Supporting Information

$B(C_6F_5)_3$-catalyzed O−H insertion reactions of diazoalkanes with phosphinic acids

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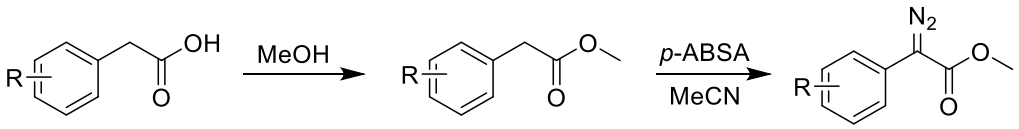
Contents

1. General Information

All the reactions were monitored by thin layer chromatography (TLC), carried out on 0.25 mm silica gel plates using UV light as visualizing agent. Column chromatography was carried out on silica gel (particle size 300-400 mesh). Unless stated otherwise, all the yields refer to isolated products after flash column chromatography. The solvent mixtures employed in flash column chromatography purifications are reported as volume by volume and in percentages. LEDs used in this manuscript were purchased from Taobao. Jia lamp, SF, 25W, 460-470nm. NMR spectra were recorded with BrukerAvance III HD500 spectrometer at 500 MHz. All ^{1}H, ^{19}F, ^{31}P and ^{13}C NMR spectra were recorded using $CDCl_3$ or DMSO-d_6 as solvent. Tetramethylsilane (TMS) signals or residual solvent signals were used [TMS $\delta = 0.00$ (1H NMR), $CDCl_3$ $\delta = 7.26$ ppm (^{1}H NMR), 77.16 ppm (^{13}C NMR), DMSO-d6 $\delta = 2.50$ ppm (^{1}H NMR), 39.52 ppm (^{13}C NMR)] as internal standards. Coupling constants (*J*) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet, td = triplet doublet, qd = quartet doublet. HRMS (ESI) Mass spectra were recorded on Thermo Fisher Scientific LTQ FT Ultra. The relative configuration of **3a** was determined by NMR Data and molecular weight compared with literature data.[1]

2. Experiment Section

2.1 General procedure for synthesis of aryldiazoacetates[2-3]

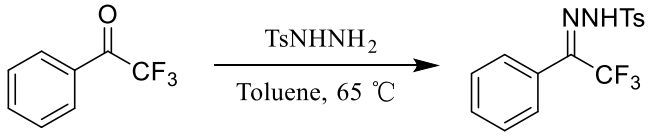


To a 100 mL round bottom flask was charged with 6 mL methanol. At 0 ºC thionyl chloride of 1.6 mL was added dropwise and the solution in an ice bath was stirred for 30 min. Then the corresponding aryl acetic acid (1.54 g, 10 mmol) solution in 15.4 mL methanol was added dropwise and the solution in an ice bath was stirred for 30 min. The reaction mixture was stirred under 60 °C and monitored by TLC. After completion of the reaction, the product was extracted with ethyl acetate, washed with aqueous $NaHCO_3$, water and brine, dried over anhydrous Na_2SO_4, crude methyl arylacetate which were used to next step without further purification.

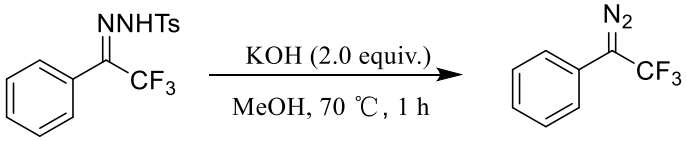
Methyl arylacetate (10 mmol), *p*-cetamidobenzenesulfonyl azide (*p*-ABSA) (3.6 g, 15 mmol) and acetonitrile (15 mL) were added to a dried flask. The mixture was

cooled with an ice-bath and a solution of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (2.3 mL, 2.4 g, 15 mmol) in acetonitrile (5 mL) was added dropwise. Then the ice-bath was removed and the mixture was stirred at room temperature overnight. The reaction was then quenched with saturated aqueous NH_4Cl and the mixture was extracted with diethyl ether (3 × 25 mL). The organic phases were combined, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The filtrate was evaporated and purified by silica gel chromatography (petroleum ether/ethyl acetate =100:1~50:1) to provide product α-diazoester (red-brown oil).

2.2 Synthesis of (1-diazo-2,2,2-trifluoroethyl)benzene[4]

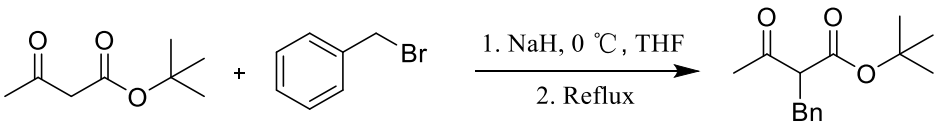


To a round bottom flask equipped with a reflux condenser was added tosylhydrazide (1.0 equiv.) and the minimum quantity of solvent (either methanol or toluene according to individual substrates) needed to dissolve the hydrazide at reflux (approximately 1.5 M). Subsequently the reaction was cooled to room temperature and trifluoroacetophenone (1.0 equiv.) was added in one portion. The reaction mixture was then stirred at 65 °C (Toluene) over 4-16 h (monitored by TLC). The solution was cooled to room temperature or 0 °C, at which point the product precipitated out of solution (precipitation can be induced by addition of pentane). The precipitate was collected by vacuum filtration and washed with pentane, in which case it was used without further purification. If no precipitation occurred, the solvent was removed under reduced pressure and the residue used in the next step without further purification.

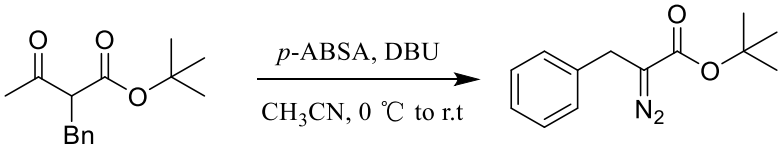


In a round bottom flask was added tosyl hydrazone (1.0 equiv.) and a solution of KOH (2.0 equiv.) in MeOH (0.4 M). A condenser was attached and the reaction mixture refluxed for 1 h or until the colour of the solution no longer intensified. The reaction was cooled to room temperature and diluted with water. The crude product was extracted with DCM, washed with a saturated solution of $NaHCO_3$, brine, dried with $MgSO_4$, concentrated under reduced pressure, and purified by silica gel chromatography.

2.3 Synthesis of 2-substituted *tert*-butyldiazoacetates[5]

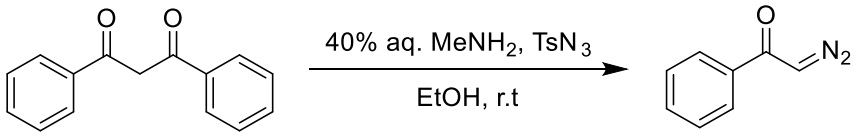


A 100 mL round bottom flask fitted with a rubber septum was charged with NaH (60%, dispersion in mineral oil, 1.56 g, 39 mmol) in 30 mL of freshly distilled THF. At 0 ºC *tert*-butyl acetoacetate (30 mmol) was added dropwise and the solution was stirred for 10 min. The reaction mixture was moved to ambient temperature then benzyl bromide (33 mmol) was added to the mixture in one portion. The resulting solution was refluxed and monitored by TLC. After completion of the reaction, the reaction mixture was quenched with sat. aq. NH_4Cl solution (20 mL) and H_2O (2 mL). The product was extracted with DCM (3 × 15 mL) and dried with Na_2SO_4. The volatiles were evaporated and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 9:1) to give 2-substituted *tert*-butyl acetoacetates clear colorless liquid.



To a stirred solution of 2-substituted *tert*-butyl acetoacetate (10 mmol) in acetonitrile (30 mL) were added a 4-acetamidobenzenesulfonyl azide (2.88 g, 12 mmol) and DBU (2.24 mL, 15 mmol) at 0 ºC. The reaction mixture was stirred under ambient temperature and monitored by TLC. After completion of the reaction, the reaction mixture was quenched with sat. aq. NH_4Cl solution (10 mL). The product was extracted with ethyl acetate (3 × 30 mL) and dried with Na_2SO_4. The volatiles were evaporated and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give corresponding 2-substituted *tert*-butyldiazoacetateas clear yellow liquid.

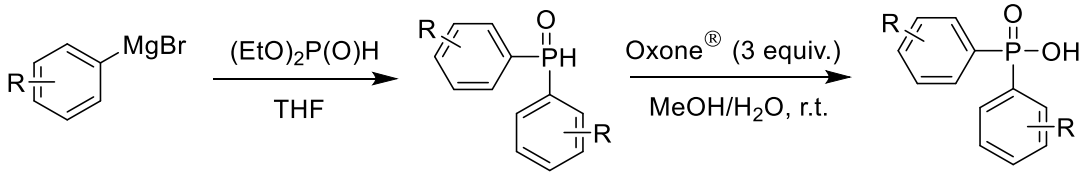
2.4 Synthesis of 2-diazo-1-phenylethanone[6]



To a solution of 1,3-diphenylpropane-1,3-dione (1 mmol, 224 mg) and TsN_3 (1 mmol, 197 mg) in EtOH (1 mL) was added $MeNH_2$ (40% aqueous solution, 1.2 mmol, 93 mg). After the mixture was stirred at room temperature for 25 min (monitored by TLC), the solvent was removed. The residue was purified by silica gel column

chromatography (petroleum ether/ethyl acetate = 20:1) to give product as a yellow solid.

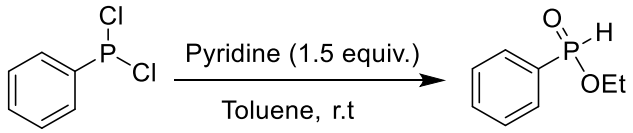
2.5 Preparation for synthesis of phosphinic acids[7,8]



To a solution of arylmagnesium bromide (0.1 mol) in THF (100 mL), diethyl phosphate (4.1 g, 0.03 mol) in THF (20 mL) was added dropwise with vigorous stirring under the cooling of ice-water bath. Then the resulting mixture stirred at r.t. for 2 h. After the reaction, the resulting reaction mixture was cooled to 0 °C, and sat. aq. NH_4Cl solution was added slowly upon stirring. The solution was then evaporated under reduced pressure. The residue was extracted with ethyl acetate (150 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give the product H-phosphine oxide as a white solid.

The H-phosphine oxide (3.0 mmol, 1 equiv.) was dissolved in MeOH (12 mL) and charged into a 100 mL flask under air atmosphere. Oxone® (5.5 g, 7.5 mmol, 3 equiv.) was dissolved in H_2O (12 mL) and poured into the MeOH solution containing the secondary phosphine oxide, resulting in a slurry. The mixture was stirred at r.t. for 24 h and diluted with H_2O (50 mL). The aqueous phase was extracted with $CHCl_3$ (3 x 75 mL) and the combined organic fractions washed with brine (100 mL). The organic fractions were then extracted with 1 M aq. NaOH solution (3 x 100 mL). The combined aqueous fractions were acidified with conc. HCl and extracted with $CHCl_3$ (3 x 150 mL). The combined organic fractions were dried over $MgSO_4$ and concentrated in vacuo to afford the target compound phosphinic acids as a white solid.

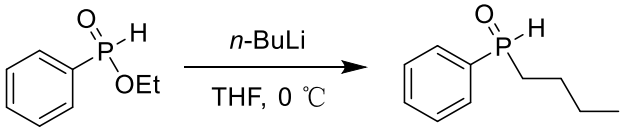
2.6 Preparation for synthesis of butyl(phenyl)phosphinic acid[8,9]



The phenylphosphinate was made from dichlorophenylphosphine and the appropriate alcohol. For example, in the synthesis of ethyl phenylphosphinate, a solution of ethanol (22.1 mL, 540 mmol) and pyridine (26.2 mL, 325 mmol) in toluene (36 mL) was added dropwise over 30 min to a solution of dichlorophenylphosphine (34 mL, 250 mmol) in toluene (175 mL). The mixture was

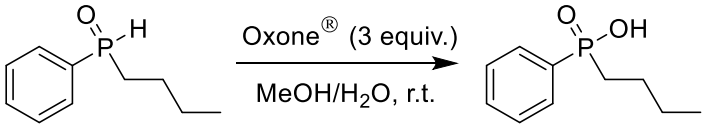
stirred for 1.5 h and allowed to sit without stirring for 1 day. The solution and resulting white solid were washed with saturated sodium bicarbonate (80 mL), and the aqueous layer was back-extracted with DCM (70 mL). The combined organic fractions dried over magnesium sulfate, filtered, and then concentrated down to give ethyl phenylphosphinate.

Synthesis of butyl(phenyl)phosphine oxide



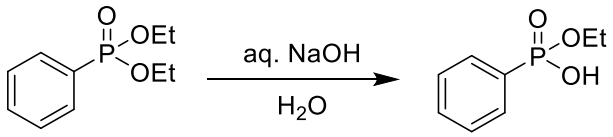
The crude ethyl phenylphosphinate dissolved in freshly distilled THF (12 mL) under a nitrogen atmosphere. A flame-dried flask was charged with commercially available *n*-BuLi Solution (9.2 mL, 22 mmol, 2.4 M in hexanes) under nitrogen atmosphere and cooled to -78 °C. The ethyl phenylphosphinate solution was added dropwise over 30 min and the resulting mixture stirred at room temperature for 2 h. The reaction was then quenched with sat. aq. NH_4Cl solution and subsequently diluted with H_2O (100 mL). The aqueous phase was extracted with $CHCl_3$ (3 x 150 mL) and the combined organic fractions dried over $MgSO_4$, concentrated and dried in vacuo. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give the product *n*-butyl(phenyl)phosphine oxide.

Synthesis of butyl(phenyl)phosphinic acid



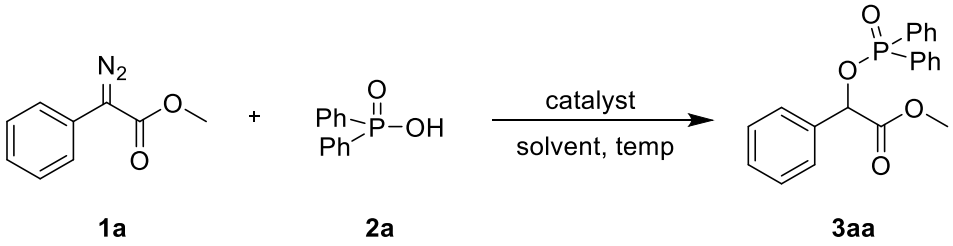
The butyl(phenyl)phosphine oxide (455.5 mg, 2.5 mmol, 1 equiv.) was dissolved in MeOH (10 mL) and charged into a 100 mL flask under air atmosphere. Oxone® (4.6 g, 7.5 mmol, 3 eq.) was dissolved in H_2O (10 mL) and poured into the MeOH solution containing the secondary phosphine oxide, resulting in a slurry. The mixture was stirred at r.t. for 24 h and diluted with H_2O (50 mL). The aqueous phase was extracted with $CHCl_3$ (3 x 75 mL) and the combined organic fractions washed with brine (100 mL). The organic fractions were then extracted with 1 M aq. NaOH solution (3 x 100 mL). The combined aqueous fractions were acidified with conc. HCl and extracted with $CHCl_3$ (3 x 150 mL). The combined organic fractions were dried over $MgSO_4$ and concentrated in vacuo to afford the title compound butyl(phenyl)phosphinic acid (382 mg, 1.9 mmol, 77%) as a colorless oil.

2.7 Preparation for synthesis of ethyl hydrogen phenylphosphonate[10]



The corresponding diethyl phosphonate (3.0 mmol), NaOH (6.0 mmol) and H_2O (15.0 mL) were stirred at 80 °C for 6-12 hours. The reaction solution was evaporated in vacuo to remove the ethanol and diluted with H_2O (10 mL). The solution was neutralized with cooled concentrated hydrochloric acid and extracted with ethyl acetate. The extracts were evaporated under reduced pressure to give the title compound ethyl hydrogen phenylphosphonate (281 mg, 1.5 mmol, 50%) as a colorless oil.

3. Screening the Optimum Reaction Conditions for the Synthesis of 3aa



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

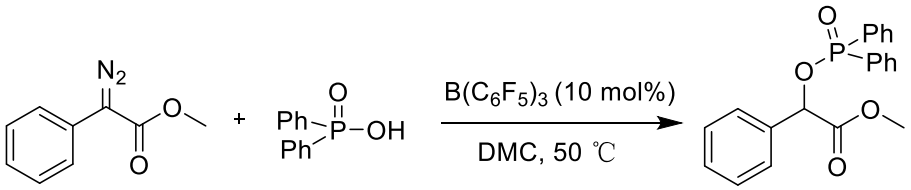
Table S2. Screening the optimum conditions for the synthesis of **3aa**

Entry	Catalyst	Solvent	Temp. (°C)	Time (hour)	Yield(%)[b]
1[c]	$Rh_2(OCT)_4$	DCM	RT	5min	63
2[c]	$Cu(OAc)_2$	DCM	RT	72	27
3[c]	$Pd(OAc)_2$	DCM	RT	10	36
4[c]	AgOAc	DCM	RT	20	76
5[c]	$FeSO_4·7H_2O$ +NaBArF	DCM	RT	10	74
6	Blue LEDs	DCM	RT	3	5
7[c]	$B(OCH_3)_3$	DCM	RT	168	36
8[c]	BBr_3	DCM	RT	20	11
9[c]	$PhB(OH)_2$	DCM	RT	168	49
10[c]	$B(C_6F_5)_3$	DCM	RT	12	93
11	$B(C_6F_5)_3$	DCM	RT	7	96
12	$B(C_6F_5)_3$	DMSO	RT	120	N.R.
13	$B(C_6F_5)_3$	Toluene	RT	48	38
14	$B(C_6F_5)_3$	Acetonitrile	RT	3	16

15	$B(C_6F_5)_3$	Ethanol	RT	192	55
16	$B(C_6F_5)_3$	Methanol	RT	40	55
17	$B(C_6F_5)_3$	Acetone	RT	3	20
18	$B(C_6F_5)_3$	Cyclohexanone	RT	45	14
19	$B(C_6F_5)_3$	EA	RT	3	52
20	$B(C_6F_5)_3$	DEC	RT	4	36
21	$B(C_6F_5)_3$	DMC	RT	2	87
22[d]	$B(C_6F_5)_3$	DMC	RT	0.8	60
23	$B(C_6F_5)_3$	DMC	50	1.5	98
24	-	DMC	50	168	Trace

[a] Reaction conduction: **1a** (0.15 mmol, 1.5 equiv.), **2a** (0.1 mmol, 1.0 equiv.), catalyst (10 mol%), solvent (1 mL), 50 °C. [b] Isolated yield. [c] catalyst (5 mol%) [d] catalyst (20 mol%). DCM = Dichloromethane. EA = Ethyl Acetate. DMSO = Dimethyl Sulfoxide. DEC = Diethyl Carbonate. DMC = Dimethyl Carbonate. N.R. = No Reaction. symbol "-" means no catalyst. Blue LEDs: 460-470 nm light (25 W).

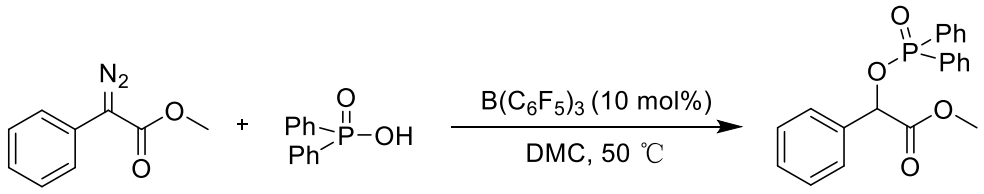
4. Typical Procedure for O-H Insertion of Phosphoric Acid



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

A typical procedure for the synthesis of 3aa: To the test tube was charged with diphenylphosphinic acid **2a** (0.1 mmol, 21.8 mg), catalyst $B(C_6F_5)_3$ (5.12 mg, 10 mol%), and dimethyl carbonate (0.5 mL). Then the diazoalkane **1a** (0.15 mmol, 26.4 mg) solution in dimethyl carbonate (0.5 mL) was added dropwise. The reaction mixture was reacted at 50 ℃ for 1.5 h until the diazoalkane **1a** was completely consumed. After the reaction, the solution was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the product **3aa** (36 mg, 98%) as a colorless oil.

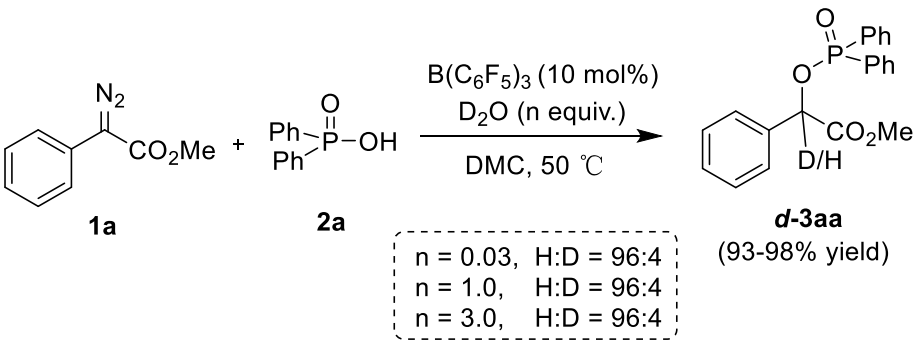
5. A Gram-scale Experiment



1a (1.32 g, 7.5 mmol) **2a** (1.09 g, 5.0 mmol) **3aa** (1.81 g, 99% yield)

Gram-scale experiment for the synthesis of 3aa: To a 100 mL round bottom flask was charged with diphenylphosphinic acid **2a** (5 mmol, 1.09 g), catalyst $B(C_6F_5)_3$ (256 mg, 10 mol%), and dimethyl carbonate of (25 mL). Then the 2-diazo-2-phenylacetate **1a** (15 mmol, 1.32 g) solution in dimethyl carbonate of 25 mL was added dropwise. The reaction mixture was reacted at 50 °C for 1 h until the diazoalkane **1a** was completely consumed. After the reaction, the solution was concentrated in vacuo and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the product **3aa** (1.81 g, 99%) as a colorless oil.

6. Deuterium Labelling Experiments



1a **2a** ***d*-3aa** (93-98% yield)

A dried test tube was loaded with $B(C_6F_5)_3$ (5.12 mg, 10 mol%) and diphenylphosphinic acid **2a** (0.1 mmol, 21.8 mg) and dry dimethyl carbonate (0.5 mL) and D_2O (n equiv.). The test tube was flushed and refilled with N_2 for three times. Than methyl 2-diazo-2-phenylacetate **1a** (0.15 mmol, 26.4 mg) dissolved in 0.5 mL dry dimethyl carbonate was added dropwise at once. The reaction mixture was stirred at 50 °C for 1.5 h until the orange color of the diazoalkane disappeared. Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the product ***d*-3aa** (36 mg, 98%). Deuterium is not incorporated in the reaction product. H:D = 96:4

7. Evaluation of Green metrics of the process.

Atom economy defined as “how much of the reactants remain in the final desired product”

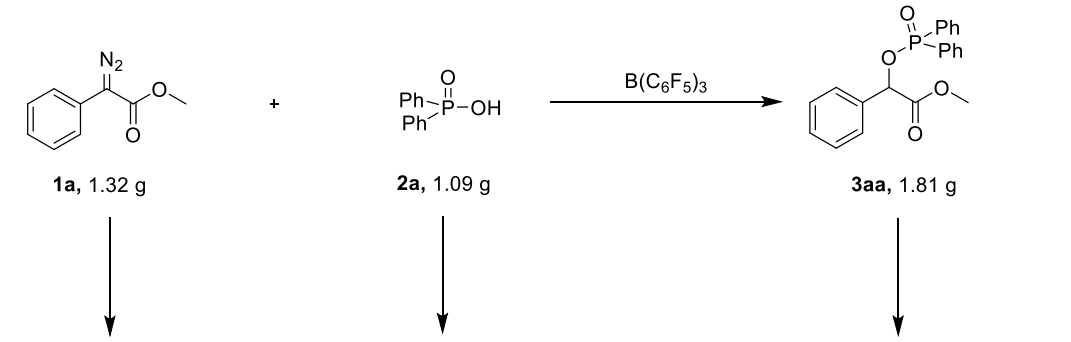
$$\text{Atom economy (\%) (AE)} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of all reactants}} \times 100$$

Reaction mass efficiency (RME) defined as “the percentage of the mass of the reactants that remain in the product”

$$\text{Reaction mass efficiency (\%) (RME)} = \frac{\text{mass of desired product}}{\text{mass of all reatatants}} \times 100$$

Evaluation of Green metrics for the current process

Reaction Scheme



1a, 1.32 g

2a, 1.09 g

3aa, 1.81 g

Chemical Formula: $C_9H_8N_2O_2$
Molecular Weight: 176.18

Chemical Formula: $C_{12}H_{11}O_2P$
Molecular Weight: 218.19

Chemical Formula: $C_{21}H_{19}O_4P$
Molecular Weight:366.35

Total = 176.18 + 218.19 = 394.37

Product Yield: 99%

Reactant 1	Methyl 2-diazo-2-phenylacetate	1.32 g	0.007492 mol	FW 176.18
Reactant 2	Diphenylphosphinic acid	1.09 g	0.004996 mol	FW 218.19
Catalyst	Tris(pentafluorophenyl)borane	0.256 g	0.0005 mol	FW 511.98
Solvent	Dimethyl carbonate	51.25g (50 mL)	---------	---------
Auxiliary	----------	---------	---------	---------
Product	Methyl 2-((diphenylphosphoryl)oxy) -2-phenylacetate	1.81 g	0.004941 mol	FW 366.35

$$\text{E-factor} = \frac{1.32\text{ g} + 1.09\text{ g} + 0.256\text{ g} + 51.25\text{ g} - 1.81\text{ g}}{1.81\text{ g}} = 28.79\text{ kg waste/1 kg product}$$

$$\text{Atom economy} = \frac{366.35}{394.37} \times 100 = 92.89\%$$

$$\text{Atom efficiency} = \frac{99 \times 92.89}{100} = 91.96\%$$

$$\text{Carbon efficiency} = \frac{9 + 12}{21} = 100\%$$

$$\text{Reaction mass efficiency} = \frac{1.81\text{ g}}{1.32\text{ g} + 1.09\text{ g}} \times 100 = 75.10\%$$

E-factor of the synthesis method is 28.79 kg waste per kg product, with 92.89% atom economy, 91.96% atom efficiency, 75.10% reaction mass efficiency and 100% carbon efficiency.

8. References

[1] B. Xiong, Q. Ye, X. Feng, L. Zhu, T. Chen, Y. Zhou, C.-T. Au and S.-F. Yin, *Tetrahedron*, 2014, **70**, 9057.

[2] J. E. Park, C. Song, K. Choi, T. Sim, B. Moon, E. J. Roh, *Bioorg. Med. Chem. Lett.* 2013, **23**, 5515.

[3] M. Zhang, T. Zhang, D. Zhang, W. Hu, *Adv. Synth. Catal*. 2020, **362**, 4662.

[4] E. Emer, J. Twilton, M. Tredwell, S. Calderwood, T. L. Collier, B. Liégault, M. Taillefer, V. Gouverneur, *Org. Lett.* 2014, **16**, 6004.

[5] I. S. Lee, B. C. Kang, G. S. Hwang, D. H. Ryu, *Org. Lett.* 2013, **15**, 1428.

[6] J. Zhang, W. Chen, D. Huang, X. Zeng, X. Wang, Y. Hu, *J. Org. Chem.* 2017, **82**, 9171.

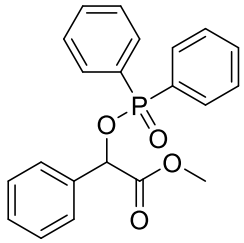
[7] J. Wang, G. Deng, C. Liu, Z. Chen, K. Yu, W. Chen, H. Zhang, X. Yang, *Adv. Synth. Catal*. 2020, **362**, 2268.

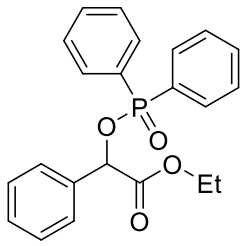
[8] B. M. Trost, S. M. Spohr, A. B. Rolka, C. A. Kalnmals, *J. Am. Chem. Soc.* 2019, **141**, 14098.

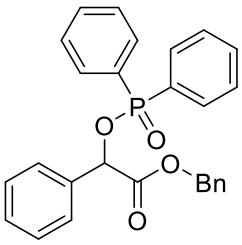
[9] L. Y. Kuo, D. C. Baker, A. K. Dortignacq, K. M. Dill, *Organometallics.* 2013, **32**, 4759.

[10] J. Seo, Y. Park, I. Jeon, T. Ryu, S. Park, P. H. Lee, *Org. Lett*. 2013, **15**, 3358.

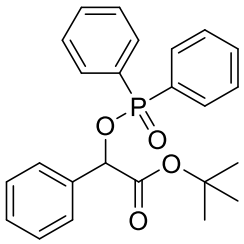
9. Characterization data for compounds

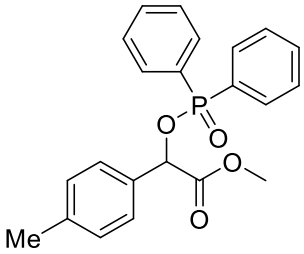
Methyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3aa). Colorless oil, 35.9 mg, 98% yield.  **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.91 – 7.87 (m, 2H), 7.74 – 7.70 (m, 2H), 7.54 – 7.51 (m, 1H), 7.47 – 7.41 (m, 5H), 7.36 – 7.32 (m, 2H), 7.31 – 7.29 (m, 3H), 5.84 (d, *J* = 10.0 Hz, 1H), 3.64 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.47 (d, *J* = 4.2 Hz), 135.22 (d, *J* = 4.9 Hz), 132.39 (d, *J* = 2.8 Hz), 132.30 (d, *J* = 2.8 Hz), 131.75 (d, *J* = 2.9 Hz), 131.67 (d, *J* = 3.2 Hz), 131.50 (d, *J* = 32.9 Hz), 130.42 (d, *J* = 32.7 Hz), 129.07, 128.64, 128.46 (d, *J* = 9.7 Hz), 128.35 (d, *J* = 9.5 Hz), 127.22, 74.12 (d, *J* = 5.0 Hz), 52.52. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.21. **HRMS** (ESI) m/z calcd for $C_{21}H_{20}O_4P$ $[M+H]^+$: 367.1094, found: 367.1093.

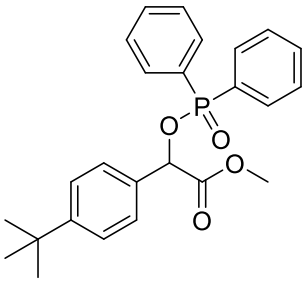
Ethyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3ba). Colorless oil, 33.1 mg, 87% yield.  **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.92 – 7.87 (m, 2H), 7.75 – 7.71 (m, 2H), 7.54 – 7.51 (m, 1H), 7.47 – 7.42 (m, 5H), 7.37-7.33 (m, 2H), 7.31 – 7.29 (m, 3H), 5.82 (d, *J* = 10.0 Hz, 1H), 4.17 – 4.05 (m, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.05 (d, *J* = 4.3 Hz), 135.37 (d, *J* = 4.8 Hz), 132.37 (d, *J* = 2.8 Hz), 132.29 (d, *J* = 2.8 Hz), 131.81 (d, *J* = 2.8 Hz), 131.72 (d, *J* = 2.6 Hz), 131.58 (d, *J* = 29.9 Hz), 130.50 (d, *J* = 29.9 Hz), 129.00, 128.61, 128.47 (d, *J* = 9.2 Hz), 128.36 (d, *J* = 9.1 Hz), 127.24, 74.23 (d, *J* = 5.1 Hz), 61.70, 13.91. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.09. **HRMS** (ESI) m/z calcd for $C_{22}H_{22}O_4P$ $[M+H]^+$: 381.1250, found: 381.1263.

Benzyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3ca). White solid, 42.9 mg, 97% yield.  **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.88 – 7.83 (m, 2H), 7.74 – 7.70 (m, 2H), 7.51 – 7.48 (m, 1H), 7.46 – 7.44 (m, 1H), 7.43 – 7.38 (m, 4H), 7.35 – 7.31 (m, 2H), 7.29 – 7.26 (m, 6H), 7.16 – 7.13 (m, 2H), 5.88 (d, *J* = 10.1 Hz, 1H), 5.09 (d, *J* = 2.8 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.88 (d, *J* = 4.4 Hz), 135.16 (d, *J* = 4.7 Hz), 135.05, 132.37 (d, *J* = 2.8 Hz), 132.29 (d, *J* = 2.8 Hz), 131.74 (d, *J* = 10.6 Hz), 131.47 (d, *J* = 20.1 Hz), 130.38 (d, *J* = 20.0 Hz), 129.05, 128.61, 128.45 (d, *J* = 10.4 Hz), 128.42, 128.39, 128.27 (d, *J* = 10.6 Hz), 127.93, 127.28, 74.21 (d, *J* = 5.0 Hz), 67.19. **^{31}P NMR** (202

MHz, Chloroform-*d*) δ 34.22. **HRMS** (ESI) m/z calcd for $C_{24}H_{24}O_4P$ $[M+H]^+$: 443.1407, found: 443.1410.

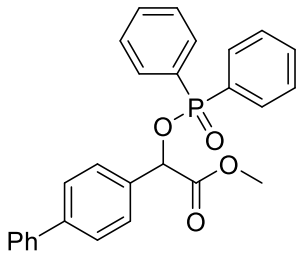
***Tert*-butyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3da).** Colorless oil, 20.9 mg, 51% yield.  **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.93 – 7.88 (m, 2H), 7.77 – 7.73 (m, 2H), 7.54 – 7.51 (m, 1H), 7.47 – 7.41 (m, 5H), 7.37 – 7.33 (m, 2H), 7.32 – 7.28 (m, 3H), 5.71 (d, *J* = 10.2 Hz, 1H), 1.33 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.01 (d, *J* = 4.4 Hz), 135.82 (d, *J* = 4.7 Hz), 132.28 (d, *J* = 2.8 Hz), 132.19 (d, *J* = 2.8 Hz), 131.88 (d, *J* = 10.7 Hz), 131.78 (d, *J* = 22.7 Hz), 131.75 (d, *J* = 10.4 Hz), 130.69 (d, *J* = 22.7 Hz), 128.74, 128.49, 128.34 (d, *J* = 13.2 Hz), 127.15, 82.47, 74.38 (d, *J* = 5.1 Hz), 27.75. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 33.46. **HRMS** (ESI) m/z calcd for $C_{24}H_{26}O_4P$ $[M+H]^+$: 409.1563, found: 409.1572.

Methyl 2-((diphenylphosphoryl)oxy)-2-(p-tolyl)acetate (3ea). Colorless oil, 28.9 mg, 76% yield.  **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 – 7.86 (m, 2H), 7.74 – 7.70 (m, 2H), 7.54 – 7.51 (m, 1H), 7.48 – 7.44 (m, 3H), 7.37 – 7.34 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.79 (d, *J* = 9.9 Hz, 1H), 3.64 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.69 (d, *J* = 4.3 Hz), 139.06, 132.36 (d, *J* = 3.0 Hz), 132.30, 132.25 (d, *J* = 2.8 Hz), 131.82 (d, *J* = 6.2 Hz), 131.73 (d, *J* = 6.3 Hz), 131.61 (d, *J* = 32.7 Hz), 130.52 (d, *J* = 31.4 Hz), 129.36, 128.46 (d, *J* = 10.4 Hz), 128.35 (d, *J* = 10.3 Hz), 127.28, 74.10 (d, *J* = 5.1 Hz), 52.54, 21.21. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.06. **HRMS** (ESI) m/z calcd for $C_{22}H_{22}O_4P$ $[M+H]^+$: 381.1250, found: 381.1254.

Methyl 2-(4-(*tert*-butyl)phenyl)-2-((diphenylphosphoryl)oxy)acetate (3fa).  Colorless oil, 40.1 mg, 95% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 – 7.86 (m, 2H), 7.73 – 7.69 (m, 2H), 7.54 – 7.50 (m, 1H), 7.47 – 7.43 (m, 3H), 7.34 – 7.29 (m, 6H), 5.81 (d, *J* = 9.7 Hz, 1H), 3.65 (s, 3H), 1.28 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.66 (d, *J* = 4.6 Hz), 152.10, 132.34 (d, *J* = 2.9 Hz), 132.20 (d, *J* = 2.8 Hz), 132.13 (d, *J* = 4.8 Hz), 131.76 (t, *J* = 10.2 Hz), 131.60 (d, *J* = 35.7 Hz), 130.51 (d, *J* =

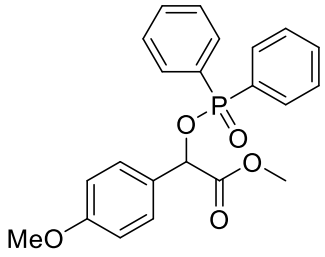
34.5 Hz), 128.44 (d, *J* = 13.5 Hz), 128.31 (d, *J* = 13.4 Hz), 127.08, 125.59, 74.07 (d, *J* = 5.0 Hz), 52.50, 34.60, 31.21. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 33.86. **HRMS** (ESI) m/z calcd for $C_{25}H_{28}O_4P$ $[M+H]^+$: 423.1720, found: 423.1728.

Methyl 2-([1,1'-biphenyl]-4-yl)-2-((diphenylphosphoryl)oxy)acetate (3ga).



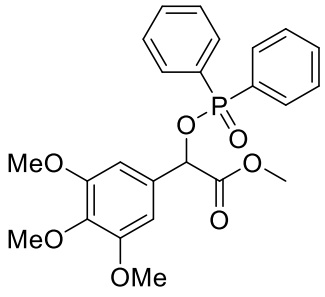
Colorless oil, 42.0 mg, 95% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.93 – 7.89 (m, 2H), 7.76 – 7.72 (m, 2H), 7.54 – 7.51 (m, 5H), 7.49 – 7.40 (m, 7H), 7.36 – 7.32 (m, 3H), 5.89 (d, *J* = 9.8 Hz, 1H), 3.67 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.49 (d, *J* = 4.6 Hz), 142.01, 140.34, 134.15 (d, *J* = 4.7 Hz), 132.42 (d, *J* = 2.8 Hz), 132.29 (d, *J* = 2.8 Hz), 131.80 (d, *J* = 4.5 Hz), 131.72 (d, *J* = 4.7 Hz), 131.52 (d, *J* = 28.5 Hz), 130.43 (d, *J* = 27.4 Hz), 128.79, 128.49 (d, *J* = 12.1 Hz), 128.38 (d, *J* = 12.1 Hz), 127.76, 127.58, 127.39, 127.08, 73.97 (d, *J* = 5.0 Hz), 52.62. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.25. **HRMS** (ESI) m/z calcd for $C_{27}H_{24}O_4P$ $[M+H]^+$: 443.1407, found: 443.1414.

Methyl 2-((diphenylphosphoryl)oxy)-2-(4-methoxyphenyl)acetate (3ha). White solid, 38.1 mg, 96% yield.



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 – 7.85 (m, 2H), 7.73 – 7.69 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.43 (m, 3H), 7.37 – 7.32 (m, 4H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.79 (d, *J* = 9.8 Hz, 1H), 3.76 (s, 3H), 3.64 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.72 (d, *J* = 4.6 Hz), 160.18, 132.35 (d, *J* = 2.8 Hz), 132.24 (d, *J* = 2.8 Hz), 131.78 (d, *J* = 8.3 Hz), 131.70 (d, *J* = 8.5 Hz), 131.51 (d, *J* = 29.4 Hz), 130.54 (d, *J* = 29.0 Hz), 128.84, 128.45 (d, *J* = 11.6 Hz), 128.35 (d, *J* = 11.4 Hz), 127.38 (d, *J* = 4.8 Hz), 114.07, 73.88 (d, *J* = 5.1 Hz), 55.26, 52.50. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 33.90. **HRMS** (ESI) m/z calcd for $C_{22}H_{22}O_5P$ $[M+H]^+$: 397.1199, found: 397.1205.

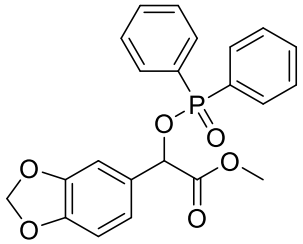
Methyl 2-((diphenylphosphoryl)oxy)-2-(3,4,5-trimethoxyphenyl)acetate (3ia).



White solid, 42.0 mg, 92% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 – 7.85 (m, 2H), 7.72 – 7.68 (m, 2H), 7.56 – 7.53 (m, 1H), 7.49 – 7.45 (m, 3H), 7.38 – 7.34 (m, 2H), 6.59 (s, 2H), 5.79 (d, *J* = 9.9 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 6H), 3.70 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.43 (d, *J* = 5.5 Hz), 153.27, 138.52,

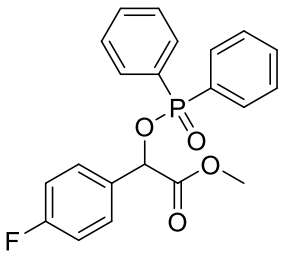
132.47 (d, *J* = 2.8 Hz), 132.31 (d, *J* = 2.8 Hz), 131.81 (d, *J* = 10.5 Hz), 131.68 (d, *J* = 10.7 Hz), 131.56 (d, *J* = 11.9 Hz), 130.55 (d, *J* = 4.0 Hz), 130.47 (d, *J* = 9.4 Hz), 128.51 (d, *J* = 13.6 Hz), 128.28 (d, *J* = 13.4 Hz), 104.67, 74.24 (d, *J* = 4.9 Hz), 60.74, 56.12, 52.67. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.12. **HRMS** (ESI) m/z calcd for $C_{24}H_{26}O_7P$ $[M+H]^+$: 457.1411, found: 457.1416.

Methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-((diphenylphosphoryl)oxy)acetate (3ja).



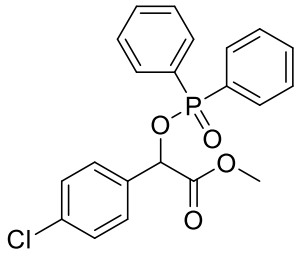
Colorless oil, 39.8 mg, 97% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 – 7.85 (m, 2H), 7.74 – 7.70 (m, 2H), 7.54 – 7.51 (m, 1H), 7.49 – 7.43 (m, 3H), 7.39 – 7.35 (m, 2H), 6.92 (d, *J* = 1.7 Hz, 1H), 6.85 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.92 (s, 2H), 5.73 (d, *J* = 9.8 Hz, 1H), 3.65 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.53 (d, *J* = 4.7 Hz), 148.33, 147.89, 132.42 (d, *J* = 2.8 Hz), 132.31 (d, *J* = 2.8 Hz), 131.79 (d, *J* = 8.1 Hz), 131.70 (d, *J* = 8.3 Hz), 131.55 (d, *J* = 24.3 Hz), 130.46 (d, *J* = 23.1 Hz), 128.94 (d, *J* = 4.8 Hz), 128.43 (t, *J* = 13.0 Hz), 121.64, 108.28, 107.66, 101.33, 73.99 (d, *J* = 5.0 Hz), 52.59. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 33.97. **HRMS** (ESI) m/z calcd for $C_{22}H_{20}O_6P$ $[M+H]^+$: 411.0992, found: 411.0998.

Methyl 2-((diphenylphosphoryl)oxy)-2-(4-fluorophenyl)acetate (3ka). White solid,

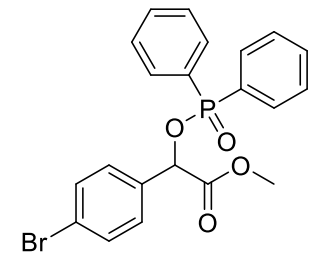


36.9 mg, 96% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 – 7.86 (m, 2H), 7.73 – 7.69 (m, 2H), 7.56 – 7.52 (m, 1H), 7.49 – 7.45 (m, 3H), 7.42 – 7.35 (m, 4H), 6.99 (t, *J* = 8.7 Hz, 2H), 5.82 (d, *J* = 10.0 Hz, 1H), 3.66 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.37 (d, *J* = 4.6 Hz), 163.06 (d, *J* = 248.4 Hz), 132.49 (d, *J* = 2.8 Hz), 132.40 (d, *J* = 2.8 Hz), 131.78 (d, *J* = 2.2 Hz), 131.69 (d, *J* = 2.0 Hz), 131.44 (d, *J* = 19.0 Hz), 131.24 (dd, *J* = 4.5, 3.4 Hz), 130.35 (d, *J* = 18.3 Hz), 129.27 (d, *J* = 8.5 Hz), 128.53 (d, *J* = 11.1 Hz), 128.42 (d, *J* = 11.1 Hz), 115.69 (d, *J* = 21.8 Hz), 73.43 (d, *J* = 4.9 Hz), 52.66. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.27. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -112.11. **HRMS** (ESI) m/z calcd for $C_{21}H_{19}FO_4P$ $[M+H]^+$: 385.1000, found: 385.1009.

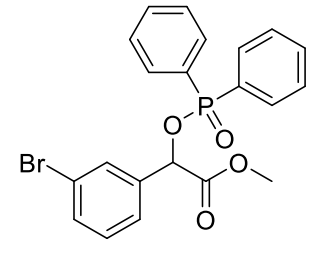
Methyl 2-(4-chlorophenyl)-2-((diphenylphosphoryl)oxy)acetate (3la). White solid, 39.3 mg, 98% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 – 7.86 (m, 2H), 7.74 – 7.69 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.39 –7.35 (m, 4H), 7.28 (d, *J* = 7.7 Hz, 2H), 5.81 (d, *J* = 10.0 Hz, 1H), 3.65 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.16 (d, *J* = 4.6 Hz), 135.11, 133.82 (d, *J* = 4.7 Hz), 132.51 (d, *J* = 2.8 Hz), 132.42 (d, *J* = 2.9 Hz), 131.76 (d, *J* = 5.2 Hz), 131.68 (d, *J* = 5.0 Hz), 131.34 (d, *J* = 17.8 Hz), 130.25 (d, *J* = 17.2 Hz), 128.88, 128.65, 128.54 (d, *J* = 8.1 Hz), 128.43 (d, *J* = 7.9 Hz), 73.40 (d, *J* = 4.9 Hz), 52.70. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.48. **HRMS** (ESI) m/z calcd for $C_{21}H_{19}ClO_4P$ $[M+H]^+$: 401.0704, found: 401.0709.



Methyl 2-(4-bromophenyl)-2-((diphenylphosphoryl)oxy)acetate (3ma). White solid, 43.2 mg, 97% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 – 7.86 (m, 2H), 7.73 – 7.69 (m, 2H), 7.56 – 7.52 (m, 1H), 7.50 – 7.42 (m, 5H), 7.39 –7.35 (m, 2H), 7.31 – 7.29 (m, 2H), 5.79 (d, *J* = 9.9 Hz, 1H), 3.65 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.05 (d, *J* = 4.6 Hz), 134.30 (d, *J* = 4.8 Hz), 132.52 (d, *J* = 2.8 Hz), 132.43 (d, *J* = 2.8 Hz), 131.83, 131.73 (d, *J* = 5.5 Hz), 131.65 (d, *J* = 5.2 Hz), 131.27 (d, *J* = 18.0 Hz), 130.19 (d, *J* = 17.4 Hz), 128.91, 128.54 (d, *J* = 7.1 Hz), 128.43 (d, *J* = 6.9 Hz), 123.33, 73.45 (d, *J* = 4.9 Hz), 52.70. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.54. **HRMS** (ESI) m/z calcd for $C_{21}H_{19}BrO_4P$ $[M+H]^+$: 445.0199, found: 445.0206.



Methyl 2-(3-bromophenyl)-2-((diphenylphosphoryl)oxy)acetate (3na). Colorless oil, 42.7 mg, 96% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 – 7.86 (m, 2H), 7.74 – 7.70 (m, 2H), 7.57 – 7.53 (m, 2H), 7.50 – 7.46 (m, 3H), 7.44 – 7.42 (m, 1H), 7.40 – 7.35 (m, 3H), 7.17 (t, *J* = 7.9 Hz, 1H), 5.79 (d, *J* = 9.9 Hz, 1H), 3.67 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.98 (d, *J* = 4.6 Hz), 137.31 (d, *J* = 4.6 Hz), 132.54 (d, *J* = 2.9 Hz), 132.50 (d, *J* = 2.9 Hz), 132.21, 131.77 (d, *J* = 1.5 Hz), 131.68 (d, *J* = 1.3 Hz), 131.21 (d, *J* = 27.1 Hz), 130.21, 130.12 (d, *J* = 25.6 Hz), 128.54 (d, *J* = 9.4 Hz), 128.43 (d, *J* = 9.2 Hz), 125.93, 122.62, 73.30 (d, *J* = 4.9 Hz), 52.77. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.65. **HRMS** (ESI) m/z calcd for $C_{21}H_{19}BrO_4P$ $[M+H]^+$: 445.0199, found: 445.0208.



Methyl 2-(2-bromophenyl)-2-((diphenylphosphoryl)oxy)acetate (3oa). Colorless oil, 40.9 mg, 92% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.92 – 7.88 (m, 2H), 7.71 – 7.67 (m, 2H), 7.56 – 7.52 (m, 2H), 7.48 – 7.43 (m, 4H), 7.34 – 7.29 (m, 2H), 7.28 – 7.26 (m, 1H), 7.17 – 7.13 (m, 1H), 6.24 (d, *J* = 10.2 Hz, 1H), 3.67 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.05 (d, *J* = 5.2 Hz), 135.31 (d, *J* = 4.3 Hz), 133.03, 132.39 (d, *J* = 2.9 Hz), 132.27 (d, *J* = 2.9 Hz), 131.75 (t, *J* = 10.6 Hz), 131.42 (d, *J* = 43.5 Hz), 130.49, 130.34 (d, *J* = 42.4 Hz), 129.76, 128.46 (d, *J* = 13.5 Hz), 128.30 (d, *J* = 13.4 Hz), 127.74, 123.28, 73.35 (d, *J* = 4.9 Hz), 52.76. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.21. **HRMS** (ESI) m/z calcd for $C_{21}H_{19}BrO_4P$ $[M+H]^+$: 445.0199, found: 445.0202.

Methyl 2-((diphenylphosphoryl)oxy)-2-(4-(trifluoromethyl)phenyl)acetate (3pa). Colorless oil, 41.7 mg, 96% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.92 – 7.87 (m, 2H), 7.74 – 7.70 (m, 2H), 7.58 – 7.55 (m, 5H), 7.50 – 7.47 (m, 3H), 7.39 – 7.35 (m, 2H), 5.90 (d, *J* = 9.9 Hz, 1H), 3.67 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.90 (d, *J* = 4.7 Hz), 139.12 (d, *J* = 4.5 Hz), 132.64 (d, *J* = 2.9 Hz), 132.55 (d, *J* = 2.8 Hz), 131.79 (d, *J* = 10.8 Hz), 131.69 (d, *J* = 10.5 Hz), 131.20 (q, *J* = 11.3 Hz), 130.15, 130.06, 128.61 (d, *J* = 10.0 Hz), 128.50 (d, *J* = 9.9 Hz), 127.63, 125.66 (q, *J* = 3.7 Hz), 123.80 (q, *J* = 272.4 Hz), 73.45 (d, *J* = 4.9 Hz), 52.85. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.80. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.83. **HRMS** (ESI) m/z calcd for $C_{22}H_{19}F_3O_4P$ $[M+H]^+$: 435.0968, found: 435.0979.

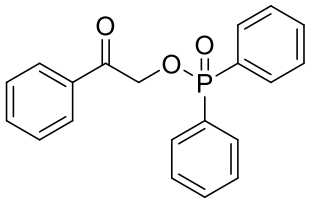
Methyl 2-((diphenylphosphoryl)oxy)-2-(naphthalen-1-yl)acetate (3qa). White solid, 39.9 mg, 96% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.3 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.80 – 7.76 (m, 2H), 7.54 – 7.49 (m, 4H), 7.48 – 7.44 (m, 4H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.15 – 7.11 (m, 2H), 6.44 (d, *J* = 10.2 Hz, 1H), 3.61 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.93 (d, *J* = 5.2 Hz), 133.85, 132.35 (d, *J* = 2.8 Hz), 132.04 (d, *J* = 2.8 Hz), 131.63 (t, *J* = 10.4 Hz), 131.51 (d, *J* = 86.0 Hz), 131.25 (d, *J* = 3.9 Hz), 130.57, 130.42 (d, *J* = 82.3 Hz), 130.00, 128.66, 128.45 (d, *J* = 13.6 Hz), 128.01 (d, *J* = 13.3 Hz), 127.65, 126.76, 125.92, 125.06, 123.89, 73.30 (d, *J* = 5.1 Hz), 52.69. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.36. **HRMS** (ESI) m/z calcd for $C_{25}H_{22}O_4P$ $[M+H]^+$: 417.1250, found: 417.1259.

Methyl 2-((diphenylphosphoryl)oxy)-2-(thiophen-2-yl)acetate (3ra). Brown oil, 20.1 mg, 54% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 – 7.85 (m, 2H), 7.77 – 7.73 (m, 2H), 7.55 – 7.50 (m, 1H), 7.48 – 7.44 (m, 3H), 7.40 – 7.36 (m, 2H), 7.29 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.07 (d, *J* = 3.5 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.12 (d, *J* = 9.7 Hz, 1H), 3.70 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.69 (d, *J* = 4.3 Hz), 137.14 (d, *J* = 5.6 Hz), 132.45 (d, *J* = 2.9 Hz), 132.38 (d, *J* = 2.8 Hz), 131.77 (d, *J* = 9.6 Hz), 131.69 (d, *J* = 10.0 Hz), 131.37 (d, *J* = 33.2 Hz), 130.29 (d, *J* = 31.4 Hz), 128.49 (d, *J* = 9.1 Hz), 128.38 (d, *J* = 8.9 Hz), 127.81, 127.25, 126.82, 69.89 (d, *J* = 4.9 Hz), 52.81. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.54. **HRMS** (ESI) m/z calcd for $C_{19}H_{18}O_4PS$ $[M+H]^+$: 373.0658, found: 373.0663.

***Tert*-butyl 2-((diphenylphosphoryl)oxy)-3-phenylpropanoate (3sa).** Colorless oil, 11.9 mg, 28% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 2H), 7.63 – 7.58 (m, 2H), 7.50 – 7.45 (m, 2H), 7.43 – 7.39 (m, 2H), 7.36 – 7.32 (m, 2H), 7.25 – 7.19 (m, 5H), 4.97 – 4.93 (m, 1H), 3.25 – 3.16 (m, 2H), 1.29 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.80 (d, *J* = 3.4 Hz), 135.59, 132.16 (d, *J* = 2.8 Hz), 132.04 (d, *J* = 2.8 Hz), 131.90 (d, *J* = 10.6 Hz), 131.57 (d, *J* = 10.4 Hz), 131.36 (d, *J* = 135.7 Hz), 130.29(d, *J* = 137.5 Hz), 129.80, 128.35(d, *J* = 12.4 Hz), 128.29, 126.90, 82.21, 73.76 (d, *J* = 5.8 Hz), 39.93 (d, *J* = 4.9 Hz), 27.75. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 33.11. **HRMS** (ESI) m/z calcd for $C_{25}H_{28}O_4P$ $[M+H]^+$: 423.1720, found: 423.1726.

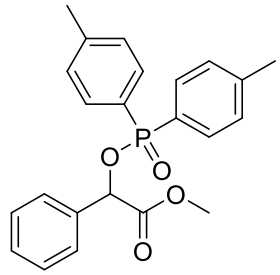
2,2,2-trifluoro-1-phenylethyl diphenylphosphinate (3ta). Colorless oil, 6.1 mg, 16% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.87 – 7.83 (m, 2H), 7.62 – 7.56 (m, 3H), 7.51 – 7.48 (m, 2H), 7.45 – 7.39 (m, 3H), 7.35 – 7.28 (m, 5H), 5.74 – 5.68 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 132.69 (d, *J* = 2.9 Hz), 132.40 (d, *J* = 2.9 Hz), 131.67 (d, *J* = 3.3 Hz), 131.65, 131.59 (d, *J* = 3.4 Hz), 130.57 (d, *J* = 136.3 Hz), 130.45 (d, *J* = 138.1 Hz), 129.84, 128.61 (d, *J* = 13.6 Hz), 128.48, 128.31 (d, *J* = 13.6 Hz), 128.13, 126.58 – 119.86 (m), 73.58 (qd, *J* = 33.8, 5.0 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 35.30. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -76.48. **HRMS** (ESI) m/z calcd for $C_{20}H_{17}F_3O_2P$ $[M+H]^+$: 377.0913, found: 377.0921.

2-oxo-2-phenylethyl diphenylphosphinate (3ua). Yellow oil, 30.9 mg, 92% yield.



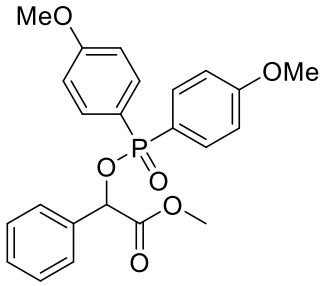
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.90 (m, 4H), 7.88 – 7.86 (m, 2H), 7.59 – 7.52 (m, 3H), 7.48 – 7.43 (m, 6H), 5.31 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 192.31 (d, *J* = 6.8 Hz), 134.07, 133.91, 132.50 (d, *J* = 2.9 Hz), 131.80 (d, *J* = 10.4 Hz), 130.70 (d, *J* = 137.4 Hz), 128.85, 128.64 (d, *J* = 13.3 Hz), 127.74, 65.78 (d, *J* = 5.6 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.35. **HRMS** (ESI) m/z calcd for $C_{20}H_{18}O_3P$ $[M+H]^+$: 337.0988, found: 337.0991.

Methyl 2-((di-p-tolylphosphoryl)oxy)-2-phenylacetate (3ab). Colorless oil, 35.1 mg, 89% yield.

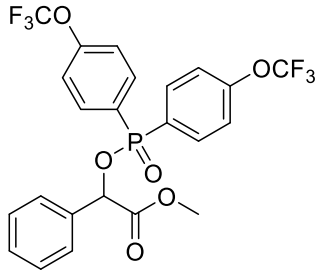


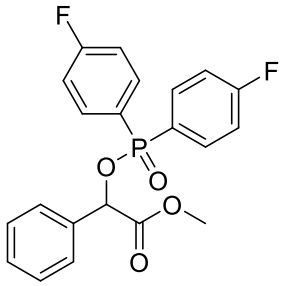
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 12.5, 8.1 Hz, 2H), 7.62 (dd, *J* = 12.3, 8.1 Hz, 2H), 7.45 – 7.43 (m, 2H), 7.34 – 7.32 (m, 3H), 7.29 – 7.27 (m, 2H), 7.18 (dd, *J* = 7.8, 3.4 Hz, 2H), 5.82 (d, *J* = 10.1 Hz, 1H), 3.67 (s, 3H), 2.40 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.68 (d, *J* = 4.1 Hz), 142.83 (d, *J* = 3.0 Hz), 142.76 (d, *J* = 2.9 Hz), 135.47 (d, *J* = 5.0 Hz), 131.82 (d, *J* = 2.2 Hz), 131.73 (d, *J* = 2.5 Hz), 129.19 (d, *J* = 7.8 Hz), 129.08 (d, *J* = 7.7 Hz), 128.96, 128.62, 128.53 (d, *J* = 35.4 Hz), 127.42 (d, *J* = 34.8 Hz), 127.22, 74.00 (d, *J* = 5.0 Hz), 52.53, 21.66 (d, *J* = 1.1 Hz), 21.60 (d, *J* = 1.1 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 35.26. **HRMS** (ESI) m/z calcd for $C_{23}H_{24}O_4P$ $[M+H]^+$: 395.1407, found: 395.1417.

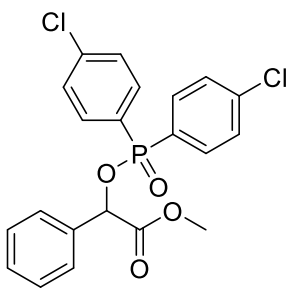
Methyl 2-((bis(4-methoxyphenyl)phosphoryl)oxy)-2-phenylacetate (3ac). Colorless oil, 40.9 mg, 96% yield.



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.77 (m, 2H), 7.66 – 7.62 (m, 2H), 7.43 – 7.41 (m, 2H), 7.32 – 7.30 (m, 3H), 6.96 (dd, *J* = 8.8, 2.8 Hz, 2H), 6.85 (dd, *J* = 8.8, 2.8 Hz, 2H), 5.78 (d, *J* = 10.2 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.66 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.75 (d, *J* = 4.1 Hz), 162.72 (d, *J* = 3.1 Hz), 162.66 (d, *J* = 3.1 Hz), 135.53 (d, *J* = 4.9 Hz), 133.75, 133.65, 128.96, 128.63, 127.22, 123.19 (d, *J* = 40.8 Hz), 122.04 (d, *J* = 40.2 Hz), 113.99 (d, *J* = 7.6 Hz), 113.87 (d, *J* = 7.5 Hz), 73.92, 55.32, 55.29, 52.54. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 35.11. **HRMS** (ESI) m/z calcd for $C_{23}H_{24}O_6P$ $[M+H]^+$: 427.1305, found: 427.1318.

Methyl 2-((bis(4-(trifluoromethoxy)phenyl)phosphoryl)oxy)-2-phenylacetate (3ad). 
Colorless oil, 52.3 mg, 98% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.97 – 7.92 (m, 2H), 7.75 – 7.70 (m, 2H), 7.39 – 7.37 (m, 2H), 7.34 – 7.28 (m, 5H), 7.19 – 7.17 (m, 2H), 5.85 (d, *J* = 9.7 Hz, 1H), 3.68 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.27 (d, *J* = 5.1 Hz), 152.47 (dd, *J* = 3.4, 1.7 Hz), 152.32 (dd, *J* = 3.4, 1.6 Hz), 134.80 (d, *J* = 4.4 Hz),133.92 (d, *J* = 3.4 Hz), 133.83 (d, *J* = 3.1 Hz), 129.44, 129.38 (d, *J* = 141.5 Hz), 129.21 (d, *J* = 139.3 Hz), 128.84, 127.47, 120.58 (t, *J* = 15.0 Hz), 120.29 (qd, *J* = 259.0, 6.7 Hz), 74.52 (d, *J* = 5.0 Hz), 52.76. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 31.00. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.64, -57.68. **HRMS** (ESI) m/z calcd for $C_{23}H_{18}F_6O_6P$ $[M+H]^+$: 535.0740, found: 535.0742.

Methyl 2-((bis(4-fluorophenyl)phosphoryl)oxy)-2-phenylacetate (3ae). 
Colorless oil, 36.6 mg, 91% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.92 – 7.86 (m, 2H), 7.72 – 7.66 (m, 2H), 7.41 – 7.38 (m, 2H), 7.33 – 7.30 (m, 3H), 7.17 (td, *J* = 8.8, 2.6 Hz, 2H), 7.04 (td, *J* = 8.6, 2.4 Hz, 2H), 5.82 (d, *J* = 10.0 Hz, 1H), 3.67 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.39 (d, *J* = 4.7 Hz), 166.36 (dd, *J* = 12.9, 3.5 Hz), 164.34 (dd, *J* = 12.9, 3.5 Hz), 135.00 (d, *J* = 4.7 Hz), 134.40 (dd, *J* = 9.1, 2.1 Hz), 134.31 (dd, *J* = 9.1, 1.8 Hz), 129.29, 128.78, 127.48(dd, *J* = 29.3, 3.4 Hz), 127.34, 126.36 (dd, *J* = 29.3, 3.4 Hz), 116.13 – 115.96 (m), 115.90 – 115.73 (m), 74.28 (d, *J* = 5.0 Hz), 52.70. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 32.30. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -105.42 (d, *J* = 1.3 Hz), -105.53(d, *J* = 1.0 Hz). **HRMS** (ESI) m/z calcd for $C_{21}H_{18}F_2O_4P$ $[M+H]^+$: 403.0905, found: 403.0911.

Methyl 2-((bis(4-chlorophenyl)phosphoryl)oxy)-2-phenylacetate (3af). 
Colorless oil, 41.8 mg, 96% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 2H), 7.63 – 7.59 (m, 2H), 7.47 – 7.45 (m, 2H), 7.40 – 7.38 (m, 2H), 7.35 – 7.30 (m, 5H), 5.83 (d, *J* = 9.9 Hz, 1H), 3.68 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.27 (d, *J* = 4.6 Hz), 139.28 (d, *J* = 3.7 Hz), 139.17 (d, *J* = 3.6 Hz), 134.87 (d, *J* = 4.7 Hz), 133.14 (d, *J* = 3.6 Hz), 133.05 (d, *J* = 3.4 Hz), 129.79 (d, *J* = 24.4 Hz),

129.33, 128.92 (t, *J* = 14.1 Hz), 128.79, 128.68 (d, *J* = 23.1 Hz), 127.34, 74.37 (d, *J* = 5.0 Hz), 52.72. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 32.16. **HRMS** (ESI) m/z calcd for $C_{21}H_{18}Cl_2O_4P$ $[M+H]^+$: 435.0314, found: 435.0321.

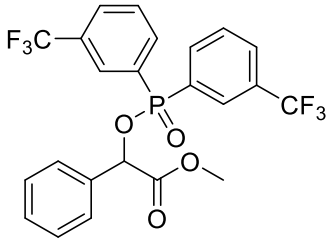
Methyl 2-((bis(4-bromophenyl)phosphoryl)oxy)-2-phenylacetate (3ag). Colorless oil, 39.8 mg, 76% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 2H), 7.63 – 7.61 (m, 2H), 7.55 – 7.53 (m, 1H), 7.51 – 7.48 (m, 3H), 7.40 – 7.35 (m, 2H), 7.34 – 7.30 (m, 3H), 5.82 (d, *J* = 9.8 Hz, 1H), 3.68 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.25 (d, *J* = 4.7 Hz), 134.84 (d, *J* = 4.7 Hz), 133.21 (d, *J* = 4.0 Hz), 133.12 (d, *J* = 3.8 Hz), 131.88 (t, *J* = 14.0 Hz), 130.24 (d, *J* = 23.1 Hz), 129.34, 129.13 (d, *J* = 21.5 Hz), 128.80, 127.95 (d, *J* = 3.7 Hz), 127.84 (d, *J* = 3.7 Hz), 127.34, 74.38 (d, *J* = 5.0 Hz), 52.73. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 32.45. **HRMS** (ESI) m/z calcd for $C_{21}H_{18}Br_2O_4P$ $[M+H]^+$: 522.9304, found: 522.9308.

Methyl 2-((bis(3-fluoro-4-methylphenyl)phosphoryl)oxy)-2-phenylacetate (3ah). Colorless oil, 41.7 mg, 97% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.56 – 7.49 (m, 2H), 7.42 – 7.40 (m, 2H), 7.39 – 7.34 (m, 1H), 7.34 – 7.28 (m, 5H), 7.20 – 7.16 (m, 1H), 5.82 (d, *J* = 9.9 Hz, 1H), 3.68 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.35 (d, *J* = 4.5 Hz), 161.93 (dd, *J* = 19.5, 14.7 Hz), 159.96 (dd, *J* = 19.5, 14.9 Hz), 135.03 (d, *J* = 4.8 Hz), 132.04 (dd, *J* = 12.2, 3.7 Hz), 131.90 (dd, *J* = 12.0, 3.7 Hz), 130.83 (dd, *J* = 22.9, 6.0 Hz), 130.34 (dd, *J* = 12.8, 2.8 Hz), 130.21 (dd, *J* = 12.8, 2.8 Hz), 129.71 (dd, *J* = 21.6, 6.0 Hz), 129.25, 128.75, 127.31, 127.27 (d, *J* = 3.7 Hz), 127.19 (d, *J* = 3.7 Hz), 118.20 (dd, *J* = 11.7, 1.6 Hz), 118.02 (dd, *J* = 11.7, 1.5 Hz), 74.39 (d, *J* = 5.0 Hz), 52.68, 14.81 (d, *J* = 3.6 Hz), 14.74 (d, *J* = 3.6 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 31.45 (t, *J* = 6.4 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -115.59 (d, *J* = 6.4 Hz), -115.73 (d, *J* = 6.6 Hz). **HRMS** (ESI) m/z calcd for $C_{23}H_{22}F_2O_4P$ $[M+H]^+$: 431.1218, found: 431.1226.

Methyl 2-((bis(4-(trifluoromethyl)phenyl)phosphoryl)oxy)-2-phenylacetate (3ai). Colorless oil, 48.2 mg, 96% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 12.4, 8.0 Hz, 2H), 7.80 (dd, *J* = 12.3, 8.0 Hz, 2H), 7.76 (dd, *J* = 8.2, 2.9 Hz, 2H), 7.61 (dd, *J* = 8.2, 2.9 Hz, 2H), 7.40 – 7.38 (m, 2H), 7.35 – 7.29 (m,

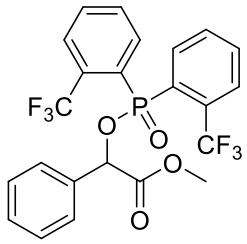
3H), 5.89 (d, *J* = 9.5 Hz, 1H), 3.69 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.09 (d, *J* = 5.0 Hz), 135.29 (d, *J* = 12.1 Hz), 134.62 – 134.43 (m), 134.36 – 134.17 (m), 132.27 (d, *J* = 6.4 Hz), 132.18 (d, *J* = 6.3 Hz), 129.56, 128.89, 127.48, 125.64 (q, *J* = 3.8 Hz), 125.57 – 125.44 (m), 125.37 (q, *J* = 3.7 Hz), 123.36 (q, *J* = 272.7 Hz), 123.44 (q, *J* = 272.7 Hz), 74.75 (d, *J* = 5.1 Hz), 52.83. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 30.11. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -63.36, -63.43. **HRMS** (ESI) m/z calcd for $C_{23}H_{18}F_6O_4P$ $[M+H]^+$: 503.0841, found: 503.0847.

Methyl 2-((bis(3-(trifluoromethyl)phenyl)phosphoryl)oxy)-2-phenylacetate (3aj).



Colorless oil, 45.2 mg, 90% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 13.0 Hz, 1H), 8.09 (dd, *J* = 12.4, 7.7 Hz, 1H), 7.93 (d, *J* = 12.8 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.65 (td, *J* = 7.8, 3.4 Hz, 1H), 7.51 (td, *J* = 7.8, 3.3 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.32 – 7.28 (m, 3H), 5.90 (d, *J* = 9.8 Hz, 1H), 3.70 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.03 (d, *J* = 5.4 Hz), 135.03 (dd, *J* = 10.2, 7.7 Hz), 134.52 (d, *J* = 4.1 Hz), 132.06 (d, *J* = 140.2 Hz), 131.92 (d, *J* = 137.9 Hz), 131.80 – 131.27 (m), 131.26 – 130.73 (m), 129.61, 129.56 – 129.51 (m), 129.43 (d, *J* = 13.5 Hz), 129.27 (d, *J* = 13.4 Hz), 128.91, 128.58 (q, *J* = 3.9 Hz), 128.49 (q, *J* = 3.9 Hz), 127.53, 123.53 (qd, *J* = 272.7, 2.0 Hz), 123.38 (qd, *J* = 272.6, 1.9 Hz), 74.82 (d, *J* = 5.1 Hz), 52.83. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 29.92. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.88, -62.97. **HRMS** (ESI) m/z calcd for $C_{23}H_{18}F_6O_4P$ $[M+H]^+$: 503.0841, found: 503.0847.

Methyl 2-((bis(2-(trifluoromethyl)phenyl)phosphoryl)oxy)-2-phenylacetate (3ak).



Colorless oil, 46.2 mg, 92% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.60 (dd, *J* = 14.3, 7.7 Hz, 1H), 8.05 (dd, *J* = 14.7, 7.7 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.39 (m, 2H), 7.31 – 7.27 (m, 3H), 6.00 (d, *J* = 8.6 Hz, 1H), 3.61 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.32 (d, *J* = 4.2 Hz), 135.32 (d, *J* = 6.6 Hz), 134.96 (d, *J* = 8.0 Hz), 134.55 (d, *J* = 5.7 Hz), 132.45 (d, *J* = 2.7 Hz), 132.26 (d, *J* = 2.7 Hz), 131.88 (dd, *J* = 10.5, 8.5 Hz), 131.62 (dd, *J* = 10.6, 8.5 Hz), 131.39 (d, *J* = 11.7 Hz), 131.13 (d, *J* = 12.6 Hz), 130.73 – 129.66 (m), 130.46 – 129.37 (m), 129.20, 128.62, 127.55, 127.35 – 127.24 (m), 127.23 – 127.11 (m), 123.36 (qd, *J* = 274.5, 3.8 Hz), 123.16 (qd, *J* = 274.5, 3.7 Hz), 75.28 (d, *J* = 5.2 Hz), 52.59. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 28.77. **^{19}F NMR**

(471 MHz, Chloroform-*d*) δ -56.99, -57.16. **HRMS** (ESI) m/z calcd for $C_{23}H_{18}F_6O_4P$ $[M+H]^+$: 503.0841, found: 503.0844.

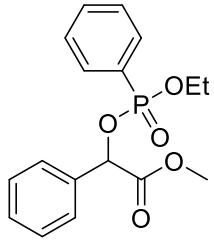
Methyl 2-((di(naphthalen-2-yl)phosphoryl)oxy)-2-phenylacetate (3al). Colorless oil, 42.9 mg, 92% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 14.6 Hz, 1H), 8.41 (d, *J* = 14.4 Hz, 1H), 7.92 (t, *J* = 7.3 Hz, 3H), 7.85 – 7.78 (m, 4H), 7.70 (t, *J* = 9.4 Hz, 1H), 7.58 – 7.49 (m, 4H), 7.47 – 7.46 (m, 2H), 7.32 – 7.27 (m, 3H), 5.93 (dd, *J* = 10.0, 3.2 Hz, 1H), 3.64 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.56 (d, *J* = 4.3 Hz), 135.29 (d, *J* = 4.8 Hz), 134.97 (d, *J* = 2.5 Hz), 134.87 (d, *J* = 2.5 Hz), 134.06 (d, *J* = 10.2 Hz), 133.93 (d, *J* = 10.5 Hz), 132.36 (d, *J* = 11.5 Hz), 132.24 (d, *J* = 11.4 Hz), 129.12, 129.07, 128.99, 128.68, 128.65 (d, *J* = 31.7 Hz), 128.45, 128.37 (d, *J* = 1.9 Hz), 128.34 (d, *J* = 1.9 Hz), 128.27, 127.81, 127.75, 127.55 (d, *J* = 30.7 Hz), 127.34, 126.88, 126.85, 126.44 (d, *J* = 4.6 Hz), 126.35 (d, *J* = 4.5 Hz), 74.33 (d, *J* = 5.0 Hz), 52.60. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.66. **HRMS** (ESI) m/z calcd for $C_{29}H_{24}O_4P$ $[M+H]^+$: 467.1407, found: 467.1413.

Methyl 2-((dibenzylphosphoryl)oxy)-2-phenylacetate (3am). Colorless oil, 35.9 mg, 91% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.41 – 7.39 (m, 2H), 7.36 – 7.31 (m, 5H), 7.30 – 7.26 (m, 2H), 7.24 (d, *J* = 2.1 Hz, 1H), 7.17 – 7.11 (m, 3H), 7.01 – 7.00 (m, 2H), 5.55 (d, *J* = 8.8 Hz, 1H), 3.66 (s, 3H), 3.42 – 3.26 (m, 2H), 2.99 – 2.86 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.17 (d, *J* = 3.2 Hz), 135.40 (d, *J* = 5.5 Hz), 131.34 (d, *J* = 7.1 Hz), 130.45 (d, *J* = 8.5 Hz), 130.13 (d, *J* = 6.0 Hz), 129.93 (d, *J* = 5.7 Hz), 129.01, 128.66 (d, *J* = 2.7 Hz), 128.61, 128.45 (d, *J* = 2.6 Hz), 127.40, 127.00 (d, *J* = 3.3 Hz), 126.80 (d, *J* = 3.1 Hz), 74.42 (d, *J* = 6.4 Hz), 52.56, 37.15 (d, *J* = 85.0 Hz), 36.03 (d, *J* = 85.3 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 51.80. **HRMS** (ESI) m/z calcd for $C_{23}H_{24}O_4P$ $[M+H]^+$: 395.1407, found: 395.1410.

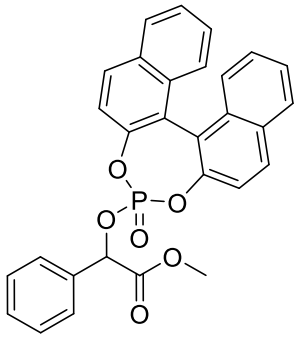
Methyl 2-((butyl(phenyl)phosphoryl)oxy)-2-phenylacetate (3an). Colorless oil, 23.1 mg, 67% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.91 – 7.87 (m, 2H), 7.59 – 7.56 (m, 1H), 7.52 – 7.49 (m, 4H), 7.41 – 7.35 (m, 3H), 5.79 (d, *J* = 10.4 Hz, 1H), 3.54 (s, 3H), 1.93 – 1.83 (m, 2H), 1.48 – 1.36 (m, 2H), 1.32 – 1.24 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.59 (d, *J* = 4.7 Hz), 135.80 (d, *J* = 4.0 Hz), 132.41 (d, *J* =

2.7 Hz), 131.57 (d, *J* = 10.1 Hz), 130.72 (d, *J* = 123.4 Hz), 129.10, 128.75, 128.49 (d, *J* = 12.6 Hz), 127.23, 73.56 (d, *J* = 5.5 Hz), 52.39, 29.79 (d, *J* = 98.1 Hz), 23.67 (d, *J* = 16.6 Hz), 23.51 (d, *J* = 3.7 Hz), 13.44. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 48.00. **HRMS** (ESI) m/z calcd for $C_{19}H_{24}O_4P$ $[M+H]^+$: 347.1407, found: 347.1413.

Methyl 2-((ethoxy(phenyl)phosphoryl)oxy)-2-phenylacetate (3ao). Colorless oil, 27.1 mg, 81% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.93 – 7.88 (m, 2H), 7.72 – 7.68 (m, 2H), 7.58 – 7.54 (m, 1H), 7.51 – 7.46 (m, 5H), 7.41 – 7.33 (m, 7H), 7.31 – 7.28 (m, 3H), 5.93 (d, *J* = 9.2 Hz, 1H), 5.83 (d, *J* = 8.7 Hz, 1H), 4.36 – 4.24 (m, 2H), 4.03 – 3.89 (m, 2H), 3.74 (s, 3H), 3.62 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.72 (d, *J* = 4.1 Hz), 169.34 (d, *J* = 5.4 Hz), 135.41 (d, *J* = 4.8 Hz), 134.90 (d, *J* = 6.0 Hz), 132.59 (d, *J* = 3.1 Hz), 132.47 (d, *J* = 3.1 Hz), 131.76 (d, *J* = 10.3 Hz), 131.63 (d, *J* = 10.2 Hz), 129.21, 129.09, 128.76, 128.62, 128.41 (d, *J* = 11.8 Hz), 128.29 (d, *J* = 11.7 Hz), 127.92 (d, *J* = 192.1 Hz), 127.87 (d, *J* = 192.8 Hz), 127.29, 127.19, 75.41 (t, *J* = 4.5 Hz), 62.72 (d, *J* = 6.2 Hz), 62.30 (d, *J* = 6.1 Hz), 52.64, 52.54, 16.28 (d, *J* = 6.6 Hz), 16.08 (d, *J* = 6.6 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 19.31, 19.15. **HRMS** (ESI) m/z calcd for $C_{17}H_{20}O_5P$ $[M+H]^+$: 335.1043, found: 335.1050.

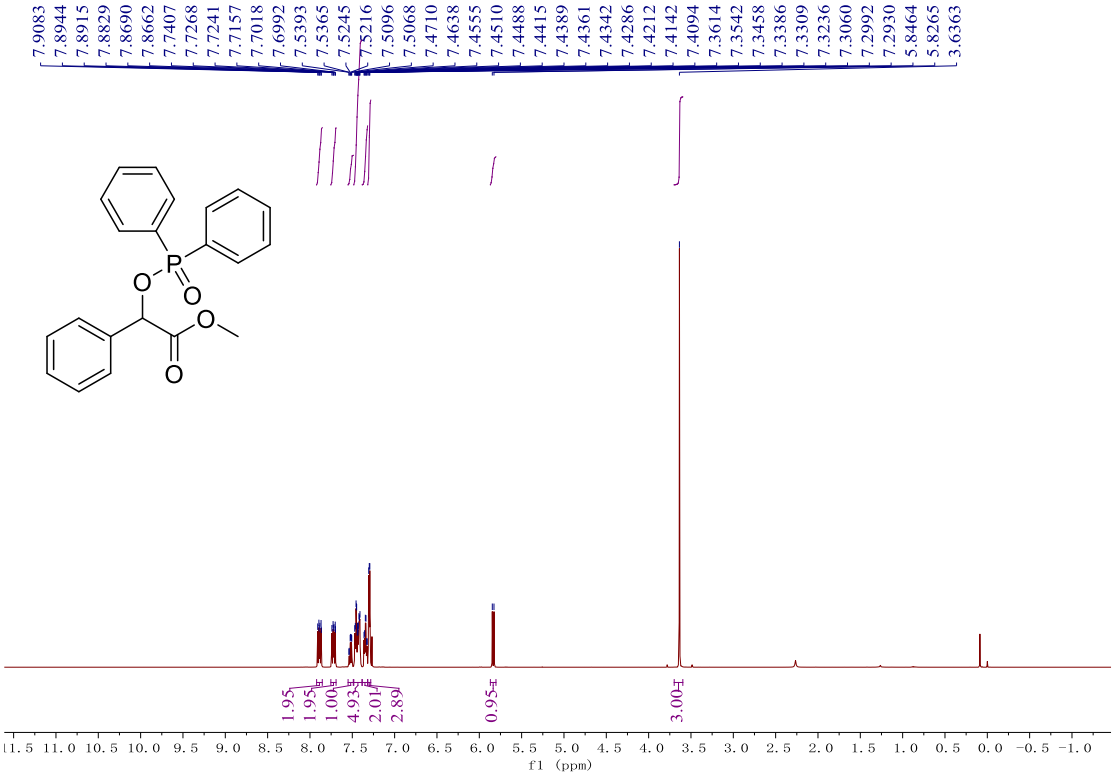


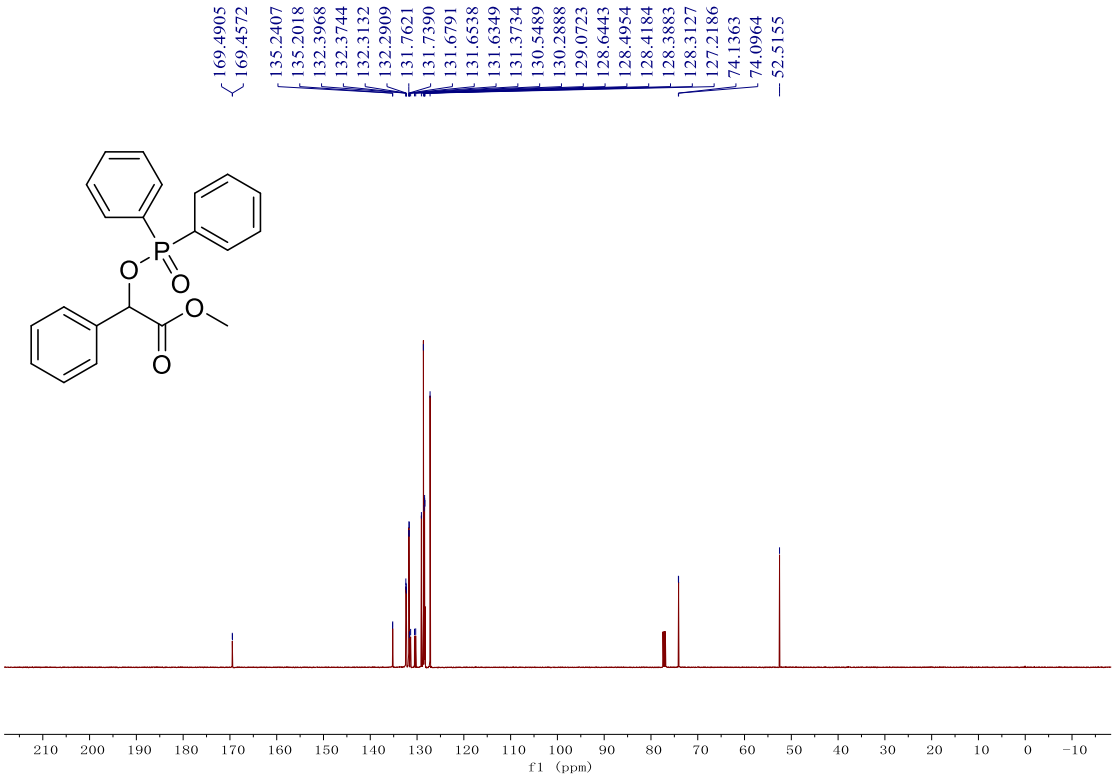
Methyl 2-((4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)oxy)-2-phenylacetate (3ap). Colorless oil, 27.8 mg, 56% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.9 Hz, 1H), 8.01 (d, *J* = 8.9 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.40 – 7.36 (m, 4H), 7.34 – 7.28 (m, 5H), 6.07 (d, *J* = 7.5 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.83 (d, *J* = 4.1 Hz), 146.87 (d, *J* = 169.1 Hz), 146.79 (d, *J* = 166.0 Hz), 134.09 (d, *J* = 7.4 Hz), 132.20 (dd, *J* = 7.0, 0.9 Hz), 131.85 (dd, *J* = 12.9, 1.1 Hz), 131.38 (d, *J* = 0.72 Hz), 131.12, 129.47, 128.78, 128.48, 127.23, 127.19, 127.15, 126.72 (d, *J* = 15.6 Hz), 125.81 (d, *J* = 12.5 Hz), 120.85 (d, *J* = 3.0 Hz), 120.56 (d, *J* = 3.0 Hz), 78.49 (d, *J* = 4.4 Hz), 53.00. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 1.96. **HRMS** (ESI) m/z calcd for $C_{29}H_{22}O_6P$ $[M+H]^+$: 497.1149, found: 497.1155.

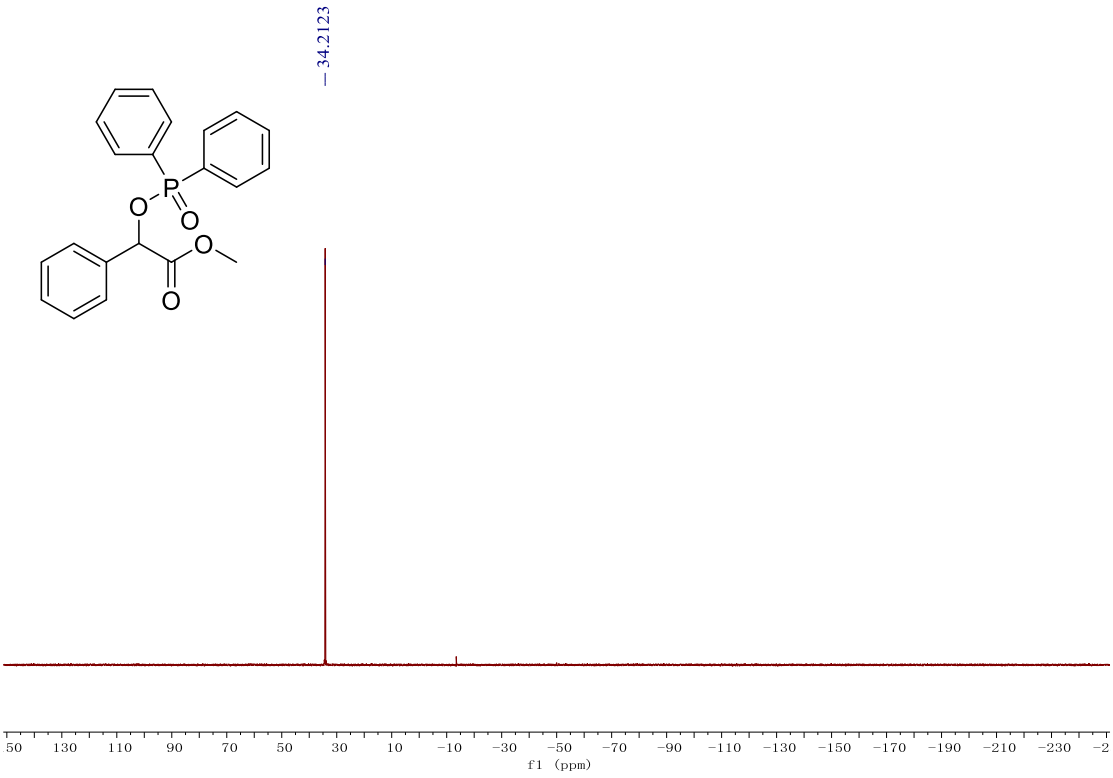


10. Copies of NMR Spectra

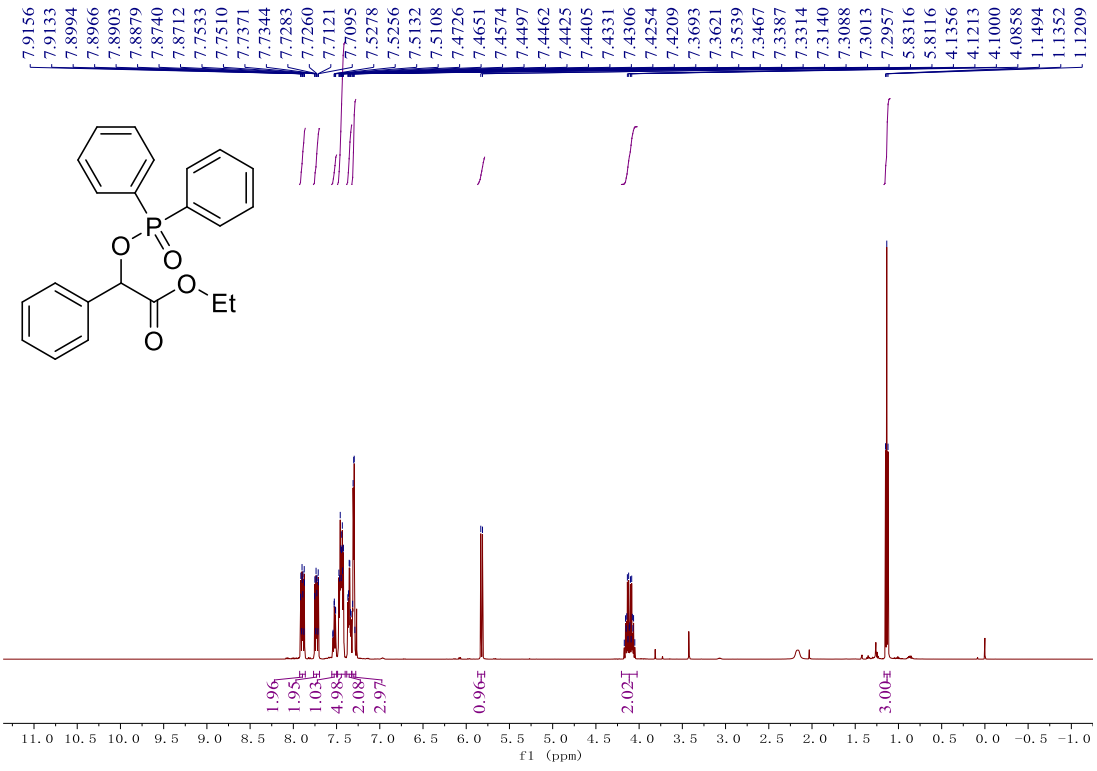
Methyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3aa)

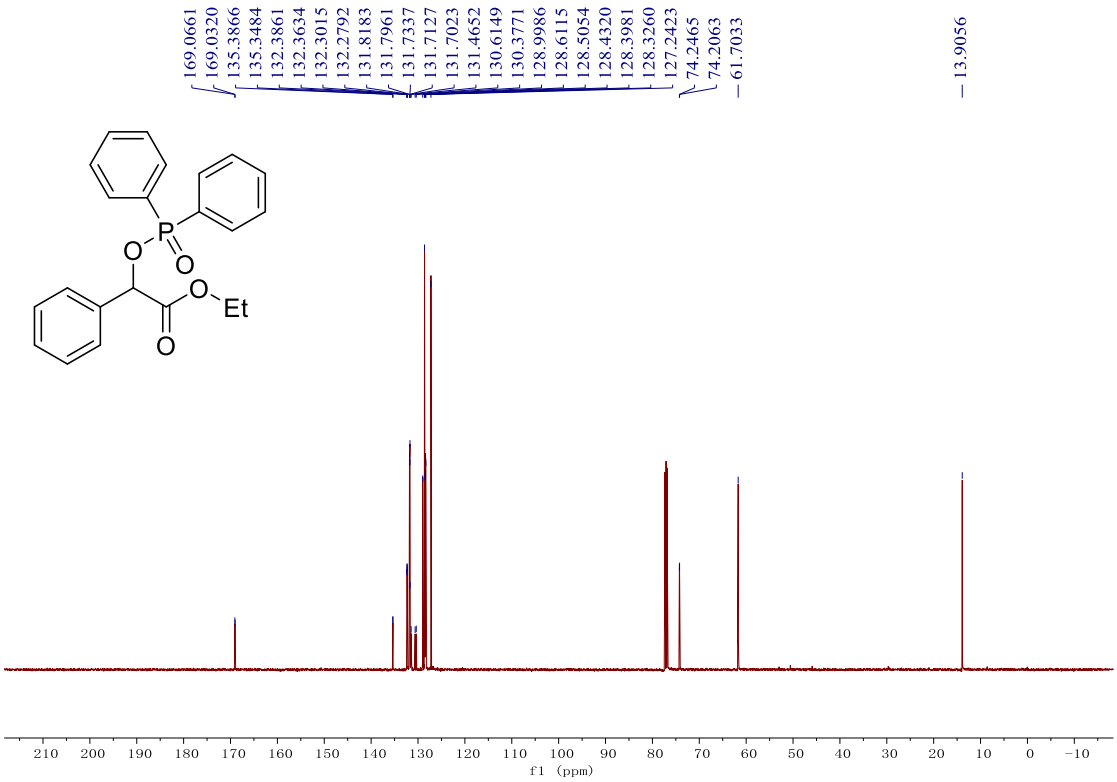






Ethyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3ba)

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74.2063
61.7033
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O
O
O
Et
O
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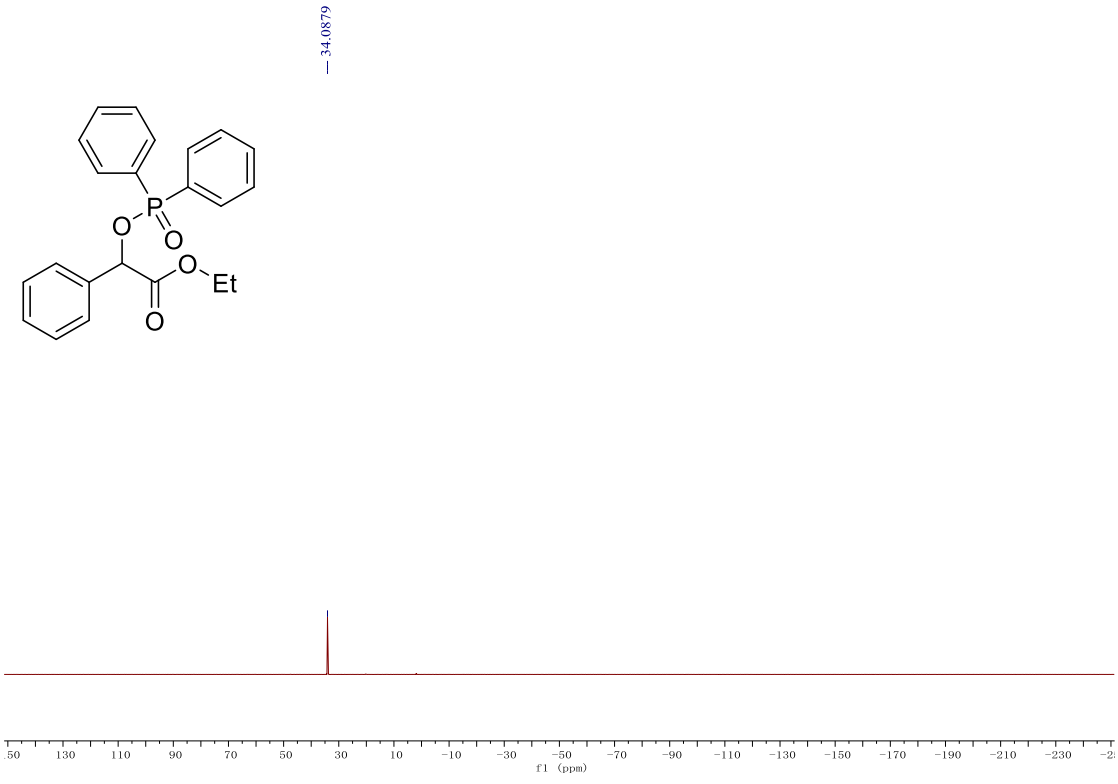
f1 (ppm)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P
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Et
O
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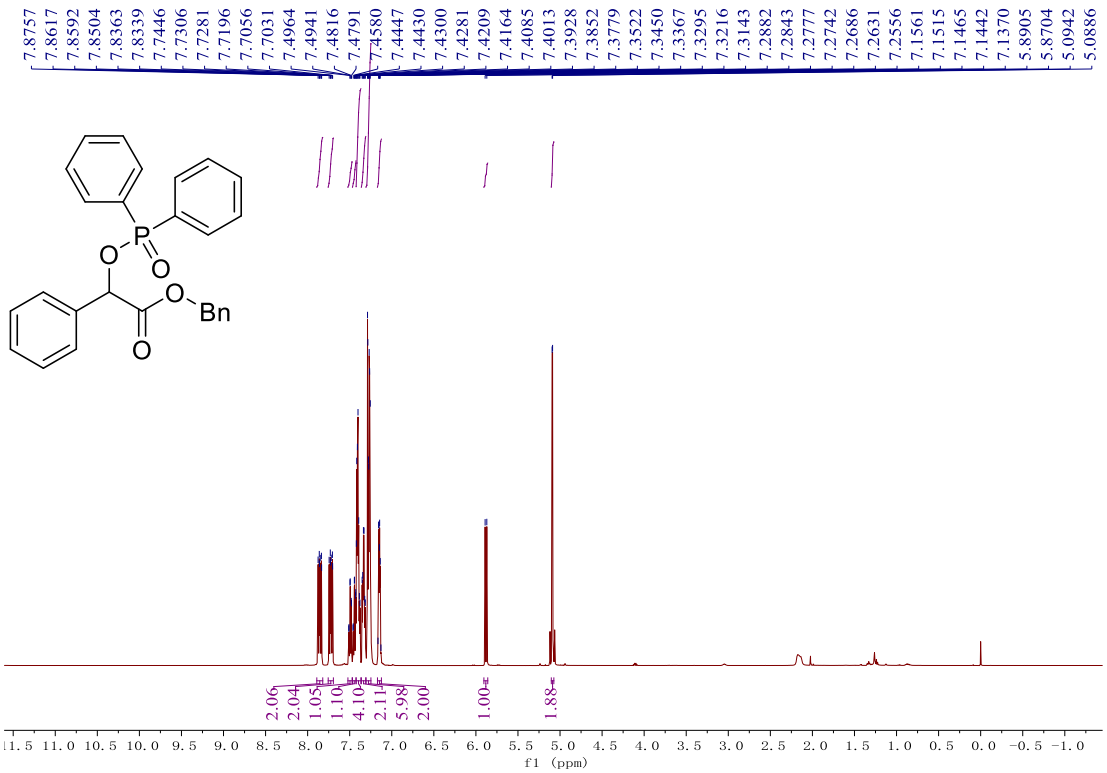
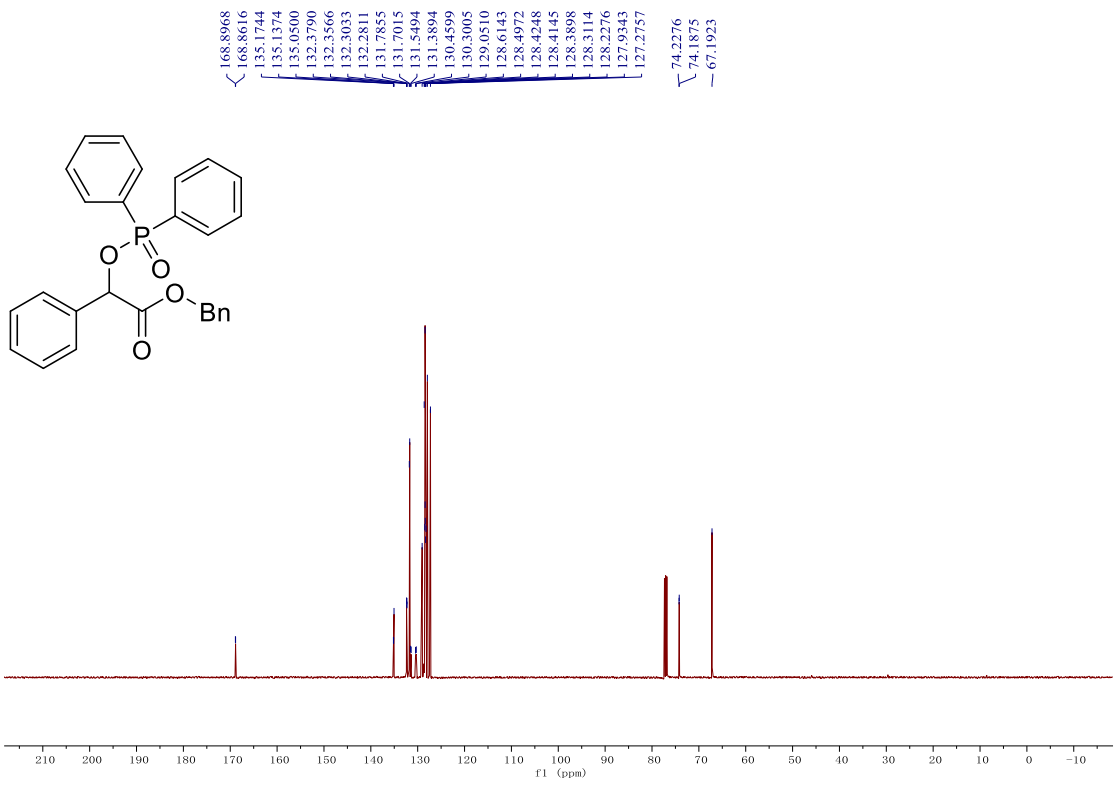
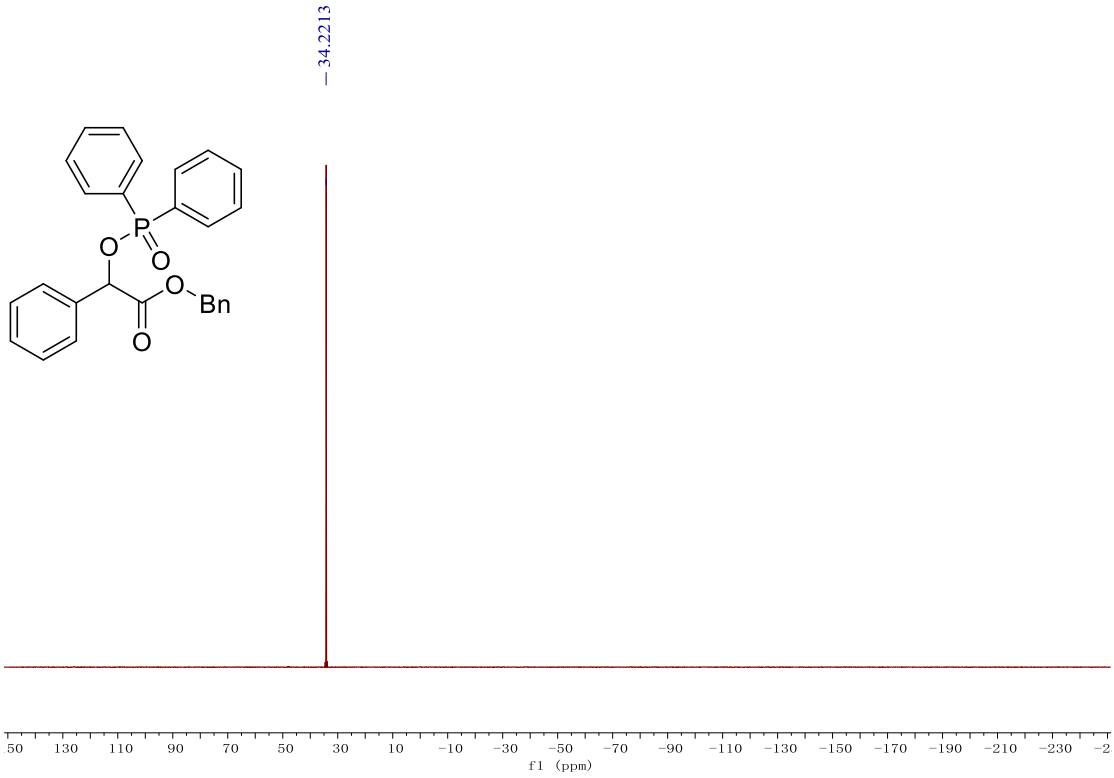
f1 (ppm)

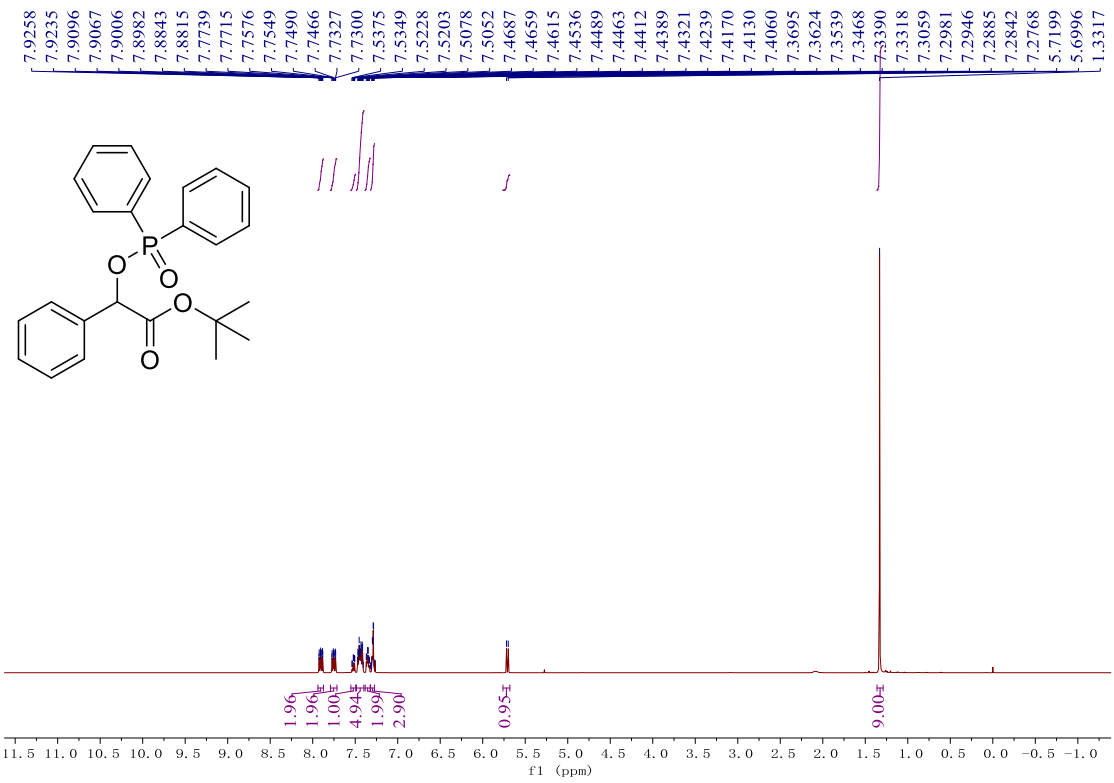
Benzyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3ca)

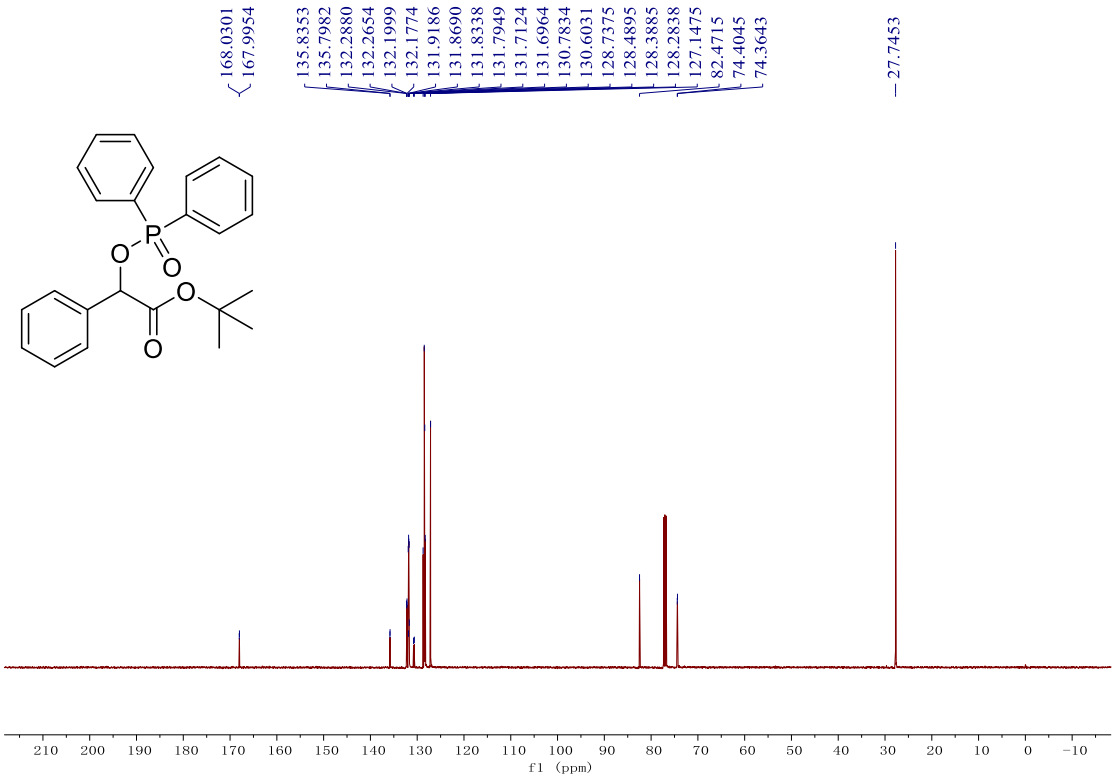






Tert-butyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3da)

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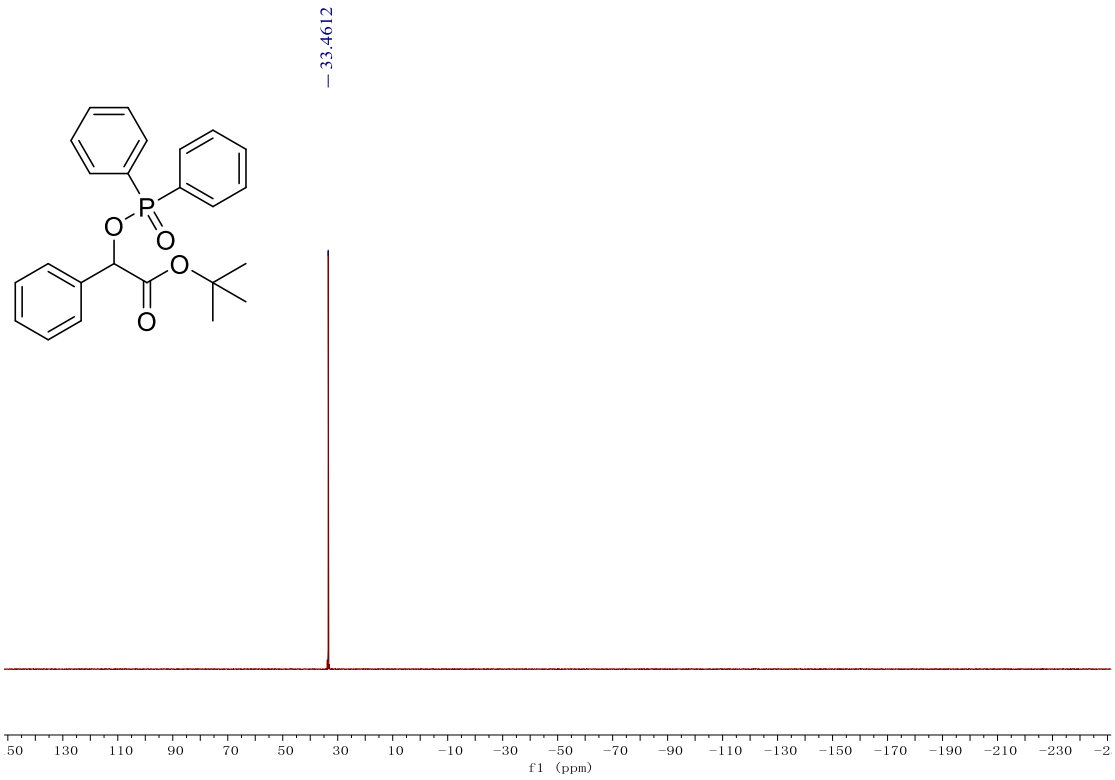
f1 (ppm)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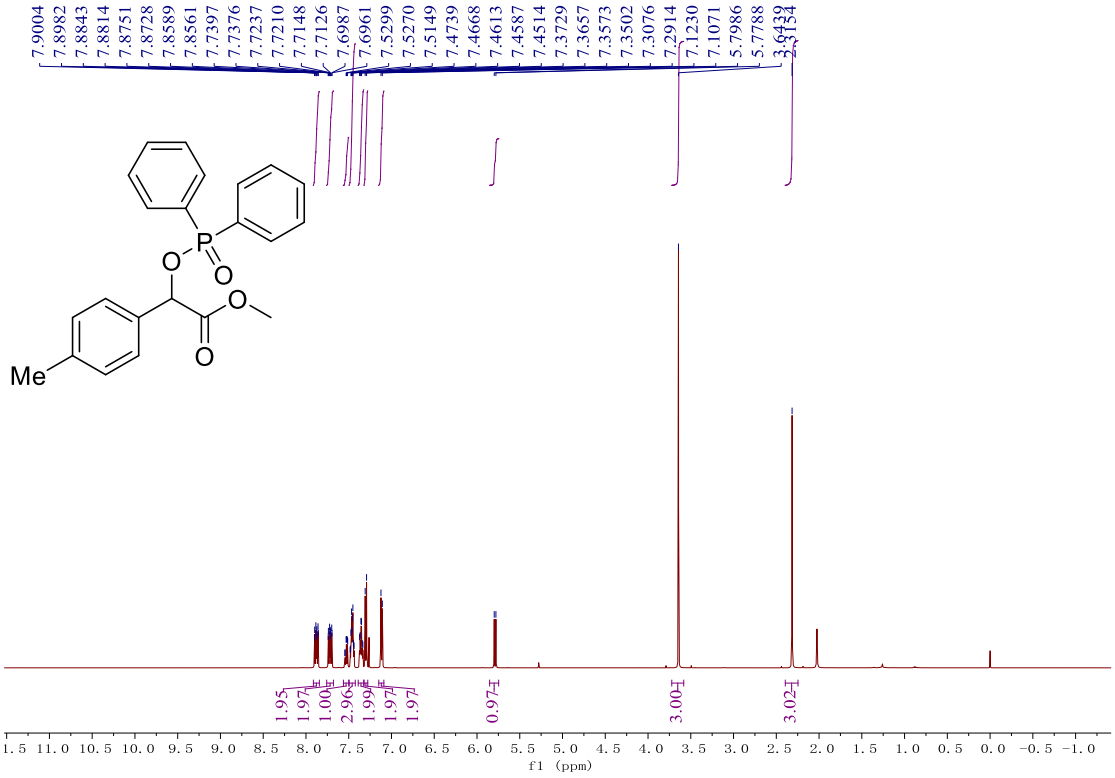
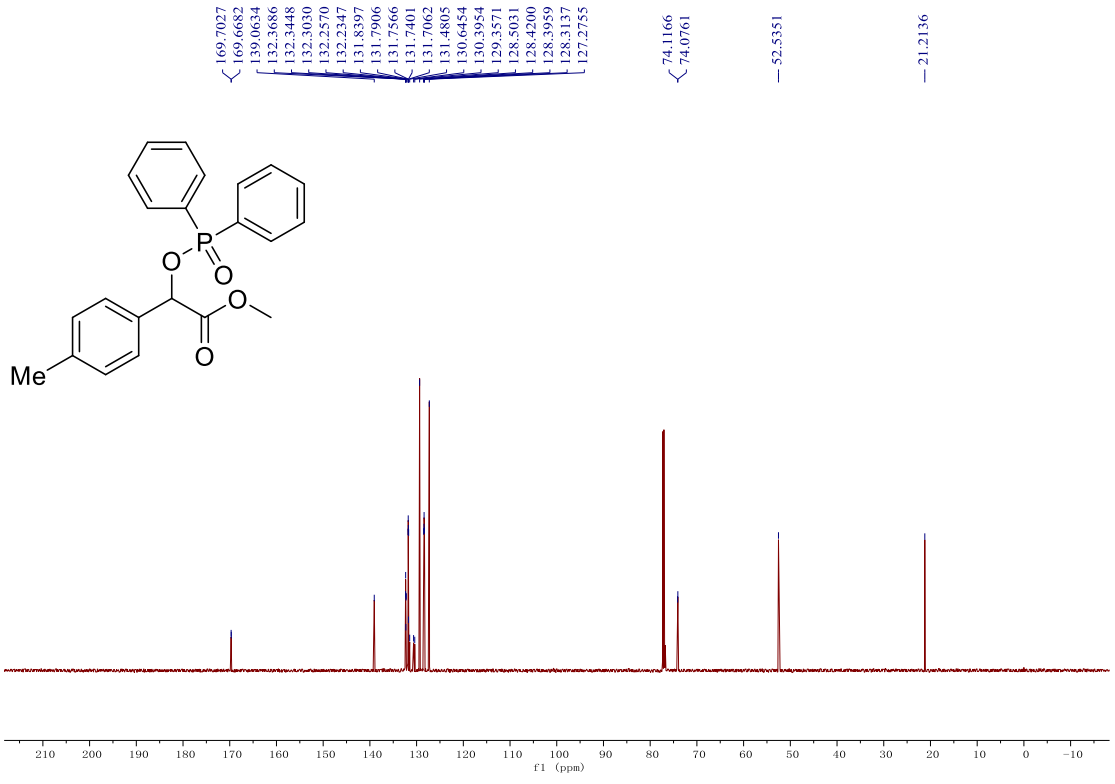
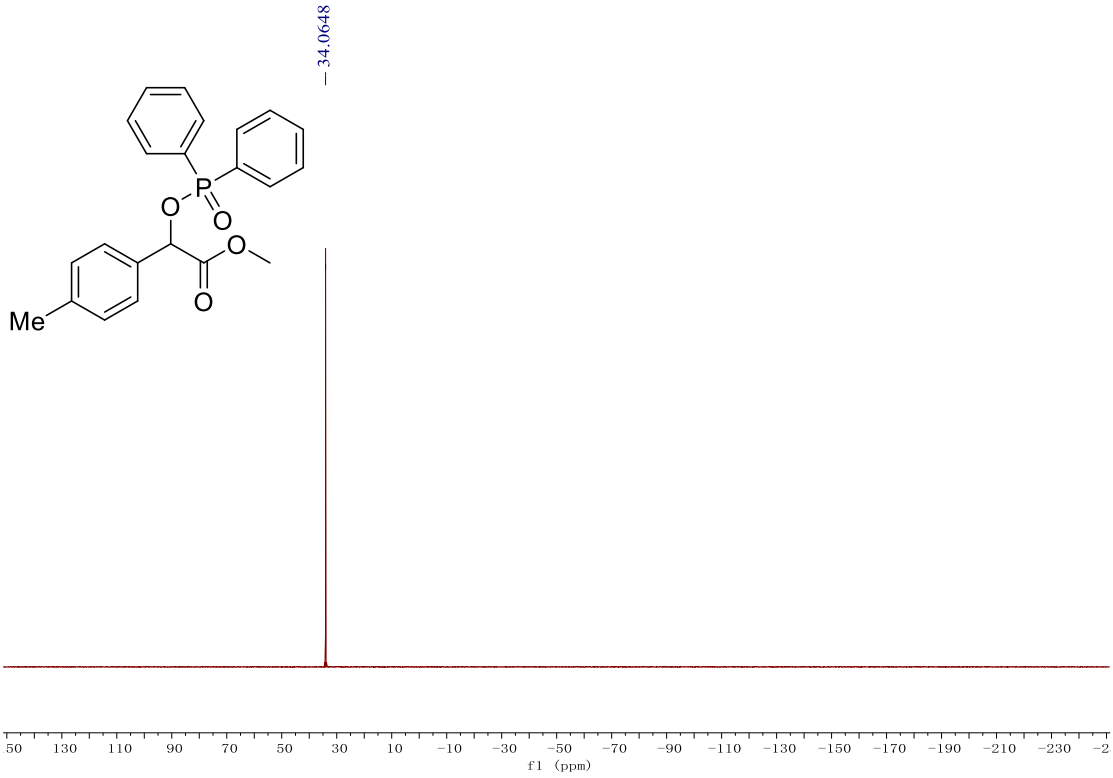
f1 (ppm)

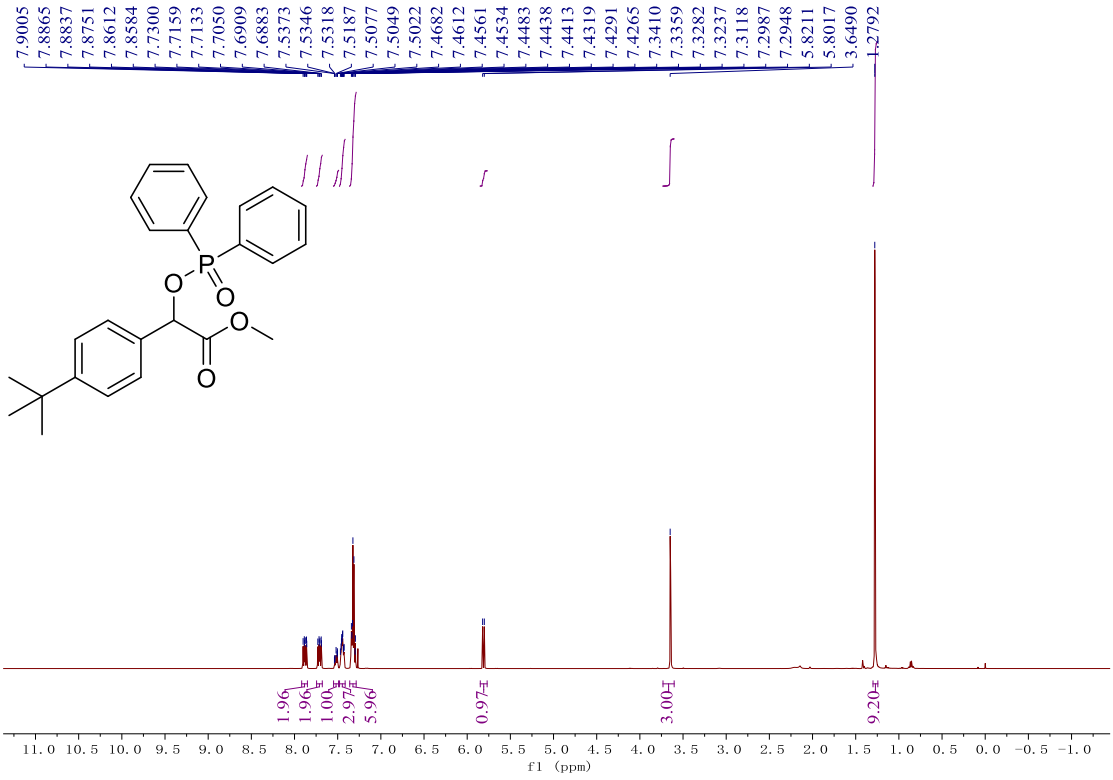
Methyl 2-((diphenylphosphoryl)oxy)-2-(p-tolyl)acetate (3ea)

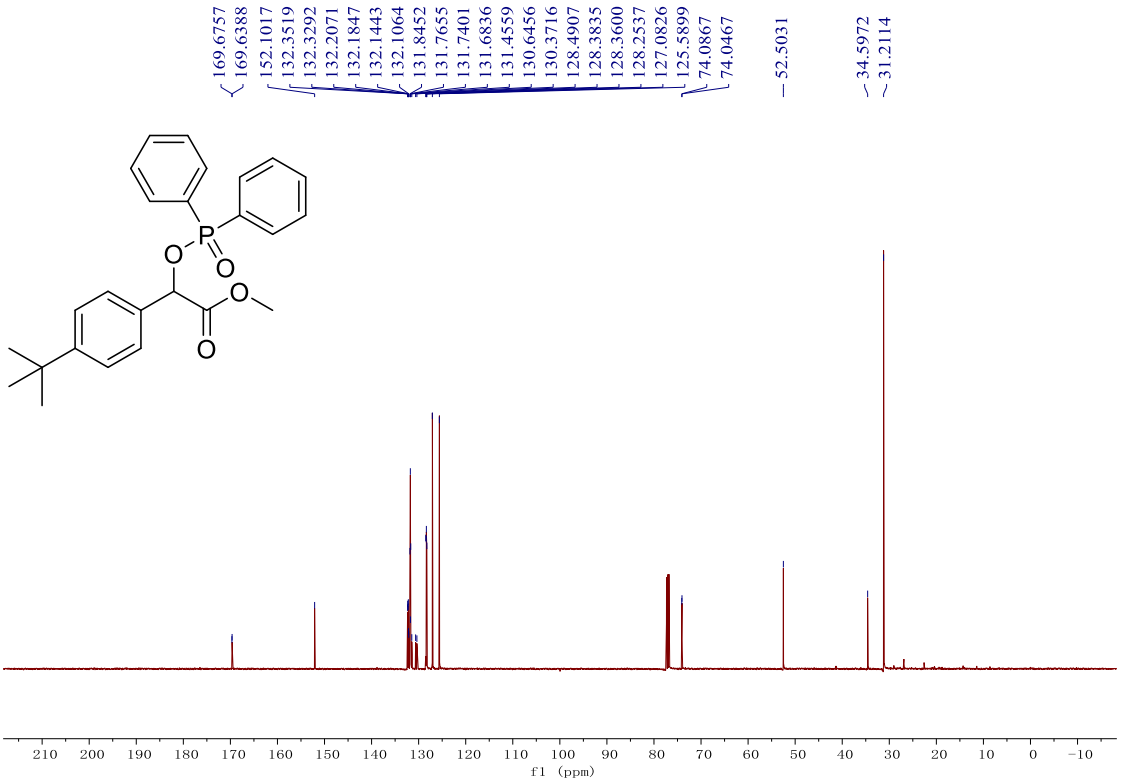


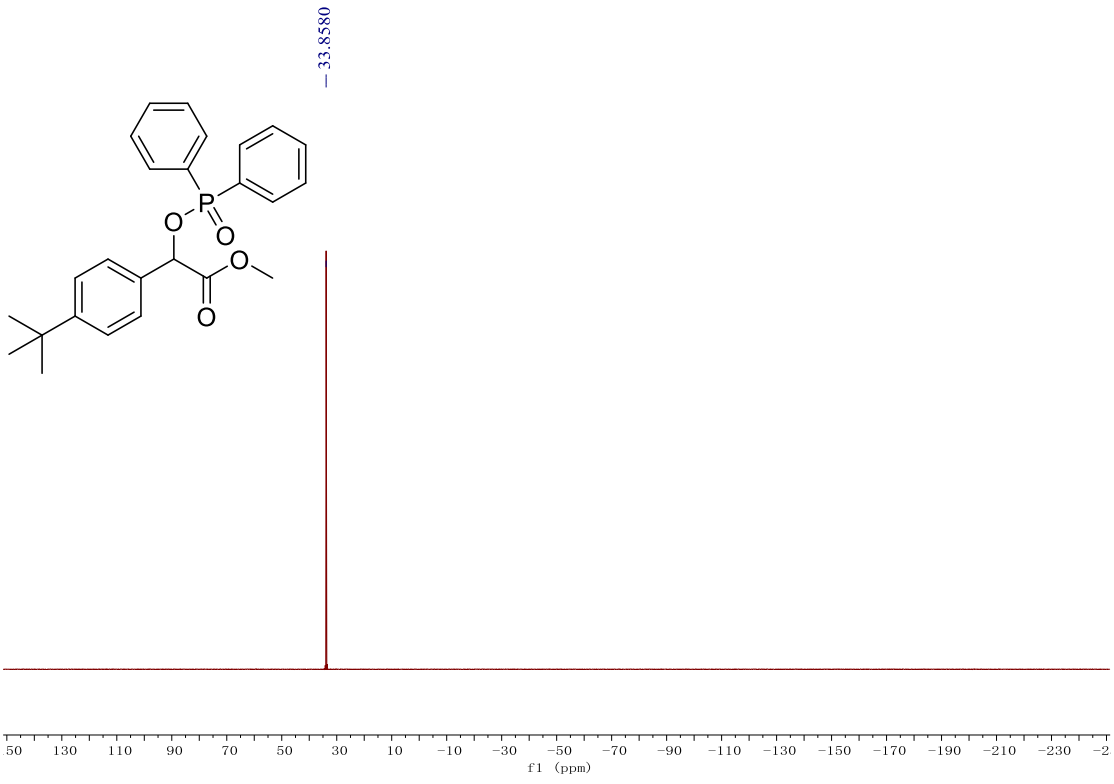




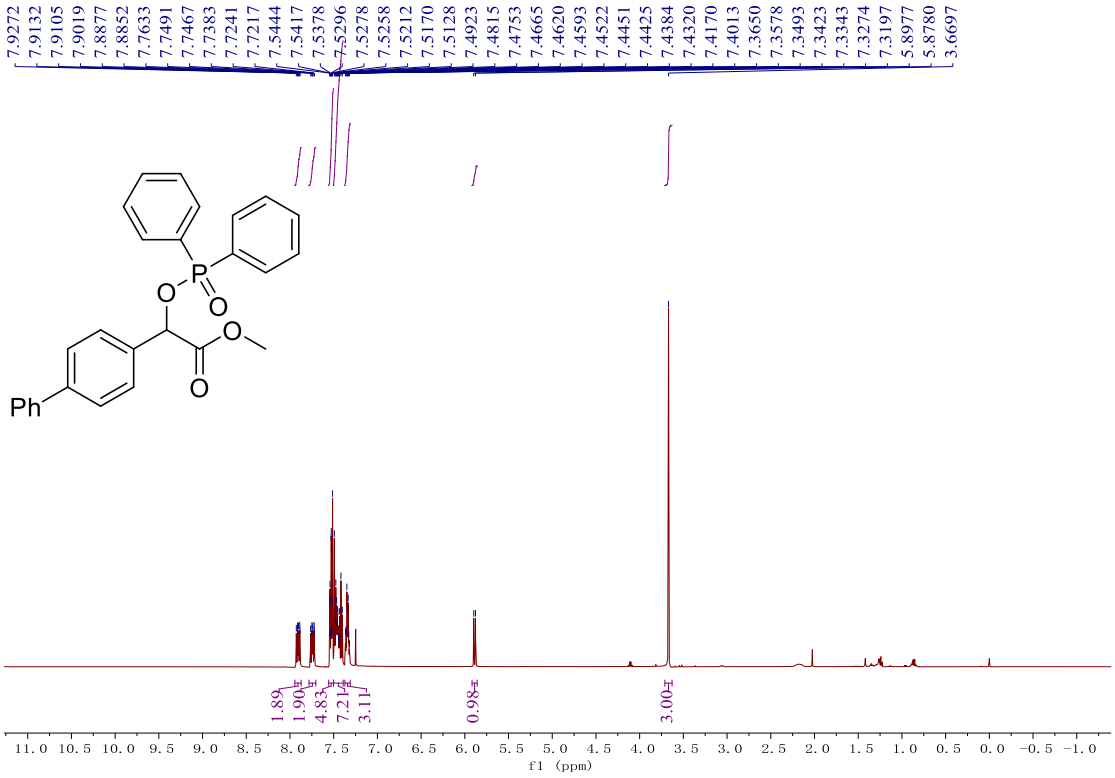
Methyl 2-(4-(*tert*-butyl)phenyl)-2-((diphenylphosphoryl)oxy)acetate (3fa)

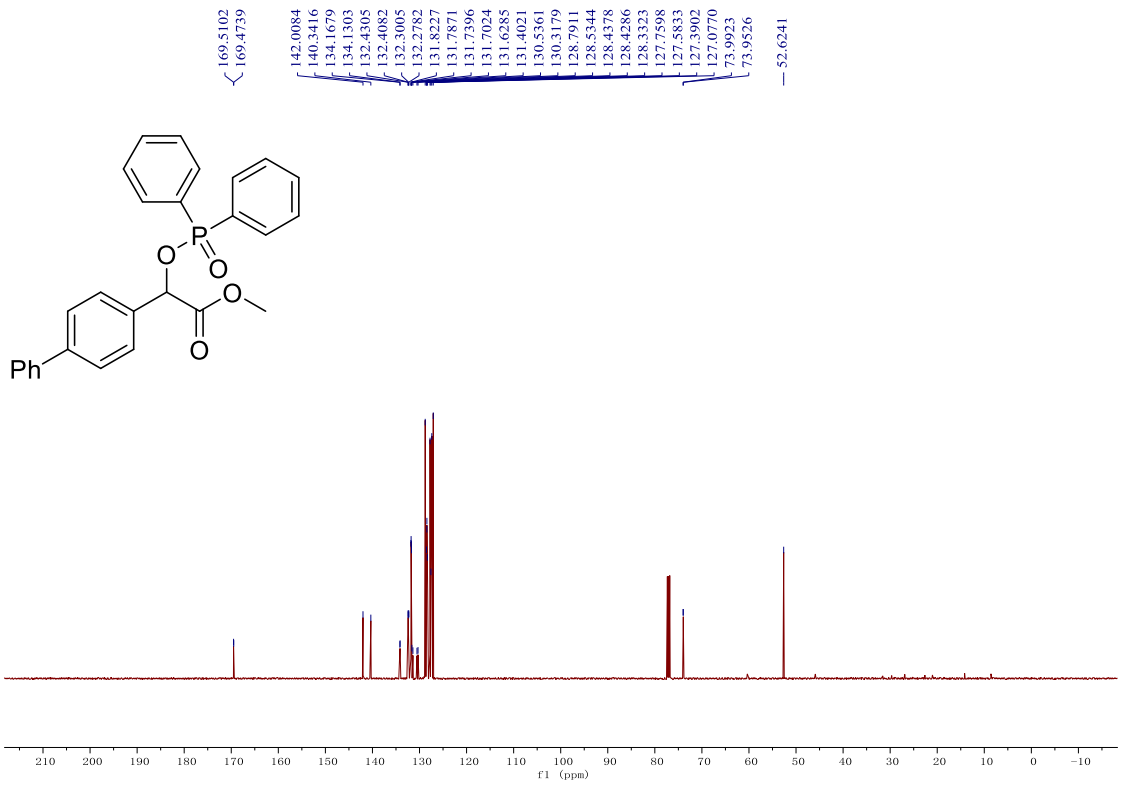


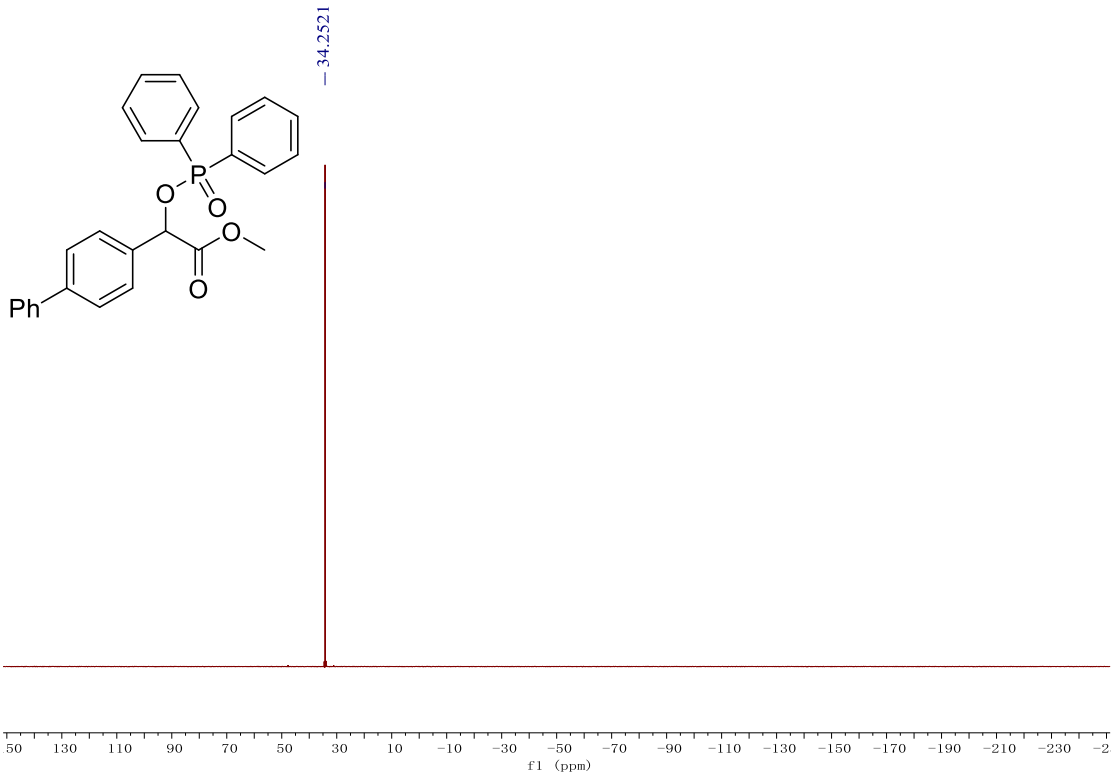

169.6757
169.6388
152.1017
132.3519
132.3292
132.2071
132.1847
132.1443
132.1064
131.8452
131.7655
131.7401
131.6836
131.4559
130.6456
130.3716
128.4907
128.3835
128.3600
128.2537
127.0826
125.5899
74.0867
74.0467
52.5031
34.5972
31.2114
f1 (ppm)


33.8580
f1 (ppm)

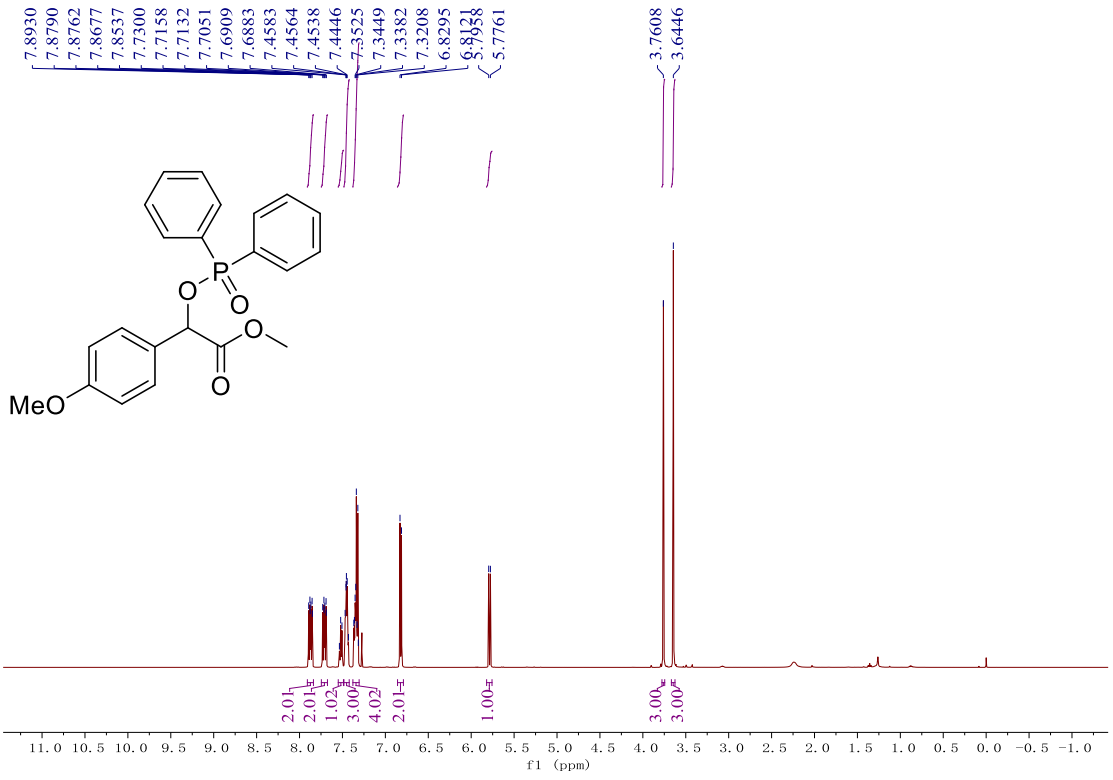
Methyl 2-([1,1'-biphenyl]-4-yl)-2-((diphenylphosphoryl)oxy)acetate (3ga)

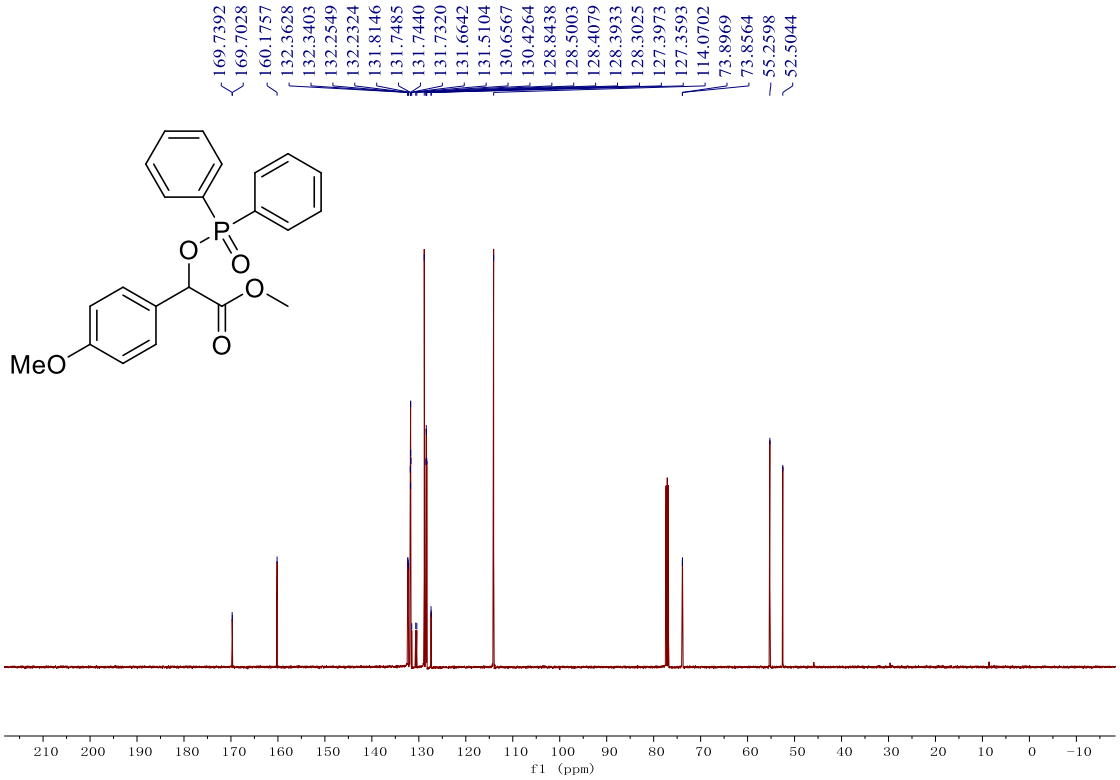


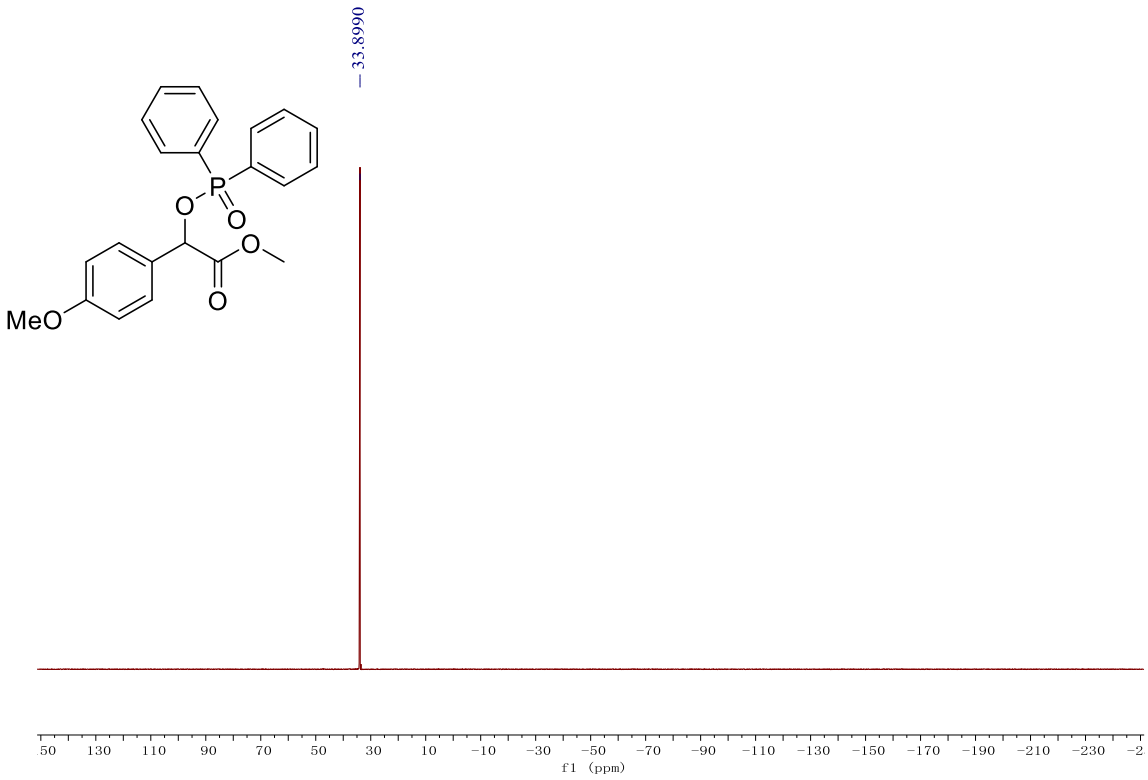




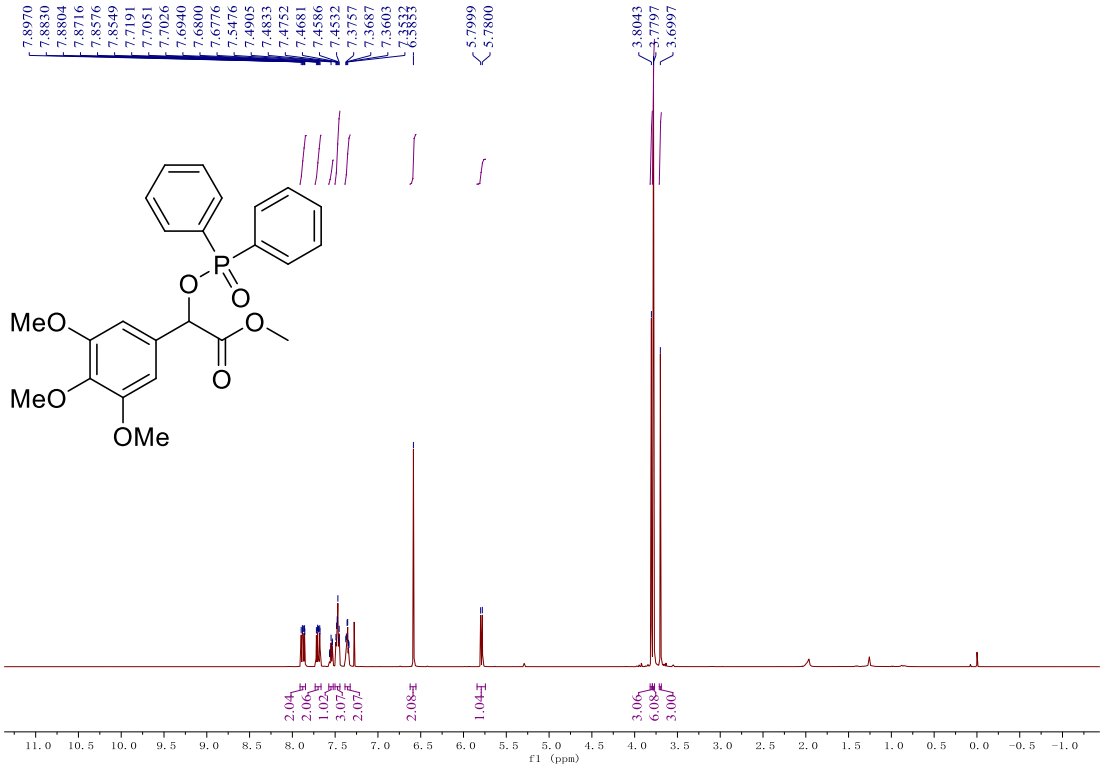
methyl 2-((diphenylphosphoryl)oxy)-2-(4-methoxyphenyl)acetate (3ha)

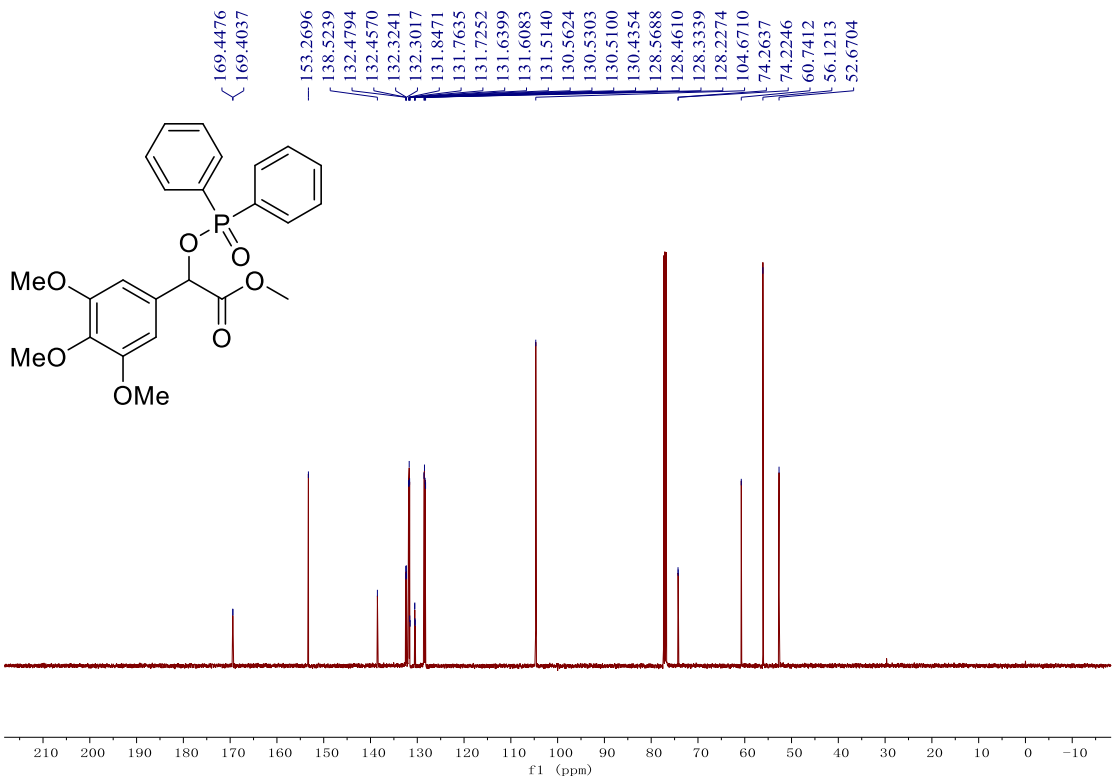


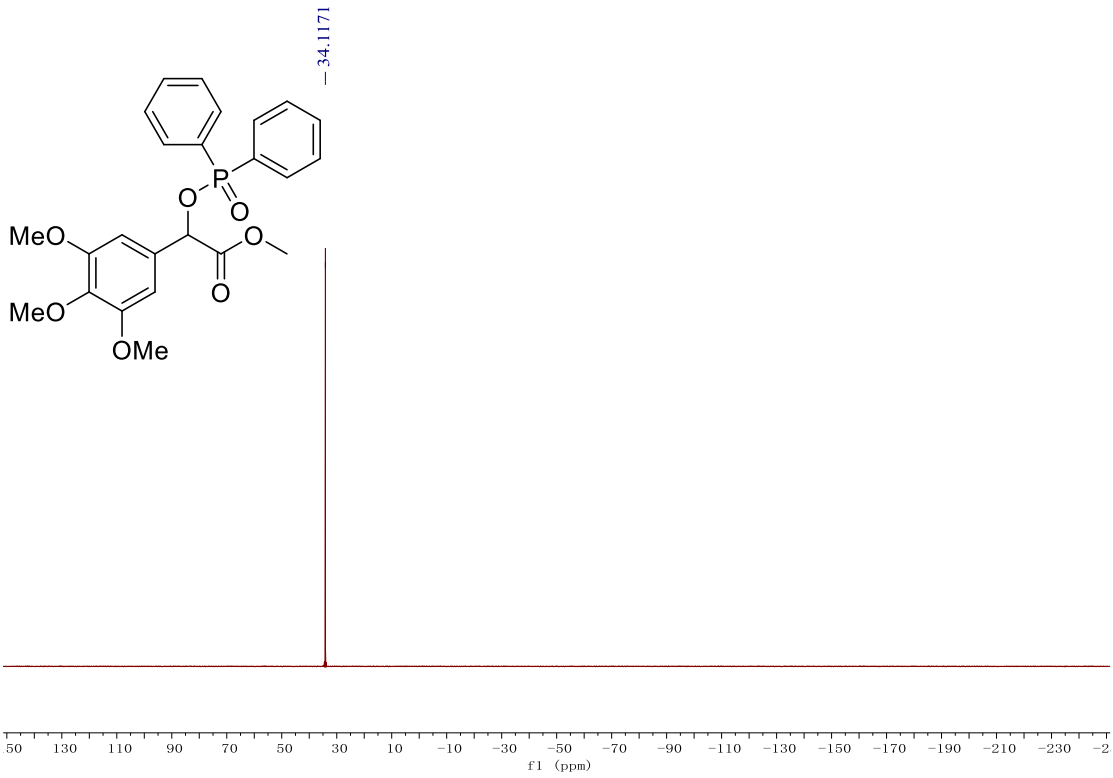

169.7392
169.7028
160.1757
132.3628
132.3403
132.2549
132.2324
131.8146
131.7485
131.7440
131.7320
131.6642
131.5104
130.6567
130.4264
128.8438
128.5003
128.4079
128.3933
128.3025
127.3973
127.3593
114.0702
73.8969
73.8564
55.2598
52.5044
MeO
f1 (ppm)


33.8990
MeO
f1 (ppm)

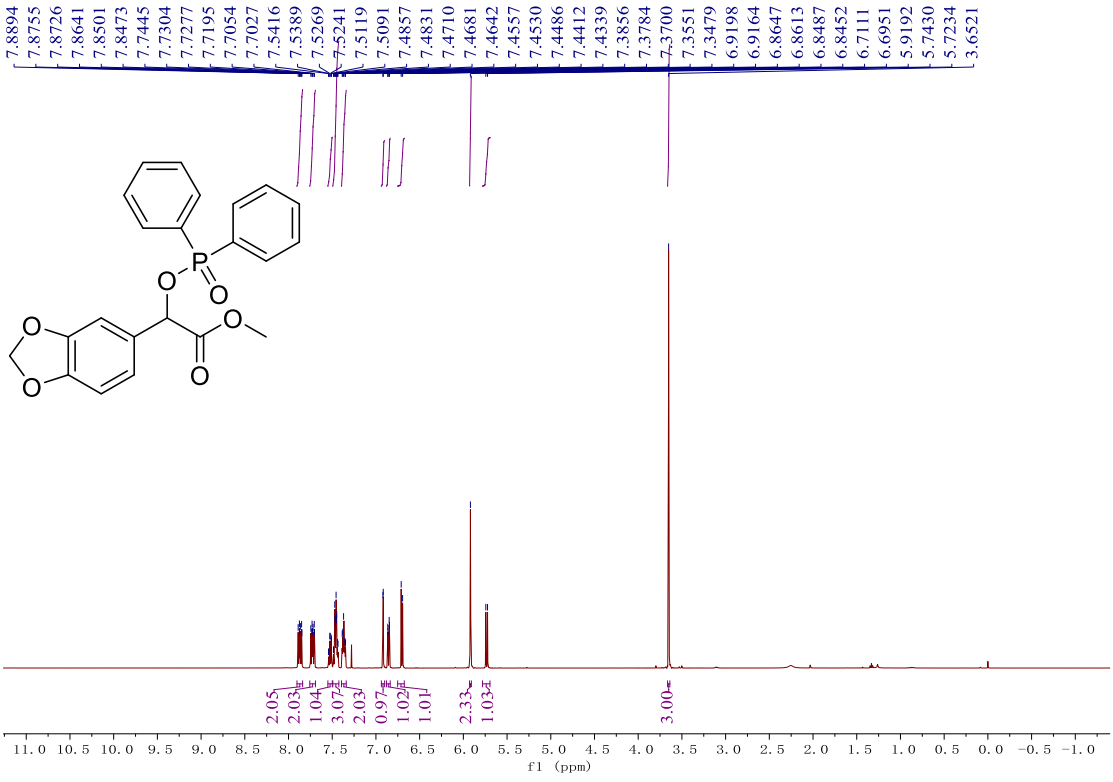
Methyl 2-((diphenylphosphoryl)oxy)-2-(3,4,5-trimethoxyphenyl)acetate (3ia)

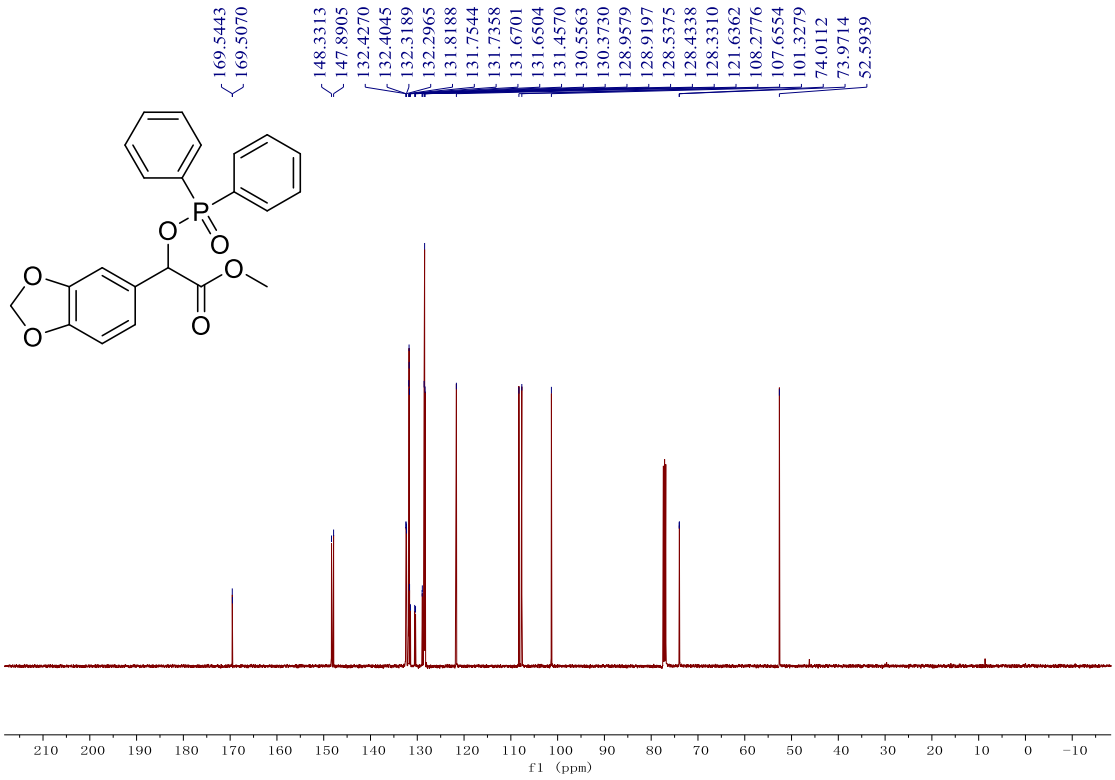


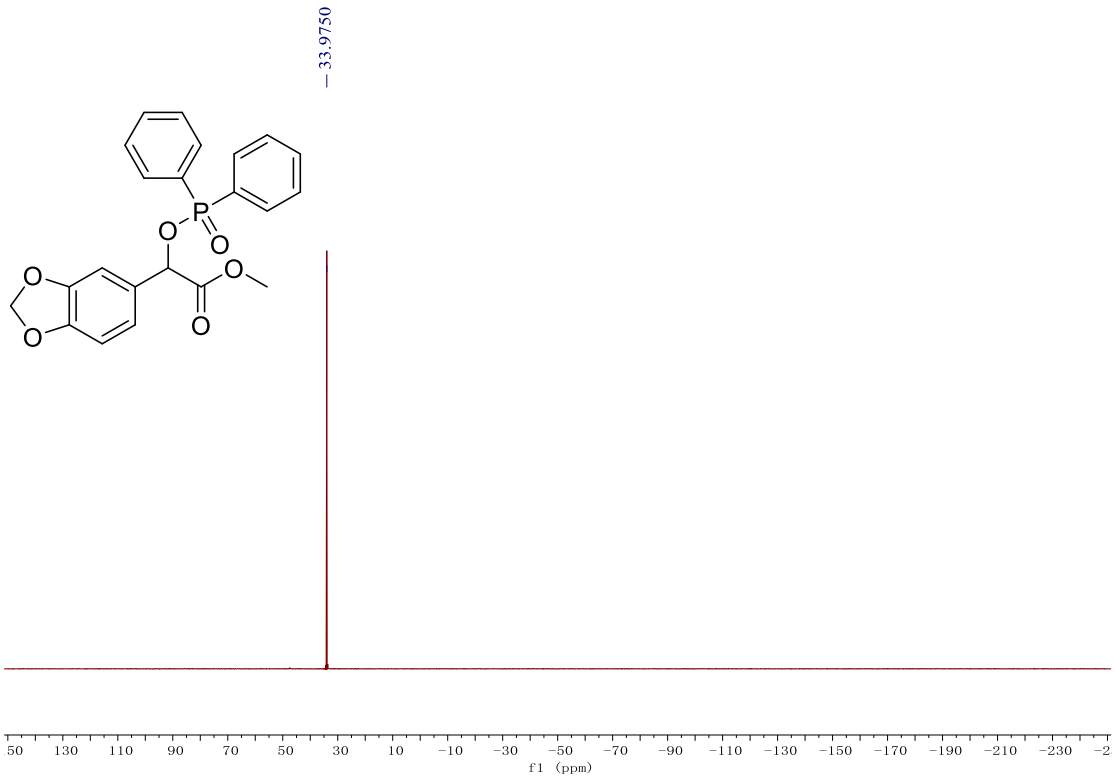




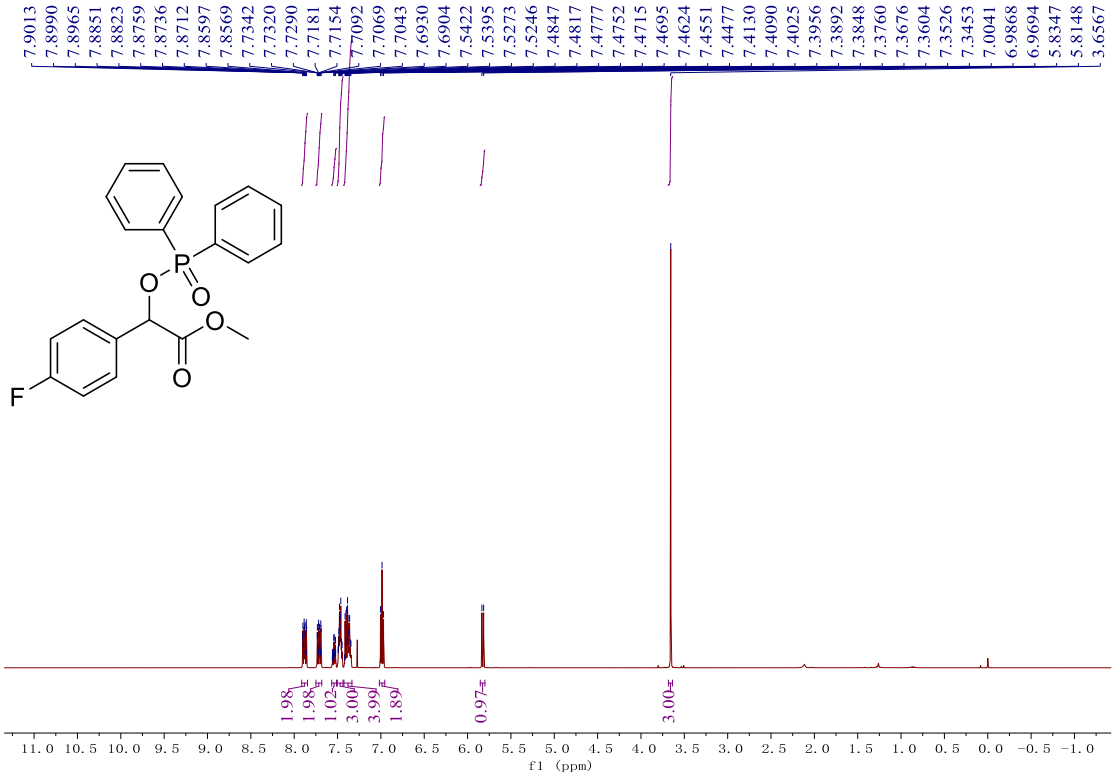
Methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-((diphenylphosphoryl)oxy)acetate (3ja)

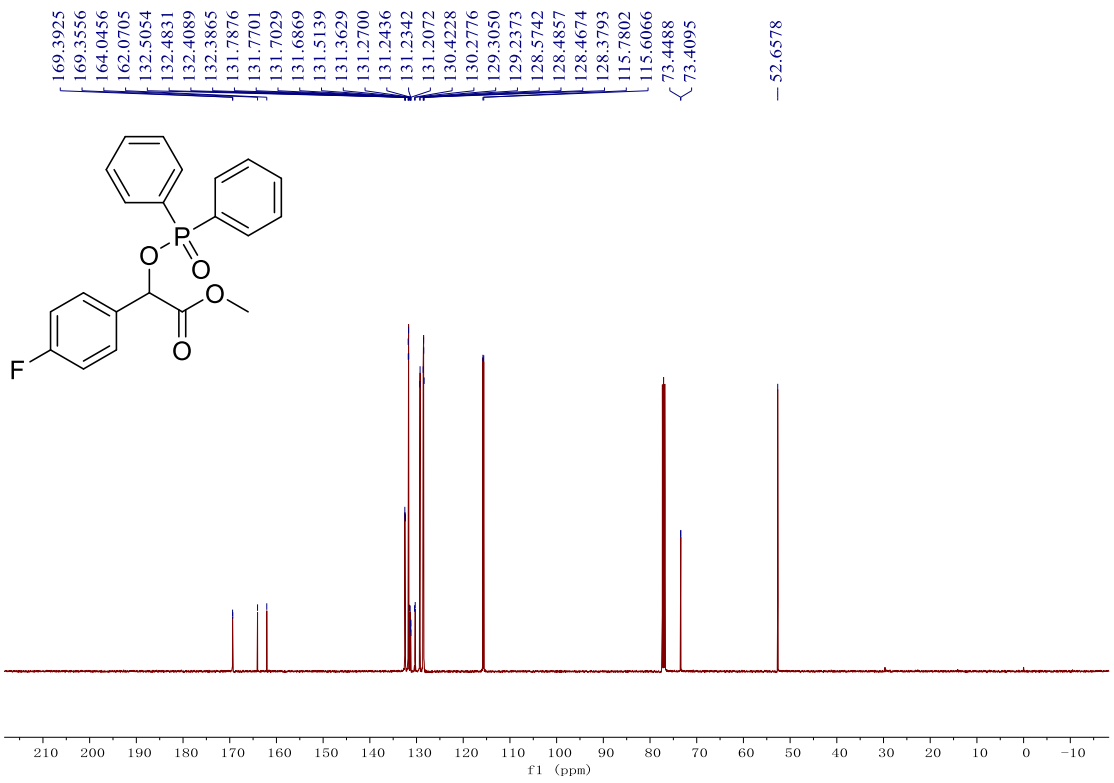


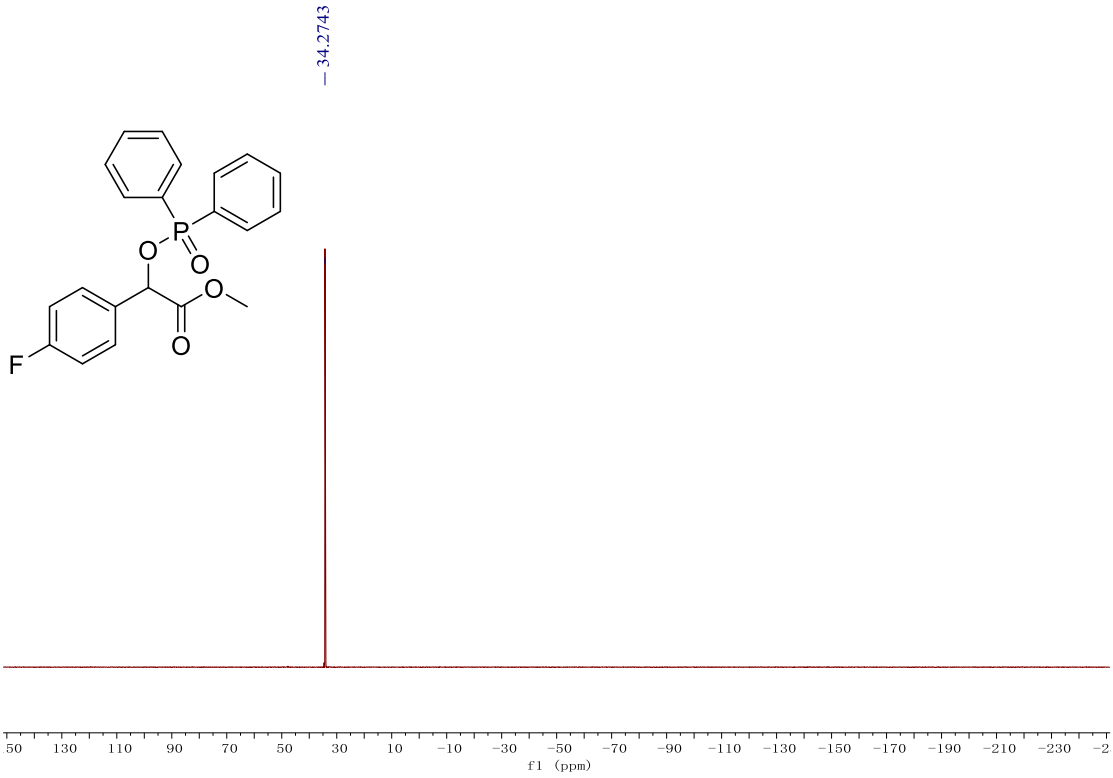

169.5443
169.5070
148.3313
147.8905
132.4270
132.4045
132.3189
132.2965
131.8188
131.7544
131.7358
131.6701
131.6504
131.4570
130.5563
130.3730
128.9579
128.9197
128.5375
128.4338
128.3310
121.6362
108.2776
107.6554
101.3279
74.0112
73.9714
52.5939
f1 (ppm)

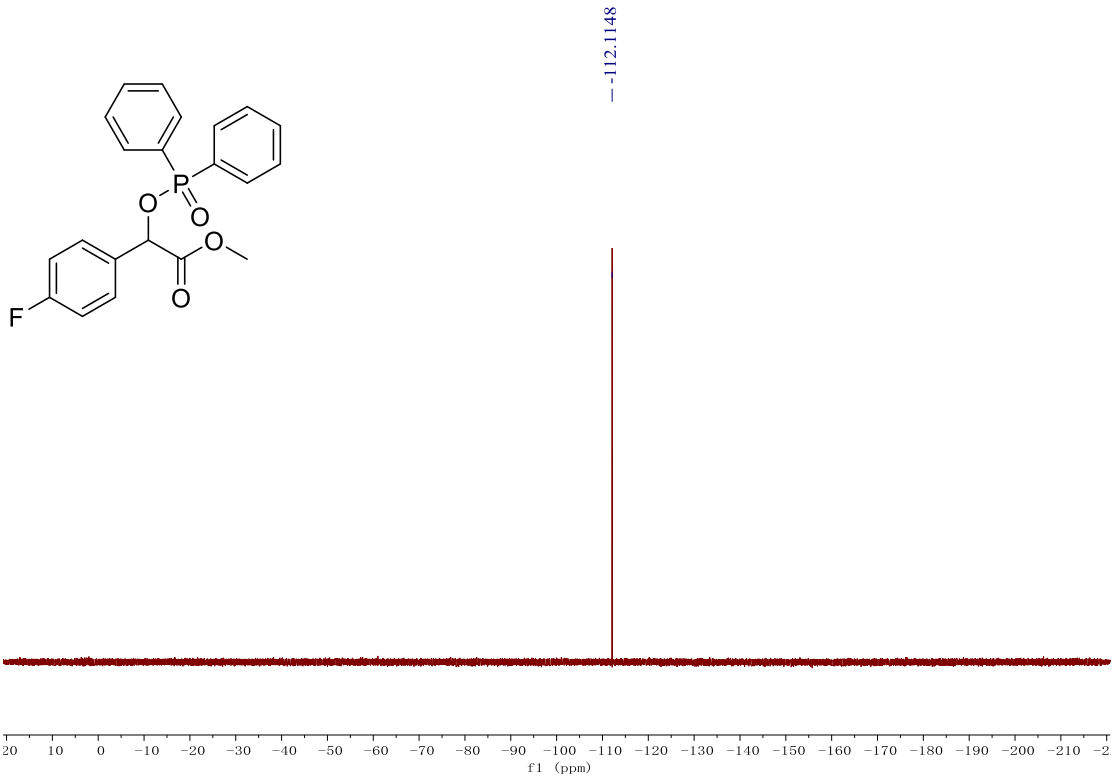

33.9750
f1 (ppm)

Methyl 2-((diphenylphosphoryl)oxy)-2-(4-fluorophenyl)acetate (3ka)

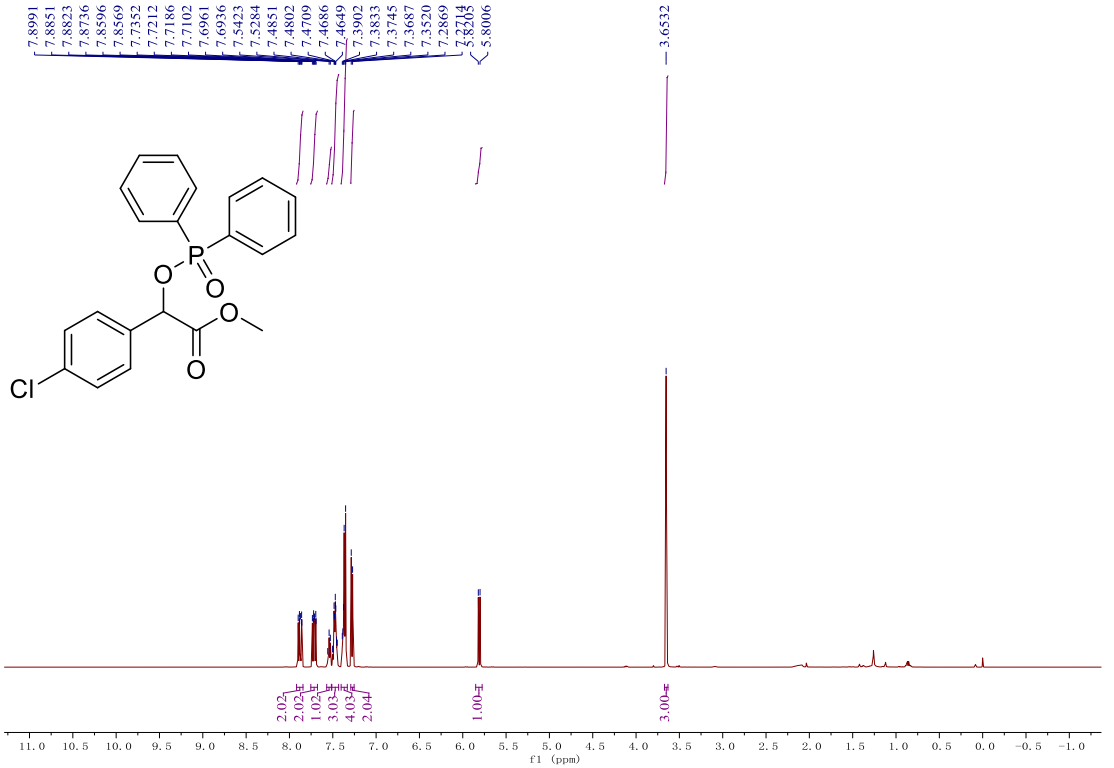


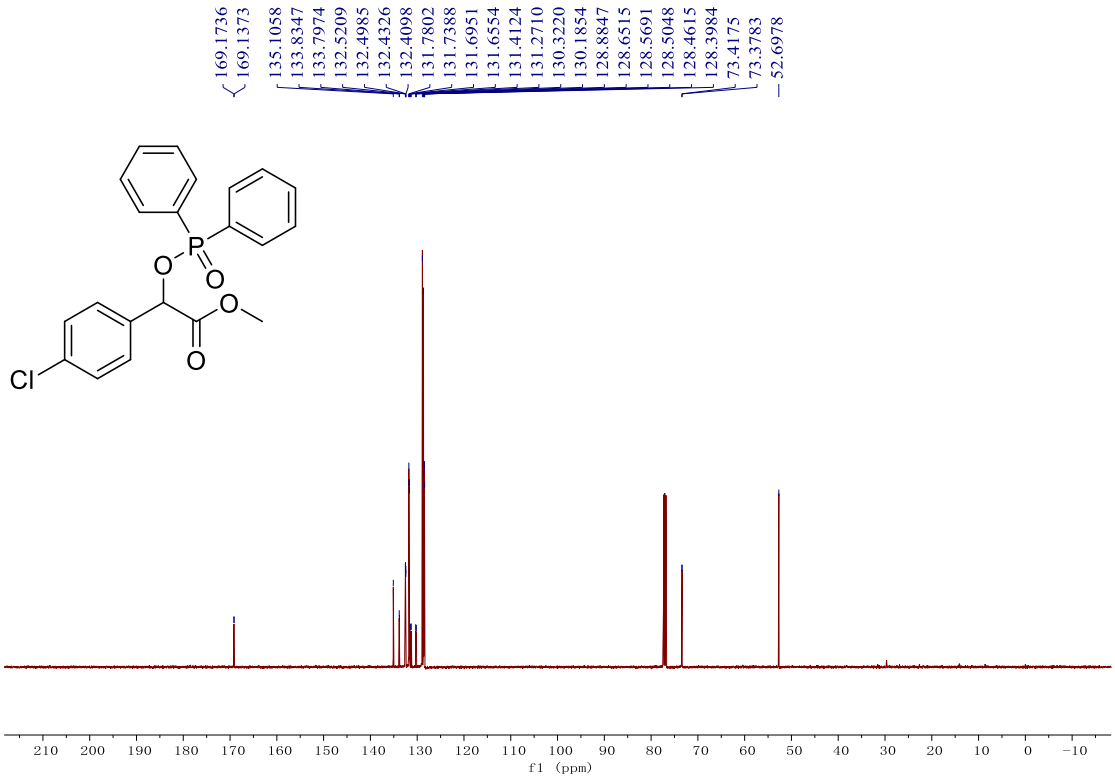


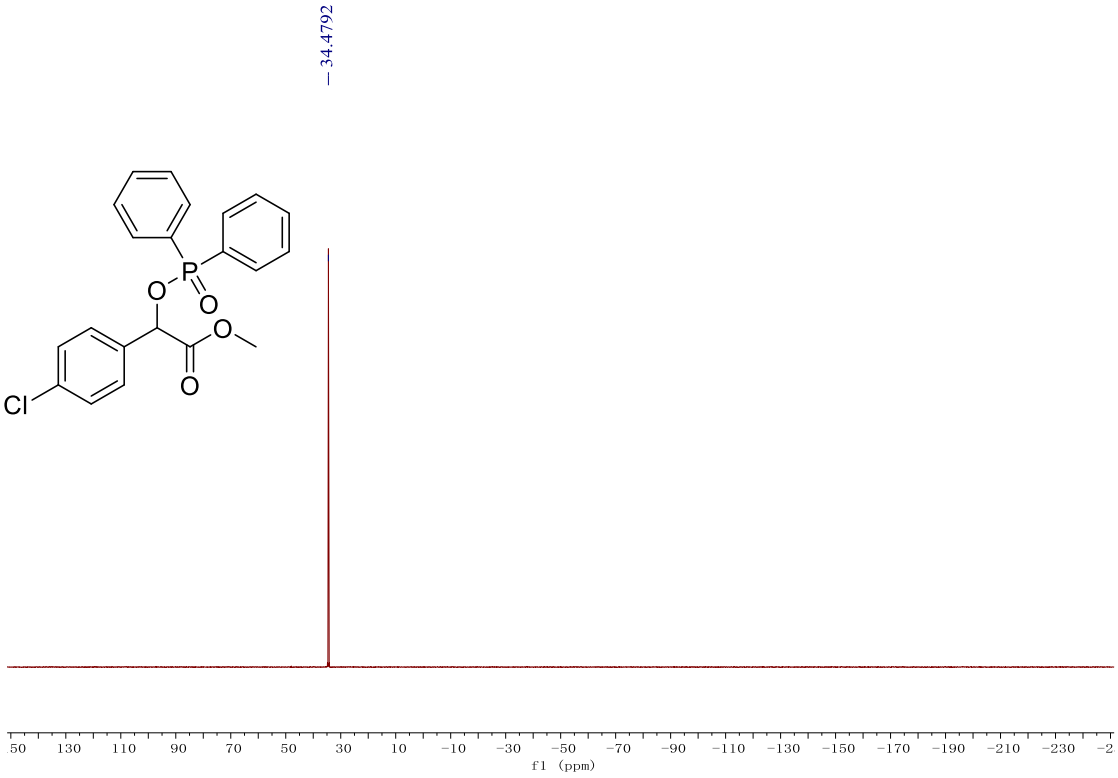

34.2743
O
P
O
O
O
F
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)


-112.1148
O
P
O
O
O
F
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

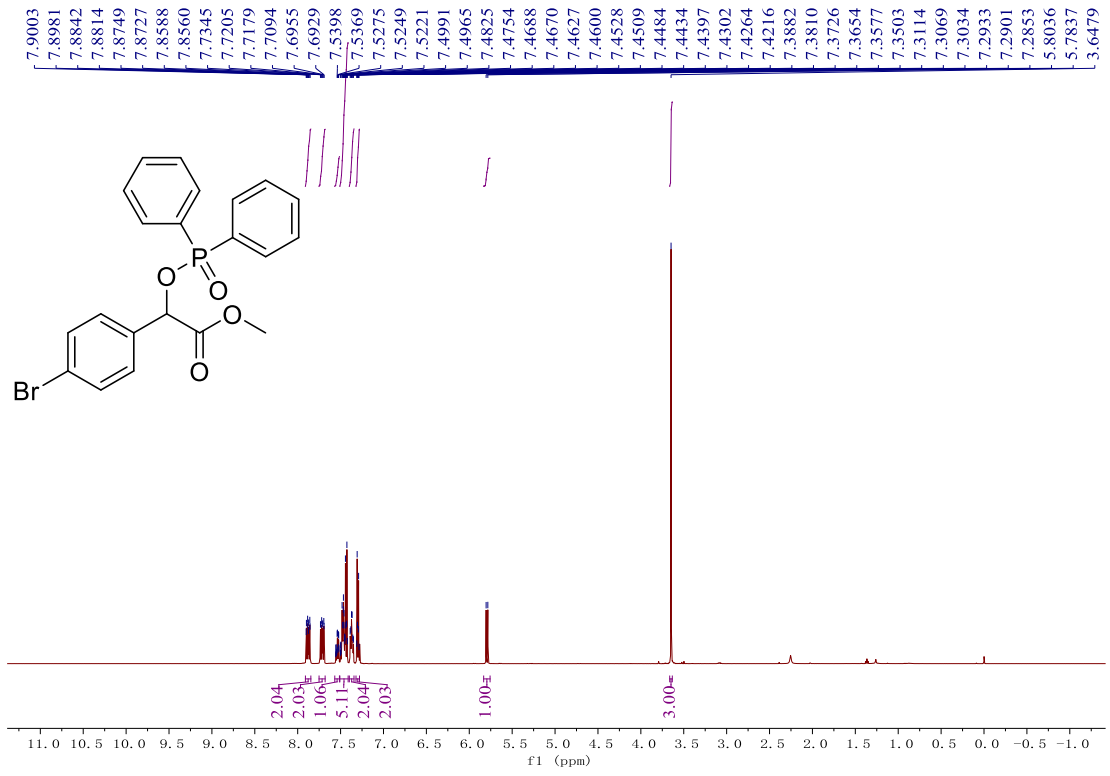
Methyl 2-(4-chlorophenyl)-2-((diphenylphosphoryl)oxy)acetate (3la)

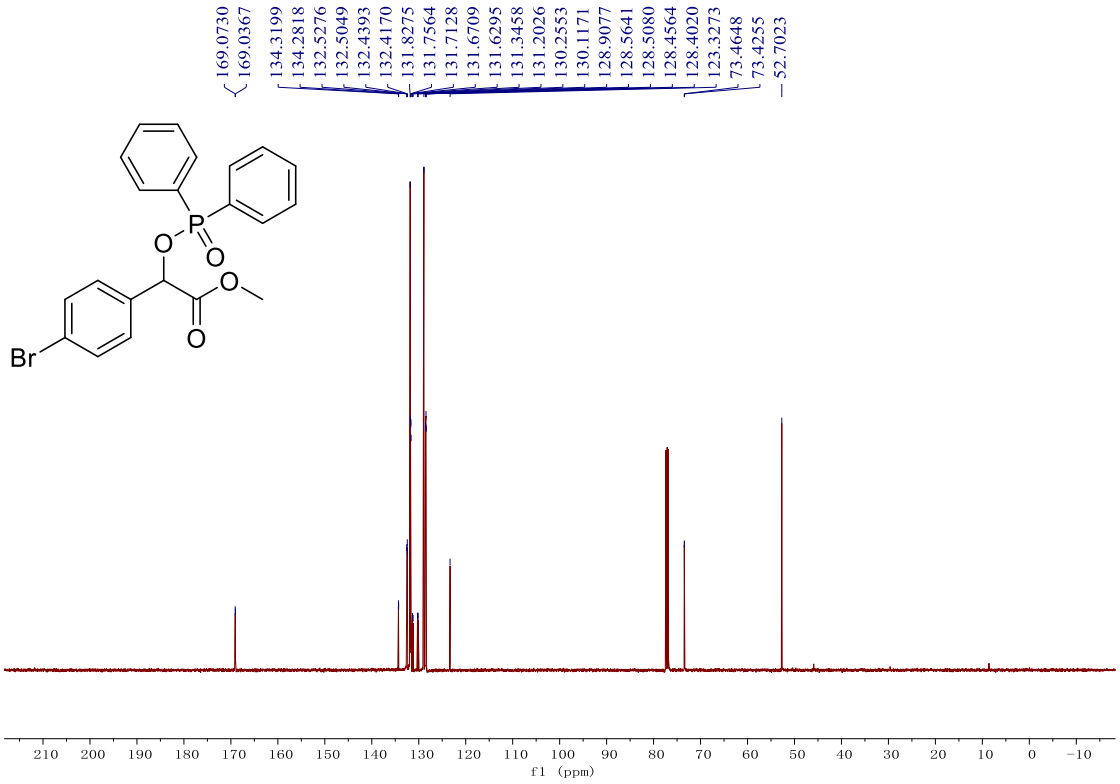


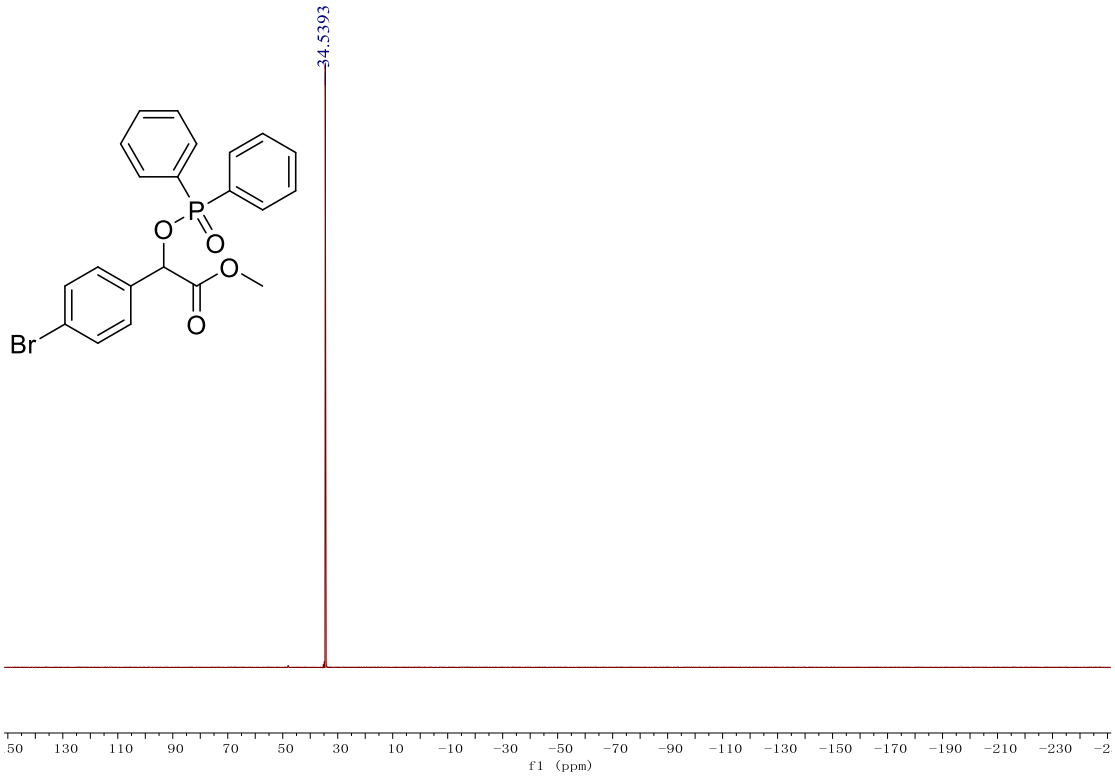




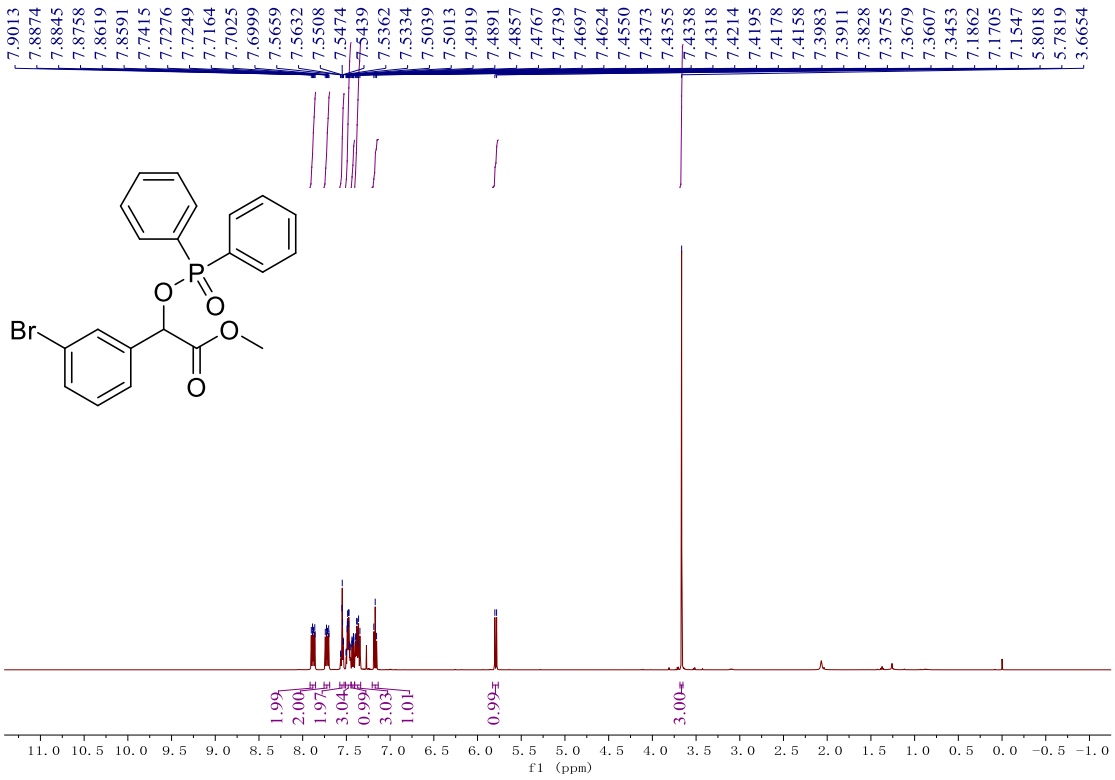
Methyl 2-(4-bromophenyl)-2-((diphenylphosphoryl)oxy)acetate (3ma)

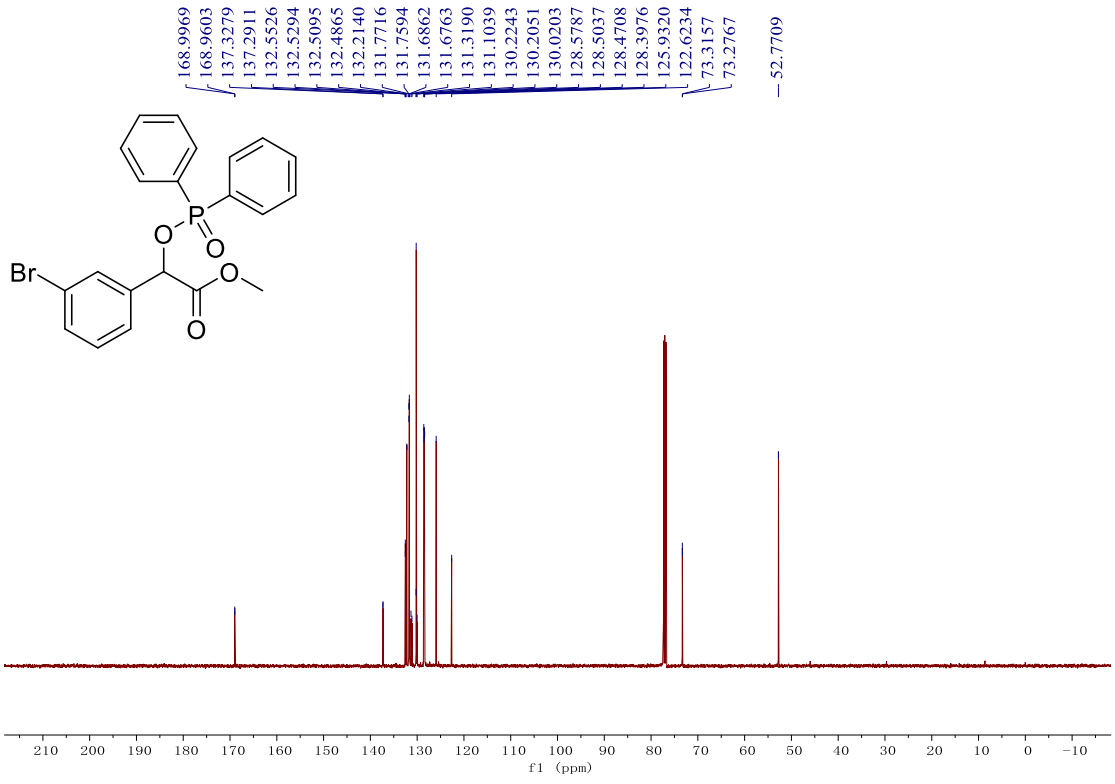


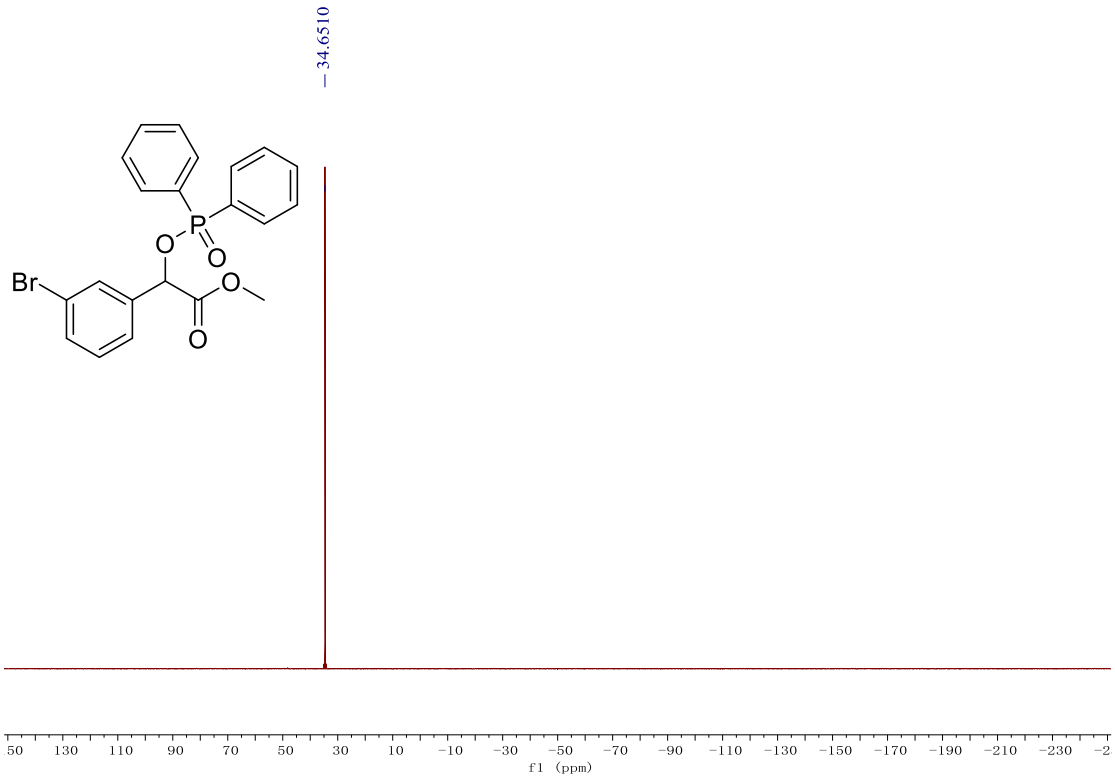

169.0730
169.0367
134.3199
134.2818
132.5276
132.5049
132.4393
132.4170
131.8275
131.7564
131.7128
131.6709
131.6295
131.3458
131.2026
130.2553
130.1171
128.9077
128.5641
128.5080
128.4564
128.4020
123.3273
73.4648
73.4255
52.7023
Br
f1 (ppm)


34.5393
Br
f1 (ppm)

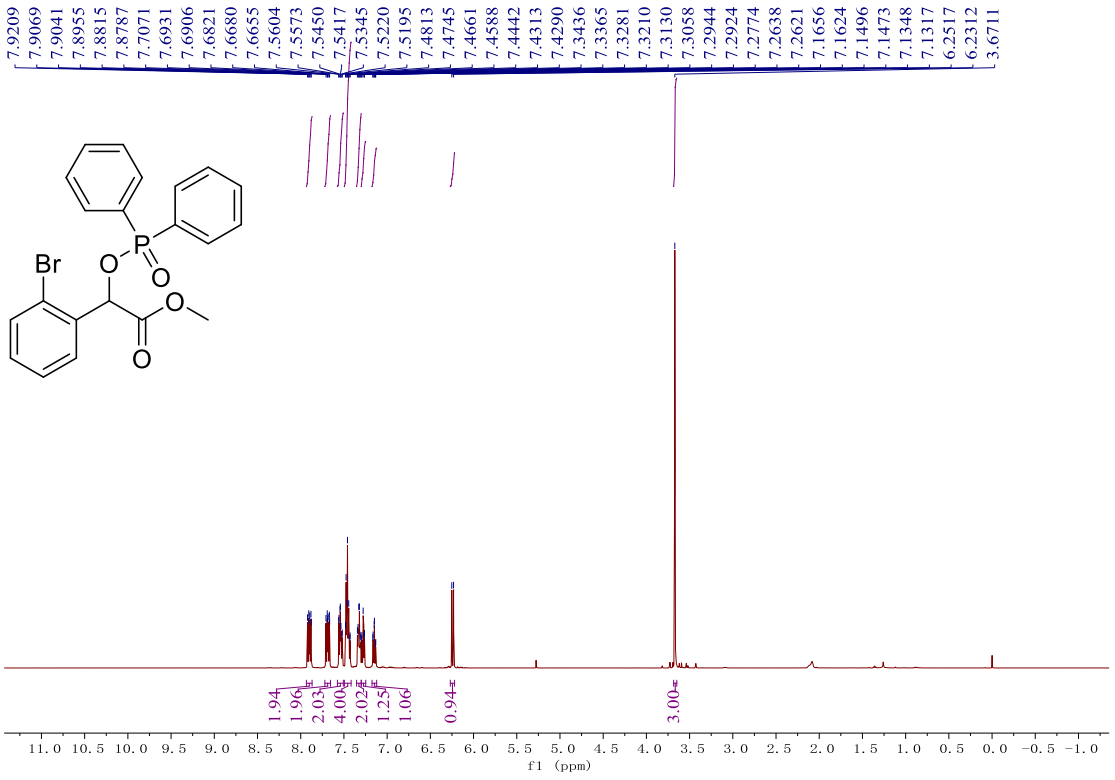
Methyl 2-(3-bromophenyl)-2-((diphenylphosphoryl)oxy)acetate (3na)

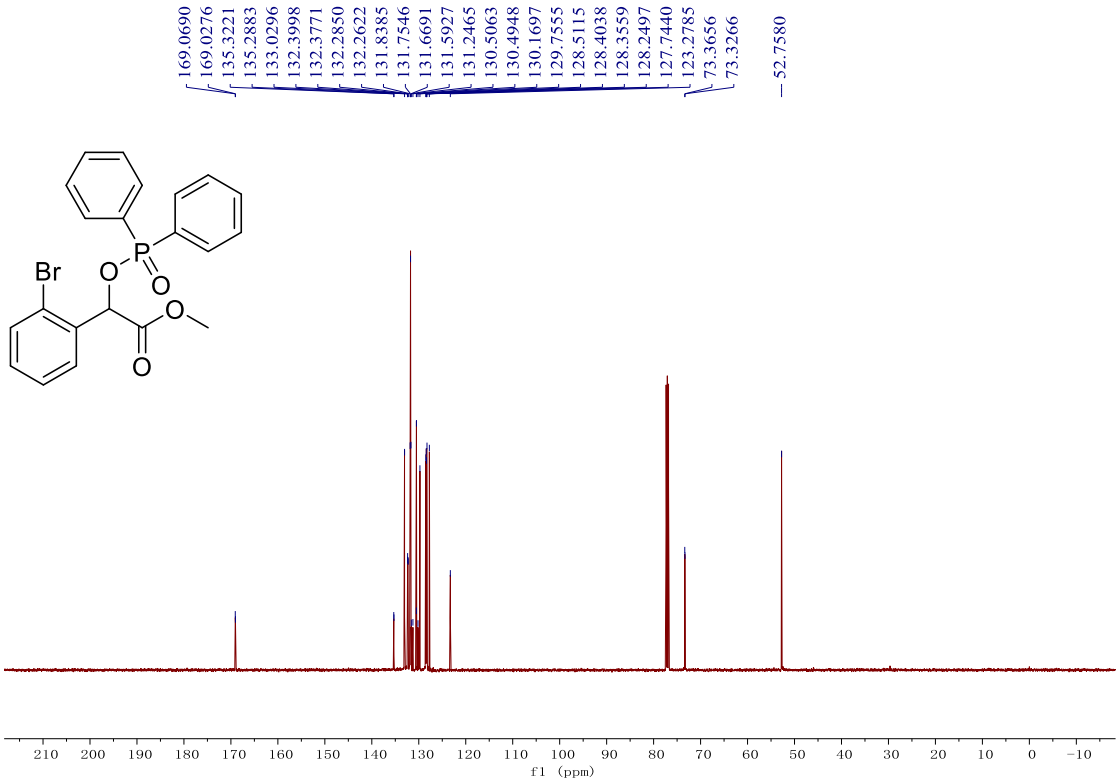


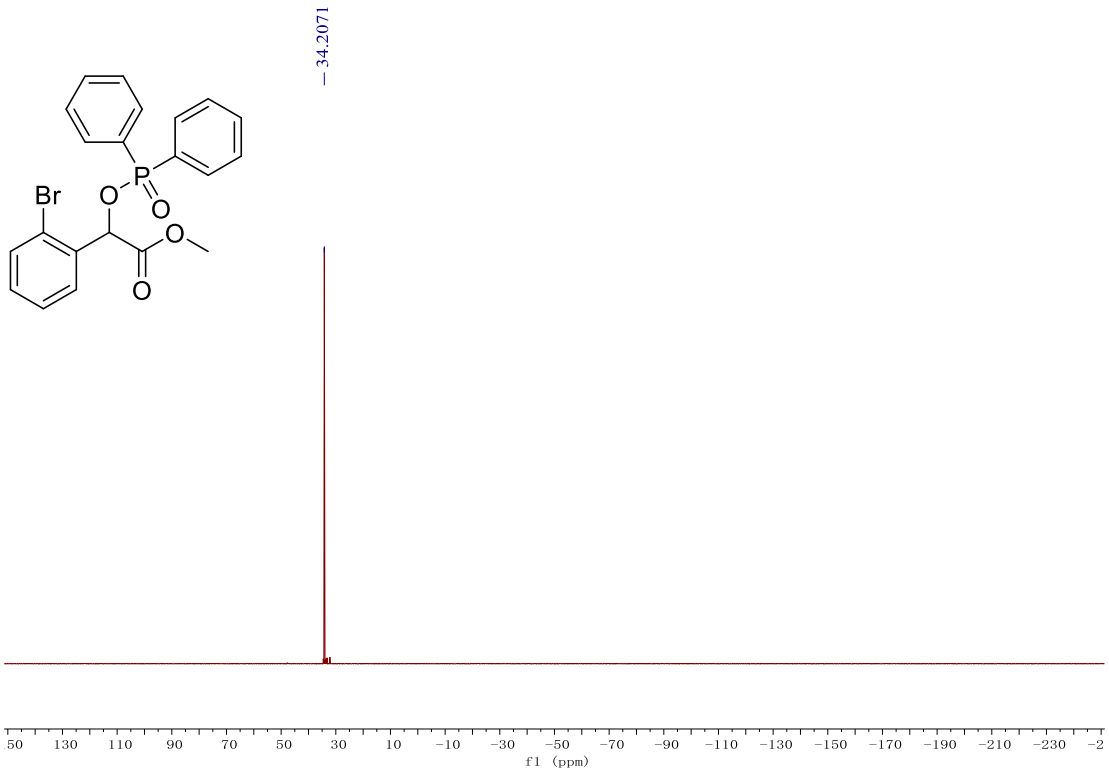




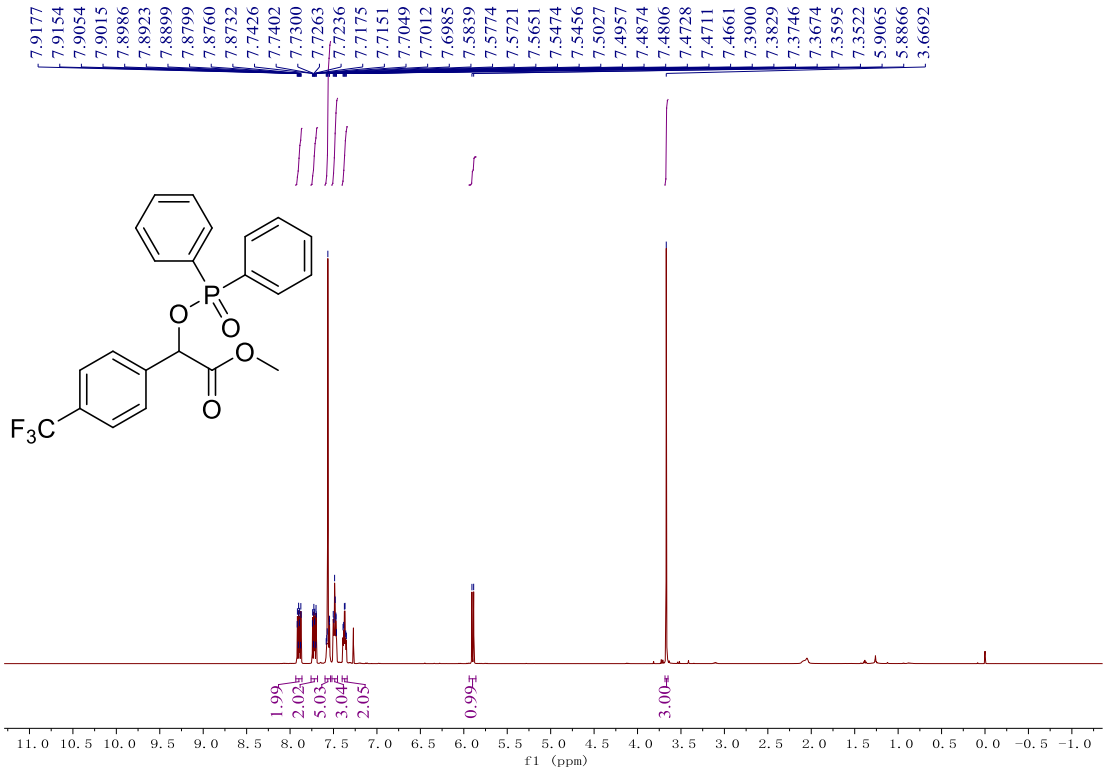
Methyl 2-(2-bromophenyl)-2-((diphenylphosphoryl)oxy)acetate acetate (3oa)

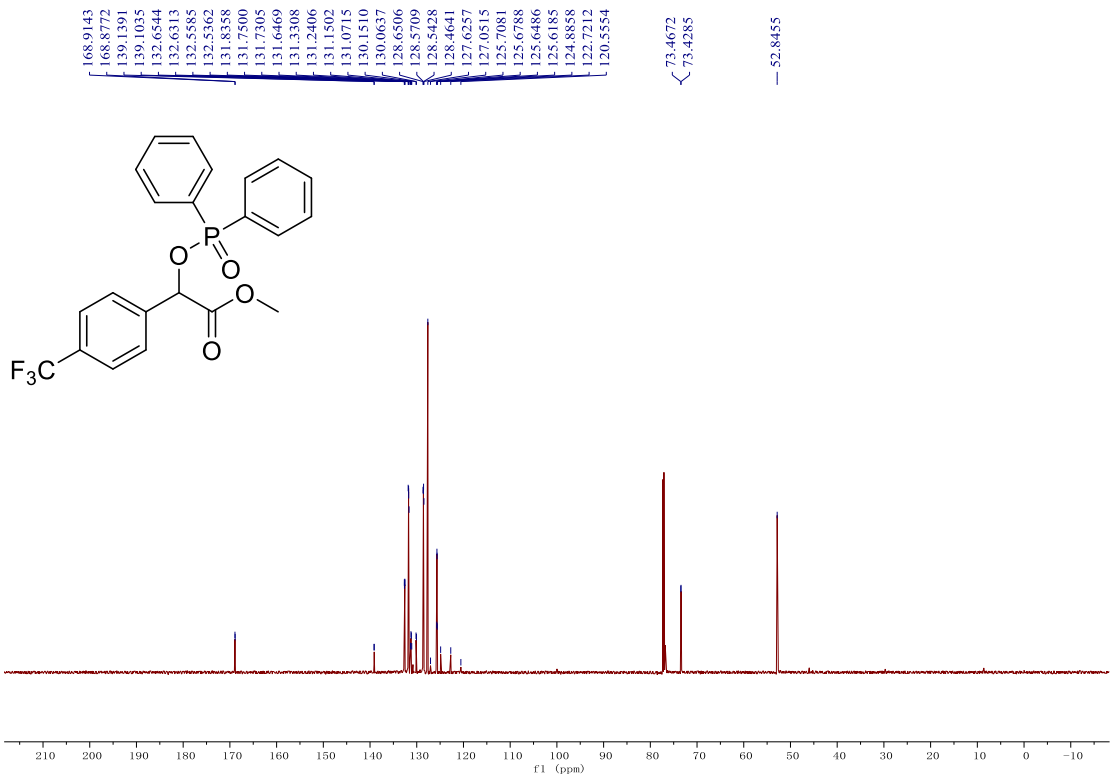


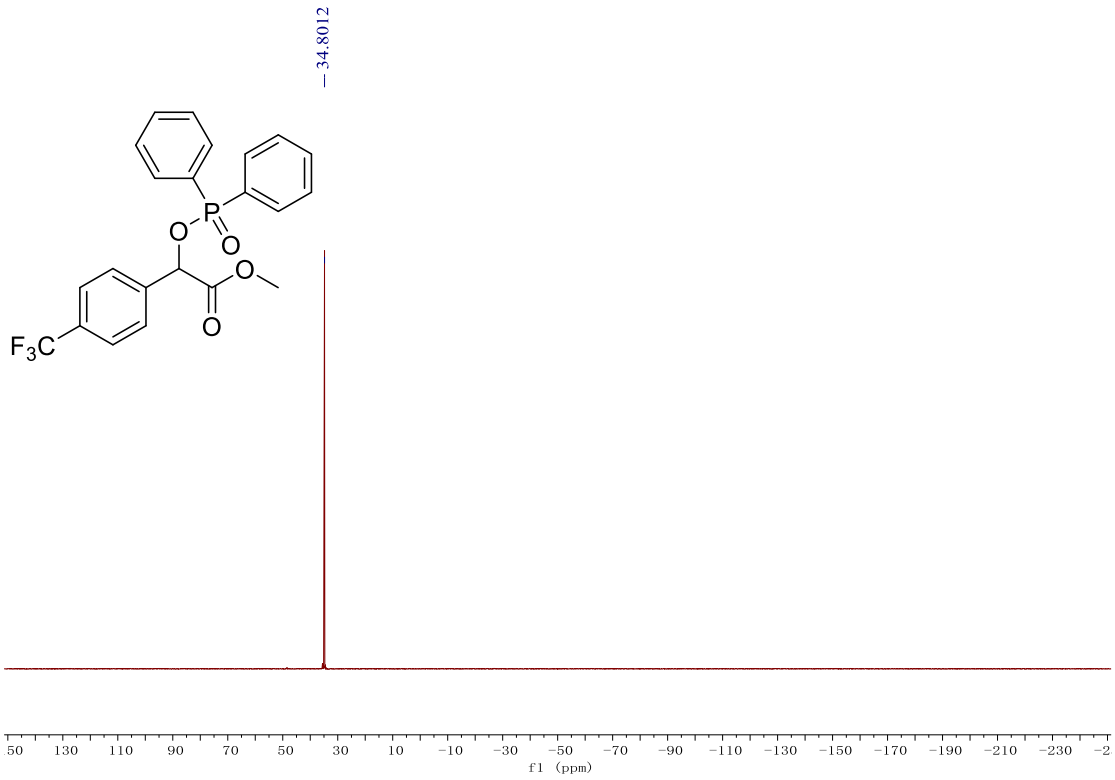

169.0690
169.0276
135.3221
135.2883
133.0296
132.3998
132.3771
132.2850
132.2622
131.8385
131.7546
131.6691
131.5927
131.2465
130.5063
130.4948
130.1697
129.7555
128.5115
128.4038
128.3559
128.2497
127.7440
123.2785
73.3656
73.3266
52.7580
Br
O
P
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

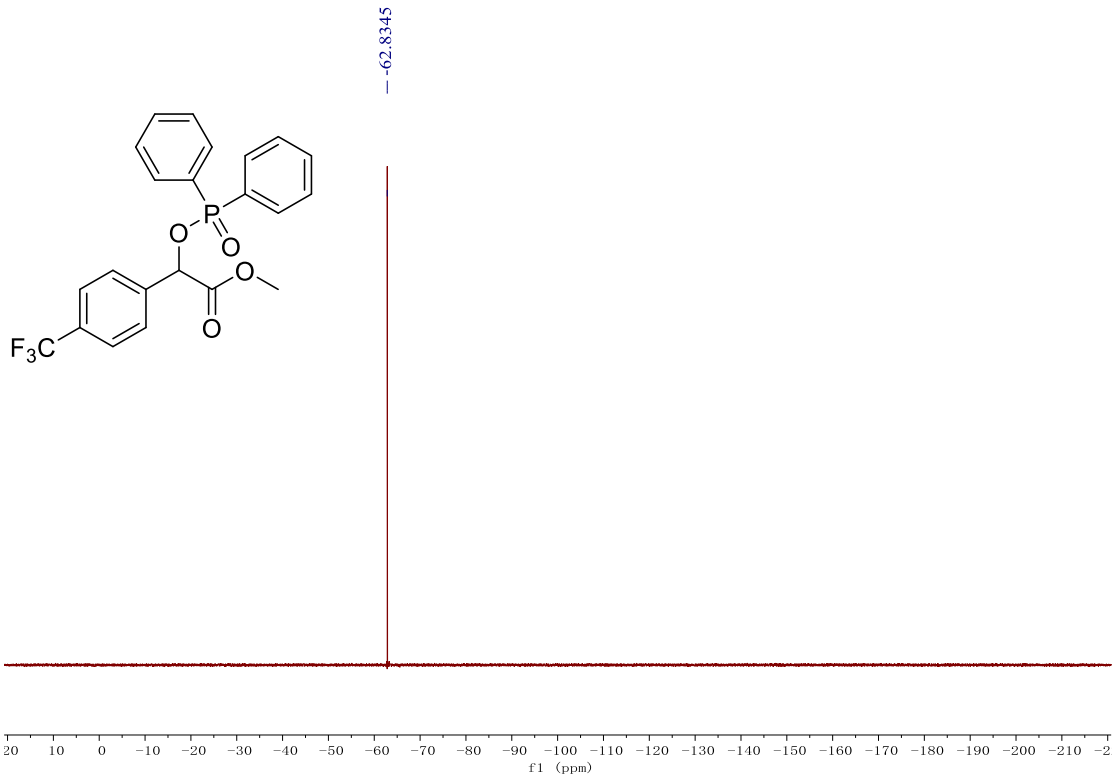

34.2071
Br
O
P
O
O
O
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)

Methyl 2-((diphenylphosphoryl)oxy)-2-(4-(trifluoromethyl)phenyl)acetate (3pa).

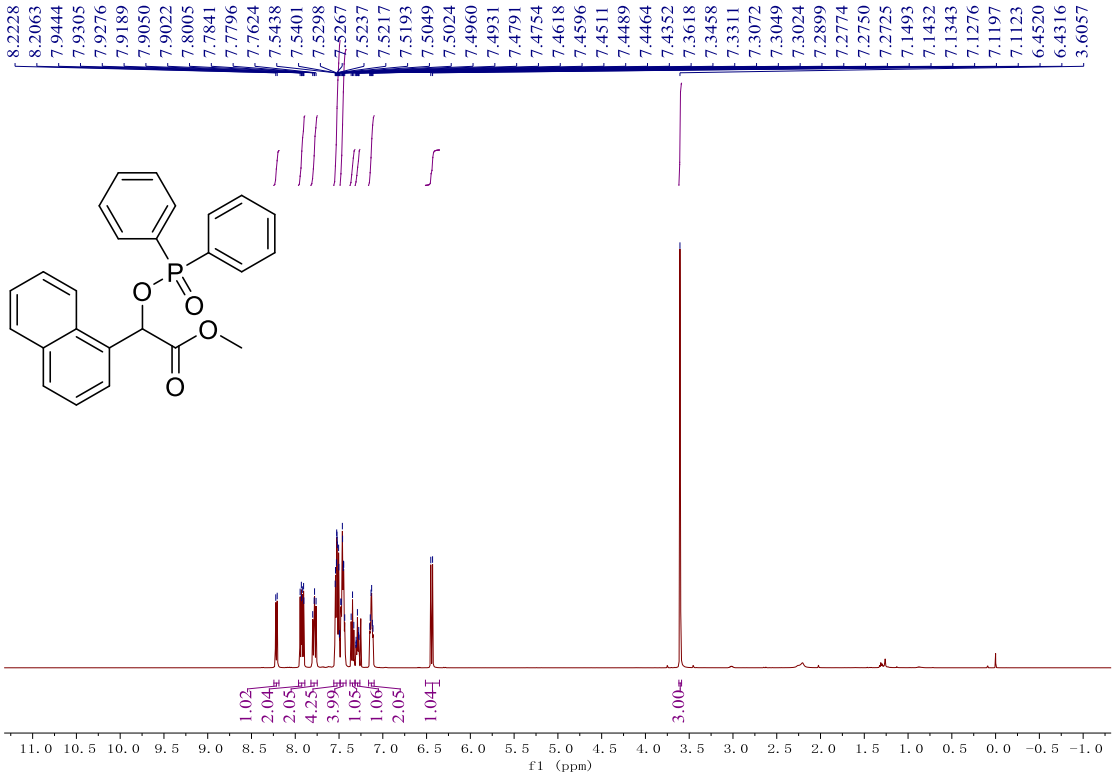


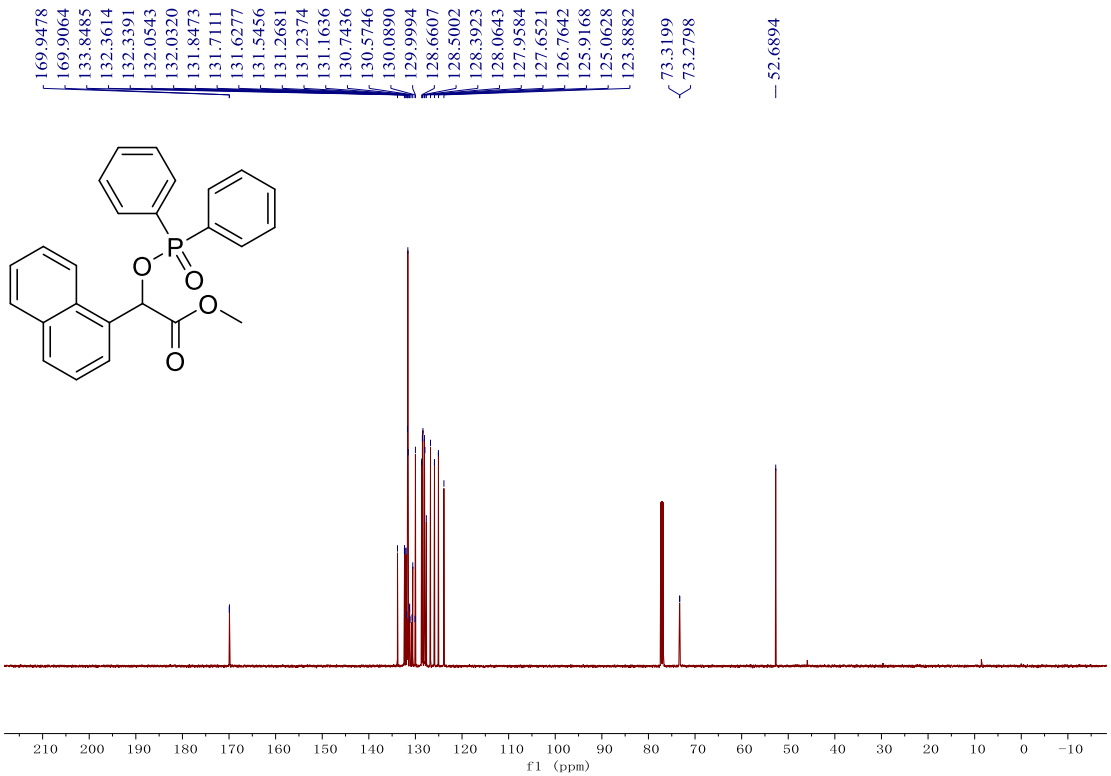


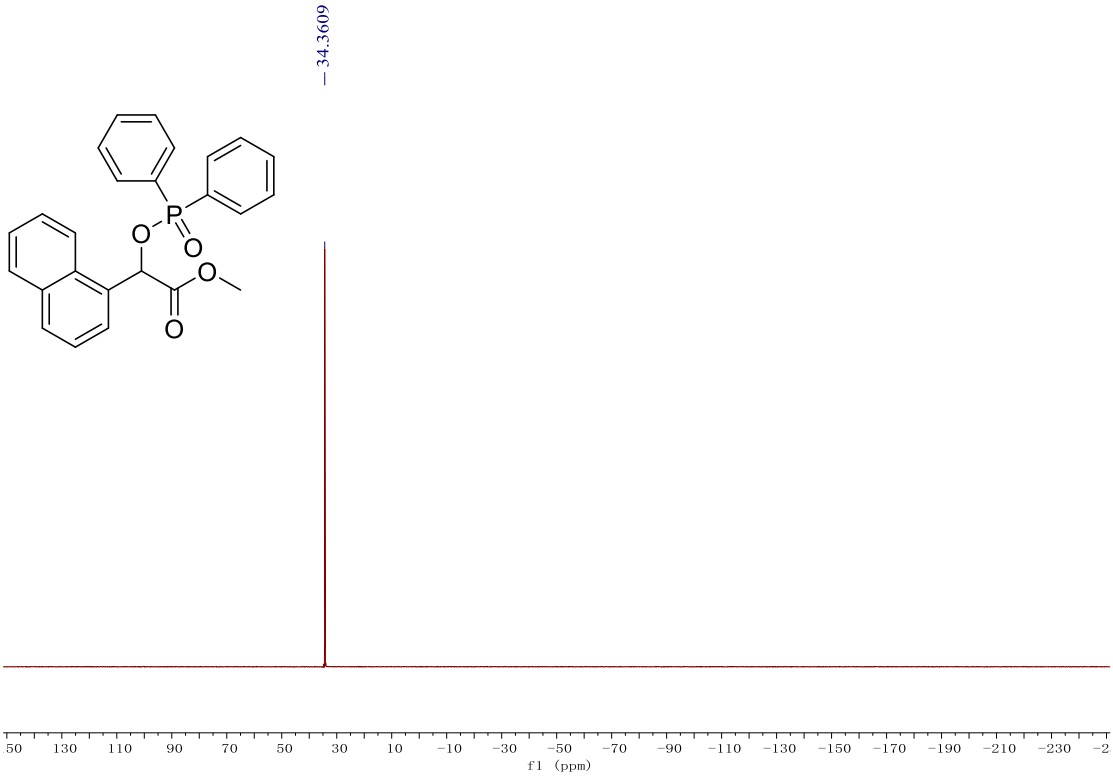

34.8012
O
P
O
O
O
O
F3C
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)


-62.8345
O
P
O
O
O
O
F3C
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

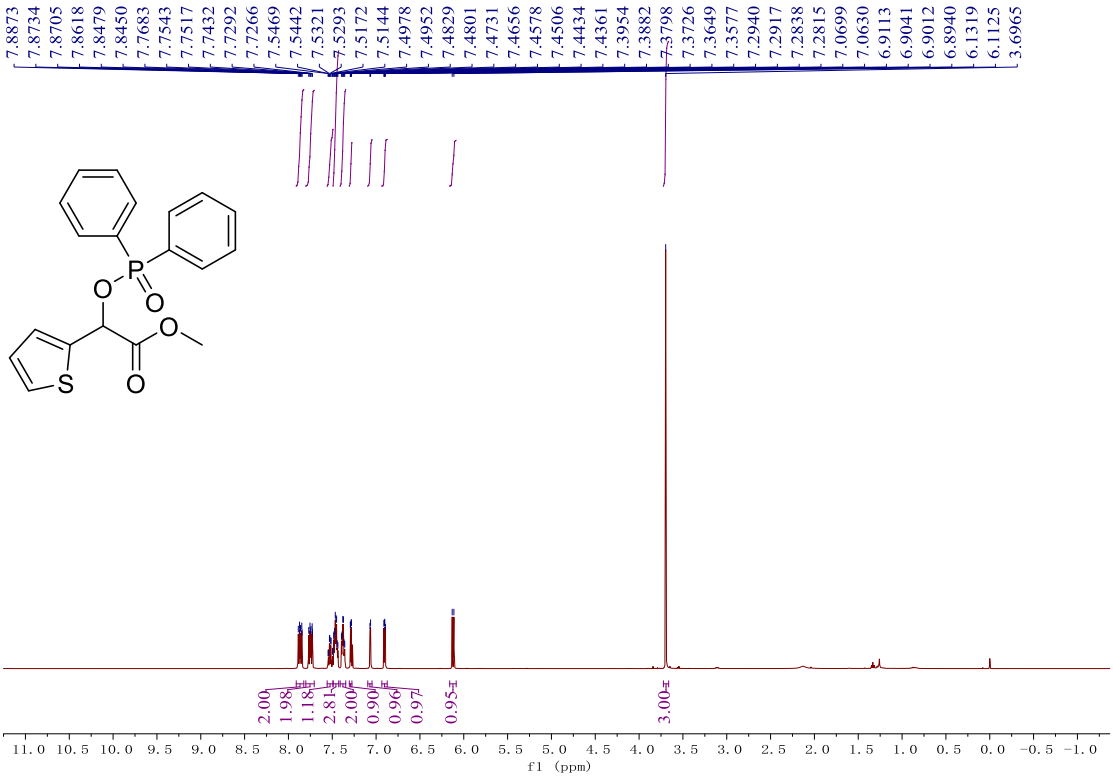
Methyl 2-((diphenylphosphoryl)oxy)-2-(naphthalen-1-yl)acetate (3qa).

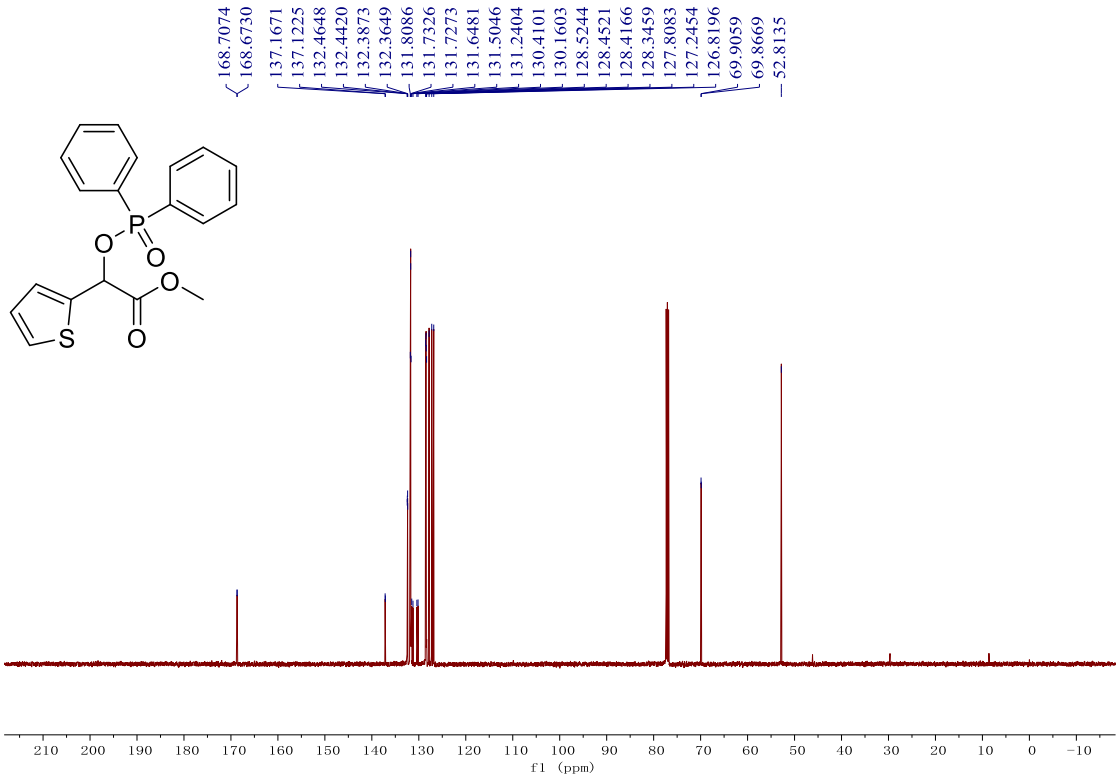


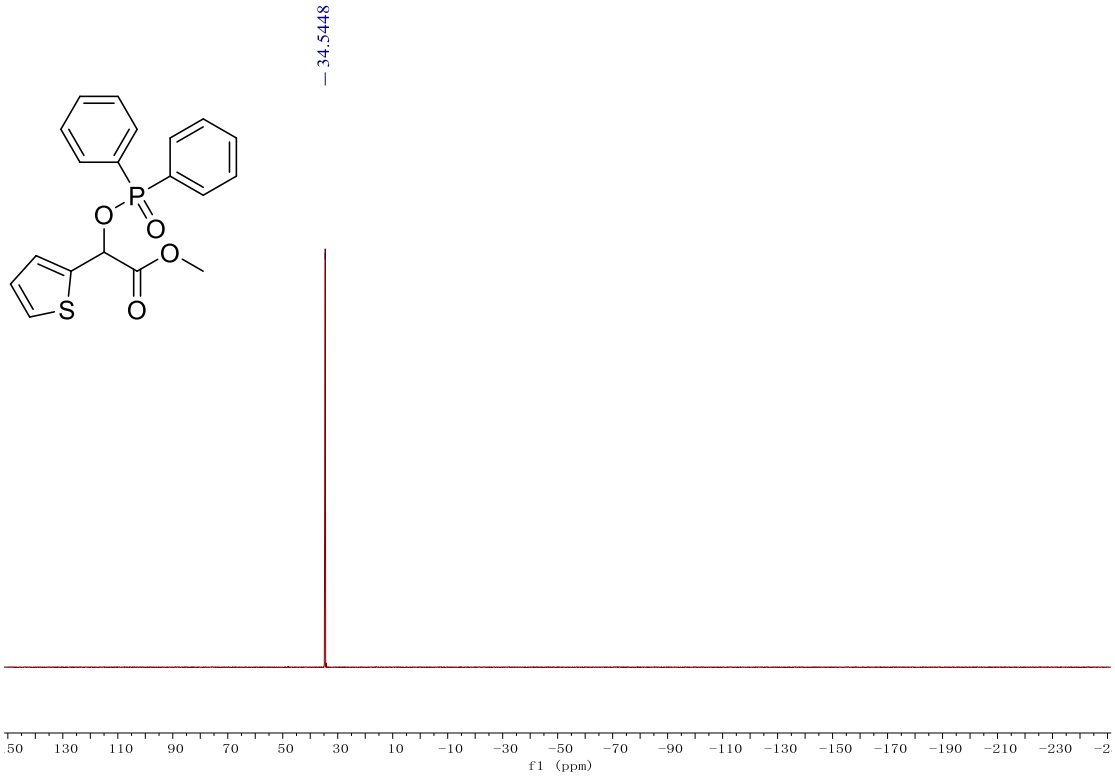




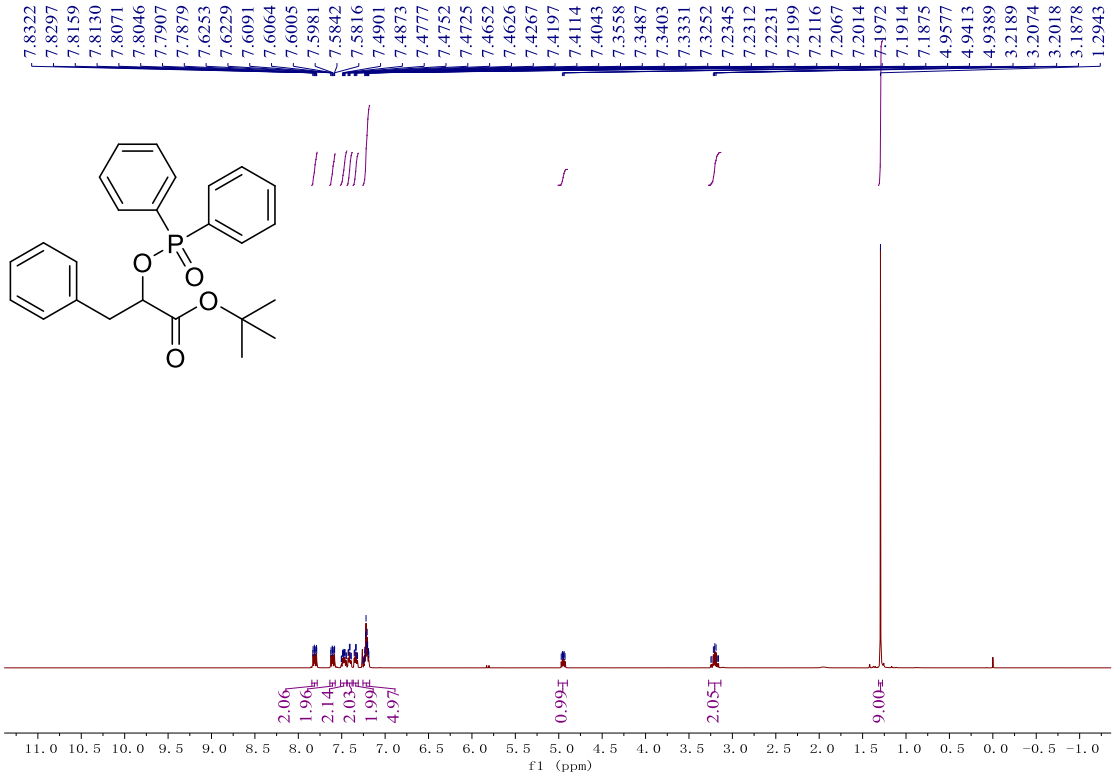
Methyl 2-((diphenylphosphoryl)oxy)-2-(thiophen-2-yl)acetate (3ra)

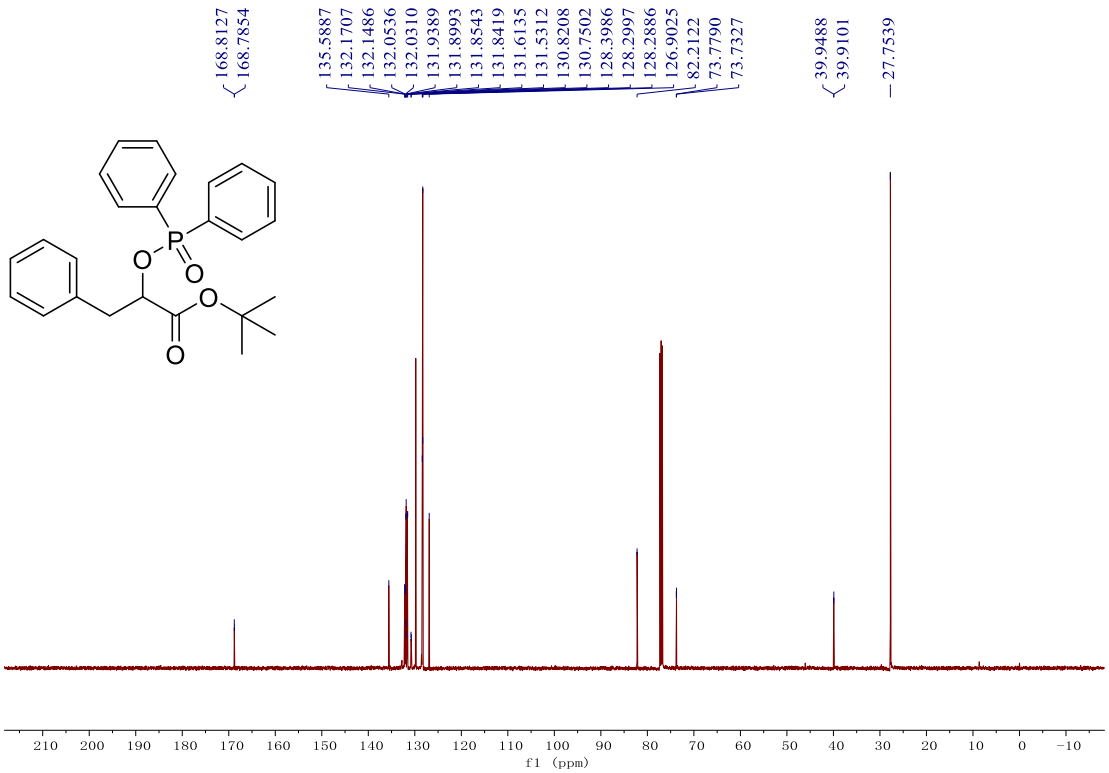


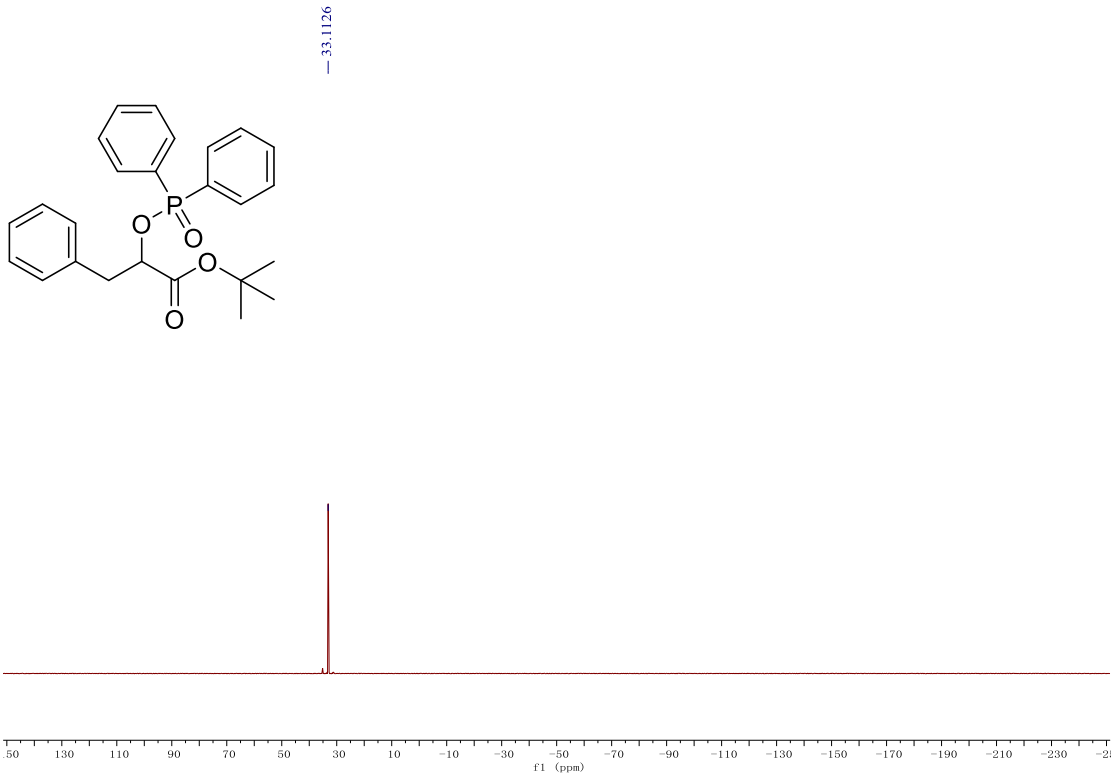

168.7074
168.6730
137.1671
137.1225
132.4648
132.4420
132.3873
132.3649
131.8086
131.7326
131.7273
131.6481
131.5046
131.2404
130.4101
130.1603
128.5244
128.4521
128.4166
128.3459
127.8083
127.2454
126.8196
69.9059
69.8669
52.8135
O
P
O
O
O
S
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


34.5448
O
P
O
O
O
S
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)

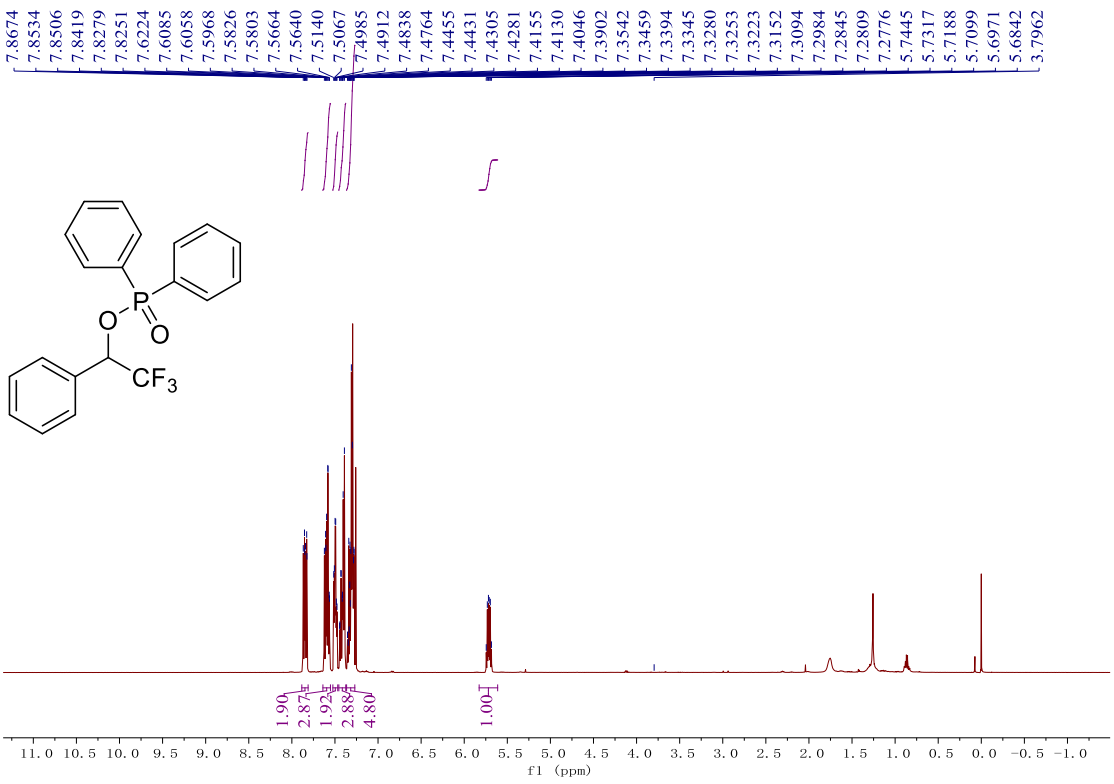
***Tert*-butyl 2-((diphenylphosphoryl)oxy)-3-phenylpropanoate (3sa).**

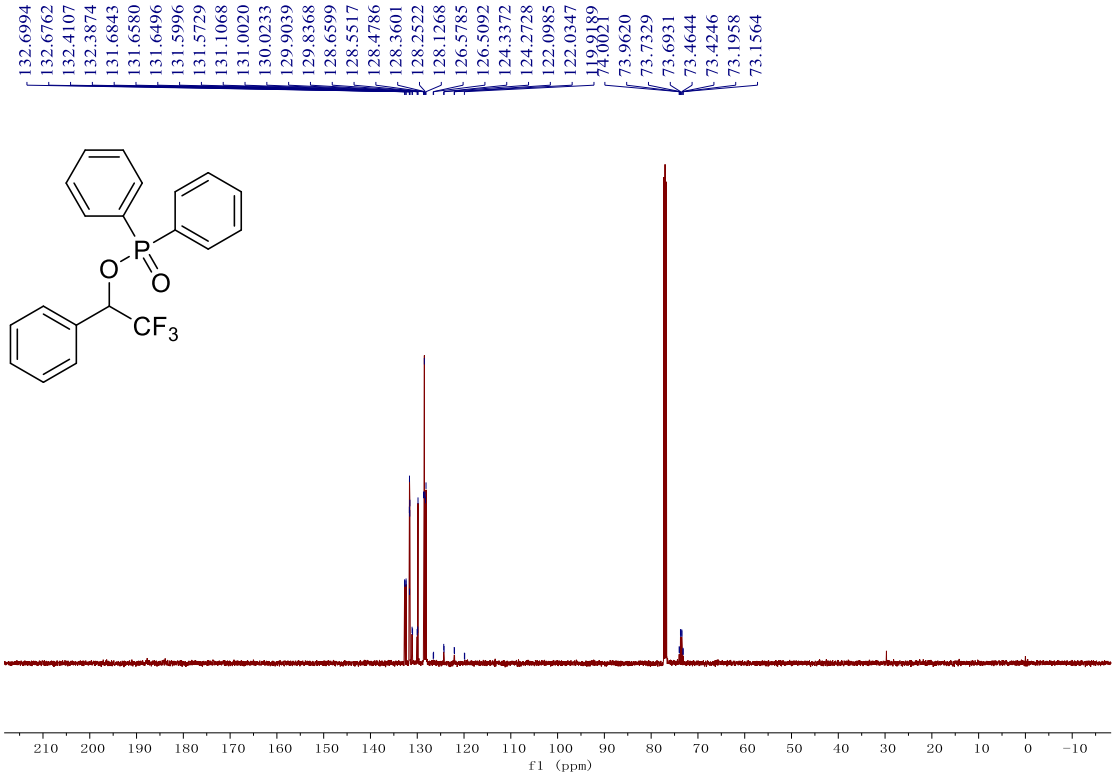


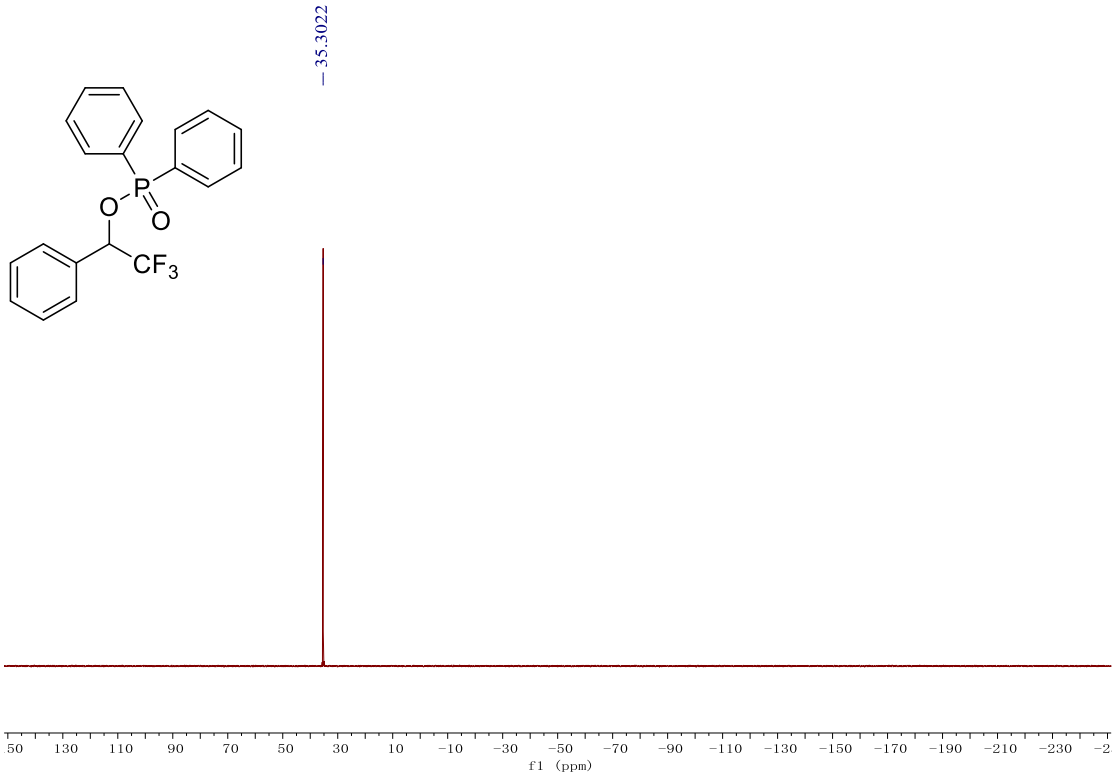


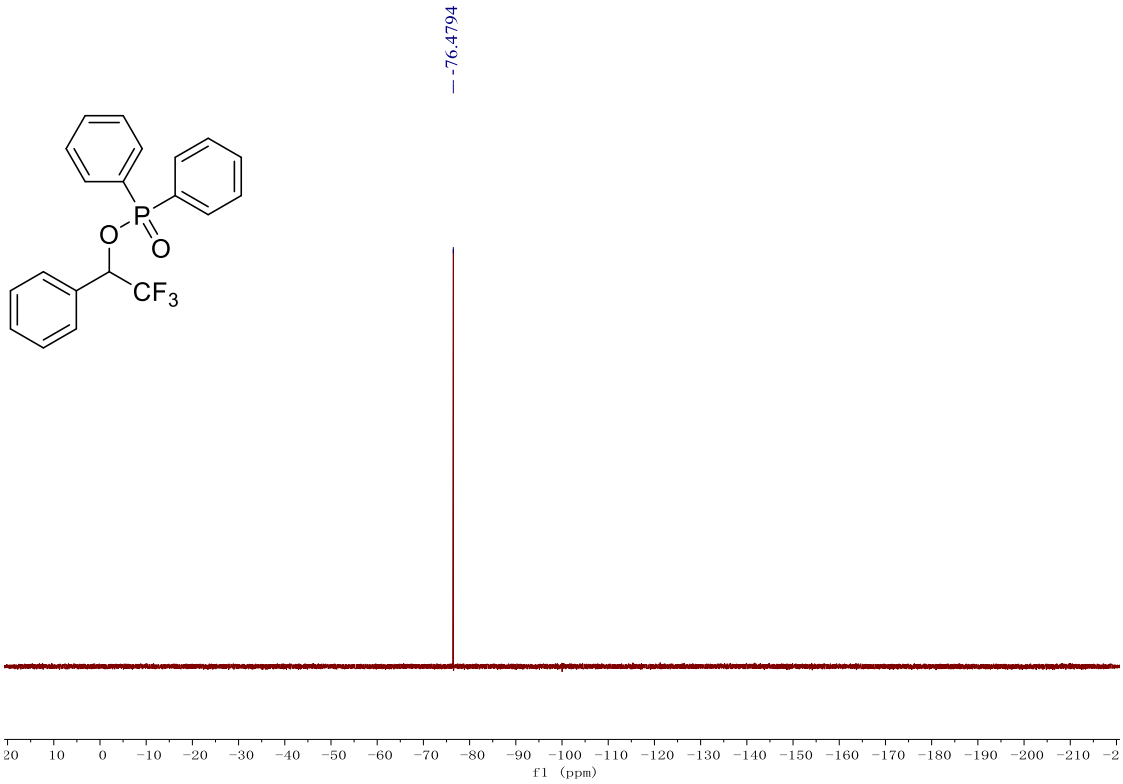


2,2,2-trifluoro-1-phenylethyl diphenylphosphinate (3ta)

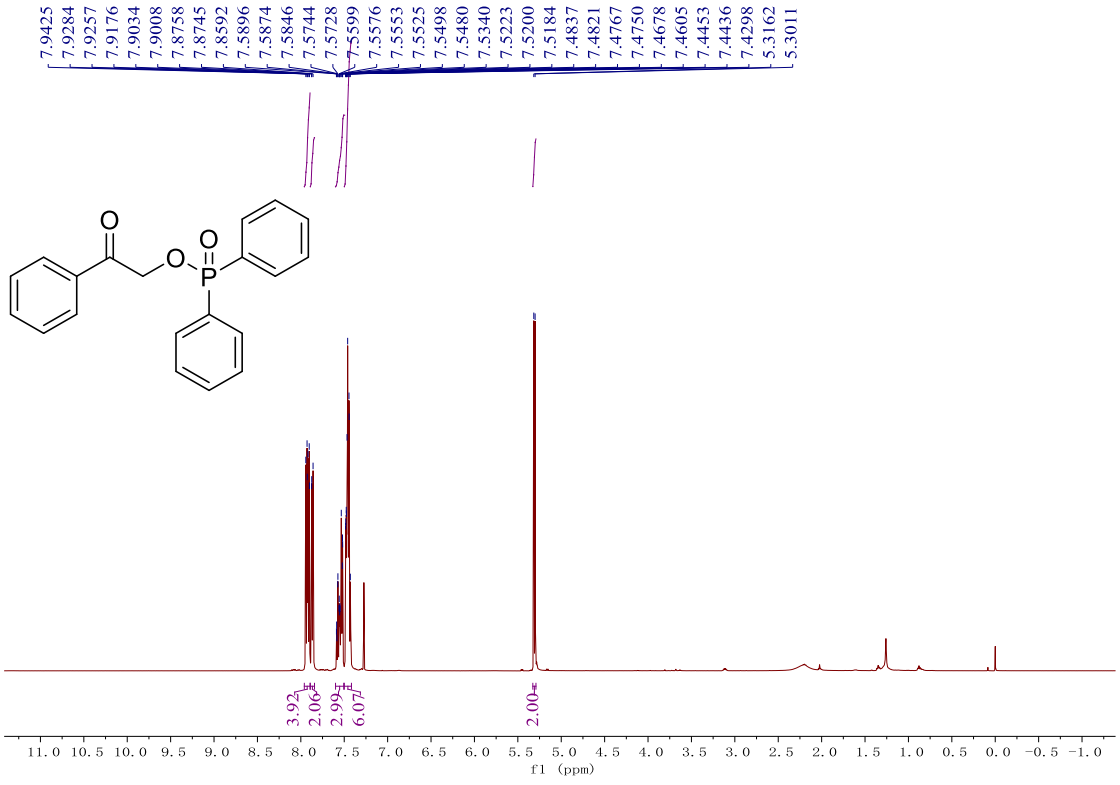


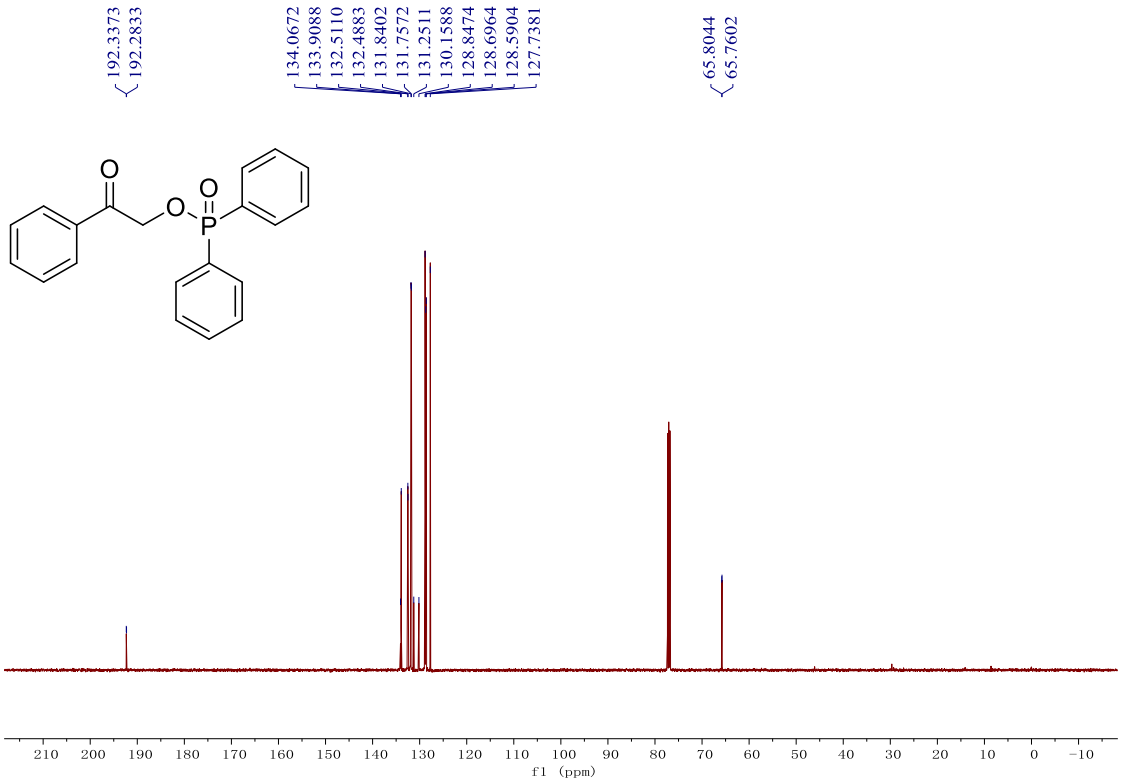

132.6994
132.6762
132.4107
132.3874
131.6843
131.6580
131.6496
131.5996
131.5729
131.1068
131.0020
130.0233
129.9039
129.8368
128.6599
128.5517
128.4786
128.3601
128.2522
128.1268
126.5785
126.5092
124.3372
124.2728
122.0985
122.0347
119.9189
74.0021
73.9620
73.7329
73.6931
73.4644
73.4246
73.1958
73.1564
O
P
O
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

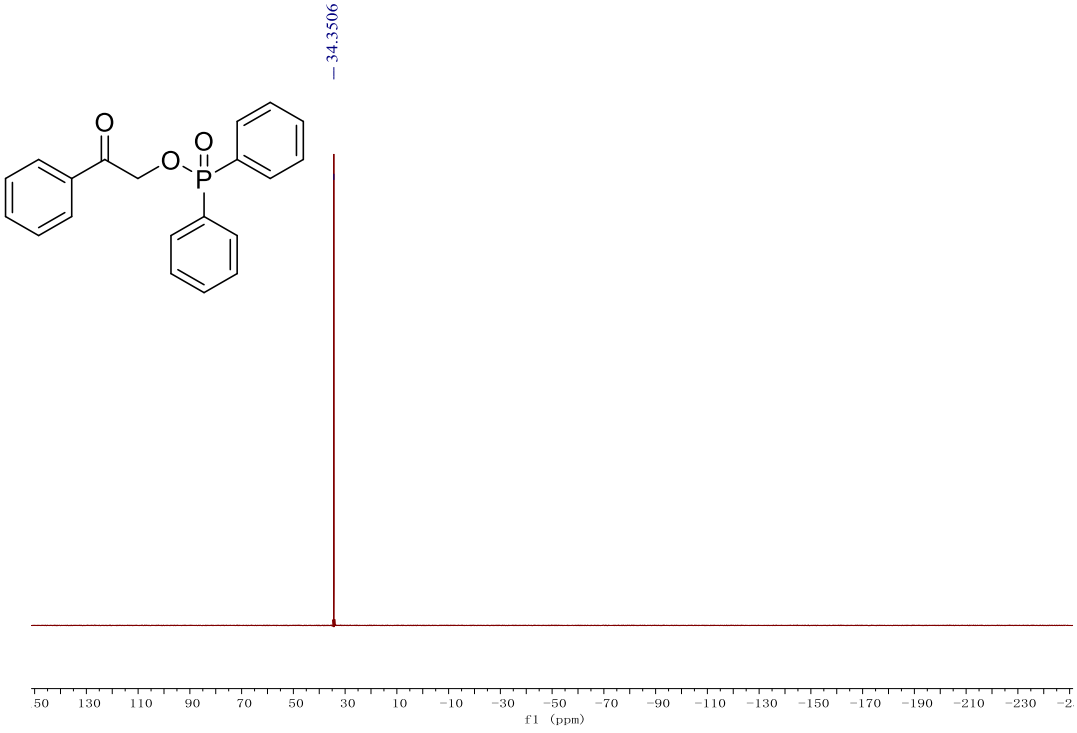

35.3022
O
P
O
CF3
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)



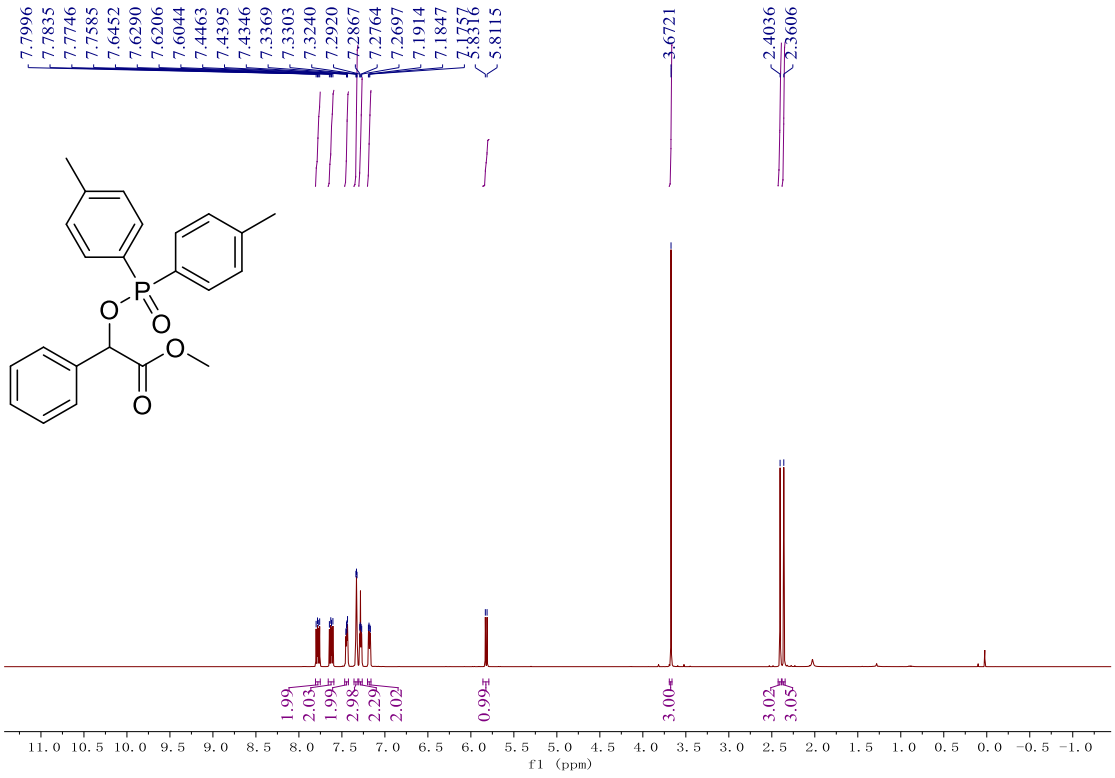
2-oxo-2-phenylethyl diphenylphosphinate (3ua)

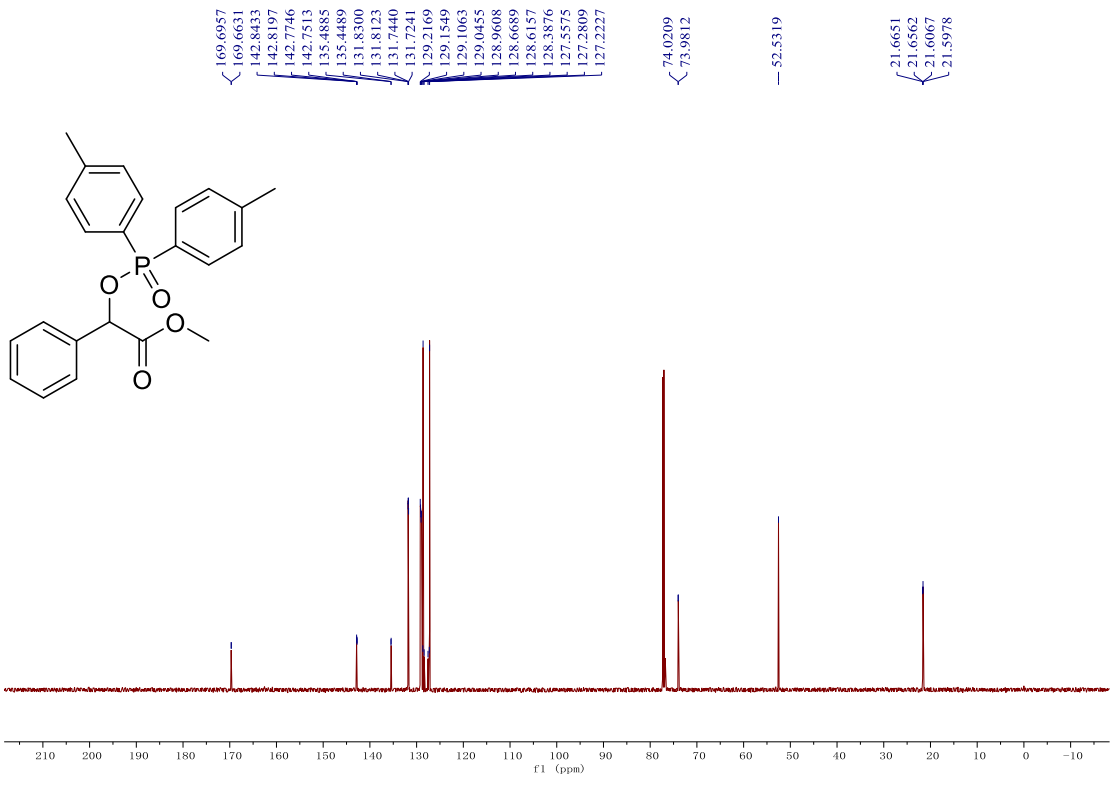


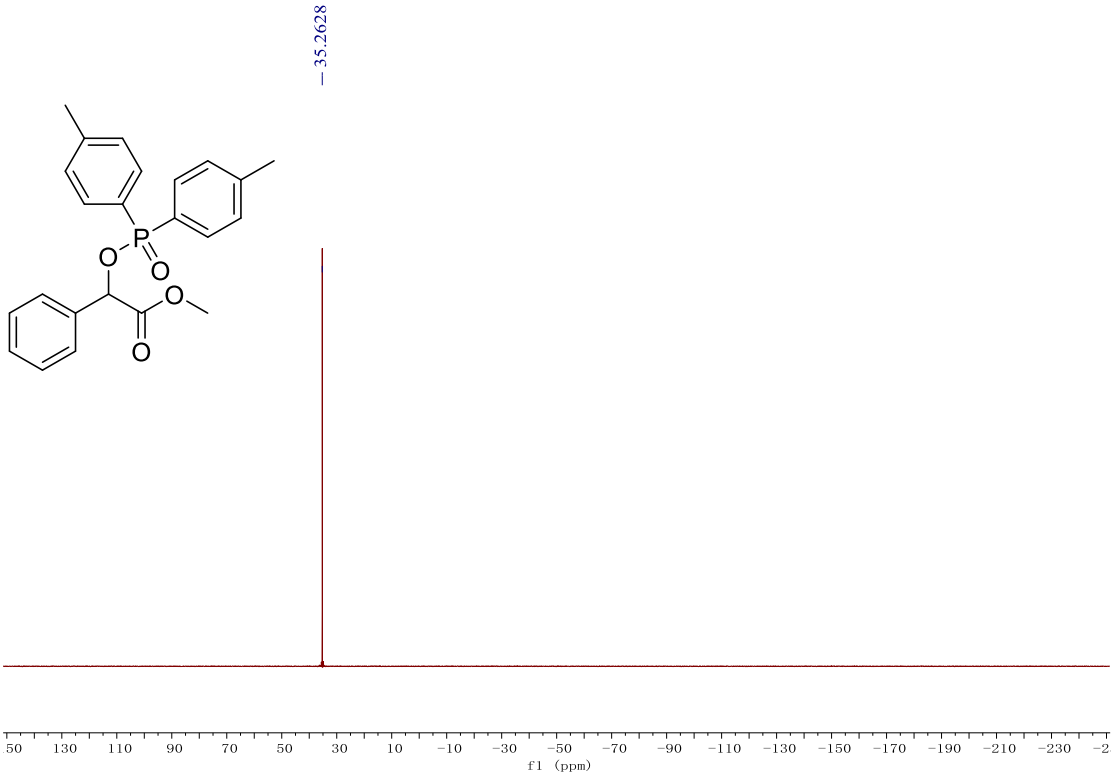

192.3373
192.2833
134.0672
133.9088
132.5110
132.4883
131.8402
131.7572
131.2511
130.1588
128.8474
128.6964
128.5904
127.7381
65.8044
65.7602
O
O
O
P
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


34.3506
O
O
O
P
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)

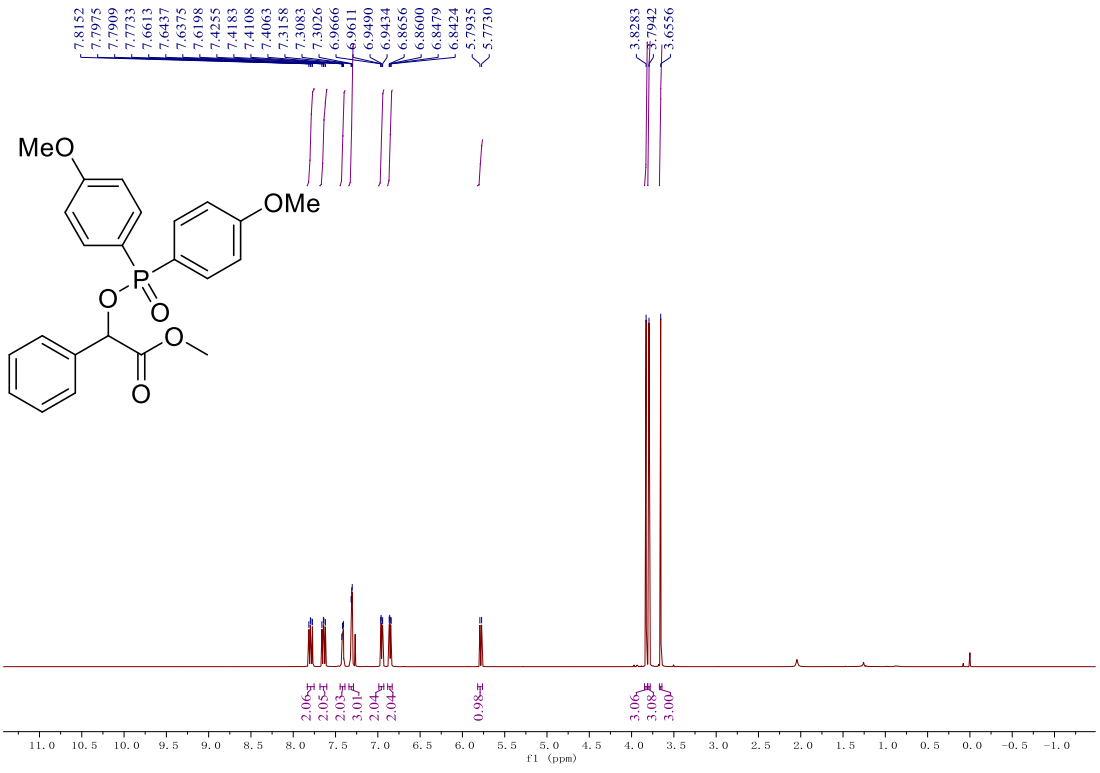
Methyl 2-((di-p-tolylphosphoryl)oxy)-2-phenylacetate (3ab)

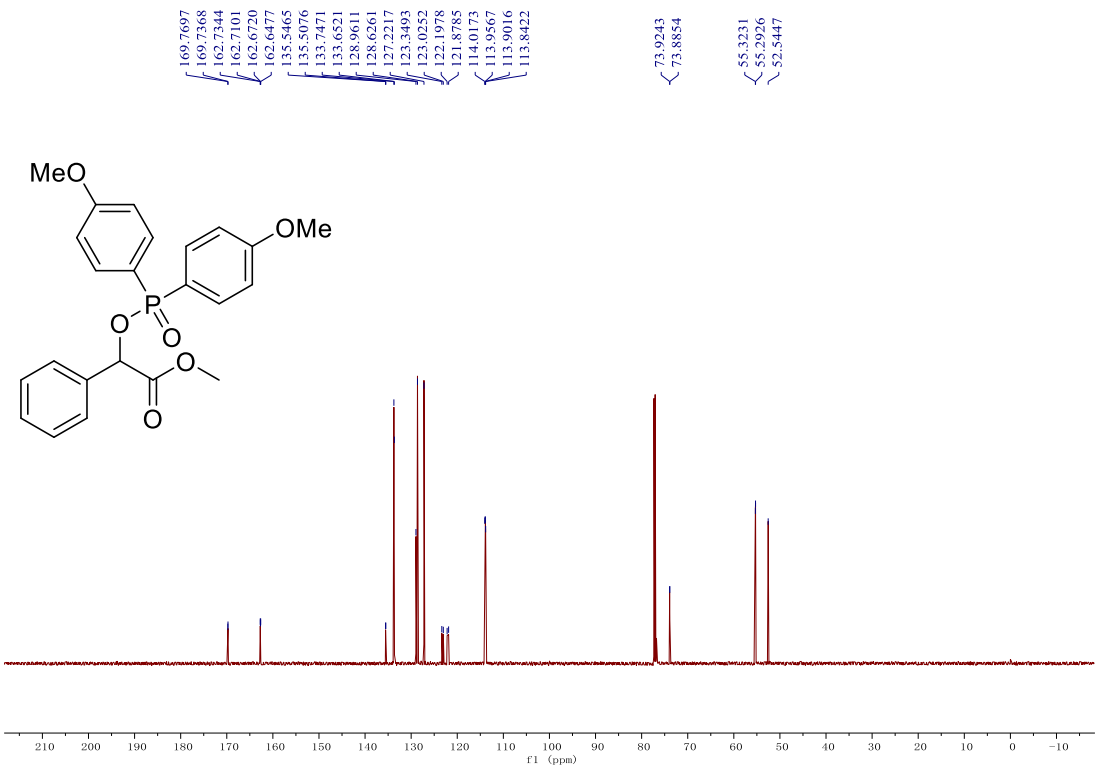


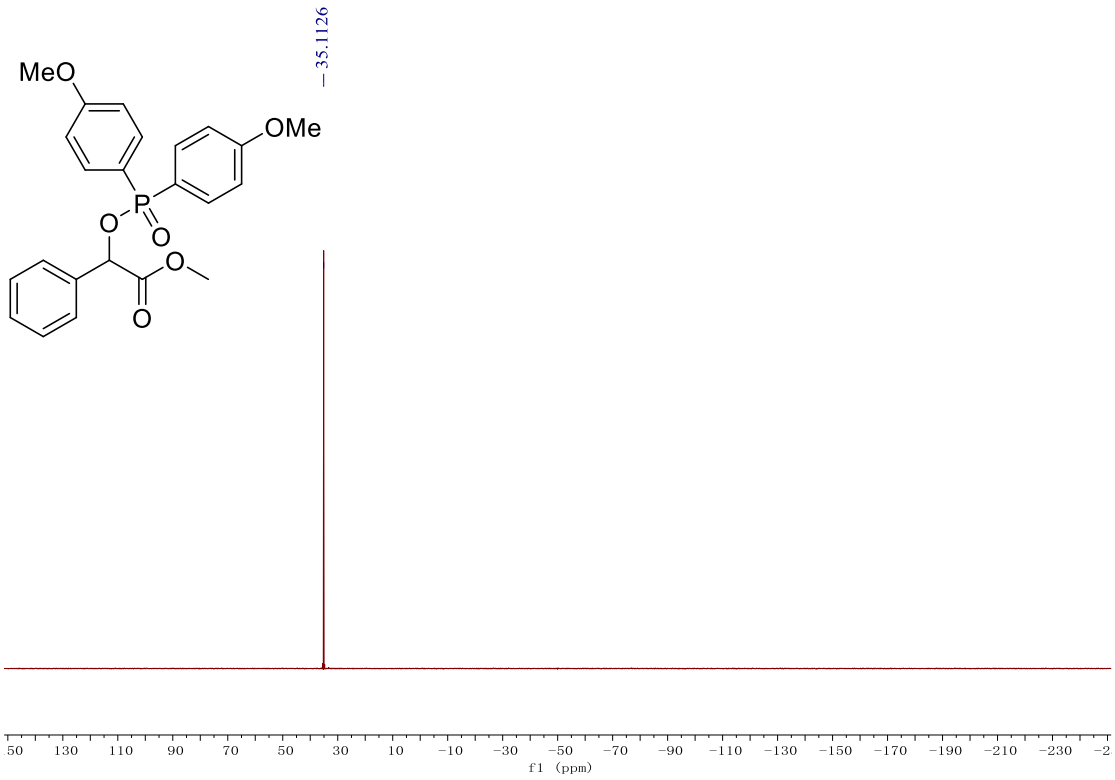




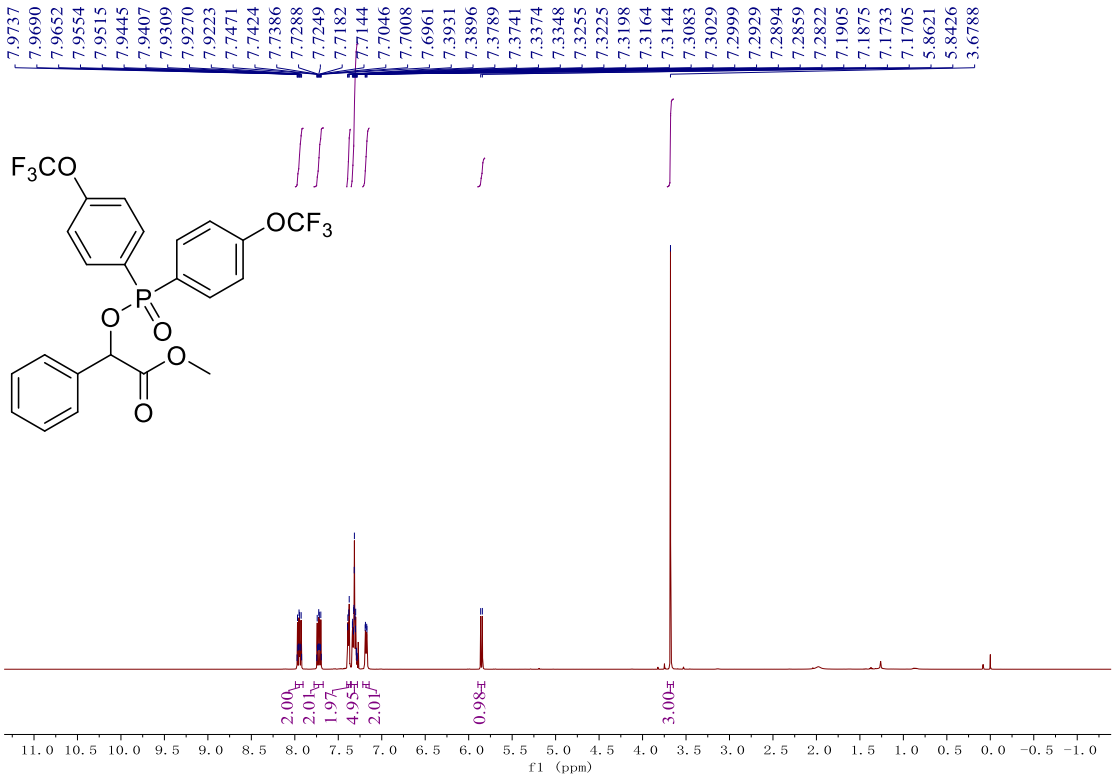
Methyl 2-((bis(4-methoxyphenyl)phosphoryl)oxy)-2-phenylacetate (3ac)

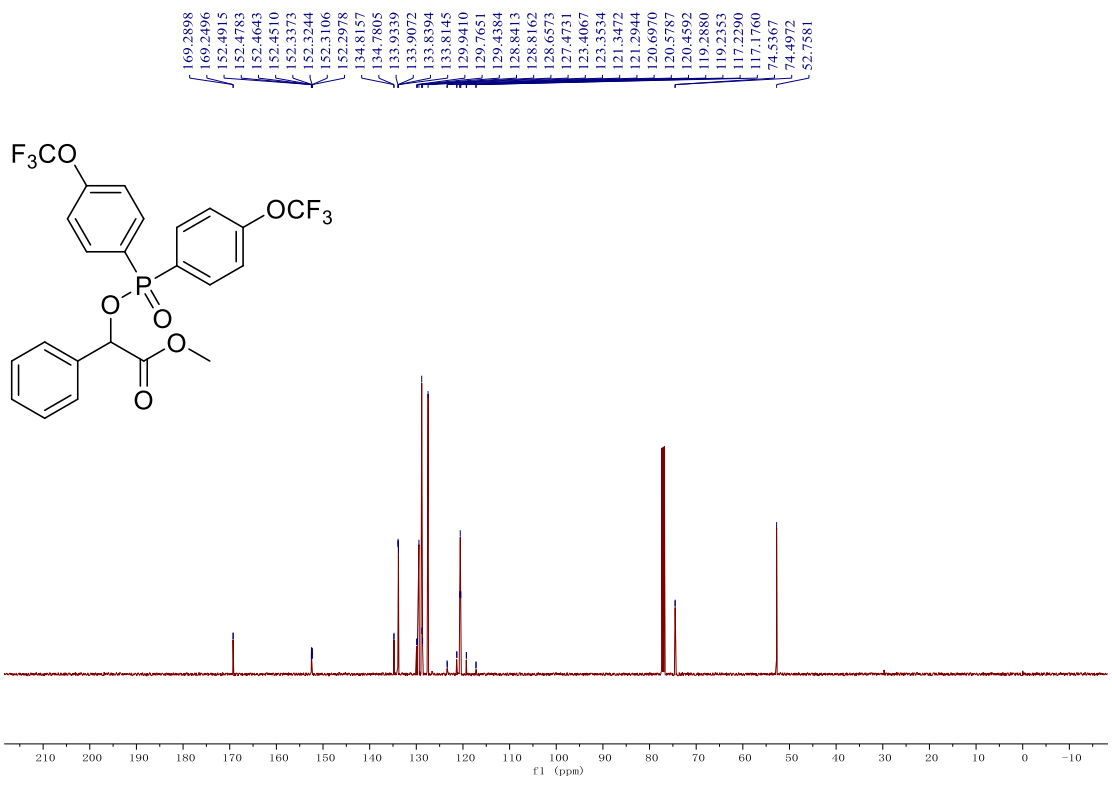


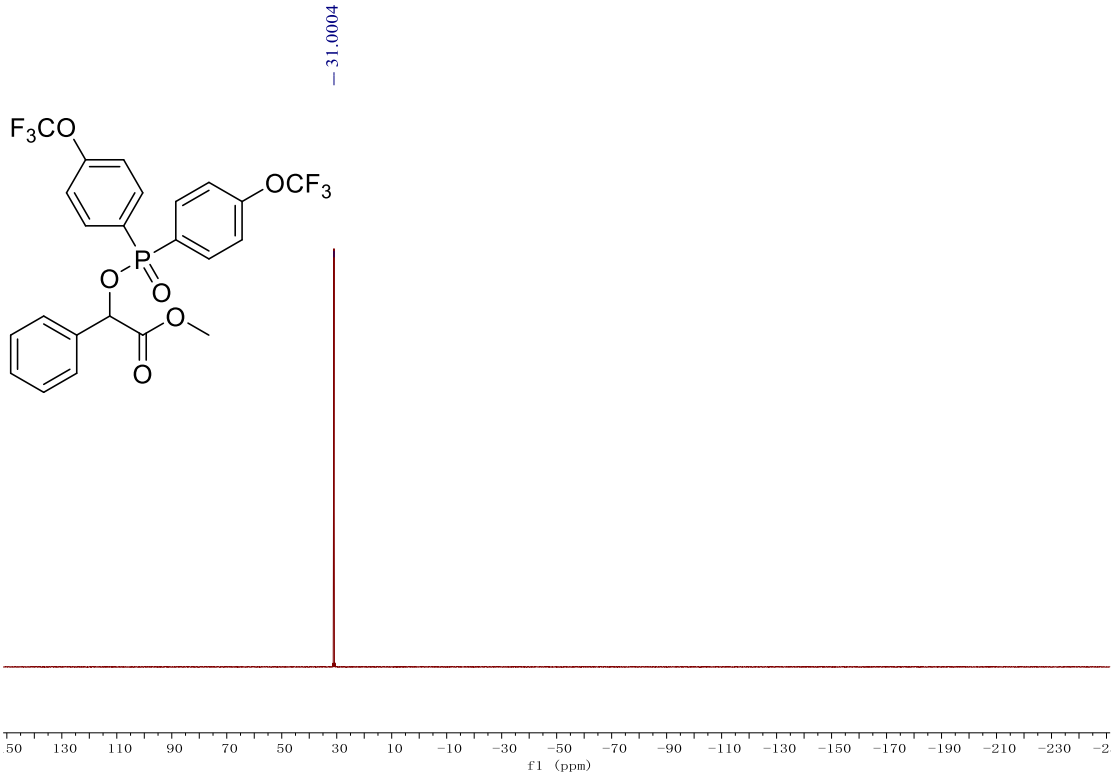

169.7697
169.7368
162.7344
162.7101
162.6720
162.6477
135.5465
135.5076
133.7471
133.6521
128.9611
128.6261
127.2217
123.3493
123.0252
122.1978
121.8785
114.0173
113.9567
113.9016
113.8422
73.9243
73.8854
55.3231
55.2926
52.5447
MeO
OMe
O
P
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

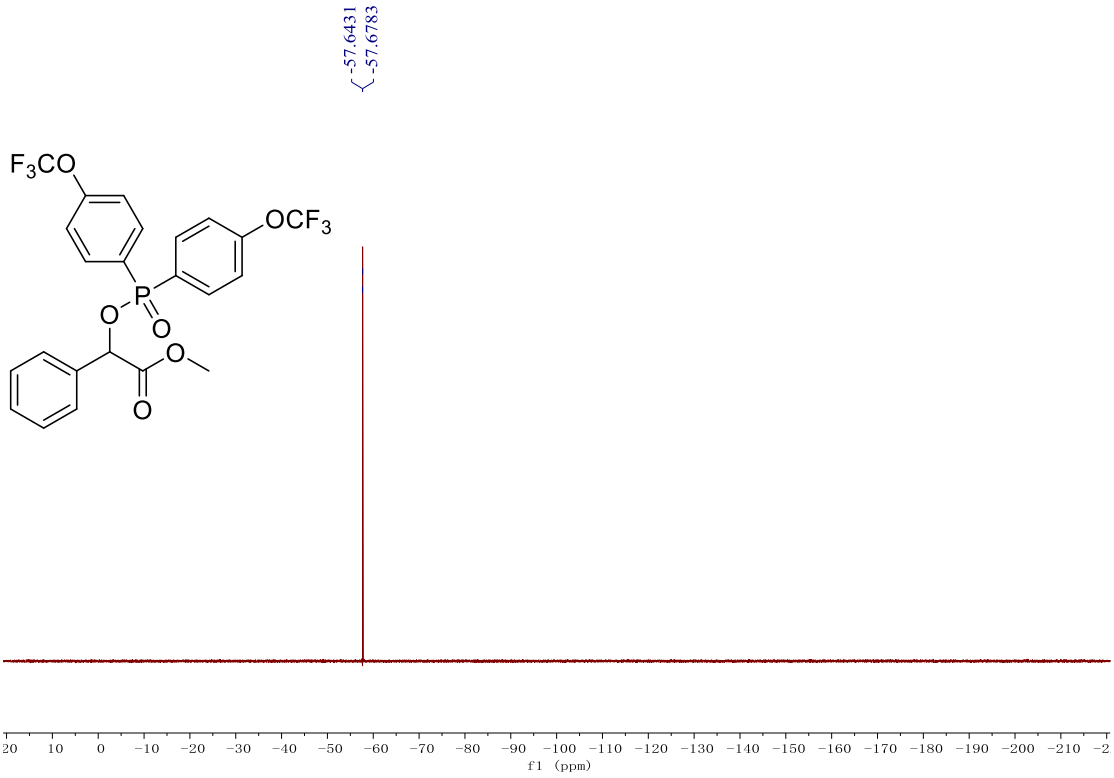

35.1126
MeO
OMe
O
P
O
O
O
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)

Methyl 2-((bis(4-(trifluoromethoxy)phenyl)phosphoryl)oxy)-2-phenylacetate (3ad)

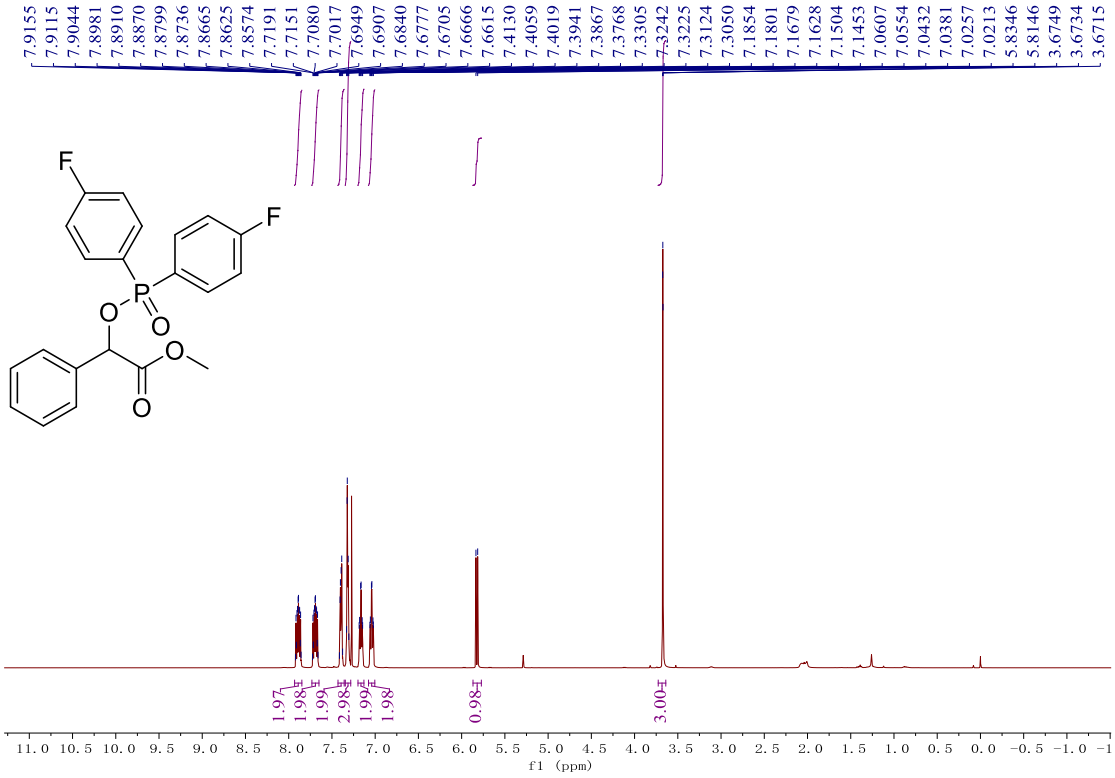


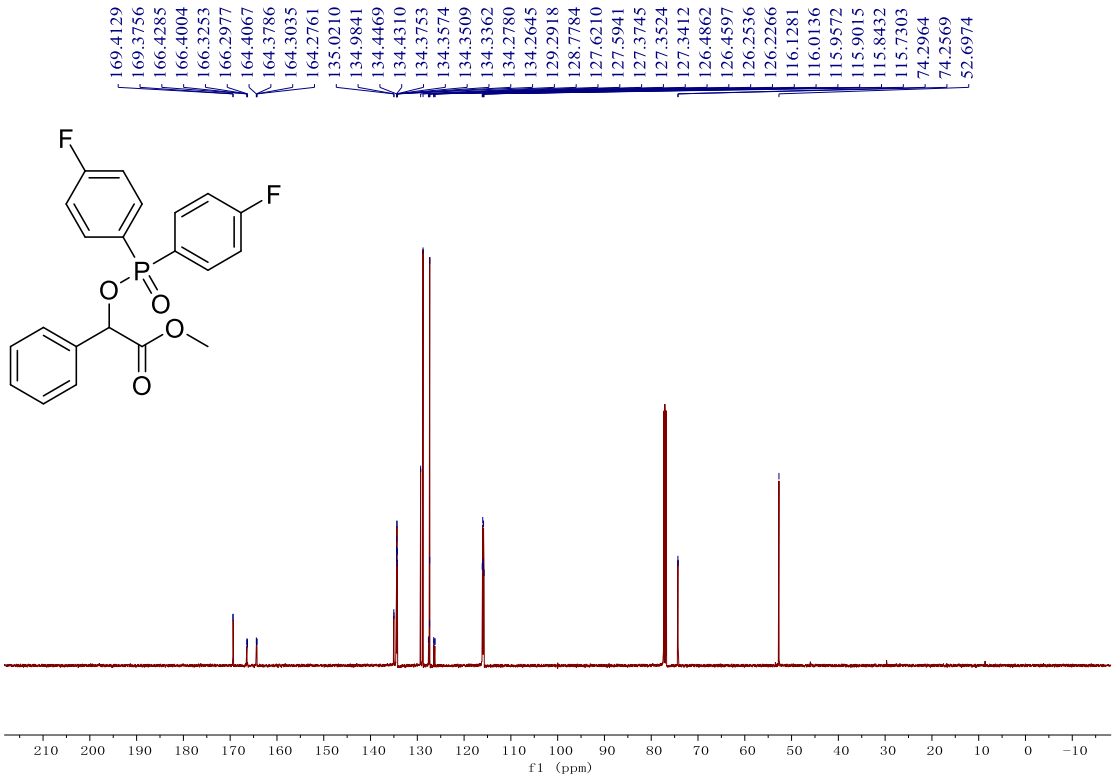


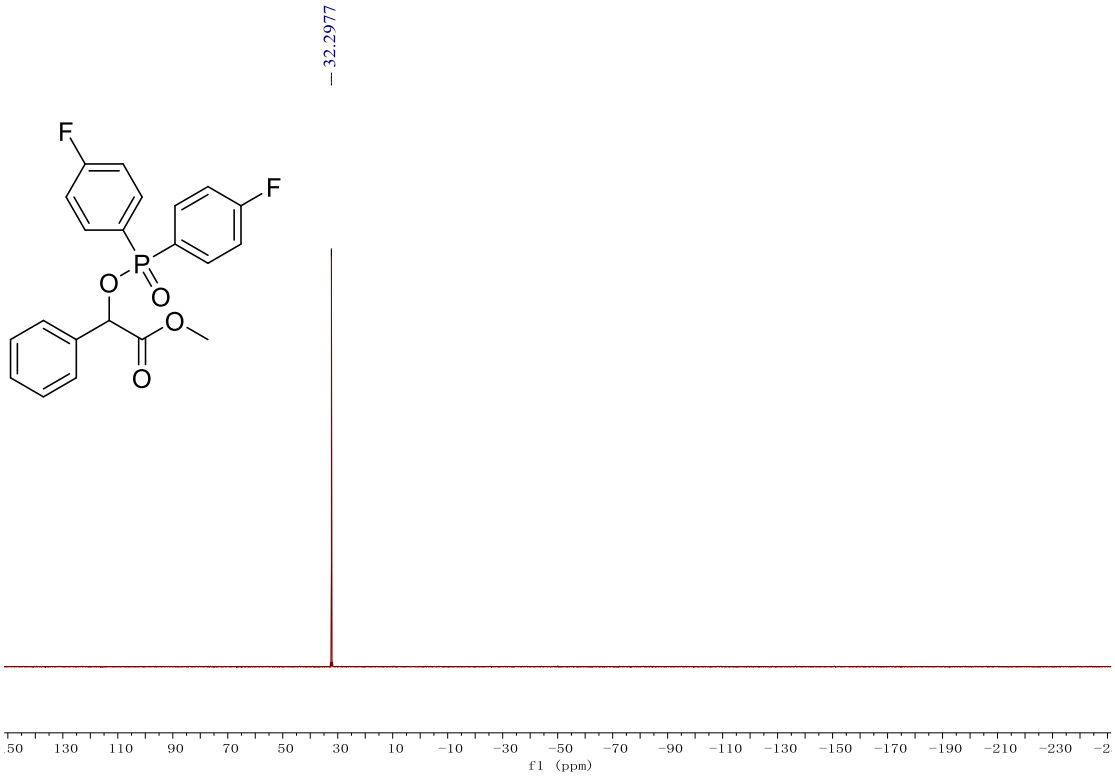

31.0004
F3CO
OCF3
P
O
O
O
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)

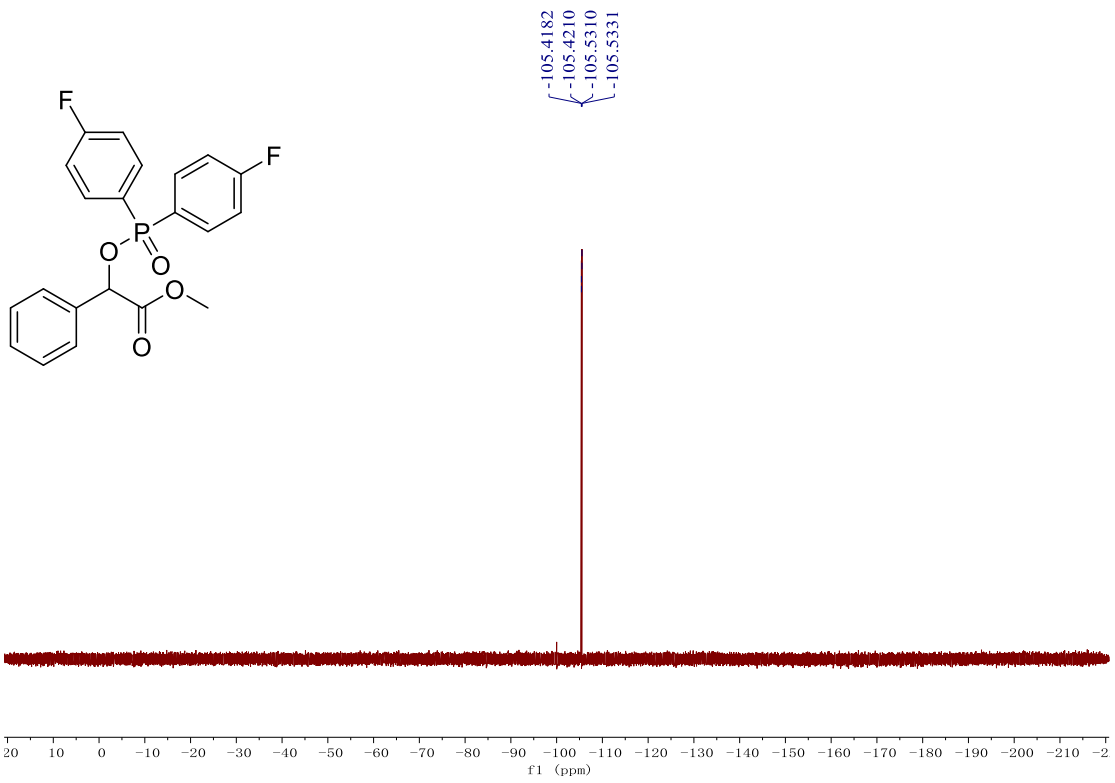

-57.6431
-57.6783
F3CO
OCF3
P
O
O
O
O
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

Methyl 2-((bis(4-fluorophenyl)phosphoryl)oxy)-2-phenylacetate (3ae)

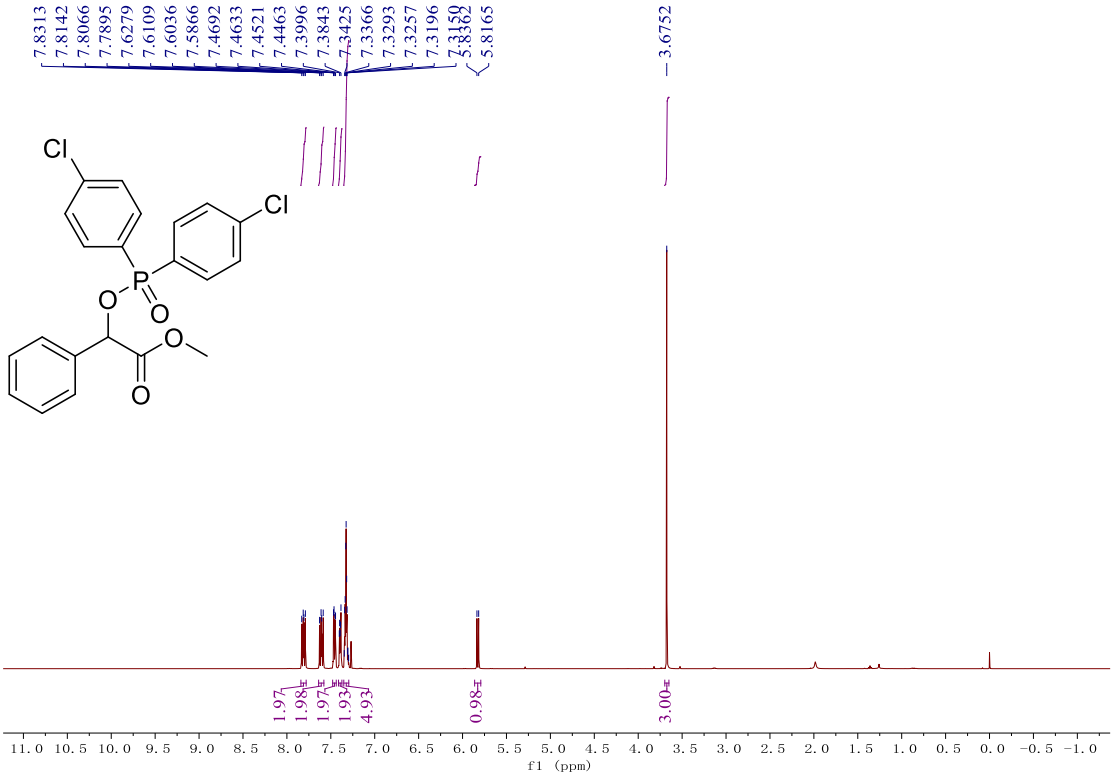


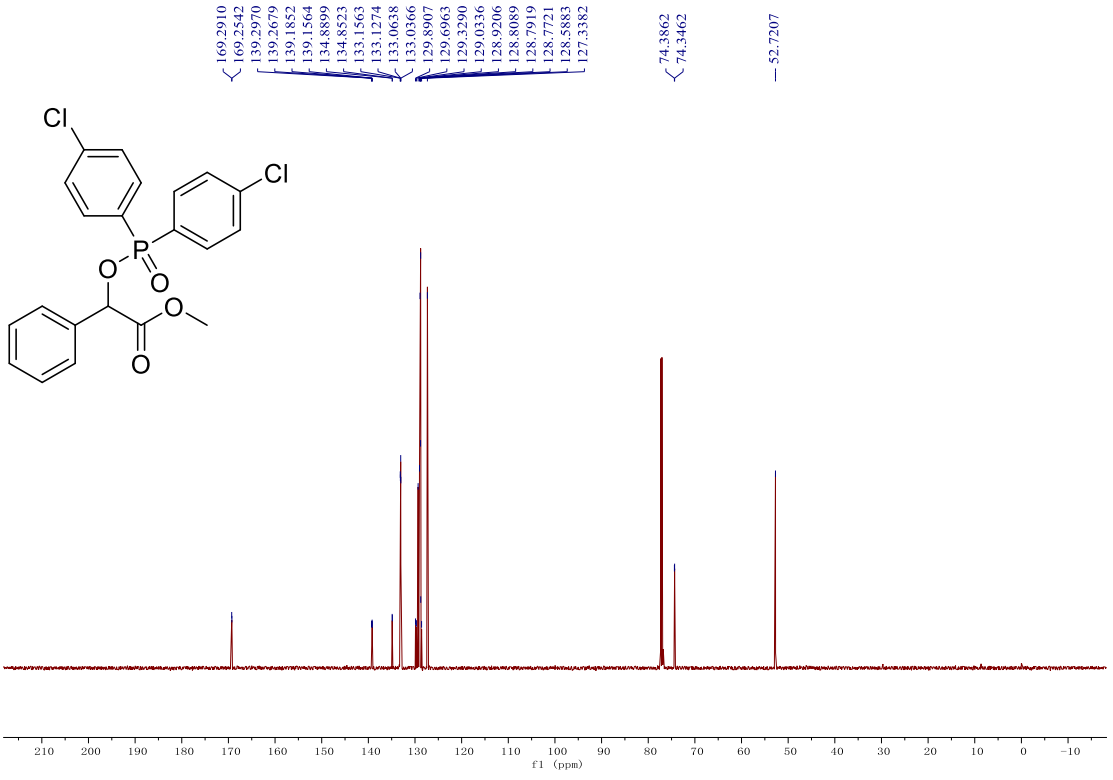


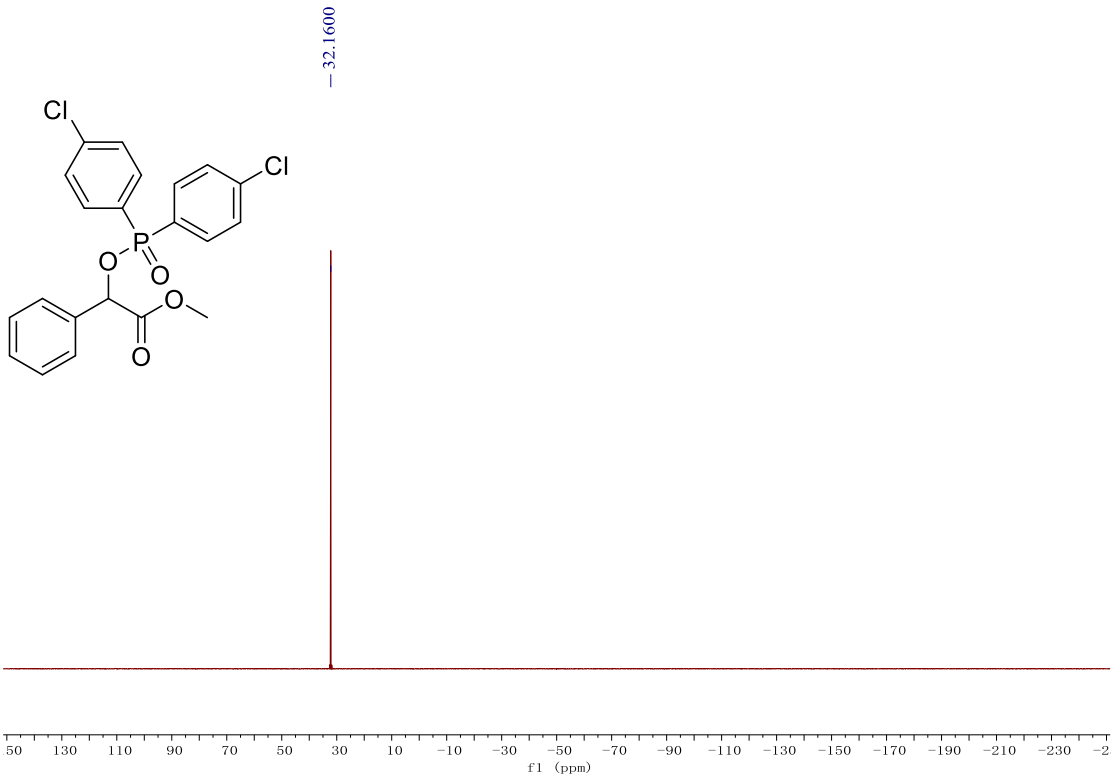

32.2977
F
F
P
O
O
O
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)


-105.4182
-105.4210
-105.5310
-105.5331
F
F
P
O
O
O
O
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

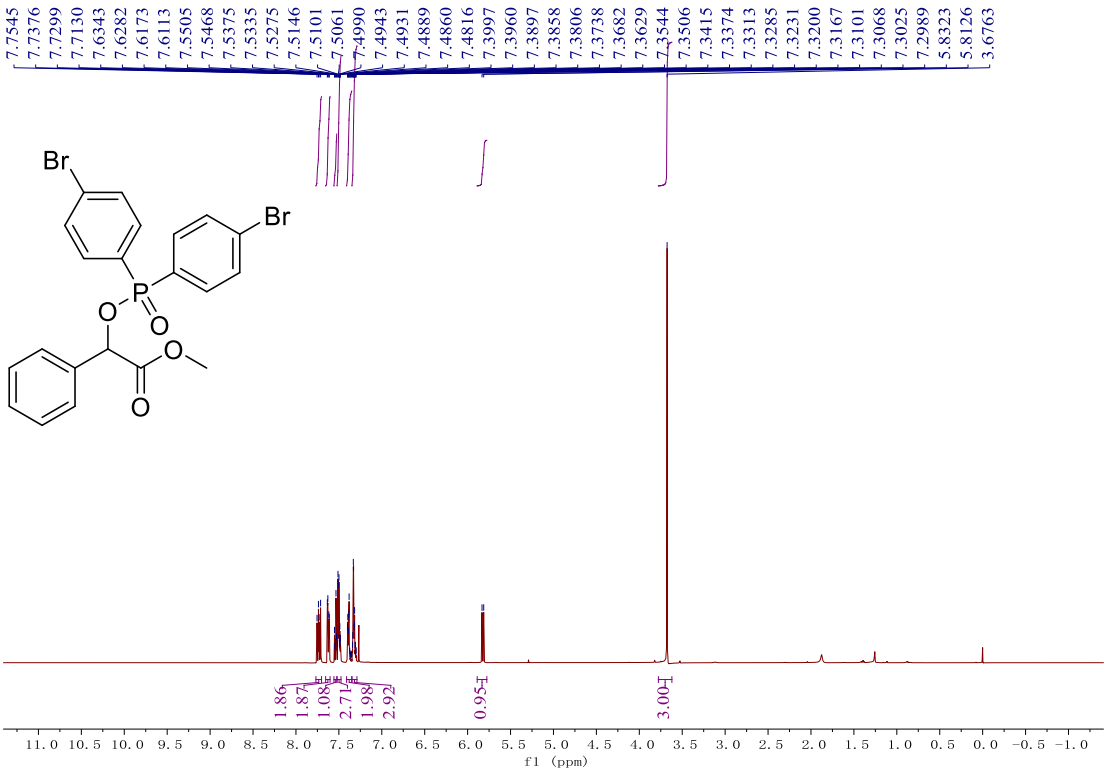
Methyl 2-((bis(4-chlorophenyl)phosphoryl)oxy)-2-phenylacetate (3af)

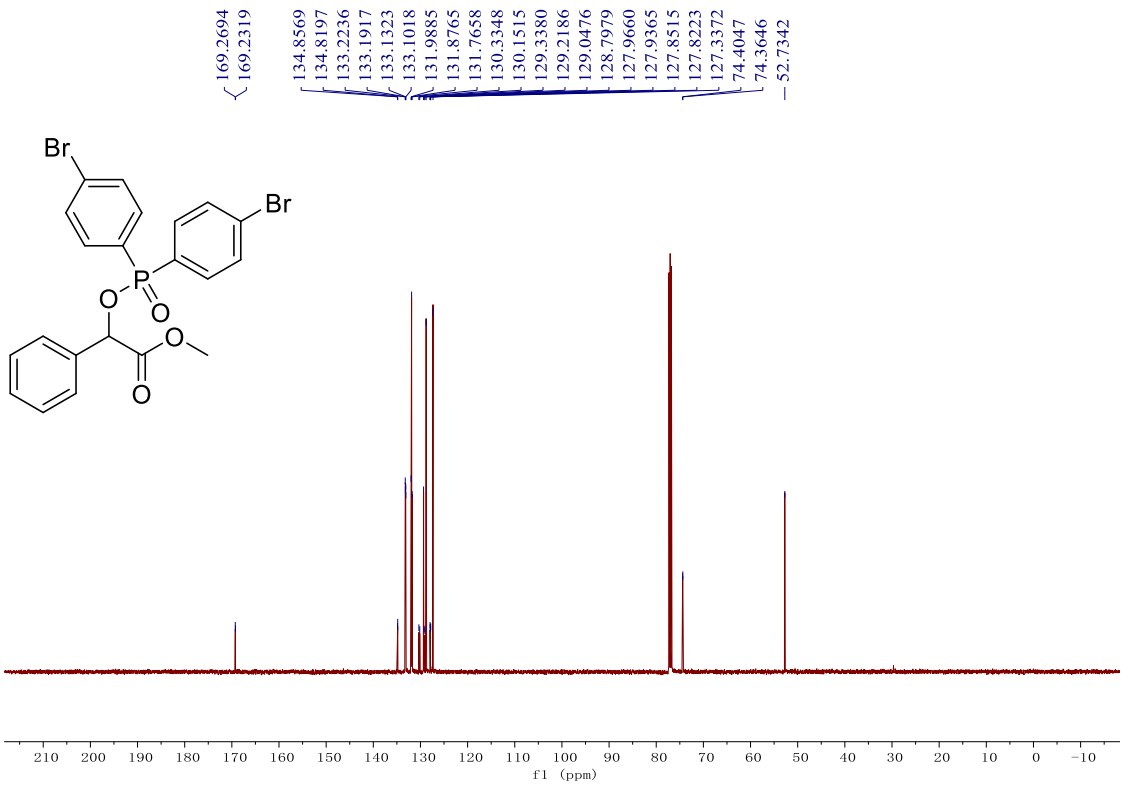


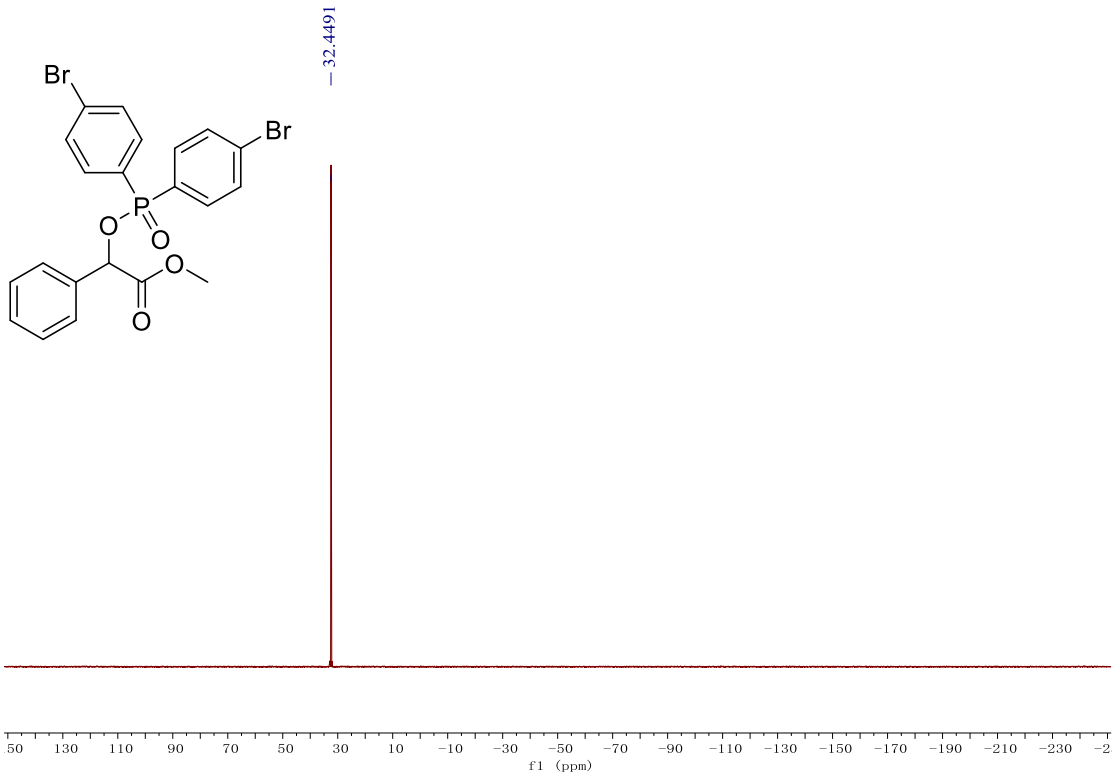




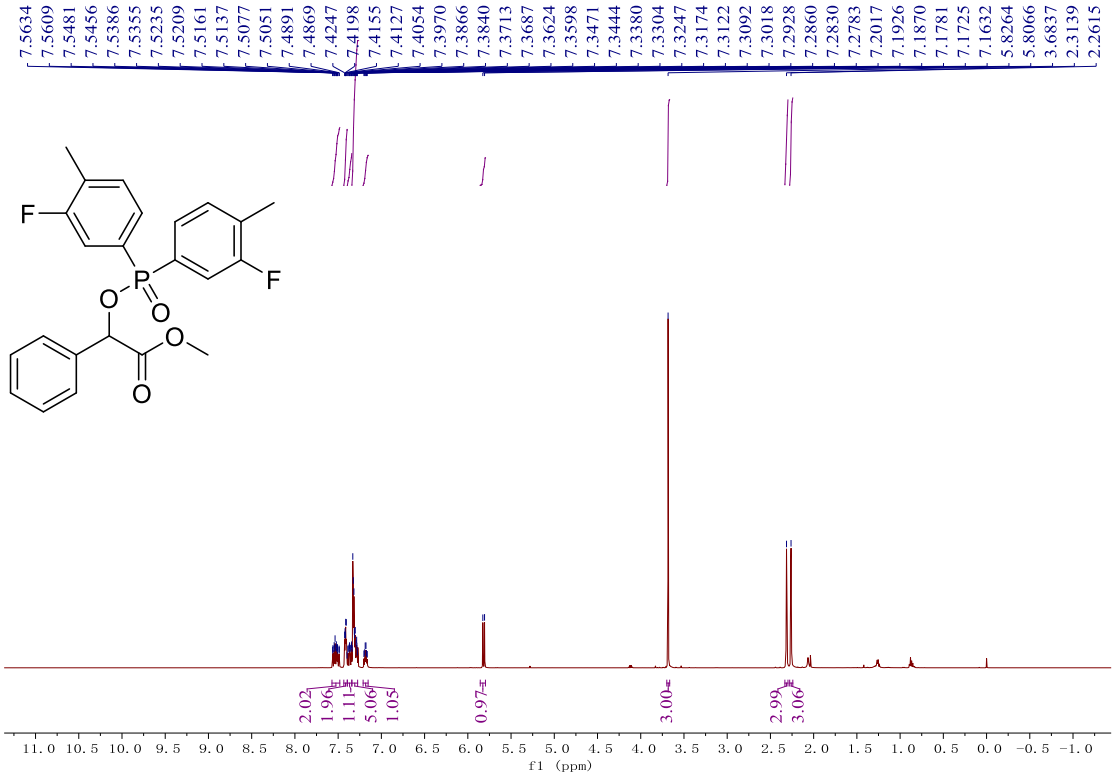
Methyl 2-((bis(4-bromophenyl)phosphoryl)oxy)-2-phenylacetate (3ag)

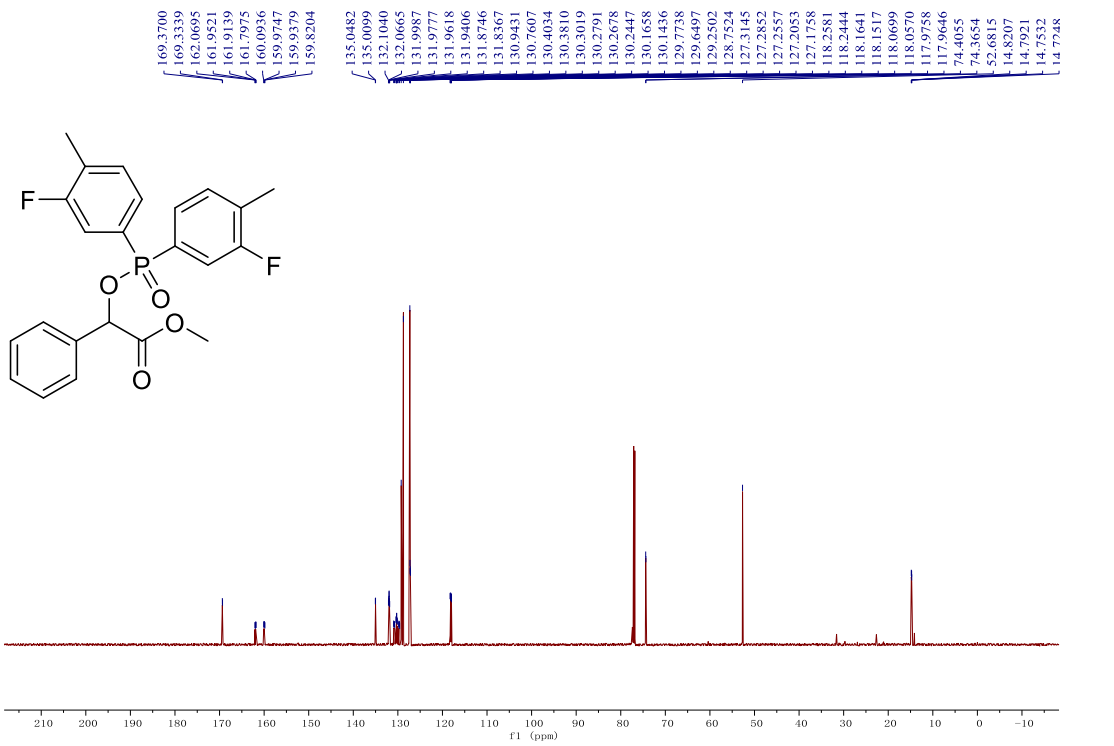


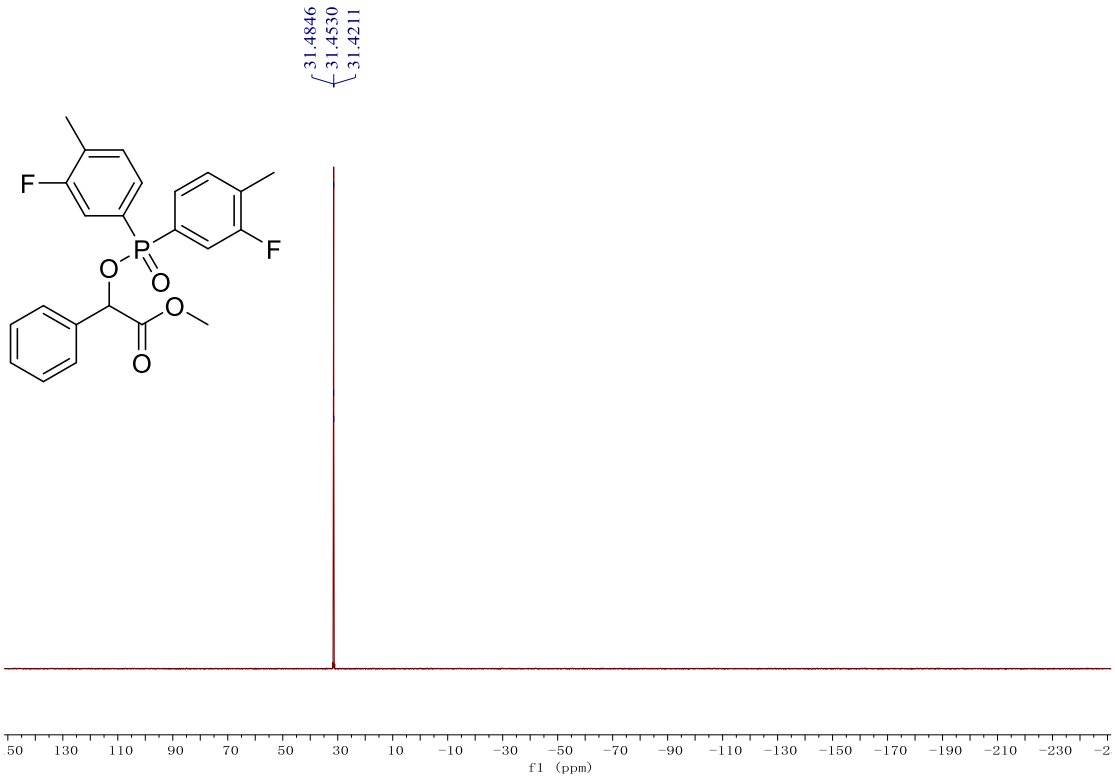

169.2694
169.2319
134.8569
134.8197
133.2236
133.1917
133.1323
133.1018
131.9885
131.8765
131.7658
130.3348
130.1515
129.3380
129.2186
129.0476
128.7979
127.9660
127.9365
127.8515
127.8223
127.3372
74.4047
74.3646
52.7342
Br
Br
P
O
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

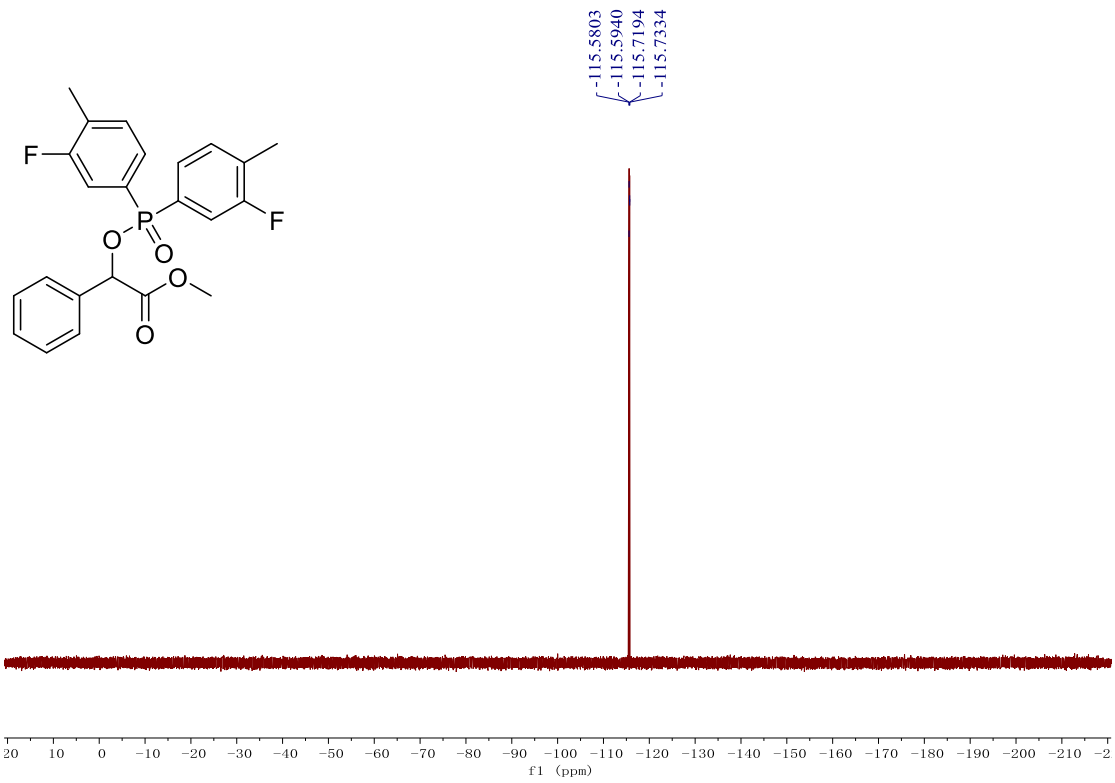

32.4491
Br
Br
P
O
O
O
O
O
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -2
f1 (ppm)

Methyl 2-((bis(3-fluoro-4-methylphenyl)phosphoryl)oxy)-2-phenylacetate (3ah)

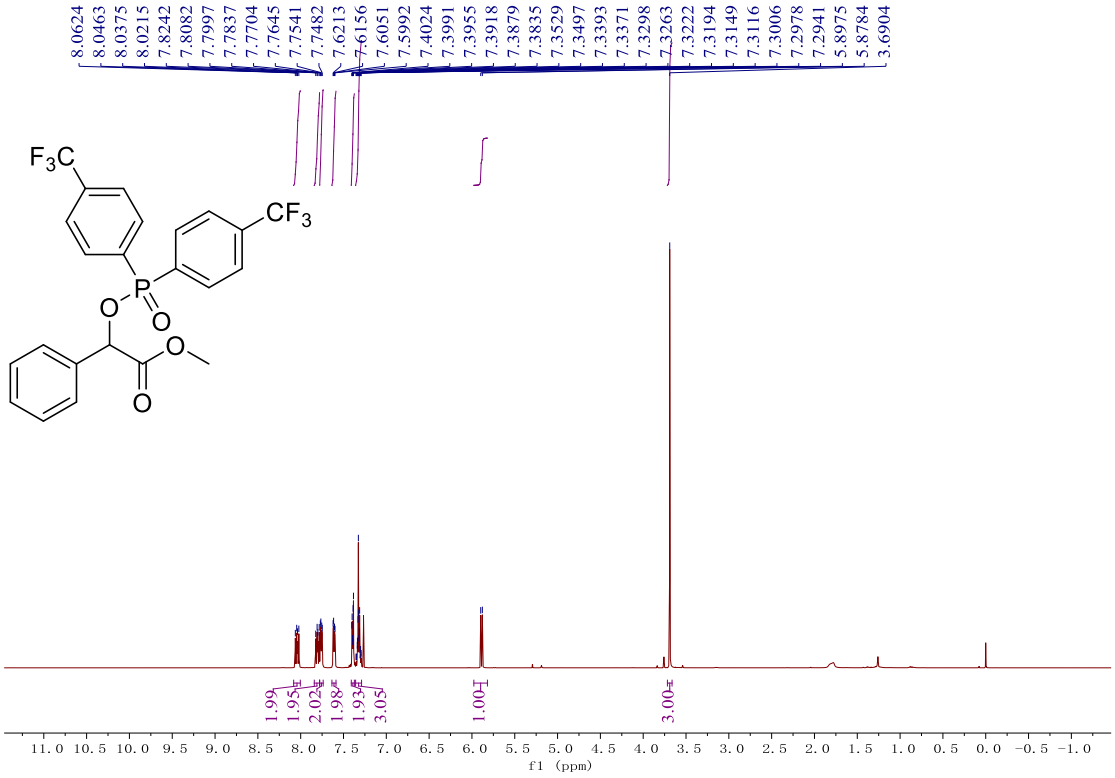


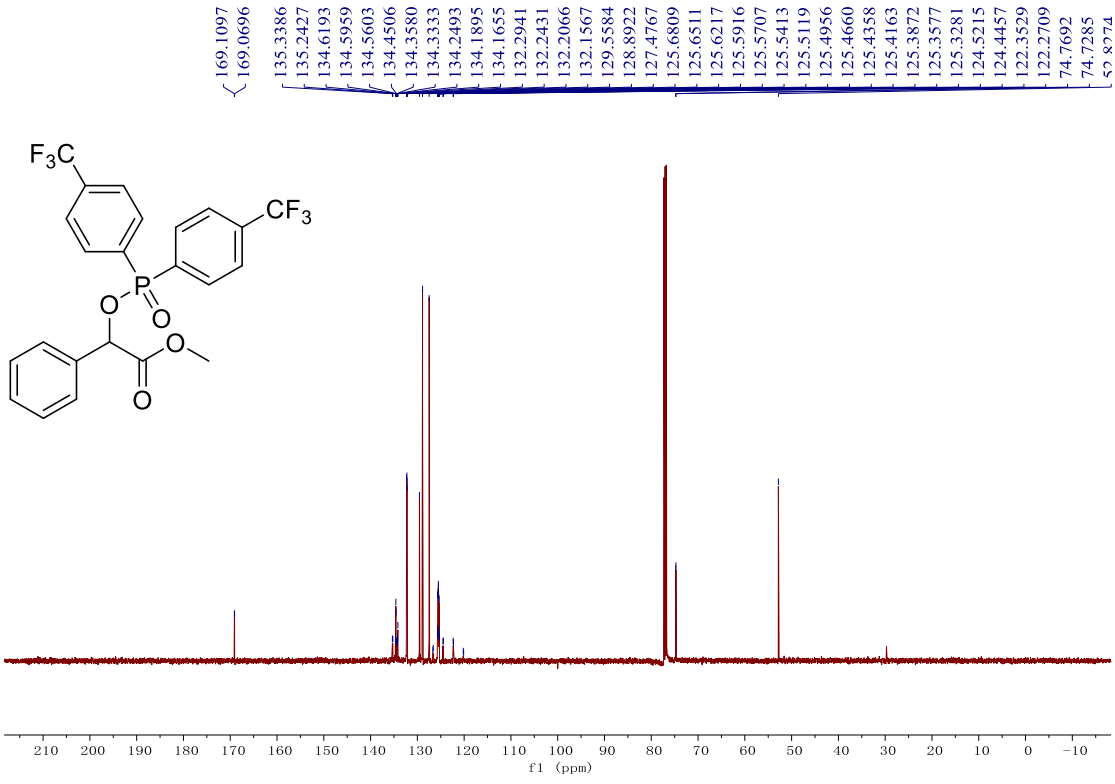


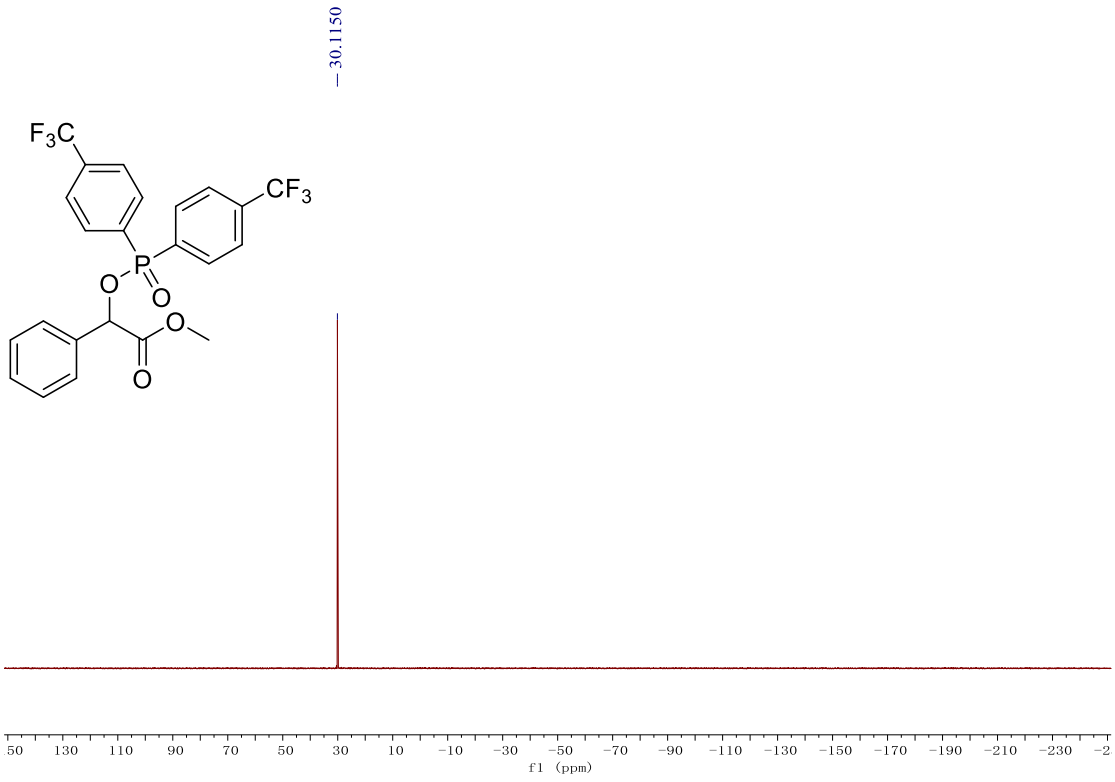

31.4846
31.4530
31.4211
F
F
P
O
O
O
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)

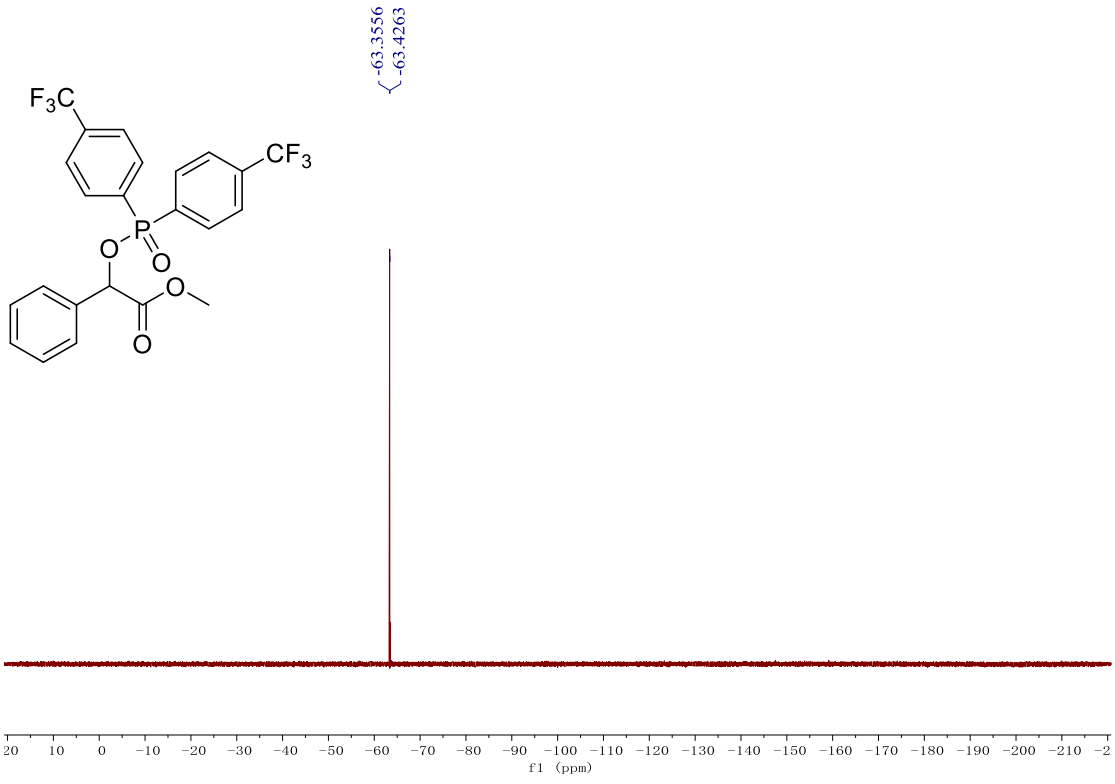

-115.5803
-115.5940
-115.7194
-115.7334
F
F
P
O
O
O
O
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

Methyl 2-((bis(4-(trifluoromethyl)phenyl)phosphoryl)oxy)-2-phenylacetate (3ai)

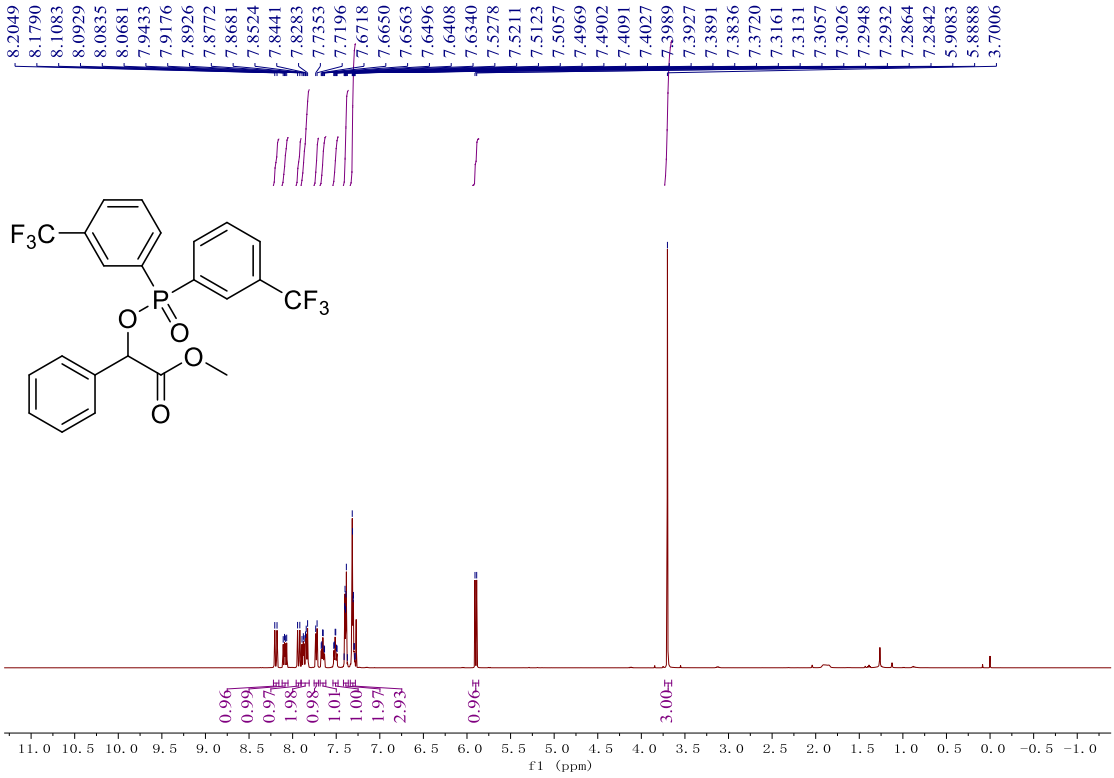


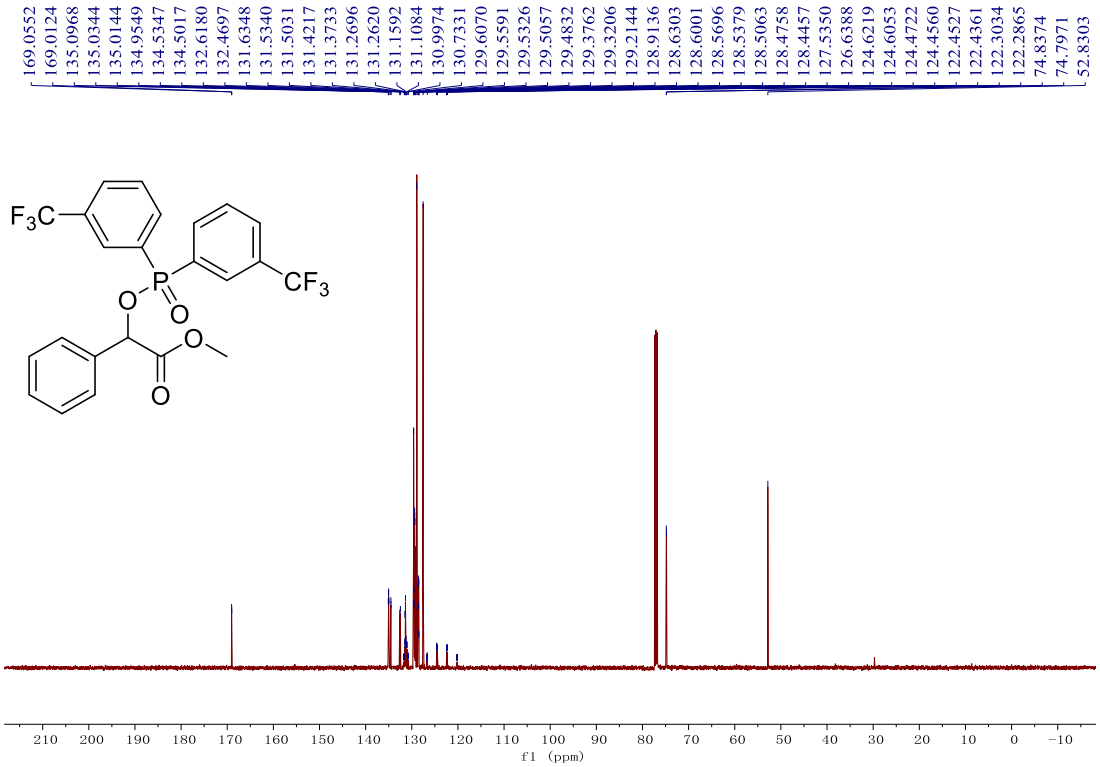


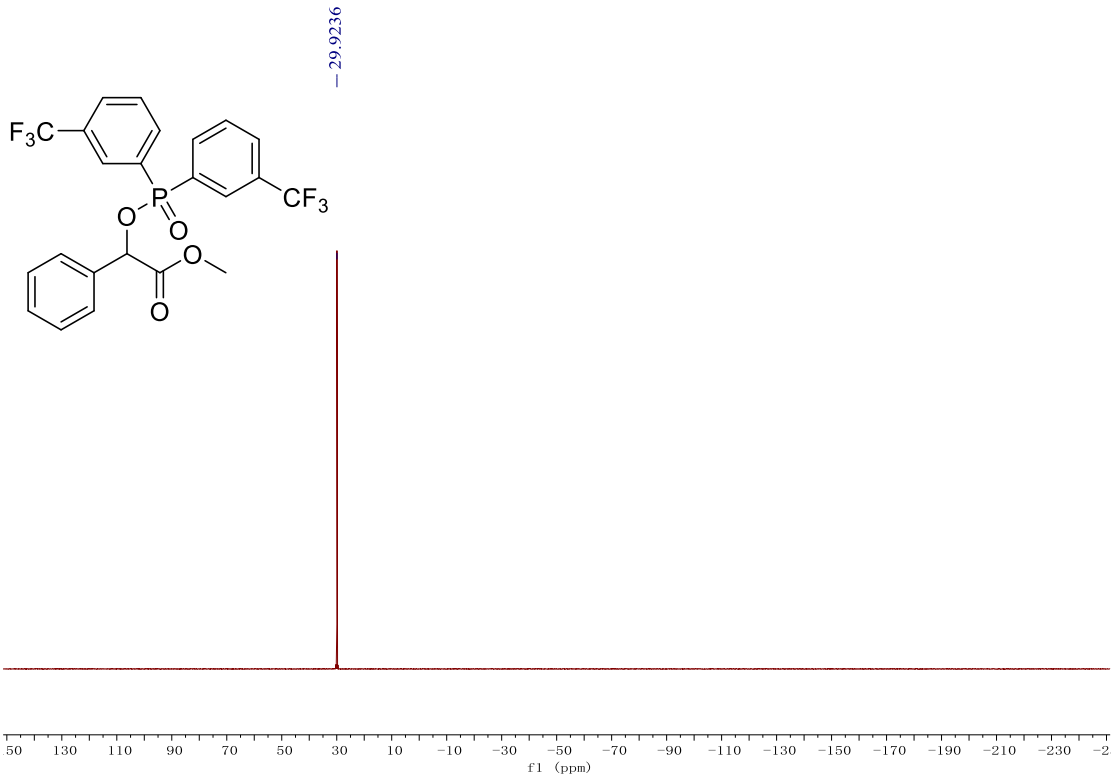

30.1150
F3C
CF3
P
O
O
O
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)

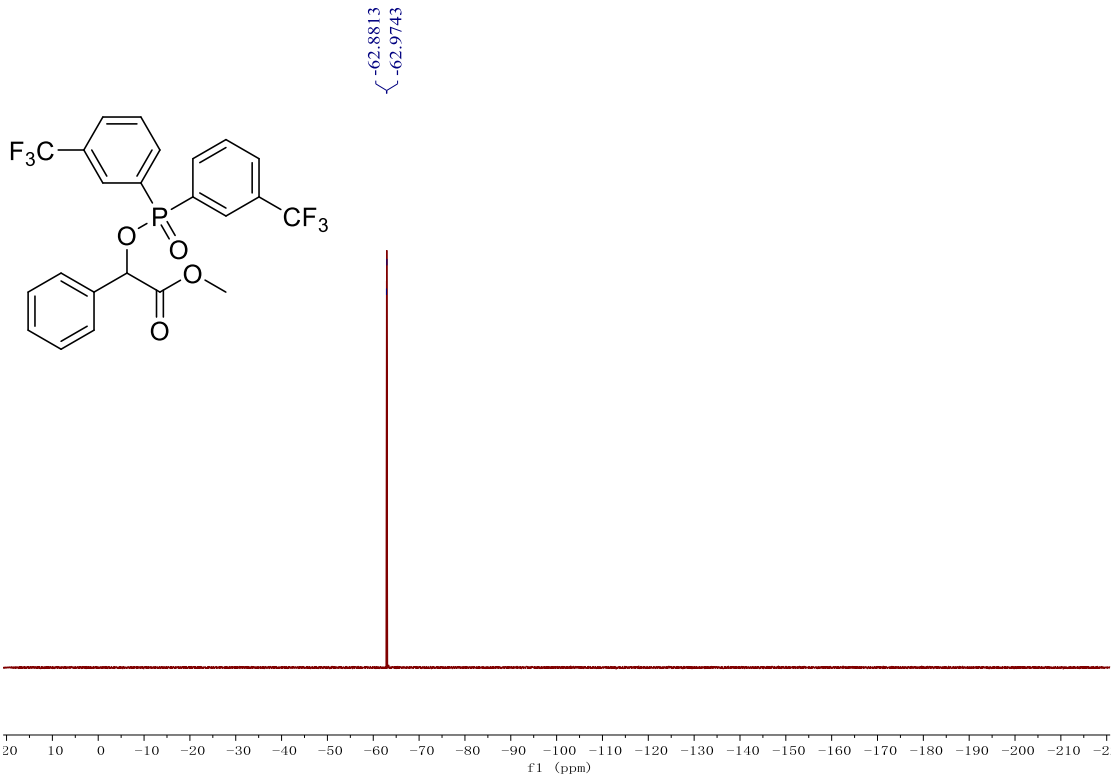

-63.3556
-63.4263
F3C
CF3
P
O
O
O
O
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

Methyl 2-((bis(3-(trifluoromethyl)phenyl)phosphoryl)oxy)-2-phenylacetate (3aj)

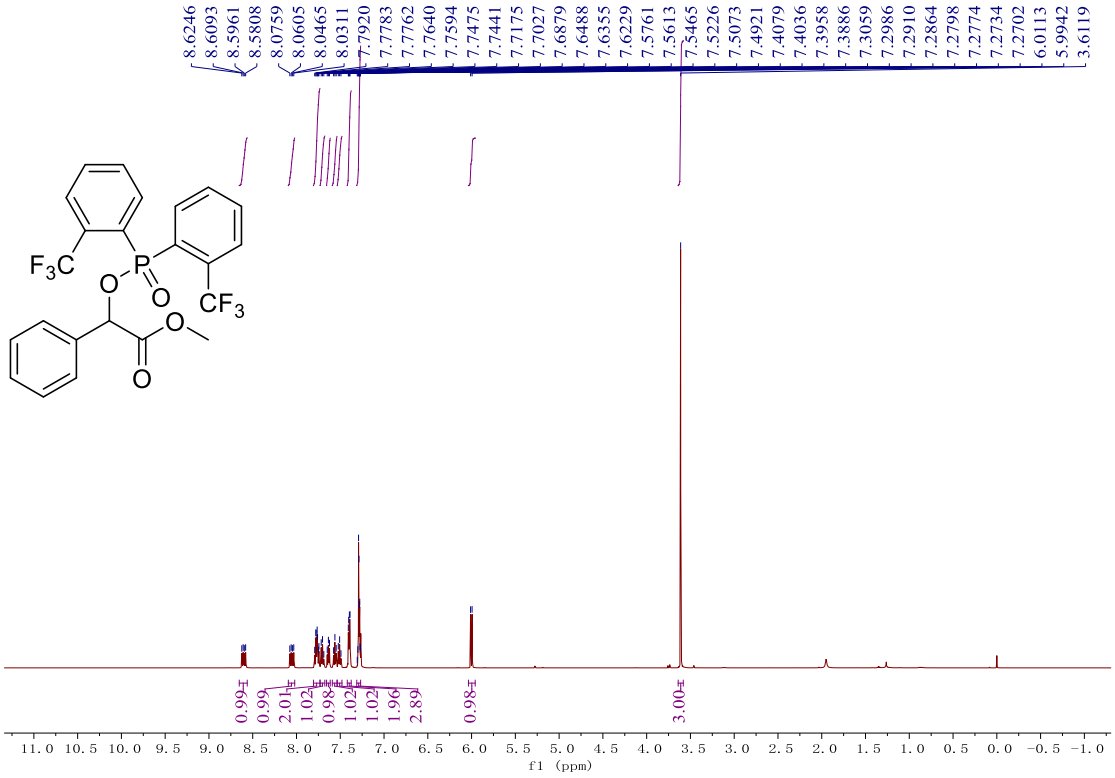


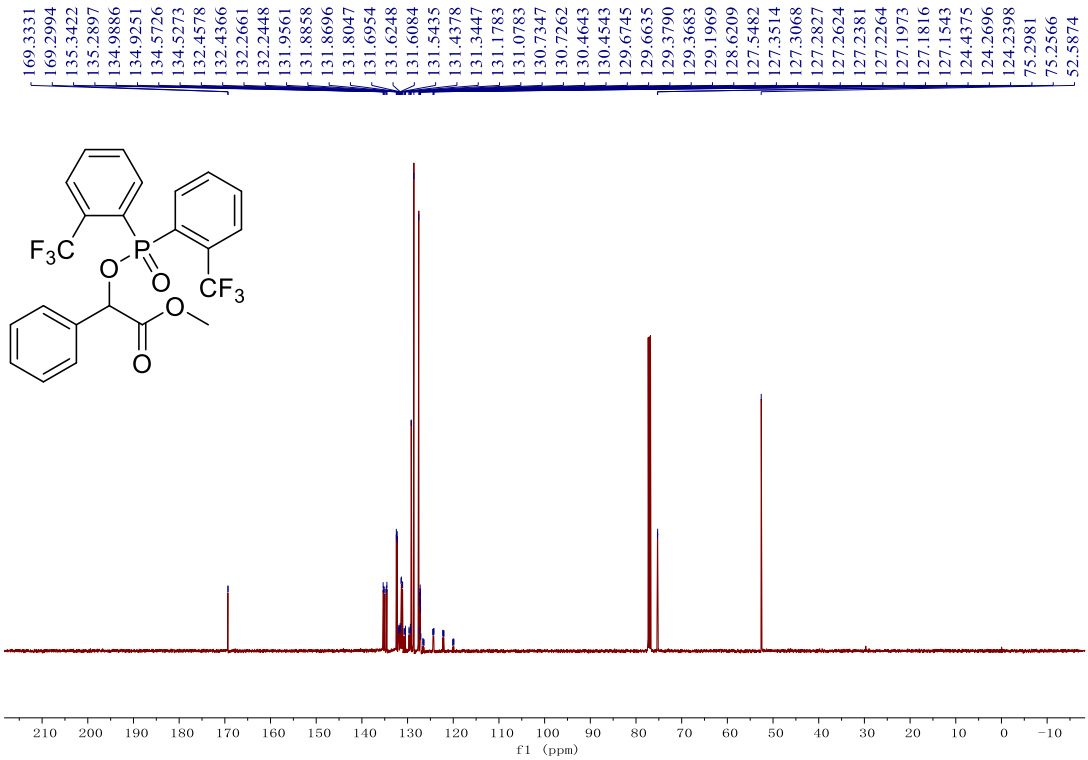


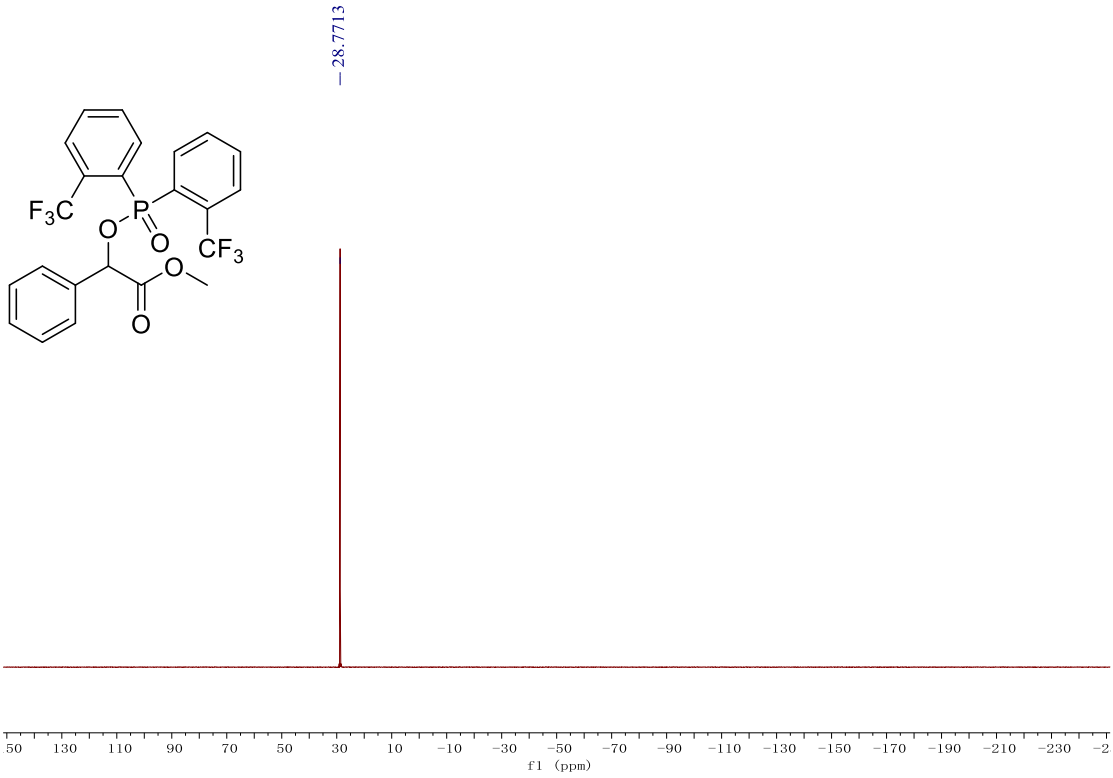

29.9236
F3C
CF3
O
P
O
O
O
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)

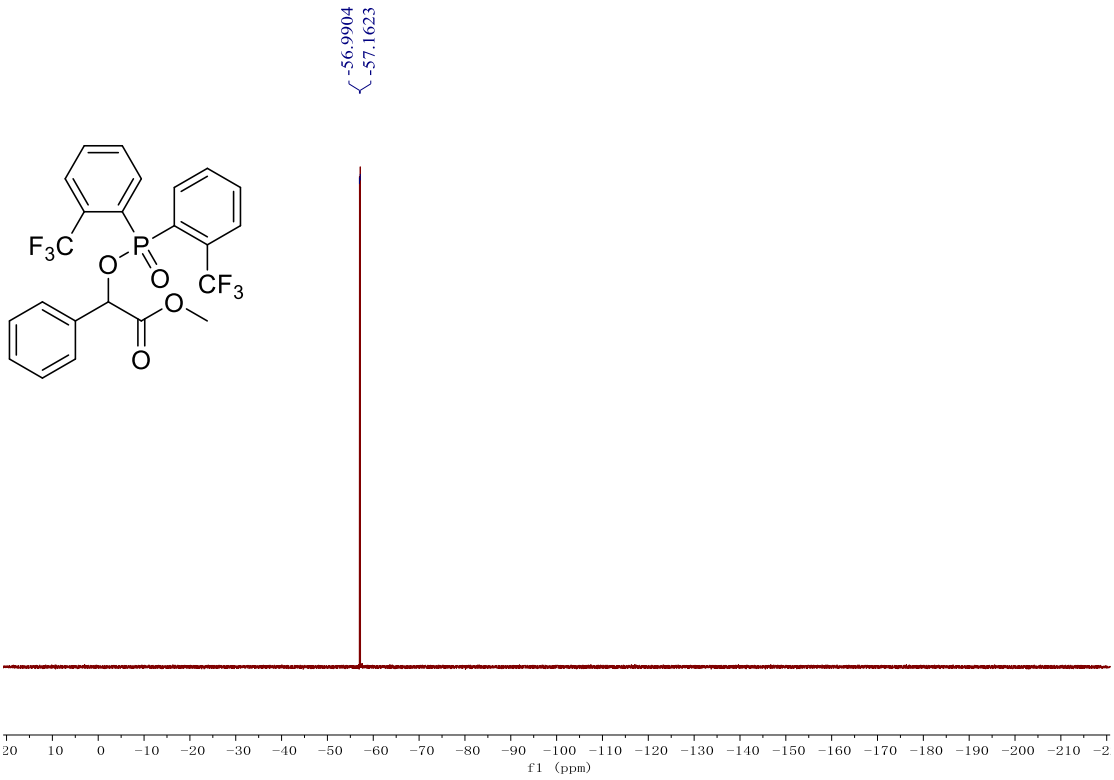

-62.8813
-62.9743
F3C
CF3
O
P
O
O
O
O
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

Methyl 2-((bis(2-(trifluoromethyl)phenyl)phosphoryl)oxy)-2-phenylacetate (3ak)

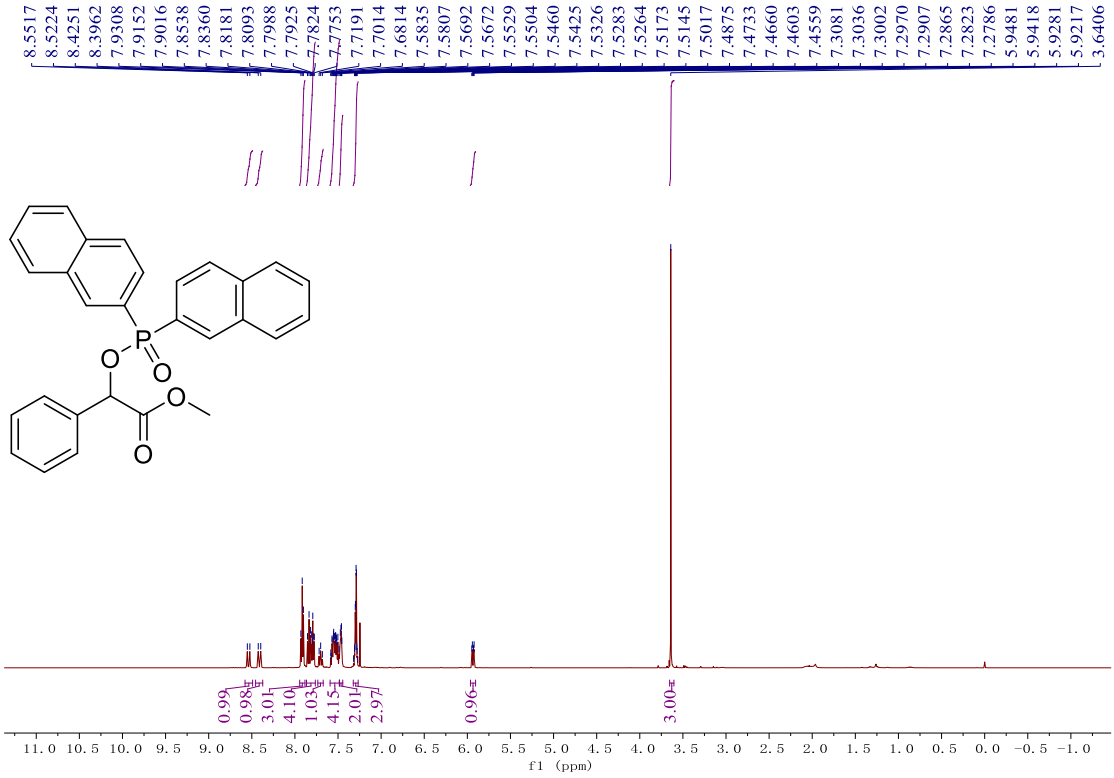


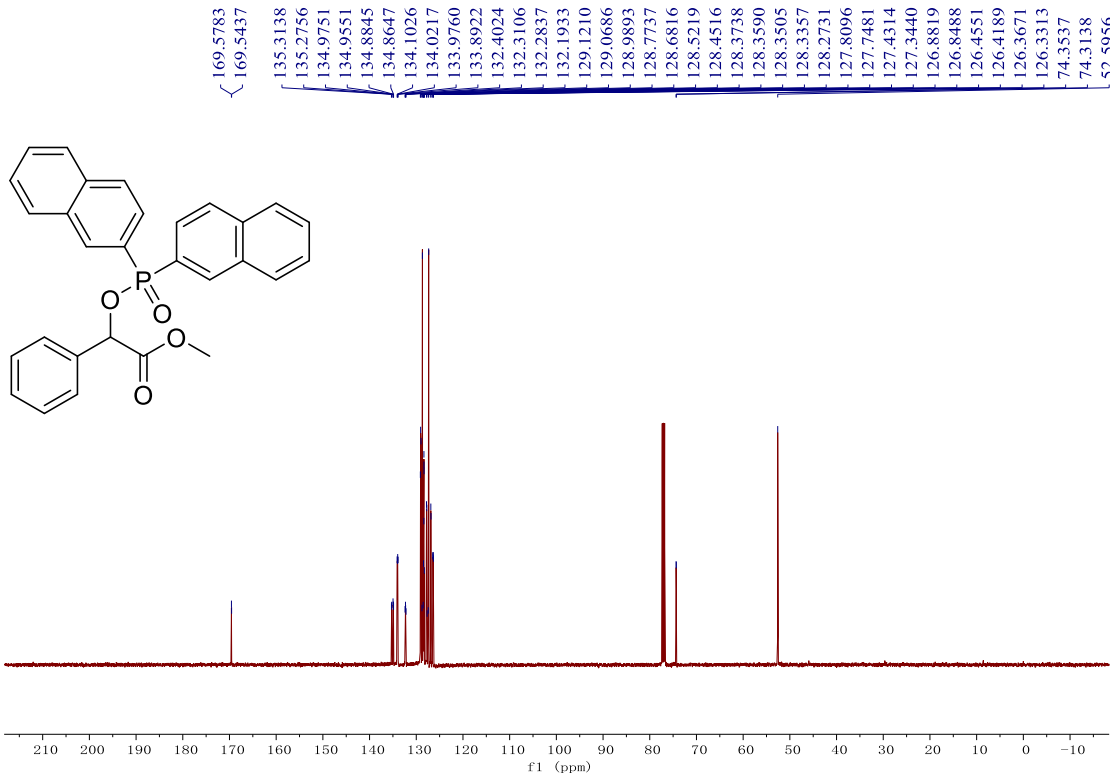


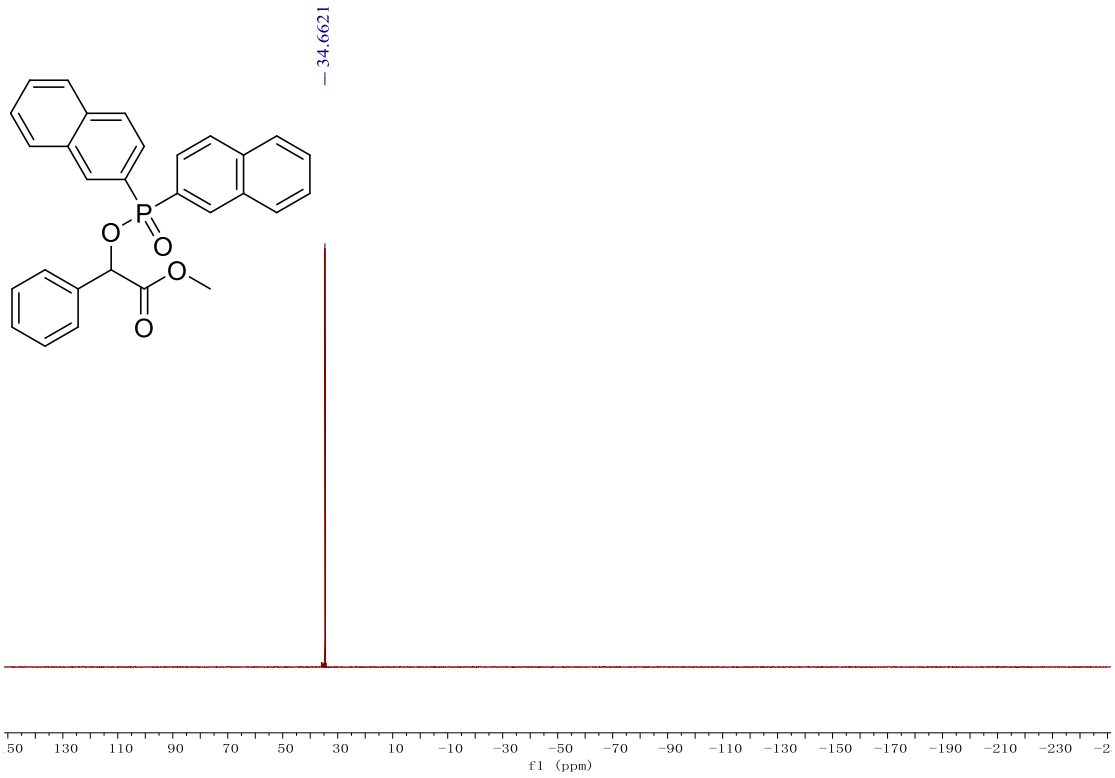

-28.7713
F3C
P
O
O
CF3
O
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)


-56.9904
-57.1623
F3C
P
O
O
CF3
O
O
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

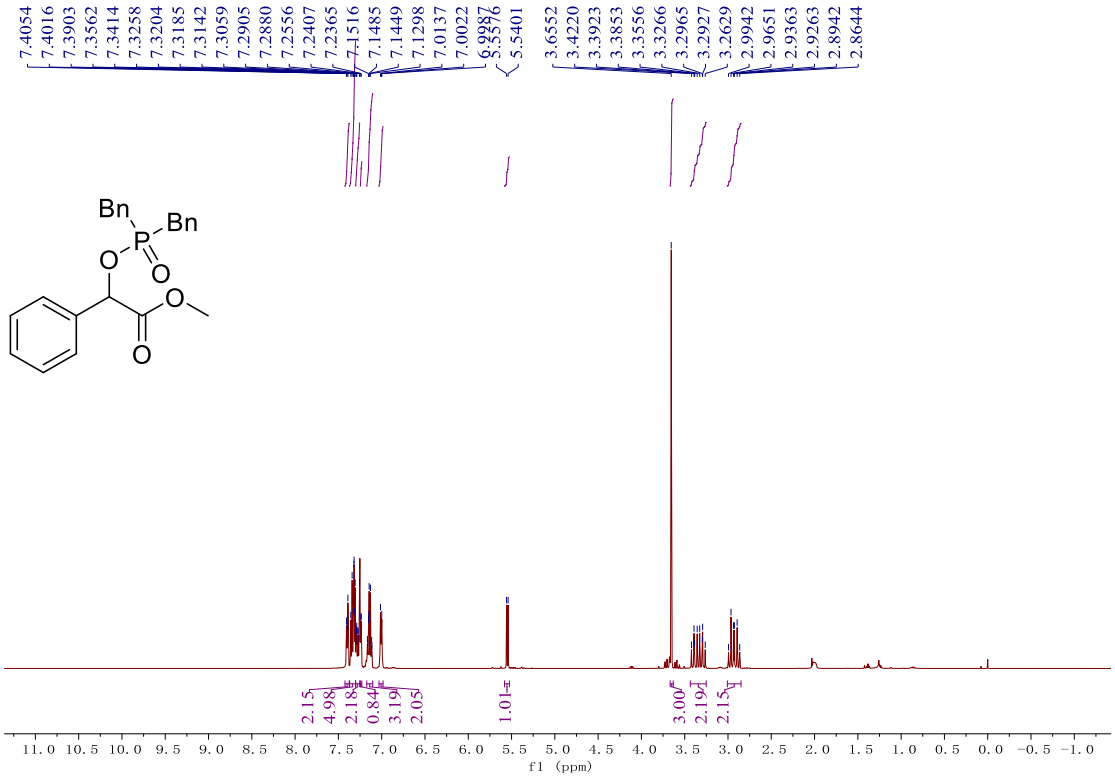
Methyl 2-((di(naphthalen-2-yl)phosphoryl)oxy)-2-phenylacetate (3al)

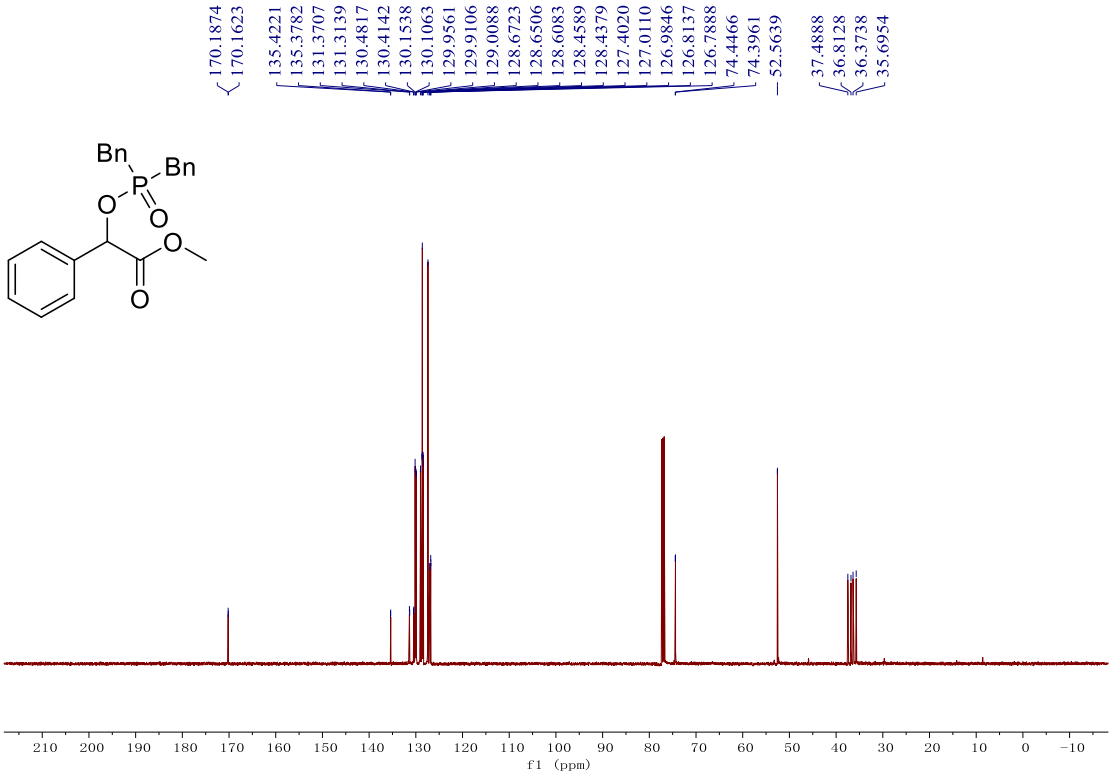


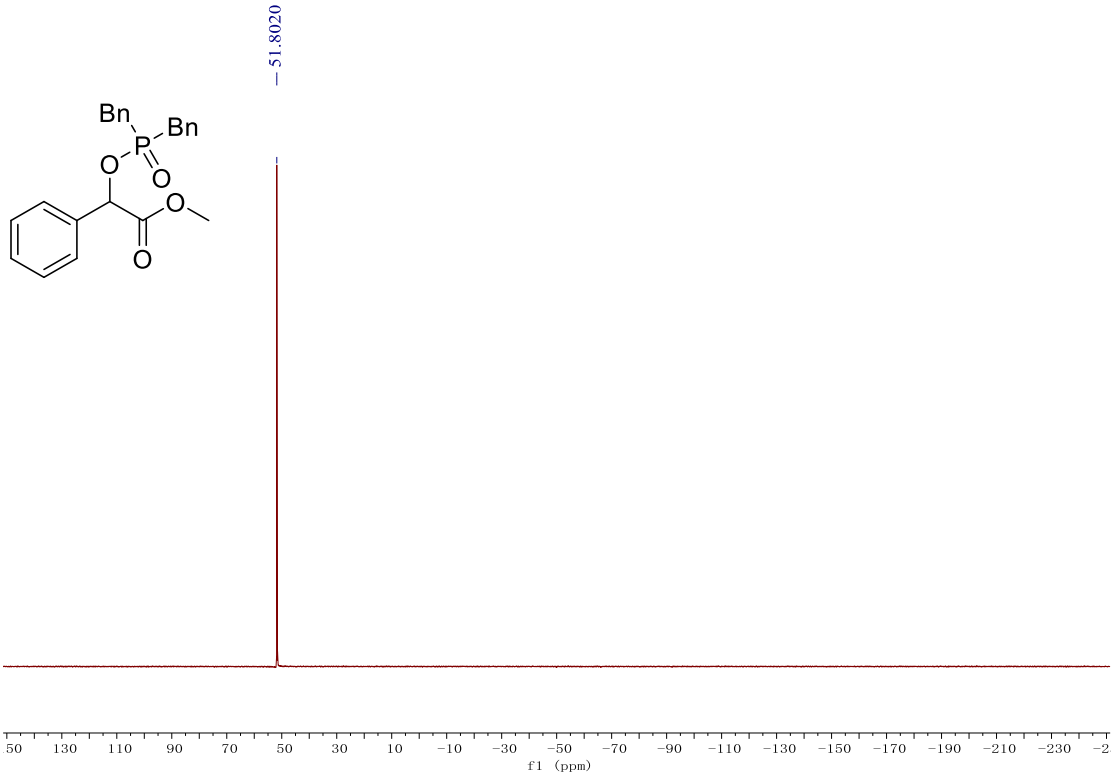




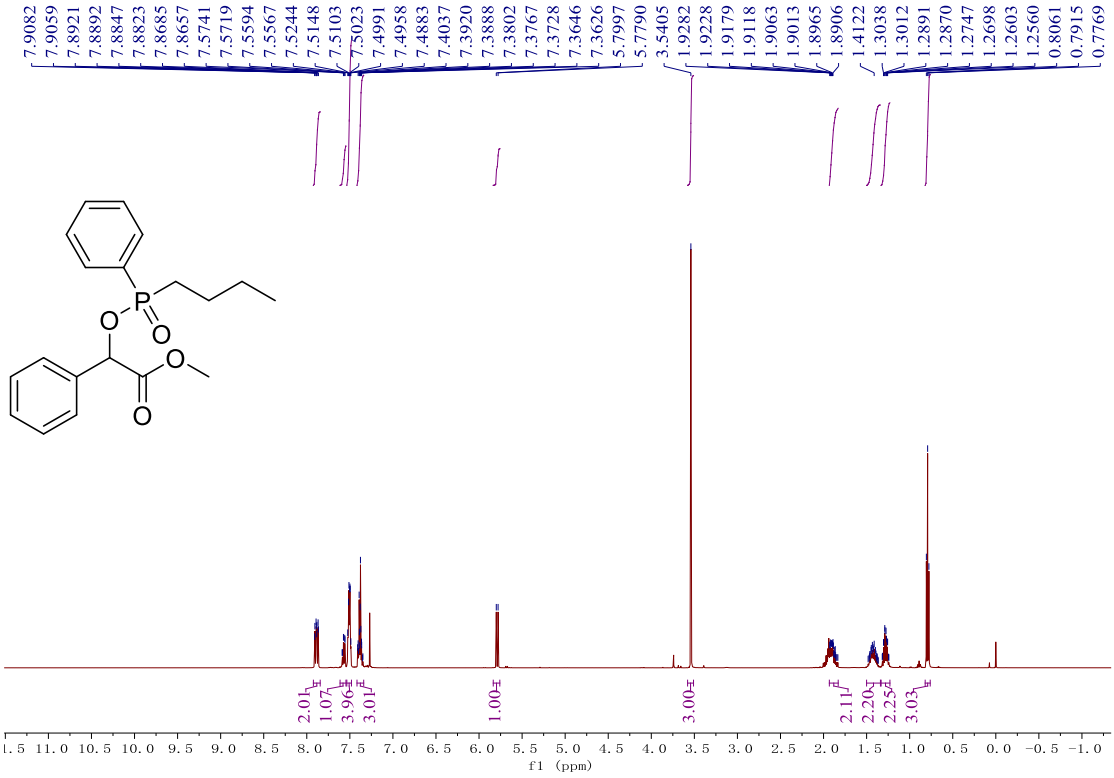
Methyl 2-((dibenzylphosphoryl)oxy)-2-phenylacetate (3am)

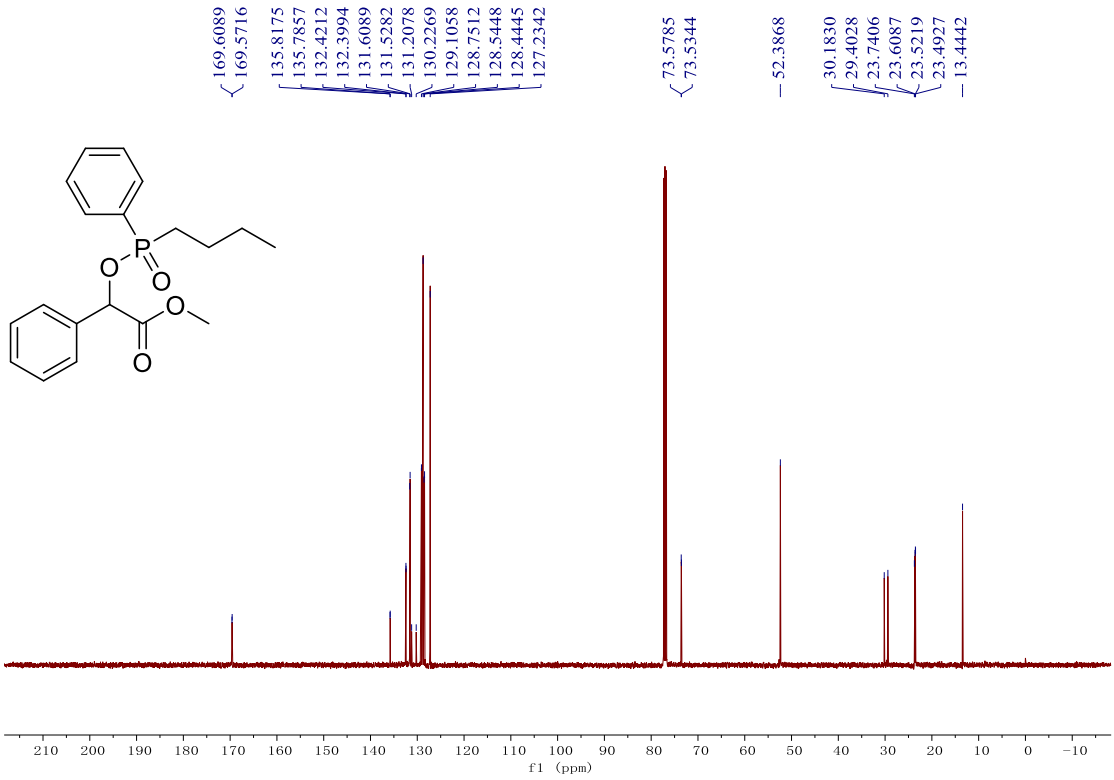


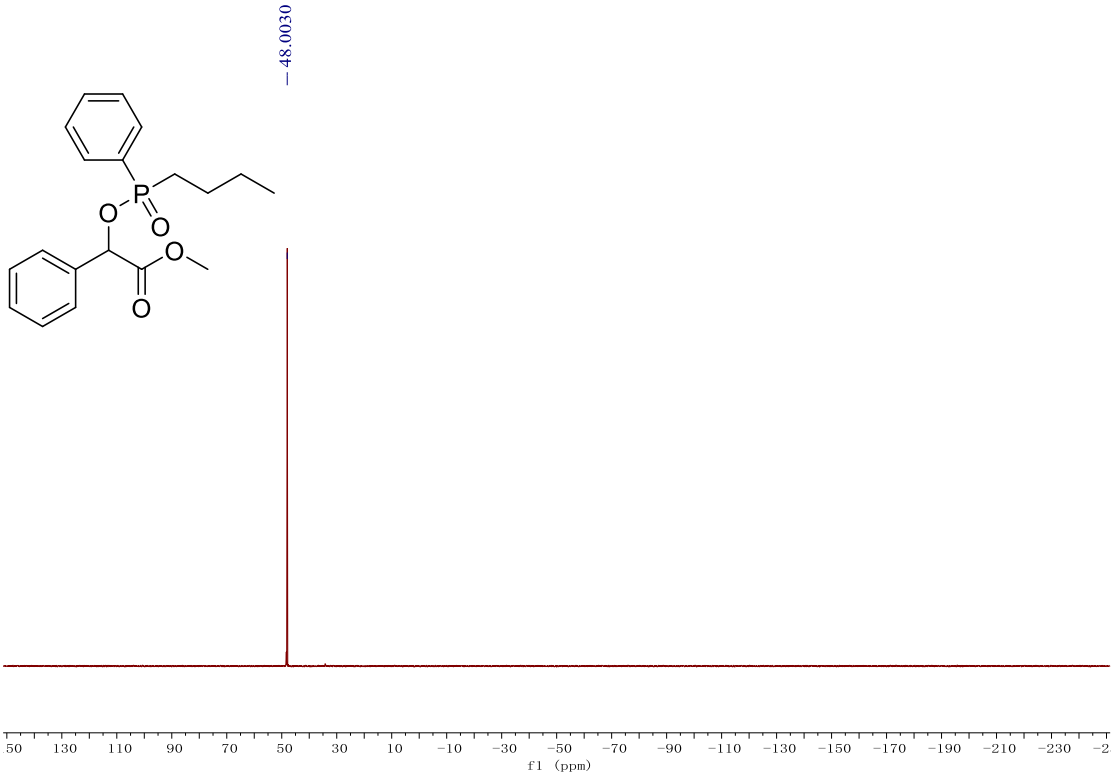

170.1874
170.1623
135.4221
135.3782
131.3707
131.3139
130.4817
130.4142
130.1538
130.1063
129.9561
129.9106
129.0088
128.6723
128.6506
128.6083
128.4589
128.4379
127.4020
127.0110
126.9846
126.8137
126.7888
74.4466
74.3961
52.5639
37.4888
36.8128
36.3738
35.6954
Bn
Bn
P
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


51.8020
Bn
Bn
P
O
O
O
O
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -2
f1 (ppm)

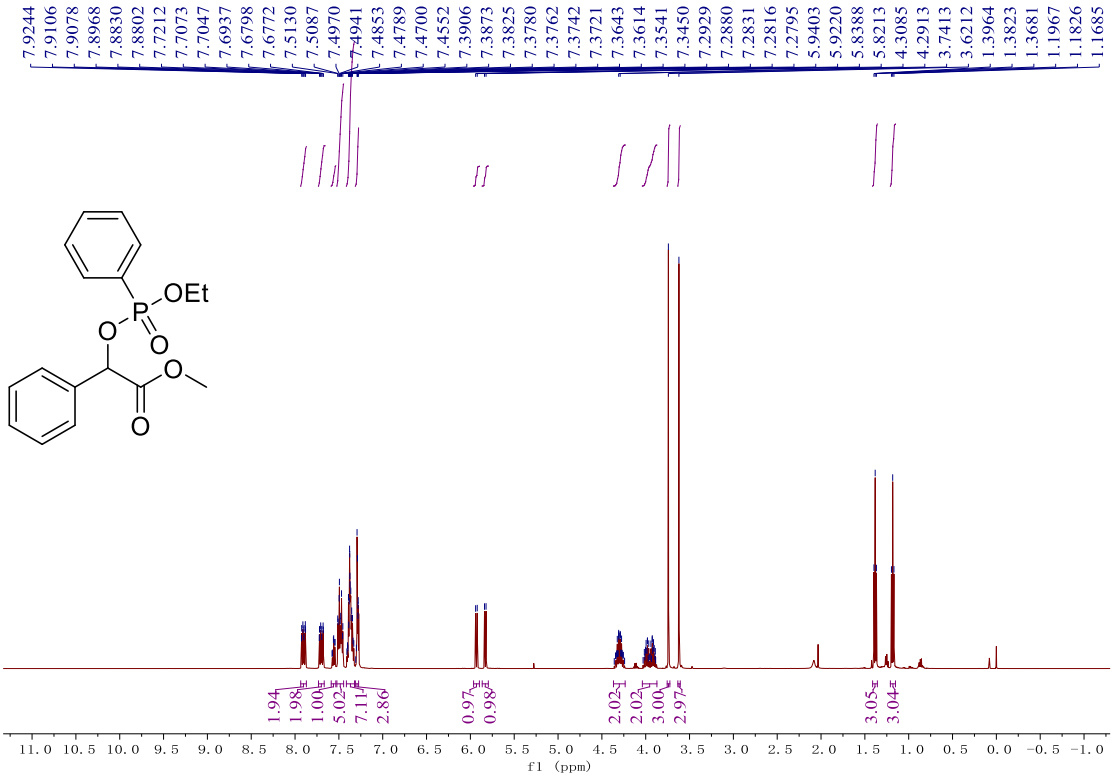
Methyl 2-((butyl(phenyl)phosphoryl)oxy)-2-phenylacetate (3an)

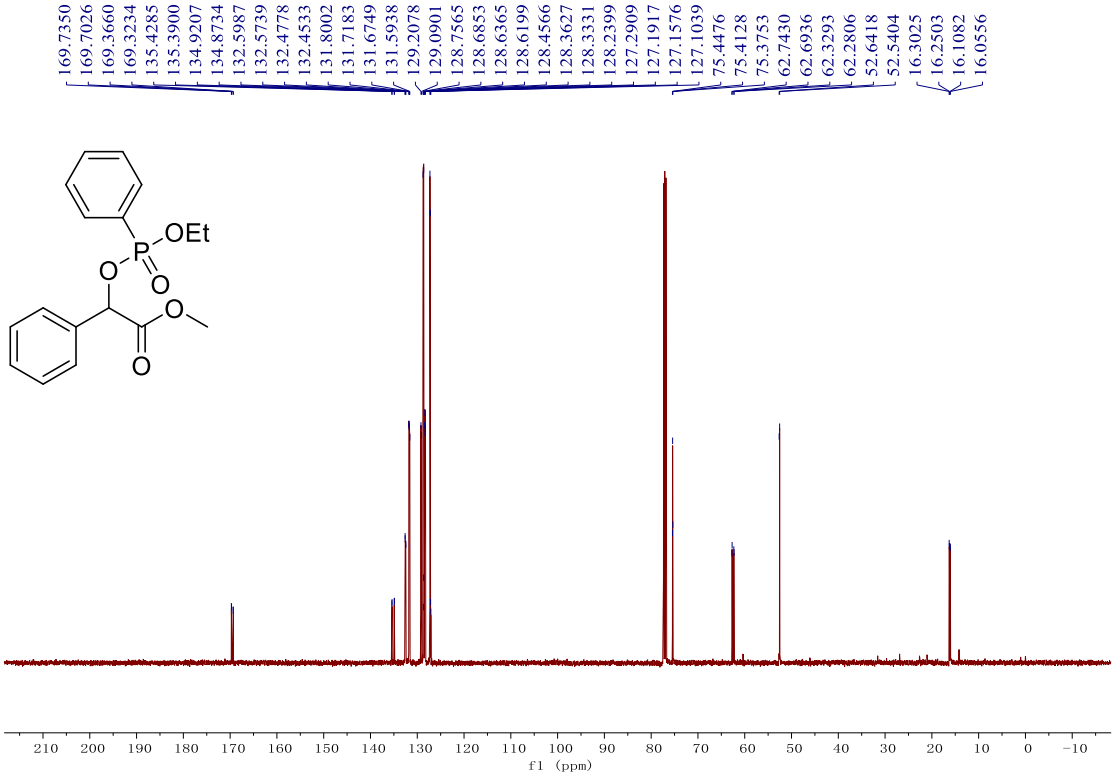


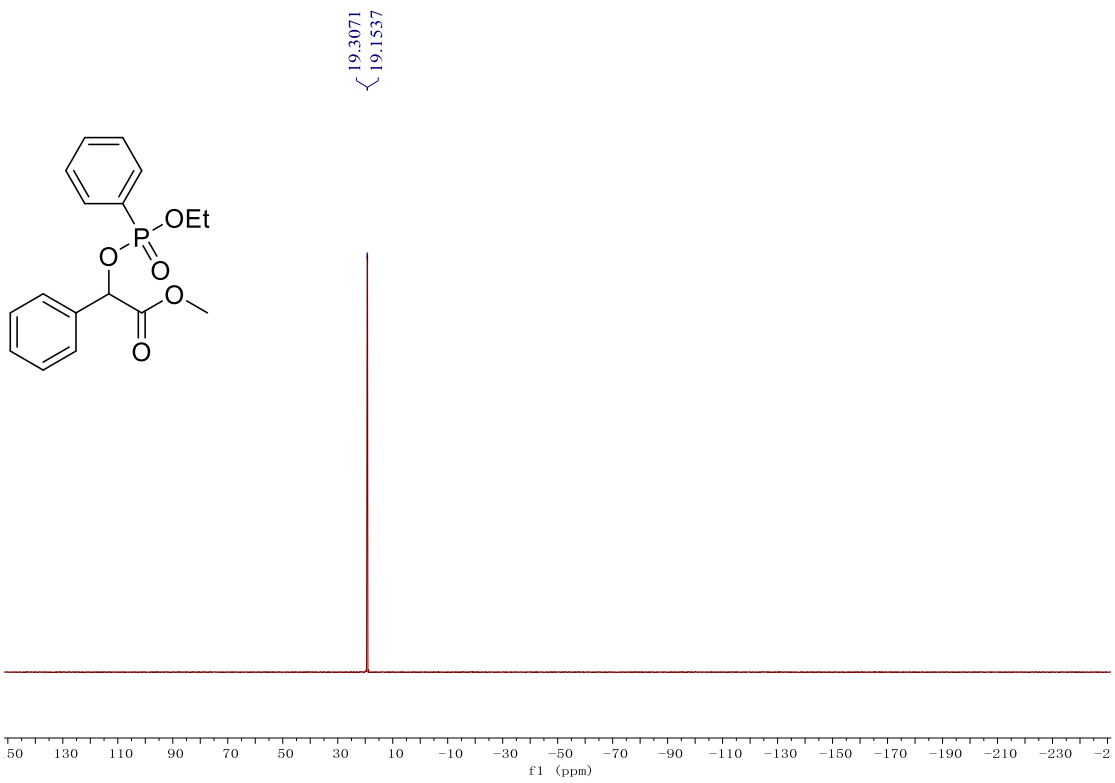




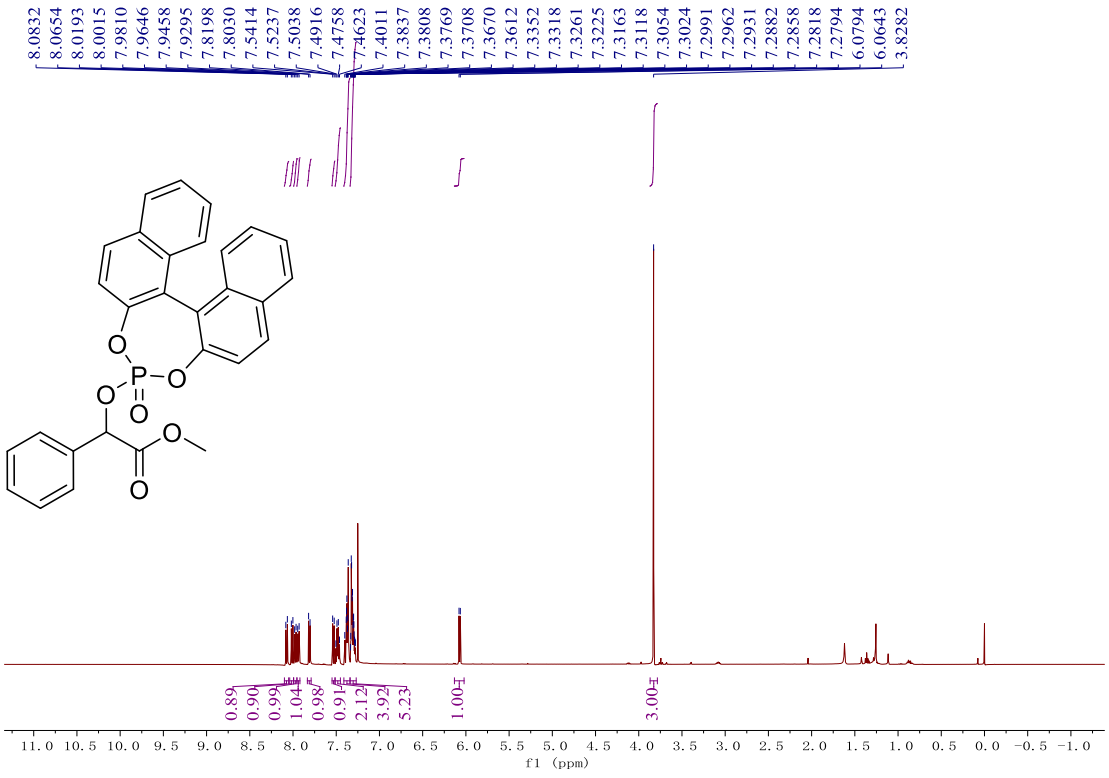
Methyl 2-((ethoxy(phenyl)phosphoryl)oxy)-2-phenylacetate (3ao)

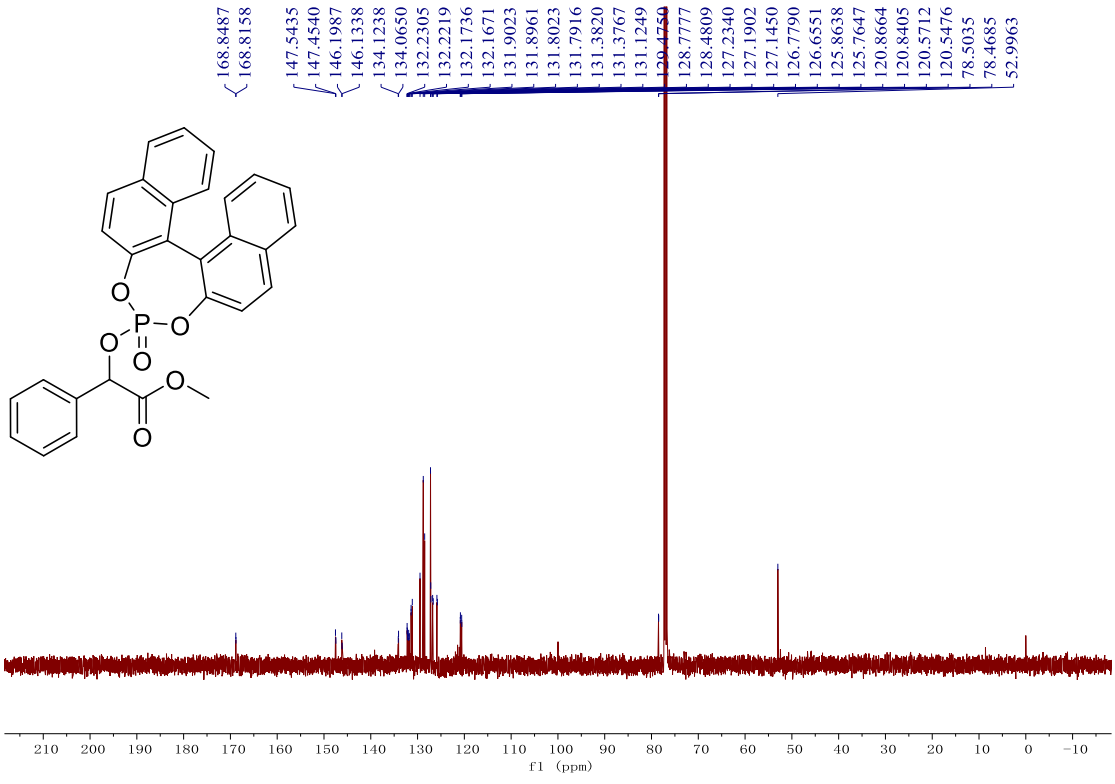


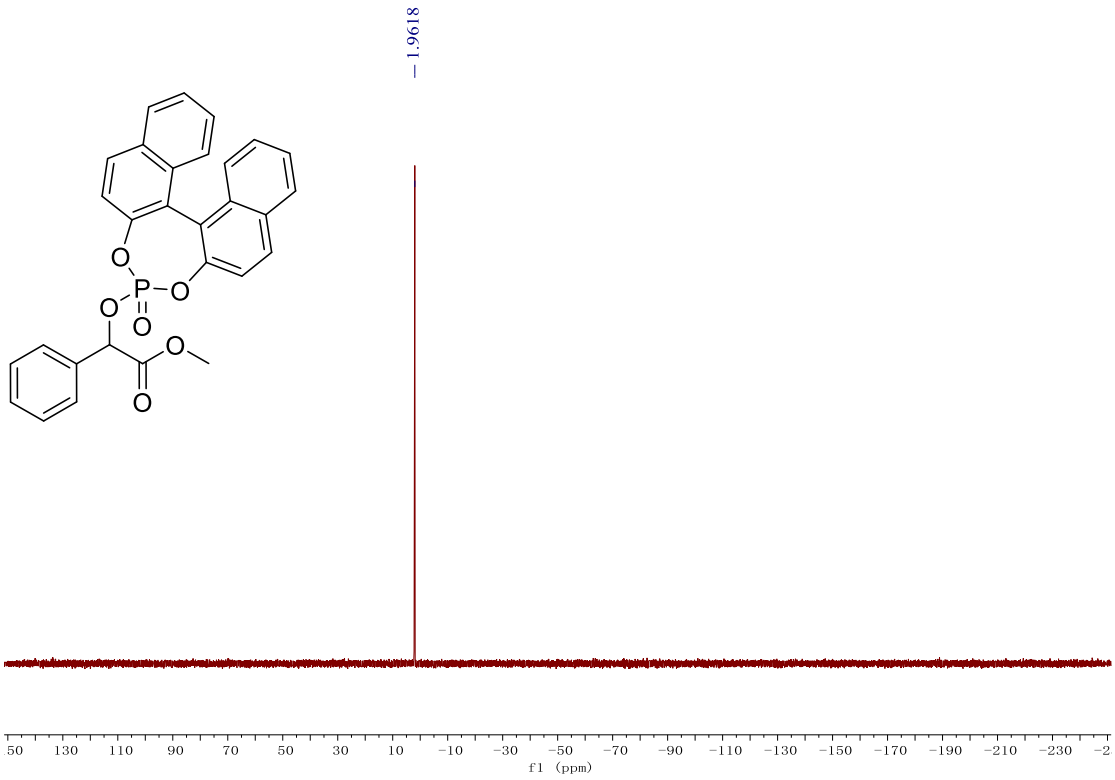

169.7350
169.7026
169.3660
169.3234
135.4285
135.3900
134.9207
134.8734
132.5987
132.5739
132.4778
132.4533
131.8002
131.7183
131.6749
131.5938
129.2078
129.0901
128.7565
128.6853
128.6365
128.6199
128.4566
128.3627
128.3331
128.2399
127.2909
127.1917
127.1576
127.1039
75.4476
75.4128
75.3753
62.7430
62.6936
62.3293
62.2806
52.6418
52.5404
16.3025
16.2503
16.1082
16.0556
OEt
O
P
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


19.3071
19.1537
OEt
O
P
O
O
O
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)

Methyl 2-((4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)oxy)-2-phenylacetate (3ap)






1.9618
O
P
O
O
O
O
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −2
f1 (ppm)