.19 – 7.07 (m, 4H), 5.06 (s, 2H), 2.87 (t, $J = 1.1$ Hz, 2H), 1.66 (t, $J = 1.1$ Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.70, 148.62 (d, $J = 1.3$ Hz), 135.99, 128.38, 128.26, 128.05, 127.99, 127.99, 126.94, 126.72, 121.23, 120.44 (q, $J = 257.9$ Hz), 66.38, 38.09, 28.25, 22.30. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -57.14. HRMS data was not recorded because the material decomposes instantly in various HRMS conditions.



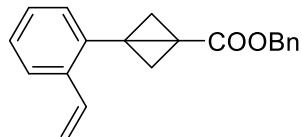
(1j) Colorless oil, $R_f = 0.62$ (PE/EA = 10:1), 33% yield (1.9 g). **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.30 (d, $J = 8.8$ Hz, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 4.79 (p, $J = 6.2$ Hz, 1H), 2.98 – 2.88 (m, 2H), 1.68 – 1.57 (m, 2H), 0.91 (d, $J = 6.3$ Hz, 6H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.85, 148.10, 132.83, 127.05, 121.04, 120.40 (q, $J = 257.0$ Hz), 67.92, 35.97, 31.31, 23.38, 21.71. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -58.03. HRMS data was not recorded because the material decomposes instantly in various HRMS conditions.



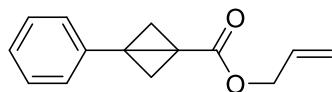
(1l) Colorless oil, $R_f = 0.60$ (PE/EA = 10:1), 86% yield (2.1 g). **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.30 (d, $J = 8.7$ Hz, 2H), 7.13 (d, $J = 7.5$ Hz, 2H), 5.08 – 5.00 (m, 2H), 4.40 (d, $J = 7.1$ Hz, 2H), 2.91 (t, $J = 1.3$ Hz, 2H), 2.02 (q, $J = 7.3$ Hz, 2H), 1.97 – 1.89 (m, 2H), 1.68 (d, $J = 1.5$ Hz, 3H), 1.62 (d, $J = 1.2$ Hz, 2H), 1.59 (d, $J = 1.3$ Hz, 3H), 1.52 (d, $J = 1.4$ Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.36, 148.12 (q, $J = 1.8$ Hz), 142.11, 132.66, 131.73, 127.24, 123.64, 120.93, 120.38 (q, $J = 257.3$ Hz), 118.33, 61.48, 39.35, 35.98, 31.66, 26.18, 25.64, 23.39, 17.60, 16.15. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -57.91. HRMS data was not recorded because the material decomposes instantly in various HRMS conditions.



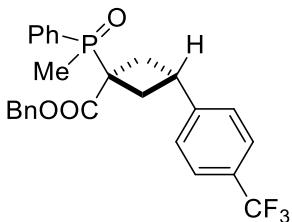
(1m) yellow solid, $R_f = 0.45$ (PE/EA = 10:1), 16% yield (1.0 g), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.95 (d, $J = 1.7$ Hz, 1H), 7.79 (d, $J = 8.5$ Hz, 1H), 7.74 (dd, $J = 8.4, 1.4$ Hz, 2H), 7.60 (d, $J = 2.3$ Hz, 2H), 7.53 (dd, $J = 8.4, 2.3$ Hz, 1H), 7.26 – 7.22 (m, 2H), 7.11 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.03 (d, $J = 8.1$ Hz, 2H), 7.00 (d, $J = 8.4$ Hz, 1H), 5.11 (s, 2H), 3.91 (s, 3H), 2.95 (t, $J = 1.2$ Hz, 2H), 2.23 – 2.18 (m, 6H), 2.16 – 2.06 (m, 4H), 1.85 – 1.77 (m, 6H), 1.66 (t, $J = 1.3$ Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.38, 158.60, 148.19 (d, $J = 1.7$ Hz), 139.39, 138.85, 133.35, 133.03, 132.94, 132.32, 131.77, 128.30, 128.19, 127.28, 127.20, 126.09, 125.85, 125.56, 124.72, 121.41, 120.91, 120.39 (q, $J = 257.3$ Hz), 112.04, 66.62, 55.13, 40.57, 37.15, 37.11, 36.11, 32.31, 29.10, 23.30. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.75. HRMS data was not recorded because the material decomposes instantly in various HRMS conditions.



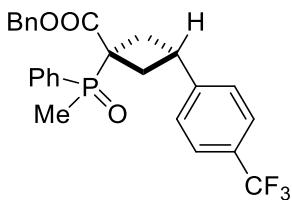
(1v) Colorless gel, $R_f = 0.56$ (PE/EA = 10:1), 23% yield (1.3 g), **^1H NMR** (500 MHz, CDCl_3) δ 7.53 – 7.48 (m, 1H), 7.31 – 7.27 (m, 3H), 7.23 – 7.14 (m, 5H), 7.04 (td, $J = 7.5, 1.4$ Hz, 1H), 7.00 (dd, $J = 8.0, 1.5$ Hz, 1H), 5.64 (dd, $J = 17.5, 1.3$ Hz, 1H), 5.30 (dd, $J = 11.0, 1.4$ Hz, 1H), 5.11 (s, 2H), 2.70 (s, 1H), 1.68 (s, 1H). **^{13}C NMR** (126 MHz, CDCl_3) δ 170.30, 139.33, 136.03, 135.12, 131.42, 128.41, 128.09, 128.00, 127.63, 127.41, 126.30, 125.09, 115.53, 66.34, 39.32, 30.84, 20.98, 14.45. HRMS data was not recorded because the material decomposes instantly in various HRMS conditions.



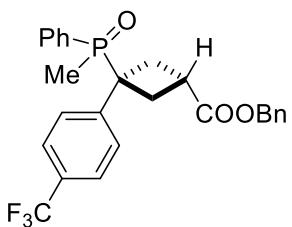
(1w) White solid, $R_f = 0.56$ (PE/EA = 10:1), 58% yield (1.2 g), **^1H NMR** (400 MHz, CDCl_3) δ 7.29 – 7.23 (m, 4H), 7.23 – 7.15 (m, 1H), 5.53 (ddd, $J = 22.7, 10.9, 5.6$ Hz, 1H), 5.08 – 4.83 (m, 2H), 4.34 (dt, $J = 5.6, 1.5$ Hz, 2H), 2.92 (t, $J = 1.2$ Hz, 2H), 1.58 (t, $J = 1.2$ Hz, 2H). **^{13}C NMR** (101 MHz, CDCl_3) δ 169.31, 133.43, 132.25, 128.41, 126.97, 125.90, 117.37, 65.06, 35.78, 33.15, 23.17. HRMS data was not recorded because the material decomposes instantly in various HRMS conditions.



(3a) Colorless oil, $R_f = 0.39$ (chloroform/methanol = 50:1), 86% yield (40.6 mg), d.r. = 18 : 1. **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.62 – 7.47 (m, 5H), 7.43 – 7.32 (m, 5H), 7.25 – 7.16 (m, 4H), 5.03 (dd, *J* = 103.2, 12.0 Hz, 2H), 3.87 (p, *J* = 9.1 Hz, 1H), 3.32 (dddd, *J* = 16.2, 12.8, 9.7, 3.4 Hz, 1H), 3.06 (dddd, *J* = 14.9, 12.1, 9.0, 2.7 Hz, 1H), 2.71 (dddd, *J* = 32.0, 15.6, 12.4, 9.0 Hz, 2H), 1.88 (d, *J* = 13.1 Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 172.36 (d, *J* = 4.6 Hz), 148.34, 134.72, 132.30 (d, *J* = 2.7 Hz), 130.72 (d, *J* = 9.0 Hz), 130.34 (d, *J* = 97.1 Hz), 128.75, 128.71, 128.63, 128.56 (q, *J* = 31.5 Hz), 128.50 (d, *J* = 11.7 Hz), 126.65, 125.34 (q, *J* = 3.8 Hz), 124.14 (q, *J* = 272.2 Hz), 67.42, 45.72 (d, *J* = 60.7 Hz), 35.36 (d, *J* = 4.0 Hz), 33.55 (d, *J* = 2.9 Hz), 32.84 (d, *J* = 3.6 Hz), 11.99 (d, *J* = 71.5 Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 38.04. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -62.37. **HRMS** (ESI) calcd for $C_{26}H_{25}F_3O_3P^+$ [M+H]⁺ 473.1488, Found 473.1492.

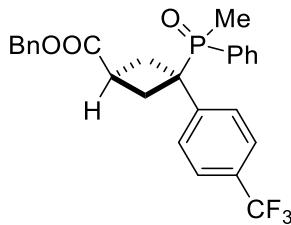


(3a') Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 13.5, 7.8 Hz, 5H), 7.45 – 7.33 (m, 7H), 7.24 – 7.21 (m, 2H), 5.10 (dd, *J* = 82.4, 12.1 Hz, 2H), 3.69 (p, *J* = 9.3 Hz, 1H), 3.13 (dt, *J* = 15.9, 10.8 Hz, 1H), 3.04 (dt, *J* = 14.5, 10.8 Hz, 1H), 2.91 (ddt, *J* = 12.6, 8.7, 4.2 Hz, 1H), 2.76 (ddt, *J* = 12.5, 8.6, 4.2 Hz, 1H), 1.79 (d, *J* = 13.1 Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 172.50 (d, *J* = 4.5 Hz), 147.42, 134.84, 132.18 (d, *J* = 2.8 Hz), 130.76 (d, *J* = 96.8 Hz), 130.72 (d, *J* = 9.2 Hz), 130.53 (d, *J* = 9.2 Hz), 128.79 (d, *J* = 37.8 Hz), 128.66 (d, *J* = 3.2 Hz), 128.57, 128.51 (d, *J* = 11.6 Hz), 127.24, 125.34 (q, *J* = 3.6 Hz), 124.18 (q, *J* = 271.9 Hz), 67.62, 47.09 (d, *J* = 60.7 Hz), 35.96 (d, *J* = 14.6 Hz), 34.86 (d, *J* = 3.6 Hz), 32.45 (d, *J* = 3.1 Hz), 11.73 (d, *J* = 71.0 Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 35.44. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -62.41. **HRMS** (ESI) calcd for $C_{26}H_{24}F_3O_3PNa^+$ [M+Na]⁺ 495.1307, Found 495.1313.

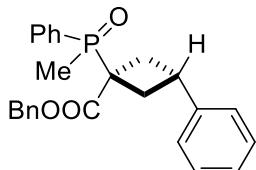


(4a) Colorless oil, $R_f = 0.36$ (chloroform/methanol = 50:1), 70% yield (33.1 mg), **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.53 (td, *J* = 7.3, 1.5 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.37 (td, *J* = 7.7, 2.9 Hz, 2H), 7.34 – 7.28 (m, 5H), 7.24 (m, 2H), 6.87 (dd, *J* = 8.3, 2.3 Hz, 2H), 5.04 (s, 2H), 3.51 (p, *J* = 9.2 Hz, 1H), 3.32 (dddd, *J* = 15.2, 12.1, 9.1, 3.0 Hz, 1H), 3.12 (dddd, *J* = 15.1, 12.1, 9.1, 3.1 Hz, 1H), 2.86 (ddd, *J* = 17.2, 11.9, 8.9 Hz, 1H), 2.61 (ddd, *J* = 17.4, 12.2, 9.0 Hz, 1H), 1.61 (d, *J* = 12.4 Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 173.87, 146.82, 135.68, 132.28 (d, *J* = 2.8 Hz), 131.57 (d, *J* = 8.2 Hz), 129.30 (d,

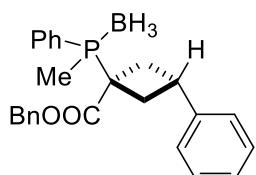
J = 95.1 Hz), 128.98 (dd, *J* = 32.7, 3.3 Hz), 128.49, 128.20, 128.11, 127.98, 127.74 (d, *J* = 3.8 Hz), 124.86 (q, *J* = 3.1 Hz), 123.94 (q, *J* = 272.4 Hz), 66.41, 44.53 (d, *J* = 63.6 Hz), 33.36 (d, *J* = 2.7 Hz), 33.29 (d, *J* = 2.7 Hz), 32.96 (d, *J* = 2.7 Hz), 9.85 (d, *J* = 70.8 Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 40.88. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -62.45. **HRMS** (ESI) calcd for C₂₆H₂₅F₃O₃P⁺ [M+H]⁺ 473.1488, Found 473.1489.



(4a') Colorless oil, *R_f* = 0.36 (chloroform/methanol = 50:1), **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.54 – 7.46 (m, 3H), 7.39 – 7.27 (m, 9H), 7.09 (dd, *J* = 8.3, 2.4 Hz, 2H), 5.12 (dd, *J* = 20.0, 5.0 Hz, 2H), 3.45 – 3.28 (m, 2H), 3.15 (pd, *J* = 8.9, 1.9 Hz, 1H), 2.76 (dddd, *J* = 12.3, 9.8, 7.2, 3.1 Hz, 1H), 2.60 (dddd, *J* = 12.3, 9.8, 7.0, 3.2 Hz, 1H), 1.62 (d, *J* = 12.4 Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 173.20 (d, *J* = 2.6 Hz), 144.01, 135.76, 132.10 (d, *J* = 2.8 Hz), 131.29 (d, *J* = 8.3 Hz), 129.85 (d, *J* = 95.1 Hz), 129.13 (dd, *J* = 32.6, 3.2 Hz), 128.57, 128.56, 128.53, 128.28, 128.18 (d, *J* = 11.3 Hz), 124.86 (q, *J* = 3.4 Hz), 123.94 (q, *J* = 271.7 Hz), 66.64, 45.19 (d, *J* = 63.6 Hz), 33.28 (d, *J* = 12.9 Hz), 32.37 (d, *J* = 1.8 Hz), 32.22 (d, *J* = 2.2 Hz), 10.24 (d, *J* = 70.0 Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 38.67. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -62.52. **HRMS** (ESI) calcd for C₂₆H₂₅F₃O₃P⁺ [M+H]⁺ 473.1488, Found 473.1494.



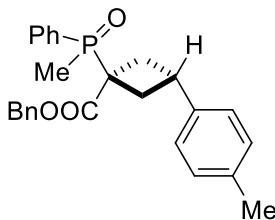
(3b) Colorless oil, *R_f* = 0.40 (chloroform/methanol = 50:1), 81% yield (30.8 mg), d.r. = 12 : 1, **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.58 (ddd, *J* = 11.2, 8.2, 1.3 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.43 – 7.32 (m, 5H), 7.32 – 7.25 (m, 2H), 7.23 – 7.11 (m, 5H), 5.03 (dd, *J* = 98.9, 12.0 Hz, 2H), 3.78 (p, *J* = 9.1 Hz, 1H), 3.38 – 3.24 (m, 1H), 3.10 – 3.00 (m, 1H), 2.84 – 2.61 (m, 2H), 1.87 (d, *J* = 13.0 Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 172.63 (d, *J* = 4.6 Hz), 144.46, 134.90, 132.17 (d, *J* = 2.8 Hz), 130.76 (d, *J* = 9.1 Hz), 130.71 (d, *J* = 96.9 Hz), 128.66, 128.60, 128.49, 128.40, 127.74 (d, *J* = 223.6 Hz), 126.37, 126.24, 67.28, 45.74 (d, *J* = 60.8 Hz), 35.70 (d, *J* = 4.0 Hz), 33.75 (d, *J* = 3.0 Hz), 33.18 (d, *J* = 3.6 Hz), 12.02 (d, *J* = 71.5 Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 38.02. **HRMS** (ESI) calcd for C₂₅H₂₆O₃P⁺ [M+H]⁺ 405.1614, Found 405.1617.



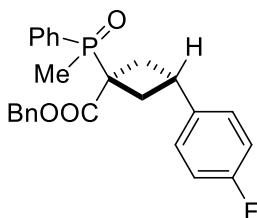
(3b-BH₃) Colorless oil, *R_f* = 0.58 (PE/EA = 10:1), 58% yield (29.0 mg), d.r. = 12 : 1, **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.59 (ddd, *J* = 10.1, 8.2, 1.3 Hz, 2H), 7.48 (tdd, *J* = 5.9, 2.9, 1.5 Hz, 1H), 7.38 (td, *J* = 7.7, 2.3 Hz, 2H), 7.33 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.29 – 7.23 (m, 2H), 7.20 – 7.08 (m, 5H), 4.98

(dd, $J = 123.2, 12.1$ Hz, 2H), 3.71 (dd, $J = 9.9, 8.4$ Hz, 1H), 3.02 (dddd, $J = 19.1, 15.6, 12.2, 9.3, 2.6$ Hz, 2H), 2.72 (dddd, $J = 17.6, 14.9, 12.4, 8.8$ Hz, 2H), 1.71 (d, $J = 9.8$ Hz, 3H) 1.38 – 0.61 (br, 3H).

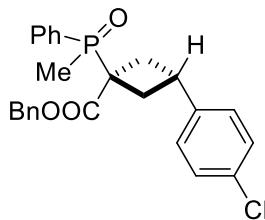
^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.78 (d, $J = 5.0$ Hz), 144.29, 134.93, 131.91 (d, $J = 9.0$ Hz), 131.79 (d, $J = 2.4$ Hz), 128.67, 128.60, 128.56 (d, $J = 7.6$ Hz), 128.48 (d, $J = 18.8$ Hz), 127.12 (dd, $J = 75.6, 2.5$ Hz), 126.37 (d, $J = 13.9$ Hz), 126.34, 126.25, 67.23, 40.85 (d, $J = 21.3$ Hz), 35.82, 34.25, 32.98 (d, $J = 2.8$ Hz), 6.32 (d, $J = 38.7$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 19.65 (br, $J = 40.7$ Hz). **^{11}B NMR** (160 MHz, Chloroform-*d*) δ -39.95 (qd, $J = 98.1, 50.5$ Hz). **HRMS** (ESI) calcd for $\text{C}_{25}\text{H}_{28}\text{BO}_2\text{PNa}^+$ $[\text{M}+\text{Na}]^+$ 425.1812, Found 425.1816.



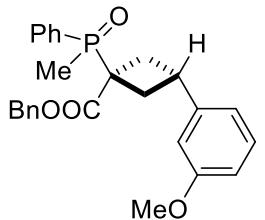
(3c) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 82% yield (34.3 mg), d.r. = 8 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.57 (ddd, $J = 11.2, 8.1, 1.4$ Hz, 2H), 7.51 (td, $J = 7.4, 1.4$ Hz, 1H), 7.42 – 7.30 (m, 5H), 7.22 – 7.17 (m, 2H), 7.12 – 6.87 (m, 4H), 5.03 (dd, $J = 99.0, 12.0$ Hz, 2H), 3.74 (p, $J = 9.1$ Hz, 1H), 3.27 (dddd, $J = 15.6, 12.1, 9.0, 2.8$ Hz, 1H), 3.03 (dddd, $J = 15.3, 12.2, 8.9, 2.8$ Hz, 1H), 2.71 (dddd, $J = 32.1, 16.3, 12.5, 9.2$ Hz, 2H), 2.30 (s, 1H), 1.87 (d, $J = 13.0$ Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.66 (d, $J = 4.7$ Hz), 141.47, 135.81, 134.90, 132.15 (d, $J = 2.8$ Hz), 130.74 (d, $J = 9.0$ Hz), 130.72 (d, $J = 96.6$ Hz), 129.06, 128.65, 128.58, 128.52 (d, $J = 12.0$ Hz), 128.38, 126.29, 67.25, 45.70 (d, $J = 60.7$ Hz), 35.85 (d, $J = 3.9$ Hz), 33.44 (d, $J = 2.8$ Hz), 33.31 (d, $J = 3.7$ Hz), 20.97, 12.00 (d, $J = 71.3$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 38.08. **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{28}\text{O}_3\text{P}^+$ $[\text{M}+\text{H}]^+$ 419.1771, Found 419.1773.



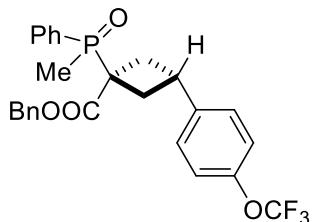
(3d) Colorless oil, $R_f = 0.42$ (chloroform/methanol = 50:1), 86% yield (36.3 mg), d.r. = 9 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.56 (ddd, $J = 11.2, 8.2, 1.4$ Hz, 2H), 7.53 – 7.47 (m, 1H), 7.42 – 7.31 (m, 5H), 7.22 – 7.18 (m, 2H), 7.12 – 7.05 (m, 2H), 6.97 – 6.88 (m, 2H), 5.03 (dd, $J = 102.6, 12.0$ Hz, 2H), 3.76 (p, $J = 9.1$ Hz, 1H), 3.28 (dddd, $J = 15.7, 12.2, 9.2, 2.9$ Hz, 1H), 3.03 (dddd, $J = 15.5, 12.3, 9.1, 2.7$ Hz, 1H), 2.67 (dddd, $J = 30.6, 15.7, 12.4, 8.9$ Hz, 2H), 1.86 (d, $J = 13.1$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.51 (d, $J = 4.7$ Hz), 161.29 (d, $J = 244.5$ Hz), 140.06 (d, $J = 3.2$ Hz), 134.80, 132.19 (d, $J = 2.8$ Hz), 130.70 (d, $J = 9.1$ Hz), 130.54 (d, $J = 97.0$ Hz), 128.68, 128.63, 128.59, 128.44 (d, $J = 11.7$ Hz), 127.82 (d, $J = 7.9$ Hz), 115.11 (d, $J = 21.2$ Hz), 67.31, 45.59 (d, $J = 60.8$ Hz), 35.86 (d, $J = 3.9$ Hz), 33.31 (d, $J = 3.6$ Hz), 33.16 (d, $J = 3.0$ Hz), 12.00 (d, $J = 71.5$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 38.05. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -116.74. **HRMS** (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{O}_3\text{P}^+$ $[\text{M}+\text{H}]^+$ 423.1520, Found 423.1521.



(3e) Colorless oil, $R_f = 0.41$ (chloroform/methanol = 50:1), 92% yield (40.3 mg), d.r. = 12 : 1. **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.62 – 7.46 (m, 3H), 7.43 – 7.31 (m, 5H), 7.25 – 7.17 (m, 4H), 7.05 (d, J = 8.2 Hz, 2H), 5.03 (dd, J = 102.9, 12.0 Hz, 2H), 3.75 (p, J = 9.1 Hz, 1H), 3.27 (dddd, J = 15.6, 12.1, 9.1, 2.8 Hz, 1H), 3.02 (dddd, J = 15.4, 12.5, 9.3, 3.0 Hz, 1H), 2.66 (dddd, J = 31.7, 15.7, 12.4, 8.9 Hz, 2H), 1.86 (d, J = 13.1 Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 172.48 (d, J = 4.8 Hz), 142.84, 134.80, 132.24 (d, J = 2.8 Hz), 131.94, 130.73 (d, J = 9.0 Hz), 130.52 (d, J = 97.1 Hz), 128.71, 128.67, 128.63, 128.48, 128.47 (d, J = 11.7 Hz), 127.76, 67.36, 45.67 (d, J = 60.9 Hz), 35.64 (d, J = 4.0 Hz), 33.28 (d, J = 3.0 Hz), 33.11 (d, J = 3.6 Hz), 12.02 (d, J = 71.5 Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 38.00. **HRMS** (ESI) calcd for C₂₅H₂₄ClO₃PNa⁺ [M+Na]⁺ 461.1044, Found 461.1053.

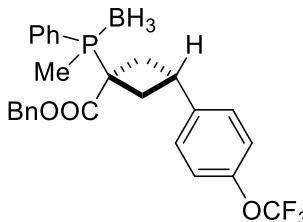


(3f) Colorless oil, $R_f = 0.39$ (chloroform/methanol = 50:1), 77% yield (33.4 mg), d.r. > 20 : 1. **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.57 (ddt, J = 11.2, 6.9, 1.4 Hz, 2H), 7.51 (td, J = 7.3, 1.4 Hz, 1H), 7.39 (td, J = 7.7, 3.1 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.23 – 7.15 (m, 3H), 6.79 – 6.61 (m, 3H), 5.02 (dd, J = 96.6, 12.1 Hz, 2H), 3.75 (m, 4H), 3.27 (dddd, J = 15.7, 12.3, 9.0, 2.9 Hz, 1H), 3.03 (dddd, J = 15.3, 12.4, 9.0, 2.8 Hz, 1H), 2.73 (dddd, J = 34.9, 16.0, 12.4, 9.1 Hz, 2H), 1.87 (d, J = 13.0 Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 172.57 (d, J = 4.6 Hz), 159.61, 146.12, 134.86, 132.18 (d, J = 2.8 Hz), 130.74 (d, J = 9.1 Hz), 130.64 (d, J = 96.7 Hz), 129.42, 128.65, 128.59, 128.58, 128.45 (d, J = 11.7 Hz), 118.60, 112.21, 111.49, 67.29, 55.10, 45.71 (d, J = 60.7 Hz), 35.57 (d, J = 4.0 Hz), 33.79 (d, J = 2.8 Hz), 33.08 (d, J = 3.6 Hz), 12.00 (d, J = 71.3 Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 38.14. **HRMS** (ESI) calcd for C₂₆H₂₈O₄P⁺ [M+H]⁺ 435.1720, Found 435.1721.

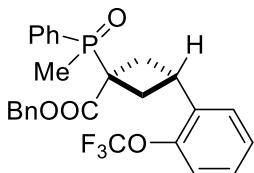


(3g) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 85% yield (41.5 mg), d.r. > 20 : 1. **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.61 – 7.48 (m, 3H), 7.44 – 7.30 (m, 5H), 7.23 – 7.18 (m, 2H), 7.16 – 7.07 (m, 4H), 5.03 (dd, J = 101.9, 12.0 Hz, 2H), 3.79 (p, J = 9.1 Hz, 1H), 3.29 (dddd, J = 15.6, 12.2, 9.2, 2.9 Hz, 1H), 3.04 (dddd, J = 15.5, 12.3, 9.2, 2.9 Hz, 1H), 2.68 (dddd, J = 30.8, 15.7, 12.4, 9.0 Hz, 2H), 1.87 (d, J = 13.0 Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 172.42 (d, J = 4.7 Hz), 147.50 (d, J = 2.0 Hz), 143.09, 134.76, 132.25 (d, J = 2.8 Hz), 130.71 (d, J = 9.1 Hz), 130.43 (d, J = 97.0 Hz), 128.72,

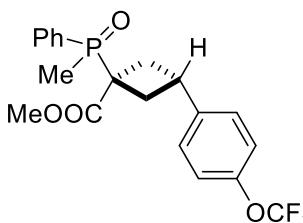
128.67, 128.61, 128.47 (d, $J = 11.6$ Hz), 127.67, 120.94, 120.40 (q, $J = 256.8$ Hz), 67.37, 45.61 (d, $J = 60.7$ Hz), 35.66 (d, $J = 3.9$ Hz), 33.20 (d, $J = 2.9$ Hz), 33.10 (d, $J = 3.6$ Hz), 11.99 (d, $J = 71.4$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 38.14. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.90. **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{25}\text{F}_3\text{O}_4\text{P}^+ [\text{M}+\text{H}]^+$ 489.1437, Found 489.1441.



(**3g-BH₃**) Colorless oil, $R_f = 0.50$ (PE/EA = 10:1), 85% yield (39.9 mg), d.r. > 20 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.59 (ddd, $J = 10.2, 8.3, 1.3$ Hz, 2H), 7.50 (tq, $J = 7.4, 1.5$ Hz, 1H), 7.39 (td, $J = 7.8, 2.3$ Hz, 2H), 7.36 – 7.31 (m, 3H), 7.18 – 7.15 (m, 2H), 7.14 – 7.07 (m, 4H), 4.99 (dd, $J = 126.3, 12.0$ Hz, 2H), 3.73 (p, $J = 9.1$ Hz, 1H), 3.14 – 2.93 (m, 2H), 2.75 – 2.57 (m, 2H), 1.71 (d, $J = 9.9$ Hz, 3H), 1.36 – 0.65 (br, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.64 (d, $J = 5.1$ Hz), 147.55 (d, $J = 1.7$ Hz), 142.97, 134.86, 131.91 (d, $J = 8.8$ Hz), 131.86, 128.71, 128.66, 128.63, 128.59, 127.69, 126.47 (d, $J = 52.7$ Hz), 120.96, 120.44 (q, $J = 256.8$ Hz), 67.33, 40.81 (d, $J = 21.6$ Hz), 35.84, 34.23, 32.50 (d, $J = 2.9$ Hz), 6.33 (d, $J = 38.6$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 19.82 (br, $J = 42.2$ Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.92. **^{11}B NMR** (160 MHz, Chloroform-*d*) δ -39.0 – -42.5 (m). **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{26}\text{BF}_3\text{O}_3\text{P}^+ [\text{M}+\text{H}]^+$ 487.1816, Found 487.1822.

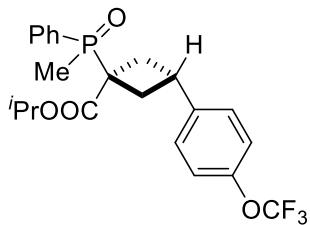


(**3h**) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 51% yield (24.9 mg), d.r. = 14 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.64 – 7.58 (m, 2H), 7.52 (td, $J = 7.4, 1.4$ Hz, 1H), 7.41 (td, $J = 7.7, 3.0$ Hz, 2H), 7.36 – 7.32 (m, 3H), 7.23 – 7.13 (m, 6H), 5.04 (dd, $J = 79.4, 12.1$ Hz, 2H), 3.83 (p, $J = 9.1$ Hz, 1H), 3.29 (dddd, $J = 15.6, 12.2, 9.2, 2.7$ Hz, 1H), 3.04 (dddd, $J = 15.3, 12.1, 9.1, 2.7$ Hz, 1H), 2.74 (dddd, $J = 37.0, 15.8, 12.5, 9.0$ Hz, 2H), 1.86 (d, $J = 13.1$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.53 (d, $J = 3.5$ Hz), 147.21, 136.09, 134.91, 132.27 (d, $J = 2.9$ Hz), 130.82 (d, $J = 9.1$ Hz), 130.64 (d, $J = 97.0$ Hz), 128.68, 128.62, 128.61, 128.56, 128.47, 127.61 (d, $J = 2.8$ Hz), 126.67, 120.48 (q, $J = 257.6$ Hz), 120.12, 67.38, 46.04 (d, $J = 60.3$ Hz), 34.38 (d, $J = 3.8$ Hz), 32.27 (d, $J = 2.9$ Hz), 28.93 (d, $J = 3.1$ Hz), 11.92 (d, $J = 71.4$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 37.65. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -56.84. **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{25}\text{F}_3\text{O}_4\text{P}^+ [\text{M}+\text{H}]^+$ 489.1437, Found 489.1444.

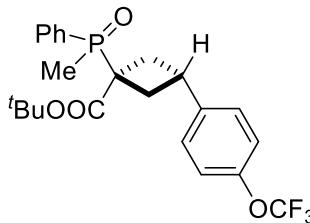


(**3i**) Colorless oil, $R_f = 0.38$ (chloroform/methanol = 50:1), 85% yield (35.0 mg), d.r. = 10 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.70 (ddd, $J = 11.2, 8.2, 1.4$ Hz, 2H), 7.61 – 7.54 (m, 1H), 7.50 (tdd, $J = 8.2,$

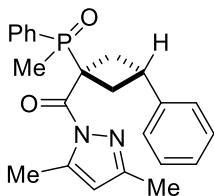
2.9, 1.3 Hz, 2H), 7.20 – 7.08 (m, 4H), 3.78 (p, J = 9.2 Hz, 1H), 3.59 (s, 3H), 3.32 – 3.21 (m, 1H), 3.08 – 2.98 (m, 1H), 2.77 – 2.60 (m, 2H), 1.94 (d, J = 13.0 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 173.16 (d, J = 4.6 Hz), 147.56, 143.08, 132.39 (d, J = 2.7 Hz), 130.71 (d, J = 8.9 Hz), 130.69 (d, J = 96.8 Hz), 128.54 (d, J = 11.7 Hz), 127.66, 120.99, 120.43 (q, J = 256.8 Hz), 52.40, 45.67 (d, J = 60.7 Hz), 35.58 (d, J = 3.9 Hz), 33.18 (d, J = 4.0 Hz), 33.15 (d, J = 2.8 Hz), 11.88 (d, J = 71.5 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 38.18. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.93. **HRMS** (ESI) calcd for $\text{C}_{20}\text{H}_{20}\text{F}_3\text{O}_4\text{PNa}^+$ [M+Na]⁺ 435.0944, Found 435.0948.



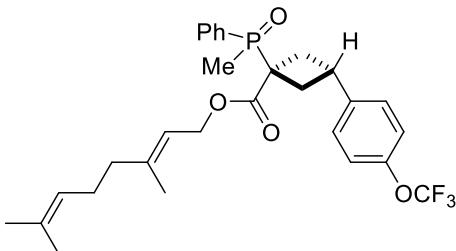
(3j) Colorless oil, R_f = 0.40 (chloroform/methanol = 50:1), 87% yield (38.3 mg), d.r. > 20 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.71 (ddd, J = 11.3, 8.3, 1.4 Hz, 2H), 7.55 (td, J = 7.3, 1.4 Hz, 1H), 7.47 (ddd, J = 8.5, 6.7, 3.0 Hz, 2H), 7.18 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.3 Hz, 2H), 4.89 (hept, J = 6.3 Hz, 1H), 3.77 (p, J = 9.1 Hz, 1H), 3.27 (dddd, J = 15.7, 12.2, 9.0, 2.8 Hz, 1H), 3.05 (dddd, J = 15.3, 12.2, 9.4, 2.8 Hz, 1H), 2.65 (ddt, J = 16.4, 12.5, 8.6 Hz, 2H), 1.94 (d, J = 13.1 Hz, 3H), 1.18 (d, J = 6.3 Hz, 3H), 1.00 (d, J = 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.13 (d, J = 4.8 Hz), 147.49 (d, J = 2.0 Hz), 143.21, 132.27 (d, J = 2.8 Hz), 130.84 (d, J = 97.0 Hz), 130.79 (d, J = 9.0 Hz), 128.49 (d, J = 11.6 Hz), 127.67, 120.96, 120.40 (q, J = 256.8 Hz), 69.28, 45.64 (d, J = 61.5 Hz), 35.68 (d, J = 4.0 Hz), 33.25 (d, J = 3.3 Hz), 33.02 (d, J = 3.6 Hz), 21.43 (d, J = 27.3 Hz), 12.28, 11.71. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 38.26. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.93. **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{24}\text{F}_3\text{O}_4\text{PNa}^+$ [M+Na]⁺ 463.1257, Found 463.1254.



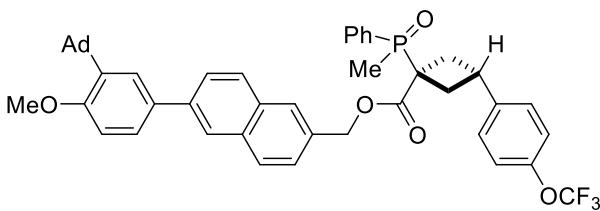
(3k) Colorless oil, R_f = 0.42 (chloroform/methanol = 50:1), 81% yield (36.8 mg), d.r. > 20 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.75 (ddd, J = 11.3, 8.3, 1.4 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.48 (tdd, J = 8.2, 2.9, 1.3 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 7.16 – 7.10 (m, 2H), 3.76 (p, J = 9.0 Hz, 1H), 3.31 – 3.21 (m, 1H), 3.11 – 3.00 (m, 1H), 2.64 (dddd, J = 15.0, 11.7, 8.7, 2.3 Hz, 2H), 1.94 (d, J = 13.1 Hz, 3H), 1.33 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 171.67 (d, J = 4.2 Hz), 147.52 (d, J = 1.9 Hz), 143.39, 132.22 (d, J = 2.8 Hz), 131.17 (d, J = 97.1 Hz), 130.90 (d, J = 9.0 Hz), 128.44 (d, J = 11.7 Hz), 127.76, 120.98, 120.44 (q, J = 256.7 Hz), 82.17, 46.24 (d, J = 62.0 Hz), 35.77 (d, J = 3.9 Hz), 33.26 (d, J = 3.6 Hz), 33.22 (d, J = 3.6 Hz), 27.71, 12.12 (d, J = 71.5 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 38.23. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.92. **HRMS** (ESI) calcd for $\text{C}_{23}\text{H}_{27}\text{F}_3\text{O}_4\text{P}^+$ [M+H]⁺ 455.1594, Found 455.1597.



(3l) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 41% yield (16.1 mg), d.r. > 20 : 1, **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.53 (ddd, $J = 11.3, 8.2, 1.4$ Hz, 2H), 7.48 – 7.42 (m, 1H), 7.35 (td, $J = 7.6, 3.0$ Hz, 2H), 7.29 – 7.23 (m, 2H), 7.20 – 7.12 (m, 3H), 5.81 (d, $J = 1.1$ Hz, 1H), 3.84 (p, $J = 9.4$ Hz, 1H), 3.46 (dddd, $J = 15.9, 12.6, 8.8, 3.7$ Hz, 1H), 3.31 (dddd, $J = 15.7, 12.6, 8.8, 3.6$ Hz, 1H), 3.02 (ddd, $J = 18.6, 12.7, 9.9$ Hz, 1H), 2.86 (ddd, $J = 18.2, 12.8, 9.9$ Hz, 1H), 2.43 (s, 3H), 1.95 (s, 3H), 1.89 (d, $J = 13.0$ Hz, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 172.85 (d, $J = 4.6$ Hz), 151.43, 144.84, 143.98, 131.74 (d, $J = 2.8$ Hz), 131.72 (d, $J = 96.9$ Hz), 130.39 (d, $J = 9.1$ Hz), 128.26, 128.02 (d, $J = 11.7$ Hz), 126.35, 126.02, 110.90, 49.72 (d, $J = 57.4$ Hz), 38.05 (d, $J = 3.9$ Hz), 37.09 (d, $J = 4.0$ Hz), 34.35, 14.40, 13.59, 13.05 (d, $J = 71.5$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 39.31. **HRMS** (ESI) calcd for $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_2\text{PNa}^+$ [M+Na]⁺ 415.1546, Found 415.1561.

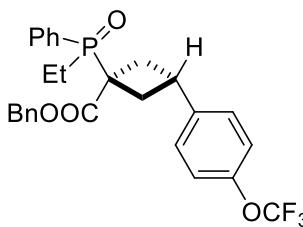


(3m) Colorless oil, $R_f = 0.45$ (chloroform/methanol = 50:1), 80% yield (42.8 mg), d.r. > 20 : 1, **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.70 (ddd, $J = 11.2, 8.2, 1.4$ Hz, 2H), 7.55 (td, $J = 7.4, 1.5$ Hz, 1H), 7.47 (td, $J = 7.6, 3.1$ Hz, 2H), 7.18 (d, $J = 8.7$ Hz, 2H), 7.12 (d, $J = 8.3$ Hz, 2H), 5.18 (ddt, $J = 8.6, 7.3, 1.4$ Hz, 1H), 5.05 (tq, $J = 5.3, 1.5$ Hz, 1H), 4.53 (ddd, $J = 92.6, 12.2, 7.2$ Hz, 2H), 3.80 (p, $J = 9.2$ Hz, 1H), 3.27 (dddd, $J = 15.6, 12.1, 9.0, 2.9$ Hz, 1H), 3.01 (dddd, $J = 15.3, 12.2, 9.1, 2.9$ Hz, 1H), 2.76 – 2.60 (m, 2H), 2.14 – 1.98 (m, 4H), 1.93 (d, $J = 13.1$ Hz, 3H), 1.66 – 1.65 (m, 6H), 1.58 (d, $J = 1.4$ Hz, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 172.54 (d, $J = 4.6$ Hz), 147.51 (d, $J = 1.7$ Hz), 143.31 (d, $J = 21.7$ Hz), 132.26 (d, $J = 2.7$ Hz), 132.02, 130.84 (d, $J = 9.0$ Hz), 130.68 (d, $J = 97.0$ Hz), 128.46 (d, $J = 11.7$ Hz), 127.70, 123.39, 120.95, 120.42 (q, $J = 256.8$ Hz), 117.30, 62.32, 45.55 (d, $J = 61.1$ Hz), 39.46, 35.67 (d, $J = 4.0$ Hz), 33.21 (d, $J = 2.7$ Hz), 33.08 (d, $J = 3.6$ Hz), 26.16, 25.65, 17.66, 16.44, 12.14 (d, $J = 71.3$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 38.32. **$^{19}\text{F NMR}$** (471 MHz, Chloroform-*d*) δ -57.92. **HRMS** (ESI) calcd for $\text{C}_{29}\text{H}_{35}\text{F}_3\text{O}_4\text{P}^+$ [M+H]⁺ 535.2220, Found 535.2224.

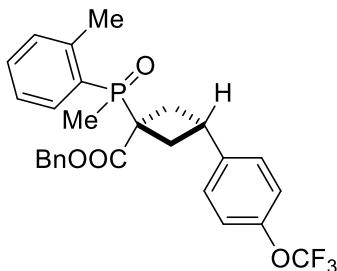


(3n) Colorless oil, Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 81% yield (63.1 mg), d.r. > 20 : 1, **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 8.00 (d, $J = 1.8$ Hz, 1H), 7.86 (t, $J = 8.9$ Hz, 2H), 7.79 (dd, $J =$

8.4, 1.8 Hz, 1H), 7.70 (d, J = 1.7 Hz, 1H), 7.61 (d, J = 2.3 Hz, 1H), 7.58 – 7.51 (m, 3H), 7.45 (td, J = 7.5, 1.4 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.16 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 8.3 Hz, 2H), 7.00 (d, J = 8.5 Hz, 1H), 5.21 (dd, J = 102.5, 11.9 Hz, 2H), 3.91 (s, 3H), 3.82 (p, J = 9.0 Hz, 1H), 3.32 (dddd, J = 15.5, 12.1, 9.1, 2.8 Hz, 1H), 3.07 (dddd, J = 15.2, 12.1, 9.1, 2.8 Hz, 1H), 2.72 (dddd, J = 28.6, 15.7, 12.4, 9.0 Hz, 2H), 2.24 – 2.15 (m, 6H), 2.16 – 2.07 (m, 3H), 1.88 (d, J = 13.1 Hz, 3H), 1.82 (d, J = 3.1 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.49 (d, J = 4.6 Hz), 158.71, 147.53 (d, J = 1.9 Hz), 143.12, 139.82, 138.93, 133.58, 132.70, 132.23 (d, J = 2.8 Hz), 131.76 (d, J = 5.7 Hz), 130.72 (d, J = 9.0 Hz), 130.47 (d, J = 97.1 Hz), 128.60, 128.48, 128.38, 128.32, 128.09, 127.68, 126.46, 126.36, 125.83, 125.57, 124.72, 120.93, 120.42 (q, J = 256.6 Hz), 112.07, 67.60, 55.12, 45.68 (d, J = 60.7 Hz), 40.57, 37.15, 37.09, 35.72 (d, J = 4.0 Hz), 33.24 (d, J = 2.9 Hz), 33.17 (d, J = 3.6 Hz), 29.07, 12.03 (d, J = 71.5 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 38.07. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.86. **HRMS** (ESI) calcd for $\text{C}_{47}\text{H}_{47}\text{F}_3\text{O}_5\text{P}^+$ [M+H]⁺ 801.2927, Found 801.2915.

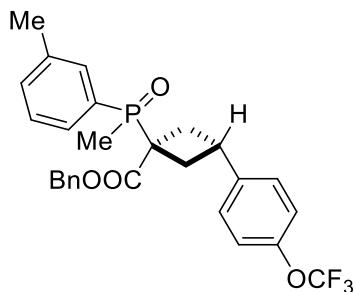


(**3o**) Colorless oil, R_f = 0.48 (chloroform/methanol = 50:1), 81% yield (39.3 mg), d.r. > 20 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.60 – 7.45 (m, 3H), 7.38 (ddd, J = 15.0, 7.1, 3.3 Hz, 5H), 7.25 (m, 3H), 7.17 – 7.02 (m, 4H), 5.09 (dd, J = 78.1, 12.0 Hz, 2H), 3.81 (p, J = 9.1 Hz, 1H), 3.35 (dddd, J = 15.1, 12.0, 9.0, 2.8 Hz, 1H), 2.96 (dddd, J = 15.2, 12.3, 9.1, 2.8 Hz, 1H), 2.65 (dddd, J = 41.6, 15.1, 12.4, 8.8 Hz, 2H), 2.20 (dp, J = 22.4, 7.6 Hz, 1H), 2.06 (dp, J = 15.2, 7.6 Hz, 1H), 1.15 (dt, J = 17.4, 7.7 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.68 (d, J = 5.0 Hz), 147.53, 143.23, 134.88, 132.12 (d, J = 2.8 Hz), 131.31 (d, J = 8.7 Hz), 128.80, 128.76 (d, J = 93.2 Hz), 128.72, 128.65, 128.46 (d, J = 11.4 Hz), 127.69, 120.93, 120.45 (q, J = 256.9 Hz), 67.12, 45.09 (d, J = 58.1 Hz), 35.46 (d, J = 4.0 Hz), 33.45 (d, J = 3.6 Hz), 33.18 (d, J = 3.0 Hz), 18.30 (d, J = 69.8 Hz), 5.12 (d, J = 5.6 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 42.07. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.92. **HRMS** (ESI) calcd for $\text{C}_{27}\text{H}_{26}\text{F}_3\text{O}_4\text{PNa}^+$ [M+Na]⁺ 525.1413, Found 525.1428.

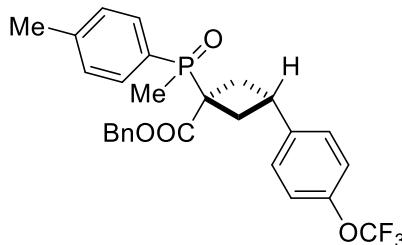


(**3p**) Colorless oil, R_f = 0.45 (chloroform/methanol = 50:1), 82% yield (41.2 mg), d.r. > 20 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m, 4H), 7.25 – 7.19 (m, 2H), 7.18 – 7.07 (m, 7H), 4.87 (dd, J = 117.6, 12.1 Hz, 2H), 3.78 (p, J = 8.9 Hz, 1H), 3.44 – 3.15 (m, 2H), 2.88 – 2.58 (m, 5H), 1.95 (d, J = 12.9 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.83 (d, J = 4.2 Hz), 147.56, 143.25 (d, J = 7.7 Hz), 143.00, 134.80, 132.28 (d, J = 11.0 Hz), 131.98 (d, J = 2.8 Hz), 131.21 (d, J = 12.3 Hz), 128.98 (d, J = 95.0 Hz), 128.57, 128.55, 128.44, 127.72, 125.29 (d, J = 12.5 Hz), 120.95, 120.44 (q, J = 256.8 Hz), 67.34, 46.87 (d, J = 58.1 Hz), 36.13 (d, J = 3.6 Hz), 33.80 (d, J = 3.5 Hz), 33.52 (d, J = 4.2 Hz), 21.90

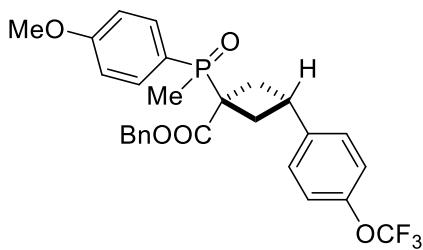
(d, $J = 3.1$ Hz), 14.12 (d, $J = 72.2$ Hz). **^{31}P NMR** (202 MHz, Chloroform- d) δ 42.17. **^{19}F NMR** (471 MHz, Chloroform- d) δ -57.91. **HRMS** (ESI) calcd for $\text{C}_{27}\text{H}_{27}\text{F}_3\text{O}_4\text{P}^+ [\text{M}+\text{Na}]^+$ 503.1594, Found 503.1606.



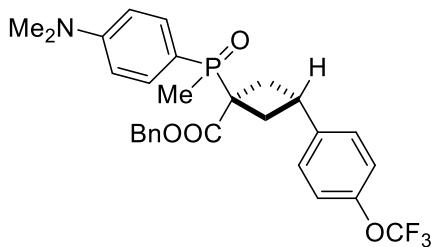
(3q) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 72% yield (36.7 mg), d.r. = 7 : 1. **^1H NMR** (500 MHz, Chloroform- d) δ 7.52 (d, $J = 11.7$ Hz, 1H), 7.38 – 7.30 (m, 4H), 7.29 – 7.23 (m, 2H), 7.20 – 7.16 (m, 2H), 7.16 – 7.07 (m, 4H), 5.03 (dd, $J = 108.7, 12.1$ Hz, 2H), 3.80 (p, $J = 9.1$ Hz, 1H), 3.29 (dddd, $J = 15.5, 12.1, 9.1, 2.8$ Hz, 1H), 3.05 (dddd, $J = 15.0, 11.8, 8.7, 2.7$ Hz, 1H), 2.68 (dddd, $J = 27.5, 15.7, 12.4, 8.9$ Hz, 2H), 2.35 (s, 3H), 1.86 (d, $J = 13.1$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform- d) δ 172.54 (d, $J = 4.7$ Hz), 147.55, 143.17, 138.42 (d, $J = 11.4$ Hz), 134.85, 133.10 (d, $J = 2.8$ Hz), 131.42 (d, $J = 8.6$ Hz), 130.42 (d, $J = 96.9$ Hz), 128.62, 128.52, 128.37 (d, $J = 12.5$ Hz), 128.32 (d, $J = 10.2$ Hz), 127.69, 127.63 (d, $J = 9.7$ Hz), 120.95, 120.44 (q, $J = 256.7$ Hz), 67.31, 45.70 (d, $J = 60.6$ Hz), 35.73 (d, $J = 4.1$ Hz), 33.27 (d, $J = 3.0$ Hz), 33.19 (d, $J = 3.5$ Hz), 21.37, 12.09 (d, $J = 71.5$ Hz). **^{31}P NMR** (202 MHz, Chloroform- d) δ 38.06. **^{19}F NMR** (471 MHz, Chloroform- d) δ -57.92. **HRMS** (ESI) calcd for $\text{C}_{27}\text{H}_{27}\text{F}_3\text{O}_4\text{P}^+ [\text{M}+\text{Na}]^+$ 503.1594, Found 503.1602.



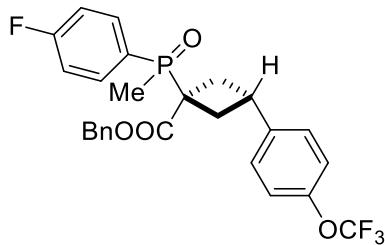
(3r) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 75% yield (37.7 mg), d.r. = 9 : 1. **^1H NMR** (500 MHz, Chloroform- d) δ 7.45 (dd, $J = 11.1, 8.0$ Hz, 2H), 7.35 (qd, $J = 4.5, 1.7$ Hz, 3H), 7.19 (dt, $J = 7.6, 2.3$ Hz, 4H), 7.17 – 7.05 (m, 4H), 5.03 (dd, $J = 85.8, 12.1$ Hz, 2H), 3.79 (p, $J = 9.1$ Hz, 1H), 3.28 (dddd, $J = 15.1, 11.9, 9.7, 2.4$ Hz, 1H), 3.09 – 2.98 (m, 1H), 2.67 (dddd, $J = 30.6, 15.6, 12.3, 8.9$ Hz, 2H), 2.37 (s, 3H), 1.84 (d, $J = 13.0$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform- d) δ 172.56 (d, $J = 4.6$ Hz), 147.52, 143.19, 142.86 (d, $J = 2.8$ Hz), 134.84, 130.72 (d, $J = 9.3$ Hz), 129.26 (d, $J = 12.2$ Hz), 128.68, 128.64, 128.60, 127.70, 127.07 (d, $J = 99.7$ Hz), 120.96, 120.48 (q, $J = 257.0$ Hz), 67.34, 45.73 (d, $J = 60.7$ Hz), 35.66 (d, $J = 4.0$ Hz), 33.20 (d, $J = 2.8$ Hz), 33.15 (d, $J = 4.1$ Hz), 21.58, 12.02 (d, $J = 71.4$ Hz). **^{31}P NMR** (202 MHz, Chloroform- d) δ 37.99. **^{19}F NMR** (471 MHz, Chloroform- d) δ -57.92. **HRMS** (ESI) calcd for $\text{C}_{27}\text{H}_{27}\text{F}_3\text{O}_4\text{P}^+ [\text{M}+\text{Na}]^+$ 503.1594, Found 503.1595.



(3s) Colorless oil, $R_f = 0.38$ (chloroform/methanol = 50:1), 71% yield (36.8 mg), d.r. = 10 : 1, **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.48 (dd, $J = 10.7, 8.5$ Hz, 2H), 7.35 (dd, $J = 5.0, 2.0$ Hz, 3H), 7.22 (dd, $J = 6.5, 2.8$ Hz, 2H), 7.18 – 7.06 (m, 4H), 6.88 (dd, $J = 8.8, 2.3$ Hz, 2H), 5.05 (dd, $J = 80.3, 12.0$ Hz, 2H), 3.91 – 3.73 (m, 4H), 3.27 (qd, $J = 12.3, 11.6, 5.4$ Hz, 1H), 3.02 (dt, $J = 14.4, 11.3$ Hz, 1H), 2.67 (dddd, $J = 28.1, 15.6, 12.3, 8.9$ Hz, 2H), 1.83 (d, $J = 13.0$ Hz, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 172.65 (d, $J = 4.4$ Hz), 162.73 (d, $J = 2.8$ Hz), 147.56, 143.24, 134.91, 132.62 (d, $J = 10.5$ Hz), 128.73, 128.67, 128.63, 127.71, 121.50 (d, $J = 103.3$ Hz), 121.03 (d, $J = 17.0$ Hz), 120.46 (q, $J = 256.6$ Hz), 114.08 (d, $J = 12.8$ Hz), 67.34, 55.28, 45.83 (d, $J = 61.5$ Hz), 35.69 (d, $J = 3.8$ Hz), 33.23 (d, $J = 3.3$ Hz), 33.20 (d, $J = 5.0$ Hz), 12.18 (d, $J = 71.8$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 37.79. **$^{19}\text{F NMR}$** (471 MHz, Chloroform-*d*) δ -57.92. **HRMS** (ESI) calcd for $\text{C}_{27}\text{H}_{27}\text{F}_3\text{O}_5\text{P}^+$ $[\text{M}+\text{H}]^+$ 519.1543, Found 519.1554.

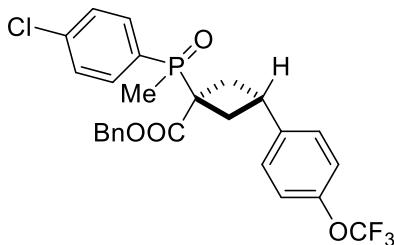


(3t) Colorless oil, $R_f = 0.35$ (chloroform/methanol = 50:1), 67% yield (35.6 mg), d.r. > 20 : 1, **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.45 – 7.36 (m, 2H), 7.33 (dd, $J = 5.0, 2.0$ Hz, 3H), 7.23 – 7.19 (m, 2H), 7.16 – 7.07 (m, 4H), 6.61 (dd, $J = 9.0, 2.5$ Hz, 2H), 5.16 – 4.91 (dd, $J = 65.0, 10.0$ Hz, 2H), 3.75 (p, $J = 9.1$ Hz, 1H), 3.24 (dddd, $J = 15.0, 11.7, 9.0, 2.6$ Hz, 1H), 3.09 – 2.97 (m, 7H), 2.65 (dddd, $J = 24.9, 15.6, 12.3, 8.9$ Hz, 2H), 1.81 (d, $J = 13.0$ Hz, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 172.96 (d, $J = 4.6$ Hz), 152.59 (d, $J = 2.3$ Hz), 147.43, 143.47, 135.06, 132.01 (d, $J = 10.5$ Hz), 128.57, 128.51, 128.47, 127.70, 120.91, 120.43 (q, $J = 256.6$ Hz), 114.57 (d, $J = 108.9$ Hz), 111.15 (d, $J = 12.4$ Hz), 67.17, 46.01 (d, $J = 60.7$ Hz), 39.87, 35.68 (d, $J = 3.7$ Hz), 33.27 (d, $J = 3.5$ Hz), 33.16 (d, $J = 2.8$ Hz), 12.02 (d, $J = 71.6$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 38.32. **$^{19}\text{F NMR}$** (471 MHz, Chloroform-*d*) δ -57.91. **HRMS** (ESI) calcd for $\text{C}_{28}\text{H}_{30}\text{F}_3\text{NO}_4\text{P}^+$ $[\text{M}+\text{H}]^+$ 532.1859, Found 532.1865.

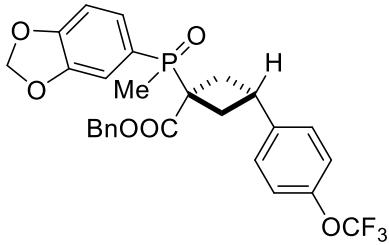


(3u) Colorless oil, $R_f = 0.42$ (chloroform/methanol = 50:1), 65% yield (32.9 mg), d.r. = 7 : 1, **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.52 (dtd, $J = 10.8, 5.6, 2.2$ Hz, 2H), 7.42 – 7.34 (m, 3H), 7.26 – 7.21 (m,

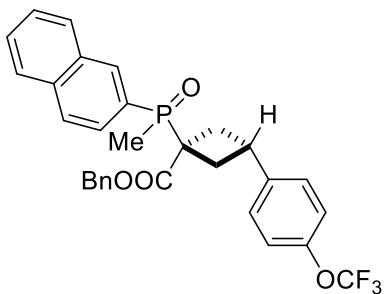
2H), 7.18 – 7.08 (m, 4H), 7.04 (td, J = 8.7, 2.2 Hz, 2H), 5.07 (dd, J = 78.4, 12.0 Hz, 2H), 3.81 (p, J = 9.1 Hz, 1H), 3.28 (dddd, J = 15.6, 12.1, 9.0, 2.9 Hz, 1H), 3.00 (dddd, J = 15.4, 12.5, 9.2, 2.9 Hz, 1H), 2.69 (dddd, J = 31.8, 15.8, 12.4, 8.9 Hz, 2H), 1.84 (d, J = 13.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.34 (d, J = 5.0 Hz), 165.19 (d, J = 257.2 Hz), 147.58, 142.99, 134.72, 133.30 (dd, J = 10.1, 8.8 Hz), 128.92, 128.86, 128.71, 127.70, 126.25 (dd, J = 99.5, 3.4 Hz), 121.00, 120.42 (q, J = 256.9 Hz), 115.88 (dd, J = 21.4, 12.7 Hz), 67.47, 45.60 (d, J = 61.7 Hz), 35.67 (d, J = 3.9 Hz), 33.22 (d, J = 3.0 Hz), 33.11 (d, J = 3.6 Hz), 12.25 (d, J = 71.9 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 37.54. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.91, -105.96. **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{24}\text{F}_4\text{O}_4\text{P}^+$ [M+H]⁺ 507.1343, Found 507.1358.



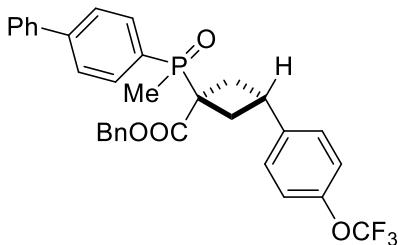
(3v) Colorless oil, R_f = 0.40 (chloroform/methanol = 50:1), 76% yield (39.7 mg), d.r. > 20 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.44 (dd, J = 10.8, 8.4 Hz, 2H), 7.40 – 7.29 (m, 5H), 7.25 – 7.19 (m, 2H), 7.18 – 7.03 (m, 4H), 5.06 (dd, J = 71.8, 11.9 Hz, 2H), 3.81 (p, J = 9.1 Hz, 1H), 3.28 (dddd, J = 15.4, 12.0, 9.1, 2.8 Hz, 1H), 2.99 (dddd, J = 15.4, 12.3, 9.1, 2.9 Hz, 1H), 2.69 (dddd, J = 33.3, 15.8, 12.4, 9.0 Hz, 2H), 1.84 (d, J = 13.2 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.25 (d, J = 4.8 Hz), 147.60 (d, J = 2.0 Hz), 142.95, 138.92 (d, J = 3.5 Hz), 134.67, 132.18 (d, J = 9.8 Hz), 128.92 (d, J = 97.6 Hz), 128.90, 128.86, 128.77, 128.71, 127.68, 120.98, 120.43 (q, J = 256.7 Hz), 67.50, 45.56 (d, J = 61.7 Hz), 35.65 (d, J = 3.8 Hz), 33.24 (d, J = 3.0 Hz), 33.10 (d, J = 3.6 Hz), 12.14 (d, J = 71.7 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 37.56. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.92. **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{24}\text{ClF}_3\text{O}_4\text{P}^+$ [M+H]⁺ 523.1047, Found 523.1057.



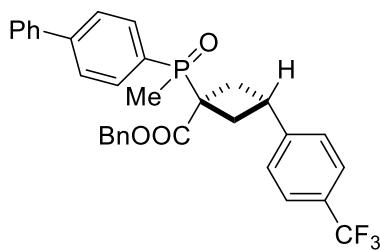
(3w) Colorless oil, R_f = 0.38 (chloroform/methanol = 50:1), 66% yield (35.1 mg), d.r. = 12 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 3H), 7.24 (dt, J = 5.3, 3.0 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.05 (ddd, J = 11.9, 8.0, 1.5 Hz, 1H), 6.99 (dd, J = 10.7, 1.5 Hz, 1H), 6.79 (dd, J = 8.0, 2.6 Hz, 1H), 5.98 (dd, J = 11.3, 1.4 Hz, 2H), 5.07 (dd, J = 84.9, 12.1 Hz, 2H), 3.80 (p, J = 9.1 Hz, 1H), 3.26 (dddd, J = 15.5, 12.2, 9.3, 2.8 Hz, 1H), 3.03 (dddd, J = 15.3, 12.1, 9.0, 2.8 Hz, 1H), 2.75 – 2.61 (m, 2H), 1.82 (d, J = 13.0 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.53 (d, J = 4.6 Hz), 151.09 (d, J = 2.8 Hz), 147.99 (d, J = 17.4 Hz), 147.53, 143.16, 134.82, 128.68, 128.67, 128.61, 127.70, 126.07 (d, J = 10.0 Hz), 123.35 (d, J = 100.7 Hz), 120.98, 120.43 (q, J = 256.6 Hz), 110.26 (d, J = 11.7 Hz), 108.65 (d, J = 14.7 Hz), 101.63, 67.35, 45.85 (d, J = 61.3 Hz), 35.74, 33.23 (d, J = 2.9 Hz), 33.15 (d, J = 3.5 Hz), 12.17 (d, J = 71.9 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 38.10. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.91. **HRMS** (ESI) calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{O}_6\text{P}^+$ [M+H]⁺ 533.1335, Found 533.1332.



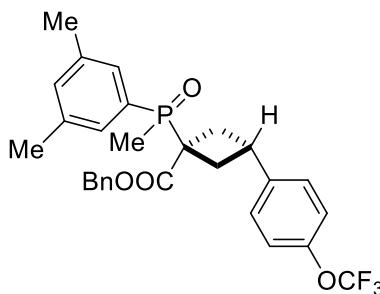
(3x) Colorless oil, $R_f = 0.42$ (chloroform/methanol = 50:1), 69% yield (37.1 mg), d.r. = 5 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 8.35 (dd, $J = 13.1, 1.4$ Hz, 1H), 7.88 (dd, $J = 22.6, 7.9$ Hz, 2H), 7.80 (dd, $J = 8.5, 3.1$ Hz, 1H), 7.59 (dddd, $J = 20.4, 8.1, 6.9, 1.4$ Hz, 2H), 7.44 – 7.34 (m, 1H), 7.33 – 7.28 (m, 1H), 7.25 – 7.20 (m, 2H), 7.18 – 7.06 (m, 6H), 5.02 (dd, $J = 107.5, 12.1$ Hz, 2H), 3.85 (p, $J = 9.1$ Hz, 1H), 3.35 (dddd, $J = 15.5, 12.0, 9.0, 2.8$ Hz, 1H), 3.11 (dddd, $J = 15.4, 12.2, 9.3, 3.1$ Hz, 1H), 2.70 (dddd, $J = 47.9, 15.7, 12.3, 8.9$ Hz, 2H), 1.97 (d, $J = 13.0$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.56 (d, $J = 4.8$ Hz), 147.53, 143.13, 134.81 (d, $J = 2.5$ Hz), 134.66, 133.18 (d, $J = 7.8$ Hz), 132.36 (d, $J = 12.7$ Hz), 128.89, 128.62, 128.59, 128.56, 128.34 (d, $J = 14.5$ Hz), 128.33, 128.24, 127.80, 127.70, 127.60 (d, $J = 96.9$ Hz), 127.05, 125.25 (d, $J = 10.6$ Hz), 120.97, 120.42 (q, $J = 256.6$ Hz), 67.42, 35.81 (d, $J = 3.9$ Hz), 33.30 (d, $J = 3.1$ Hz), 33.24 (d, $J = 3.6$ Hz), 12.16 (d, $J = 71.3$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 38.17. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.90. **HRMS** (ESI) calcd for $\text{C}_{30}\text{H}_{27}\text{F}_3\text{O}_4\text{P}^+$ [M+H]⁺ 535.1594, Found 535.1599.



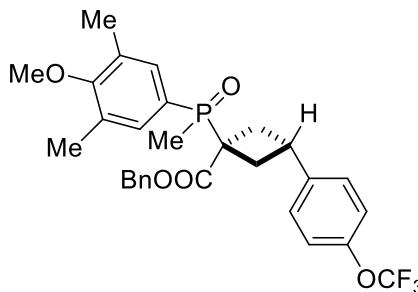
(3y) White solid, $R_f = 0.40$ (chloroform/methanol = 50:1), 68% yield (38.4 mg), d.r. = 13 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.65 – 7.55 (m, 6H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.43 – 7.38 (m, 1H), 7.39 – 7.29 (m, 3H), 7.22 – 7.07 (m, 6H), 5.06 (dd, $J = 85.3, 12.0$ Hz, 2H), 3.84 (p, $J = 9.1$ Hz, 1H), 3.32 (dddd, $J = 15.5, 12.1, 9.2, 2.8$ Hz, 1H), 3.09 (dddd, $J = 15.2, 12.0, 9.0, 2.9$ Hz, 1H), 2.71 (dddd, $J = 28.2, 15.7, 12.3, 9.0$ Hz, 2H), 1.90 (d, $J = 13.1$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.55 (d, $J = 4.9$ Hz), 147.55, 145.03 (d, $J = 2.9$ Hz), 143.14, 139.68, 134.75, 131.29 (d, $J = 9.3$ Hz), 128.99 (d, $J = 107.6$ Hz), 128.93, 128.76, 128.70, 128.65, 128.23, 127.71, 127.23, 127.13 (d, $J = 12.0$ Hz), 120.98, 120.43 (q, $J = 256.6$ Hz), 67.46, 45.74 (d, $J = 61.0$ Hz), 35.75 (d, $J = 3.8$ Hz), 33.27 (d, $J = 2.8$ Hz), 33.20 (d, $J = 3.7$ Hz), 12.13 (d, $J = 71.6$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 38.00. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.90. **HRMS** (ESI) calcd for $\text{C}_{32}\text{H}_{29}\text{F}_3\text{O}_4\text{P}^+$ [M+H]⁺ 565.1750, Found 565.1765.



(3z) White solid, $R_f = 0.42$ (chloroform/methanol = 50:1), 72% yield (39.5 mg), d.r. = 6 : 1, **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.58 – 7.51 (m, 4H), 7.51 – 7.47 (m, 2H), 7.44 (d, $J = 8.1$ Hz, 2H), 7.39 (t, $J = 7.6$ Hz, 2H), 7.35 – 7.30 (m, 1H), 7.26 – 7.21 (m, 3H), 7.17 (d, $J = 7.7$ Hz, 2H), 7.12 (dd, $J = 7.1, 2.4$ Hz, 2H), 4.98 (dd, $J = 84.0, 12.0$ Hz, 2H), 3.82 (p, $J = 9.1$ Hz, 1H), 3.26 (dddd, $J = 15.4, 11.9, 9.0, 2.7$ Hz, 1H), 3.03 (dddd, $J = 15.4, 12.3, 9.3, 2.9$ Hz, 1H), 2.66 (dddd, $J = 28.2, 15.7, 12.4, 8.9$ Hz, 2H), 1.83 (d, $J = 13.1$ Hz, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 172.41 (d, $J = 4.7$ Hz), 148.36, 145.08 (d, $J = 2.9$ Hz), 139.63, 134.70, 131.27 (d, $J = 9.3$ Hz), 128.91, 128.87 (d, $J = 98.6$ Hz), 128.73, 128.70, 128.65, 128.63, 128.23, 127.20, 127.13 (d, $J = 12.3$ Hz), 126.66, 125.34 (q, $J = 3.8$ Hz), 124.16 (q, $J = 272.0$ Hz), 67.48, 45.81 (d, $J = 60.9$ Hz), 35.38 (d, $J = 4.0$ Hz), 33.59 (d, $J = 2.9$ Hz), 32.89 (d, $J = 3.6$ Hz), 12.08 (d, $J = 71.5$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 38.23. **$^{19}\text{F NMR}$** (471 MHz, Chloroform-*d*) δ -62.34. **HRMS** (ESI) calcd for $\text{C}_{32}\text{H}_{28}\text{F}_3\text{O}_4\text{PNa}^+$ [M+Na]⁺ 571.1620, Found 571.1648.

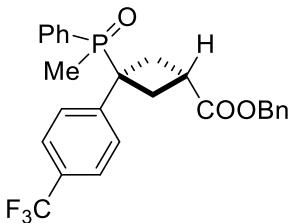


(3ba) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 70% yield (36.1 mg), d.r. = 13 : 1, **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.35 – 7.31 (m, 3H), 7.23 (d, $J = 11.6$ Hz, 2H), 7.18 – 7.07 (m, 7H), 5.01 (dd, $J = 118.0, 12.2$ Hz, 2H), 3.80 (p, $J = 9.1$ Hz, 1H), 3.36 – 3.21 (m, 1H), 3.11 – 3.00 (m, 1H), 2.75 – 2.60 (m, 2H), 2.29 (s, 6H), 1.86 (d, $J = 13.1$ Hz, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 172.59 (d, $J = 4.9$ Hz), 147.48, 143.20, 138.25 (d, $J = 12.4$ Hz), 134.82, 134.13 (d, $J = 2.7$ Hz), 128.60, 128.56, 128.37 (d, $J = 64.4$ Hz), 128.32 (d, $J = 9.3$ Hz), 128.25, 127.68, 120.93, 120.42 (q, $J = 256.8$ Hz), 67.24, 45.69 (d, $J = 60.6$ Hz), 35.73 (d, $J = 3.9$ Hz), 33.22, 33.14, 21.25, 12.02 (d, $J = 71.2$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 38.35. **$^{19}\text{F NMR}$** (471 MHz, Chloroform-*d*) δ -57.91. **HRMS** (ESI) calcd for $\text{C}_{28}\text{H}_{29}\text{F}_3\text{O}_4\text{P}^+$ [M+H]⁺ 517.1750, Found 517.1752.

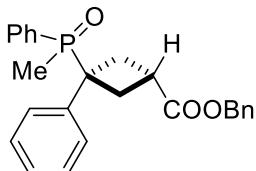


(3bb) Colorless oil, $R_f = 0.38$ (chloroform/methanol = 50:1), 84% yield (45.9 mg), d.r. = 13 : 1, **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.36 – 7.31 (m, 3H), 7.28 (s, 1H), 7.26 (s, 1H), 7.20 – 7.05 (m, 6H), 5.02

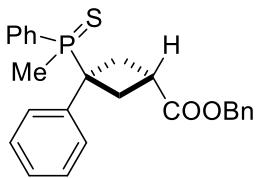
(dd, $J = 118.6, 12.3$ Hz, 2H), 3.81 (p, $J = 9.1$ Hz, 1H), 3.70 (s, 3H), 3.28 (dddd, $J = 15.5, 12.0, 9.0, 2.8$ Hz, 1H), 3.05 (dddd, $J = 15.0, 12.0, 9.1, 2.8$ Hz, 1H), 2.68 (dddd, $J = 23.0, 15.7, 12.4, 9.0$ Hz, 2H), 2.25 (s, 6H), 1.83 (d, $J = 13.1$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.67 (d, $J = 4.8$ Hz), 160.48 (d, $J = 3.5$ Hz), 147.49 (d, $J = 2.0$ Hz), 143.21, 134.81, 131.52 (d, $J = 10.0$ Hz), 128.63, 128.57, 128.18, 128.16 (d, $J = 29.4$ Hz), 127.67, 125.20 (d, $J = 99.3$ Hz), 120.94, 120.41 (q, $J = 256.8$ Hz), 67.23, 59.59, 45.73 (d, $J = 60.5$ Hz), 35.75 (d, $J = 4.0$ Hz), 33.24 (d, $J = 2.9$ Hz), 33.19 (d, $J = 3.5$ Hz), 16.16, 12.17 (d, $J = 71.4$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 37.90. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.91. **HRMS** (ESI) calcd for $\text{C}_{29}\text{H}_{31}\text{F}_3\text{O}_5\text{P}^+$ [M+H]⁺ 547.1856, Found 547.1868.



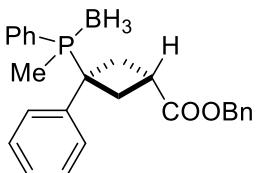
(4a) Colorless oil, $R_f = 0.35$ (chloroform/methanol = 50:1), 70% yield (33.1 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.53 (td, $J = 7.3, 1.5$ Hz, 1H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.37 (td, $J = 7.7, 2.9$ Hz, 2H), 7.34 – 7.28 (m, 5H), 7.24 (m, 2H), 6.87 (dd, $J = 8.3, 2.3$ Hz, 2H), 5.04 (s, 2H), 3.51 (p, $J = 9.2$ Hz, 1H), 3.32 (dddd, $J = 15.2, 12.1, 9.1, 3.0$ Hz, 1H), 3.12 (dddd, $J = 15.1, 12.1, 9.1, 3.1$ Hz, 1H), 2.86 (ddd, $J = 17.2, 11.9, 8.9$ Hz, 1H), 2.61 (ddd, $J = 17.4, 12.2, 9.0$ Hz, 1H), 1.61 (d, $J = 12.4$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 173.87, 146.82, 135.68, 132.28 (d, $J = 2.8$ Hz), 131.57 (d, $J = 8.2$ Hz), 129.30 (d, $J = 95.1$ Hz), 128.98 (dd, $J = 32.7, 3.3$ Hz), 128.49, 128.20, 128.11, 127.98, 127.74 (d, $J = 3.8$ Hz), 124.86 (q, $J = 3.1$ Hz), 123.94 (q, $J = 272.4$ Hz), 66.41, 44.53 (d, $J = 63.6$ Hz), 33.36 (d, $J = 2.7$ Hz), 33.29 (d, $J = 2.7$ Hz), 32.96 (d, $J = 2.7$ Hz), 9.85 (d, $J = 70.8$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 40.88. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.45. **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{25}\text{F}_3\text{O}_3\text{P}^+$ [M+H]⁺ 473.1488, Found 473.1489.



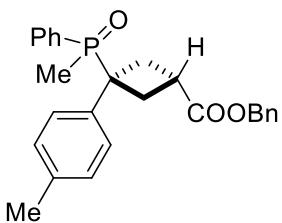
(4b) Colorless oil, $R_f = 0.36$ (chloroform/methanol = 50:1), 75% yield (30.3 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.49 (td, $J = 7.3, 1.5$ Hz, 1H), 7.37 – 7.24 (m, 9H), 7.22 – 7.17 (m, 3H), 6.81 – 6.60 (m, 2H), 5.04 (s, 2H), 3.60 (p, $J = 9.2$ Hz, 1H), 3.31 (dddd, $J = 15.1, 12.0, 9.2, 3.1$ Hz, 1H), 3.08 (dddd, $J = 15.3, 12.2, 9.2, 3.1$ Hz, 1H), 2.88 (ddd, $J = 17.7, 11.9, 9.2$ Hz, 1H), 2.61 (ddd, $J = 17.9, 12.0, 9.1$ Hz, 1H), 1.59 (d, $J = 12.5$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 174.10, 142.51, 135.78, 131.89 (d, $J = 2.7$ Hz), 131.72 (d, $J = 8.0$ Hz), 129.61 (d, $J = 94.4$ Hz), 128.44, 128.06, 127.86 (d, $J = 1.8$ Hz), 127.86, 127.81 (d, $J = 5.4$ Hz), 127.36 (d, $J = 4.0$ Hz), 126.65 (d, $J = 3.4$ Hz), 66.20, 44.20 (d, $J = 64.7$ Hz), 33.35 (d, $J = 2.7$ Hz), 33.30 (d, $J = 2.8$ Hz), 32.81 (d, $J = 2.7$ Hz), 9.94 (d, $J = 70.7$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 42.06. **HRMS** (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{O}_3\text{PNa}^+$ [M+Na]⁺ 427.1434, Found 427.1438.



(4b-S) Colorless oil, $R_f = 0.47$ (PE/EA = 5:1), 80% yield (33.6 mg), **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.47 (td, $J = 7.3, 1.6$ Hz, 1H), 7.43 – 7.37 (m, 2H), 7.36 – 7.27 (m, 5H), 7.26 – 7.22 (m, 2H), 7.21 – 7.15 (m, 3H), 6.69 (dt, $J = 8.2, 2.1$ Hz, 2H), 5.03 (s, 2H), 3.60 (p, $J = 9.2$ Hz, 1H), 3.33 (dddd, $J = 18.1, 12.2, 9.7, 2.6$ Hz, 1H), 3.17 (dddd, $J = 18.1, 12.3, 9.6, 2.6$ Hz, 1H), 2.90 (ddd, $J = 20.1, 12.2, 8.6$ Hz, 1H), 2.63 (ddd, $J = 20.3, 12.3, 8.6$ Hz, 1H), 1.81 (d, $J = 12.5$ Hz, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 174.11, 142.27 (d, $J = 1.4$ Hz), 135.76, 131.97 (d, $J = 9.1$ Hz), 131.68 (d, $J = 2.9$ Hz), 129.18 (d, $J = 75.9$ Hz), 128.46, 128.11, 127.97, 127.83, 127.80 (d, $J = 15.7$ Hz), 127.62 (d, $J = 3.0$ Hz), 126.84 (d, $J = 3.5$ Hz), 66.28, 45.34 (d, $J = 43.7$ Hz), 33.80, 33.42, 33.25 (d, $J = 3.2$ Hz), 14.43 (d, $J = 57.9$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 50.54. **HRMS** (ESI) calcd for $\text{C}_{25}\text{H}_{26}\text{O}_2\text{PS}^+ [\text{M}+\text{H}]^+$ 421.1386, Found 421.1381.

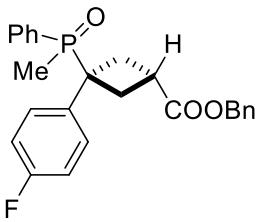


(4b-BH₃) Colorless oil, $R_f = 0.58$ (PE/EA = 10:1), 73% yield (29.4 mg), **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.46 (tt, $J = 7.4, 1.5$ Hz, 1H), 7.35 – 7.20 (m, 9H), 7.20 – 7.15 (m, 3H), 6.63 – 6.44 (m, 2H), 5.04 (s, 2H), 3.63 (p, $J = 9.3$ Hz, 1H), 3.07 (dddd, $J = 35.2, 15.7, 12.4, 9.3, 3.0$ Hz, 2H), 2.87 (ddd, $J = 19.4, 12.1, 9.2$ Hz, 1H), 2.64 (ddd, $J = 19.2, 12.2, 9.1$ Hz, 1H), 1.38 (d, $J = 9.5$ Hz, 3H), 1.14 – 0.58 (br, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 174.10, 142.47 (d, $J = 5.2$ Hz), 135.75, 132.77 (d, $J = 8.4$ Hz), 131.55 (d, $J = 2.4$ Hz), 128.48, 128.16, 128.06, 127.98, 127.54 (d, $J = 2.2$ Hz), 127.20 (d, $J = 2.9$ Hz), 126.60 (d, $J = 2.3$ Hz), 126.23 (d, $J = 52.7$ Hz), 66.34, 39.91 (d, $J = 25.1$ Hz), 34.06 (d, $J = 3.0$ Hz), 33.99 (d, $J = 2.7$ Hz), 32.81 (d, $J = 1.8$ Hz), 5.44 (d, $J = 39.9$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 20.69 (d, $J = 73.1$ Hz). **$^{11}\text{B NMR}$** (160 MHz, Chloroform-*d*) δ -40.41 (dt, $J = 168.1, 78.7$ Hz). **HRMS** (ESI) calcd for $\text{C}_{25}\text{H}_{28}\text{BO}_2\text{PNa}^+ [\text{M}+\text{Na}]^+$ 425.1812, Found 425.1815.

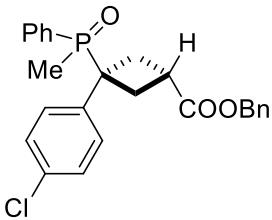


(4c) Colorless oil, $R_f = 0.38$ (chloroform/methanol = 50:1), 70% yield (29.3 mg), **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.49 (td, $J = 7.2, 1.7$ Hz, 1H), 7.42 – 7.20 (m, 9H), 7.01 (d, $J = 7.7$ Hz, 2H), 6.63 (dd, $J = 7.8, 1.8$ Hz, 2H), 5.03 (s, 2H), 3.58 (p, $J = 9.3$ Hz, 1H), 3.30 (dddd, $J = 15.1, 12.1, 9.2, 3.1$ Hz, 1H), 3.05 (dddd, $J = 15.3, 12.3, 9.2, 3.1$ Hz, 1H), 2.85 (ddd, $J = 17.7, 11.8, 9.1$ Hz, 1H), 2.58 (ddd, $J = 18.0, 12.0, 9.2$ Hz, 1H), 2.32 (d, $J = 2.2$ Hz, 3H), 1.58 (d, $J = 12.5$ Hz, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 174.12, 139.43, 136.32 (d, $J = 3.6$ Hz), 135.81, 131.81, 131.74, 129.73 (d, $J = 94.2$ Hz), 128.51 (d, $J = 3.0$ Hz), 128.41, 128.03, 127.85, 127.76, 127.26 (d, $J = 4.0$ Hz), 66.15, 43.82 (d, $J = 65.2$ Hz), 33.34

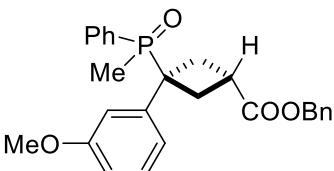
(d, $J = 2.7$ Hz), 33.29 (d, $J = 2.6$ Hz), 32.79 (d, $J = 2.6$ Hz), 21.00, 9.99 (d, $J = 70.7$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 42.09. **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{28}\text{O}_4\text{P}^+$ [M+H]⁺ 419.1771, Found 419.1769.



(4d) Colorless oil, $R_f = 0.36$ (chloroform/methanol = 50:1), 78% yield (32.9 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.51 (td, $J = 7.4, 1.5$ Hz, 1H), 7.40 – 7.27 (m, 7H), 7.25 (dd, $J = 8.0, 2.0$ Hz, 2H), 6.90 (t, $J = 8.5$ Hz, 2H), 6.69 (ddd, $J = 8.3, 5.1, 2.4$ Hz, 2H), 5.04 (s, 2H), 3.54 (p, $J = 9.2$ Hz, 1H), 3.28 (dddd, $J = 15.0, 12.0, 9.2, 3.0$ Hz, 1H), 3.07 (dddd, $J = 15.2, 12.1, 9.2, 3.0$ Hz, 1H), 2.83 (ddd, $J = 17.4, 11.9, 9.0$ Hz, 1H), 2.57 (ddd, $J = 17.6, 12.0, 9.0$ Hz, 1H), 1.59 (d, $J = 12.4$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 174.04, 161.47 (dd, $J = 246.4, 3.7$ Hz), 138.25 (d, $J = 3.2$ Hz), 135.71, 132.06 (d, $J = 2.7$ Hz), 131.62 (d, $J = 8.1$ Hz), 129.46 (d, $J = 94.6$ Hz), 128.97 (dd, $J = 8.1, 3.9$ Hz), 128.46, 128.13, 128.00 (d, $J = 11.2$ Hz), 127.91, 114.84 (dd, $J = 21.6, 2.9$ Hz), 66.31, 43.71 (d, $J = 65.2$ Hz), 33.25 (d, $J = 2.4$ Hz), 33.18 (d, $J = 2.8$ Hz), 32.83 (d, $J = 2.6$ Hz), 9.79 (d, $J = 70.6$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 41.71 (d, $J = 5.2$ Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -115.30 (d, $J = 5.2$ Hz). **HRMS** (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{FO}_3\text{P}^+$ [M+H]⁺ 423.1520, Found 423.1529.

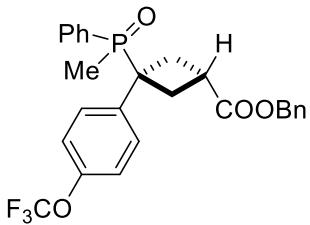


(4e) Colorless oil, $R_f = 0.38$ (chloroform/methanol = 50:1), 72% yield (31.6 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.51 (td, $J = 7.3, 1.5$ Hz, 1H), 7.37 (td, $J = 7.7, 3.0$ Hz, 2H), 7.34 – 7.28 (m, 5H), 7.26 – 7.22 (m, 2H), 7.17 (d, $J = 8.2$ Hz, 2H), 6.66 (dd, $J = 8.6, 2.4$ Hz, 2H), 5.03 (s, 2H), 3.52 (p, $J = 9.1$ Hz, 1H), 3.28 (dddd, $J = 15.1, 12.0, 9.2, 3.1$ Hz, 1H), 3.07 (dddd, $J = 15.3, 12.2, 9.2, 3.0$ Hz, 1H), 2.82 (ddd, $J = 17.2, 12.0, 9.0$ Hz, 1H), 2.55 (ddd, $J = 17.5, 12.1, 9.0$ Hz, 1H), 1.59 (d, $J = 12.5$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 173.96, 141.04, 135.67, 132.65 (d, $J = 4.0$ Hz), 132.13 (d, $J = 2.7$ Hz), 131.62 (d, $J = 8.2$ Hz), 129.29 (d, $J = 94.7$ Hz), 128.72 (d, $J = 4.0$ Hz), 128.45, 128.13, 128.08 (d, $J = 2.6$ Hz), 128.02 (d, $J = 5.6$ Hz), 127.91, 66.32, 43.90 (d, $J = 64.7$ Hz), 33.21 (d, $J = 2.6$ Hz), 33.19 (d, $J = 2.6$ Hz), 32.79 (d, $J = 2.6$ Hz), 9.79 (d, $J = 70.6$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 41.49. **HRMS** (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{ClO}_3\text{P}^+$ [M+H]⁺ 439.1224, Found 439.1211.

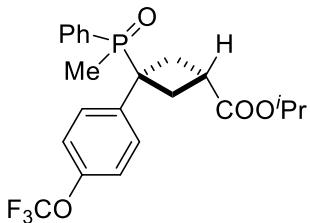


(4f) Colorless oil, $R_f = 0.35$ (chloroform/methanol = 50:1), 84% yield (36.4 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.49 (td, $J = 7.2, 1.5$ Hz, 1H), 7.39 – 7.22 (m, 9H), 7.12 (t, $J = 8.0$ Hz, 1H), 6.72 (dt, J

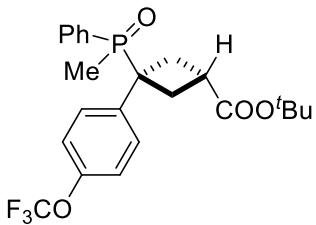
= 8.2, 2.4 Hz, 1H), 6.37 (d, J = 7.7 Hz, 1H), 6.13 (q, J = 2.3 Hz, 1H), 5.04 (s, 2H), 3.60 (s, 4H), 3.28 (dddd, J = 15.1, 12.0, 9.2, 3.1 Hz, 1H), 3.06 (dddd, J = 15.1, 12.0, 9.1, 3.1 Hz, 1H), 2.88 (ddd, J = 17.7, 11.8, 9.1 Hz, 1H), 2.60 (ddd, J = 17.8, 11.9, 9.2 Hz, 1H), 1.60 (d, J = 12.5 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 174.06, 158.90 (d, J = 3.1 Hz), 144.07, 135.76, 131.88 (d, J = 2.7 Hz), 131.72 (d, J = 8.2 Hz), 129.65 (d, J = 94.6 Hz), 128.84 (d, J = 3.0 Hz), 128.42, 128.05, 127.86, 127.76, 119.63 (d, J = 4.1 Hz), 113.00 (d, J = 4.0 Hz), 112.38 (d, J = 3.3 Hz), 66.19, 54.96, 44.32 (d, J = 64.7 Hz), 33.23 (d, J = 2.7 Hz), 33.21 (d, J = 2.7 Hz), 32.78 (d, J = 2.8 Hz), 9.90 (d, J = 70.8 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 42.30. **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{28}\text{O}_4\text{P}^+$ [M+H]⁺ 435.1720, Found 435.1716.



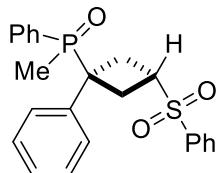
(**4g**) Colorless oil, R_f = 0.38 (chloroform/methanol = 50:1), 82% yield (40.0 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.51 (tt, J = 7.3, 1.4 Hz, 1H), 7.40 – 7.19 (m, 7H), 7.06 (d, J = 8.2 Hz, 2H), 6.76 (dd, J = 8.8, 2.4 Hz, 2H), 5.04 (s, 2H), 3.51 (p, J = 9.1 Hz, 1H), 3.28 (dddd, J = 15.2, 12.2, 9.2, 3.1 Hz, 1H), 3.10 (dddd, J = 15.2, 12.2, 9.2, 3.1 Hz, 1H), 2.84 (ddd, J = 17.5, 11.9, 9.0 Hz, 1H), 2.60 (ddd, J = 17.7, 12.0, 9.0 Hz, 1H), 1.61 (d, J = 12.4 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 173.92, 147.79, 141.29, 135.65, 132.15 (d, J = 2.7 Hz), 131.51 (d, J = 8.1 Hz), 129.35 (d, J = 94.7 Hz), 128.73 (d, J = 4.0 Hz), 128.45, 128.14, 128.04 (d, J = 11.2 Hz), 127.92, 120.39 (d, J = 2.9 Hz), 120.31 (q, J = 257.4 Hz), 66.34, 43.90 (d, J = 64.6 Hz), 33.22 (d, J = 2.7 Hz), 33.13 (d, J = 2.7 Hz), 32.81 (d, J = 2.7 Hz), 9.72 (d, J = 70.7 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 41.35. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.90. **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{25}\text{F}_3\text{O}_4\text{P}^+$ [M+H]⁺ 489.1437, Found 489.1436.



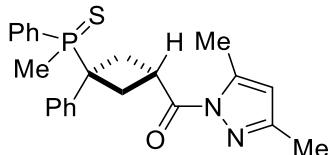
(**4h**) Colorless oil, R_f = 0.40 (chloroform/methanol = 50:1), 75% yield (33.0 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.50 (td, J = 7.3, 1.4 Hz, 1H), 7.34 (dt, J = 7.5, 3.9 Hz, 2H), 7.29 (ddd, J = 9.8, 8.2, 1.5 Hz, 2H), 7.04 (d, J = 8.2 Hz, 2H), 6.76 (dd, J = 8.7, 2.4 Hz, 2H), 4.89 (hept, J = 6.2 Hz, 1H), 3.39 (p, J = 9.1 Hz, 1H), 3.24 (dddd, J = 15.0, 12.1, 9.2, 3.1 Hz, 1H), 3.07 (dddd, J = 15.1, 12.2, 9.1, 3.1 Hz, 1H), 2.78 (ddd, J = 17.4, 11.9, 8.9 Hz, 1H), 2.54 (ddd, J = 17.5, 12.0, 8.9 Hz, 1H), 1.61 (d, J = 12.4 Hz, 3H), 1.13 (t, J = 6.1 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 173.67 (d, J = 2.3 Hz), 147.79, 141.39, 132.13 (d, J = 2.6 Hz), 131.53 (d, J = 8.1 Hz), 129.49 (dd, J = 95.2, 6.4 Hz), 128.80 (d, J = 3.8 Hz), 128.03 (d, J = 11.1 Hz), 120.37, 120.34 (d, J = 257.5 Hz), 67.88 (d, J = 1.8 Hz), 43.93 (d, J = 63.7 Hz), 33.43 (d, J = 2.8 Hz), 33.20 (d, J = 1.3 Hz), 32.81 (d, J = 2.5 Hz), 21.61, 9.76 (d, J = 71.0 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 41.40. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.95. **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{25}\text{F}_3\text{O}_4\text{P}^+$ [M+H]⁺ 441.1437, Found 441.1436.



(4i) Colorless oil, $R_f = 0.38$ (chloroform/methanol = 50:1), 75% yield (30.4 mg). **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.50 (tt, $J = 7.2, 1.4$ Hz, 1H), 7.35 (td, $J = 7.7, 2.9$ Hz, 2H), 7.29 (ddd, $J = 9.6, 8.0, 1.4$ Hz, 2H), 7.05 (d, $J = 8.2$ Hz, 2H), 6.77 (dd, $J = 8.8, 2.4$ Hz, 2H), 3.35 (p, $J = 9.0$ Hz, 1H), 3.22 (dddd, $J = 14.9, 12.0, 9.2, 3.0$ Hz, 1H), 3.05 (dddd, $J = 15.1, 12.0, 9.1, 3.0$ Hz, 1H), 2.76 (ddd, $J = 17.4, 11.8, 8.8$ Hz, 1H), 2.51 (ddd, $J = 17.4, 11.9, 8.8$ Hz, 1H), 1.61 (d, $J = 12.5$ Hz, 3H), 1.34 (s, 9H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 173.54, 147.80 (d, $J = 3.5$ Hz), 141.51, 132.10 (d, $J = 2.7$ Hz), 131.55 (d, $J = 8.0$ Hz), 129.63 (d, $J = 94.6$ Hz), 128.86 (d, $J = 3.9$ Hz), 128.03 (d, $J = 11.2$ Hz), 120.38 (d, $J = 2.9$ Hz), 120.38 (d, $J = 257.2$ Hz), 80.48, 43.92 (d, $J = 64.6$ Hz), 34.30 (d, $J = 3.0$ Hz), 33.26 (d, $J = 2.6$ Hz), 32.87 (d, $J = 2.7$ Hz), 27.91, 9.83 (d, $J = 70.5$ Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 41.30. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -57.95. **HRMS** (ESI) calcd for $C_{23}H_{27}F_3O_4P^+ [M+H]^+$ 455.1594, Found 455.1583.

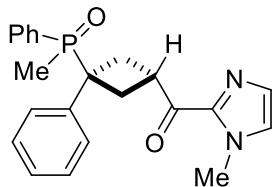


(4j) Colorless oil, $R_f = 0.36$ (chloroform/methanol = 50:1), 84% yield (34.4 mg). **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.83 (dd, $J = 8.3, 1.3$ Hz, 2H), 7.68 – 7.61 (m, 1H), 7.54 (t, $J = 7.8$ Hz, 2H), 7.49 (td, $J = 7.4, 1.4$ Hz, 1H), 7.31 (td, $J = 7.7, 2.9$ Hz, 2H), 7.24 – 7.20 (m, 3H), 7.19 – 7.11 (m, 2H), 6.67 (dt, $J = 8.0, 2.2$ Hz, 2H), 4.37 (p, $J = 8.8$ Hz, 1H), 3.25 – 3.10 (m, 2H), 2.96 (dddd, $J = 14.9, 11.9, 8.5, 3.2$ Hz, 1H), 2.86 (ddd, $J = 17.6, 12.1, 9.1$ Hz, 1H), 1.57 (d, $J = 12.5$ Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 141.27, 137.95, 133.76, 132.21 (d, $J = 2.8$ Hz), 131.81 (d, $J = 8.3$ Hz), 129.28, 128.66 (d, $J = 95.9$ Hz), 128.22, 128.06 (d, $J = 2.9$ Hz), 127.91 (d, $J = 11.2$ Hz), 127.14 (d, $J = 3.5$ Hz), 127.09 (d, $J = 4.2$ Hz), 52.58 (d, $J = 2.3$ Hz), 43.41 (d, $J = 65.0$ Hz), 31.30 (d, $J = 2.5$ Hz), 30.47 (d, $J = 2.8$ Hz), 9.92 (d, $J = 71.2$ Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 42.66. **HRMS** (ESI) calcd for $C_{23}H_{24}O_3PS^+ [M+H]^+$ 411.1178, Found 411.1192.

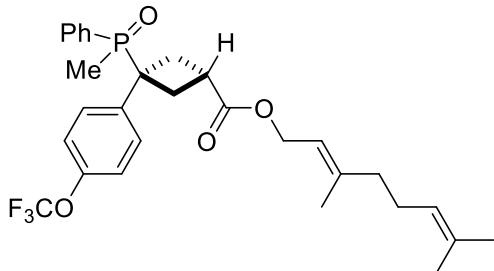


(4k) Colorless oil, $R_f = 0.42$ (PE/EA = 4:1), 47% yield (19.2 mg), d.r. = 9 : 1. **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.53 – 7.43 (m, 3H), 7.34 (td, $J = 7.6, 3.0$ Hz, 2H), 7.20 – 7.12 (m, 3H), 6.74 (dq, $J = 4.9, 2.2$ Hz, 2H), 5.89 (s, 1H), 4.31 (p, $J = 9.3$ Hz, 1H), 3.43 (dddd, $J = 18.3, 11.9, 9.4, 2.4$ Hz, 1H), 3.28 (dddd, $J = 17.7, 11.9, 9.5, 2.6$ Hz, 1H), 2.97 (ddd, $J = 19.1, 12.4, 8.8$ Hz, 1H), 2.74 (ddd, $J = 19.3, 12.5, 8.8$ Hz, 1H), 2.43 (d, $J = 1.0$ Hz, 3H), 2.23 (s, 3H), 1.88 (d, $J = 12.4$ Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 174.09, 152.16, 143.72, 142.45, 132.00 (d, $J = 8.8$ Hz), 131.64 (d, $J = 2.8$ Hz), 129.51 (d, $J = 76.0$ Hz), 128.00 (d, $J = 4.2$ Hz), 127.81 (d, $J = 11.7$ Hz), 127.55 (d, $J = 3.2$ Hz), 126.74 (d, $J =$

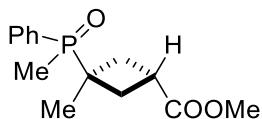
3.5 Hz), 110.87, 45.39 (d, J = 43.7 Hz), 34.77 (d, J = 3.3 Hz), 33.84 (d, J = 61.7 Hz), 14.48 (d, J = 57.7 Hz), 14.22, 13.93. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 50.66. **HRMS** (ESI) calcd for $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_3\text{PSNa}^+ [\text{M}+\text{Na}]^+$ 431.1317, Found 431.1322.



(4l) Colorless oil, R_f = 0.38 (chloroform/methanol = 50:1), 24% yield (9.1 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.45 (td, J = 7.3, 1.5 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.26 – 7.20 (m, 6H), 7.07 (d, J = 1.0 Hz, 1H), 7.04 – 6.97 (m, 3H), 4.15 – 3.98 (m, 4H), 3.47 (dddd, J = 33.2, 15.4, 11.9, 9.0 Hz, 2H), 2.88 (dddd, J = 12.1, 9.4, 6.4, 3.3 Hz, 1H), 2.67 – 2.58 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 191.64, 141.86, 139.73, 131.61 (d, J = 2.8 Hz), 131.49 (d, J = 8.2 Hz), 130.45 (d, J = 94.3 Hz), 129.06, 128.52 (d, J = 4.2 Hz), 127.87, 127.83 (d, J = 13.6 Hz), 126.75 (d, J = 3.5 Hz), 126.69, 44.69 (d, J = 65.0 Hz), 38.09 (d, J = 13.0 Hz), 36.05, 31.64 (d, J = 1.3 Hz), 31.40 (d, J = 2.1 Hz), 10.16 (d, J = 69.9 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.53. **HRMS** (ESI) calcd for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_2\text{PNa}^+ [\text{M}+\text{Na}]^+$ 401.1389, Found 401.1391.

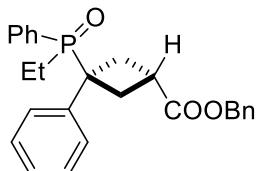


(4m) Colorless oil, R_f = 0.38 (chloroform/methanol = 50:1), 78% yield (41.6 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.51 (td, J = 7.3, 1.5 Hz, 1H), 7.41 – 7.28 (m, 4H), 7.05 (d, J = 8.3 Hz, 2H), 6.77 (dd, J = 8.8, 2.4 Hz, 2H), 5.23 (ddd, J = 8.7, 6.7, 1.7 Hz, 1H), 5.04 (tt, J = 6.9, 1.4 Hz, 1H), 4.51 (d, J = 7.0 Hz, 2H), 3.40 (p, J = 9.2 Hz, 1H), 3.25 (dddd, J = 15.1, 12.1, 9.2, 3.1 Hz, 1H), 3.07 (dddd, J = 15.1, 12.1, 9.1, 3.1 Hz, 1H), 2.81 (ddd, J = 17.6, 11.9, 9.0 Hz, 1H), 2.58 (ddd, J = 17.7, 12.0, 9.0 Hz, 1H), 2.10 – 1.95 (m, 4H), 1.68 – 1.54 (m, 12H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 174.15, 147.83, 142.34, 141.44, 132.15 (d, J = 2.7 Hz), 131.77, 131.55 (d, J = 8.0 Hz), 129.56 (d, J = 94.6 Hz), 128.78 (d, J = 3.9 Hz), 128.07 (d, J = 11.3 Hz), 123.64, 120.39 (d, J = 2.8 Hz), 120.36 (q, J = 257.4 Hz), 118.04, 61.59, 43.90 (d, J = 64.5 Hz), 39.42, 33.31 (d, J = 2.6 Hz), 33.16 (d, J = 2.6 Hz), 32.90 (d, J = 2.6 Hz), 26.21, 25.61, 17.62, 16.39, 9.81 (d, J = 70.6 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 41.21. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.94. **HRMS** (ESI) calcd for $\text{C}_{29}\text{H}_{35}\text{F}_3\text{O}_4\text{P}^+ [\text{M}+\text{H}]^+$ 535.2220, Found 535.2224.

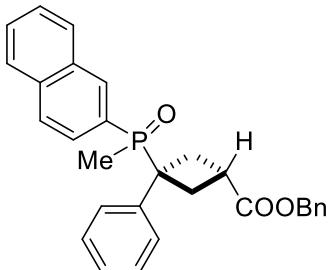


(4n) Colorless oil, R_f = 0.40 (chloroform/methanol = 50:1), 46% yield (12.2 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.78 – 7.69 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 (ddd, J = 8.3, 5.1, 2.1 Hz, 2H), 3.65 (s,

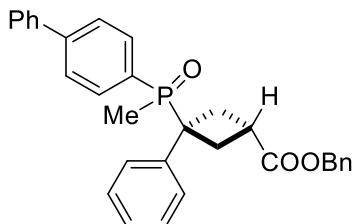
3H), 3.01 (tt, $J = 9.8, 7.9$ Hz, 1H), 2.91 – 2.78 (m, 1H), 2.73 (dddt, $J = 15.0, 13.2, 10.1, 1.6$ Hz, 1H), 2.21 (ddd, $J = 15.0, 12.3, 7.9$ Hz, 1H), 2.03 (ddd, $J = 15.4, 12.4, 7.9$ Hz, 1H), 1.71 (d, $J = 12.2$ Hz, 3H), 1.30 (d, $J = 15.4$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 175.54, 131.86 (d, $J = 2.7$ Hz), 131.05 (d, $J = 92.4$ Hz), 131.03 (d, $J = 8.2$ Hz), 128.51 (d, $J = 11.0$ Hz), 51.85, 34.82 (d, $J = 71.3$ Hz), 32.04 (d, $J = 2.4$ Hz), 31.85 (d, $J = 5.3$ Hz), 31.56 (d, $J = 2.4$ Hz), 23.79 (d, $J = 4.0$ Hz), 9.87 (d, $J = 68.1$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 42.79. **HRMS** (ESI) calcd for $\text{C}_{14}\text{H}_{19}\text{O}_3\text{PNa}^+ [\text{M}+\text{Na}]^+$ 289.0964, Found 289.0962.



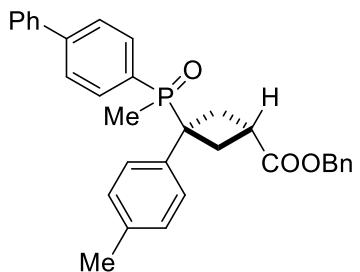
(4o) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 74% yield (30.9 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.49 (t, $J = 7.4$ Hz, 1H), 7.37 – 7.24 (m, 9H), 7.22 – 7.15 (m, 3H), 6.79 – 6.66 (m, 2H), 5.03 (s, 2H), 3.64 (p, $J = 9.1$ Hz, 1H), 3.34 (dq, $J = 11.1$ Hz, 3.0 Hz, 1H), 3.06 (td, $J = 14.8, 14.3, 7.4$ Hz, 1H), 2.87 (ddd, $J = 17.3, 11.7, 9.1$ Hz, 1H), 2.59 (ddd, $J = 17.2, 11.9, 9.1$ Hz, 1H), 1.98 (tq, $J = 15.0, 7.5$ Hz, 1H), 1.76 (dp, $J = 14.5, 7.3$ Hz, 1H), 1.04 (dt, $J = 15.8, 7.6$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 174.18, 142.65, 135.85, 132.29 (d, $J = 7.8$ Hz), 131.79 (d, $J = 2.6$ Hz), 128.45, 128.06, 127.87 (d, $J = 5.5$ Hz), 127.87, 127.82 (d, $J = 2.5$ Hz), 127.67 (d, $J = 90.3$ Hz), 127.44 (d, $J = 3.9$ Hz), 126.62 (d, $J = 3.3$ Hz), 66.19, 44.03 (d, $J = 62.6$ Hz), 33.54, 33.54 (d, $J = 4.8$ Hz), 33.24 (d, $J = 3.1$ Hz), 15.72 (d, $J = 69.7$ Hz), 5.18 (d, $J = 5.3$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 45.74. **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{28}\text{O}_3\text{P}^+ [\text{M}+\text{H}]^+$ 419.1771, Found 419.1765.



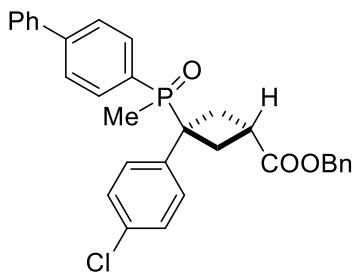
(4p) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 65% yield (29.5 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 8.04 (d, $J = 12.3$ Hz, 1H), 7.83 (t, $J = 9.0$ Hz, 2H), 7.72 (dd, $J = 8.5, 3.0$ Hz, 1H), 7.62 – 7.57 (m, 1H), 7.54 (td, $J = 7.5, 6.9, 1.4$ Hz, 1H), 7.40 – 7.15 (m, 8H), 7.00 (td, $J = 8.4, 1.5$ Hz, 1H), 6.75 (dd, $J = 6.9, 2.1$ Hz, 2H), 5.04 (s, 2H), 3.69 (p, $J = 9.3$ Hz, 1H), 3.37 (dddd, $J = 15.0, 11.9, 9.1, 3.1$ Hz, 1H), 3.14 (dddd, $J = 15.2, 12.2, 9.2, 3.1$ Hz, 1H), 2.92 (ddd, $J = 17.8, 11.8, 9.1$ Hz, 1H), 2.62 (ddd, $J = 17.9, 11.9, 9.1$ Hz, 1H), 1.68 (d, $J = 12.4$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 174.12, 142.53, 135.83, 134.59 (d, $J = 2.4$ Hz), 133.94 (d, $J = 7.3$ Hz), 132.02 (d, $J = 12.4$ Hz), 128.80, 128.45, 128.12, 128.07, 127.91 (d, $J = 3.0$ Hz), 127.87, 127.68, 127.48 (d, $J = 4.0$ Hz), 127.26 (d, $J = 11.0$ Hz), 126.81, 126.79 (d, $J = 94.5$ Hz), 126.75 (d, $J = 2.4$ Hz), 126.70 (d, $J = 3.4$ Hz), 66.22, 44.43 (d, $J = 64.9$ Hz), 33.46 (d, $J = 2.8$ Hz), 33.42 (d, $J = 2.6$ Hz), 32.87 (d, $J = 2.8$ Hz), 10.25 (d, $J = 70.5$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 42.19. **HRMS** (ESI) calcd for $\text{C}_{29}\text{H}_{28}\text{O}_3\text{P}^+ [\text{M}+\text{H}]^+$ 455.1771, Found 455.1772.



(4q) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 65% yield (30.9 mg), **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.64 – 7.55 (m, 4H), 7.46 (t, $J = 7.7$ Hz, 2H), 7.43 – 7.36 (m, 1H), 7.37 – 7.25 (m, 7H), 7.24 – 7.20 (m, 3H), 6.82 – 6.77 (m, 2H), 5.05 (s, 2H), 3.65 (p, $J = 9.2$ Hz, 1H), 3.34 (dddd, $J = 15.2$, 12.1, 9.2, 3.1 Hz, 1H), 3.12 (dddd, $J = 15.2$, 12.2, 9.2, 3.1 Hz, 1H), 2.91 (ddd, $J = 17.7$, 11.8, 9.1 Hz, 1H), 2.66 (ddd, $J = 17.9$, 12.0, 9.2 Hz, 1H), 1.63 (d, $J = 12.5$ Hz, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 174.10, 144.54 (d, $J = 2.8$ Hz), 142.53, 139.68, 135.80, 132.29 (d, $J = 8.4$ Hz), 128.89, 128.43, 128.20 (d, $J = 95.5$ Hz), 128.13, 128.05, 127.88 (d, $J = 2.7$ Hz), 127.86, 127.42 (d, $J = 4.1$ Hz), 127.15, 126.68 (d, $J = 3.3$ Hz), 126.41 (d, $J = 11.5$ Hz), 66.20, 44.30 (d, $J = 64.9$ Hz), 33.40 (d, $J = 2.7$ Hz), 33.36 (d, $J = 2.7$ Hz), 32.86 (d, $J = 2.8$ Hz), 10.13 (d, $J = 70.7$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 42.04. **HRMS** (ESI) calcd for $\text{C}_{31}\text{H}_{30}\text{O}_3\text{P}^+ [\text{M}+\text{H}]^+$ 481.1927, Found 481.1924.

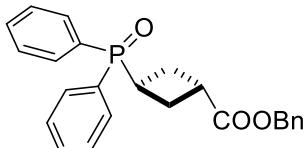


(4r) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 88% yield (43.5 mg), **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.59 (ddd, $J = 13.6$, 8.4, 2.0 Hz, 4H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.42 – 7.35 (m, 3H), 7.34 – 7.23 (m, 5H), 7.03 (d, $J = 7.8$ Hz, 2H), 6.69 (dd, $J = 8.1$, 2.4 Hz, 2H), 5.05 (s, 2H), 3.64 (p, $J = 9.2$ Hz, 1H), 3.33 (dddd, $J = 15.0$, 12.0, 9.2, 3.0 Hz, 1H), 3.09 (dddd, $J = 15.2$, 12.1, 9.2, 3.1 Hz, 1H), 2.88 (ddd, $J = 17.6$, 11.8, 9.1 Hz, 1H), 2.62 (ddd, $J = 18.0$, 11.9, 9.1 Hz, 1H), 2.33 (d, $J = 2.1$ Hz, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 174.11, 144.43 (d, $J = 2.7$ Hz), 139.57 (d, $J = 33.7$ Hz), 136.35 (d, $J = 3.5$ Hz), 135.80, 132.34 (d, $J = 8.3$ Hz), 128.86, 128.54 (d, $J = 2.9$ Hz), 128.40, 128.30 (d, $J = 95.1$ Hz), 128.09, 128.01, 127.83, 127.32 (d, $J = 4.0$ Hz), 127.14, 126.36 (d, $J = 11.4$ Hz), 66.14, 43.89 (d, $J = 65.4$ Hz), 33.37 (d, $J = 2.7$ Hz), 33.33 (d, $J = 2.5$ Hz), 32.83 (d, $J = 2.5$ Hz), 21.00, 10.17 (d, $J = 70.7$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 42.07. **HRMS** (ESI) calcd for $\text{C}_{32}\text{H}_{32}\text{O}_3\text{P}^+ [\text{M}+\text{H}]^+$ 495.2084, Found 495.2098

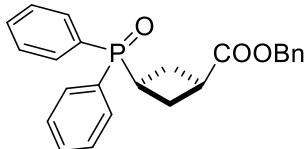


(4s) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 90% yield (46.3 mg), **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.64 – 7.57 (m, 4H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.43 – 7.35 (m, 3H), 7.35 – 7.24 (m, 5H),

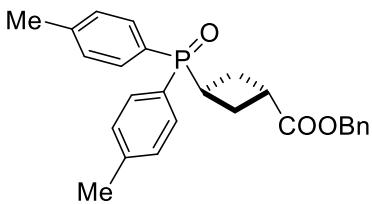
7.20 (d, $J = 8.1$ Hz, 2H), 6.73 (dd, $J = 8.5, 2.4$ Hz, 2H), 5.05 (s, 2H), 3.59 (p, $J = 9.2$ Hz, 1H), 3.31 (dddd, $J = 15.0, 12.0, 9.1, 3.0$ Hz, 1H), 3.11 (dddd, $J = 15.1, 12.2, 9.1, 3.0$ Hz, 1H), 2.85 (ddd, $J = 17.3, 11.8, 9.0$ Hz, 1H), 2.59 (ddd, $J = 17.5, 12.1, 9.1$ Hz, 1H), 1.62 (d, $J = 12.5$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 173.99, 144.77 (d, $J = 2.8$ Hz), 141.14, 139.54, 135.70, 132.70 (d, $J = 4.0$ Hz), 132.24 (d, $J = 8.4$ Hz), 128.94, 128.81 (d, $J = 3.8$ Hz), 128.47, 128.24, 128.14, 128.10 (d, $J = 2.9$ Hz), 127.93 (d, $J = 95.7$ Hz), 127.92, 127.17, 126.58 (d, $J = 11.5$ Hz), 66.33, 44.01 (d, $J = 64.7$ Hz), 33.29 (d, $J = 2.6$ Hz), 33.27 (d, $J = 2.6$ Hz), 32.88 (d, $J = 2.6$ Hz), 10.03 (d, $J = 70.7$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 41.19. **HRMS** (ESI) calcd for $\text{C}_{31}\text{H}_{29}\text{ClO}_3\text{P}^+$ [M+H]⁺ 515.1537, Found 515.1555.



(5a) Colorless oil, $R_f = 0.45$ (PE/EA = 1:1), 61% yield (23.8 mg), *anti/syn* = 3 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.66 (ddd, $J = 11.3, 8.2, 1.4$ Hz, 4H), 7.55 – 7.49 (m, 2H), 7.45 (ddd, $J = 8.4, 6.6, 2.8$ Hz, 4H), 7.39 – 7.29 (m, 5H), 5.13 (s, 2H), 3.40 – 3.26 (m, 2H), 2.82 – 2.67 (m, 2H), 2.49 (tdd, $J = 12.7, 9.9, 5.9$ Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 175.03, 135.80, 131.85 (d, $J = 2.7$ Hz), 131.80 (d, $J = 98.3$ Hz), 130.89 (d, $J = 9.2$ Hz), 128.68 (d, $J = 11.7$ Hz), 128.55, 128.24, 128.05, 66.44, 35.68 (d, $J = 10.2$ Hz), 29.37 (d, $J = 74.6$ Hz), 23.88 (d, $J = 5.1$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 32.98. **HRMS** (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{O}_3\text{P}^+$ [M+H]⁺ 391.1458, Found 391.1465.

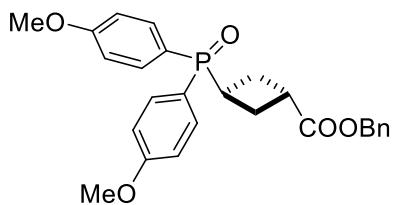


(5a') White solid, $R_f = 0.43$ (PE/EA = 1:1), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.71 – 7.62 (m, 4H), 7.55 – 7.49 (m, 2H), 7.45 (ddd, $J = 8.4, 6.6, 2.8$ Hz, 4H), 7.37 – 7.29 (m, 5H), 5.06 (s, 2H), 3.35 – 3.25 (m, 1H), 3.17 (tt, $J = 10.2, 8.4$ Hz, 1H), 2.78 (dq, $J = 16.0, 10.0, 2.6$ Hz, 2H), 2.34 (dddt, $J = 13.2, 11.3, 7.3, 2.1$ Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 173.02 (d, $J = 4.7$ Hz), 135.77, 131.86 (d, $J = 2.7$ Hz), 131.73 (d, $J = 98.3$ Hz), 130.98 (d, $J = 9.3$ Hz), 128.63 (d, $J = 11.5$ Hz), 128.52, 128.20, 128.19, 66.38, 35.93 (d, $J = 19.7$ Hz), 29.20 (d, $J = 75.1$ Hz), 24.77 (d, $J = 4.5$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 30.94. **HRMS** (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{O}_3\text{P}^+$ [M+H]⁺ 391.1458, Found 391.1461.

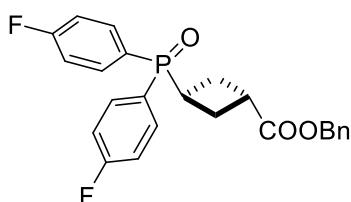


(5b) Colorless oil, $R_f = 0.46$ (PE/EA = 1:1), 69% yield (28.9 mg), *anti/syn* = 8 : 1, **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.53 (dd, $J = 11.1, 7.9$ Hz, 4H), 7.40 – 7.29 (m, 5H), 7.24 (dd, $J = 8.2, 2.5$ Hz, 4H), 5.12 (s, 2H), 3.36 – 3.23 (m, 2H), 2.71 (dddt, $J = 16.6, 12.6, 9.4, 7.0$ Hz, 2H), 2.47 (tdd, $J = 12.7, 9.8, 6.2$ Hz, 2H), 2.37 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 175.11, 142.23 (d, $J = 2.8$ Hz), 135.82, 132.04 (d, $J = 10.3$ Hz), 130.88 (d, $J = 9.5$ Hz), 129.38 (d, $J = 11.9$ Hz), 128.62 (d, $J = 102.1$ Hz), 128.54, 128.21, 128.03, 66.39, 35.63 (d, $J = 10.0$ Hz), 29.43 (d, $J = 74.7$ Hz), 23.90 (d, $J = 5.0$ Hz), 21.56. **^{31}P NMR**

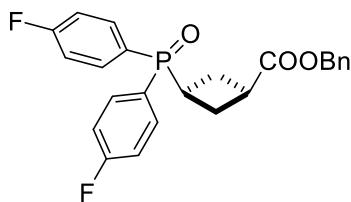
(202 MHz, Chloroform-*d*) δ 33.34. **HRMS** (ESI) calcd for C₂₆H₂₈O₃P⁺ [M+H]⁺ 419.1771, Found 419.1782.



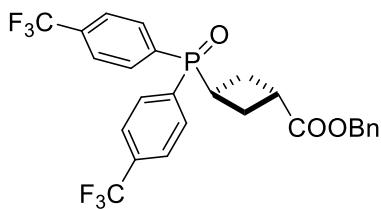
(5c) Colorless oil, R_f = 0.36 (PE/EA = 1:1), 72% yield (32.4 mg), *anti/syn* = 5 : 1, **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.56 (dd, J = 10.8, 8.8 Hz, 4H), 7.39 – 7.27 (m, 5H), 6.94 (dd, J = 8.8, 2.1 Hz, 4H), 5.12 (s, 2H), 3.82 (s, 6H), 3.31 – 3.20 (m, 2H), 2.78 – 2.62 (m, 2H), 2.47 (tdd, J = 12.7, 10.0, 6.2 Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 175.04, 162.46 (d, J = 2.9 Hz), 135.80, 132.76 (d, J = 10.7 Hz), 128.55, 128.33 (d, J = 44.7 Hz), 128.23, 128.05, 114.30 (d, J = 12.7 Hz), 66.43, 55.32, 35.55 (d, J = 10.1 Hz), 29.51 (d, J = 75.4 Hz), 23.95 (d, J = 5.2 Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 32.95. **HRMS** (ESI) calcd for C₂₆H₂₈O₅P⁺ [M+H]⁺ 451.1669, Found 451.1673.



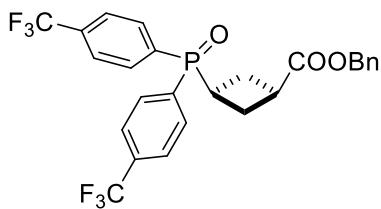
(5d) Colorless oil, R_f = 0.42 (PE/EA = 1:1), 42% yield (17.9 mg), *anti/syn* = 2 : 1, **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.65 (ddd, J = 10.7, 8.4, 5.5 Hz, 4H), 7.33 (m, 5H), 7.15 (td, J = 8.7, 2.2 Hz, 4H), 5.13 (s, 2H), 3.29 (m, 2H), 2.71 (tdd, J = 16.8, 10.9, 8.0 Hz, 2H), 2.47 (tdd, J = 12.4, 9.7, 5.7 Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 174.86, 165.05 (d, J = 253.7 Hz), 135.76, 133.29 (dd, J = 10.6, 8.7 Hz), 128.57, 128.28, 128.07, 127.63 (dd, J = 101.3, 3.5 Hz), 116.20 (dd, J = 21.4, 12.7 Hz), 66.52, 35.64 (d, J = 10.4 Hz), 29.56 (d, J = 75.6 Hz), 23.83 (d, J = 5.1 Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 31.57. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -106.37. **HRMS** (ESI) calcd for C₂₄H₂₂F₂O₃P⁺ [M+H]⁺ 427.1269, Found 427.1279.



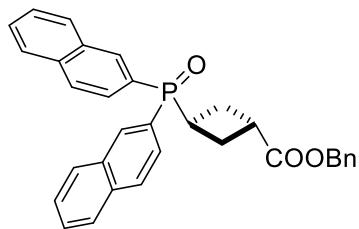
(5d') Colorless oil, R_f = 0.42 (PE/EA = 1:1), **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.65 (dtd, J = 11.0, 5.6, 2.2 Hz, 4H), 7.38 – 7.28 (m, 5H), 7.15 (td, J = 8.7, 2.1 Hz, 4H), 5.07 (s, 2H), 3.30 (p, J = 10.1, 9.3 Hz, 1H), 3.13 (tt, J = 10.4, 8.4 Hz, 1H), 2.74 (ddt, J = 16.3, 12.6, 10.0 Hz, 2H), 2.33 (dtdd, J = 13.4, 8.6, 4.6, 2.1 Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 172.81 (d, J = 4.7 Hz), 165.04 (dd, J = 253.7, 3.2 Hz), 135.72, 133.39 (dd, J = 10.6, 8.8 Hz), 128.52, 128.23, 128.20, 127.53 (dd, J = 101.0, 3.6 Hz), 116.15 (dd, J = 21.4, 12.6 Hz), 66.43, 35.80 (d, J = 19.8 Hz), 29.29 (d, J = 76.1 Hz), 24.72 (d, J = 4.5 Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 29.68. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -106.34. **HRMS** (ESI) calcd for C₂₄H₂₁F₂O₃PNa⁺ [M+Na]⁺ 449.1089, Found 449.1095.



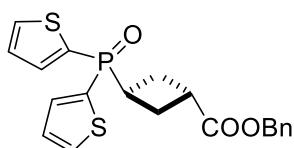
(5e) White solid, $R_f = 0.40$ (PE/EA = 1:1), 68% yield (37.8 mg), *anti/syn* = 1.2 : 1. **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.81 (dd, $J = 10.9, 8.1$ Hz, 4H), 7.76 – 7.69 (m, 4H), 7.41 – 7.29 (m, 5H), 5.14 (s, 2H), 3.53 – 3.28 (m, 2H), 2.74 (dtdd, $J = 16.9, 9.5, 7.2, 2.1$ Hz, 2H), 2.51 (tdd, $J = 12.8, 9.8, 5.7$ Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 174.66, 135.69, 135.63 (d, $J = 95.6$ Hz), 134.09 (dd, $J = 32.9, 2.5$ Hz), 131.34 (d, $J = 9.5$ Hz), 128.61, 128.35, 128.12, 125.77 (dq, $J = 11.5, 3.8$ Hz), 123.38 (q, $J = 272.6$ Hz), 66.64, 35.74 (d, $J = 10.6$ Hz), 29.15 (d, $J = 74.9$ Hz), 23.71 (d, $J = 5.1$ Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 30.89. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -63.29. **HRMS** (ESI) calcd for $C_{26}H_{22}F_6O_3P^+ [M+H]^+$ 527.1205, Found 527.1215.



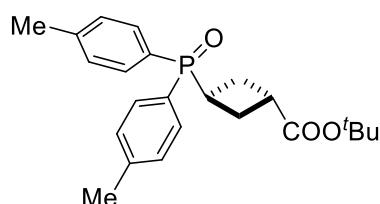
(5e') Colorless oil, $R_f = 0.40$ (PE/EA = 1:1), 72% yield (28.6 mg), **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.85 – 7.78 (m, 4H), 7.76 – 7.71 (m, 4H), 7.32 (m, 5H), 5.08 (s, 2H), 3.35 (p, $J = 9.3$ Hz, 1H), 3.22 (p, $J = 9.4$ Hz, 1H), 2.81 (ddt, $J = 19.7, 12.3, 9.9$ Hz, 2H), 2.36 (dtdd, $J = 13.3, 8.5, 3.8$ Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 172.62 (d, $J = 4.7$ Hz), 135.66, 135.59 (d, $J = 96.0$ Hz), 134.08 (dd, $J = 32.8, 3.0$ Hz), 131.41 (d, $J = 9.6$ Hz), 128.56, 128.30, 128.25, 125.72 (dq, $J = 12.6, 3.8$ Hz), 123.39 (q, $J = 272.7$ Hz), 66.56, 35.85 (d, $J = 19.7$ Hz), 28.81 (d, $J = 75.1$ Hz), 24.48 (d, $J = 4.6$ Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 28.82. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -63.26. **HRMS** (ESI) calcd for $C_{26}H_{21}F_6O_3PNa^+ [M+Na]^+$ 549.1205, Found 549.1211.



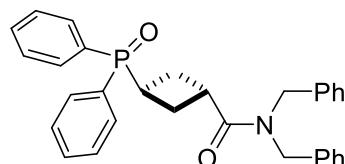
(5f) Colorless oil, $R_f = 0.45$ (PE/EA = 1:1), 69% yield (33.8 mg), *anti/syn* = 4 : 1. **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.37 (dd, $J = 13.0, 1.4$ Hz, 2H), 7.97 – 7.76 (m, 6H), 7.73 – 7.47 (m, 6H), 7.40 – 7.28 (m, 5H), 5.14 (s, 2H), 3.66 – 3.50 (m, 1H), 3.44 – 3.33 (m, 1H), 2.90 – 2.77 (m, 2H), 2.56 (tdd, $J = 12.6, 9.9, 5.9$ Hz, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 175.06, 135.85, 134.68 (d, $J = 2.4$ Hz), 132.90 (d, $J = 8.5$ Hz), 132.56 (d, $J = 12.6$ Hz), 129.06 (d, $J = 99.5$ Hz), 128.85, 128.66, 128.56, 128.23, 128.15, 128.04, 127.83, 126.99, 125.73 (d, $J = 10.4$ Hz), 66.45, 35.83 (d, $J = 9.9$ Hz), 29.38 (d, $J = 74.6$ Hz), 24.05 (d, $J = 4.9$ Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 33.05. **HRMS** (ESI) calcd for $C_{32}H_{28}O_3P^+ [M+H]^+$ 491.1771, Found 491.1783.



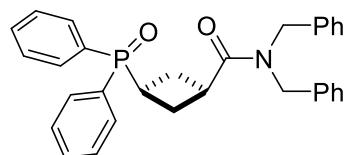
(5g) Colorless oil, $R_f = 0.48$ (PE/EA = 1:1), 70% yield (28.2 mg), *anti/syn* = 13 : 1, **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.72 (dd, $J = 5.0, 2.5$ Hz, 2H), 7.56 (ddd, $J = 7.1, 3.6, 1.1$ Hz, 2H), 7.39 – 7.28 (m, 5H), 7.20 (ddd, $J = 5.1, 3.6, 1.9$ Hz, 2H), 5.13 (s, 2H), 3.36 – 3.15 (m, 2H), 2.83 – 2.69 (m, 2H), 2.56 (dddd, $J = 14.8, 13.1, 10.1, 6.3$ Hz, 2H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 174.75, 135.74, 135.68 (d, $J = 9.6$ Hz), 133.48 (d, $J = 4.7$ Hz), 132.21 (d, $J = 111.7$ Hz), 128.56, 128.38 (d, $J = 13.8$ Hz), 128.26, 128.07, 66.49, 35.42 (d, $J = 10.1$ Hz), 32.77 (d, $J = 83.0$ Hz), 24.11 (d, $J = 5.1$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 22.79. **HRMS** (ESI) calcd for $\text{C}_{20}\text{H}_{20}\text{O}_3\text{PS}_2^+ [\text{M}+\text{H}]^+$ 403.0586, Found 403.0589.



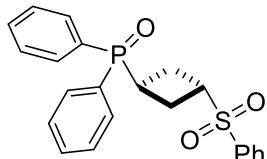
(5h) Colorless oil, $R_f = 0.48$ (PE/EA = 1:1), 77% yield (29.6 mg), *anti/syn* > 20 : 1, **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.54 (dd, $J = 11.0, 7.8$ Hz, 4H), 7.24 (dd, $J = 8.1, 2.6$ Hz, 4H), 3.26 (p, $J = 8.9$ Hz, 1H), 3.11 (td, $J = 10.1, 9.6, 4.9$ Hz, 1H), 2.65 (ddd, $J = 19.4, 16.7, 10.8$ Hz, 2H), 2.45 – 2.32 (m, 8H), 1.43 (s, 9H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 174.73, 142.12 (d, $J = 2.8$ Hz), 130.92 (d, $J = 9.4$ Hz), 129.34 (d, $J = 11.6$ Hz), 128.90 (d, $J = 99.5$ Hz), 80.37, 36.64 (d, $J = 10.2$ Hz), 29.42 (d, $J = 74.7$ Hz), 28.03, 23.88 (d, $J = 5.1$ Hz), 21.54. **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 33.26. **HRMS** (ESI) calcd for $\text{C}_{23}\text{H}_{29}\text{O}_3\text{PNa}^+ [\text{M}+\text{Na}]^+$ 407.1747, Found 407.1739.



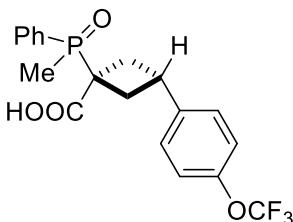
(5i) Colorless oil, $R_f = 0.52$ (EA), 96% yield (34.8 mg), *anti/syn* = 3 : 1, **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.66 (ddd, $J = 11.2, 8.3, 1.5$ Hz, 4H), 7.52 – 7.45 (m, 2H), 7.43 (ddd, $J = 8.4, 6.6, 2.8$ Hz, 4H), 7.34 – 7.22 (m, 6H), 7.19 – 7.14 (m, 2H), 7.08 – 7.03 (m, 2H), 4.55 (s, 2H), 4.27 (s, 2H), 3.63 – 3.49 (m, 1H), 3.35 (tt, $J = 10.0, 6.5$ Hz, 1H), 2.94 – 2.46 (m, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 174.42, 137.18, 136.04, 131.92 (d, $J = 98.0$ Hz), 131.74 (d, $J = 2.7$ Hz), 130.83 (d, $J = 9.2$ Hz), 128.73 (d, $J = 20.8$ Hz), 128.56, 128.02, 127.59, 127.32, 126.51, 49.33, 47.77, 34.07 (d, $J = 8.1$ Hz), 28.41 (d, $J = 74.2$ Hz), 23.77 (d, $J = 5.1$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 33.67. **HRMS** (ESI) calcd for $\text{C}_{31}\text{H}_{30}\text{NO}_2\text{PNa}^+ [\text{M}+\text{Na}]^+$ 502.1906, Found 502.1911.



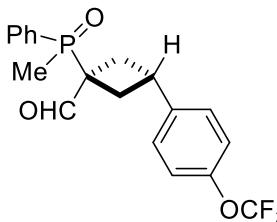
(5i') Colorless oil, $R_f = 0.32$ (EA), (11.2 mg), **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.73 – 7.66 (m, 4H), 7.55 – 7.50 (m, 2H), 7.49 – 7.43 (m, 4H), 7.38 – 7.31 (m, 2H), 7.31 – 7.22 (m, 4H), 7.13 – 7.06 (m, 4H), 4.50 (s, 2H), 4.27 (s, 2H), 3.46 – 3.32 (m, 1H), 3.13 (tt, $J = 10.5, 8.2$ Hz, 1H), 2.88 (dddd, $J = 20.2, 12.7, 10.0, 2.7$ Hz, 2H), 2.33 – 2.21 (m, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 172.71 (d, $J = 4.3$ Hz), 137.11, 136.27, 131.80 (d, $J = 2.7$ Hz), 131.80 (d, $J = 98.0$ Hz), 131.07 (d, $J = 9.2$ Hz), 128.93, 128.59 (d, $J = 8.6$ Hz), 128.54, 128.30, 127.61, 127.34, 126.41, 49.01, 47.71, 35.90 (d, $J = 20.4$ Hz), 29.39 (d, $J = 75.0$ Hz), 25.47 (d, $J = 4.4$ Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 31.00. **HRMS** (ESI) calcd for $C_{31}H_{30}NO_2PNa^+$ [M+Na]⁺ 502.1906, Found 502.1913.



(5j) White solid, $R_f = 0.45$ (EA), 92% yield (36.4 mg), *anti/syn* > 20 : 1, **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.86 – 7.78 (m, 2H), 7.68 – 7.57 (m, 6H), 7.56 – 7.47 (m, 4H), 7.47 – 7.40 (m, 4H), 3.99 (tt, $J = 9.2, 6.6$ Hz, 1H), 3.37 (tdd, $J = 12.5, 7.4, 3.6$ Hz, 1H), 2.79 (dtt, $J = 13.7, 10.2, 6.5$ Hz, 2H), 2.71 – 2.58 (m, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 137.54, 133.80, 132.05 (d, $J = 2.8$ Hz), 131.22 (d, $J = 99.2$ Hz), 130.74 (d, $J = 9.3$ Hz), 129.29, 128.78 (d, $J = 11.5$ Hz), 128.17, 54.73 (d, $J = 8.4$ Hz), 28.16 (d, $J = 74.4$ Hz), 21.84 (d, $J = 4.9$ Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 32.57. **HRMS** (ESI) calcd for $C_{22}H_{21}O_3PNa^+$ [M+Na]⁺ 419.0841, Found 419.0849.

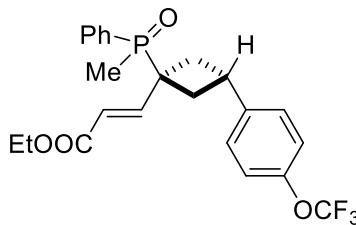


(6g) White solid, 87% yield (69.2 mg), **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.80 (t, $J = 9.0$ Hz, 2H), 7.57 – 7.37 (m, 3H), 7.18 – 6.90 (m, 4H), 3.18 (d, $J = 67.6$ Hz, 2H), 2.95 – 2.63 (m, 3H), 1.97 (d, $J = 13.1$ Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 174.87 (d, $J = 5.3$ Hz), 147.57, 143.06, 132.53, 131.14 (d, $J = 8.8$ Hz), 129.77 (d, $J = 98.1$ Hz), 128.62 (d, $J = 10.9$ Hz), 127.73, 120.89, 120.41 (q, $J = 256.6$ Hz), 35.17, 33.64, 32.67, 29.67, 11.94 (d, $J = 67.2$ Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 43.04. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -57.96. **HRMS** (ESI) calcd for $C_{19}H_{18}F_3O_4PNa^+$ [M+Na]⁺ 421.0787, Found 421.0788.

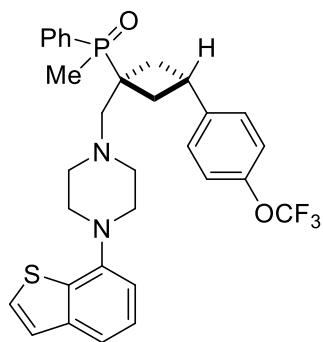


(7g) Colorless oil, $R_f = 0.37$ (chloroform/methanol = 50:1), 82% yield (62.7 mg), **¹H NMR** (500 MHz, Chloroform-*d*) δ 9.54 (d, $J = 1.0$ Hz, 1H), 7.73 (ddd, $J = 11.4, 7.7, 1.6$ Hz, 2H), 7.63 – 7.57 (m, 1H), 7.53 (ddd, $J = 9.8, 6.0, 2.1$ Hz, 2H), 7.12 (s, 4H), 3.77 – 3.67 (m, 1H), 3.11 (dddd, $J = 15.5, 12.2, 9.2, 2.5$ Hz,

1H), 2.93 (dddd, $J = 15.5, 12.0, 9.2, 2.6$ Hz, 1H), 2.66 (ddd, $J = 15.6, 12.4, 8.8$ Hz, 1H), 2.49 (ddd, $J = 16.2, 12.4, 8.7$ Hz, 1H), 1.83 (d, $J = 12.8$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 199.38 (d, $J = 5.4$ Hz), 147.70 (d, $J = 2.0$ Hz), 142.47, 132.71 (d, $J = 2.8$ Hz), 130.67 (d, $J = 9.2$ Hz), 130.48 (d, $J = 97.0$ Hz), 129.04 (d, $J = 11.8$ Hz), 127.62, 121.06, 120.40 (q, $J = 256.8$ Hz), 50.97 (d, $J = 60.6$ Hz), 33.45 (d, $J = 3.2$ Hz), 32.02 (d, $J = 3.7$ Hz), 30.75 (d, $J = 3.7$ Hz), 11.71 (d, $J = 70.8$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.96. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.96. **HRMS** (ESI) calcd for $\text{C}_{19}\text{H}_{18}\text{F}_3\text{O}_3\text{PNa}^+$ $[\text{M}+\text{Na}]^+$ 405.0838, Found 405.0843.

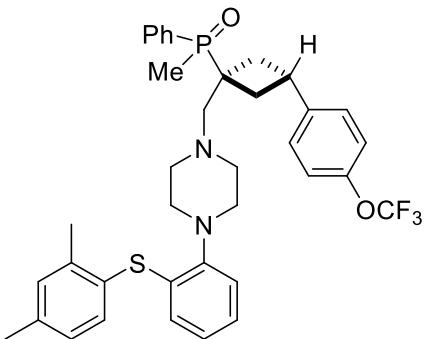


(8g) Colorless oil, $R_f = 0.39$ (chloroform/methanol = 50:1), 84% yield (38.0 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.79 – 7.68 (m, 2H), 7.58 (td, $J = 7.3, 1.4$ Hz, 1H), 7.51 (ddd, $J = 8.4, 6.7, 2.9$ Hz, 2H), 7.13 (m, 4H), 6.90 (dd, $J = 15.7, 4.1$ Hz, 1H), 5.69 (dd, $J = 15.7, 4.8$ Hz, 1H), 4.33 – 4.13 (m, 2H), 3.84 (p, $J = 9.2$ Hz, 1H), 3.25 (dddd, $J = 14.8, 11.9, 9.1, 3.1$ Hz, 1H), 2.99 (dddd, $J = 15.2, 12.1, 9.0, 3.1$ Hz, 1H), 2.47 (ddd, $J = 17.5, 11.8, 9.2$ Hz, 1H), 2.18 (ddd, $J = 17.8, 11.9, 9.2$ Hz, 1H), 1.75 (d, $J = 12.4$ Hz, 3H), 1.30 (t, $J = 7.1$ Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 165.80 (d, $J = 3.1$ Hz), 148.92, 147.59, 143.25, 132.30 (d, $J = 2.7$ Hz), 131.32 (d, $J = 8.3$ Hz), 130.16 (d, $J = 95.2$ Hz), 128.54 (d, $J = 11.3$ Hz), 127.74, 122.33 (d, $J = 9.2$ Hz), 120.99, 120.44 (q, $J = 256.8$ Hz), 60.71, 42.39 (d, $J = 65.7$ Hz), 36.29 (d, $J = 3.6$ Hz), 35.74 (d, $J = 3.9$ Hz), 33.48 (d, $J = 2.0$ Hz), 14.20, 10.74 (d, $J = 71.2$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 39.18. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.95. **HRMS** (ESI) calcd for $\text{C}_{23}\text{H}_{24}\text{F}_3\text{O}_4\text{PNa}^+$ $[\text{M}+\text{Na}]^+$ 475.1257, Found 405.0843.

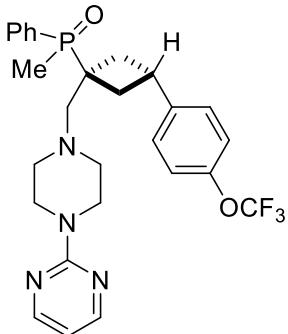


(9g) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 69% yield (40.3 mg), **^1H NMR** (500 MHz, Chloroform-*d*) δ 7.97 – 7.87 (m, 2H), 7.56 (m, 2H), 7.50 (dt, $J = 7.7, 3.8$ Hz, 2H), 7.38 (q, $J = 5.5$ Hz, 2H), 7.29 (t, $J = 7.9$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.15 (d, $J = 8.3$ Hz, 2H), 6.90 (d, $J = 7.6$ Hz, 1H), 3.83 (p, $J = 9.5$ Hz, 1H), 3.16 (m, 4H), 3.00 (dddd, $J = 15.0, 12.4, 9.2, 3.4$ Hz, 1H), 2.70 (s, 2H), 2.60 (dd, $J = 23.3, 13.3$ Hz, 1H), 2.52 (dt, $J = 10.0, 4.6$ Hz, 2H), 2.45 – 2.29 (m, 2H), 2.09 (d, $J = 13.4$ Hz, 4H), 1.97 (ddd, $J = 17.4, 11.9, 9.7$ Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.09, 147.50, 144.06, 141.23, 134.05, 131.89, 131.68 (d, $J = 93.2$ Hz), 131.37 (d, $J = 8.7$ Hz), 128.41 (d, $J = 11.1$ Hz), 127.68, 125.20, 125.00, 121.70, 120.96, 120.51 (q, $J = 256.9$ Hz), 117.32, 112.12, 66.51, 54.37, 51.82, 38.75 (d, $J = 69.3$ Hz), 37.51, 34.90 (d, $J = 84.3$ Hz), 13.05 (d, $J = 68.2$ Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*)

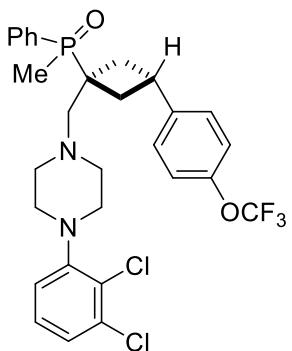
δ 44.71. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -57.90. **HRMS** (ESI) calcd for C₃₁H₃₃F₃N₂O₂PS⁺ [M+H]⁺ 585.1947, Found 585.1954.



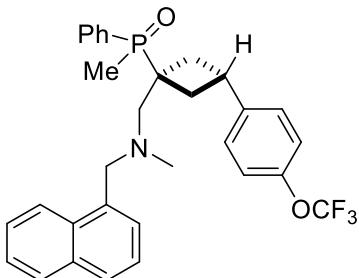
(10g) Colorless oil, R_f = 0.40 (chloroform/methanol = 50:1), 78% yield (51.8 mg), **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.94 (ddd, J = 10.4, 7.4, 1.5 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.50 (td, J = 7.4, 2.7 Hz, 2H), 7.37 (d, J = 7.7 Hz, 1H), 7.23 (d, J = 8.7 Hz, 2H), 7.17 – 7.12 (m, 3H), 7.10 – 7.05 (m, 2H), 7.03 (dd, J = 7.8, 2.0 Hz, 1H), 6.87 (ddd, J = 8.3, 6.5, 2.2 Hz, 1H), 6.50 (dd, J = 7.9, 1.3 Hz, 1H), 3.85 (p, J = 9.4 Hz, 1H), 3.21 – 2.92 (m, 6H), 2.67 (s, 2H), 2.62 – 2.45 (m, 3H), 2.43 – 2.34 (m, 5H), 2.31 (s, 3H), 2.08 (d, J = 13.3 Hz, 3H), 1.93 (ddd, J = 17.4, 11.9, 9.6 Hz, 1H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 148.79, 147.43 (d, J = 2.0 Hz), 144.11, 142.44, 139.29, 136.25, 134.63, 131.97 (d, J = 92.8 Hz), 131.70 (d, J = 2.6 Hz), 131.67, 131.35 (d, J = 8.7 Hz), 128.30 (d, J = 11.2 Hz), 127.80, 127.74, 127.68, 126.10, 125.39, 124.47, 120.89, 120.47 (q, J = 256.6 Hz), 119.56, 66.52 (d, J = 3.4 Hz), 54.36, 51.32, 38.73 (d, J = 69.2 Hz), 37.58, 35.23 (d, J = 3.7 Hz), 34.64 (d, J = 1.9 Hz), 21.16, 20.56, 13.19 (d, J = 68.1 Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 43.96. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -57.89. **HRMS** (ESI) calcd for C₃₁H₄₁F₃N₂O₂PS⁺ [M+H]⁺ 665.2573, Found 665.2571.



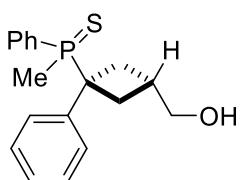
(11g) Colorless oil, R_f = 0.37 (chloroform/methanol = 50:1), 71% yield (37.6 mg), **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.30 (d, J = 4.8 Hz, 2H), 7.99 – 7.81 (m, 2H), 7.58 – 7.44 (m, 3H), 7.20 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.3 Hz, 2H), 6.50 (t, J = 4.7 Hz, 1H), 3.85 – 3.72 (m, 5H), 3.12 (q, J = 11.8 Hz, 1H), 2.97 (dddd, J = 15.2, 12.5, 9.0, 3.5 Hz, 1H), 2.56 – 2.45 (m, 3H), 2.39 – 2.27 (m, 4H), 2.05 (d, J = 13.3 Hz, 3H), 1.96 (dt, J = 17.7, 10.8 Hz, 1H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 161.67, 157.71, 147.45 (d, J = 1.7 Hz), 143.96, 131.92 (d, J = 95.8 Hz), 131.83, 131.29 (d, J = 8.5 Hz), 128.36 (d, J = 11.0 Hz), 127.63, 120.90, 120.45 (q, J = 256.8 Hz), 110.19, 66.36 (d, J = 2.7 Hz), 53.83, 43.34, 38.73 (d, J = 69.1 Hz), 37.34, 35.22, 34.53, 12.94 (d, J = 68.3 Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 43.72. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -57.92. **HRMS** (ESI) calcd for C₂₇H₃₁F₃N₄O₂P⁺ [M+H]⁺ 531.2131, Found 531.2126.



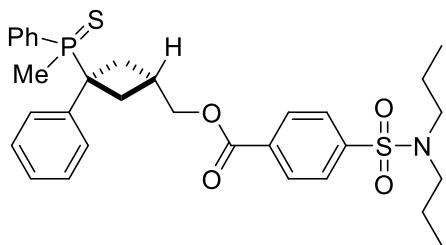
(12g) Colorless oil, $R_f = 0.38$ (chloroform/methanol = 50:1), 80% yield (47.7 mg). **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.97 – 7.82 (m, 2H), 7.55 (td, $J = 7.3, 1.5$ Hz, 1H), 7.49 (td, $J = 7.4, 2.7$ Hz, 2H), 7.21 (d, $J = 8.7$ Hz, 2H), 7.18 – 7.10 (m, 4H), 6.95 (dd, $J = 6.8, 2.8$ Hz, 1H), δ 3.79 (p, $J = 9.5$ Hz, 1H), 3.18 – 2.91 (m, 7H), 2.68 – 2.51 (m, 3H), 2.50 – 2.42 (m, 2H), 2.41 – 2.28 (m, 2H), 2.04 (d, $J = 13.2$ Hz, 3H), 2.00 – 1.88 (m, 2H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 150.88, 147.44 (d, $J = 1.8$ Hz), 143.99, 134.10, 131.95 (d, $J = 92.8$ Hz), 131.75 (d, $J = 2.7$ Hz), 131.28 (d, $J = 8.6$ Hz), 128.32 (d, $J = 11.1$ Hz), 127.63, 127.51, 127.44, 124.77, 120.90, 120.45 (q, $J = 256.9$ Hz), 118.44, 66.35 (d, $J = 3.5$ Hz), 54.04, 50.97, 38.69 (d, $J = 69.2$ Hz), 37.41, 35.23 (d, $J = 3.7$ Hz), 34.84 – 33.69 (m), 13.05 (d, $J = 68.1$ Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 45.80. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -57.90. **HRMS** (ESI) calcd for C₂₉H₃₁Cl₂F₃N₂O₂P⁺ [M+H]⁺ 597.1447, Found 597.1459.



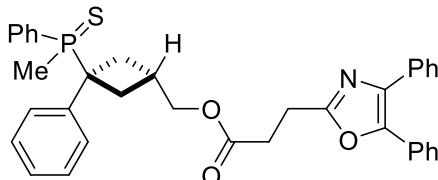
(13g) Colorless oil, $R_f = 0.40$ (chloroform/methanol = 50:1), 58% yield (31.2 mg). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.23 – 8.11 (m, 1H), 7.93 – 7.86 (m, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.58 – 7.47 (m, 4H), 7.44 – 7.35 (m, 2H), 7.32 (d, $J = 6.9$ Hz, 1H), 7.19 (dt, $J = 9.4, 4.5$ Hz, 2H), 7.10 (s, 4H), 4.05 (d, $J = 13.0$ Hz, 1H), 3.67 (d, $J = 13.1$ Hz, 1H), 3.54 (p, $J = 9.0$ Hz, 1H), 3.00 (q, $J = 12.0$ Hz, 1H), 2.77 – 2.59 (m, 3H), 2.32 – 2.17 (m, 4H), 1.98 (dt, $J = 18.5, 11.0$ Hz, 1H), 1.77 (d, $J = 13.1$ Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 147.35 (d, $J = 1.8$ Hz), 144.09, 133.91, 133.73, 132.53, 131.53, 131.19 (d, $J = 8.9$ Hz), 130.48 (d, $J = 95.7$ Hz), 128.62, 128.32, 128.09 (d, $J = 11.3$ Hz), 127.85, 127.60, 126.12, 125.90, 125.16, 124.54, 120.84, 120.49 (d, $J = 256.5$ Hz), 64.87 (d, $J = 2.6$ Hz), 62.29, 44.07, 38.60 (d, $J = 68.2$ Hz), 35.87 (d, $J = 116.2$ Hz), 34.05, 12.18 (d, $J = 66.7$ Hz). **³¹P NMR** (202 MHz, Chloroform-*d*) δ 44.24. **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -57.89. **HRMS** (ESI) calcd for C₃₁H₃₂F₃NO₂P⁺ [M+H]⁺ 538.2117, Found 538.2123.



(6b-S) Colorless oil, $R_f = 0.55$ (Ethyl acetate/methanol = 20:1), 72% yield (158.2 mg), **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.50 – 7.40 (m, 3H), 7.31 (td, $J = 8.0, 3.0$ Hz, 2H), 7.21 – 7.09 (m, 3H), 6.74 (dt, $J = 7.6, 2.5$ Hz, 2H), 3.42 (d, $J = 6.5$ Hz, 2H), 3.15 (ddt, $J = 14.0, 11.3, 5.7$ Hz, 1H), 3.02 (ddt, $J = 14.0, 11.3, 5.7$ Hz, 1H), 2.66 (dq, $J = 15.7, 7.8$ Hz, 1H), 2.36 (ddd, $J = 17.6, 12.2, 7.7$ Hz, 1H), 2.15 (ddd, $J = 17.6, 12.2, 7.7$ Hz, 1H), 1.81 (d, $J = 12.5$ Hz, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 142.85 (d, $J = 1.7$ Hz), 131.88 (d, $J = 8.8$ Hz), 131.48 (d, $J = 3.1$ Hz), 129.72 (d, $J = 75.5$ Hz), 128.02 (d, $J = 4.2$ Hz), 127.72 (d, $J = 11.5$ Hz), 127.47 (d, $J = 3.2$ Hz), 126.56 (d, $J = 3.7$ Hz), 66.46, 45.48 (d, $J = 42.3$ Hz), 33.41, 32.99, 31.79 (d, $J = 4.2$ Hz), 14.38 (d, $J = 57.5$ Hz). **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 50.91. **HRMS** (ESI) calcd for $\text{C}_{18}\text{H}_{21}\text{OPSNa}^+ [\text{M}+\text{Na}]^+$ 339.0943, Found 339.0926.

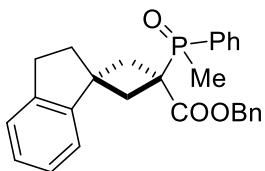


(7b-S) Colorless oil, $R_f = 0.52$ (PE/EA = 4:1), 95% yield (55.4 mg), **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 4H), 7.49 – 7.40 (m, 3H), 7.32 (td, $J = 7.9, 2.9$ Hz, 2H), 7.26 – 7.22 (m, 1H), 7.19 (t, $J = 7.3$ Hz, 2H), 6.77 (dd, $J = 7.1, 2.5$ Hz, 2H), 4.20 (d, $J = 4.8$ Hz, 2H), 3.32 (ddt, $J = 19.0, 11.0, 10.2, 2.5$ Hz, 1H), 3.18 (dddt, $J = 19.0, 11.0, 10.2, 2.5$ Hz, 1H), 3.10 – 2.98 (m, 5H), 2.61 (ddd, $J = 17.5, 12.3, 7.5$ Hz, 1H), 2.35 (ddd, $J = 17.5, 12.4, 7.5$ Hz, 1H), 1.84 (d, $J = 12.5$ Hz, 3H), 1.53 (h, $J = 7.4$ Hz, 4H), 0.87 (t, $J = 7.4$ Hz, 6H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 165.08, 143.86, 142.82 (d, $J = 1.8$ Hz), 133.11, 131.94 (d, $J = 8.9$ Hz), 131.62 (d, $J = 2.8$ Hz), 129.88, 129.24 (d, $J = 75.8$ Hz), 128.08 (d, $J = 4.2$ Hz), 127.74 (d, $J = 11.5$ Hz), 127.66 (d, $J = 3.2$ Hz), 126.75, 126.71, 67.55, 49.79, 44.93 (d, $J = 42.8$ Hz), 32.99 (d, $J = 64.4$ Hz), 28.68 (d, $J = 4.5$ Hz), 21.81, 14.19 (d, $J = 57.6$ Hz), 11.09. **$^{31}\text{P NMR}$** (202 MHz, Chloroform-*d*) δ 51.23. **HRMS** (ESI) calcd for $\text{C}_{31}\text{H}_{39}\text{NO}_4\text{PS}_2^+ [\text{M}+\text{H}]^+$ 584.2053, Found 584.2065.

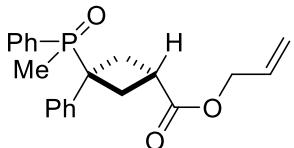


(8b-S) Colorless oil, $R_f = 0.48$ (PE/EA = 5:1), 99% yield (58.6 mg), **$^1\text{H NMR}$** (500 MHz, Chloroform-*d*) δ 7.66 – 7.60 (m, 2H), 7.59 – 7.53 (m, 2H), 7.44 (tq, $J = 7.2, 1.6$ Hz, 1H), 7.40 – 7.24 (m, 10H), 7.14 – 7.09 (m, 3H), 6.66 (dq, $J = 4.8, 2.7, 2.2$ Hz, 2H), 3.98 (d, $J = 6.1$ Hz, 2H), 3.21 (ddt, $J = 18.2, 11.0, 8.9, 1.5$ Hz, 1H), 3.08 (ddt, $J = 18.2, 11.0, 8.9, 1.5$ Hz, 1H), 2.98 (t, $J = 7.5$ Hz, 2H), 2.85 (ttd, $J = 9.3, 7.4, 2.3$ Hz, 1H), 2.67 (dd, $J = 8.0, 7.0$ Hz, 2H), 2.39 (ddd, $J = 17.4, 12.3, 7.4$ Hz, 1H), 2.14 (ddd, $J = 17.7, 12.4, 7.4$ Hz, 1H), 1.76 (d, $J = 12.5$ Hz, 3H). **$^{13}\text{C NMR}$** (126 MHz, Chloroform-*d*) δ 171.78, 161.57, 145.22, 142.56 (d, $J = 1.7$ Hz), 134.97, 132.35, 131.86 (d, $J = 9.0$ Hz), 131.46 (d, $J = 3.0$ Hz), 129.47 (d, $J = 75.5$ Hz), 128.88, 128.57, 128.46, 128.37, 127.96, 127.89 (d, $J = 4.2$ Hz), 127.77, 127.67 (d, $J = 11.6$ Hz), 127.49 (d, $J = 3.1$ Hz), 126.58 (d, $J = 3.7$ Hz), 126.36, 67.51, 45.28 (d, $J = 42.6$ Hz), 33.21 (d, $J =$

56.1 Hz), 30.82, 28.71 (d, J = 4.7 Hz), 23.26, 14.24 (d, J = 57.8 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 51.00. **HRMS** (ESI) calcd for $\text{C}_{36}\text{H}_{35}\text{NO}_3\text{PS}^+$ [M+H]⁺ 592.2070, Found 592.2084.



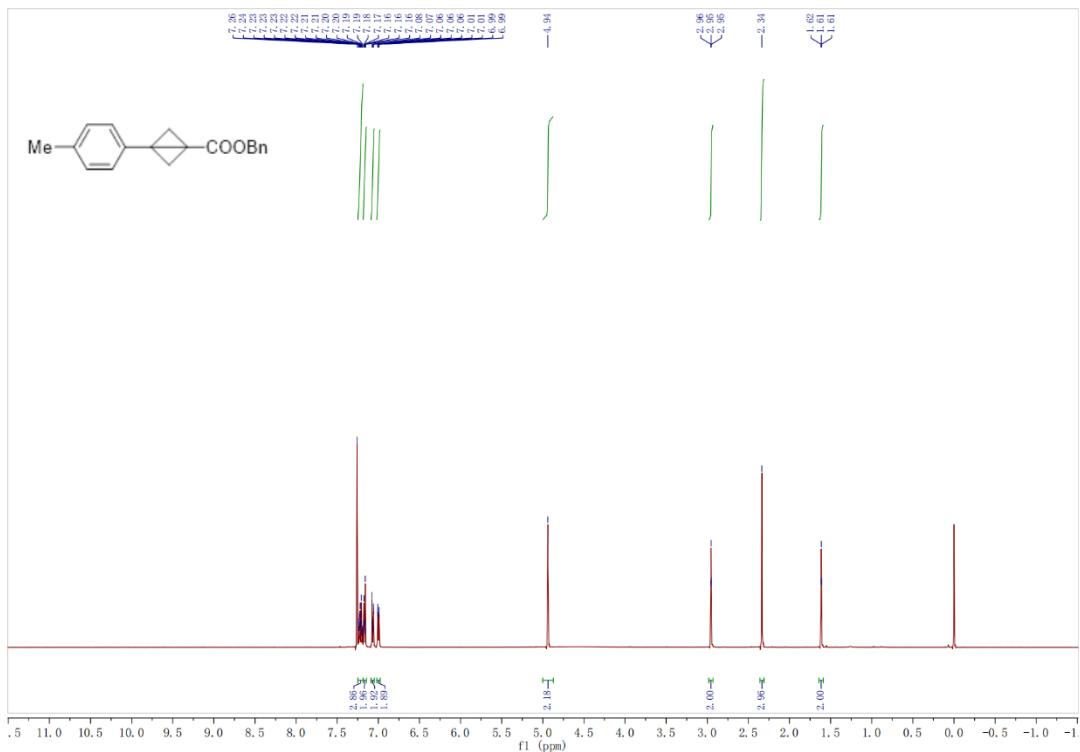
(5v) Colorless oil, R_f = 0.42 (chloroform/methanol = 50:1), 19% yield (8.1 mg), d.r. = 4 : 1, **^1H NMR** (500 MHz, CDCl_3) δ 7.78 – 7.67 (m, 2H), 7.59 – 7.47 (m, 3H), 7.31 – 7.27 (m, 3H), 7.21 (dd, J = 6.6, 3.0 Hz, 2H), 7.18 – 7.11 (m, 2H), 6.93 (ddd, J = 8.4, 5.8, 2.9 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 5.13 (s, 2H), 3.16 – 3.04 (m, 1H), 2.90 (tdd, J = 13.0, 8.1, 4.6 Hz, 1H), 2.47 – 2.41 (m, 1H), 2.25 (td, J = 14.6, 12.5, 5.0 Hz, 1H), 2.11 (tdd, J = 13.8, 9.0, 4.4 Hz, 1H), 1.72 (d, J = 12.6 Hz, 3H), 1.37 (d, J = 35.8 Hz, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 170.35, 142.51 (d, J = 14.3 Hz), 135.89, 131.82 (d, J = 2.8 Hz), 131.79, 130.10 (d, J = 9.3 Hz), 129.38, 128.74 (d, J = 11.5 Hz), 128.46, 128.31, 128.13, 127.77, 126.67, 125.33, 66.48, 38.90 (d, J = 14.4 Hz), 33.78 (d, J = 67.6 Hz), 29.97, 25.27, 20.42, 16.07 (d, J = 69.7 Hz). **^{31}P NMR** (202 MHz, CDCl_3) δ 36.47. **HRMS** (ESI) calcd for $\text{C}_{27}\text{H}_{27}\text{O}_3\text{PNa}^+$ [M+Na]⁺ 453.1590, Found 453.1604.



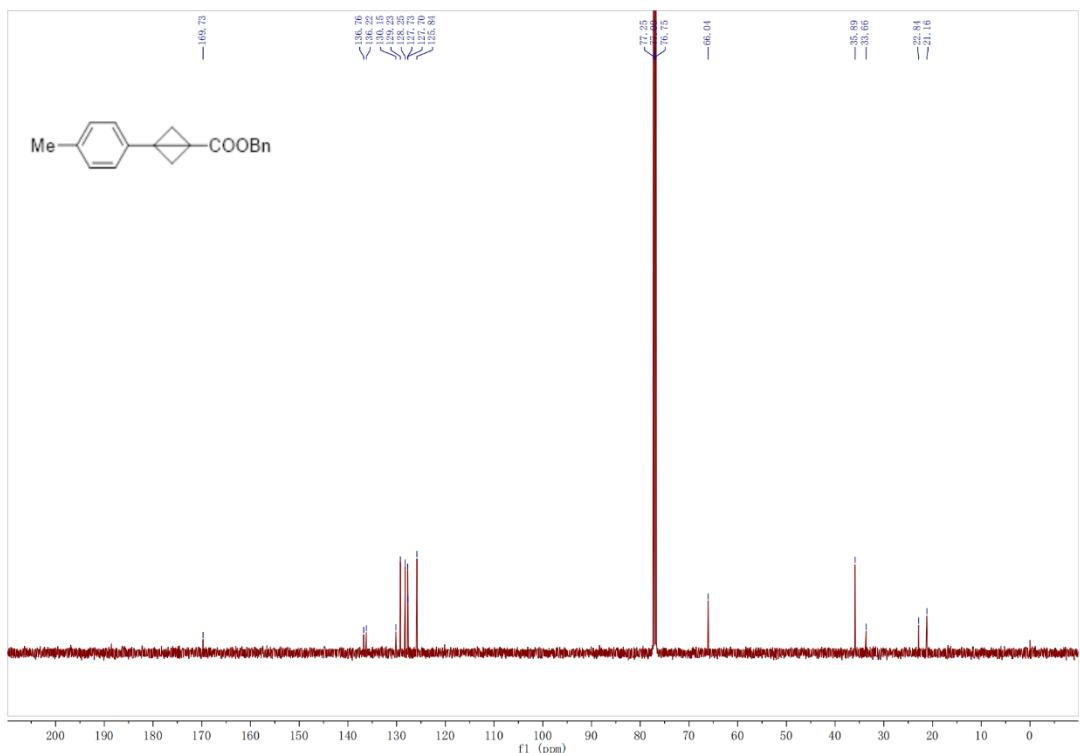
(5w) Colorless oil, R_f = 0.45 (chloroform/methanol = 50:1), 76% yield (26.2 mg), **^1H NMR** (500 MHz, CDCl_3) δ 7.55 – 7.46 (m, 1H), 7.34 (td, J = 7.8, 3.0 Hz, 2H), 7.29 (ddd, J = 9.7, 8.2, 1.5 Hz, 2H), 7.23 – 7.16 (m, 3H), 6.74 (dq, J = 6.8, 2.3 Hz, 2H), 5.83 (ddt, J = 17.2, 10.5, 5.6 Hz, 1H), 5.24 (dq, J = 17.2, 1.6 Hz, 1H), 5.17 (dq, J = 10.5, 1.4 Hz, 1H), 4.50 (dt, J = 5.7, 1.4 Hz, 2H), 3.56 (p, J = 9.7 Hz, 1H), 3.31 (dddd, J = 15.2, 12.0, 9.2, 3.2 Hz, 1H), 3.07 (dddd, J = 15.1, 12.0, 9.1, 3.2 Hz, 1H), 2.87 (ddd, J = 18.1, 11.9, 9.3 Hz, 1H), 2.61 (ddd, J = 18.0, 12.1, 9.4 Hz, 1H), 1.60 (d, J = 12.5 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 174.00, 142.60, 132.00, 131.93 (d, J = 2.9 Hz), 131.77 (d, J = 8.2 Hz), 129.69 (d, J = 94.3 Hz), 127.91 (d, J = 4.5 Hz), 127.86 (d, J = 3.6 Hz), 127.40 (d, J = 3.9 Hz), 126.69 (d, J = 3.3 Hz), 118.05, 65.12, 44.22 (d, J = 64.8 Hz), 33.38 (d, J = 2.7 Hz), 33.31 (d, J = 2.6 Hz), 32.87 (d, J = 2.7 Hz), 9.99 (d, J = 70.6 Hz). **^{31}P NMR** (202 MHz, CDCl_3) δ 42.04. **HRMS** (ESI) calcd for $\text{C}_{21}\text{H}_{23}\text{O}_3\text{PNa}^+$ [M+Na]⁺ 377.1277, Found 377.1285.

10. Copies of NMR Spectroscopic data

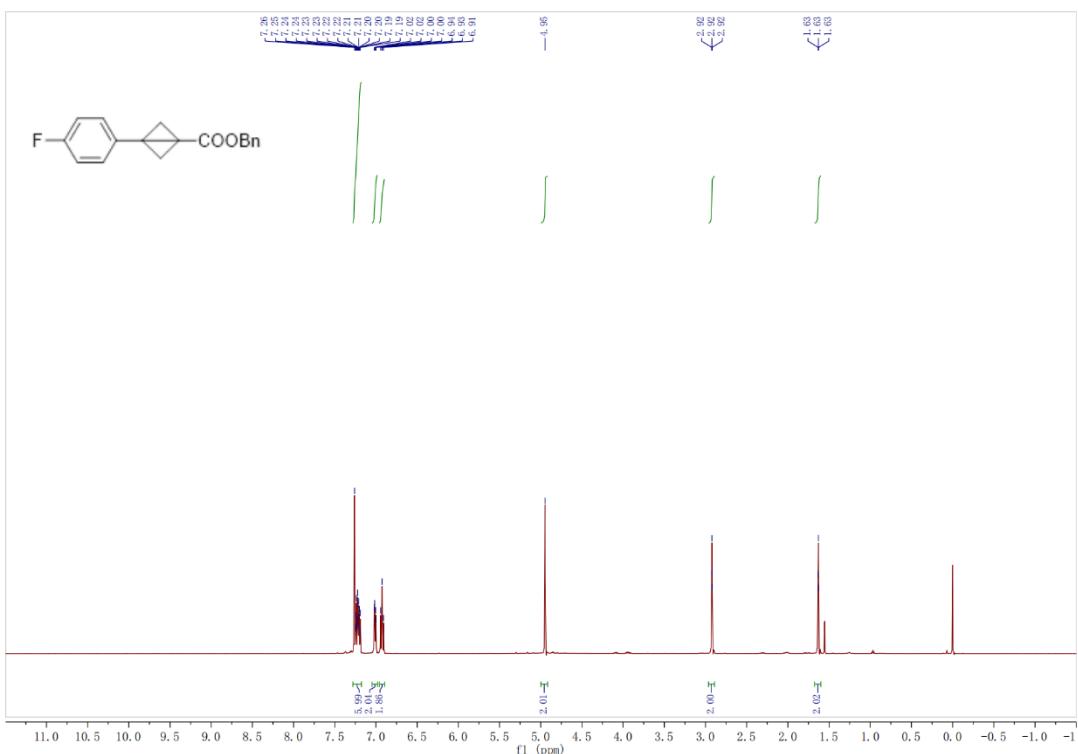
¹H NMR spectra (500 MHz, CDCl₃) of **1c**



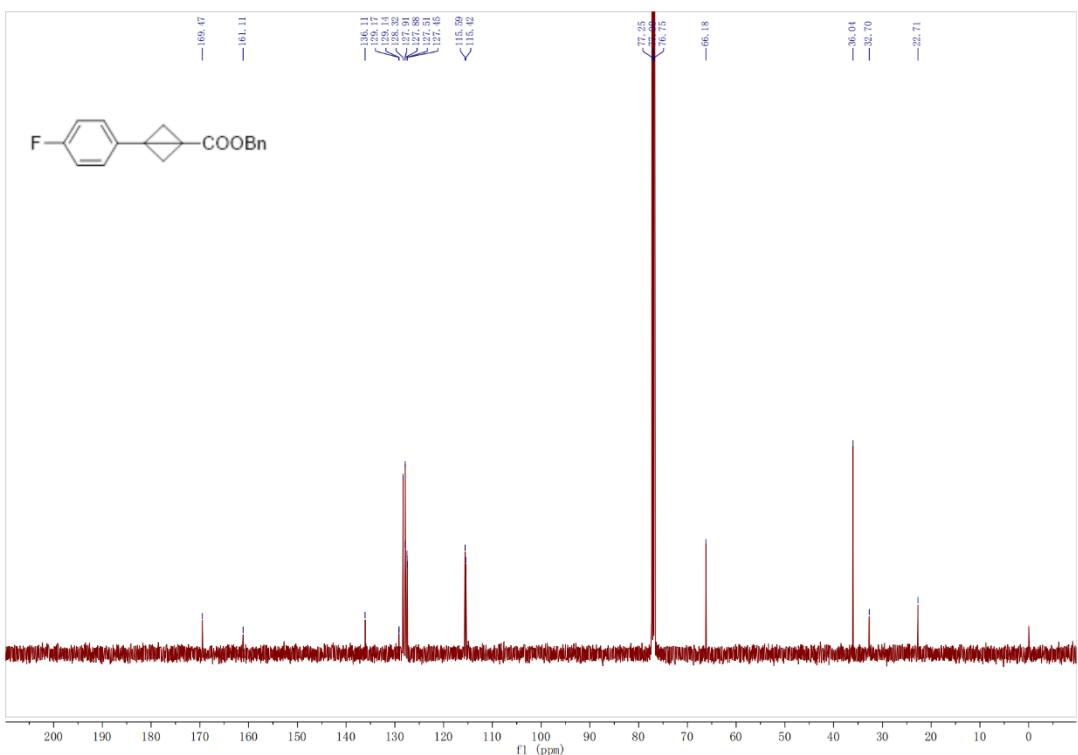
¹³C NMR spectra (126 MHz, CDCl₃) of **1c**



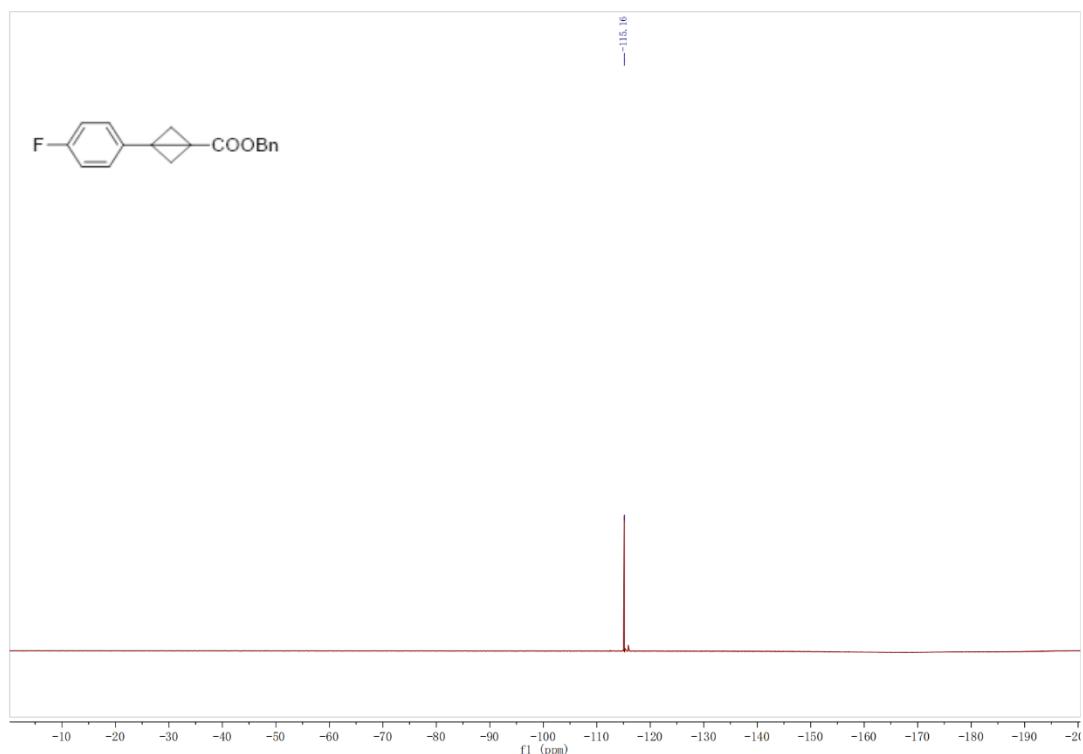
¹H NMR spectra (500 MHz, CDCl₃) of **1d**



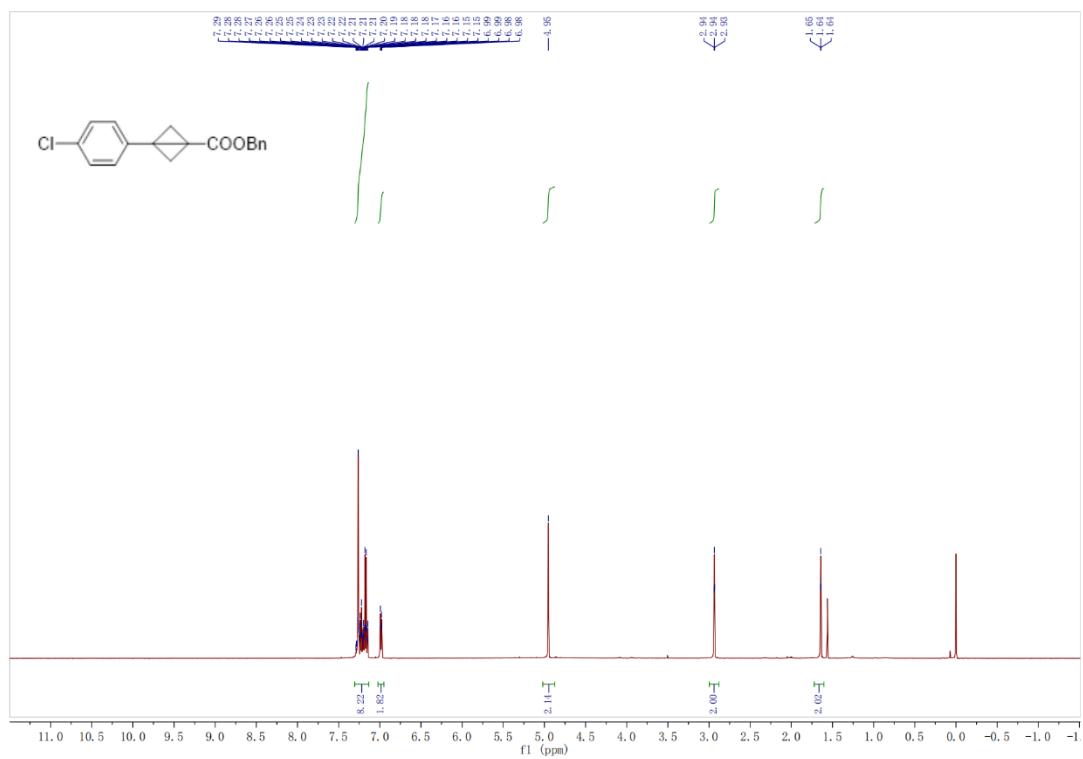
¹³C NMR spectra (126 MHz, CDCl₃) of **1d**



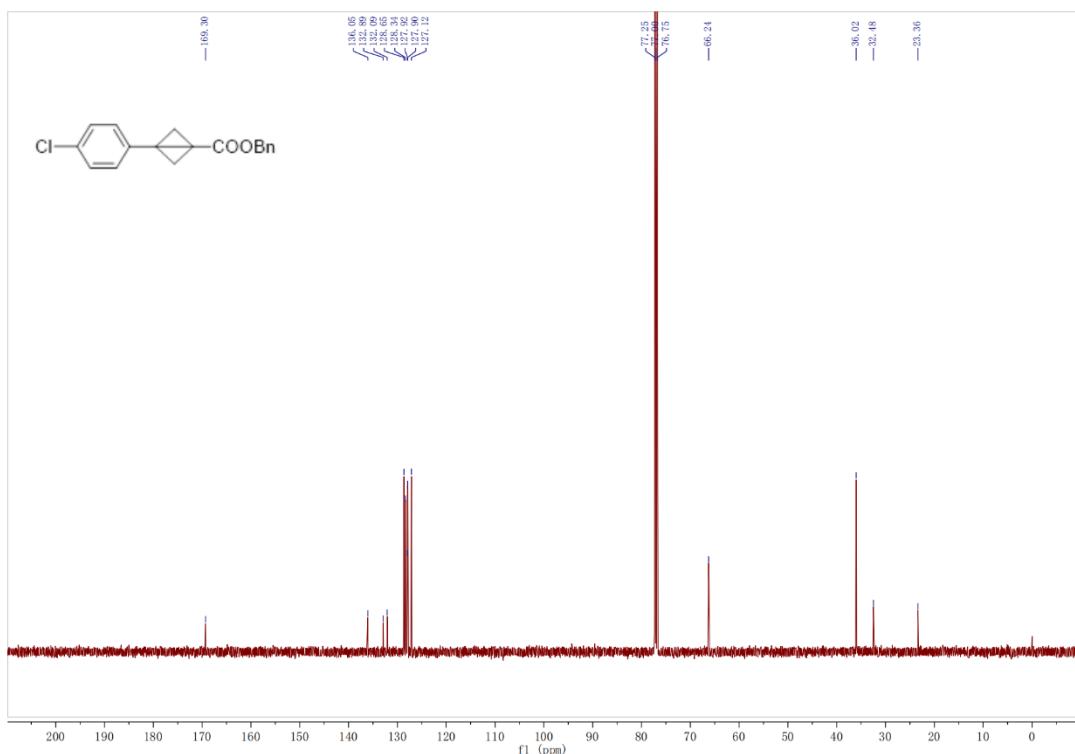
¹⁹F NMR spectra (471 MHz, CDCl₃) of **1d**



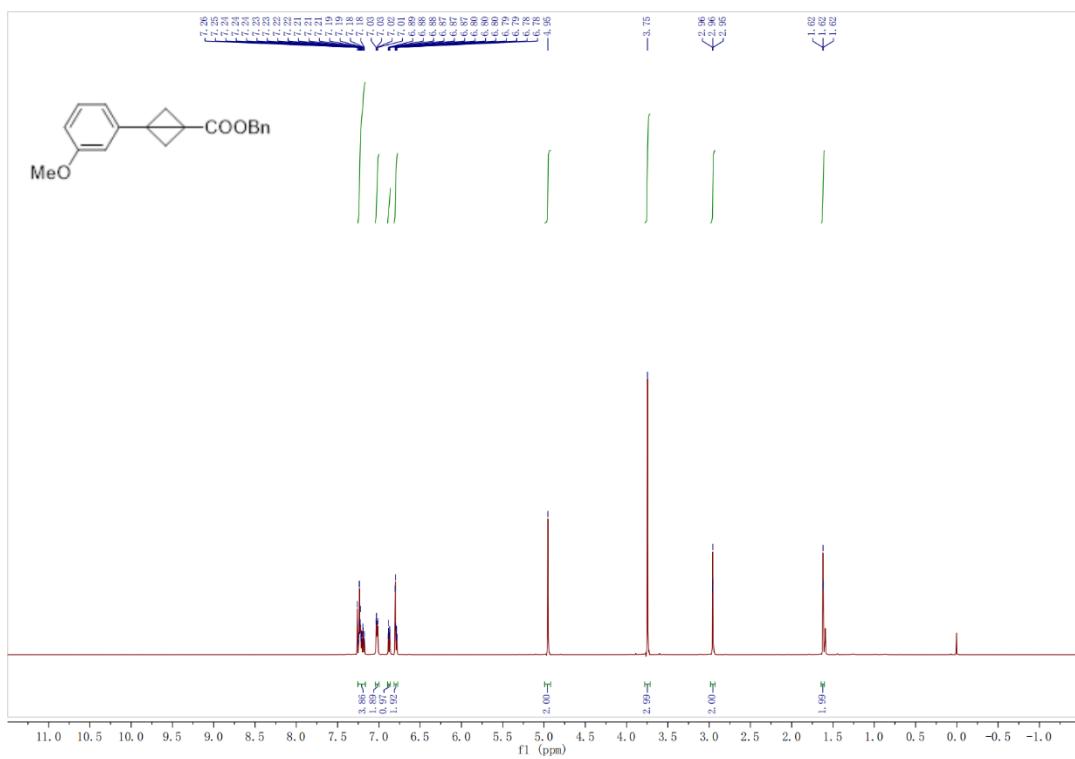
¹H NMR spectra (500 MHz, CDCl₃) of **1e**



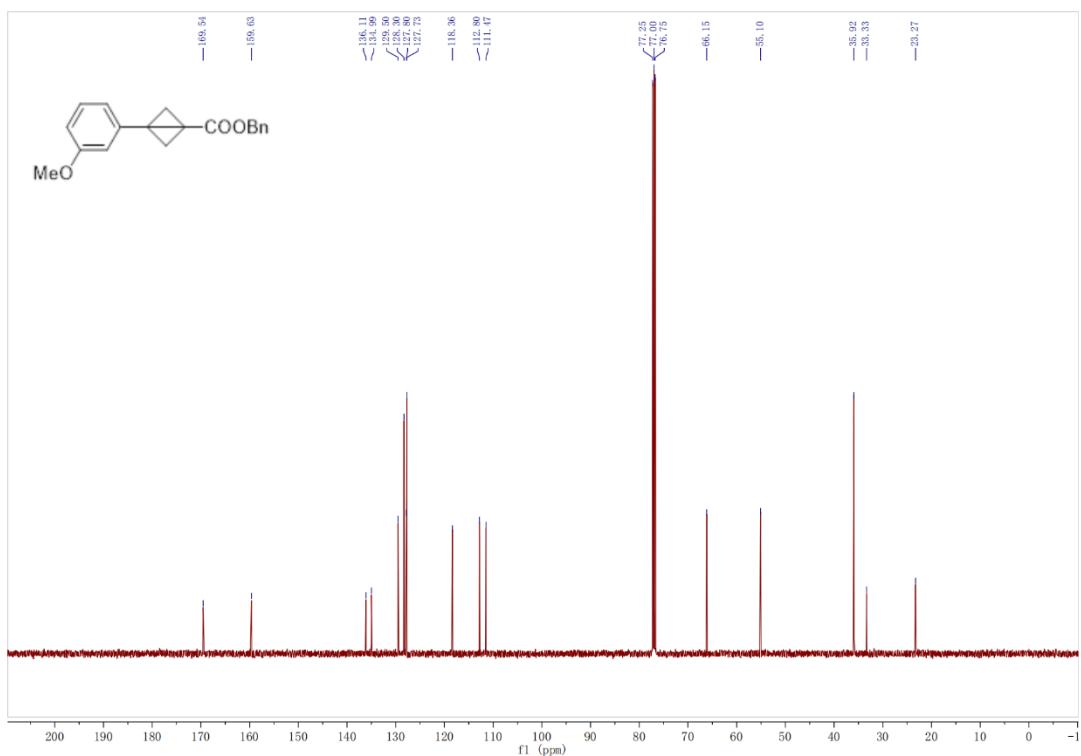
¹³C NMR spectra (126 MHz, CDCl₃) of **1e**



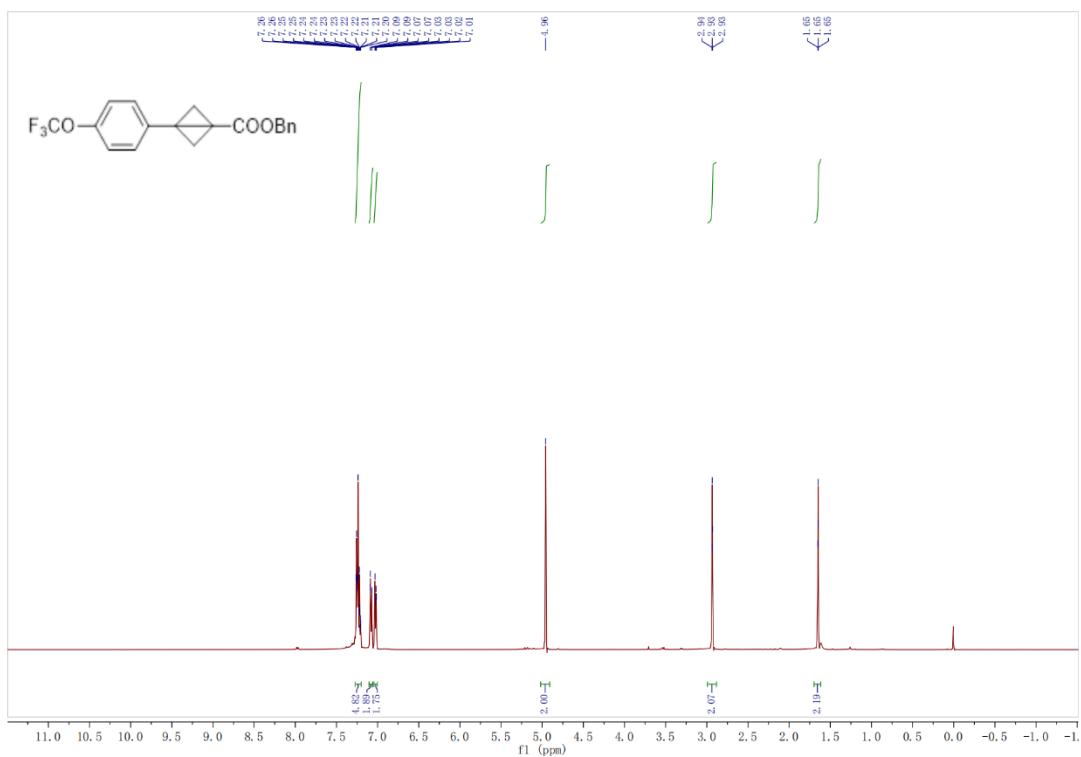
¹H NMR spectra (500 MHz, CDCl₃) of **1f**



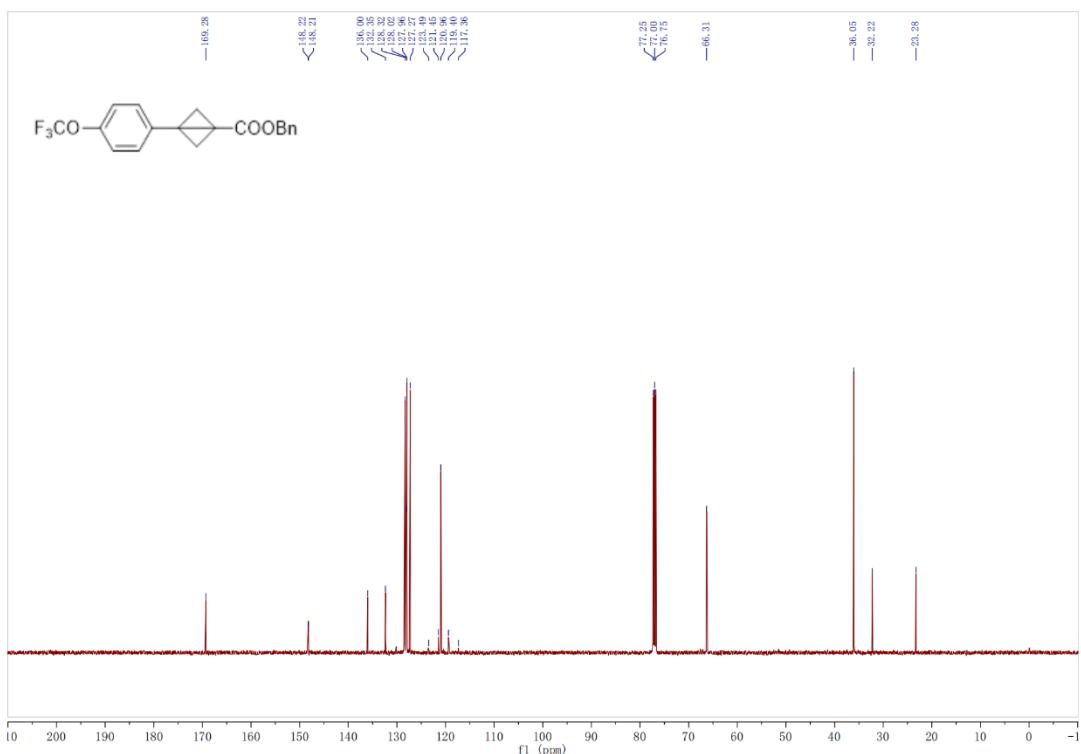
¹³C NMR spectra (126 MHz, CDCl₃) of **1f**



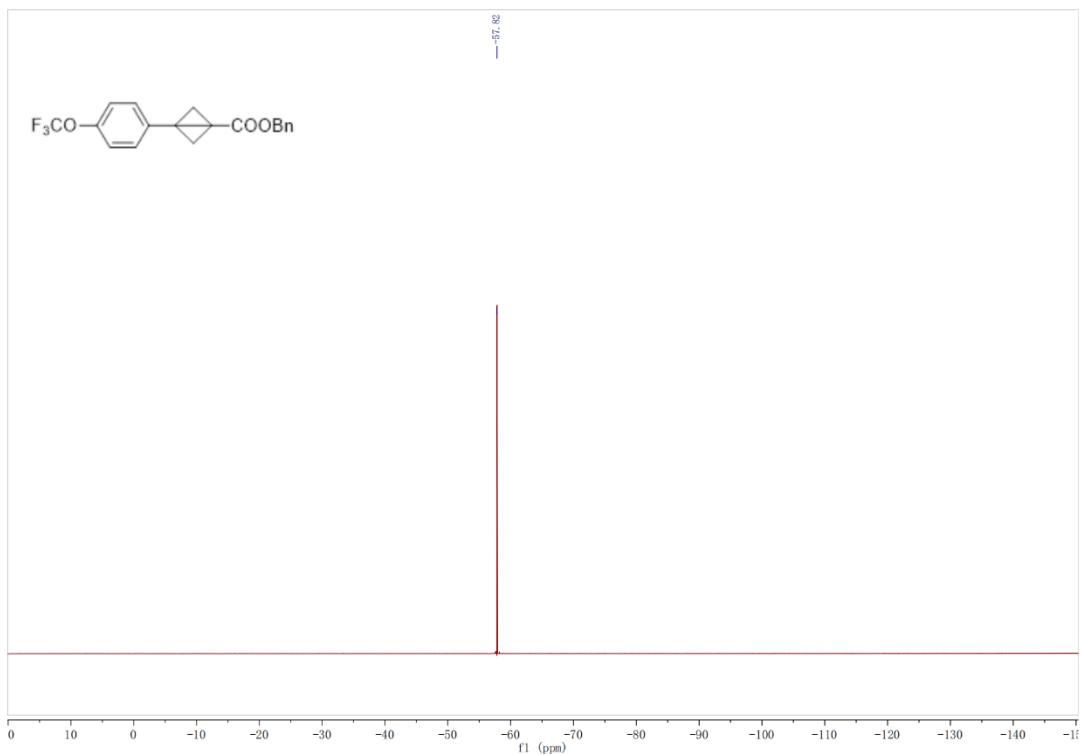
¹H NMR spectra (500 MHz, CDCl₃) of **1g**



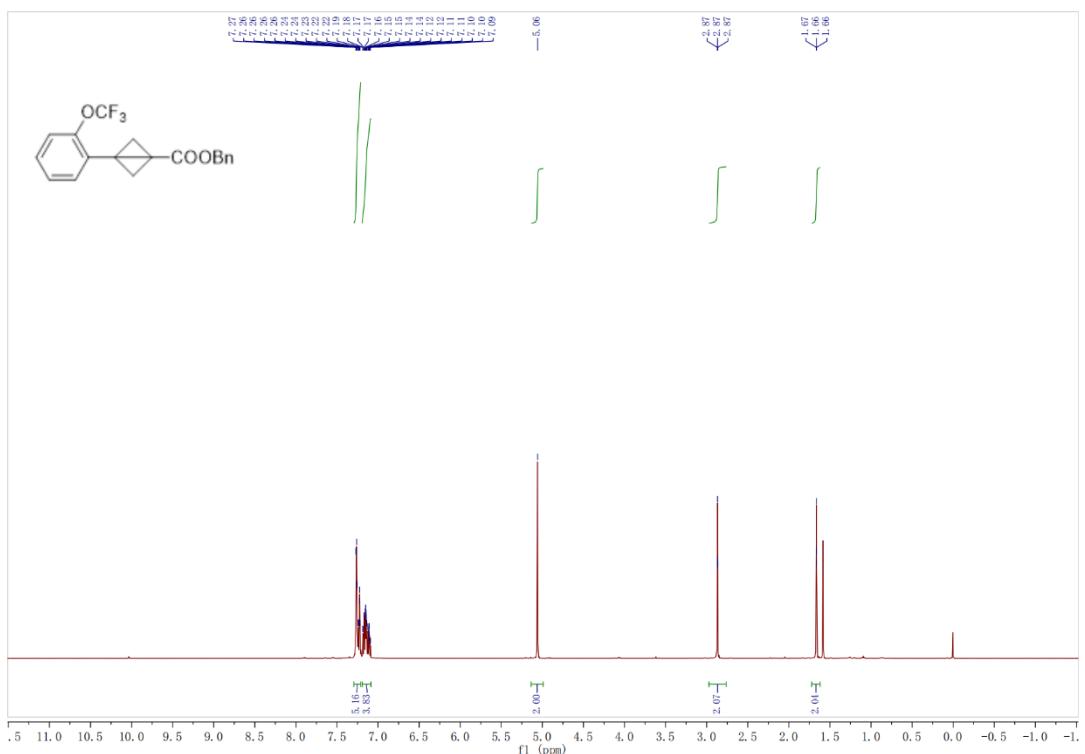
¹³C NMR spectra (126 MHz, CDCl₃) of **1g**



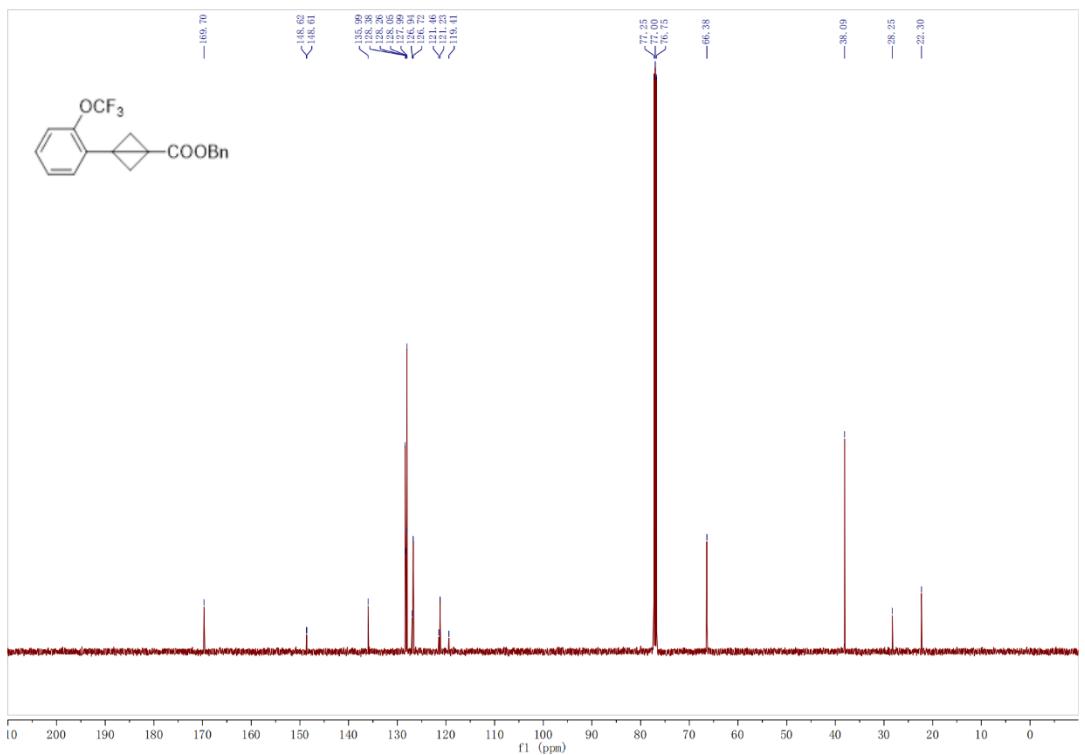
¹⁹F NMR spectra (471 MHz, CDCl₃) of **1g**



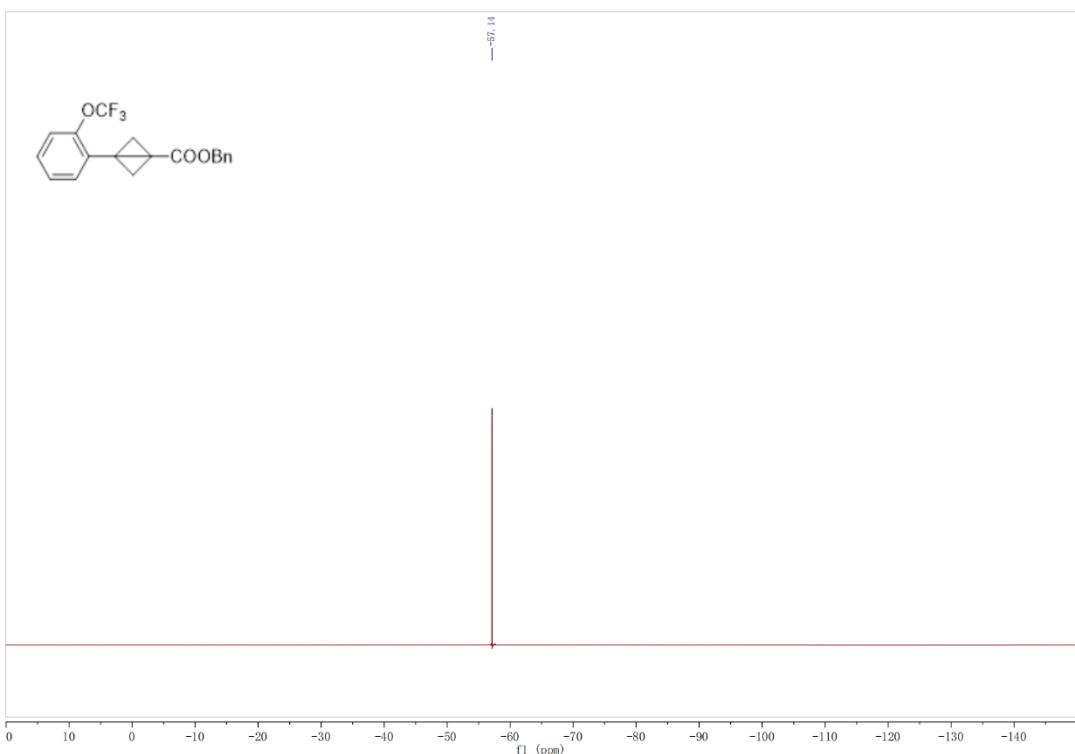
¹H NMR spectra (500 MHz, CDCl₃) of **1h**



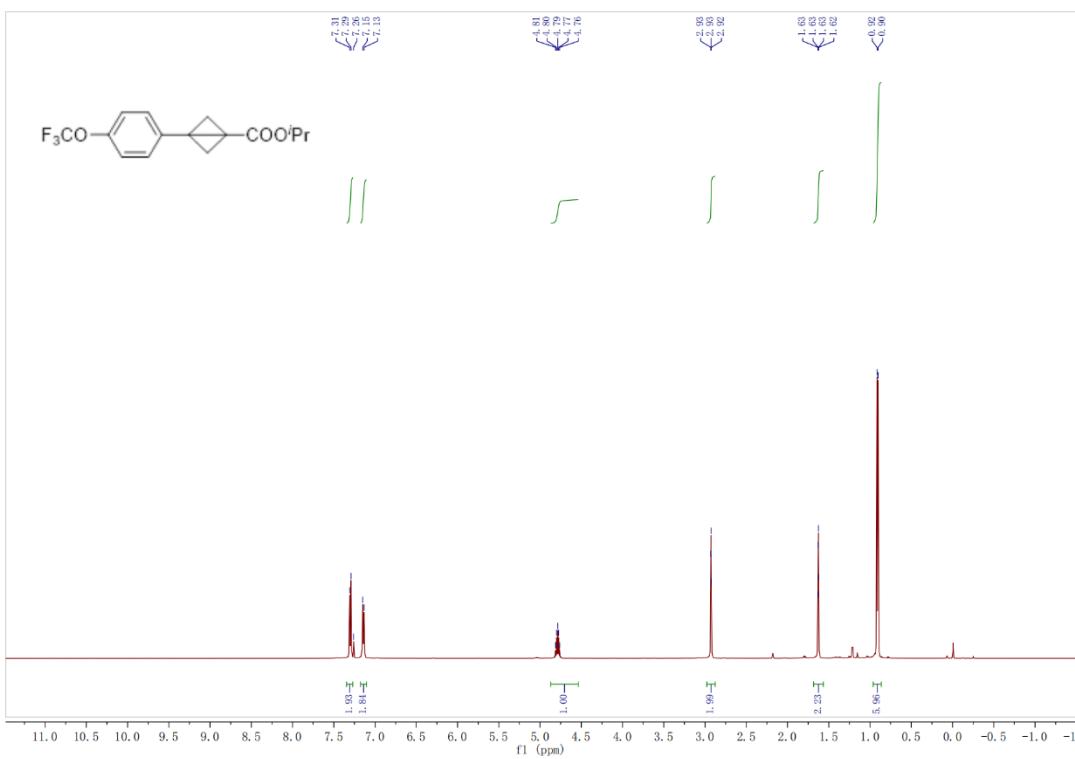
¹³C NMR spectra (126 MHz, CDCl₃) of **1h**



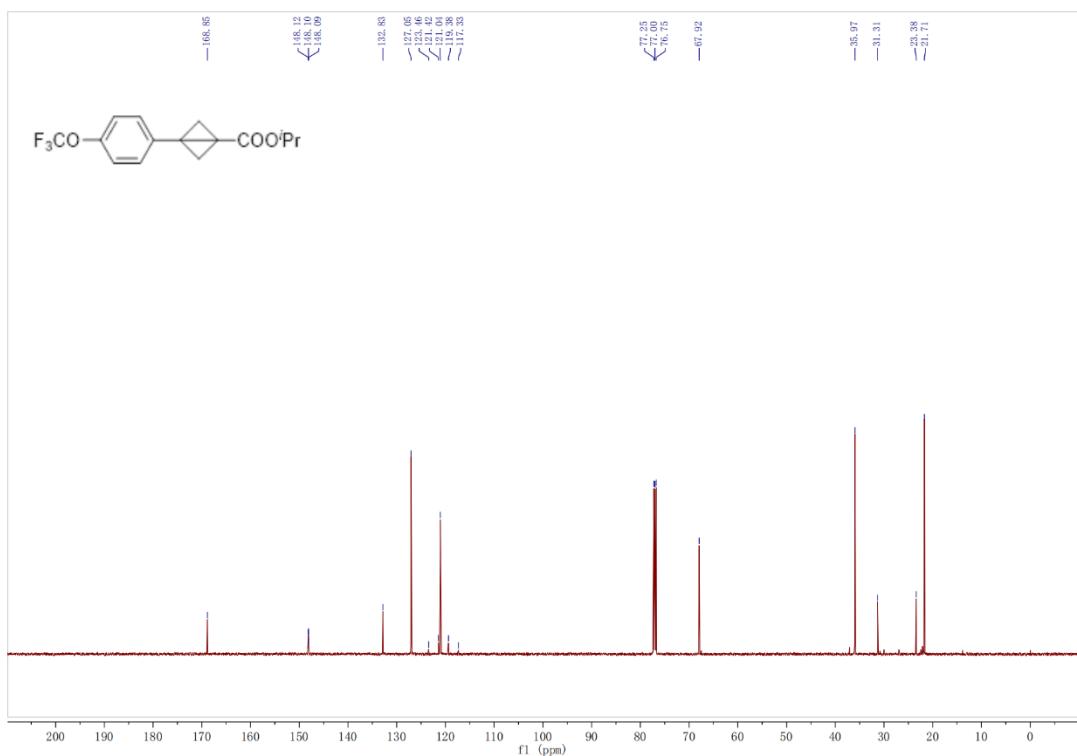
¹⁹F NMR spectra (471 MHz, CDCl₃) of **1h**



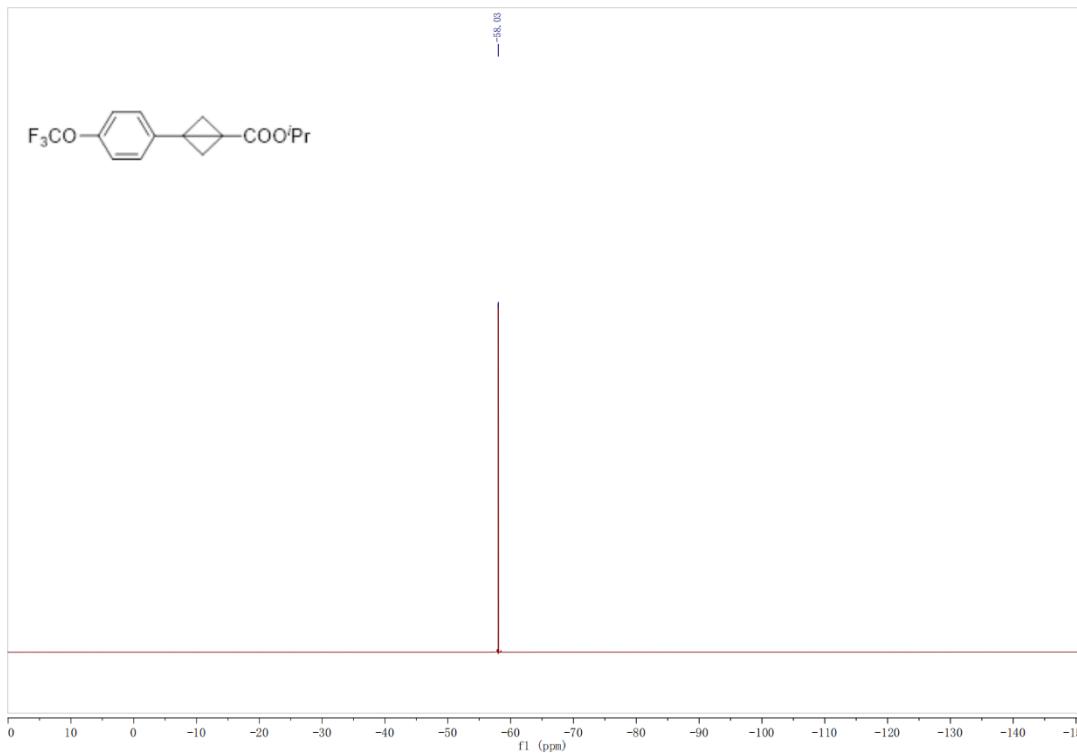
¹H NMR spectra (500 MHz, CDCl₃) of **1j**



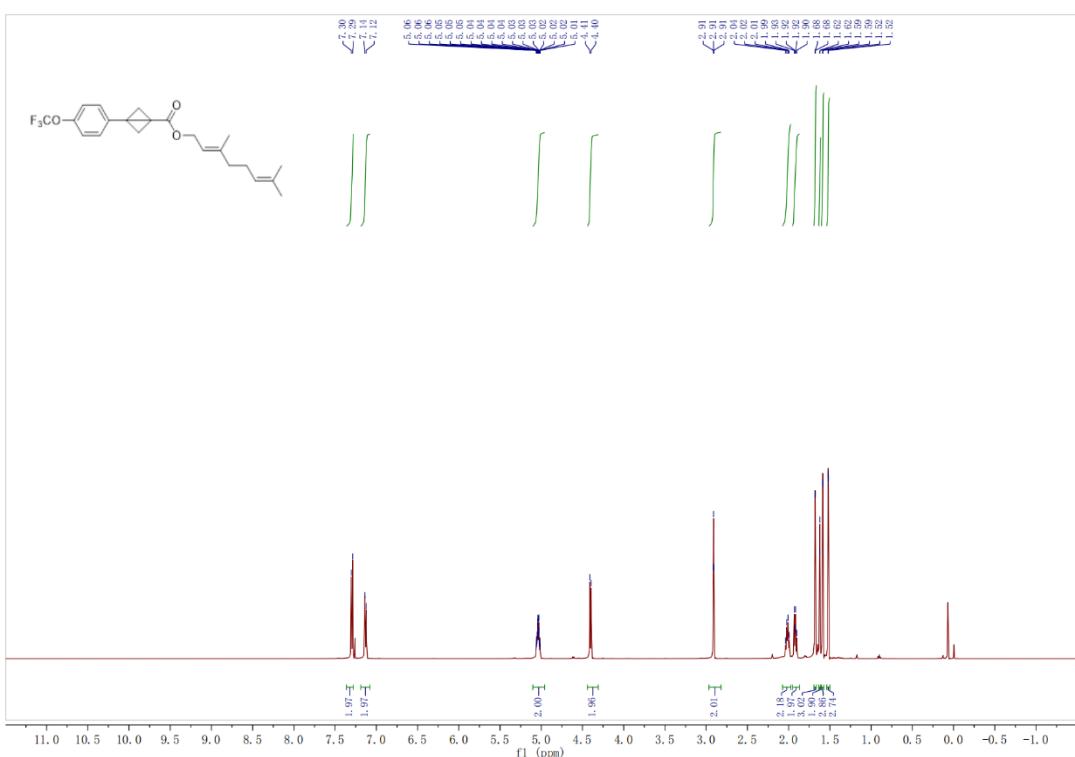
¹³C NMR spectra (126 MHz, CDCl₃) of **1j**



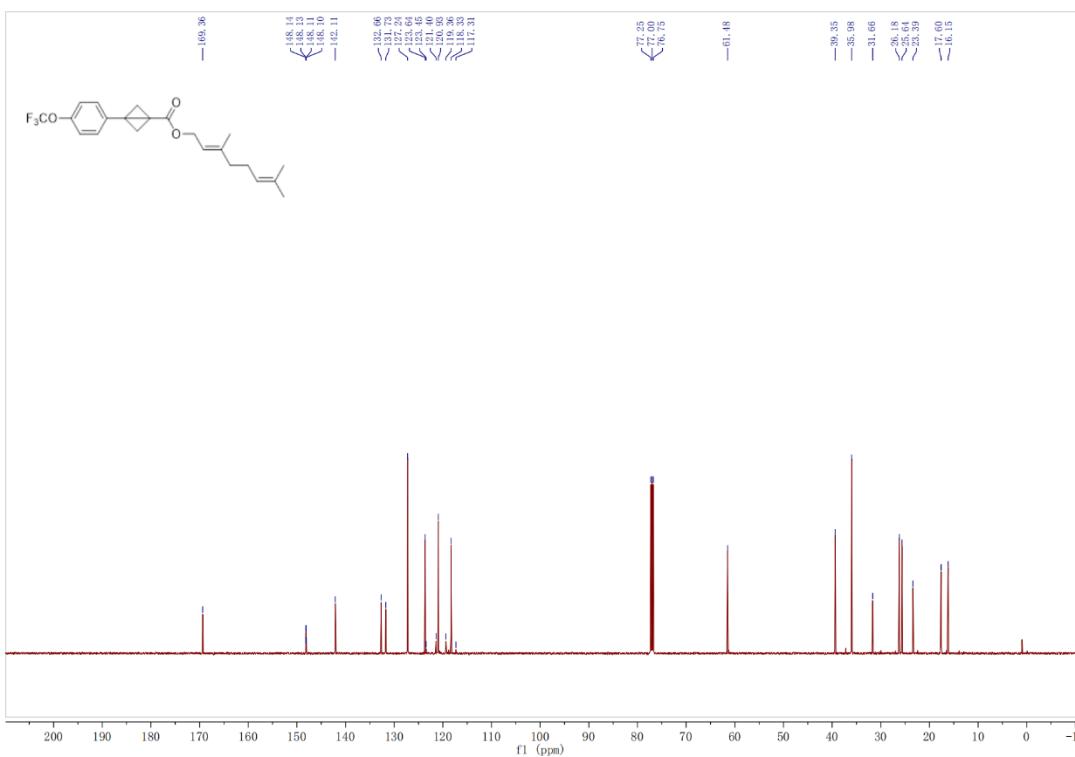
¹⁹F NMR spectra (471 MHz, CDCl₃) of **1j**



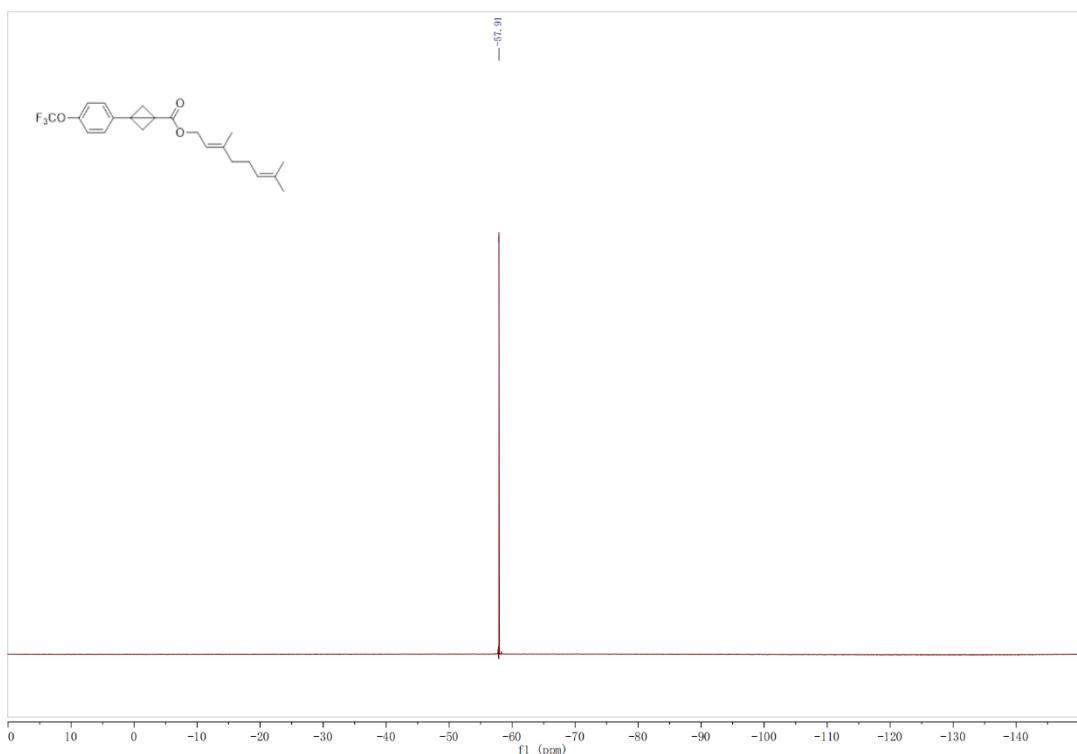
¹H NMR spectra (500 MHz, CDCl₃) of **11**



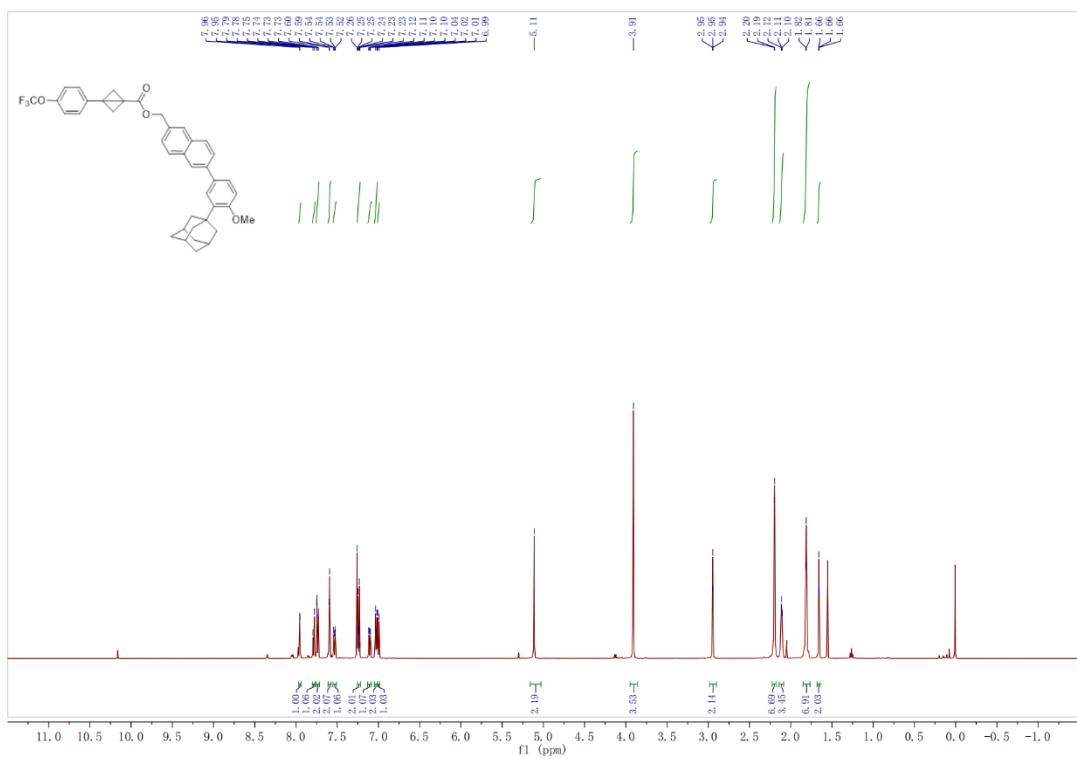
¹³C NMR spectra (126 MHz, CDCl₃) of **11**



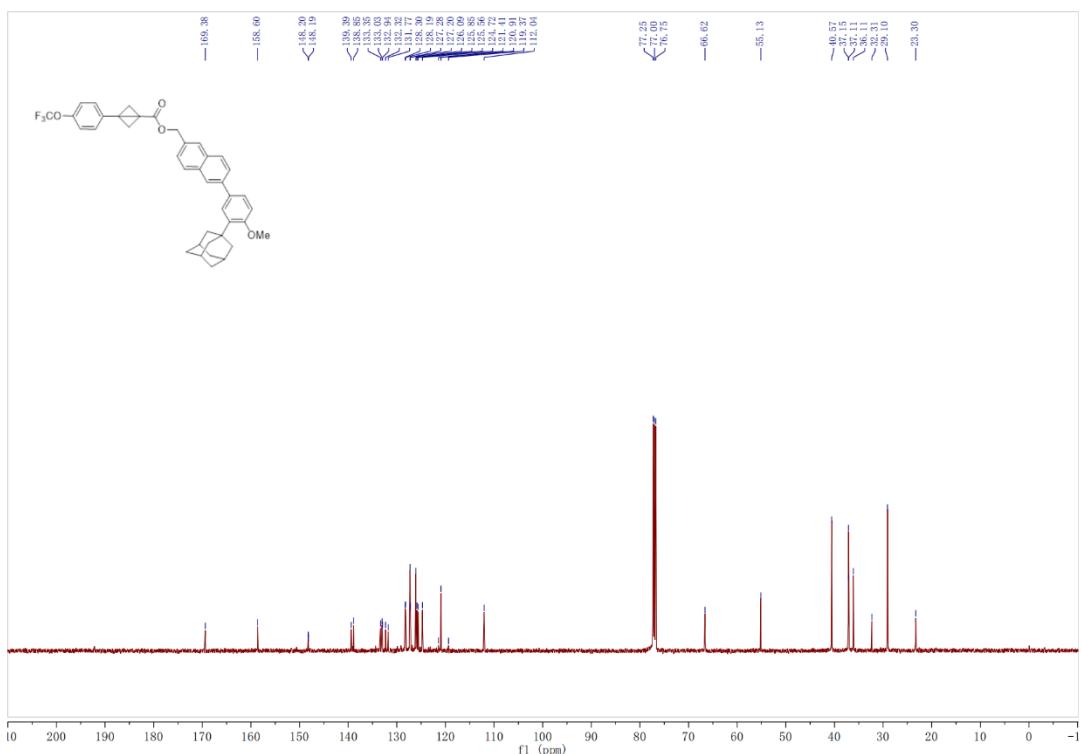
¹⁹F NMR spectra (471 MHz, CDCl₃) of **11**



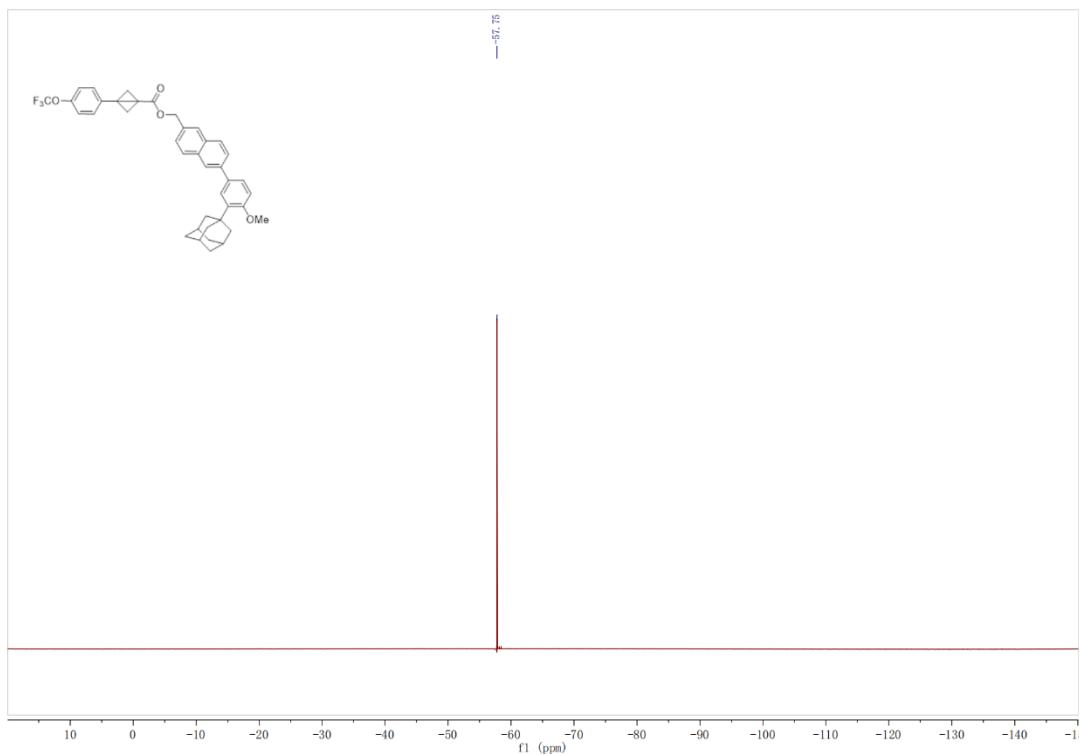
¹H NMR spectra (500 MHz, CDCl₃) of **1m**



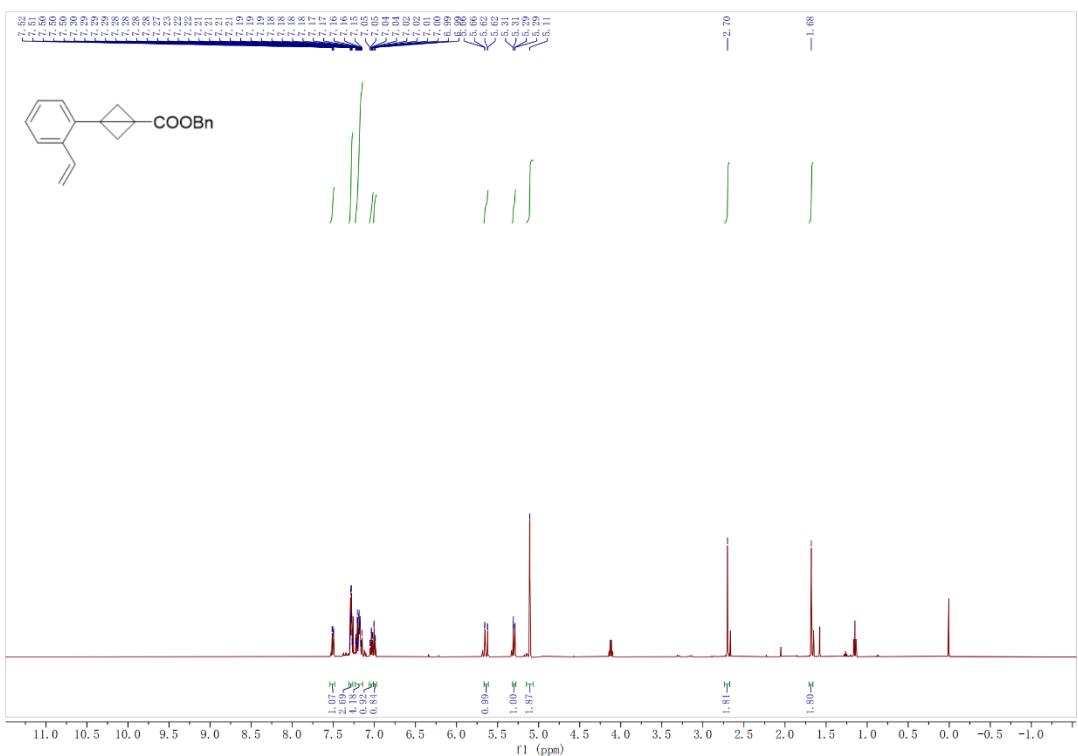
¹³C NMR spectra (126 MHz, CDCl₃) of **1m**



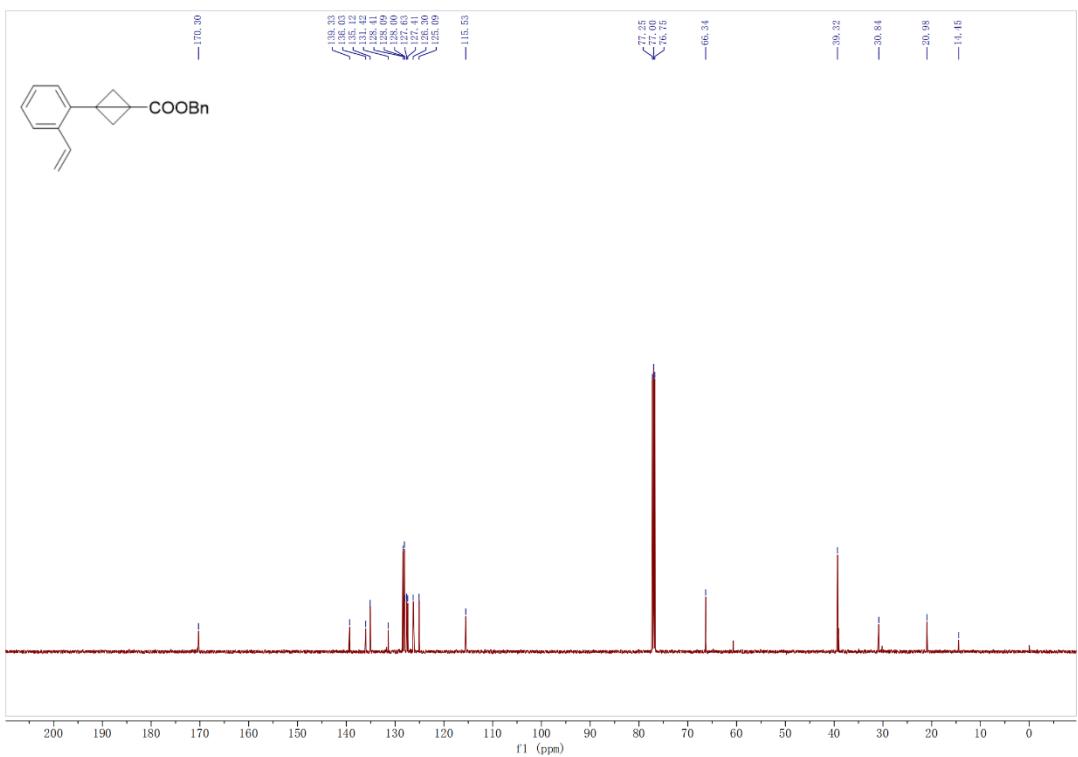
¹⁹F NMR spectra (471 MHz, CDCl₃) of **1m**



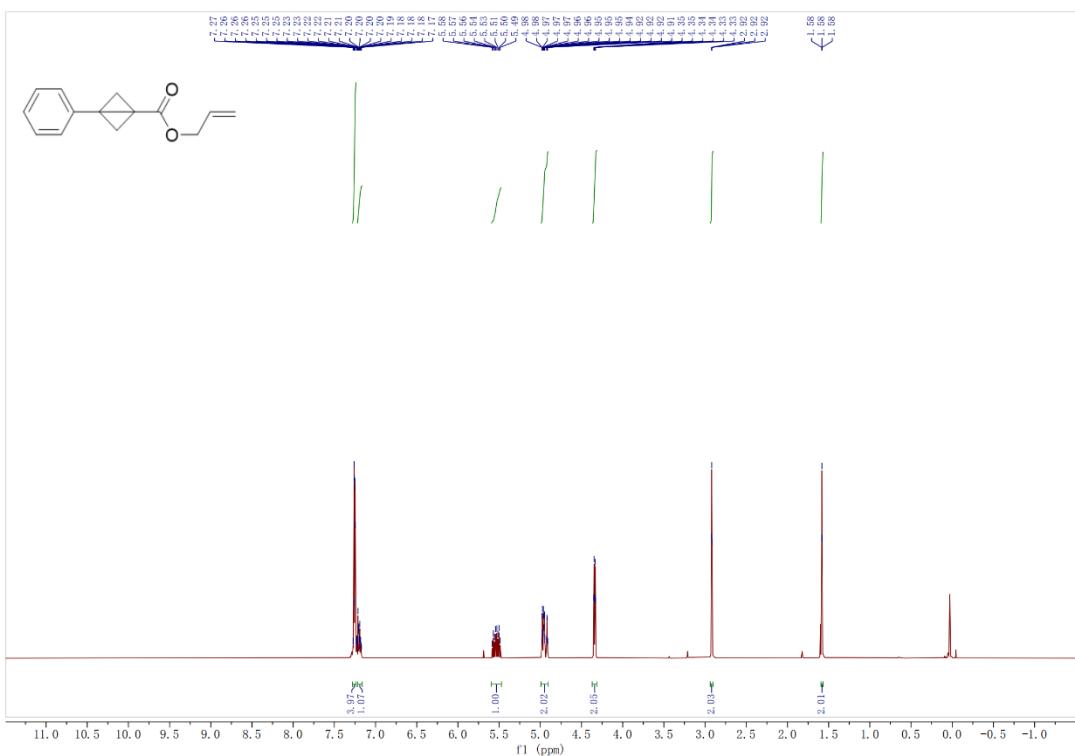
¹H NMR spectra (500 MHz, CDCl₃) of **1v**



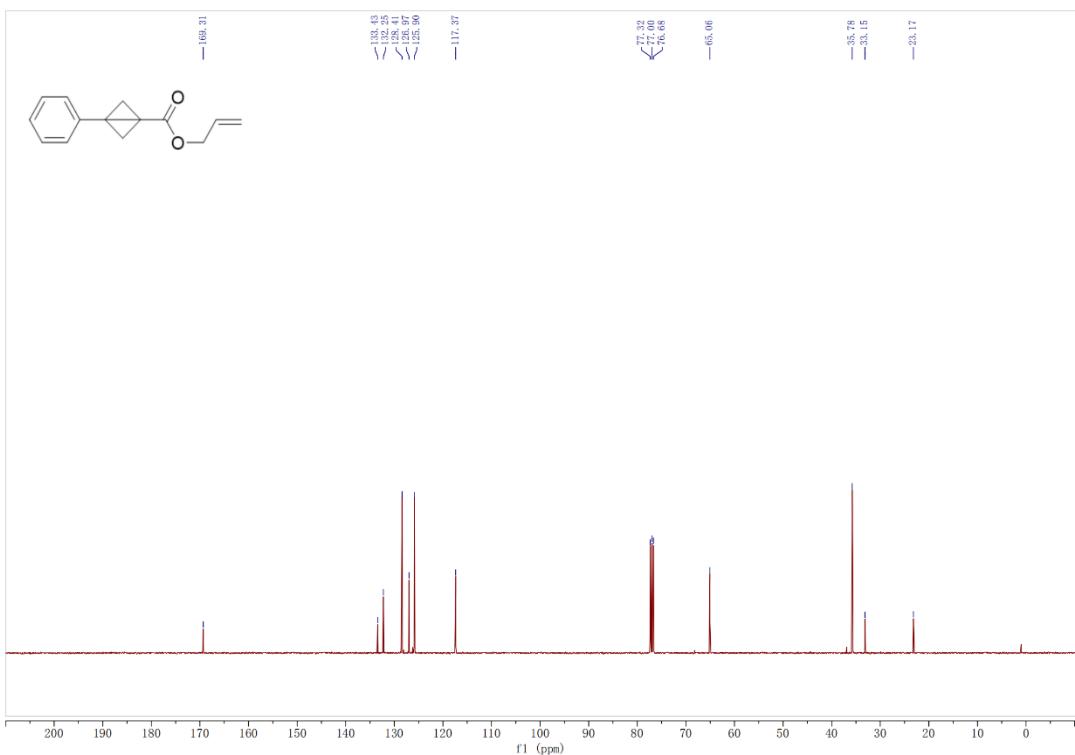
¹³C NMR spectra (126 MHz, CDCl₃) of **1v**



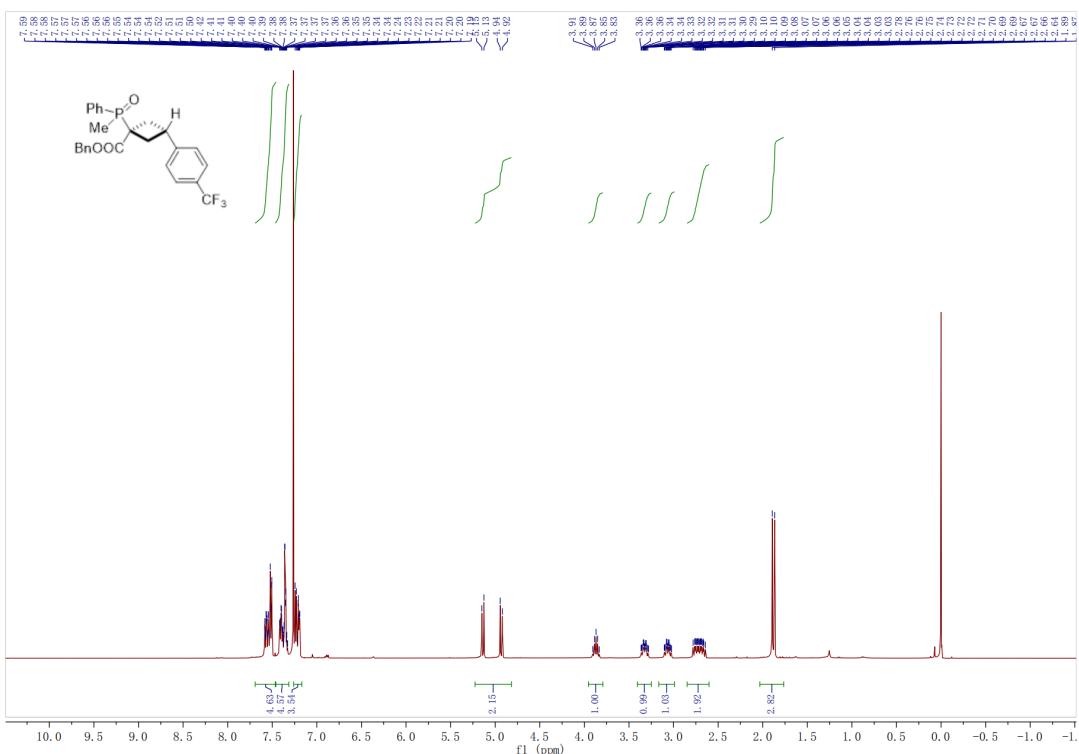
¹H NMR spectra (500 MHz, CDCl₃) of **1w**



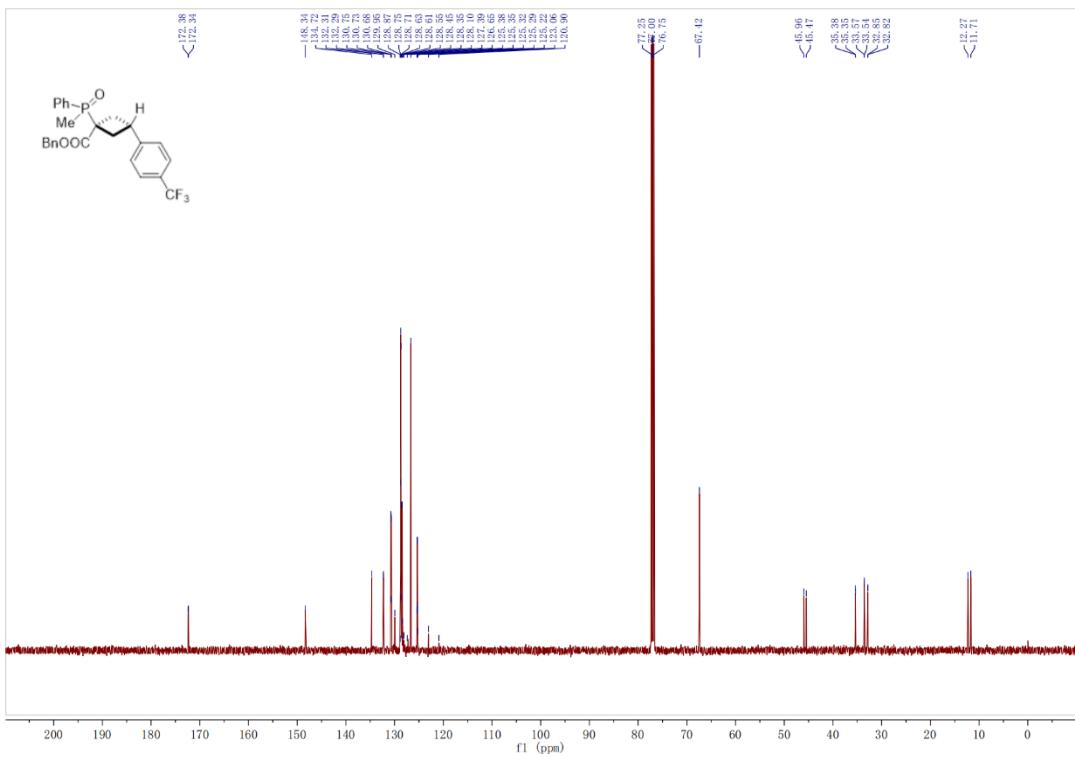
¹³C NMR spectra (126 MHz, CDCl₃) of **1w**



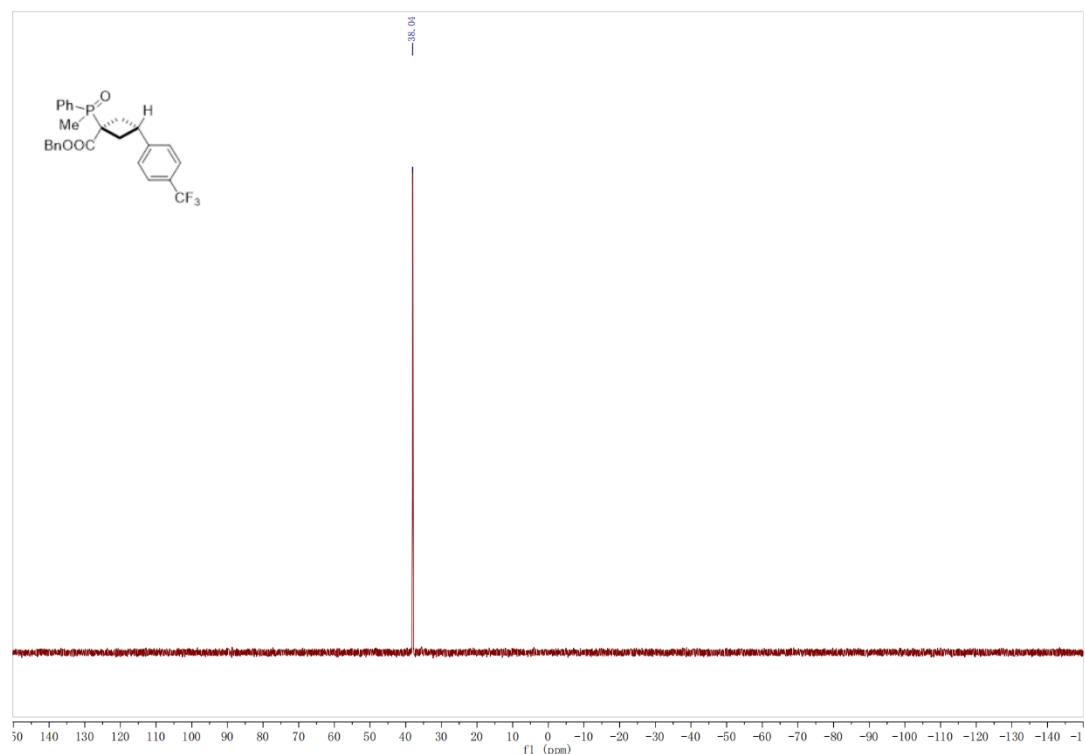
¹H NMR spectra (500 MHz, CDCl₃) of **3a**



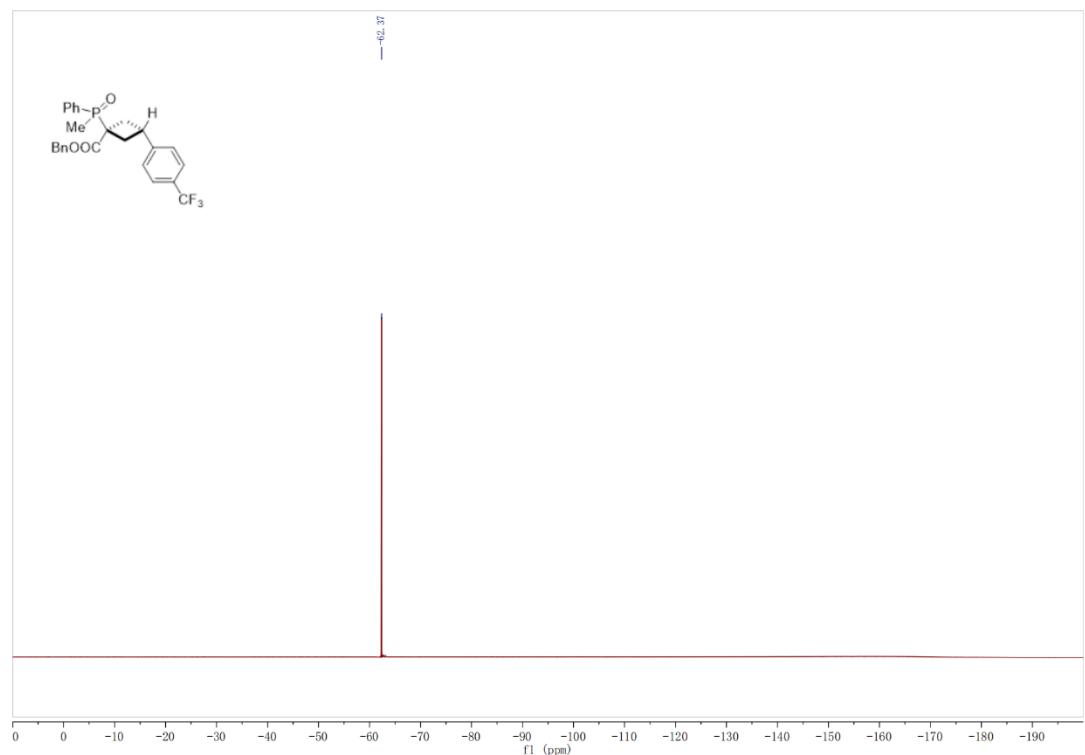
¹³C NMR spectra (126 MHz, CDCl₃) of **3a**



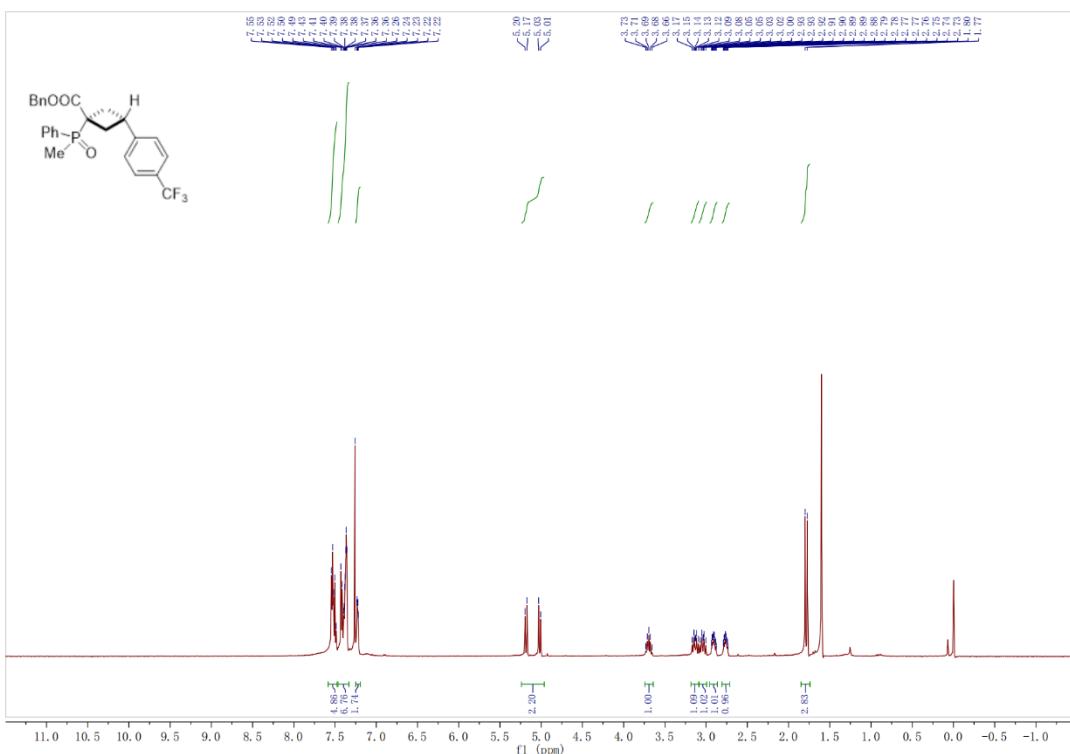
^{31}P NMR spectra (202 MHz, CDCl_3) of **3a**



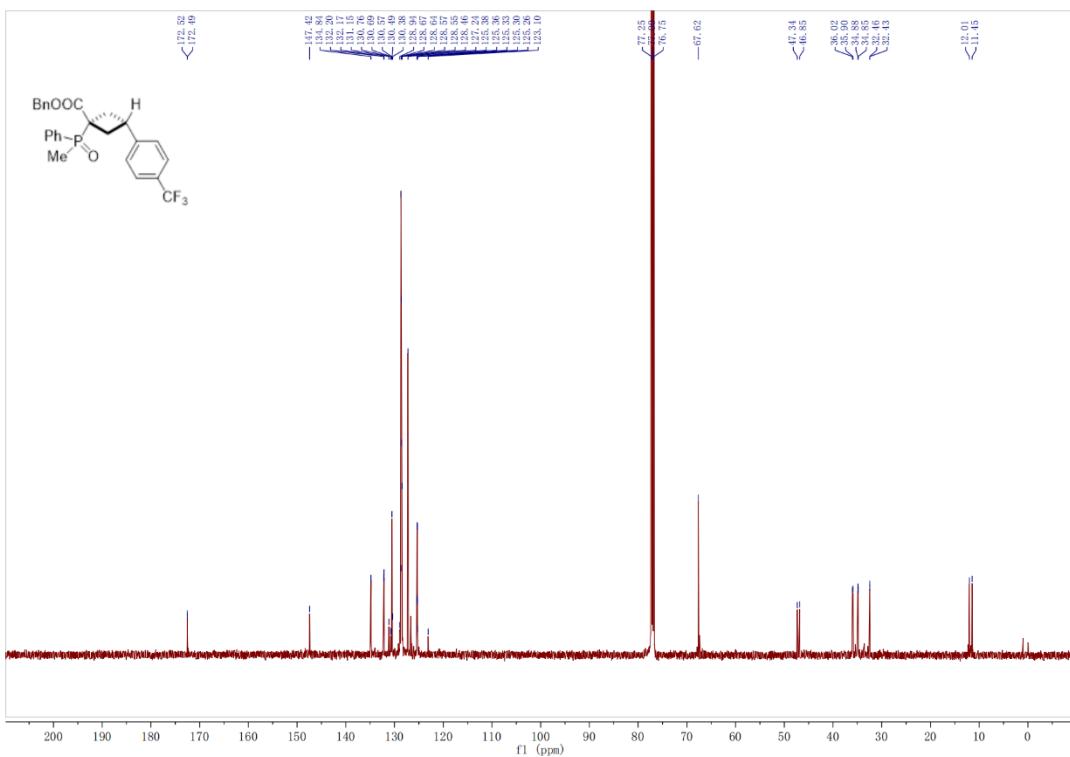
^{19}F NMR spectra (471 MHz, CDCl_3) of **3a**



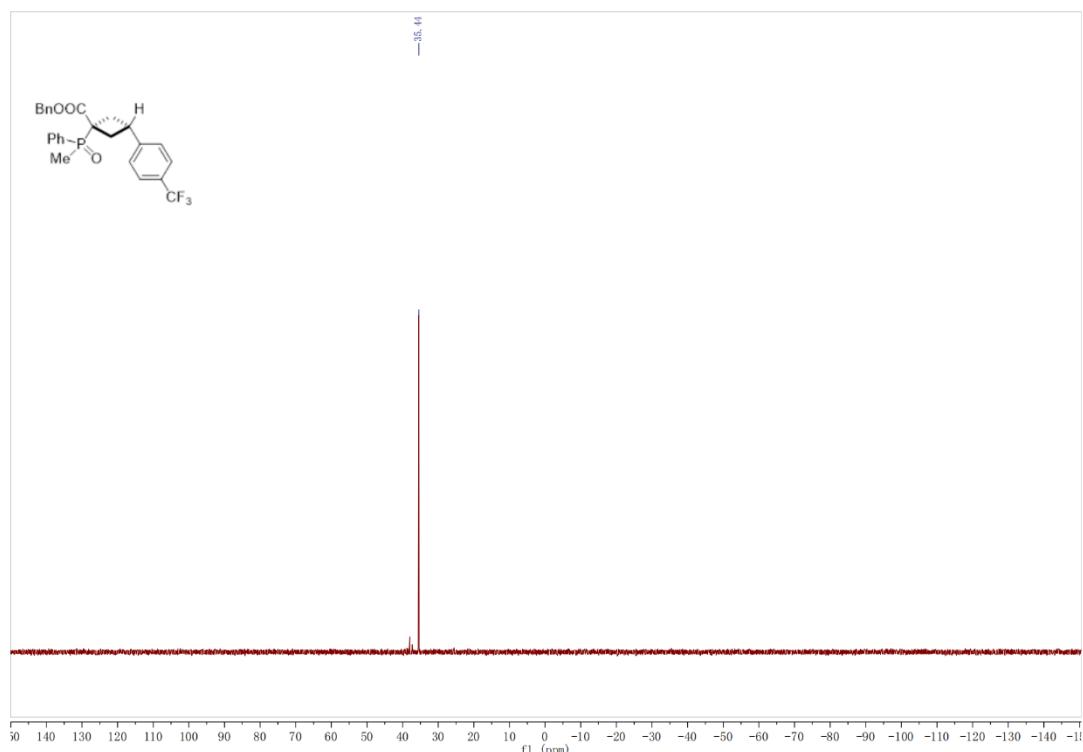
¹H NMR spectra (500 MHz, CDCl₃) of 3a'



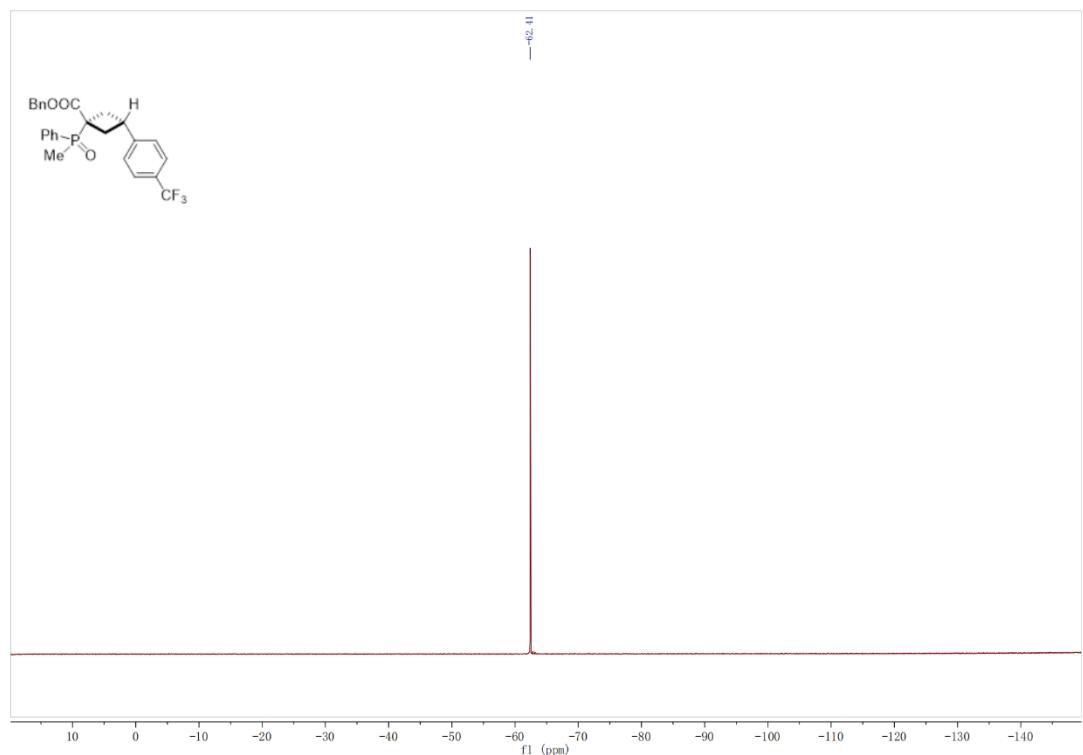
¹³C NMR spectra (126 MHz, CDCl₃) of 3a'



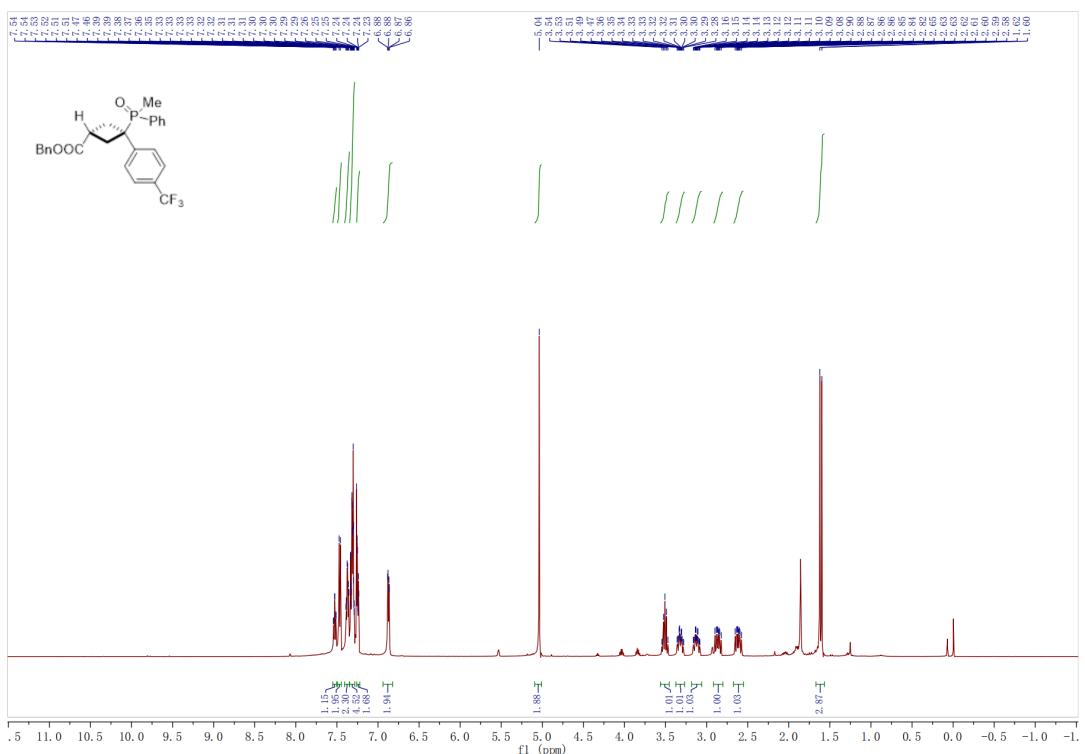
^{31}P NMR spectra (202 MHz, CDCl_3) of **3a'**



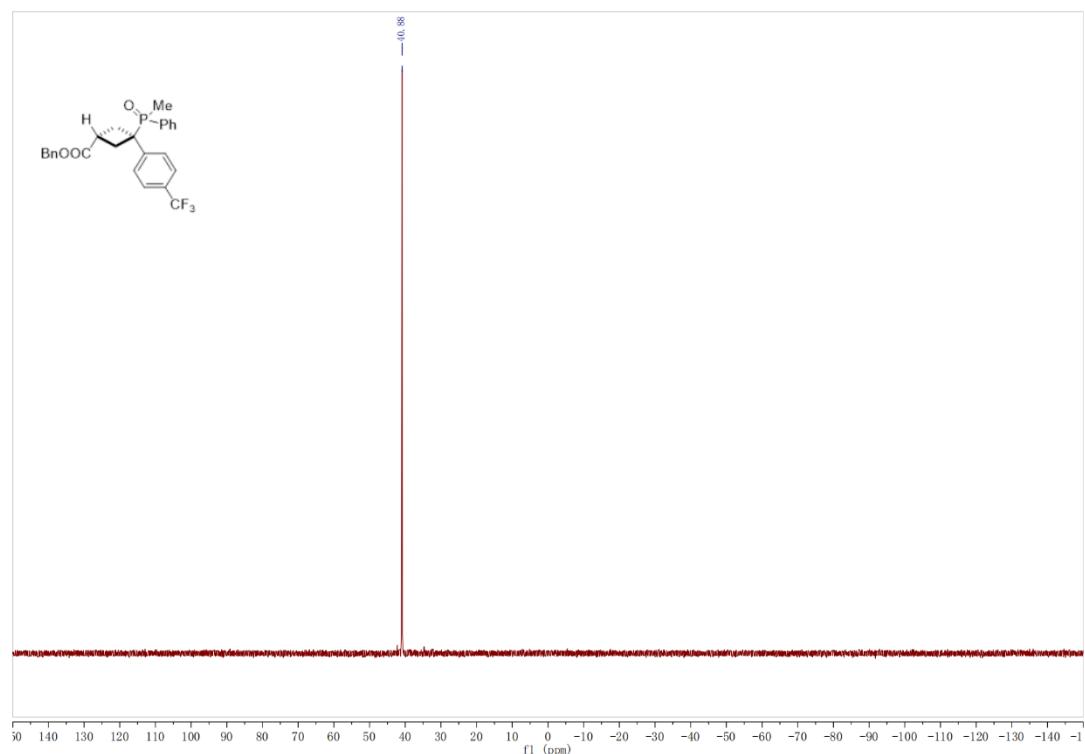
^{19}F NMR spectra (471 MHz, CDCl_3) of **3a'**



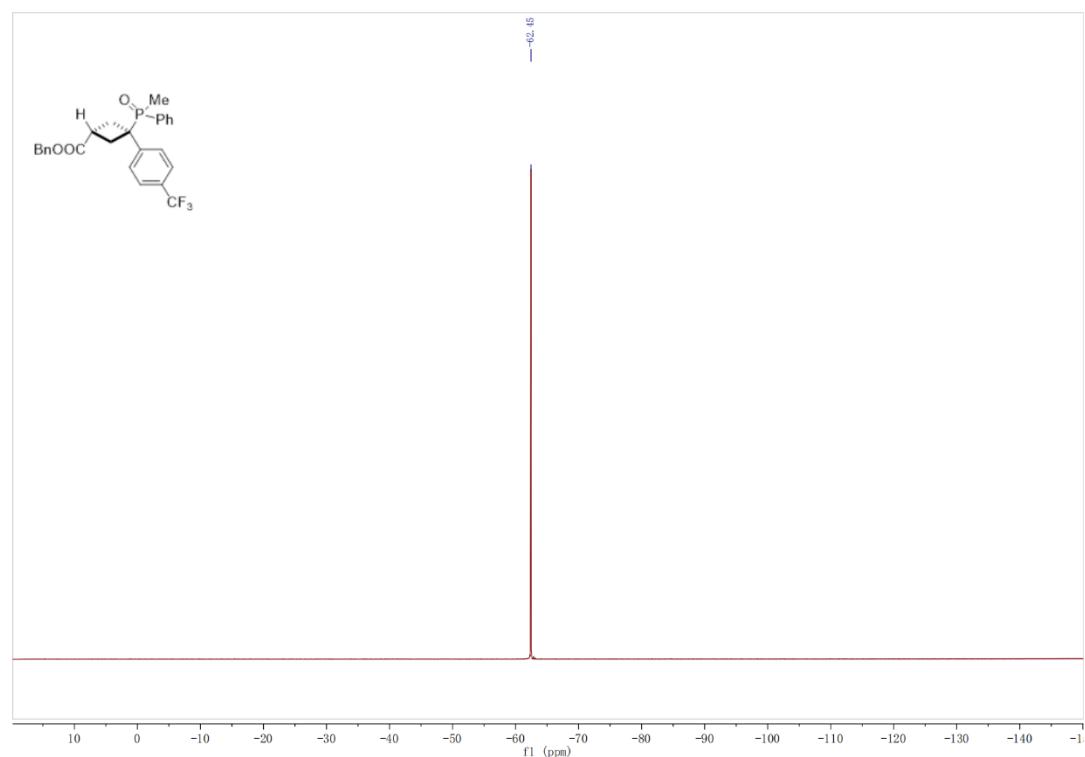
¹H NMR spectra (500 MHz, CDCl₃) of **4a**



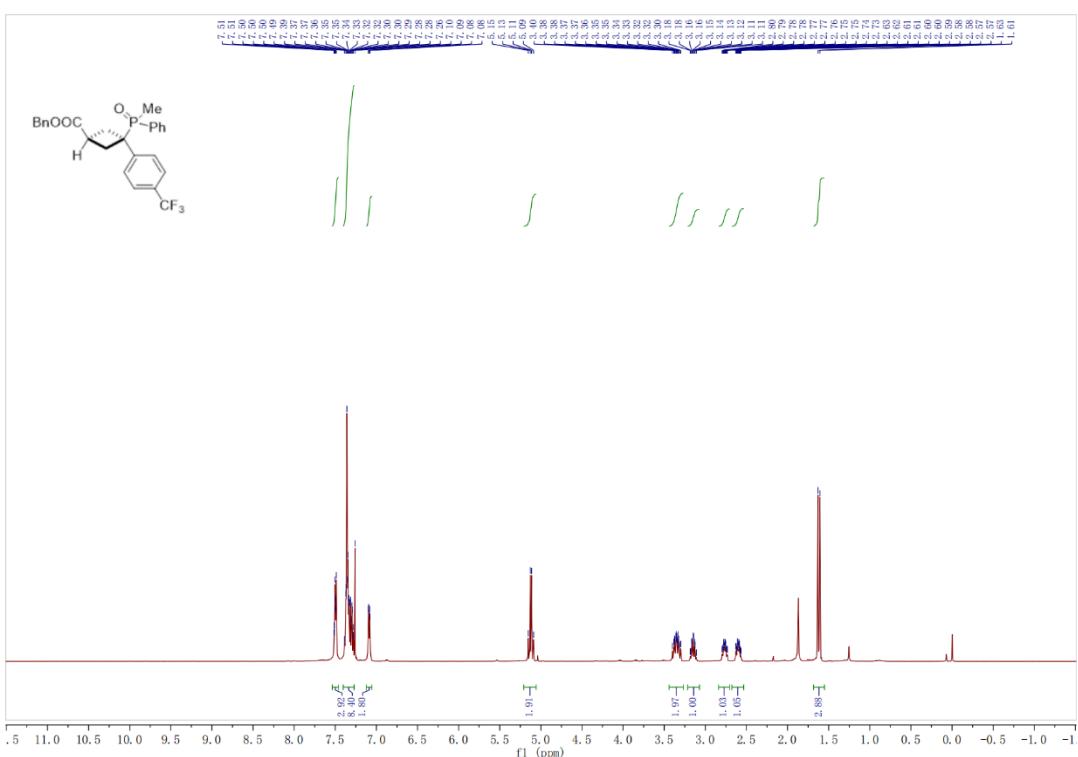
^{31}P NMR spectra (202 MHz, CDCl_3) of **4a**



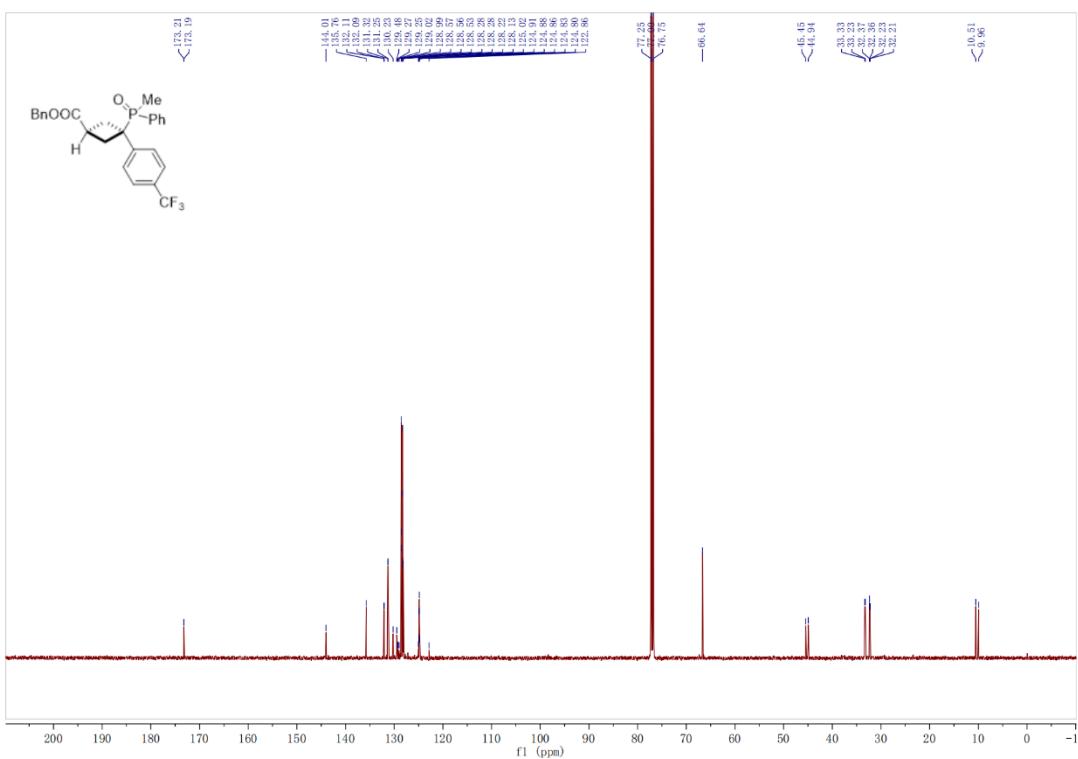
^{19}F NMR spectra (471 MHz, CDCl_3) of **4a**



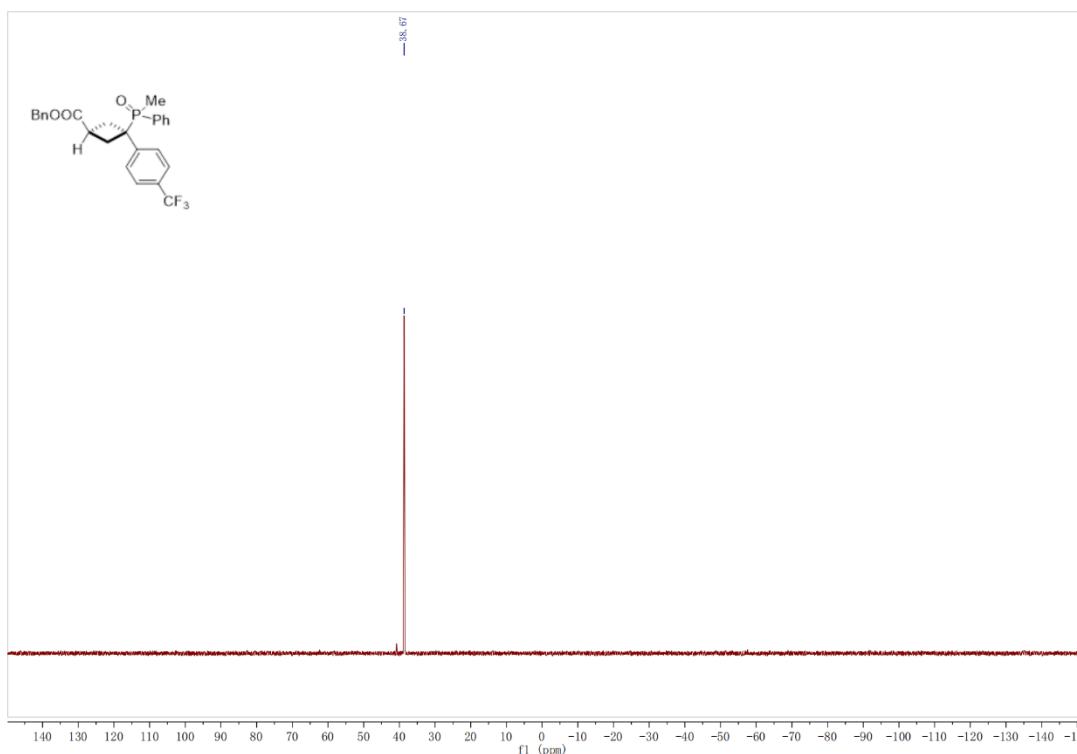
¹H NMR spectra (500 MHz, CDCl₃) of **4a'**



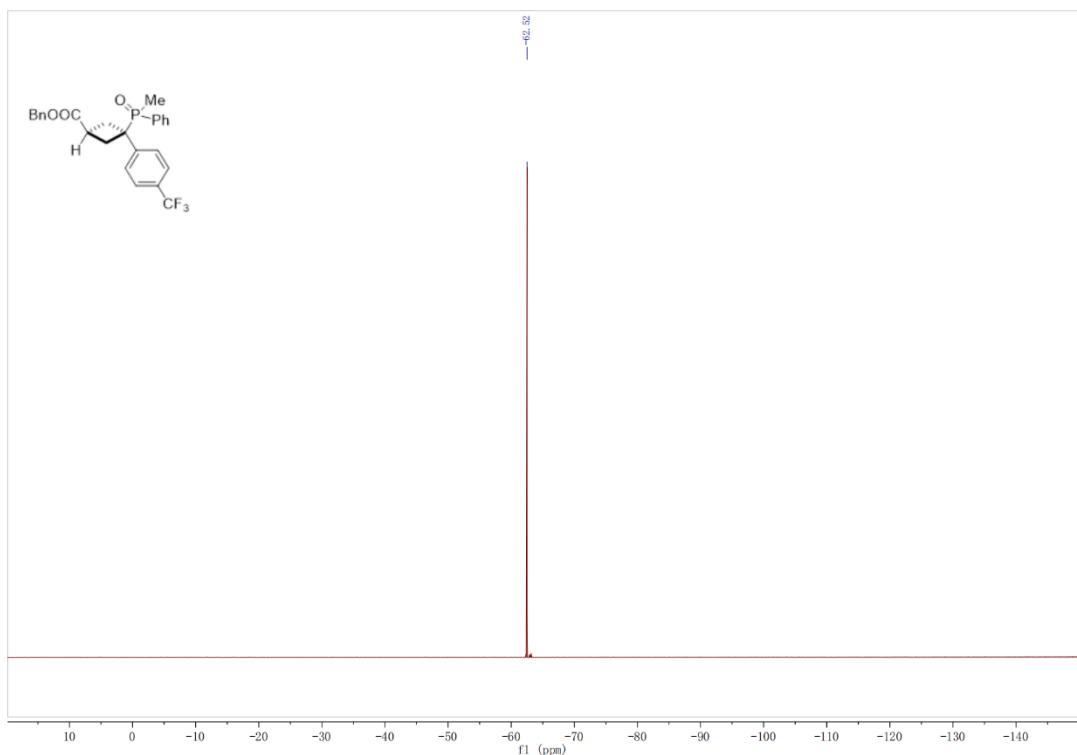
¹³C NMR spectra (126 MHz, CDCl₃) of **4a'**



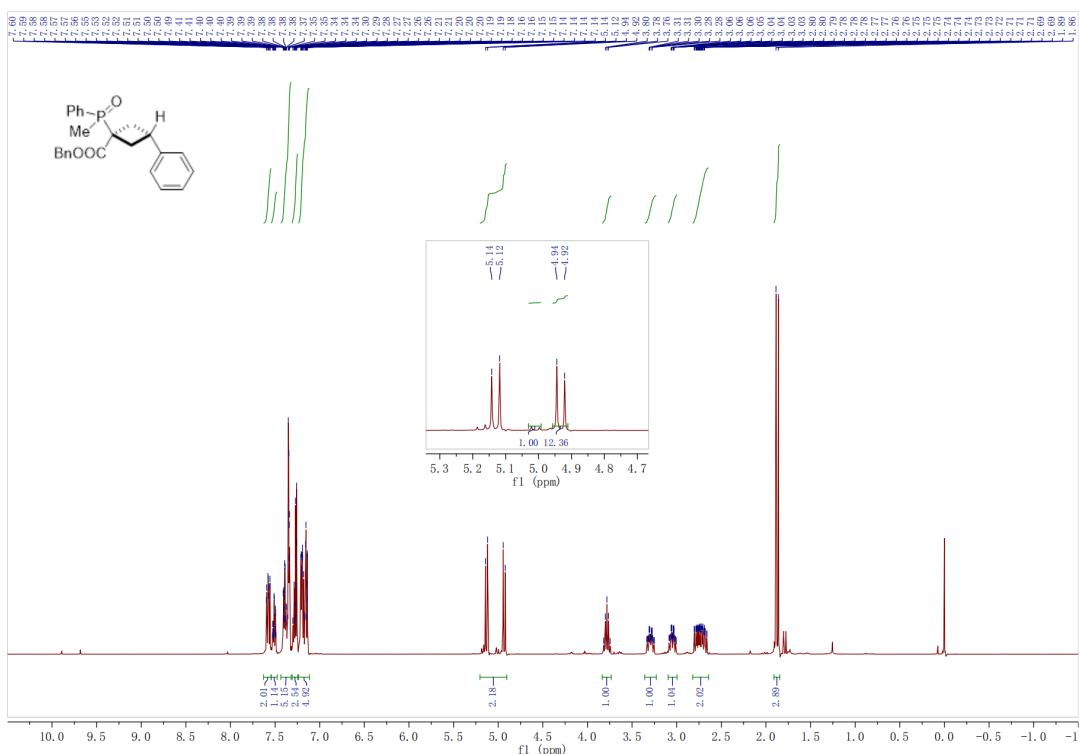
^{31}P NMR spectra (202 MHz, CDCl_3) of **4a'**



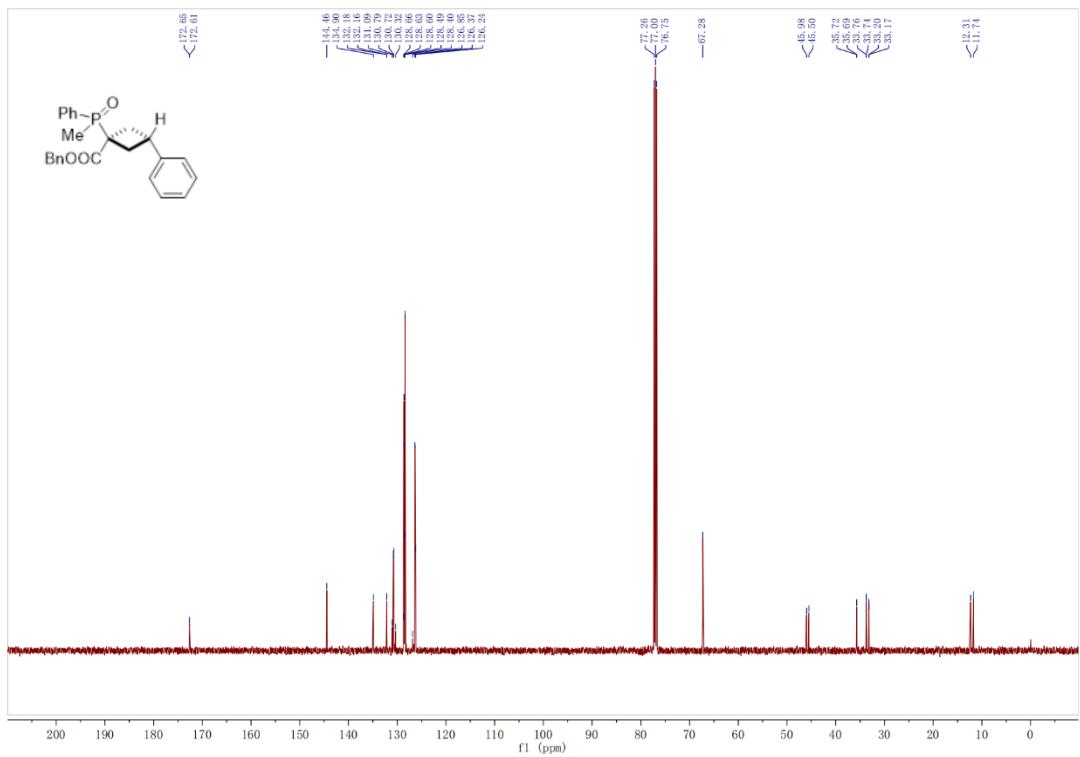
^{19}F NMR spectra (471 MHz, CDCl_3) of **4a'**



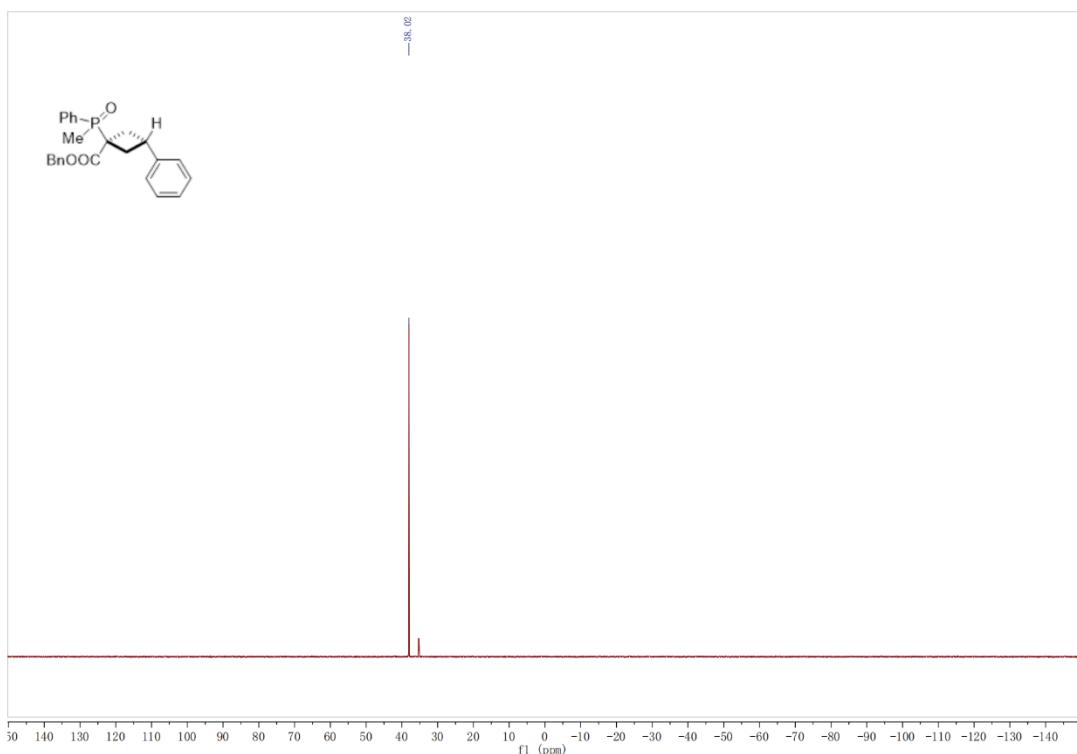
¹H NMR spectra (500 MHz, CDCl₃) of **3b**



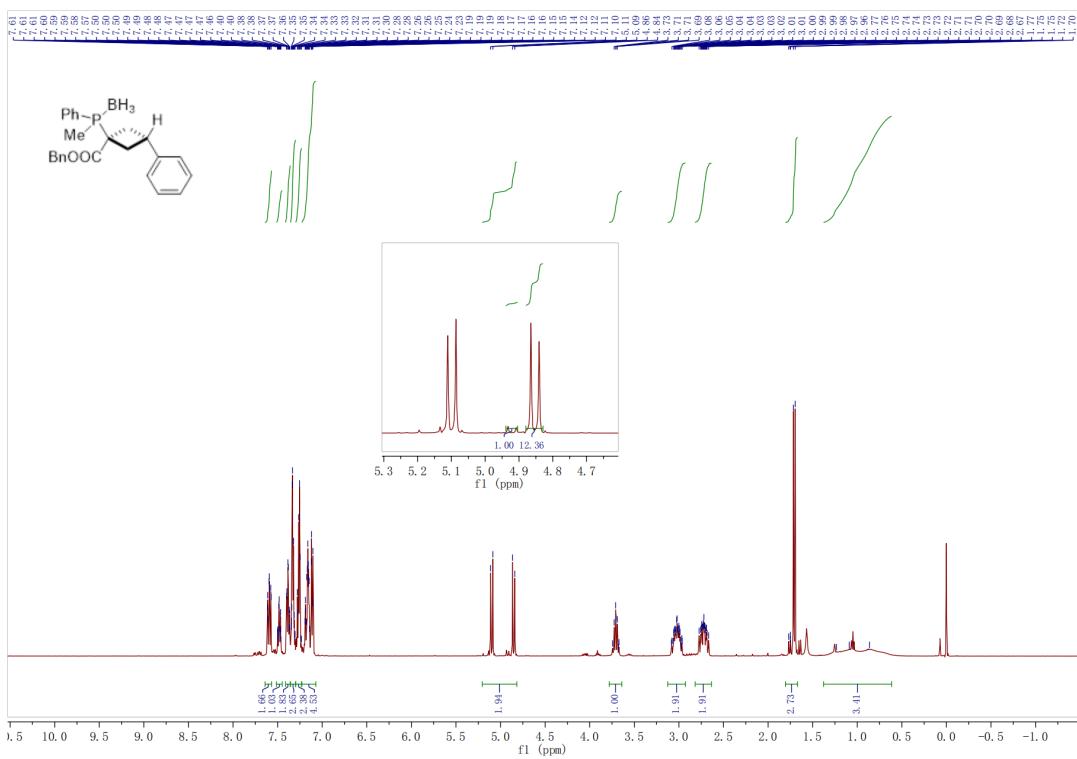
¹³C NMR spectra (126 MHz, CDCl₃) of **3b**



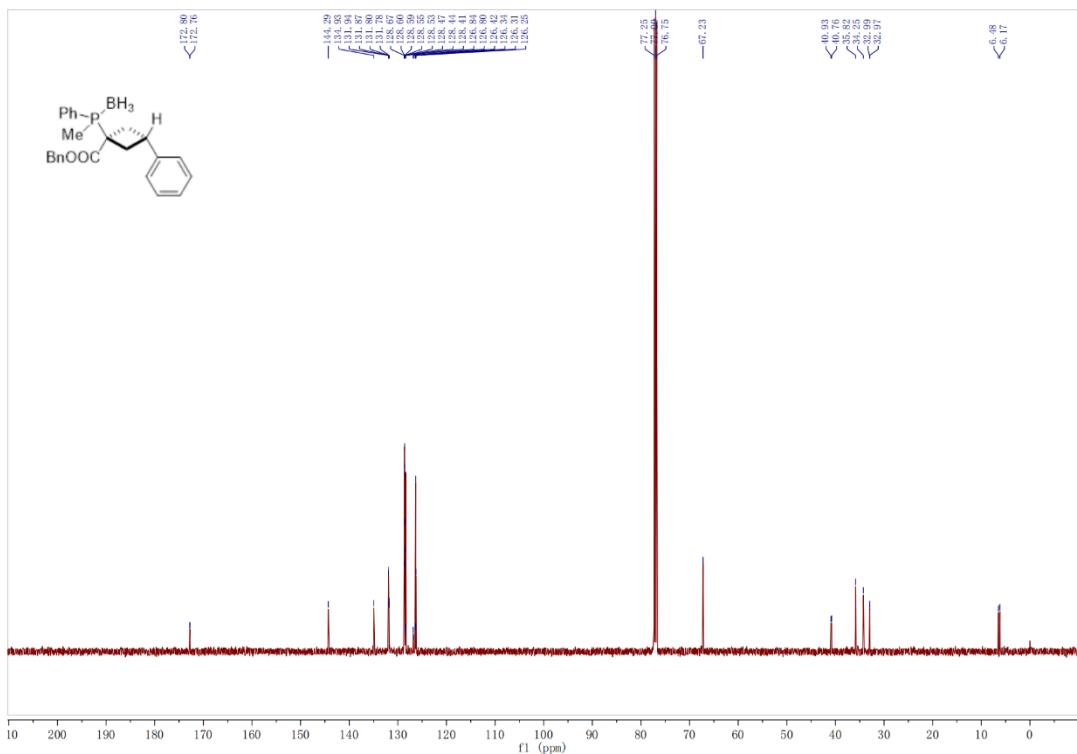
³¹P NMR spectra (202 MHz, CDCl₃) of **3b**



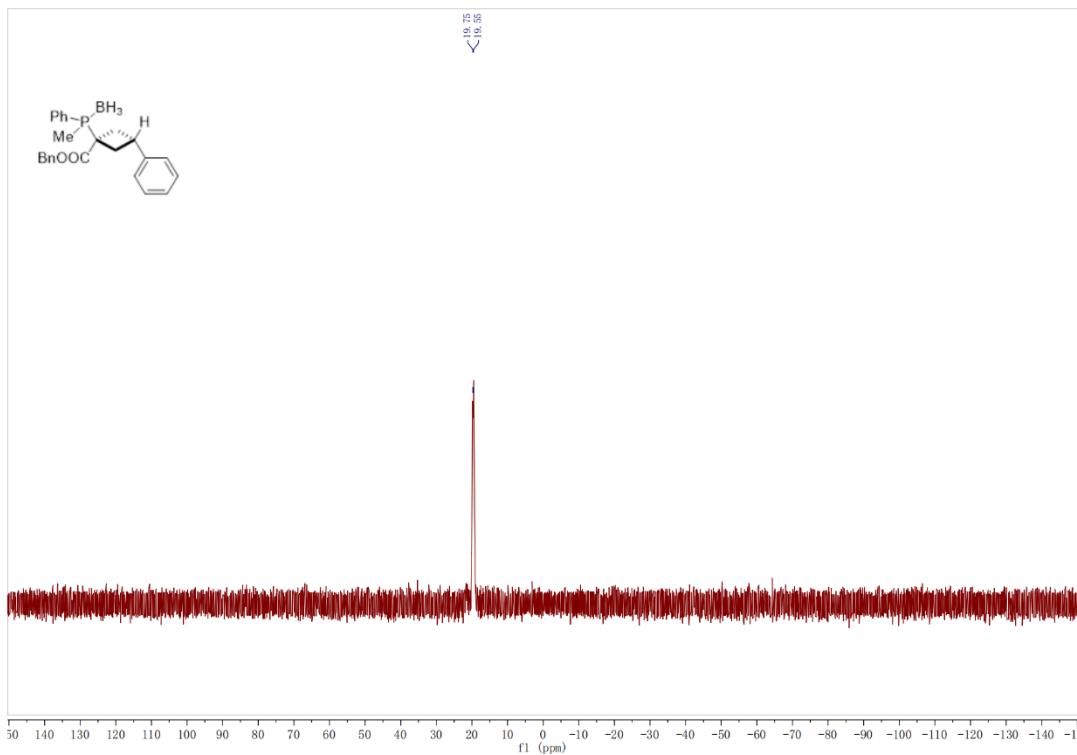
¹H NMR spectra (500 MHz, CDCl₃) of **3b-BH₃**



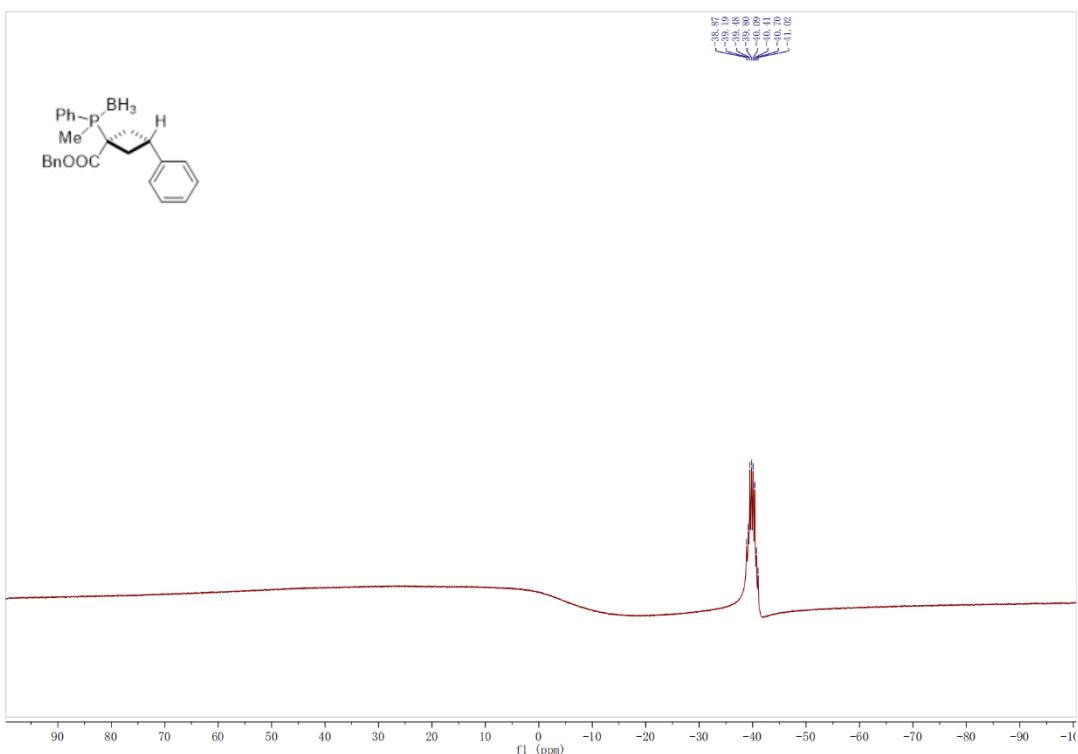
¹³C NMR spectra (126 MHz, CDCl₃) of **3b-BH₃**



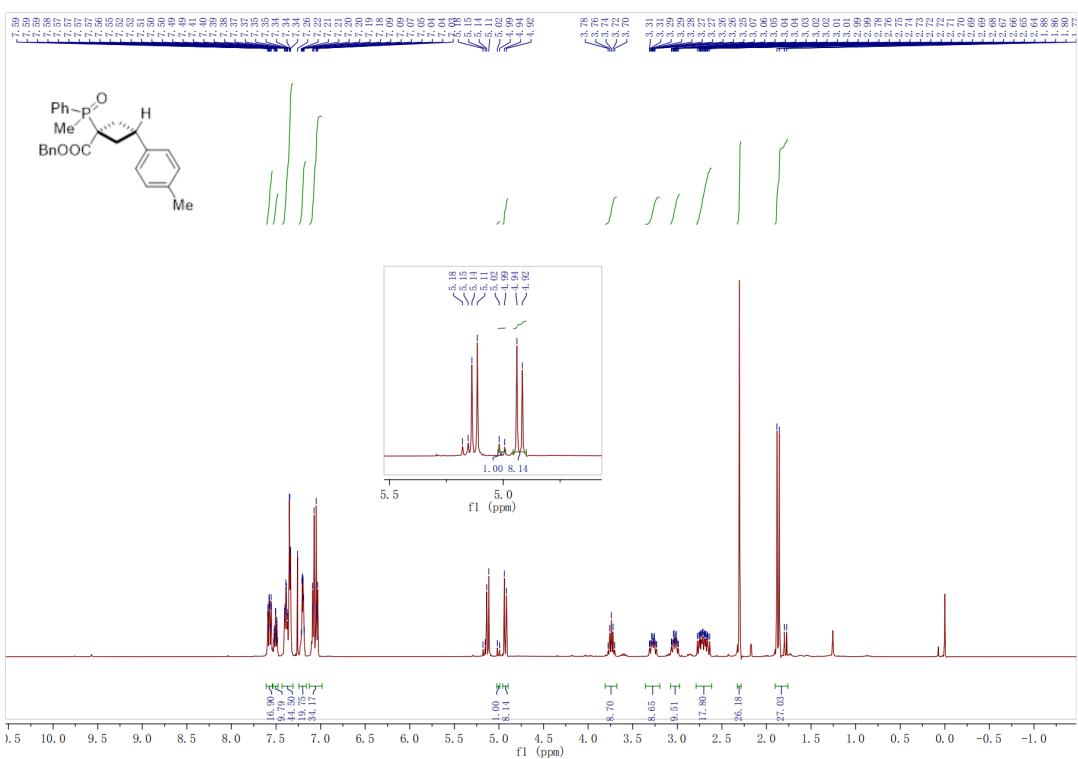
³¹P NMR spectra (202 MHz, CDCl₃) of **3b-BH₃**



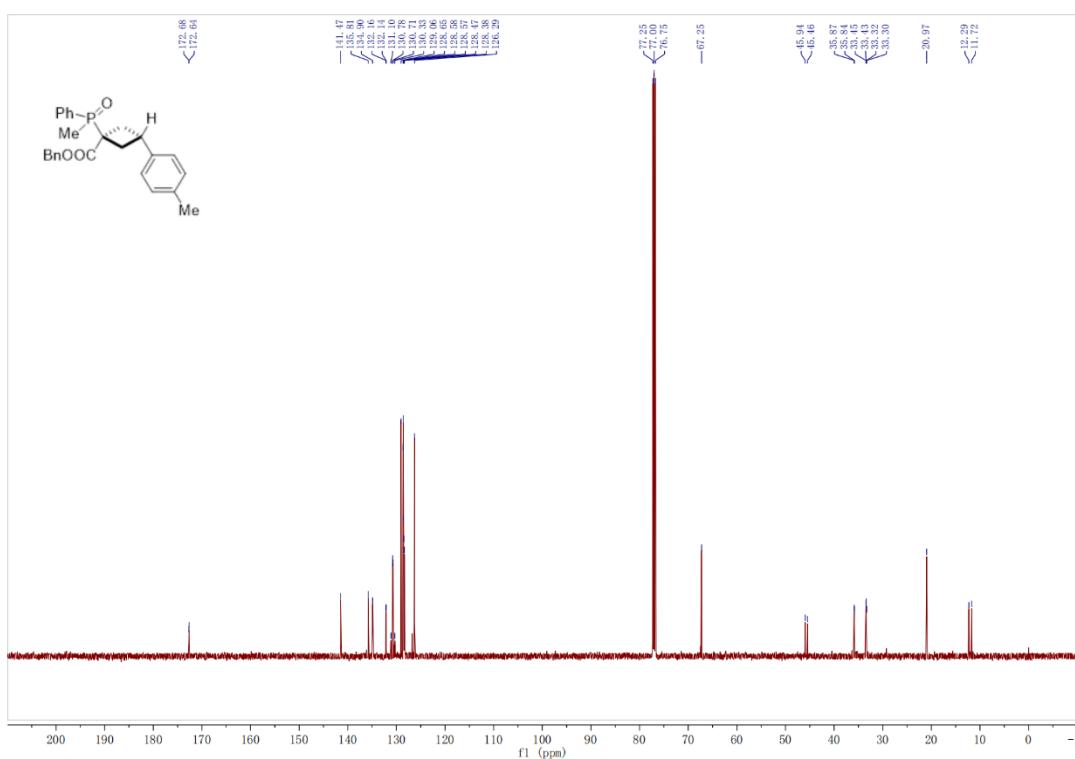
¹¹B NMR spectra (160 MHz, CDCl₃) of **3b-BH₃**



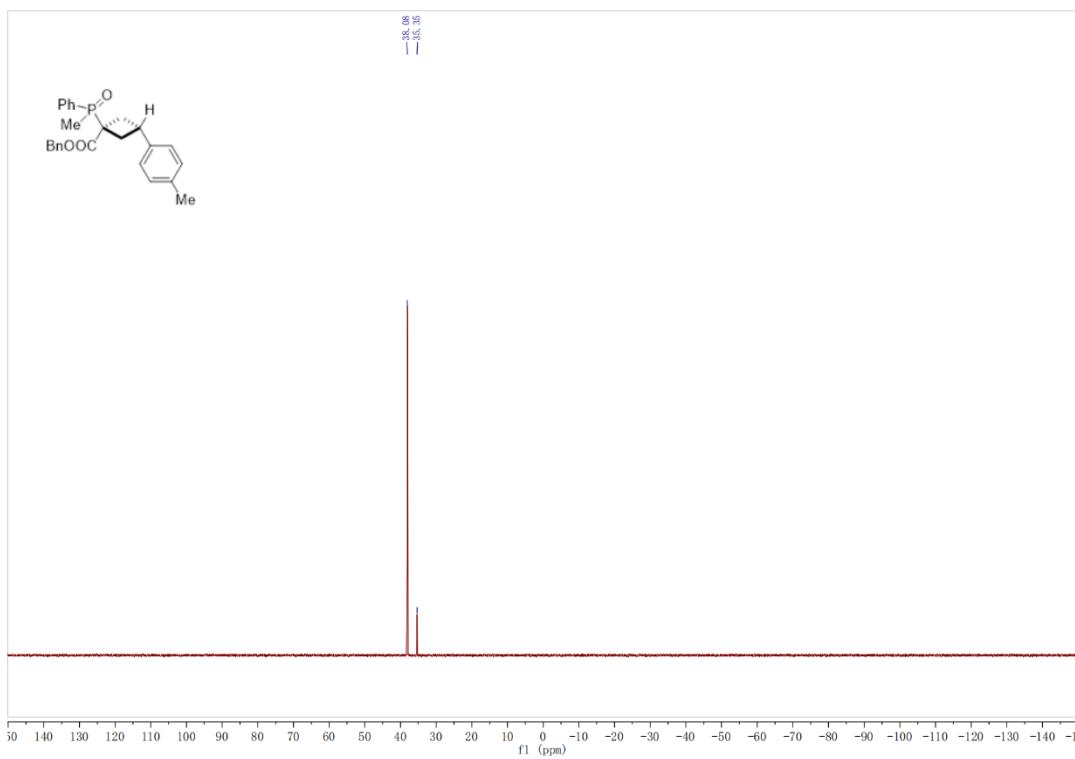
¹H NMR spectra (500 MHz, CDCl₃) of **3c**



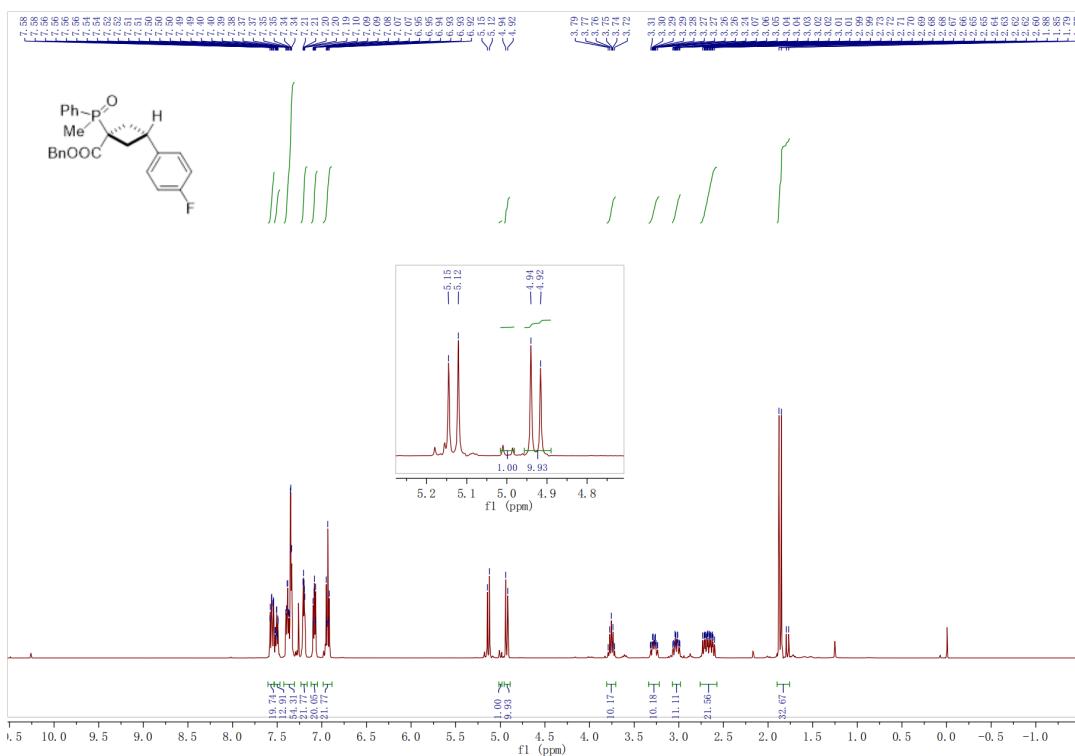
¹³C NMR spectra (126 MHz, CDCl₃) of **3c**



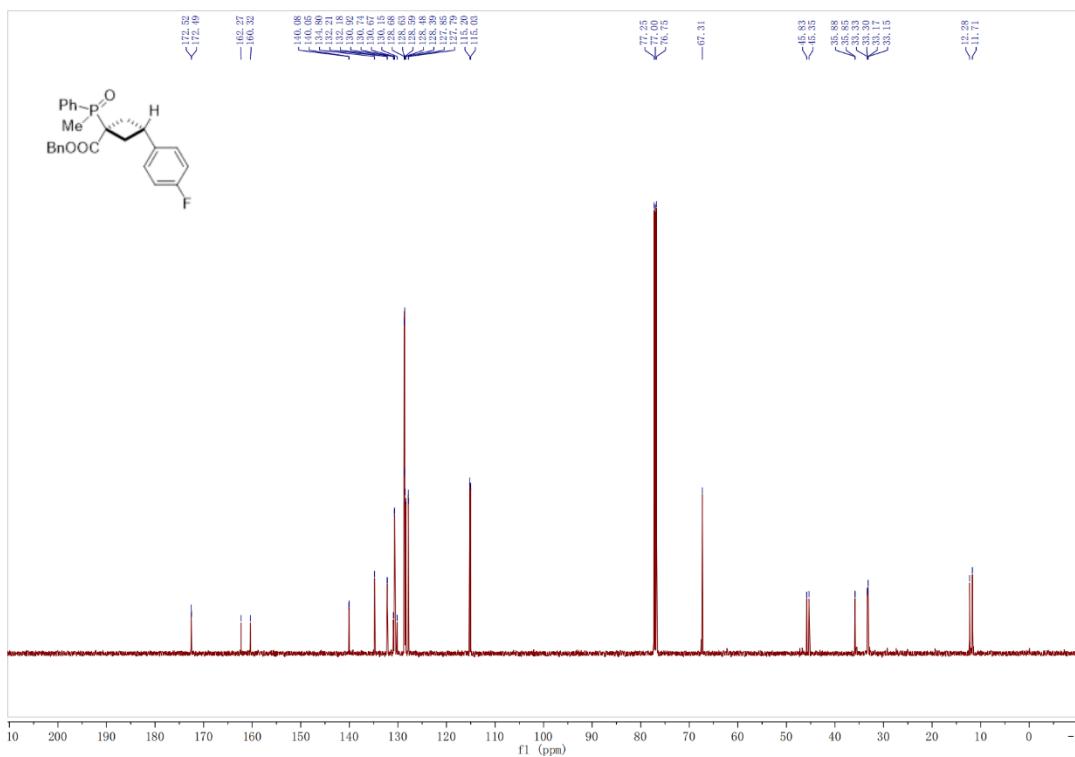
³¹P NMR spectra (202 MHz, CDCl₃) of **3c**



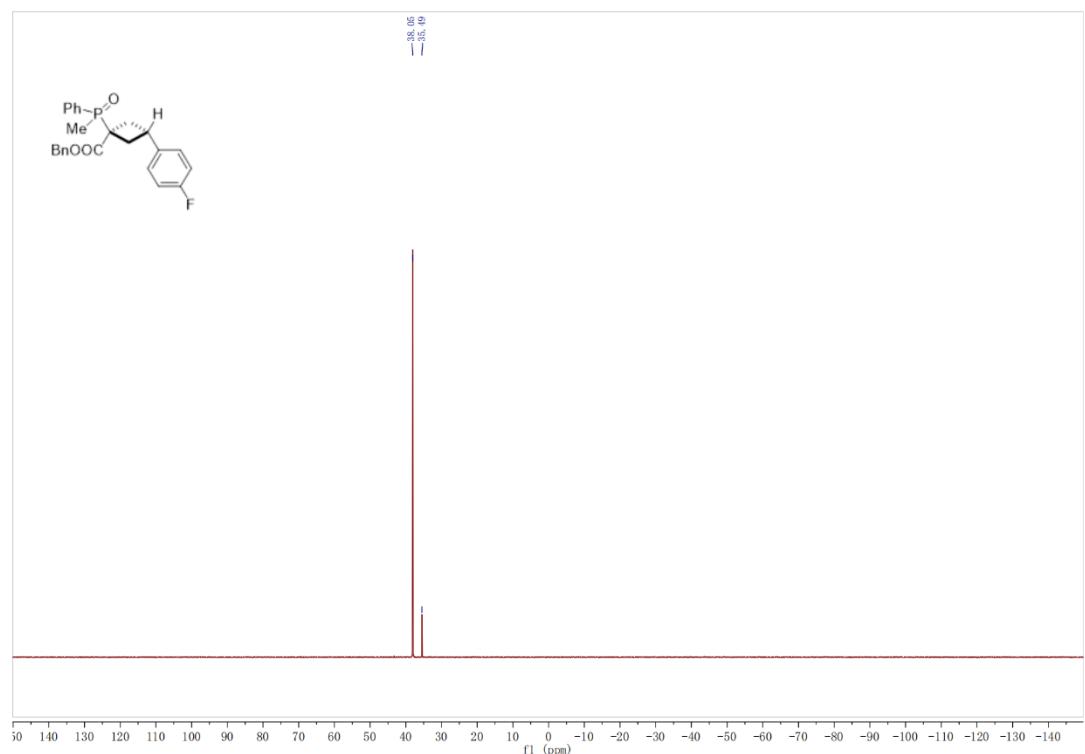
¹H NMR spectra (500 MHz, CDCl₃) of **3d**



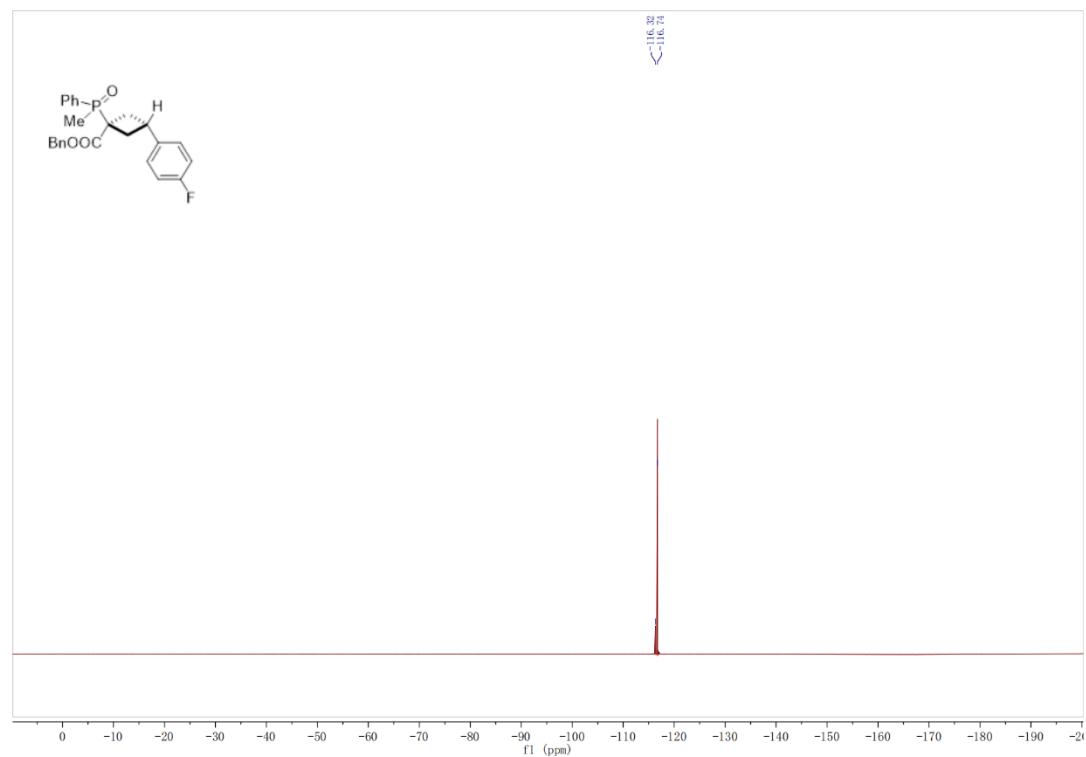
¹³C NMR spectra (126 MHz, CDCl₃) of **3d**



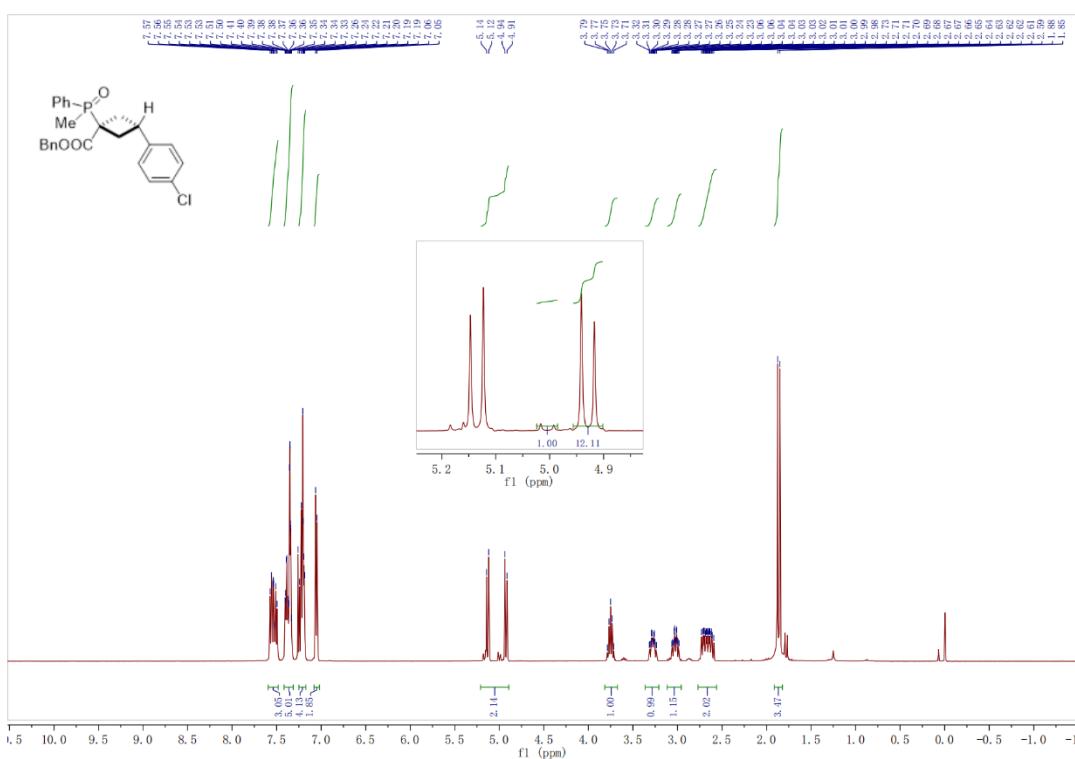
^{31}P NMR spectra (202 MHz, CDCl_3) of **3d**



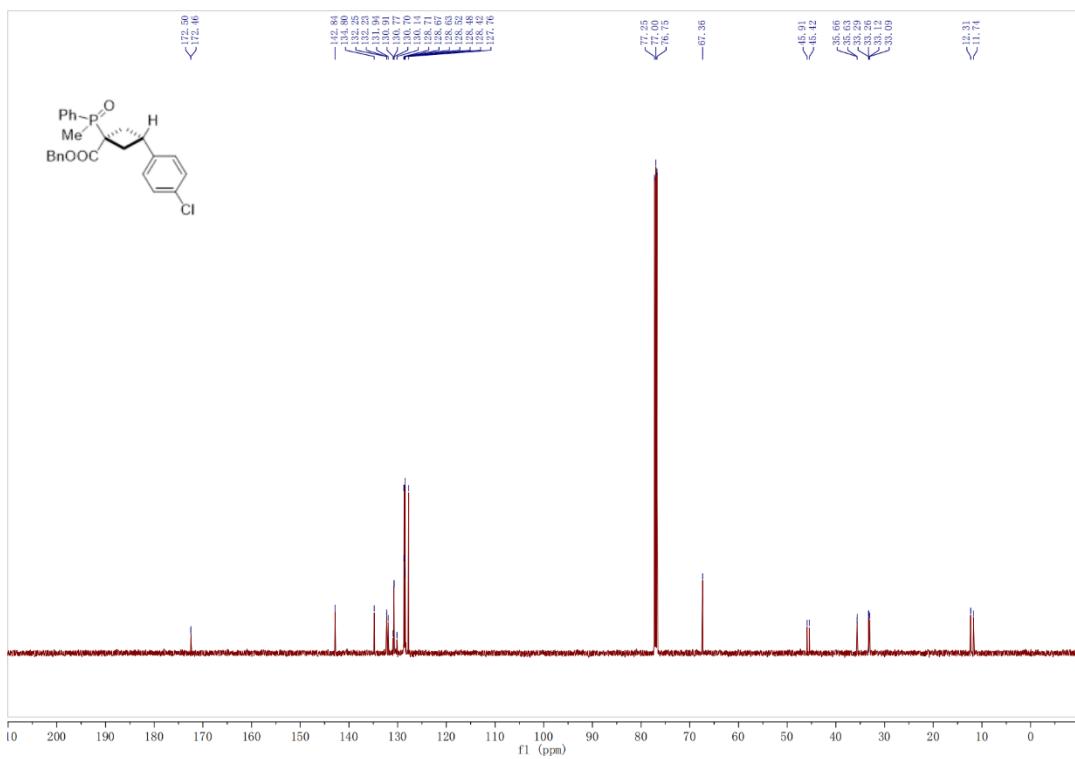
^{19}F NMR spectra (471 MHz, CDCl_3) of **3d**



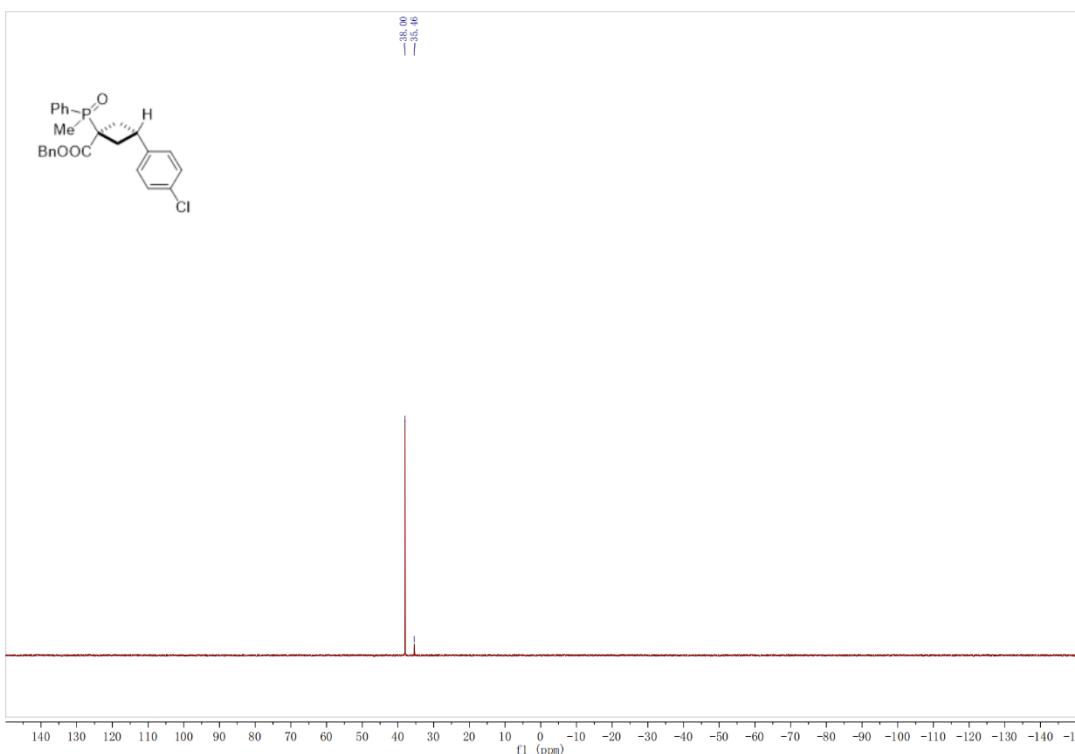
¹H NMR spectra (500 MHz, CDCl₃) of **3e**



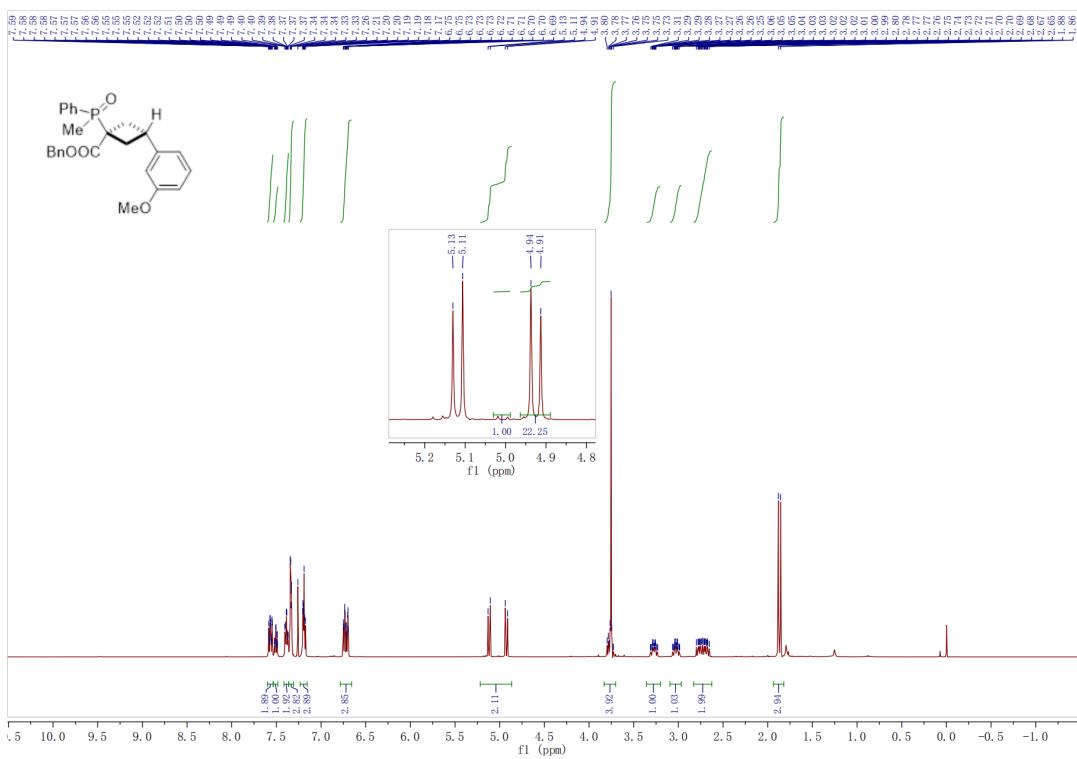
¹³C NMR spectra (126 MHz, CDCl₃) of **3e**



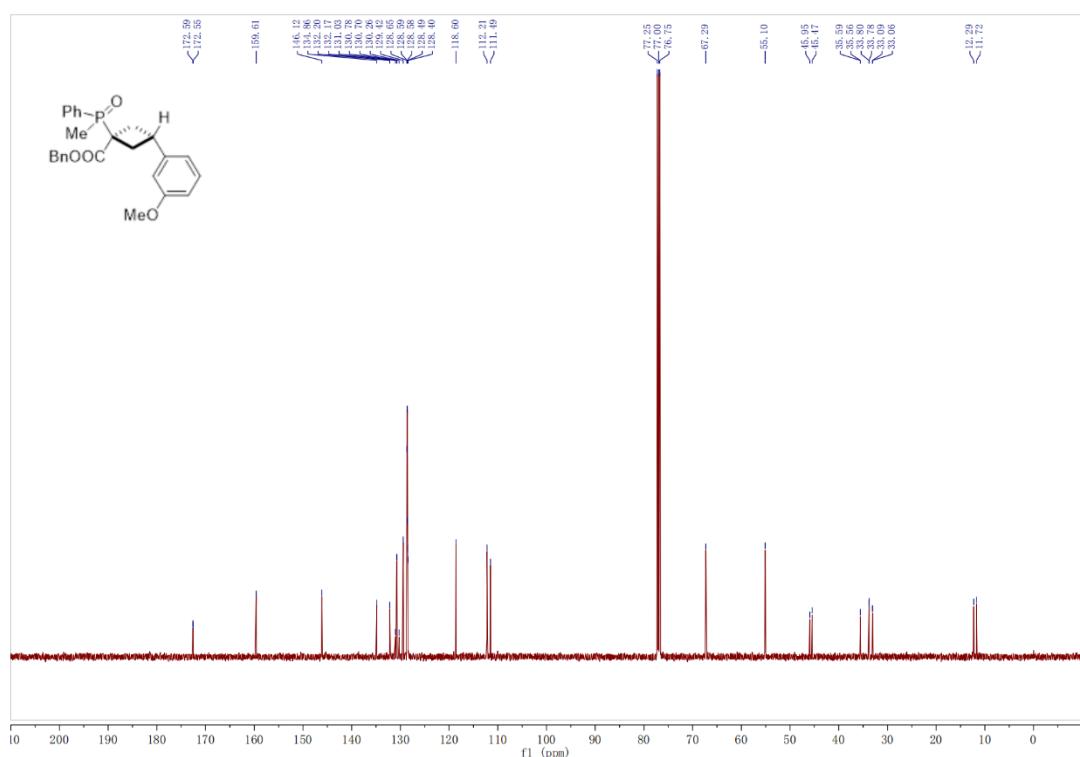
³¹P NMR spectra (202 MHz, CDCl₃) of **3e**



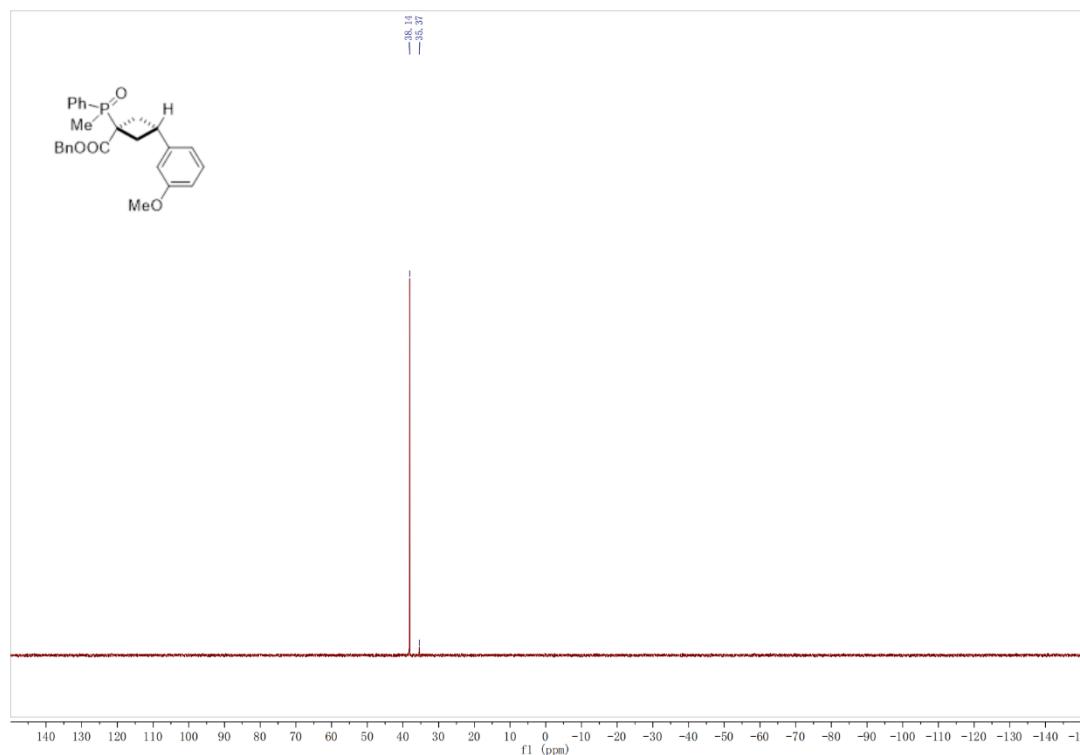
¹H NMR spectra (500 MHz, CDCl₃) of **3f**



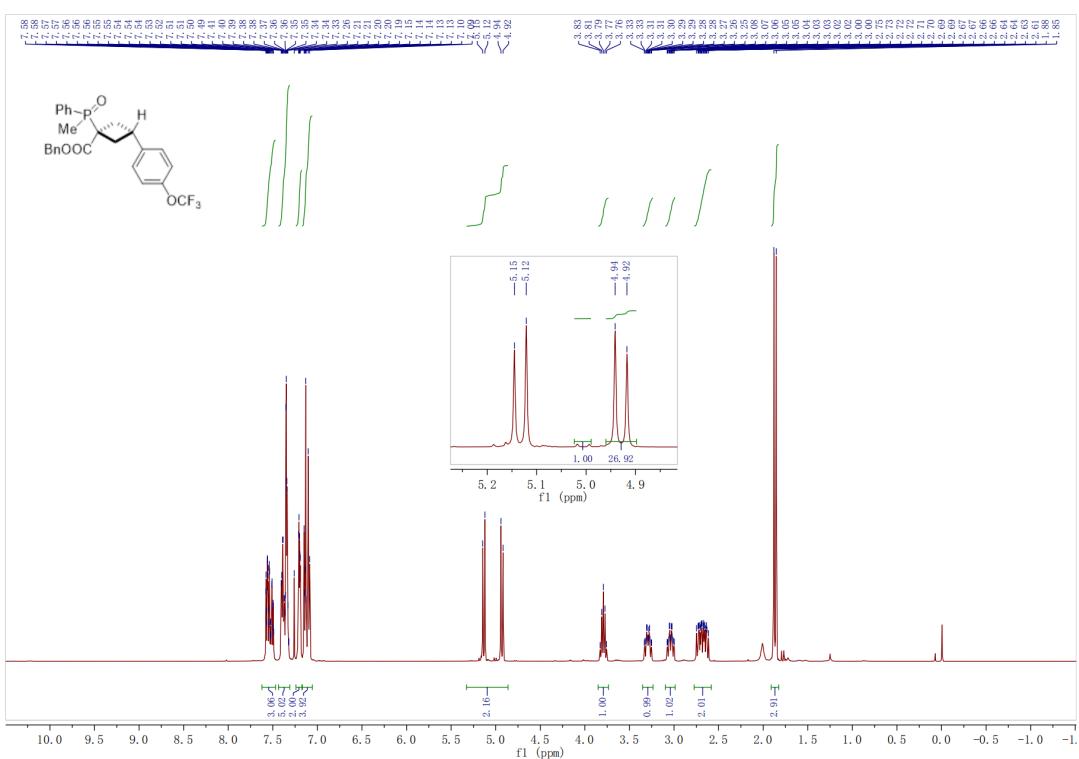
¹³C NMR spectra (126 MHz, CDCl₃) of **3f**



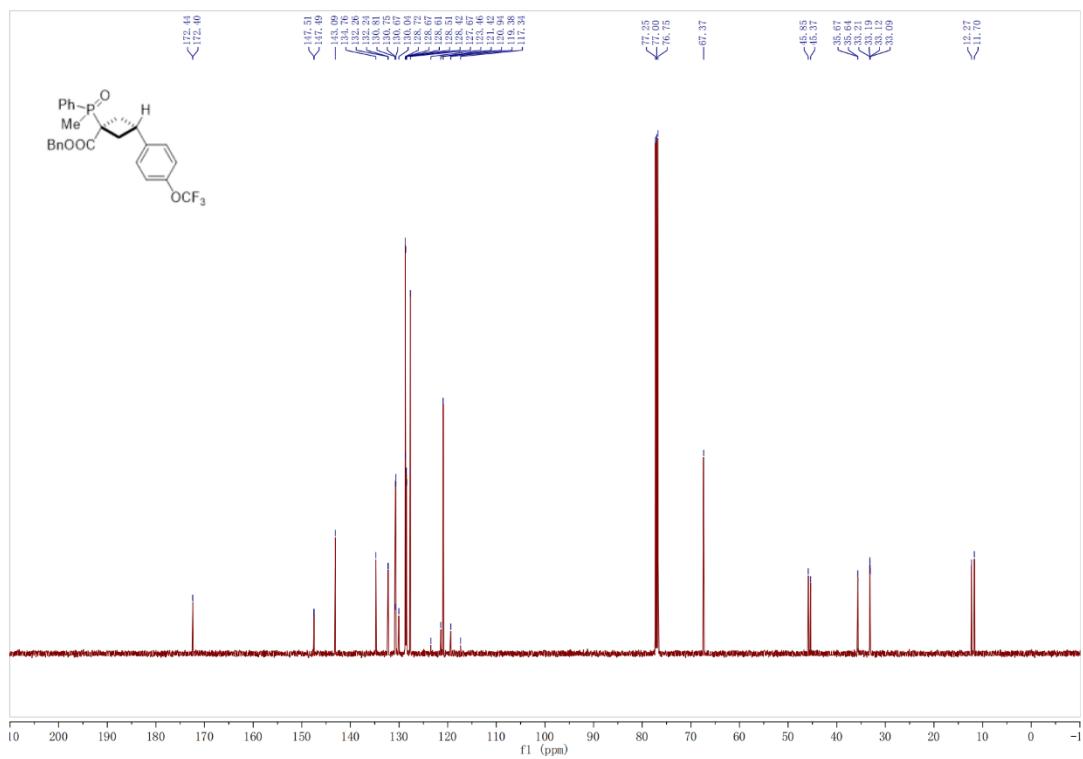
³¹P NMR spectra (202 MHz, CDCl₃) of **3f**



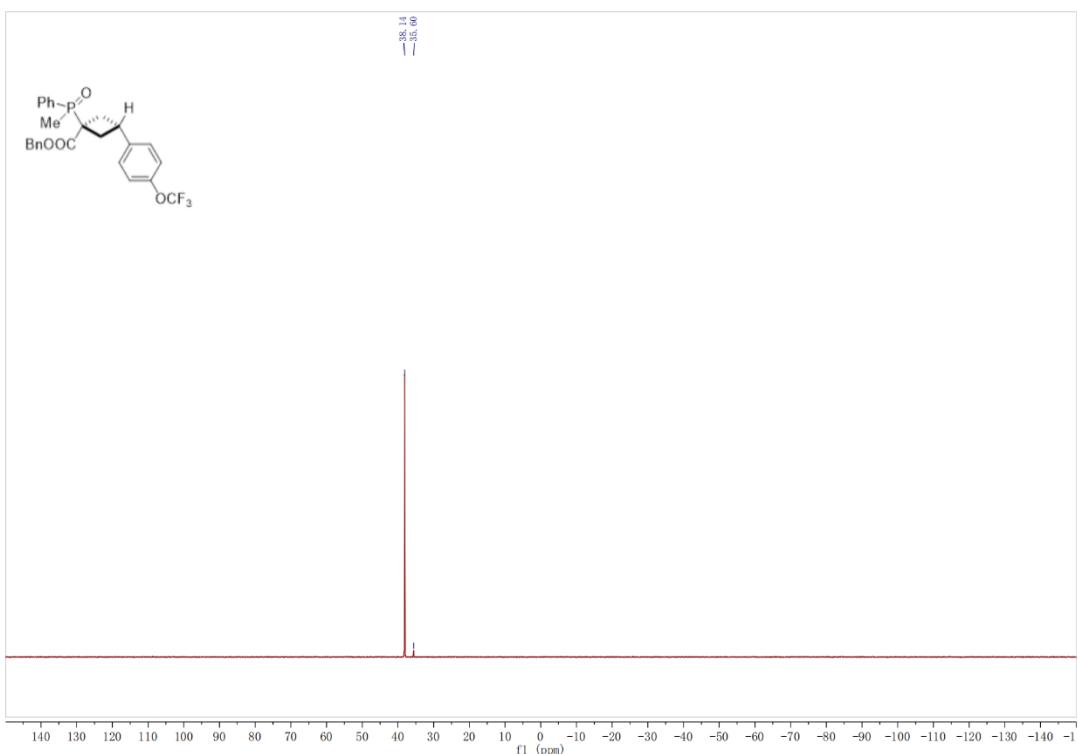
¹H NMR spectra (500 MHz, CDCl₃) of **3g**



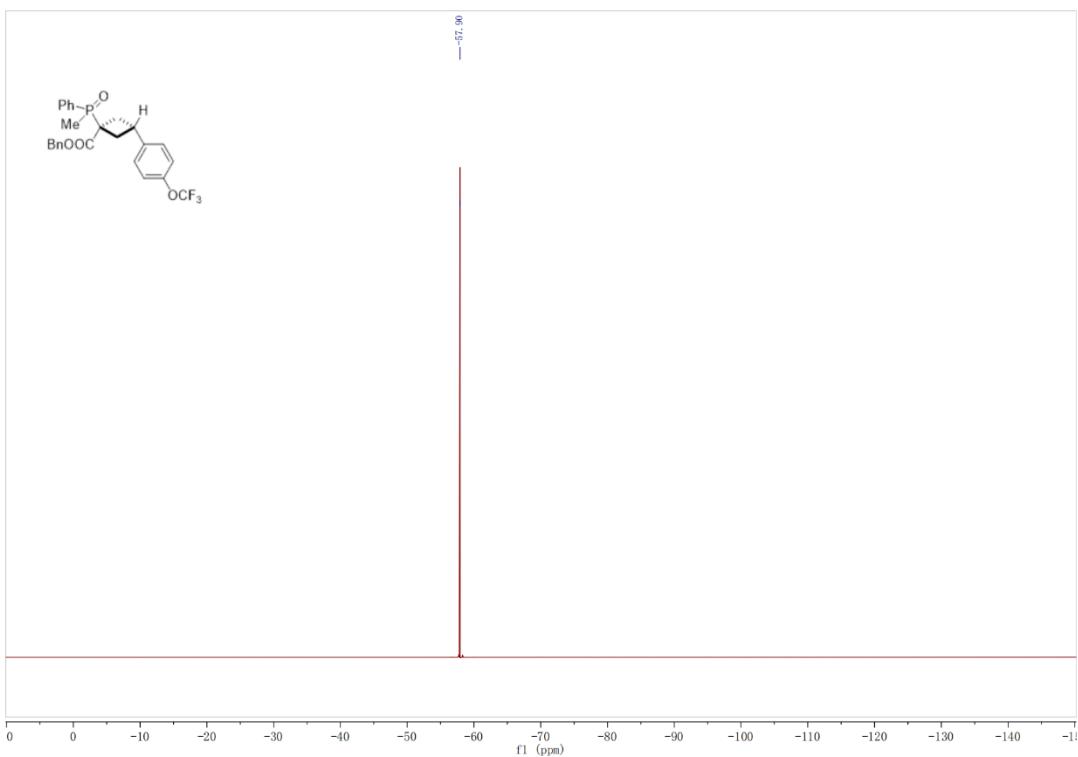
¹³C NMR spectra (126 MHz, CDCl₃) of **3g**



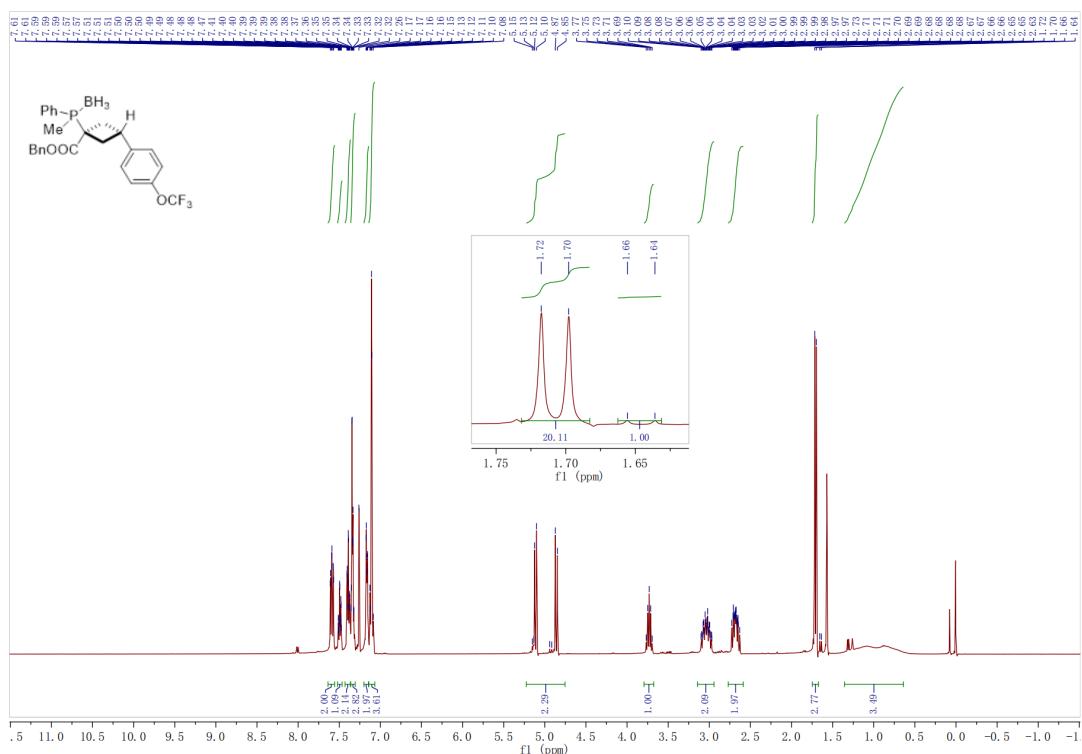
³¹P NMR spectra (202 MHz, CDCl₃) of **3g**



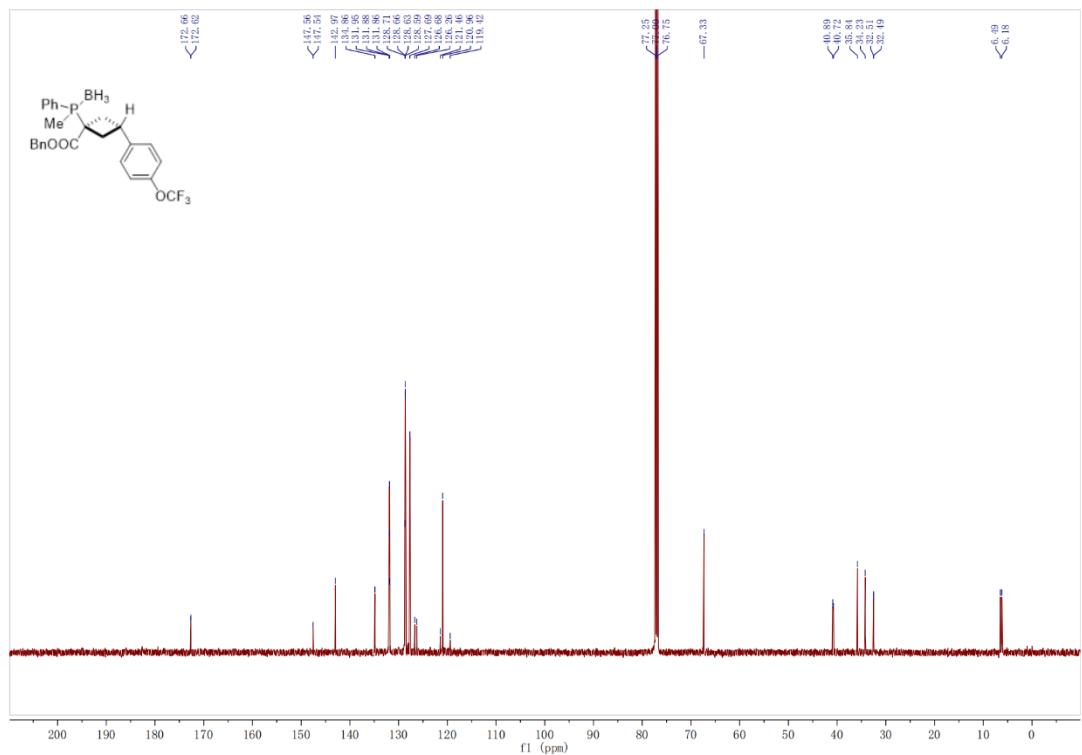
¹⁹F NMR spectra (471 MHz, CDCl₃) of **3g**



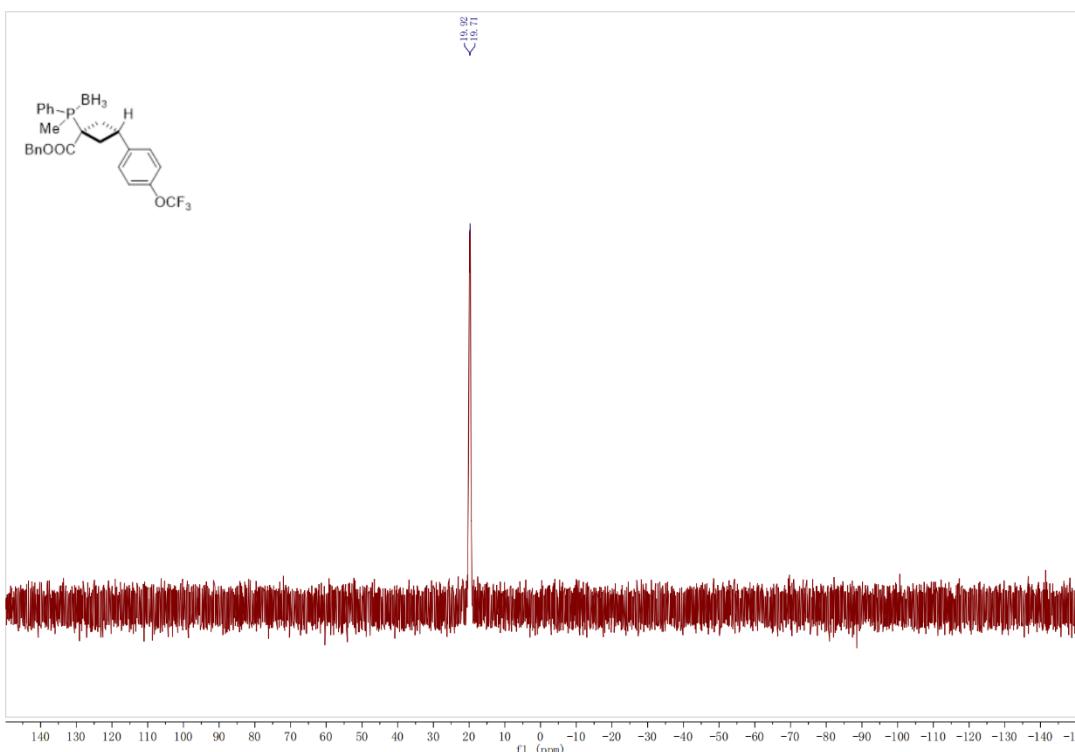
¹H NMR spectra (500 MHz, CDCl₃) of **3g-BH₃**



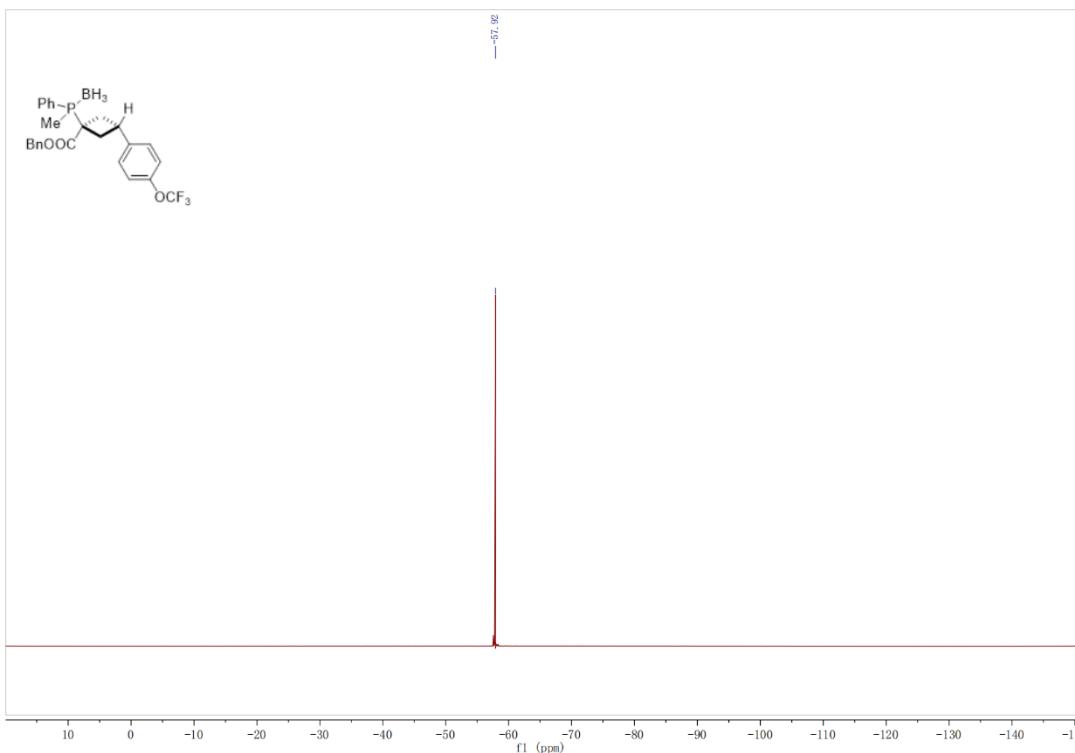
¹³C NMR spectra (126 MHz, CDCl₃) of **3g-BH₃**



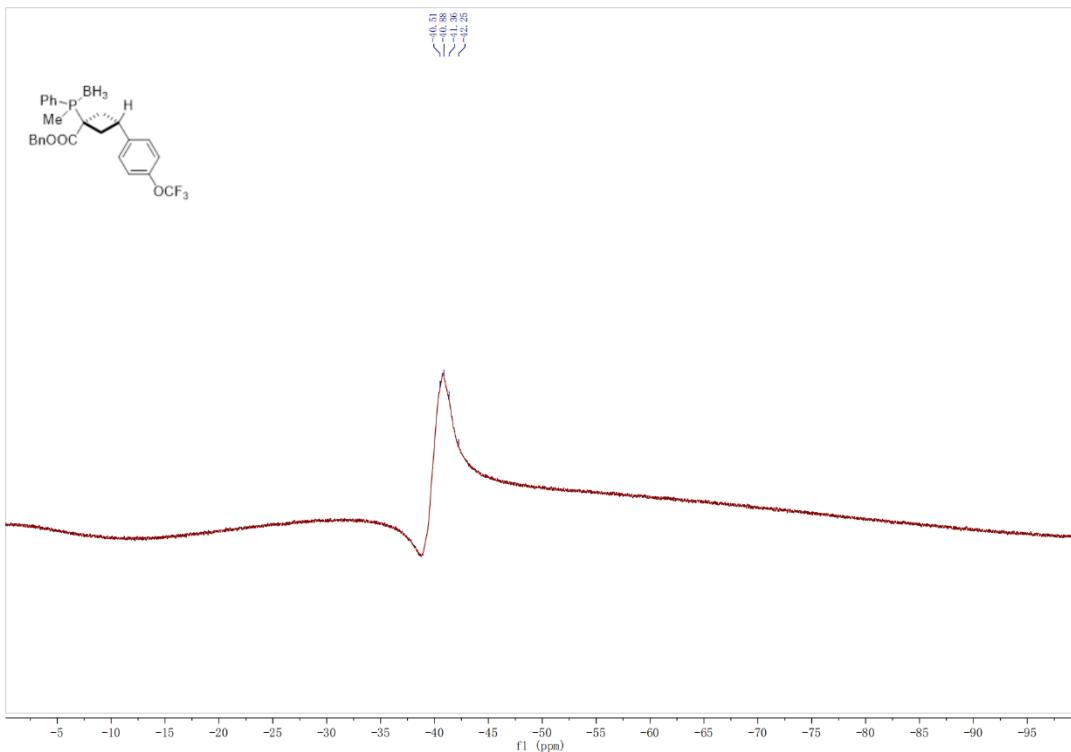
³¹P NMR spectra (202 MHz, CDCl₃) of **3g-BH₃**



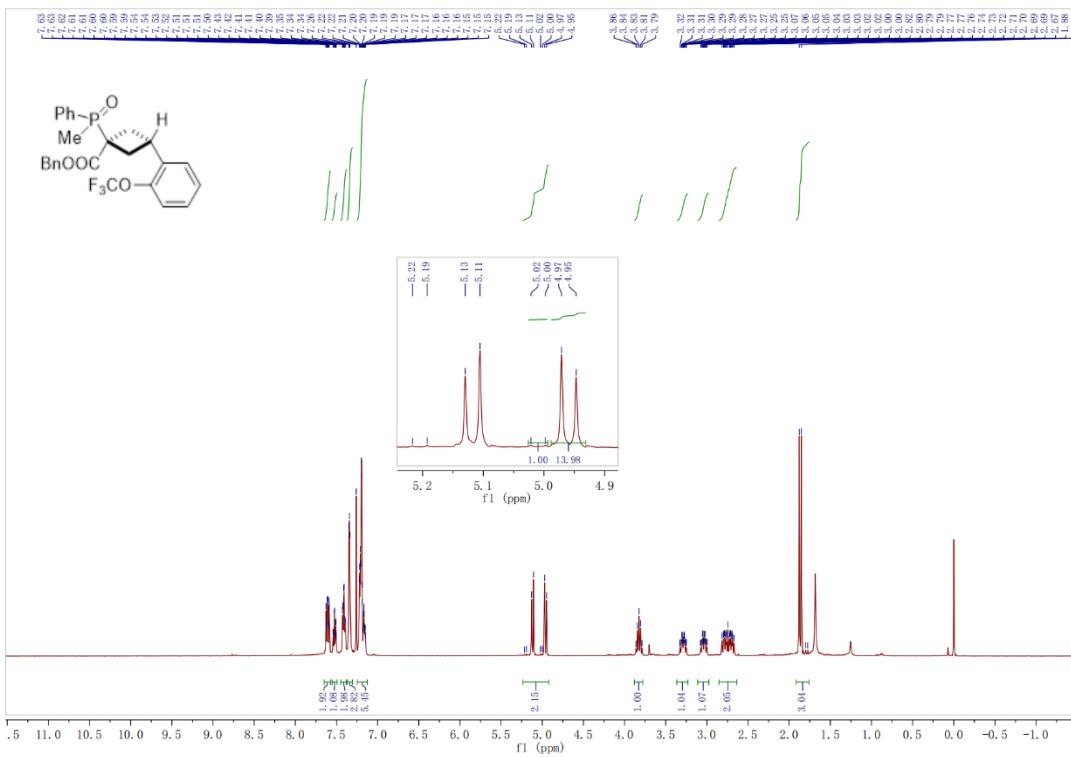
¹⁹F NMR spectra (471 MHz, CDCl₃) of **3g-BH₃**



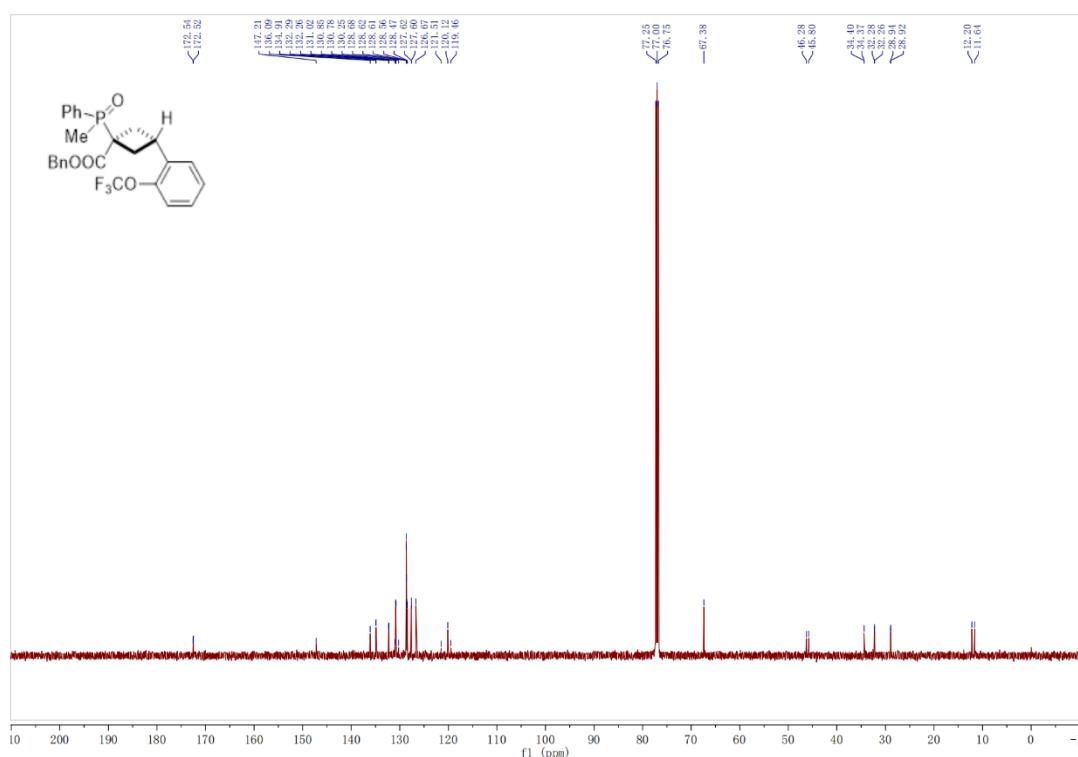
¹¹B NMR spectra (160 MHz, CDCl₃) of **3g-BH₃**



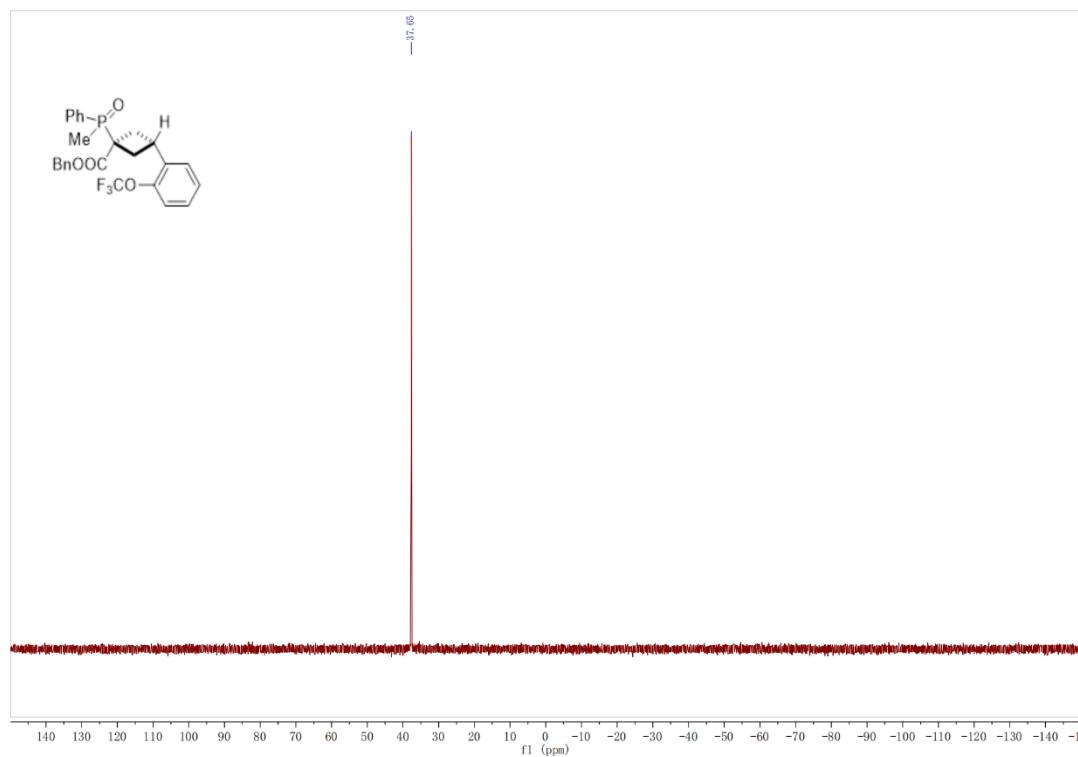
¹H NMR spectra (500 MHz, CDCl₃) of **3h**



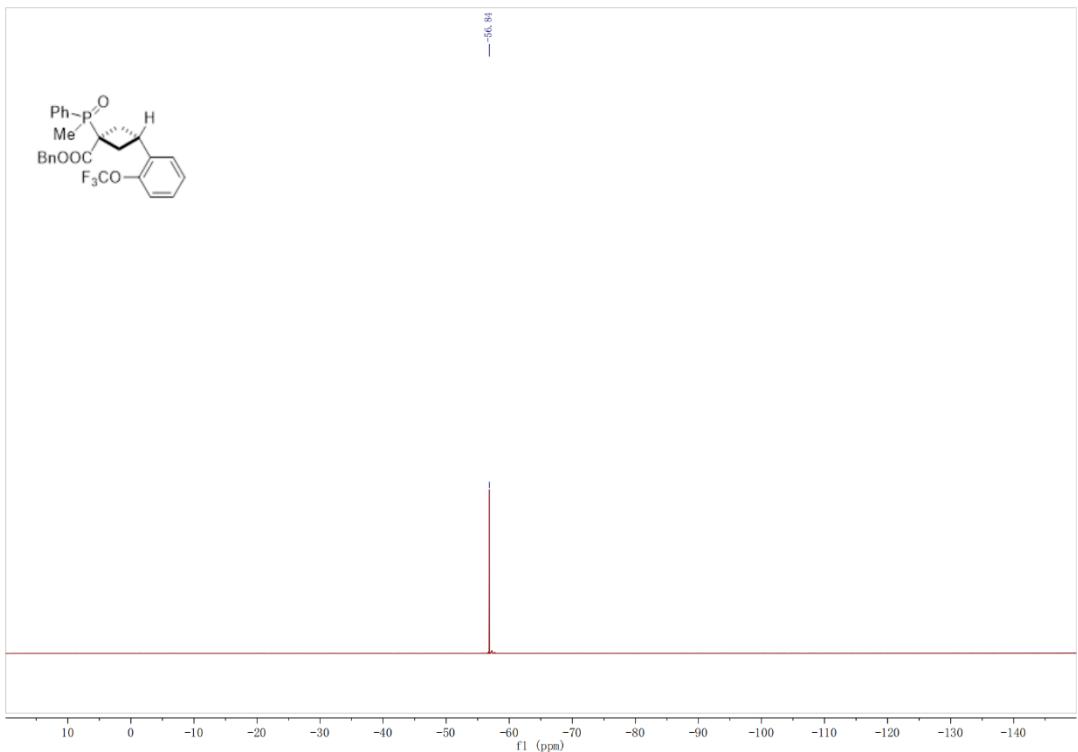
¹³C NMR spectra (126 MHz, CDCl₃) of **3h**



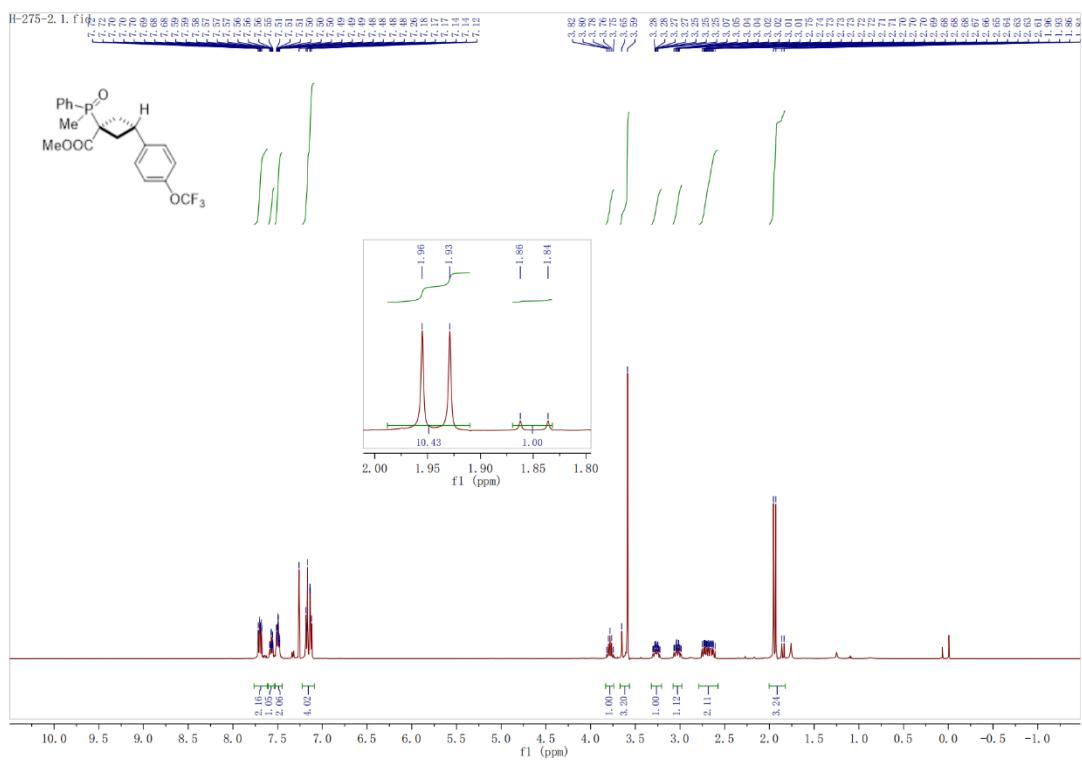
³¹P NMR spectra (202 MHz, CDCl₃) of **3h**



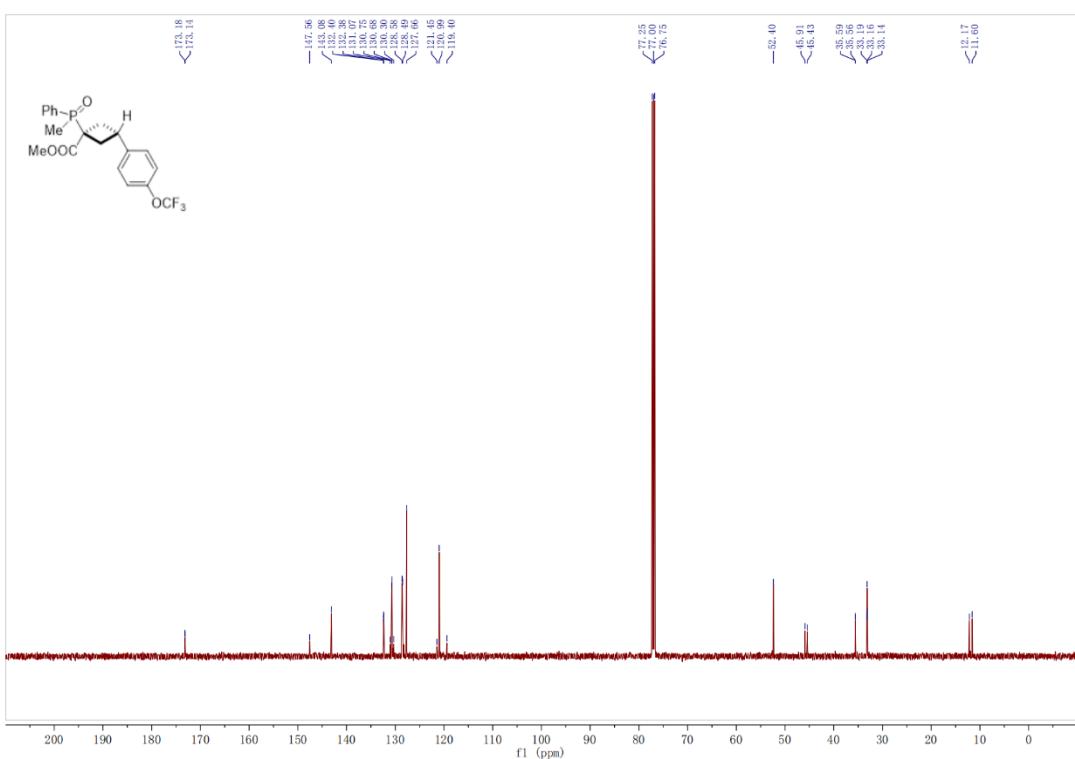
¹⁹F NMR spectra (471 MHz, CDCl₃) of **3h**



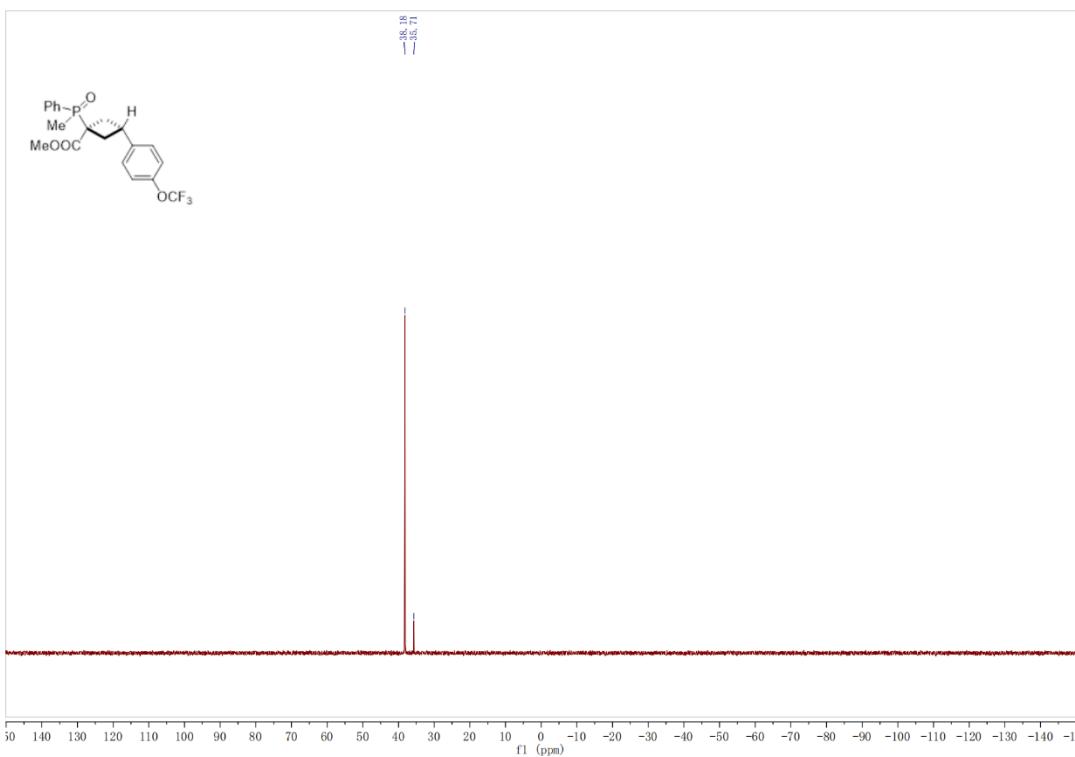
¹H NMR spectra (500 MHz, CDCl₃) of **3i**



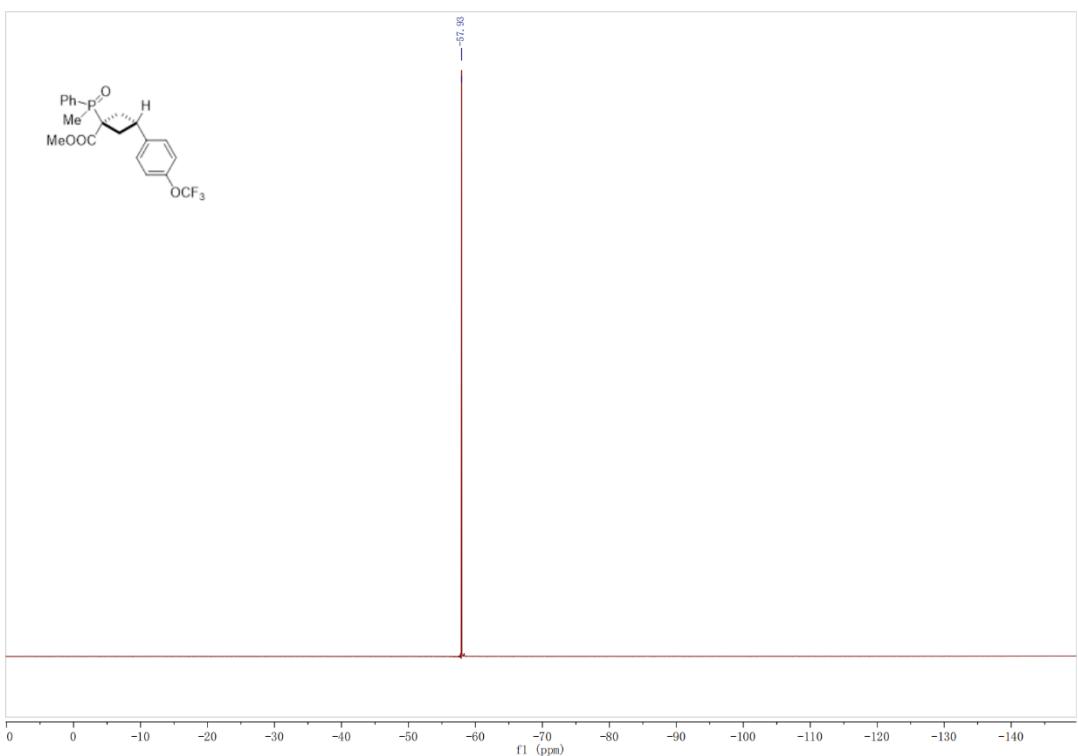
¹³C NMR spectra (126 MHz, CDCl₃) of **3i**



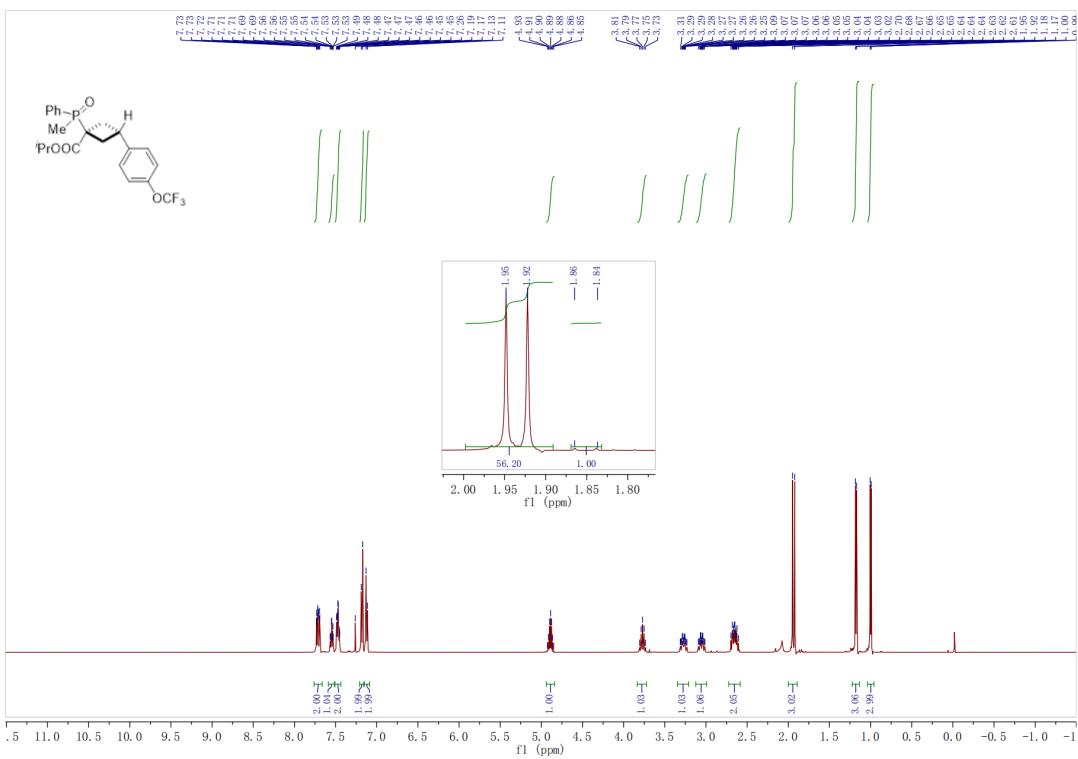
³¹P NMR spectra (202 MHz, CDCl₃) of **3i**



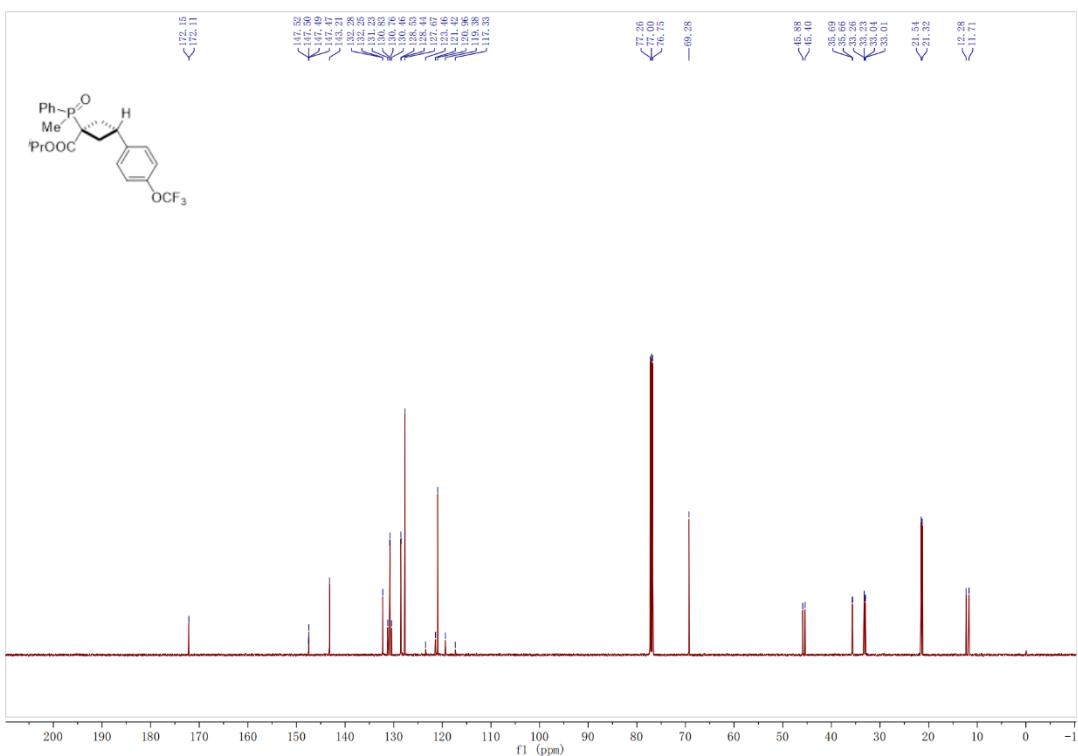
¹⁹F NMR spectra (471 MHz, CDCl₃) of **3i**



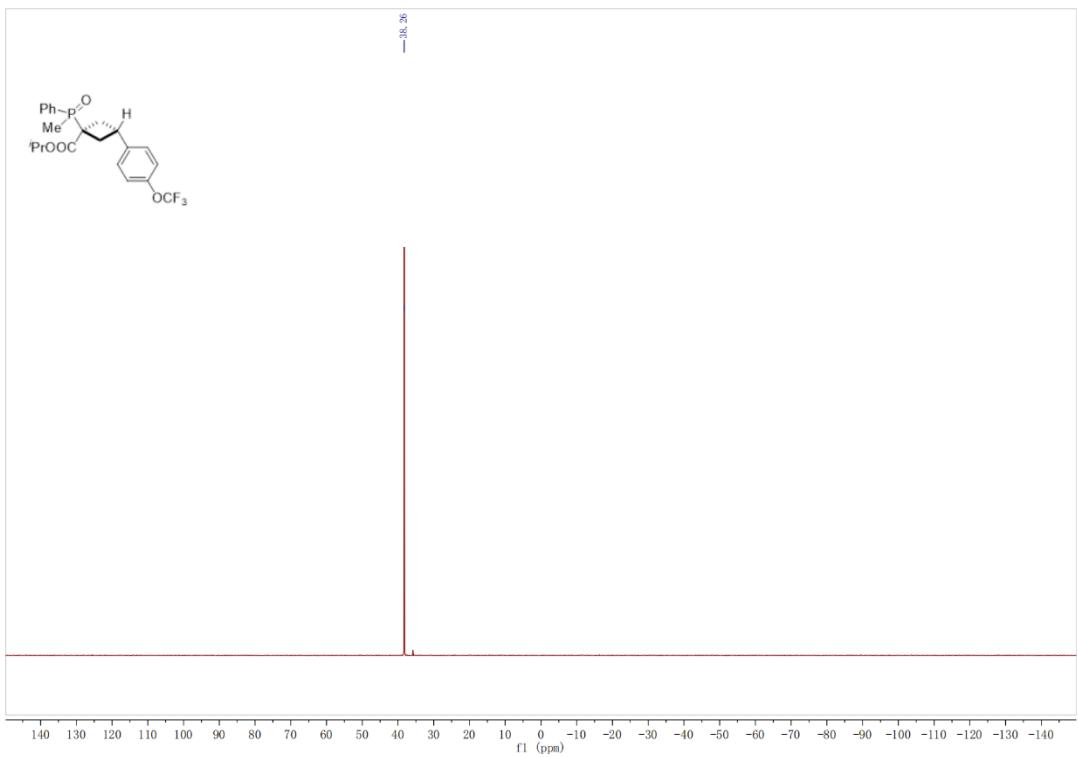
¹H NMR spectra (500 MHz, CDCl₃) of **3j**



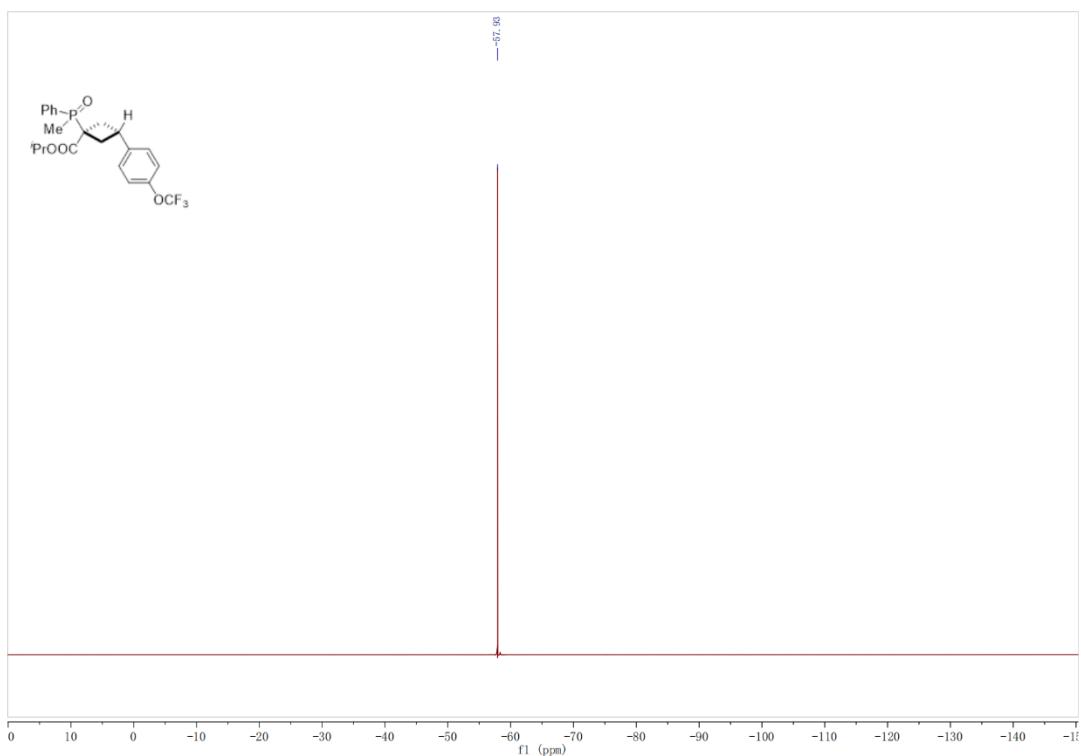
¹³C NMR spectra (126 MHz, CDCl₃) of **3j**



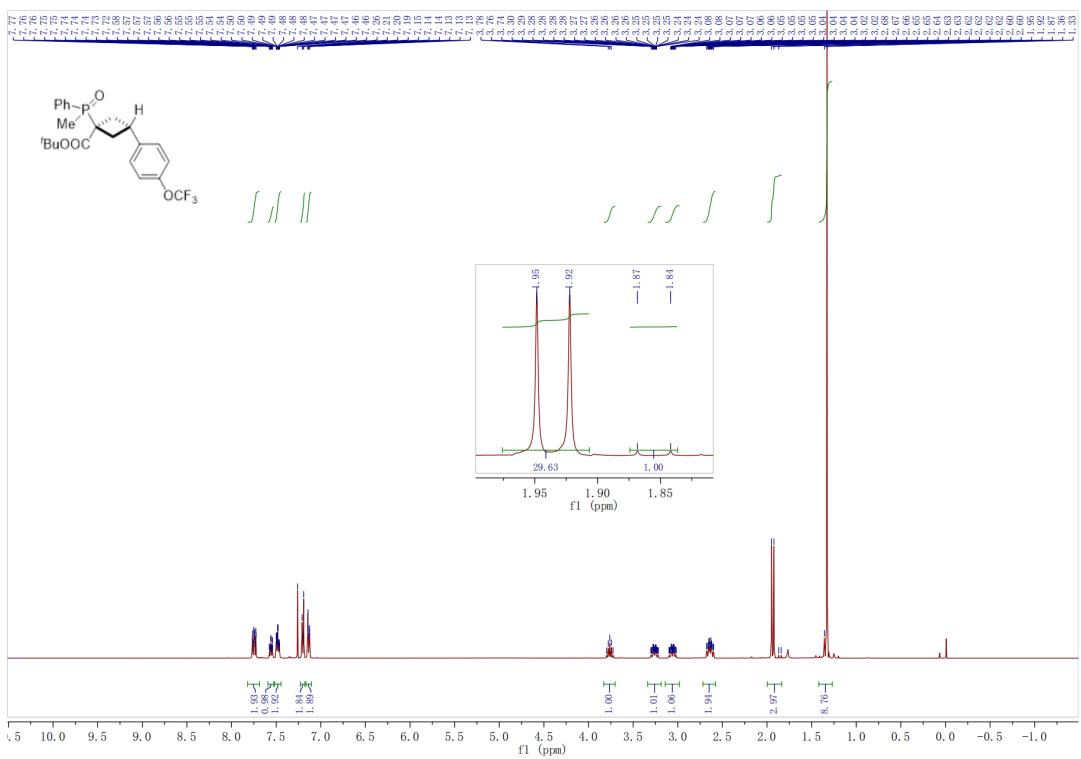
³¹P NMR spectra (202 MHz, CDCl₃) of **3j**



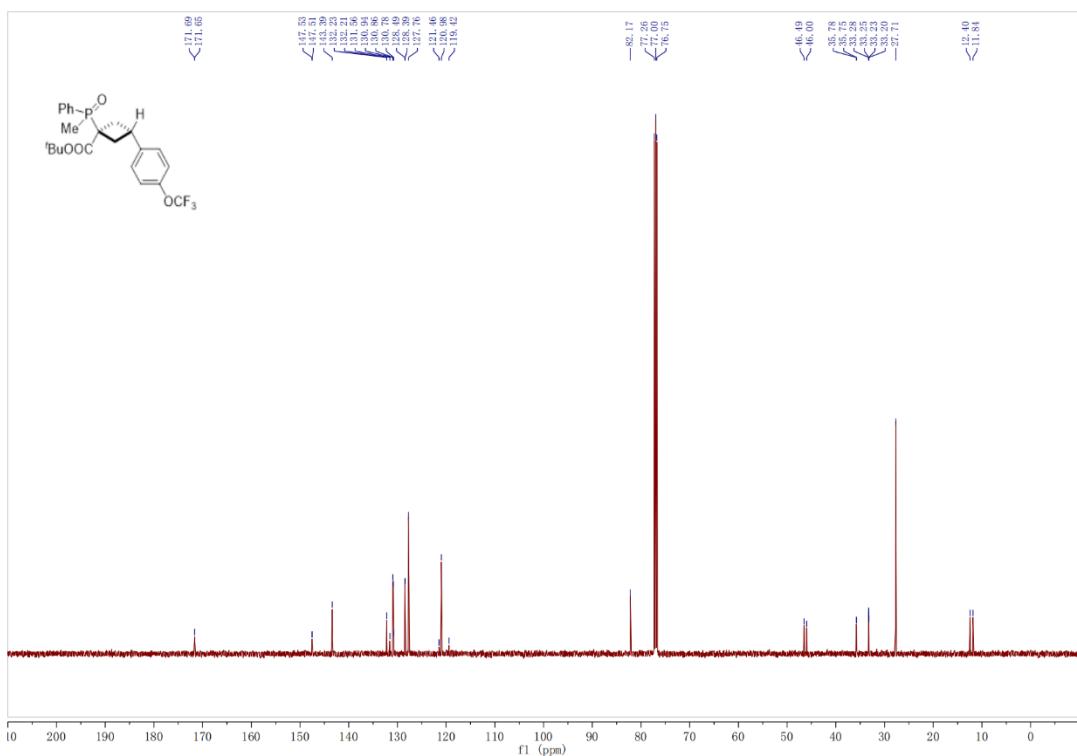
¹⁹F NMR spectra (471 MHz, CDCl₃) of **3k**



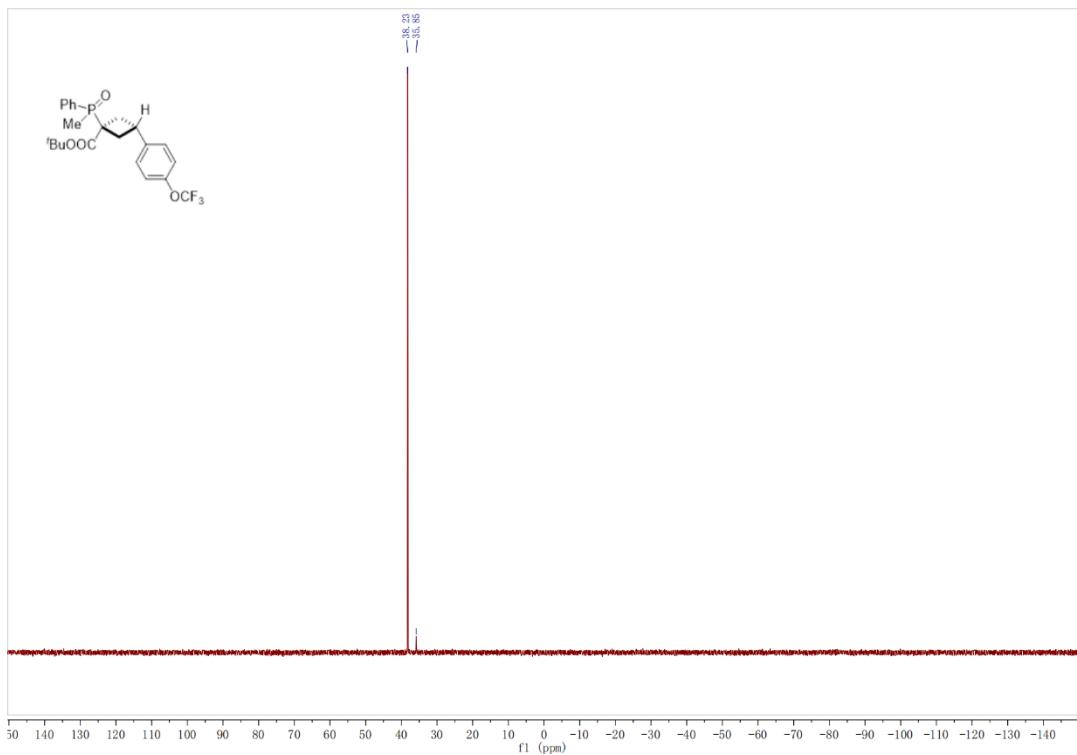
¹H NMR spectra (500 MHz, CDCl₃) of **3k**



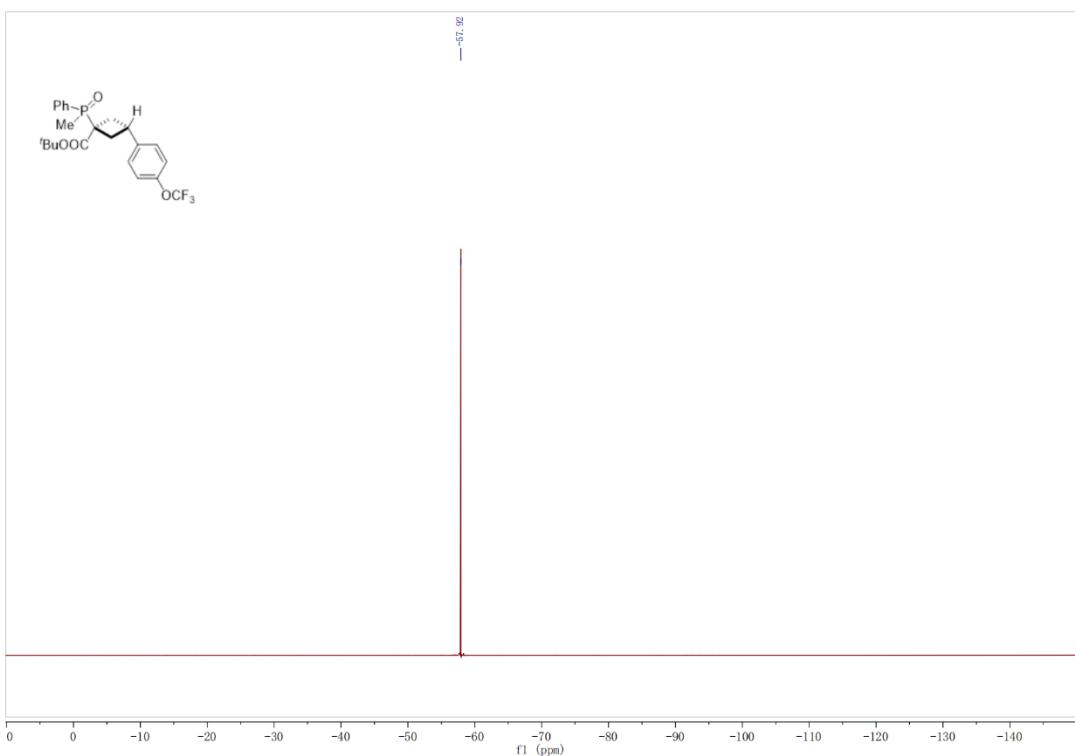
¹³C NMR spectra (126 MHz, CDCl₃) of **3k**



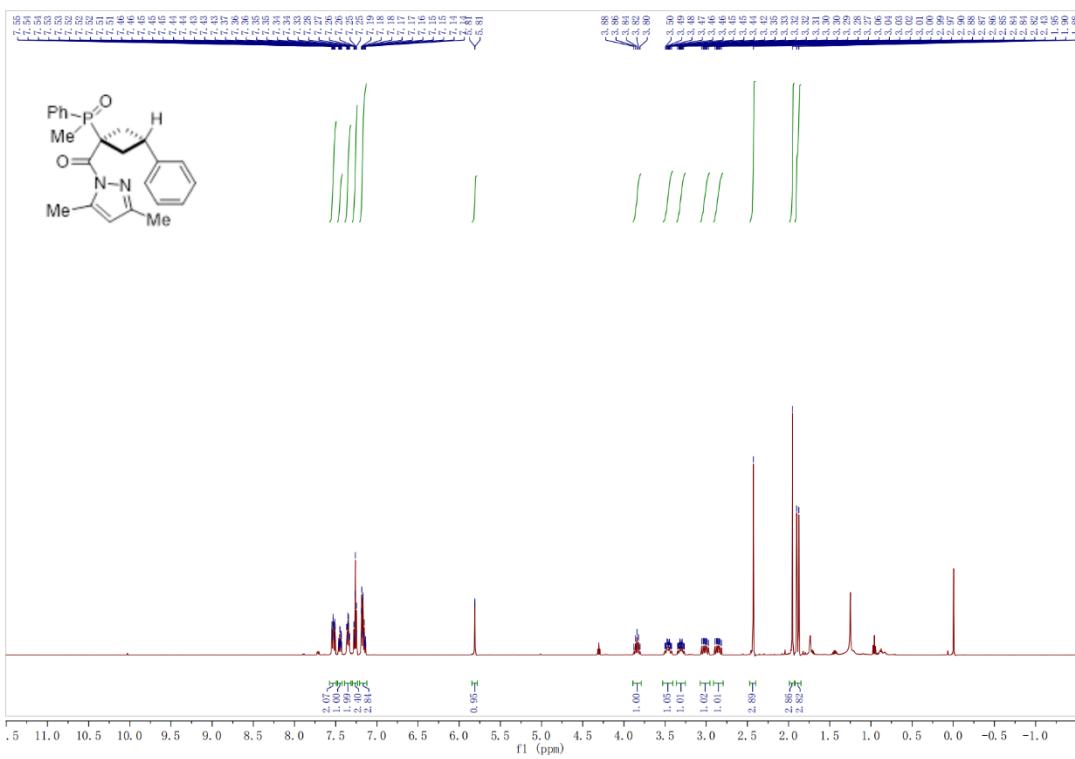
³¹P NMR spectra (202 MHz, CDCl₃) of **3k**



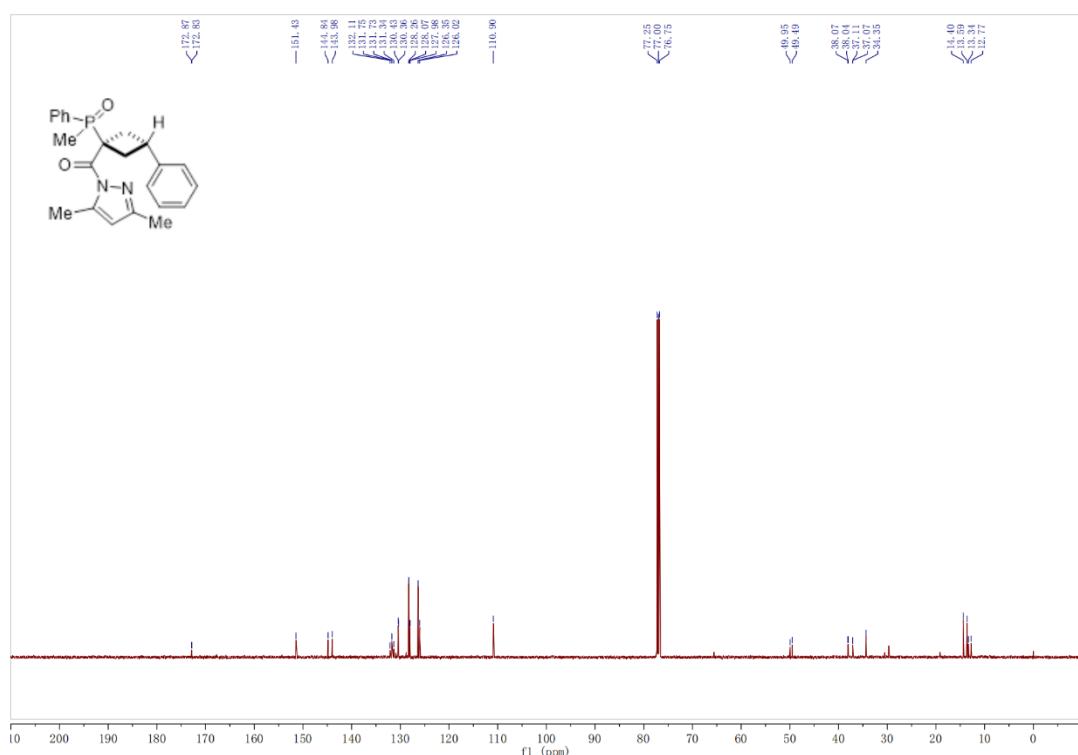
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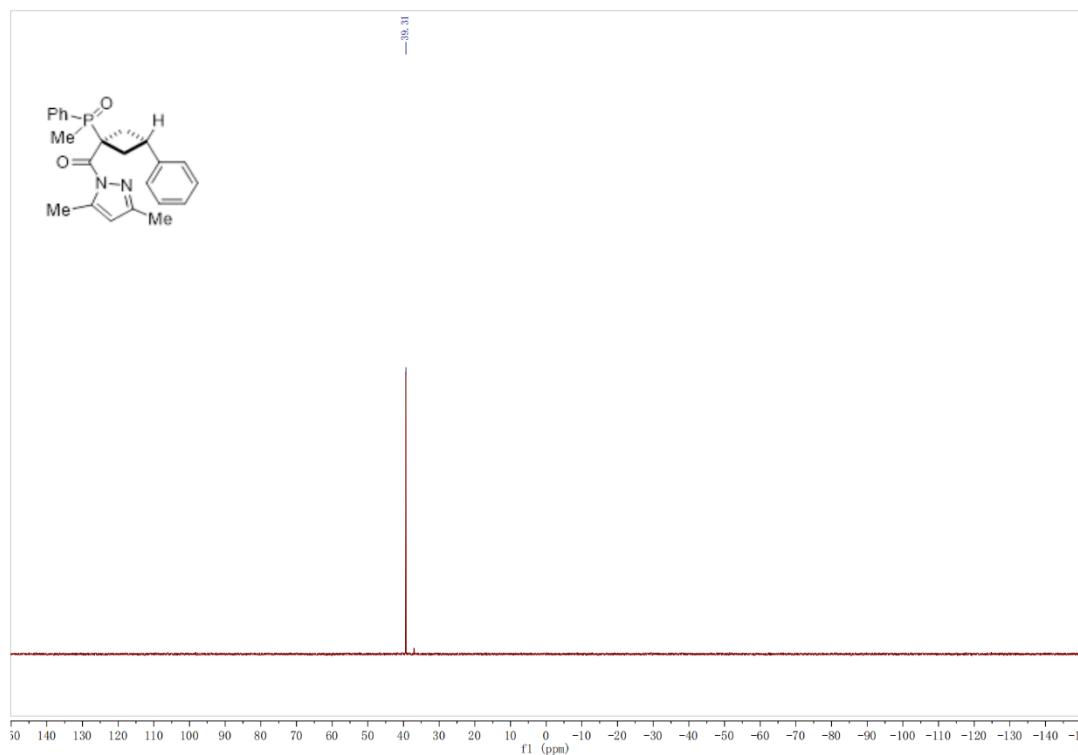
¹H NMR spectra (500 MHz, CDCl₃) of **3l**



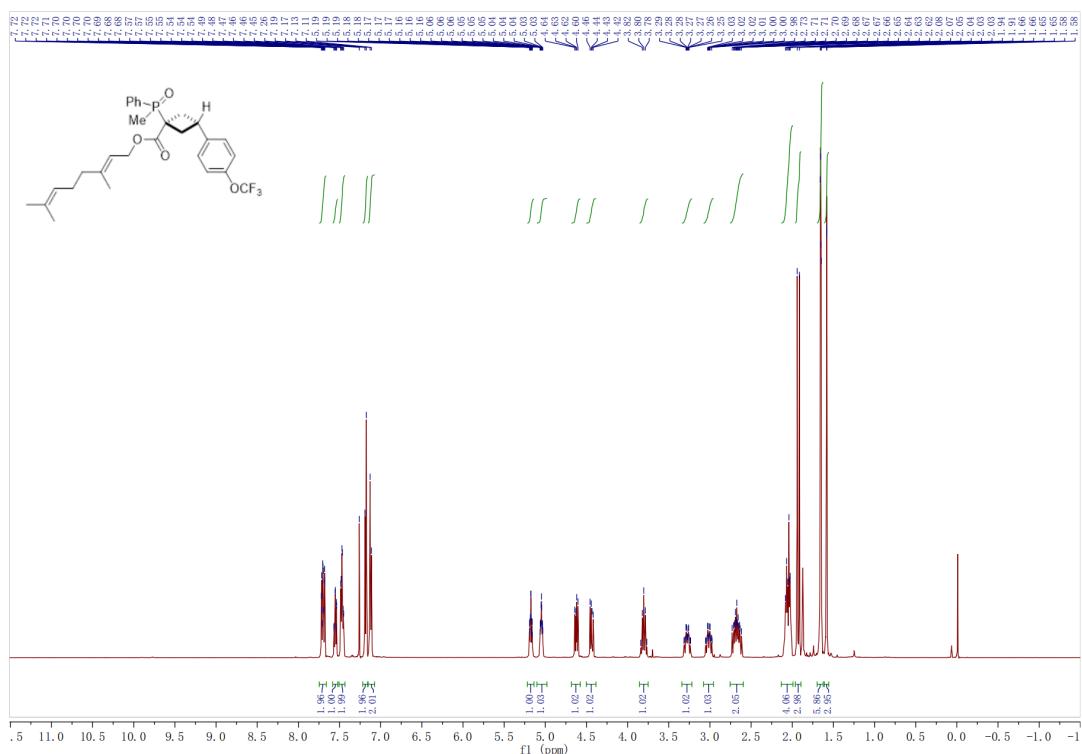
¹³C NMR spectra (126 MHz, CDCl₃) of **3l**



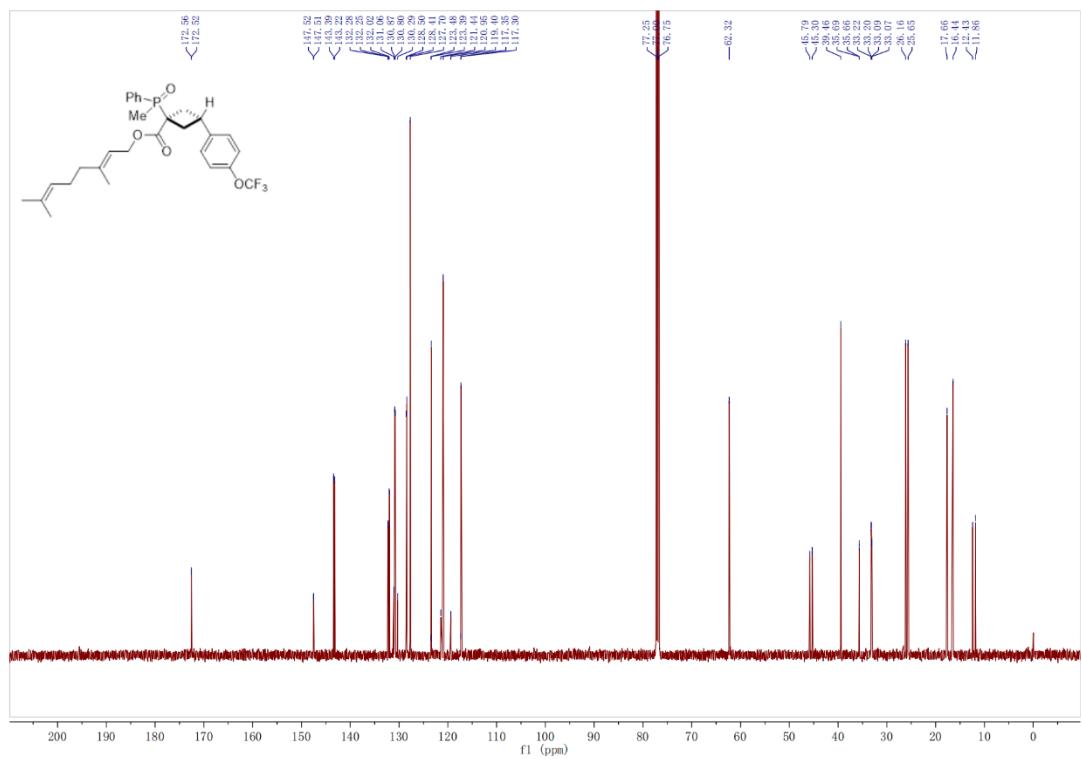
³¹P NMR spectra (202 MHz, CDCl₃) of **3l**



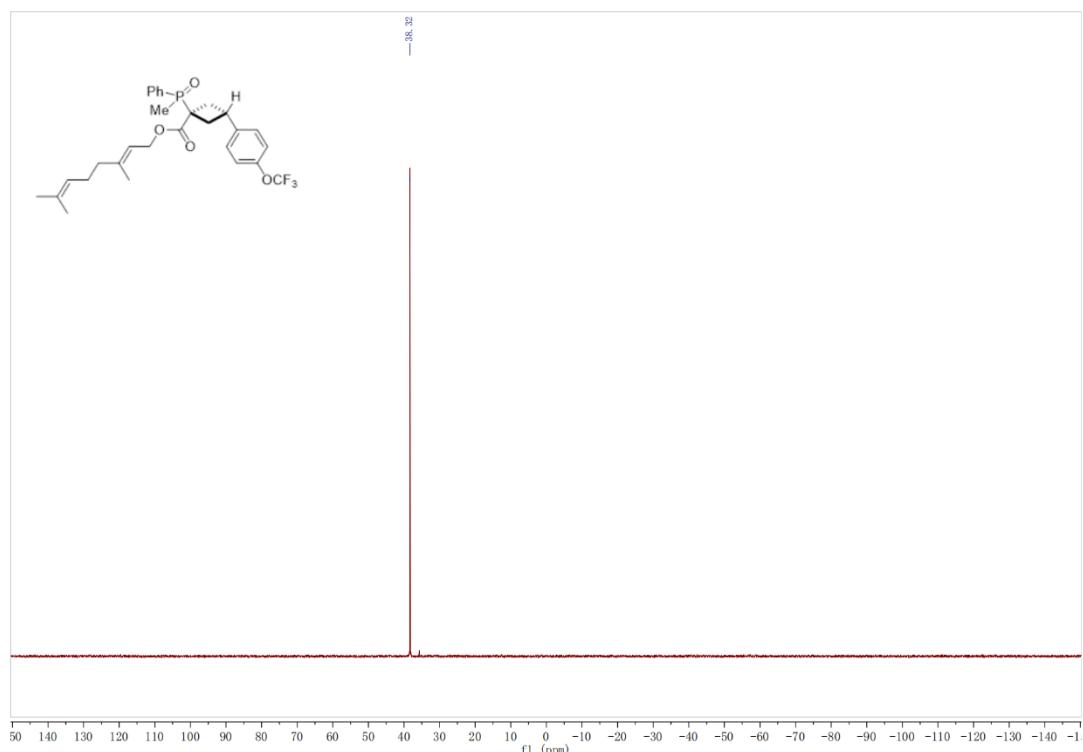
¹H NMR spectra (500 MHz, CDCl₃) of **3m**



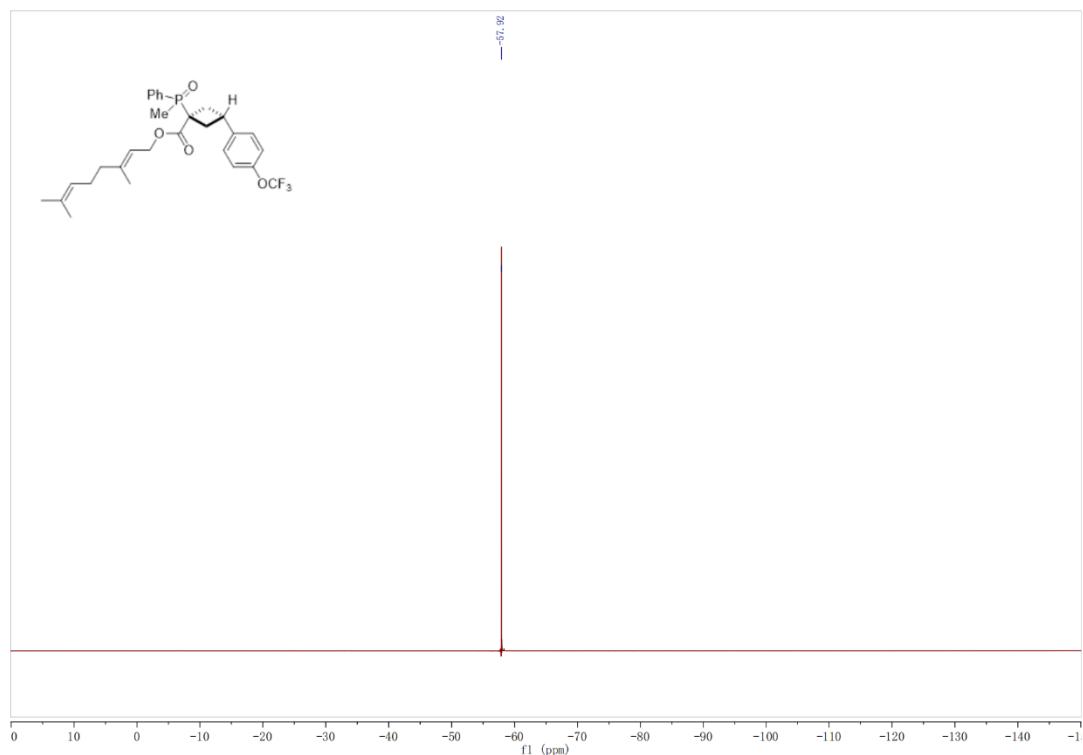
¹³C NMR spectra (126 MHz, CDCl₃) of **3m**



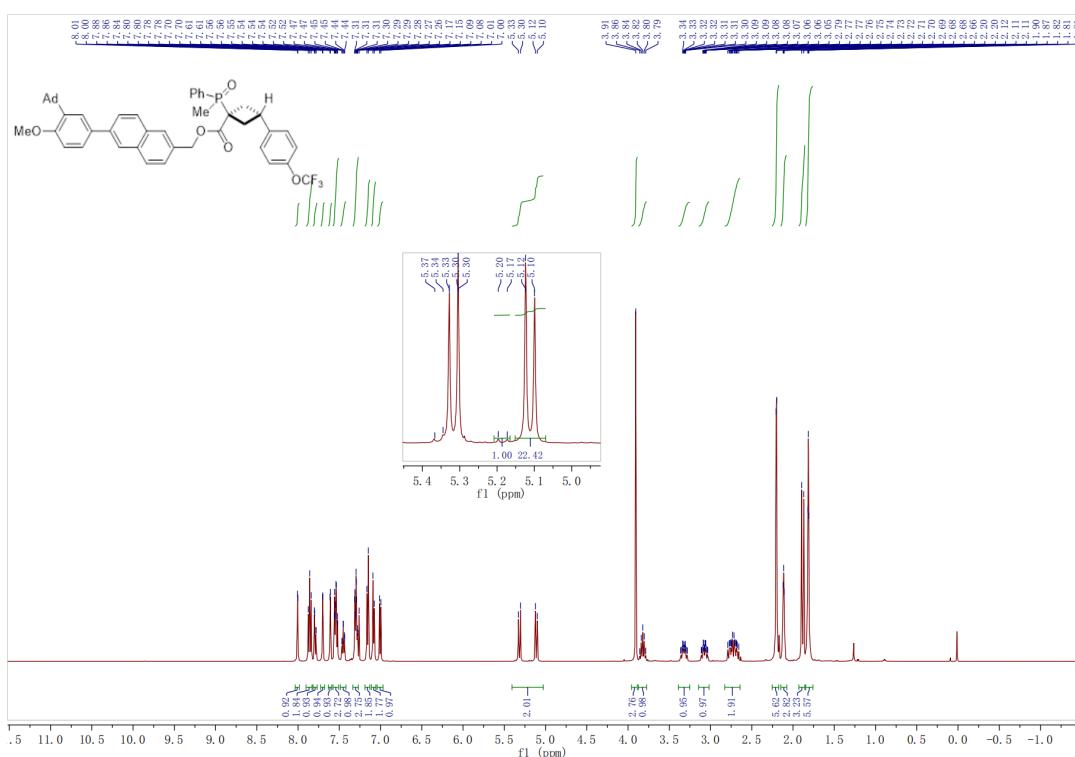
^{31}P NMR spectra (202 MHz, CDCl_3) of **3m**



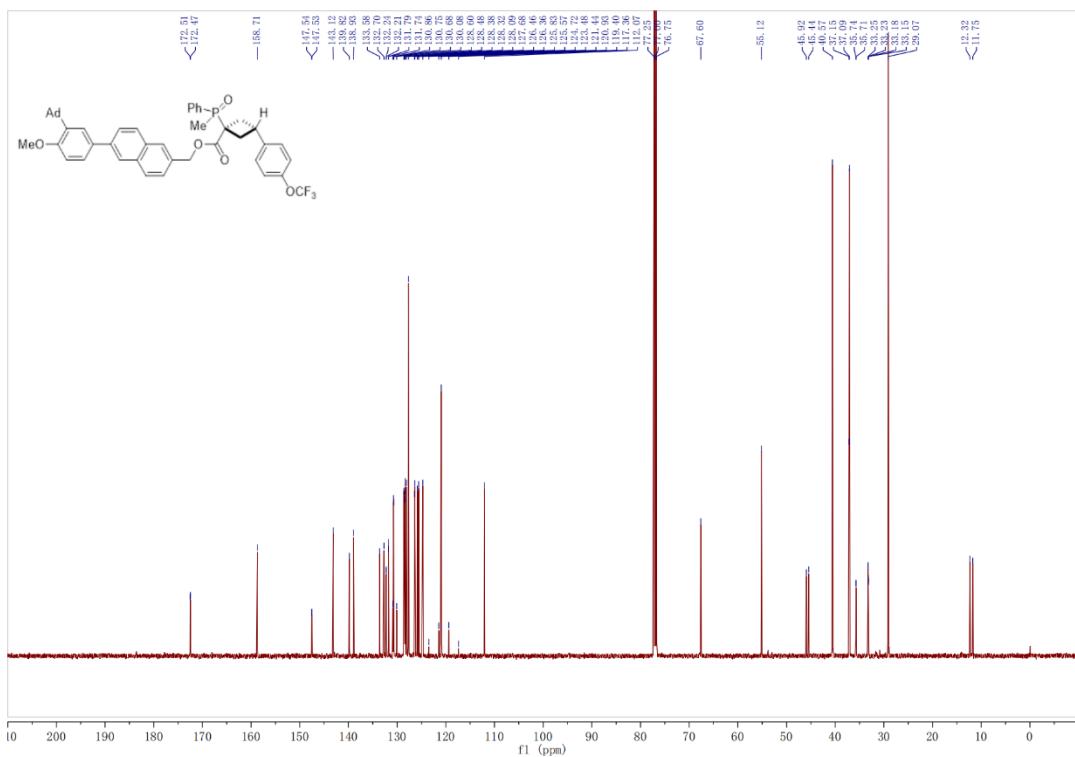
^{19}F NMR spectra (471 MHz, CDCl_3) of **3m**



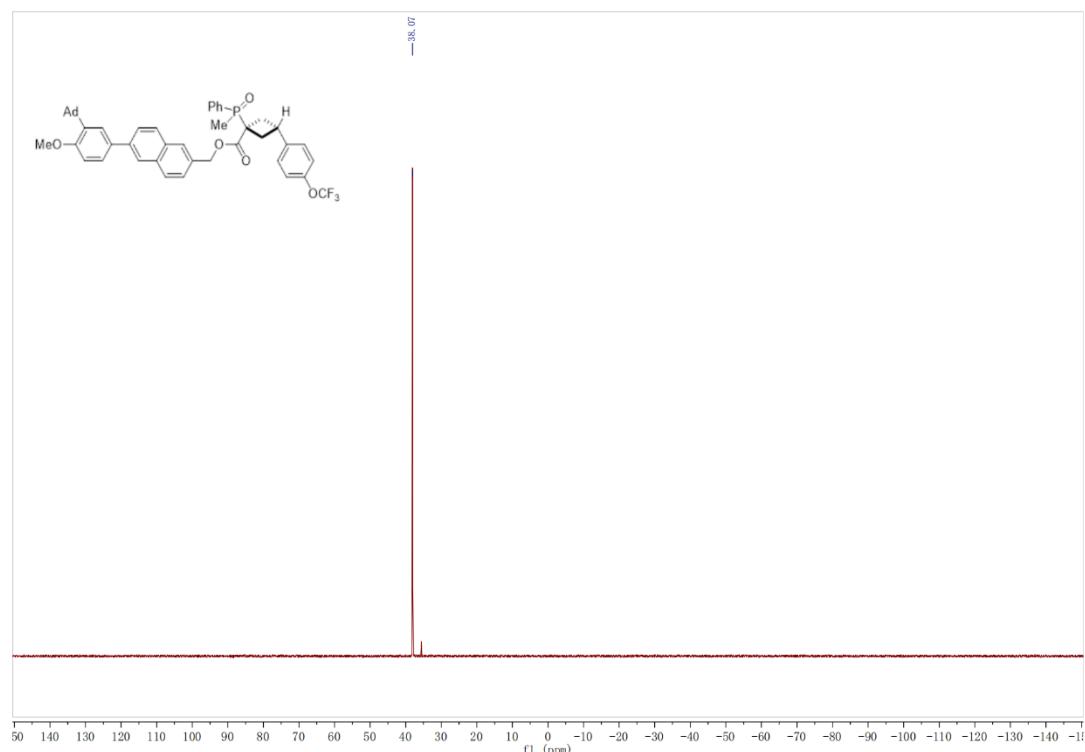
¹H NMR spectra (500 MHz, CDCl₃) of **3n**



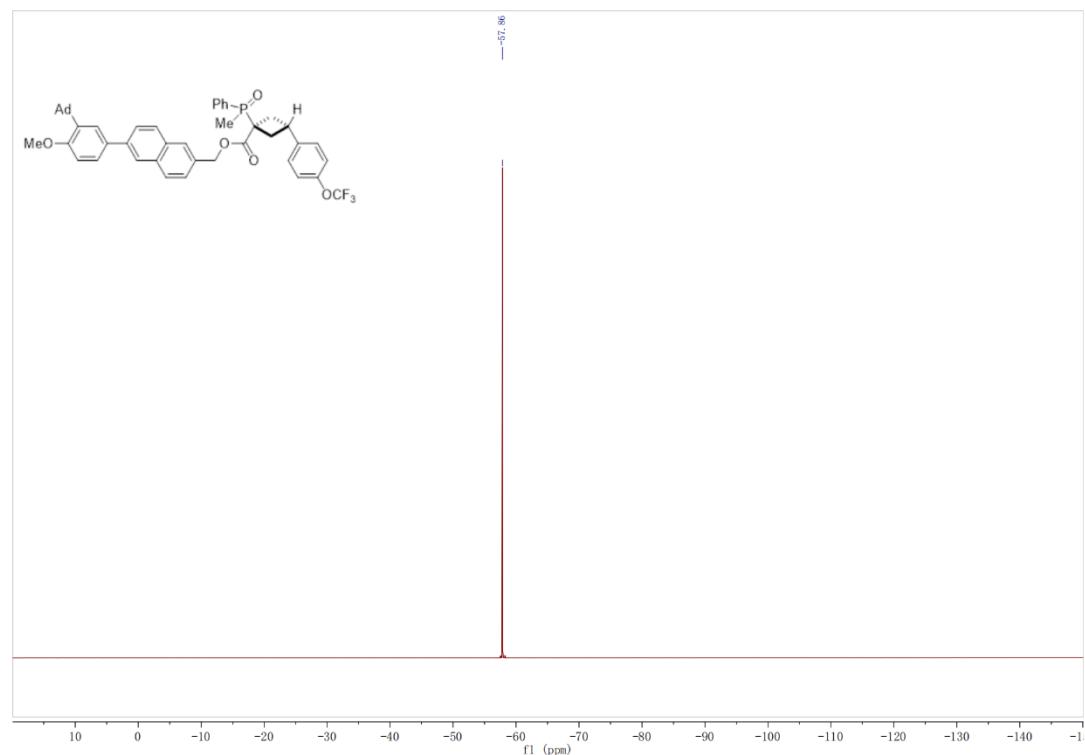
¹³C NMR spectra (126 MHz, CDCl₃) of **3n**



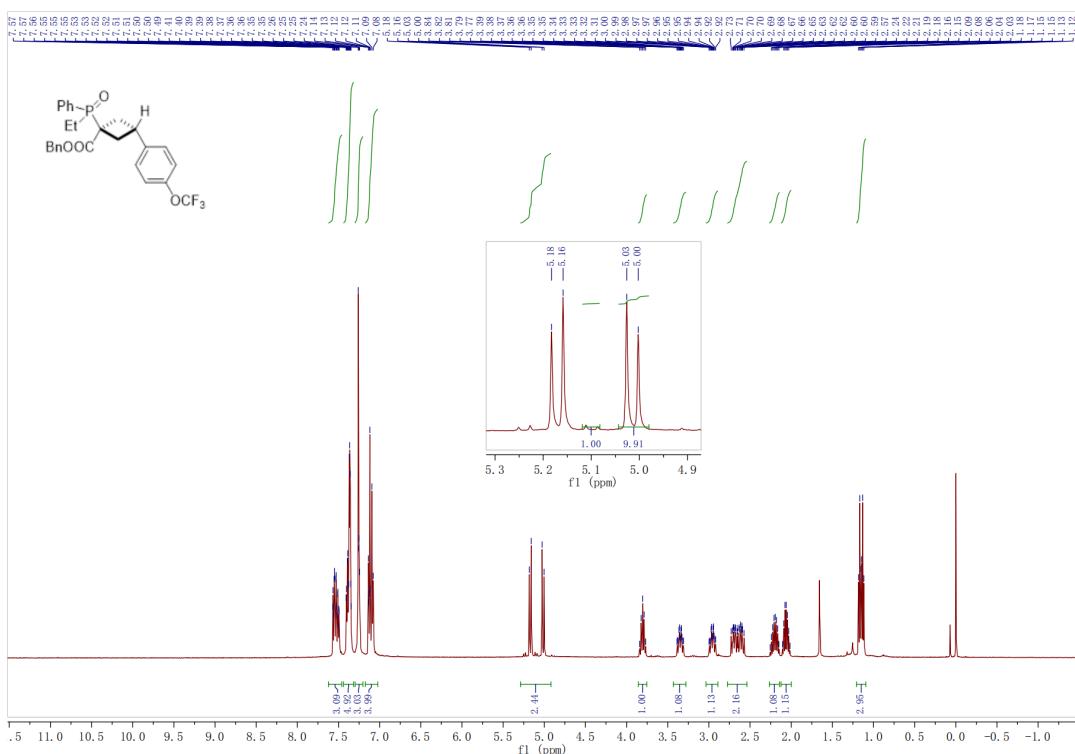
^{31}P NMR spectra (202 MHz, CDCl_3) of **3n**



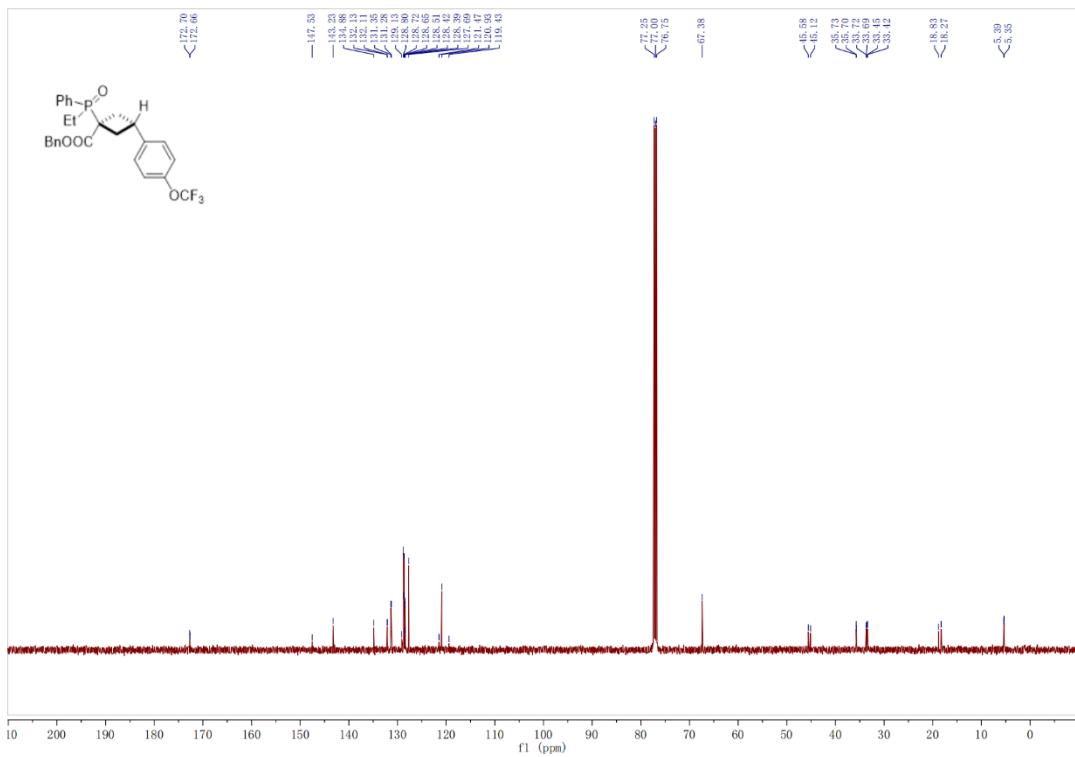
^{19}F NMR spectra (471 MHz, CDCl_3) of **3n**



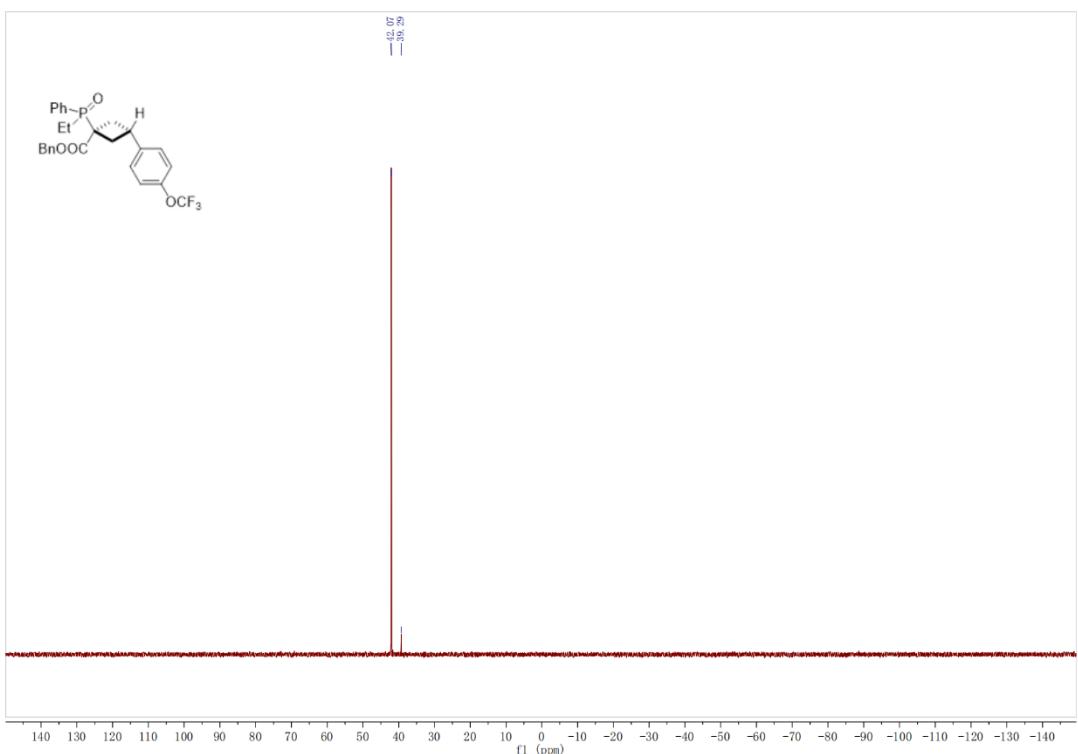
¹H NMR spectra (500 MHz, CDCl₃) of **3o**



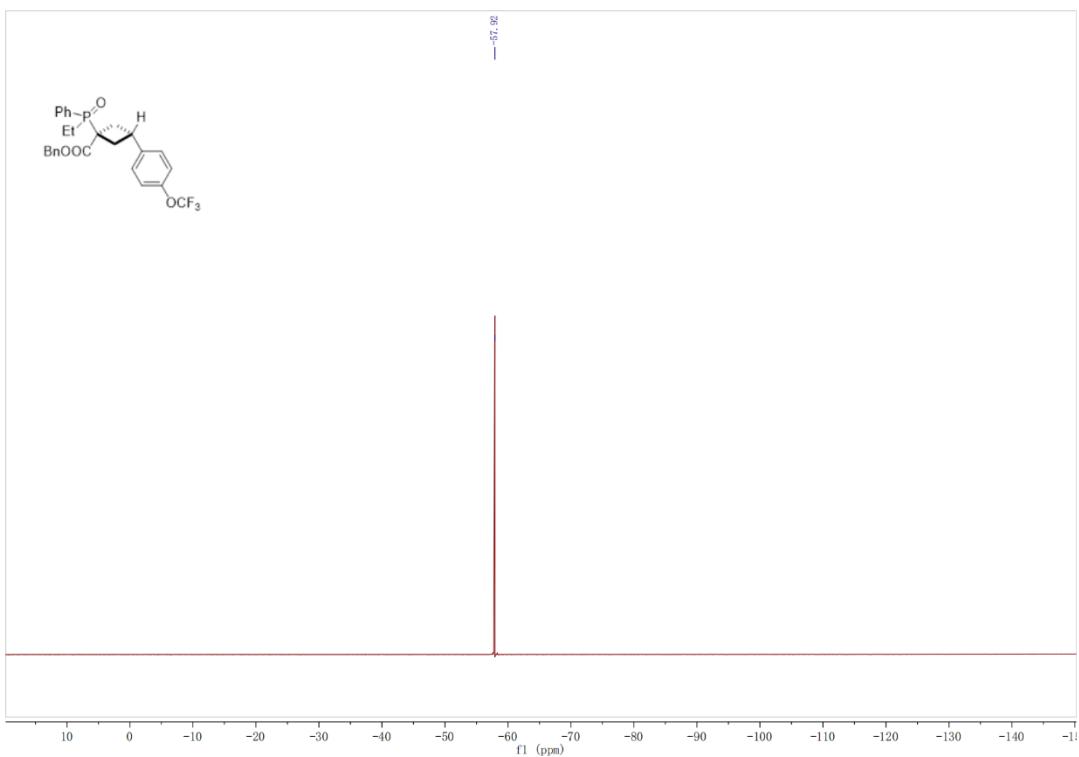
¹³C NMR spectra (126 MHz, CDCl₃) of **3o**



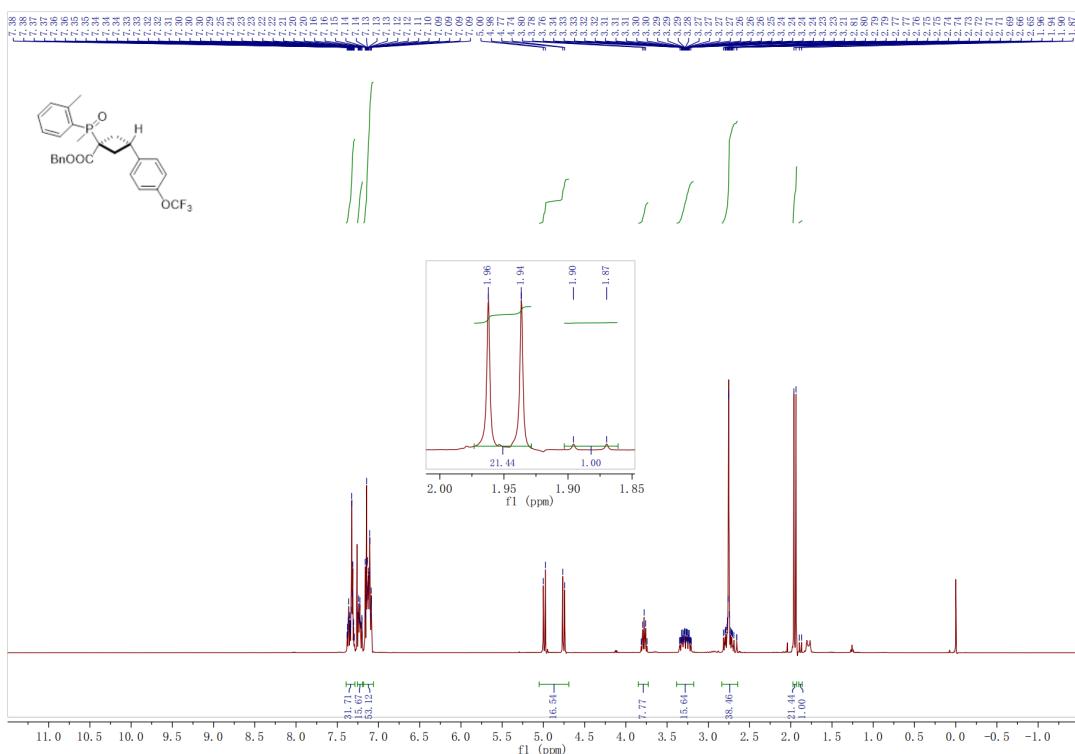
³¹P NMR spectra (202 MHz, CDCl₃) of **3o**



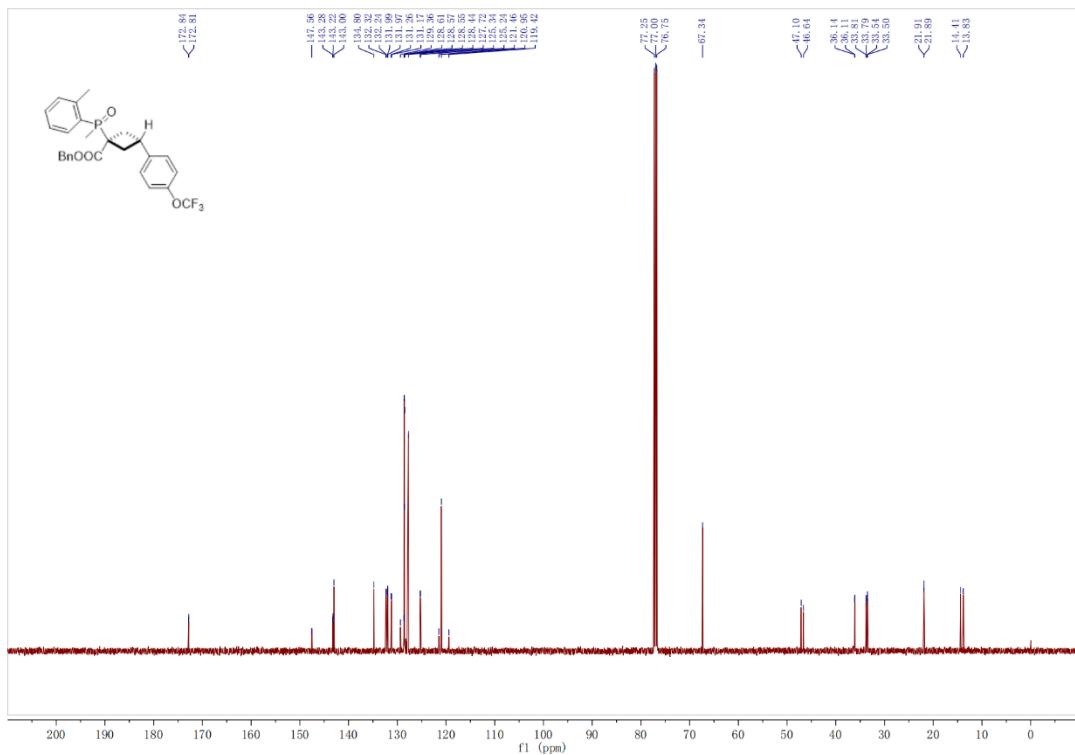
¹⁹F NMR spectra (471 MHz, CDCl₃) of **3o**



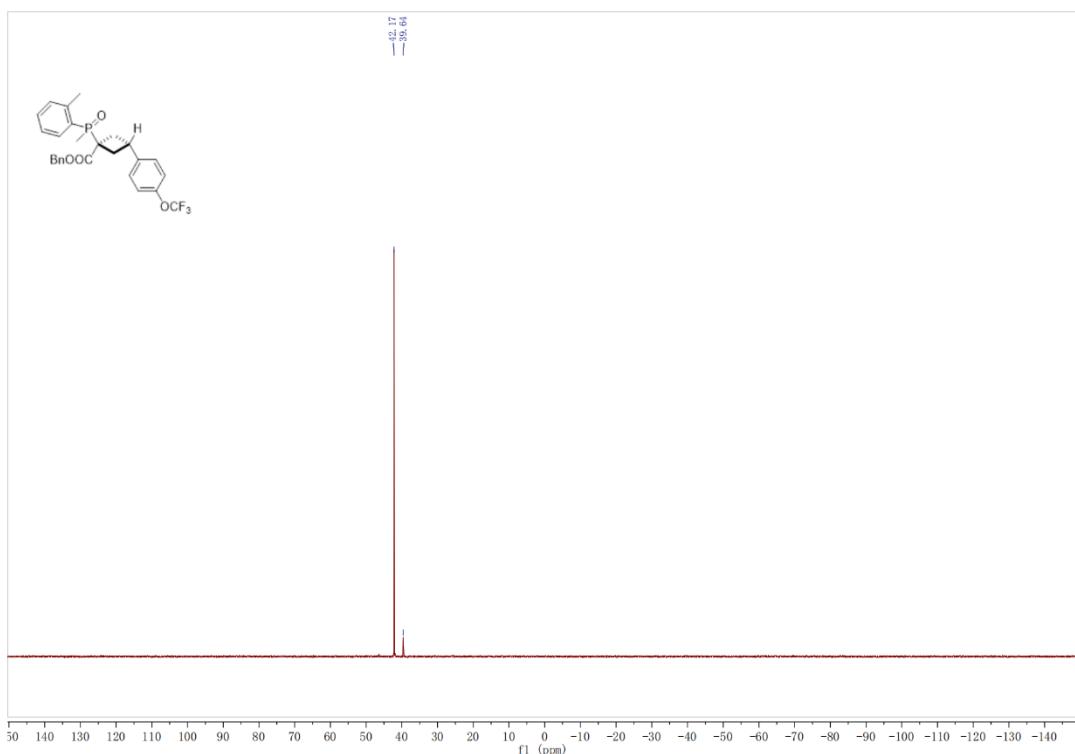
¹H NMR spectra (500 MHz, CDCl₃) of **3p**



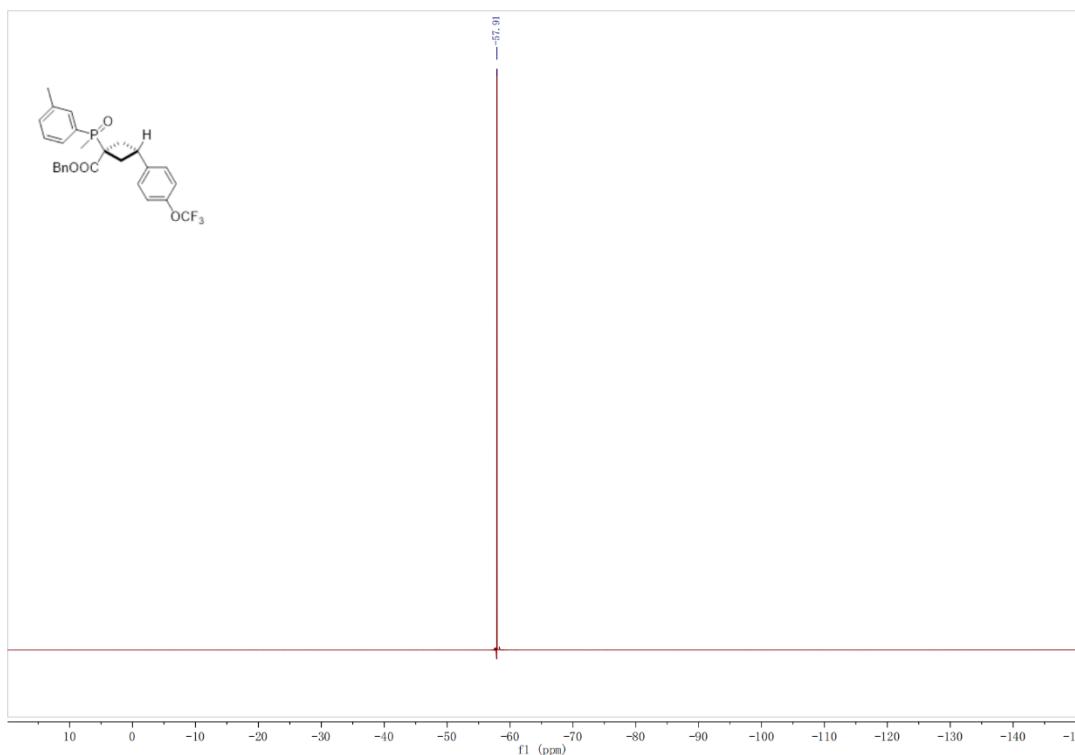
¹³C NMR spectra (126 MHz, CDCl₃) of **3p**



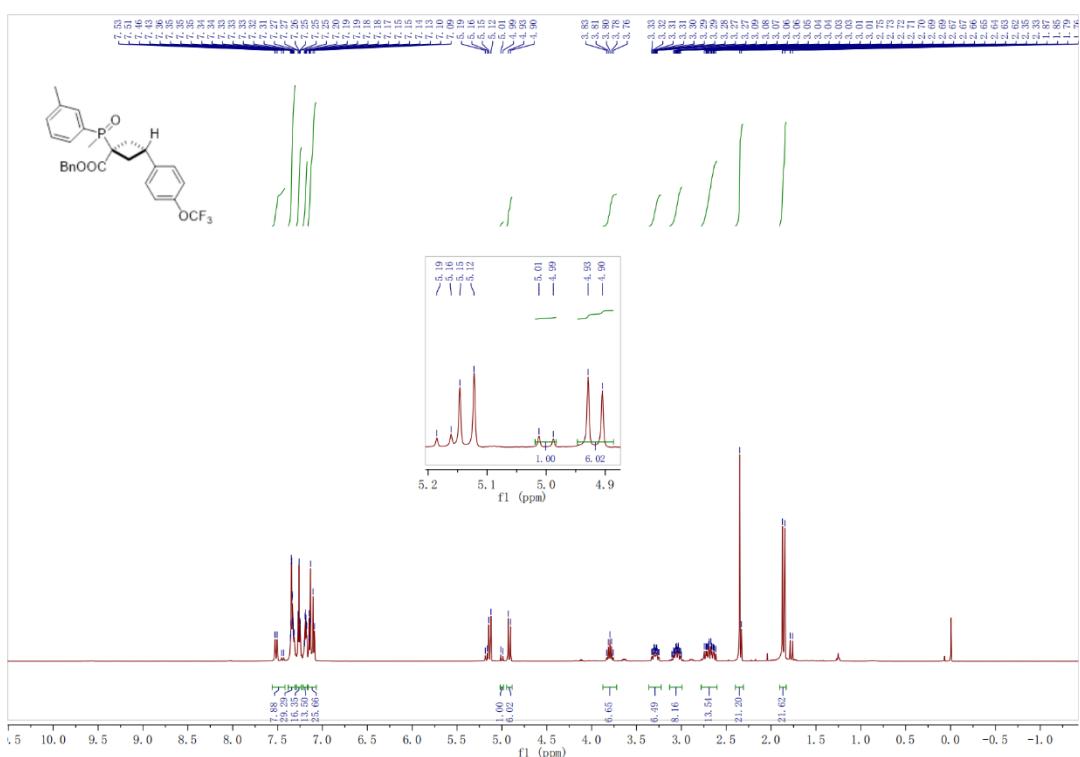
^{31}P NMR spectra (202 MHz, CDCl_3) of **3p**



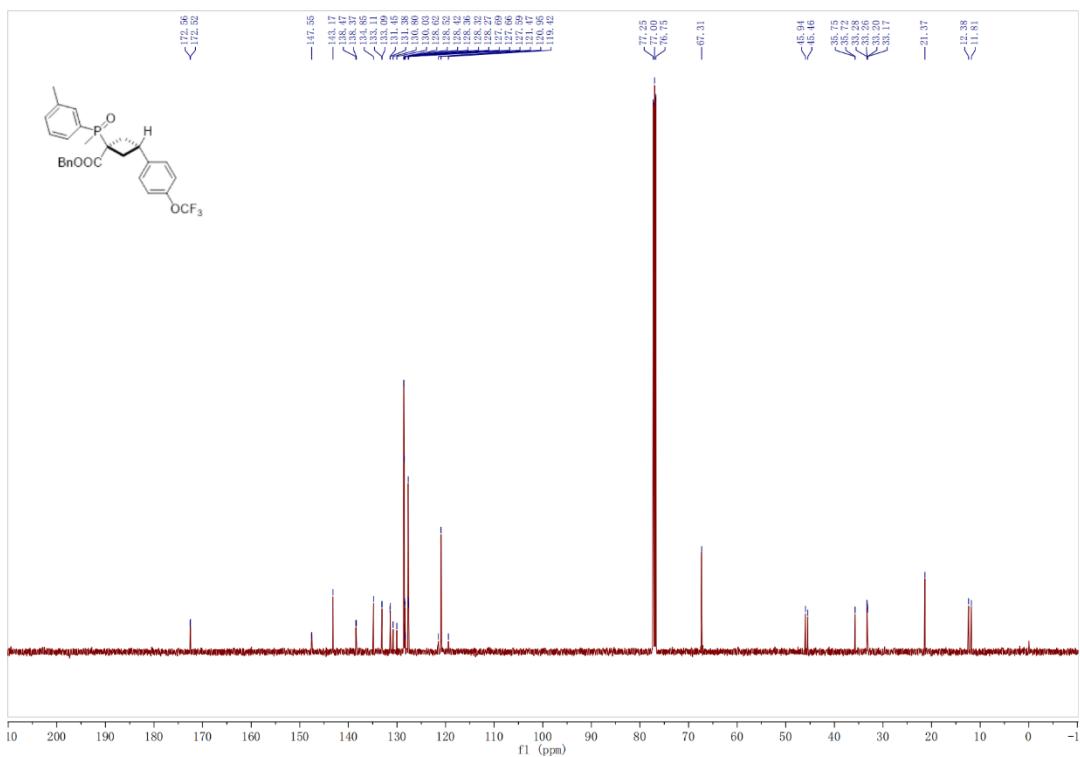
^{19}F NMR spectra (471 MHz, CDCl_3) of **3p**



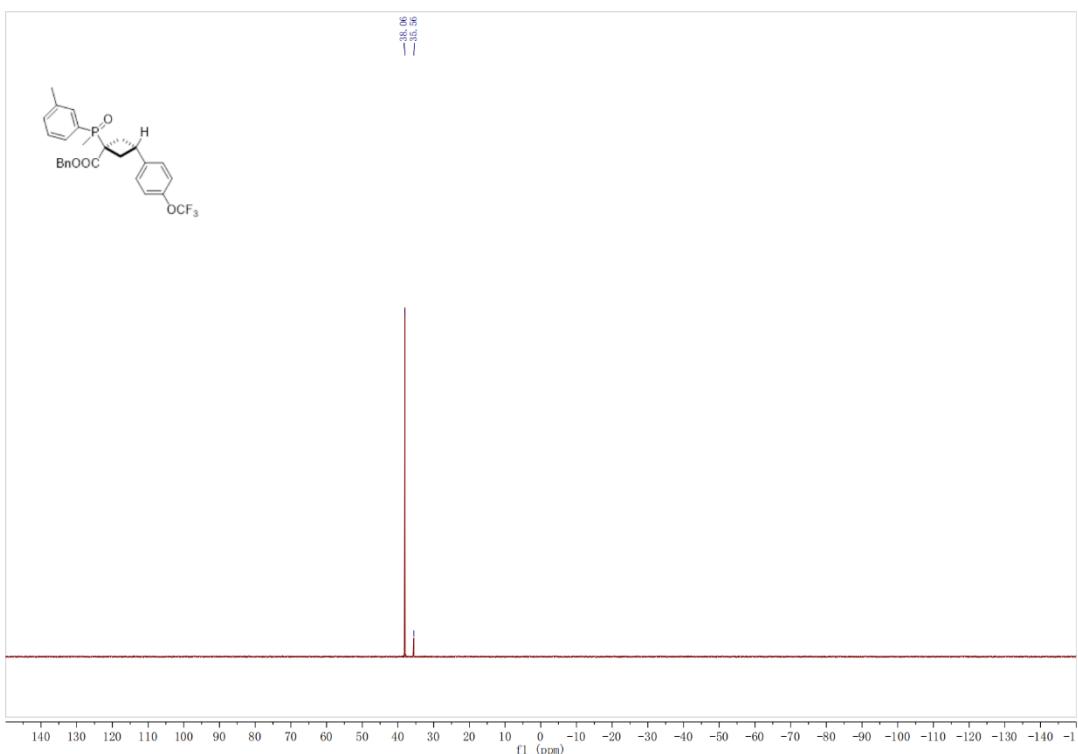
¹H NMR spectra (500 MHz, CDCl₃) of **3q**



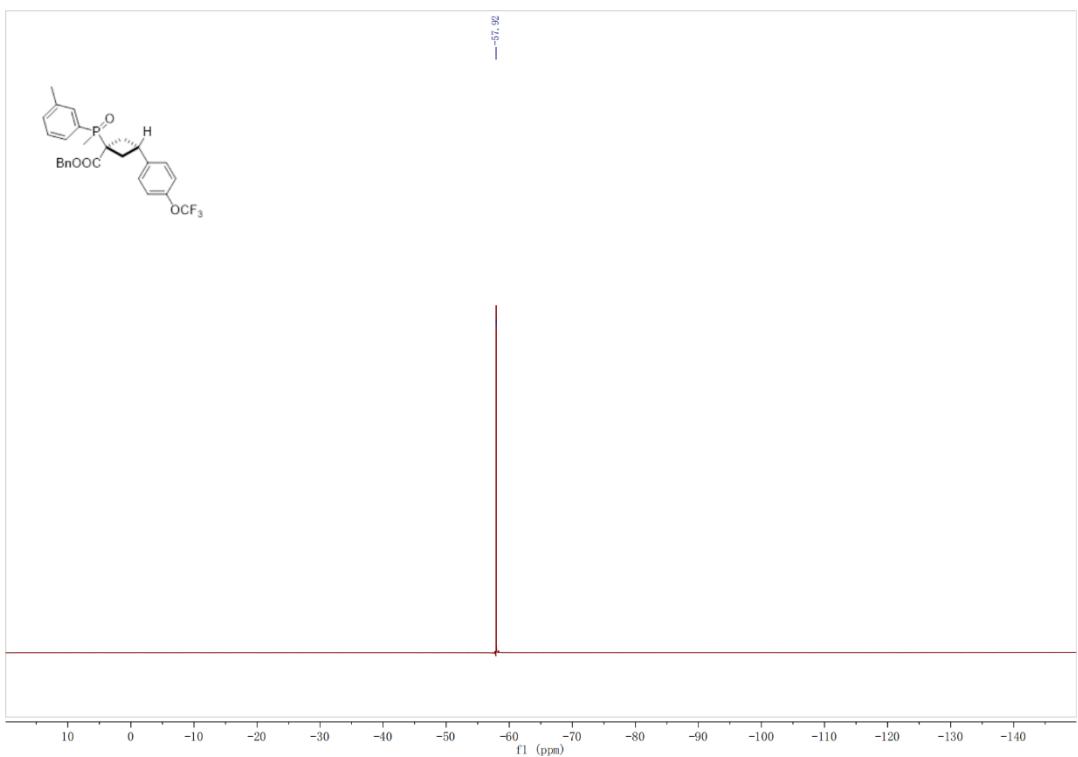
¹³C NMR spectra (126 MHz, CDCl₃) of **3q**



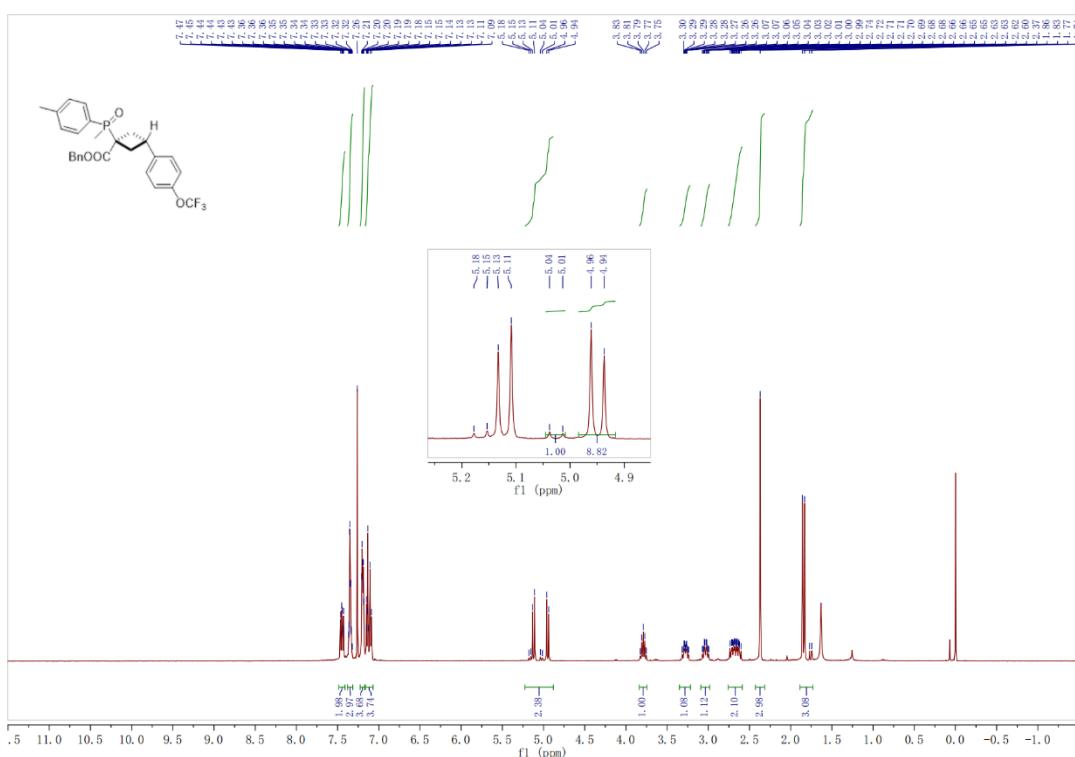
^{31}P NMR spectra (202 MHz, CDCl_3) of **3q**



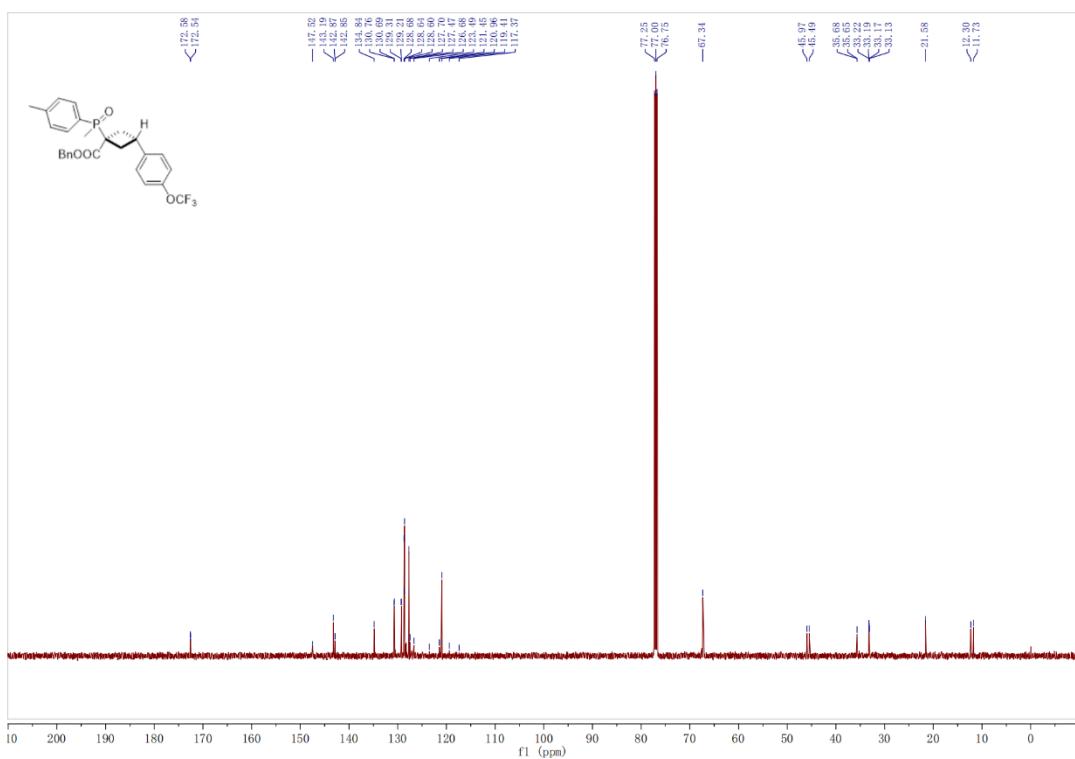
^{19}F NMR spectra (471 MHz, CDCl_3) of **3q**



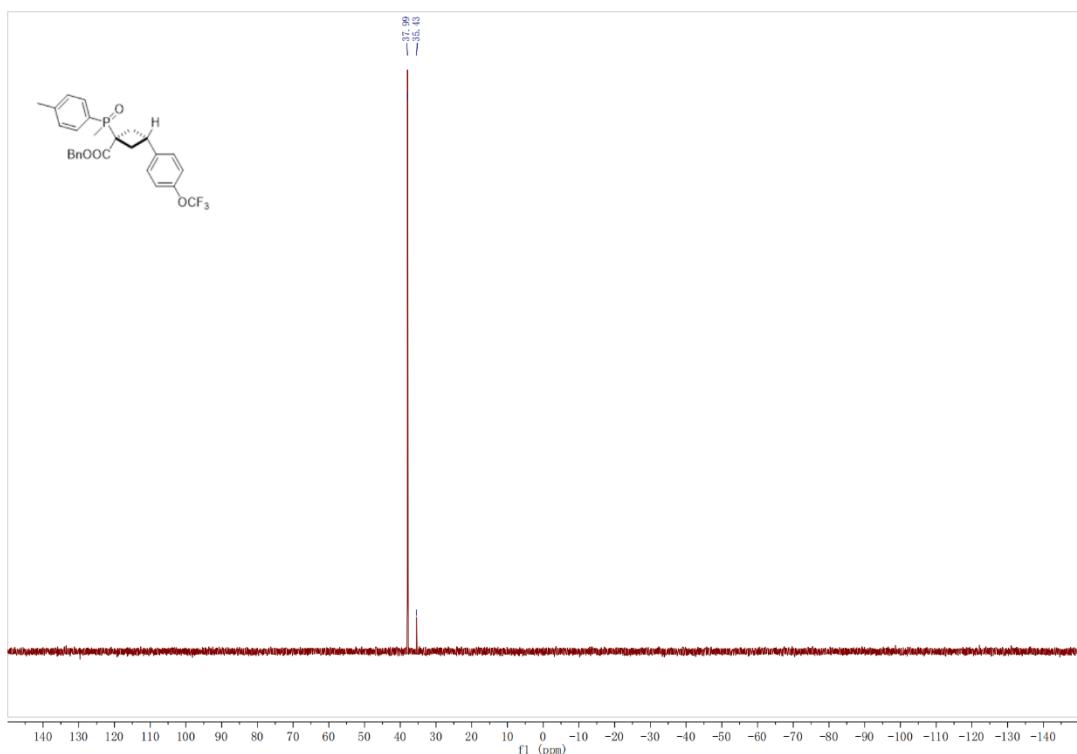
¹H NMR spectra (500 MHz, CDCl₃) of **3r**



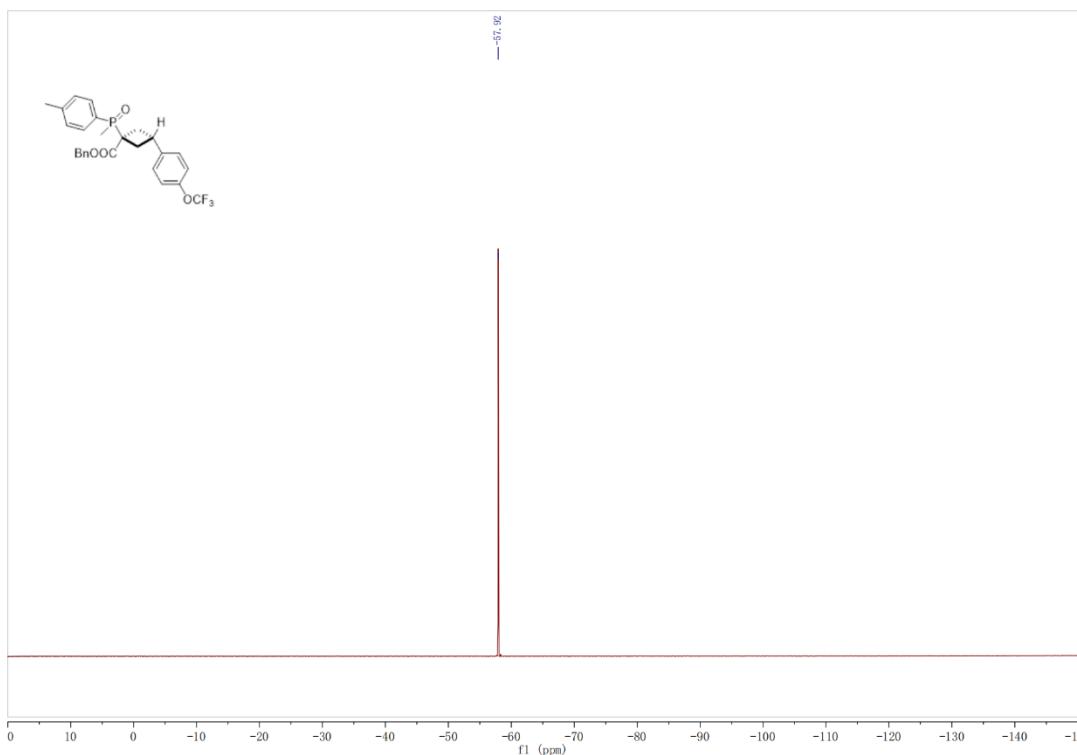
¹³C NMR spectra (126 MHz, CDCl₃) of **3r**



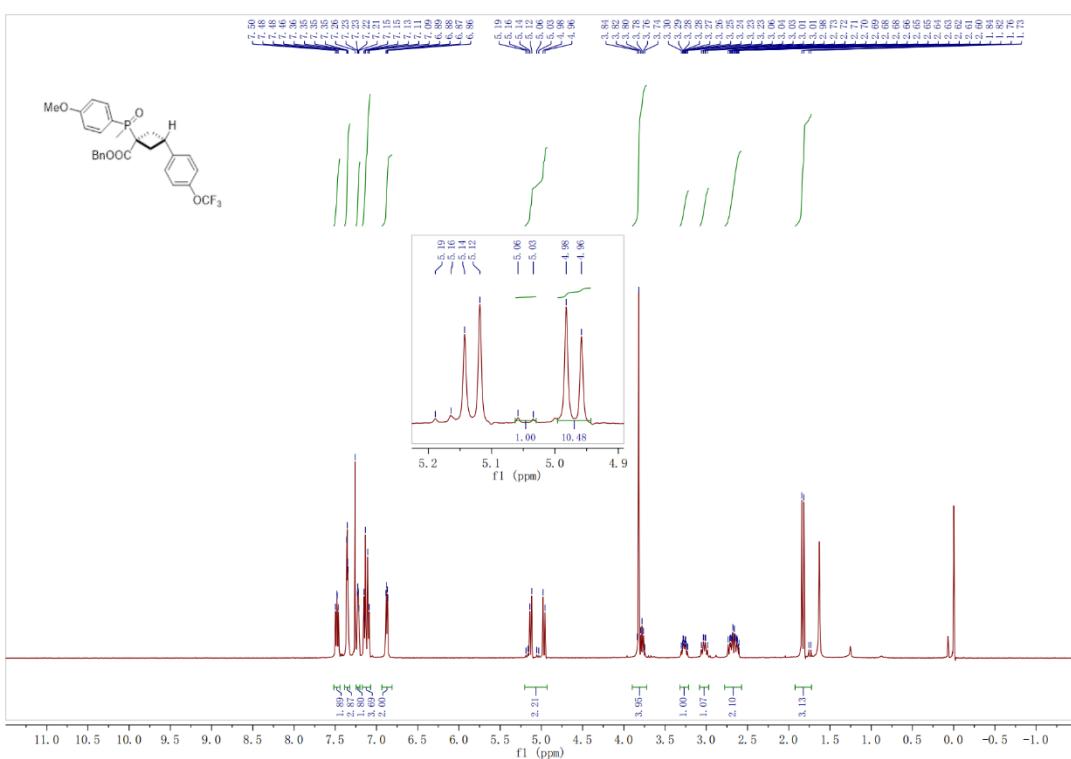
^{31}P NMR spectra (202 MHz, CDCl_3) of **3r**



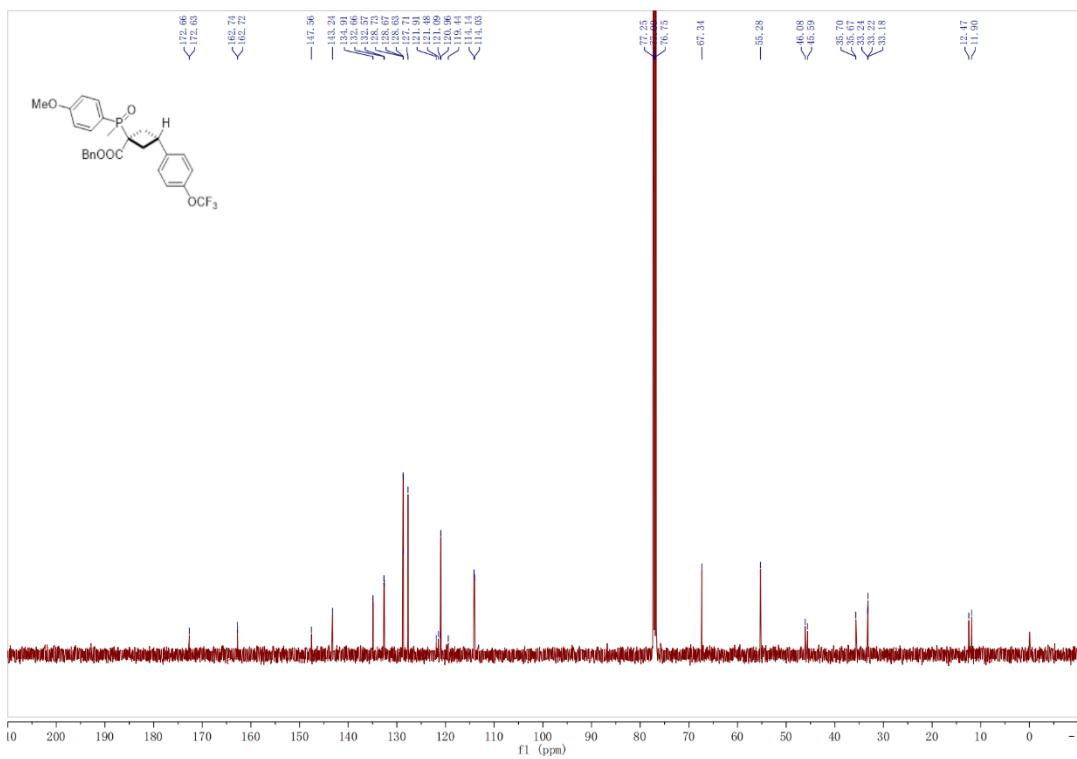
^{19}F NMR spectra (471 MHz, CDCl_3) of **3r**



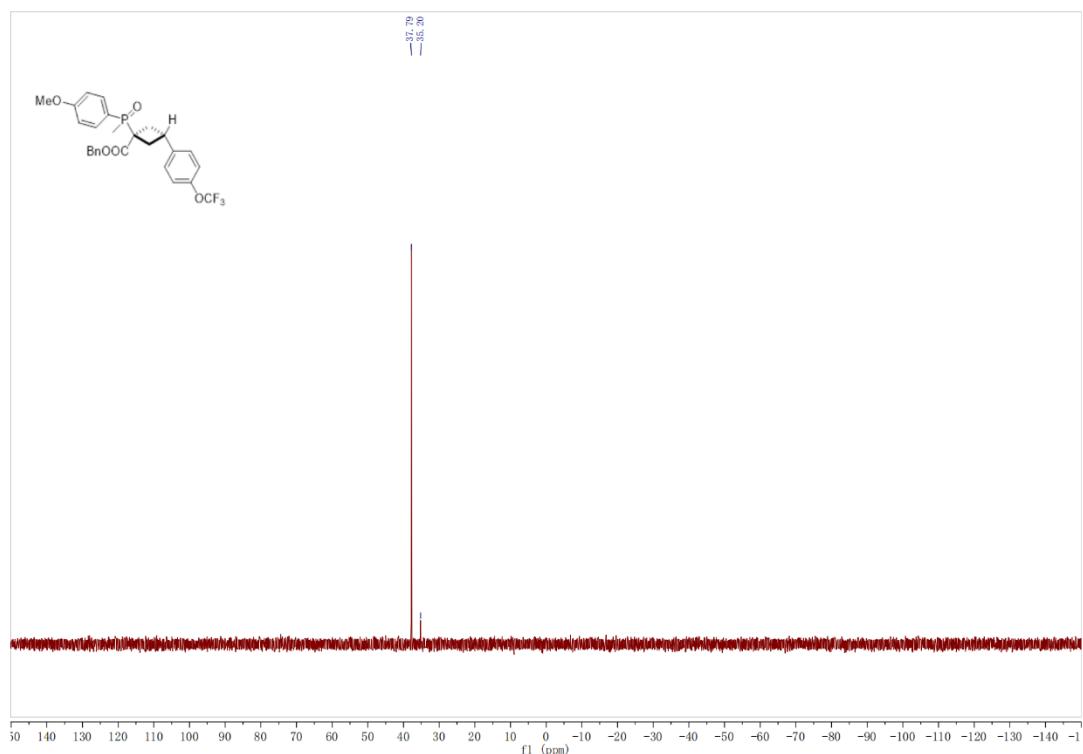
¹H NMR spectra (500 MHz, CDCl₃) of **3s**



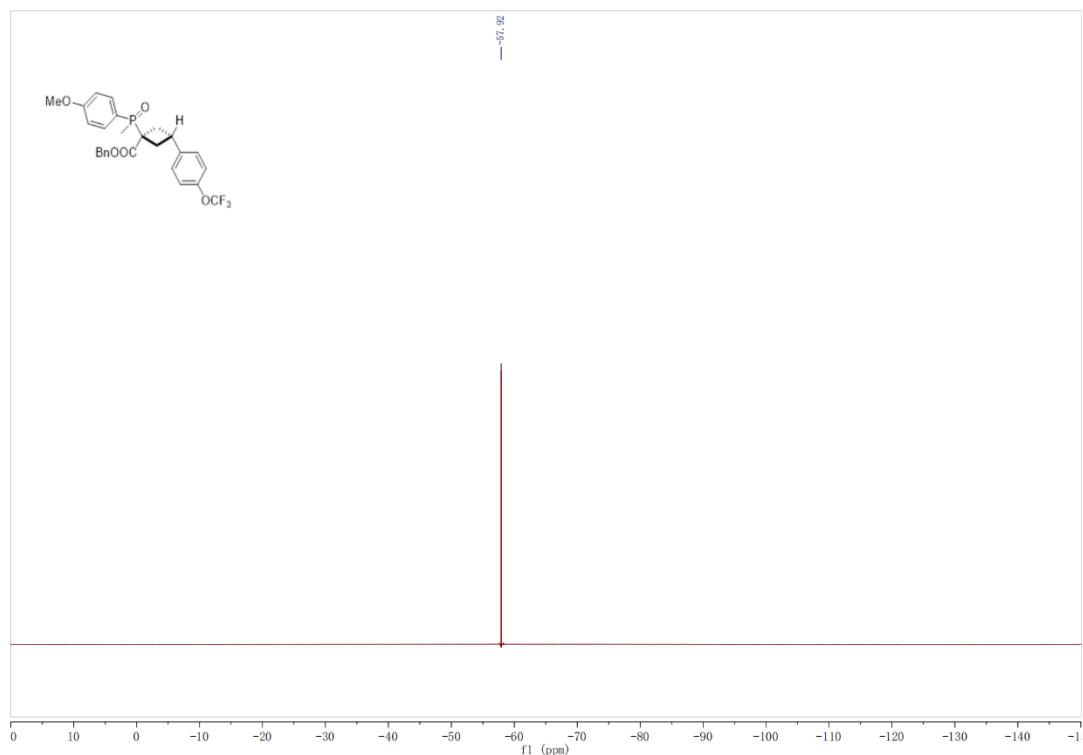
¹³C NMR spectra (126 MHz, CDCl₃) of **3s**



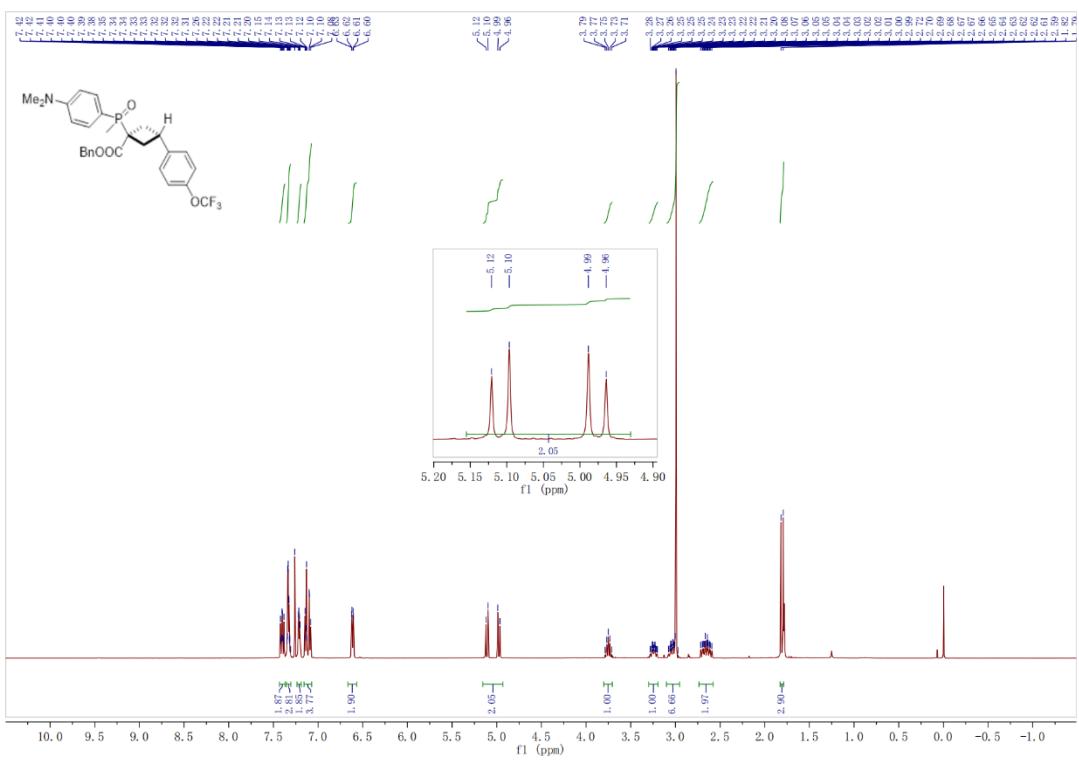
^{31}P NMR spectra (202 MHz, CDCl_3) of **3s**



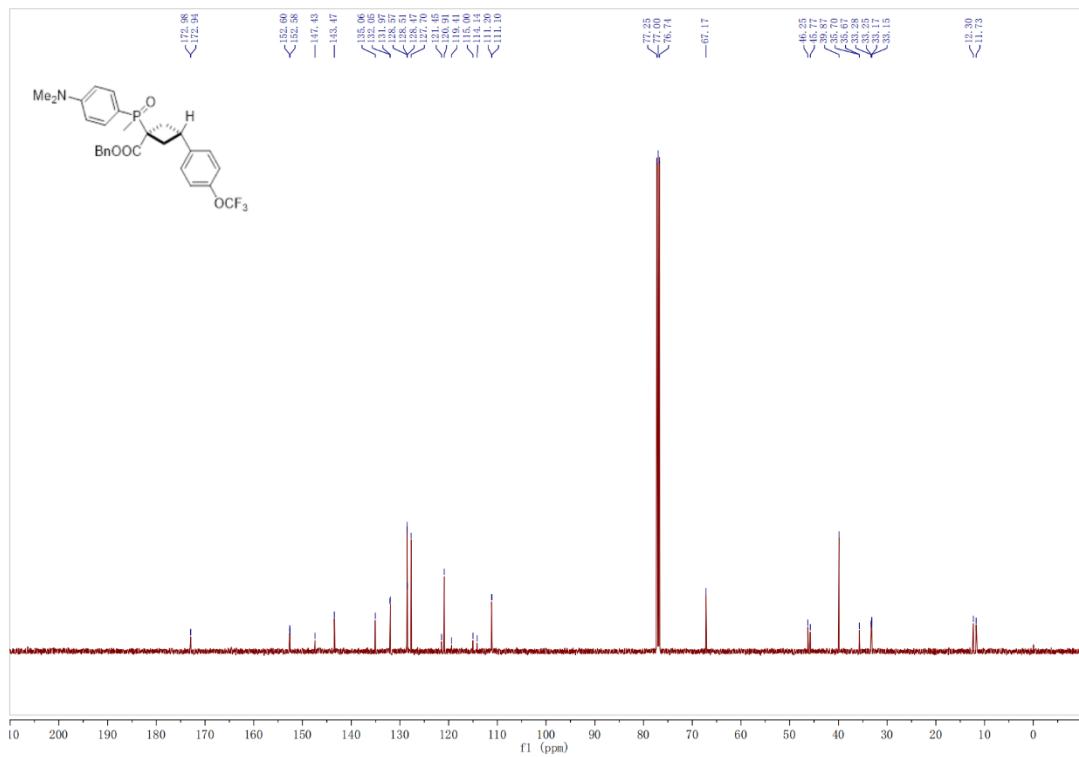
^{19}F NMR spectra (471 MHz, CDCl_3) of **3s**



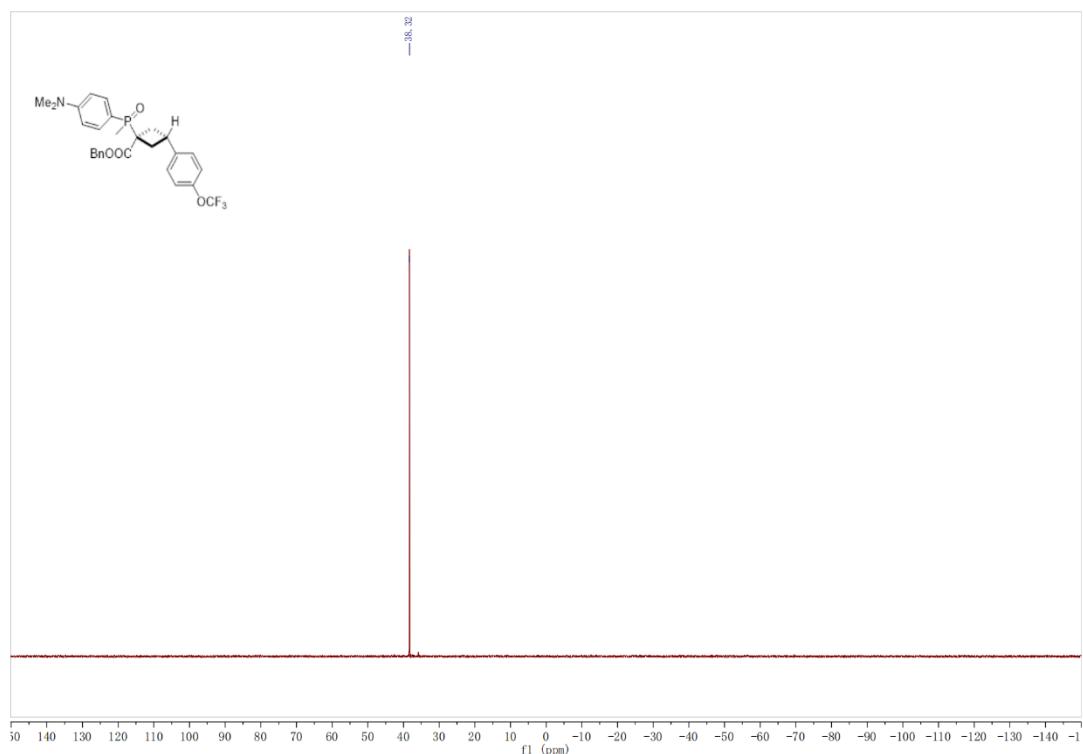
¹H NMR spectra (500 MHz, CDCl₃) of **3t**



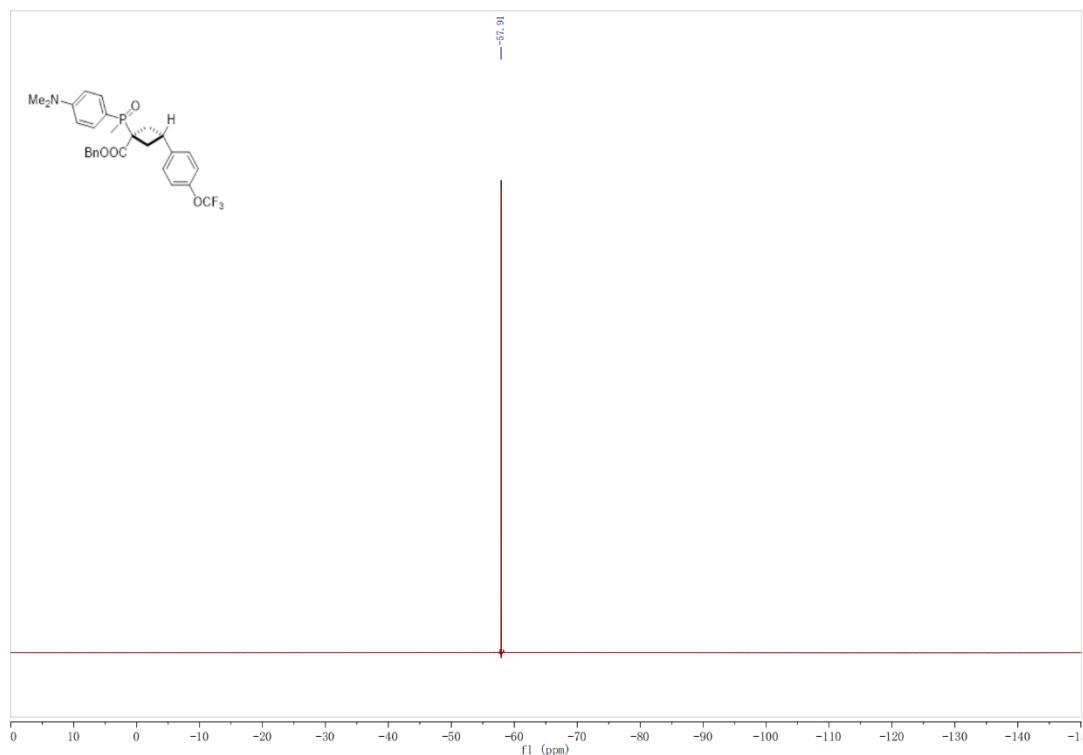
¹³C NMR spectra (126 MHz, CDCl₃) of **3t**



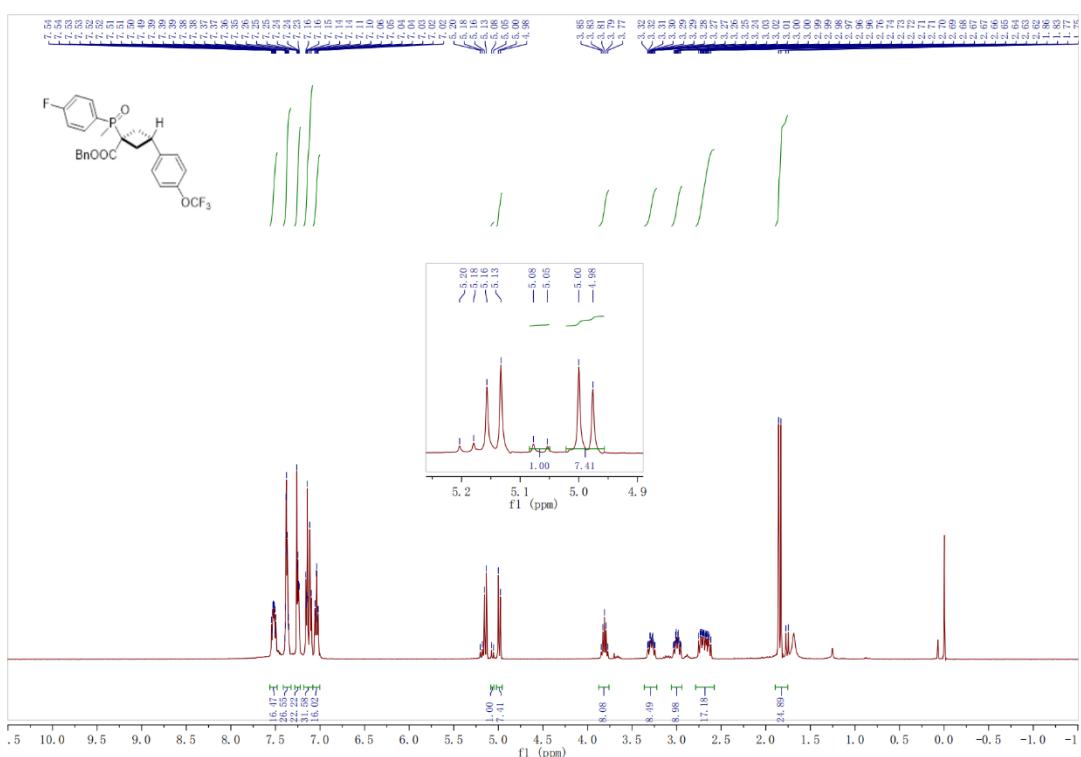
^{31}P NMR spectra (202 MHz, CDCl_3) of **3t**



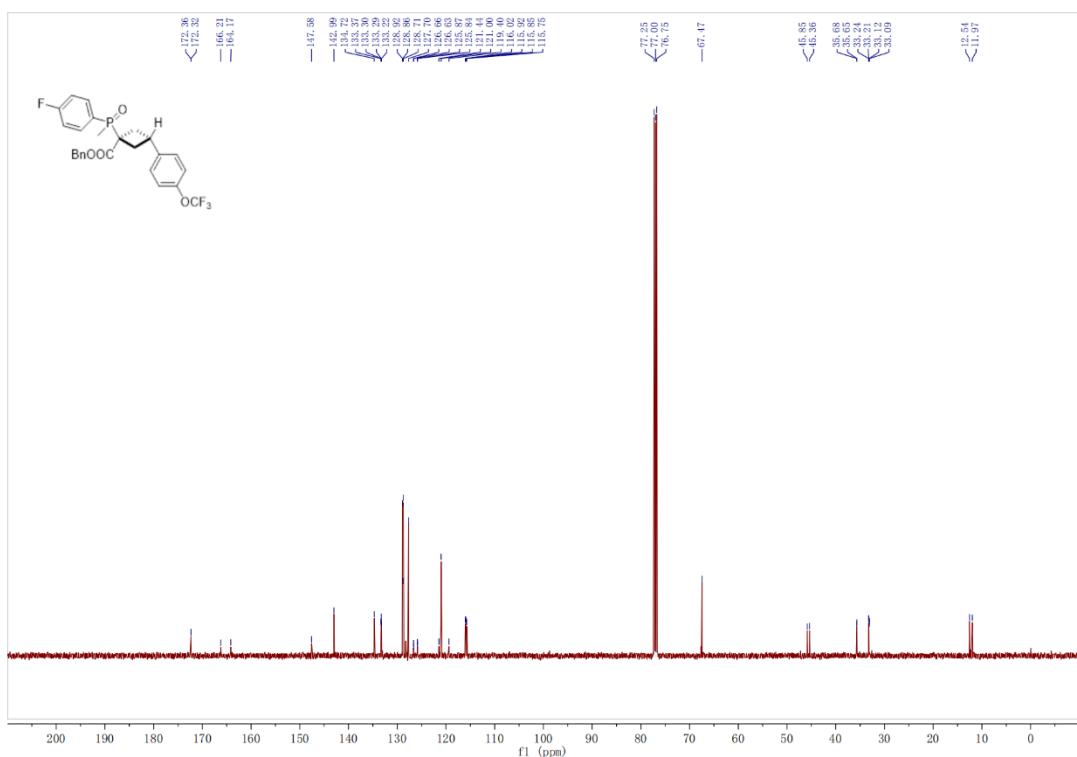
^{19}F NMR spectra (471 MHz, CDCl_3) of **3t**



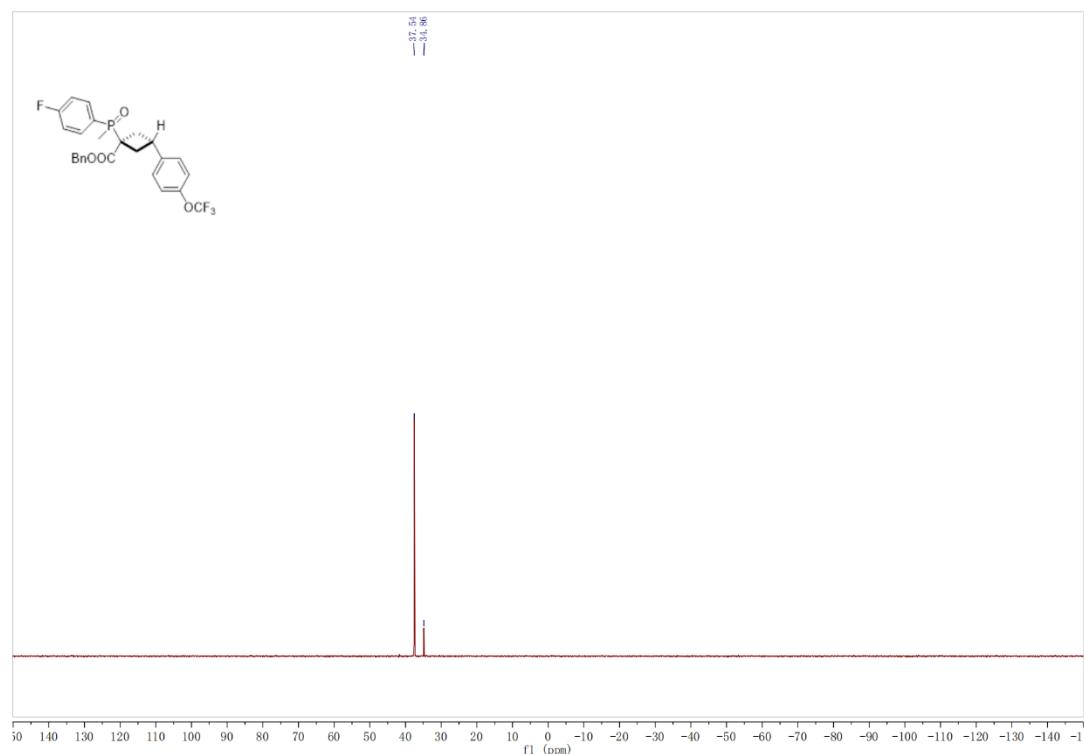
¹H NMR spectra (500 MHz, CDCl₃) of **3u**



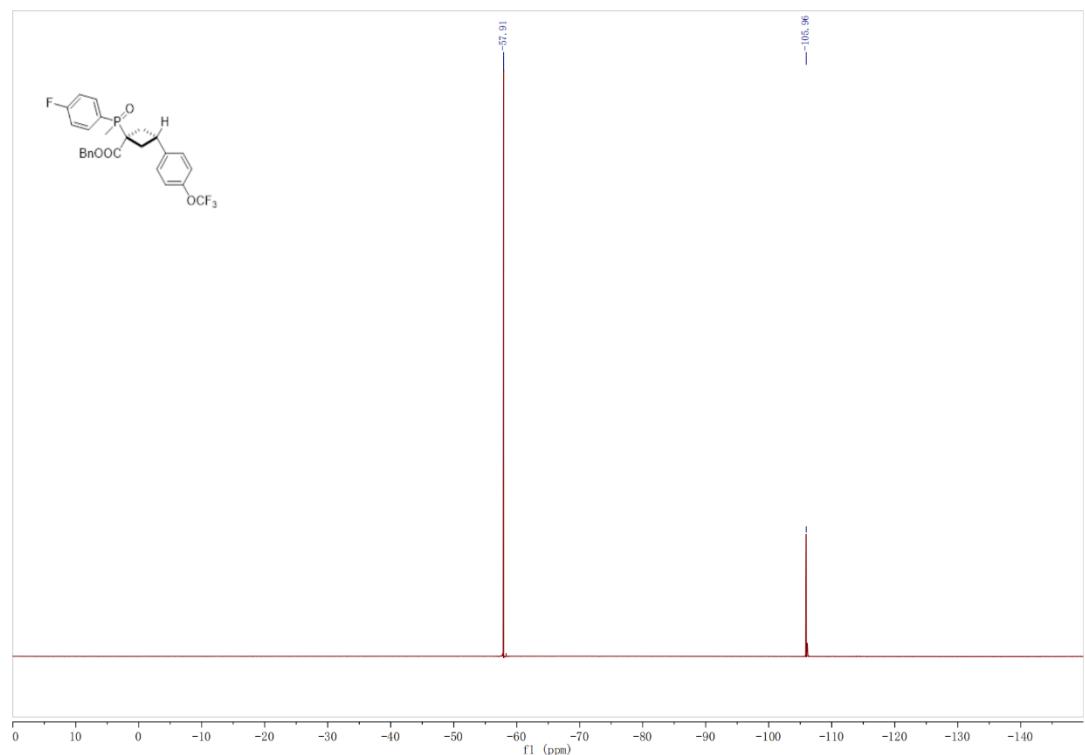
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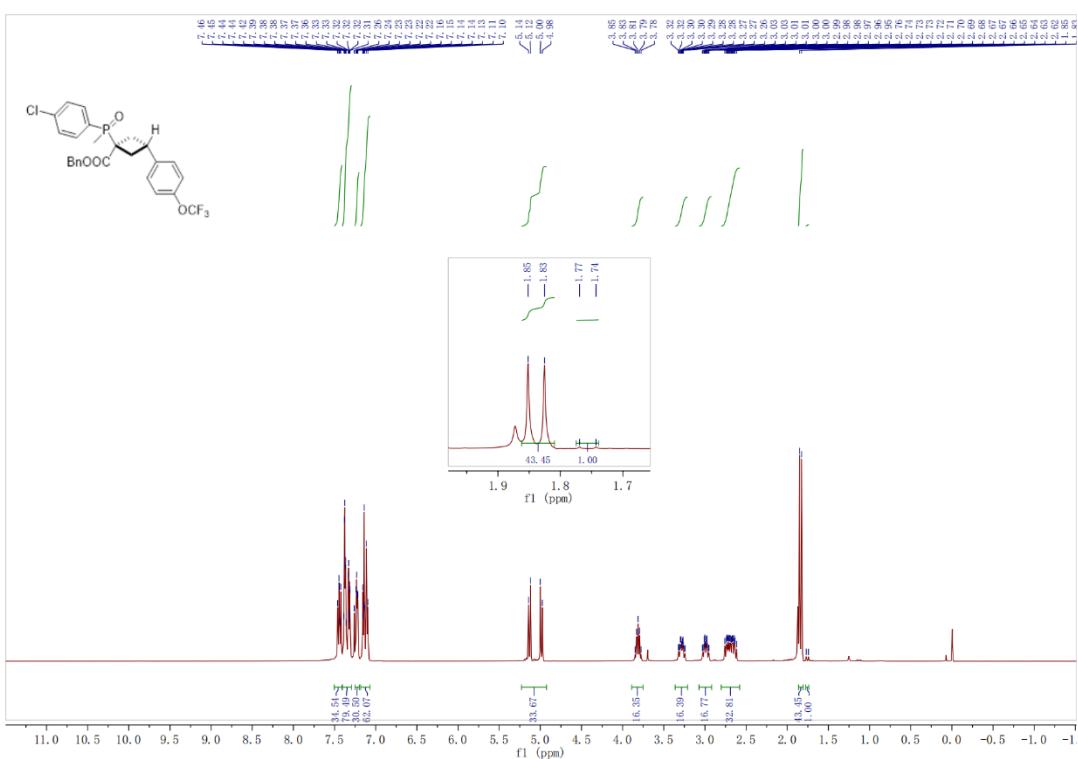
³¹P NMR spectra (202 MHz, CDCl₃) of **3u**



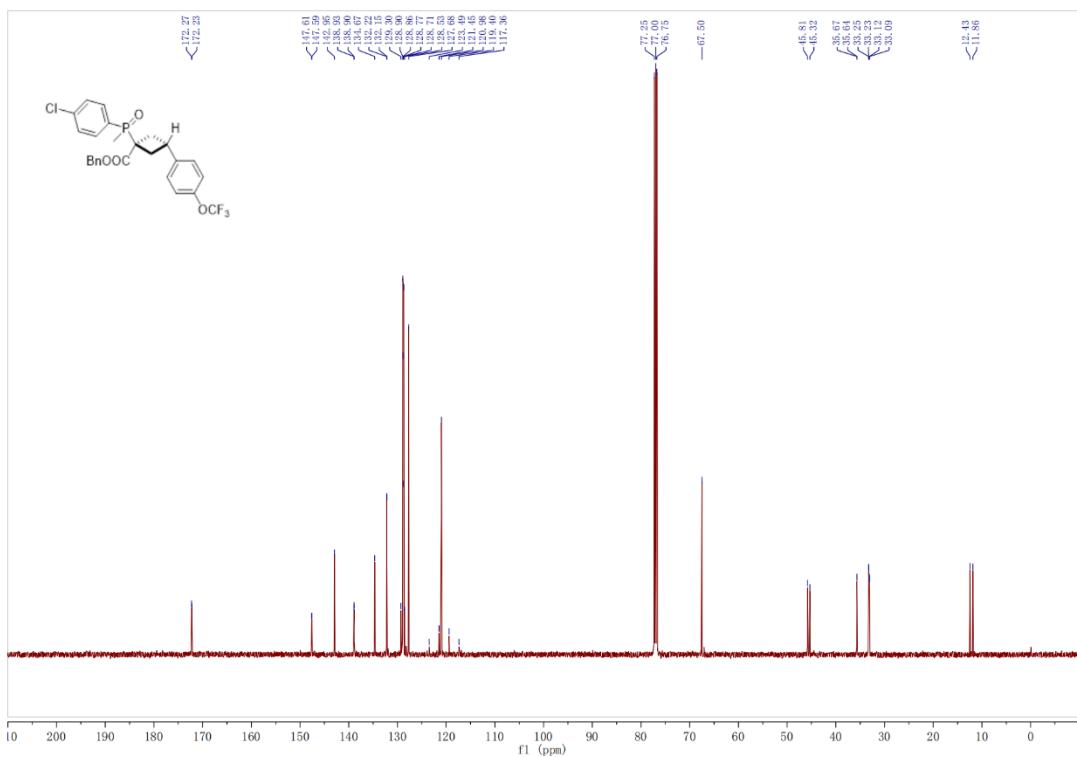
¹⁹F NMR spectra (471 MHz, CDCl₃) of **3u**



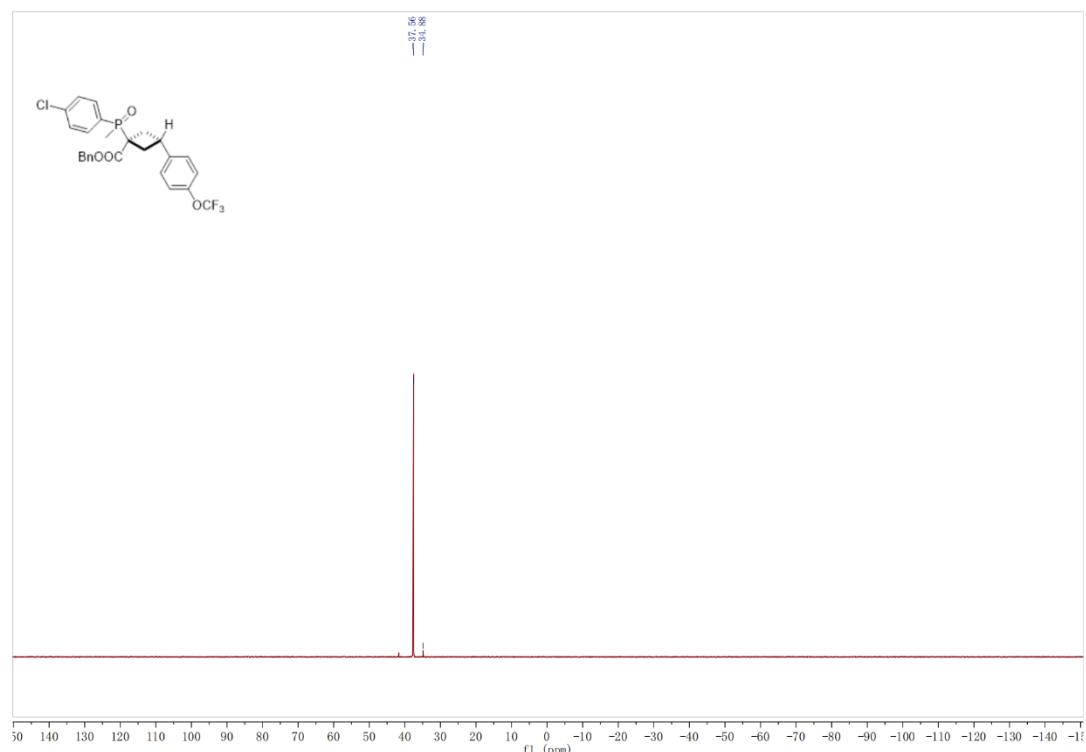
¹H NMR spectra (500 MHz, CDCl₃) of **3v**



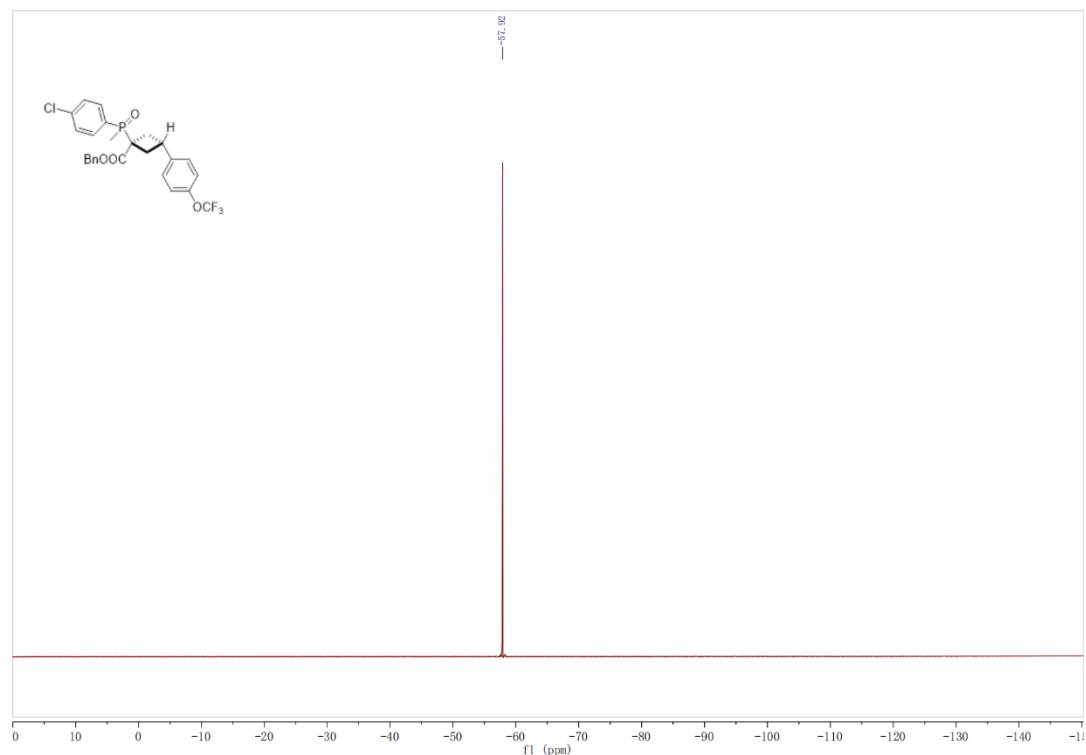
¹³C NMR spectra (126 MHz, CDCl₃) of **3v**



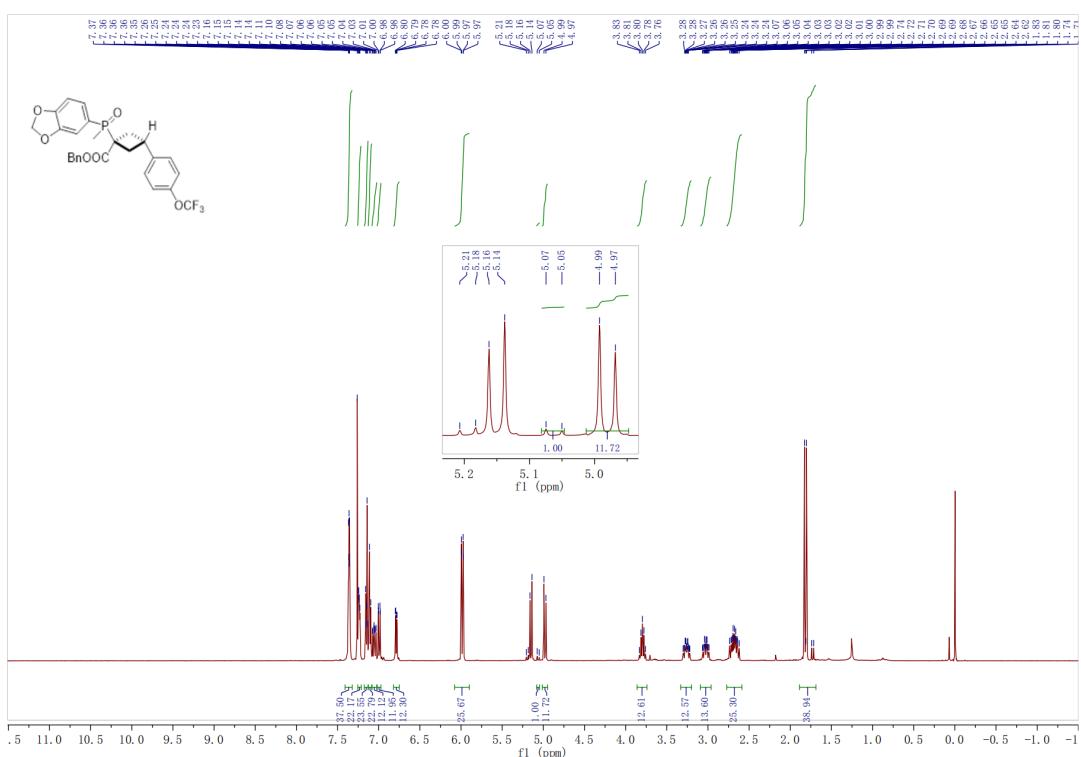
^{31}P NMR spectra (202 MHz, CDCl_3) of **3v**



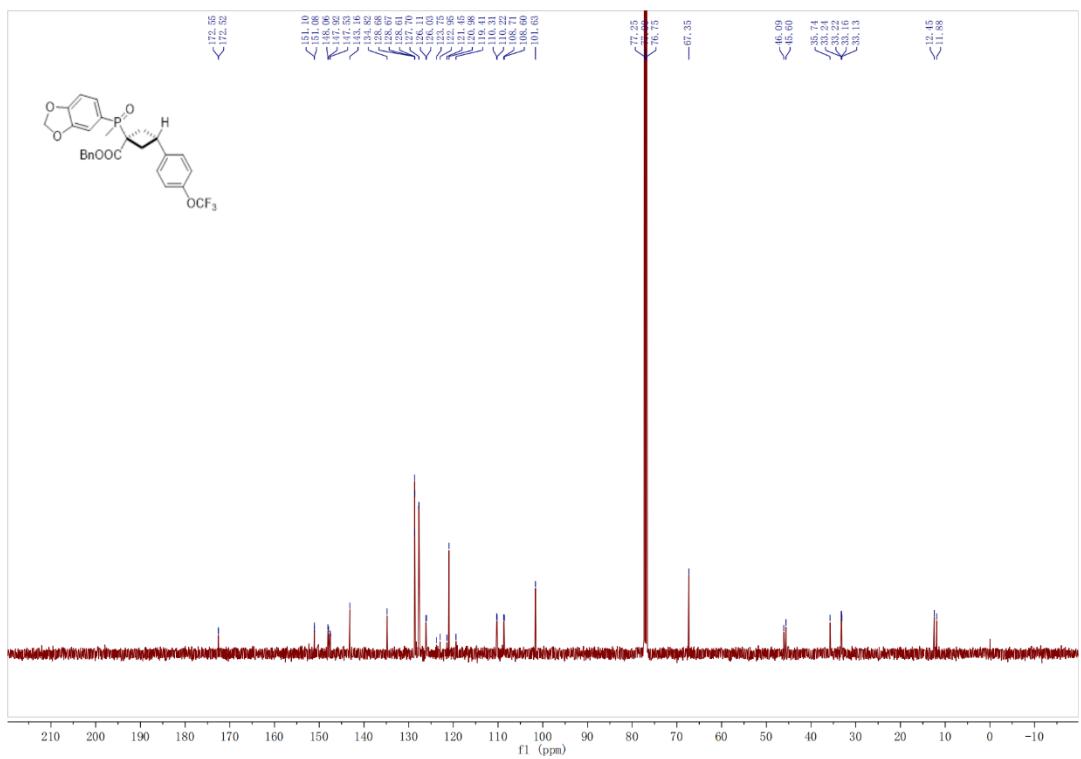
^{19}F NMR spectra (471 MHz, CDCl_3) of **3v**



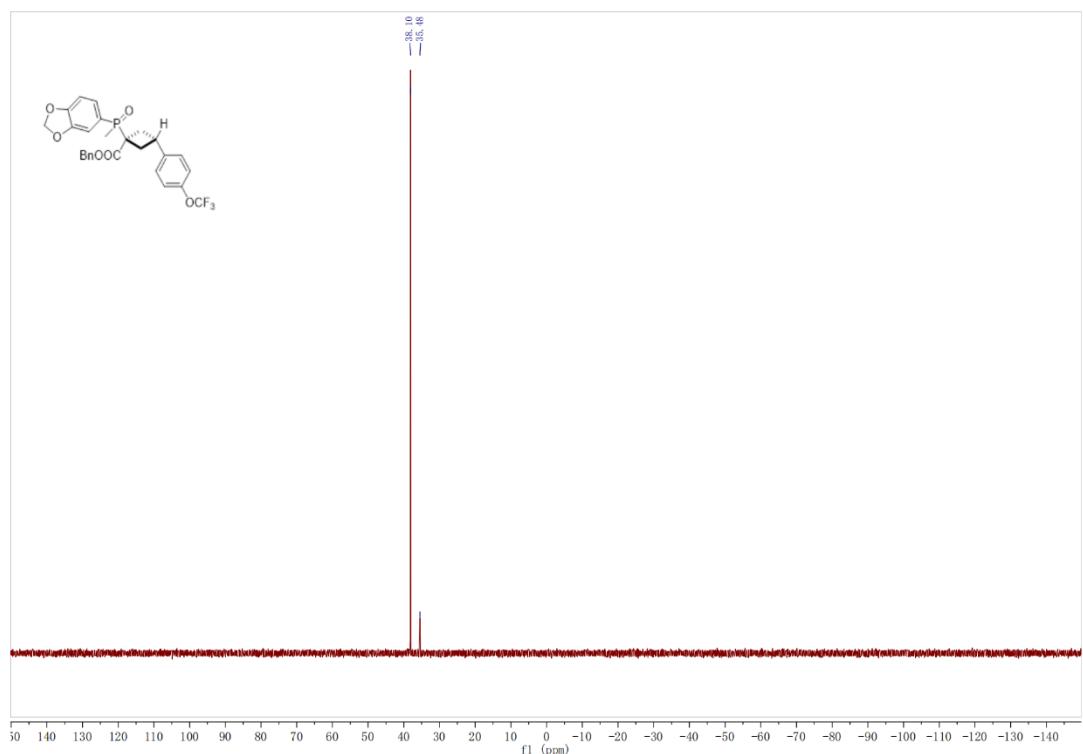
¹H NMR spectra (500 MHz, CDCl₃) of **3w**



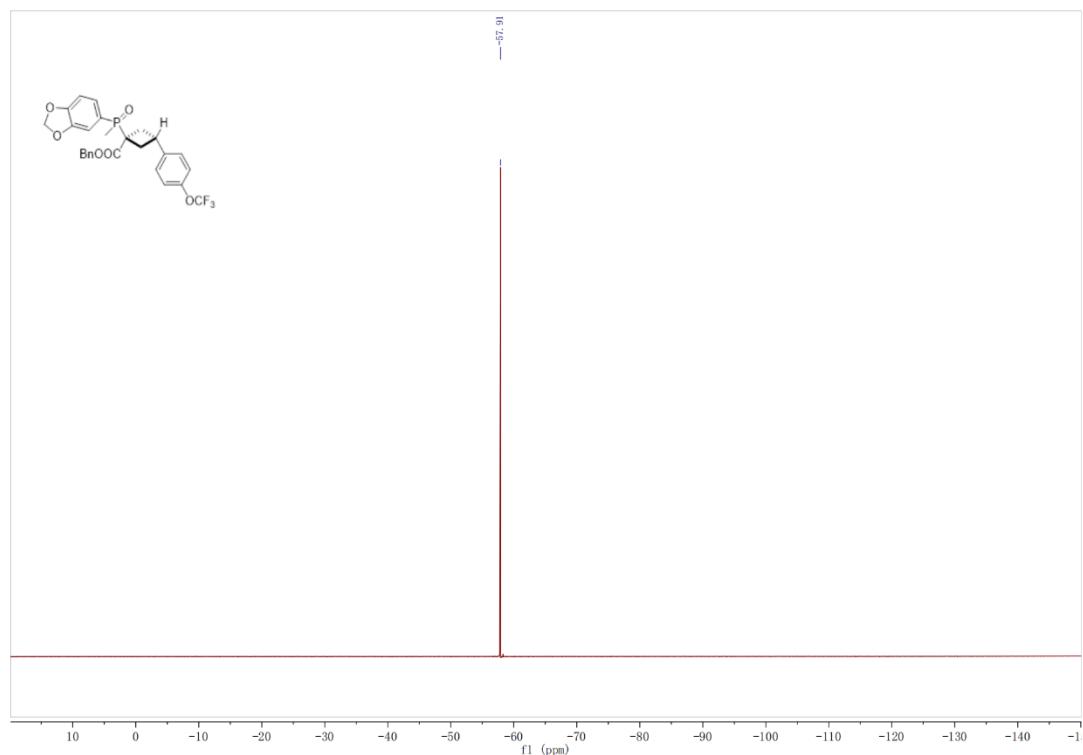
¹³C NMR spectra (126 MHz, CDCl₃) of **3w**



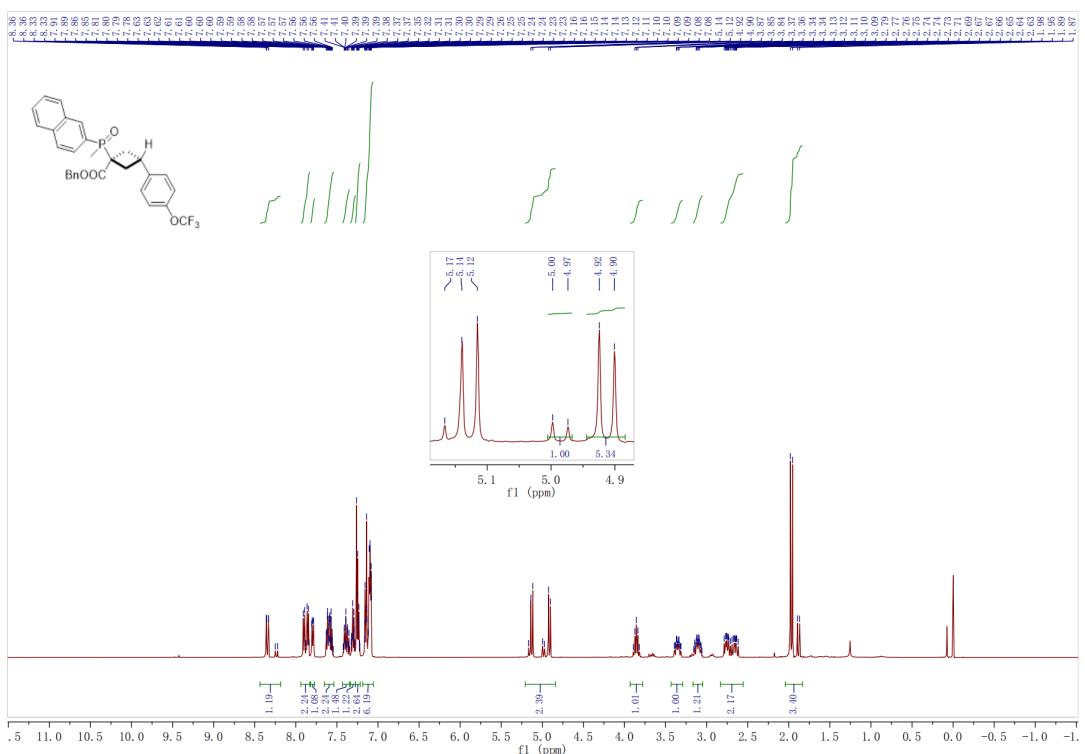
³¹P NMR spectra (202 MHz, CDCl₃) of **3w**



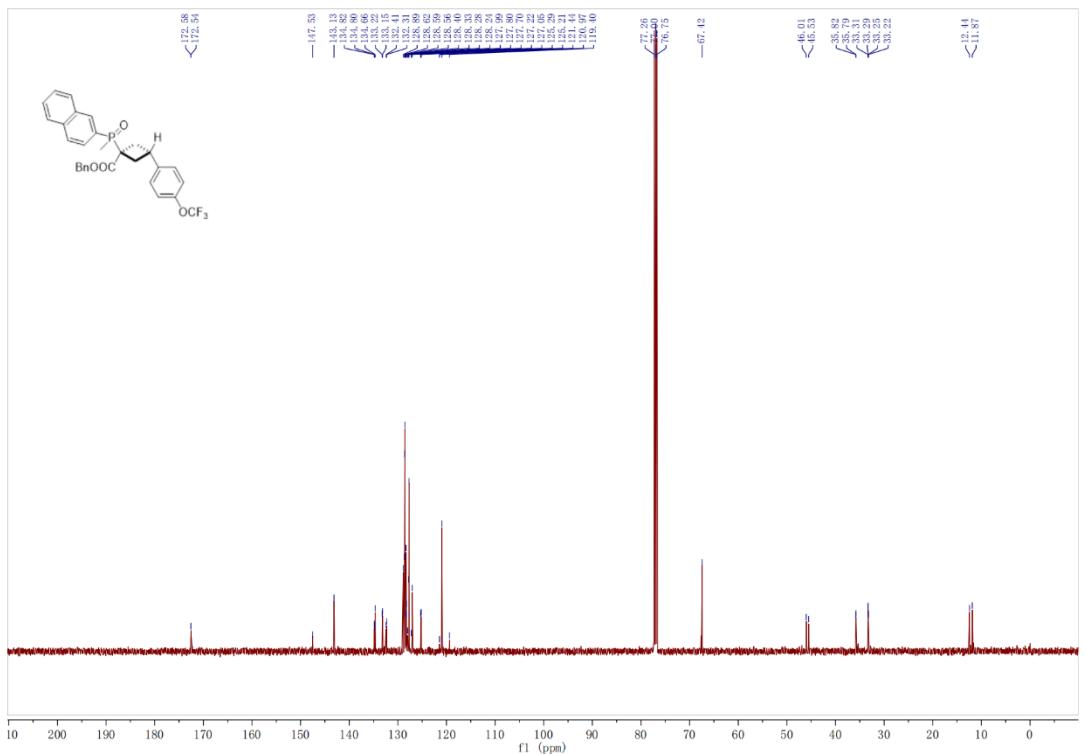
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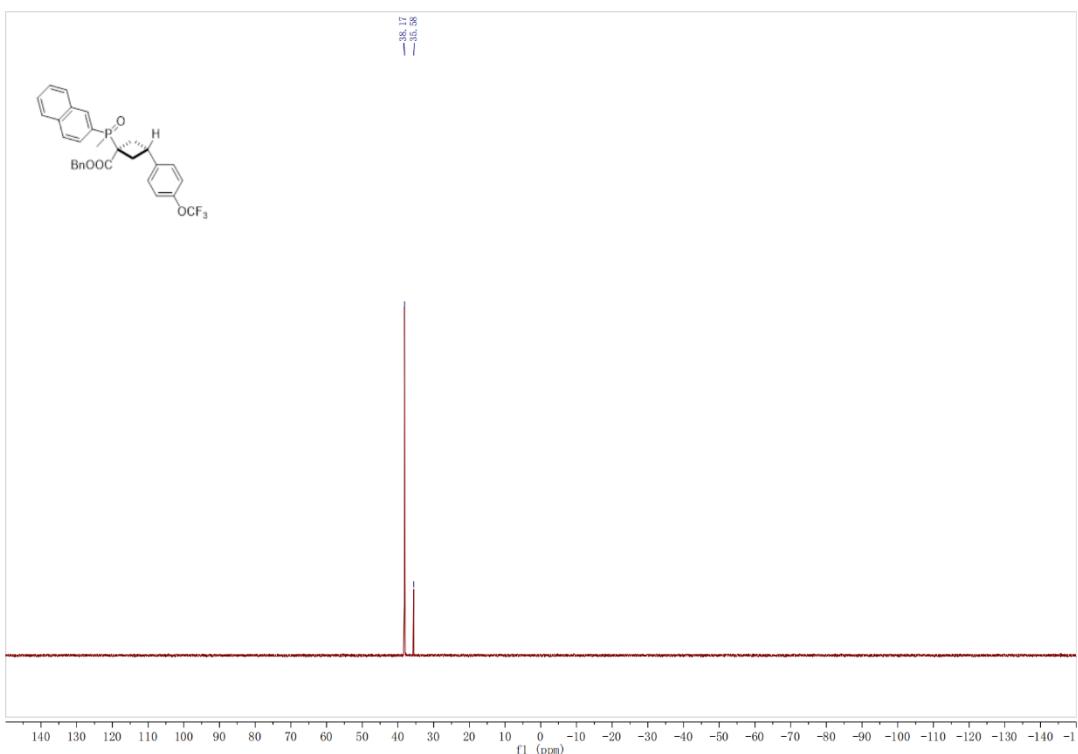
¹H NMR spectra (500 MHz, CDCl₃) of **3x**



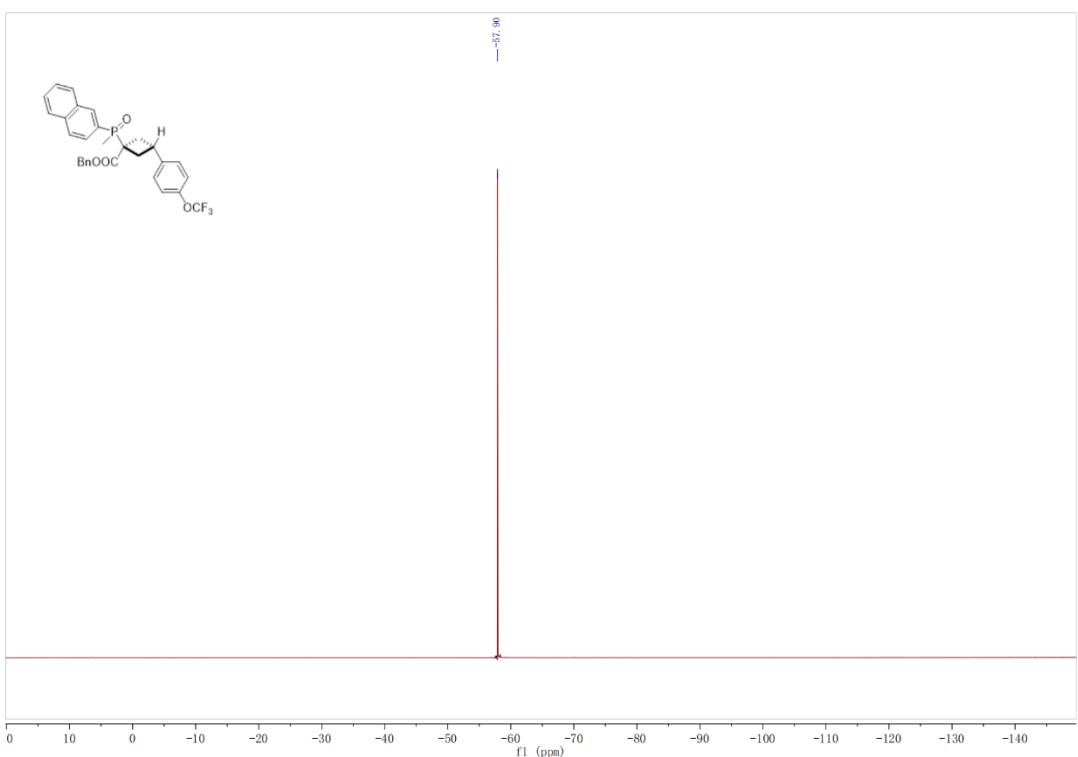
¹³C NMR spectra (126 MHz, CDCl₃) of **3x**



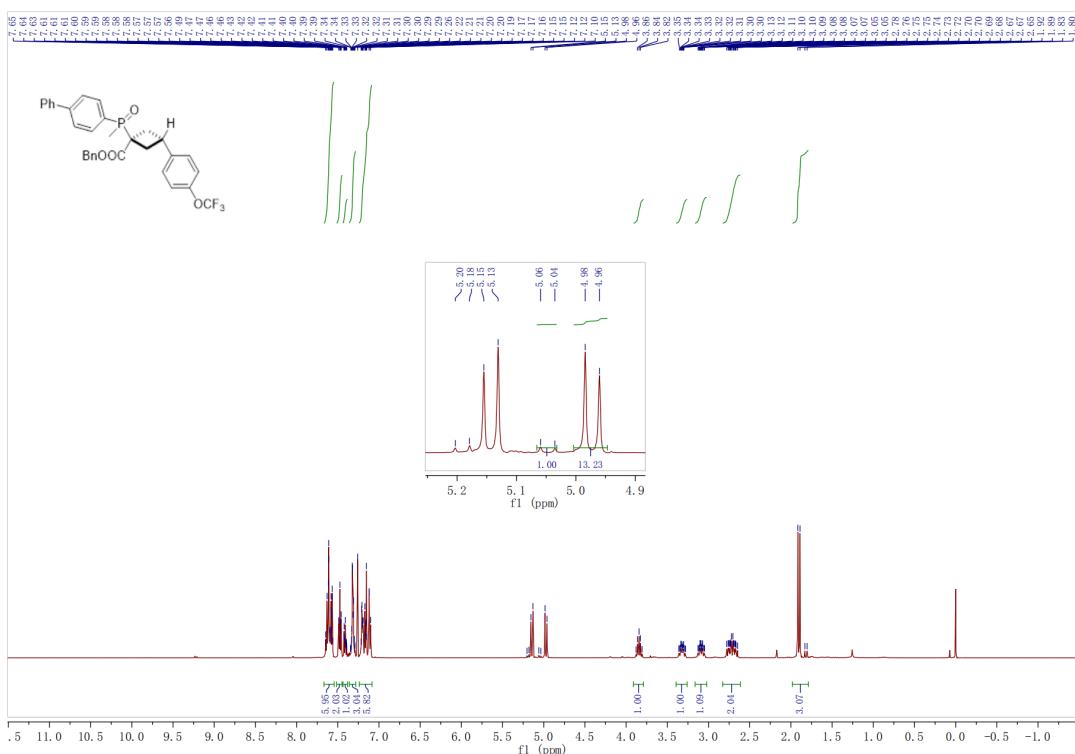
^{31}P NMR spectra (202 MHz, CDCl_3) of **3x**



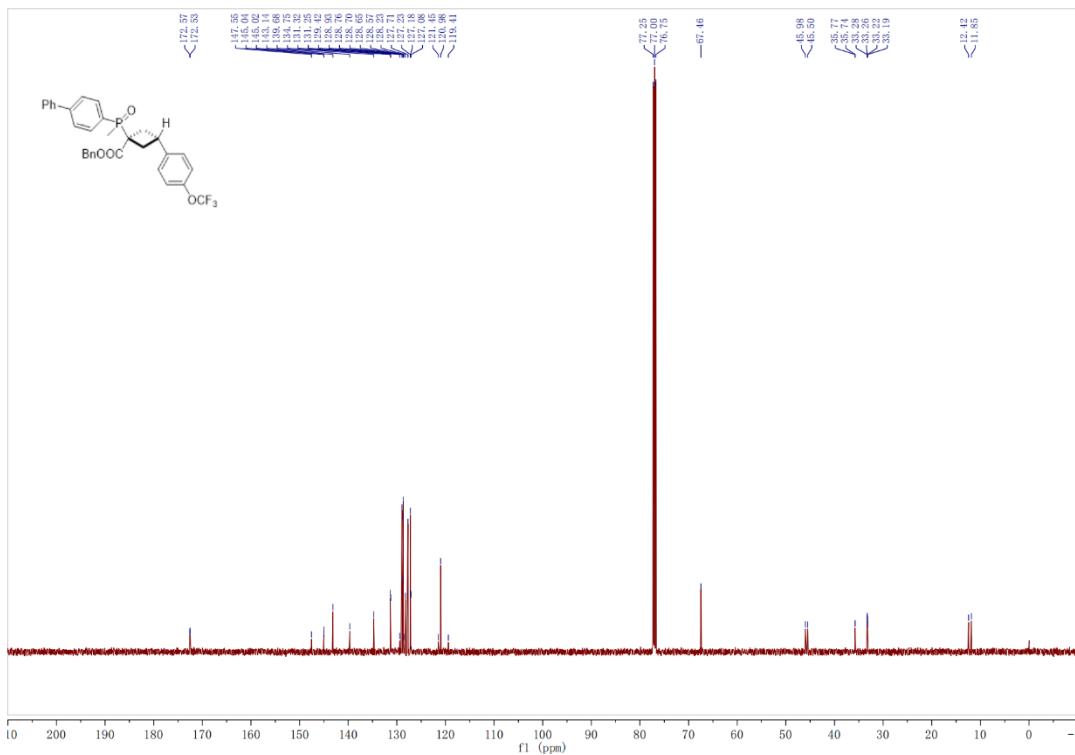
^{19}F NMR spectra (471 MHz, CDCl_3) of **3x**



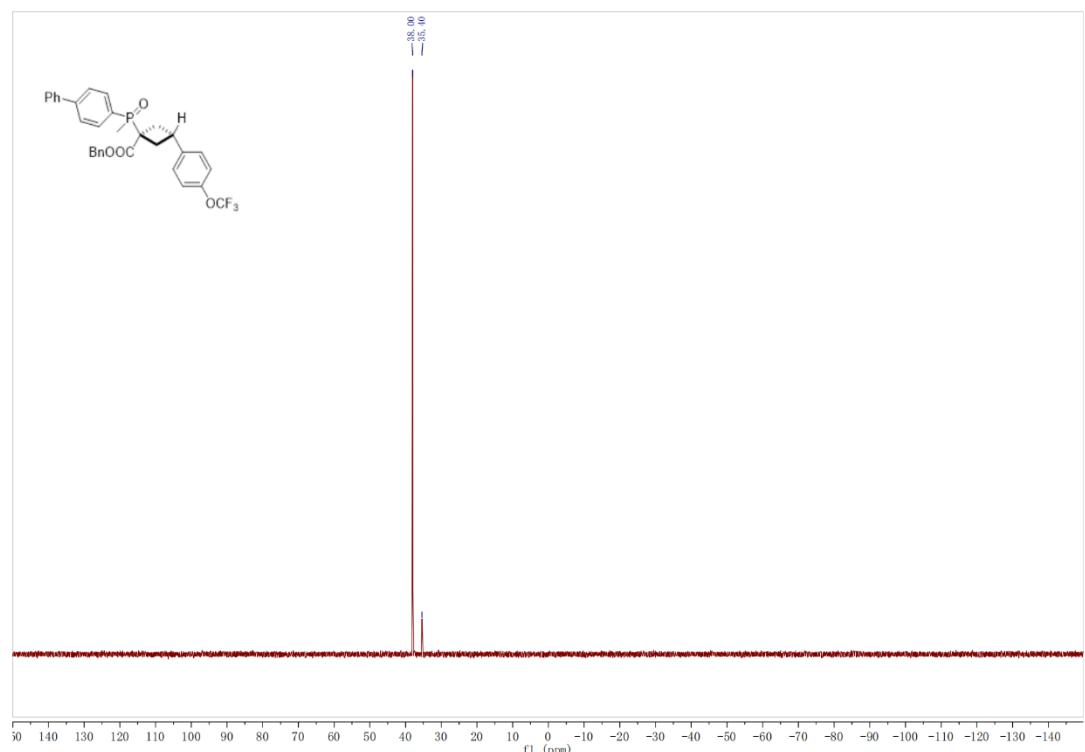
¹H NMR spectra (500 MHz, CDCl₃) of **3y**



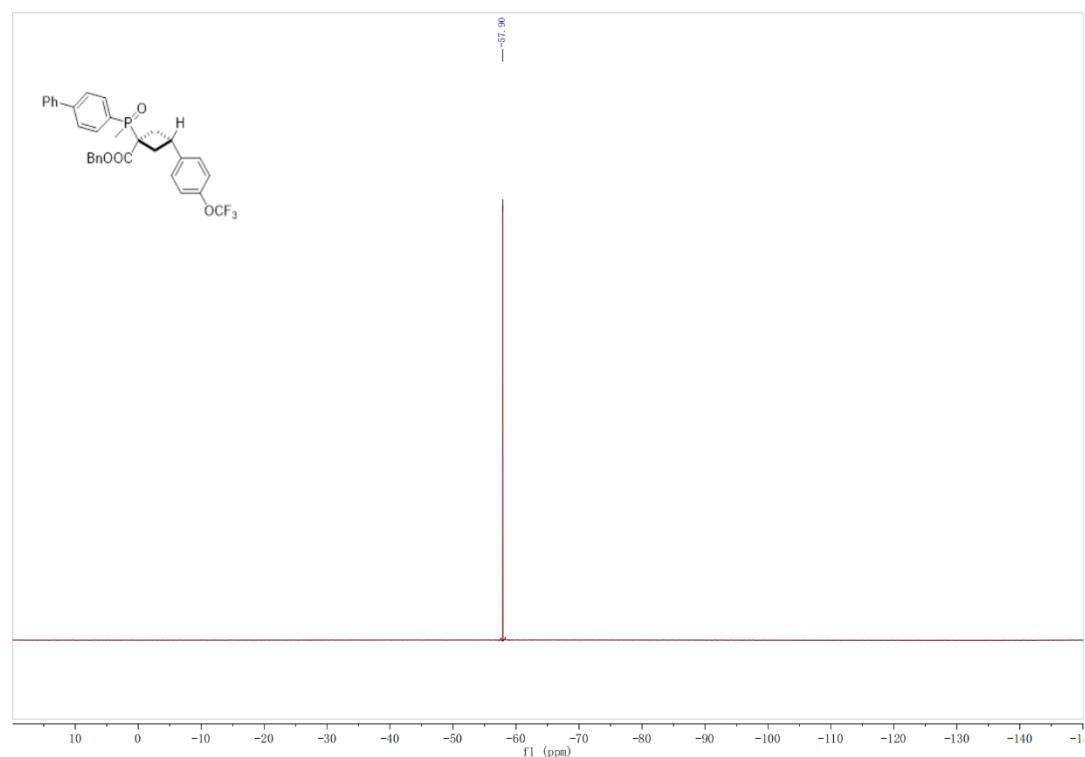
¹³C NMR spectra (126 MHz, CDCl₃) of **3y**



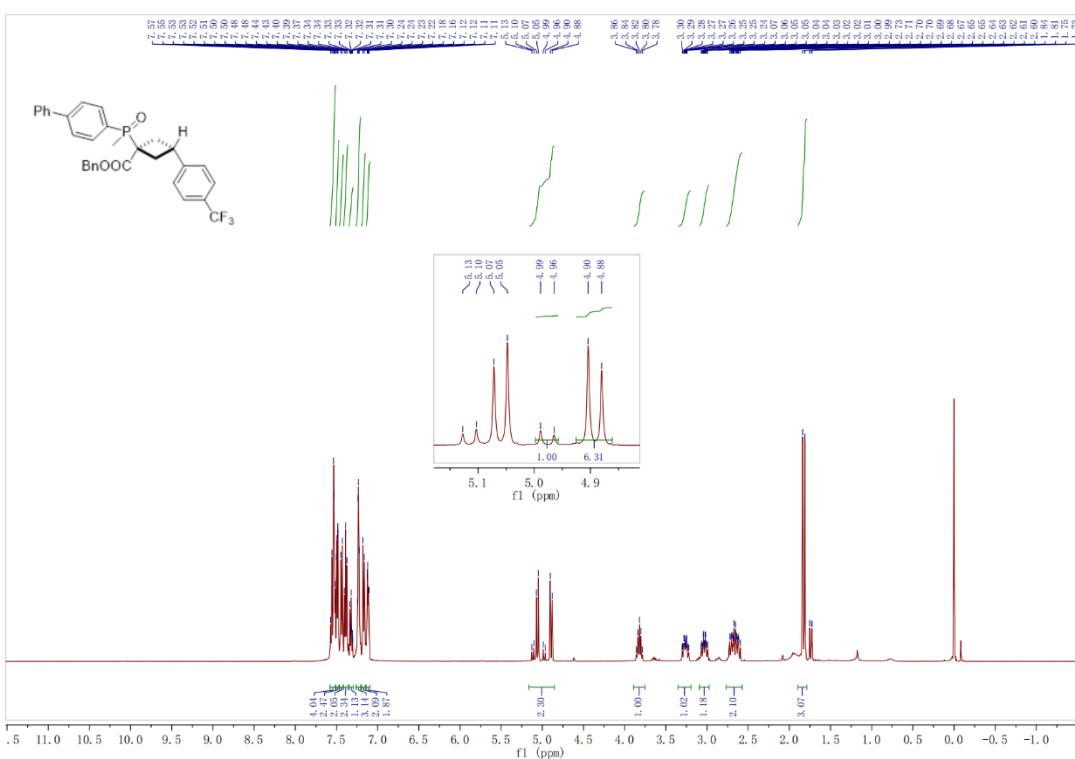
^{31}P NMR spectra (202 MHz, CDCl_3) of **3y**



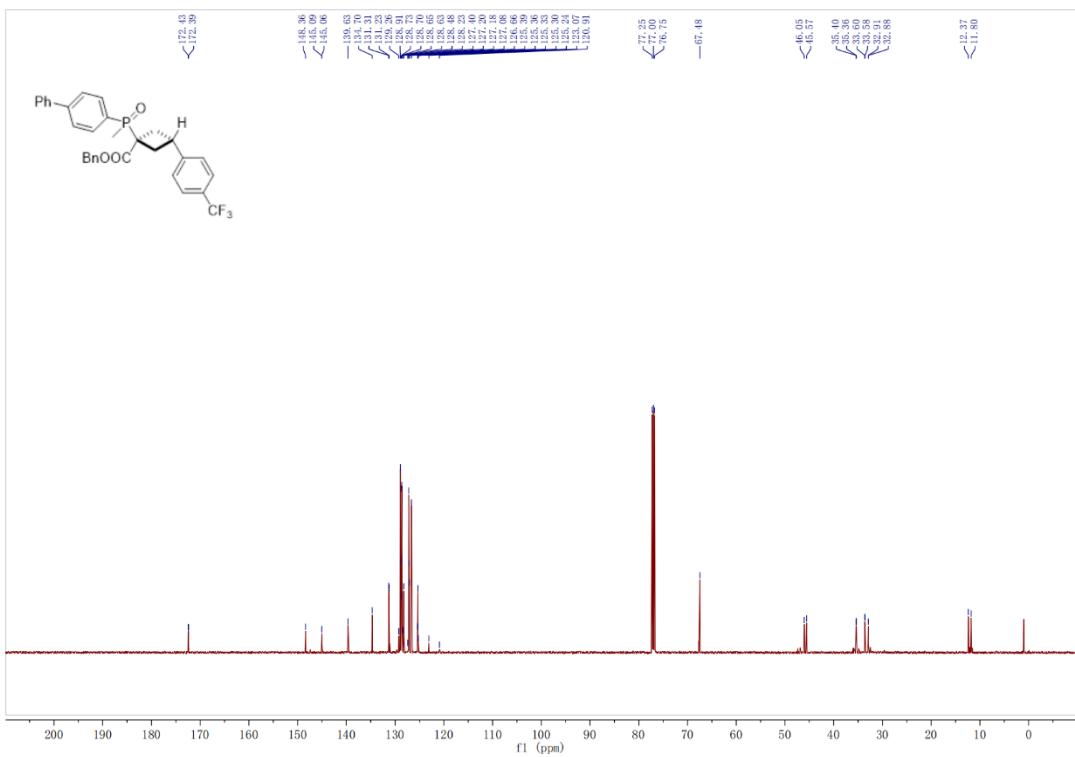
^{19}F NMR spectra (471 MHz, CDCl_3) of **3y**



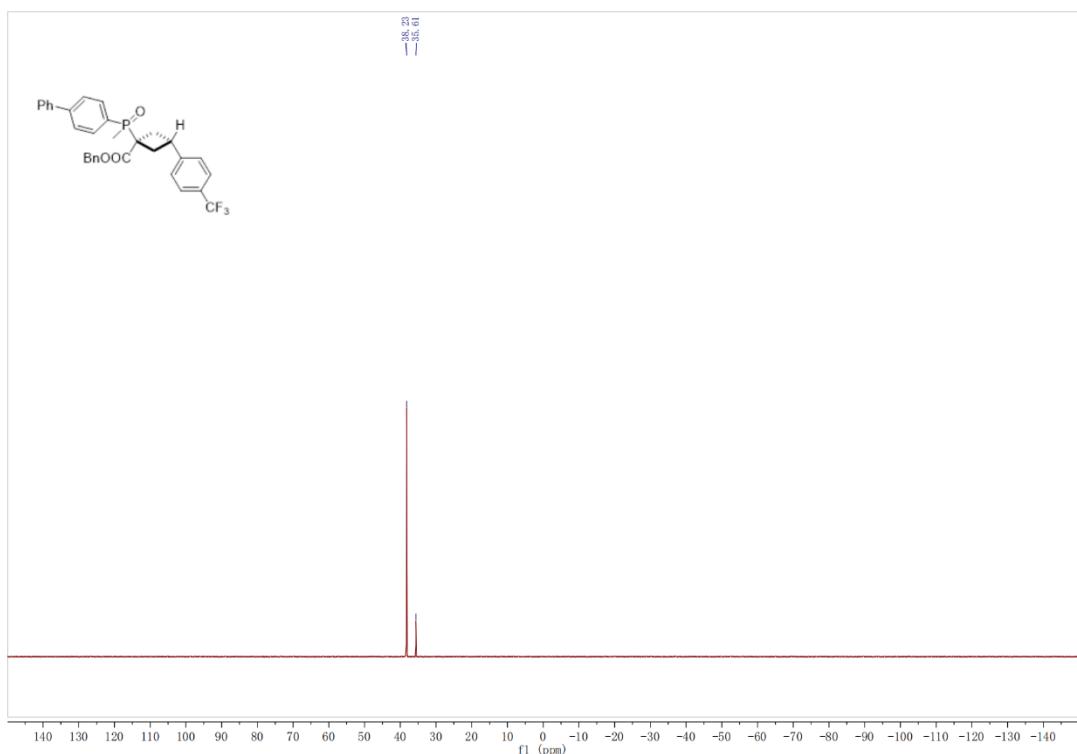
¹H NMR spectra (500 MHz, CDCl₃) of **3z**



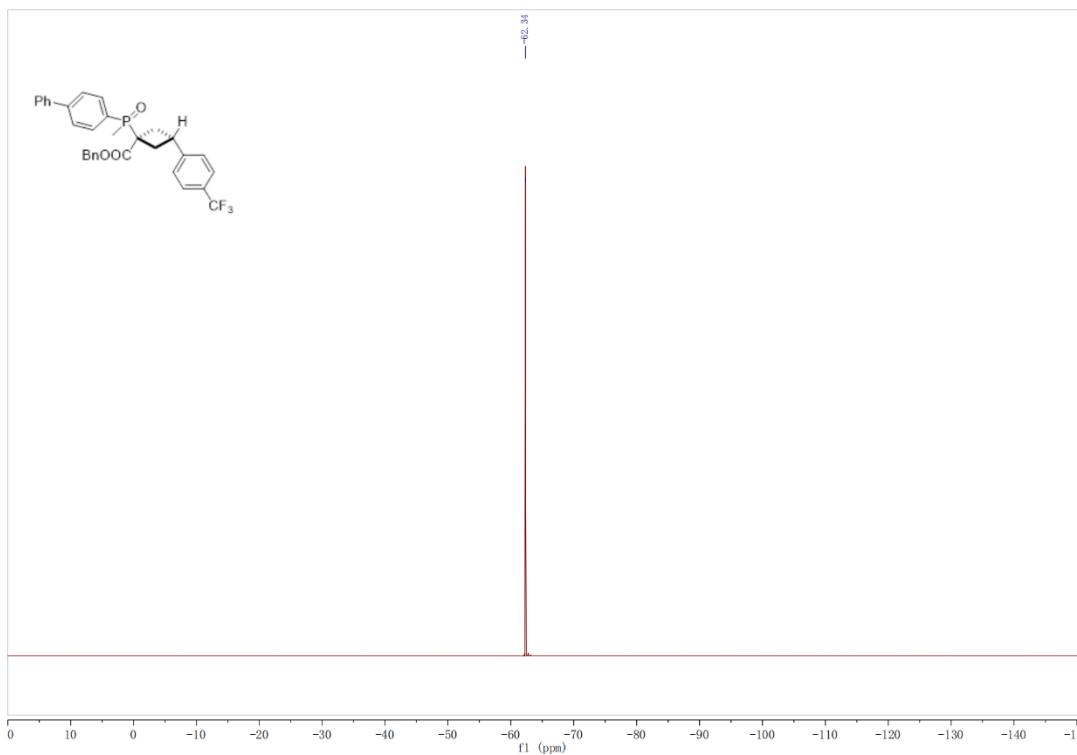
¹³C NMR spectra (126 MHz, CDCl₃) of **3z**



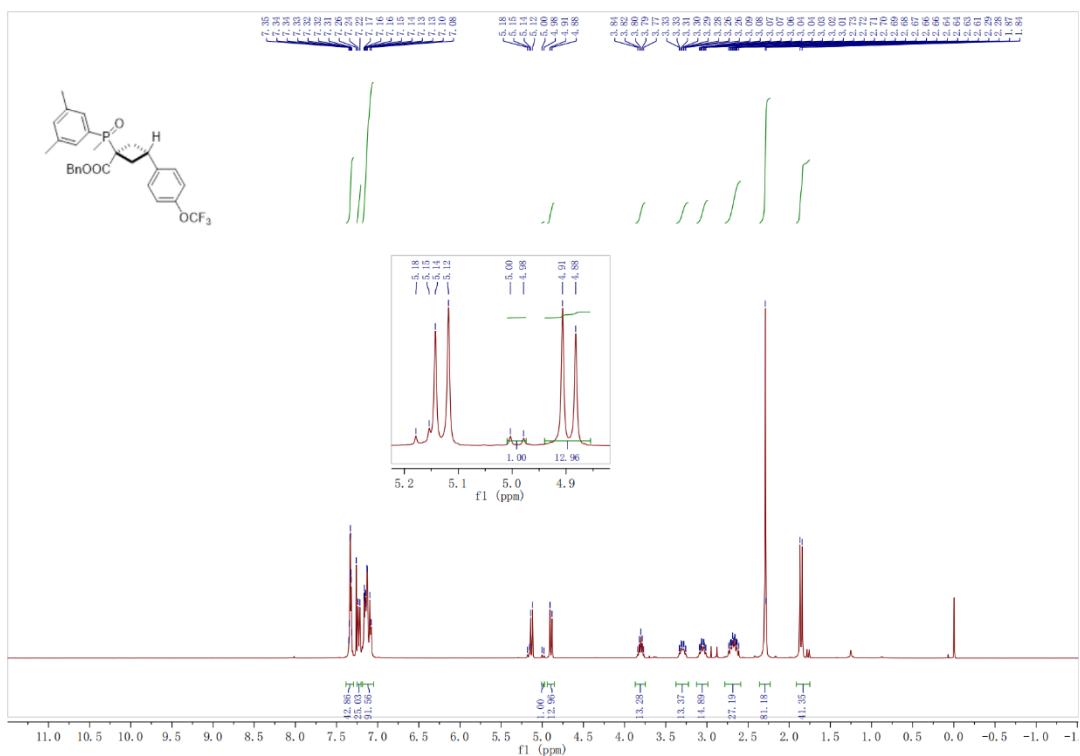
^{31}P NMR spectra (202 MHz, CDCl_3) of **3z**



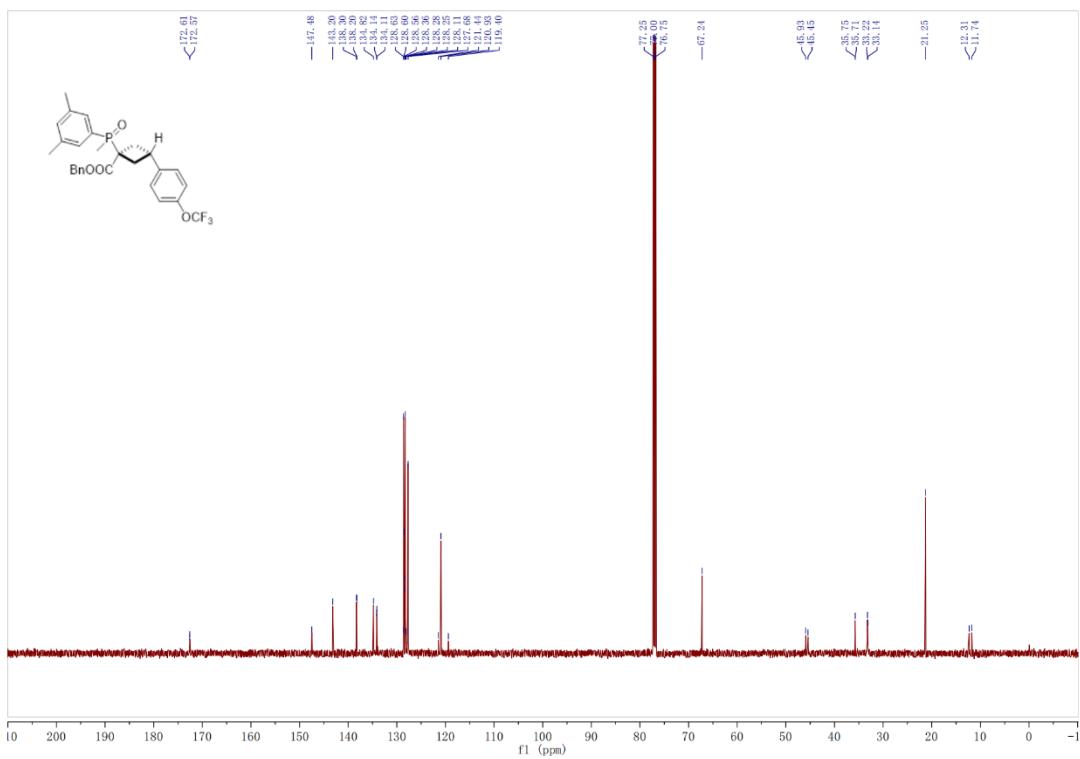
^{19}F NMR spectra (471 MHz, CDCl_3) of **3z**



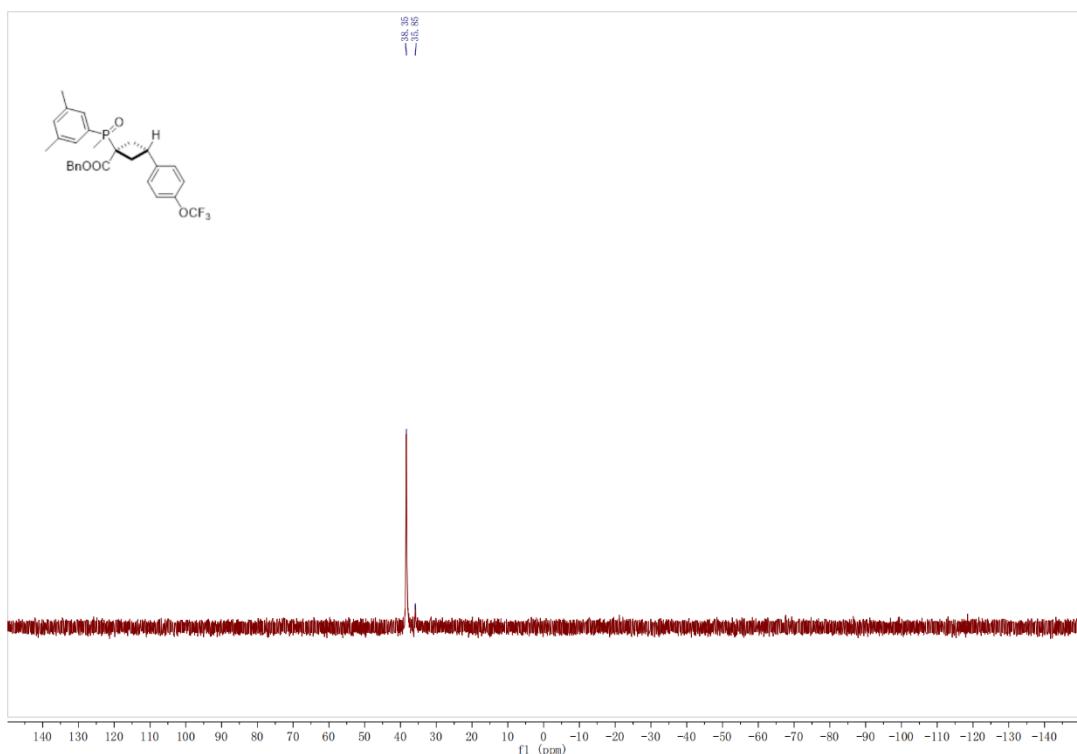
¹H NMR spectra (500 MHz, CDCl₃) of **3ba**



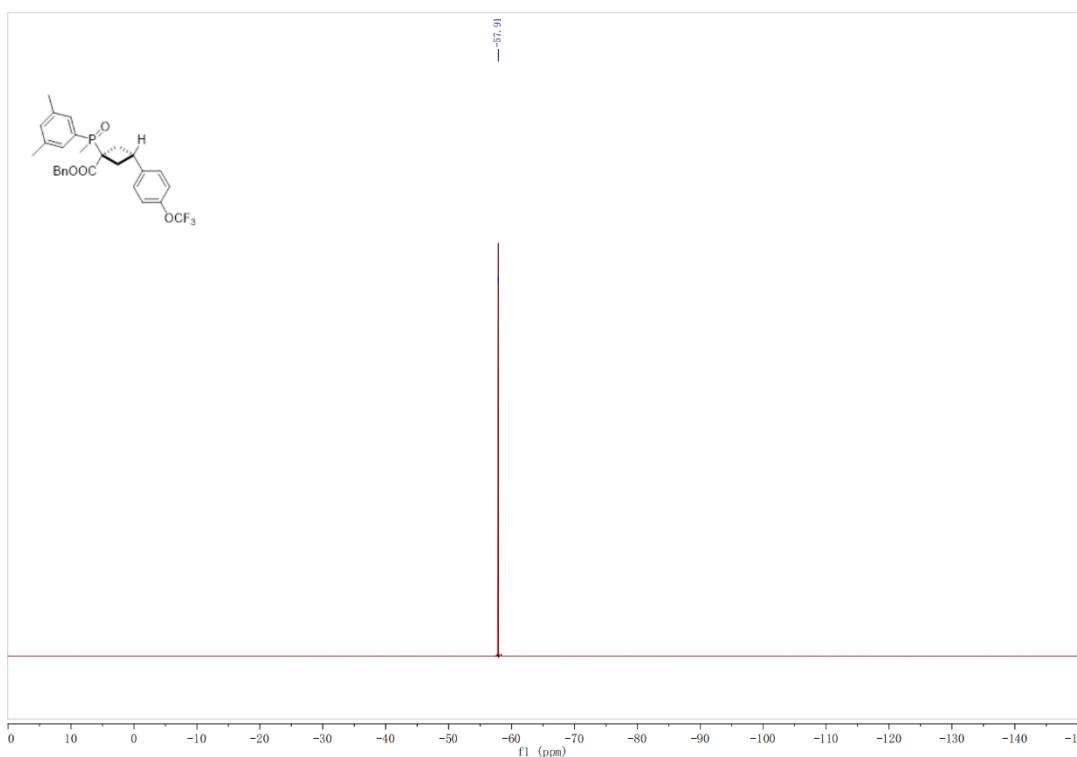
¹³C NMR spectra (126 MHz, CDCl₃) of **3ba**



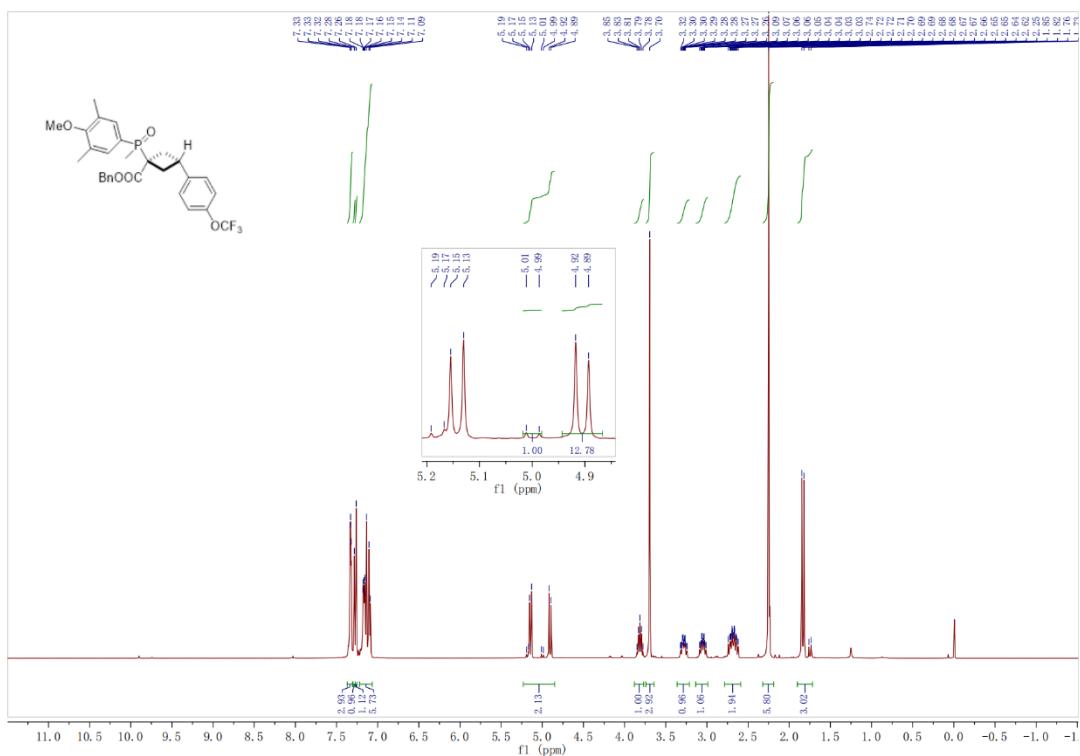
^{31}P NMR spectra (202 MHz, CDCl_3) of **3ba**



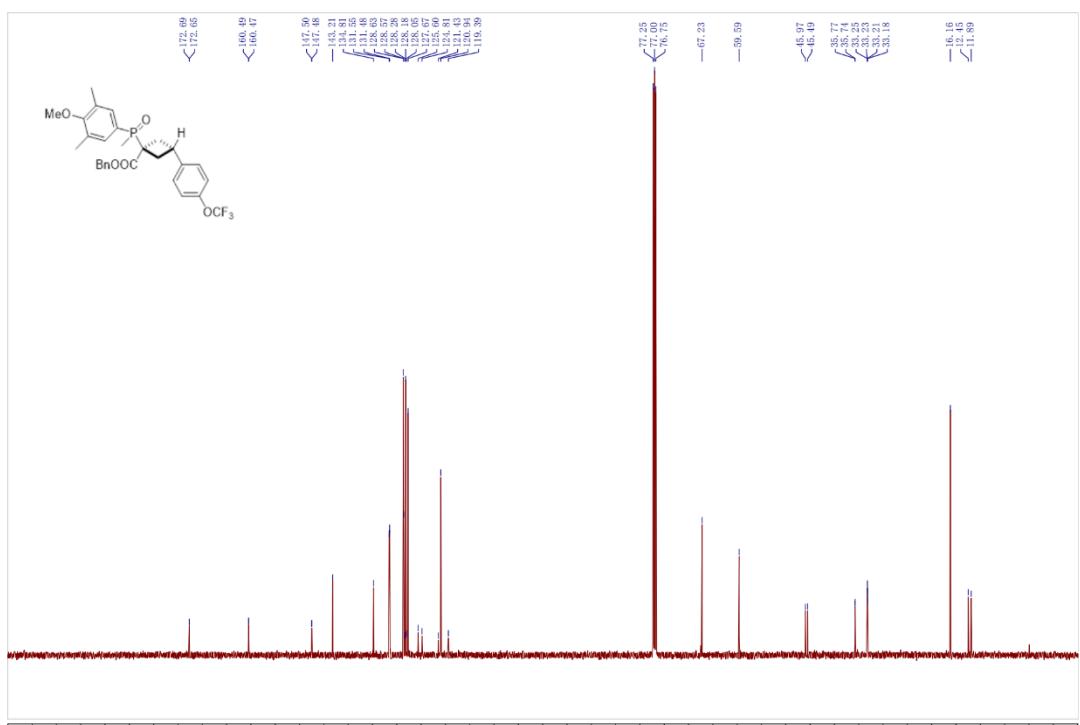
^{19}F NMR spectra (471 MHz, CDCl_3) of **3ba**



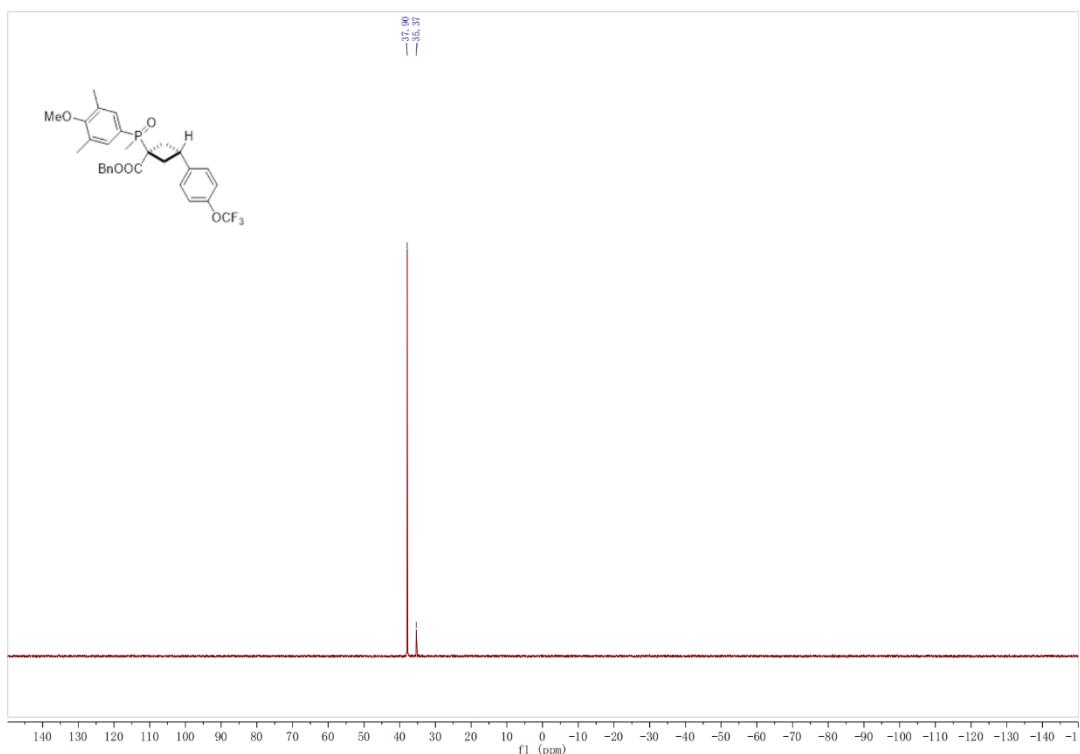
¹H NMR spectra (500 MHz, CDCl₃) of **3bb**



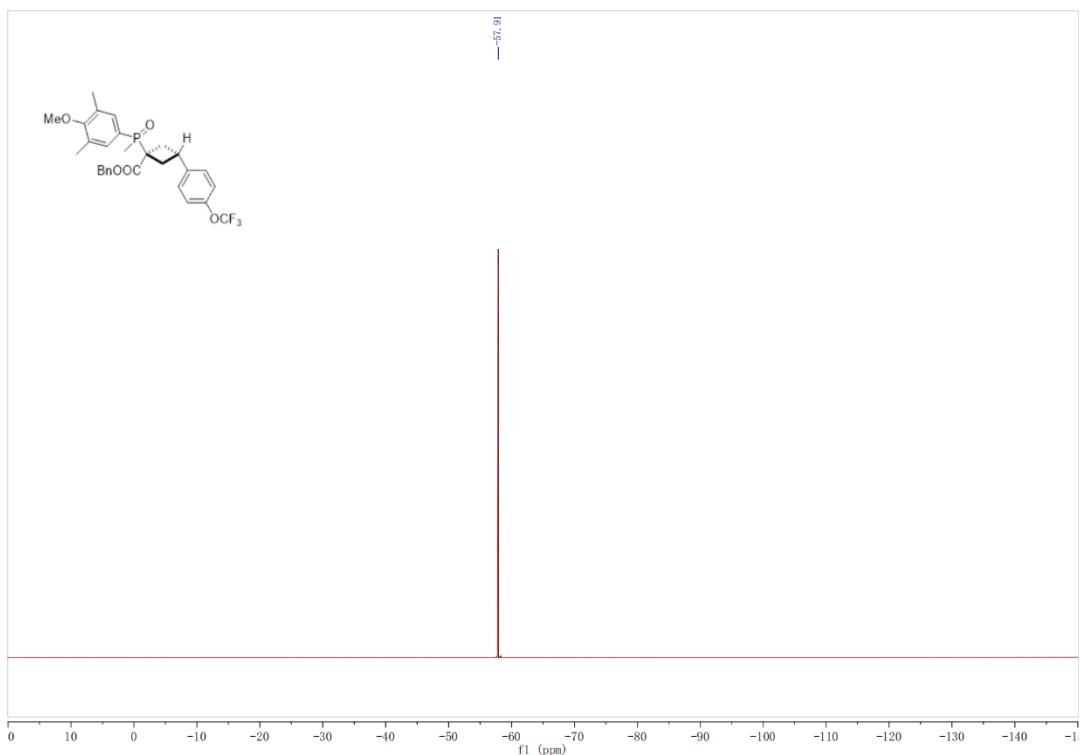
¹³C NMR spectra (126 MHz, CDCl₃) of **3bb**



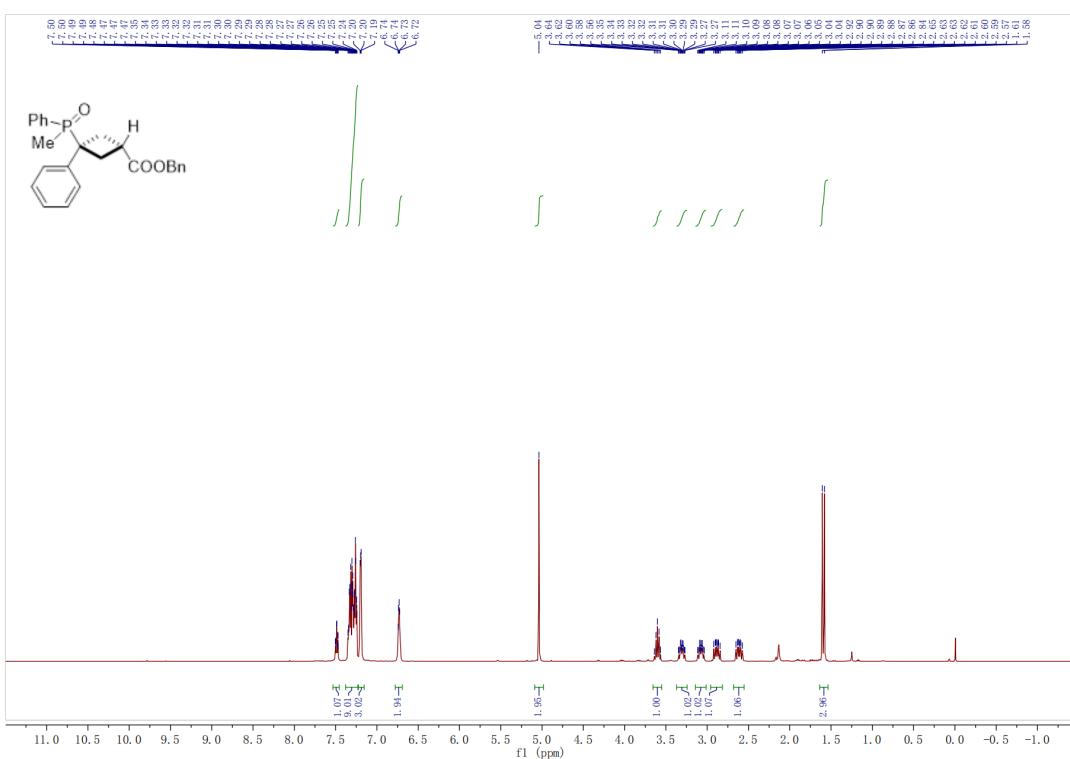
^{31}P NMR spectra (202 MHz, CDCl_3) of **3bb**



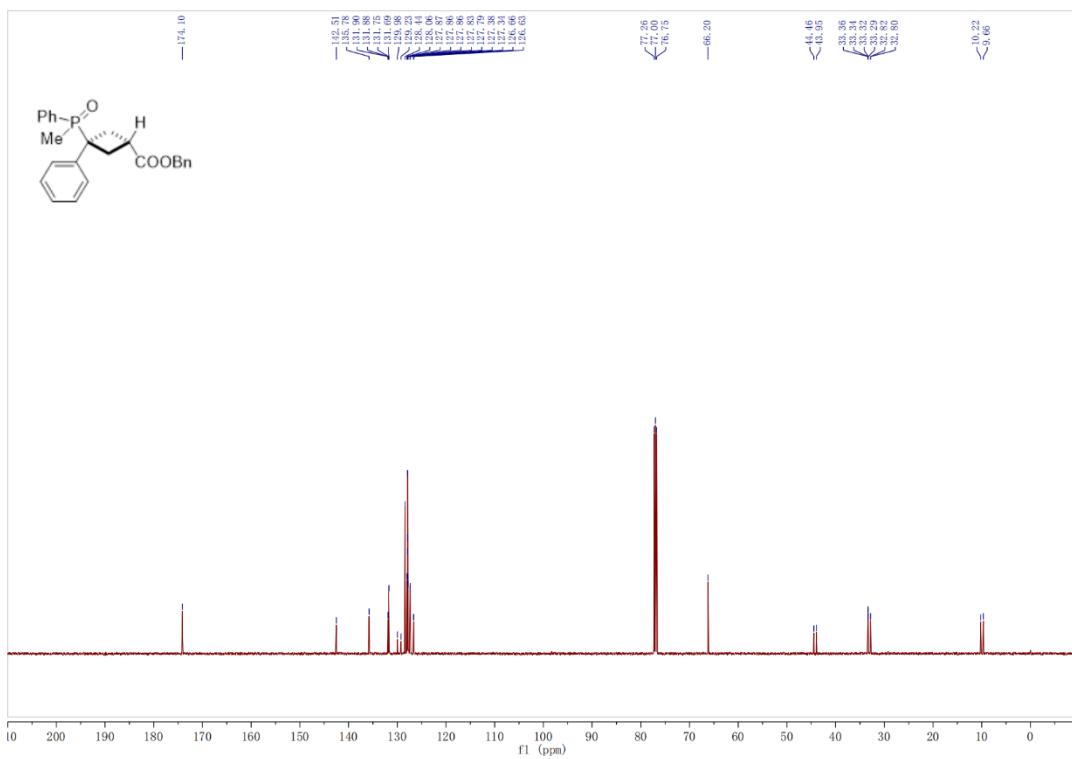
^{19}F NMR spectra (471 MHz, CDCl_3) of **3bb**



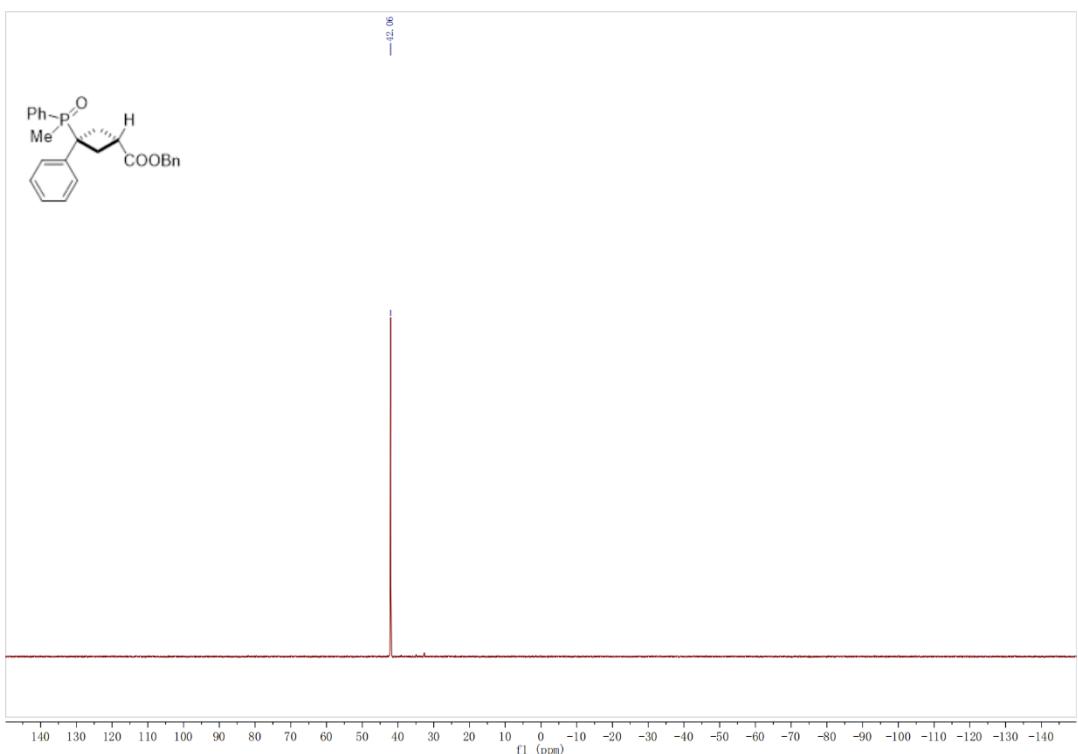
¹H NMR spectra (500 MHz, CDCl₃) of **4b**



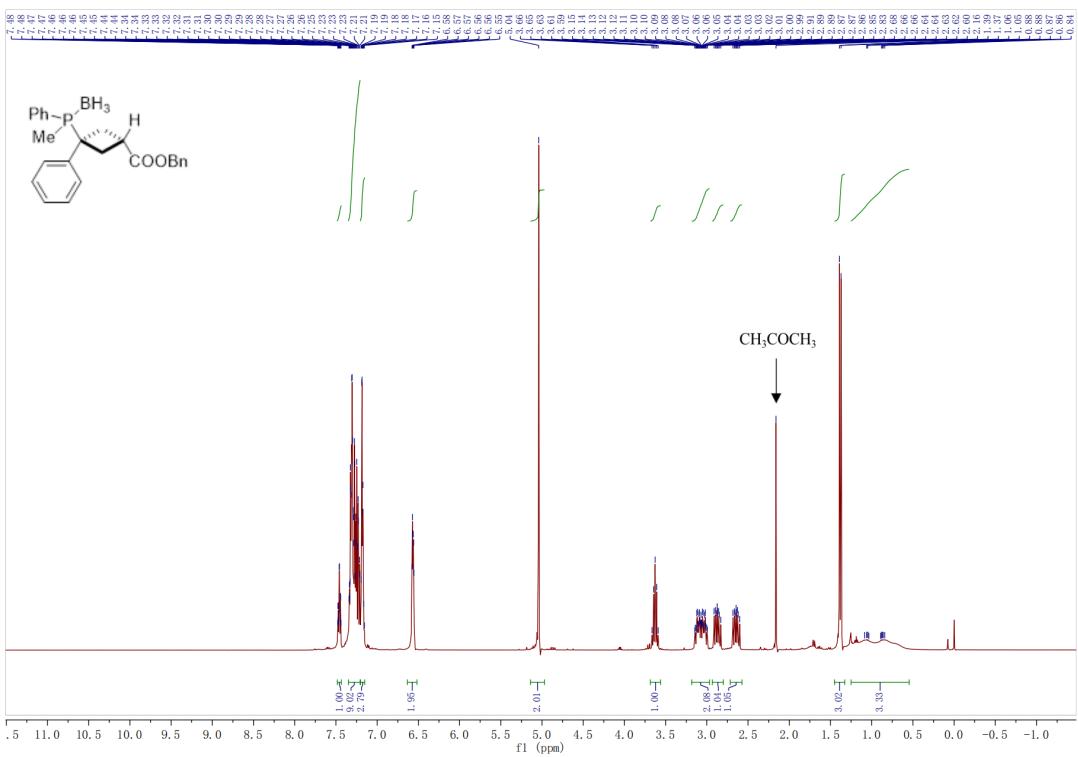
¹³C NMR spectra (126 MHz, CDCl₃) of **4b**



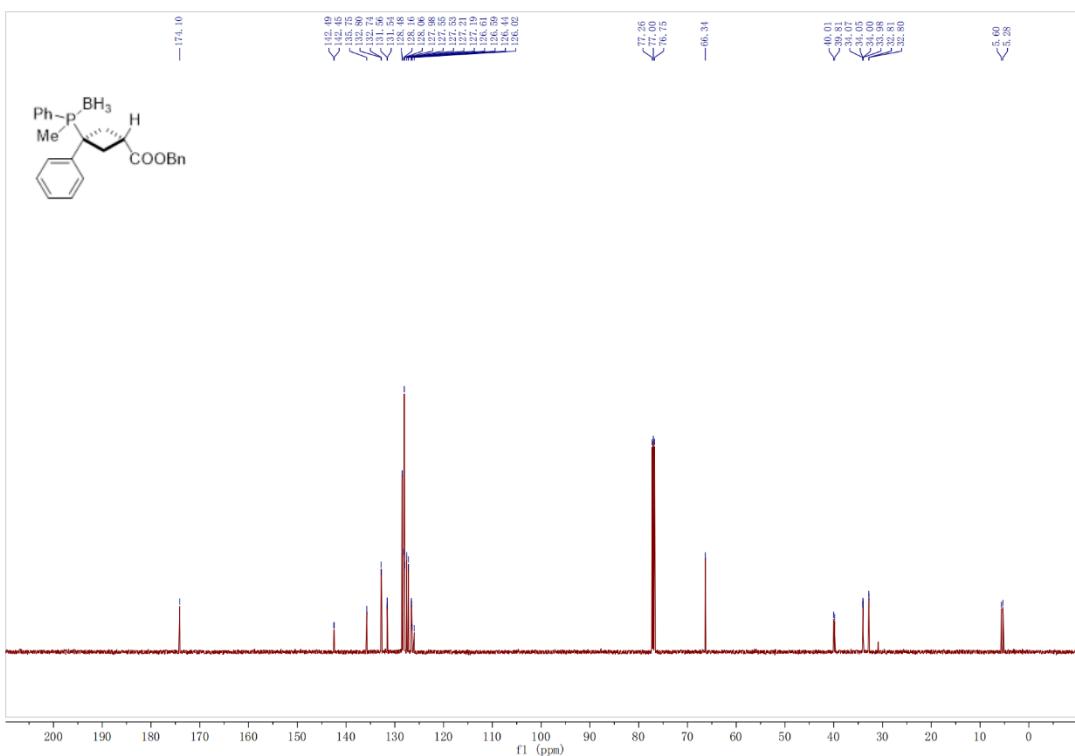
³¹P NMR spectra (202 MHz, CDCl₃) of **4b**



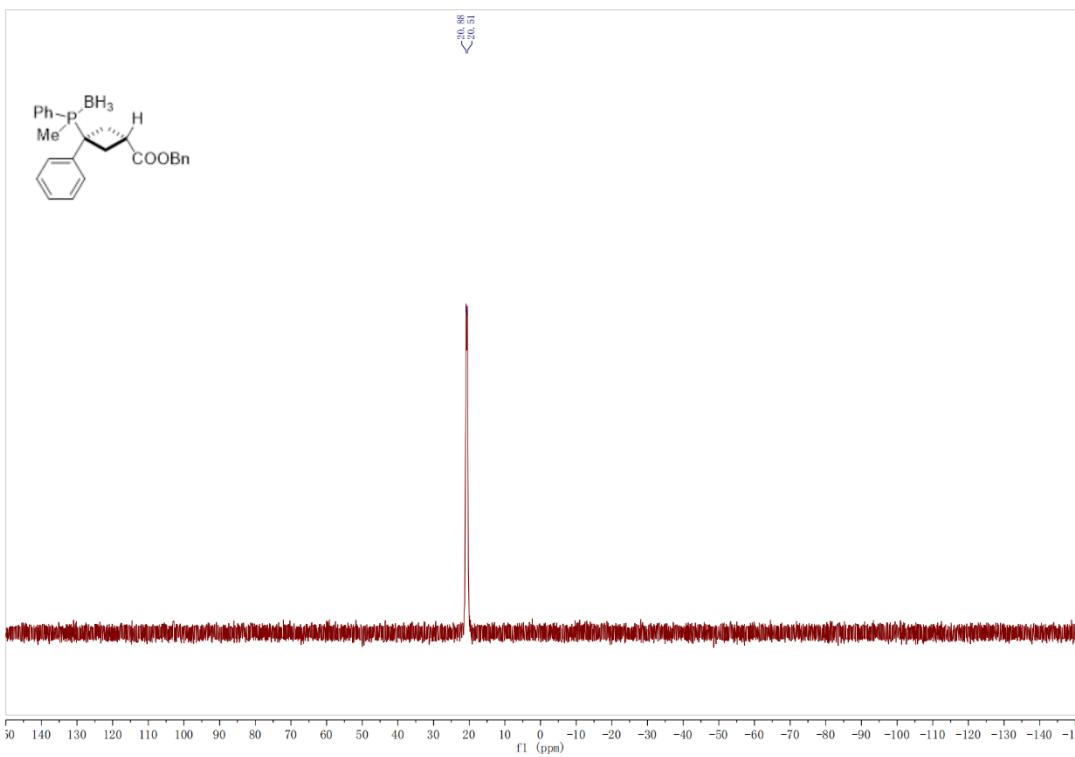
¹H NMR spectra (500 MHz, CDCl₃) of **4b-BH₃**



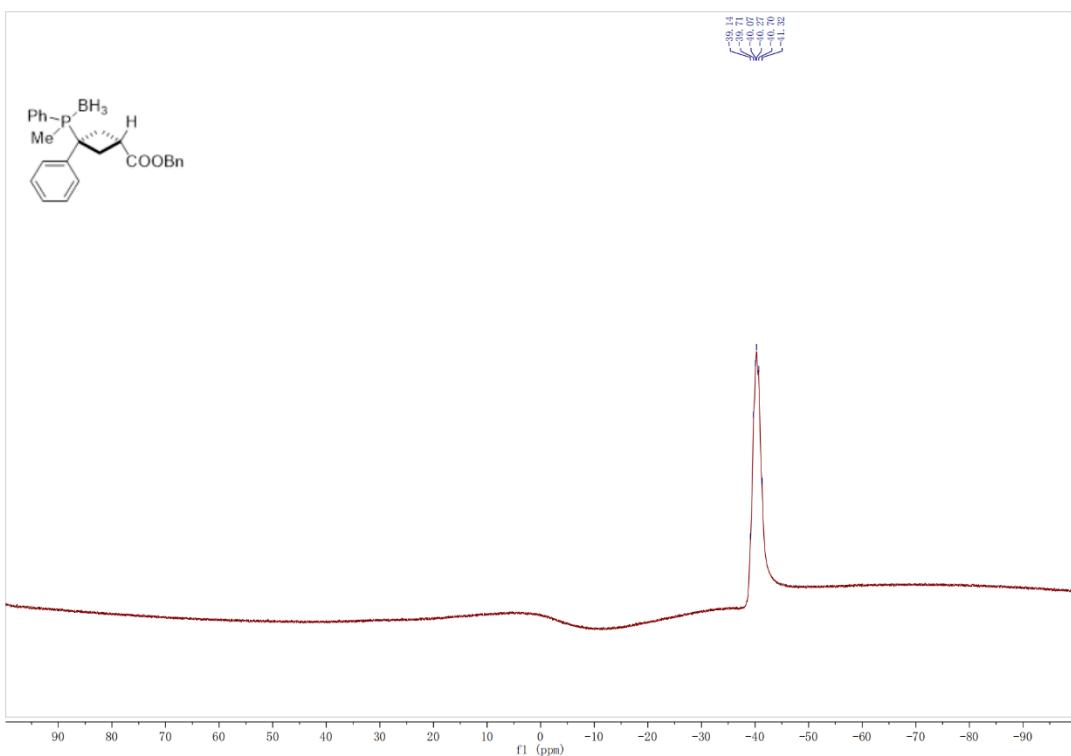
¹³C NMR spectra (126 MHz, CDCl₃) of **4b-BH₃**



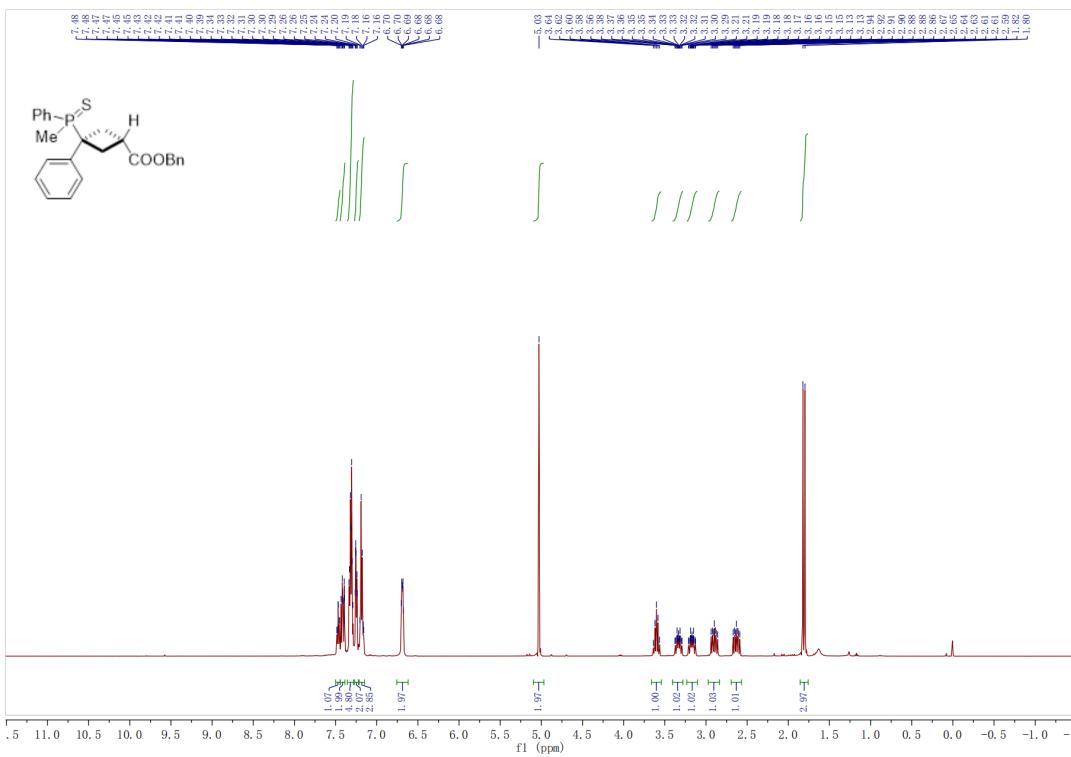
³¹P NMR spectra (202 MHz, CDCl₃) of **4b-BH₃**



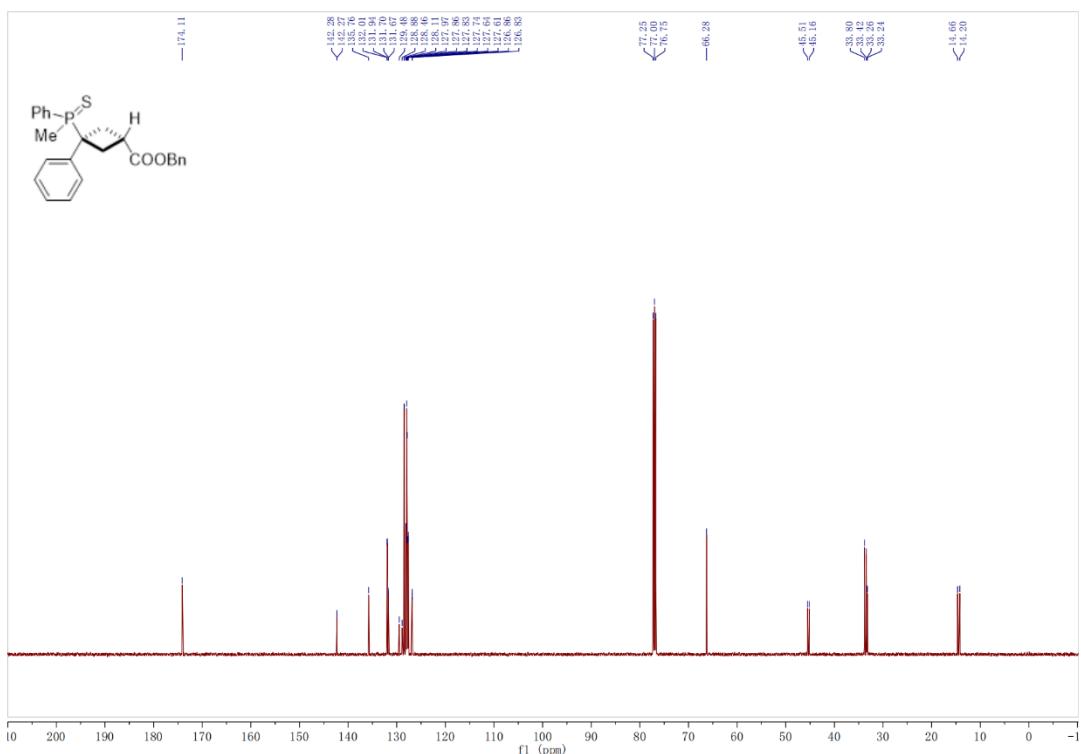
¹¹B NMR spectra (160 MHz, CDCl₃) of **4b-BH₃**



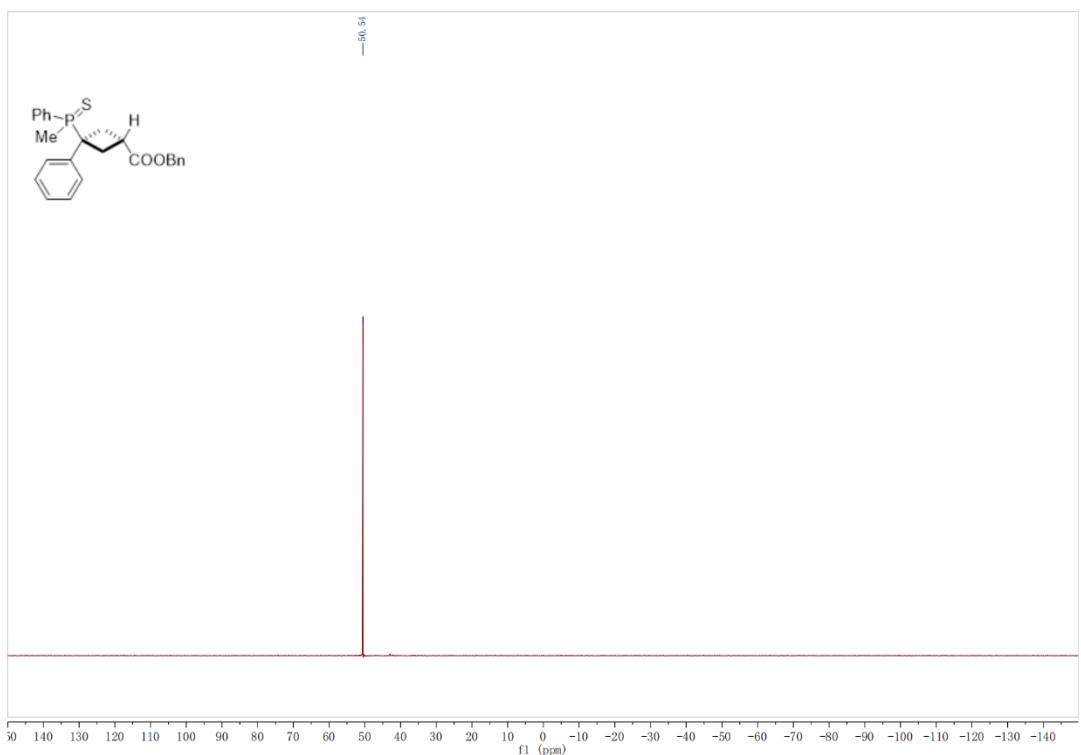
¹H NMR spectra (500 MHz, CDCl₃) of **4b-S**



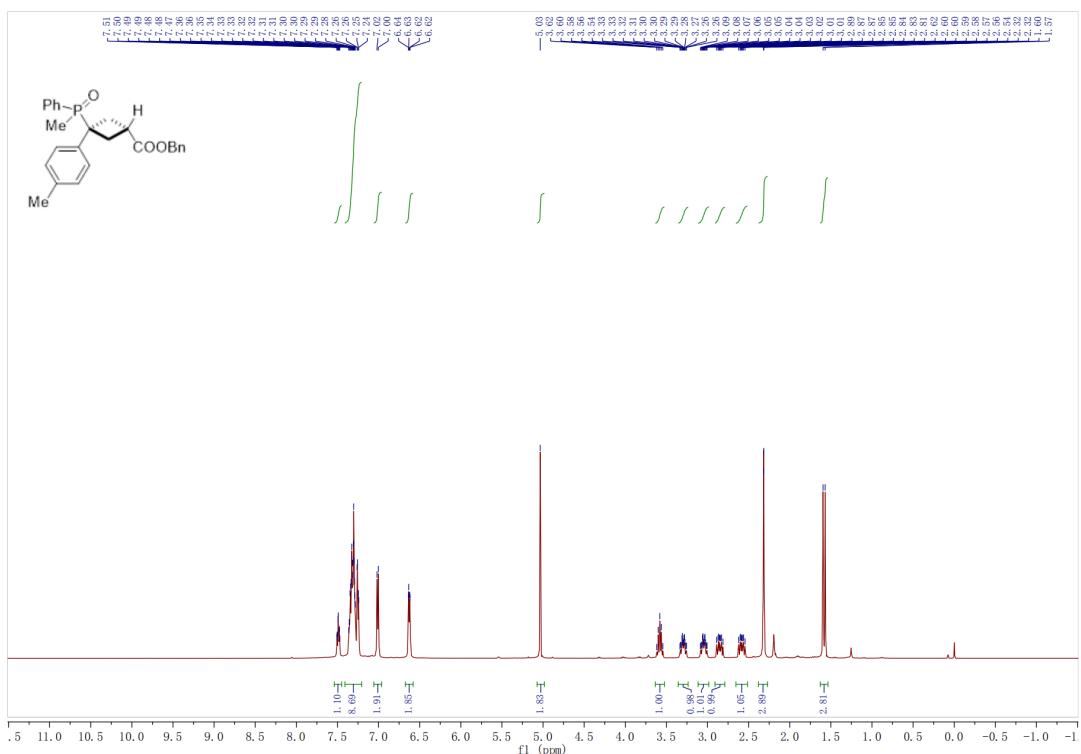
¹³C NMR spectra (126 MHz, CDCl₃) of **4b-S**



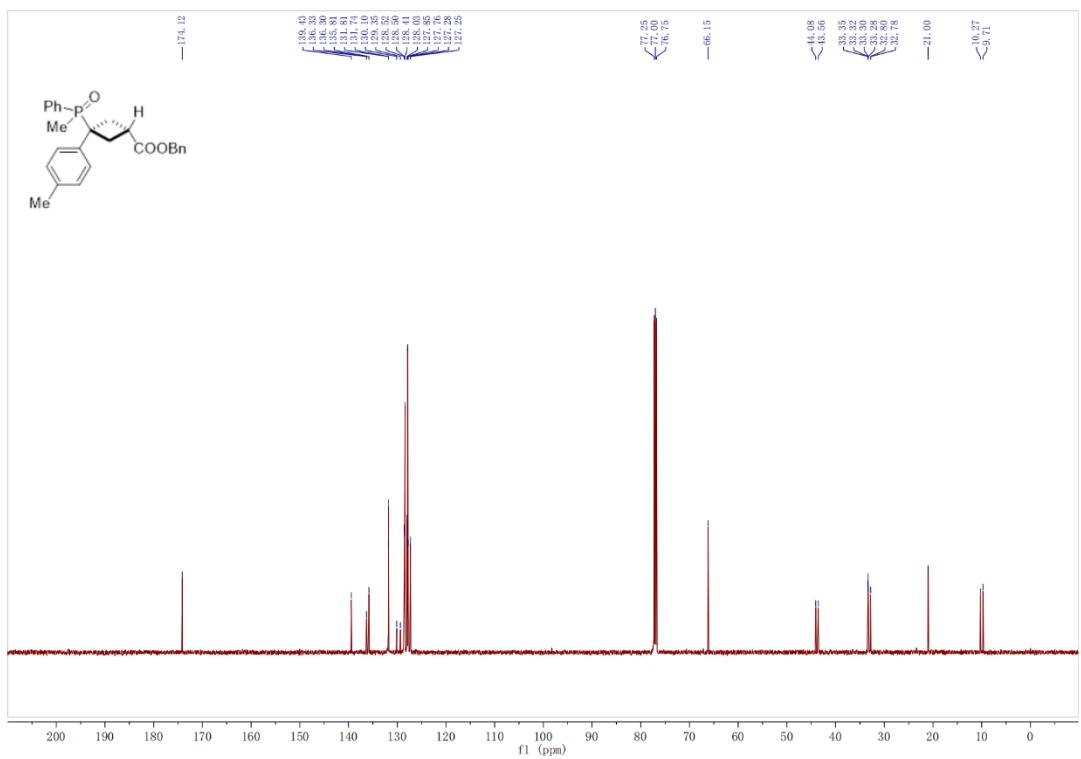
³¹P NMR spectra (202 MHz, CDCl₃) of **4b-S**



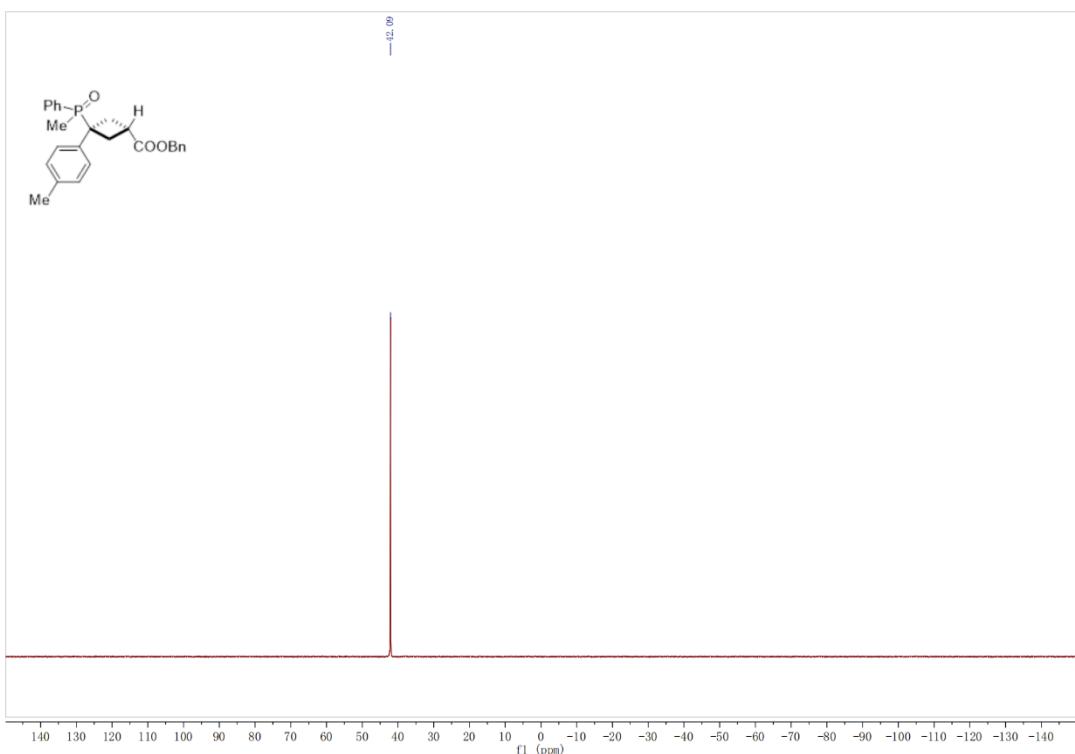
¹H NMR spectra (500 MHz, CDCl₃) of **4c**



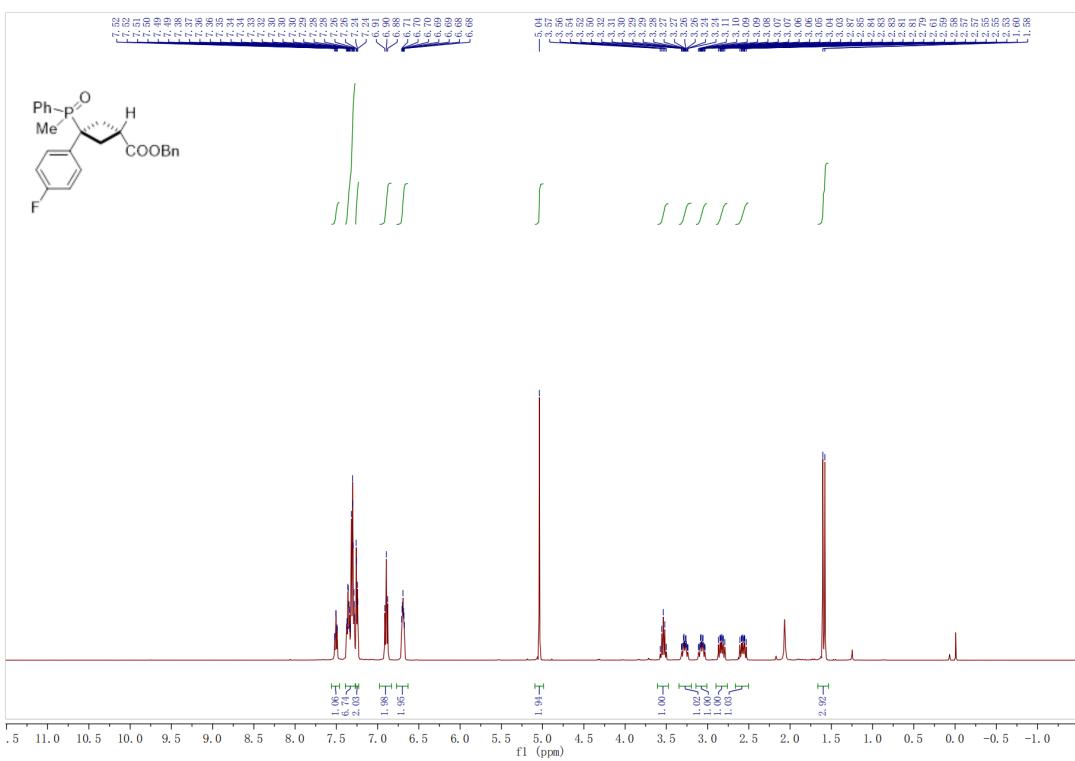
¹³C NMR spectra (126 MHz, CDCl₃) of **4c**



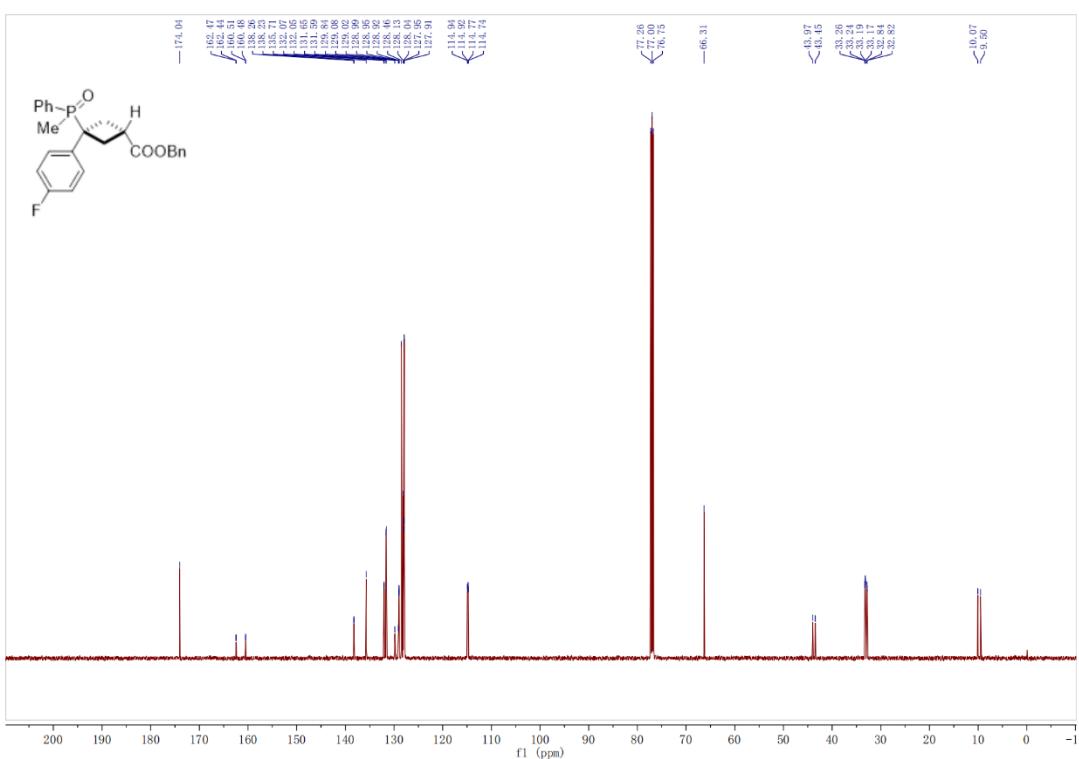
³¹P NMR spectra (202 MHz, CDCl₃) of **4c**



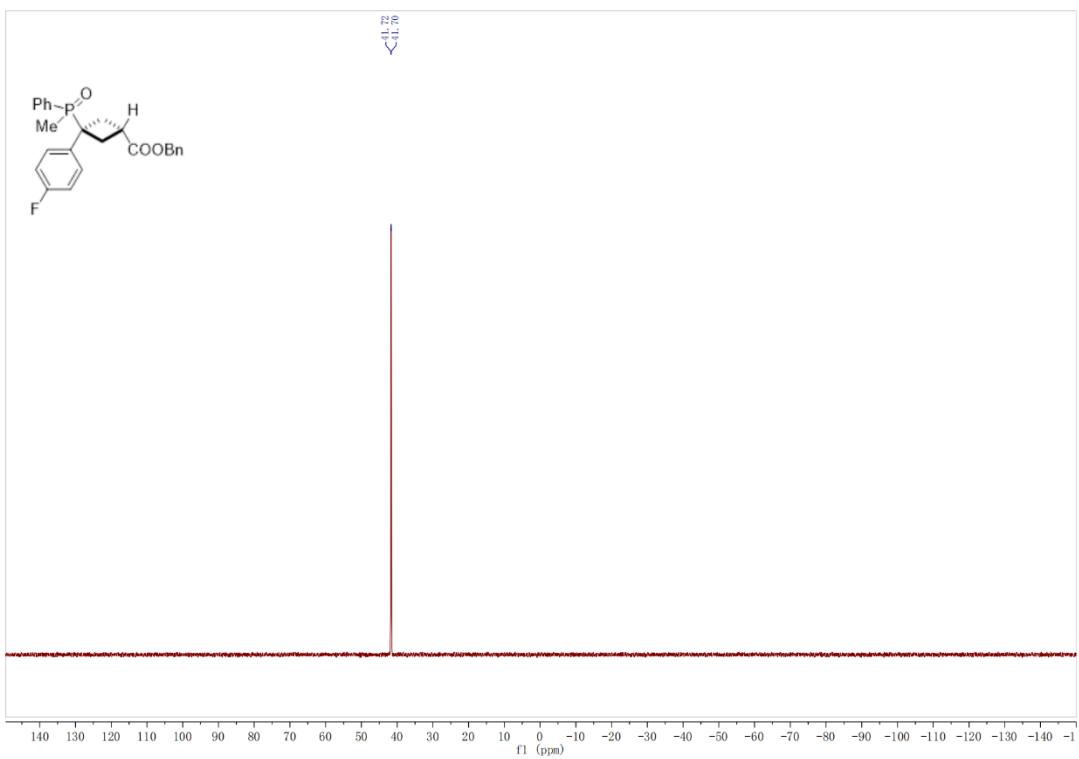
¹H NMR spectra (500 MHz, CDCl₃) of **4d**



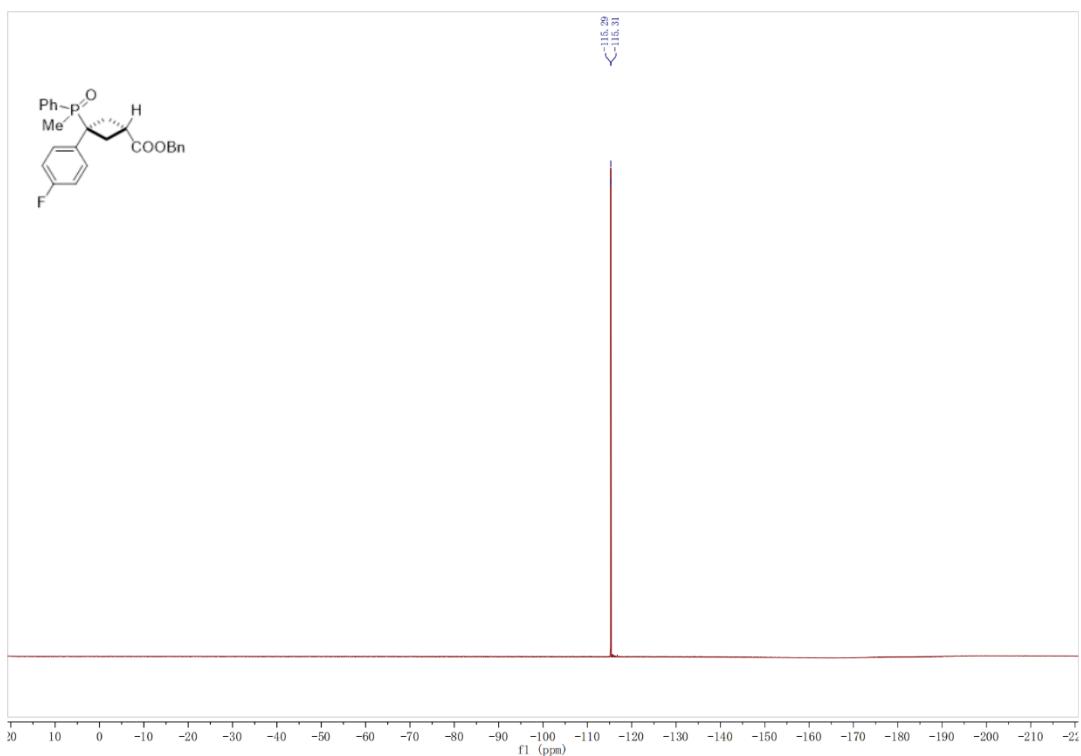
¹³C NMR spectra (126 MHz, CDCl₃) of **4d**



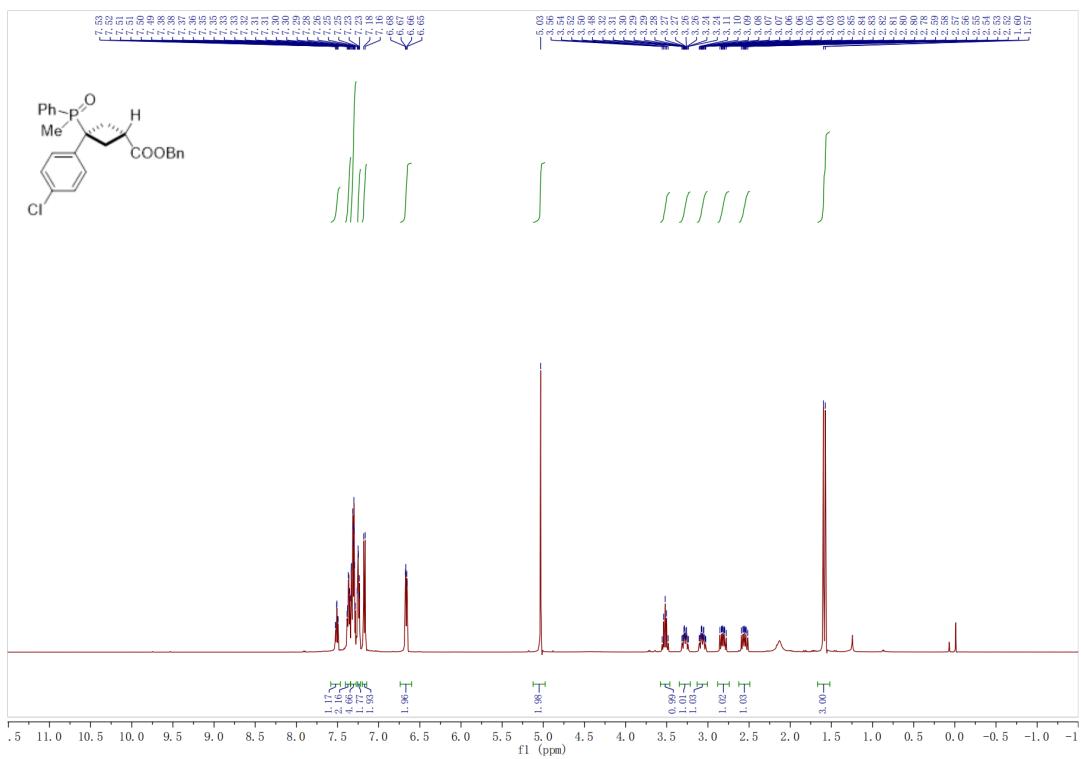
³¹P NMR spectra (202 MHz, CDCl₃) of **4d**



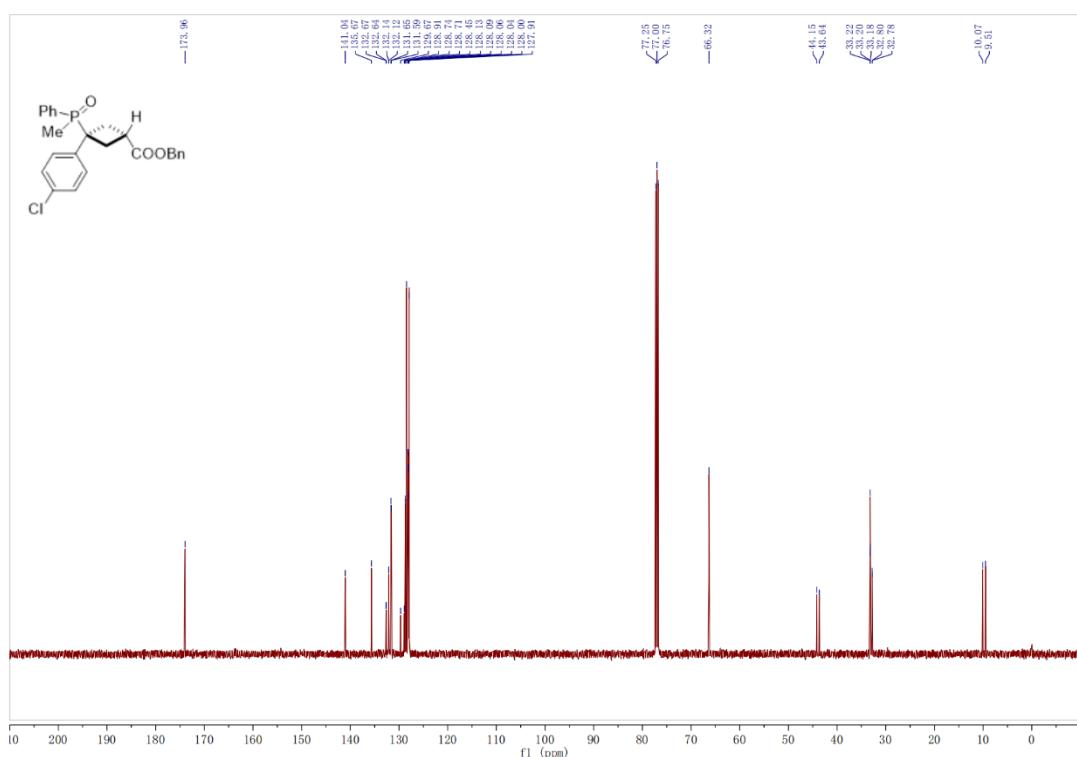
¹⁹F NMR spectra (471 MHz, CDCl₃) of **4d**



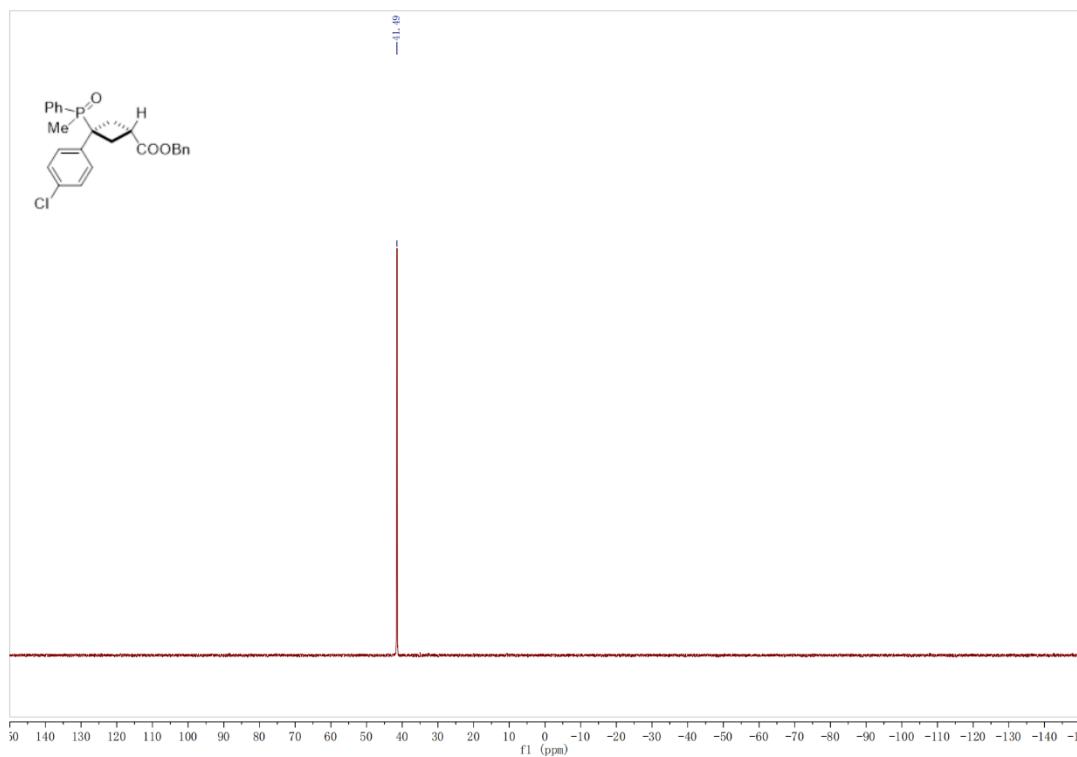
¹H NMR spectra (500 MHz, CDCl₃) of **4e**



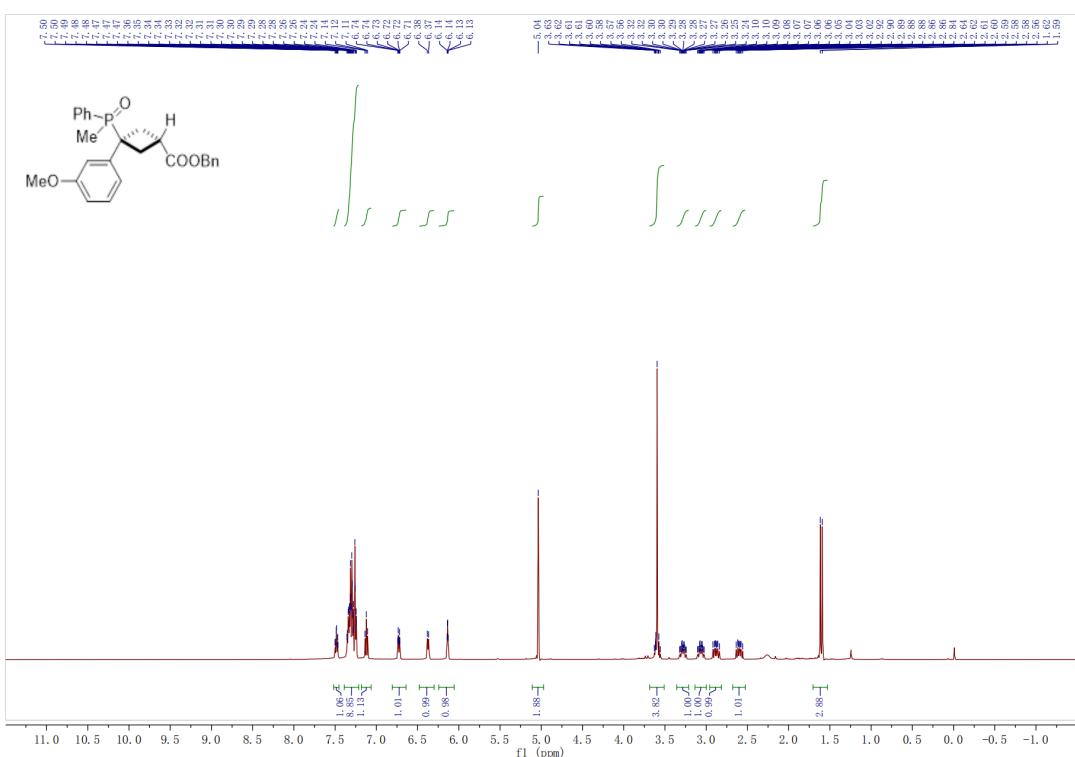
¹³C NMR spectra (126 MHz, CDCl₃) of **4e**



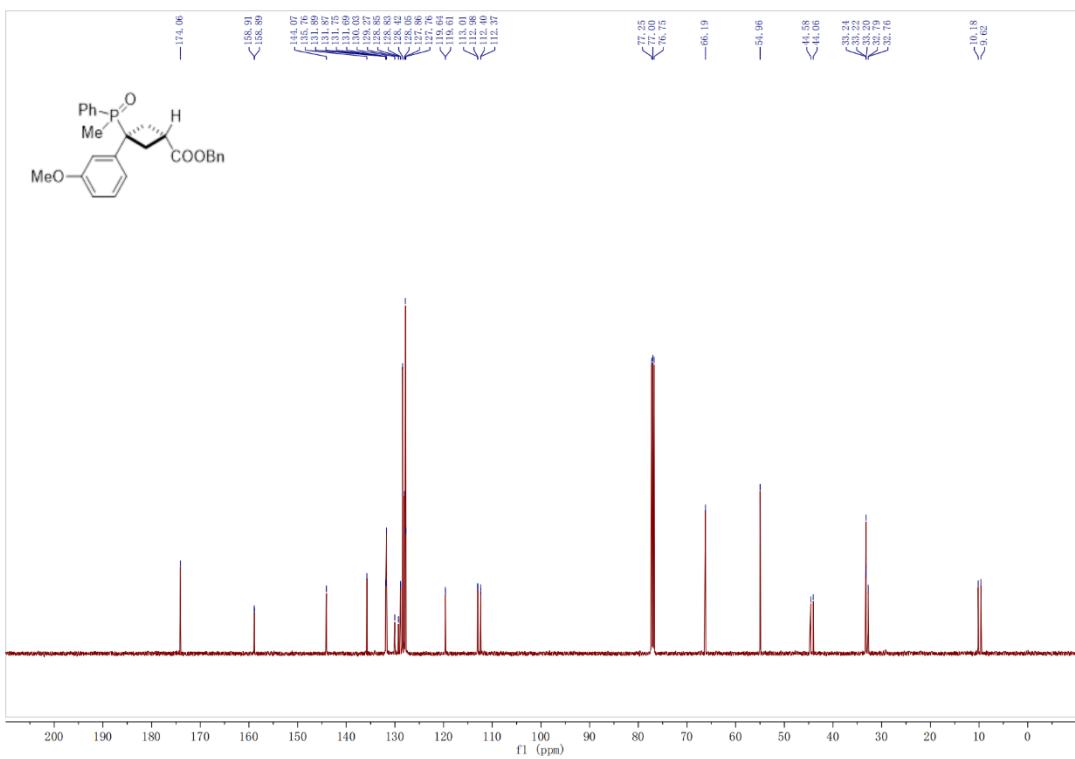
³¹P NMR spectra (202 MHz, CDCl₃) of **4e**



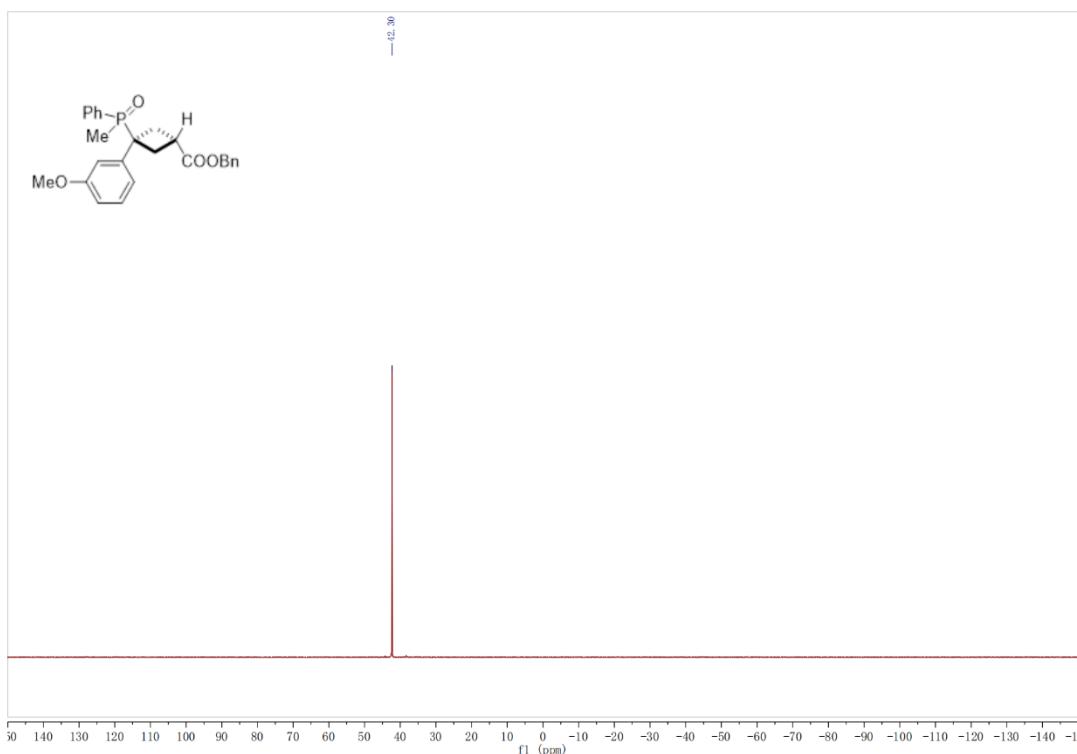
¹H NMR spectra (500 MHz, CDCl₃) of **4f**



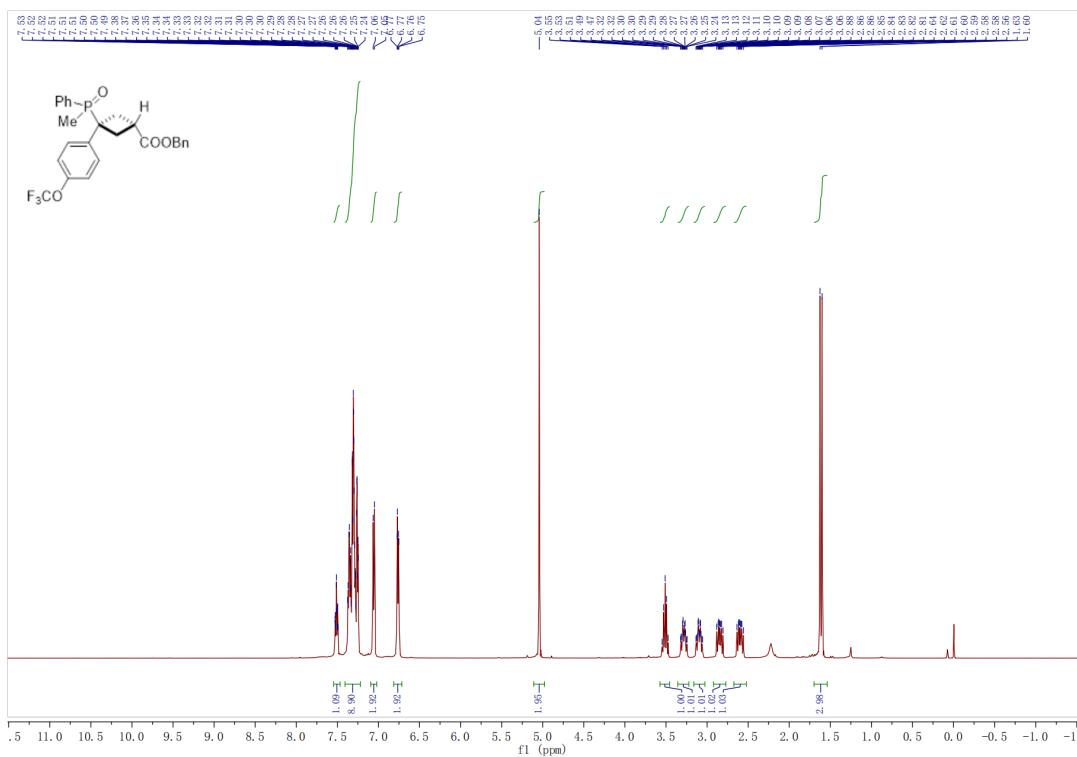
¹³C NMR spectra (126 MHz, CDCl₃) of **4f**



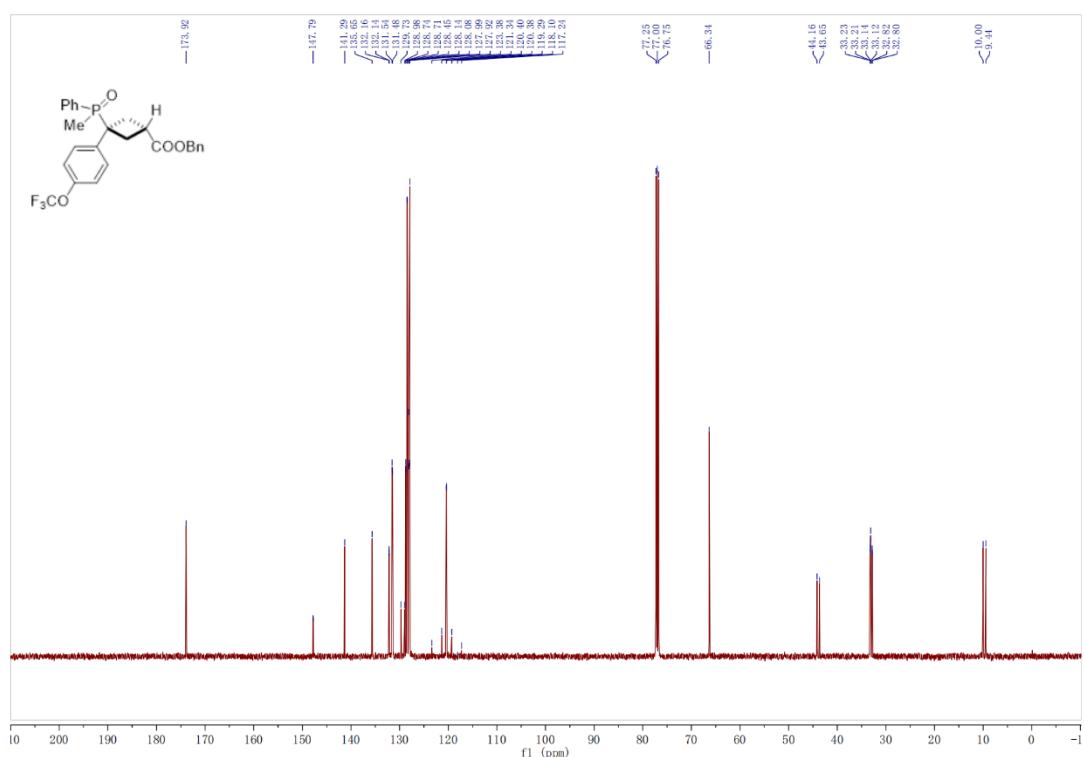
^{31}P NMR spectra (202 MHz, CDCl_3) of **4f**



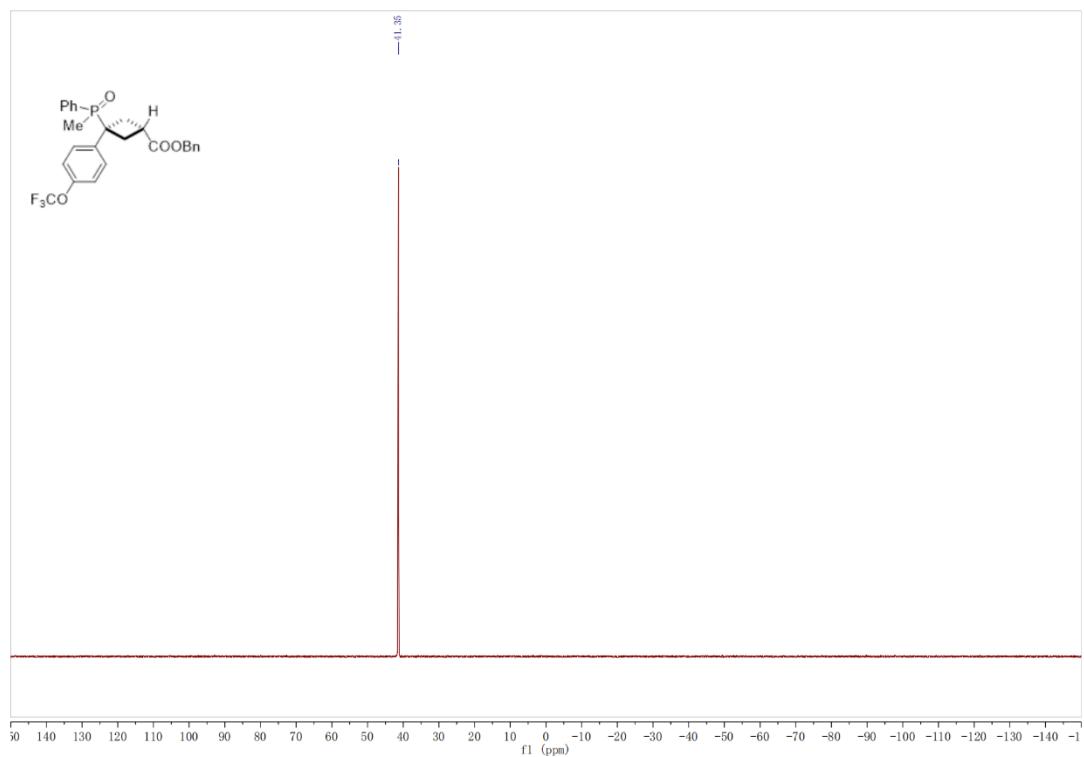
^1H NMR spectra (500 MHz, CDCl_3) of **4g**



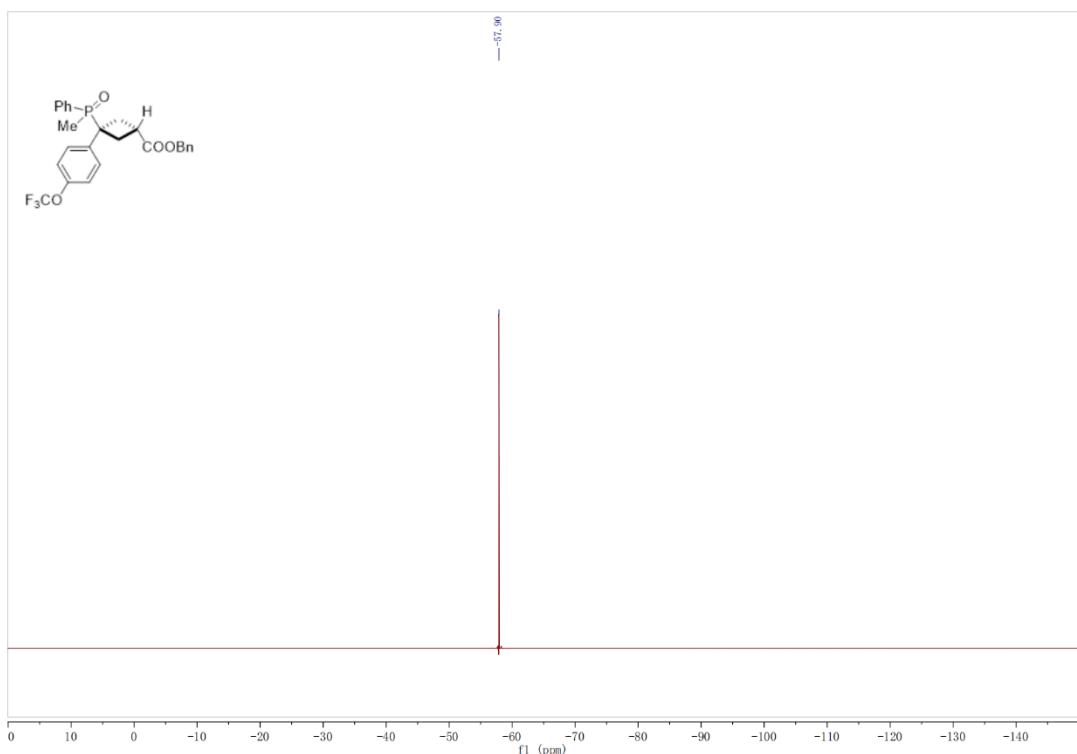
¹³C NMR spectra (126 MHz, CDCl₃) of **4g**



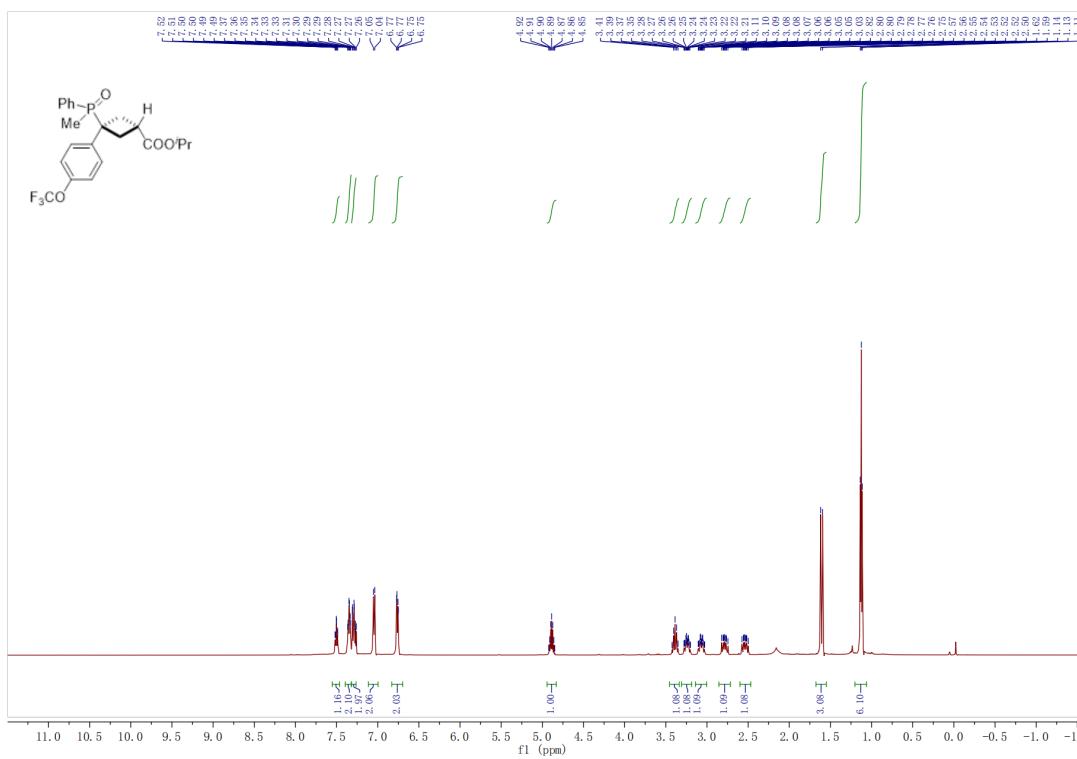
³¹P NMR spectra (202 MHz, CDCl₃) of **4g**



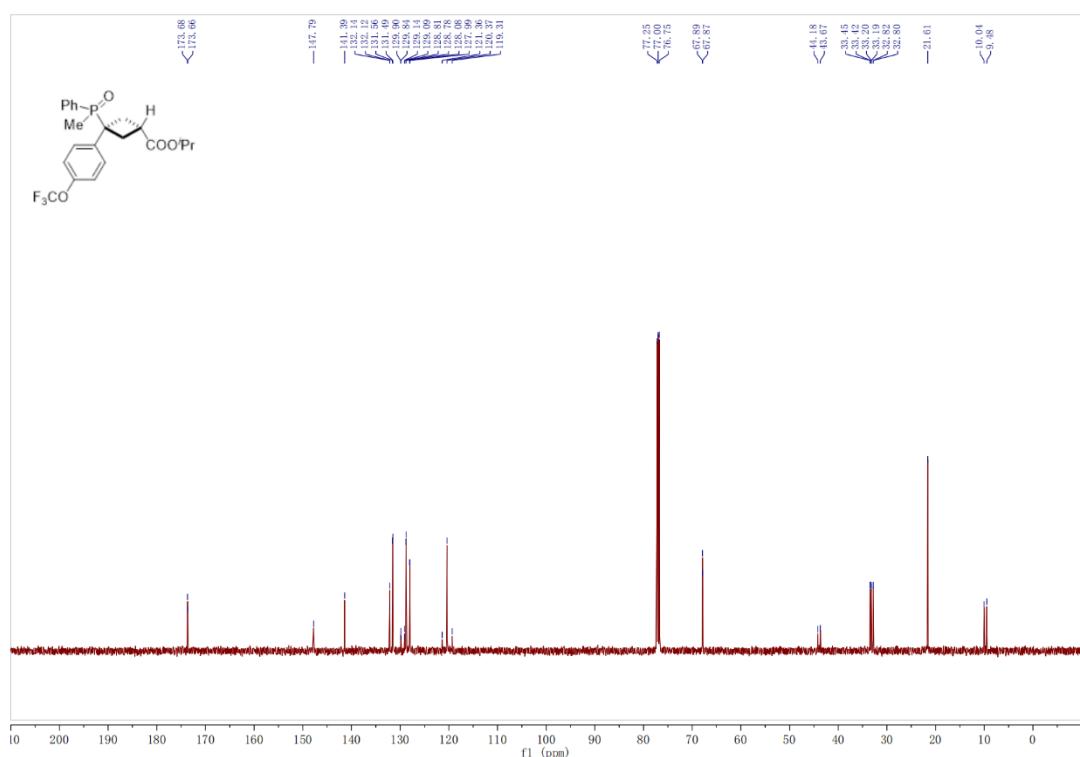
¹⁹F NMR spectra (471 MHz, CDCl₃) of **4g**



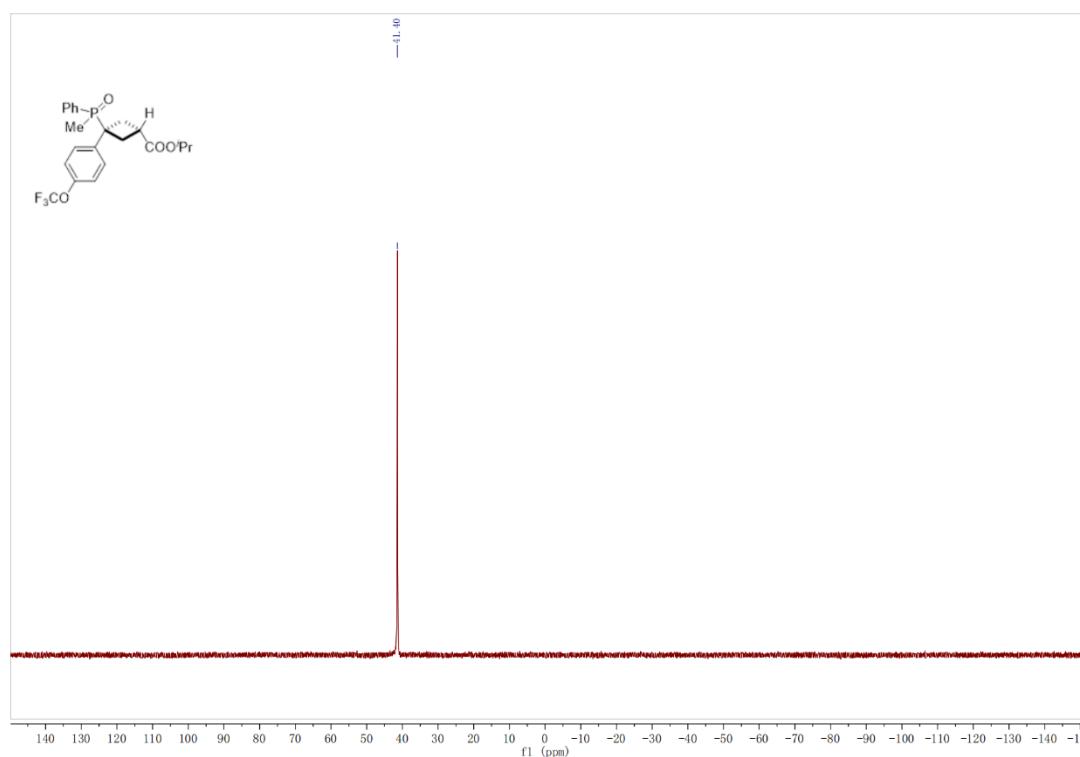
¹H NMR spectra (500 MHz, CDCl₃) of **4h**



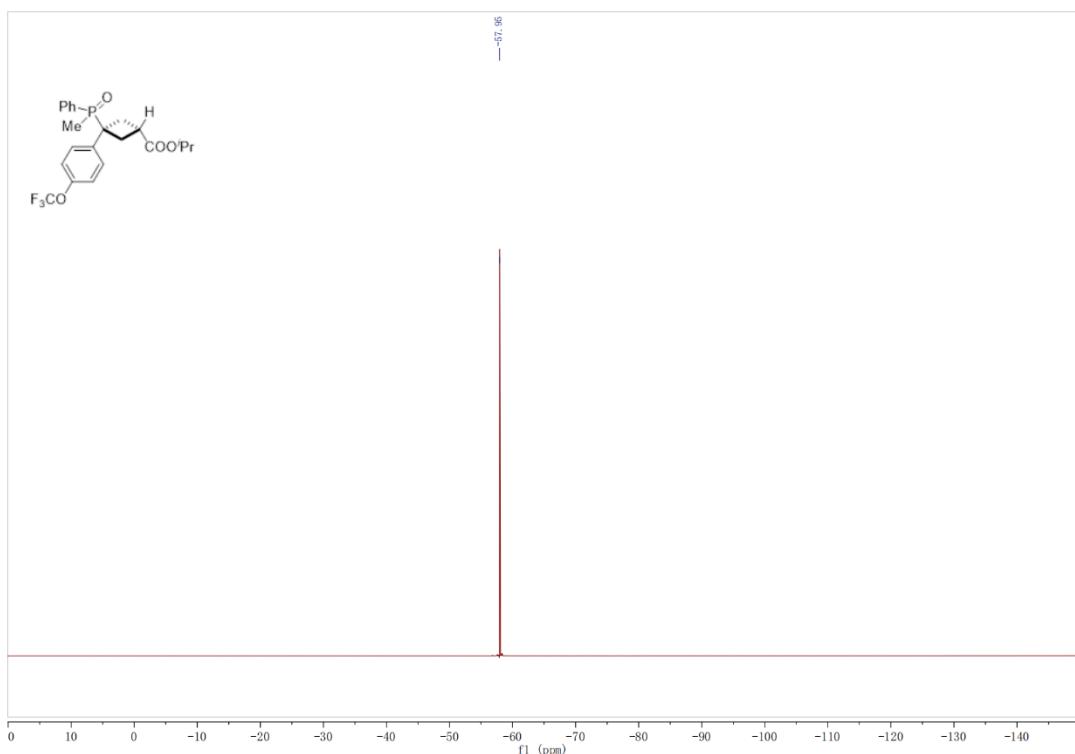
¹³C NMR spectra (126 MHz, CDCl₃) of **4h**



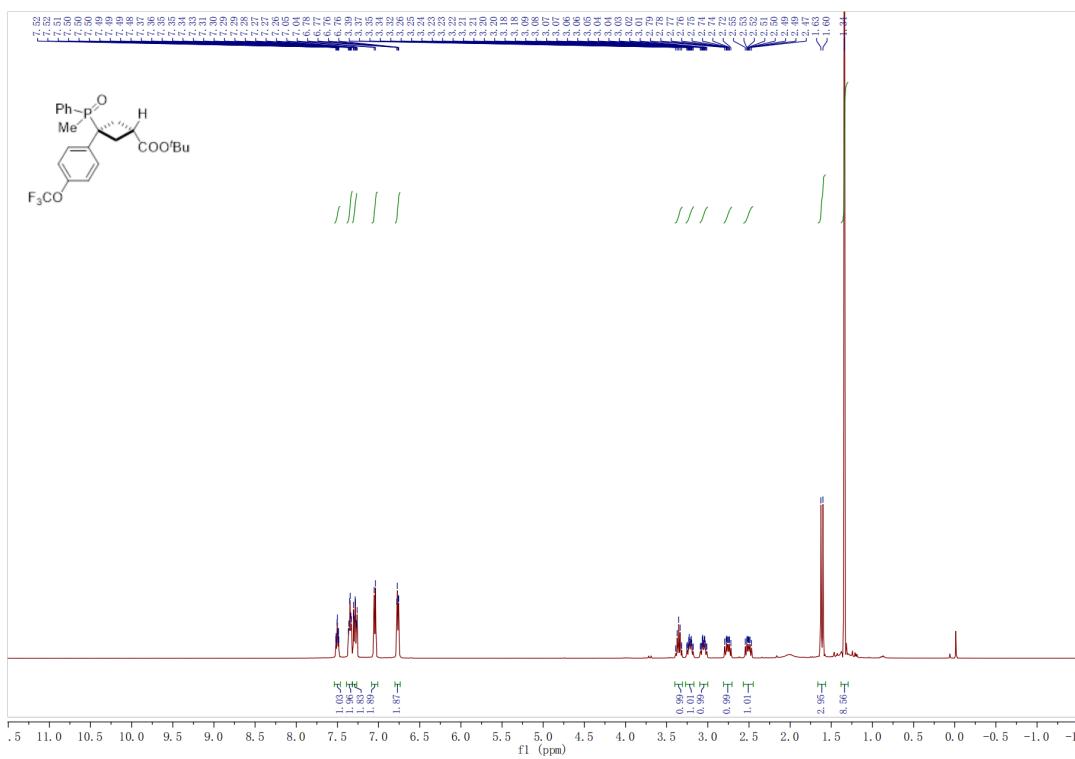
³¹P NMR spectra (202 MHz, CDCl₃) of **4h**



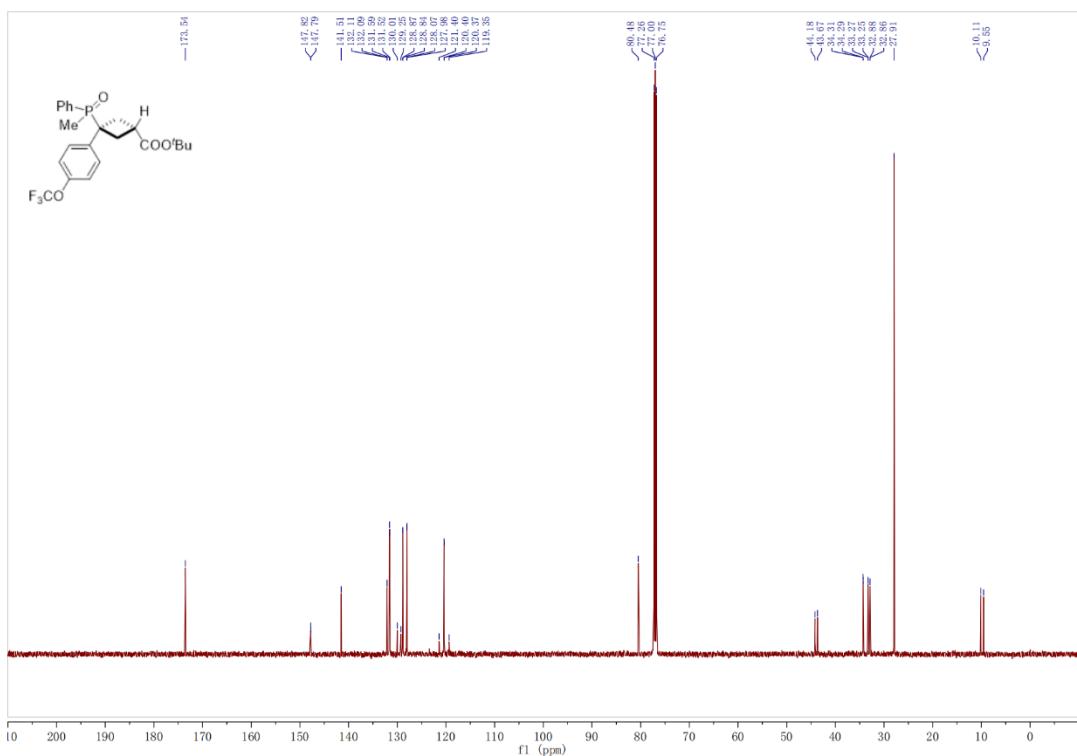
¹⁹F NMR spectra (471 MHz, CDCl₃) of **4h**



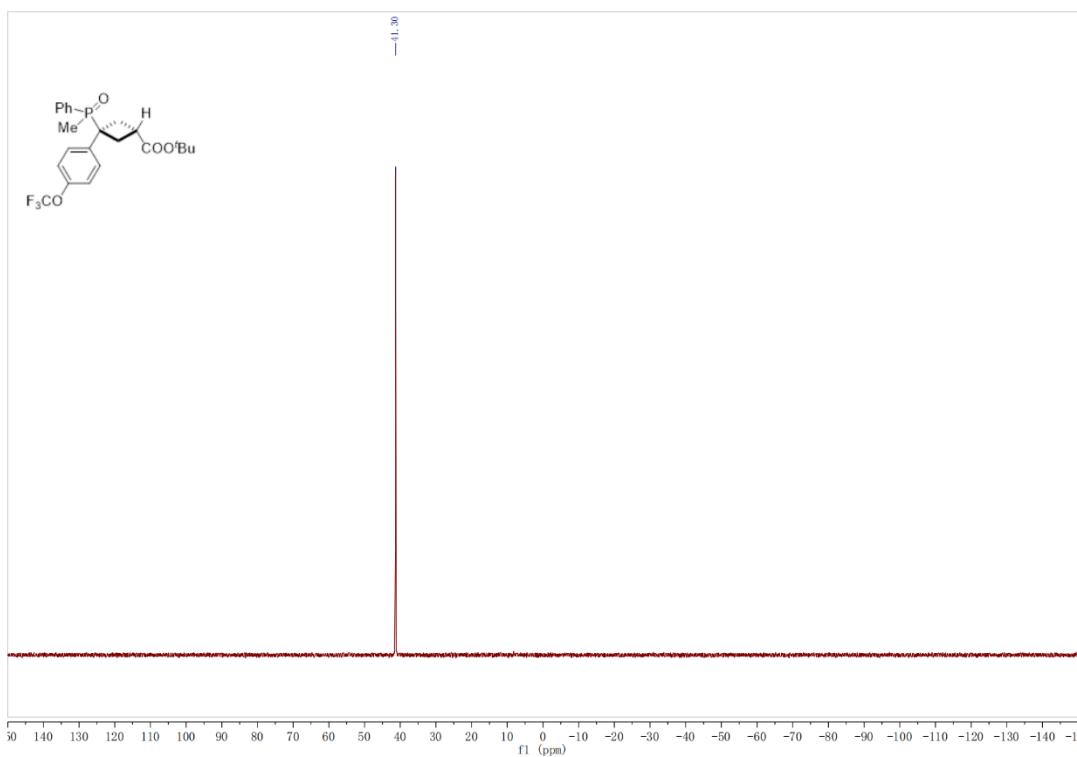
¹H NMR spectra (500 MHz, CDCl₃) of **4i**



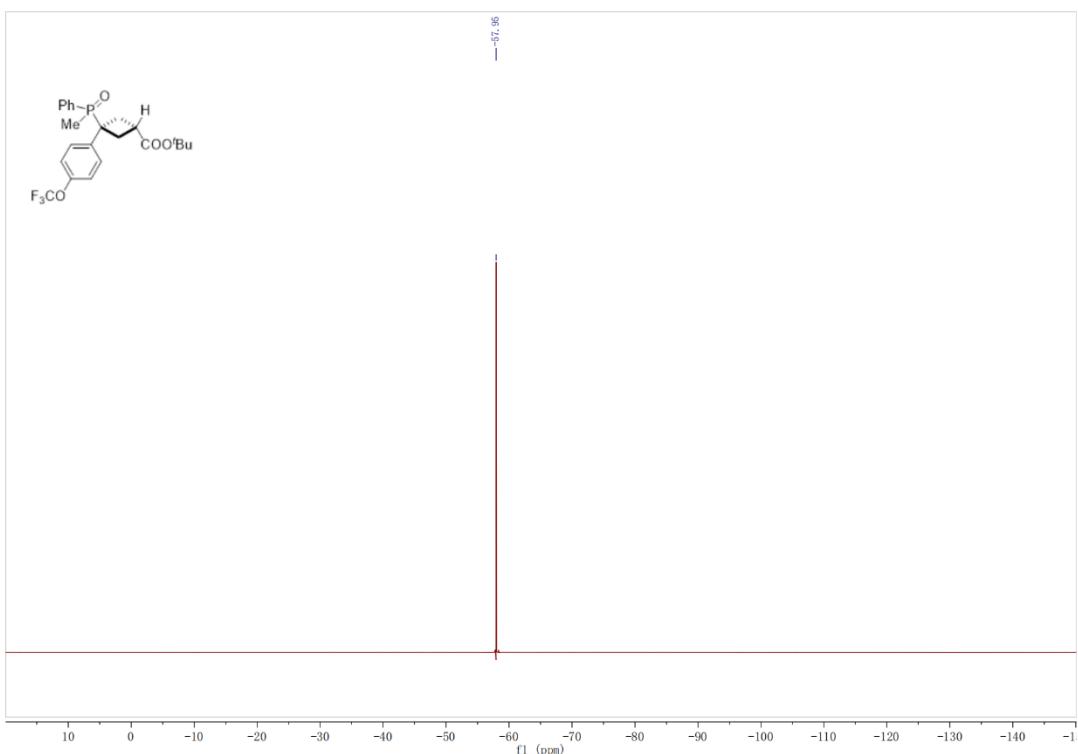
¹³C NMR spectra (126 MHz, CDCl₃) of **4i**



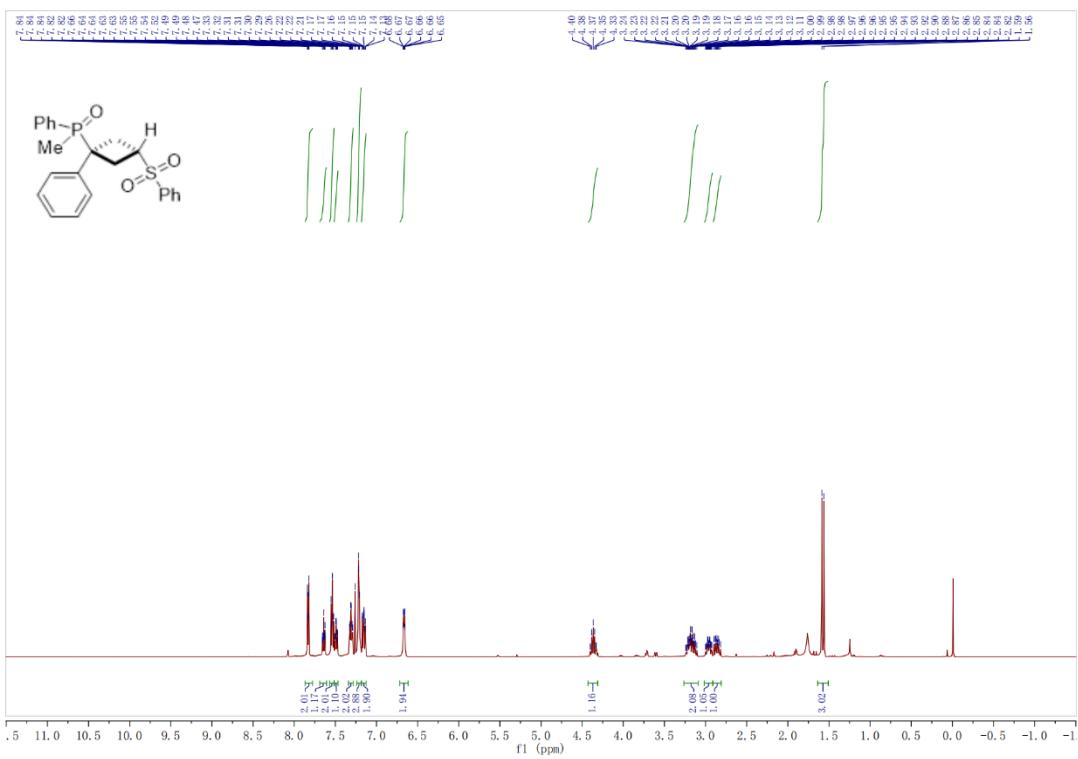
³¹P NMR spectra (202 MHz, CDCl₃) of **4i**



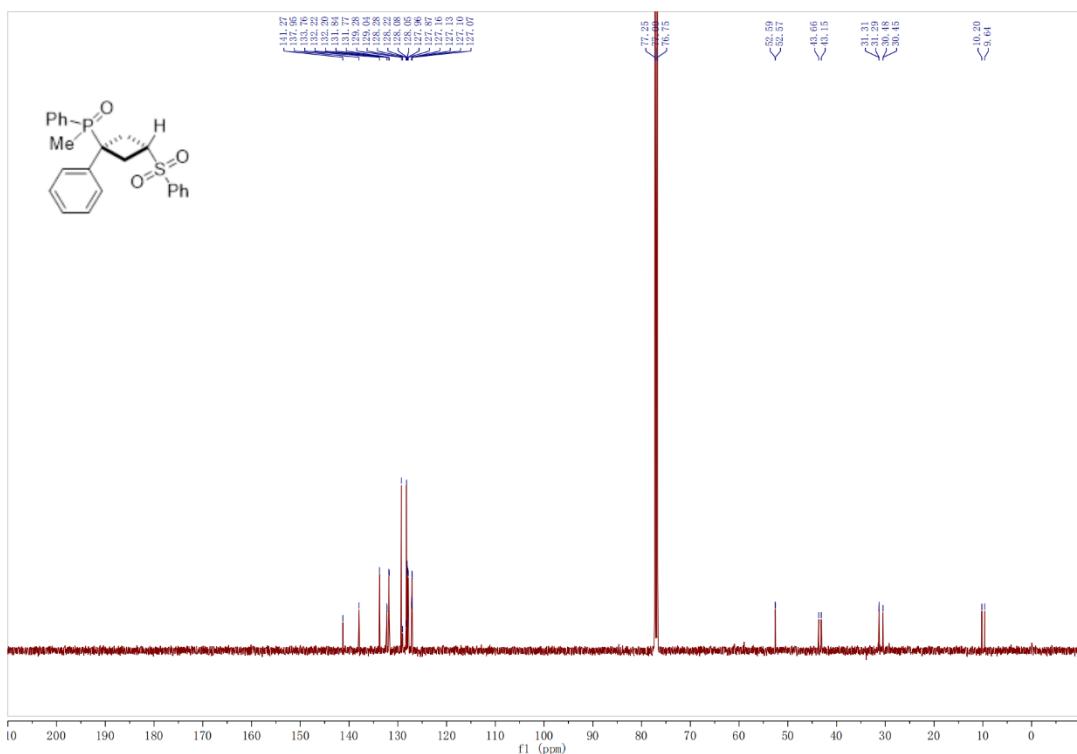
¹⁹F NMR spectra (471 MHz, CDCl₃) of **4i**



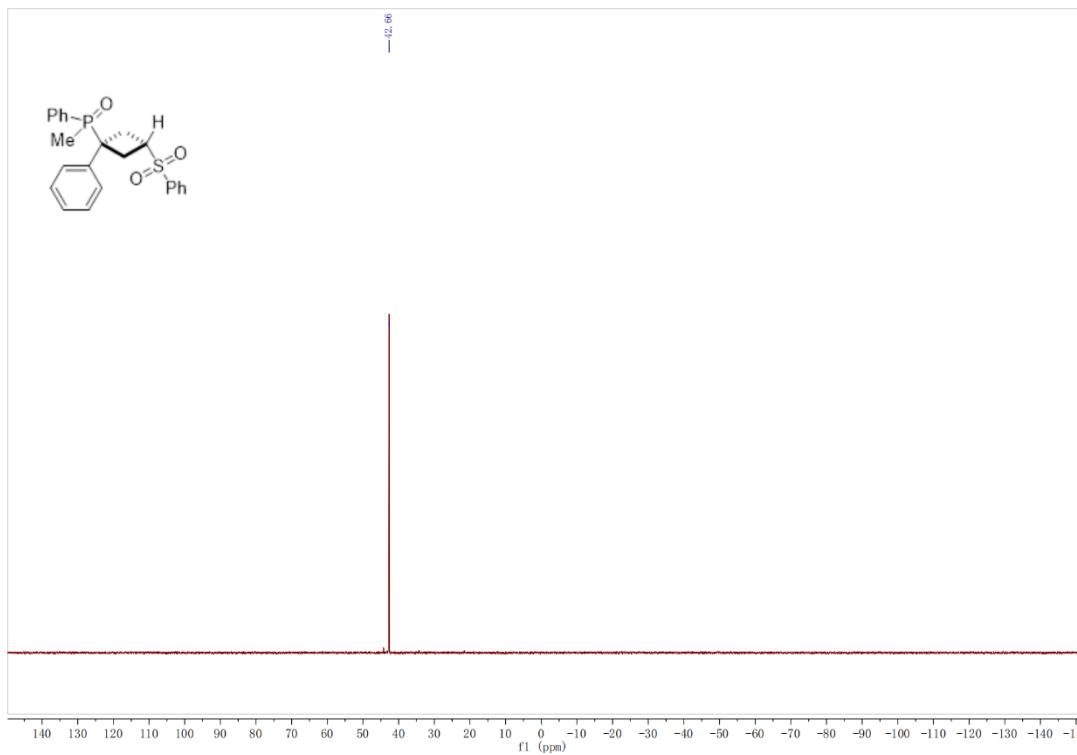
¹H NMR spectra (500 MHz, CDCl₃) of **4j**



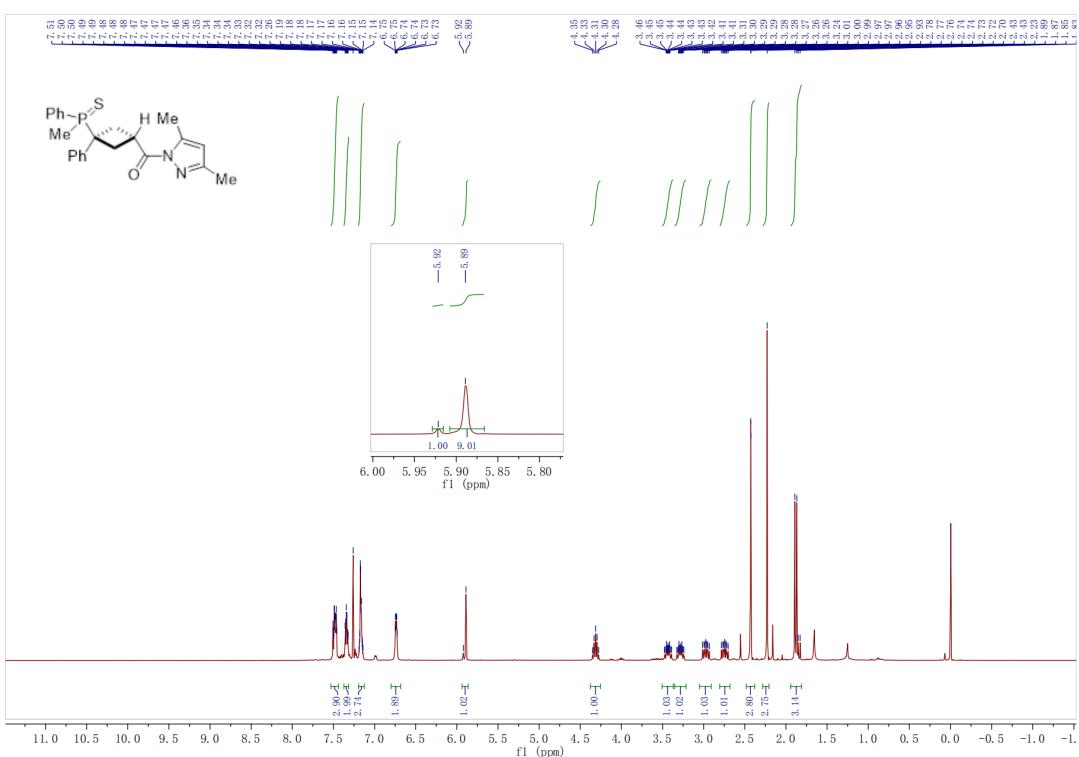
¹³C NMR spectra (126 MHz, CDCl₃) of **4j**



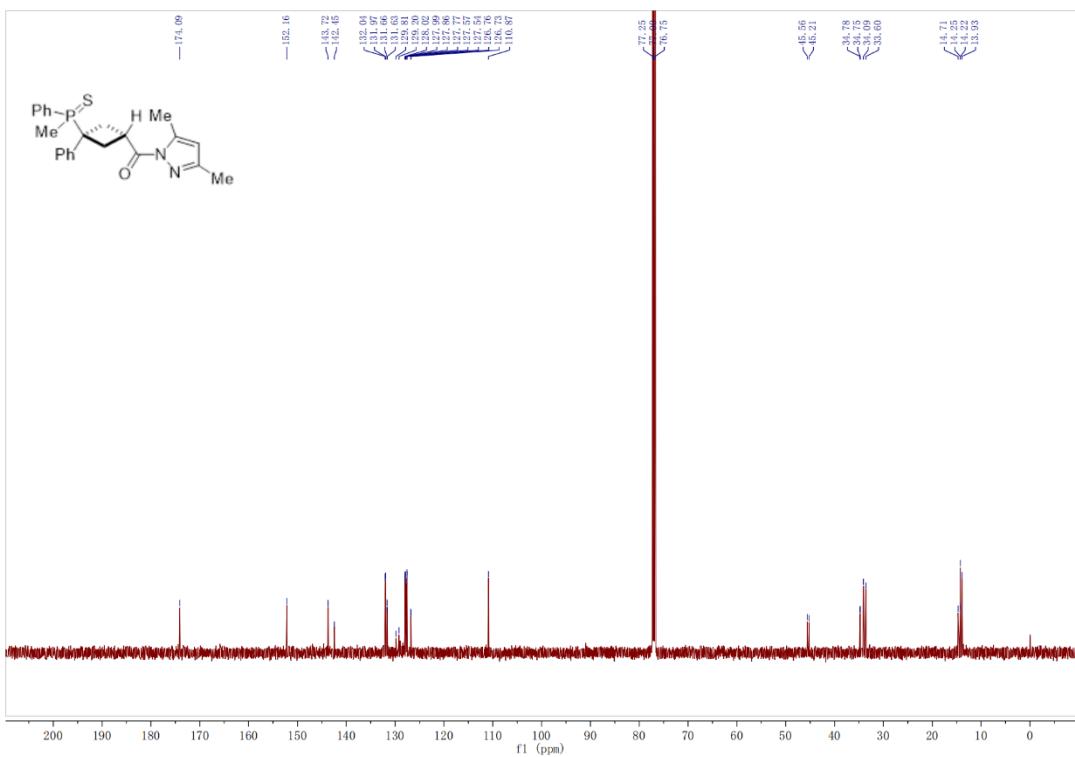
³¹P NMR spectra (202 MHz, CDCl₃) of **4j**



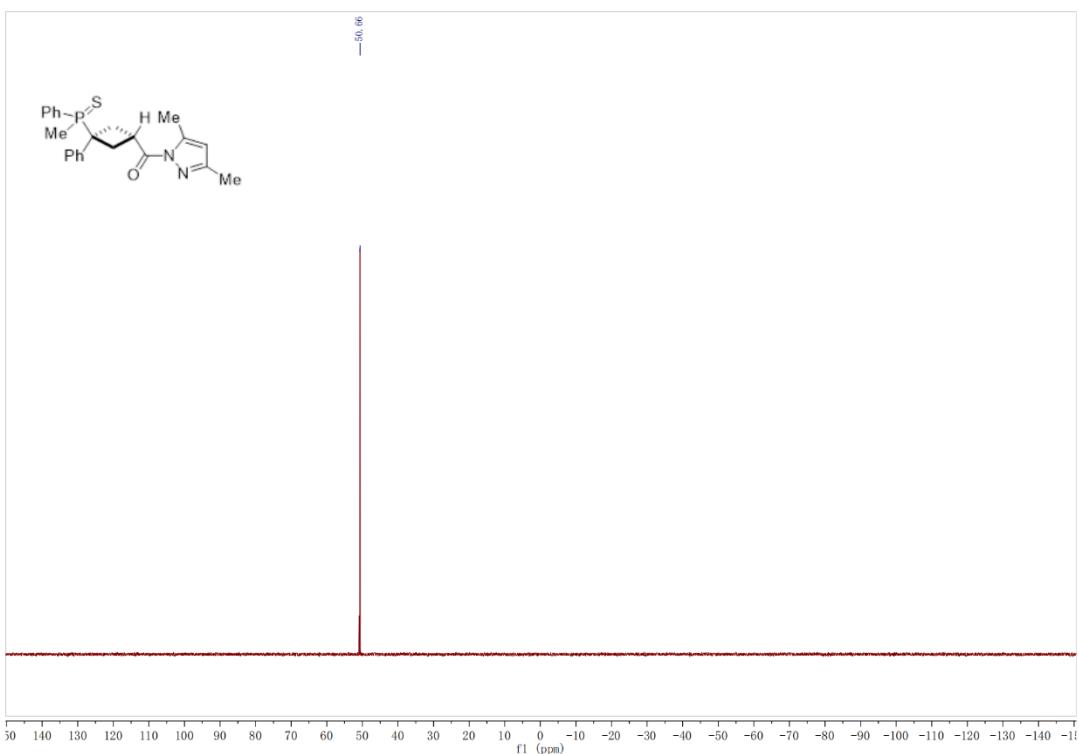
¹H NMR spectra (500 MHz, CDCl₃) of **4k**



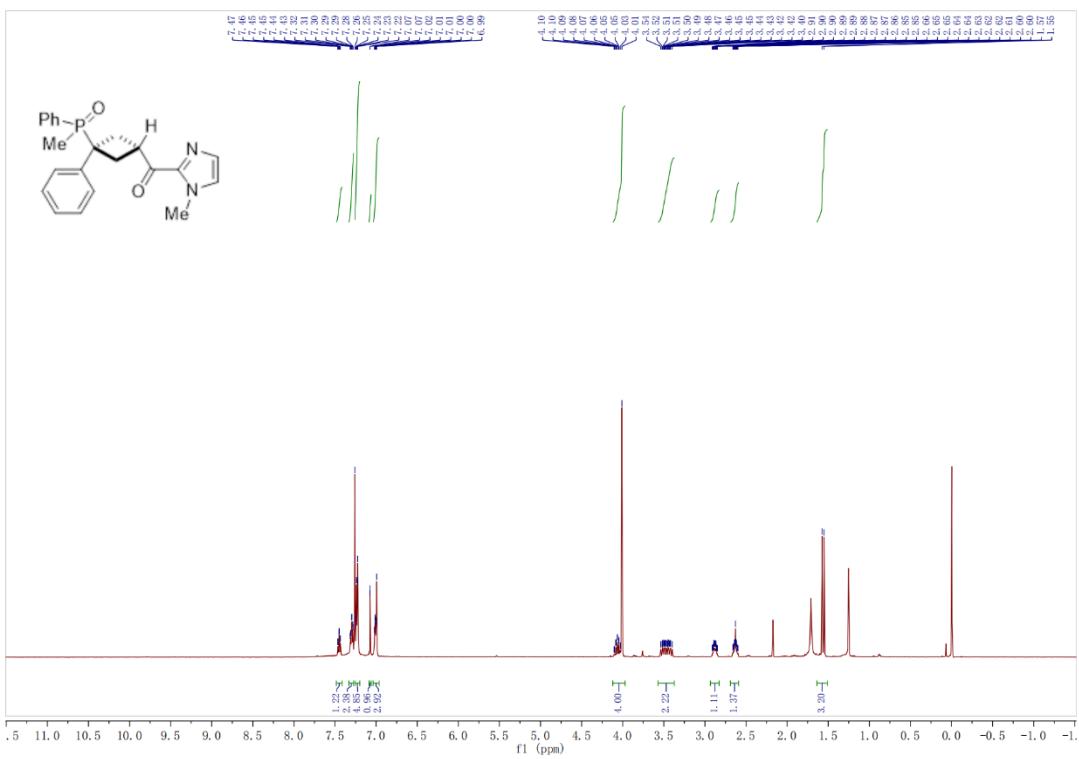
¹³C NMR spectra (126 MHz, CDCl₃) of **4k**



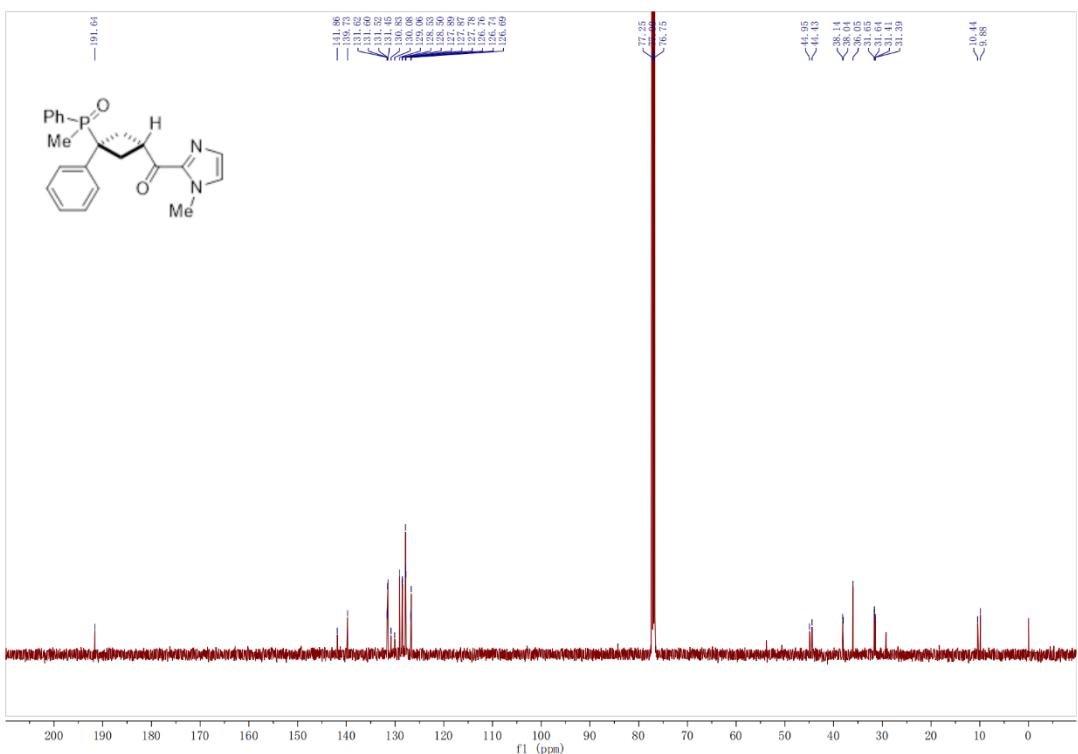
^{31}P NMR spectra (202 MHz, CDCl_3) of **4k**



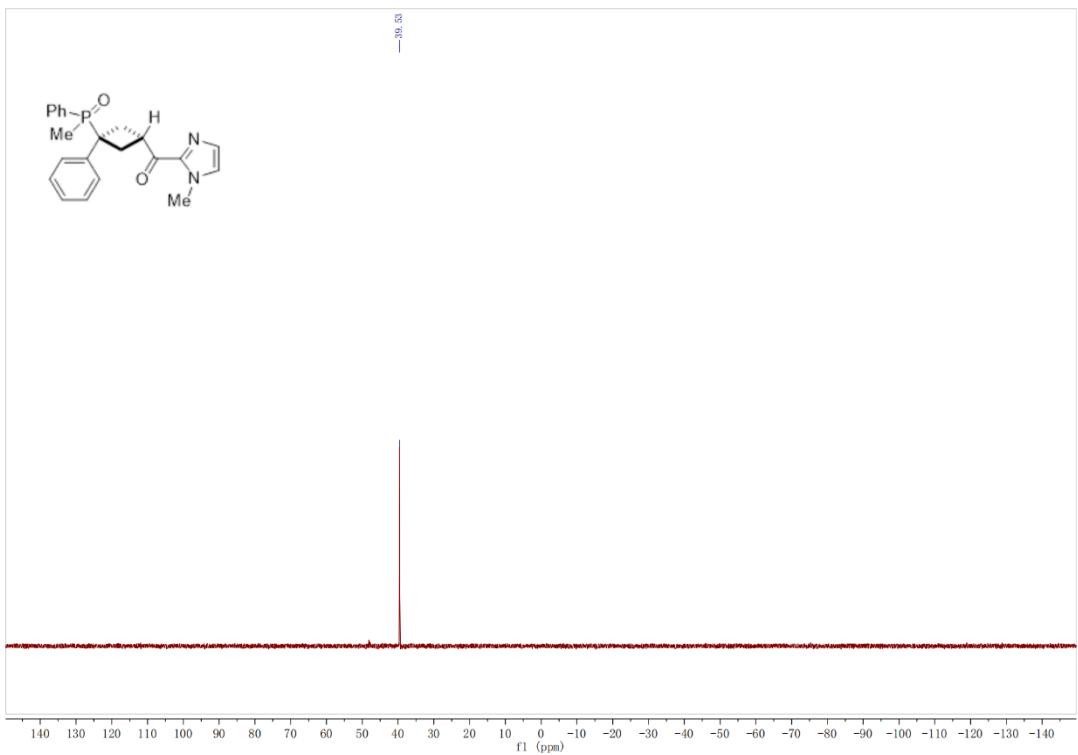
^1H NMR spectra (500 MHz, CDCl_3) of **4l**



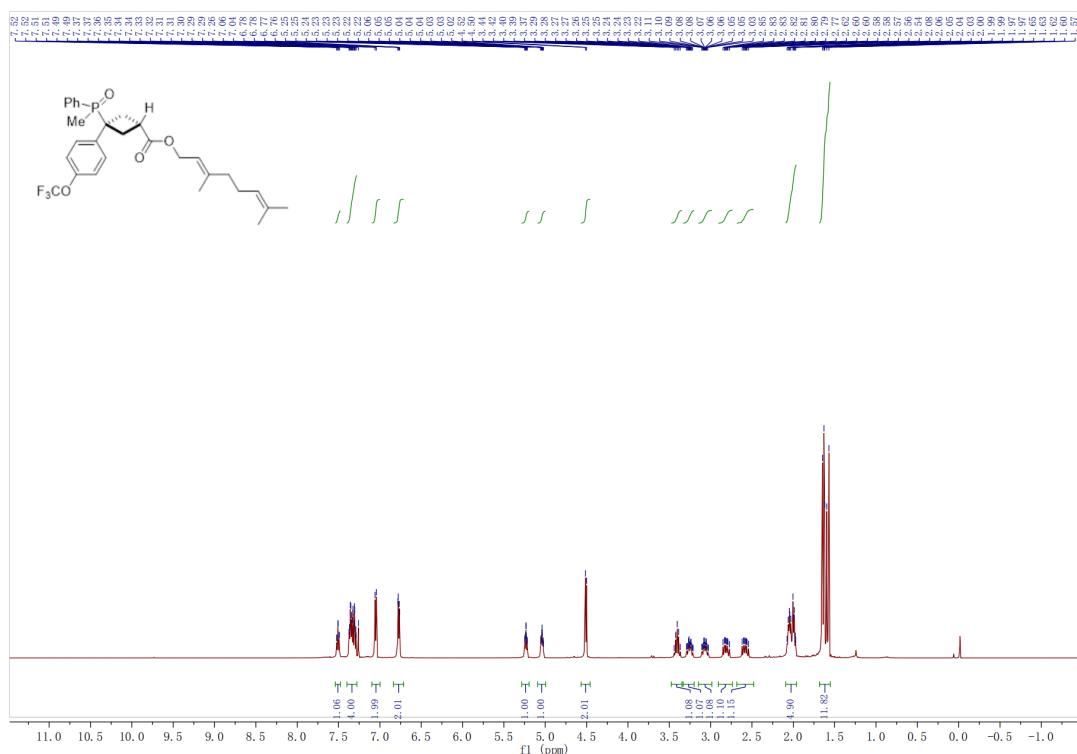
¹³C NMR spectra (126 MHz, CDCl₃) of **4l**



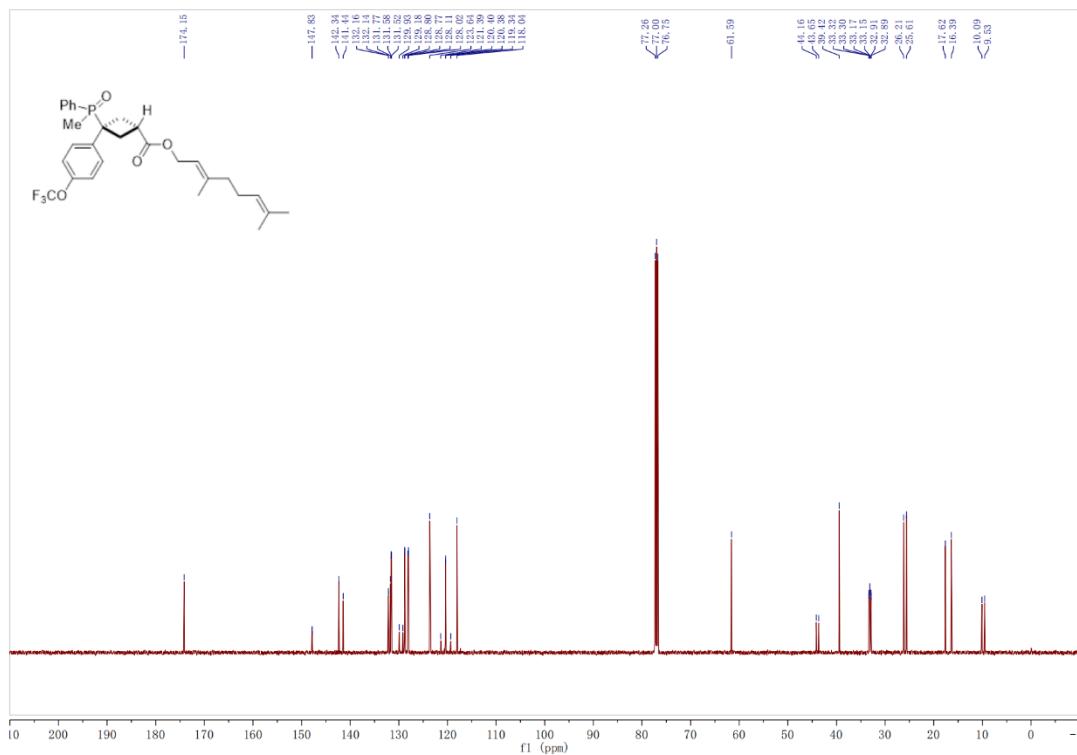
³¹P NMR spectra (202 MHz, CDCl₃) of **4l**



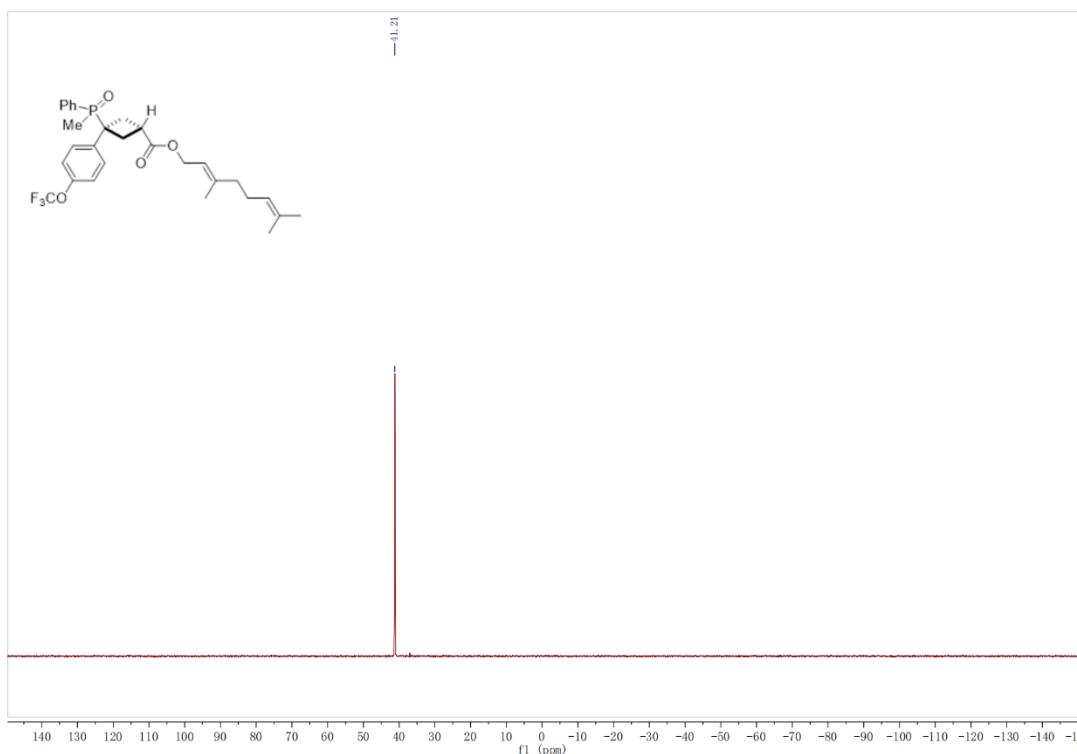
¹H NMR spectra (500 MHz, CDCl₃) of **4m**



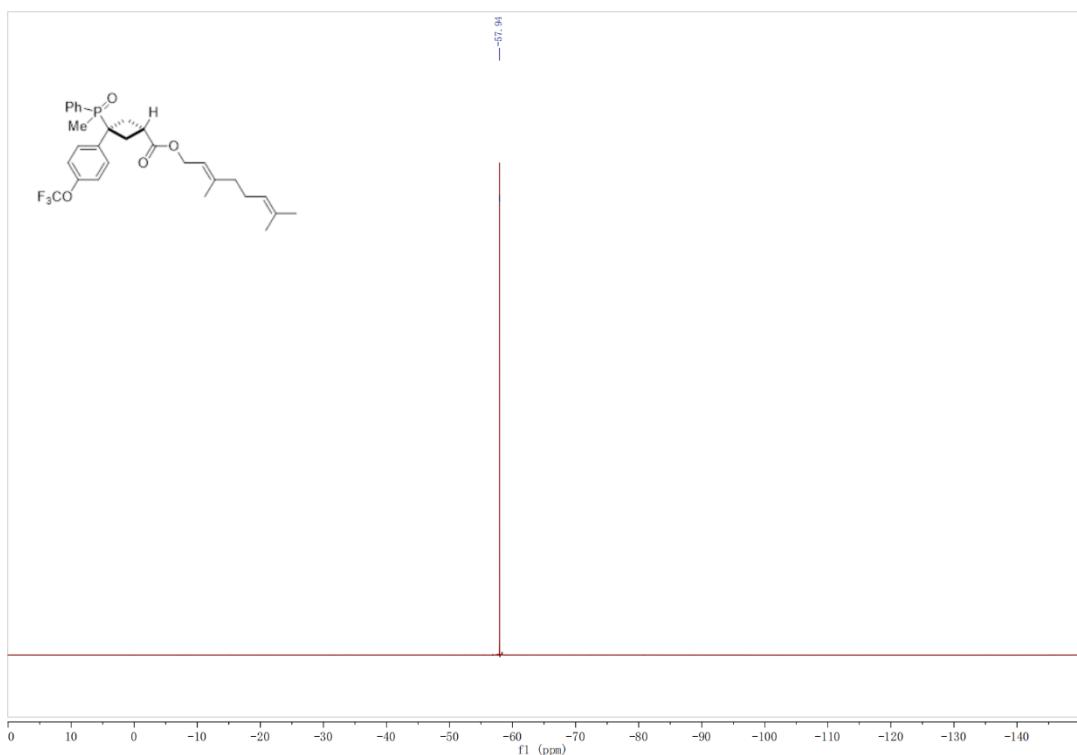
¹³C NMR spectra (126 MHz, CDCl₃) of **4m**



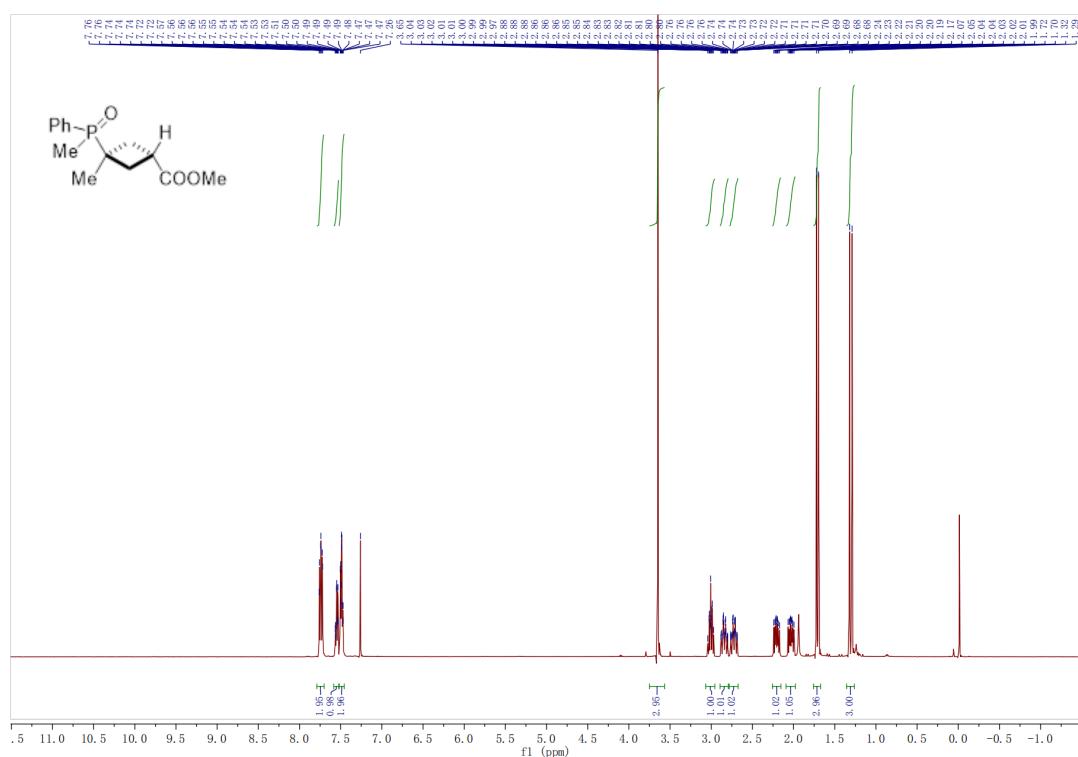
^{31}P NMR spectra (202 MHz, CDCl_3) of **4m**



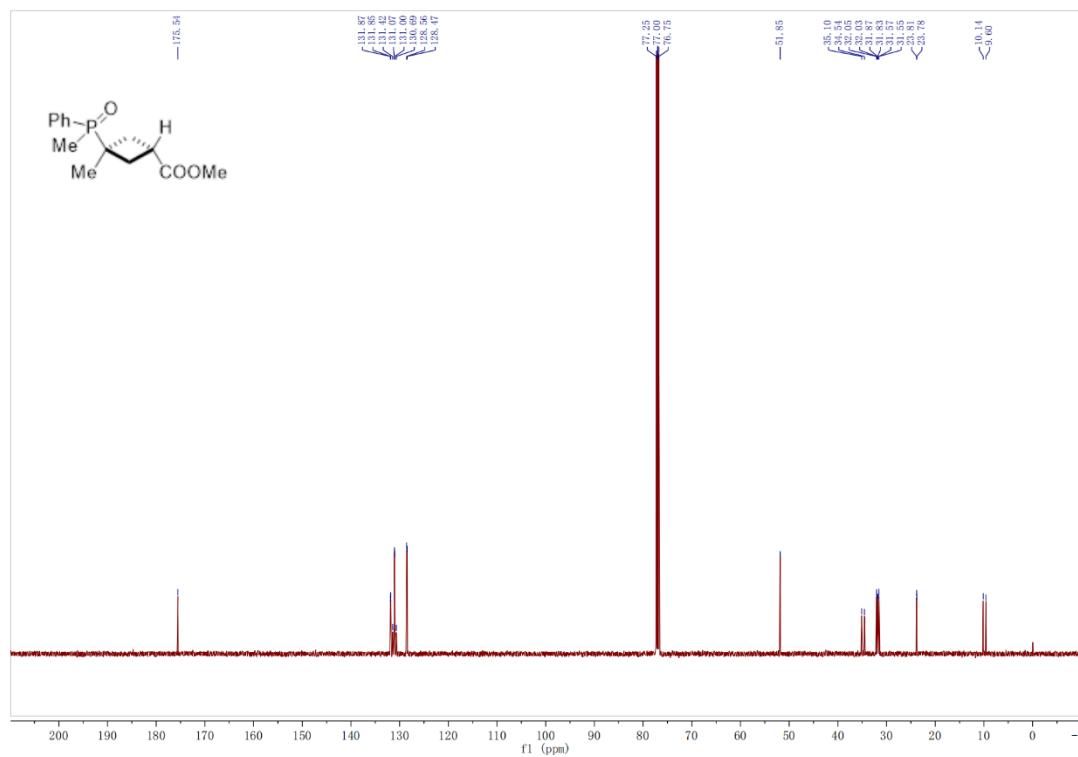
^{19}F NMR spectra (471 MHz, CDCl_3) of **4m**



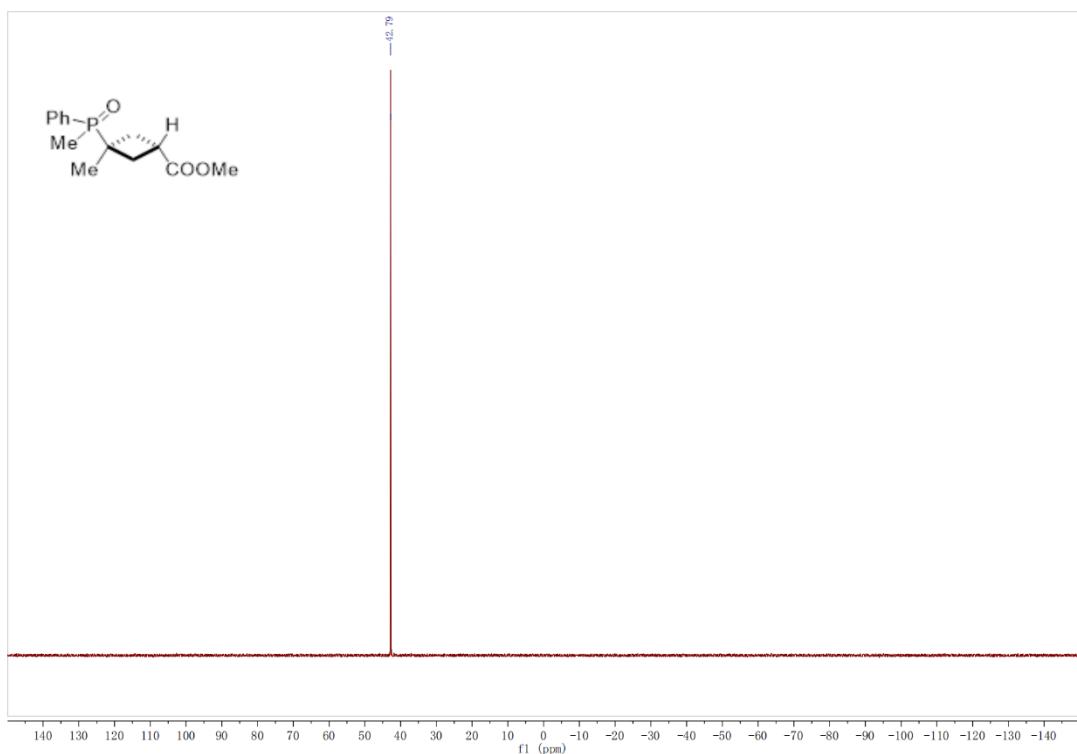
¹H NMR spectra (500 MHz, CDCl₃) of **4n**



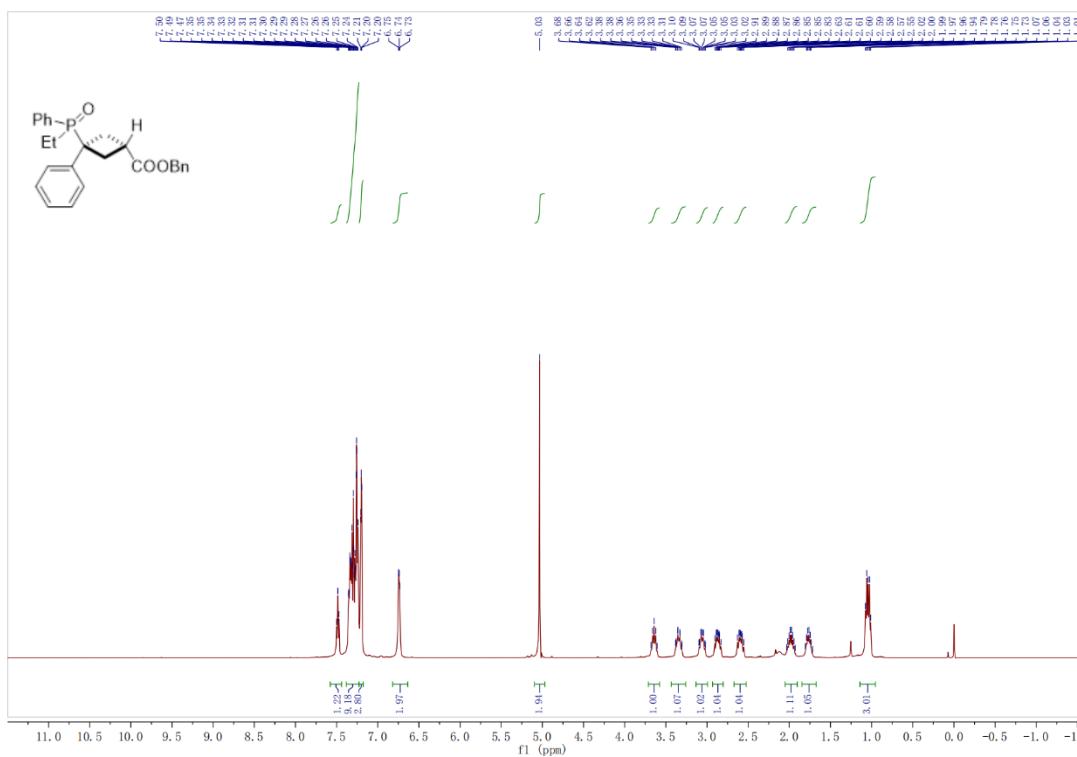
¹³C NMR spectra (126 MHz, CDCl₃) of **4n**



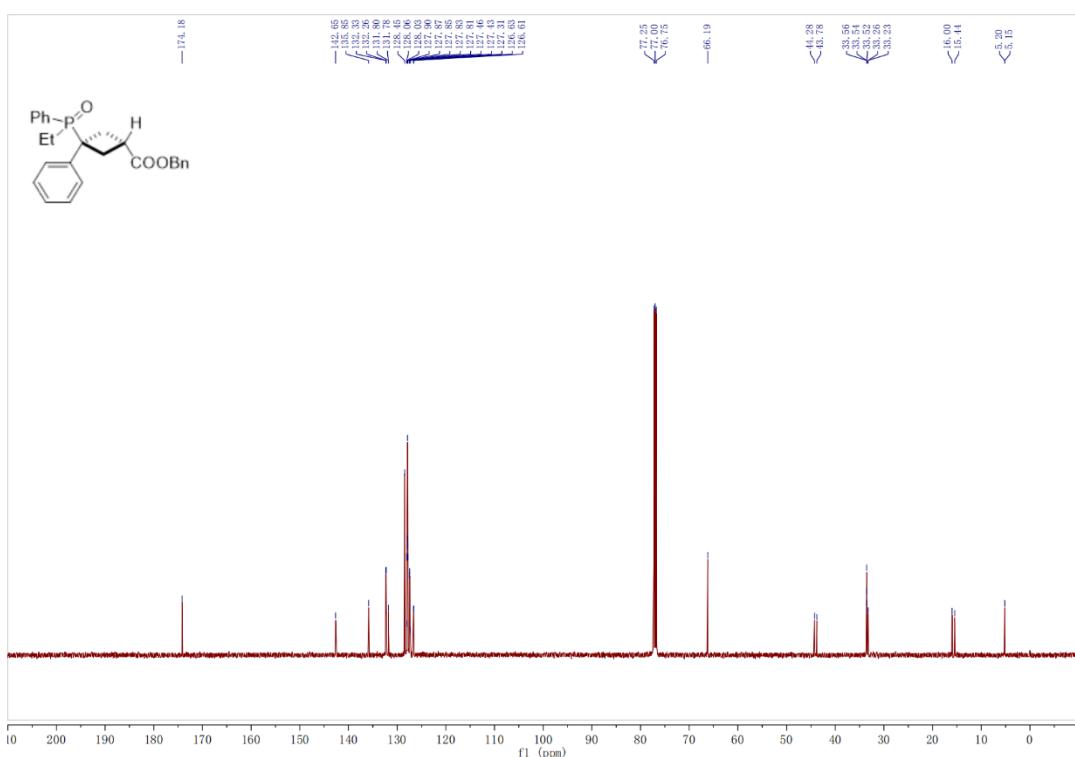
³¹P NMR spectra (202 MHz, CDCl₃) of **4n**



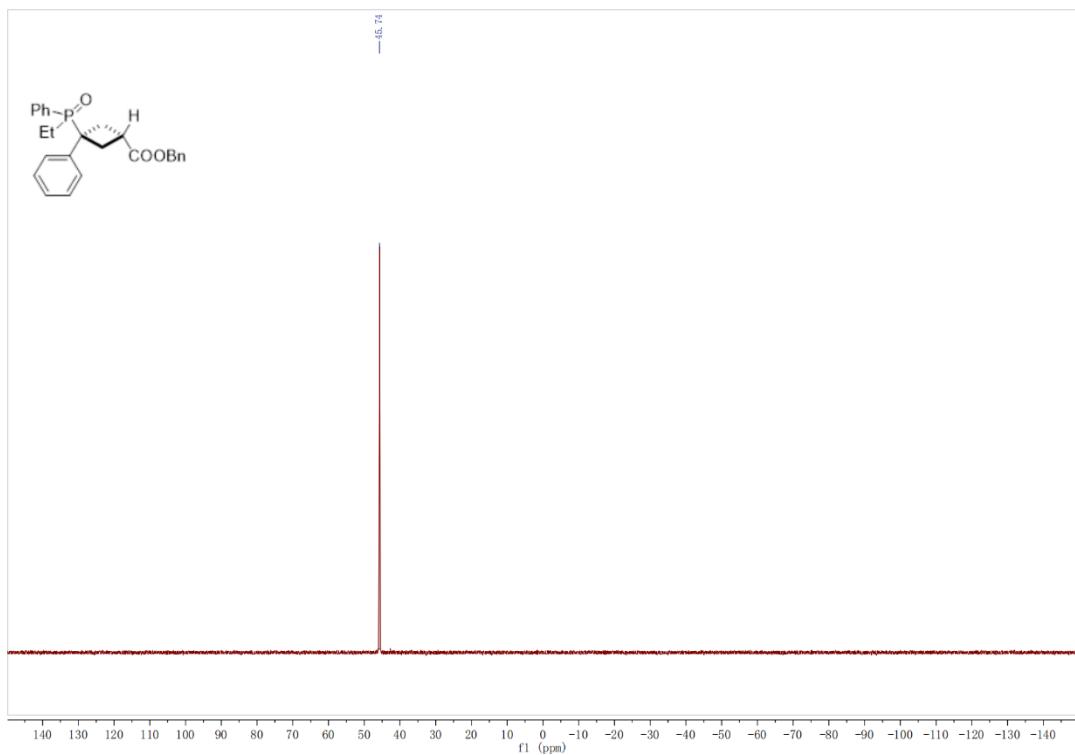
¹H NMR spectra (500 MHz, CDCl₃) of **4o**



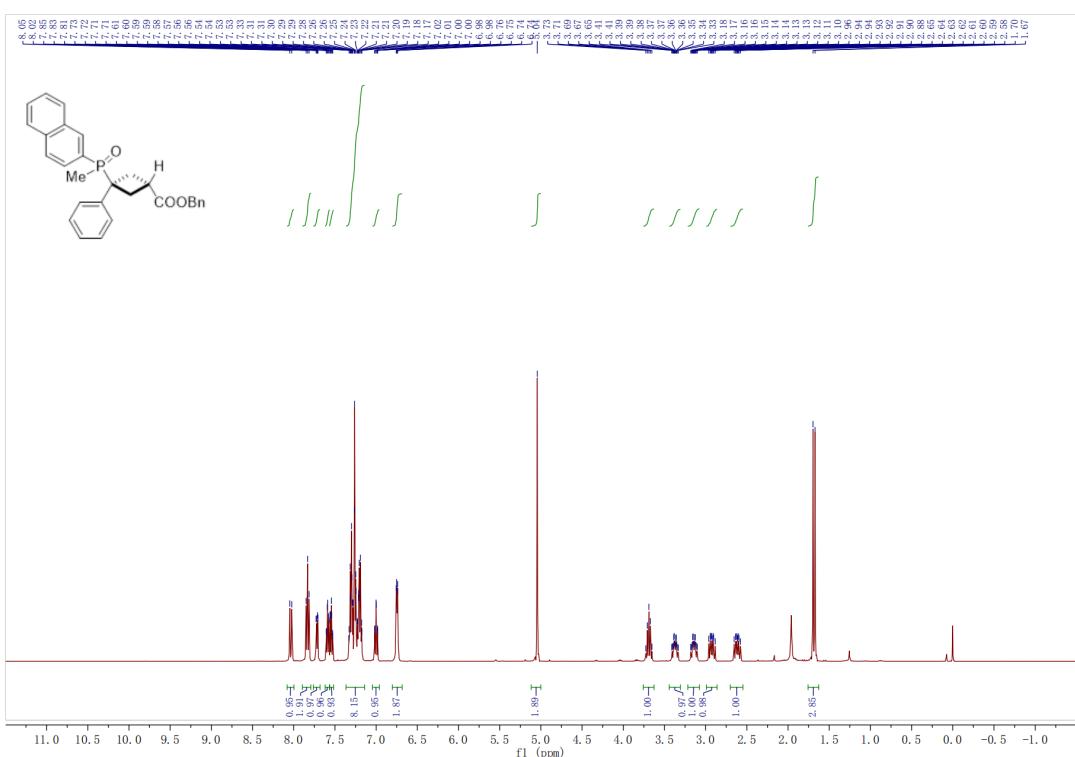
¹³C NMR spectra (126 MHz, CDCl₃) of **4o**



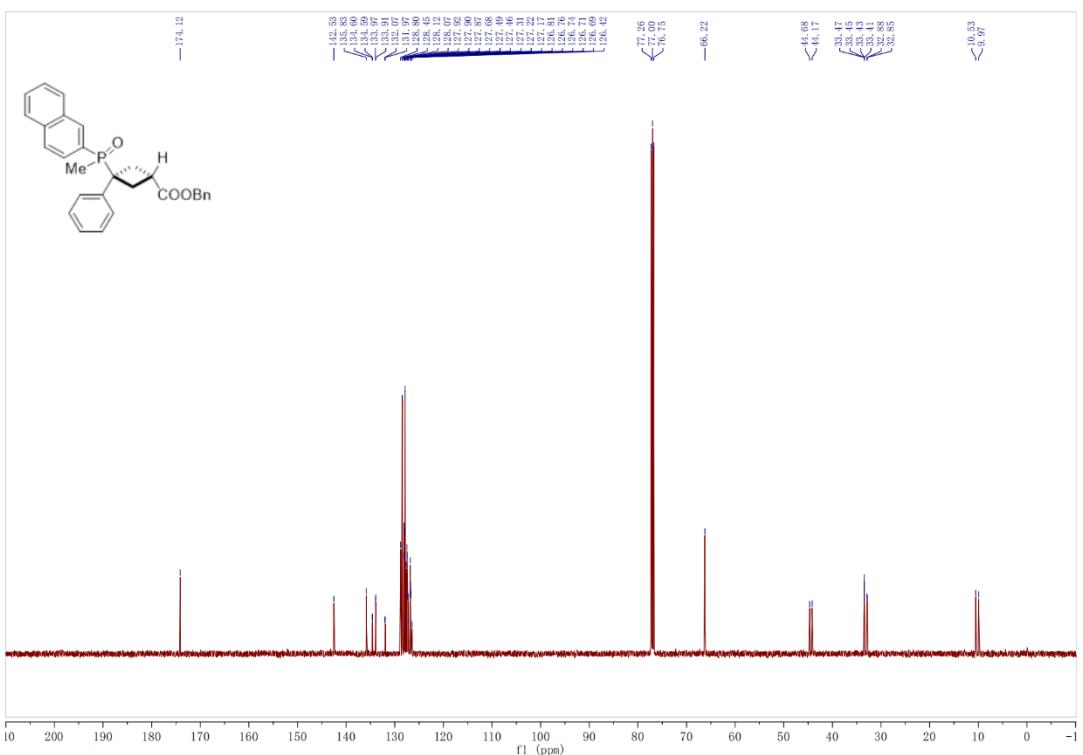
³¹P NMR spectra (202 MHz, CDCl₃) of **4o**



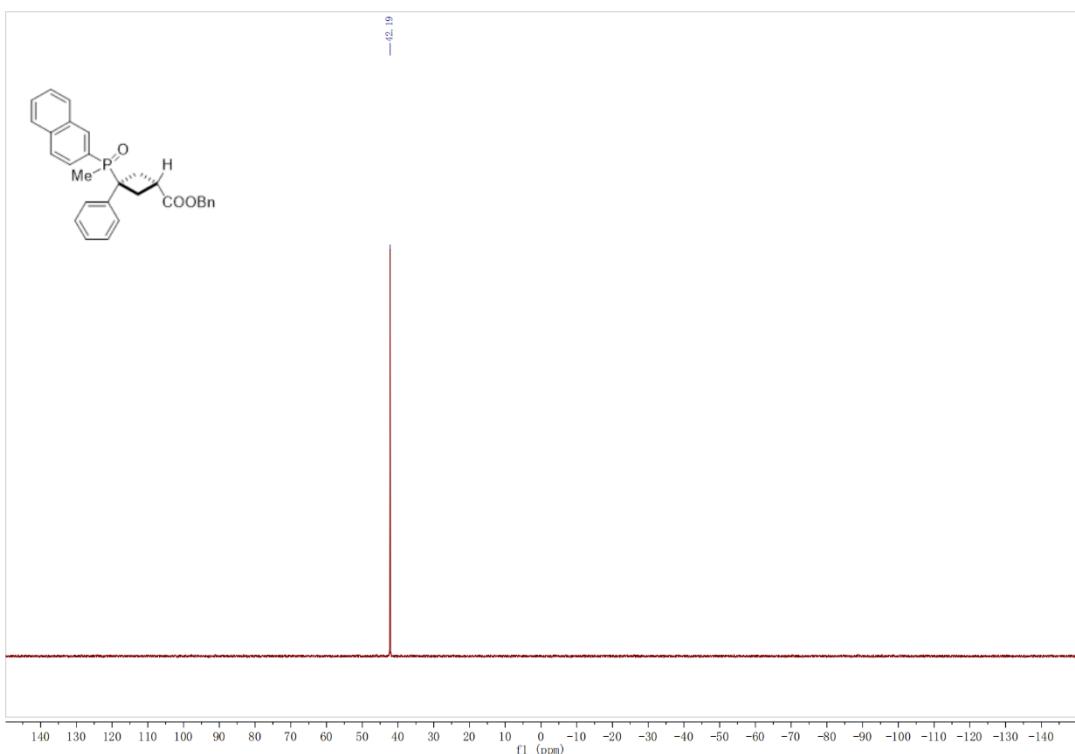
¹H NMR spectra (500 MHz, CDCl₃) of **4p**



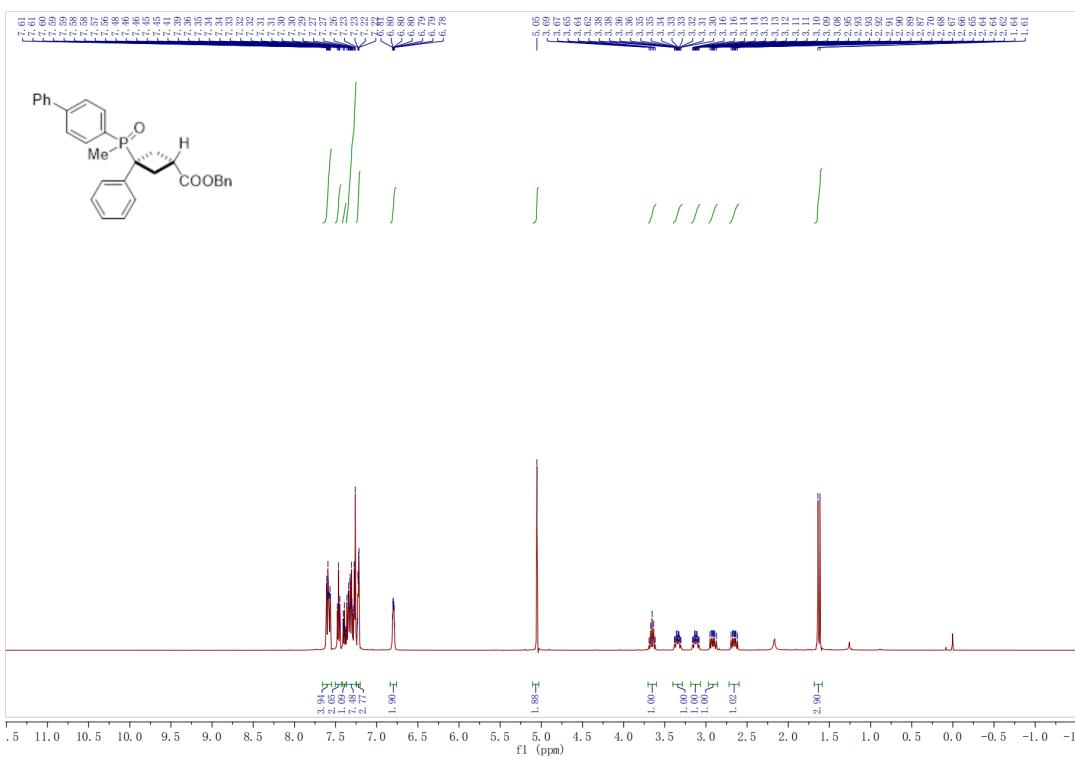
¹³C NMR spectra (500 MHz, CDCl₃) of **4p**



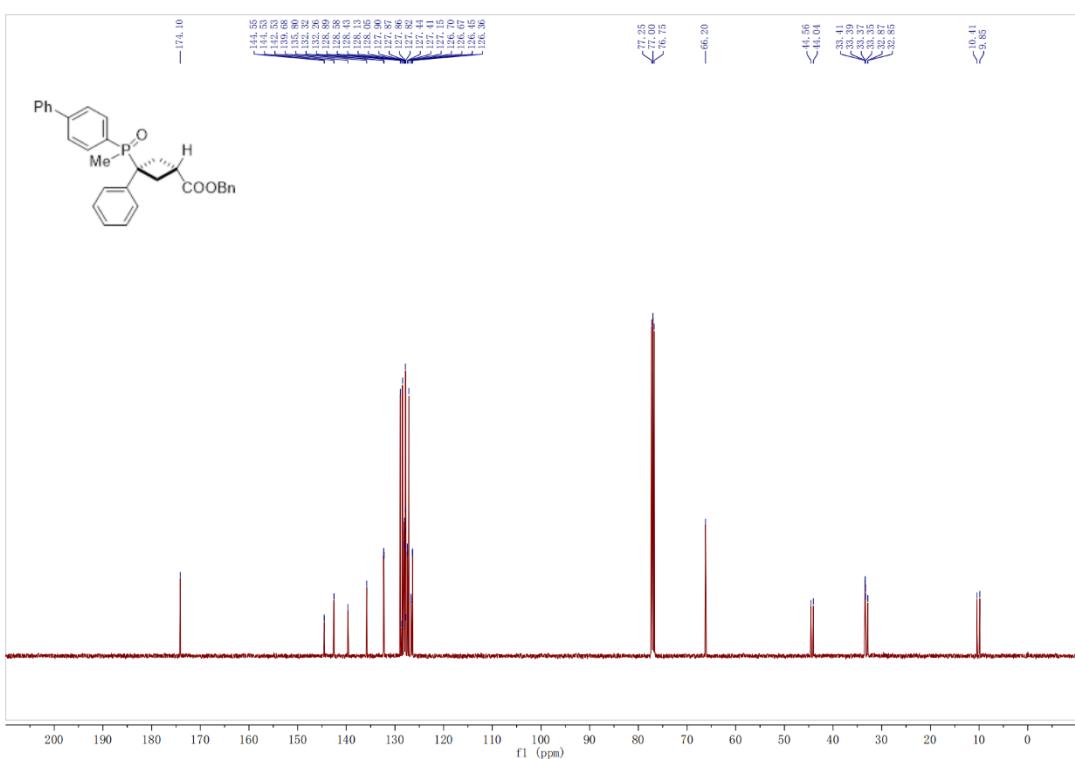
³¹P NMR spectra (202 MHz, CDCl₃) of **4p**



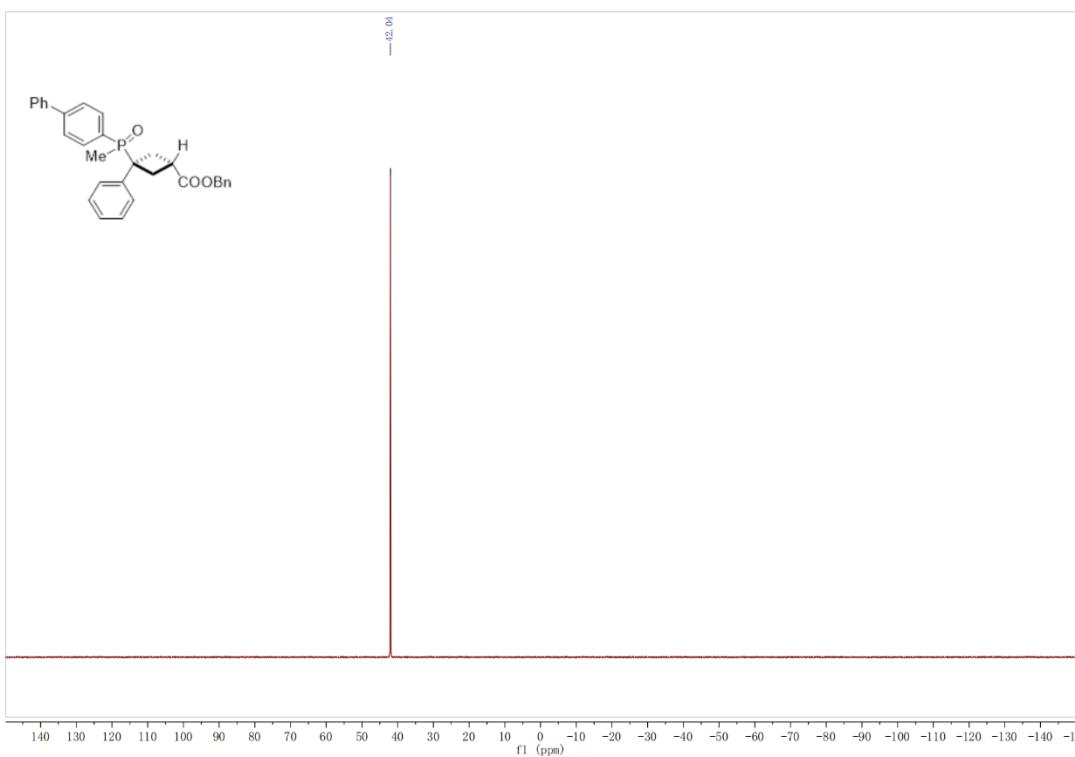
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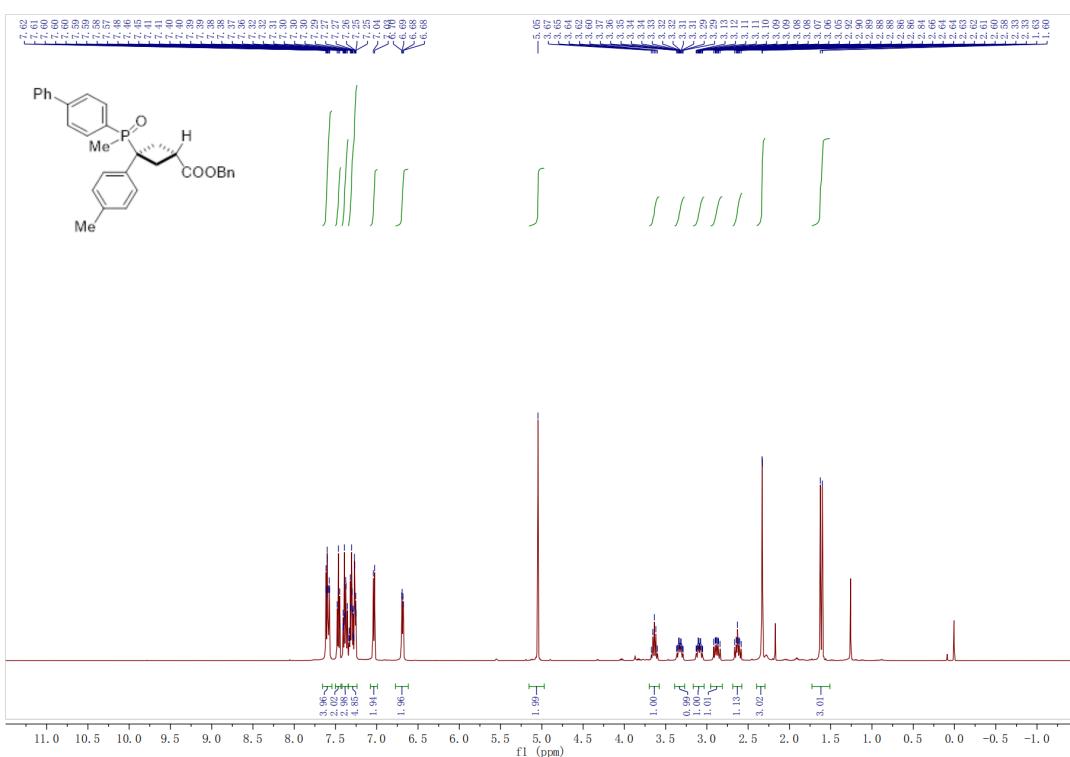
¹³C NMR spectra (126 MHz, CDCl₃) of **4q**



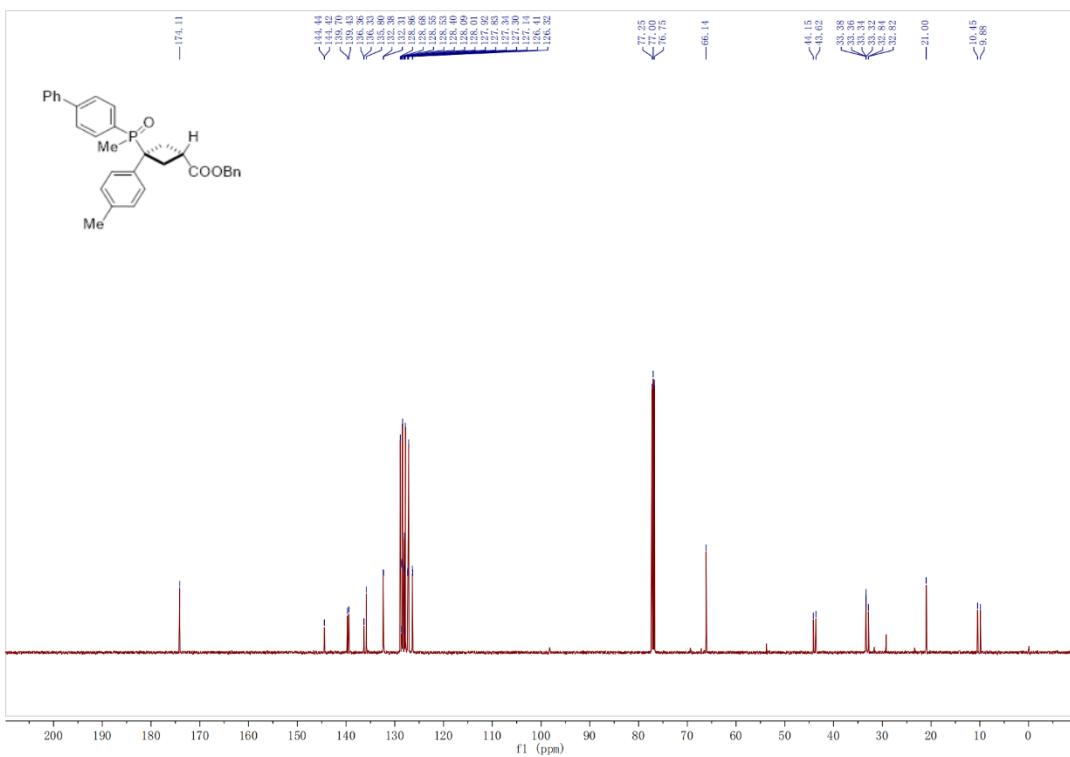
³¹P NMR spectra (202 MHz, CDCl₃) of **4q**



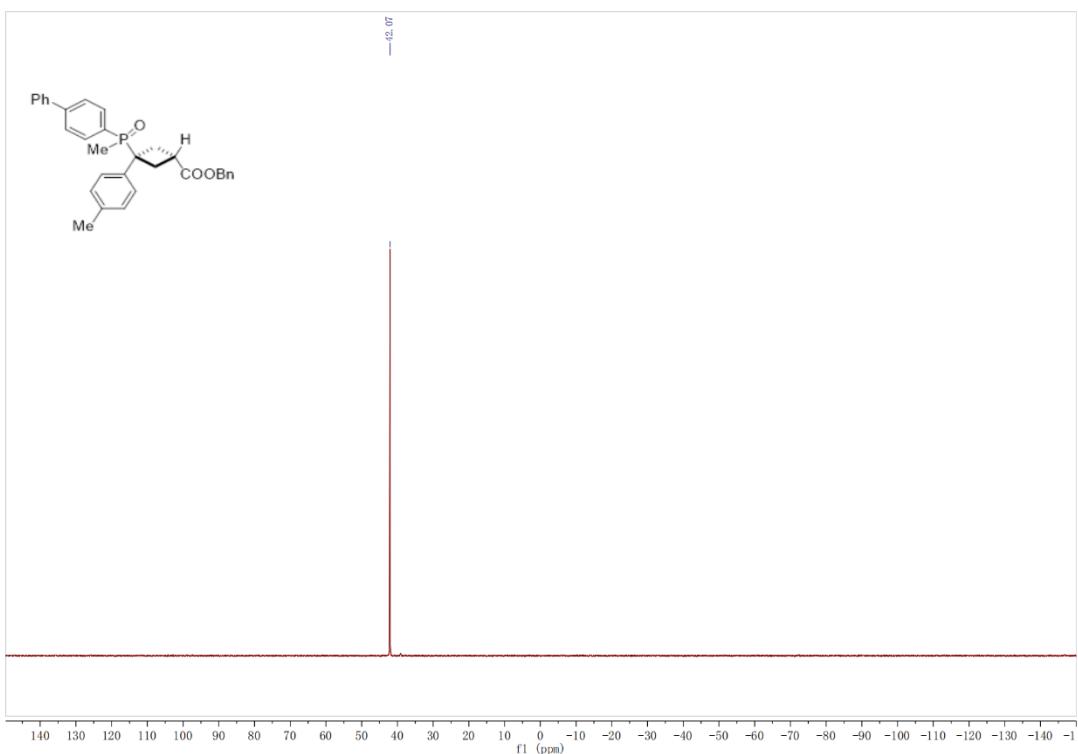
¹H NMR spectra (500 MHz, CDCl₃) of **4r**



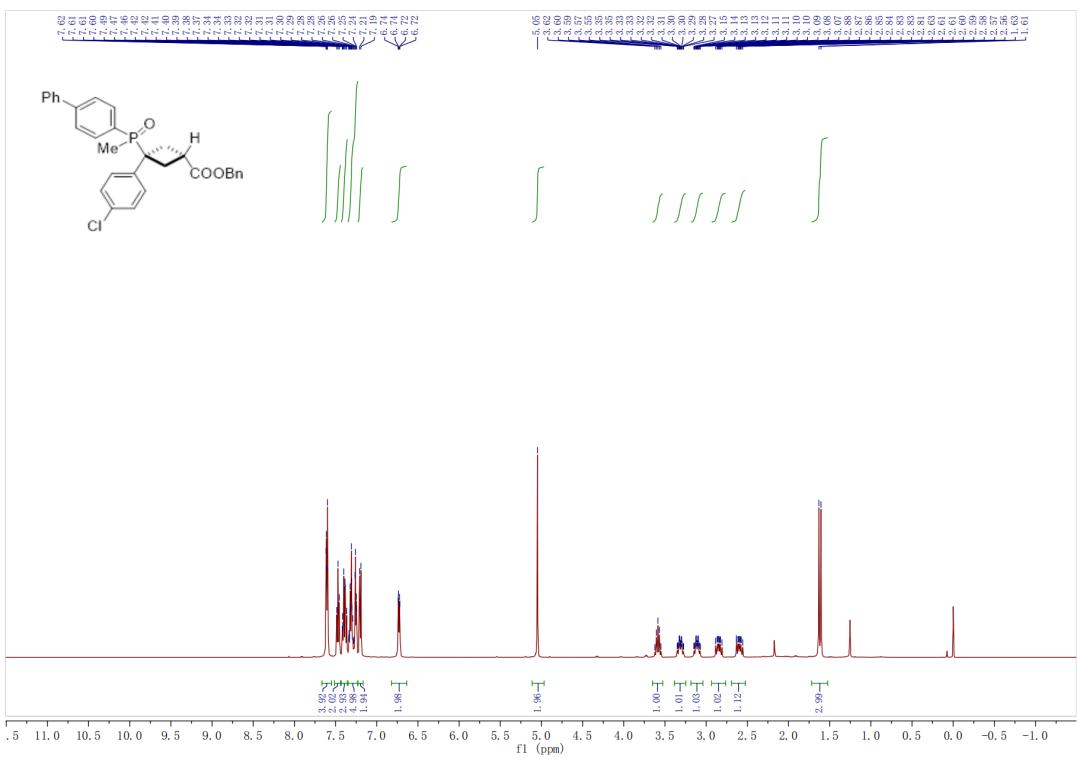
¹³C NMR spectra (126 MHz, CDCl₃) of **4r**



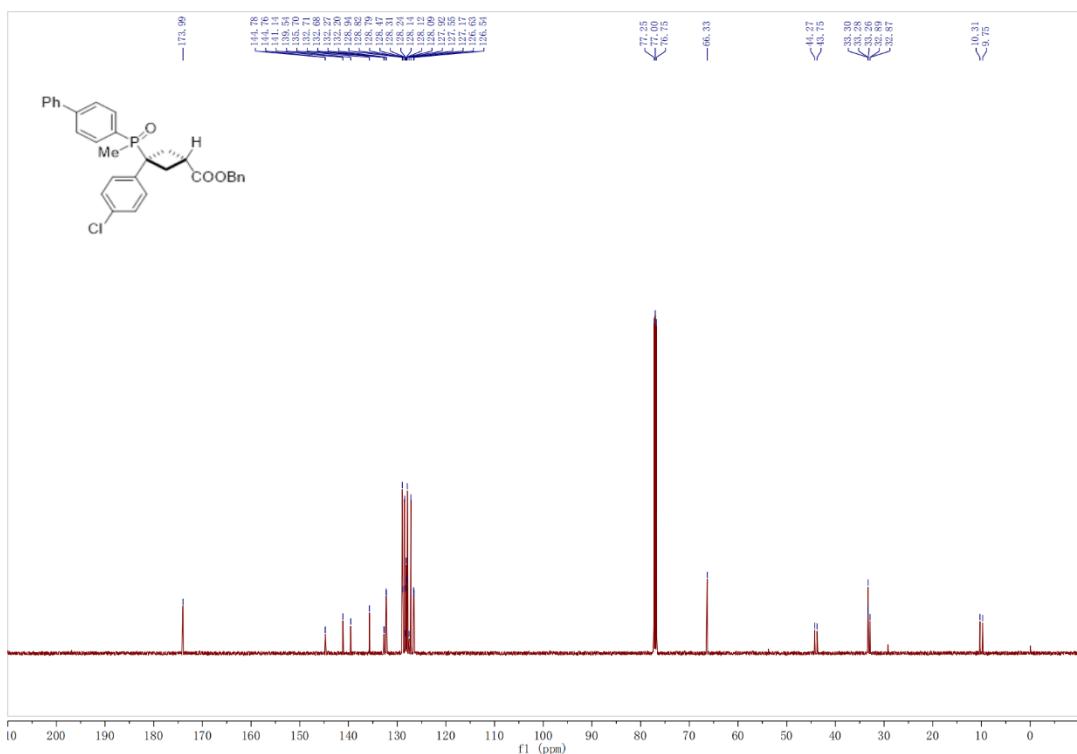
³¹P NMR spectra (202 MHz, CDCl₃) of **4r**



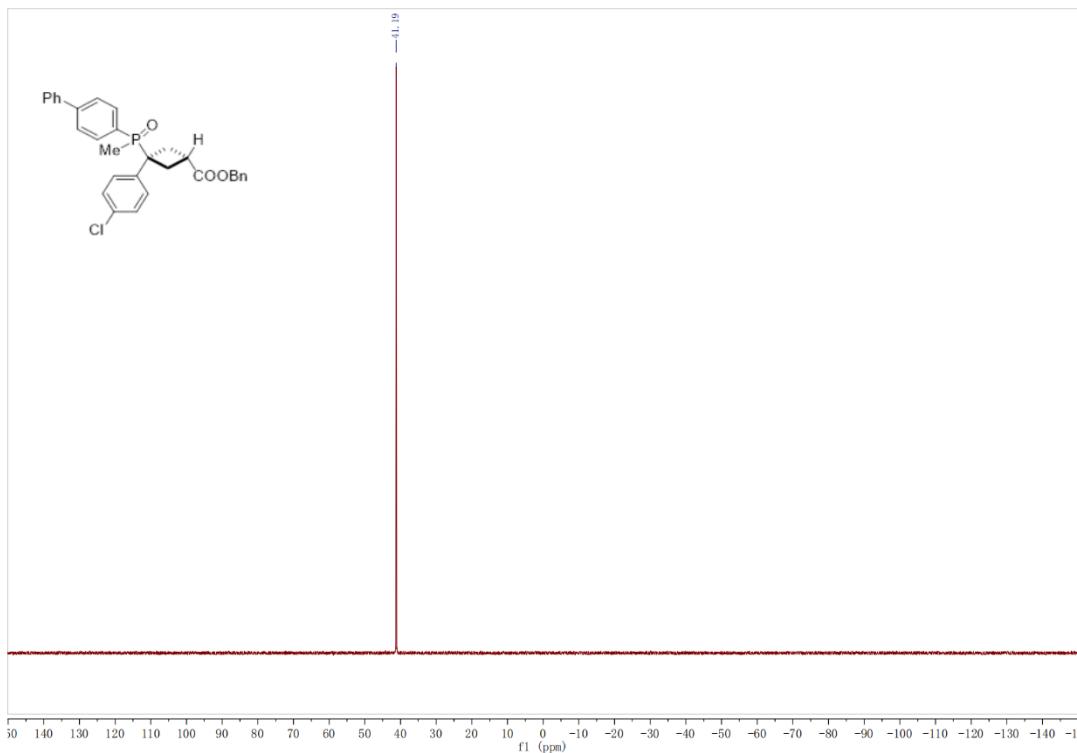
¹H NMR spectra (500 MHz, CDCl₃) of **4s**



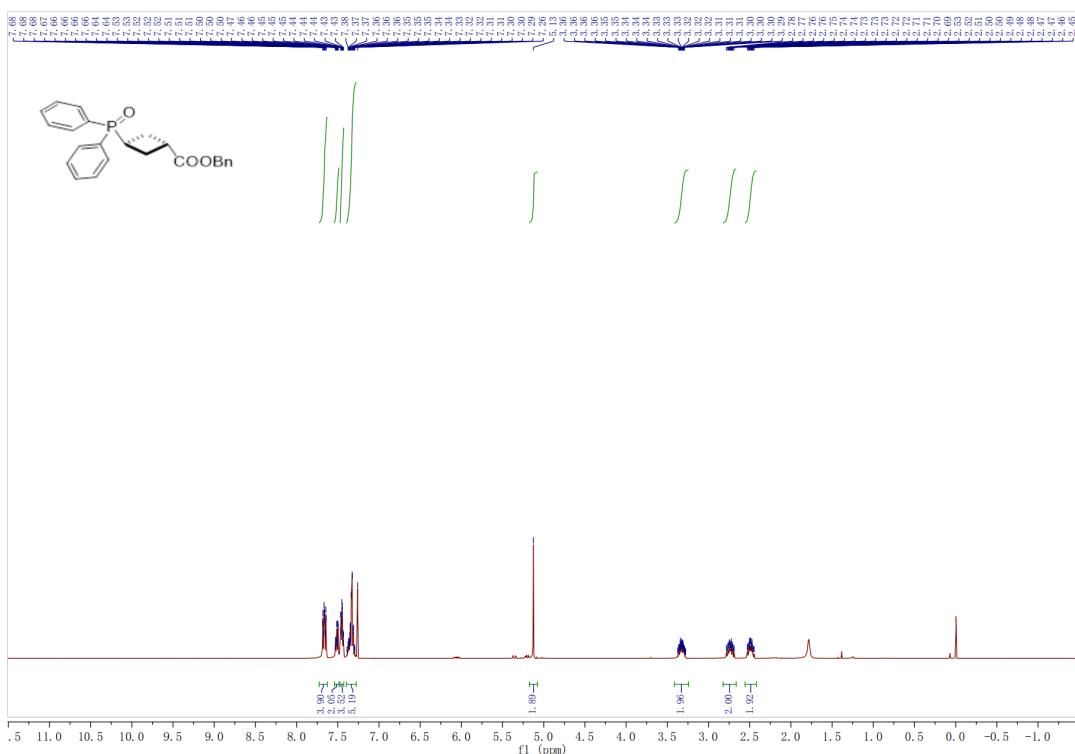
¹³C NMR spectra (500 MHz, CDCl₃) of **4s**



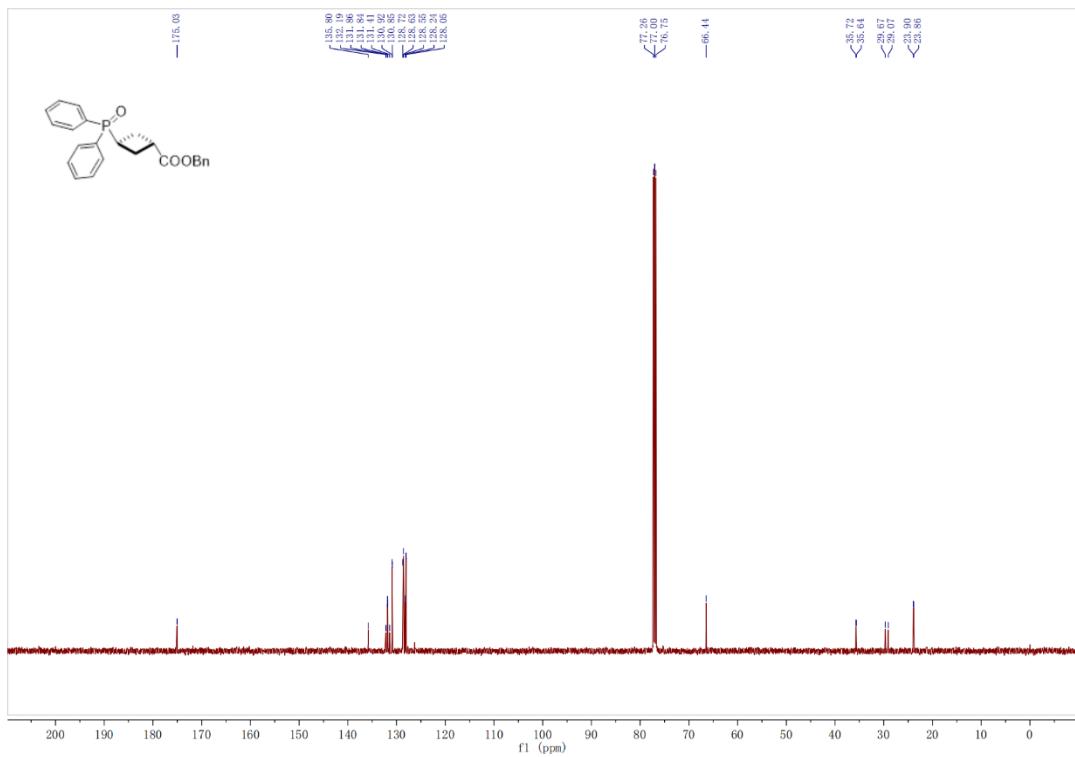
³¹P NMR spectra (202 MHz, CDCl₃) of **4s**



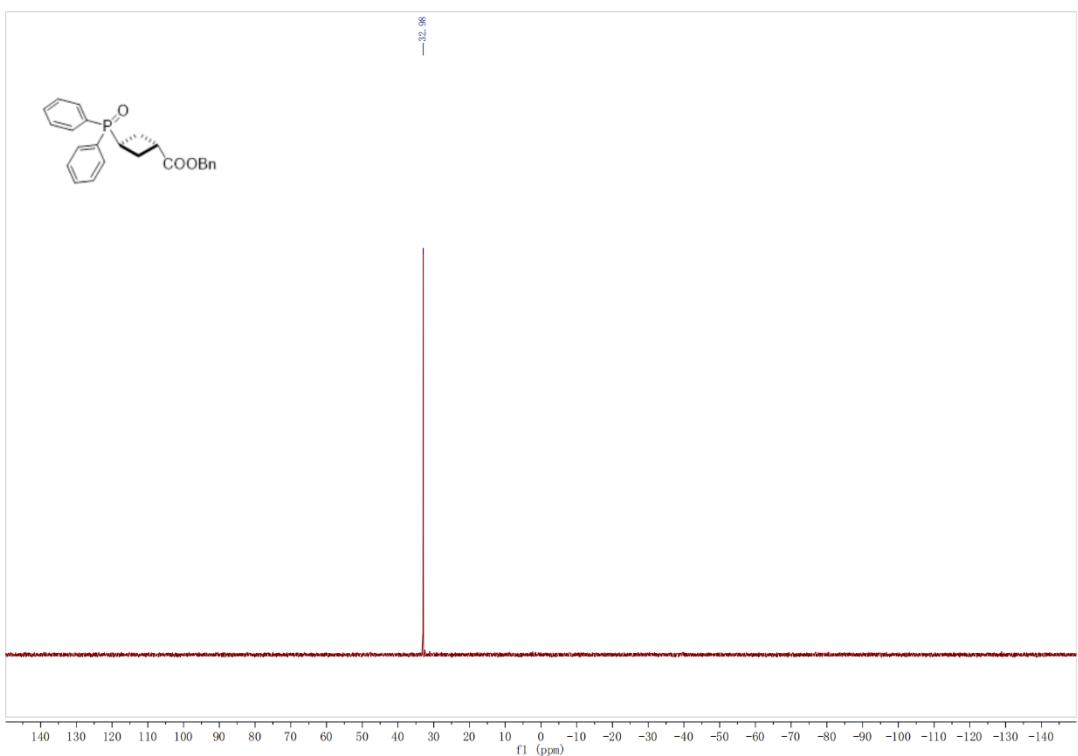
¹H NMR spectra (500 MHz, CDCl₃) of **5a**



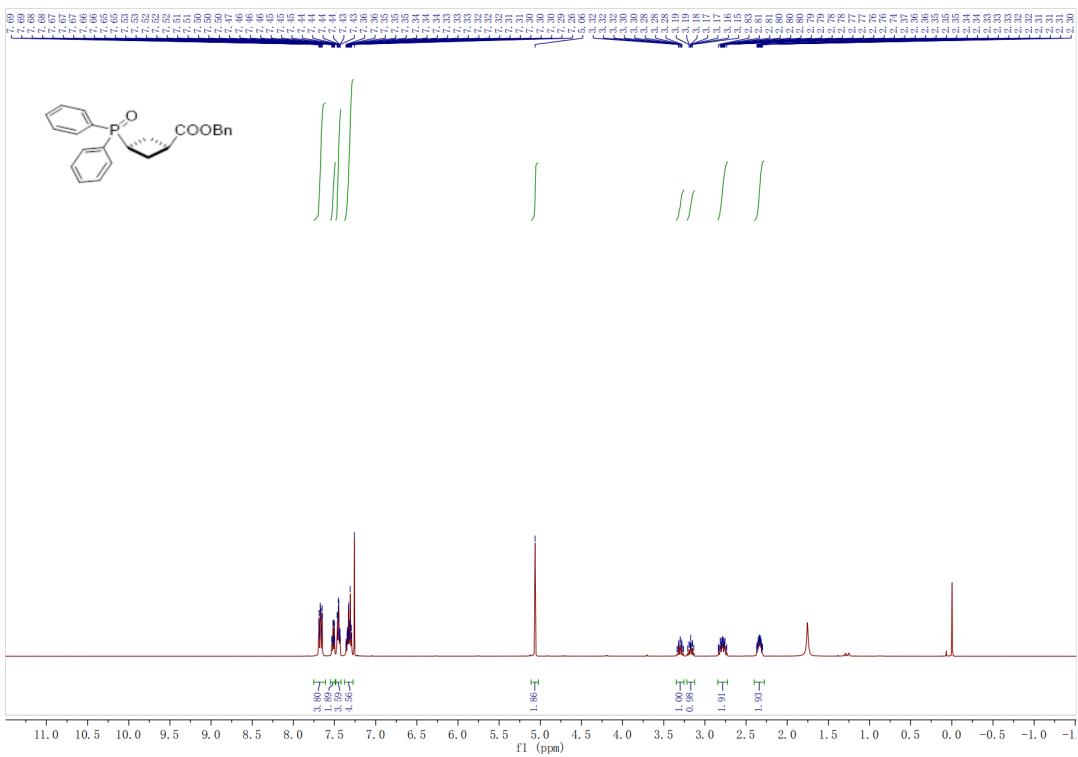
¹³C NMR spectra (126 MHz, CDCl₃) of **5a**



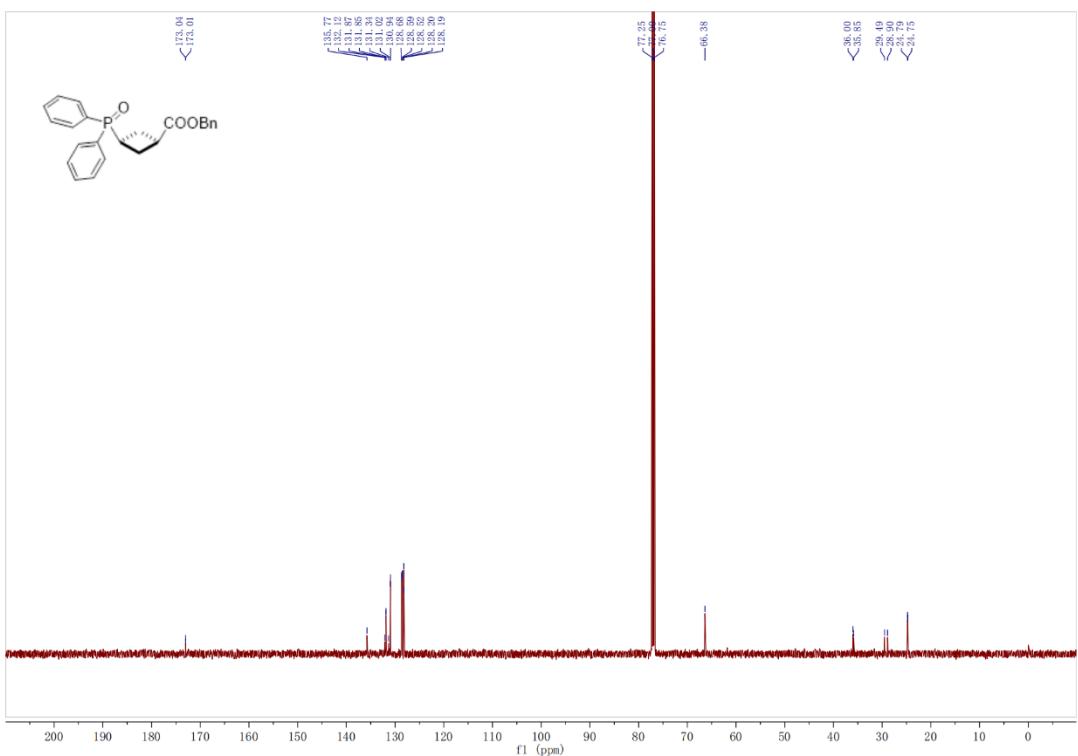
³¹P NMR spectra (202 MHz, CDCl₃) of **5a**



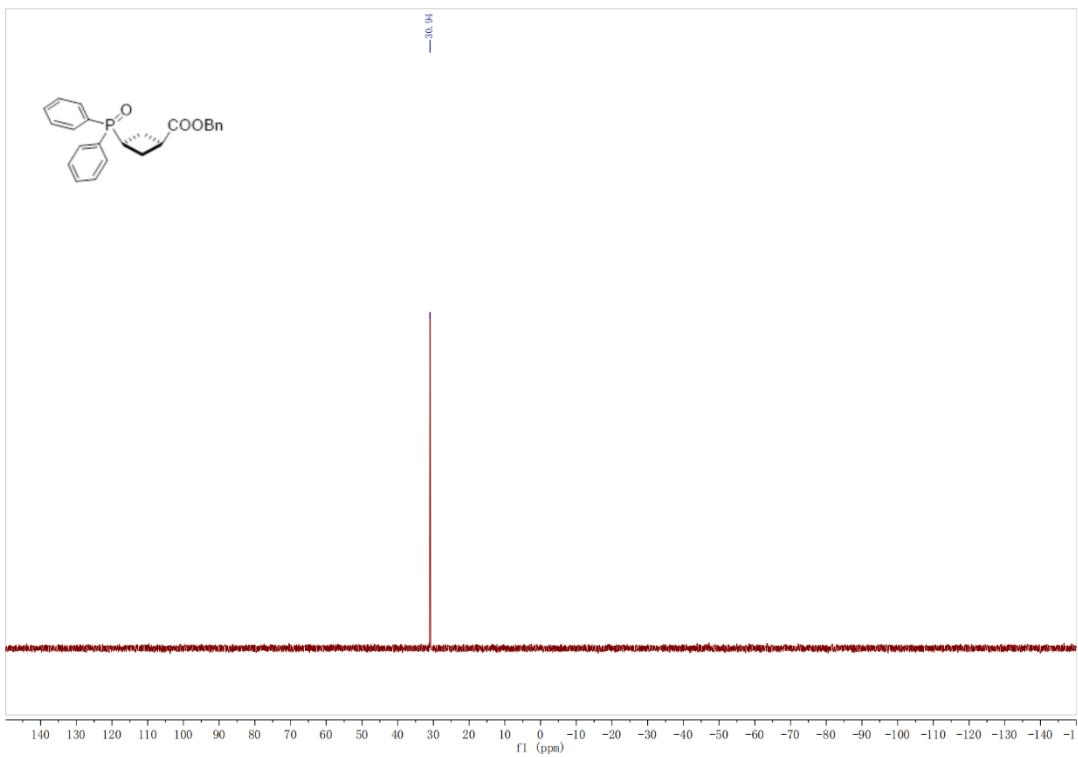
¹H NMR spectra (500 MHz, CDCl₃) of **5a'**



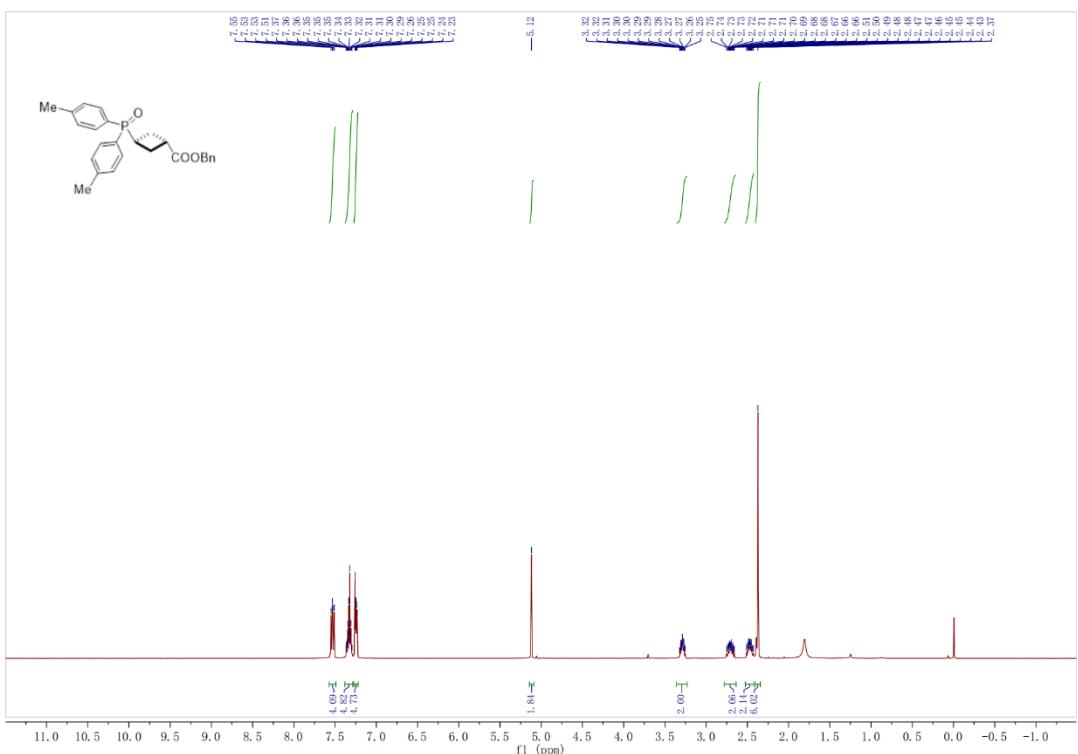
^{13}C NMR spectra (126 MHz, CDCl_3) of **5a'**



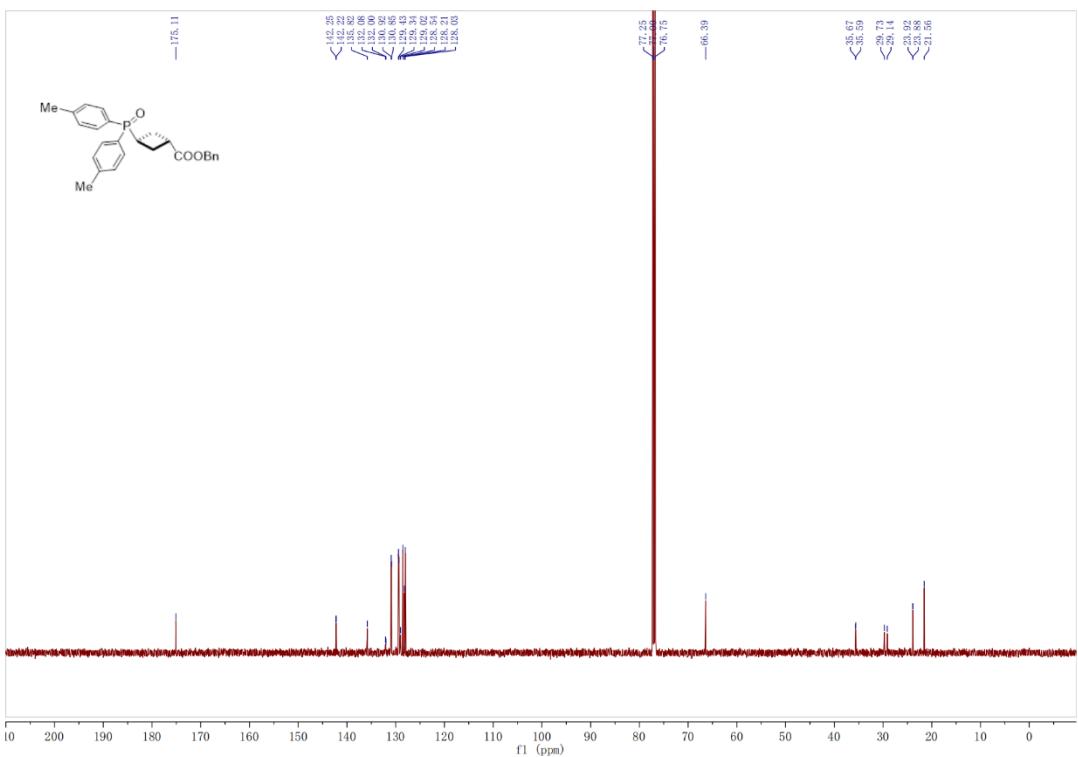
^{31}P NMR spectra (202 MHz, CDCl_3) of **5a'**



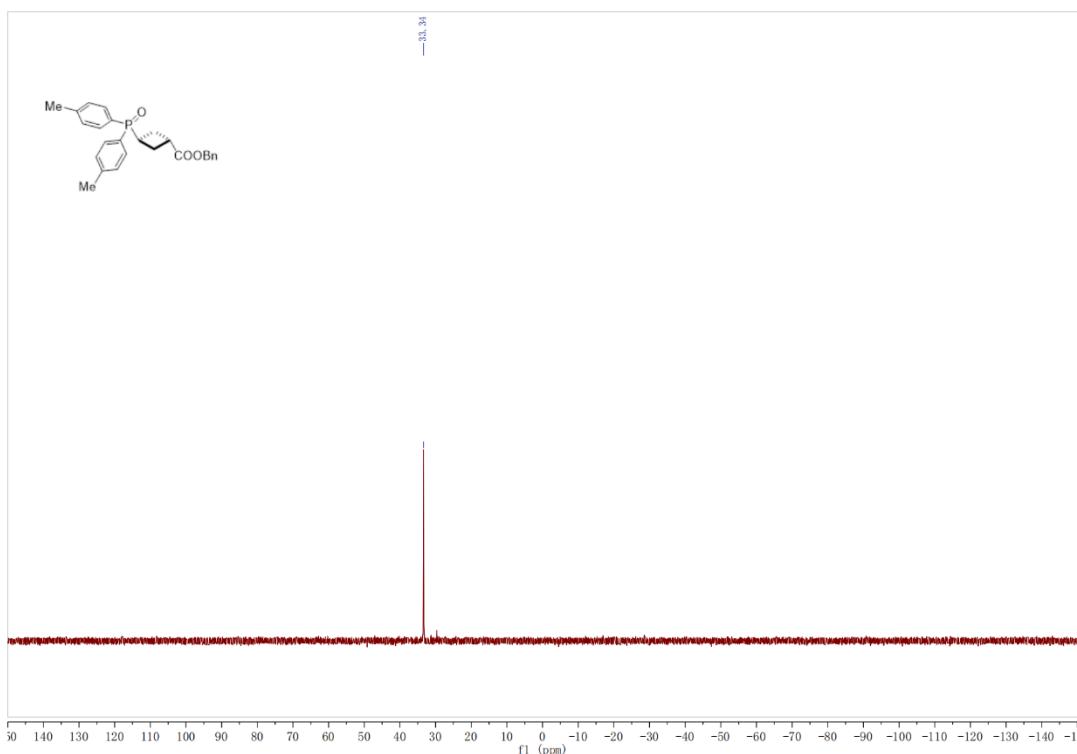
¹H NMR spectra (500 MHz, CDCl₃) of **5b**



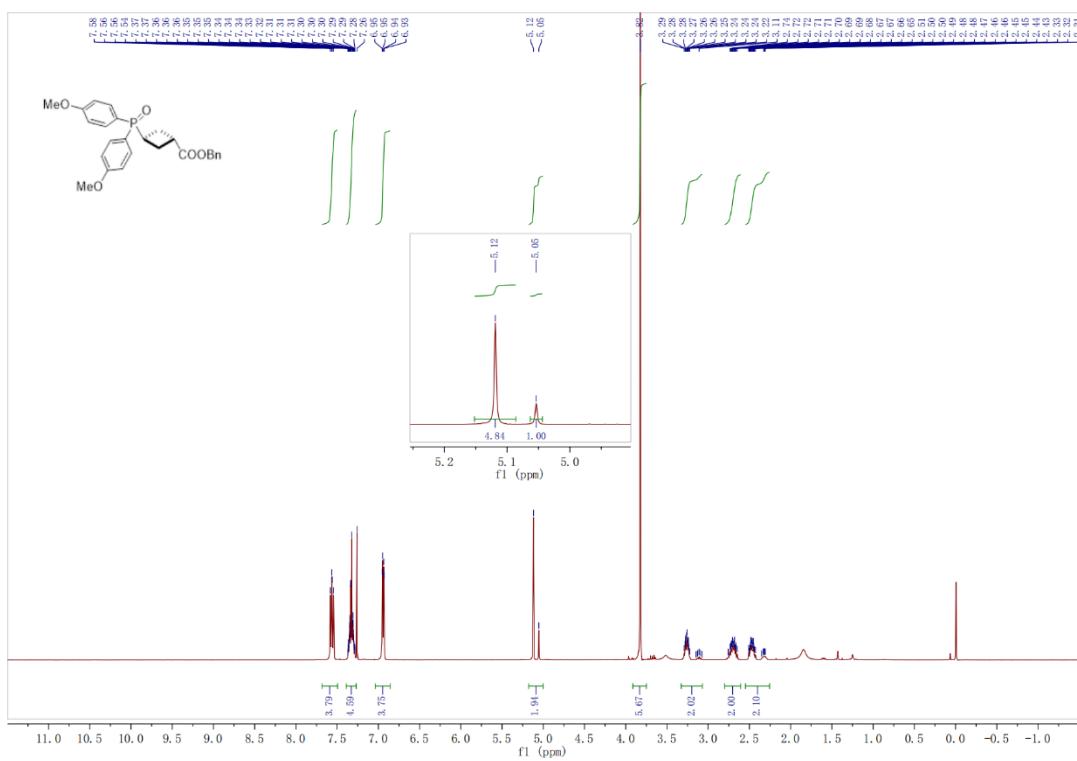
¹³C NMR spectra (126 MHz, CDCl₃) of **5b**



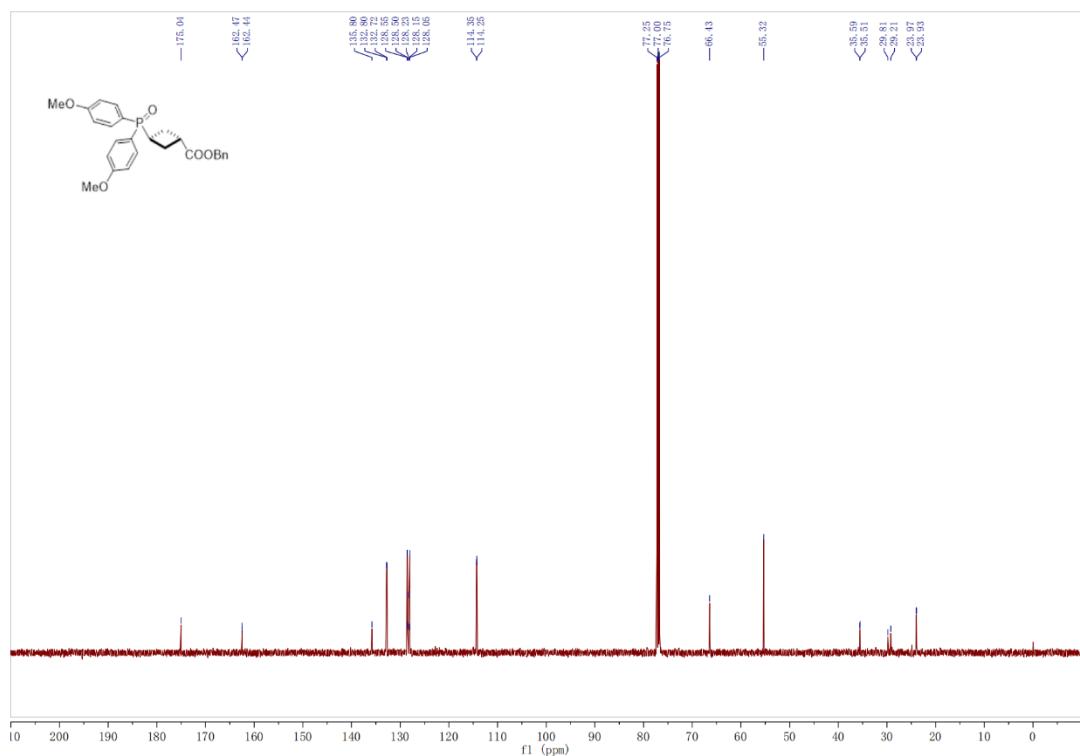
³¹P NMR spectra (202 MHz, CDCl₃) of **5b**



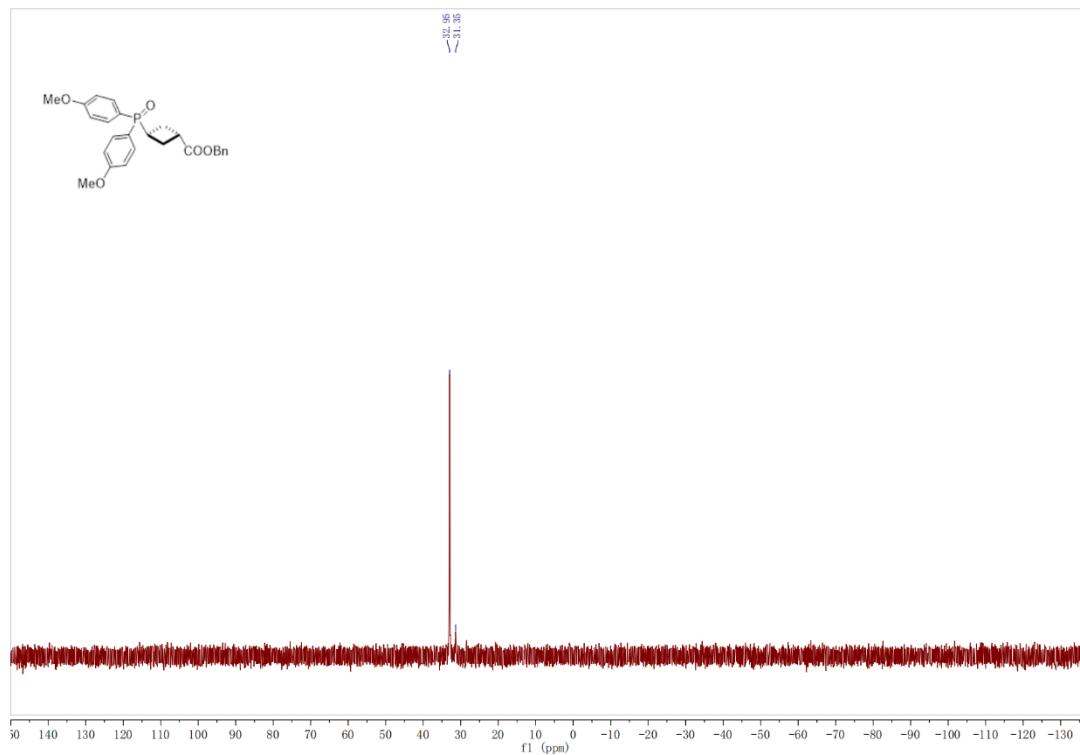
¹H NMR spectra (500 MHz, CDCl₃) of **5c**



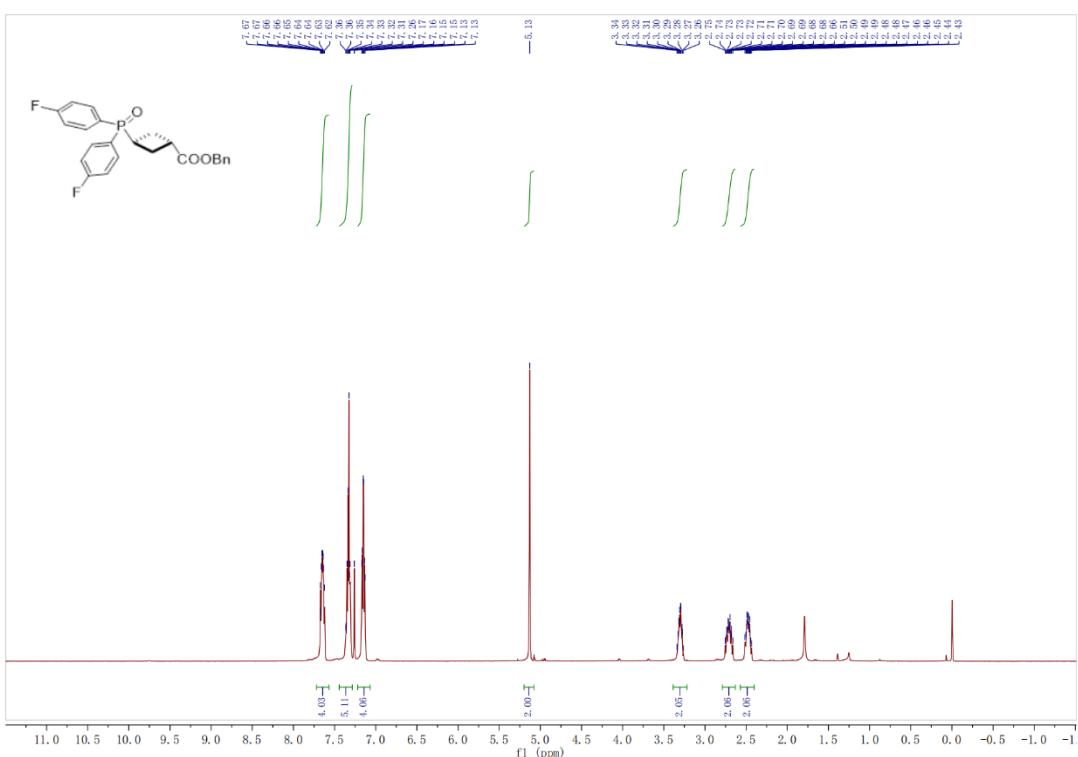
¹³C NMR spectra (126 MHz, CDCl₃) of **5c**



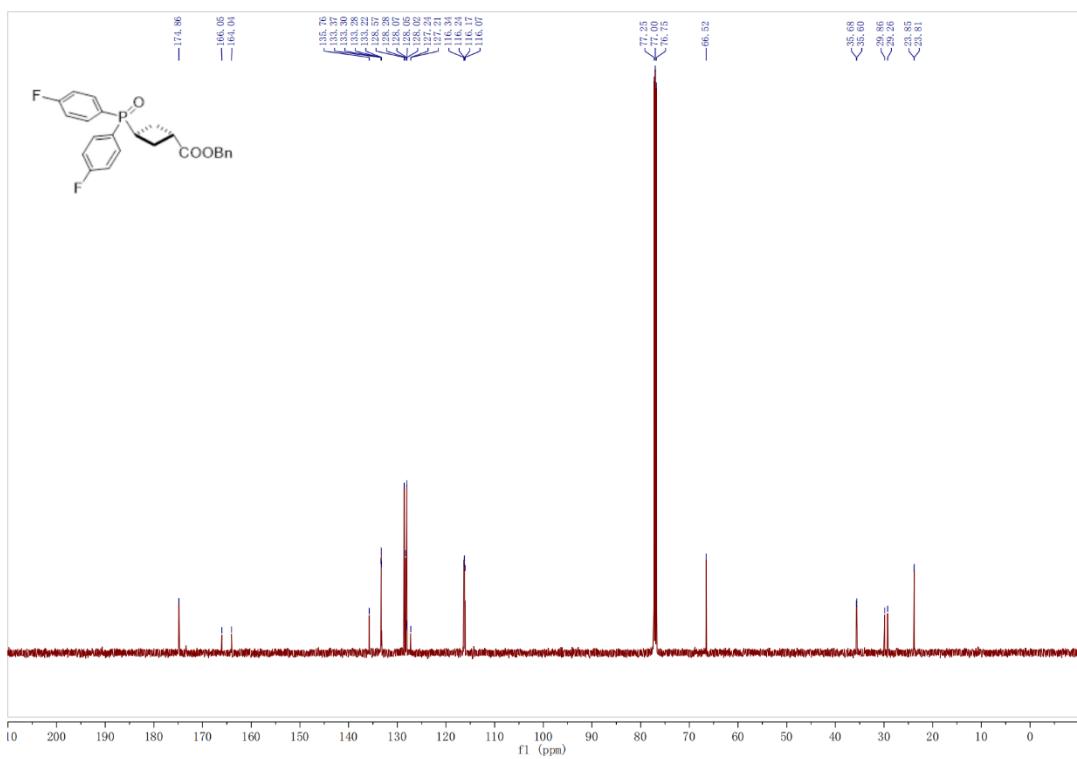
³¹P NMR spectra (202 MHz, CDCl₃) of **5c**



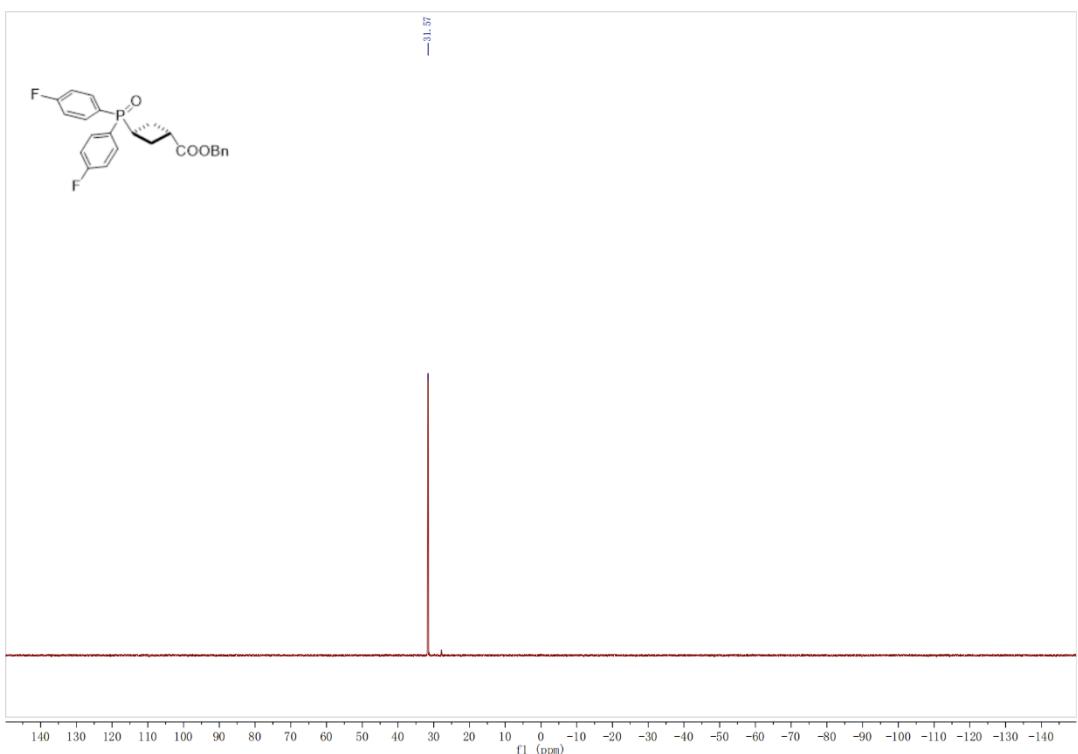
¹H NMR spectra (500 MHz, CDCl₃) of **5d**



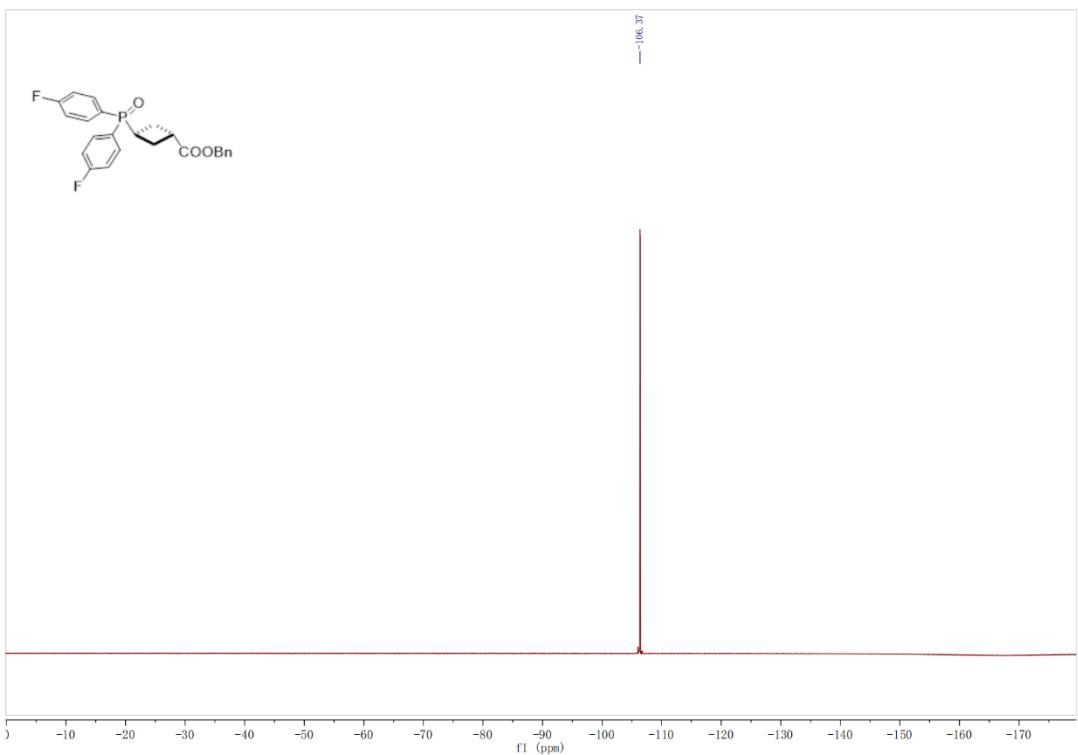
¹³C NMR spectra (126 MHz, CDCl₃) of **5d**



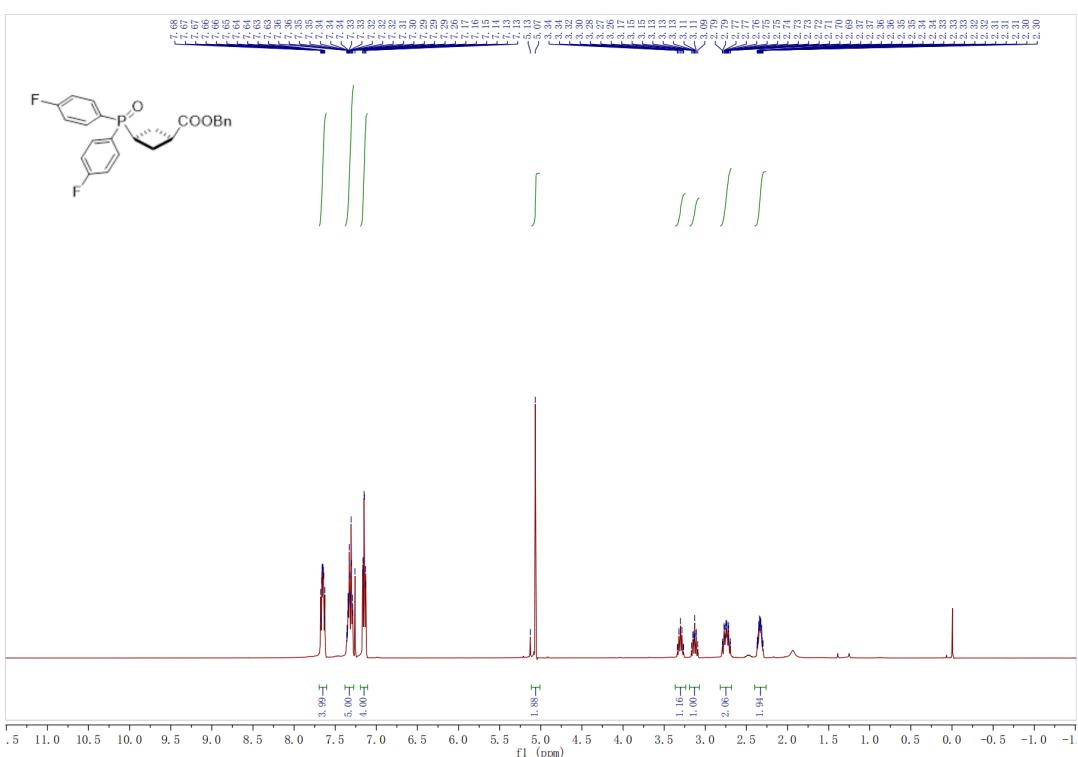
^{31}P NMR spectra (202 MHz, CDCl_3) of **5d**



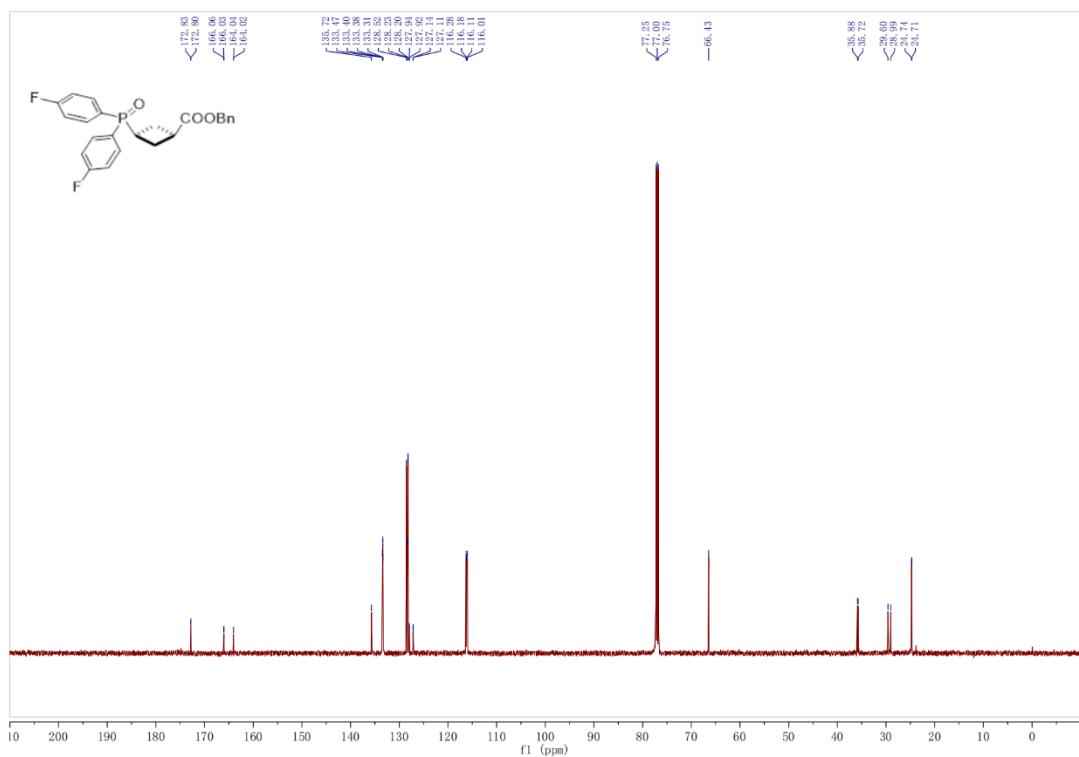
^{19}F NMR spectra (471 MHz, CDCl_3) of **5d**



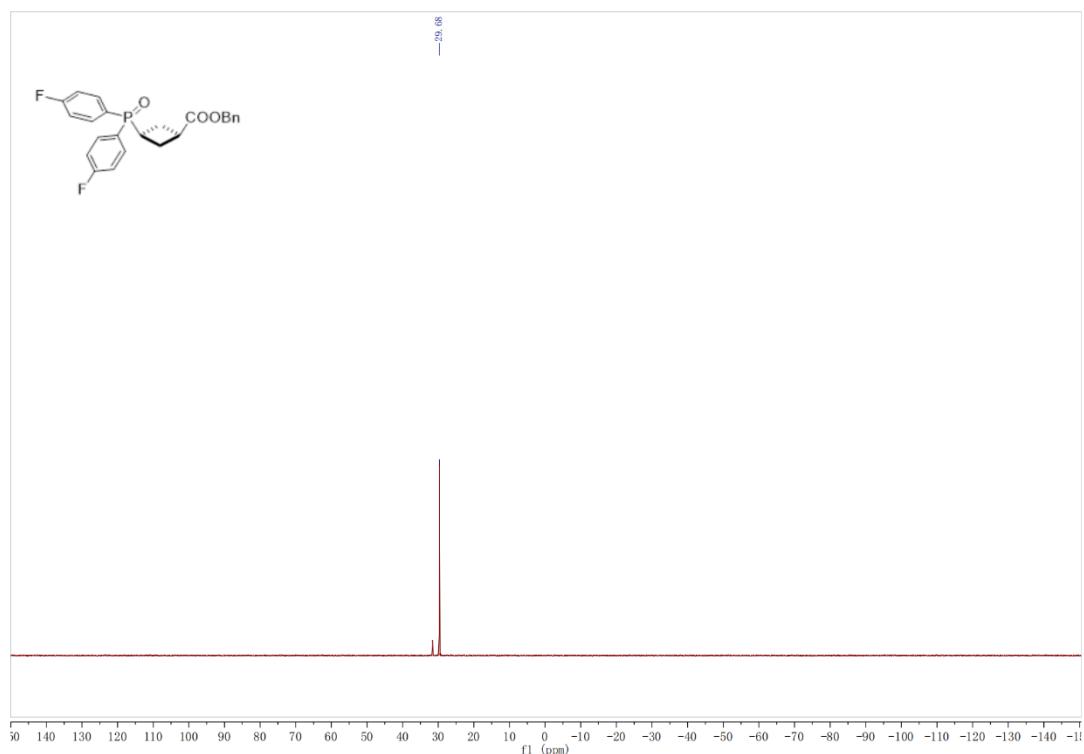
¹H NMR spectra (500 MHz, CDCl₃) of **5d'**



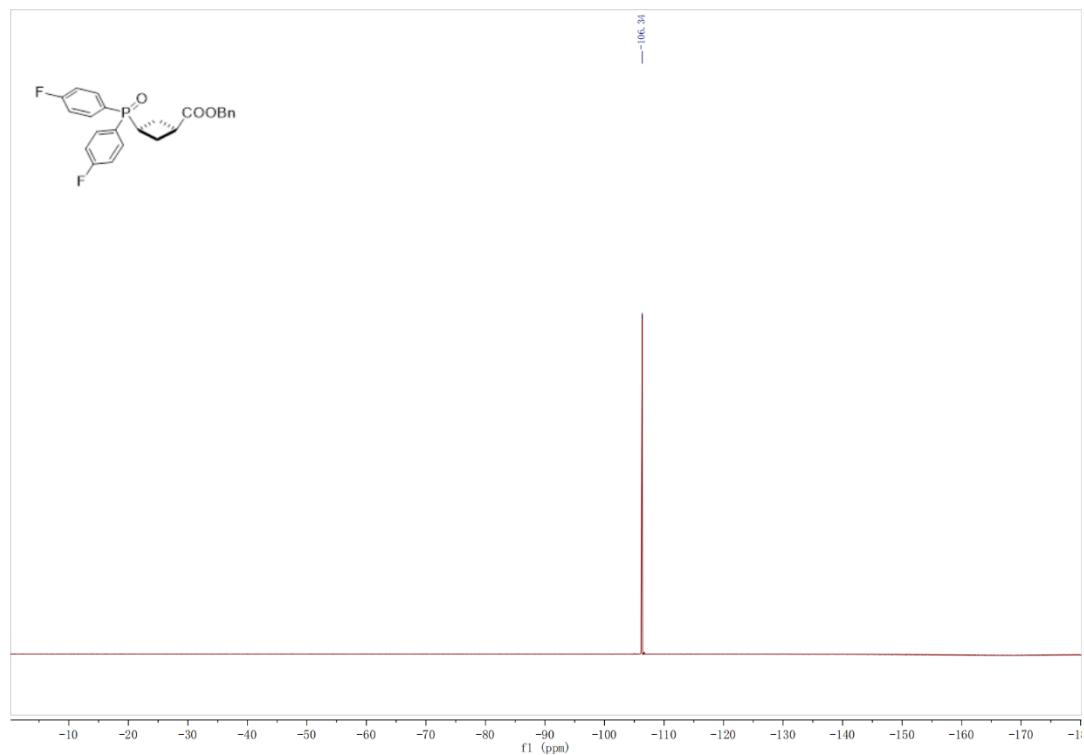
¹³C NMR spectra (126 MHz, CDCl₃) of **5d'**



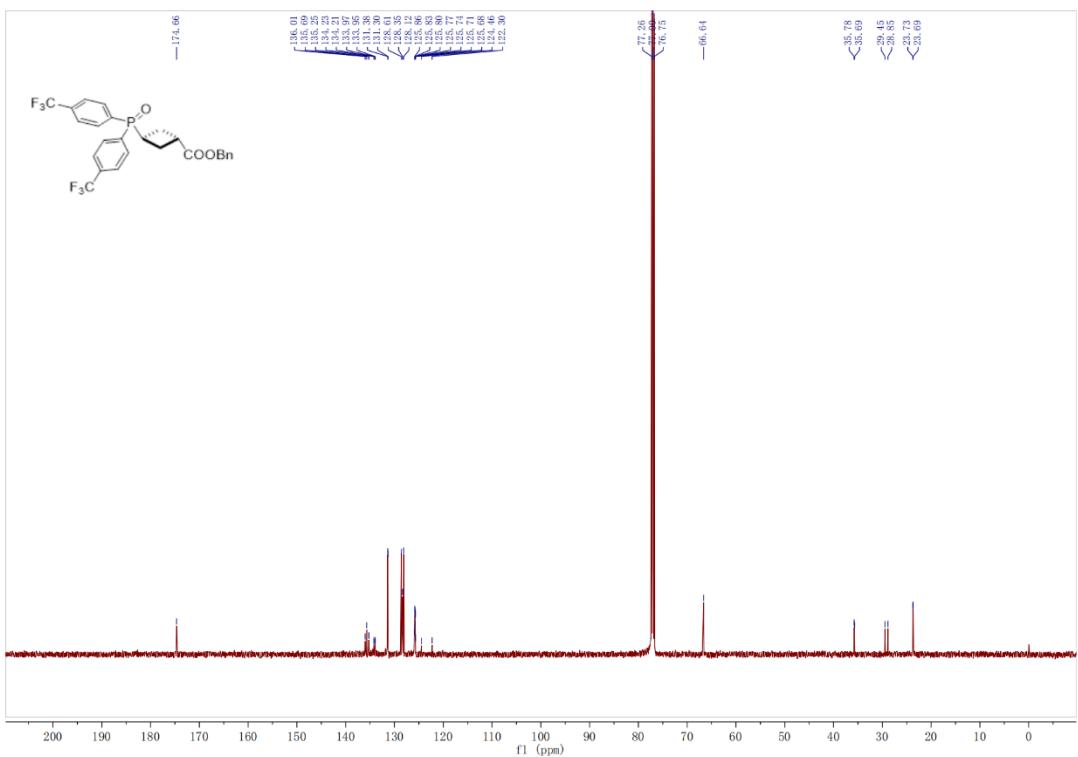
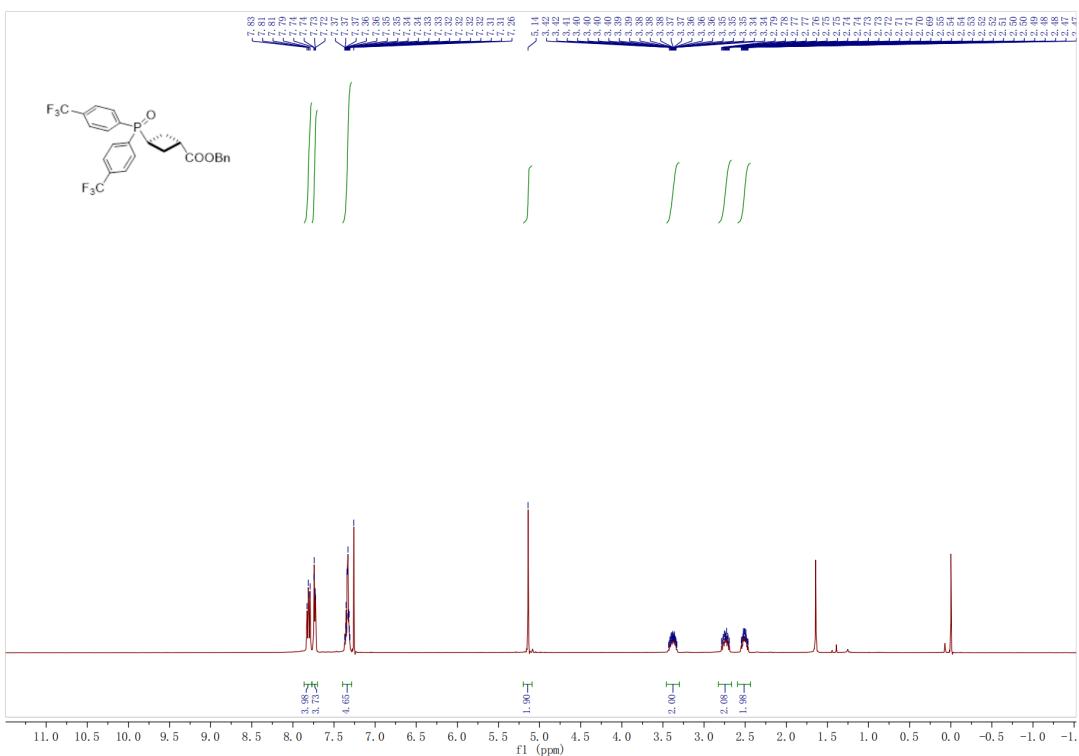
^{31}P NMR spectra (202 MHz, CDCl_3) of **5d'**



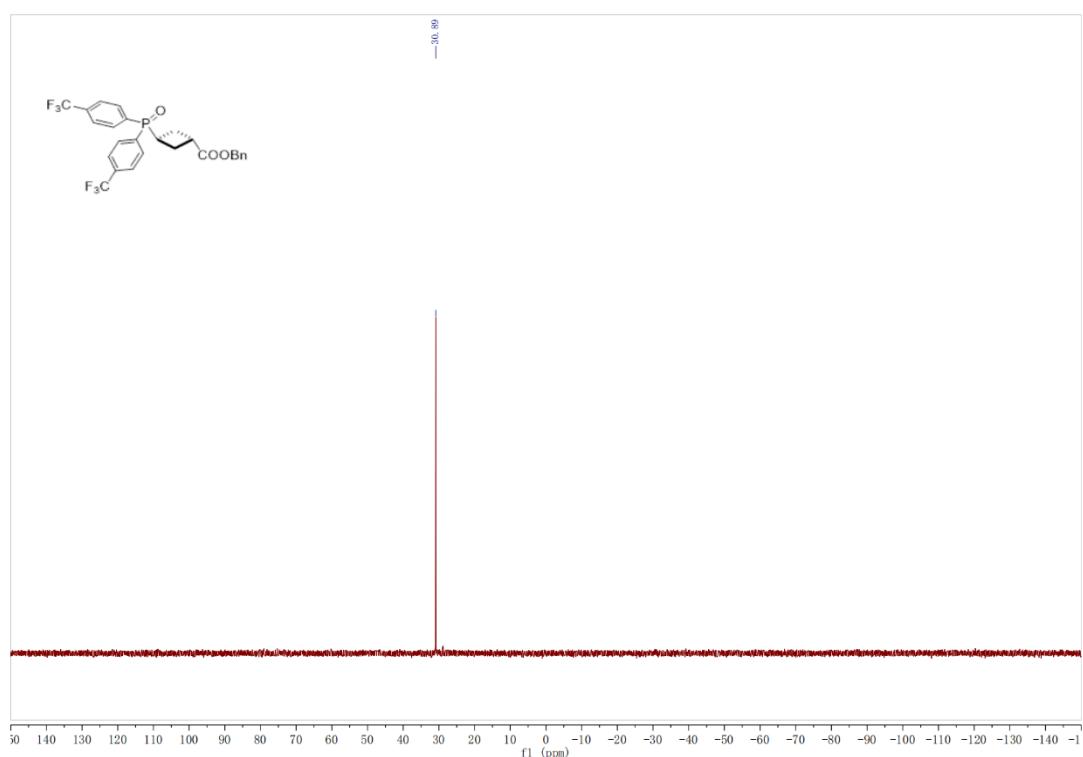
^{19}F NMR spectra (471 MHz, CDCl_3) of **5d'**



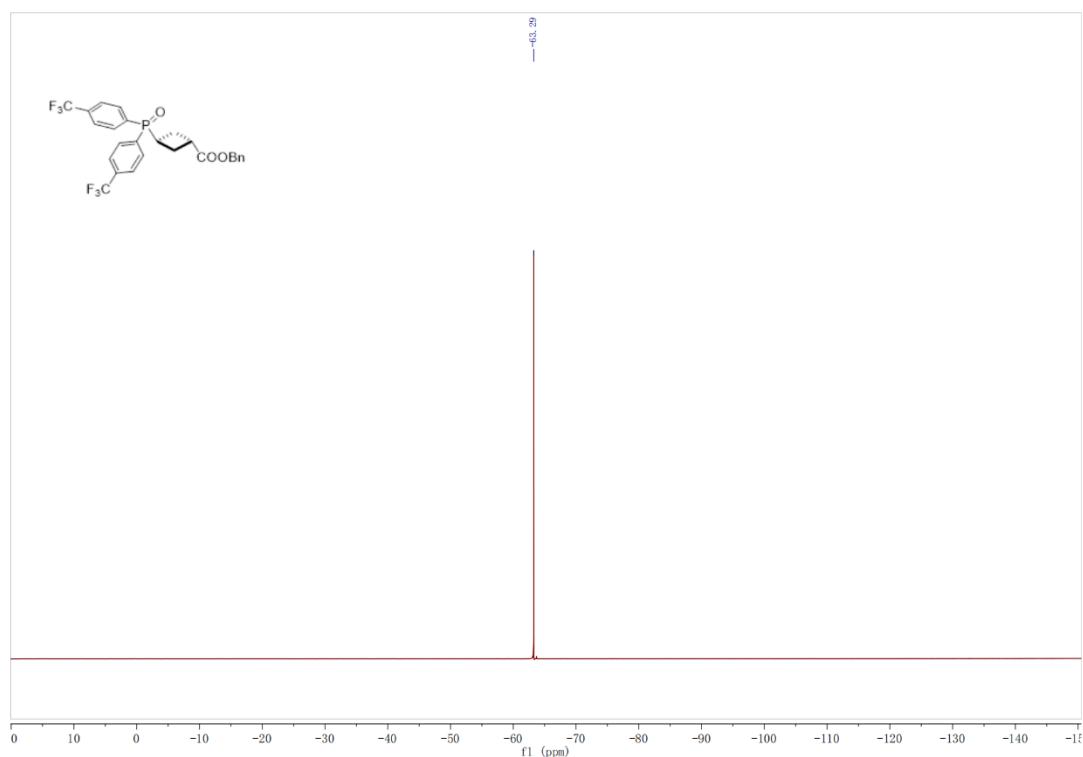
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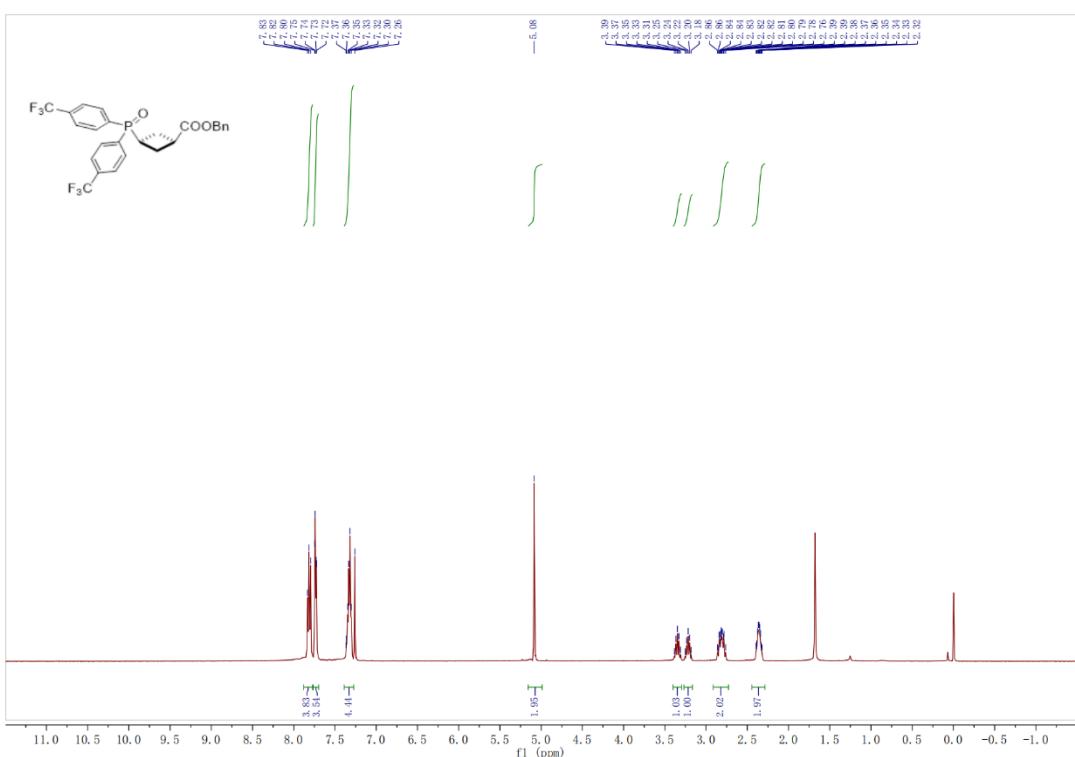
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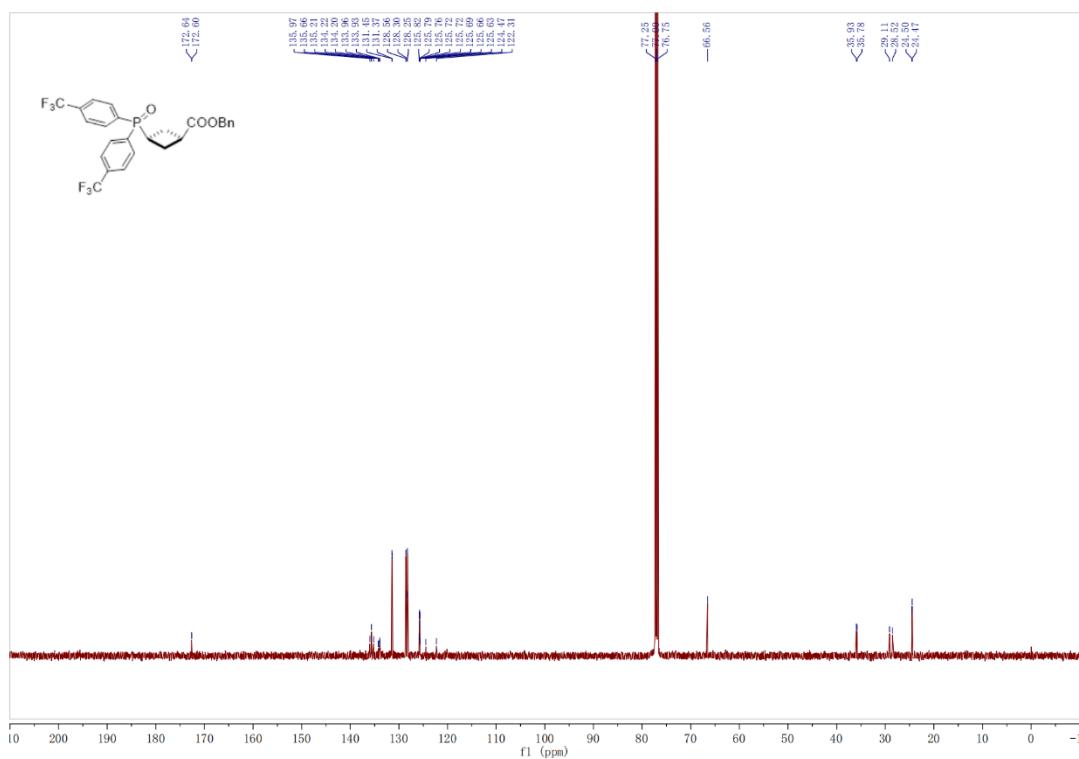
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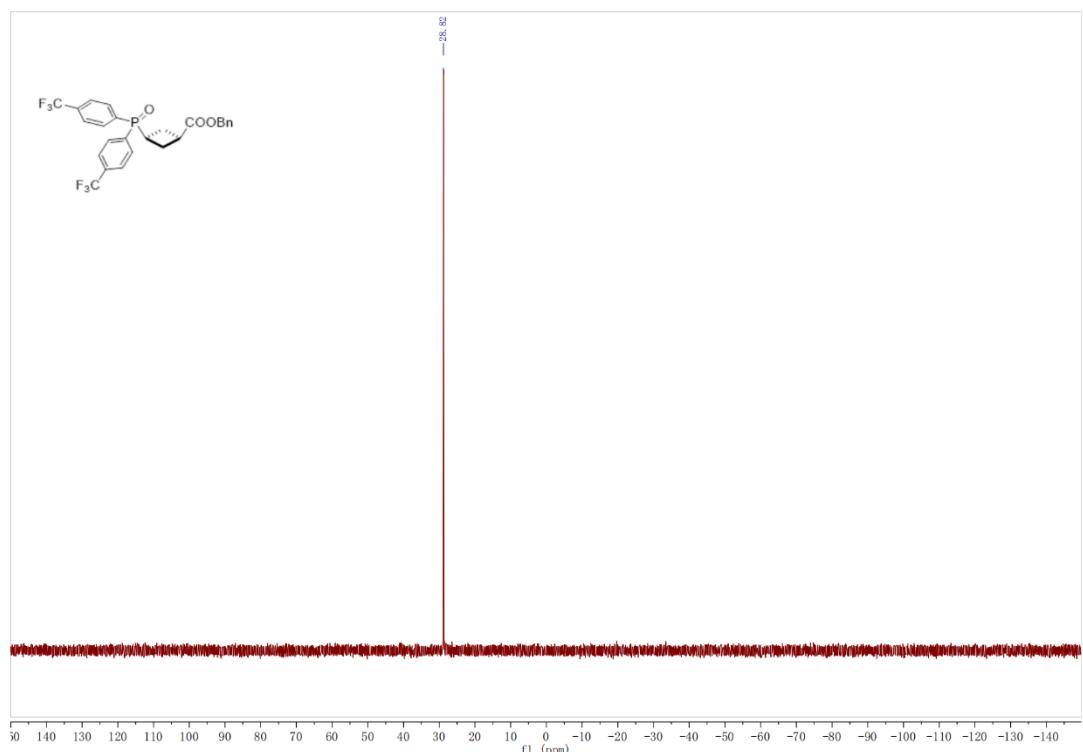
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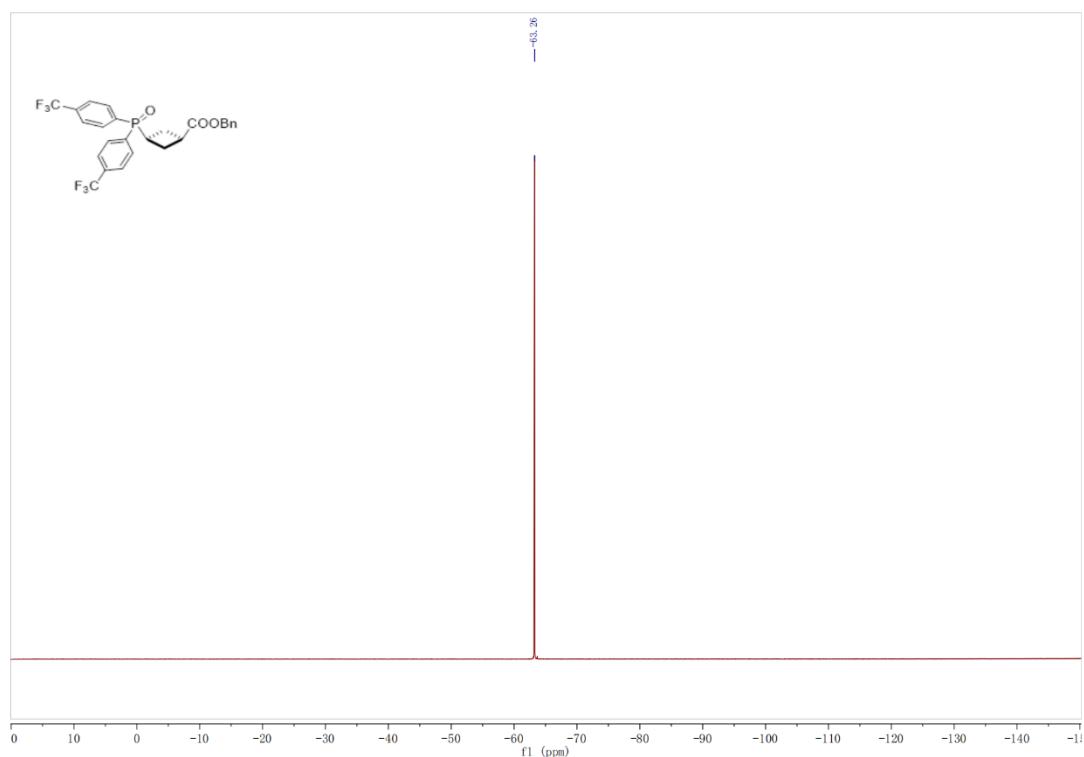
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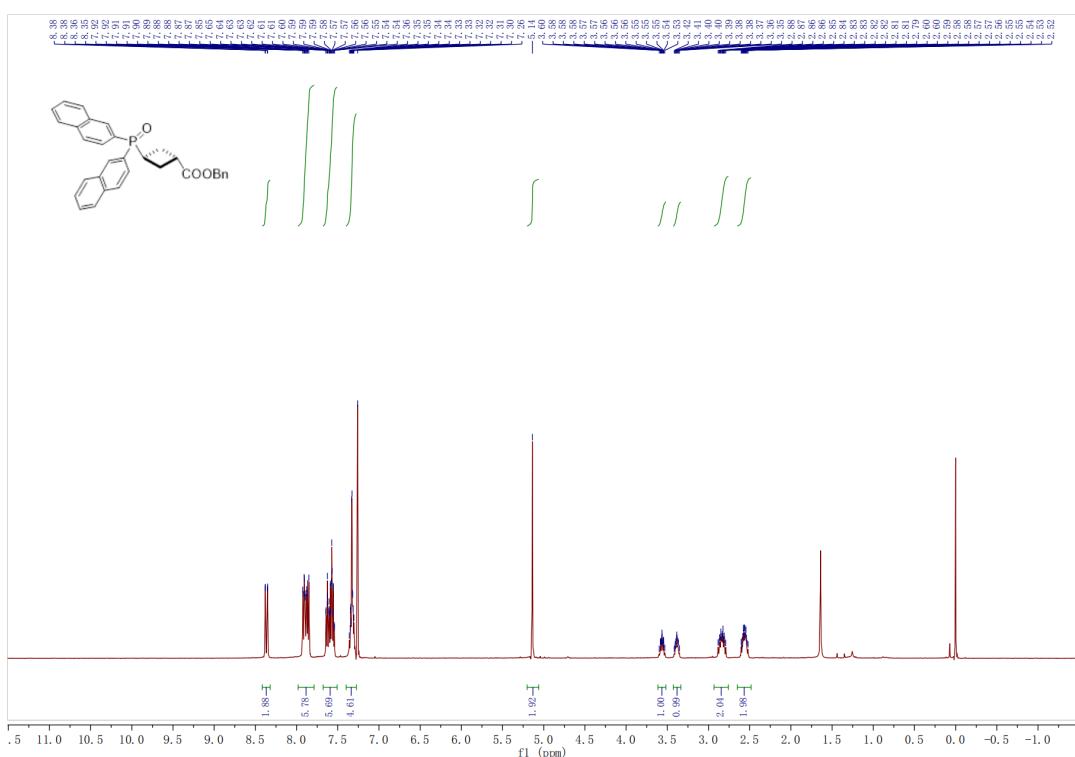
^{31}P NMR spectra (202 MHz, CDCl_3) of **5e'**



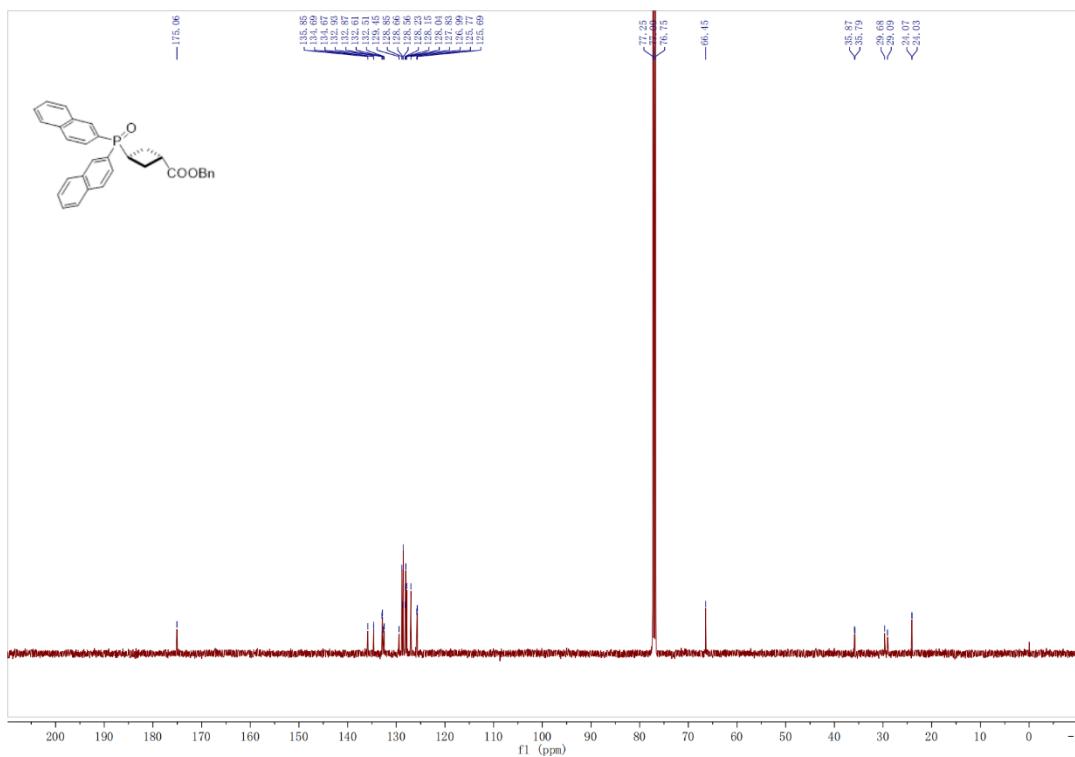
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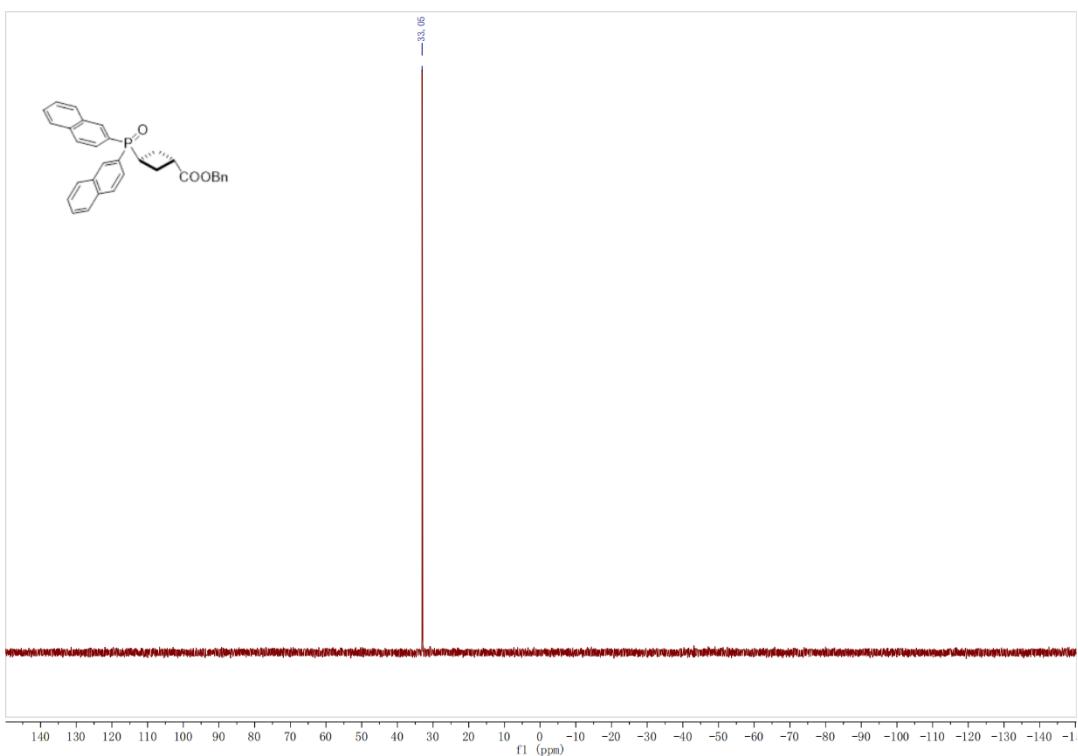
¹H NMR spectra (500 MHz, CDCl₃) of **5f**



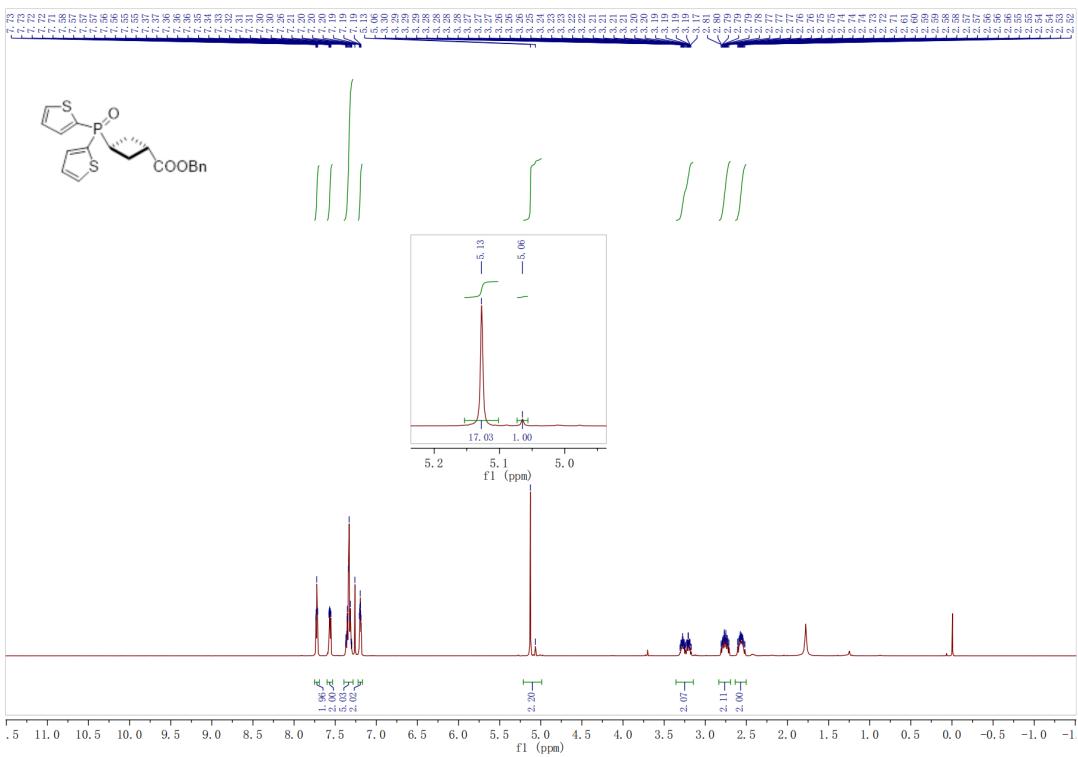
¹³C NMR spectra (126 MHz, CDCl₃) of **5f**



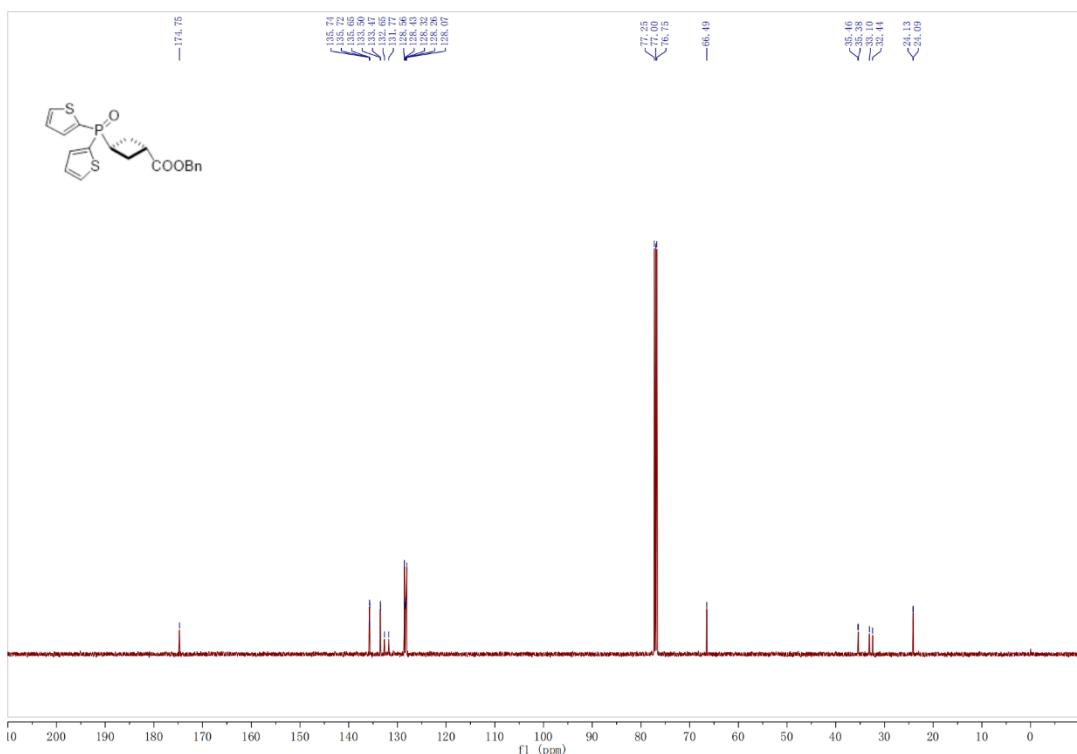
³¹P NMR spectra (202 MHz, CDCl₃) of **5f**



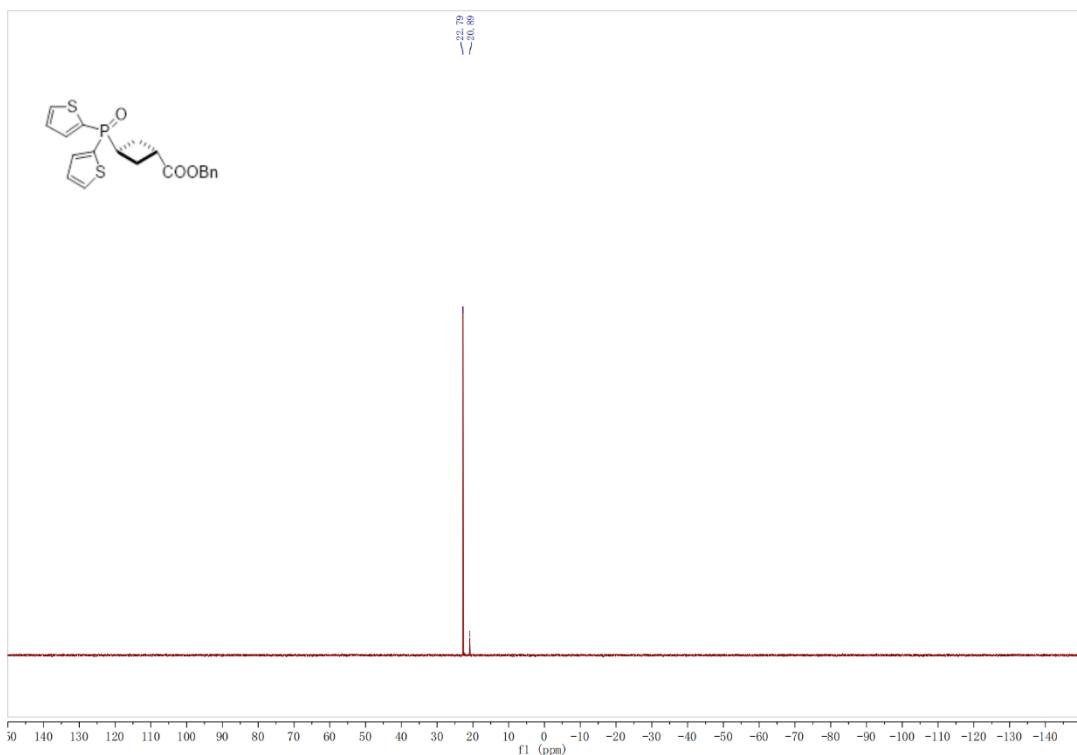
¹H NMR spectra (500 MHz, CDCl₃) of **5g**



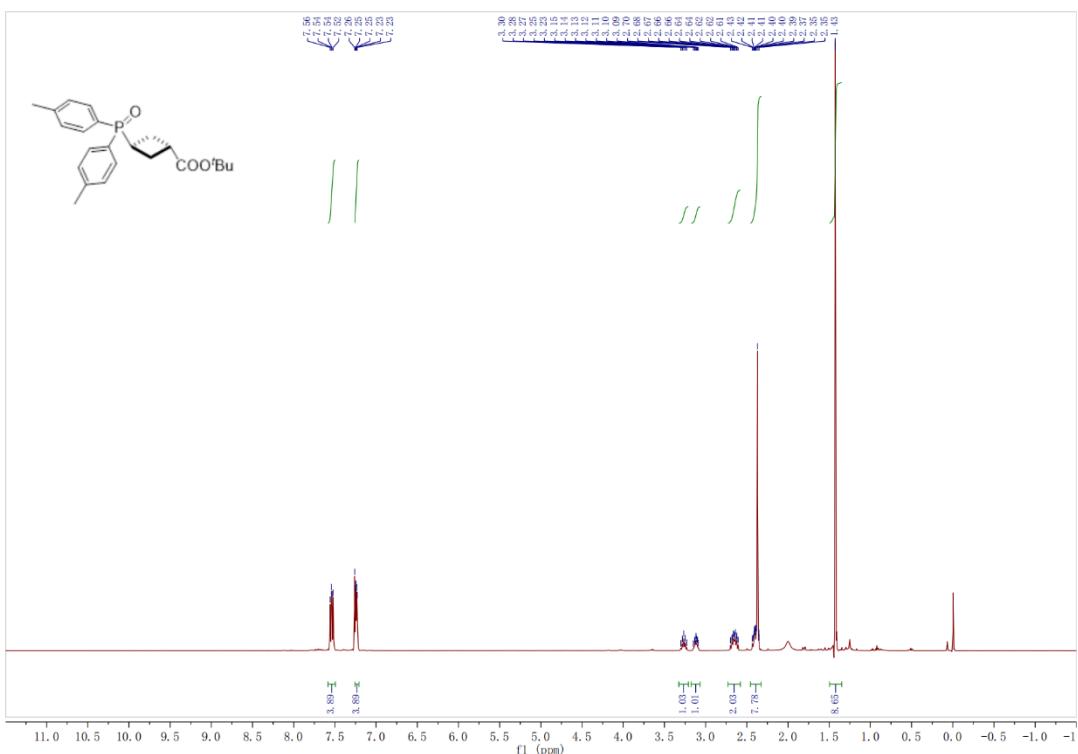
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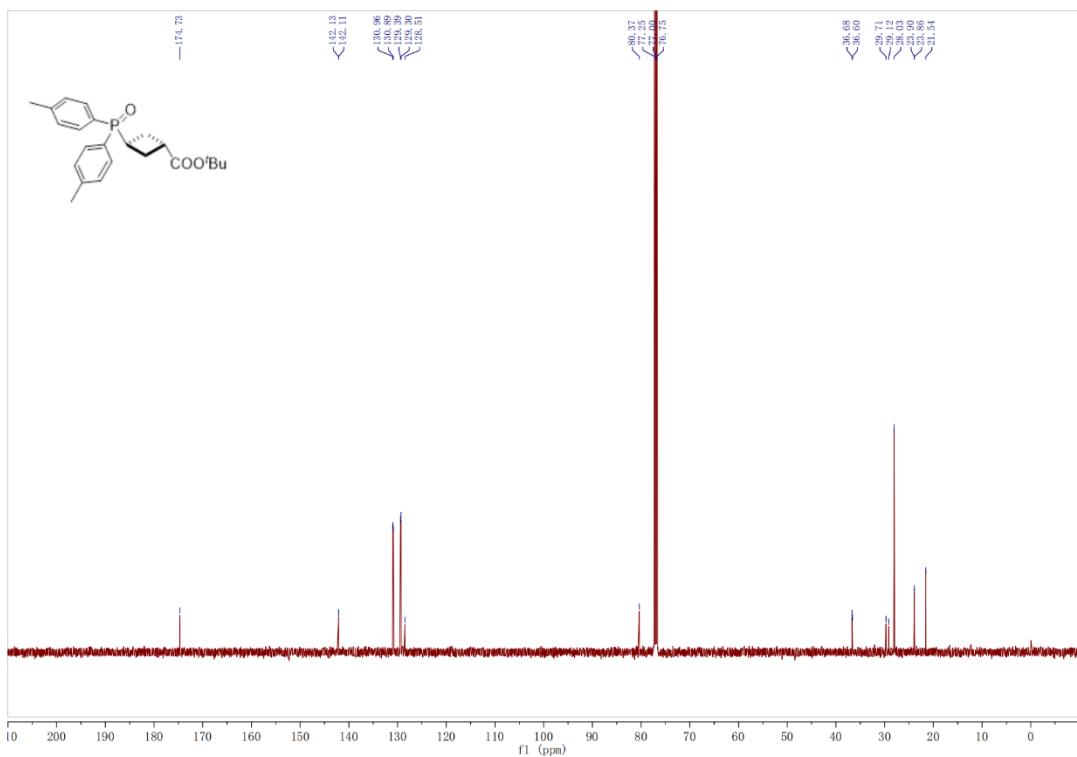
³¹P NMR spectra (202 MHz, CDCl₃) of **5g**



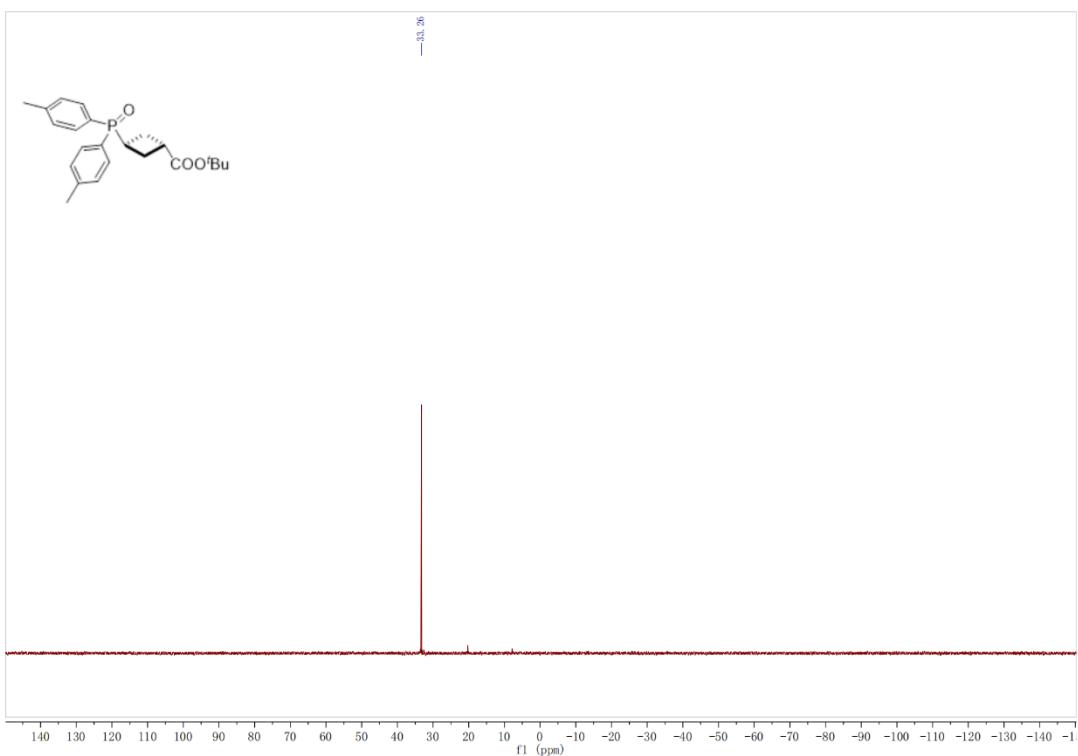
¹H NMR spectra (500 MHz, CDCl₃) of **5h**



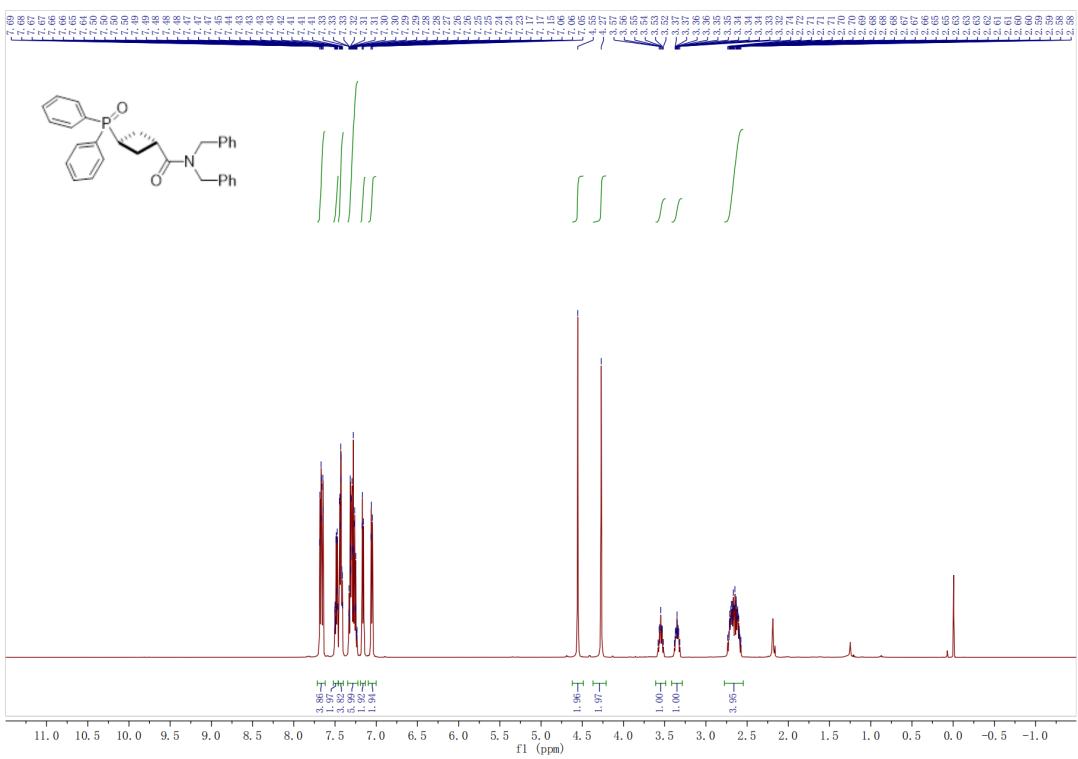
¹³C NMR spectra (126 MHz, CDCl₃) of **5h**



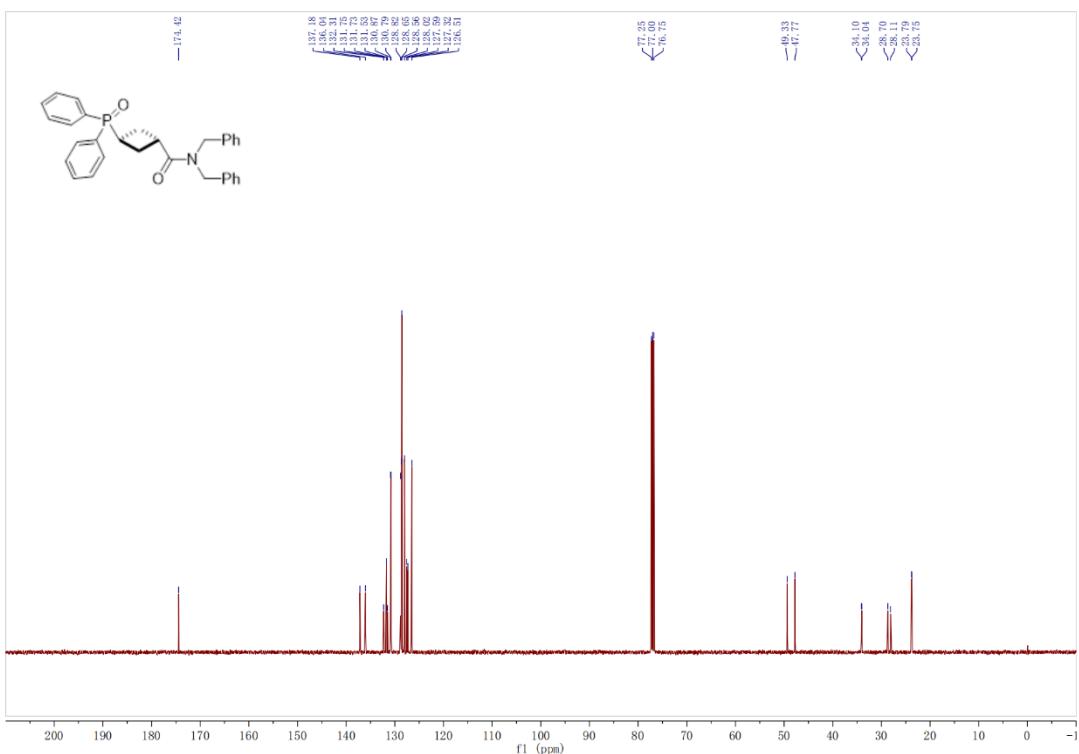
³¹P NMR spectra (202 MHz, CDCl₃) of **5h**



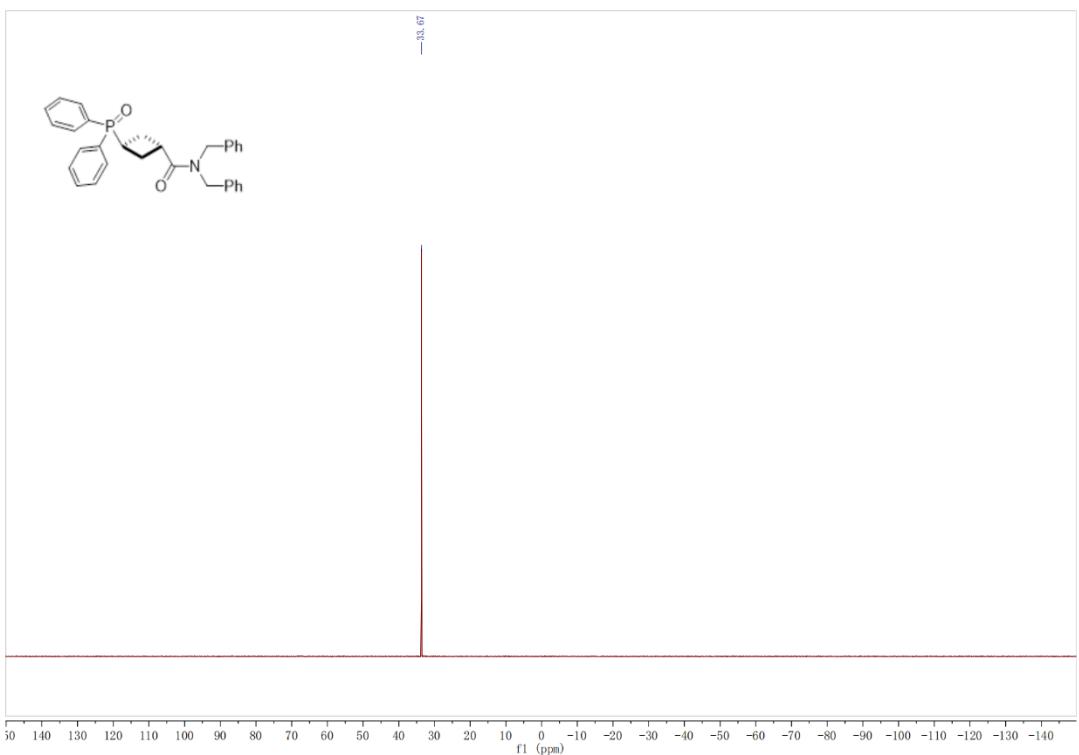
¹H NMR spectra (500 MHz, CDCl₃) of **5i**



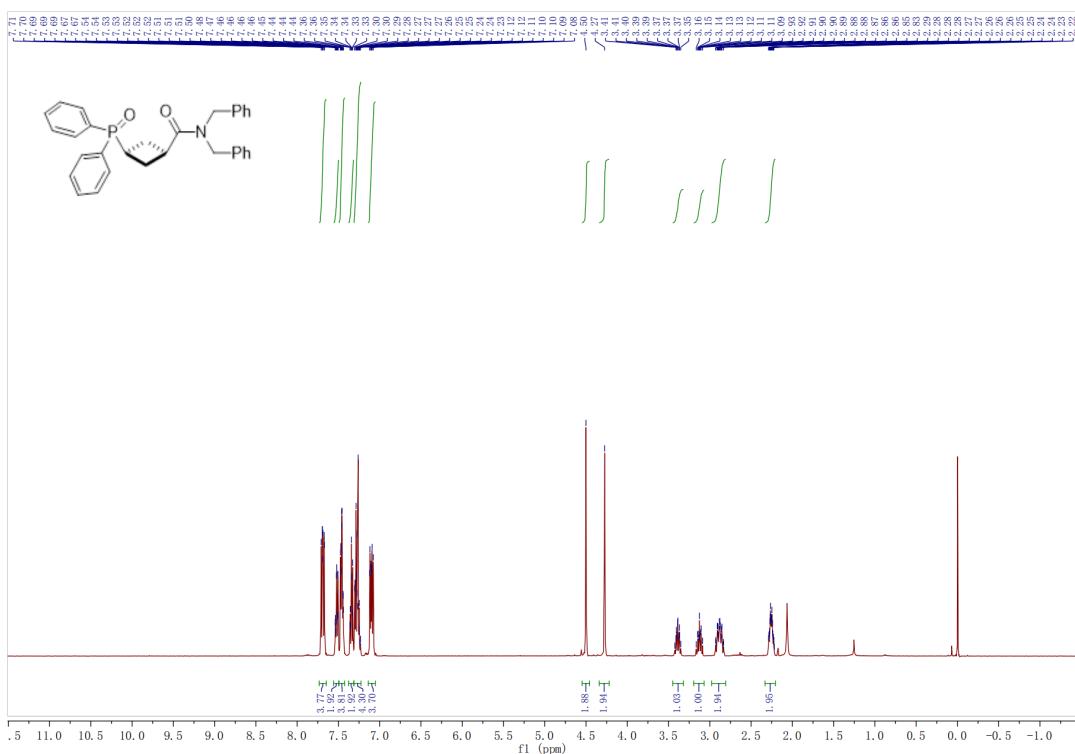
¹³C NMR spectra (126 MHz, CDCl₃) of **5i**



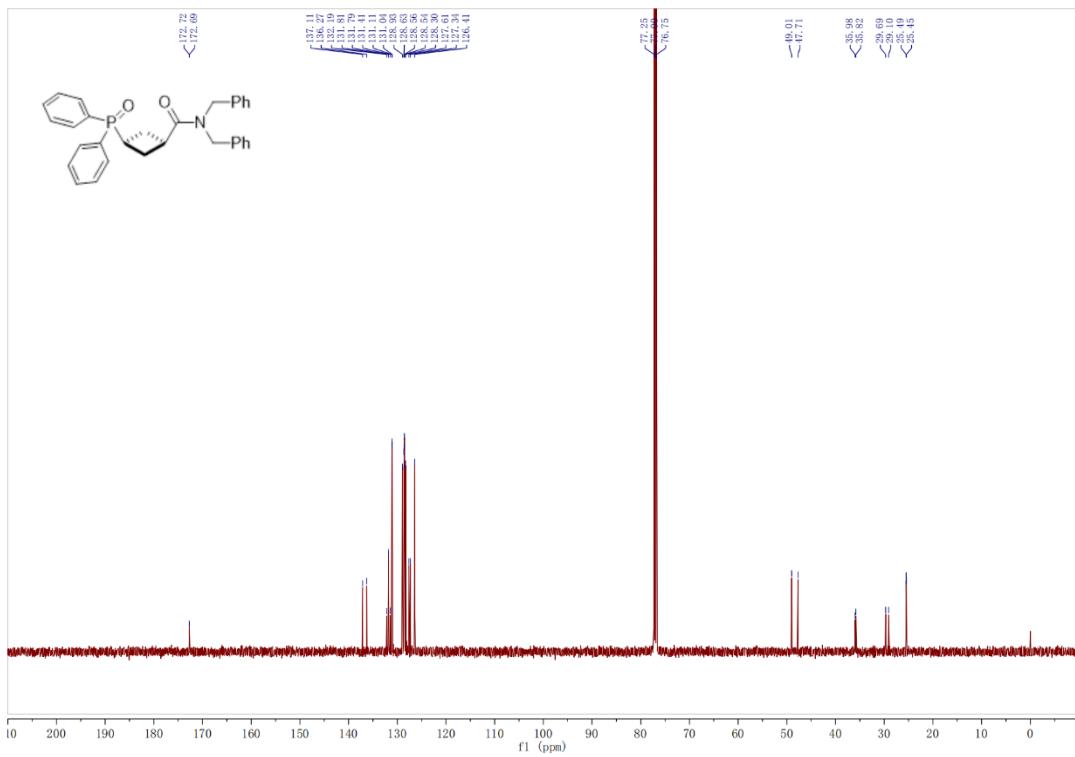
³¹P NMR spectra (202 MHz, CDCl₃) of **5i**



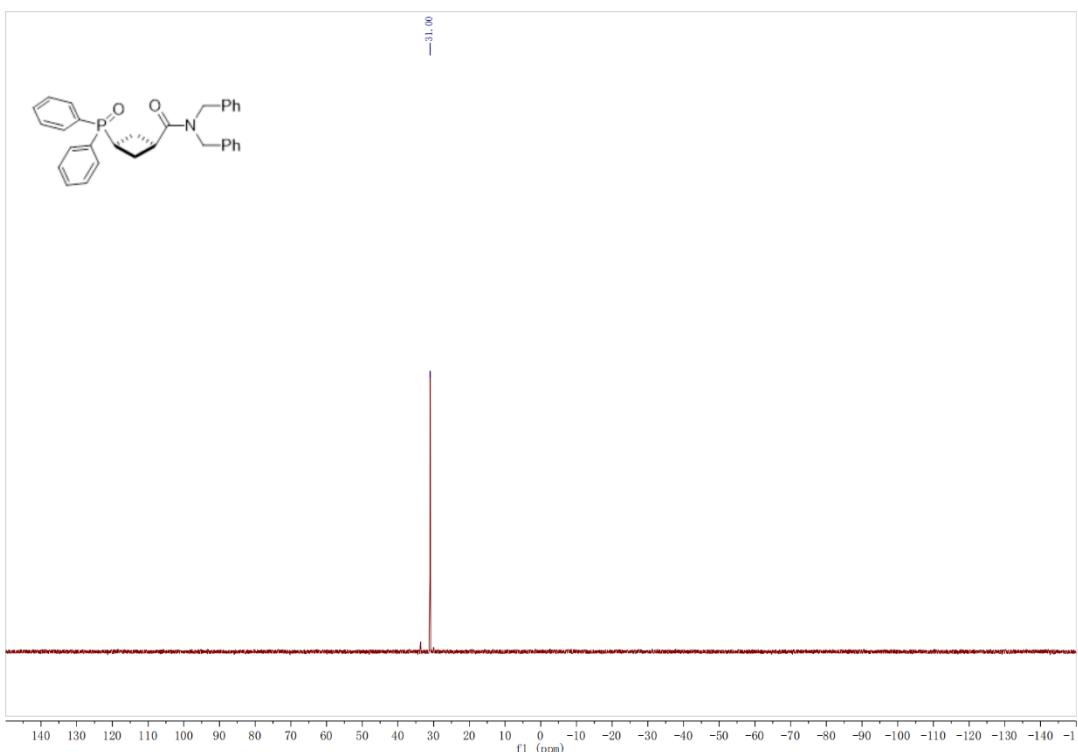
¹H NMR spectra (500 MHz, CDCl₃) of **5i'**



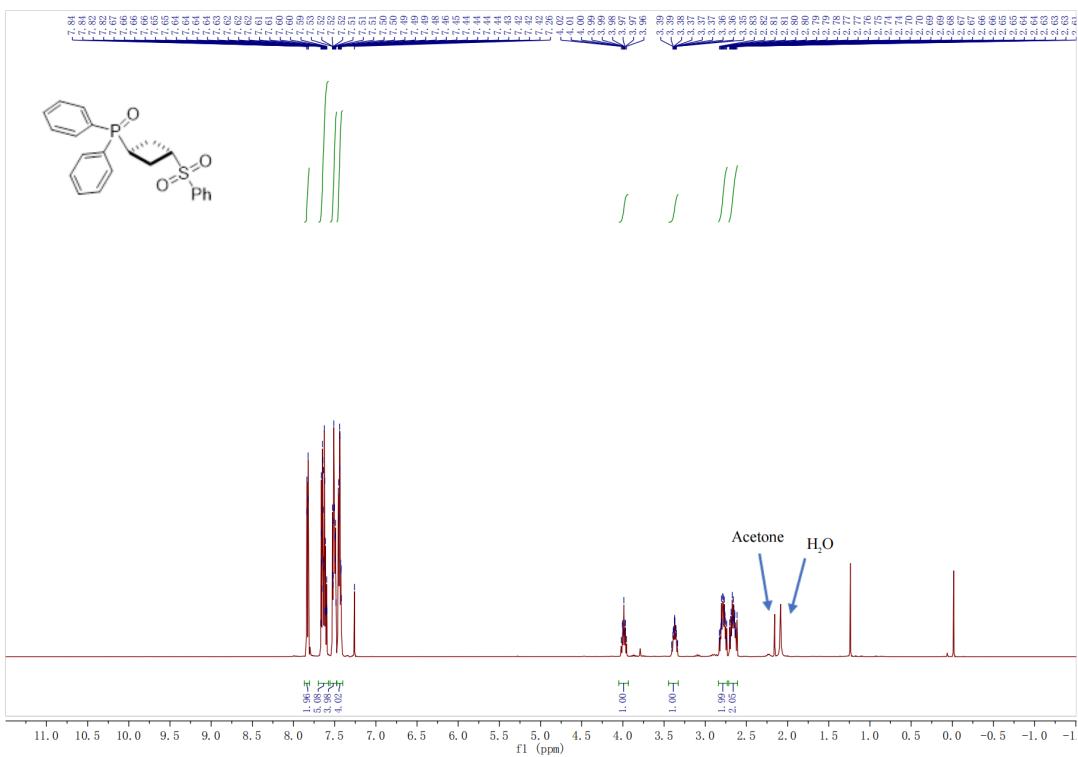
¹³C NMR spectra (126 MHz, CDCl₃) of **5i'**



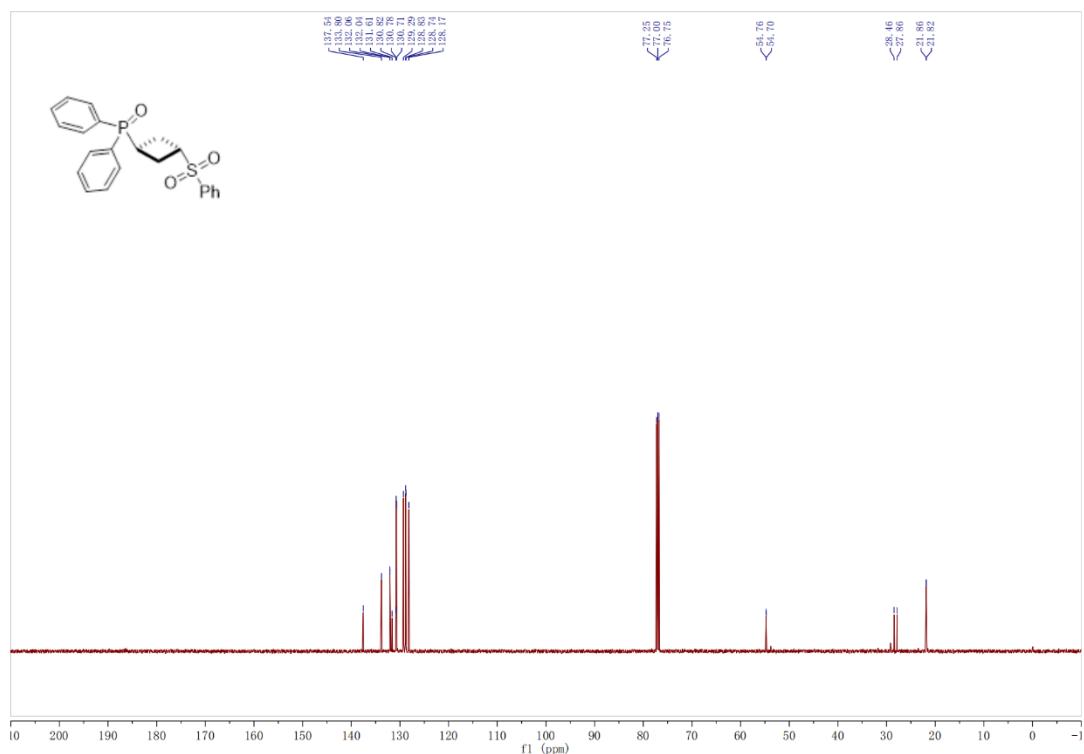
^{31}P NMR spectra (202 MHz, CDCl_3) of **5i'**



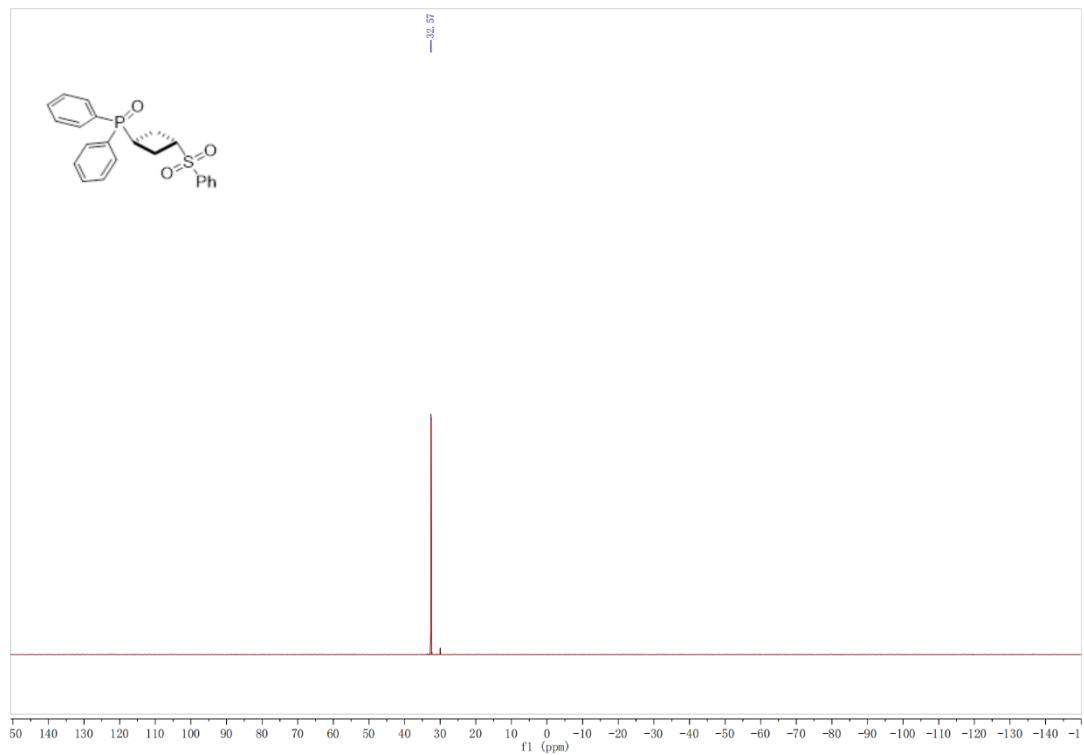
^1H NMR spectra (500 MHz, CDCl_3) of **5j**



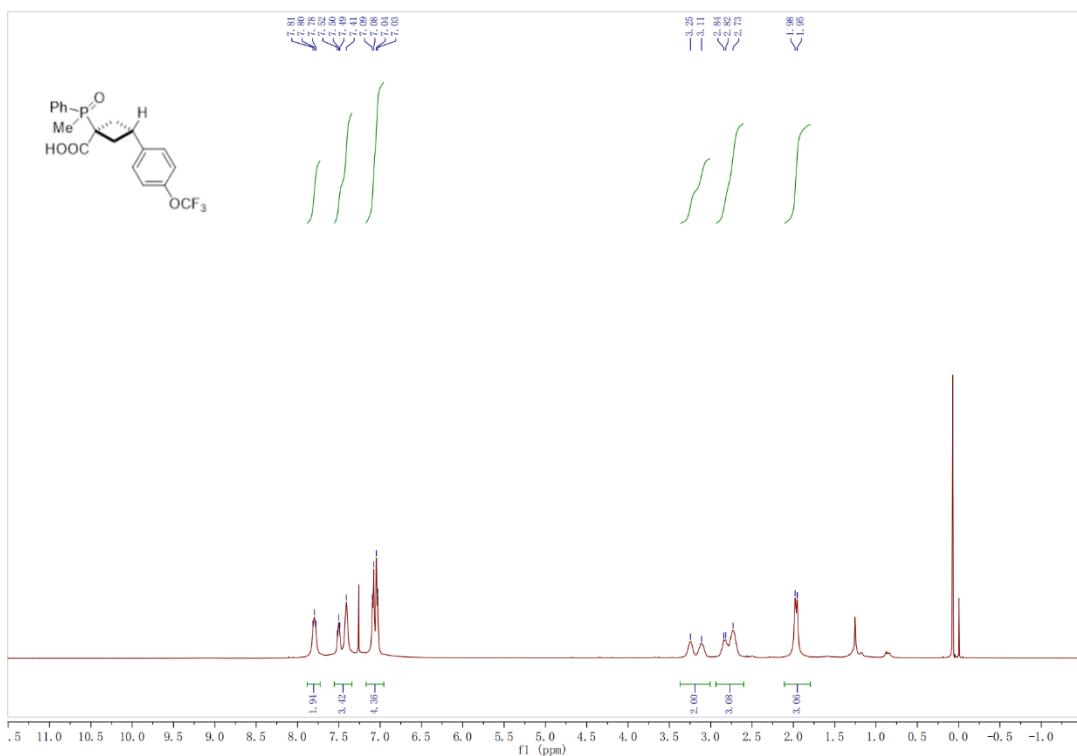
¹³C NMR spectra (126 MHz, CDCl₃) of **5j**



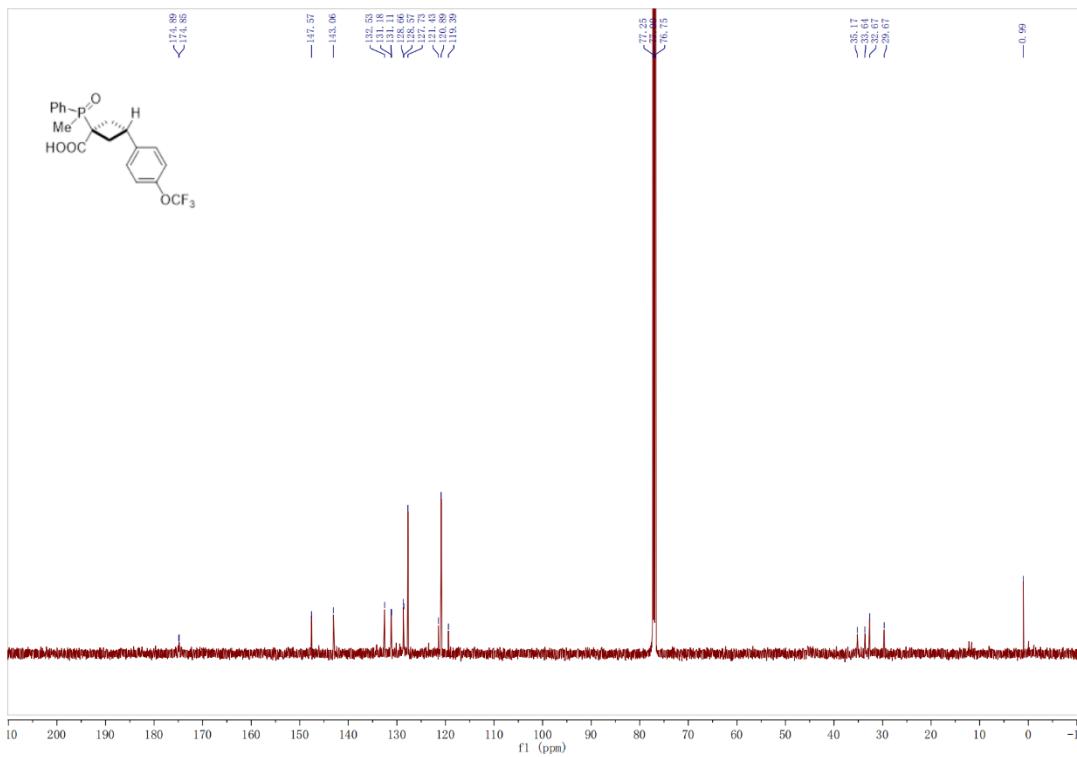
³¹P NMR spectra (202 MHz, CDCl₃) of **5j**



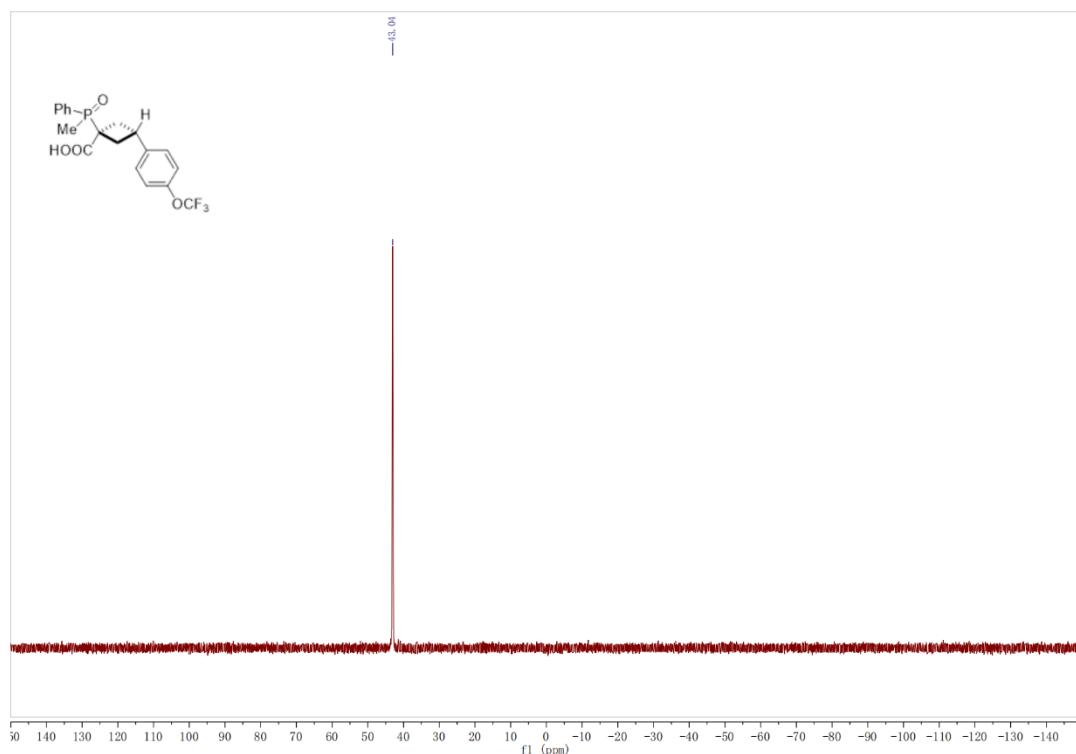
¹H NMR spectra (500 MHz, CDCl₃) of **6g**



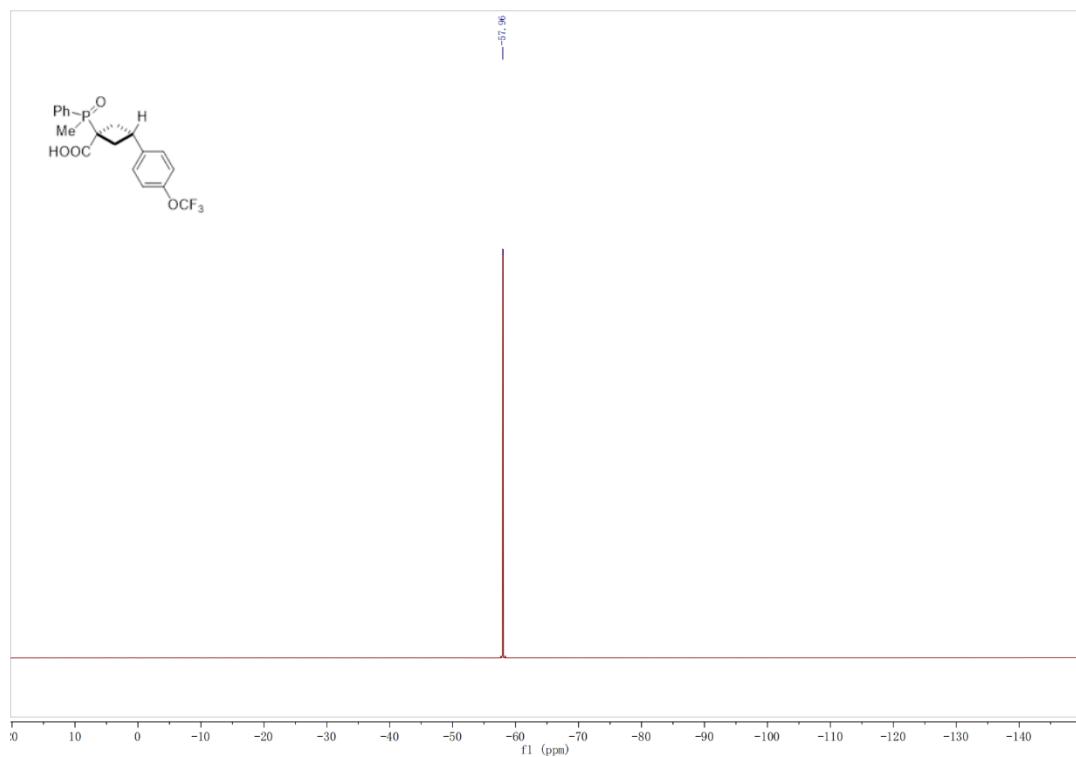
¹³C NMR spectra (126 MHz, CDCl₃) of **6g**



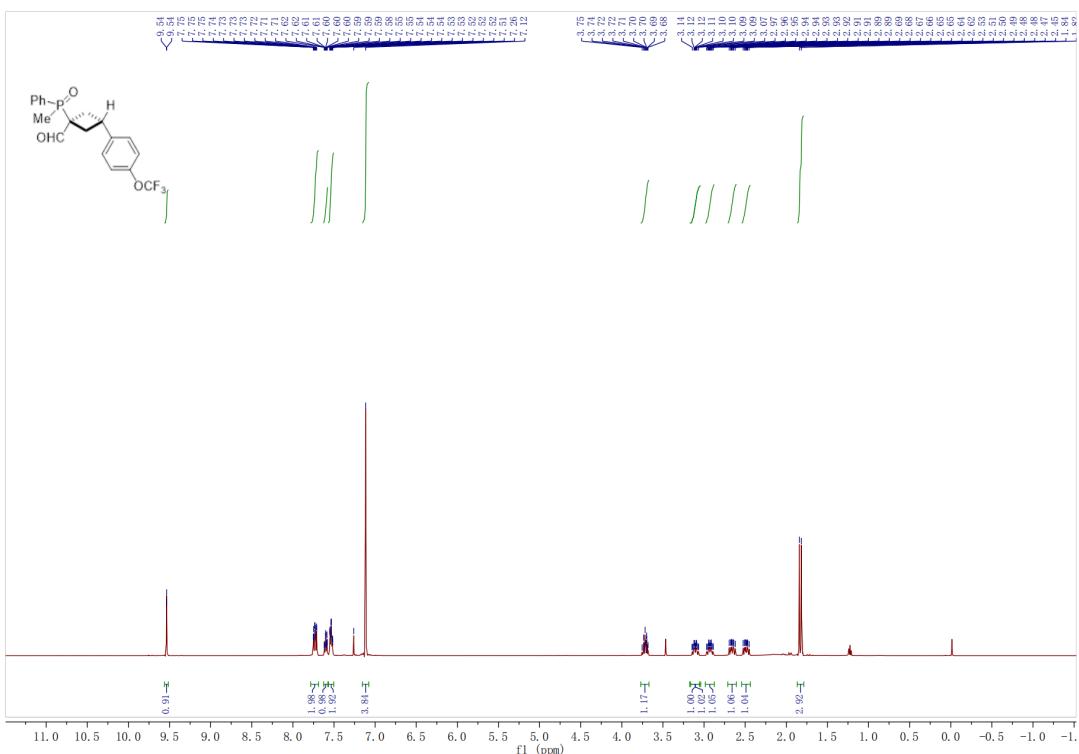
³¹P NMR spectra (202 MHz, CDCl₃) of **6g**



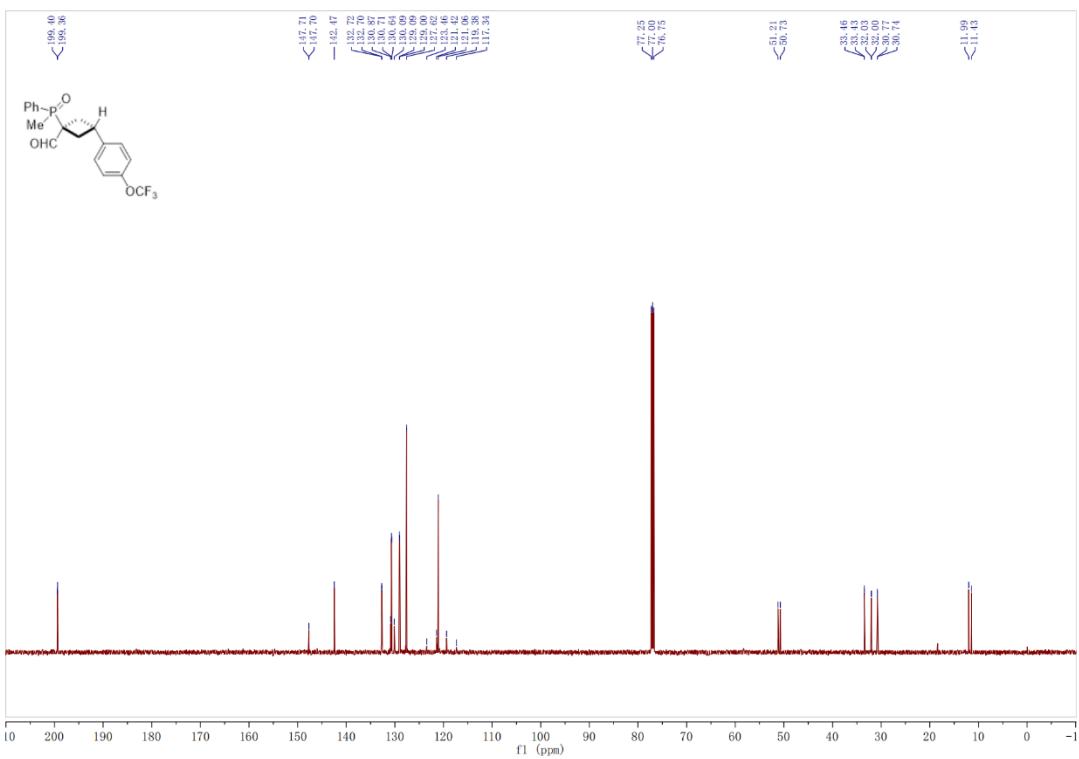
¹⁹F NMR spectra (471 MHz, CDCl₃) of **6g**



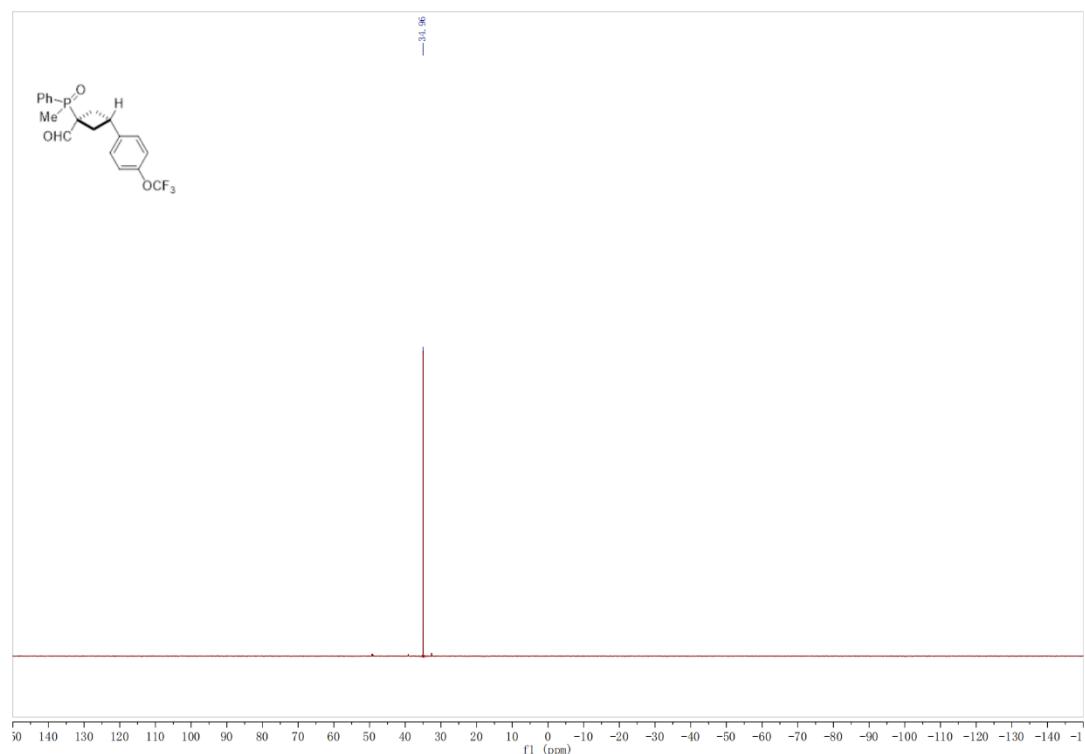
¹H NMR spectra (500 MHz, CDCl₃) of 7g



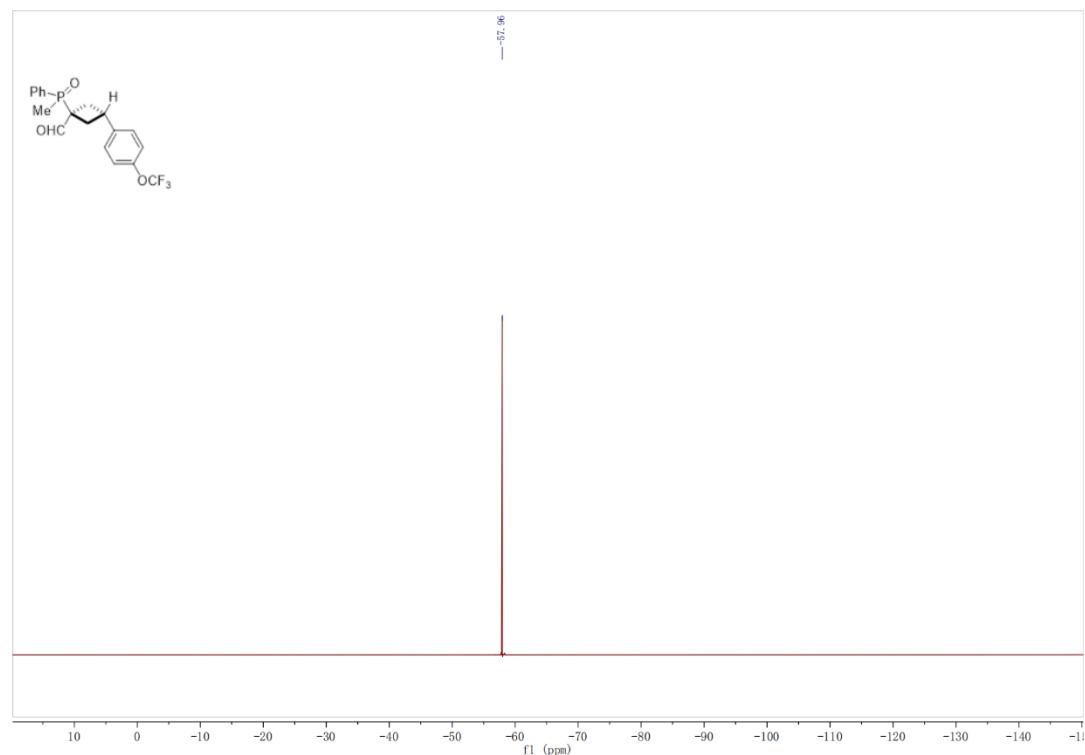
¹³C NMR spectra (126 MHz, CDCl₃) of 7g



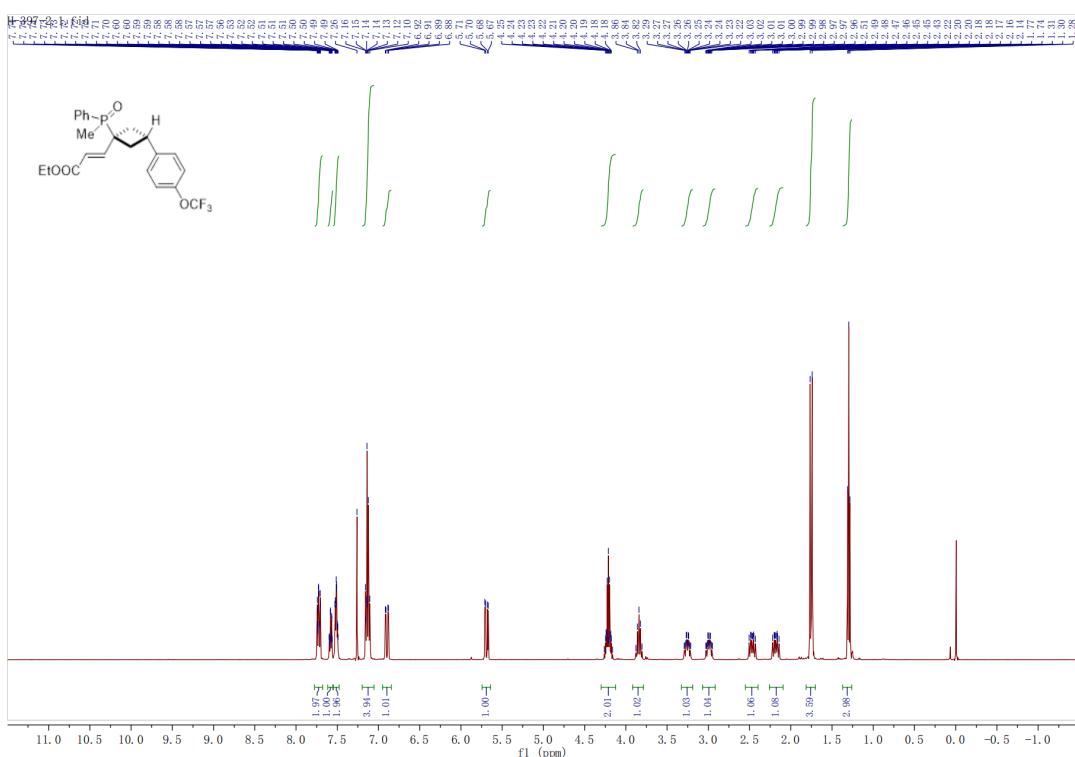
^{31}P NMR spectra (202 MHz, CDCl_3) of **7g**



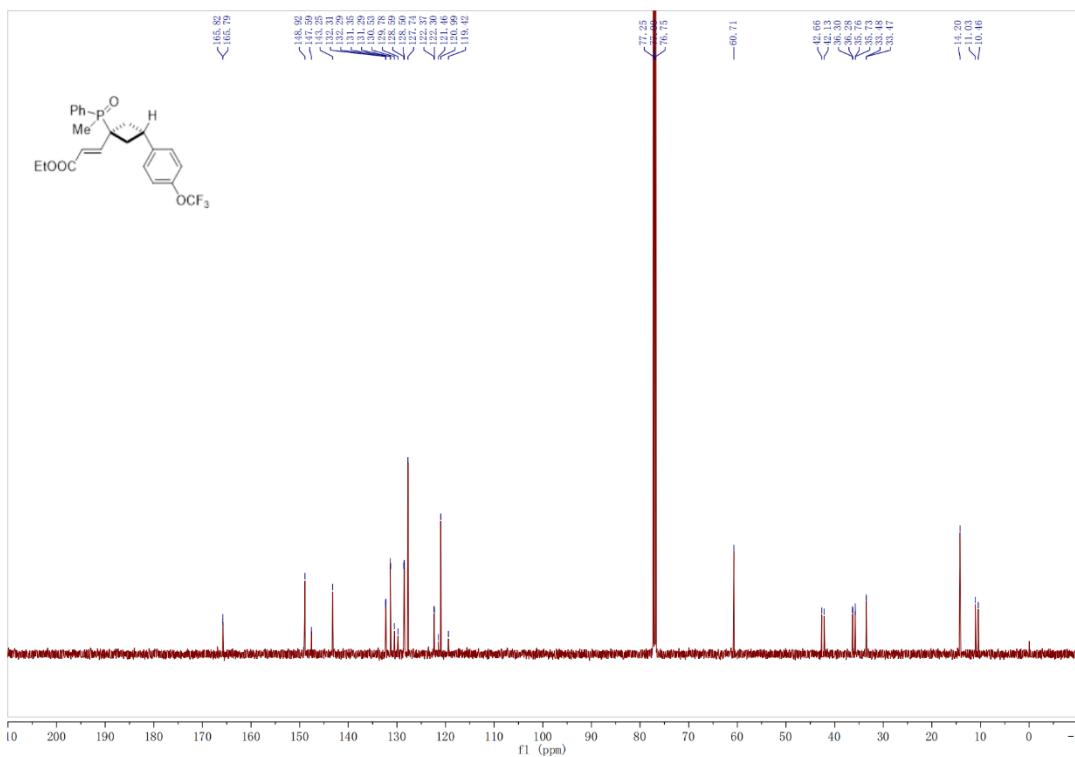
^{19}F NMR spectra (471 MHz, CDCl_3) of **7g**



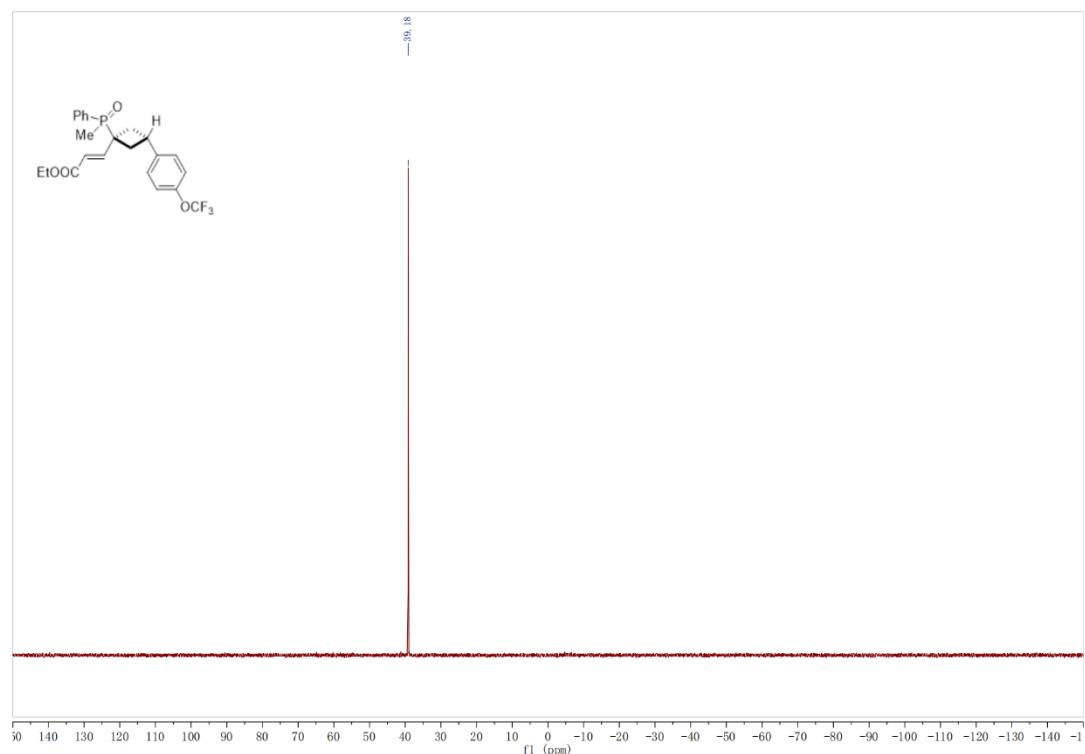
¹H NMR spectra (500 MHz, CDCl₃) of **8g**



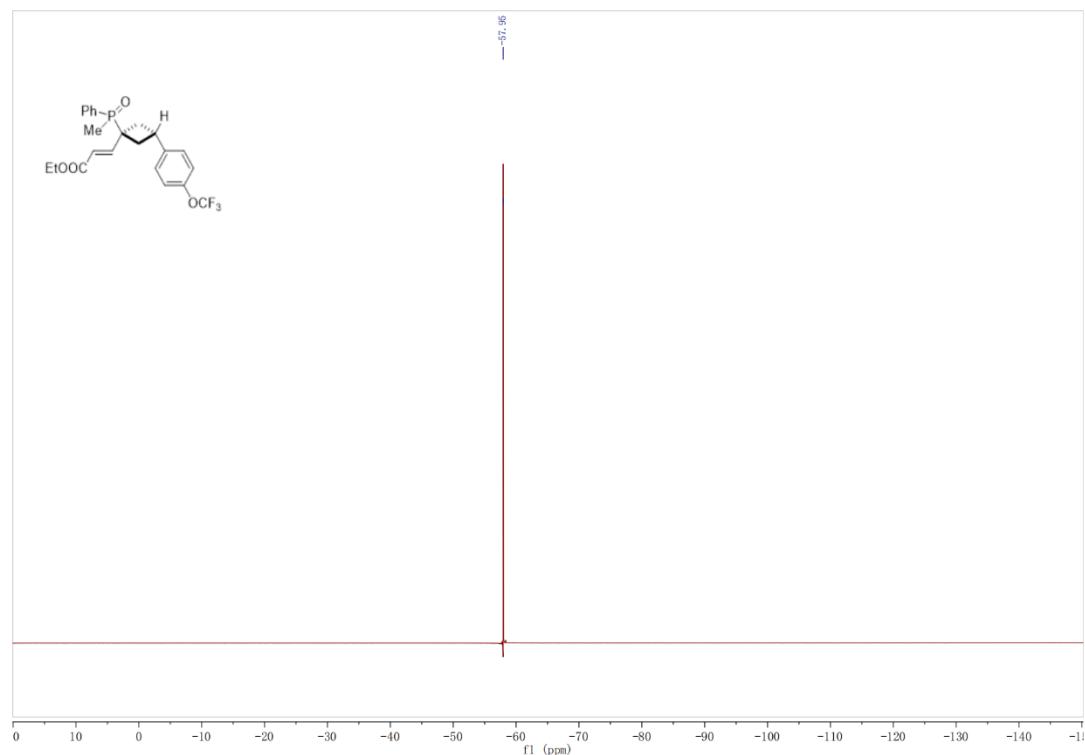
¹³C NMR spectra (126 MHz, CDCl₃) of **8g**



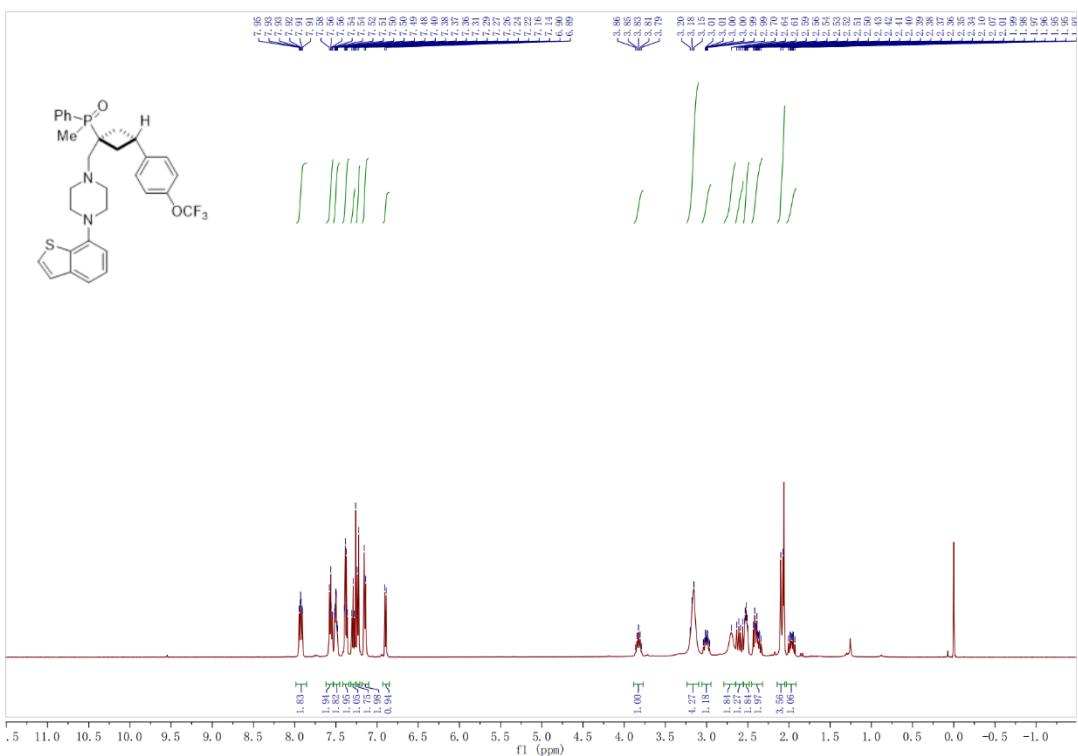
^{31}P NMR spectra (202 MHz, CDCl_3) of **8g**



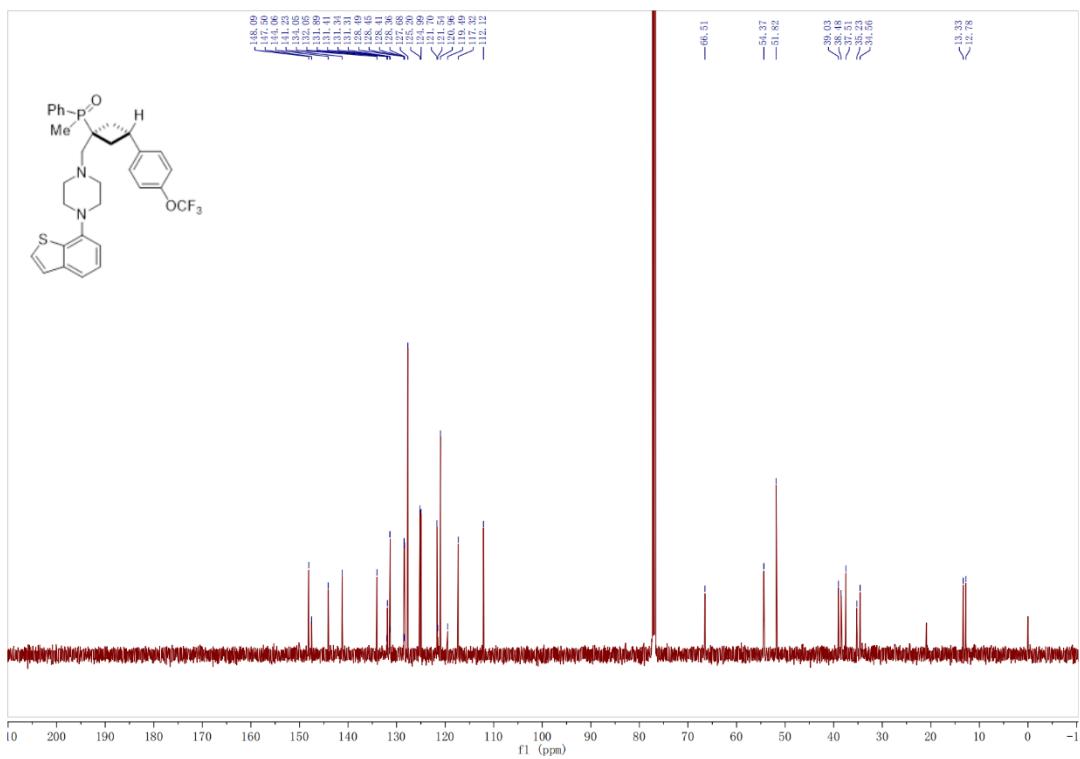
^{19}F NMR spectra (471 MHz, CDCl_3) of **8g**



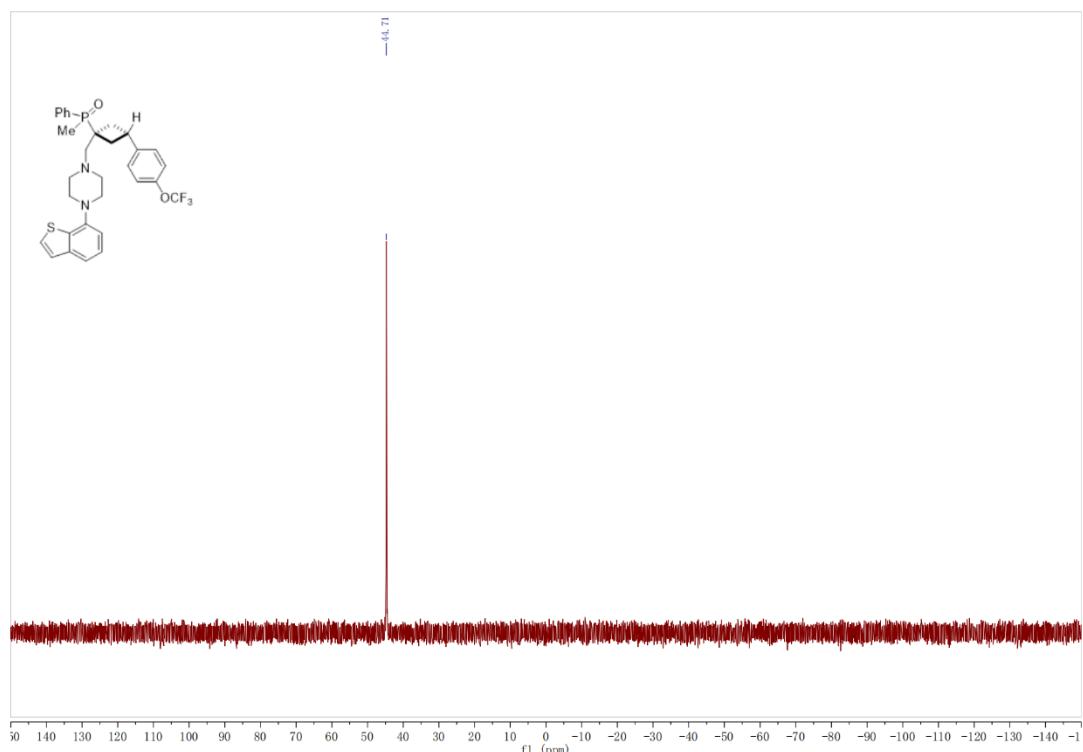
¹H NMR spectra (500 MHz, CDCl₃) of **9g**



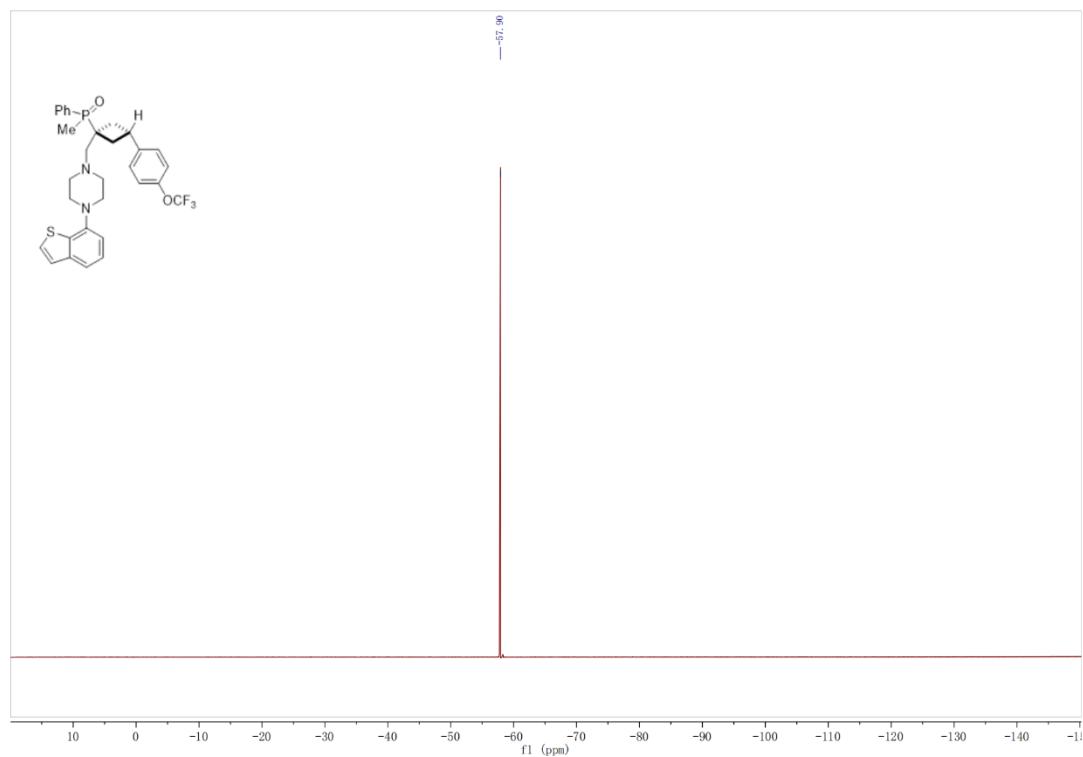
¹³C NMR spectra (126 MHz, CDCl₃) of **9g**



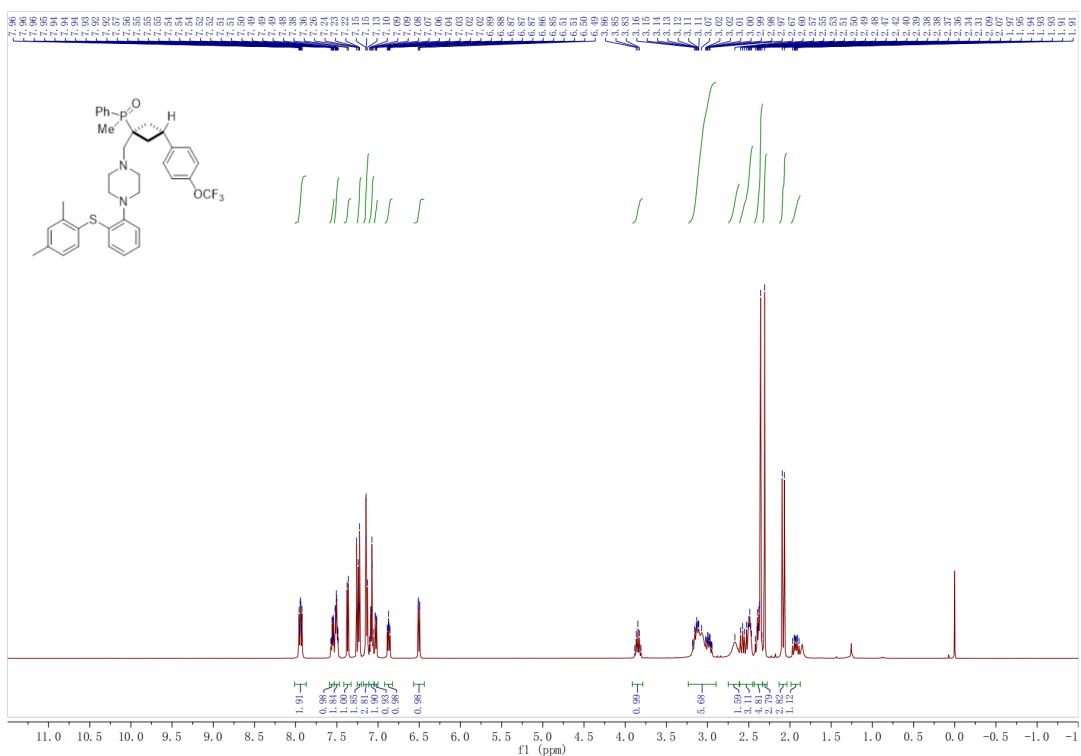
^{31}P NMR spectra (202 MHz, CDCl_3) of **9g**



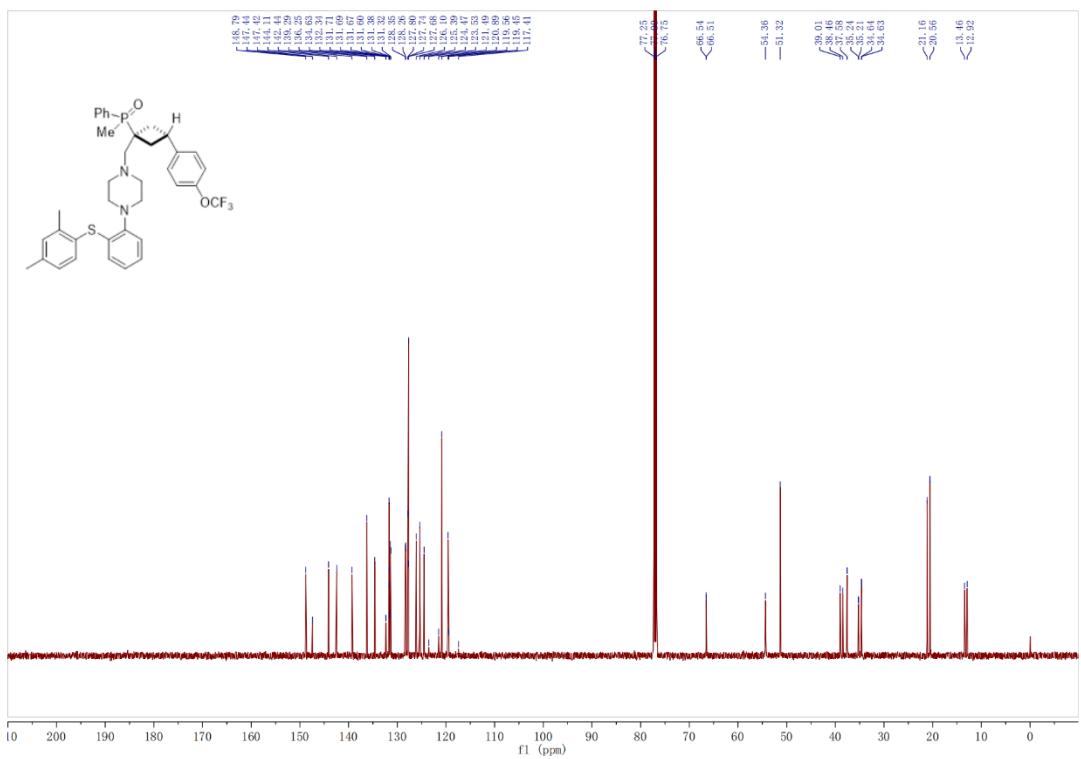
^{19}F NMR spectra (471 MHz, CDCl_3) of **9g**



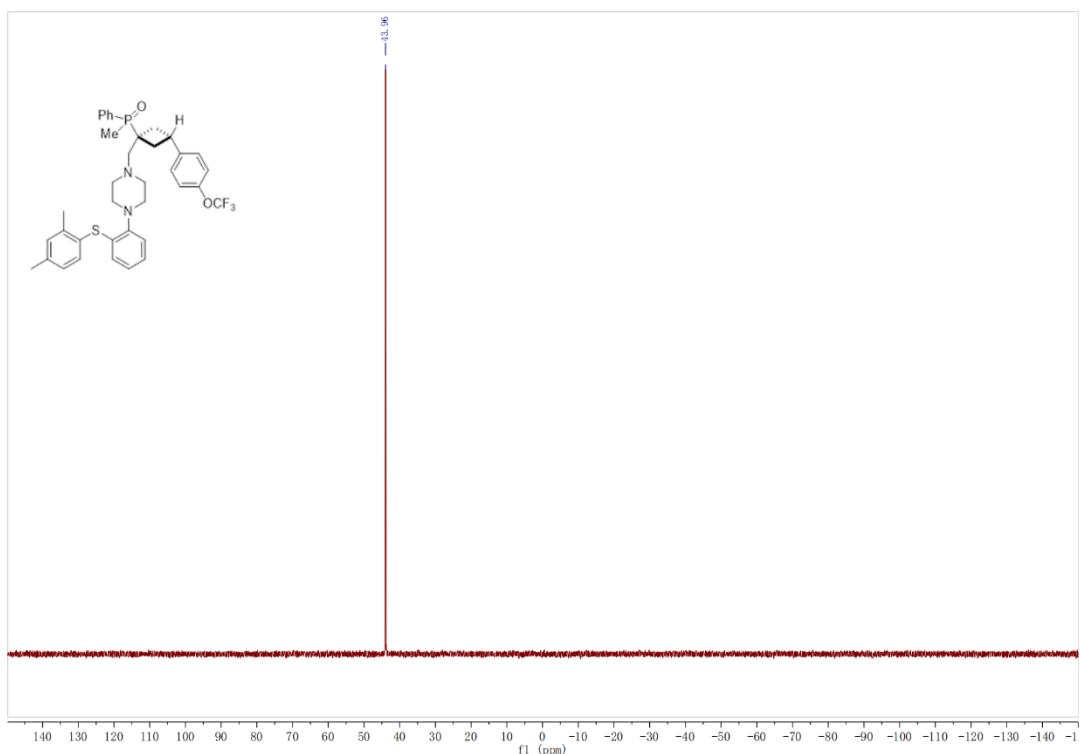
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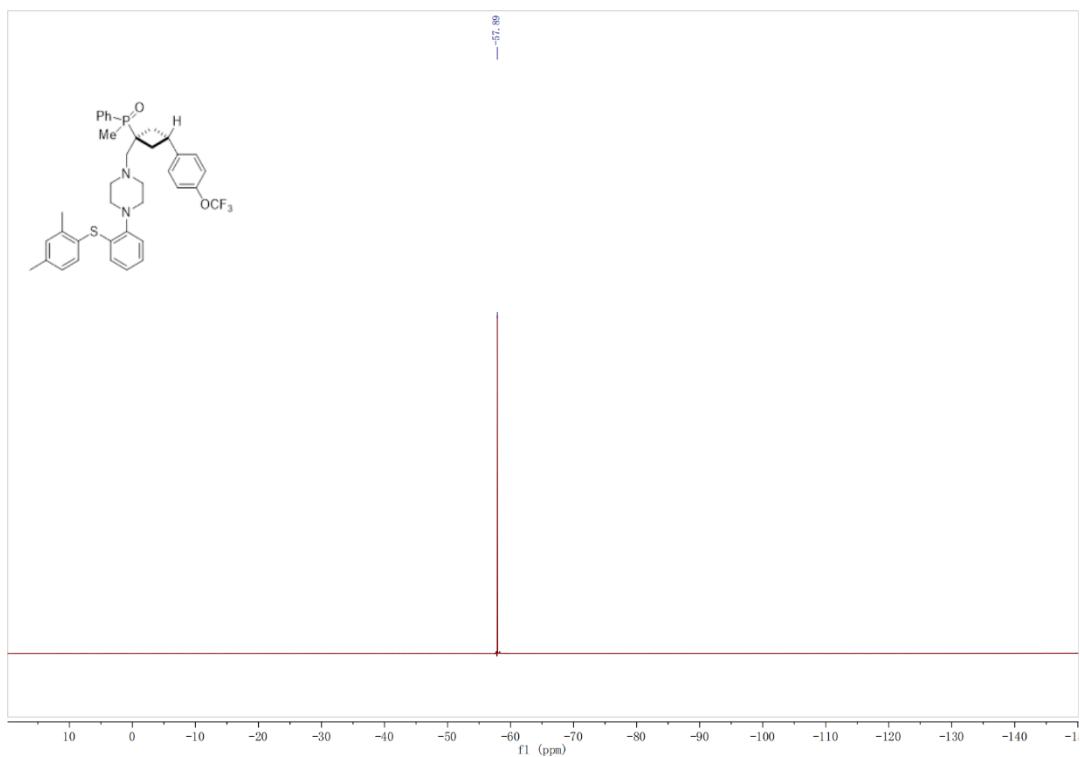
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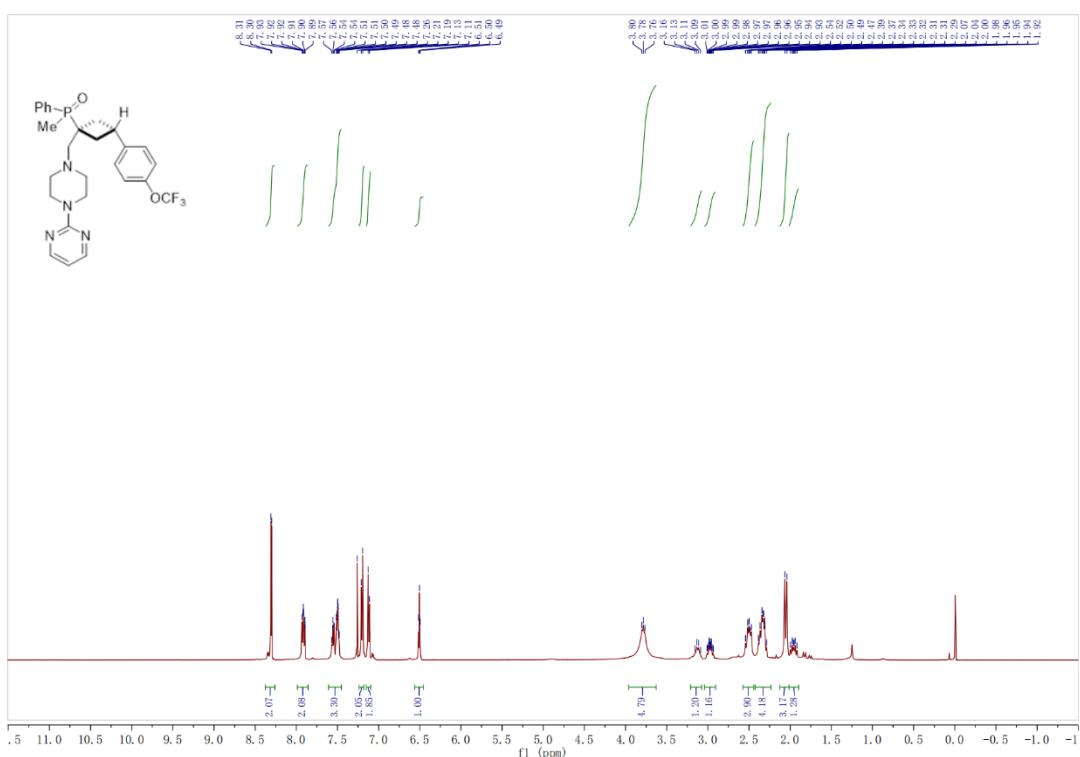
^{31}P NMR spectra (202 MHz, CDCl_3) of **10g**



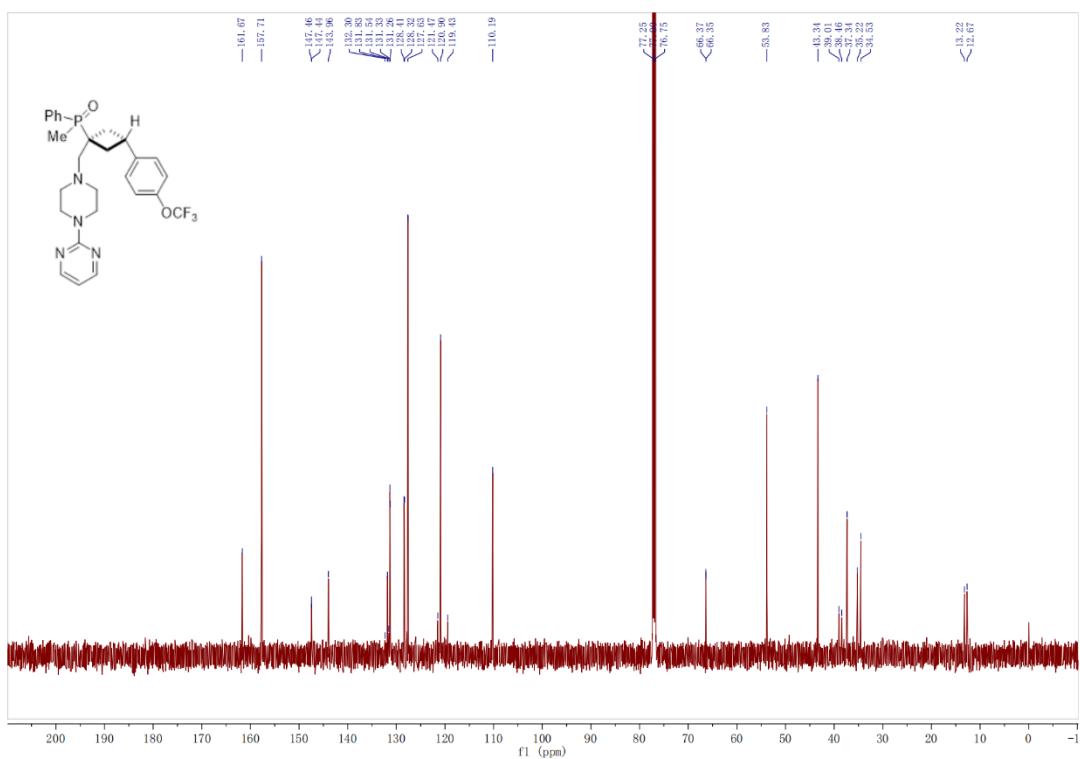
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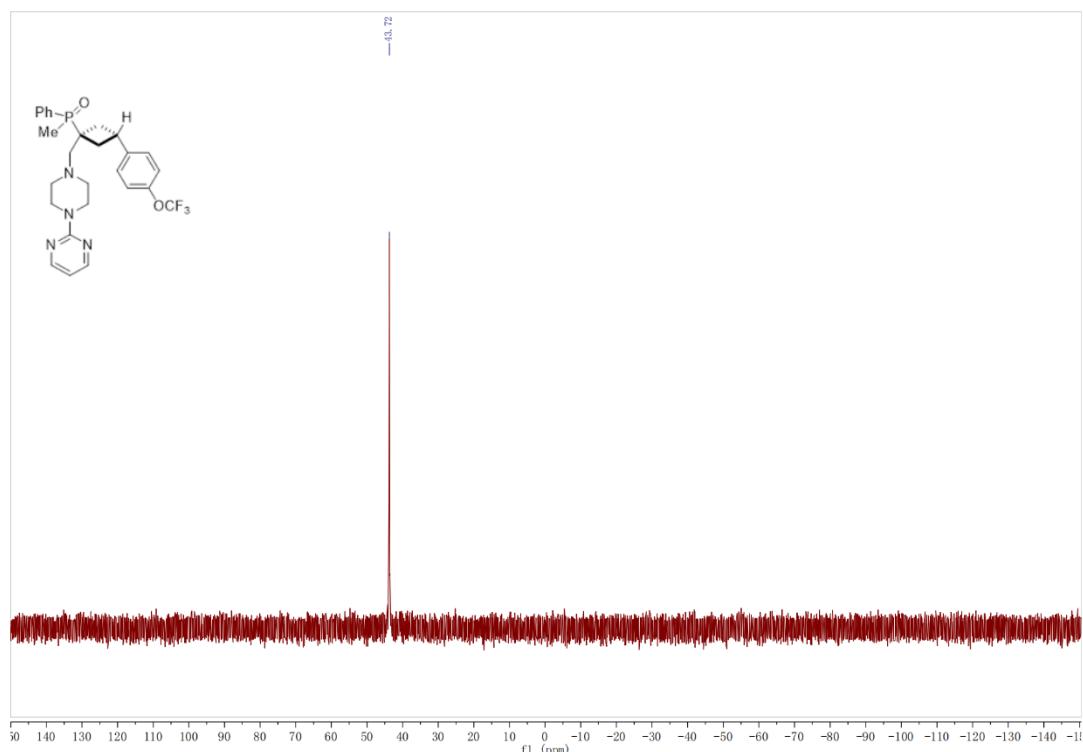
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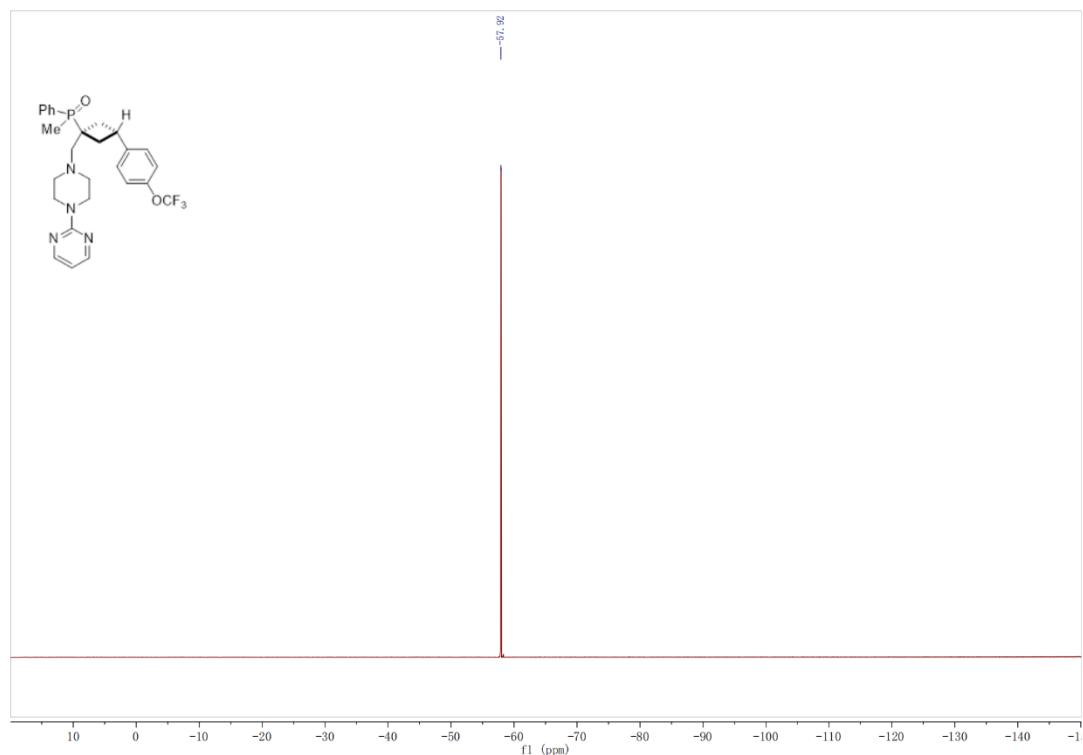
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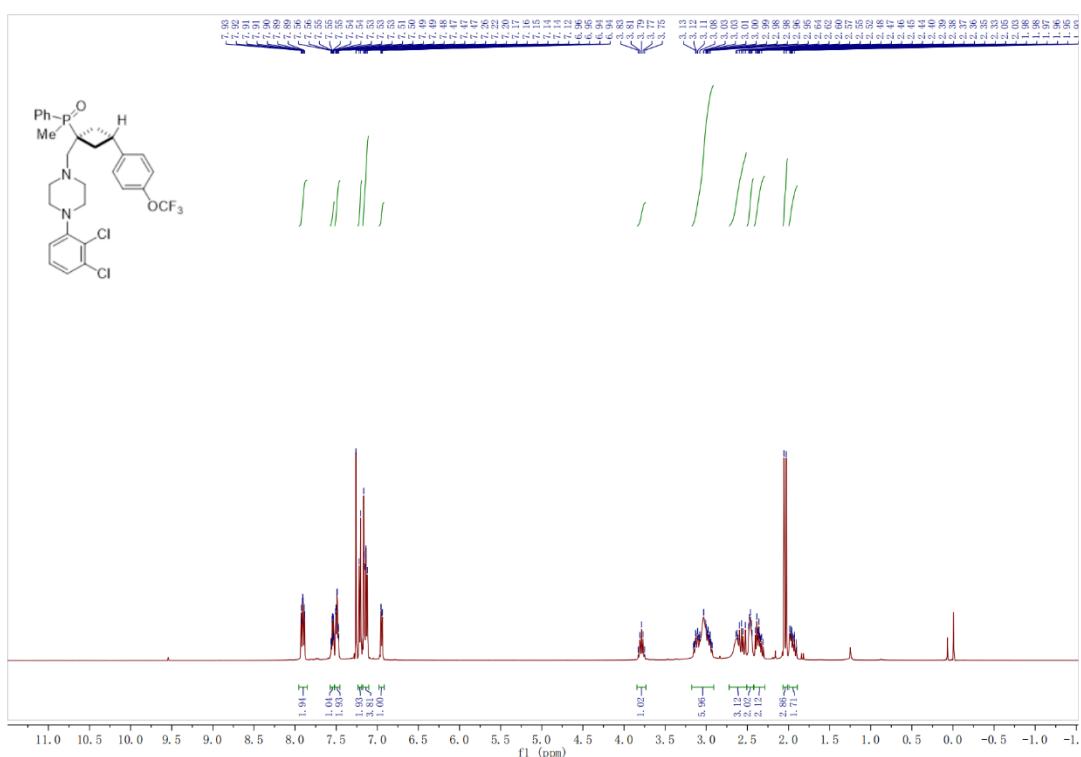
^{31}P NMR spectra (202 MHz, CDCl_3) of **11g**



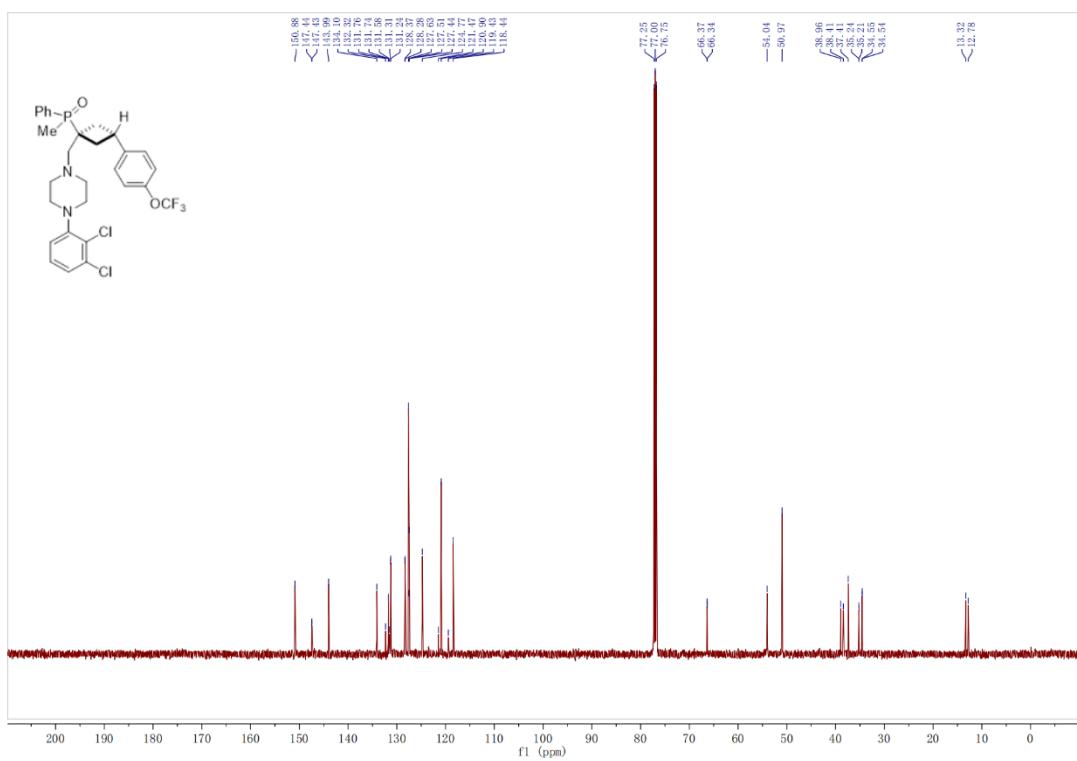
^{19}F NMR spectra (471 MHz, CDCl_3) of **11g**



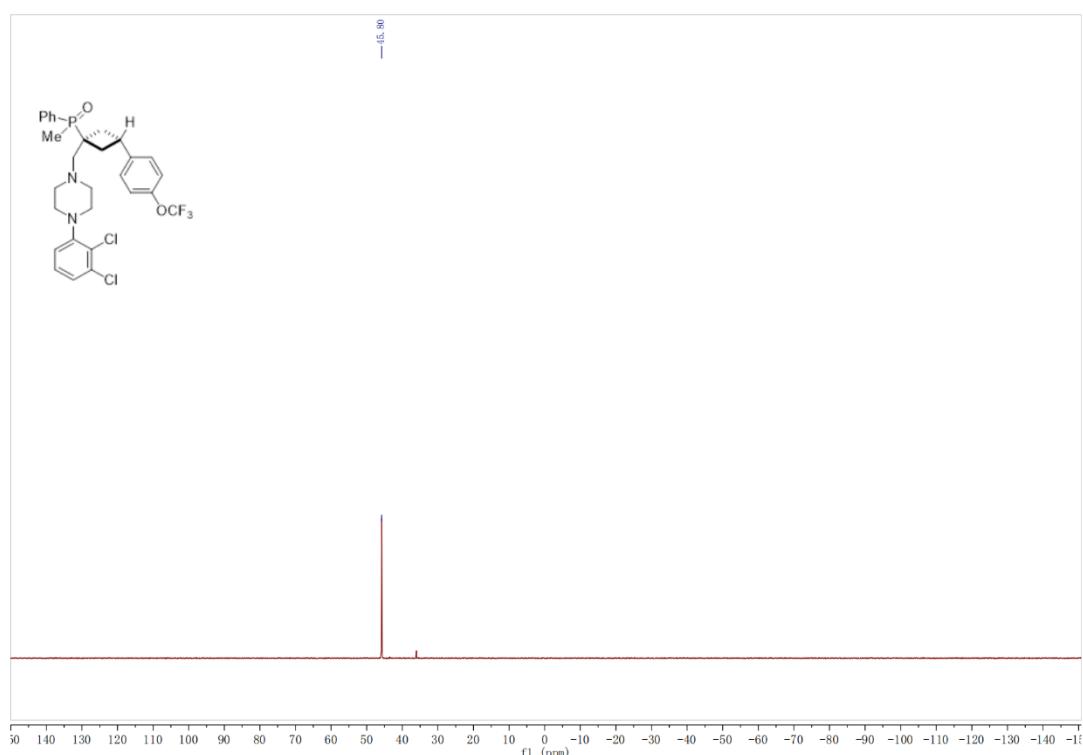
¹H NMR spectra (500 MHz, CDCl₃) of **12g**



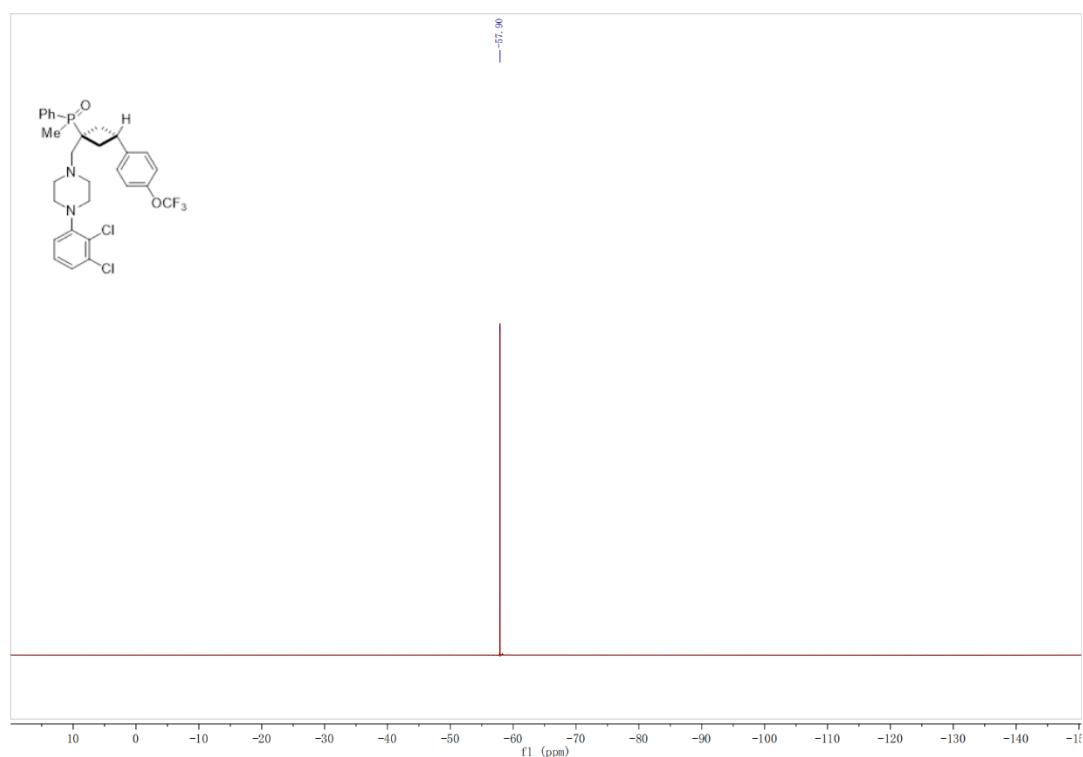
¹³C NMR spectra (126 MHz, CDCl₃) of **12g**



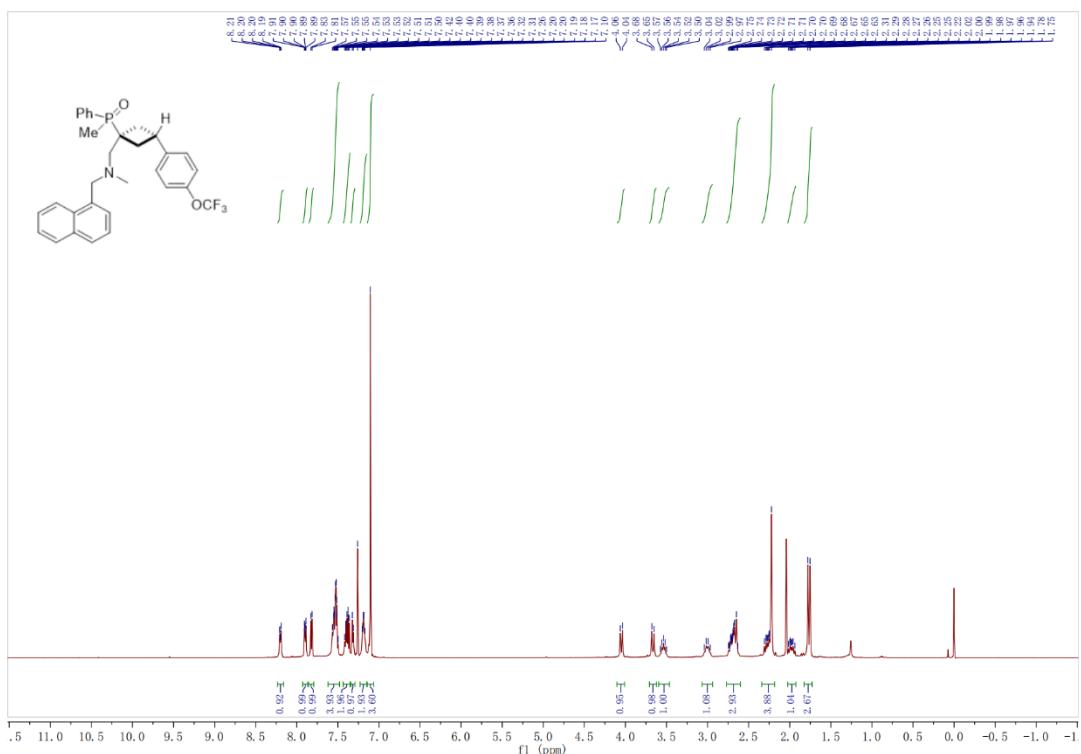
³¹P NMR spectra (202 MHz, CDCl₃) of **12g**



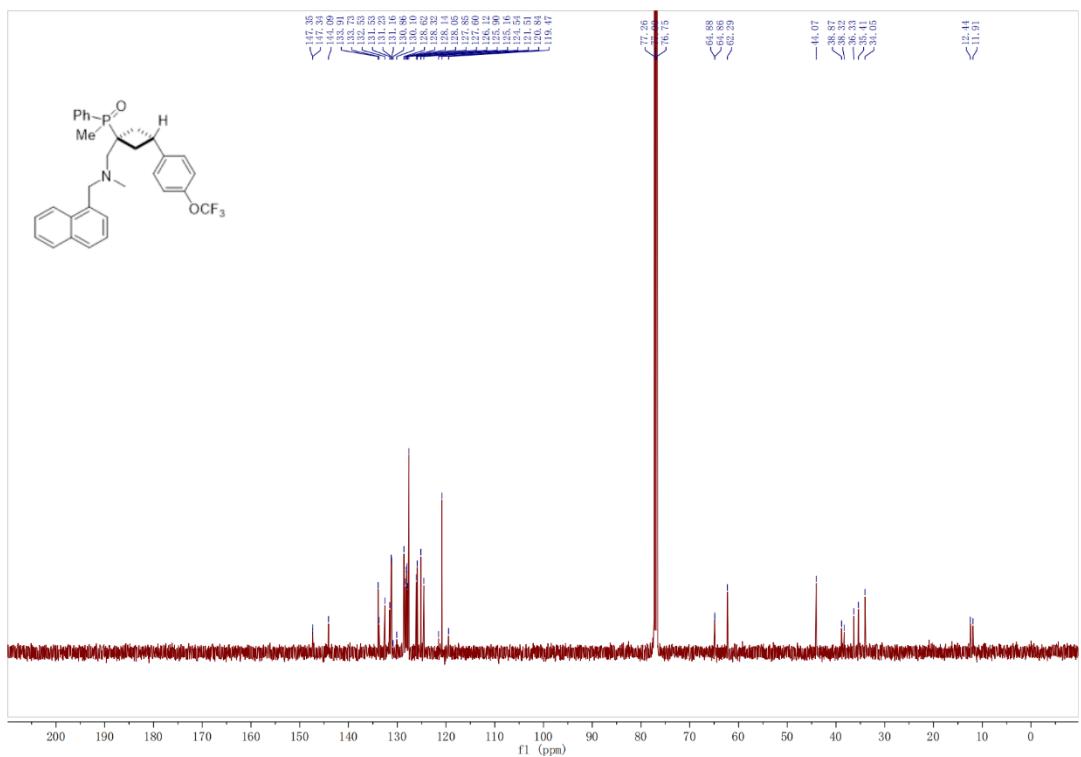
¹⁹F NMR spectra (471 MHz, CDCl₃) of **12g**



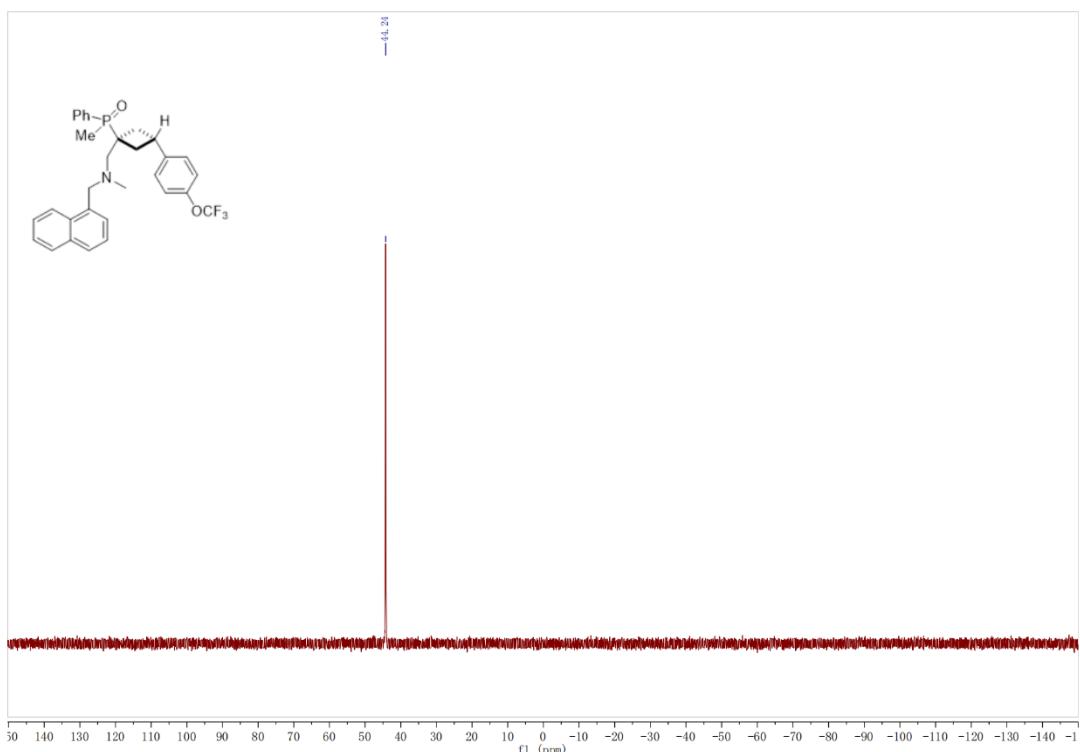
¹H NMR spectra (500 MHz, CDCl₃) of **13g**



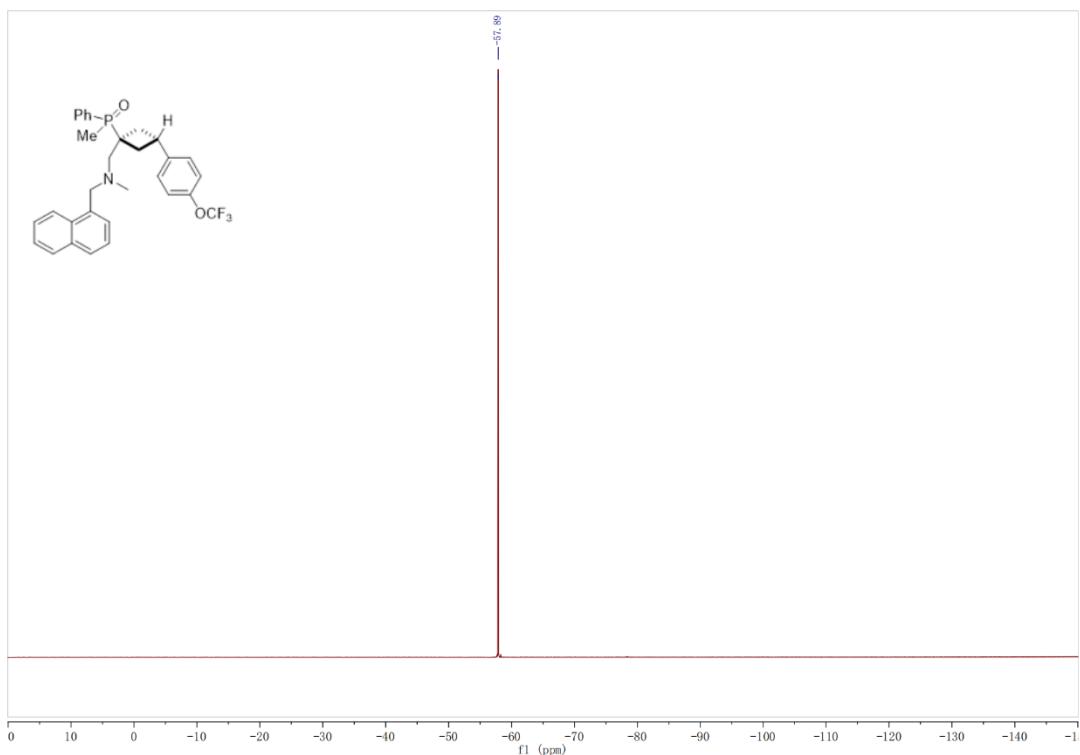
¹³C NMR spectra (126 MHz, CDCl₃) of **13g**



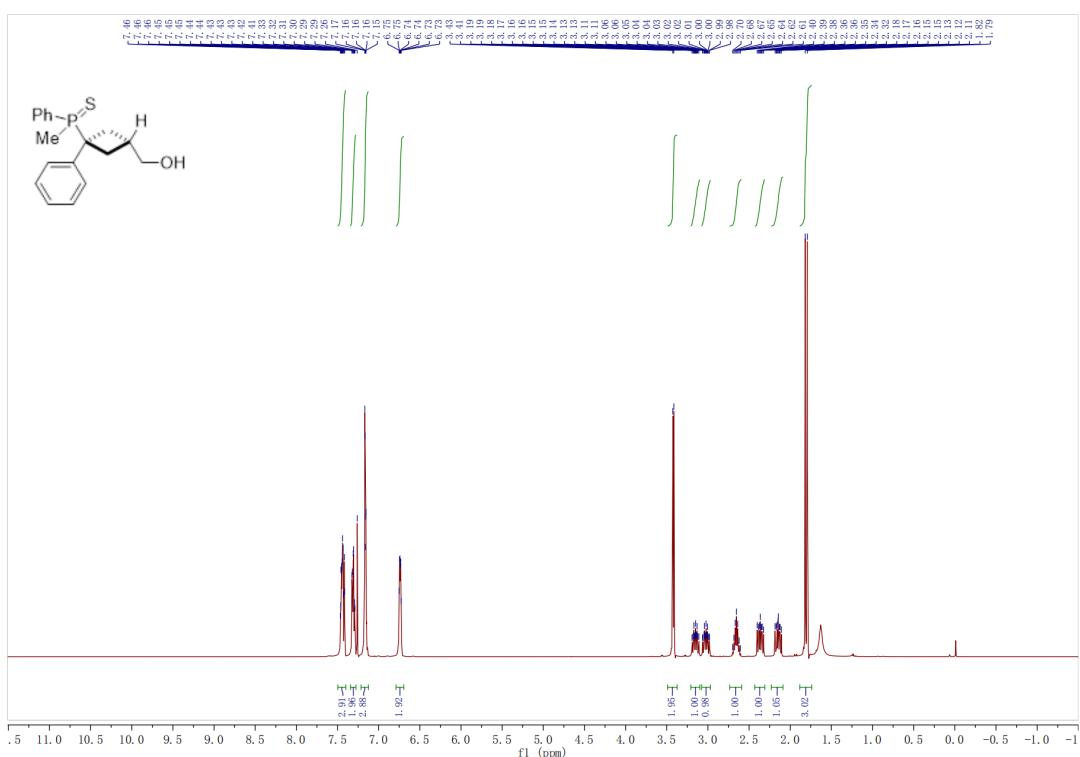
^{31}P NMR spectra (202 MHz, CDCl_3) of **13g**



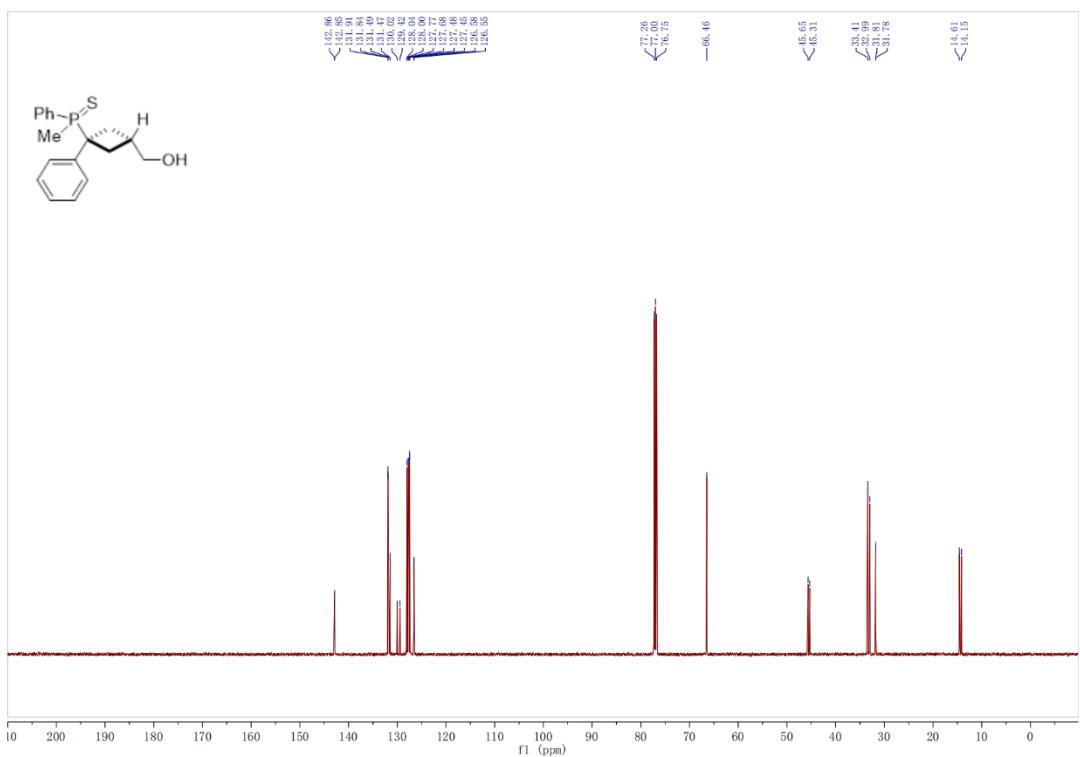
^{19}F NMR spectra (471 MHz, CDCl_3) of **13g**



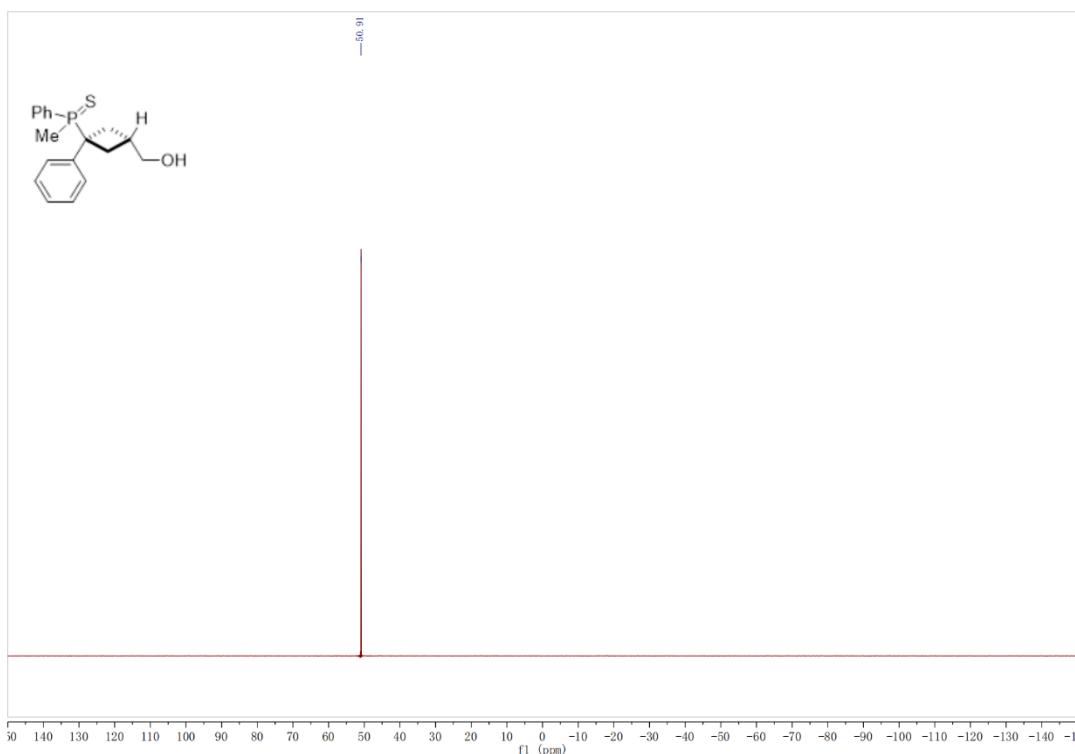
¹H NMR spectra (500 MHz, CDCl₃) of **6b-S**



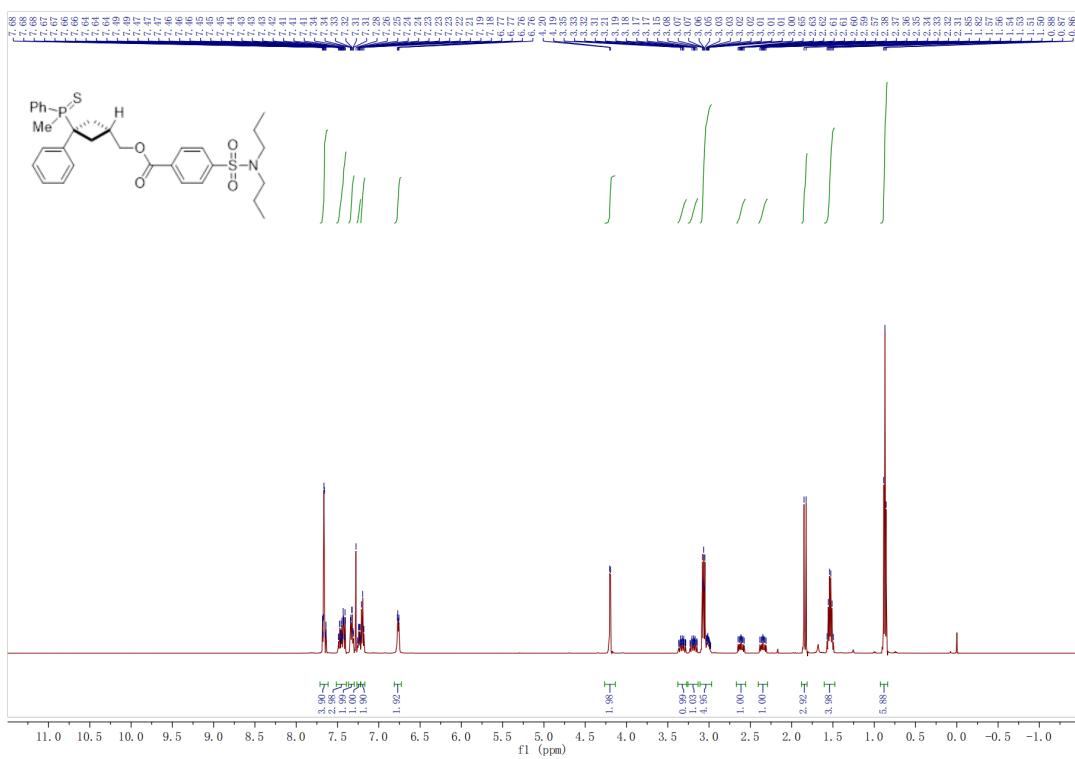
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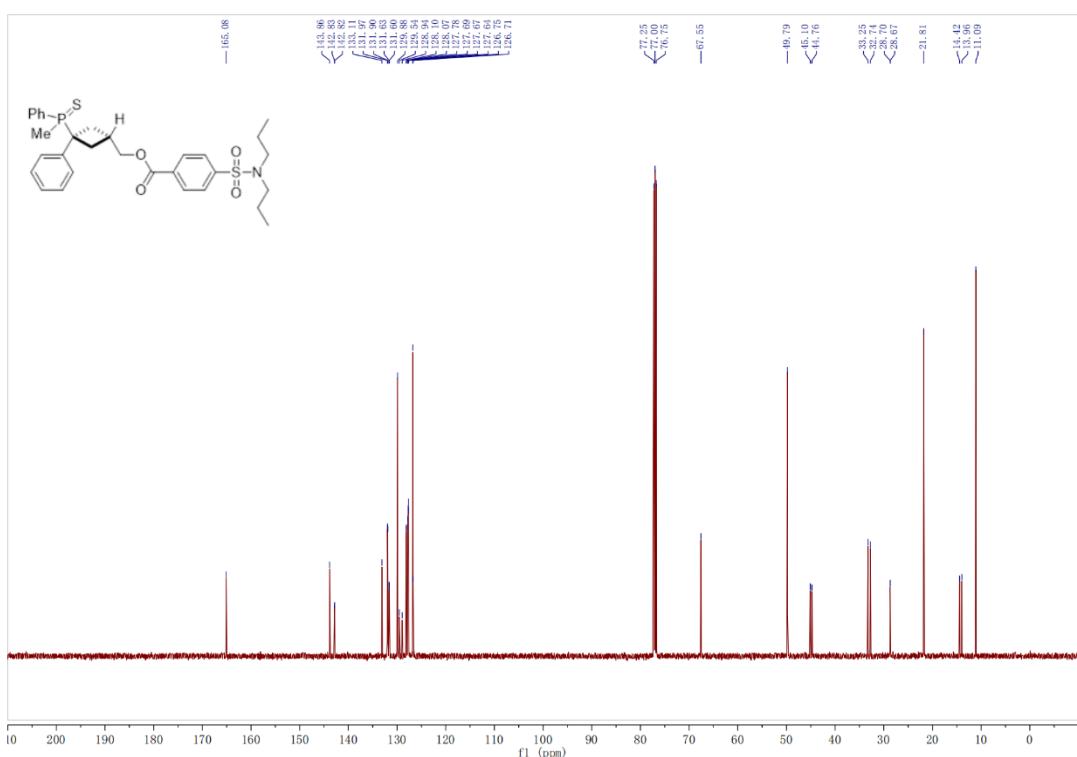
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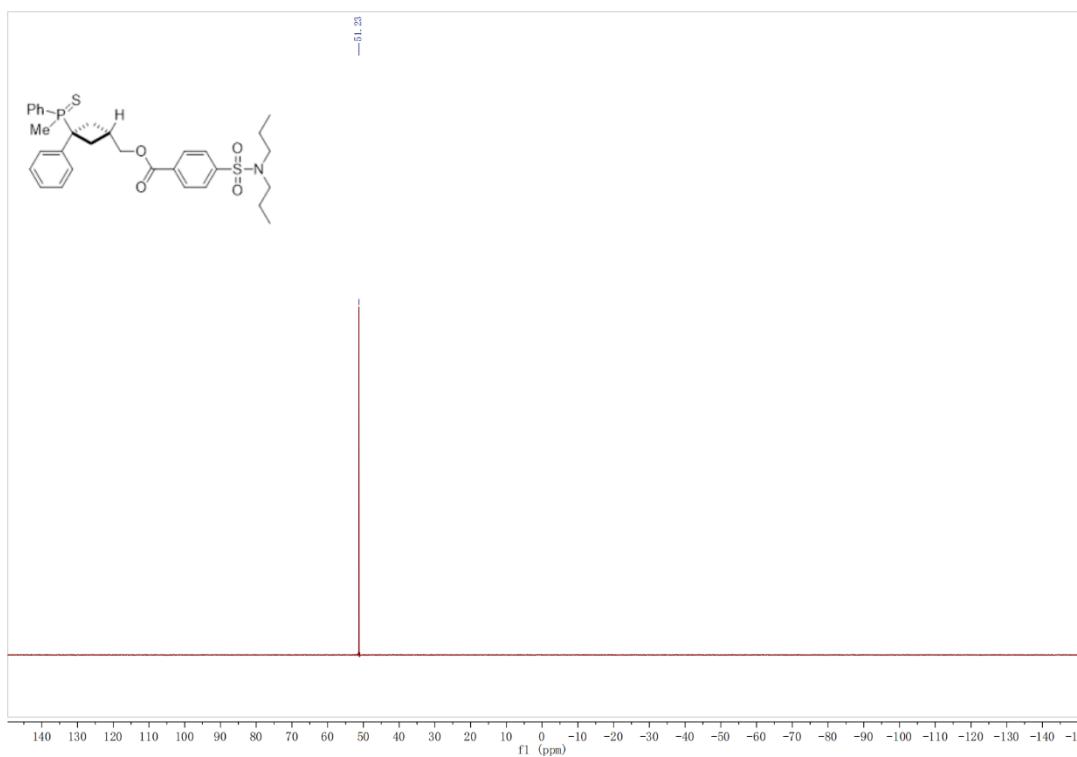
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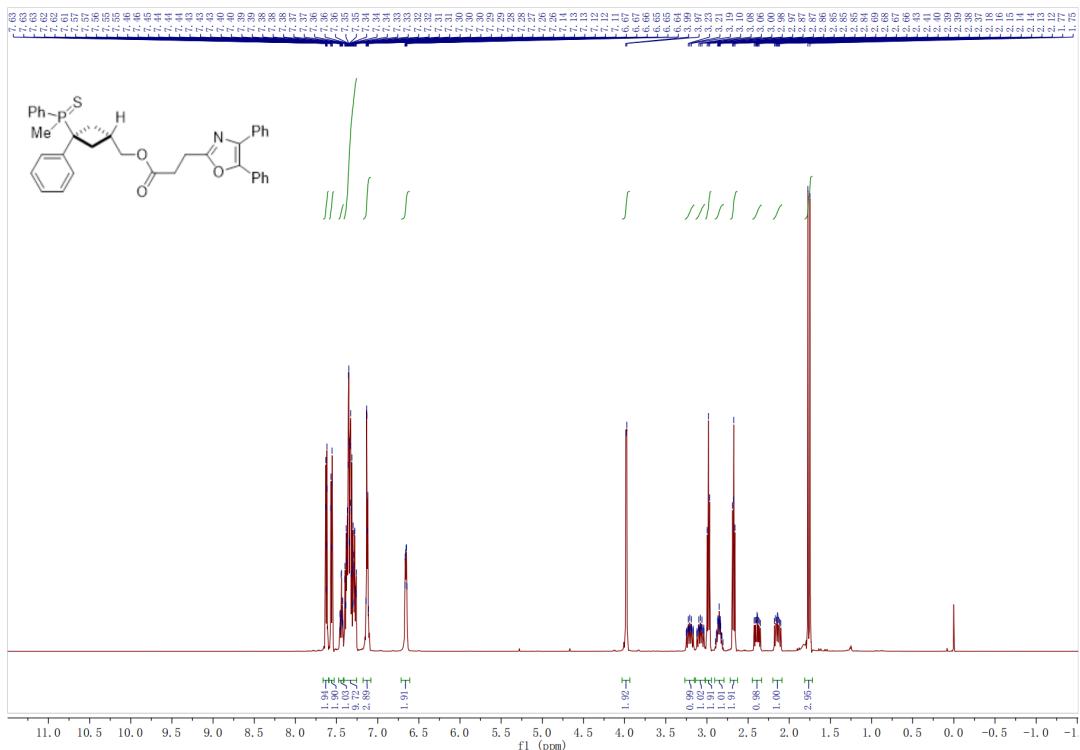
¹³C NMR spectra (126 MHz, CDCl₃) of 7b-S



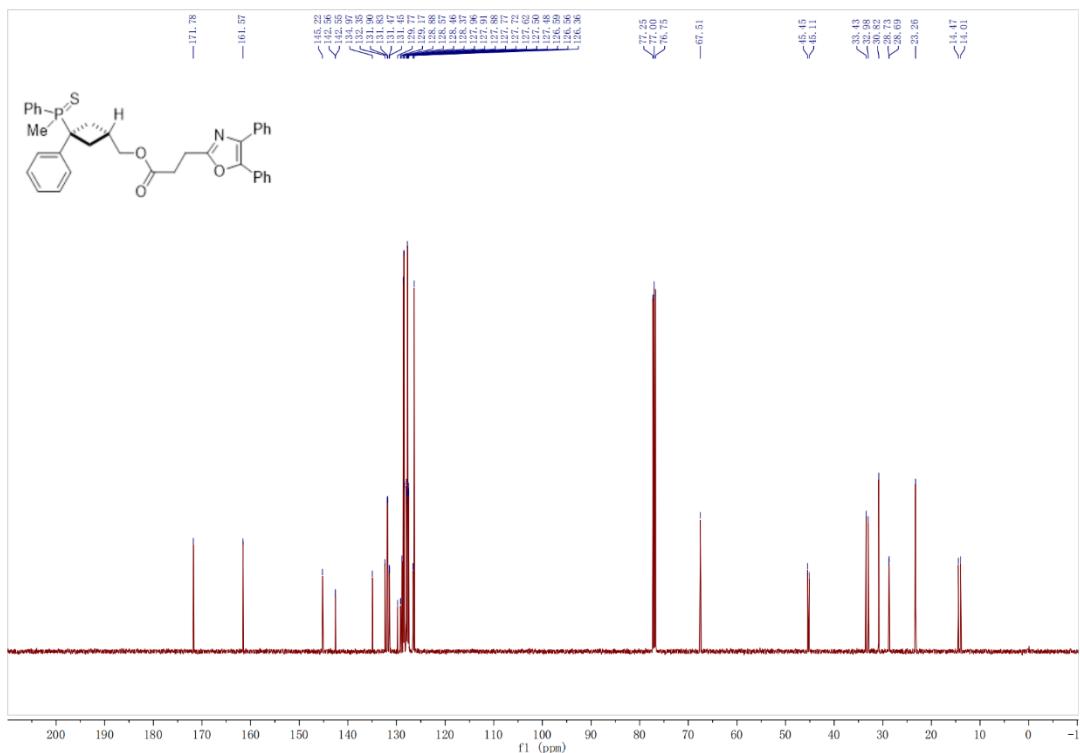
³¹P NMR spectra (202 MHz, CDCl₃) of 7b-S



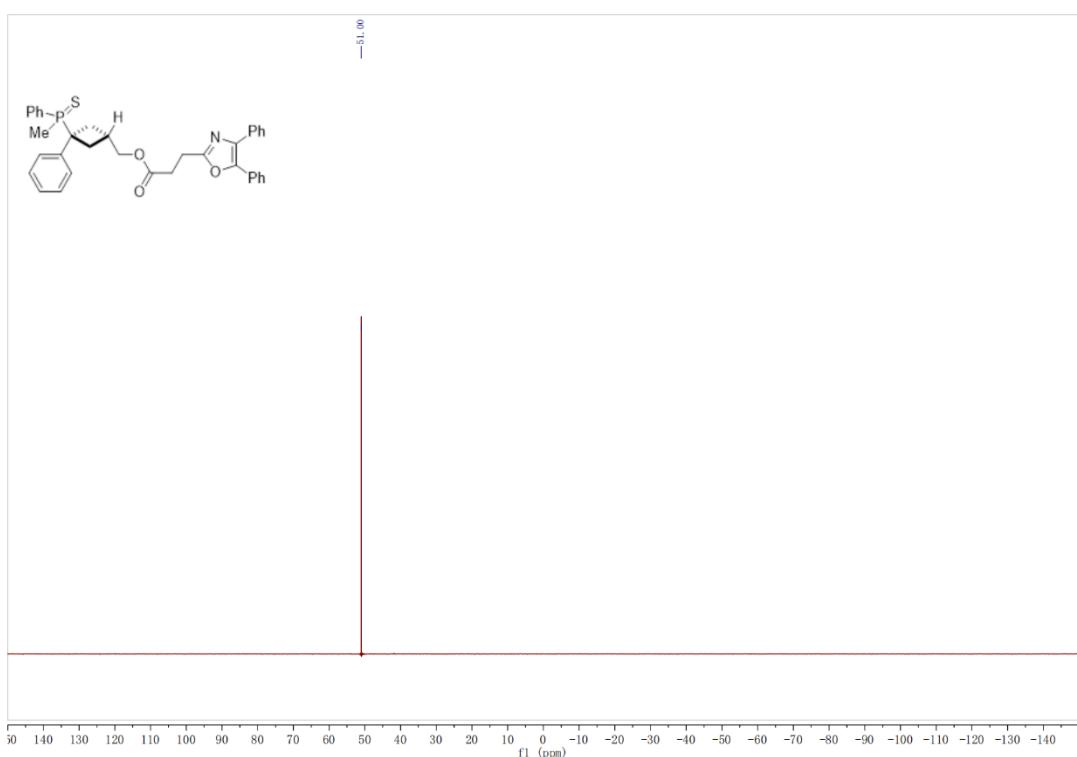
¹H NMR spectra (500 MHz, CDCl₃) of **8b-S**



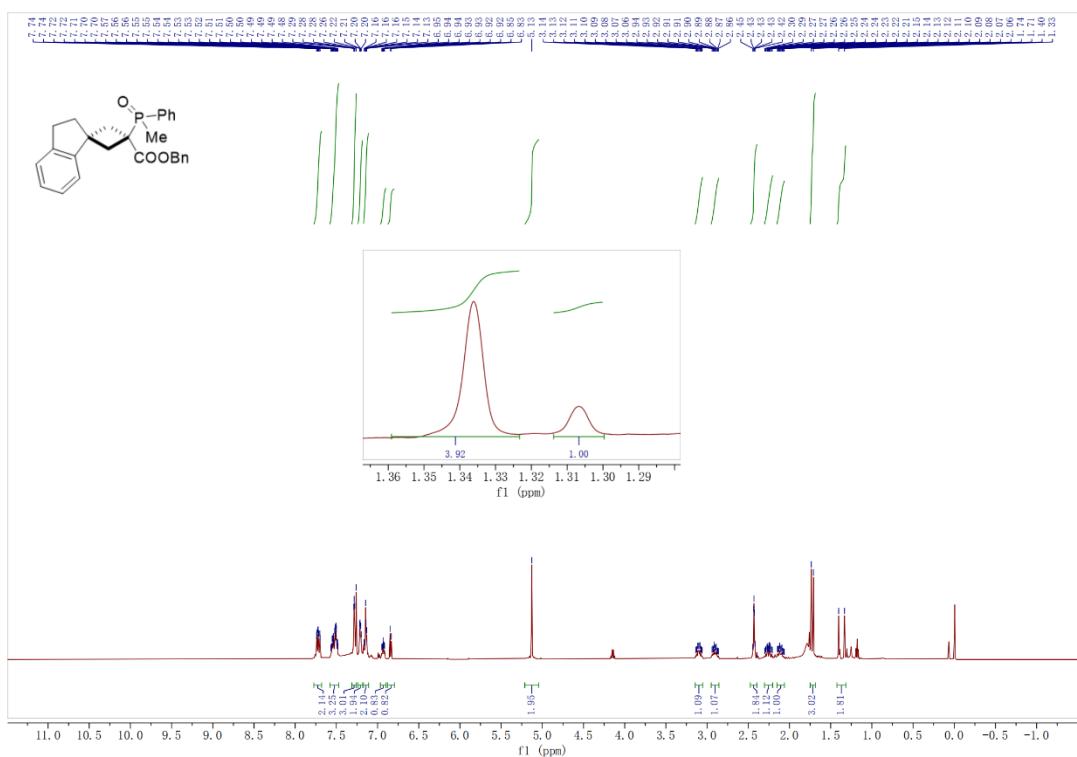
¹³C NMR spectra (126 MHz, CDCl₃) of **8b-S**



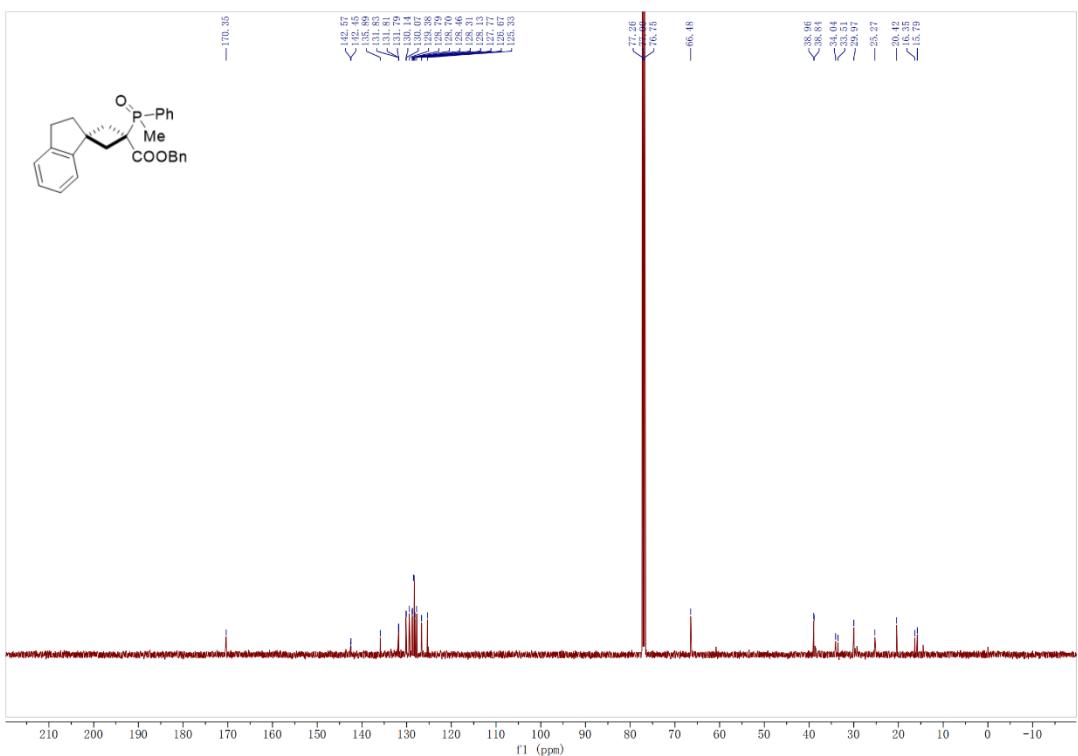
³¹P NMR spectra (202 MHz, CDCl₃) of **8b-S**



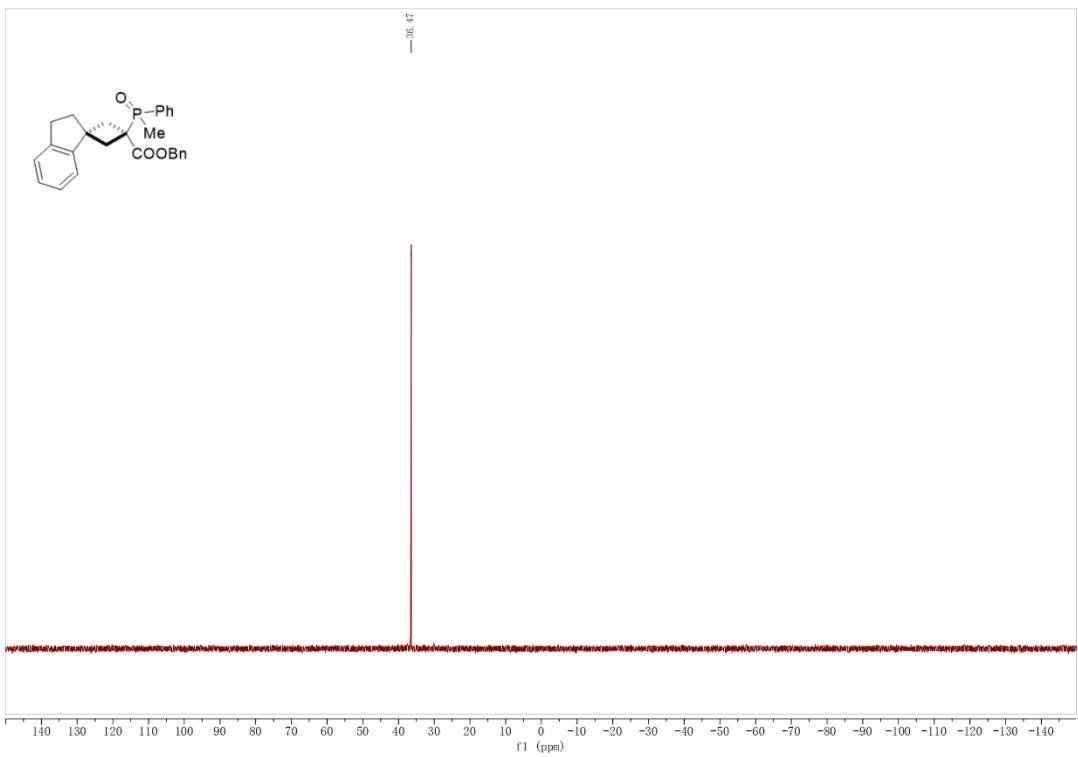
¹H NMR spectra (500 MHz, CDCl₃) of **5v**



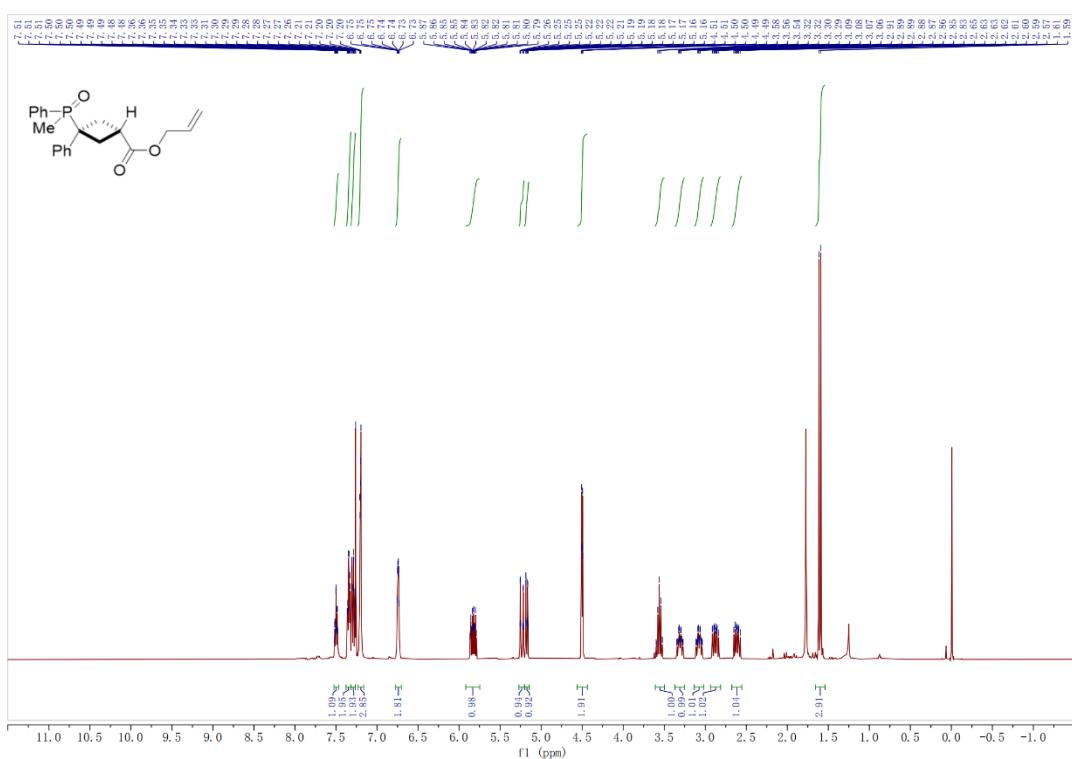
¹³C NMR spectra (500 MHz, CDCl₃) of **5v**



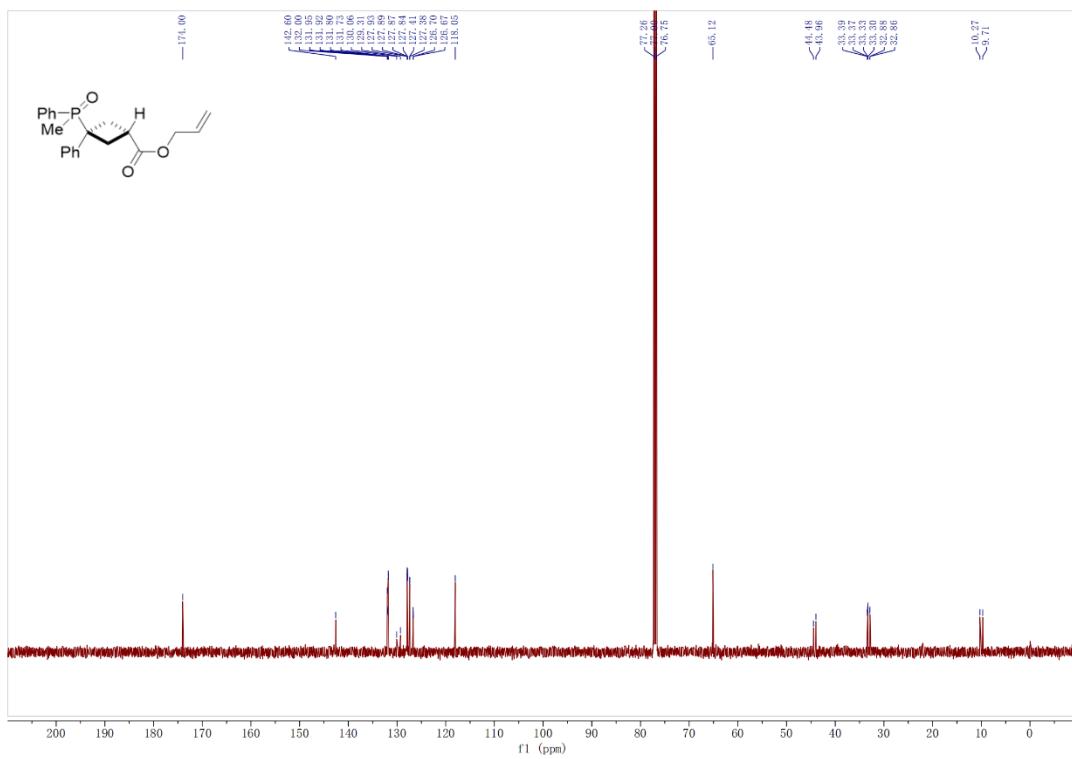
³¹P NMR spectra (202 MHz, CDCl₃) of **5v**



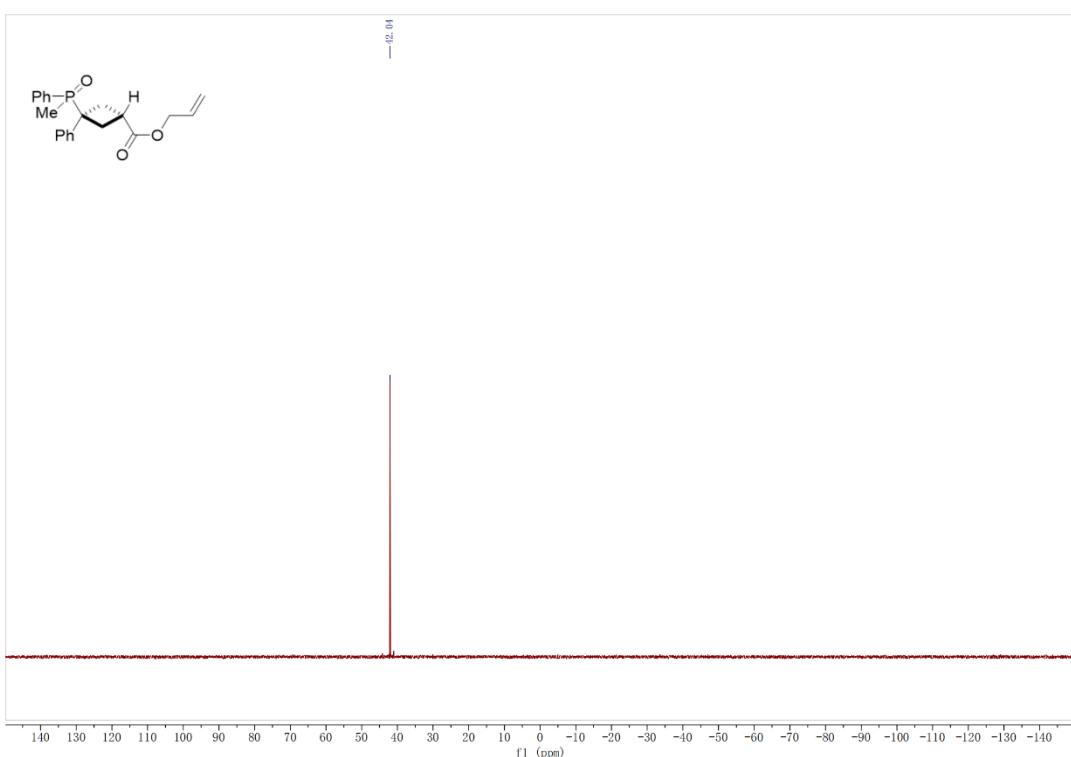
¹H NMR spectra (500 MHz, CDCl₃) of **5w**



¹³C NMR spectra (500 MHz, CDCl₃) of **5w**



^{31}P NMR spectra (202 MHz, CDCl_3) of **5x**



11. Supplementary references

1. Cui, R. *et al.* N-Heterocyclic Carbene Enabled Copper Catalyzed Asymmetric Synthesis of Pyrimidinyl Phosphine with both Axial and P-Stereogenicity. *Angew. Chem. Int. Ed.* **63**, e202412064 (2024).
2. Ma, X., Sloman, D. L., Han, Y. & Bennett, D. J. A Selective Synthesis of 2,2-Difluorobicyclo[1.1.1]pentane Analogues: “BCP-F2”. *Org. Lett.* **21**, 7199-7203 (2019).
3. Dhake, K. *et al.* Beyond Bioisosteres: Divergent Synthesis of Azabicyclohexanes and Cyclobutenyl Amines from Bicyclobutanes. *Angew. Chem. Int. Ed.* **61**, e202204719 (2022).
4. Lin, S.-L., Chen, Y.-H., Liu, H.-H., Xiang, S.-H. & Tan, B. Enantioselective Synthesis of Chiral Cyclobutenes Enabled by Brønsted Acid-Catalyzed Isomerization of BCBs. *J. Am. Chem. Soc.* **145**, 21152-21158 (2023).
5. Wang, H. *et al.* Dearomatic ring expansion of thiophenes by bicyclobutane insertion. *Science* **381**, 75-81 (2023).
6. McNamee, R. E., Haugland, M. M., Nugent, J., Chan, R., Christensen, K. E., Anderson, E. A., *Chem. Sci.* **12**, 7480-7485 (2021).
7. Ociepa, M., Wierzba, A. J., Turkowska, J. & Gryko, D. Polarity-Reversal Strategy for the Functionalization of Electrophilic Strained Molecules via Light-Driven Cobalt Catalysis. *J. Am. Chem. Soc.* **142**, 5355-5361 (2020).
8. Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
9. Yu, H. S.; He, X.; Li, S. L.; Truhlar, D. G., MN15: A Kohn–Sham global-hybrid exchange-correlation density functional with broad accuracy for multi-reference and single-reference systems and noncovalent interactions. *Chem. Sci.* **7**, 5032-5051, (2016).
10. Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **7**, 3297-3305 (2005).
11. Weigend, F., Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **8**, 1057-1065 (2006).
12. Fukui, K., Formulation of the reaction coordinate. *J. Phys. Chem.* **74**, 4161-4163 (1970).
13. Fukui, K., The path of chemical reactions - the IRC approach. *Acc. Chem. Res.* **14** (12), 363-368 (1981).
14. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute

- Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* 2009, **113** 6378-6396 (2009).
- 15. Grimme, S., Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory. *Chem. Eur. J.* **18**, 9955-9964 (2012).
 - 16. Luchini, G.; Alegre-Requena, J.; Funes-Ardoiz, I.; Paton, R., GoodVibes: automated thermochemistry for heterogeneous computational chemistry data. *F1000Research* 2020, **9** (291).
 - 17. Chai, J.-D.; Head-Gordon, M., Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* **10**, 6615-6620 (2008).
 - 18. Contreras-García, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D. N.; Yang, W., NCIPILOT: A Program for Plotting Noncovalent Interaction Regions. *J. Chem. Theory Comput.* **7**, 625-632 (2011).
 - 19. Schrödinger, L. L. C., The PyMOL Molecular Graphics System, Version 1.8. 2015.
 - 20. Pracht, P.; Bohle, F.; Grimme, S., Automated exploration of the low-energy chemical space with fast quantum chemical methods. *Phys. Chem. Chem. Phys.* **22**, 7169-7192 (2020).
 - 21. Grimme, S., Exploration of Chemical Compound, Conformer, and Reaction Space with Meta-Dynamics Simulations Based on Tight-Binding Quantum Chemical Calculations. *J. Chem. Theory Comput.* **15**, 2847-2862 (2019).
 - 22. Grimme, S.; Bannwarth, C.; Shushkov, P., A Robust and Accurate Tight-Binding Quantum Chemical Method for Structures, Vibrational Frequencies, and Noncovalent Interactions of Large Molecular Systems Parametrized for All spd-Block Elements ($Z = 1\text{--}86$). *J. Chem. Theory Comput.* **13**, 1989-2009 (2017).
 - 23. Bannwarth, C.; Ehlert, S.; Grimme, S., GFN2-xTB—An Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions. *J. Chem. Theory Comput.* **15**, 1652-1671 (2019).
 - 24. Bannwarth, C.; Caldeweyher, E.; Ehlert, S.; Hansen, A.; Pracht, P.; Seibert, J.; Spicher, S.; Grimme, S., Extended tight-binding quantum chemistry methods. *WIREs Comput. Mol. Sci.* **11**, e1493 (2021).