Tunable vicinal, geminal diphosphorylation and C-N bond phosphorylation of enaminones toward divergent phosphorylated ketone derivatives

Dingsheng Cao,[a] Chaoli Wang,[a] Jie-Ping Wan,[a] Chengping Wen,[b,*] Yunyun Liu[a,*]

[a]National Engineering Research Center for Carbohydrate Synthesis, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China.

[b]Institute of Basic Research in Clinical Medicine, College of Basic Medical Science, Zhejiang Chinese Medical University, Hangzhou, China.

Email: chemliuyunyun@jxnu.edu.cn; wengcp@yeah.net

Contents

General experimental information……S2

Data of optimization on selective reactions……S2-S4

Deuterium isotope labelling experiments……S5-S7

General procedure for the synthesis of **3**……S7

Procedure for the 1 mmol scale reaction for the synthesis of **3a**……S8

Characterization data of compounds **3**……S8-S25

General procedure for the synthesis of **4**……S15

Procedure for the 1 mmol scale reaction for the synthesis of **4a**……S16

Characterization data of compounds **4**……S16-S24

General procedure for the synthesis of **3**……S24

Procedure for the 1 mmol scale reaction for the synthesis of **5a**……S24-S25

Characterization data of compounds **5**……S25-S30

Synthetic procedure and characterization data of compound **7**……S30-S31

Synthetic procedure and characterization data of compound **8**……S31-S32

Synthetic procedure and characterization data of compound **10**……S32-S33

Synthetic procedure and characterization data of compound **12**……S33

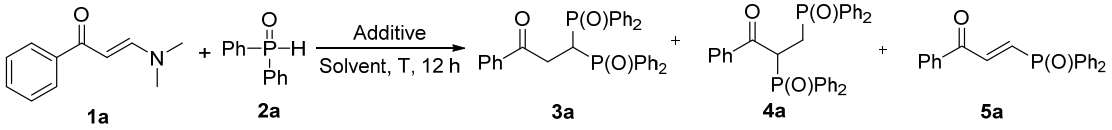
References……S33

NMR spectra of all products……S34-S116

General experimental information

All enaminones **1** were synthesized following literature process.[1] All other chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. The NMR spectra were recorded in 400 MHz apparatus in DMSO-d_6 or $CDCl_3$. The frequencies for ^1H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR test are 400 MHz, 100 MHz, 162 MHz and 376 MHz, respectively. The chemical shifts were reported in ppm with TMS as internal standard. Melting points were tested in X-4A instrument without correcting temperature and the HRMS data for all new products were obtained under ESI model with TOF analyzer.

Table S1 Optimization on the conditions for the geminal diphosphorylation[a]

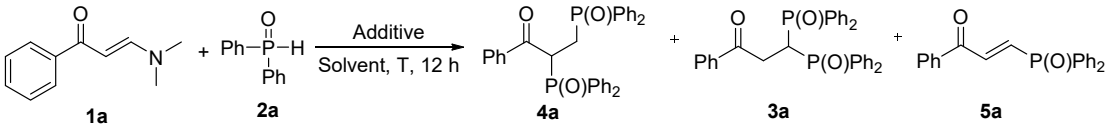


Entry	Promoter	Solvent	T (°C)	Yield (**3a**/**4a**/**5a**%)[b]
1	-	MeCN	50	17/0/0
2	TMSCl	MeCN	50	63/trace/0
3	AcOH	MeCN	50	39/trace/0
4	$KHSO_4$	MeCN	50	75/trace/0
5	TFA	MeCN	50	80/0/0
6	TFA	EtOH	50	75/0/0
7	TFA	THF	50	78/0/0
8	TFA	DMF	50	69/0/trace
9	TFA	DMSO	50	78/0/0
10	TFA	DCM	50	76/0/0
11	TFA	toluene	50	77/0/0
12[c]	TFA	MeCN	50	87/0/0
13[d]	TFA	MeCN	50	85/0/0
14[c]	TFA	MeCN	60	91/0/0
15[c]	TFA	MeCN	70	90/0/0

[a]General conditions: **1a** (0.2 mmol), **2a** (3.0 equiv), promoter (2.0 equiv), solvent (2 mL), stirred at 60 °C for 12 h. [b]Isolated yields based on **1a**. [c]With 3.0 equiv TFA. [d]With

4.0 equiv TFA.

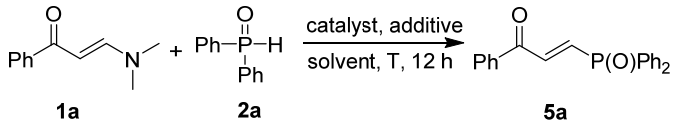
Table S2 Optimization data for the selective vicinal diphosphorylation[a]



Entry	base	Solvent	T (°C)	Yield (**3a**/**4a**/**5a**%)[b]
1	Cs_2CO_3	MeCN	60	52/10/0
2	^{t}BuONa	MeCN	60	55/5/0
3	^{t}BuOK	MeCN	60	60/5/0
4	TBAH	MeCN	60	20/50/0
5	NH_2Na	MeCN	60	trace /20/0
6	^{t}BuOK	THF	60	50/trace/0
7	^{t}BuOK	DCM	60	10/10/0
8	^{t}BuOK	DMSO	60	50/5/0
9	^{t}BuOK	toluene	60	40/5/0
10	^{t}BuOK	DCM/DMF (1:1)	60	55/trace /0
11	^{t}BuOK	DMF/THF (1:1)	60	66/trace/0
12	^{t}BuOK	DMF/THF (1:3)	60	72/trace/0
13	^{t}BuOK	DMF/THF (1:3)	50	85/trace/0
14	^{t}BuOK	DMF/THF (1:3)	70	70/trace/0
15[c]	^{t}BuOK	DMF/THF (1:3)	50	90/trace/0

[a]General conditions: **1a** (0.2 mmol), **2a** (4.0 equiv), base (3.0 equiv), solvent (4 mL), stirred for 12 h. [b]Isolated yield. [c]With 4.0 equiv ^{t}BuOK.

Table S3 Optimization data for the C-N bond phosphorylation[a]



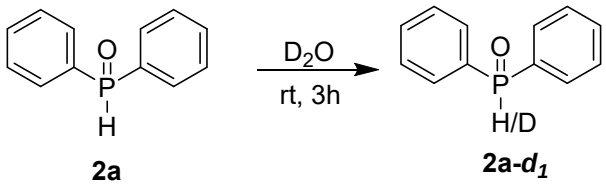
1a **2a** **5a**

Entry	Solvent	Catalyst	Additive	T (°C)	Yield (**3a**/**4a**/**5a**%)[b]
1	MeCN	I_2	oxalic acid	50	40/0/10
2	DCM	I_2	oxalic acid	50	30/0/20
3	DMSO	I_2	oxalic acid	50	35/0/trace
4	acetone	I_2	oxalic acid	50	20/0/15
5	DMF	I_2	oxalic acid	50	25/0/35
6	DMF	I_2	TFA	50	50/0/trace
7	DMF	I_2	AcOH	50	20/0/55
8	DMF		AcOH	50	
	DMF	I_2	HCl(aq)	50	30/0/30
9	DMF	I_2	$AlCl_3$	50	10/0/0
10	DMF	NIS	AcOH	50	10/0/trace
11	DMF	KI	AcOH	50	10/0/trace
12	DMF	KIO_3	AcOH	50	30/0/5
13	DMF	$PhI(OAc)_2$	AcOH	50	0/0/trace
14	DMF	I_2	AcOH	60	25/0/40
15	DMF	I_2	AcOH	40	20/0/45

[a]General conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), catalyst (0.2 equiv), additive (2.0 equiv), solvent (2 mL), stirred for 12 h. [b]Isolated yield.

Deuterium isotope labelling experiments

Procedure for the preparation of D-labelled diphenyl phosphine oxide 2a-*d*$_1$



To a 15 mL test tube were added diphenyl phosphine oxide **2a** (3.0mmol), D_20 (0.6 mL). The mixture was stirred at room temperature for 3 h. Removing the water under reduced pressure provided mixed **2a** and **2a-*d*$_1$** with 97% yield wherein the proportion of D-labelled compound was 81% (Figure S1).

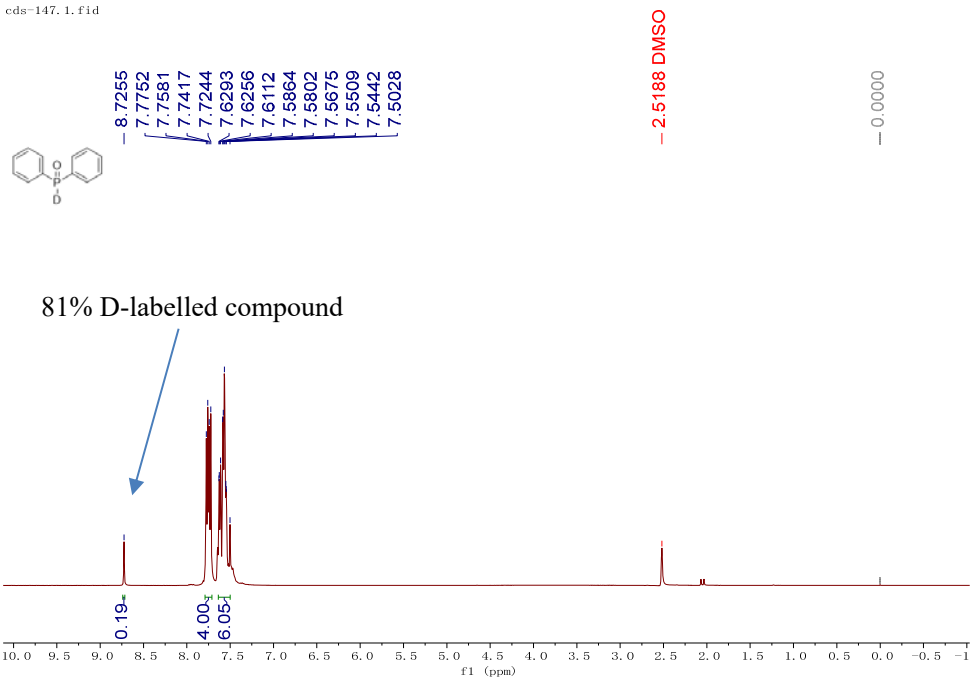


Figure S1 The ^{1}H NMR spectrum of mixed **2a** and **2a-*d*$_1$**

Procedures for the geminal and vicinal dephosphorylation of enaminone 1a with D-labelled diphenyl phosphine oxide

The D-labelling experiments were performed following the standard procedures for the geminal and vicinal diphosphorylation reactions using the prior prepared **2a-*d*$_1$** as substrate. The 1H NMR spectra for the products resulting from the reaction shows the formation of D-labelled products **3a-*d*$_1$** and **4a-*d*$_1$** in formed of mixture with corresponding product **3a** and **4a**, respectively (Figure S2-Figure S5).

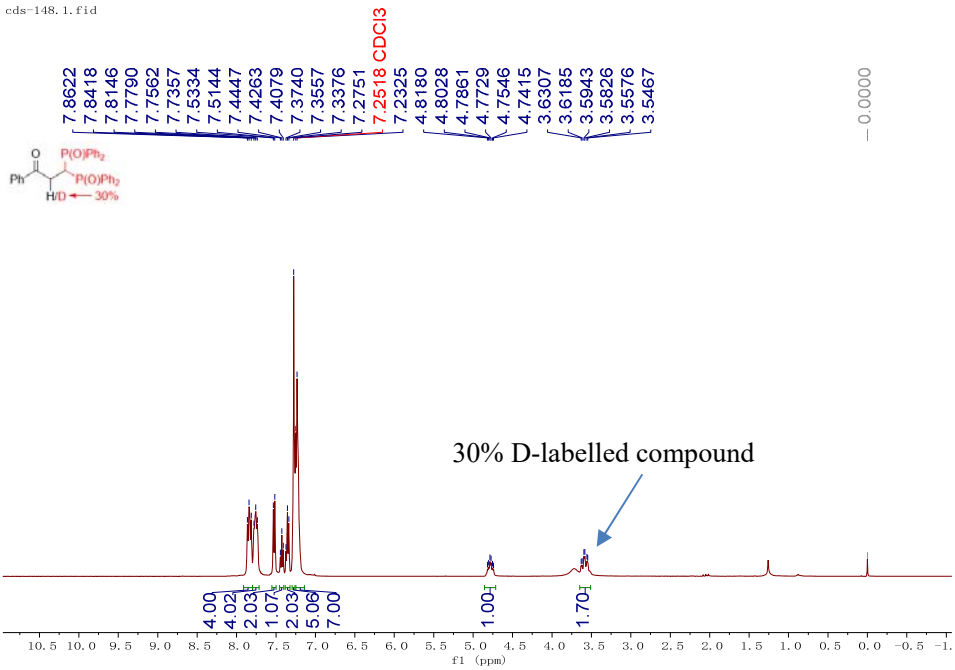


Figure S2 The ^{1}H NMR spectrum of mixed **3a** and **3a-*d*$_1$**

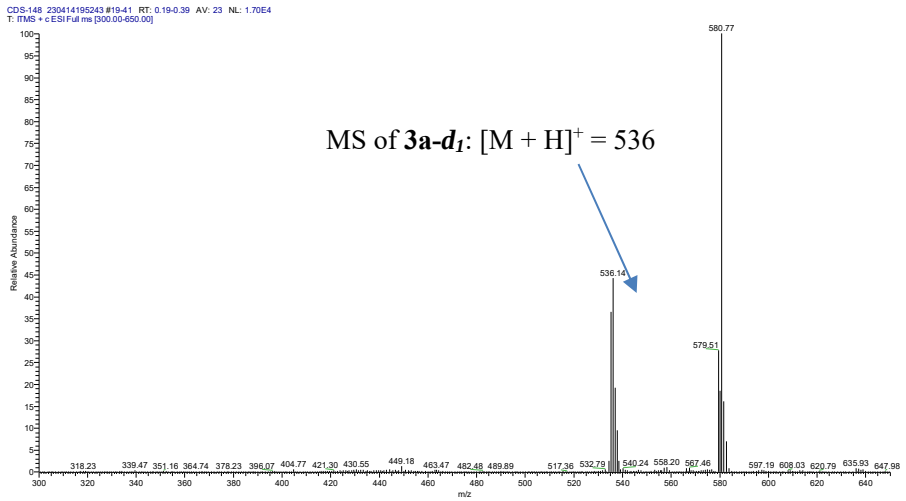


Figure S3 The ESI-MS spectrum of mixed **3a** and **3a-*d*$_1$**

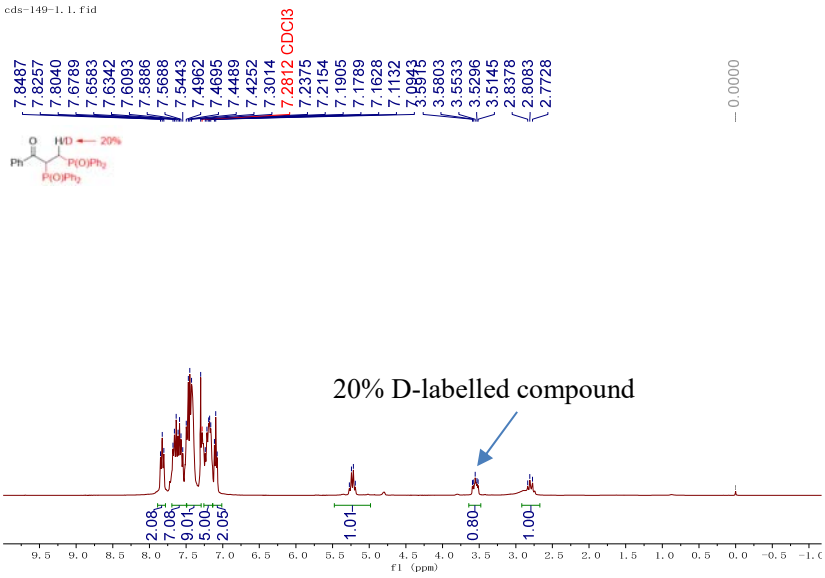


Figure S4 The ^{1}H NMR spectrum of mixed **4a** and **4a-*d*$_1$**

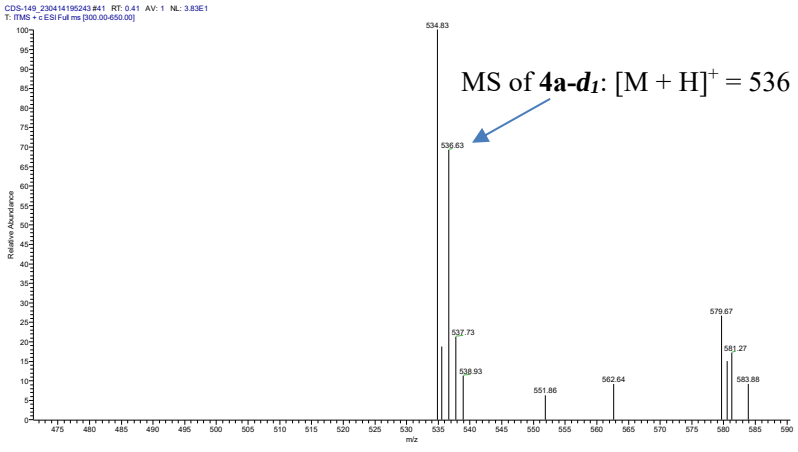


Figure S5 The ESI-MS spectrum of mixed **4a** and **4a-*d*$_1$**

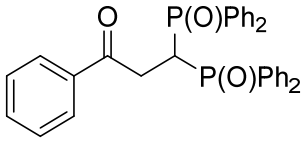
General procedure for the synthesis of 3

In a 25 mL sealed tube were added enaminone **1** (0.2 mmol, 1 equiv), phosphine oxide/phosphonate **2** (0.6 mmol, 3 equiv), TFA (0.6 mmol, 3 equiv) and CH_3CN (2 mL, 0.1 M). After sealing the tube with Teflon cap, the mixture was stirred at 60 °C with oil bath heating for 12 h. After being cooled down to room temperature, the mixture was transferred into the round bottom flask, and solvent was removed at reduced pressure. The residue obtained therein was subjected to flash silica gel column chromatography

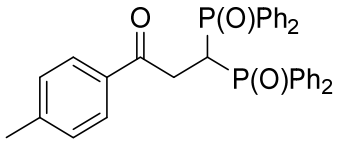
to provide pure products with the elution of mixed ethyl acetate and methanol or dichloromethane (DCM) and methanol (v/v = 10:1~40:1).

Procedure for the 1 mmol scale reaction for the synthesis of 3a

In a 50 mL sealed tube were added enaminone **1a** (1.0 mmol, 1 equiv), dialkyl phosphonate **2a** (3.0 mmol, 3 equiv), TFA (3.0 mmol, 3 equiv) and CH_3CN (6 mL, 0.17 M). After sealing the tube with Teflon cap, the mixture was stirred at 60 °C with oil bath heating for 12 h. After being cooled down to room temperature, the mixture was transferred into the round bottom flask, and solvent was removed at reduced pressure. The residue was dissolved with methanol (2 mL), and water (80 mL) was added dropwise into the mixture while stirring. The precipitates formed thereby were collected by filtration. The solid was washed subsequently with water and then washed by petroleum ether, dried at vacuum to give pure product **3a** (459.4 mg, 86% yield).

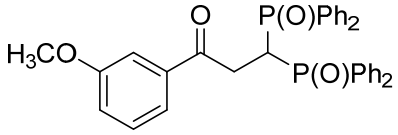


3,3-Bis(diphenylphosphoryl)-1-phenylpropan-1-one (**3a**).[2] Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (97.6 mg, 91% yield); mp 168-170 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.82 (m, 4H), 7.79-7.71 (m, 4H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 4.0 Hz, 5H), 7.22 (s, 7H), 4.83-4.73 (m, 1H), 3.62-3.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8 (t, *J* = 4.4 Hz), 135.4, 133.4, 131.8, 131.7, 131.63, 131.58, 131.5, 130.9, 130.6, 128.3, 128.2, 127.8, 36.6 (t, *J* = 59.2 Hz), 34.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.5.

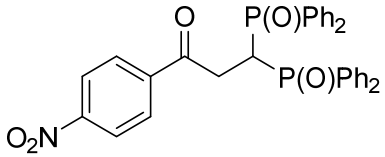


3,3-Bis(diphenylphosphoryl)-1-(p-tolyl)propan-1-one (**3b**). Eluent: V_{EA}/V_{MeOH} = 10:1; Yellow liquid (89.7 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) ; δ 7.88-7.76 (m, 8H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.34-7.30 (m, 2H), 7.23 (d, *J* = 5.2 Hz, 10H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.83-4.76 (m, 1H), 3.66-3.58 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 144.3, 132.7, 131.9, 131.7, 131.5, 131.4, 130.4, 130.3, 128.9,

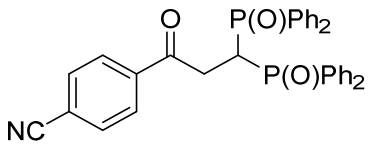
128.4, 128.2, 128.0, 35.6, 34.0, 21.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{31}O_3P_2$ 549.1743; Found 549.1745.



3,3-Bis(diphenylphosphoryl)-1-(3-methoxyphenyl)propan-1-one (**3c**). Eluent: V_{EA}/V_{MeOH} = 10:1; Yellow liquid (84.5 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.77 (m, 8H), 7.32 (t, *J* = 7.1 Hz, 2H), 7.25 (s, 10H), 7.13 (s, 2H), 7.05 (s, 1H), 6.97 (s, 1H), 4.82-4.73 (m, 1H), 3.8 (s, 3H), 3.70-3.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 159.4, 136.6, 132.0, 131.8, 131.6, 131.5, 129.3, 128.5, 128.4, 128.3, 120.7, 120.1, 111.9, 55.4, 35.3, 34.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{31}O_4P_2$ 565.1692; Found 565.1697.

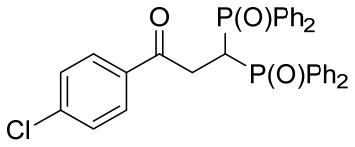


3,3-Bis(diphenylphosphoryl)-1-(4-nitrophenyl)propan-1-one (**3d**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (90.7 mg, 78% yield); mp 188-190 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) ; δ 8.12 (d, *J* = 7.0 Hz, 2H), 7.90-7.80 (m, 4H), 7.80-7.68 (m, 6H), 7.37 (d, *J* = 6.3 Hz, 2H), 7.26 (s, 10H), 4.74-4.67 (m, 1H), 3.70-3.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0 (t, *J* = 5.4 Hz), 150.3, 139.6, 132.1, 131.9, 131.6 (d, *J* = 3.0 Hz), 131.5 (d, *J* = 3.5 Hz), 129.0, 128.6, 128.5, 128.4, 128.3, 123.5, 36.6 (d, *J* = 57.6 Hz), 34.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{28}NO_5P_2$ 580.1437; Found 580.1439.

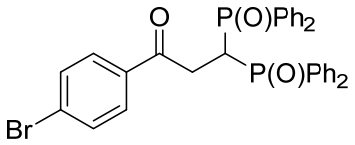


4-(3,3-Bis(diphenylphosphoryl)propanoyl)benzonitrile (**3e**). Eluent: V_{EA}/V_{MeOH} = 10:1; Yellow liquid (89.3 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.72 (m, 8H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.3 Hz, 3H), 7.27-7.18 (m, 9H), 4.72-4.66 (m, 1H), 3.90-3.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

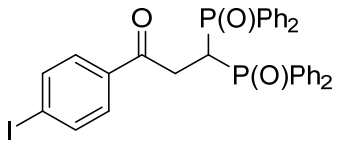
195.3 (t, J = 4.4 Hz), 138.0, 132.1, 131.9, 131.52, 131.47, 131.4, 130.9, 129.9, 128.6, 128.5, 128.3, 117.8, 116.5, 36.0 (t, J = 59.5 Hz), 34.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{28}NO_3P_2$ 560.1539; Found 560.1537.



1-(4-Chlorophenyl)-3,3-bis(diphenylphosphoryl)propan-1-one (**3f**). Eluent: V_{EA}/V_{MeOH} = 10:1; Yellow liquid (77.7 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.69 (m, 8H), 7.49 (d, J = 8.5 Hz, 2H), 7.34 (t, J = 7.0 Hz, 2H), 7.29 (s, 2H), 7.26-7.19 (m, 10H), 4.78-4.69 (m, 1H), 3.62-3.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9 (t, J = 4.9 Hz), 139.9, 133.5, 132.0, 131.8, 131.6, 131.49, 131.47, 129.3, 128.6, 128.5, 128.4, 128.3, 36.2 (t, J = 59.2 Hz), 34.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{28}ClO_3P_2$ 569.1197; Found 569.1197.

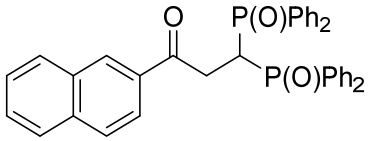


1-(4-Bromophenyl)-3,3-bis(diphenylphosphoryl)propan-1-one (**3g**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (101.3 mg, 83% yield); mp 172-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.72 (m, 8H), 7.41 (s, 4H), 7.36 (t, J = 7.1 Hz, 2H), 7.27 (d, J = 12.9 Hz, 10H), 4.75-4.68 (m, 1H), 3.59-3.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1 (t, J = 5.0 Hz), 134.0, 131.9, 131.7, 131.6, 131.4, 130.3, 129.4, 128.6, 128.44, 128.37, 128.3, 128.2, 36.4 (t, J = 59.7 Hz), 34.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{28}BrO_3P_2$ 613.0692; Found 613.0696.

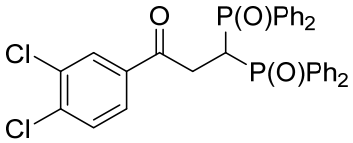


3,3-Bis(diphenylphosphoryl)-1-(4-iodophenyl)propan-1-one (**3h**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (117.9 mg, 89% yield); mp 144-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.72 (m, 8H), 7.58 (d, J = 8.0 Hz, 2H), 7.35-7.27 (m, 4H), 7.24 (s,

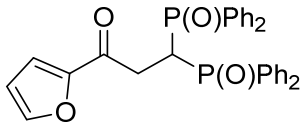
10H), 4.76-4.69 (m, 1H), 3.66-3.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 137.5, 134.4, 132.1, 131.8, 131.5, 131.4, 130.1, 129.3, 128.6, 128.44, 128.39, 128.3, 35.7, 34.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{28}IO_3P_2$ 661.0553; Found 661.0553.



3,3-Bis(diphenylphosphoryl)-1-(naphthalen-2-yl)propan-1-one (**3i**). Eluent: V_{EA}/V_{MeOH} = 10:1; Yellow liquid (95.5 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) ; δ 8.09 (s, 1H), 7.88-7.75 (m, 10H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.26-7.11 (m, 9H), 4.89-4.80 (m, 1H), 3.84-3.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 135.6, 132.5, 132.1, 132.0, 131.8, 131.6, 131.52, 131.48, 130.1, 129.8, 128.7, 128.5, 128.4, 128.3, 128.0, 127.5, 126.7, 123.3, 41.8, 34.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{31}O_3P_2$ 585.1743; Found 585.1749.

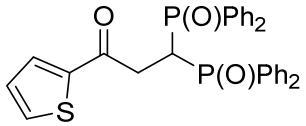


1-(3,4-Dichlorophenyl)-3,3-bis(diphenylphosphoryl)propan-1-one (**3j**). Eluent: V_{EA}/V_{MeOH} = 10:1; Yellow liquid (110.1 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 16.3 Hz, 8H), 7.57 (s, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.33-7.27 (m, 6H), 7.25-7.23 (m, 7H), 4.72-4.63 (m, 1H), 3.65-5.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 138.0, 134.8, 132.9, 132.0, 131.8, 131.6, 131.5, 131.1, 130.4, 129.7, 128.6, 128.4, 128.3, 127.2, 36.3, 34.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{27}Cl_2O_3P_2$ 603.0807; Found 603.0806.

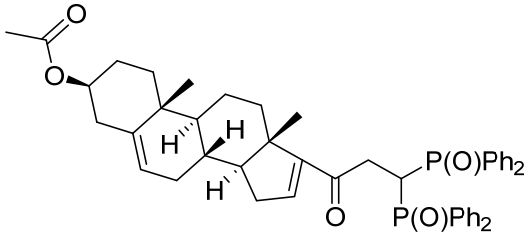


3,3-Bis(diphenylphosphoryl)-1-(furan-2-yl)propan-1-one (**3k**). Eluent: V_{EA}/V_{MeOH} = 10:1; Black liquid (79.0 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.73 (m,

8H), 7.36-7.28 (m, 4H), 7.22 (d, J = 6.8 Hz, 9H), 6.93 (s, 1H), 6.29 (s, 1H), 4.69-4.60 (m, 1H), 3.54-3.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5 (t, J = 5.3 Hz), 150.9, 146.8, 131.9, 131.7, 131.6, 131.5, 131.4, 128.5, 128.3, 128.2, 118.6, 112.1, 35.3 (t, J = 59.4 Hz), 33.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{27}O_4P_2$ 525.1379; Found 525.1378.

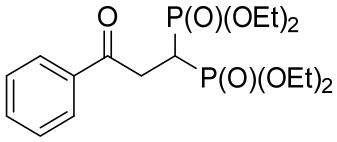


3,3-Bis(diphenylphosphoryl)-1-(thiophen-2-yl)propan-1-one (**3l**). Eluent: V_{EA}/V_{MeOH} = 10:1; Yellow liquid (84.6 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.70 (m, 9H), 7.47 (s, 1H), 7.33 (d, J = 22.6 Hz, 4H), 7.23 (s, 8H), 6.83 (s, 1H), 4.75-4.67 (m, 1H), 3.62-3,53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8 (t, J = 4.7 Hz), 141.8, 134.4, 133.1, 131.9, 131.7, 131.5, 130.3, 128.5, 128.4, 128.3, 128.2, 127.9, 35.8 (t, J = 59.8 Hz), 34.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{27}O_3P_2S$ 541.1151; Found 541.1152.

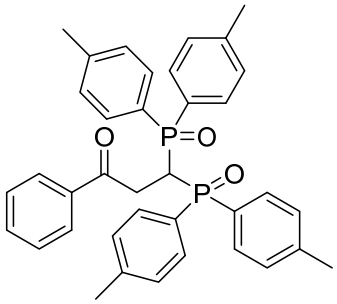


(3S, 8R, 9S, 10R, 13S, 14S)-17-(3,3-Bis(diphenylphosphoryl)propanoyl)-10,13-dimethyl-2, 3, 4, 7, 8, 9, 10, 11, 12, 13, 14, 15-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (**3m**). Eluent: V_{DCM}/V_{MeOH} = 40:1; Yellow liquid (53.7 mg, 35% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.79 (m, 4H), 7.77-7.69 (m, 4H), 7.39-7.28 (m, 8H), 7.27 (s, 4H), 6.30 (s, 1H), 5.34 (d, J = 4.5 Hz, 1H), 4.67-4.54 (m, 2H), 3.35-3.08 (m, 2H), 2.57 (s, 1H), 2.35-2.27 (m, 2H), 2.17-2.09 (m, 2H), 2.03 (s, 3H), 1.87-1.81 (m, 2H), 1.76 (d, J = 16.8 Hz, 1H), 1.55 (s, 2H), 1.53 (s, 2H), 1.38-1.23 (m, 2H), 1.13 (d, J = 10.5 Hz, 2H), 1.02 (s, 3H), 0.96-0.92 (m, 1H), 0.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 170.5, 144.9, 140.1, 131.61, 131.60, 131.54, 131.49, 128.3, 128.23, 128.20, 128.17, 128.1, 121.9, 73.7, 55.8, 50.2, 46.1, 38.1, 38.0, 36.7, 34.5, 34.3, 32.1, 31.3, 29.9, 27.6, 21.4, 21.3, 20.4, 19.1, 15.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.7

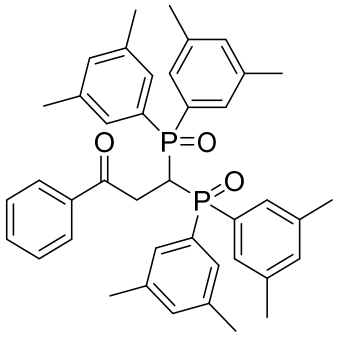
(d, J = 85.5 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{48}H_{53}O_5P_2$ 771.3363; Found 771.3363.



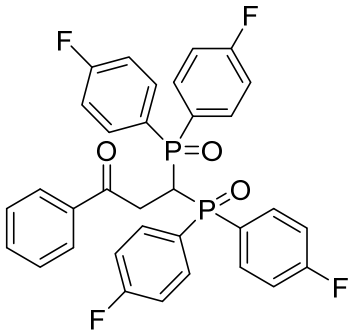
Tetraethyl (3-oxo-3-phenylpropane-1,1-diyl)bis(phosphonate) (**3n**). Eluent: V_{EA}/V_{PE} = 1:1; Yellow liquid (32.8 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.7 Hz, 2H), 7.34 (d, J = 7.4 Hz, 3H), 5.66 (d, J = 8.0 Hz, 1H), 4.29-4.01 (m, 8H), 3.11-2.88 (m, 2H), 1.33 (t, J = 7.0 Hz, 6H), 1.24 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 128.8, 128.4, 128.3, 125.7, 64.6 (d, J = 6.0 Hz), 62.1 (d, J = 6.5 Hz), 16.4 (d, J = 6.0 Hz), 16.0 (d, J = 7.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{29}O_7P_2$ 407.1383; Found 407.1385.



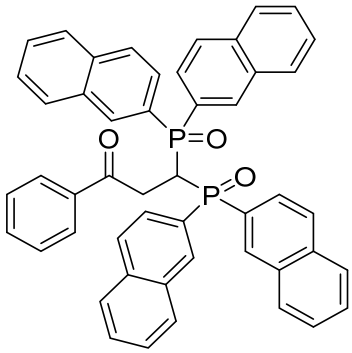
3,3-Bis(di-*p*-tolylphosphoryl)-1-phenylpropan-1-one (**3o**). Eluent: V_{EA}/V_{MeOH} = 10:1; Yellow liquid (97.6 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.59 (m, 8H), 7.52 (d, J = 7.7 Hz, 2H), 7.39 (d, J = 7.4 Hz, 1H), 7.18 (t, J = 7.6 Hz, 2H), 6.96 (s, 8H), 4.64-4.58 (m, 1H), 3.73-3.58 (m, 2H), 2.27 (s, 6H), 2.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2 (t, J = 5.0 Hz), 142.4, 142.0, 135.1, 133.2, 131.5, 131.4, 129.2, 129.1, 128.8, 128.7, 128.0, 127.1, 36.1 (t, J = 60.2 Hz), 33.8, 21.5, 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{37}O_3P_2$ 591.2212; Found 591.2211.



3,3-Bis(bis(3,5-dimethylphenyl)phosphoryl)-1-phenylpropan-1-one (**3p**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (68.9 mg, 53% yield); mp 130-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.38-7.25 (m, 10H), 6.82 (d, *J* = 23.8 Hz, 4H), 4.57-4.50 (m, 1H), 3.74-3.65 (m, 2H), 2.16 (s, 12H), 2.09 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 138.4, 138.2, 137.8, 137.7, 135.1, 133.7, 133.5, 133.4, 130.0, 128.7, 128.1, 128.0, 35.6, 33.6, 21.2, 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{41}H_{45}O_3P_2$ 647.2838; Found 647.2846.



3,3-Bis(bis(4-fluorophenyl)phosphoryl)-1-phenylpropan-1-one (**3q**). Eluent: V_{EA}/V_{MeOH} = 10:1; Yellow liquid (70.7 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.72 (m, 8H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.48 (t, *J* = 6.9 Hz, 1H), 7.35-7.25 (m, 2H), 7.19-7.13 (m, 1H), 7.01-6.87 (m, 7H), 4.69-4.62 (m, 1H), 3.70-3.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 166.4 (d, *J* = 4.7 Hz), 163.9 (d, *J* = 6.0 Hz), 134.7, 134.2, 134.1, 134.0, 128.4, 128.0, 116.3, 116.1, 116.0, 115.8, 36.4, 33.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -105.56; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{25}F_4O_3P_2$ 607.1210; Found 607.1210.



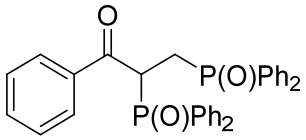
3,3-Bis(di(naphthalen-2-yl)phosphoryl)-1-phenylpropan-1-one (**3r**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (95.9 mg, 65% yield); mp 86-88 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 13.2 Hz, 2H), 8.34 (d, *J* = 13.6 Hz, 2H), 7.87 (s, 4H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.50-7.44 (m, 4H), 7.38-7.25 (m, 12H), 7.18 (t, *J* = 7.1 Hz, 2H), 7.01 (t, *J* = 7.0 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 2H), 5.14-5.09 (m, 1H), 3.96-3.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3 (t, *J* = 4.6 Hz), 134.7, 134.4, 134.2, 134.0, 133.9, 133.1, 132.3, 132.1, 132.0, 131.9, 128.8, 128.6, 128.3, 128.1, 127.8, 127.52, 127.47, 127.3, 126.8, 126.6, 125.9, 125.8, 125.6, 125.5, 36.3 (t, *J* = 59.7 Hz), 33.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{49}H_{37}O_3P_2$ 735.2212; Found 735.2217.

General procedure for the synthesis of 4

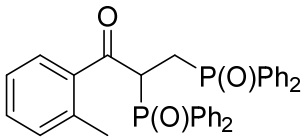
In a 25 mL sealed tube were added enaminone **1** (0.2 mmol, 1 equiv), phosphine oxide **2** (0.8 mmol, 4 equiv), ^{t}BuOK (0.8 mmol, 4 equiv) and DMF/THF (1 mL/3 mL). After sealing the tube with Teflon cap, the mixture was stirred at 50 °C with oil bath heating for 12 h. After being cooled down to room temperature, 5 mL of water was added, and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The organic phases were collected and washed with a small amount of water for three times. After being dried with anhydrous Na_2SO_4, the solid was removed by filtration. The solvent in the resulting solution was removed at reduced pressure. The residue obtained therein was subjected to flash silica gel column chromatography to provide pure products with the elution of mixed ethyl acetate and methanol or dichloromethane and methanol (v/v = 10:1~200:3).

Procedure for the 1 mmol scale reaction for the synthesis of 4a

In a 50 mL sealed tube were added enaminone **1a** (1.0 mmol, 1 equiv), phosphine oxide **2a** (4.0 mmol, 4 equiv), ^{t}BuOK (4.0 mmol, 4 equiv) and DMF/THF (2 mL/6 mL). After sealing the tube with Teflon cap, the mixture was stirred at 50 °C with oil bath heating for 12 h. After being cooled down to room temperature, 20 mL of water was added, and the resulting mixture was extracted with ethyl acetate (3 × 40 mL). The combined organic phases were concentrated at reduced pressure. Mixed methanol (2 mL) and water (80 mL) was then added dropwise into the residue at stirring. The precipitates formed thereby were collected by filtration. The solid was washed subsequently with water and petroleum ether, dried at vacuum to give pure product **4a** (470.1 mg, 88% yield).

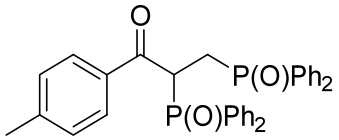


2,3-Bis(diphenylphosphoryl)-1-phenylpropan-1-one (**4a**).[2] Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (95.9 mg, 90% yield); mp 201-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.79 (m, 2H), 7.69-7.55 (m, 7H), 7.50-7.43 (m, 9H), 7.25-7.15 (m, 5H), 7.10 (t, *J* = 7.3 Hz, 2H), 5.27-5.19 (m, 1H), 3.59-3.51 (m, 1H), 2.84-2.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1 (d, *J* = 2.3 Hz), 137.5, 132.6, 132.4, 132.1 (d, *J* = 3.9 Hz), 131.9, 131.7, 131.6 (d, *J* = 2.6 Hz), 131.5, 131.3, 131.2, 130.6, 130.5, 128.9, 128.85, 128.77, 128.7, 128.4, 128.3, 128.2, 127.8, 42.9 (d, *J* = 49.2 Hz), 28.0 (d, *J* = 63.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.9 (d, *J* = 42.0 Hz), 30.4 (d, *J* = 41.8 Hz).

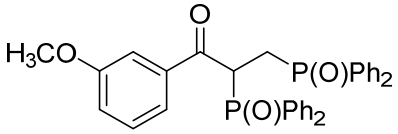


2,3-Bis(diphenylphosphoryl)-1-(o-tolyl)propan-1-one (**4b**). Eluent: V_{EA}/V_{MeOH} = 10:1; Yellow solid (85.9 mg, 78% yield); mp 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, *J* = 8.4 Hz, 2H), 7.72-7.65 (m, 2H), 7.64-7.54 (m, 5H), 7.51-7.45 (m, 2H), 7.41 (d, *J* = 6.6 Hz, 4H), 7.37-7.28 (m, 3H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.16-7.07 (m, 3H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 7.2 Hz, 1H), 5.31-5.07 (m, 1H), 3.67 (s, 1H), 2.66

(d, J = 13.7 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7 (d, J = 3.4 Hz), 138.6, 138.1, 132.2, 132.0, 131.8, 131.32, 131.28, 131.2, 131.1, 130.6, 130.5, 129.3, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 128.1, 125.1, 45.8 (d, J = 50.5 Hz), 26.7 (d, J = 63.3 Hz), 20.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.0 (d, J = 41.3 Hz), 30.5 (d, J = 40.5 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{31}O_3P_2$ 549.1743; Found 549.1753.

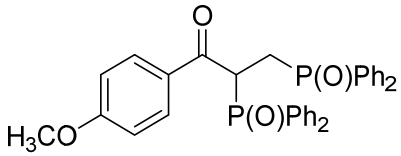


2,3-Bis(diphenylphosphoryl)-1-(p-tolyl)propan-1-one (**4c**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (93.5 mg, 85% yield); mp 220-222 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, J = 9.3 Hz, 2H), 7.67-7.48 (m, 8H), 7.46-7.28 (m, 8H), 7.23-7.17 (m, 4H), 6.90 (d, J = 7.7 Hz, 2H), 5.24-5.15 (m, 1H), 3.57-3.49 (m, 1H), 2.78 (d, J = 14.0 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6 (d, J = 3.2 Hz), 143.5 (d, J = 3.0 Hz), 135.0 (d, J = 3.3 Hz), 132.3, 132.0, 131.9, 131.8, 131.7, 131.6, 131.4, 131.3, 130.7, 130.62 (d, J = 2.9 Hz), 130.56, 128.8, 128.7, 128.6 (d, J = 2.8 Hz), 128.5, 128.4, 128.3, 128.1, 42.7 (d, J = 50.7 Hz), 27.9 (d, J = 63.9 Hz), 21.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.4 (d, J = 42.3 Hz), 30.6 (d, J = 42.3 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{31}O_3P_2$ 549.1743; Found 549.1750. .

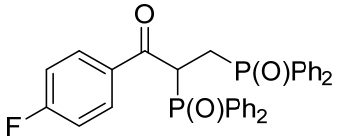


2,3-Bis(diphenylphosphoryl)-1-(3-methoxyphenyl)propan-1-one (**4d**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (89.5 mg, 79% yield); mp 200-202 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (t, J = 9.1 Hz, 2H), 7.69-7.58 (m, 6H), 7.57-7.48 (m, 6H), 7.42 (d, J = 7.2 Hz, 1H), 7.36 (d, J = 7.4 Hz, 3H), 7.27-7.15 (m, 4H), 7.03-6.90 (m, 2H), 5.23-4.93 (m, 1H), 3.69 (s, 3H), 3.36 (d, J = 11.0 Hz, 1H), 2.69-2.57 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 195.1 (d, J = 3.1 Hz), 159.1, 139.5, 132.8, 132.5, 132.3, 131.9, 131.8, 131.6, 131.5, 131.04, 130.95, 130.86, 129.5, 129.4, 129.3 (d, J = 2.9 Hz), 129.0, 128.9, 128.8, 128.7, 121.5, 119.3, 113.1, 55.6, 43.7 (d, J = 51.7 Hz), 28.2 (d, J = 65.3

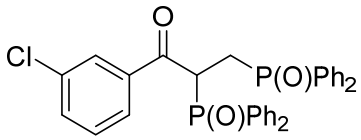
Hz); ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.3 (d, J = 44.3 Hz), 28.4 (d, J = 44.4 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{31}O_4P_2$ 565.1692; Found 565.1690.



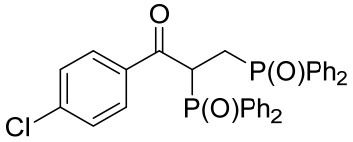
2,3-Bis(diphenylphosphoryl)-1-(4-methoxyphenyl)propan-1-one (**4e**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (90.6 mg, 80% yield); mp 198-200 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (t, J = 9.3 Hz, 2H), 7.66 (s, 4H), 7.58-7.49 (m, 6H), 7.46-7.39 (m, 5H), 7.37-7.27 (m, 2H), 7.24-7.13 (m, 3H), 6.59 (d, J = 8.4 Hz, 2H), 5.22-5.13 (m, 1H), 3.76 (s, 3H), 3.56-3.47 (m, 1H), 2.83-2.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2 (d, J = 2.9 Hz), 163.2, 132.4, 132.1, 131.9, 131.8, 131.69, 131.67, 131.6, 131.4, 131.3, 130.9, 130.6, 130.5, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 113.0, 55.4, 42.4 (d, J = 53.0 Hz), 28.0 (d, J = 65.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.7 (d, J = 42.6 Hz), 30.8 (d, J = 42.6 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{31}O_4P_2$ 565.1692; Found 565.1699.



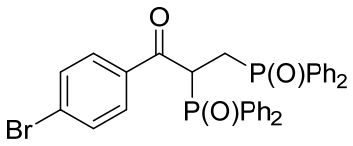
2,3-Bis(diphenylphosphoryl)-1-(4-fluorophenyl)propan-1-one (**4f**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (66.5 mg, 60% yield); mp 223-225 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.78 (m, 2H), 7.69-7.55 (m, 6H), 7.53-7.50 (m, 4H), 7.47-7.40 (m, 5H), 7.34 (t, J = 8.0 Hz, 1H), 7.27-7.24 (m, 2H), 7.22-7.15 (m, 2H), 6.79 (t, J = 8.6 Hz, 2H), 5.21-5.12 (m, 1H), 3.62-3.38 (m, 1H), 2.81-2.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6 (d, J = 3.2 Hz), 132.5 (d, J = 2.0 Hz), 132.2 (d, J = 2.3 Hz), 132.1 (d, J = 2.1 Hz), 132.0 (d, J = 2.1 Hz), 131.8, 131.7, 131.6, 131.5, 131.3 (d, J = 9.2 Hz), 131.1 (d, J = 9.4 Hz), 130.6, 130.5, 128.9 (d, J = 3.1 Hz), 128.8 (d, J = 2.9 Hz), 128.5, 128.4, 128.3, 128.2, 115.0 (d, J = 21.4 Hz), 114.9 (d, J = 21.9 Hz), 43.1 (d, J = 49.4 Hz), 28.1 (d, J = 60.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.1 (d, J = 41.8 Hz), 30.5 (d, J = 41.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.39; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{28}FO_3P_2$ 553.1492; Found 553.1491.



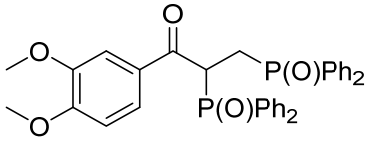
1-(3-Chlorophenyl)-2,3-bis(diphenylphosphoryl)propan-1-one (**4g**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (85.5 mg, 75% yield); mp 210-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, *J* = 9.0 Hz, 2H), 7.69-7.60 (m, 4H), 7.60-7.50 (m, 4H), 7.45 (t, *J* = 6.6 Hz, 5H), 7.36-7.30 (m, 2H), 7.27 (s, 1H), 7.26-7.18 (m, 5H), 7.07 (t, *J* = 8.1 Hz, 1H), 5.11 (d, *J* = 10.8 Hz, 1H), 3.55-3.48 (m, 1H), 2.77 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2 (d, *J* = 2.5 Hz), 139.1, 134.1, 132.6, 132.4, 132.3, 132.2, 132.0, 131.7 (d, *J* = 1.9 Hz), 131.6 (d, *J* = 1.9 Hz), 131.55 (d, *J* = 1.9 Hz), 131.48 (d, *J* = 2.1 Hz), 131.4 (d, *J* = 2.2 Hz), 131.3 (d, *J* = 2.2 Hz), 130.7 (d, *J* = 2.2 Hz), 130.6 (d, *J* = 2.3 Hz), 129.1, 129.0-128.8 (m), 128.5 (d, *J* = 2.8 Hz), 128.4-128.4 (m), 128.3 (d, *J* = 2.8 Hz), 128.2, 126.5, 43.6 (d, *J* = 50.5 Hz), 28.1 (d, *J* = 65.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.7 (d, *J* = 41.2 Hz), 30.4 (d, *J* = 41.3 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{28}ClO_3P_2$ 569.1197; Found 569.1199.



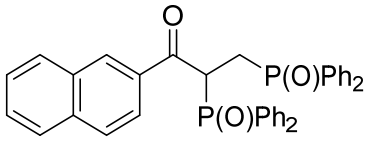
1-(4-Chlorophenyl)-2,3-bis(diphenylphosphoryl)propan-1-one (**4h**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (77.6 mg, 68% yield); mp 222-224 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 9.2 Hz, 2H), 7.68-7.50 (m, 8H), 7.43 (t, *J* = 8.0 Hz, 6H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.29-7.18 (m, 5H), 7.09 (d, *J* = 8.2 Hz, 2H), 5.19-5.11 (m, 1H), 3.62-3.43 (m, 1H), 2.81-2.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1 (d, *J* = 3.0 Hz), 139.1, 135.9, 132.5, 132.3 (d, *J* = 2.7 Hz), 132.1 (d, *J* = 14.9 Hz), 131.8, 131.7, 131.6, 131.5, 131.3 (d, *J* = 9.1 Hz), 130.6, 130.5, 129.8, 128.9 (d, *J* = 4.5 Hz), 128.8 (d, *J* = 4.4 Hz), 128.6, 128.44, 128.36, 128.2, 128.1, 43.2 (d, *J* = 49.6 Hz), 28.1 (d, *J* = 64.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.0 (d, *J* = 41.8 Hz), 30.5 (d, *J* = 41.8 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{28}ClO_3P_2$ 569.1197; Found 569.1192.



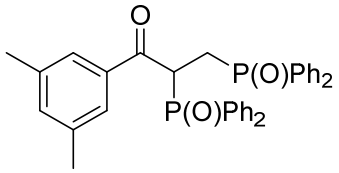
1-(4-Bromophenyl)-2,3-bis(diphenylphosphoryl)propan-1-one (**4i**). Eluent: V_{DCM}/V_{MeOH} = 200:3; Yellow liquid (48.8 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 3H), 7.71-7.49 (m, 10H), 7.48-7.41 (m, 4H), 7.38-7.28 (m, 5H), 7.25 (s, 2H), 5.27-5.04 (m, 1H), 2.83-2.72 (m, 1H), 2.47-2.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3 (d, *J* = 3.0 Hz), 136.3, 132.5, 132.3 (d, *J* = 2.1 Hz), 132.1, 132.0 (d, *J* = 2.3 Hz), 131.7, 131.6 (d, *J* = 6.8 Hz), 131.5, 131.4, 131.3, 131.1, 130.6 (d, *J* = 8.8 Hz), 129.9, 128.9 (d, *J* = 4.9 Hz), 128.8 (d, *J* = 5.0 Hz), 128.6, 128.5, 128.4, 128.3, 127.9, 43.3 (d, *J* = 44.0 Hz), 29.5 (d, *J* = 37.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.0 (d, *J* = 41.8 Hz), 30.5 (d, *J* = 42.0 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{28}BrO_3P_2$ 613.0692; Found 613.0698.



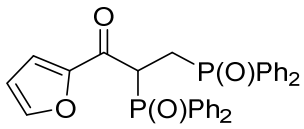
1-(3,4-Dimethoxyphenyl)-2,3-bis(diphenylphosphoryl)propan-1-one (**4j**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (94.8 mg, 80% yield); mp 215-217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.79 (m, 2H), 7.71-7.63 (m, 4H), 7.60-7.53 (m, 2H), 7.52-7.47 (m, 2H), 7.42 (d, *J* = 6.7 Hz, 4H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.30 (s, 2H), 7.25 (d, *J* = 4.4 Hz, 2H), 7.19 (t, *J* = 6.6 Hz, 2H), 6.92 (d, *J* = 1.9 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 5.31-5.05 (m, 1H), 3.80 (d, *J* = 39.8 Hz, 6H), 3.55-3.44 (m, 1H), 2.79 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4 (d, *J* = 3.5 Hz), 153.0, 148.2, 132.3, 132.1, 131.8, 131.70, 131.67, 131.6, 131.3 (d, *J* = 9.4 Hz), 130.8, 130.6, 130.5, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 123.7, 110.4, 109.4, 55.9, 55.7, 42.7 (d, *J* = 52.9 Hz), 28.0 (d, *J* = 66.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.4 (d, *J* = 42.6 Hz), 30.6 (d, *J* = 42.6 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{33}O_5P_2$ 595.1798; Found 595.1800.



2,3-Bis(diphenylphosphoryl)-1-(naphthalen-2-yl)propan-1-one (**4k**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (95.5 mg, 82% yield); mp 196-198 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.88 (t, *J* = 9.1 Hz, 2H), 7.78-7.64 (m, 6H), 7.62-7.54 (m, 3H), 7.53-7.41 (m, 10H), 7.11 (d, *J* = 20.3 Hz, 5H), 5.46-5.30 (m, 1H), 3.69-3.50 (m, 1H), 2.86 (d, *J* = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0 (d, *J* = 2.9 Hz), 135.1, 134.8, 132.5, 132.1, 131.9, 131.81, 131.77, 131.7, 131.6, 131.5, 131.4, 131.3, 130.7, 130.6, 130.5, 129.7, 128.9 (d, *J* = 2.7 Hz), 128.8 (d, *J* = 2.8 Hz), 128.44, 128.40, 128.3, 128.2, 127.7, 127.4, 126.4, 123.9, 43.2 (d, *J* = 50.3 Hz), 28.0 (d, *J* = 64.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.6 (d, *J* = 42.0 Hz), 31.0 (d, *J* = 42.0 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{31}O_3P_2$ 585.1743; Found 585.1749.

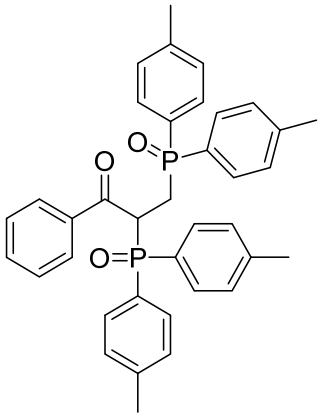


1-(3,5-Dimethylphenyl)-2,3-bis(diphenylphosphoryl)propan-1-one (**4l**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (87.5 mg, 78% yield); mp 144-146 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (t, *J* = 9.1 Hz, 2H), 7.71-7.56 (m, 6H), 7.53-7.41 (m, 7H), 7.34-7.27 (m, 2H), 7.21 (d, *J* = 8.7 Hz, 3H), 6.91 (d, *J* = 14.4 Hz, 3H), 5.30-5.04 (m, 1H), 3.65-3.36 (m, 1H), 2.81 (t, *J* = 13.5 Hz, 1H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5 (d, *J* = 2.8 Hz), 137.6, 137.2, 134.3, 132.4, 132.1, 131.79, 131.75, 131.7, 131.6, 131.4, 131.3, 130.7, 130.6, 128.8, 128.7, 128.6, 128.3 (d, *J* = 2.0 Hz), 128.2, 126.1, 123.6, 43.4 (d, *J* = 49.7 Hz), 27.8 (d, *J* = 65.2 Hz), 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.5 (d, *J* = 42.1 Hz), 31.0 (d, *J* = 42.0 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{33}O_3P_2$ 563.1899; Found 563.1912.

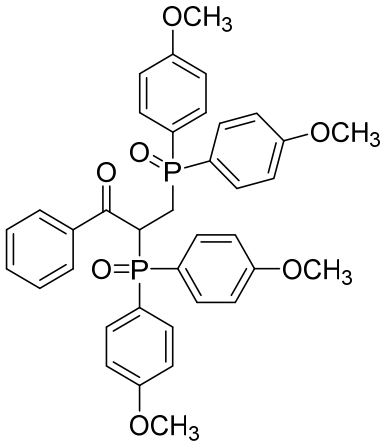


2,3-Bis(diphenylphosphoryl)-1-(furan-2-yl)propan-1-one (**4m**). Eluent: V_{EA}/V_{MeOH} = 10:1; White solid (81.5 mg, 78% yield); mp 233-235 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (t, *J* = 9.2 Hz, 2H), 7.73-7.63 (m, 4H), 7.58 (t, *J* = 9.5 Hz, 2H), 7.52 (d, *J* = 6.6

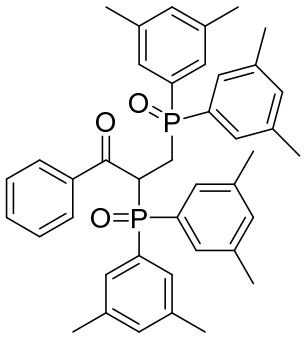
Hz, 2H), 7.44 (d, *J* = 9.5 Hz, 4H), 7.36-7.19 (m, 7H), 6.73 (d, *J* = 2.8 Hz, 1H), 6.24-6.13 (m, 1H), 5.17-4.90 (m, 1H), 3.58-3.38 (m, 1H), 2.81-2.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.5 (d, *J* = 3.2 Hz), 152.3, 146.2, 132.4, 132.1, 131.9, 131.7, 131.6, 131.5, 131.4, 131.3, 131.2, 130.8, 130.7, 128.9, 128.8, 128.7, 128.3, 128.2, 128.1, 117.7, 112.5, 43.0 (d, *J* = 49.8 Hz), 27.1 (d, *J* = 63.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.3 (d, *J* = 41.7 Hz), 30.7 (d, *J* = 41.7 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{27}O_4P_2$ 525.1379; Found 525.1379.



2,3-Bis(di-p-tolylphosphoryl)-1-phenylpropan-1-one (**4n**). Eluent: V_{DCM}/V_{MeOH} = 40:1; White solid (101.3 mg, 86% yield); mp 210-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.65 (m, 2H), 7.57-7.48 (m, 4H), 7.47-7.38 (m, 4H), 7.31 (d, *J* = 6.1 Hz, 1H), 7.21 (d, *J* = 7.1 Hz, 4H), 7.10 (t, *J* = 7.8 Hz, 2H), 7.05-6.98 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.26-5.04 (m, 1H), 3.45 (t, *J* = 16.3 Hz, 1H), 2.81-2.68 (m, 1H), 2.35 (s, 6H), 2.18 (d, *J* = 30.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5 (d, *J* = 3.3 Hz), 142.8 (d, *J* = 2.4 Hz), 142.5 (d, *J* = 2.6 Hz), 142.4, 142.2 (d, *J* = 2.5 Hz), 137.6, 132.2, 131.8, 131.70, 131.66, 131.6, 131.4, 131.3, 130.7, 130.6, 129.5 (d, *J* = 2.0 Hz), 129.4 (d, *J* = 1.7 Hz), 129.1, 129.0, 128.8, 128.5, 127.5, 43.3 (d, *J* = 52.0 Hz), 28.4 (d, *J* = 66.0 Hz), 21.5, 21.4, 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.8 (d, *J* = 41.3 Hz), 31.0 (d, *J* = 41.8 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{37}O_3P_2$ 591.2212; Found 591.2221.



2,3-Bis(bis(4-methoxyphenyl)phosphoryl)-1-phenylpropan-1-one (**4o**). Eluent: V_{DCM}/V_{MeOH} = 40:1; Yellow liquid (65.8 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.69 (m, 2H), 7.60-7.53 (m, 4H), 7.51-7.40 (m, 4H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 3H), 6.92 (d, *J* = 7.3 Hz, 4H), 6.80-6.53 (m, 3H), 5.21-5.08 (m, 1H), 3.81 (d, *J* = 1.7 Hz, 6H), 3.72 (s, 3H), 3.64 (s, 3H), 3.43-3.34 (m, 1H), 2.79-2.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6 (d, *J* = 3.1 Hz), 162.7 (d, *J* = 2.7 Hz), 162.5 (t, *J* = 2.5 Hz), 162.3 (d, *J* = 2.6 Hz), 137.6, 133.7, 133.6, 133.5, 133.4, 133.2, 132.9, 132.8, 132.5, 132.43, 132.37, 128.5, 127.6, 114.3, 114.2, 114.0, 113.9, 113.8, 113.7, 55.3, 55.2, 55.1, 43.3 (d, *J* = 52.1 Hz), 28.7 (d, *J* = 65.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.6 (d, *J* = 41.7 Hz), 30.9 (d, *J* = 41.9 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{37}O_7P_2$ 655.2009; Found 655.2022.



2,3-Bis(bis(3,5-dimethylphenyl)phosphoryl)-1-phenylpropan-1-one (**4p**). Eluent: V_{DCM}/V_{MeOH} = 40:1; Yellow solid (107.7 mg, 83% yield); mp 202-204 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61-7.51 (m, 2H), 7.48-7.37 (m, 3H), 7.28-7.08 (m, 10H), 6.94 (s, 1H), 6.84 (s, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 3.35 (d, *J* = 11.8 Hz, 1H), 2.59 (t, *J* = 12.9 Hz, 1H), 2.25 (s, 12H), 2.07 (d, *J* = 31.3 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ 195.0 (d, *J* = 3.3 Hz), 138.6, 138.5, 138.4, 138.3, 138.0, 137.9, 137.84, 137.79, 137.6, 134.0, 133.6, 133.5 (d, *J* = 2.3 Hz), 133.3 (d, *J* = 2.2 Hz), 132.2, 129.2, 129.14, 129.07 (d, *J* = 3.5 Hz), 129.0 (d, *J* = 3.3 Hz), 128.2, 128.1, 128.0, 127.3, 42.5 (d, *J* = 49.8 Hz), 27.9 (d, *J* = 64.1 Hz), 21.3, 21.2, 21.0, 20.9 ; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.5 (d, *J* = 42.6 Hz), 28.5 (d, *J* = 42.8 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{41}H_{45}O_3P_2$ 647.2838; Found 647.2847.

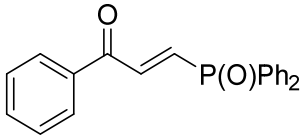
General procedure for the synthesis of 5

In a 25 mL sealed tube were added enaminone **1** (0.2 mmol, 1 equiv), dialkyl phosphonate/phosphine oxide **2** (0.3 mmol, 1.5 equiv), CH_3COOH (0.4 mmol, 2 equiv), I_2 (20 mol%) and DMF (2 mL, 0.1 M). After sealing the tube with Teflon cap, the mixture was stirred at 50 °C with oil bath heating for 12 h. After being cooled down to room temperature, 5 mL of water was added, and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The organic phases were collected and washed with a small amount of water for three times. After being dried with anhydrous Na_2SO_4, the solid was removed by filtration. The solvent in the resulting solution was removed at reduced pressure. The residue obtained therein was subjected to flash silica gel column chromatography to provide pure products with the elution of mixed ethyl acetate and petroleum ether (v/v = 1:1~2:1).

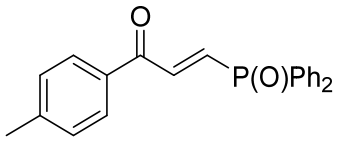
Procedure for the 1 mmol scale reaction for the synthesis of 5a

In a 50 mL sealed tube were added enaminone **1a** (1 mmol, 1 equiv), diphenyl phosphine oxide **2a** (1.5 mmol, 1.5 equiv), CH_3COOH (2 mmol, 2 equiv), I_2 (0.2 mmol, 20 mol%) and DMF (6 mL, 0.17 M). After sealing the tube with Teflon cap, the mixture was stirred at 50 °C with oil bath heating for 12 h. After being cooled down to room temperature, 20 mL of water was added, and the resulting mixture was extracted with ethyl acetate (3 × 40 mL). The organic phases were collected and washed with a small amount of water for three times. After being dried with anhydrous Na_2SO_4, the solid was removed by filtration. The solvent in the resulting solution was removed at reduced pressure. The residue obtained therein was subjected to flash silica gel column

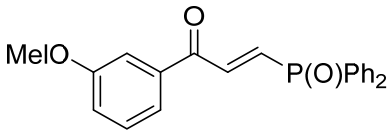
chromatography to provide pure product **5a** (166.0 mg, 50% yield) with the elution of mixed ethyl acetate and petroleum ether (v/v = 1:2).



(*E*)-3-(Diphenylphosphoryl)-1-phenylprop-2-en-1-one (**5a**). Eluent: V_{EA}/V_{PE} = 1:2; White solid (36.8 mg, 55% yield); mp 108-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.01 (m, 3H), 7.79-7.70 (m, 4H), 7.69-7.62 (m, 1H), 7.62-7.55 (m, 3H), 7.50 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1 (d, *J* = 16.5 Hz), 139.3, 137.3, 136.4 (d, *J* = 6.2 Hz), 133.9, 132.4, 131.3 (d, *J* = 9.9 Hz), 129.0, 128.94, 128.89, 128.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}O_2P$ 333.1039; Found 333.1043.

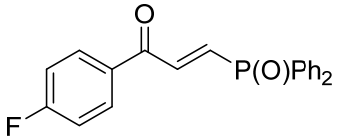


(*E*)-3-(Diphenylphosphoryl)-1-(p-tolyl)prop-2-en-1-one (**5b**). Eluent: V_{EA}/V_{PE} = 1:2; White solid (34.8 mg, 50% yield); mp 176-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (t, *J* = 17.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.80-7.70 (m, 4H), 7.69-7.60 (m, 1H), 7.59-7.47 (m, 6H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 145.1, 139.5, 136.8, 135.9, 134.0, 132.3, 131.3 (d, *J* = 9.4 Hz), 129.6, 129.2, 128.9 (d, *J* = 11.9 Hz), 21.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}O_2P$ 347.1195; Found 347.1205.

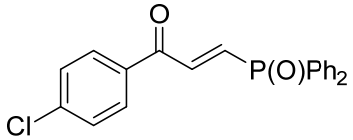


(*E*)-3-(Diphenylphosphoryl)-1-(3-methoxyphenyl)prop-2-en-1-one (**5c**). Eluent: V_{EA}/V_{PE} = 2:3; Yellow liquid (32.4 mg, 45% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (t, *J* = 16.9 Hz, 1H), 7.79-7.71 (m, 4H), 7.71-7.61 (m, 2H), 7.60-7.48 (m, 7H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.20-7.10 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9 (d, *J* = 16.1 Hz), 160.1, 139.4, 137.8, 137.3, 136.3, 132.4, 131.3 (d, *J* = 9.6 Hz), 129.9,

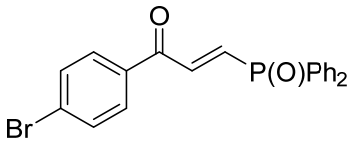
128.9 (d, J = 12.1 Hz), 121.8, 120.8, 112.8, 55.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}O_3P$ 363.1145; Found 363.1146.



(*E*)-3-(Diphenylphosphoryl)-1-(4-fluorophenyl)prop-2-en-1-one (**5d**). Eluent: V_{EA}/V_{PE} = 1:2; White solid (42.3 mg, 60% yield); mp143-145 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-7.98 (m, 3H), 7.75 (t, J = 9.6 Hz, 4H), 7.70-7.60 (m, 1H), 7.57 (t, J = 7.3 Hz, 2H), 7.50 (t, J = 7.4 Hz, 4H), 7.17 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.5 (d, J = 18.1 Hz), 166.2 (d, J = 256.8 Hz), 138.9, 137.6, 136.7 (d, J = 2.8 Hz), 132.9 (d, J = 2.3 Hz), 132.4, 131.8 (d, J = 9.6 Hz), 131.3 (d, J = 9.2 Hz), 128.9 (d, J = 11.6 Hz), 116.1 (d, J = 22.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.20; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}FO_2P$ 351.0945; Found 351.0945.

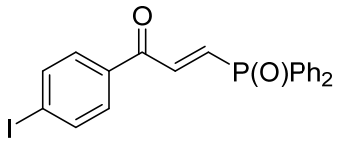


(*E*)-1-(4-Chlorophenyl)-3-(diphenylphosphoryl)prop-2-en-1-one (**5e**). Eluent: V_{EA}/V_{PE} = 1:2; White solid (42.3 mg, 58% yield); mp 177-179 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-7.96 (m, 3H), 7.78-7.71 (m, 4H), 7.69-7.54 (m, 3H), 7.54-7.43 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9 (d, J = 16.6 Hz), 140.6, 138.7, 137.8, 136.9, 134.7, 132.5, 131.3 (d, J = 10.0 Hz), 130.4, 129.3, 128.9 (d, J = 12.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}ClO_2P$ 367.0649; Found 367.0651.

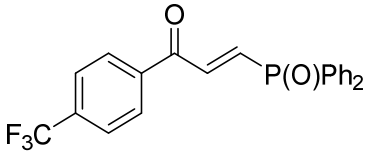


(*E*)-1-(4-Bromophenyl)-3-(diphenylphosphoryl)prop-2-en-1-one (**5f**). Eluent: V_{EA}/V_{PE} = 2:3; White solid (45.7 mg, 56% yield); mp 182-184 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (t, J = 16.8 Hz, 1H), 7.91 (d, J = 8.2 Hz, 2H), 7.78-7.71 (m, 4H), 7.64

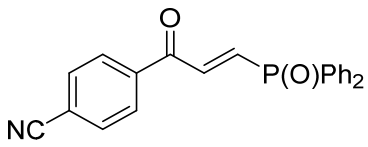
(d, J = 8.1 Hz, 3H), 7.60-7.55 (m, 2H), 7.50 (t, J = 7.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1 (d, J = 16.5 Hz), 138.7, 137.9, 137.0, 135.1, 132.4, 132.2, 131.3 (d, J = 9.7 Hz), 130.5, 129.3, 128.9 (d, J = 12.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}BrO_2P$ 411.0144; Found 411.0143.



(*E*)-3-(Diphenylphosphoryl)-1-(4-iodophenyl)prop-2-en-1-one (**5g**). Eluent: V_{EA}/V_{PE} = 2:3; White solid (48.8 mg, 53% yield); mp 204-206 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (t, J = 16.1 Hz, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.4 Hz, 7H), 7.58 (t, J = 7.3 Hz, 2H), 7.50 (t, J = 7.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3(d, J = 14.0 Hz), 138.6, 138.3, 138.0, 135.7, 132.5, 132.2, 131.3 (d, J = 7.7 Hz), 130.3, 128.9 (d, J = 10.3 Hz), 102.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}IO_2P$ 459.0005; Found 459.0009.

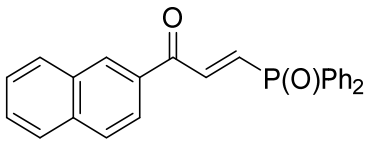


(*E*)-3-(Diphenylphosphoryl)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**5h**). Eluent: V_{EA}/V_{PE} = 2:3; White solid (46.6 mg, 58% yield); mp 155-157 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.0 Hz, 2H), 8.06 (t, J = 16.3 Hz, 1H), 7.76 (t, J = 9.2 Hz, 7H), 7.61-7.56 (m, 2H), 7.52 (t, J = 7.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3 (d, J = 16.1 Hz), 139.1, 138.8, 138.5, 137.9, 135.0 (d, J = 33.0 Hz), 132.5, 131.3 (d, J = 7.7 Hz), 129.3, 129.0 (d, J = 10.7 Hz), 126.0 – 125.8 (m), 123.4 (d, J = 272.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.24; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}F_3O_2P$ 401.0913; Found 401.0914.

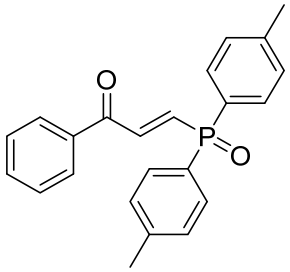


(*E*)-4-(3-(Diphenylphosphoryl)acryloyl)benzonitrile (**5i**). Eluent: V_{EA}/V_{PE} = 1:1; Yellow liquid (37.3 mg, 52% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-7.98 (m, 3H),

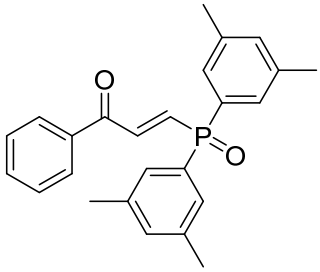
7.85-7.64 (m, 7H), 7.61-7.52 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9 (d, *J* = 16.8 Hz), 139.3 (d, *J* = 22.7 Hz), 138.1 (d, *J* = 16.4 Hz), 132.7, 132.6, 131.7, 131.2 (d, *J* = 10.1 Hz), 130.6, 129.3, 129.0 (d, *J* = 12.4 Hz), 117.7, 117.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}NO_2P$ 358.0991; Found 358.0996.



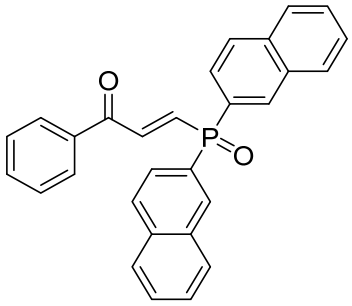
(*E*)-3-(Diphenylphosphoryl)-1-(naphthalen-2-yl)prop-2-en-1-one (**5j**). Eluent: V_{EA}/V_{PE} = 2:3; White solid (38.5 mg, 50% yield); mp 175-177 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.30 (t, *J* = 16.7 Hz, 1H), 8.10 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.94-7.85 (m, 2H), 7.82-7.69 (m, 5H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.60-7.54 (m, 3H), 7.51 (t, *J* = 7.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8 (d, *J* = 14.3 Hz), 139.3, 137.1, 136.2 (d, *J* = 2.4 Hz), 135.9, 133.8, 132.5, 132.4, 131.5, 131.3 (d, *J* = 8.6 Hz), 129.8, 129.1, 129.0, 128.9, 127.8, 127.1, 124.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}O_2P$ 383.1195; Found 383.1205.



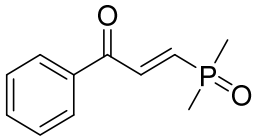
(*E*)-3-(Di-p-tolylphosphoryl)-1-phenylprop-2-en-1-one (**5k**). Eluent: V_{EA}/V_{PE} = 1:1; Yellow liquid (36.3 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 3H), 7.67-7.58 (m, 6H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 4H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3 (d, *J* = 16.5 Hz), 142.9, 138.9, 137.9, 136.9, 136.5, 133.8, 131.3 (d, *J* = 10.1 Hz), 129.6 (d, *J* = 12.5 Hz), 128.9 (d, *J* = 17.6 Hz), 128.0, 21.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{22}O_2P$ 361.1352; Found 361.1359.



(*E*)-3-(Bis(3,5-dimethylphenyl)phosphoryl)-1-phenylprop-2-en-1-one (**5l**). Eluent: V_{EA}/V_{PE} = 2:3; White solid (40.6 mg, 52% yield); mp 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 3H), 7.61 (t, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 9.0 Hz, 4H), 7.17 (s, 2H), 2.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3 (d, *J* = 11.5 Hz), 138.9, 138.81, 138.77, 136.5, 134.2, 134.1, 133.8, 129.1, 128.9, 128.8, 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}O_2P$ 389.1665; Found 389.1667.

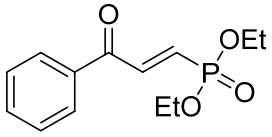


(*E*)-3-(Di(naphthalen-2-yl)phosphoryl)-1-phenylprop-2-en-1-one (**5m**). Eluent: V_{EA}/V_{PE} = 1:1; White solid (38.7 mg, 45% yield); mp 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 13.1 Hz, 2H), 8.18 (t, *J* = 16.8 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.95-7.81 (m, 7H), 7.71 (t, *J* = 8.4 Hz, 2H), 7.63-7.55 (m, 5H), 7.49 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2 (d, *J* = 15.0 Hz), 139.6, 137.3, 136.5, 134.9, 133.9, 133.4 (d, *J* = 7.5 Hz), 132.6 (d, *J* = 12.2 Hz), 129.4, 129.1, 129.0, 128.9, 128.8, 128.5, 127.9, 127.2, 125.9 (d, *J* = 9.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{22}O_2P$ 433.1352; Found 433.1351.

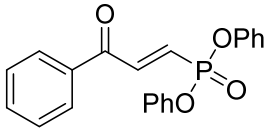


(*E*)-3-(Dimethylphosphoryl)-1-phenylprop-2-en-1-one (**5n**). Eluent: V_{EA}/V_{PE} = 1:2; Yellow liquid (25.1 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.01 (m, 2H),

8.00-7.90 (m, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.26-7.13 (m, 1H), 1.68 (d, J = 13.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2 (d, J = 16.3 Hz), 138.9, 138.5, 137.6, 136.3, 133.9, 128.9 (d, J = 9.5 Hz), 17.2 (d, J = 73.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{14}O_2P$ 209.0726; Found 209.0726.



Diethyl (*E*)-(3-oxo-3-phenylprop-1-en-1-yl)phosphonate (5o).[3] Eluent: V_{EA}/V_{PE}=1:3; Colorless liquid (21.3 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.7 Hz, 2H), 7.90-7.78 (m, 1H), 7.63 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.04-6.87 (m, 1H), 4.31-4.08 (m, 4H), 1.37 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5 (d, J = 22.9 Hz), 140.2 (d, J = 6.2 Hz), 136.3, 133.9, 131.6, 129.8, 128.9 (d, J = 3.3 Hz), 62.5 (d, J = 5.5 Hz), 16.4 (d, J = 6.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.8.

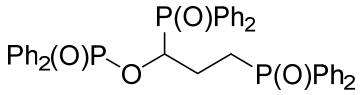


Diphenyl (*E*)-(3-oxo-3-phenylprop-1-en-1-yl)phosphonate (5p). Eluent: V_{EA}/V_{PE}=1:8; Yellow liquid (29.3 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.91 (m, 3H), 7.61 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.34 (t, J = 7.9 Hz, 4H), 7.27-7.10 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9 (d, J = 23.1 Hz), 149.9 (d, J = 7.7 Hz), 142.5 (d, J = 6.7 Hz), 136.0, 134.1, 130.0, 129.9, 129.0 (d, J = 4.5 Hz), 128.0, 125.6, 120.6 (d, J = 4.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.9 (t, J = 21.8 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}O_4P$ 365.0937; Found 365.0950.

Procedure for the synthesis of 7

In a 25 mL sealed tube were added enaminal **6** (0.2 mmol, 1 equiv), phosphine oxide **2a** (0.6 mmol, 3 equiv), TFA (0.6 mmol, 3 equiv) and CH_3CN (2 mL, 0.1 M). After sealing the tube with Teflon cap, the mixture was stirred at 60 °C with oil bath heating for 12 h. Upon completion (TLC), the reaction mixture was diluted with ethyl

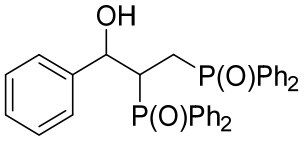
acetate, and transferred into a round bottom flask. After removing the solvent at reduced temperature, the resulting mixture was purified by silica gel column chromatography with the election of mixed dichloromethane and methanol (v: v=40:1).



1,3-Bis(diphenylphosphoryl)propyl diphenylphosphinate (**7**). Eluent: V_{DCM}/V_{MeOH} = 40:1; Yellow liquid (79.7 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) ; δ 7.89-7.79 (m, 2H), 7.76-7.65 (m, 4H), 7.57-7.43 (m, 8H), 7.43-7.33 (m, 10H), 7.33-7.28 (m, 4H), 7.23-7.17 (m, 2H), 5.68-5.49 (m, 1H), 2.60-2.35 (m, 2H), 2.28-2.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.51, 132.49, 132.46, 132.4, 132.0, 131.9, 131.8, 131.4, 131.33, 131.30, 131.2, 131.1, 131.0, 130.8, 130.72, 130.69, 130.6, 128.9, 128.8, 128.6, 128.5, 128.4, 128.2, 100.0, 25.8 (d, J = 64.6 Hz), 23.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.7, 33.5, 31.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{36}O_4P_3$ 661.1821; Found 661.1835.

Procedure for the synthesis of 8

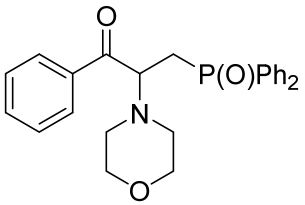
Compound **4a** (0.2 mmol) was dissolved in MeOH (2 mL) in a 25 mL round-bottom flask. To this solution was slowly added $NaBH_4$ (0.4 mmol) in 3 mins. The mixture was stirred at room temperature for 12 h. The pH was then adjusted to 3 with 10% (m/m) aqueous HCl solution. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phase was successively washed with saturated sodium bicarbonate solution and brine for three times and dried with anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure, and the resulting residue was purified by flash column chromatography to give pure product by using mixed ethyl acetate and petroleum ether (v/v = 1:1) as eluent.



(3-Hydroxy-3-phenylpropane-1,2-diyl)bis(diphenylphosphine oxide) (**8**). Eluent: V_{EA}/V_{PE} = 1:1; White solid (66.9 mg, 62% yield); mp 201-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.71 (m, 2H), 7.58-7.51 (m, 5H), 7.47 (d, *J* = 7.6 Hz, 3H), 7.43-7.32 (m, 10H), 7.31-7.27 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 9.8 Hz, 1H), 5.34-5.11 (m, 1H), 3.45-3.25 (m, 1H), 2.97-2.82 (m, 1H), 2.40-2.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 132.3 (d, *J* = 2.4 Hz), 132.0 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 2.4 Hz), 131.6 (d, *J* = 2.5 Hz), 131.1, 131.0, 130.7, 130.64, 130.57, 128.93, 128.90, 128.84, 128.81, 128.78, 128.72, 128.67, 127.8, 127.1, 126.9, 72.7, 40.4 (d, *J* = 64.0 Hz), 25.0 (d, *J* = 67.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.9 (d, *J* = 33.5 Hz), 33.9 (d, *J* = 33.6 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{31}O_3P_2$ 537.1743; Found 537.1746.

Procedure for the synthesis of 10

In a 15 mL reaction tube was equipped with **5a** (0.2 mmol), morpholine **9** (0.4 mmol) and MeCN (2 mL). The mixture was then stirred at room temperature for 4 h. Upon completion (TLC), the reaction mixture was diluted with ethyl acetate, and transferred into a round bottom flask. After removing the solvent at reduced temperature, the resulting mixture was purified by silica gel column chromatography with the elution of mixed petroleum ether and ethyl acetate (v:v = 1:2).

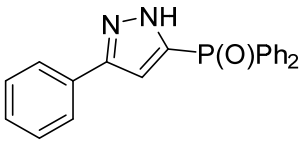


3-(Diphenylphosphoryl)-2-morpholino-1-phenylpropan-1-one (**10**). Eluent: V_{EA}/V_{PE}=1:2; White solid (73.5 mg, 88% yield); mp 167-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.82 (m, 6H), 7.57-7.47 (m, 4H), 7.42 (d, *J* = 15.3 Hz, 5H), 4.52-4.47 (m, 1H), 3.78-3.70 (m, 1H), 3.45 (s, 4H), 3.16-3.08 (m, 1H), 2.96-2.89 (m, 2H), 2.56-2.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8 (d, *J* = 11.8 Hz), 136.2, 133.5, 131.9 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 2.8 Hz), 131.5, 131.4, 131.0 (d, *J* = 8.5 Hz), 128.8, 128.6, 128.3, 128.2, 128.1, 67.2, 59.5 (d, *J* = 89.2 Hz), 51.4 (d, *J* = 6.5 Hz), 31.5 (d, *J* = 8.1

Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{27}NO_3P$ 420.1723; Found 420.1727.

Procedure for the synthesis of 12

In a 15 mL reaction tube was equipped with **5a** (0.2 mmol), hydrazine hydrate (0.4 mmol) and toluene (2 mL). The mixture was then stirred at room temperature for 12 h. Upon completion (TLC), the reaction mixture was diluted with ethyl acetate, and transferred into a round bottom flask. After removing the solvent at reduced pressure, the resulting mixture was purified by silica gel column chromatography with the election of mixed petroleum ether and ethyl acetate (v: v=1:1).



Diphenyl(3-phenyl-1H-pyrazol-5-yl)phosphine oxide (**12**). Eluent: V_{EA}/V_{PE}=1:1; White solid (48.2 mg, 70% yield); mp 179-181 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 6H), 7.54 (t, *J* = 7.3 Hz, 2H), 7.47 – 7.41 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 10.6 Hz), 130.8 (d, *J* = 9.5 Hz), 128.9, 128.8, 128.6, 128.5, 128.3, 128.1, 125.9, 109.6 (d, *J* = 17.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}N_2OP$ 345.1151; Found 345.1154.

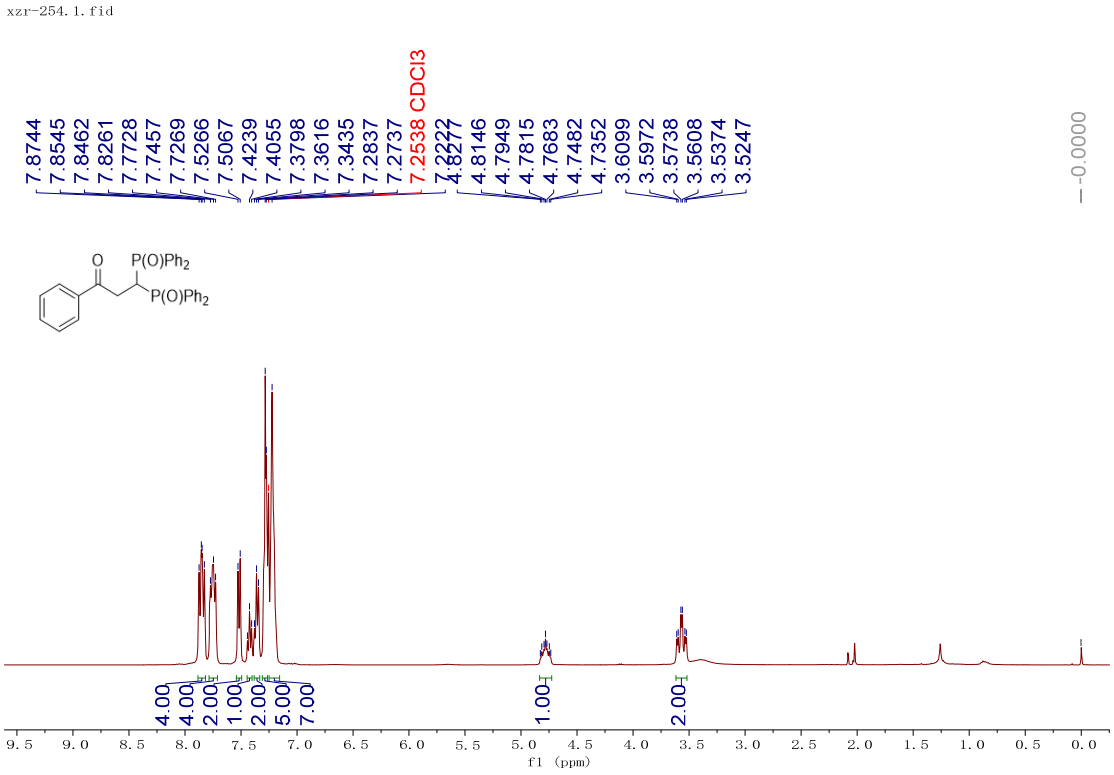
References

1. (a) H. Guo, L. Tian, Y. Liu and J.-P. Wan, *Org. Lett*., 2022, **24**, 228-233. (b) J. Ying, T. Liu, Y. Liu and J.-P. Wan, *Org. Lett*., 2022, **24**, 2404-2408.

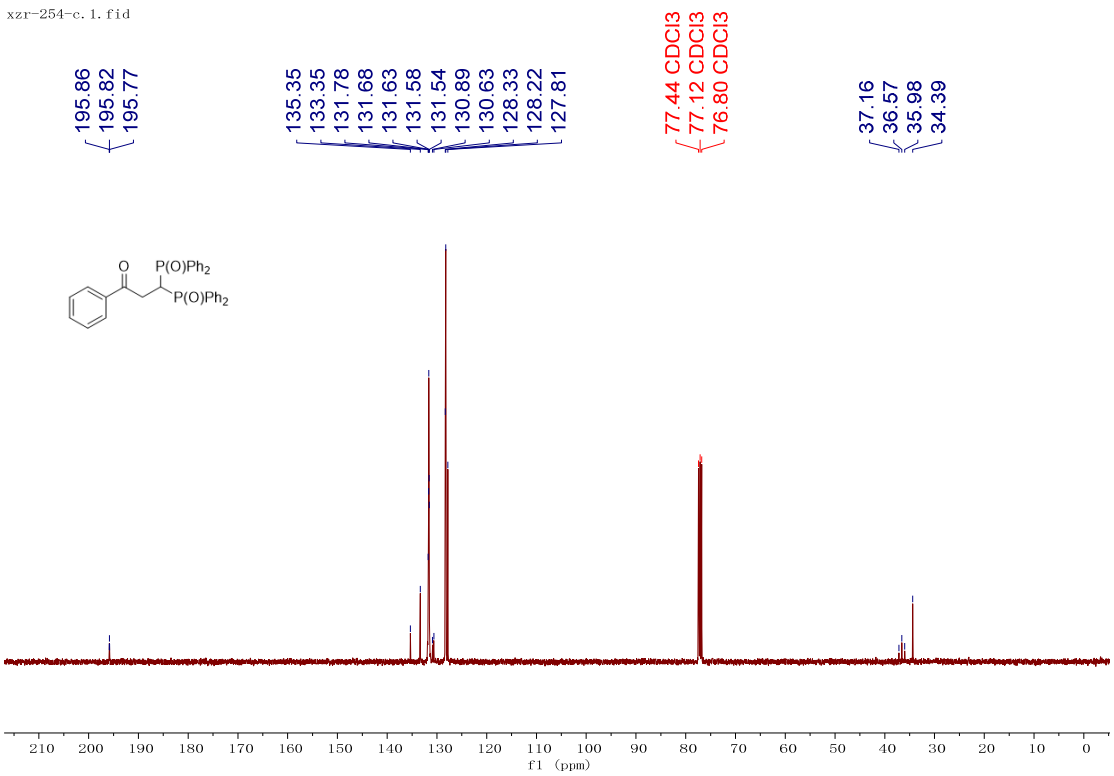
2. E. T. Glotova, M. Y. Dvorko, N. S. Arbuzova, A. I. Ushakov, I. S. Verkhoturova, K. N. Gusarova and A. B. Trofimov, *Lett. Org. Chem.*, 2007, **4**, 109-111.

3. T. Liu, L. Wei, B. Zhao, Y. Liu and J.-P. Wan, *J. Org. Chem.*, 2021, **86**, 9861-9868.

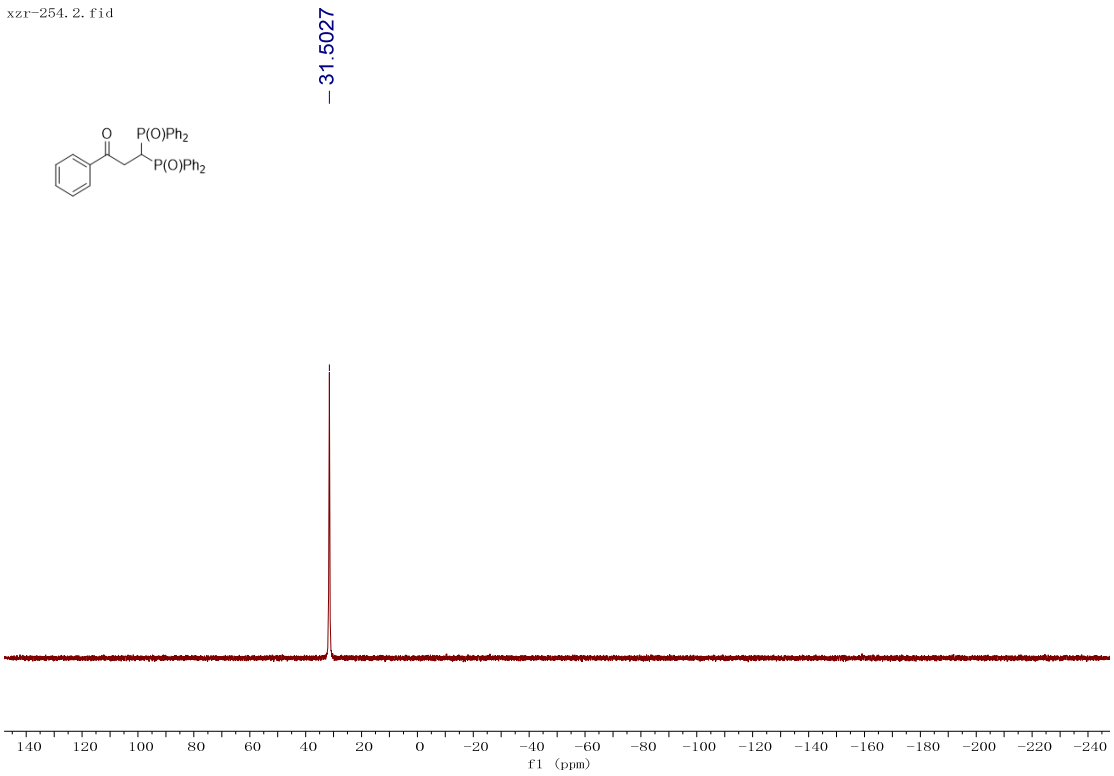
NMR spectra of all products



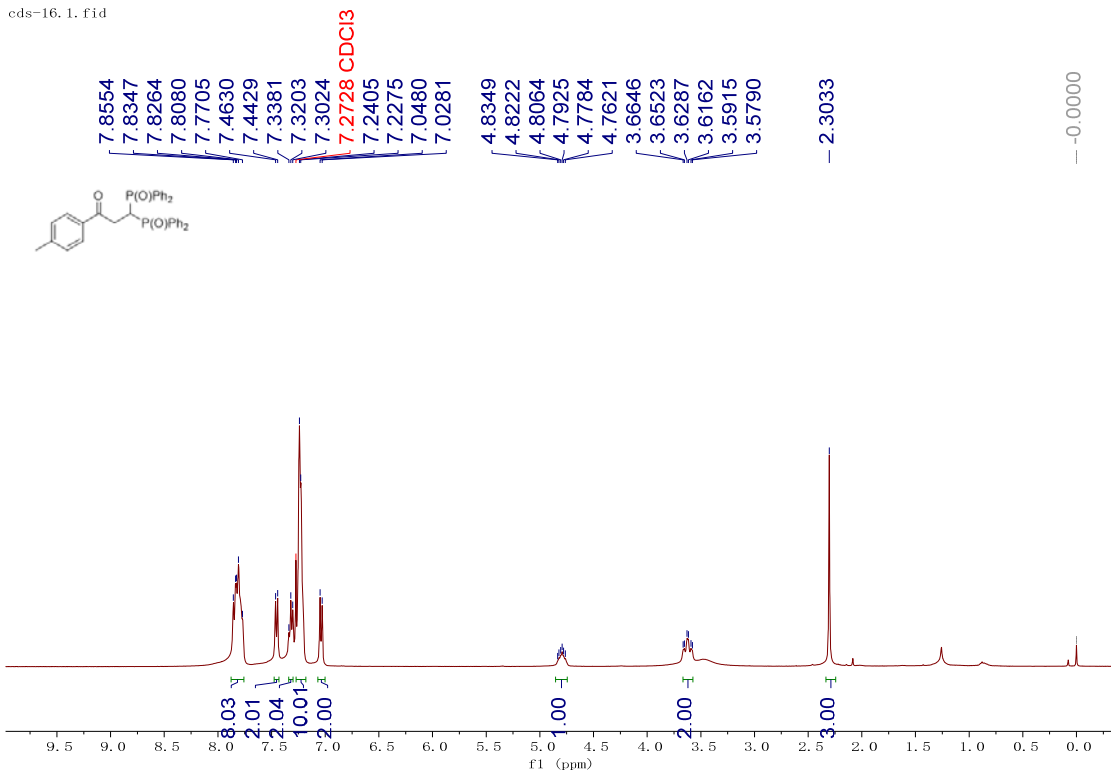
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



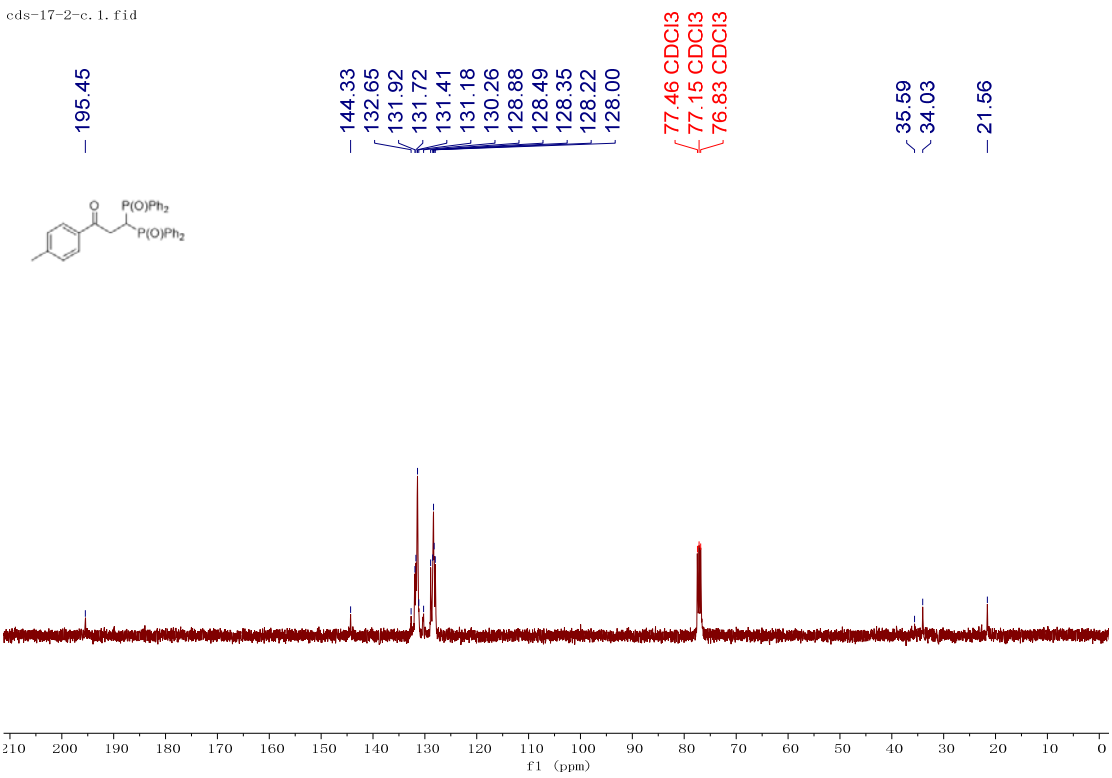
^{13}C NMR spectrum of **3a** (100 MHz, $CDCl_3$)



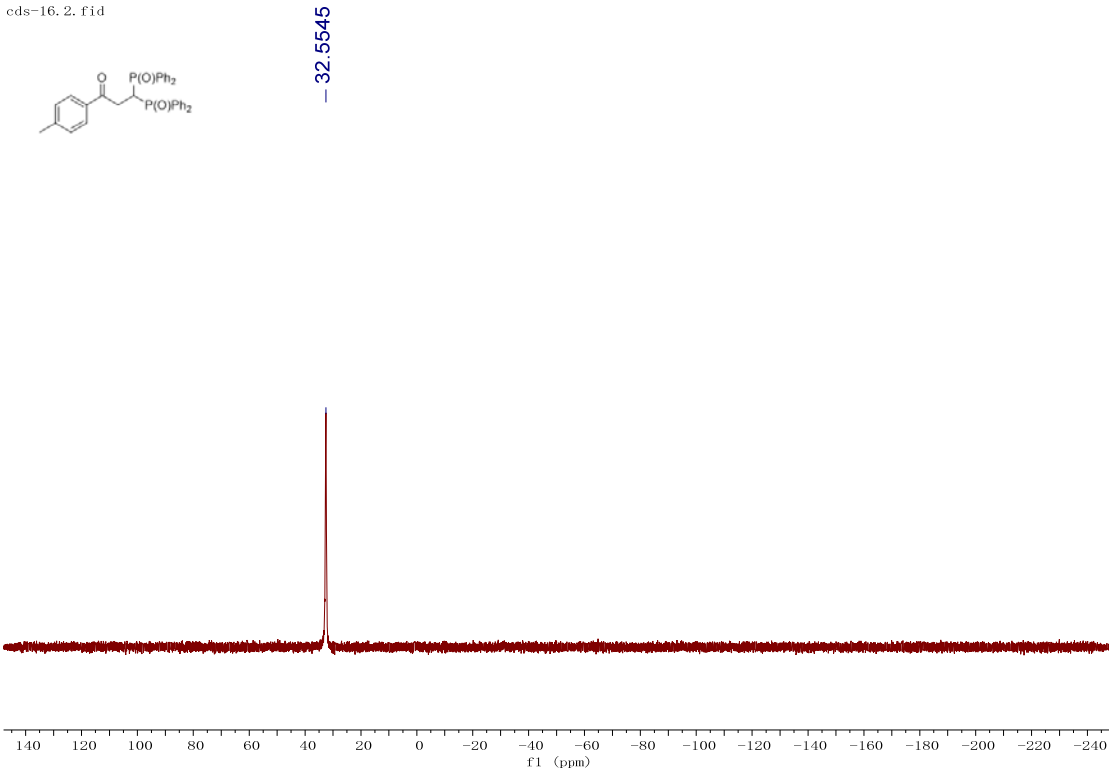
^{31}P NMR spectrum of **3a** (162 MHz, $CDCl_3$)



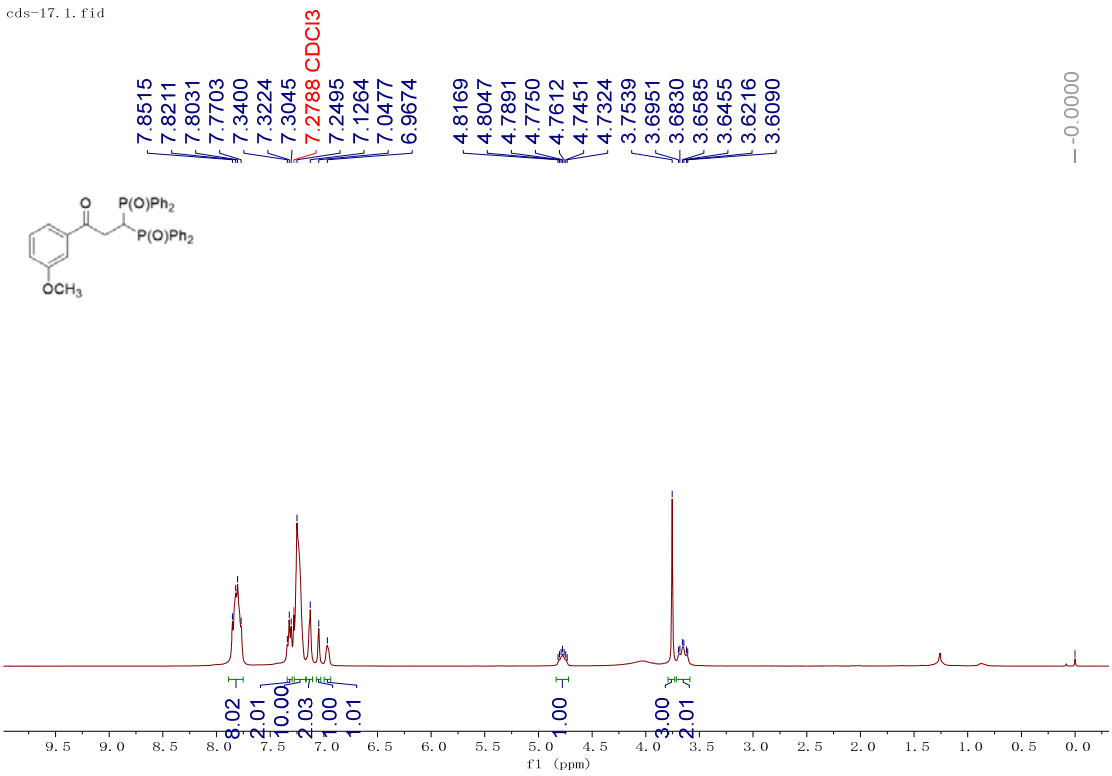
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)



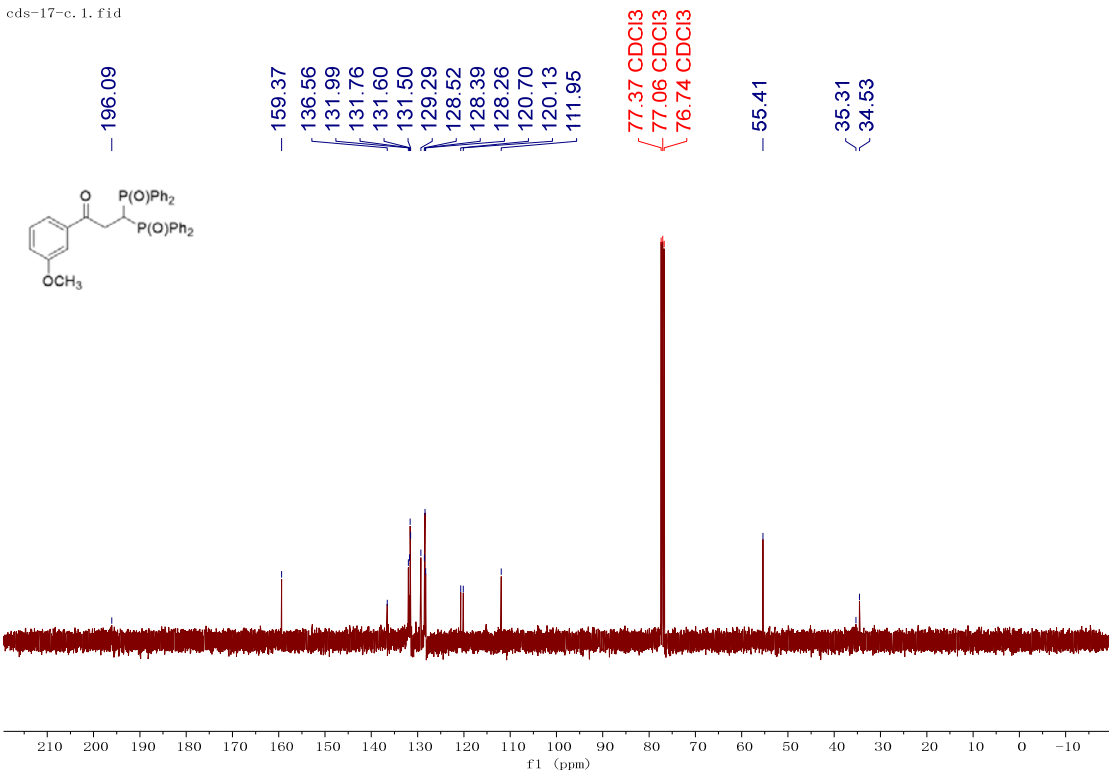
^{13}C NMR spectrum of **3b** (100 MHz, $CDCl_3$)



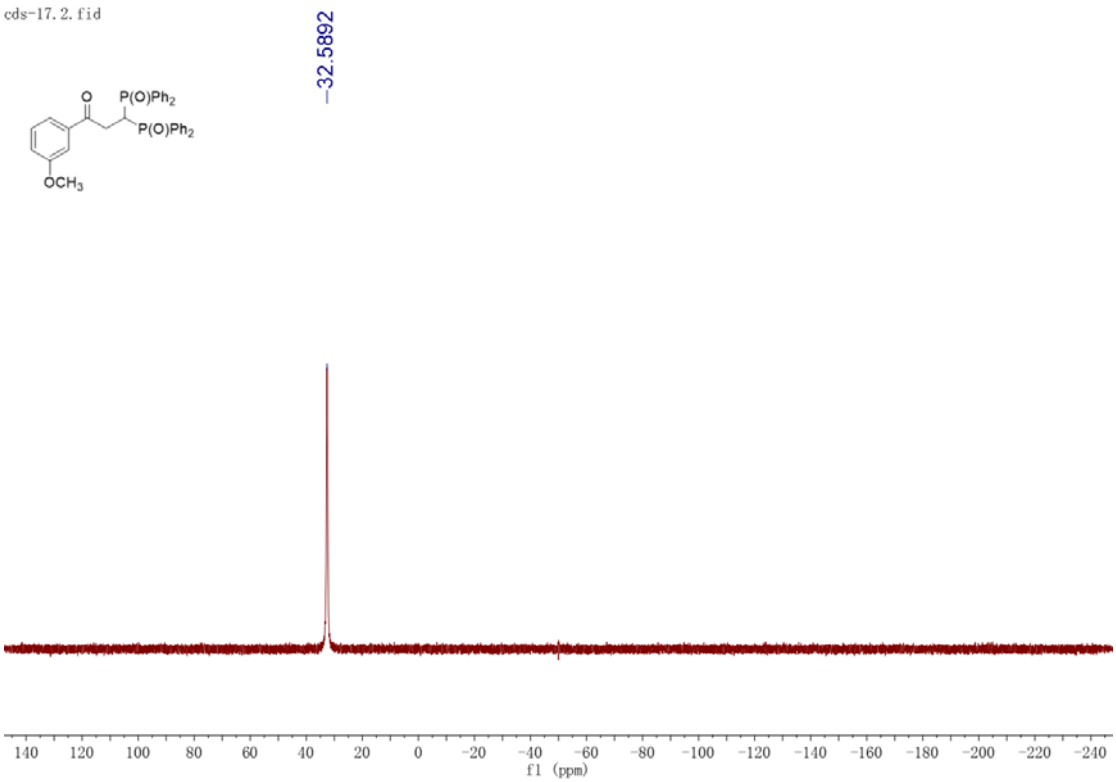
^{31}P NMR spectrum of **3b** (162 MHz, $CDCl_3$)



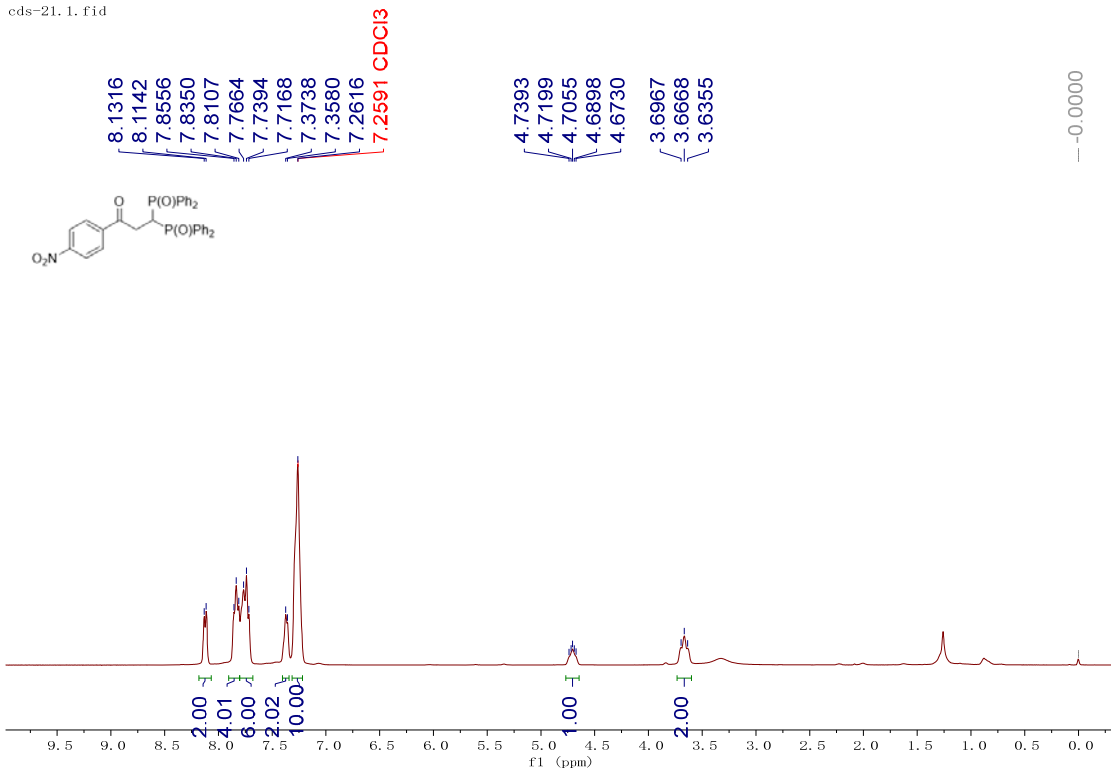
^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)



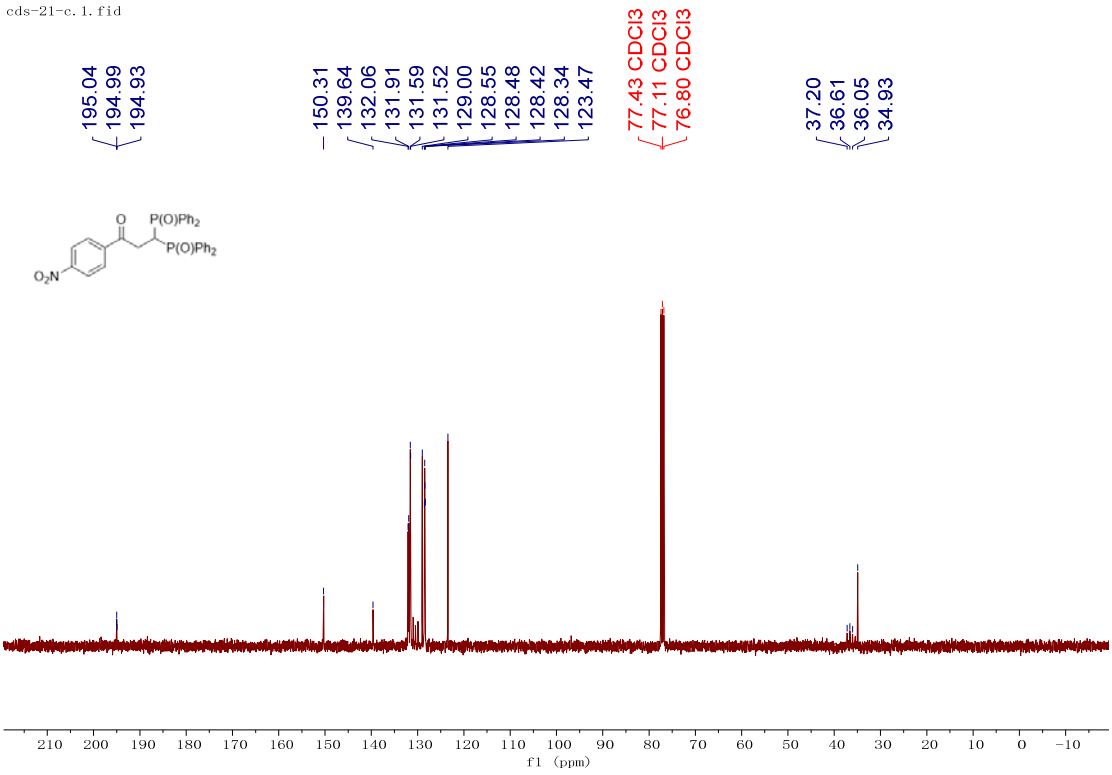
^{13}C NMR spectrum of **3c** (100 MHz, $CDCl_3$)



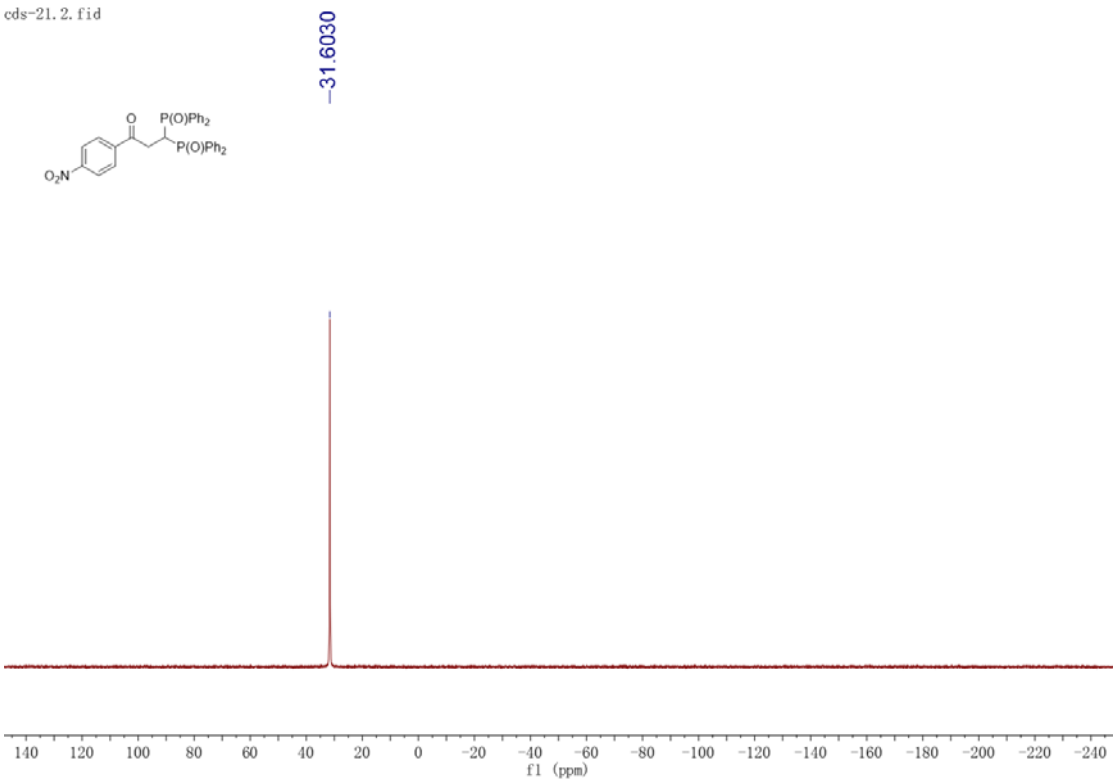
^{31}P NMR spectrum of **3c** (162 MHz, $CDCl_3$)



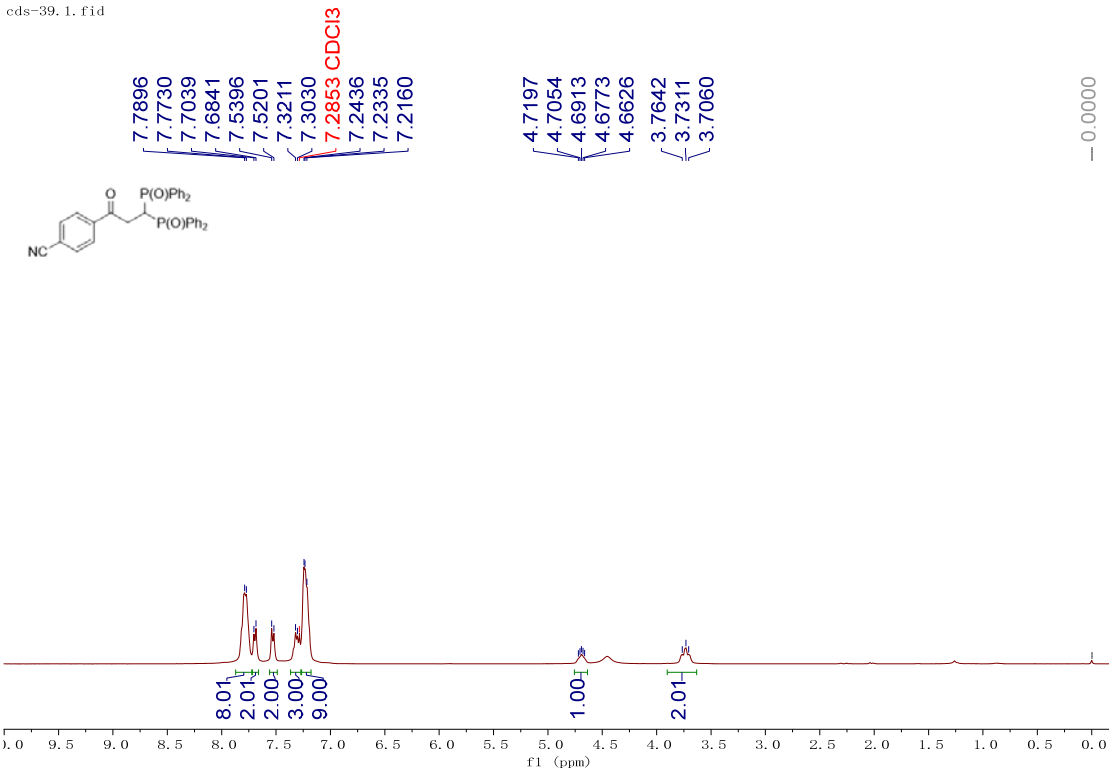
^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$)



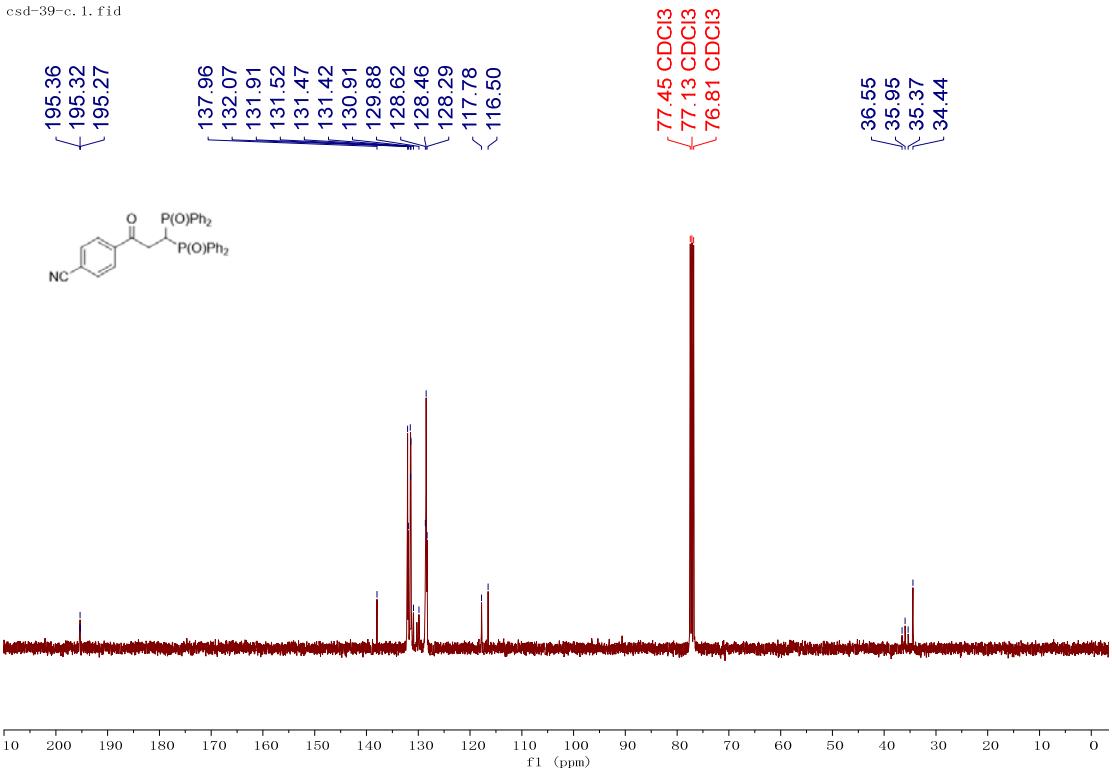
^{13}C NMR spectrum of **3d** (100 MHz, $CDCl_3$)



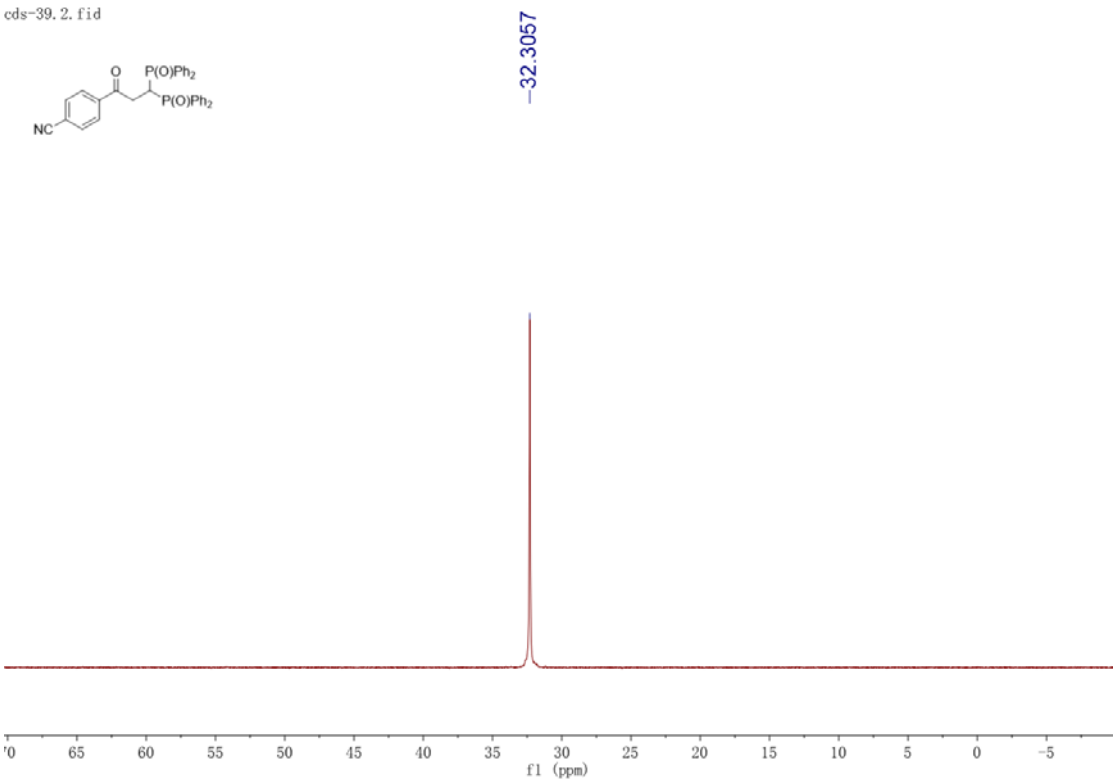
^{31}P NMR spectrum of **3d** (162 MHz, $CDCl_3$)



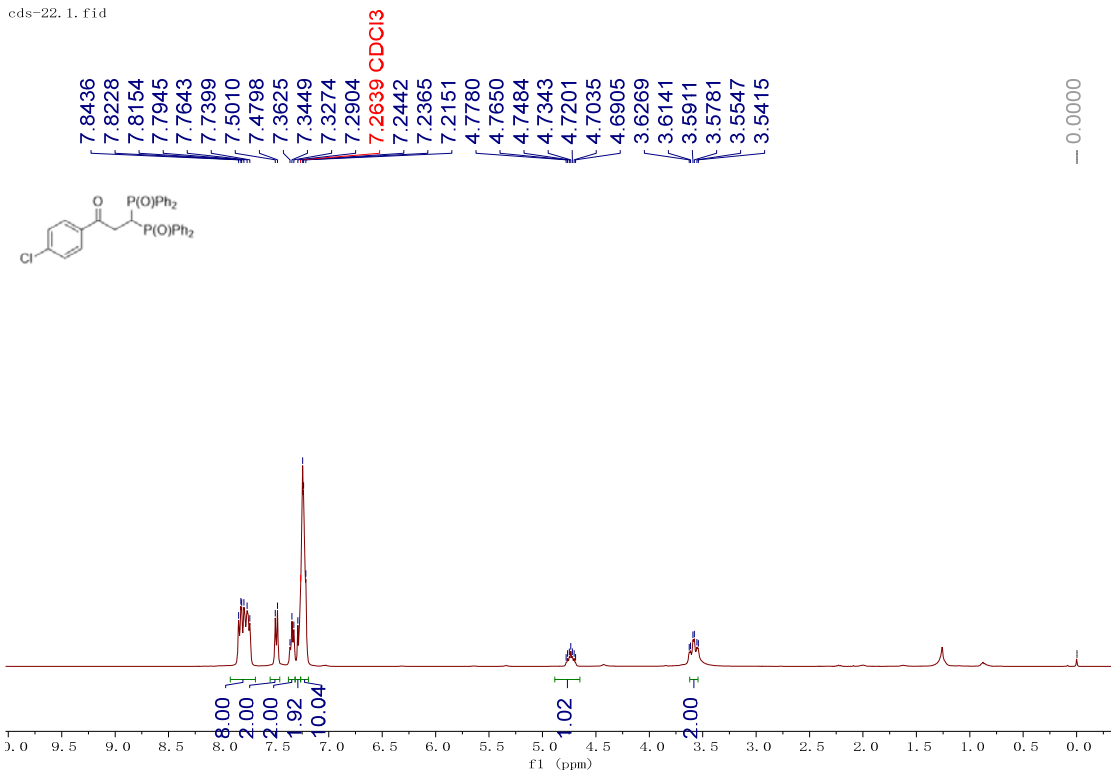
^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)



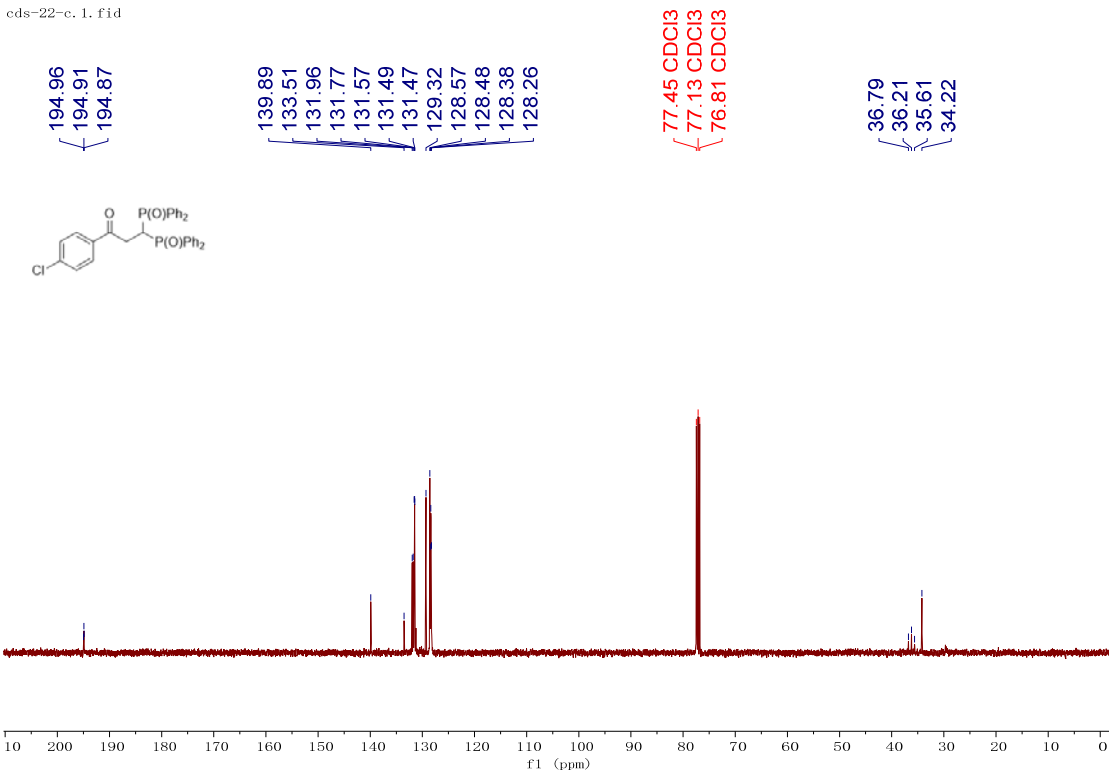
^{13}C NMR spectrum of **3e** (100 MHz, $CDCl_3$)



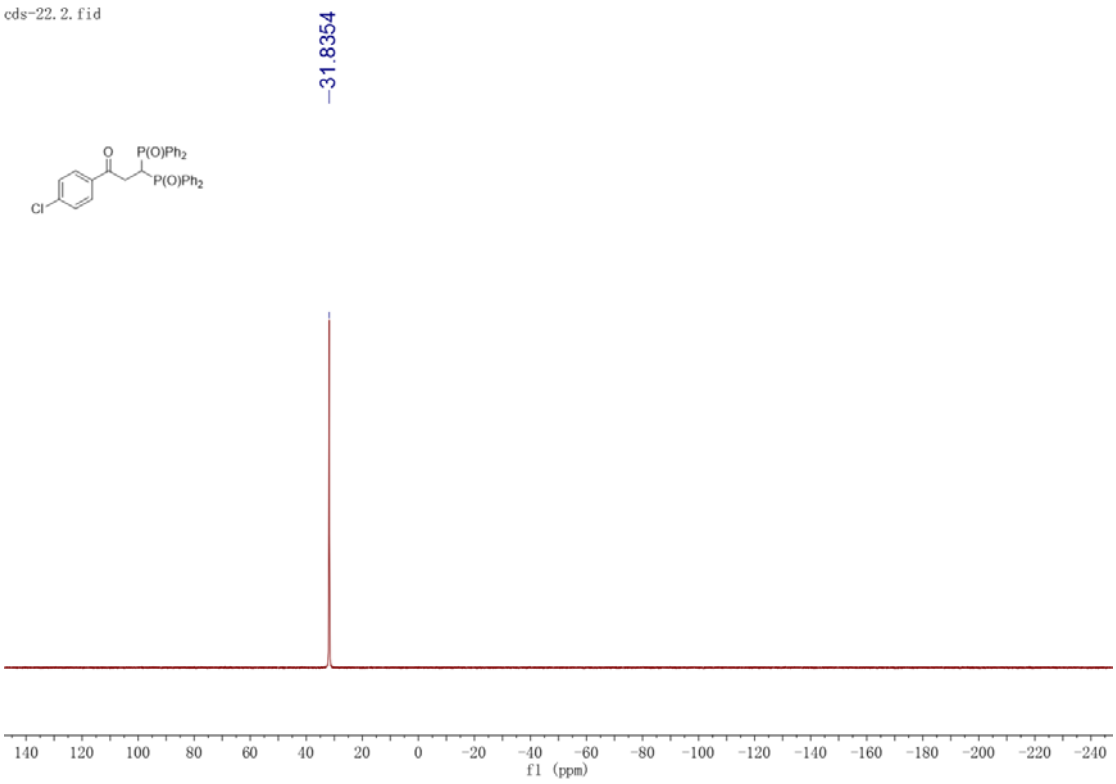
^{31}P NMR spectrum of **3e** (162 MHz, $CDCl_3$)



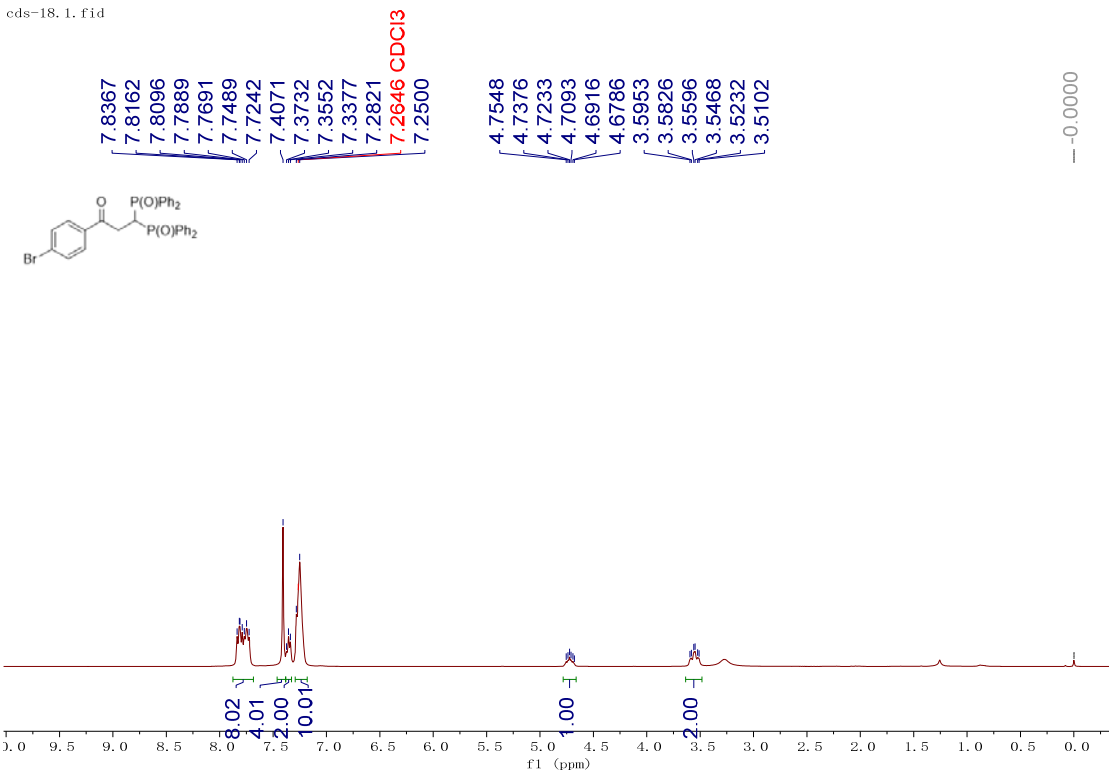
^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)



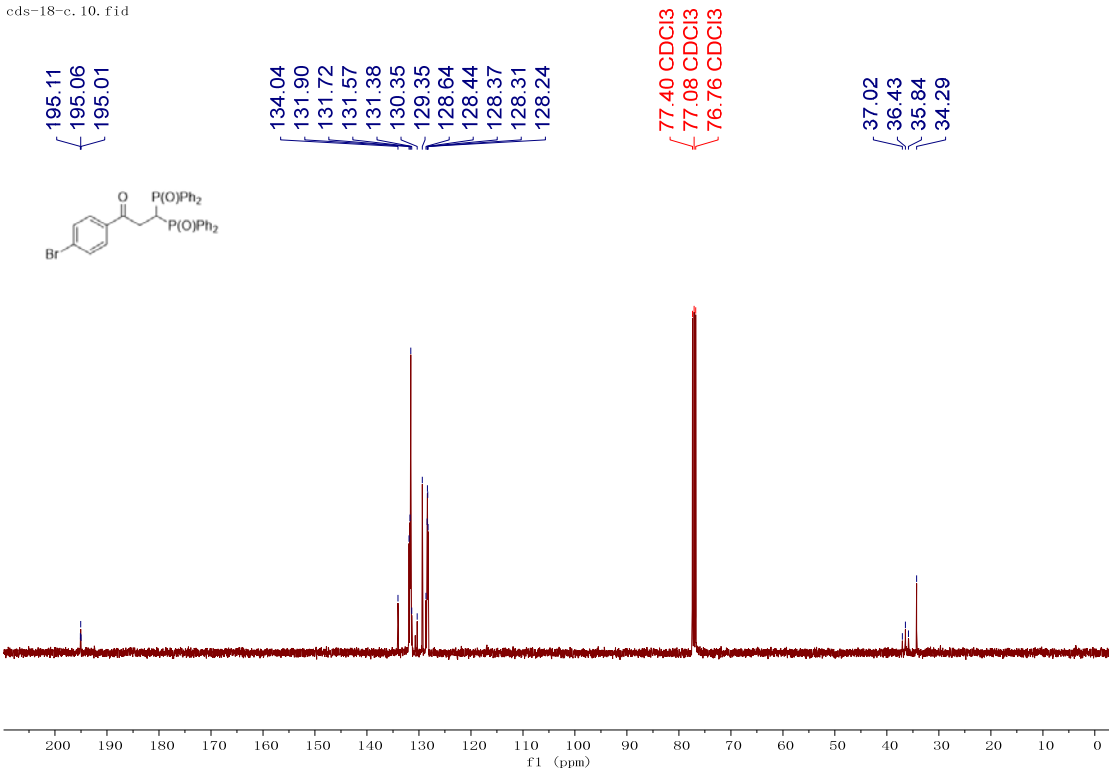
^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$)



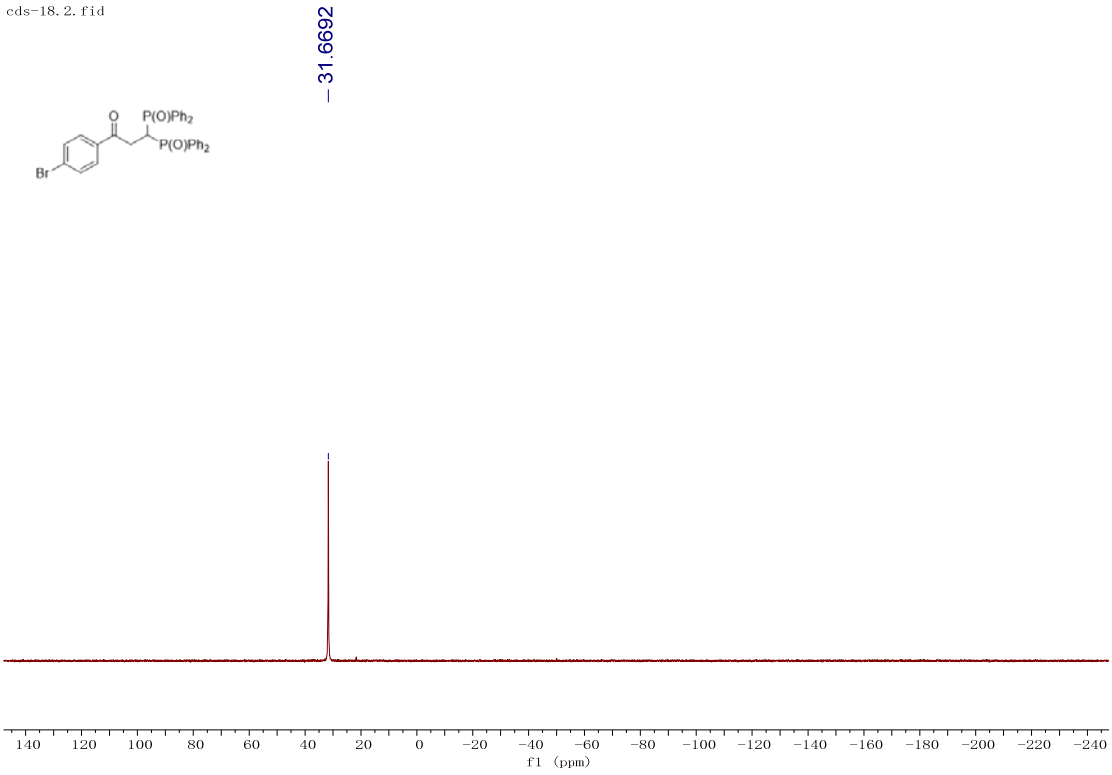
^{31}P NMR spectrum of **3f** (162 MHz, $CDCl_3$)



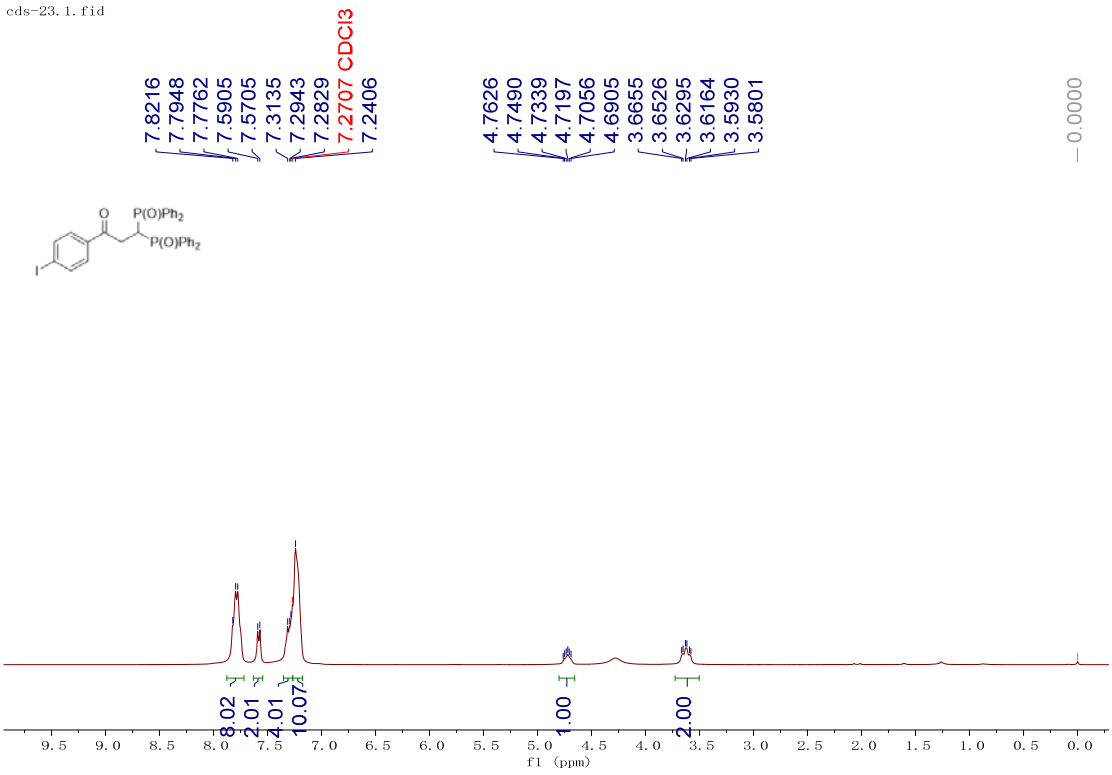
^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)



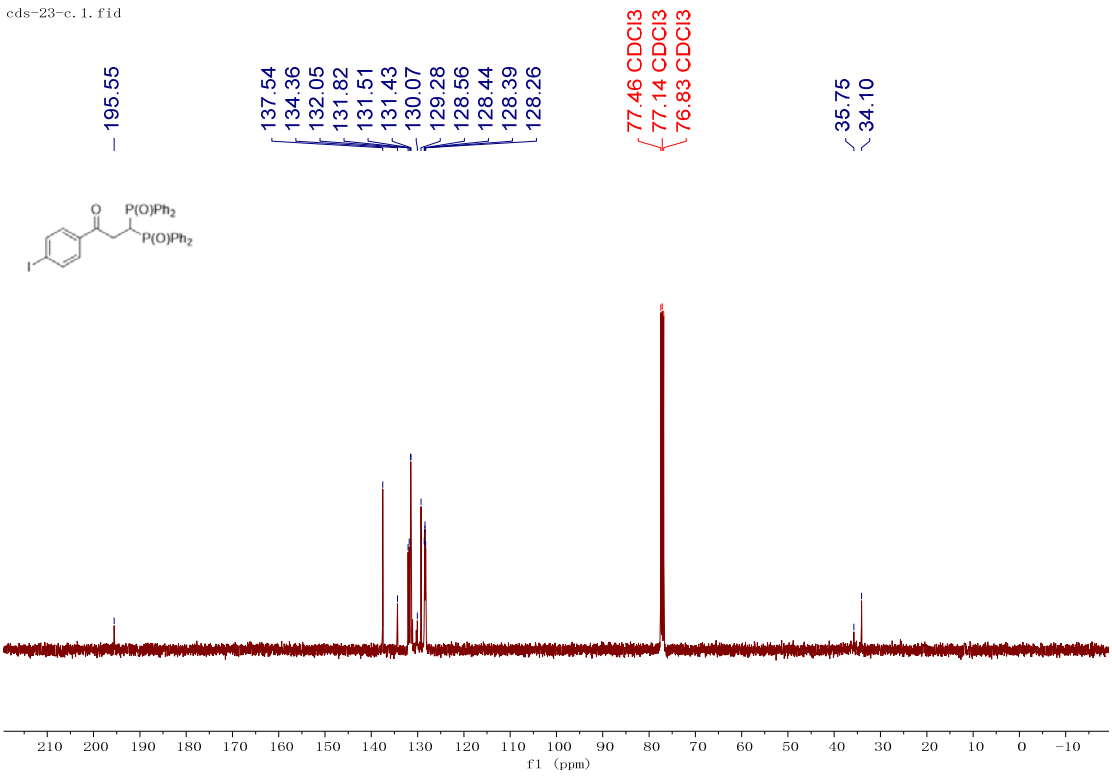
^{13}C NMR spectrum of **3g** (100 MHz, $CDCl_3$)



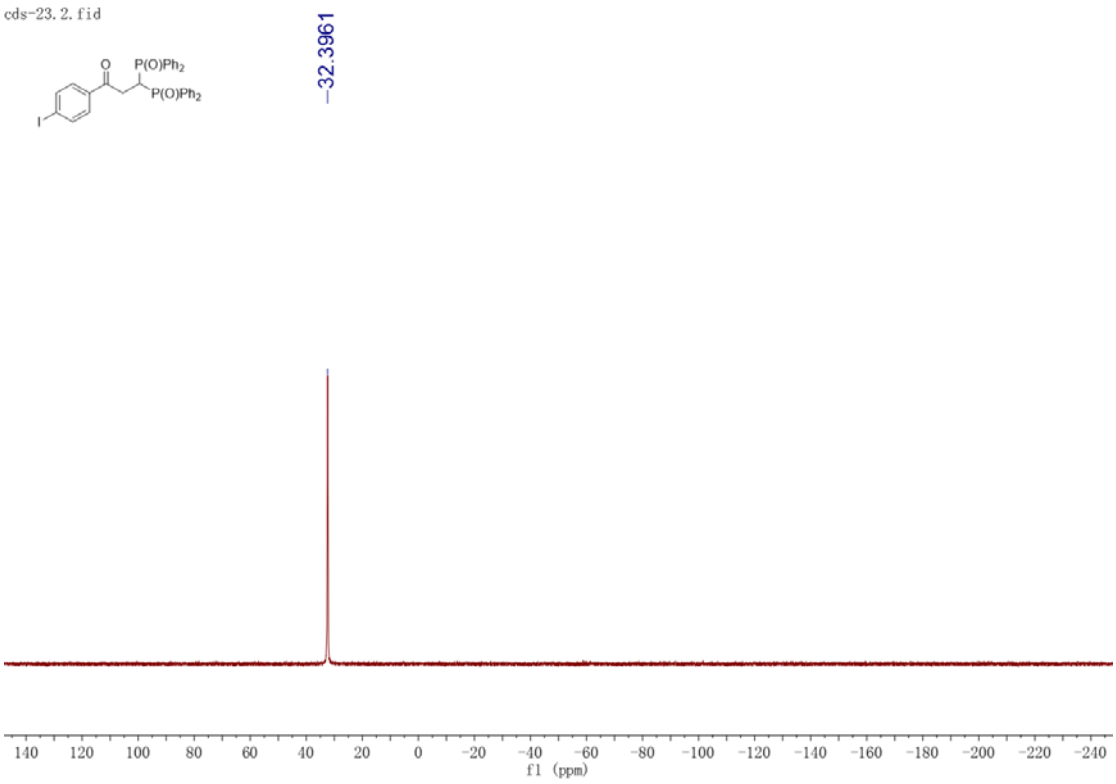
^{31}P NMR spectrum of **3g** (162 MHz, $CDCl_3$)



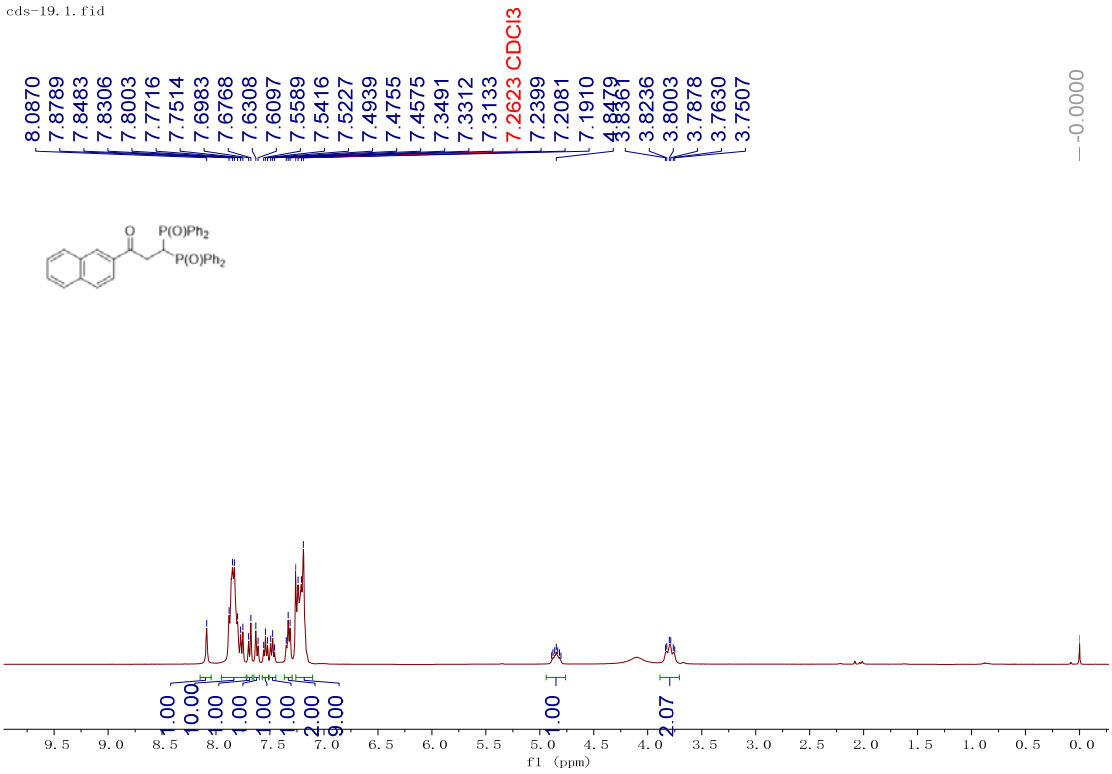
^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)



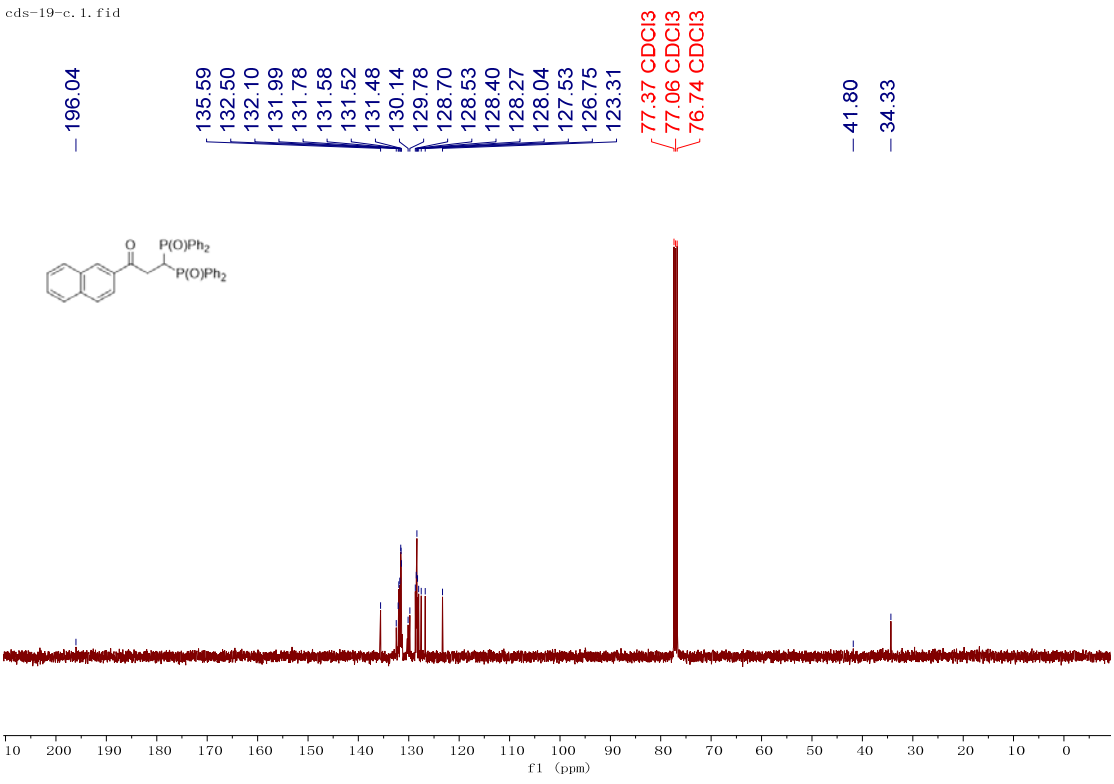
^{13}C NMR spectrum of **3h** (100 MHz, $CDCl_3$)



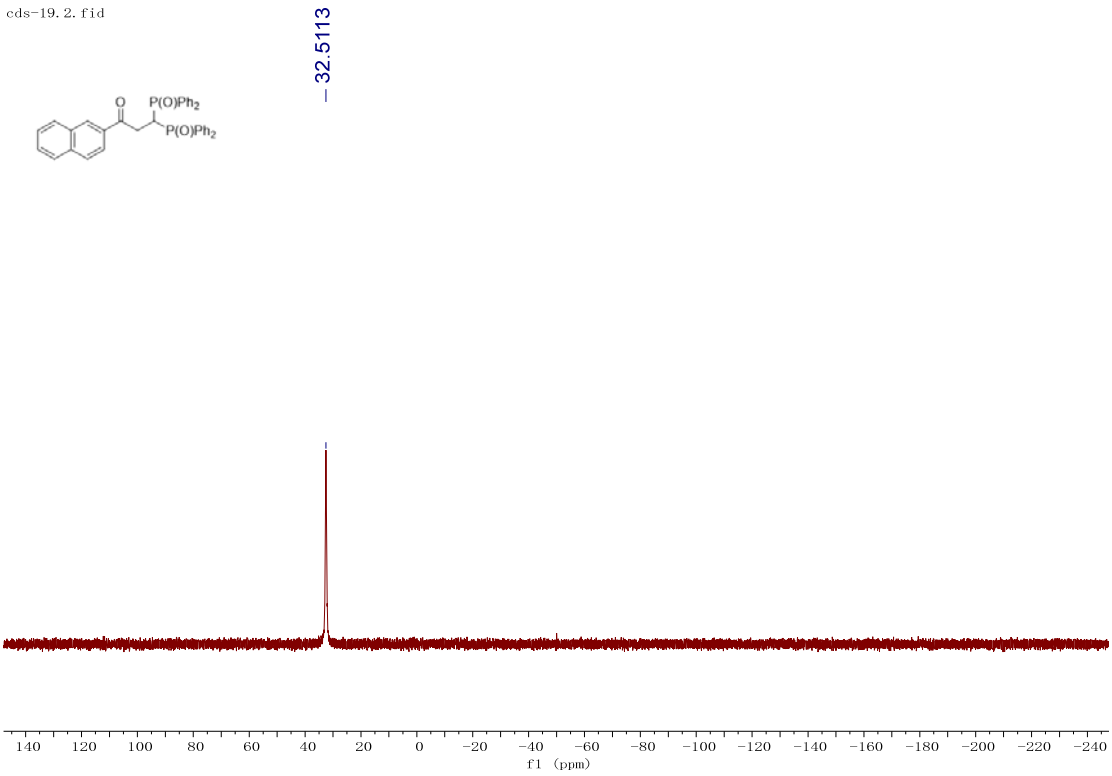
^{31}P NMR spectrum of **3h** (162 MHz, $CDCl_3$)



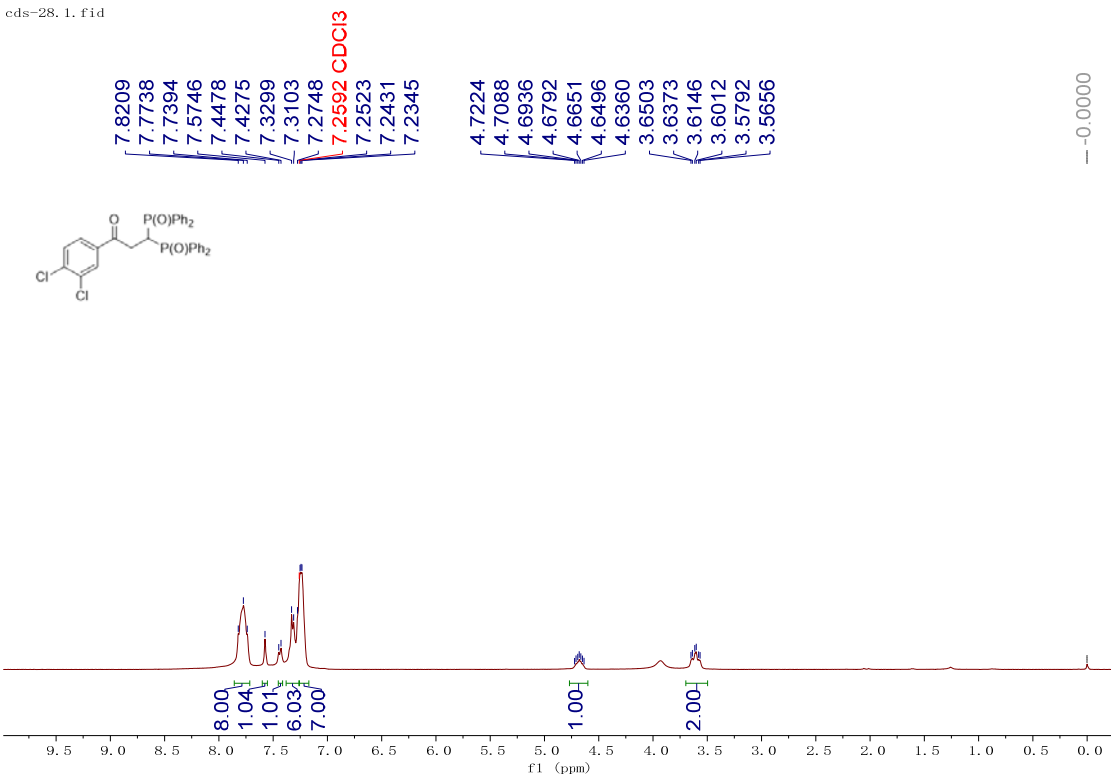
^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$)



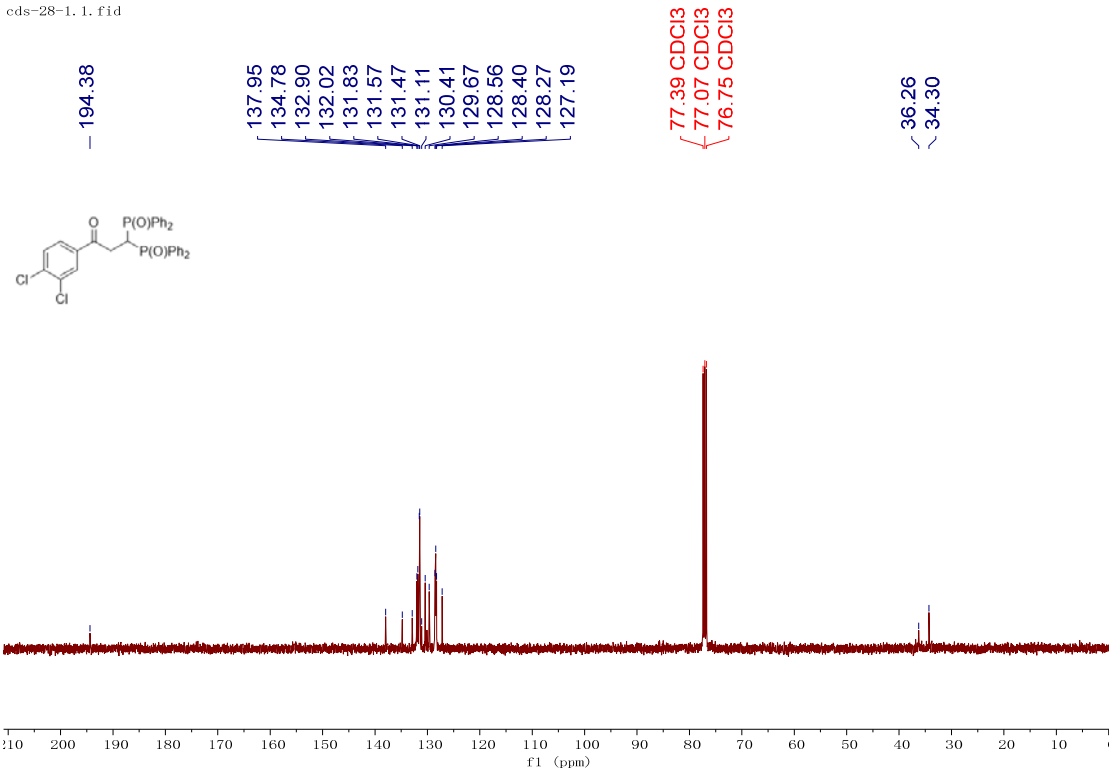
^{13}C NMR spectrum of **3i** (100 MHz, $CDCl_3$)



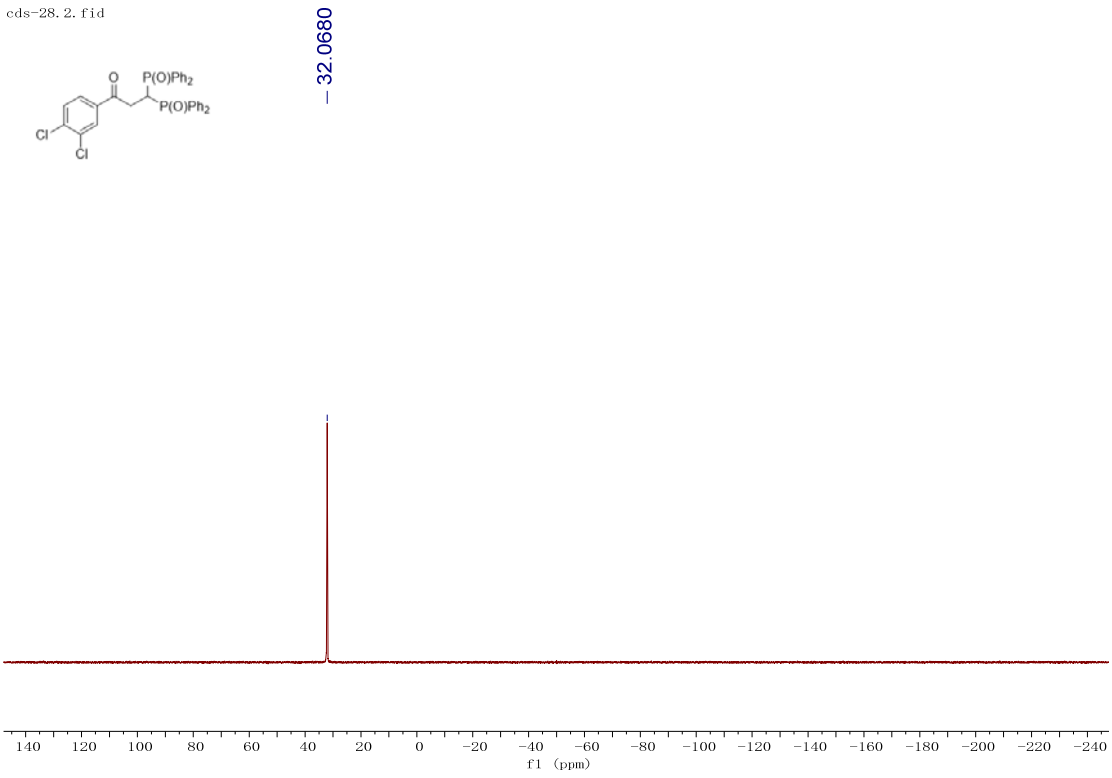
^{31}P NMR spectrum of **3i** (162 MHz, $CDCl_3$)



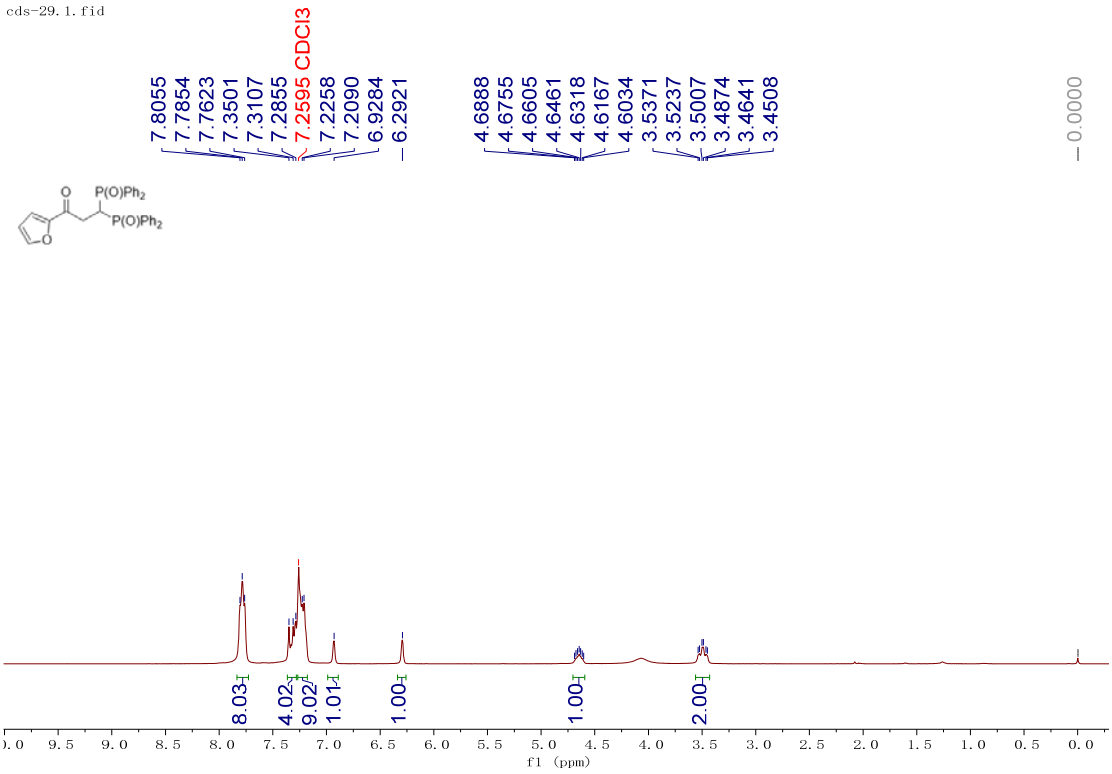
^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$)



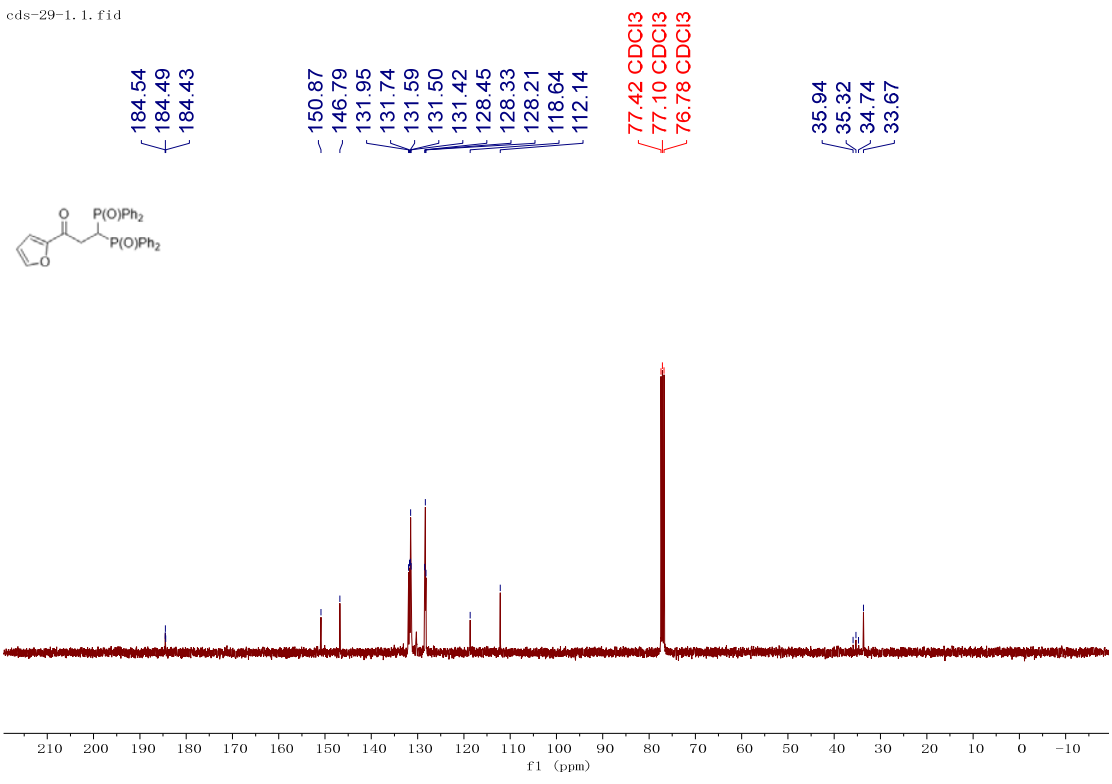
^{13}C NMR spectrum of **3j** (100 MHz, $CDCl_3$)



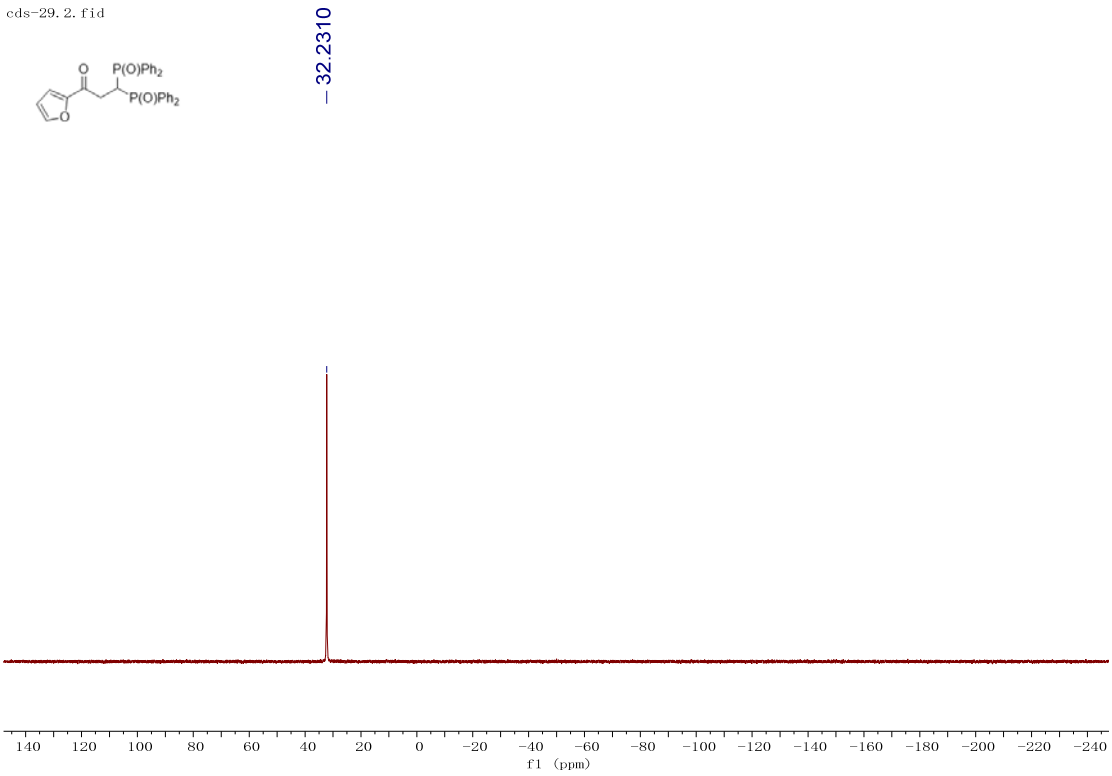
^{31}P NMR spectrum of **3j** (162 MHz, $CDCl_3$)



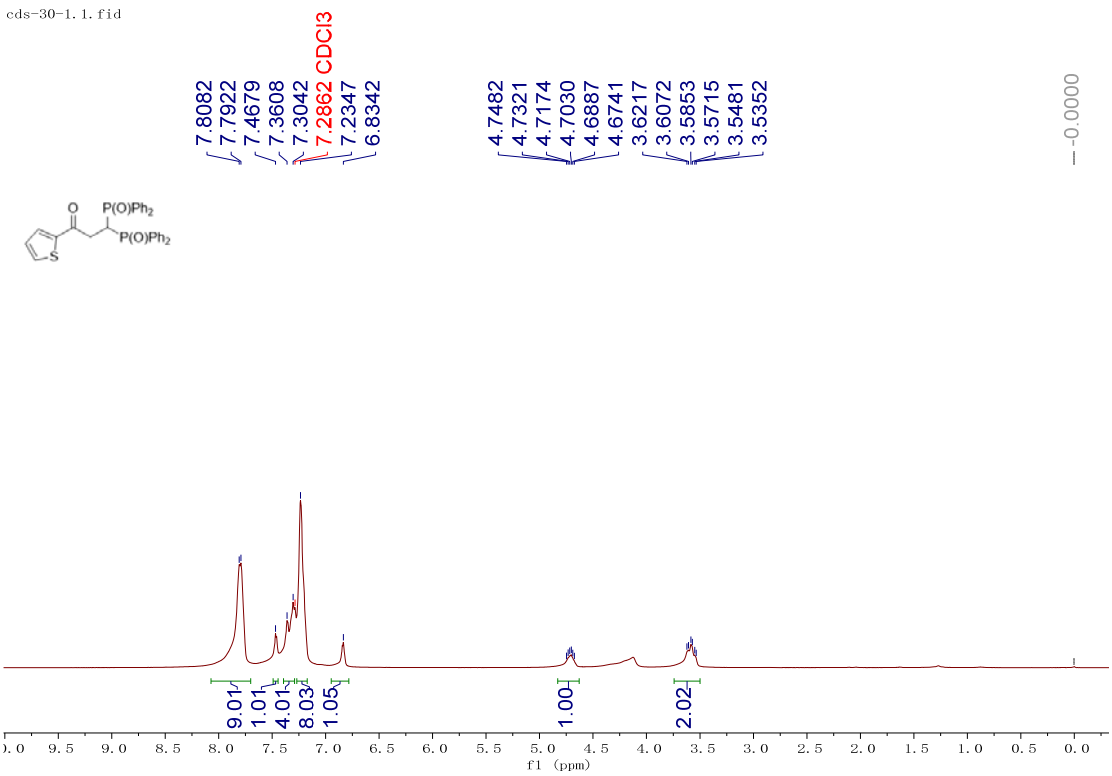
^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)



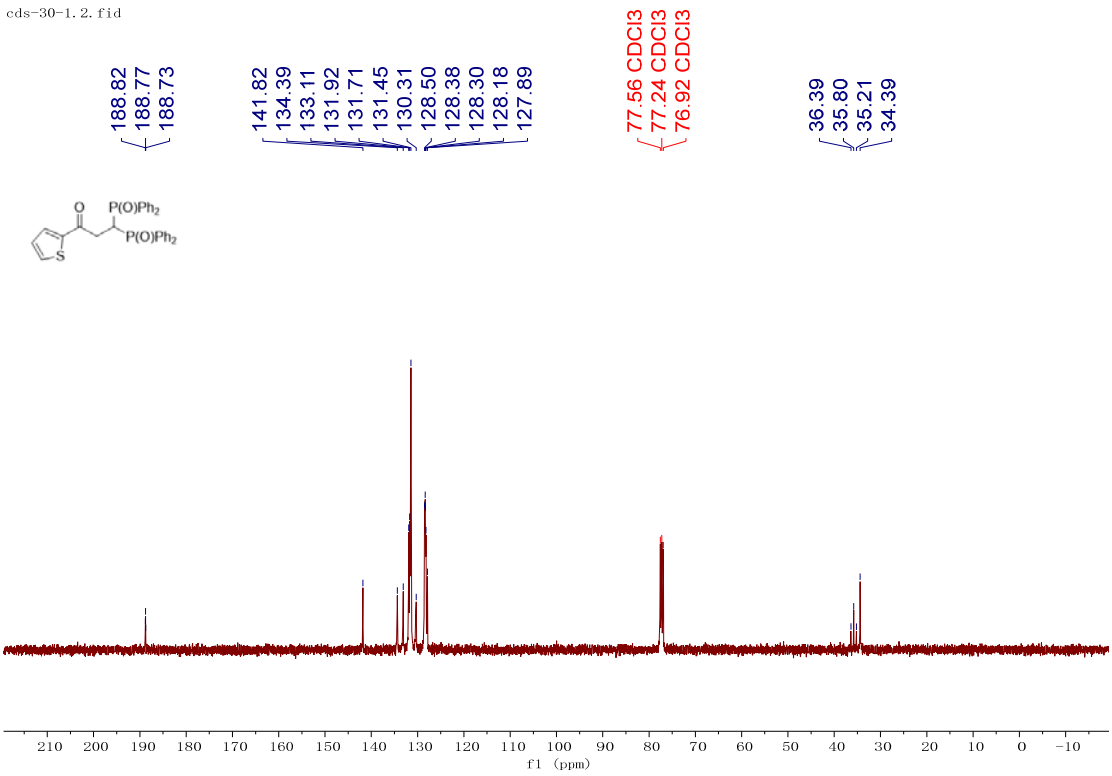
^{13}C NMR spectrum of **3k** (100 MHz, $CDCl_3$)



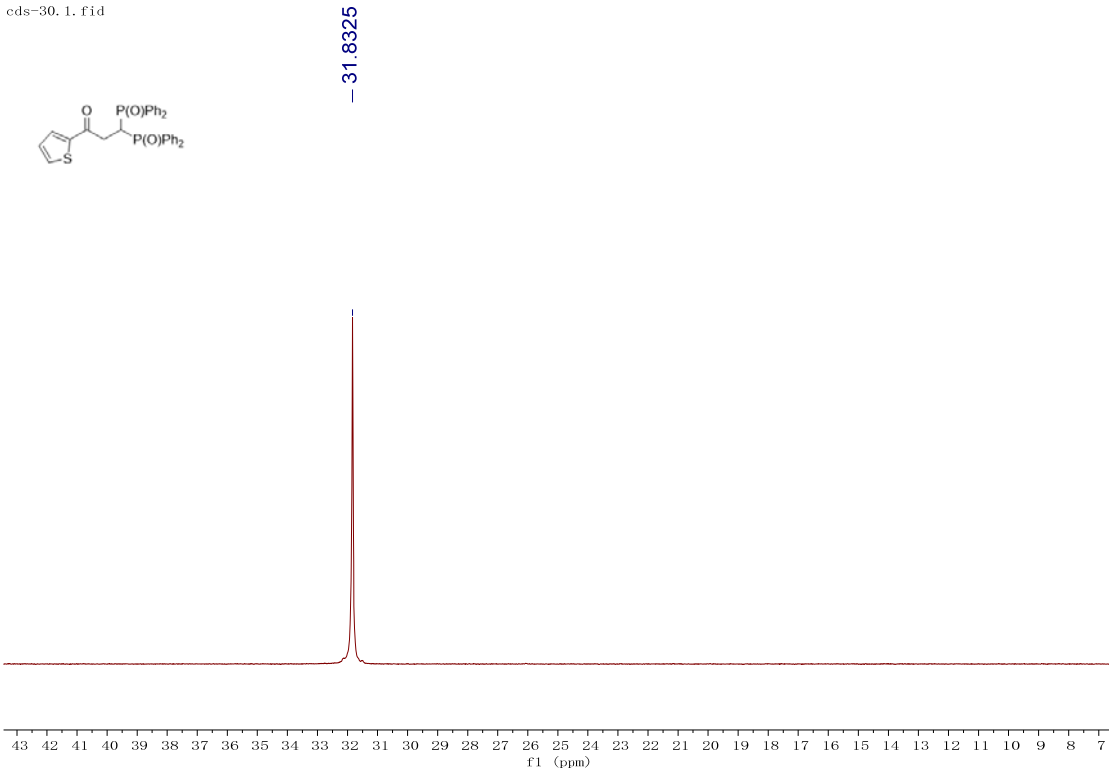
^{31}P NMR spectrum of **3k** (162 MHz, $CDCl_3$)



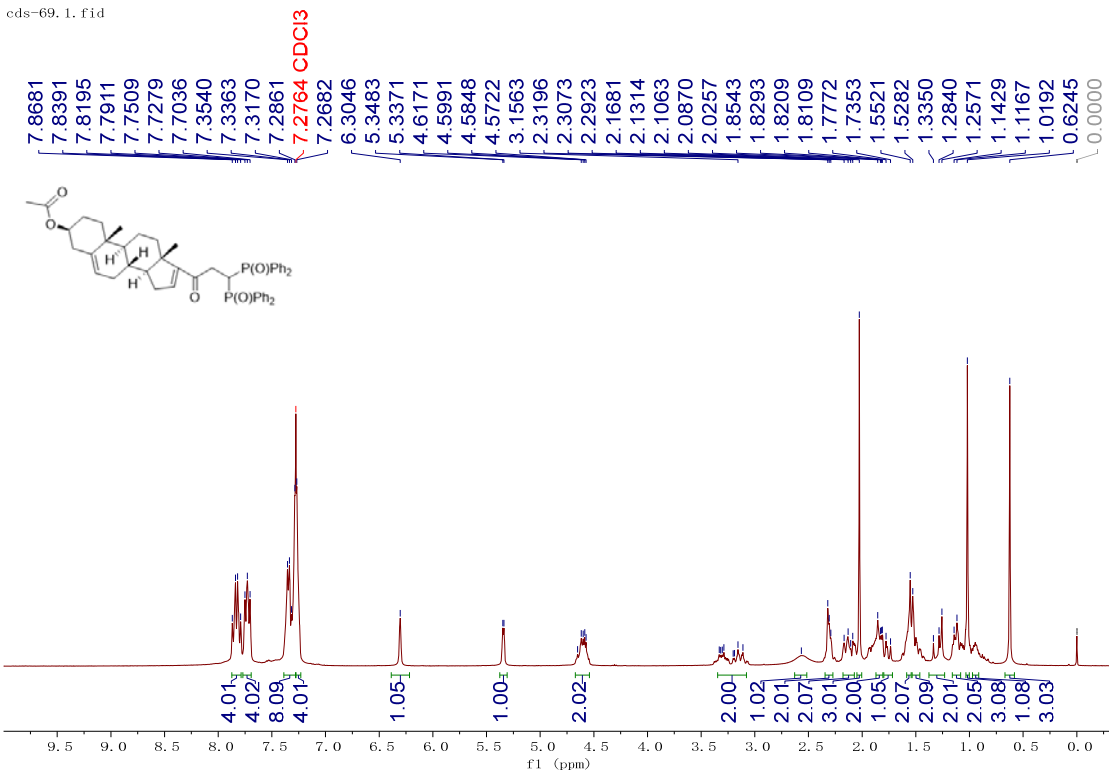
^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)



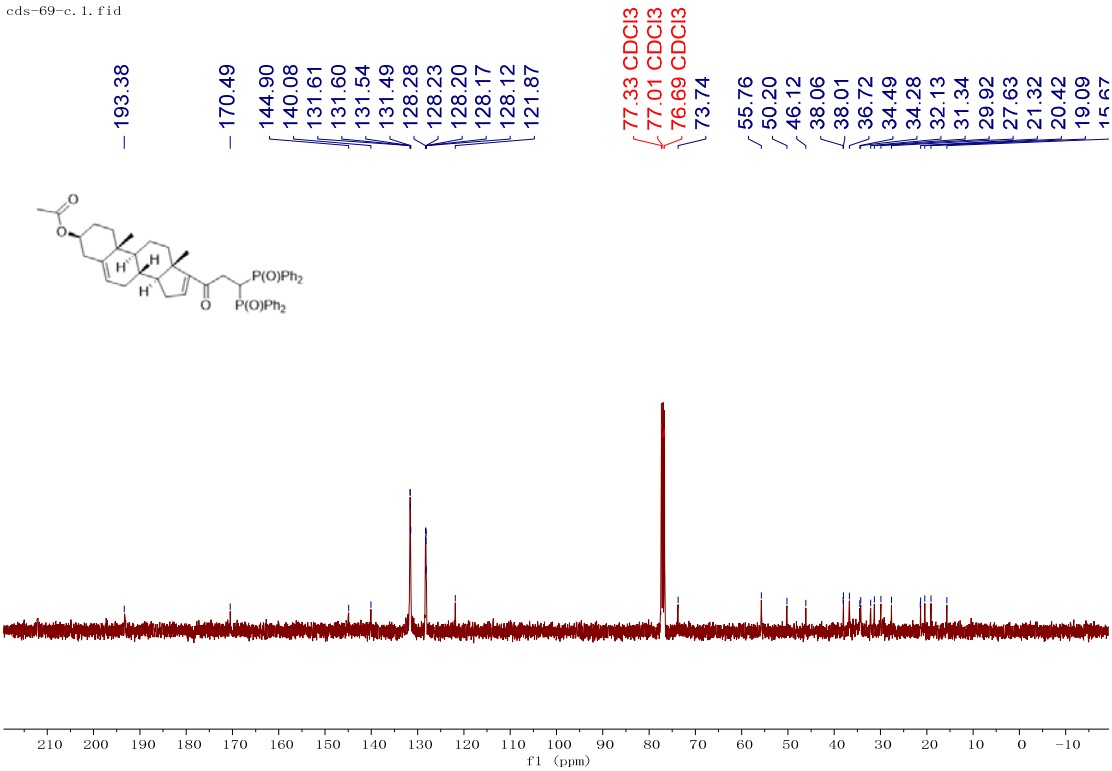
^{13}C NMR spectrum of **3l** (100 MHz, $CDCl_3$)



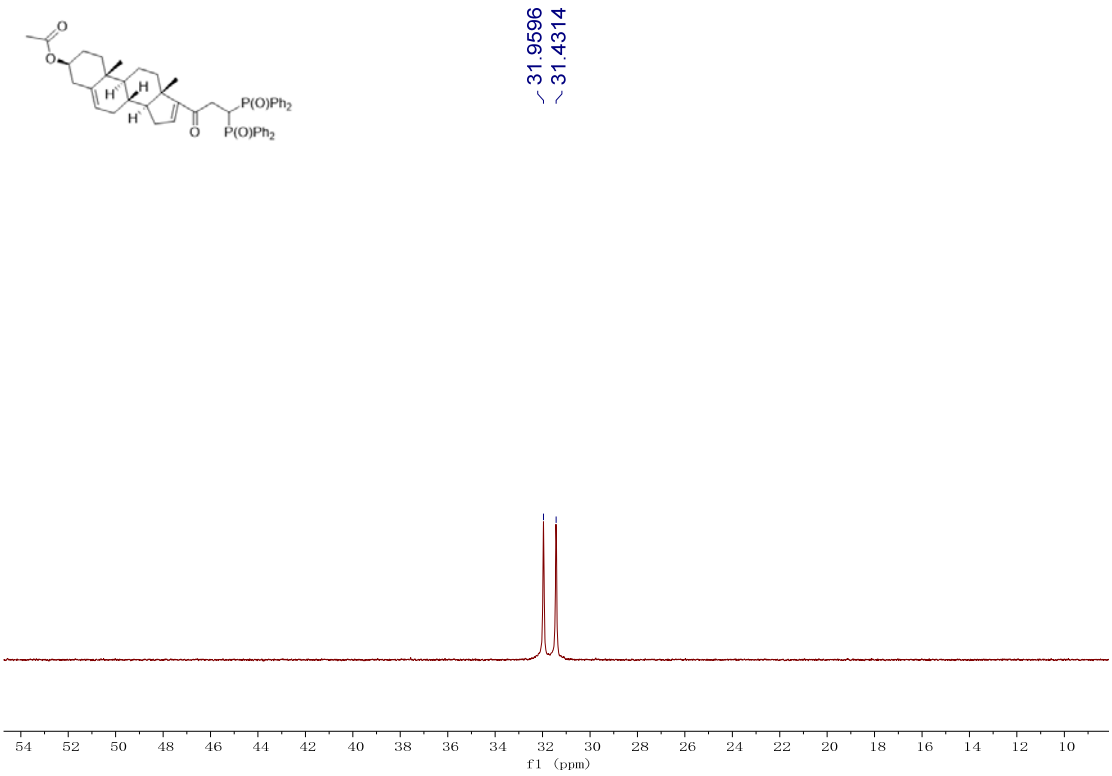
^{31}P NMR spectrum of **3l** (162 MHz, $CDCl_3$)



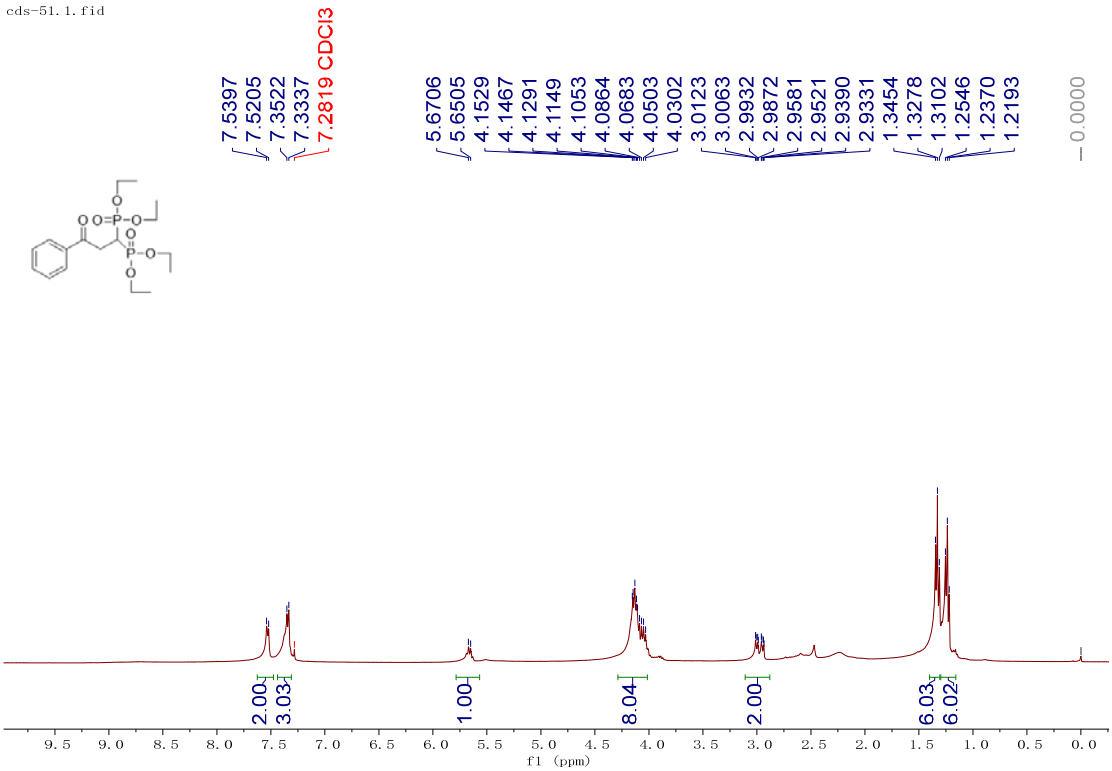
^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)



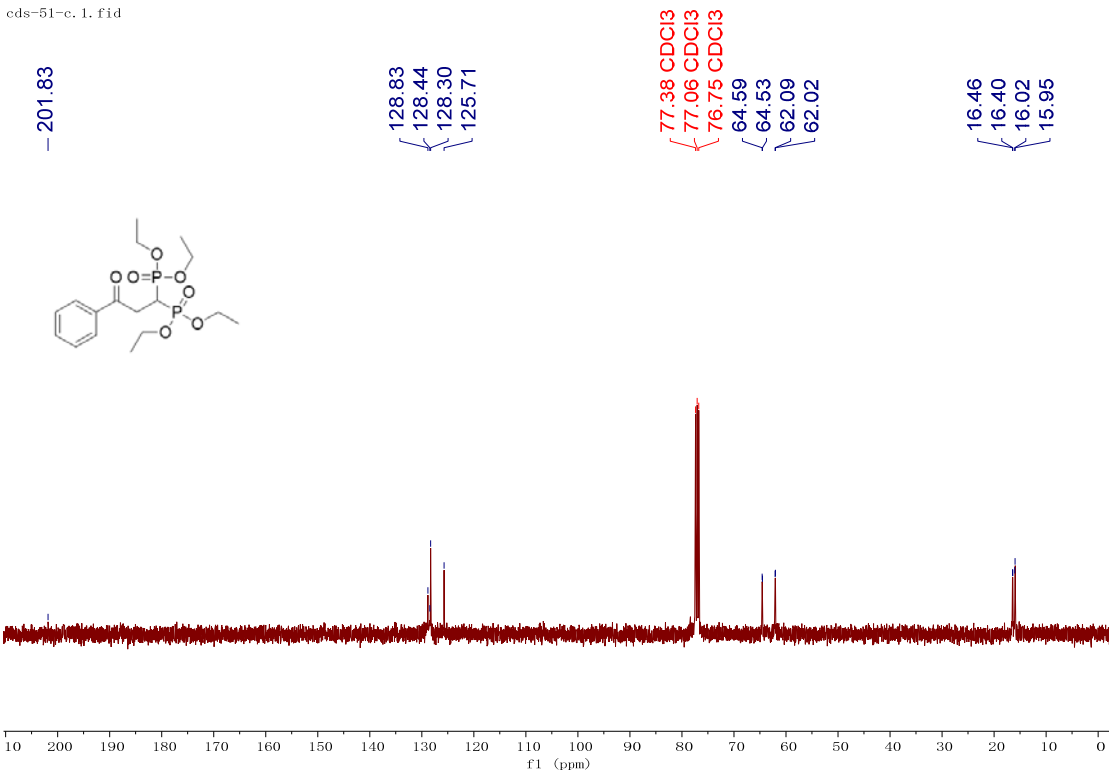
^{13}C NMR spectrum of **3m** (100 MHz, $CDCl_3$)



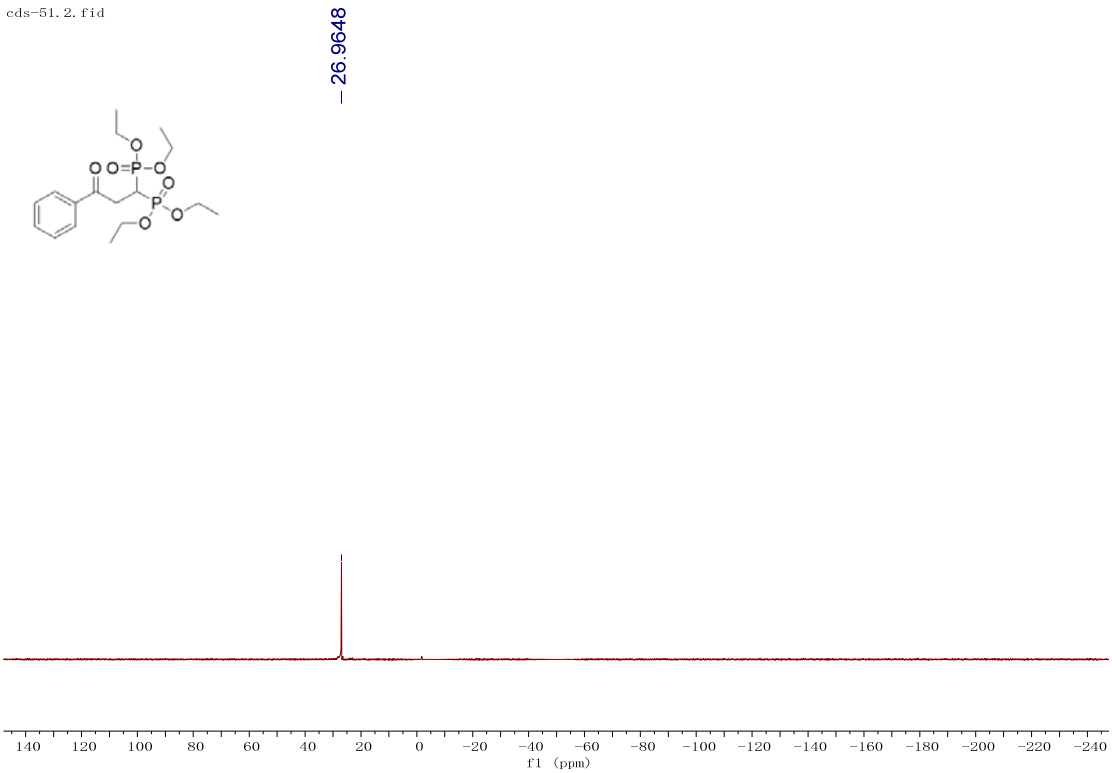
^{31}P NMR spectrum of **3m** (162 MHz, $CDCl_3$)



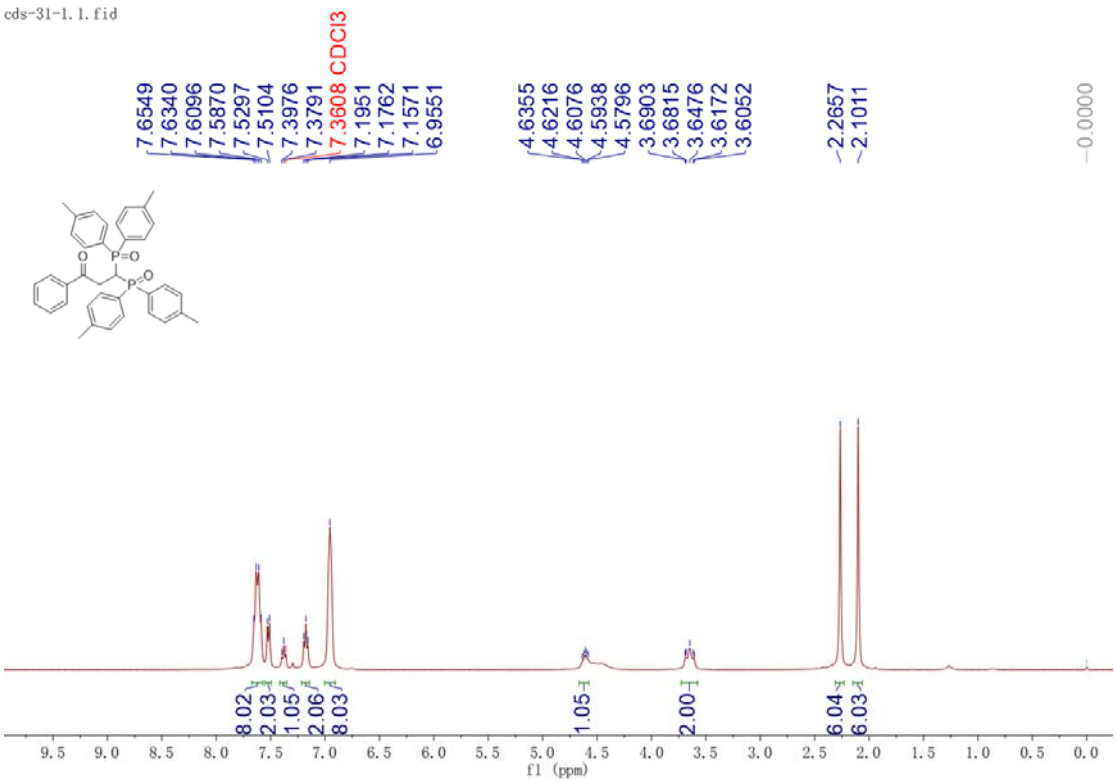
^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$)



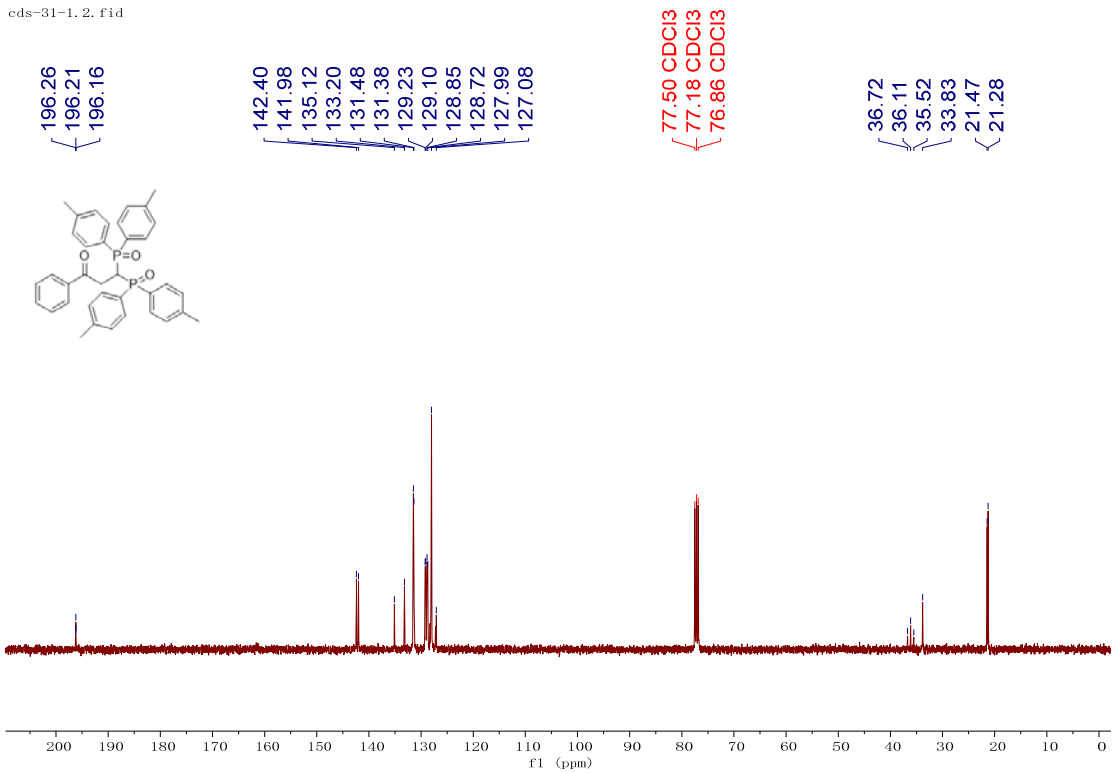
^{13}C NMR spectrum of **3n** (100 MHz, $CDCl_3$)



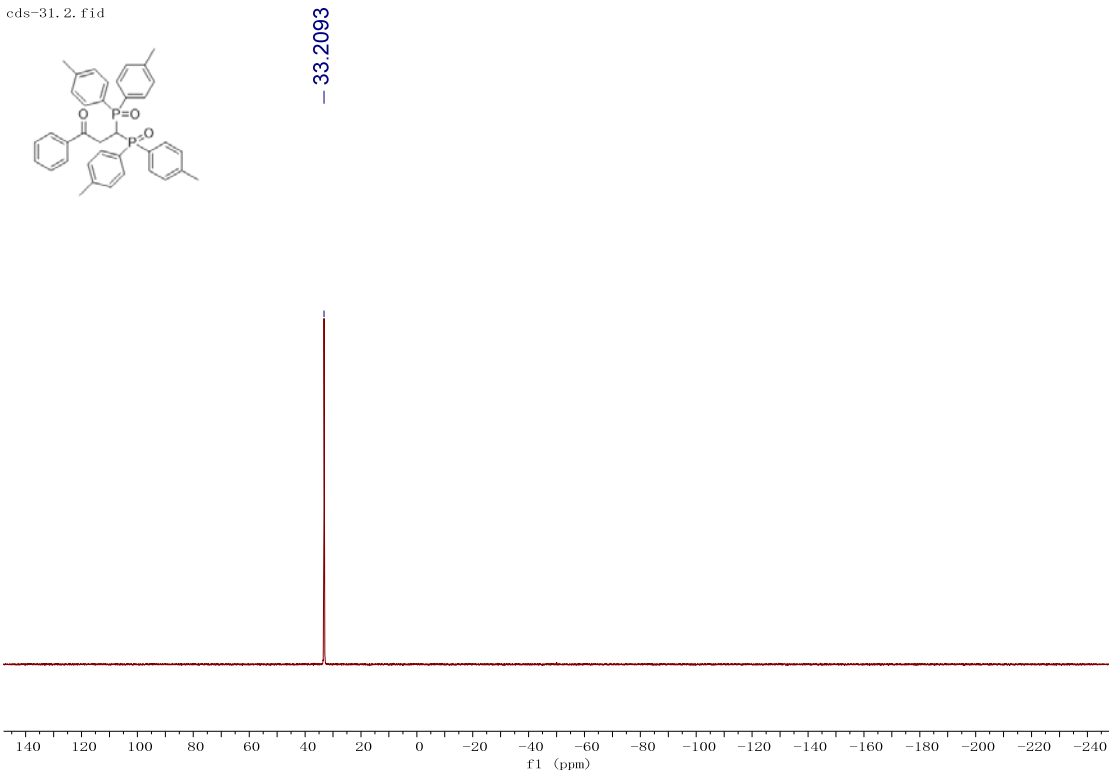
^{31}P NMR spectrum of **3n** (162 MHz, $CDCl_3$)



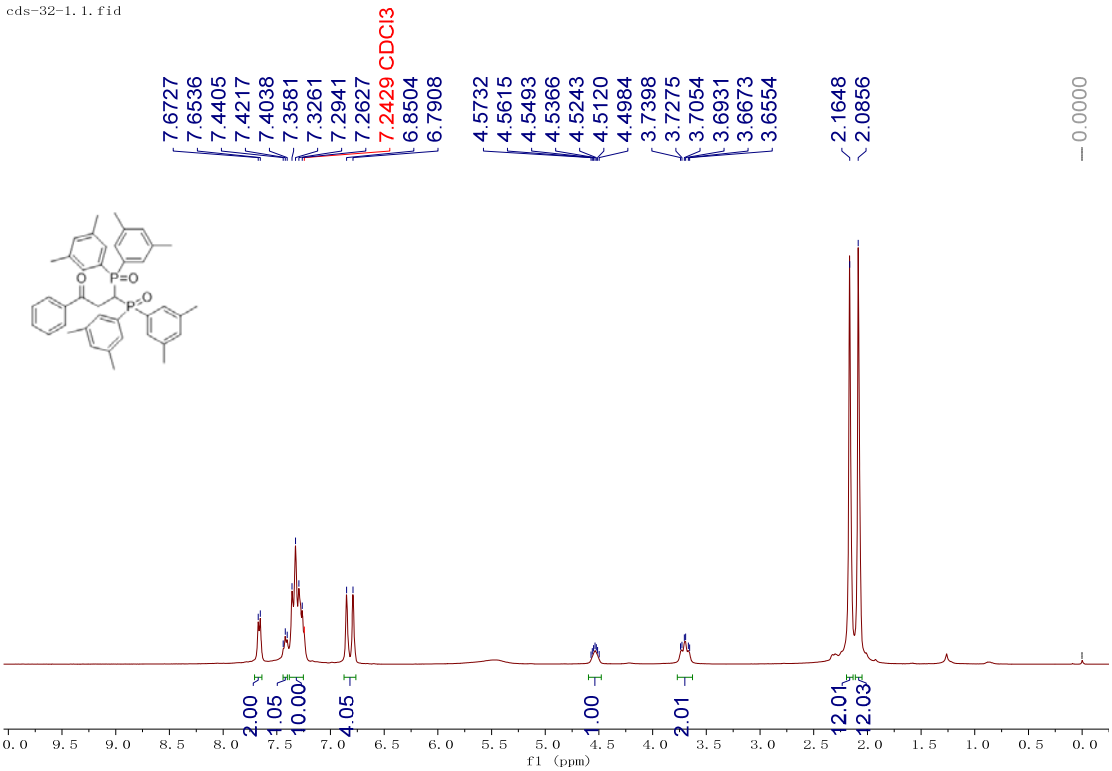
^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$)



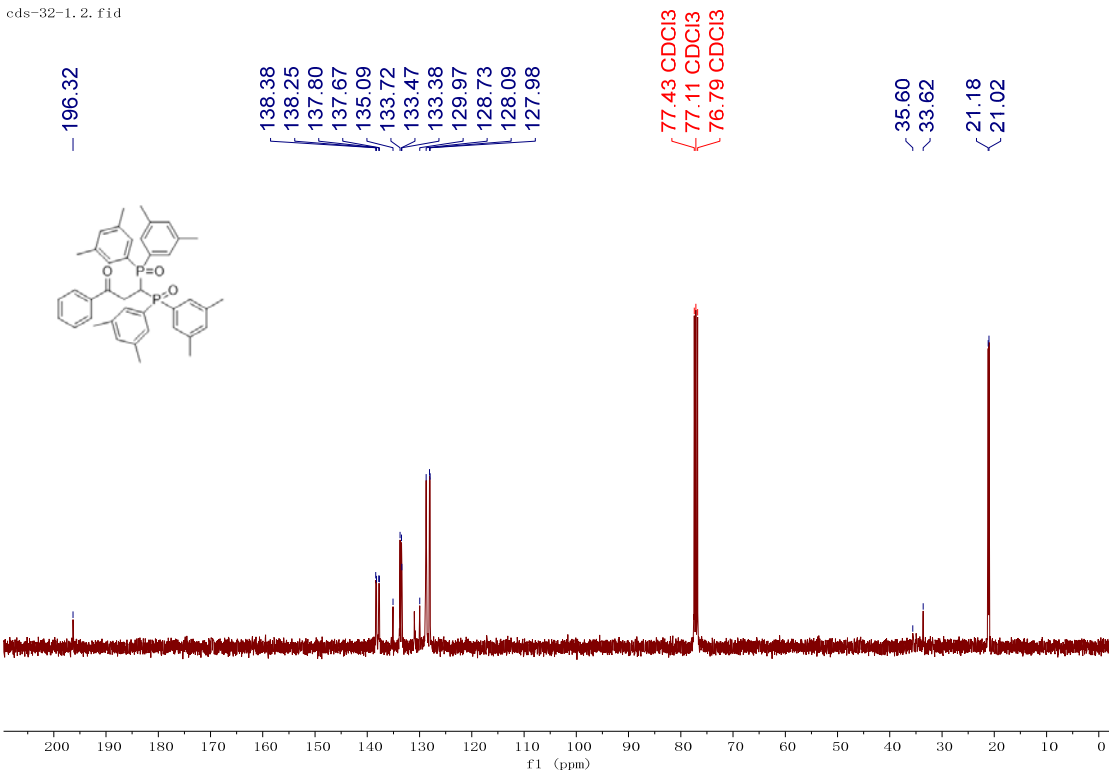
^{13}C NMR spectrum of **3o** (100 MHz, $CDCl_3$)



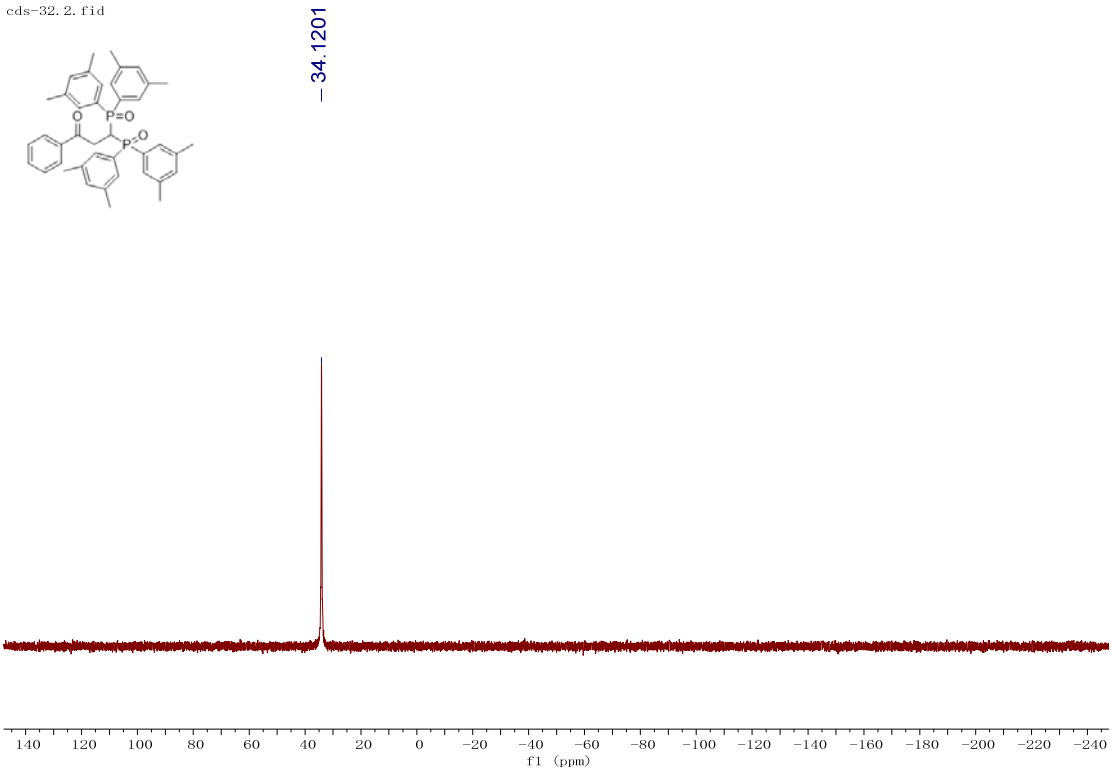
^{31}P NMR spectrum of **3o** (162 MHz, $CDCl_3$)



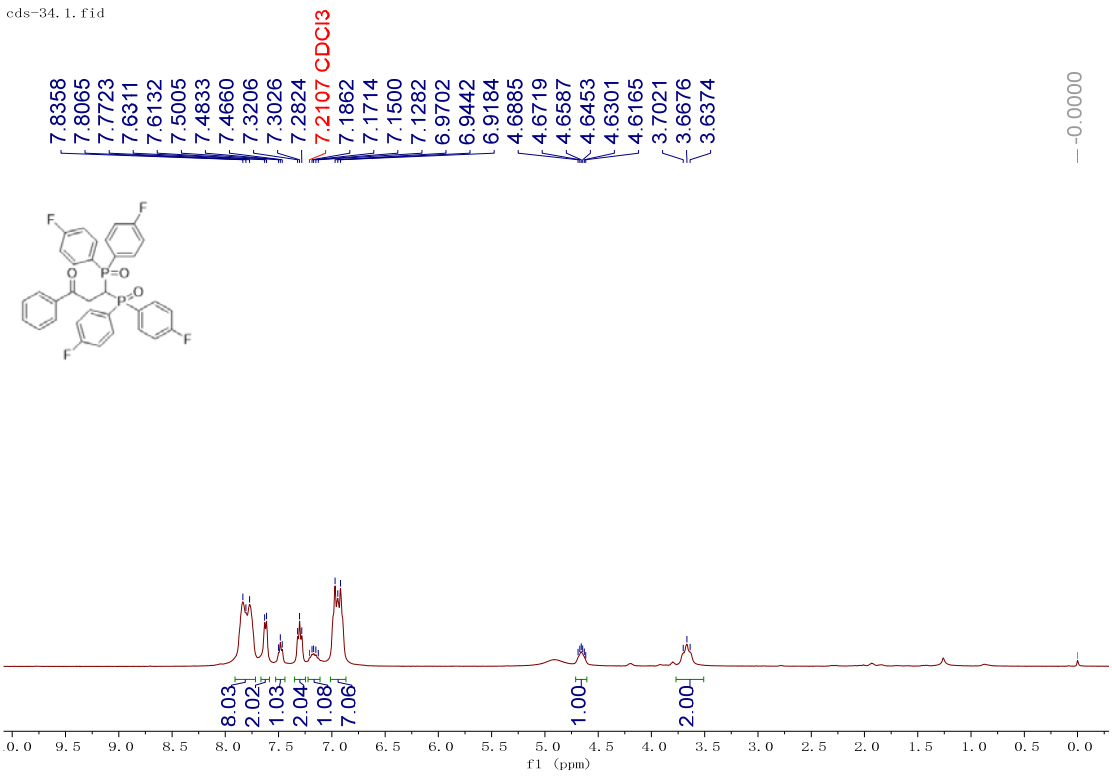
^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$)



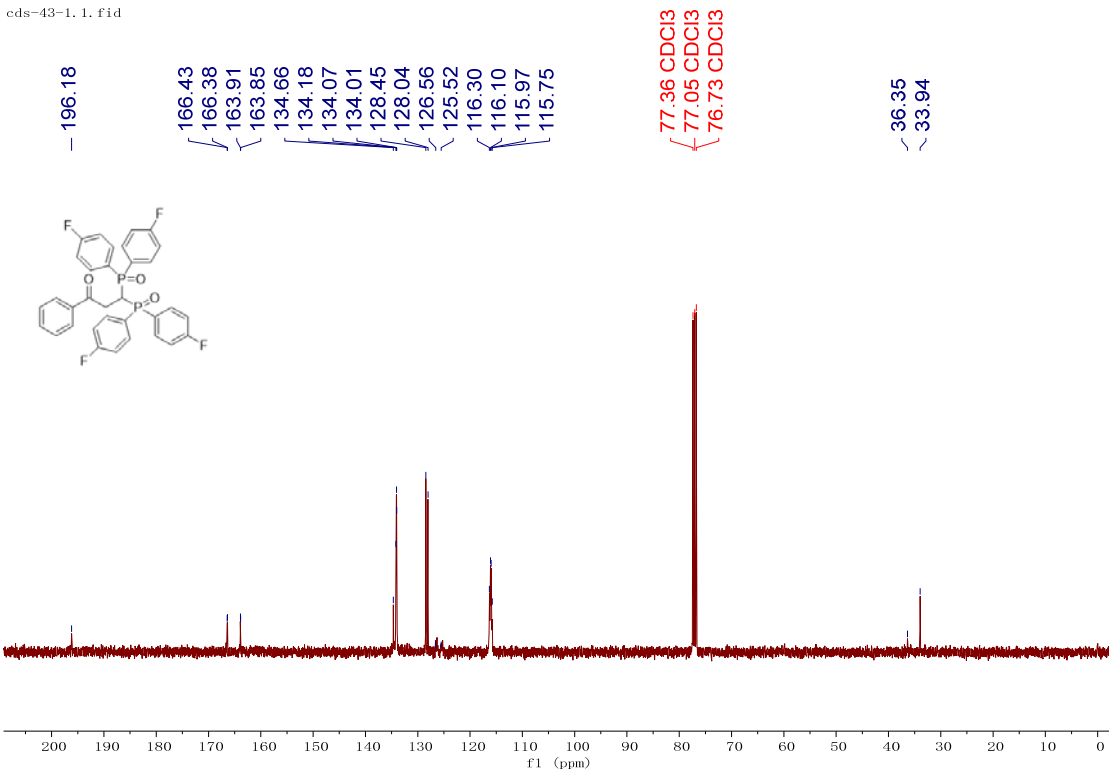
^{13}C NMR spectrum of **3p** (100 MHz, $CDCl_3$)



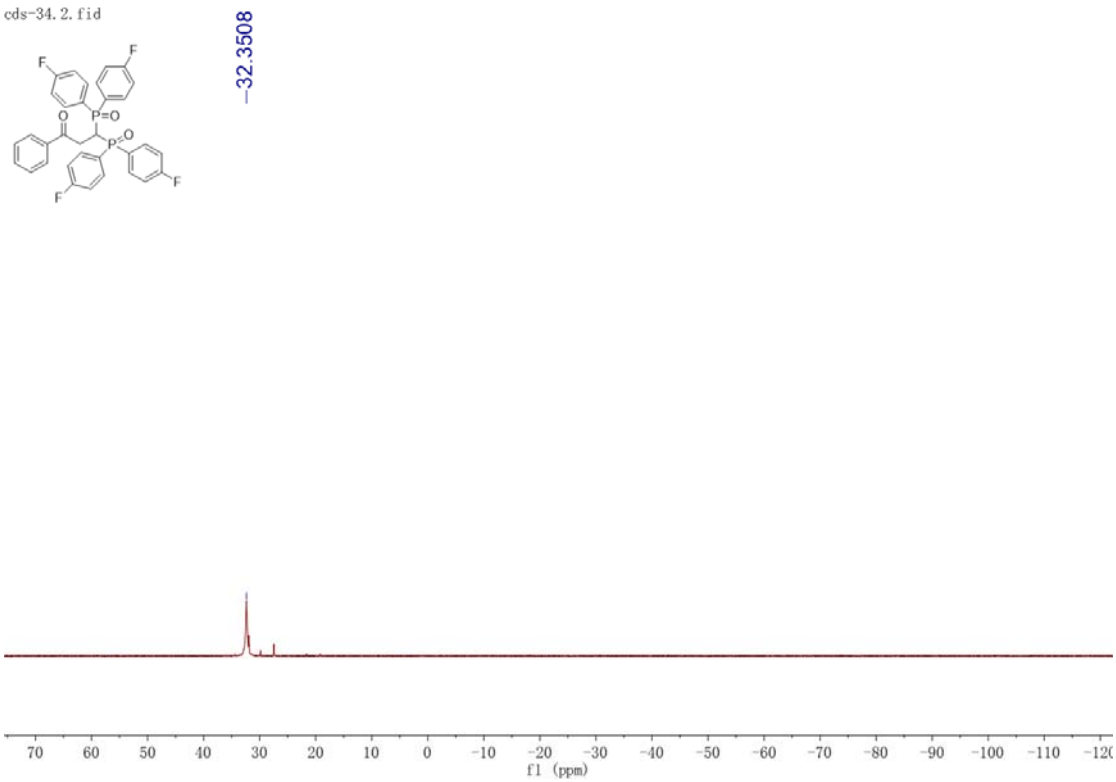
^{31}P NMR spectrum of **3p** (162 MHz, $CDCl_3$)



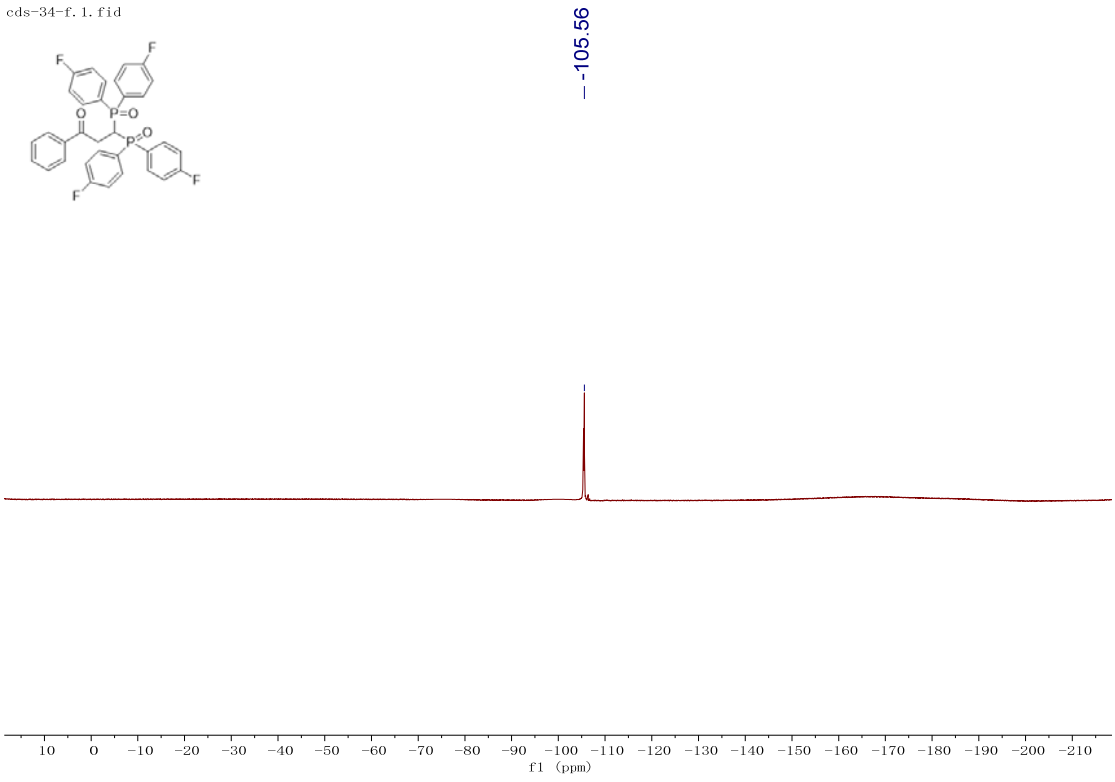
^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$)



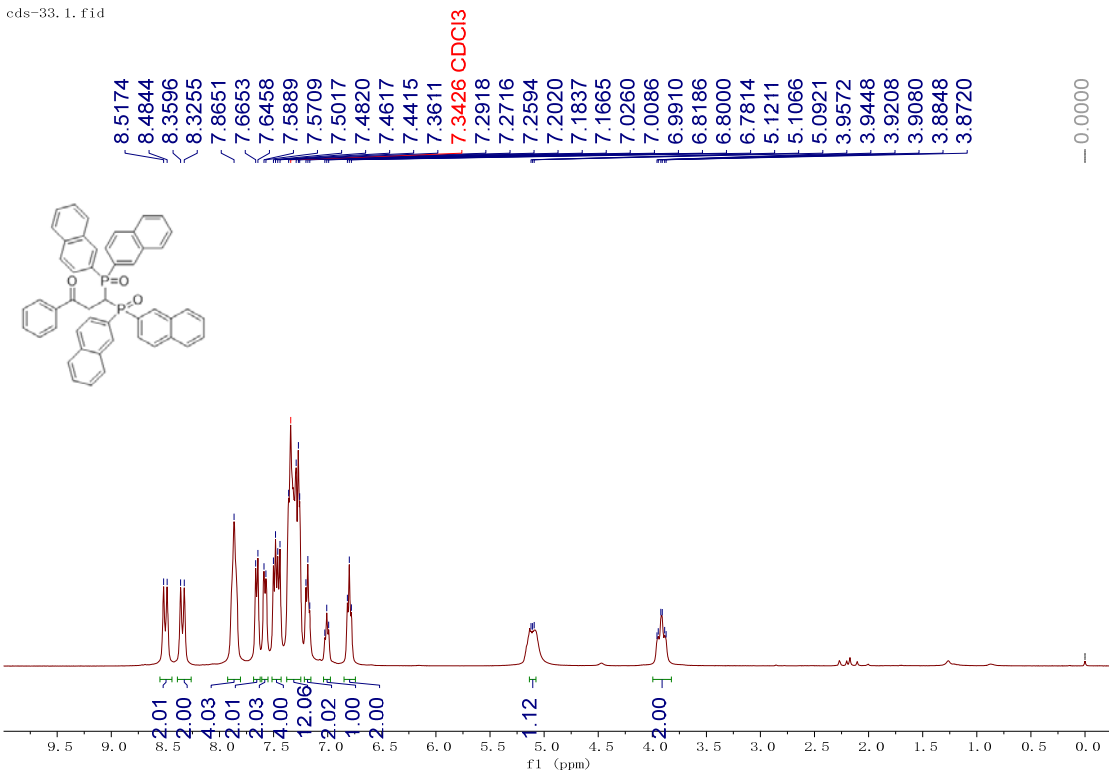
^{13}C NMR spectrum of **3q** (100 MHz, $CDCl_3$)



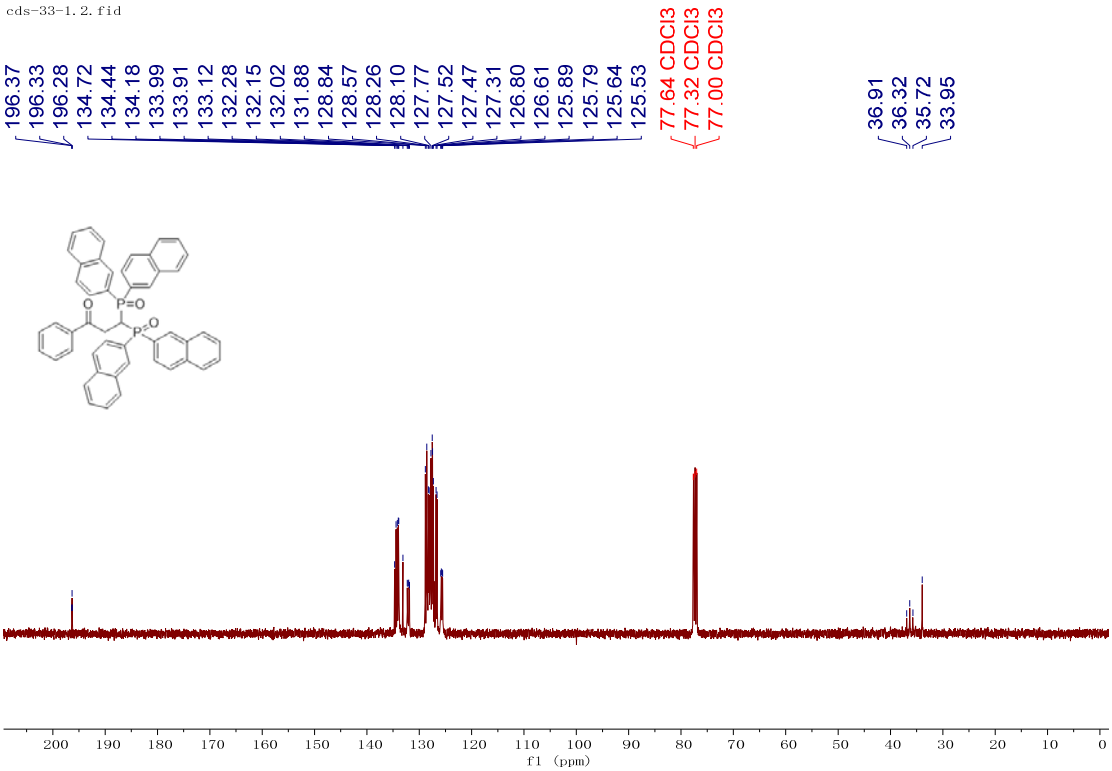
^{31}P NMR spectrum of **3q** (162 MHz, $CDCl_3$)



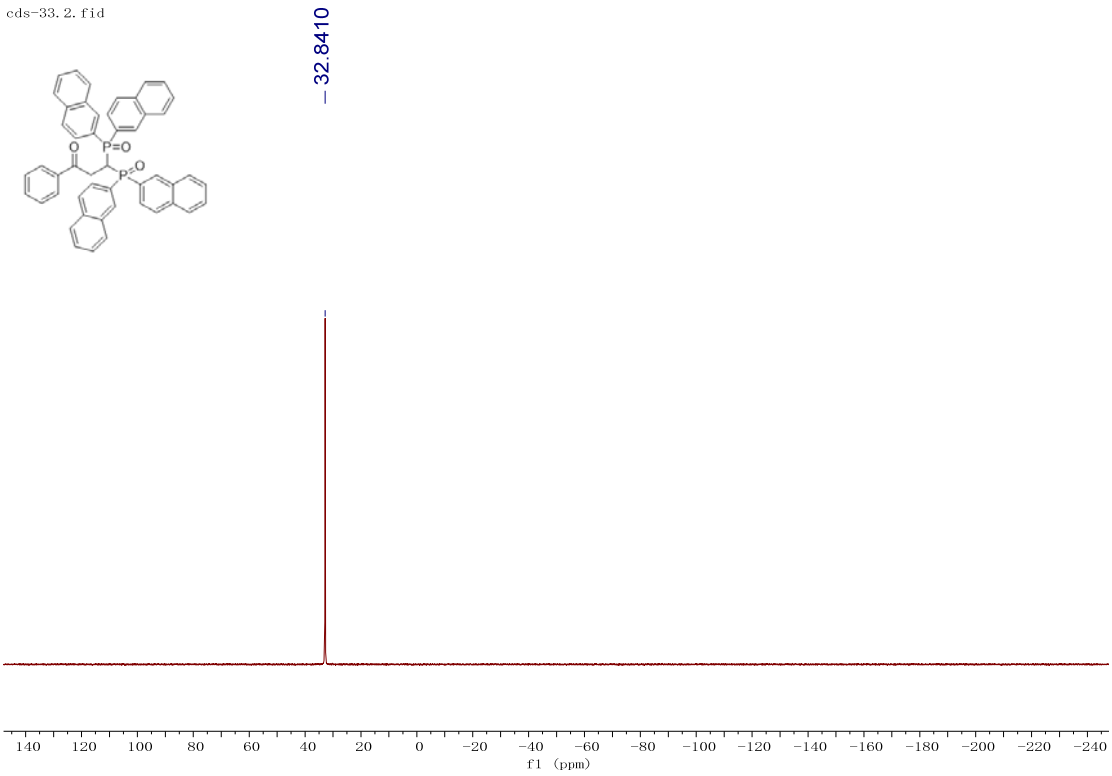
^{19}F NMR spectrum of **3q** (376 MHz, $CDCl_3$)



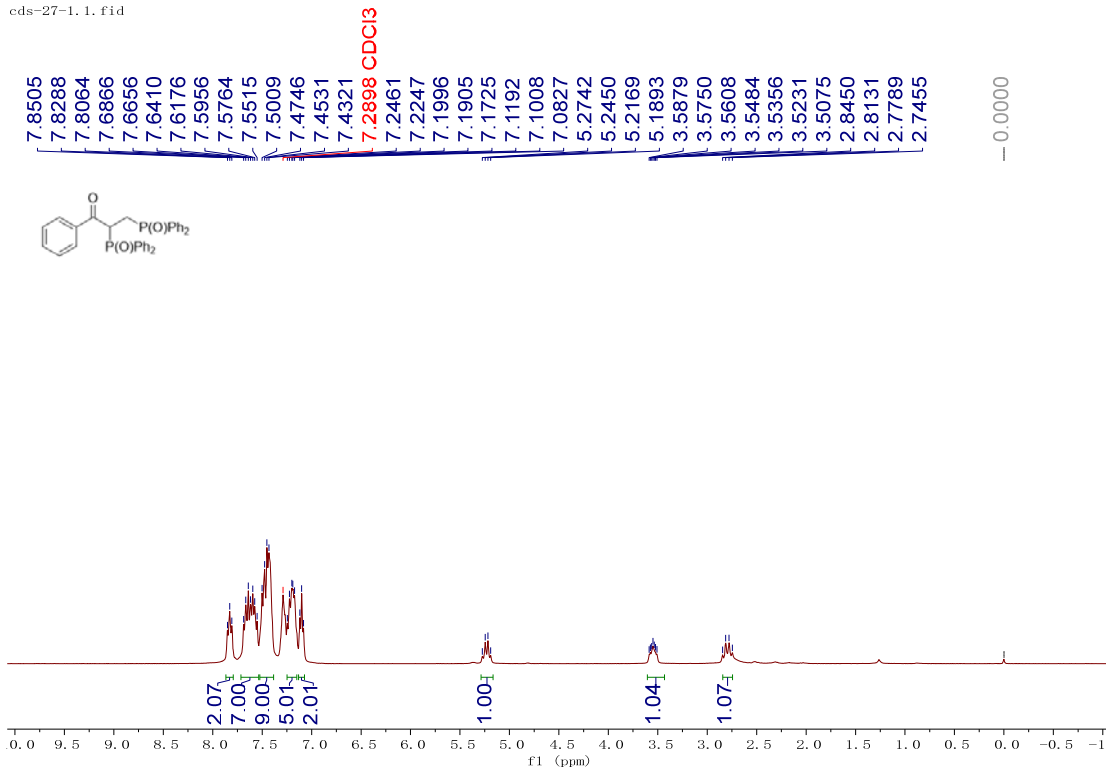
^{1}H NMR spectrum of **3r** (400 MHz, $CDCl_3$)



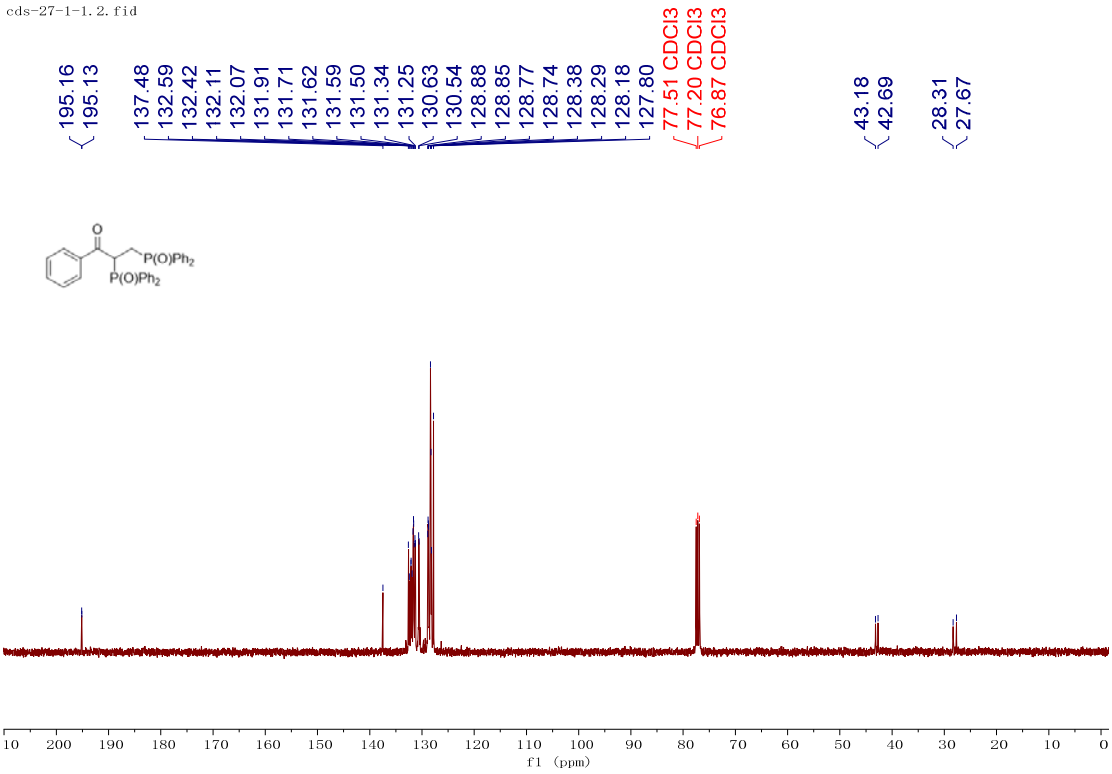
^{13}C NMR spectrum of **3r** (100 MHz, $CDCl_3$)



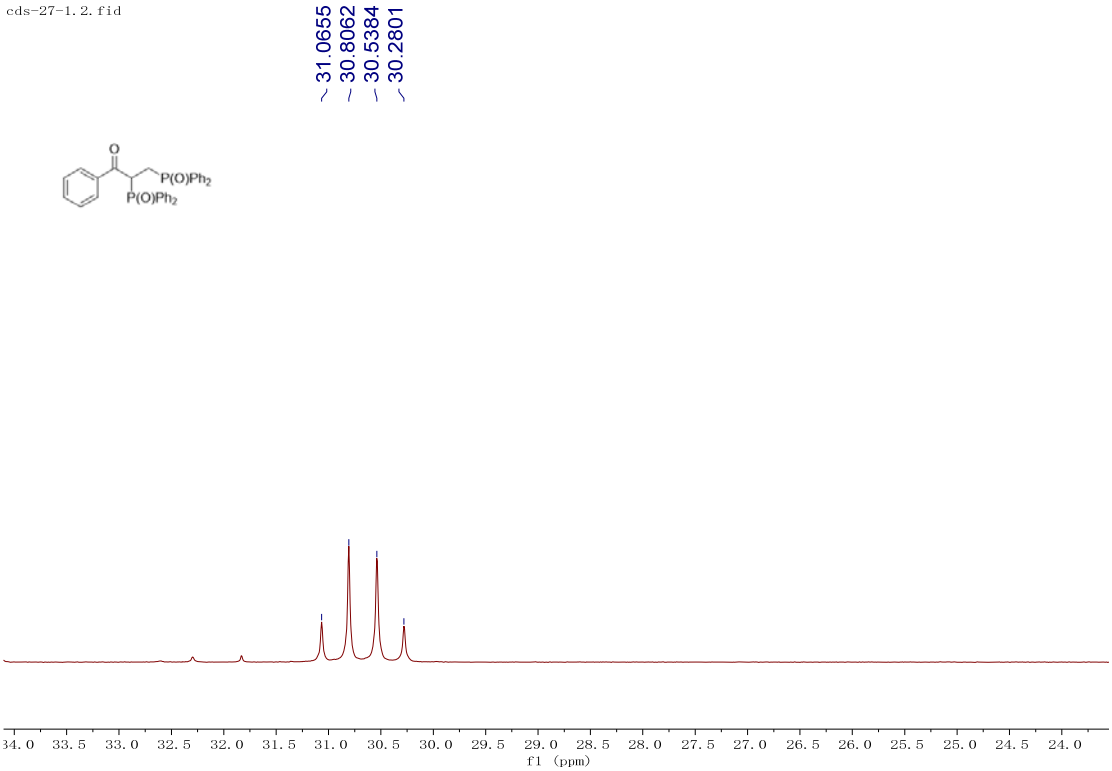
^{31}P NMR spectrum of **3r** (162 MHz, $CDCl_3$)



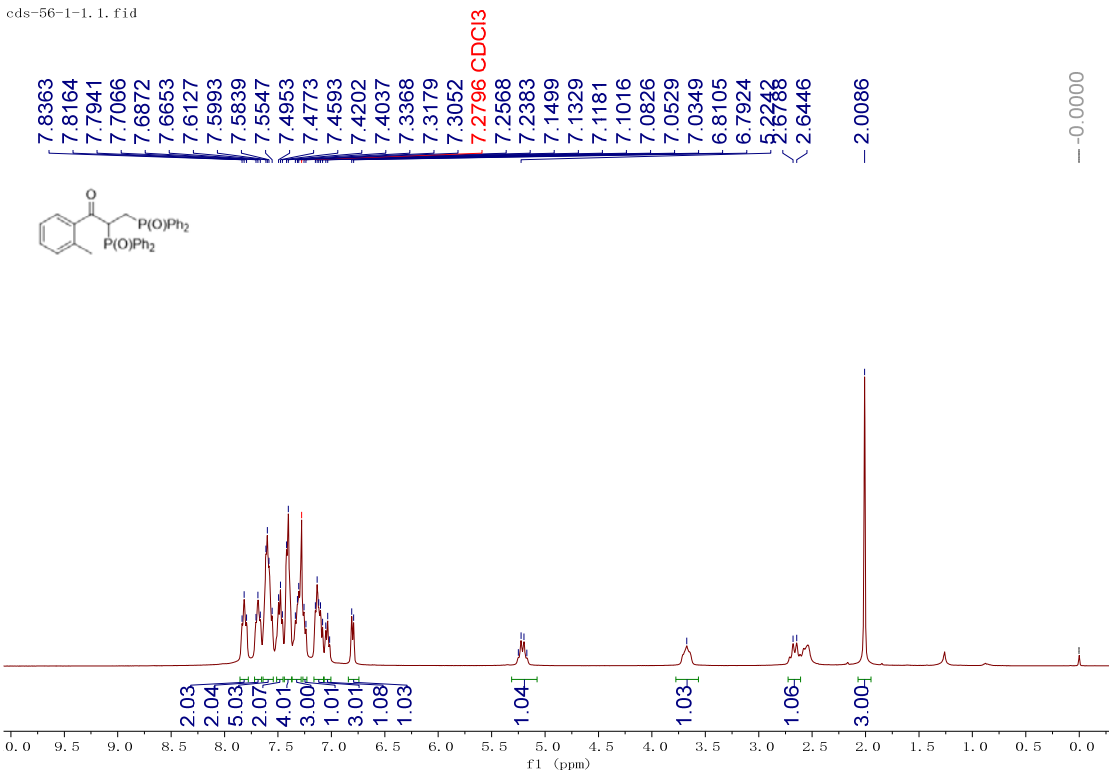
^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)



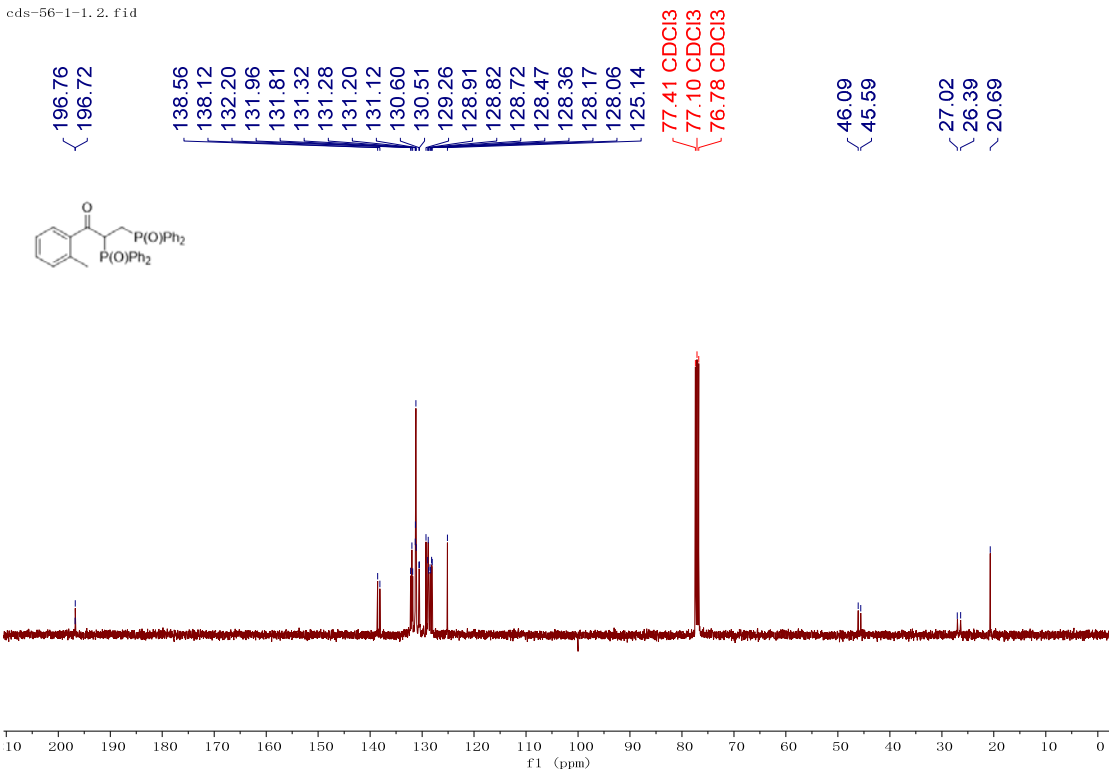
^{13}C NMR spectrum of **4a** (100 MHz, $CDCl_3$)



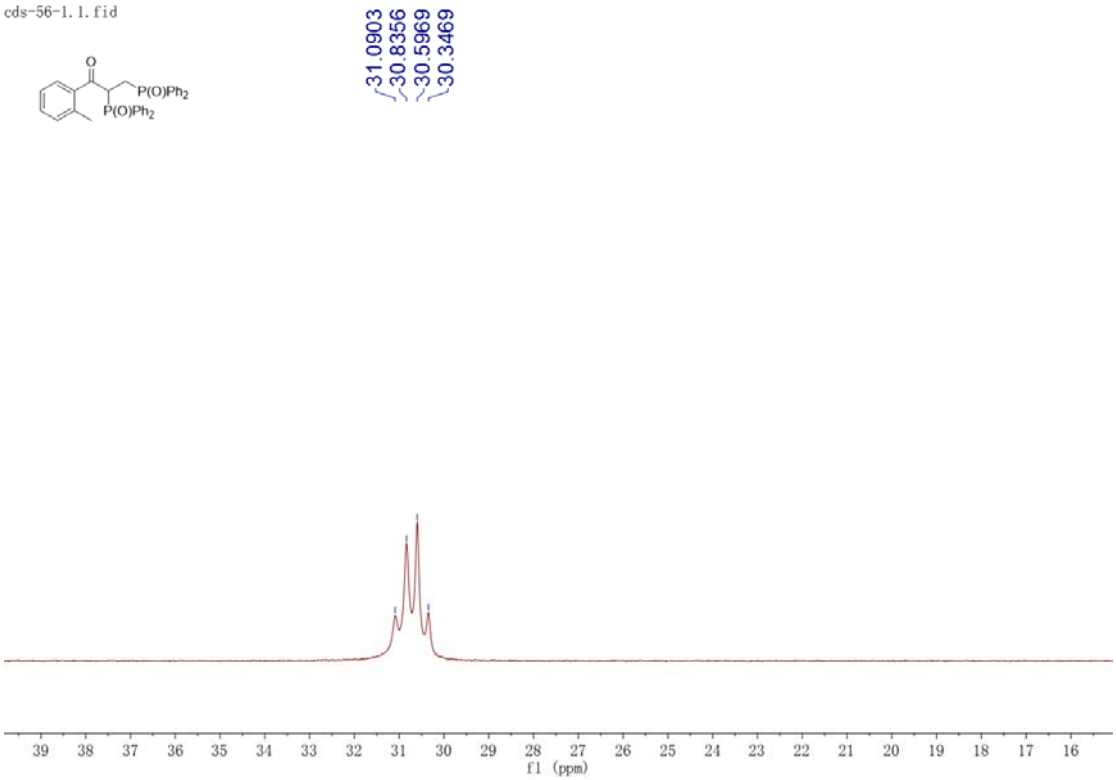
^{31}P NMR spectrum of **4a** (162 MHz, $CDCl_3$)



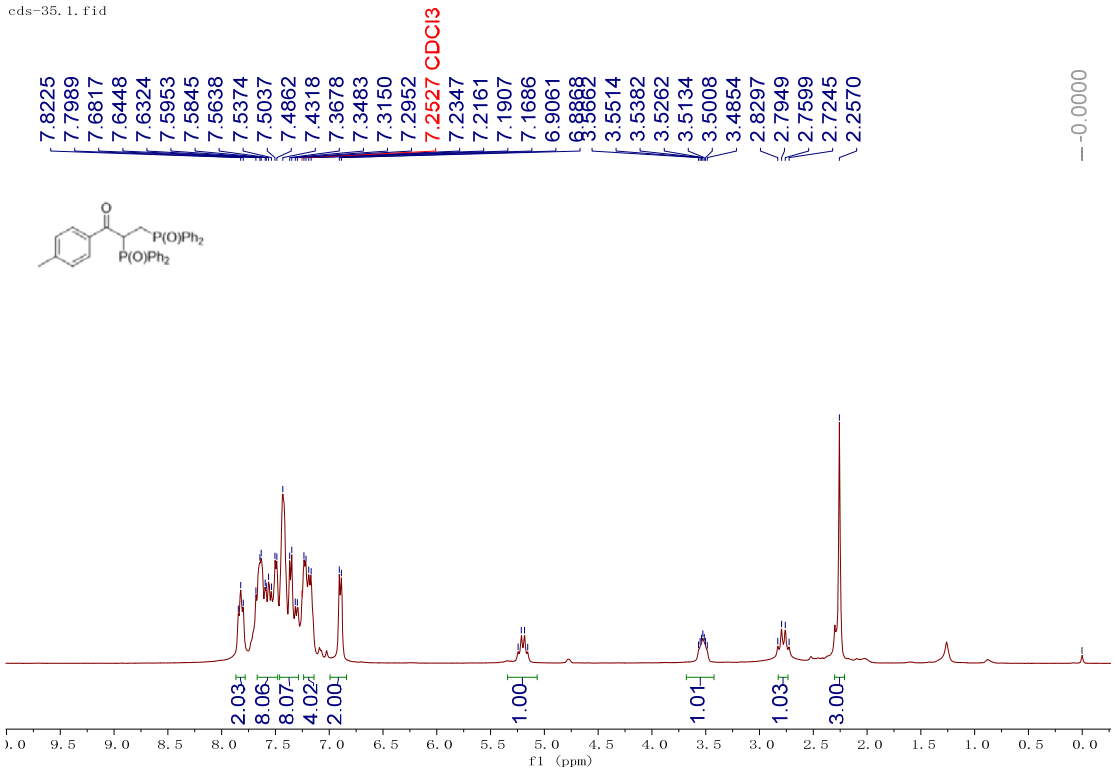
^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$)



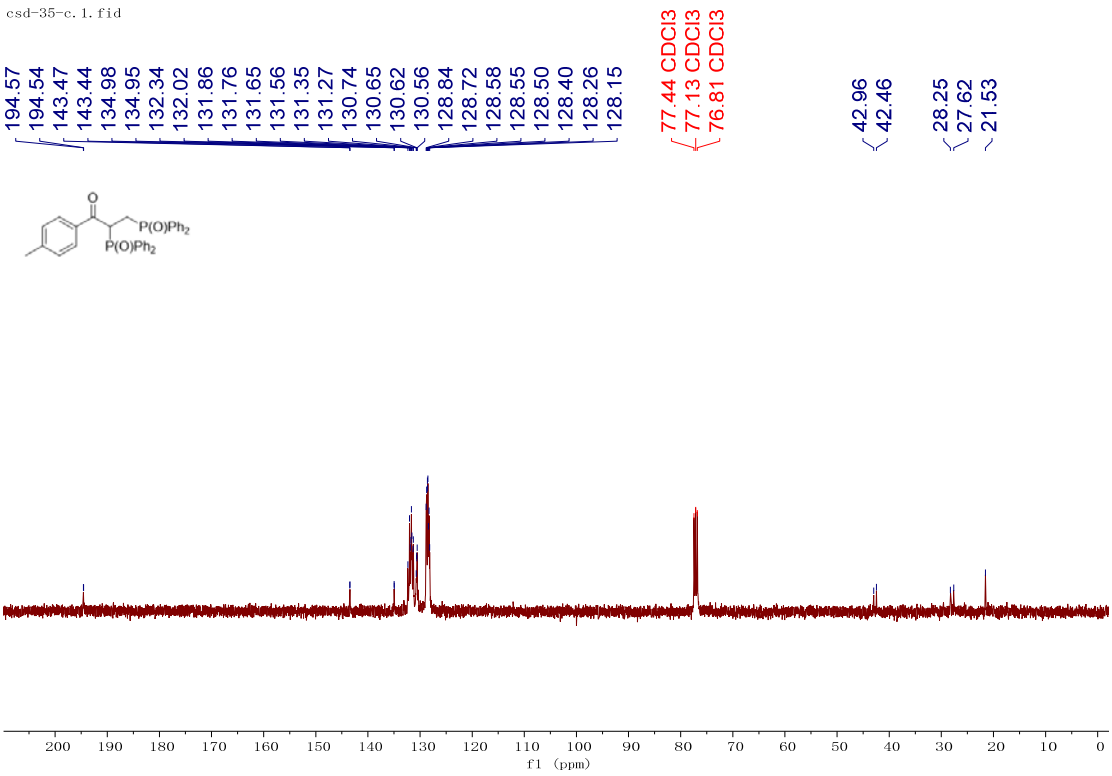
^{13}C NMR spectrum of **4b** (100 MHz, $CDCl_3$)



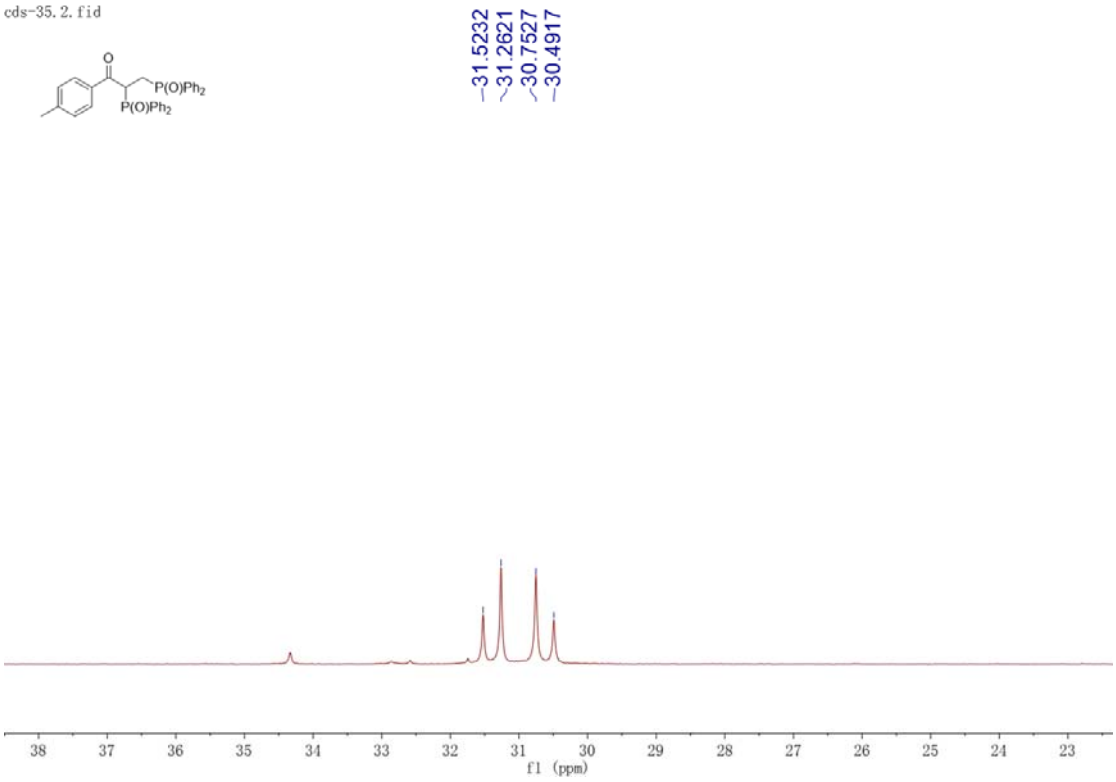
^{31}P NMR spectrum of **4b** (162 MHz, $CDCl_3$)



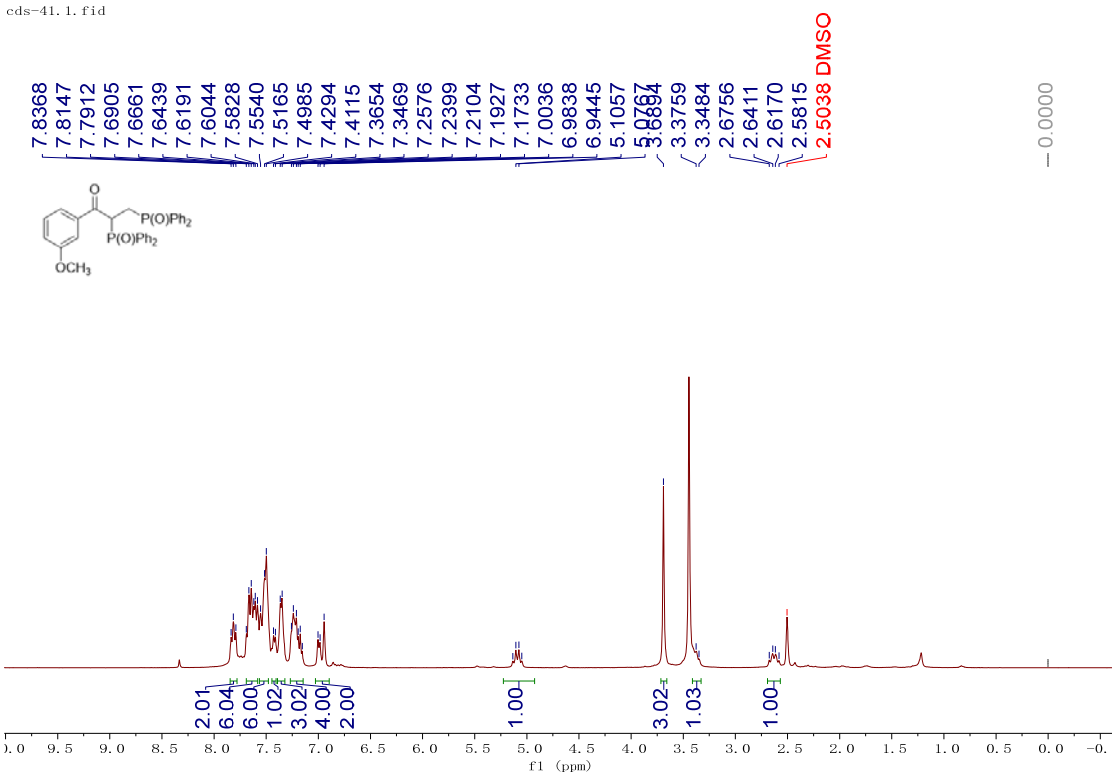
^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$)



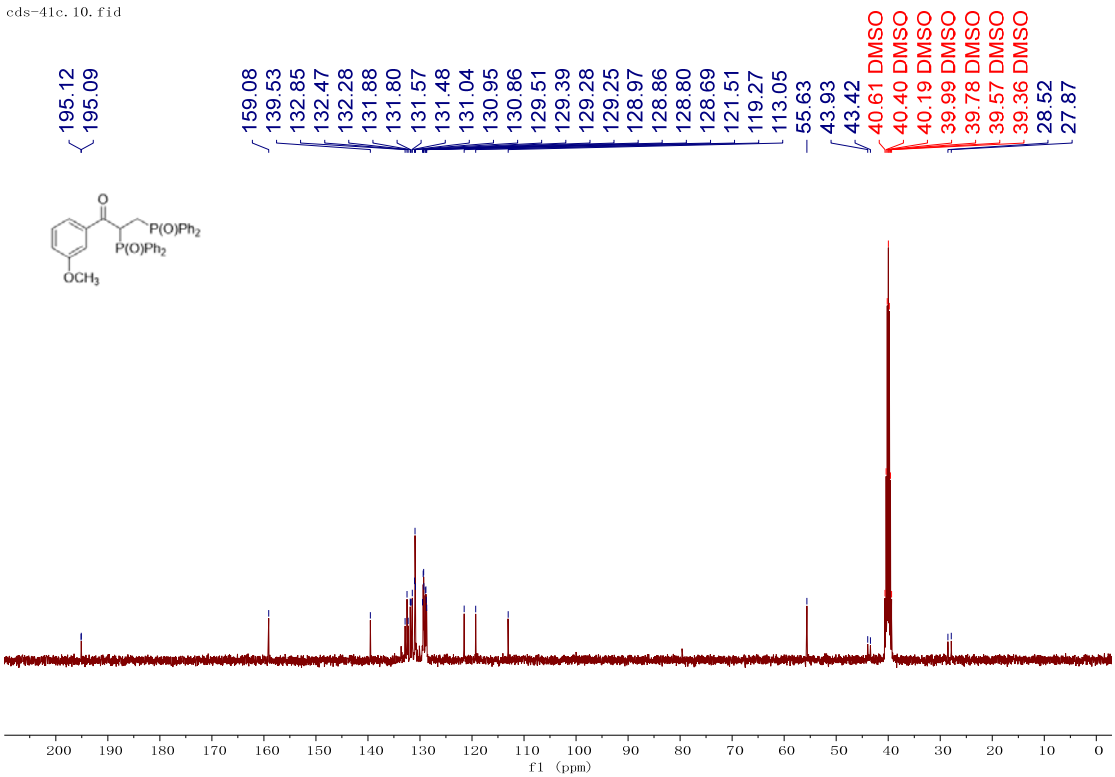
^{13}C NMR spectrum of **4c** (100 MHz, $CDCl_3$)



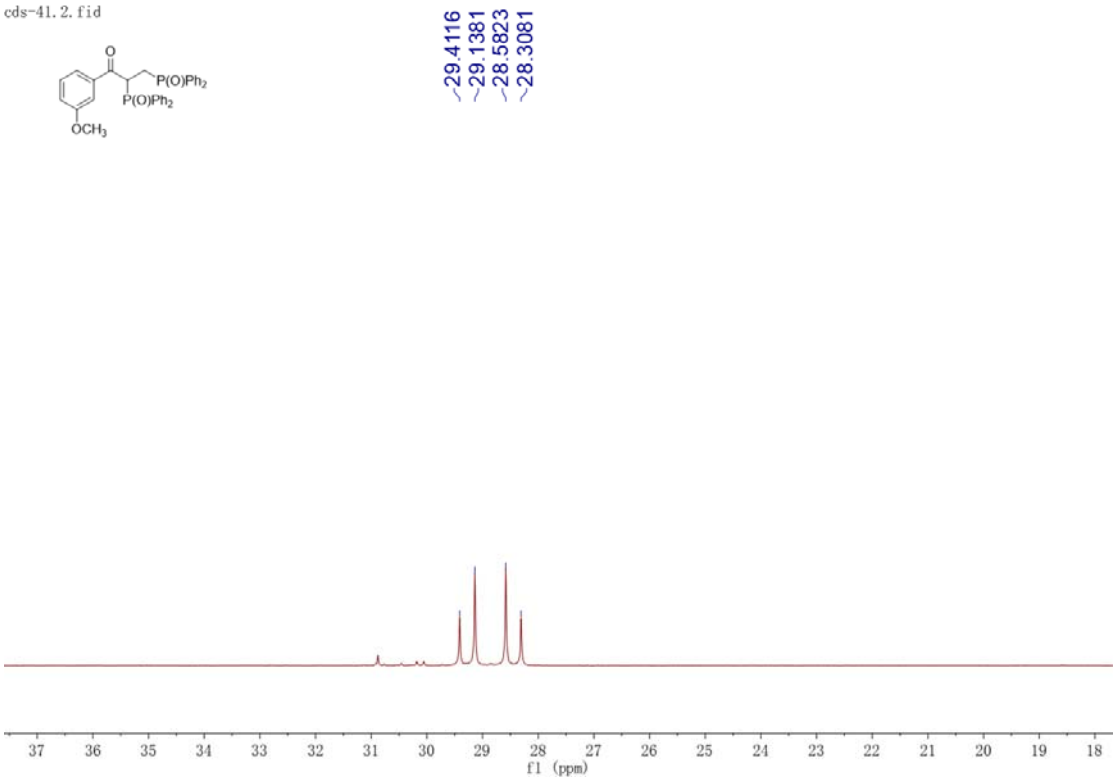
^{31}P NMR spectrum of **4c** (162 MHz, $CDCl_3$)



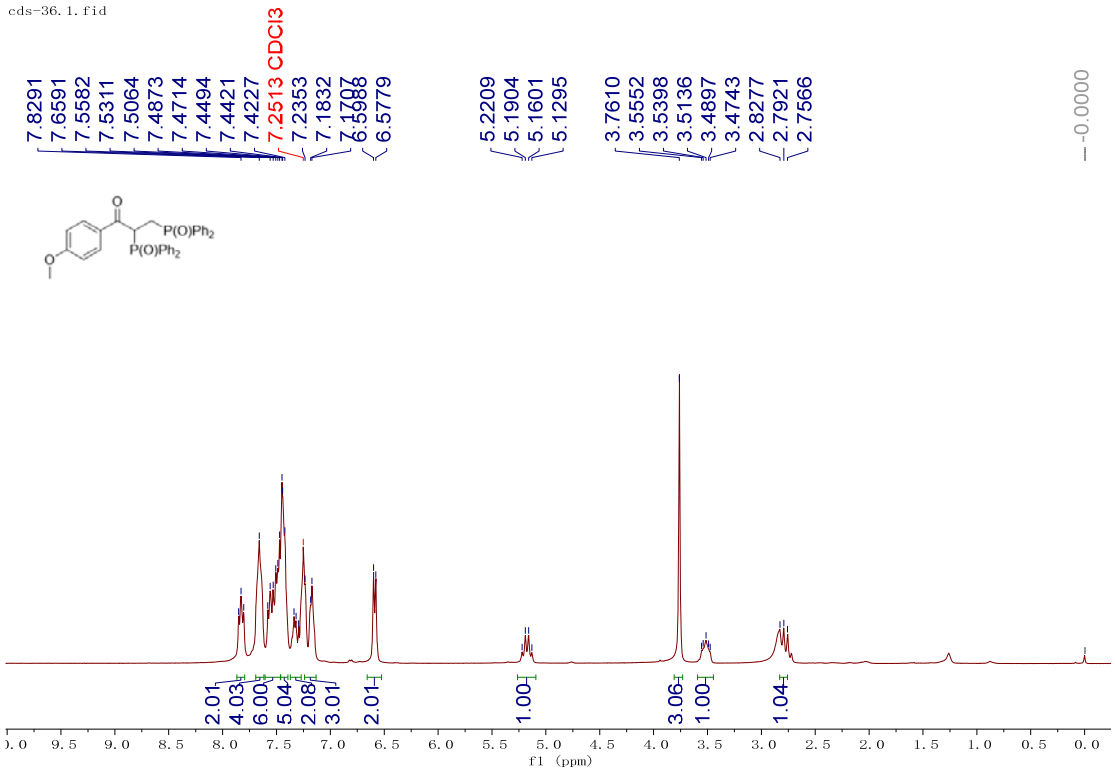
^{1}H NMR spectrum of **4d** (400 MHz, DMSO-d_6)



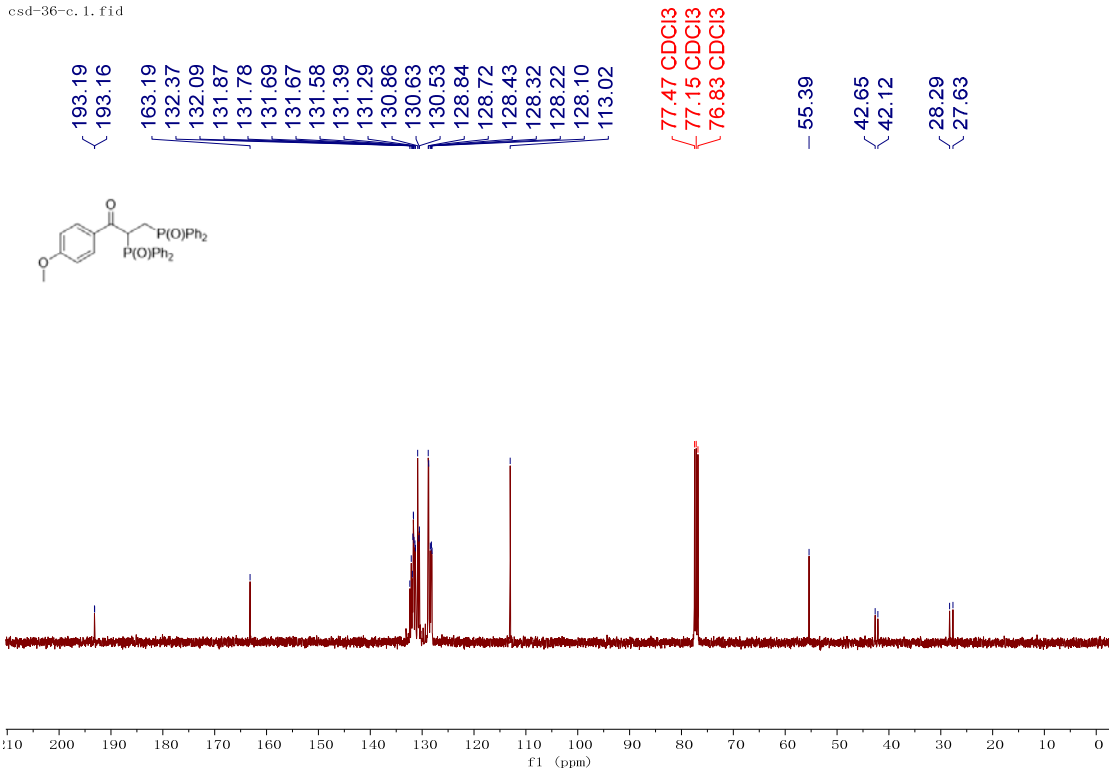
^{13}C NMR spectrum of **4d** (100 MHz, DMSO-d_6)



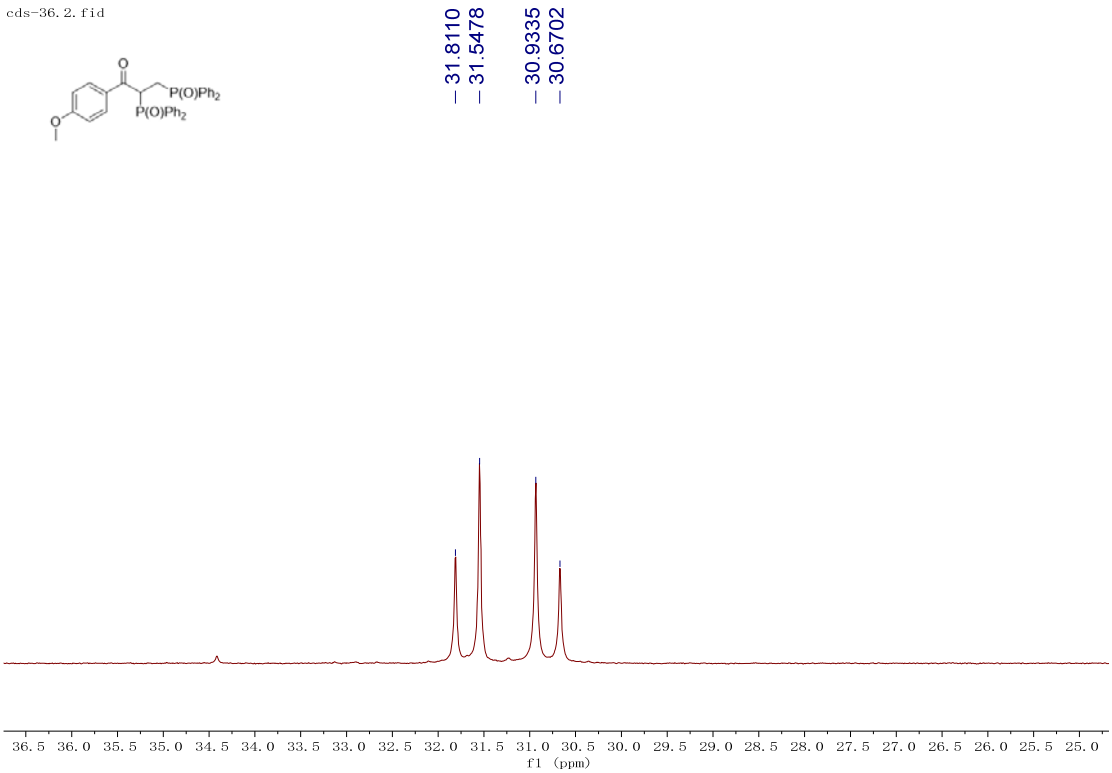
^{31}P NMR spectrum of **4d** (162 MHz, DMSO-d_6)



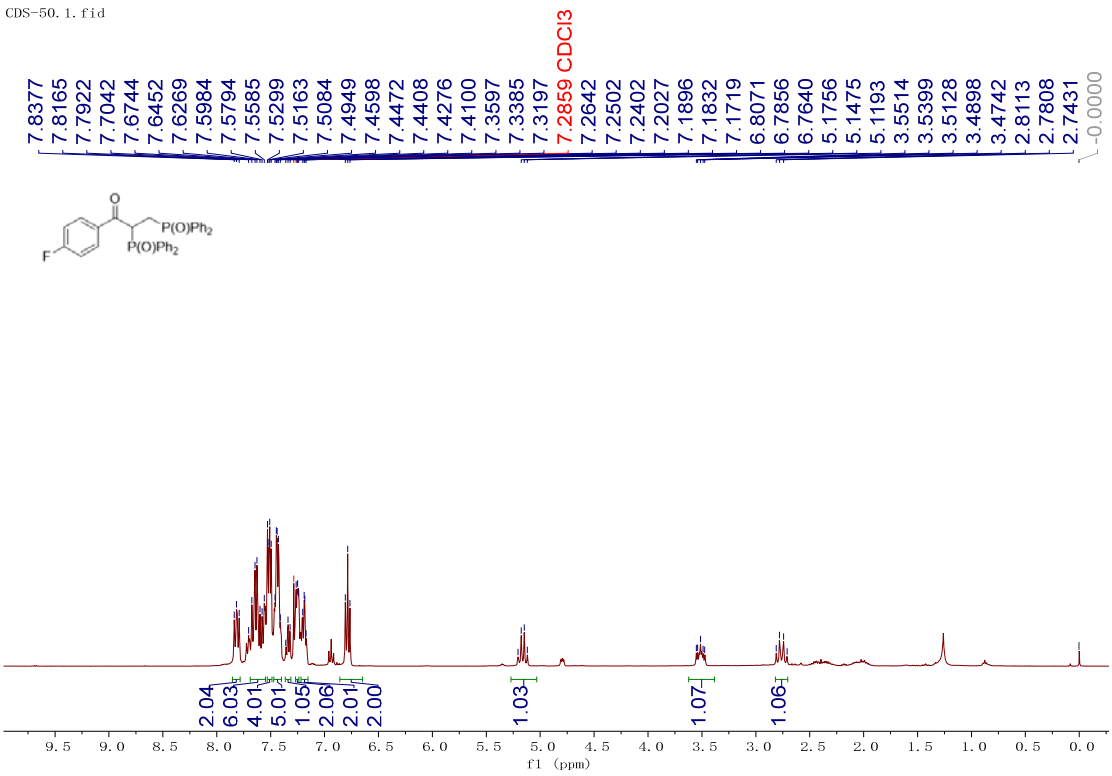
^{1}H NMR spectrum of **4e** (400 MHz, $CDCl_3$)



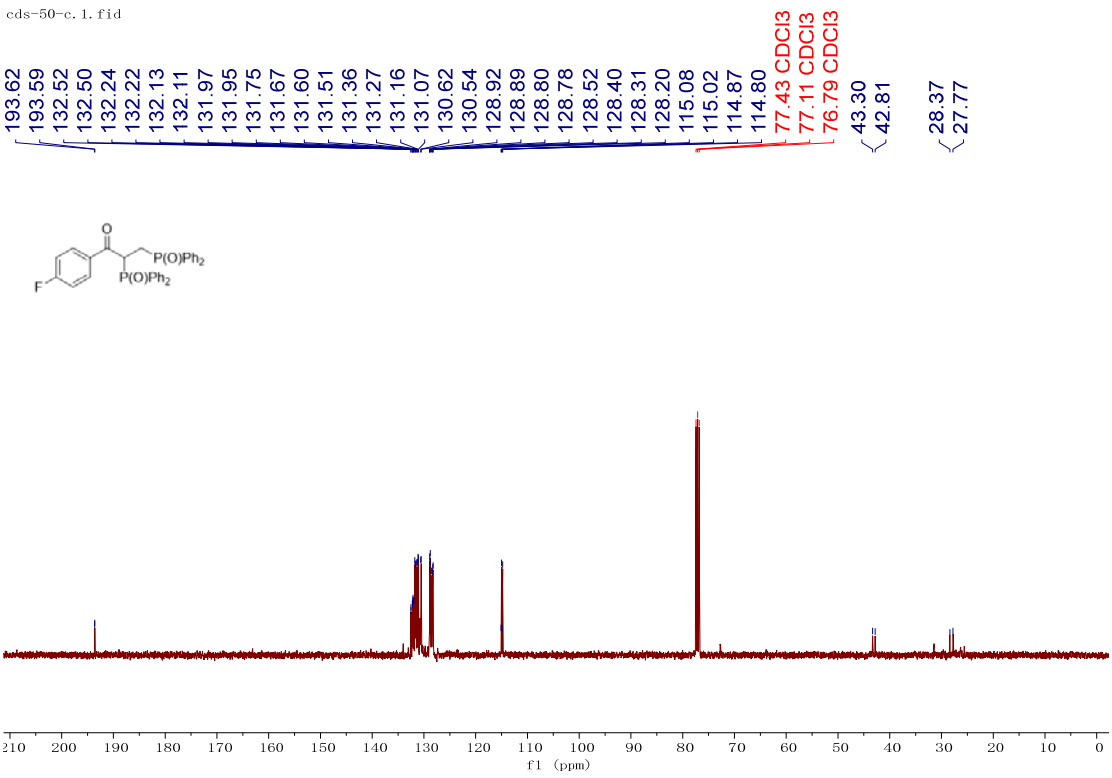
^{13}C NMR spectrum of **4e** (100 MHz, $CDCl_3$)



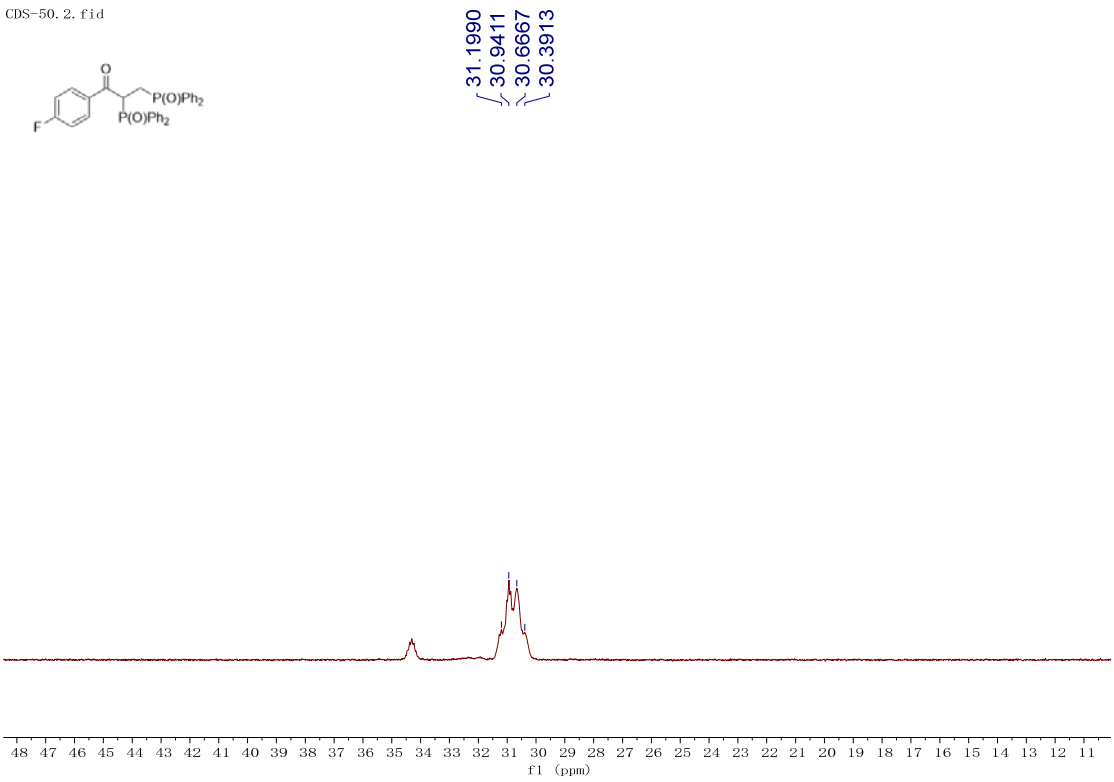
^{31}P NMR spectrum of **4e** (162 MHz, $CDCl_3$)



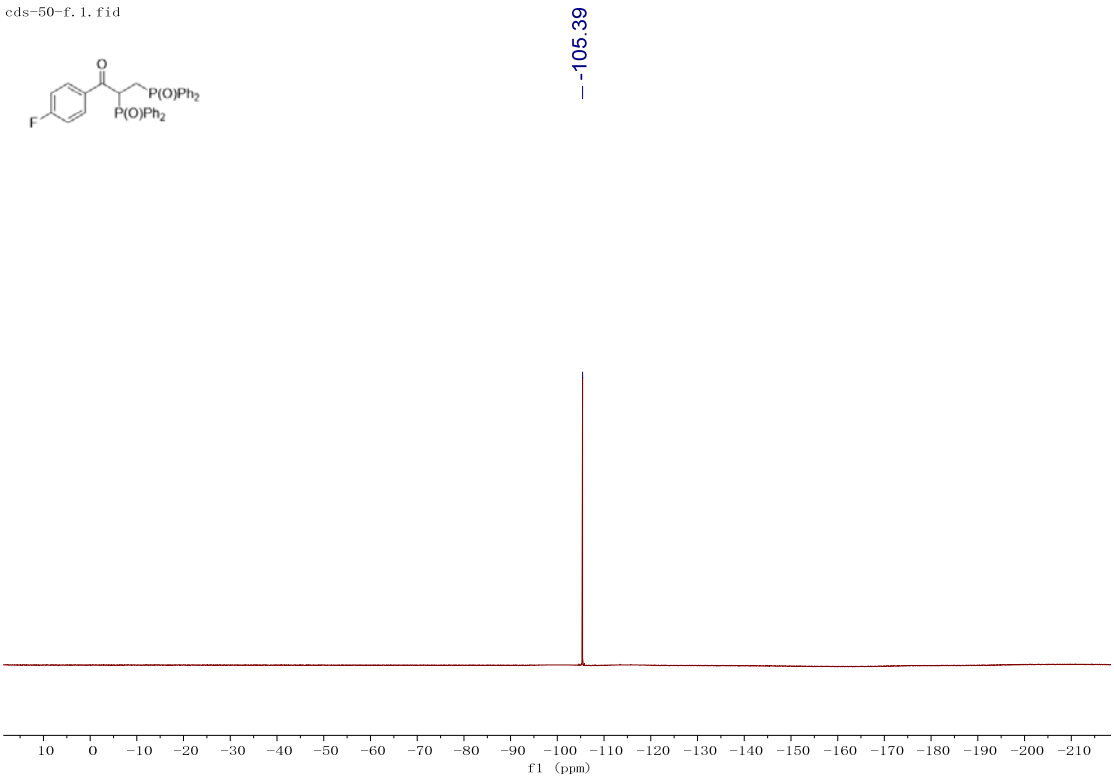
^{1}H NMR spectrum of **4f** (400 MHz, $CDCl_3$)



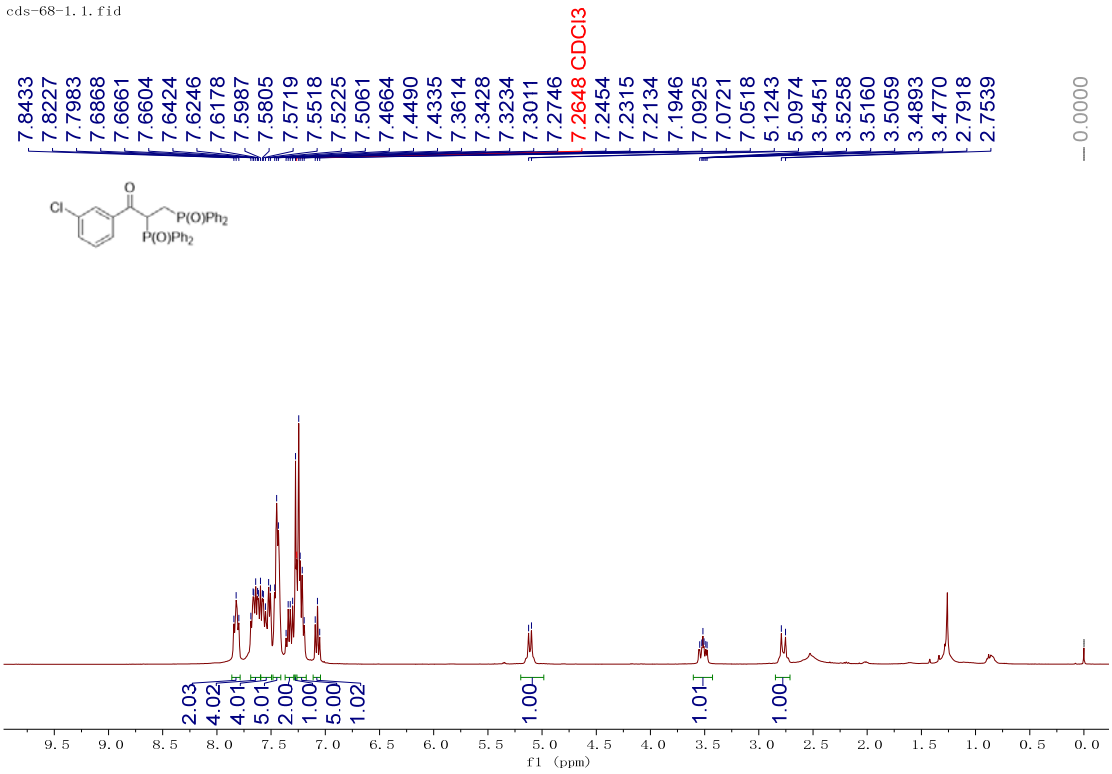
^{13}C NMR spectrum of **4f** (100 MHz, $CDCl_3$)



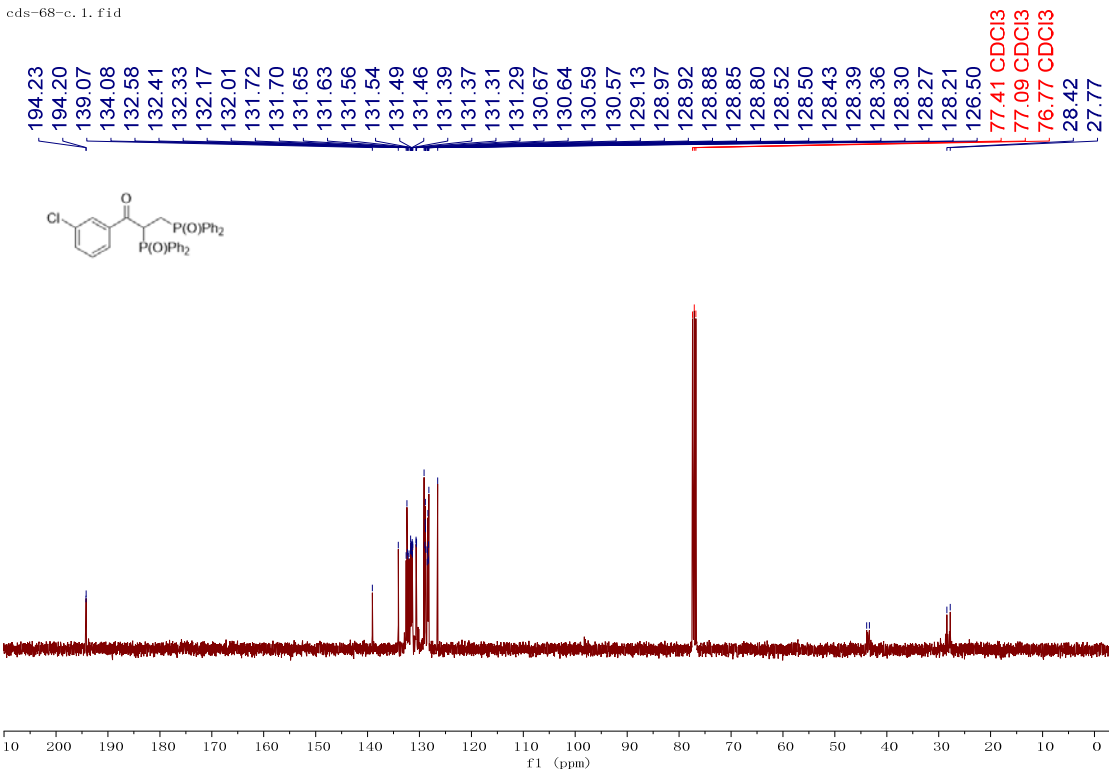
^{31}P NMR spectrum of **4f** (162 MHz, $CDCl_3$)



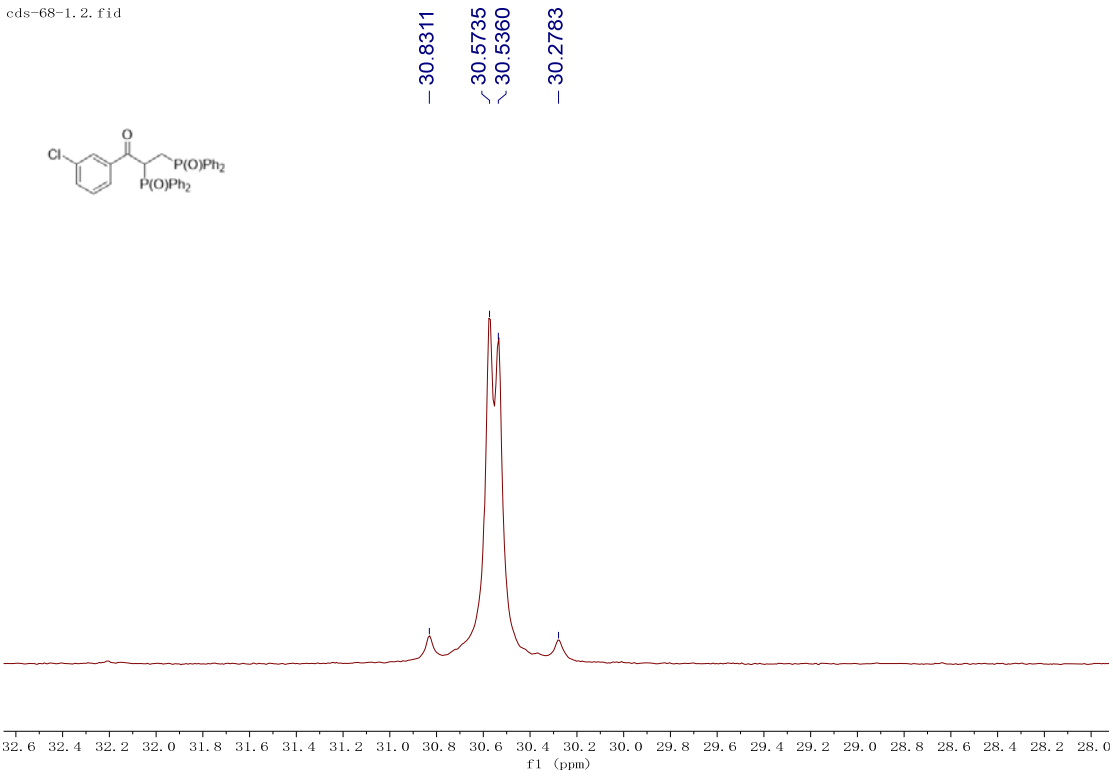
^{19}F NMR spectrum of **4f** (376 MHz, $CDCl_3$)



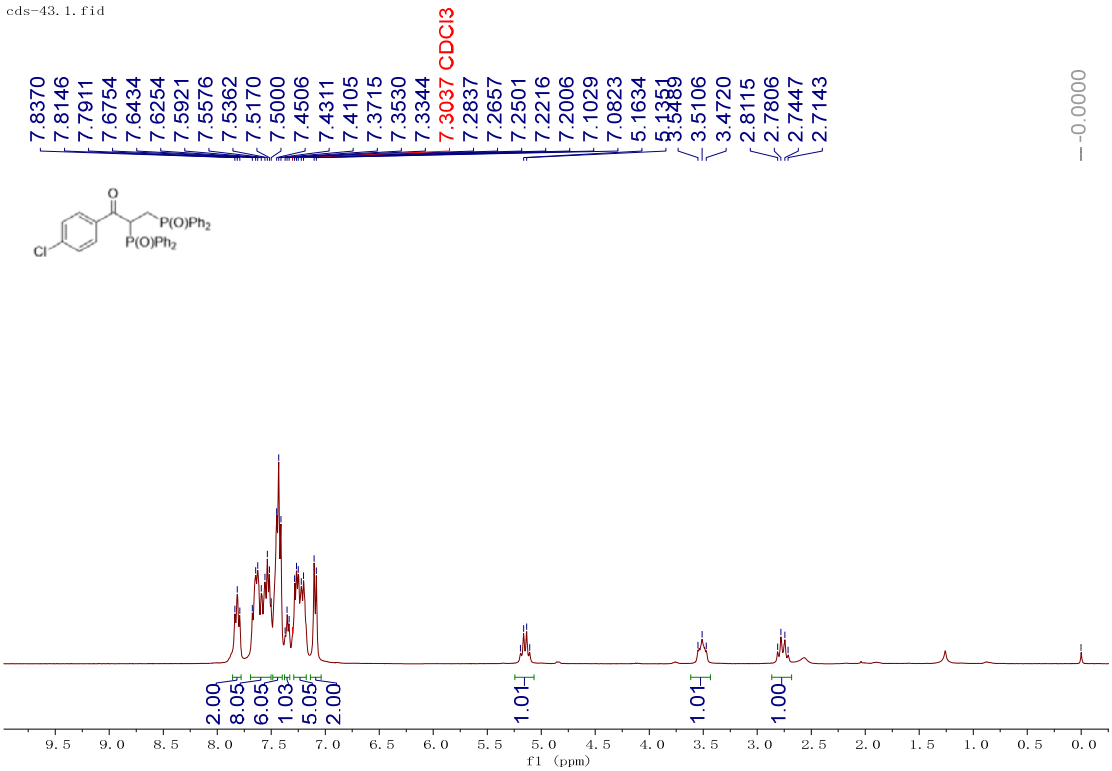
^{1}H NMR spectrum of **4g** (400 MHz, $CDCl_3$)



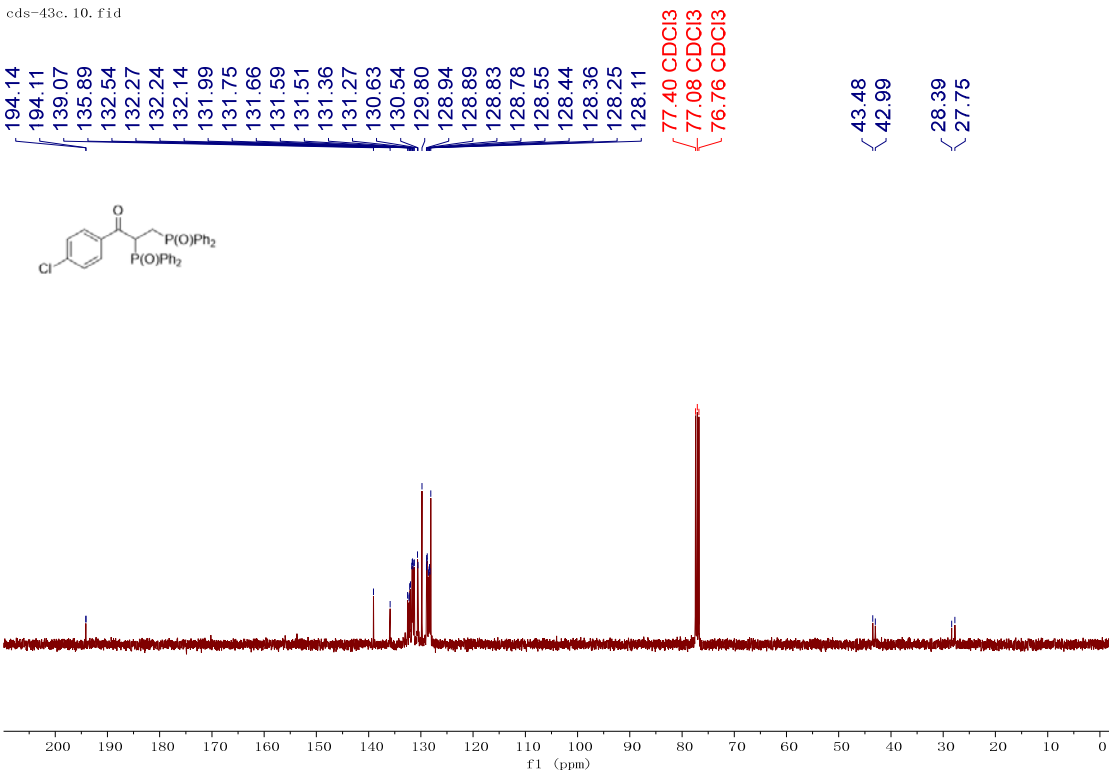
^{13}C NMR spectrum of **4g** (100 MHz, $CDCl_3$)



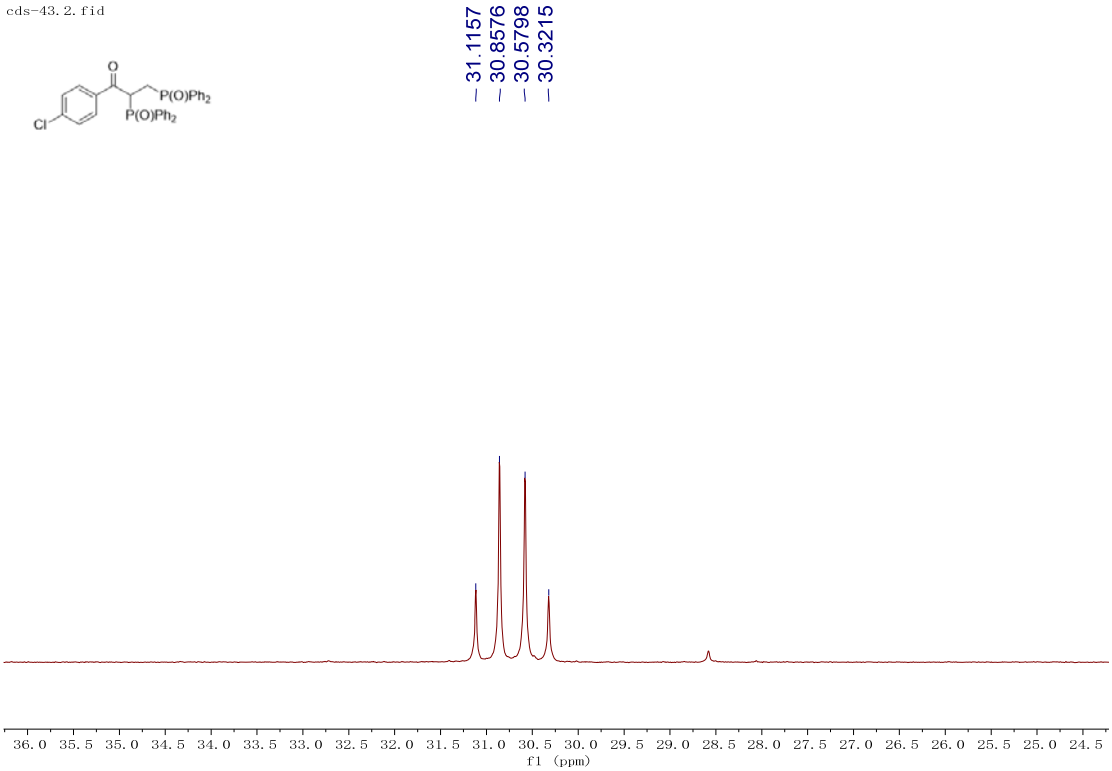
^{31}P NMR spectrum of **4g** (162 MHz, $CDCl_3$)



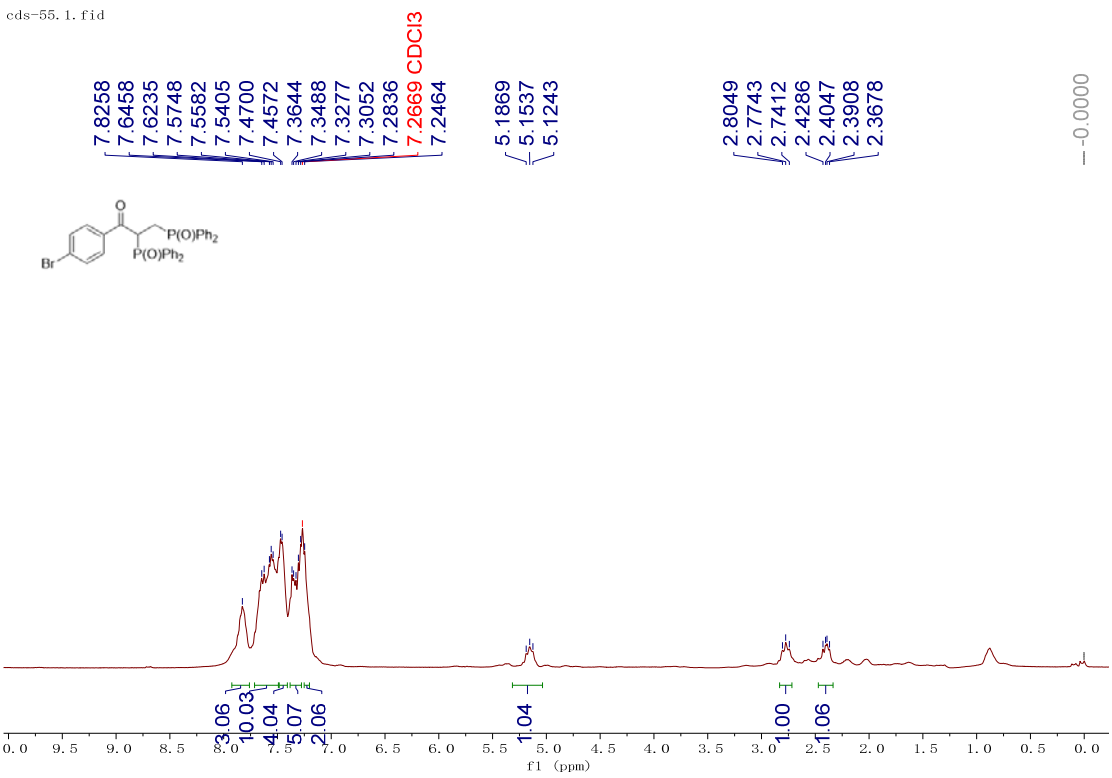
^{1}H NMR spectrum of **4h** (400 MHz, $CDCl_3$)



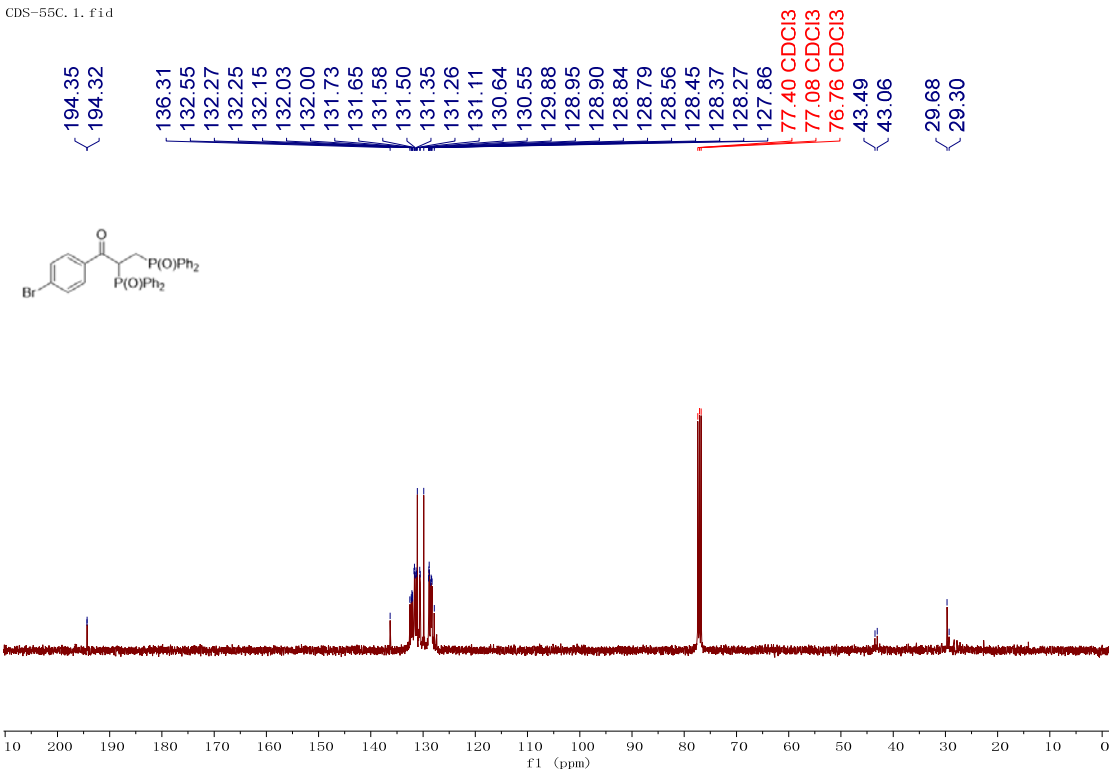
^{13}C NMR spectrum of **4h** (100 MHz, $CDCl_3$)



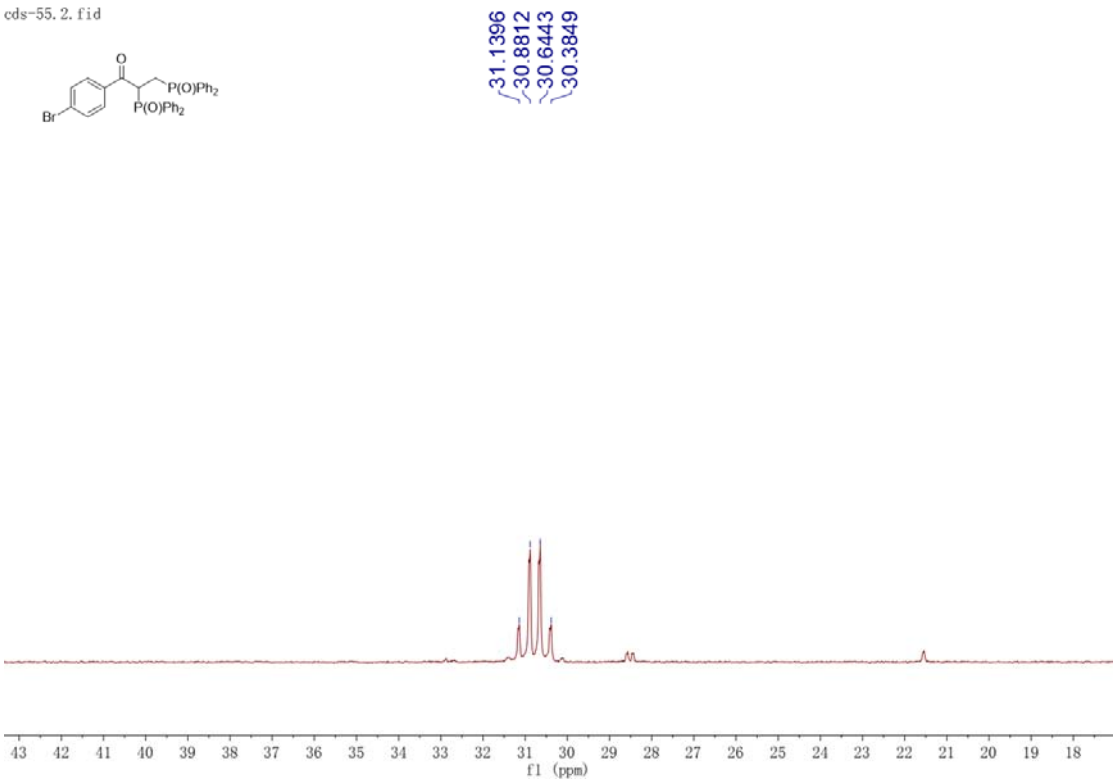
^{31}P NMR spectrum of **4h** (162 MHz, $CDCl_3$)



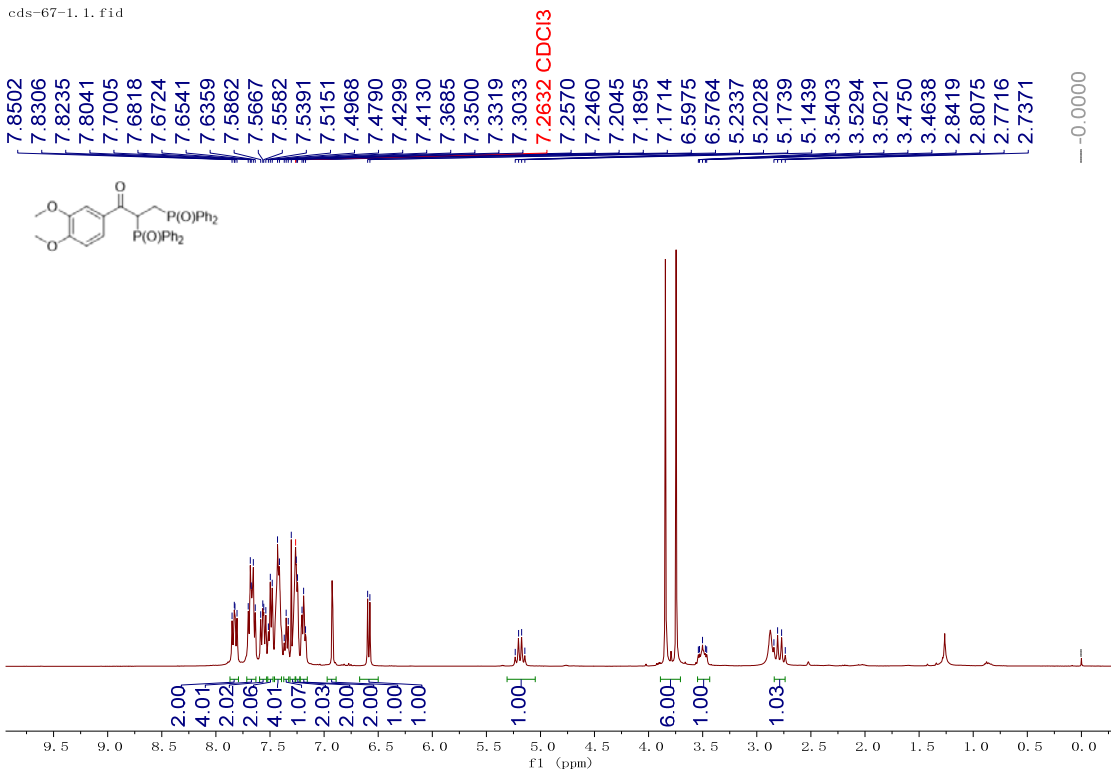
^{1}H NMR spectrum of **4i** (400 MHz, $CDCl_3$)



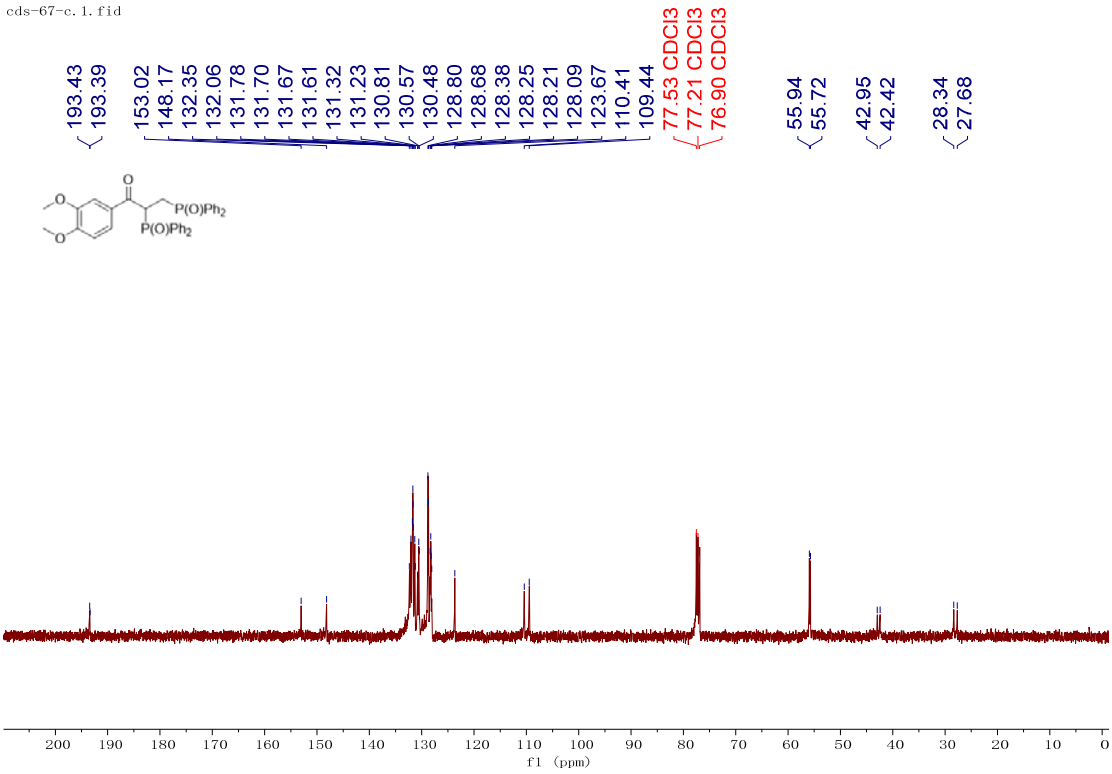
^{13}C NMR spectrum of **4i** (100 MHz, $CDCl_3$)



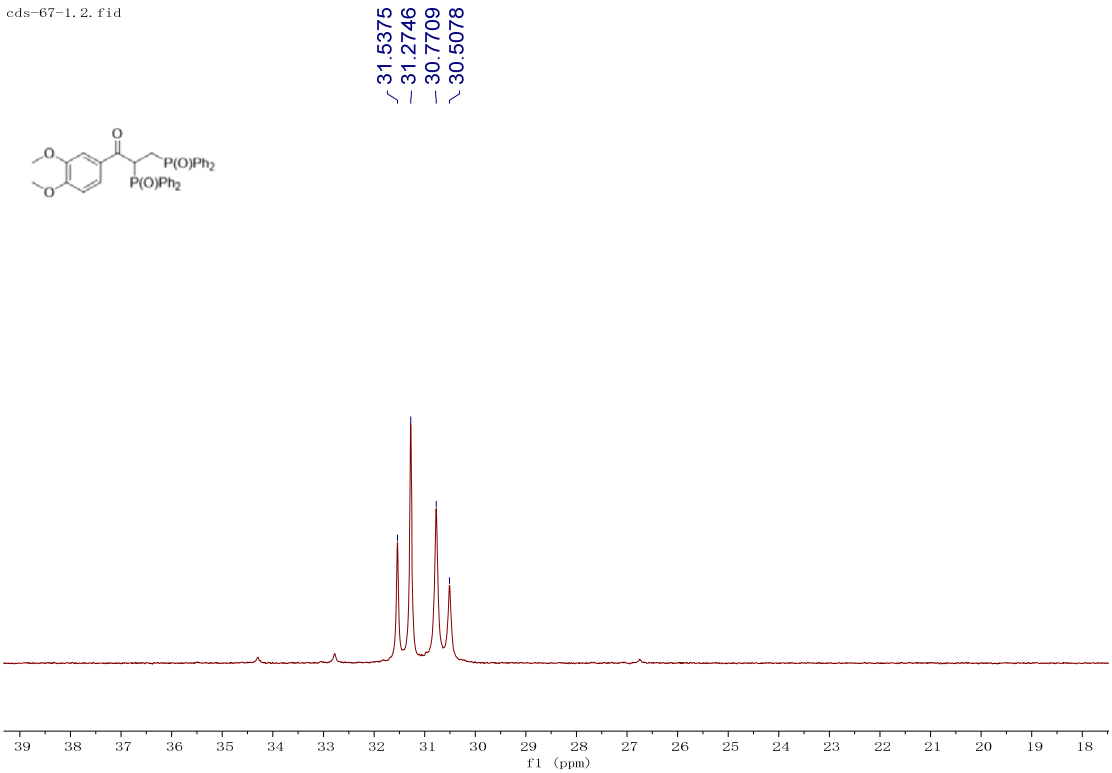
^{31}P NMR spectrum of **4i** (162 MHz, $CDCl_3$)



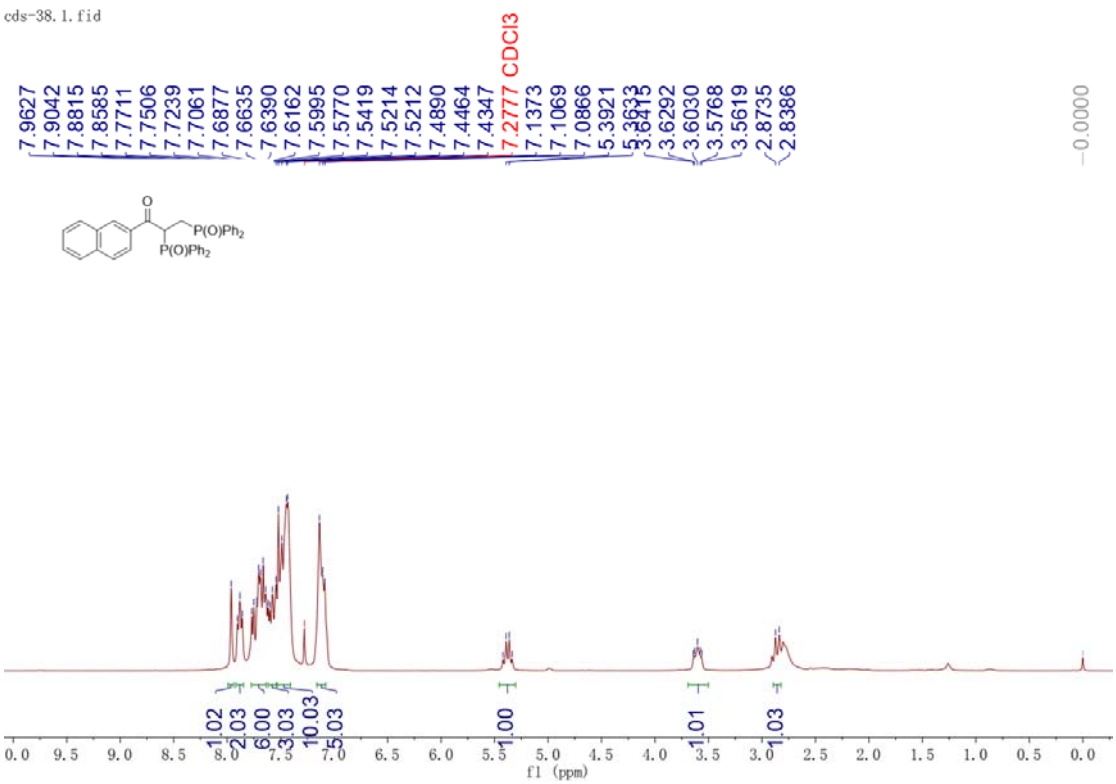
^{1}H NMR spectrum of **4j** (400 MHz, $CDCl_3$)



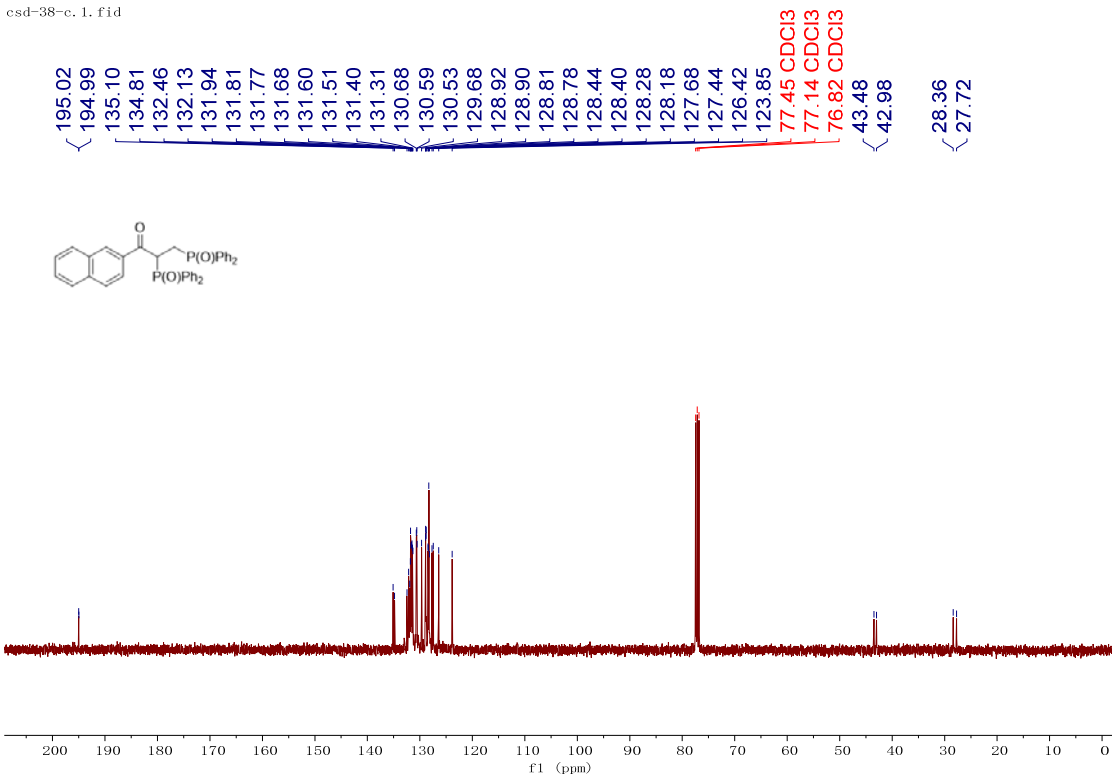
^{13}C NMR spectrum of **4j** (100 MHz, $CDCl_3$)



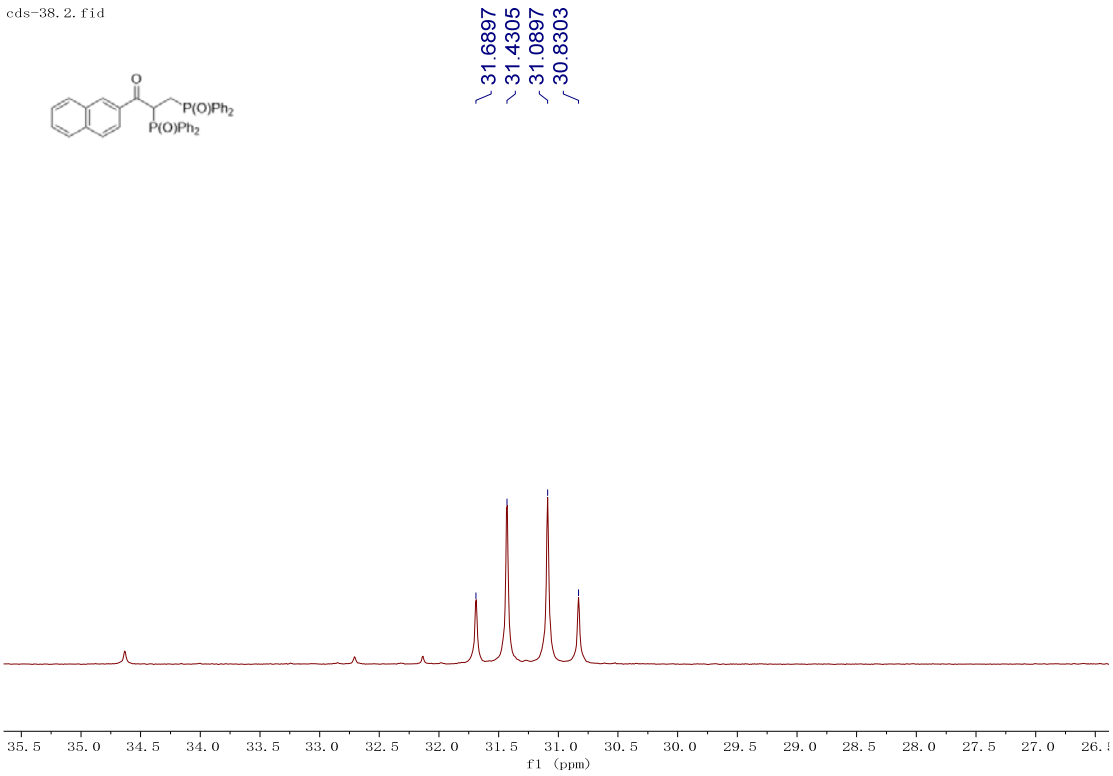
^{31}P NMR spectrum of **4j** (162 MHz, $CDCl_3$)



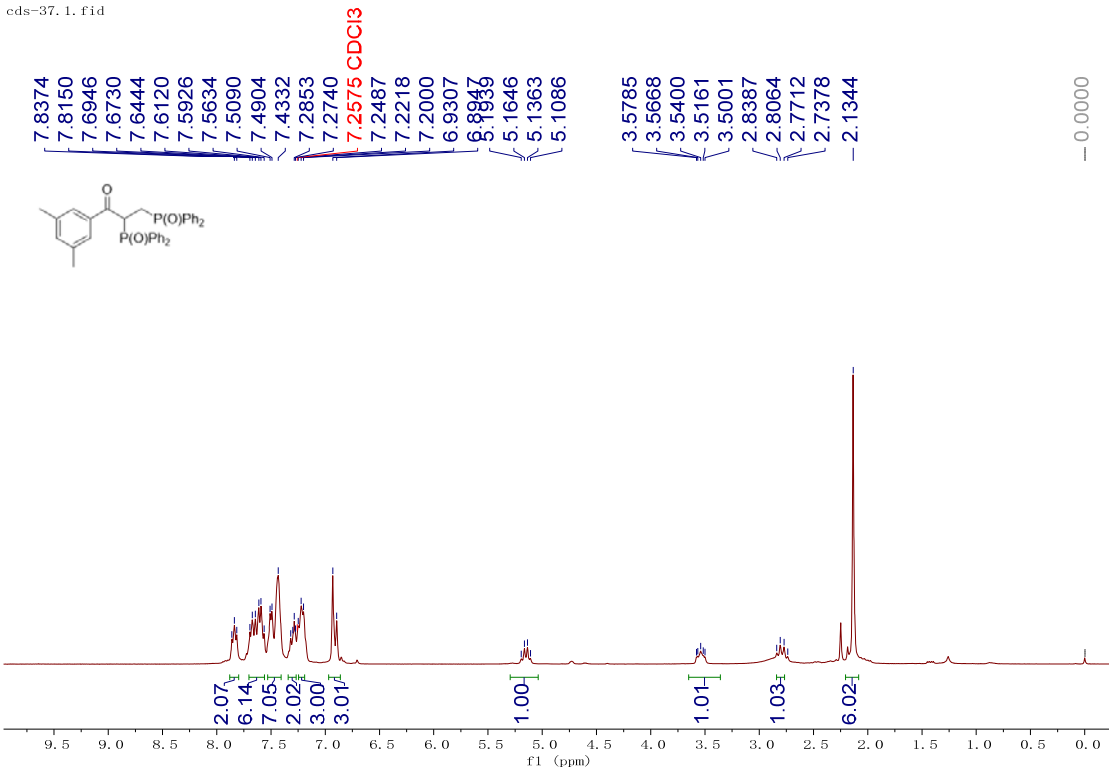
^{1}H NMR spectrum of **4k** (400 MHz, $CDCl_3$)



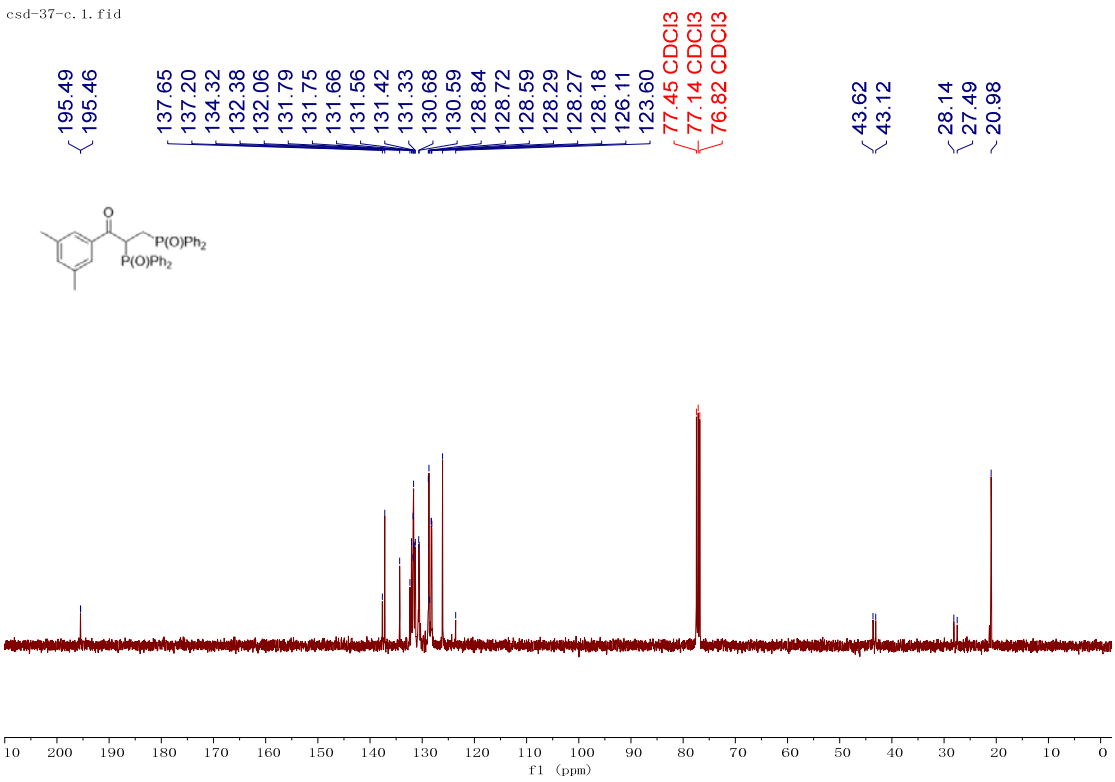
^{13}C NMR spectrum of **4k** (100 MHz, $CDCl_3$)



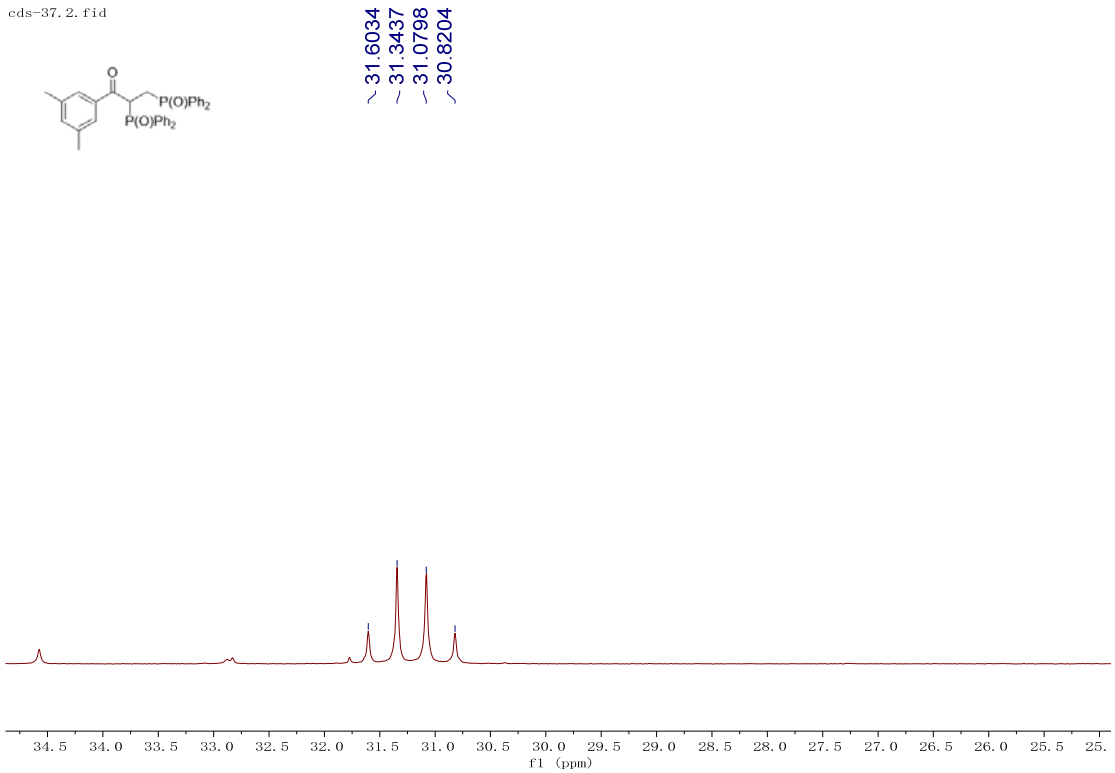
^{31}P NMR spectrum of **4k** (162 MHz, $CDCl_3$)



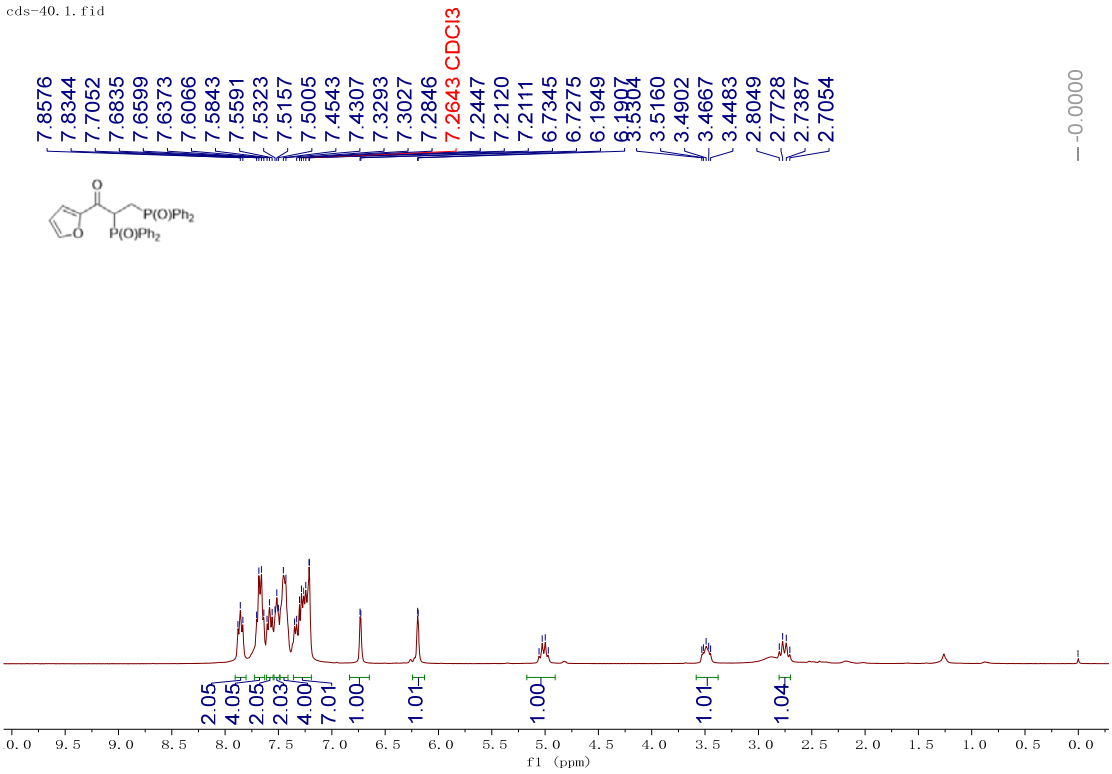
^{1}H NMR spectrum of **4l** (400 MHz, $CDCl_3$)



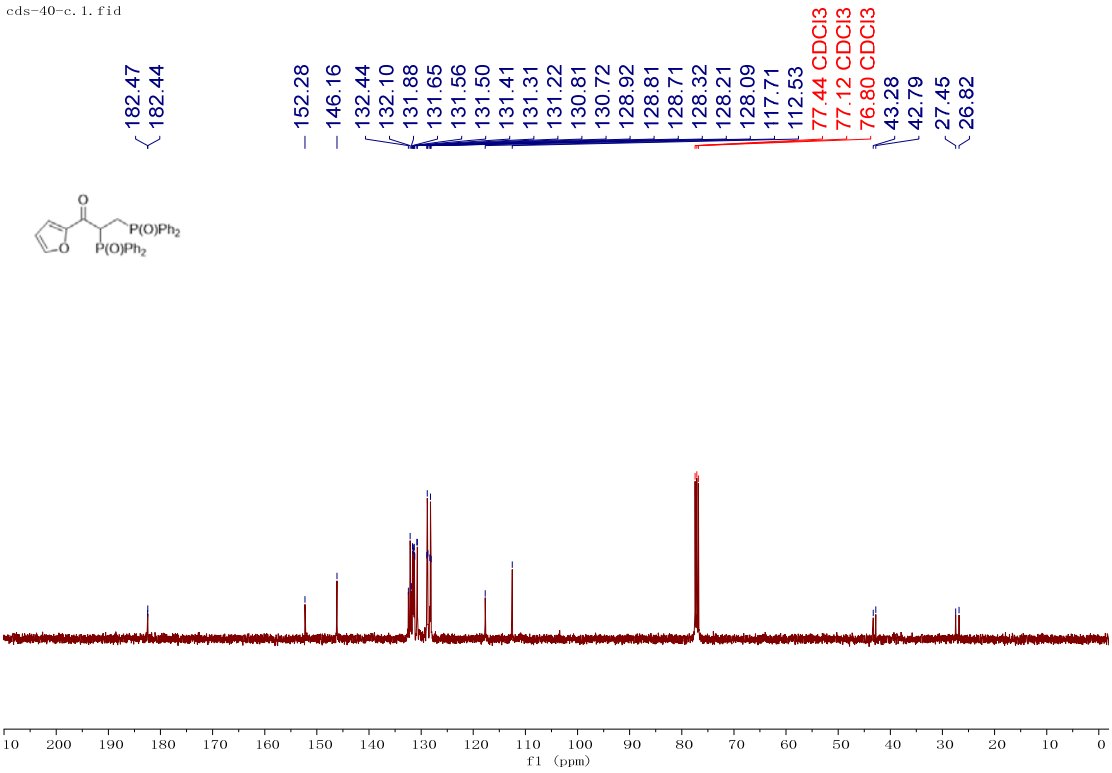
^{13}C NMR spectrum of **4l** (100 MHz, $CDCl_3$)



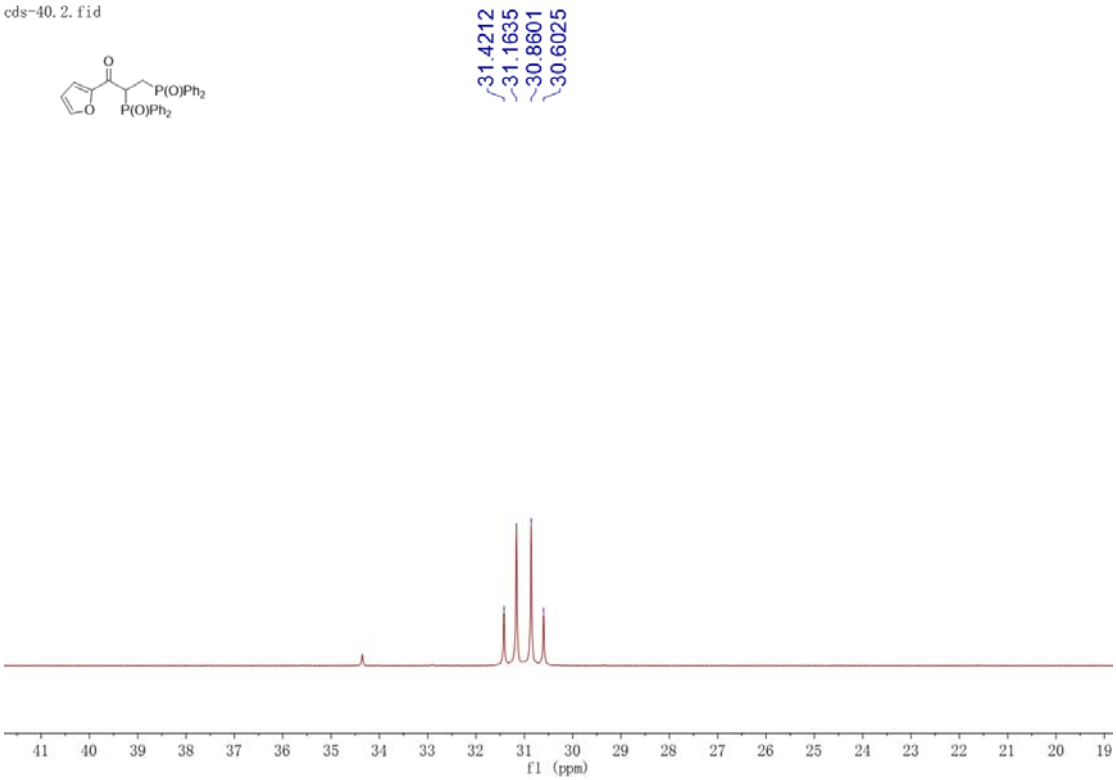
^{31}P NMR spectrum of **4l** (162 MHz, $CDCl_3$)



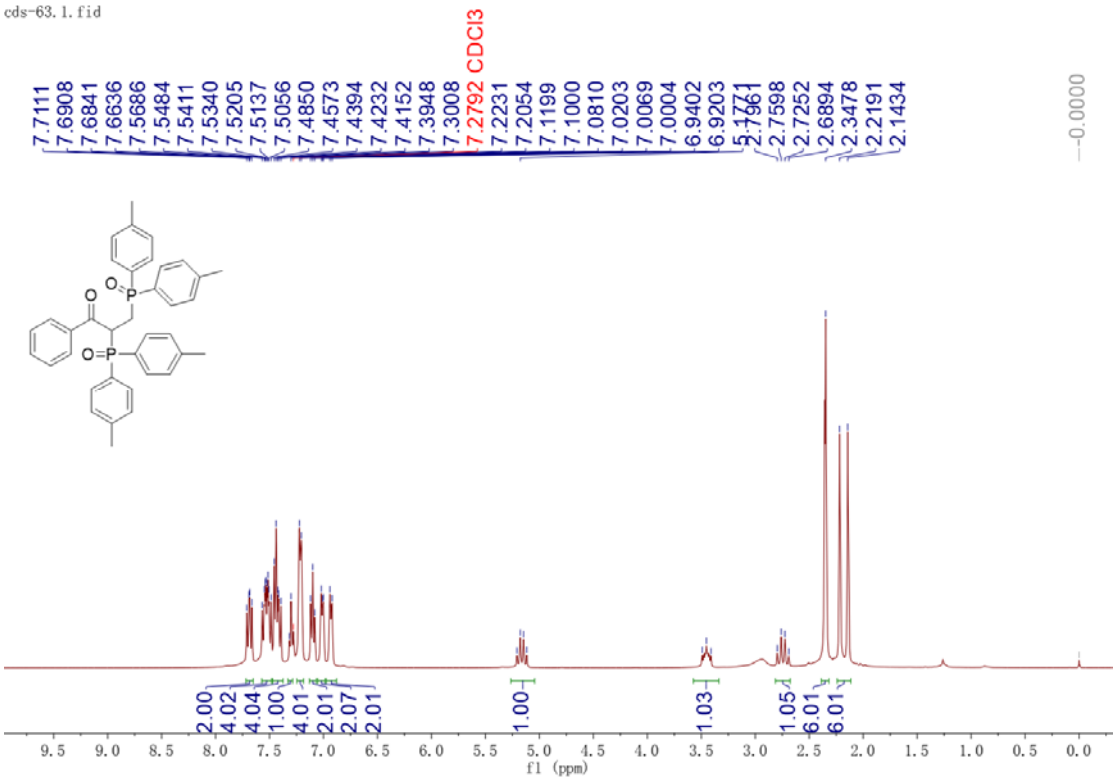
^{1}H NMR spectrum of **4m** (400 MHz, $CDCl_3$)



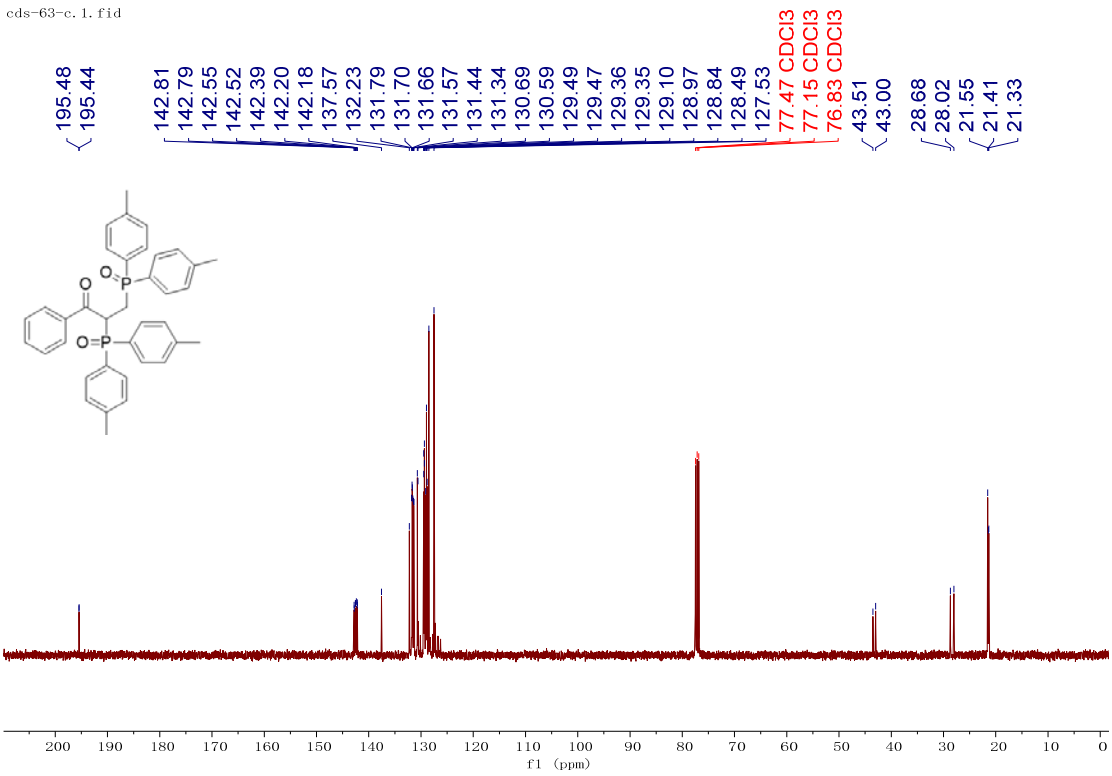
^{13}C NMR spectrum of **4m** (100 MHz, $CDCl_3$)



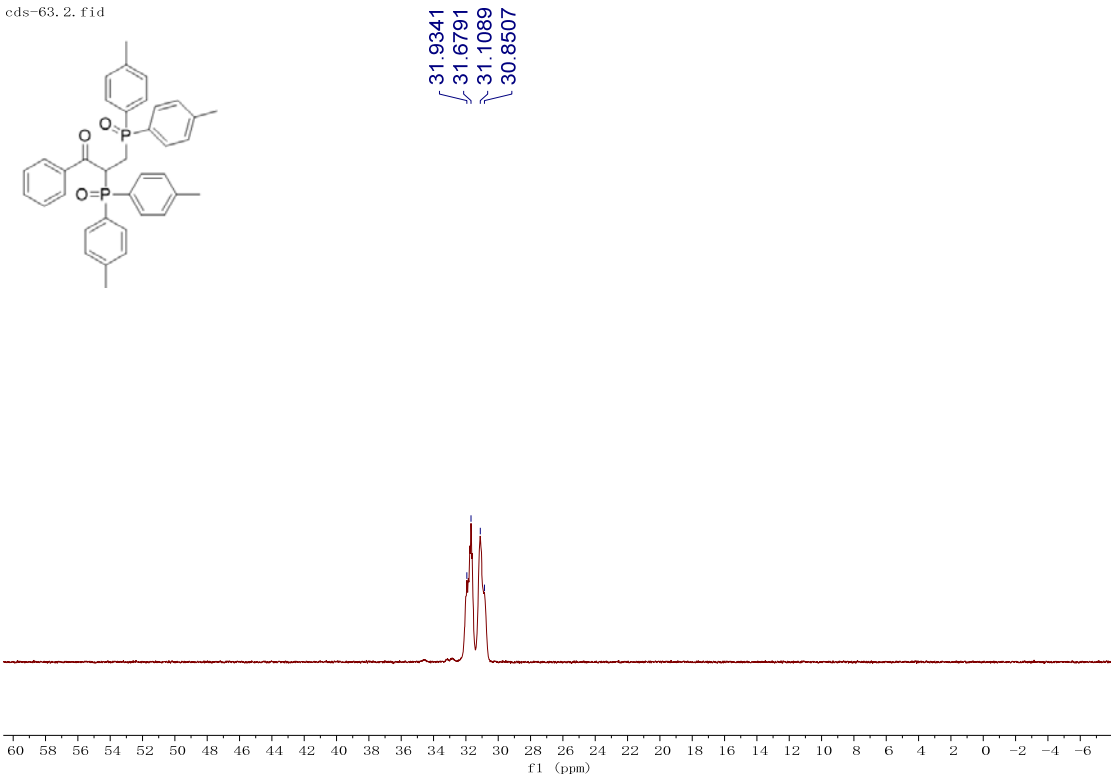
^{31}P NMR spectrum of **4m** (162 MHz, $CDCl_3$)



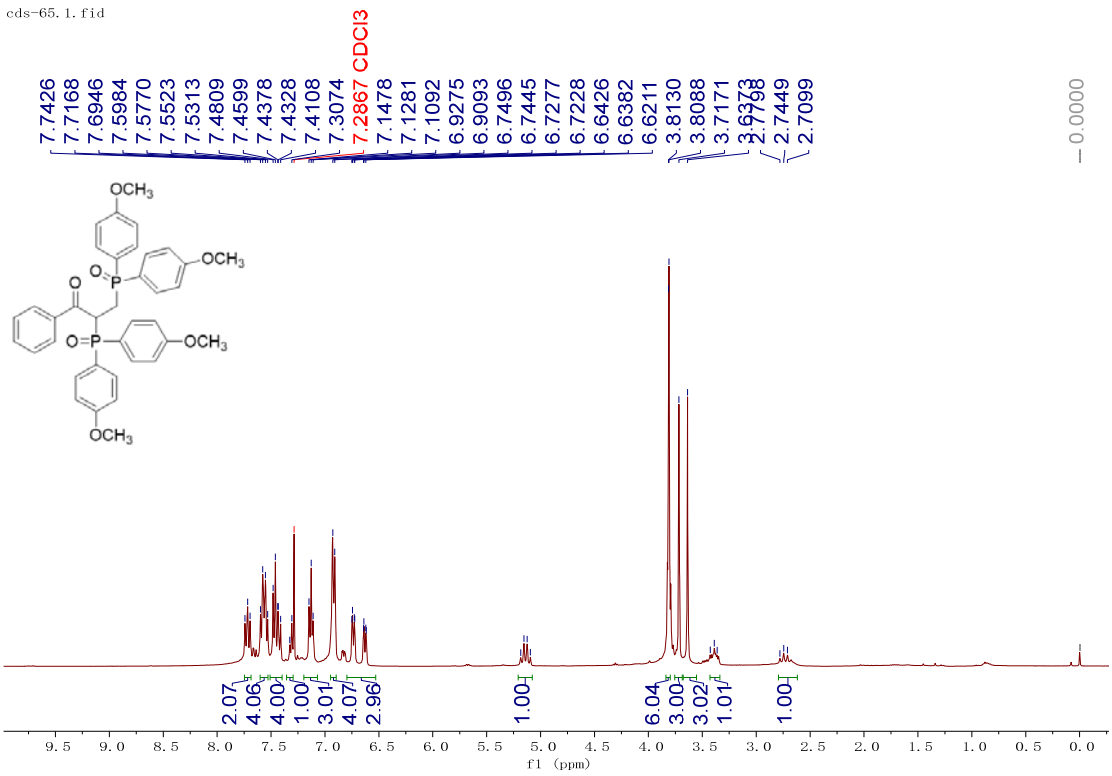
^{1}H NMR spectrum of **4n** (400 MHz, $CDCl_3$)



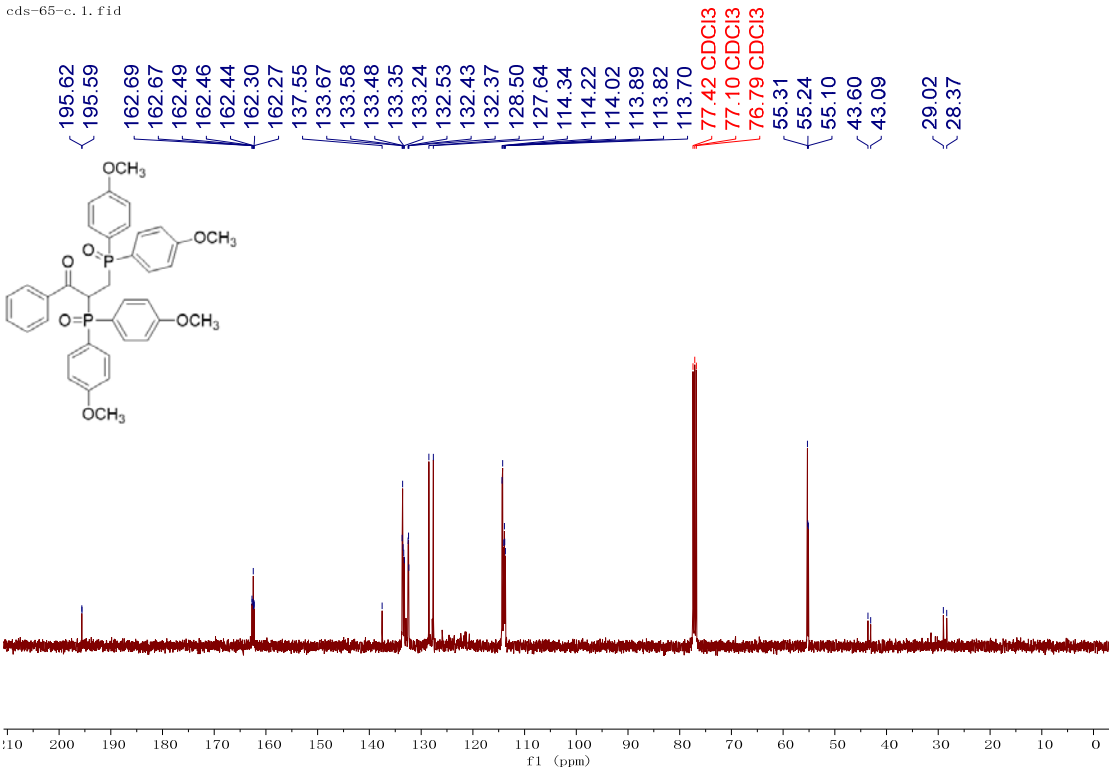
^{13}C NMR spectrum of **4n** (100 MHz, $CDCl_3$)



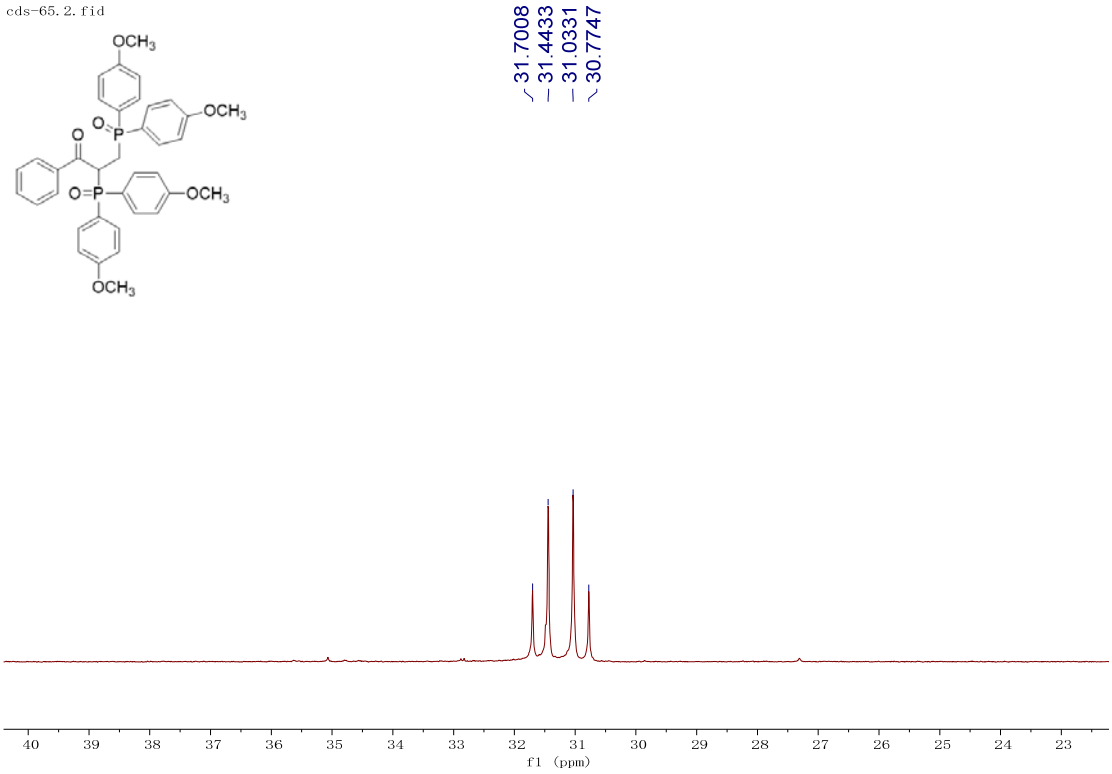
^{31}P NMR spectrum of **4n** (162 MHz, $CDCl_3$)



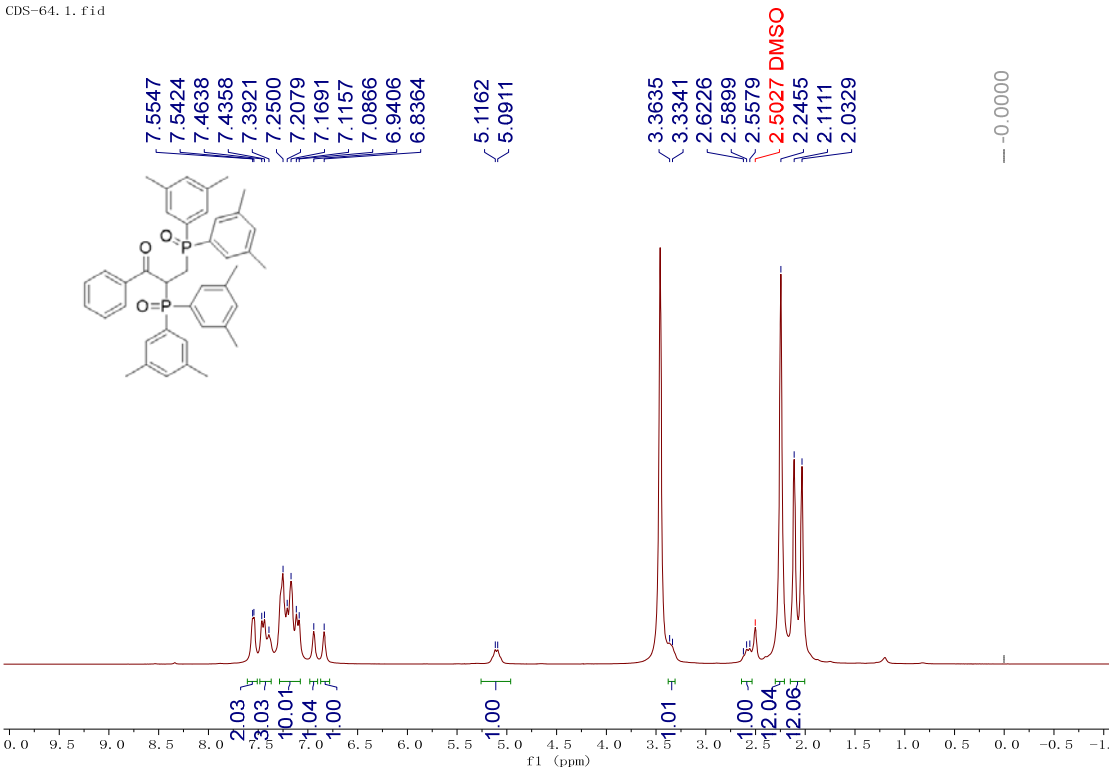
^{1}H NMR spectrum of **4o** (400 MHz, $CDCl_3$)



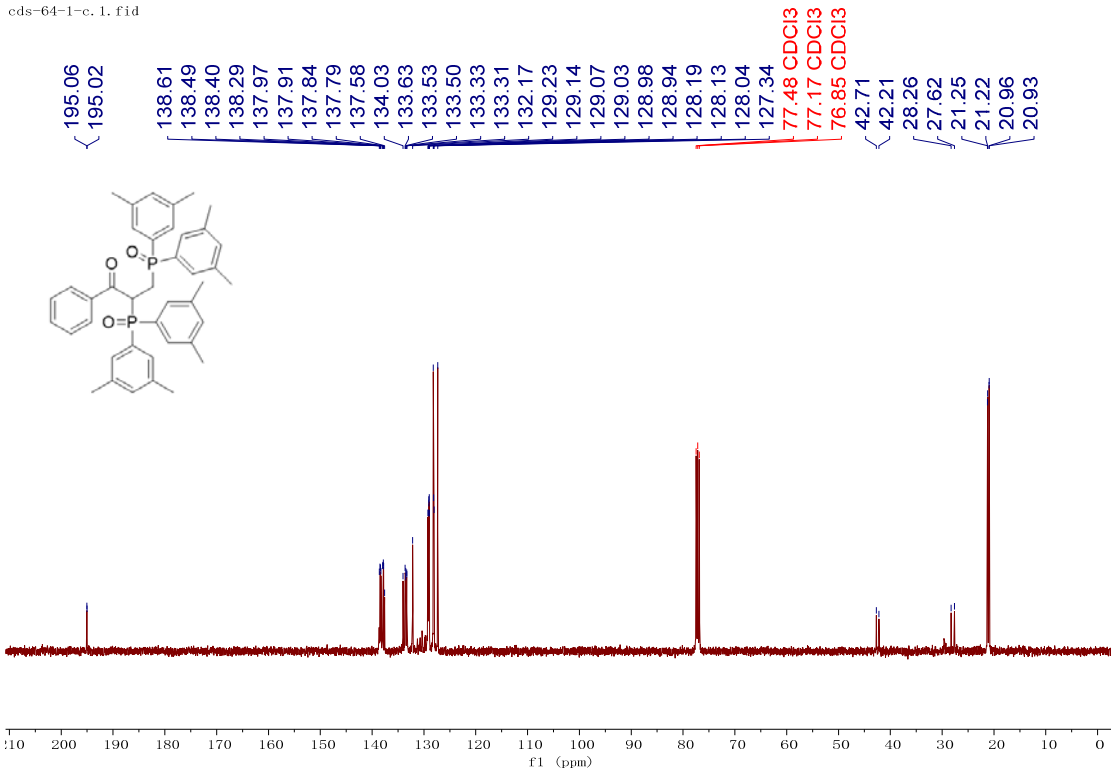
^{13}C NMR spectrum of **4o** (100 MHz, $CDCl_3$)



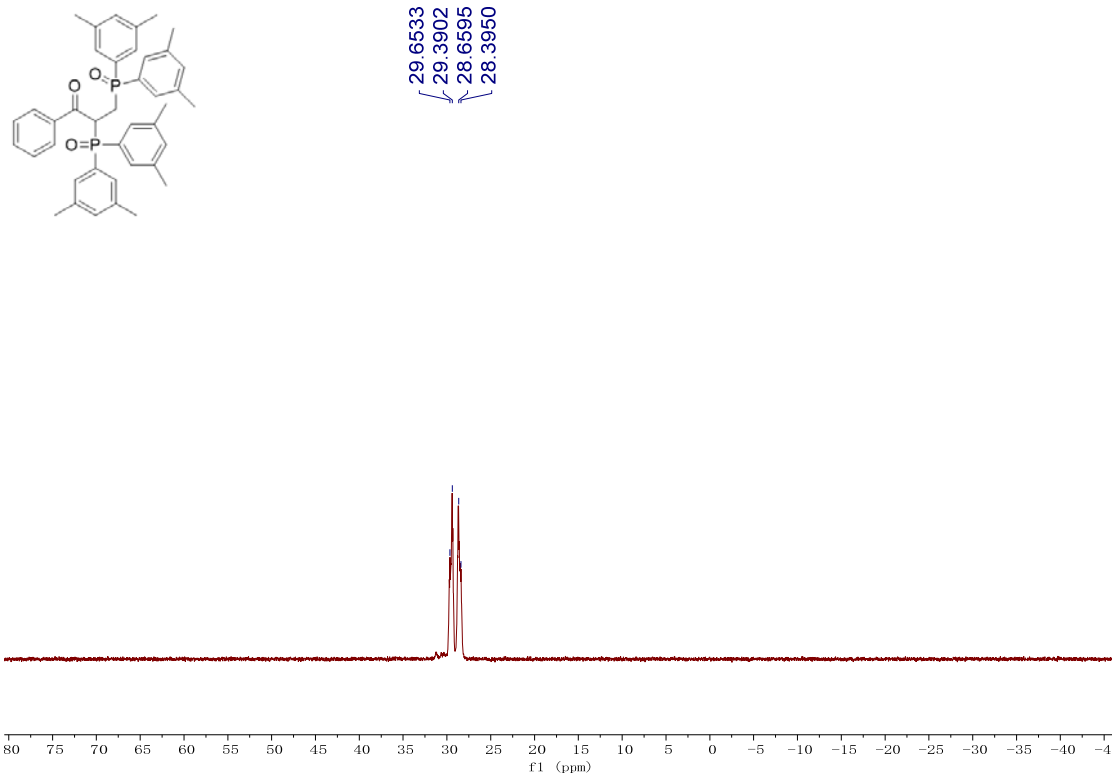
^{31}P NMR spectrum of **4o** (162 MHz, $CDCl_3$)



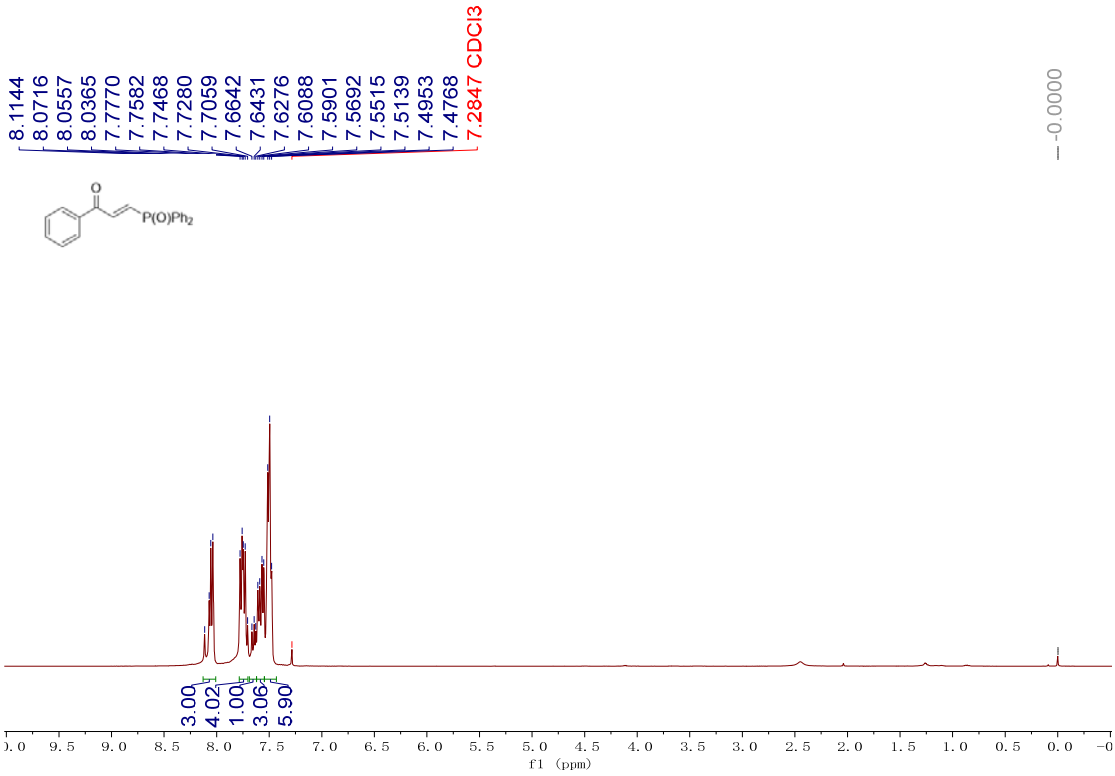
^{1}H NMR spectrum of **4p** (400 MHz, DMSO-d_6)



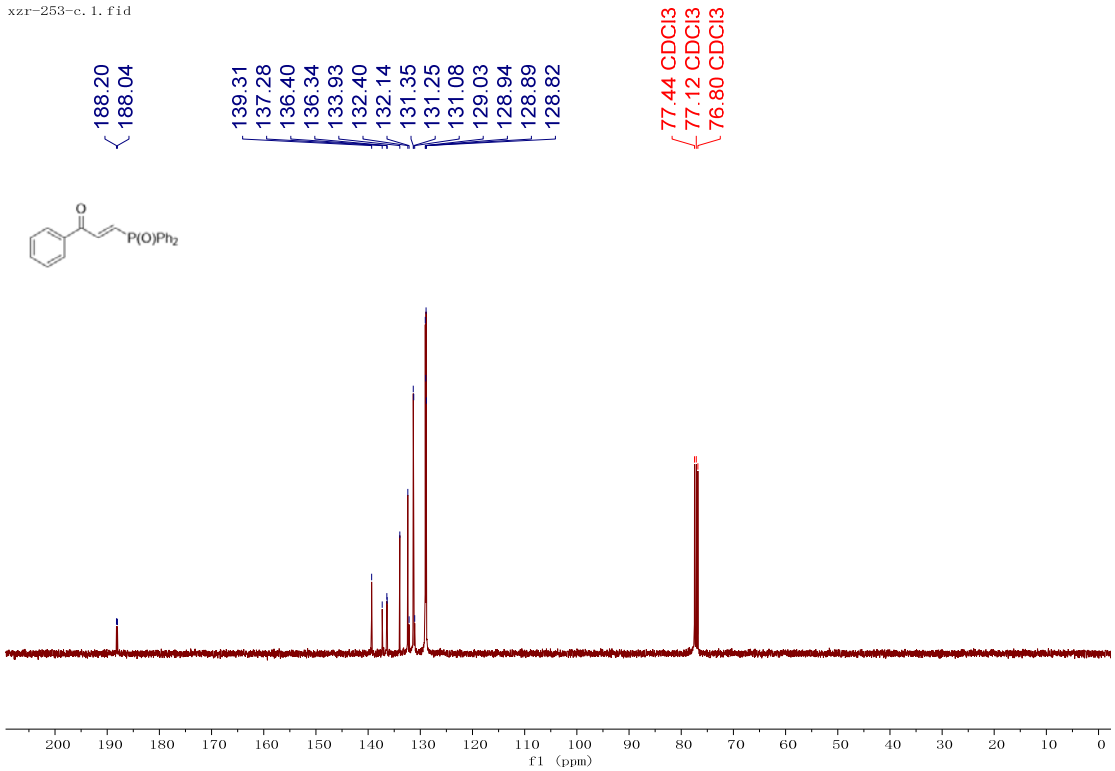
^{13}C NMR spectrum of **4p** (100 MHz, $CDCl_3$)



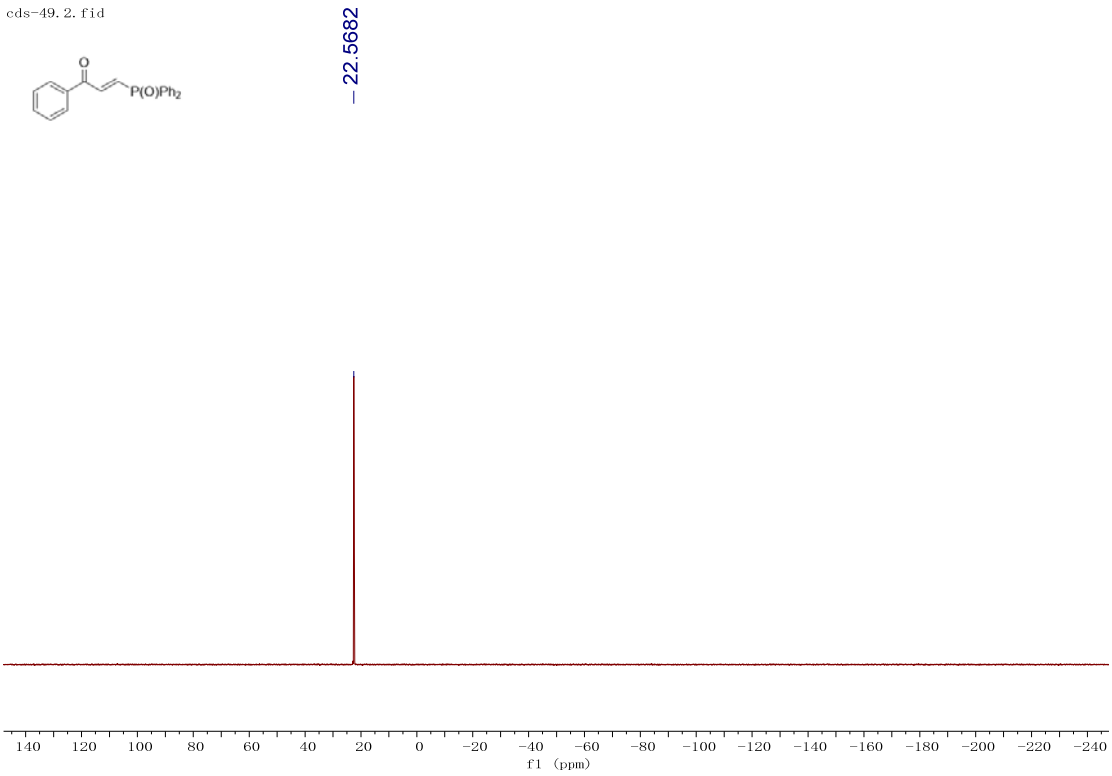
^{31}P NMR spectrum of **4p** (162 MHz, DMSO-d_6)



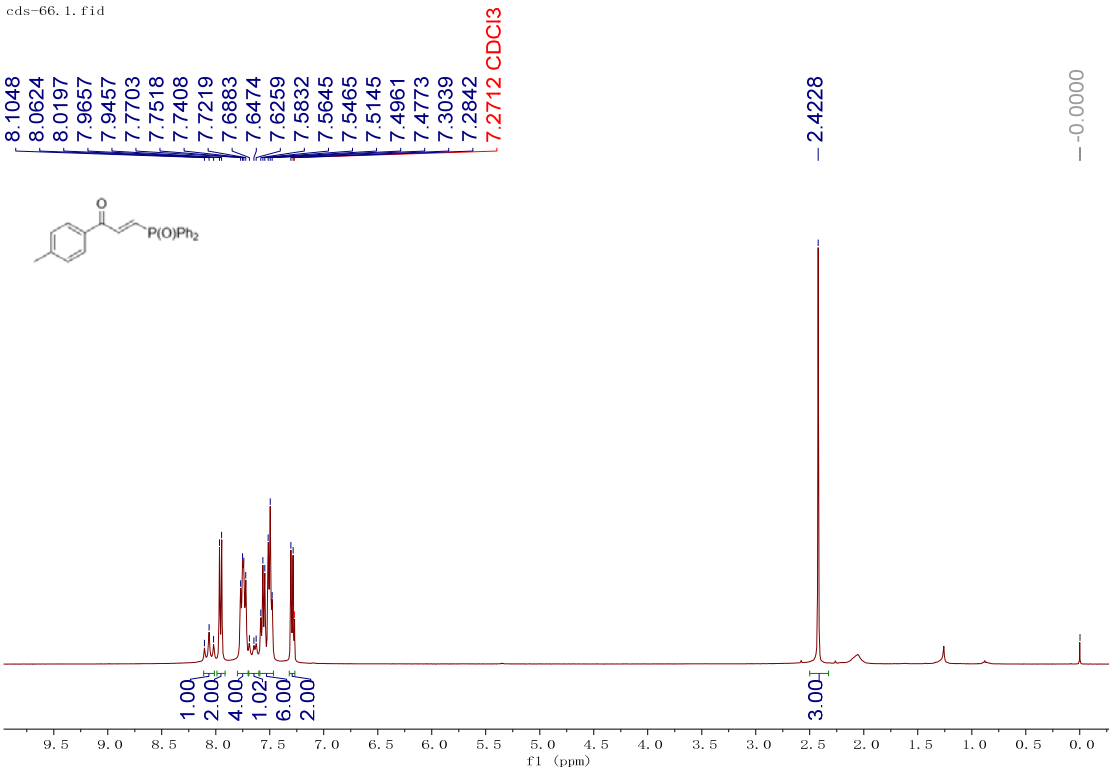
^{1}H NMR spectrum of **5a** (400 MHz, $CDCl_3$)



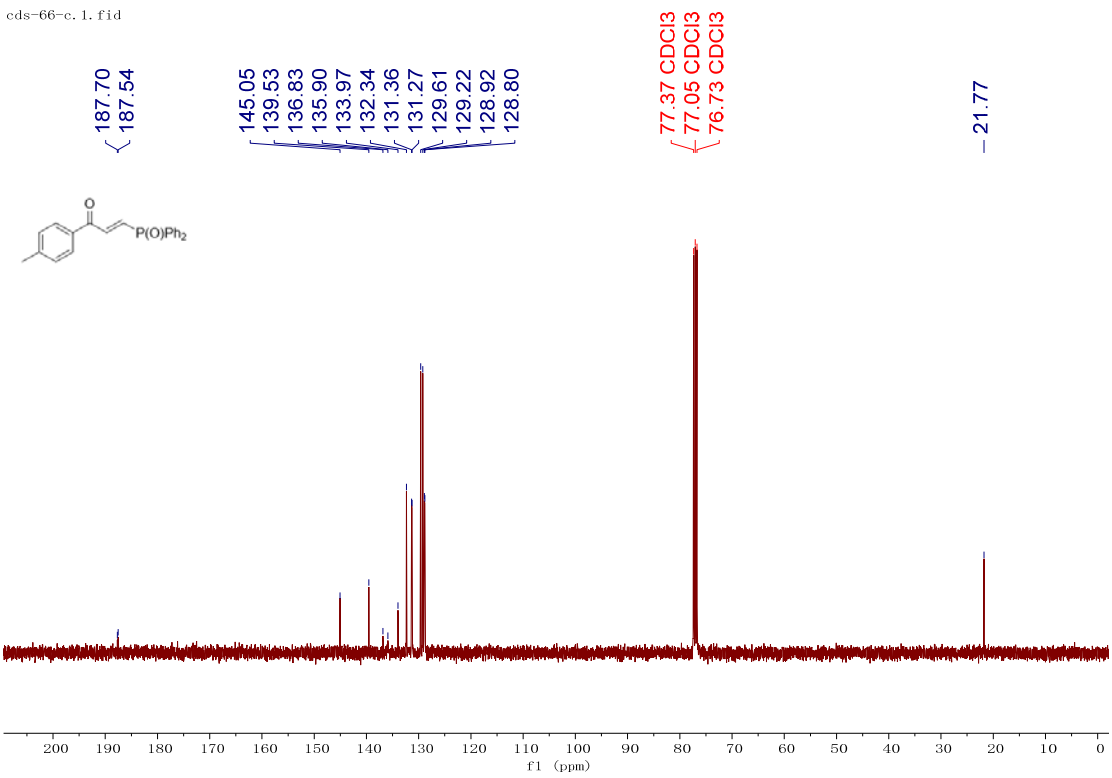
^{13}C NMR spectrum of **5a** (100 MHz, $CDCl_3$)



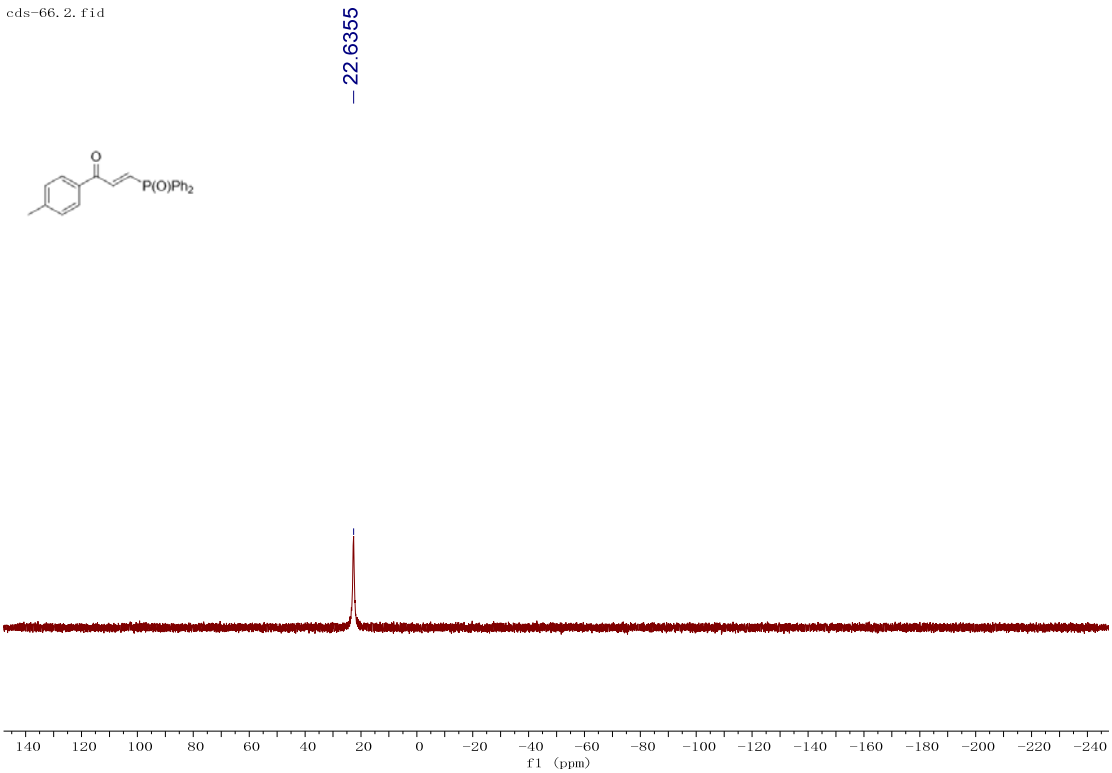
^{31}P NMR spectrum of **5a** (162 MHz, $CDCl_3$)



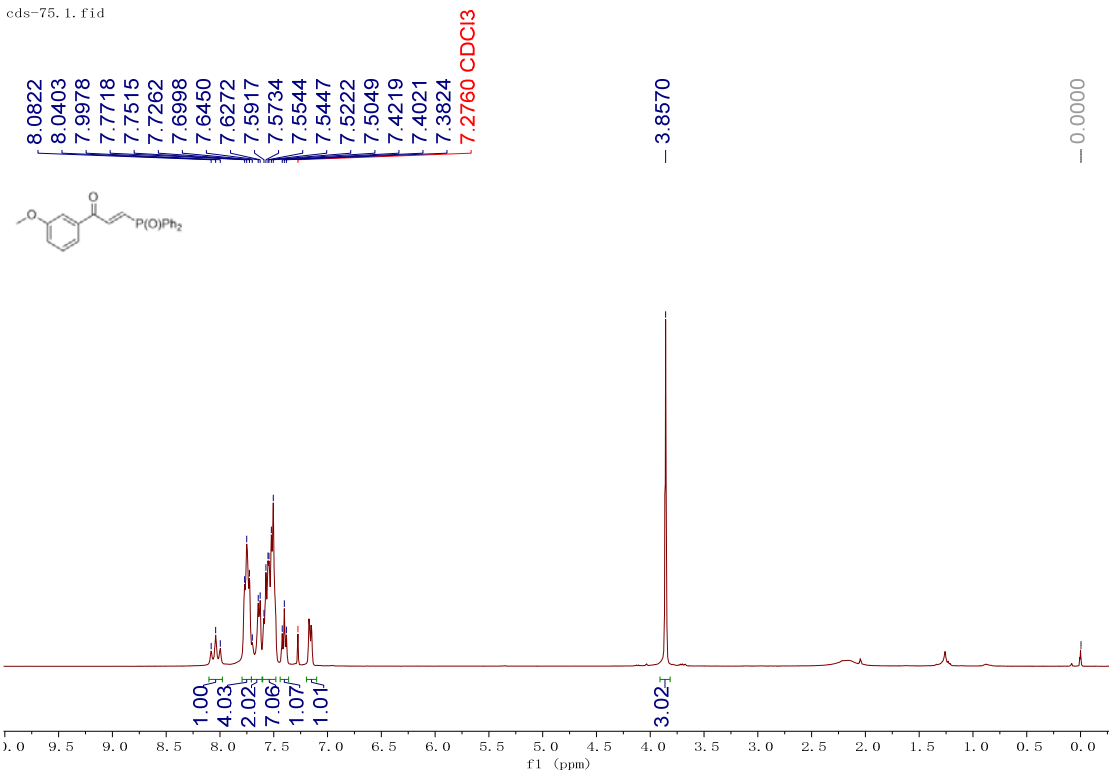
^{1}H NMR spectrum of **5b** (400 MHz, $CDCl_3$)



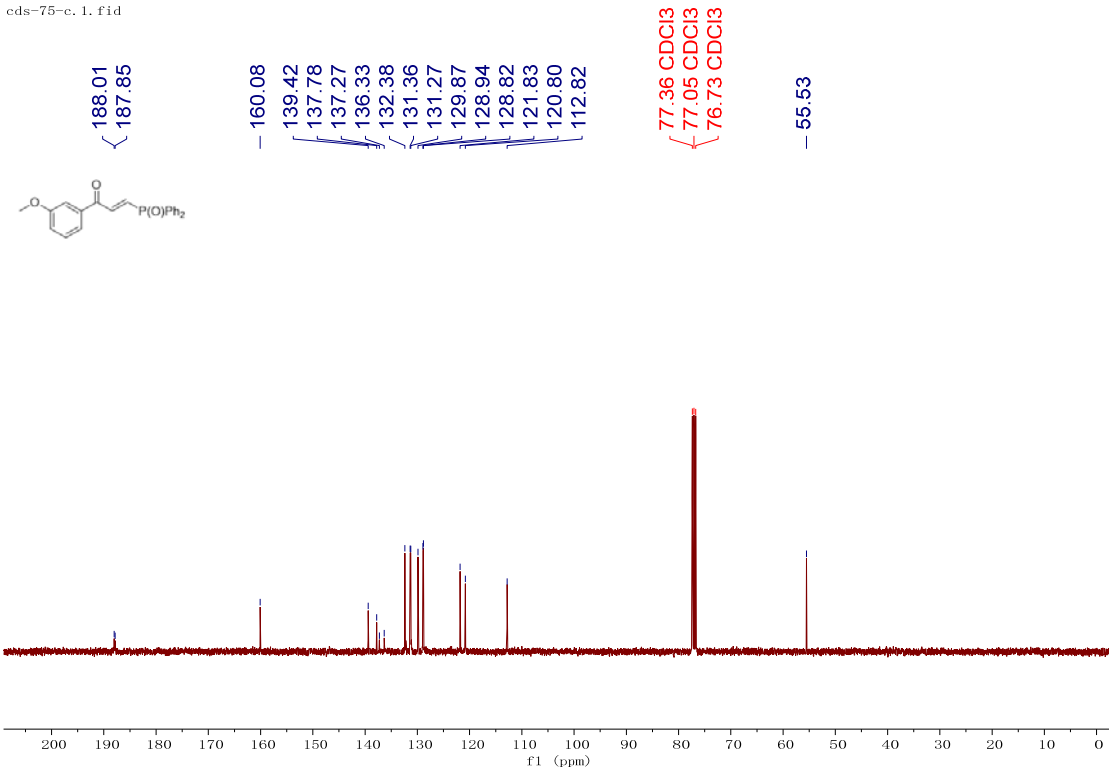
^{13}C NMR spectrum of **5b** (100 MHz, $CDCl_3$)



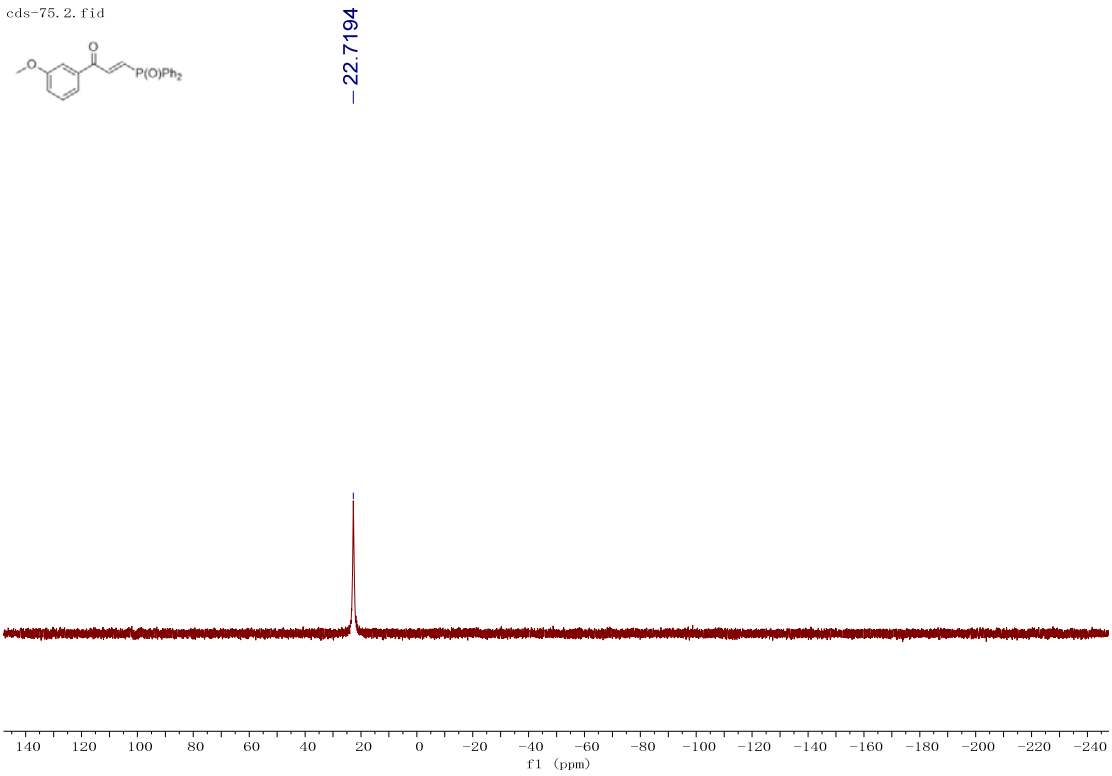
^{31}P NMR spectrum of **5b** (162 MHz, $CDCl_3$)



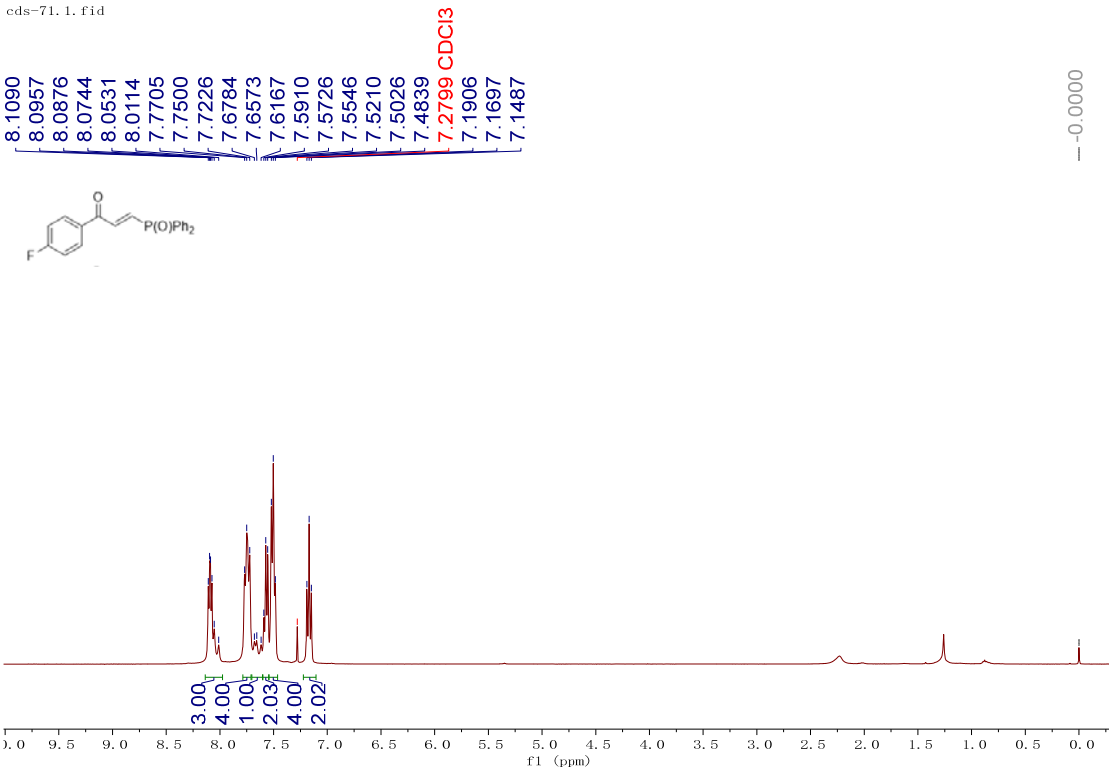
^{1}H NMR spectrum of **5c** (400 MHz, $CDCl_3$)



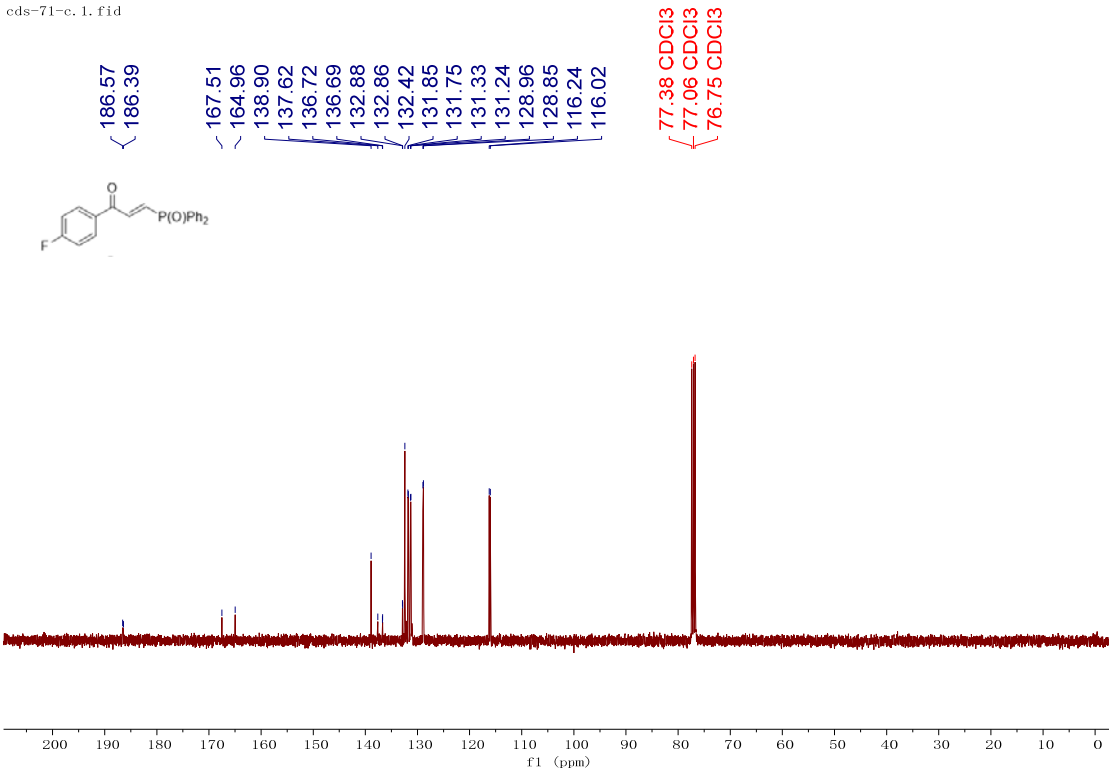
^{13}C NMR spectrum of **5c** (100 MHz, $CDCl_3$)



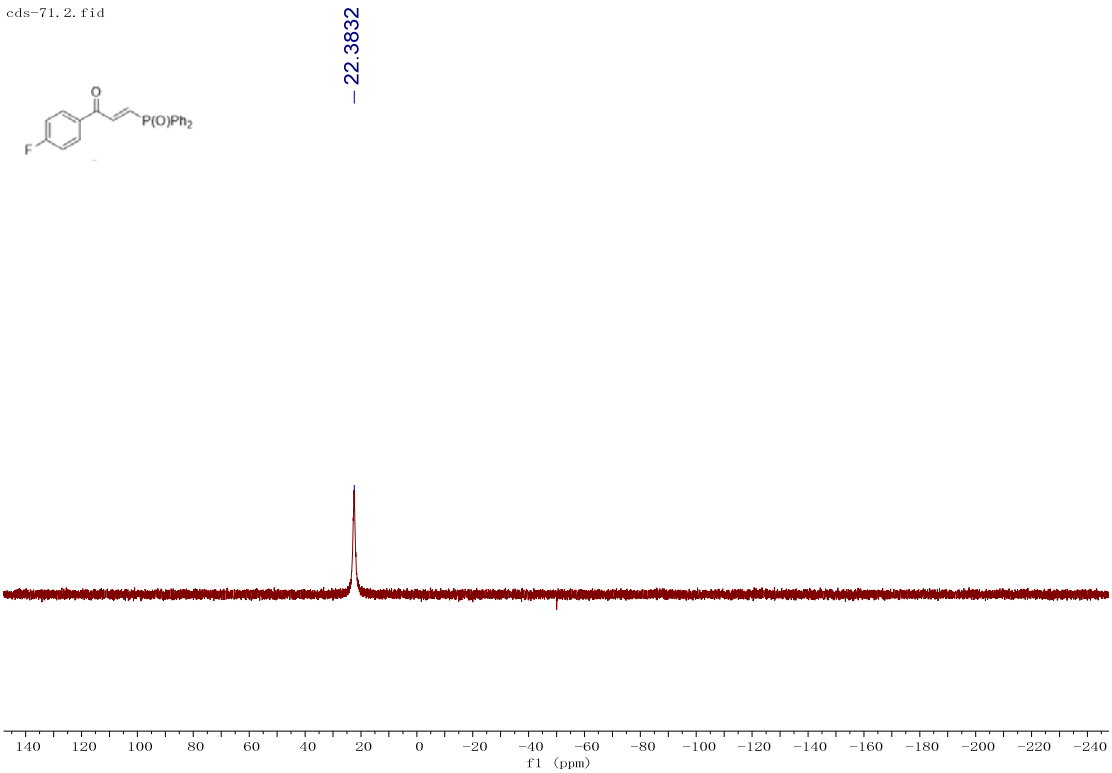
^{31}P NMR spectrum of **5c** (162 MHz, $CDCl_3$)



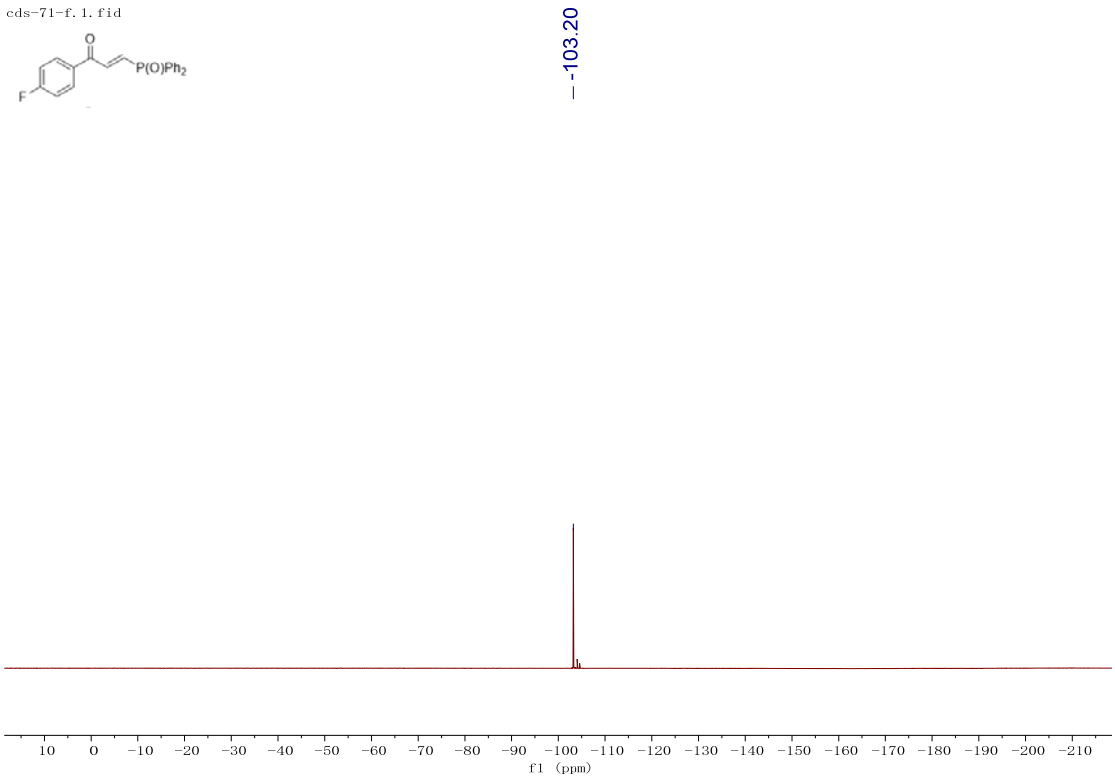
^{1}H NMR spectrum of **5d** (400 MHz, $CDCl_3$)



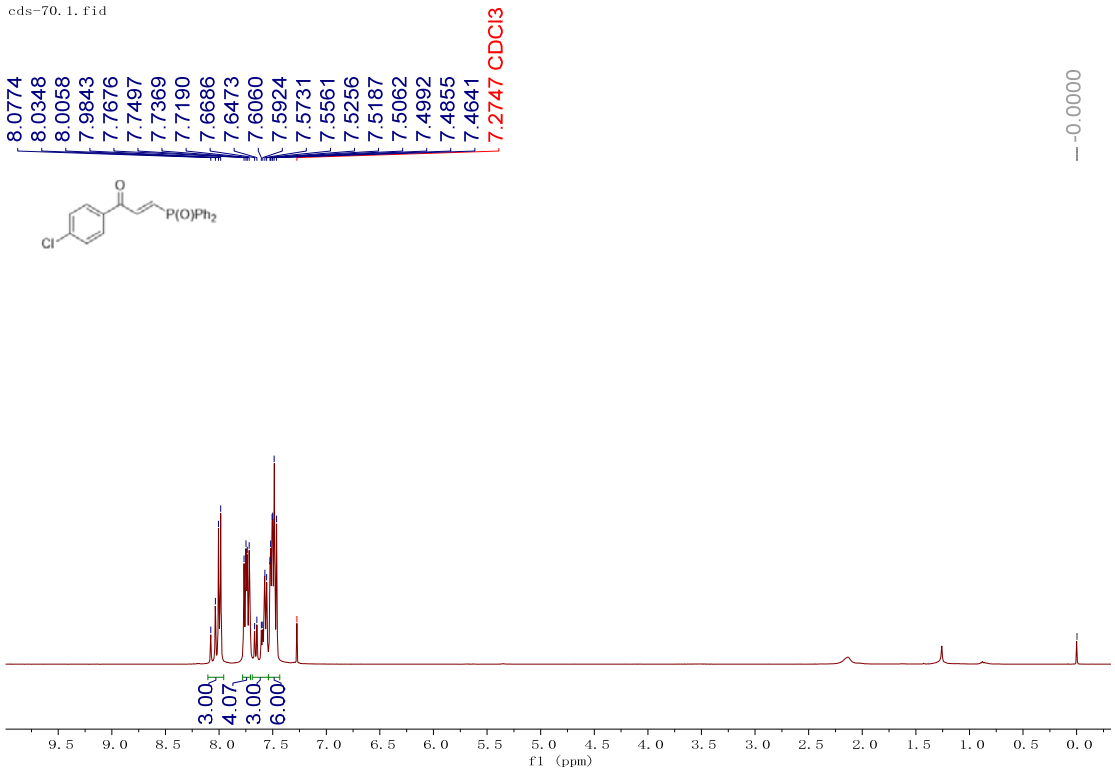
^{13}C NMR spectrum of **5d** (100 MHz, $CDCl_3$)



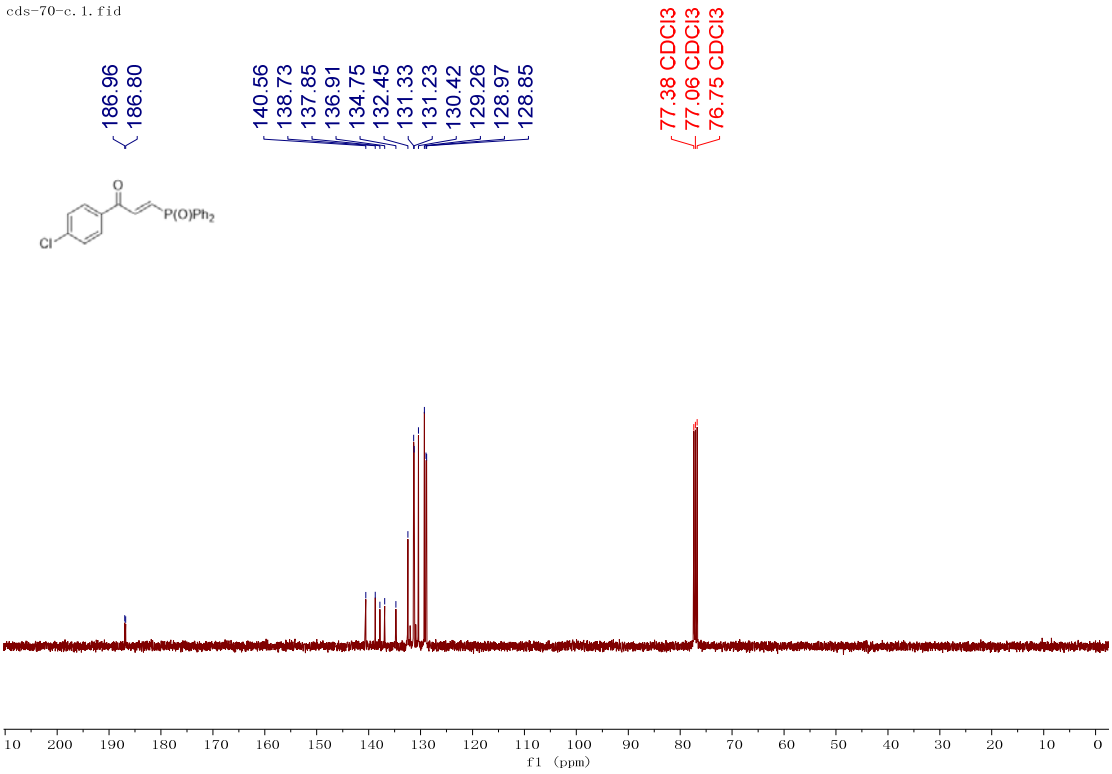
^{31}P NMR spectrum of **5d** (162 MHz, $CDCl_3$)



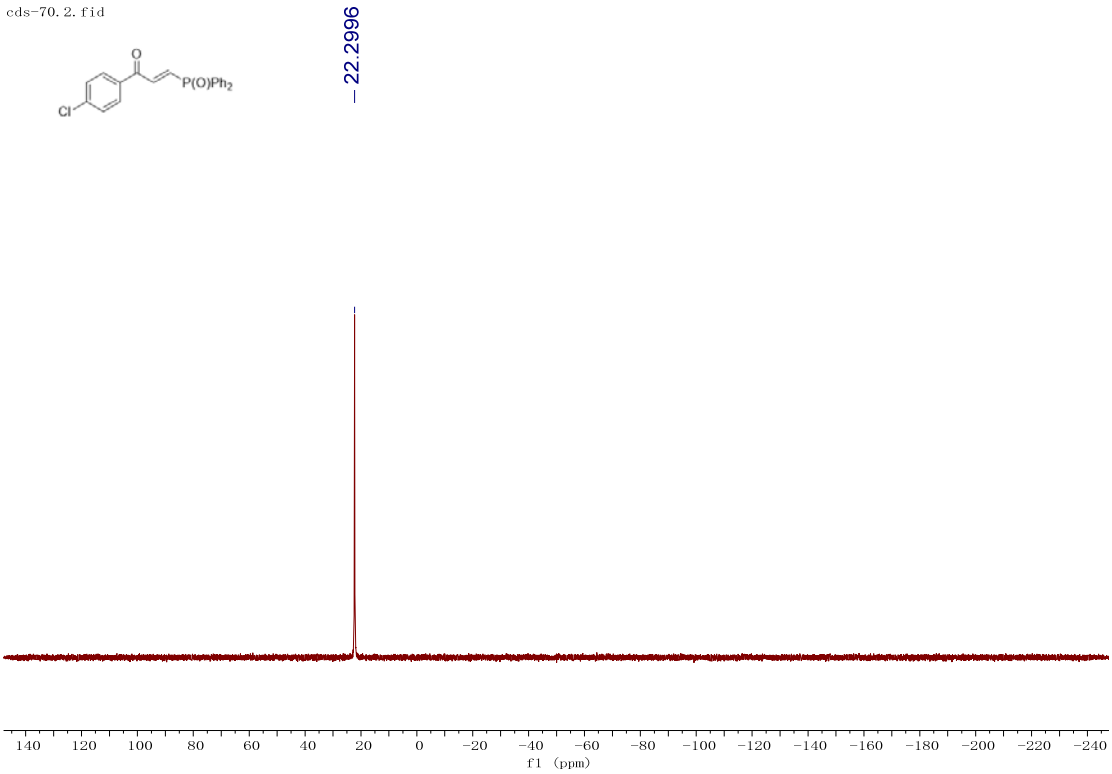
^{19}F NMR spectrum of **5d** (376 MHz, $CDCl_3$)



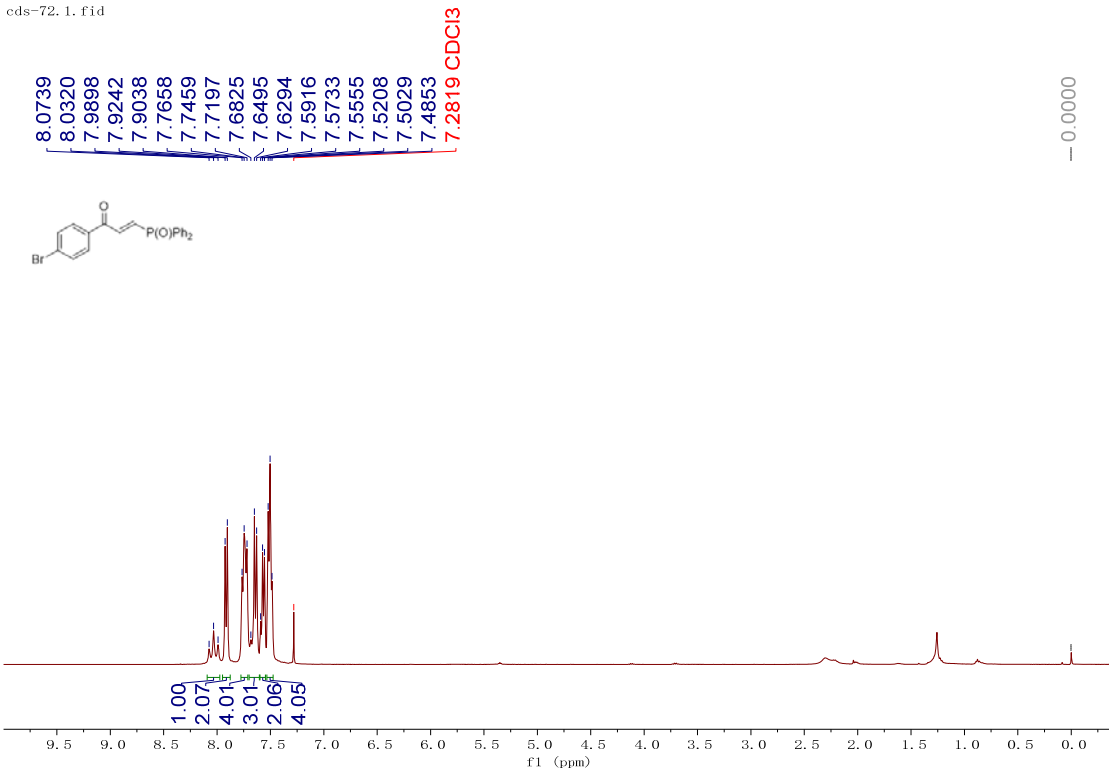
^{1}H NMR spectrum of **5e** (400 MHz, $CDCl_3$)



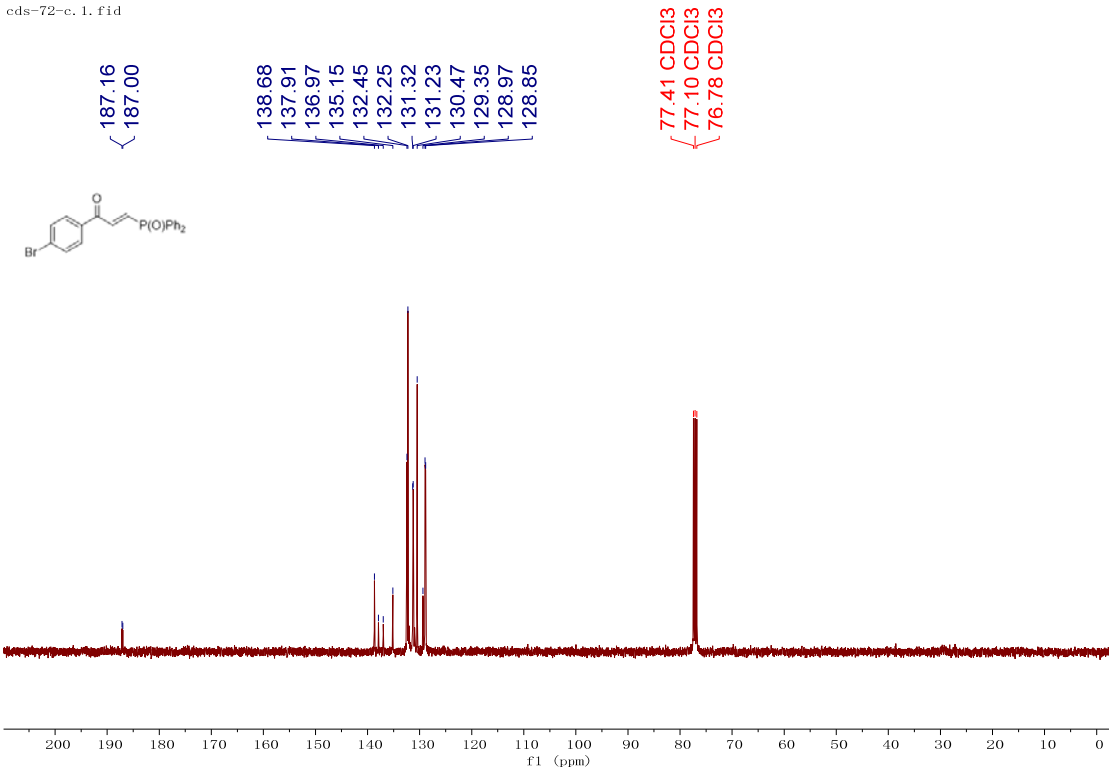
^{13}C NMR spectrum of **5e** (100 MHz, $CDCl_3$)



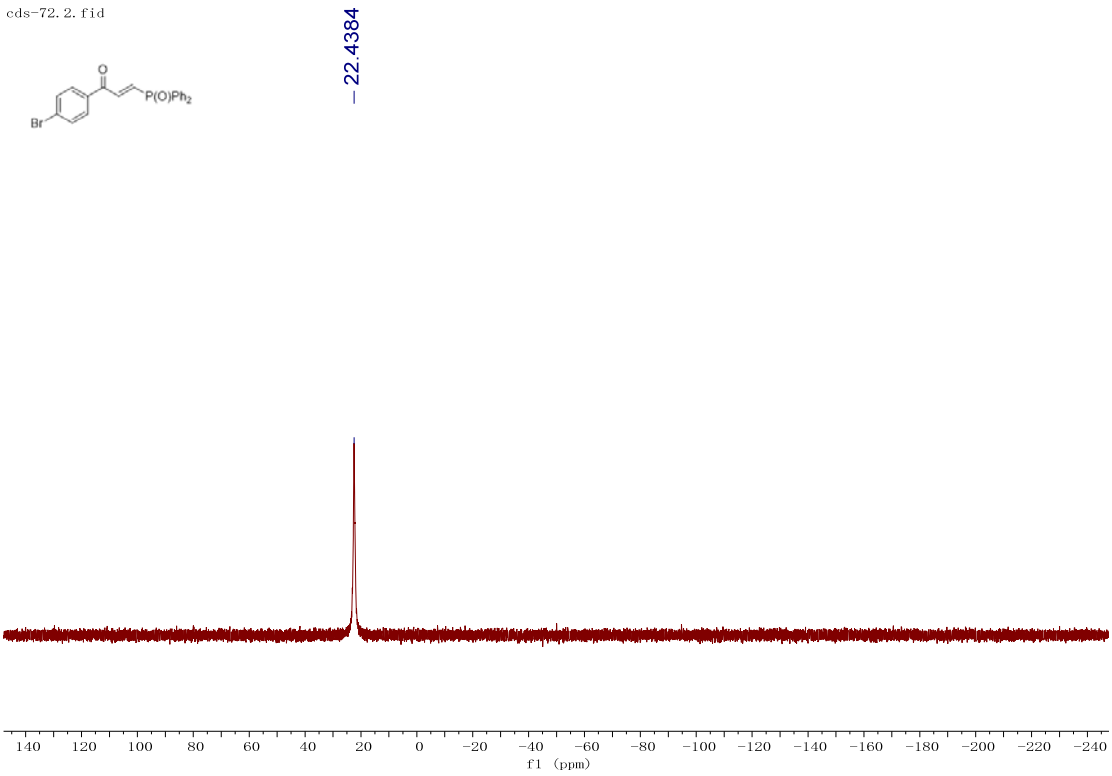
^{31}P NMR spectrum of **5e** (162 MHz, $CDCl_3$)



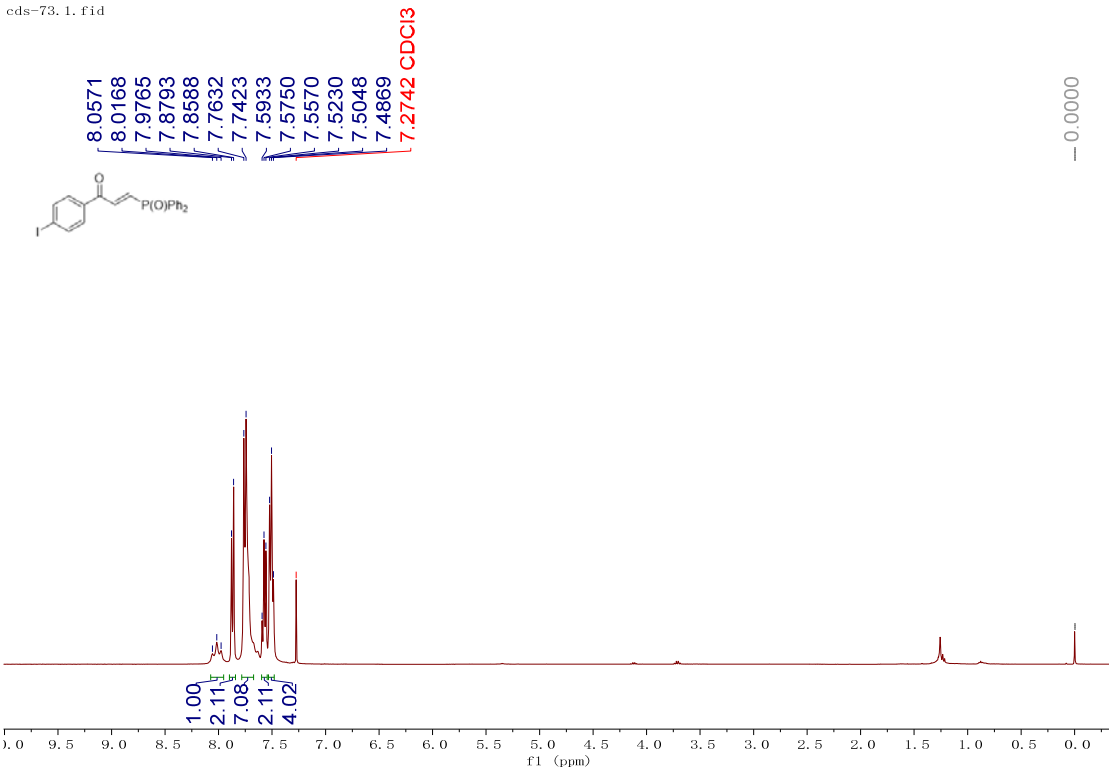
^{1}H NMR spectrum of **5f** (400 MHz, $CDCl_3$)



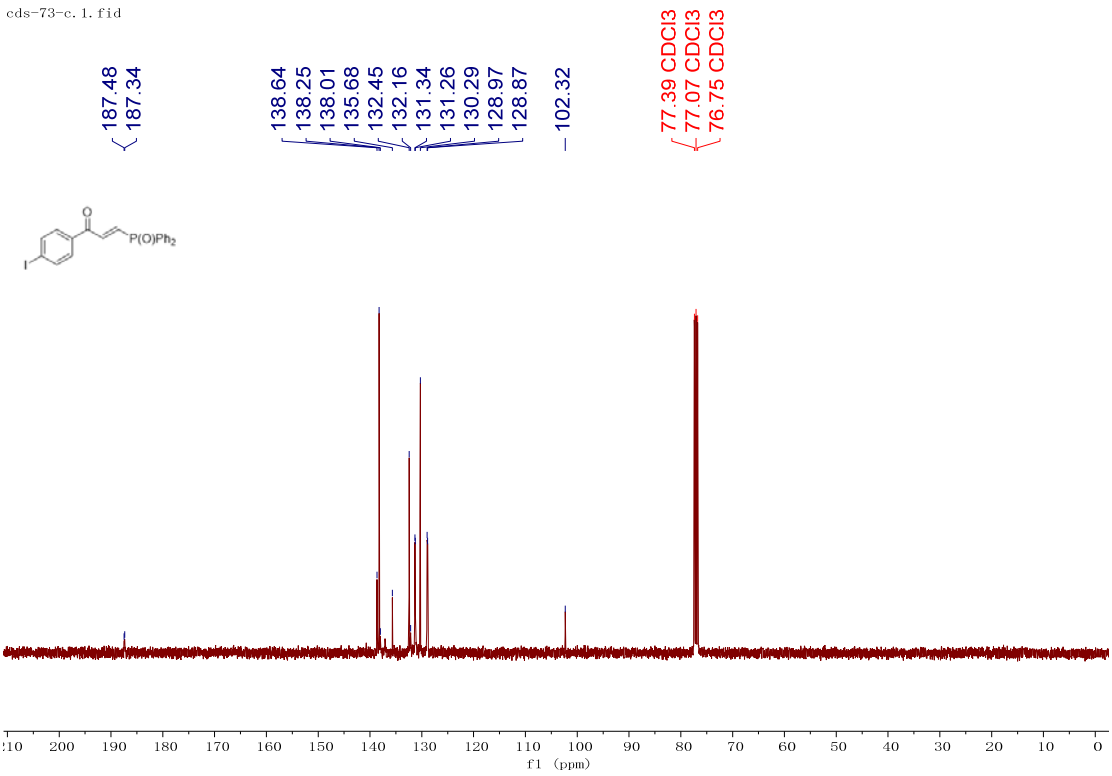
^{13}C NMR spectrum of **5f** (100 MHz, $CDCl_3$)



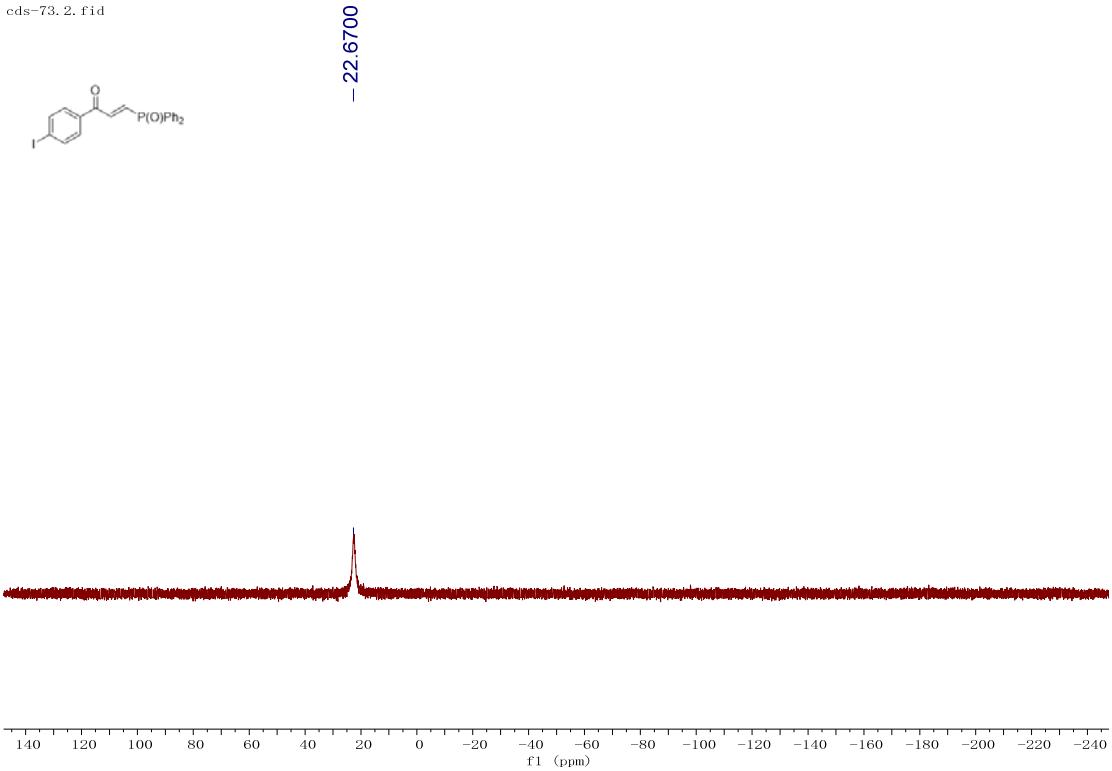
^{31}P NMR spectrum of **5f** (162 MHz, $CDCl_3$)



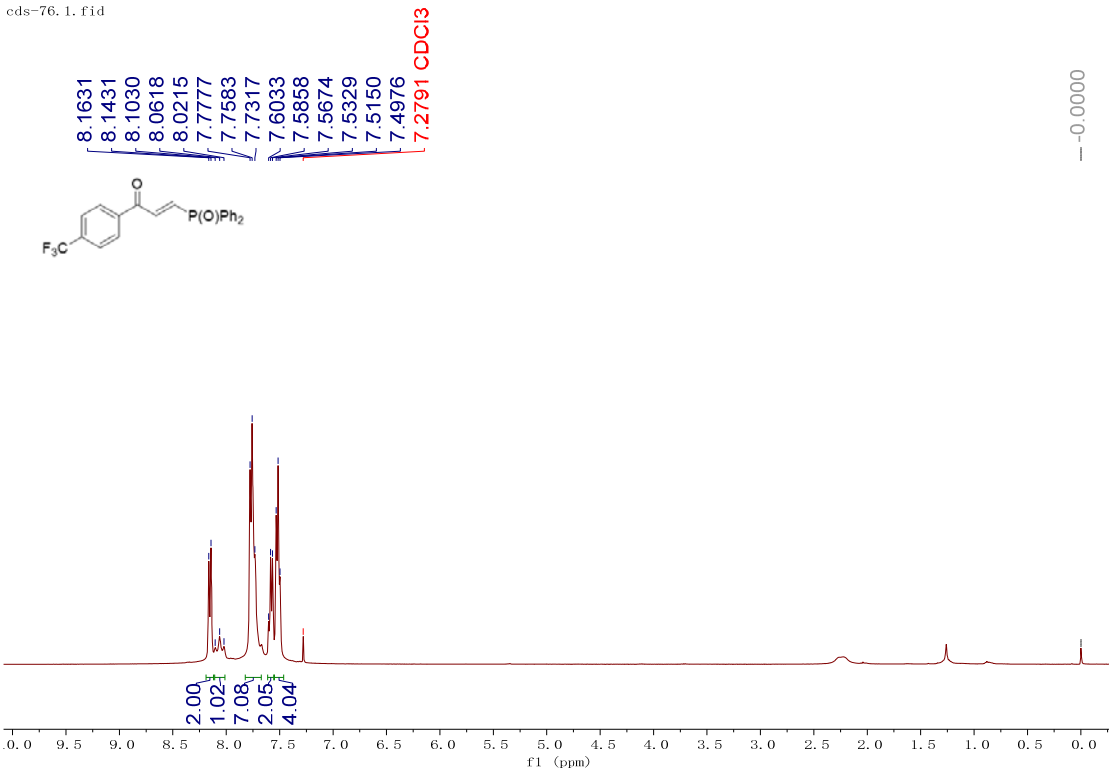
^{1}H NMR spectrum of **5g** (400 MHz, $CDCl_3$)



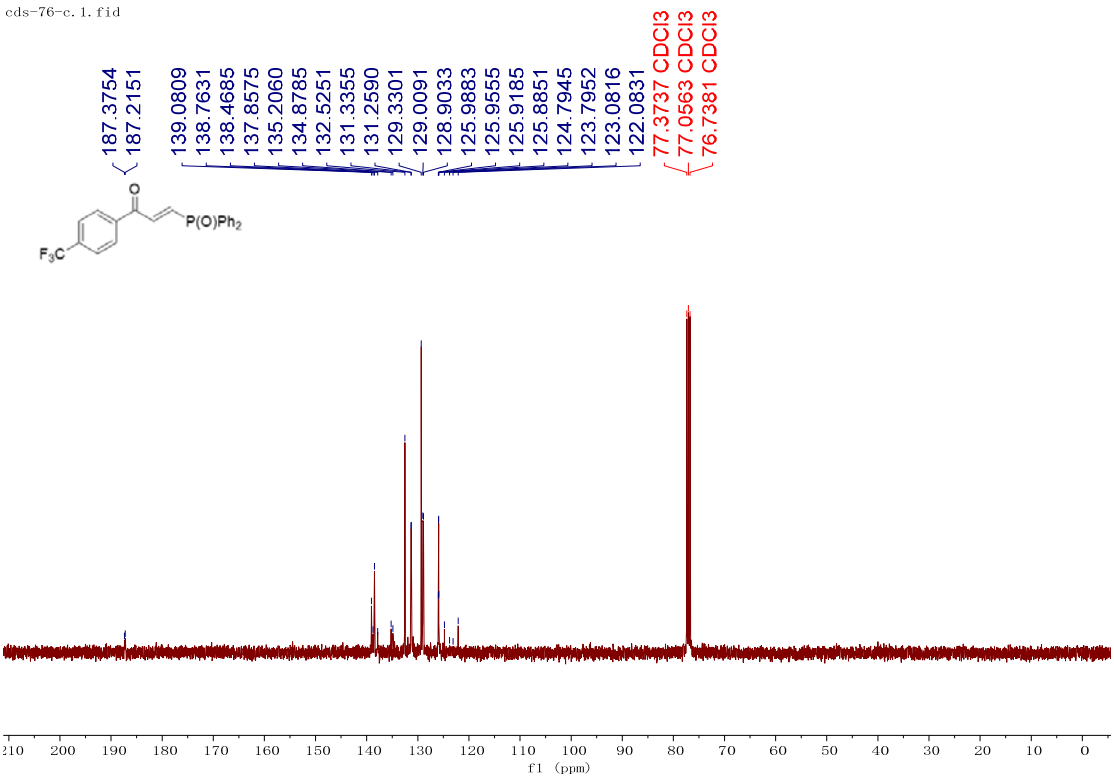
^{13}C NMR spectrum of **5g** (100 MHz, $CDCl_3$)



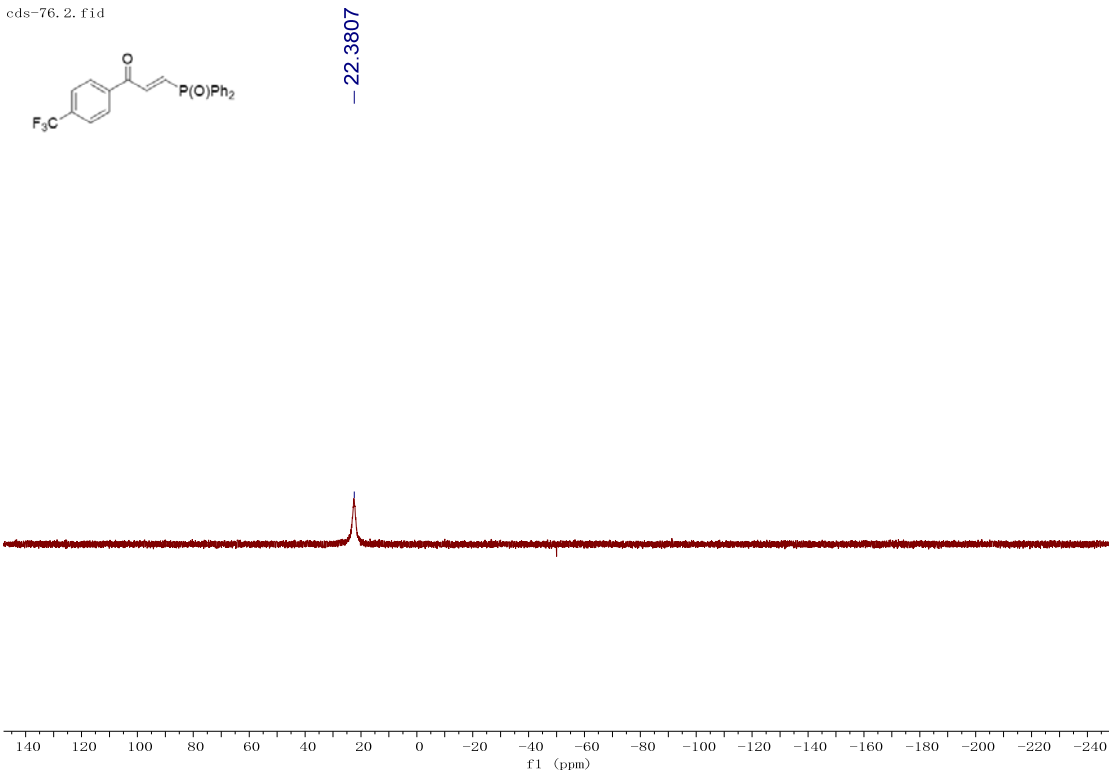
^{31}P NMR spectrum of **5g** (162 MHz, $CDCl_3$)



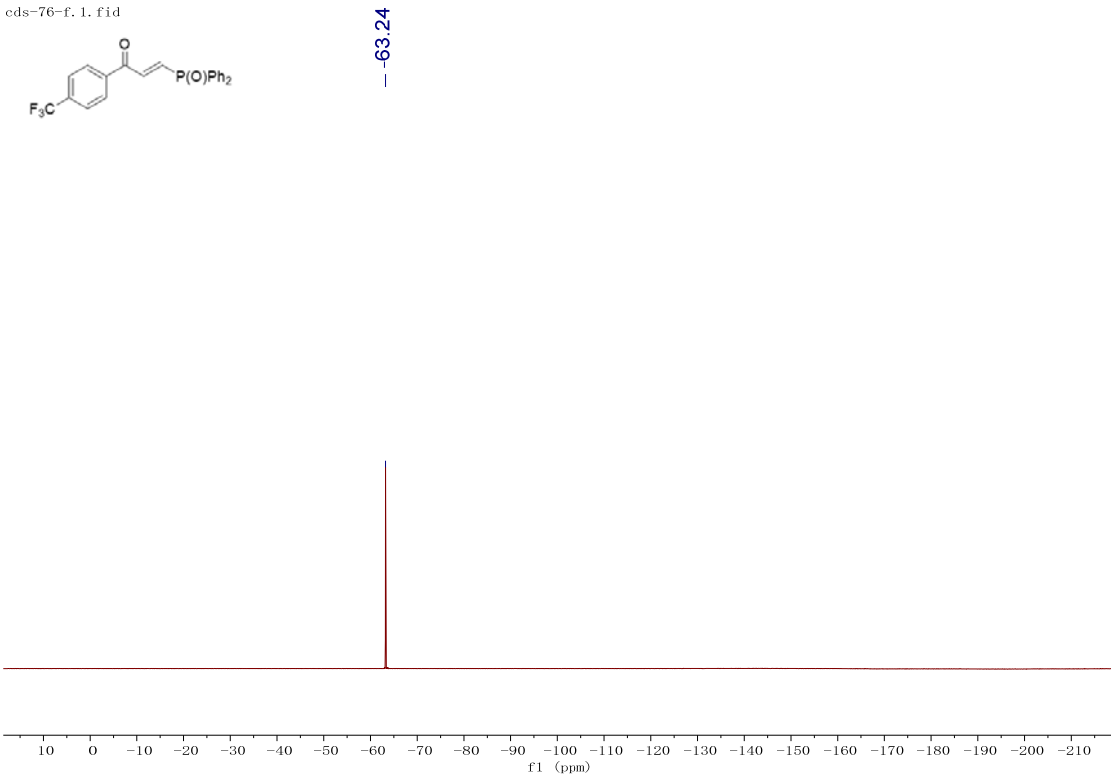
^{1}H NMR spectrum of **5h** (400 MHz, $CDCl_3$)



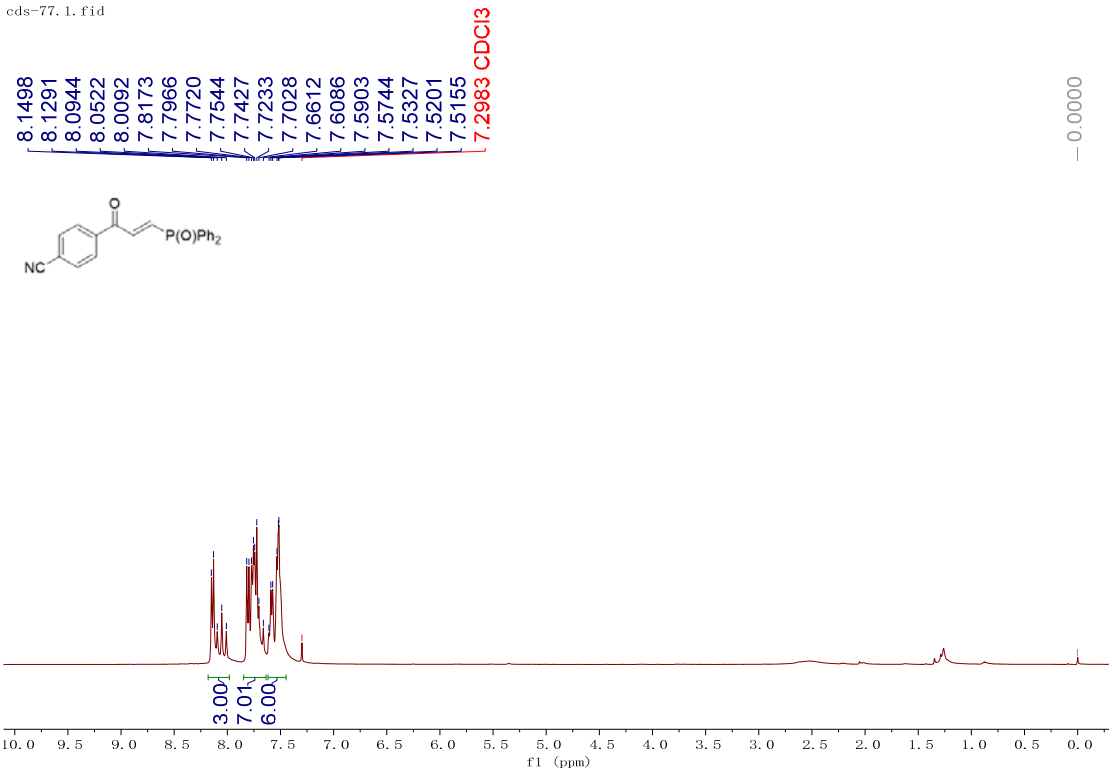
^{13}C NMR spectrum of **5h** (100 MHz, $CDCl_3$)



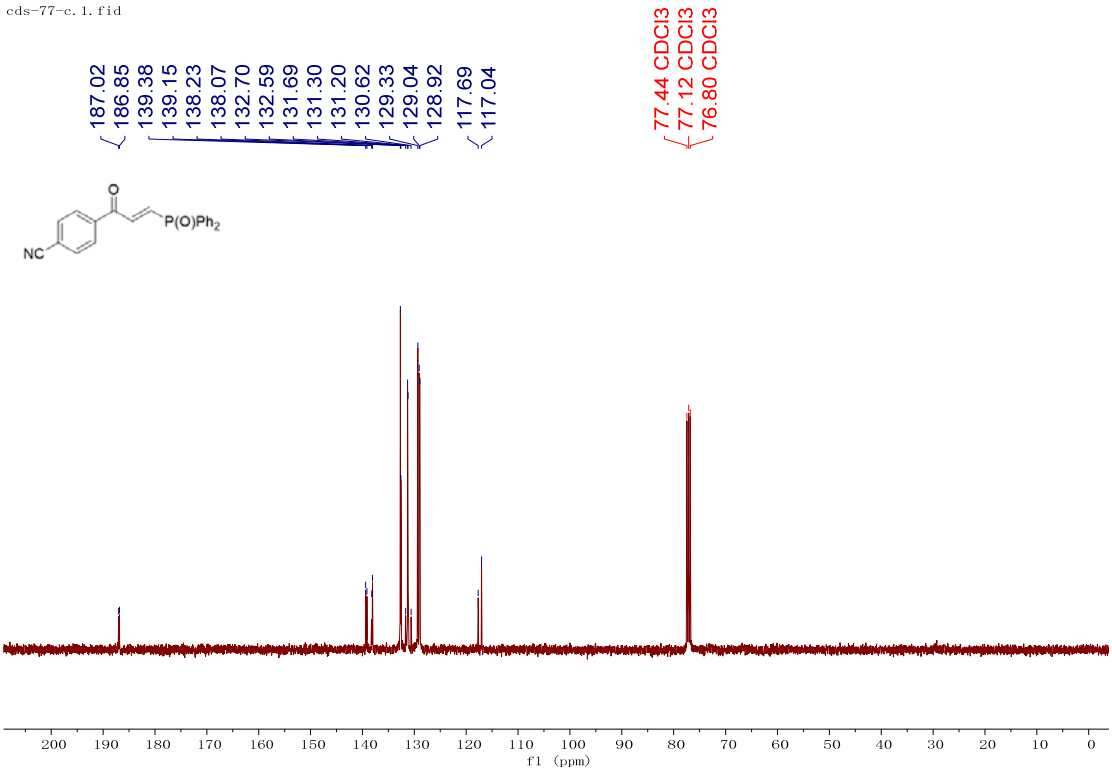
^{31}P NMR spectrum of **5h** (162 MHz, $CDCl_3$)



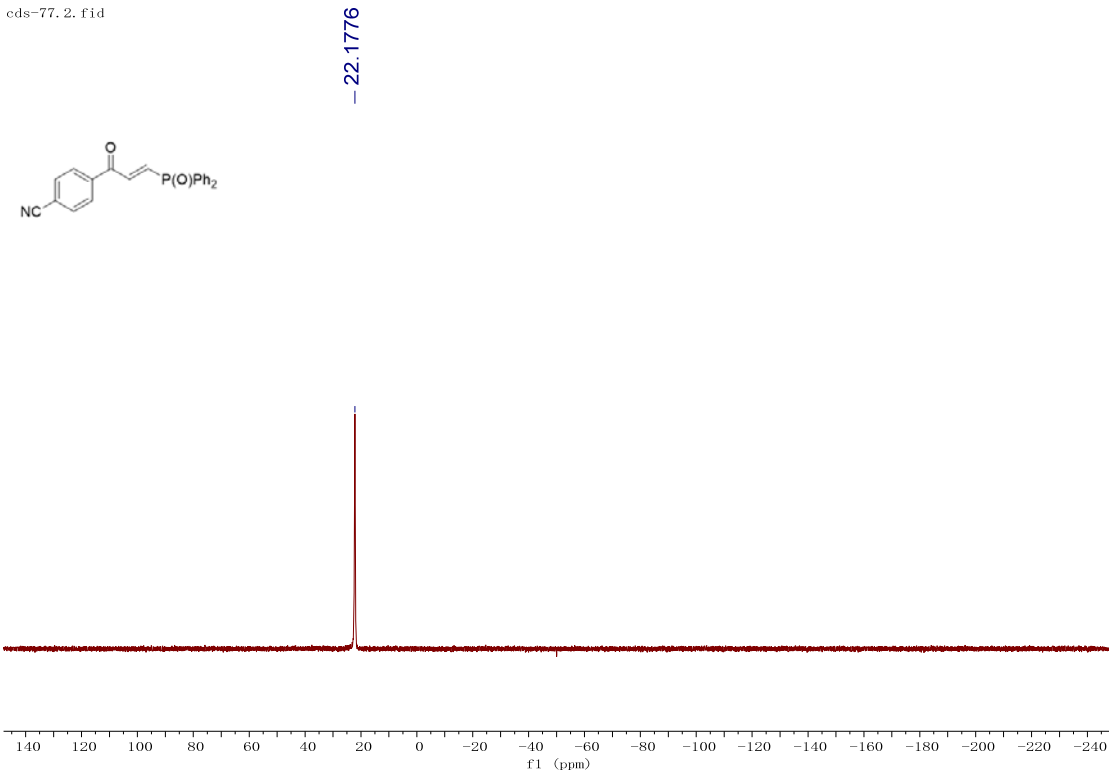
^{19}F NMR spectrum of **5h** (376 MHz, $CDCl_3$)



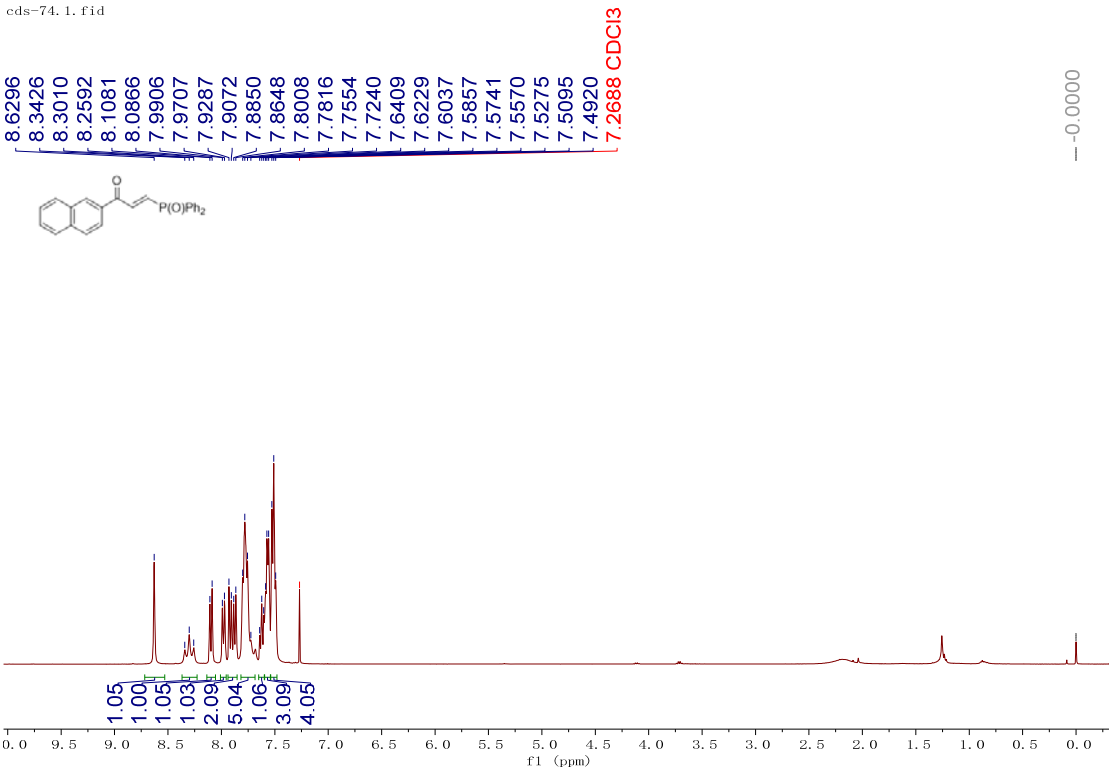
^{1}H NMR spectrum of **5i** (400 MHz, $CDCl_3$)



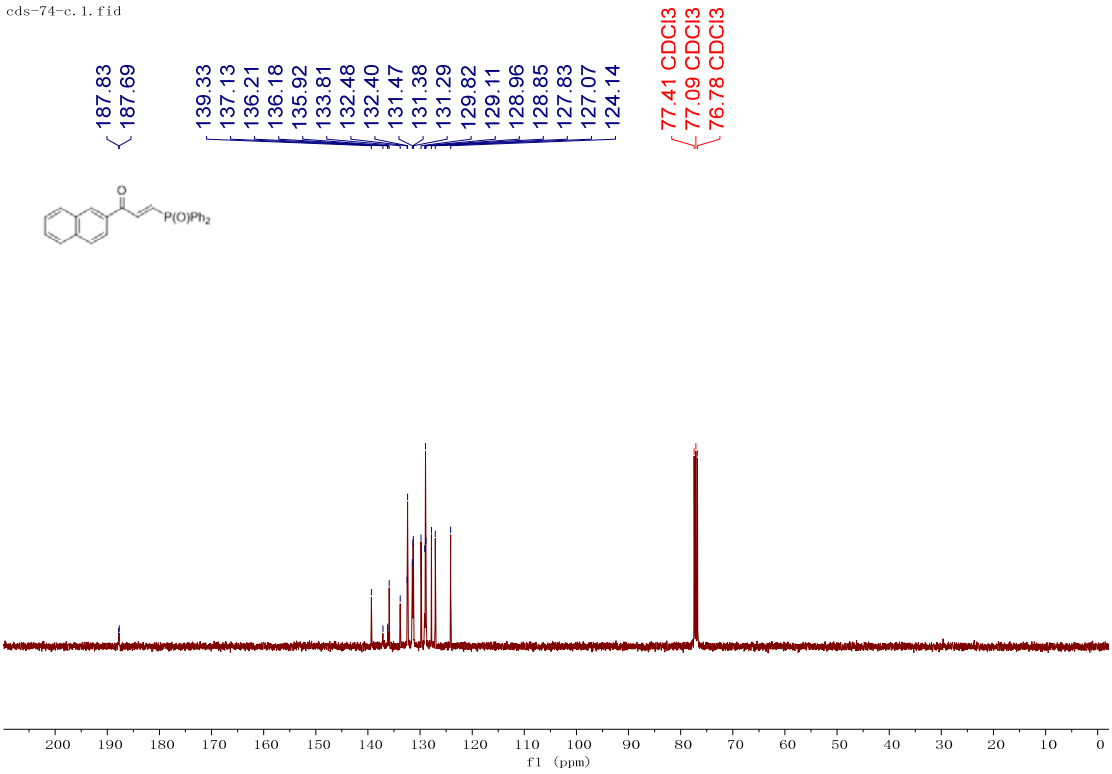
^{13}C NMR spectrum of **5i** (100 MHz, $CDCl_3$)



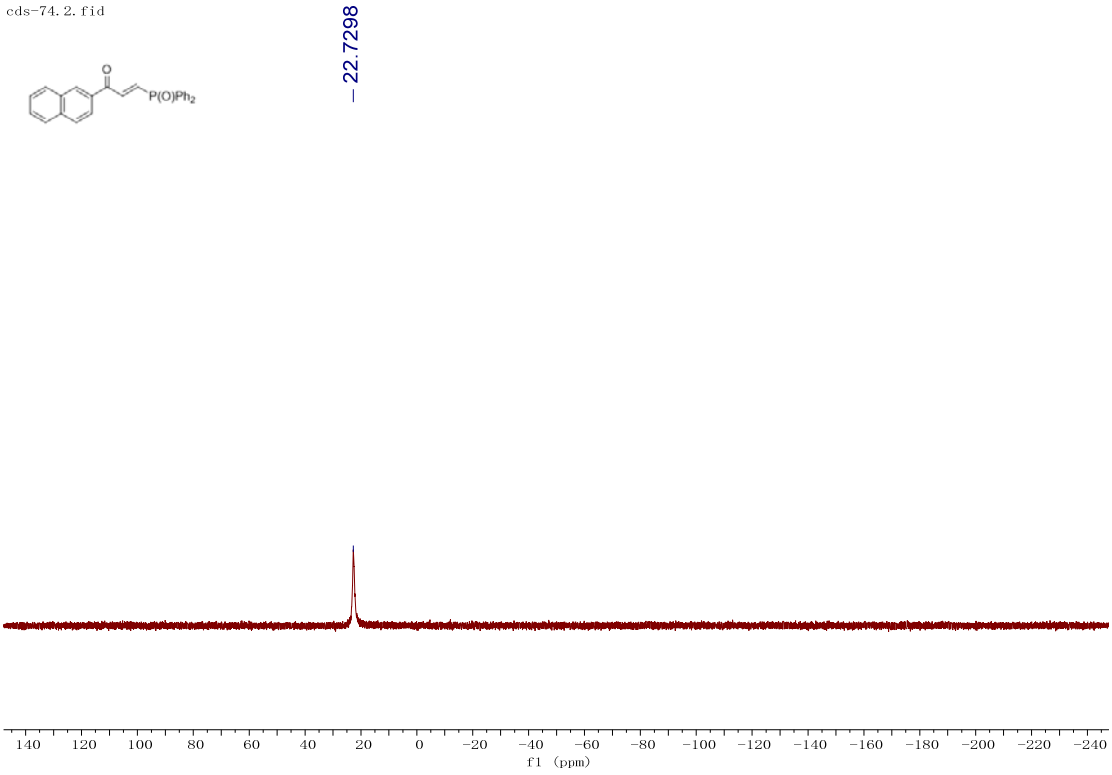
^{31}P NMR spectrum of **5i** (162 MHz, $CDCl_3$)



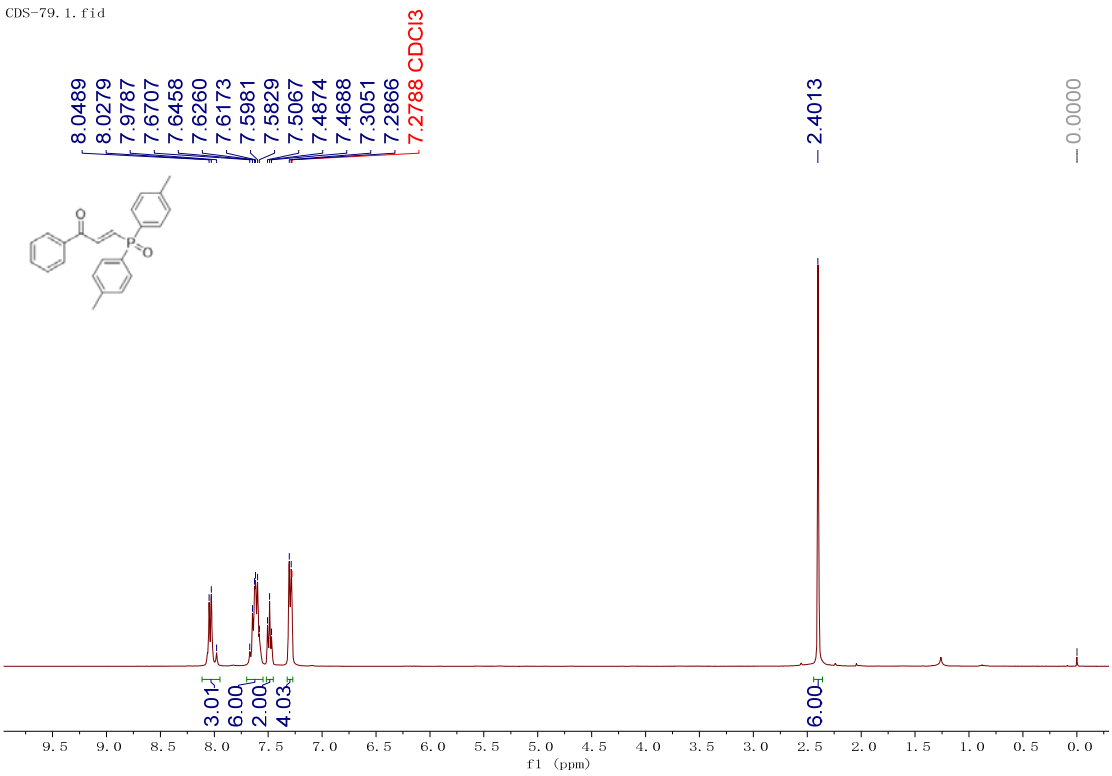
^{1}H NMR spectrum of **5j** (400 MHz, $CDCl_3$)



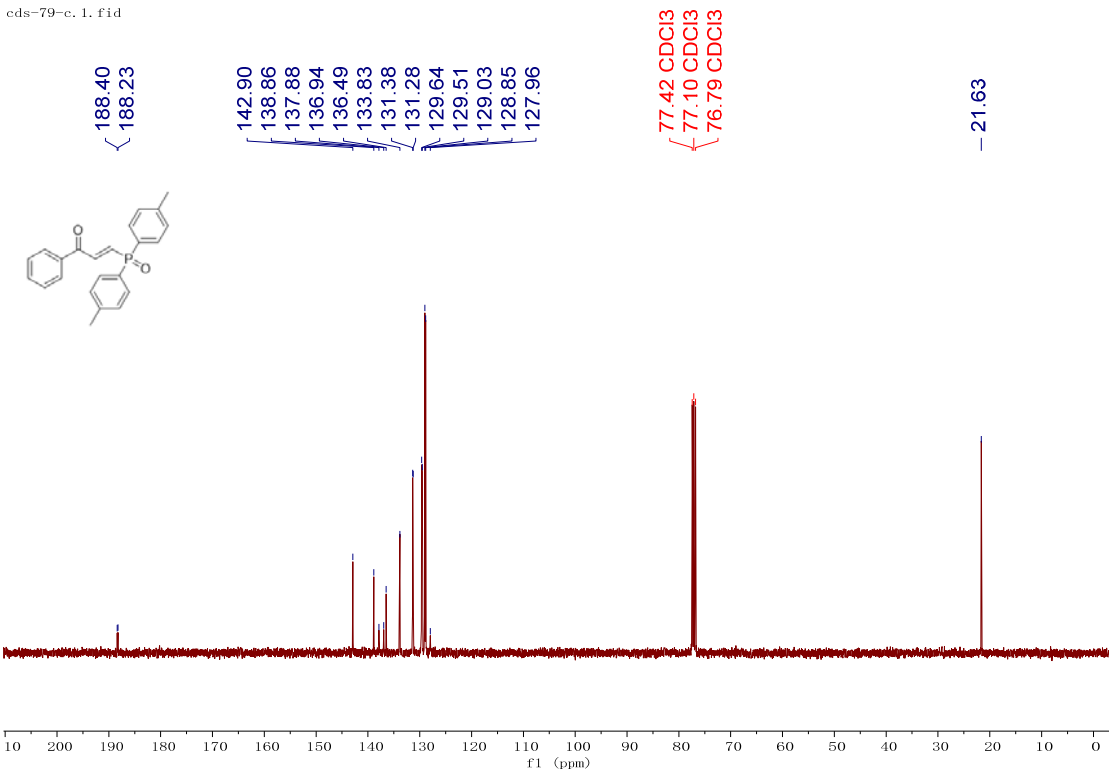
^{13}C NMR spectrum of **5j** (100 MHz, $CDCl_3$)



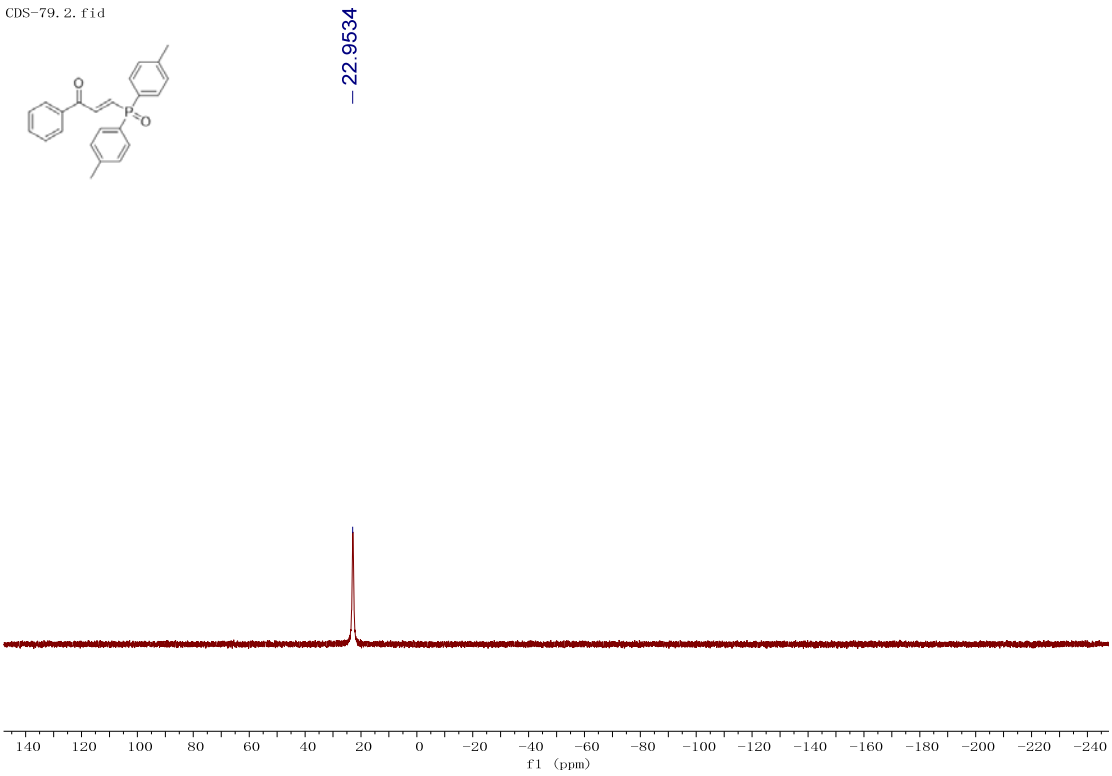
^{31}P NMR spectrum of **5j** (162 MHz, $CDCl_3$)



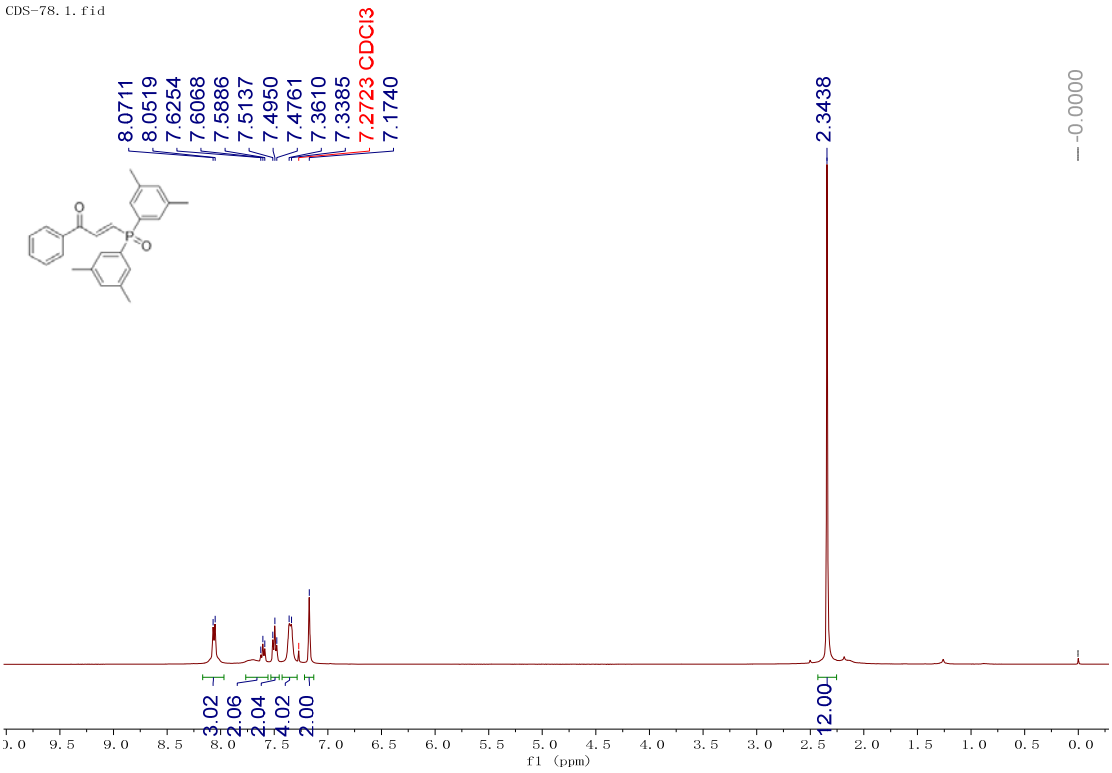
^{1}H NMR spectrum of **5k** (400 MHz, $CDCl_3$)



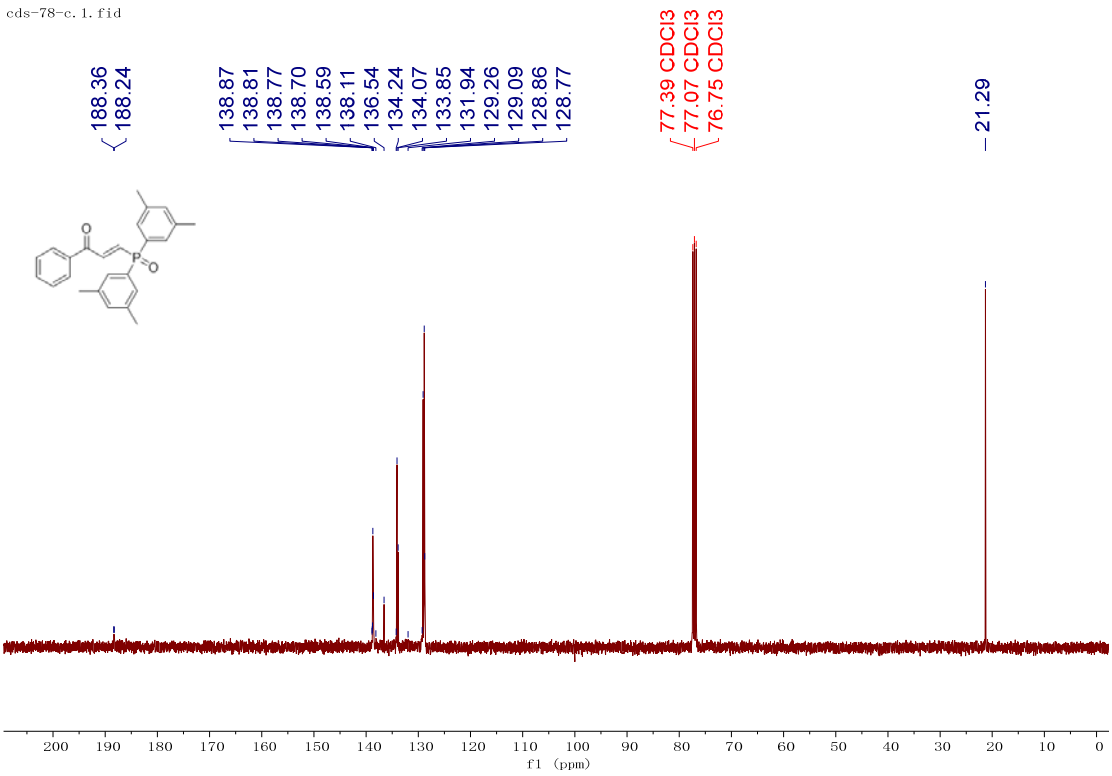
^{13}C NMR spectrum of **5k** (100 MHz, $CDCl_3$)



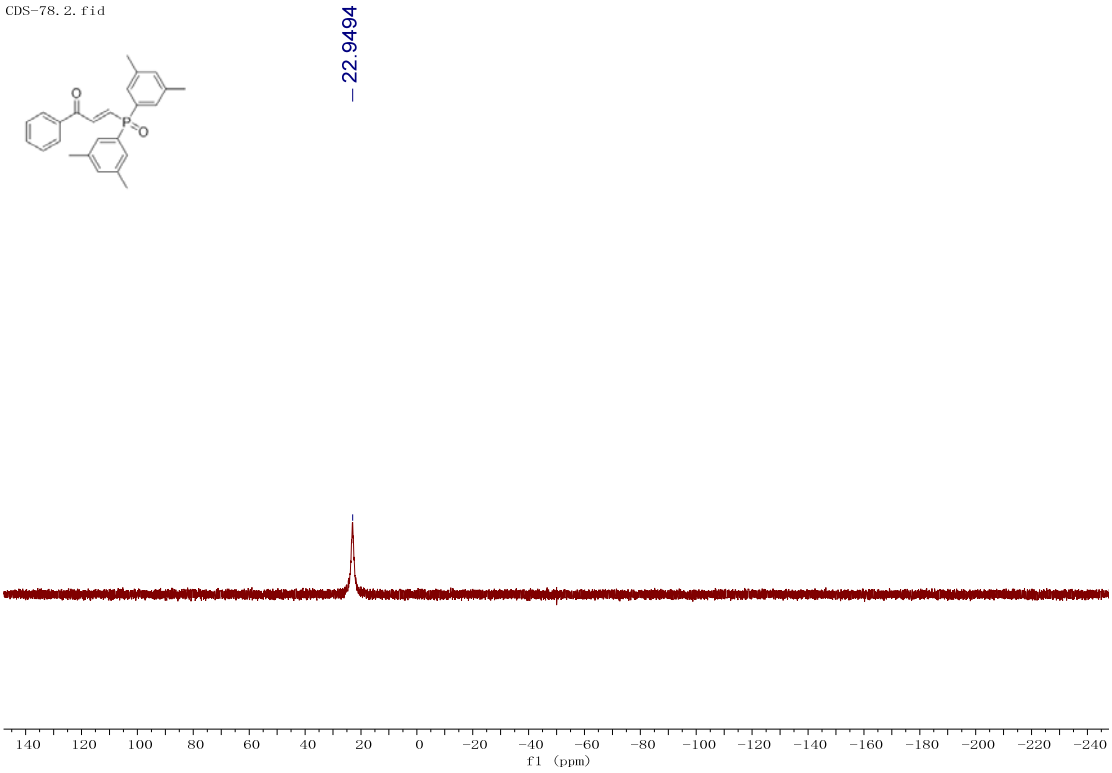
^{31}P NMR spectrum of **5k** (162 MHz, $CDCl_3$)



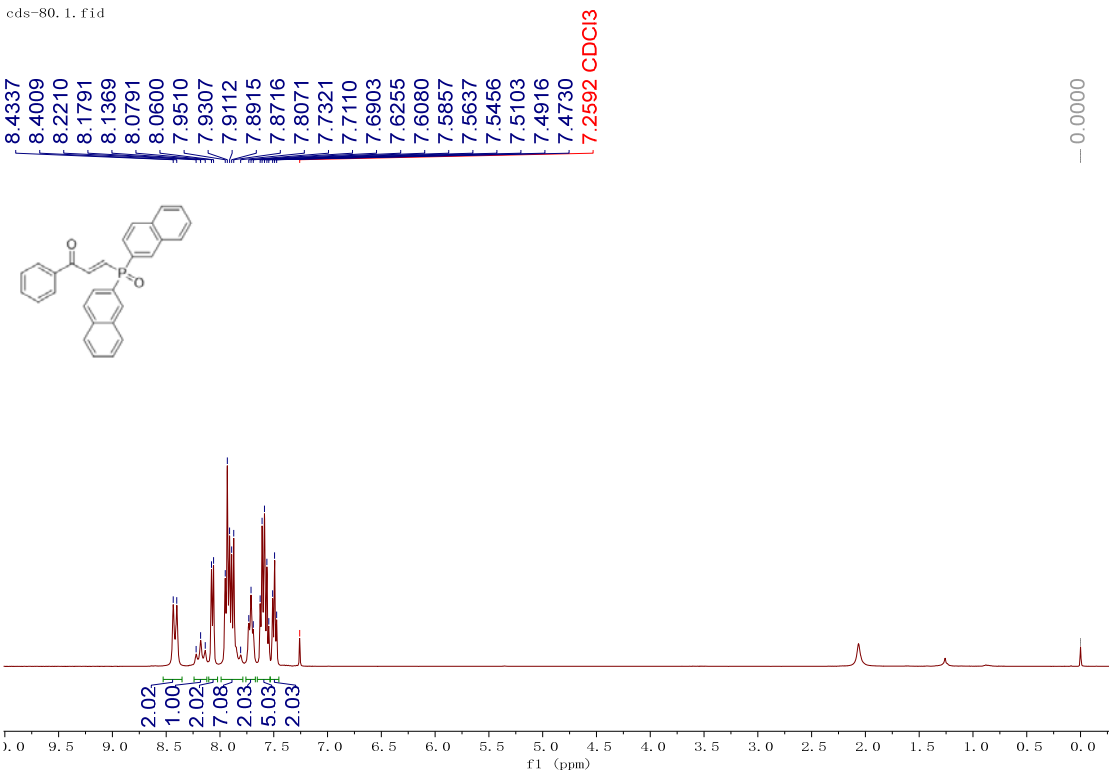
^{1}H NMR spectrum of **5l** (400 MHz, $CDCl_3$)



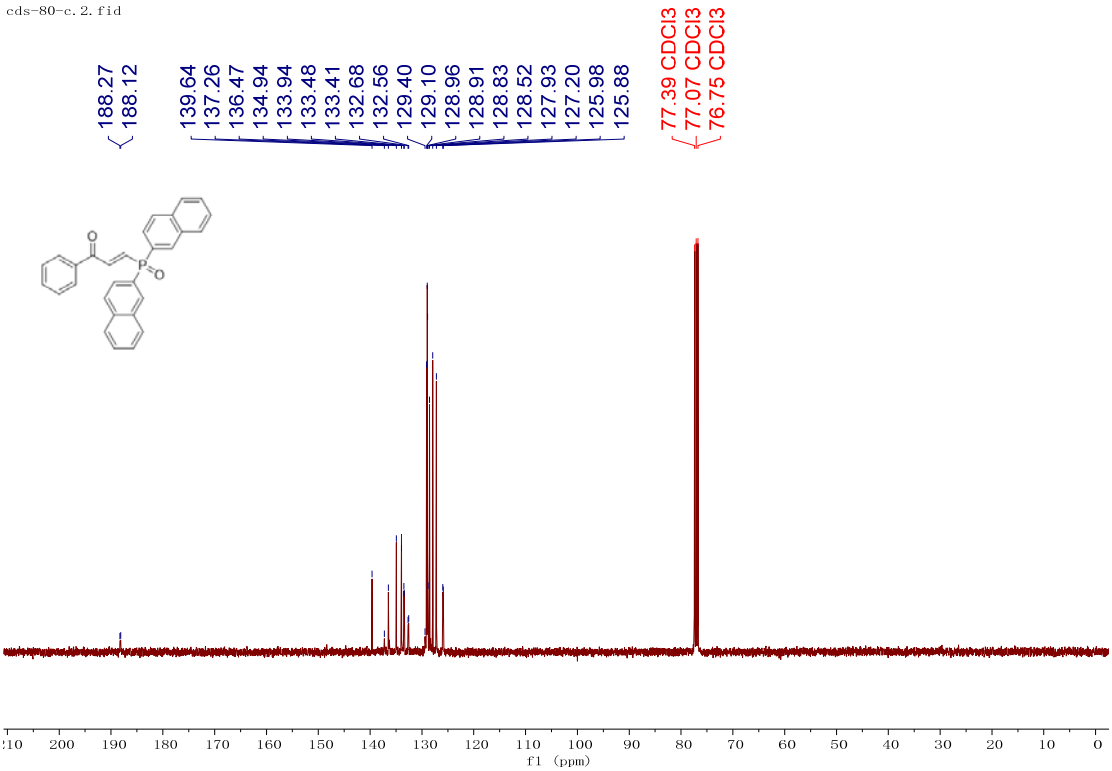
^{13}C NMR spectrum of **5l** (100 MHz, $CDCl_3$)



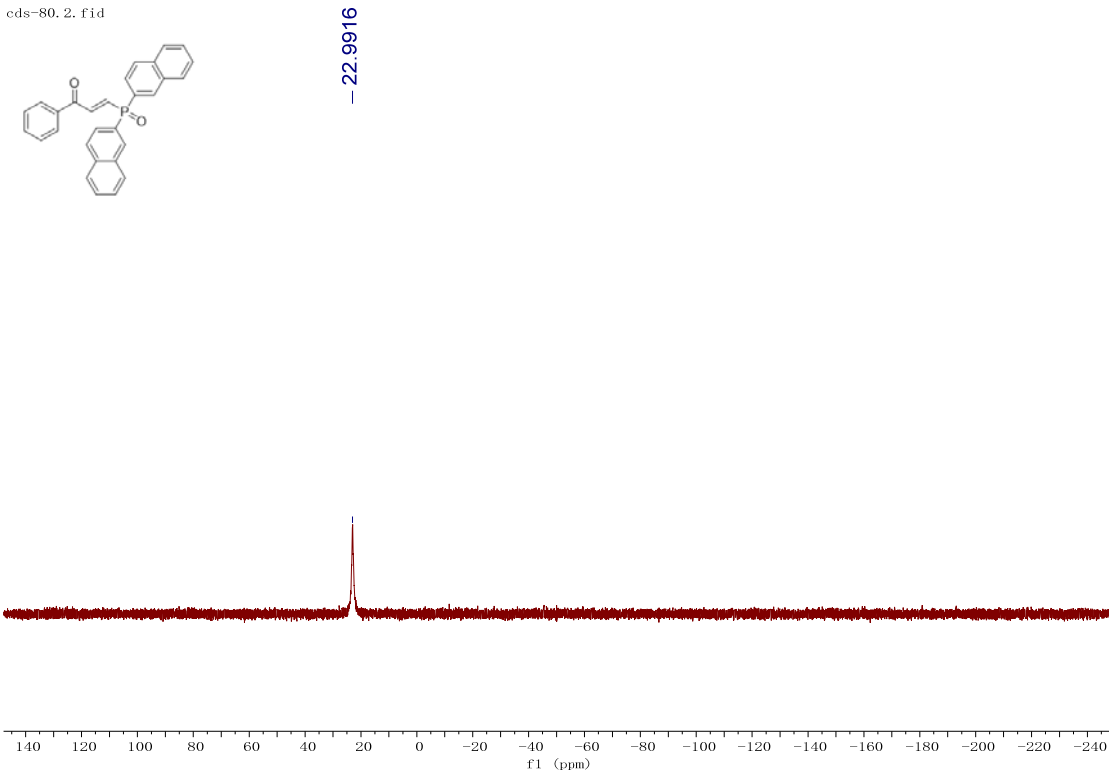
^{31}P NMR spectrum of **5l** (162 MHz, $CDCl_3$)



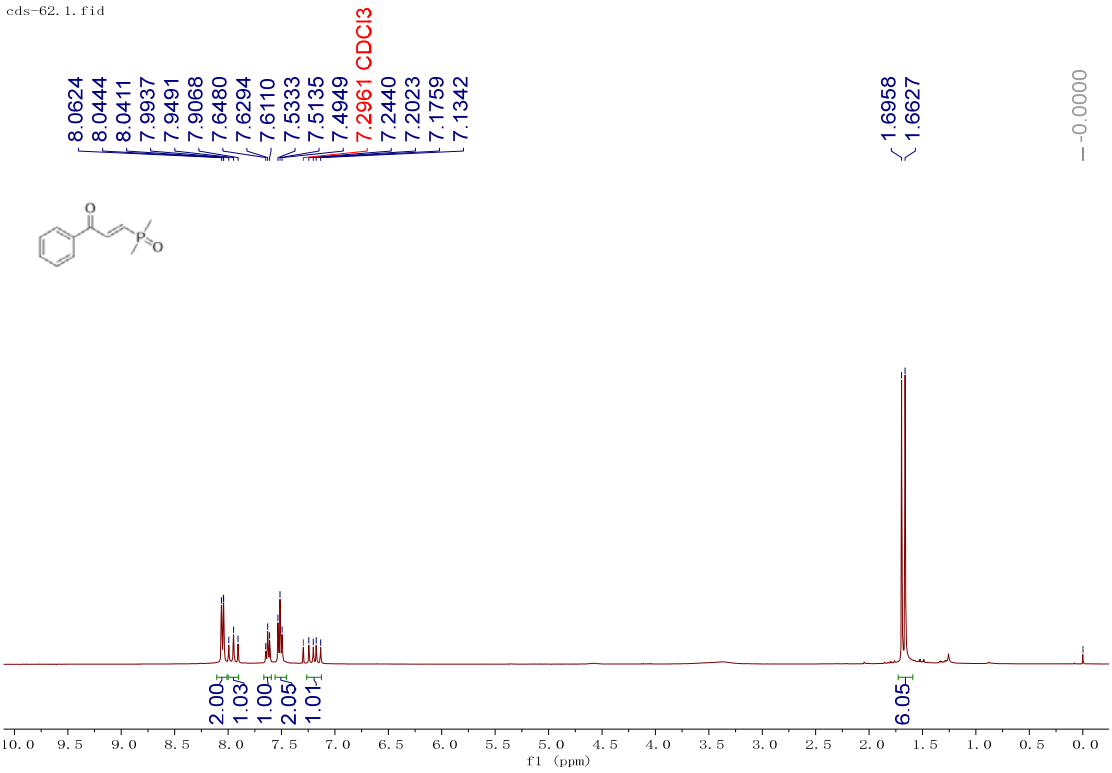
^{1}H NMR spectrum of **5m** (400 MHz, $CDCl_3$)



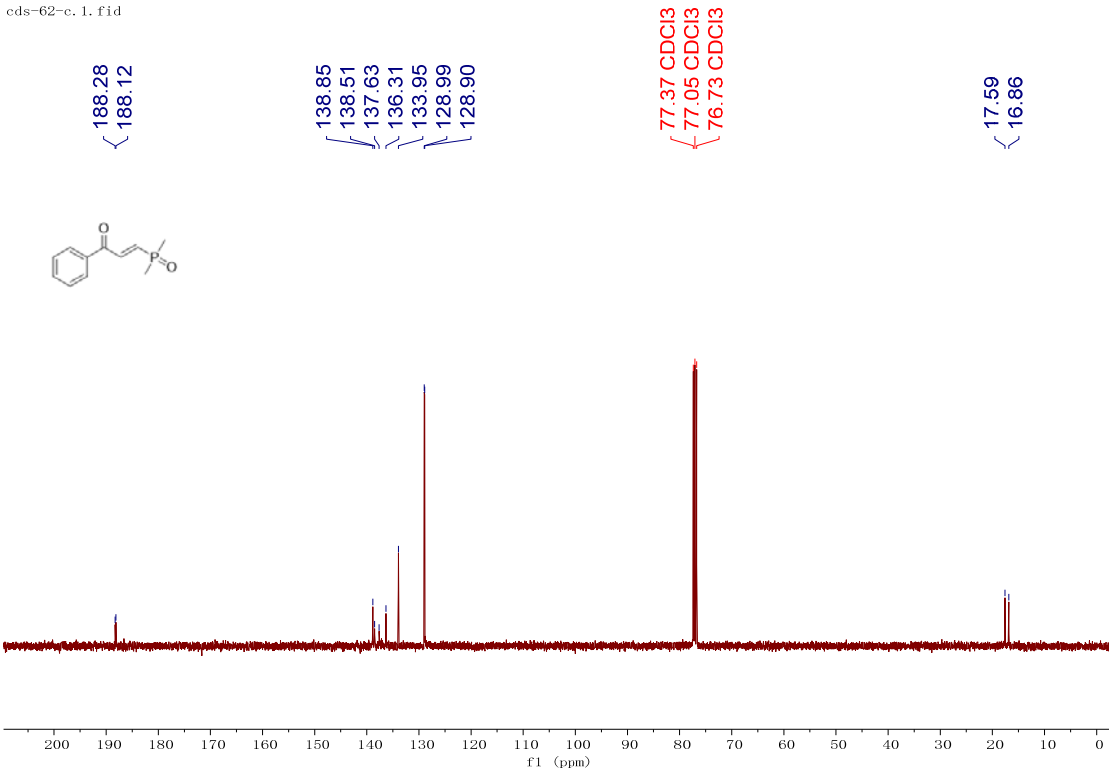
^{13}C NMR spectrum of **5m** (100 MHz, $CDCl_3$)



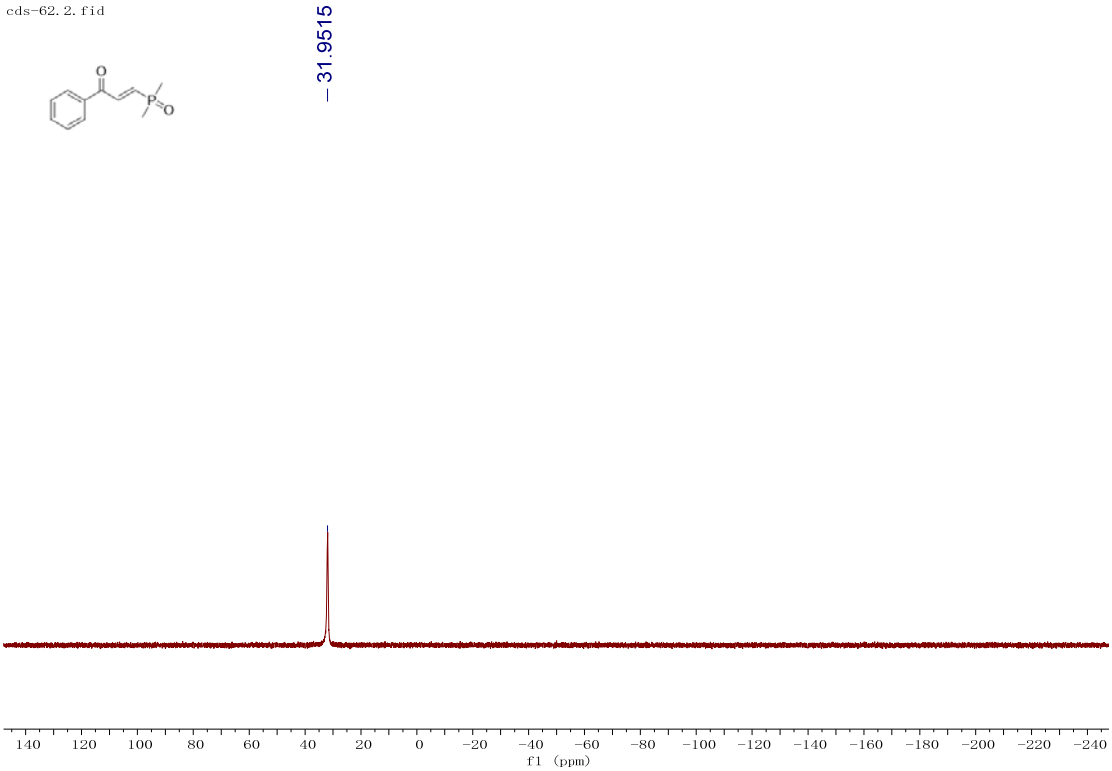
^{31}P NMR spectrum of **5m** (162 MHz, $CDCl_3$)



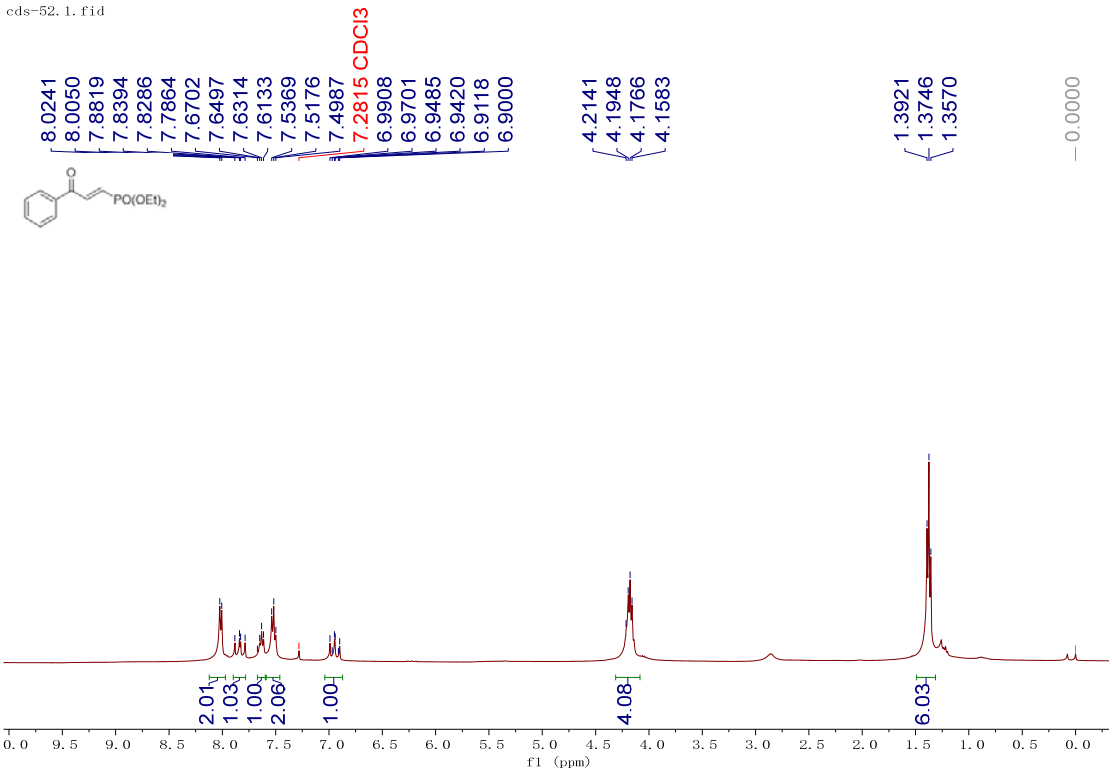
^{1}H NMR spectrum of **5n** (400 MHz, $CDCl_3$)



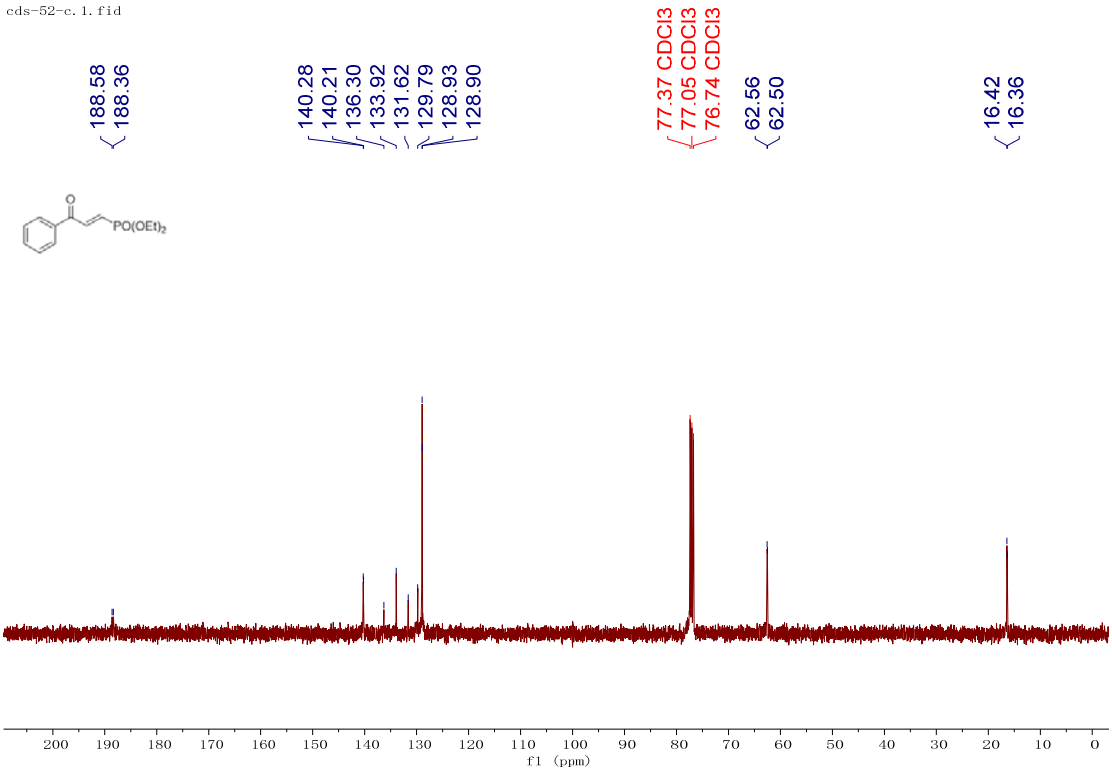
^{13}C NMR spectrum of **5n** (100 MHz, $CDCl_3$)



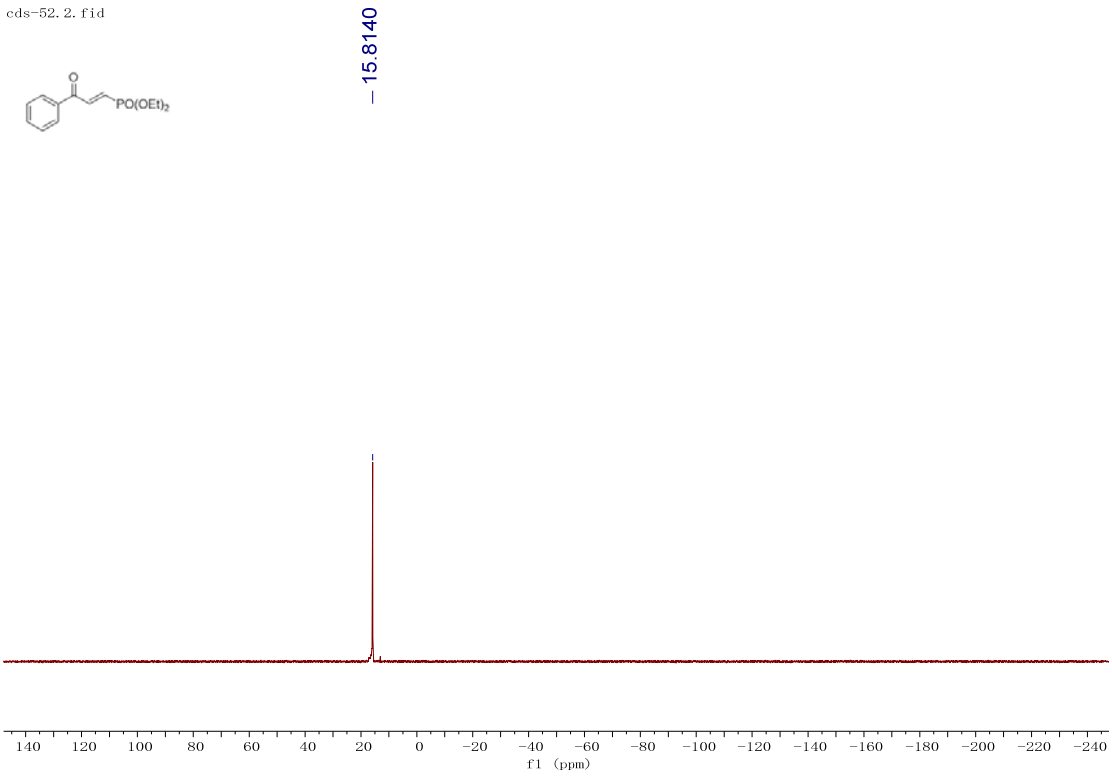
^{31}P NMR spectrum of **5n** (162 MHz, $CDCl_3$)



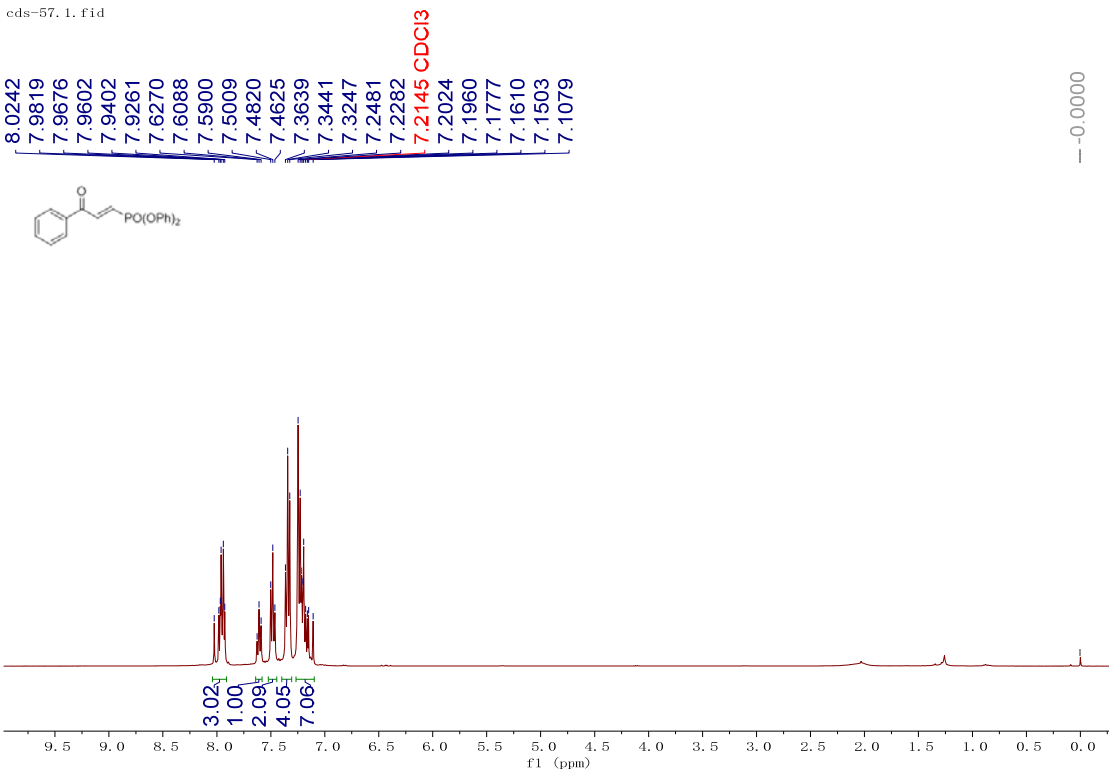
^{1}H NMR spectrum of **5o** (400 MHz, $CDCl_3$)



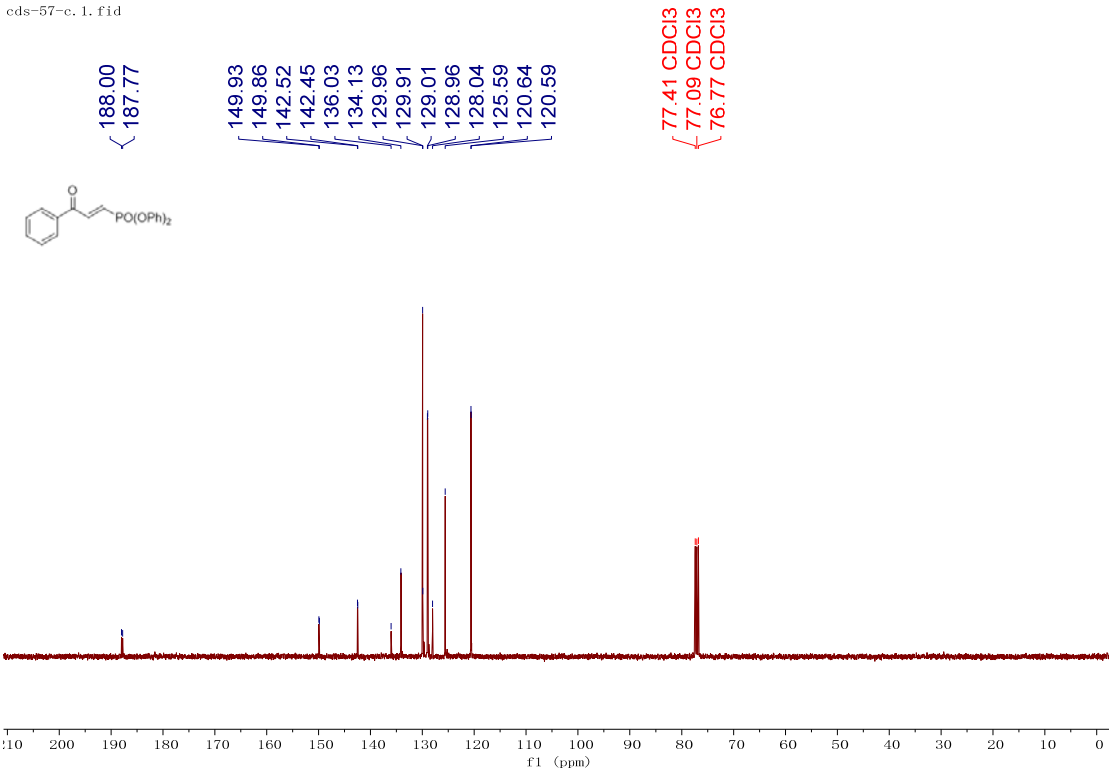
^{13}C NMR spectrum of **5o** (100 MHz, $CDCl_3$)



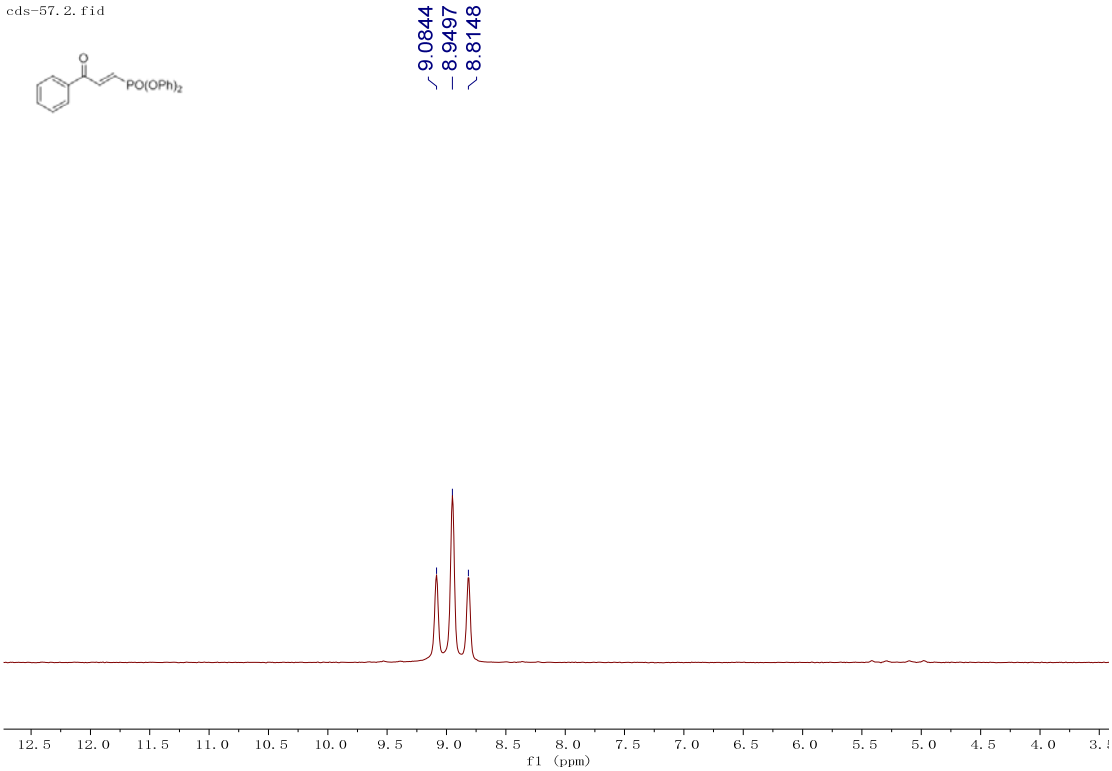
^{31}P NMR spectrum of **5o** (162 MHz, $CDCl_3$)



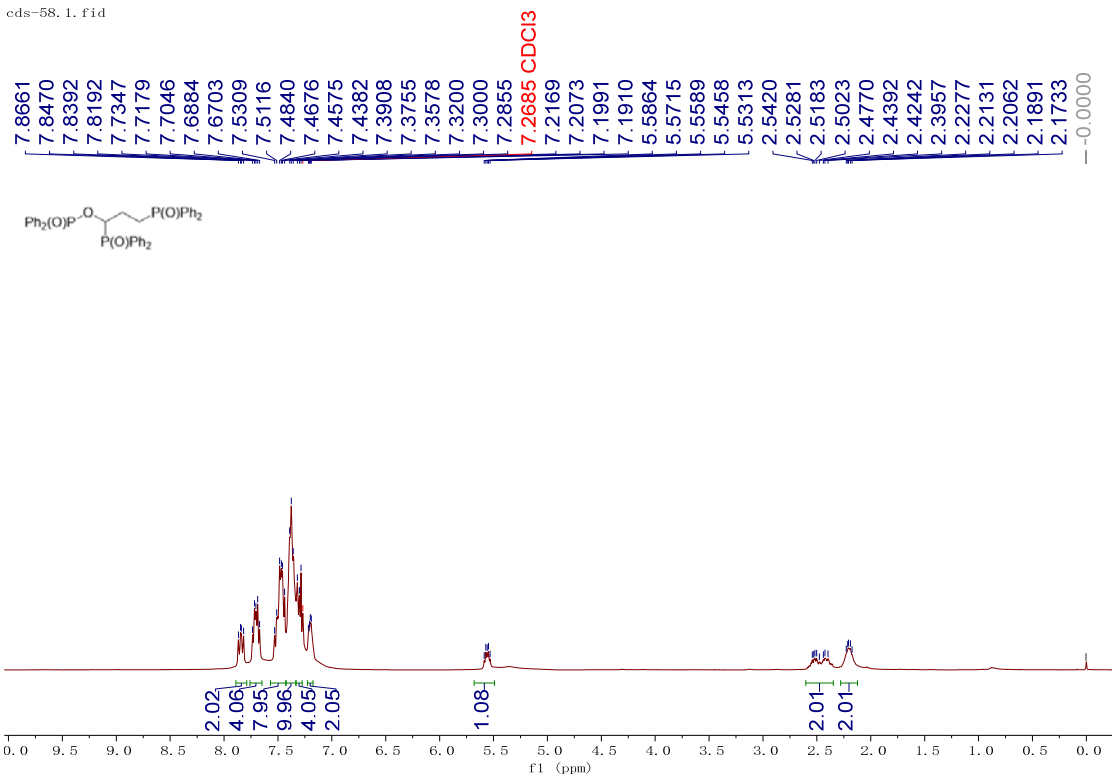
^{1}H NMR spectrum of **5p** (400 MHz, $CDCl_3$)



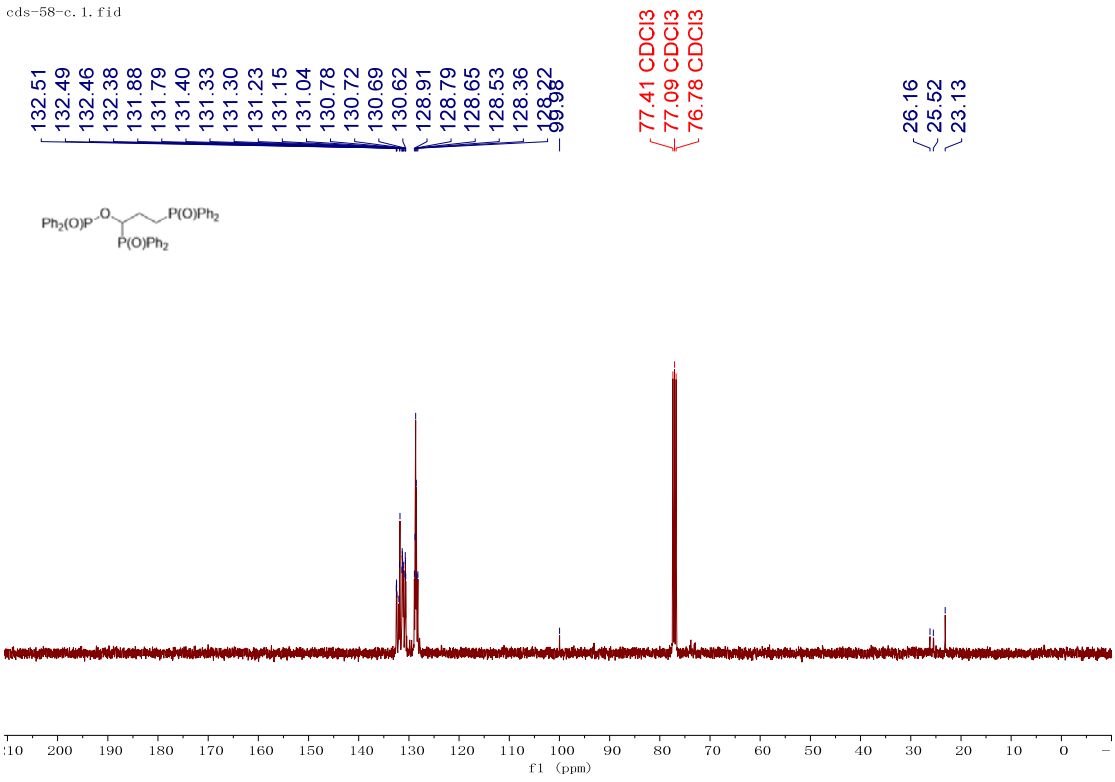
^{13}C NMR spectrum of **5p** (100 MHz, $CDCl_3$)



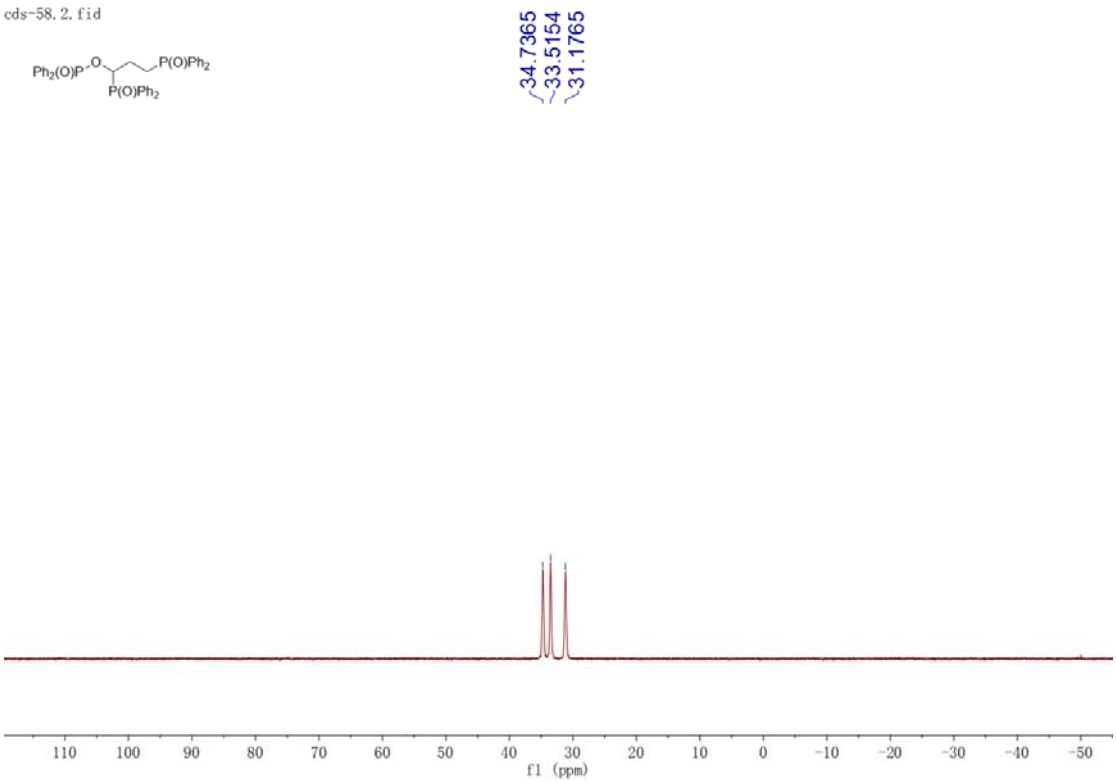
^{31}P NMR spectrum of **5p** (162 MHz, $CDCl_3$)



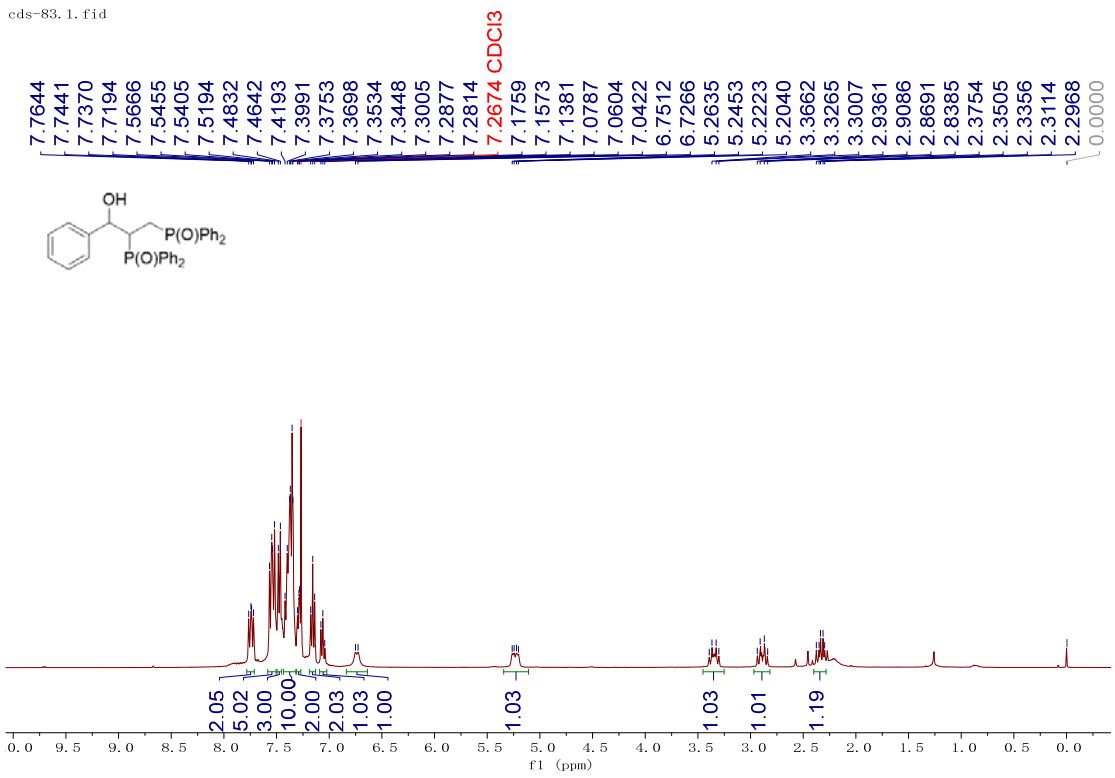
^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$)



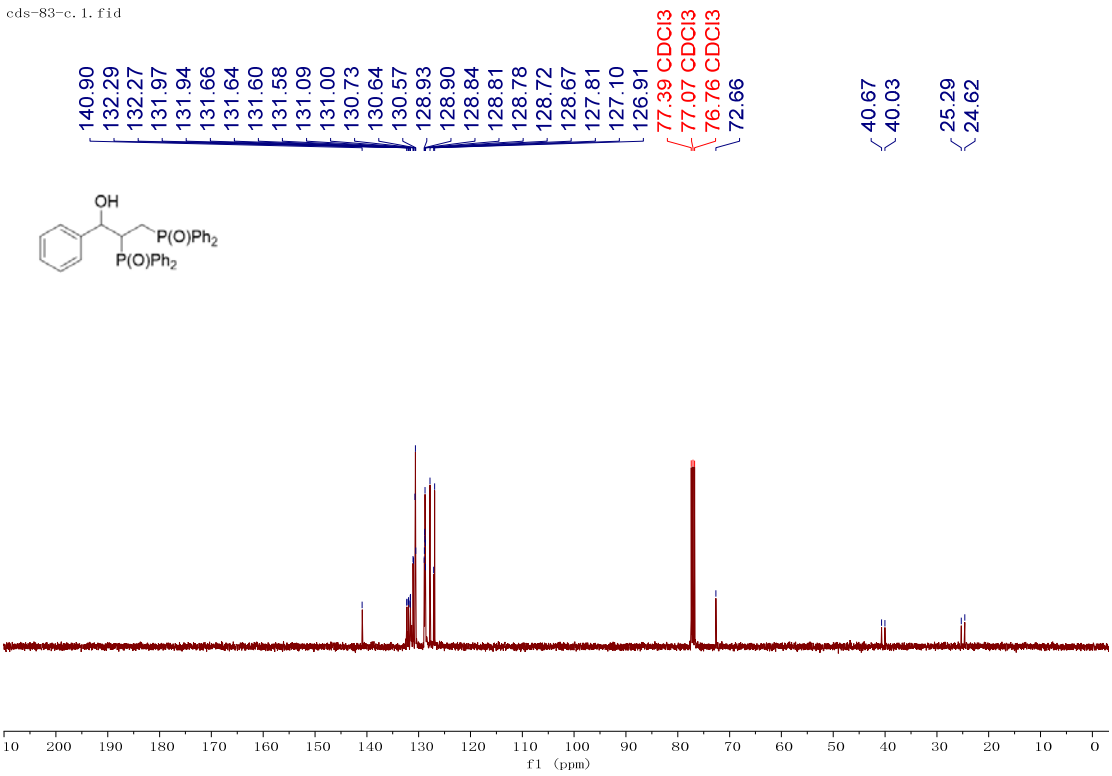
^{13}C NMR spectrum of **7** (100 MHz, $CDCl_3$)



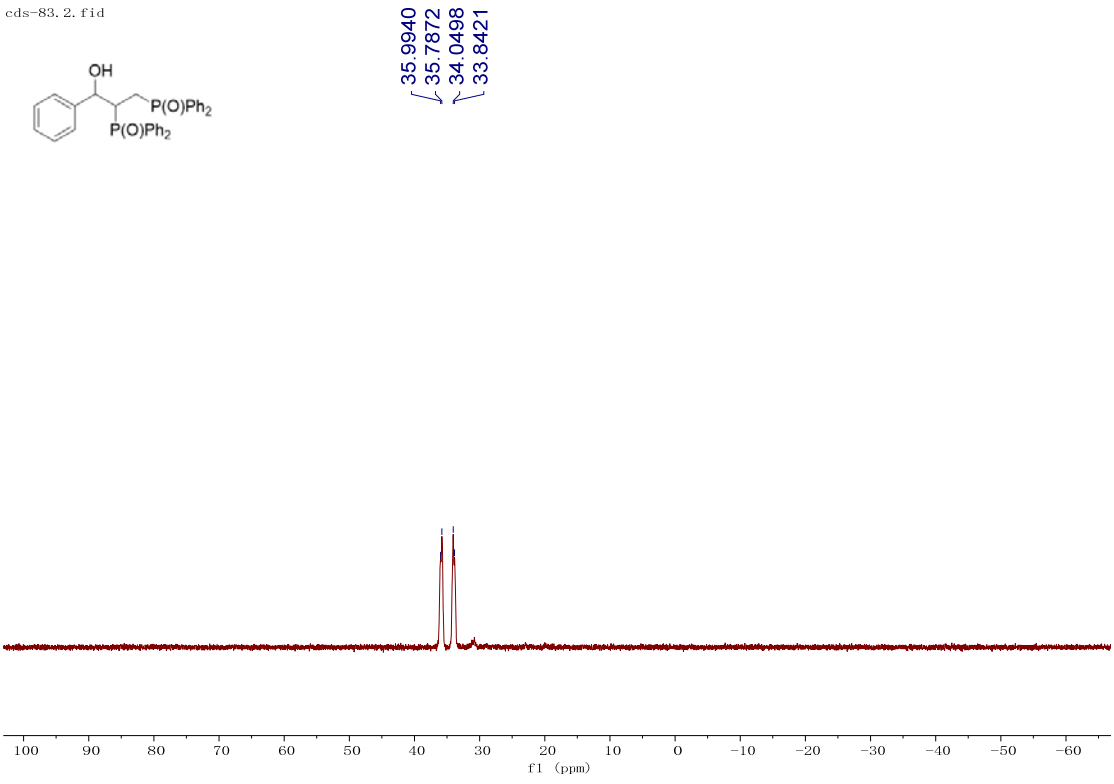
^{31}P NMR spectrum of **7** (162 MHz, $CDCl_3$)



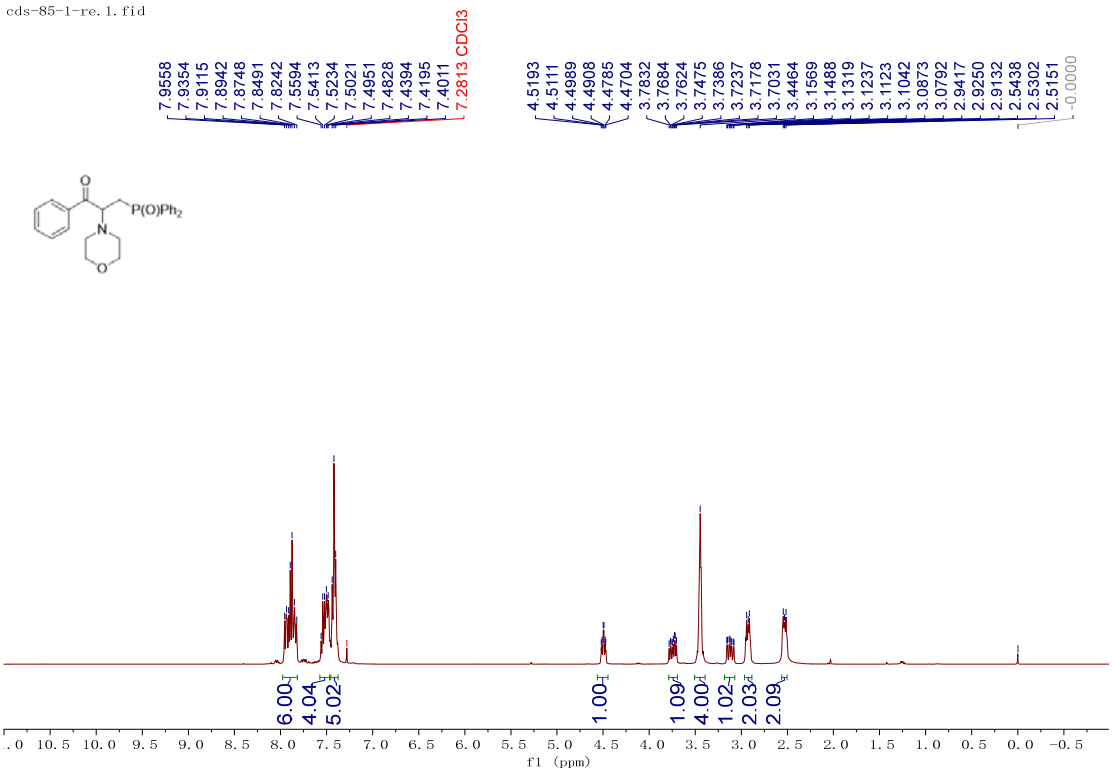
^{1}H NMR spectrum of **8** (400 MHz, $CDCl_3$)



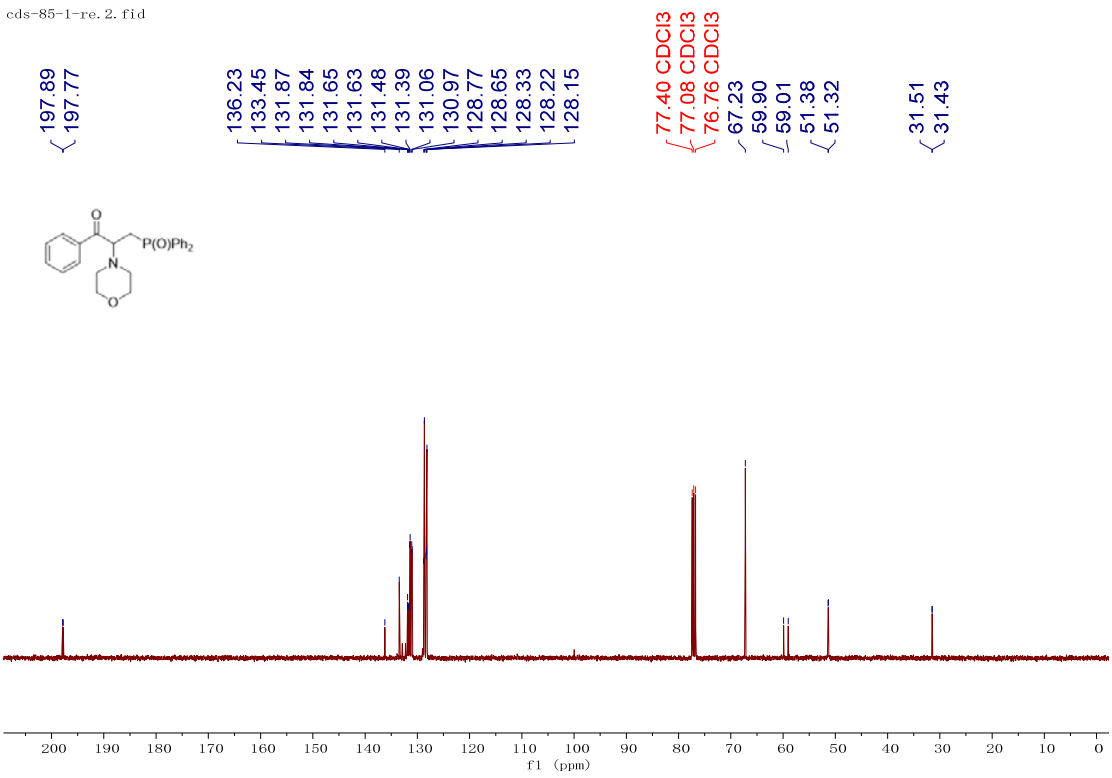
^{13}C NMR spectrum of **8** (100 MHz, $CDCl_3$)



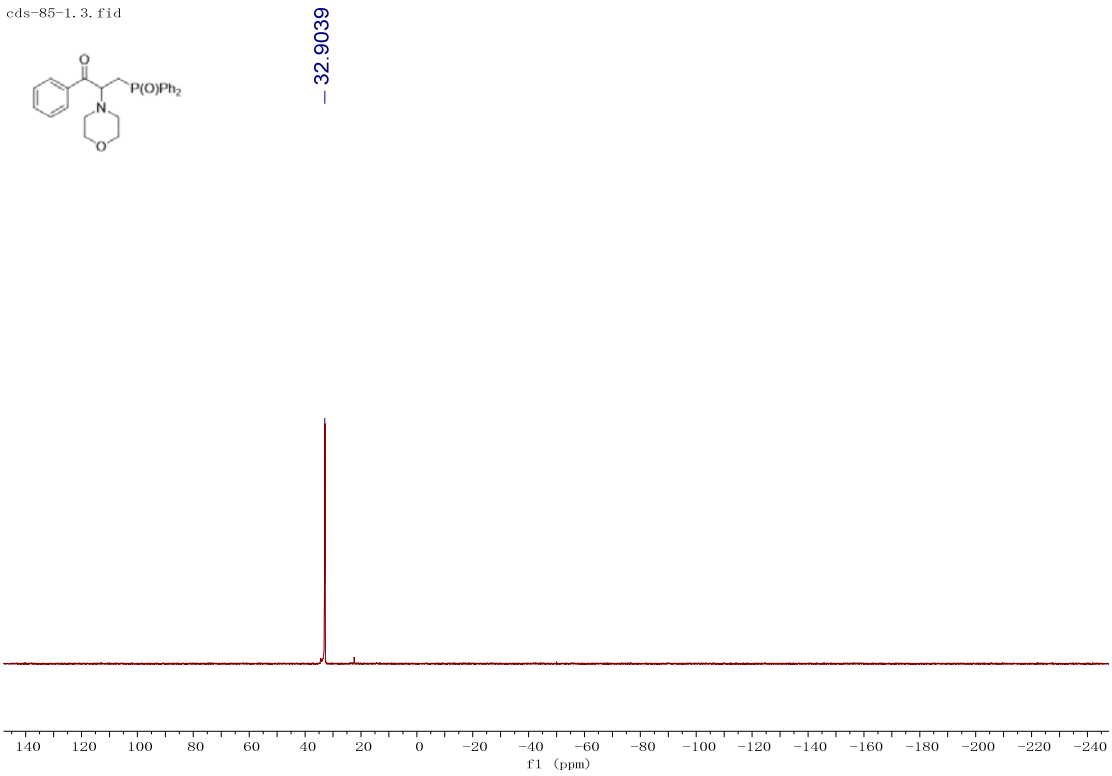
^{31}P NMR spectrum of **8** (162 MHz, $CDCl_3$)



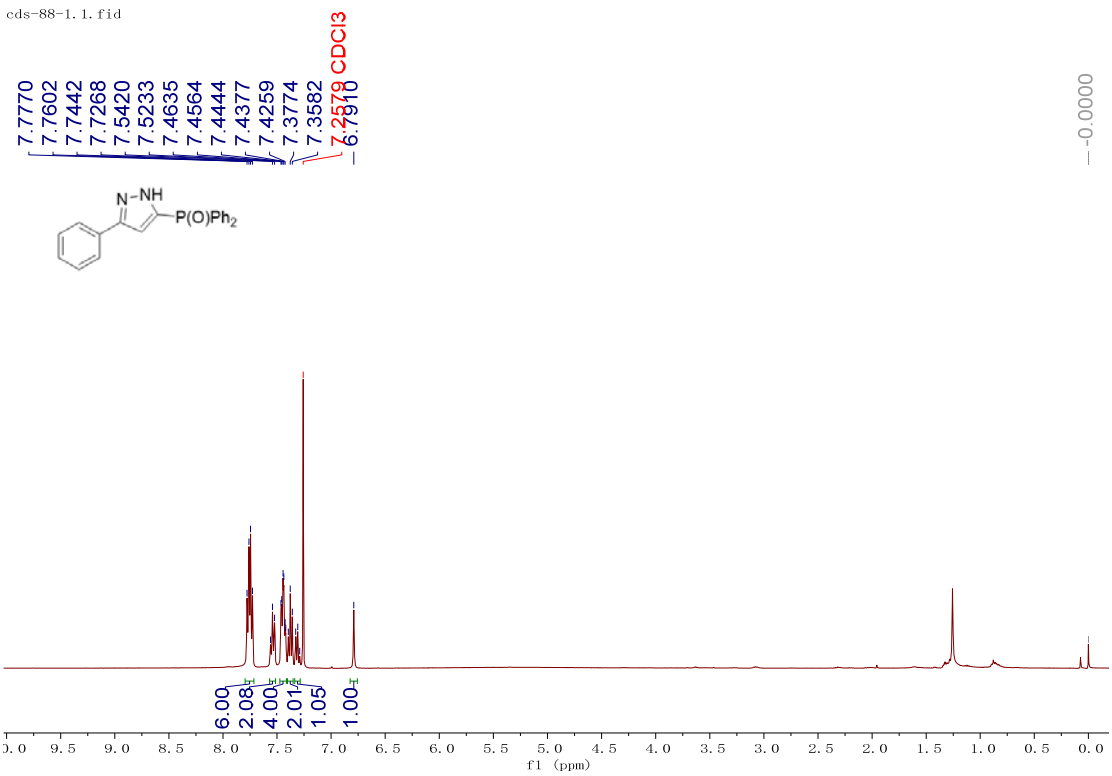
^{1}H NMR spectrum of **10** (400 MHz, $CDCl_3$)



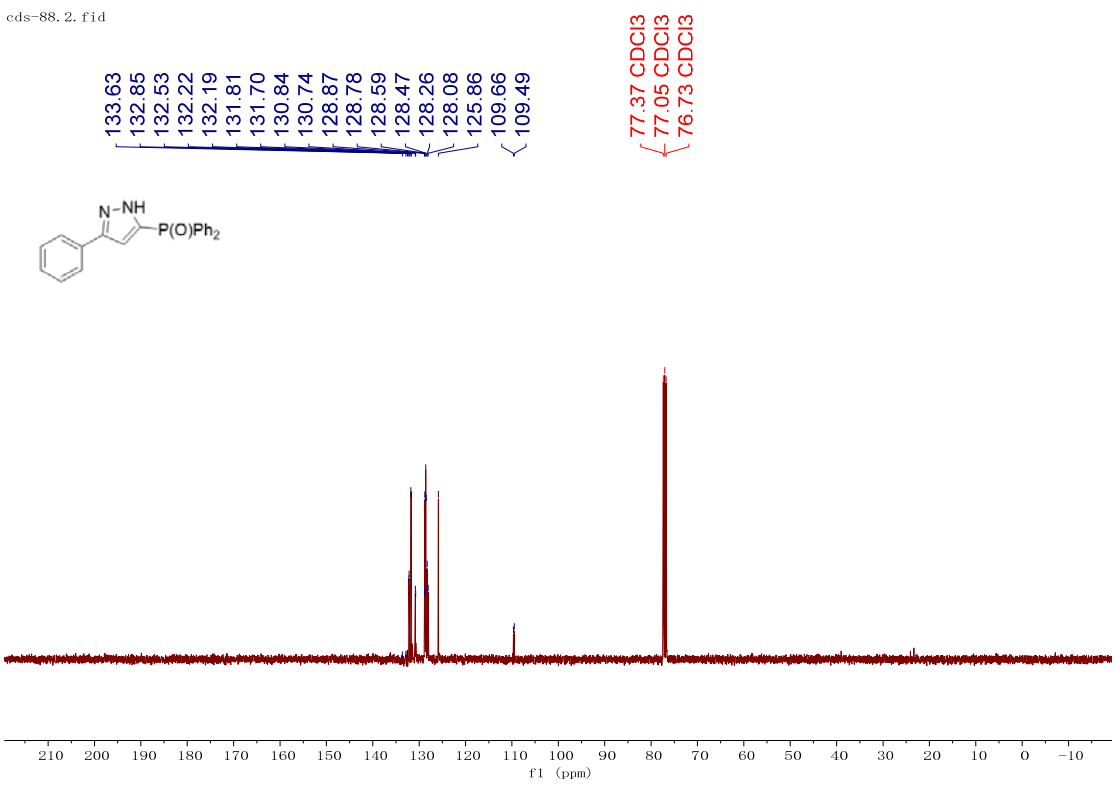
^{13}C NMR spectrum of **10** (100 MHz, $CDCl_3$)



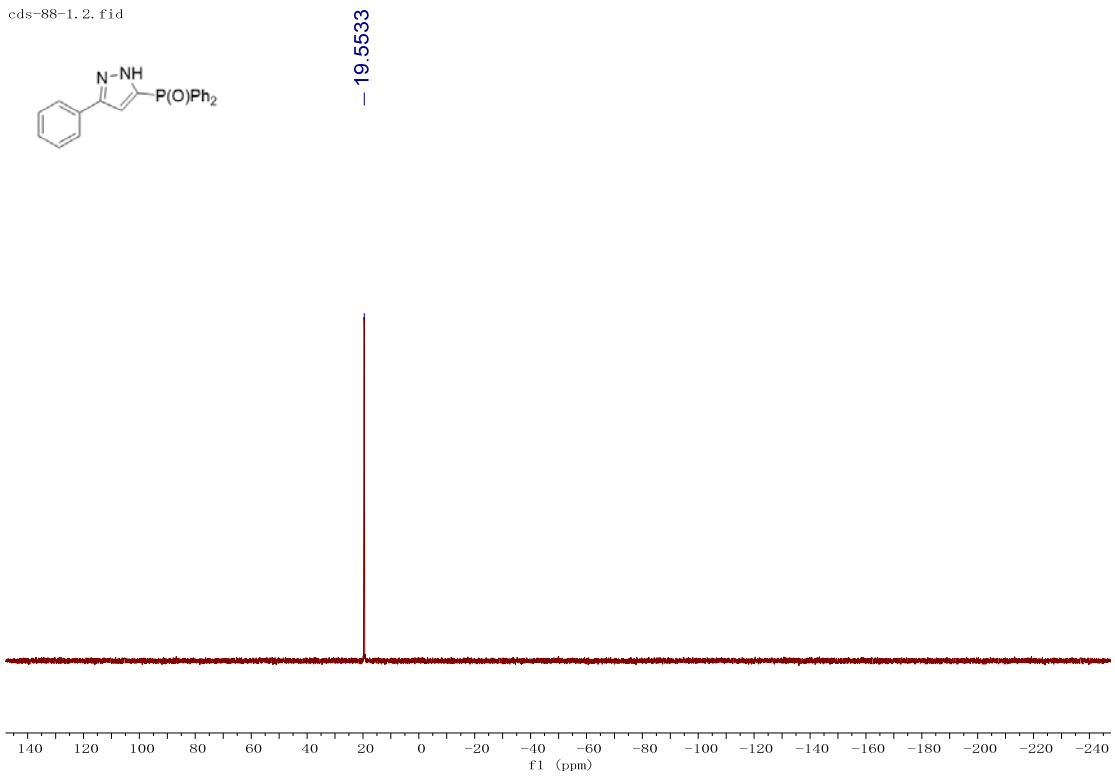
^{31}P NMR spectrum of **10** (162 MHz, $CDCl_3$)



^{1}H NMR spectrum of **12** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **12** (100 MHz, $CDCl_3$)



^{31}P NMR spectrum of **12** (162 MHz, $CDCl_3$)