Electronic Supplementary Information

Catalyst-Controlled Switchable Phosphination of α-Diazoesters

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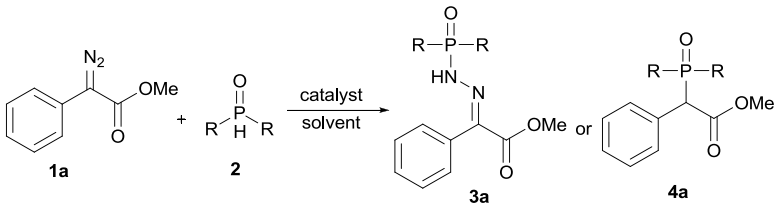
General Information

All reagents were obtained from commercial suppliers and used without further purification except as indicated below. Solvents were dried and distilled prior to use according to the standard method. For thin-layer chromatography (TLC), compounds were visualized by irradiation with UV light on GF 254 silica gel plates. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at Bruker ARX-300 MHz spectrometer with chemical shifts referenced to $SiMe_4$ as internal standard. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constant (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = double, t = triplet, dd = double doublet, tt = triple triplet, q = quartet, m = multiplet, b = broad. HRMS were recorded on an Agilent 6210 TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode.

Table 1: Optimization of reaction conditions.[a]



Entry	Cat(mol%)	Solvent	R	Yield[%] [c]
1	K_2CO_3/CuBr [b]	DMF	OMe	**3a**/20
2	K_2CO_3(20)	DMF	OMe	**3a**/20
3	-	DMF	OMe	**3a**/0
4	Li_2CO_3(20)	DMF	OMe	**3a**/trace
5	KOBu^t(20)	DMF	OMe	**3a**/trace
6	DBU(20)	DMF	OMe	**3a**/55
7	DMAP(20)	DMF	OMe	**3a**/0
8	DABCO(20)	DMF	OMe	**3a**/0
9	DMEDA(20)	DMF	OMe	**3a**/0
10	Hexamethylenetetramine	DMF	OMf	**3a**/0
11	**DBU**(20)	**CH_3CN**	**OMe**	**3a/66**
12	DBU(20)	$MeNO_2$	OMe	**3a**/trace
13	DBU(20)	DMSO	OMe	**3a**/45
14	DBU(20)	THF	OMe	**3a**/24
15	DBU(20)	EtOAc	OMe	**3a**/26
16	DBU(20)	Hexane	OMe	**3a**/43
17	CuBr(5)	CH_2Cl_2	OMe	**4a**/0
18	CuBr(5)	CH_2Cl_2	OEt	**4a**/0
19	CuBr(5)	CH_2Cl_2	O*i*Pr	**4a**/0
20	CuBr(5)	CH_2Cl_2	OPh	**4a**/45
21	**CuBr**(5)	**$ClCH_2CH_2Cl$**	**OPh**	**4a/87**
22	CuBr(5)	toluene	OPh	**4a**/12
23	CuBr(5)	hexane	OPh	**4a**/0
24	CuCl(5)	$ClCH_2CH_2Cl$	OPh	**4a**/58
25	CuI(5)	$ClCH_2CH_2Cl$	OPh	**4a**/61
26	CuOTf(5)	$ClCH_2CH_2Cl$	OPh	**4a**/68

[a] mixture of **1a** (0.5 mmol), **2** (0.55 mmol) and catalyst in solvent (2 mL) was stirred at room temperature for 48 h (**3a**), 12h (**4a**). [b] K_2CO_3 (20 mol%) and CuBr (5 mol%). [c] Yield of isolated products.

General procedure A for the N−P bond formation:

A 10 mL reaction tube was charged with α–Diazoacetates (0.5mmol) in the dry acetonitrile under air. Next, phosphorous compounds (0.55mmol) and DBU (0.1

mmol, 20 mol%) were added. The tube was then sealed and the resulting mixture was stirred at room temperature. After the indicated time the crude products were purified by silica gel chromatography to yield the desired product **3**. It should be noted that the silica gel should be treated with NEt_3.

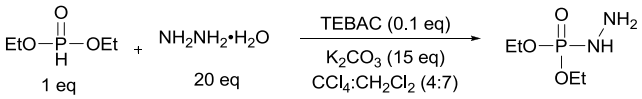
General procedure B for the C−P bond formation:

A solution of α-Diazoacetates (0.5 mmol), phosphorous compounds (0.55mmol), and CuBr (0.025 mmol, 5 mol%) in dry $ClCH_2CH_2Cl$(2.0 mL) was stirred at room temperature under argon for 12h in a reaction tube. After the reaction, the mixture was concentrated in vacuo. The residue was purified by columnchromatography (silica gel, petroleum ether/EtOAc) to afford the corresponding products **4**.

The other procedure for the synthesis of products 3

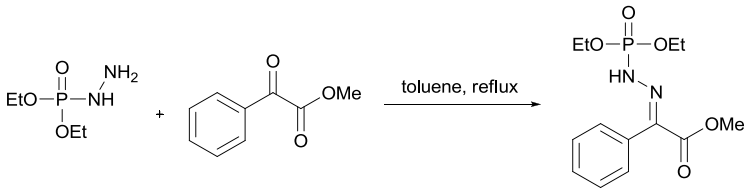
In order to further make sure the product 3, we tried our best to synthesis the compound **3l**.

(1) Preparation of diethyl phosphorohydrazidate[1].



Hydrazine hydrate (20 equiv) was added dropwise to a stirred solution of K_2CO_3 (15 equiv) and triethylbenzyl ammonium chloride (0.1 equiv) in CCl_4–CH_2Cl_2 (4:7) at room temperature. Diethylphosphite (1 equiv) was then added in dropwise. The mixture was stirred for one night and the residue was filtered off and washed with CH_2Cl_2. The solvents were removed and kept under high vacuum until the solvents were removed. The pale yellow liquid was used without further purification.

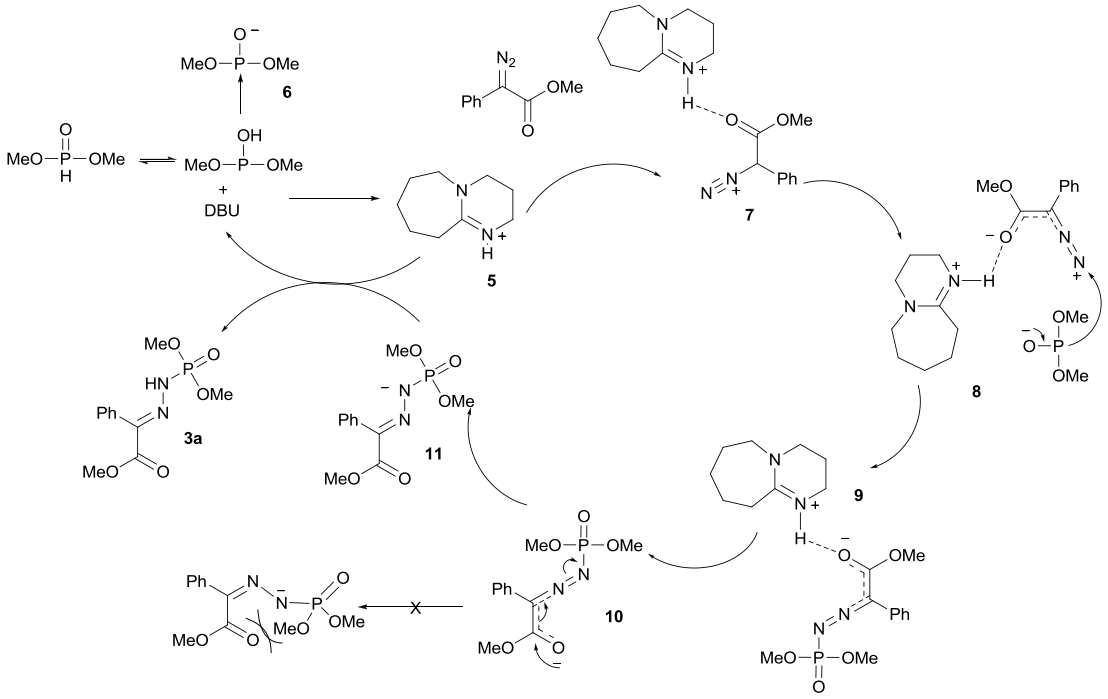
(2) The product 3l was prepared by a modified method[2].



Diethyl phosphorohydrazidate (10 mol) was added into a stirred solution of methyl 2-oxo-2-phenylacetate (10 mol) in toluene 80mL. The mixture was heated to reflux for one night, and the Dean-Stark apparatus was applied to remove the water from the reaction. When the reaction finished, the residue was purified by silica gel chromatography to yield the desired product **3l** in 31% yield. It should be noted that the silica gel should be treated with NEt_3.

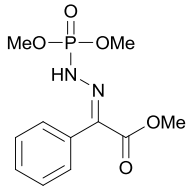
Ref: (1) V. A. Sauro and M. S. Workentin, *Can. J. Chem.* 2002, **80**, 250; (2) K. Anna, T. Krzysztof and Z. Andrzej, *Synthesis*. 1986, **4**, 298.

Proposed catalytic process for the catalytic N–P bond formation.



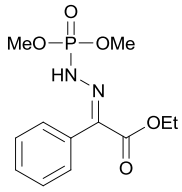
The spectroscopic data of phosphinamide compounds

(E)-methyl 2-(2-(dimethyoxyphosphoryl)hydraono)-2-phenylacetate (3a).



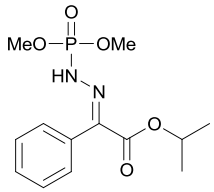
White solid, 66% yield, mp. 93–95°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.56–7.44 (m, 3H), 7.30–7.19 (m, 2H), 7.07 (d, *J* = 30.5, 1H), 3.86 (s, 3H), 3.83 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.8, 143.5(d, *J* = 16.9), 130.2, 129.6, 128.3, 128.2, 54.3 (d, *J* = 5.9), 52.6; ^{31}P NMR (202 MHz, CDCl3): δ = 1.6 (s); HRMS: calculated for $C_{11}H_{15}N_2O_5PNa$: 309.0611. $[M+Na]^+$; found: 309.0616.

(E)-ethyl 2-(2-(dimethoxyphosphoryl)hydrazono)-2-phenylacetate (3b).



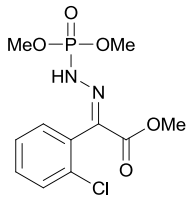
White solid, 67% yield, mp. 69–71°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.53–7.41 (m, 3H), 7.26–7.19 (m, 2H), 7.05 (d, *J* = 30.5, 1H), 4.27 (q, *J* = 7.1, 2H), 3.83 (d, *J* = 11.3), 1.28 (t, *J* = 7.1, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.3, 143.7(d, *J* = 17.0), 130.1, 129.5, 128.4, 128.2, 61.7, 54.3 (d, *J* = 5.9), 14.0; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 1.5; HRMS: calculated for $C_{12}H_{17}N_2O_5PNa$: 323.0767. $[M+Na]^+$; found: 323.0762.

(E)-isopropyl 2-(2-(dimethoxyphosphoryl)hydrazono)-2-phenylacetate (3c).



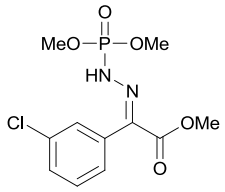
White solid, 72% yield, mp. 87–89°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.55–7.41 (m, 3H), 7.26–7.18 (m, 2H), 7.05 (d, *J* = 30.5, 1H), 5.24–4.96 (m, 6H), 3.85 (d, *J* = 11.3, 3H), 1.27 (s, 1H), 1.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.81, 143.96 (d, *J* = 17.0 Hz), 130.04, 129.44, 128.52, 128.15, 77.40, 76.98, 76.56, 69.38, 54.42 (d, *J* = 6.1), 21.59; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 1.3; HRMS: calculated for $C_{13}H_{19}N_2O_5PNa$: 337.0924. $[M+Na]^+$; found: 337.0927.

(E)-methyl 2-(2-chlorophenyl)-2-(2-(dimethoxyphosphoryl)hydrazono)acetate (3d).



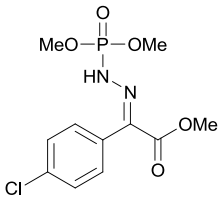
White solid, 93% yield, mp. 144–145°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.52–7.36 (m, 3H), 7.19–7.16 (m, 1H), 6.88 (d, *J* = 30, 1H), 3.87–3.77 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.1, 141.0 (d, *J* = 17.3 Hz), 133.0, 131.7, 130.4, 130.1, 127.8, 77.4, 77.0, 76.6, 54.3 (d, *J* = 15.1), 52.71; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 1.0; HRMS: calculated for $C_{11}H_{14}ClN_2O_5PNa$: 343.0221. $[M+Na]^+$; found: 343.0228.

(E)-methyl 2-(3-chlorophenyl)-2-(2-(dimethoxyphosphoryl)hydrazono)acetate (3e).



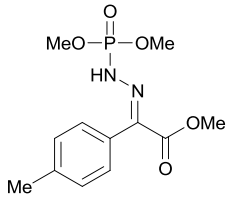
White solid, 80% yield, mp. 134–136°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42–7.41 (m, 2H), 7.25–7.08 (m, 3H), 3.81–3.77 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.4, 141.7(d, *J* = 17.2), 135.5, 130.8 130.4 130.2 128.4, 126.4, 54.3 (d, *J* = 5.9), 52.7. ^{31}P NMR (202 MHz, $CDCl_3$) δ = 1.0; HRMS: calculated for $C_{11}H_{14}ClN_2O_5PNa$: 343.0221. $[M+Na]^+$; found: 343.0229.

(E)-methyl 2-(4-chlorophenyl)-2-(2-(dimethoxyphophoryl)hydrazono)acetate (***3f***).



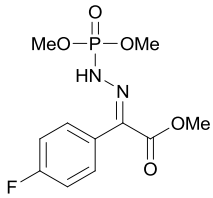
White solid, 75% yield, mp. 159–162°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.51–7.44 (m, 2H), 7.22–7.07 (m, 3H), 3.83 (s, 3H), 3.80 (d, *J* = 2.6, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.6, 142.1 (d, *J* = 17.0), 136.4, 129.8, 129.8, 126.6, 54.3 (d, *J* = 5.9), 52.7; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 1.0; HRMS: calculated for $C_{11}H_{14}ClN_2O_5PNa$: 343.0221. $[M+Na]^+$; found: 343.0212.

(E)-methyl 2-(2-(dimethoxyphosphoryl)hydrazono)-2-p-tolyacetate (***3g***).



White solid, 65% yield, mp. 92–94°C. ^{1}H NMR (300 MHz, CDCl3) δ = 7.33–7.27(m, 2H), 7.15–7.03(m, 3H), 3.86–3.78(m, 9H), 2.40–2.37(d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.9, 143.7 (d, *J* = 17.0), 140.5, 130.3, 128.0, 125.2, 54.3 (d, *J* = 5.5 Hz) 52.6, 21.3; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 1.7; HRMS: calculated for $C_{18}H_{16}O_4Na$: 323.0767. $[M+Na]^+$; found: 323.0761.

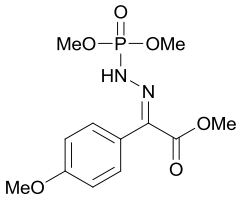
(E)-methyl 2-(2-(dimethoxyphosphoryl)hydrazono)-2-(4-fluorophenyl)acetate (***3h***).



White solid, 72% yield, mp. 143–146°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43–6.88 (m, 5H), 3.84–3.77 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.1, 162.7 (d, *J* = 151.1), 142.3 (d, *J* = 17.3), 130.6 (d, *J* = 8.5), 124.2, 116.8 (d, *J* = 21.9), 54.3 (d, *J* = 5.8), 52.7; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 1.5; HRMS: calculated for $C_{11}H_{14}FN_2O_5PNa$: 327.0517. $[M+Na]^+$; found: 327.0514.

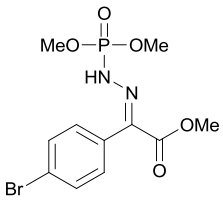
(E)-methyl 2-(2-(dimethoxyphosphoryl)hydrazono)-2-(4-methoxyphenyl)acetate (***3i***).

White solid, 78% yield, mp. 157–159°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.18–7.07



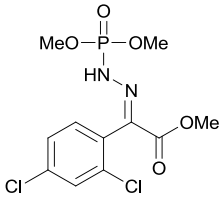
(m, 3H), 6.98 (d, *J* = 8.7, 2 H), 3.83–3.79 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.1, 160.8, 143.4 (d, *J* = 17.2), 129.8, 120.0, 115.0, 77.5, 77.0, 76.6, 54.24 (d, *J* = 5.9), 54.2, 52.6. ^{31}P NMR (202 MHz, $CDCl_3$) δ = 1.8. HRMS: calculated for $C_{12}H_{17}N_2O_6PNa$: 339.0716. $[M+Na]^+$; found: 339.0722.

(E)-methyl 2-(4-bromophenyl)-2-(2-(dimethoxyphosphoryl)hydrazono)acetate (3j).



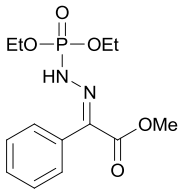
White solid, 83% yield, mp. 150–152°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1, 2H), 7.18–7.11 (m, 3H), 3.84–3.80 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.5, 142.1 (d, *J* = 17.3), 132.8, 130.0, 127.1, 124.7, 142.1 (d, *J* = 17.3), 52.7; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 1.3; HRMS: calculated for $C_{11}H_{14}BrN_2O_5PNa$: 386.9716. $[M+Na]^+$; found: 386.9703.

(E)-methyl 2-(2,4-dichlorophenyl)-2-(2-(dimethoxyphosphoryl)hydrazono)acetate (***3k***).



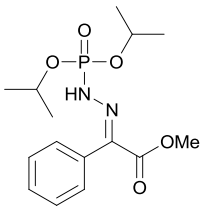
White solid, 91% yield, mp. 152–154°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.49–7.44(m, 3H), 7.13–7.09 (m, 1H), 3.78 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.0, 139.7 (d, *J* = 17.8), 137.0, 134.1, 131.1, 130.2, 128.1, 126.8, 54.2 (d, *J* = 7.1), 52.7; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 0.9; HRMS: calculated for $C_{11}H_{13}Cl_2N_2O_5PNa$: 376.9831. $[M+Na]^+$; found: 376.9838.

(E)-methy 2-(2-(diethoxyphosphoryl)hydrazono)-2-phenylacetate (***3l***).



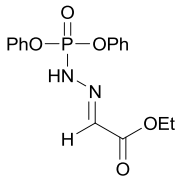
White solid, 70% yield, mp. 59–61°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.55–7.45 (m, 3H), 7.26–7.21 (m, 2H), 7.07 (d, *J* = 30.4, 1H), 4.27–4.12 (m, 4H), 3.82 (s, 3H), 1.37 (tt, *J* = 6.2, 3.1, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.0, 142.9 (d, *J* = 17.0), 130.2, 129.6, 128.4, 128.2, 64.0 (d, *J* = 5.8), 52.6, 16.0 (d, *J* = 6.6); ^{31}P NMR (202 MHz, $CDCl_3$) δ = -1.0; HRMS: calculated for $C_{13}H_{19}N_2O_5PNa$: 337.0924. $[M+Na]^+$; found: 337.0924.

(E)-methyl 2-(2-(diisopropoxyphosphoryl)hydrazono)-2-phenylacetate (***3m***).



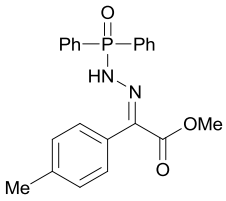
White solid, 75% yield, mp. 70–72°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.54–7.41 (m, 3H), 7.22–7.19 (m, 2H), 7.05 (d, *J* = 30.5, 1H), 4.69 (dq, *J* = 12.5, 6.2, 1H), 3.80 (s, 3H), 1.35 (dd, *J* = 8.1, 6.3, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.1, 142.3 (d, *J* = 17.1), 130.1, 129.5, 128.6, 128.2, 72.9 (d, *J* = 5.8), 52.4, 23.6 (d, *J* = 4.6), 23.4 (d, *J* = 4.9); ^{31}P NMR (202 MHz, $CDCl_3$) δ = -3.0; HRMS: calculated for $C_{15}H_{23}N_2O_5PNa$: 365.1237. $[M+Na]^+$; found: 365.1228.

(E)-methyl 2-(2-(diphenoxyphosphoryl)hydrazono)acetate (***3n***).



Light yellow solid, 90% yield, mp. 70-72°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.32–7.27 (m, 4H), 7.22–7.12 (m, 7H), 4.30 (q, *J* = 7.1, 1H), 1.35 (t, *J* = 7.1, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.7, 149.9 (d, *J* = 6.9), 136.8, 136.6, 129.6, 125.5, 120.6 (d, *J* = 4.5), 61.2, 14.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ = -8.3; HRMS: calculated for $C_{15}H_{15}N_2O_5PNa$: 371.0767. $[M+Na]^+$; found: 371.0761.

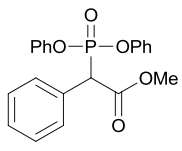
(E)-methyl 2-(2-(diphenylphosphoryl)hydrazono)-2-p-tolylacetate (***3o***).



White solid, 98% yield, mp. 184–186°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.90–7.83 (m, 4H), 7.63–7.40 (m, 6H), 7.31–7.28 (m, 2H), 7.19–7.17 (d, *J* = 8.1 Hz, 2H), 3.75 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 142.9 (d, *J* = 13.9), 140.3, 132.4, 132.4, 132.1, 131.9, 131.5, 130.2, 129.8, 128.5, 128.3 (d, *J* = 5.4), 125.4, 52.4, 21.3; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 25.43; HRMS: calculated for $C_{22}H_{21}N_2O_3PNa$: 415.1182. $[M+Na]^+$; found: 415.1189.

The spectroscopic data of compounds from C–P bond formation.

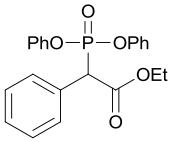
Methyl 2-(diphenoxyphosphoryl)-2-phenylacetate (***4a***).



Colorless oil, 87% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.66–7.62 (m, 2H), 7.45–7.08 (m, 11H), 7.00–6.94 (m, 2H), 4.67 (d, *J* = 23.7, 1H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, CDCl3) δ = 167.2, 150.2 (d, *J* = 9.4), 130.0, 129.9, 129.8, 129.7, 129.5, 128.8, 128.8, 128.5, 128.4, 125.3, 125.2,

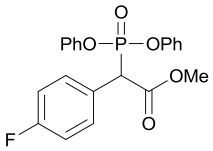
120.5, 120.4, 120.4, 53.0, 51.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 11.24; HRMS (ESI): calculated for $C_{21}H_{19}O_5PNa$: 405.0862 $[M+Na]^+$; found: 405.0869.

Ethyl 2-(diphenoxyphosphoryl)-2-phenylacetate (***4b***).



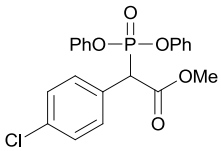
White solid, 92% yield, mp. 80–82°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.65–7.61 (m, 2H), 7.44–7.08 (m, 11H), 7.00–6.93 (m, 2H), 4.62 (d, *J* = 23.7, 1H), 4.43–4.11 (m, 2H), 1.26 (t, *J* = 7.1, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.7, 150.3 (d, *J* = 9.3), 129.9, 129.9, 129.6, 129.5, 128.7, 128.4, 128.3, 125.2, 125.1, 120.4, 120.4, 120.34, 62.5, 52.26 (d, *J* = 138.3), 13.5; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 11.32; HRMS (ESI): calculated for $C_{22}H_{21}O_5PNa$: 419.1016 $[M+Na]^+$; found: 419.1026.

Methyl 2-(diphenoxyphosphoryl)-2-(4-fluorophenyl)acetate (***4c***).



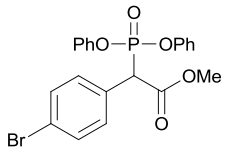
White solid, 95% yield, mp. 88–90°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.68–7.53 (m, 2H), 7.36–6.90 (m, 12H), 4.65 (d, *J* = 24.1, 1H), 3.76 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.1 (d, *J* = 2.0), 164.4 (d, *J* = 3.1), 161.1 (d, *J* = 3.0), 150.2 (dd, *J* = 9.3, 3.8), 131.8, 131.7, 131.6, 129.7, 129.6, 125.7 (d, *J* = 3.0), 125.6 (d, *J* = 3.1), 120.4, 120.3, 120.3, 115.8 (d, *J* = 1.6), 115.6 (d, *J* = 1.6), 53.1, 51.1 (d, *J* = 138.6). ^{31}P NMR (202 MHz, $CDCl_3$) δ = 11.23; HRMS (ESI): calculated for $C_{21}H_{18}FO_5PNa$: 423.0768 $[M+Na]^+$; found: 423.0786.

Methyl 2-(4-chlorophenyl)-2-(diphenoxyphosphoryl)acetate (***4d***).



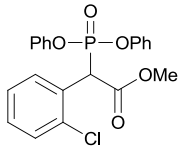
Colorless oil, 89% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.59–7.56 (m, 2H), 7.40–7.09 (m, 11H), 7.00–6.98 (m, 2H), 4.64 (d, *J* = 24.1, 1H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.9, 150.2 (d, *J* = 4.4), 150.1 (d, *J* = 4.1), 134.6, 134.5, 131.3, 131.2, 129.7, 129.6, 128.9, 128.9, 128.5, 128.4, 125.4, 125.3, 120.4, 120.3, 120.3, 53.1, 52.24, 51.32 (d, *J* = 138.2); ^{31}P NMR (202 MHz, $CDCl_3$) δ = 10.55; HRMS (ESI): calculated for $C_{21}H_{18}ClO_5PNa$: 439.0473 $[M+Na]^+$; found: 439.0478.

Methyl 2-(4-bromophenyl)-2-(diphenoxyphosphoryl)acetate (***4e***).



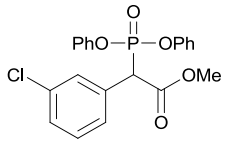
Colorless oil, 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.51 (s, 4H), 7.37–7.08 (m, 8H), 7.00–6.97 (m, 2H), 4.63 (d, *J* = 24.1, 1H), 3.76 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8 (d, *J* = 3.0 Hz), 150.2 (d, *J* = 4.1 Hz), 150.0 (d, *J* = 3.9 Hz), 131.9 (d, *J* = 1.6 Hz), 131.6 (d, *J* = 6.8 Hz), 129.7, 129.7, 129.0, 128.9, 125.4 (d, *J* = 4.2 Hz), 122.8 (d, *J* = 3.8 Hz), 120.4, 120.3, 120.3, 53.2, 51.4 (d, *J* = 138.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ = 10.31; HRMS (ESI): calculated for $C_{21}H_{18}BrO_5PNa$: 482.9967 $[M+Na]^+$; found: 482.9958.

Methyl 2-(2-chlorophenyl)-2-(diphenoxyphosphoryl)acetate (***4f***).



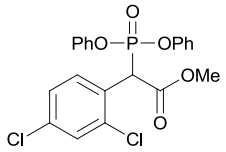
Colorless oil, 93% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.07–8.03 (m, 1H), 7.45–7.42 (m, 1H), 7.35–7.08 (m, 10H), 6.97–6.97 (m, 2H), 5.45 (d, *J* = 25.6, 1H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.7 (d, *J* = 2.7), 150.2 (t, *J* = 9.2), 134.5 (d, *J* = 10.0), 131.6 (d, *J* = 4.7), 129.7, 129.6, 128.1 (d, *J* = 7.0), 127.1 (d, *J* = 2.2), 125.3 (d, *J* = 10.4), 120.4 (d, *J* = 4.4), 120.2 (d, *J* = 4.4), 53.2, 47.4 (d, *J* = 140.7); ^{31}P NMR (202 MHz, $CDCl_3$) δ = 10.67; HRMS (ESI): calculated for $C_{21}H_{18}ClO_5PNa$: 439.0473 $[M+Na]^+$; found: 439.0478.

Methyl 2-(3-chlorophenyl)-2-(diphenoxyphosphoryl)acetate (***4g***).



Colorless oil, 91% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.56 – 7.50 (m, 1H), 7.35 – 7.10 (m, 10H), 7.04 – 6.99 (m, 2H), 4.64 (d, *J* = 24.0, 1H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.7 (d, *J* = 3.3), 150.1 (d, *J* = 7.5), 134.5 (d, *J* = 2.2), 131.7 (d, *J* = 8.7), 130.0, 130.0, 129.7, 129.6, 128.7 (d, *J* = 2.5), 128.2 (d, *J* = 6.7), 125.41 (d, *J* = 3.7), 120.4, 120.3, 120.3, 53.2, 51.6 (d, *J* = 137.9); ^{31}P NMR (202 MHz, $CDCl_3$) δ = 10.64; HRMS (ESI): calculated for $C_{21}H_{18}ClO_5PNa$: 439.0473 $[M+Na]^+$; found: 439.0444.

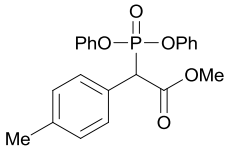
Methyl 2-(2,4-dichlorophenyl)-2-(diphenoxyphosphoryl)acetate (***4h***).



Colorless oil, 91% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00 (dd, *J* = 8.6, 2.5, 1H), 7.45 (s, 1H), 7.36–7.10 (m, 9H), 7.01–6.98 (m, 2H), 5.37 (d, *J* = 25.8, 1H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.3, 150.2 (d, *J* = 9.7), 150.0 (d, *J* = 9.6), 135.2 (d, *J* = 10.0), 135.0 (d, *J* = 3.0), 132.6 (d, *J* = 4.5), 129.7 (d, *J* = 7.1), 129.3, 127.5, 126.8 (d, *J* = 7.1), 125.4 (d, *J* = 7.1), 120.3 (d, *J* = 4.3), 120.1 (d, *J* = 4.3), 53.3, 46.9 (d, *J* = 140.0); ^{31}P NMR (202

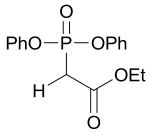
MHz, $CDCl_3$) δ = 10.00; HRMS (ESI): calculated for $C_{21}H_{17}Cl_2O_5PNa$: 473.0083 $[M+Na]^+$; found: 473.0044.

Methyl 2-(diphenoxyphosphoryl)-2-p-tolylacetate (***4i***).



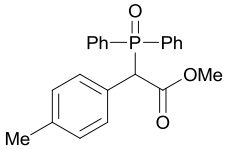
White solid, 90% yield, mp. 94–96°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56–7.53 (m, 2H), 7.36–7.08 (m, 10H), 7.03–7.00 (m, 2H), 4.65 (d, *J* = 23.6, 1H), 3.75 (s, 3H), 2.37 (d, *J* = 1.8, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.3, 150.4 (d, *J* = 1.7), 150.2 (d, *J* = 1.3), 138.3 (d, *J* = 2.9), 129.8, 129.7, 129.7, 129.5, 129.5, 126.8 (d, *J* = 8.8 H), 125.2 (d, *J* = 5.8), 120.5, 120.5, 120.4, 52.9, 51.7 (d, *J* = 139.2), 21.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 11.51; HRMS (ESI): calculated for $C_{22}H_{22}O_5PNa$: 419.1019 $[M+Na]^+$; found: 419.1018.

Ethyl 2-(diphenoxyphosphoryl)acetate (4j).



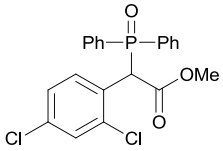
Colorless oil, 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.58–6.92 (m, 10H), 4.23 (q, *J* = 7.1, 2H), 3.27 (d, *J* = 21.6, 1H), 1.28 (t, *J* = 7.1, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.7, 149.9 (d, *J* = 8.6), 129.8, 125.5, 120.5 (d, *J* = 4.3), 61.9, 34.0 (d, *J* = 137.2), 14.0; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 13.03; HRMS (ESI): calculated for $C_{16}H_{17}O_5PNa$: 343.0706 $[M+Na]^+$; found: 343.0744.

Methyl 2-(diphenylphosphoryl)-2-(4-methoxyphenyl)acetate (***4k***).



White solid, 93% yield, mp. 192–194°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.96–7.83 (m, 2H), 7.66–7.29 (m, 10H), 6.76 (d, *J* = 8.6, 2H), 4.66 (d, *J* = 11.4, 1H), 3.74 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.5, 159.24, 132.03 (d, *J* = 1.7 Hz), 131.79 (d, *J* = 1.8 Hz), 131.7, 131.5, 131.3, 131.3, 131.2, 130.1 (d, *J* = 21.0), 128.4, 128.3, 128.1, 121.94 (d, *J* = 6.3 Hz), 113.7, 55.1, 54.6 (d, *J* = 59.4), 52.4; ^{31}P NMR (202 MHz, $CDCl_3$) δ = 27.25; HRMS (ESI): calculated for $C_{22}H_{21}O_3PNa$: 403.1070 $[M+Na]^+$; found: 403.1074.

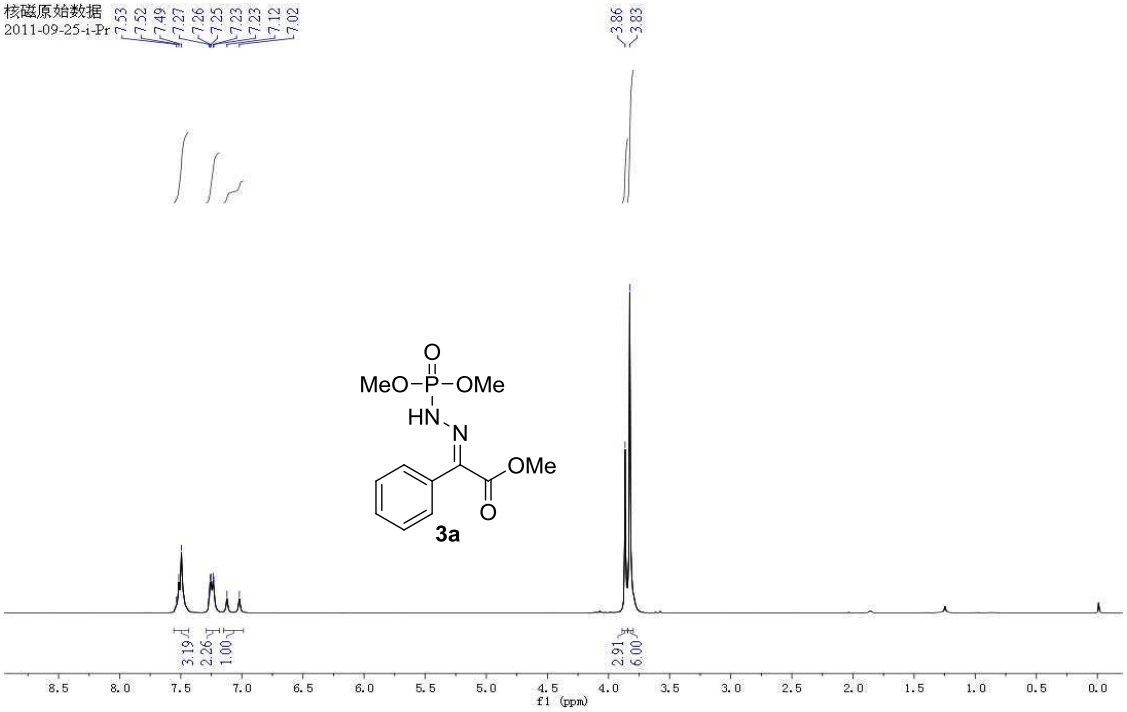
Methyl 2-(2,4-dichlorophenyl)-2-(diphenylphosphoryl)acetate (***4l***).

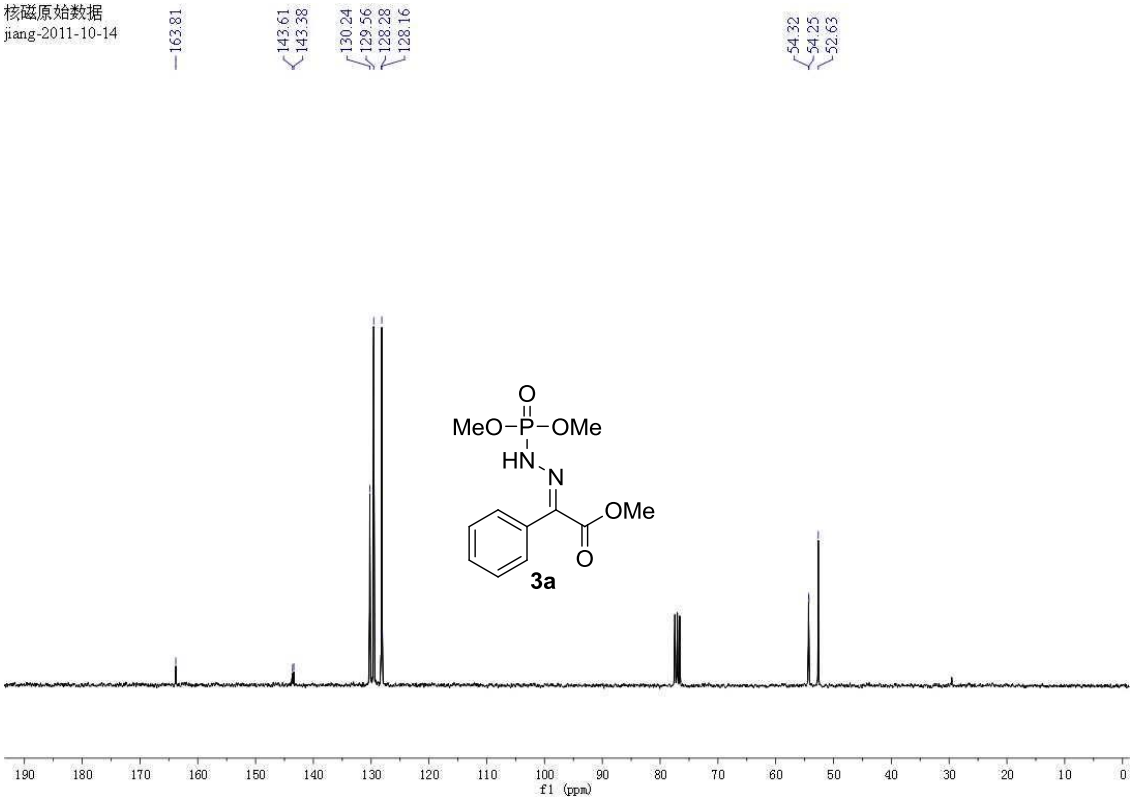


White solid, 96% yield, mp. 136–138°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.4, 1H), 8.04–7.89 (m, 2H), 8.00–7.93 (m,

5H), 7.47–7.17 (m, 5H), 5.40 (d, *J* = 10.6 Hz, 1H), 3.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.8, 134.5, 133.54 (d, *J* = 3.8), 132.2, 132.1, 131.3 (d, *J* = 9.1), 130.9, 130.8, 128.6, 128.4, 128.4, 128.2, 127.5, 127.4, 127.3, 52.7, 49.3 (d, *J* = 57.5); ^{31}P NMR (202 MHz, $CDCl_3$) δ = 28.64; HRMS (ESI): calculated for $C_{21}H_{17}Cl_2O_3PNa$: 441.0185 $[M+Na]^+$; found: 441.0190.

PDF file of copies ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra for new phosphinamide compounds.





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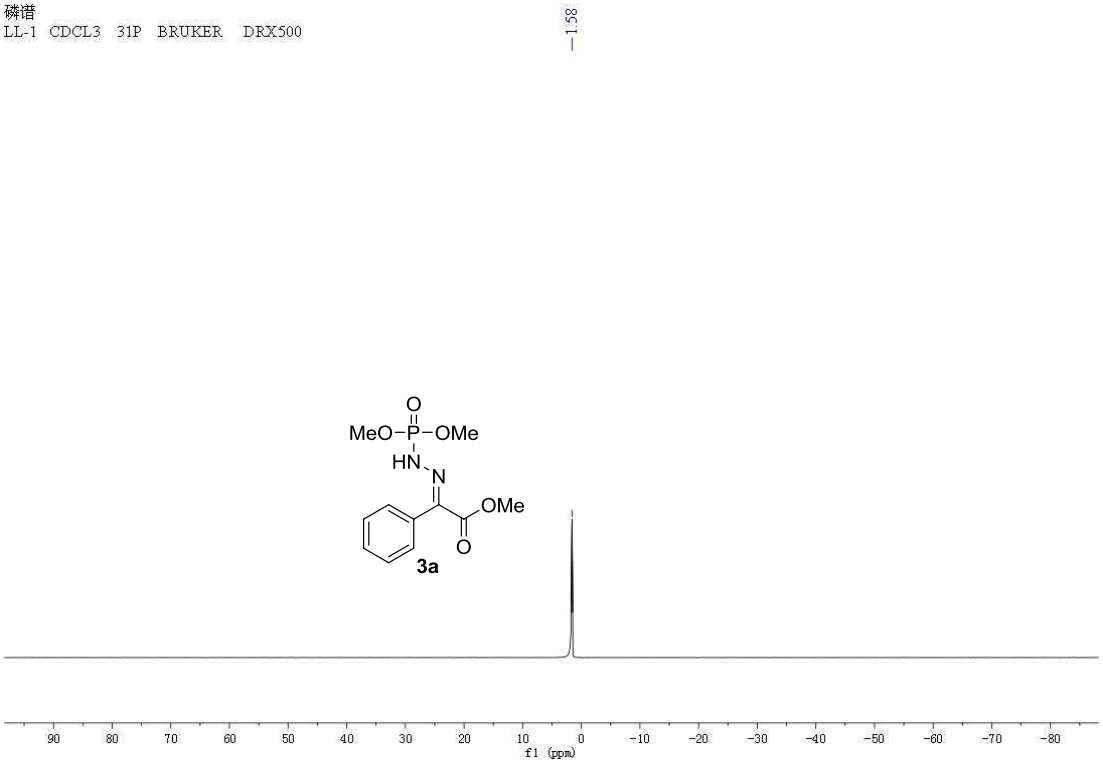

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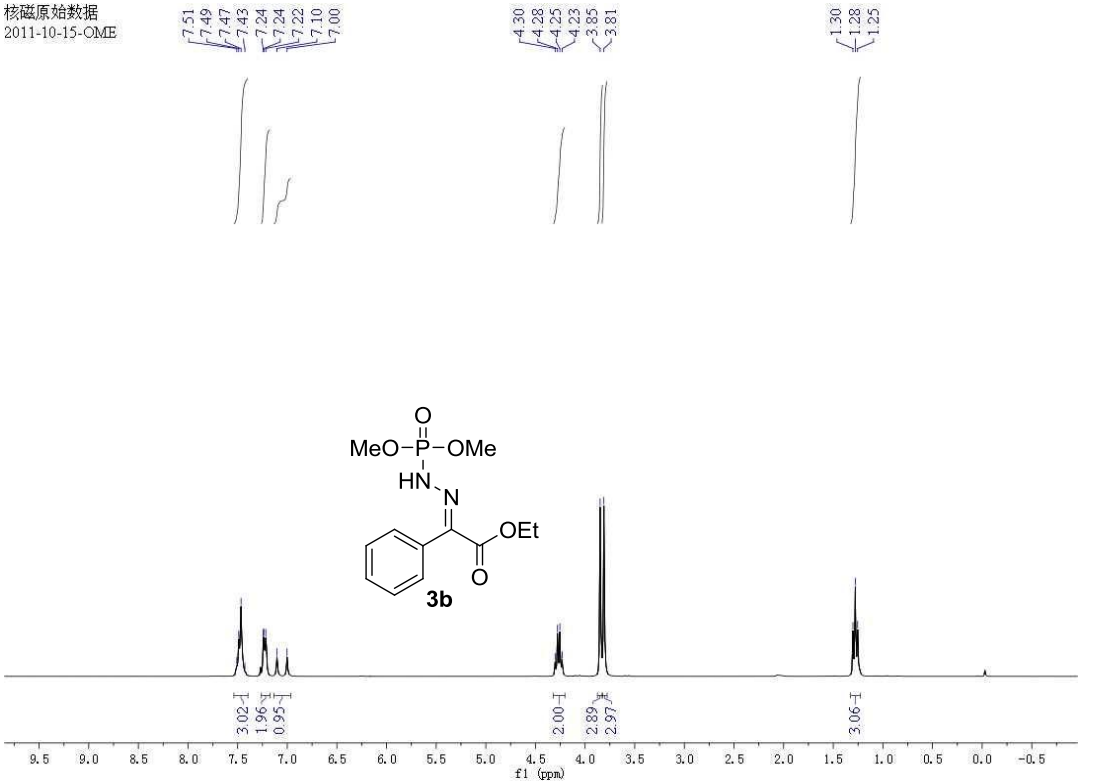

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jiang-2011-10-19

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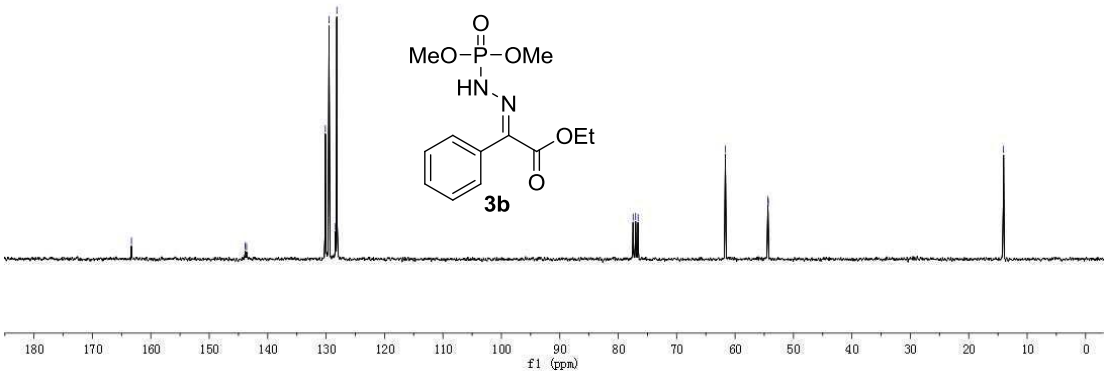

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LL-1 CDCL3 31P BRUKER DRX500

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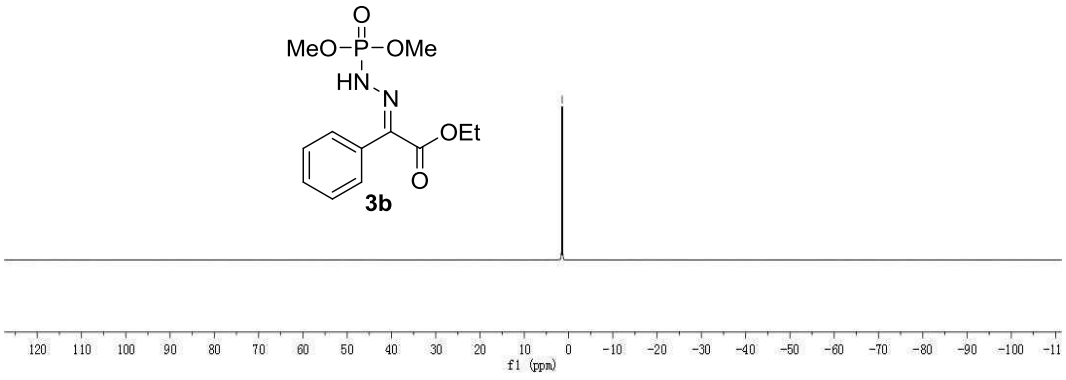

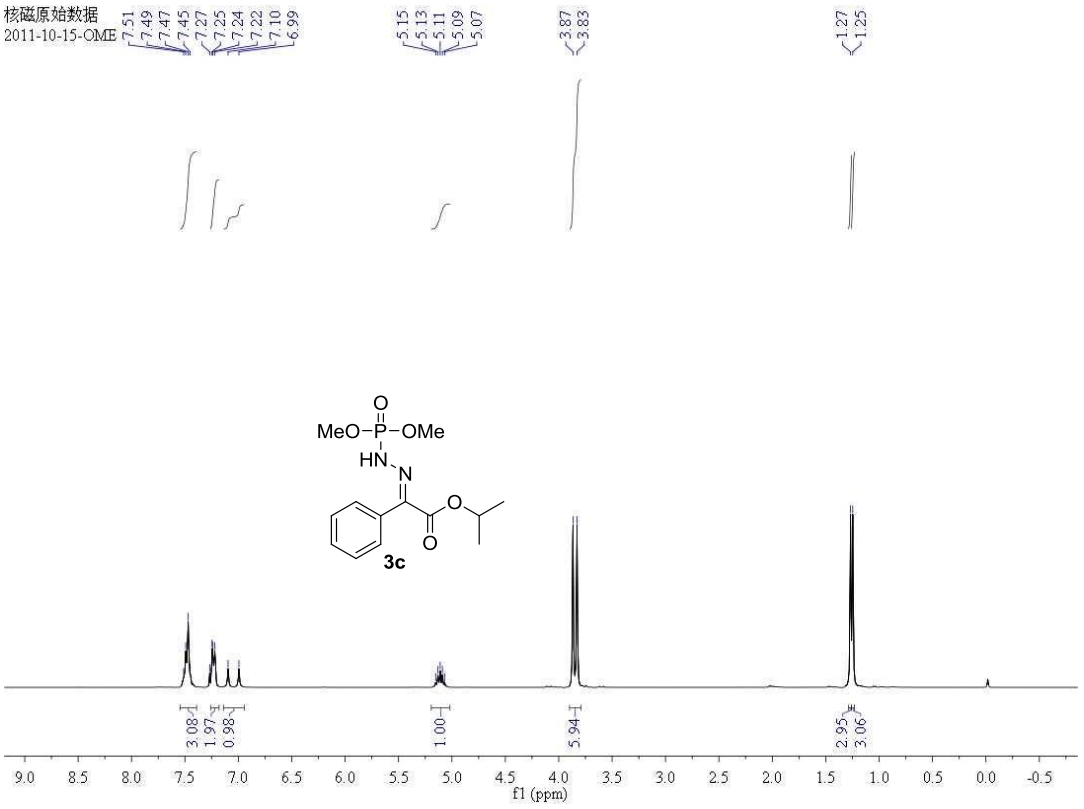

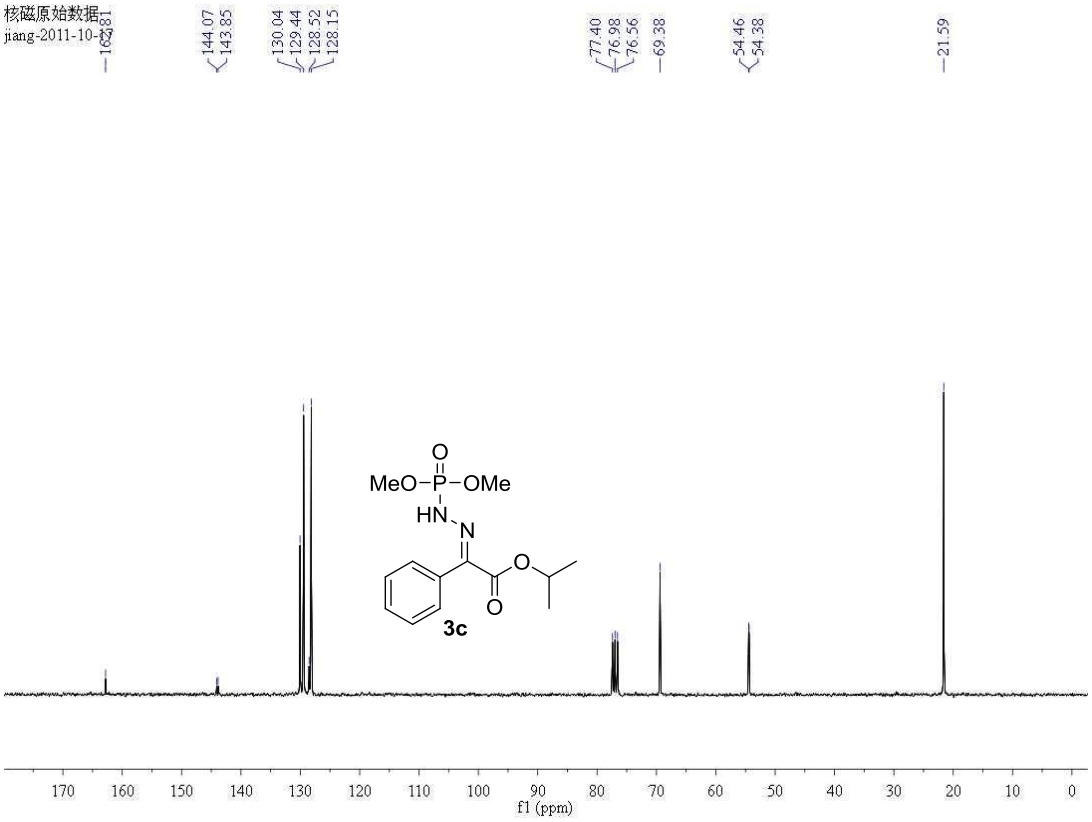

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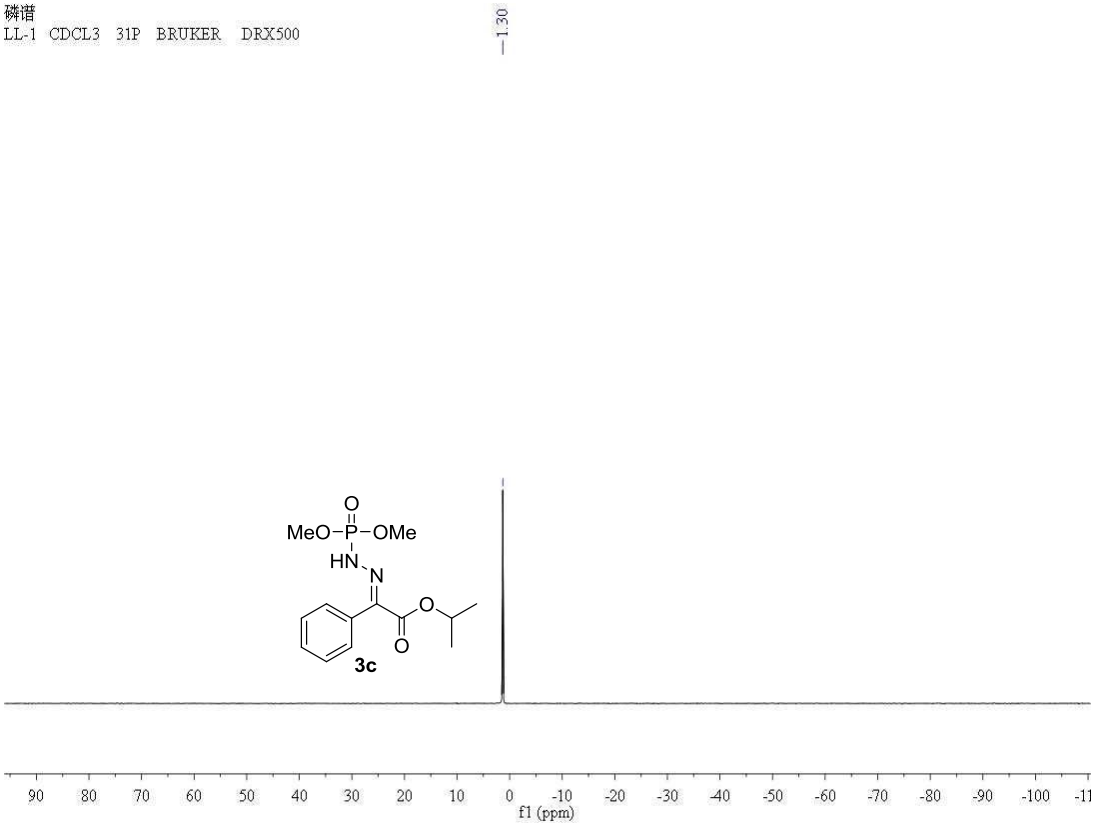

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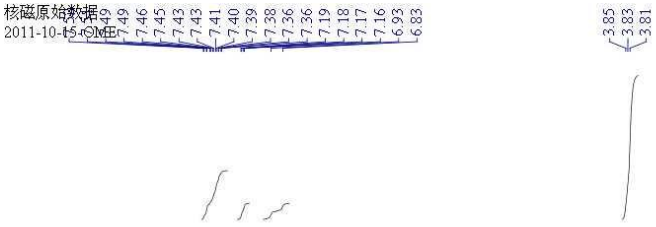
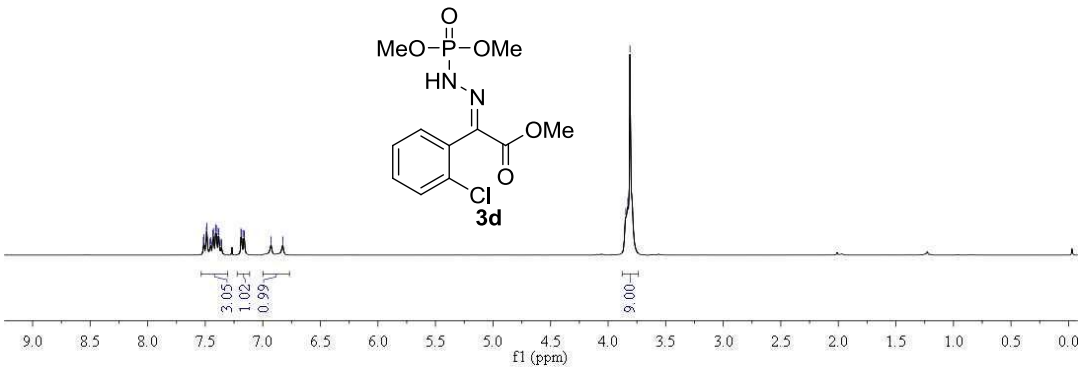
2011-10-t5-OMe





核磁原始数据
jiang-2011-10-19

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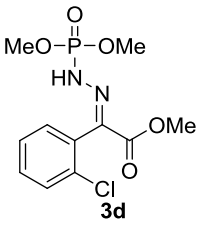

3d

磷谱
LL-1 CDCL3 31P BRUKER DRX500

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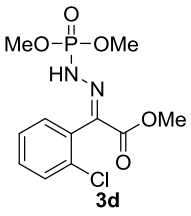

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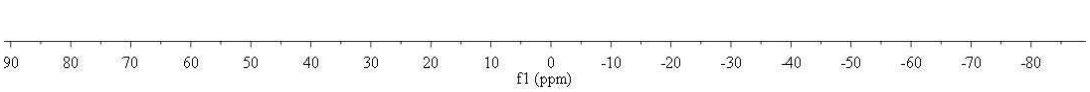

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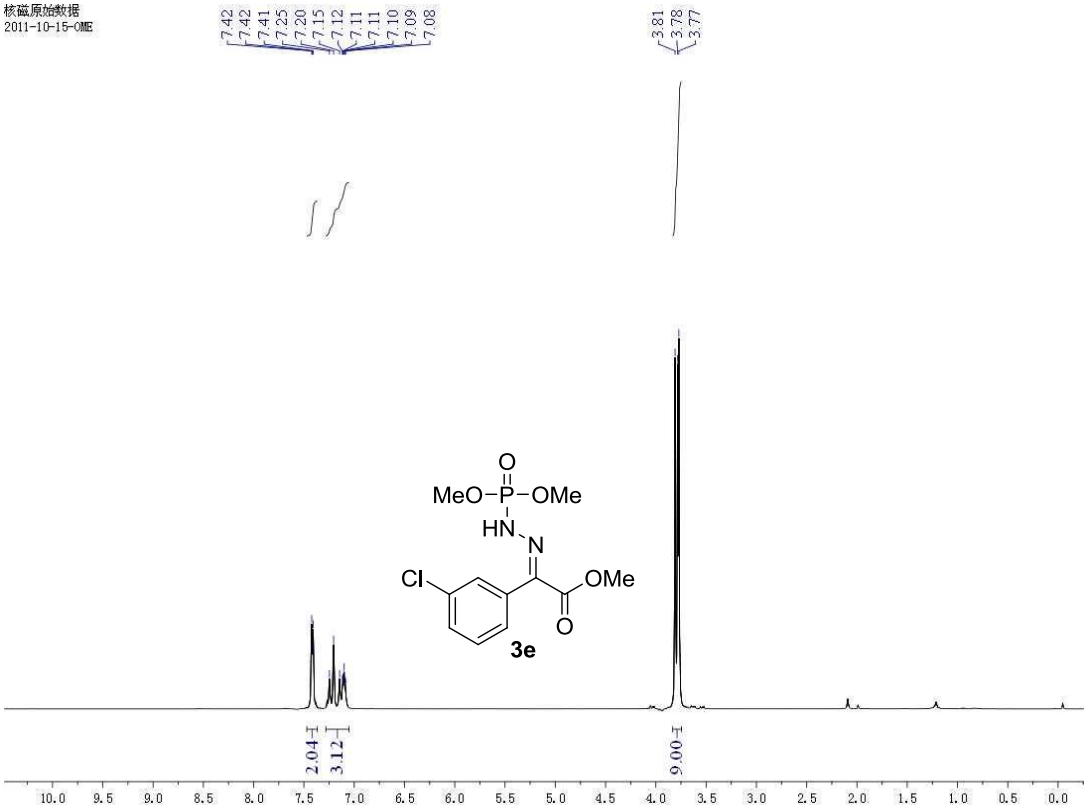

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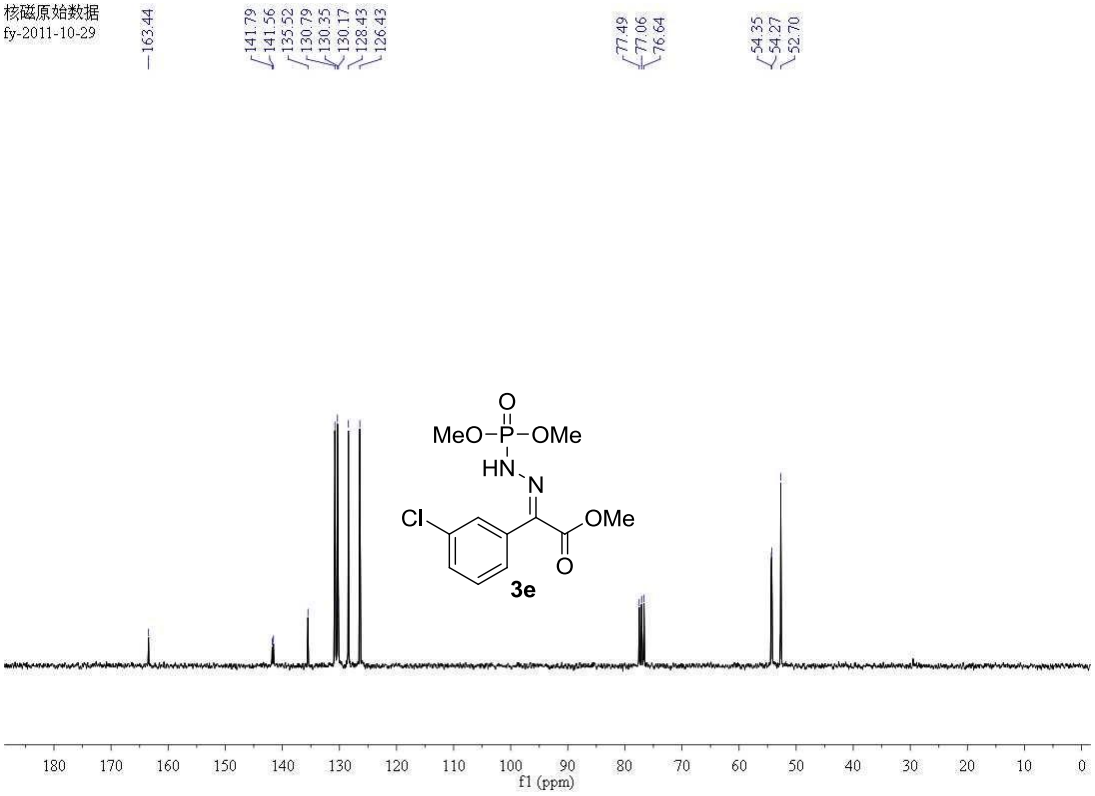
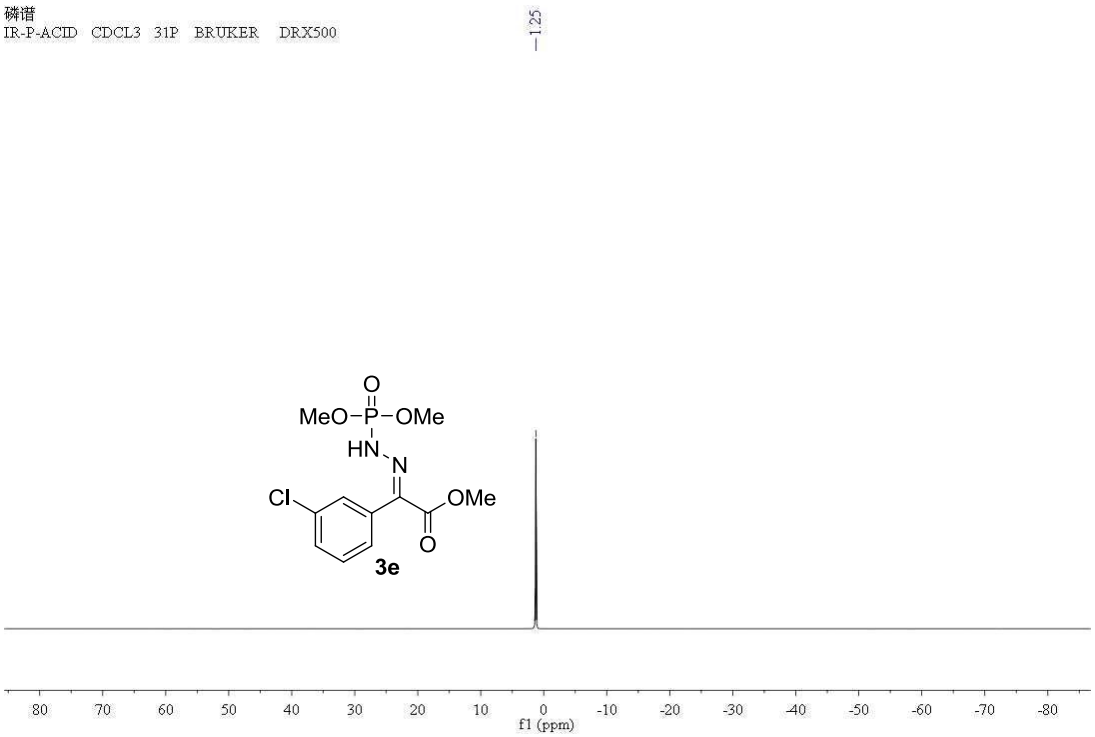


磷谱
IR-P-ACID CDCL3 31P BRUKER DRX500



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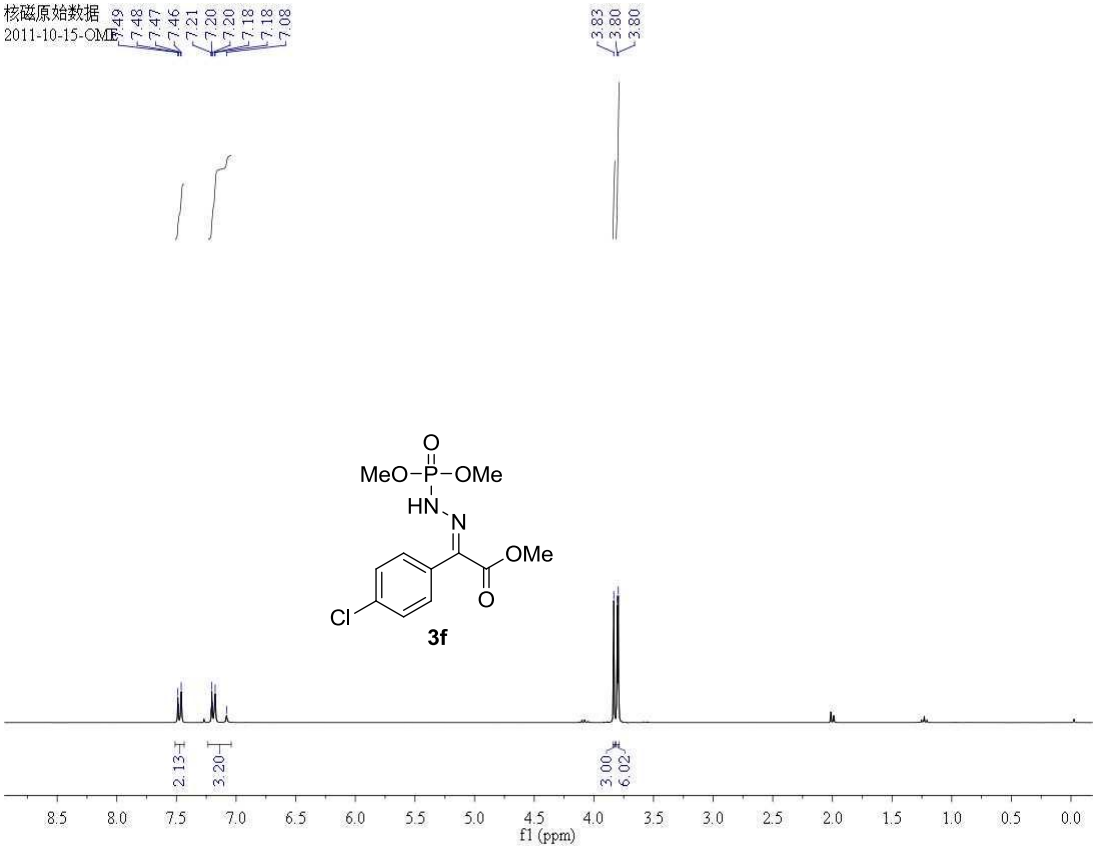

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jiang-2011-10-19

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54.29
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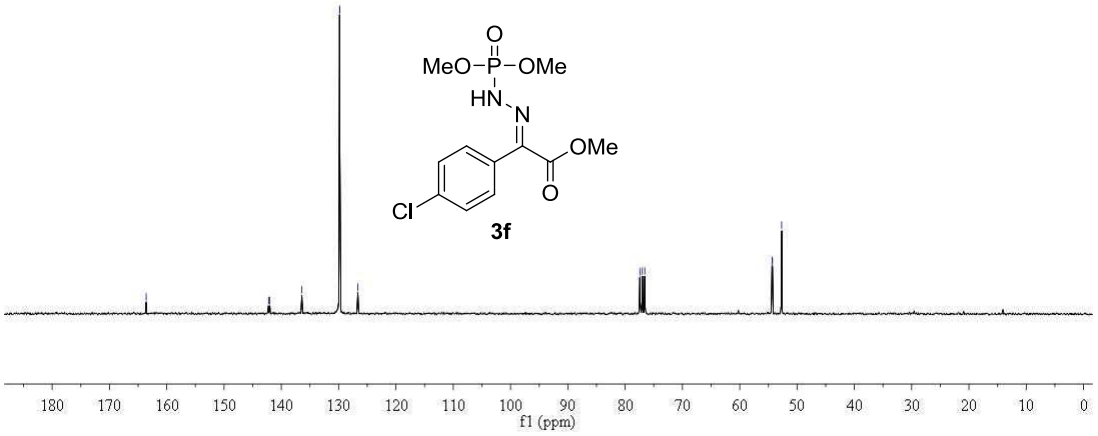
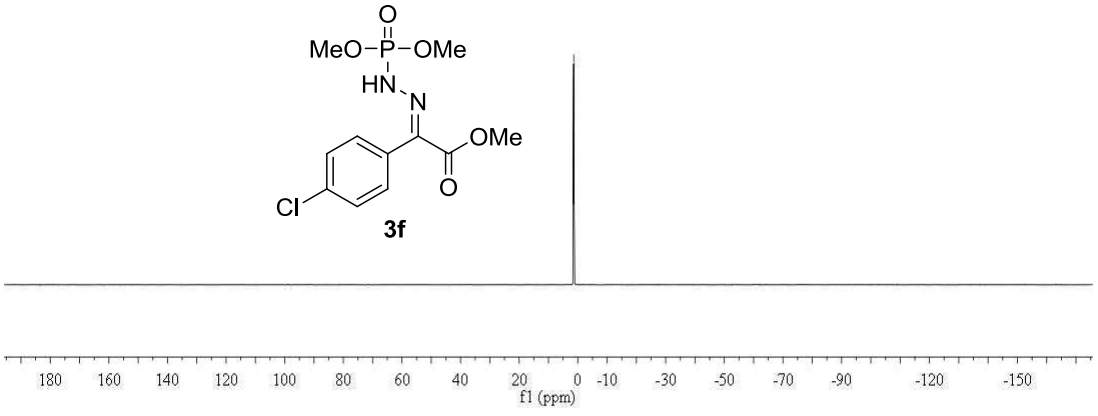


磷谱
IR-P-ACID CDCL3 31P BRUKER DRX500

1.36



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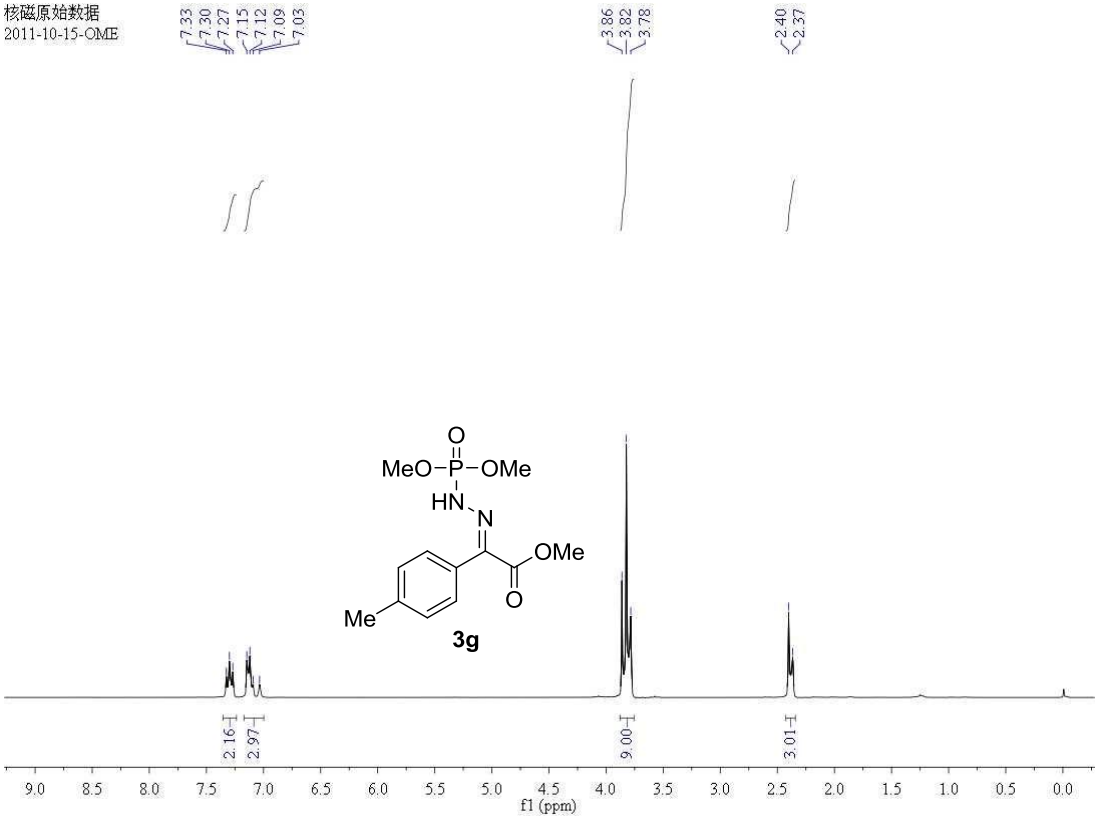

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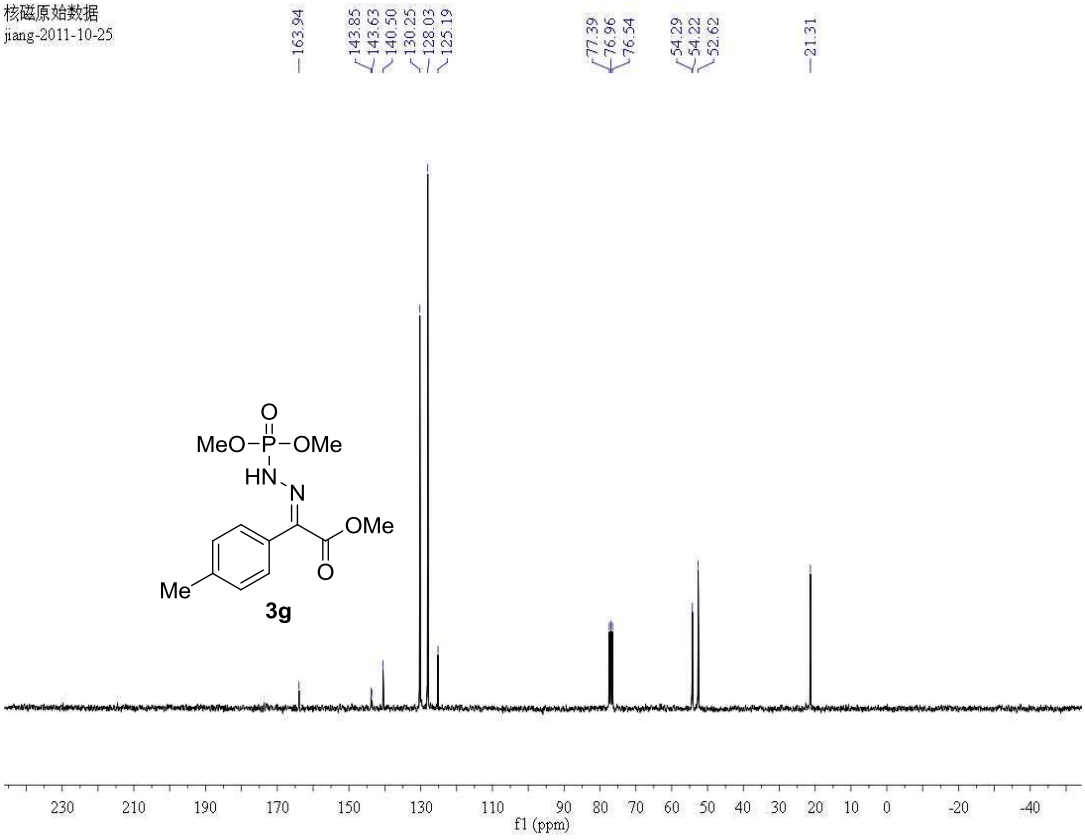

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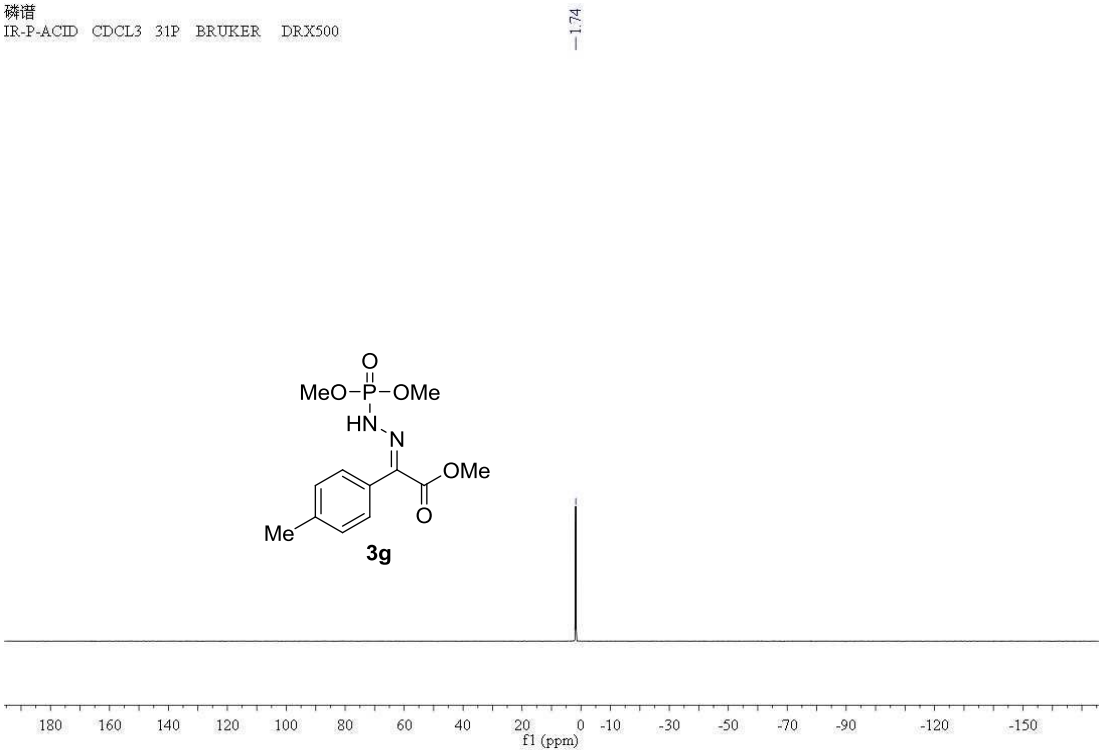
IR-P-ACID CDCL3 31P BRUKER DRX500



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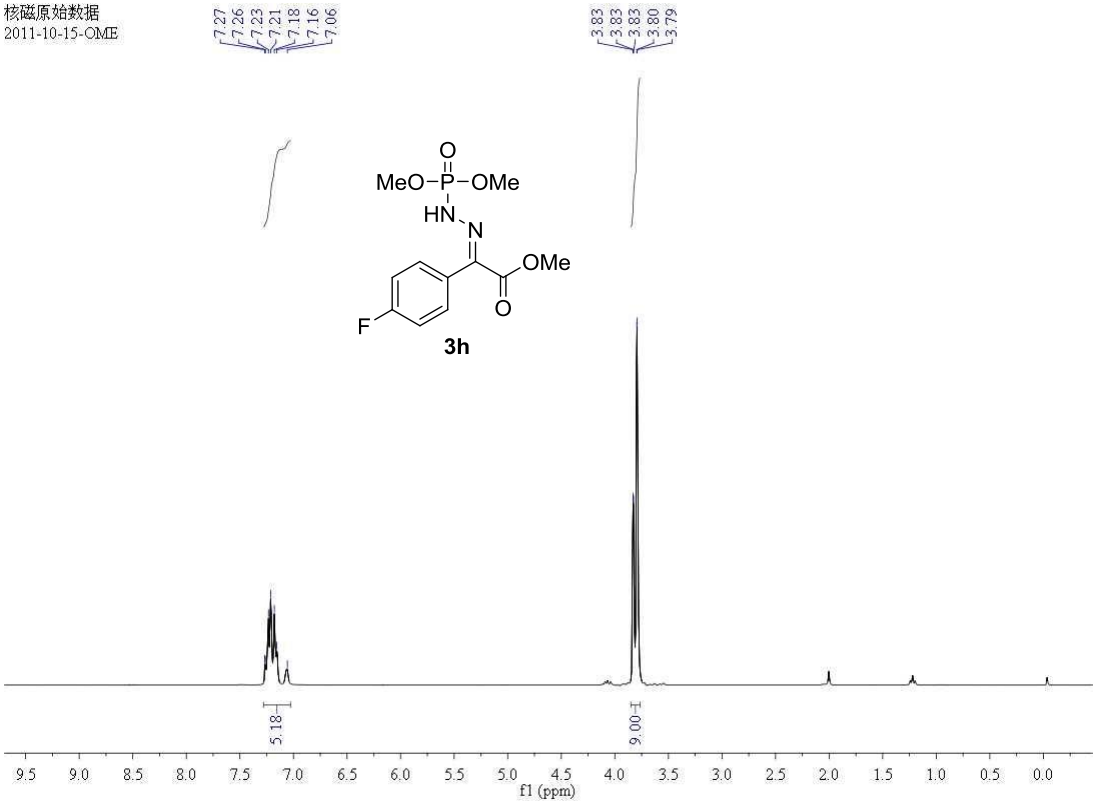

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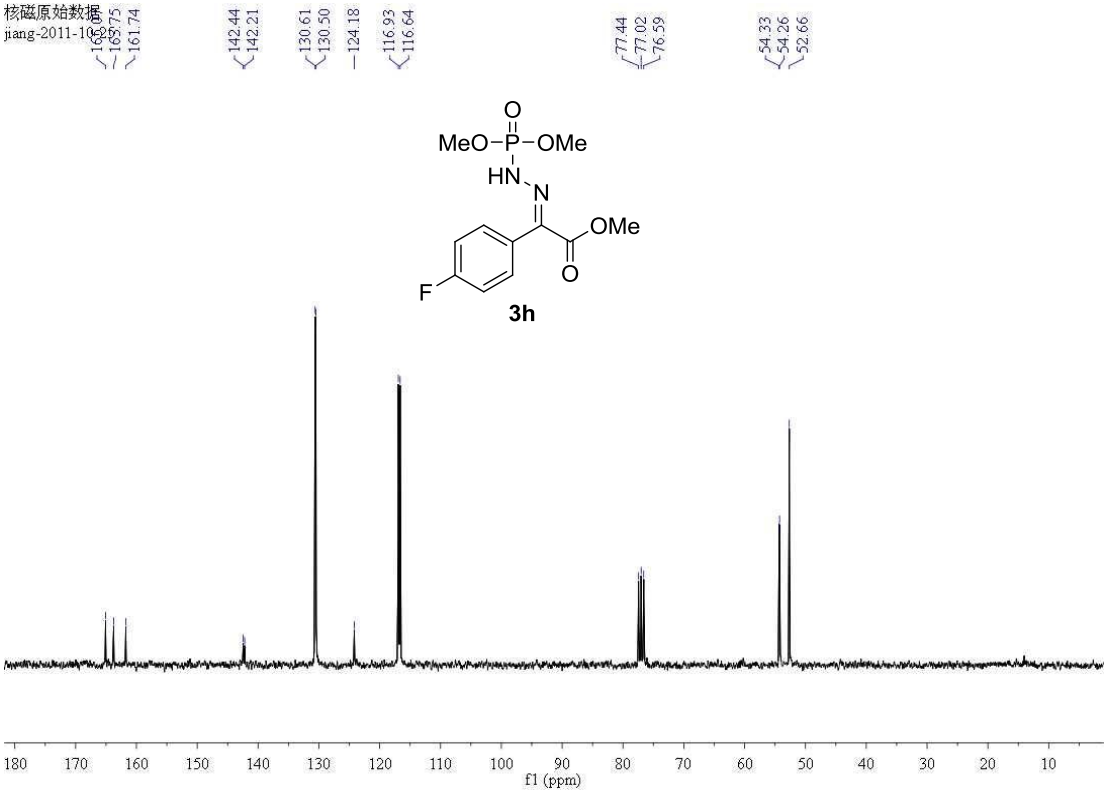

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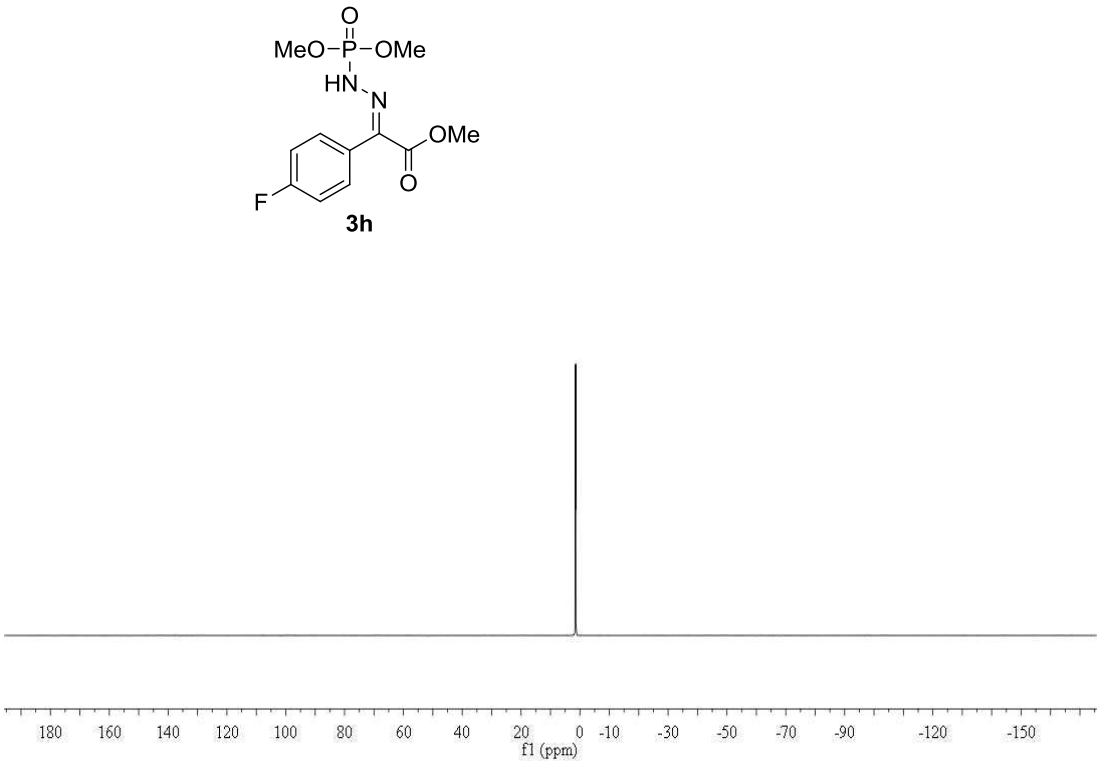
IR-P-ACID CDCL3 31P BRUKER DRX500



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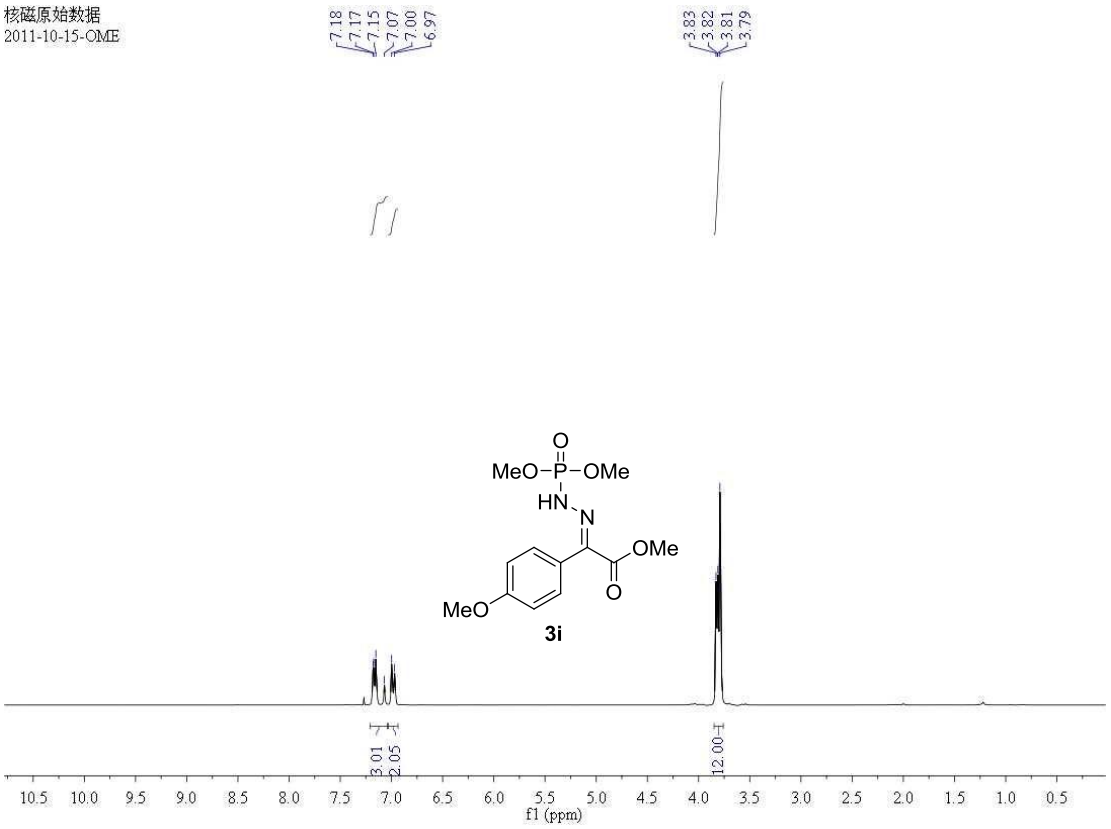

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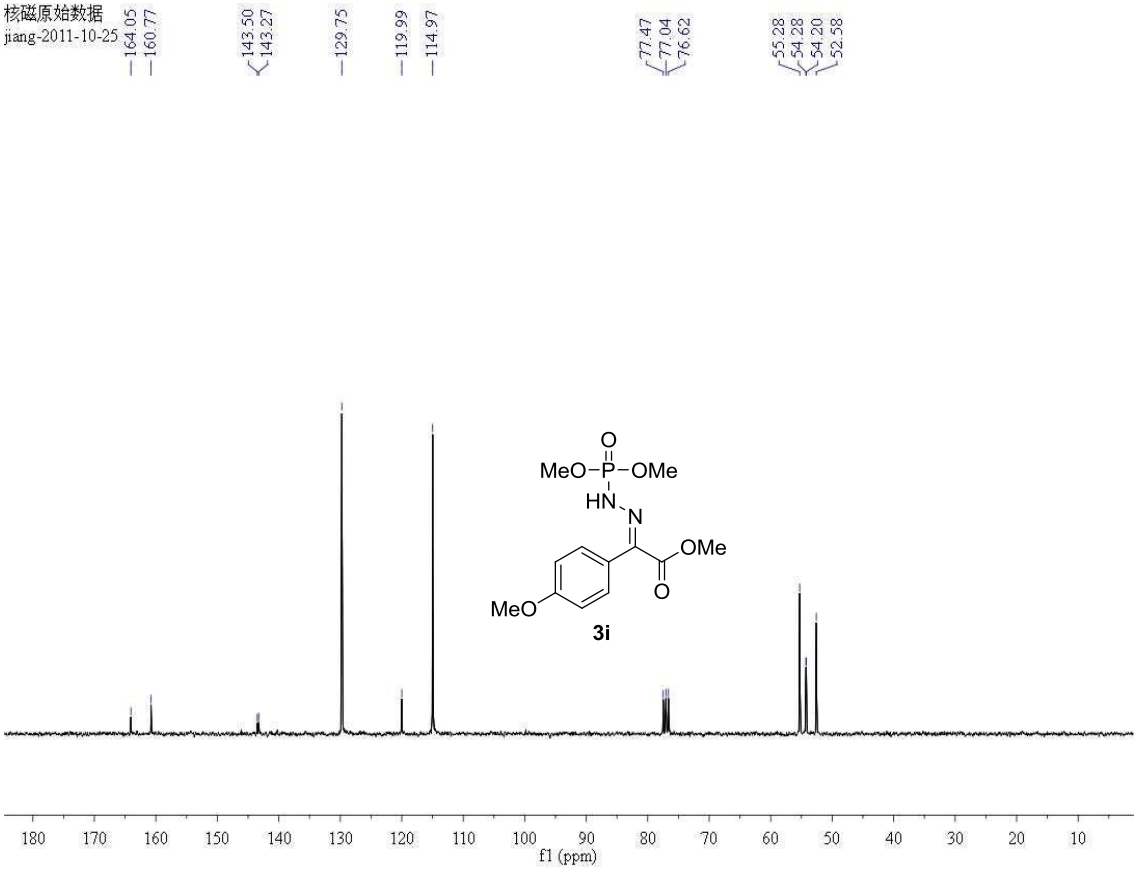

磷谱
IR-P-ACID CDCL3 31P BRUKER DRX500

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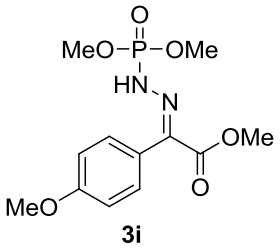

3i

核磁原始数据
2011-10-15-OME

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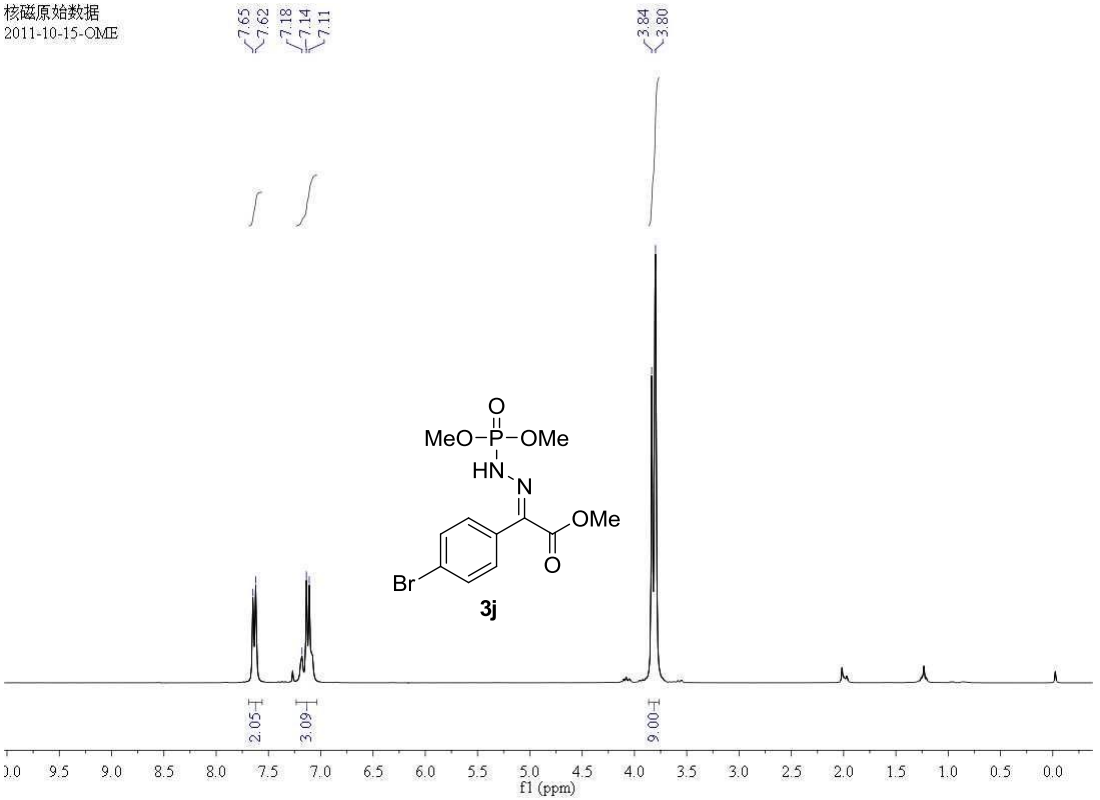
3.84
3.80



3j

核磁原始数据
fy-2011-10-29

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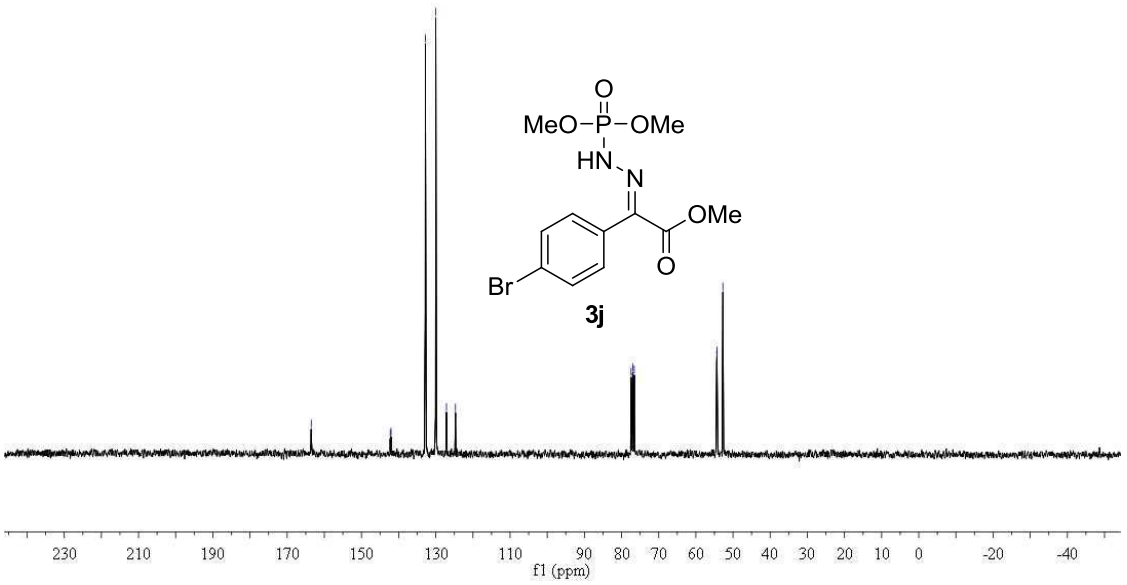
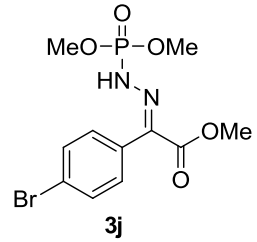
54.30
52.71



3j

磷谱
IR-P-ACID CDCL3 31P BRUKER DRX500

1.34



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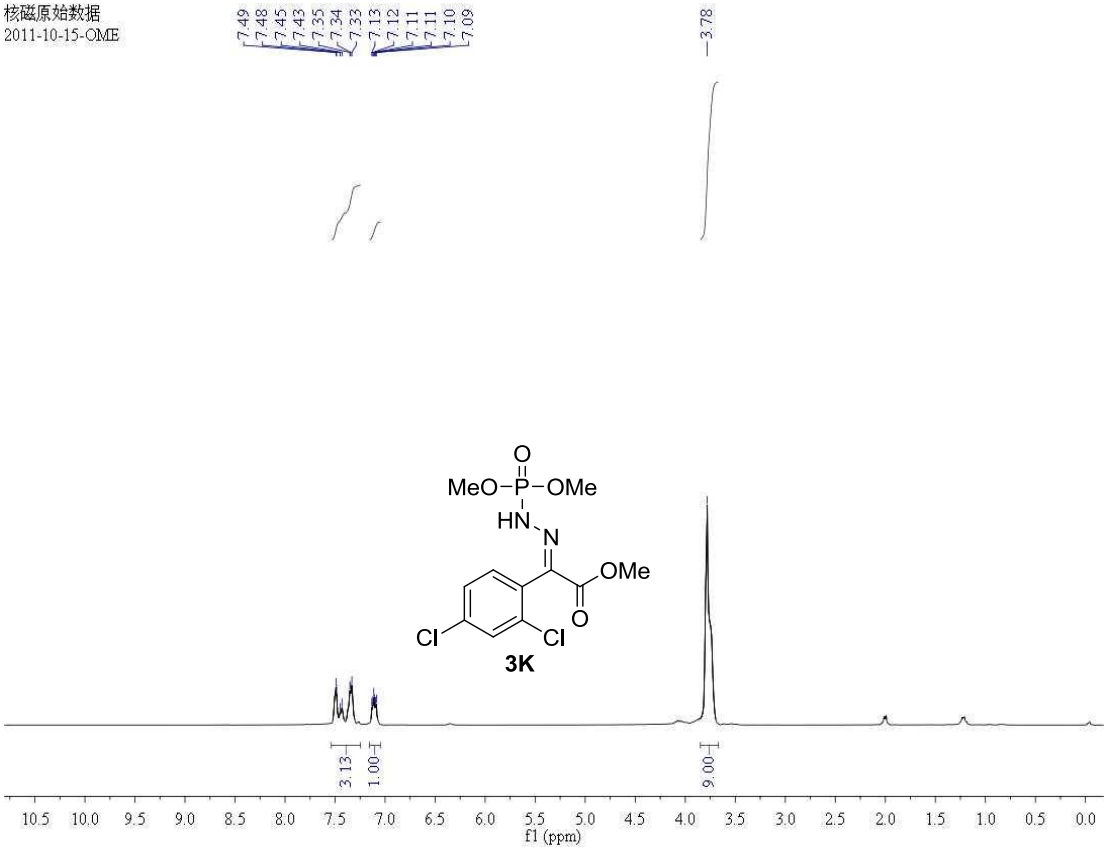

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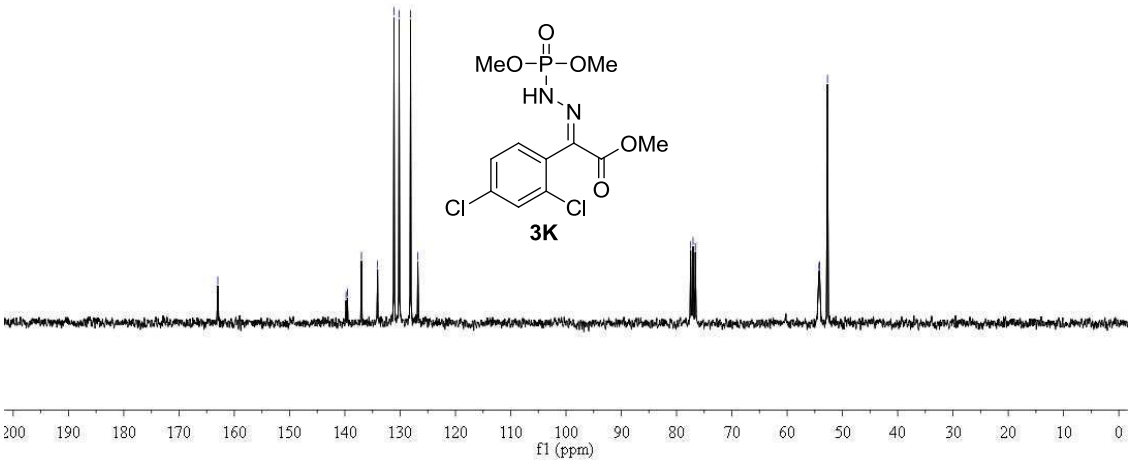
jiang-2011-10-25



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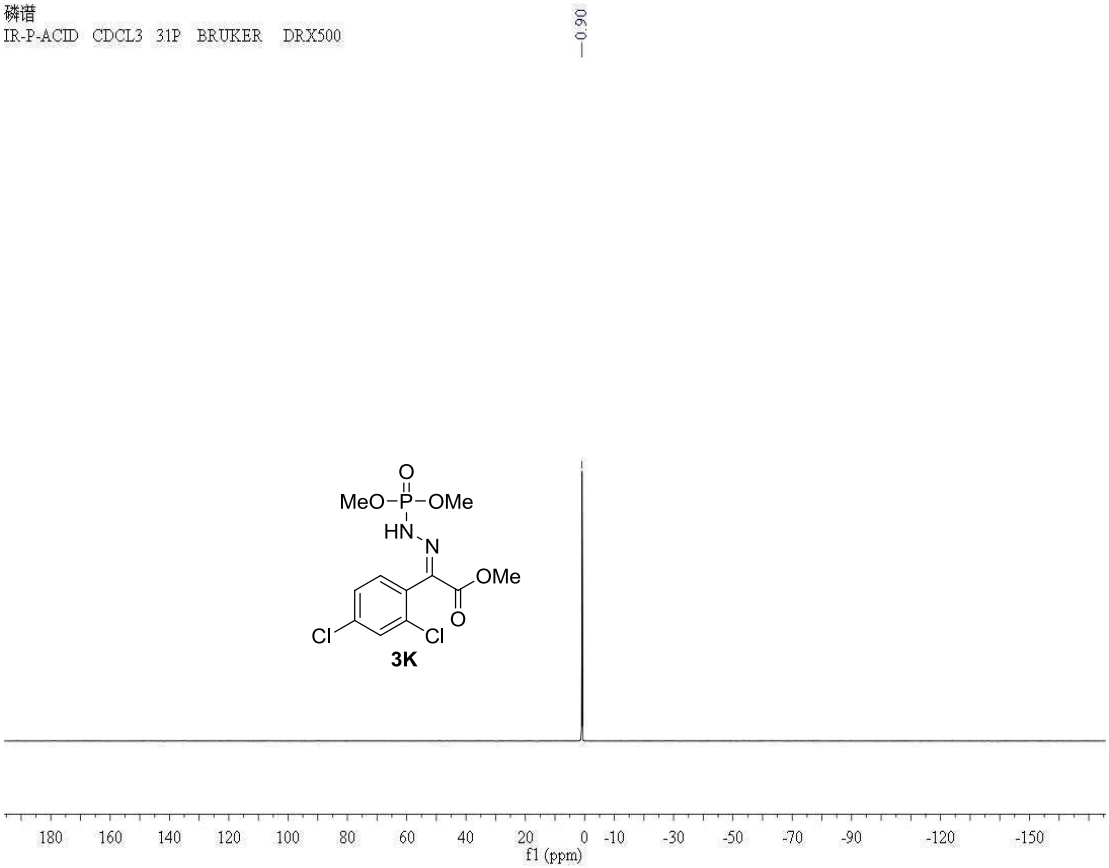
IR-P-ACID CDCL3 31P BRUKER DRX500



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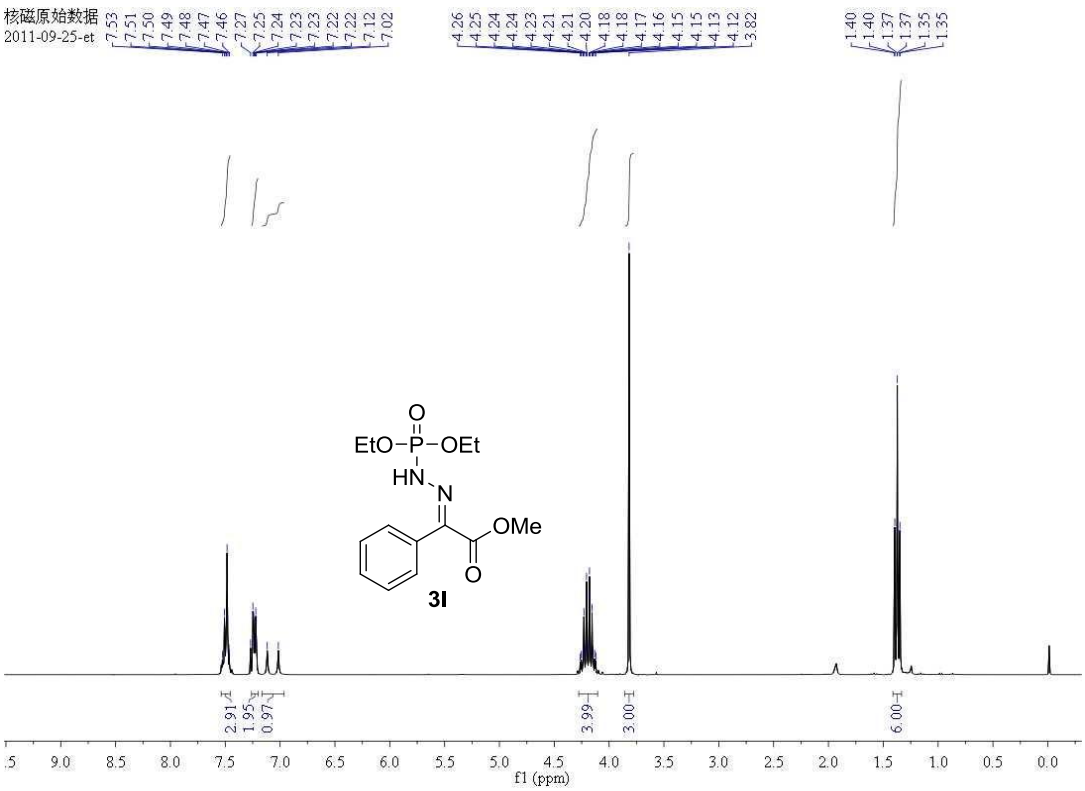

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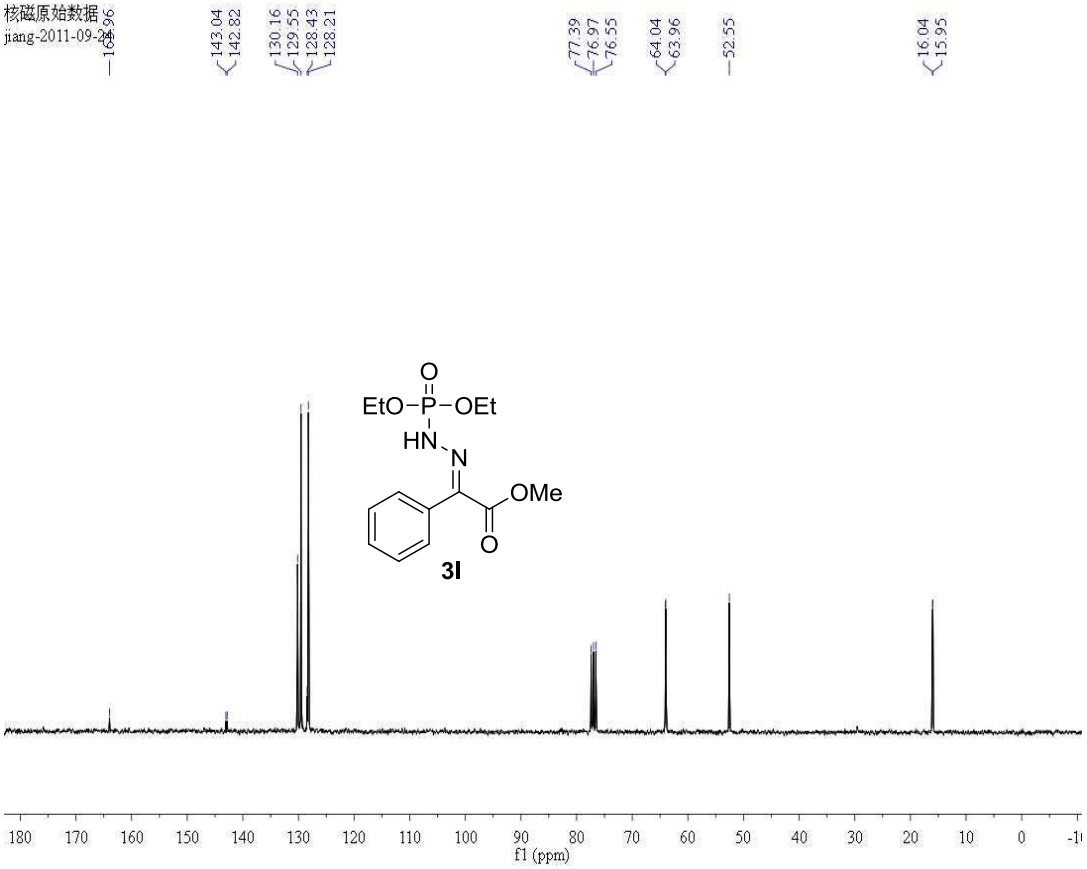
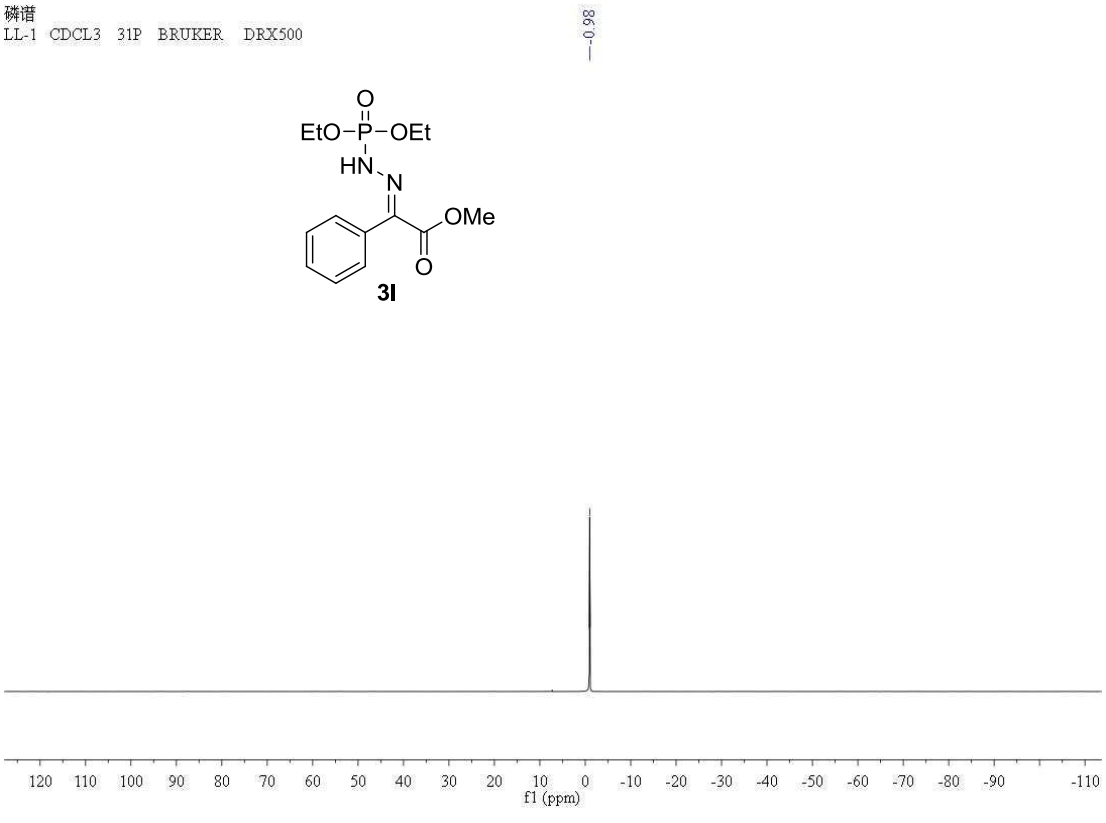
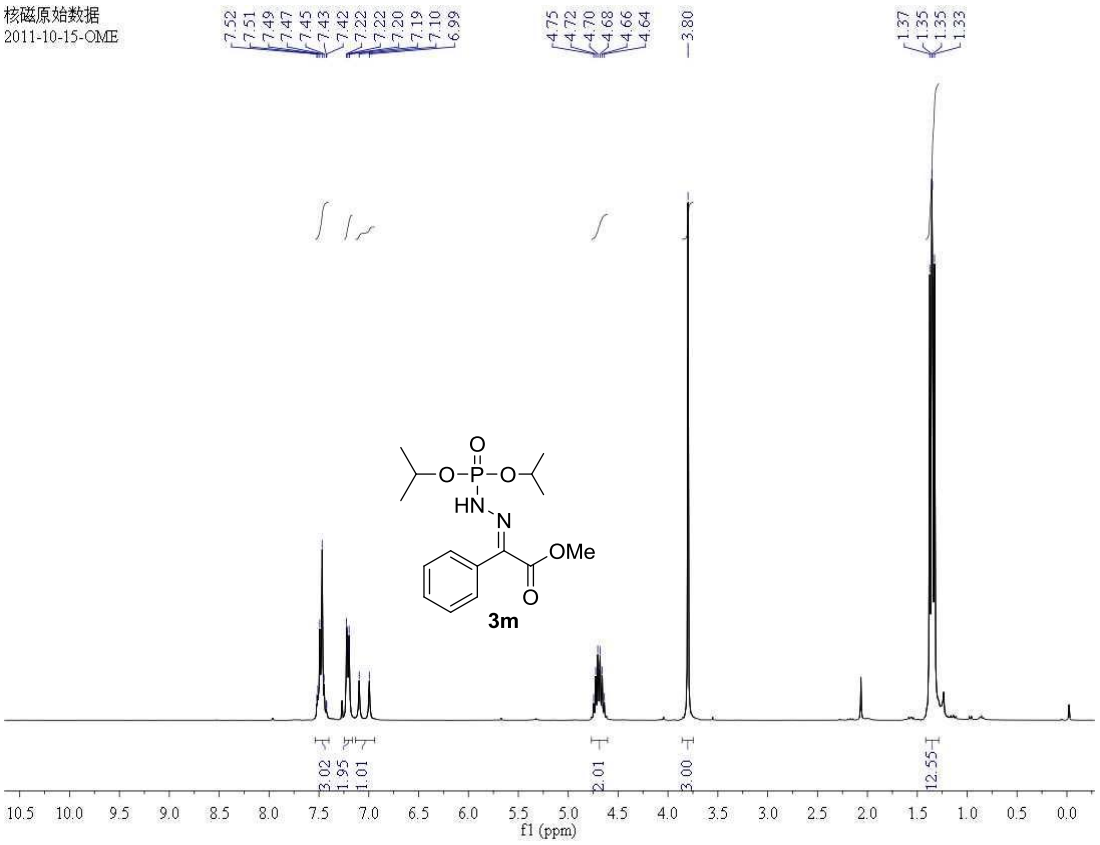
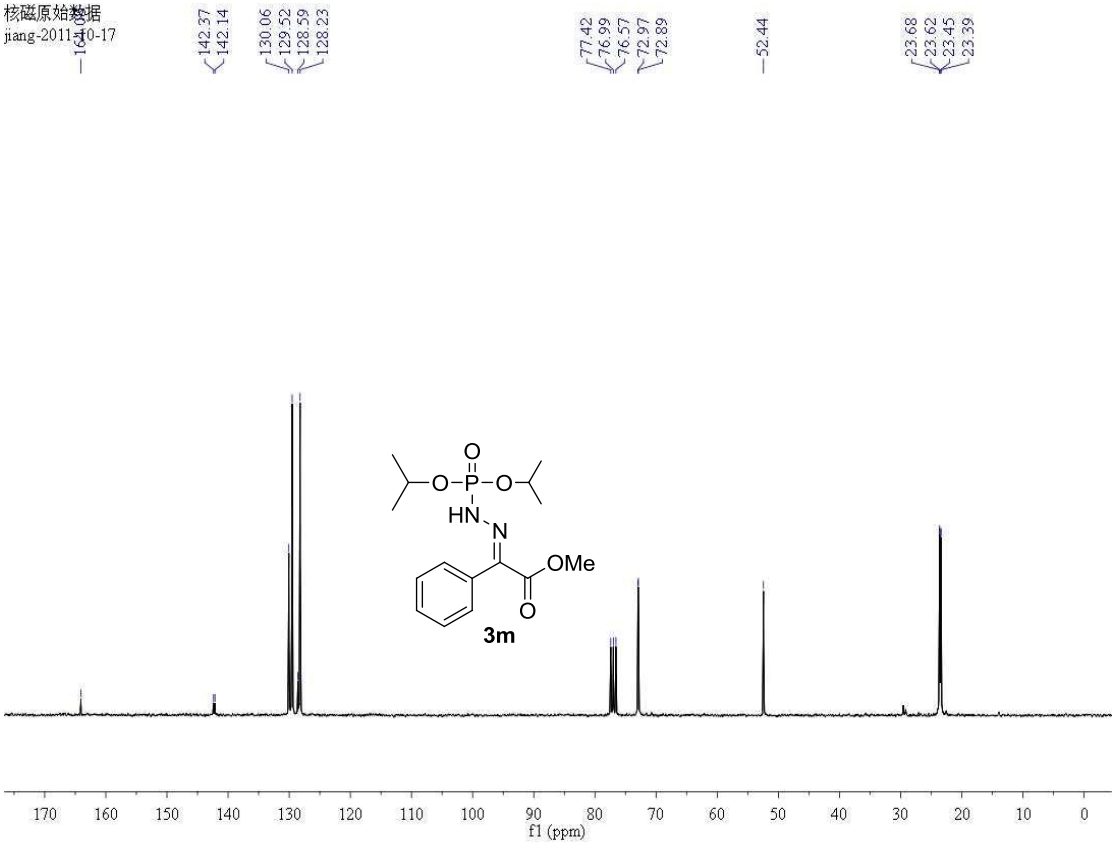


磷谱
LL-1 CDCL3 31P BRUKER DRX500







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LL-1 CDCL3 31P BRUKER DRX500

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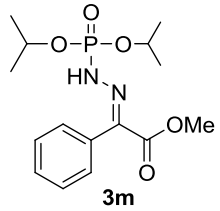

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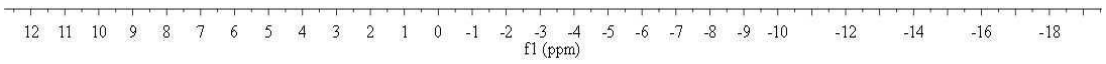
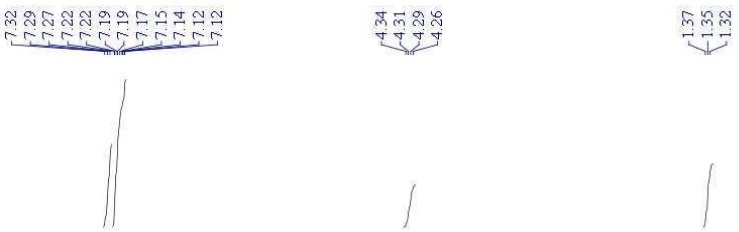
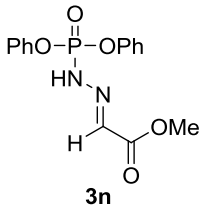


核磁原始数据
2011-10-15-OME





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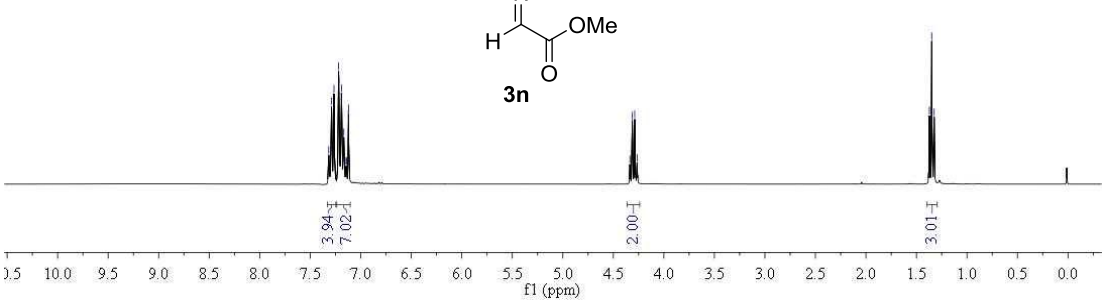

核磁原始数据
jiang-2011-10-25

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120.56
77.39
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76.54
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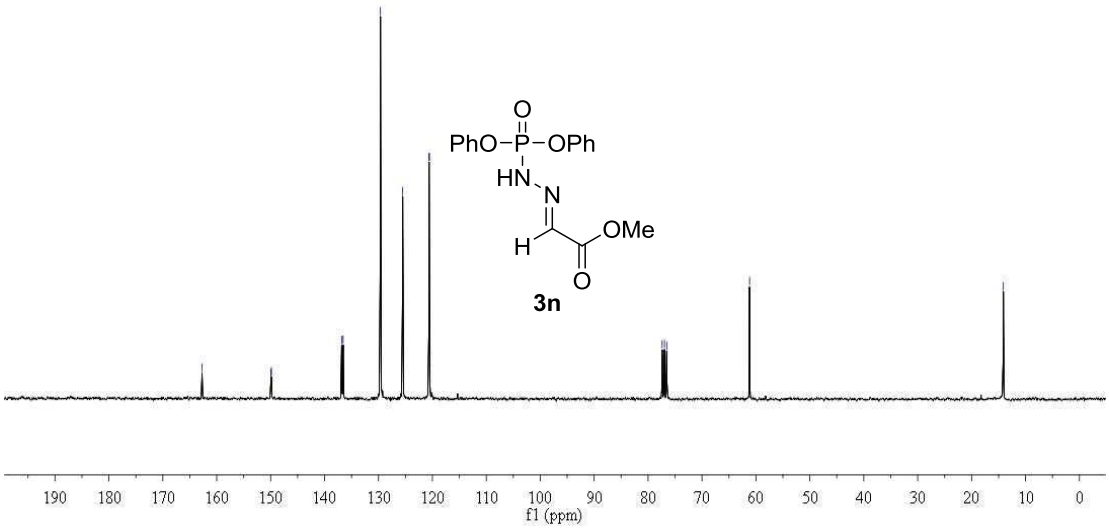
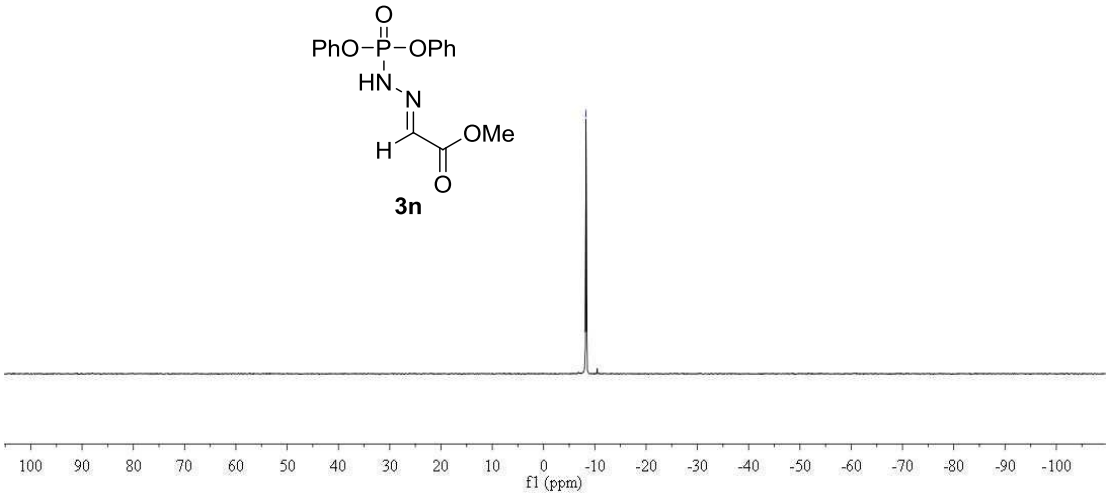
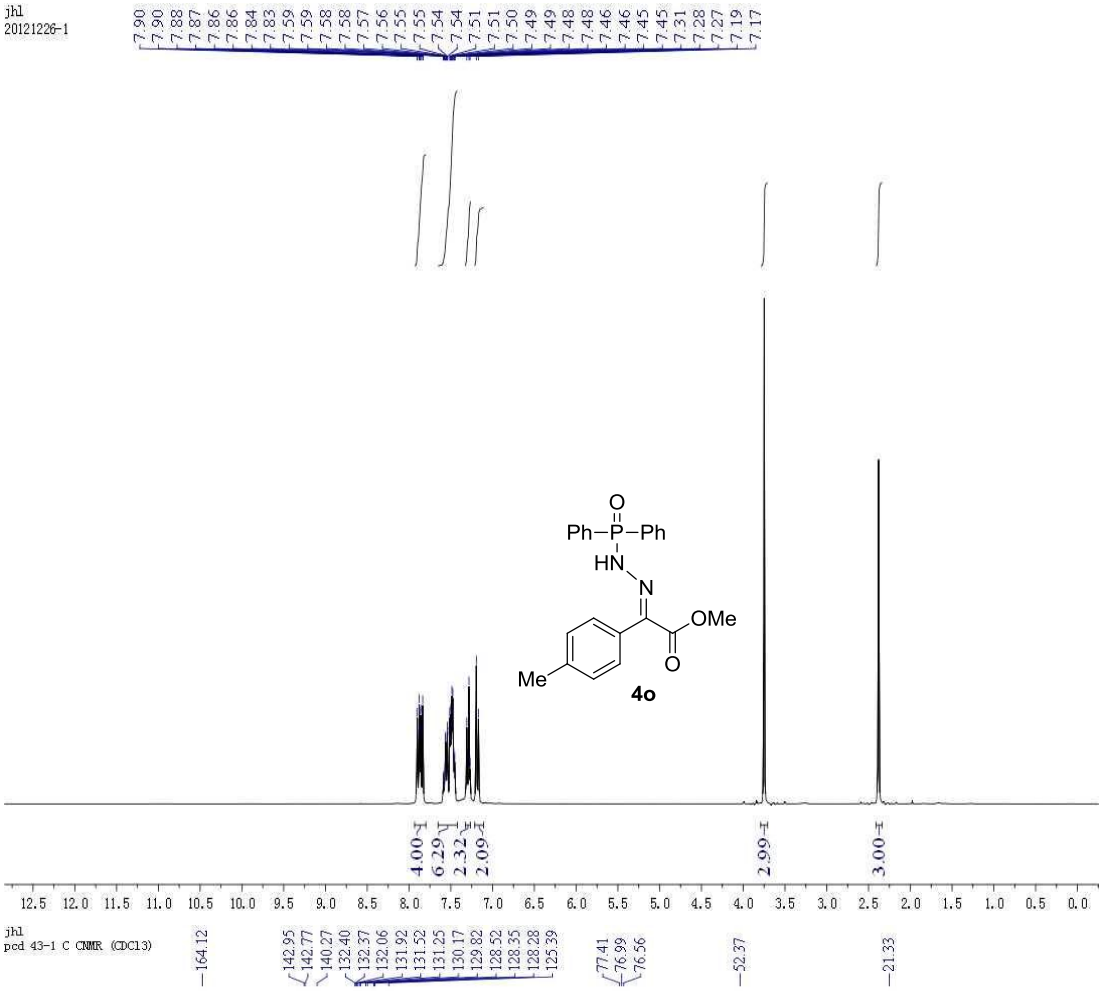
14.11



磷谱
IR-P-ACID CDCL3 31P BRUKER DRX500

8.27

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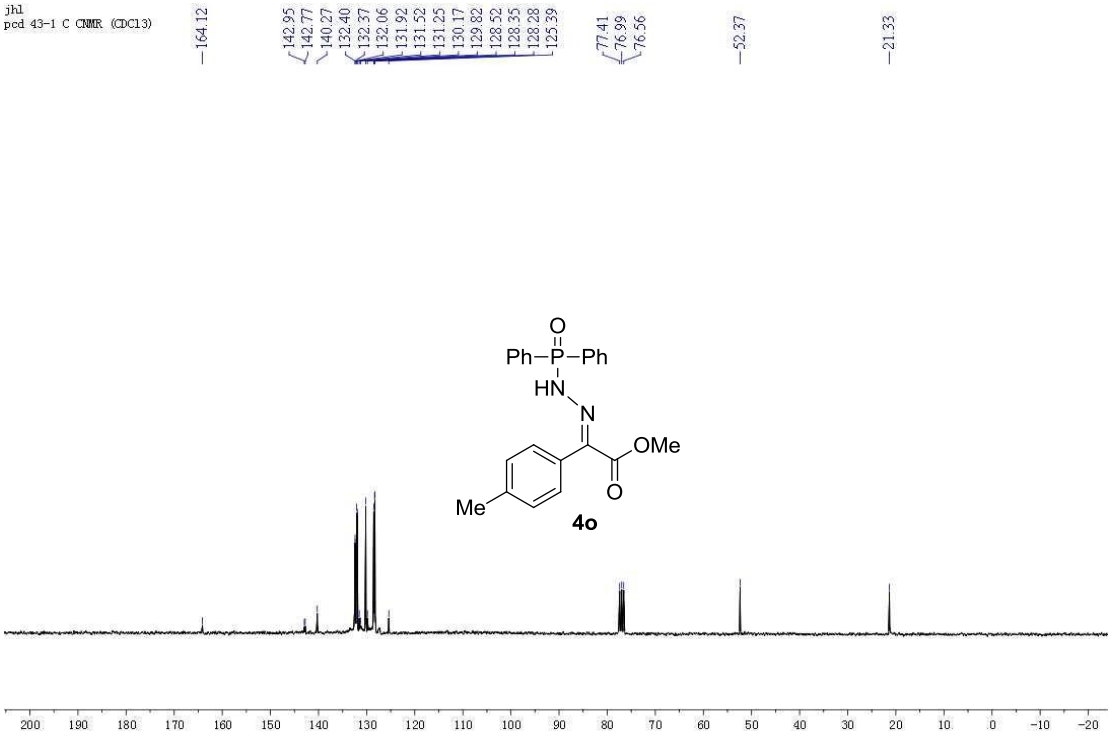
7.48
7.48
7.46
7.46
7.45
7.45
7.31
7.28
7.27
7.19
7.17
O
Ph–P–Ph
HN
N
OMe
O
Me
4o
4.00
6.29
2.32
2.09
2.99
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


jhl
pcd 43-1 C CNMR (CDCl3)
164.12
142.95
142.77
140.27
132.40
132.37
132.06
131.92
131.52
131.25
130.17
129.82
128.52
128.35
128.28
125.39
77.41
76.99
76.56
52.37
21.33
O
Ph–P–Ph
HN
N
OMe
O
Me
4o
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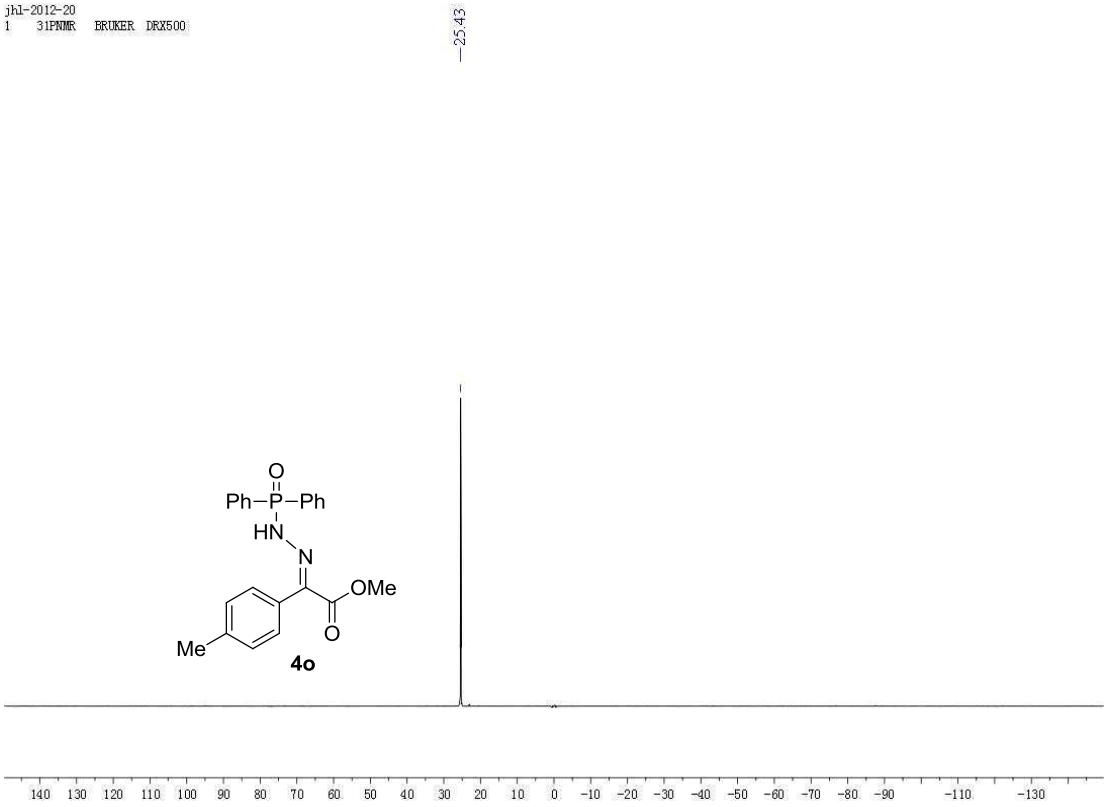
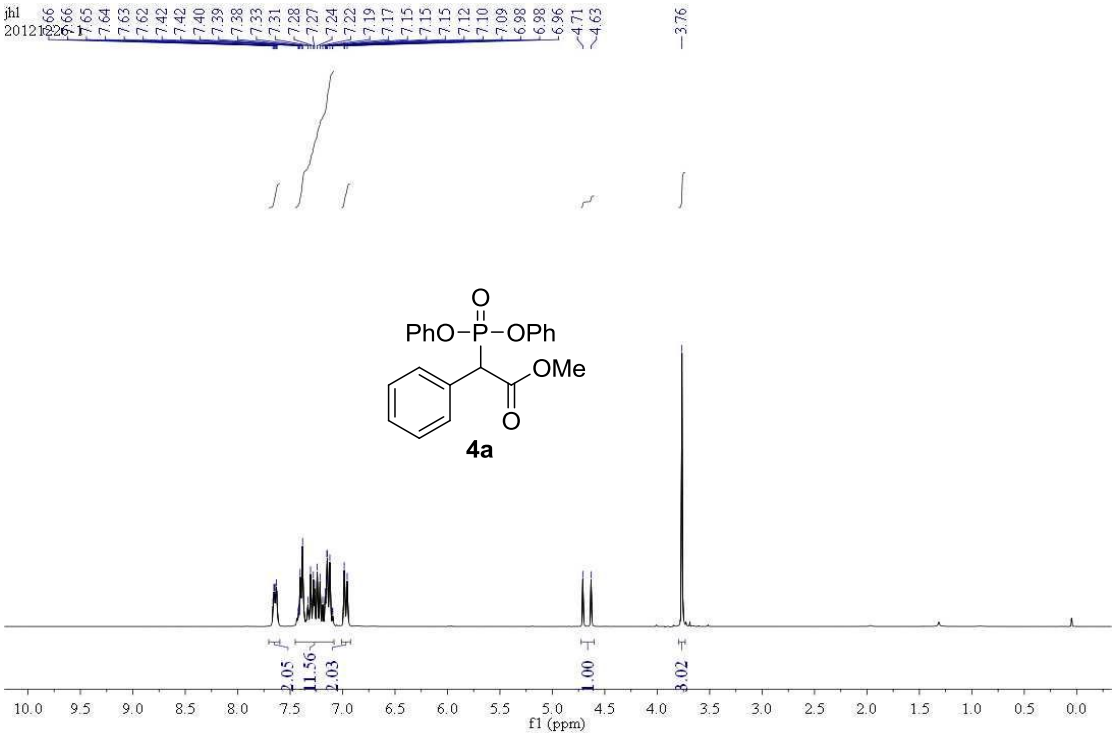


PDF file of copies ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra for new compounds form P–H insertion.



jh1
31-3 CNMR (CDCl3)

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128.45
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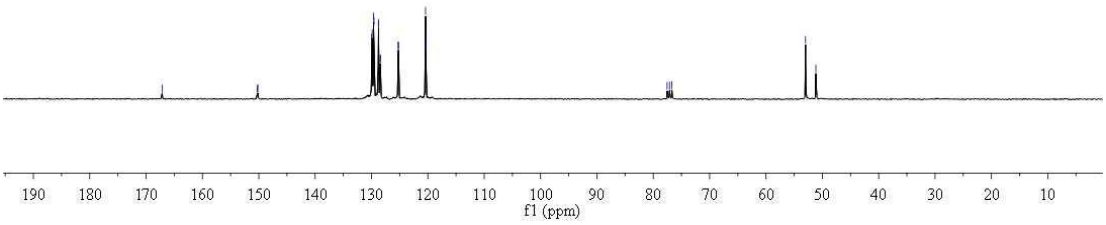
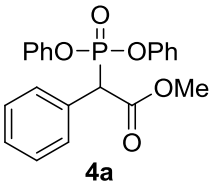
51.14

4a

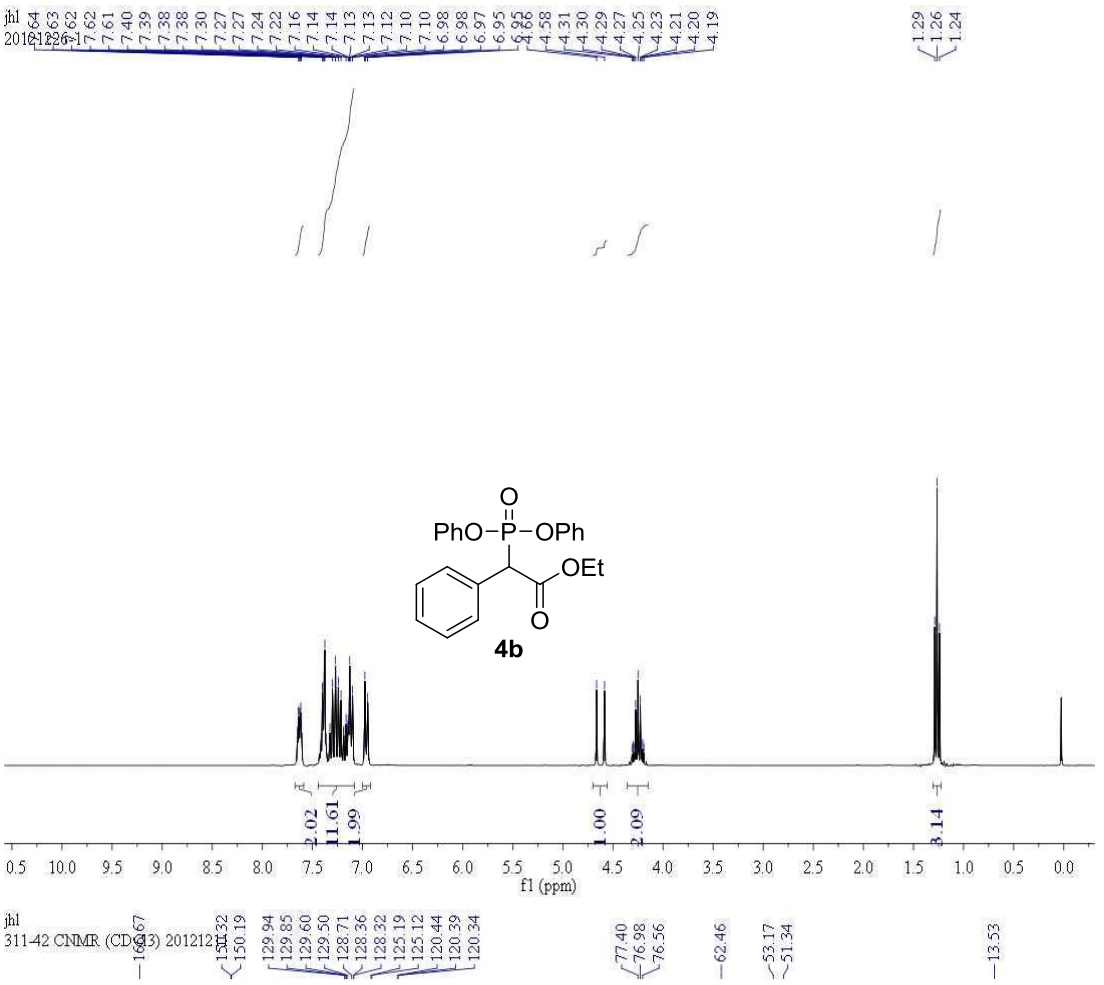


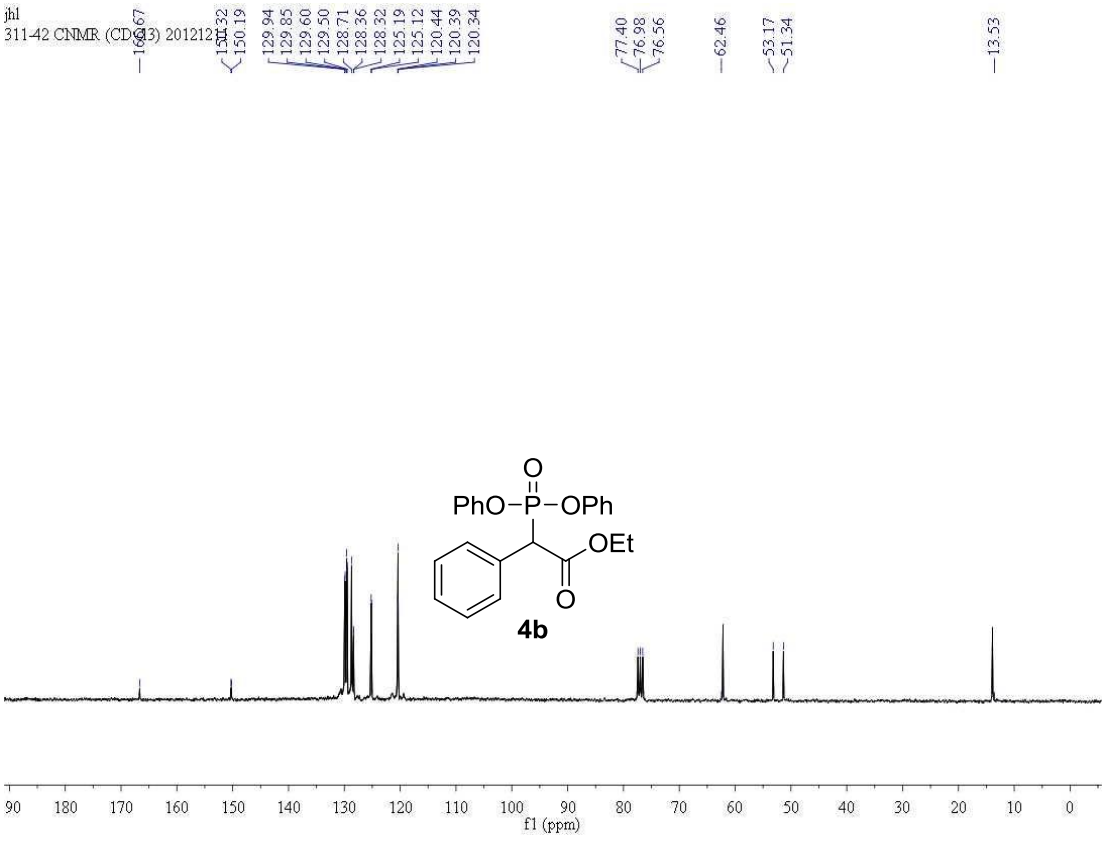
jh1-2012-20
1 31PNMR BRUKER DRX500

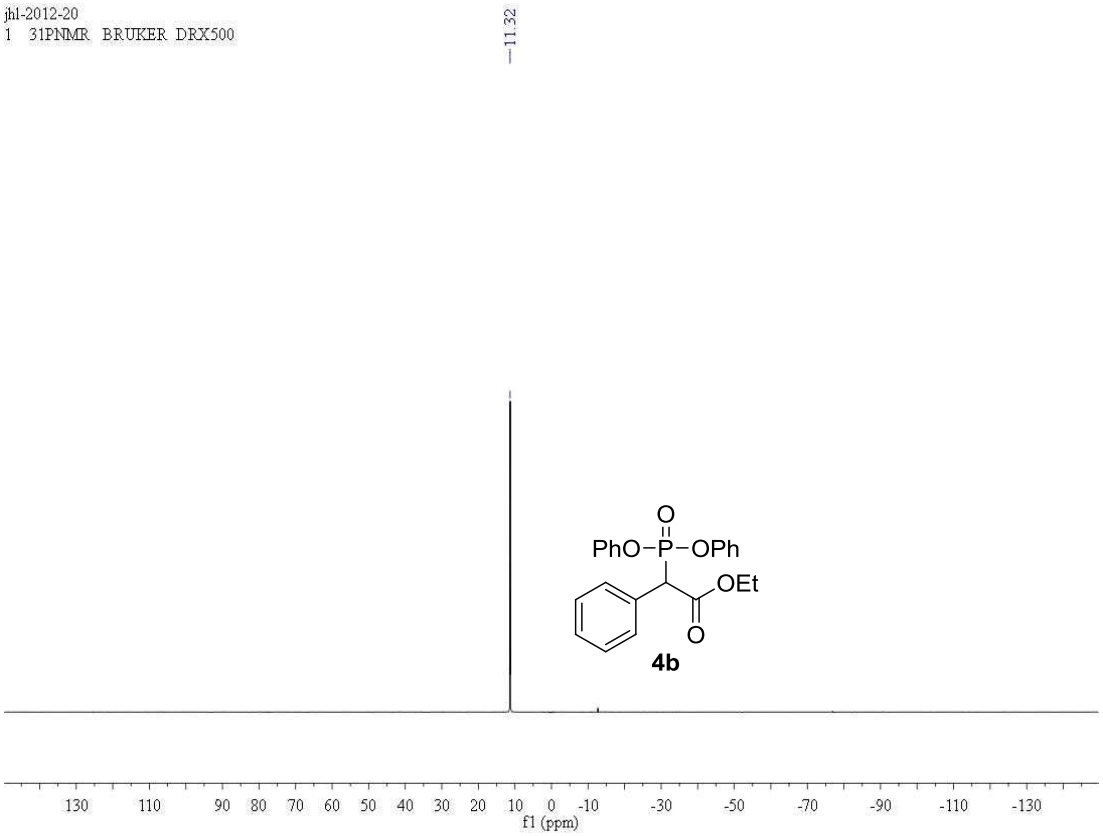
11.24

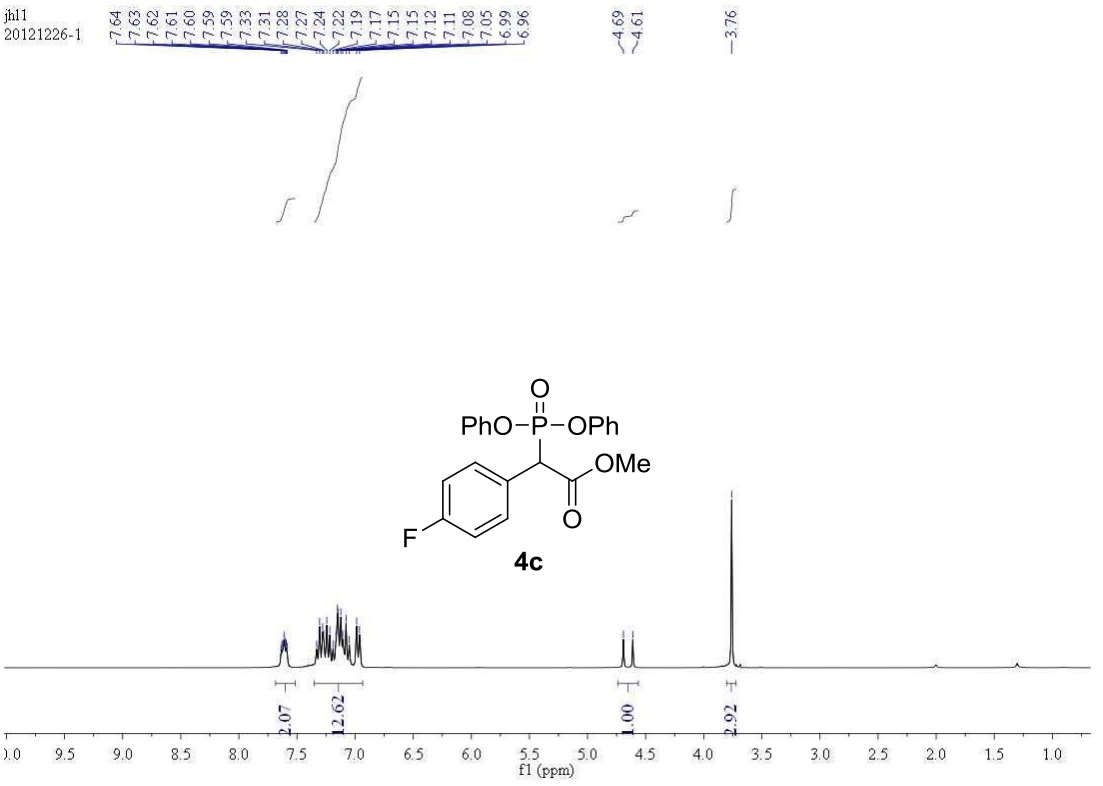


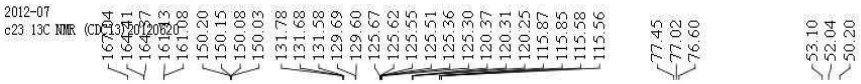
4a

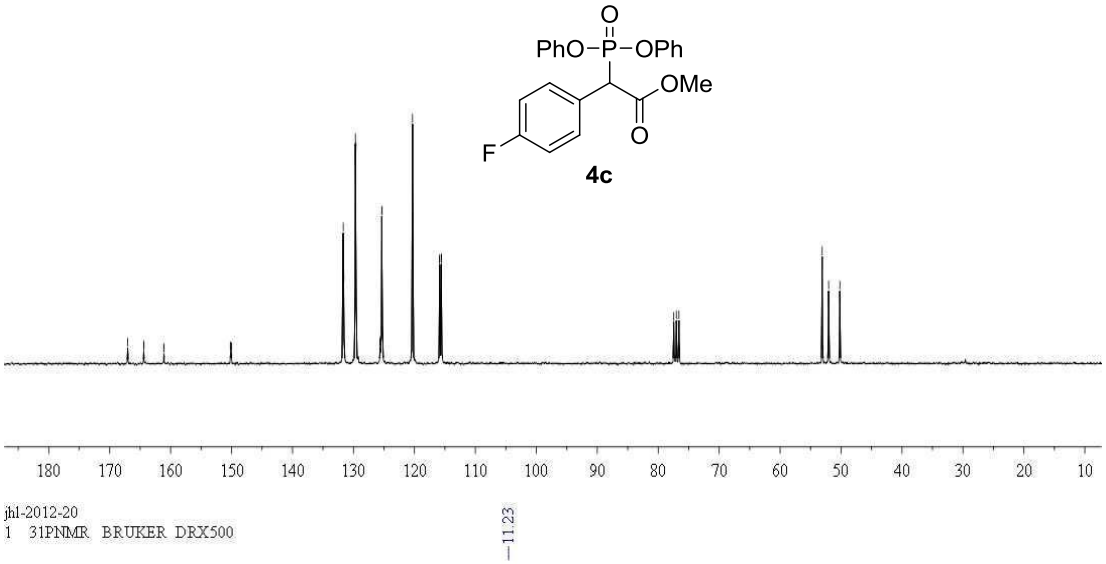




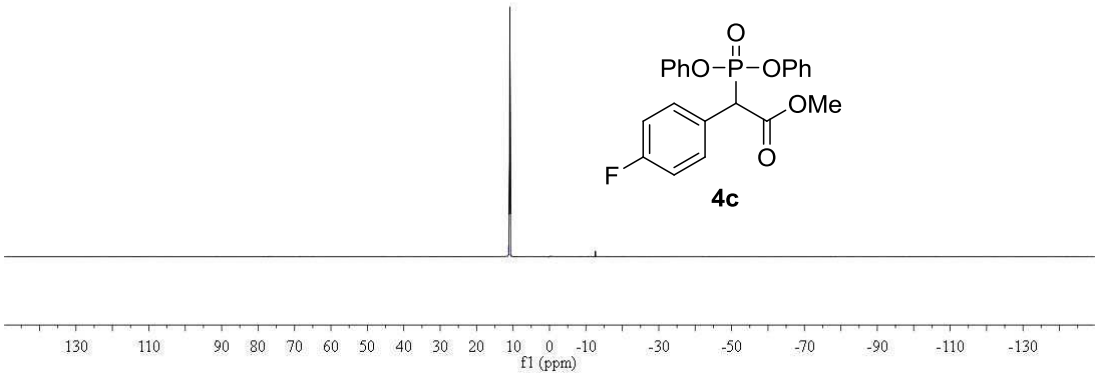


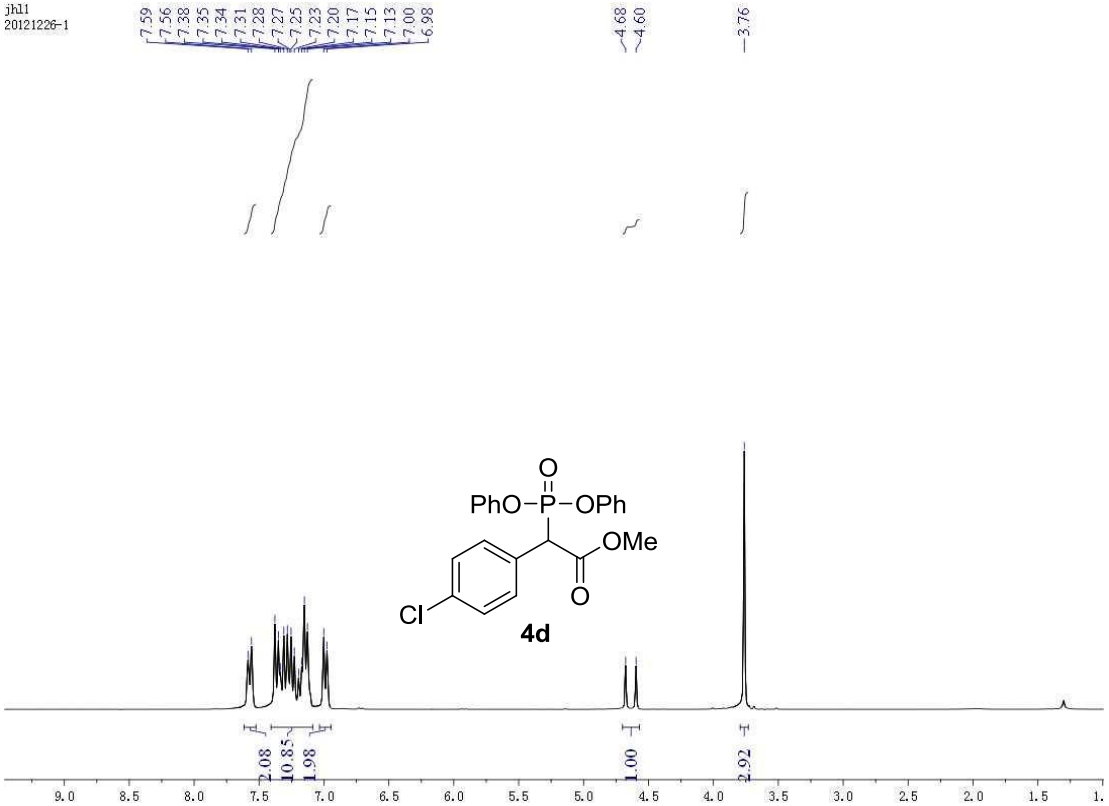


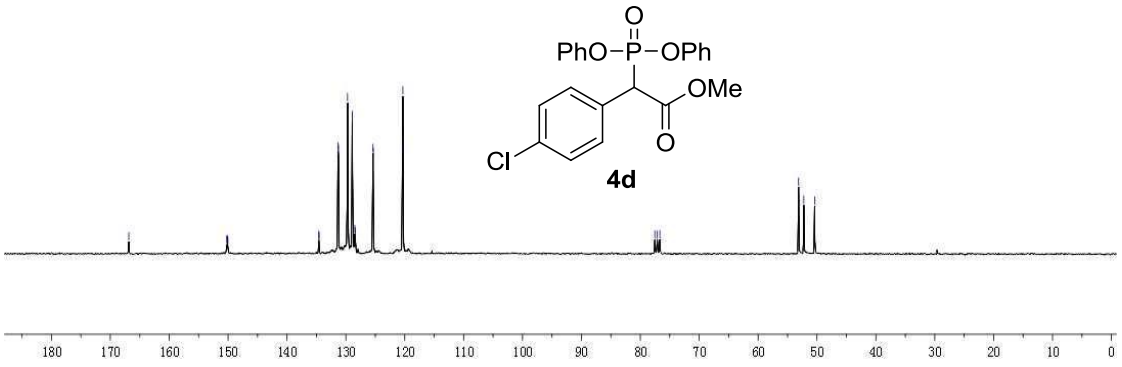

2012-07
c23 13C NMR (CDCl3,20120625)
167.84
164.11
164.07
161.73
161.08
150.20
150.15
150.08
150.03
131.78
131.68
131.58
129.69
129.60
125.67
125.62
125.55
125.51
125.36
125.30
120.37
120.31
120.25
115.87
115.85
115.58
115.56
77.45
77.02
76.60
53.10
52.04
50.20

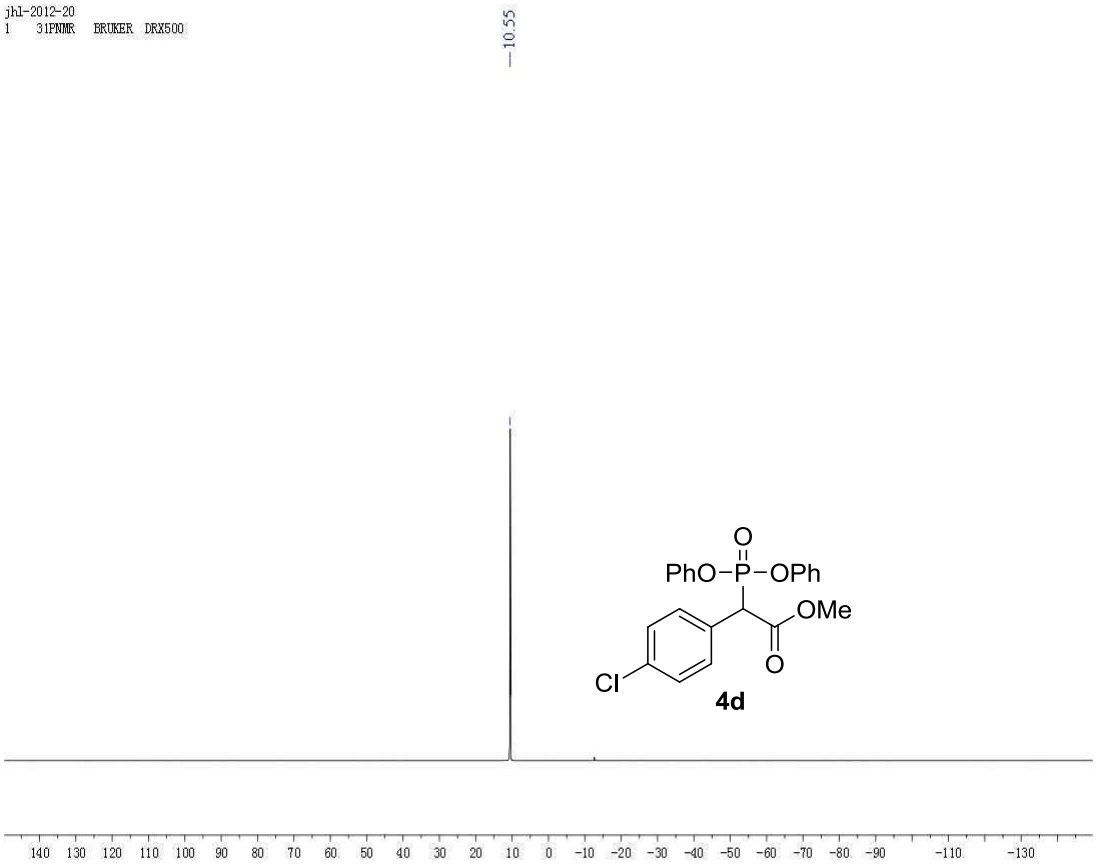

O
PhO−P−OPh
OMe
O
F
4c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

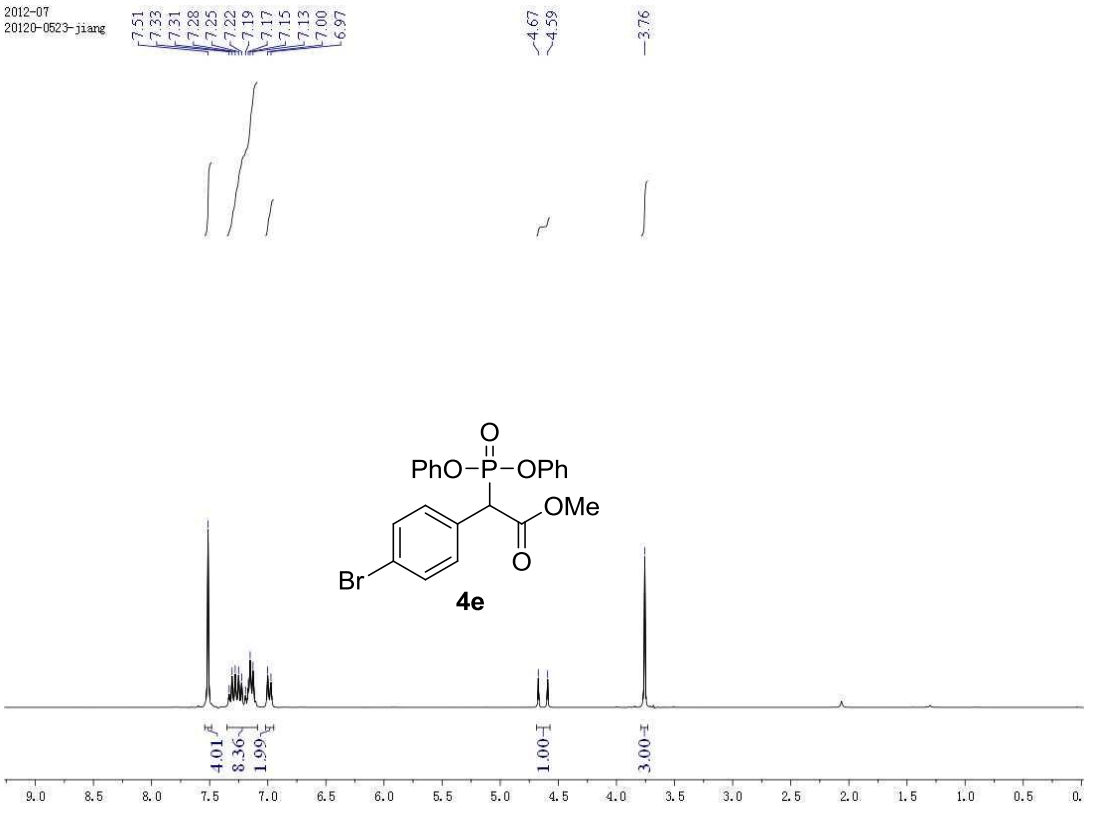
jh1-2012-20
1 31PNMR BRUKER DRX500
11.23

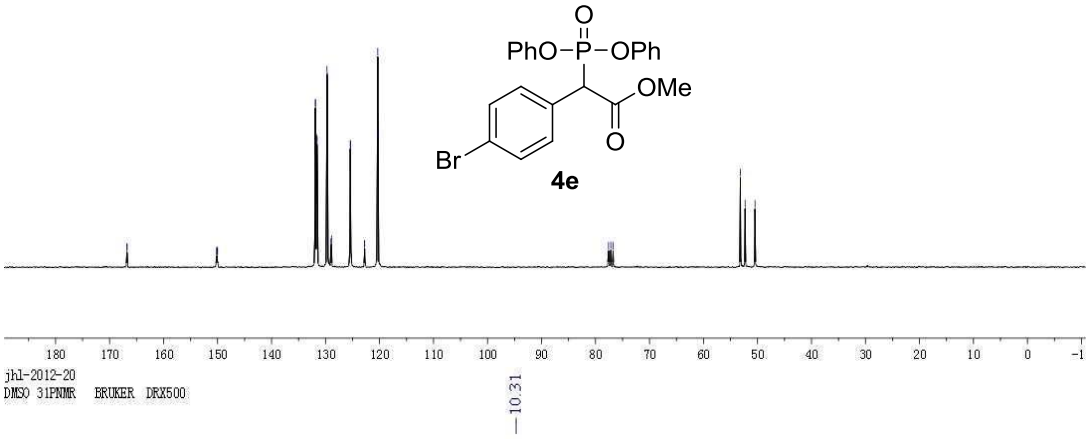

O
PhO−P−OPh
OMe
O
F
4c
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
f1 (ppm)

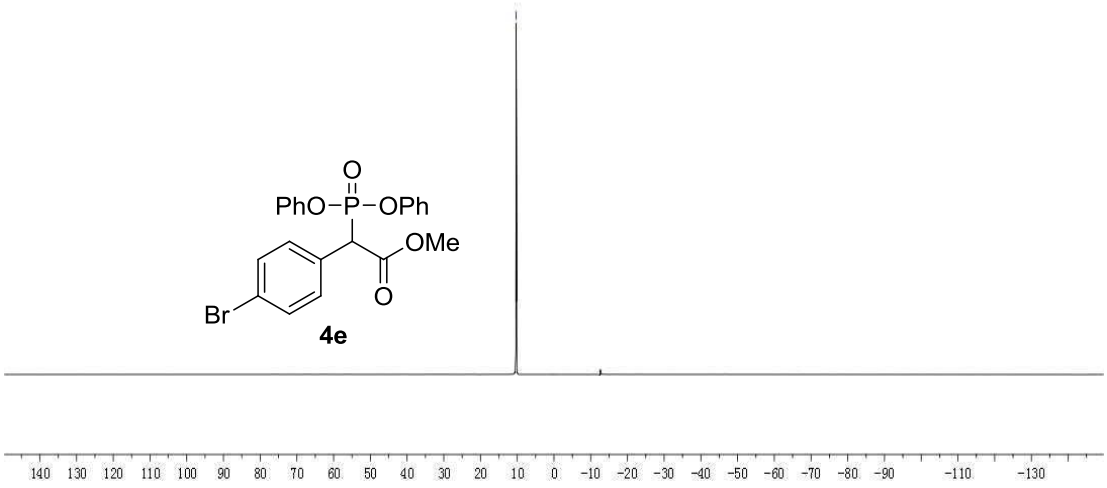


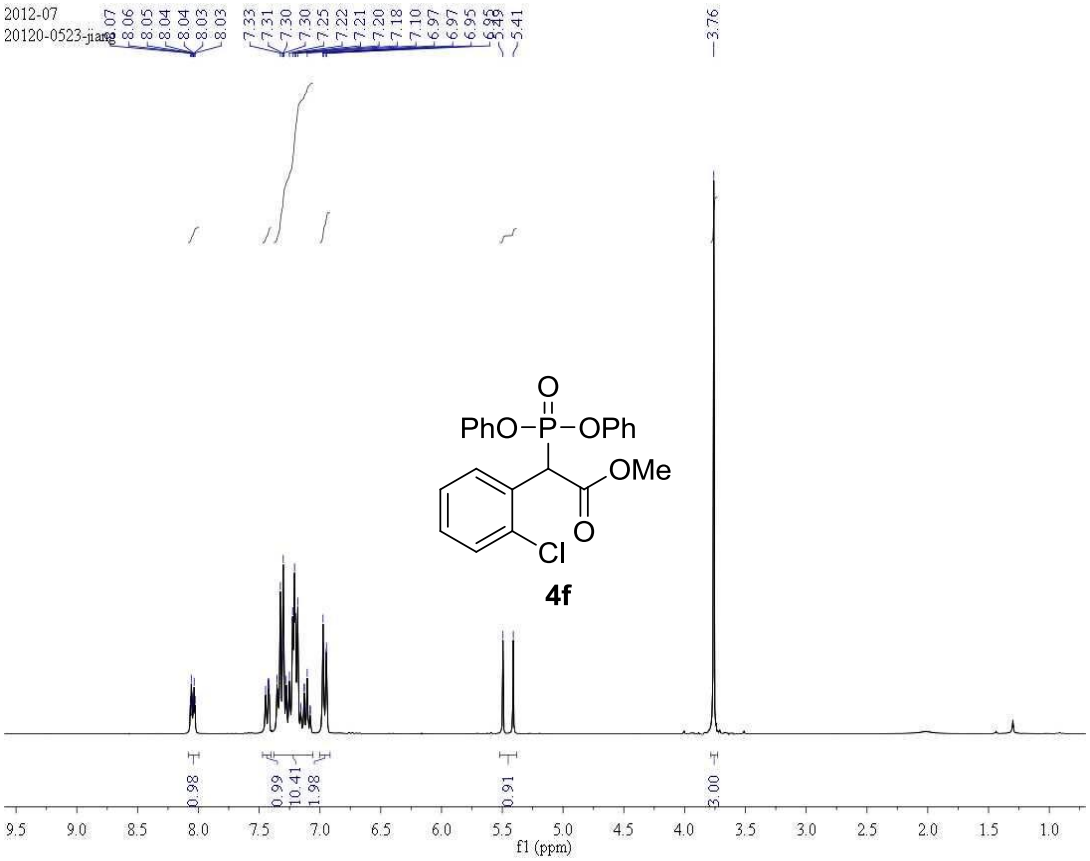


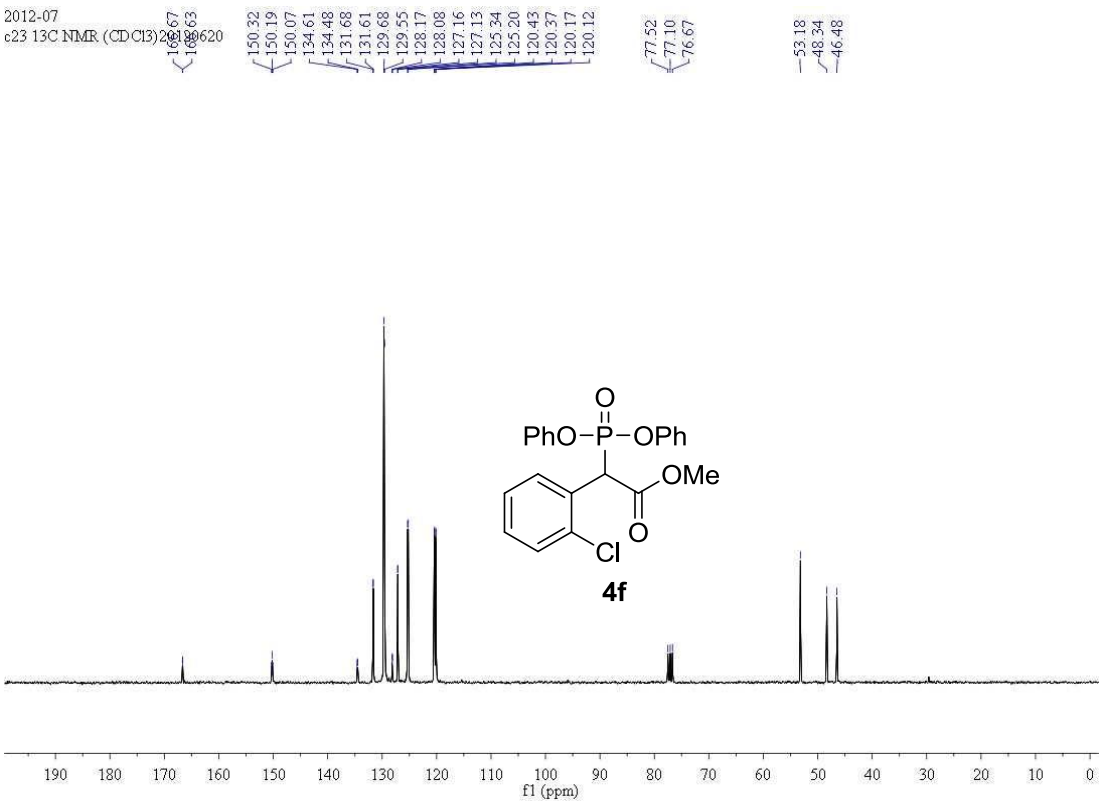

jhl-2012-20
1 31PNMR BRUKER DRX500
10.55
PhO−P−OPh
O
OMe
O
Cl
4d
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130

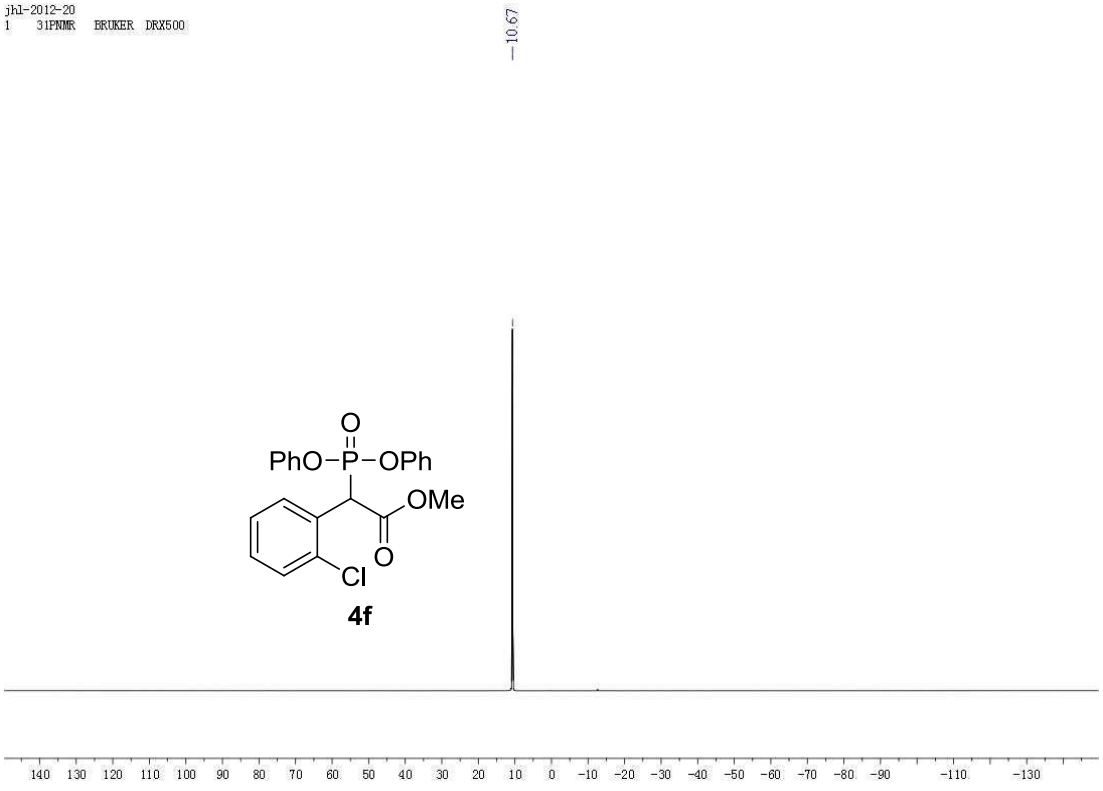

2012-07
20120-0523-jiang
7.51
7.33
7.31
7.28
7.25
7.22
7.19
7.17
7.15
7.13
7.00
6.97
4.67
4.59
3.76
PhO−P−OPh
O
OMe
O
Br
4e
4.01
8.36
1.99
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.

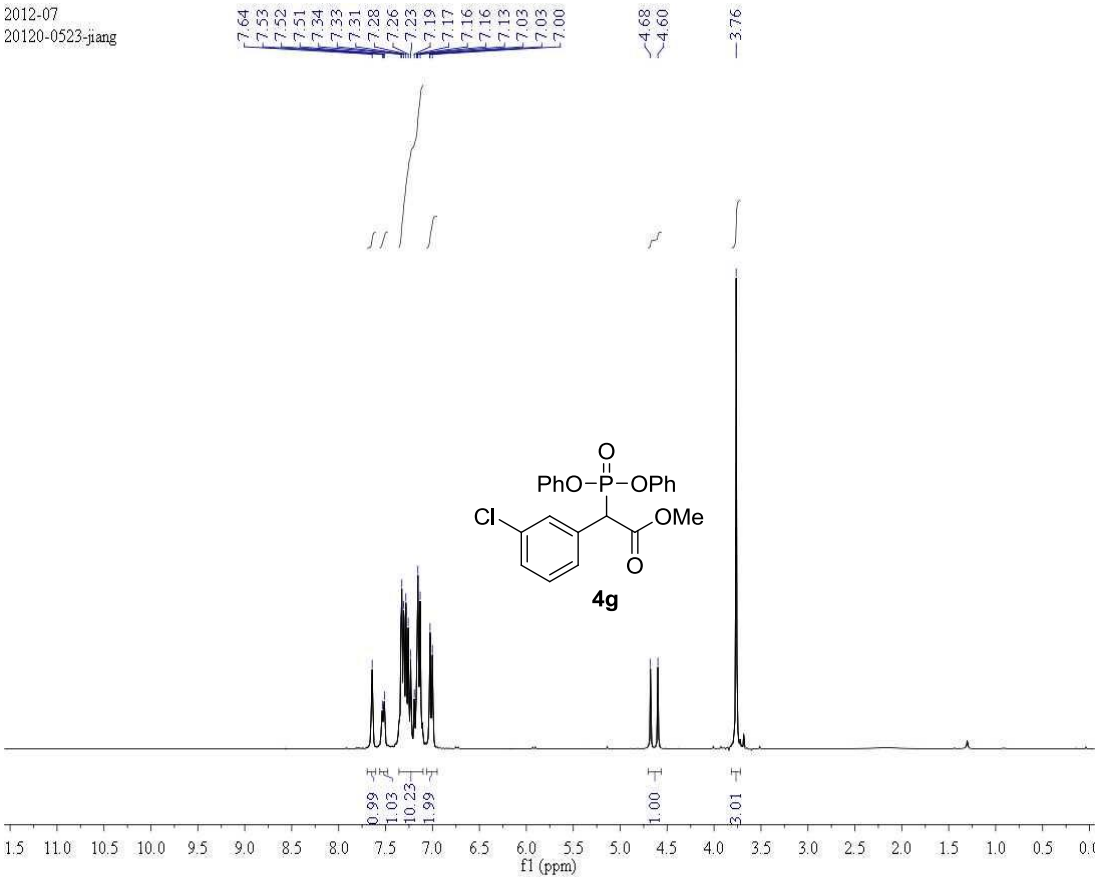


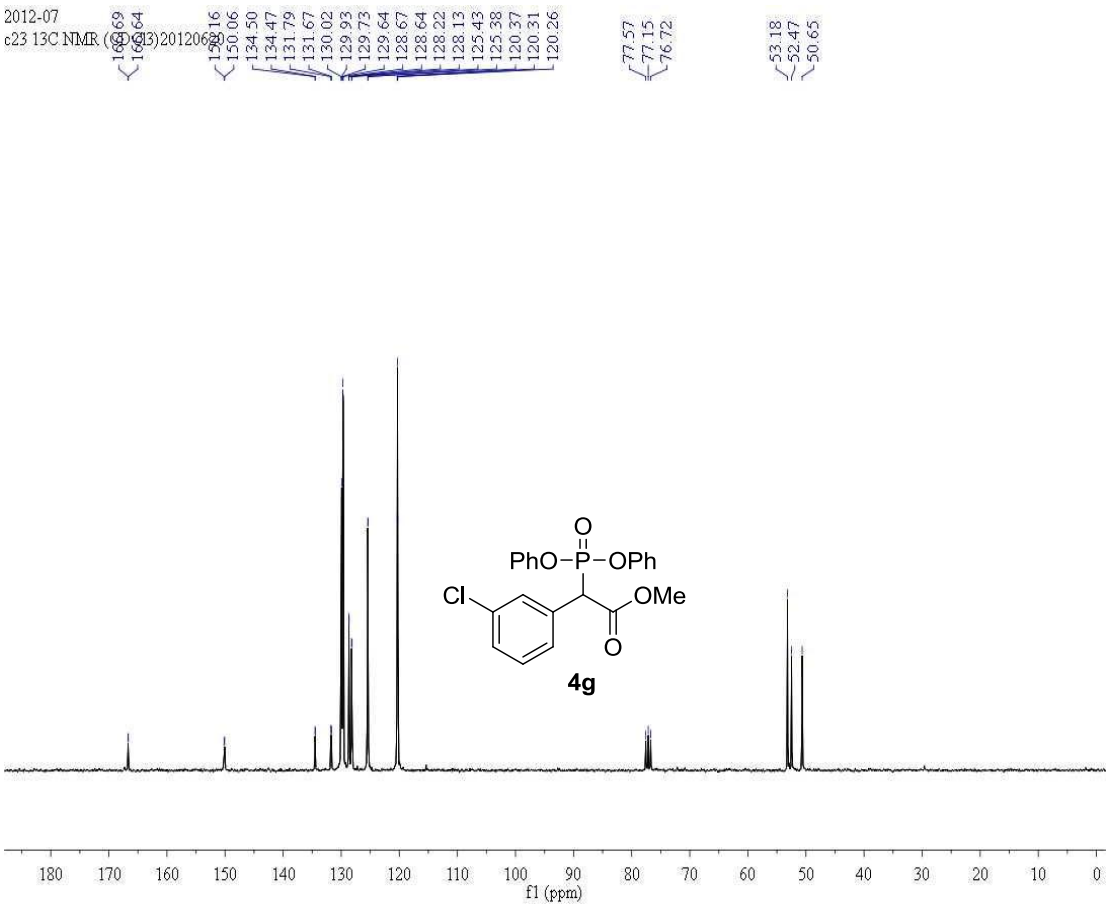


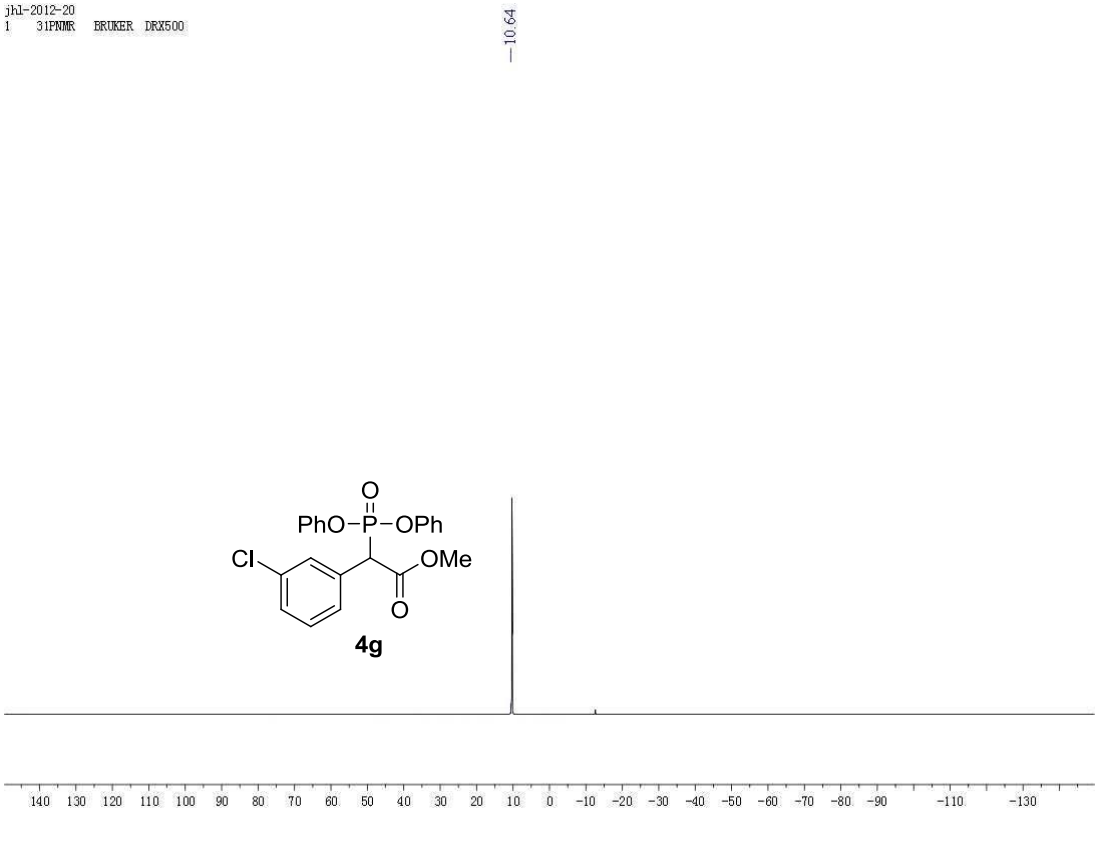

2012-07
20120-0523-jiang
8.07
8.06
8.05
8.04
8.04
8.03
8.03
7.33
7.31
7.30
7.30
7.25
7.22
7.21
7.20
7.18
7.10
6.97
6.97
6.95
5.41
3.76
PhO−P−OPh
OMe
O
O
Cl
4f
0.98
0.99
10.41
1.98
0.91
3.00
f1 (ppm)

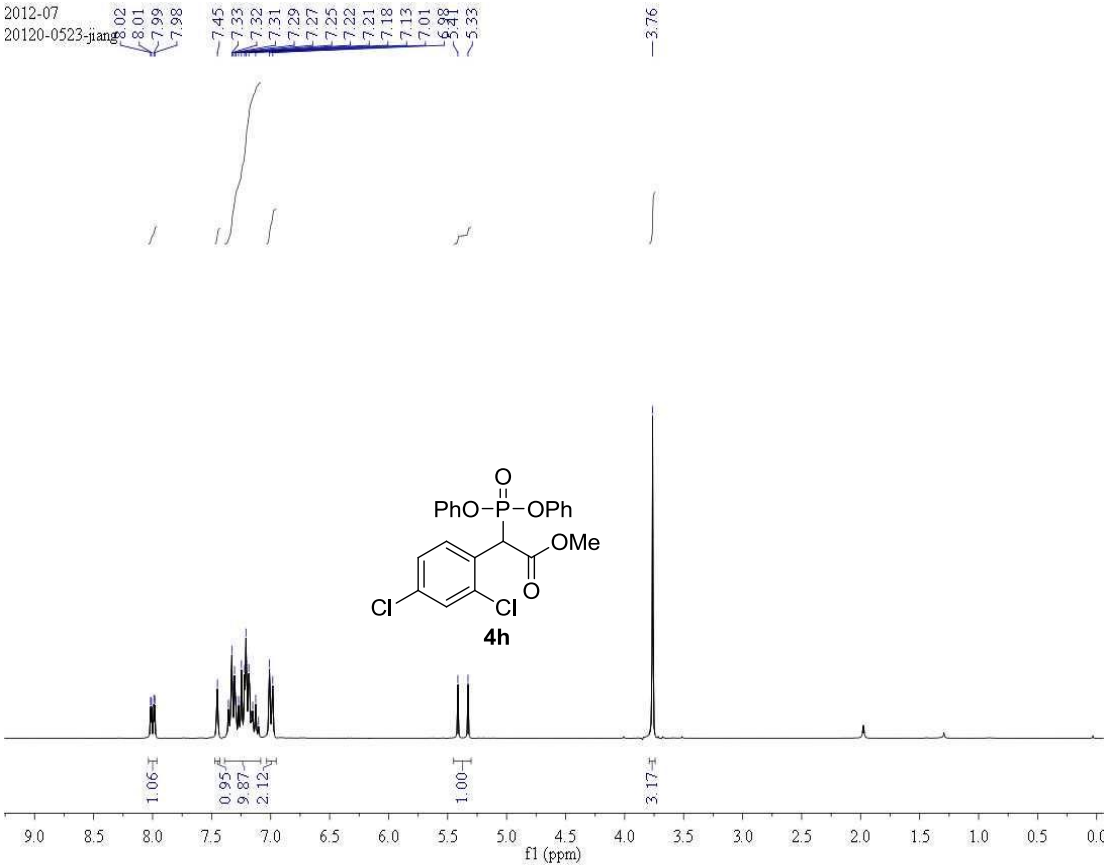

2012-07
c23 13C NMR (CDCl3) 20130620
166.67
166.63
150.32
150.19
150.07
134.61
134.48
131.68
131.61
129.68
129.55
128.17
128.08
127.16
127.13
125.34
125.20
120.43
120.37
120.17
120.12
77.52
77.10
76.67
53.18
48.34
46.48
PhO−P−OPh
OMe
O
O
Cl
4f
f1 (ppm)

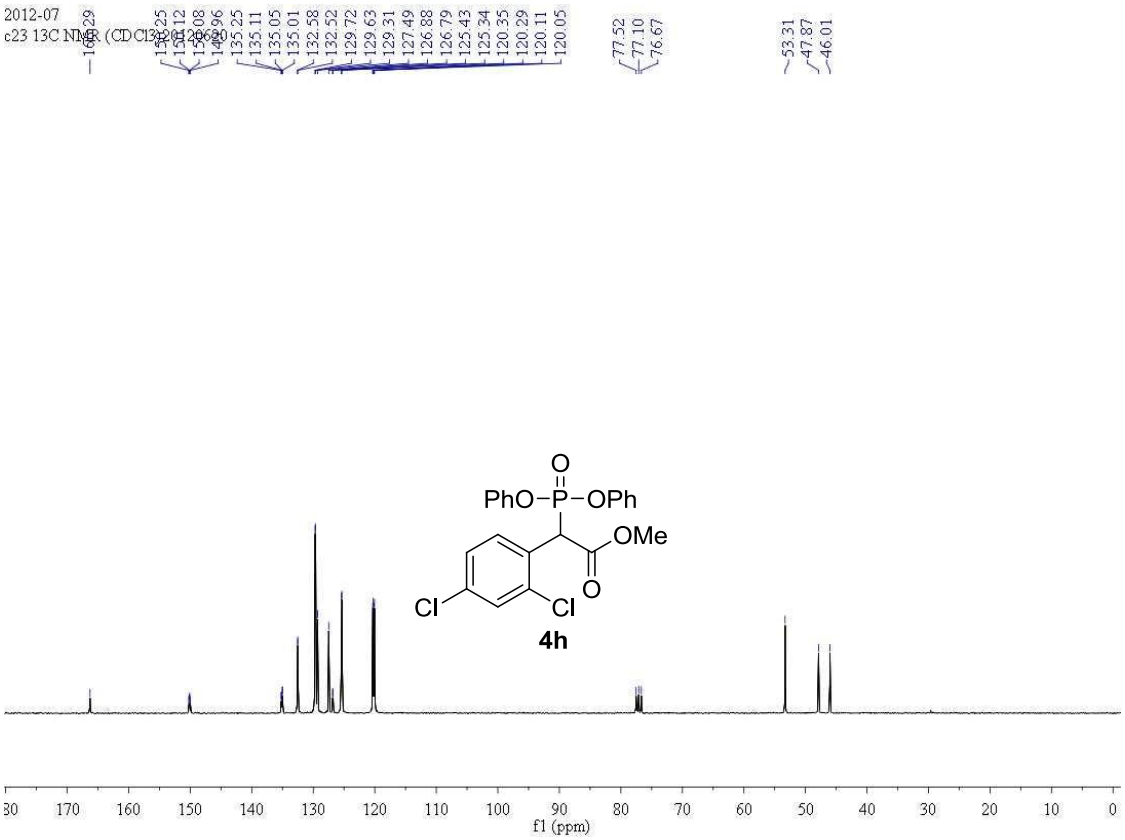


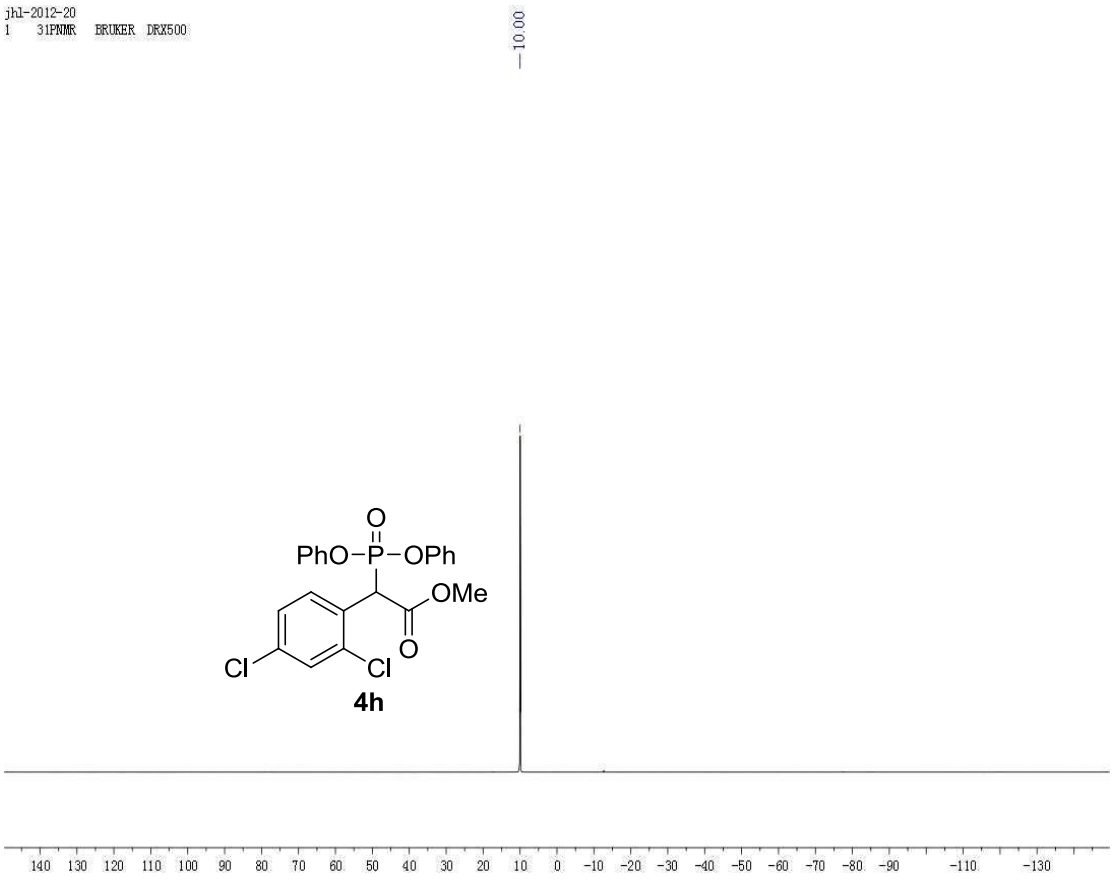


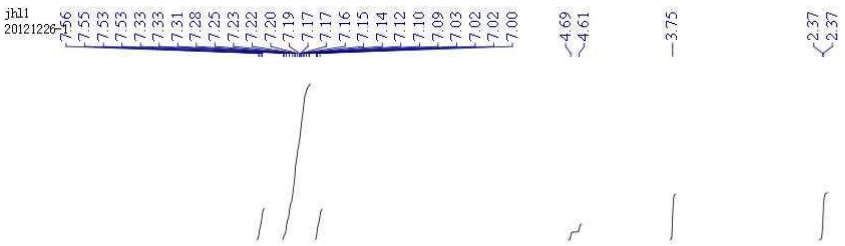


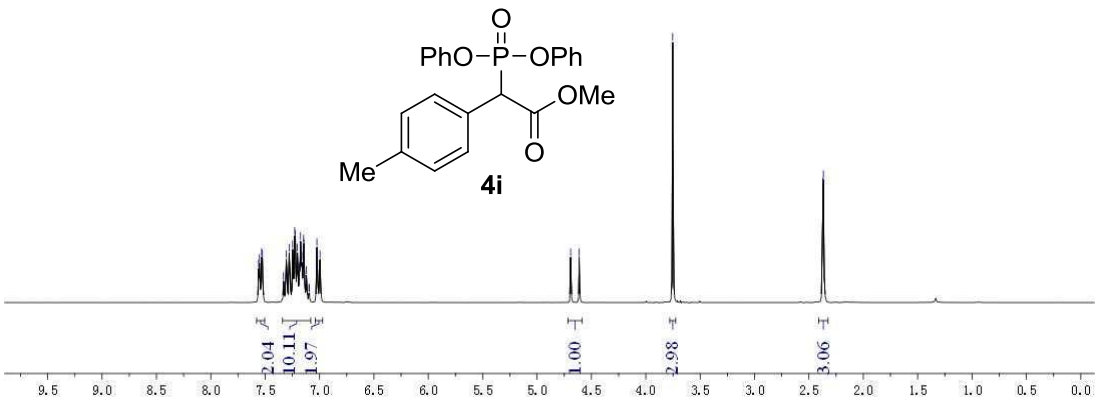


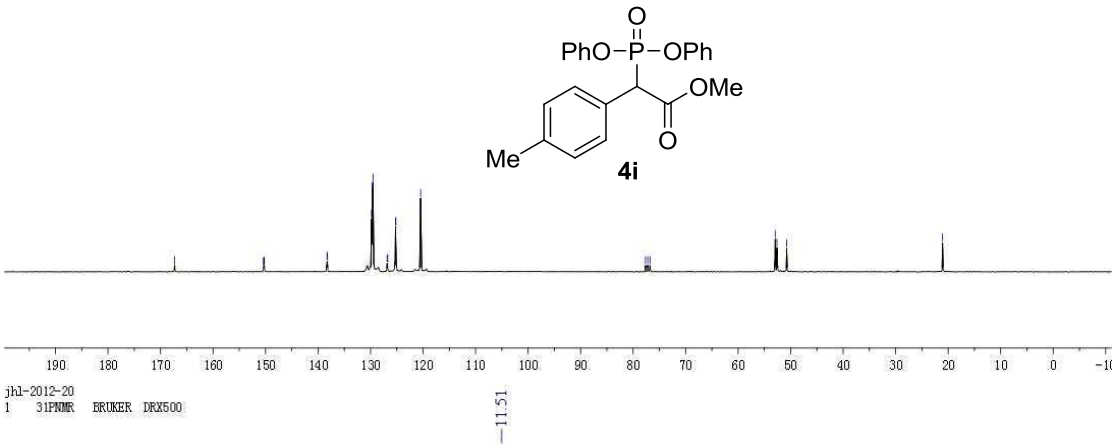


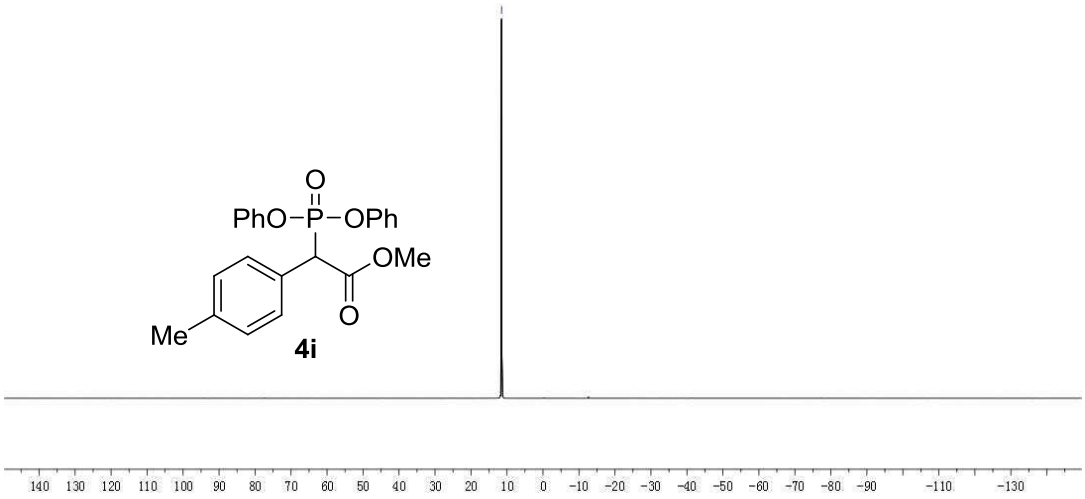


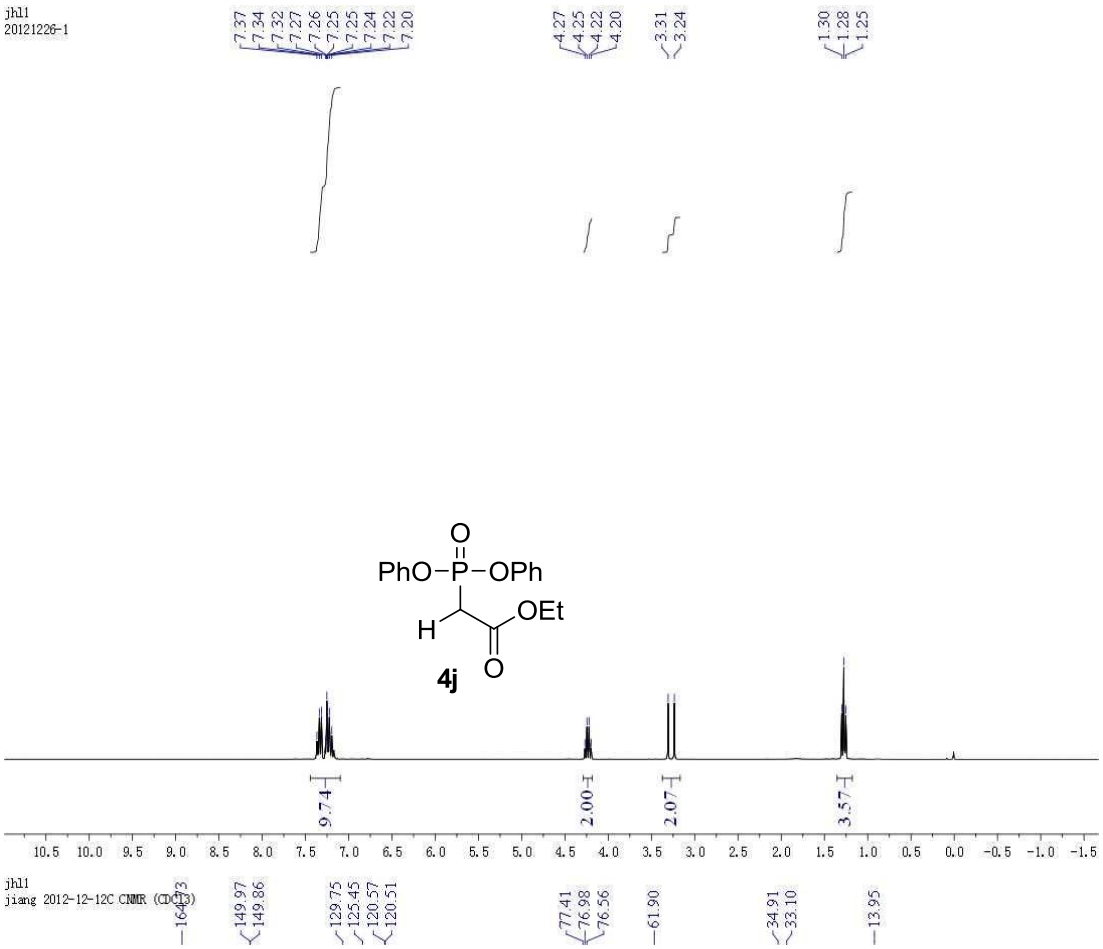

jhl-2012-20
1 31PNMR BRUKER DRX500
10.00
O
PhO−P−OPh
OMe
O
Cl
Cl
4h
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130

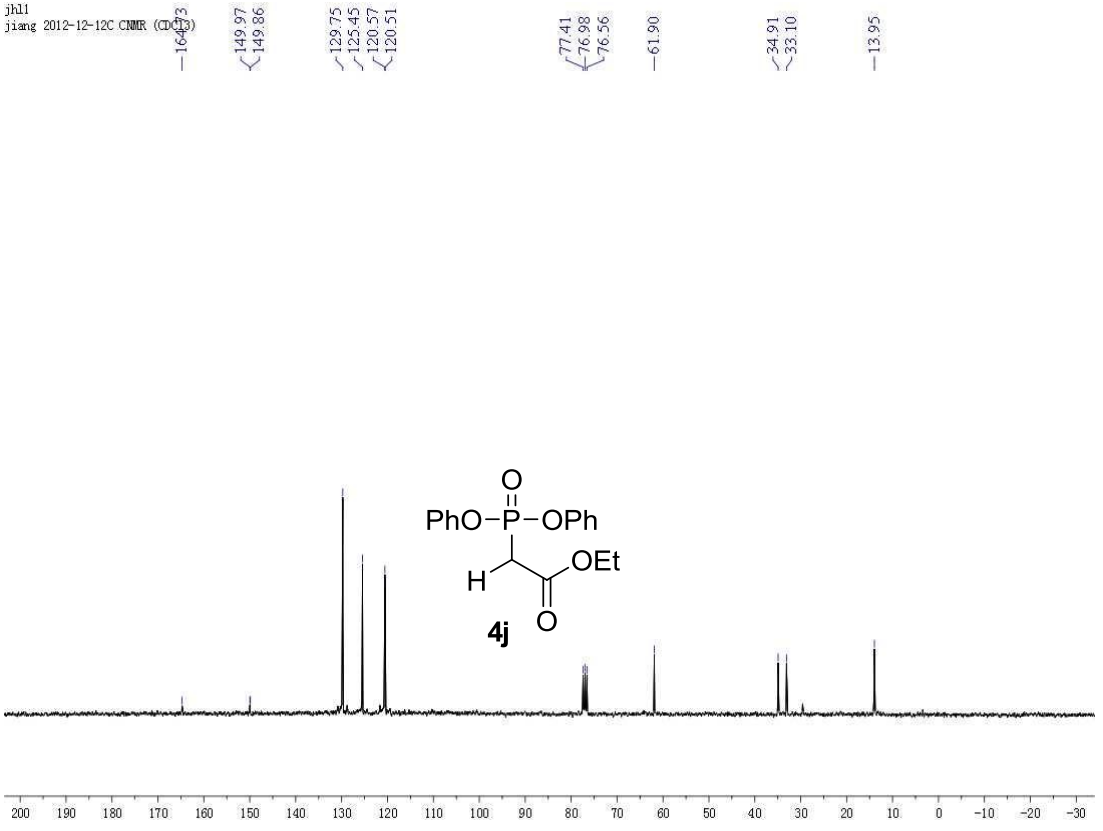

jhl
20121226-1
7.56 7.55 7.53 7.53 7.33 7.33 7.31 7.28 7.25 7.23 7.22 7.20 7.19 7.17 7.17 7.16 7.15 7.14 7.12 7.10 7.09 7.03 7.02 7.02 7.00
4.69 4.61
3.75
2.37 2.37

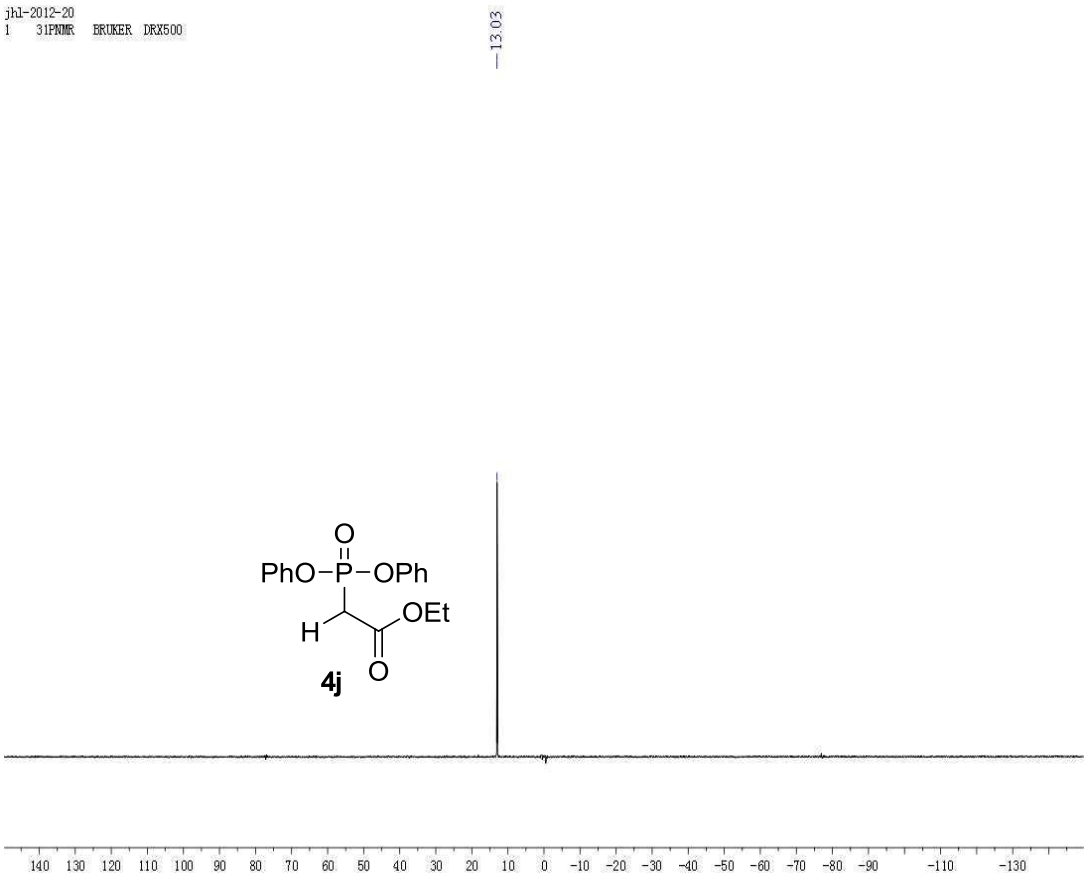

O
PhO−P−OPh
OMe
O
Me
4i
2.04 10.11 1.97 1.00 2.98 3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

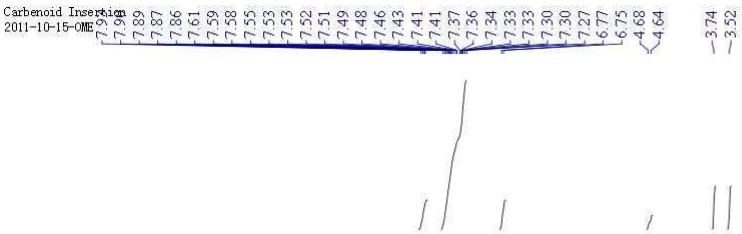


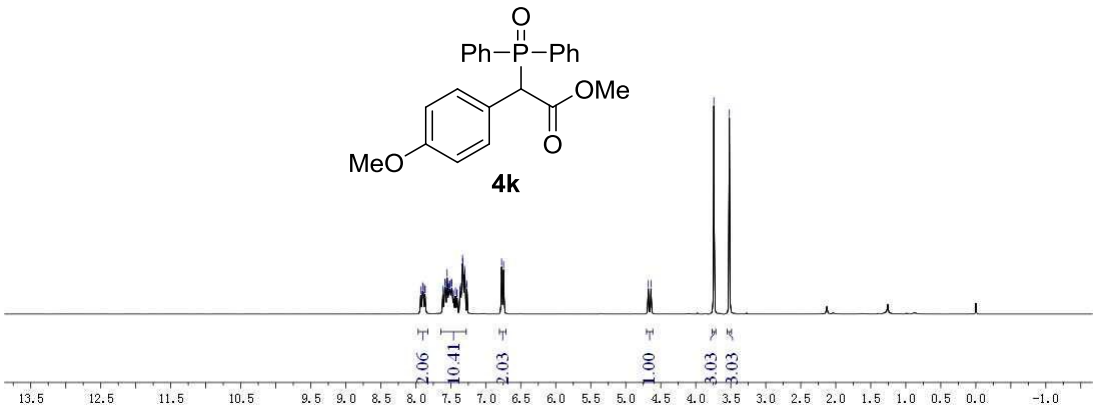


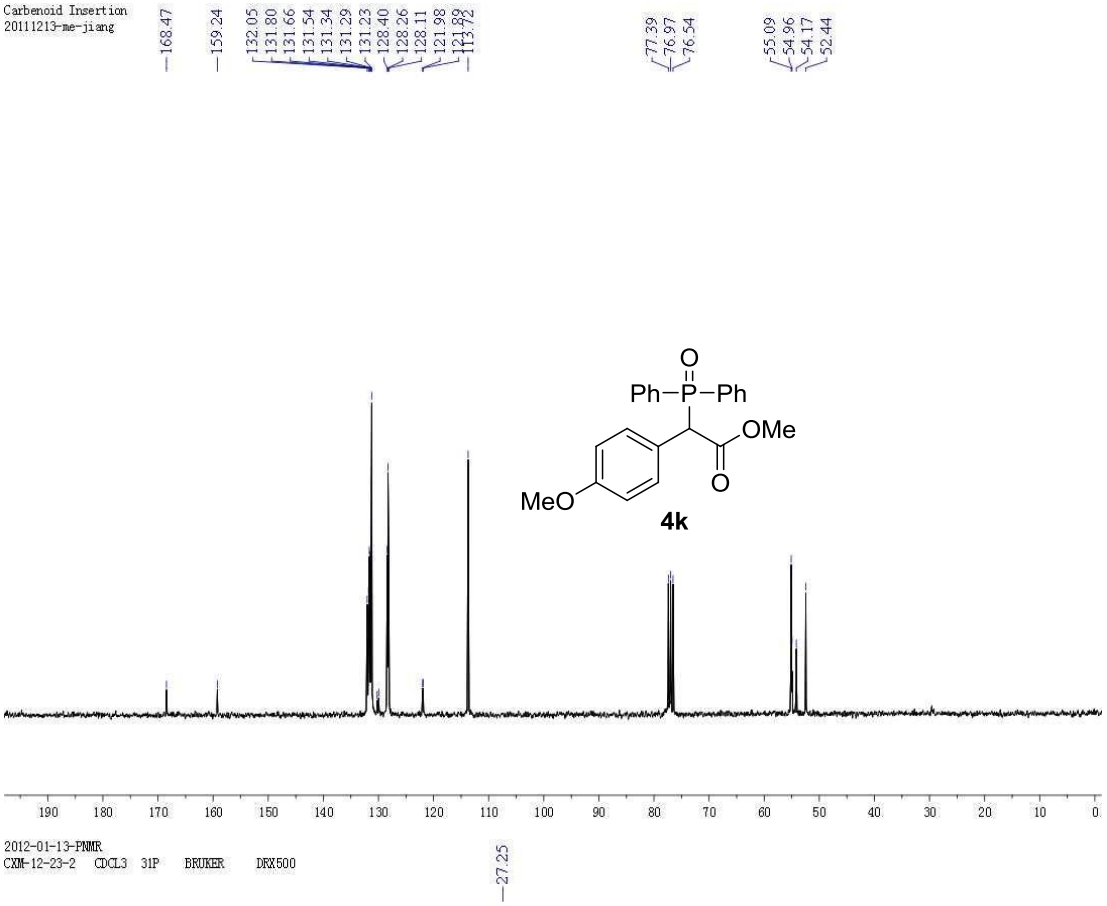


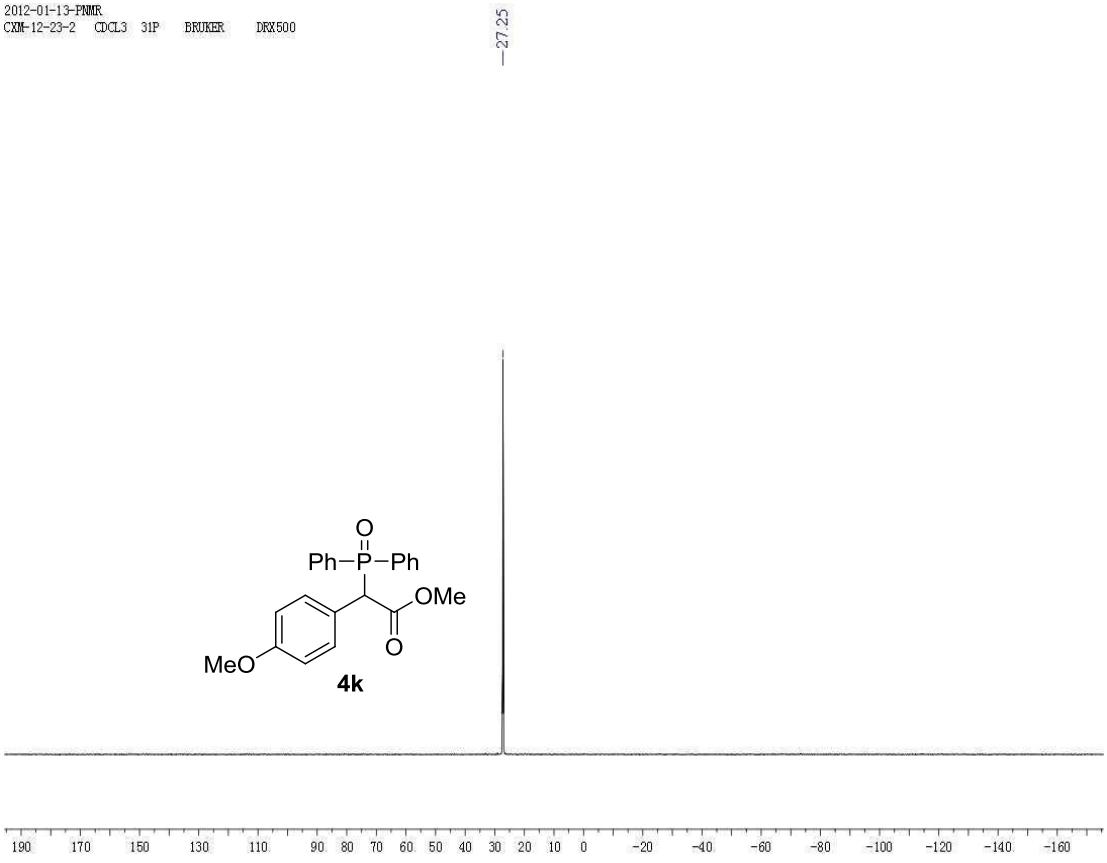


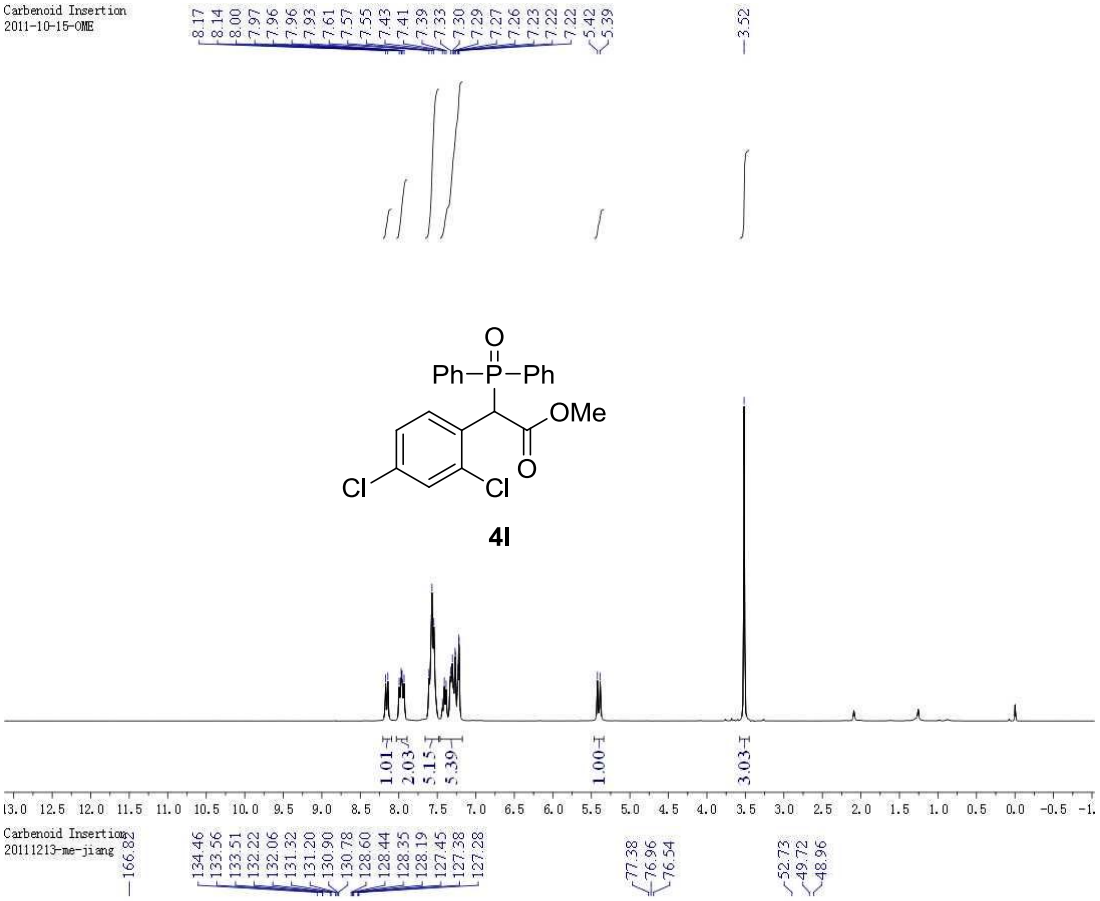

jhl-2012-20
1 31PNMR BRUKER DRX500
13.03
O
PhO–P–OPh
H
OEt
O
4j


Carbenoid Insertion
2011-10-15-OME
7.99
7.89
7.87
7.86
7.61
7.59
7.58
7.55
7.53
7.53
7.52
7.51
7.49
7.48
7.46
7.43
7.41
7.41
7.37
7.36
7.34
7.33
7.33
7.30
7.30
7.27
6.77
6.75
4.68
4.64
3.74
3.52

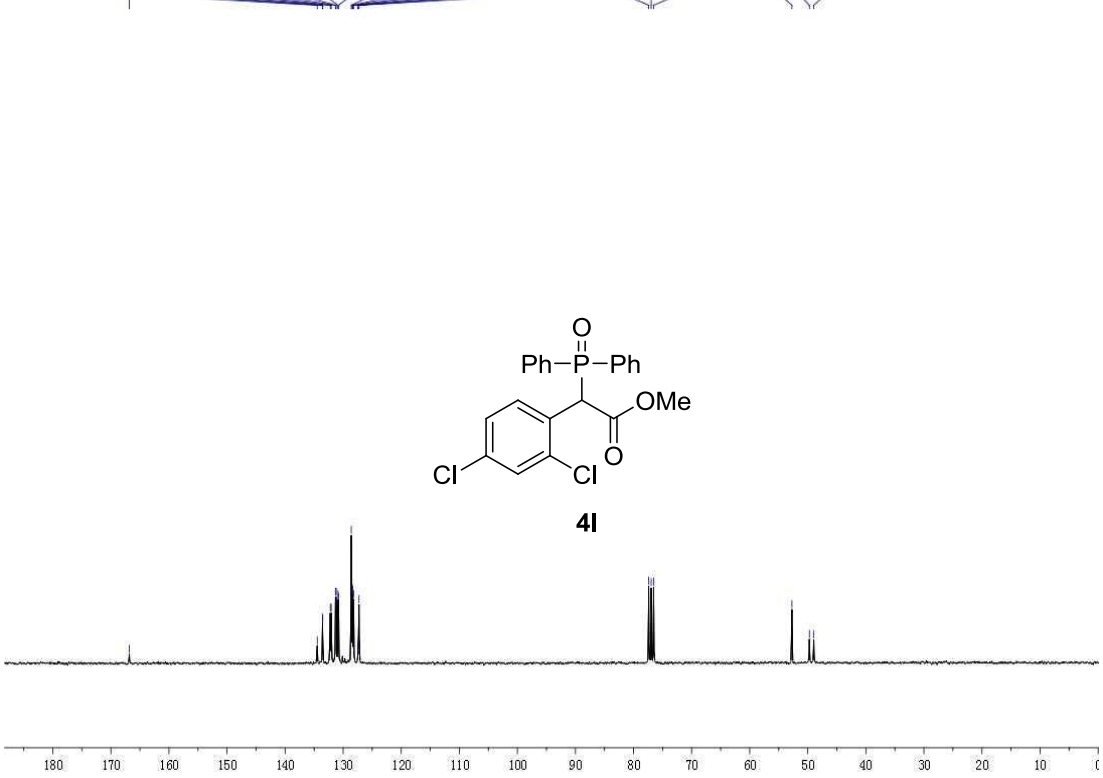

O
Ph–P–Ph
OMe
O
MeO
4k
2.06
10.41
2.03
1.00
3.03
3.03


Carbenoid Insertion
20111213-me-jiang
168.47
159.24
132.05
131.80
131.66
131.54
131.34
131.29
131.23
128.40
128.26
128.11
121.98
121.89
113.72
77.39
76.97
76.54
55.09
54.96
54.17
52.44
O
Ph–P–Ph
OMe
O
MeO
4k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


2012-01-13-PNMR
CXM-12-23-2 CDCL3 31P BRUKER DRX500
27.25
O
Ph–P–Ph
OMe
O
MeO
4k
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160

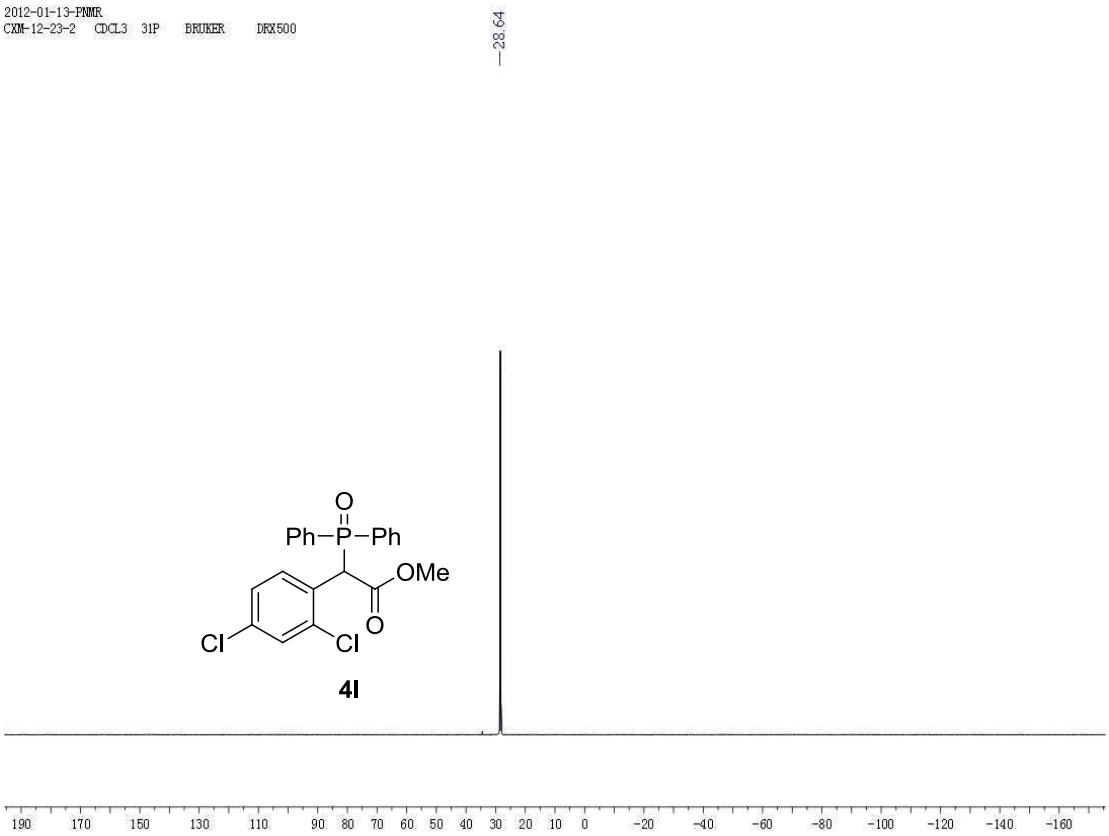

Carbenoid Insertion
2011-10-15-OME
8.17
8.14
8.00
7.97
7.96
7.96
7.93
7.61
7.57
7.55
7.43
7.41
7.39
7.33
7.30
7.29
7.27
7.26
7.23
7.22
7.22
5.42
5.39
3.52
O
Ph–P–Ph
OMe
O
Cl
Cl
1.01
2.03
5.15
5.39
1.00
3.03

4l


Carbenoid Insertion
20111213-me-jiang
166.82
134.46
133.56
133.51
132.22
132.06
131.32
131.20
130.90
130.78
128.60
128.44
128.35
128.19
127.45
127.38
127.28
77.38
76.96
76.54
52.73
49.72
48.96

O
Ph–P–Ph
OMe
O
Cl
Cl

4l



4l