Supporting Information

"On-Water" Defluorinative Cyclization of Trifluoromethyl Enones with Phosphine Oxides: Synthesis of Polysubstituted Furans

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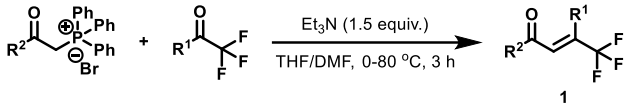
General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Melting points were recorded on an electrothermal digital melting point apparatus. ^{1}H, ^{19}F, ^{31}P, and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance or Joel 400 MHz spectrometers. NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublets (dd), doublet of triplets (dt), doublet of quartets (dq), triplet of doublets (td), triplet of triplets (tt), quartet of doublets (qd), and doublet of doublet (ddd), *etc*. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QTof) using electrospray ionization (ESI) in positive or negative mode. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

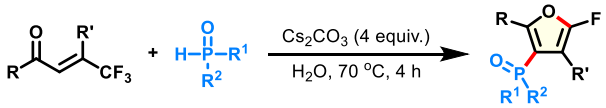
General procedure for the synthesis of trifluoromethylated enones 1[1-2]



1

A solution of triphenylphosphonium salt (7.5 mmol, 1.5 equiv.) and triethylamine (758.9 mg, 7.5 mmol, 1.5 equiv.) in THF (20 mL) was added a solution of a trifluoromethyl ketone (5.0 mmol, 1 equiv.) in DMF (1.6 mL) at 0 °C (ice bath) under air. The mixture was stirred for 15 min at this temperature. After warming to room temperature, the solution was heated at 80 °C (oil bath) for 3 h. The solution was quenched with saturated aqueous NH_4Cl solution (30 mL) and extracted with ethyl acetate (50 mL x 3). The organic extract was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate: 100/1) to give the pure trifluoromethylated enones **1**.

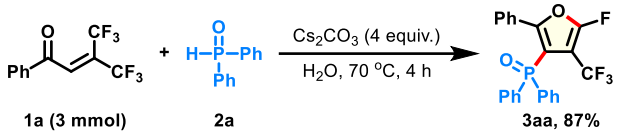
General procedure for the reaction of trifluoromethylated enones 1 with phosphine oxides 2



1 2 3

A solution of trifluoromethylated enone (0.3 mmol, 1 equiv., **1**), phosphine oxide (0.45 mmol, 1.5 equiv., **2**), and Cs_2CO_3 (391.0 mg, 1.2 mmol, 4 equiv.) in H_2O (2 mL) was stirred at 70 °C (oil bath) for 4 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The combined organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (6/1~3/1) as eluent to afford the pure products **3**.

Scale-up synthesis of product 3aa

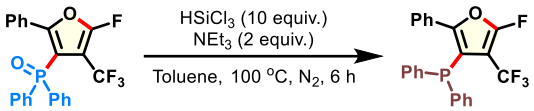


1a (3 mmol) 2a 3aa, 87%

A solution of 4,4,4-trifluoro-1-phenyl-3-(trifluoromethyl)but-2-en-1-one (804.1 mg, 3 mmol, 1 equiv., **1a**), diphenylphosphine oxide (909.9 mg, 4.5 mmol, 1.5 equiv., **2a**), and Cs_2CO_3 (3910.0 mg, 12 mmol, 4 equiv.) in H_2O (10 mL) was stirred at 70 °C (oil bath) for 4 h. The reaction was then quenched by saturated NH_4Cl solution (40 mL) and extracted with EtOAc (40 mL x 3). The combined organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (6/1~3/1) as eluent to afford the pure product **3aa** (1122.5 mg, 87% yield).

Further transformations of product 3aa

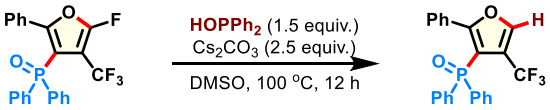
a) Reduction of product 3aa by $HSiCl_3$



3aa 4, 89%

To an oven-dried vial equipped with a stir bar was added (5-fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (129.0 mg, 0.3 mmol, 1 equiv., **3aa**) at room temperature under air. The vial was capped with a rubber septum, evacuated and refilled with nitrogen (3 times). Anhydrous toluene (4 mL), trichlorosilane (1354.5 mg, 10 equiv., 3 mmol,), and Et_3N (60.7 mg, 2 equiv., 0.6 mmol) were added sequentially via syringe. The reaction mixture was placed in an oil bath at 100 °C and stirred for 6 h. After cooling the vial to room temperature, the reaction vial was opened to air and quenched with saturated NH_4Cl solution (20 mL). The resulting mixture was extracted with EtOAc (20 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether as eluent to afford the pure product **4** (110.6 mg, 89% yield).

b) Reduction of product 3aa by $HOPPh_2$

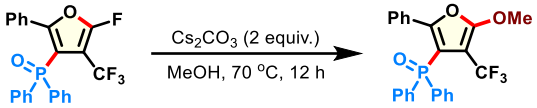


3aa 5, 92%

A solution of (5-fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (129.0 mg, 0.3 mmol, 1 equiv., **3aa**), diphenylphosphine oxide (91.0 mg, 0.45 mmol, 1.5 equiv.), and Cs_2CO_3 (244.4 mg, 0.75 mmol, 2.5 equiv.) in DMSO (2 mL) was stirred at 100 °C under air for 12 h. The reaction was then quenched by saturated NH_4Cl solution (10 mL) and extracted with EtOAc (10 mL x 3). The combined organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash

silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (6/1~2/1) as eluent to afford the pure product **5** (113.7 mg, 92% yield).

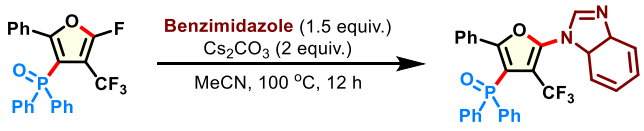
c) Reaction of product 3aa with MeOH



3aa **6**, 85%

A solution of (5-fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (129.0 mg, 0.3 mmol, 1 equiv., **3aa**), and Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv.) in MeOH (2 mL) was stirred at 70 °C under air for 12 h. The reaction was then quenched by saturated NH_4Cl solution (10 mL) and extracted with EtOAc (10 mL x 3). The combined organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (5/1~1/1) as eluent to afford the pure product **6** (112.7 mg, 85% yield).

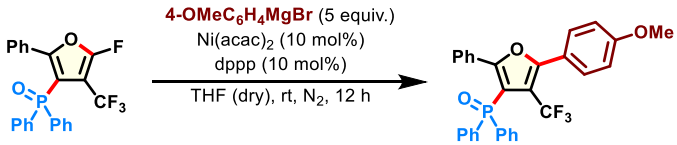
d) Reaction of product 3aa with benzimidazole



3aa **7**, 67%

A solution of (5-fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (129.0 mg, 0.3 mmol, 1 equiv., **3aa**), benzimidazole (53.2 mg, 0.45 mmol, 1.5 equiv.), and Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv.) in MeCN (2 mL) was stirred at 100 °C under air for 12 h. The reaction was then quenched by saturated NH_4Cl solution (10 mL) and extracted with EtOAc (10 mL x 3). The combined organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (4/1~1/1) as eluent to afford the pure product **7** (106.2 mg, 67% yield).

e) Reaction of product 3aa with Grignard reagent



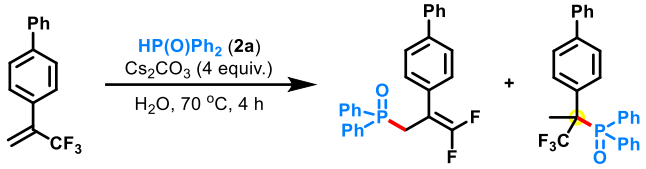
3aa **8**, 82%

To an oven-dried vial equipped with a stir bar was added (5-fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (129.0 mg, 0.3 mmol, 1 equiv., **3aa**), $Ni(acac)_2$ (7.7 mg, 0.03 mmol, 0.1 equiv.), and dppp (12.4 mg, 0.03 mmol, 0.1 equiv.) at room temperature under air. The vial was capped with a rubber septum, evacuated and refilled with nitrogen (3 times). Anhydrous THF (1 mL) and 4-$OMeC_6H_4MgBr$ (1 mL, 1.5 mmol, 1.5 mol/L in THF, 5 equiv.) were added sequentially via syringe. The reaction was stirred at room temperature for 12 h. The reaction was then quenched by saturated NH_4Cl solution (10 mL) and

extracted with EtOAc (10 mL x 3). The combined organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (6/1~1/1) as eluent to afford the pure product **8** (127.7 mg, 82% yield).

Mechanistic studies

a) The reactivity of trifluoromethylated alkene 9

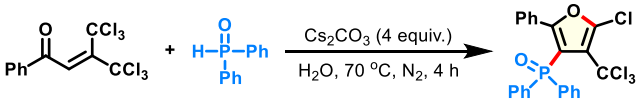


9 **10**, 40% **11**, <5%

A solution of 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (74.4 mg, 0.3 mmol, 1 equiv., **9**), diphenylphosphine oxide (91.0 mg, 0.45 mmol, 1.5 equiv., **2a**), and Cs_2CO_3 (391.0 mg, 1.2 mmol, 4 equiv.) in H_2O (2 mL) was stirred at 70 °C (oil bath) for 4 h. The reaction was then quenched by saturated NH_4Cl solution (10 mL) and extracted with EtOAc (10 mL x 3). The combined organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (6/1~1/1) as eluent to afford the pure product **10** (51.7 mg, 40% yield) and product **11** (<5% yield).

This result indicated that the reaction might initiate via the intermolecular S_N2'-type defluorinative substitution.

b) The reactivity of β,β-di-trichloromethylated alkene 12

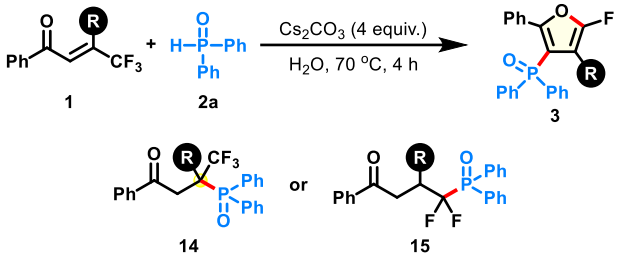


12 **2a** **13**, trace

A solution of 4,4,4-trichloro-1-phenyl-3-(trichloromethyl)but-2-en-1-one (109.2 mg, 0.3 mmol, 1 equiv., **12**), diphenylphosphine oxide (91.0 mg, 0.45 mmol, 1.5 equiv., **2a**), and Cs_2CO_3 (391.0 mg, 1.2 mmol, 4 equiv.) in H_2O (2 mL) was stirred at 70 °C (oil bath) under N_2 for 4 h. Only trace amount of the product **13** was formed.

This result suggested that the trifluoromethyl groups were discovered to be crucial in enhancing substrate reactivity.

c) The influence of *β*-substituted group on the reaction efficiency

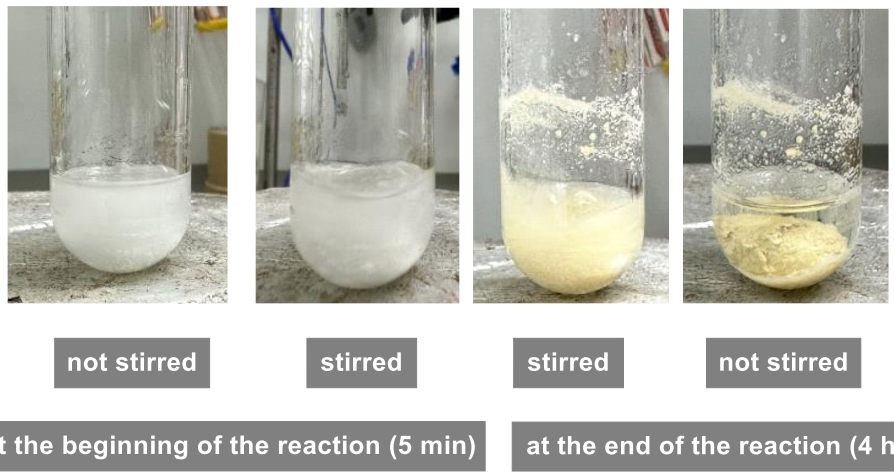


Entry	R	Products	Yield (%)
1	Me	**3ra/14a/15a**	0/95/0
2	Et	**3sa/14b/15b**	0/96/0
3	CO_2Et	**3ta/14c/15c**	0/0/8
4	H	**3ua/14d/15d**	0/60/0
5	Ph	**3oa/14e/15e**	trace/trace/0

A solution of β-trifluoromethyl enone (0.3 mmol, 1 equiv., **1q-t** and **1n**), diphenylphosphine oxide (91.0 mg, 0.45 mmol, 1.5 equiv., **2a**), and Cs_2CO_3 (391.0 mg, 1.2 mmol, 4 equiv.) in H_2O (2 mL) was stirred at 70 °C (oil bath) under air for 4 h. The reaction was then quenched by saturated NH_4Cl solution (10 mL) and extracted with EtOAc (10 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (10/1~2/1) as eluent to afford the pure products **14a** (118.6 mg, 95% yield), **14b** (123.9 mg, 96% yield), **14d** (72.4 mg, 60% yield), and **15c** (10.9 mg, 8% yield).

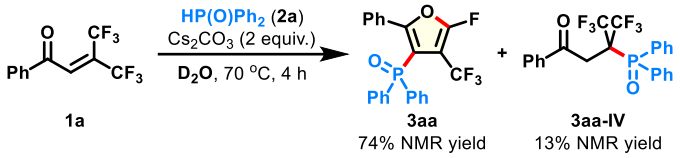
When R is Me, Et, CO_2Et, H, or Ph, only phospha-Michael addition byproducts 14 and ipso-defluorinative byproduct 15c were formed. These outcomes underscore the importance of the trifluoromethyl group in fine-tuning the reaction selectivity.

d) The heterogeneity of the reaction



Insoluble reactants tend to aggregate during the reaction course, and the heterogeneity of the reaction was observed.

e) The isotope kinetic effect (in D_2O)

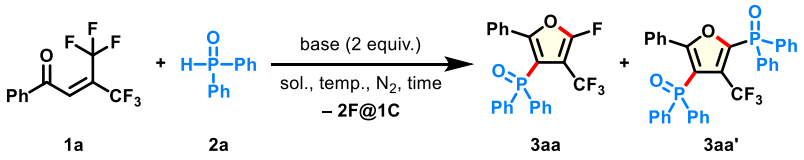


A solution of 4,4,4-trifluoro-1-phenyl-3-(trifluoromethyl)but-2-en-1-one (80.4 mg, 0.3 mmol, 1 equiv., **1a**), diphenylphosphine oxide (91.0 mg, 0.45 mmol, 1.5 equiv., **2a**), and Cs_2CO_3 (195.5 mg, 0.6 mmol, 2 equiv.) in D_2O (2 mL) was stirred at 70 °C (oil bath) for 4 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The combined organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. ^1H NMR analysis of the obtained residue by using 4-fluoroanisole (0.1 mmol) as an internal standard indicated the formation of product **3aa** (74% NMR yield) and byproduct **3aa-IV** (13% NMR yield), respectively.

A discernible isotope kinetic effect was observed. This result also supported the specific property of the "on-water" reaction.

Optimization of Reaction Conditions

Table S1. Optimization of reaction conditions[a]



Entry	**1a/2a**	Base (2 equiv)	Solvent	Temp. (°C)	Time (h)	Yield of **3aa** (%)[b]	Yield of **3aa'** (%)[b]
1	1/1.5	Cs_2CO_3	H_2O	100	24	85	15
2	1/1.5	Cs_2CO_3	H_2O	100	12	88	12
3	1/1.5	Cs_2CO_3	H_2O	70	12	94	6
4	1/3	Cs_2CO_3	H_2O	70	12	91	9
5	1/1.2	Cs_2CO_3	H_2O	70	12	86	1
6	1/1.5	Cs_2CO_3	H_2O	50	12	88	0
7	1/1.5	Cs_2CO_3	H_2O	rt	12	71	0
8	1/1.5	Cs_2CO_3	H_2O	70	8	90	2
9	**1/1.5**	**Cs_2CO_3**	**H_2O**	**70**	**4**	**97 (94)[c]**	**1**
10	1/1.5	K_3PO_4	H_2O	70	4	76	0
11	1/1.5	DBU	H_2O	70	4	62	8
12	1/1.5	LiOH	H_2O	70	4	65	1
13	1/1.5	Cs_2CO_3	MeOH	70	4	8	8
14	1/1.5	Cs_2CO_3	MeCN	70	4	71	19
15	1/1.5	Cs_2CO_3	DMSO	70	4	20	0

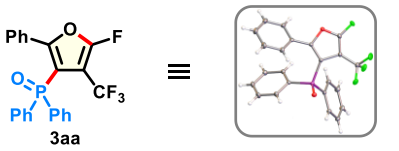
[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.36-0.9 mmol), and base (0.6 mmol) in solvent (2 mL) at r.t.-100 °C under N_2. [b] Yields were determined by ^{19}F NMR analysis with $PhOCF_3$ (0.1 mmol) as an internal standard. [c] Isolated yield.

The X-ray crystal structure of products

The single crystal was grown from the mixed solution of EtOAc/DCM/DMSO by slowly

evaporating the above solvents at room temperature.

(5-Fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (**3aa**; displacement ellipsoids are drawn at the 50% probability levels):



CCDC 2284384 (3aa)

Table S2. Crystal data and structure refinement for **3aa**

Identification code	**3aa**
Empirical formula	$C_{23}H_{15}F_4O_2P$
Formula weight	430.32
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.8764(3)
b/Å	20.6631(4)
c/Å	11.3864(2)
α/°	90
β/°	92.772(2)
γ/°	90
Volume/Å^3	3966.00(13)
Z	8
ρ_{calc}g/cm^3	1.441
μ/mm^{-1}	1.726
F(000)	1760.0
Crystal size/mm^3	0.15 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.242 to 147.124
Index ranges	-20 ≤ h ≤ 20, -25 ≤ k ≤ 24, -8 ≤ l ≤ 13
Reflections collected	16062
Independent reflections	7786 [R_{int} = 0.0411, R_{sigma} = 0.0510]
Data/restraints/parameters	7786/0/541
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0491, wR_2 = 0.1286
Final R indexes [all data]	R_1 = 0.0615, wR_2 = 0.1415
Largest diff. peak/hole / e Å^{-3}	0.34/-0.30

Crystal structure determination of [3aa]

Crystal Data for $C_{23}H_{15}F_4O_2P$ (*M* =430.32 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* =

16.8764(3) Å, *b* = 20.6631(4) Å, *c* = 11.3864(2) Å, *β* = 92.772(2)°, *V* = 3966.00(13) Å^3, *Z* = 8, *T* = 169.99(10) K, μ(Cu Kα) = 1.726 mm^{-1}, *Dcalc* = 1.441 g/cm^3, 16062 reflections measured (5.242° ≤ 2Θ ≤ 147.124°), 7786 unique (R_{int} = 0.0411, R_{sigma} = 0.0510) which were used in all calculations. The final R_1 was 0.0491 (I > 2σ(I)) and wR_2 was 0.1415 (all data).

(5-Fluoro-2,4-diphenylfuran-3-yl)diphenylphosphine oxide (**3oa**; displacement ellipsoids are drawn at the 50% probability levels):

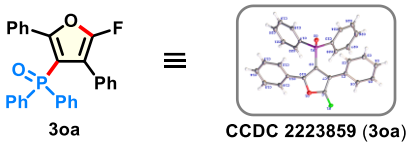


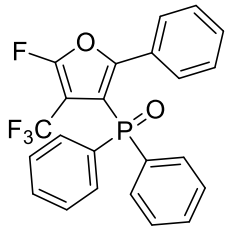
Table S3. Crystal data and structure refinement for **3oa**

Identification code	**3oa**
Empirical formula	$C_{28}H_{20}FO_2P$
Formula weight	438.41
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.9054(3)
b/Å	15.6356(3)
c/Å	11.0833(2)
α/°	90
β/°	105.718(2)
γ/°	90
Volume/Å^3	2152.80(8)
Z	4
ρ_{calc}g/cm^3	1.353
μ/mm^{-1}	1.397
F(000)	912.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.116 to 147.664
Index ranges	-16 ≤ h ≤ 12, -19 ≤ k ≤ 18, -13 ≤ l ≤ 12
Reflections collected	8405
Independent reflections	4247 [R_{int} = 0.0212, R_{sigma} = 0.0279]
Data/restraints/parameters	4247/0/299
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0431, wR_2 = 0.1104
Final R indexes [all data]	R_1 = 0.0474, wR_2 = 0.1130
Largest diff. peak/hole / e Å^{-3}	0.28/-0.39

Crystal structure determination of [3oa]

Crystal Data for $C_{28}H_{20}FO_2P$ (M =438.41 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 12.9054(3) Å, b = 15.6356(3) Å, c = 11.0833(2) Å, β = 105.718(2)°, V = 2152.80(8) Å^3, Z = 4, T = 150.00(10) K, μ(Cu Kα) = 1.397 mm^{-1}, *Dcalc* = 1.353 g/cm^3, 8405 reflections measured (7.116° ≤ 2Θ ≤ 147.664°), 4247 unique (R_{int} = 0.0212, R_{sigma} = 0.0279) which were used in all calculations. The final R_1 was 0.0431 (I > 2σ(I)) and wR_2 was 0.1130 (all data).

Characterization data for products



(5-Fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3aa):

Yield = 94% (121.6 mg). White solid. M.p. 156.0–157.9 ºC.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

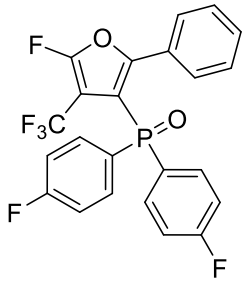
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.68–7.59 (m, 4H), 7.41–7.35 (m, 2H), 7.32–7.24 (m, 4H), 7.22–7.18 (m, 2H), 7.18–7.12 (m, 1H), 7.06–6.99 (m, 2H) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -54.72 (d, J = 16.4 Hz, 3F), -105.76 (qd, J = 15.3, 4.5Hz, 1F) ppm.

^{31}P NMR (162 MHz, CDCl$_3$): δ = 18.82 ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 157.3–154.2 (m, 1C), 152.0 (d, J = 14.0 Hz), 132.2 (d, J = 2.6 Hz), 131.8 (d, J = 10.3 Hz), 131.6 (d, J = 109.1 Hz), 129.9, 129.7, 128.4 (d, J = 12.9 Hz), 127.9, 127.4, 120.6 (qd, J = 263.4, 5.9 Hz), 112.1 (d, J = 106.2 Hz), 92.9–92.6 (m, 1C) ppm.

HRMS (m/z): calcd for $C_{23}H_{16}F_4O_2P$ $[M+H]^+$ 431.0819, found: 431.0816.



(5-Fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)bis(4-fluorophenyl)phosphine oxide (3ab):

Yield = 90% (126.1 mg). White solid. M.p. 152.7–153.9 ºC.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 8/1~2/1).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.65–7.57 (m, 4H), 7.25–7.18 (m, 3H), 7.11–7.07 (m, 2H), 7.01–6.96 (m, 4H) ppm.

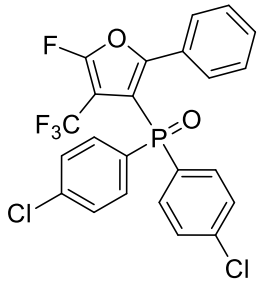
^{19}F NMR (376 MHz, CDCl$_3$): δ = -54.74 (d, J = 15.5 Hz, 3F), -105.33 (qd, J = 15.8, 3.7 Hz, 1F), -105.72– -105.84 (m, 2F) ppm.

^{31}P NMR (162 MHz, CDCl$_3$): δ = 16.99 ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 165.3 (dd, J = 254.5, 3.5 Hz), 157.4–154.3 (m, 1C), 152.2 (d, J

= 14.4 Hz), 134.3 (dd, *J* = 11.8, 9.0 Hz), 130.2, 129.8, 128.1, 127.3, 126.9 (d, *J* = 3.7 Hz), 120.6 (qd, *J* = 268.5, 5.3 Hz), 115.9 (dd, *J* = 21.6, 14.0 Hz), 112.0 (d, *J* = 110.1 Hz), 93.0–92.4 (m, 1C) ppm.

HRMS (m/z): calcd for $C_{23}H_{14}F_6O_2P$ $[M+H]^+$ 467.0630, found: 467.0627.



Bis(4-chlorophenyl)(5-fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)phosphine oxide (3ac):

Yield = 89% (133.2 mg). White solid. M.p. 153.8–155.5 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

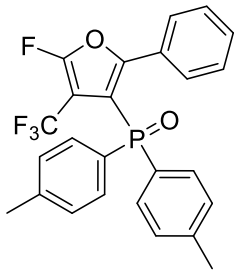
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.51 (m, 4H), 7.31–7.25 (m, 5H), 7.22–7.18 (m, 2H), 7.13–7.08 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.62 (d, *J* = 16.1 Hz, 3F), -105.87 (qd, *J* = 16.3, 2.9 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 16.97 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4–154.3 (m, 1C), 152.3 (d, *J* = 14.4 Hz), 139.2 (d, *J* = 3.6 Hz), 133.1 (d, *J* = 11.1 Hz), 130.2, 129.9 (d, *J* = 113.6 Hz), 129.8, 128.9 (d, *J* = 13.5 Hz), 128.1, 127.1, 120.6 (qd, *J* = 266.7, 5.2 Hz), 111.6 (d, *J* = 111.5 Hz), 93.4–91.7 (m, 1C) ppm.

HRMS (m/z): calcd for $C_{23}H_{14}Cl_2F_4O_2P$ $[M+H]^+$ 499.0039, found: 499.0039.



(5-Fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)di-*p*-tolylphosphine oxide (3ad):

Yield = 96% (132.2 mg). White solid. M.p. 157.9–158.8 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

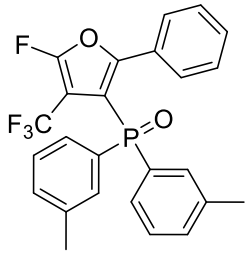
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.44 (m, 4H), 7.18–7.13 (m, 3H), 7.06 (dd, *J* = 8.1, 2.9 Hz, 4H), 7.04–6.98 (m, 2H), 2.28 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.71 (d, *J* = 16.0 Hz, 3F), -105.97 (qd, *J* = 16.2, 3.0 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.57 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2–154.1 (m, 1C), 151.6 (d, *J* = 14.0 Hz), 142.7 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 10.6 Hz), 129.7, 129.4, 129.1, 129.0 (d, *J* = 13.4 Hz), 127.8, 127.7 (d, *J* = 43.5 Hz), 120.8 (qd, *J* = 267.5, 10.1 Hz), 112.7 (d, *J* = 107.3 Hz), 93.0–92.5 (m, 1C), 21.5 ppm.

HRMS (m/z): calcd for $C_{25}H_{20}F_4O_2P$ $[M+H]^+$ 459.1132, found: 459.1126.



(5-Fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)di-*m*-tolylphosphine oxide (3ae):

Yield = 90% (124.0 mg). White solid. M.p. 148.9–150.8 ºC.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 7/1~2/1).

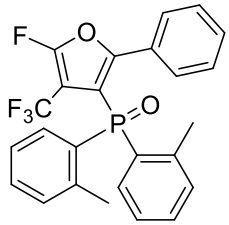
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.42 (m, 2H), 7.41–7.33 (m, 2H), 7.20–7.11 (m, 7H), 7.03 (dd, *J* = 8.4, 7.0 Hz, 2H), 2.22 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.72 (d, *J* = 15.0 Hz, 3F), -105.94 (qd, *J* = 16.1, 3.6 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.32 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4–154.2 (m, 1C), 151.7 (d, *J* = 14.2 Hz), 138.2 (d, *J* = 12.8 Hz), 132.9 (d, *J* = 2.9 Hz), 132.3 (d, *J* = 10.0 Hz), 131.5 (d, *J* = 111.0 Hz), 129.8, 129.5, 128.8 (d, *J* = 10.5 Hz), 128.2 (d, *J* = 13.6 Hz), 127.7, 127.5, 120.8 (qd, *J* = 267.5, 5.3 Hz), 112.4 (d, *J* = 106.5 Hz), 93.1–92.5 (m, 1C), 11.3 ppm.

HRMS (m/z): calcd for $C_{25}H_{20}F_4O_2P$ $[M+H]^+$ 459.1132, found: 459.1138.



(5-Fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)di-*o*-tolylphosphine oxide (3af):

Yield = 81% (111.6 mg). White solid. M.p. 151.2–153.1 ºC.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~2/1).

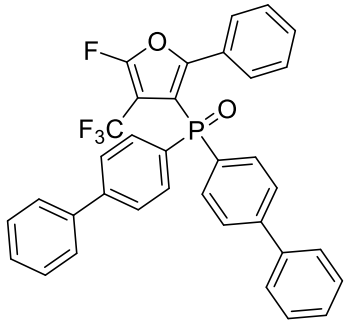
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.27 (m, 3H), 7.24–7.10 (m, 5H), 7.10–6.81 (m, 5H), 2.53 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.92 (d, *J* = 16.1 Hz, 3F), -105.23 (qd, *J* = 16.4, 3.0 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.41 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6–154.1 (m, 1C), 150.8 (d, *J* = 13.6 Hz), 143.8, 132.8, 132.4, 132.0 (d, *J* = 11.0 Hz), 129.8, 129.3, 128.8, 127.7, 127.1, 125.3 (d, *J* = 13.6 Hz), 120.7 (qd, *J* = 268.4, 5.3 Hz), 112.1 (dd, *J* = 105.4, 3.6 Hz), 93.8–92.4 (m, 1C), 21.7 (d, *J* = 4.8 Hz) ppm.

HRMS (m/z): calcd for $C_{25}H_{20}F_4O_2P$ $[M+H]^+$ 459.1132, found: 459.1131.



Di([1,1'-biphenyl]-4-yl)(5-fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)phosphine oxide (3ag):

Yield = 82% (143.5 mg). White solid. M.p. 166.1–167.9 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~3/1).

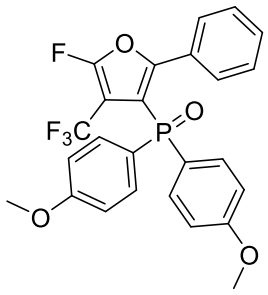
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.70 (m, 4H), 7.56–7.50 (m, 8H), 7.49–7.42 (m, 4H), 7.42–7.35 (m, 2H), 7.27–7.20 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.08–7.01 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.56 (d, *J* = 15.2 Hz, 3F), -105.62 (qd, *J* = 14.9, 3.3 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.73 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4–154.3 (m, 1C), 151.8 (d, *J* = 14.2 Hz), 145.0 (d, *J* = 2.9 Hz), 139.9, 132.4 (d, *J* = 10.6 Hz), 130.2 (d, *J* = 113.2 Hz), 129.9, 129.7, 129.0, 128.3, 127.9, 127.5, 127.3, 127.1 (d, *J* = 13.2 Hz), 120.8 (qd, *J* = 267.4, 5.0 Hz), 112.5 (d, *J* = 108.2 Hz), 93.6–92.0 (m, 1C) ppm.

HRMS (m/z): calcd for $C_{35}H_{24}F_4O_2P$ $[M+H]^+$ 583.1445, found: 583.1451.



(5-Fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)bis(4-methoxyphenyl)phosphine oxide (3ah):

Yield = 87% (128.2 mg). White solid. M.p. 144.0–145.1 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 4/1~1/1).

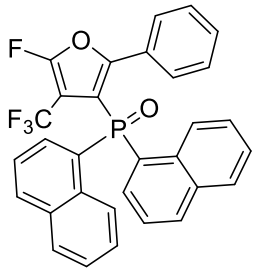
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.46 (m, 4H), 7.20–7.13 (m, 3H), 7.08–7.01 (m, 2H), 6.80–6.73 (m, 4H), 3.75 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.78 (d, *J* = 16.3 Hz, 3F), -106.02 (qd, *J* = 14.9, 3.0 Hz, 1F) ppm.

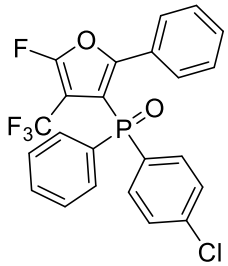
^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.20 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6 (d, *J* = 3.0 Hz), 157.2–154.1 (m, 1C), 151.5 (d, *J* = 14.0 Hz), 133.7 (d, *J* = 11.8 Hz), 129.8, 129.6, 127.8, 127.6, 123.1 (d, *J* = 118.8 Hz), 120.7 (qd, *J* = 268.6, 5.4 Hz), 113.9 (d, *J* = 14.0 Hz), 113.0 (d, *J* = 108.8 Hz), 92.9–92.4 (m, 1C), 55.3 ppm.

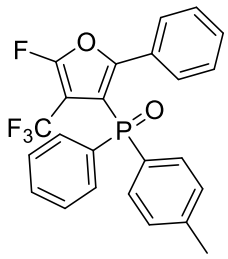
HRMS (m/z): calcd for $C_{25}H_{20}F_4O_4P$ $[M+H]^+$ 491.1030, found: 491.1028.



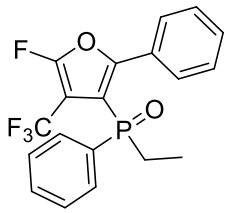
(5-Fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)di(naphthalen-1-yl)phosphine oxide (3ai):
Yield = 91% (145.0 mg). White solid. M.p. 166.6–168.5 °C.
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 5/1~2/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (dt, *J* = 14.8, 1.9 Hz, 2H), 7.84–7.68 (m, 6H), 7.63 (ddd, *J* = 10.2, 8.5, 1.6 Hz, 2H), 7.56–7.44 (m, 4H), 7.23–7.15 (m, 2H), 6.85–6.72 (m, 3H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.62 (d, *J* = 16.3 Hz, 3F), -103.60 (qd, *J* = 16.4, 2.8 Hz, 1F) ppm.
^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.02 ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3–154.3 (m, 1C), 152.0 (d, *J* = 14.4 Hz), 134.7 (d, *J* = 2.6 Hz), 134.1 (d, *J* = 9.7 Hz), 132.3 (d, *J* = 14.1 Hz), 129.62, 129.57, 128.9, 128.8 (d, *J* = 98.2 Hz), 128.4, 128.2, 127.7, 127.5, 127.1, 126.9 (qd, *J* = 266.9, 5.3 Hz), 126.2 (d, *J* = 11.1 Hz), 120.2 (m, 1C), 112.4 (d, *J* = 109.2 Hz), 93.2–92.6 (m, 1C) ppm.
HRMS (m/z): calcd for $C_{31}H_{20}F_4O_2P$ $[M+H]^+$ 531.1132, found: 531.1135.



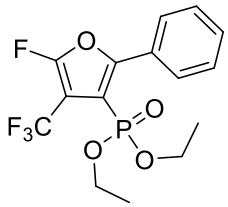
(4-Chlorophenyl)(5-fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)(phenyl)phosphine oxide (3aj):
Yield = 93% (129.7 mg). White solid. M.p. 153.9–155.4 °C.
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~2/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.59 (m, 2H), 7.56–7.49 (m, 2H), 7.45–7.39 (m, 1H), 7.34–7.29 (m, 2H), 7.25–7.16 (m, 5H), 7.09–7.03 (m, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.67 (d, *J* = 15.0 Hz, 3F), -105.49 (qd, *J* = 15.5, 4.0 Hz, 1F) ppm.
^{31}P NMR (162 MHz, $CDCl_3$): δ = 17.87 ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3–154.3 (m, 1C), 152.1 (d, *J* = 14.3 Hz), 138.9 (d, *J* = 3.5 Hz), 133.3 (d, *J* = 11.1 Hz), 132.4 (d, *J* = 2.9 Hz), 131.8, 131.6 (d, *J* = 10.3 Hz), 130.8 (d, *J* = 11.6 Hz), 130.0, 129.8, 128.62 (d, *J* = 26.3 Hz), 128.61, 128.0, 127.3, 120.6 (qd, *J* = 268.6, 5.3 Hz), 111.9 (d, *J* = 109.5 Hz), 93.0–92.5 (m, 1C) ppm.
HRMS (m/z): calcd for $C_{23}H_{15}ClF_4O_2P$ $[M+H]^+$ 465.0429, found: 465.0430.



(5-Fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)(phenyl)(*p*-tolyl)phosphine oxide (3ak):
Yield = 87% (116.2 mg). White solid. M.p. 158.5–160.3 °C.
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~2/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.57 (m, 2H), 7.54–7.46 (m, 2H), 7.41–7.33 (m, 1H), 7.29–7.24 (m, 2H), 7.20–7.13 (m, 3H), 7.08 (dd, *J* = 8.0, 3.0 Hz, 2H), 7.05–6.99 (m, 2H), 2.29 (s, 3H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.71 (d, *J* = 16.4 Hz, 3F), -105.89 (qd, *J* = 15.6, 3.8 Hz, 1F) ppm.
^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.21 ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3–154.2 (m, 1C), 151.8 (d, *J* = 14.0 Hz), 142.8 (d, *J* = 3.0 Hz), 132.1 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 111.5 Hz), 131.83, 131.82 (d, *J* = 19.4 Hz), 129.72, 129.67, 129.1 (d, *J* = 13.3 Hz), 128.3 (d, *J* = 12.8 Hz), 128.2 (d, *J* = 114.1 Hz), 127.9, 127.5, 120.6 (qd, *J* = 268.7, 5.3 Hz), 112.4 (d, *J* = 106.8 Hz), 93.0–92.6 (m, 1C), 21.6 ppm.
HRMS (m/z): calcd for $C_{24}H_{18}F_4O_2P$ $[M+H]^+$ 445.0975, found: 445.0975.



Ethyl(5-fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)(phenyl)phosphine oxide (3al):
Yield = 86% (98.8 mg). Yellow oil.
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~2/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.53 (m, 2H), 7.47–7.43 (m, 2H), 7.42–7.22 (m, 6H), 2.25–2.12 (m, 1H), 2.06–1.94 (m, 1H), 1.02 (dt, *J* = 18.7, 7.6 Hz, 3H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.66 (d, *J* = 16.4 Hz, 3F), -105.64 (qd, *J* = 18.1, 2.9 Hz, 1F) ppm.
^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.19 ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2–154.1 (m, 1C), 151.7 (d, *J* = 13.0 Hz), 132.0 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 105.1 Hz), 130.9 (d, *J* = 9.9 Hz), 130.5, 130.1, 128.4 (d, *J* = 12.3 Hz), 128.1, 127.9, 121.0 (qd, *J* = 267.8, 5.4 Hz), 112.3 (d, *J* = 99.2 Hz), 91.8 (d, *J* = 40.0 Hz), 23.2 (d, *J* = 77.2 Hz), 5.3 (d, *J* = 5.1 Hz) ppm.
HRMS (m/z): calcd for $C_{19}H_{16}F_4O_2P$ $[M+H]^+$383.0819, found: 383.0818.



Diethyl (5-fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)phosphonate (3am):

Yield = 43% (47.4 mg). Colourless oil.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 5/1~2/1).

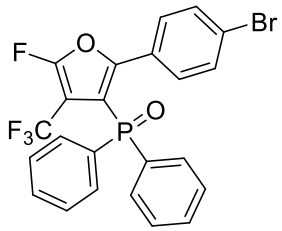
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.68 (m, 2H), 7.49–7.36 (m, 3H), 4.15–3.96 (m, 4H), 1.19 (t, *J* = 7.1 Hz, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -56.52 (d, *J* = 17.3 Hz, 3F), -106.32 (qd, *J* = 16.4, 4.5 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.07 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0–153.5 (m, 1C), 151.7 (d, *J* = 20.4 Hz), 130.5, 129.3, 128.3, 127.6, 120.8 (qd, *J* = 267.8, 5.4 Hz), 107.4 (d, *J* = 213.0 Hz), 92.8–92.0 (m, 1C), 62.9 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 6.8 Hz) ppm.

HRMS (m/z): calcd for $C_{15}H_{16}F_4O_4P$ $[M+H]^+$367.0717, found: 367.0715.



(2-(4-Bromophenyl)-5-fluoro-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3ba):

Yield = 90% (137.4 mg). White solid. M.p. 156.0–157.5 ºC.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

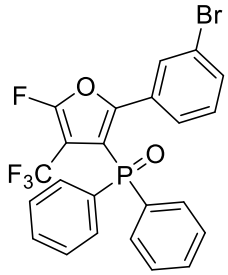
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.60 (m, 4H), 7.48–7.41 (m, 2H), 7.32 (td, *J* = 7.7, 3.2 Hz, 4H), 7.21–7.16 (m, 2H), 7.15–7.08 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.73 (d, *J* = 15.6 Hz, 3F), -105.16 (qd, *J* = 15.0, 2.9 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.85 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3–154.3 (m, 1C), 150.8 (d, *J* = 13.4 Hz), 132.3 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 10.2 Hz), 131.5 (d, *J* = 111.5 Hz), 131.13, 131.09, 128.5 (d, *J* = 12.8 Hz), 126.3, 124.7, 120.4 (qd, *J* = 262.4, 5.1 Hz), 112.9 (d, *J* = 107.2 Hz), 93.7–91.7 (m, 1C) ppm.

HRMS (m/z): calcd for $C_{23}H_{15}BrF_4O_2P$ $[M+H]^+$ 508.9924, found: 508.9924.



(2-(3-Bromophenyl)-5-fluoro-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3ca):

Yield = 85% (129.8 mg). White solid. M.p. 155.1–156.9 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

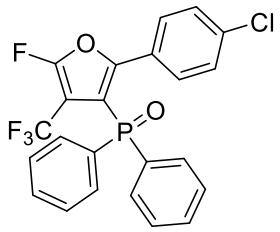
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.60 (m, 4H), 7.45–7.38 (m, 2H), 7.37–7.25 (m, 6H), 7.21 (dt, *J* = 7.8, 1.4 Hz, 1H), 6.98–6.88 (m, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.76 (d, *J* = 15.7 Hz, 3F), -105.07 (qd, *J* = 14.9, 4.5 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.35 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4–154.3 (m, 1C), 150.0 (d, *J* = 13.8 Hz), 133.0, 132.7, 132.5 (d, *J* = 3.1 Hz), 131.7 (d, *J* = 10.3 Hz), 131.3 (d, *J* = 111.6 Hz), 129.4, 129.1 (d, *J* = 2.8 Hz), 128.5 (d, *J* = 12.7 Hz), 128.3, 121.9, 120.5 (qd, *J* = 268.7, 5.7 Hz), 113.5 (d, *J* = 106.7 Hz), 93.2–92.8 (m, 1C) ppm.

HRMS (m/z): calcd for $C_{23}H_{15}BrF_4O_2P$ $[M+H]^+$ 508.9924, found: 508.9920.



(2-(4-Chlorophenyl)-5-fluoro-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3da):

Yield = 93% (129.7 mg). White solid. M.p. 149.9–151.6 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 5/1~2/1).

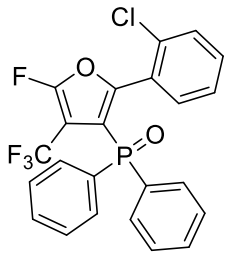
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.58 (m, 4H), 7.48–7.41 (m, 2H), 7.34–7.30 (m, 4H), 7.22–7.16 (m, 2H), 7.07–7.00 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.71 (d, *J* = 16.4 Hz, 3F), -105.23 (qd, *J* = 15.7, 3.6 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.35 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2–153.8 (m, 1C), 150.8 (d, *J* = 13.4 Hz), 136.3, 132.4 (d, *J* = 2.9 Hz), 132.1, 131.9 (d, *J* = 10.3 Hz), 130.9, 128.5 (d, *J* = 12.9 Hz), 128.2, 125.9, 120.5 (qd, *J* = 267.4, 9.2 Hz), 112.9 (d, *J* = 109.0 Hz), 93.8–91.8 (m, 1C) ppm.

HRMS (m/z): calcd for $C_{23}H_{15}ClF_4O_2P$ $[M+H]^+$ 465.0429, found: 465.0435.



(2-(2-Chlorophenyl)-5-fluoro-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3ea):

Yield = 91% (127.0 mg). White solid. M.p. 148.8–150.6 °C

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 5/1~2/1).

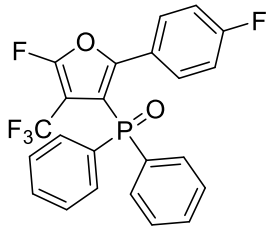
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.55 (m, 4H), 7.38–7.30 (m, 2H), 7.24 (ddd, *J* = 8.7, 6.8, 3.3 Hz, 4H), 7.14–7.04 (m, 2H), 6.92–6.80 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.89 (d, *J* = 14.8 Hz, 3F), -104.87 (qd, *J* = 15.0, 4.1 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.26 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5–154.4 (m, 1C), 147.8 (d, *J* = 14.7 Hz), 134.8, 133.5, 132.3, 131.7, 131.6, 131.2 (d, *J* = 111.9 Hz), 129.3, 128.3 (d, *J* = 13.0 Hz), 126.7, 126.4, 120.7 (qd, *J* = 268.6, 5.1 Hz), 115.2 (d, *J* = 106.9 Hz), 92.7–92.2 (m, 1C) ppm.

HRMS (m/z): calcd for $C_{23}H_{15}ClF_4O_2P$ $[M+H]^+$ 465.0429, found: 465.0427.



(5-Fluoro-2-(4-fluorophenyl)-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3fa):

Yield = 88% (118.6 mg). Grey solid. M.p. 150.8–151.9 ºC.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 7/1~2/1).

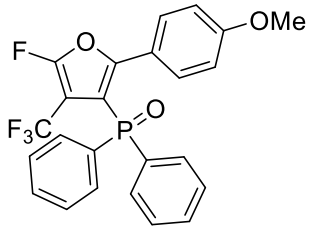
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.58 (m, 4H), 7.46–7.39 (m, 2H), 7.31 (td, *J* = 7.7, 3.2 Hz, 4H), 7.27–7.21 (m, 2H), 6.74 (t, *J* = 8.6 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.75 (d, *J* = 15.0 Hz, 3F), -105.56 (qd, *J* = 14.9, 3.0 Hz, 1F), -109.2– -109.3 (m, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.70 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5 (d, *J* = 251.8 Hz), 157.3–154.2 (m, 1C), 151.0 (d, *J* = 13.8 Hz), 132.3 (d, *J* = 2.9 Hz), 131.84 (d, *J* = 10.6 Hz), 131.82, 131.6 (d, *J* = 111.5 Hz), 128.5 (d, *J* = 12.9 Hz), 123.7 (d, *J* = 3.4 Hz), 120.5 (qd, *J* = 268.5, 5.1 Hz), 115.2 (d, *J* = 22.2 Hz), 112.4 (d, *J* = 106.1 Hz), 94.5–90.8 (m, 1C) ppm.

HRMS (m/z): calcd for $C_{23}H_{15}F_5O_2P$ $[M+H]^+$ 449.0724, found: 449.0729.



(5-Fluoro-2-(4-methoxyphenyl)-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3ga):

Yield = 94% (130.0 mg). White solid. M.p. 143.9–145.3 ºC.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

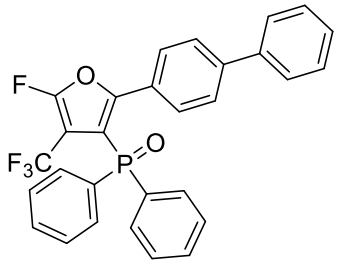
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.58 (m, 4H), 7.44–7.36 (m, 2H), 7.30 (ddd, *J* = 8.6, 6.9, 3.3 Hz, 4H), 7.20–7.12 (m, 2H), 6.58–6.52 (m, 2H), 3.69 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.70 (d, *J* = 16.3 Hz, 3F), -106.23 (qd, *J* = 15.4, 3.3 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.89 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 157.1–154.0 (m, 1C), 152.3 (d, *J* = 13.9 Hz), 132.2 (d, *J* = 2.8 Hz), 131.91 (d, *J* = 111.4 Hz), 131.85 (d, *J* = 10.1 Hz), 131.2, 128.4 (d, *J* = 12.6 Hz), 120.6 (qd, *J* = 268.6, 5.3 Hz), 119.8, 113.4, 111.0 (d, *J* = 109.0 Hz), 92.9–92.3 (m, 1C), 55.3 ppm.

HRMS (m/z): calcd for $C_{24}H_{18}F_4O_3P$ $[M+H]^+$ 461.0924, found: 461.0923.



(2-([1,1'-Biphenyl]-4-yl)-5-fluoro-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3ha):

Yield = 86% (131.2 mg). White solid. M.p. 144.2–144.9 ºC.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

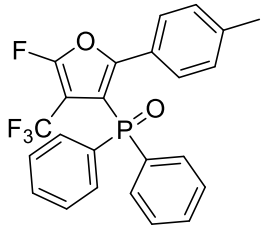
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.64 (m, 4H), 7.47–7.35 (m, 7H), 7.33–7.23 (m, 8H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.67 (d, J = 15.1 Hz, 3F), -105.56 (qd, J = 15.6, 3.5 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.88 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3–154.1 (m, 1C), 151.8 (d, J = 13.7 Hz), 142.6, 140.0, 132.1 (d, J = 2.8 Hz), 131.9 (d, J = 10.3 Hz), 131.7 (d, J = 111.5 Hz), 130.1, 129.0, 128.4 (d, J = 12.8 Hz), 128.0, 127.1, 126.5, 126.2, 120.6 (qd, J = 268.7, 5.1 Hz), 112.3 (d, J = 106.4 Hz), 93.1–92.6 (m, 1C) ppm.

HRMS (m/z): calcd for $C_{29}H_{20}F_4O_2P$ $[M+H]^+$ 507.1132, found: 507.1129.



(5-Fluoro-2-(*p*-tolyl)-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3ia):

Yield = 91% (121.5 mg). White solid. M.p. 150.1–151.6 ºC.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

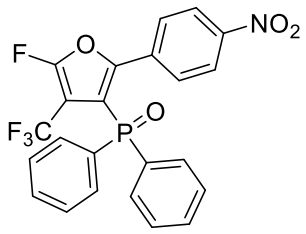
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.59 (m, 4H), 7.43–7.36 (m, 2H), 7.29 (ddd, J = 8.7, 7.0, 3.3 Hz, 4H), 7.12–7.07 (m, 2H), 6.83 (d, J = 7.9 Hz, 2H), 2.21 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.71 (d, J = 15.1 Hz, 3F), -106.02 (qd, J = 15.3, 3.0 Hz, 1F) ppm.

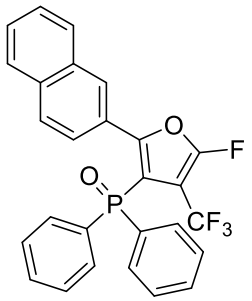
^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.05 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8–153.4 (m, 1C), 152.4 (d, J = 14.1 Hz), 140.2, 132.0 (d, J = 2.9 Hz), 131.9 (d, J = 10.2 Hz), 131.8 (d, J = 111.4 Hz), 129.6, 128.6, 128.3 (d, J = 12.8 Hz), 124.5, 120.6 (qd, J = 268.4, 5.3 Hz), 111.6 (d, J = 108.2 Hz), 93.2–92.0 (m, 1C), 21.4 ppm.

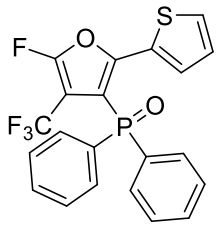
HRMS (m/z): calcd for $C_{24}H_{18}F_4O_2P$ $[M+H]^+$ 445.0975, found: 445.0978.



(5-Fluoro-2-(4-nitrophenyl)-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3ja):
Yield = 63% (90.0 mg). White solid. M.p. 149.7–150.2 °C.
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 4/1~1/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01–7.93 (m, 2H), 7.72–7.62 (m, 4H), 7.61–7.54 (m, 2H), 7.51–7.44 (m, 2H), 7.39–7.34 (m, 4H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.71 (d, *J* = 16.3 Hz, 3F), -103.69 (qd, *J* = 16.4, 2.8 Hz, 1F) ppm.
^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.06 ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0–154.4 (m, 1C), 149.4 (d, *J* = 12.8 Hz), 148.2, 132.8, 132.7, 132.6 (d, *J* = 178.2 Hz), 131.9 (d, *J* = 10.4 Hz), 130.6 (d, *J* = 2.8 Hz), 128.7 (d, *J* = 13.0 Hz), 123.0, 120.3 (qd, *J* = 261.9, 5.5 Hz), 115.1 (d, *J* = 102.0 Hz), 94.6–92.6 (m, 1C) ppm.
HRMS (m/z): calcd for $C_{24}H_{15}F_4NO_4P$ $[M+H]^+$ 476.0669, found: 476.0667.



(5-Fluoro-2-(naphthalen-2-yl)-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3ka):
Yield = 88% (126.4 mg). White solid. M.p. 163.2–164.9 °C.
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~2/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.63 (m, 6H), 7.62–7.50 (m, 2H), 7.43 (dddd, *J* = 17.5, 8.2, 6.9, 1.5 Hz, 2H), 7.30 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.25–7.12 (m, 6H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.64 (d, *J* = 16.0 Hz, 3F), -106.02 (qd, *J* = 15.6, 2.9 Hz, 1F) ppm.
^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.70 ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5–154.0 (m, 1C), 152.0 (d, *J* = 13.9 Hz), 133.3, 132.2, 132.0 (d, *J* = 2.9 Hz), 131.8, 131.6 (d, *J* = 10.2 Hz), 131.1, 130.8, 128.5, 128.3 (d, *J* = 12.9 Hz), 127.7, 127.5, 126.6, 125.4, 124.4, 120.6 (qd, *J* = 268.7, 5.3 Hz), 112.6 (d, *J* = 107.8 Hz), 93.3–92.5 (m, 1C) ppm.
HRMS (m/z): calcd for $C_{27}H_{18}F_4O_2P$ $[M+H]^+$ 481.0975, found: 481.0975.



(5-Fluoro-2-(thiophen-2-yl)-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3la):
Yield = 66% (86.5 mg). White solid. M.p. 142.7–143.9 °C.
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

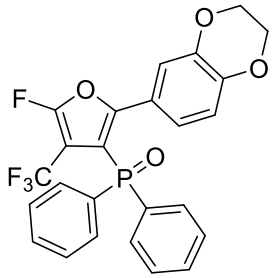
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.59 (m, 4H), 7.47 (ddd, *J* = 7.3, 5.2, 1.6 Hz, 2H), 7.37 (td, *J* = 7.6, 3.3 Hz, 4H), 7.28–7.23 (m, 1H), 7.12 (dd, *J* = 3.8, 1.2 Hz, 1H), 6.69 (dd, *J* = 5.1, 3.7 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.82 (d, *J* = 16.4 Hz, 3F), -104.98 (qd, *J* = 16.5, 3.4 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.67 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7–153.2 (m, 1C), 146.1 (d, *J* = 13.3 Hz), 132.5, 132.4 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 10.7 Hz), 130.9, 129.5, 128.5 (d, *J* = 13.0 Hz), 127.7, 127.4, 120.5 (qd, *J* = 268.0, 5.3 Hz), 113.1 (d, *J* = 86.8 Hz), 93.9–92.0 (m, 1C) ppm.

HRMS (m/z): calcd for $C_{24}H_{14}F_4O_2PS$ $[M+H]^+$ 437.0383, found: 437.0385.



(2-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-5-fluoro-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3ma):

Yield = 73% (107.1 mg). White solid. M.p. 138.6–140.4 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 4/1~1/1).

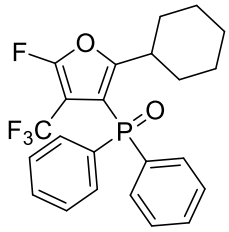
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.59 (m, 4H), 7.46–7.39 (m, 2H), 7.32 (ddd, *J* = 8.7, 7.1, 3.2 Hz, 4H), 6.71 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.61 (d, *J* = 2.1 Hz, 1H), 6.53 (d, *J* = 8.3 Hz, 1H), 4.18–4.07 (m, 4H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.76 (d, *J* = 15.8 Hz, 3F), -106.06 (qd, *J* = 15.6, 3.5 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.97 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0–154.0 (m, 1C), 151.6 (d, *J* = 14.1 Hz), 143.8 (d, *J* = 268.9 Hz), 132.04, 132.01, 131.82 (d, *J* = 10.2 Hz), 131.77 (d, *J* = 111.6 Hz), 128.4 (d, *J* = 13.0 Hz), 123.2, 120.7 (qd, *J* = 269.0, 4.9 Hz), 120.3, 119.2, 116.9, 111.5 (d, *J* = 108.7 Hz), 93.1–92.0 (m, 1C), 64.4, 64.1 ppm.

HRMS (m/z): calcd for $C_{25}H_{18}F_4O_4P$ $[M+H]^+$ 489.0873, found: 489.0873.



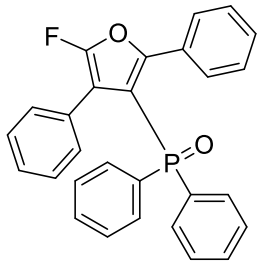
(2-Cyclohexyl-5-fluoro-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (3na):

Yield = 82% (107.5 mg). Colourless oil.

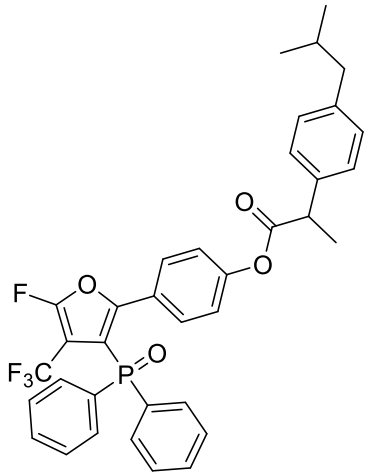
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.64 (m, 4H), 7.60–7.53 (m, 2H), 7.49–7.44 (m, 4H), 2.34–2.25 (m, 1H), 1.63–1.50 (m, 5H), 1.44–1.33 (m, 2H), 1.12–1.00 (m, 1H), 0.93–0.76 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.90 (d, J = 16.0 Hz, 3F), -106.68 (q, J = 16.0 Hz, 1F) ppm.
^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.21 ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0 (dd, J = 15.6, 2.5 Hz), 156.7–153.2 (m, 1C), 132.6 (d, J = 2.9 Hz), 132.2 (d, J = 111.3 Hz), 131.9 (d, J = 10.5 Hz), 128.7 (d, J = 12.7 Hz), 120.7 (qd, J = 268.1, 5.5 Hz), 109.1 (d, J = 111.6 Hz), 90.4, 36.2, 31.2, 25.8, 25.4 ppm.
HRMS (m/z): calcd for $C_{23}H_{22}F_4O_2P$ $[M+H]^+$ 437.1288, found: 437.1286.



(5-Fluoro-2,4-diphenylfuran-3-yl)diphenylphosphine oxide (3oa):
Yield = 42% (55.3 mg). White solid. M.p. 121.6–122.5 °C.
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.52 (m, 4H), 7.48–7.39 (m, 2H), 7.32–7.23 (m, 2H), 7.15–7.08 (m, 3H), 7.07–7.00 (m, 9H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -120.64 (d, J = 4.1 Hz, 1F) ppm.
^{31}P NMR (162 MHz, $CDCl_3$): δ = 16.86 ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2 (dd, J = 281.1, 16.1 Hz), 151.5 (d, J = 15.9 Hz), 132.7 (d, J = 109.4 Hz), 131.3 (d, J = 9.6 Hz), 131.2, 131.1, 129.9, 129.2, 129.1, 128.7, 128.5 (d, J = 3.8 Hz), 128.0 (d, J = 6.5 Hz), 127.8 (d, J = 11.3 Hz), 127.2, 113.3 (d, J = 113.7 Hz), 102.1 (t, J = 9.3 Hz) ppm.
HRMS (m/z): calcd for $C_{28}H_{21}FO_2P$ $[M+H]^+$ 439.1258, found: 439.1259.



4-(3-(Diphenylphosphoryl)-5-fluoro-4-(trifluoromethyl)furan-2-yl)phenyl 2-(4-isobutylphenyl)propanoate (3pa):
Yield = 69% (131.5 mg). White solid. M.p. 149.3–150.1 °C.
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~3/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (ddd, J = 12.8, 8.4, 1.4 Hz, 4H), 7.42–7.37 (m, 2H), 7.34–7.23 (m, 6H), 7.23–7.08 (m, 4H), 6.75–6.64 (m, 2H), 3.89 (q, J = 7.1 Hz, 1H), 2.47 (d, J =

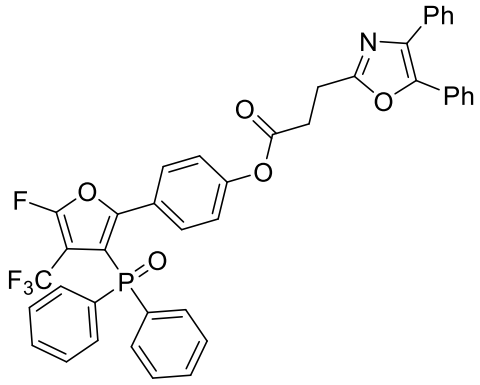
7.2 Hz, 2H), 1.87 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.57 (d, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.73 (d, *J* = 15.8 Hz, 3F), -105.55 (qd, *J* = 15.1, 3.1 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.78 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.6, 157.2–154.1 (m, 1C), 152.0, 151.0 (d, *J* = 13.9 Hz), 141.0, 137.0, 132.4 (d, *J* = 3.0 Hz), 131.7, 131.5 (d, *J* = 111.6 Hz), 130.8, 129.6, 128.4 (d, *J* = 12.7 Hz), 127.2, 124.8, 121.4, 120.5 (qd, *J* = 273.6, 5.0 Hz), 112.6 (d, *J* = 107.9 Hz), 93.1–92.6 (m, 1C), 45.2, 45.1, 30.3, 22.4, 18.5 ppm.

HRMS (m/z): calcd for $C_{36}H_{32}F_4O_4P$ $[M+H]^+$ 635.1969, found: 635.1967.



4-(3-(Diphenylphosphoryl)-5-fluoro-4-(trifluoromethyl)furan-2-yl)phenyl 3-(4,5-diphenyloxazol-2-yl)propanoate (3qa):

Yield = 71% (153.8 mg). White solid. M.p. 157.8–159.3 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/3).

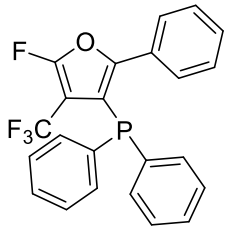
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.55 (m, 8H), 7.45–7.27 (m, 12H), 7.23–7.18 (m, 2H), 6.83–6.77 (m, 2H), 3.28 (t, *J* = 7.5 Hz, 2H), 3.13 (t, *J* = 7.0 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.74 (d, *J* = 15.2 Hz, 3F), -105.41 (qd, *J* = 16.3, 3.5 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.81 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 161.4, 154.4–153.9 (m, 1C), 151.7, 151.0 (d, *J* = 13.8 Hz), 145.7, 135.2, 132.5, 132.4, 131.8 (d, *J* = 10.2 Hz), 131.4 (d, *J* = 111.6 Hz), 131.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 127.9, 126.6, 125.1, 121.3, 120.5 (qd, *J* = 273.6, 5.0 Hz), 112.7 (d, *J* = 107.4 Hz), 93.2–92.5 (m, 1C), 31.2, 23.5 ppm.

HRMS (m/z): calcd for $C_{41}H_{29}F_4NO_5P$ $[M+H]^+$ 722.1714, found: 722.1718.



(5-Fluoro-2-phenyl-4-(trifluoromethyl)furan-3-yl)diphenylphosphane (4):

Yield = 89% (110.6 mg). White solid. M.p. 134.8–135.3 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

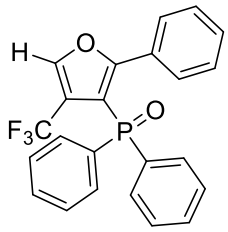
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.57 (m, 2H), 7.49–7.43 (m, 4H), 7.42–7.32 (m, 9H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -55.44 (dd, *J* = 15.7, 7.1 Hz, 3F), -105.28 (q, *J* = 15.7 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = -24.98 (q, *J* = 7.7 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0 (dt, *J* = 289.8, 3.8 Hz), 151.6 (d, *J* = 34.1 Hz), 133.9 (d, *J* = 8.6 Hz), 132.6 (d, *J* = 19.3 Hz), 129.5, 129.0 (d, *J* = 7.1 Hz), 128.8, 128.5 (d, *J* = 6.6 Hz), 128.32, 128.26, 121.1 (qd, *J* = 268.3, 5.3 Hz), 112.4 (dd, *J* = 31.6, 4.2 Hz), 93.3 (q, *J* = 39.5 Hz) ppm.

HRMS (m/z): calcd for $C_{23}H_{16}F_4OP$ $[M+H]^+$ 415.0869, found: 415.0865.



Diphenyl(2-phenyl-4-(trifluoromethyl)furan-3-yl)phosphine oxide (5):

Yield = 92% (113.7 mg). White solid. M.p. 138.6–140.3 ºC.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

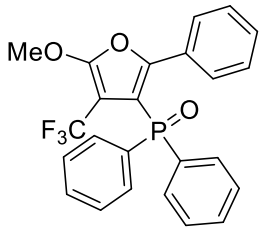
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.94 (m, 1H), 7.68–7.55 (m, 4H), 7.41–7.34 (m, 2H), 7.32–7.23 (m, 6H), 7.20–7.12 (m, 1H), 7.10–7.00 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -55.96 (s, 3F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.82 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9 (d, *J* = 16.0 Hz), 143.9 (td, *J* = 14.0, 6.9 Hz), 132.2 (d, *J* = 111.0 Hz), 132.0 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 10.2 Hz), 129.7, 129.5, 128.7, 128.2 (d, *J* = 12.7 Hz), 127.8, 121.6 (q, *J* = 268.9 Hz), 121.0 (dd, *J* = 37.6, 8.0 Hz), 110.3 (d, *J* = 110.3 Hz) ppm.

HRMS (m/z): calcd for $C_{23}H_{17}F_3O_2P$ $[M+H]^+$ 413.0913, found: 413.0909.



(5-Methoxy-2-phenyl-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (6):

Yield = 85% (112.7 mg). White solid. M.p. 121.6–122.5 ºC.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

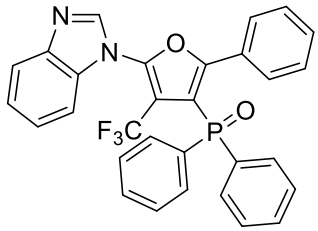
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.58 (m, 4H), 7.34 (td, *J* = 7.3, 1.5 Hz, 2H), 7.28–7.18 (m, 6H), 7.14–7.08 (m, 1H), 7.04–6.95 (m, 2H), 4.06 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -53.47 (s, 3F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.00 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8–158.7 (m, 1C), 151.8 (d, *J* = 14.7 Hz), 132.5 (d, *J* = 110.8 Hz), 131.81, 131.75 (d, *J* = 7.4 Hz), 129.7, 129.3, 128.6, 128.2 (d, *J* = 12.8 Hz), 127.8, 122.0 (q, *J* = 268.0 Hz), 111.7 (d, *J* = 110.6 Hz), 93.1–92.7 (m, 1C), 59.2 ppm.

HRMS (m/z): calcd for $C_{24}H_{19}F_3O_3P$ $[M+H]^+$ 443.1018, found: 443.1018.



(5-(1*H*-benzo[*d*]imidazol-1-yl)-2-phenyl-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (7):

Yield = 67% (106.2 mg). White solid. M.p. 121.6–122.5 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 3/1~1/1).

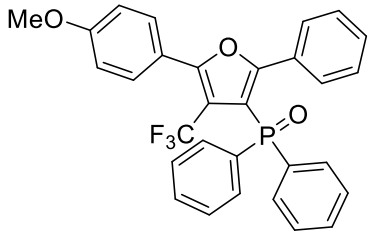
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (s, 1H), 7.89–7.81 (m, 1H), 7.78– 7.66 (m, 4H), 7.46 (dt, *J* = 6.9, 2.9 Hz, 1H), 7.43–7.27 (m, 10H), 7.23–7.13 (m, 1H), 7.06 (t, *J* = 7.7 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -54.21 (s, 3F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 18.65 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2 (d, *J* = 14.1 Hz), 143.1, 143.0–142.5 (m, 1C), 142.2, 133.7, 132.2 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 111.4 Hz), 131.7 (d, *J* = 10.1 Hz), 130.3, 129.7, 128.4 (d, *J* = 12.9 Hz), 128.0, 127.6, 125.1, 124.2, 121.0, 120.9 (q, *J* = 270.0 Hz), 112.7 (d, *J* = 106.6 Hz), 111.5 (qd, *J* = 38.2, 7.8 Hz), 111.4 (qd, *J* = 38.2, 7.8 Hz), 110.9 ppm.

HRMS (m/z): calcd for $C_{30}H_{21}F_3N_2O_2P$ $[M+H]^+$ 529.1287, found: 529.1285.



(5-(4-Methoxyphenyl)-2-phenyl-4-(trifluoromethyl)furan-3-yl)diphenylphosphine oxide (8):

Yield = 82% (127.7 mg). White solid. M.p. 121.6–122.5 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

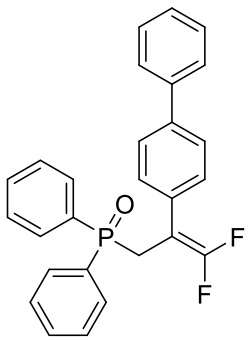
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.66 (m, 4H), 7.64–7.57 (m, 2H), 7.38–7.31 (m, 2H), 7.31–7.22 (m, 6H), 7.17–7.10 (m, 1H), 7.08–6.99 (m, 2H), 6.99–6.90 (m, 2H), 3.83 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -51.84 (s, 3F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.13 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 160.5 (d, *J* = 15.7 Hz), 155.3 (m, 1C), 132.9 (d, *J* = 110.8 Hz), 131.8, 131.70, 131.66, 130.2, 129.7, 129.5, 128.9, 128.2 (d, *J* = 12.7 Hz), 127.8, 122.3 (q, *J* = 269.6 Hz), 120.8, 114.1, 112.0 (d, *J* = 110.1 Hz), 55.4 ppm.

HRMS (m/z): calcd for $C_{30}H_{23}F_3O_3P$ $[M+H]^+$ 519.1331, found: 519.1331.



(2-([1,1'-Biphenyl]-4-yl)-3,3-difluoroallyl)diphenylphosphine oxide (10):

Yield = 40% (51.7 mg). White solid. 150.0–150.9 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 6/1~2/1).

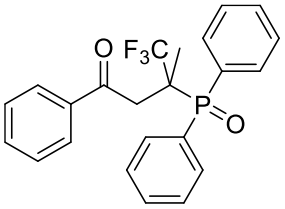
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.66 (m, 4H), 7.55–7.51 (m, 2H), 7.49–7.43 (m, 4H), 7.42–7.33 (m, 8H), 7.28 (d, *J* = 1.0 Hz, 1H), 3.47–3.43 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -86.1 (dd, *J* = 34.3, 8.9 Hz, 1F), -87.6 (dd, *J* = 32.8, 13.4 Hz, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.58 (dd, *J* = 14.2, 8.3 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7 (td, *J* = 291.4, 10.6 Hz), 140.7, 140.3, 132.5, 132.0 (d, *J* = 2.5 Hz), 131.8, 131.5, 131.1 (d, *J* = 9.4 Hz), 129.1, 128.9, 128.6 (d, *J* = 11.8 Hz), 127.5, 127.1 (d, *J* = 2.3 Hz), 85.5–85.0 (m, 1C), 31.2 (d, *J* = 69.4 Hz) ppm.

HRMS (m/z): calcd for $C_{27}H_{22}F_2OP$ $[M+H]^+$ 431.1371, found: 431.1371.



3-(Diphenylphosphoryl)-4,4,4-trifluoro-3-methyl-1-phenylbutan-1-one (14a):

Yield = 95% (118.6 mg). White solid. M.p. 121.6–122.5 °C.

Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 5/1~3/1).

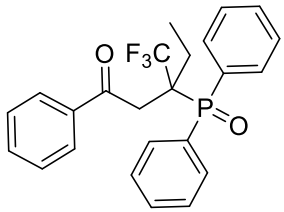
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12–8.07 (m, 4H), 7.90–7.83 (m, 2H), 7.61–7.48 (m, 7H), 7.42 (t, *J* = 7.7 Hz, 2H), 3.62 (dd, *J* = 15.2, 9.0 Hz, 1H), 3.35 (dd, *J* = 15.2, 8.3 Hz, 1H), 1.76 (d, *J* = 14.9 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -63.46 (d, *J* = 4.0 Hz, 3F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.06 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5 (d, *J* = 10.6 Hz), 137.6, 133.4, 132.7–132.3 (m, 3C), 129.6 (dd, *J* = 95.3, 10.1 Hz), 128.7 (d, *J* = 5.3 Hz), 128.5 (d, *J* = 16.9 Hz), 129.0 (q, *J* = 283.4 Hz), 49.8 (dd, *J* = 61.4, 24.8 Hz), 36.4, 15.7 ppm.

HRMS (m/z): calcd for $C_{23}H_{21}F_3O_2P$ $[M+H]^+$ 417.1226, found: 417.1224.



3-(Diphenylphosphoryl)-1-phenyl-3-(trifluoromethyl)pentan-1-one (14b):

Yield = 96% (123.9 mg). White solid. M.p. 120.1–121.5 °C.

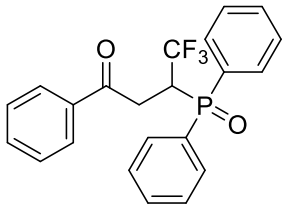
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 5/1~3/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12–7.96 (m, 4H), 7.91–7.85 (m, 2H), 7.60–7.39 (m, 9H), 3.91 (dd, *J* = 16.6, 7.7 Hz, 1H), 3.55 (dd, *J* = 16.6, 13.2 Hz, 1H), 2.52–2.26 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H) ppm.

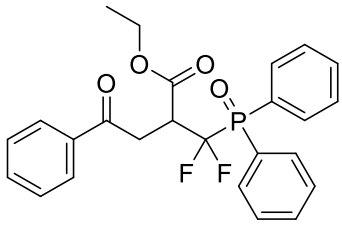
^{19}F NMR (376 MHz, $CDCl_3$): δ = -61.16 (s, 3F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.49 ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.1 (d, *J* = 8.2 Hz), 137.6, 133.2, 132.4 (dd, *J* = 23.0, 8.6 Hz), 132.3 (d, *J* = 7.3 Hz), 130.5 (dd, *J* = 130.0, 93.9 Hz), 128.6, 128.6 (dd, *J* = 11.5, 9.7 Hz), 128.2, 127.2 (q, *J* = 283.6 Hz), 54.2 (dd, *J* = 59.7, 23.1 Hz), 33.5, 22.3, 9.2 (d, *J* = 5.8 Hz) ppm.
HRMS (m/z): calcd for $C_{24}H_{23}F_3O_2P$ $[M+H]^+$ 431.1382, found: 431.1377.



3-(Diphenylphosphoryl)-4,4,4-trifluoro-1-phenylbutan-1-one (14d):
Yield = 60% (72.4 mg). White solid. M.p. 116.7–118.4 ºC.
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~3/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.89 (m, 2H), 7.88–7.80 (m, 4H), 7.59–7.48 (m, 4H), 7.47–7.37 (m, 5H), 4.57–4.43 (m, 1H), 3.63 (dt, *J* = 18.9, 6.9 Hz, 1H), 3.43 (ddd, *J* = 18.8, 14.9, 3.8 Hz, 1H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -60.48 (dd, *J* = 9.6, 5.2 Hz, 3F) ppm.
^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.72–28.45 (m, 1P) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.6 (d, *J* = 6.7 Hz), 135.5, 134.0, 132.6 (dd, *J* = 8.3, 2.9 Hz), 131.2 (dd, *J* = 21.6, 9.5 Hz), 130.5 (dd, *J* = 103.5, 49.4 Hz), 128.9 (dd, *J* = 27.5, 12.3 Hz), 128.8, 128.3, 127.0 (q, *J* = 281.3 Hz), 39.3 (dd, *J* = 66.2, 26.7 Hz), 33.0 ppm.
HRMS (m/z): calcd for $C_{22}H_{19}F_3O_2P$ $[M+H]^+$ 403.1069, found: 403.1068.



Ethyl 2-((diphenylphosphoryl)difluoromethyl)-4-oxo-4-phenylbutanoate (15c):
Yield = 8% (10.9 mg). Colourless oil.
Purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 10/1~3/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.75 (m, 2H), 7.74–7.66 (m, 4H), 7.44–7.29 (m, 7H), 7.25–7.18 (m, 2H), 5.05 (ddd, *J* = 16.3, 11.5, 2.6 Hz, 1H), 4.00 (qd, *J* = 7.2, 0.9 Hz, 2H), 3.42 (ddd, *J* = 17.7, 11.5, 5.0 Hz, 1H), 2.86 (ddd, *J* = 17.6, 9.0, 2.6 Hz, 1H), 1.10 (t, *J* = 7.2 Hz, 3H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -102.16 (d, *J* = 3.7 Hz, 2F) ppm.
^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.61 ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.0 (d, *J* = 2.5 Hz), 171.5 (d, *J* = 16.6 Hz), 138.1, 132.9, 132.4 (d, *J* = 3.0 Hz), 131.6 (dd, *J* = 34.5, 9.3 Hz), 130.0 (dd, *J* = 100.5, 37.3 Hz), 128.7 (d, *J* = 3.7 Hz), 128.60, 128.56, 128.3, 61.4, 47.5 (d, *J* = 56.3 Hz), 32.7, 14.0 ppm.
HRMS (m/z): calcd for $C_{25}H_{24}F_2O_4P$ $[M+H]^+$ 457.1375, found: 457.1373.

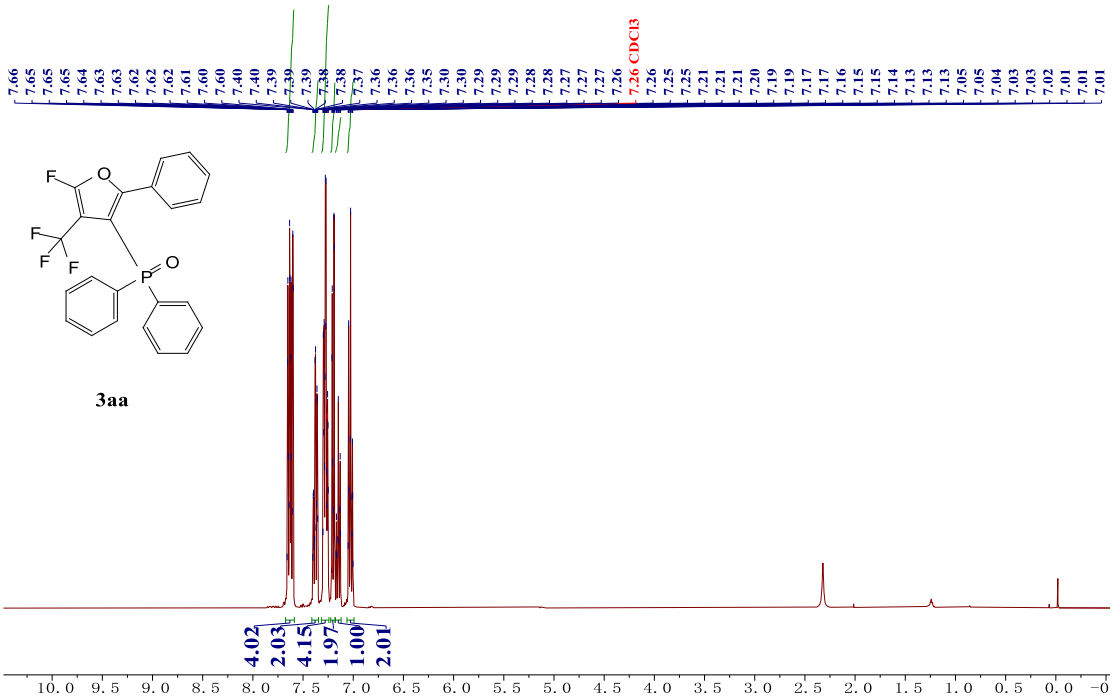
References

[1] Wu, X.; Xie, F.; Gridnev, I. D.; Zhang, W. *Org. Lett.* **2018**, *20*, 1638−1642.

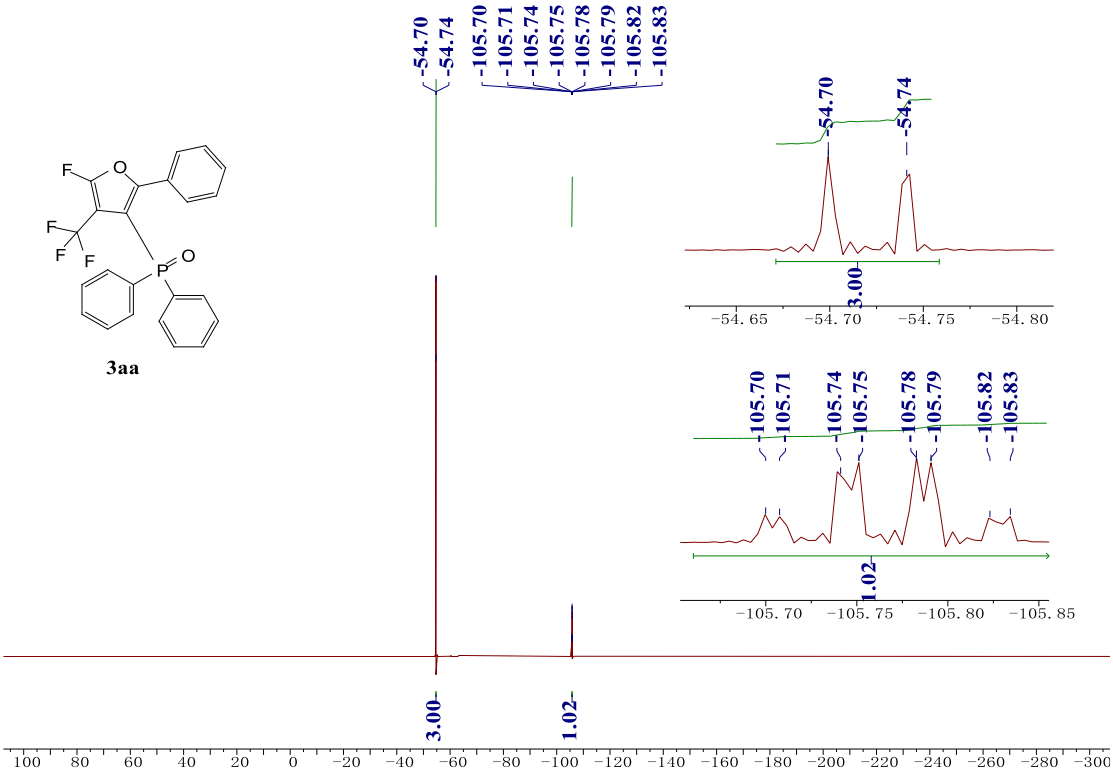
[2] Chu, X.-Q.; Sun, L.-W.; Chen, Y.-L.; Chen, *J*.-W.; Ying, X.; Ma, M.; Shen, Z.-L. *Green Chem.* **2022**, *24*, 2777–2782.

H, ^{19}F, ^{31}P, and ^{13}C NMR spectra of products

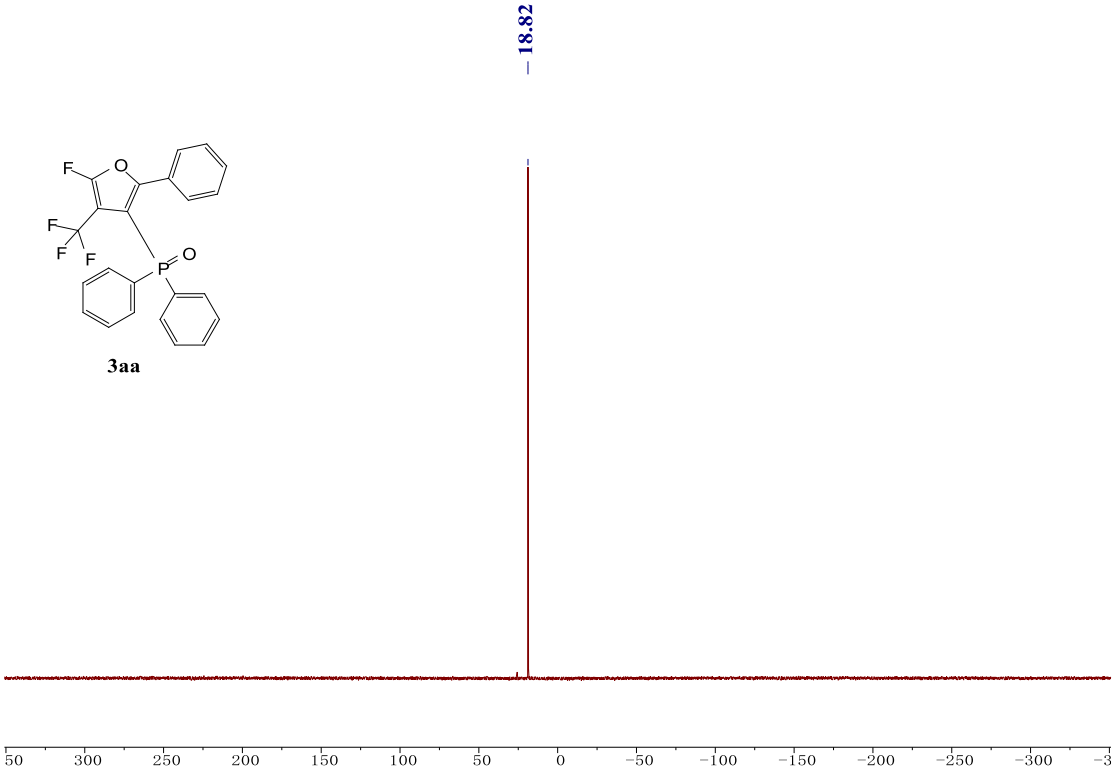
^{1}H NMR spectra of the product **3aa** (400 MHz, $CDCl_3$):



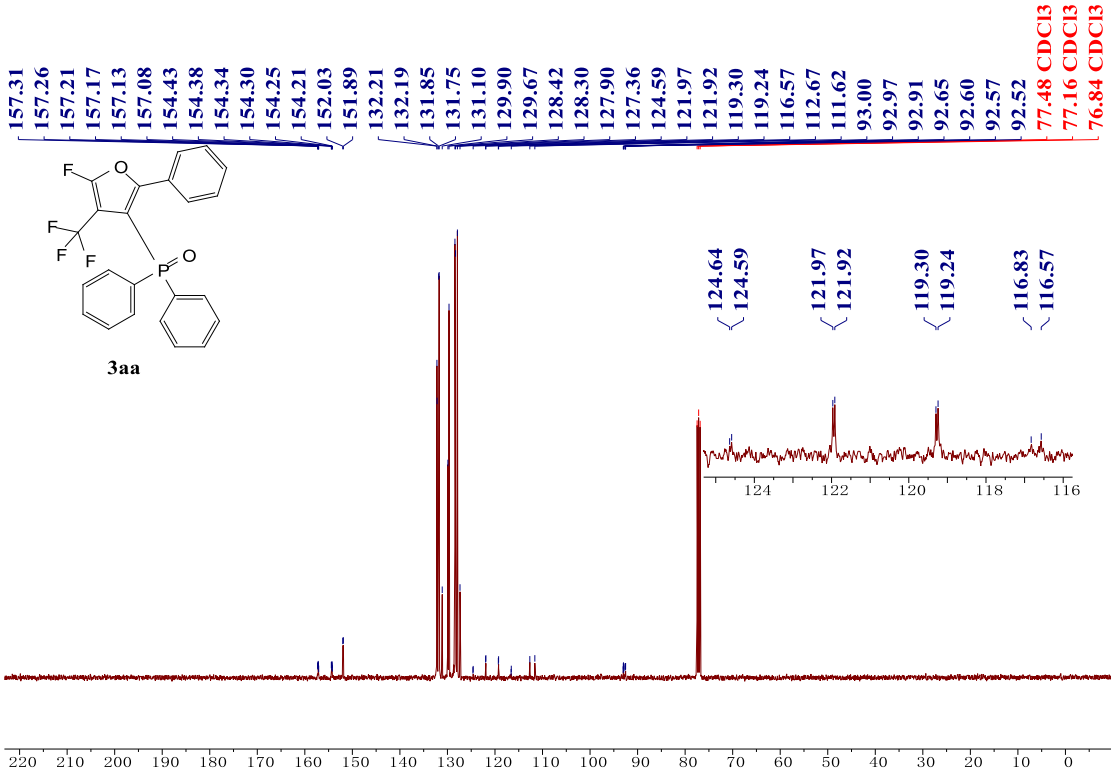
^{19}F NMR spectra of the product **3aa** (376 MHz, $CDCl_3$):



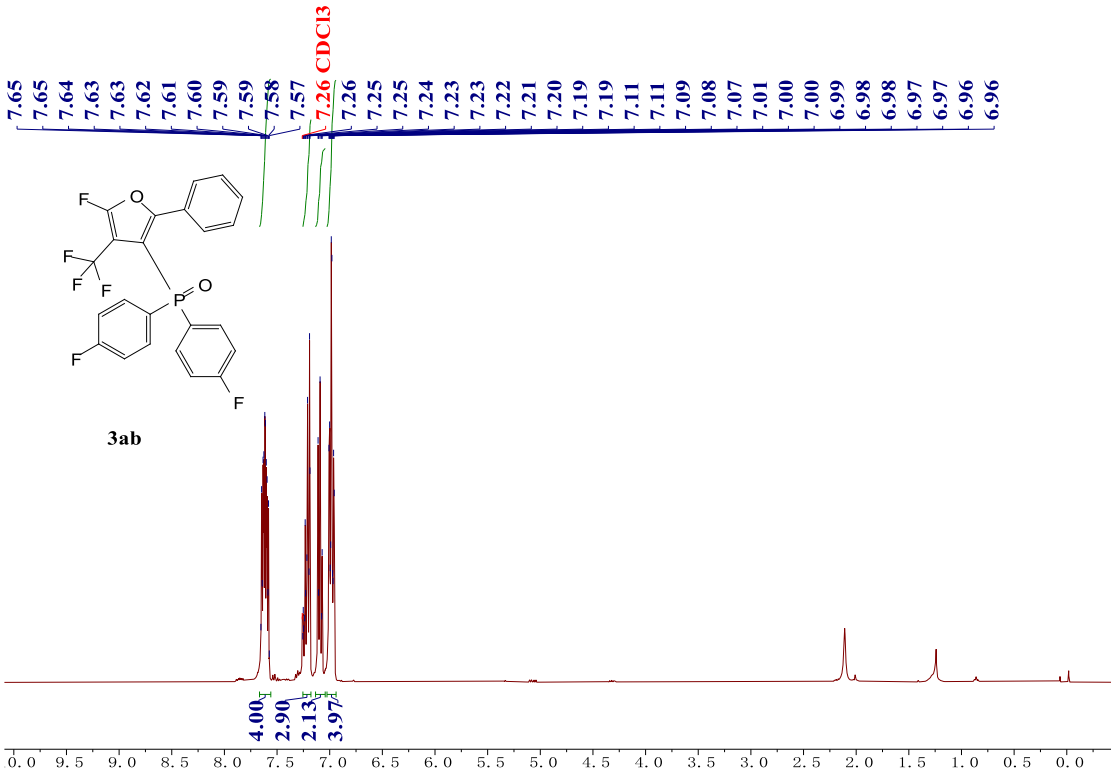
^{31}P NMR spectra of the product **3aa** (162 MHz, $CDCl_3$):



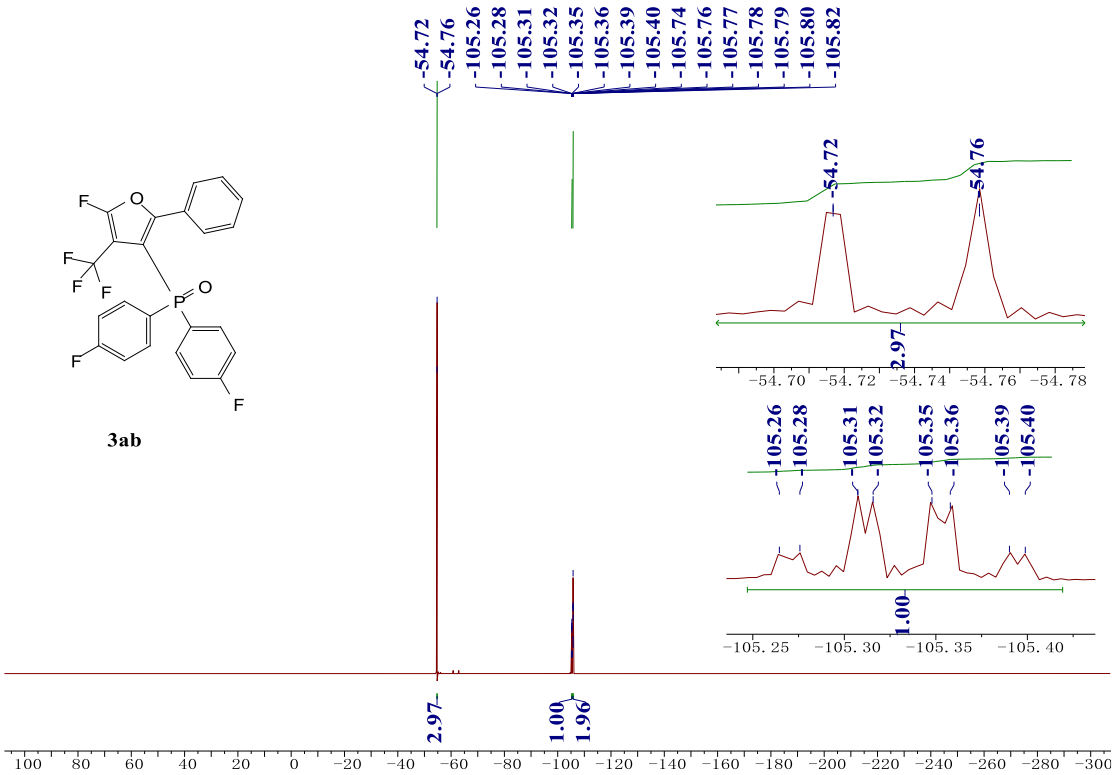
^{13}C NMR spectra of the product **3aa** (100 MHz, $CDCl_3$):



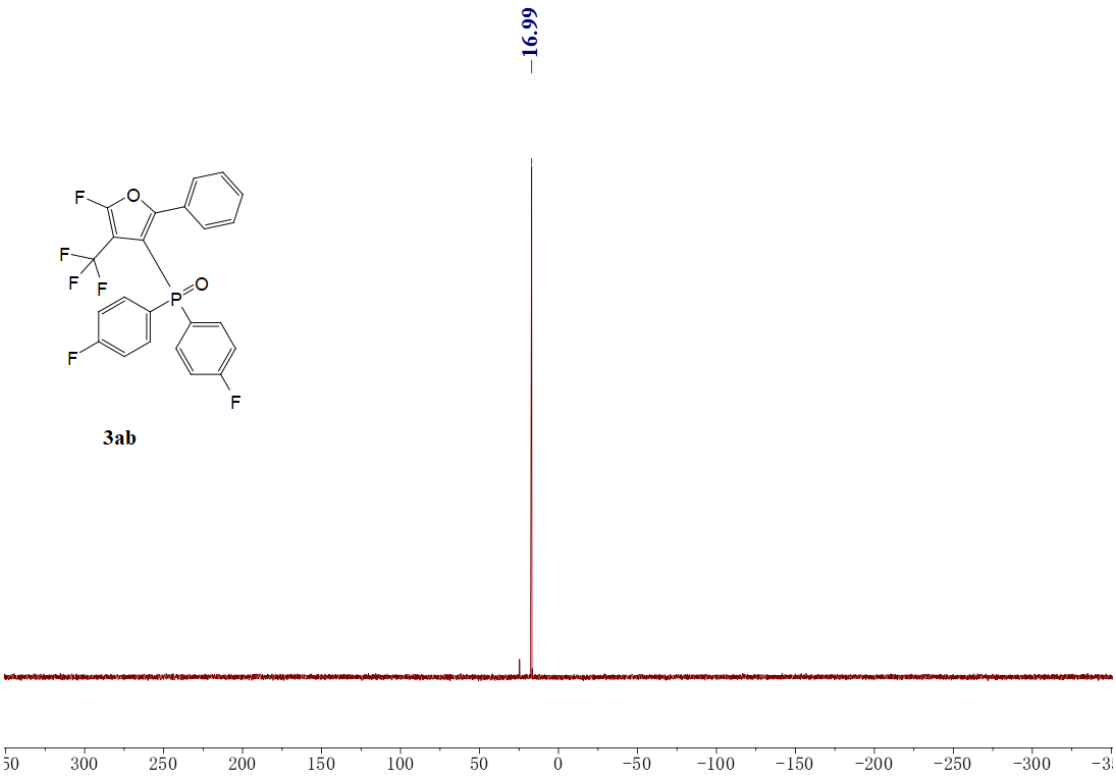
^{1}H NMR spectra of the product **3ab** (400 MHz, $CDCl_3$):



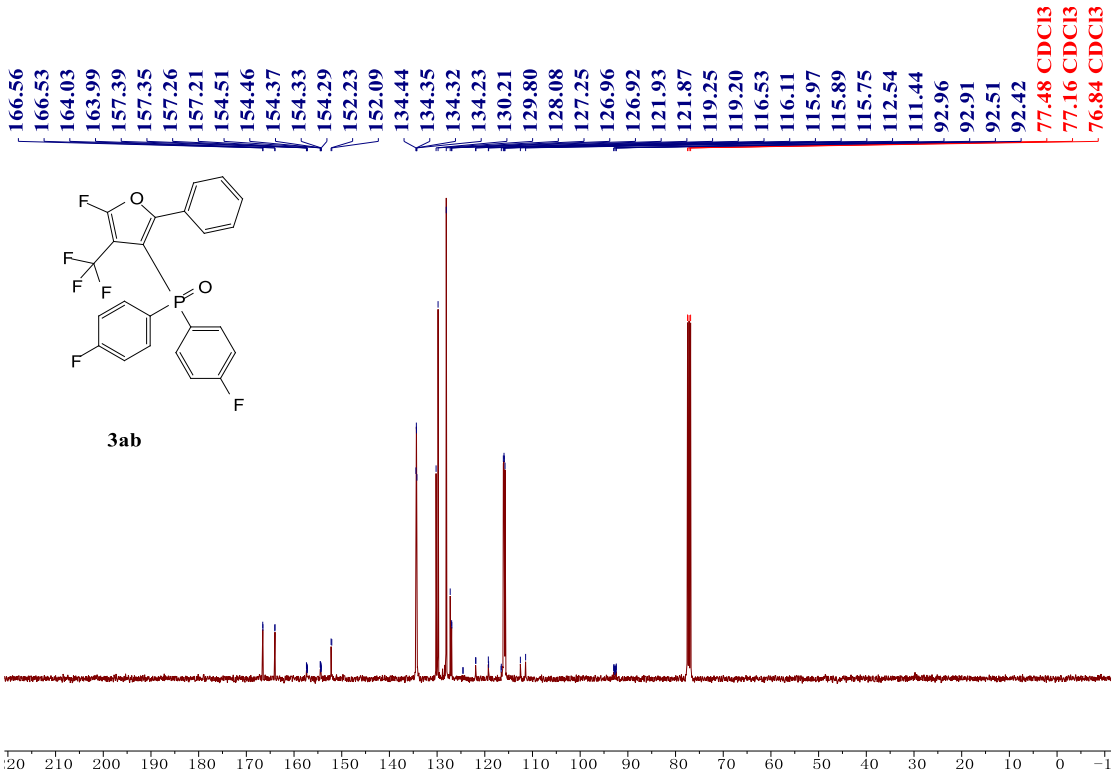
^{19}F NMR spectra of the product **3ab** (376 MHz, $CDCl_3$):



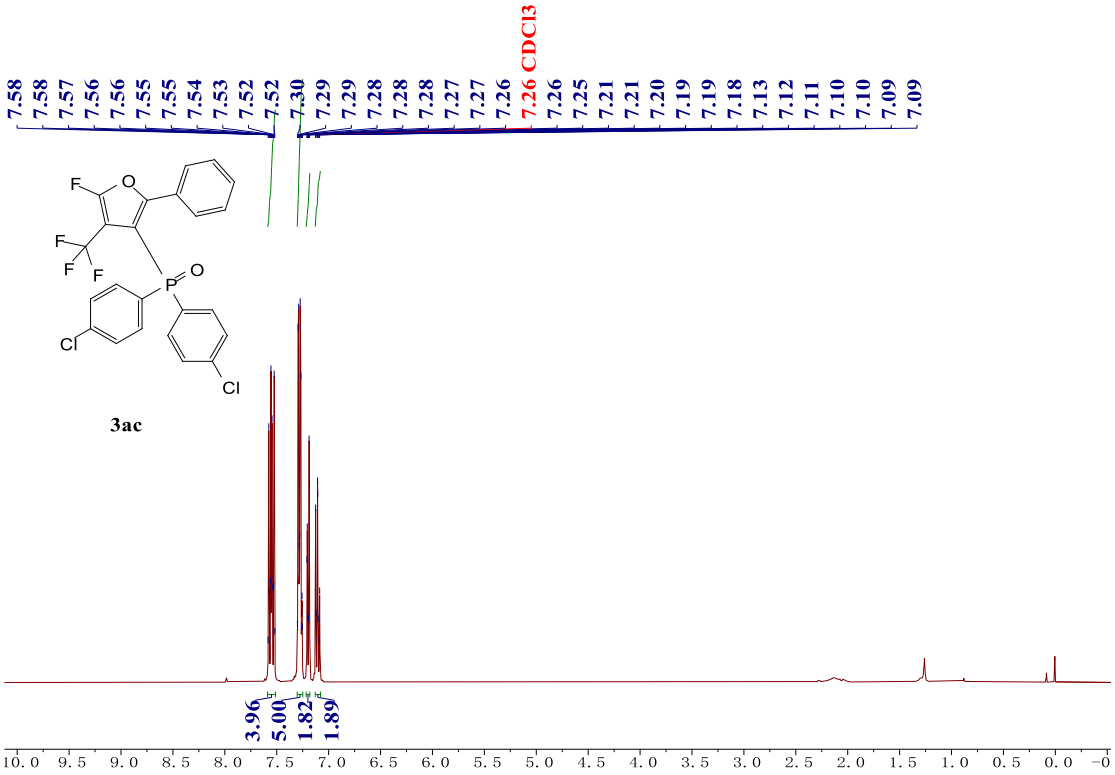
^{31}P NMR spectra of the product **3ab** (162 MHz, $CDCl_3$):



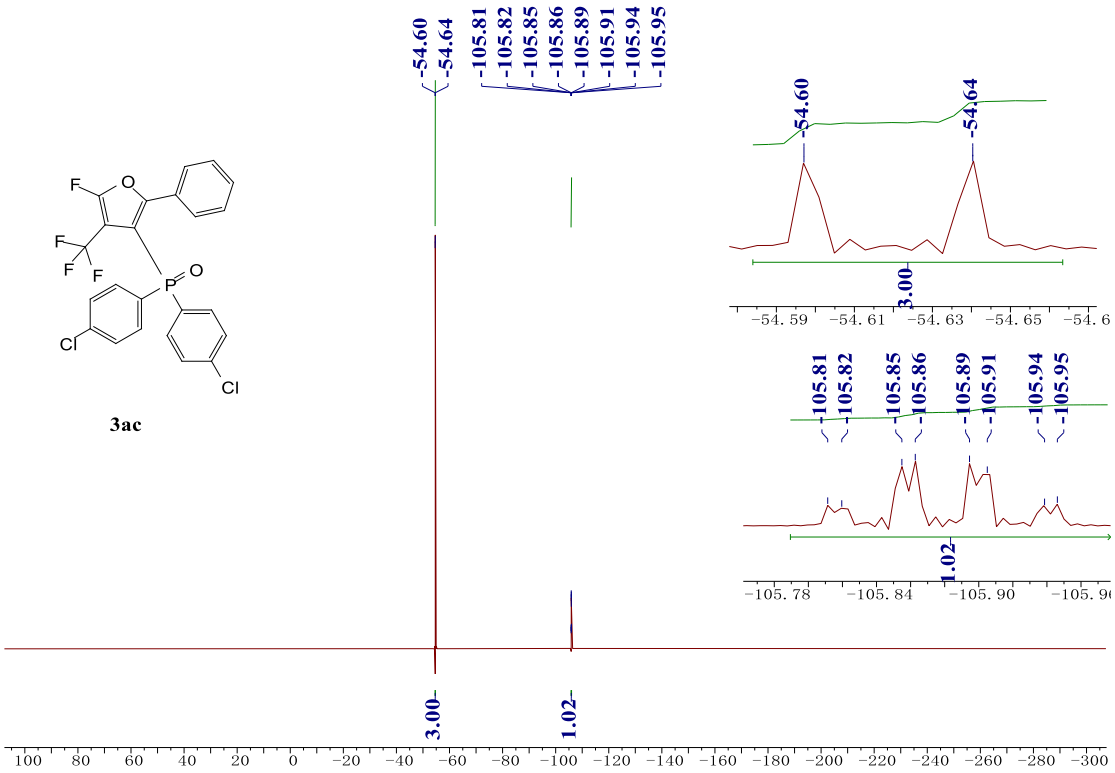
^{13}C NMR spectra of the product **3ab** (100 MHz, $CDCl_3$):



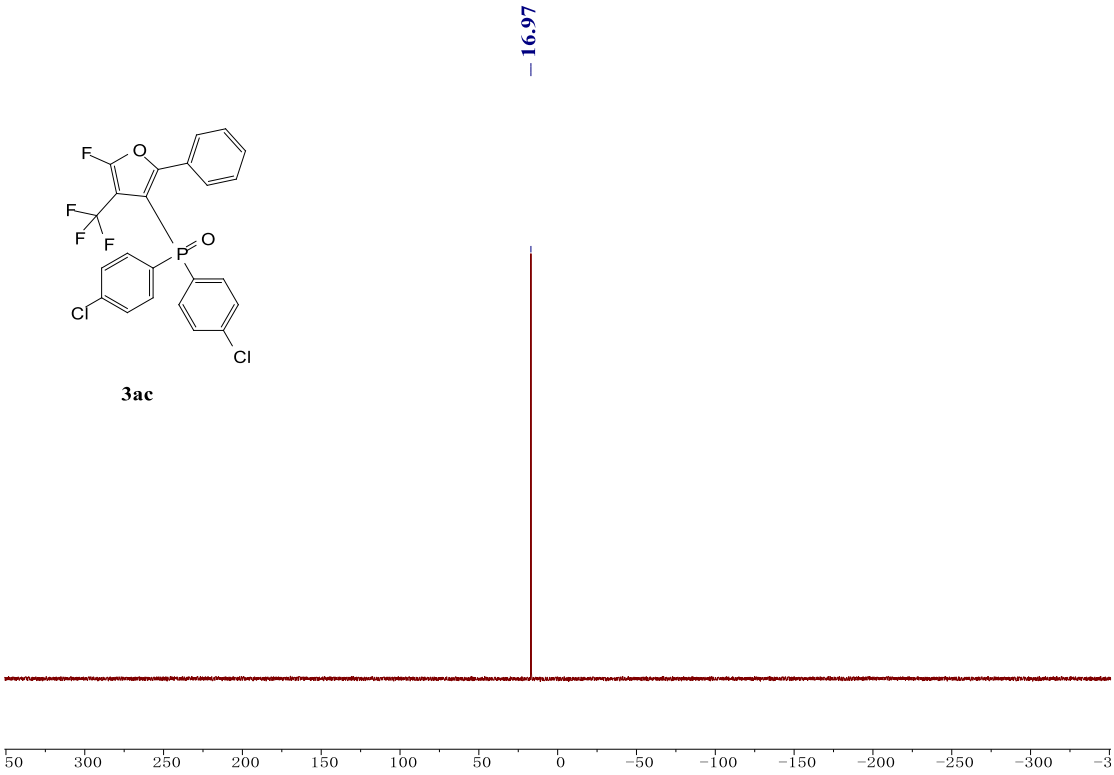
^{1}H NMR spectra of the product **3ac** (400 MHz, $CDCl_3$):



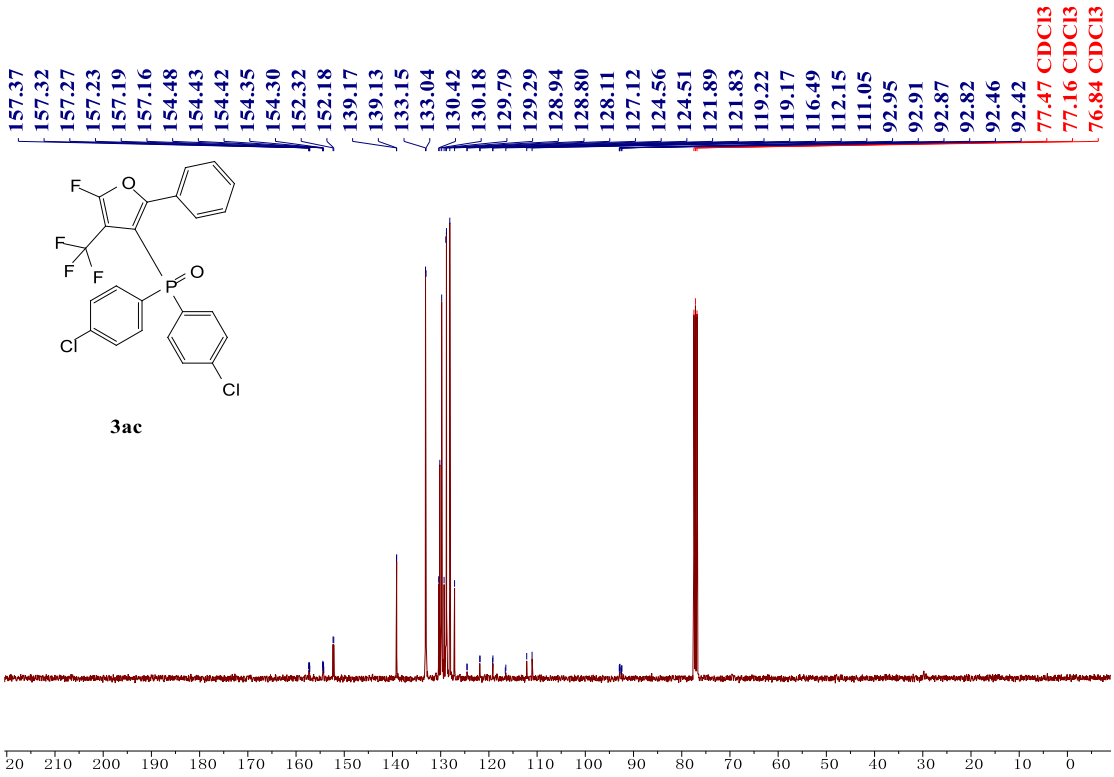
^{19}F NMR spectra of the product **3ac** (376 MHz, $CDCl_3$):



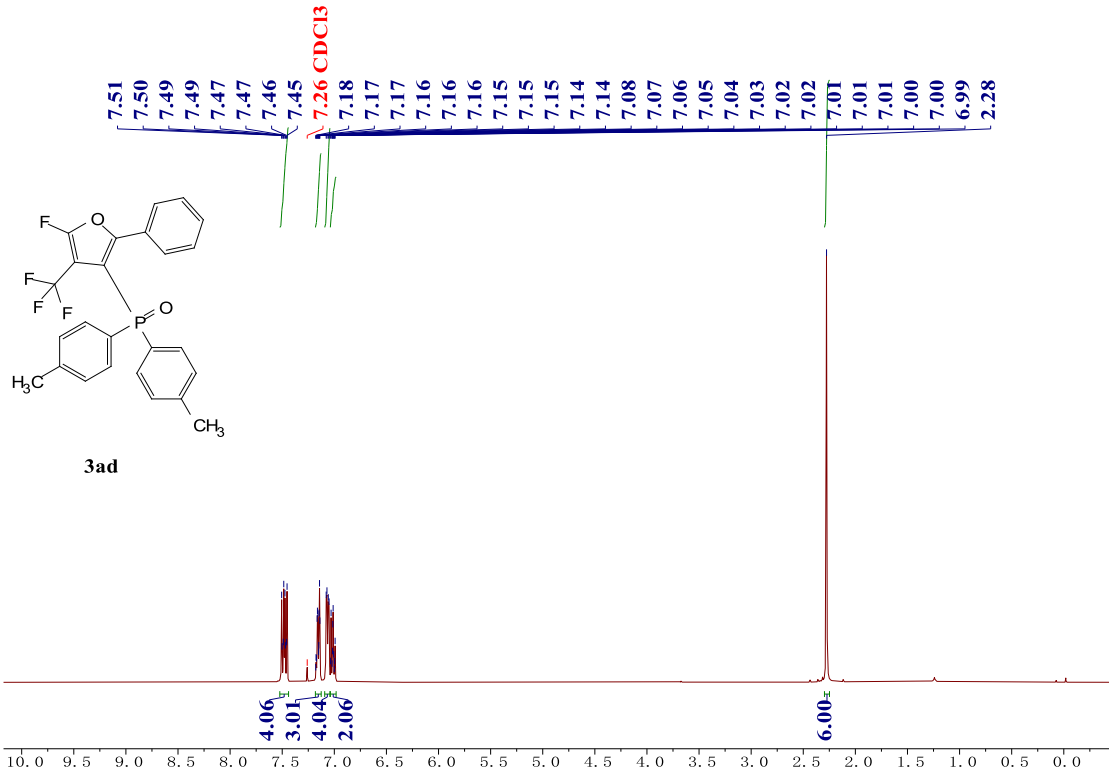
^{31}P NMR spectra of the product **3ac** (162 MHz, $CDCl_3$):



^{13}C NMR spectra of the product **3ac** (100 MHz, $CDCl_3$):

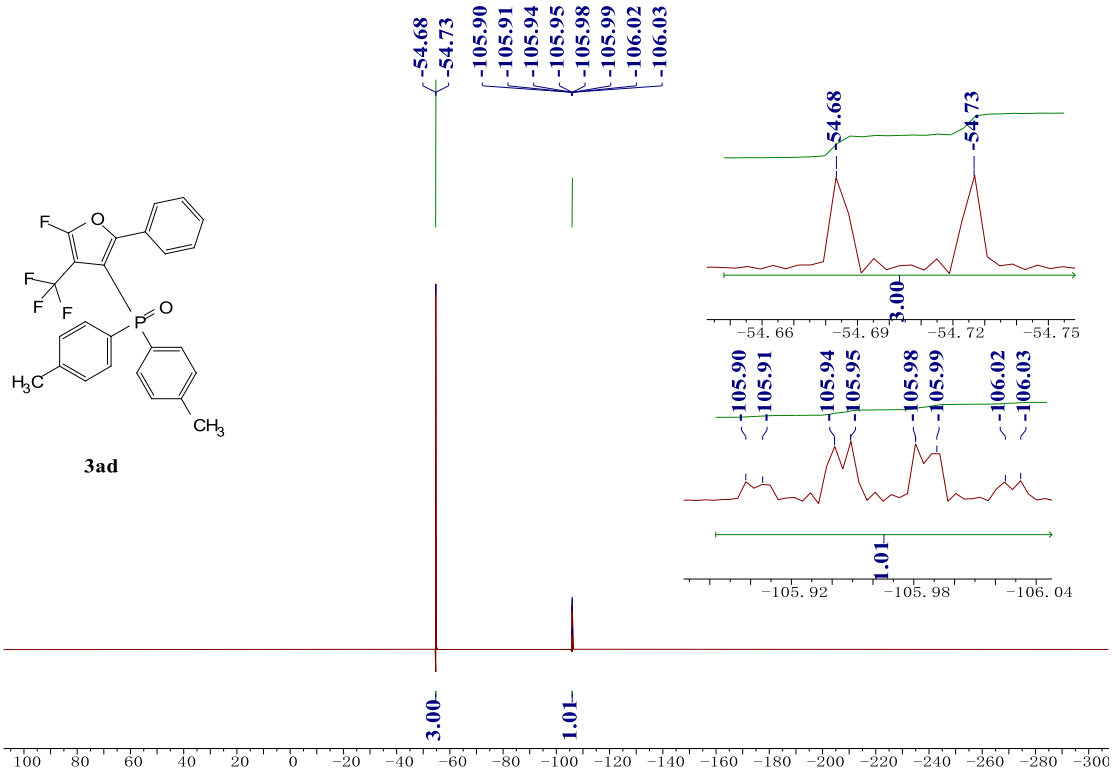


^{1}H NMR spectra of the product **3ad** (400 MHz, $CDCl_3$):



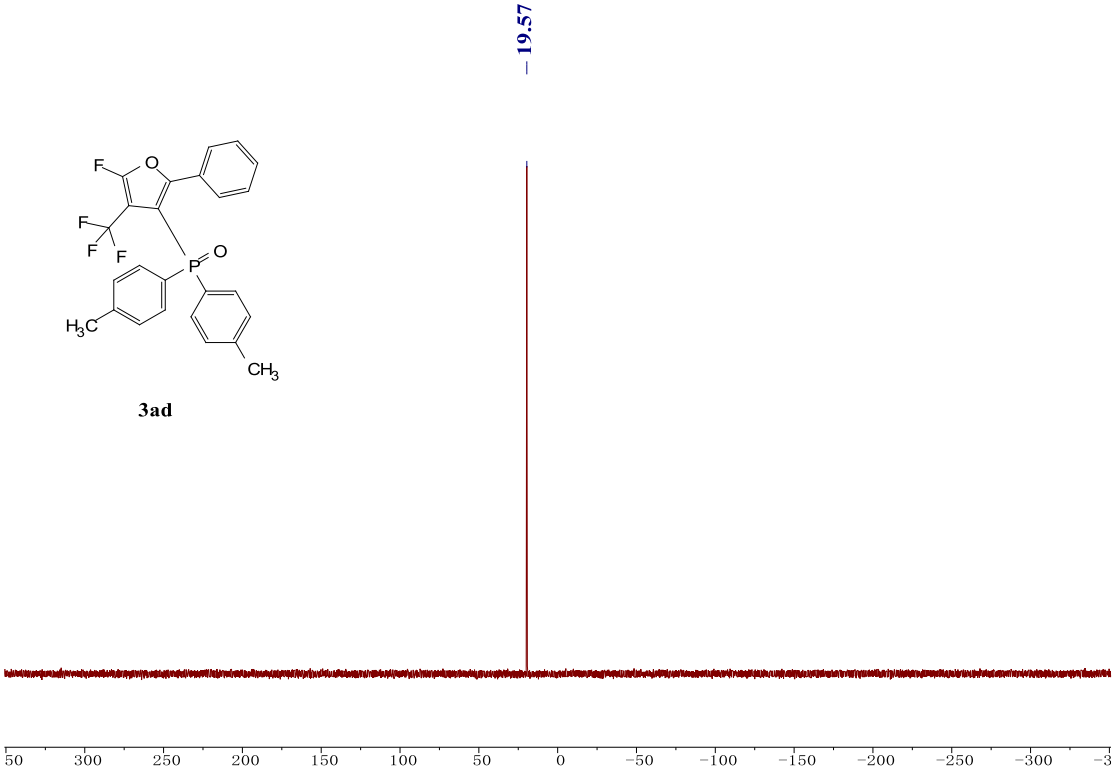
3ad

^{19}F NMR spectra of the product **3ad** (376 MHz, $CDCl_3$):

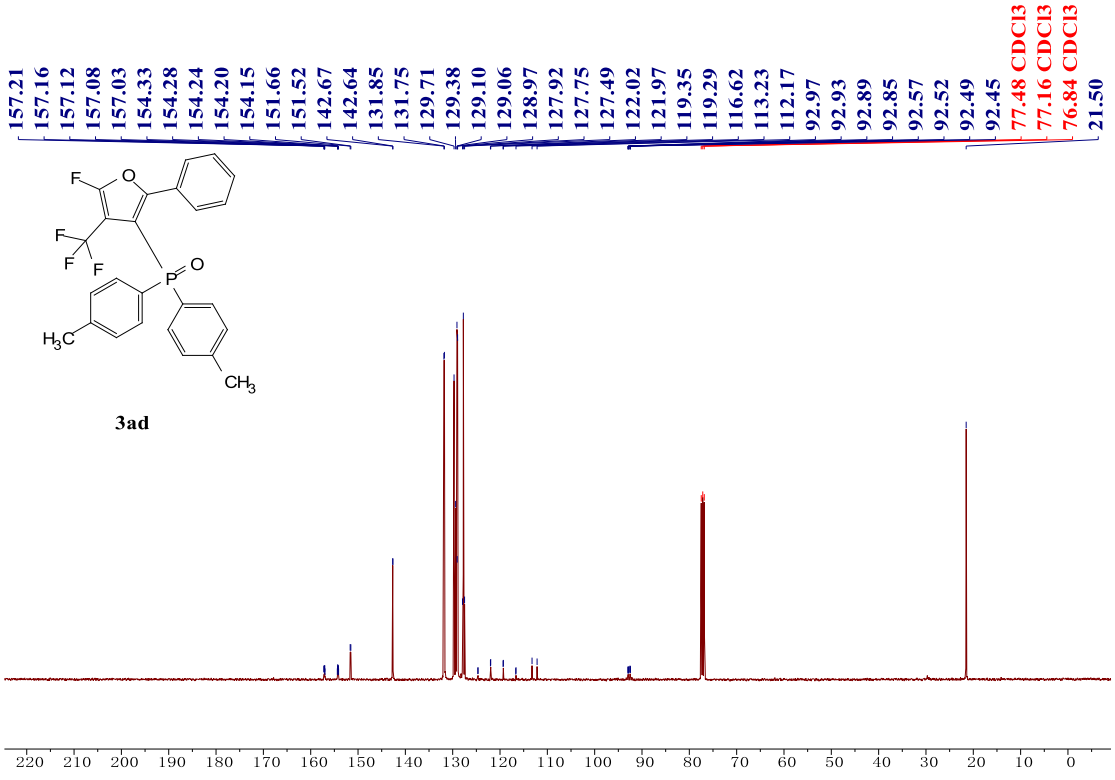


3ad

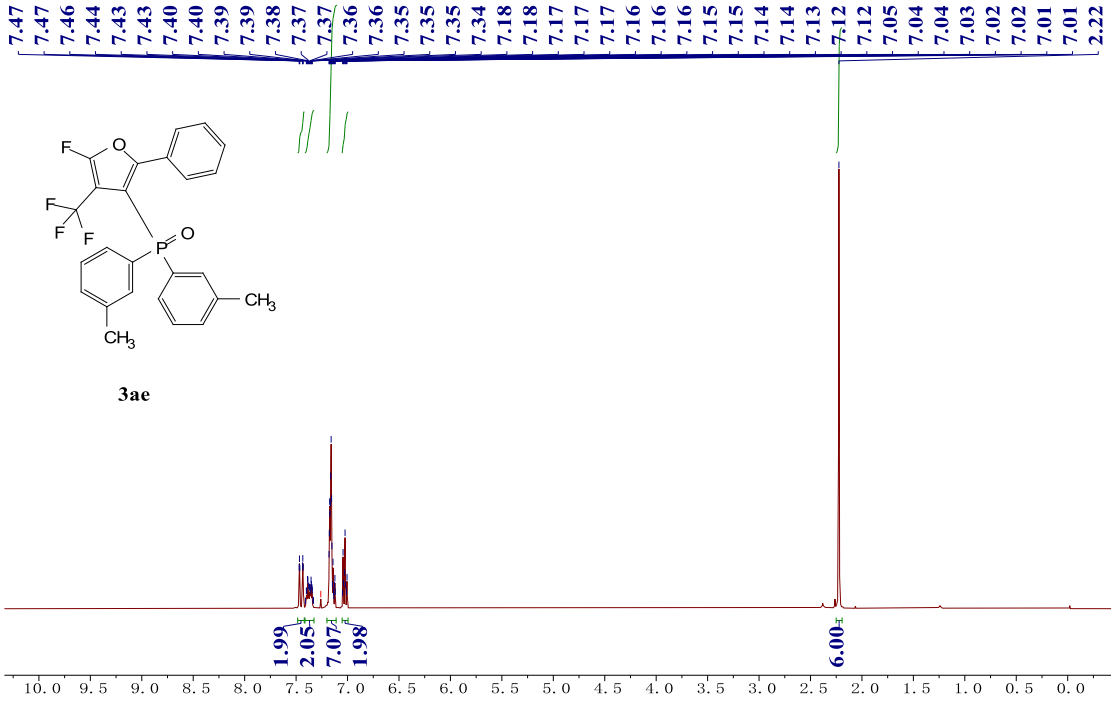
^{31}P NMR spectra of the product **3ad** (162 MHz, $CDCl_3$):



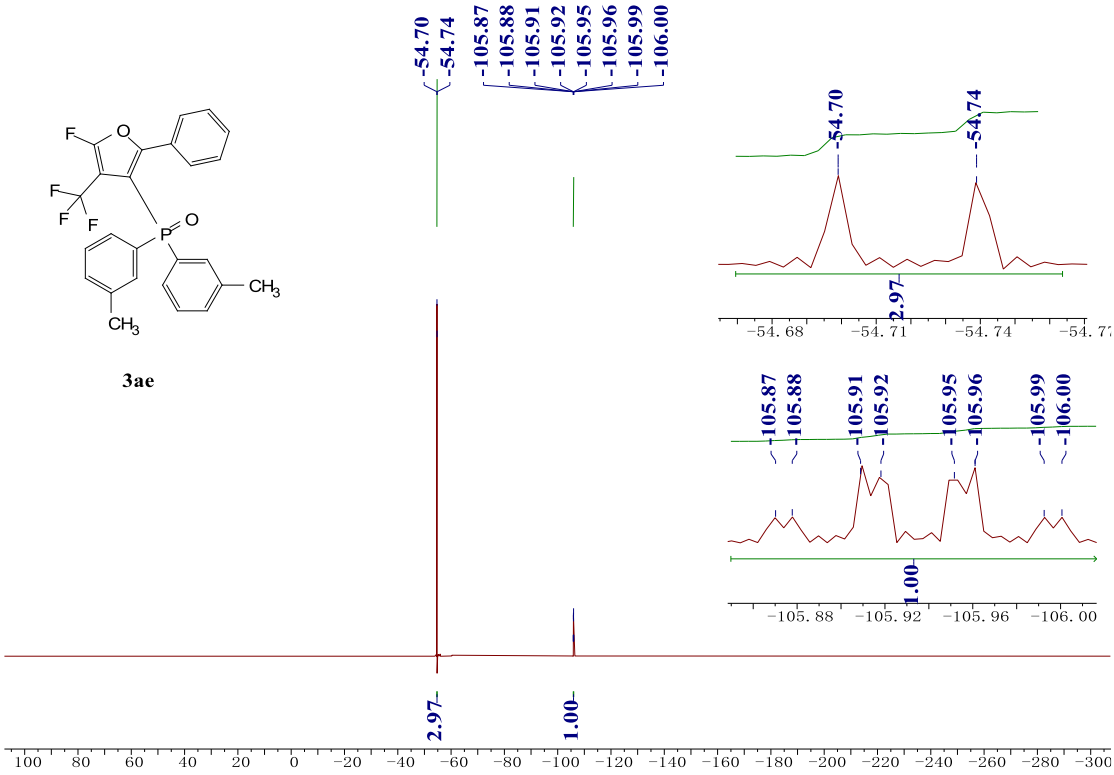
^{13}C NMR spectra of the product **3ad** (100 MHz, $CDCl_3$):



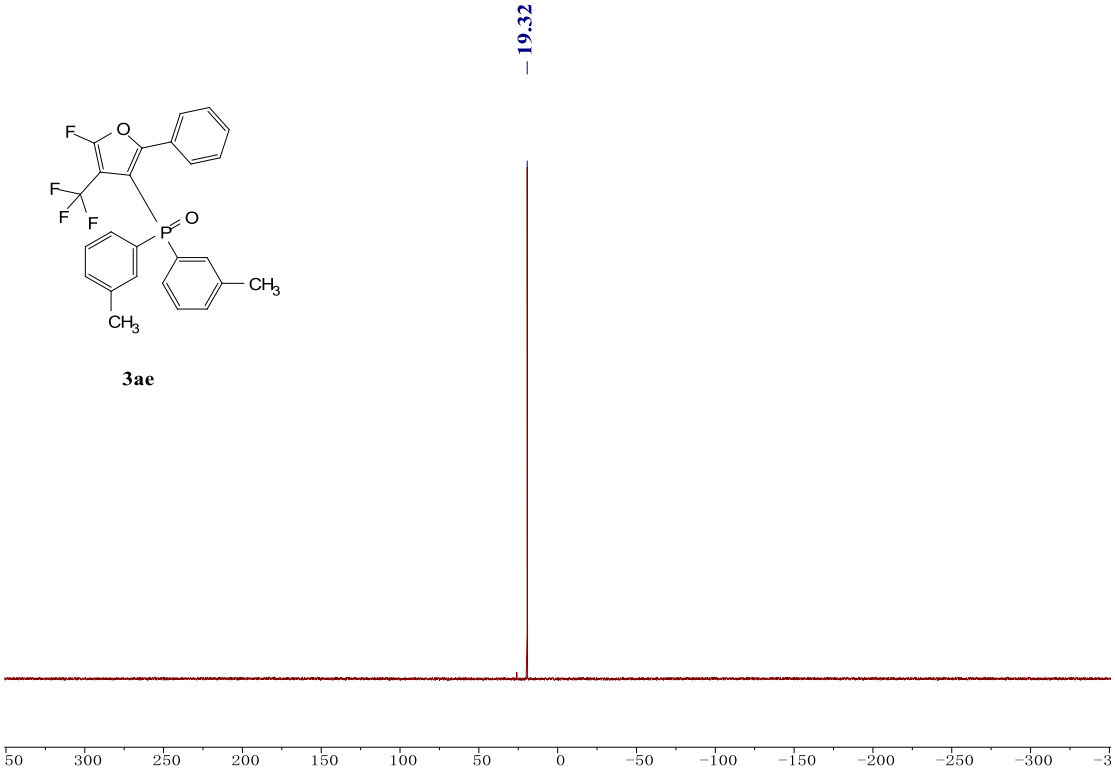
^{1}H NMR spectra of the product **3ae** (400 MHz, $CDCl_3$):



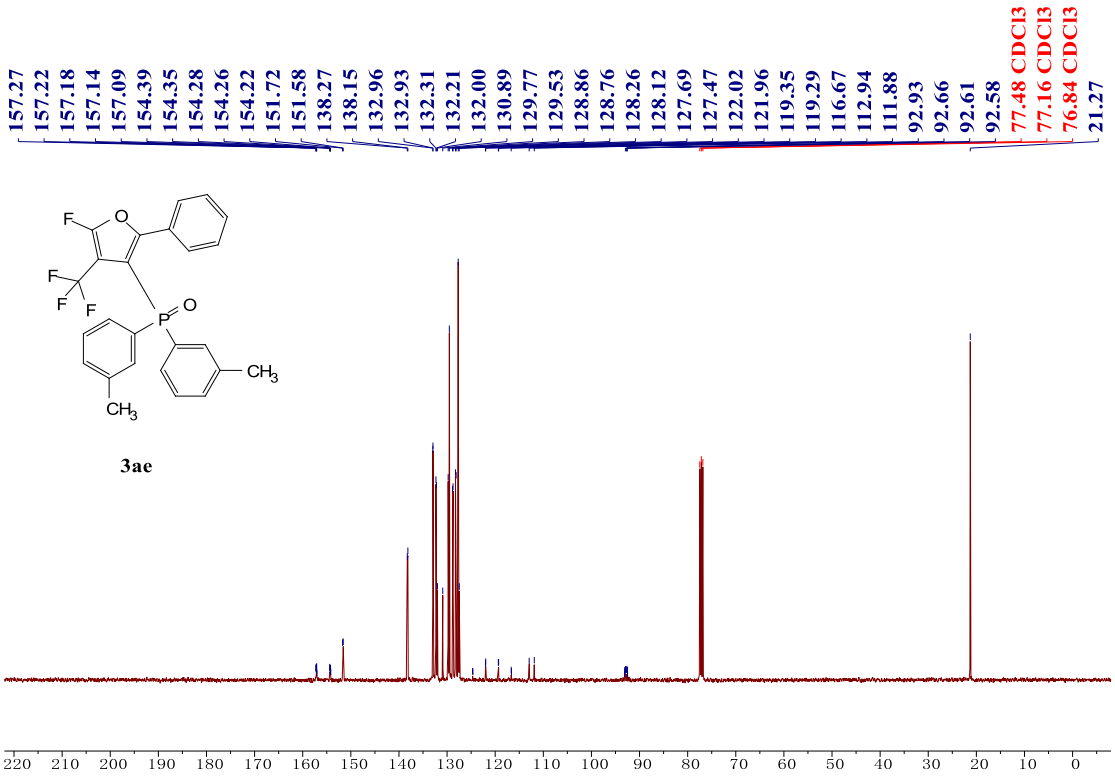
^{19}F NMR spectra of the product **3ae** (376 MHz, $CDCl_3$):



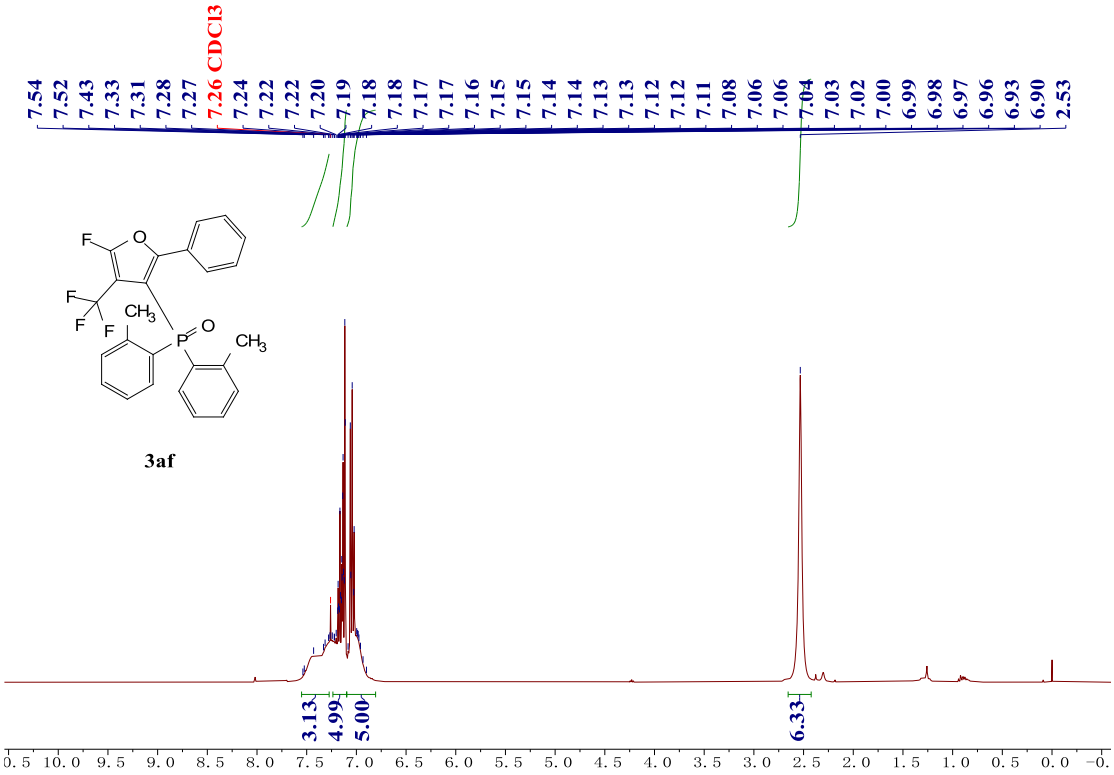
^{31}P NMR spectra of the product **3ae** (162 MHz, $CDCl_3$):



^{13}C NMR spectra of the product **3ae** (100 MHz, $CDCl_3$):

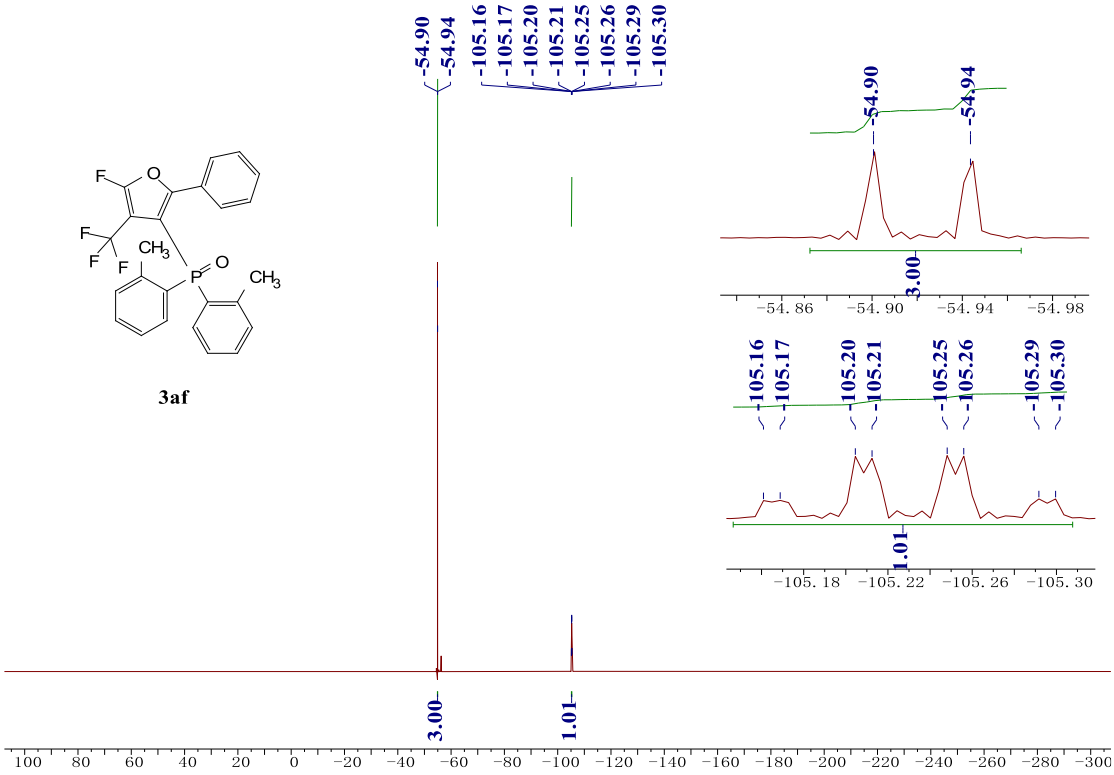


^{1}H NMR spectra of the product **3af** (400 MHz, $CDCl_3$):



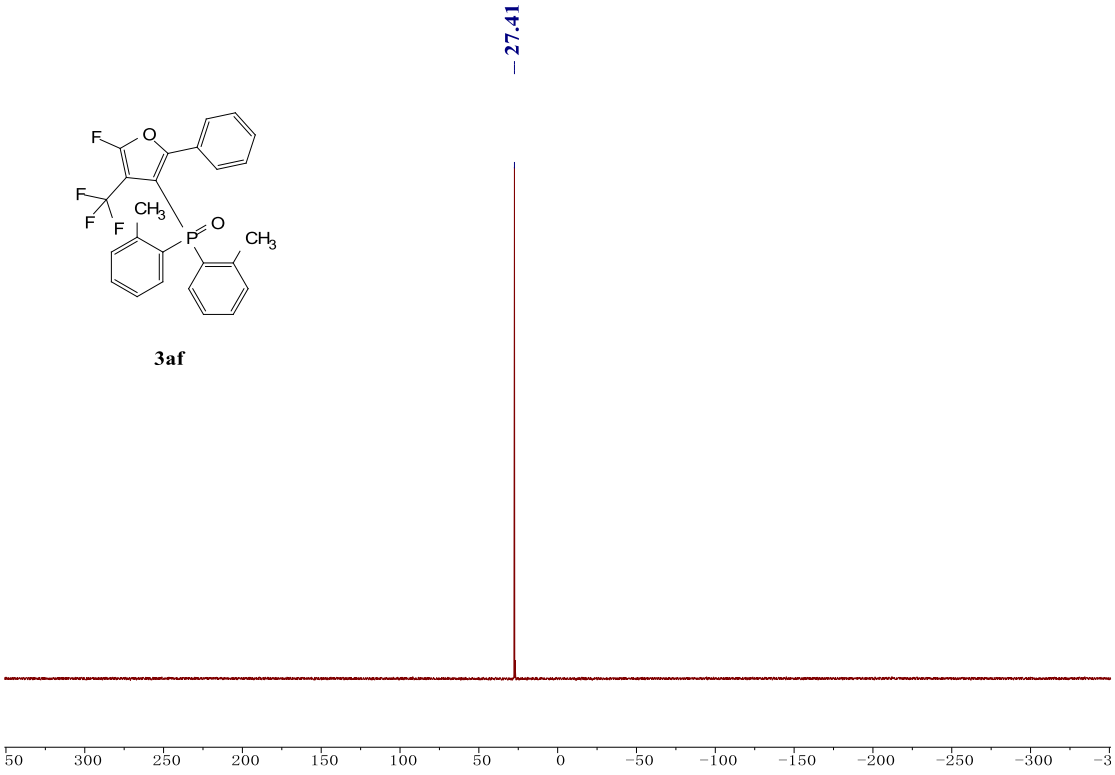
3af

^{19}F NMR spectra of the product **3af** (376 MHz, $CDCl_3$):

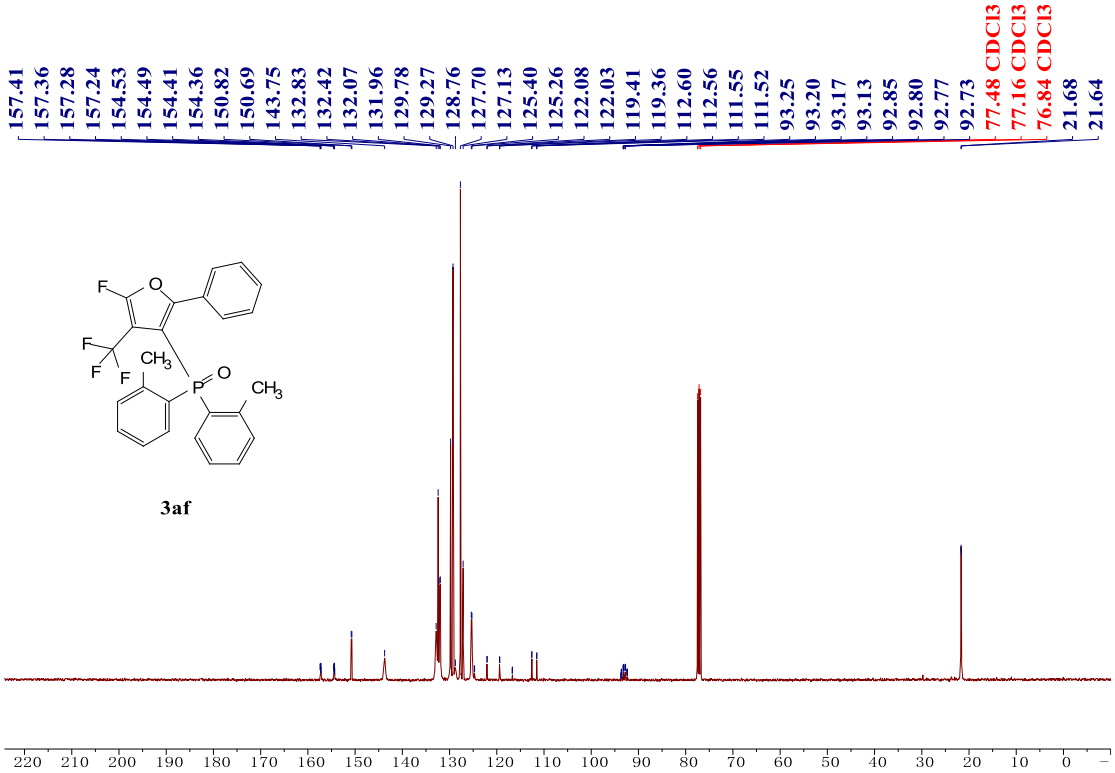


3af

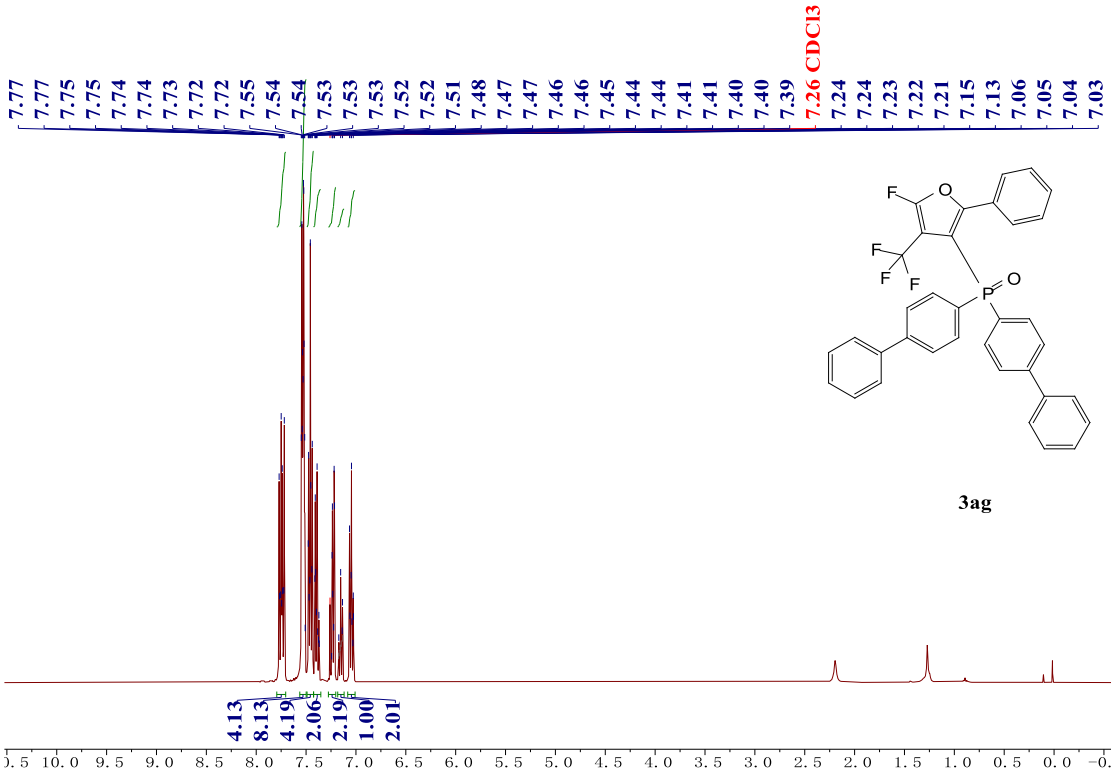
^{31}P NMR spectra of the product **3af** (162 MHz, $CDCl_3$):



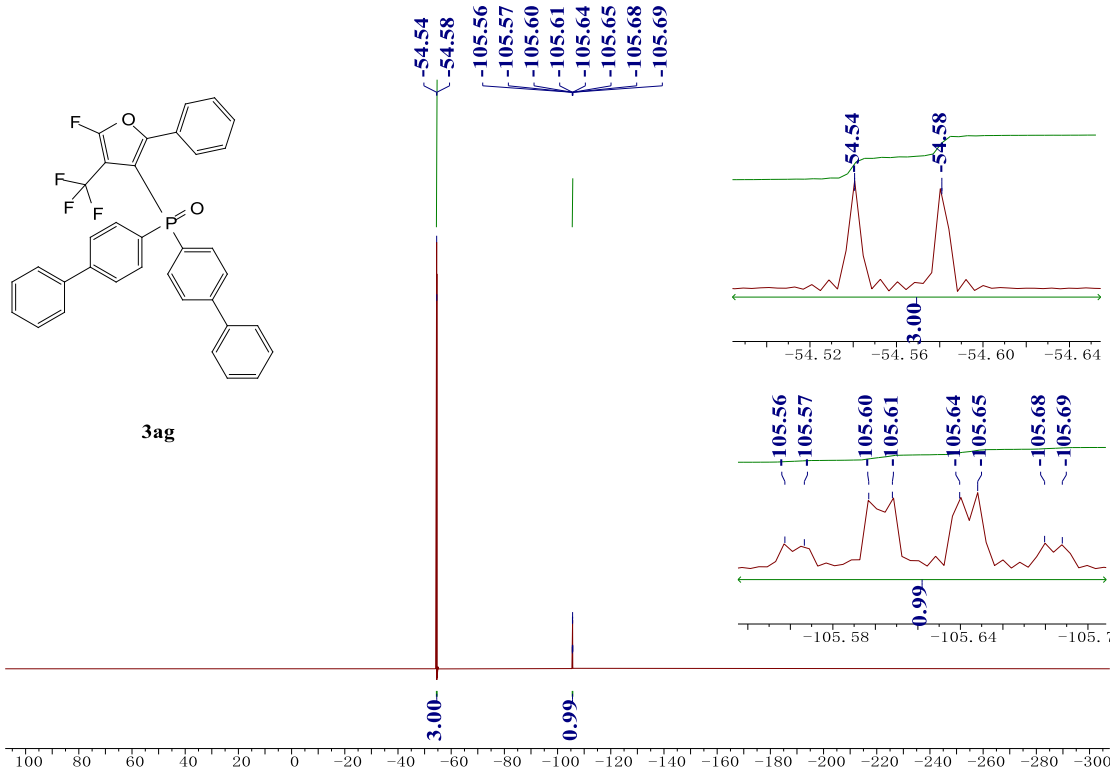
^{13}C NMR spectra of the product **3af** (100 MHz, $CDCl_3$):



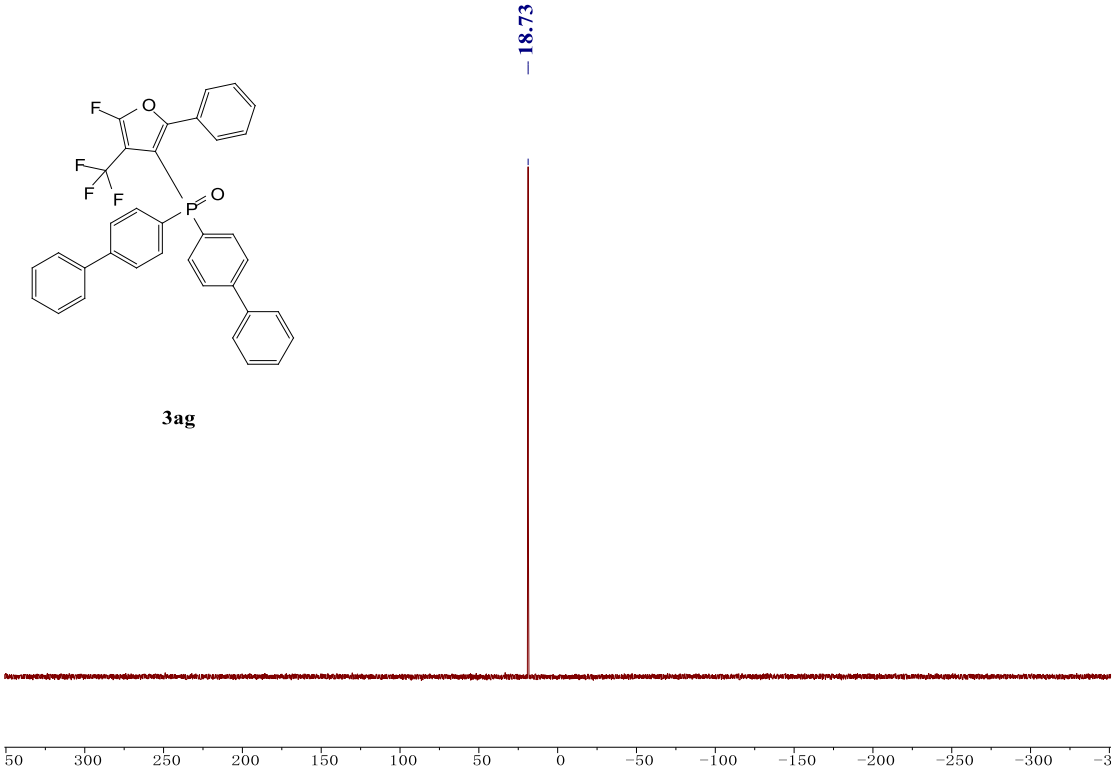
^{1}H NMR spectra of the product **3ag** (400 MHz, $CDCl_3$):



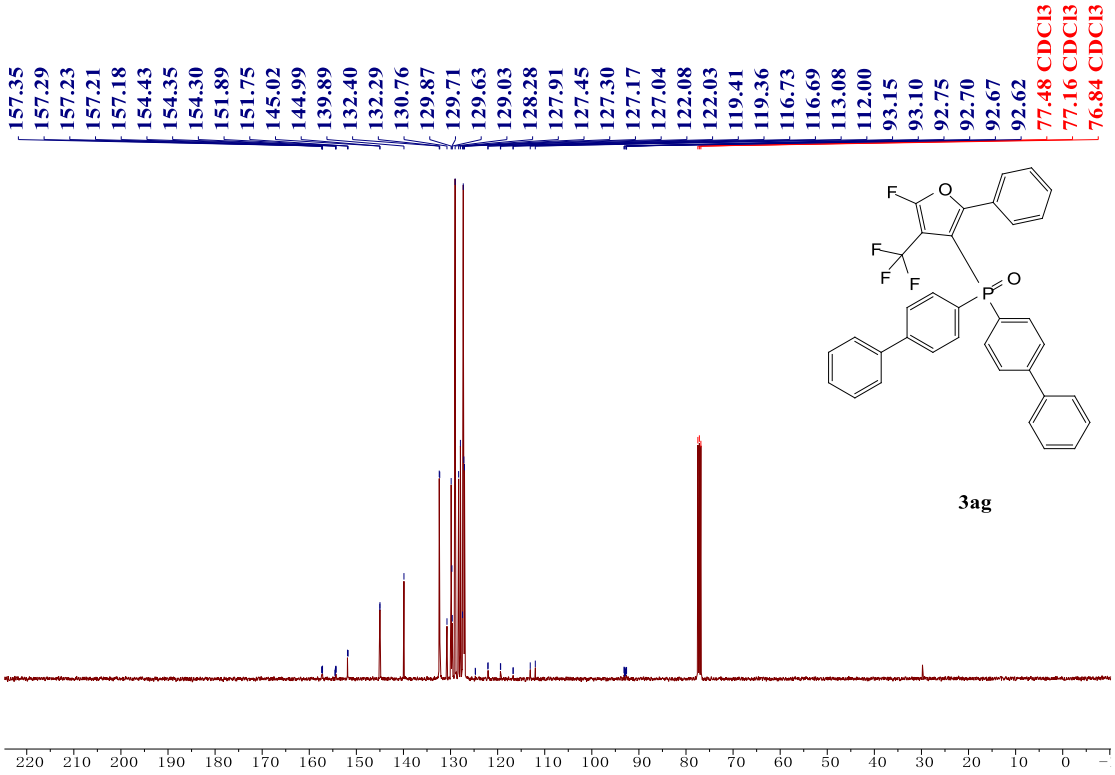
^{19}F NMR spectra of the product **3ag** (376 MHz, $CDCl_3$):



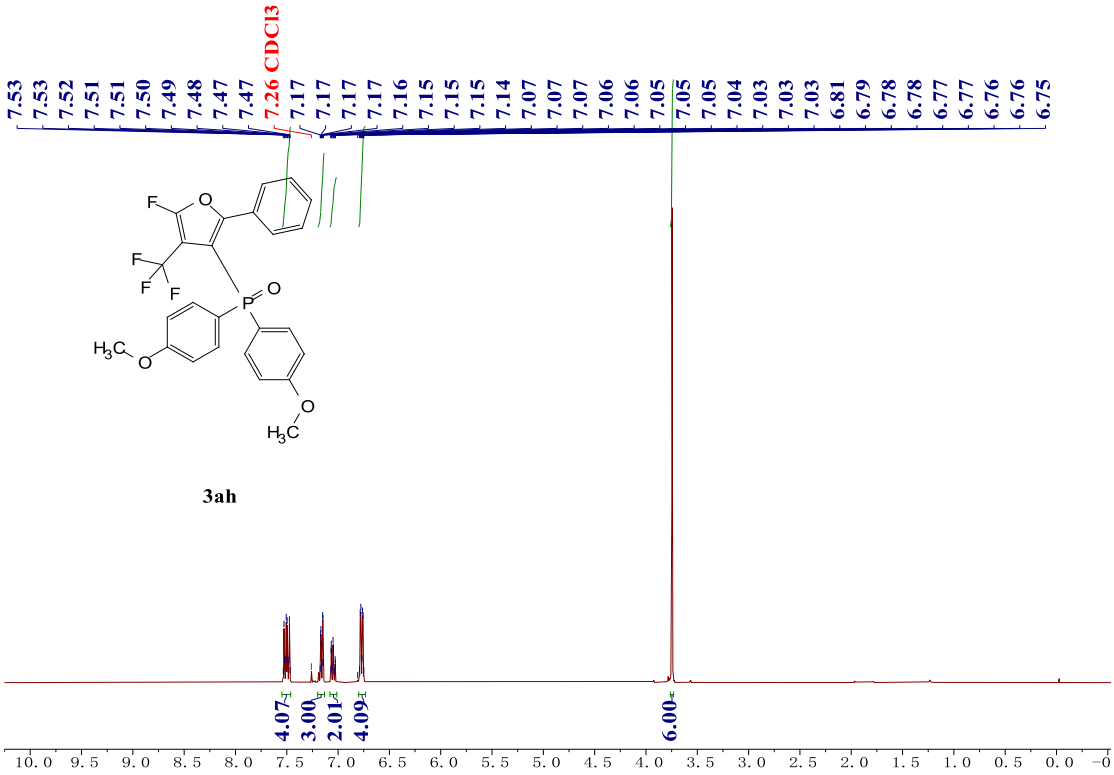
^{31}P NMR spectra of the product **3ag** (162 MHz, $CDCl_3$):



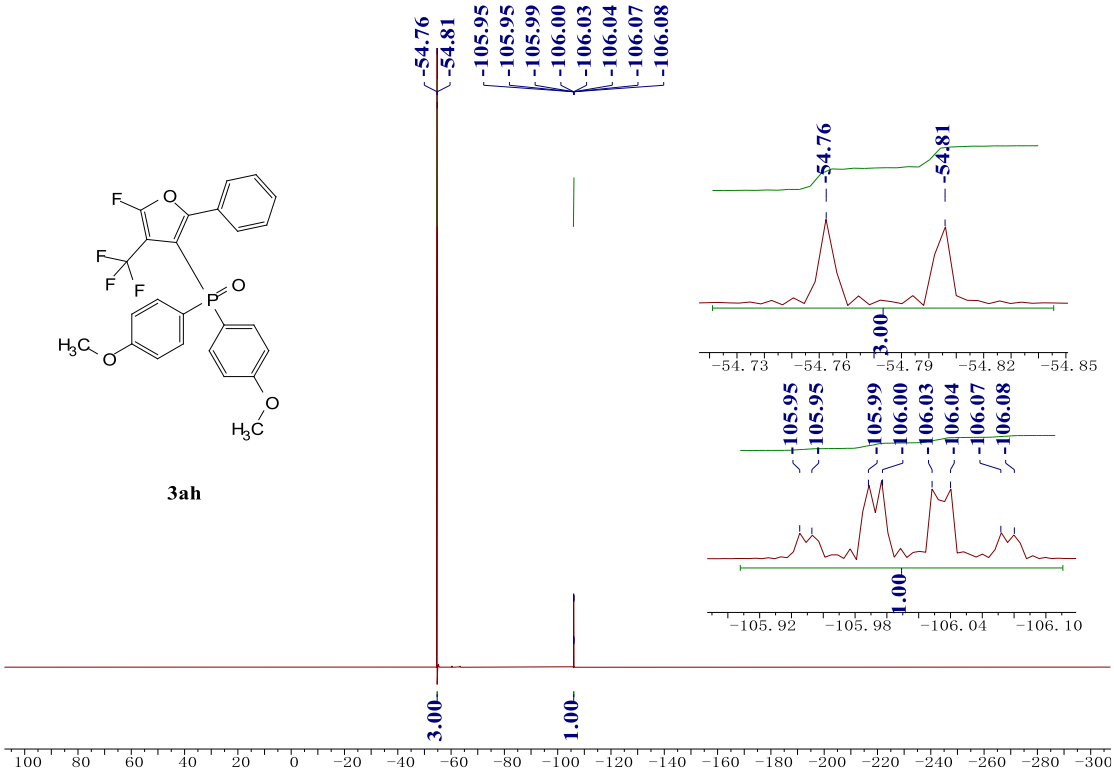
^{13}C NMR spectra of the product **3ag** (100 MHz, $CDCl_3$):



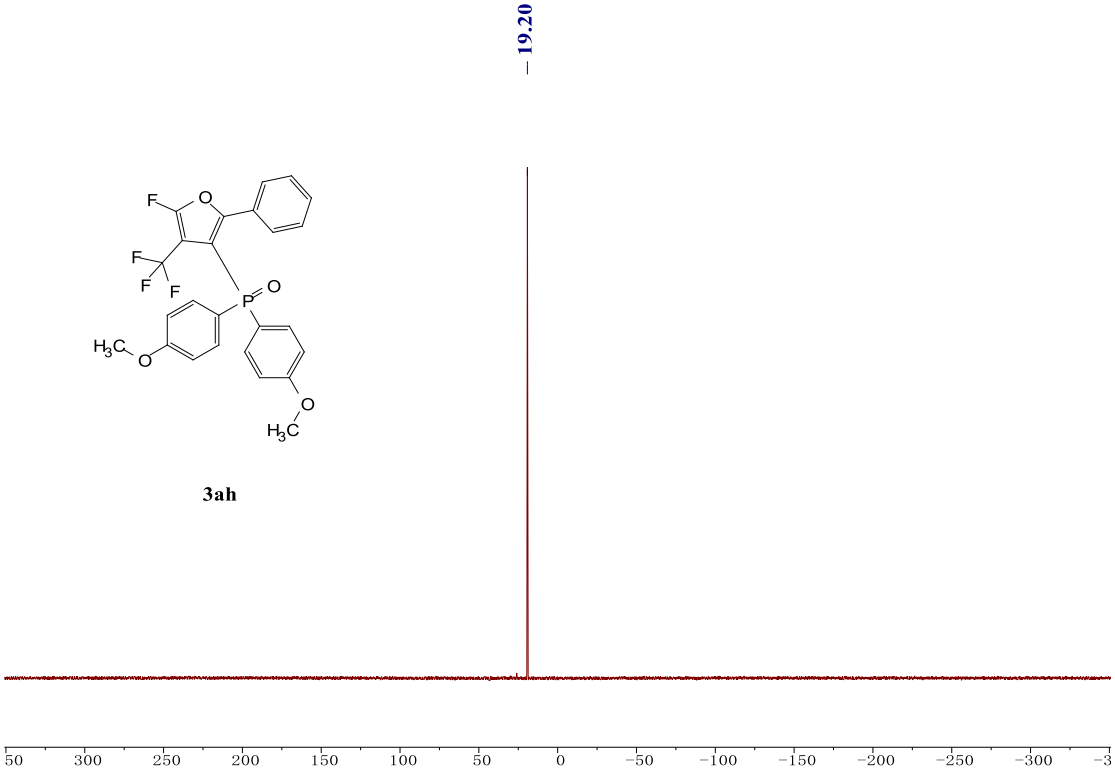
^{1}H NMR spectra of the product **3ah** (400 MHz, $CDCl_3$):



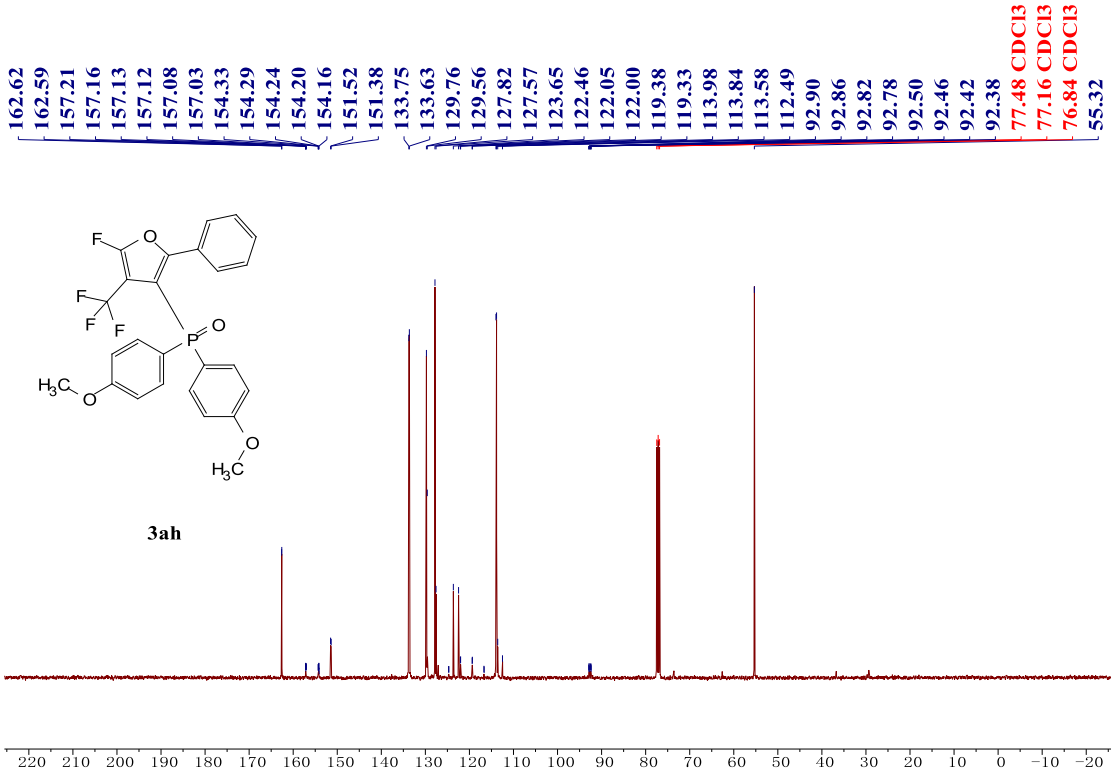
^{19}F NMR spectra of the product **3ah** (376 MHz, $CDCl_3$):



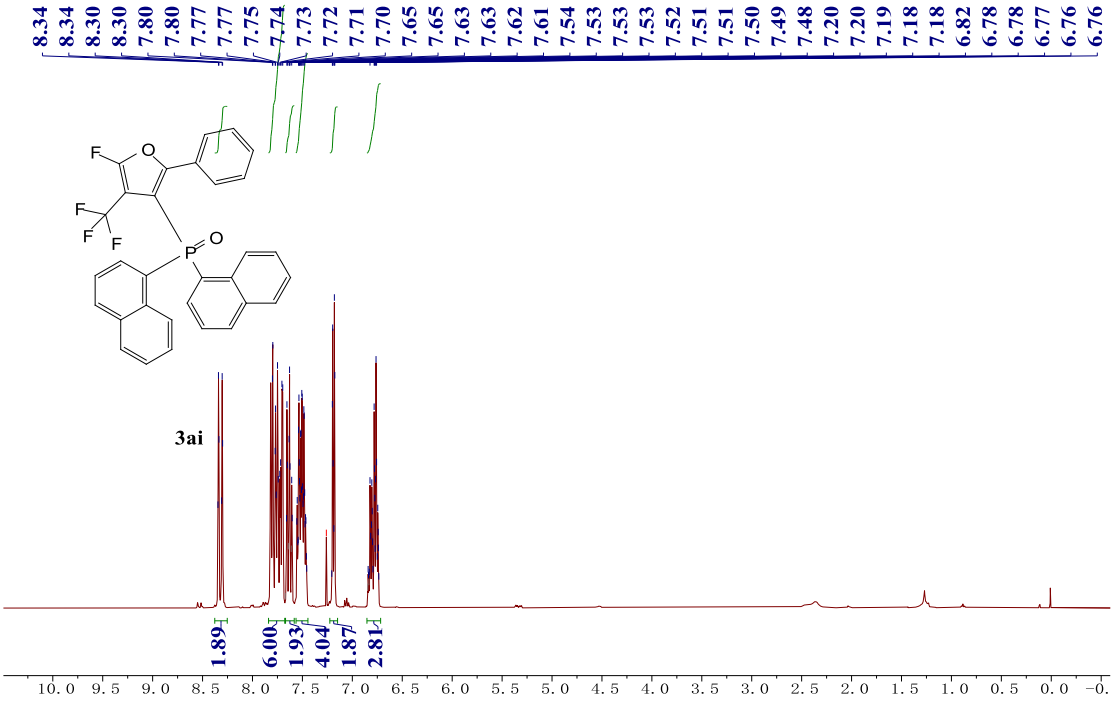
^{31}P NMR spectra of the product **3ah** (162 MHz, $CDCl_3$):



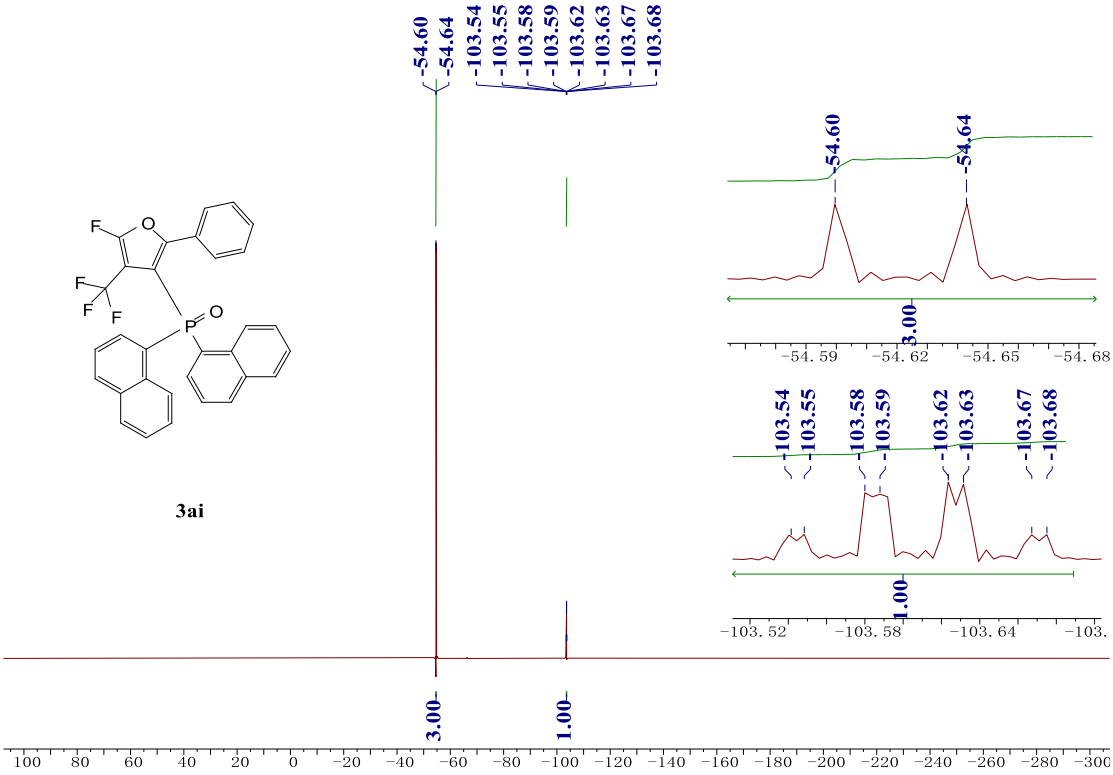
^{13}C NMR spectra of the product **3ah** (100 MHz, $CDCl_3$):



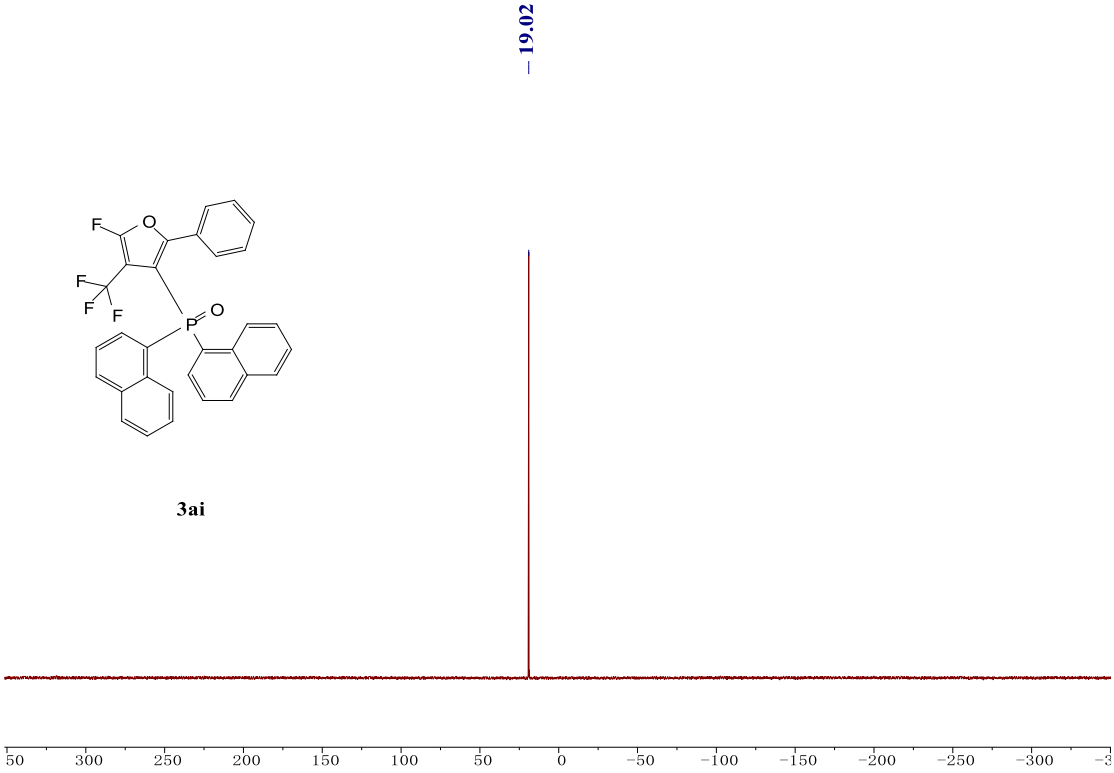
^{1}H NMR spectra of the product **3ai** (400 MHz, $CDCl_3$):



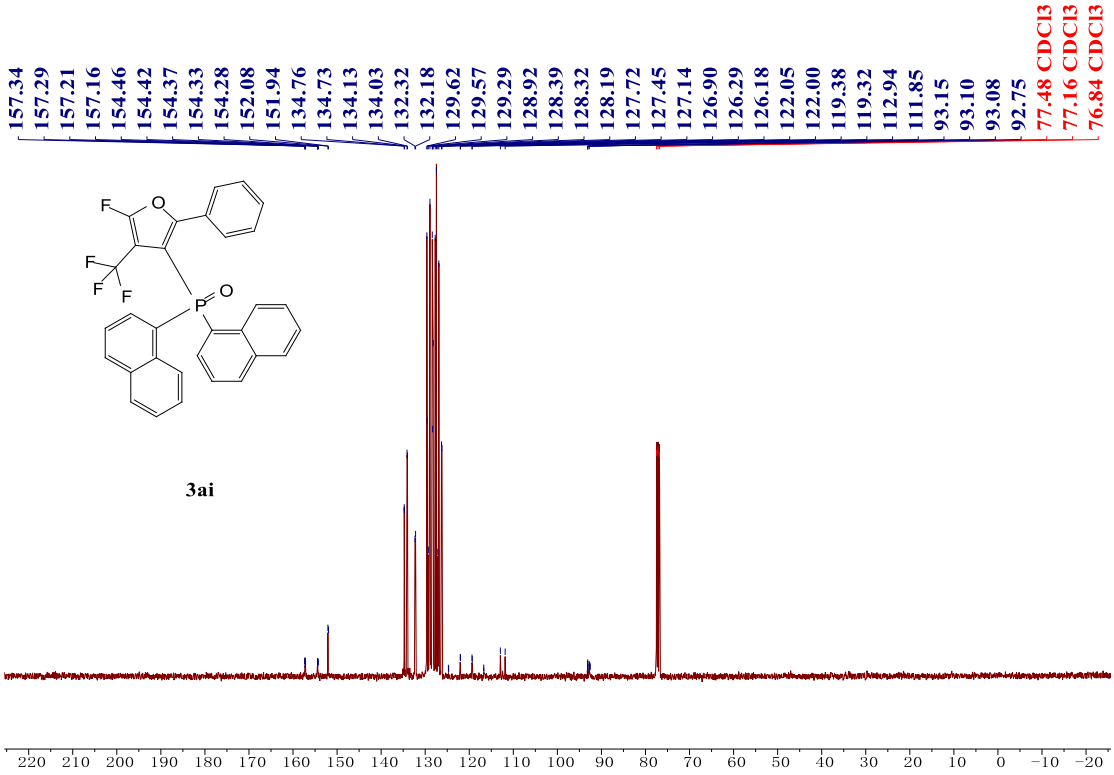
^{19}F NMR spectra of the product **3ai** (376 MHz, $CDCl_3$):



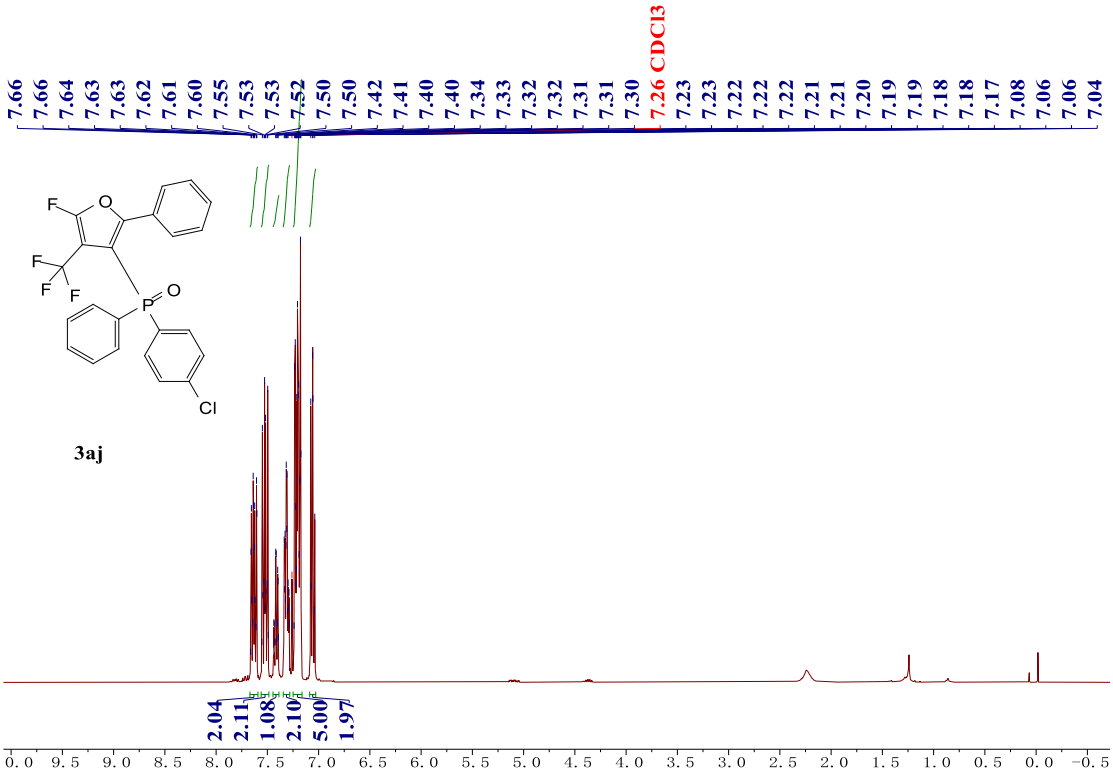
^{31}P NMR spectra of the product **3ai** (162 MHz, $CDCl_3$):



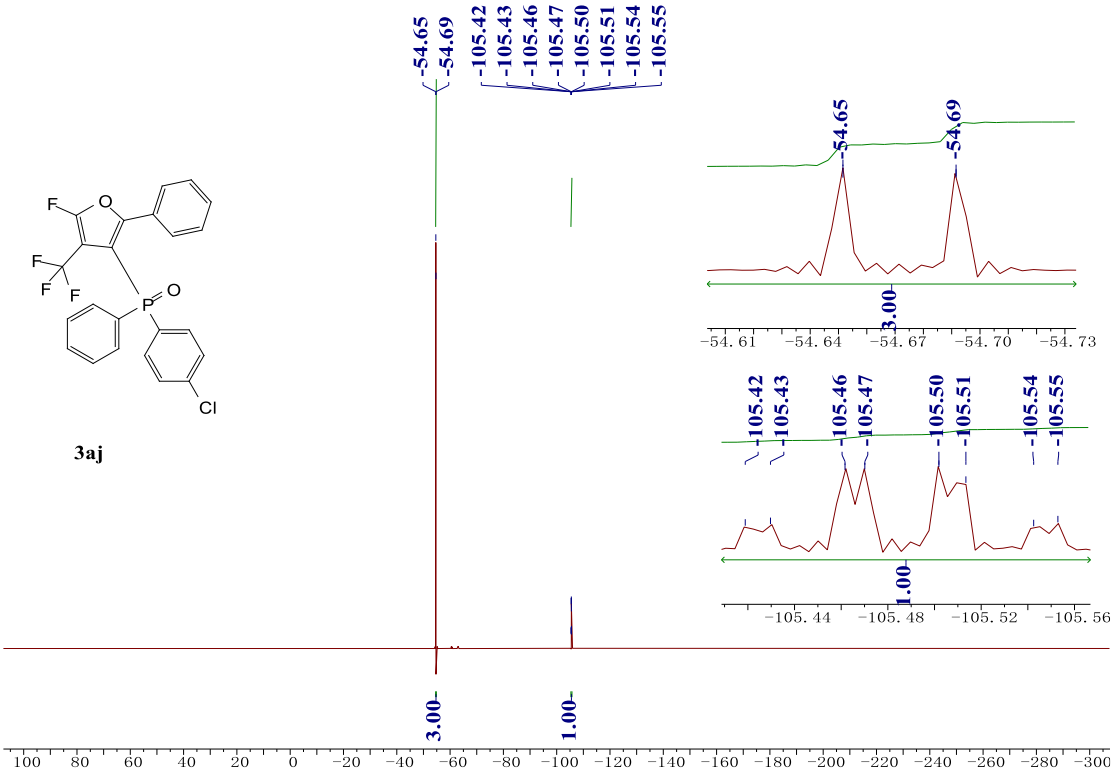
^{13}C NMR spectra of the product **3ai** (100 MHz, $CDCl_3$):



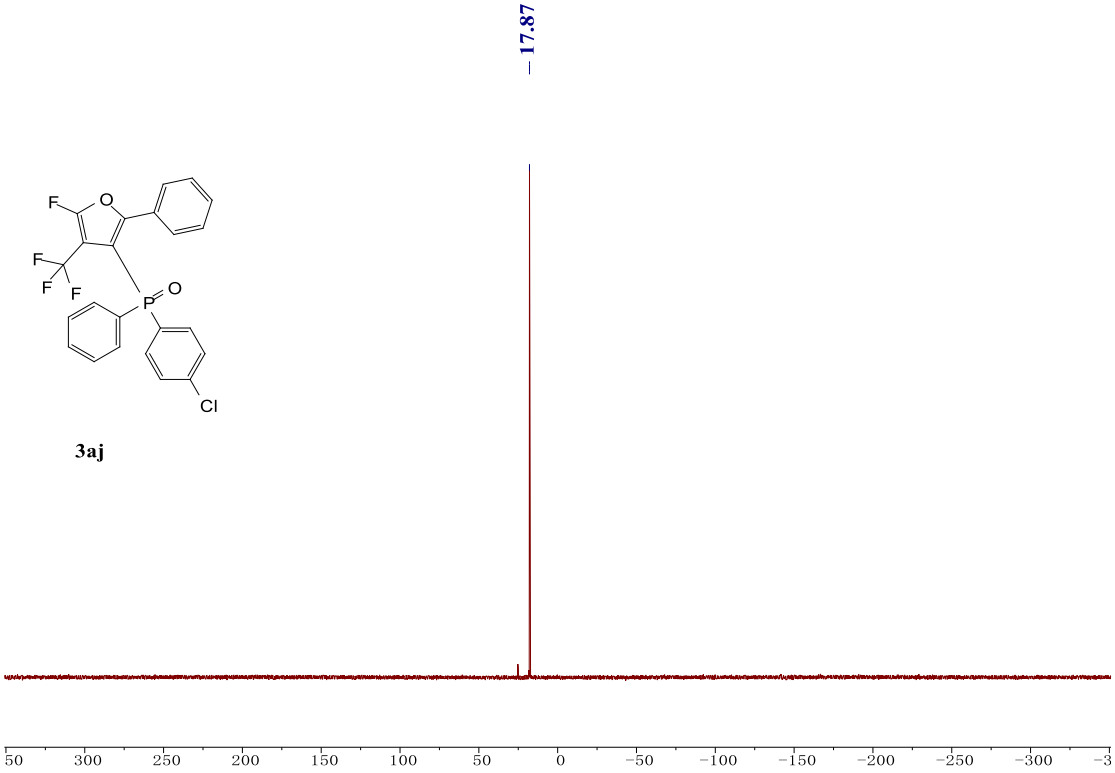
^{1}H NMR spectra of the product **3aj** (400 MHz, $CDCl_3$):



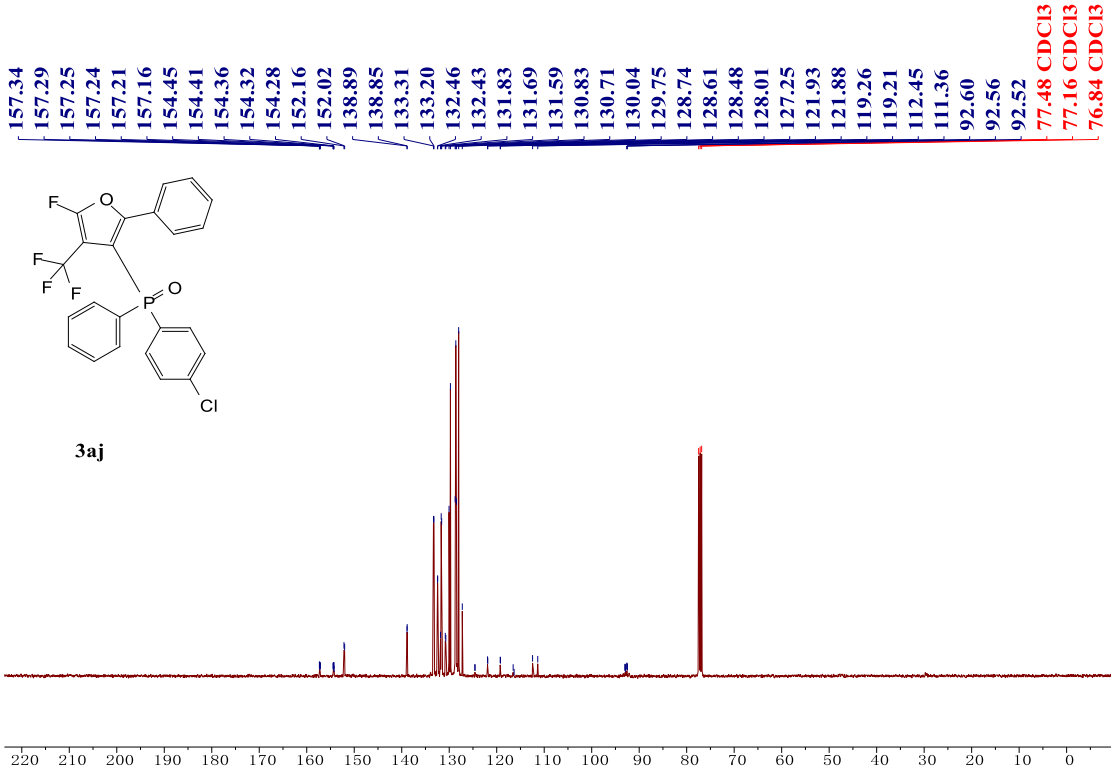
^{19}F NMR spectra of the product **3aj** (376 MHz, $CDCl_3$):



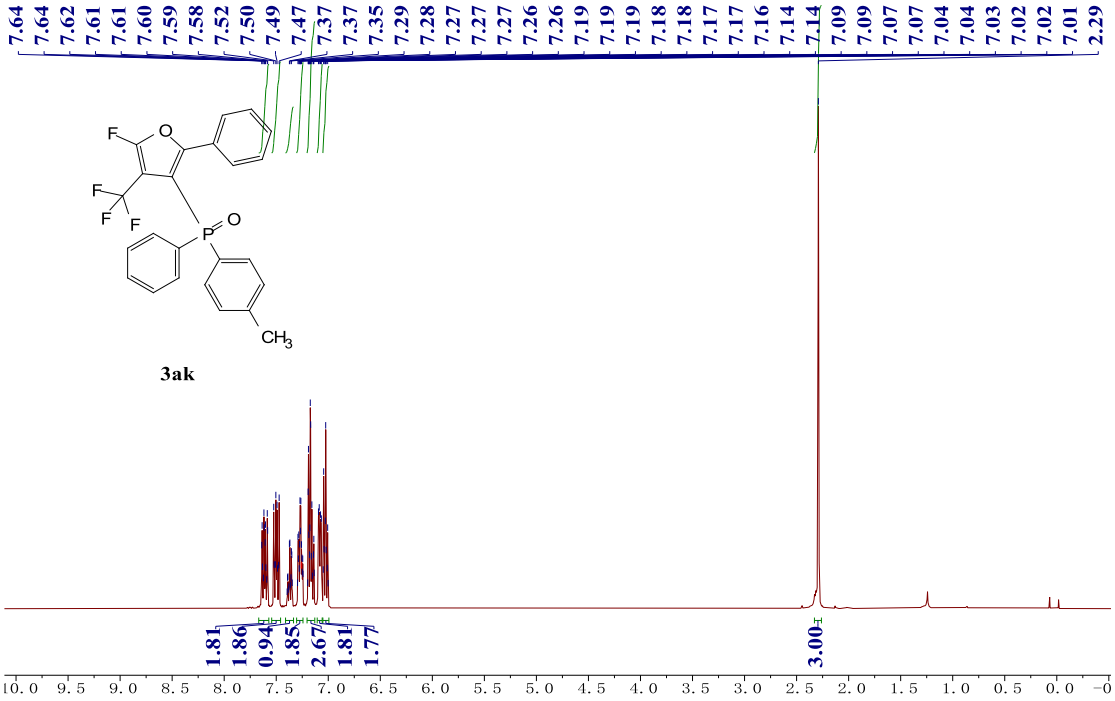
^{31}P NMR spectra of the product **3aj** (162 MHz, $CDCl_3$):



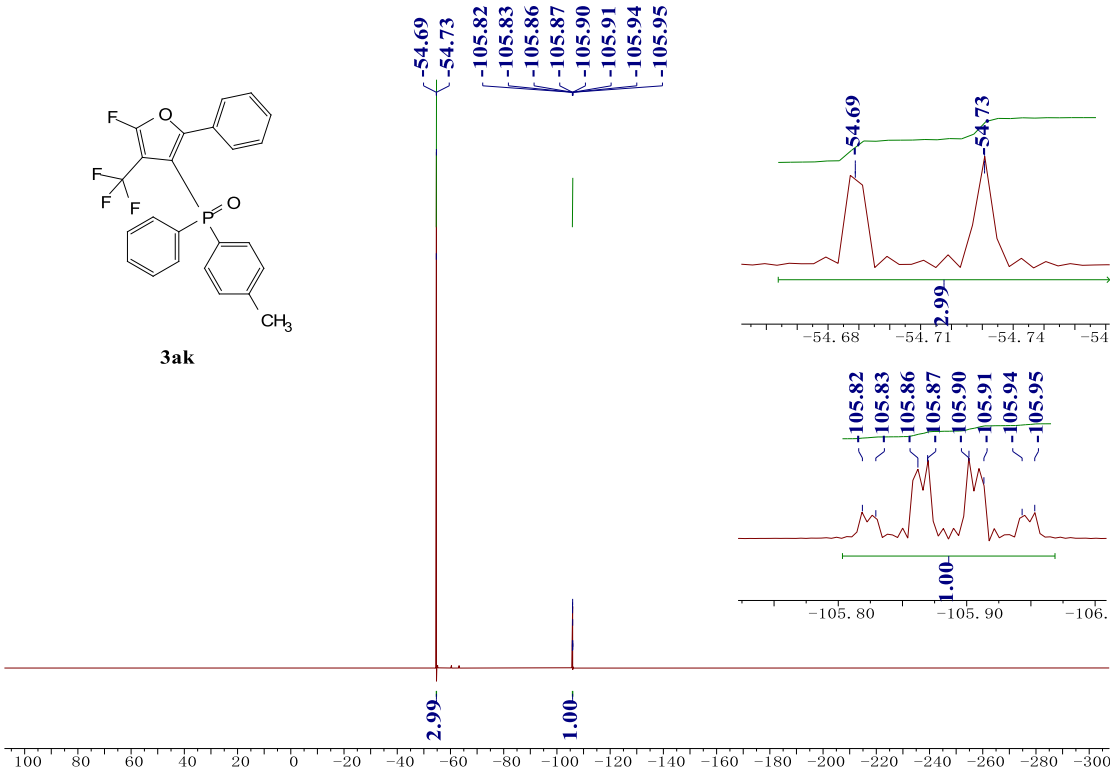
^{13}C NMR spectra of the product **3aj** (100 MHz, $CDCl_3$):



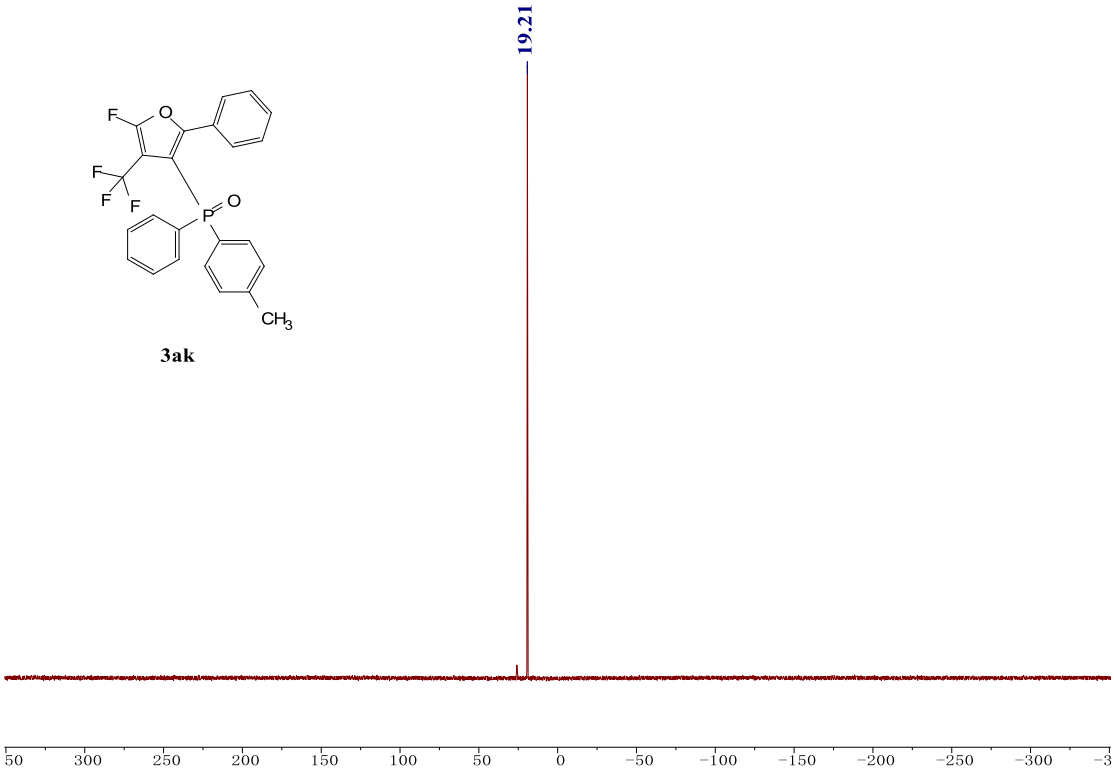
^{1}H NMR spectra of the product **3ak** (400 MHz, $CDCl_3$):



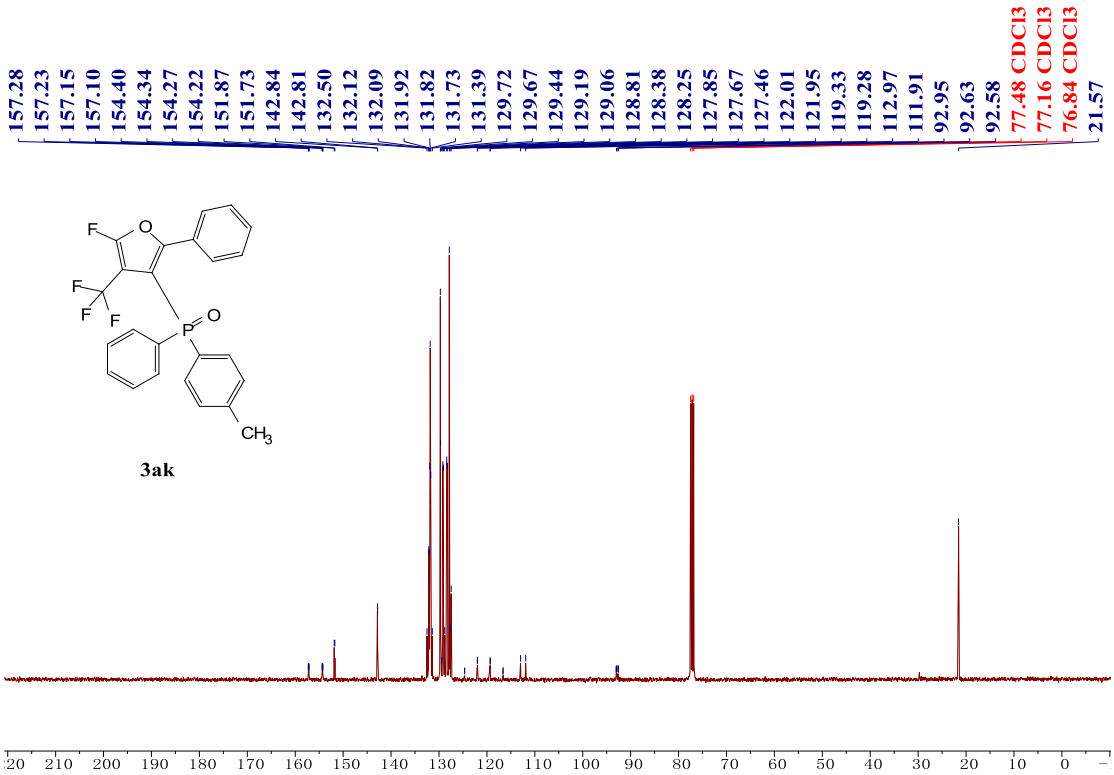
^{19}F NMR spectra of the product **3ak** (376 MHz, $CDCl_3$):



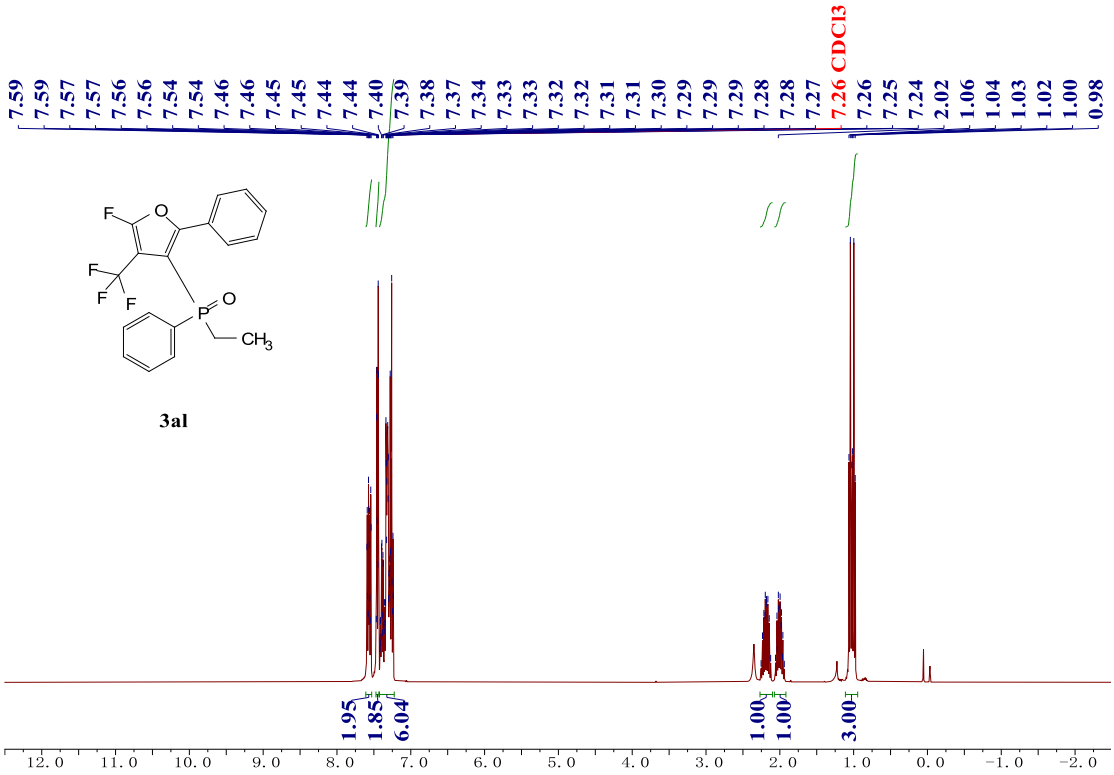
^{31}P NMR spectra of the product **3ak** (162 MHz, $CDCl_3$):



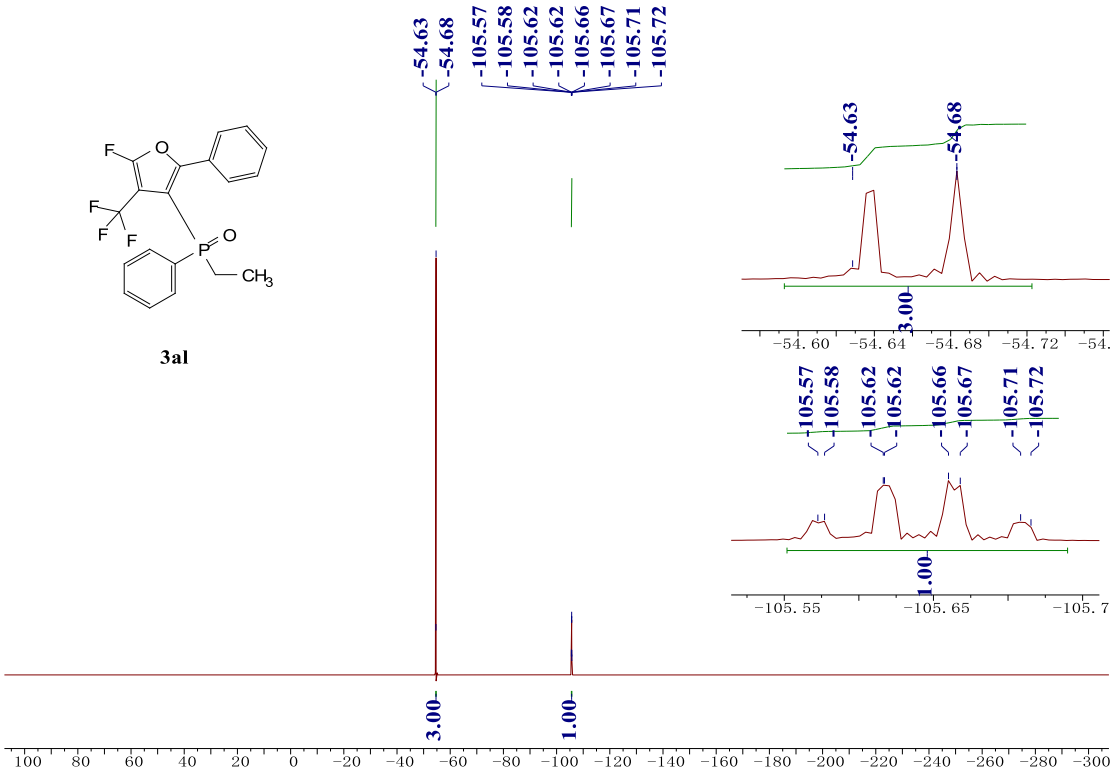
^{13}C NMR spectra of the product **3ak** (100 MHz, $CDCl_3$):



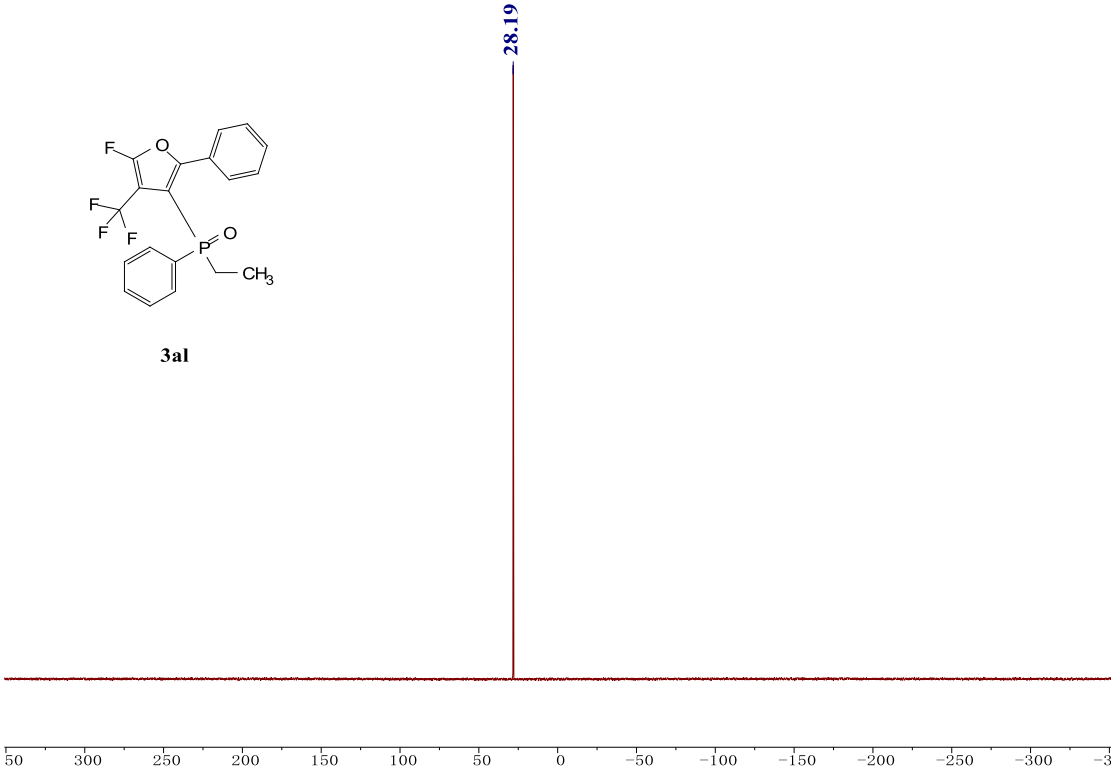
^{1}H NMR spectra of the product **3al** (400 MHz, $CDCl_3$):



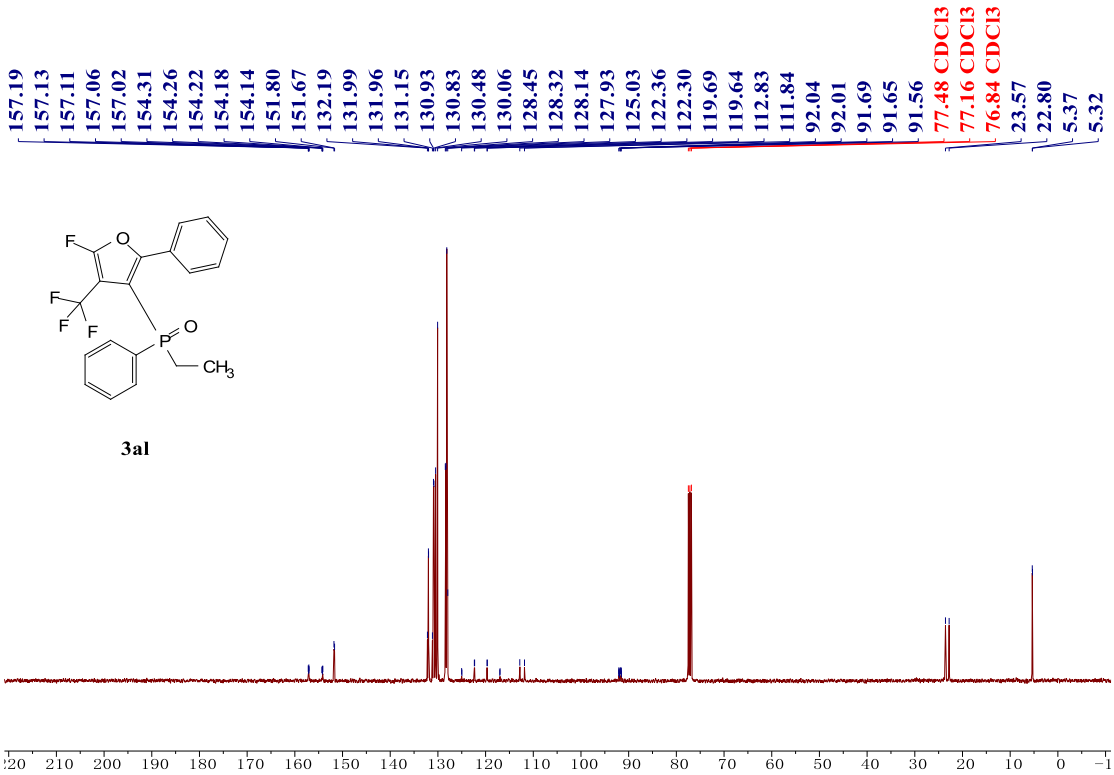
^{19}F NMR spectra of the product **3al** (376 MHz, $CDCl_3$):



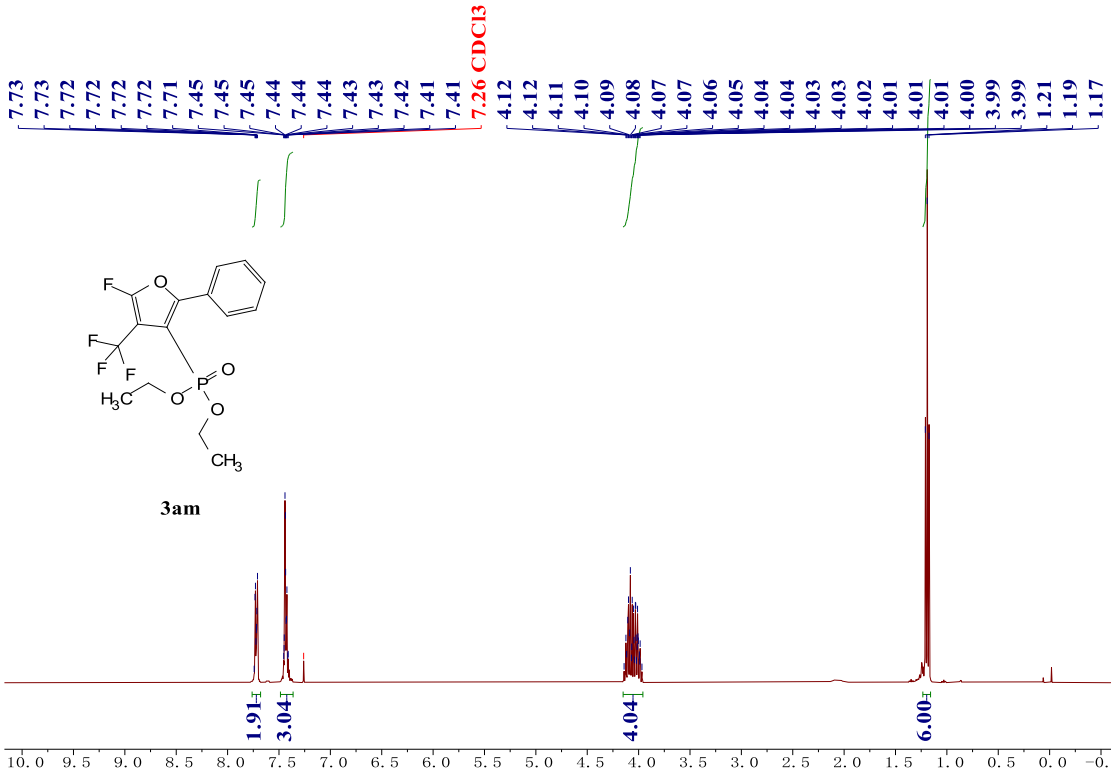
^{31}P NMR spectra of the product **3al** (162 MHz, $CDCl_3$):



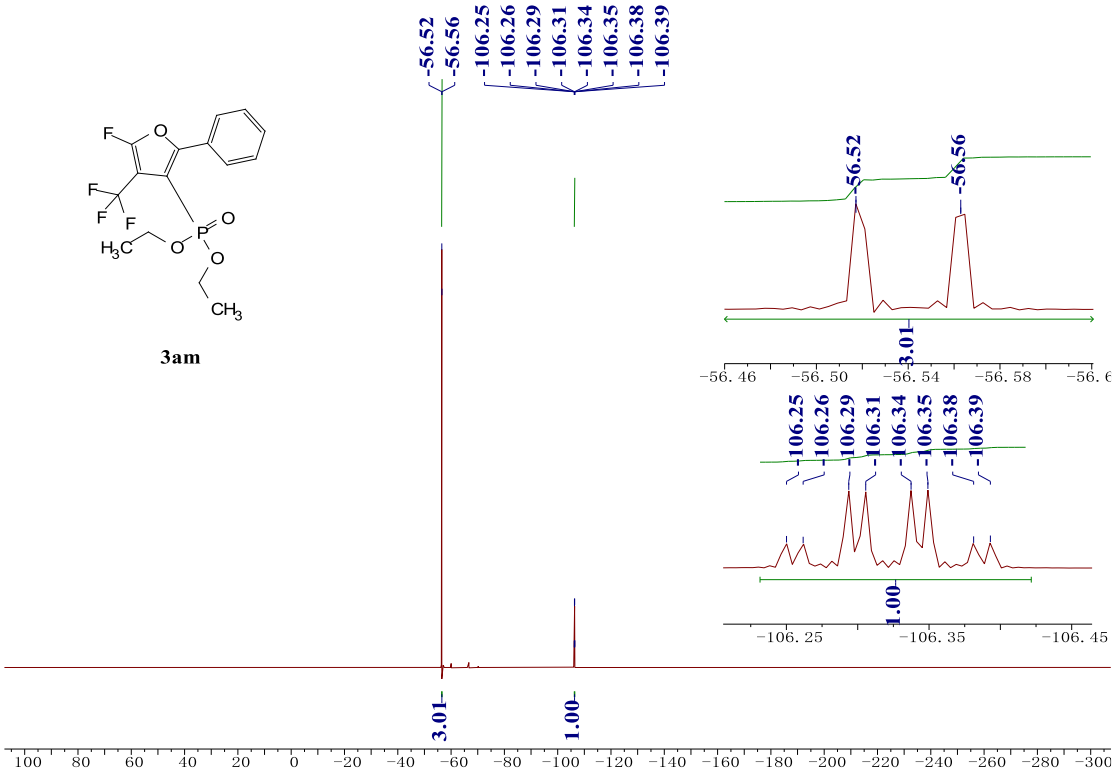
^{13}C NMR spectra of the product **3al** (100 MHz, $CDCl_3$):



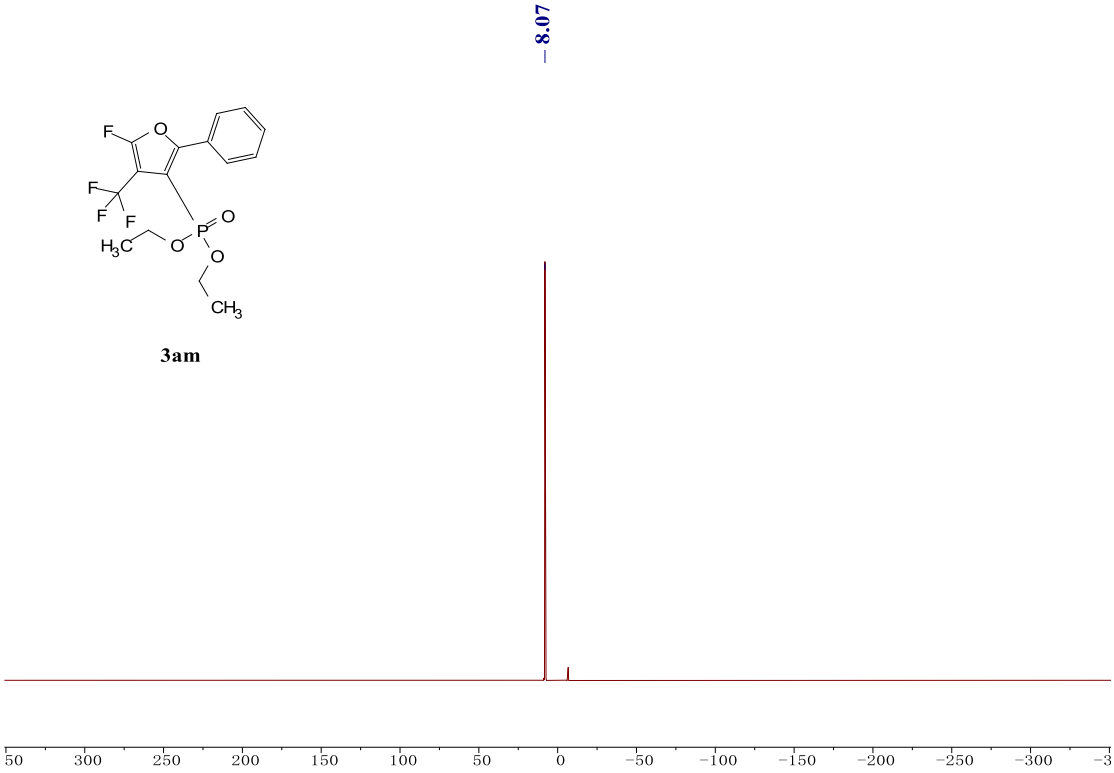
^{1}H NMR spectra of the product **3am** (400 MHz, $CDCl_3$):



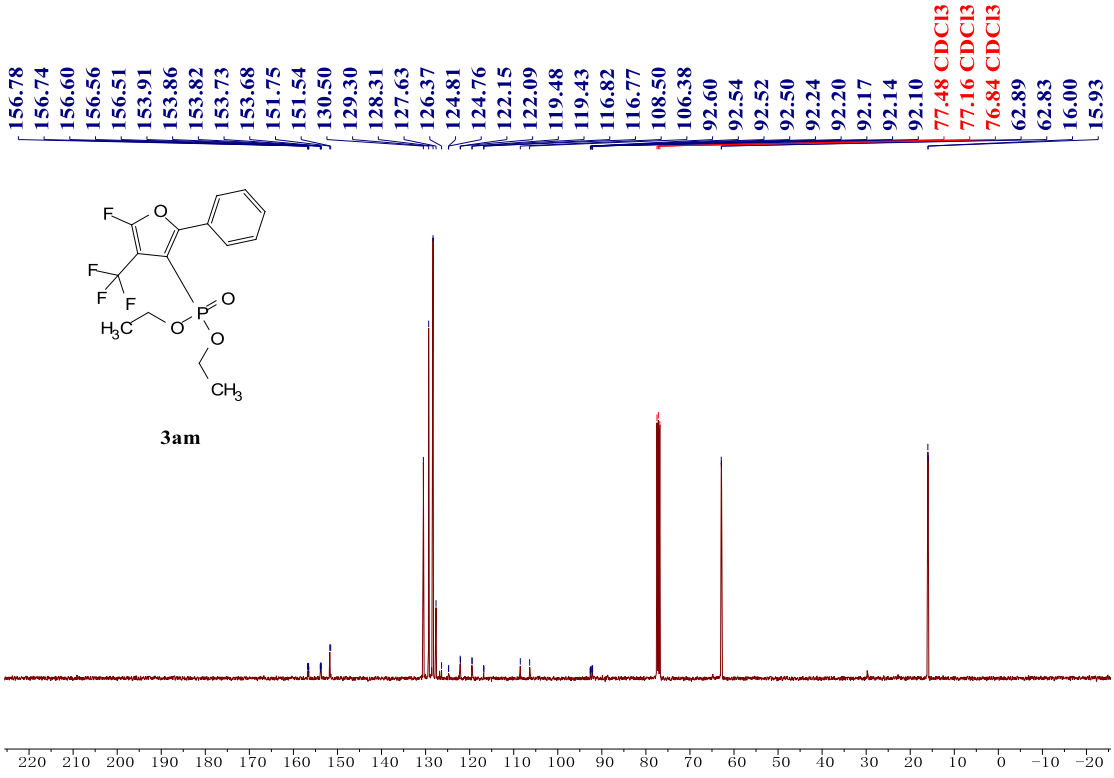
^{19}F NMR spectra of the product **3am** (376 MHz, $CDCl_3$):



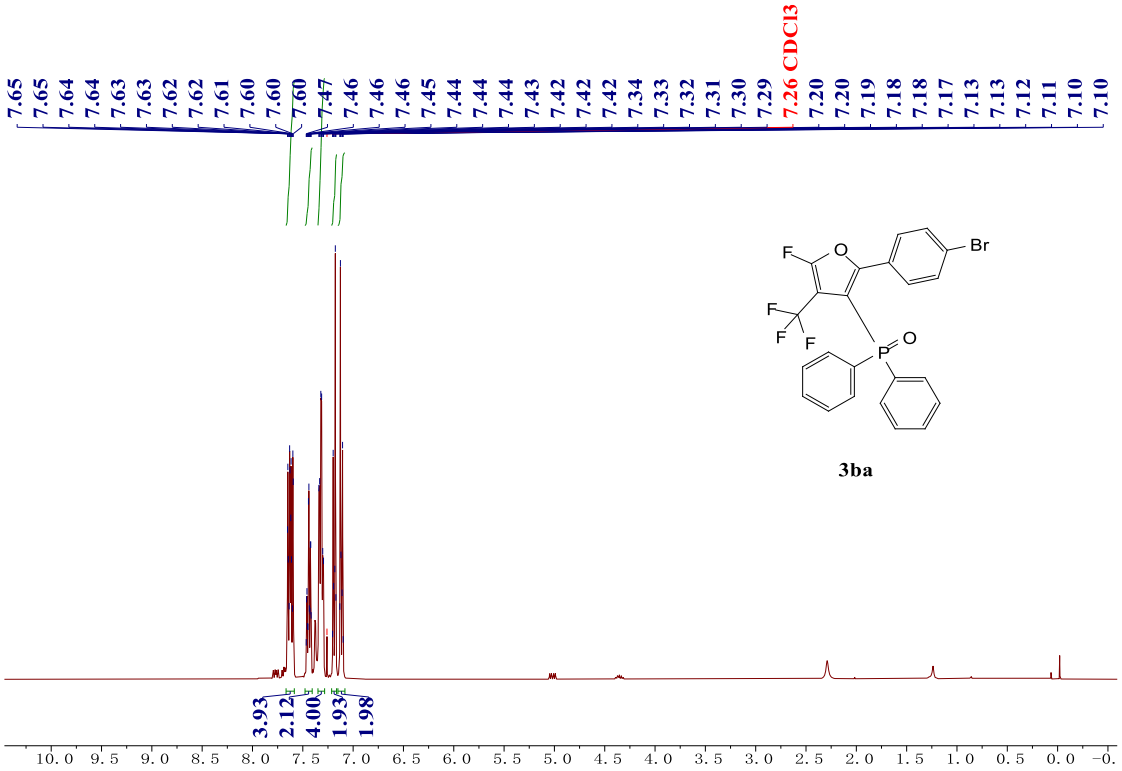
^{31}P NMR spectra of the product **3am** (162 MHz, $CDCl_3$):



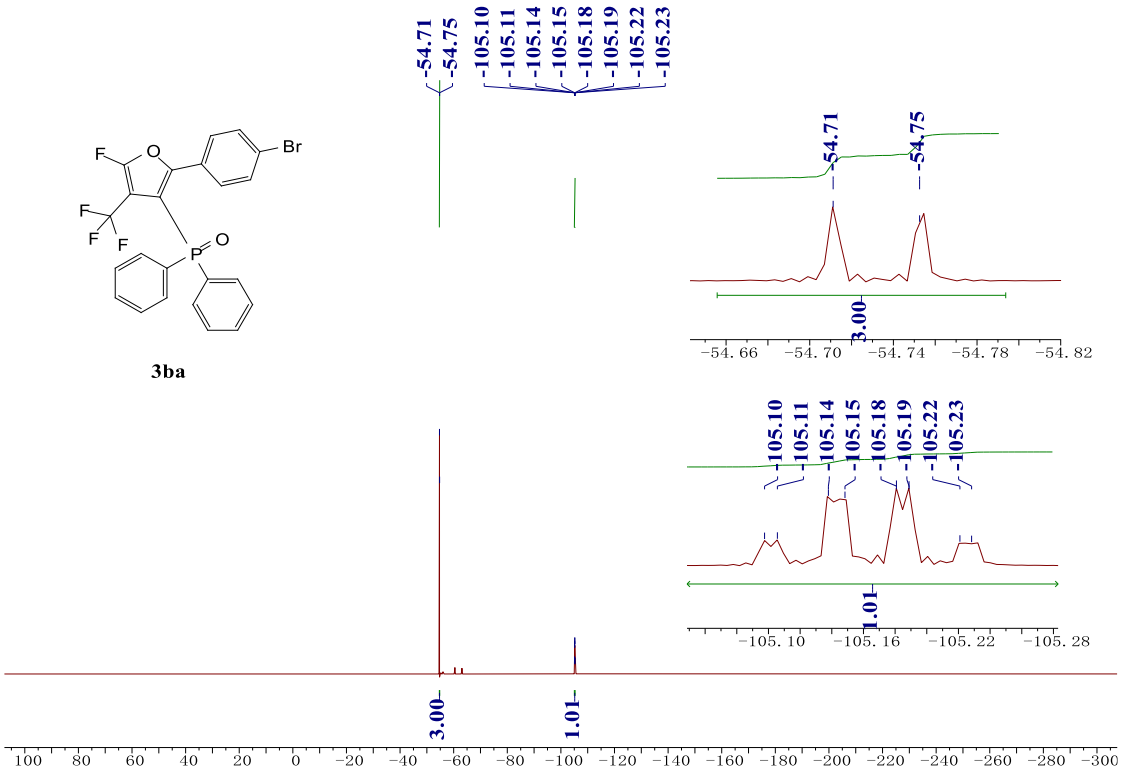
^{13}C NMR spectra of the product **3am** (100 MHz, $CDCl_3$):



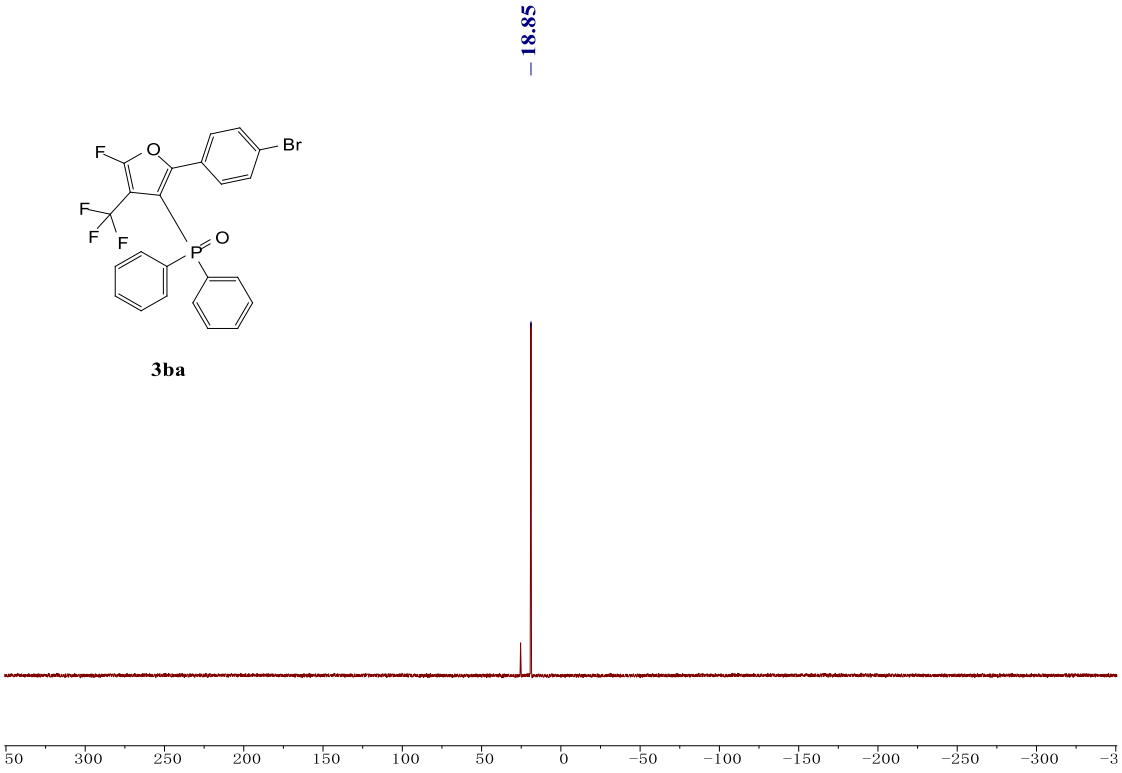
^{1}H NMR spectra of the product **3ba** (400 MHz, $CDCl_3$):



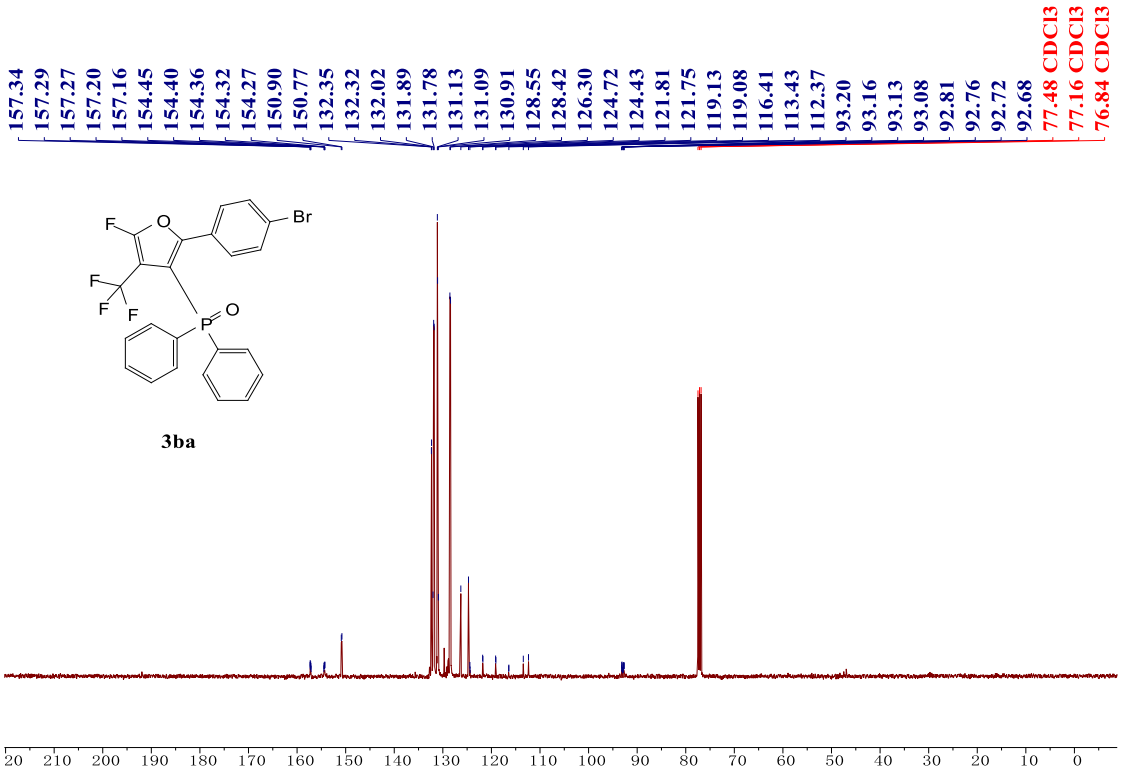
^{19}F NMR spectra of the product **3ba** (376 MHz, $CDCl_3$):



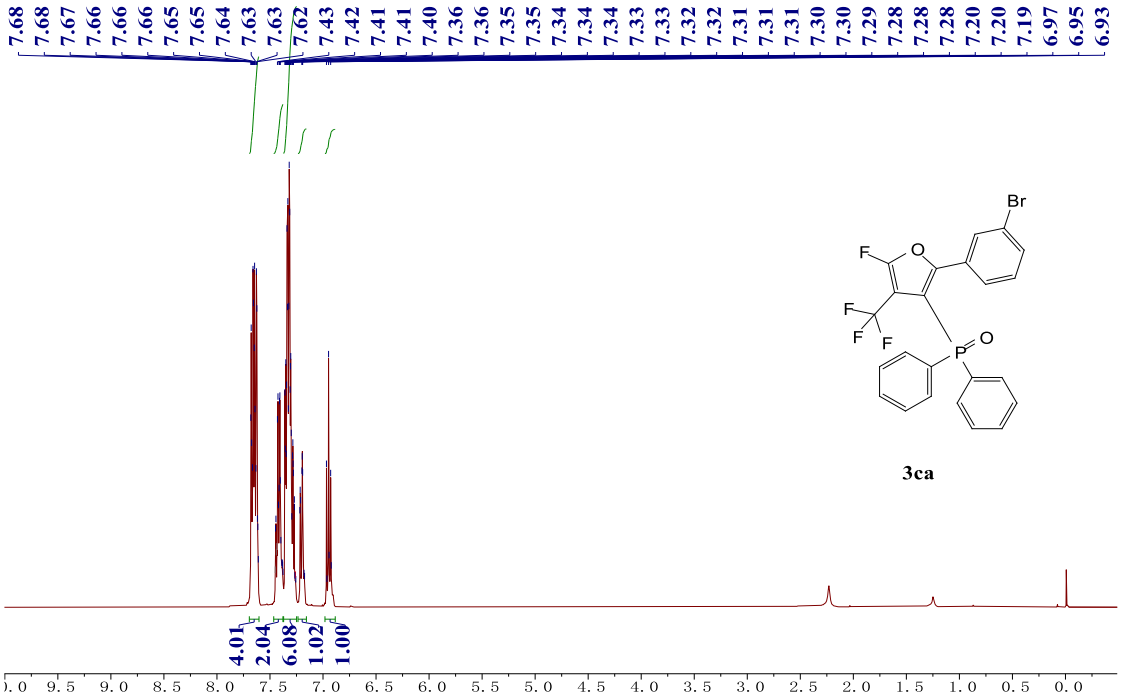
^{31}P NMR spectra of the product **3ba** (162 MHz, $CDCl_3$):



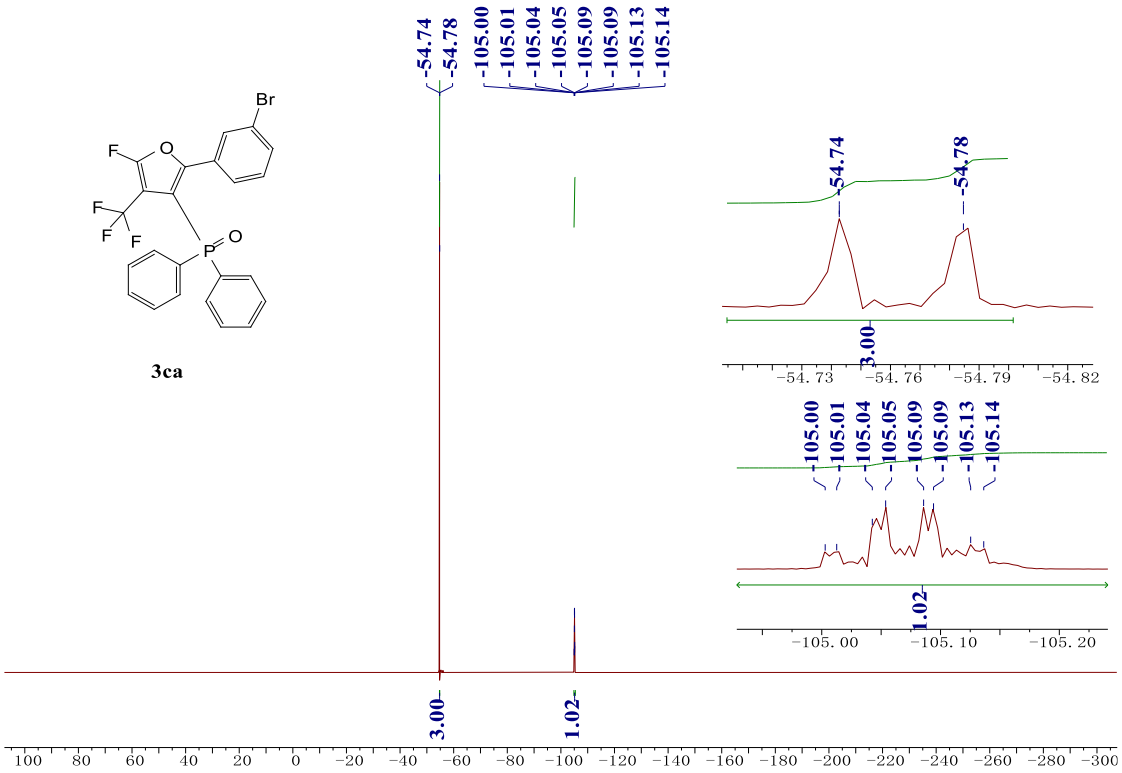
^{13}C NMR spectra of the product **3ba** (100 MHz, $CDCl_3$):



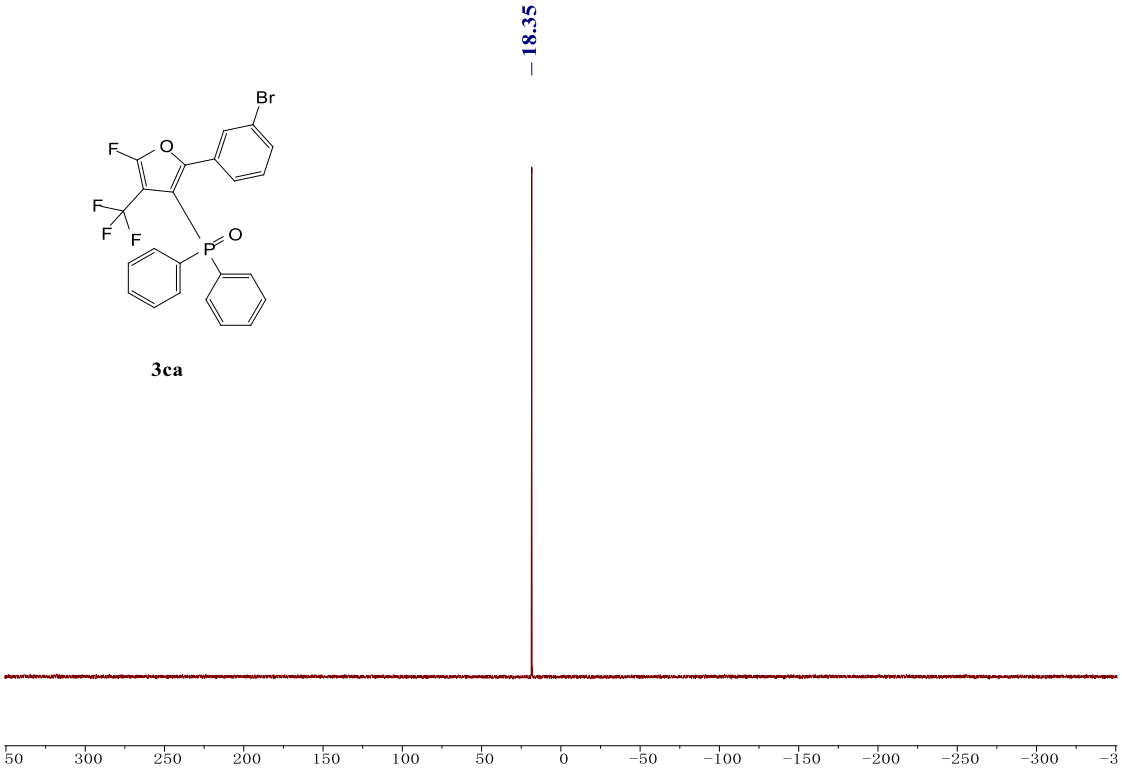
^{1}H NMR spectra of the product **3ca** (400 MHz, $CDCl_3$):



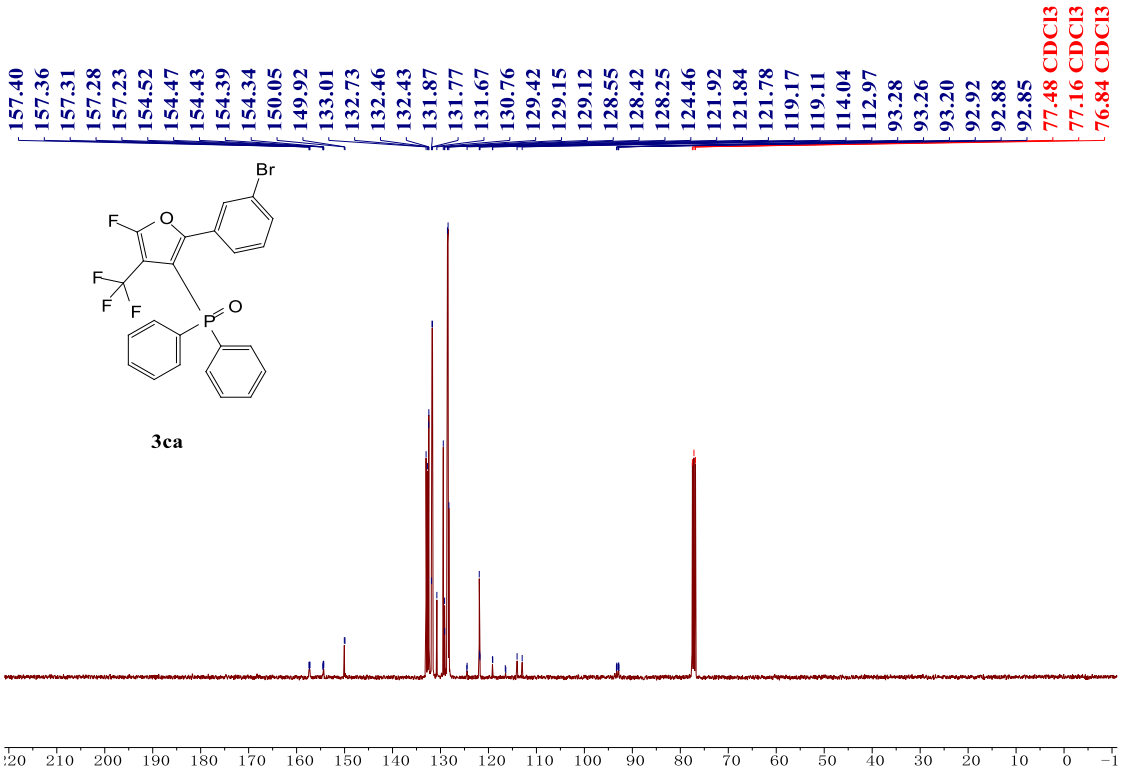
^{19}F NMR spectra of the product **3ca** (376 MHz, $CDCl_3$):



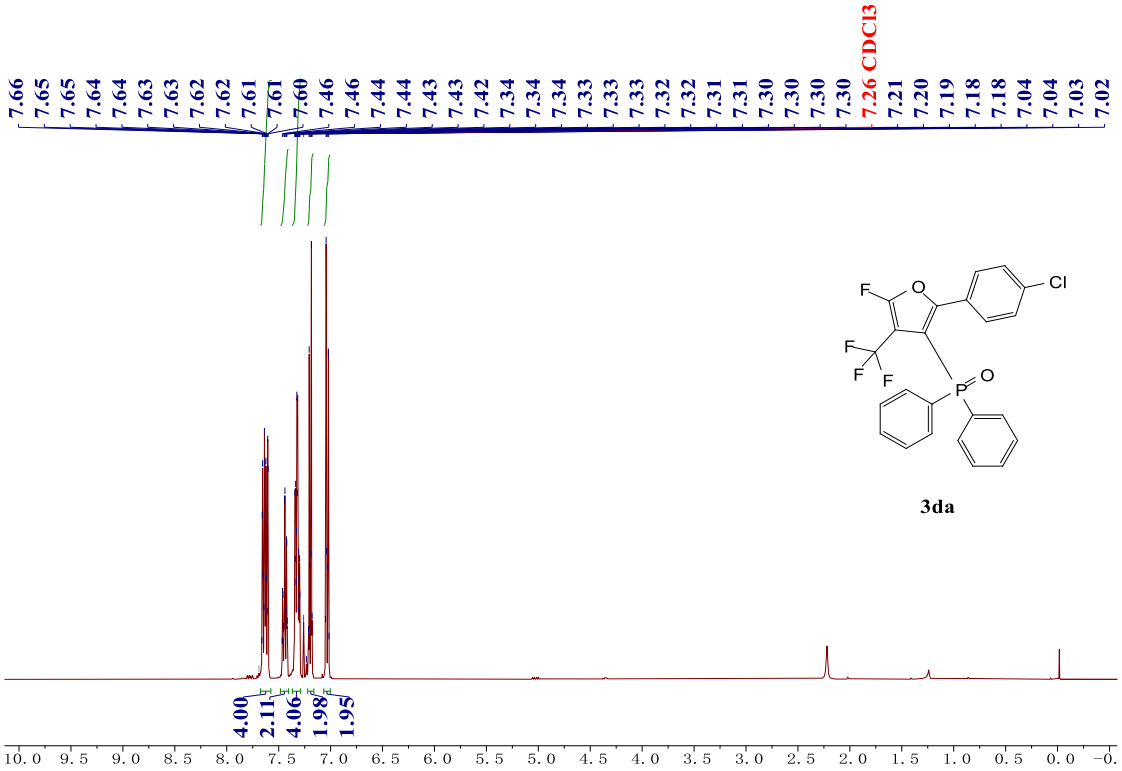
^{31}P NMR spectra of the product **3ca** (162 MHz, $CDCl_3$):



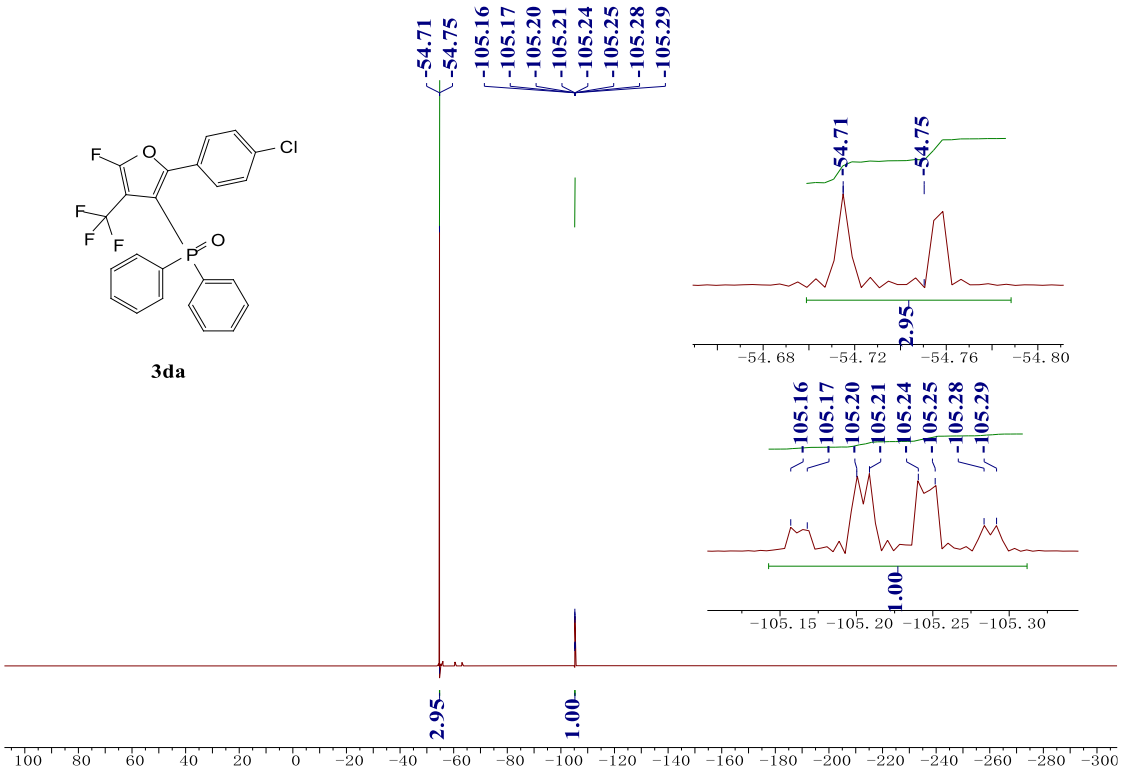
^{13}C NMR spectra of the product **3ca** (100 MHz, $CDCl_3$):



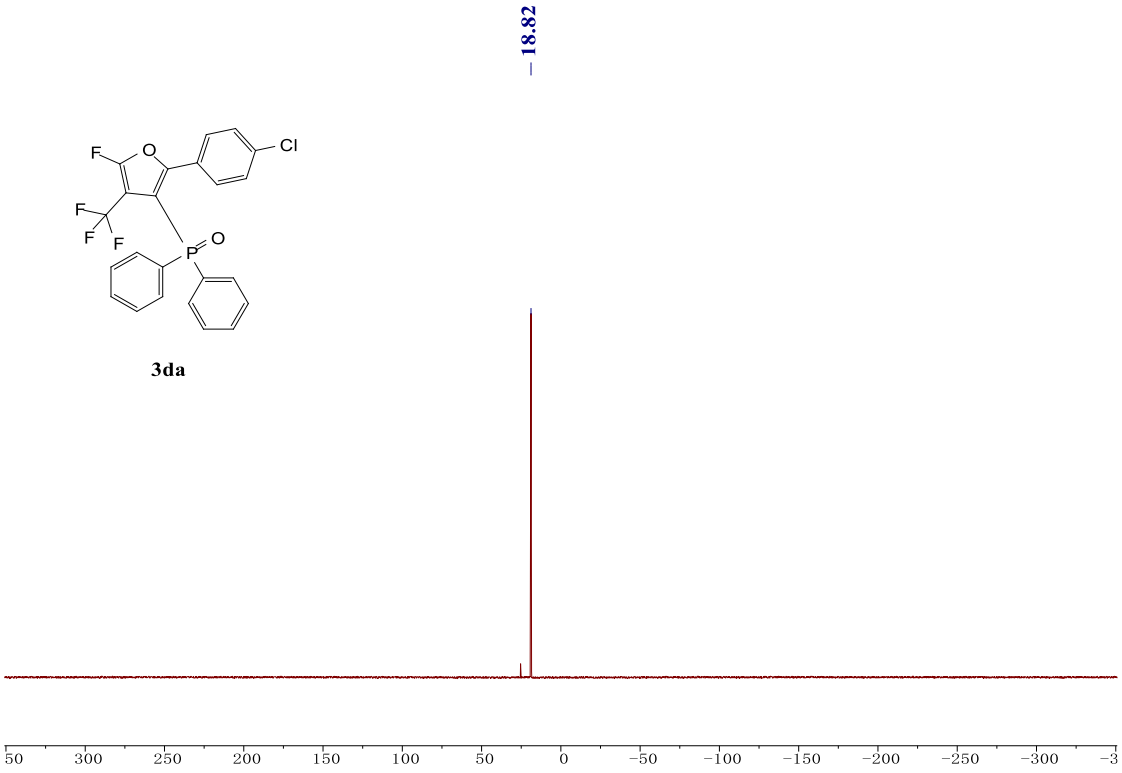
^{1}H NMR spectra of the product **3da** (400 MHz, $CDCl_3$):



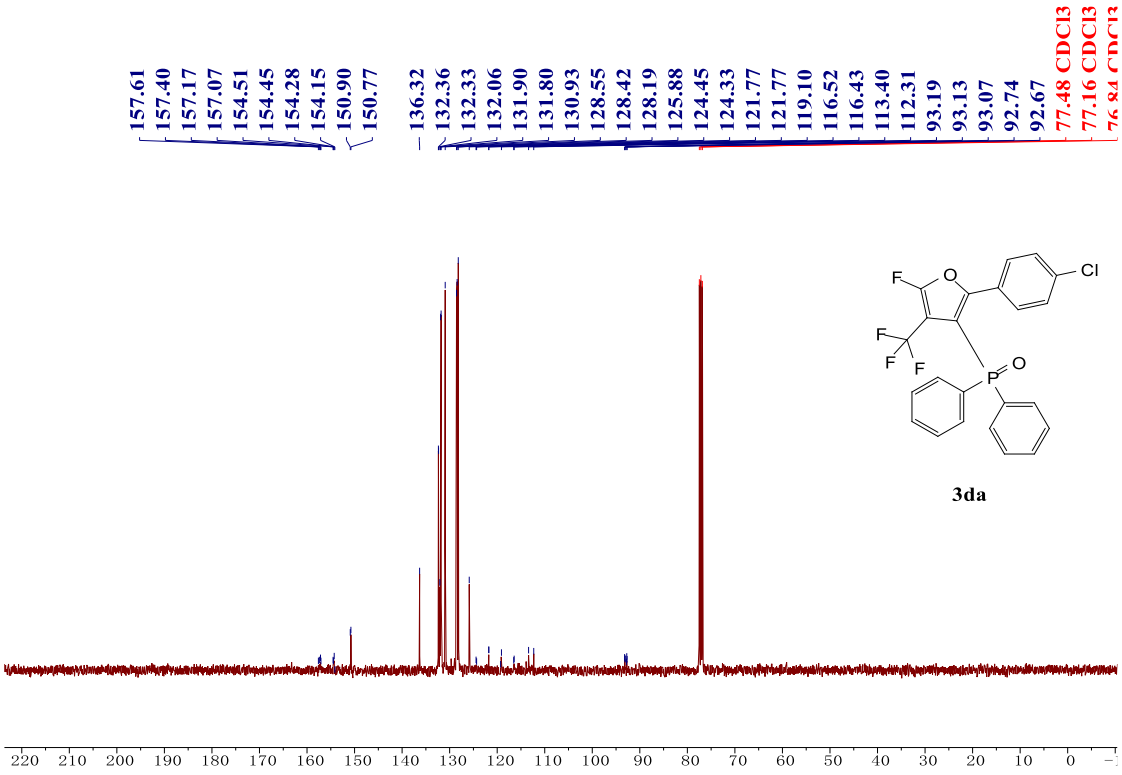
^{19}F NMR spectra of the product **3da** (376 MHz, $CDCl_3$):



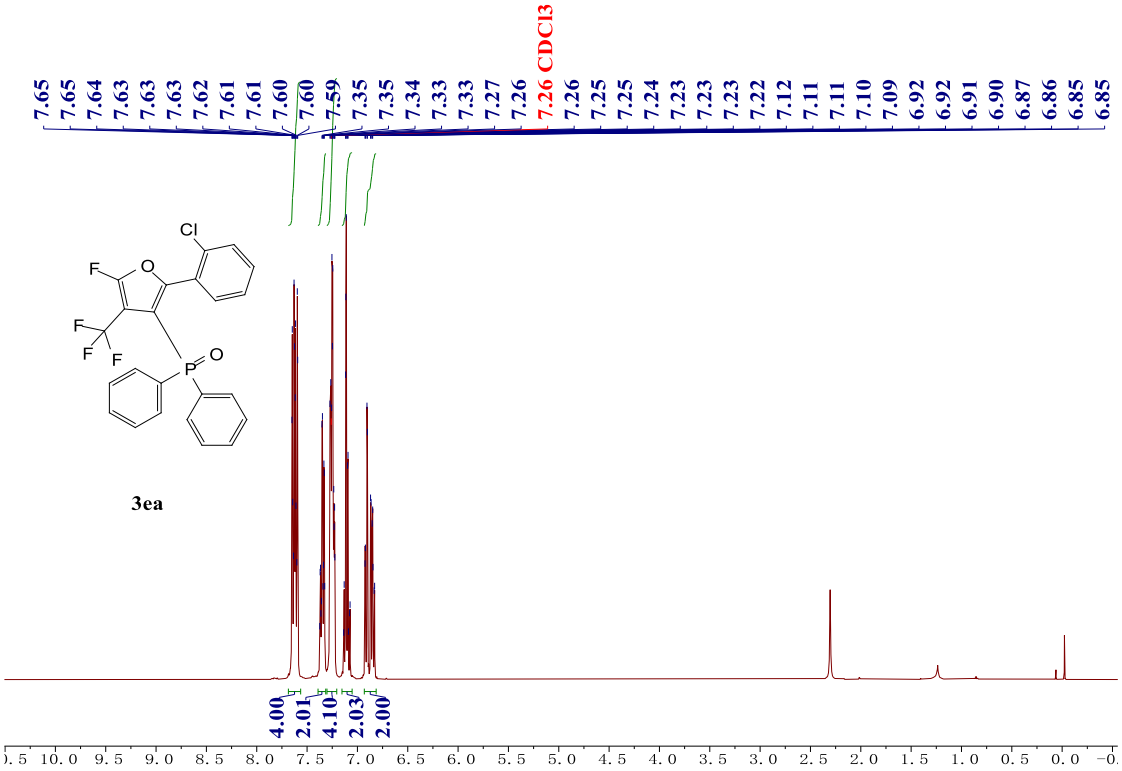
^{31}P NMR spectra of the product **3da** (162 MHz, $CDCl_3$):



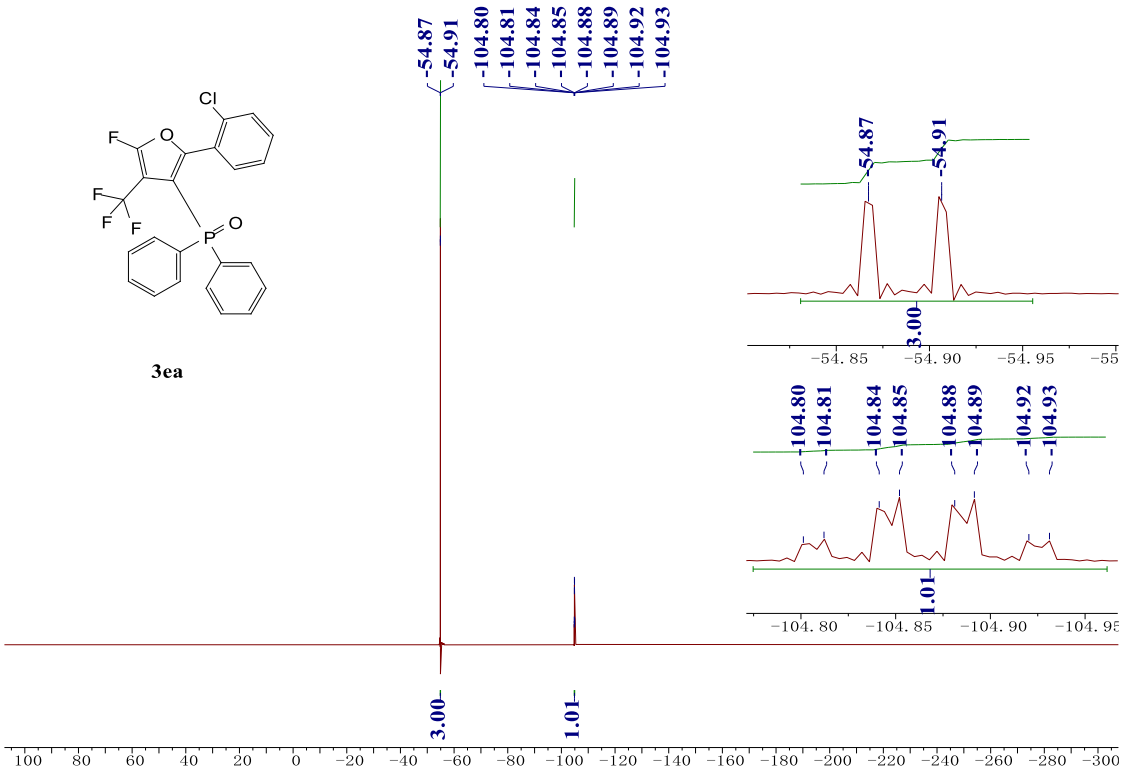
^{13}C NMR spectra of the product **3da** (100 MHz, $CDCl_3$):



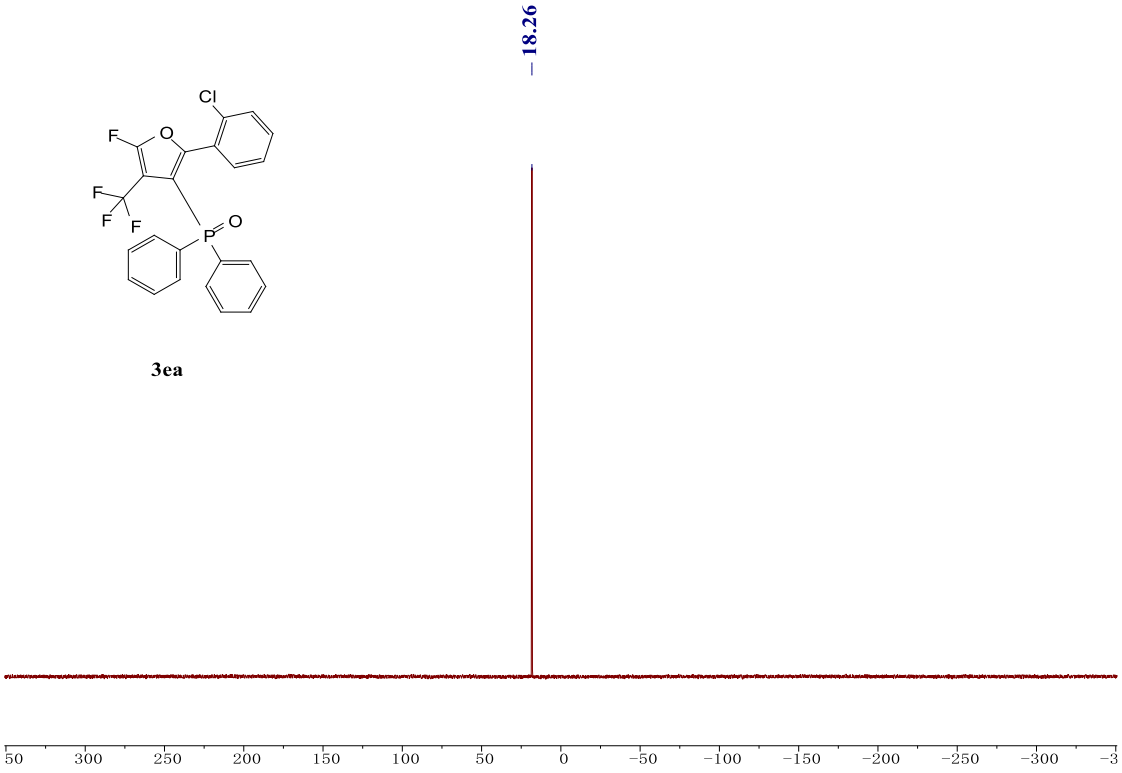
^{1}H NMR spectra of the product **3ea** (400 MHz, $CDCl_3$):



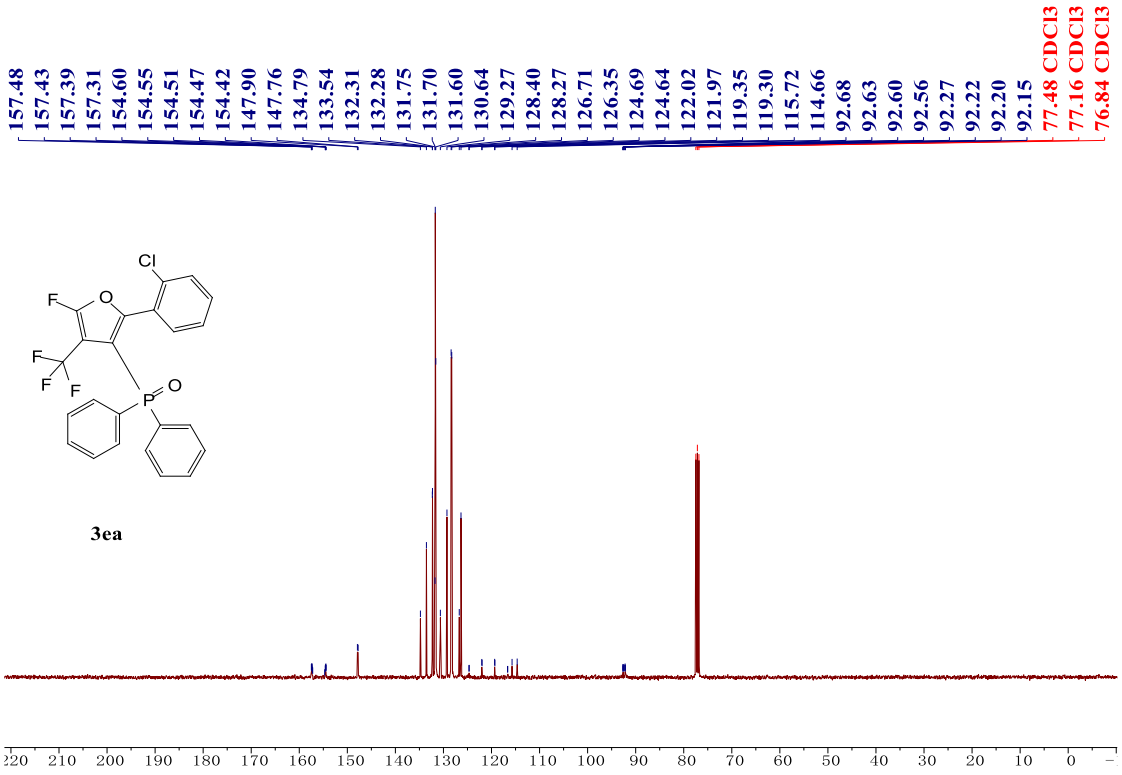
^{19}F NMR spectra of the product **3ea** (376 MHz, $CDCl_3$):



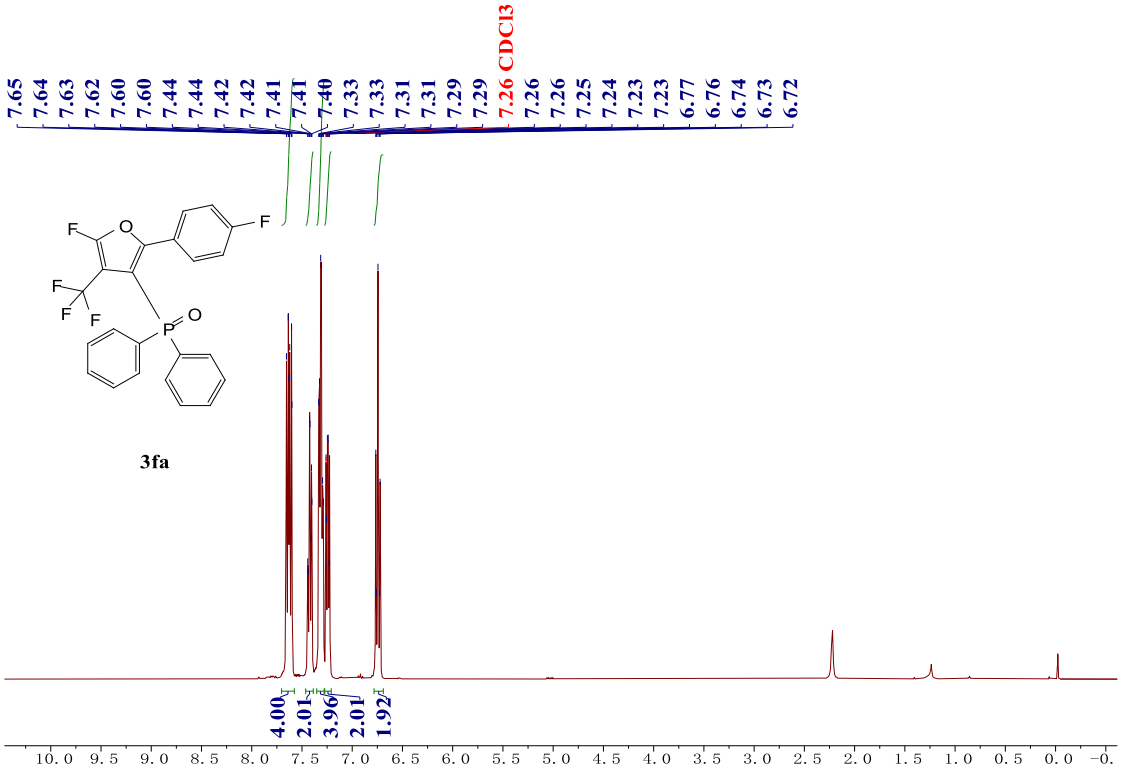
^{31}P NMR spectra of the product **3ea** (162 MHz, $CDCl_3$):



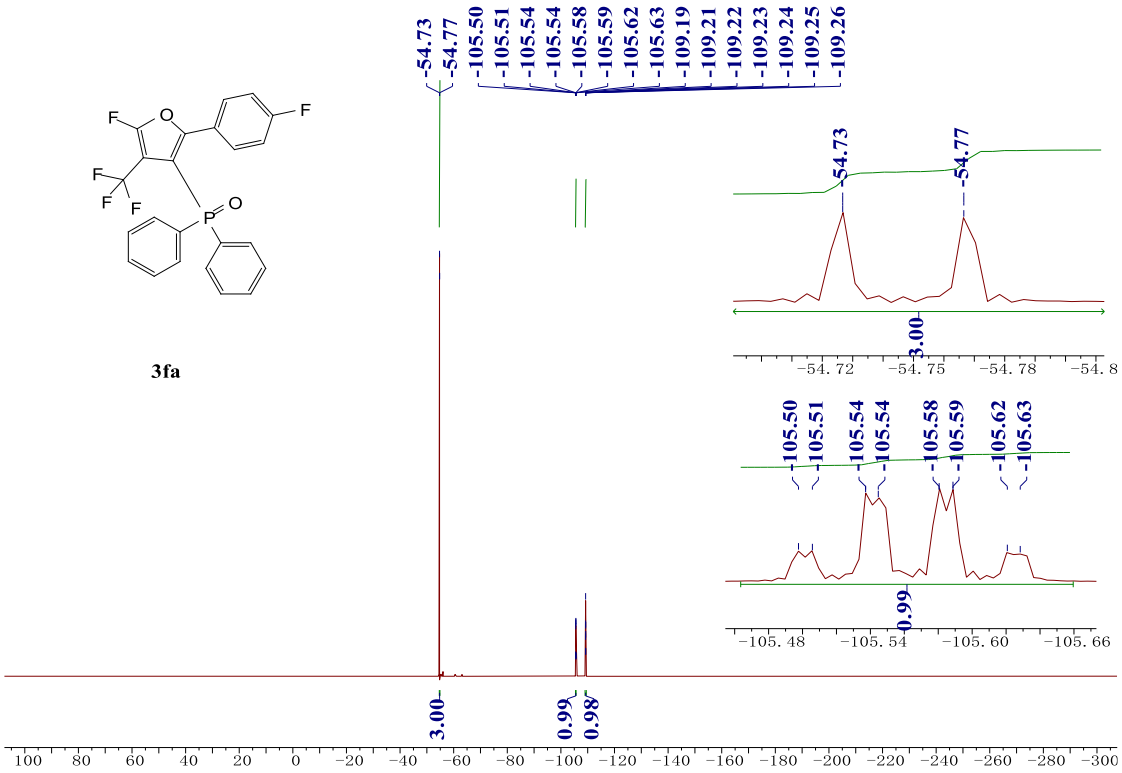
^{13}C NMR spectra of the product **3ea** (100 MHz, $CDCl_3$):



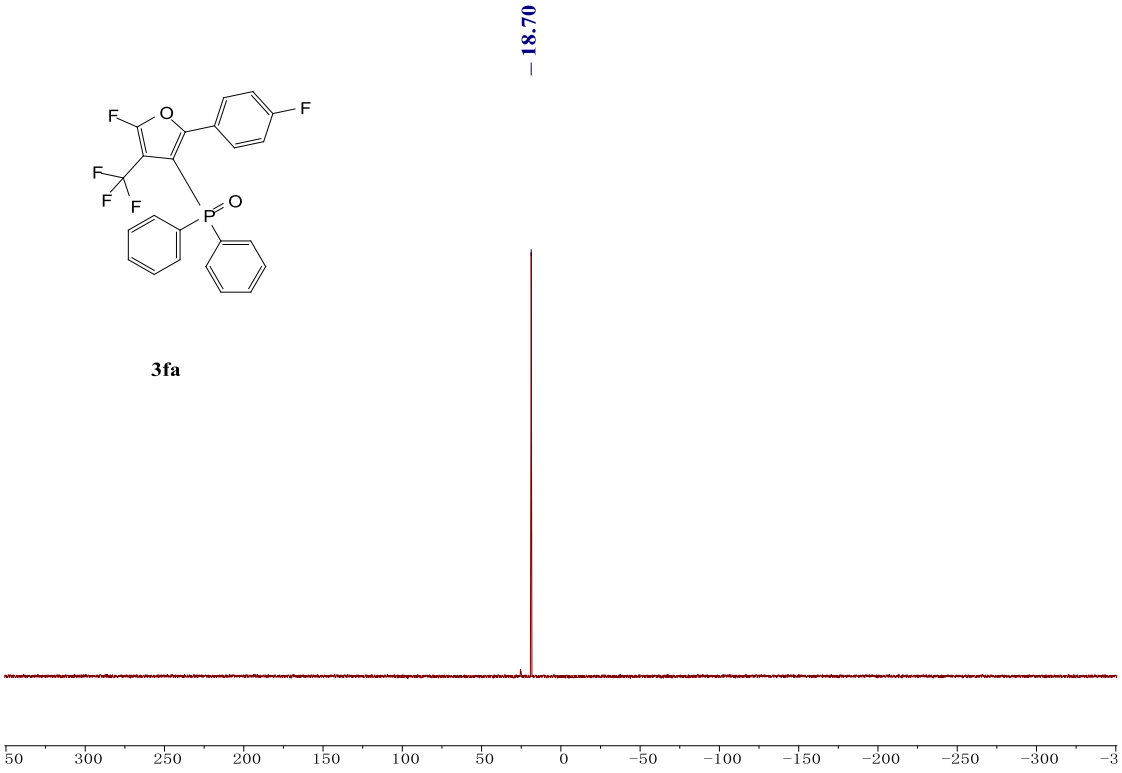
^{1}H NMR spectra of the product **3fa** (400 MHz, $CDCl_3$):



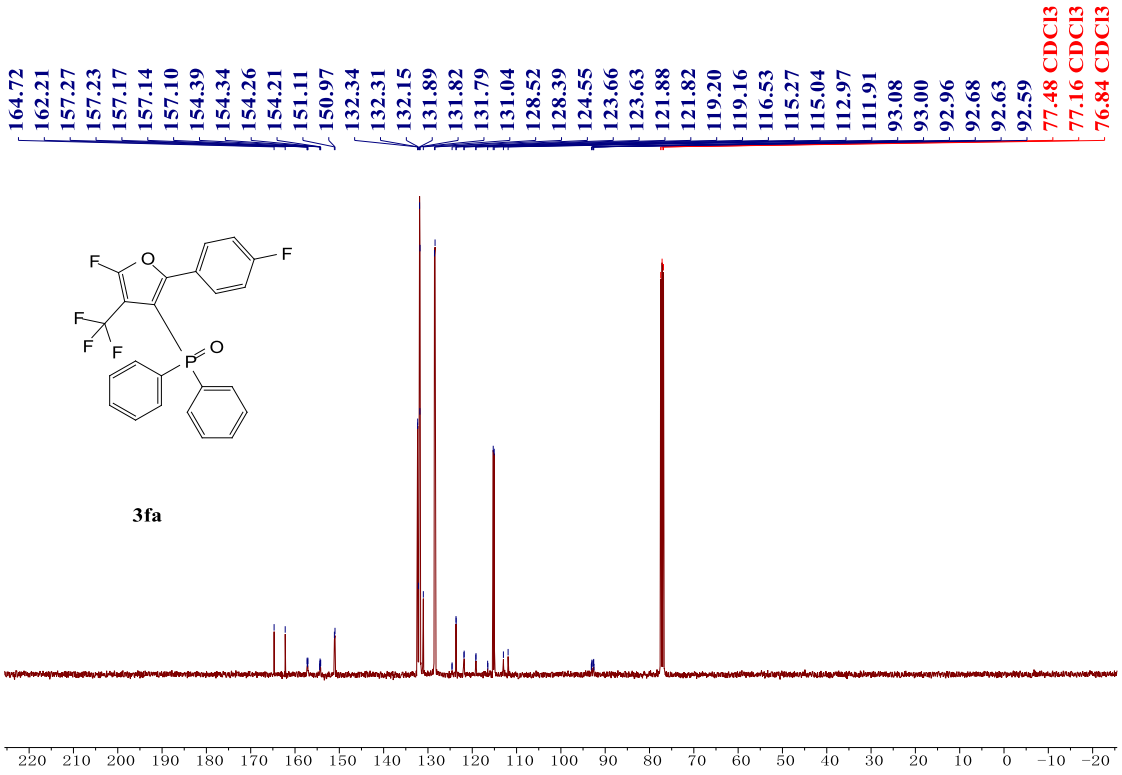
^{19}F NMR spectra of the product **3fa** (376 MHz, $CDCl_3$):



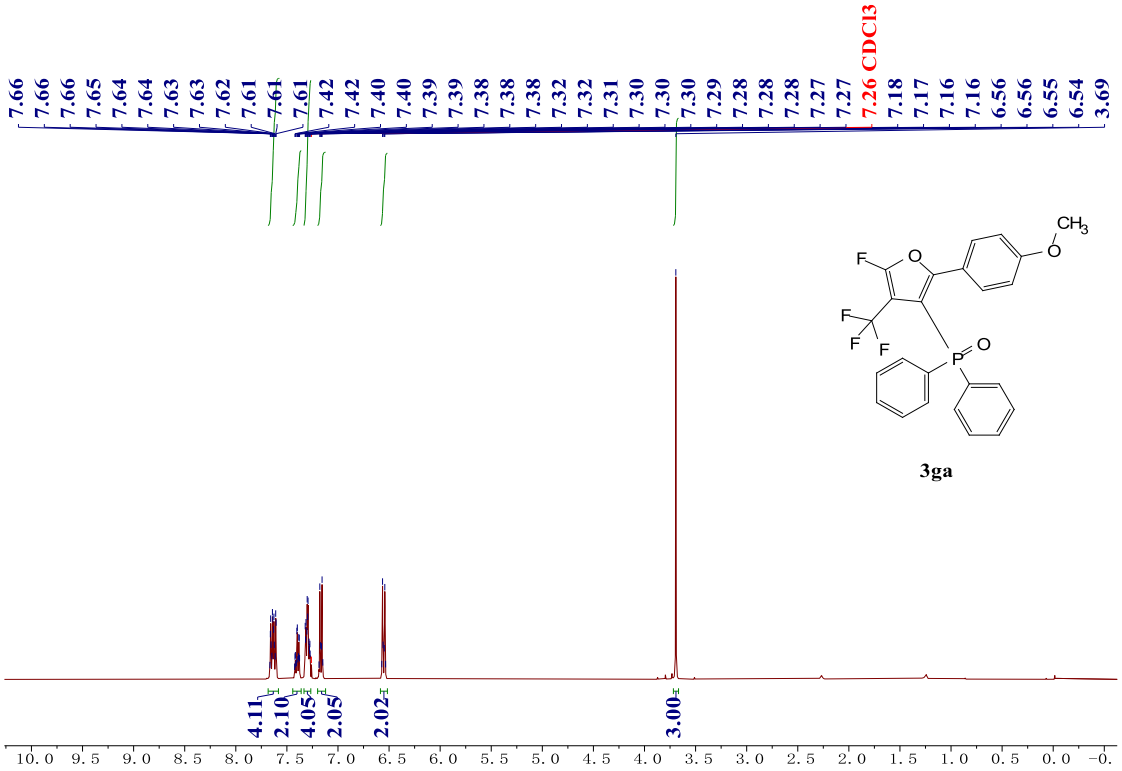
^{31}P NMR spectra of the product **3fa** (162 MHz, $CDCl_3$):



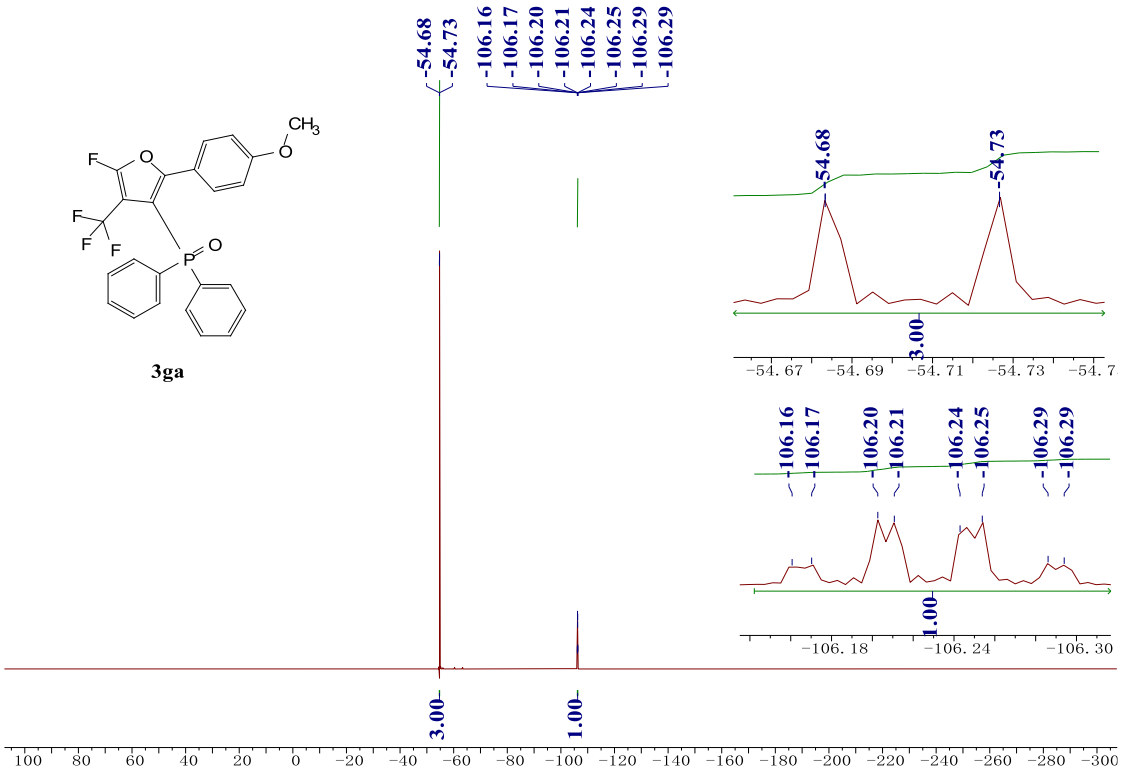
^{13}C NMR spectra of the product **3fa** (100 MHz, $CDCl_3$):



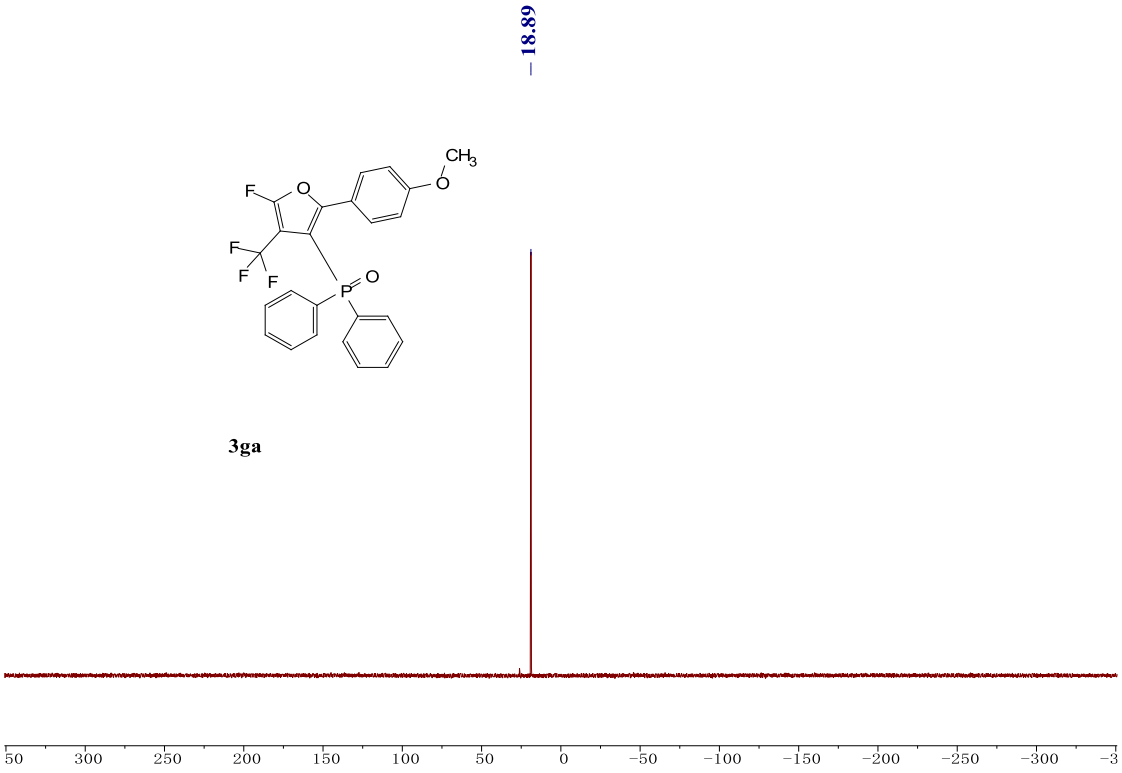
^{1}H NMR spectra of the product **3ga** (400 MHz, $CDCl_3$):



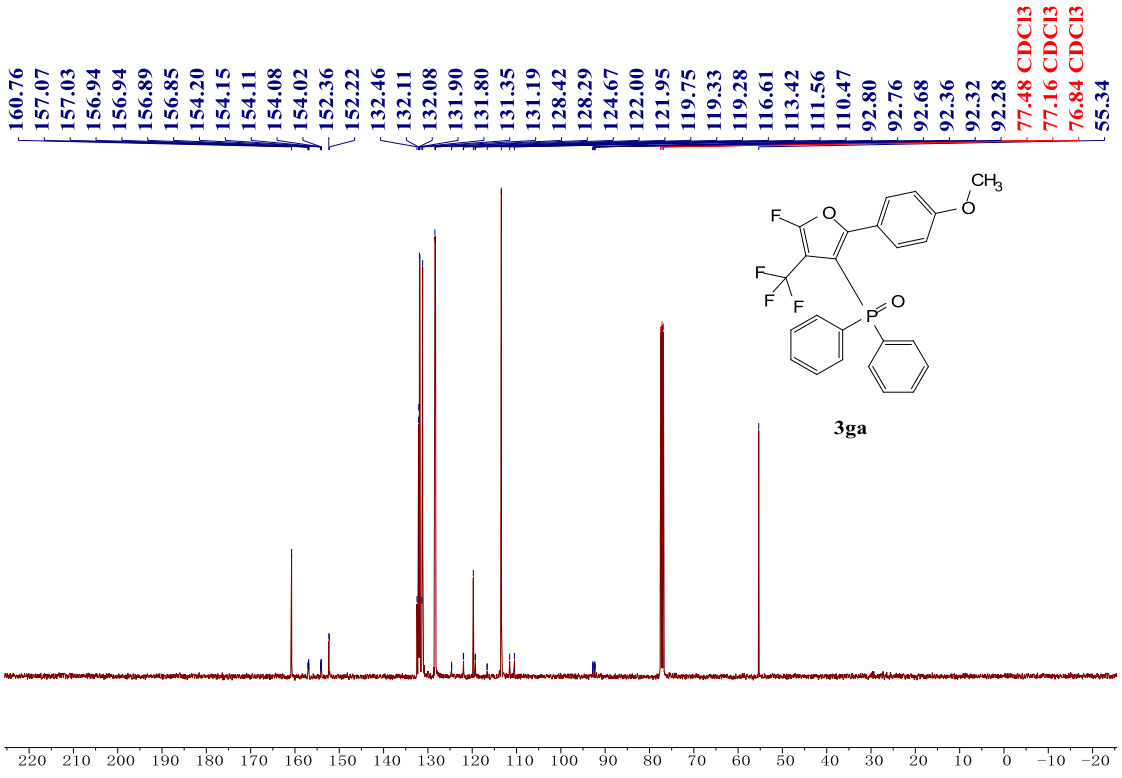
^{19}F NMR spectra of the product **3ga** (376 MHz, $CDCl_3$):



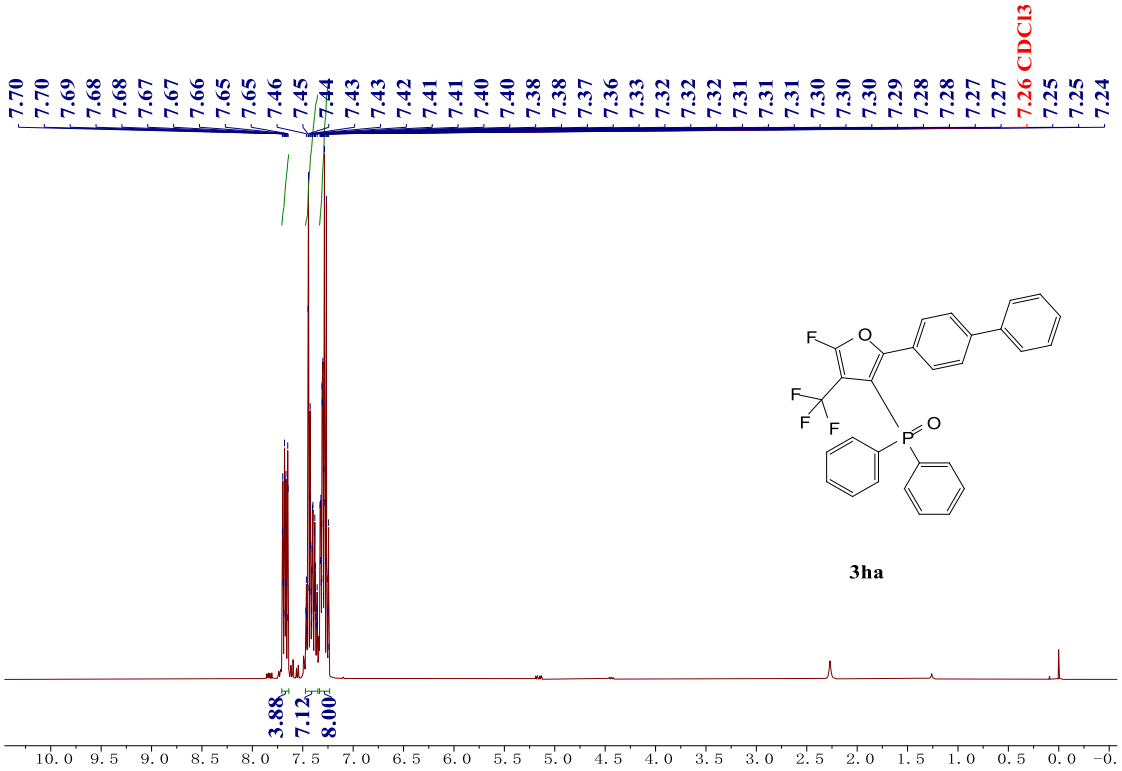
^{31}P NMR spectra of the product **3ga** (162 MHz, $CDCl_3$):



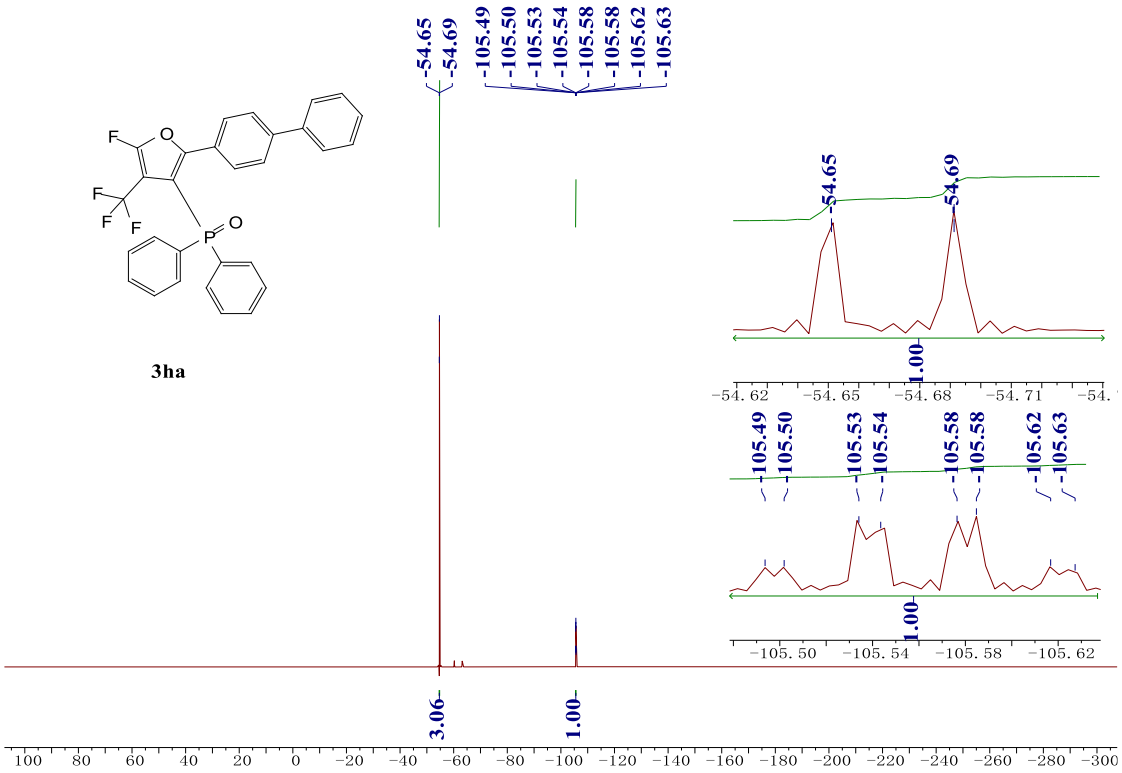
^{13}C NMR spectra of the product **3ga** (100 MHz, $CDCl_3$):



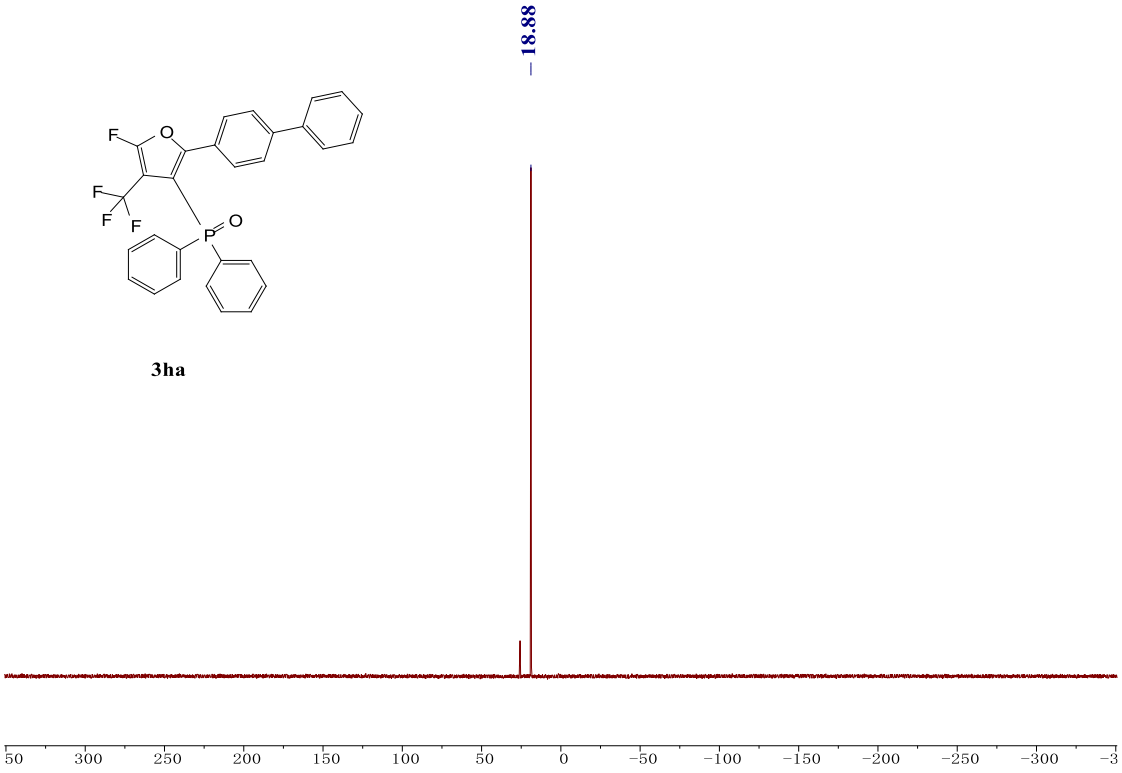
^{1}H NMR spectra of the product **3ha** (400 MHz, $CDCl_3$):



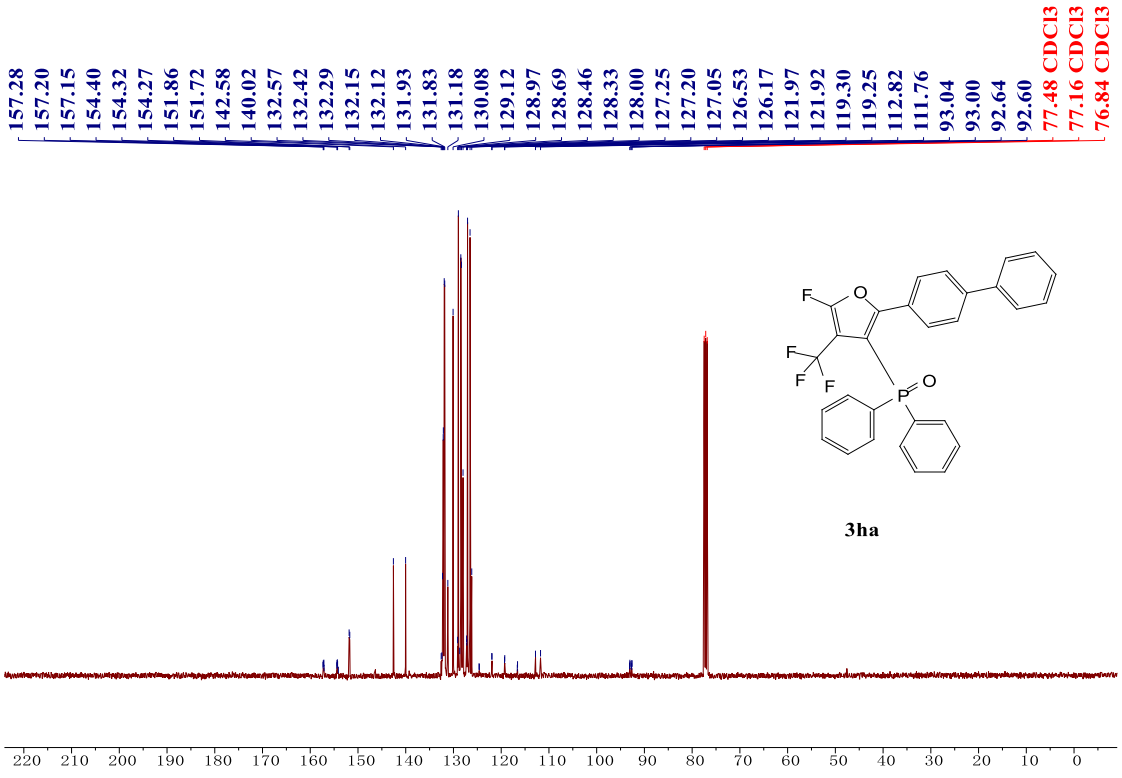
^{19}F NMR spectra of the product **3ha** (376 MHz, $CDCl_3$):



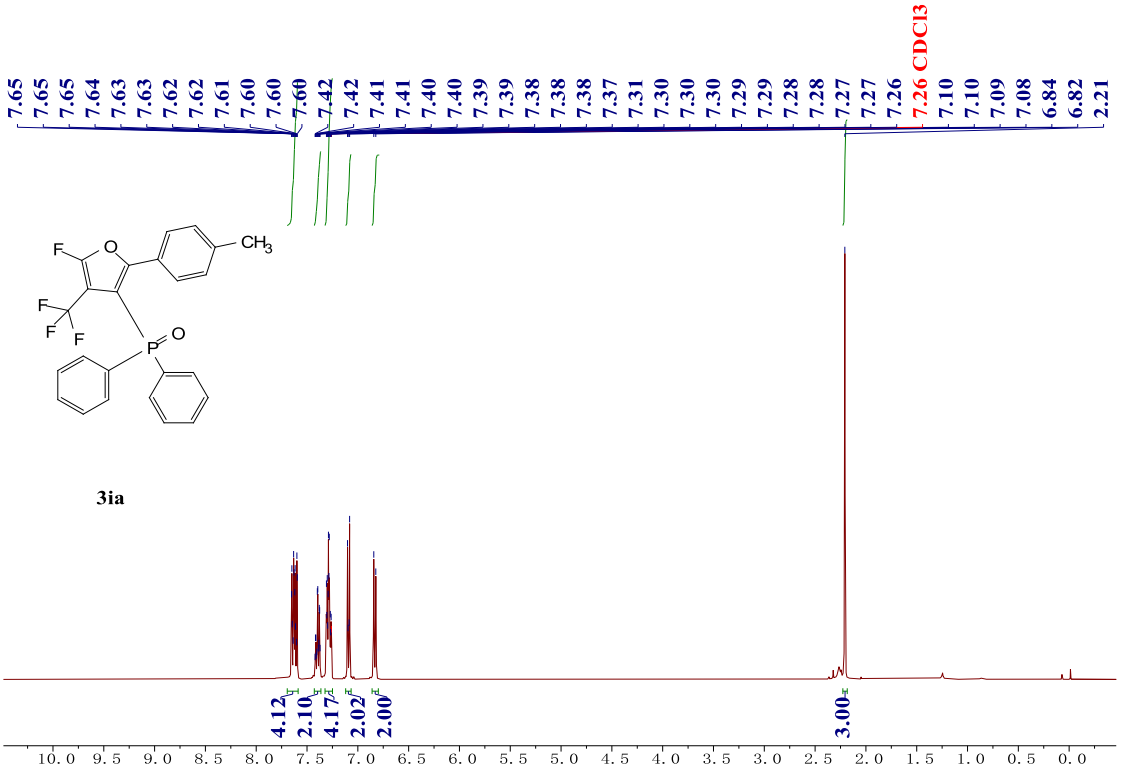
^{31}P NMR spectra of the product **3ha** (162 MHz, $CDCl_3$):



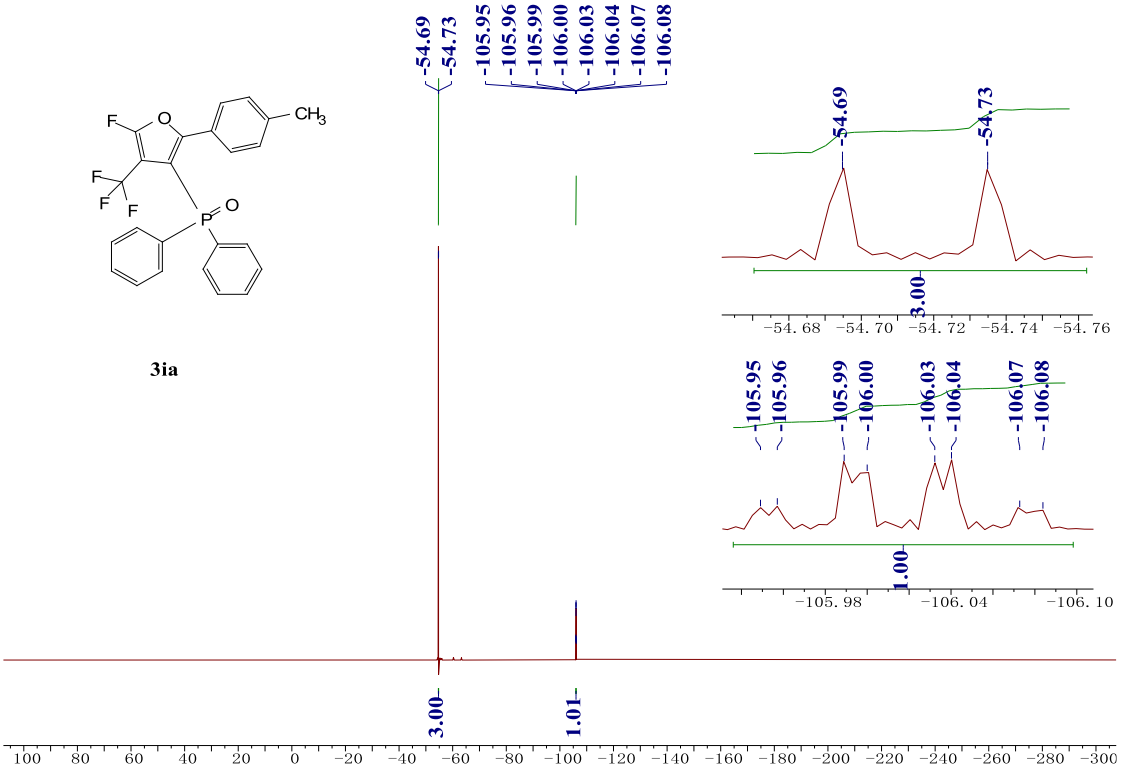
^{13}C NMR spectra of the product **3ha** (100 MHz, $CDCl_3$):



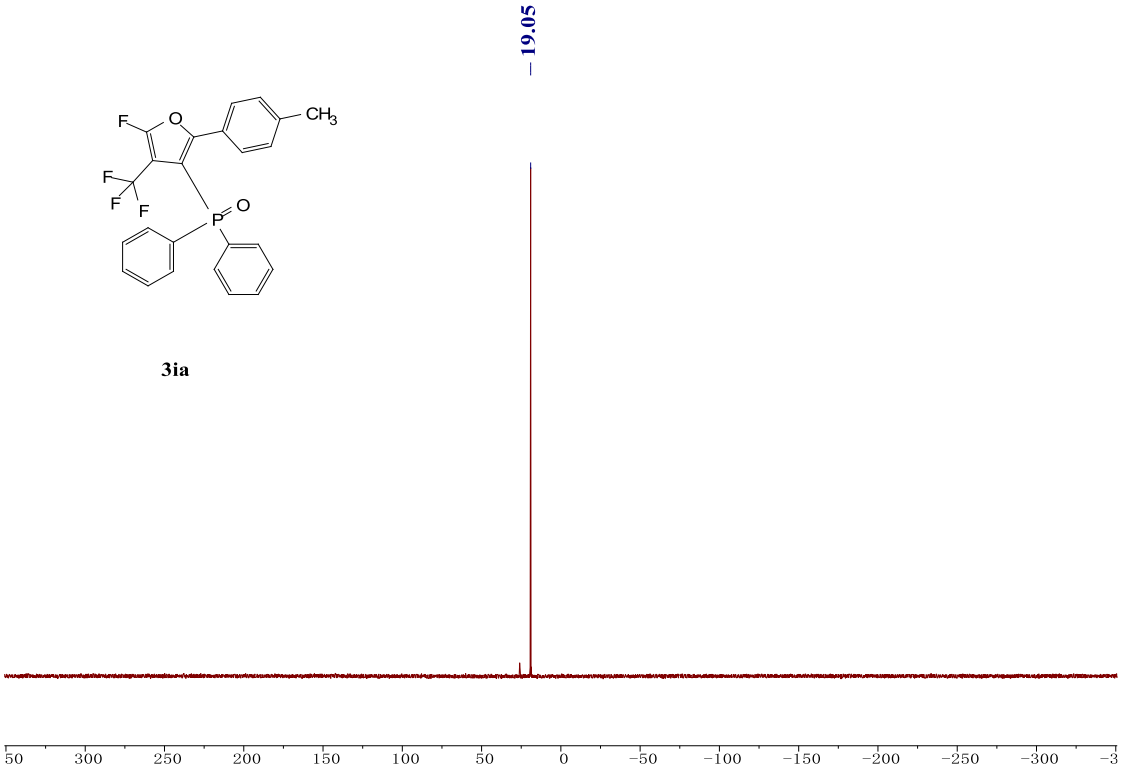
^{1}H NMR spectra of the product **3ia** (400 MHz, $CDCl_3$):



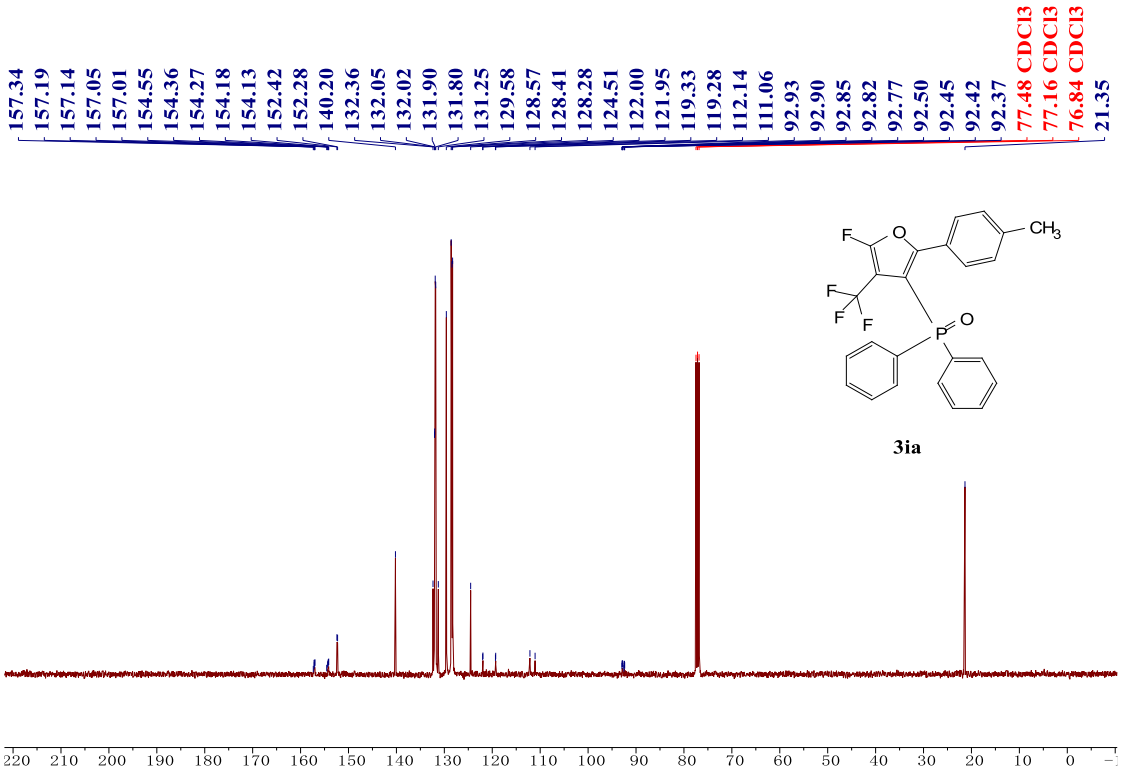
^{19}F NMR spectra of the product **3ia** (376 MHz, $CDCl_3$):



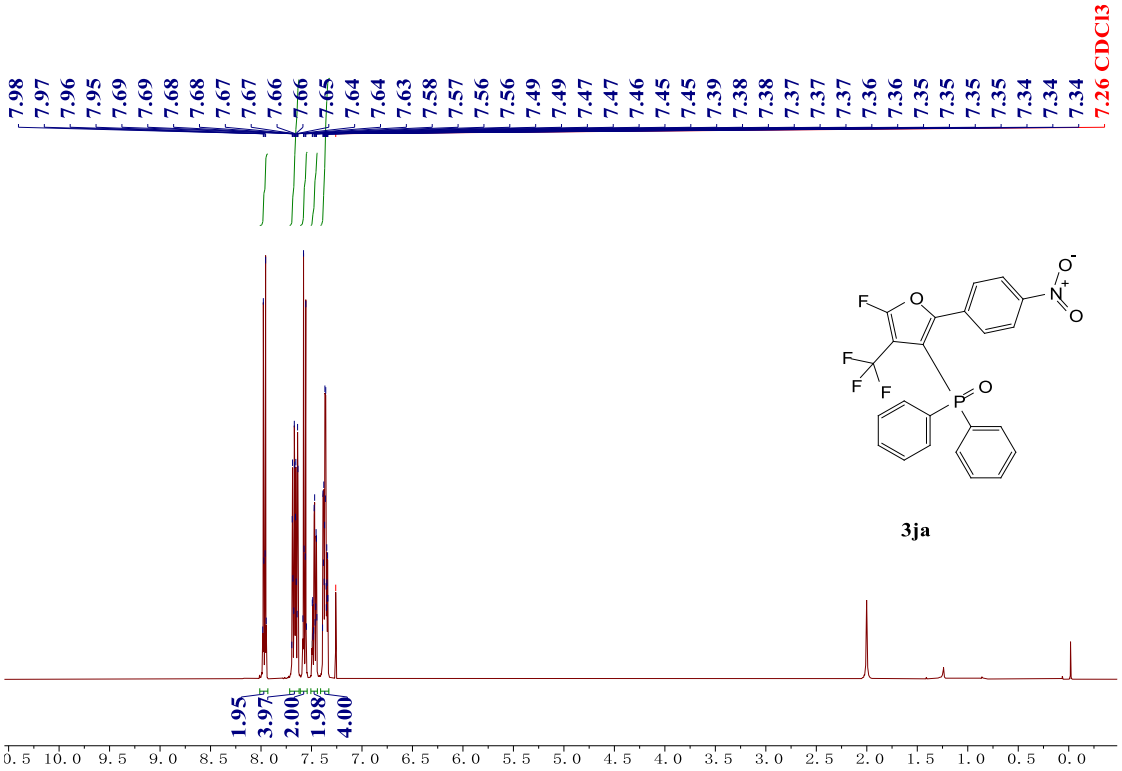
^{31}P NMR spectra of the product **3ia** (162 MHz, $CDCl_3$):



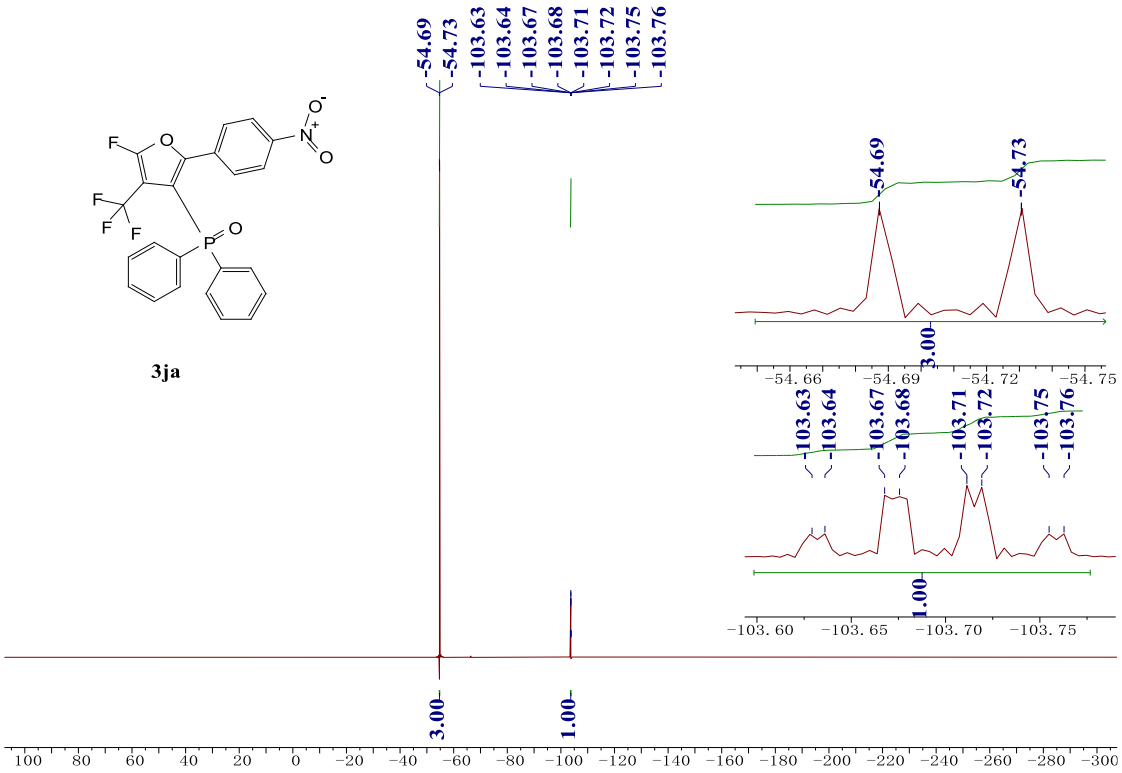
^{13}C NMR spectra of the product **3ia** (100 MHz, $CDCl_3$):



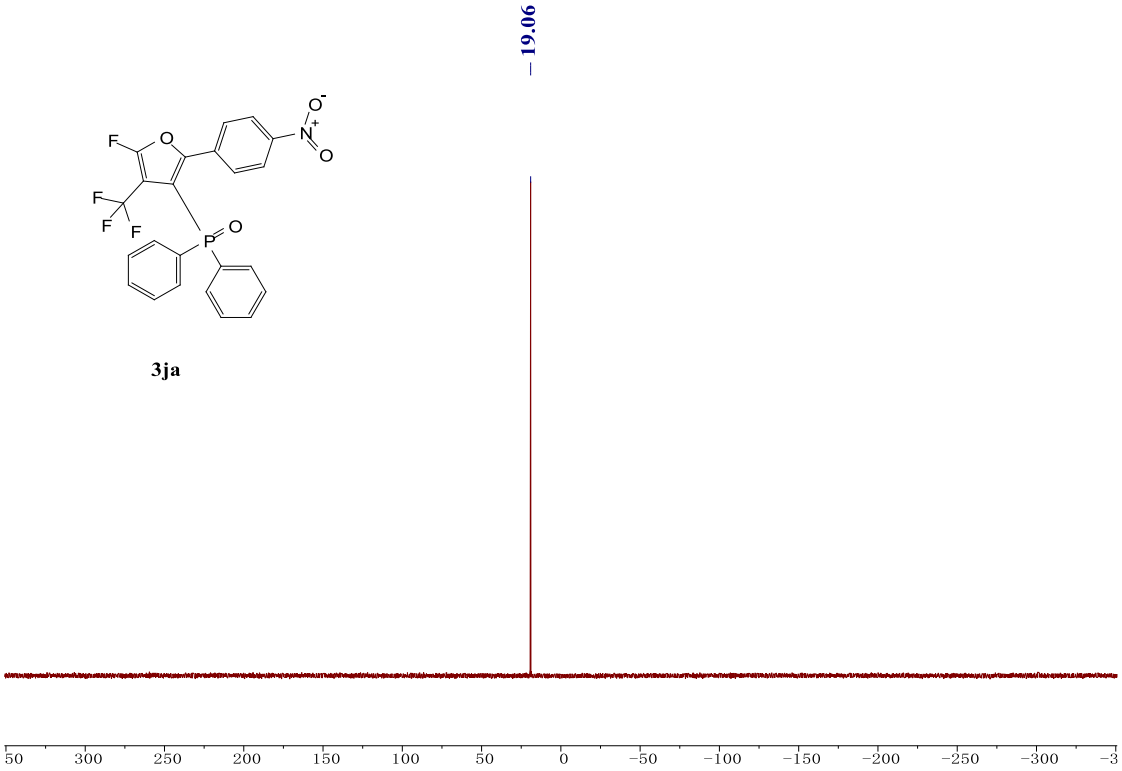
^{1}H NMR spectra of the product **3ja** (400 MHz, $CDCl_3$):



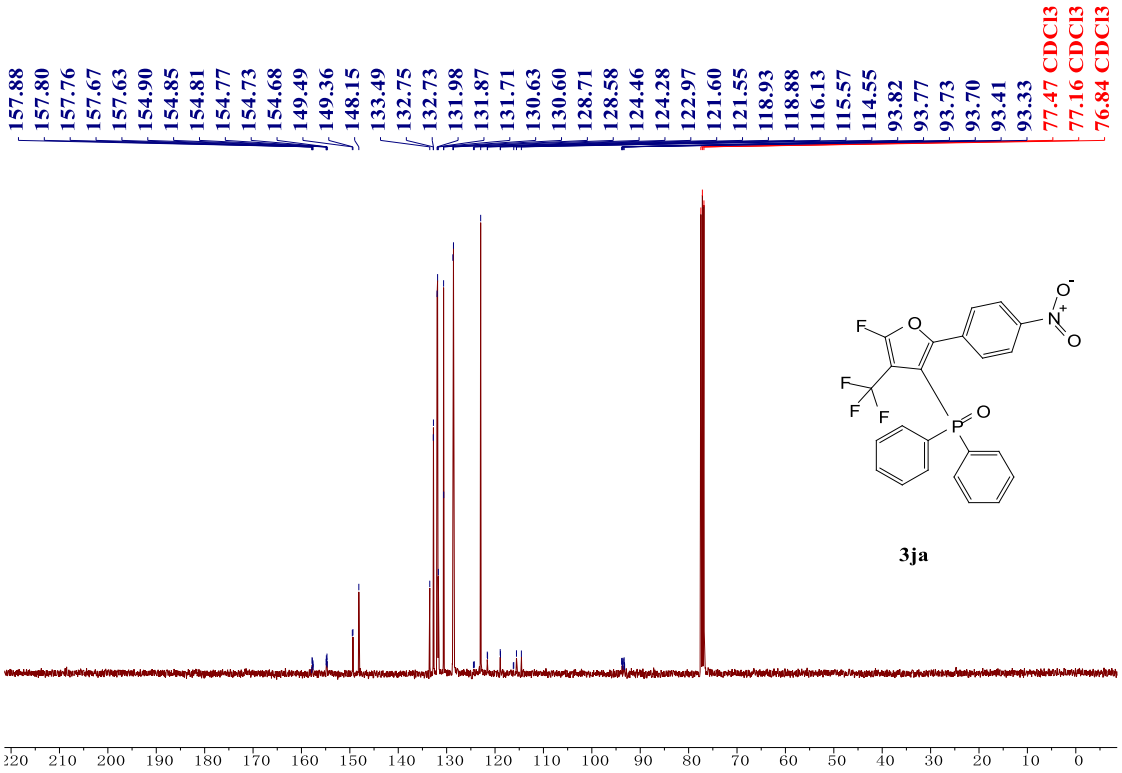
^{19}F NMR spectra of the product **3ja** (376 MHz, $CDCl_3$):



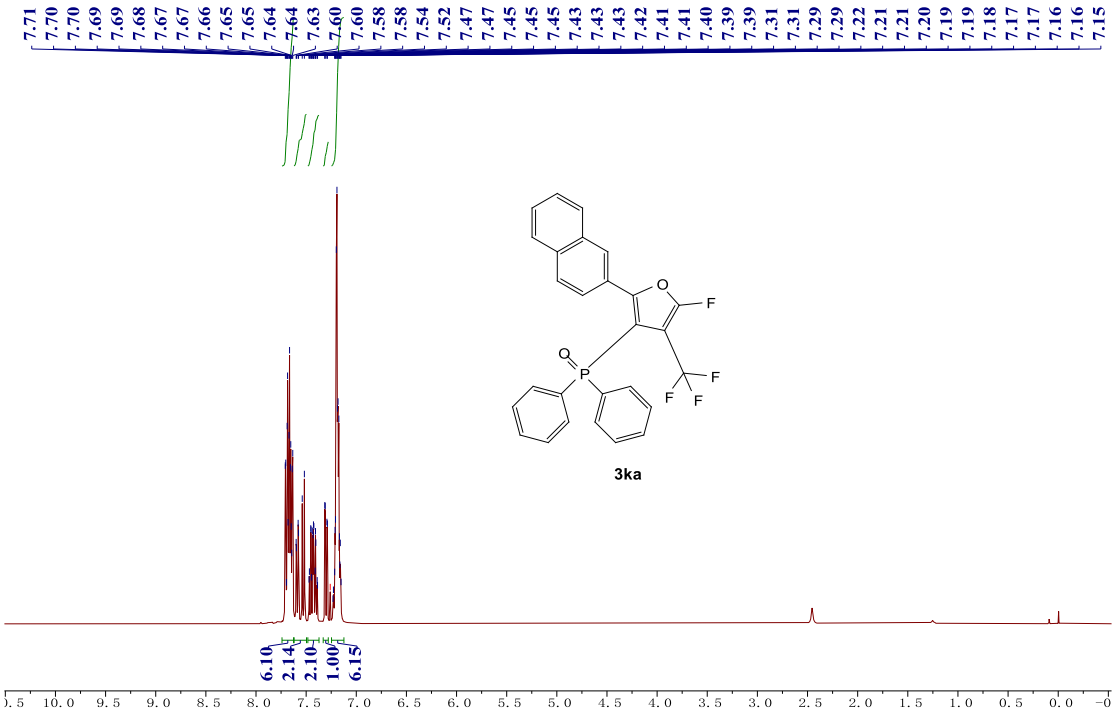
^{31}P NMR spectra of the product **3ja** (162 MHz, $CDCl_3$):



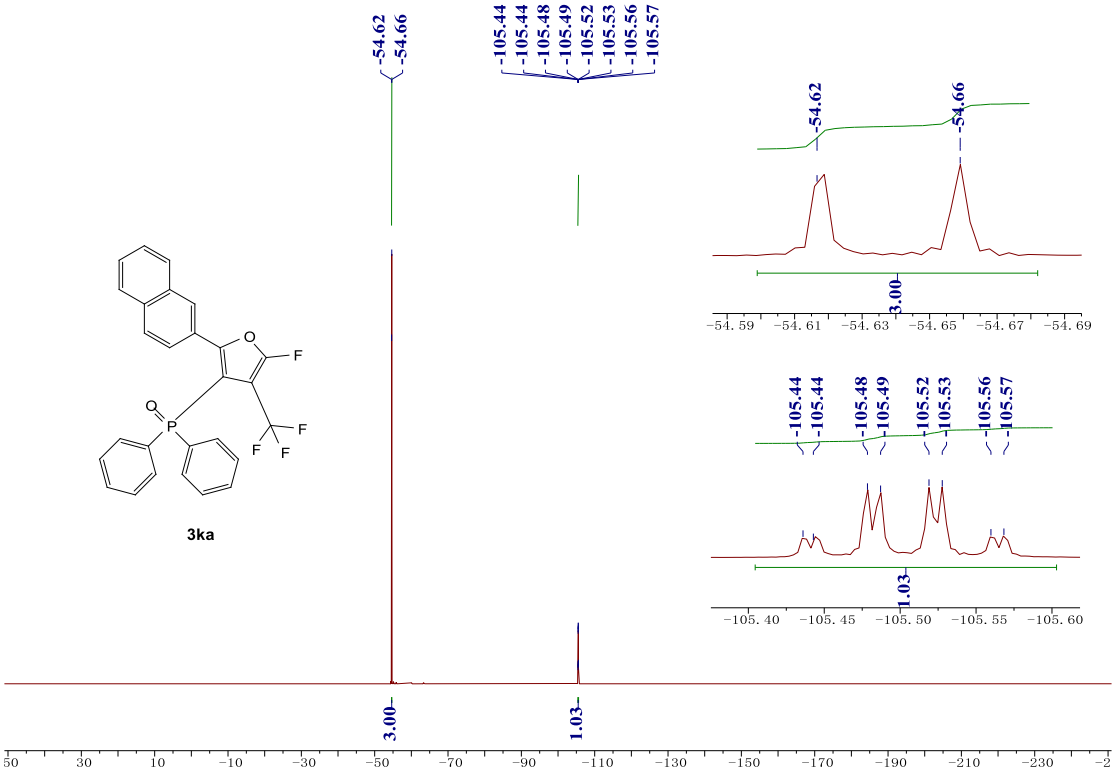
^{13}C NMR spectra of the product **3ja** (100 MHz, $CDCl_3$):



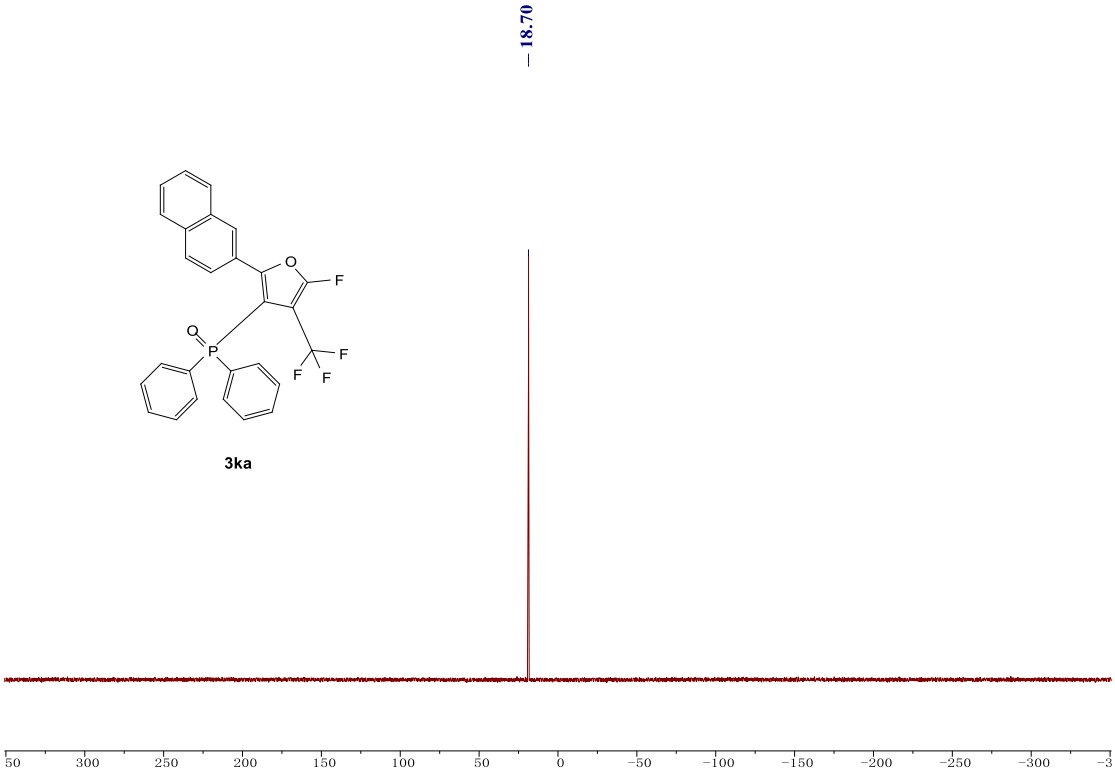
^{1}H NMR spectra of the product **3ka** (400 MHz, $CDCl_3$):



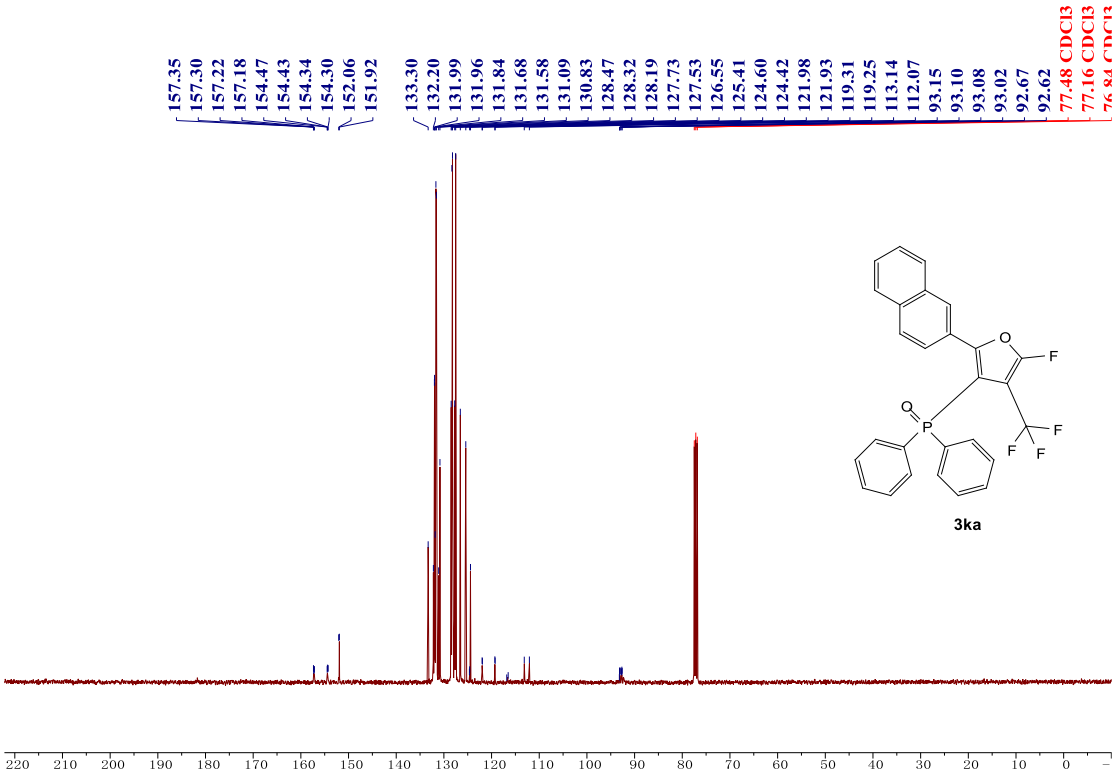
^{19}F NMR spectra of the product **3ka** (376 MHz, $CDCl_3$):



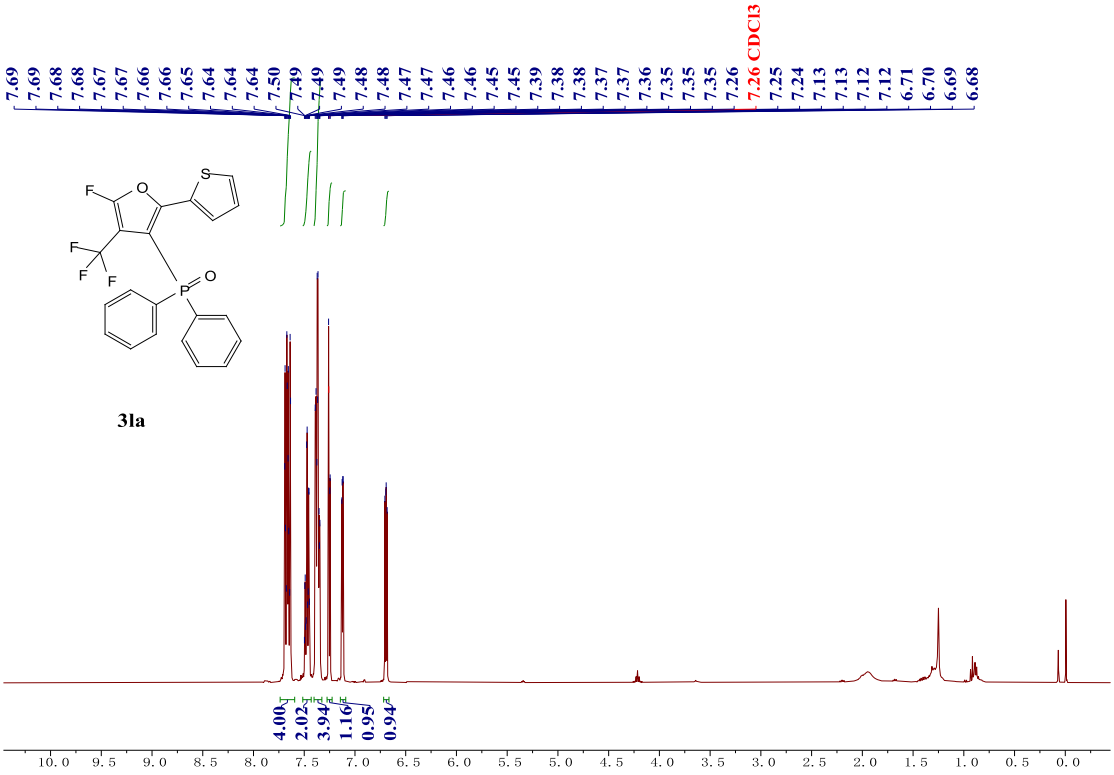
^{31}P NMR spectra of the product **3ka** (162 MHz, $CDCl_3$):



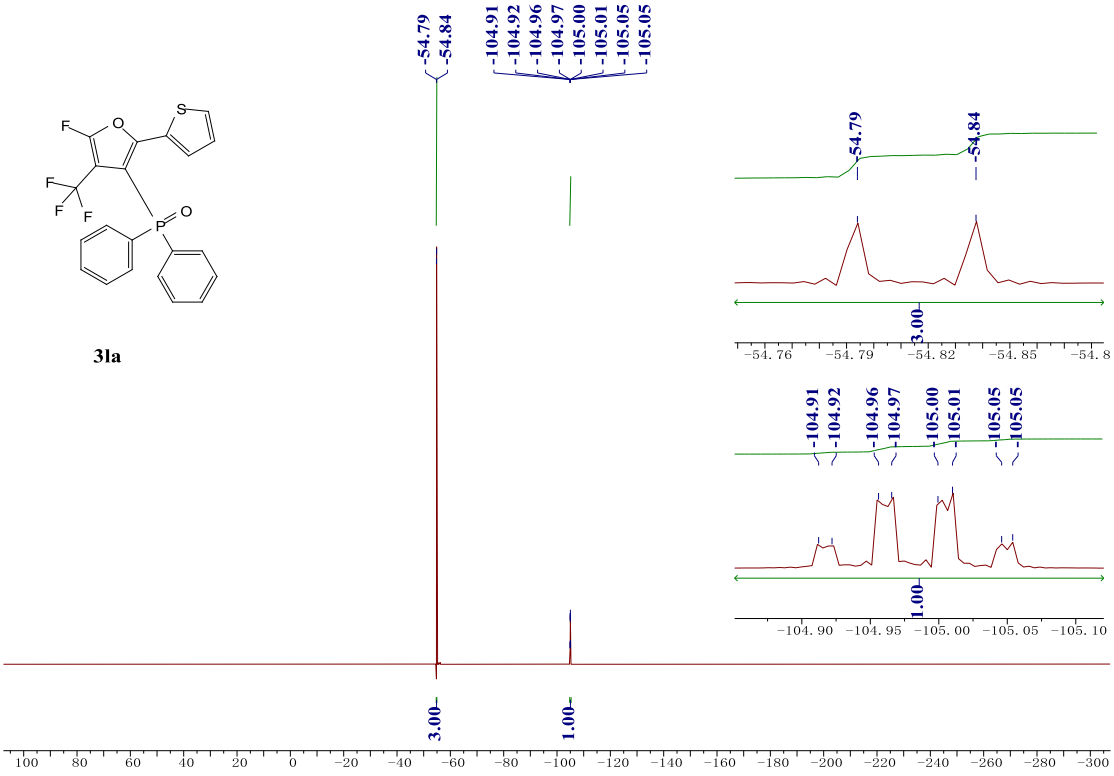
^{13}C NMR spectra of the product **3ka** (100 MHz, $CDCl_3$):



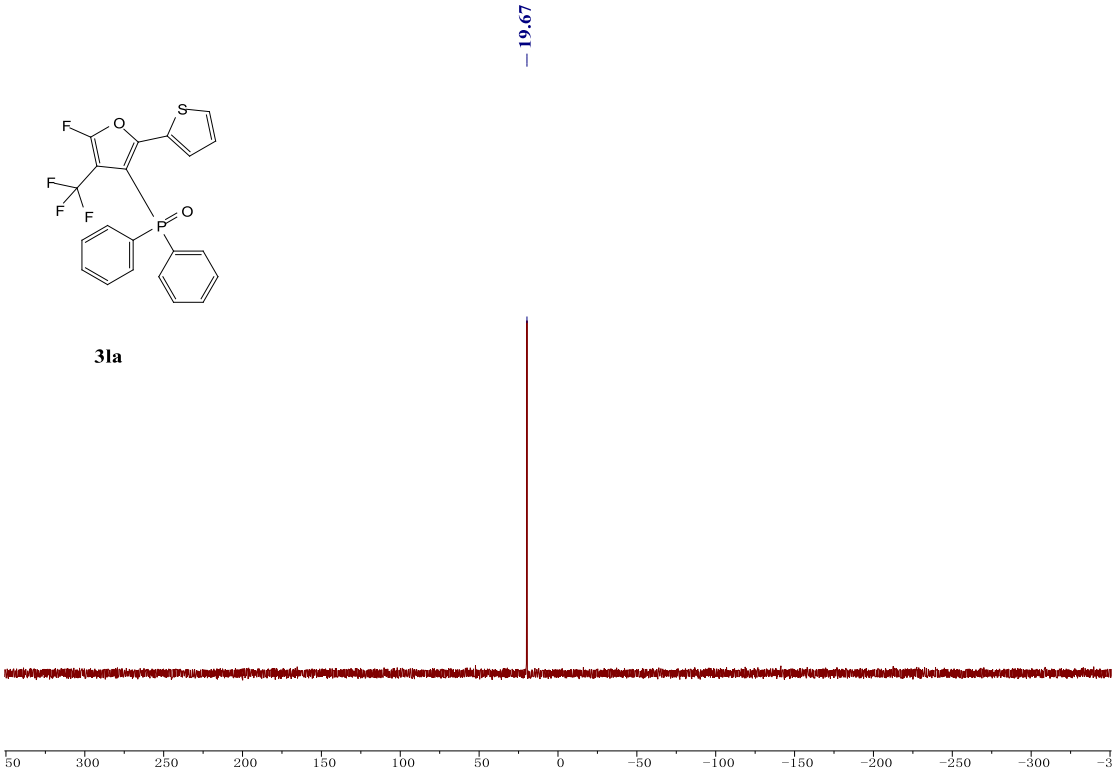
^{1}H NMR spectra of the product **3la** (400 MHz, $CDCl_3$):



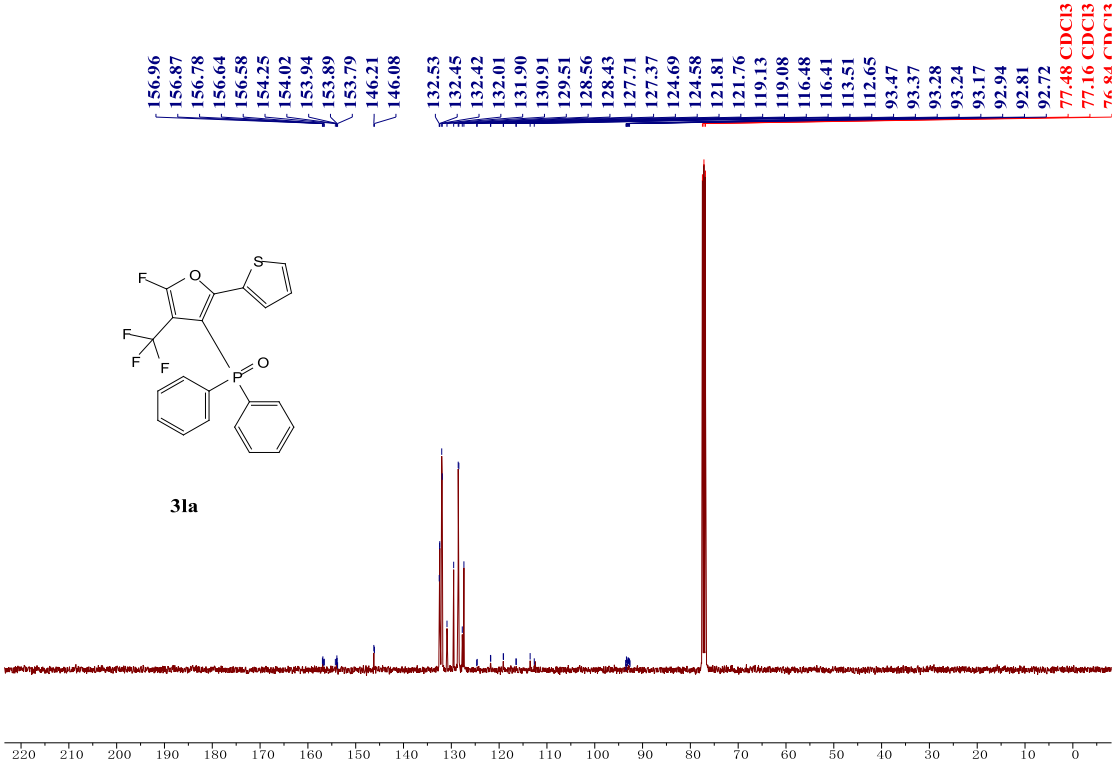
^{19}F NMR spectra of the product **3la** (376 MHz, $CDCl_3$):



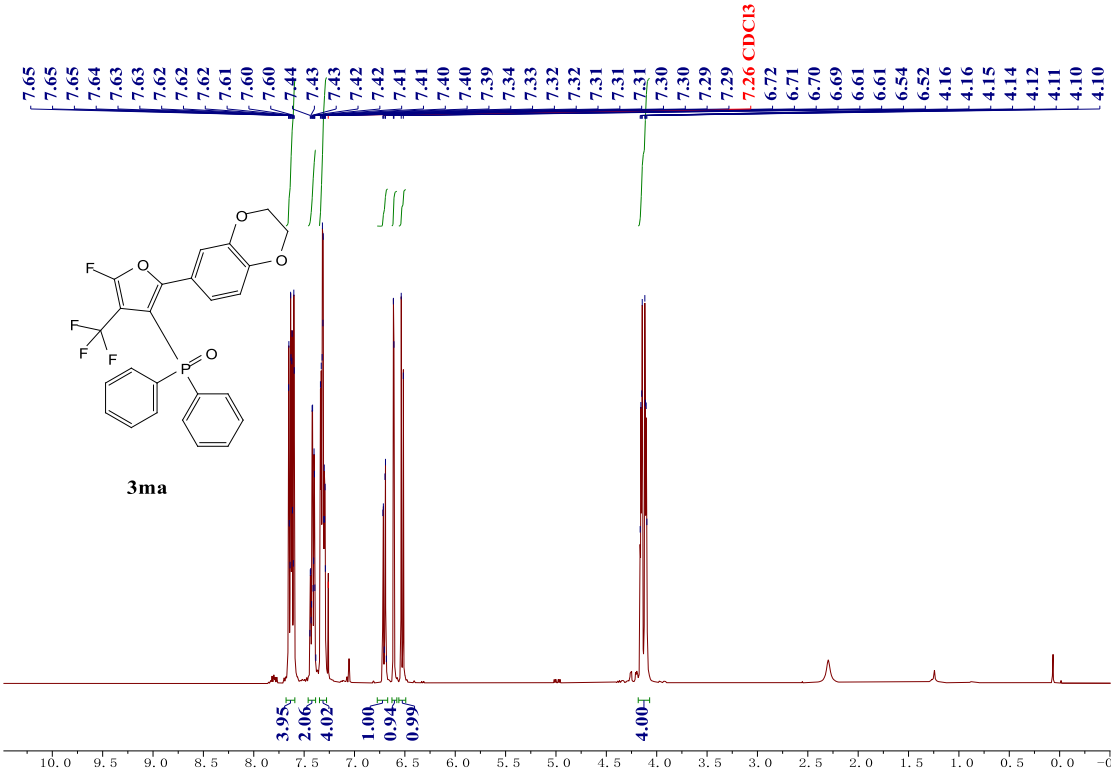
^{31}P NMR spectra of the product **3la** (162 MHz, $CDCl_3$):



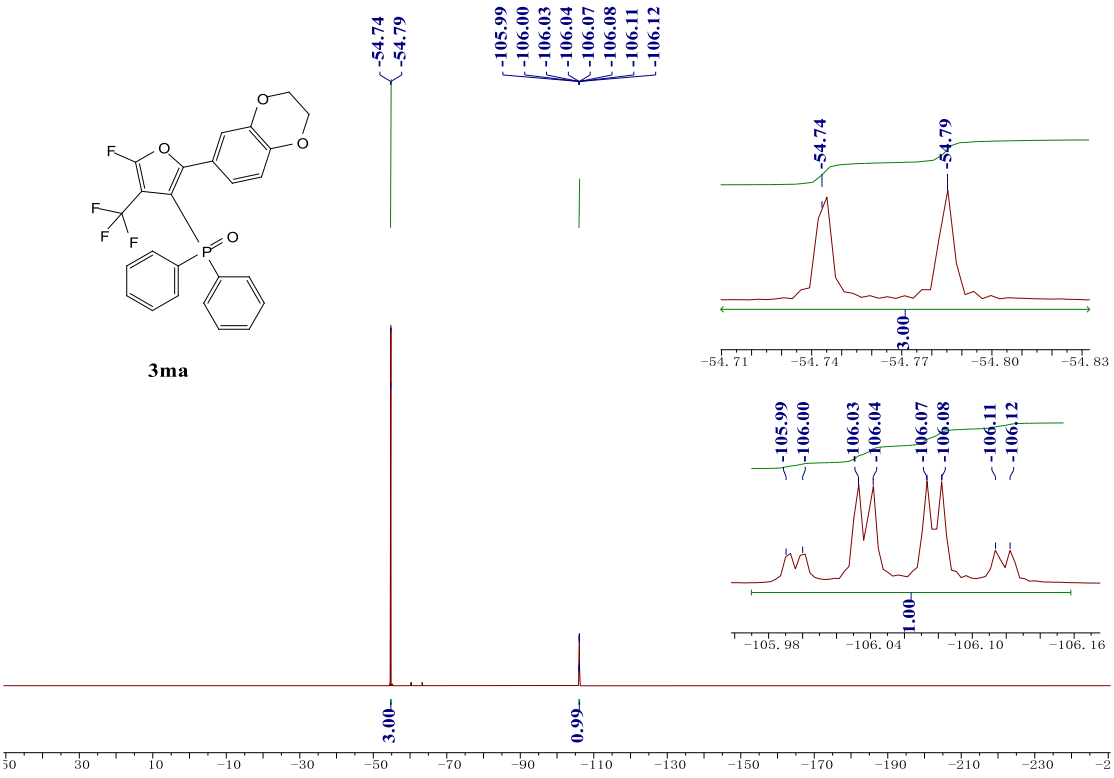
^{13}C NMR spectra of the product **3la** (100 MHz, $CDCl_3$):



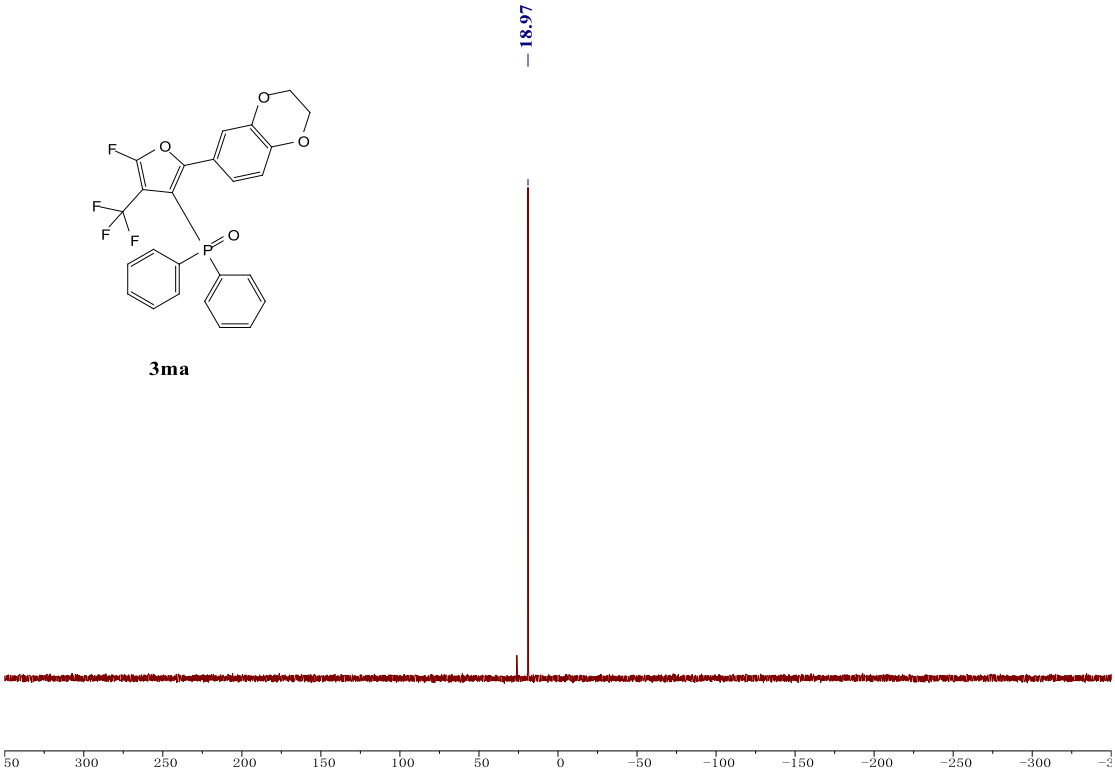
^{1}H NMR spectra of the product **3ma** (400 MHz, $CDCl_3$):



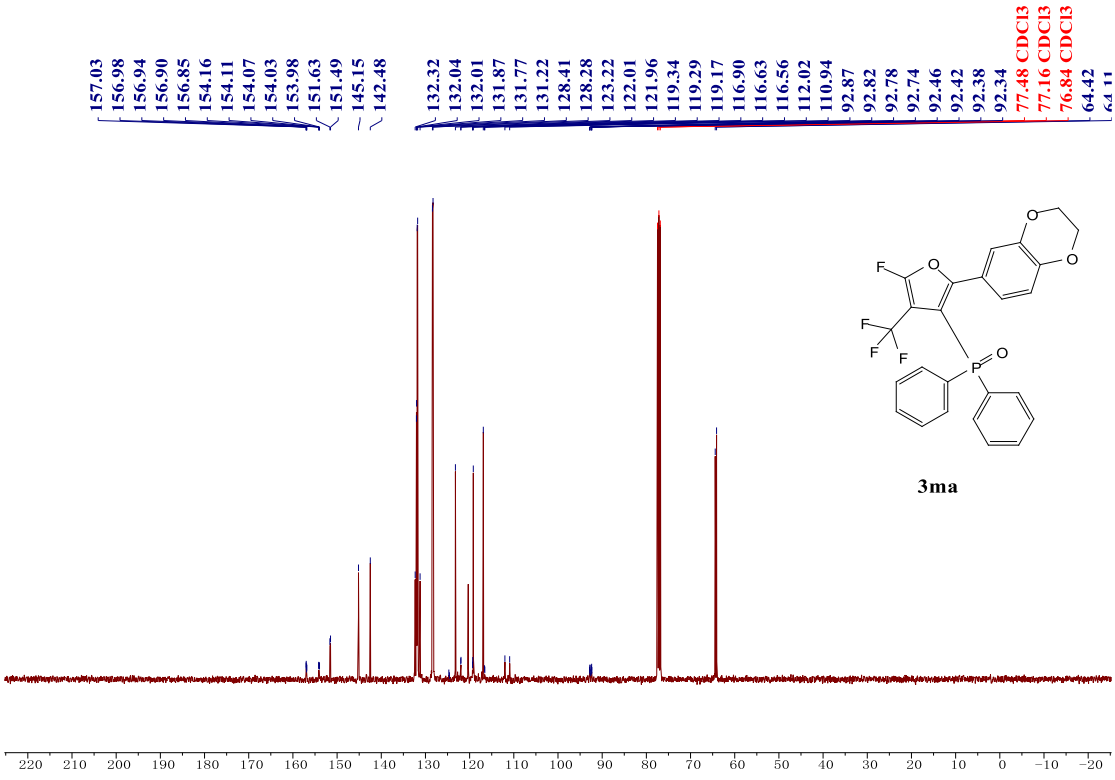
^{19}F NMR spectra of the product **3ma** (376 MHz, $CDCl_3$):



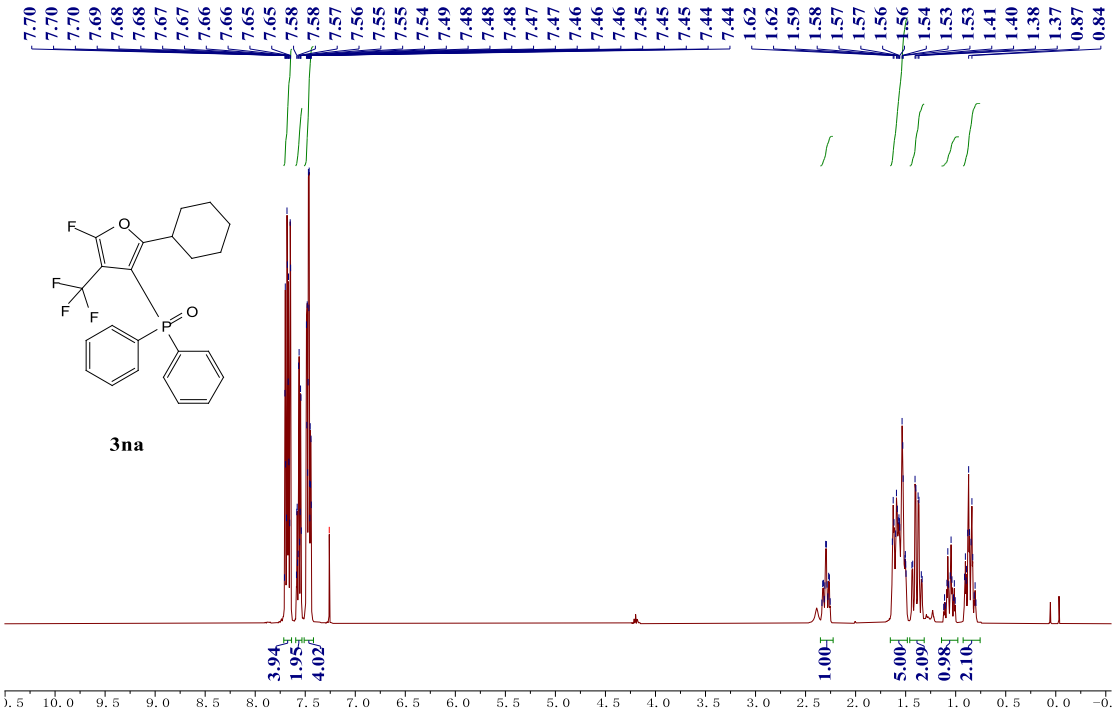
^{31}P NMR spectra of the product **3ma** (162 MHz, $CDCl_3$):



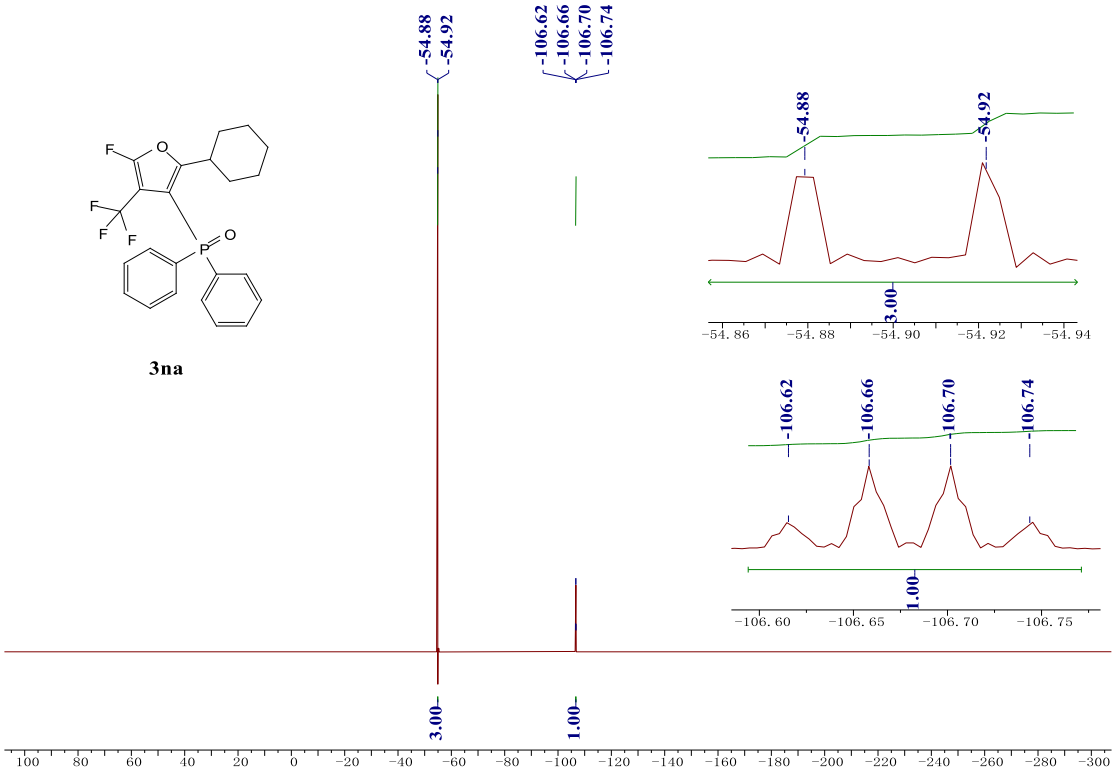
^{13}C NMR spectra of the product **3ma** (100 MHz, $CDCl_3$):



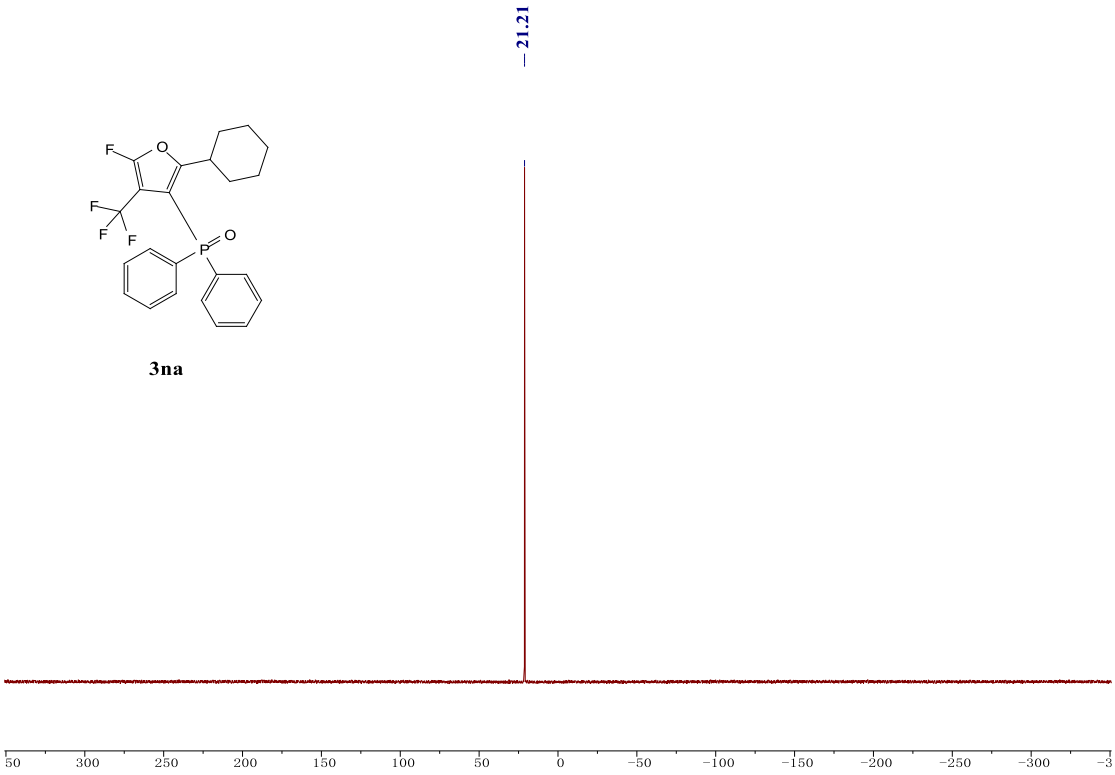
^{1}H NMR spectra of the product **3na** (400 MHz, $CDCl_3$):



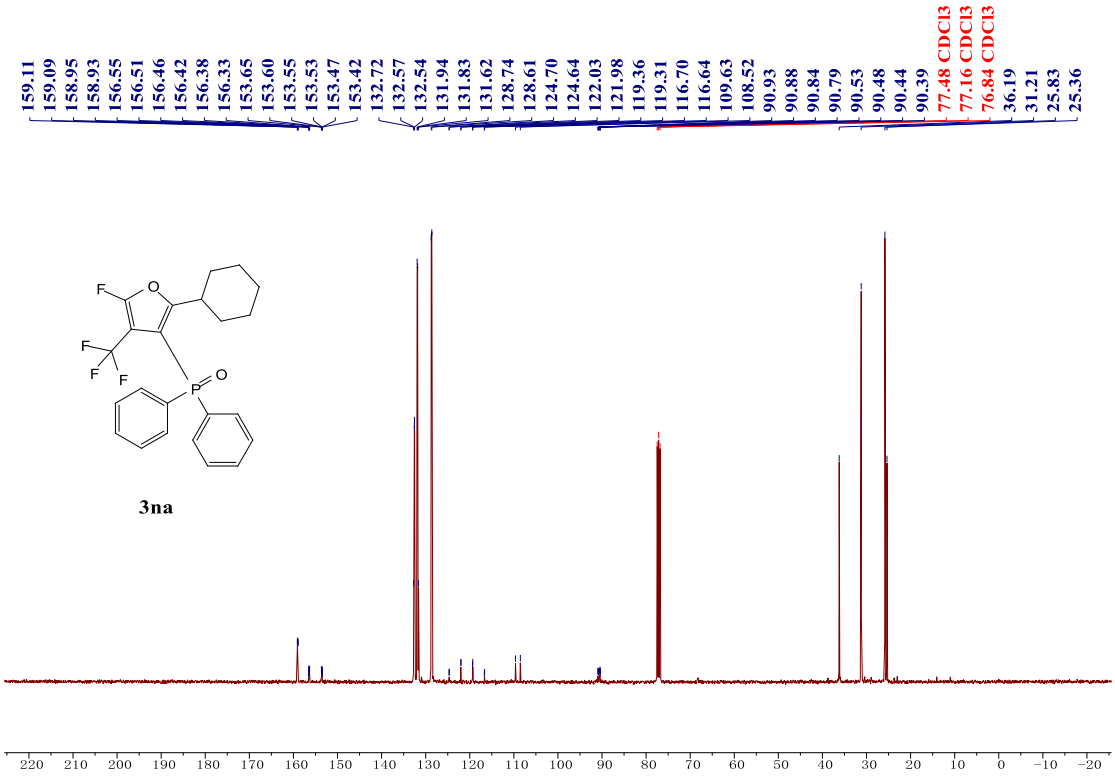
^{19}F NMR spectra of the product **3na** (376 MHz, $CDCl_3$):



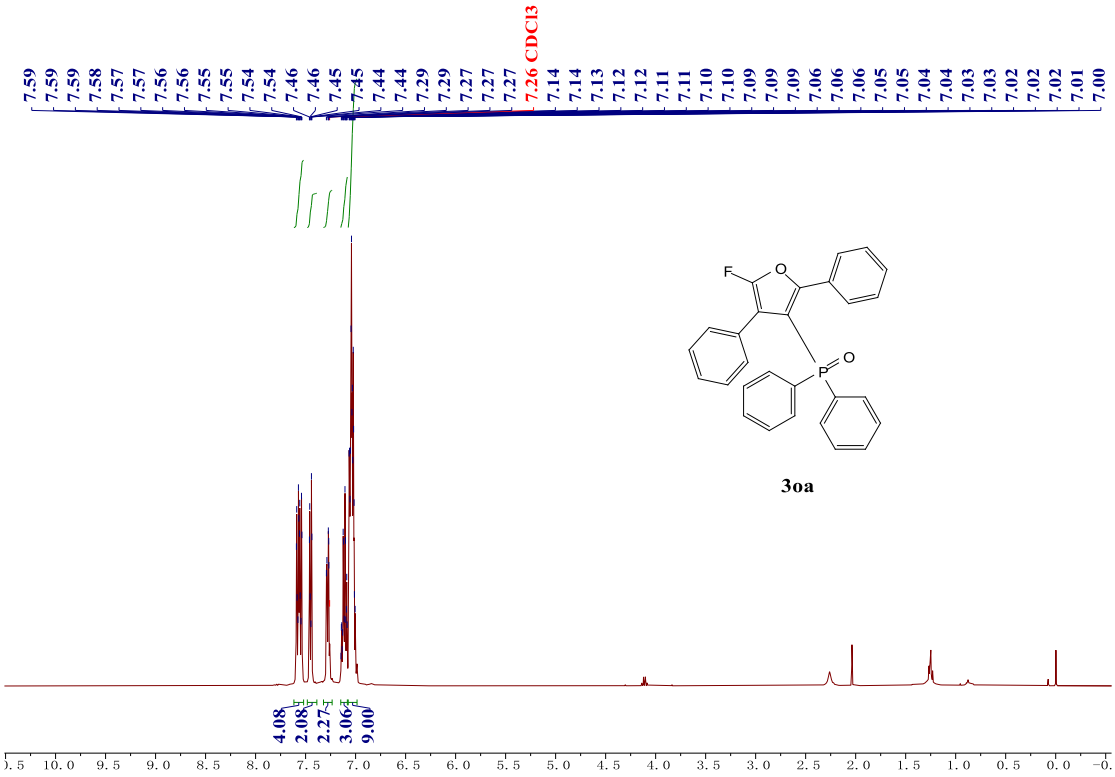
^{31}P NMR spectra of the product **3na** (162 MHz, $CDCl_3$):



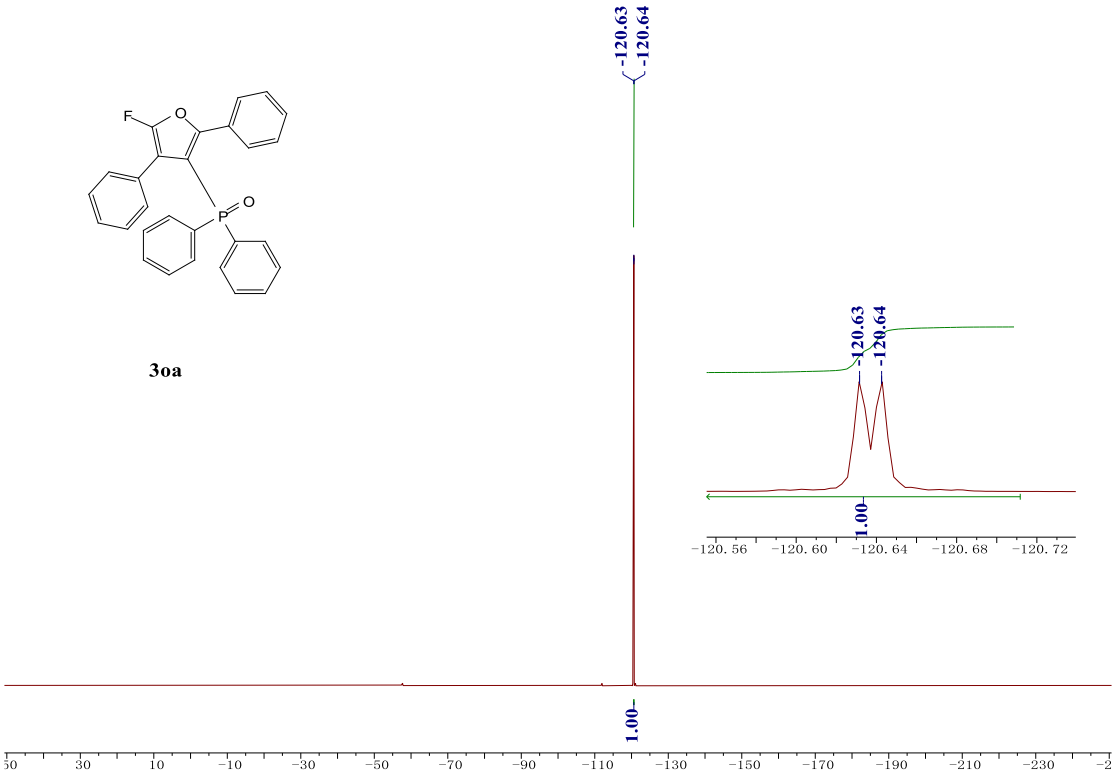
^{13}C NMR spectra of the product **3na** (100 MHz, $CDCl_3$):



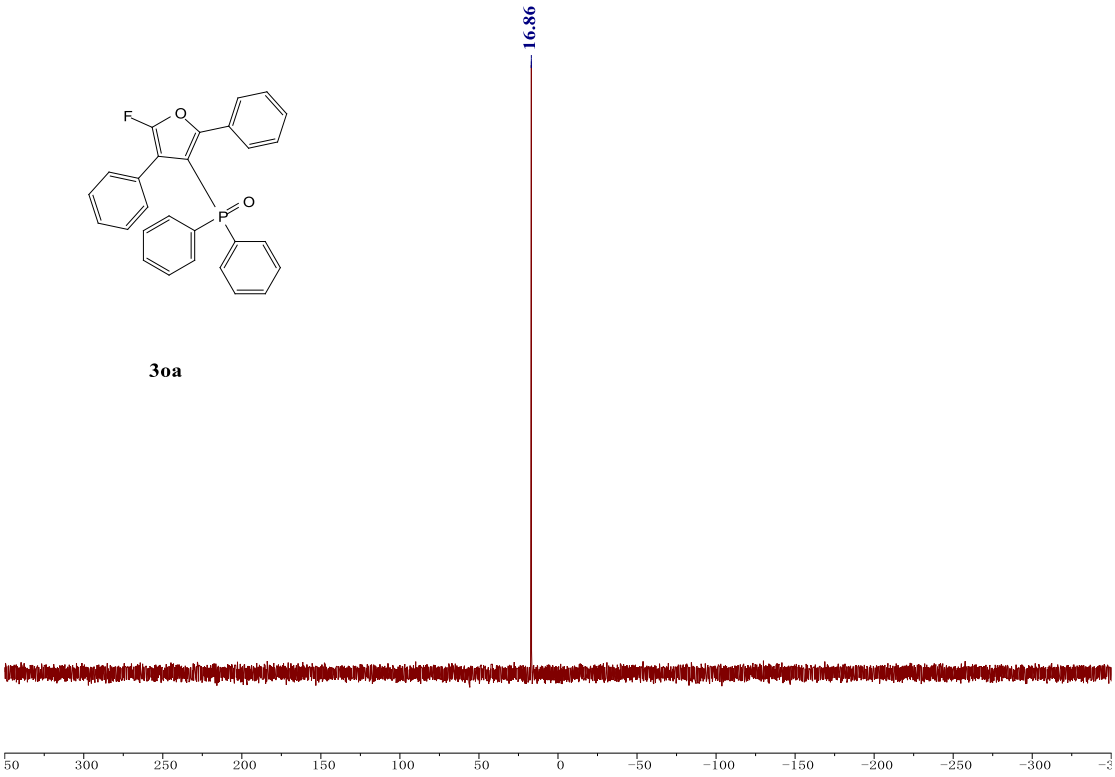
^{1}H NMR spectra of the product **3oa** (400 MHz, $CDCl_3$):



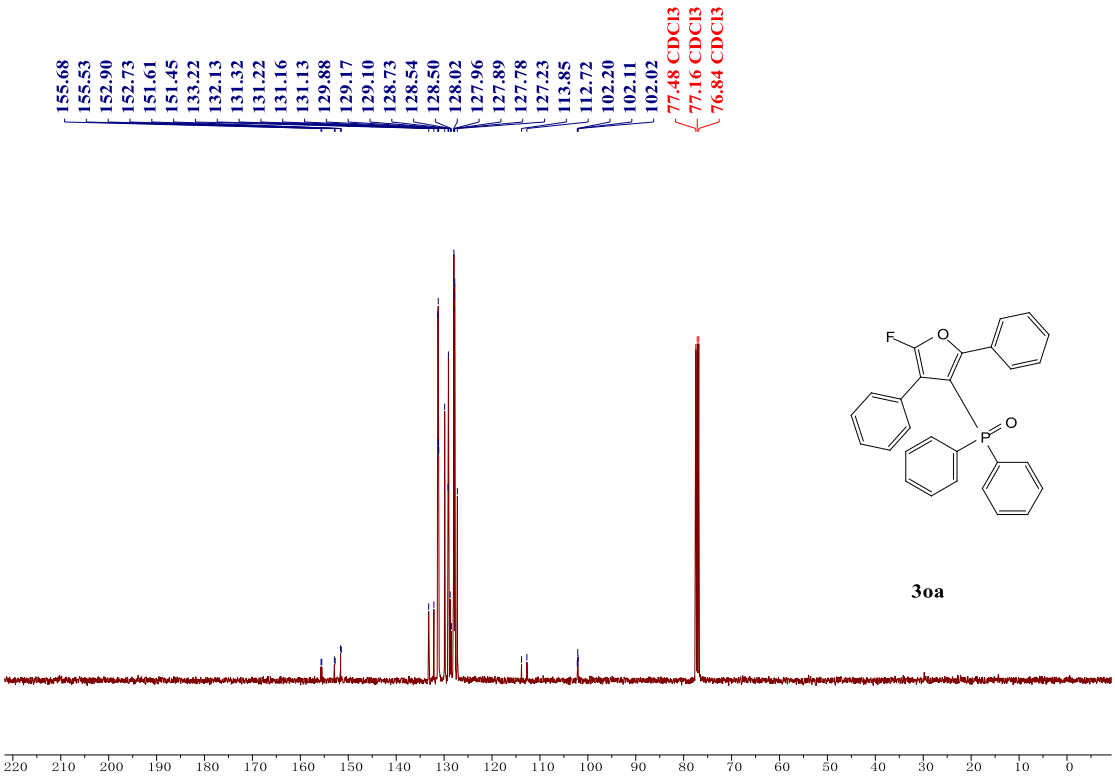
^{19}F NMR spectra of the product **3oa** (376 MHz, $CDCl_3$):



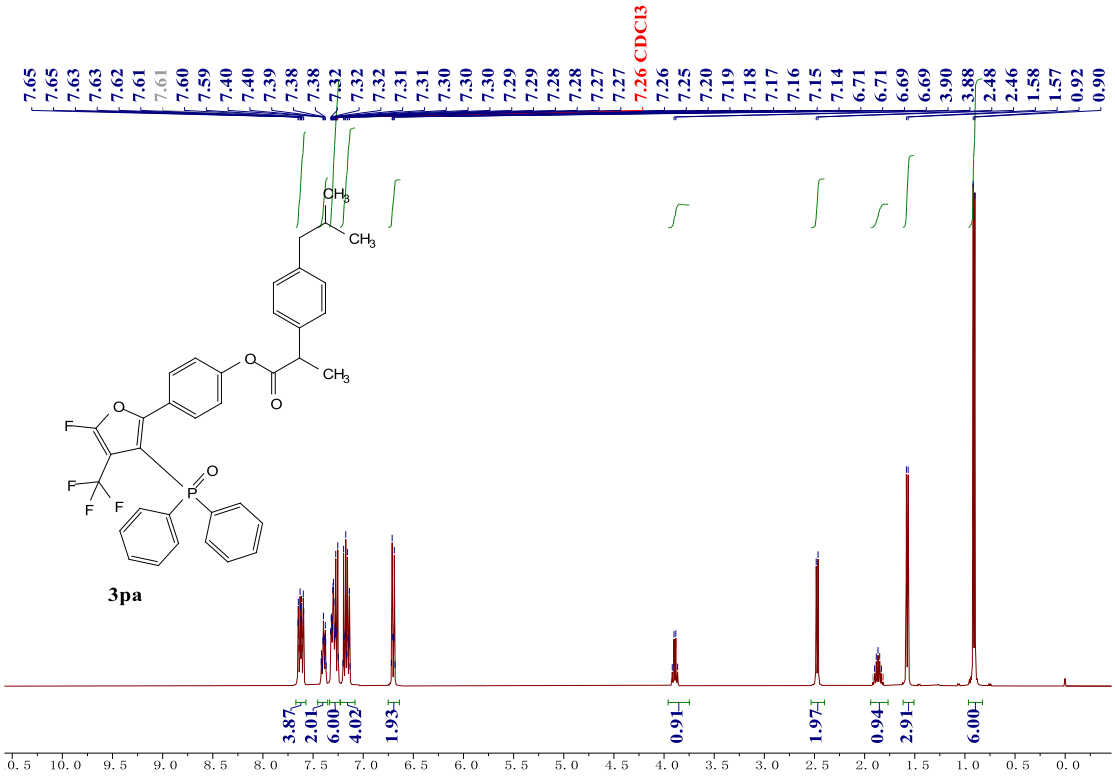
^{31}P NMR spectra of the product **3oa** (162 MHz, $CDCl_3$):



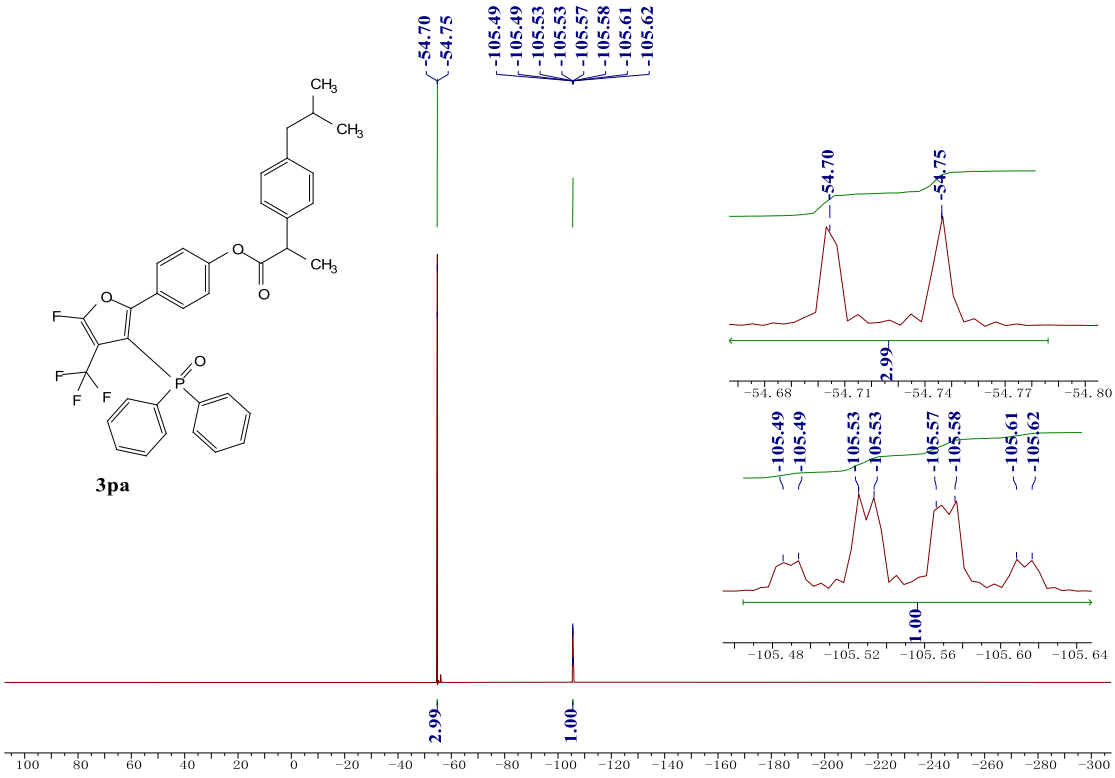
^{13}C NMR spectra of the product **3oa** (100 MHz, $CDCl_3$):



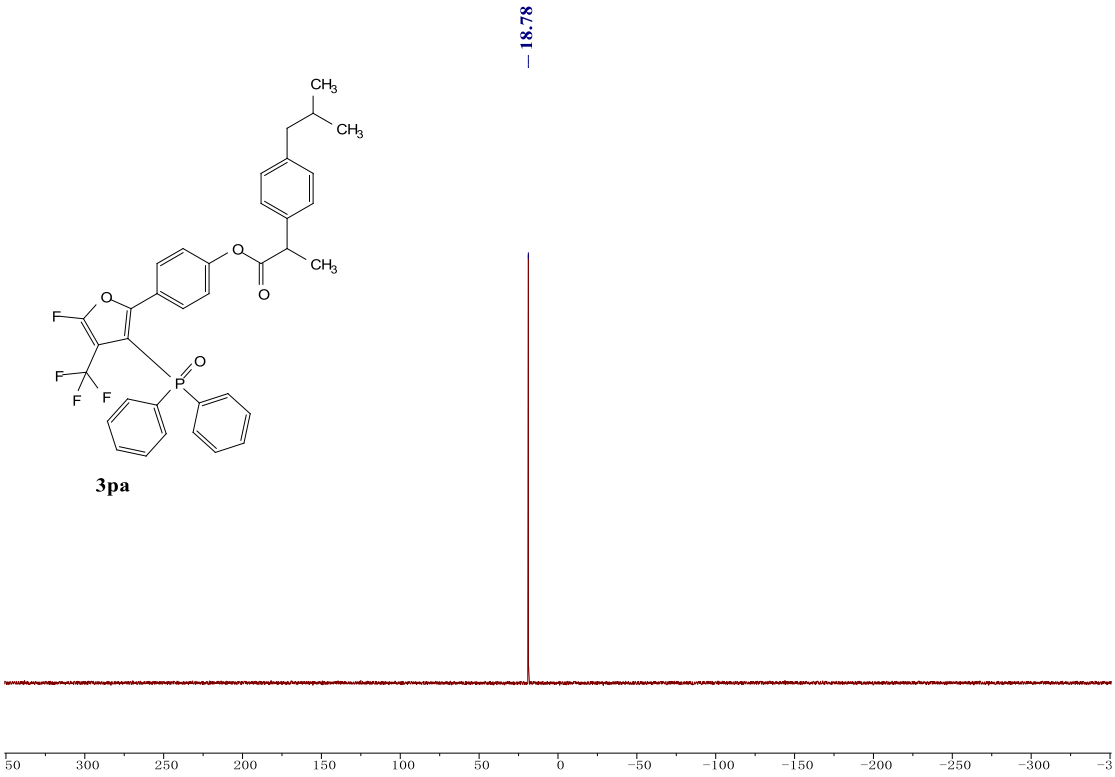
^{1}H NMR spectra of the product **3pa** (400 MHz, $CDCl_3$):



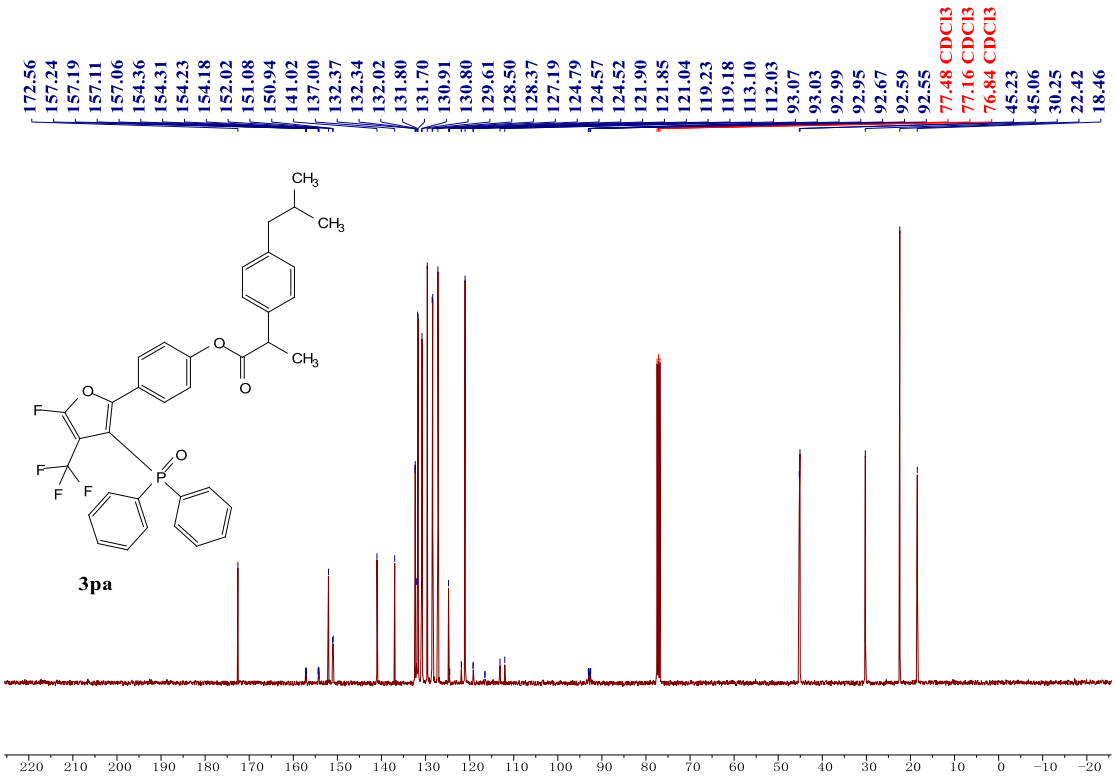
^{19}F NMR spectra of the product **3pa** (376 MHz, $CDCl_3$):



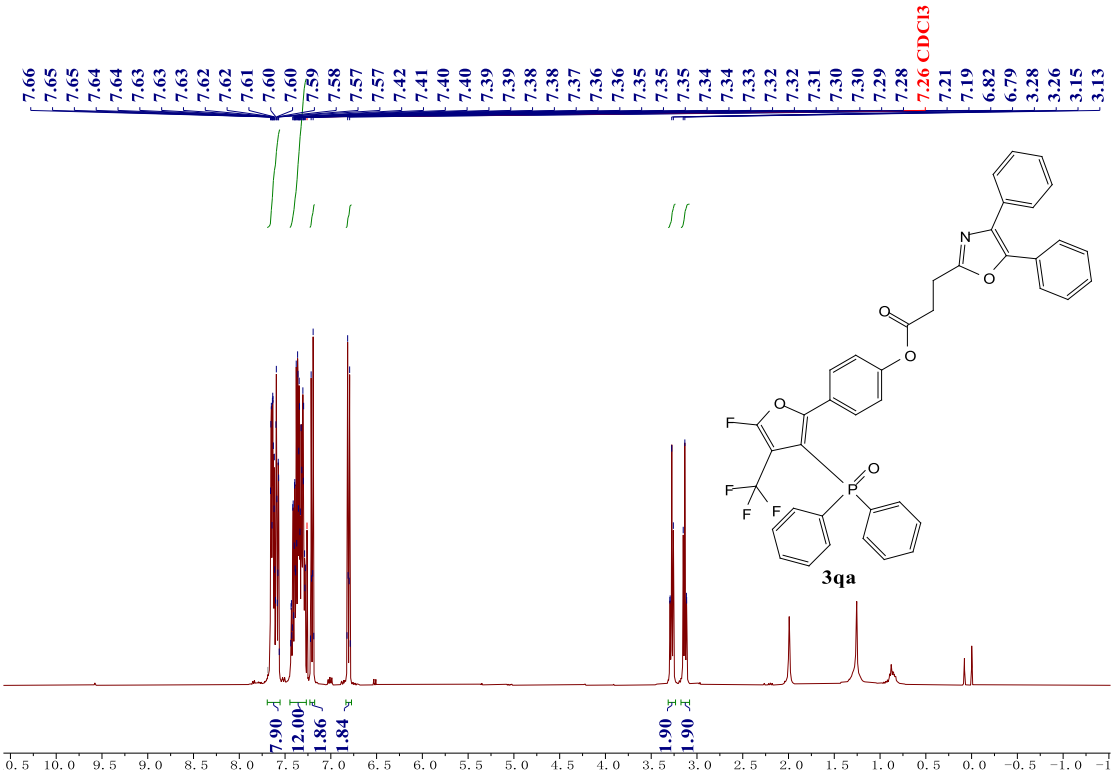
^{31}P NMR spectra of the product **3pa** (162 MHz, $CDCl_3$):



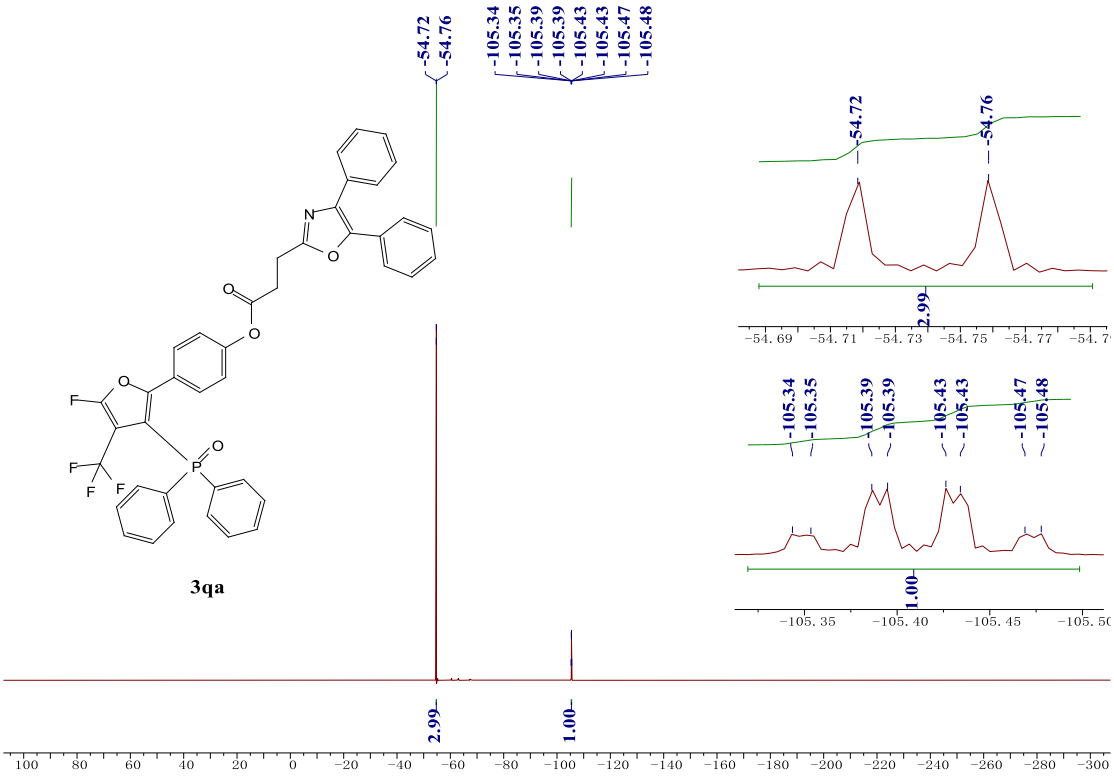
^{13}C NMR spectra of the product **3pa** (100 MHz, $CDCl_3$):



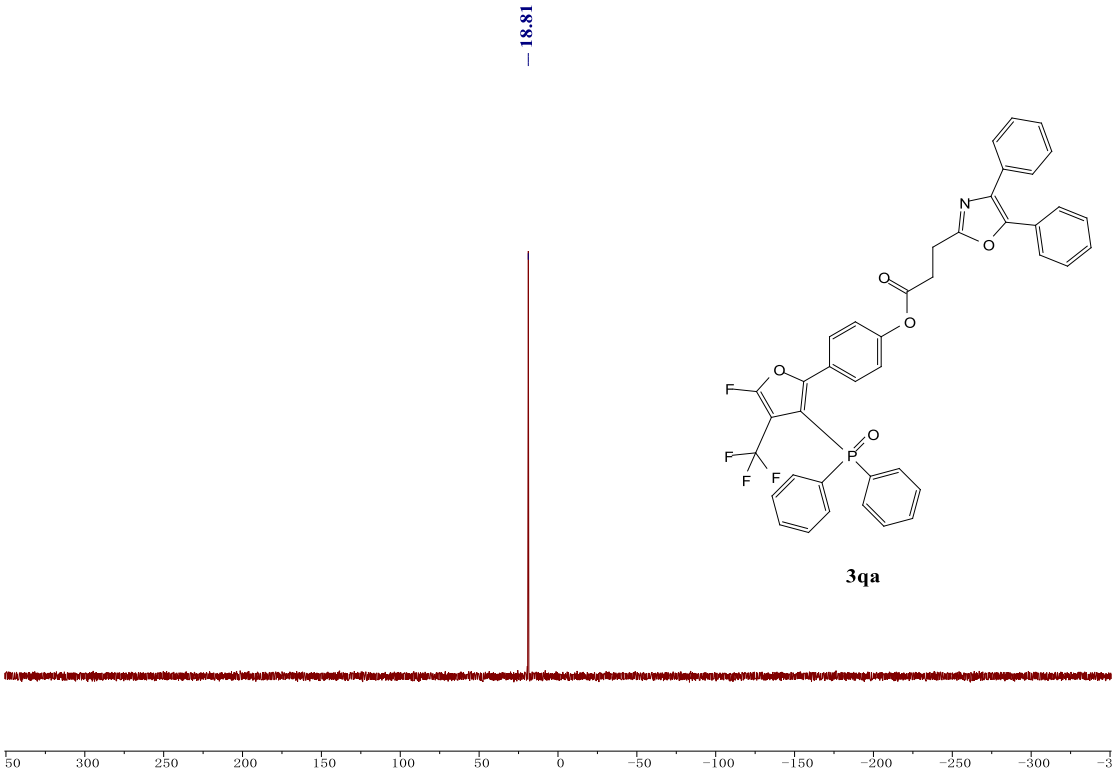
^{1}H NMR spectra of the product **3qa** (400 MHz, $CDCl_3$):



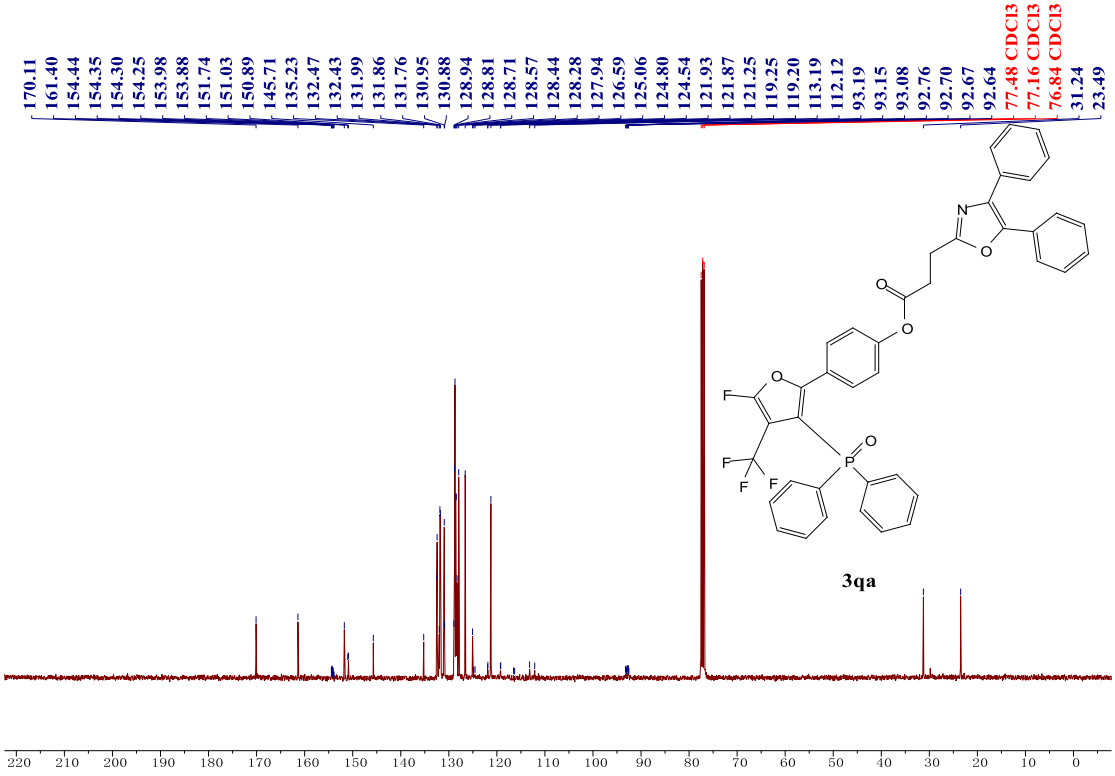
^{19}F NMR spectra of the product **3qa** (376 MHz, $CDCl_3$):



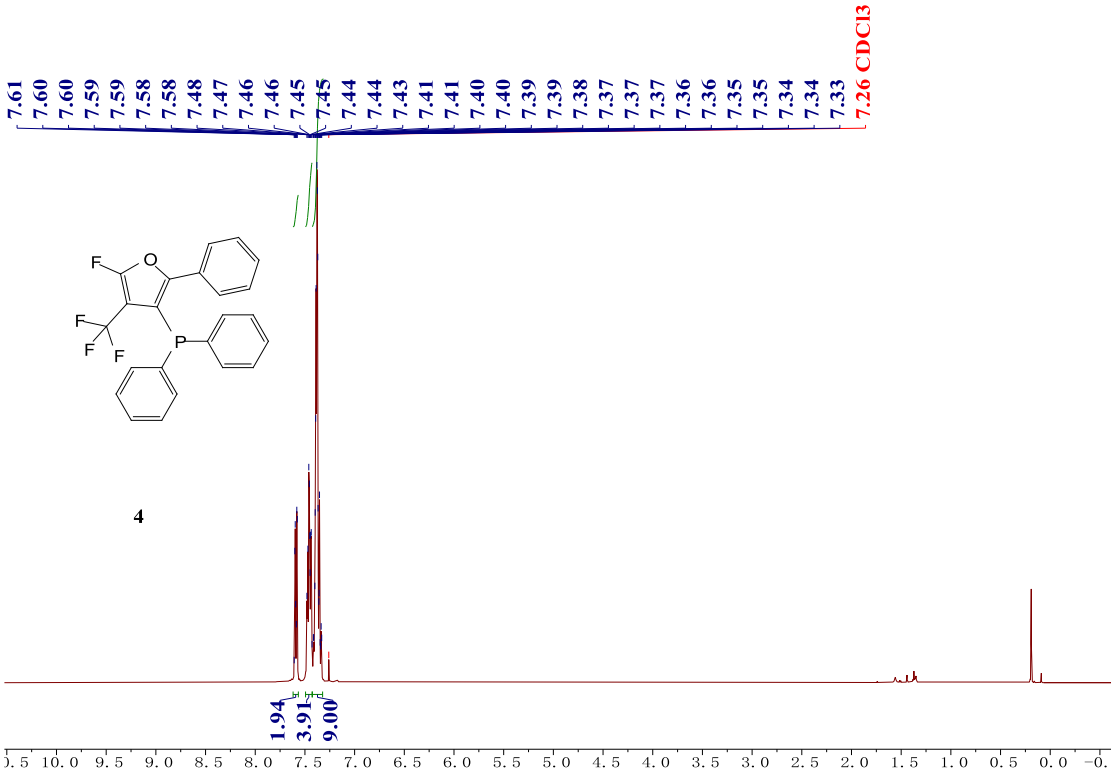
^{31}P NMR spectra of the product **3qa** (162 MHz, $CDCl_3$):



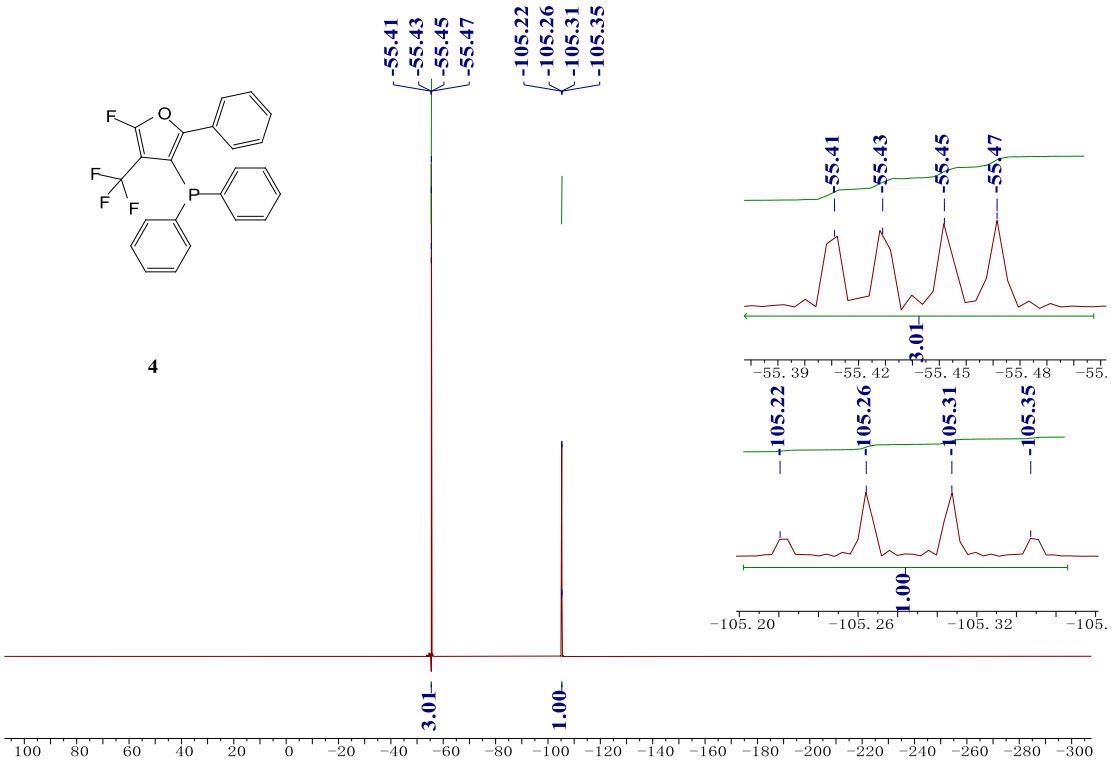
^{13}C NMR spectra of the product **3qa** (100 MHz, $CDCl_3$):



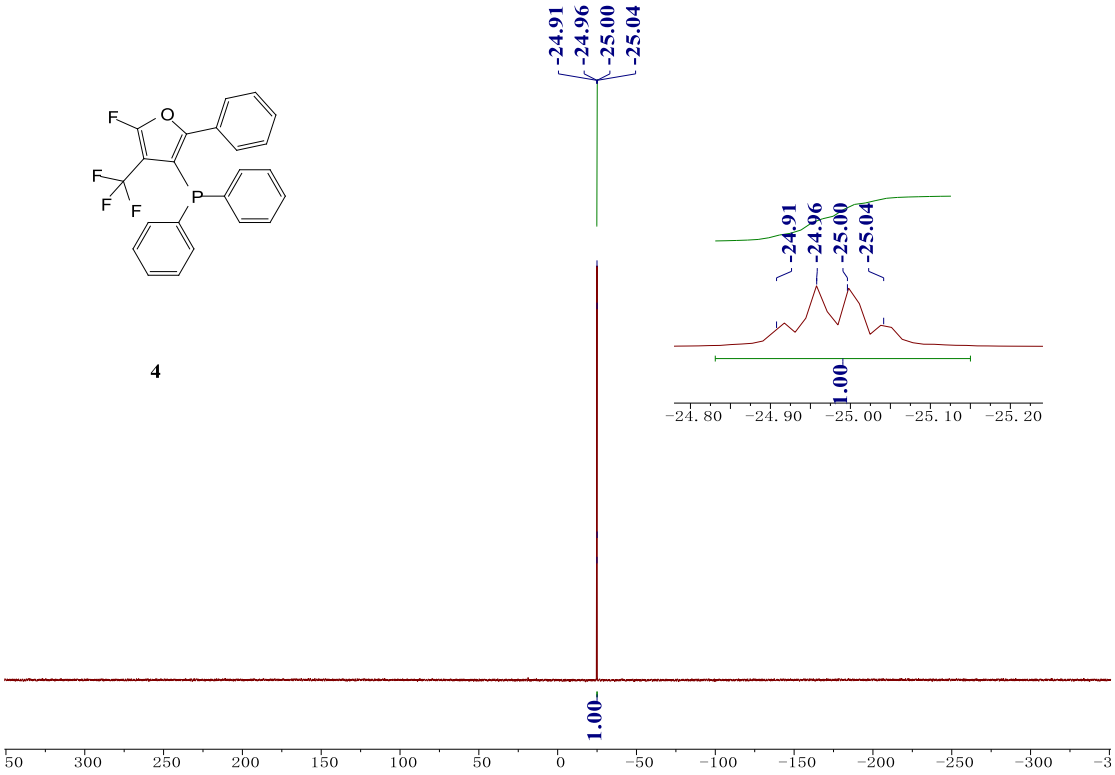
^{1}H NMR spectra of the product **4** (400 MHz, $CDCl_3$):



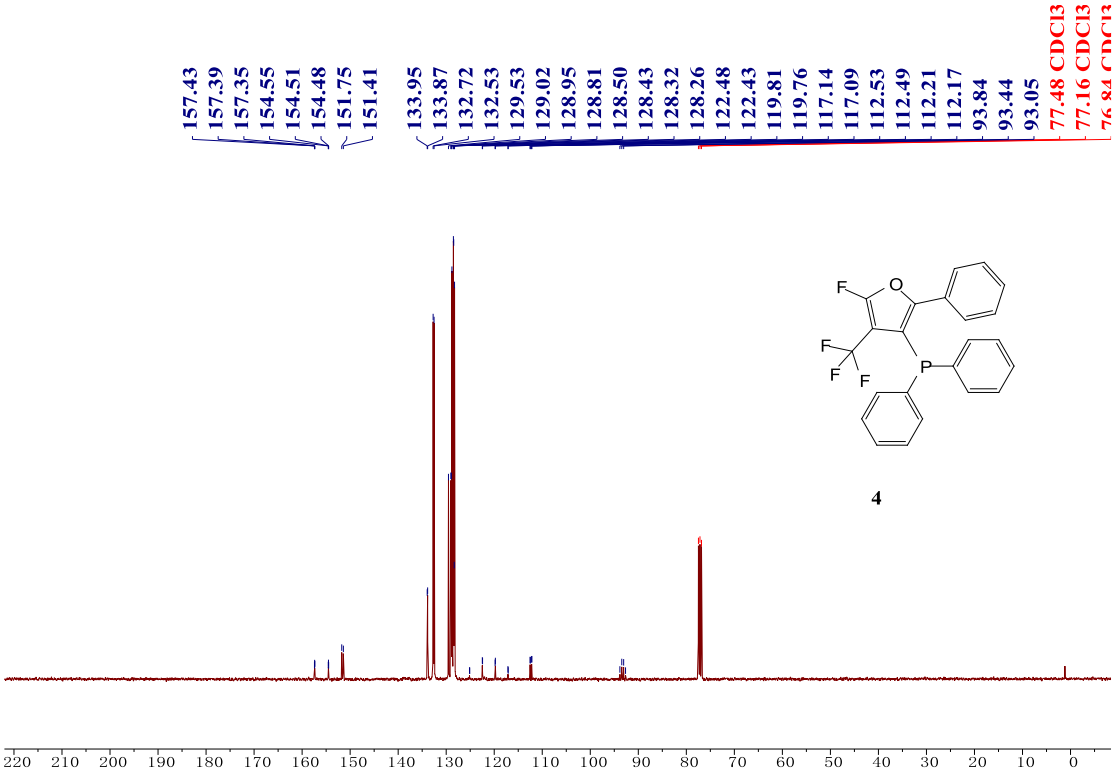
^{19}F NMR spectra of the product **4** (376 MHz, $CDCl_3$):



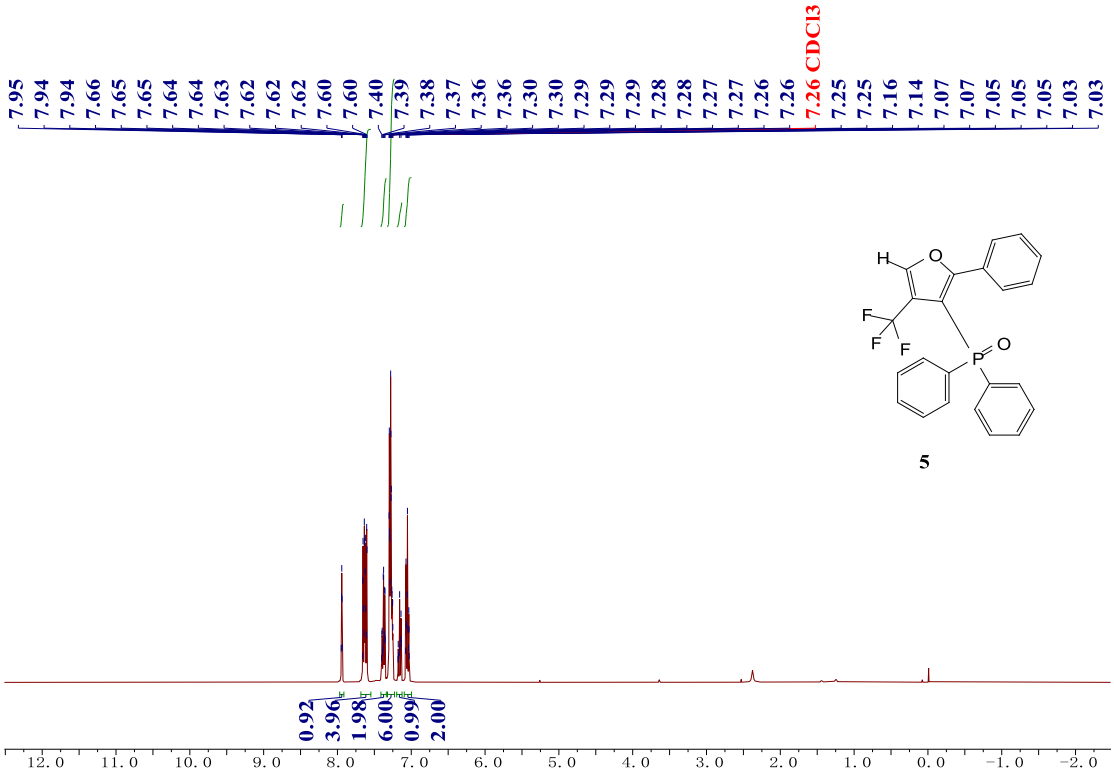
^{31}P NMR spectra of the product **4** (162 MHz, $CDCl_3$):



^{13}C NMR spectra of the product **4** (100 MHz, $CDCl_3$):

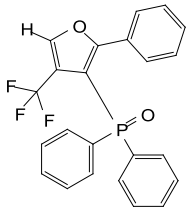


^{1}H NMR spectra of the product **5** (400 MHz, $CDCl_3$):



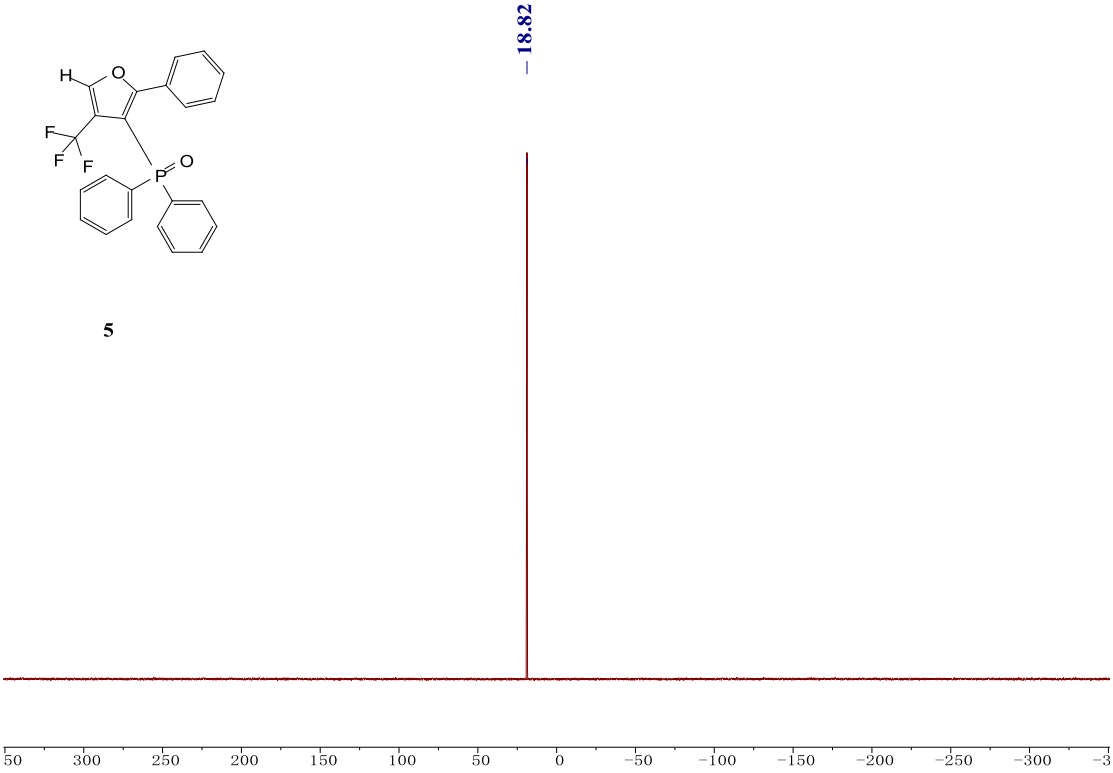
5

^{19}F NMR spectra of the product **5** (376 MHz, $CDCl_3$):

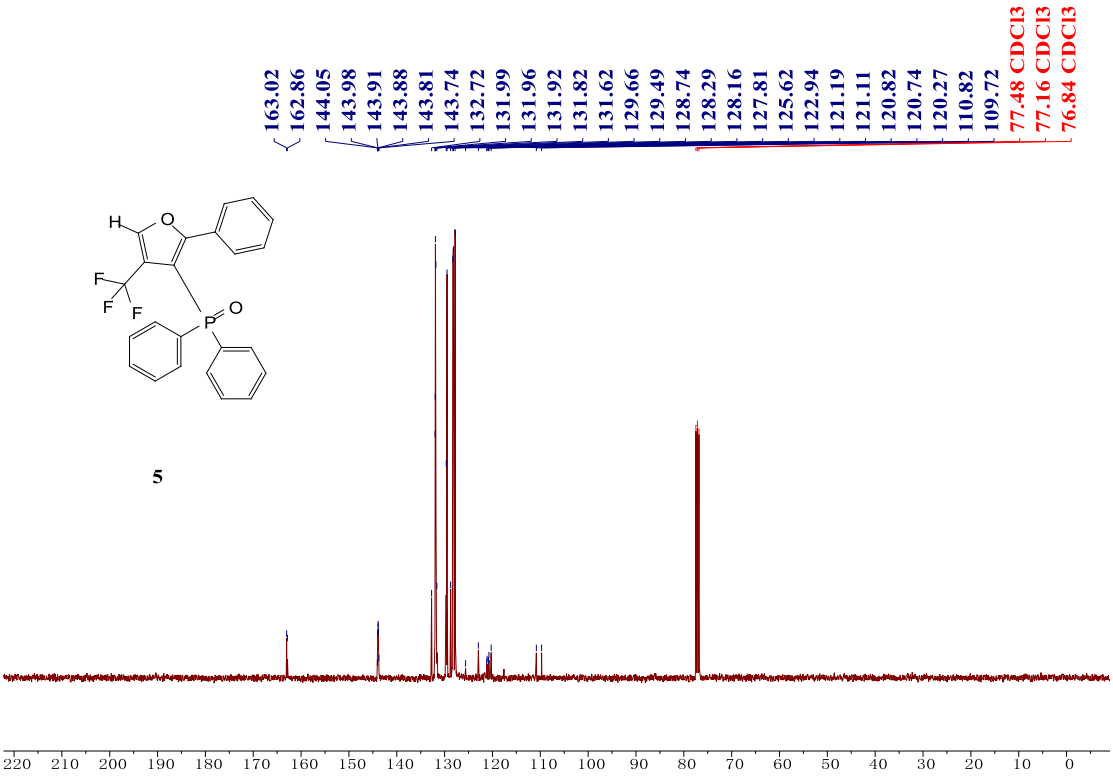


5

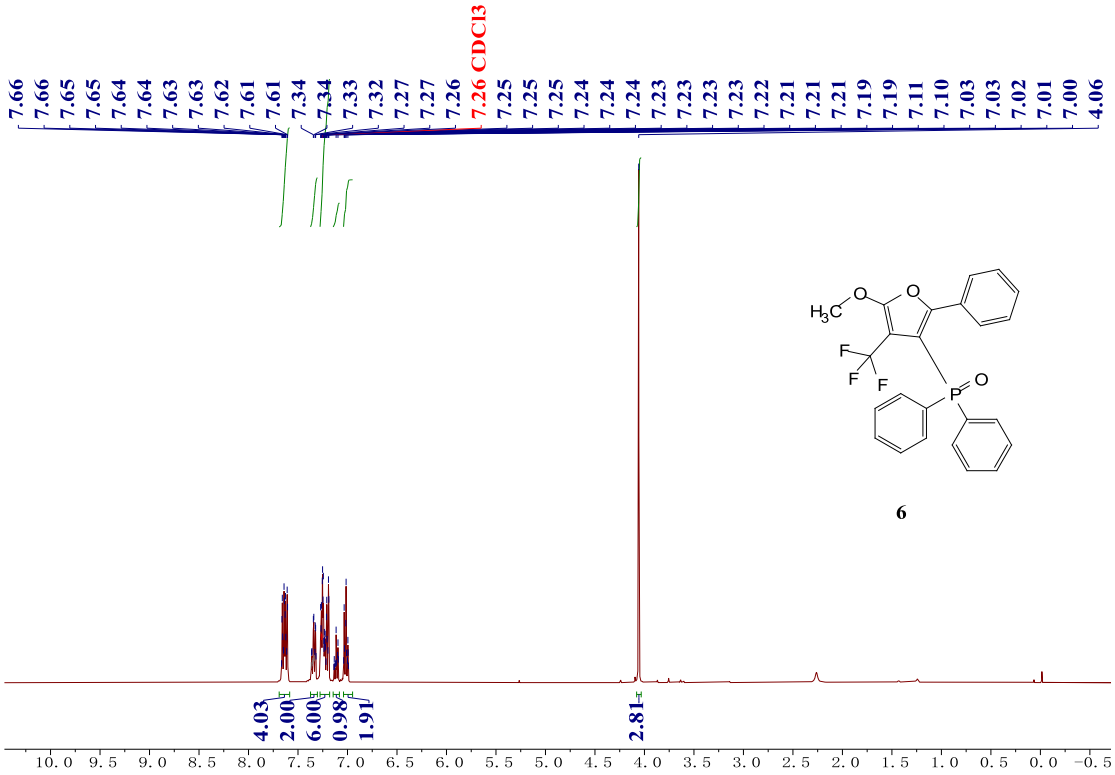
^{31}P NMR spectra of the product **5** (162 MHz, $CDCl_3$):



^{13}C NMR spectra of the product **5** (100 MHz, $CDCl_3$):

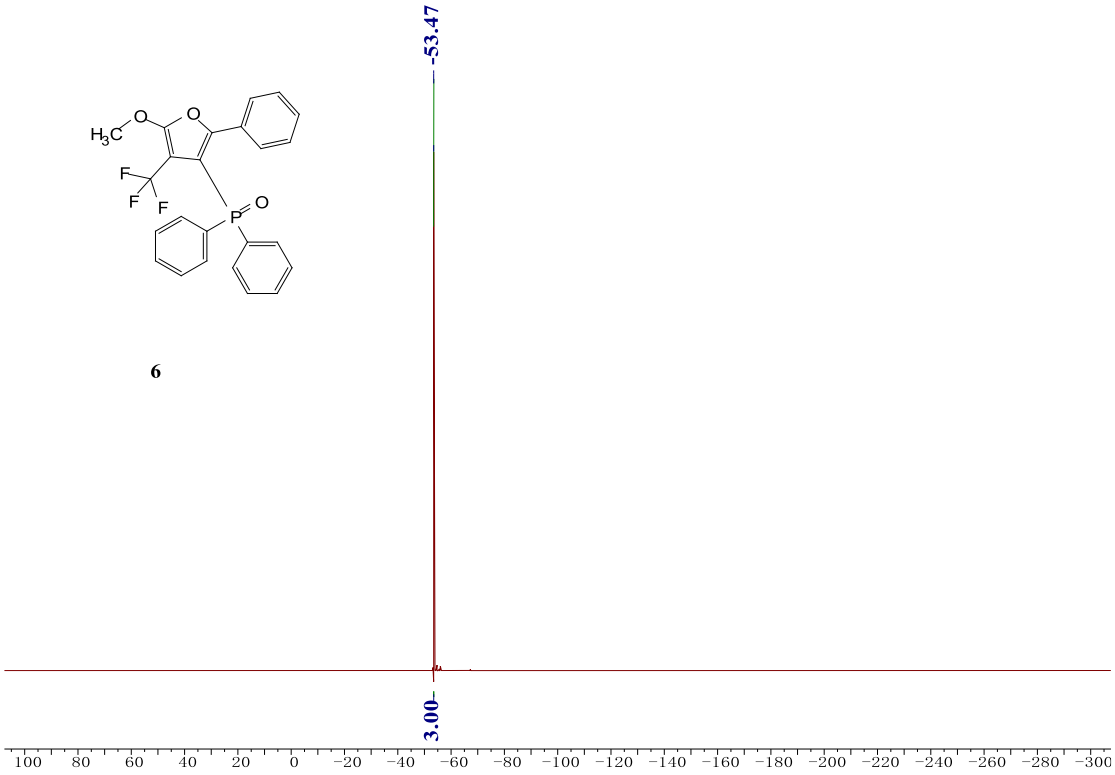


^{1}H NMR spectra of the product **6** (400 MHz, $CDCl_3$):



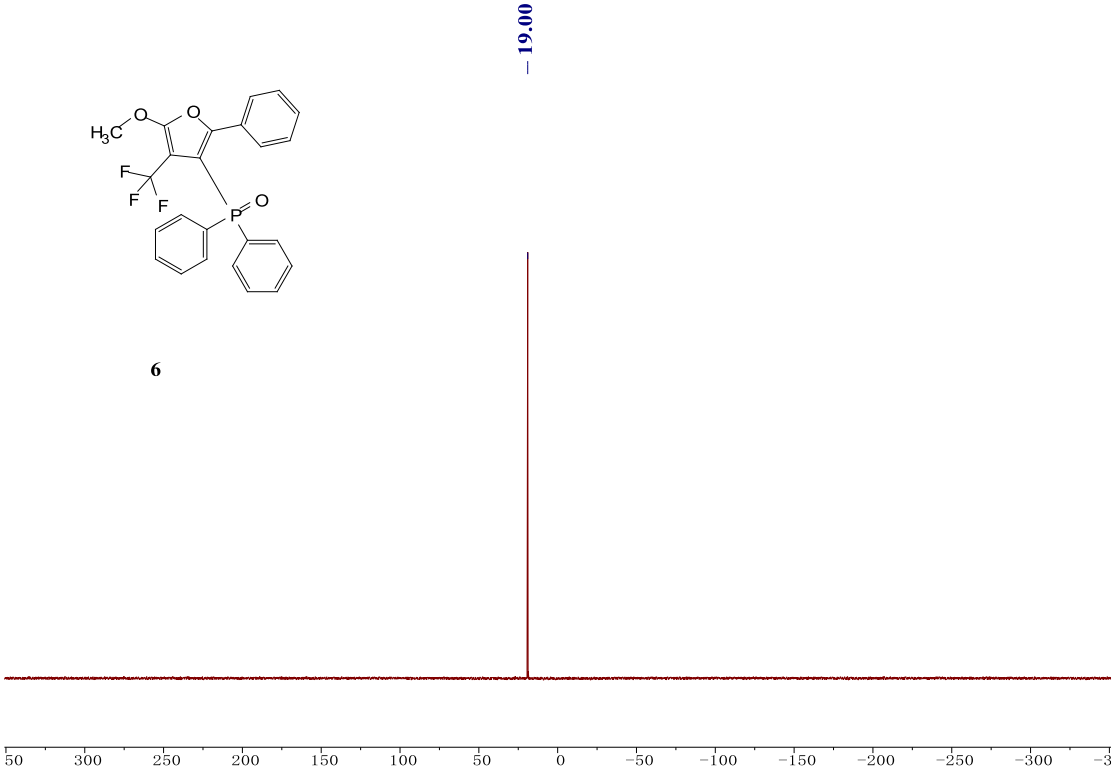
6

^{19}F NMR spectra of the product **6** (376 MHz, $CDCl_3$):

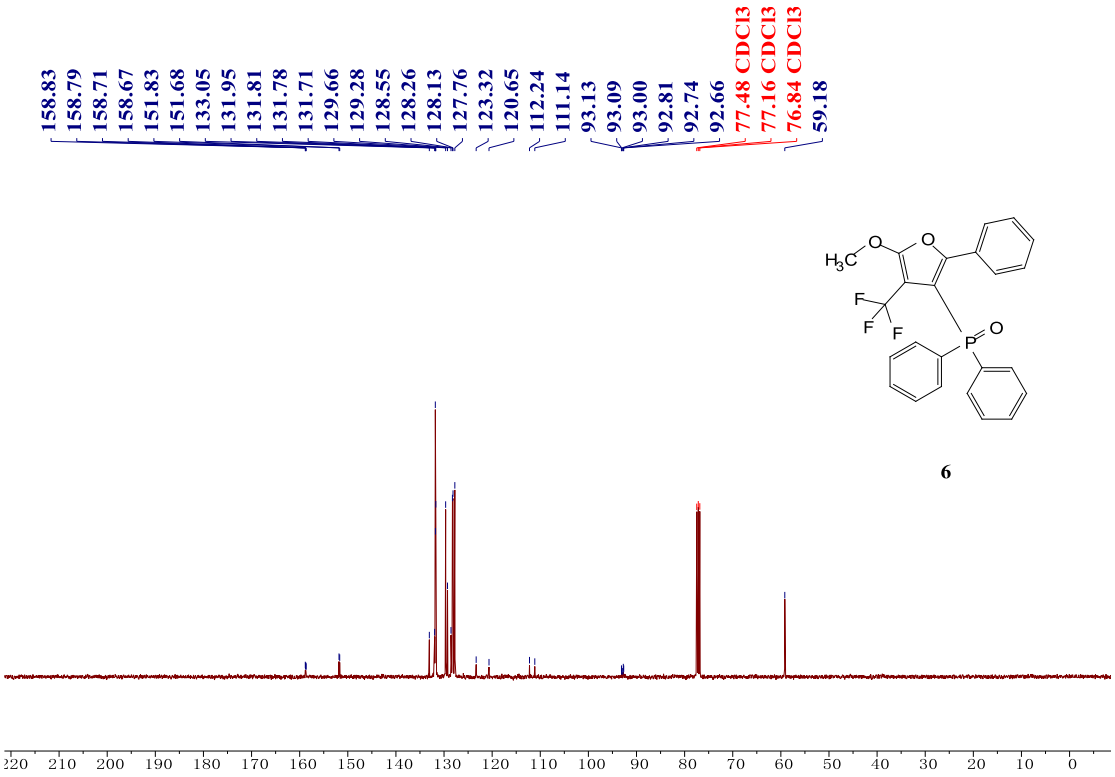


6

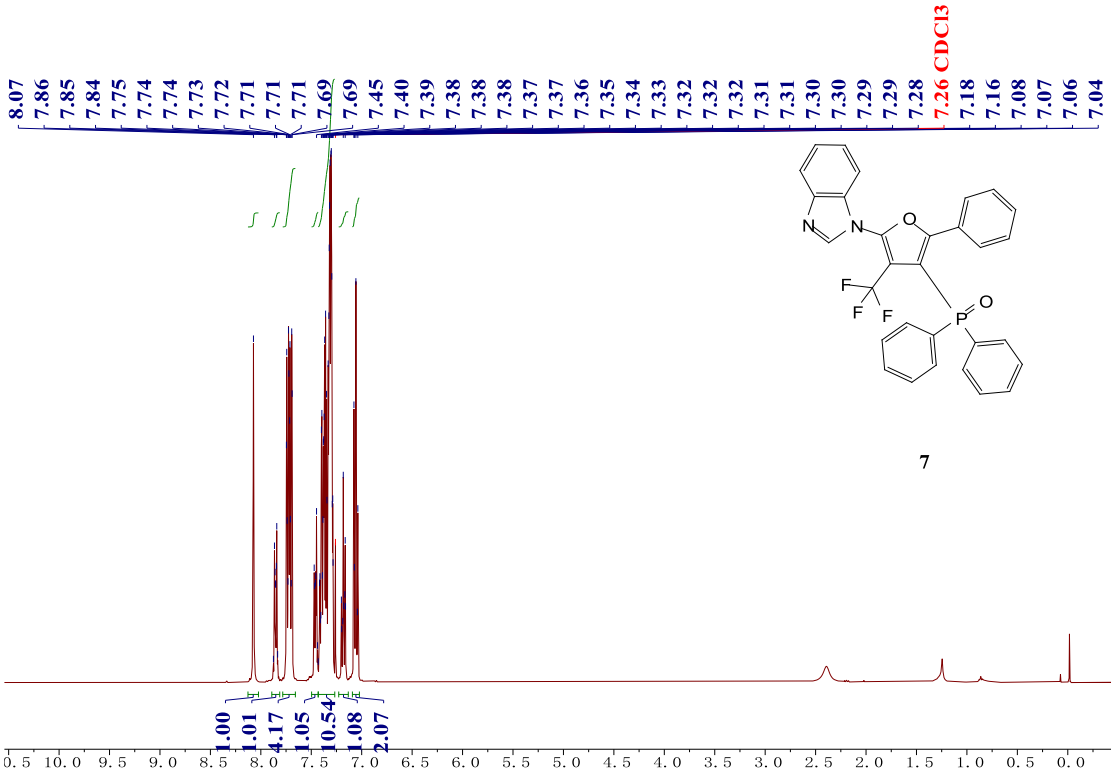
^{31}P NMR spectra of the product **6** (162 MHz, $CDCl_3$):



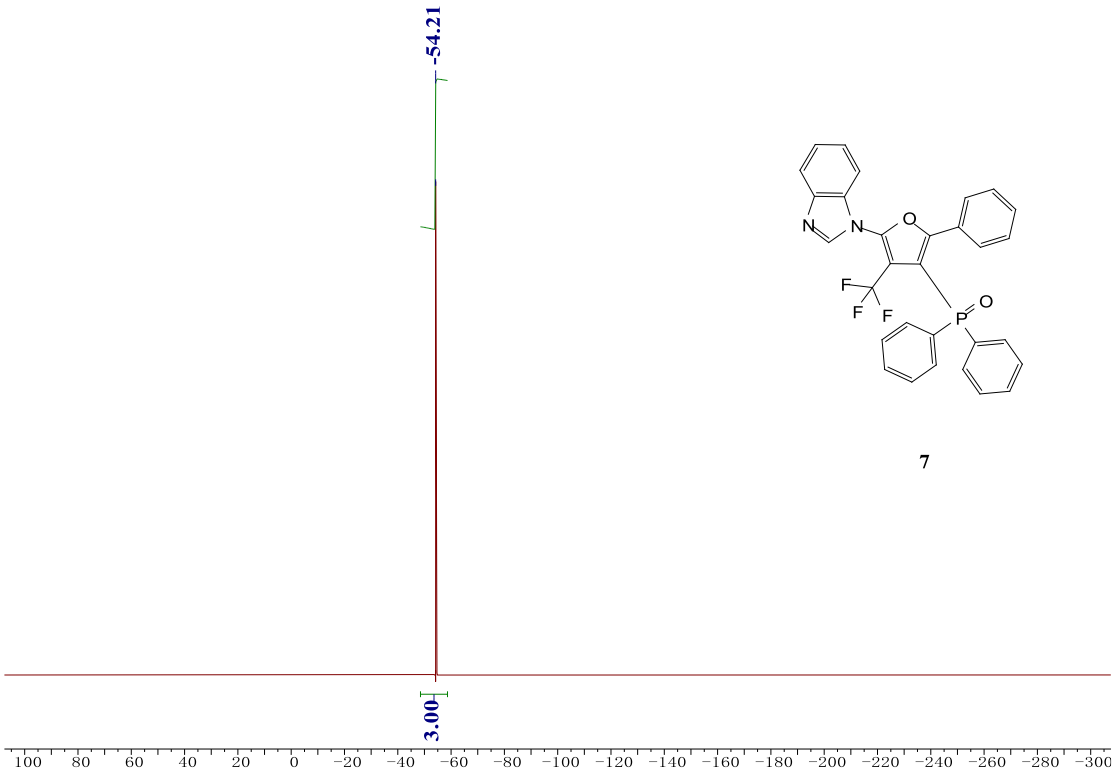
^{13}C NMR spectra of the product **6** (100 MHz, $CDCl_3$):



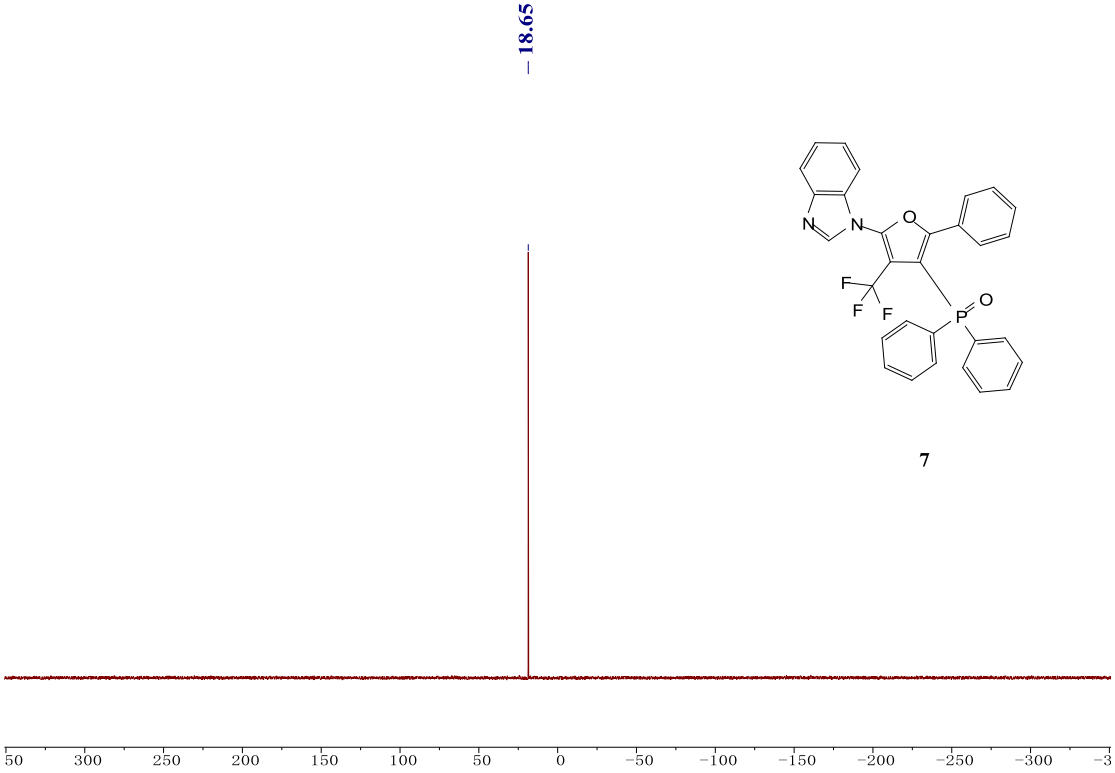
^{1}H NMR spectra of the product **7** (400 MHz, $CDCl_3$):



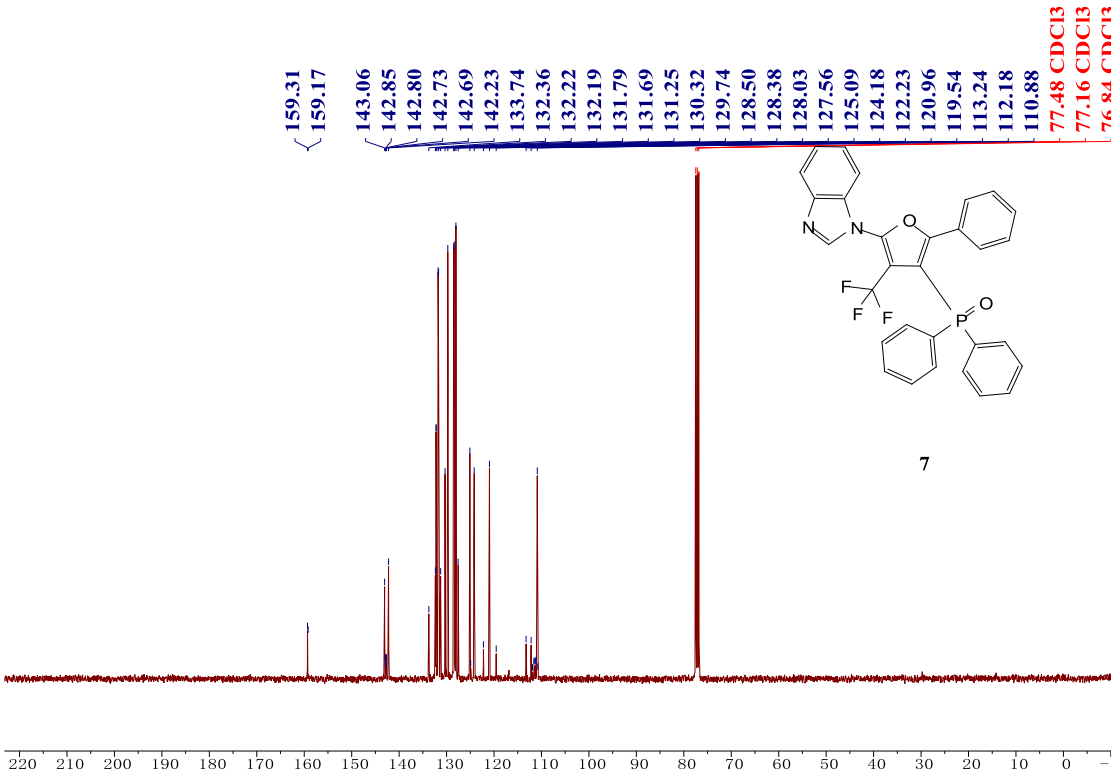
^{19}F NMR spectra of the product **7** (376 MHz, $CDCl_3$):



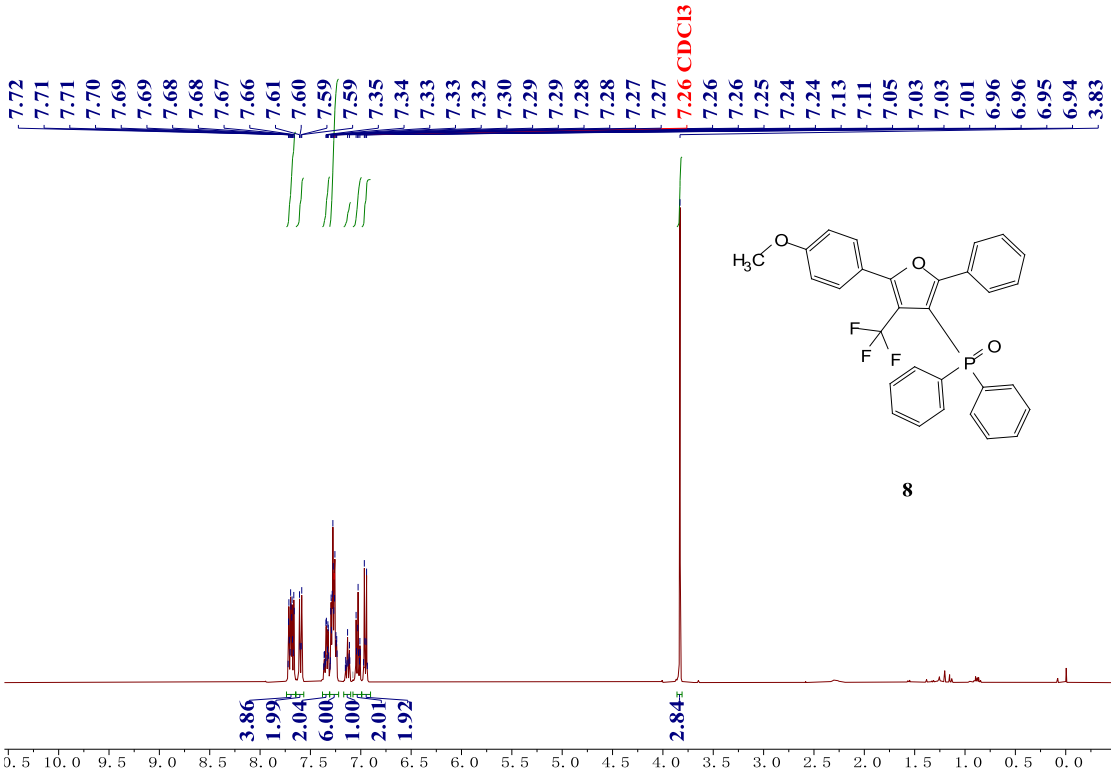
^{31}P NMR spectra of the product **7** (162 MHz, $CDCl_3$):



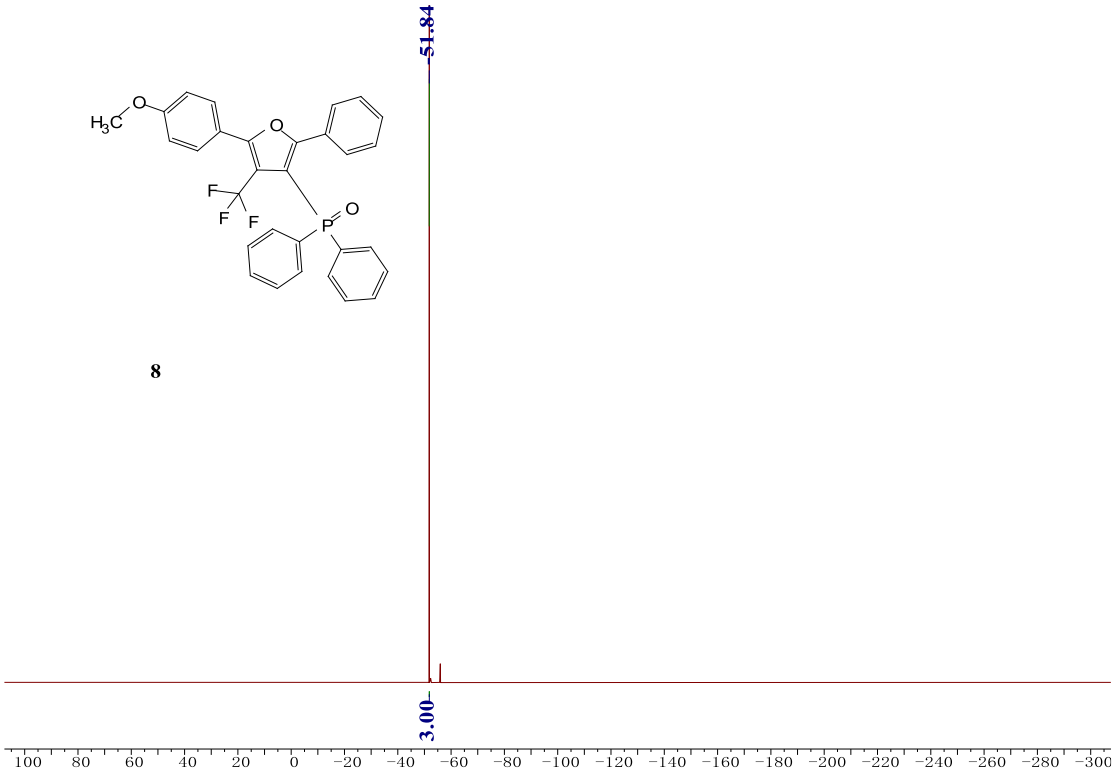
^{13}C NMR spectra of the product **7** (100 MHz, $CDCl_3$):



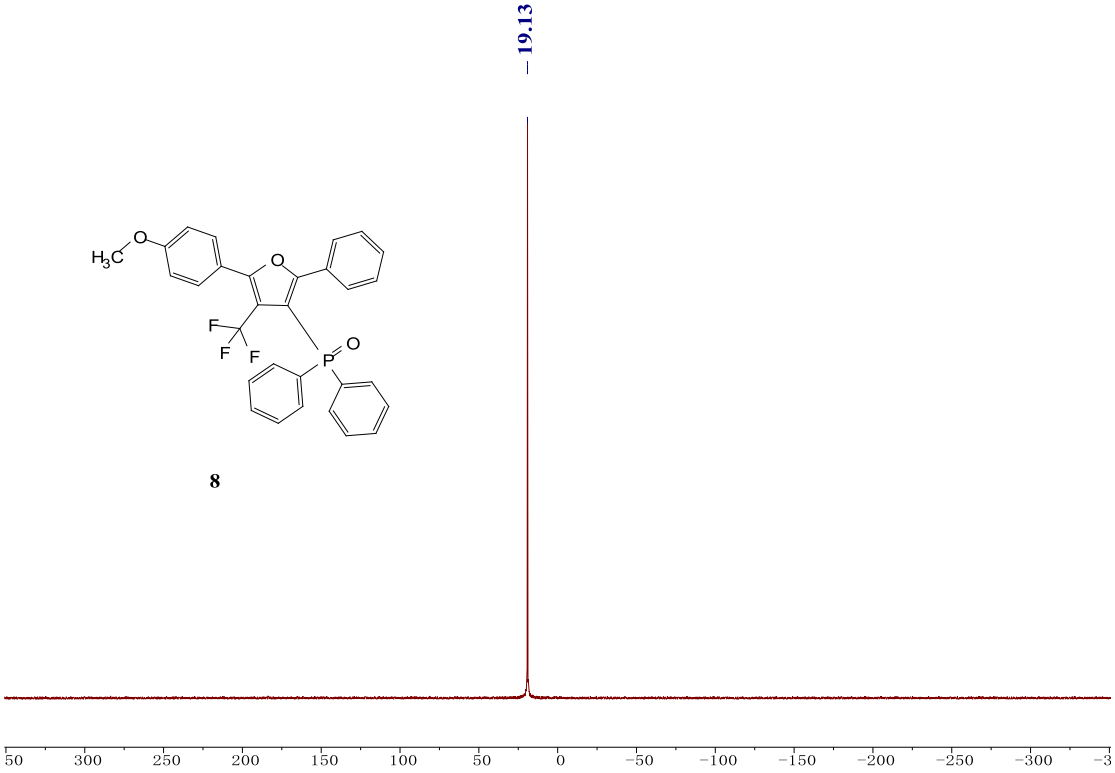
^{1}H NMR spectra of the product **8** (400 MHz, $CDCl_3$):



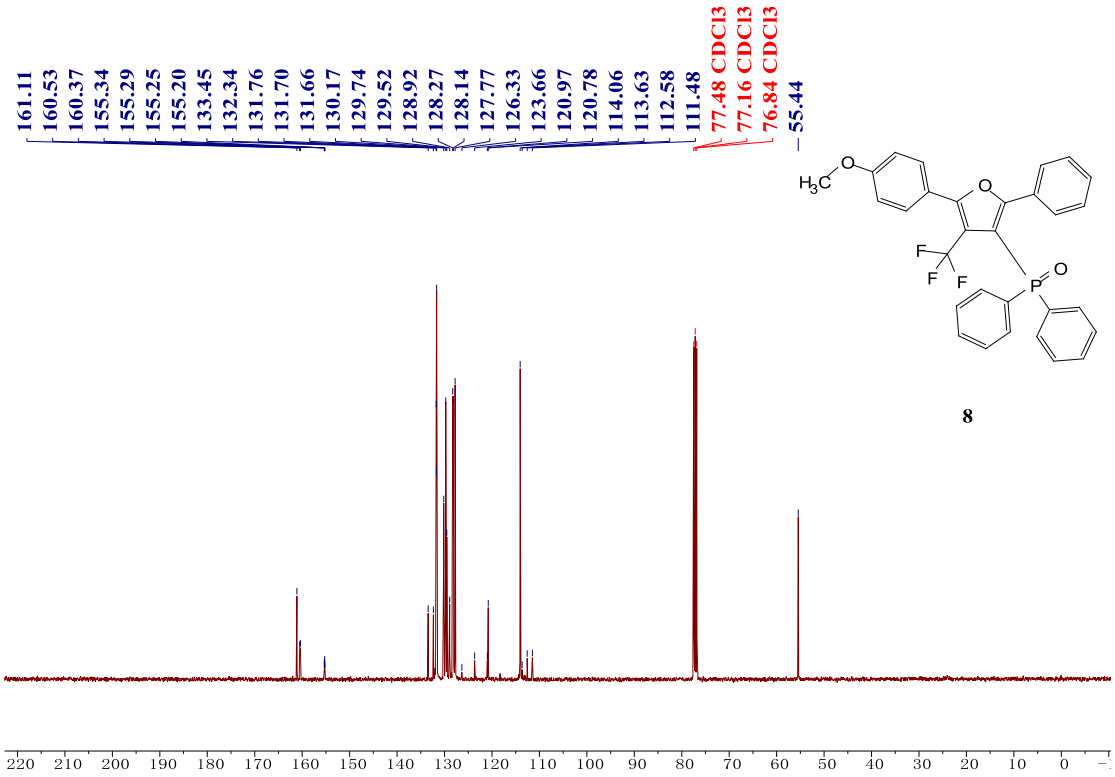
^{19}F NMR spectra of the product **8** (376 MHz, $CDCl_3$):



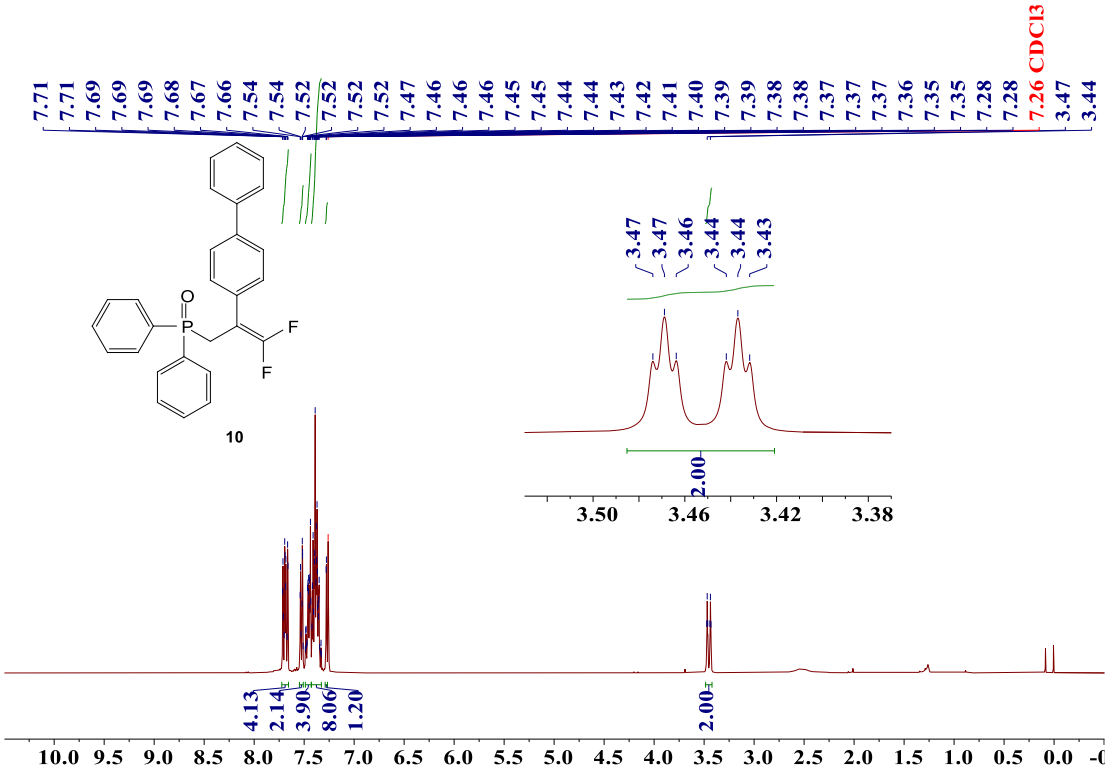
^{31}P NMR spectra of the product **8** (162 MHz, $CDCl_3$):



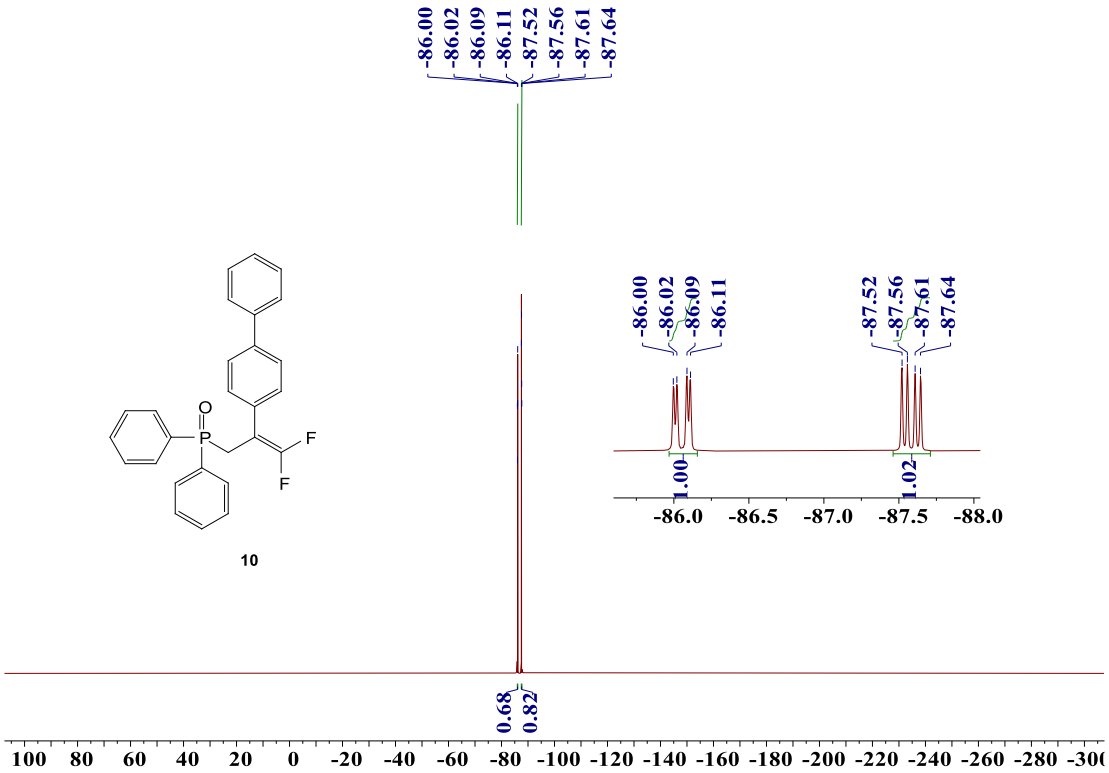
^{13}C NMR spectra of the product **8** (100 MHz, $CDCl_3$):



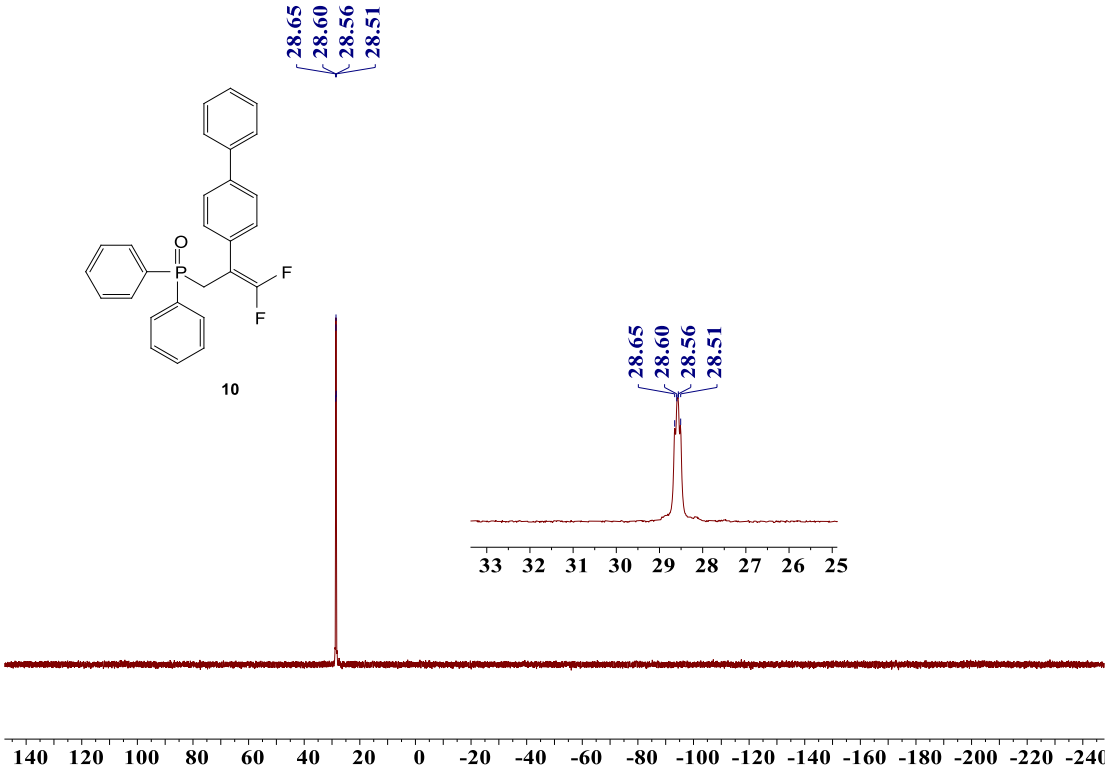
^{1}H NMR spectra of the product **10** (400 MHz, $CDCl_3$)



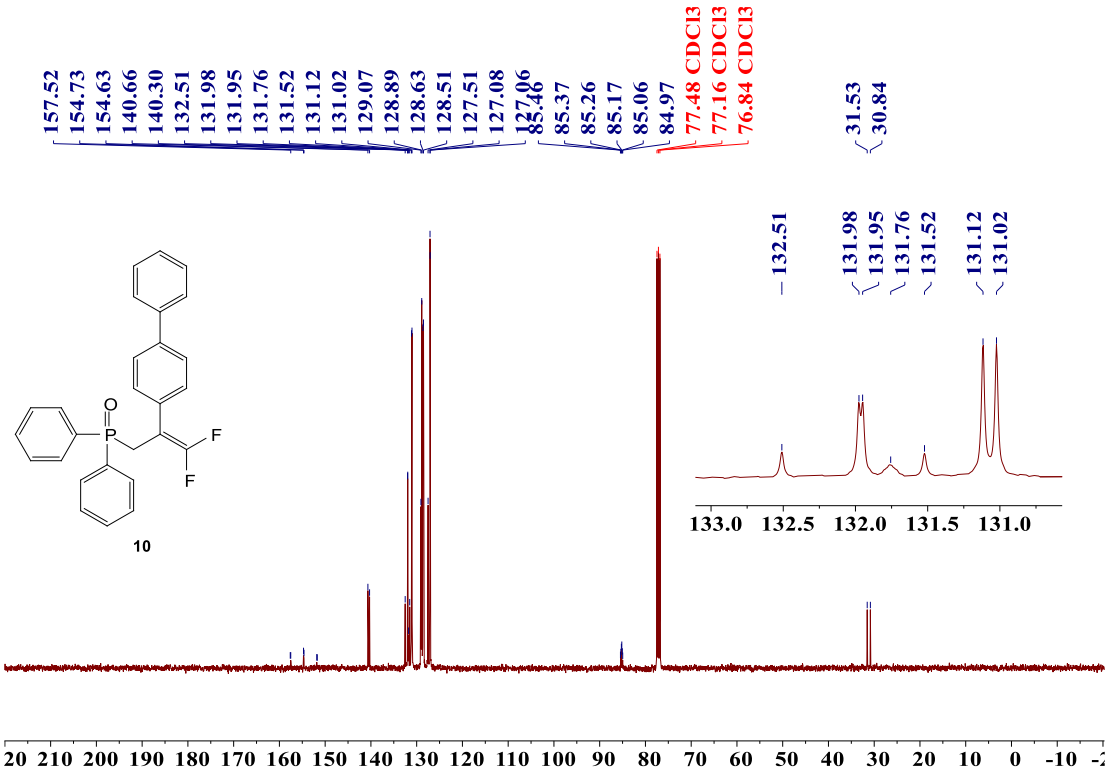
^{19}F NMR spectra of the product **10** (376 MHz, $CDCl_3$)



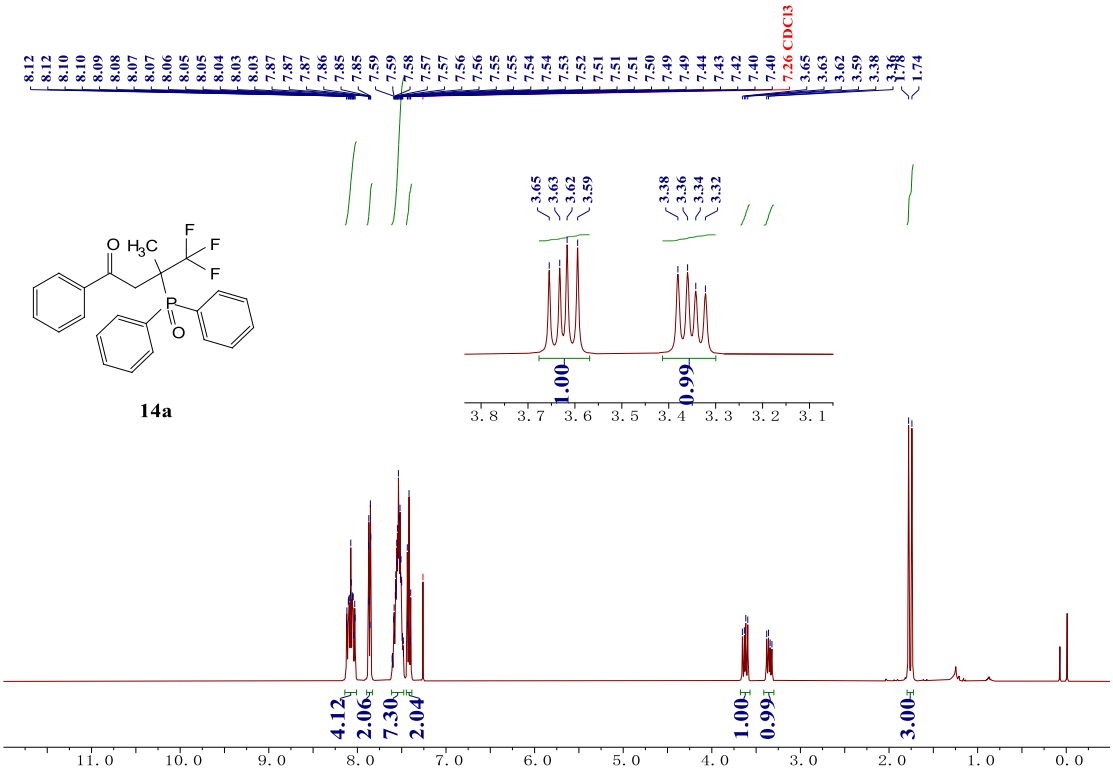
^{31}P NMR spectra of the product **10** (162 MHz, $CDCl_3$)



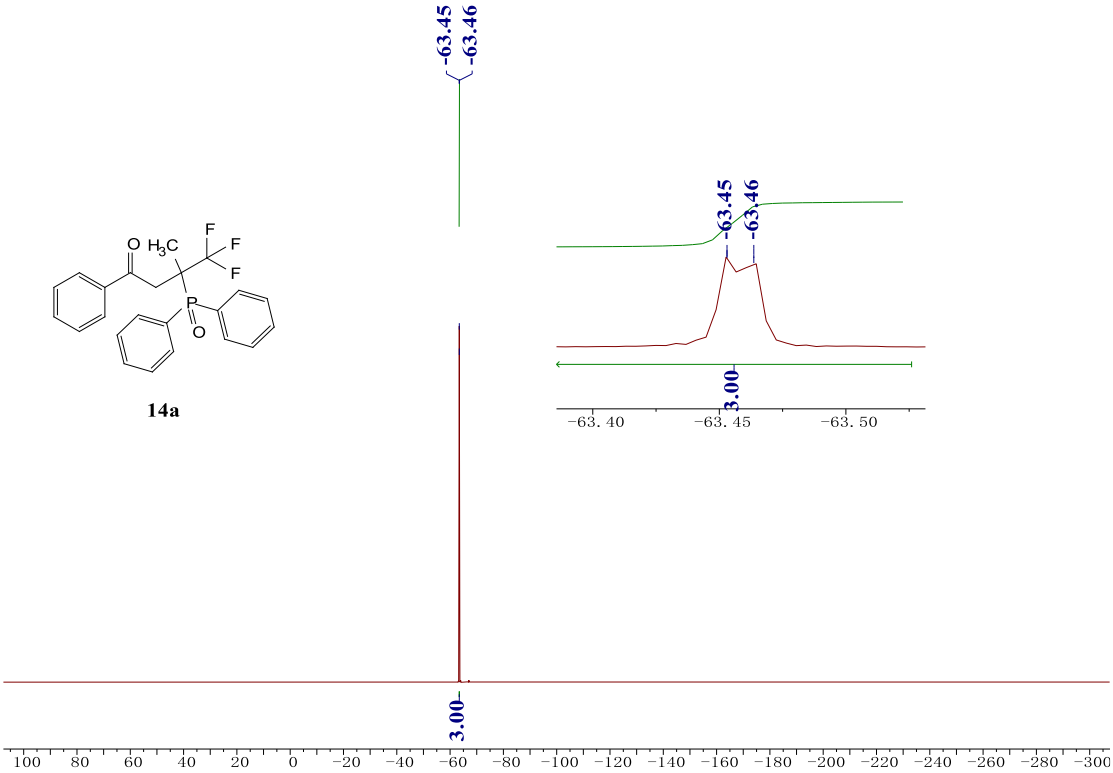
^{13}C NMR spectra of the product **10** (100 MHz, $CDCl_3$)



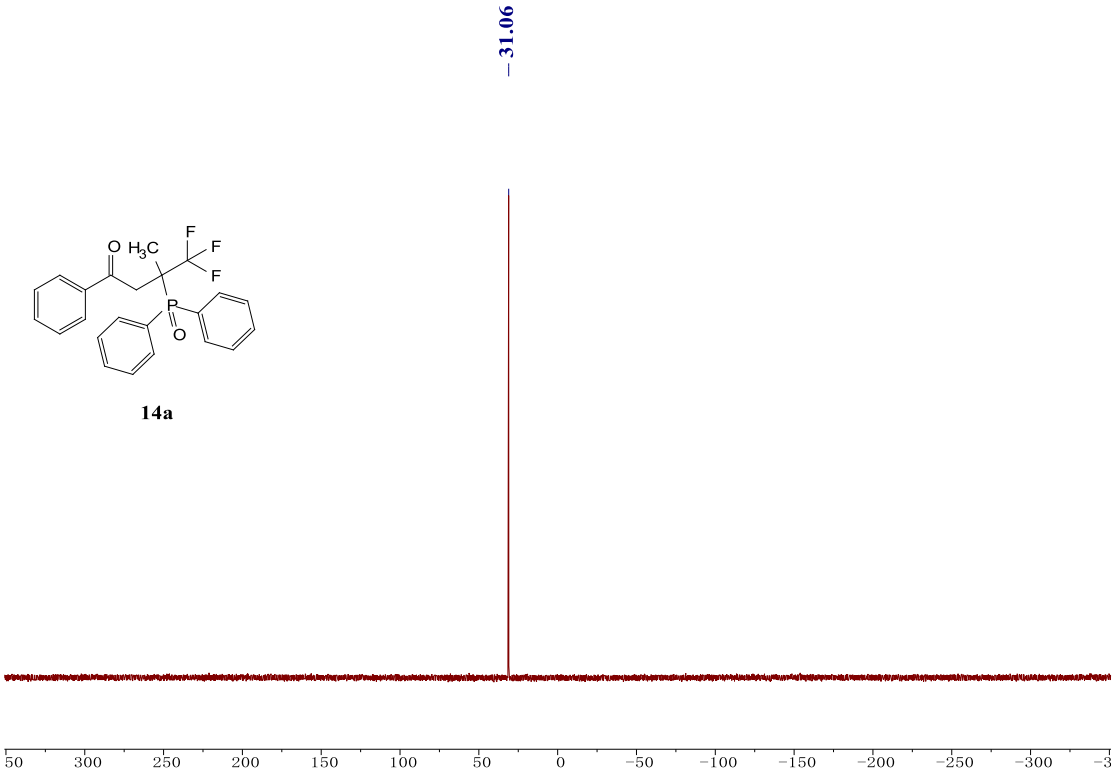
^{1}H NMR spectra of the product **14a** (400 MHz, $CDCl_3$)



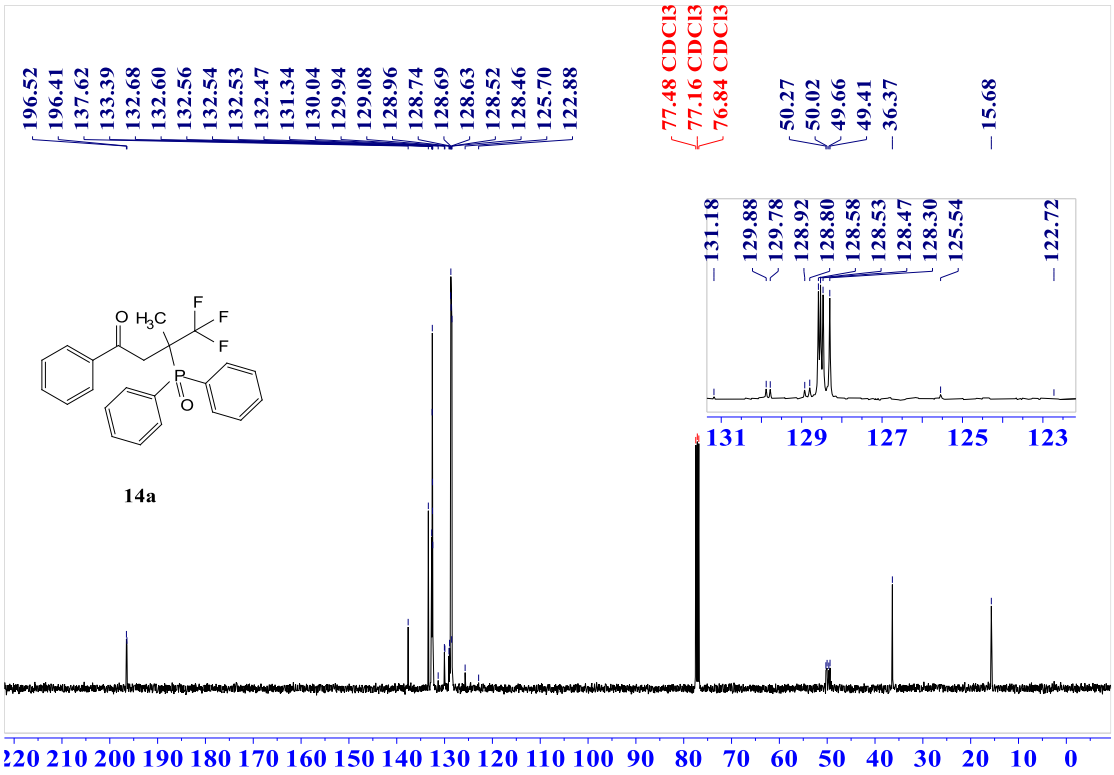
^{19}F NMR spectra of the product **14a** (376 MHz, $CDCl_3$)



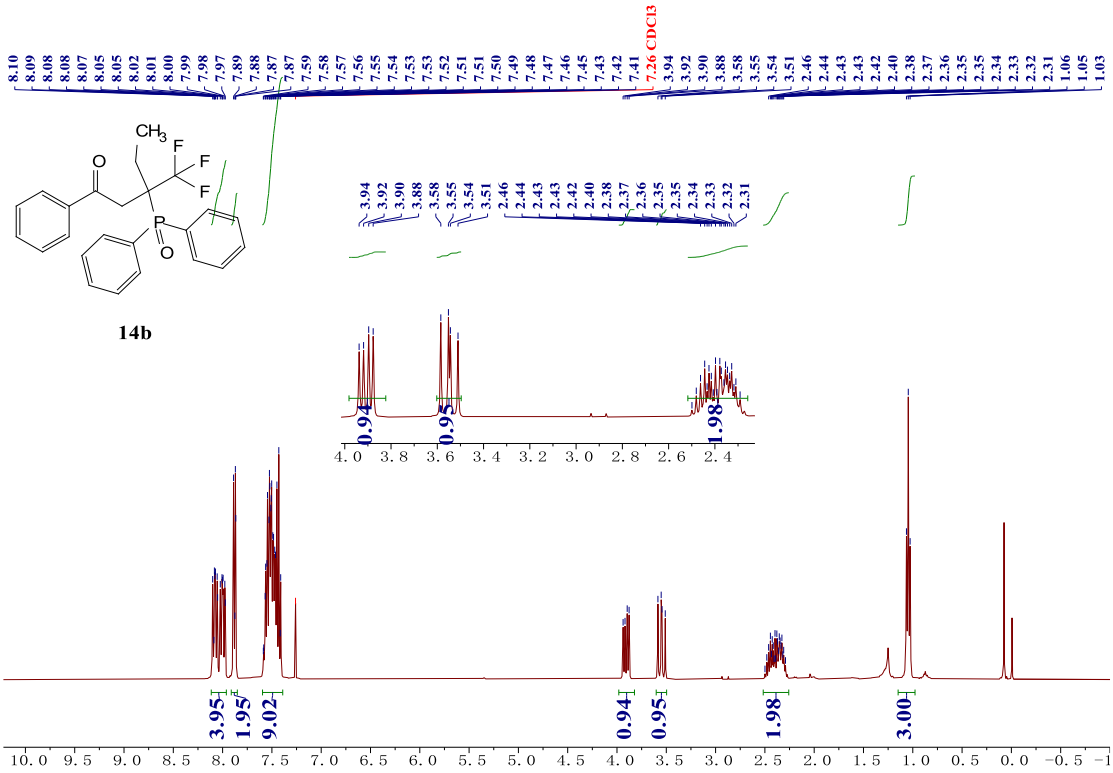
^{31}P NMR spectra of the product **14a** (162 MHz, $CDCl_3$)



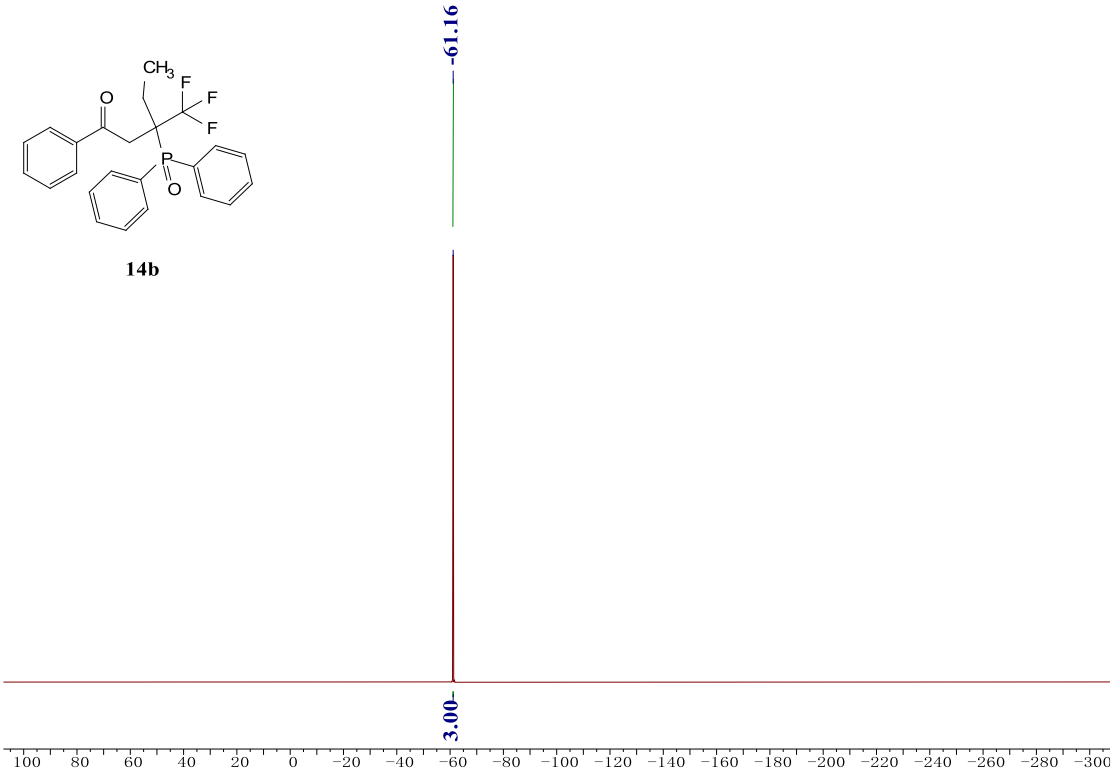
^{13}C NMR spectra of the product **14a** (100 MHz, $CDCl_3$)



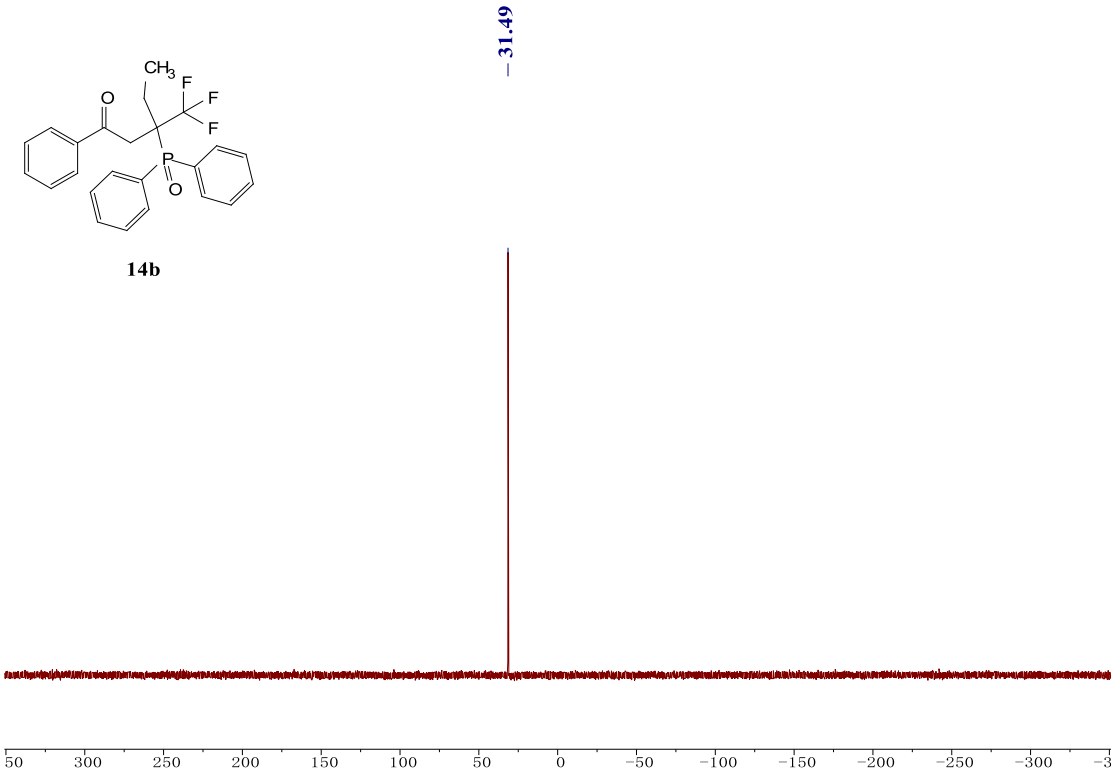
^{1}H NMR spectra of the product **14b** (400 MHz, $CDCl_3$)



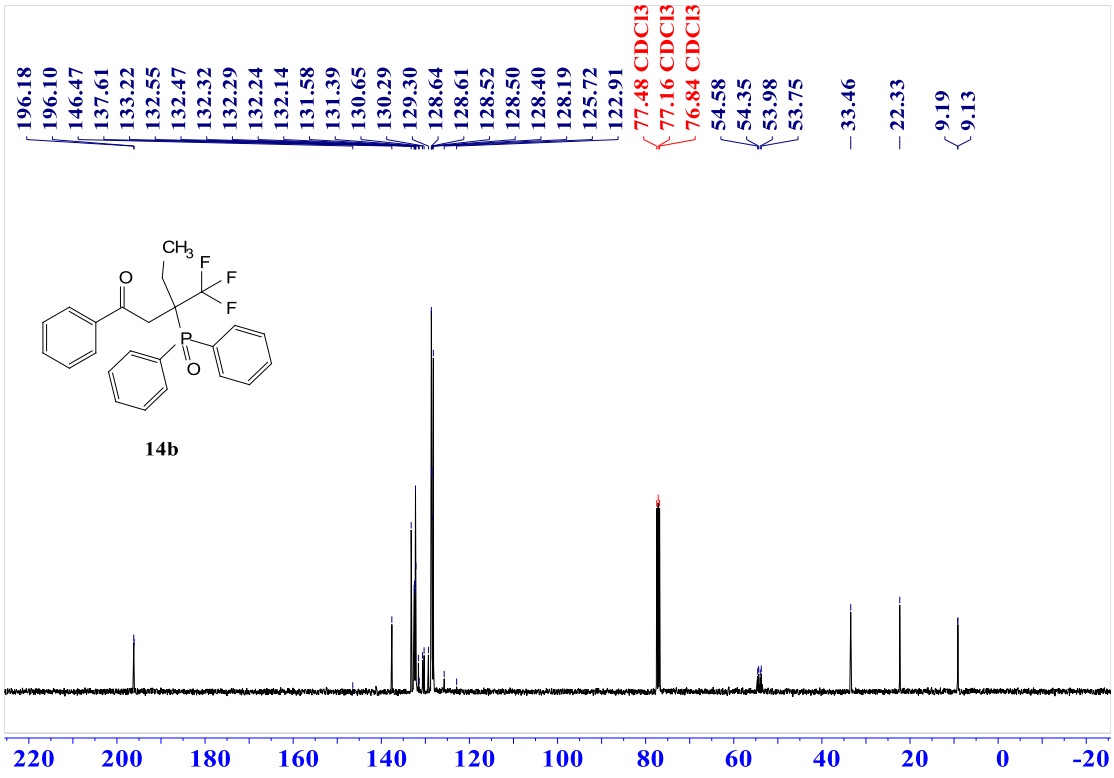
^{19}F NMR spectra of the product **14b** (376 MHz, $CDCl_3$)



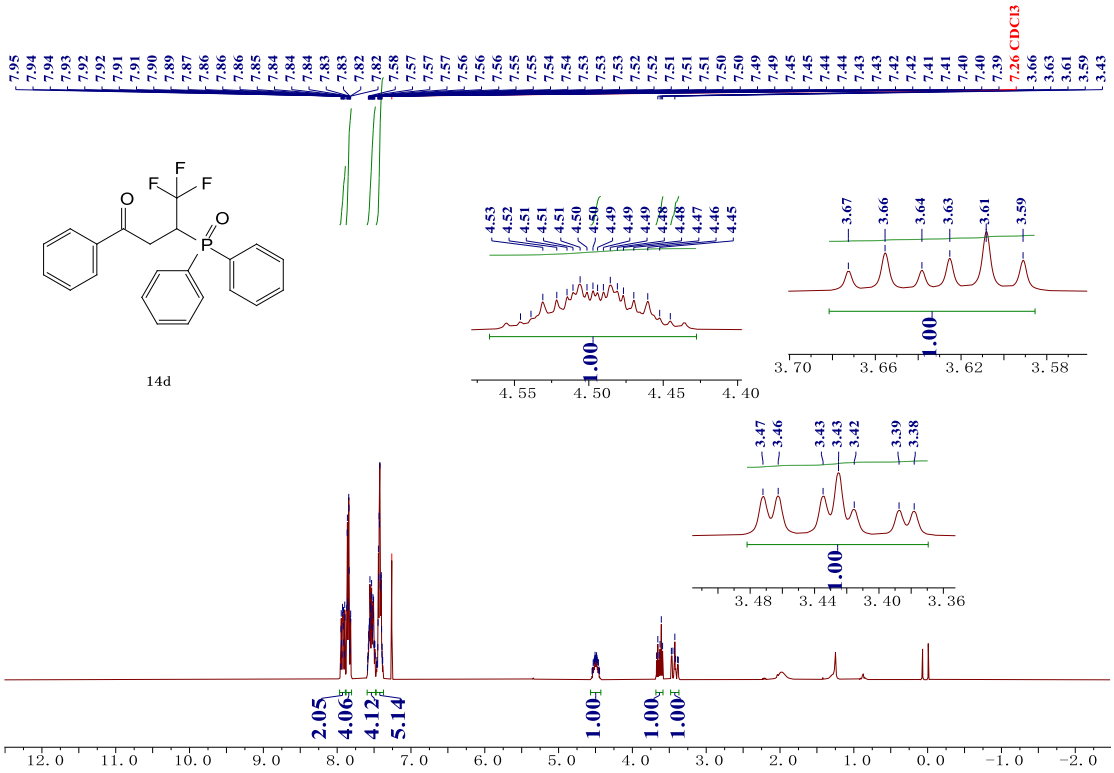
^{31}P NMR spectra of the product **14b** (162 MHz, $CDCl_3$)



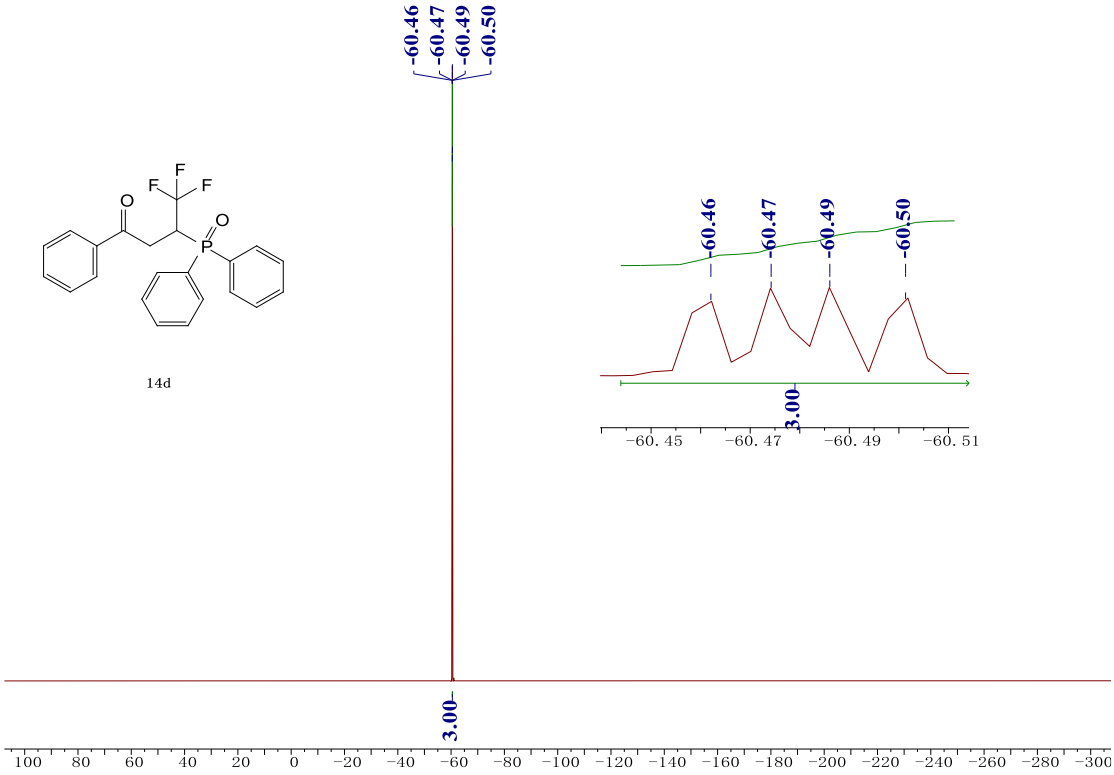
^{13}C NMR spectra of the product **14b** (100 MHz, $CDCl_3$)



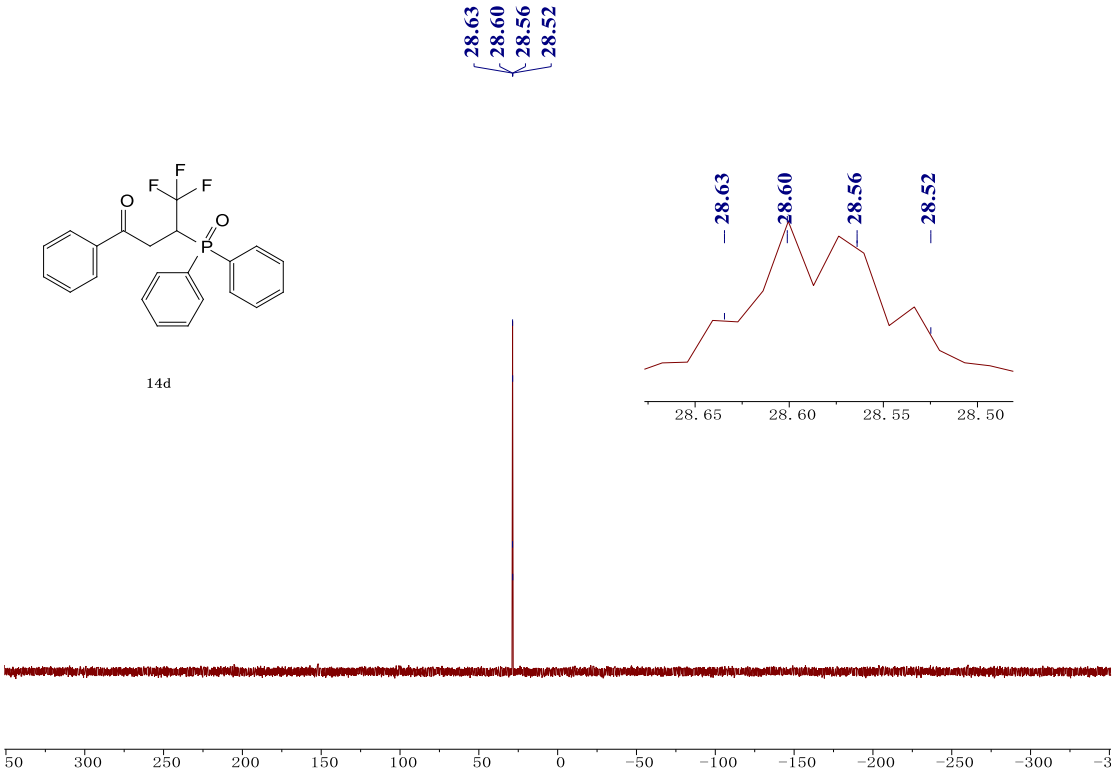
^{1}H NMR spectra of the product **14d** (400 MHz, $CDCl_3$)



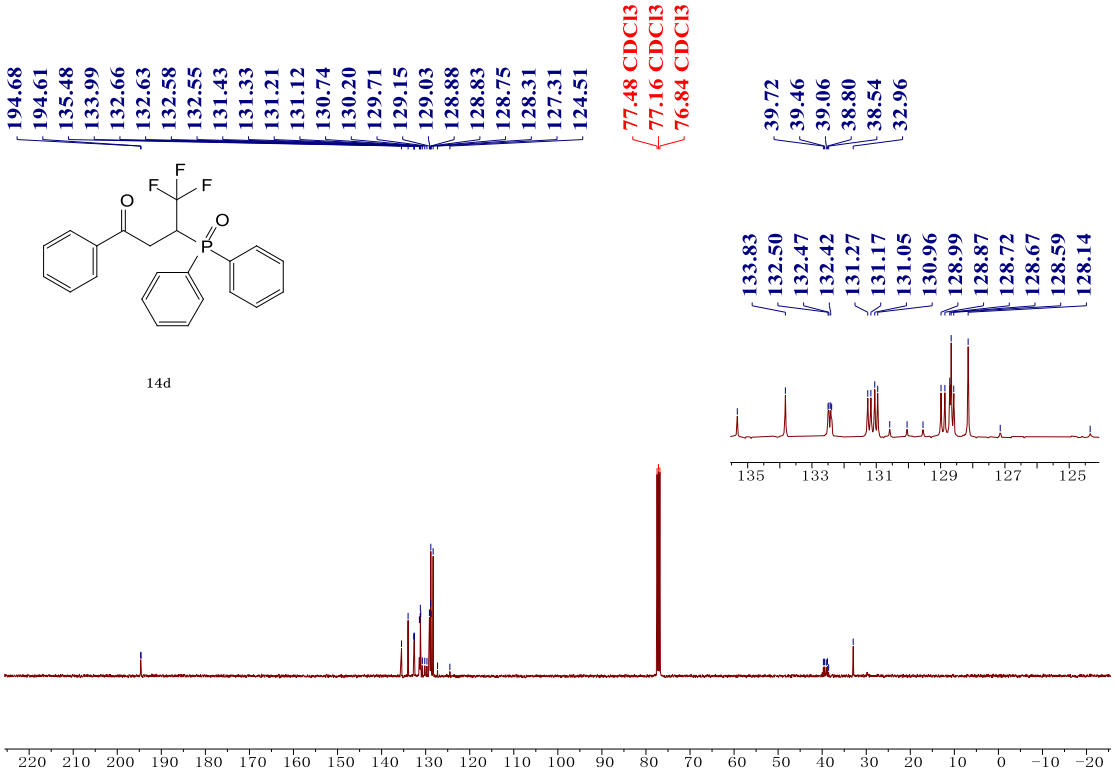
^{19}F NMR spectra of the product **14d** 376 MHz, $CDCl_3$)



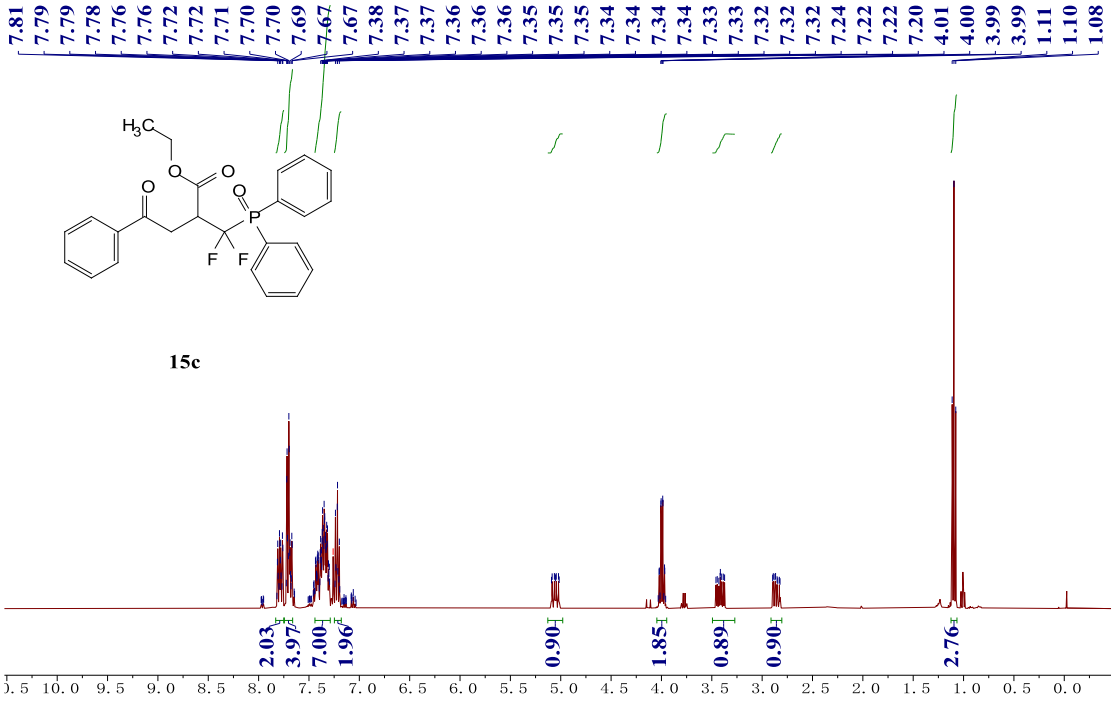
^{31}P NMR spectra of the product **14d** (162 MHz, $CDCl_3$)



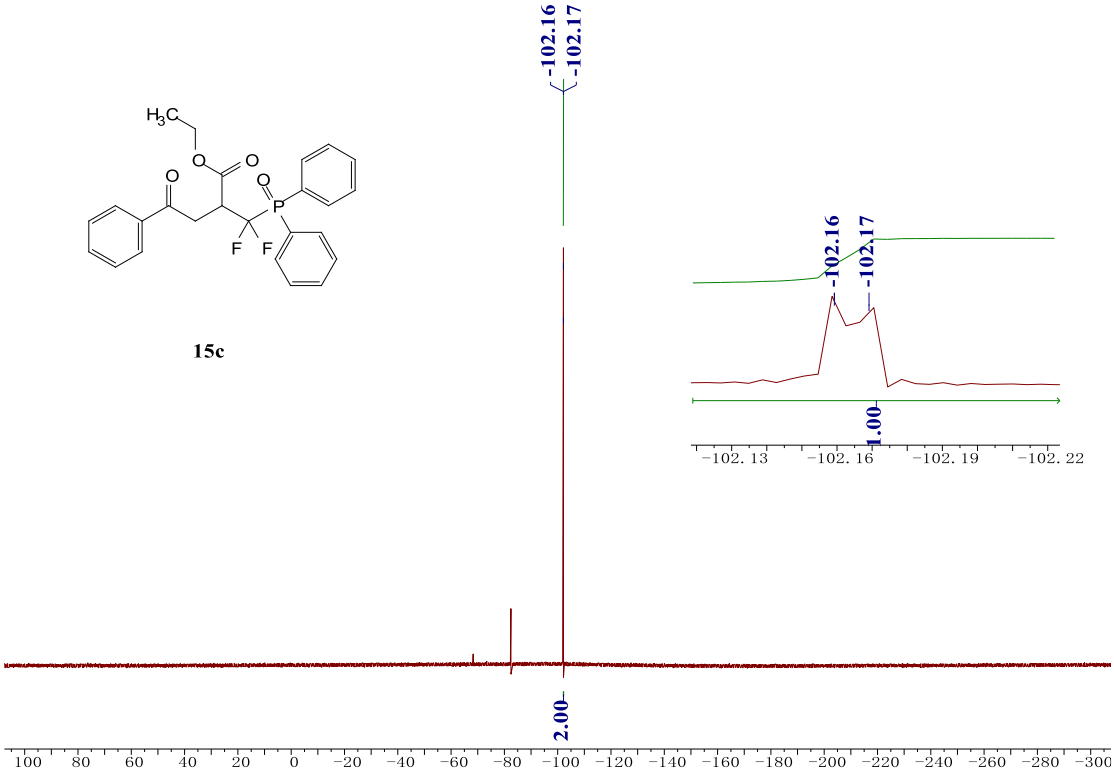
^{13}C NMR spectra of the product **14d** (100 MHz, $CDCl_3$)



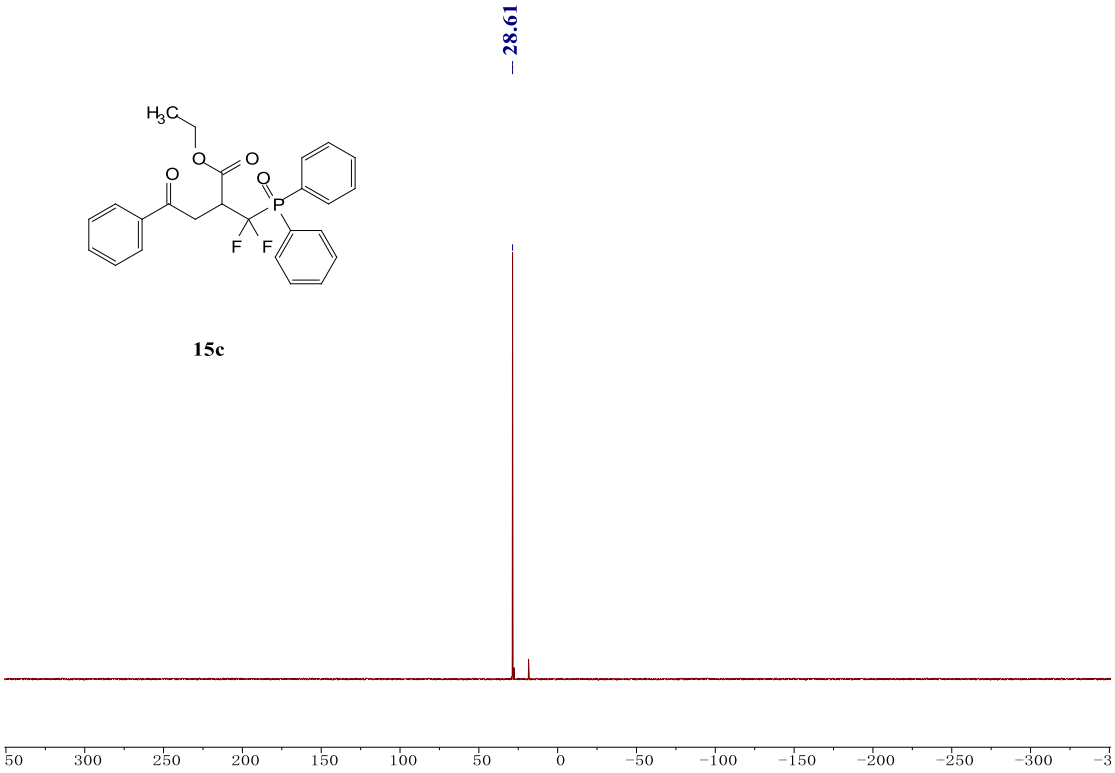
^{1}H NMR spectra of the product **15c** (400 MHz, $CDCl_3$)



^{19}F NMR spectra of the product **15c** 376 MHz, $CDCl_3$)



^{31}P NMR spectra of the product **15c** (162 MHz, $CDCl_3$)



^{13}C NMR spectra of the product **15c** (100 MHz, $CDCl_3$)