Copper-Catalyzed P-H Insertion Reactions of Sulfoxonium Ylides

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Supporting Information

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). 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. 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 $CDCl_3$ as solvent. Tetramethylsilane (TMS) signals or residual solvent signals were used [TMS $\delta = 0.00$ppm (^{1}H NMR), $CDCl_3$ $\delta = 7.26$ppm (^{1}H NMR), $CDCl_3$ $\delta = 77.16$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. HRMS (ESI) Mass spectra were recorded on Thermo Fisher Scientific LTQ FT Ultra. Melting points were determined on a microscopic apparatus and were uncorrected. The relative configuration of **3a** was determined by NMR Data and molecular weight compared with literature data.[1] Sulfoxonium ylides **1** and H-phosphine oxides **2** were prepared according to the published procedures.[2, 3]

Table S1. Common abbreviations in the article

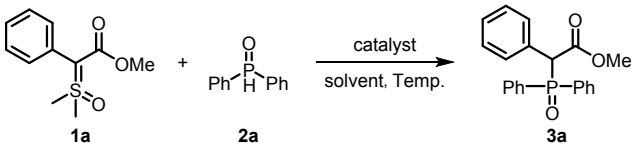
Abbreviation	Full name
PE	Petroleum Ether
EA	Ethyl Acetate
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
DMF	N,N-Dimethylformamide

2. General Procedures

2.1 General Procedure for Optimization of Reaction Conditions (Table 1 and Table S2):

A 10 mL test tube was charged with diphenylphosphine oxide **2a** (0.2 mmol), catalyst (10 mol%), and DCM of 0.5 mL. Then, a solution of sulfoxonium ylides **1a** (0.1 mmol) in DCM (1.5 mL) was added dropwise. The reaction mixture was reacted under the indicated temperature in Table 1 and Table S2. Upon completion, the solution was purified by flash column chromatography on silica gel (PE: EA = 1:1) to give the product **3a** as white solid.

Table S2. Optimization of the Reaction Conditions[a-c]



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

Entry	Catalyst	Solvent	Temp.(℃)	Yield(%)
1	$[Ir(COD)Cl]_2$	DCM	RT	N.R.[d]
2	RuCl[(R,R)-Tsdpen](p-cymene)	DCM	RT	N.R.
3	[RuCl(p-cymene)((S)-xylbinap)]Cl	DCM	RT	N.R.
4	[RuCl(p-cymene)((S)-binap)]Cl	DCM	RT	N.R.
5	$[Ru(p\text{-cymene})]Cl_2$	DCM	RT	N.R.
6	AuCl	DCM	RT	N.R.
7	$RhCp^*Cl_2$	DCM	RT	N.R.
8	CuCl	DCM	RT	29
9	$Cu(acac)_2$	DCM	RT	43
10	CuCN	DCM	RT	29
11	CuI	DCM	RT	37
12	$CuBr_2$	DCM	RT	40
13	CuTc	DCM	RT	29
14	$Cu(OTf)_2$	DCM	RT	43
15	$[(CH_3CN)_4Cu]PF_6$	DCM	RT	46
16	$Cu(OAc)_2$	DCM	RT	63
17	$Cu(OAc)_2$	DMSO	RT	N.R.
18	$Cu(OAc)_2$	DMF	RT	N.R.
19	$Cu(OAc)_2$	$CHCl_3$	RT	40
20	$Cu(OAc)_2$	DCM	40	43
21	$Cu(OAc)_2$	DCM	50	48
22	-	DCM	RT	N.R.

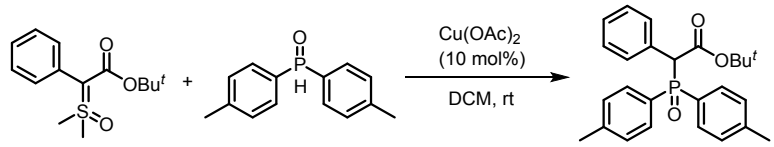
[a] Reaction conduction: **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (10 mol %), solvent (2.0 mL). [b] Isolated yield. [c] React for 18-36 h. [d] N.R.=no reaction.

2.2 General Procedure for the Synthesis of Compounds 3a-u (Scheme 2, Scheme 3):

A 10 mL test tube was charged with diphenylphosphine oxide **2** (0.2 mmol), $Cu(OAc)_2$ (10 mol %), and DCM (0.5 mL). Then a solution of sulfoxonium ylides **1**

(0.1 mmol) in DCM (1.5 mL) was added dropwise. The reaction mixture was reacted at room temperature for 18-36 h until the sulfoxonium ylides **1** was completely consumed. After the reaction, the solution was purified by flash column chromatography on silica gel (PE: EA = 1:1) to give the product **3**.

2.3 Scaled-Up Reaction



1i (4.0 mmol, 1.072g) **2b** **3i** (1.546g, 92% yield)

To a 250 mL round bottom flask was charged with diphenylphosphine oxide **2b** (8 mmol, 1.840g), catalyst $Cu(OAc)_2$ (72.0 mg, 10 mol%), and DCM (20.0 mL). Then the sulfoxonium ylides **1i** (4 mmol, 1.072g) solution in DCM (60.0 mL) was added dropwise. The reaction mixture was reacted at room temperature for 24 h until the sulfoxonium ylides **1i** was completely consumed. After the reaction, the solution was concentrated in vacuo and was purified by flash column chromatography on silica gel (PE: EA = 1:1) to give the product **3i** (1.546 g, 92%) as a white solid.

3. References

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(2) H. Zhang, J. Huang and S. Yang, Copper(I) Bromide-Catalyzed for the Synthesis of Sulfoxonium Ylides, *Chin. J. Org. Chem.* 2015, **35** (9), 1961.

(3) (a) J. Wang, G. Deng, C. Liu, Z. Chen, K. Yu, W. Chen, H. Zhang and X. Yang, Transition Metal-Free Synthesis of α-Aminophosphine Oxides through C(Sp^3)−P Coupling of 2-Azaallyls, *Adv. Synth. Catal*. 2020, **362** (11), 2268. (b) L. Y. Kuo, D. C. Baker, A. K. Dortignacq and K. M. Dill, Phosphonothioate Hydrolysis by Molybdocene Dichlorides: Importance of Metal Interaction with the Sulfur of the Thiolate Leaving Group, *Organometallics* 2013, **32** (17), 4759. (c) B. M. Trost, S. M. Spohr, A. B. Rolka and C. A. Kalnmals, Desymmetrization of Phosphinic Acids via Pd-Catalyzed Asymmetric Allylic Alkylation: Rapid Access to *P*-Chiral Phosphinates, *J. Am. Chem. Soc.* 2019, **141** (36), 14098.

4. Characterization datas for compounds

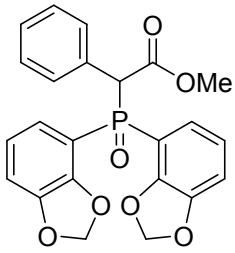
Methyl 2-(diphenylphosphoryl)-2-phenylacetate (3a): White solid, m.p. 206.5-208.0 ℃, 22.0 mg, Yield: 63%; **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.94 – 7.88 (m, 2H), 7.61 – 7.53 (m, 3H), 7.53 – 7.46 (m, 2H), 7.46 – 7.36 (m, 3H), 7.36 – 7.30 (m, 2H), 7.24 – 7.19 (m, 3H), 4.71 (d, *J* = 11.4 Hz, 1H), 3.53 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 168.31 (d, *J* = 3.1 Hz), 132.18 (d, *J* = 2.8 Hz), 131.92 (d, *J*= 2.9 Hz), 131.71 (d, *J* = 9.1 Hz), 131.36 (d, *J* = 9.1 Hz), 130.86 (d, *J* = 102.4 Hz), 130.56 (d, *J* = 100.4 Hz), 130.23 (d, *J* = 5.3 Hz), 130.18(d, *J* = 5.1 Hz),128.40 (d, *J* = 20.5 Hz), 128.30 (d, *J* = 21.2 Hz),128.33,(d, *J* = 2.3 Hz) 127.92 (d, *J* = 2.3 Hz), 55.59 (d, *J* = 58.4 Hz), 52.60 . **^{31}P NMR** (202 MHz, Chloroform-d) δ 27.32. **HRMS** (ESI) m/z: calcd for $C_{21}H_{20}O_3P$ $[M+H]^+$: 351.1145; found: 351.1153.

Methyl 2-(di-p-tolylphosphoryl)-2-phenylacetate (3b): White solid, m.p. 181.6-182.8 ℃, 29.1 mg, Yield: 77%; **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.79 – 7.72 (m, 2H), 7.47 – 7.40 (m, 2H), 7.40 – 7.36 (m, 2H), 7.30 – 7.26 (m, 2H), 7.24 – 7.19 (m, 3H), 7.15 – 7.10 (m, 2H), 4.66 (d, *J* = 11.5 Hz, 1H), 3.54 (s, 3H), 2.40 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 168.51 (d, *J* = 3.0 Hz), 142.58 (d, *J* = 2.8 Hz), 142.32 (d, *J* = 2.9 Hz), 131.71 (d, *J* = 9.5 Hz), 131.39 (d, *J* = 9.4 Hz), 130.47 (d, *J* = 6.4 Hz), 130.24 (d, *J* = 5.1 Hz), 129.14 (d, *J* = 12.4 Hz), 128.98 (d, *J* = 12.5 Hz), 128.28 (d, *J* = 1.8 Hz), 128.00 (d, *J* = 45.7 Hz), 127.81(d, *J* = 2.2 Hz) , 127.17 (d, *J* = 44.1 Hz), 55.77 (d, *J* = 58.3 Hz), 52.57 , 21.62 (d, *J* = 0.9 Hz), 21.52 (d, *J* = 1.0 Hz).**^{31}P NMR** (202 MHz, Chloroform-d) δ 27.72 .**HRMS** (ESI) m/z: calcd for $C_{23}H_{24}O_3P$ $[M+H]^+$: 379.1458; found: 379.1468.

Methyl 2-(bis(4-methoxyphenyl)phosphoryl)-2-phenylacetate (3c): White solid, m.p. 124.8-126.0 ℃, 25.8 mg, Yield: 63%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.81 – 7.74 (m, 2H), 7.50 – 7.43 (m, 2H), 7.39 – 7.33 (m, 2H), 7.24 – 7.20 (m, 3H), 7.01 – 6.95 (m, 2H), 6.87 – 6.81 (m, 2H), 4.64 (d, *J* = 12.3 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.56 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.67 (d, *J* = 2.8 Hz), 162.59 (d, *J* = 2.8 Hz), 162.35 (d, *J* = 2.9 Hz), 133.71 (d, *J* = 10.4 Hz), 133.33 (d, *J* = 10.5 Hz), 130.59 (d, *J* = 6.4 Hz), 130.19 (d, *J* = 5.0 Hz), 128.29 (d, *J* = 2.0 Hz), 127.81 (d, *J* = 2.5 Hz), 122.32 (d, *J* = 109.4 Hz), 121.62 (d, *J* = 107.6 Hz), 113.95 (d, *J* = 13.0 Hz), 113.79 (d,

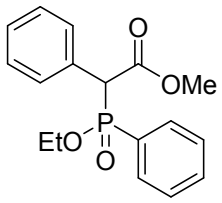
J = 13.1 Hz), 56.16 (d, *J* = 58.7 Hz), 55.34 , 55.28 , 52.59 .**^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.68. **HRMS** (ESI) m/z: calcd for $C_{23}H_{24}O_5P$ $[M+H]^+$: 411.1356; found: 411.1362.

Methyl 2-(bis(benzo[d][1,3]dioxol-4-yl)phosphoryl)-2-phenylacetate (3d): White



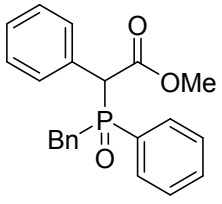
solid, m.p. 172.8-174.5 ℃, 18.0 mg, Yield: 41%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.43 – 7.37 (m, 3H), 7.30 – 7.23 (m, 4H), 7.10 – 7.05 (m, 1H), 6.97 – 6.89 (m, 2H), 6.77 – 6.74 (m, 1H), 6.03 (s, 2H), 5.97 – 5.94 (m, 2H), 4.61 (d, *J* = 11.9 Hz, 1H), 3.59 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.53 (d, *J* = 2.8 Hz), 151.14 (d, *J* = 3.0 Hz), 150.86 (d, *J* = 2.9 Hz), 148.05 (d, *J* = 18.4 Hz), 147.87 (d, *J* = 18.4 Hz), 130.48 (d, *J* = 6.4 Hz), 130.29 (d, *J* = 5.2 Hz), 128.49 (d, *J* = 1.8 Hz), 128.08 (d, *J* = 2.3 Hz), 127.31 (d, *J* = 10.0 Hz), 127.02 (d, *J* = 10.1 Hz), 124.33 (d, *J* = 69.2 Hz), 123.48 (d, *J* = 67.2 Hz), 111.30 (d, *J* = 12.0 Hz), 110.97 (d, *J* = 12.0 Hz), 108.77 (d, *J* = 15.1 Hz), 108.59 (d, *J* = 15.2 Hz), 101.80 , 101.70 , 55.96 (d, *J* = 59.9 Hz), 52.83 .**^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.71 .**HRMS** (ESI) m/z: calcd for $C_{23}H_{20}O_7P$ $[M+H]^+$: 439.0941; found: 439.0952.

Methyl 2-(ethoxy(phenyl)phosphoryl)-2-phenylacetate (3e): colorless oil, 28.0 mg,



Yield: 88%; **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.54 – 7.49 (m, 3H), 7.37 – 7.33 (m, 4H), 7.27 – 7.24 (m, 3H), 4.35 (d, J = 2.4 Hz, 1H), 4.06 – 3.98 (m, 2H), 3.65 (s, 3H), 1.32 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.24 (d, *J* = 2.3 Hz), 132.59 (d, *J* = 2.9 Hz), 132.51 (d, *J* = 2.7 Hz),130.47 (d, *J* = 6.0 Hz), 129.84 (d, *J* = 5.4 Hz), 129.33 (d, *J* = 36.4 Hz), 128.30 (d, *J* = 2.3 Hz), 128.14 (d, *J* = 13.2 Hz), 127.85 (d, *J* = 2.8 Hz),61.99 (d, *J* = 6.6 Hz), 55.76 (d, *J* = 86.9 Hz), 52.55 , 16.38 (d, *J* = 6.3 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.32 . **HRMS** (ESI) m/z: calcd for $C_{17}H_{20}O_4P$ $[M+H]^+$: 319.1094; found: 319.1099.

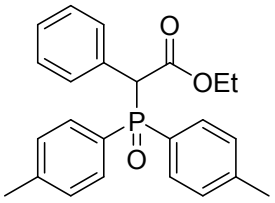
Methyl 2-(benzyl(phenyl)phosphoryl)-2-phenylacetate (3f): White solid, m.p.



165.0-167.3 ℃, 20.2 mg, Yield: 55%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.57 – 7.51 (m, 2H), 7.51 – 7.43 (m, 1H), 7.39 – 7.33 (m, 2H), 7.31 – 7.27 (m, 5H), 7.20 – 7.12 (m, 5H), 4.36 (d, *J* = 14.6 Hz, 1H), 3.62 (s, 3H), 3.60 – 3.50 (m, 1H), 3.41 – 3.34 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.85(d, *J* = 1.4 Hz) , 132.10 (d, *J* = 2.6 Hz), 131.80 (d, *J* = 8.7 Hz), 130.60 (d, *J* = 20.6 Hz), 130.59 (d, *J* = 7.0 Hz), 130.27 (d, *J* = 5.7 Hz), 130.16 (d, *J* = 5.4 Hz), 129.88 (d, *J* = 4.7 Hz), 128.60 (d, *J* = 1.6 Hz),

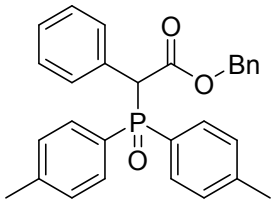
128.47 (d, *J* = 2.3 Hz), 128.07 (d, *J* = 2.0 Hz), 128.07 (d, *J* = 11.8 Hz), 126.93 (d, *J* = 2.8 Hz), 55.20 (d, *J* = 56.1 Hz), 52.67 , 35.28 (d, *J* = 64.7 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 34.68 .**HRMS** (ESI) m/z: calcd for $C_{22}H_{22}O_3P$ $[M+H]^+$: 365.1301; found: 365.1309.

Ethyl 2-(di-p-tolylphosphoryl)-2-phenylacetate (3g): White solid, m.p. 184.2-186.0



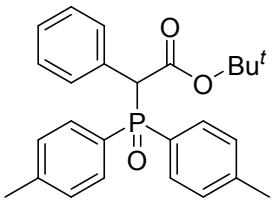
℃，31.0 mg, Yield: 79%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.81 – 7.74 (m, 2H), 7.48 – 7.37 (m, 4H), 7.31 – 7.27 (m, 2H), 7.23 – 7.21 (m, 3H), 7.15 – 7.10 (m, 2H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.02 – 3.96 (m, 2H), 2.40 (s, 3H), 2.31 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.07 (d, *J* = 3.0 Hz), 142.65 (d, *J* = 2.9 Hz), 142.38 (d, *J* = 2.8 Hz), 131.97 (d, *J* = 9.4 Hz), 131.49 (d, *J* = 9.4 Hz), 130.69 (d, *J* = 6.4 Hz), 130.39 (d, *J* = 5.1 Hz),129.19 (d, *J* = 13.0 Hz),129.09 (d, *J* = 12.9 Hz), 128.36 (d, *J* = 1.7 Hz), 128.27 (d, *J* = 67.0 Hz), 127.87 (d, *J* = 2.3 Hz), 127.44 (d, *J* = 65.1 Hz), 61.71 , 55.91 (d, *J* = 58.3 Hz), 21.73 , 21.64 , 13.86. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.58 .**HRMS** (ESI) m/z: calcd for $C_{24}H_{26}O_3P$ $[M+H]^+$: 393.1614; found: 393.1620.

Benzyl 2-(di-p-tolylphosphoryl)-2-phenylacetate (3h): White solid, m.p. 169.5-



171.5 ℃，28.1 mg, Yield: 62%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.77 – 7.71 (m, 2H), 7.46 – 7.40 (m, 4H), 7.31 – 7.25 (m, 3H), 7.24 – 7.20 (m, 5H), 7.12 – 7.07 (m, 4H), 5.03 – 4.90 (m, 2H), 4.71 (d, *J* = 11.3 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.82 (d, *J* = 2.9 Hz), 142.51 (d, *J* = 2.8 Hz), 142.29 (d, *J* = 2.8 Hz), 135.07 , 131.78 (d, *J* = 9.5 Hz), 131.34 (d, *J* = 9.4 Hz), 130.48 (d, *J* = 6.4 Hz), 130.32 (d, *J* = 5.1 Hz), 129.16 (d, *J* = 12.4 Hz), 129.01 (d, *J* = 12.5 Hz), 128.37 , 128.35 , 128.29 (d, *J* = 1.7 Hz), 128.14, 128.01 (d, *J* = 68.57 Hz) 127.82 (d, *J* = 2.2 Hz), 127.18 (d, *J* = 65.7 Hz), 67.41 , 55.57 (d, *J* = 58.0 Hz), 21.66, 21.54. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.67 .**HRMS** (ESI) m/z: calcd for $C_{29}H_{28}O_3P$ $[M+H]^+$: 455.1771; found: 455.1774.

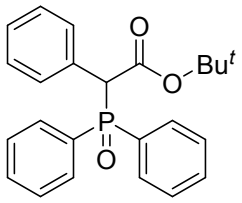
Tert-butyl 2-(di-p-tolylphosphoryl)-2-phenylacetate (3i): White solid, m.p. 212.3-



213.4 ℃，39.0 mg, Yield: 93%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.86 – 7.80 (m, 2H), 7.46 – 7.37 (m, 4H), 7.31 – 7.27 (m, 2H), 7.22 – 7.18 (m, 3H), 7.10 – 7.06 (m, 2H), 4.56 (d, *J* = 11.1 Hz, 1H), 2.39 (s, 3H), 2.28 (s, 3H), 1.18 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.76 (d, *J* = 3.1 Hz), 142.32 (d, *J* = 2.8

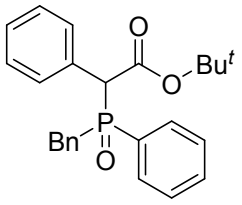
Hz), 141.98 (d, *J* = 2.7 Hz), 131.95 (d, *J* = 9.3 Hz), 131.22 (d, *J* = 9.3 Hz), 130.98 (d, *J* = 6.4 Hz), 130.28 (d, *J* = 5.2 Hz), 129.00 (d, *J* = 12.3 Hz), 128.87 (d, *J* = 12.4 Hz), 128.63(d, *J* = 89.4 Hz),128.12 (d, *J* = 1.6 Hz),127.80(d, *J* = 87.3 Hz), 127.53 (d, *J* = 2.2 Hz) , 82.21 , 56.33 (d, *J* = 58.5 Hz), 27.57 , 21.58, 21.47. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.38. **HRMS** (ESI) m/z: calcd for $C_{26}H_{30}O_3P$ $[M+H]^+$: 421.1927; found: 421.1936.

Tert-butyl 2-(diphenylphosphoryl)-2-phenylacetate (3j): White solid, m.p. 196.3-



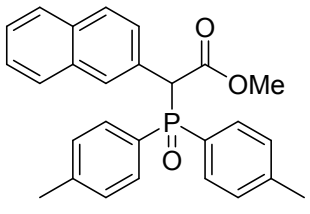
197.8 ℃, 30.6 mg, Yield: 78%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.01 – 7.96 (m, 2H), 7.58 – 7.51 (m, 5H), 7.44 – 7.35 (m, 3H), 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 4.60 (d, *J* = 11.0 Hz, 1H), 1.18 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.70 (d, *J* = 3.2 Hz), 132.10 (d, *J* = 8.9 Hz), 132.10 (d, *J* = 2.9 Hz), 131.91 (d, *J* = 78.8 Hz), 131.79 (d, *J* = 2.7 Hz), 131.35 (d, *J* = 9.0 Hz), 131.11 (d, *J* = 77.3 Hz),130.83 (d, *J* = 6.3 Hz), 130.43 (d, *J* = 5.2 Hz), 128.49 (d, *J* = 12.0 Hz), 128.34 (d, *J* = 1.9 Hz), 128.31 (d, *J* = 11.8 Hz), 127.81 (d, *J* = 2.3 Hz), 82.58 , 56.35 (d, *J* = 58.6 Hz), 27.71. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 26.89 .**HRMS** (ESI) m/z: calcd for $C_{24}H_{26}O_3P$ $[M+H]^+$: 393.1614; found: 393.1619.

Tert-butyl 2-(benzyl(phenyl)phosphoryl)-2-phenylacetate (3k): White solid, m.p.



182.8-185.0 ℃, 37.4 mg, Yield: 92%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.63 – 7.53 (m, 2H), 7.51 – 7.40 (m, 3H), 7.41 – 7.28 (m, 5H), 7.16 – 7.10 (m, 3H), 7.02 – 6.98 (m, 2H), 4.29 (d, *J* = 12.6 Hz, 1H), 3.44 – 3.36 (m, 1H), 3.26 – 3.19 (m, 1H), 1.24 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.80 (d, *J* = 2.7 Hz), 131.81 (d, *J* = 8.5 Hz), 131.79 (d, *J* = 3.2 Hz), 131.20 (d, *J* = 5.9 Hz), 130.85 (d, *J* = 7.7 Hz), 130.15 (d, *J* = 5.2 Hz), 130.09 (d, *J* = 5.5 Hz), 130.06 (d, *J* = 96.0 Hz), 128.54 (d, *J* = 1.7 Hz),128.29 (d, *J* = 2.5 Hz),127.97 (d, *J* = 11.9 Hz), 127.91 (d, *J* = 2.3 Hz) , 126.71 (d, *J* = 3.0 Hz), 82.44 , 55.75 (d, *J* = 55.8 Hz), 36.22 (d, *J* = 65.1 Hz), 27.66. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 26.89 .**HRMS** (ESI) m/z: calcd for $C_{25}H_{28}O_3P$ $[M+H]^+$: 407.1771; found: 407.1774.

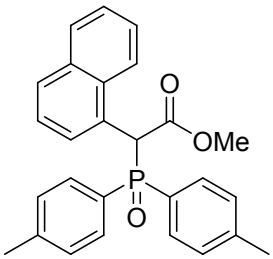
Methyl 2-(di-p-tolylphosphoryl)-2-(naphthalen-2-yl)acetate (3l): White solid, m.p.



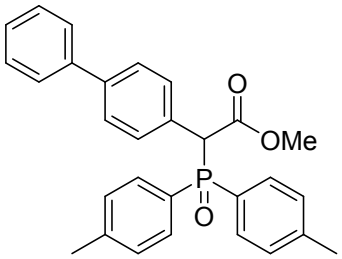
172.0-173.6 ℃, 36.4 mg, Yield: 85%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 – 7.88 (m, 1H), 7.83 – 7.68 (m, 5H), 7.56 – 7.39 (m, 5H), 7.31 – 7.27 (m, 2H), 7.12 – 7.08 (m, 2H), 4.87 (d, *J* = 11.6 Hz, 1H), 3.56 (s, 3H), 2.40

(s, 3H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.63 (d, *J* = 2.9 Hz), 142.67 (d, *J* = 2.8 Hz), 142.44 (d, *J* = 2.8 Hz), 133.13 (d, *J* = 2.0 Hz), 132.78 (d, *J* = 1.6 Hz), 131.78 (d, *J* = 9.4 Hz), 131.49 (d, *J* = 9.5 Hz), 129.63 (d, *J* = 6.3 Hz), 129.24 (d, *J* = 12.4 Hz), 129.09 (d, *J* = 12.4 Hz), 128.17 , 128.12 (d, *J* = 25.5 Hz), 127.97 – 127.88 (m), 127.54 , 127.29 (d, *J* = 23.5 Hz), 126.20 , 126.05 , 55.95 (d, *J* = 58.4 Hz), 52.69 , 21.69, 21.60. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.65. **HRMS** (ESI) m/z: calcd for $C_{27}H_{26}O_3P$ $[M+H]^+$: 429.1614; found: 429.1620.

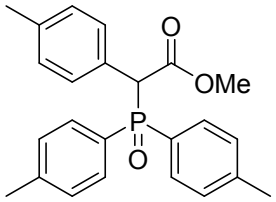
Methyl 2-(di-p-tolylphosphoryl)-2-(naphthalen-1-yl)acetate (3m): colorless oil, 36.4 mg, Yield: 85%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.25 – 8.19 (m, 1H), 7.84 – 7.77 (m, 4H), 7.56 – 7.54 (m, 1H), 7.50 – 7.44 (m, 2H), 7.44 – 7.35 (m, 3H), 7.30 – 7.26 (m, 2H), 6.97 – 6.93 (m, 2H), 6.41 (d, *J* = 10.2 Hz, 1H), 3.62 (s, 3H), 2.39 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.16 (d, *J* = 5.1 Hz), 142.87 (d, *J* = 2.9 Hz), 142.57 (d, *J* = 2.9 Hz), 133.97 , 131.83 (d, *J* = 11.1 Hz), 131.74 (d, *J* = 10.8 Hz), 131.62 (d, *J* = 3.9 Hz), 130.73 , 129.94 , 129.26 (d, *J* = 13.9 Hz), 128.85 (d, *J* = 13.9 Hz), 128.70 , 128.42 (d, *J* = 141.2 Hz), 127.75 (d, *J* = 137.9 Hz), 127.68 , 126.79 , 125.97 , 125.19 , 124.14 , 73.24 (d, *J* = 5.0 Hz), 52.76 , 21.77 (d, *J* = 1.0 Hz)., 21.58 (d, *J* = 1.1 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 35.35. **HRMS** (ESI) m/z: calcd for $C_{27}H_{26}O_3P$ $[M+H]^+$: 429.1614; found: 429.1614.



Methyl 2-([1,1'-biphenyl]-4-yl)-2-(di-p-tolylphosphoryl)acetate (3n): White solid, m.p. 181.6-183.5 ℃, 39.0 mg, Yield: 86%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.82 – 7.76 (m, 2H), 7.57 – 7.44 (m, 8H), 7.43 – 7.39 (m, 2H), 7.33 – 7.28 (m, 3H), 7.17 – 7.13 (m, 2H), 4.74 (d, *J* = 11.6 Hz, 1H), 3.56 (s, 3H), 2.41 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.54 (d, *J* = 3.2 Hz), 142.66 (d, *J* = 2.9 Hz), 142.43 (d, *J* = 2.8 Hz), 140.57 (d, *J* = 2.5 Hz), 140.50 , 131.76 (d, *J* = 9.5 Hz), 131.45 (d, *J* = 9.4 Hz), 130.64 (d, *J* = 5.1 Hz), 129.49 (d, *J* = 6.5 Hz), 129.19 (d, *J* = 12.5 Hz), 129.08 (d, *J* = 12.6 Hz), 128.75 , 127.81 (d, *J* = 98.8 Hz), 127.44 (d, *J* = 95.9 Hz), 127.38 , 127.02 , 126.98 (d, *J* = 1.8 Hz), 55.52 (d, *J* = 58.1 Hz), 52.64 , 21.66 (d, *J* = 1.0 Hz), 21.56 (d, *J* = 0.8 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.72. **HRMS** (ESI) m/z: calcd for $C_{29}H_{28}O_3P$ $[M+H]^+$: 455.1771; found: 455.1776.

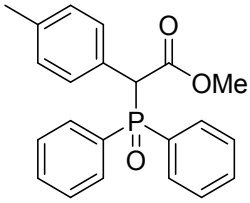


Methyl 2-(di-p-tolylphosphoryl)-2-(p-tolyl)acetate (3o): White solid, m.p. 162.9-



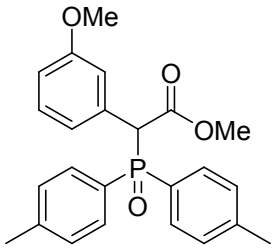
164.7 ℃, 31.0 mg, Yield: 79%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.79 – 7.70 (m, 2H), 7.50 – 7.42 (m, 2H), 7.30 – 7.25 (m, 4H), 7.17 – 7.12 (m, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 4.64 (d, *J* = 11.6 Hz, 1H), 3.53 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.71 (d, *J* = 2.7 Hz), 142.52 (d, *J* = 2.8 Hz), 142.28 (d, *J* = 2.8 Hz), 137.60 (d, *J* = 2.5 Hz), 131.72 (d, *J* = 9.4 Hz), 131.45 (d, *J* = 9.4 Hz), 130.08 (d, *J* = 5.2 Hz), 129.13 (d, *J* = 12.6 Hz), 129.06(d, *J* = 1.8 Hz) , 129.00 (d, *J* = 12.8 Hz), 128.14 (d, *J* = 40.8 Hz), 127.33 (d, *J* = 6.4 Hz), 127.32 (d, *J* = 38.6 Hz), 55.41 (d, *J* = 59.0 Hz), 52.55 , 21.64 (d, *J* = 1.4 Hz), 21.55 (d, *J* = 1.4 Hz), 21.10. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.55. **HRMS** (ESI) m/z: calcd for $C_{24}H_{26}O_3P$ $[M+H]^+$: 393.1614; found: 393.1620.

Methyl 2-(diphenylphosphoryl)-2-(p-tolyl)acetate (3p): White solid, m.p. 192.5-



194.0 ℃, 28.8 mg, Yield: 79%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.93 – 7.86 (m, 2H), 7.62 – 7.30 (m, 8H), 7.28 – 7.25 (m, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 4.68 (d, *J* = 11.5 Hz, 1H), 3.52 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.51 (d, *J* = 2.8 Hz), 137.74 (d, *J* = 2.5 Hz), 132.13 (d, *J* = 2.8 Hz), 131.89 (d, *J* = 2.7 Hz), 131.72 (d, *J* = 9.1 Hz), 131.43 (d, *J* = 9.0 Hz), 131.28 (d, *J* = 32.5 Hz), 130.47 (d, *J* = 30.6 Hz), 130.07 (d, *J* = 5.1 Hz), 129.10 (d, *J* = 1.8 Hz), 128.42 (d, *J* = 12.0 Hz), 128.28 (d, *J* = 12.1 Hz), 127.06 (d, *J* = 6.5 Hz), 55.23 (d, *J* = 59.1 Hz), 52.58 , 21.10. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.12. **HRMS** (ESI) m/z: calcd for $C_{22}H_{22}O_3P$ $[M+H]^+$: 365.1301; found: 365.1310.

Methyl 2-(di-p-tolylphosphoryl)-2-(3-methoxyphenyl)acetate (3q): White solid,



m.p. 167.3-169.3 ℃, 23.7 mg, Yield:58%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.78 – 7.72 (m, 2H), 7.49 – 7.43 (m, 2H), 7.30 – 7.26 (m, 2H), 7.18 – 7.08 (m, 3H), 6.99 – 6.97 (m, 1H), 6.94 – 6.75 (m, 2H), 4.65 (d, *J* = 11.9 Hz, 1H), 3.68 (s, 3H), 3.55 (s, 3H), 2.40 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.49 (d, *J* = 2.8 Hz), 159.30 (d, *J* = 1.9 Hz), 142.60 (d, *J* = 2.8 Hz), 142.36 (d, *J* = 2.8 Hz), 131.83(d, *J* = 5.3 Hz) , 131.77 (d, *J* = 9.3 Hz), 131.48 (d, *J* = 9.5 Hz), 129.13 (d, *J* = 12.4 Hz), 129.13 (d, *J* = 1.7 Hz), 128.98 (d, *J* = 12.5 Hz), 127.98 (d, *J* = 49.4 Hz), 127.15 (d, *J* = 47.6 Hz), 122.67 (d, *J* = 5.3 Hz), 115.13 (d, *J* = 4.9 Hz), 114.28 (d, *J* = 2.2 Hz), 55.78 (d, *J* = 58.4 Hz), 55.15 , 52.59 , 21.62(d,

J = 0.7 Hz), 21.53(d, *J* = 0.7 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.74 .**HRMS** (ESI) m/z: calcd for $C_{24}H_{26}O_4P$ $[M+H]^+$: 409.1563; found: 409.1570.

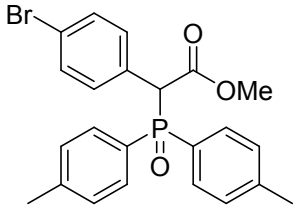
Methyl 2-(di-p-tolylphosphoryl)-2-(2-methoxyphenyl)acetate (3r): colorless oil, 37.1 mg, Yield: 91%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.00 – 7.96 (m, 1H), 7.85 – 7.76 (m, 2H), 7.49 – 7.37 (m, 2H), 7.34 – 7.25 (m, 2H), 7.17 – 7.13 (m, 1H), 7.07 – 7.03 (m, 2H), 6.94 – 6.91 (m, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 5.46 (d, *J* = 10.8 Hz, 1H), 3.55 (s, 3H), 3.51 (s, 3H), 2.38 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.39 (d, *J* = 3.7 Hz), 156.06 (d, *J* = 5.6 Hz), 142.20 (d, *J* = 2.9 Hz), 141.80 (d, *J* = 2.9 Hz), 131.84 (d, *J* = 4.5 Hz), 131.34 (d, *J* = 9.5 Hz), 131.05 (d, *J* = 9.6 Hz), 129.07 (d, *J* = 12.3 Hz), 128.92 (d, *J* = 2.1 Hz), 128.89 (d, *J* = 40.2 Hz), 128.52 (d, *J* = 12.6 Hz), 128.07 (d, *J* = 44.4 Hz), 120.62 (d, *J* = 2.0 Hz), 119.09 (d, *J* = 5.8 Hz), 109.99 (d, *J* = 1.4 Hz), 55.23 , 52.40 , 45.40 (d, *J* = 60.5 Hz), 21.55 (d, *J* = 0.8 Hz) ,21.39 (d, *J* = 0.8 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 28.68. **HRMS** (ESI) m/z: calcd for $C_{24}H_{26}O_4P$ $[M+H]^+$: 409.1563; found: 409.1570.

Methyl 2-(di-p-tolylphosphoryl)-2-(4-fluorophenyl)acetate (3s): White solid, m.p. 142.5-144.1 ℃, 36.0 mg, Yield: 91%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.81 – 7.73 (m, 2H), 7.49 – 7.42 (m, 2H), 7.41 – 7.37 (m, 2H), 7.31 – 7.28 (m, 2H), 7.16 – 7.13 (m, 2H), 6.91 (t, *J* = 8.5 Hz, 2H), 4.67 (d, *J* = 11.4 Hz, 1H), 3.53 (s, 3H), 2.40 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.37(d, *J* = 2.7 Hz) , 162.48 (dd, *J* = 247.0, 2.5 Hz), 142.74 (d, *J* = 2.9 Hz), 142.49 (d, *J* = 2.8 Hz), 131.95 (d, *J* = 5.1 Hz), 131.89 (d, *J* = 5.1 Hz), 131.65 (d, *J* = 9.5 Hz), 131.28 (d, *J* = 9.5 Hz), 129.21 (d, *J* = 12.8 Hz), 129.10 (d, *J* = 12.5 Hz) , 127.59 (d, *J* = 105.2 Hz), 127.19 (d, *J* = 103.1 Hz), 126.36 – 126.24 (m), 115.30 (d, *J* = 1.5 Hz), 115.13 (d, *J* = 1.5 Hz),54.78 (d, *J* = 57.9 Hz), 52.60 , 21.62 , 21.52. **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.75. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.31, -114.32**. HRMS** (ESI) m/z: calcd for $C_{23}H_{23}FO_3P$ $[M+H]^+$: 397.1363; found: 397.1369.

Methyl 2-(4-chlorophenyl)-2-(di-p-tolylphosphoryl)acetate (3t): colorless oil, 29.7 mg, Yield: 72%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.78 – 7.71 (m, 2H), 7.49 – 7.41 (m, 2H), 7.36 – 7.32 (m, 2H), 7.31 – 7.27 (m, 2H), 7.21 – 7.17 (m, 2H), 7.16 – 7.14 (m, 2H), 4.64 (d, *J* = 11.6 Hz, 1H), 3.52 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.19

(d, *J* = 3.0 Hz), 142.80 (d, *J* = 2.8 Hz), 142.59 (d, *J* = 2.8 Hz), 133.98 (d, *J* = 2.8 Hz), 131.66 (d, *J* = 9.5 Hz), 131.54 (d, *J* = 5.1 Hz), 131.30 (d, *J* = 9.5 Hz), 129.23 (d, *J* = 12.5 Hz), 129.16 (d, *J* = 12.5 Hz), 129.07 (d, *J* = 6.4 Hz) , 128.45 (d, *J* = 1.8 Hz), 127.69 (d, *J* = 49.5 Hz), 126.86 (d, *J* = 47.7 Hz), 55.08 (d, *J* = 57.3 Hz), 52.67 , 21.65 (d, *J* = 1.0 Hz), 21.55 (d, *J* = 1.0 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.63. **HRMS** (ESI) m/z: calcd for $C_{23}H_{23}ClO_3P$ $[M+H]^+$: 413.1068; found: 413.1071.

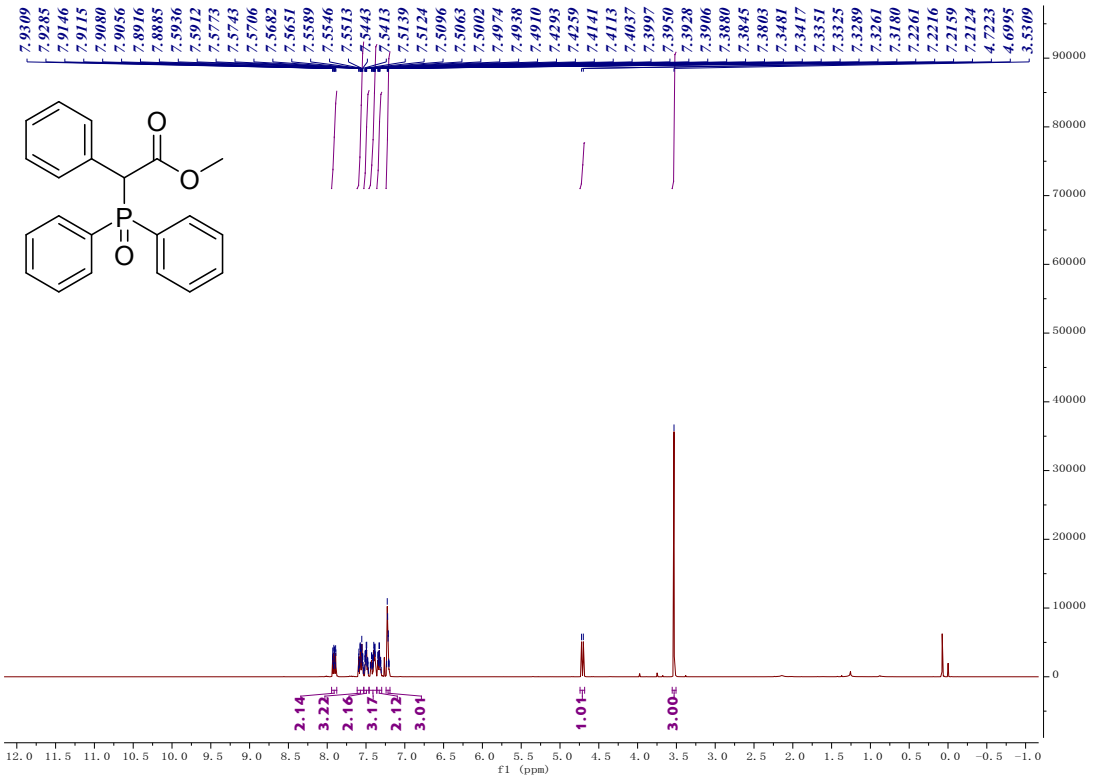
Methyl 2-(4-bromophenyl)-2-(di-p-tolylphosphoryl)acetate (3u): White solid, m.p.

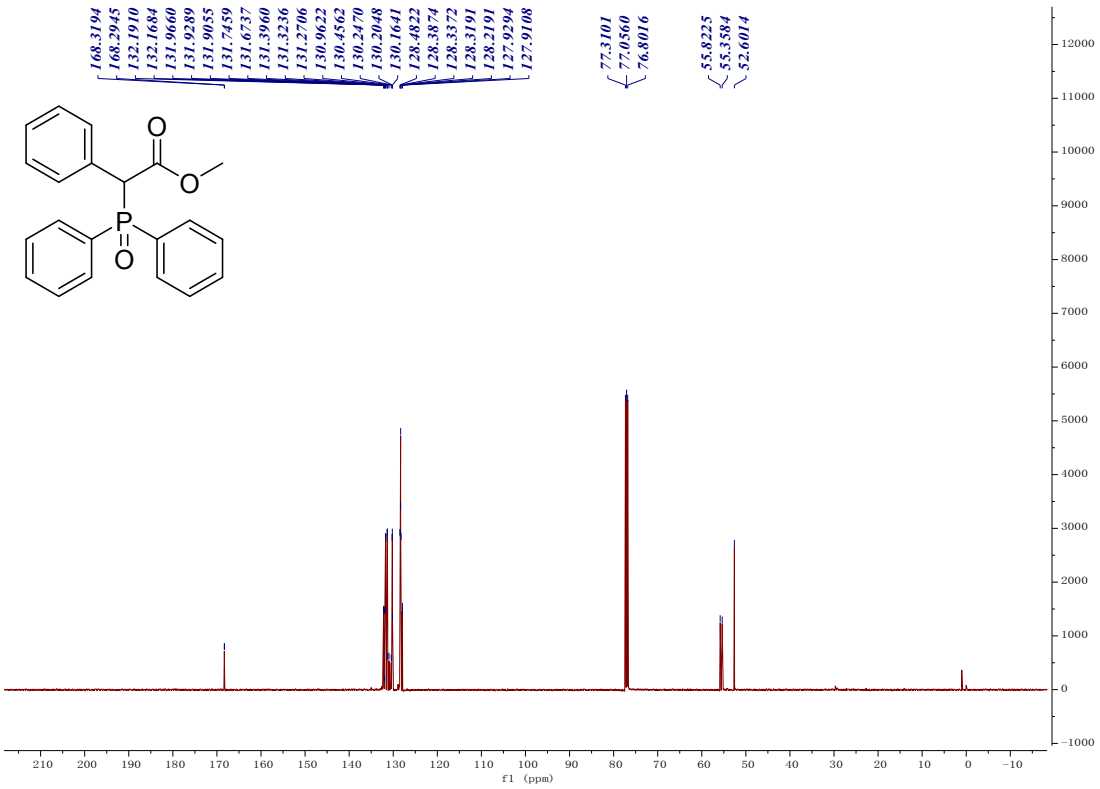


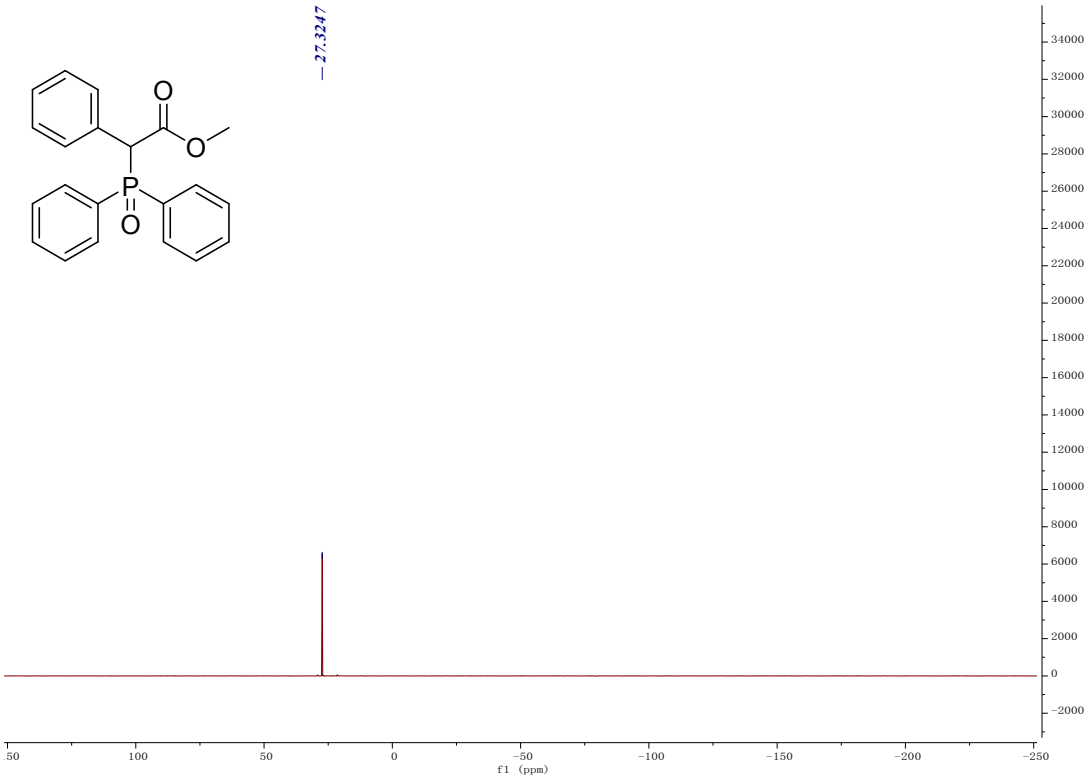
163.7-165.6 ℃, 30.1 mg, Yield: 66%; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.78 – 7.71 (m, 2H), 7.49 – 7.42 (m, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.27 (m, 4H), 7.18 – 7.14 (m, 2H), 4.62 (d, *J* = 11.6 Hz, 1H), 3.53 (s, 3H), 2.41 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.25 (d, *J* = 3.0 Hz), 142.93 (d, *J* = 2.9 Hz), 142.73 (d, *J* = 2.8 Hz), 131.99 (d, *J* = 5.1 Hz), 131.80 (d, *J* = 9.5 Hz), 131.54 (d, *J* = 1.7 Hz), 131.44 (d, *J* = 9.5 Hz), 129.74 (d, *J* = 6.4 Hz), 129.38 (d, *J* = 8.2 Hz), 129.28 (d, *J* = 8.3 Hz), 127.60 (d, *J* = 105.1 Hz), 127.20 (d, *J* = 103.4 Hz), 122.36 (d, *J* = 3.0 Hz), 55.33 (d, *J* = 57.1 Hz), 52.81 , 21.78 (d, *J* = 0.7 Hz), 21.69 (d, *J* = 1.3 Hz). **^{31}P NMR** (202 MHz, Chloroform-*d*) δ 27.40. **HRMS** (ESI) m/z: calcd for $C_{23}H_{23}BrO_3P$ $[M+H]^+$: 457.0563; found: 457.0566.

5. Copies of NMR Spectra

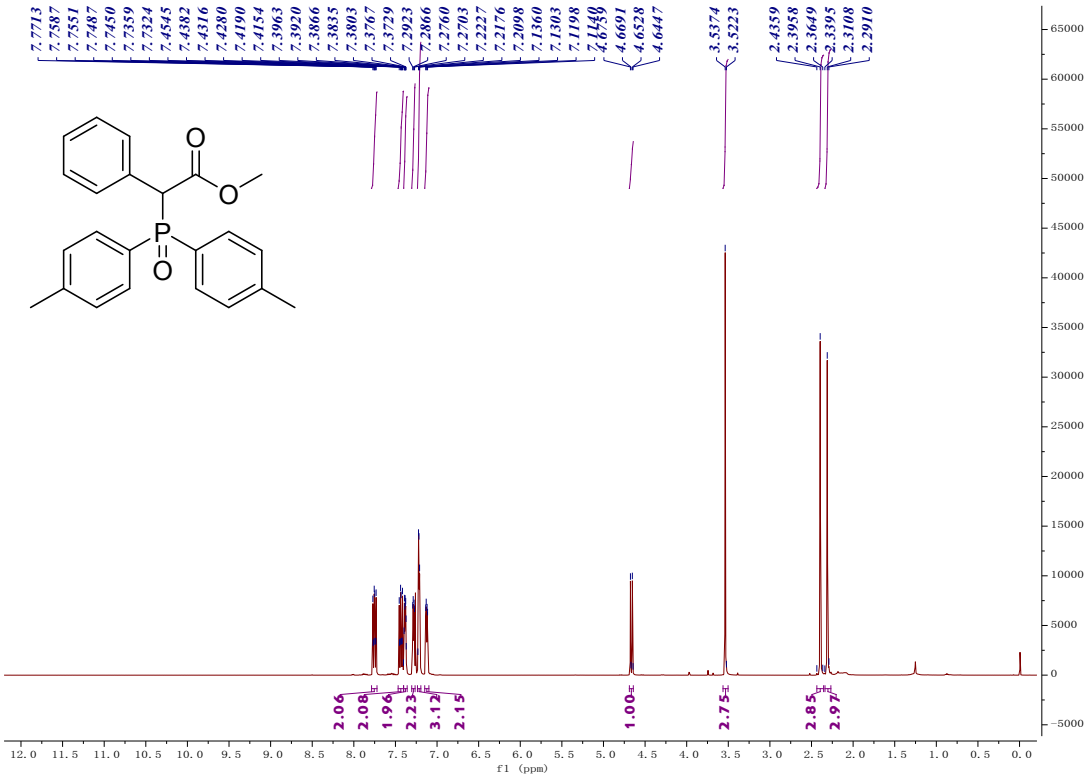
Methyl 2-(diphenylphosphoryl)-2-phenylacetate (3a)

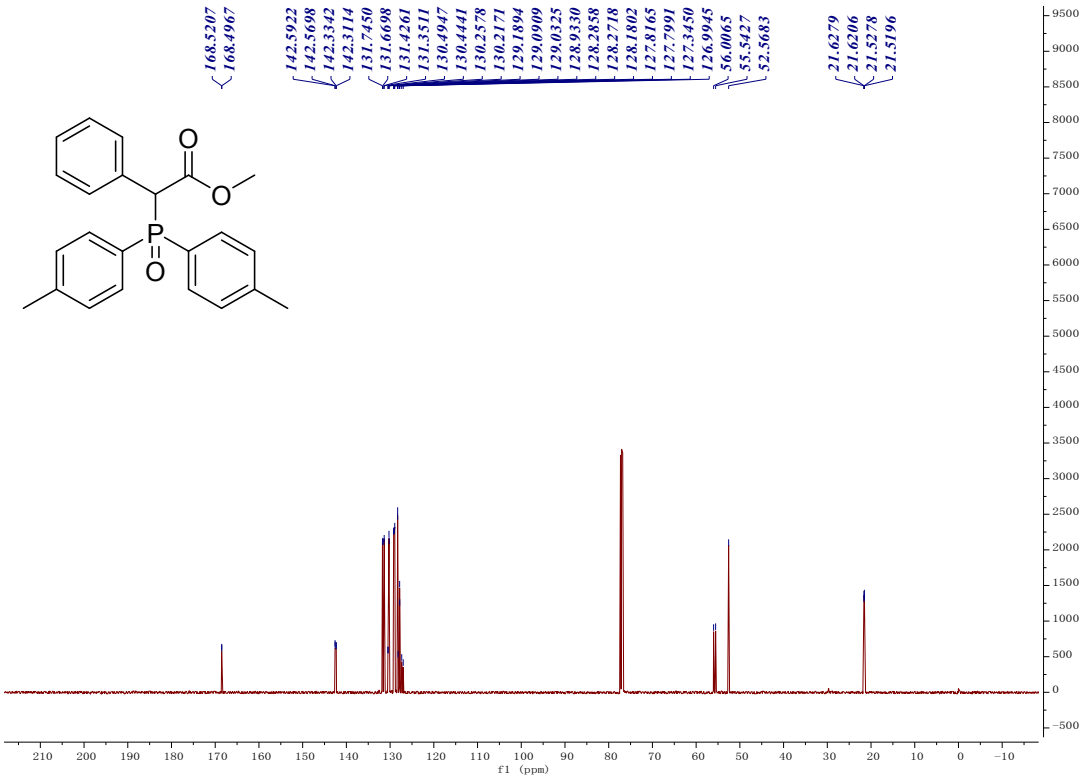


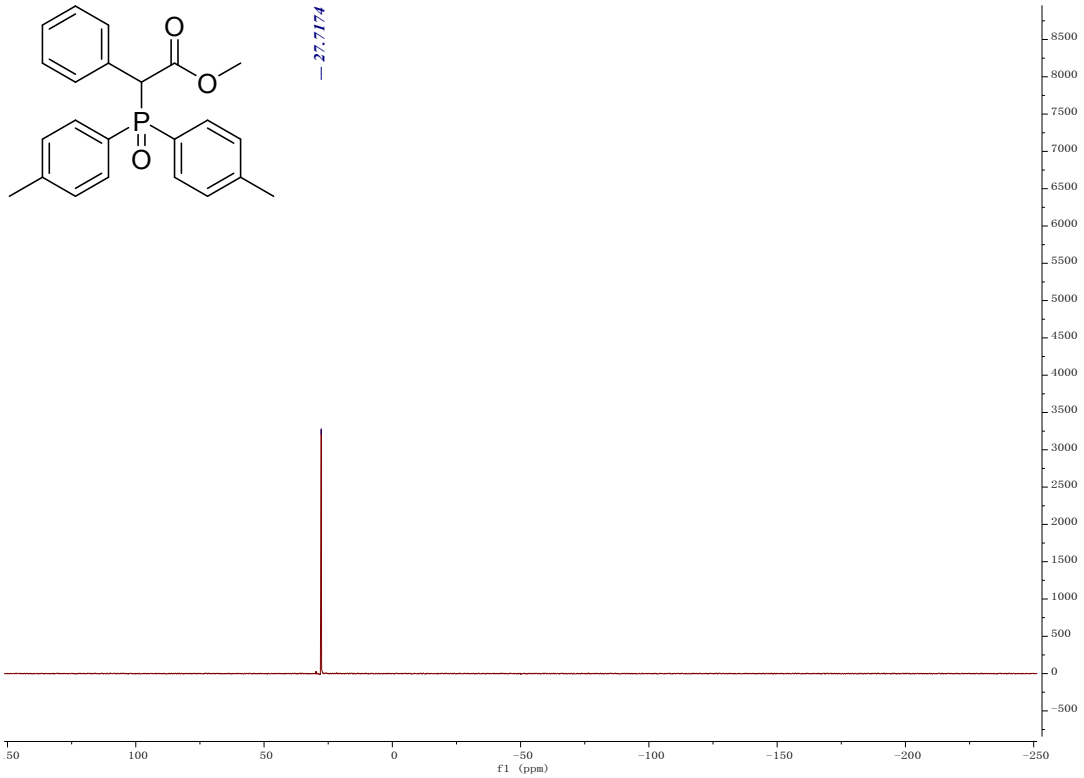




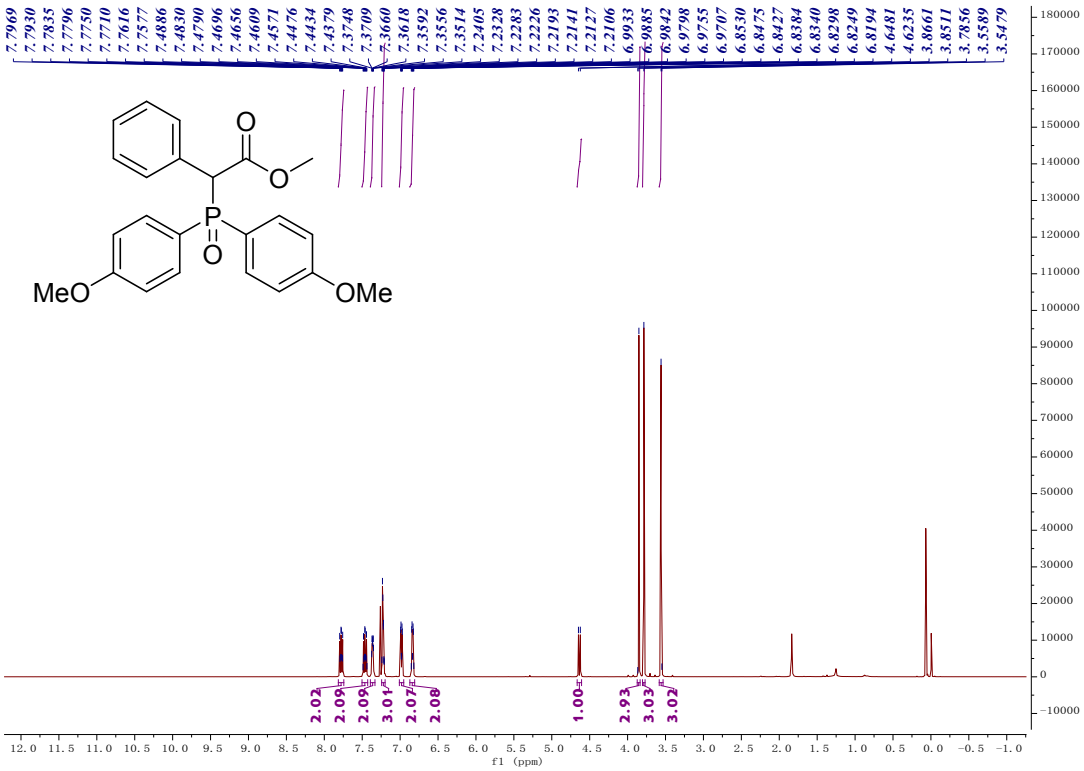
Methyl 2-(di-p-tolylphosphoryl)-2-phenylacetate (3b)







Methyl 2-(bis(4-methoxyphenyl)phosphoryl)-2-phenylacetate (3c)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7.7750
7.7710
7.7616
7.7577
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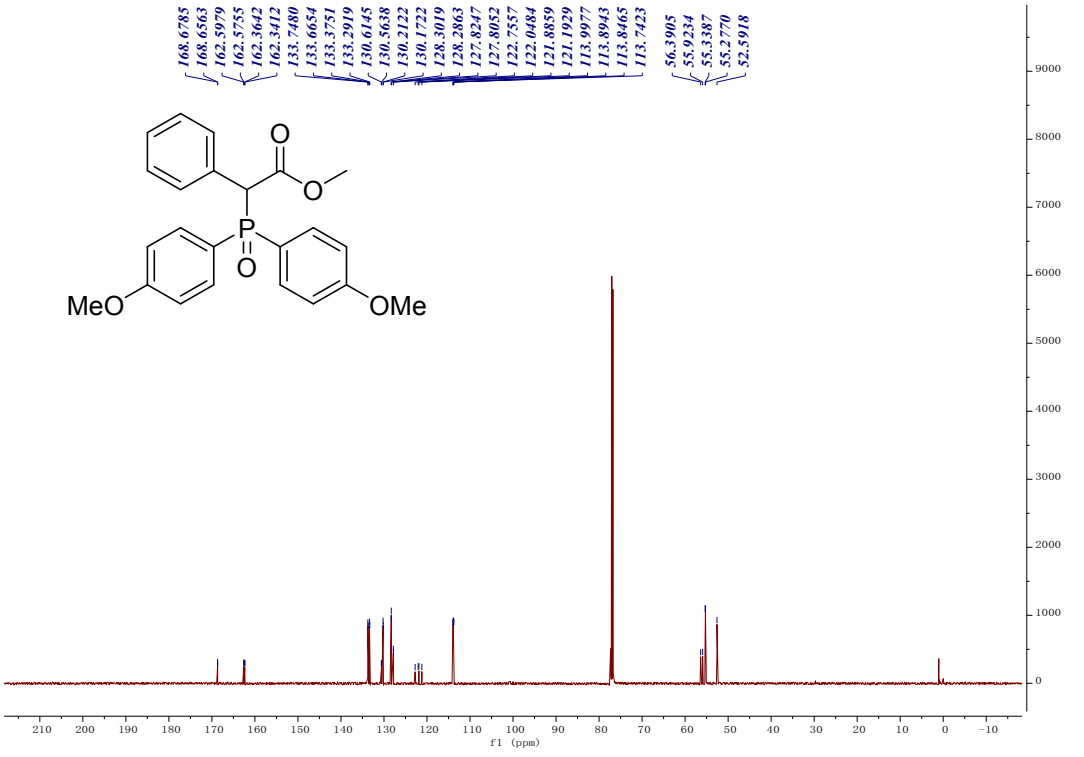
7.4830
7.4790
7.4696
7.4656
7.4609
7.4571
7.4476
7.4434
7.4379
7.3748
7.3709
7.3660
7.3618
7.3592
7.3556
7.3514
7.2405
7.2328
7.2283
7.2226
7.2193
7.2141
7.2127
7.2106
6.9933
6.9885
6.9842
6.9798
6.9755
6.9707
6.8530
6.8475
6.8427
6.8384
6.8340
6.8298
6.8249
6.8194
4.6481
4.6235
3.8661
3.8511
3.7856
3.5589
3.5479
O
O
O
P
O
MeO
OMe
2.02
2.09
2.00
3.01
2.07
2.08
1.00
2.93
3.03
3.02
f1 (ppm)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162.3642
162.3412
133.7480
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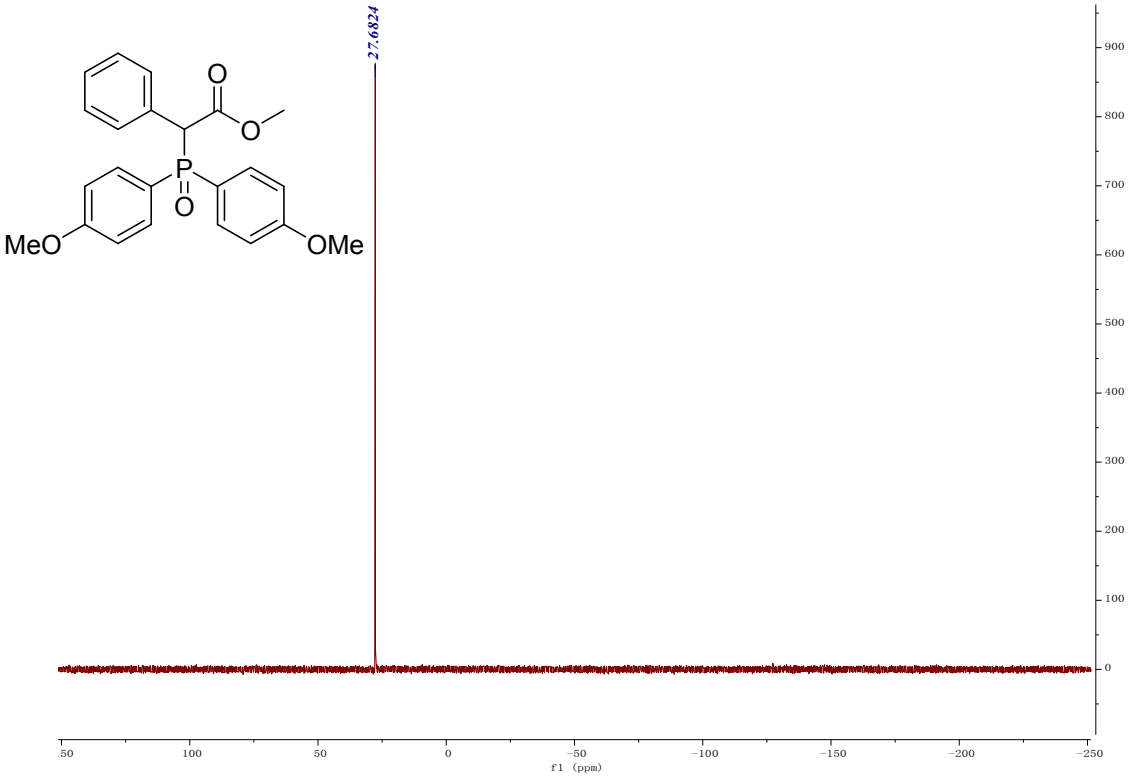
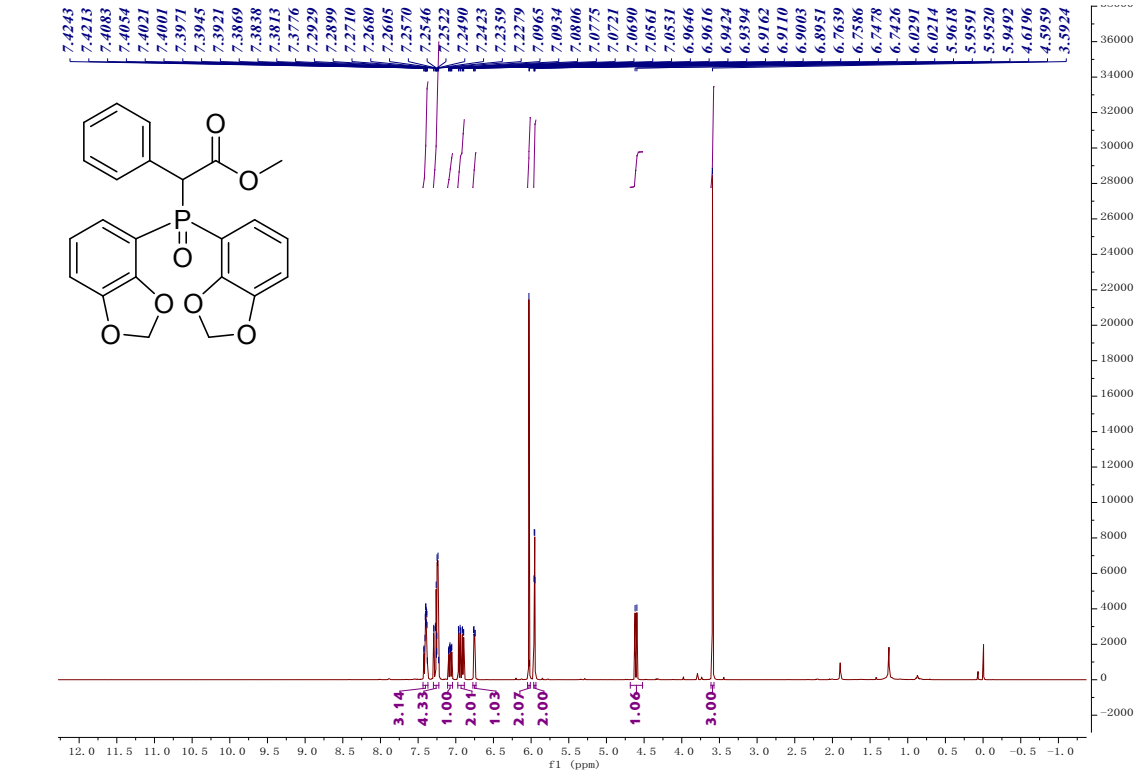
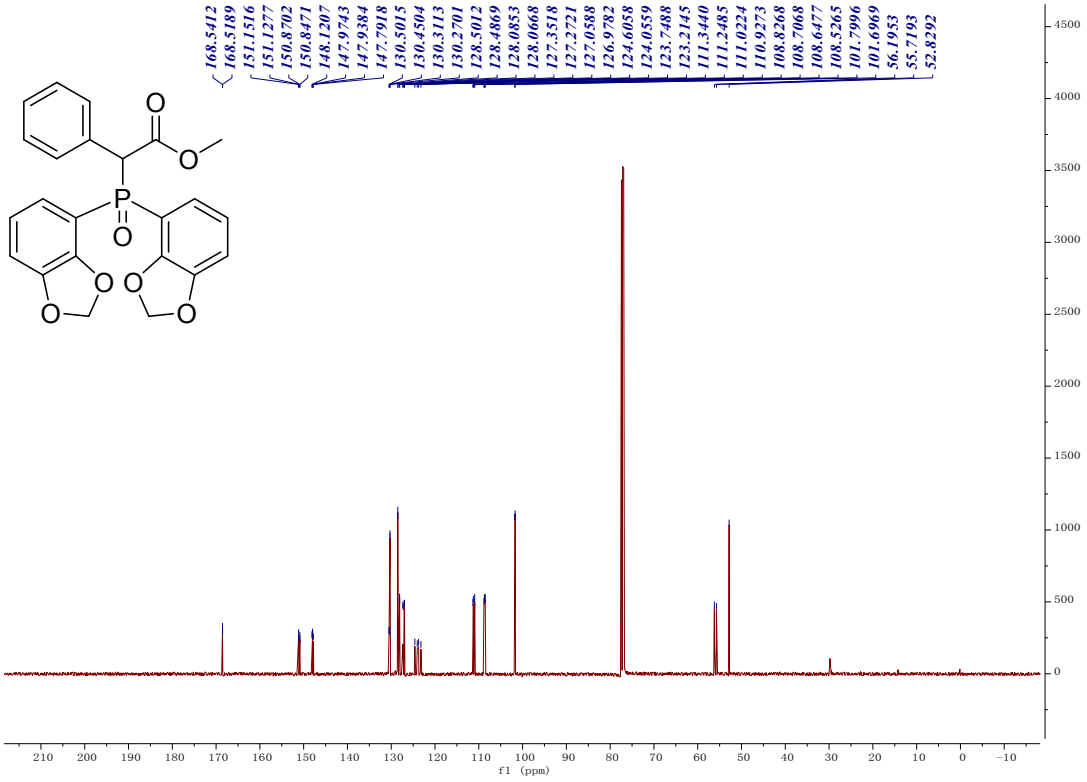
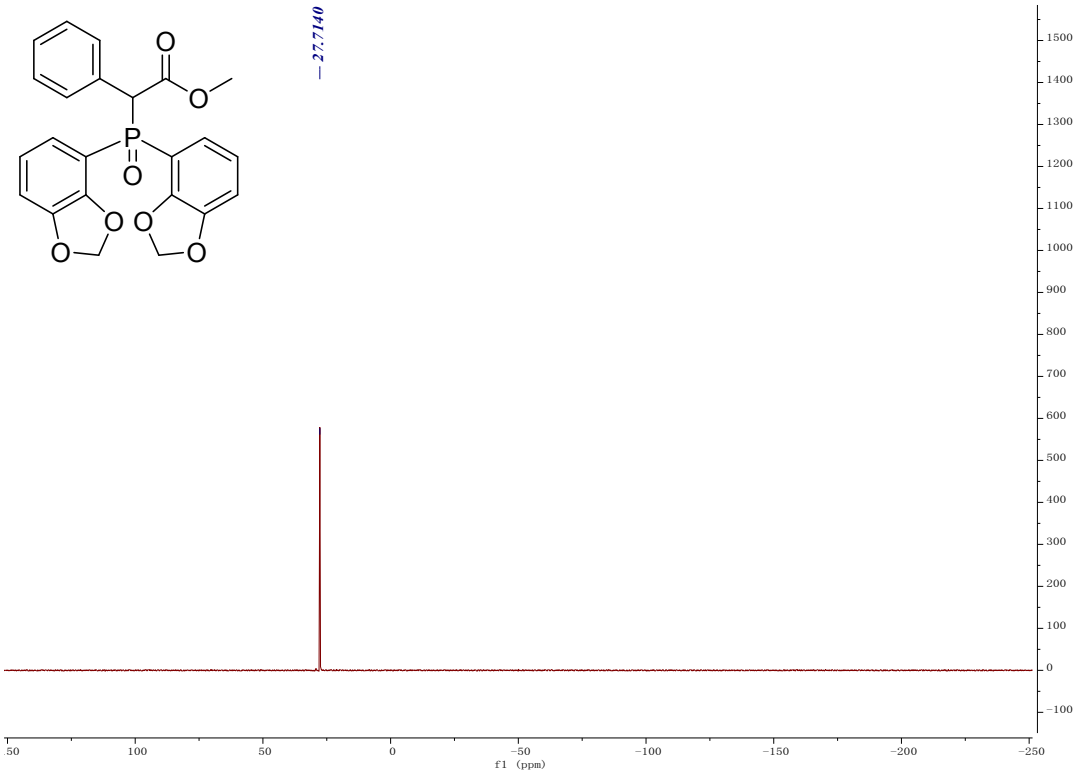
133.3751
133.2919
130.6145
130.5638
130.2122
130.1722
128.3019
128.2863
127.8247
127.8052
122.7557
122.0484
121.8859
121.1929
113.9977
113.8943
113.8465
113.7423
56.3905
55.9234
55.3387
55.2770
52.5918
O
O
O
P
O
MeO
OMe
f1 (ppm)



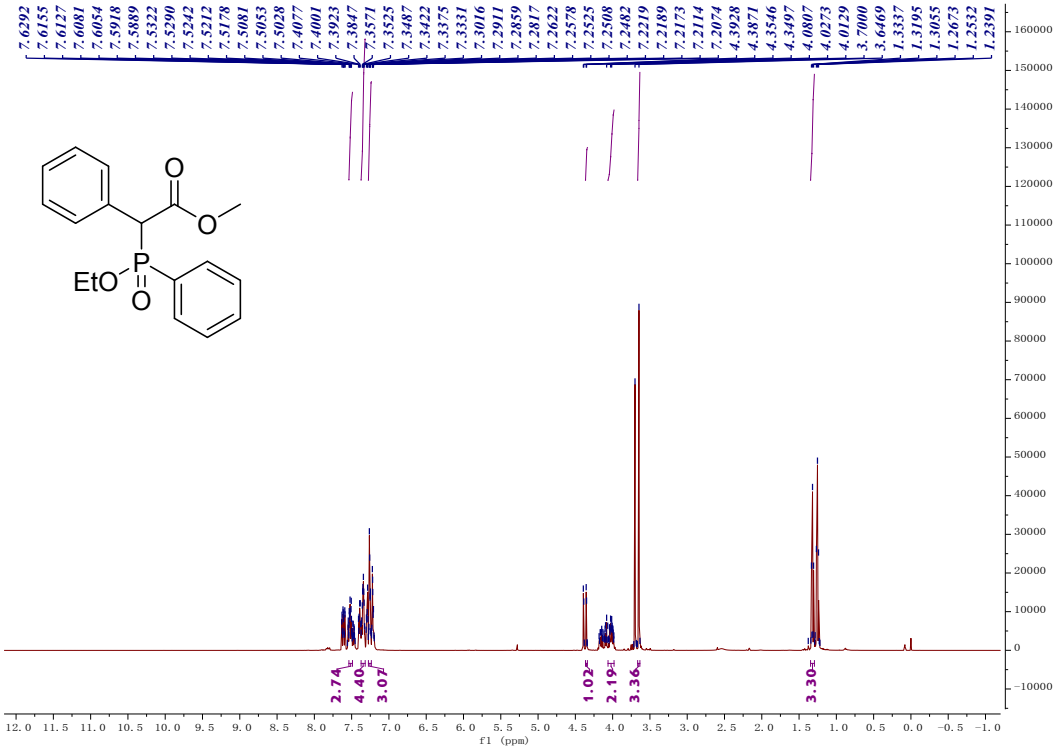
Methyl 2-(bis(benzo[d][1,3]dioxol-4-yl)phosphoryl)-2-phenylacetate (3d)







Methyl 2-(ethoxy(phenyl)phosphoryl)-2-phenylacetate (3e)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7.6127
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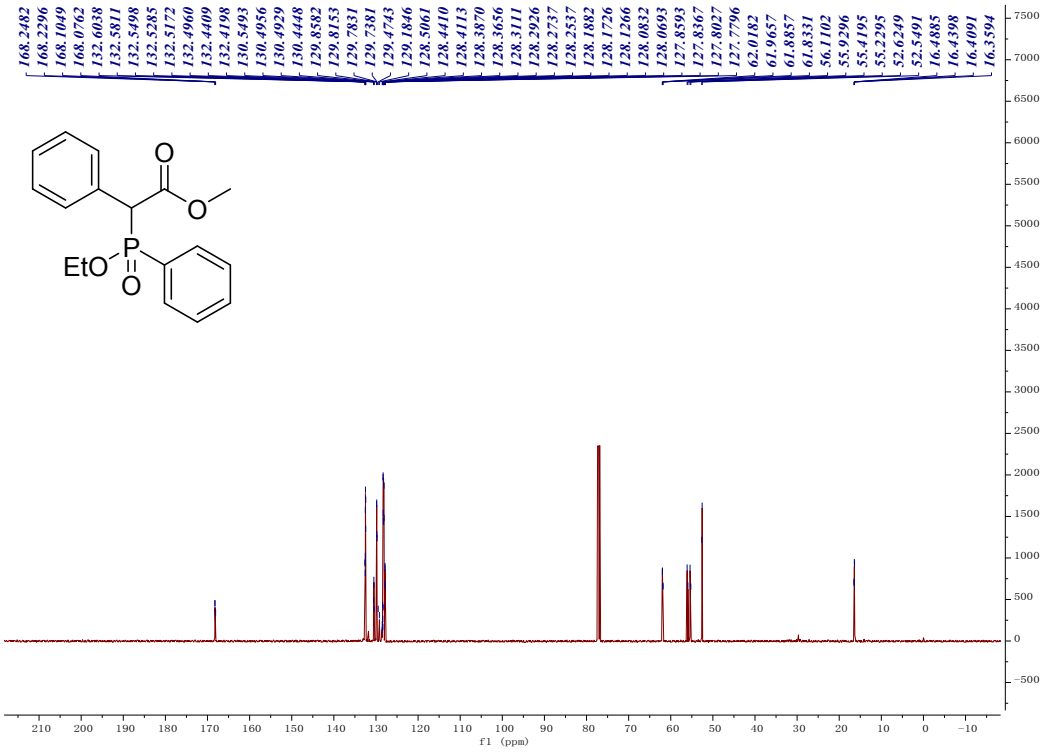
7.6054
7.5918
7.5889
7.5322
7.5290
7.5242
7.5212
7.5178
7.5081
7.5053
7.5028
7.4077
7.4001
7.3923
7.3847
7.3571
7.3525
7.3487
7.3422
7.3375
7.3331
7.3016
7.2911
7.2859
7.2817
7.2622
7.2578
7.2525
7.2508
7.2482
7.2219
7.2189
7.2173
7.2114
7.2074
4.3928
4.3871
4.3546
4.3497
4.0807
4.0273
4.0129
3.7000
3.6469
1.3337
1.3195
1.3055
1.2673
1.2532
1.2391
O
O
EtO
P
O
2.74
4.40
3.07
1.02
2.19
3.36
3.30
f1 (ppm)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168.1049
168.0762
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132.5498
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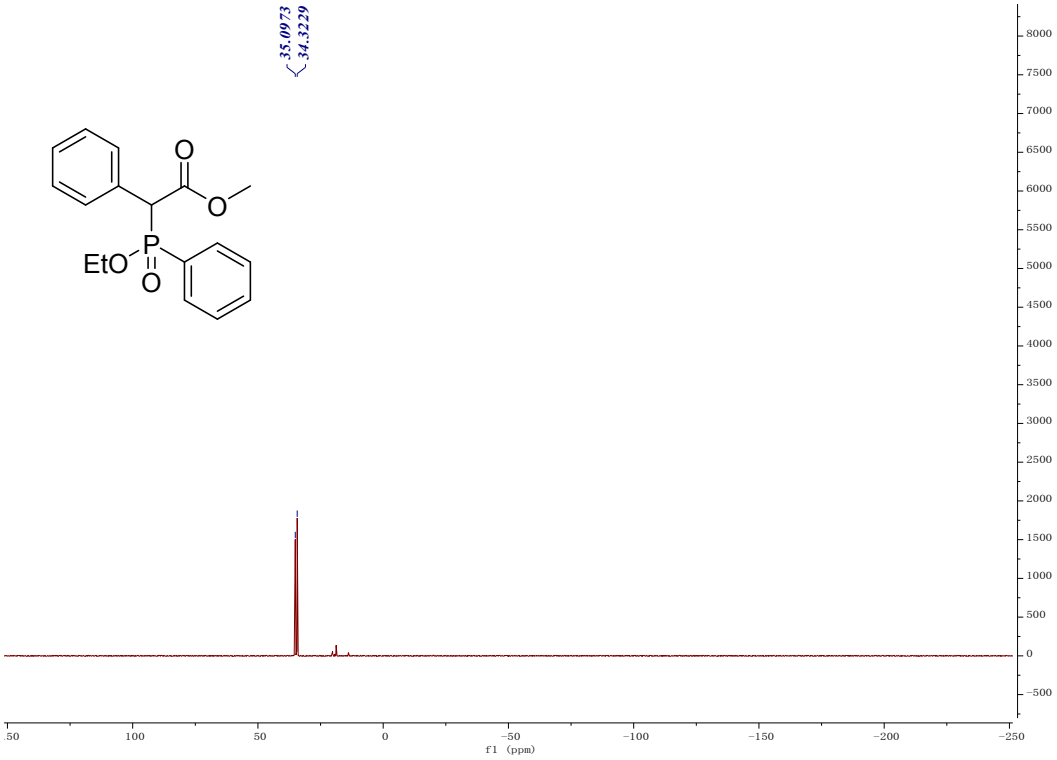
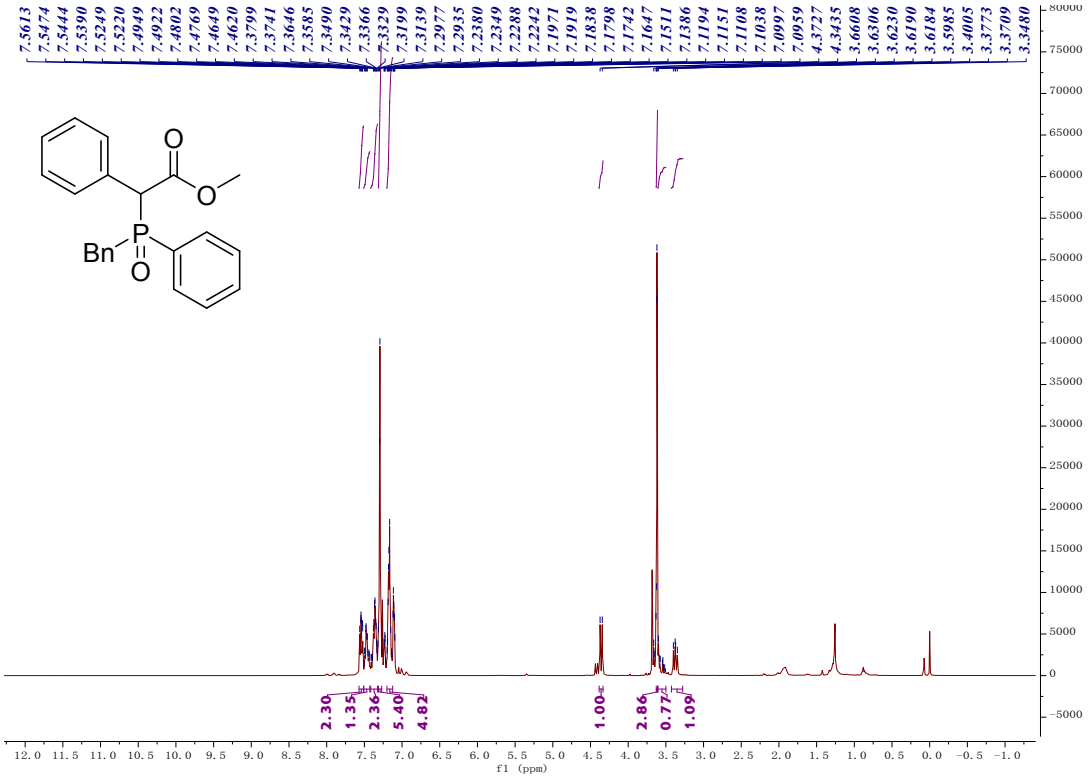
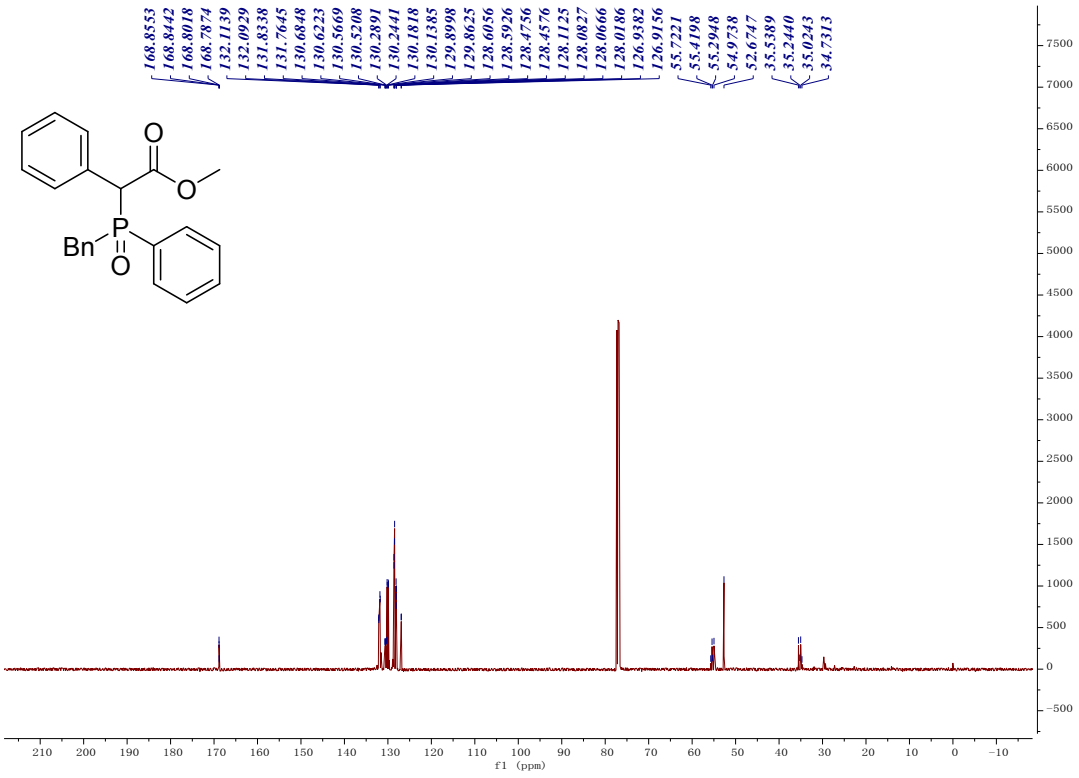
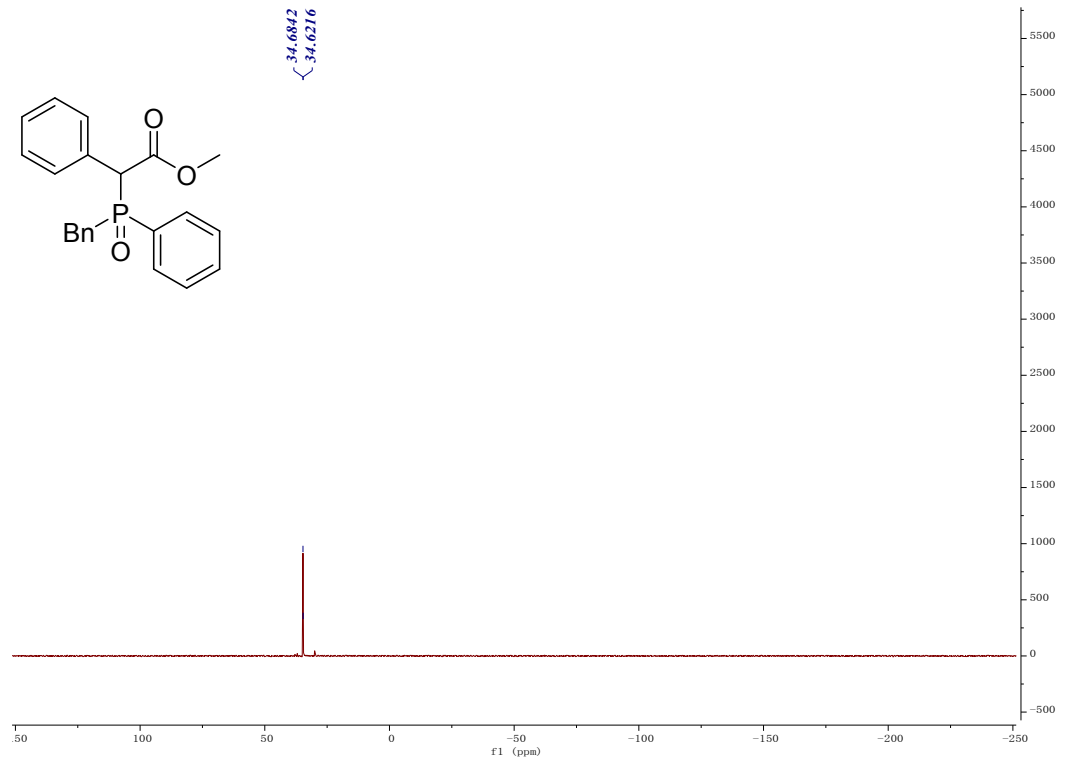
132.4409
132.4198
130.5493
130.4956
130.4929
130.4448
129.8582
129.8153
129.7831
129.7381
129.4743
129.1846
128.5061
128.4410
128.4113
128.3870
128.3656
128.3111
128.2926
128.2737
128.2537
128.1882
128.1726
128.1266
128.0832
128.0693
127.8593
127.8367
127.8027
127.7796
62.0182
61.9657
61.8857
61.8331
56.1102
55.9296
55.4195
55.2295
52.6249
52.5491
16.4885
16.4398
16.4091
16.3594
O
O
EtO
P
O
f1 (ppm)



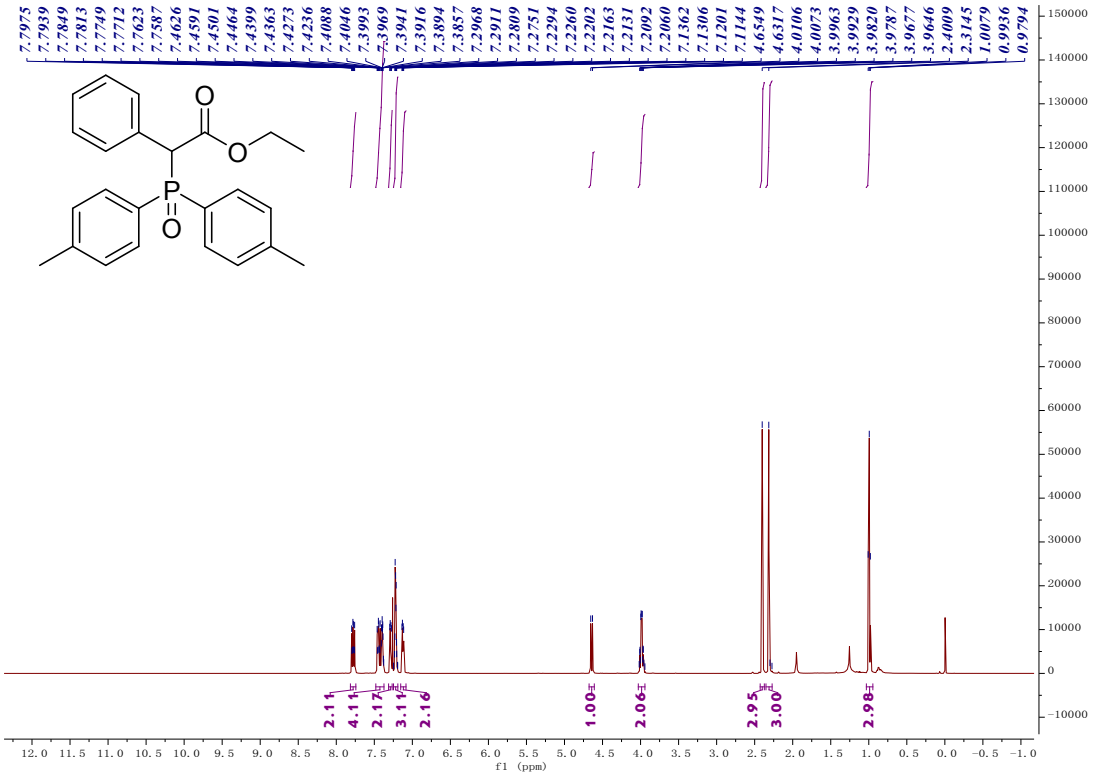
Methyl 2-(benzyl(phenyl)phosphoryl)-2-phenylacetate (3f)







Ethyl 2-(di-p-tolylphosphoryl)-2-phenylacetate (3g)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7.7813
7.7749
7.7712
7.7623
7.7587
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7.4591
7.4501
7.4464
7.4399
7.4363
7.4273
7.4236
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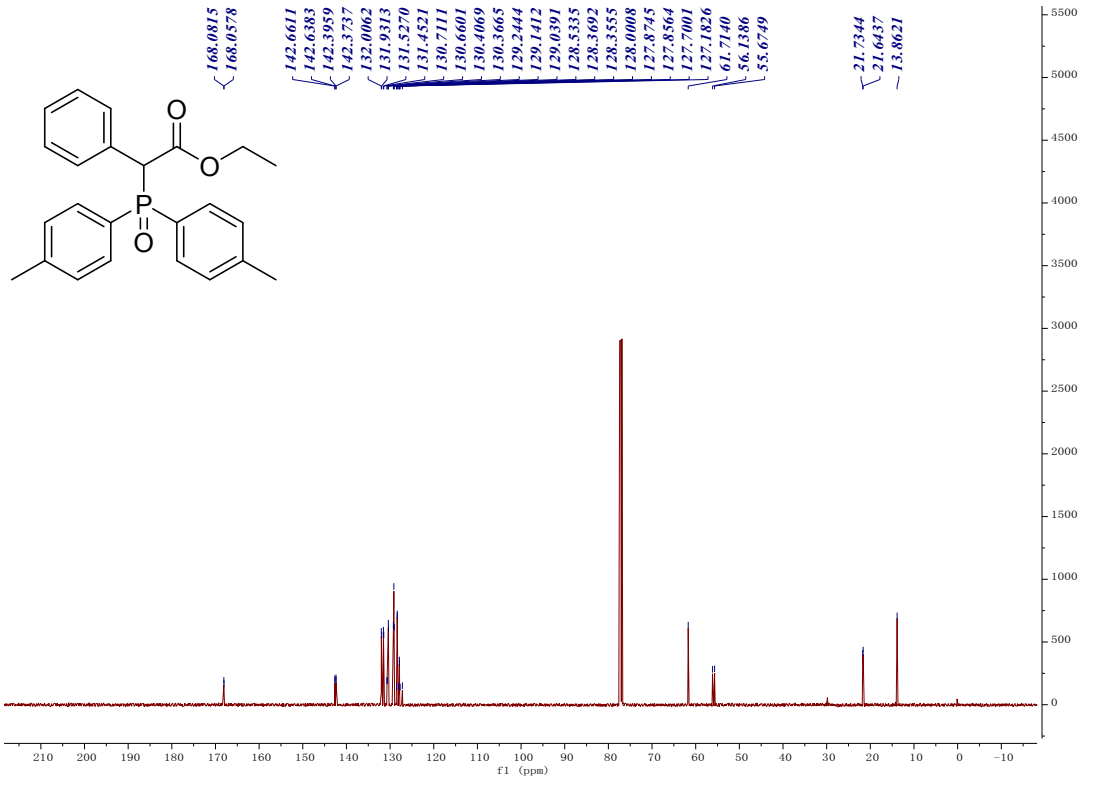
7.4046
7.3993
7.3969
7.3941
7.3916
7.3894
7.3857
7.2968
7.2911
7.2809
7.2751
7.2294
7.2260
7.2202
7.2163
7.2131
7.2092
7.2060
7.1362
7.1306
7.1201
7.1144
4.6549
4.6317
4.0106
4.0073
3.9963
3.9929
3.9820
3.9787
3.9677
3.9646
2.4009
2.3145
1.0079
0.9936
0.9794
O
O
P
O
2.11
4.11
2.17
3.11
2.16
1.00
2.06
2.95
3.00
2.98
f1 (ppm)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168.0578
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142.6383
142.3959
142.3737
132.0062
131.9313
131.5270
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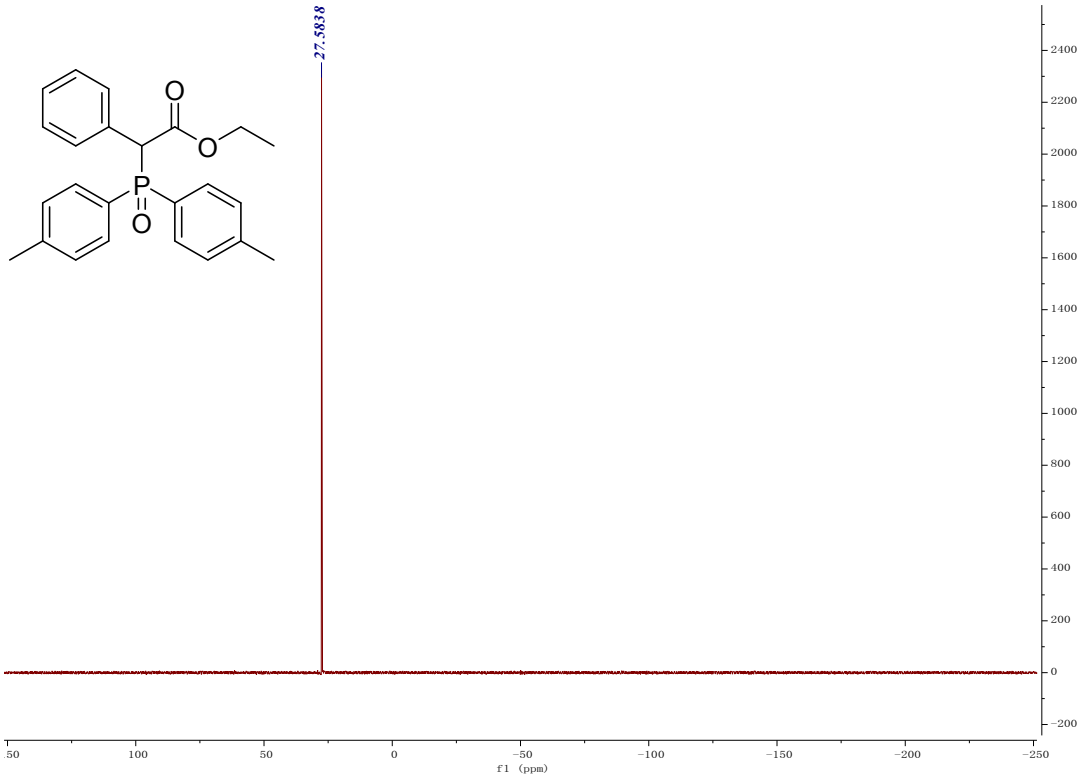
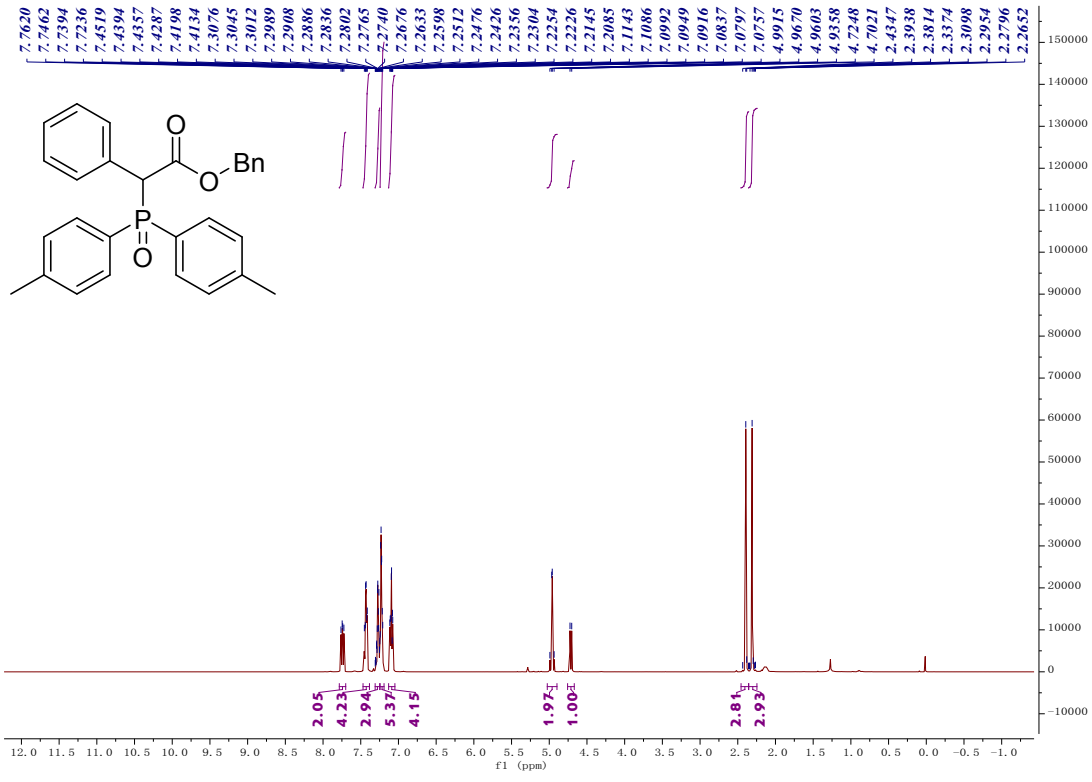
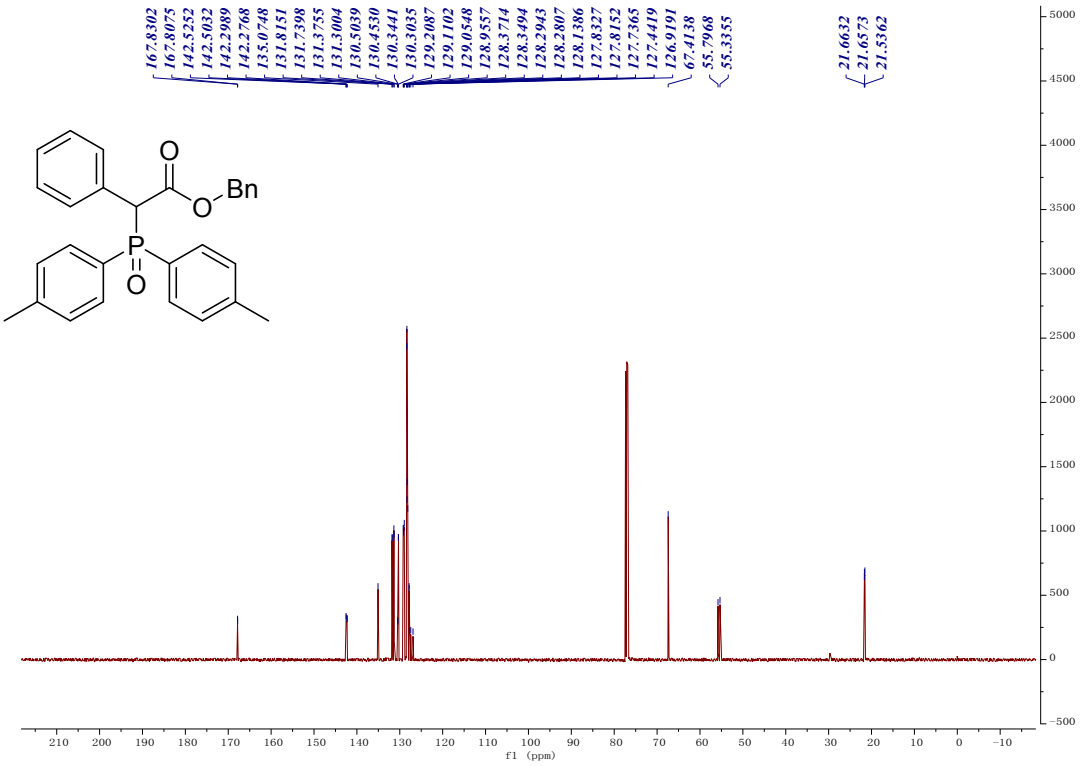
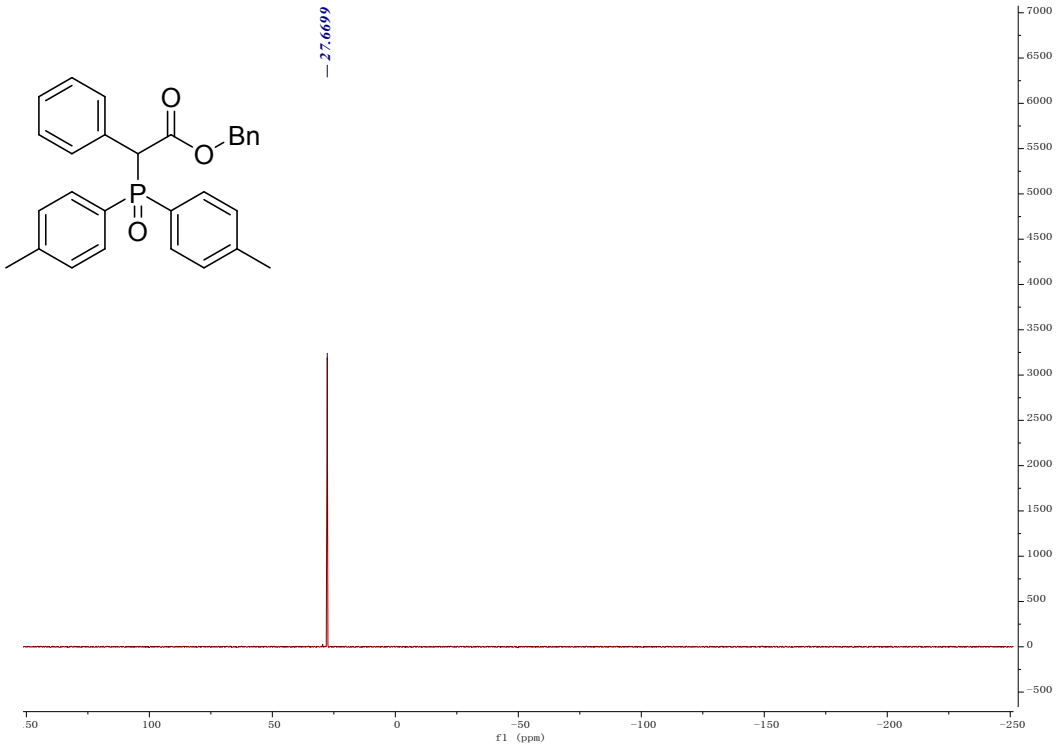
130.7111
130.6601
130.4069
130.3665
129.2444
129.1412
129.0391
128.5335
128.3692
128.3555
128.0008
127.8745
127.8564
127.7001
127.1826
61.7140
56.1386
55.6749
21.7344
21.6437
13.8621
O
O
P
O
f1 (ppm)



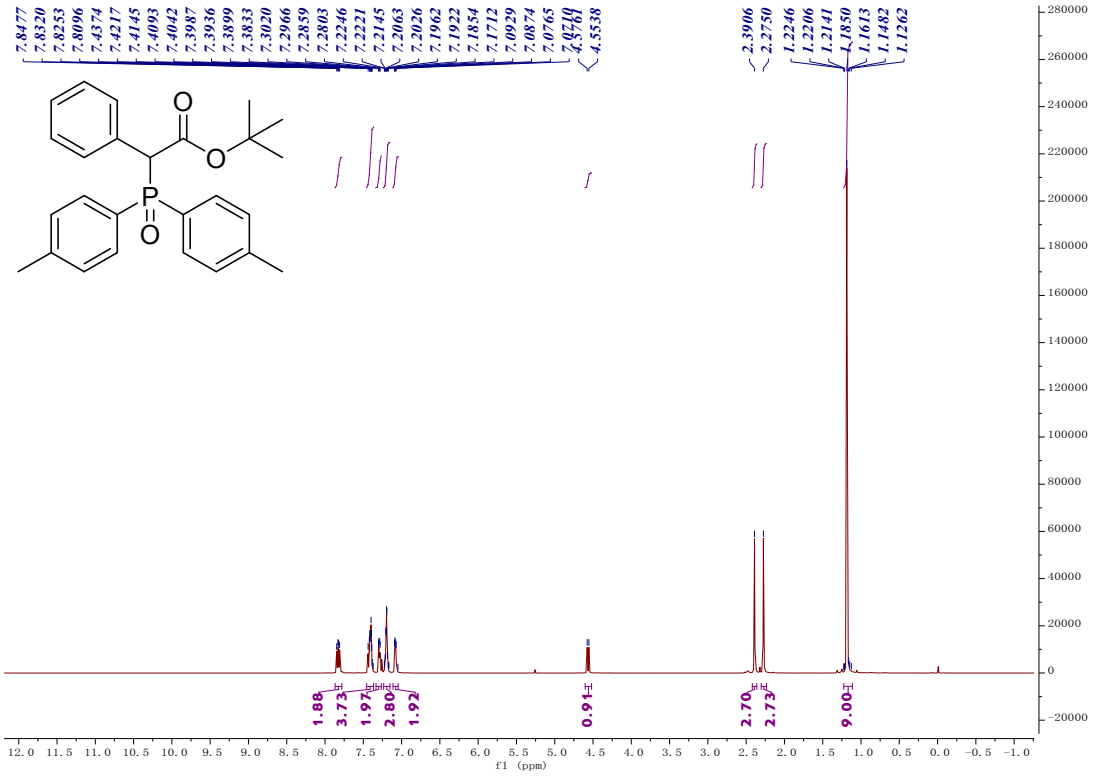
Benzyl 2-(di-p-tolylphosphoryl)-2-phenylacetate (3h)







Tert-butyl 2-(di-p-tolylphosphoryl)-2-phenylacetate (3i)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7.3899
7.3833
7.3020
7.2966
7.2859
7.2803
7.2246
7.2221
7.2145
7.2063
7.2026
7.1962
7.1922
7.1854
7.1712
7.0929
7.0874
7.0765
4.5538
2.3906
2.2750
1.2246
1.2206
1.2141
1.1850
1.1613
1.1482
1.1262
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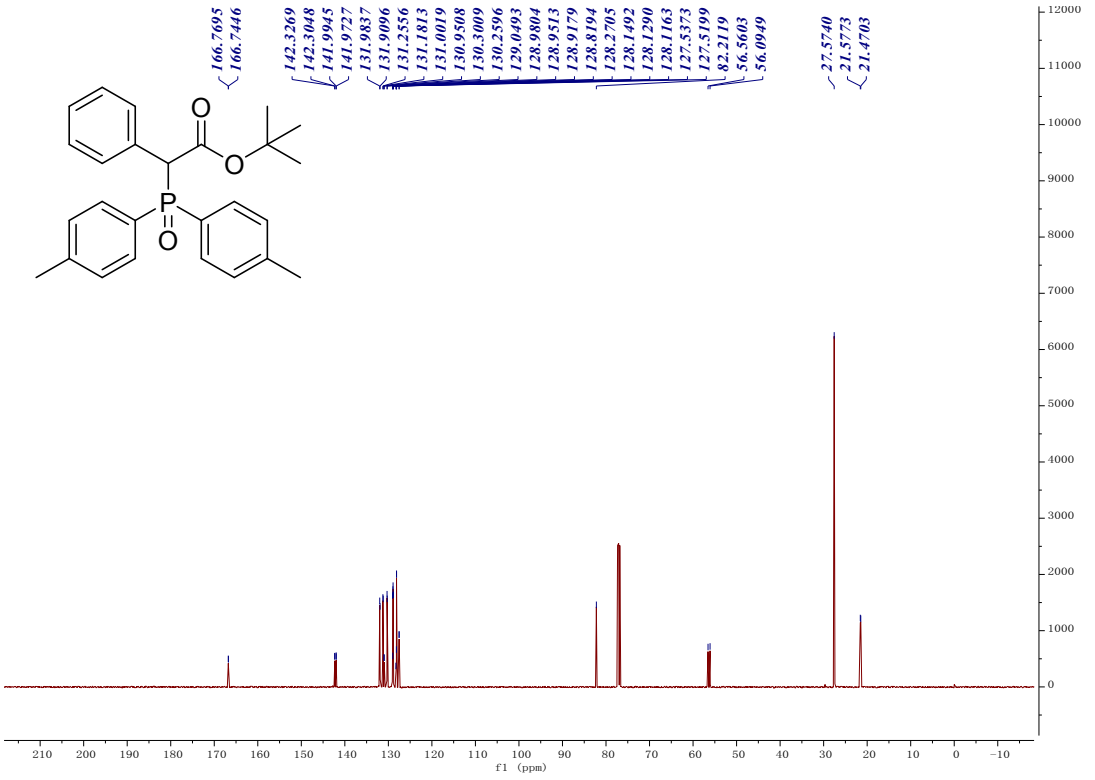
3.73
1.97
2.80
1.92
0.91
2.70
2.73
9.00
f1 (ppm)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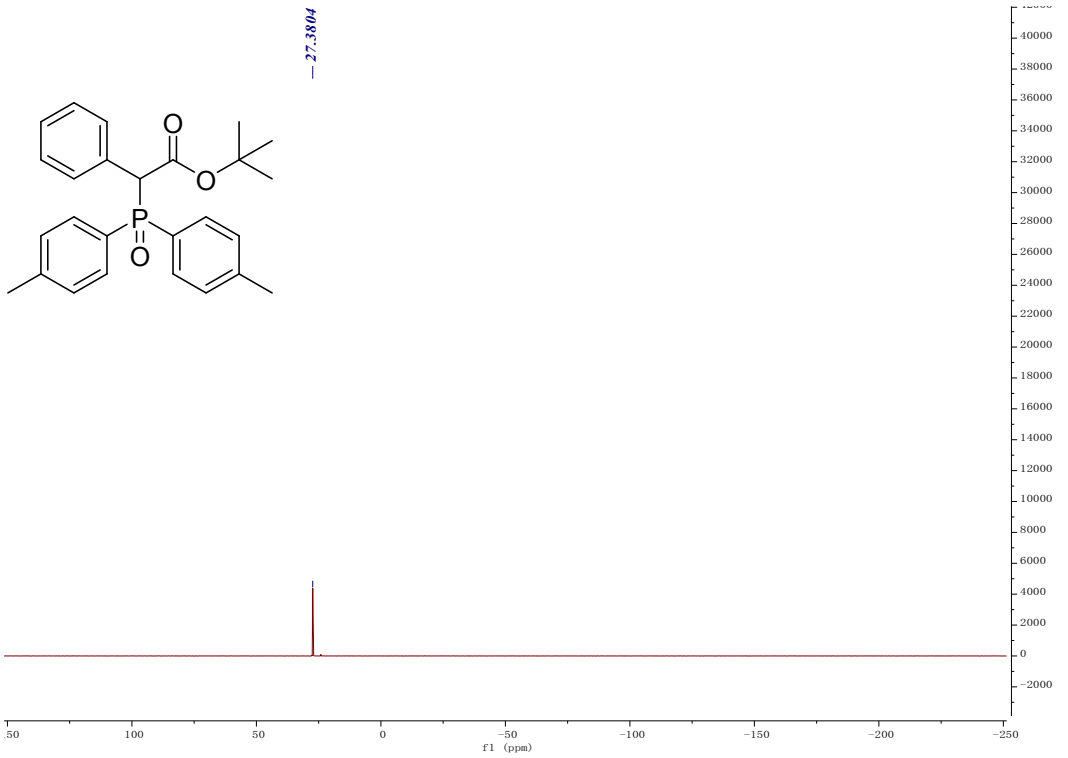
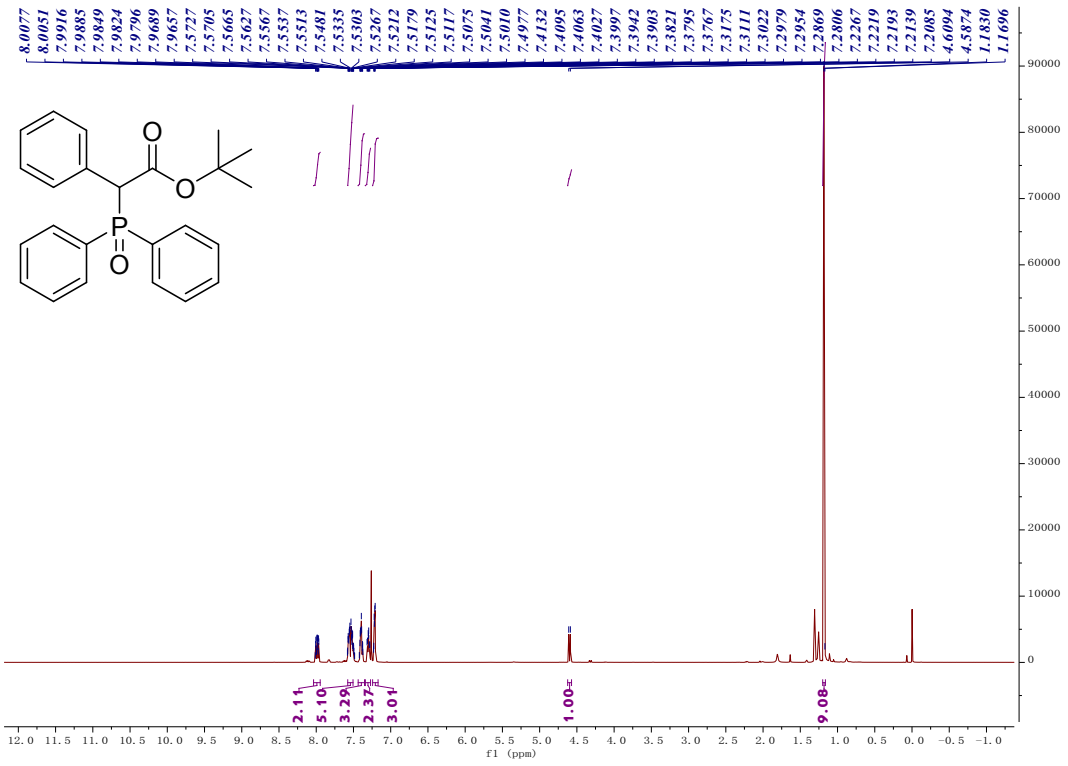
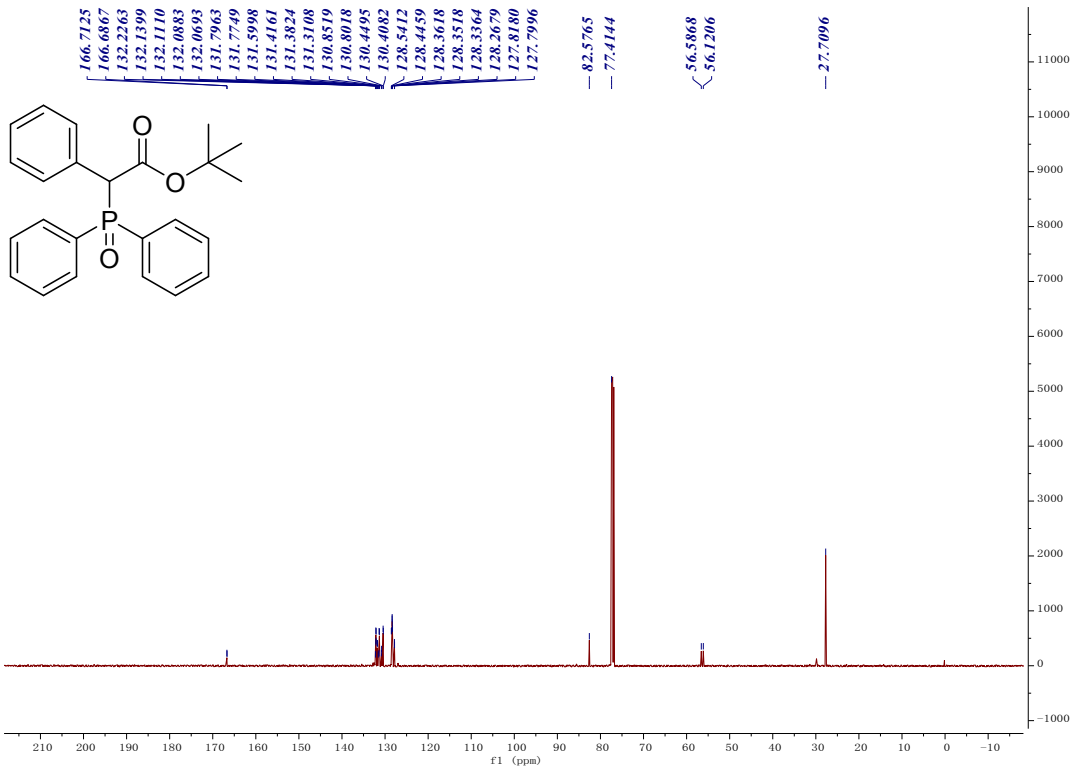
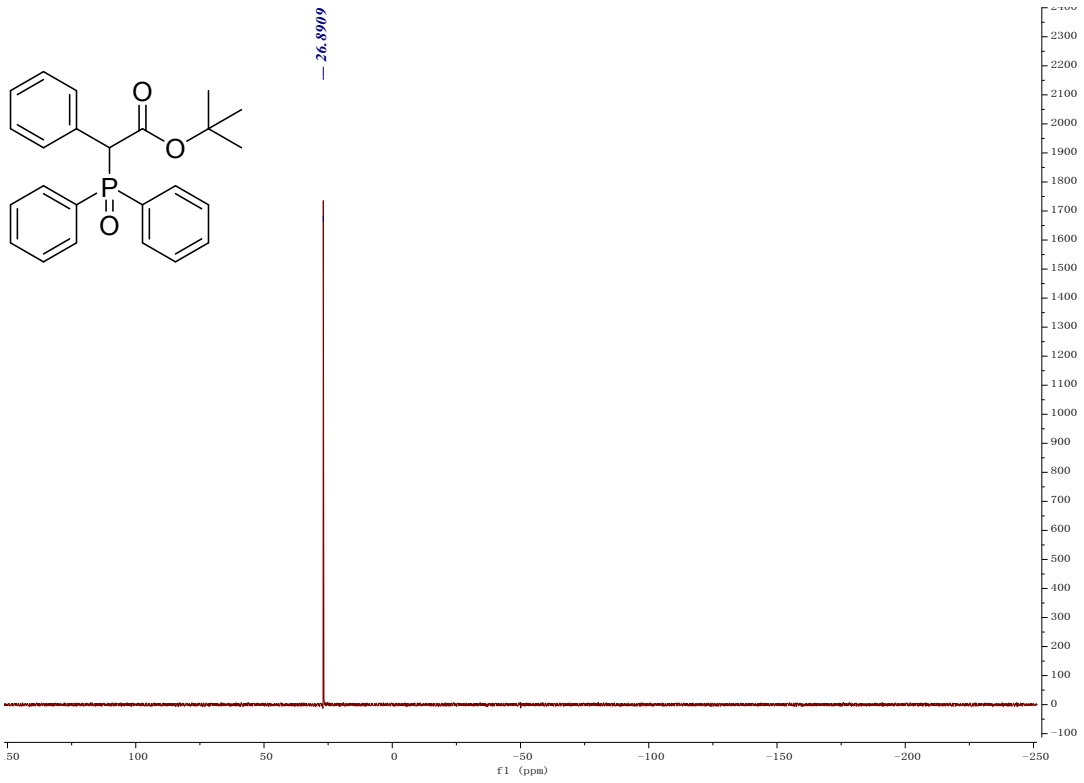
130.9508
130.3009
130.2596
129.0493
128.9804
128.9513
128.9179
128.8194
128.2705
128.1492
128.1290
128.1163
127.5373
127.5199
82.2119
56.5603
56.0949
27.5740
21.5773
21.4703
f1 (ppm)



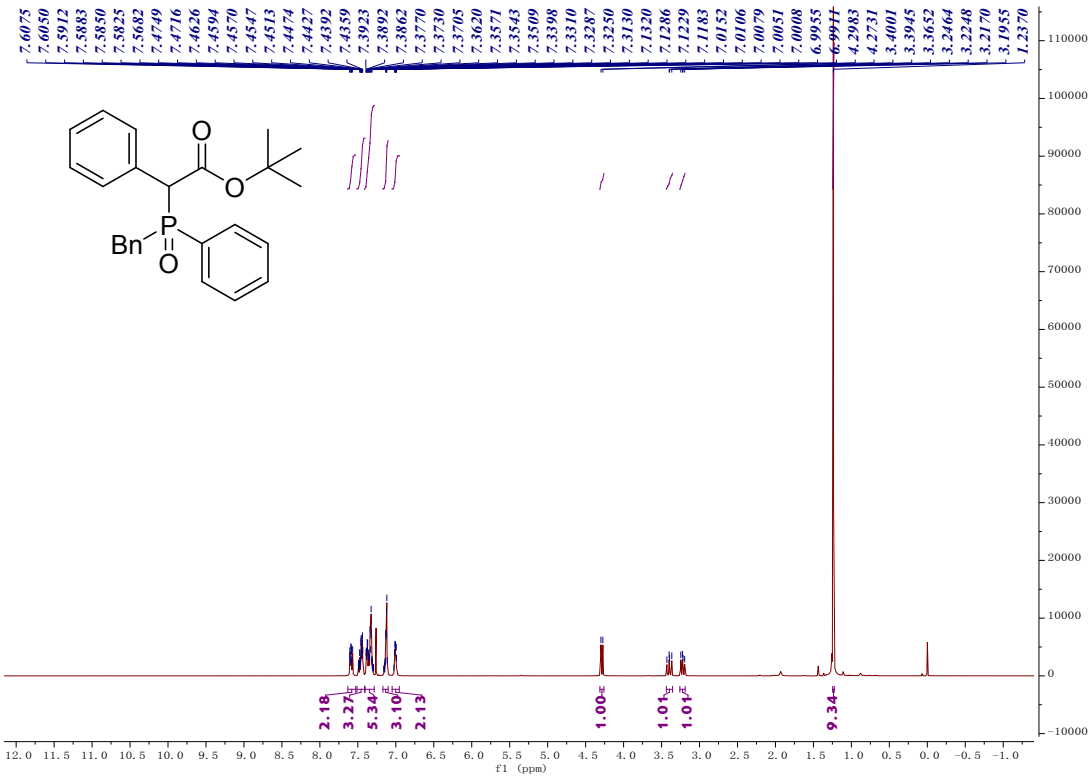
Tert-butyl 2-(diphenylphosphoryl)-2-phenylacetate (3j)







Tert-butyl 2-(benzyl(phenyl)phosphoryl)-2-phenylacetate (3k)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7.5850
7.5825
7.5682
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7.4716
7.4626
7.4594
7.4570
7.4547
7.4513
7.4474
7.4427
7.4392
7.4359
7.3923
7.3892
7.3862
7.3770
7.3730
7.3705
7.3620
7.3571
7.3543
7.3509
7.3398
7.3310
7.3287
7.3250
7.3130
7.1320
7.1286
7.1229
7.1183
7.0152
7.0106
7.0079
7.0051
7.0008
6.9955
6.9911
4.2983
4.2731
3.4001
3.3945
3.3652
3.2464
3.2248
3.2170
3.1955
1.2370
O
O
Bn
P
O
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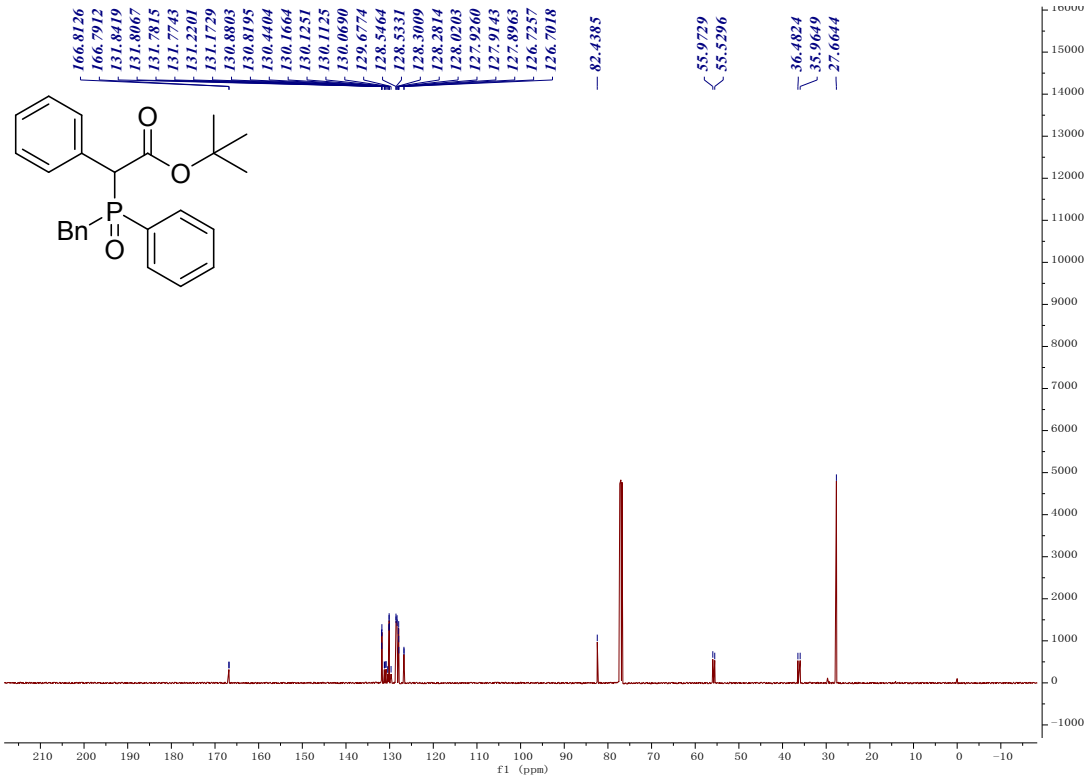
3.27
5.34
3.10
2.13
1.00
1.01
1.01
9.34
f1 (ppm)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131.8419
131.8067
131.7815
131.7743
131.2201
131.1729
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130.4404
130.1664
130.1251
130.1125
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129.6774
128.5464
128.5331
128.3009
128.2814
128.0203
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127.9143
127.8963
126.7257
126.7018
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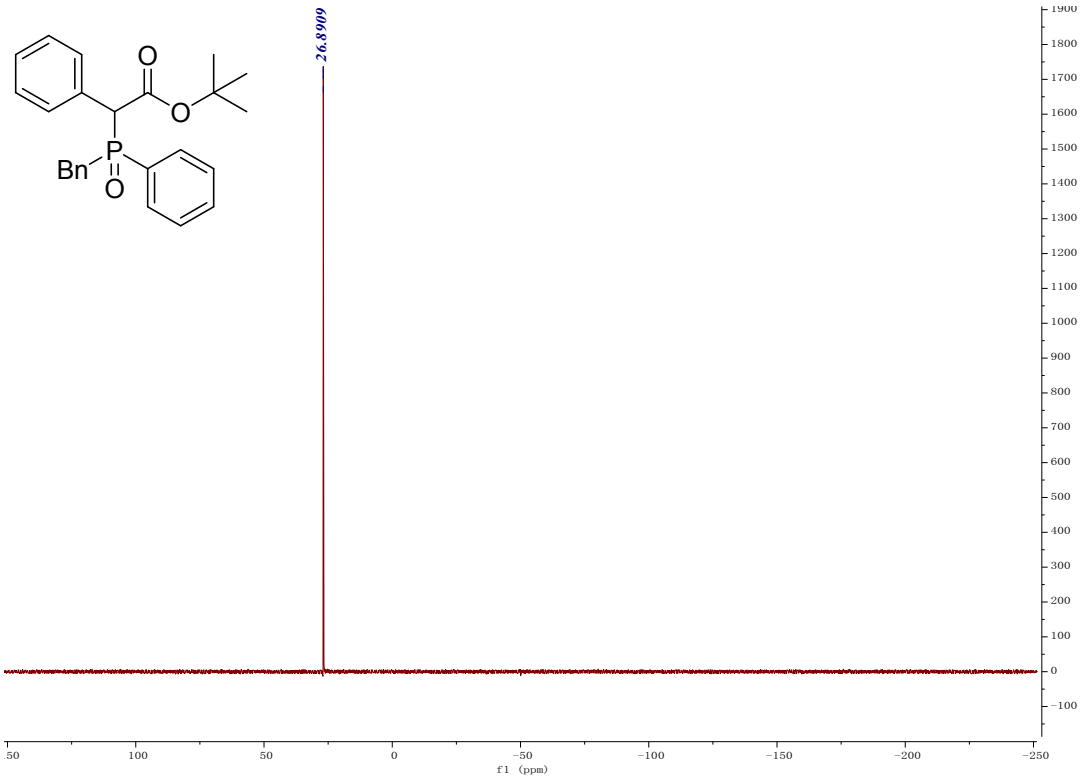
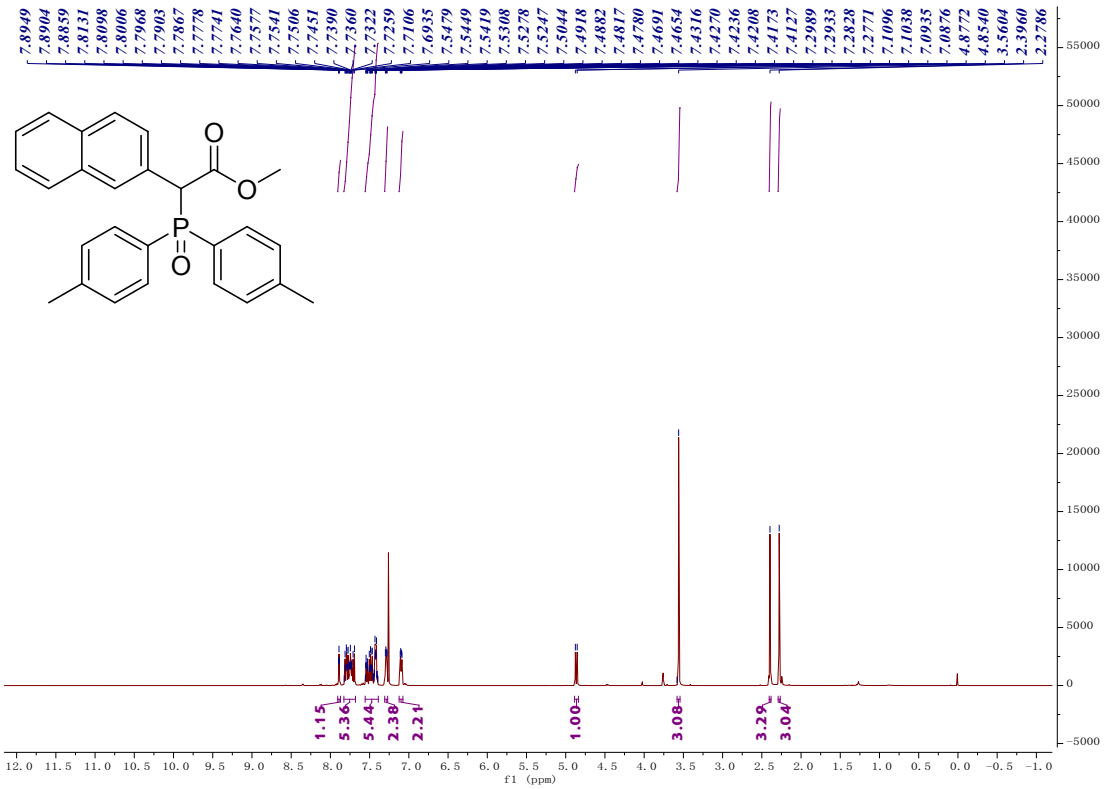
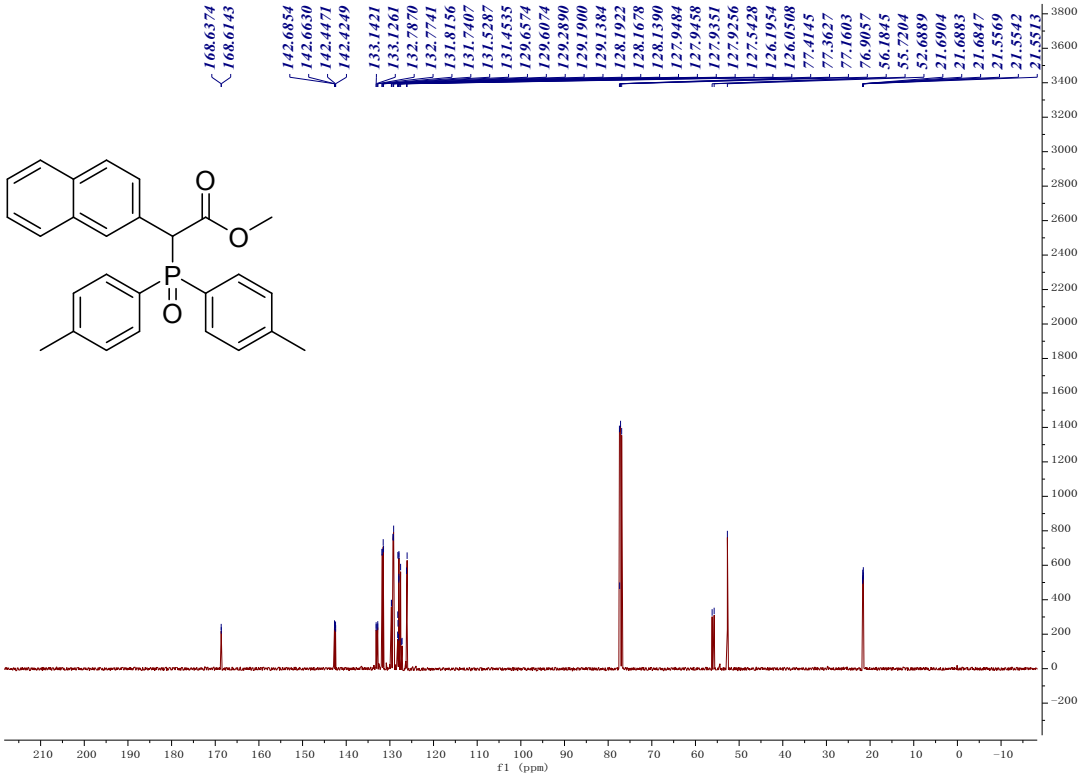
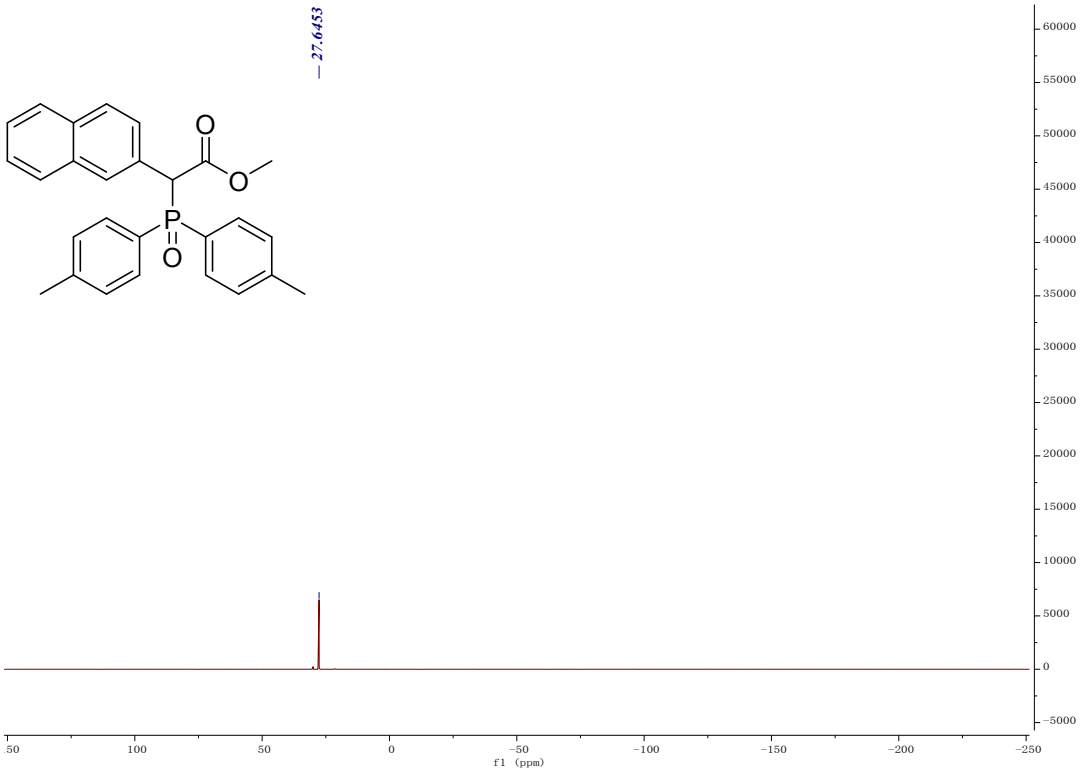
27.6644
O
O
Bn
P
O
f1 (ppm)



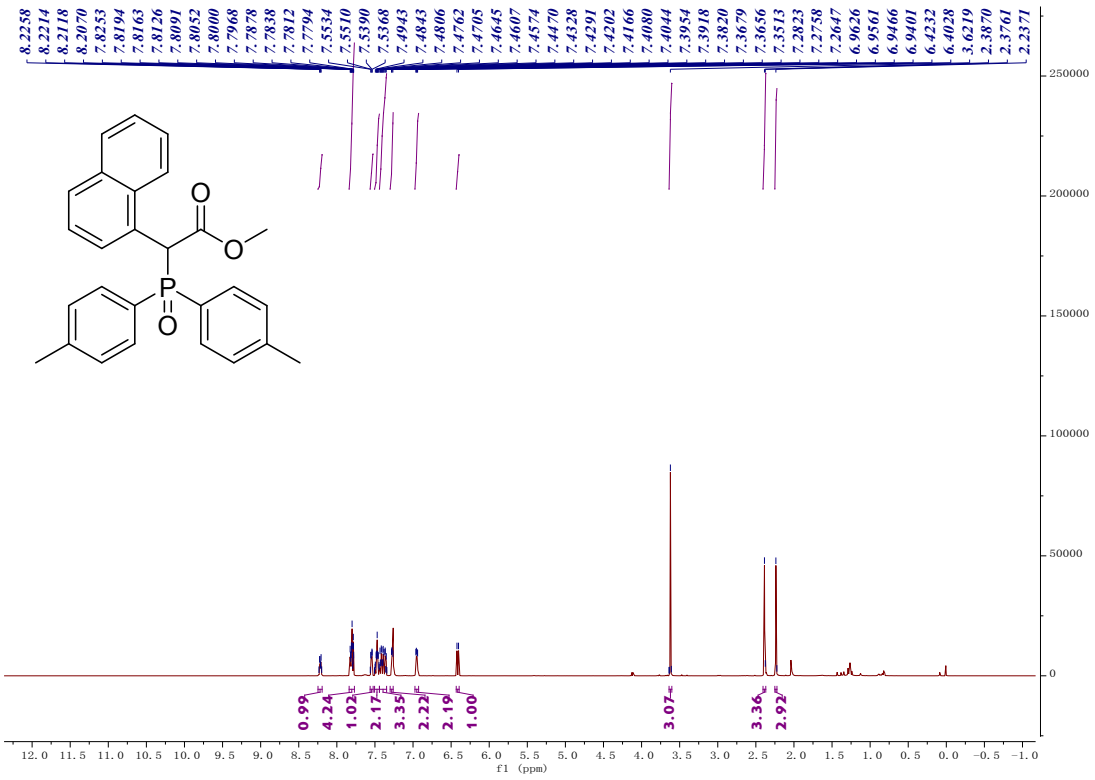
Methyl 2-(di-p-tolylphosphoryl)-2-(naphthalen-2-yl)acetate (3l)







Methyl 2-(di-p-tolylphosphoryl)-2-(naphthalen-1-yl)acetate (3m)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8.2118
8.2070
7.8253
7.8194
7.8163
7.8126
7.8091
7.8052
7.8000
7.7968
7.7878
7.7838
7.7812
7.7794
7.5534
7.5510
7.5390
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7.4943
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7.4806
7.4762
7.4705
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7.3820
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7.3656
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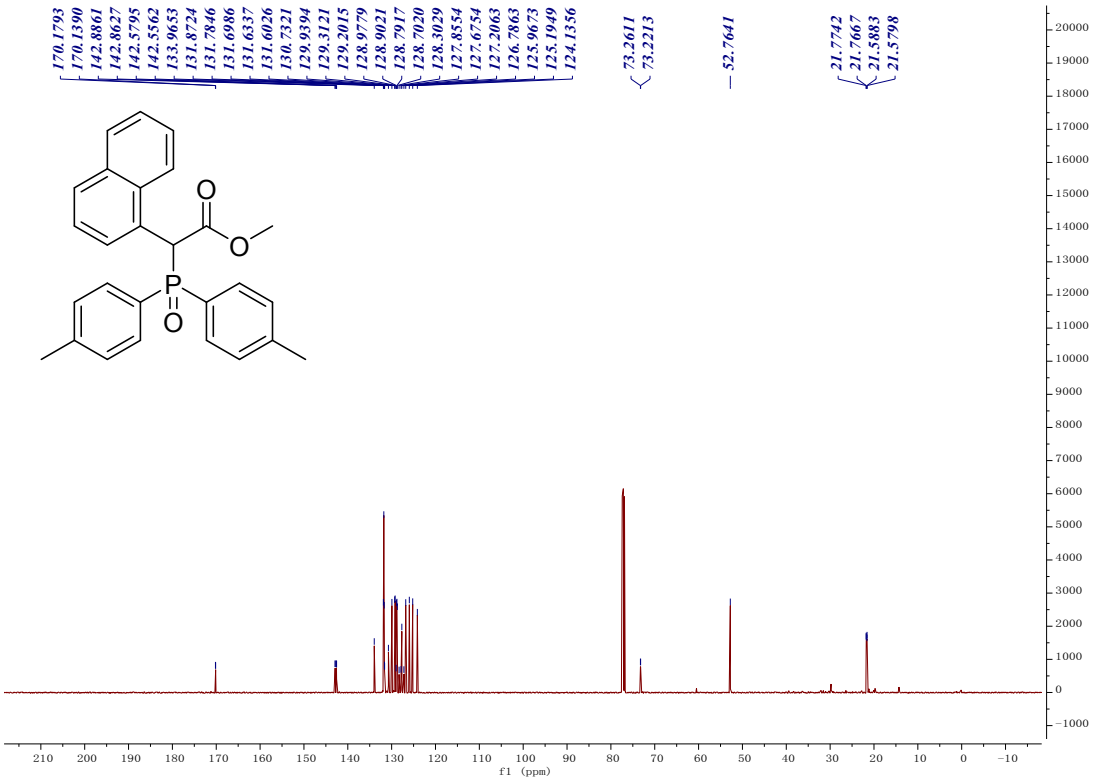
7.2647
6.9626
6.9561
6.9466
6.9401
6.4232
6.4028
3.6219
2.3870
2.3761
2.2371
O
O
P
O
0.99
4.24
1.02
2.17
3.35
2.22
2.19
1.00
3.07
3.36
2.92
f1 (ppm)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170.1390
142.8861
142.8627
142.5795
142.5562
133.9653
131.8724
131.7846
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131.6026
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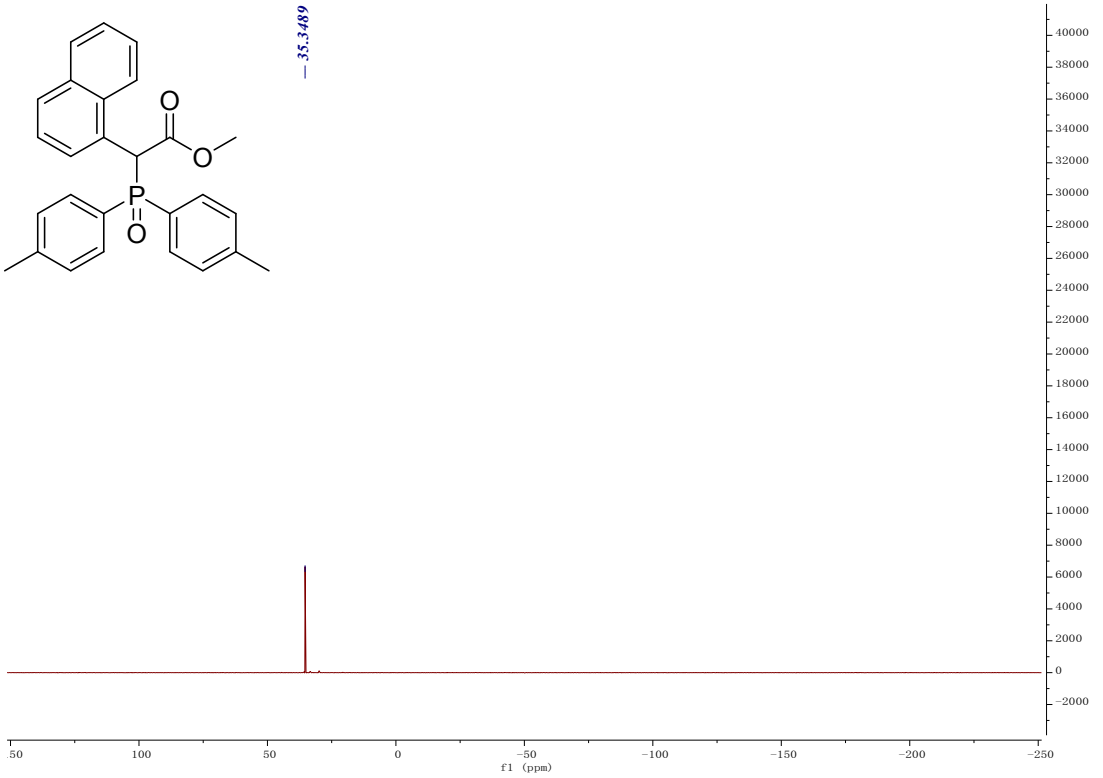
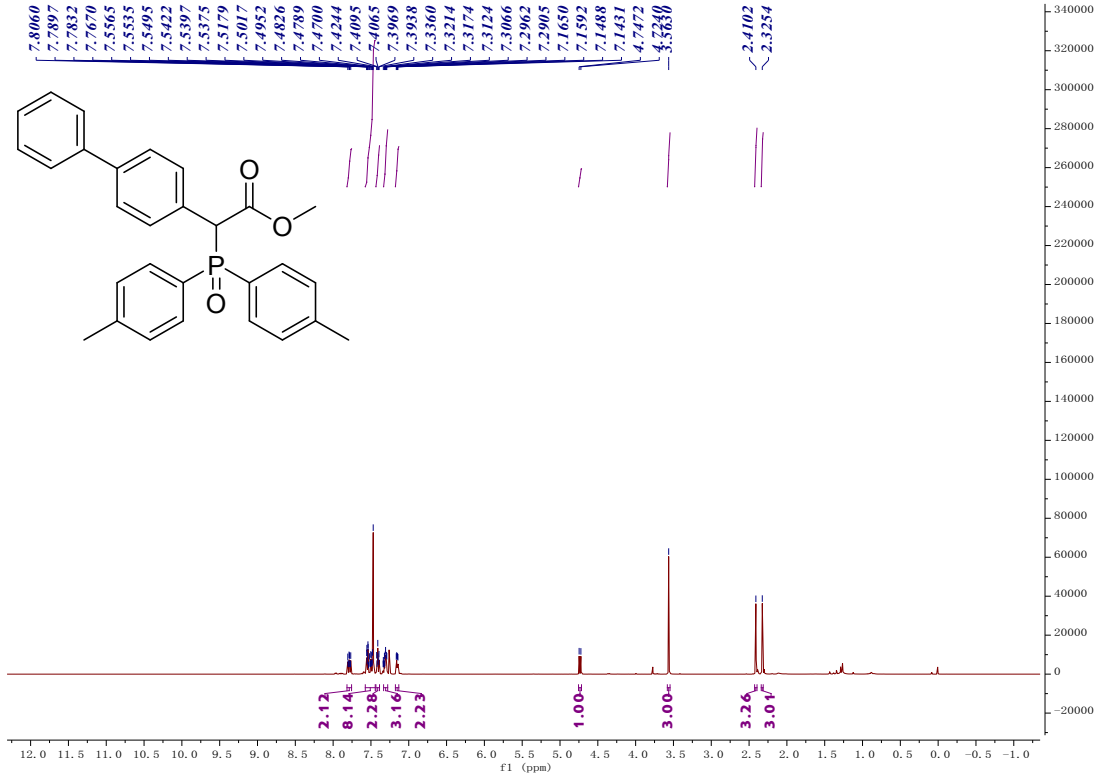
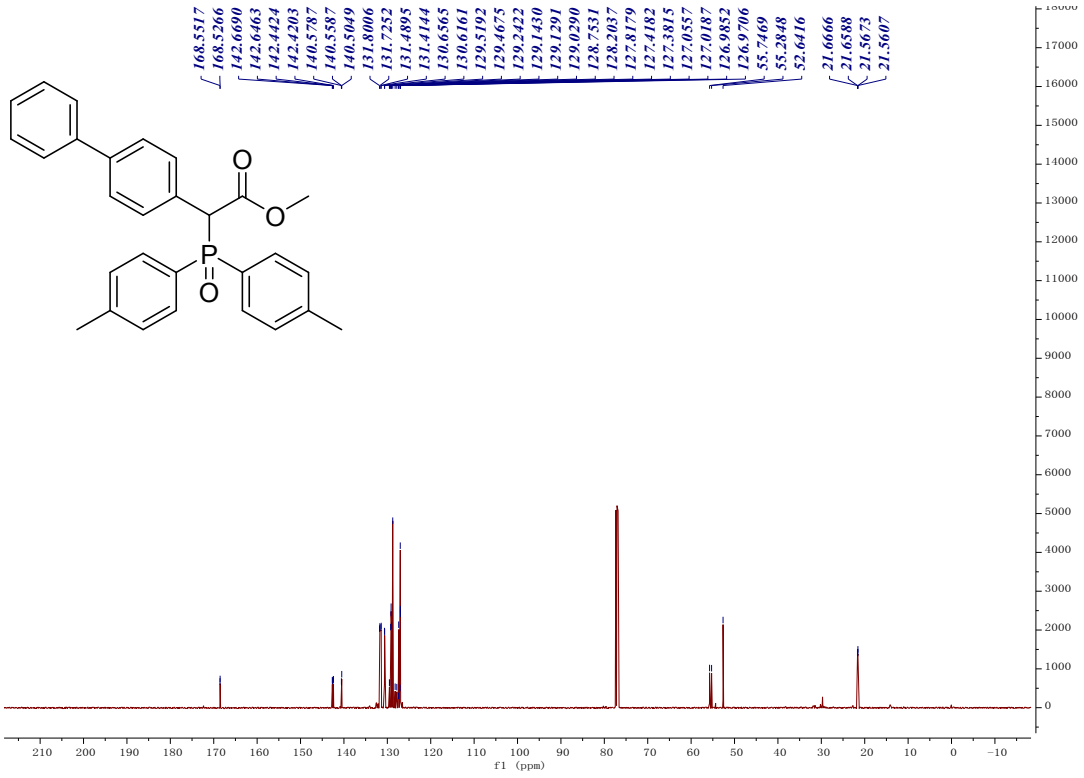
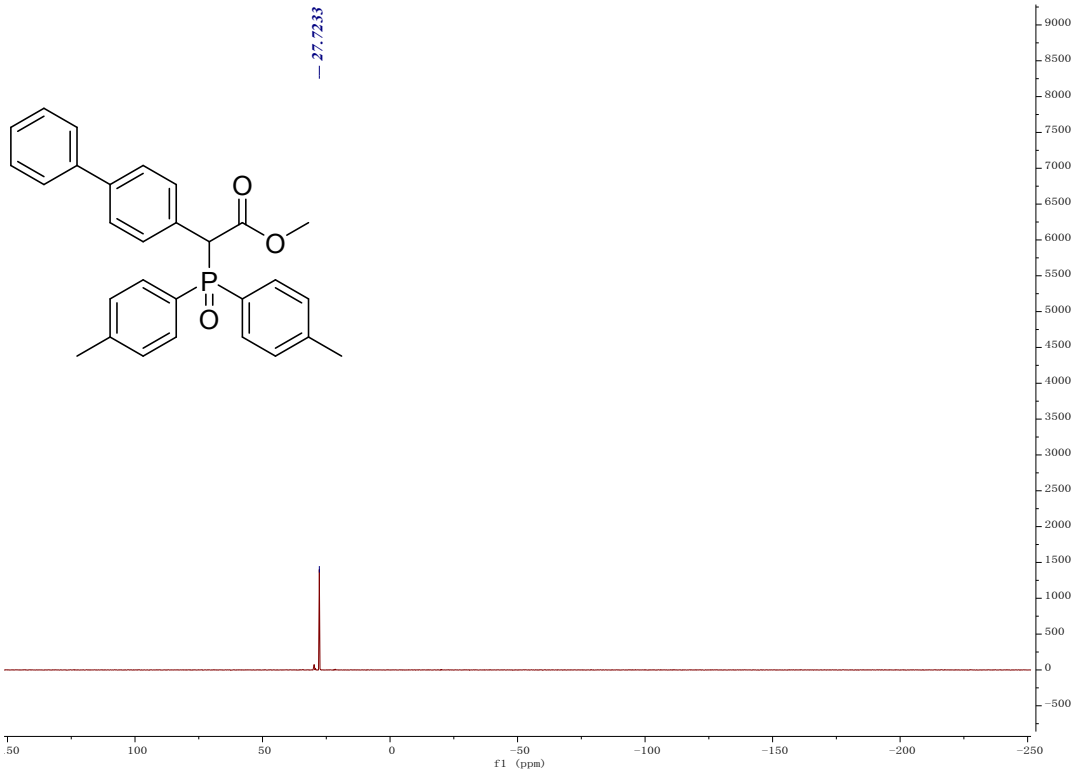
129.9394
129.3121
129.2015
128.9779
128.9021
128.7917
128.7020
128.3029
127.8554
127.6754
127.2063
126.7863
125.9673
125.1949
124.1356
73.2611
73.2213
52.7641
21.7742
21.7667
21.5883
21.5798
O
O
P
O
f1 (ppm)



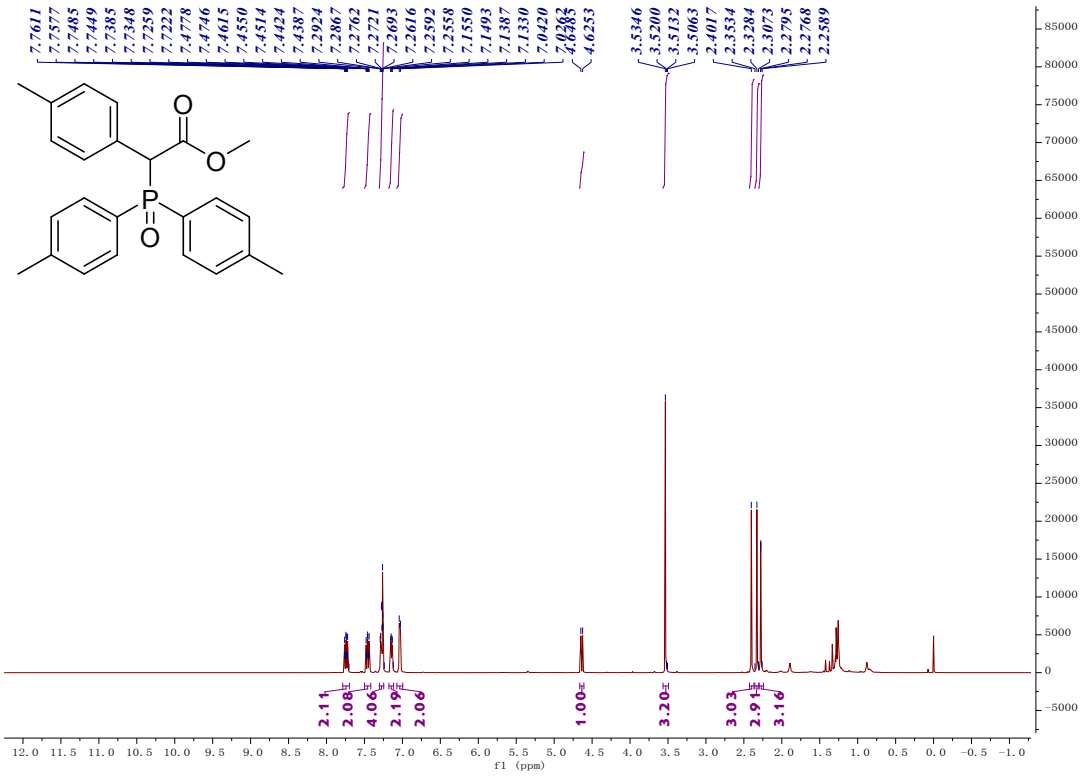
Methyl 2-([1,1'-biphenyl]-4-yl)-2-(di-p-tolylphosphoryl)acetate (3n)







Methyl 2-(di-p-tolylphosphoryl)-2-(p-tolyl)acetate (3o)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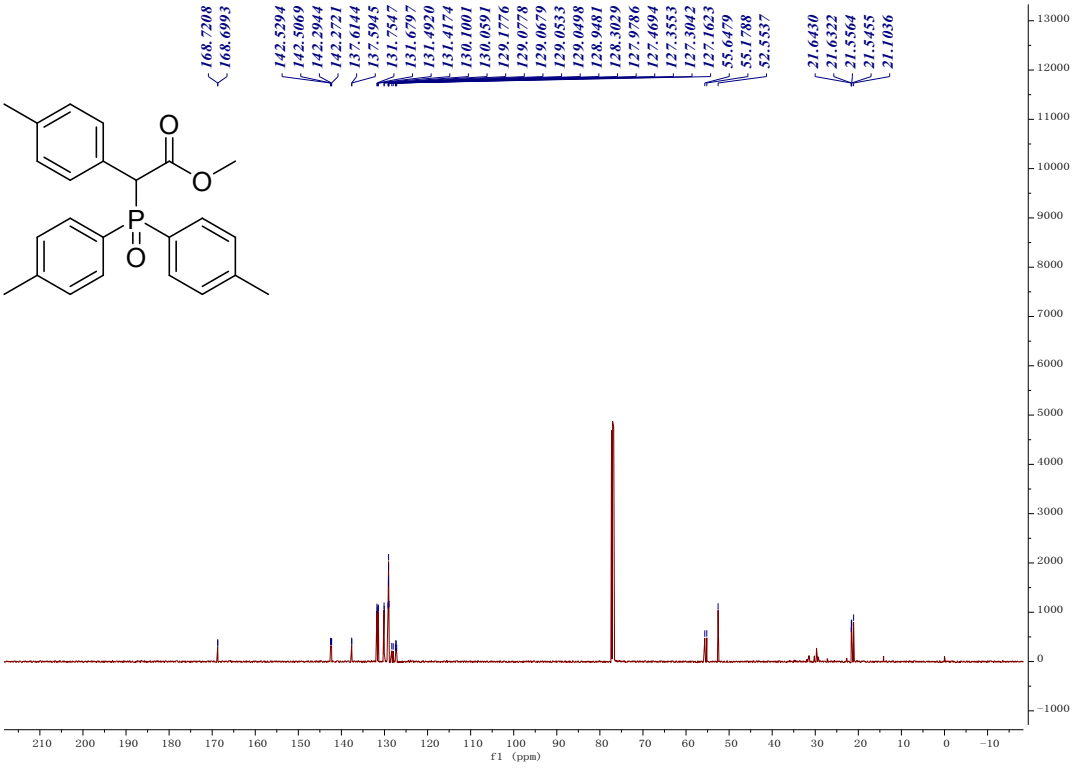
7.7385
7.7348
7.7259
7.7222
7.4778
7.4746
7.4615
7.4550
7.4514
7.4424
7.4387
7.2924
7.2867
7.2762
7.2721
7.2693
7.2616
7.2592
7.2558
7.1550
7.1493
7.1387
7.1330
7.0420
4.6253
3.5346
3.5200
3.5132
3.5063
2.4017
2.3534
2.3284
2.3073
2.2795
2.2768
2.2589
2.11
2.08
4.06
2.19
2.06
1.00
3.20
3.03
2.94
3.16
f1 (ppm)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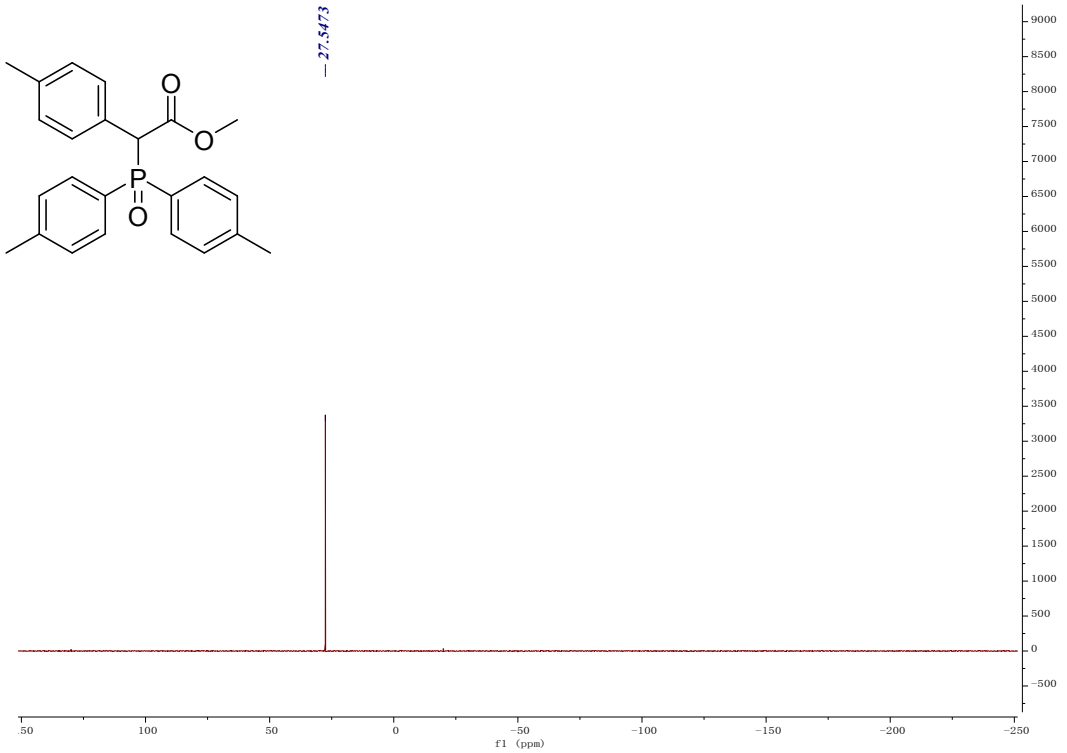
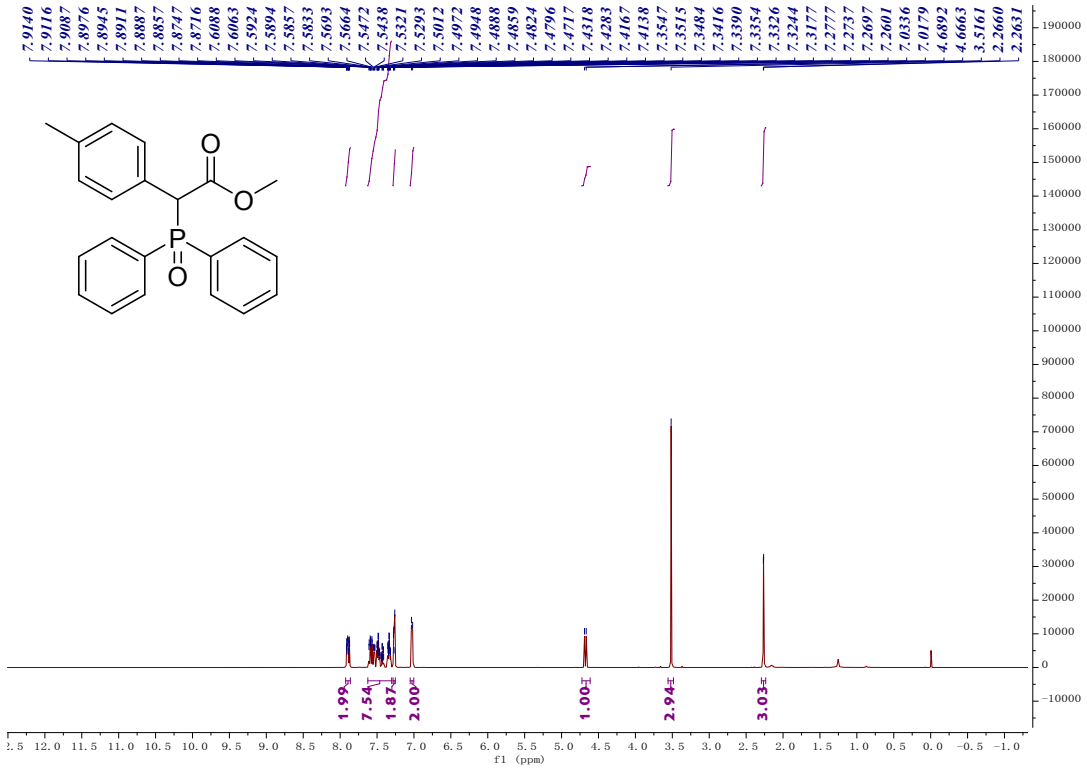
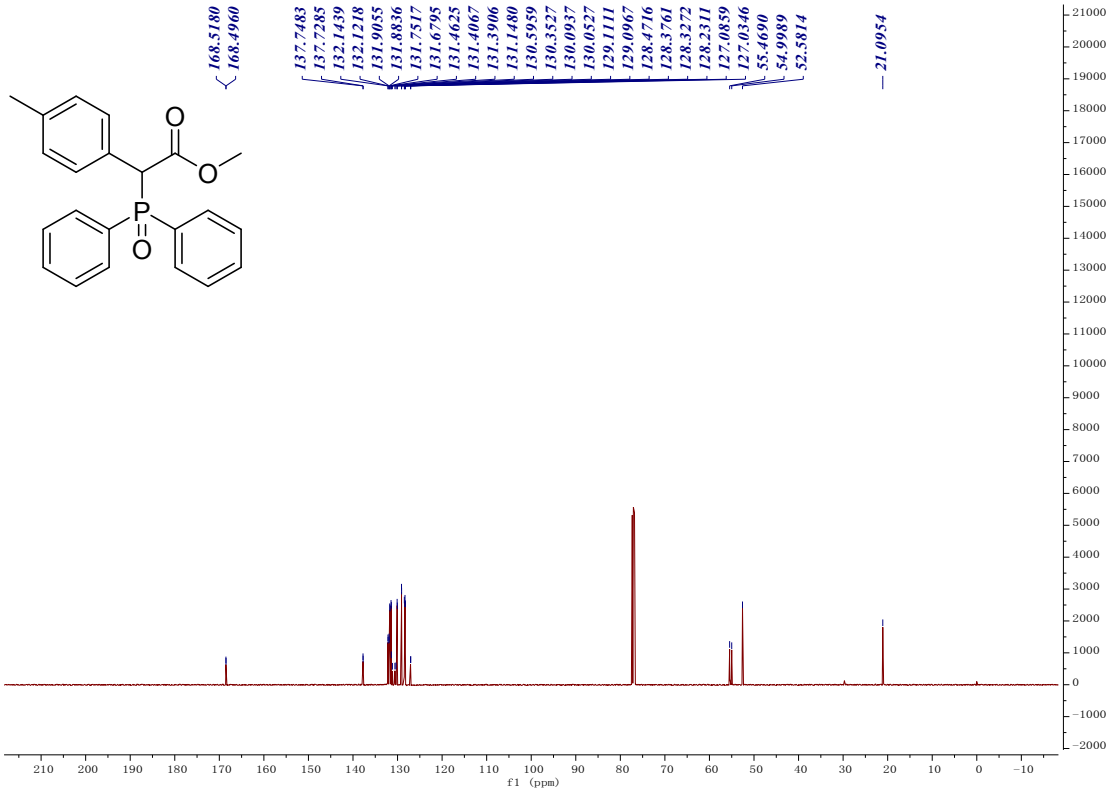
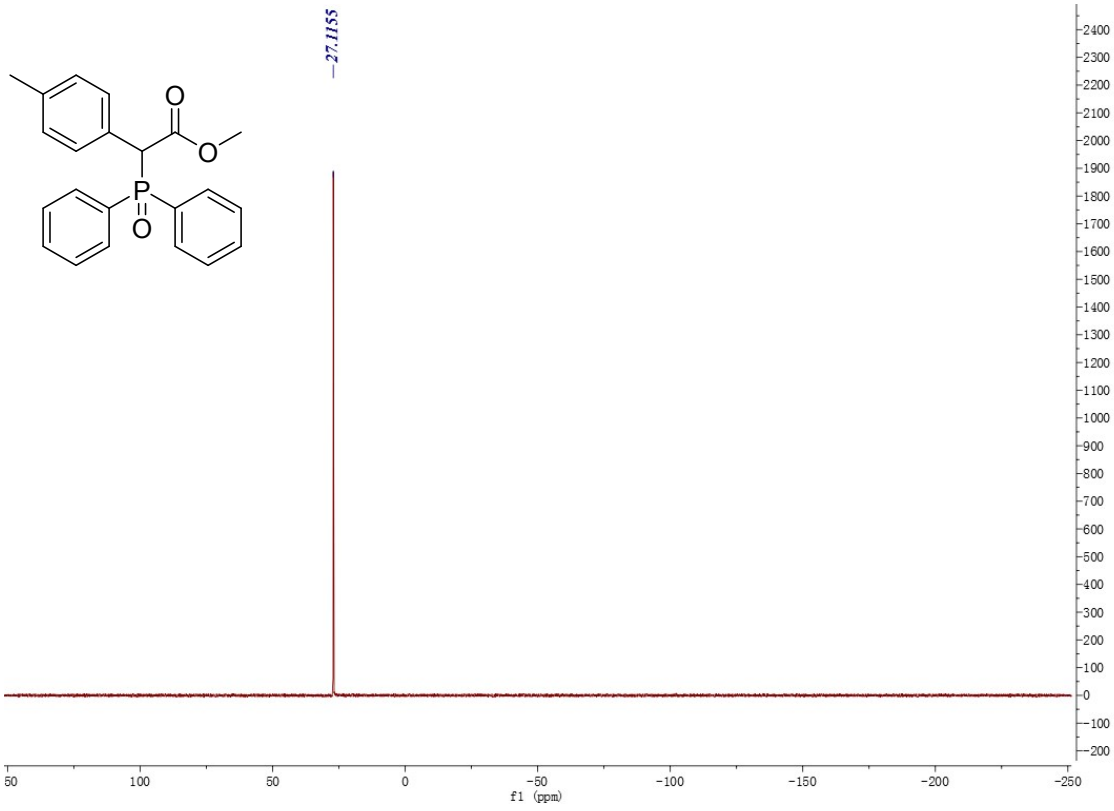
142.5294
142.5069
142.2944
142.2721
137.6144
137.5945
131.7547
131.6797
131.4920
131.4174
130.1001
130.0591
129.1776
129.0778
129.0679
129.0533
129.0498
128.9481
128.3029
127.9786
127.4694
127.3553
127.3042
127.1623
55.6479
55.1788
52.5537
21.6430
21.6322
21.5564
21.5455
21.1036
f1 (ppm)



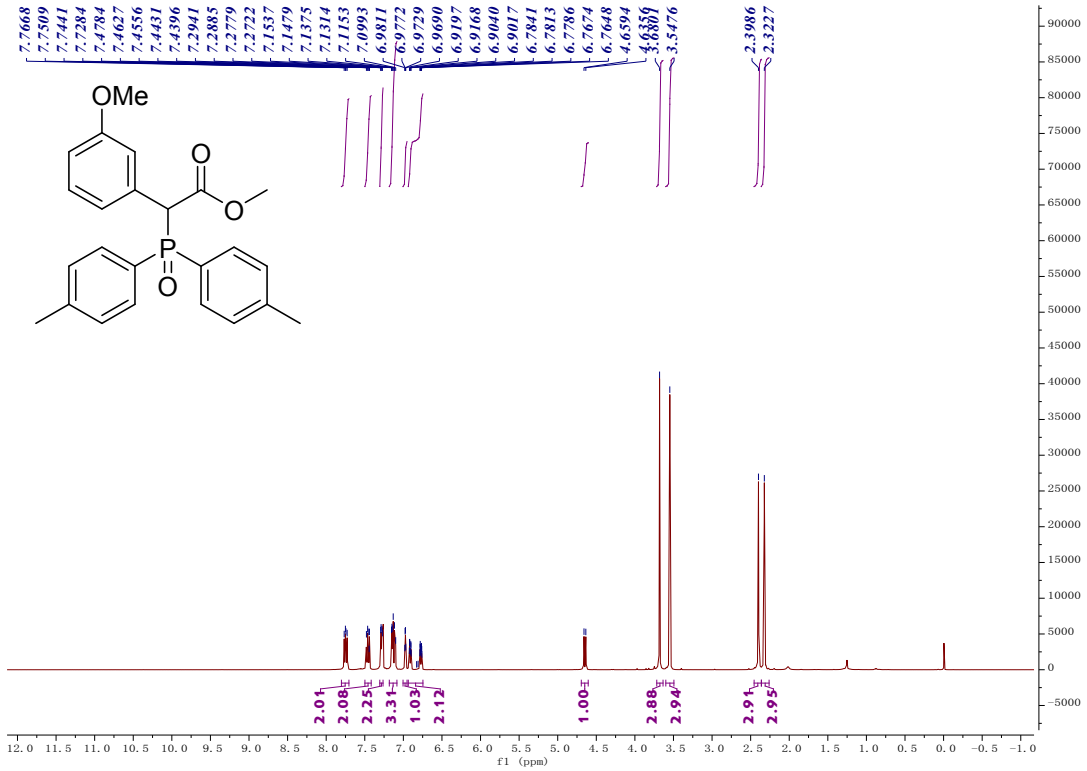
Methyl 2-(diphenylphosphoryl)-2-(p-tolyl)acetate (3p)







Methyl 2-(di-p-tolylphosphoryl)-2-(3-methoxyphenyl)acetate (3q)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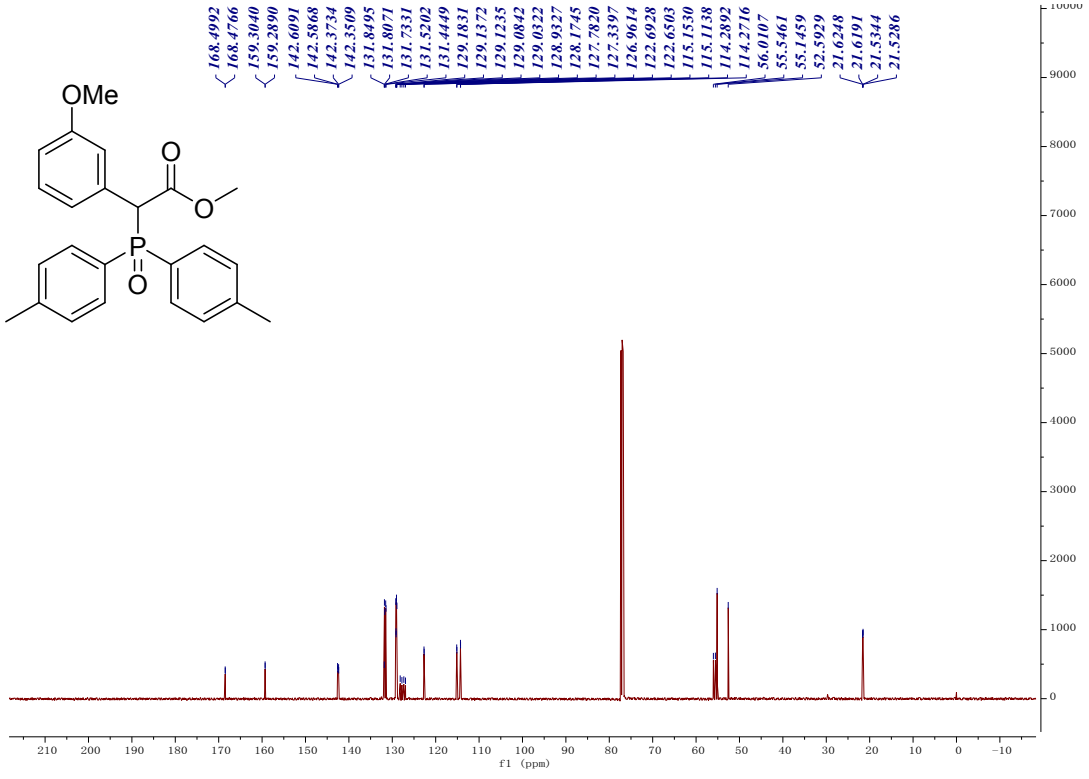
7.4784
7.4627
7.4556
7.4431
7.4396
7.2941
7.2885
7.2779
7.2722
7.1537
7.1479
7.1375
7.1314
7.1153
7.0993
6.9811
6.9772
6.9729
6.9690
6.9197
6.9168
6.9040
6.9017
6.7841
6.7813
6.7786
6.7674
6.7648
4.6594
3.6801
3.5476
2.3986
2.3227
OMe
O
O
P
O
2.01
2.08
2.25
3.31
1.03
2.12
1.00
2.88
2.94
2.91
2.95
f1 (ppm)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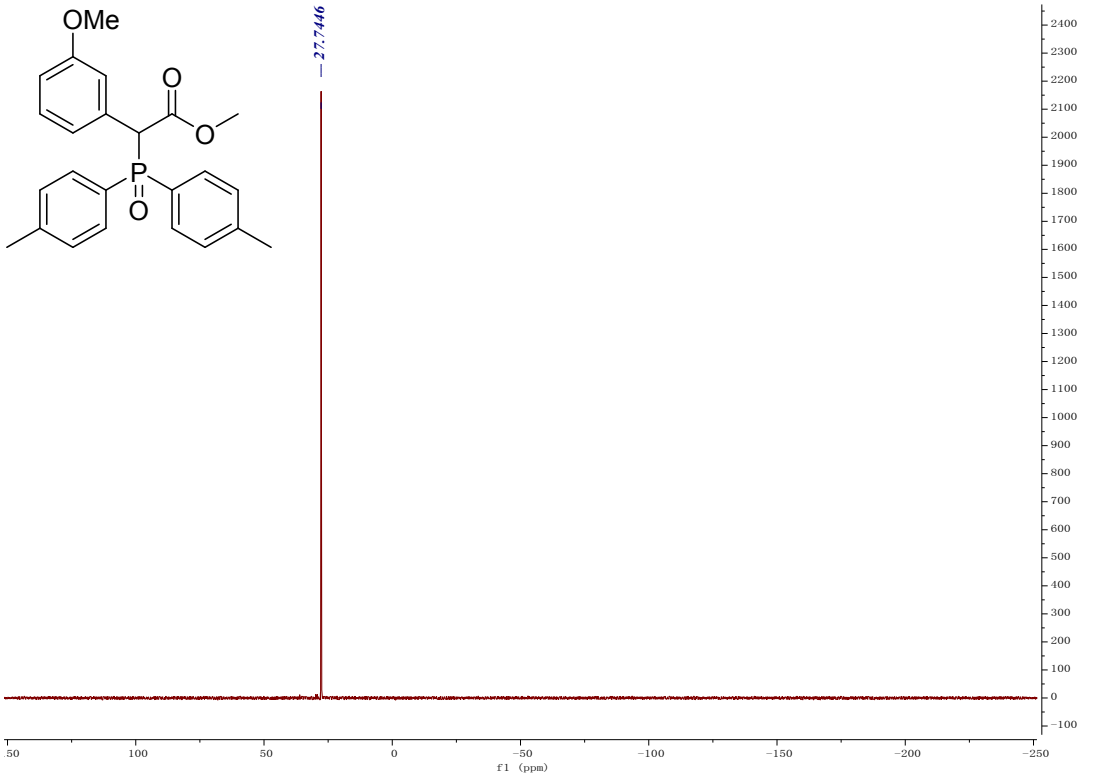
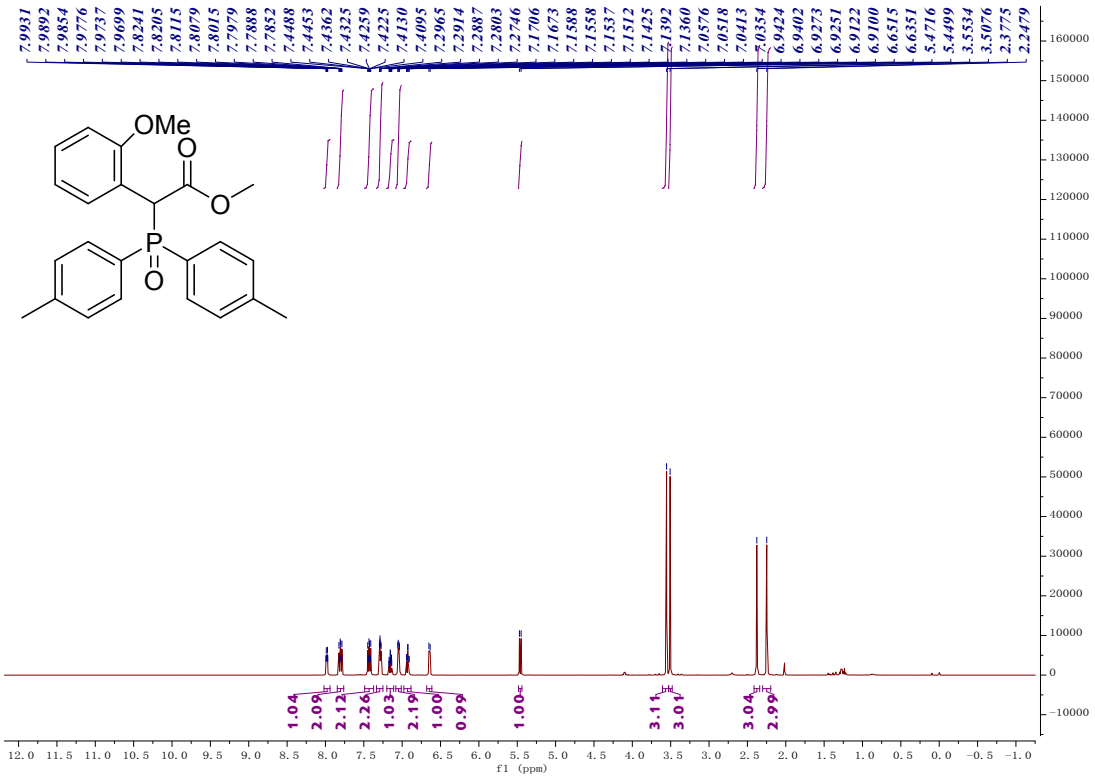
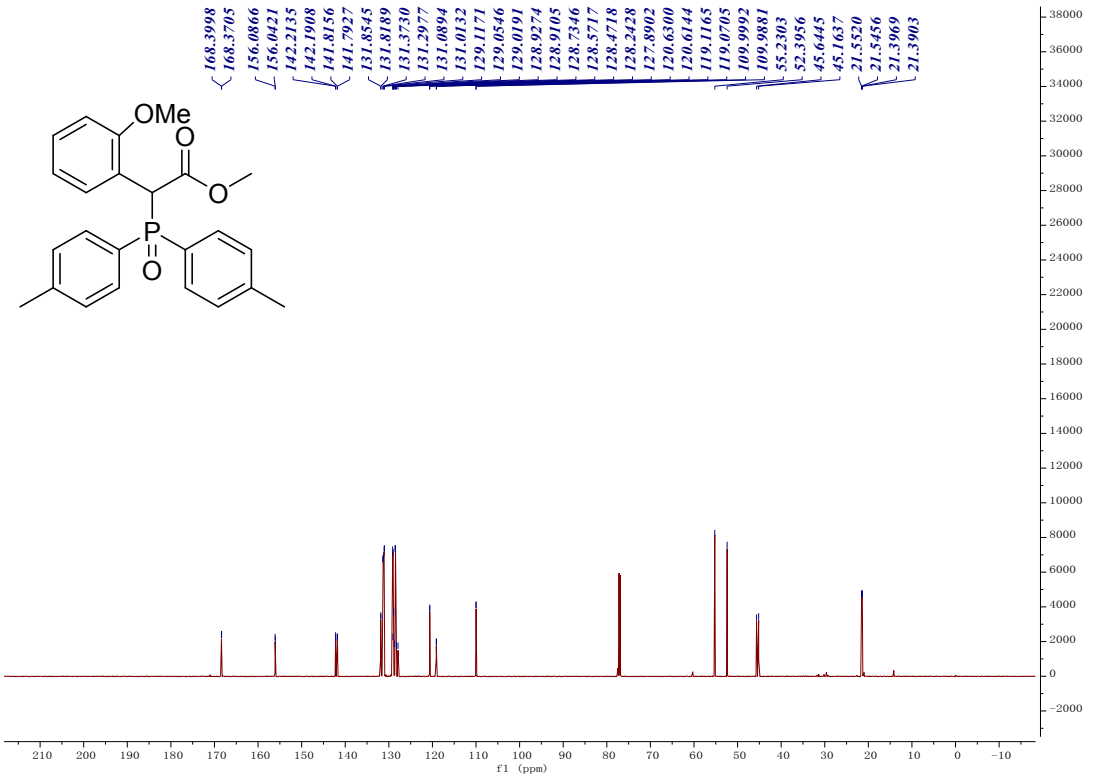
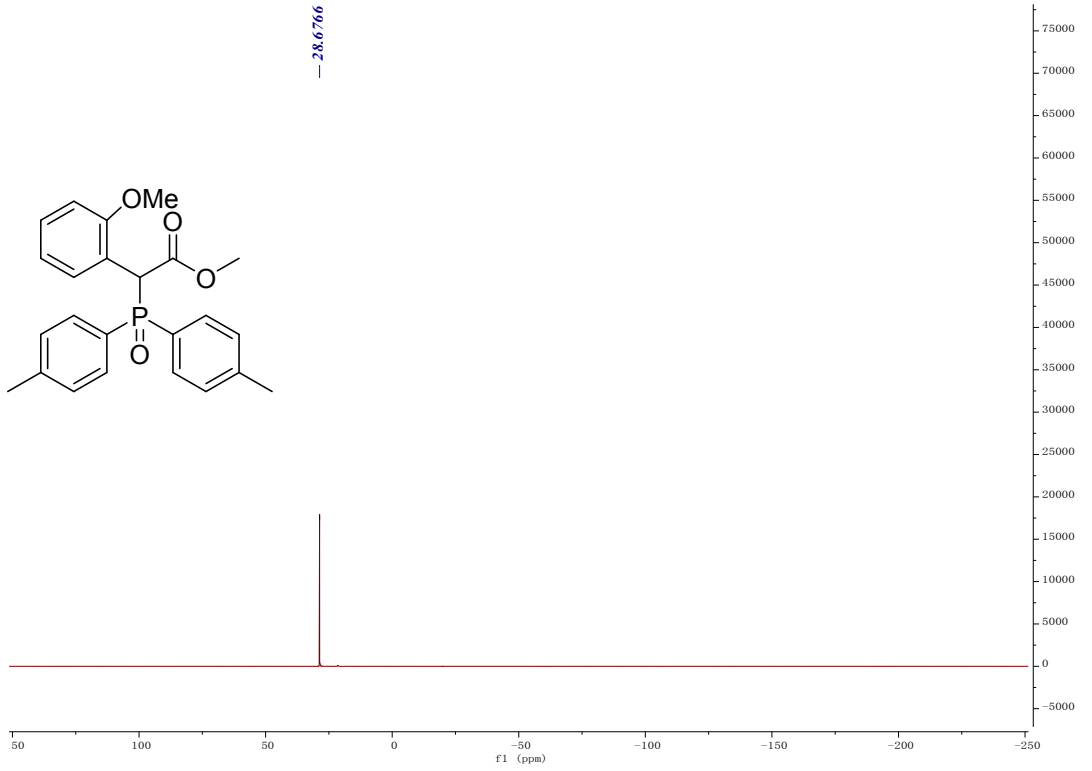
168.4766
159.3040
159.2890
142.6091
142.5868
142.3734
142.3509
131.8495
131.8071
131.7331
131.5202
131.4449
129.1831
129.1372
129.1235
129.0842
129.0322
128.9327
128.1745
127.7820
127.3397
126.9614
122.6928
122.6503
115.1530
115.1138
114.2892
114.2716
56.0107
55.5461
55.1459
52.5929
21.6248
21.6191
21.5344
21.5286
OMe
O
O
P
O
f1 (ppm)



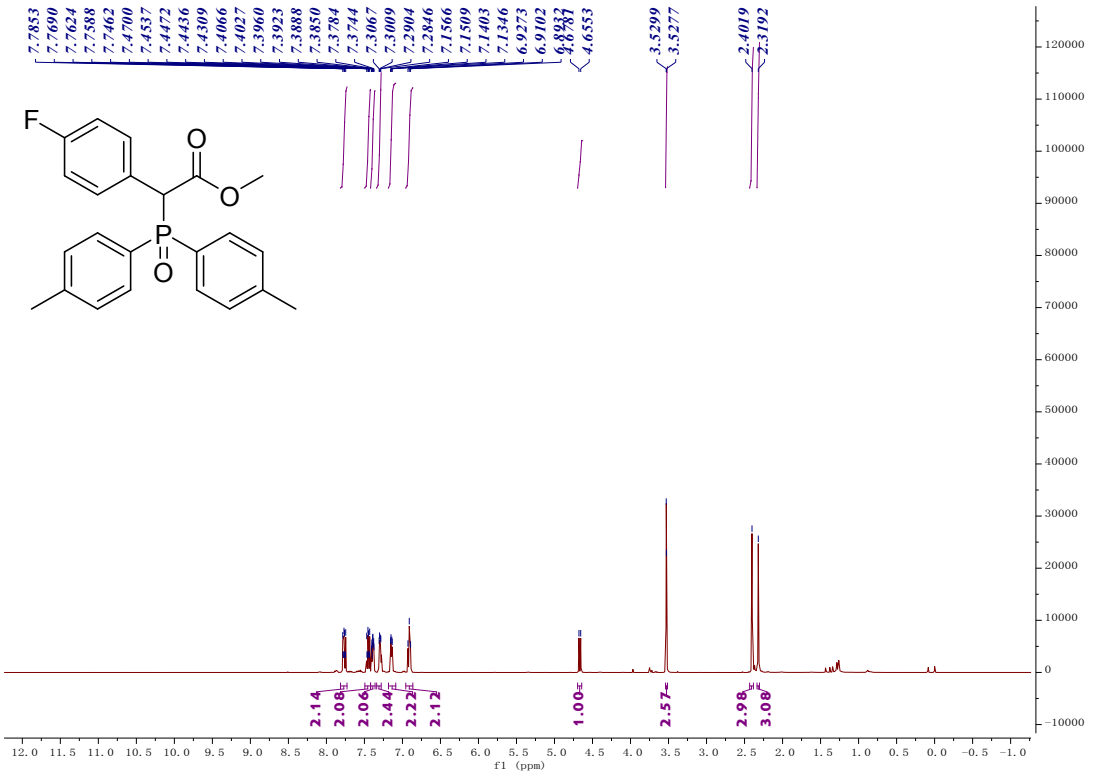
Methyl 2-(di-p-tolylphosphoryl)-2-(2-methoxyphenyl)acetate (3r)







Methyl 2-(di-p-tolylphosphoryl)-2-(4-fluorophenyl)acetate (3s)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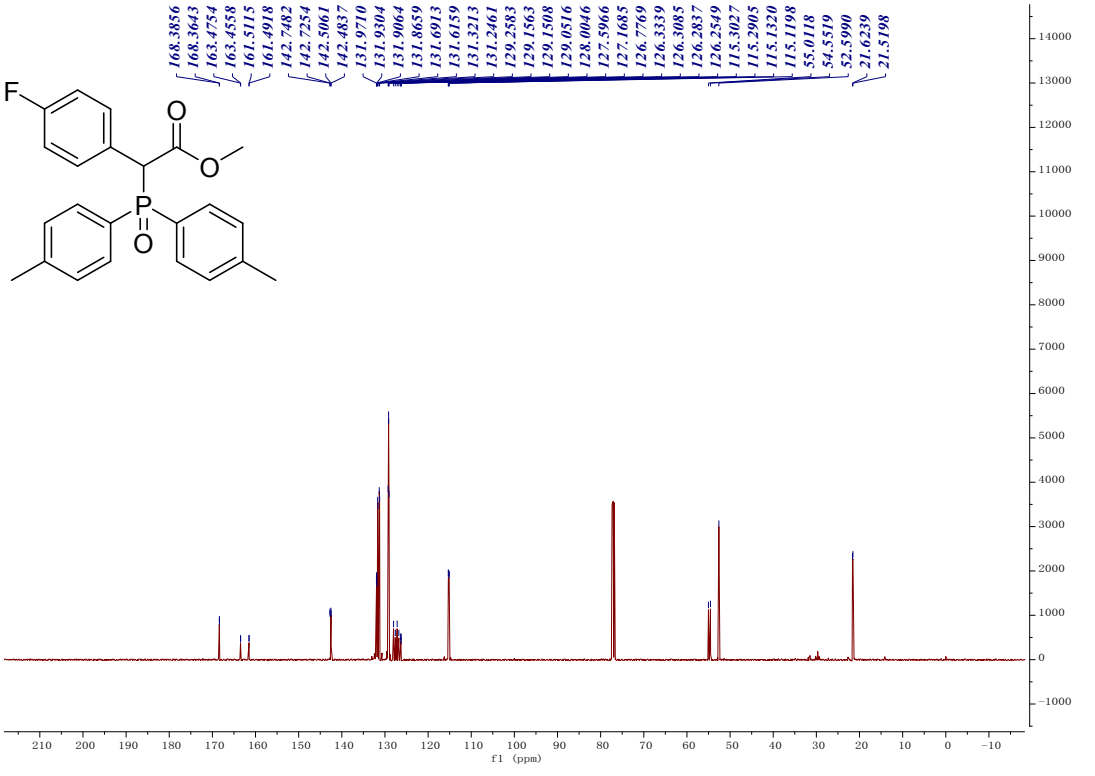
7.7690
7.7624
7.7588
7.7462
7.4700
7.4537
7.4472
7.4436
7.4309
7.4066
7.4027
7.3960
7.3923
7.3888
7.3850
7.3784
7.3744
7.3067
7.3009
7.2904
7.2846
7.1566
7.1509
7.1403
7.1346
6.9273
6.9102
4.6553
3.5299
3.5277
2.4019
2.3192
F
O
O
P
O
2.14
2.08
2.06
2.47
2.22
2.12
1.00
2.57
2.98
3.08
f1 (ppm)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142.7254
142.5061
142.4837
131.9710
131.9304
131.9064
131.8659
131.6913
131.6159
131.3213
131.2461
129.2583
129.1563
129.1508
129.0516
128.0046
127.5966
127.1685
126.7769
126.3339
126.3085
126.2837
126.2549
115.3027
115.2905
115.1320
115.1198
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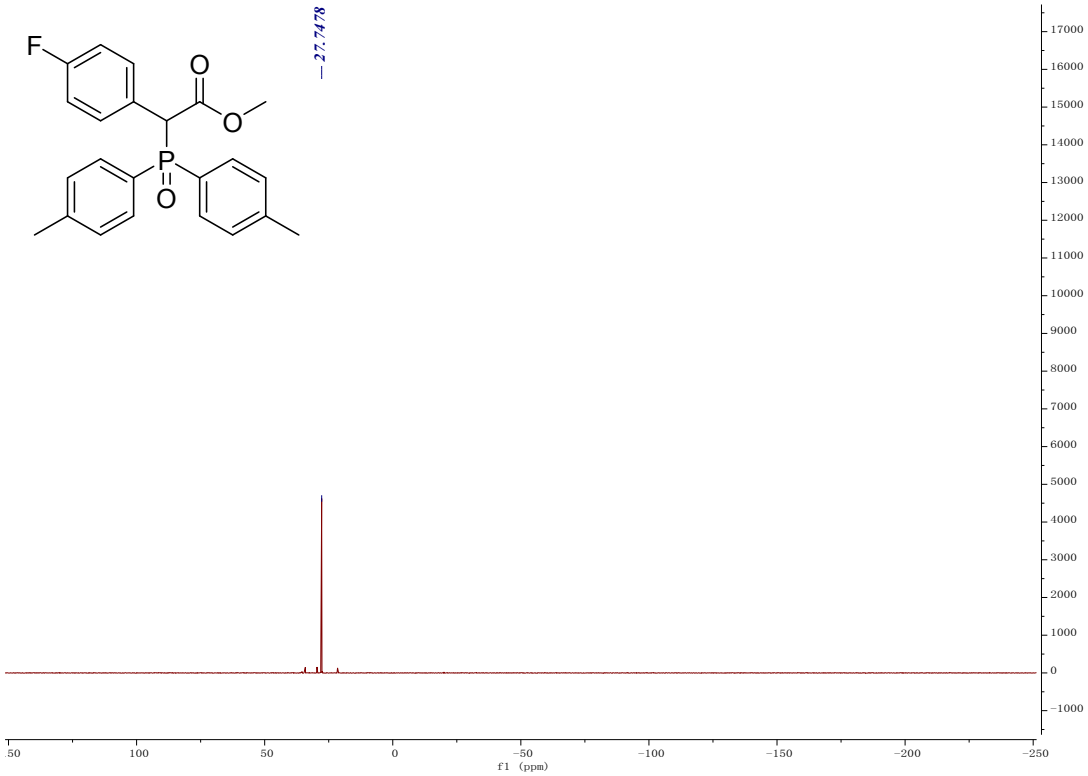
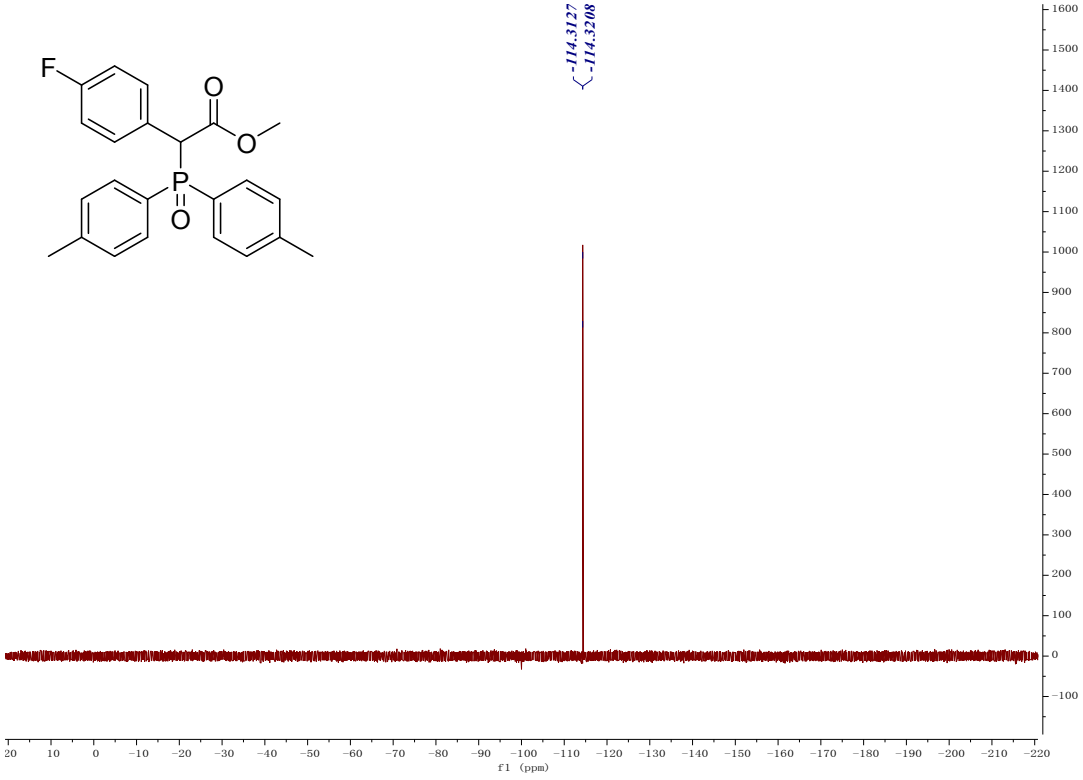
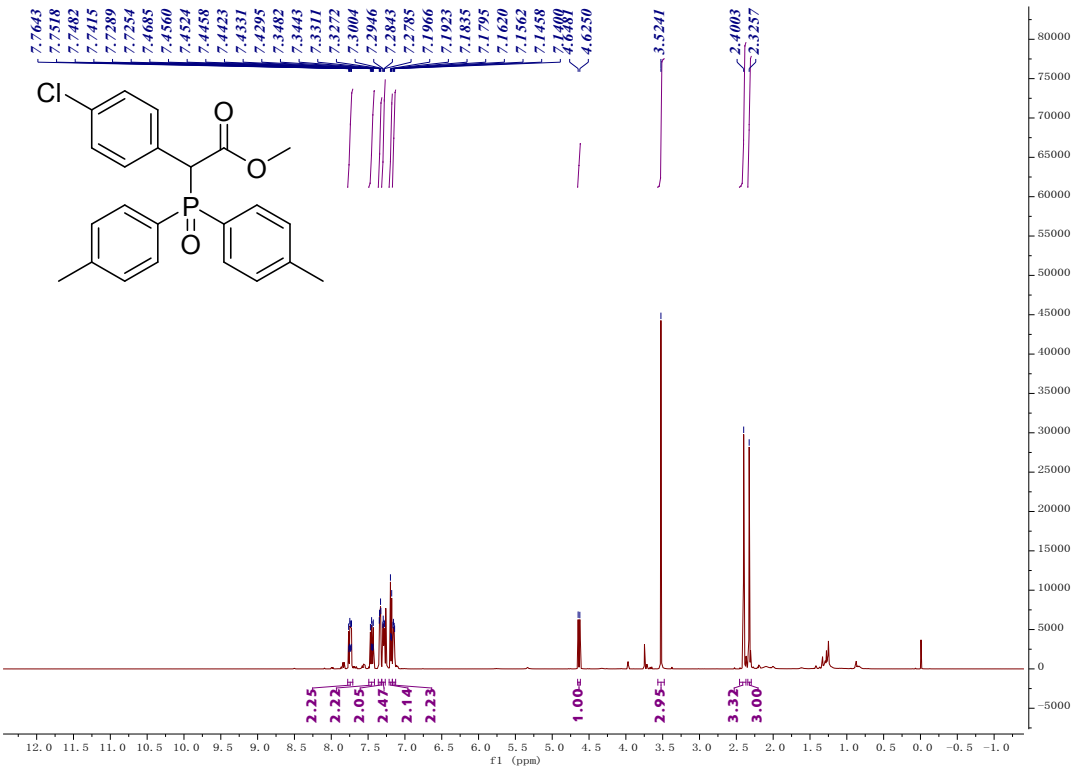
54.5519
52.5990
21.6239
21.5198
F
O
O
P
O
f1 (ppm)





Methyl 2-(4-chlorophenyl)-2-(di-p-tolylphosphoryl)acetate (3t)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7.7482
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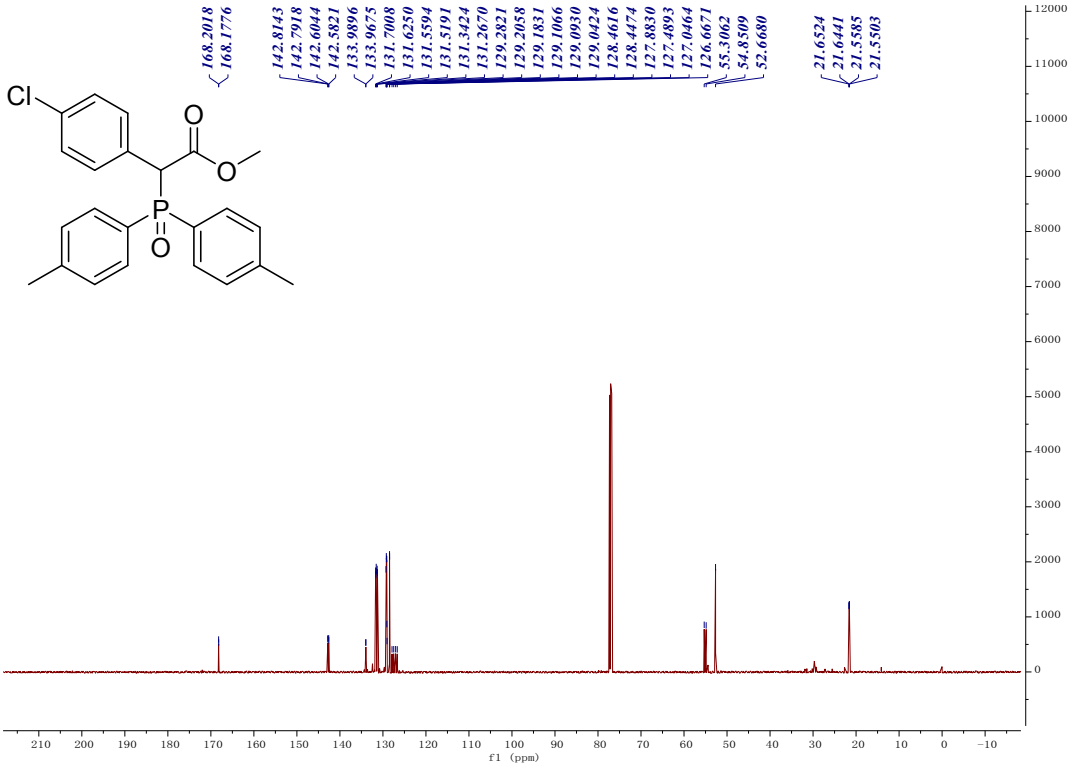
7.7289
7.7254
7.4685
7.4560
7.4524
7.4458
7.4423
7.4331
7.4295
7.3482
7.3443
7.3311
7.3272
7.3004
7.2946
7.2843
7.2785
7.1966
7.1923
7.1835
7.1795
7.1620
7.1562
7.1458
7.1400
4.6481
4.6250
3.5241
2.4003
2.3257
Cl
O
O
P
O
2.25
2.22
2.05
2.47
2.14
2.23
1.00
2.95
3.32
3.00
f1 (ppm)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142.7918
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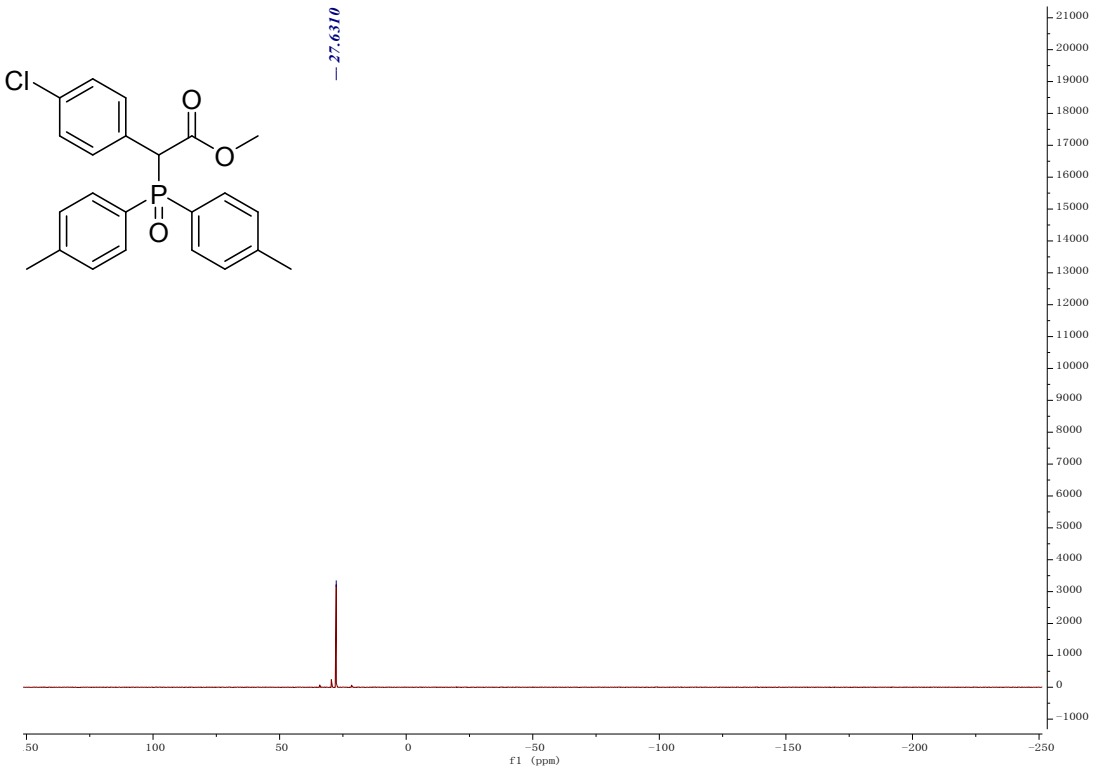
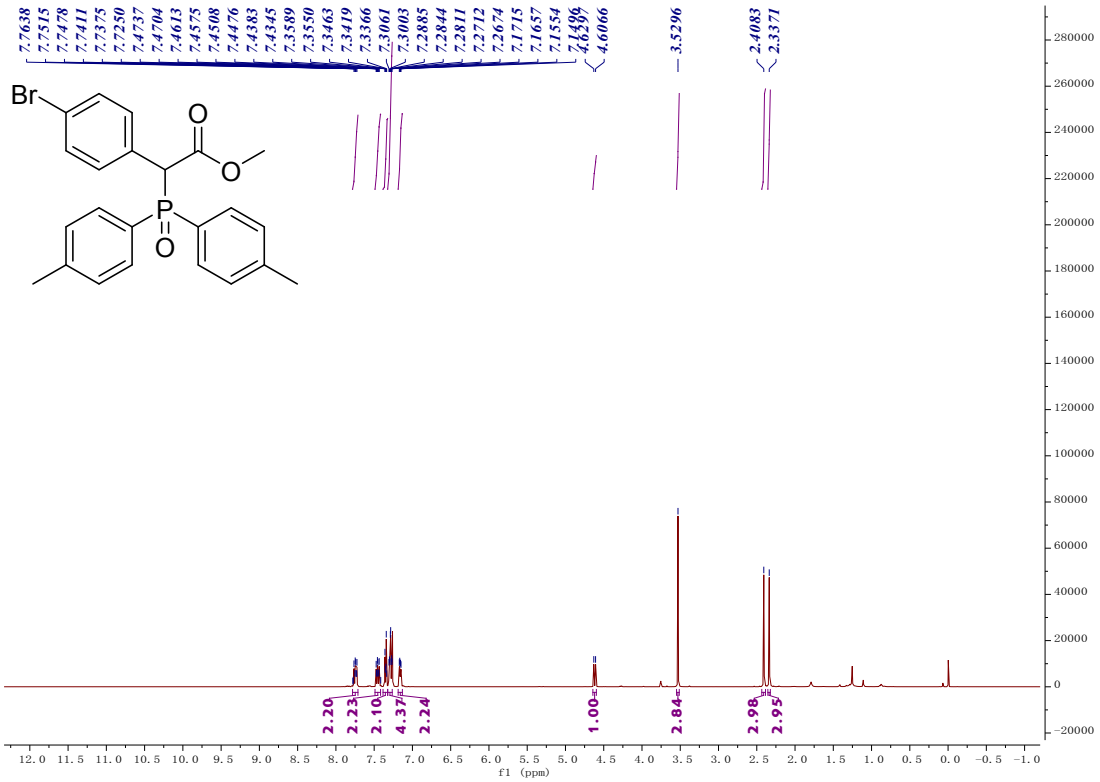
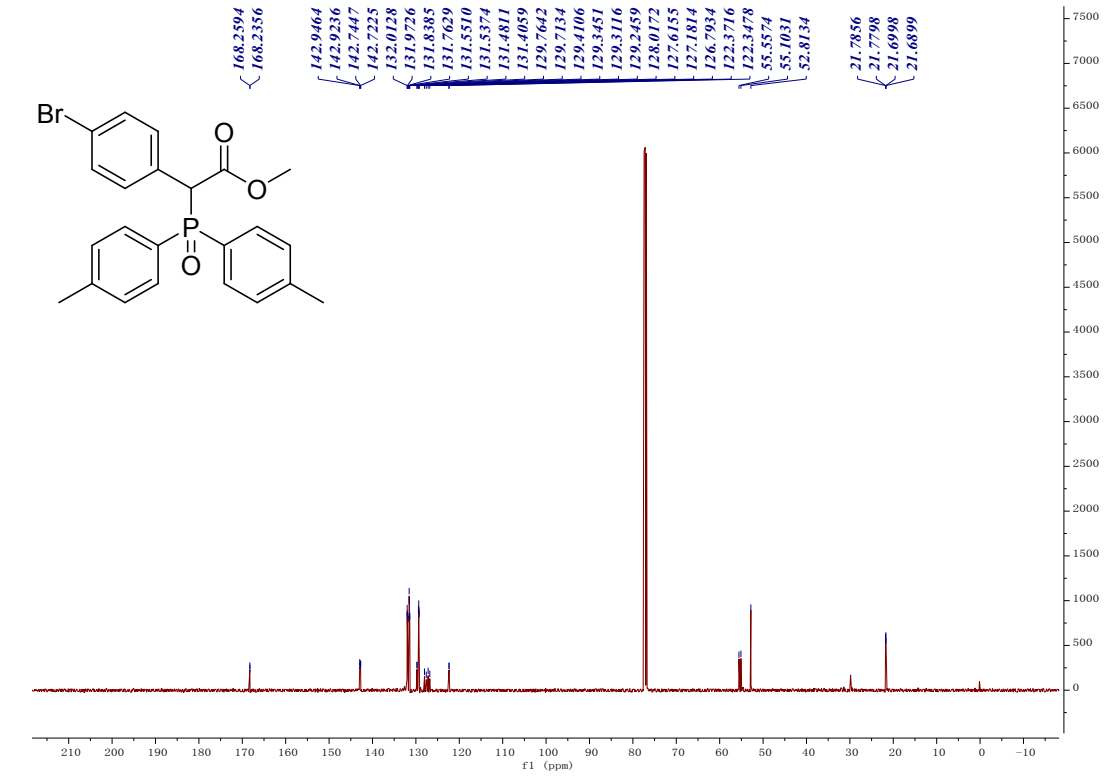
142.5821
133.9896
133.9675
131.7008
131.6250
131.5594
131.5191
131.3424
131.2670
129.2821
129.2058
129.1831
129.1066
129.0930
129.0424
128.4616
128.4474
127.8830
127.4893
127.0464
126.6671
55.3062
54.8509
52.6680
21.6524
21.6441
21.5585
21.5503
Cl
O
O
P
O
f1 (ppm)



Methyl 2-(4-bromophenyl)-2-(di-p-tolylphosphoryl)acetate (3u)

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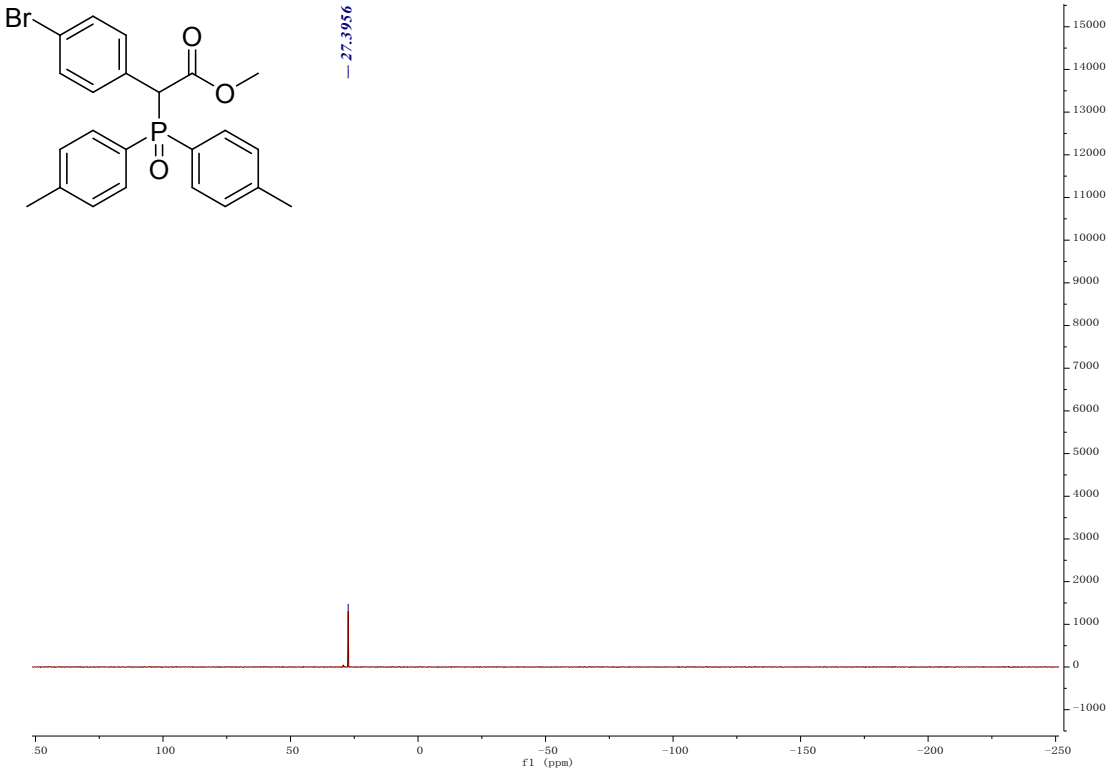
142.9236
142.7447
142.7225
132.0128
131.9726
131.8385
131.7629
131.5510
131.5374
131.4811
131.4059
129.7642
129.7134
129.4106
129.3451
129.3116
129.2459
128.0172
127.6155
127.1814
126.7934
122.3716
122.3478
55.5574
55.1031
52.8134
21.7856
21.7798
21.6998
21.6899
Br
O
O
P
O
f1 (ppm)


27.3956
Br
O
O
P
O
f1 (ppm)