Supporting Information

Palladium-Catalyzed Regio- and Enantio-selective Trifluoromethylated Allylic Alkylation of Diphenylphosphine Oxides

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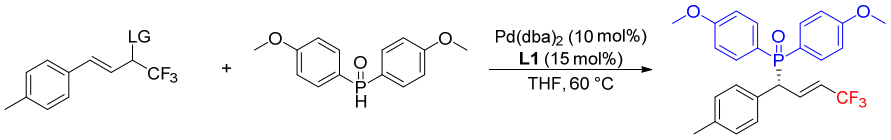
1. General Information

Unless otherwise noted, all reactions were performed under an argon atmosphere in glassware with magnetic stirring. Other reagents were purchased from commercial sources and used without further purification. All solvents used were treated prior to use according to the standard methods. Column chromatography was performed on silica gel (200 - 300 mesh) using petroleum ether/ethyl acetate as eluent. ^{1}H NMR, ^{19}F NMR, ^{13}C NMR and ^{31}P{^{1}H} NMR were obtained on Bruker Avance II 400 MHz, Varian DLG 400 and Bruker AVANCE II 500 NMR Spectroscopy recorded in ppm (δ) downfield of TMS (δ = 0) in $CDCl_3$ unless noted otherwise. Melting points were recorded on a Novel X-4 spectrometer. HRMS (ESI) were recorded on a Waters Synapt G2 *Si*. HRMS (EI) were recorded on an Agilent 7000B Triple Quadrupole GC/MS. The enantiomeric excess was determined by chiral HPLC with *n*-hexane and *i*-propanol as eluents. Optical rotations were measured on a Rudolph AUTOPOL IV polarimeter. X-ray analysis was performed on a Bruker D8 Venture diffractometer. α-(Trifluoromethyl)allyl esters (**1a–1q**) were prepared by the reaction of corresponding allylic alcohols with methyl chloroformate.[1, 2]

2. Optimization of reaction conditions

Table S1. Optimization of leaving groups[a]



1 **2a** **3a**

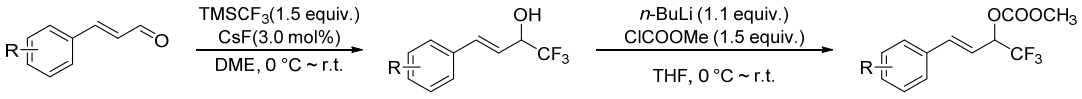
Entry	LG	Yield/%[b]	ee/%[c]
1	$OCOOCH_3$	75	92
2	OPiv	40	87
3	OTs	0	-
4	OH	0	-

[a] General conditions: under argon atmosphere, $Pd(dba)_2$ (10 mol%) and **L1** (15 mol%) were stirred in THF (2.0 mL) at 25 °C for 20 min, then **1** (3.0 equiv.), **2a** (0.2 mmol, 1.0 equiv.) and THF (2.0 mL) were added, the mixture was stirred at 60 °C for 36 h. [b] Isolated yield. [c] Determined by chiral HPLC. LG= leaving group.

As shown in Table S1, entries 1 and 2, the reaction could proceed smoothly, when the substrate was selected as (*E*)-methyl (1,1,1-trifluoro-4-(*p*-tolyl)but-3-en-2-yl) carbonate or (*E*)-1,1,1-trifluoro-4-(*p*-tolyl)but-3-en-2-yl pivalate. And a better result was obtained when the substrate with methyl carbonate as leaving group (Entry 1, 75 % yield, 92 % ee). Then, the substrate was converted to (*E*)-1,1,1-trifluoro-4-(*p*-tolyl)but-3-en-2-yl 4-methylbenzenesulfonate and (*E*)-1,1,1-trifluoro-4-(*p*-tolyl)but-3-en-2-ol (Table S1, entries 3 and 4), but the reactions didn't occur normally. So, we choose the methyl carbonate as the best leaving group.

3. Experimental procedure

2.1 Preparation of Compounds 1a–1q



1a-1q

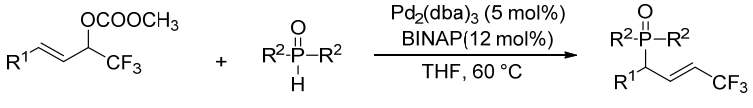
Step 1

A flame-dried 100 mL round-bottom flask was charged with *α, β*-unsaturated aldehyde (50 mmol, 1.0 equiv.), CsF (1.5 mmol, 3 mol%) and DME (50 mL) and the mixture was stirred at 0 °C, then $TMSCF_3$ (11.0 mL, 75 mmol, 1.5 equiv.) was added dropwise, and the mixture was stirred at room temperature overnight. After the reaction was completed (monitored by TLC), HCl (conc., 5 mL) was added and the mixture was stirred for 30 min. Subsequently, water (100 mL) was added to the reaction mixture and extracted with EtOAc (3 × 50 mL). The organics were combined and dried over Na_2SO_4 and concentrated under vacuum, the resulting alcohol was purified by silica-gel column chromatography.

Step 2

n-BuLi (11 mmol, 1.1 equiv) was slowly added into the solution of alcohol (10 mmol, 1.0 equiv.) in THF (30 mL) at 0 °C, and the mixture was stirred 30 min. Then, ClCOOMe (15 mmol, 1.5 equiv.) was added dropwise, and the reaction was warm to the room temperature. After 1 h, water (50 mL) was added to quench the reaction and extracted with EtOAc (3 × 50 mL). The organics were combined and dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica-gel column chromatography to give the compounds **1a-1q**.

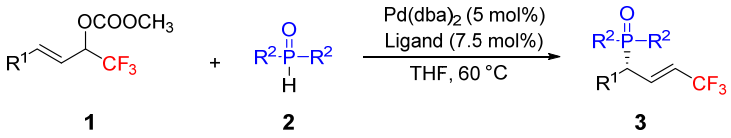
2.2 General procedure for the racemic products



1 **2** **3**

A 25 mL flame-dried Schlenck tube with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%), BINAP (12 mol%), allyl carbonate **1** (0.3 mmol, 3.0 equiv.), SPO **2** (0.1 mmol, 1.0 equiv.) and THF (2.0 mL). The mixture was stirred rapidly at 60 °C for 24 h (monitored by TLC). After the reaction was completed, the solution was concentrated under reduced pressure, and the crude was purified by column chromatography on silica gel to afford the desired racemic products.

2.3 General procedure for the chiral products



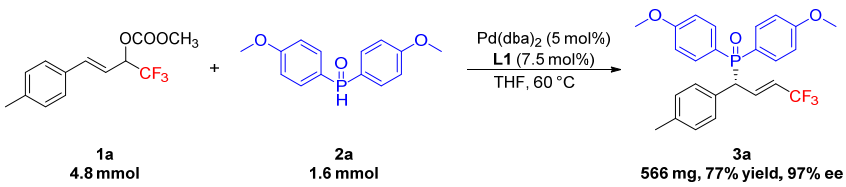
Method A

A 25 mL flame-dried Schlenck tube with a stirring bar was charged with $Pd(dba)_2$ (0.01 mmol, 5 mol%), (*R*)-MeO-BIPHEP (0.015 mmol, 7.5 mol%), allyl carbonate **1** (0.6 mmol, 3.0 equiv.), SPO **2** (0.2 mmol, 1.0 equiv.) and THF (4.0 mL). The mixture was stirred rapidly at 60 °C for 36 - 48 h (monitored by TLC). After the reaction was completed, the solution was concentrated under reduced pressure, and the crude was purified by column chromatography on silica gel to afford the desired chrial products.

Method B

A 25 mL flame-dried Schlenck tube with a stirring bar was charged with $Pd(dba)_2$ (0.01 mmol, 5 mol%), (*R*)-BINAP (0.015 mmol, 7.5 mol%), allyl carbonate **1** (0.6 mmol, 3.0 equiv.), SPO **2** (0.2 mmol, 1.0 equiv.) and THF (4.0 mL). The mixture was stirred rapidly at 60 °C for 24 h (monitored by TLC). After the reaction was completed, the solution was concentrated under reduced pressure, and the crude was purified by column chromatography on silica gel to afford the desired chrial products.

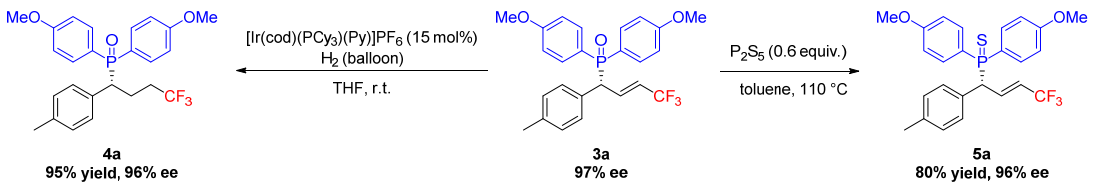
2.4 General procedure for gram-scale synthesis of 3a



Method **A**:

A 100 mL flame-dried Schlenck tube with a stirring bar was charged with $Pd(dba)_2$ (46 mg, 0.08 mmol, 5 mol%), (*R*)-MeO-BIPHEP (**L1**, 69.9 mg, 0.12 mmol, 7.5 mol%), allyl carbonate **1a** (1.32 g, 4.8 mmol, 3.0 equiv.), SPO **2a** (419 mg, 1.6 mmol, 1.0 equiv.) and THF (32 mL). The mixture was stirred rapidly at 60 °C for 36 h (monitored by TLC). After the reaction was completed, the solution was concentrated under reduced pressure, and the crude was purified by column chromatography on silica gel to afford the desired products **3a** (566 mg, 77% yield, 97% ee).

2.5 General procedure for transformation of 3a

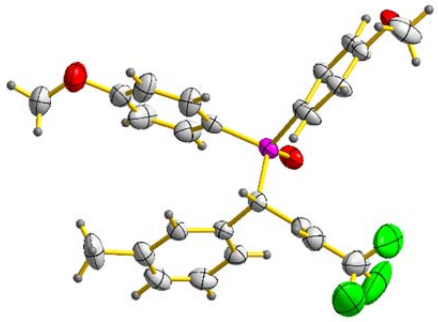


To a solution of **3a** (101 mg, 0.22 mmol, 1.0 equiv.) in THF (2.0 mL) was added $[Ir(cod)(PCy_3)(Py)]PF_6$ (26.5 mg, 15 mol%). The resulting mixture was degassed and stirred under hydrogen gas balloon pressure at 25 °C. After the completion of hydrogenation (monitored by TLC), the mixture was filtered, concentrated under reduced pressure, and the crude was purified by column chromatography on silica gel to afford the desired product **4a** (95% yield, 96% ee).

A 25 mL flame-dried Schlenck pressure tube with a stirring bar was charged with **3a** (101 mg, 0.22 mmol, 1.0 equiv.), P_2S_5 (30 mg, 0.132 mmol, 0.6 equiv.) and toluene (2 mL). Then, the reaction was heated to 110 °C and stirred overnight (monitored by TLC). After the reaction was completed, the solution was concentrated under reduced pressure, and the crude was purified by column chromatography on silica gel to afford the desired products **5a** (80% yield, 96% ee).

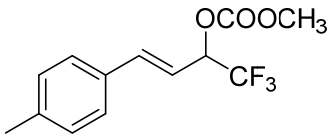
4. Crystal data and structure refinement for 3b

The crystal of **3b** was obtained by solvent diffusion method at room temperature using *n*-hex/DCM as the solvent.

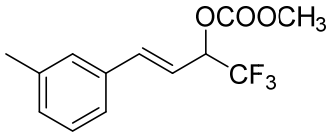


Empirical formula	$C_{25}H_2F_3O_3P$
Formula weight	460.41
Temperature/K	307
Crystal system	monoclinic
Space group	C2
a/Å	22.608(3)
b/Å	5.6779(7)
c/Å	18.838(2)
α/°	90
β/°	101.948(9)
γ/°	90
Volume/Å^3	2365.8(5)
Z	4
ρ_{calc}g/cm^3	1.293
μ/mm^{-1}	1.445
F(000)	960.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.794 to 144.862
Index ranges	-27 ≤ h ≤ 27, -6 ≤ k ≤ 7, -23 ≤ l ≤ 23
Reflections collected	26124
Independent reflections	4499 [R_{int} = 0.0336, R_{sigma} = 0.0234]
Data/restraints/parameters	4499/58/312
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0409, wR_2 = 0.1168
Final R indexes [all data]	R_1 = 0.0427, wR_2 = 0.1189
Largest diff. peak/hole / e Å^{-3}	0.21/-0.19
Flack parameter	0.043(7)

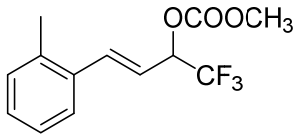
5. Experimental characterization data for compounds 1a-1q



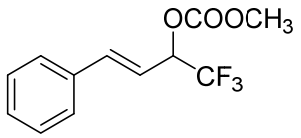
(*E*)-Methyl (1,1,1-trifluoro-4-(*p*-tolyl)but-3-en-2-yl) carbonate (1a) (known compound) [2]
Purified by Biotage flash chromatography with (PE/EtOAc 10:1), white solid, mp 65 - 67 °C, 2.33 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 15.9 Hz, 1H), 6.08 (dd, *J* = 15.9, 8.0 Hz, 1H), 5.67 – 5.56 (m, 1H), 3.84 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 139.38, 139.35, 132.1, 129.5, 127.1, 123.0 (q, *J* = 280.5 Hz), 115.5, 75.2 (q, *J* = 33.9 Hz), 55.6, 21.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.76 (d, *J* = 6.2 Hz).



(*E*)-Methyl (1,1,1-trifluoro-4-(*m*-tolyl)but-3-en-2-yl) carbonate (1b)
Purified by Biotage flash chromatography with (PE/EtOAc 10:1), colorless oil, 2.45 g, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 3H), 7.15 – 7.09 (m, 1H), 6.87 (d, *J* = 15.9 Hz, 1H), 6.12 (dd, *J* = 15.9, 7.9 Hz, 1H), 5.68 – 5.57 (m, 1H), 3.84 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 139.5, 138.4, 134.8, 130.0, 128.7, 127.8, 124.3, 122.9 (q, *J* = 281.6 Hz), 116.4, 75.1 (q, *J* = 33.8 Hz), 55.6, 21.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.74 (d, *J* = 6.6 Hz). HRMS (EI) *m/z*: calcd for $C_{13}H_{13}F_3O_3$ [$M^{+\bullet}$] 274.0817, found: 274.0814.

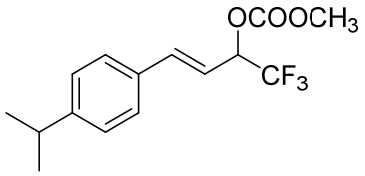


(*E*)- Methyl (1,1,1-trifluoro-4-(*o*-tolyl)but-3-en-2-yl) carbonate (1c)
Purified by Biotage flash chromatography with (PE/EtOAc 10:1), yellow oil, 2.29 g, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 1H), 7.25 – 7.11 (m, 4H), 6.02 (dd, *J* = 15.8, 7.9 Hz, 1H), 5.71 – 5.59 (m, 1H), 3.84 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 137.4, 136.3, 134.1, 130.6, 129.0, 126.3, 126.1, 123.0 (q, *J* = 280.5 Hz), 118.0, 75.2 (q, *J* = 33.8 Hz), 55.6, 19.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.73 (d, *J* = 6.3 Hz). HRMS (EI) *m/z*: calcd for $C_{13}H_{13}F_3O_3$ [$M^{+\bullet}$] 274.0817, found: 274.0813.



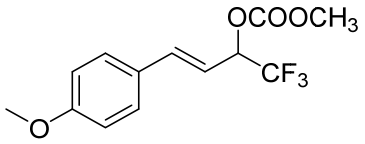
(*E*)-Methyl (1,1,1-trifluoro-4-phenylbut-3-en-2-yl) carbonate (1d) (known compound) [2]

Purified by Biotage flash chromatography with (PE/EtOAc 10:1), light yellow solid, mp 53 - 55 °C, 2.42 g, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 2H), 7.38 – 7.28 (m, 3H), 6.91 (d, *J* = 16.0 Hz, 1H), 6.13 (dd, *J* = 15.9, 7.9 Hz, 1H), 5.69 – 5.58 (m, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 139.3, 134.9, 129.2, 128.8, 127.1, 122.9 (q, *J* = 280.5 Hz), 116.6, 75.0 (q, *J* = 33.9 Hz), 55.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.73 (d, *J* = 6.4 Hz).



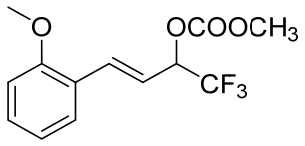
(*E*)-Methyl (1,1,1-trifluoro-4-(4-isopropylphenyl)but-3-en-2-yl) carbonate (1e)

Purified by Biotage flash chromatography with (PE/EtOAc 10:1), light yellow solid, mp 54 - 56 °C, 2.51 g, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 15.9 Hz, 1H), 6.09 (dd, *J* = 15.9, 8.0 Hz, 1H), 5.68 – 5.56 (m, 1H), 3.84 (s, 3H), 2.97 – 2.82 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 150.4, 139.4, 132.5, 127.2, 126.9, 123.0 (q, *J* = 280.5 Hz), 115.6, 75.2 (q, *J* = 33.9 Hz), 55.6, 34.0, 23.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.76 (d, *J* = 6.6 Hz). HRMS (EI) *m/z*: calcd for $C_{15}H_{17}F_3O_3$ [$M^{+\bullet}$] 302.1130, found: 302.1129.



(*E*)-Methyl (1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-yl) carbonate (1f) (known compound) [2]

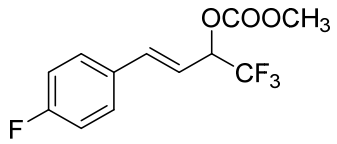
Purified by Biotage flash chromatography with (PE/EtOAc 10:1), light yellow solid, mp 48 - 50 °C, 2.26 g, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 6.94 – 6.78 (m, 3H), 5.99 (dd, *J* = 15.9, 8.1 Hz, 1H), 5.66 – 5.55 (m, 1H), 3.84 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (one aromatic carbon missing) δ 160.5, 154.3, 139.1, 128.5, 127.6, 123.0 (q, *J* = 280.5 Hz), 114.2, 75.3 (q, *J* = 33.9 Hz), 55.5, 55.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.80 (d, *J* = 6.7 Hz).



(*E*)-Methyl (1,1,1-trifluoro-4-(2-methoxyphenyl)but-3-en-2-yl) carbonate (1g)

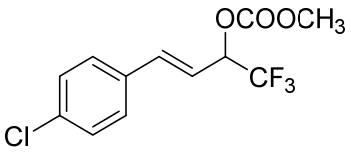
Purified by Biotage flash chromatography with (PE/EtOAc 10:1), yellow oil, 2.45 g, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.31 – 7.18 (m, 2H), 7.06 – 6.88 (m, 1H), 6.89 – 6.83 (m, 1H), 6.22 (dd, *J* = 16.0, 8.1 Hz, 1H), 5.70 – 5.57 (m, 1H), 3.82 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 154.3, 134.8, 130.4, 127.8, 123.7, 123.1 (q, *J* = 280.5 Hz), 120.7, 117.0, 111.0, 75.7 (q, *J* = 33.6 Hz), 55.5, 55.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.75 (d, *J* =

6.4 Hz). HRMS (EI) *m/z*: calcd for $C_{13}H_{13}F_3O_4$ [$M^{+\bullet}$] 290.0766, found: 290.0763.



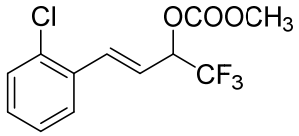
(*E*)-Methyl (1,1,1-trifluoro-4-(4-fluorophenyl)but-3-en-2-yl) carbonate (1h)

Purified by Biotage flash chromatography with (PE/EtOAc 10:1), brown yellow solid, mp 47 - 49 °C, 2.06 g, 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.12 – 6.97 (m, 2H), 6.87 (d, *J* = 15.9 Hz, 1H), 6.06 (dd, *J* = 15.9, 7.9 Hz, 1H), 5.66 – 5.58 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2 (d, *J* = 249.3 Hz), 154.2, 138.1, 131.1 (d, *J* = 3.4 Hz), 128.8 (d, *J* = 8.2 Hz), 122.8 (q, *J* = 280.4 Hz), 116.4, 115.8 (d, *J* = 21.8 Hz), 74.9 (q, *J* = 34.0 Hz), 55.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.78 (d, *J* = 6.7 Hz, 3F), -111.70 – -111.82 (m, 1F). HRMS (EI) *m/z*: calcd for $C_{12}H_{10}F_4O_3$ [$M^{+\bullet}$] 278.0566, found: 278.0564.



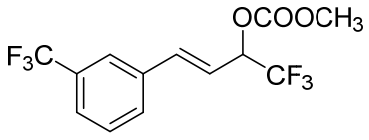
(*E*)-4-(4-Chlorophenyl)-1,1,1-trifluorobut-3-en-2-yl methyl carbonate (1i) (known compound) [2]

Purified by Biotage flash chromatography with (PE/EtOAc 10:1), white solid, mp 85 - 87 °C, 1.95 g, 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H), 6.86 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.9, 7.8 Hz, 1H), 5.67 – 5.58 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 137.9, 135.0, 133.3, 129.0, 128.3, 122.8 (q, *J* = 280.7 Hz), 117.3, 74.8 (q, *J* = 34.0 Hz), 55.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.70 (d, *J* = 6.3 Hz).



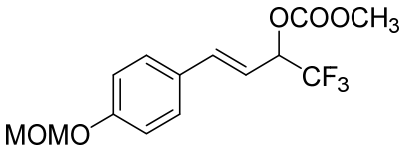
(*E*)-4-(2-Chlorophenyl)-1,1,1-trifluorobut-3-en-2-yl methyl carbonate (1j)

Purified by Biotage flash chromatography with (PE/EtOAc 10:1), light yellow oil, 1.85 g, 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 1H), 7.41 – 7.35 (m, 1H), 7.32 (d, *J* = 15.9 Hz, 1H), 7.28 – 7.21 (m, 2H), 6.13 (dd, *J* = 16.0, 7.7 Hz, 1H), 5.74 – 5.65 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 135.3, 133.8, 133.1, 130.1, 129.9, 127.2, 127.0, 122.8 (q, *J* = 280.5 Hz), 119.4, 74.7 (q, *J* = 33.9 Hz), 55.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.66 (d, *J* = 6.7 Hz). HRMS (EI) *m/z*: calcd for $C_{12}H_{10}ClF_3O_3$ [$M^{+\bullet}$] 294.0271, found: 294.0271.



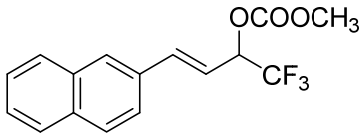
(*E*)-Methyl (1,1,1-trifluoro-4-(3-(trifluoromethyl)phenyl)but-3-en-2-yl) carbonate (1k)

Purified by Biotage flash chromatography with (PE/EtOAc 10:1), yellow oil, 1.85 g, 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 1H), 7.62 – 7.55 (m, 2H), 7.51 – 7.44 (m, 1H), 6.94 (d, *J* = 16.0 Hz, 1H), 6.22 (dd, *J* = 16.0, 7.5 Hz, 1H), 5.71 – 5.62 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 137.5, 135.6, 131.3 (q, *J* = 32.5 Hz), 130.1, 129.3, 125.7 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 272.4 Hz), 123.8 (q, *J* = 3.7 Hz), 122.7 (q, *J* = 280.6 Hz), 118.7, 74.5 (q, *J* = 34.0 Hz), 55.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.98 (s, 3F), -76.71 (d, *J* = 6.2 Hz, 3F). HRMS (EI) *m/z*: calcd for $C_{13}H_{10}F_6O_3$ [$M^{+\bullet}$] 328.0534, found: 328.0532.



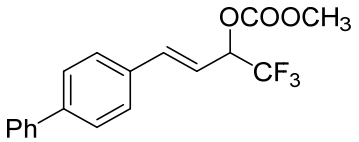
(*E*)-Methyl (1,1,1-trifluoro-4-(4-(methoxymethoxy)phenyl)but-3-en-2-yl) carbonate (1l)

Purified by Biotage flash chromatography with (PE/EtOAc 10:1), yellow oil, 2.05 g, 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.08 – 6.98 (m, 2H), 6.85 (d, *J* = 15.9 Hz, 1H), 6.01 (dd, *J* = 15.9, 8.1 Hz, 1H), 5.66 – 5.57 (m, 1H), 5.17 (s, 2H), 3.84 (s, 3H), 3.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 154.3, 138.9, 128.7, 128.5, 123.0 (q, *J* = 280.4 Hz), 116.4, 114.7, 94.2, 75.2 (q, *J* = 33.7 Hz), 56.0, 55.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.81 (d, *J* = 6.3 Hz). HRMS (EI) *m/z*: calcd for $C_{14}H_{15}F_3O_5$ [$M^{+\bullet}$] 320.0872, found: 320.0872.



(*E*)-Methyl (1,1,1-trifluoro-4-(naphthalen-2-yl)but-3-en-2-yl) carbonate (1m)

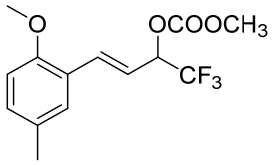
Purified by Biotage flash chromatography with (PE/EtOAc 10:1), yellow solid, mp 119 - 121 °C, 2.10 g, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 4H), 7.58 – 7.53 (m, 1H), 7.49 – 7.40 (m, 2H), 7.04 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 15.9, 7.9 Hz, 1H), 5.74 – 5.65 (m, 1H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 139.4, 133.7, 133.4, 132.3, 128.6, 128.3, 128.1, 127.8, 126.8, 126.6, 123.3, 123.0 (q, *J* = 280.7 Hz), 116.9, 75.1 (q, *J* = 33.7 Hz), 55.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.57 (d, *J* = 6.3 Hz). HRMS (EI) *m/z*: calcd for $C_{16}H_{13}F_3O_3$ [$M^{+\bullet}$] 310.0817, found: 310.0817.



(*E*)-4-([1,1'-Biphenyl]-4-yl)-1,1,1-trifluorobut-3-en-2-yl methyl carbonate (1n)

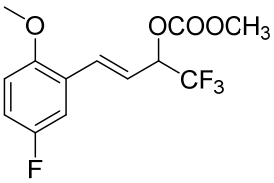
Purified by Biotage flash chromatography with (PE/EtOAc 10:1), yellow solid, mp 149 - 151 °C, 2.25 g, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 4H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.31 (m, 1H), 6.95 (d, *J* = 15.9 Hz, 1H), 6.17 (dd, *J* = 15.9, 7.9 Hz, 1H), 5.71 – 5.60 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 142.0, 140.3, 138.9, 133.8, 128.9, 127.7, 127.6, 127.4, 127.0, 122.9 (d, *J* = 280.6 Hz), 116.6, 75.1 (q, *J* = 33.9 Hz), 55.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.65 (d, *J* = 6.6 Hz). HRMS (EI) *m/z*: calcd for $C_{18}H_{15}F_3O_3$

[$M^{+\bullet}$] 336.0973, found: 336.0974.



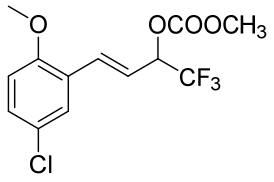
(*E*)-Methyl (1,1,1-trifluoro-4-(2-methoxy-5-methylphenyl)but-3-en-2-yl) carbonate (1o)

Purified by Biotage flash chromatography with (PE/EtOAc 10:1), light yellow solid, mp 60 - 61 °C, 2.51 g, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.22 (m, 1H), 7.19 (d, *J* = 16.0 Hz, 1H), 7.11 – 7.04 (m, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.20 (dd, *J* = 16.1, 8.2 Hz, 1H), 5.68 – 5.57 (m, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 154.3, 134.9, 130.8, 129.8, 128.3, 123.4, 123.0 (q, *J* = 280.6 Hz), 116.7, 111.0, 75.8 (q, *J* = 33.7 Hz), 55.53, 55.50, 20.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.73 (d, *J* = 6.3 Hz). HRMS (EI) *m/z*: calcd for $C_{14}H_{15}F_3O_4$ [$M^{+\bullet}$] 304.0922, found: 304.0923.



(*E*)-Methyl (1,1,1-trifluoro-4-(5-fluoro-2-methoxyphenyl)but-3-en-2-yl) carbonate (1p)

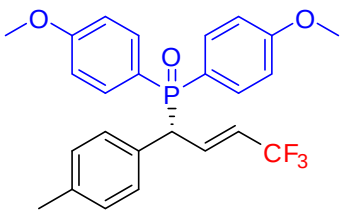
Purified by Biotage flash chromatography with (PE/EtOAc 10:1), yellow oil, 2.23 g, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.11 (m, 2H), 7.01 – 6.93 (m, 1H), 6.84 – 6.76 (m, 1H), 6.19 (dd, *J* = 16.1, 7.9 Hz, 1H), 5.70 – 5.59 (m, 1H), 3.85 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (d, *J* = 238.6 Hz), 154.3, 153.6 (d, *J* = 2.0 Hz), 133.5 (d, *J* = 2.2 Hz), 124.9 (d, *J* = 7.5 Hz), 122.9 (q, *J* = 280.6 Hz), 118.2, 116.3 (d, *J* = 23.1 Hz), 113.8 (d, *J* = 23.7 Hz), 112.1 (d, *J* = 8.3 Hz), 75.3 (q, *J* = 33.8 Hz), 55.9, 55.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.76 (d, *J* = 6.4 Hz, 3F), -123.79 – -123.93 (m, 1F). HRMS (EI) *m/z*: calcd for $C_{13}H_{12}F_4O_4$ [$M^{+\bullet}$] 308.0672, found: 308.0674.



(*E*)-4-(5-Chloro-2-methoxyphenyl)-1,1,1-trifluorobut-3-en-2-yl methyl carbonate (1q)

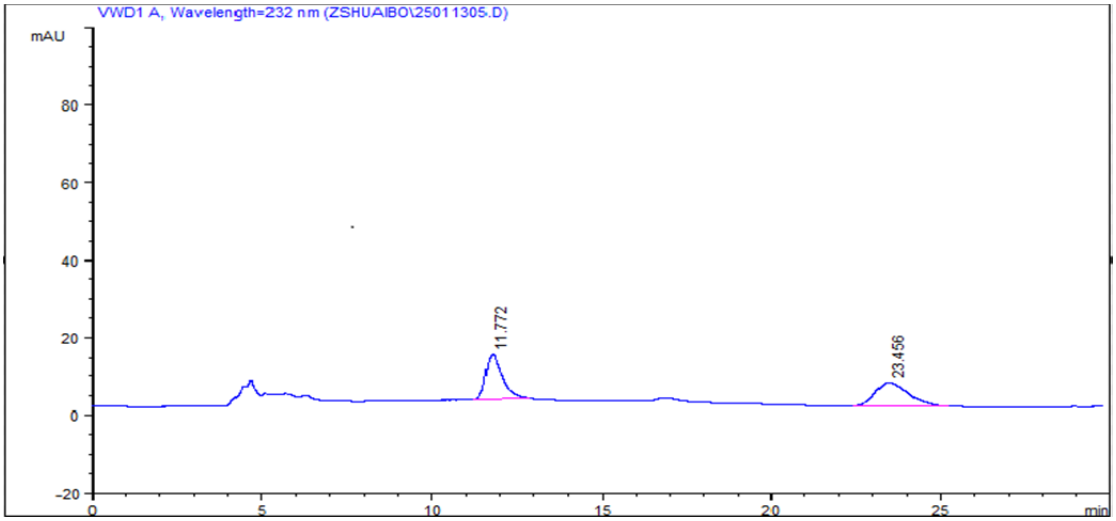
Purified by Biotage flash chromatography with (PE/EtOAc 10:1), yellow oil, 2.31 g, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 2.6 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.14 (d, *J* = 16.1 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 6.20 (dd, *J* = 16.1, 7.9 Hz, 1H), 5.70 – 5.59 (m, 1H), 3.85 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 154.2, 133.3, 129.7, 127.3, 125.7, 125.2, 122.9 (q, *J* = 280.7 Hz), 118.3, 112.2, 75.2 (q, *J* = 33.8 Hz), 55.7, 55.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.71 (d, *J* = 6.6 Hz). HRMS (EI) *m/z*: calcd for $C_{13}H_{12}ClF_3O_4$ [$M^{+\bullet}$] 324.0376, found: 324.0381.

6. Experimental characterization data for chiral products



(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(*p*-tolyl)but-2-en-1-yl)phosphine oxide (3a)

Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 225 – 226 °C, 69.9 mg, 76% yield, 97% ee, $[\alpha]^{20}_{D}$ = +26.32 (*c* 0.19, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 2H), 7.50 – 7.41 (m, 2H), 7.19 – 7.13 (m, 2H), 7.09 – 6.96 (m, 4H), 6.86 – 6.79 (m, 2H), 6.79 – 6.66 (m, 1H), 5.58 – 5.44 (m, 1H), 4.21 – 4.15 (m, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 2.9 Hz), 162.3 (d, *J* = 2.9 Hz), 137.4 (d, *J* = 2.3 Hz), 136.4 – 136.0 (m), 133.4 (d, *J* = 9.9 Hz), 133.2 (d, *J* = 10.1 Hz), 130.9 (d, *J* = 6.1 Hz), 129.5 (d, *J* = 6.9 Hz), 129.4 (d, *J* = 10.8 Hz), 122.7 (d, *J* = 48.7 Hz), 122.5 (qd, *J* = 269.8, 2.1 Hz), 121.7 (qd, *J* = 33.8, 10.3 Hz), 121.6 (d, *J* = 47.1 Hz), 114.2 (d, *J* = 12.6 Hz), 113.9 (d, *J* = 12.7 Hz), 55.4, 55.2, 51.2 (d, *J* = 64.3 Hz), 21.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -59.01 – -75.14 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 30.60. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 11.80 min, t_{minor} = 23.51 min. HRMS (ESI) m/z: calcd for $C_{25}H_{25}F_3O_3P$ $[M + H]^+$ 461.1488, found: 461.1493.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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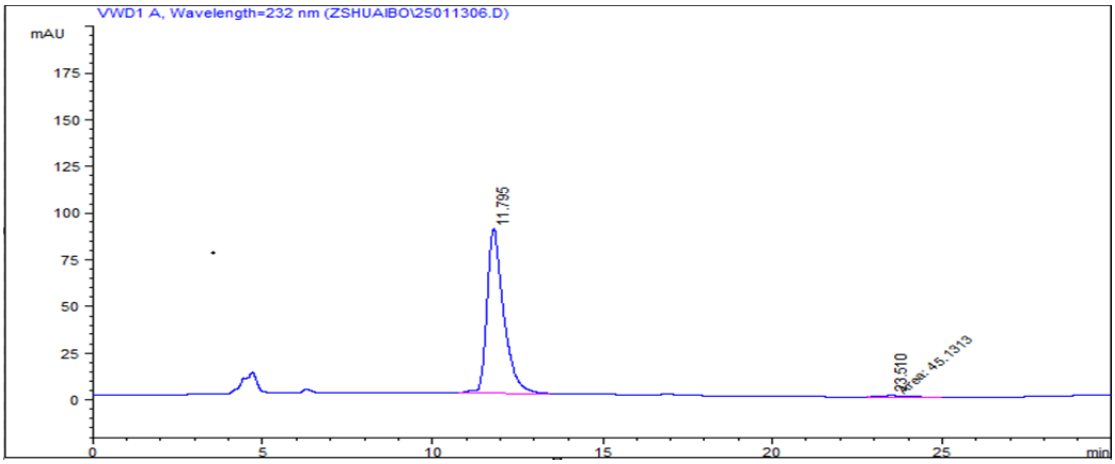
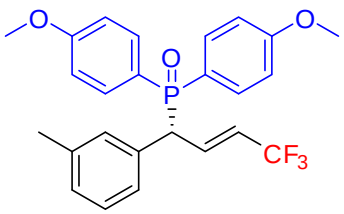
2	23.456	BB	0.8746	412.55438	6.04695	51.3949

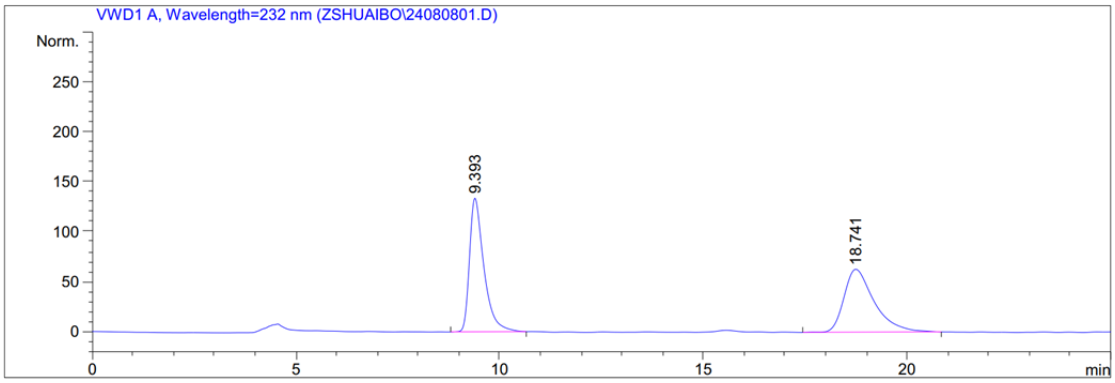


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.795	BB	0.5074	3014.21704	87.99793	98.5248
2	23.510	MM	0.9526	45.13132	7.89590e-1	1.4752



(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(*m*-tolyl)but-2-en-1-yl)phosphine oxide (3b)

Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 132 – 133 °C, 77.3 mg, 84% yield, 94% ee, $[\alpha]^{20}_{D}$ = + 19.13 (*c* 0.18, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.63 (m, 2H), 7.47 – 7.38 (m, 2H), 7.17 – 7.09 (m, 1H), 7.09 – 6.94 (m, 5H), 6.85 – 6.80 (m, 2H), 6.78 – 6.67 (m, 1H), 5.58 – 5.44 (m, 1H), 4.18 – 4.12(m, 1H), 3.86 (s, 3H), 3.77 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 2.9 Hz), 162.3 (d, *J* = 3.0 Hz), 138.5 (d, *J* = 1.7 Hz), 136.2 – 135.8 (m), 133.9 (d, *J* = 5.9 Hz), 133.5 (d, *J* = 9.9 Hz), 133.2 (d, *J* = 10.2 Hz), 130.3 (d, *J* = 5.5 Hz), 128.6 (d, *J* = 1.8 Hz), 128.4 (d, *J* = 2.2 Hz), 126.6 (d, *J* = 5.6 Hz), 122.6 (d, *J* = 57.0 Hz), 122.5 (qd, *J* = 270.9, 2.1Hz) , 121.8 (qd, *J* = 34.0, 10.3 Hz), 121.5 (d, *J* = 55.3 Hz), 114.2 (d, *J* = 12.7 Hz), 113.8 (d, *J* = 12.8 Hz), 55.4, 55.3, 51.7 (d, *J* = 64.0 Hz), 21.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.07 – -64.14 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 30.68. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 9.46 min, t_{minor} = 18.87 min. HRMS (ESI) m/z: calcd for $C_{25}H_{25}F_3O_3P$ $[M + H]^+$ 461.1488, found: 461.1492.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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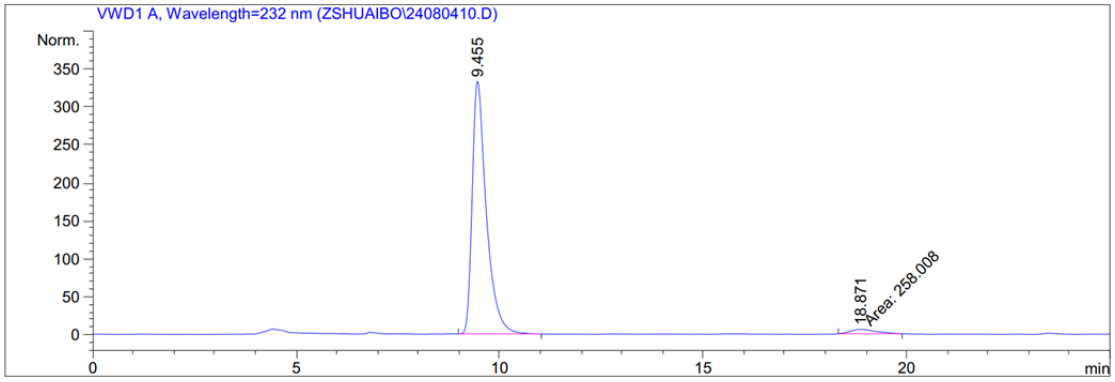
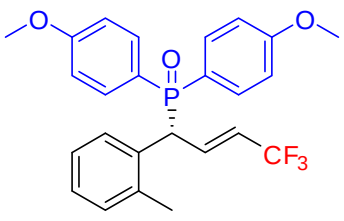
2	18.741	VB	0.7731	3262.44141	63.14365	49.7652



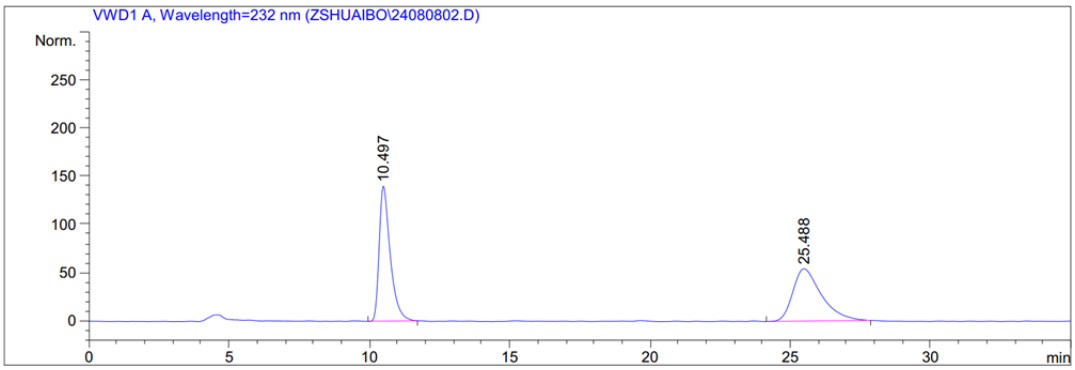
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.455	VB	0.3560	8031.71387	332.61438	96.8876
2	18.871	MM	0.7387	258.00760	5.82113	3.1124



(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(*o*-tolyl)but-2-en-1-yl)phosphine oxide (3c)

Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 172 – 173 °C, 71.8 mg, 78% yield, 94% ee, $[\alpha]^{20}_{D}$ = + 3.89 (*c* 0.23, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 3H), 7.38 – 7.27 (m, 2H), 7.24 – 7.11 (m, 2H), 7.10 – 6.99 (m, 3H), 6.82 – 6.75

(m, 2H), 6.75 – 6.61 (m, 1H), 5.57 – 5.43 (m, 1H), 4.47 – 4.41 (m, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, J = 2.9 Hz), 162.3 (d, J = 2.9 Hz), 136.2 (d, J = 6.7 Hz), 136.1 – 135.8 (m), 133.6 (d, J = 9.7 Hz), 133.0 (d, J = 10.5 Hz), 132.4 (d, J = 5.2 Hz), 130.7 (d, J = 1.5 Hz), 129.5 (d, J = 4.5 Hz), 127.7 (d, J = 2.1 Hz), 126.6 (d, J = 1.9 Hz), 122.7 (d, J = 106.3 Hz), 122.5 (qd, J = 269.8, 2.1 Hz), 121.9 (qd, J = 33.8, 10.2 Hz), 121.4 (d, J = 104.6 Hz), 114.3 (d, J = 12.5 Hz), 113.8 (d, J = 12.7 Hz), 55.4, 55.2, 46.7 (d, J = 64.9 Hz), 19.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.98 – -64.04 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 30.90. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 10.18 min, t_{minor} = 25.35 min. HRMS (ESI) m/z: calcd for $C_{25}H_{25}F_3O_3P$ [M + H]$^+$ 461.1488, found: 461.1490.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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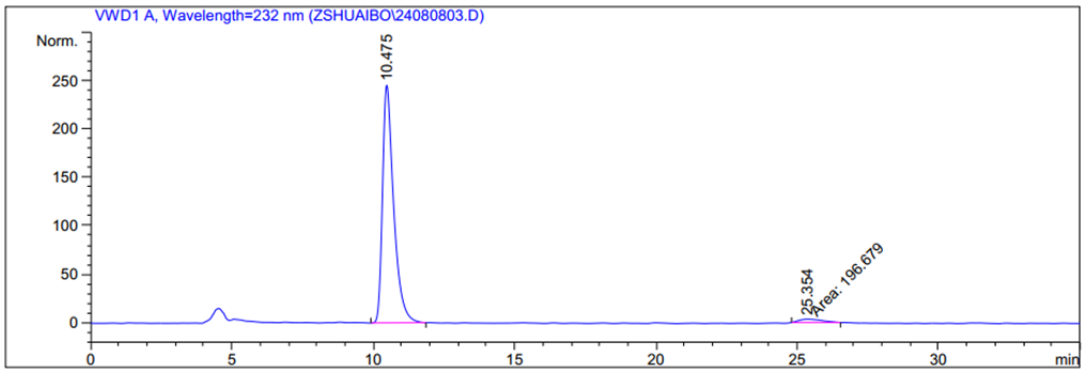
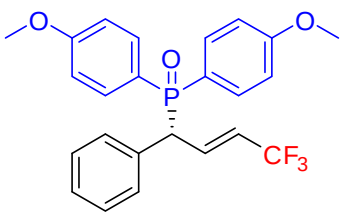
2	25.488	VB	1.0610	3871.64746	54.45560	50.2215

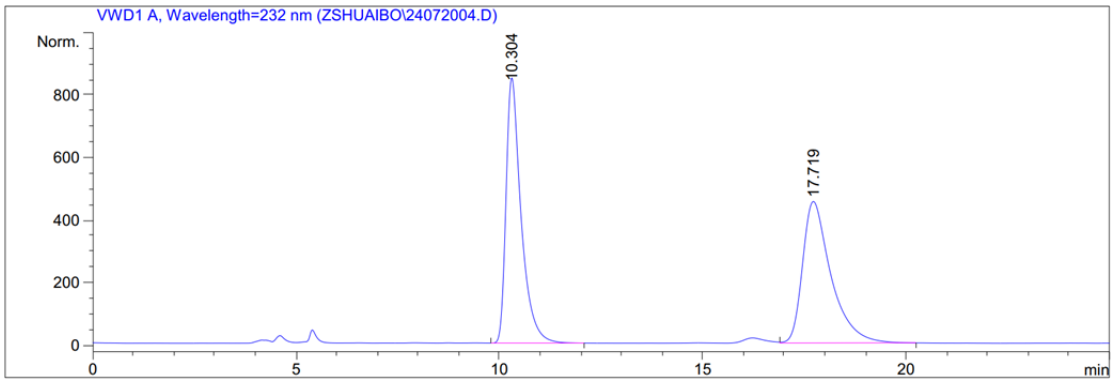


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.475	PB	0.4066	6752.09180	245.65202	97.1696
2	25.354	MM	0.9539	196.67883	3.43641	2.8304

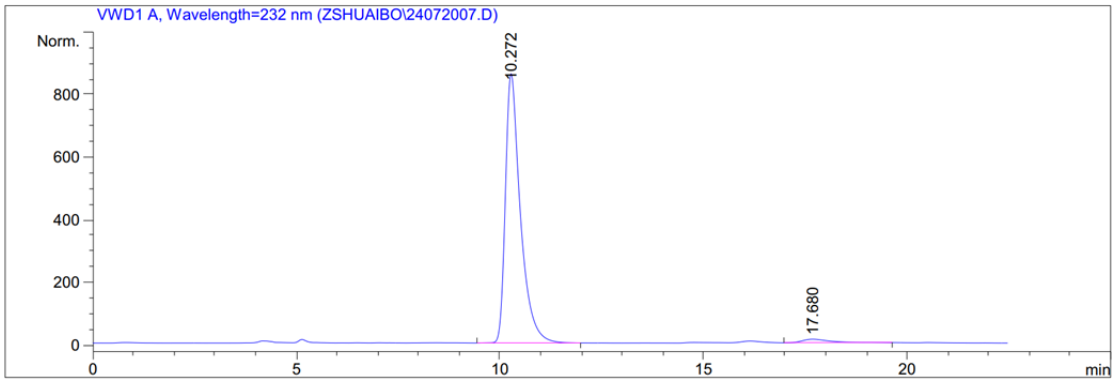


(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-phenylbut-2-en-1-yl)phosphine oxide (3d)

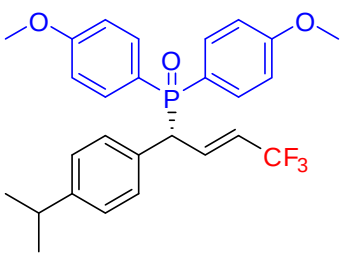
Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 181 – 183 °C, 61.6 mg, 69% yield, 95% ee, $[\alpha]^{20}_{D}$ = + 30.56 (*c* 0.18, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.65 (m, 2H), 7.48 – 7.37 (m, 2H), 7.29 – 7.18 (m, 5H), 7.13 – 6.97 (m, 2H), 6.93 – 6.68 (m, 3H), 5.60 – 5.46 (m, 1H), 4.25 – 4.15 (m, 1H), 3.85 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 2.9 Hz), 162.3 (d, *J* = 3.0 Hz), 136.1 – 135.7 (m), 134.0 (d, *J* = 6.0 Hz), 133.4 (d, *J* = 9.9 Hz), 133.1 (d, *J* = 10.1 Hz), 129.6 (d, *J* = 5.5 Hz), 128.8 (d, *J* = 1.7 Hz), 127.7 (d, *J* = 2.3 Hz), 122.6 (qd, *J* = 270.7, 1.9 Hz) , 122.5 (d, *J* = 55.2 Hz), 121.9 (qd, *J* = 33.9, 10.3 Hz), 121.4 (d, *J* = 53.4 Hz), 114.2 (d, *J* = 12.7 Hz), 113.9 (d, *J* = 12.8 Hz), 55.4, 55.2, 51.6 (d, *J* = 63.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.09 – -64.16 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 30.75. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 10.27 min, t_{minor} = 17.68 min. HRMS (ESI) m/z: calcd for $C_{24}H_{23}F_3O_3P$ $[M + H]^+$ 447.1331, found: 447.1332.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.304	VB	0.3782	2.17915e4	848.62708	49.7623
2	17.719	VB	0.7193	2.19997e4	453.13992	50.2377

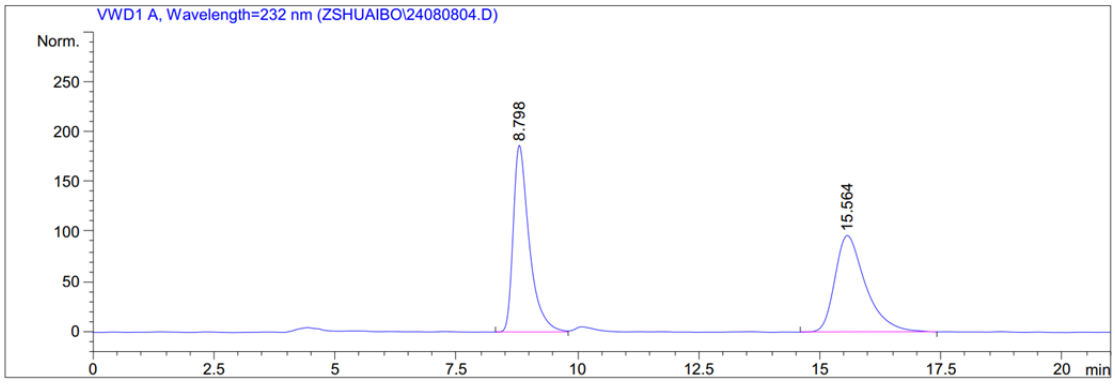


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.272	PP	0.3769	2.20070e4	860.74695	97.4451
2	17.680	VB	0.7165	576.99854	11.38426	2.5549

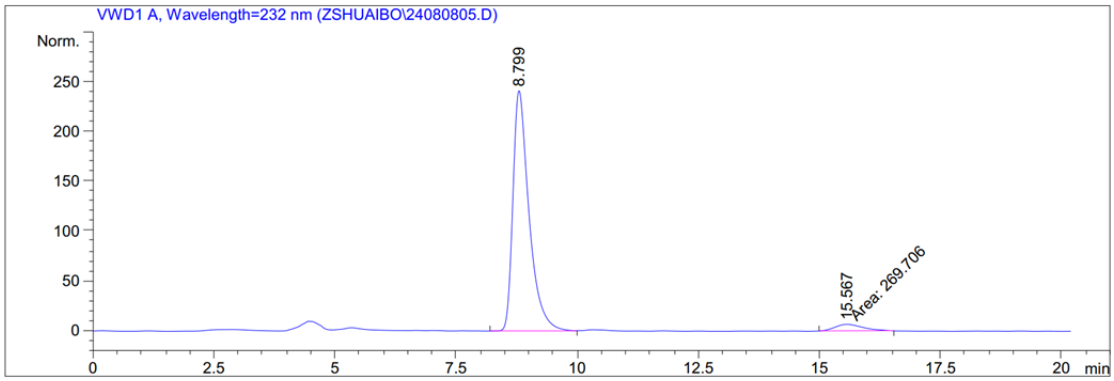


(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(4-isopropylphenyl)but-2-en-1-yl)phosphine oxide (3e)

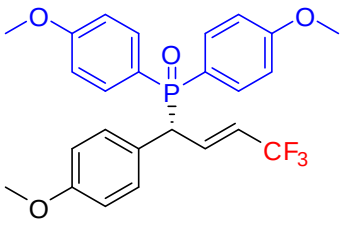
Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 188 – 190 °C, 73.2 mg, 75% yield, 91% ee, $[\alpha]^{20}_{D}$ = + 34.00 (*c* 0.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 2H), 7.45 – 7.36 (m, 2H), 7.19 – 7.14 (m, 2H), 7.12 – 7.08 (m, 2H), 7.04 – 6.96 (m, 2H), 6.84 – 6.78 (m, 2H), 6.78 – 6.68 (m, 1H), 5.60 – 5.46 (m, 1H), 4.22 – 4.13 (m, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 2.90 – 2.79 (m, 1H), 1.20 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6 (d, *J* = 3.1 Hz), 162.3 (d, *J* = 2.8 Hz), 148.4 (d, *J* = 2.4 Hz), 136.3 – 135.9 (m), 133.5 (d, *J* = 9.9 Hz), 133.2 (d, *J* = 10.1 Hz), 131.1 (d, *J* = 6.0 Hz), 129.4 (d, *J* = 5.4 Hz), 126.8 (d, *J* = 1.7 Hz), 122.5 (d, *J* = 93.6 Hz), 122.5 (qd, *J* = 269.8, 1.6 Hz), 121.8 (qd, *J* = 33.8, 10.3 Hz), 121.7 (d, *J* = 91.5 Hz), 114.2 (d, *J* = 12.5 Hz), 113.8 (d, *J* = 12.8 Hz), 55.3, 55.2, 51.3 (d, *J* = 64.1 Hz), 33.7, 23.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.06 – -64.13 (m). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ 30.88. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 8.80 min, t_{minor} = 15.57 min. HRMS (ESI) m/z: calcd for $C_{27}H_{29}F_3O_3P$ $[M + H]^+$ 489.1801, found: 489.1810.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.798	BV	0.3425	4327.56641	187.18571	50.3883
2	15.564	BB	0.6580	4260.86377	96.73208	49.6117

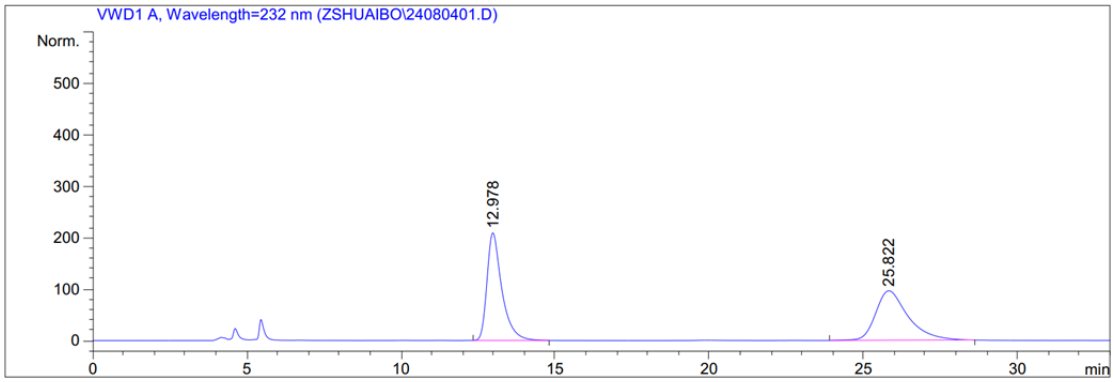


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.799	BB	0.3430	5596.02246	241.65999	95.4020
2	15.567	MM	0.6737	269.70645	6.67273	4.5980

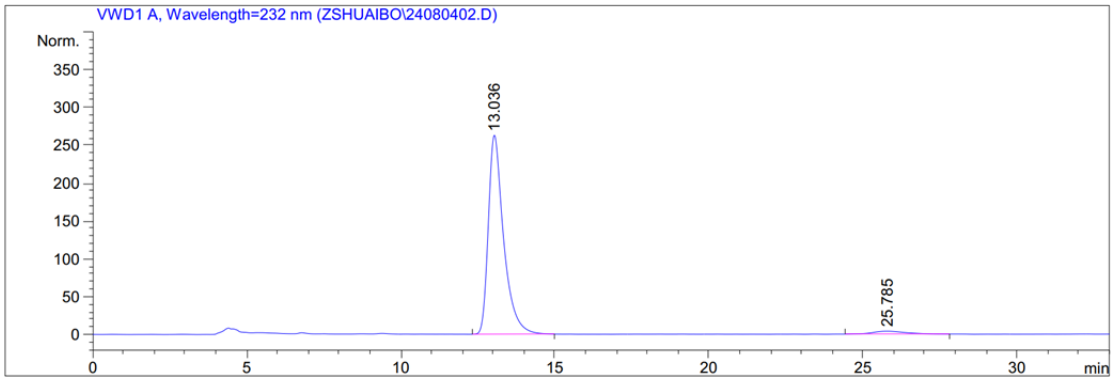


(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(4-methoxyphenyl)but-2-en-1-yl)phosphine oxide (3f)

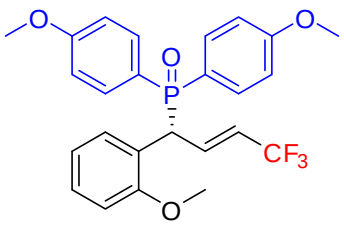
Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 188 – 190 °C, 87.6 mg, 92% yield, 94% ee, $[\alpha]^{20}_{D}$ = + 31.67 (*c* 0.18, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 2H), 7.48 – 7.40 (m, 2H), 7.22 – 7.15 (m, 2H), 7.04 – 6.97 (m, 2H), 6.86 – 6.76 (m, 4H), 6.76 – 6.65 (m, 1H), 5.57 – 5.45 (m, 1H), 4.18 (t, *J* = 10.0 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 2.9 Hz), 162.3 (d, *J* = 2.9 Hz), 159.0 (d, *J* = 2.1 Hz), 136.2 (h, *J* = 6.3 Hz), 133.4 (d, *J* = 9.9 Hz), 133.2 (d, *J* = 10.2 Hz), 130.7 (d, *J* = 5.5 Hz), 125.7 (d, *J* = 6.1 Hz), 122.6 (d, *J* = 55.7 Hz), 122.5 (qd, *J* = 270.9, 1.9 Hz), 121.8 (qd, *J* = 33.8, 10.2 Hz), 121.5 (d, *J* = 53.5 Hz), 114.2 (d, *J* = 1.6 Hz), 114.2 (d, *J* = 12.6 Hz), 113.9 (d, *J* = 12.8 Hz), 55.4, 55.2, 55.2, 50.6 (d, *J* = 64.9 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.04 – -64.11 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 30.89. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 13.04 min, t_{minor} = 25.79 min. HRMS (ESI) m/z: calcd for $C_{25}H_{25}F_3O_4P$ $[M + H]^+$ 477.1437, found: 477.1441.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.978	BB	0.4950	7021.01172	209.14665	49.9390
2	25.822	BB	1.0860	7038.15723	96.26299	50.0610



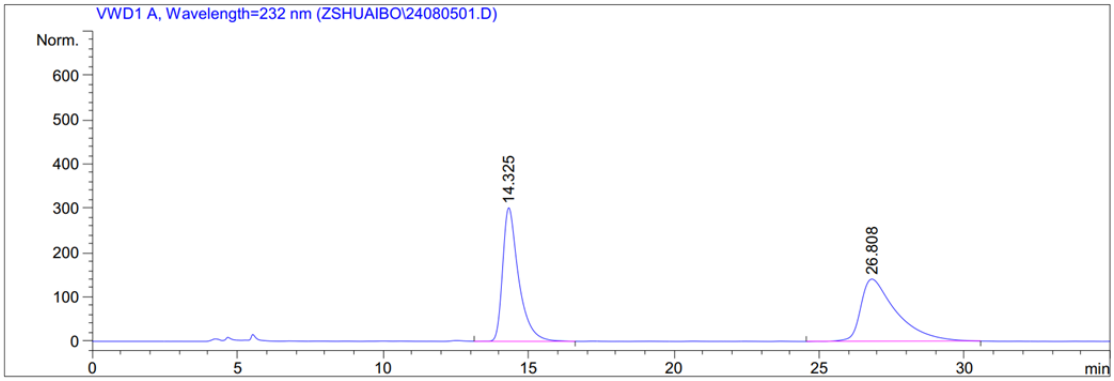
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.036	BB	0.5103	9064.54687	262.71442	96.9907
2	25.785	BP	0.8886	281.24442	3.76680	3.0093



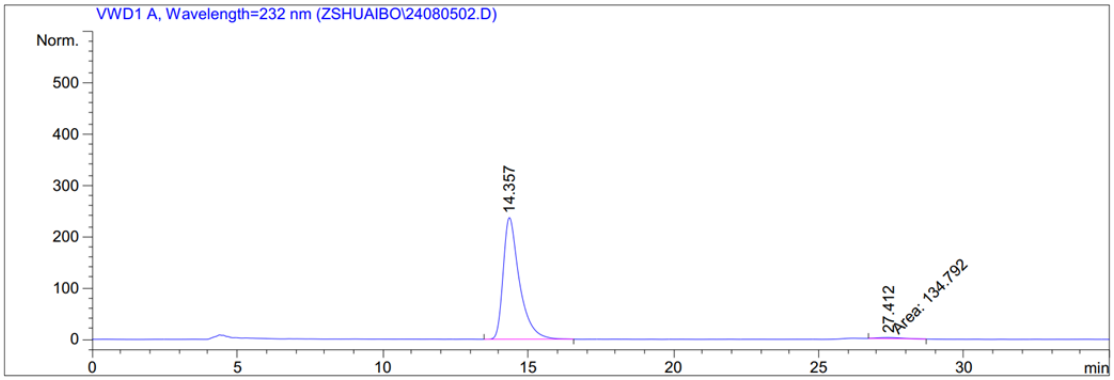
(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(2-methoxyphenyl)but-2-en-1-yl)phosphine oxide (3g)

Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 58 – 59 °C, 82.8 mg, 87% yield, 97% ee, $[\alpha]^{20}_{D}$ = - 21.77 (*c* 0.17, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.68 (m, 3H), 7.49 – 7.39 (m, 2H), 7.24 – 7.13 (m, 1H), 7.04 – 6.98 (m, 2H), 6.97 – 6.91 (m, 1H), 6.80 – 6.63 (m, 4H), 5.61 – 5.47 (m, 1H), 5.00 – 4.90 (m, 1H), 3.84 (s, 3H), 3.73 (s, 3H), 3.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 2.9 Hz), 162.1 (d, *J* = 2.9 Hz), 156.1 (d, *J* = 5.9 Hz), 136.0 – 135.6 (m), 133.3 (d, *J* = 10.0 Hz), 132.8 (d, *J* = 10.5 Hz), 130.2 (d, *J* = 4.5

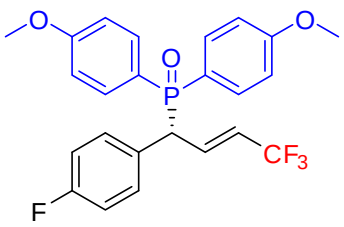
Hz), 128.7 (d, J = 2.2 Hz), 123.2 (d, J = 24.9 Hz), 122.6 (qd, J = 269.9, 2.0 Hz), 122.5 (d, J = 5.6 Hz), 122.1 (d, J = 21.8 Hz), 121.8 (qd, J = 33.7, 10.3 Hz), 121.0 (d, J = 2.2 Hz), 114.2 (d, J = 12.6 Hz), 113.5 (d, J = 12.9 Hz), 110.5 (d, J = 1.7 Hz), 55.3, 55.3, 55.2, 41.6 (d, J = 65.8 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.00 – -64.06 (m). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 31.89. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 14.36 min, t_{minor} = 27.41 min. HRMS (ESI) m/z: calcd for $C_{25}H_{25}F_3O_4P$ $[M + H]^+$ 477.1437, found: 477.1440.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.325	VB	0.5666	1.15550e4	301.43826	49.2676
2	26.808	BB	1.2213	1.18986e4	140.44829	50.7324

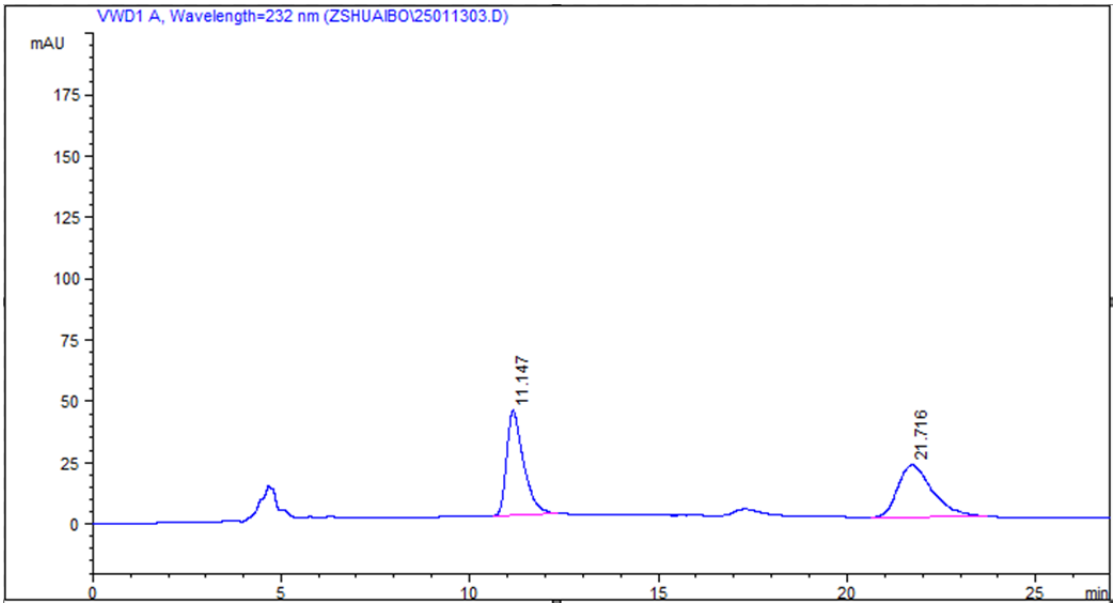


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.357	BB	0.5741	9236.01953	236.97516	98.5616
2	27.412	MM	1.0264	134.79210	2.18875	1.4384

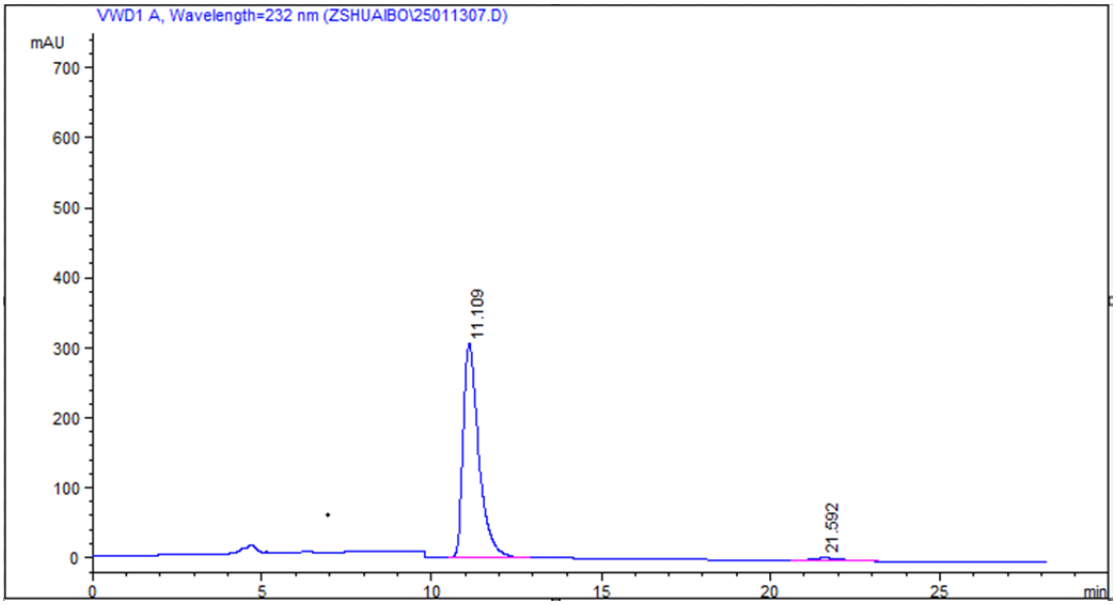


(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(4-fluorophenyl)but-2-en-1-yl)phosphine oxide (3h)

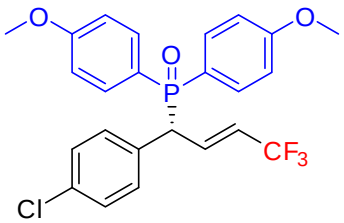
Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 164 – 166 °C, 83.5 mg, 90% yield, 95% ee, $[\alpha]^{20}_{D}$ = + 2.35 (*c* 0.17, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.66 (m, 2H), 7.47 – 7.39 (m, 2H), 7.30 – 7.22 (m, 2H), 7.06 – 6.99 (m, 2H), 6.98 – 6.91 (m, 2H), 6.91 – 6.76 (m, 2H), 6.76 – 6.62 (m, 1H), 5.59 – 5.44 (m, 1H), 4.24 – 4.15 (m, 1H), 3.86 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (dd, *J* = 30.8, 2.9 Hz), 162.2 (dd, *J* = 247.0, 2.4 Hz), 135.7 (m), 133.4 (d, *J* = 9.9 Hz), 133.0 (d, *J* = 10.2 Hz), 131.1 (dd, *J* = 8.1, 5.6 Hz), 129.8 (dd, *J* = 5.6, 3.3 Hz), 122.4 (qd, *J* = 269.9, 1.9 Hz), 122.3 (d, *J* = 56.1 Hz), 122.1 (qd, *J* = 33.9, 10.2 Hz), 121.2 (d, *J* = 54.5 Hz), 115.9 (d, *J* = 1.7 Hz), 115.6 (d, *J* = 1.8 Hz), 114.3 (d, *J* = 12.7 Hz), 114.0 (d, *J* = 12.9 Hz), 55.4, 55.3, 50.6 (d, *J* = 64.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.15 – -64.23 (m, 3F), -114.20 – -114.34 (m, 1F). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 30.71. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 11.11 min, t_{minor} = 21.59 min. HRMS (ESI) m/z: calcd for $C_{24}H_{22}F_4O_3P$ $[M + H]^+$ 465.1237, found: 465.1241.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.147	PB	0.4657	1346.22607	43.00573	49.5164
2	21.716	BB	0.9307	1372.52161	21.34725	50.4836

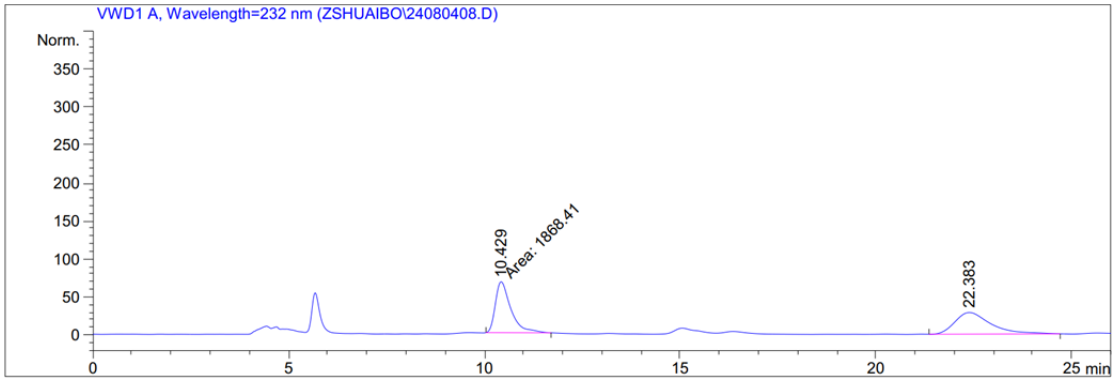


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.109	BB	0.4717	9716.90625	305.40274	97.5604
2	21.592	BB	0.7424	242.98412	3.96631	2.4396

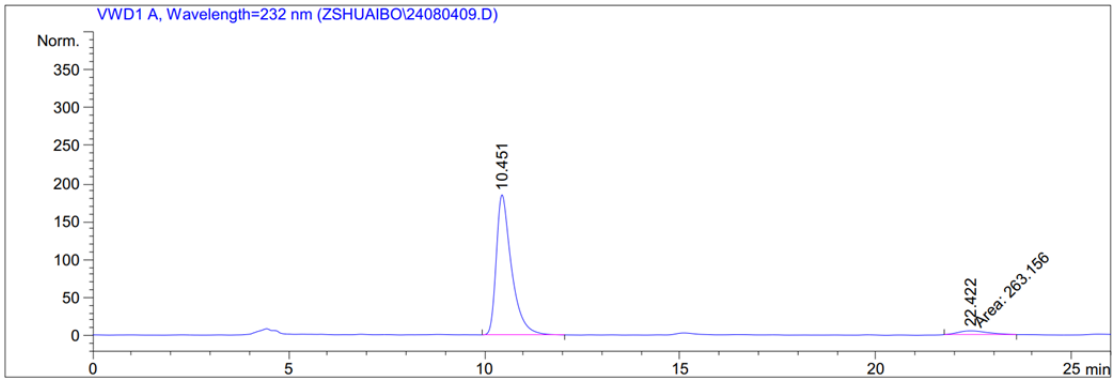


(*R*,*E*)-(1-(4-Chlorophenyl)-4,4,4-trifluorobut-2-en-1-yl)bis(4-methoxyphenyl)phosphine oxide (3i)

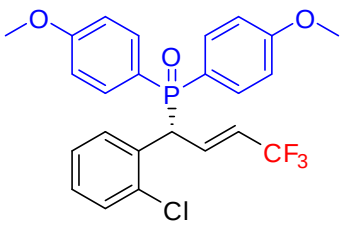
Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 109 – 110 °C, 61.5 mg, 64% yield, 90% ee, $[\alpha]^{20}_{D}$ = + 37.33 (*c* 0.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 2H), 7.49 – 7.40 (m, 2H), 7.23 (s, 4H), 7.05 – 6.98 (m, 2H), 6.87 – 6.81 (m, 2H), 6.73 – 6.62 (m, 1H), 5.57 – 5.43 (m, 1H), 4.21 – 4.12 (m, 1H), 3.86 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, *J* = 2.9 Hz), 162.4 (d, *J* = 2.9 Hz), 135.6 – 135.3 (m), 133.7 (d, *J* = 2.7 Hz), 133.4 (d, *J* = 10.0 Hz), 133.1 (d, *J* = 10.2 Hz), 132.6 (d, *J* = 5.9 Hz), 130.8 (d, *J* = 5.5 Hz), 129.0 (d, *J* = 1.8 Hz), 122.33 (qd, *J* = 269.9, 1.7 Hz), 122.26 (qd, *J* = 33.9, 10.0 Hz), 122.2 (d, *J* = 47.9 Hz), 121.1 (d, *J* = 46.3 Hz), 114.3 (d, *J* = 12.7 Hz), 114.1 (d, *J* = 12.7 Hz), 55.4, 55.3, 50.9 (d, *J* = 63.4 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.19 – -64.31 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 30.49. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 10.45 min, t_{minor} = 22.42 min. HRMS (ESI) m/z: calcd for $C_{24}H_{22}ClF_3O_3P$ $[M + H]^+$ 481.0942, found: 481.0943.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.429	MM	0.4633	1868.40503	67.20929	50.5060
2	22.383	VB	0.9360	1830.96814	28.49566	49.4940



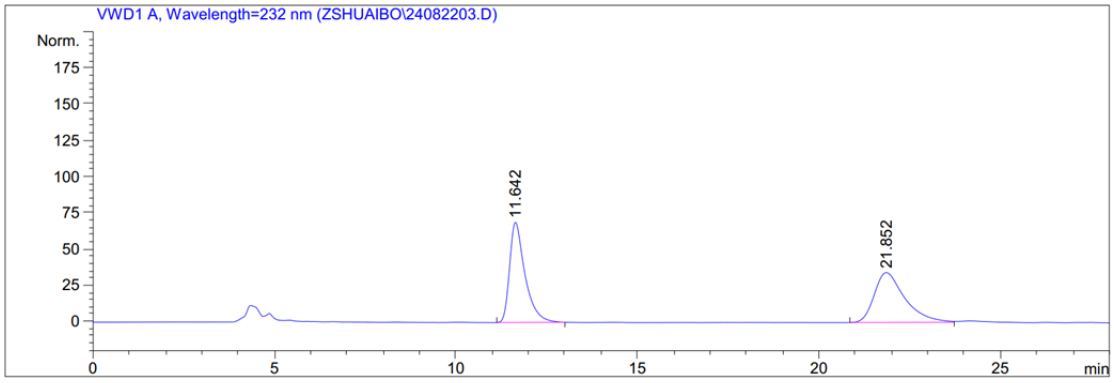
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.451	BB	0.3970	4982.62939	184.25029	94.9835
2	22.422	MM	0.8921	263.15561	4.91640	5.0165



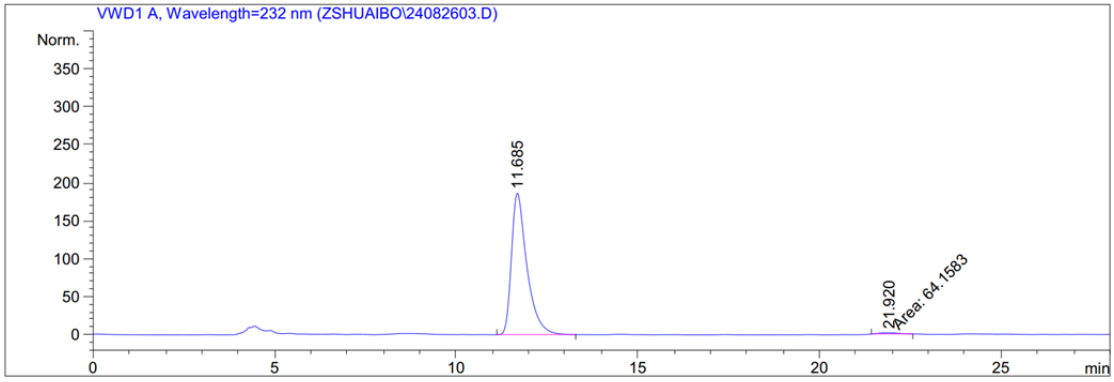
(*R*,*E*)-(1-(2-Chlorophenyl)-4,4,4-trifluorobut-2-en-1-yl)bis(4-methoxyphenyl)phosphine oxide (3j)

Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 98 – 99 °C, 69.1 mg, 72% yield, 98% ee, $[\alpha]^{20}_{D}$ = - 30.59 (*c* 0.17, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 1H), 7.80 – 7.71 (m, 2H), 7.51 – 7.41 (m, 2H), 7.29 – 7.23 (m, 2H), 7.20 – 7.11 (m, 1H), 7.07 – 7.01 (m, 2H), 6.83 – 6.76 (m, 2H), 6.69 – 6.57 (m, 1H), 5.55 – 5.44 (m, 1H), 4.96 – 4.87 (m, 1H), 3.87 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, *J* = 2.9 Hz),

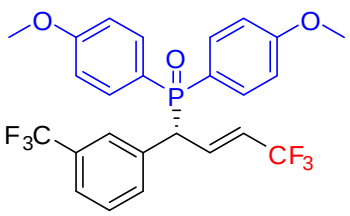
162.4 (d, J = 3.0 Hz), 135.1 – 134.6 (m), 133.8 (d, J = 7.8 Hz), 133.3 (d, J = 10.2 Hz), 132.8 (d, J = 10.4 Hz), 132.3 (d, J = 4.6 Hz), 130.9 (d, J = 4.4 Hz), 129.6 (d, J = 6.1 Hz), 128.9 (d, J = 2.0 Hz), 127.5 (d, J = 1.8 Hz), 122.5 (d, J = 12.3 Hz), 122.4 (qd, J = 34.0, 10.0 Hz), 122.3 (qd, J = 270.1, 1.7 Hz), 121.5 (d, J = 10.9 Hz), 114.4 (d, J = 12.8 Hz), 113.9 (d, J = 13.0 Hz), 55.4, 55.2, 46.2 (d, J = 64.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.09 – -64.25 (m). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 31.61. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 11.69 min, t_{minor} = 21.92 min. HRMS (ESI) m/z: calcd for $C_{24}H_{22}ClF_3O_3P$ $[M + H]^+$ 481.0942, found: 481.0943.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.642	BB	0.4375	2040.01147	69.12625	50.2822
2	21.852	BB	0.8638	2017.11682	34.44379	49.7178

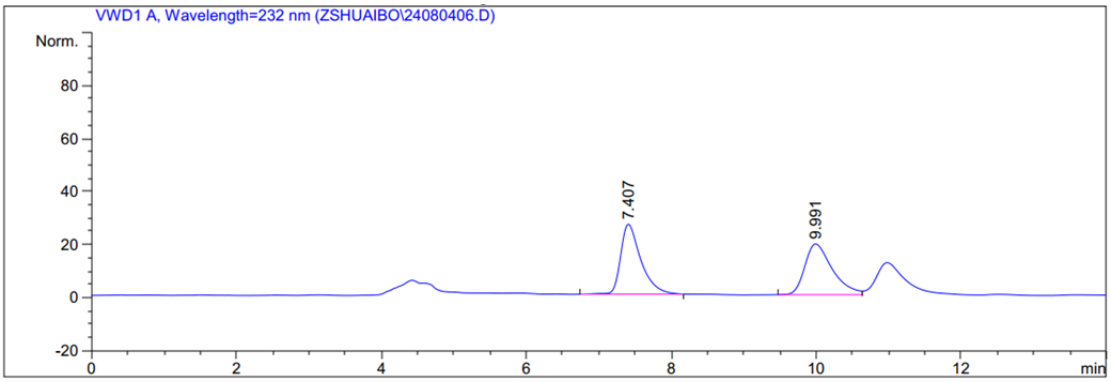


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.685	BB	0.4375	5521.53516	186.30605	98.8514
2	21.920	MM	0.6815	64.15830	1.56894	1.1486

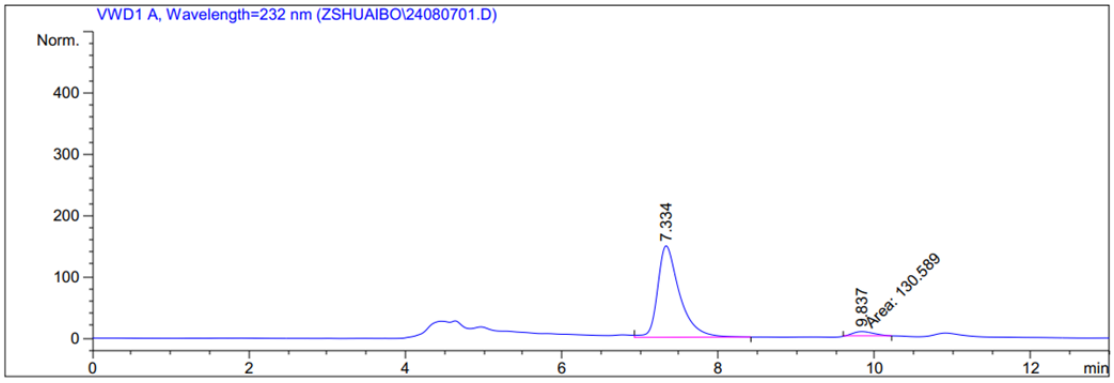


(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(3-(trifluoromethyl)phenyl)but-2-en-1-yl)phosphine oxide (3k)

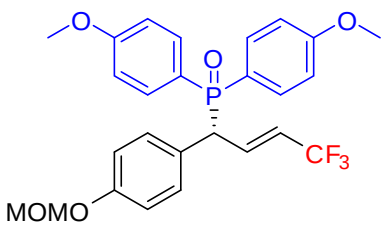
Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 136 – 137 °C, 52.4 mg, 51% yield, 92% ee, $[\alpha]^{20}_{D}$ = + 29.33 (*c* 0.15, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.31 (s, 1H), 7.06 – 7.00 (m, 2H), 6.85 – 6.79 (m, 2H), 6.79 – 6.69 (m, 1H), 5.62 – 5.52 (m, 1H), 4.31 – 4.24 (m, 1H), 3.86 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8 (d, *J* = 2.9 Hz), 162.6 (d, *J* = 2.9 Hz), 135.3 (d, *J* = 6.0 Hz), 135.2 – 134.9 (m), 133.4 (d, *J* = 10.0 Hz), 133.0 (d, *J* = 10.0 Hz), 132.7 (d, *J* = 4.9 Hz), 130.8 (qd, *J* = 32.5, 1.8 Hz), 129.2 (d, *J* = 2.0 Hz), 126.5 – 126.2 (m), 124.8, 124.5 – 124.3 (m), 122.6 (qd, *J* = 34.0, 10.1 Hz), 122.3 (qd, *J* = 270.0, 1.9 Hz), 121.7 (d, *J* = 70.8 Hz), 120.9 (d, *J* = 69.4 Hz), 114.4 (d, *J* = 12.7 Hz), 114.0 (d, *J* = 12.7 Hz), 55.4, 55.3, 51.5 (d, *J* = 62.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.75 (s, 3F), -64.28 – -64.32 (m, 3F). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) δ 30.62. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 7.33 min, t_{minor} = 9.84 min. HRMS (ESI) m/z: calcd for $C_{25}H_{22}F_6O_3P$ $[M + H]^+$ 515.1205, found: 515.1212.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.407	BB	0.2883	514.03876	26.40420	50.3358
2	9.991	BV	0.3945	507.17966	19.17206	49.6642

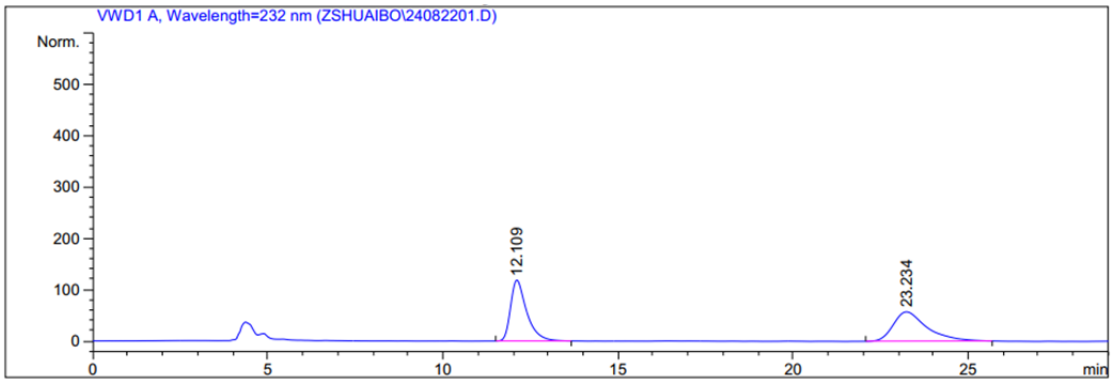


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.334	VB	0.2878	2920.42139	149.34937	95.7198
2	9.837	MM	0.3073	130.58932	7.08369	4.2802

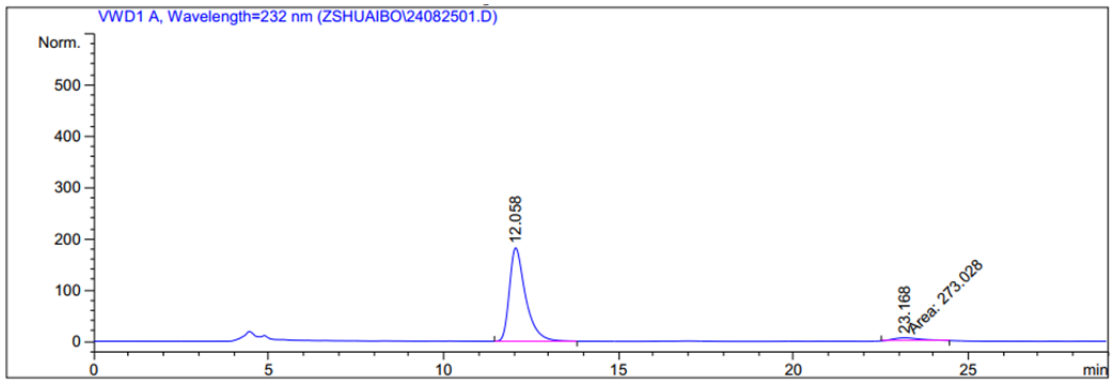


(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(4-(methoxymethoxy)phenyl)but-2-en-1-yl)phosphine oxide (3l)

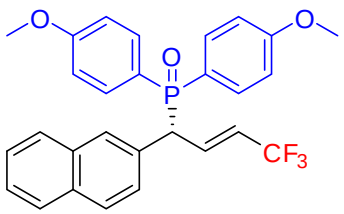
Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 155 – 116 °C, 61.8 mg, 61% yield, 91% ee, $[\alpha]^{20}_{D}$ = + 12.67 (*c* 0.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 2H), 7.50 – 7.39 (m, 2H), 7.22 – 7.14 (m, 2H), 7.04 – 6.96 (m, 2H), 6.96 – 6.89 (m, 2H), 6.87 – 6.79 (m, 2H), 6.78 – 6.63 (m, 1H), 5.58 – 5.44 (m, 1H), 5.13 (dd, *J* = 8.4, 6.8 Hz, 2H), 4.23 – 4.13 (m, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 3.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 2.9 Hz), 162.3 (d, *J* = 2.8 Hz), 156.7 (d, *J* = 2.2 Hz), 136.3 – 135.8 (m), 133.4 (d, *J* = 9.9 Hz), 133.2 (d, *J* = 10.2 Hz), 130.7 (d, *J* = 5.5 Hz), 127.0 (d, *J* = 6.0 Hz), 122.52 (d, *J* = 59.1 Hz), 12.50 (qd, *J* = 270.8, 2.0 Hz), 121.8 (qd, *J* = 33.8, 10.2 Hz), 121.5 (d, *J* = 57.0 Hz), 116.6 (d, *J* = 1.7 Hz), 114.2 (d, *J* = 12.7 Hz), 113.9 (d, *J* = 12.8 Hz), 94.4, 56.0, 55.4, 55.3, 50.7 (d, *J* = 64.7 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -53.70 – -78.06 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 30.82. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 12.06 min, t_{minor} = 23.17 min. HRMS (ESI) m/z: calcd for $C_{26}H_{27}F_3O_5P$ $[M + H]^+$ 507.1543, found: 507.1542.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.109	BB	0.4758	3801.72900	118.64249	49.8075
2	23.234	BB	0.9791	3831.11938	57.22150	50.1925



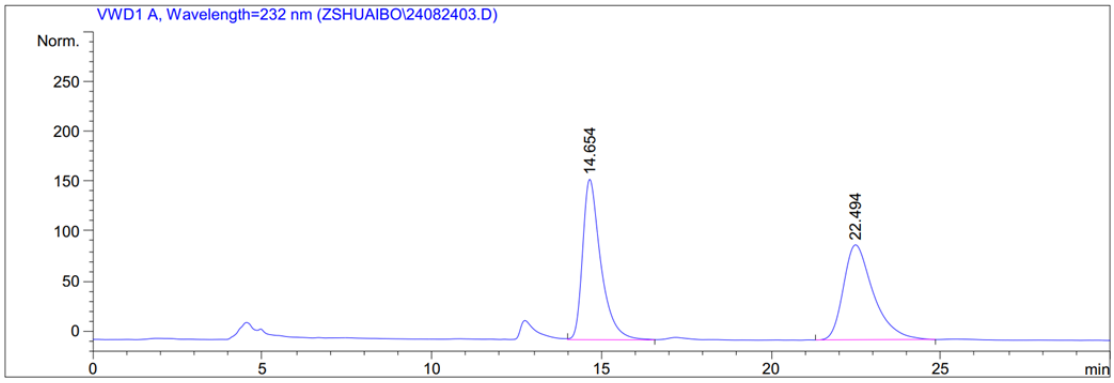
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.058	BB	0.4757	5858.63379	182.16721	95.5472
2	23.168	MM	0.8603	273.02829	5.28927	4.4528



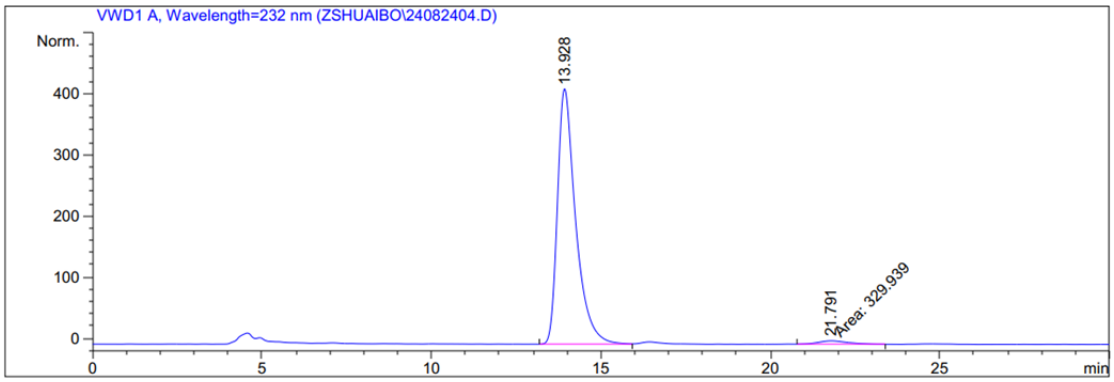
(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(naphthalen-2-yl)but-2-en-1-yl)phosphine oxide (3m)

Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 218 – 220 °C, 72.4 mg, 73% yield, 96% ee, $[\alpha]^{20}_{D}$ = + 36.15 (*c* 0.13, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.69 (m, 6H), 7.50 – 7.38 (m, 5H), 7.03 – 6.99 (m, 2H), 6.88 – 6.79 (m, 1H), 6.78

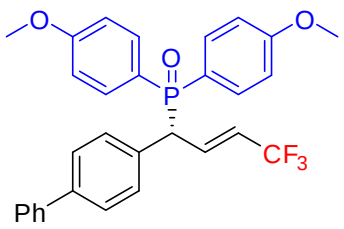
– 6.66 (m, 2H), 5.61 – 5.48 (m, 1H), 4.43 – 4.33 (m, 1H), 3.85 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (two aromatic carbon missing) δ 162.6 (d, J = 2.9 Hz), 162.3 (d, J = 2.9 Hz), 136.2 – 135.6 (m), 133.5 (d, J = 9.9 Hz), 133.3 (d, J = 1.7 Hz), 133.2 (d, J = 10.2 Hz), 132.6 (d, J = 1.6 Hz), 131.6 (d, J = 6.1 Hz), 128.8 (d, J = 6.6 Hz), 128.6 – 128.4 (d, J = 6.1 Hz), 127.8 (d, J = 30.9 Hz), 127.2 (d, J = 4.8 Hz), 126.2 (d, J = 8.7 Hz), 122.54 (d, J = 31.3 Hz), 122.49 (qd, J = 269.9, 1.9 Hz), 122.1 (qd, J = 33.8, 10.2 Hz), 121.5 (d, J = 29.7 Hz), 114.3 (d, J = 12.7 Hz), 114.0 (d, J = 12.8 Hz), 55.4, 55.2, 51.7 (d, J = 63.8 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.05 – -64.09 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 30.68. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 13.93 min, t_{minor} = 21.79 min. HRMS (ESI) m/z: calcd for $C_{28}H_{25}F_3O_3P$ $[M + H]^+$ 497.1488, found: 497.1488.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.654	BB	0.5536	6008.52930	160.88640	50.6282
2	22.494	VB	0.9190	5859.41357	95.38778	49.3718

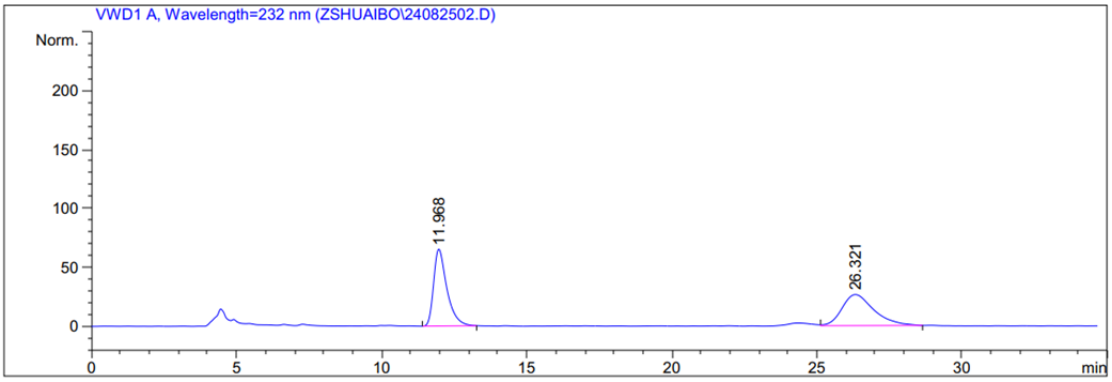


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.928	BB	0.5546	1.55716e4	417.42358	97.9251
2	21.791	MM	1.0134	329.93921	5.42639	2.0749

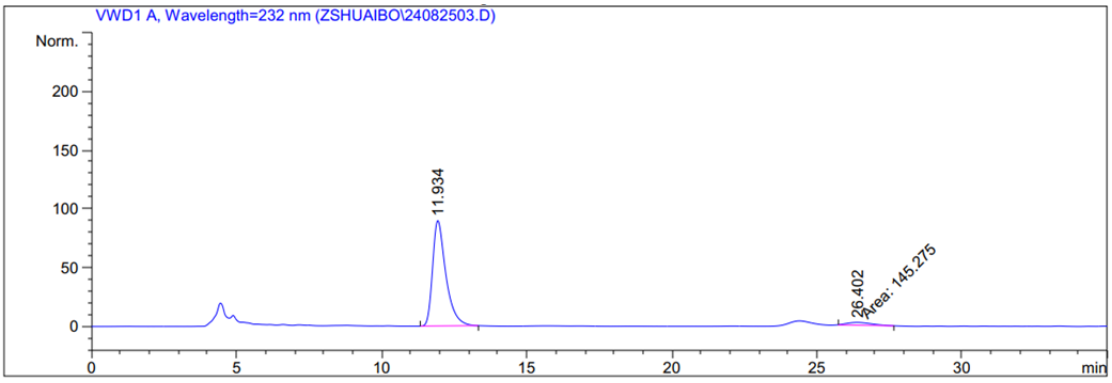


(*R*,*E*)-(1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluorobut-2-en-1-yl)bis(4-methoxyphenyl)phosphine oxide (3n)

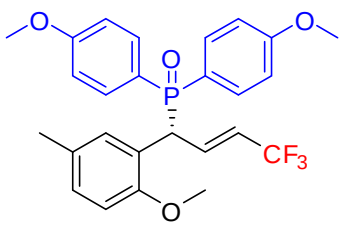
Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 254 – 255 °C, 47 mg, 45% yield, 90% ee, $[\alpha]^{20}_{D}$ = + 26.92 (*c* 0.13, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 2H), 7.60 – 7.52 (m, 2H), 7.52 – 7.39 (m, 6H), 7.37 – 7.31 (m, 3H), 7.05 – 6.97 (m, 2H), 6.86 – 6.71 (m, 3H), 5.63 – 5.49 (m, 1H), 4.30 – 4.20 (m, 1H), 3.86 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 2.8 Hz), 162.4 (d, *J* = 2.9 Hz), 140.4 (d, *J* = 2.4 Hz), 140.3, 136.1 – 135.6 (m), 133.5 (d, *J* = 9.9 Hz), 133.2 (d, *J* = 10.2 Hz), 133.0 (d, *J* = 6.2 Hz), 130.0 (d, *J* = 5.6 Hz), 128.8, 127.5, 127.4 (d, *J* = 1.8 Hz), 127.0, 122.48 (qd, *J* =270.5, 1.7 Hz), 122.47 (d, *J* = 56.5 Hz), 122.1 (qd, *J* =34.3, 10.7 Hz), 121.4 (d, *J* = 54.6 Hz), 114.3 (d, *J* = 12.7 Hz), 114.0 (d, *J* = 12.8 Hz), 55.4, 55.3, 51.3 (d, *J* = 63.7 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.07 – -64.14 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 30.72. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 11.93 min, t_{minor} = 26.40 min. HRMS (ESI) m/z: calcd for $C_{30}H_{27}F_3O_3P$ $[M + H]^+$ 523.1644, found: 523.1647.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.968	PB	0.4701	2072.77588	65.16601	50.4964
2	26.321	VB	1.1264	2032.02173	26.40430	49.5036

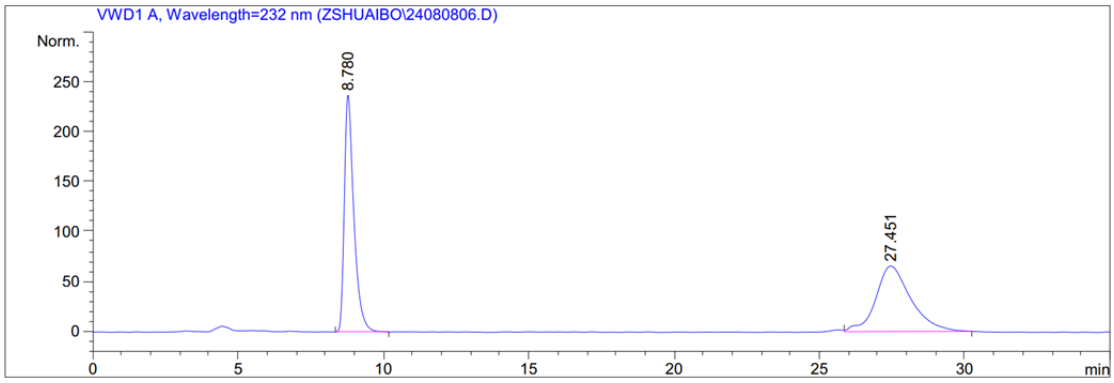


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.934	PB	0.4760	2861.04712	89.57463	95.1677
2	26.402	MM	1.0108	145.27458	2.39539	4.8323

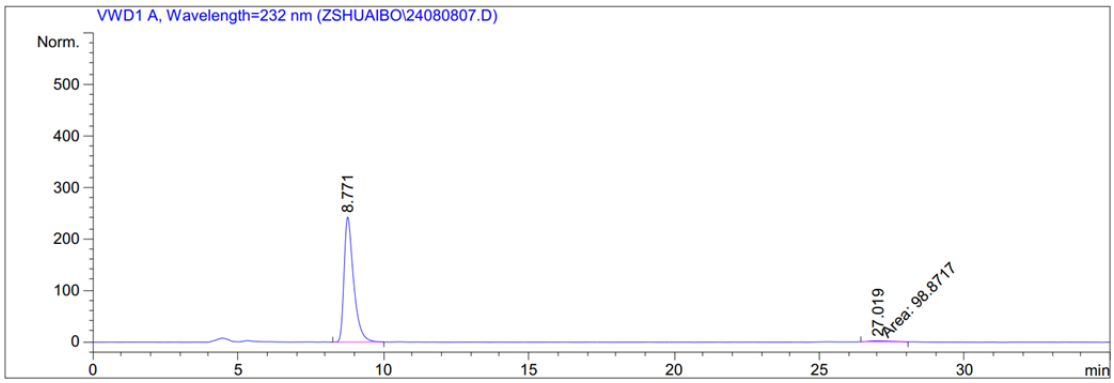


(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(2-methoxy-5-methylphenyl)but-2-en-1-yl)phosphine oxide (3o)

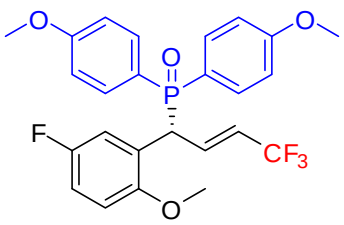
Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), light yellow solid, mp 74 – 75 °C, 77.4 mg, 79% yield, 97% ee, $[\alpha]^{20}_{D}$ = + 5.22 (*c* 0.23, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.68 (m, 2H), 7.52 – 7.40 (m, 3H), 7.04 – 6.93 (m, 3H), 6.81 – 6.75 (m, 2H), 6.75 – 6.63 (m, 1H), 6.60 (d, *J* = 8.3 Hz, 1H), 5.58 – 5.45 (m, 1H), 4.96 – 4.86 (m, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 3.59 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4 (d, *J* = 2.8 Hz), 162.1 (d, *J* = 2.9 Hz), 154.0 (d, *J* = 6.0 Hz), 136.1 – 135.8 (m), 133.3 (d, *J* = 10.0 Hz), 132.9 (d, *J* = 10.4 Hz), 130.7 (d, *J* = 4.5 Hz), 130.3 (d, *J* = 2.2 Hz), 129.0 (d, *J* = 2.3 Hz), 123.2 (d, *J* = 26.2 Hz), 122.6 (qd, *J* = 269.7, 1.9 Hz), 122.3 (d, *J* = 23.1 Hz), 122.2 (d, *J* = 5.4 Hz), 121.7 (qd, *J* = 33.7, 10.4 Hz), 114.1 (d, *J* = 12.5 Hz), 113.5 (d, *J* = 12.9 Hz), 110.4 (d, *J* = 1.7 Hz), 55.4, 55.3, 55.2, 41.6 (d, *J* = 66.0 Hz), 20.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.97 – -64.04 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 31.91. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 8.77 min, t_{minor} = 27.02 min. HRMS (ESI) m/z: calcd for $C_{26}H_{27}F_3O_4P$ $[M + H]^+$ 491.1594, found: 491.1596.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.780	PP	0.3382	5431.65039	237.50911	49.3633
2	27.451	VB	1.2150	5571.76416	65.99564	50.6367



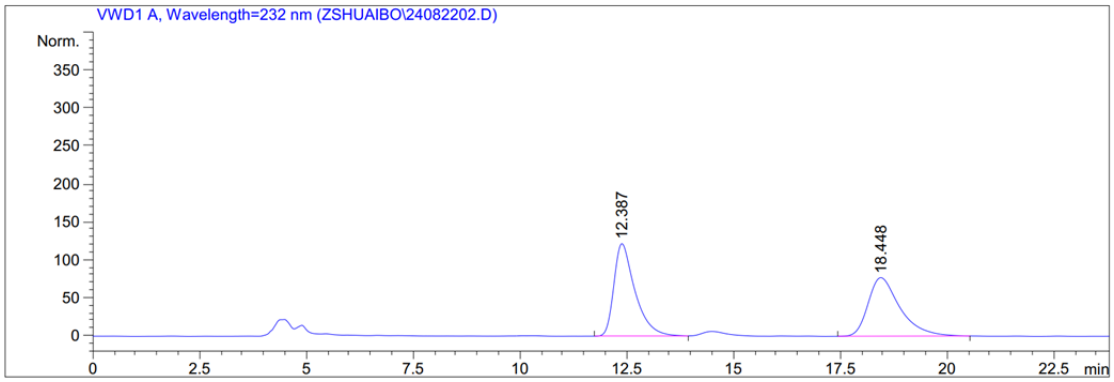
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.771	VB	0.3416	5567.04004	242.96909	98.2550
2	27.019	MM	0.9560	98.87167	1.72363	1.7450



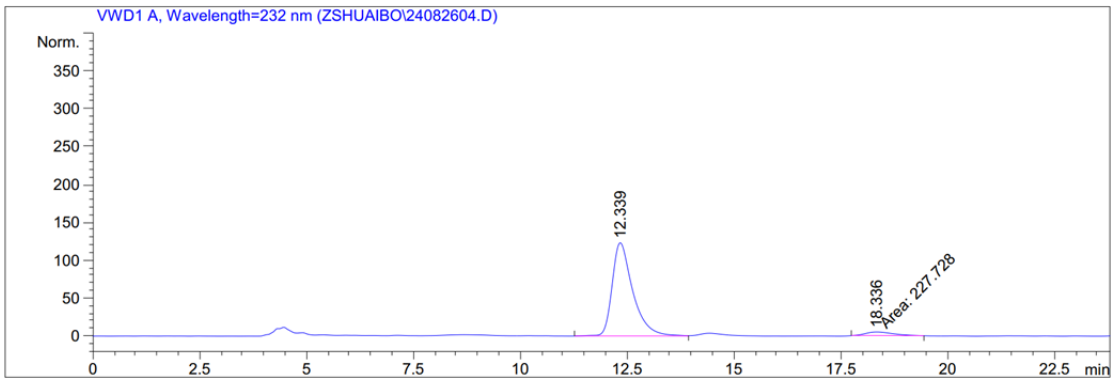
(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(5-fluoro-2-methoxyphenyl)but-2-en-1-yl)phosphine oxide (3p)

Method A, Purified by Biotage flash chromatography with (PE/EtOAc 2:1), white solid, mp 86 – 87 °C, 67.2 mg, 68% yield, 90% ee, $[\alpha]^{20}_{D}$ = - 5.83 (*c* 0.12, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.69 (m, 2H), 7.55 – 7.43 (m, 3H), 7.05 – 6.98 (m, 2H), 6.88 – 6.82 (m, 1H), 6.82 – 6.77 (m, 2H), 6.70 – 6.57 (m, 2H), 5.60 – 5.46 (m, 1H), 4.95 – 4.86 (m, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 3.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (dd, *J* = 33.0, 2.9 Hz), 156.9 (dd, *J* = 239.6, 2.5

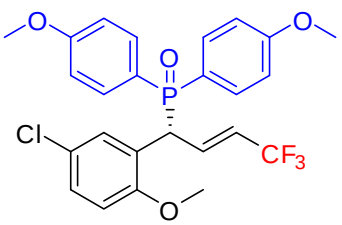
Hz), 152.3 (d, J = 2.3 Hz), 152.3 (d, J = 2.2 Hz), 135.7 – 135.0 (m), 133.2 (d, J = 10.2 Hz), 132.8 (d, J = 10.4 Hz), 124.3 – 124.1 (m), 122.9 (d, J = 22.4 Hz), 122.4 (qd, J = 269.9, 2.0 Hz), 122.2 (qd, J = 33.9, 10.1 Hz), 121.8 (d, J = 20.0 Hz), 117.1 (dd, J = 24.6, 4.6 Hz), 114.8 (dd, J = 22.9, 2.3 Hz), 114.2 (d, J = 12.7 Hz), 113.7 (d, J = 13.0 Hz), 111.3 (dd, J = 8.2, 1.7 Hz), 55.9, 55.4, 55.2, 41.7 (dd, J = 64.9, 1.1 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.10 – -64.16 (m, 3F), -121.77 – -121.88 (m, 1F). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 31.63. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 9/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 12.34 min, t_{minor} = 18.34 min. HRMS (ESI) m/z: calcd for $C_{25}H_{24}F_4O_4P$ $[M + H]^+$ 495.1343, found: 495.1349.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.387	BB	0.5070	4203.60840	121.93268	51.1749
2	18.448	BB	0.7778	4010.58350	77.21700	48.8251

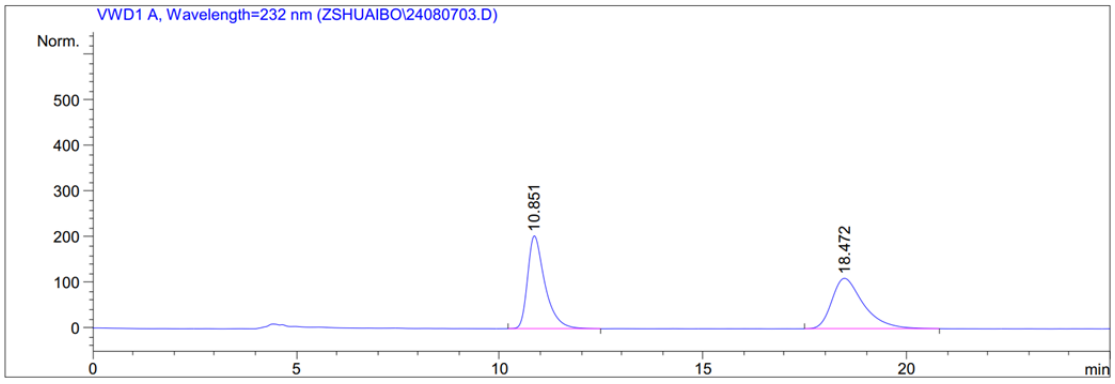


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.339	BB	0.4964	4130.44238	123.05630	94.7747
2	18.336	MM	0.7708	227.72845	4.92394	5.2253

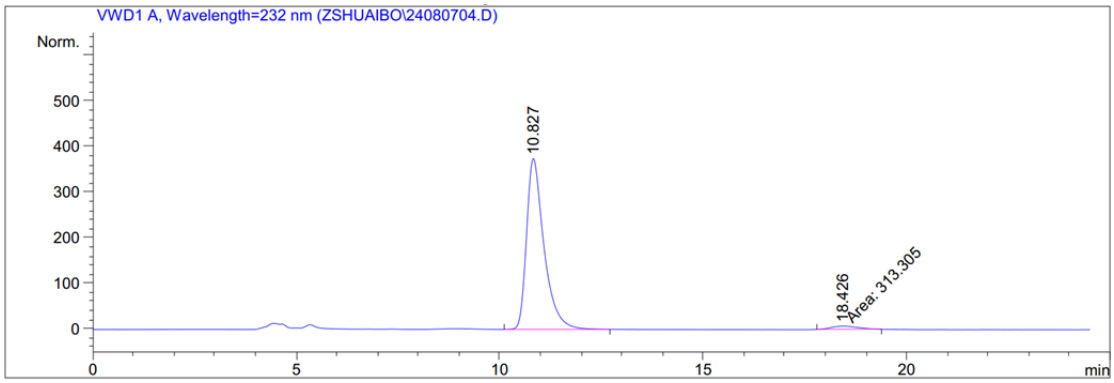


(*R*,*E*)-(1-(5-Chloro-2-methoxyphenyl)-4,4,4-trifluorobut-2-en-1-yl)bis(4-methoxyphenyl)phosphine oxide (3q)

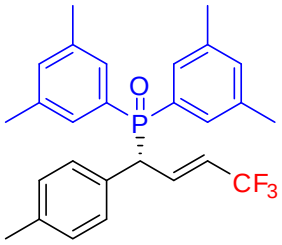
Method A, Purified by Biotage flash chromatography with (PE/EtOAc 1:1), white solid, mp 95 – 96 °C, 75.5 mg, 74% yield, 95% ee, $[\alpha]^{20}_{D}$ = + 32.94 (*c* 0.17, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.68 (m, 3H), 7.52 – 7.42 (m, 2H), 7.15 – 7.08 (m, 1H), 7.06 – 6.97 (m, 2H), 6.83 – 6.76 (m, 2H), 6.71 – 6.55 (m, 2H), 5.61 – 5.47 (m, 1H), 4.94 – 4.85 (m, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 2.9 Hz), 162.3 (d, *J* = 2.9 Hz), 154.7 (d, *J* = 5.9 Hz), 135.4 - 135.1 (m), 133.3 (d, *J* = 10.1 Hz), 132.8 (d, *J* = 10.4 Hz), 129.9 (d, *J* = 4.6 Hz), 128.5 (d, *J* = 2.4 Hz), 126.0 (d, *J* = 2.6 Hz), 124.5 (d, *J* = 5.6 Hz), 122.8 (d, *J* = 25.1 Hz), 122.4 (qd, *J* =270.9, 1.9Hz), 122.2 (qd, *J* = 33.9, 10.2 Hz), 121.7 (d, *J* = 22.6 Hz), 114.2 (d, *J* = 12.7 Hz), 113.7 (d, *J* = 12.9 Hz), 111.6 (d, *J* = 1.7 Hz), 55.7, 55.4, 55.3, 41.6 (d, *J* = 64.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.06 – -64.13 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 31.5. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 10.83 min, t_{minor} = 18.43 min. HRMS (ESI) m/z: calcd for $C_{25}H_{24}ClF_3O_4P$ $[M + H]^+$ 511.1047, found: 511.1046.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.851	BB	0.4408	6046.58154	203.76251	50.2354
2	18.472	BB	0.8102	5989.90723	110.72572	49.7646

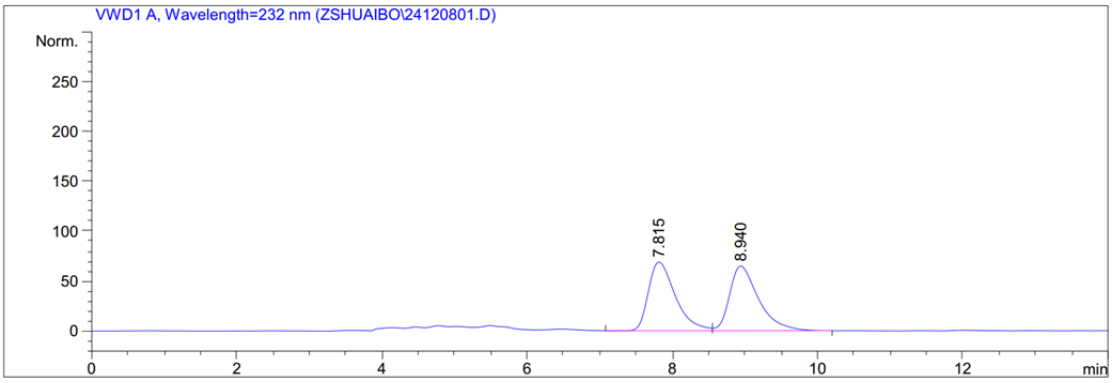


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.827	VB	0.4426	1.11796e4	374.84293	97.2739
2	18.426	MM	0.7551	313.30493	6.91517	2.7261

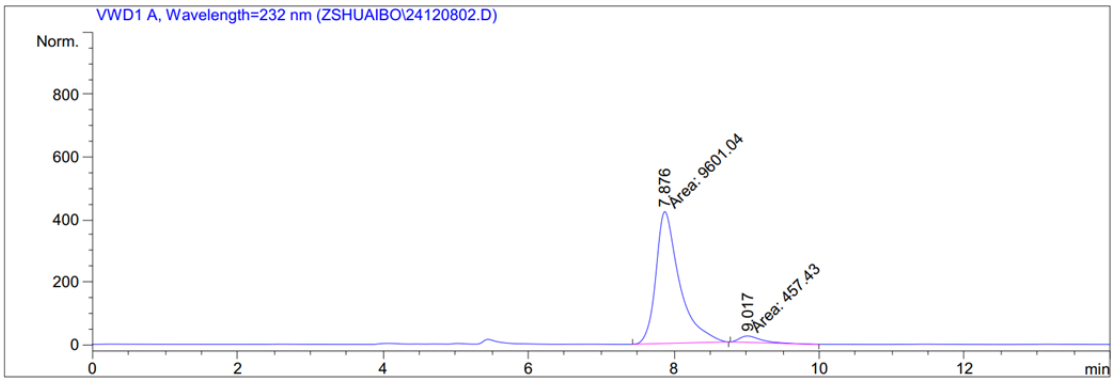


(*R*,*E*)-Bis(3,5-dimethylphenyl)(4,4,4-trifluoro-1-(*p*-tolyl)but-2-en-1-yl)phosphine oxide (3r)

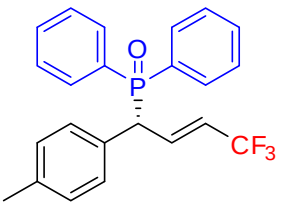
Method A, Purified by Biotage flash chromatography with (PE/EtOAc 5:1), white solid, mp 248 – 249 °C, 59.3 mg, 65% yield, 91% ee, $[\alpha]^{20}_{D}$ = + 12.00 (*c* 0.12, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 11.3 Hz, 2H), 7.21 – 7.10 (m, 5H), 7.09 – 7.00 (m, 3H), 6.77 – 6.64 (m, 1H), 5.52 – 5.39 (m, 1H), 4.23 – 4.14 (m, 1H), 2.35 (s, 6H), 2.28 (s, 3H), 2.23 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3 (d, *J* = 12.3 Hz), 137.9 (d, *J* = 12.5 Hz), 137.4 (d, *J* = 2.4 Hz), 136.3 – 135.9 (m), 133.8 (d, *J* = 2.9 Hz), 133.5 (d, *J* = 3.0 Hz), 131.0 (d, *J* = 14.4 Hz), 130.8 (d, *J* = 5.8 Hz), 130.0 (d, *J* = 12.3 Hz), 129.5 (d, *J* = 5.9 Hz), 129.4 (d, *J* = 2.1 Hz), 129.2 (d, *J* = 8.6 Hz), 129.0 (d, *J* = 8.8 Hz), 122.5 (qd, *J* = 269.8, 1.9 Hz), 121.7 (qd, *J* = 33.9, 10.3 Hz), 50.7 (d, *J* = 63.0 Hz), 21.3, 21.2, 21.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.09 – -64.21 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 31.26. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 8/2, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 7.88 min, t_{minor} = 9.02 min. HRMS (ESI) m/z: calcd for $C_{27}H_{29}F_3OP$ $[M + H]^+$ 457.1903, found: 457.1906.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.815	VV	0.3973	1794.01904	69.16217	49.7757
2	8.940	VB	0.4175	1810.18567	65.12454	50.2243



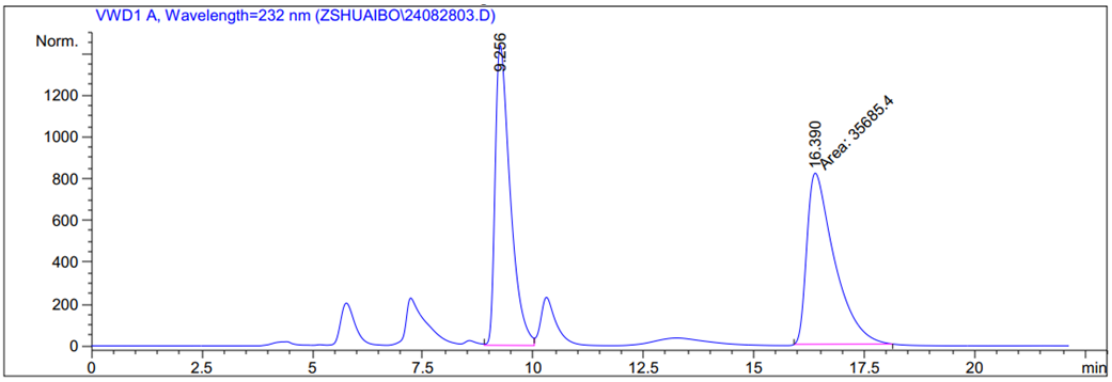
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.876	MM	0.3782	9601.03809	423.12445	95.4523
2	9.017	MM	0.3646	457.42996	20.91112	4.5477



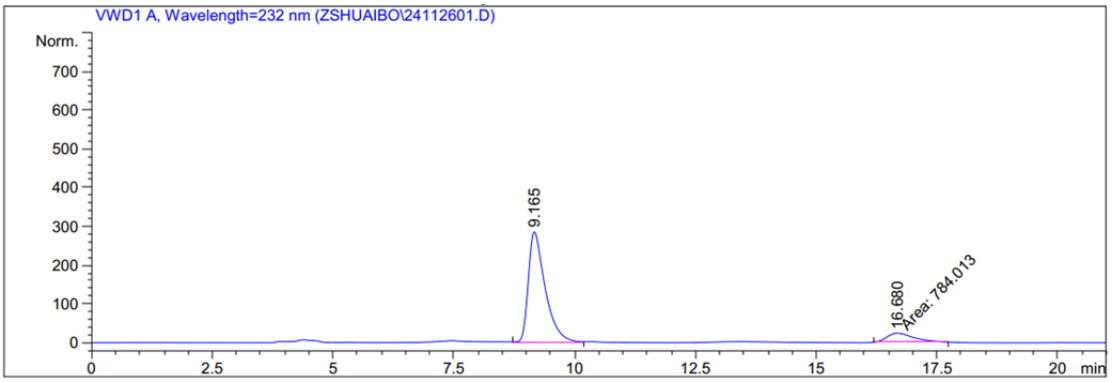
(*R*,*E*)-Diphenyl(4,4,4-trifluoro-1-(*p*-tolyl)but-2-en-1-yl)phosphine oxide (3s)

Method B, Purified by Biotage flash chromatography with (PE/EtOAc 2:1), white solid, mp 215 – 216 °C, 59.2 mg, 74% yield, 80% ee, $[\alpha]^{20}_{D}$ = + 13.57 (*c* 0.14, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.62 – 7.46 (m, 5H), 7.45 – 7.37 (m, 1H), 7.37 – 7.28 (m, 2H), 7.22 – 7.15 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.78 – 6.65 (m, 1H), 5.58 – 5.44 (m, 1H), 4.30 – 4.20 (m, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5 (d, *J* = 2.3 Hz), 136.0 – 135.5 (m), 132.2

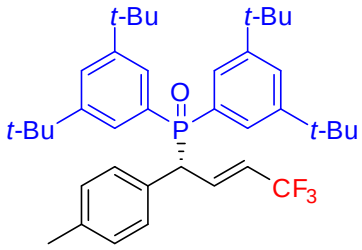
(d, J = 2.9 Hz), 131.9 (d, J = 2.8 Hz), 131.5 (d, J = 8.6 Hz), 131.3 (d, J = 20.5 Hz), 131.3 (d, J = 8.8 Hz), 130.4 (d, J = 2.3 Hz), 130.3 (d, J = 14.6 Hz), 129.6 (d, J = 1.7 Hz), 129.4 (d, J = 5.6 Hz), 128.7 (d, J = 11.7 Hz), 128.4 (d, J = 11.9 Hz), 122.4 (dd, J = 269.9, 2.0 Hz), 122.1 (qd, J = 33.8, 10.3 Hz), 50.6 (d, J = 63.8 Hz), 21.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.19 – -64.29 (m). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 30.37. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 9/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 9.17 min, t_{minor} = 16.68 min. HRMS (ESI) m/z: calcd for $C_{23}H_{21}F_3OP$ $[M + H]^+$ 401.1277, found: 401.1277.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.256	VV	0.3566	3.42465e4	1437.32837	48.9712
2	16.390	MM	0.7255	3.56854e4	819.82623	51.0288

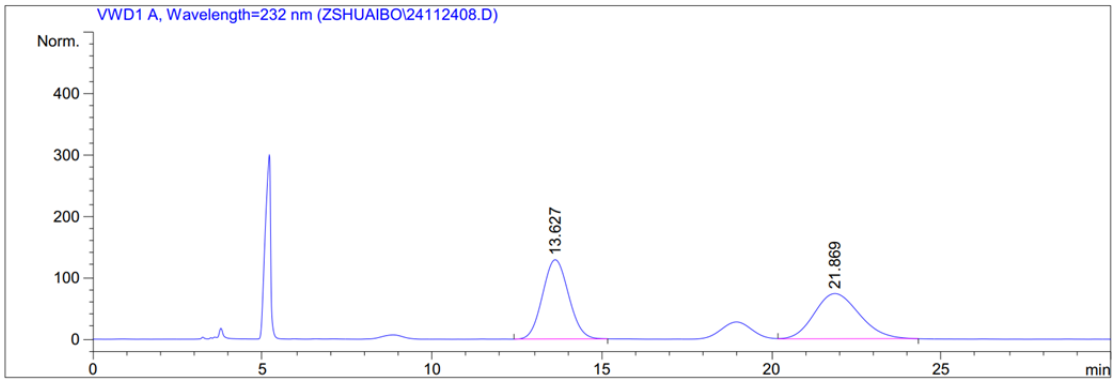


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.165	VV	0.3597	6938.67822	285.01038	89.8479
2	16.680	MM	0.5963	784.01282	21.91225	10.1521

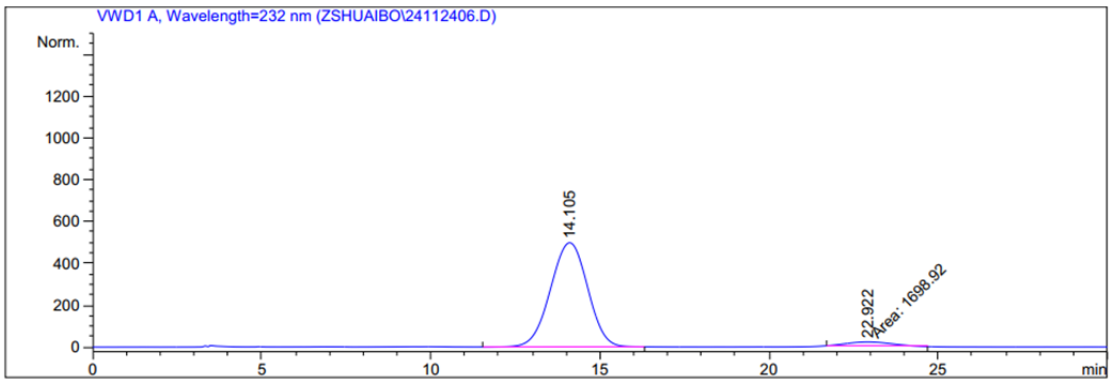


(*R*,*E*)-Bis(3,5-di-tert-butylphenyl)(4,4,4-trifluoro-1-(*p*-tolyl)but-2-en-1-yl)phosphine oxide (3t)

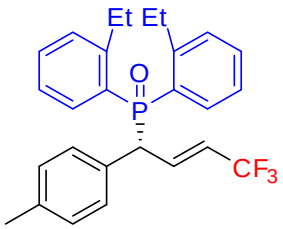
Method B, Purified by Biotage flash chromatography with (PE/EtOAc 5:1), white solid, mp 169 – 170 °C, 74.9 mg, 60% yield, 92% ee, $[\alpha]^{20}_{D}$ = + 30.42 (*c* 0.24, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 3H), 7.50 – 7.46 (m, 1H), 7.36 – 7.30 (m, 2H), 7.09 – 7.01 (m, 4H), 6.82 – 6.72 (m, 1H), 5.56 – 5.45 (m, 1H), 4.17 – 4.08 (m, 1H), 2.28 (s, 3H), 1.32 (s, 18H), 1.21 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0 (d, *J* = 11.3 Hz), 150.6 (d, *J* = 11.6 Hz), 137.3 (d, *J* = 2.3 Hz), 136.6 – 136.2 (m), 131.2 (d, *J* = 5.7 Hz), 130.1 (d, *J* = 98.5 Hz), 129.4 (d, *J* = 5.1 Hz), 129.4 (d, *J* = 1.9 Hz), 129.1 (d, *J* = 96.9 Hz), 126.2 (d, *J* = 2.8 Hz), 126.1 (d, *J* = 9.1 Hz), 126.0 (d, *J* = 2.8 Hz), 125.8 (d, *J* = 9.7 Hz), 122.5 (dd, *J* = 269.7, 1.8 Hz), 121.3 (qd, *J* = 33.9, 10.2 Hz), 52.1 (d, *J* = 62.0 Hz), 35.1, 34.9, 31.3, 31.2, 21.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.96 – -64.02 (m). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ 32.42. HPLC analysis: Daicel CHIRALPAK IG, *n*-hexane/*i*-PrOH= 50/1, flow rate = 1.0 mL/min, λ = 232 nm, retention time: t_{major} = 14.11 min, t_{minor} = 22.92 min. HRMS (ESI) m/z: calcd for $C_{39}H_{53}F_3OP$ $[M + H]^+$ 647.3600, found: 647.3604.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.627	BB	0.8388	6906.06885	129.27138	50.2738
2	21.869	VB	1.3756	6830.83984	73.88575	49.7262

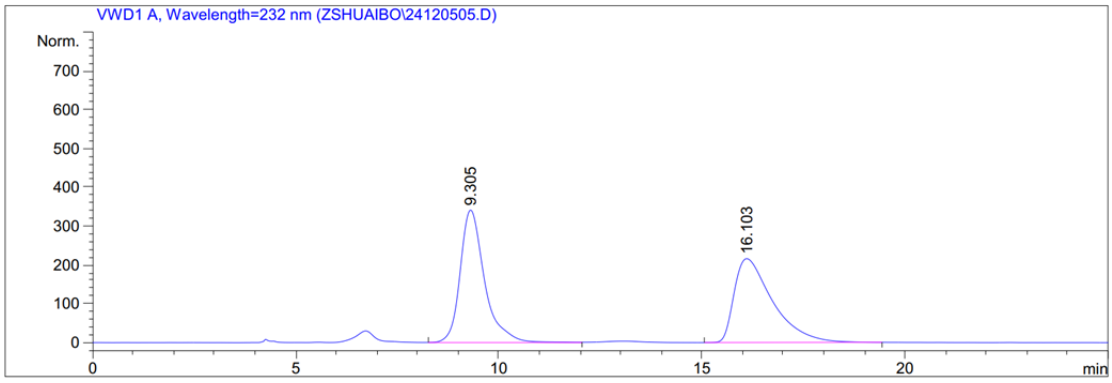


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.105	BB	1.2191	3.81975e4	498.23587	95.7417
2	22.922	MM	1.4730	1698.91541	19.22249	4.2583

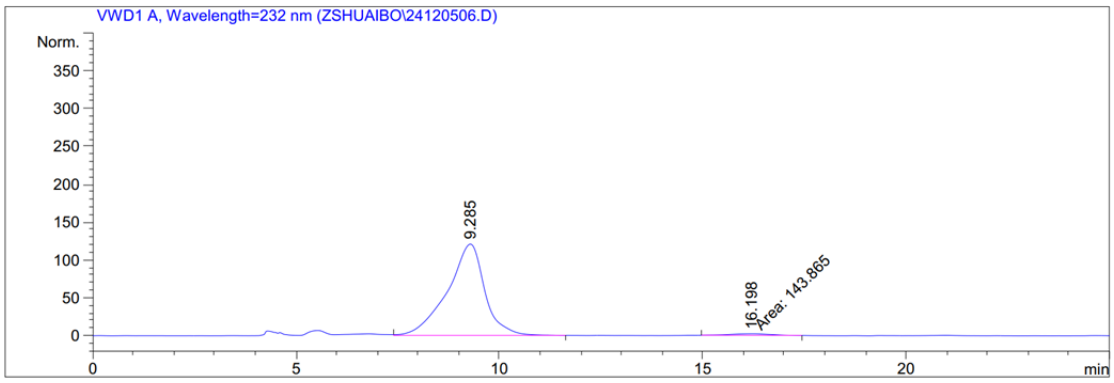


(*R*,*E*)-Bis(2-ethylphenyl)(4,4,4-trifluoro-1-(*p*-tolyl)but-2-en-1-yl)phosphine oxide (3u)

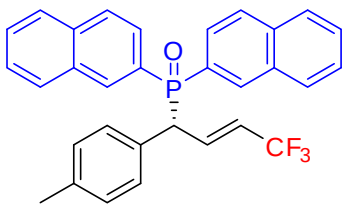
Method B, Purified by Biotage flash chromatography with (PE/EtOAc 5:1), white solid, mp 157 – 158 °C, 54.7 mg, 60% yield, 96% ee, $[\alpha]^{20}_{D}$ = + 12.00 (*c* 0.20, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 1H), 7.48 – 7.43 (m, 1H), 7.42 – 7.37 (m, 1H), 7.34 – 7.22 (m, 5H), 7.16 – 7.12 (m, 1H), 7.08 – 7.02 (m, 3H), 6.85 – 6.76 (m, 1H), 5.66 – 5.58 (m, 1H), 4.40 – 4.33 (m, 1H), 3.06 – 2.95 (m, 1H), 2.88 – 2.73 (m, 2H), 2.67 – 2.56 (m, 1H), 2.27 (s, 3H), 1.01 (t, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5 (d, *J* = 7.9 Hz), 149.3 (d, *J* = 8.0 Hz), 137.4 (d, *J* = 1.8 Hz), 136.7 (p, *J* = 6.5 Hz), 132.0 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 2.7 Hz), 131.58 (d, *J* = 4.4 Hz), 131.56 (d, *J* = 5.7 Hz), 131.4 (d, *J* = 5.3 Hz), 131.0 (d, *J* = 30.3 Hz), 130.7 (d, *J* = 10.5 Hz), 130.2 (d, *J* = 33.2 Hz), 130.2 (d, *J* = 10.7 Hz), 129.6 (d, *J* = 5.8 Hz), 129.5 (d, *J* = 1.4 Hz), 125.4 (d, *J* = 12.1 Hz), 125.0 (d, *J* = 12.3 Hz), 122.5 (qd, *J* = 270.4, 1.2 Hz), 121.9 (qd, *J* = 33.8, 10.2 Hz), 49.6 (d, *J* = 65.0 Hz), 27.2 (d, *J* = 3.7 Hz), 26.7 (d, *J* = 4.1 Hz), 21.0, 15.5, 15.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.25 – -64.35 (m). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 35.09. HPLC analysis: Daicel CHIRALPAK OD-H, *n*-hexane/*i*-PrOH= 50/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 9.29 min, t_{minor} = 16.20 min. HRMS (ESI) m/z: calcd for $C_{27}H_{29}F_3OP$ $[M + H]^+$ 457.1903, found: 457.1906.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.305	BB	0.6315	1.43006e4	341.31259	50.1253
2	16.103	PB	0.9837	1.42291e4	216.09071	49.8747



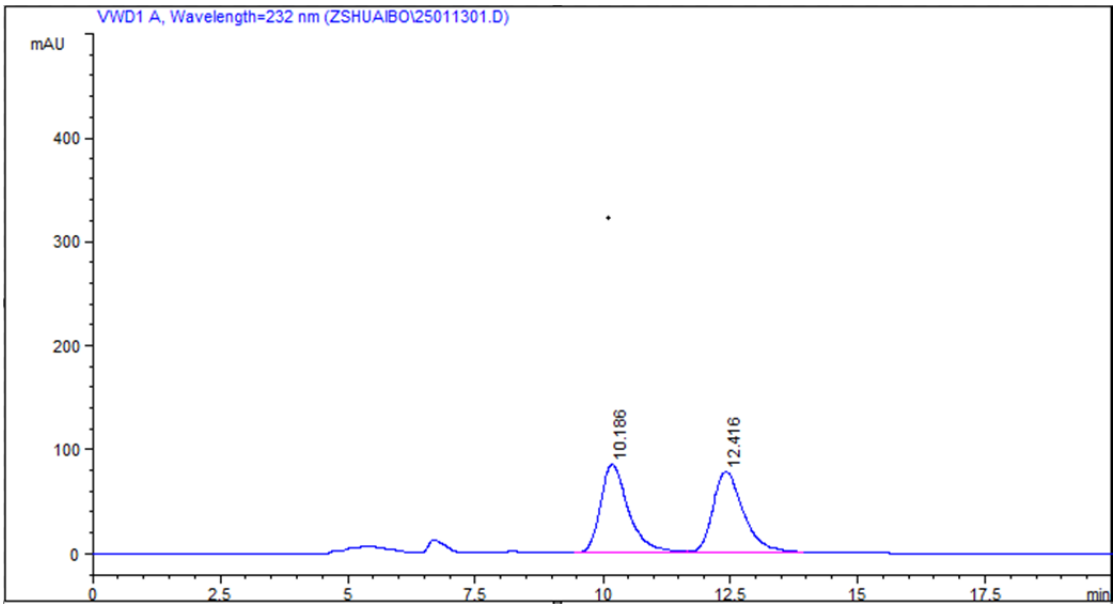
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.285	VB	0.9145	7725.52100	120.88171	98.1718
2	16.198	MM	1.1123	143.86501	2.15571	1.8282



(*R*,*E*)-Di(naphthalen-2-yl)(4,4,4-trifluoro-1-(*p*-tolyl)but-2-en-1-yl)phosphine oxide (3v)

Method B, Purified by Biotage flash chromatography with (PE/EtOAc 3:1), white solid, mp 188 – 189 °C, 60.0 mg, 60% yield, 89% ee, $[\alpha]^{20}_{D}$ = + 45.56 (*c* 0.18, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 12.9, 1.5 Hz, 1H), 8.21 (dd, *J* = 13.2, 1.4 Hz, 1H), 7.99 – 7.91 (m, 2H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.83 – 7.73 (m, 4H), 7.65 – 7.51 (m, 4H), 7.52 – 7.45 (m, 1H), 7.29 – 7.25 (m, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.91 – 6.76 (m, 1H), 5.62 – 5.50 (m, 1H), 4.51 – 4.43 (m,

1H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6 (d, *J* = 2.3 Hz), 135.0 – 134.5 (m), 133.7 (d, *J* = 2.5 Hz), 133.5 (d, *J* = 2.4 Hz), 133.2 (d, *J* = 7.7 Hz), 132.8 (d, *J* = 8.0 Hz), 131.5 (d, *J* = 12.6 Hz), 131.3 (d, *J* = 12.9 Hz), 129.4 (d, *J* = 6.0 Hz), 128.6 (d, *J* = 1.7 Hz), 128.4 (d, *J* = 5.8 Hz), 127.9 (d, *J* = 10.9 Hz), 127.6, 127.5, 127.4 (d, *J* = 5.2 Hz), 127.2, 127.1 (d, *J* = 11.7 Hz), 126.8 (d, *J* = 11.5 Hz), 126.6, 126.4, 126.1, 125.9, 125.8, 124.8 (d, *J* = 4.5 Hz), 124.7 (d, *J* = 4.5 Hz), 121.4 (dd, *J* = 269.9, 1.8 Hz), 121.1 (qd, *J* = 34.0, 10.3 Hz), 49.5 (d, *J* = 64.1 Hz), 20.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.12 – -64.18 (m). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 30.70. HPLC analysis: Daicel CHIRALPAK OD-H, *n*-hexane/*i*-PrOH= 8/2, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 9.95 min, t_{minor} = 12.21 min. HRMS (ESI) m/z: calcd for $C_{31}H_{25}F_3OP$ $[M + H]^+$ 501.1590, found: 501.1586.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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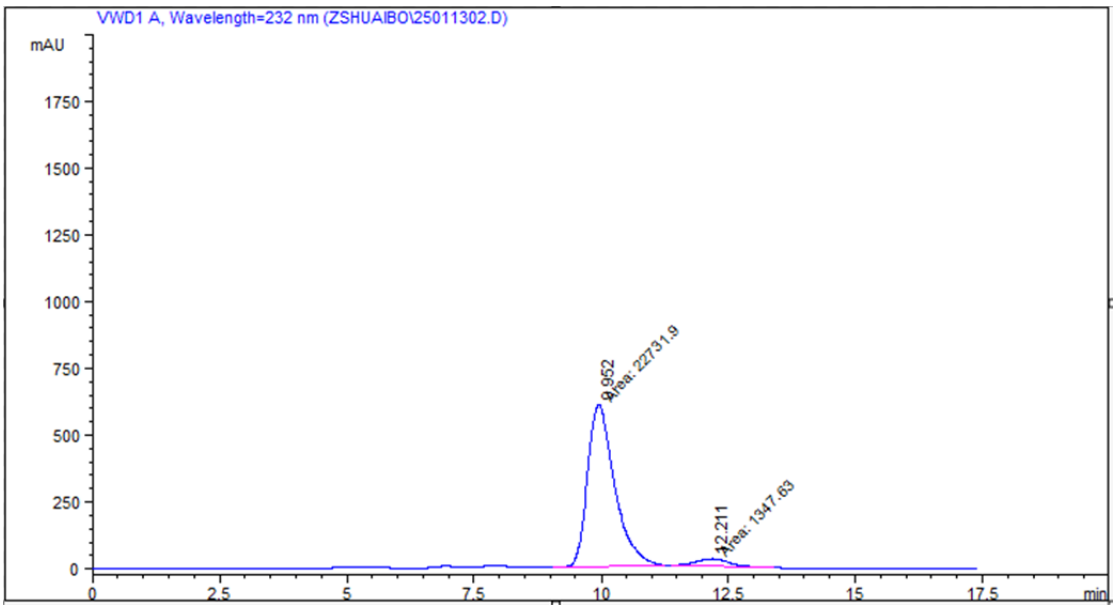
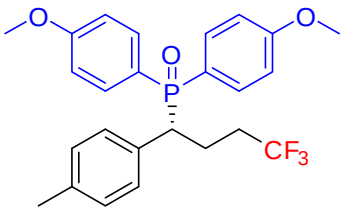
2	12.416	BB	0.6317	3229.67139	77.74278	49.7897

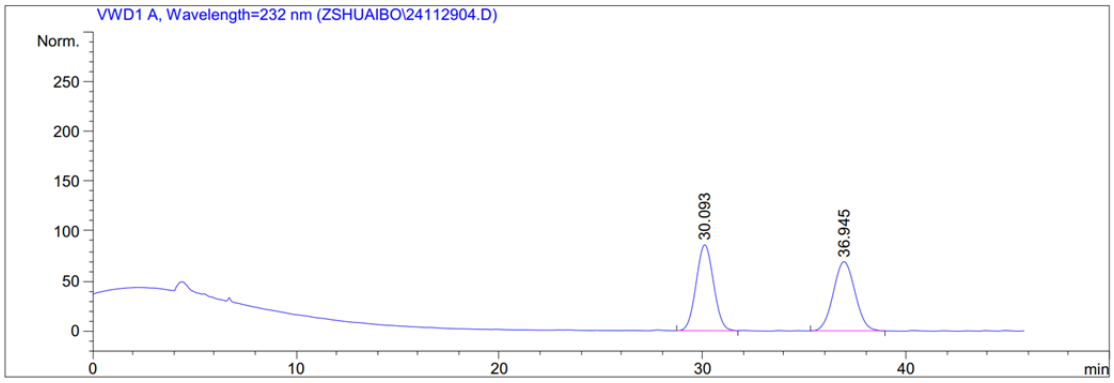


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.952	MM	0.6244	2.27319e4	606.72357	94.4034
2	12.211	MM	0.7813	1347.62537	28.74813	5.5966



(*R*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(*p*-tolyl)butyl)phosphine oxide (4a)

Purified by Biotage flash chromatography with (PE/EtOAc 1:2), white solid, mp 197 – 198 °C, 96.6 mg, 95% yield, 96% ee, $[\alpha]^{20}_{D}$ = + 111.18 (*c* 0.17, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.35 – 7.28 (m, 2H), 7.10 – 7.05 (m, 2H), 7.05 – 6.99 (m, 4H), 6.77 – 6.72 (m, 2H), 3.85 (s, 3H), 3.73 (s, 3H), 3.41 – 3.32 (m, 1H), 2.35 – 2.24 (m, 4H), 2.20 – 2.10 (m, 1H), 2.03 – 1.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 2.9 Hz), 162.0 (d, *J* = 2.9 Hz), 137.0 (d, *J* = 2.7 Hz), 133.0 (d, *J* = 8.4 Hz), 133.0 (d, *J* = 8.9 Hz), 131.5 (d, *J* = 5.5 Hz), 129.6 (d, *J* = 5.5 Hz), 129.3 (d, *J* = 2.0 Hz), 127.0 (q, *J* = 276.6 Hz), 123.3 (d, *J* = 55.8 Hz), 122.3 (d, *J* = 50.9 Hz), 114.4 (d, *J* = 12.1 Hz), 113.6 (d, *J* = 12.7 Hz), 55.3, 55.2, 45.7 (d, *J* = 68.9 Hz), 31.6 (qd, *J* = 28.7, 13.5 Hz), 22.1 (q, *J* = 3.2 Hz), 21.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.67 (t, *J* = 10.8 Hz). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ 32.34. HPLC analysis: Daicel CHIRALPAK IE, *n*-hexane/*i*-PrOH= 1/1, flow rate = 0.8 mL/min, λ = 232 nm, retention time: t_{major} = 37.50 min, t_{minor} = 30.38 min. HRMS (ESI) m/z: calcd for $C_{25}H_{27}F_3O_3P$ $[M + H]^+$ 463.1644, found: 463.1639.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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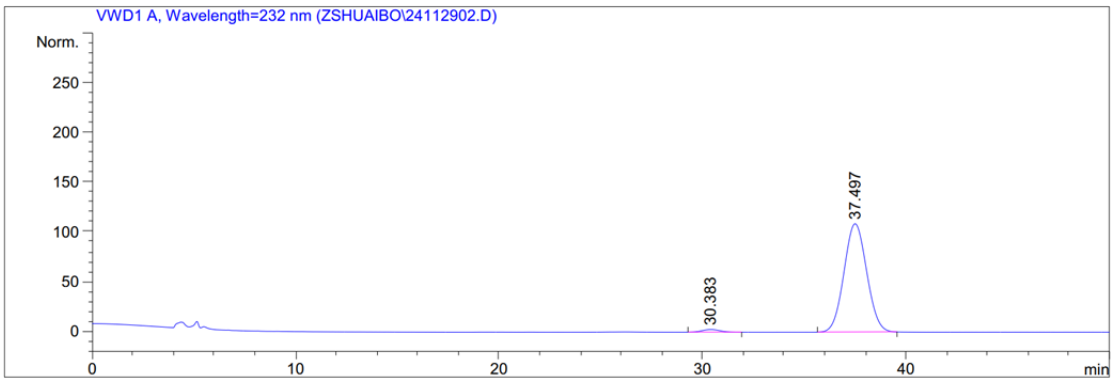
2	36.945	BB	1.1457	5165.95361	69.46948	50.0877



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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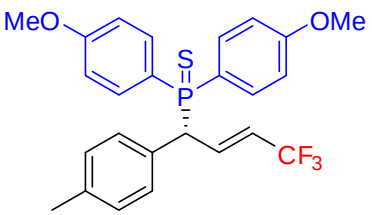
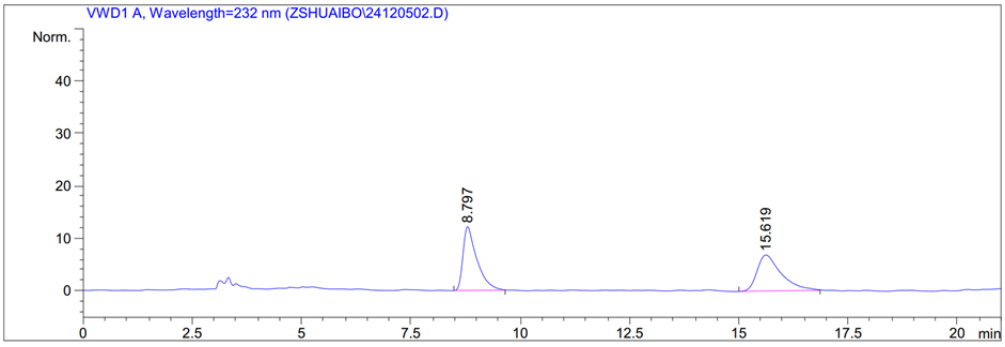
2	37.497	BB	1.1953	8476.98340	109.03558	98.0870



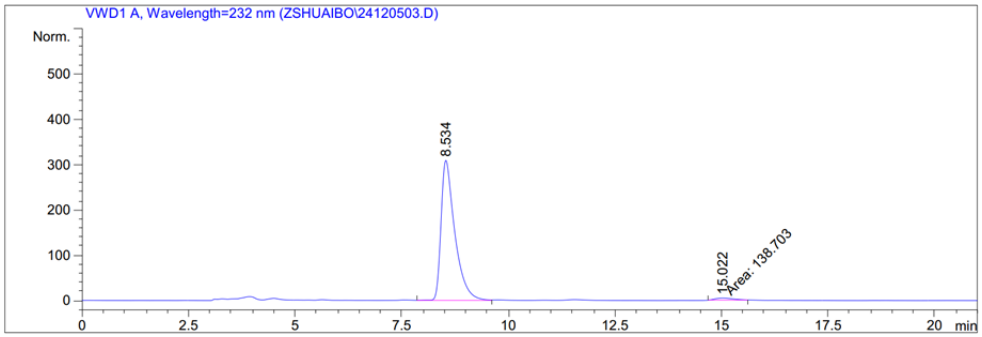
(*R*,*E*)-Bis(4-methoxyphenyl)(4,4,4-trifluoro-1-(*p*-tolyl)but-2-en-1-yl)phosphine sulfide (5a)

Purified by Biotage flash chromatography with (PE/EtOAc 5:1), colorless oil, 83.8 mg, 80% yield, 96% ee, $[\alpha]^{20}_{D}$ = + 58.33 (*c* 0.3, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 2H), 7.48 – 7.38 (m, 2H), 7.09 – 7.02 (m, 2H), 6.98 – 6.90 (m, 4H), 6.78 – 6.68 (m, 3H), 5.45 – 5.34 (m, 1H), 4.39 (t, *J* = 10.5 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, *J* = 2.9 Hz), 161.1 (d, *J* = 3.0 Hz), 136.7 (d, *J* = 3.1 Hz), 135.2 (qd, *J* = 6.8, 3.1

Hz), 133.1 (d, J = 10.7 Hz), 132.6 (d, J = 11.0 Hz), 129.6 (d, J = 5.3 Hz), 128.4 (d, J = 5.4 Hz), 128.0 (d, J = 2.3 Hz), 121.4 (qd, J = 270.0, 1.9 Hz), 121.1 (d, J = 72.4 Hz), 120.7 (qd, J = 34.2, 11.8 Hz), 120.2 (d, J = 70.1 Hz), 113.0 (d, J = 13.1 Hz), 112.7 (d, J = 13.3 Hz), 54.4, 54.3, 50.7 (d, J = 49.2 Hz), 20.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -64.10 – -64.18 (m). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 46.35. HPLC analysis: Daicel CHIRALPAK AD-H, *n*-hexane/*i*-PrOH= 8/2, flow rate = 1.0 mL/min, λ = 232 nm, retention time: t_{major} = 8.53 min, t_{minor} = 15.02 min. HRMS (ESI) m/z: calcd for $C_{25}H_{25}F_3O_2PS$ $[M + H]^+$ 477.1259, found: 477.1264.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.797	PB	0.3135	269.18704	12.16371	50.5143
2	15.619	BB	0.5521	263.70587	6.87930	49.4857



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.534	VV	0.3289	6932.85449	308.81546	98.0386
2	15.022	MM	0.5012	138.70308	4.61265	1.9614

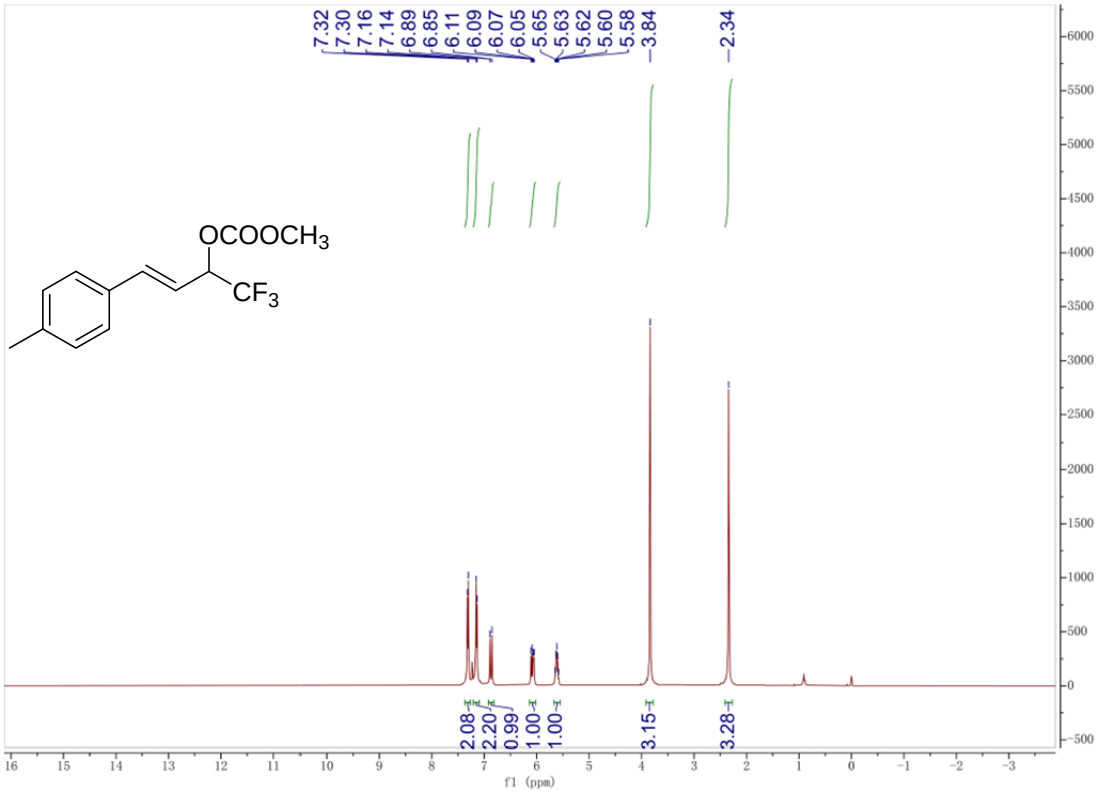
7. References

1. G. K. S. Prakash, R. Krishnamurti and G. A. Olah, *J. Am. Chem. Soc.*, 2002, **111**, 393-395.

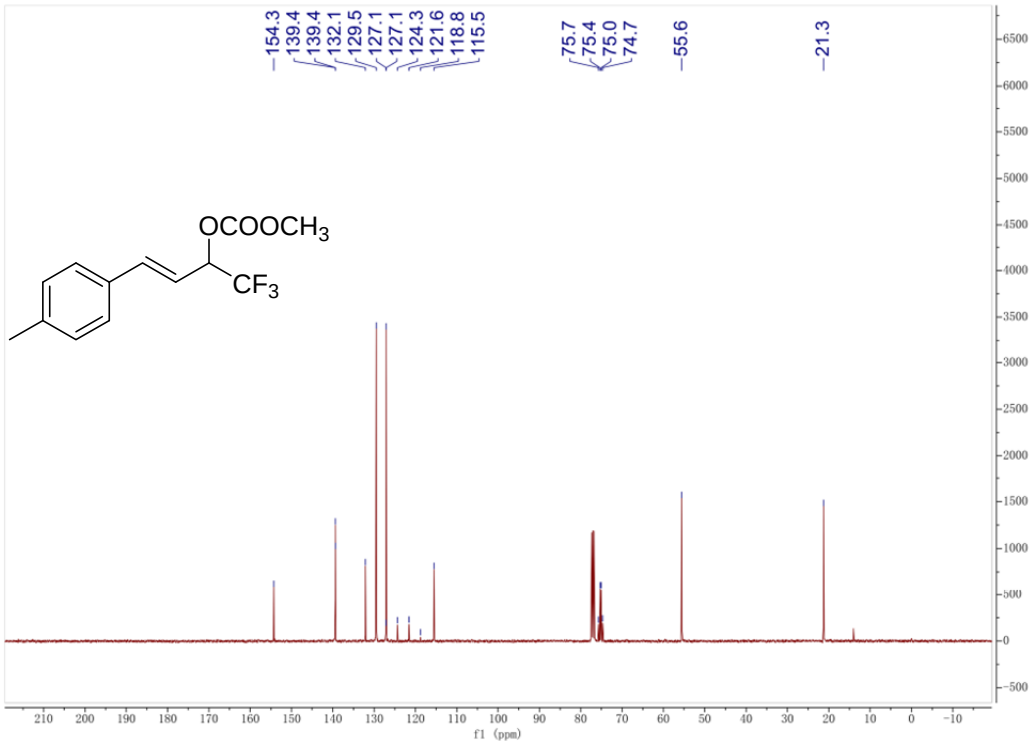
2. M. Zhou, J. Zhang, X.-G. Zhang and X. Zhang, *Org. Lett.*, 2019, **21**, 671-674.

8. Copy of NMR spectra for the products

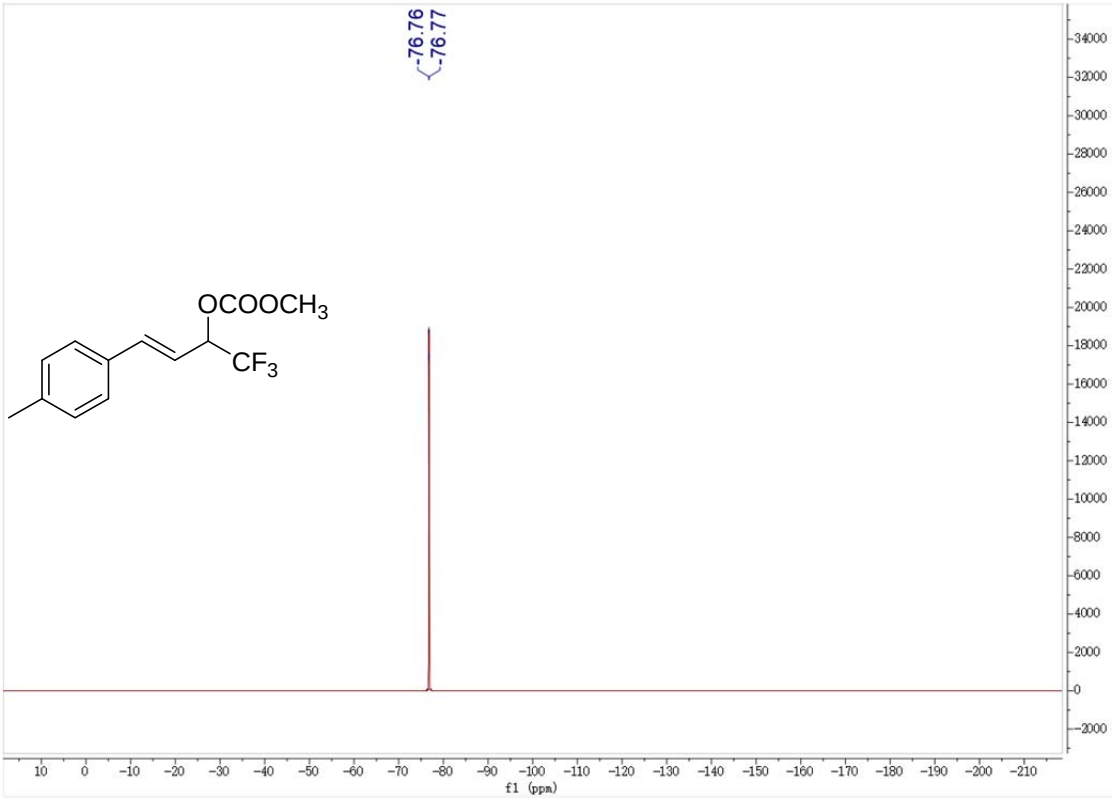
^{1}H NMR (400 MHz, $CDCl_3$) (1a)



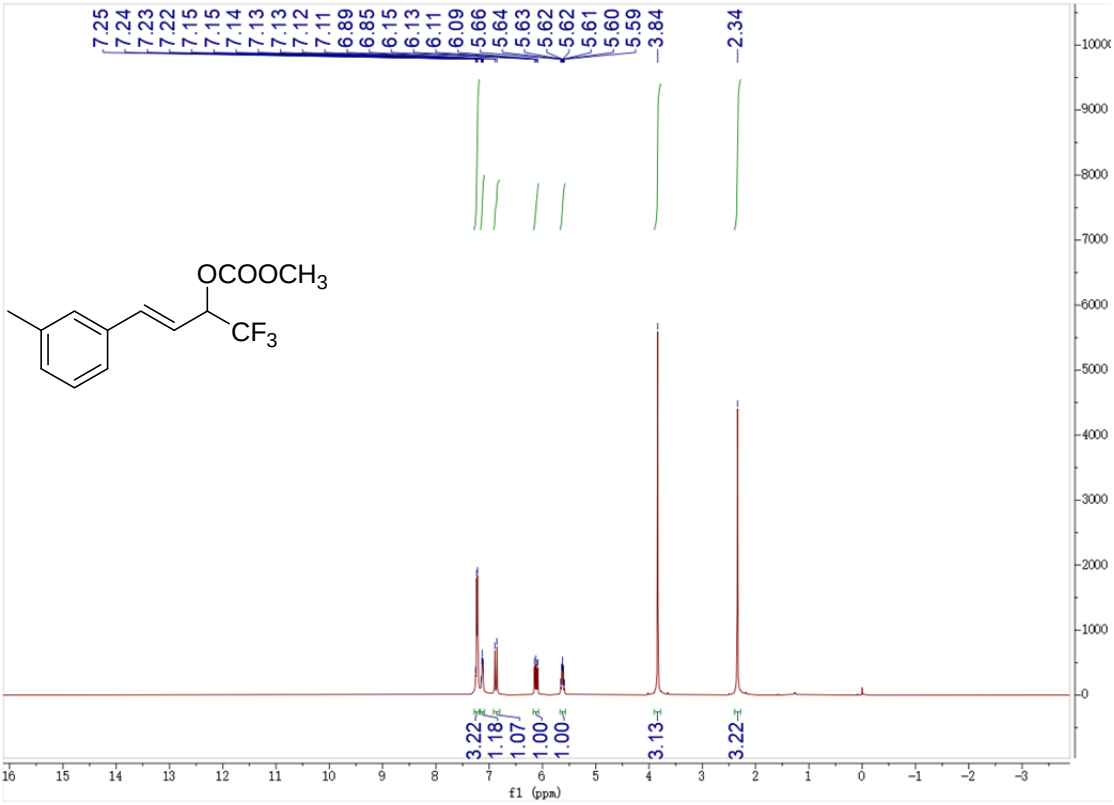
^{13}C NMR (101 MHz, $CDCl_3$) (1a)



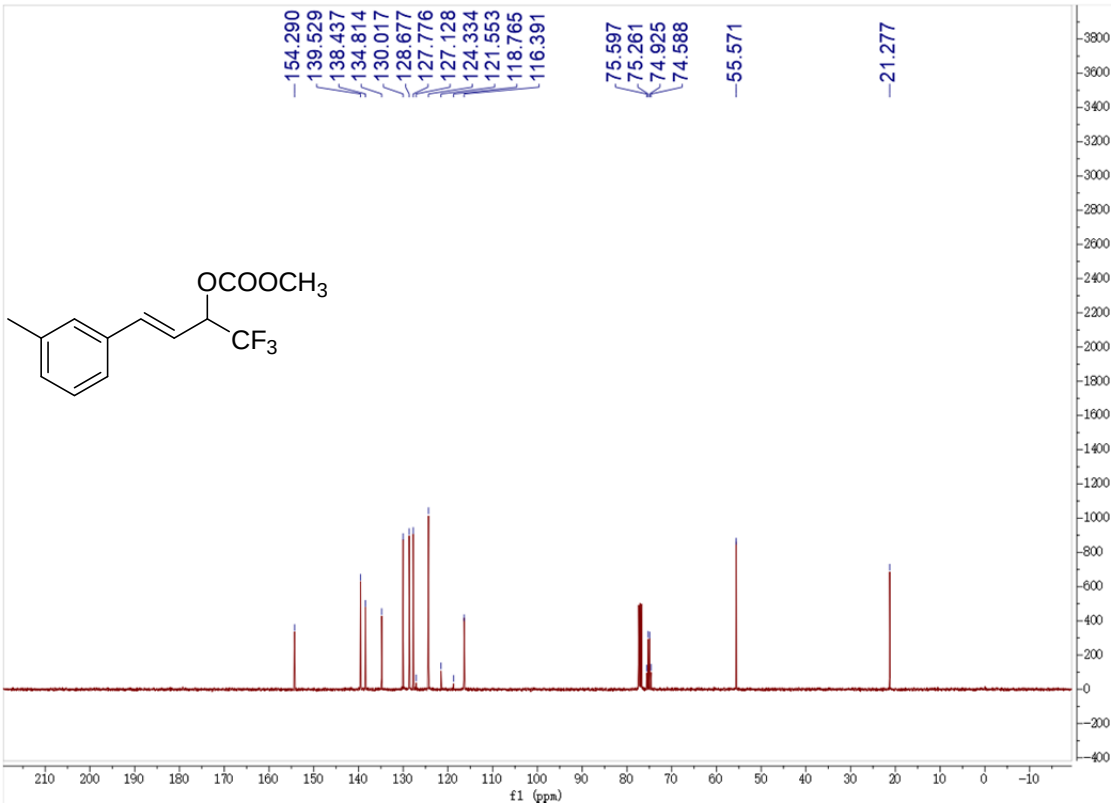
^{19}F NMR (377 MHz, $CDCl_3$) (1a)



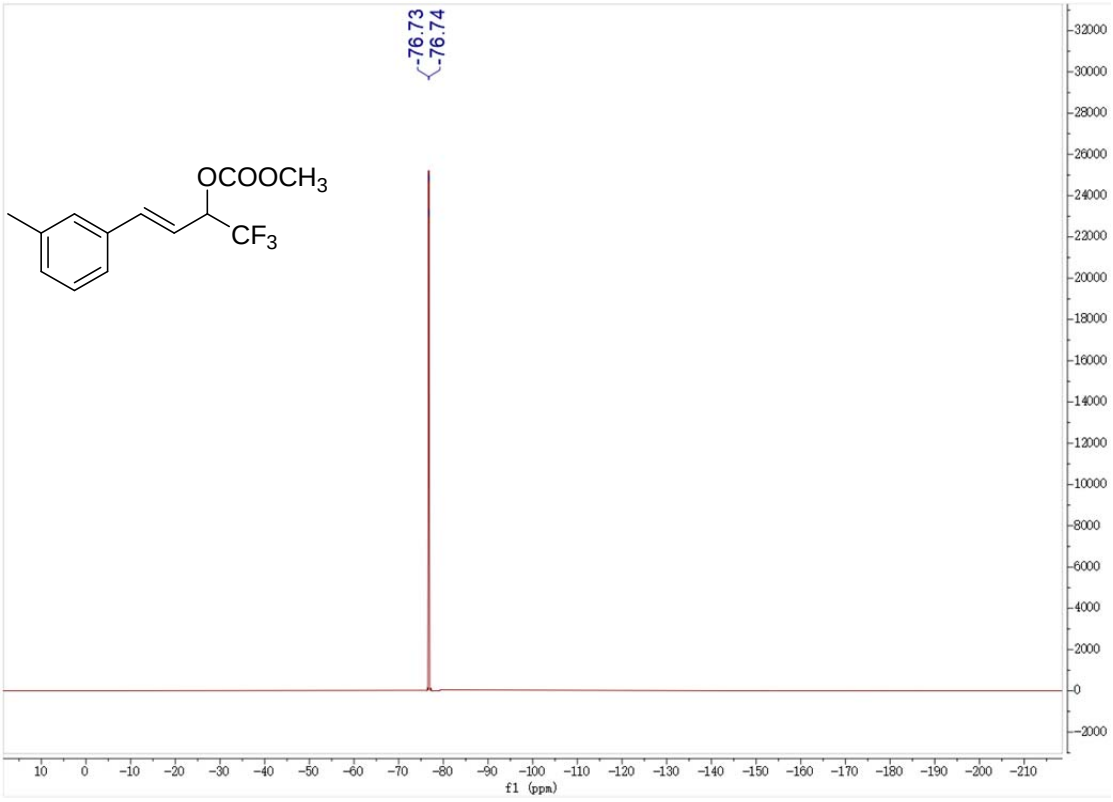
^{1}H NMR (400 MHz, $CDCl_3$) (1b)



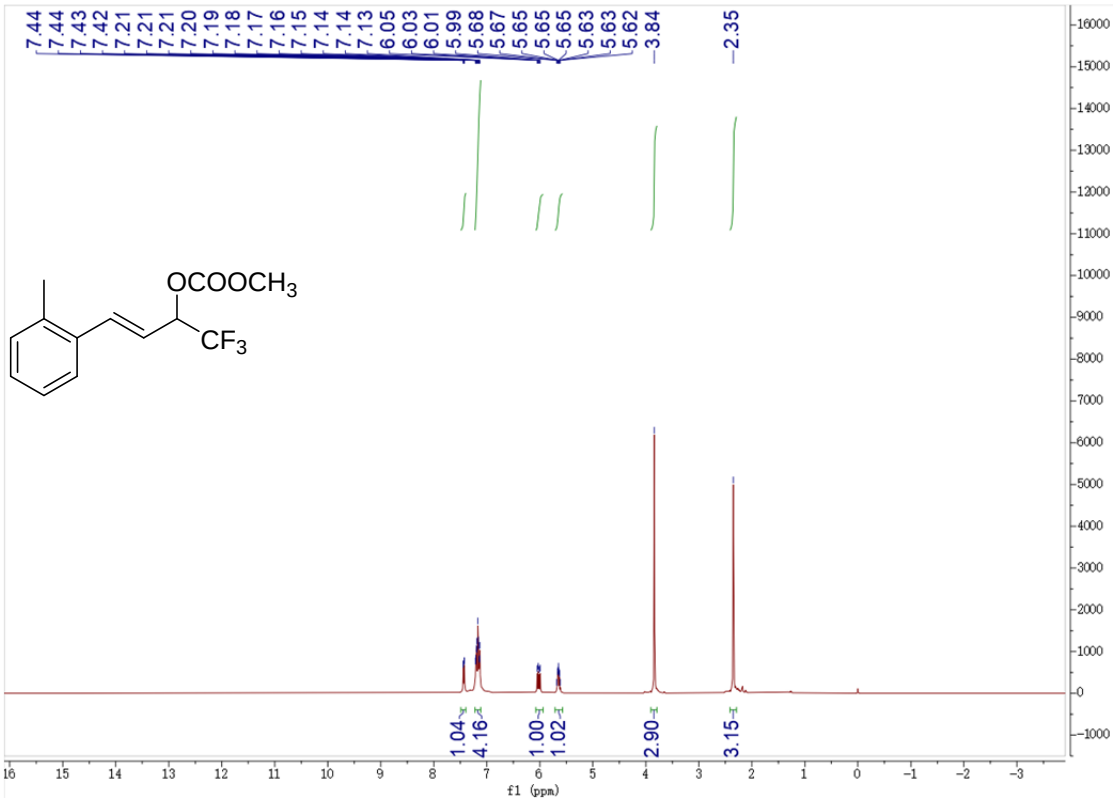
^{13}C NMR (101 MHz, $CDCl_3$) (1b)



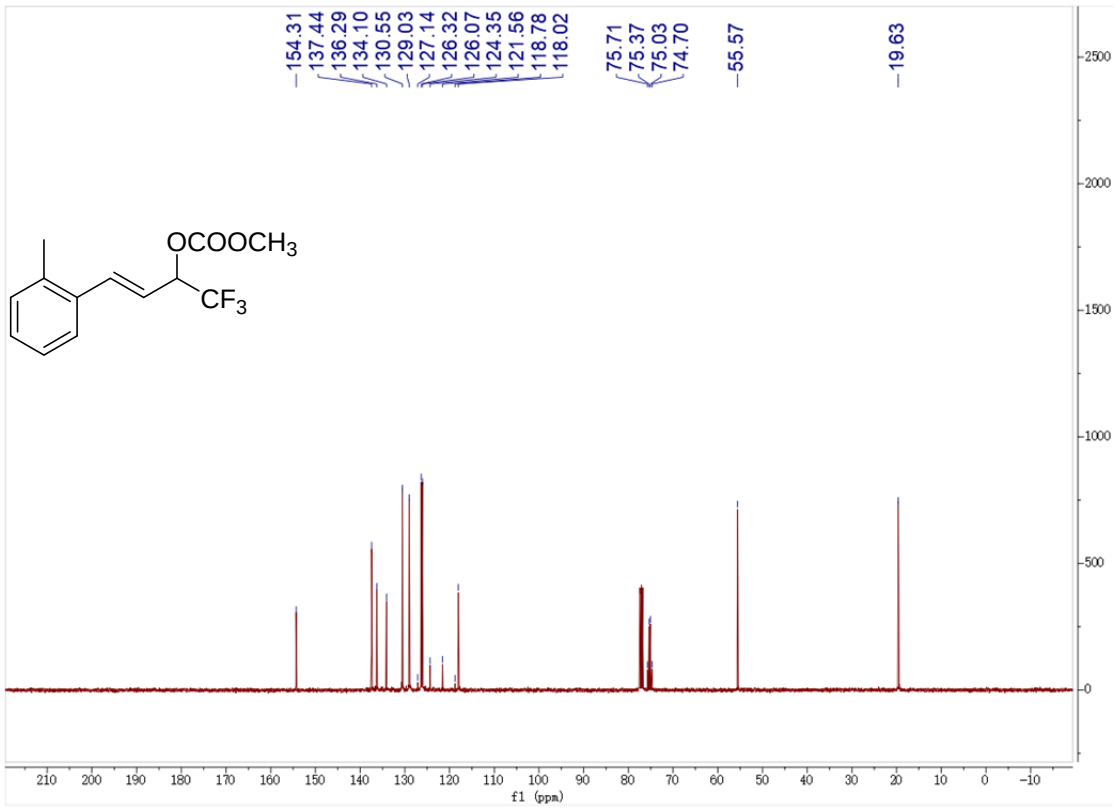
^{19}F NMR (377 MHz, $CDCl_3$) (1b)



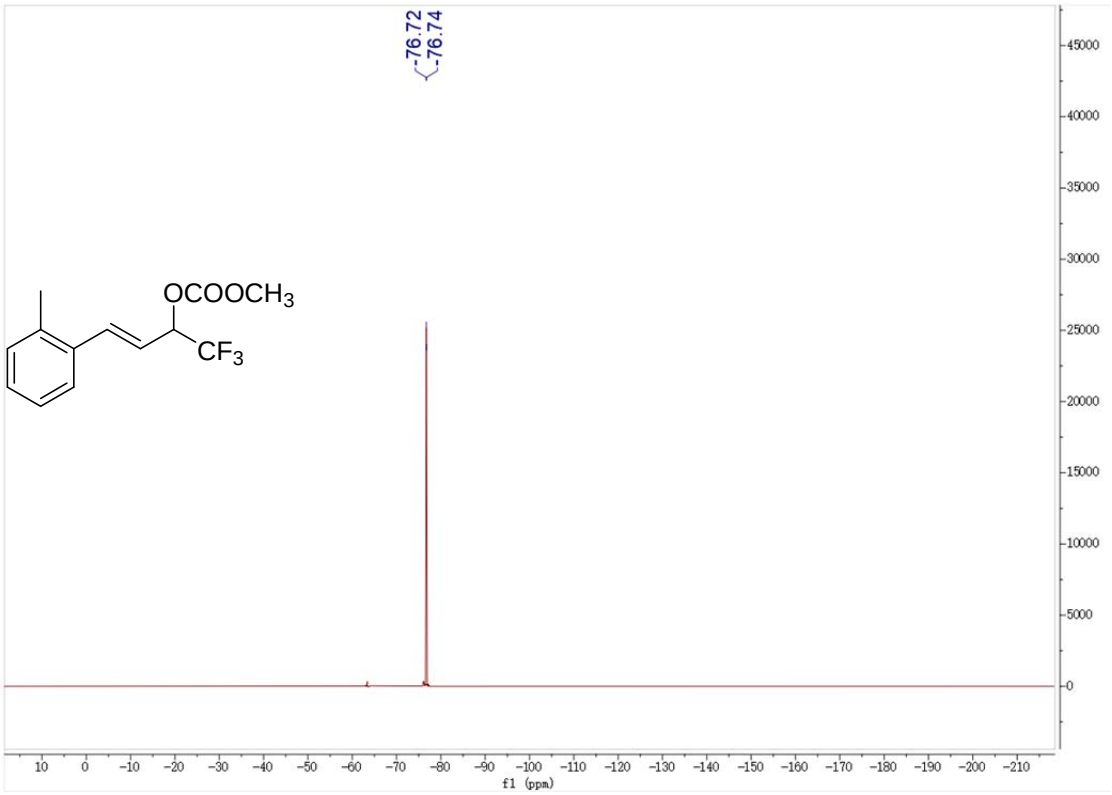
^{1}H NMR (400 MHz, $CDCl_3$) (1c)



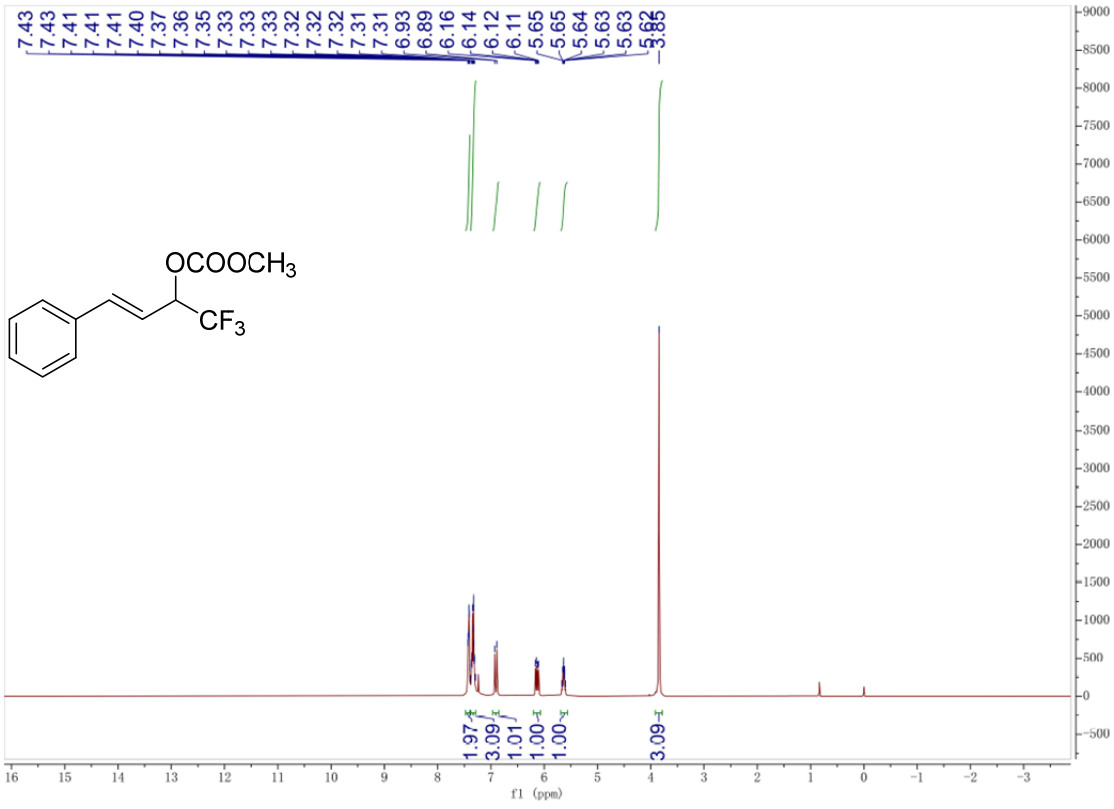
^{13}C NMR (101 MHz, $CDCl_3$) (1c)



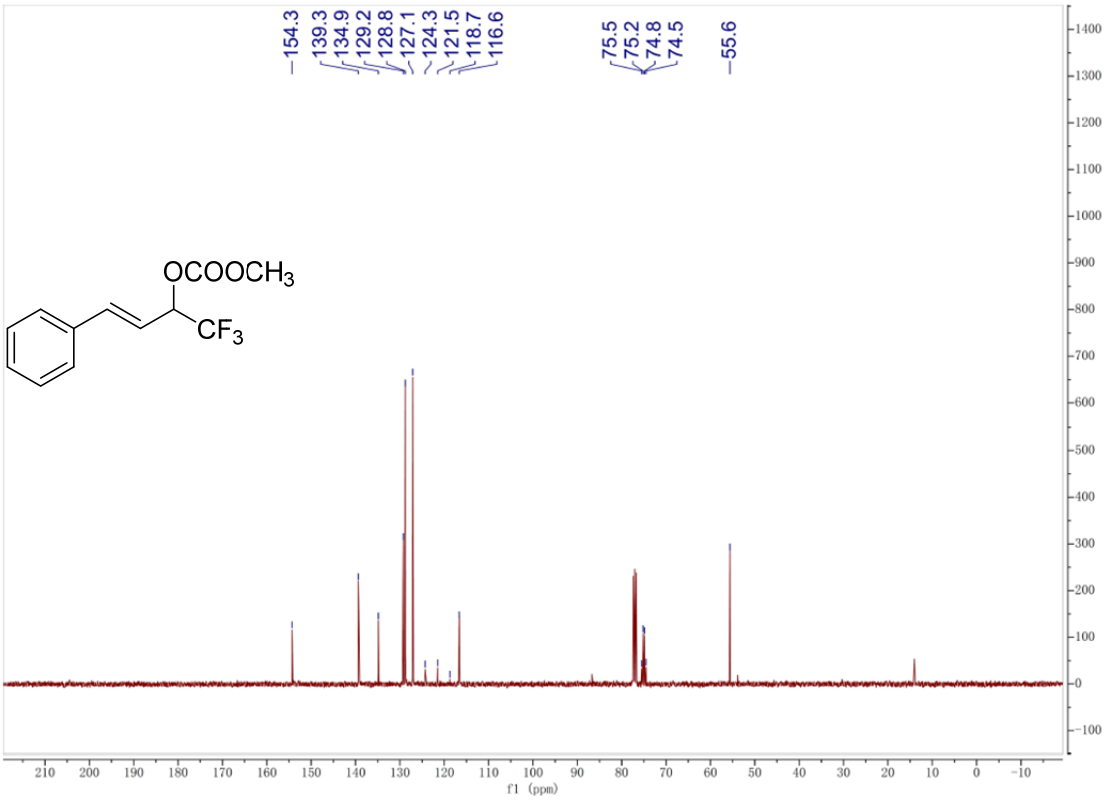
^{19}F NMR (377 MHz, $CDCl_3$) (1c)



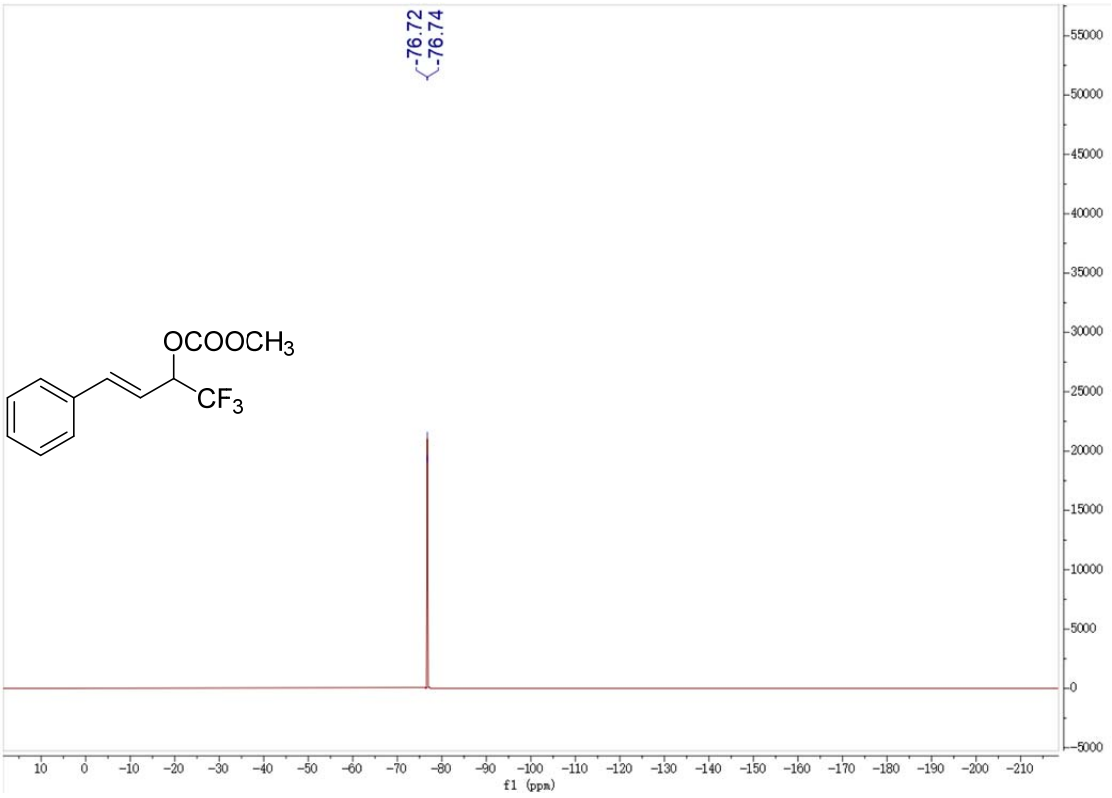
^{1}H NMR (400 MHz, $CDCl_3$) (1d)



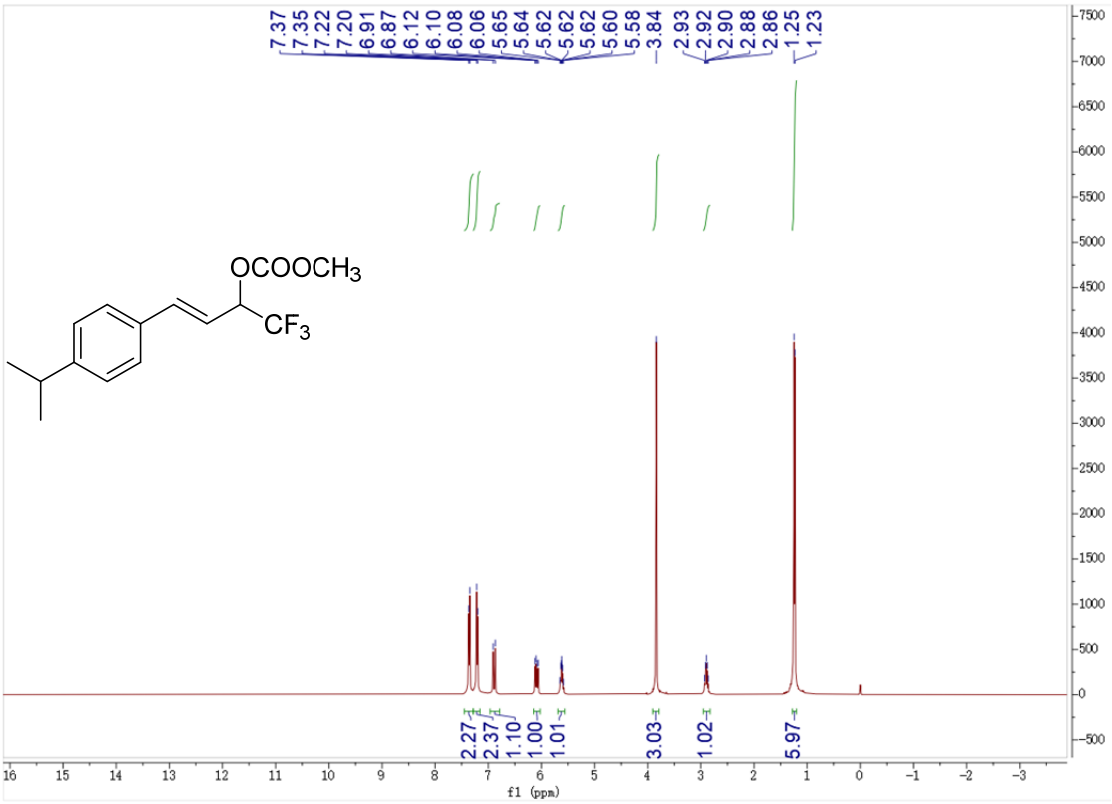
^{13}C NMR (101 MHz, $CDCl_3$) (1d)



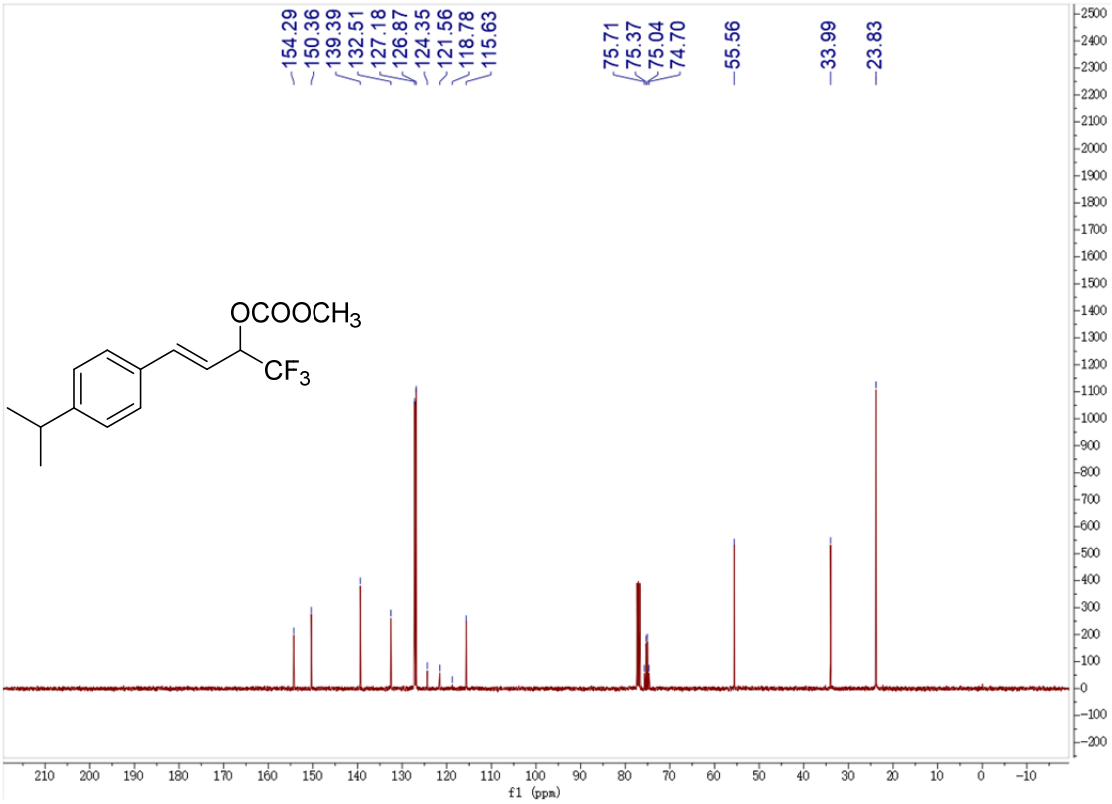
^{19}F NMR (377 MHz, $CDCl_3$) (1d)



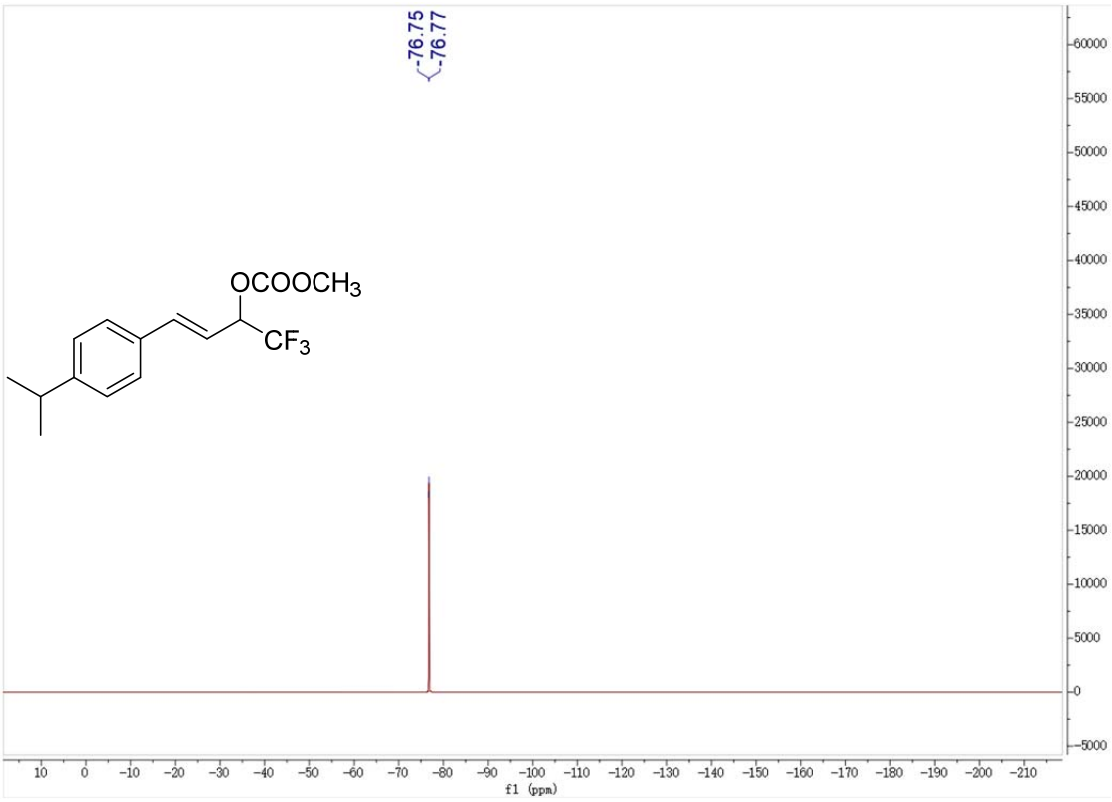
^{1}H NMR (400 MHz, $CDCl_3$) (1e)



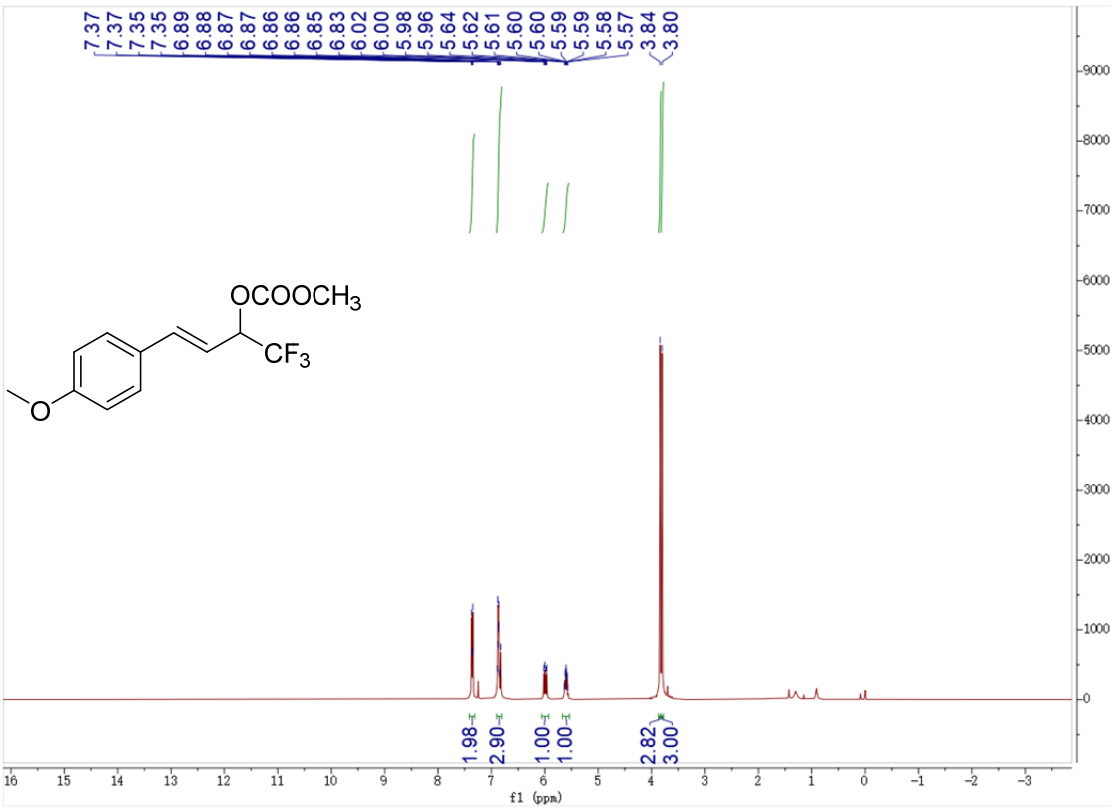
^{13}C NMR (101 MHz, $CDCl_3$) (1e)



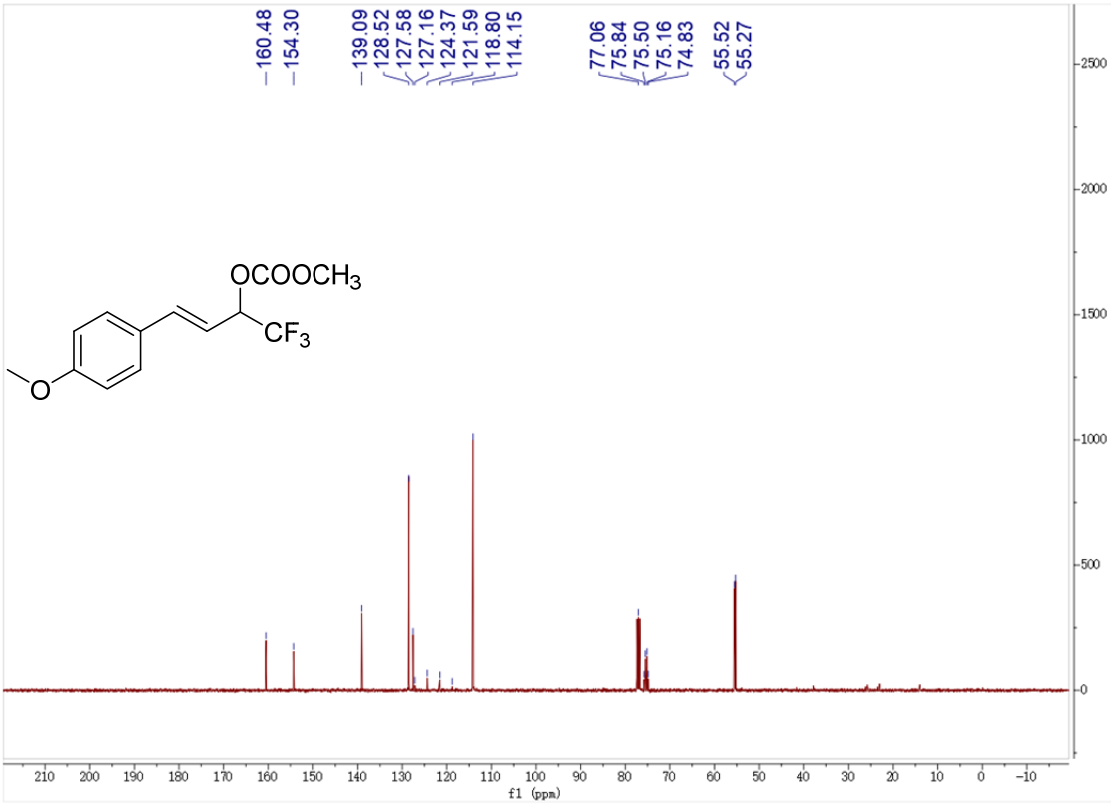
^{19}F NMR (377 MHz, $CDCl_3$) (1e)



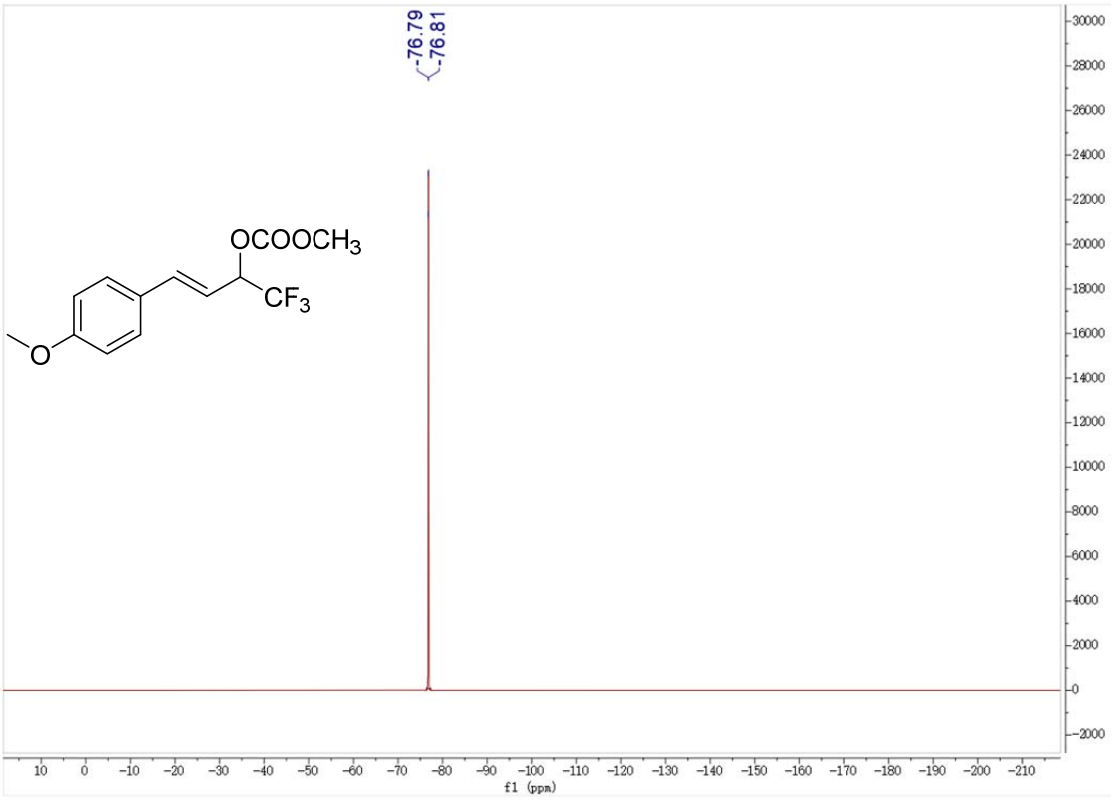
^{1}H NMR (400 MHz, $CDCl_3$) (1f)



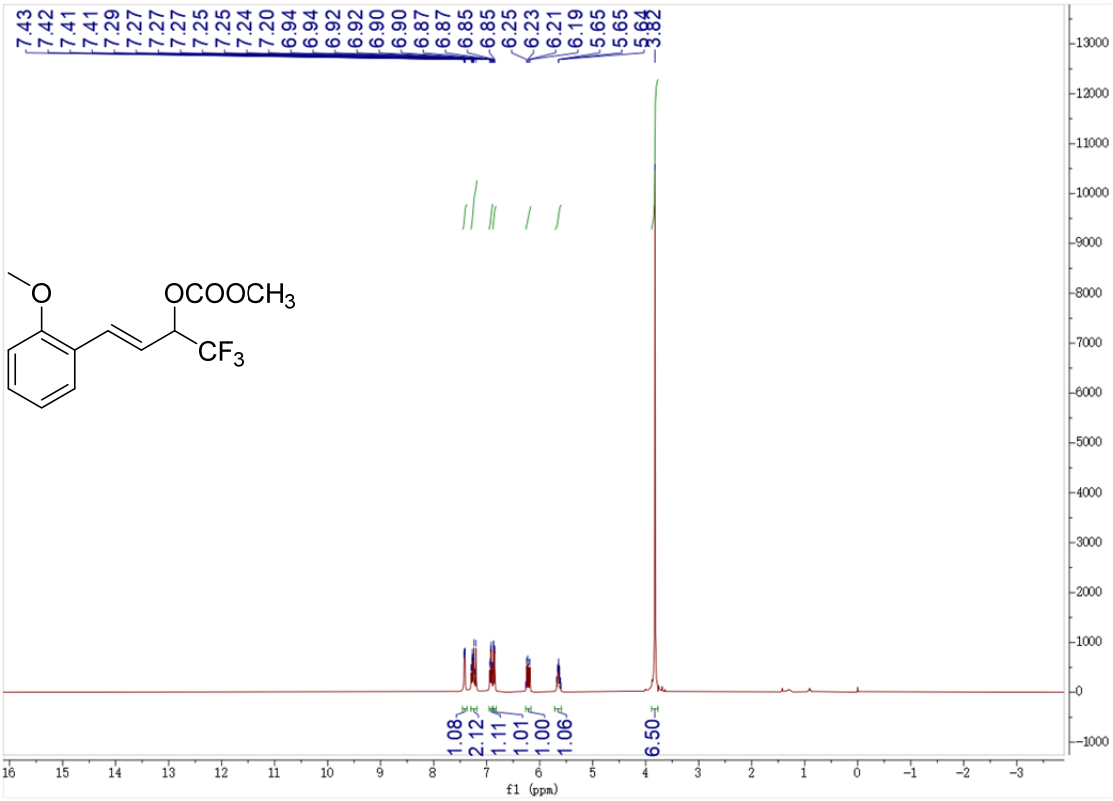
^{13}C NMR (101 MHz, $CDCl_3$) (1f)



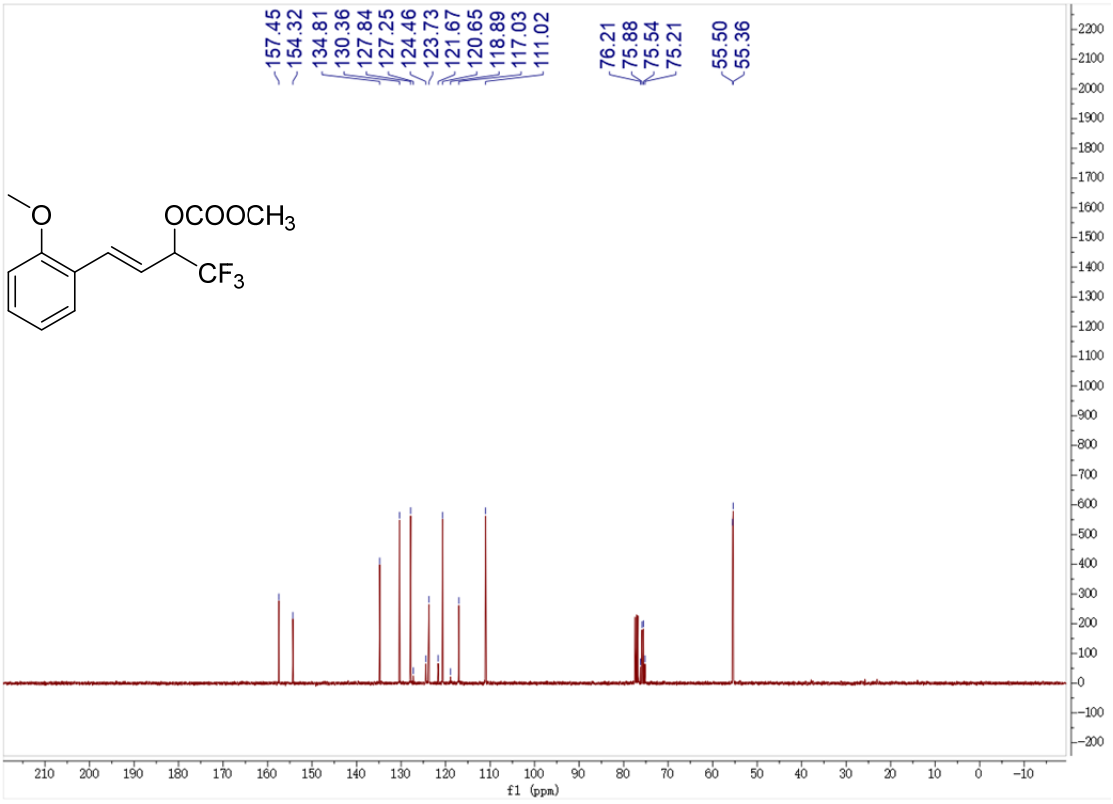
^{19}F NMR (377 MHz, $CDCl_3$) (1f)



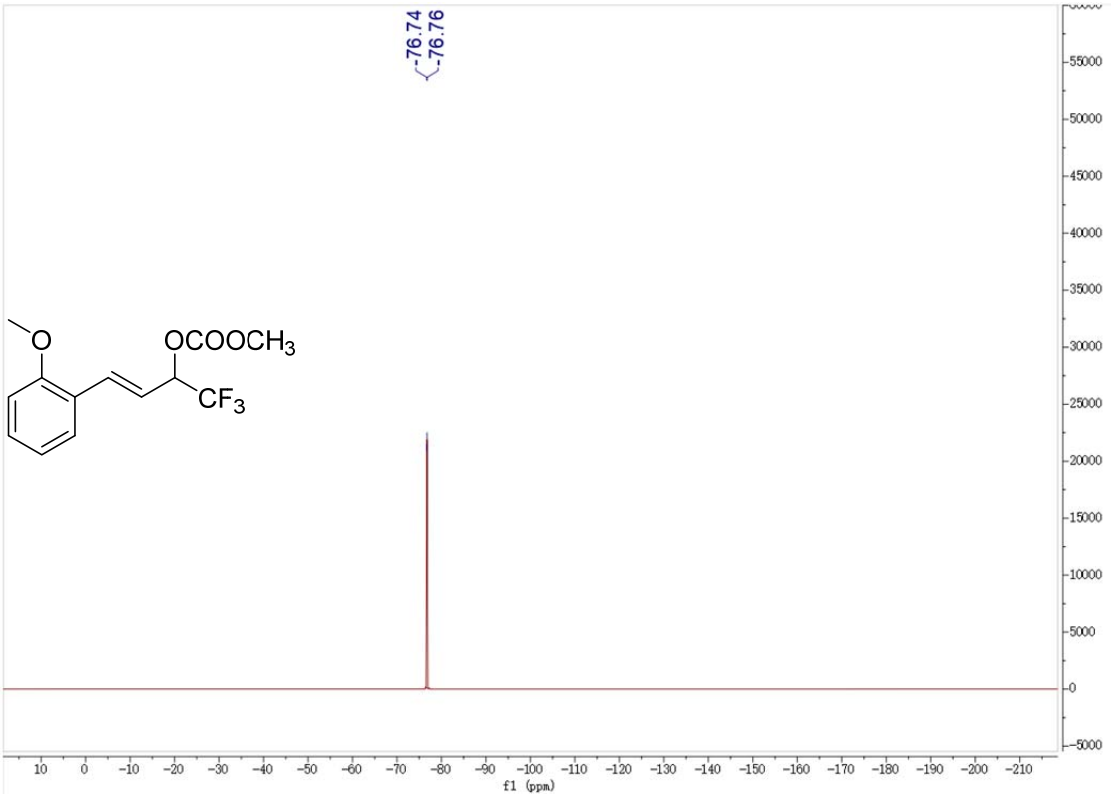
^{1}H NMR (400 MHz, $CDCl_3$) (1g)



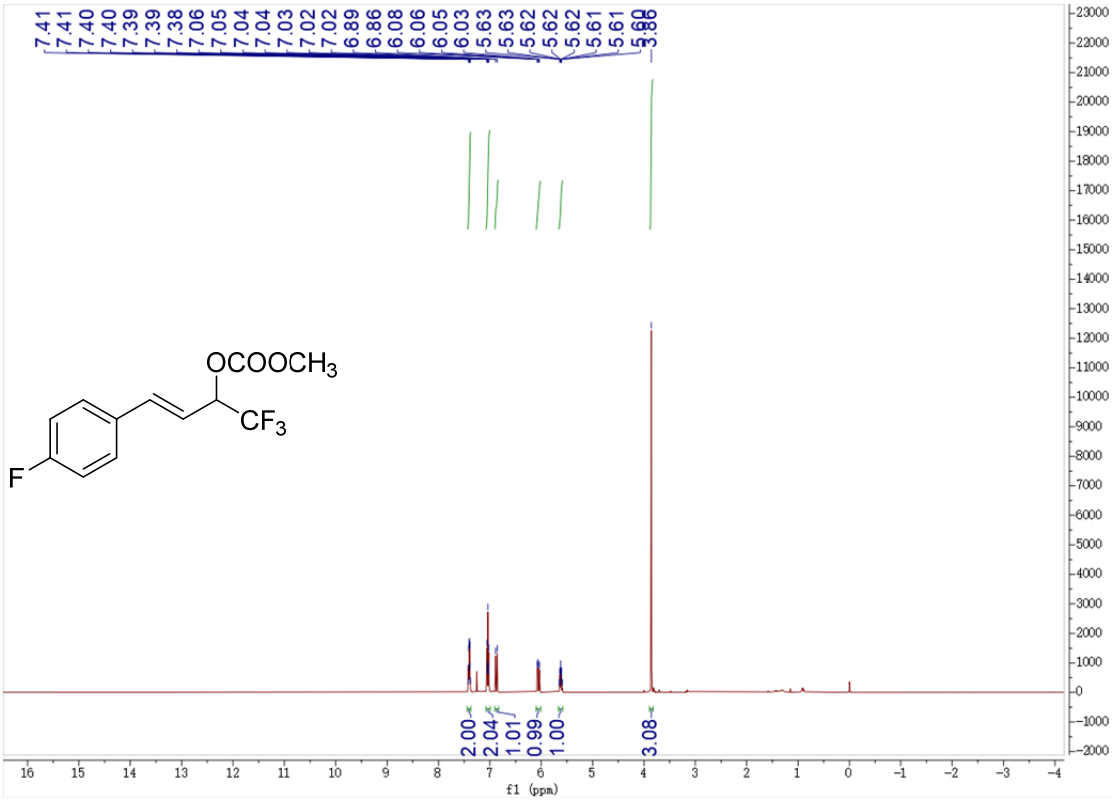
^{13}C NMR (101 MHz, $CDCl_3$) (1g)



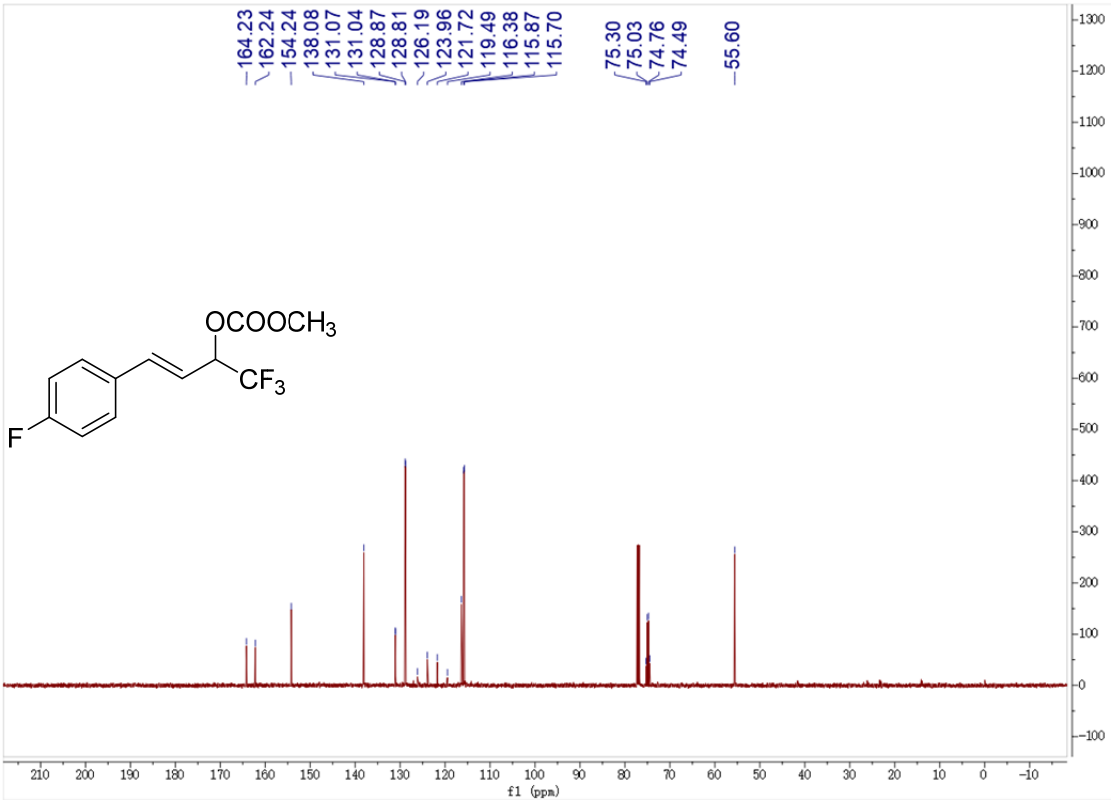
^{19}F NMR (377 MHz, $CDCl_3$) (1g)



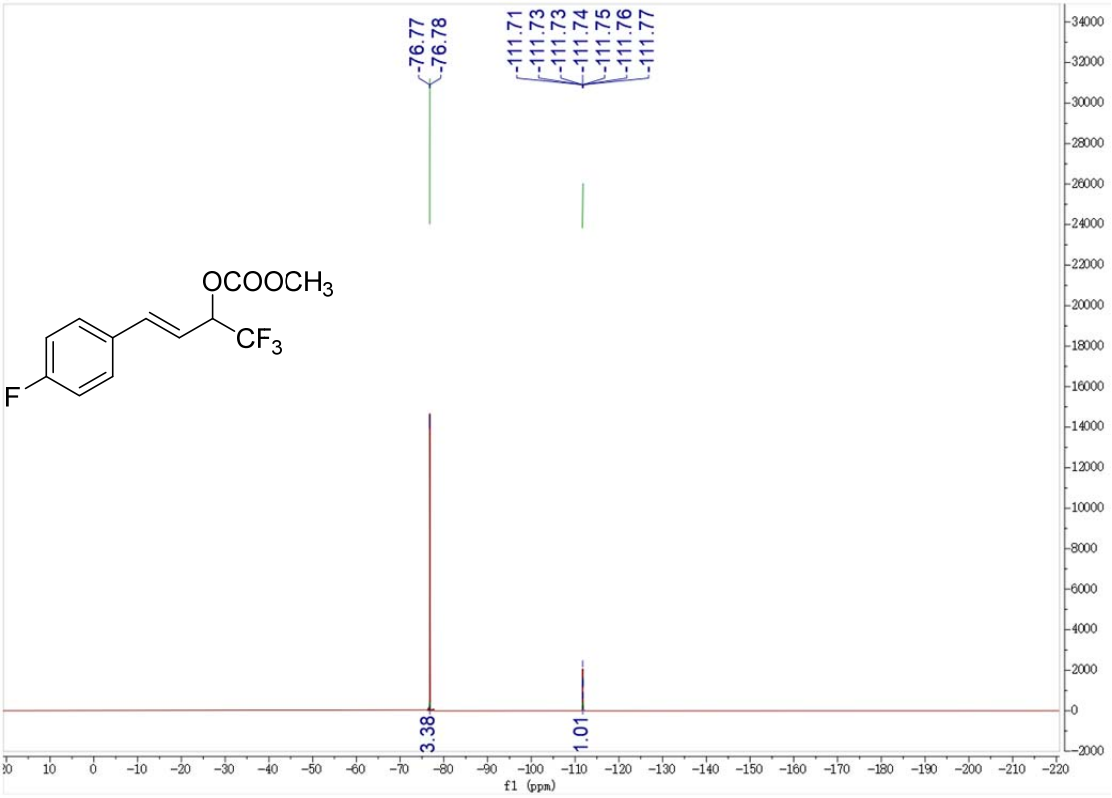
^{1}H NMR (500 MHz, $CDCl_3$) (1h)



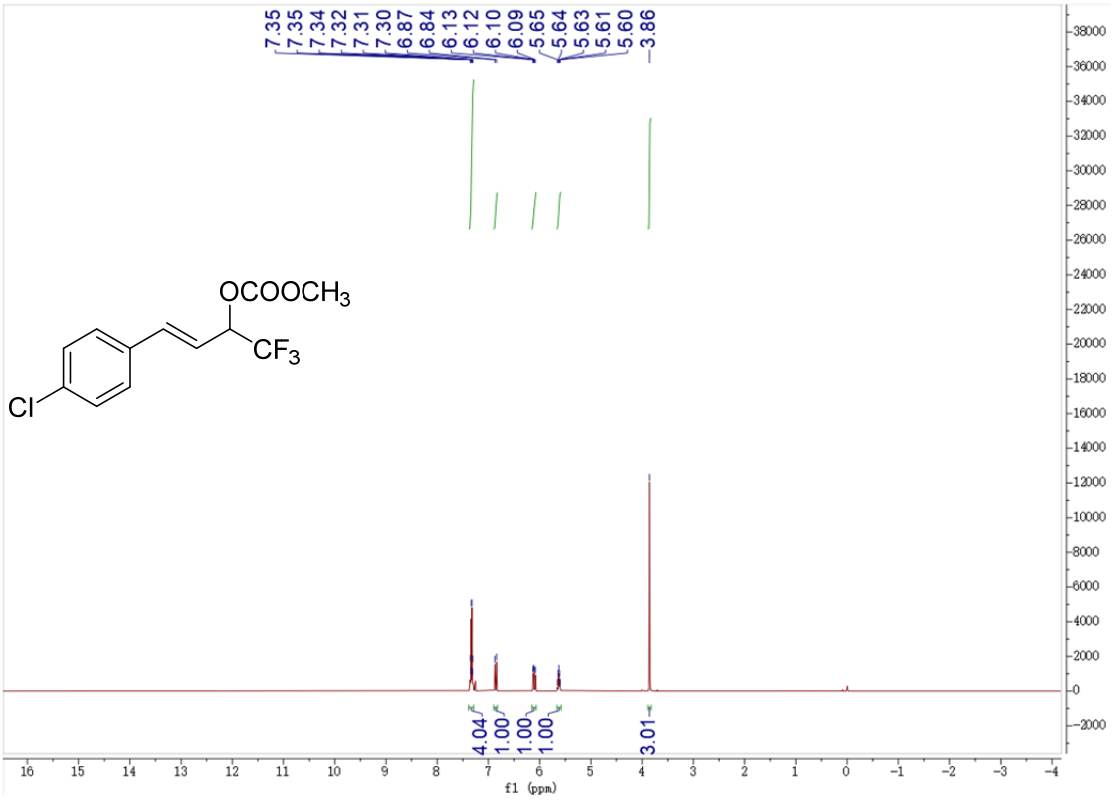
^{13}C NMR (126 MHz, $CDCl_3$) (1h)



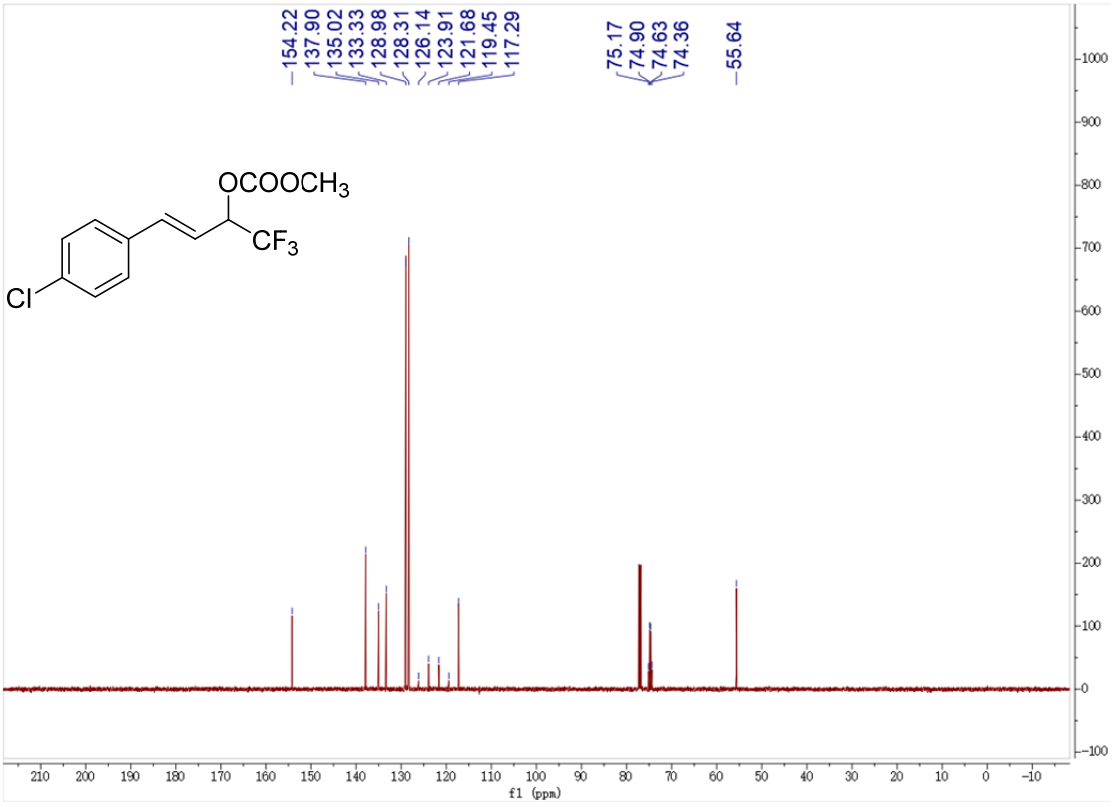
^{19}F NMR (470 MHz, $CDCl_3$) (1h)



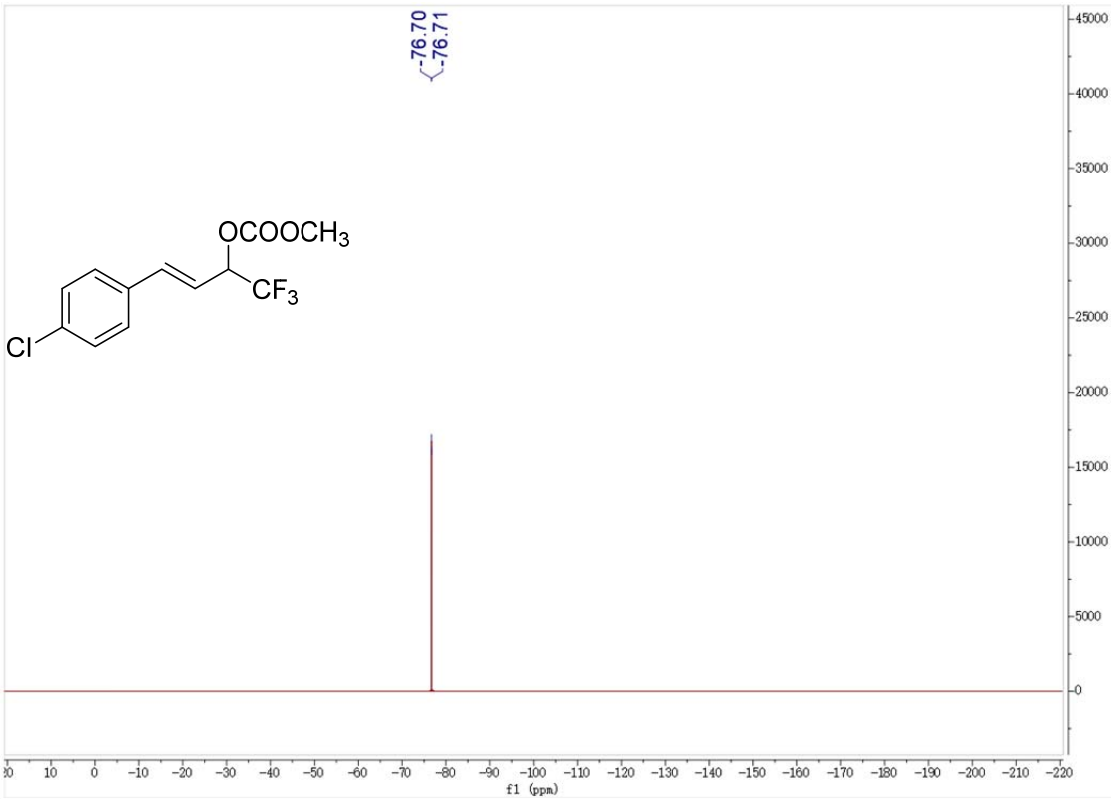
^{1}H NMR (500 MHz, $CDCl_3$) (1i)



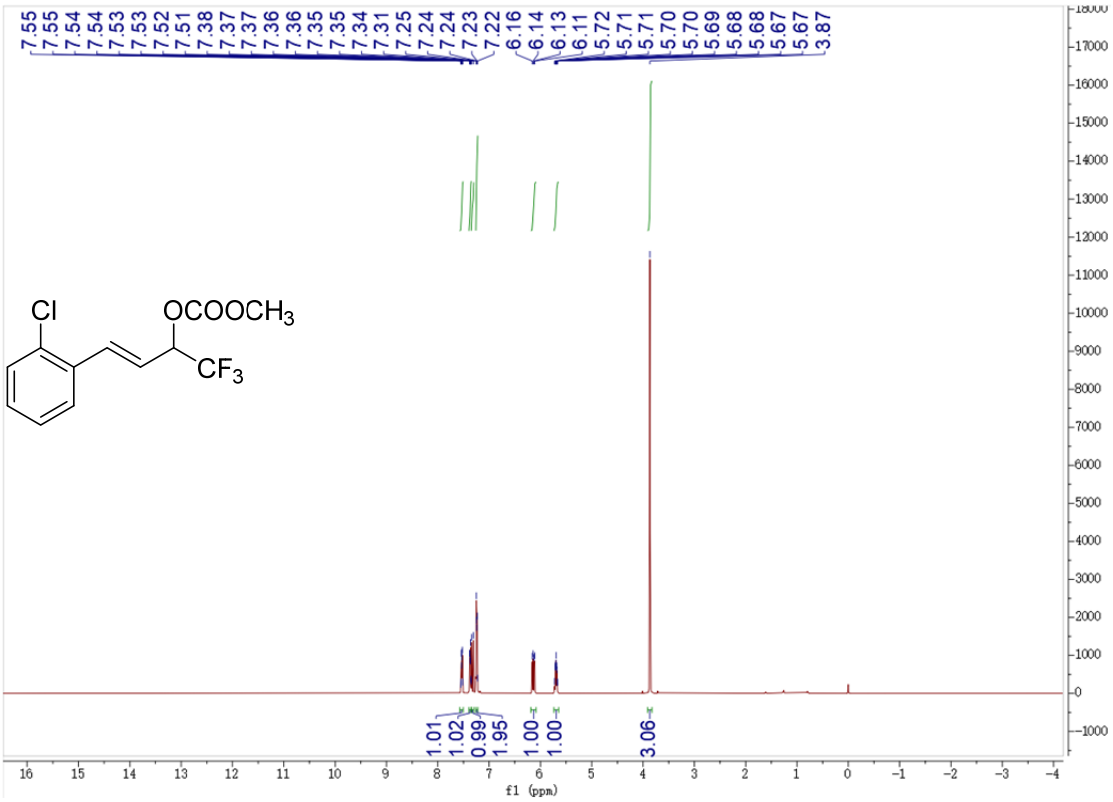
^{13}C NMR (126 MHz, $CDCl_3$) (1i)



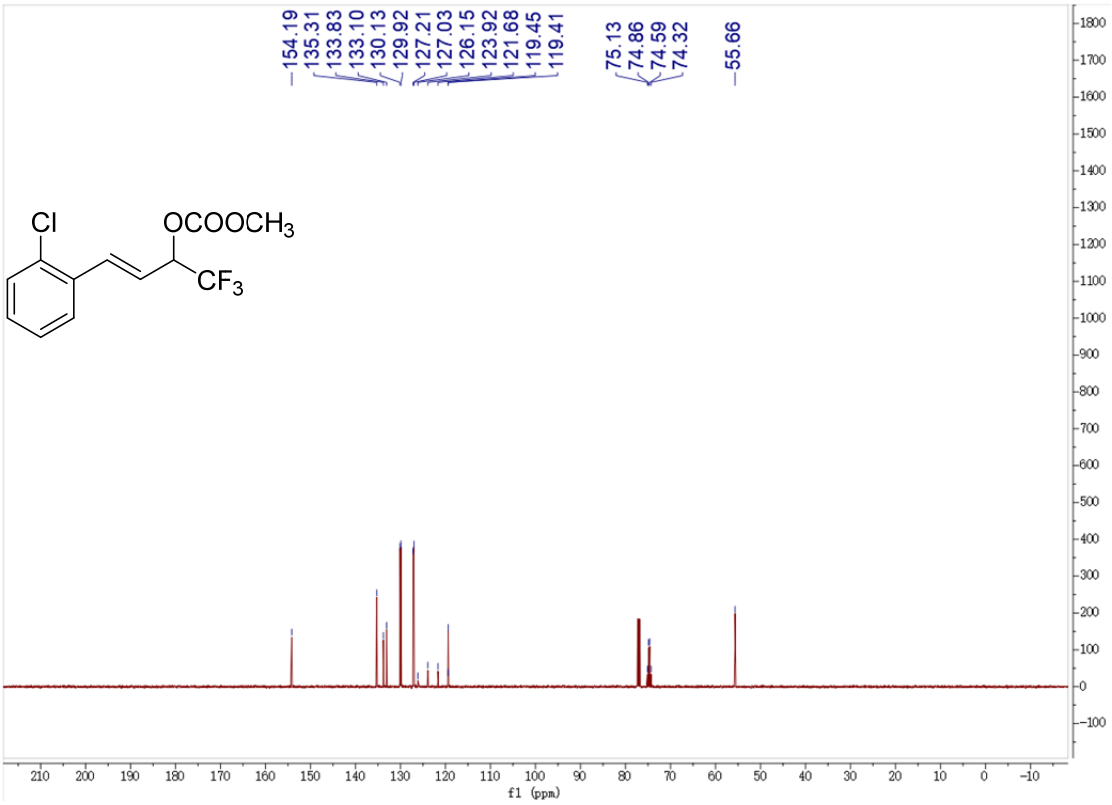
^{19}F NMR (470 MHz, $CDCl_3$) (1i)



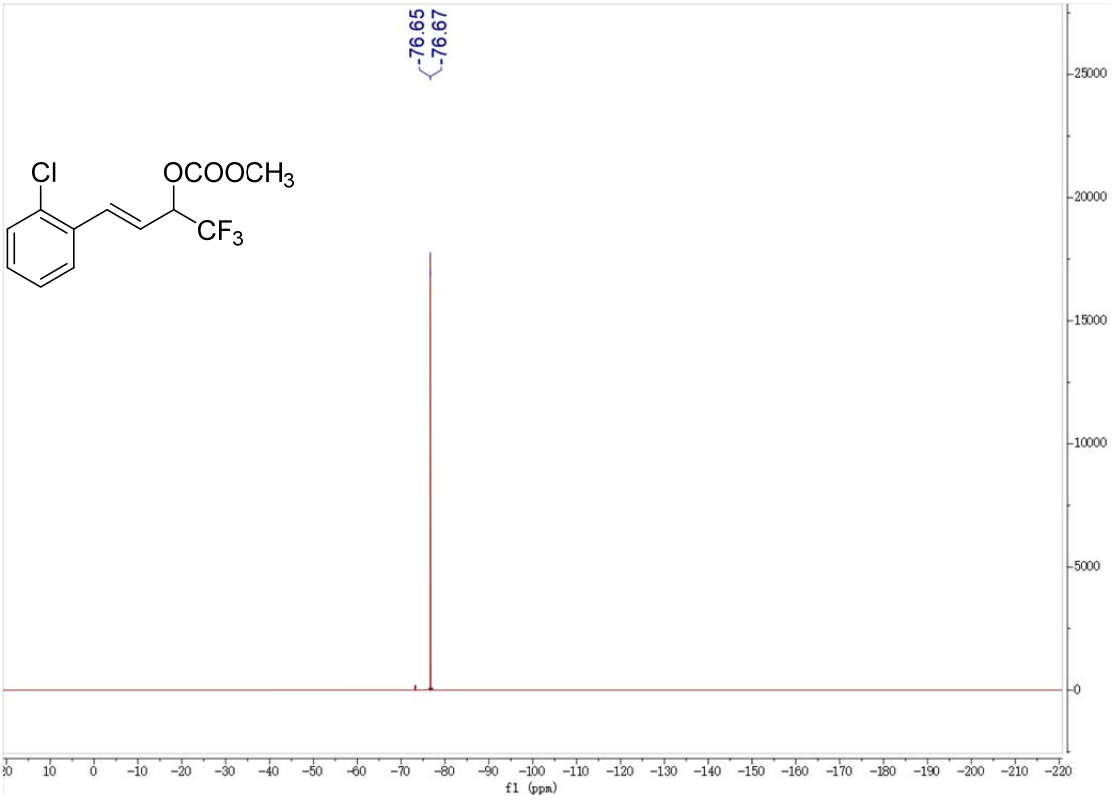
^{1}H NMR (500 MHz, $CDCl_3$) (1j)



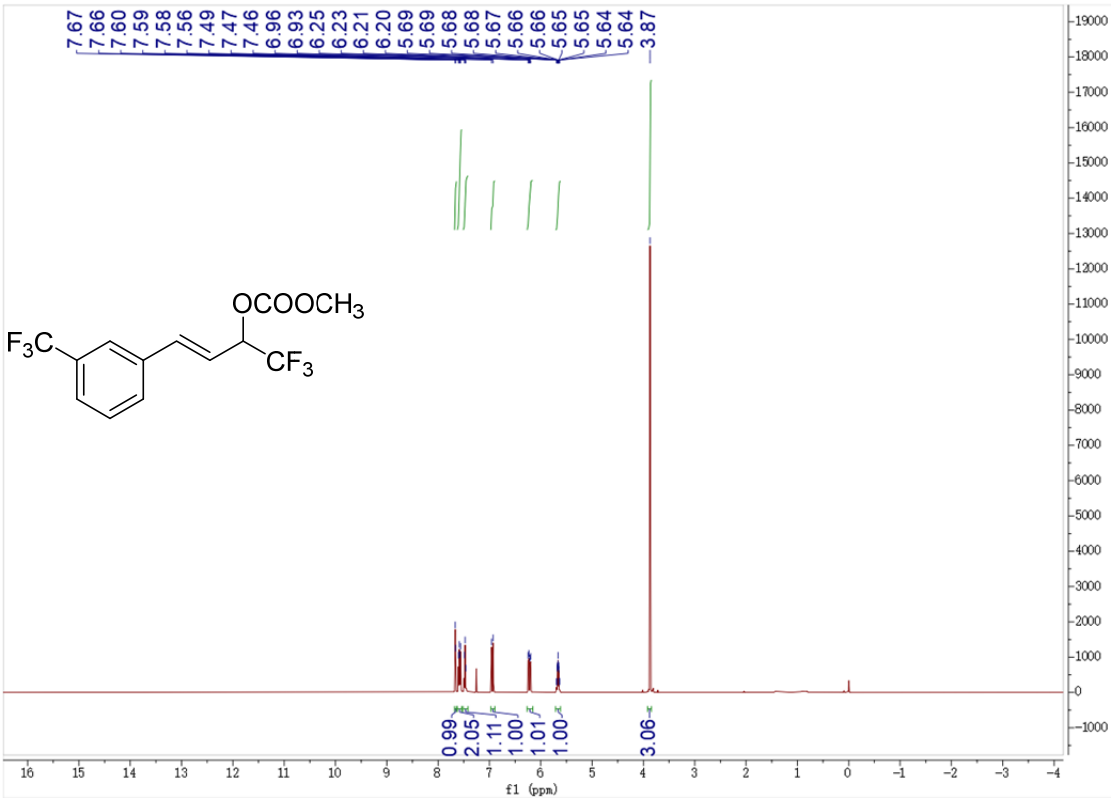
^{13}C NMR (126 MHz, $CDCl_3$) (1j)



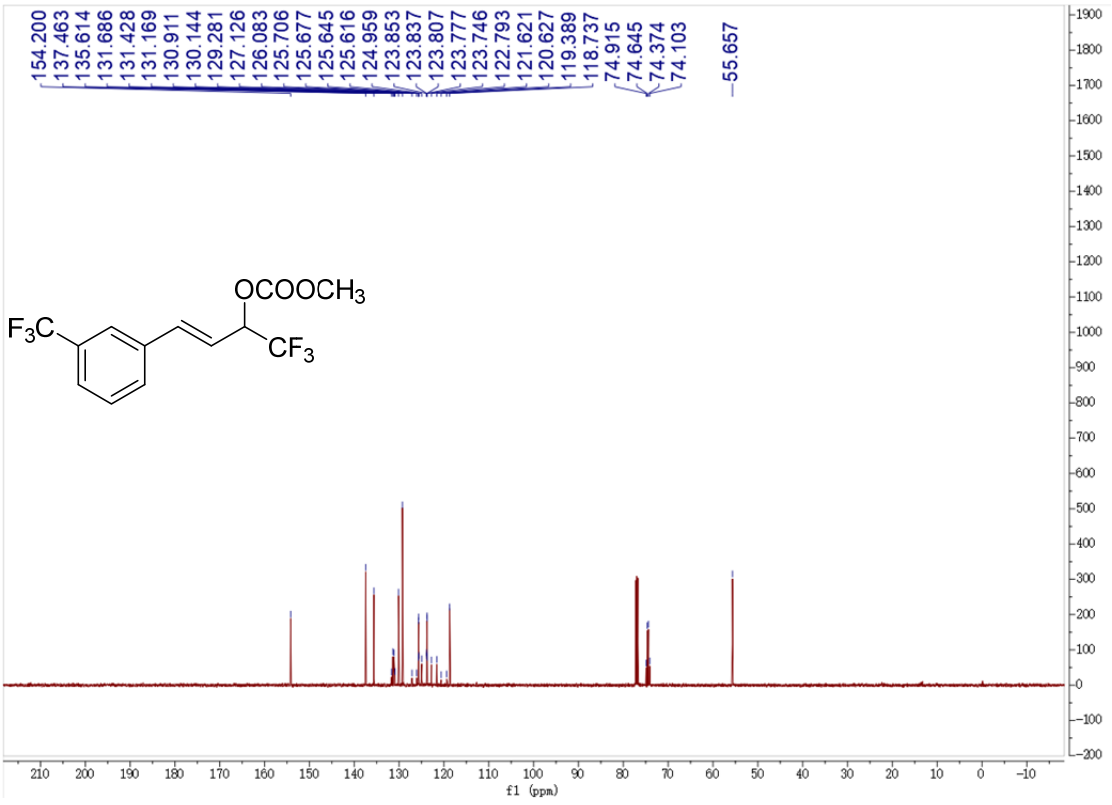
^{19}F NMR (470 MHz, $CDCl_3$) (1j)



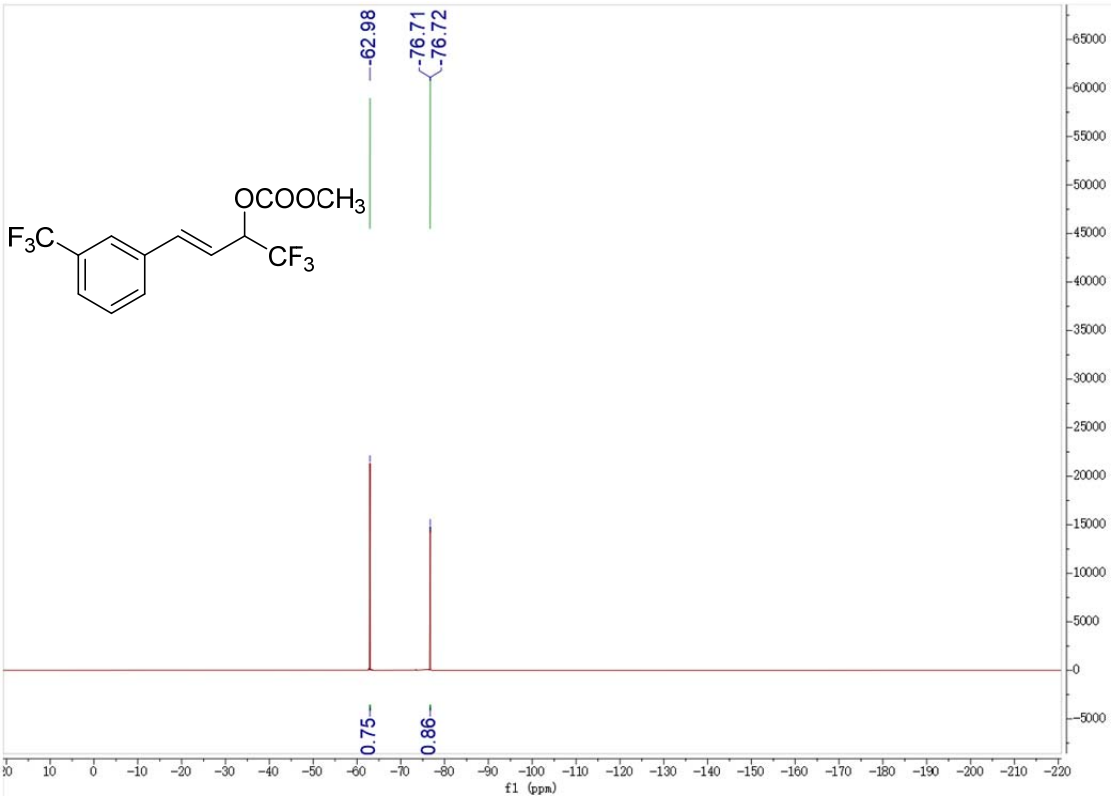
^{1}H NMR (500 MHz, $CDCl_3$) (1k)



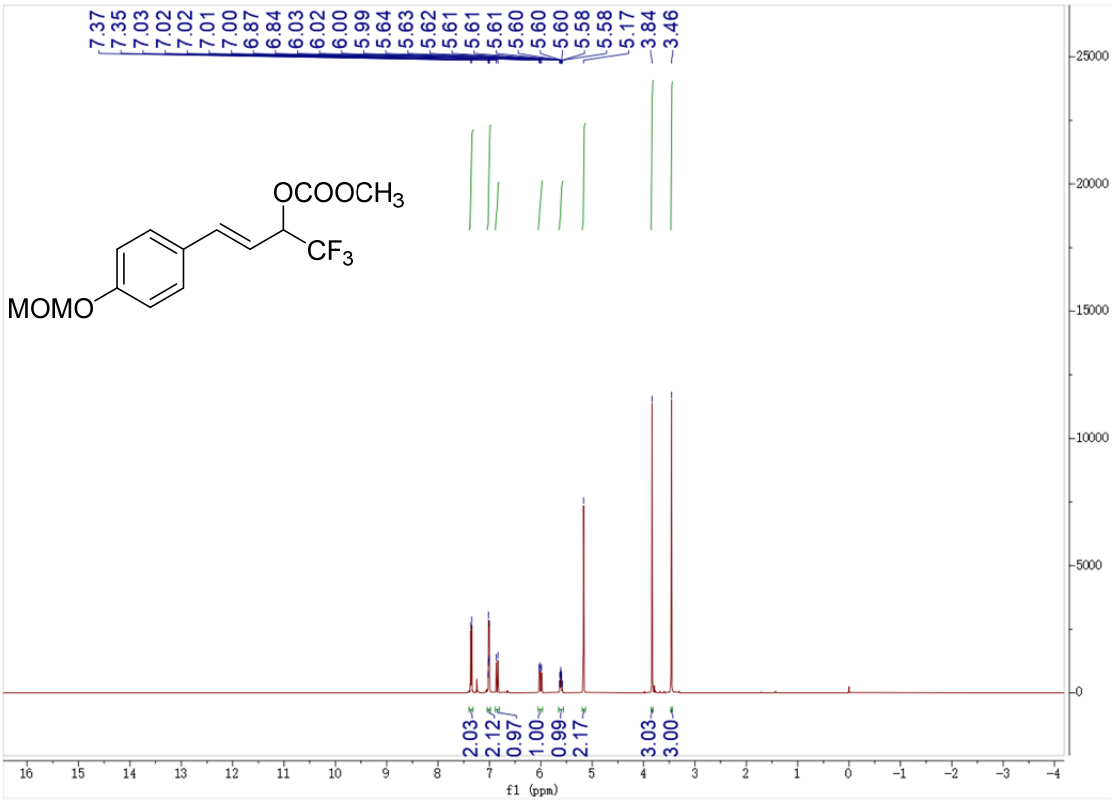
^{13}C NMR (126 MHz, $CDCl_3$) (1k)



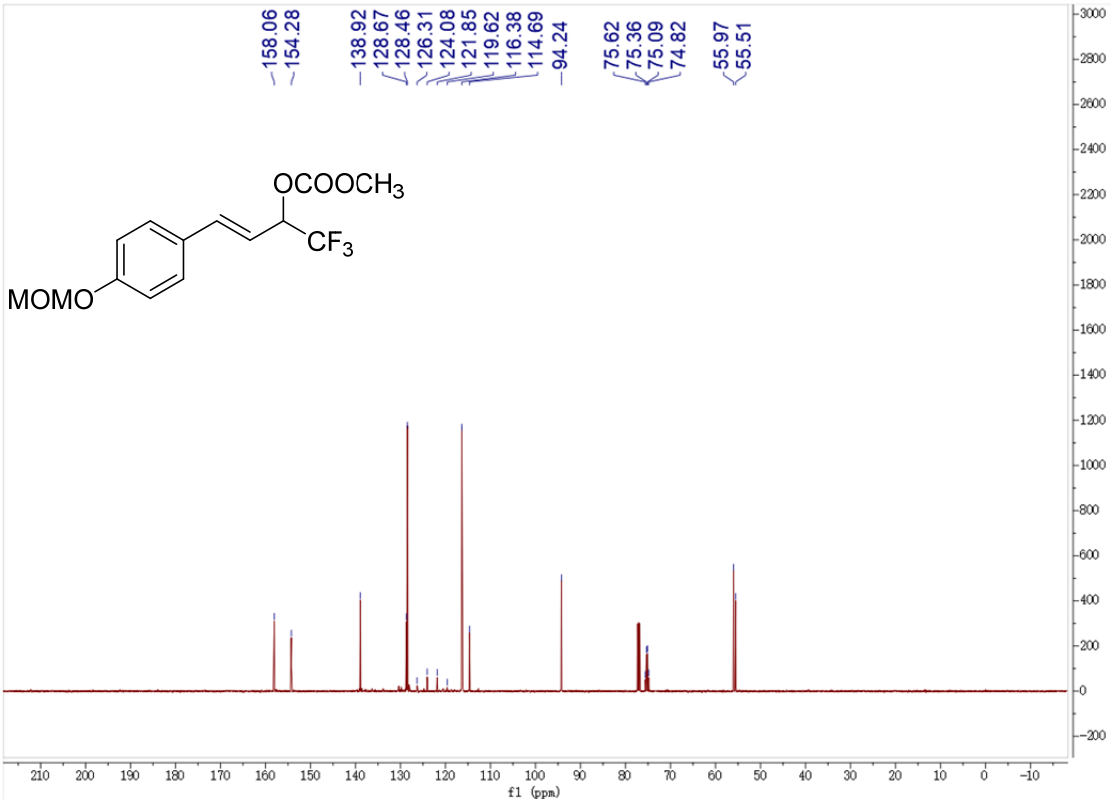
^{19}F NMR (470 MHz, $CDCl_3$) (1k)



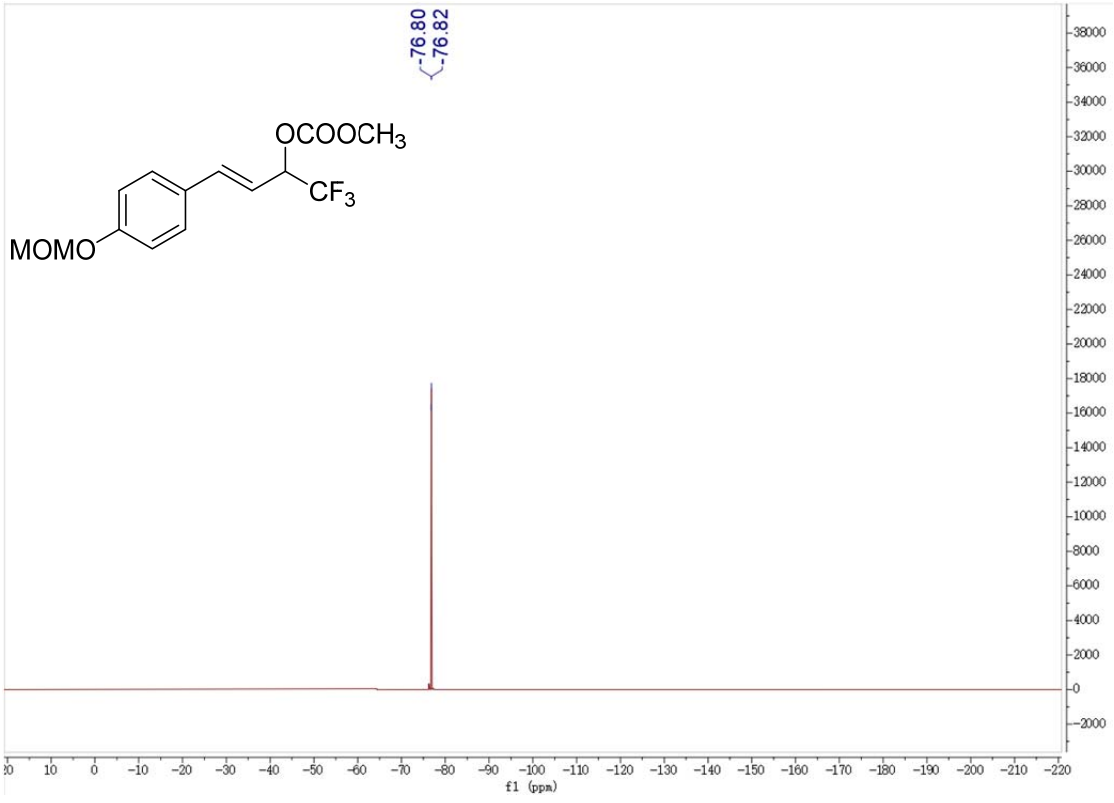
^{1}H NMR (500 MHz, $CDCl_3$) (1l)



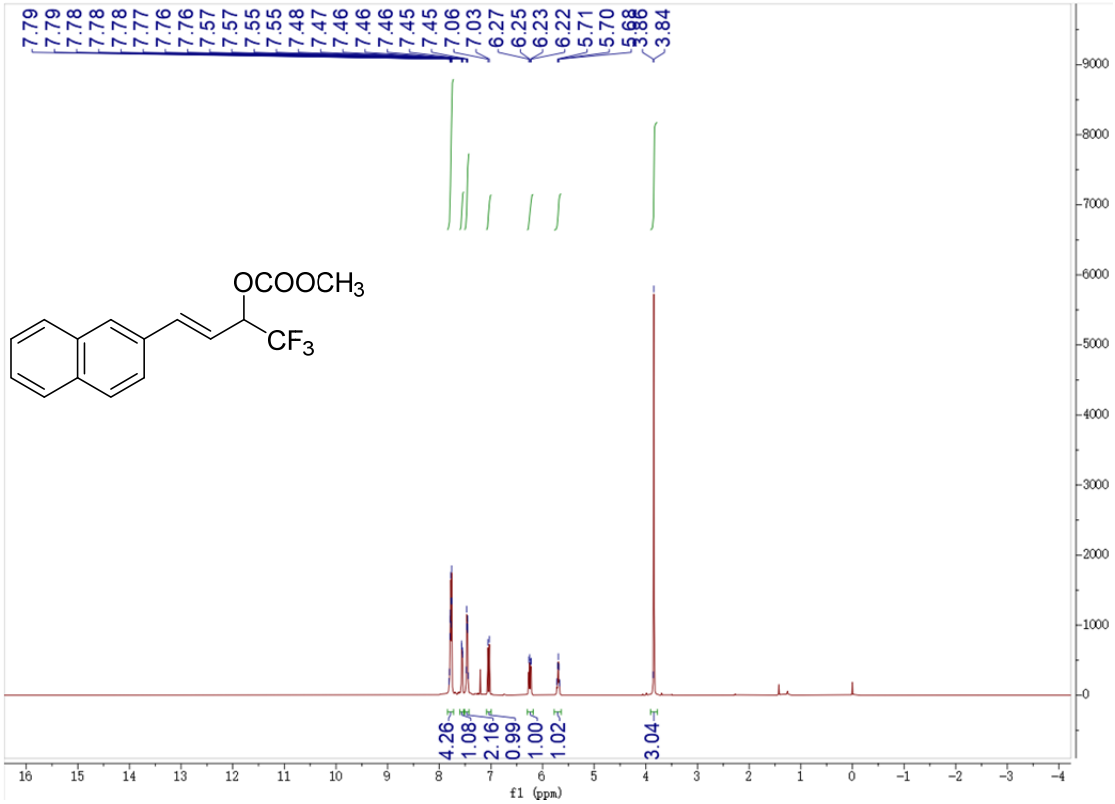
^{13}C NMR (126 MHz, $CDCl_3$) (1l)



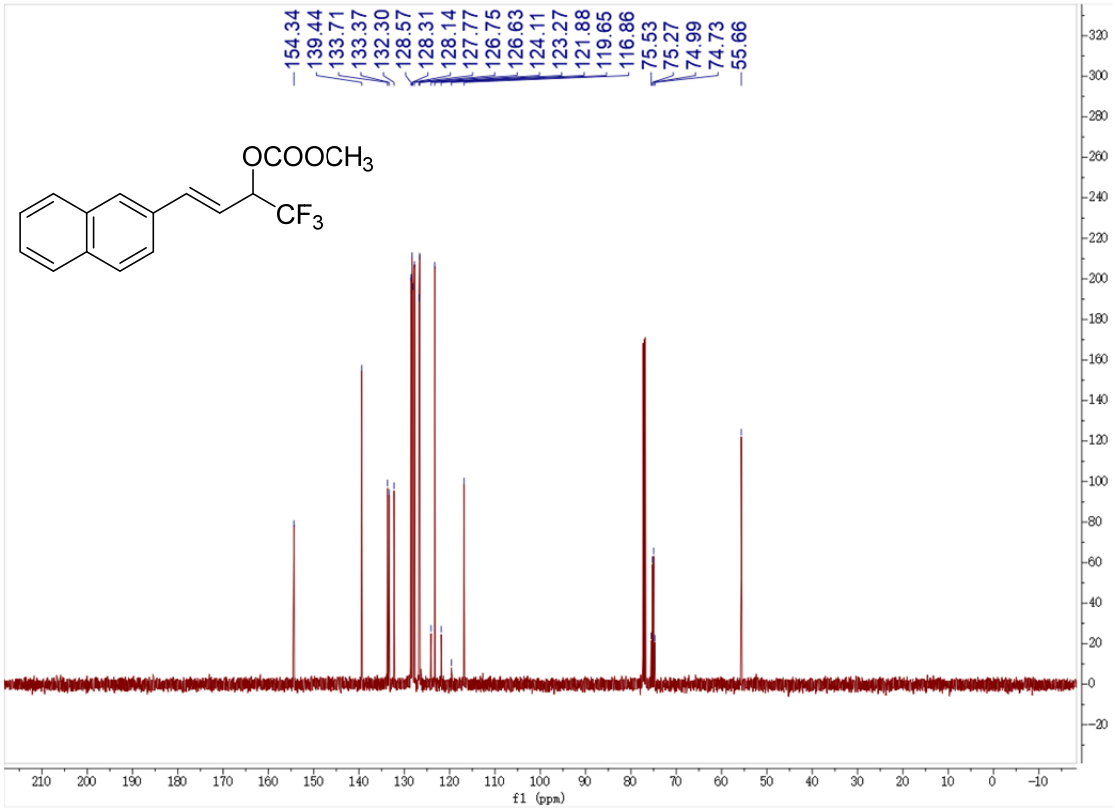
^{19}F NMR (470 MHz, $CDCl_3$) (1l)



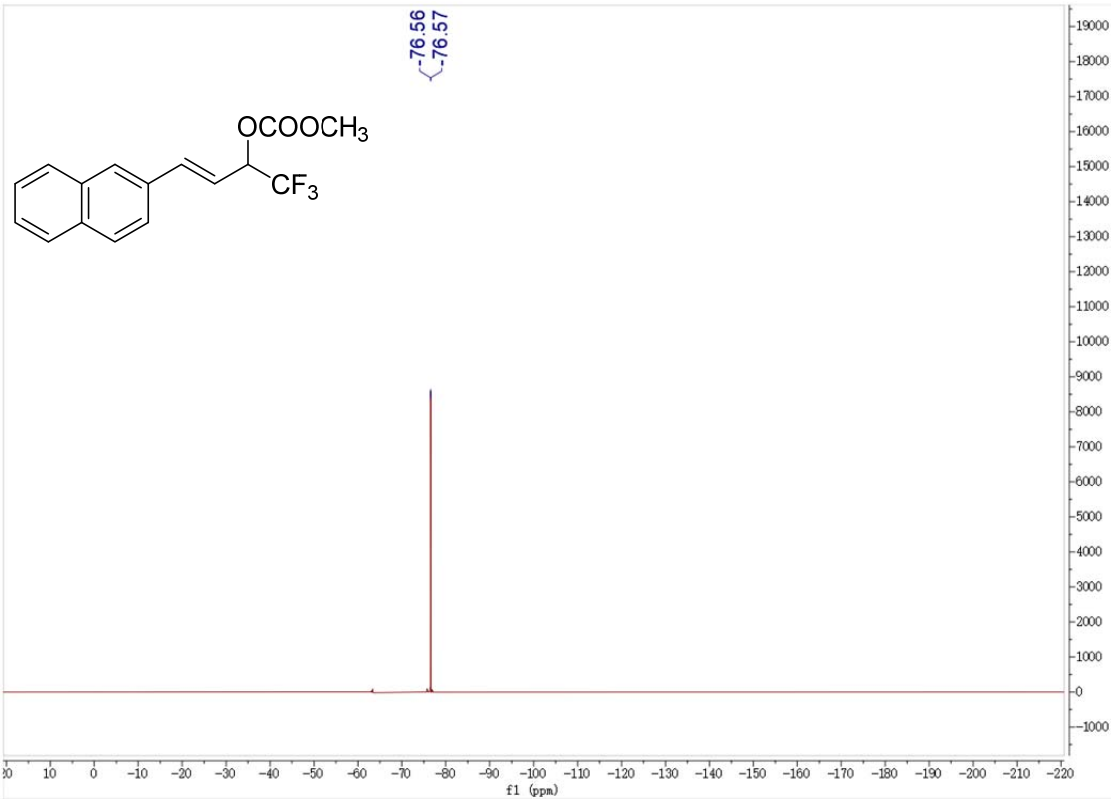
^{1}H NMR (500 MHz, $CDCl_3$) (1m)



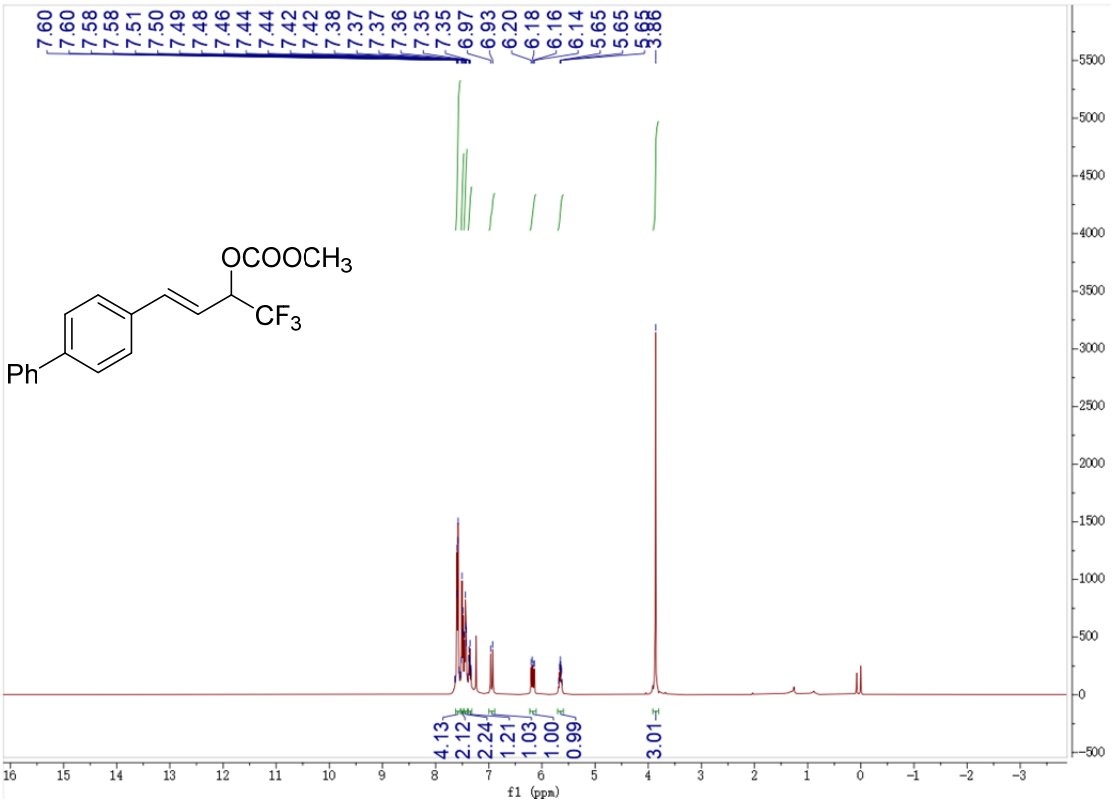
^{13}C NMR (126 MHz, $CDCl_3$) (1m)



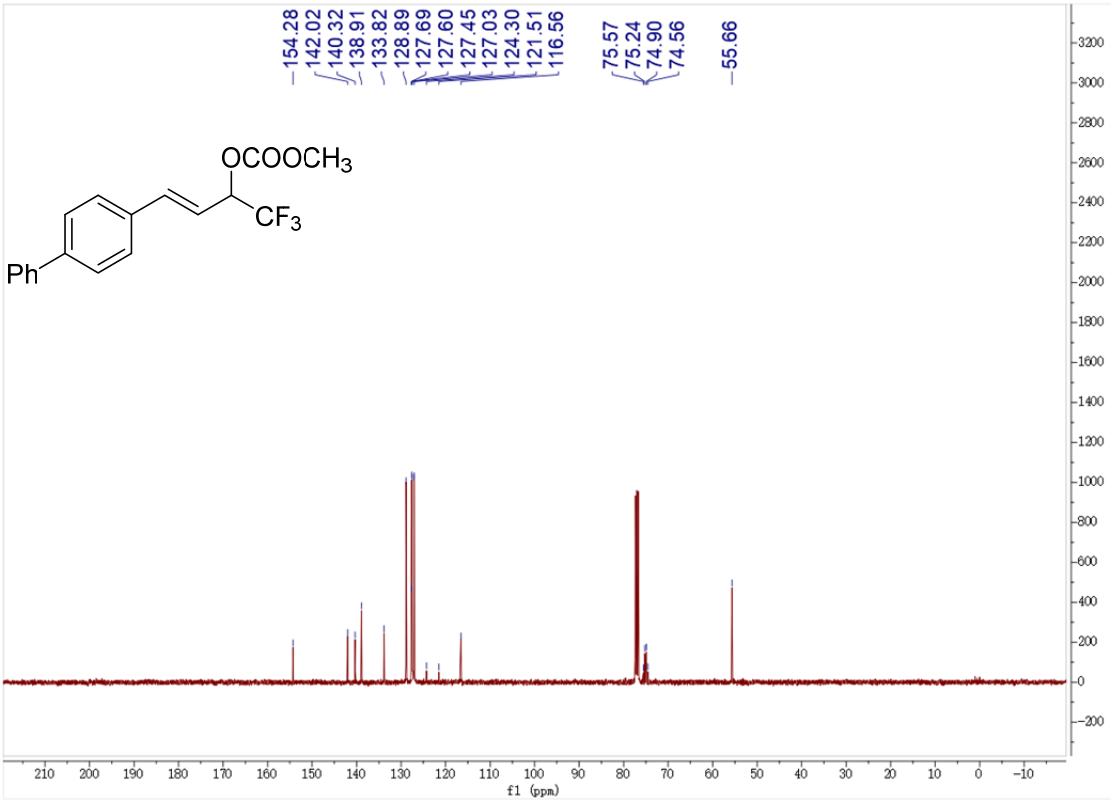
^{19}F NMR (470 MHz, $CDCl_3$) (1m)



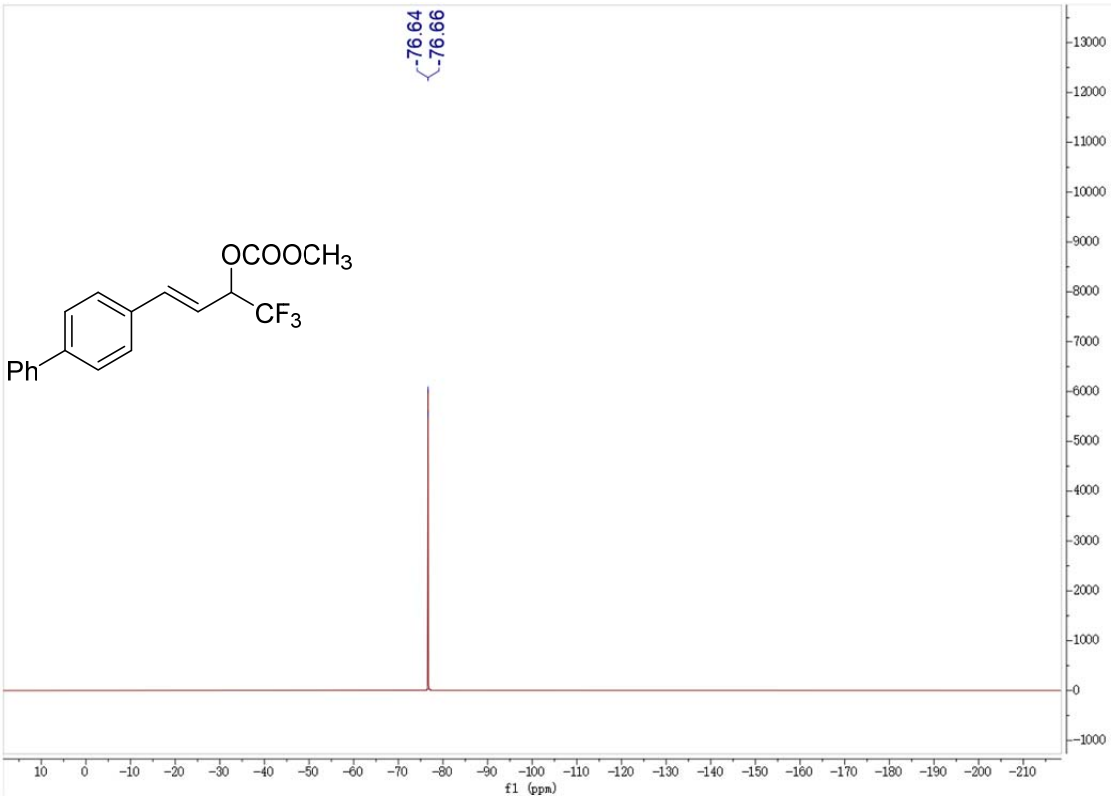
^{1}H NMR (400 MHz, $CDCl_3$) (1n)



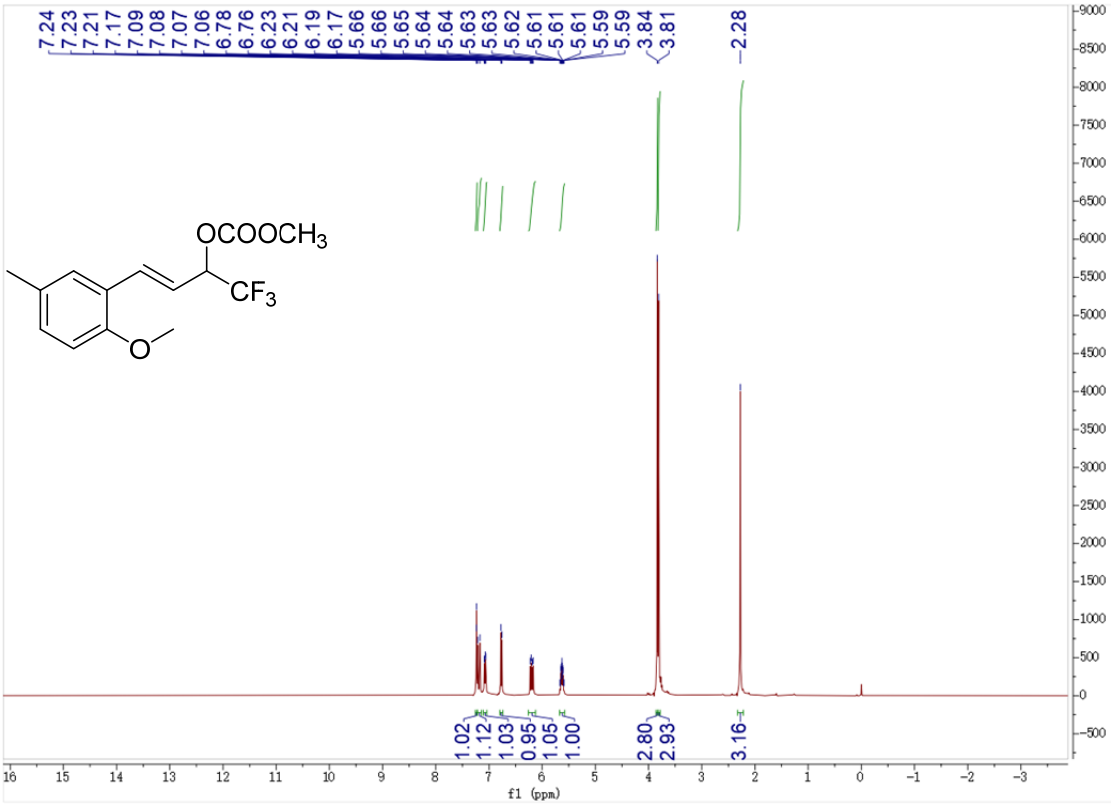
^{13}C NMR (101 MHz, $CDCl_3$) (1n)



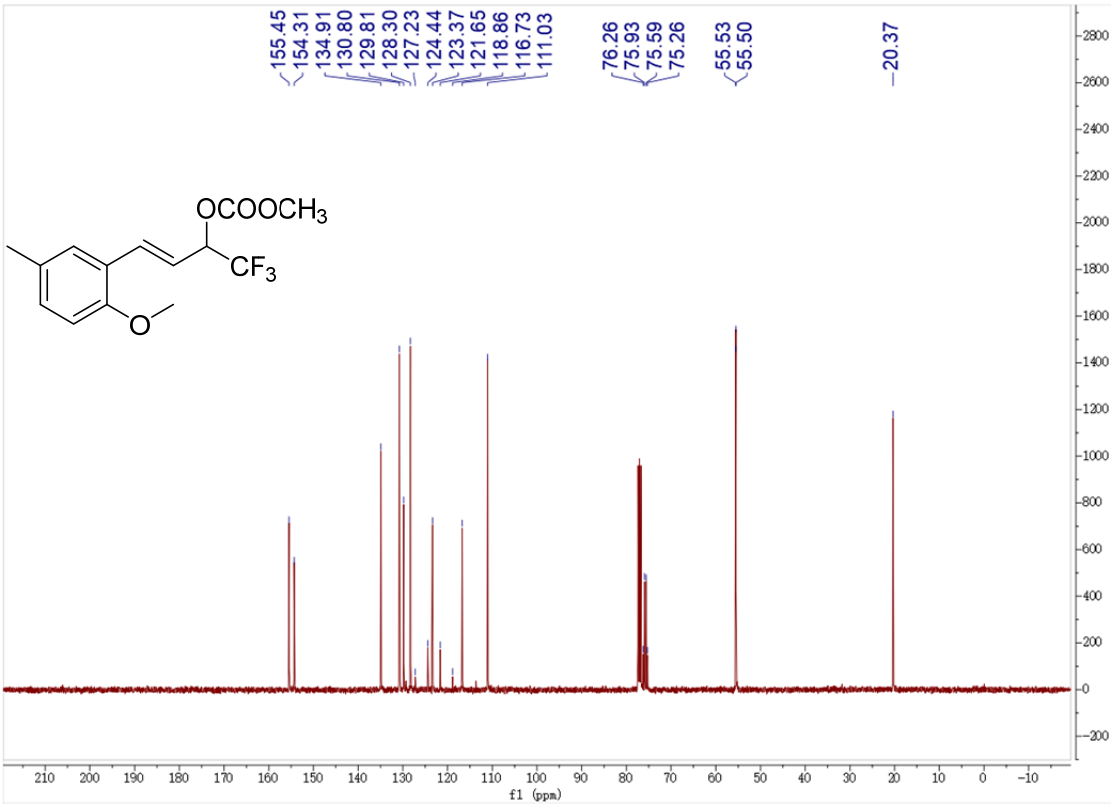
^{19}F NMR (377 MHz, $CDCl_3$) (1n)



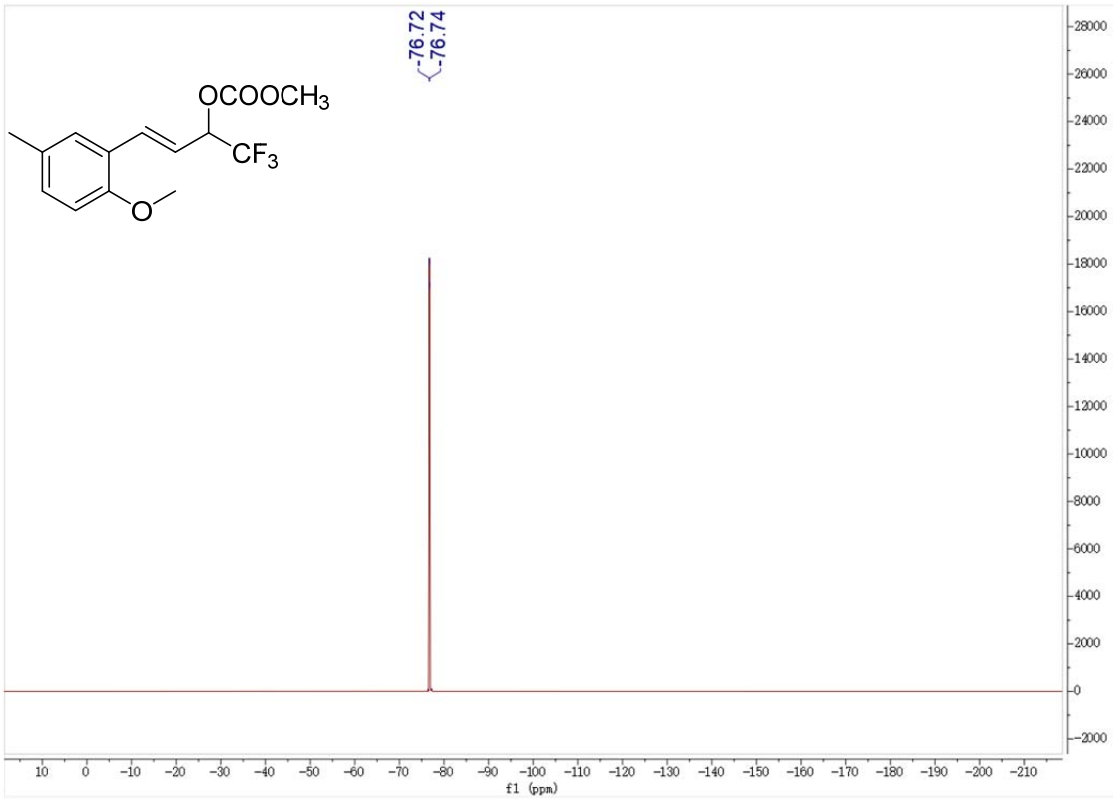
^{1}H NMR (400 MHz, $CDCl_3$) (1o)



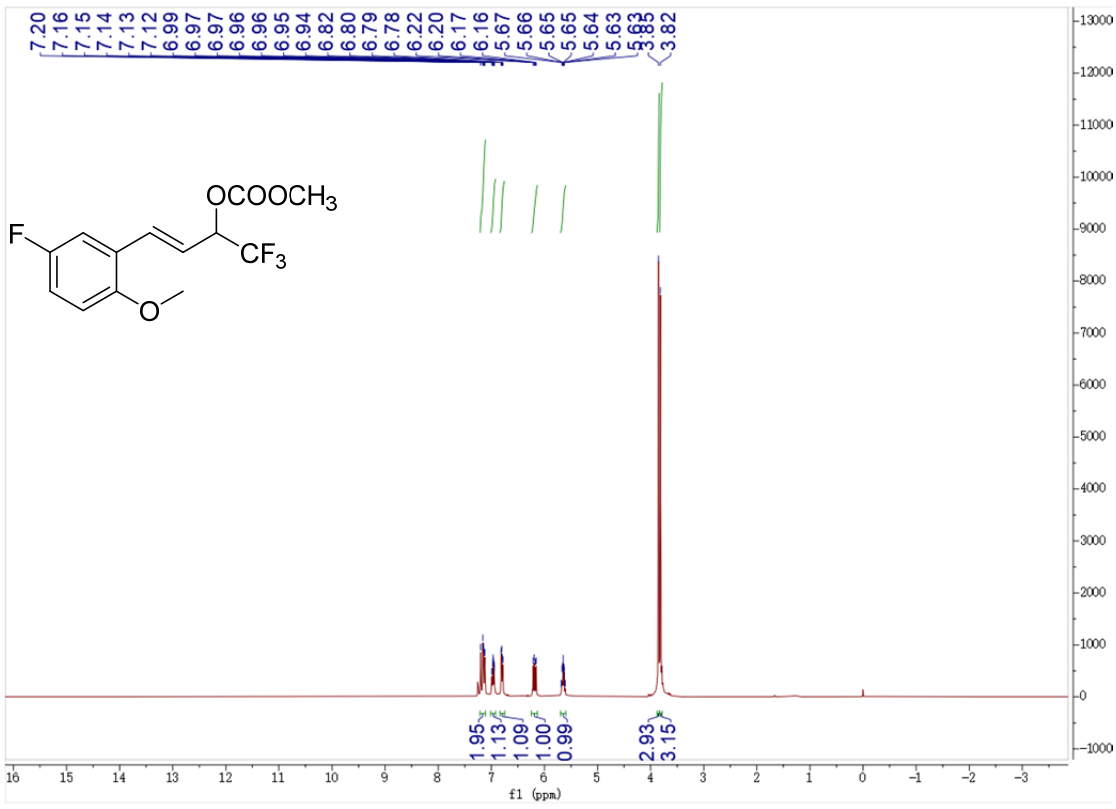
^{13}C NMR (101 MHz, $CDCl_3$) (1o)



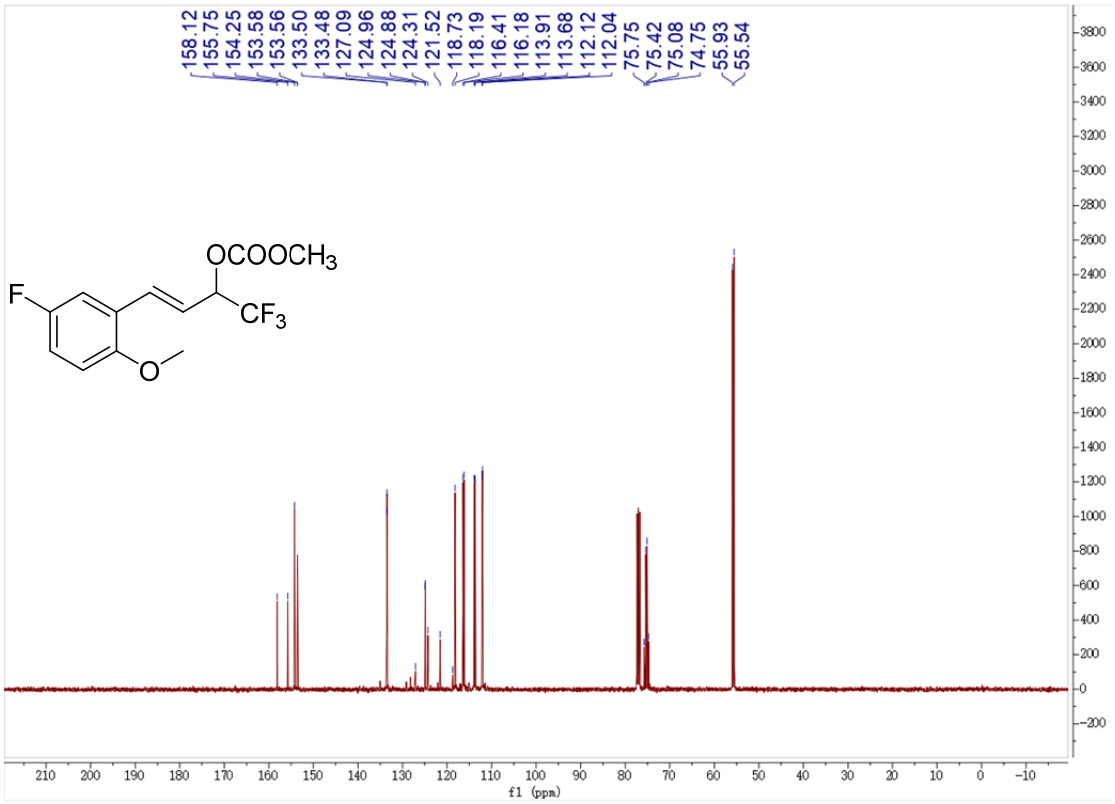
^{19}F NMR (377 MHz, $CDCl_3$) (1o)



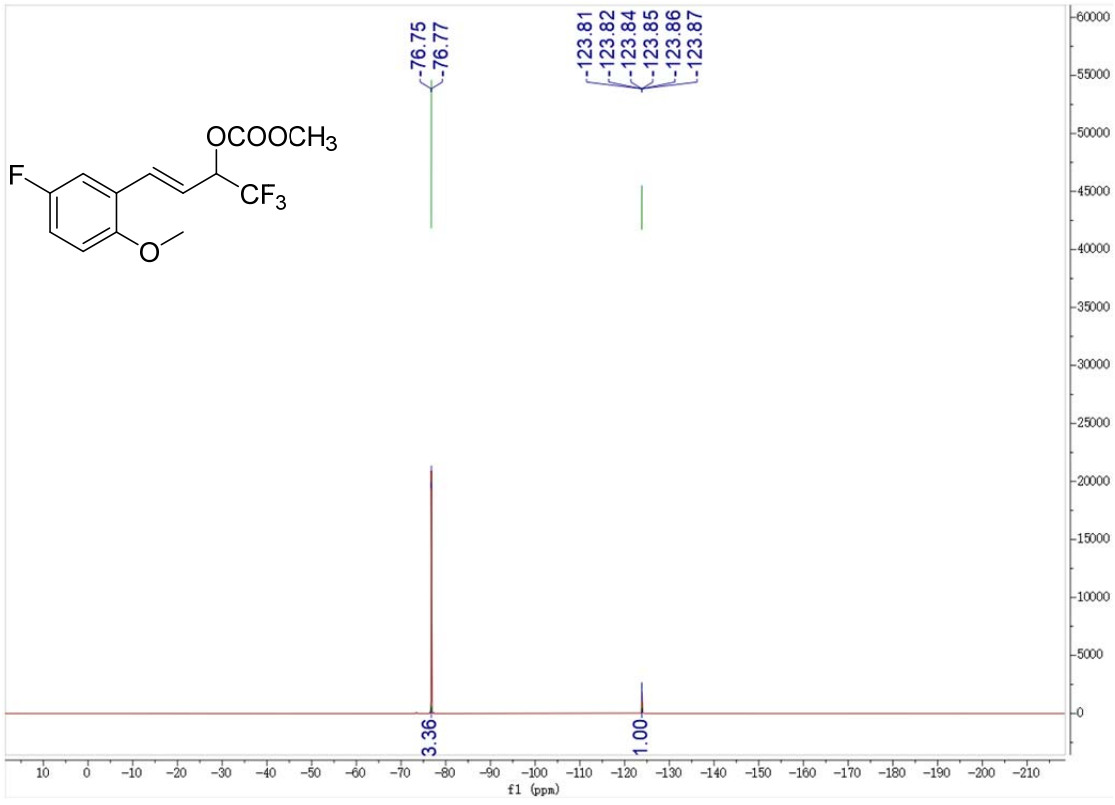
^{1}H NMR (400 MHz, $CDCl_3$) (1p)



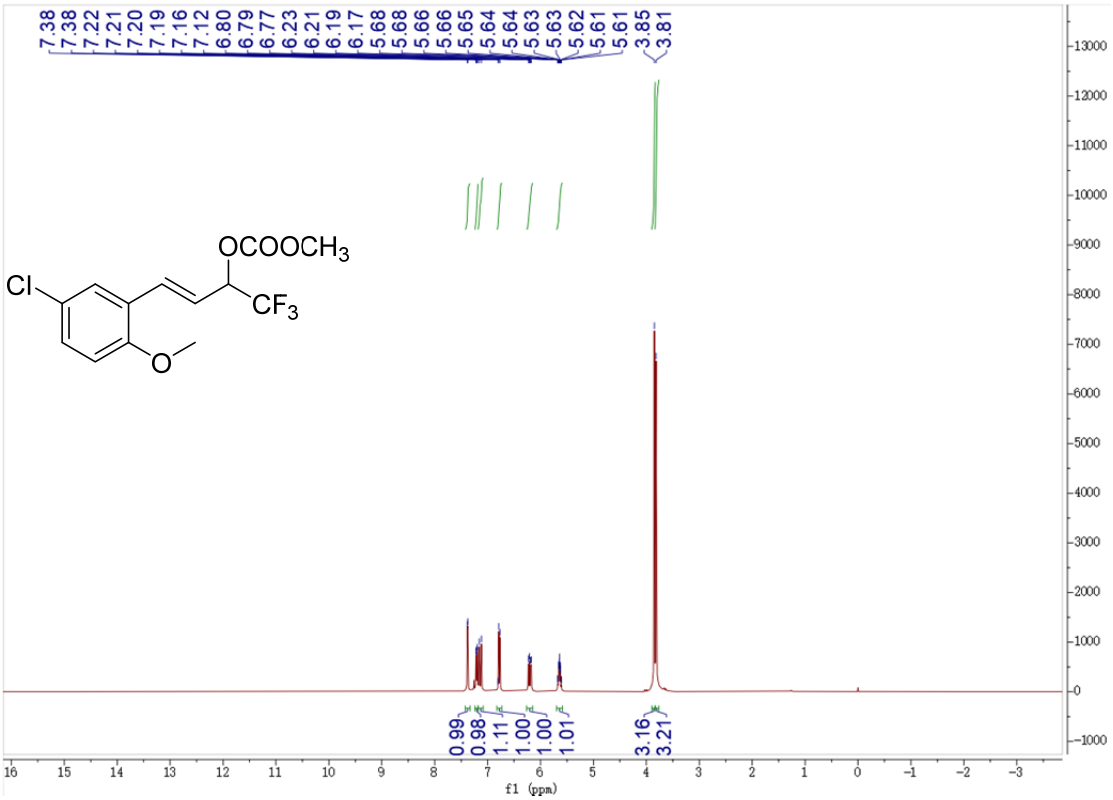
^{13}C NMR (101 MHz, $CDCl_3$) (1p)



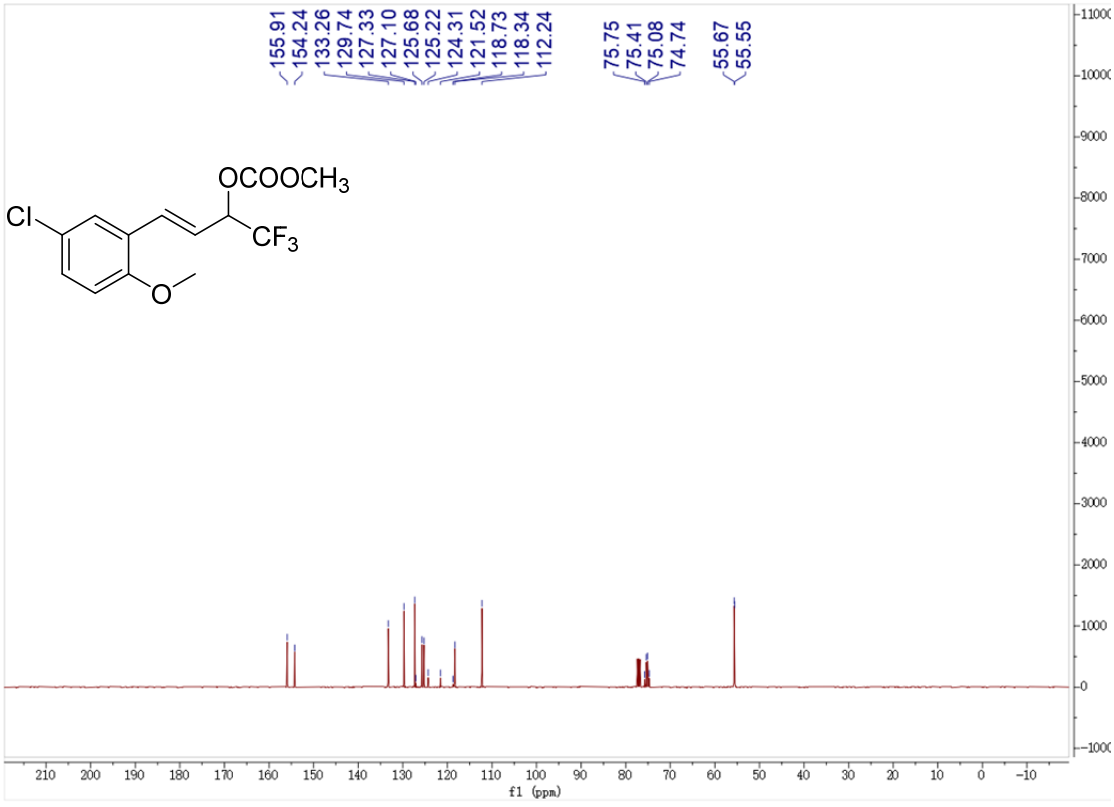
^{19}F NMR (377 MHz, $CDCl_3$) (1p)



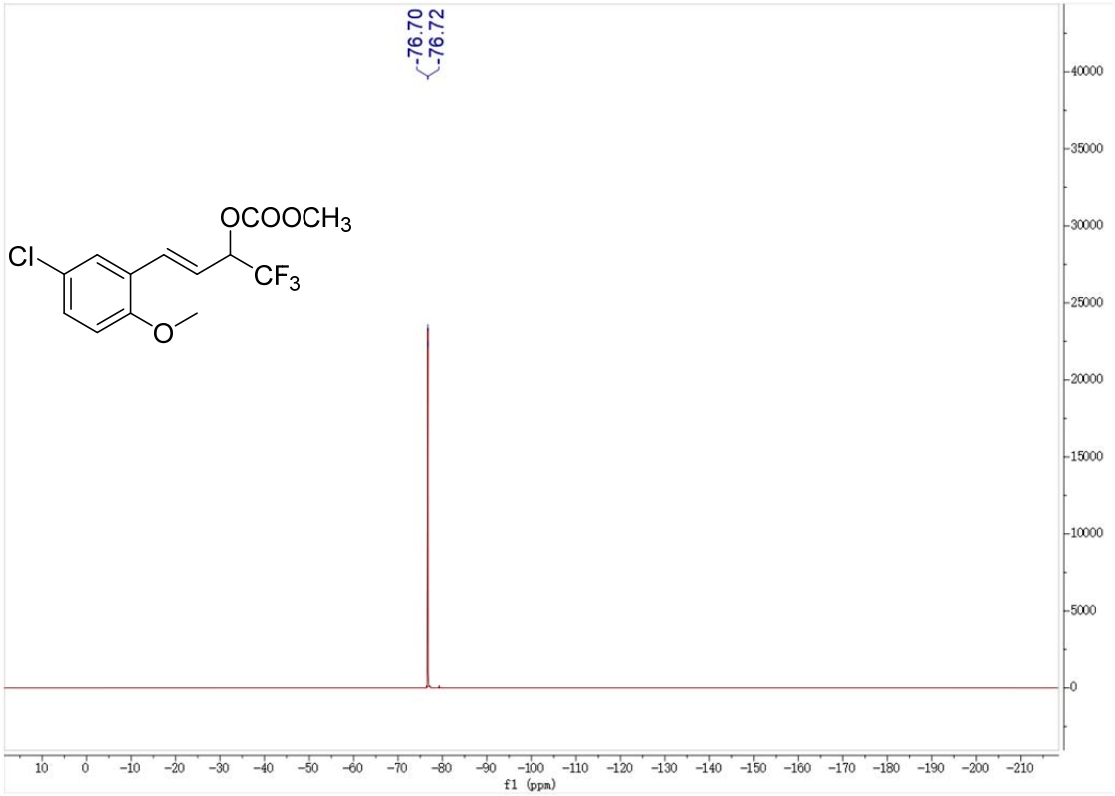
^{1}H NMR (400 MHz, $CDCl_3$) (1q)



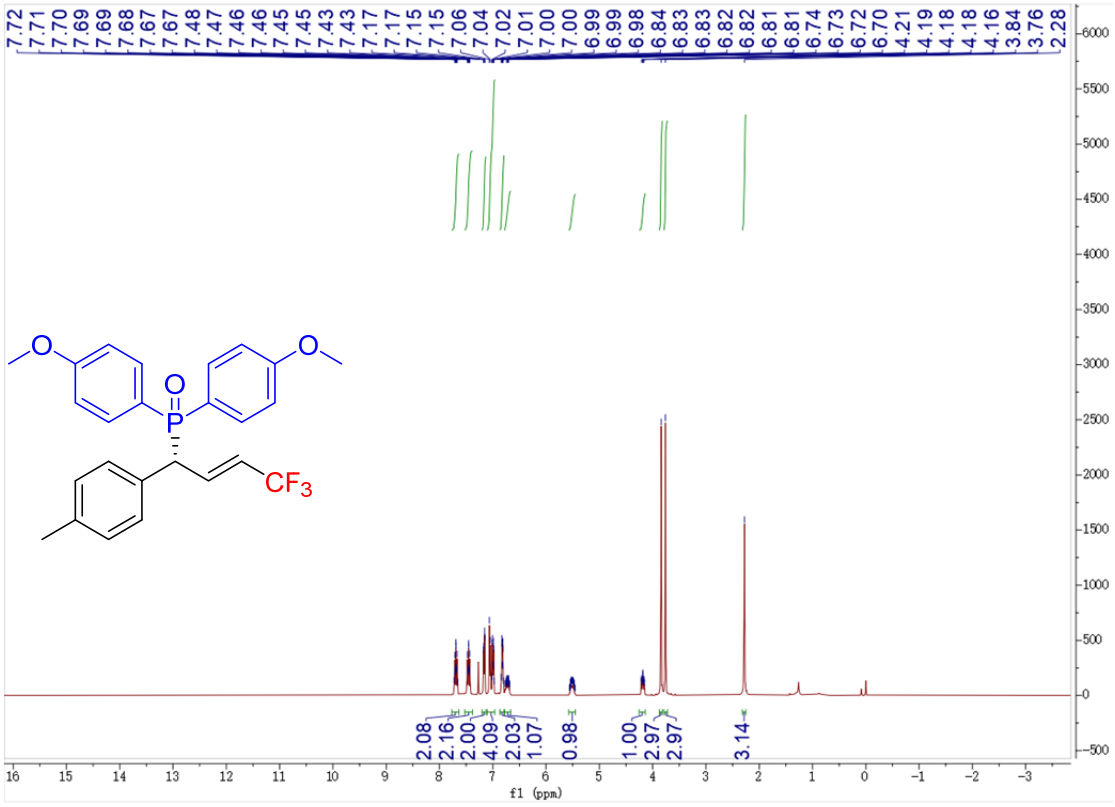
^{13}C NMR (101 MHz, $CDCl_3$) (1q)



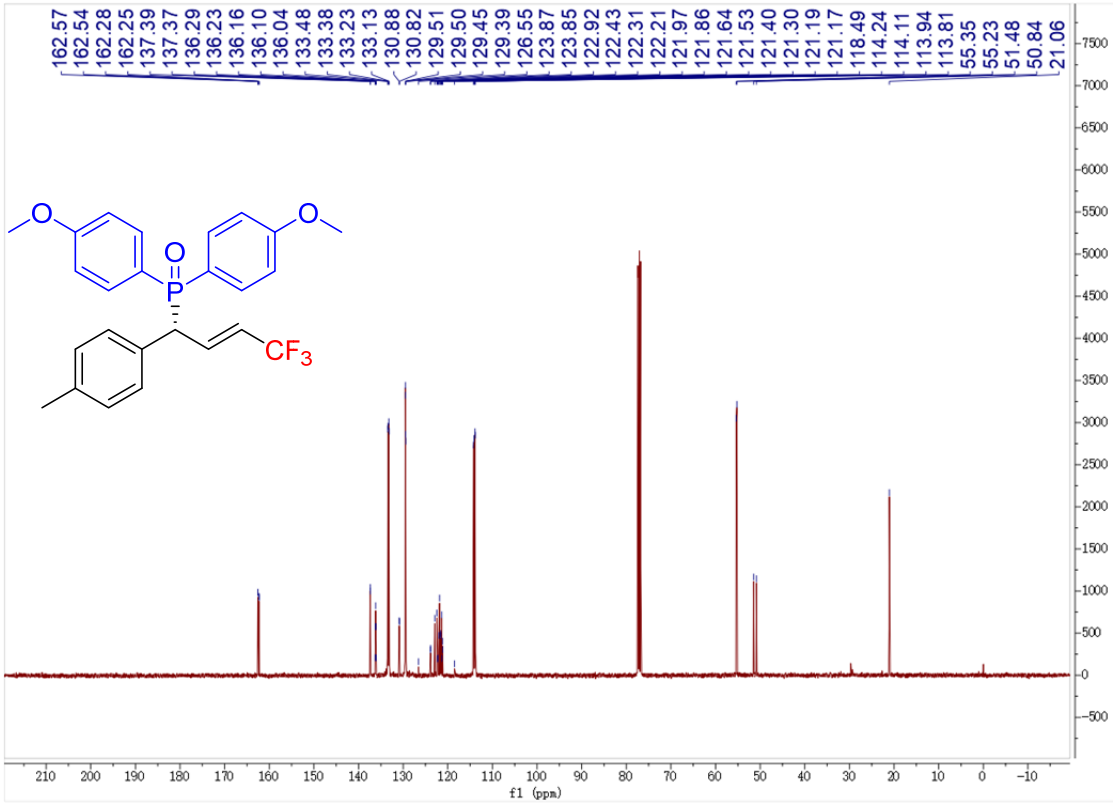
^{19}F NMR (377 MHz, $CDCl_3$) (1q)



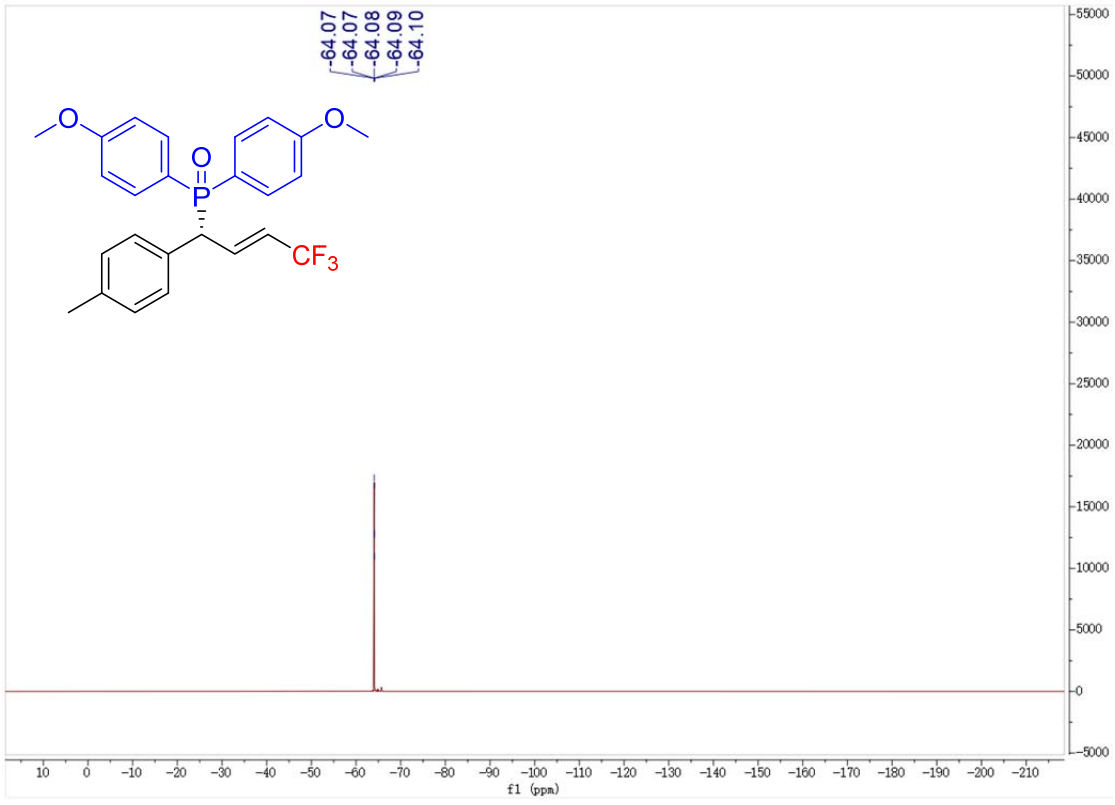
^{1}H NMR (400 MHz, $CDCl_3$) (3a)



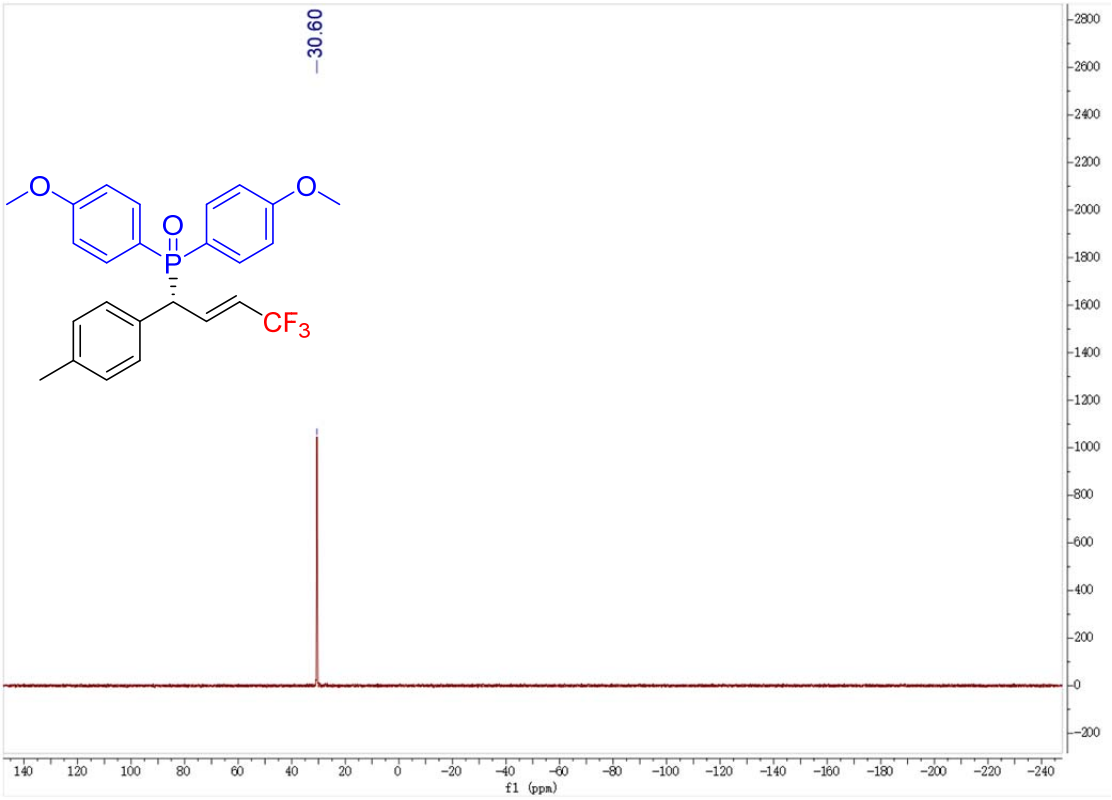
^{13}C NMR (101 MHz, $CDCl_3$) (3a)



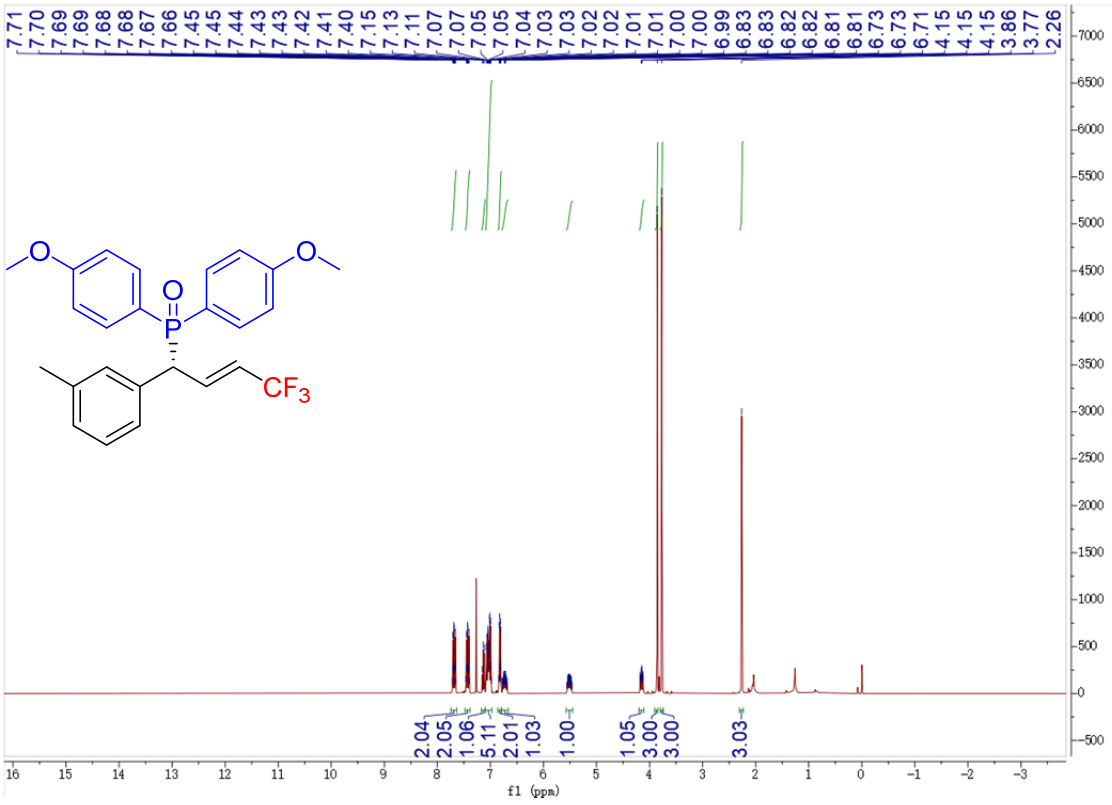
^{19}F NMR (377 MHz, $CDCl_3$) (3a)



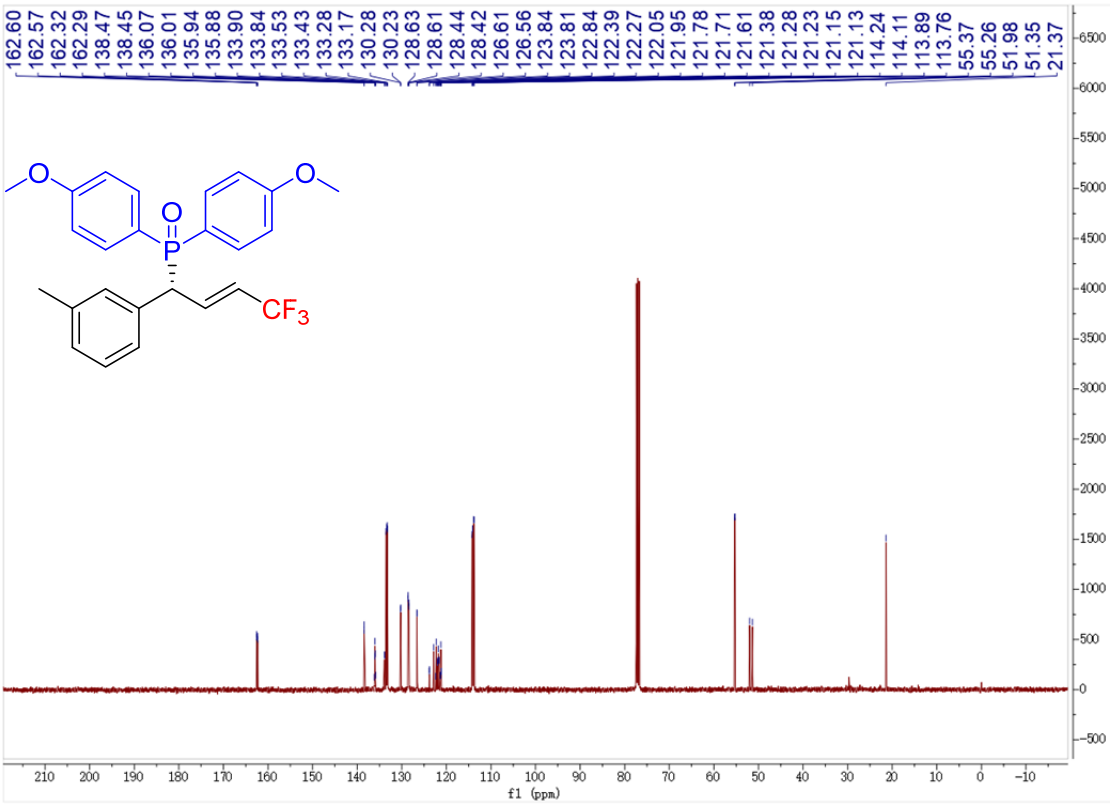
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3a)



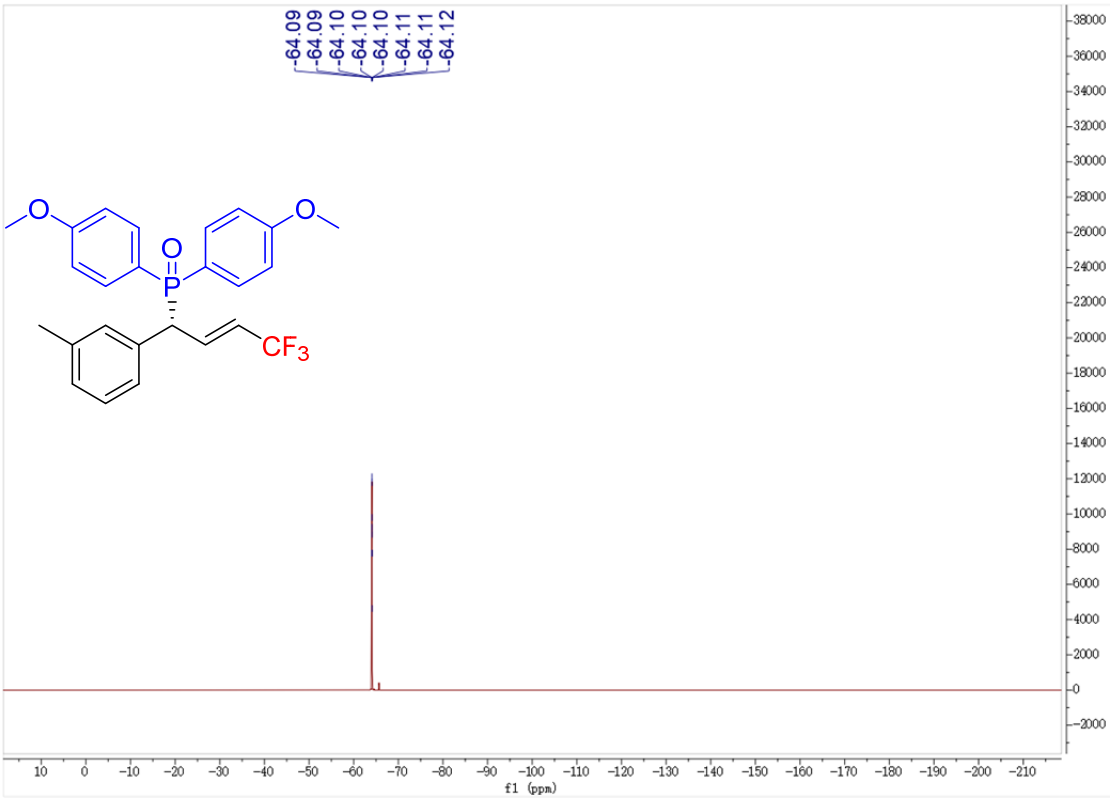
^{1}H NMR (400 MHz, $CDCl_3$) (3b)



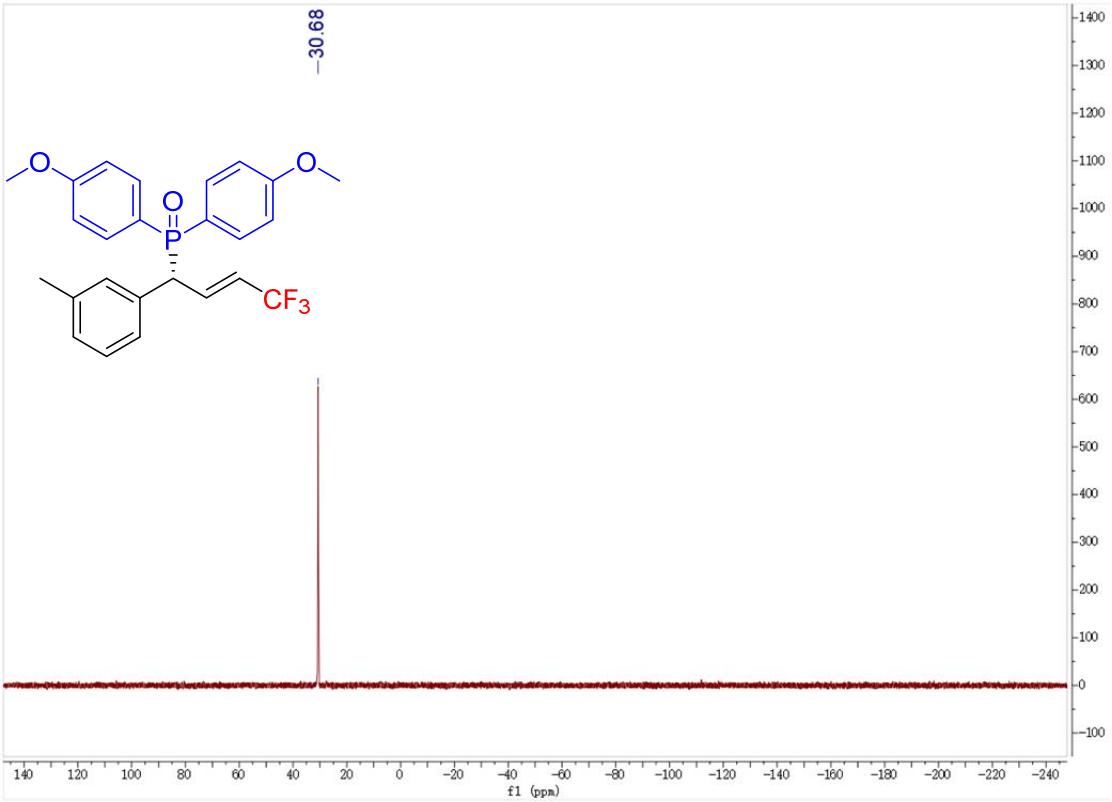
^{13}C NMR (101 MHz, $CDCl_3$) (3b)



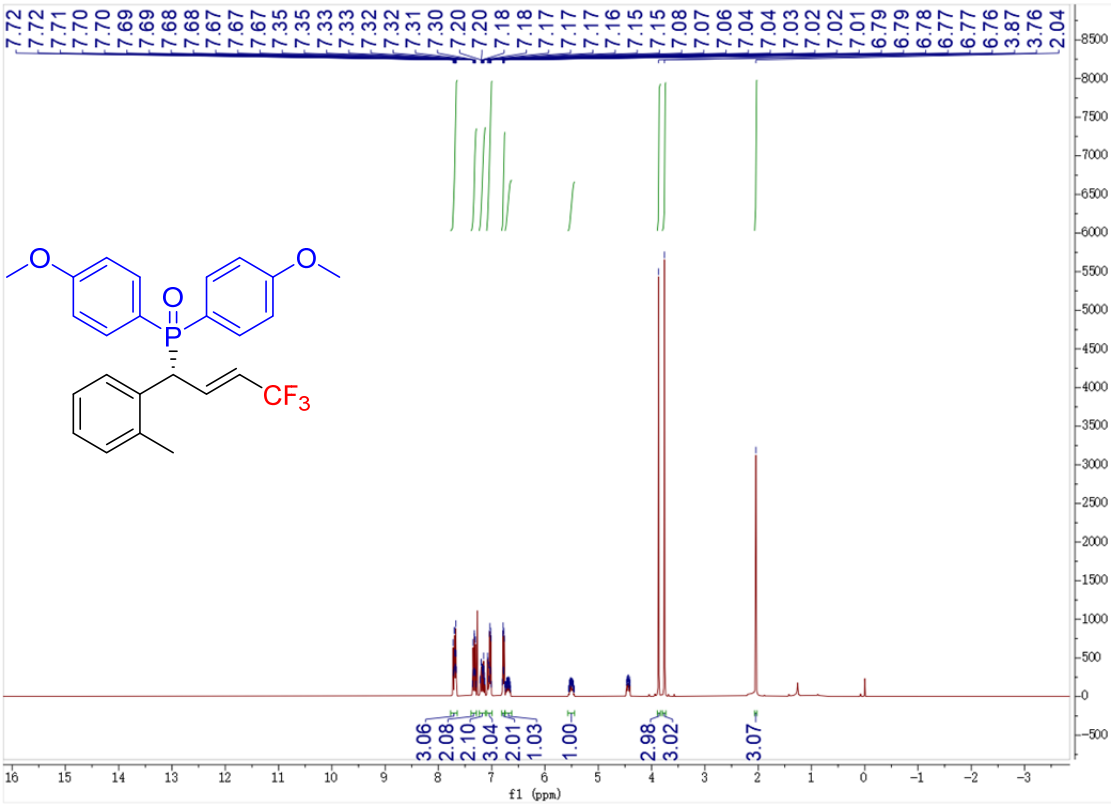
^{19}F NMR (377 MHz, $CDCl_3$) (3b)



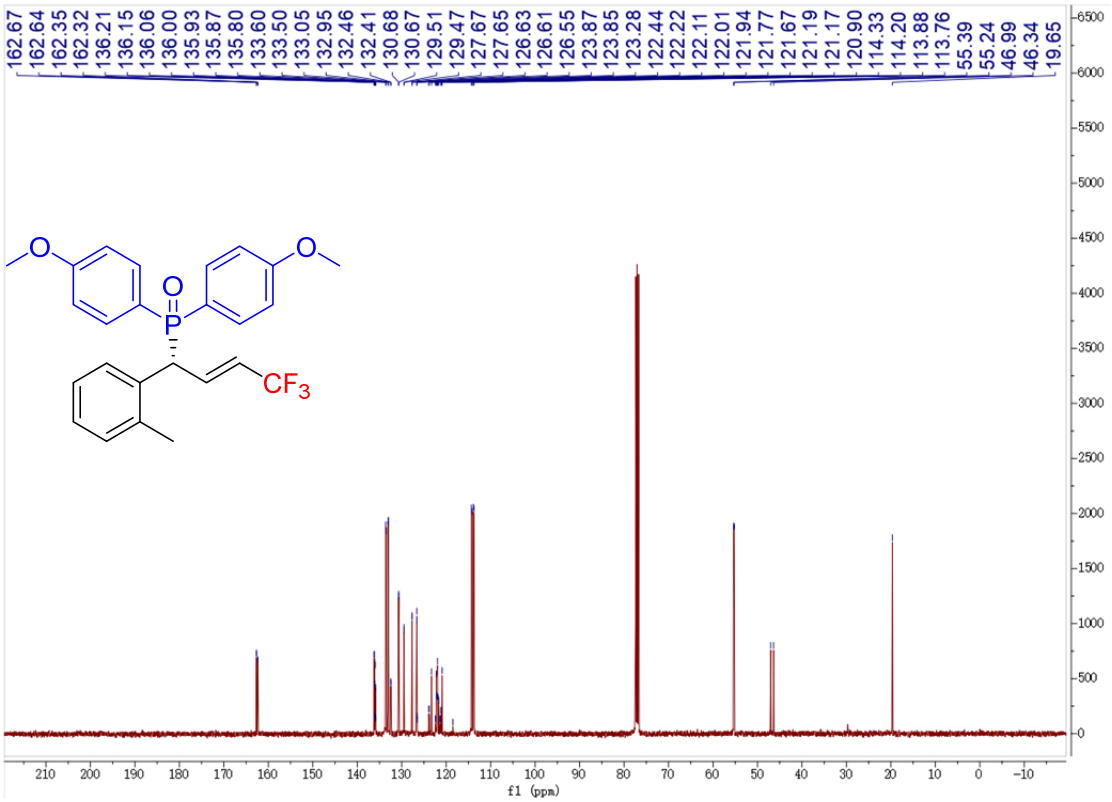
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3b)



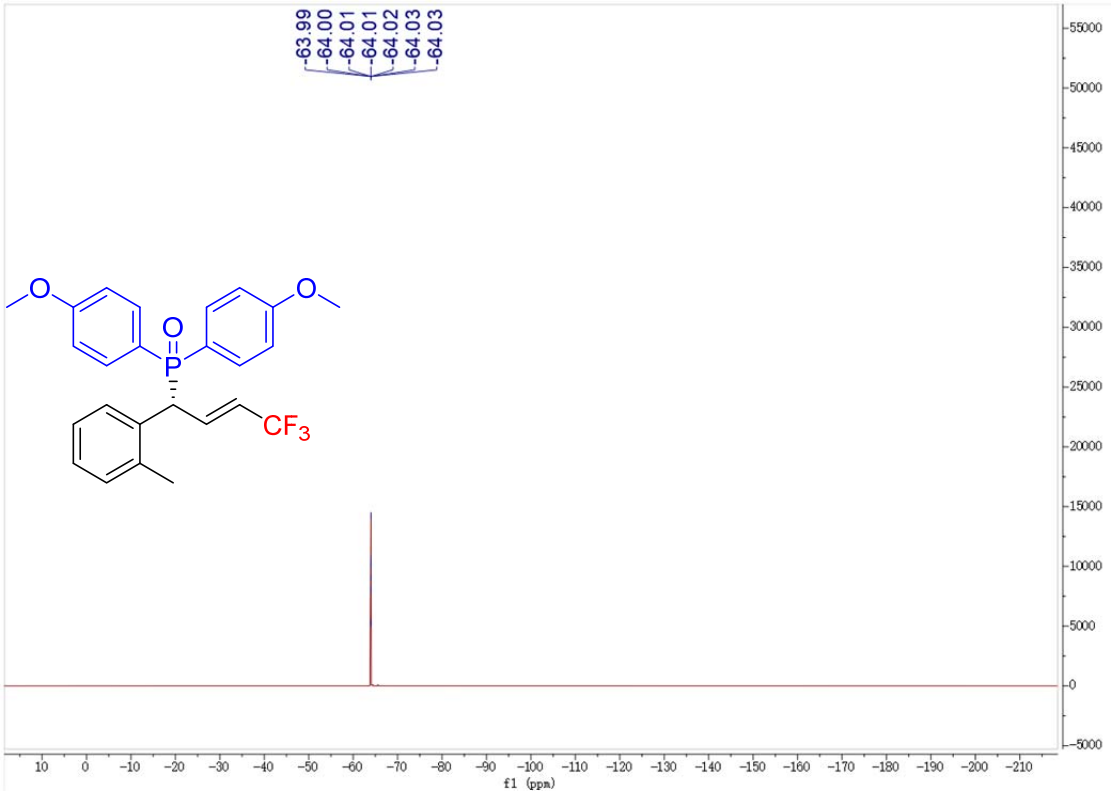
^{1}H NMR (400 MHz, $CDCl_3$) (3c)



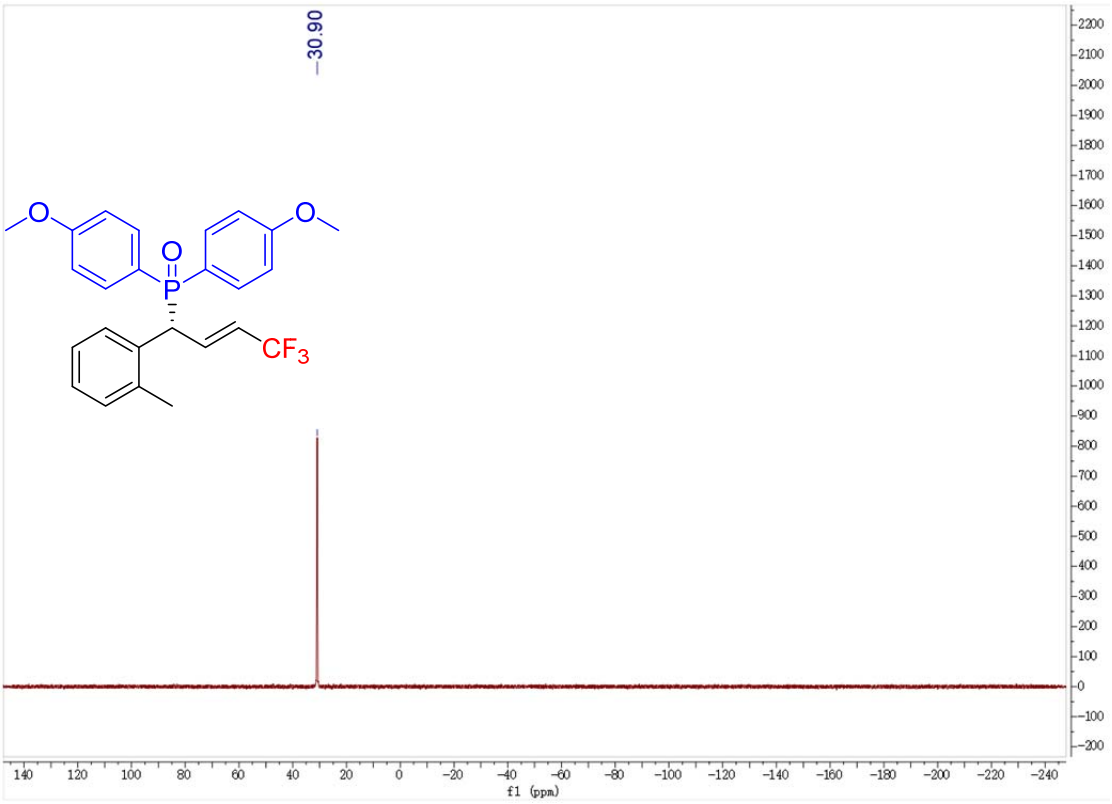
^{13}C NMR (101 MHz, $CDCl_3$) (3c)



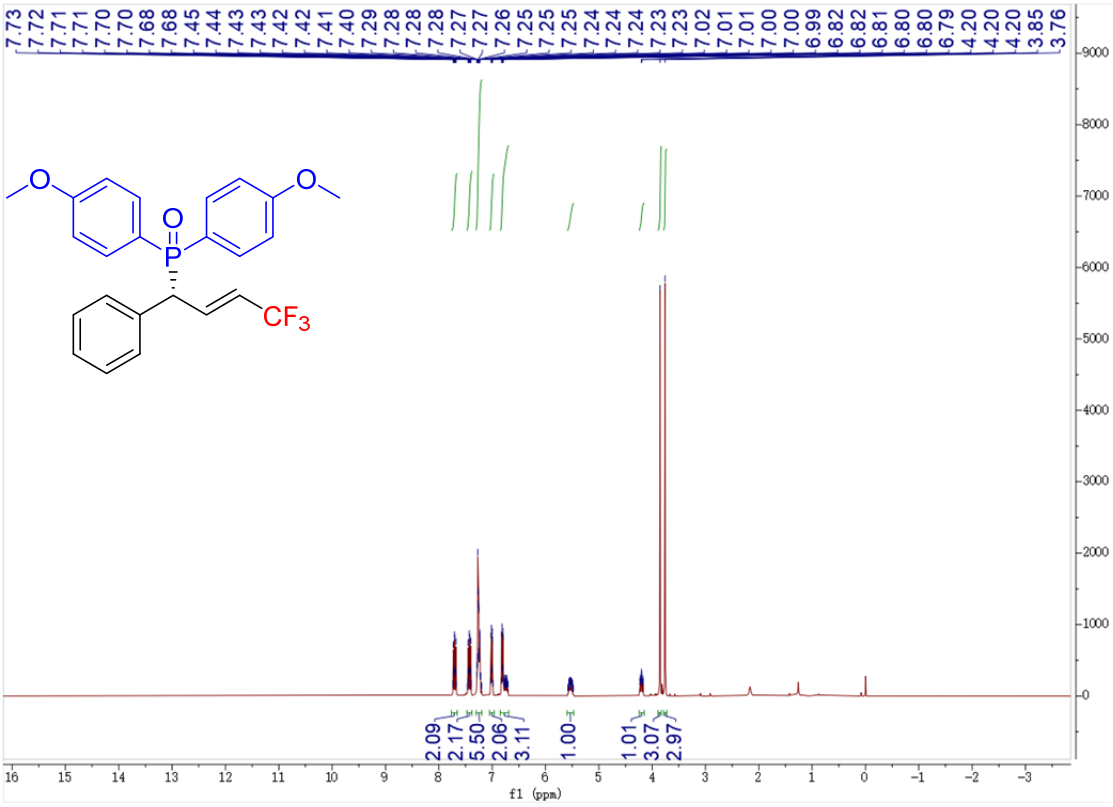
^{19}F NMR (377 MHz, $CDCl_3$) (3c)



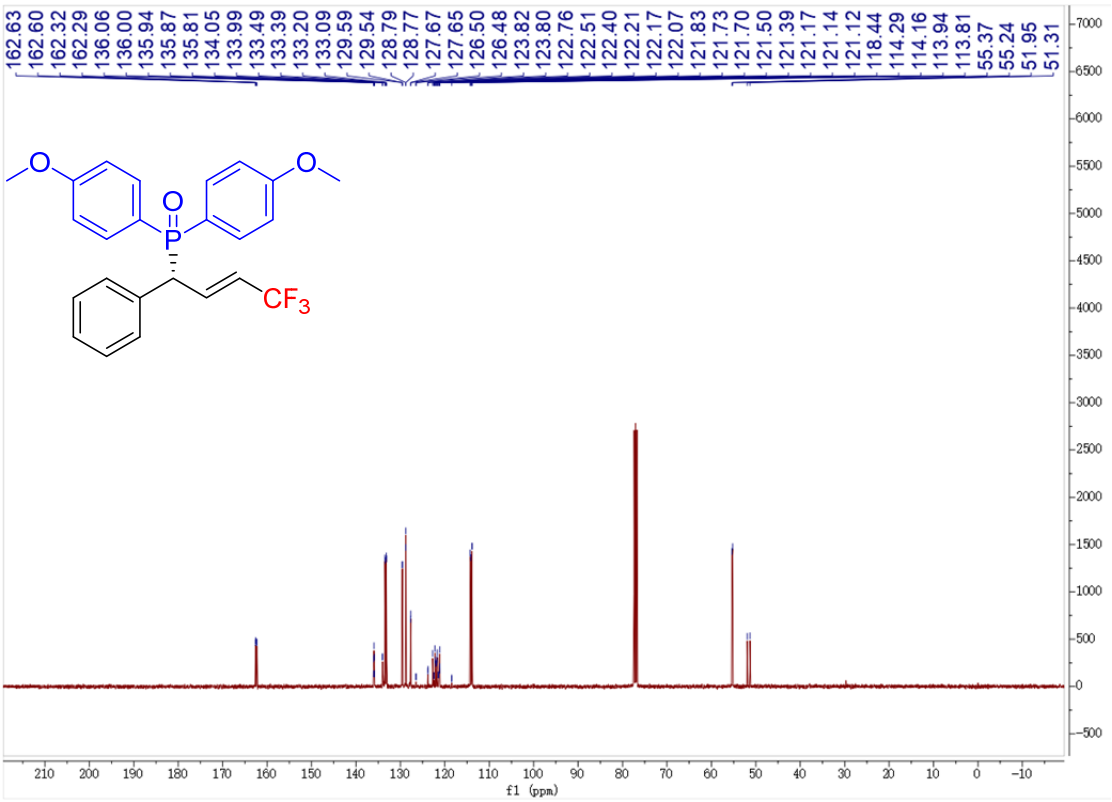
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3c)



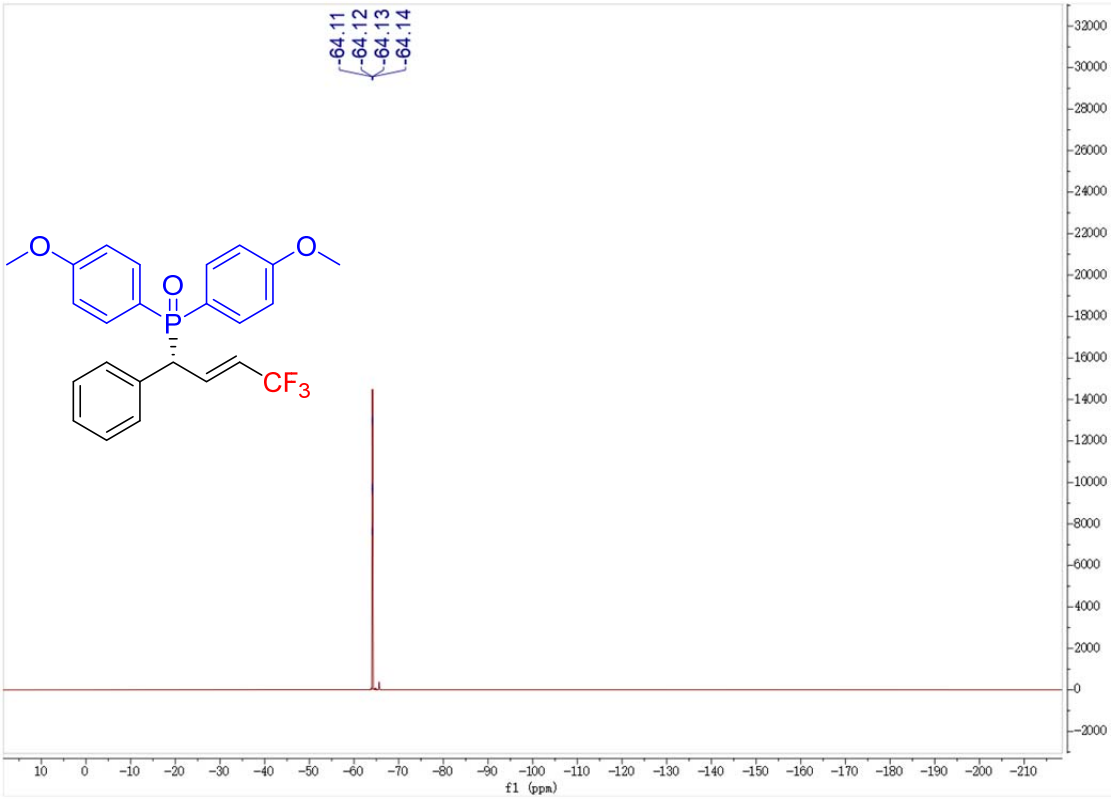
^{1}H NMR (400 MHz, $CDCl_3$) (3d)



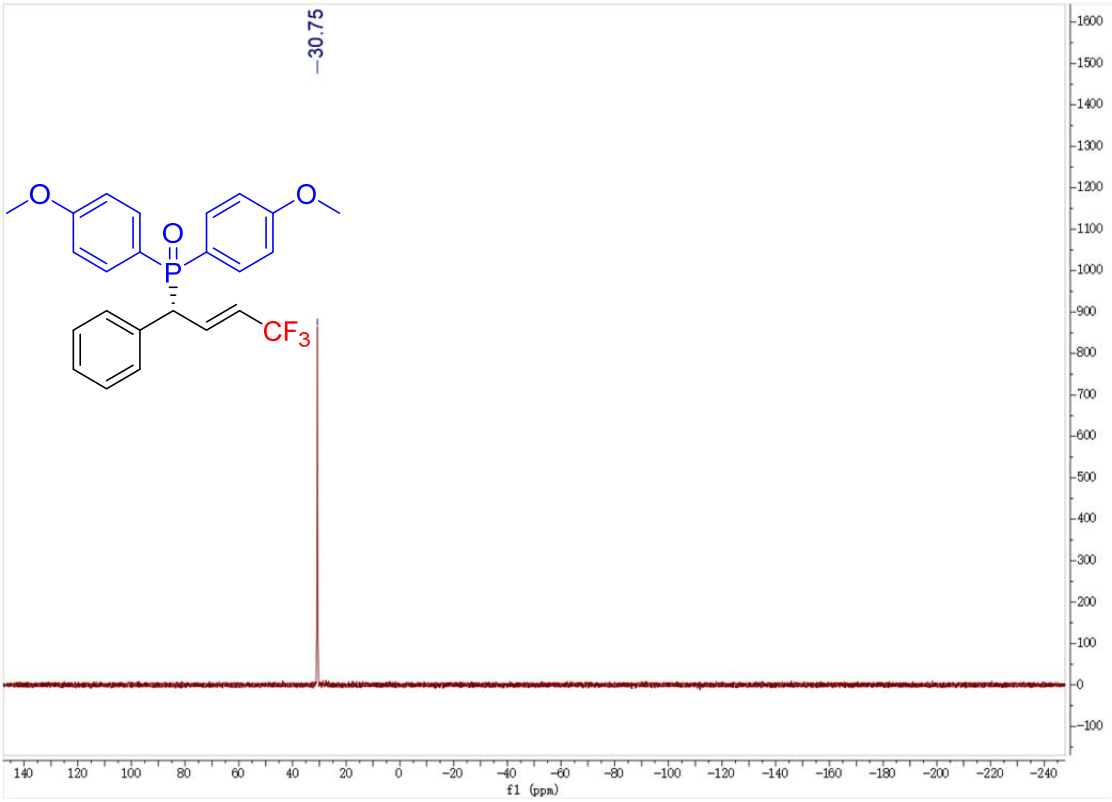
^{13}C NMR (101 MHz, $CDCl_3$) (3d)



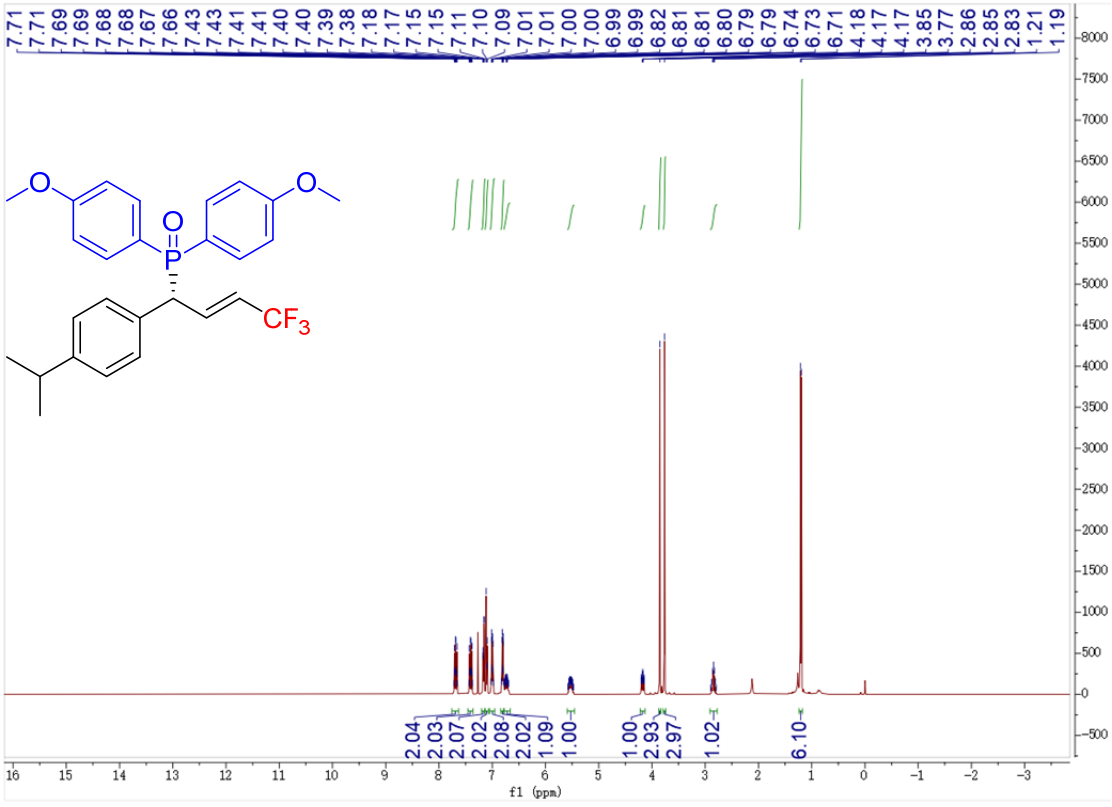
^{19}F NMR (377 MHz, $CDCl_3$) (3d)



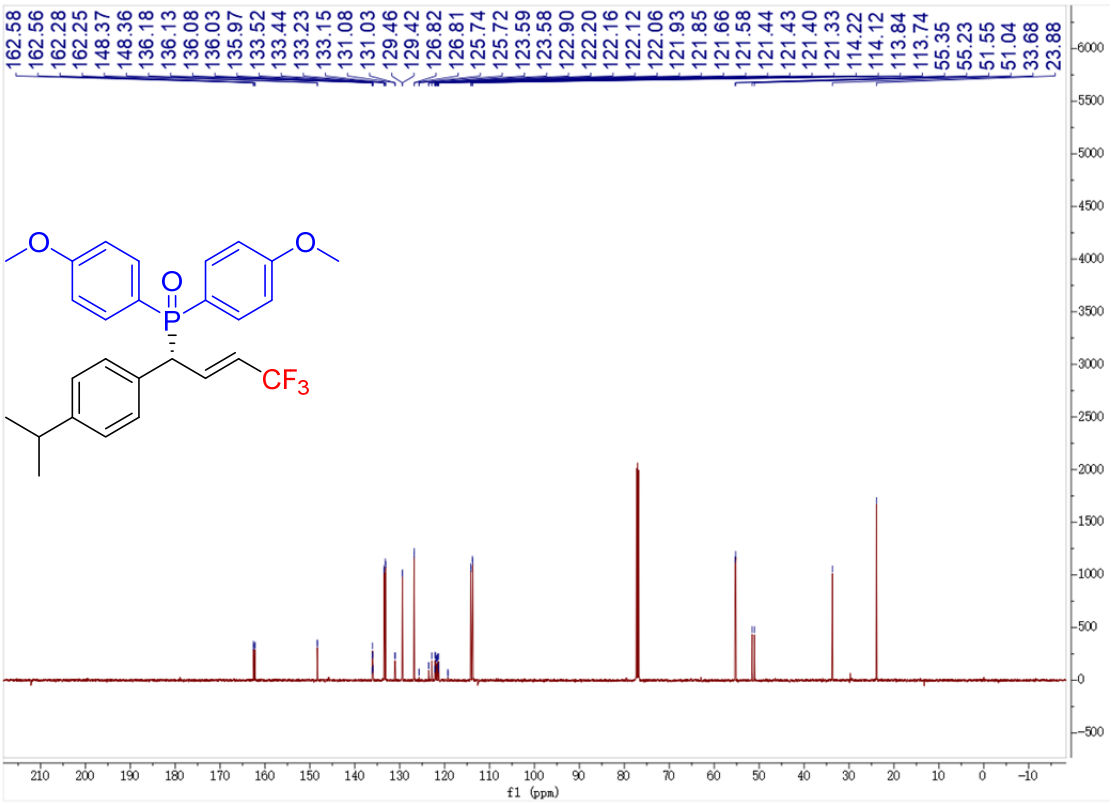
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3d)



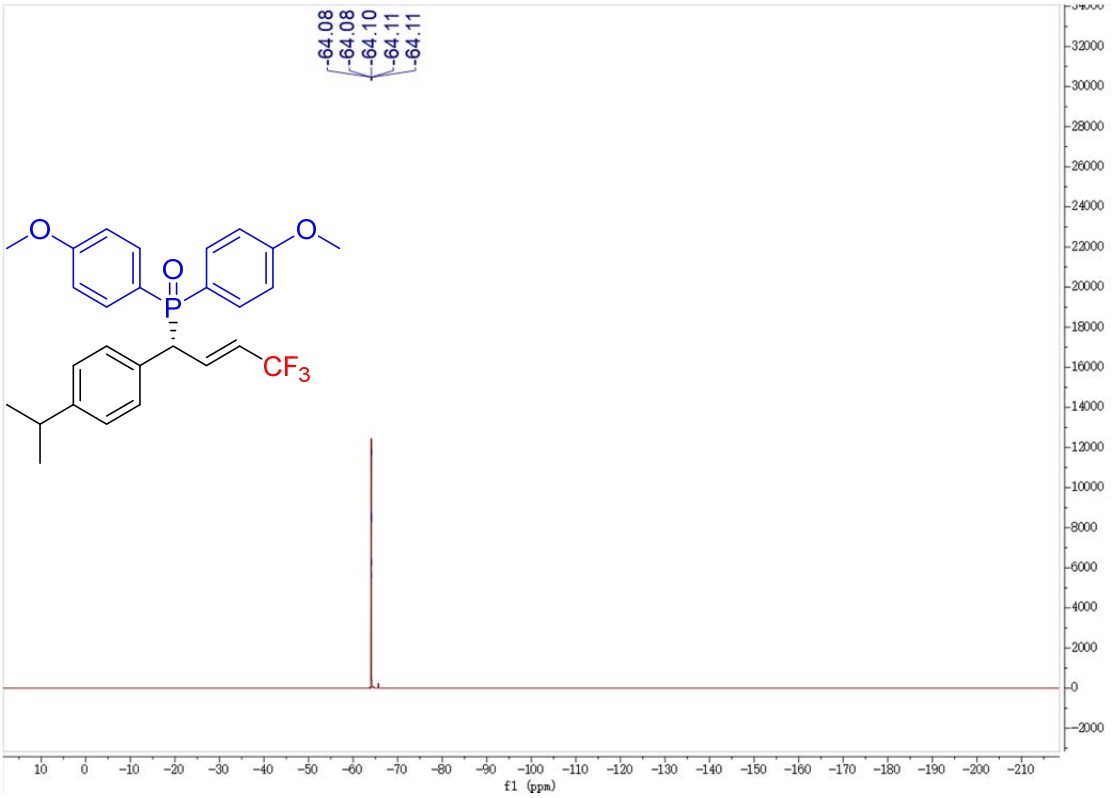
^{1}H NMR (400 MHz, $CDCl_3$) (3e)



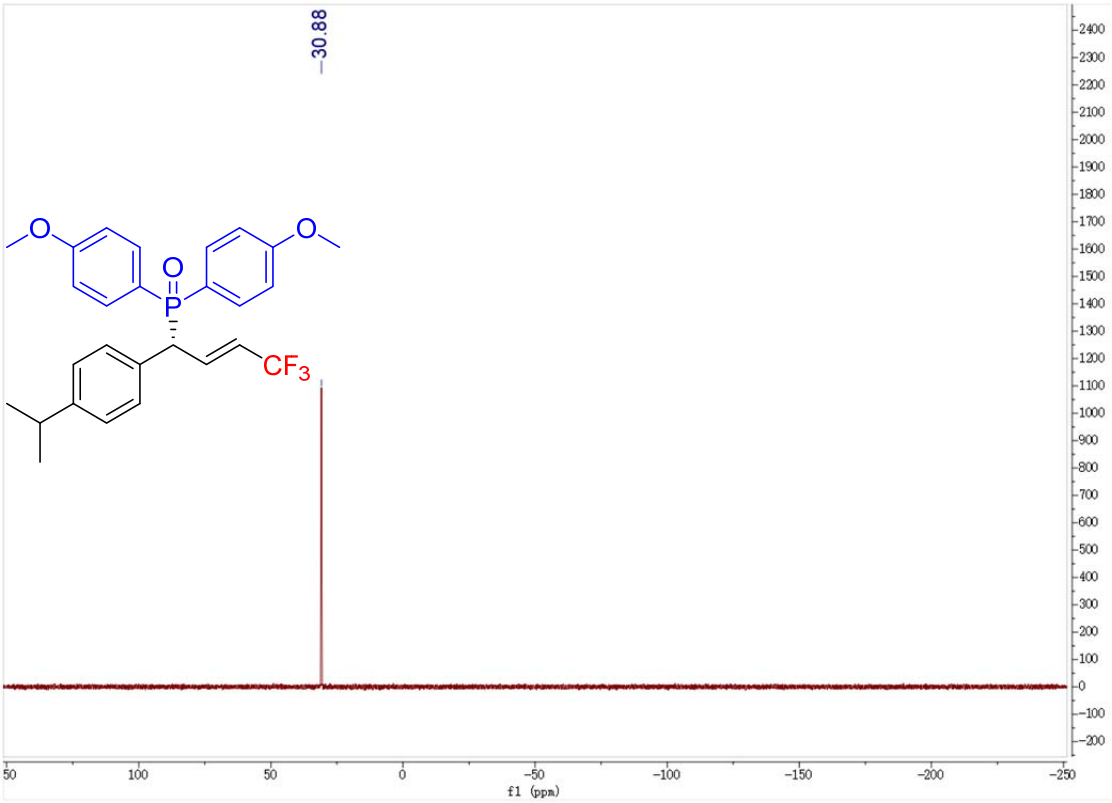
^{13}C NMR (126 MHz, $CDCl_3$) (3e)



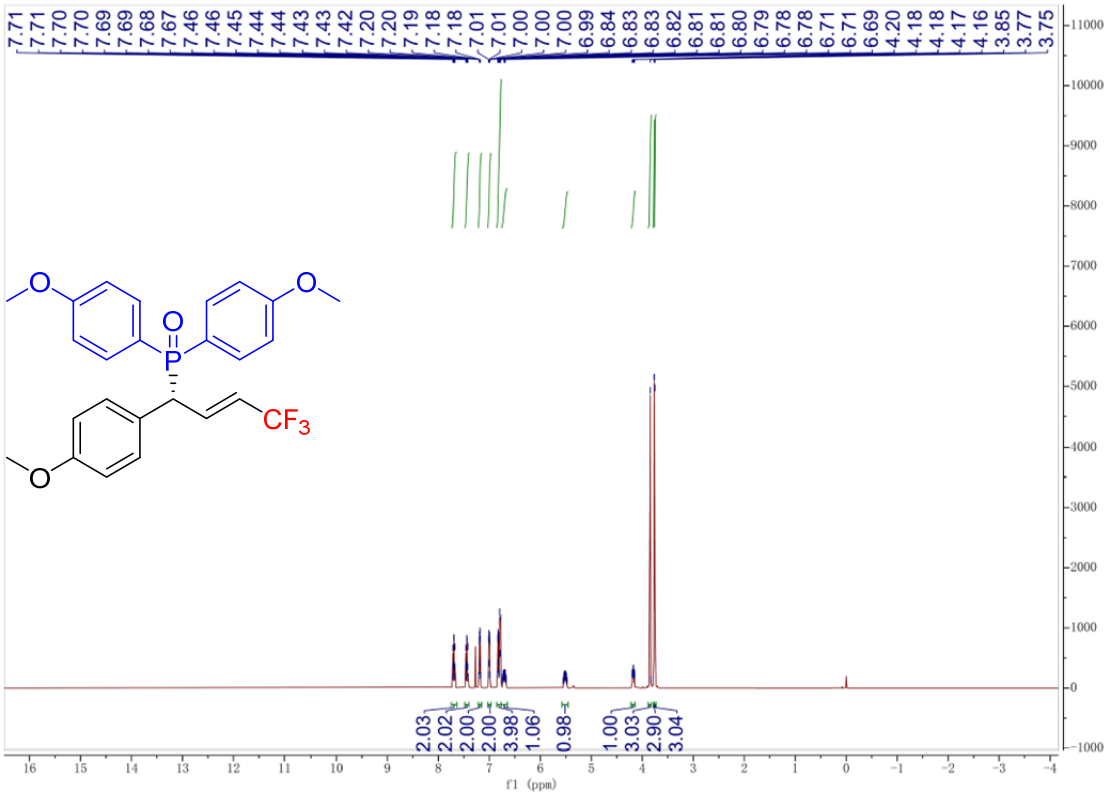
^{19}F NMR (377 MHz, $CDCl_3$) (3e)



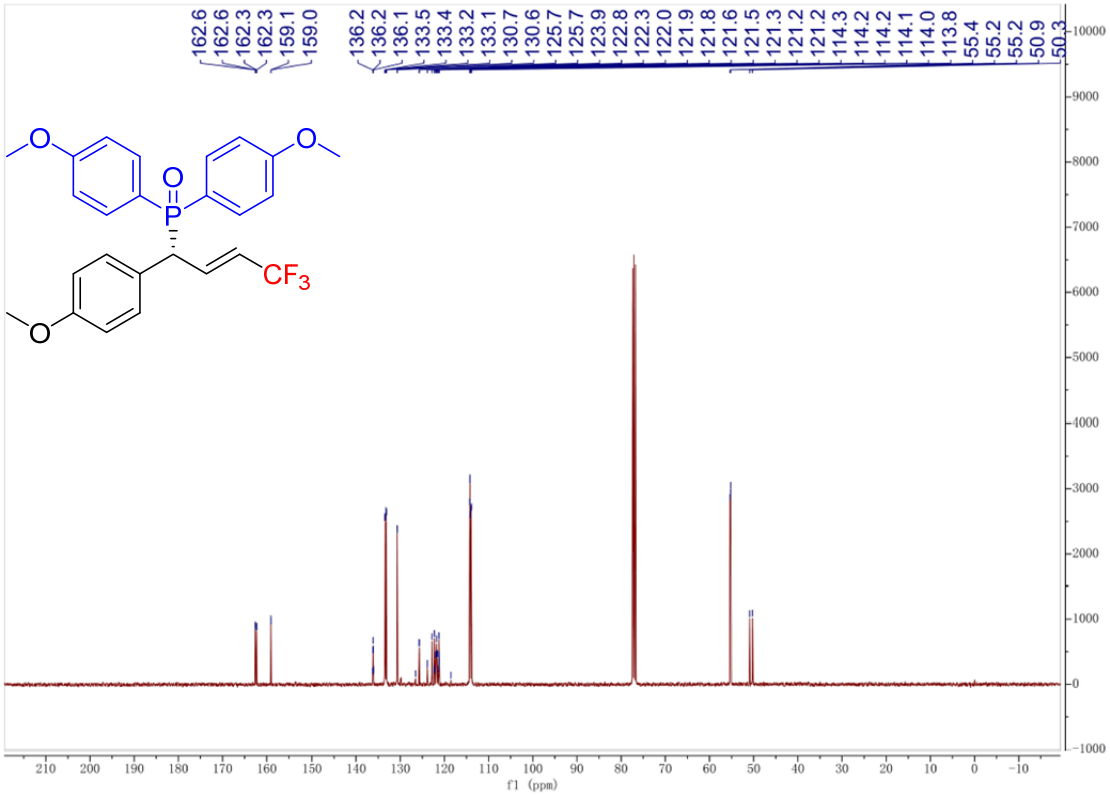
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) (3e)



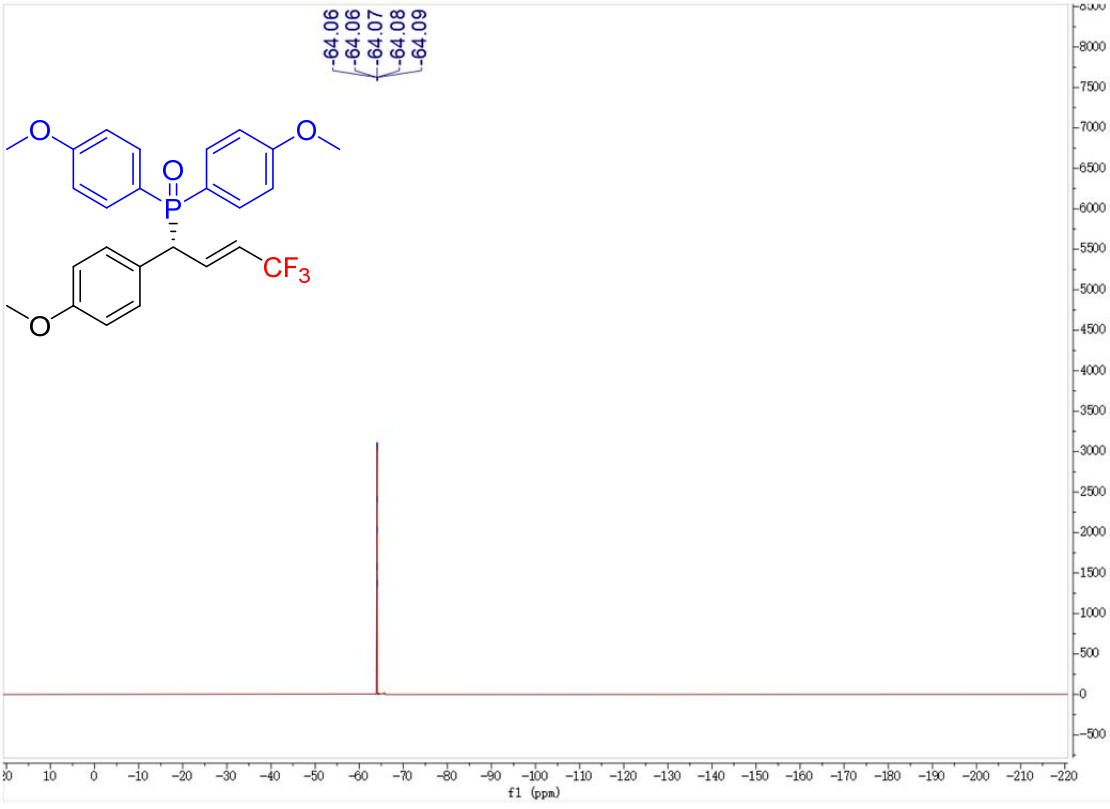
^{1}H NMR (500 MHz, $CDCl_3$) (3f)



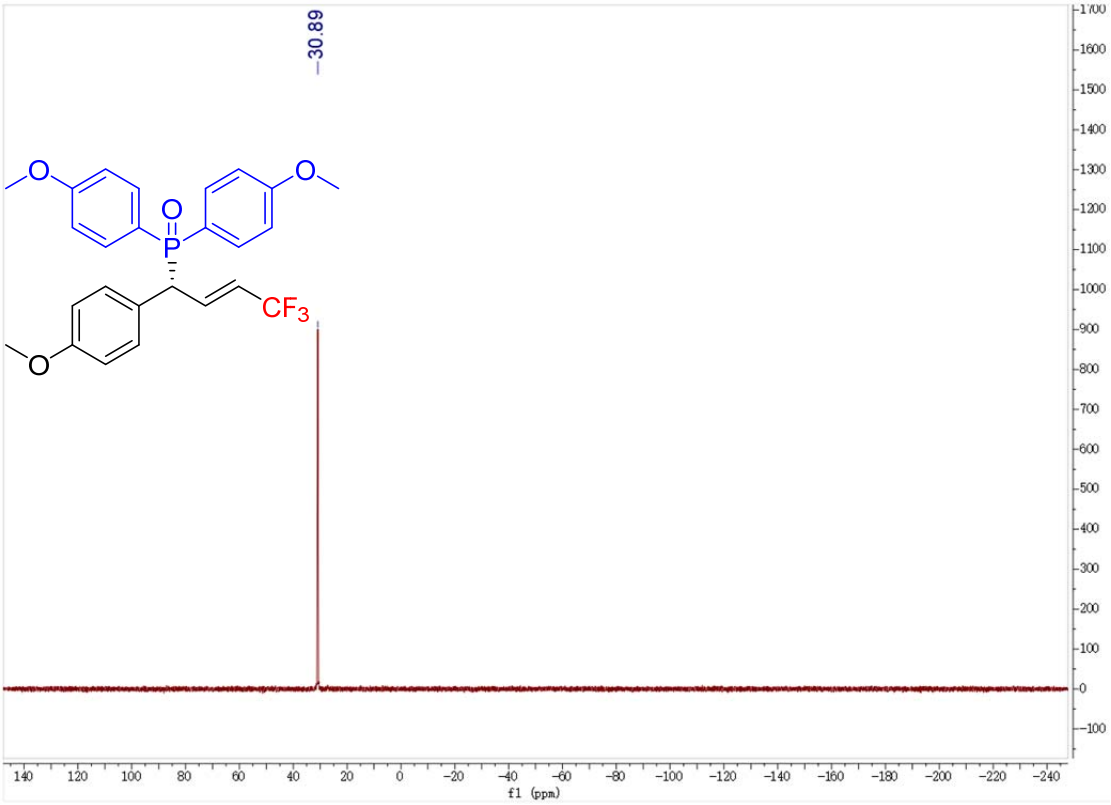
^{13}C NMR (101 MHz, $CDCl_3$) (3f)



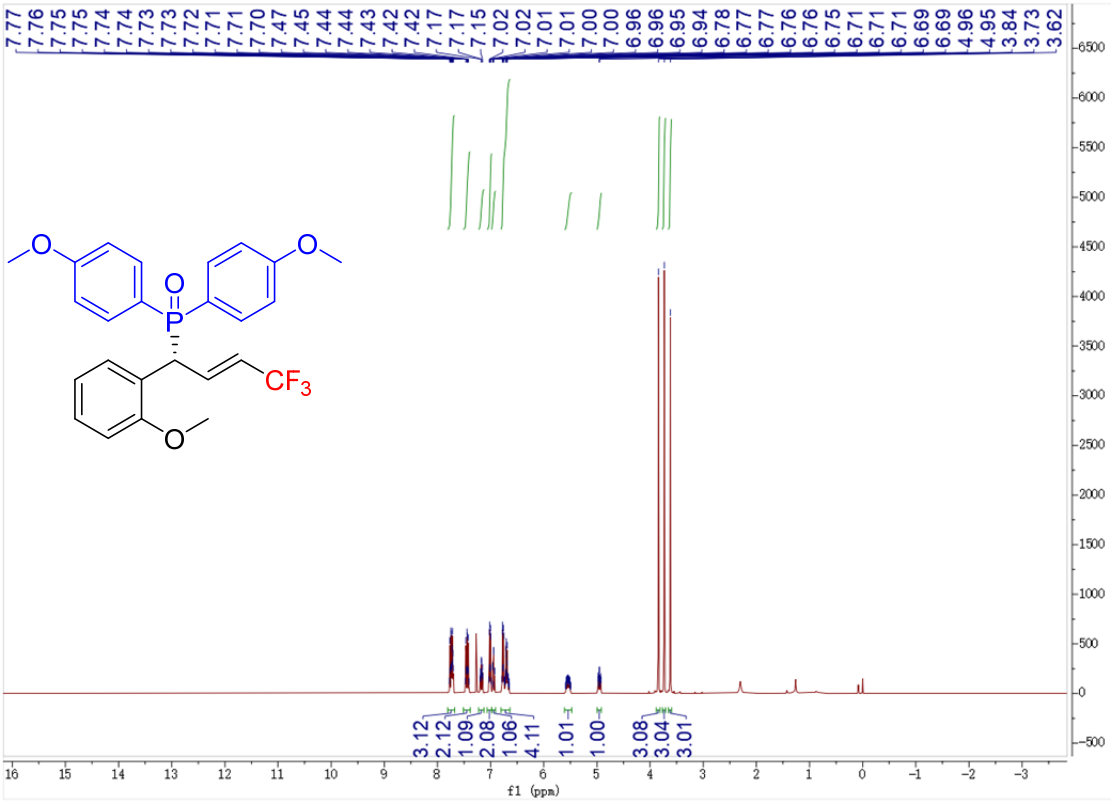
^{19}F NMR (470 MHz, $CDCl_3$) (3f)



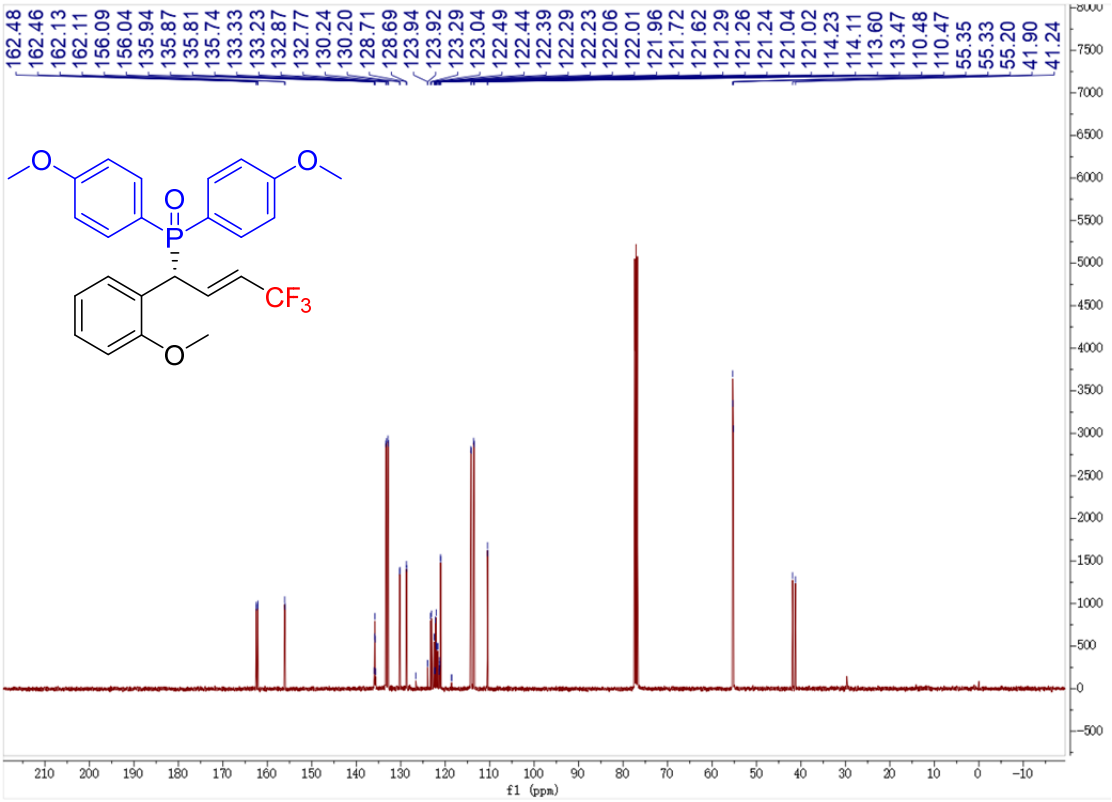
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3f)



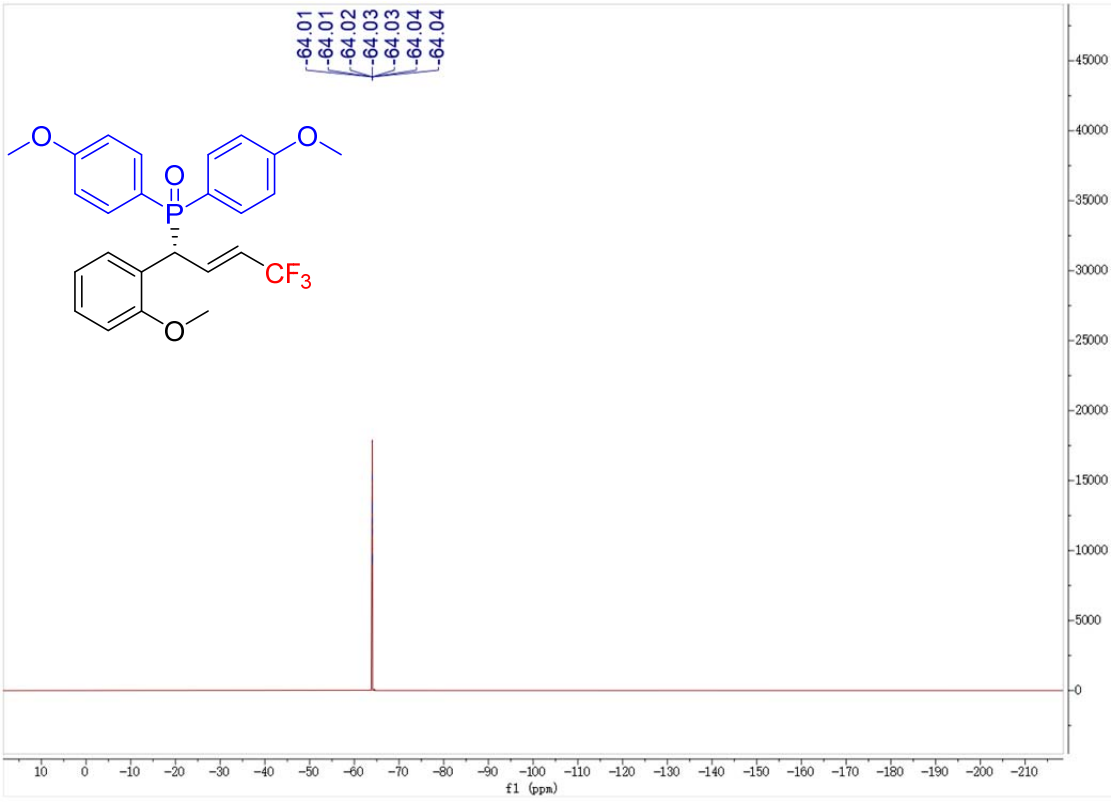
^{1}H NMR (400 MHz, $CDCl_3$) (3g)



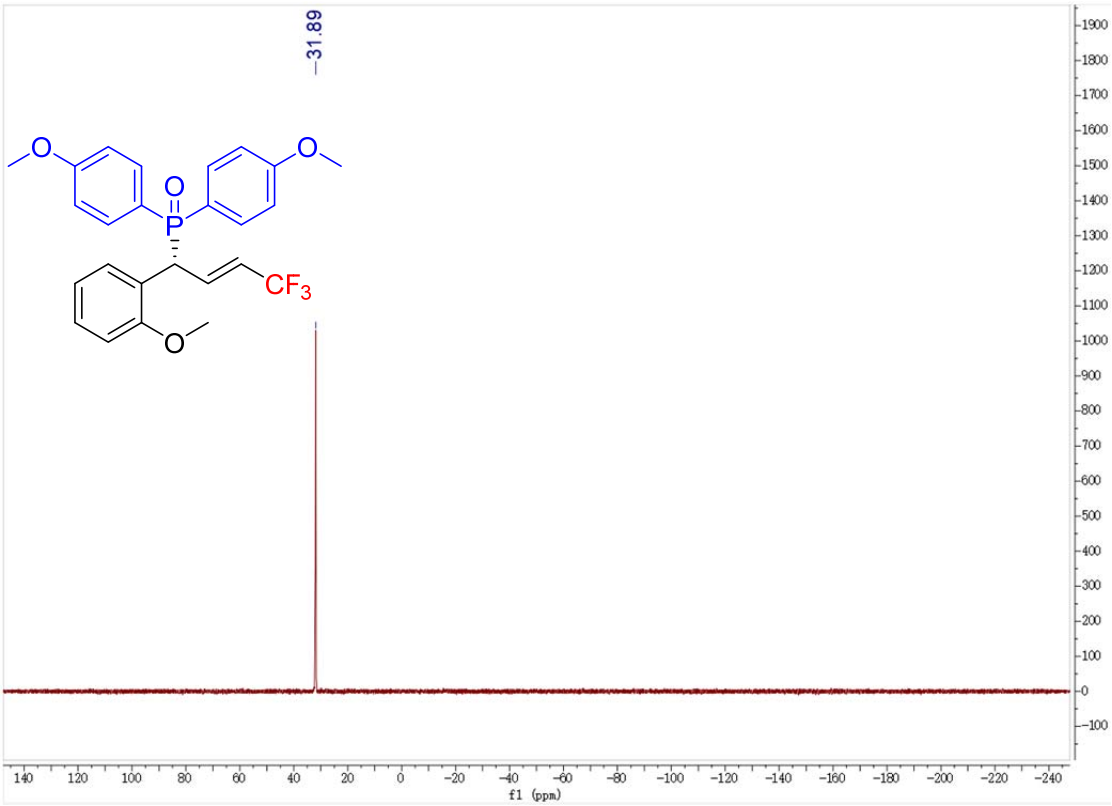
^{13}C NMR (101 MHz, $CDCl_3$) (3g)



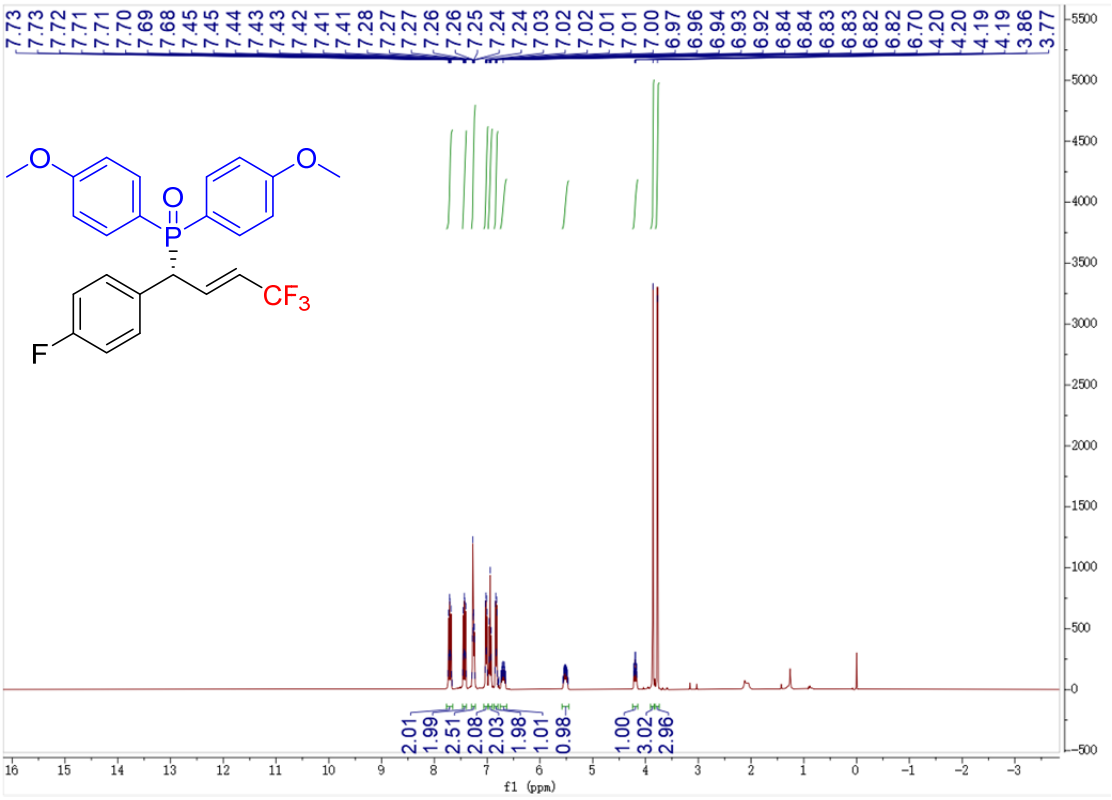
^{19}F NMR (377 MHz, $CDCl_3$) (3g)



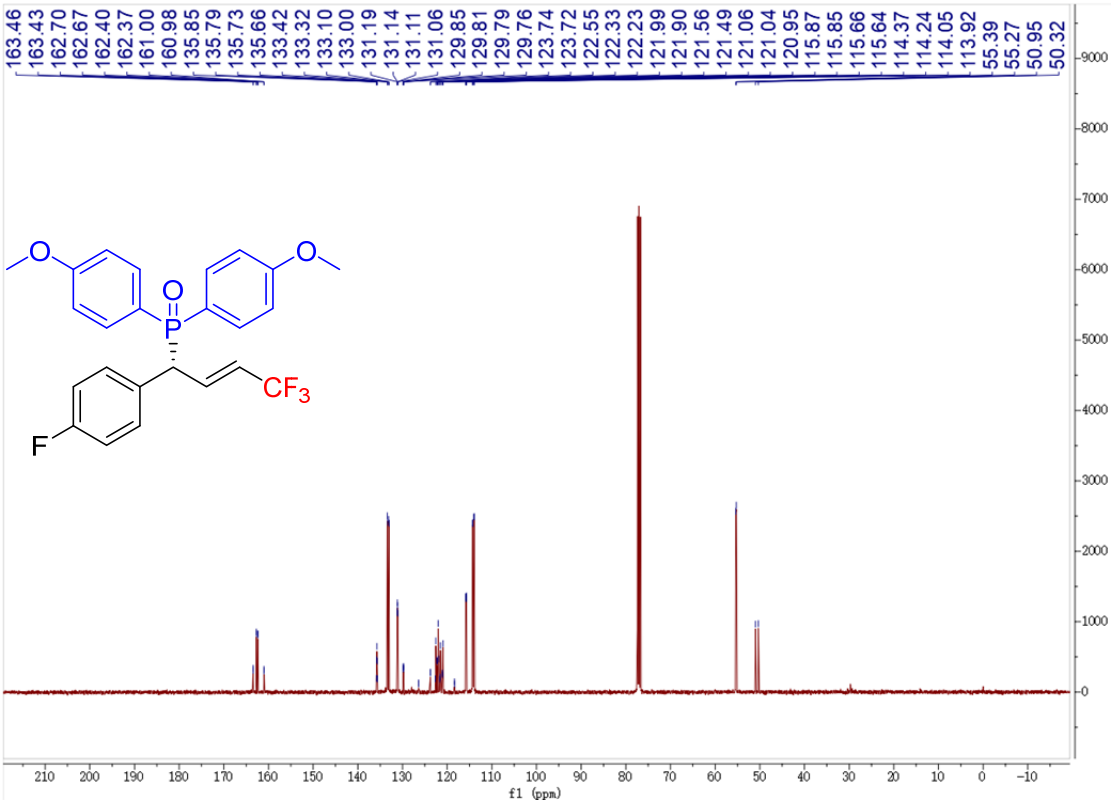
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3g)



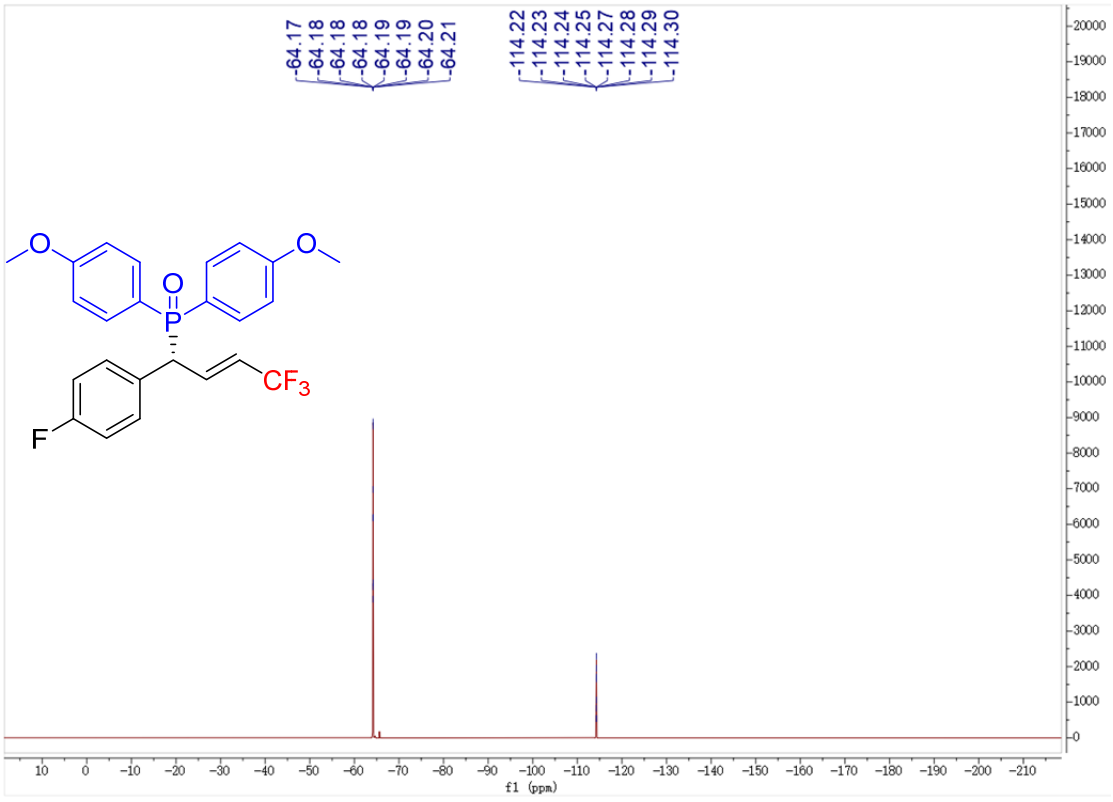
^{1}H NMR (400 MHz, $CDCl_3$) (3h)



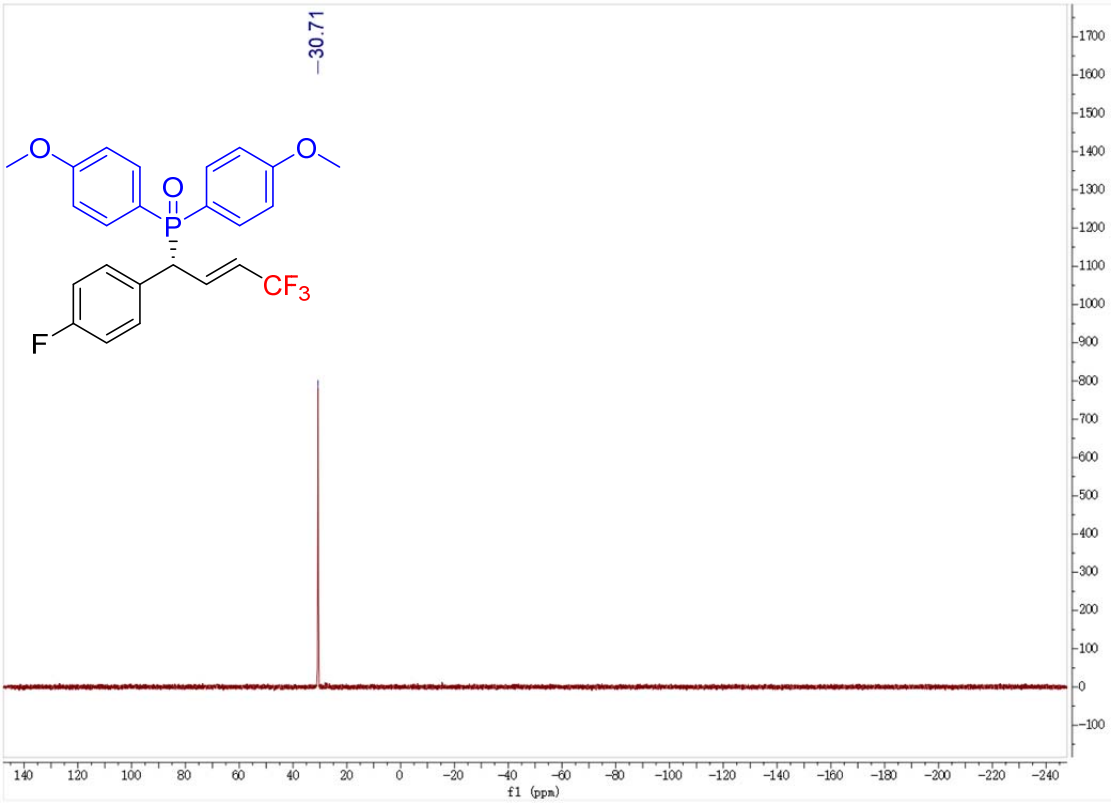
^{13}C NMR (101 MHz, $CDCl_3$) (3h)



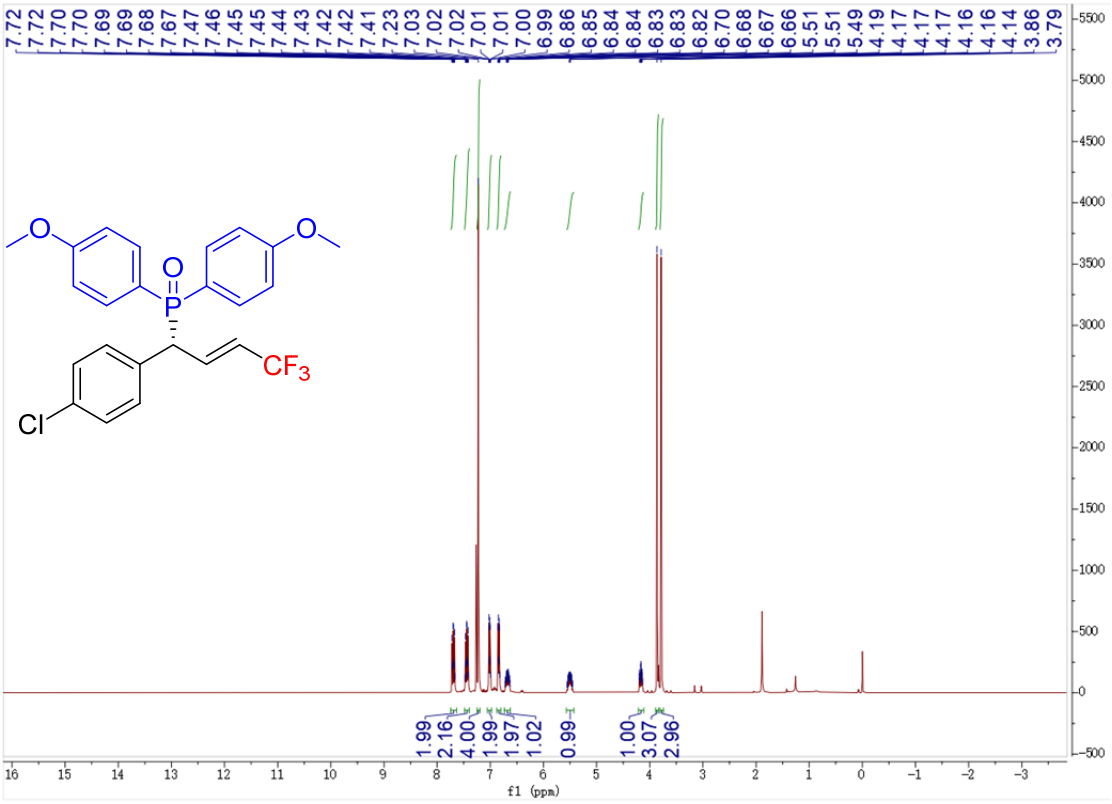
^{19}F NMR (377 MHz, $CDCl_3$) (3h)



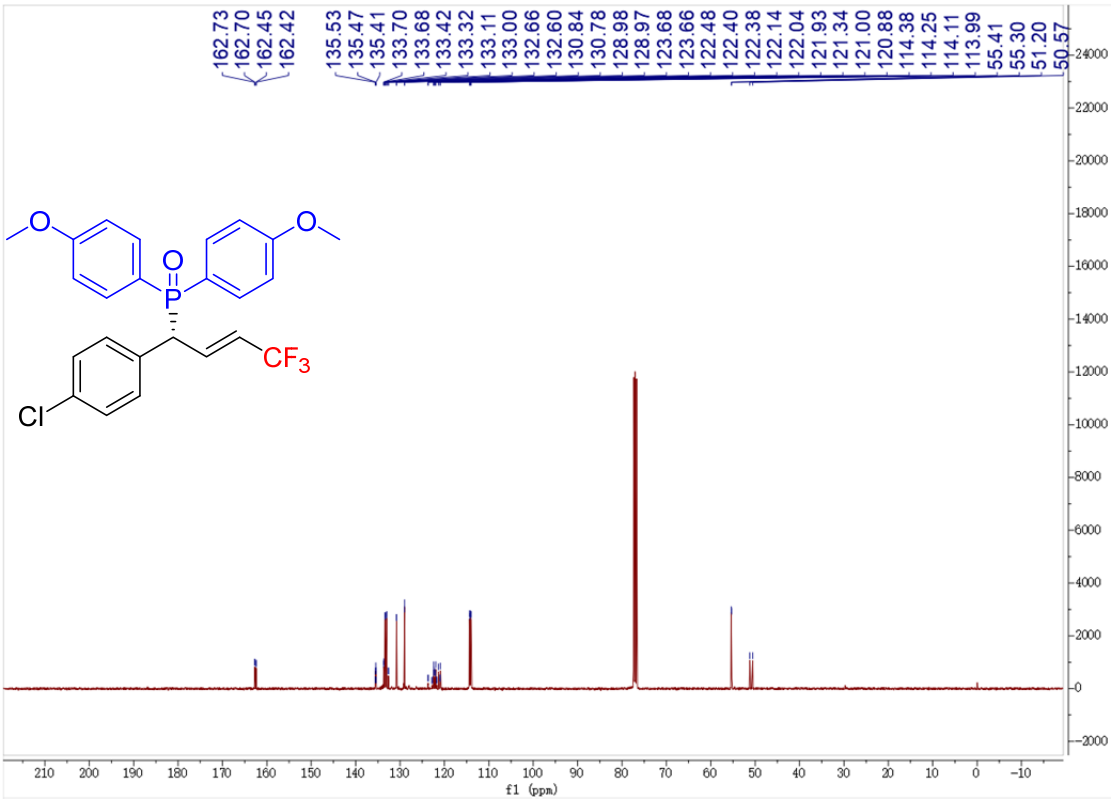
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3h)



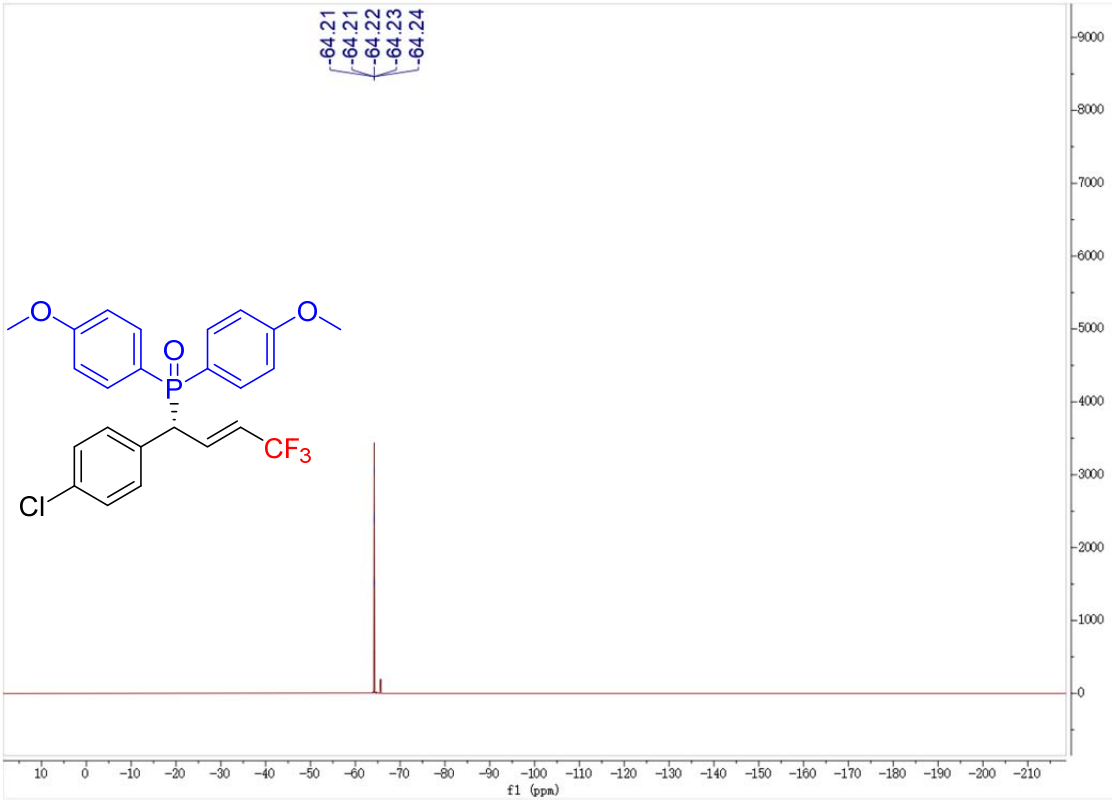
^{1}H NMR (400 MHz, $CDCl_3$) (3i)



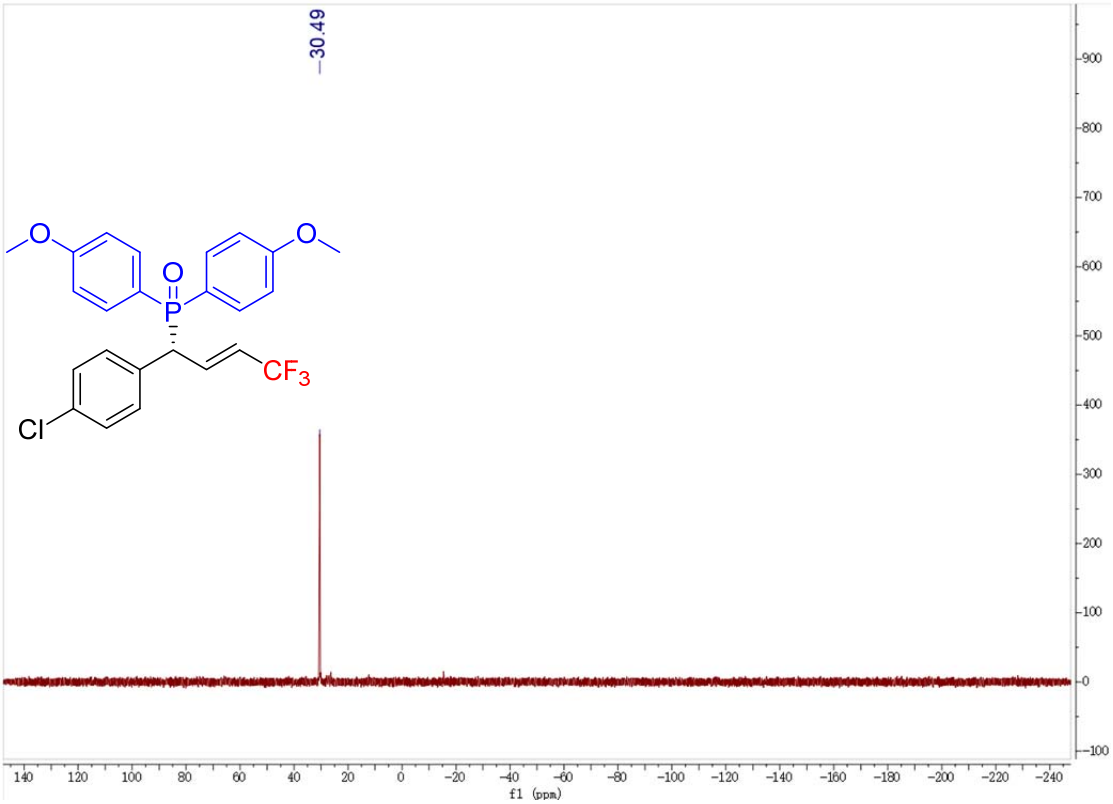
^{13}C NMR (101 MHz, $CDCl_3$) (3i)



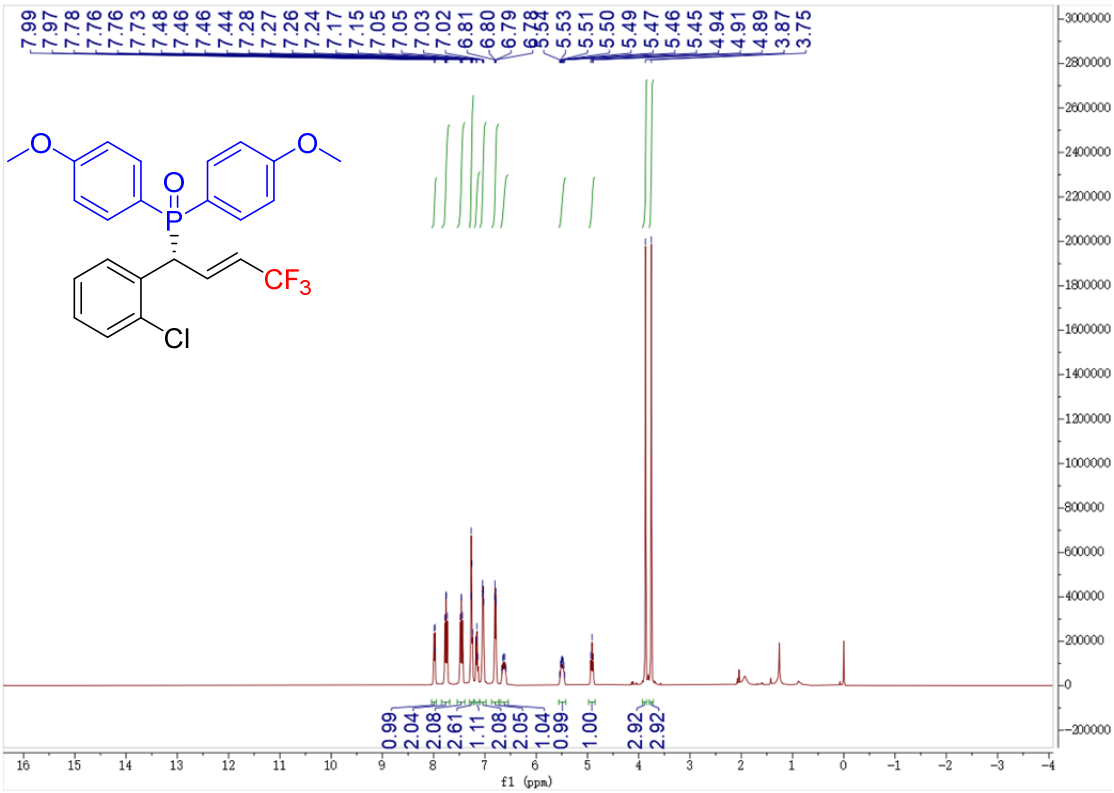
^{19}F NMR (377 MHz, $CDCl_3$) (3i)



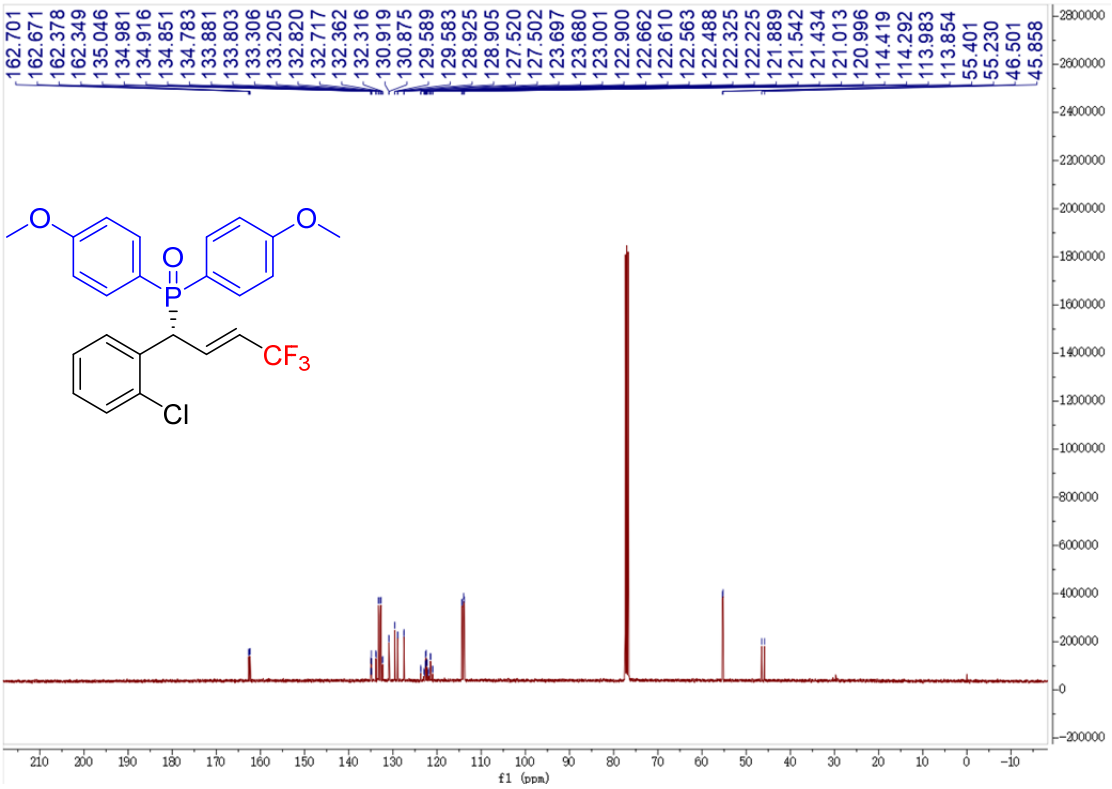
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3i)



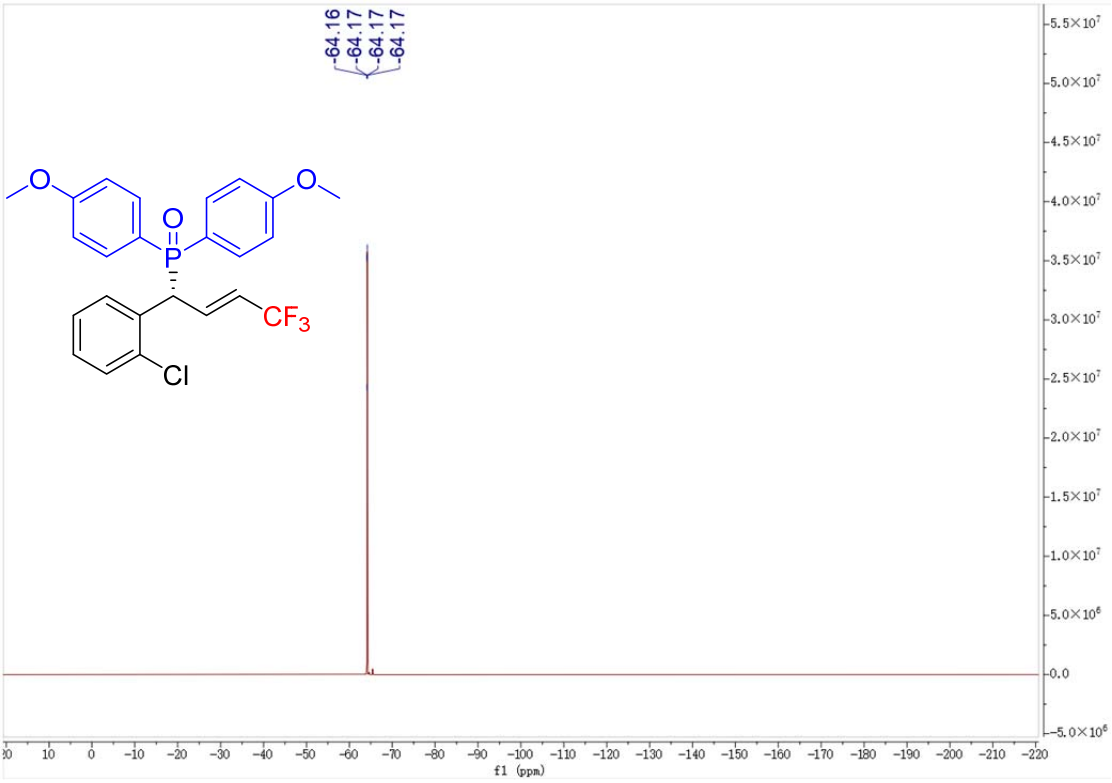
^{1}H NMR (400 MHz, $CDCl_3$) (3j)



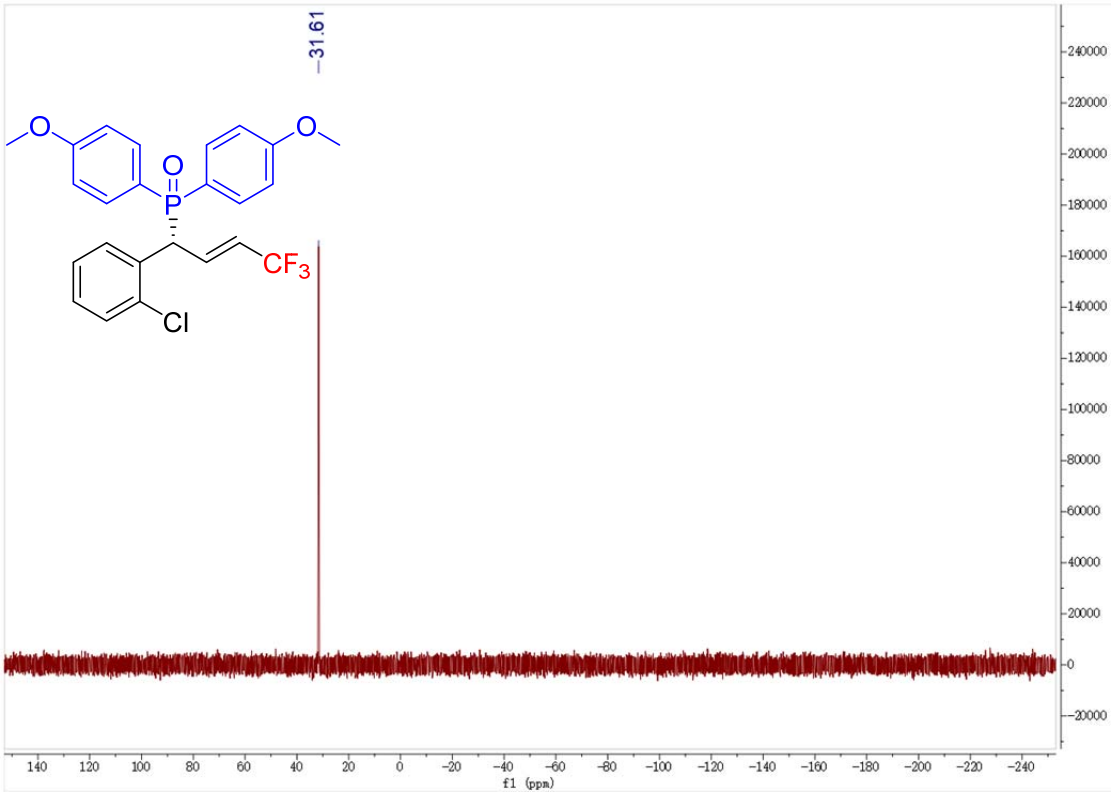
^{13}C NMR (101 MHz, $CDCl_3$) (3j)



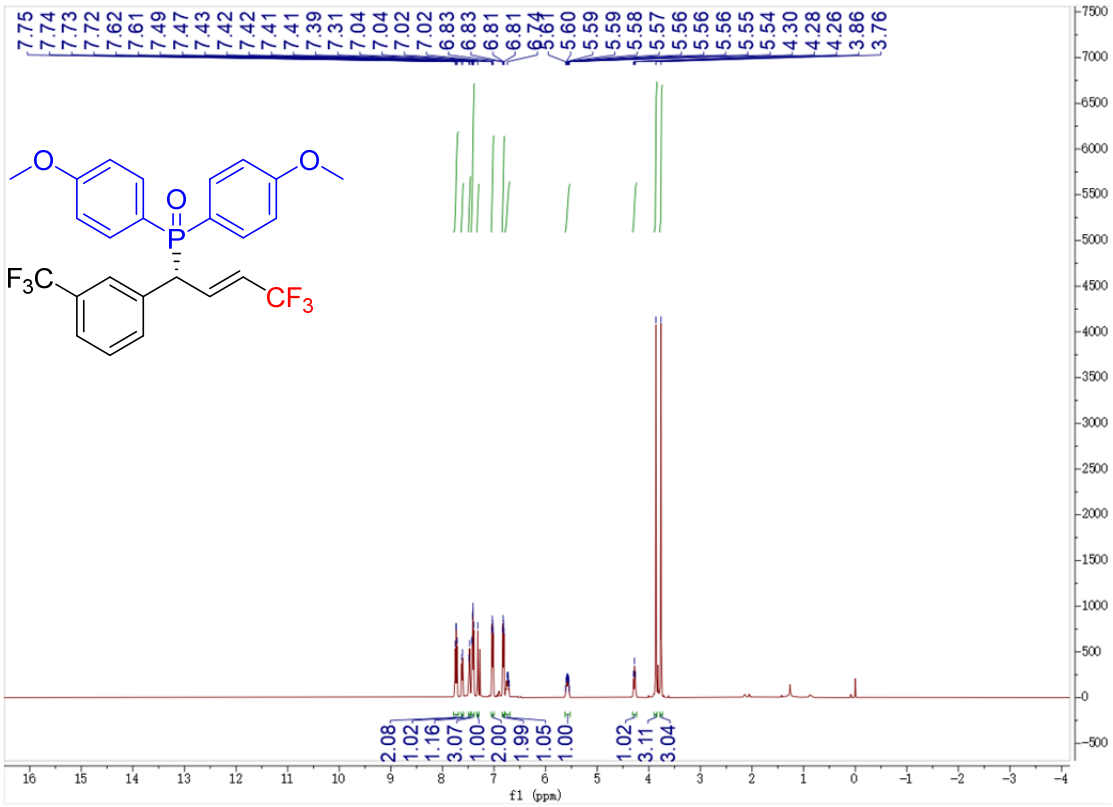
^{19}F NMR (377 MHz, $CDCl_3$) (3j)



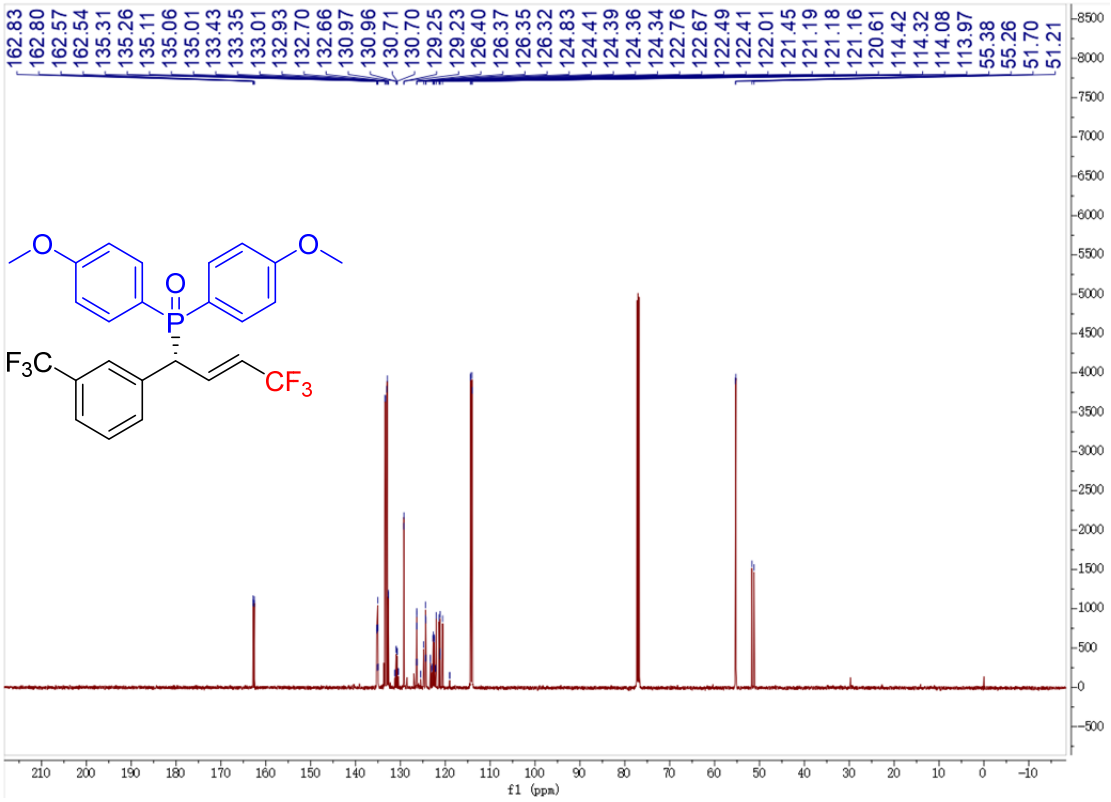
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3j)



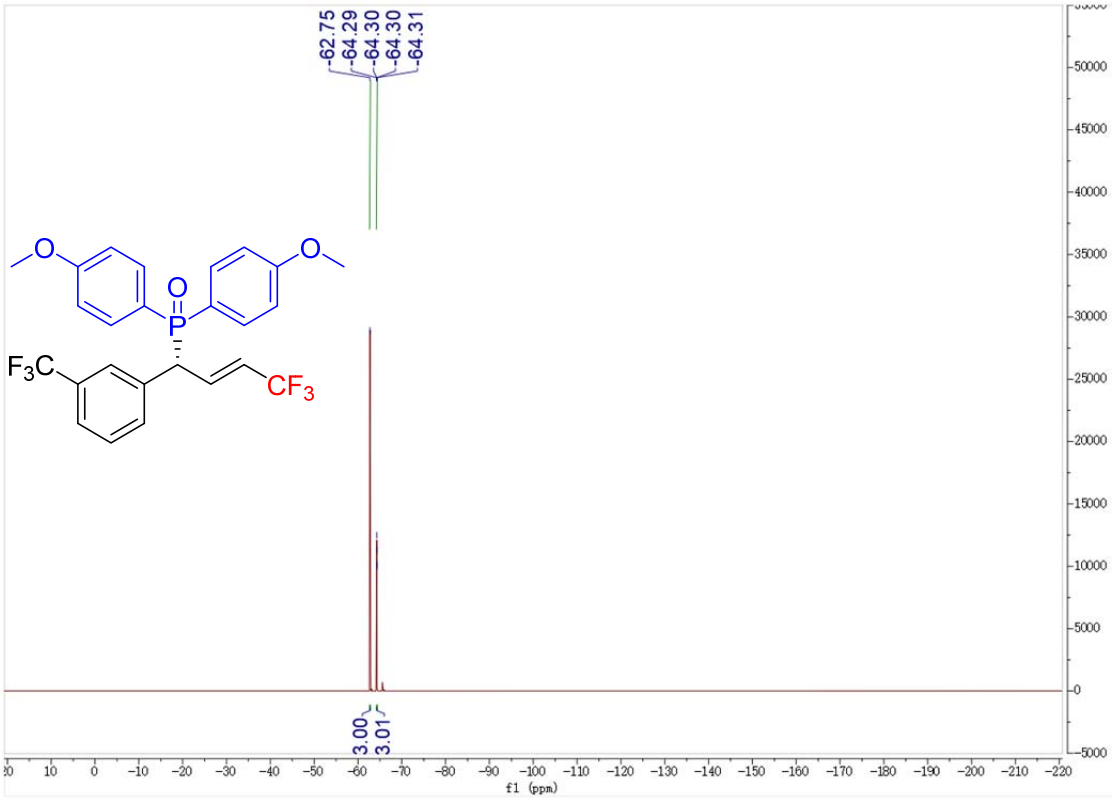
^{1}H NMR (500 MHz, $CDCl_3$) (3k)



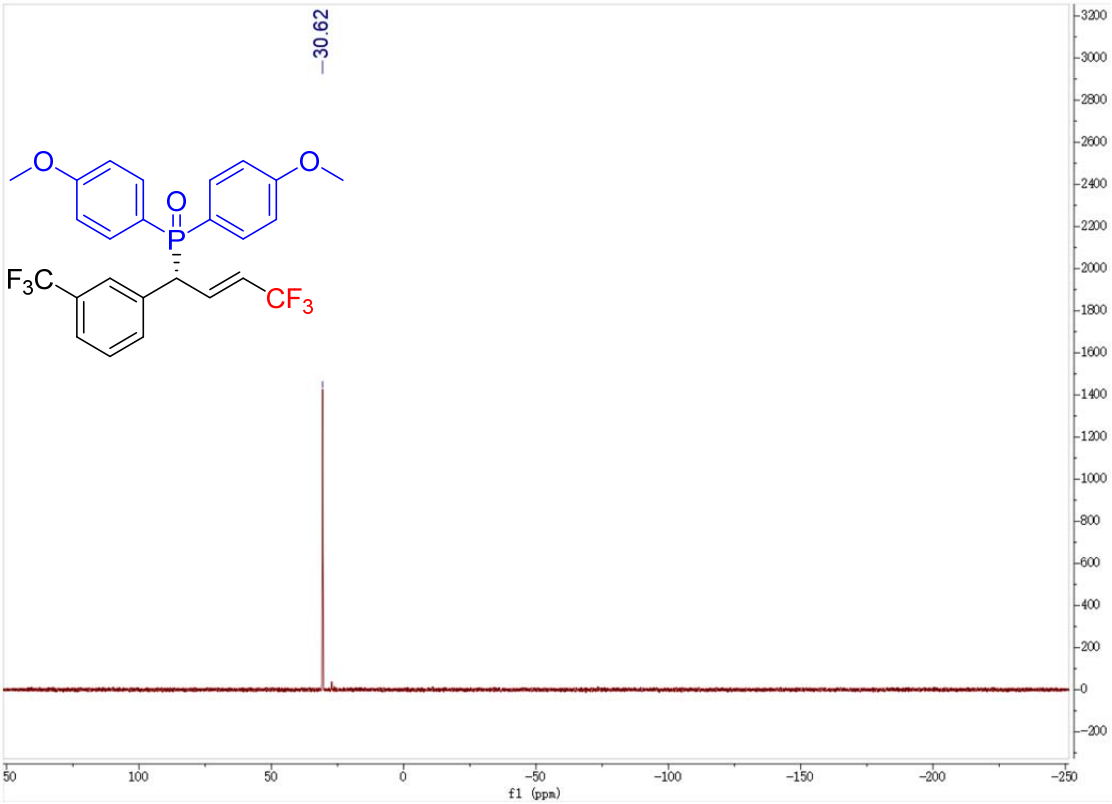
^{13}C NMR (126 MHz, $CDCl_3$) (3k)



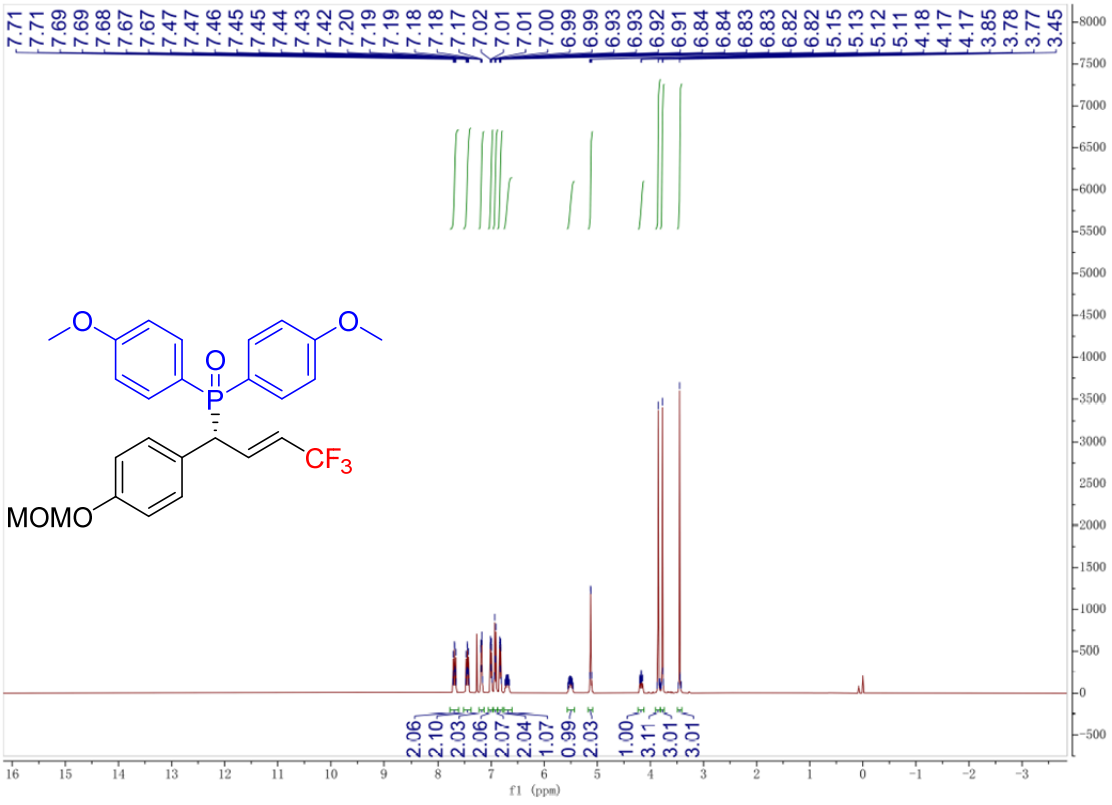
^{19}F NMR (470 MHz, $CDCl_3$) (3k)



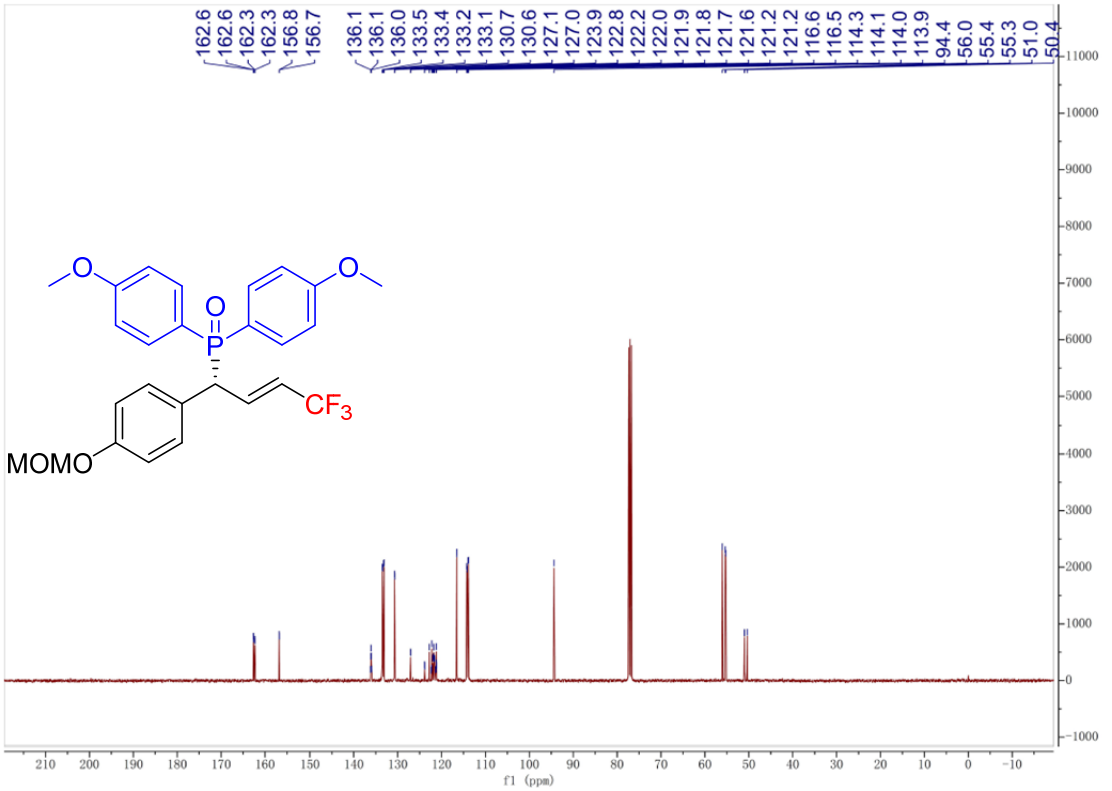
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) (3k)



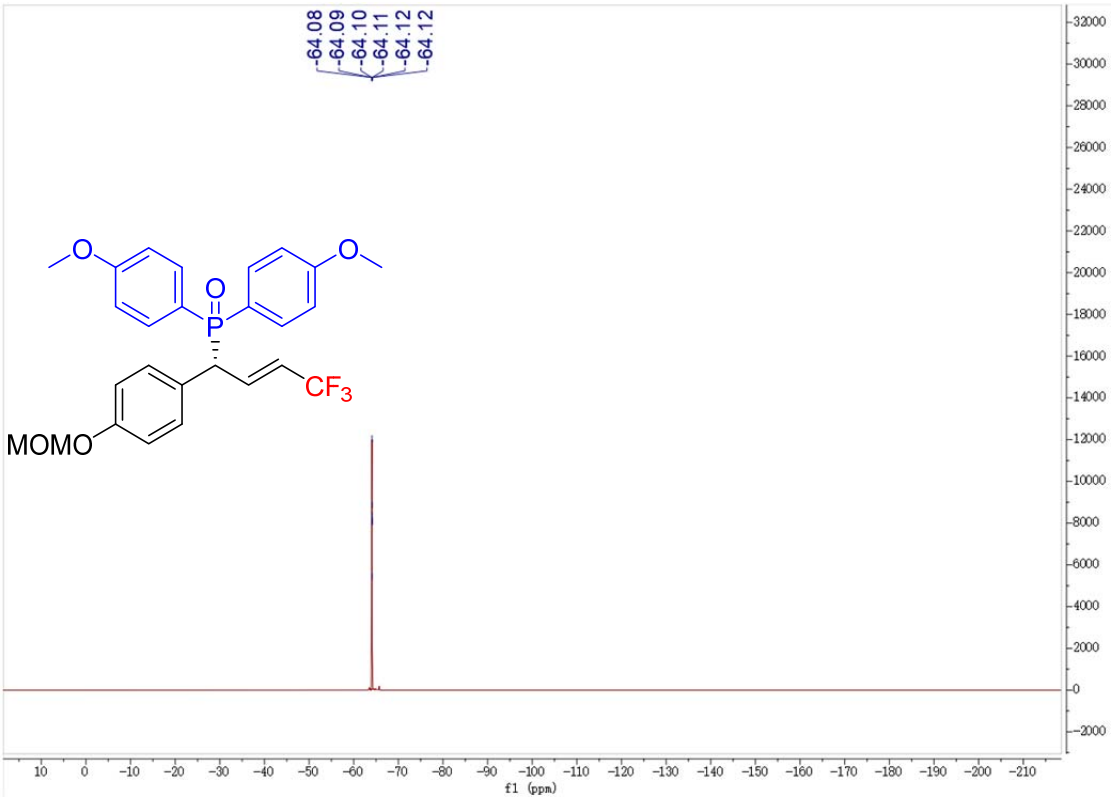
^{1}H NMR (400 MHz, $CDCl_3$) (3l)



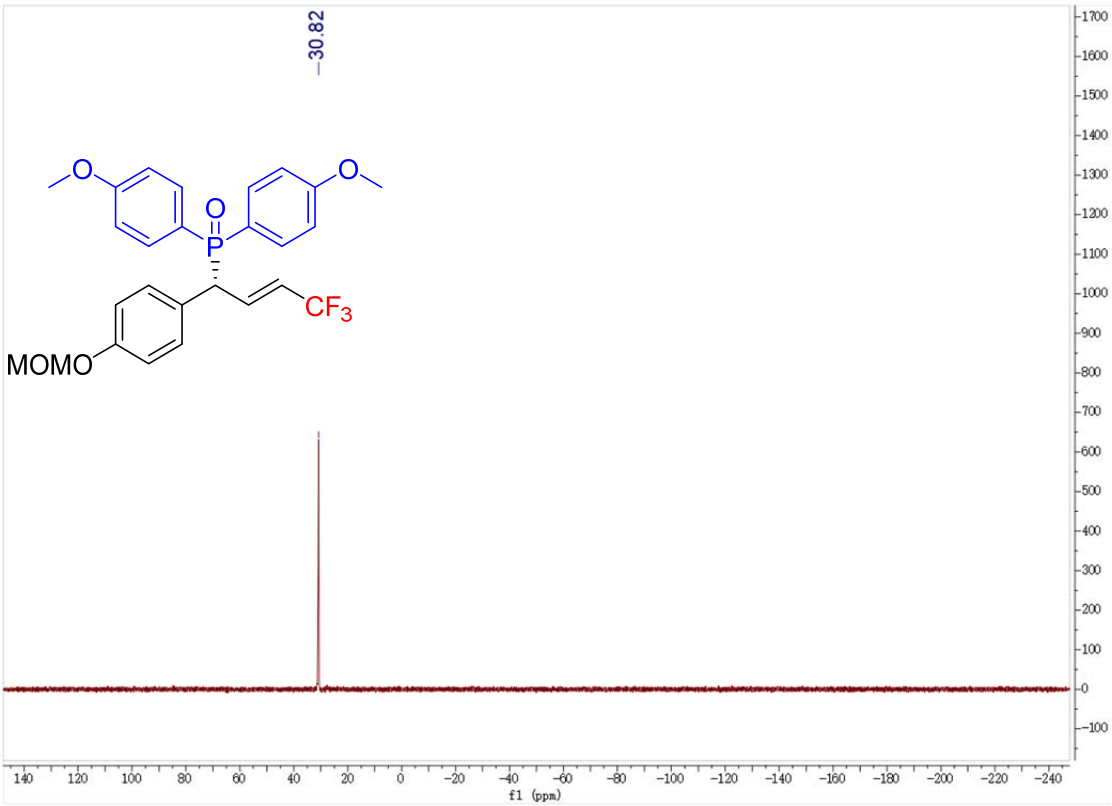
^{13}C NMR (101 MHz, $CDCl_3$) (3l)



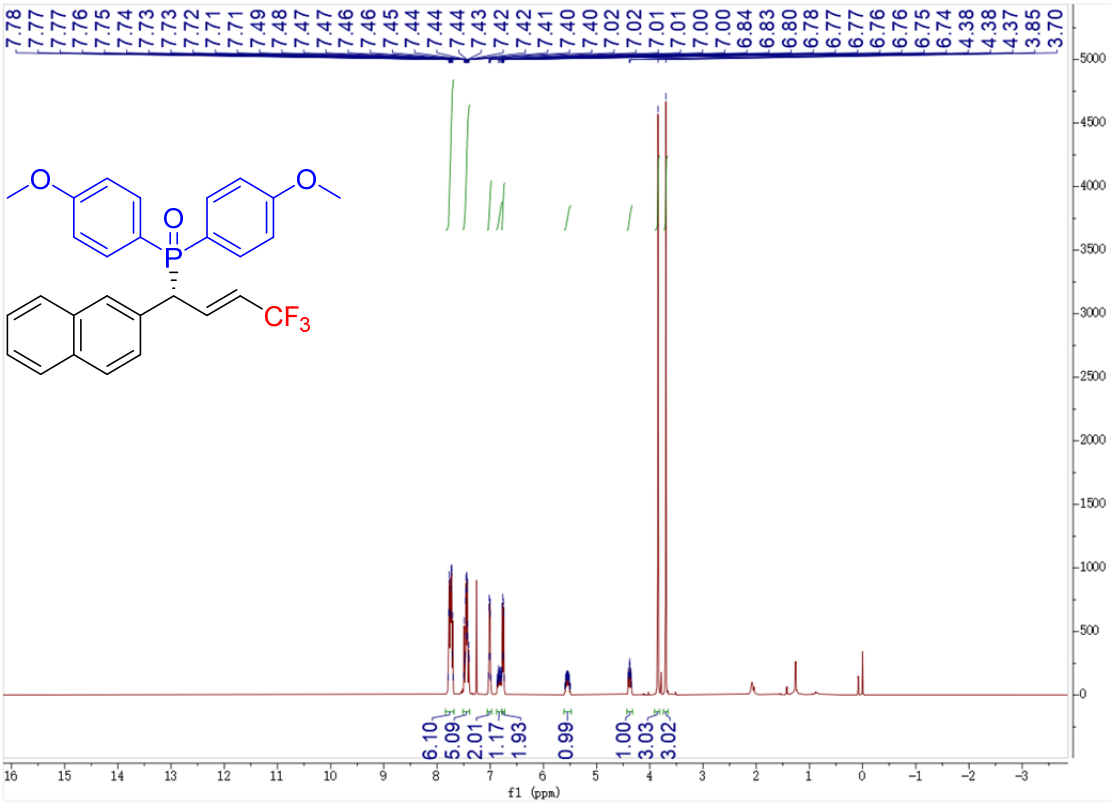
^{19}F NMR (377 MHz, $CDCl_3$) (3l)



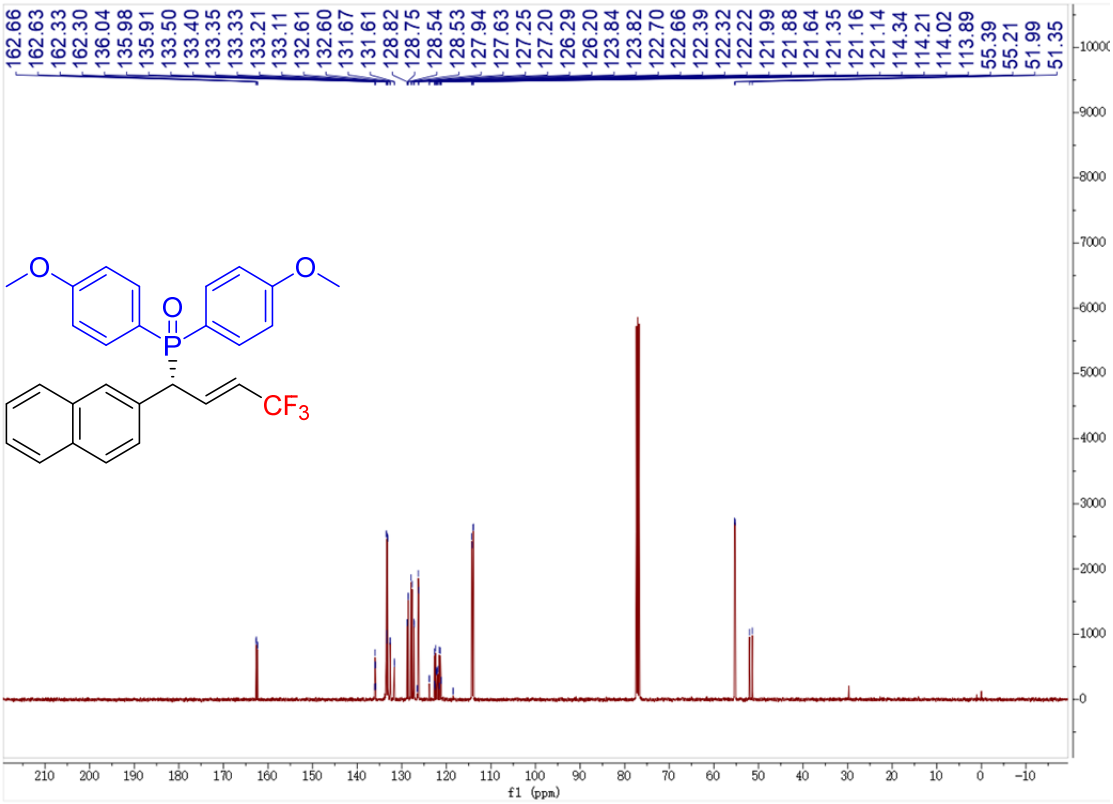
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3l)



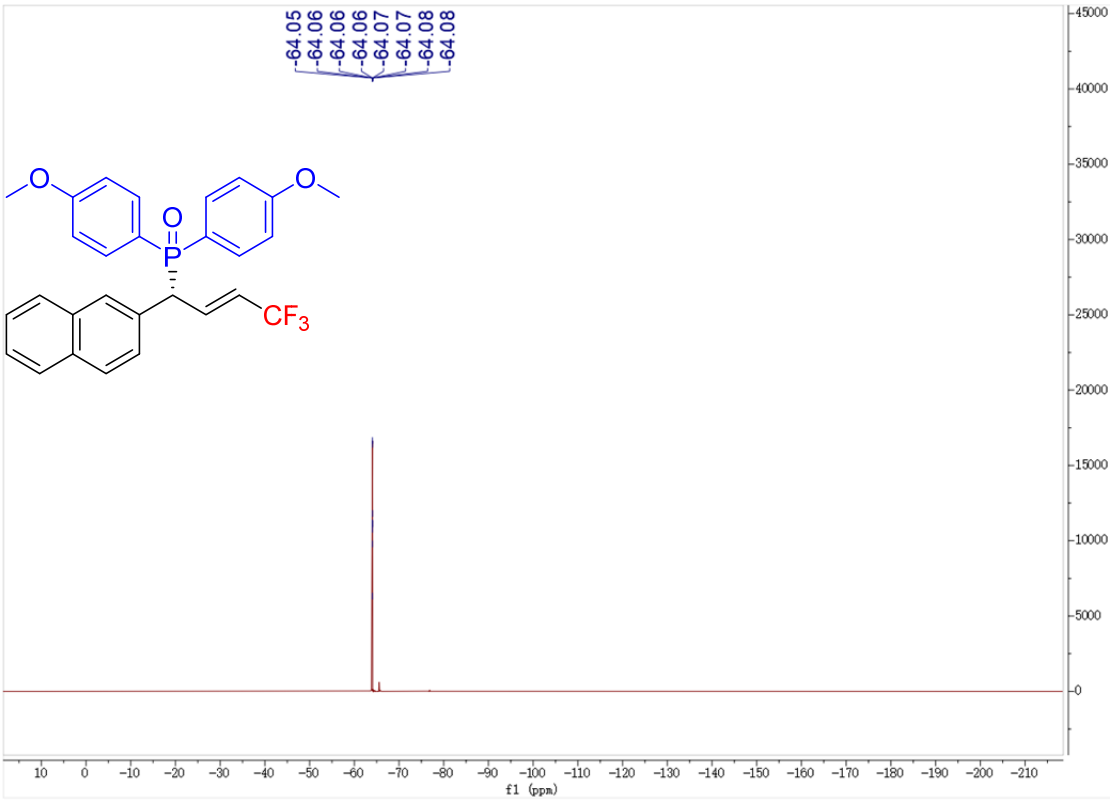
^{1}H NMR (400 MHz, $CDCl_3$) (3m)



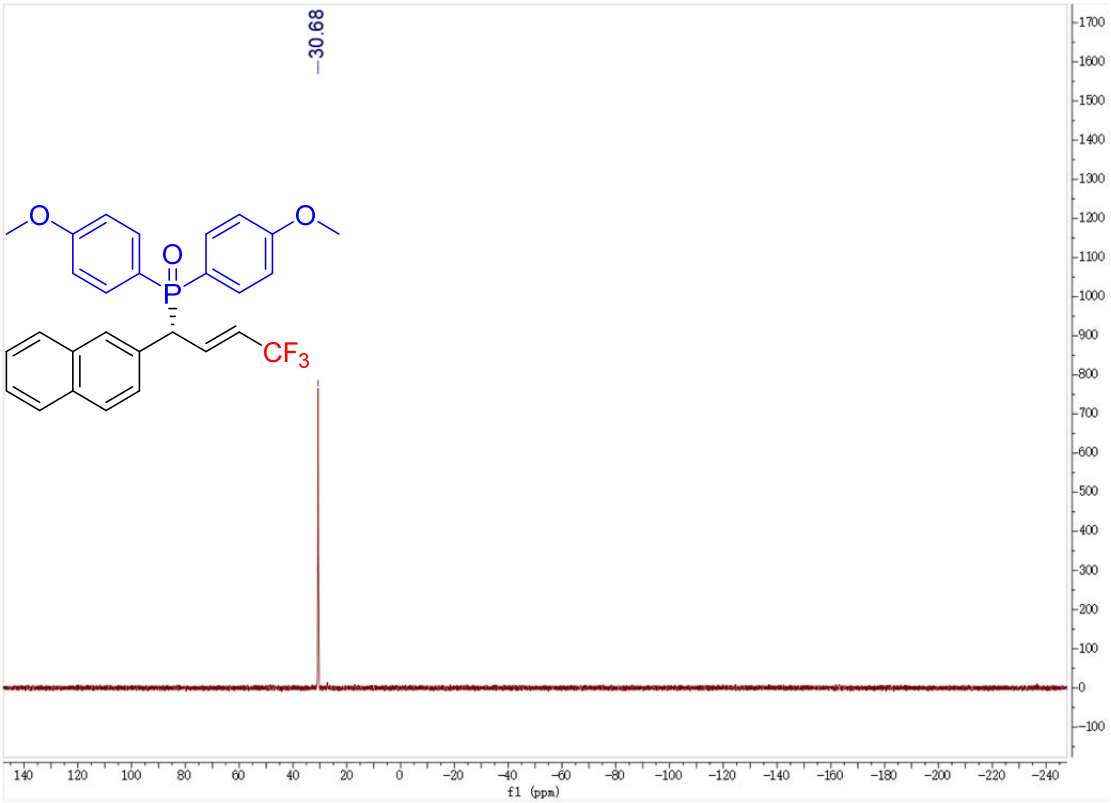
^{13}C NMR (101 MHz, $CDCl_3$) (3m)



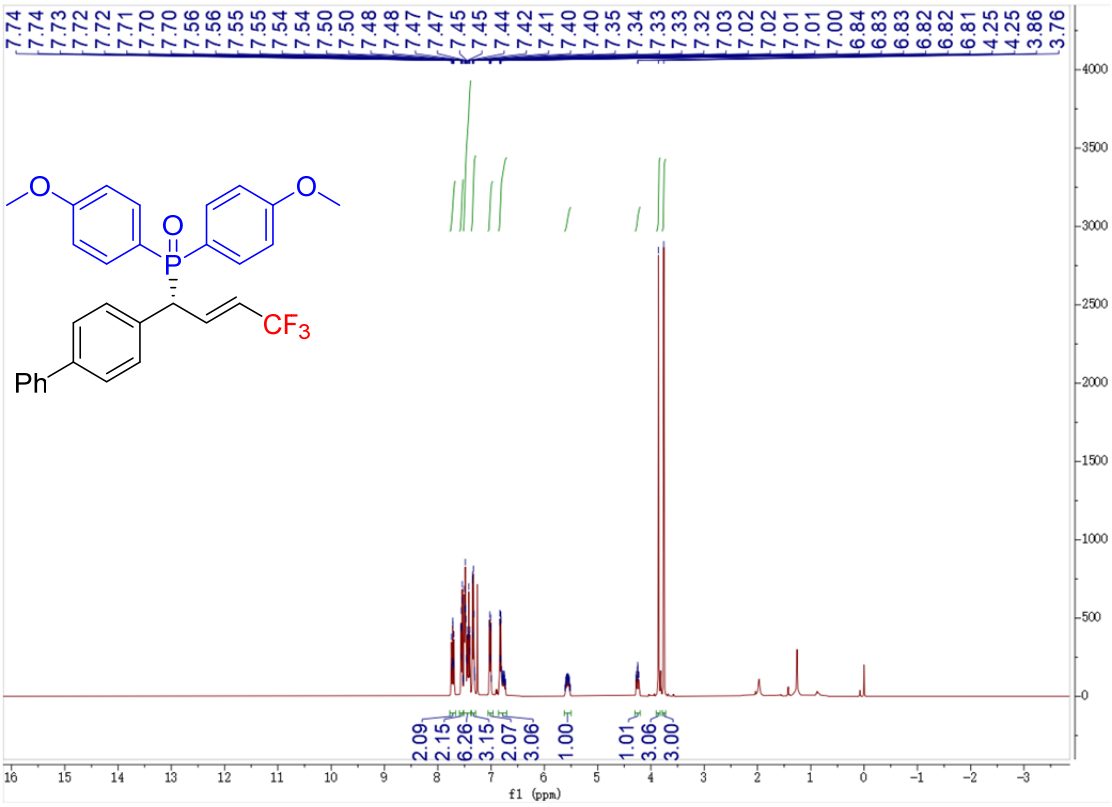
^{19}F NMR (377 MHz, $CDCl_3$) (3m)



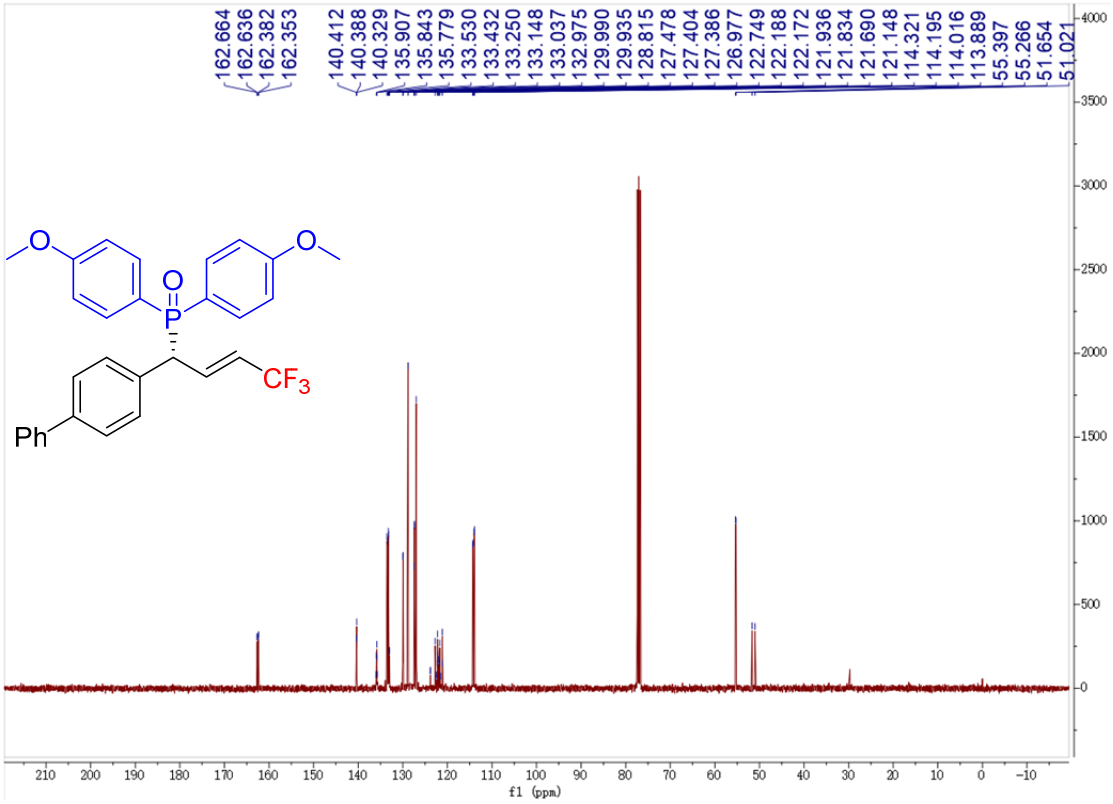
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3m)



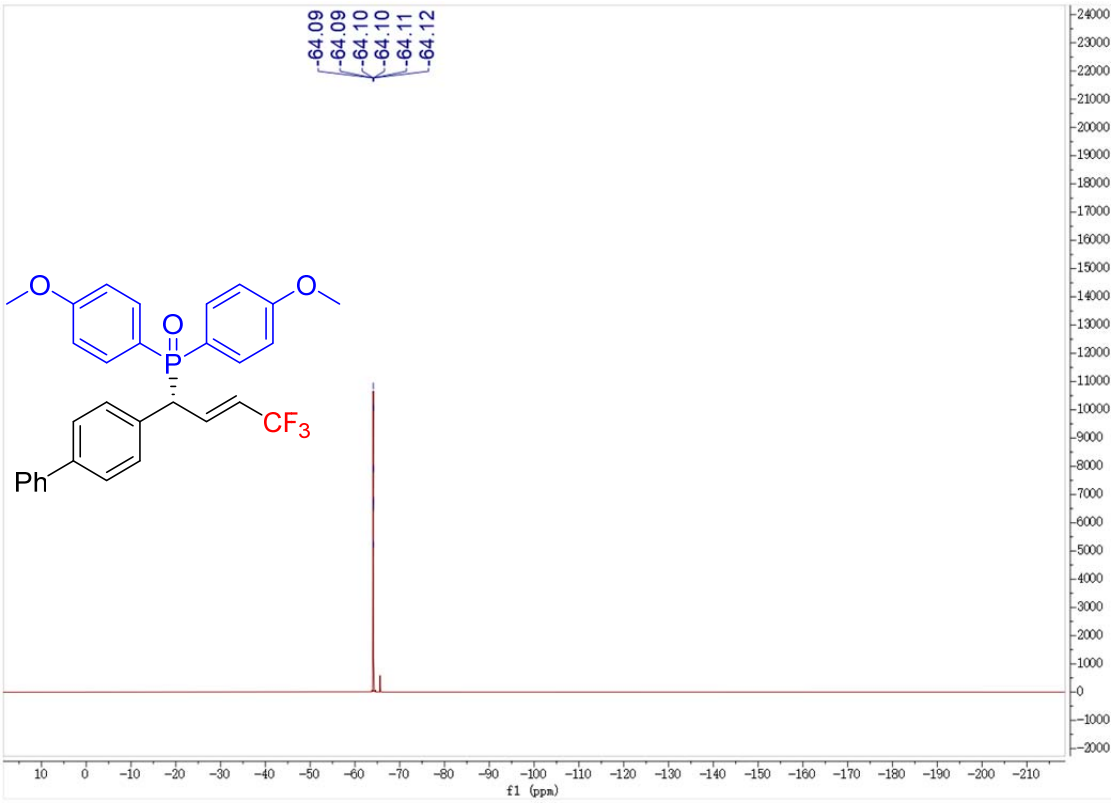
^{1}H NMR (400 MHz, $CDCl_3$) (3n)



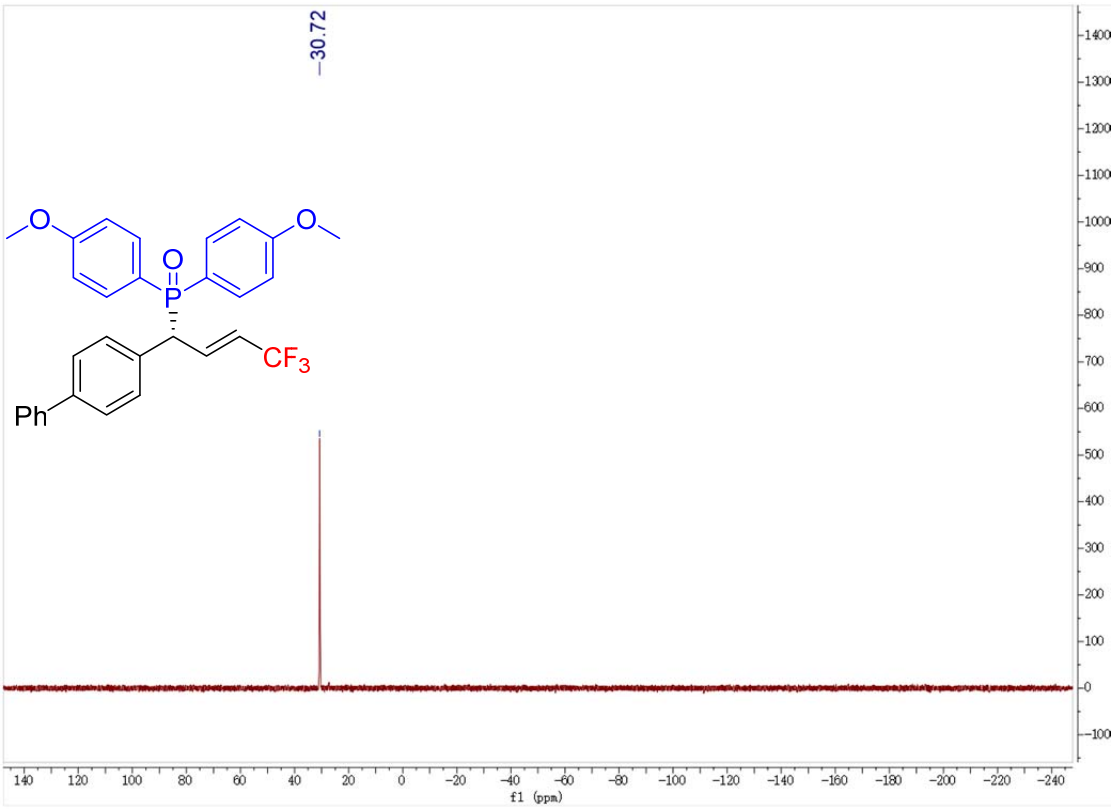
^{13}C NMR (101 MHz, $CDCl_3$) (3n)



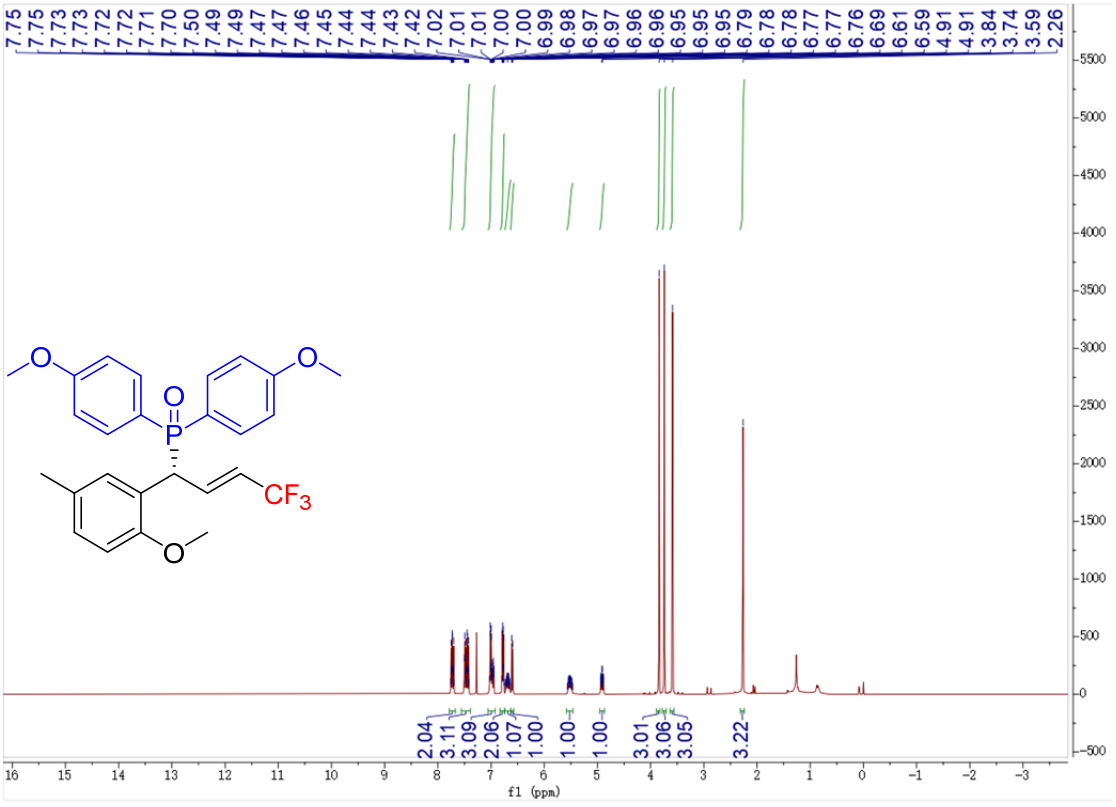
^{19}F NMR (377 MHz, $CDCl_3$) (3n)



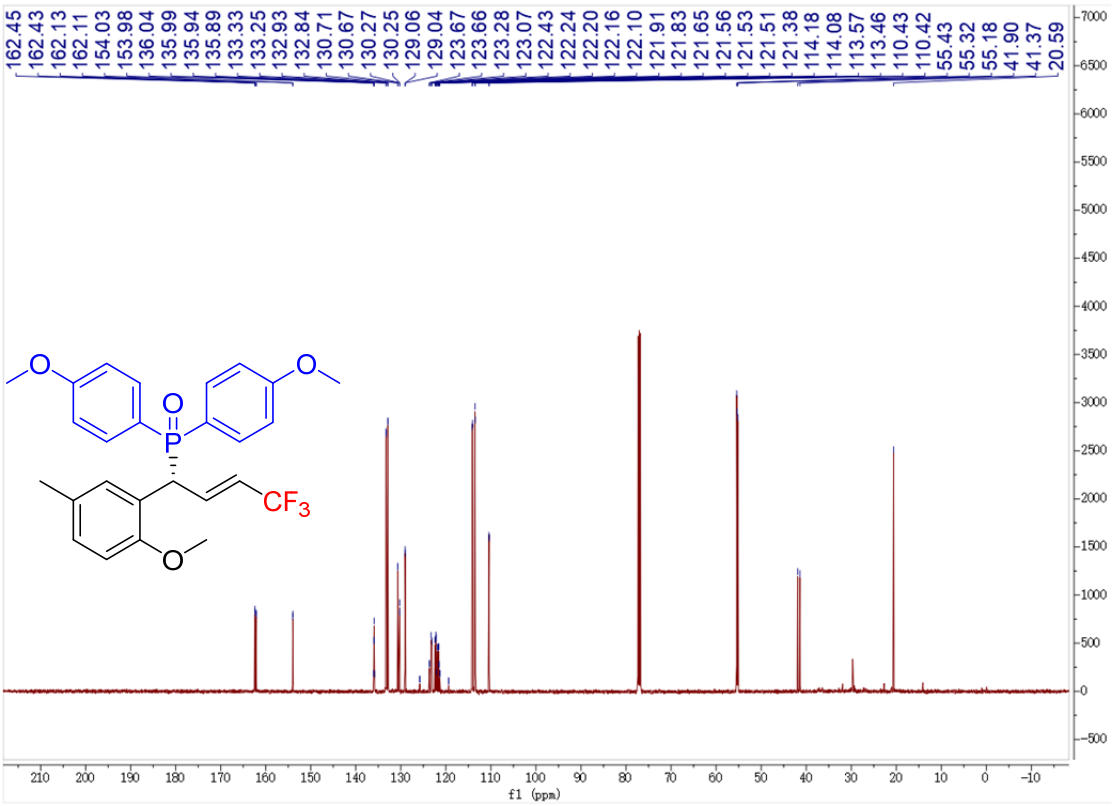
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3n)



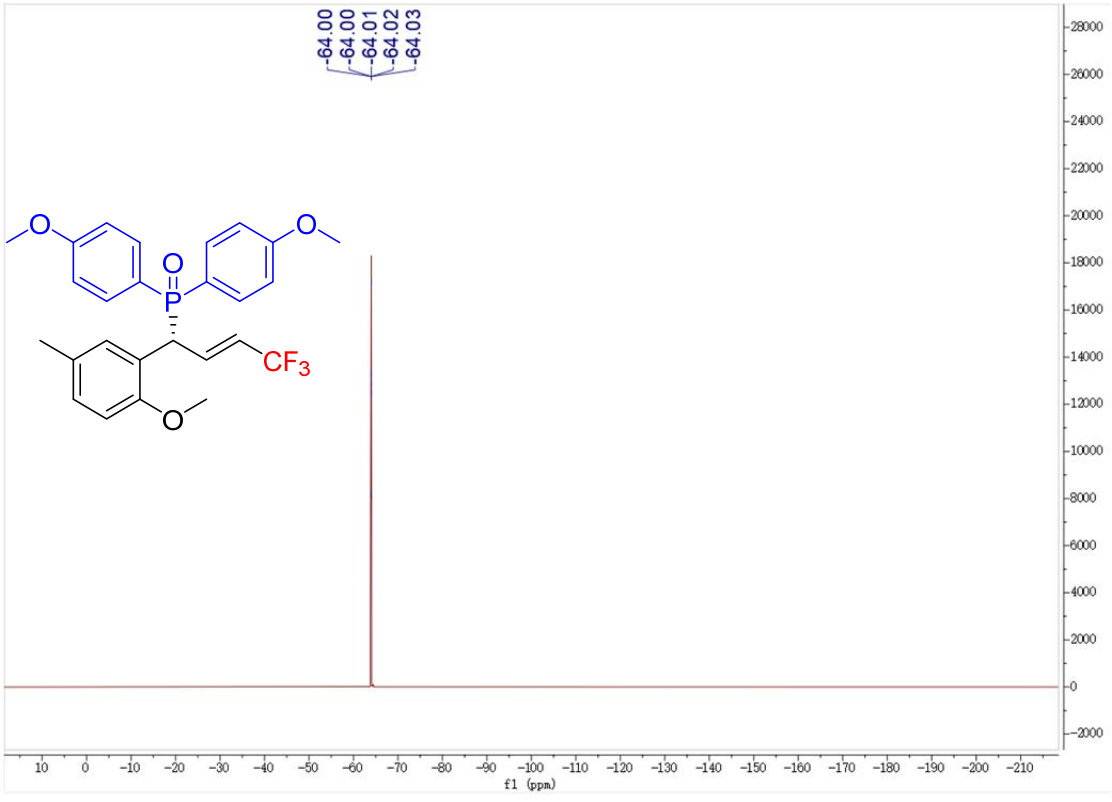
^{1}H NMR (400 MHz, $CDCl_3$) (3o)



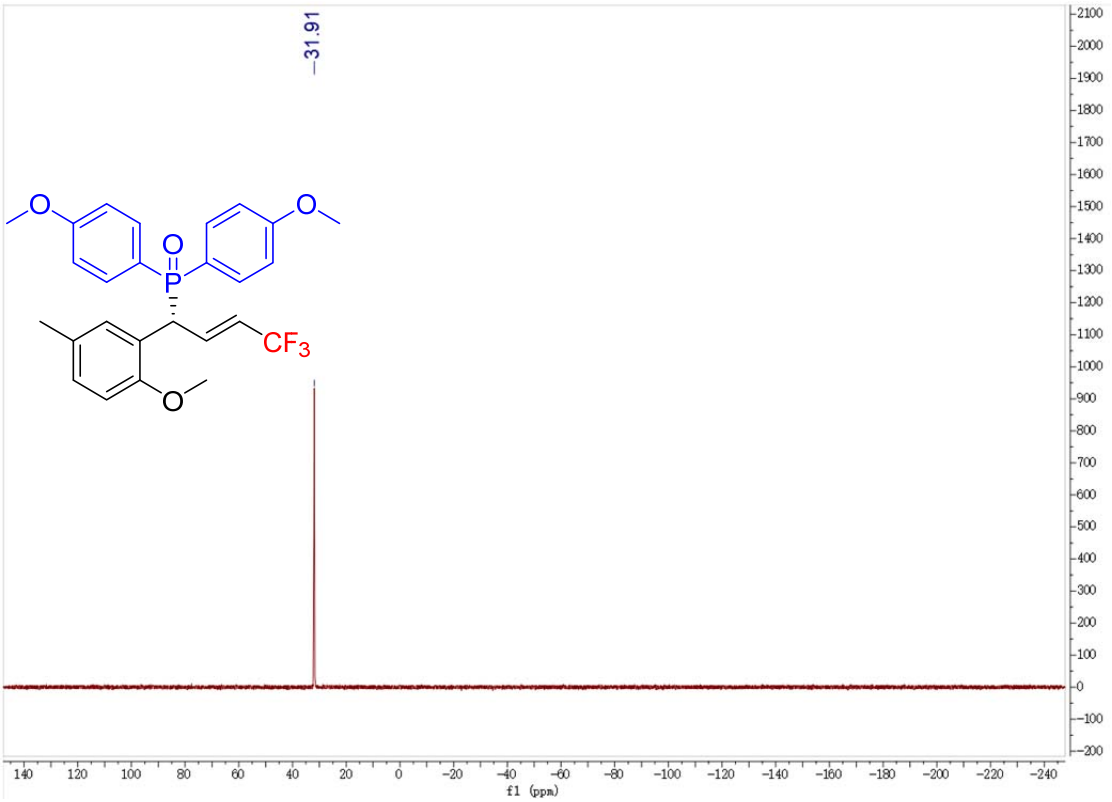
^{13}C NMR (126 MHz, $CDCl_3$) (3o)



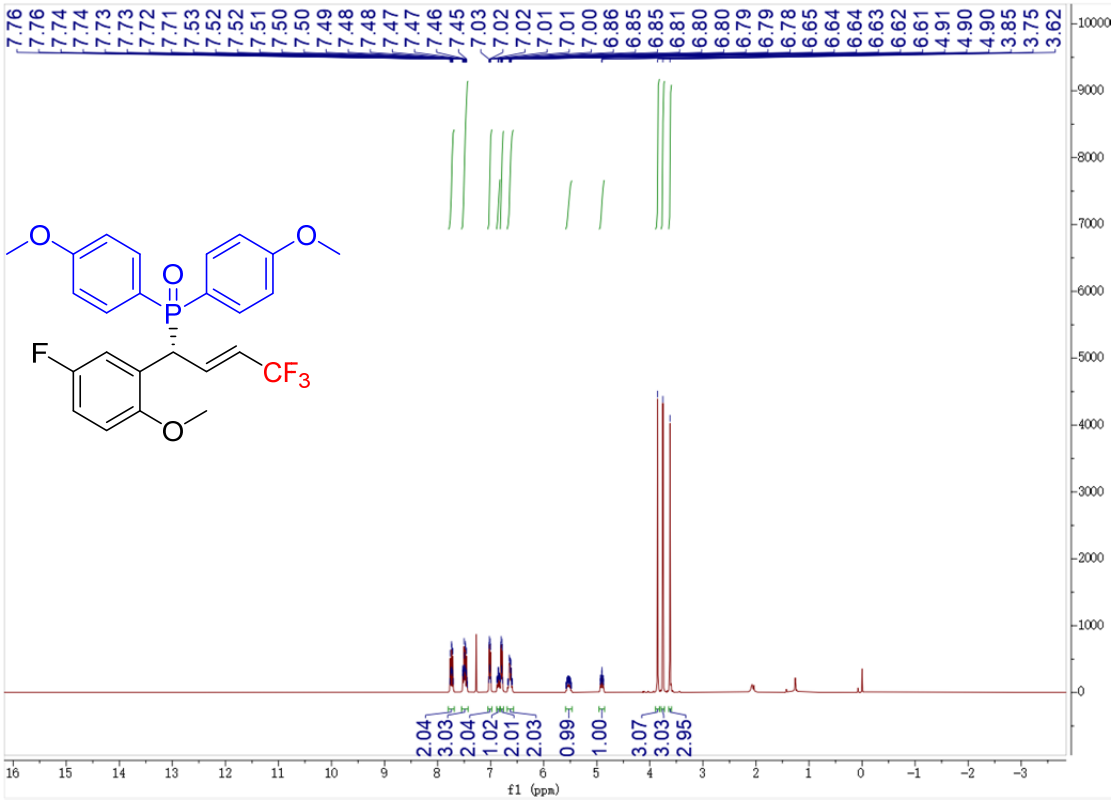
^{19}F NMR (377 MHz, $CDCl_3$) (3o)



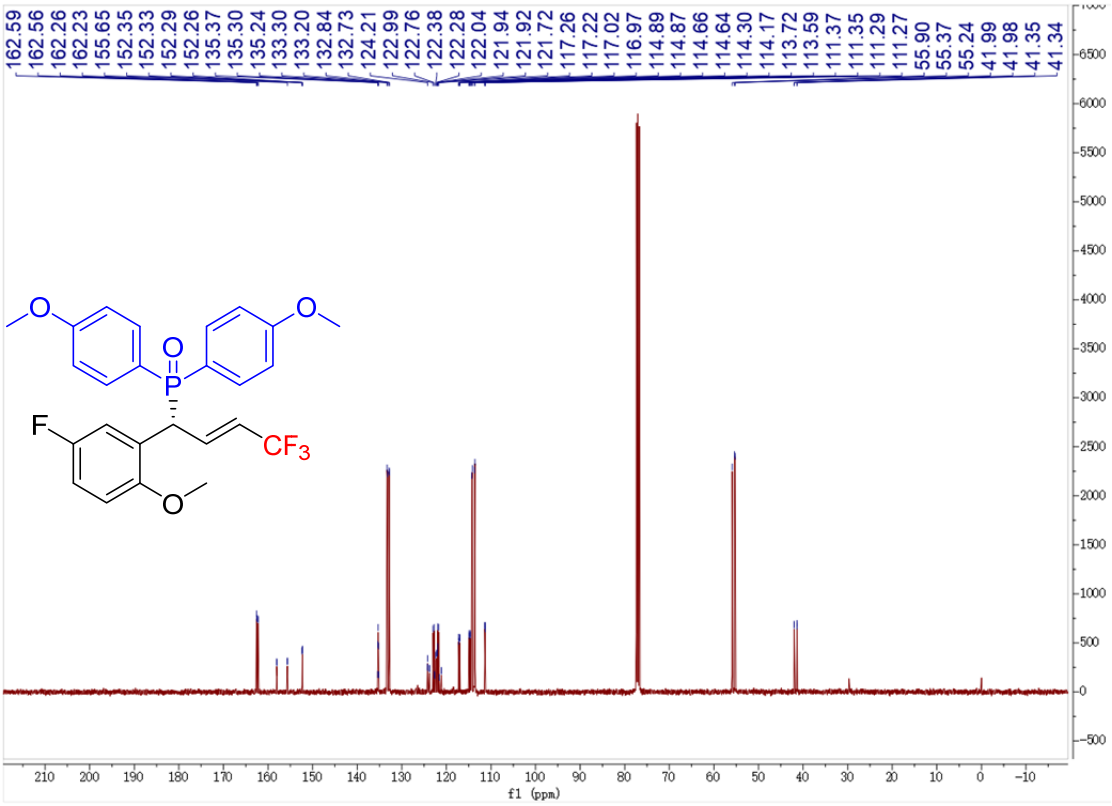
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3o)



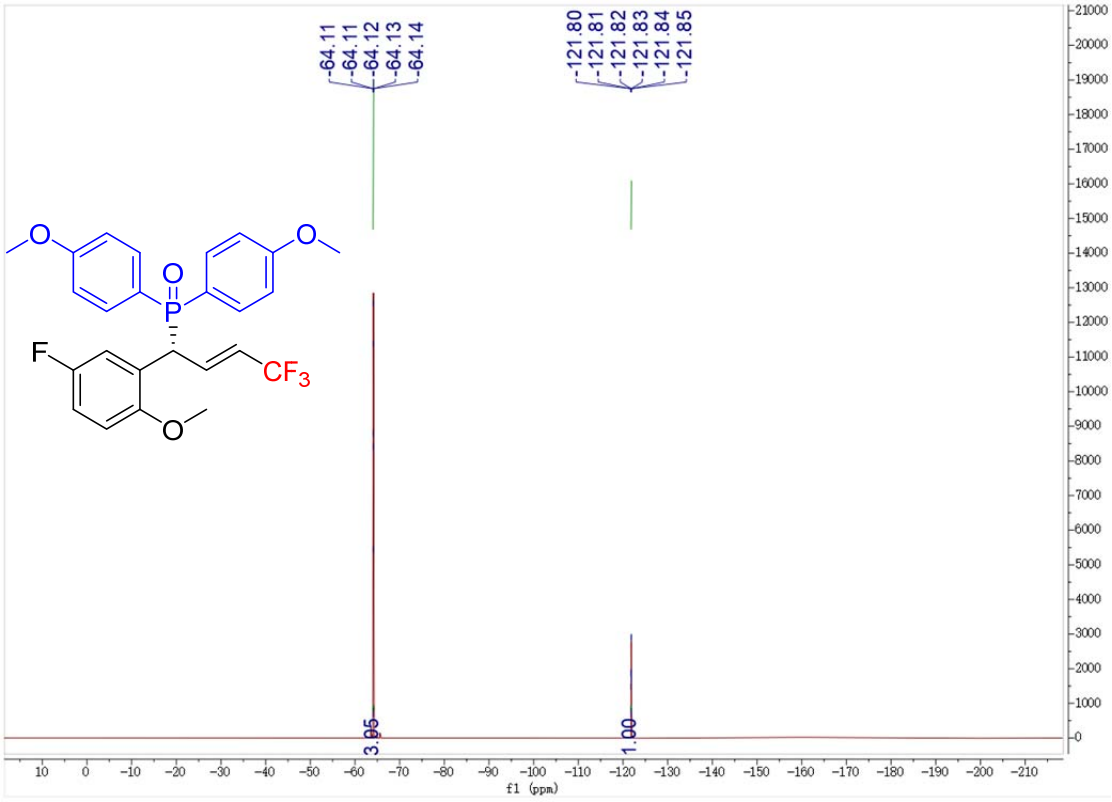
^{1}H NMR (400 MHz, $CDCl_3$) (3p)



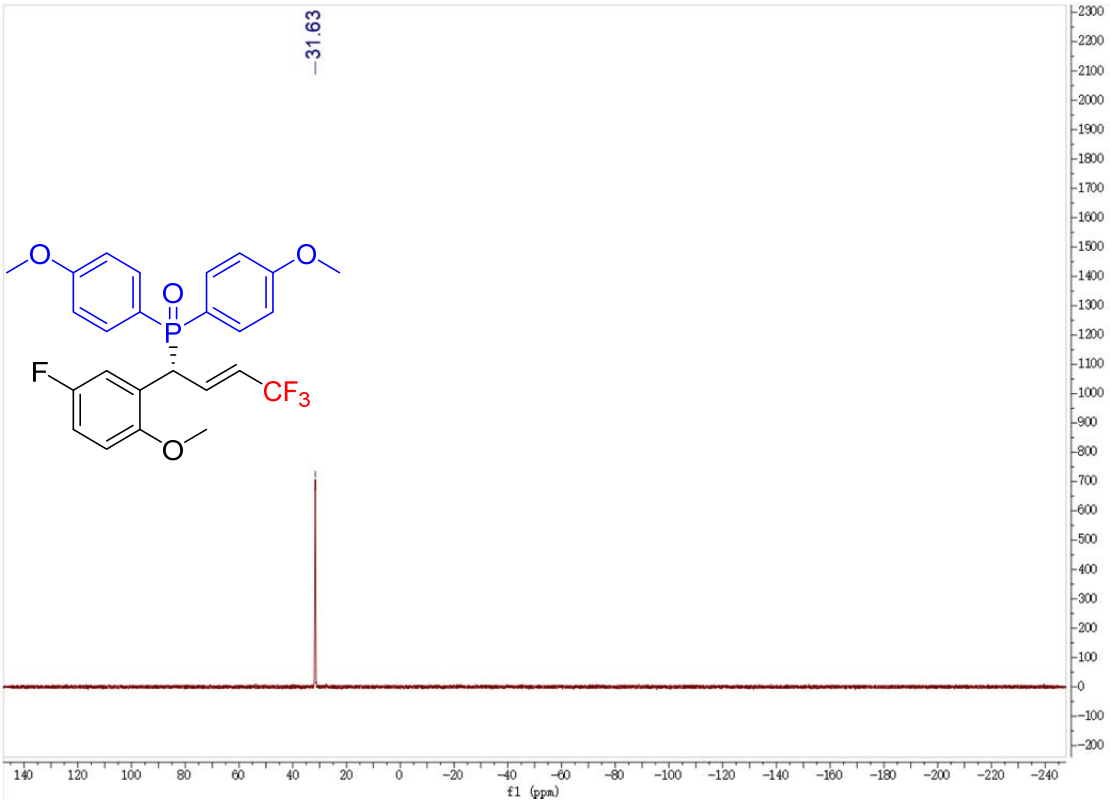
^{13}C NMR (101 MHz, $CDCl_3$) (3p)



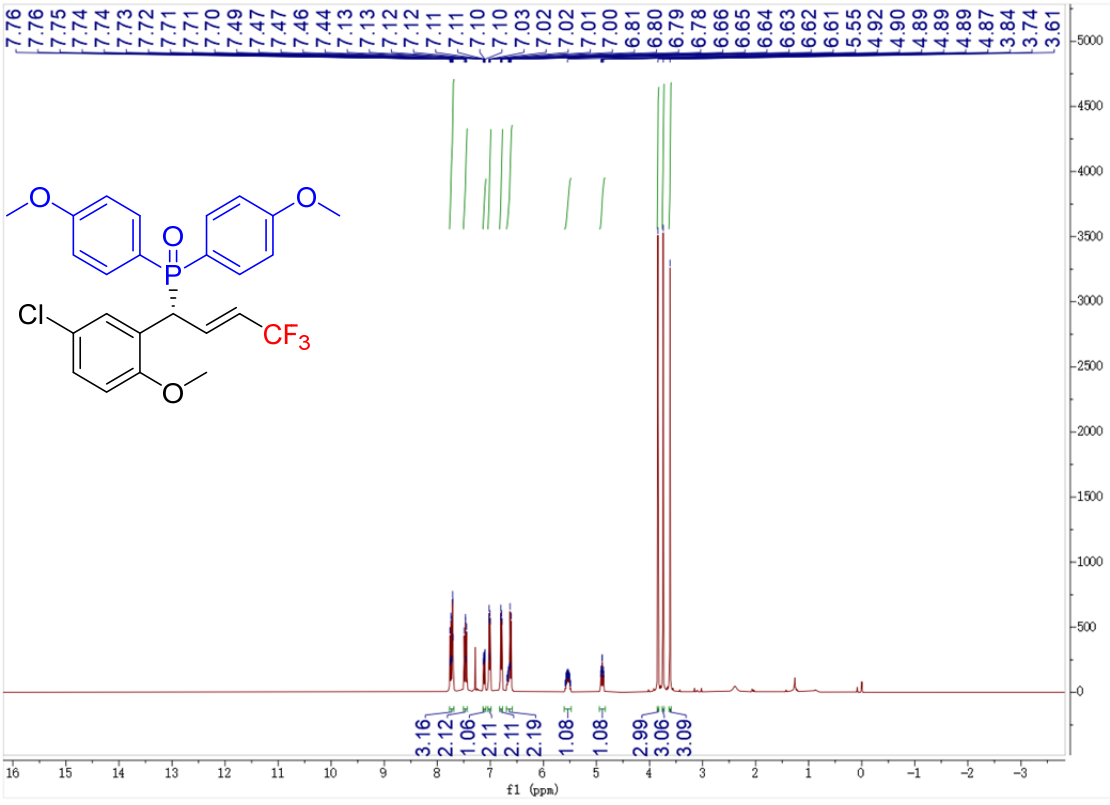
^{19}F NMR (377 MHz, $CDCl_3$) (3p)



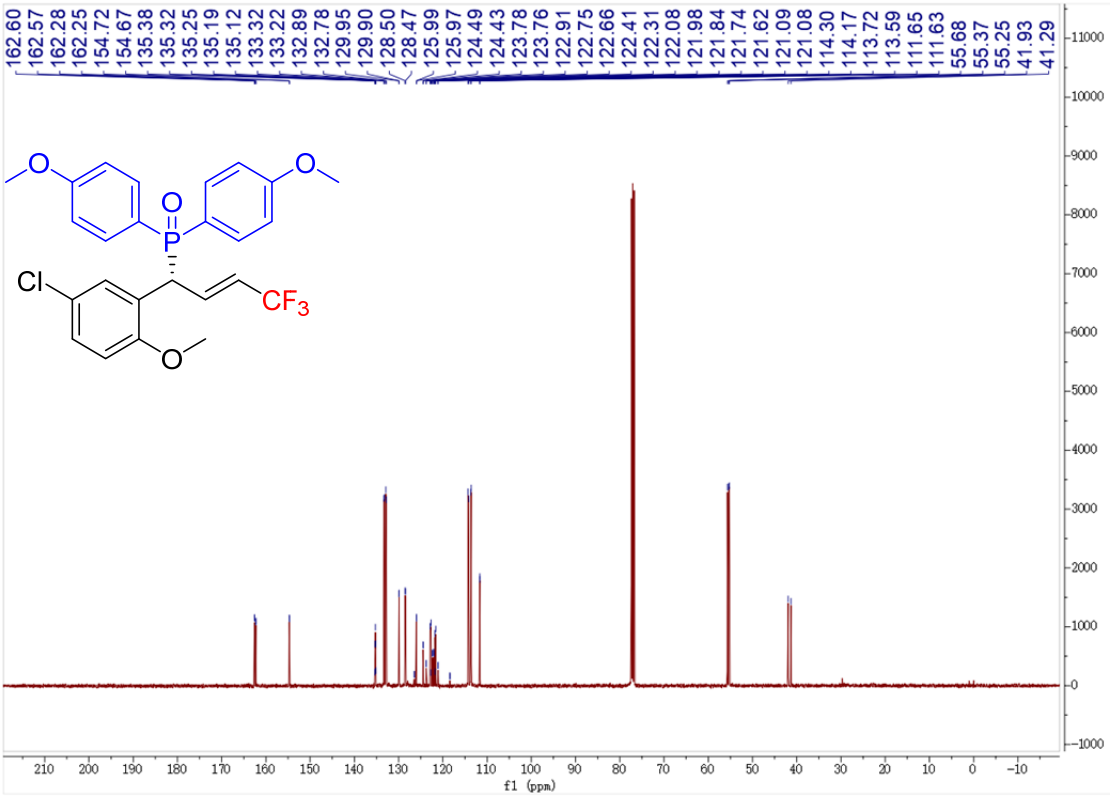
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3p)



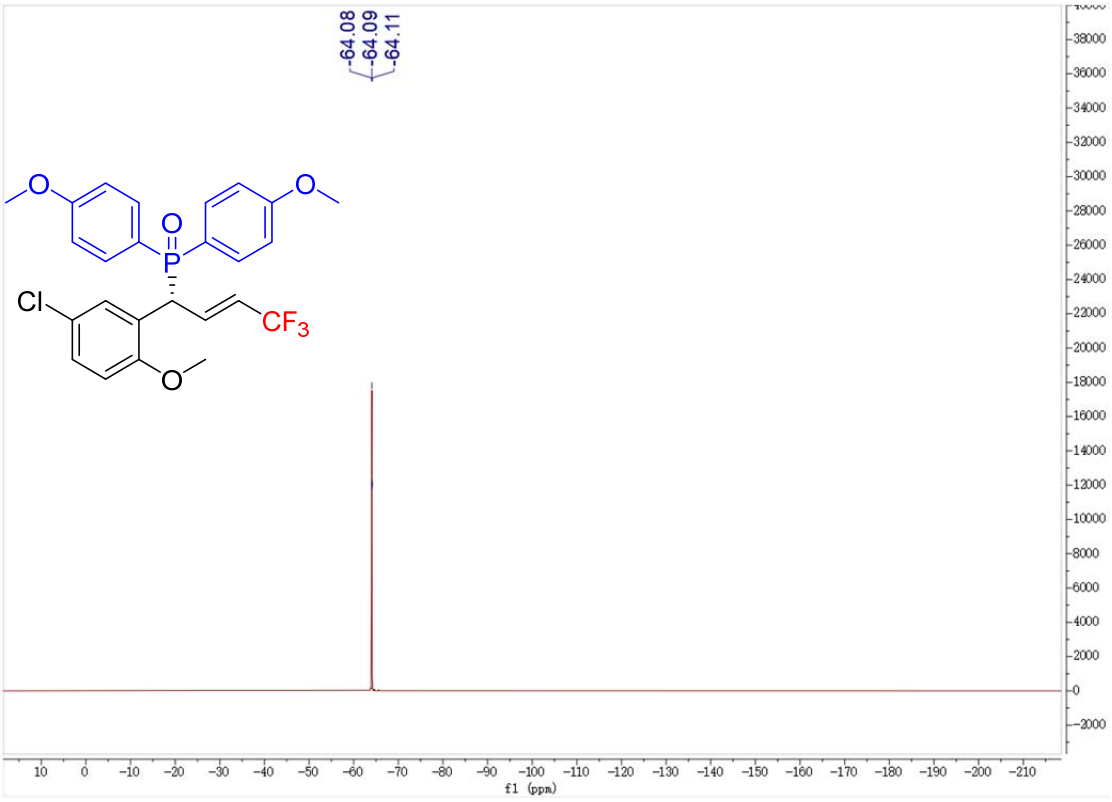
^{1}H NMR (400 MHz, $CDCl_3$) (3q)



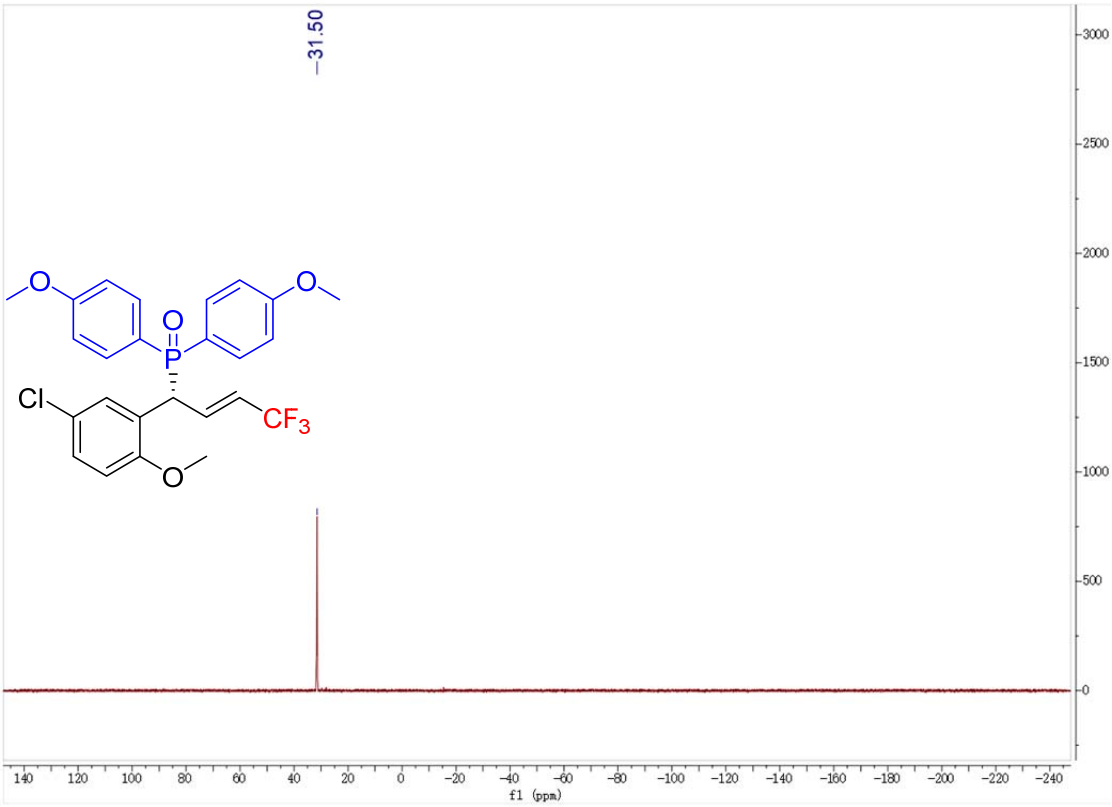
^{13}C NMR (101 MHz, $CDCl_3$) (3q)



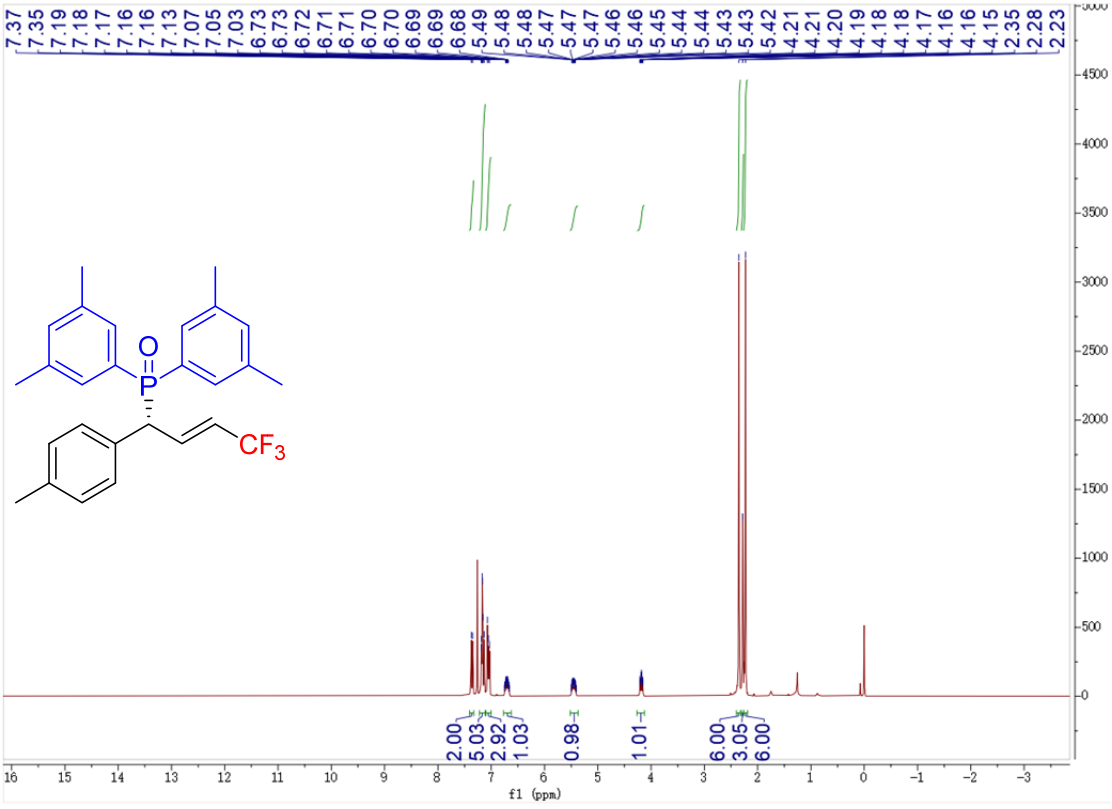
^{19}F NMR (377 MHz, $CDCl_3$) (3q)



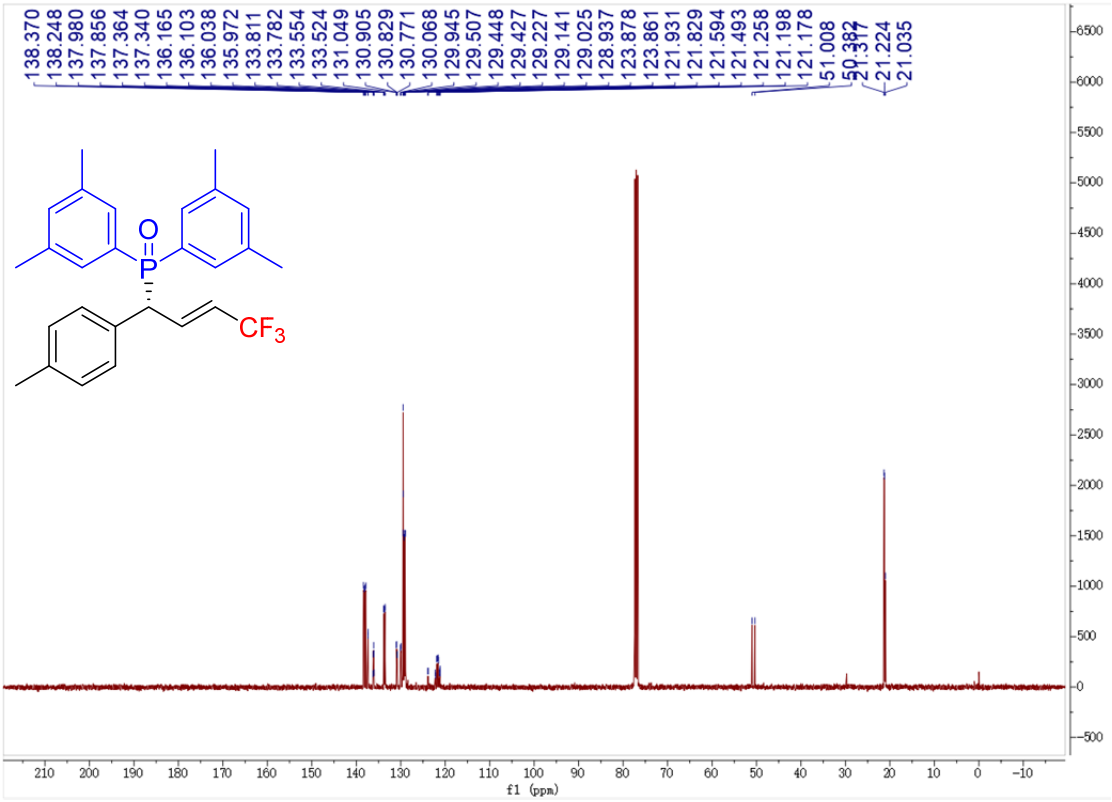
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3q)



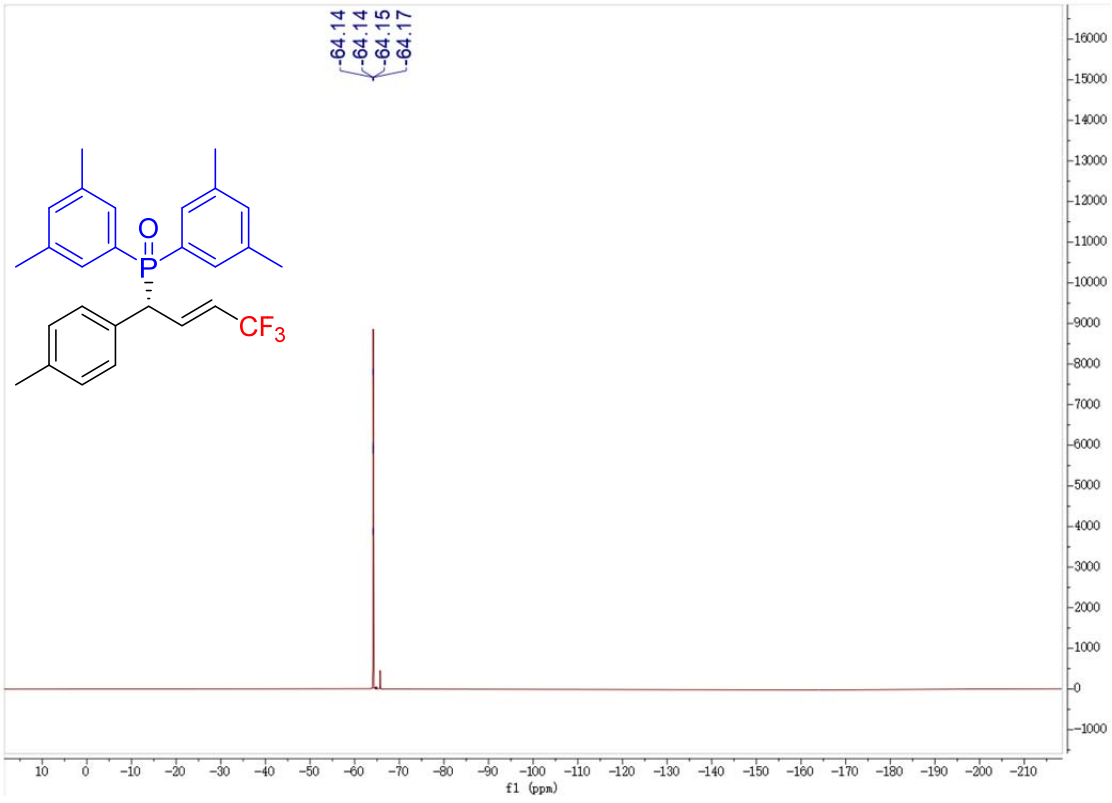
^{1}H NMR (400 MHz, $CDCl_3$) (3r)



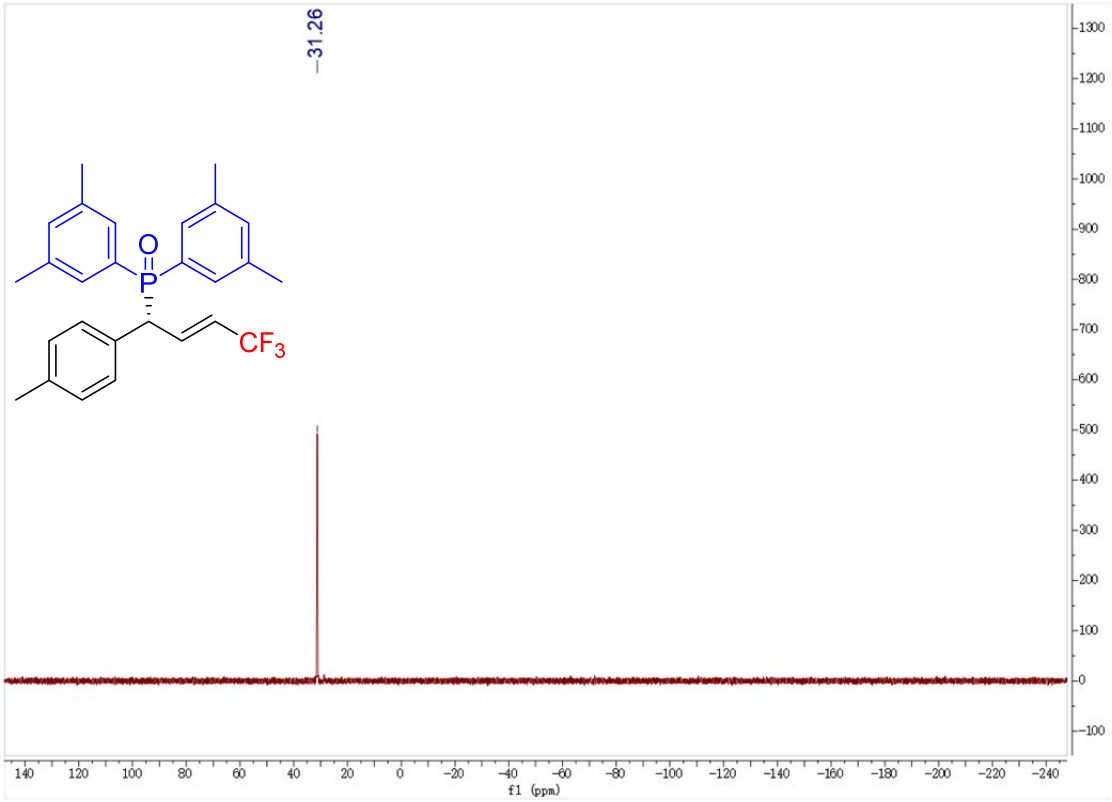
^{13}C NMR (101 MHz, $CDCl_3$) (3r)



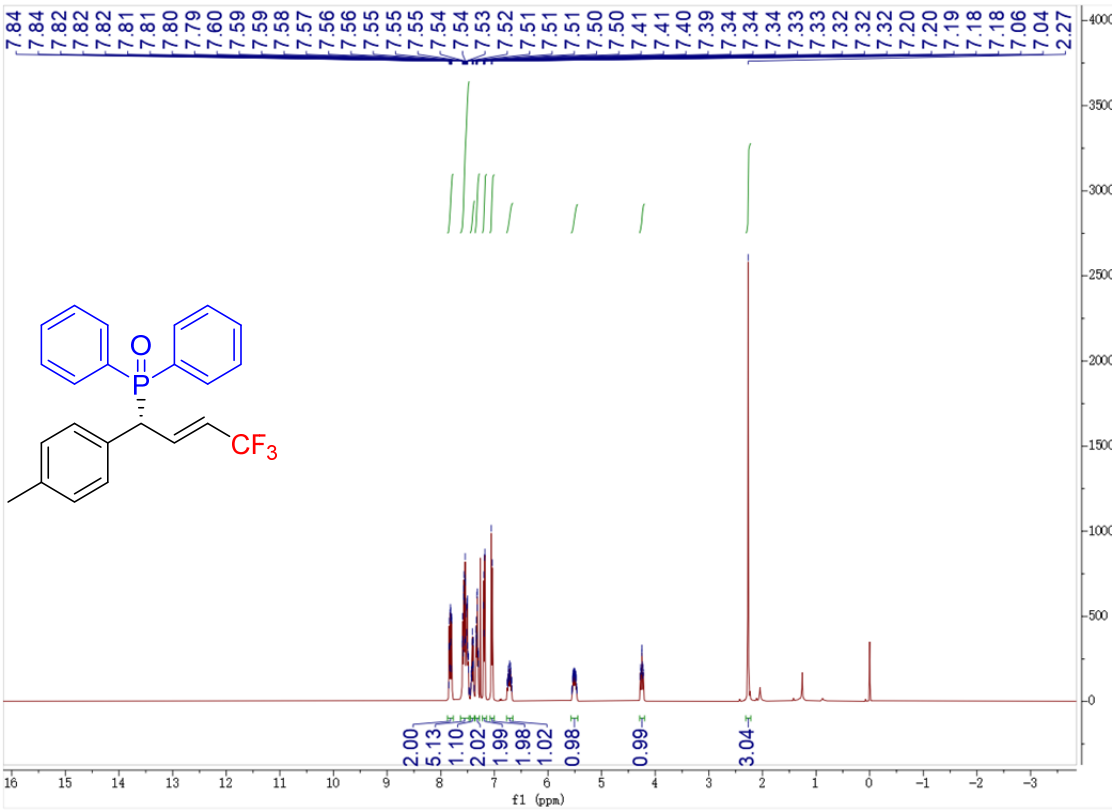
^{19}F NMR (377 MHz, $CDCl_3$) (3r)



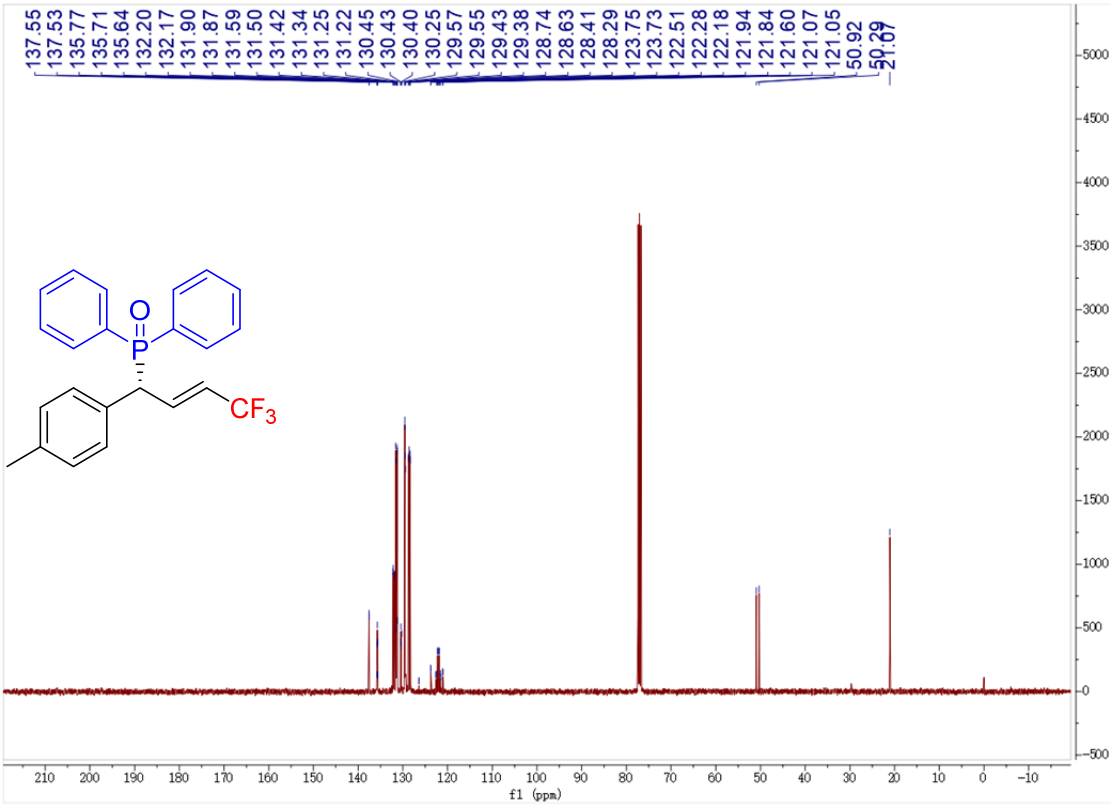
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3r)



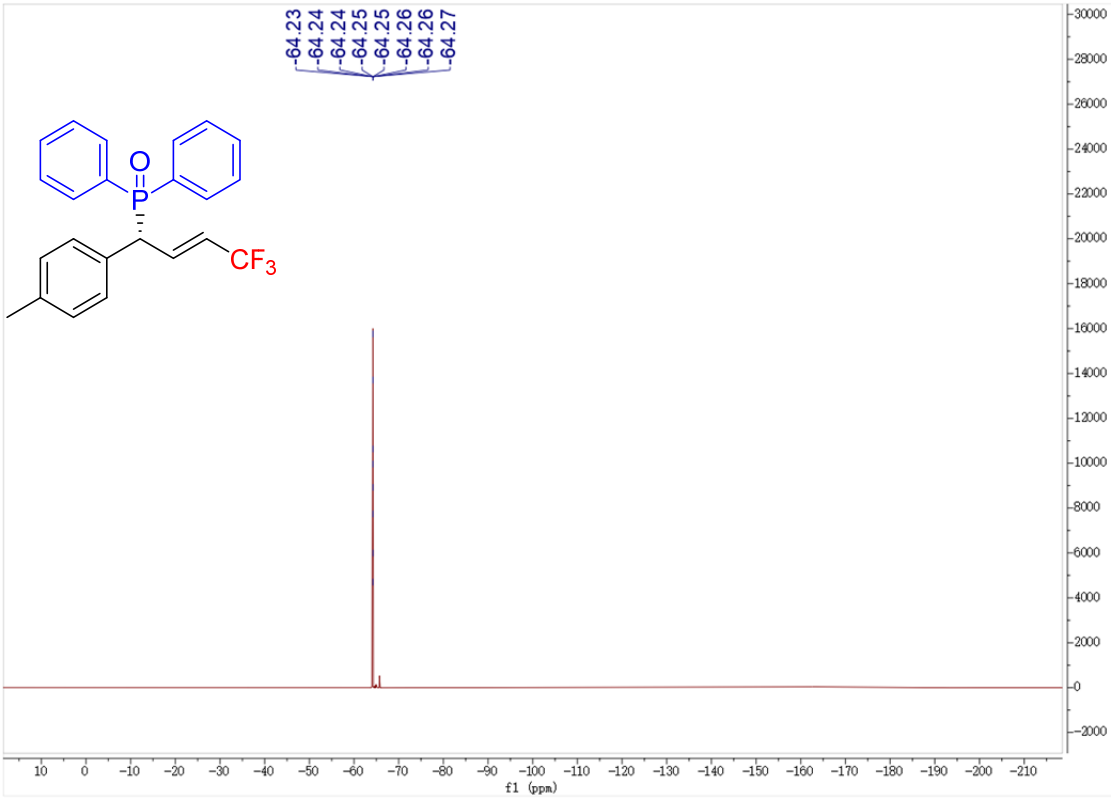
^{1}H NMR (400 MHz, $CDCl_3$) (3s)



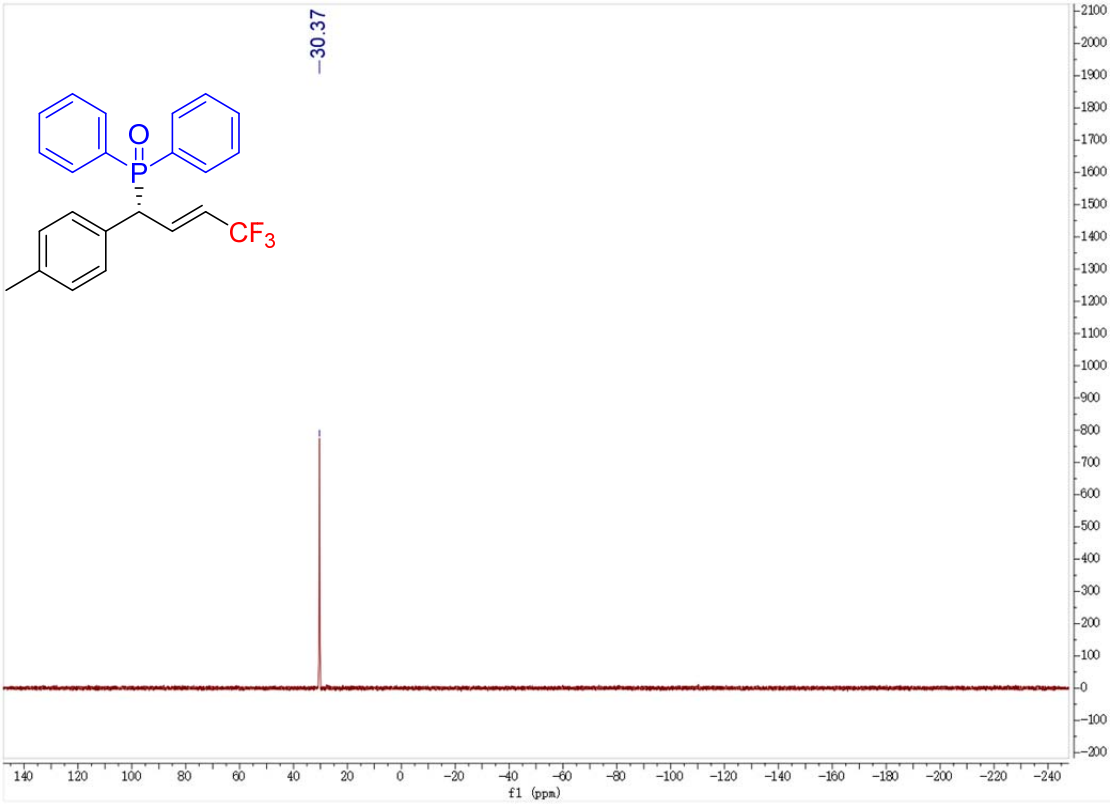
^{13}C NMR (101 MHz, $CDCl_3$) (3s)



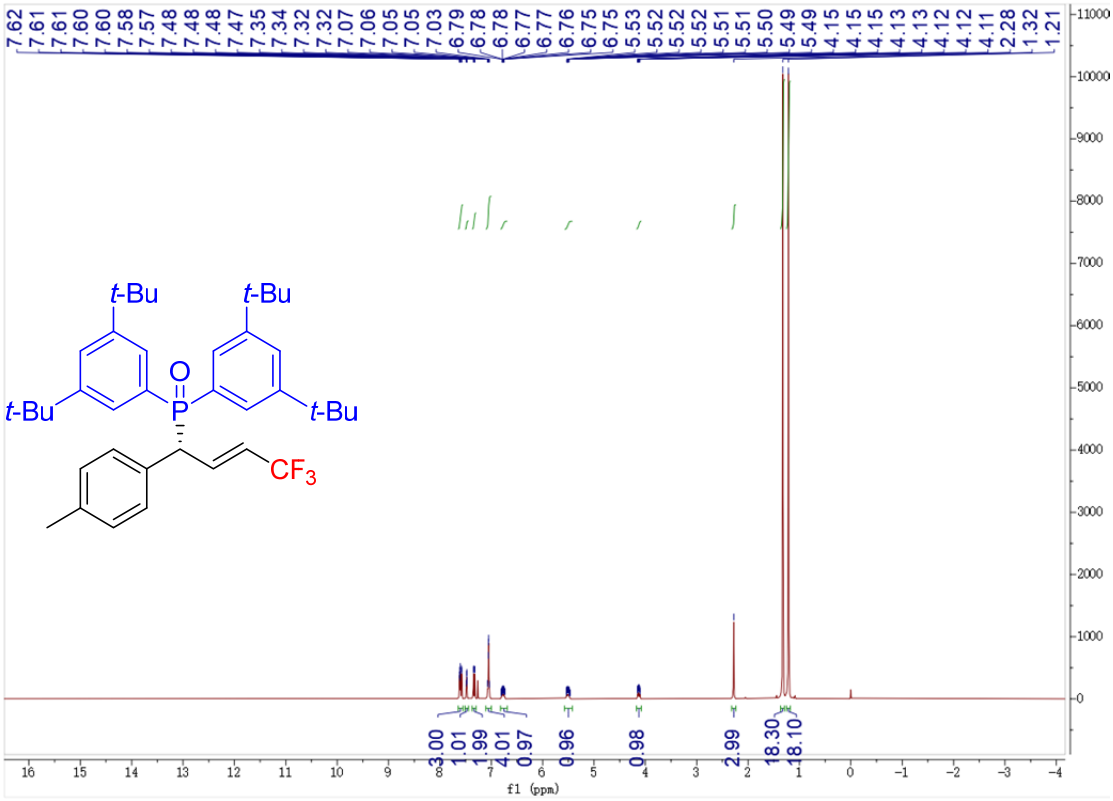
^{19}F NMR (377 MHz, $CDCl_3$) (3s)



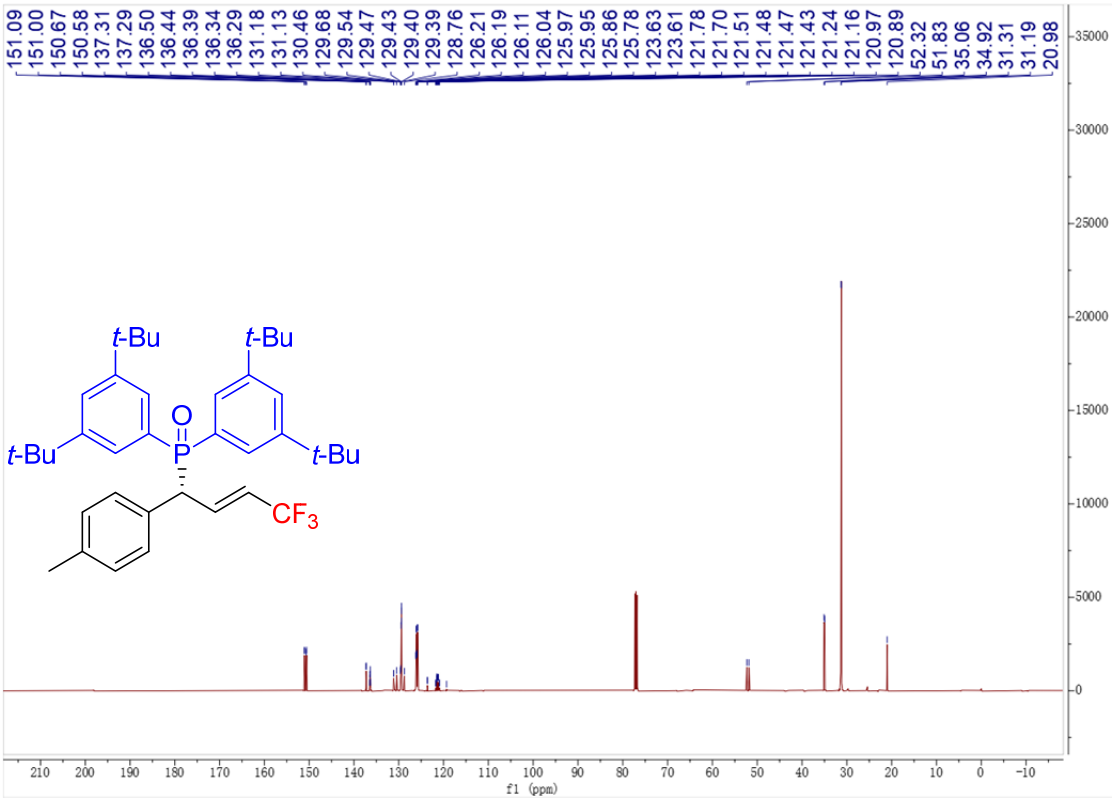
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3s)



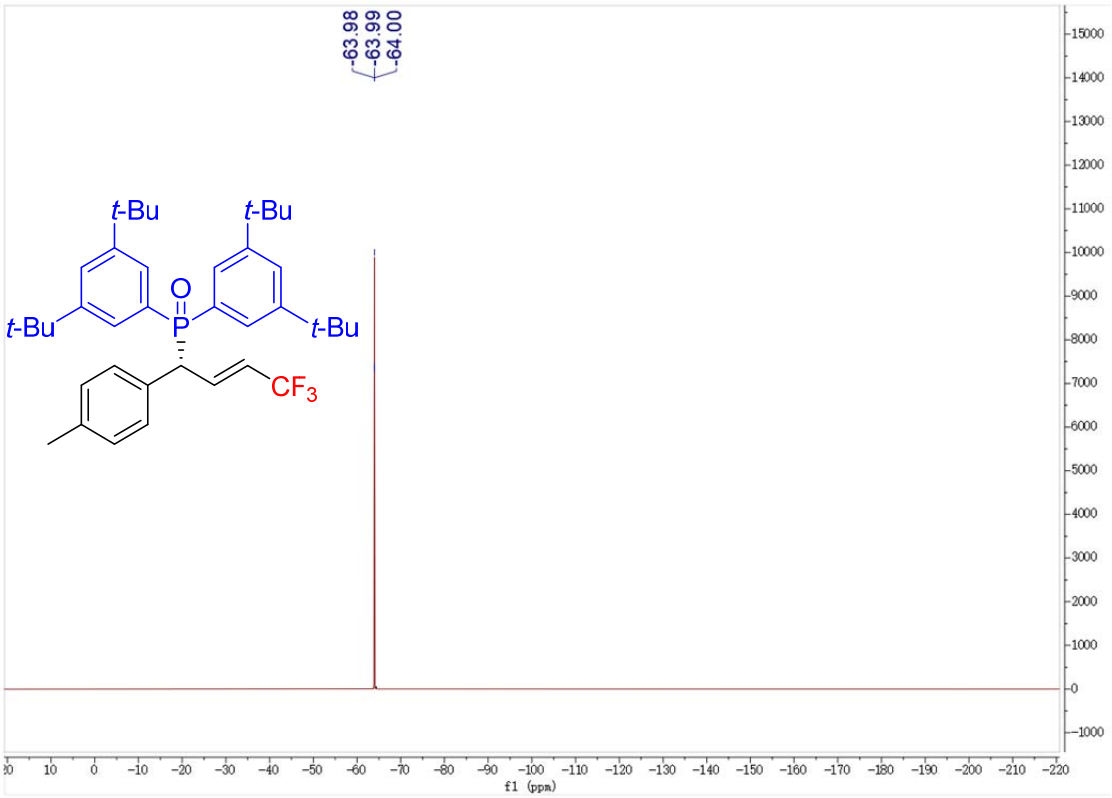
^{1}H NMR (500 MHz, $CDCl_3$) (3t)



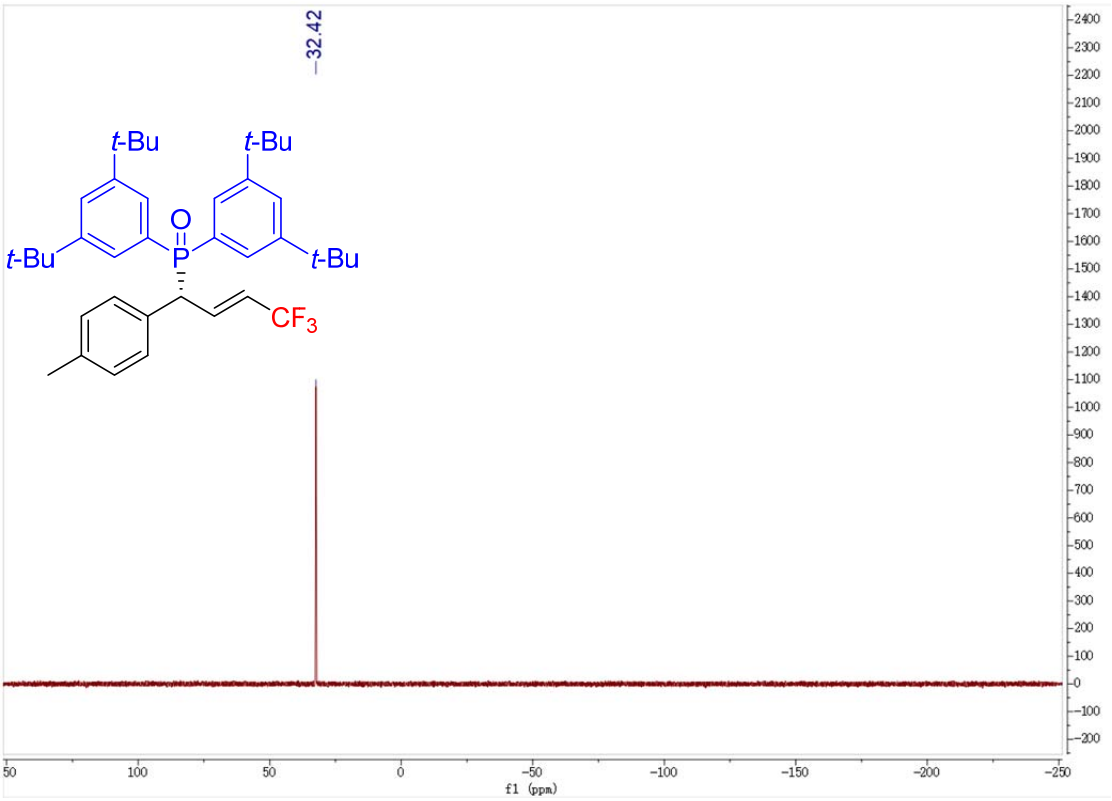
^{13}C NMR (126 MHz, $CDCl_3$) (3t)



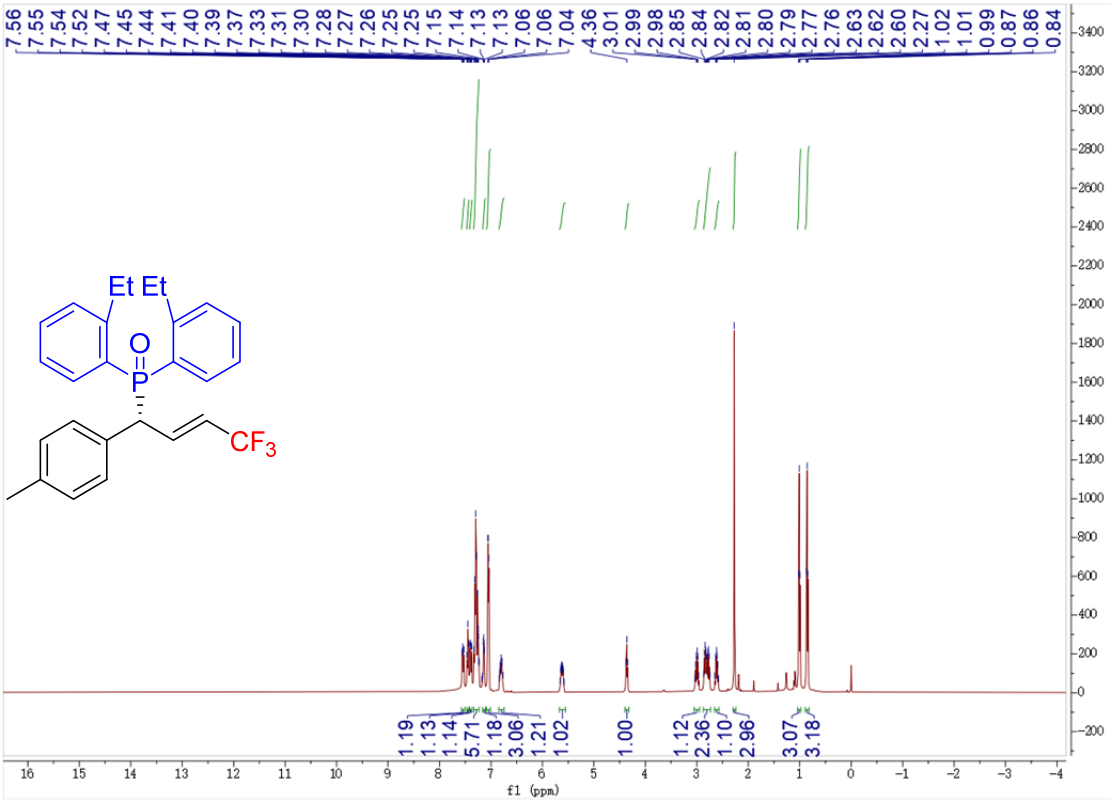
^{19}F NMR (470 MHz, $CDCl_3$) (3t)



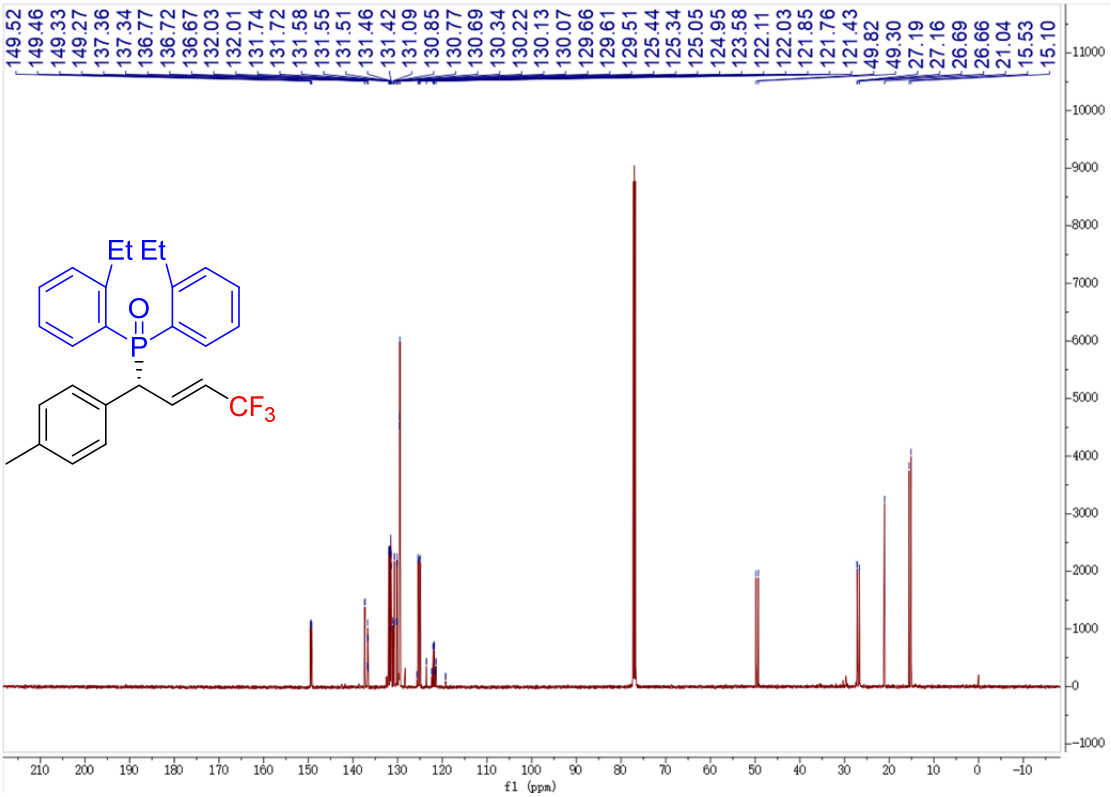
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) (3t)



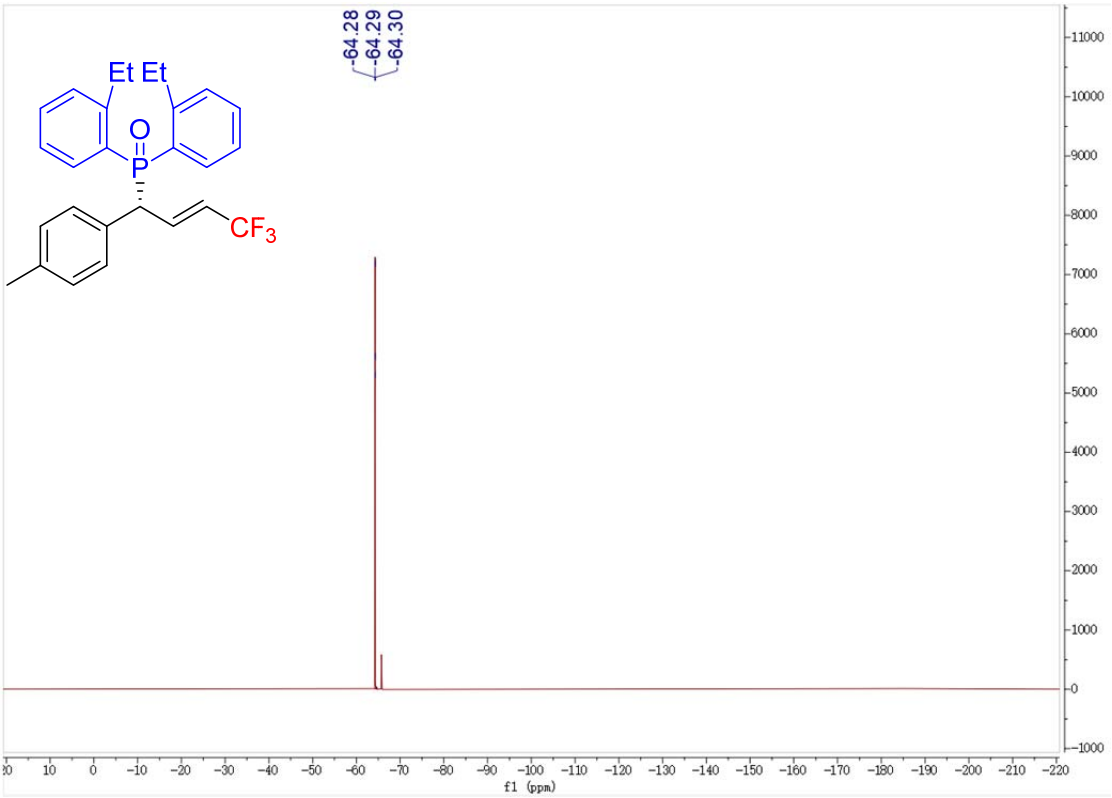
^{1}H NMR (500 MHz, $CDCl_3$) (3u)



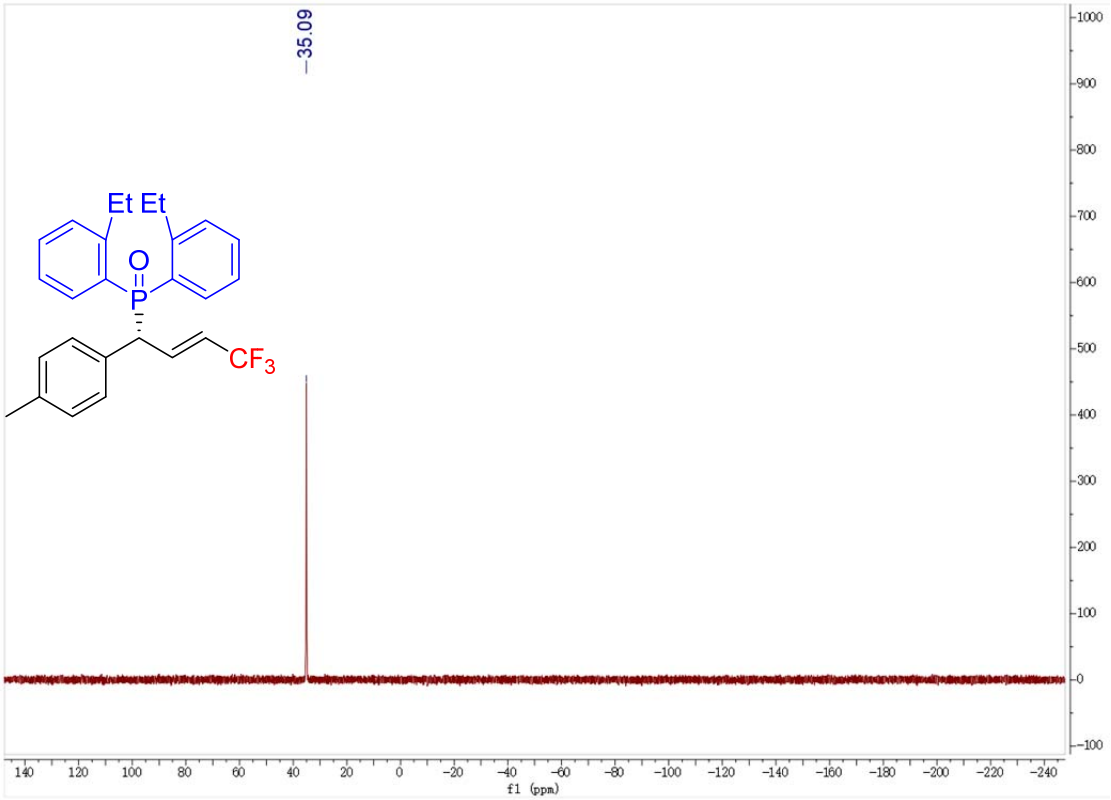
^{13}C NMR (126 MHz, $CDCl_3$) (3u)



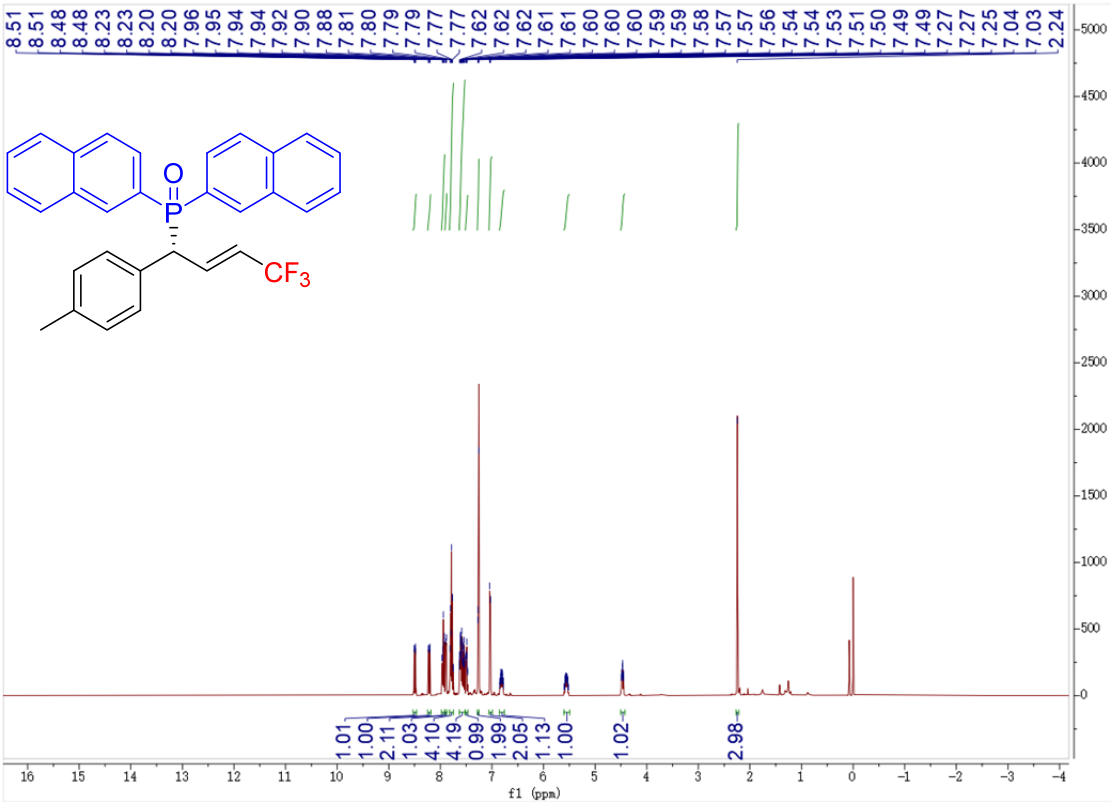
^{19}F NMR (470 MHz, $CDCl_3$) (3u)



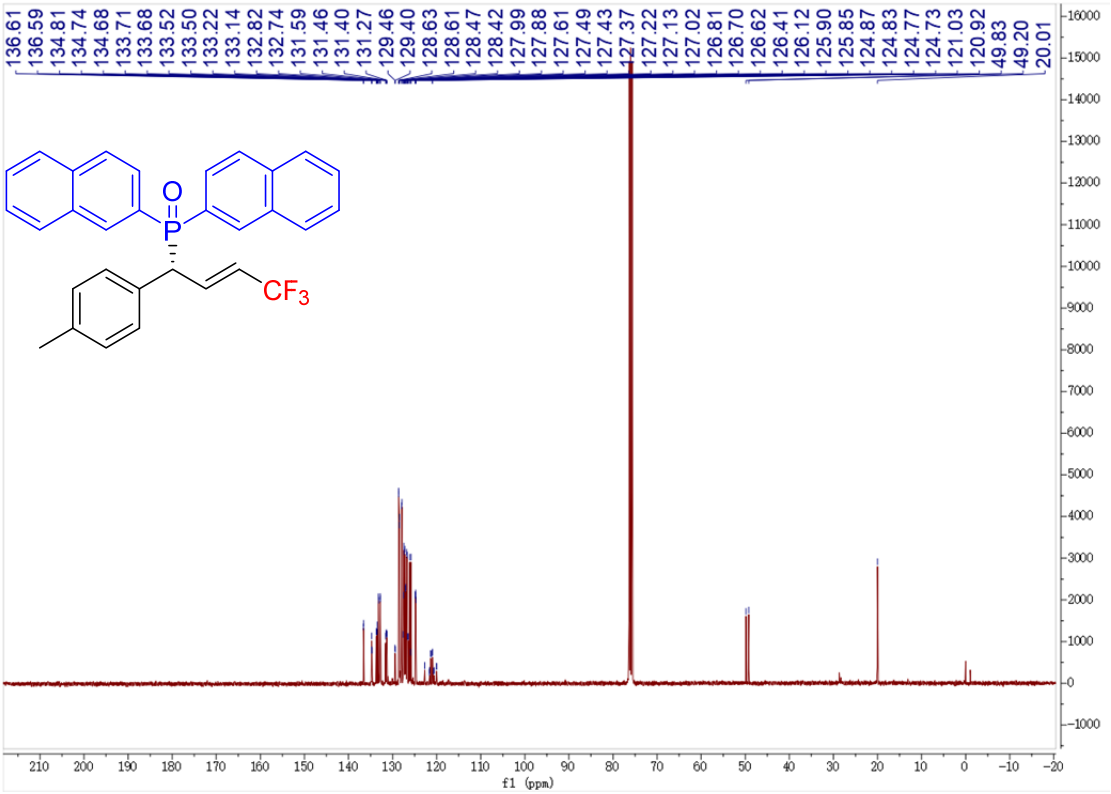
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3u)



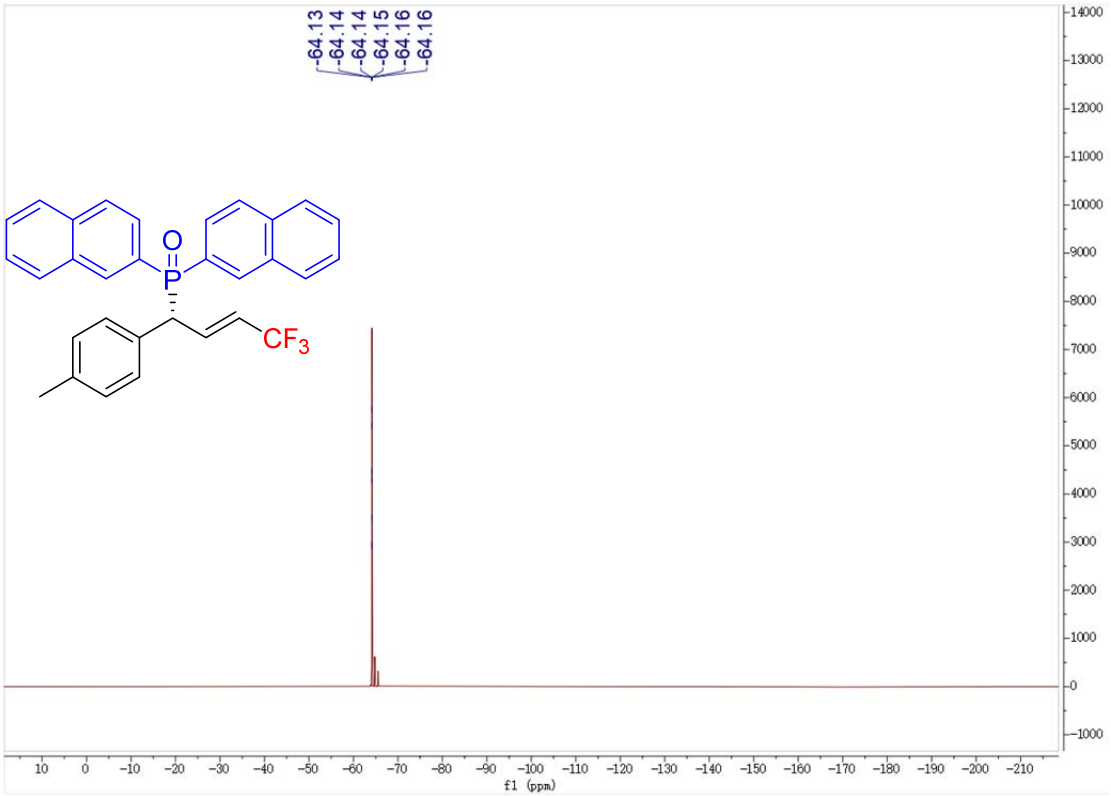
^{1}H NMR (500 MHz, $CDCl_3$) (3v)



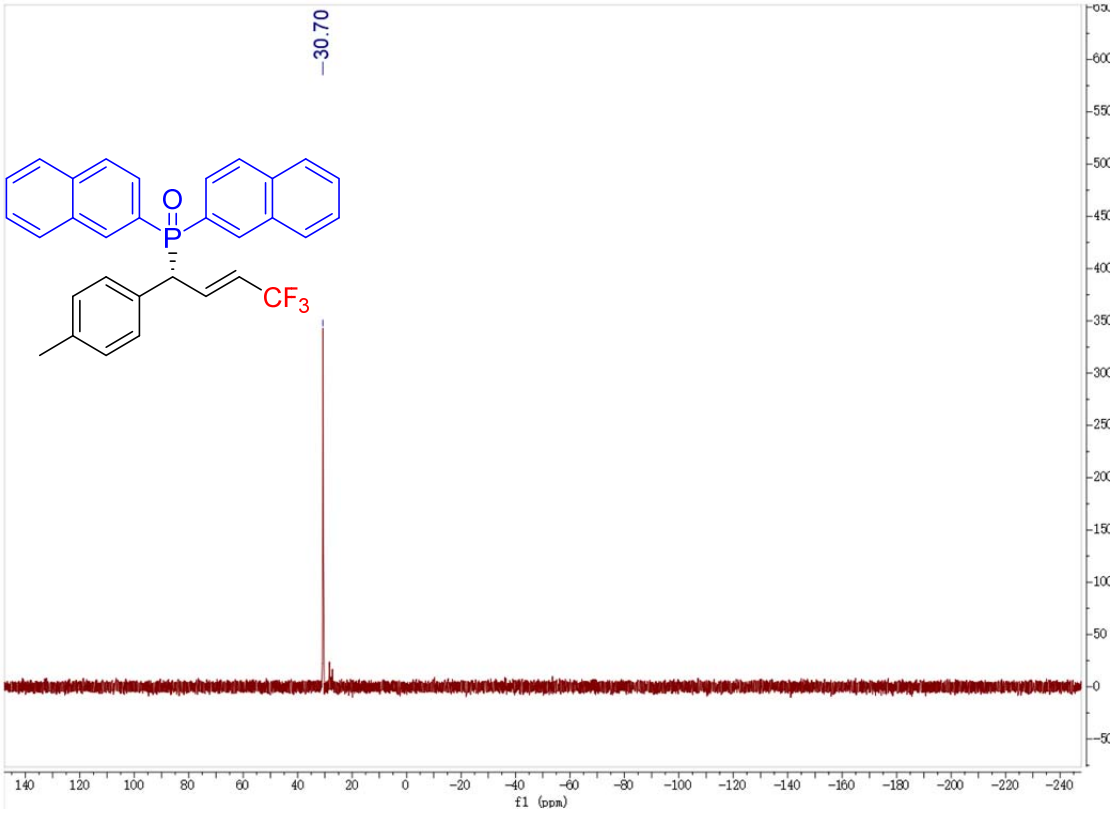
^{13}C NMR (101 MHz, $CDCl_3$) (3v)



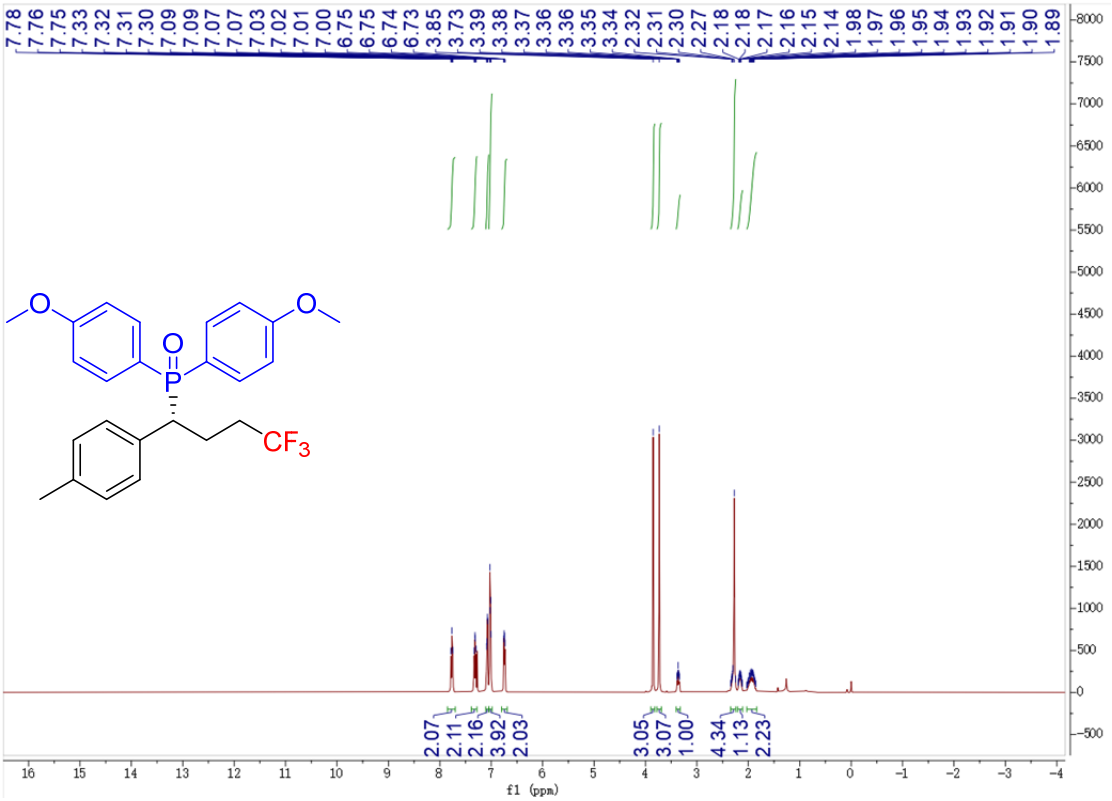
^{19}F NMR (377 MHz, $CDCl_3$) (3v)



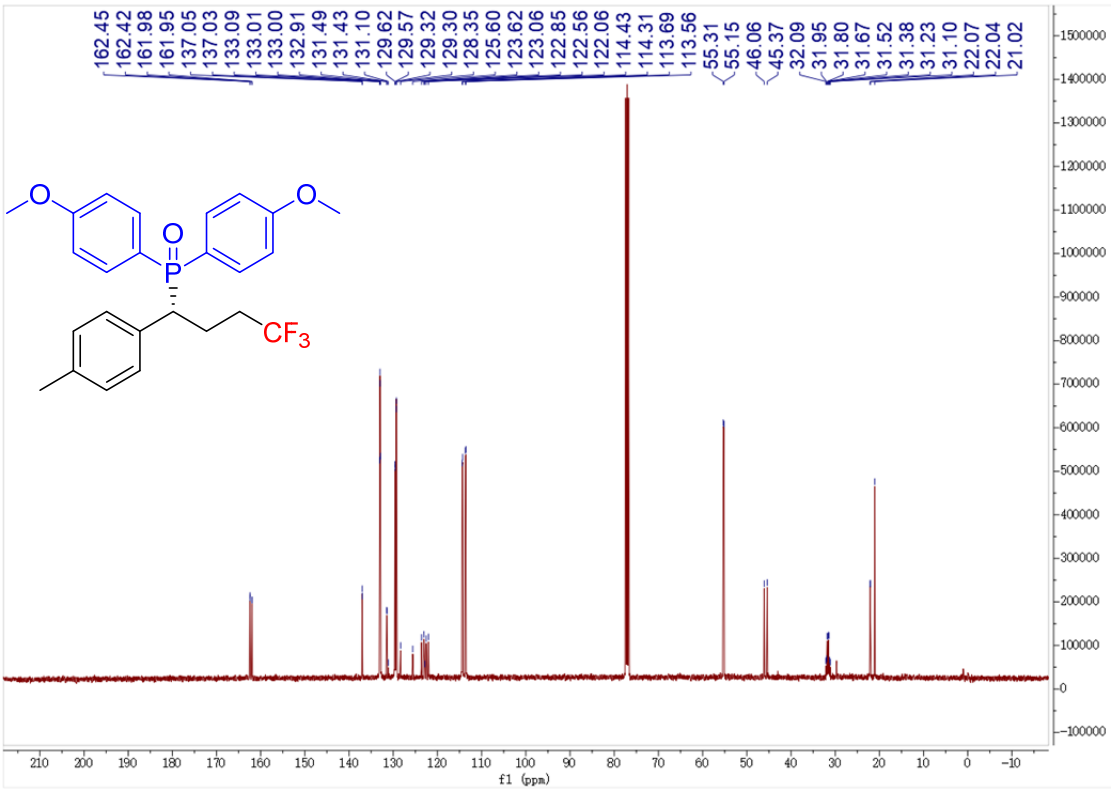
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (3v)



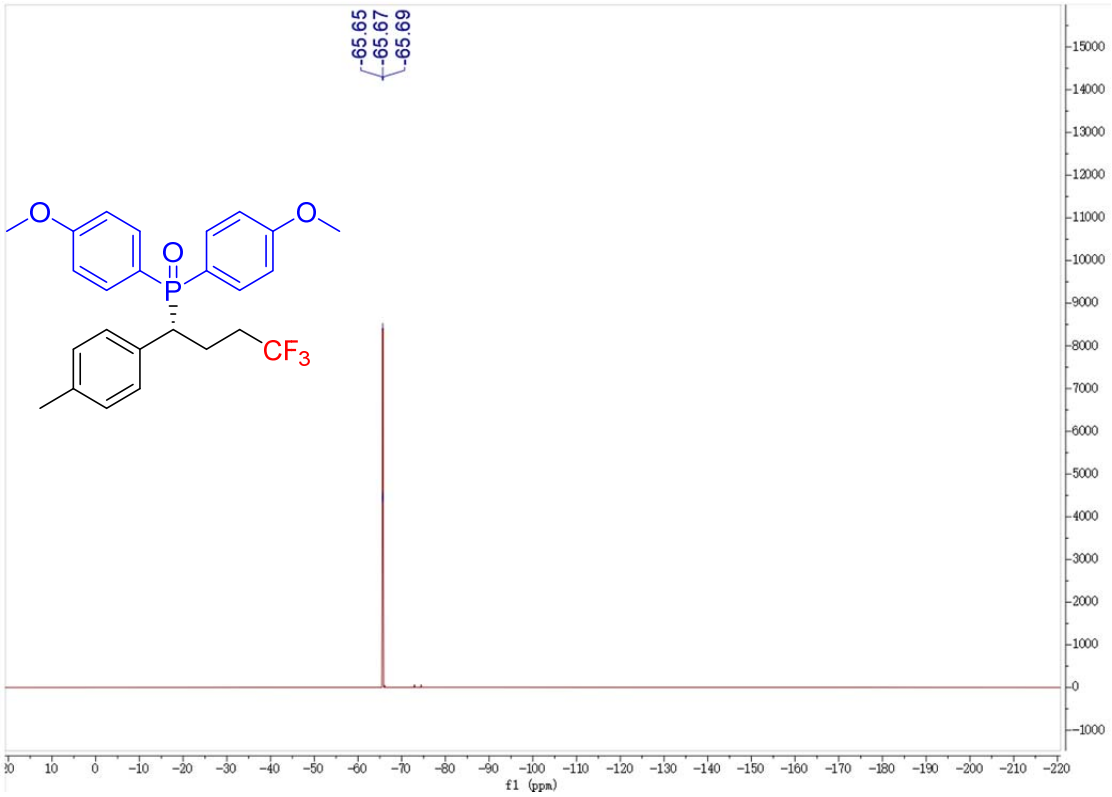
^{1}H NMR (500 MHz, $CDCl_3$) (4a)



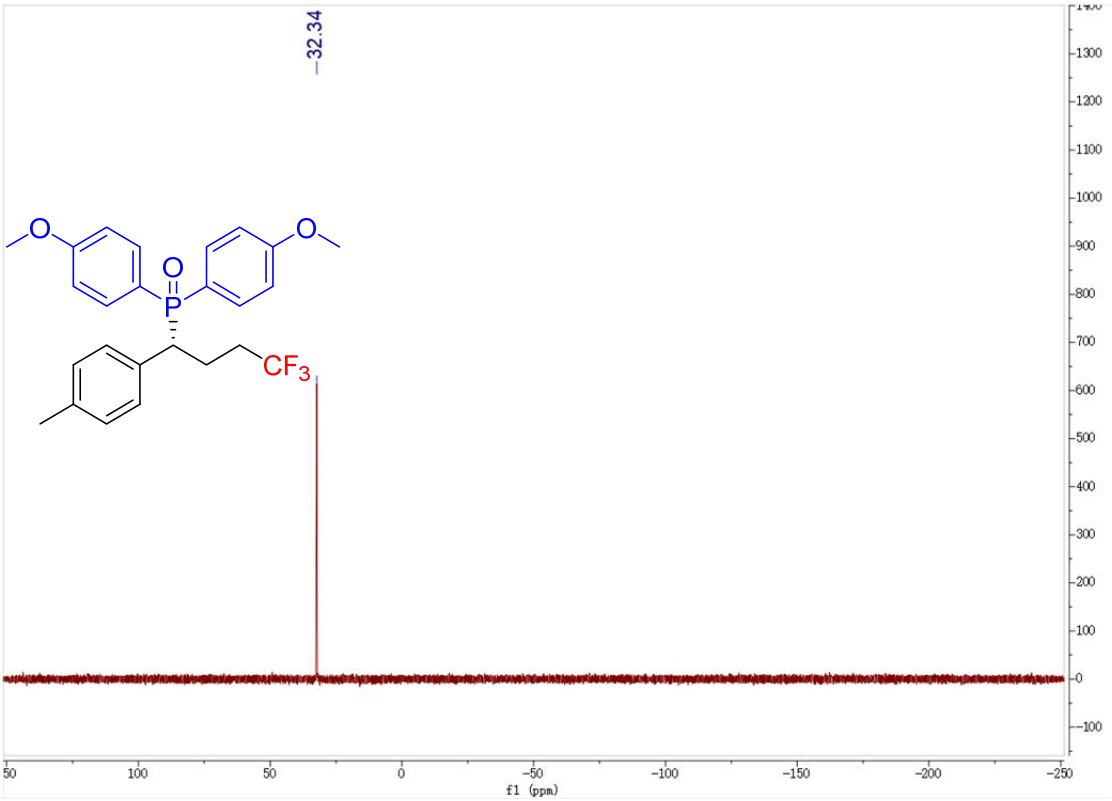
^{13}C NMR (101 MHz, $CDCl_3$) (4a)



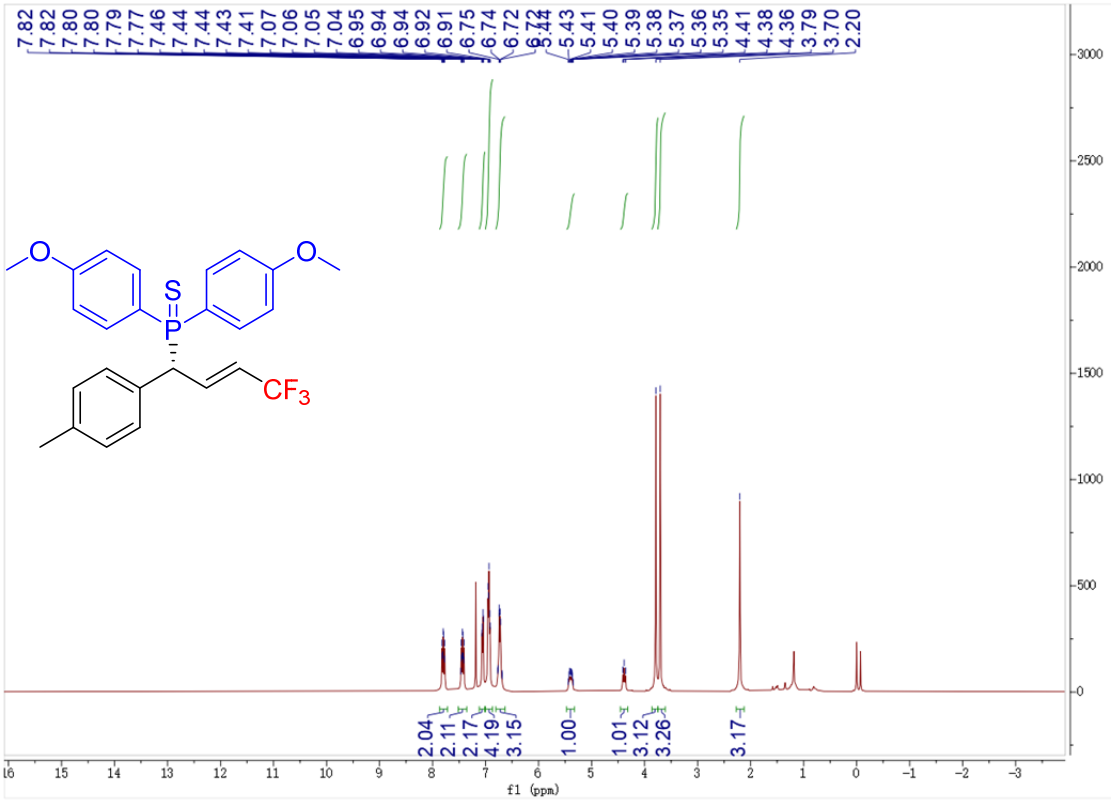
^{19}F NMR (470 MHz, $CDCl_3$) (4a)



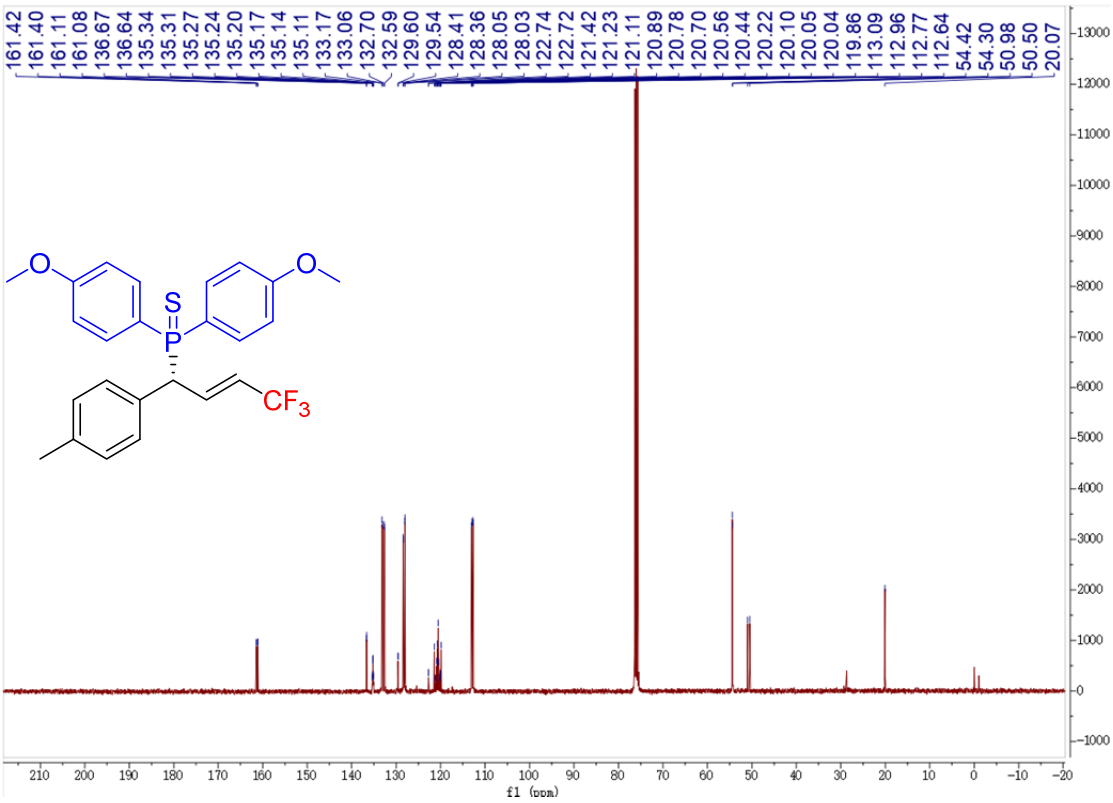
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) (4a)



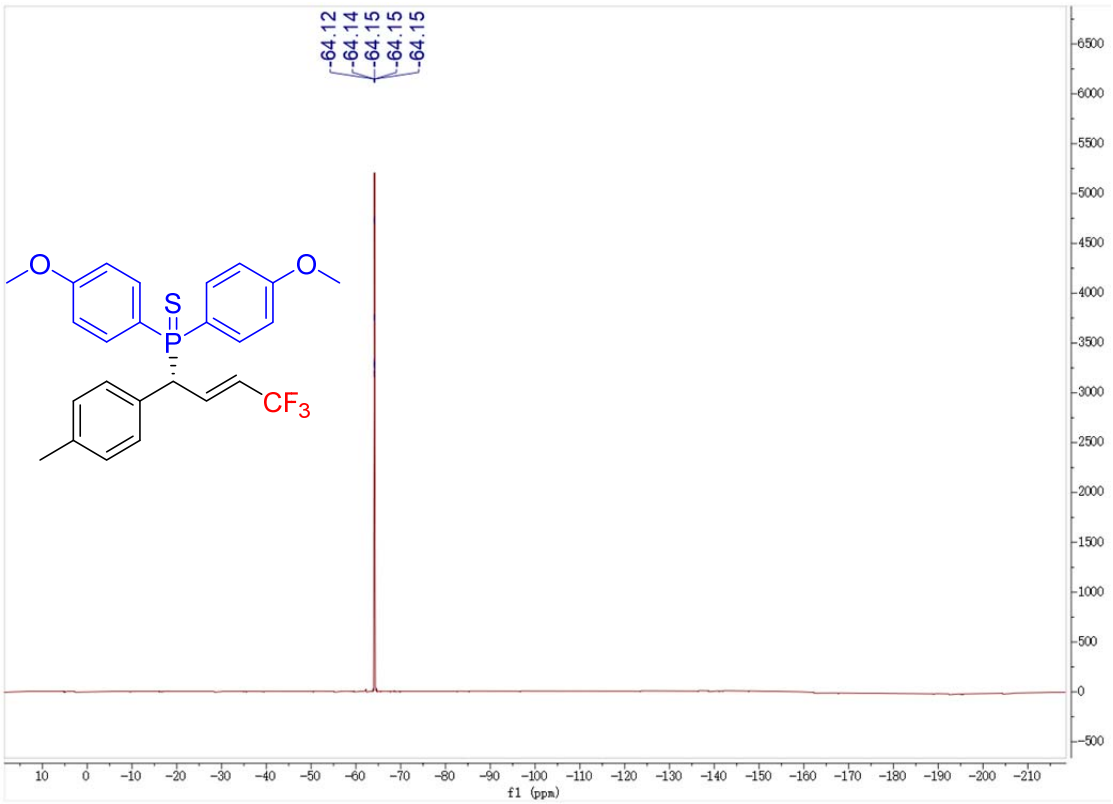
^{1}H NMR (400 MHz, $CDCl_3$) (5a)



^{13}C NMR (101 MHz, $CDCl_3$) (5a)



^{19}F NMR (377 MHz, $CDCl_3$) (5a)



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) (5a)