Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

An Efficient Direct Phosphinylation and Alkylation of Ketone to Construct C-P and C-C bonds: Access to α,α-Disubstituted γ-Ketophosphine Oxides

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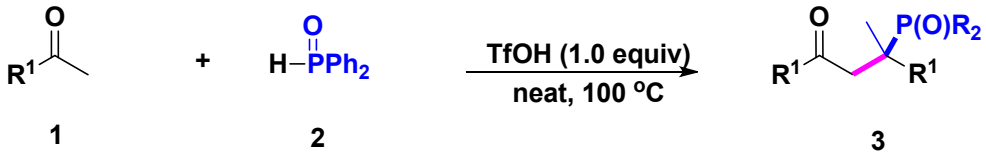
Contents

General

All reactions involving air- or moisture-sensitive reagents were carried out under an argon atmosphere. All chemicals were purchased from Chemical and used without further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Silica gel 60 (230-400 mesh) was used for column chromatography.^{1}H and ^{13}C NMR spectra were recorded using $CDCl_3$ solvent on a Bruker advance III 400 spectrometer (400 MHz for ^{1}H,162 MHz for ^{31}P and 101 MHz for ^{13}C),. The chemical shift is given indimensionless δ values and is frequency referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy.

Experimental Section

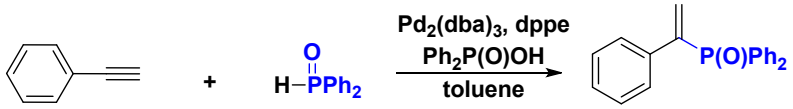
1. General procedure for synthesis of γ-ketophosphine oxides



1 2 3

An oven-dried 10 mL screw-capped vial containing **1** (0.1 mmol, 1.0 equiv), **2** (0.1 mmol, 1.0 equiv), HOTf (0.1 mmol, 1.0 equiv), and then heated to 100 °C until the starting material has disappeared for 16 hours under air condition (monitored by TLC), then was purified by column chromatography using EA/PE as eluent to afford the desired product **3**.

2. Synthesis of 4[1]



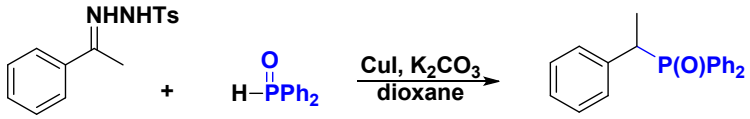
4

An oven-dried schlenck tube containing a Teflon-coated stir bar was charged with $Pd_2(dba)_3$ (1 mol%), dppe (2 mol%), diphenylphosphorus acid(4 mol%) and 0.5

1. Chen T, Zhao C-Q, Han L-B. Hydrophosphorylation of Alkynes Catalyzed by Palladium: Generality and Mechanism. *Journal of the American Chemical Society* **2018**, *140*, 3139-3155.

mL toluene under N_2 atmosphere and stirred at room temperature for 10 min, then 0.5 mmol diphenylphosphine oxide and 0.5 mmol alkynes were added and the mixture was stirred at 100 °C overnight. After removal of the solvent, the residues were passed through a short silica chromatography to afford the pure product diphenyl(1-phenylvinyl)phosphine oxide **4**.

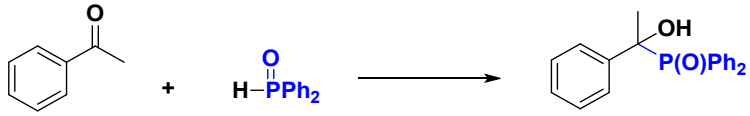
2. Synthesis of 5[2]



5

An oven-dried schlenck tube was charged with diphenylphosphine oxide (1.0 mmol), N-tosylhydrazones (1.2 equiv), CuI (10 mol %), and K_2CO_3 (3.0 equiv) in dioxane at reflux under dry argon for 5 h. then the crude product was purified by column chromatography on a short silica gel column to afford the pure product diphenyl(1-phenylethyl)phosphine oxide **5**.

3. Synthesis of 6[3]



6

A mixture of diphenylphosphine oxide (1.0 mmol) and acetophenone (1.05 mmol) as rubbed with a spatula in a round-bottomed flask (20–25 °C, 15 min, argon atmosphere) and then stirred under the same conditions for 24 h to give a solid product. The latter was washed with Et_2O (2 × 0.3 mL) and dried in vacuum to afford (1-hydroxy-1-phenylethyl)diphenylphosphine oxide **6**.

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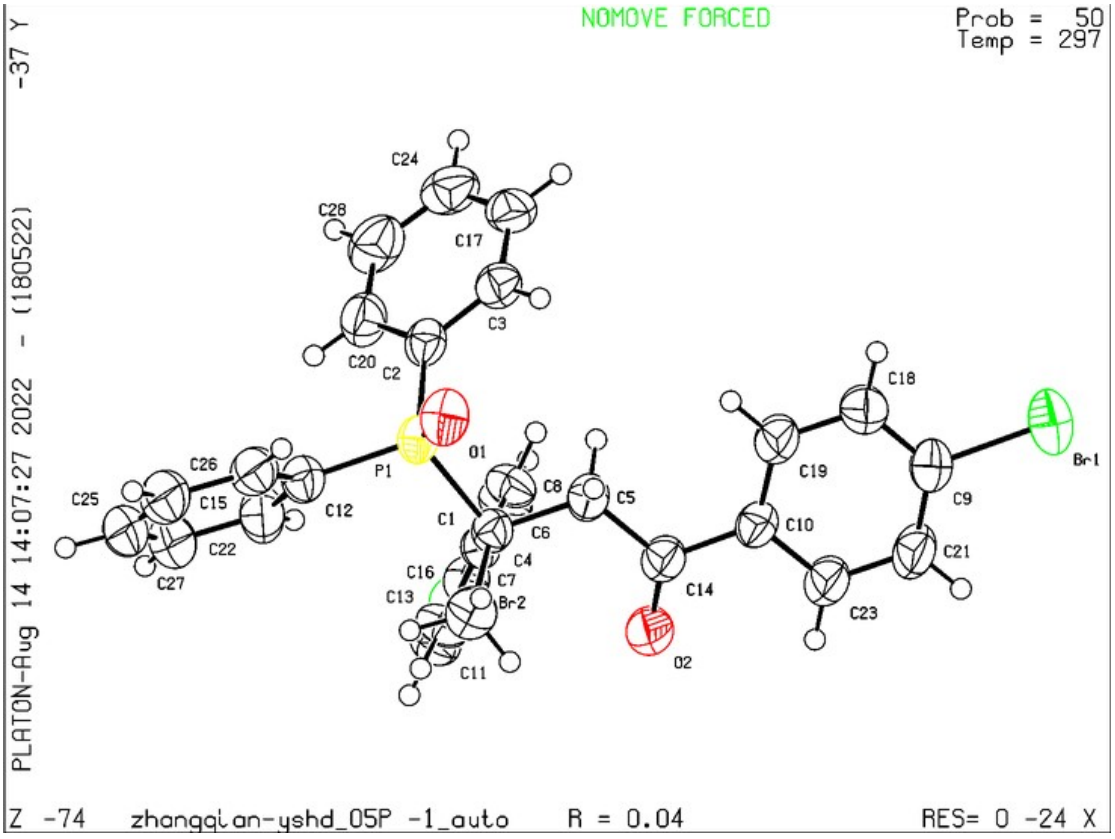
2. Chen Z-S, Zhou Z-Z, Hua H-L, Duan X-H, Luo J-Y, Wang J, Zhou P-X, Liang Y-M. Reductive coupling reactions: a new strategy for C(sp3)–P bond formation. *Tetrahedron* **2013**, *69*, 1065-1068.

3. Gusarova NK, Ivanova NI, Khrapova KO, Volkov PA, Telezhkin AA, Larina LI, Afonin AV, Pavlov DV, Trofimov BA. Catalyst- and Solvent-Free Hydrophosphorylation of Ketones with Secondary Phosphine Oxides: Green Synthesis of Tertiary α-Hydroxyphosphine Oxides. *Synthesis* **2020**, *52*, 2224-2232.

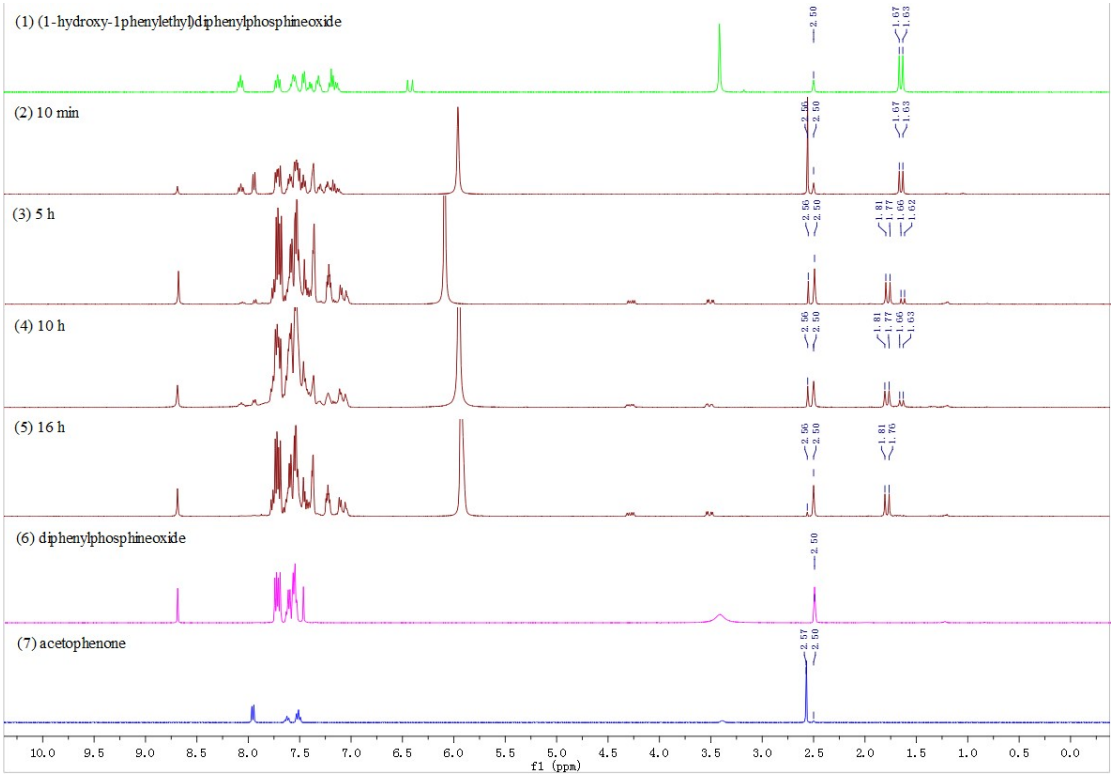
4. Crystal structure for 3fa



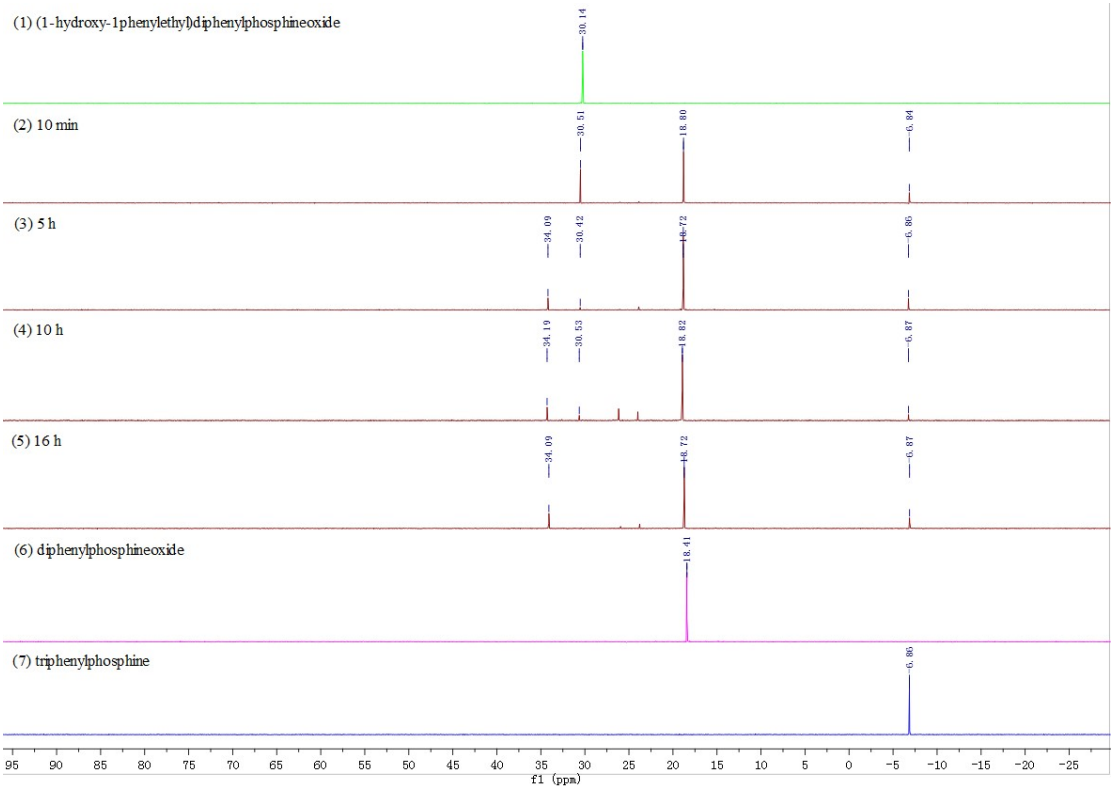
CCDC 2201338 (thermal ellipsoid is set at 50% probability)

Table 1 Crystal data and structure refinement for 3pa	
Identification code	zhangqian-yshd_0520-4_auto
Empirical formula	$C_{28}H_{23}Br_2O_2P$
Formula weight	582.25
Temperature/K	296.85(14)
Crystal system	triclinic
Space group	P-1
	13.37312(19)
Unit cell dimensions	a = 9.4895(2) Å
	10.7941(2) Å
	c = 13.7701(3) Å
	α = 96.2258(14) °
	β = 94.9520(14) °
	γ = 113.640(2) °
Volume	1234.72(4) $Å^3$
Z	2
Calculated density	1.566 g/cm^3
Absorption coefficient	4.960 mm^{-1}
F(000)	584.0
Crystal size	0.09 × 0.07 × 0.05 mm^3
Radiation	Cu Kα (λ = 1.54184)
The range for data collection/°	6.718 to 155.198
Index ranges	$-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-10 \leq l \leq 16$
Reflections collected	14374
Independent reflections	4995 [R_{int} = 0.0477, R_{sigma} = 0.0411]
Data/restraints/parameters	4995/0/299
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0446, wR_2 = 0.1255
Final R indexes [all data]	R_1 = 0.0492, wR_2 = 0.1291
Largest diff. peak/hole	0.53/-1.05 e $Å^{-3}$
Crystallization: Crystals of compound **3pa** suitable for X-ray analysis were grown from the solvent of chloroform/ethyl acetate by slow evaporation method.	

5. Time-controlled In situ ^{1}H and ^{31}P NMR spectra

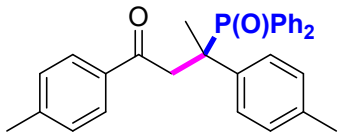


In situ ^{1}H NMR spectra



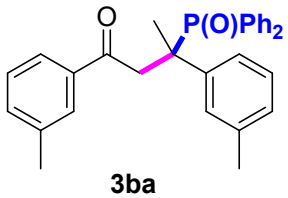
In situ ^{31}P NMR spectra

6. Analytical data of products



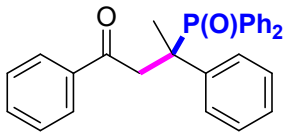
3aa

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 22.4 mg (99%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.69 – 7.56 (m, 4H), 7.56 – 7.45 (m, 2H), 7.45 – 7.34 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.92 – 6.85 (m, 2H), 4.01 (dd, *J* = 17.8, 7.9 Hz, 1H), 3.82 (dd, *J* = 17.7, 5.1 Hz, 1H), 2.37 (s, 3H), 2.31 (d, *J* = 6.2 Hz, 3H), 1.88 (d, *J* = 16.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 195.91 (d, *J* = 15.9 Hz), 143.74, 136.38 (d, *J* = 3.5 Hz), 135.41 (d, *J* = 3.4 Hz), 135.11 (d, *J* = 2.3 Hz), 133.07 (d, *J* = 7.6 Hz), 132.91 (d, *J* = 7.8 Hz), 131.73 (d, *J* = 2.7 Hz), 131.68 (d, *J* = 2.7 Hz), 129.11, 128.43 (d, *J* = 2.8 Hz), 128.24 (d, *J* = 4.8 Hz), 127.97 (d, *J* = 2.4 Hz), 127.96, 127.88 (d, *J* = 0.9 Hz), 44.51 (d, *J* = 64.0 Hz), 44.19, 41.77, 21.56, 21.02, 19.72. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 35.24. **HRMS (ESI)** Calcd. for $C_{30}H_{30}O_2P$ $[M+H]^+$: 453.1978, found 453.1970.



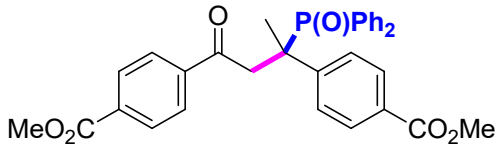
3ba

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 21.0 mg (93%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 – 7.56 (m, *J* = 9.8, 7.8 Hz, 6H), 7.55 – 7.47 (m, 2H), 7.44 – 7.28 (m, 6H), 7.12 – 7.02 (m, 2H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.69 (s, 1H), 4.01 (dd, *J* = 17.9, 7.9 Hz, 1H), 3.86 (dd, *J* = 17.8, 5.1 Hz, 1H), 2.36 (s, 3H), 2.16 (s, 3H), 1.87 (d, *J* = 16.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.44 (d, *J* = 15.9 Hz), 138.22 (d, *J* = 2.0 Hz), 137.61 (d, *J* = 2.3 Hz), 136.90 (d, *J* = 3.0 Hz), 133.69, 133.08 (d, *J* = 7.6 Hz), 132.93 (d, *J* = 7.8 Hz), 131.79 (d, *J* = 2.7 Hz), 131.73 (d, *J* = 2.8 Hz), 129.84 (d, *J* = 66.8 Hz), 129.37 (d, *J* = 4.8 Hz), 128.92 (d, *J* = 66.7 Hz), 128.35 (d, *J* = 5.3 Hz), 127.83, 127.61 (d, *J* = 3.3 Hz), 127.54 (d, *J* = 2.9 Hz), 125.39 (d, *J* = 5.0 Hz), 125.04, 53.38, 44.80 (d, *J* = 63.6 Hz), 41.98, 21.44, 21.27, 19.53. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 35.62. **HRMS (ESI)** Calcd. for $C_{30}H_{30}O_2P$ $[M+H]^+$: 453.1978, found 453.1970.



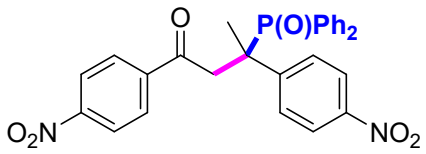
3ca

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 17.2 mg (81%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.69 – 7.31 (m, 13H), 7.24 – 7.13 (m, 3H), 7.08 – 6.99 (m, 2H), 4.12 (dd, *J* = 17.8, 8.0 Hz, 1H), 3.82 (dd, *J* = 17.9, 5.1 Hz, 1H), 1.91 (d, *J* = 16.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.18 (d, *J* = 15.9 Hz, 1H), 138.53 (d, *J* = 3.4 Hz, 1H), 137.50 (d, *J* = 2.2 Hz, 1H), 133.01 (d, *J* = 7.6 Hz, 3H), 132.98, 132.82 (d, *J* = 7.8 Hz, 2H), 131.84 (d, *J* = 2.7 Hz, 1H), 131.76 (d, *J* = 2.7 Hz, 1H), 129.88 (d, *J* = 48.3 Hz, 0H), 128.96 (d, *J* = 47.4 Hz, 1H), 128.46, 128.32 (d, *J* = 4.8 Hz, 2H), 127.95 (d, *J* = 1.9 Hz, 2H), 127.81 (d, *J* = 2.9 Hz, 3H), 127.80, 127.67 (d, *J* = 2.8 Hz, 2H), 126.86 (d, *J* = 3.3 Hz, 1H), 44.84 (d, *J* = 63.5 Hz, 1H), 42.06, 19.70. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 35.38. **HRMS (ESI)** Calcd. for $C_{28}H_{26}O_2P$ $[M+H]^+$: 425.1665, found 425.1660.



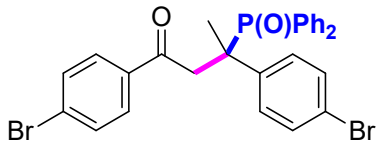
3da

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 22.1 mg (82%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.87 (t, *J* = 8.4 Hz, 4H), 7.77 – 7.66 (m, 2H), 7.66 – 7.54 (m, 3H), 7.54 – 7.44 (m, 3H), 7.44 – 7.33 (m, 2H), 7.14 (dd, *J* = 8.6, 2.0 Hz, 2H), 4.20 (dd, *J* = 18.2, 7.8 Hz, 1H), 3.92 (d, *J* = 13.0 Hz, 6H), 3.83 (dd, *J* = 18.1, 4.8 Hz, 1H), 1.92 (d, *J* = 16.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 195.55 (d, *J* = 15.7 Hz), 166.82, 166.07, 144.32, 140.35, 133.94, 132.93, 132.86, 132.70, 132.62, 132.19 (d, *J* = 2.6 Hz), 132.12 (d, *J* = 2.7 Hz), 129.81, 129.47 (d, *J* = 27.4 Hz), 128.93 (d, *J* = 2.6 Hz), 128.61 (d, *J* = 12.9 Hz), 128.49 (d, *J* = 16.3 Hz), 128.36, 128.30, 128.25, 128.21, 128.09, 127.75, 52.45, 52.08, 45.32 (d, *J* = 62.2 Hz), 42.89, 19.81. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 34.68. **HRMS (ESI)** Calcd. for $C_{32}H_{30}O_6P$ $[M+H]^+$: 541.1775, found 541.1775.



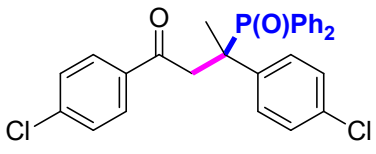
3ea

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 18.8 mg (73%) of **3aa**. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.32 – 8.23 (m, 2H), 8.02 (dd, *J* = 21.9, 8.8 Hz, 4H), 7.88 – 7.79 (m, 2H), 7.67 – 7.48 (m, 6H), 7.45 – 7.28 (m, 4H), 4.36 (dd, *J* = 18.5, 7.8 Hz, 1H), 3.75 (dd, *J* = 18.5, 4.7 Hz, 1H), 1.95 (d, *J* = 16.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.31 (d, *J* = 15.3 Hz), 150.46, 146.97 (d, *J* = 3.7 Hz), 146.54 (d, *J* = 3.5 Hz), 141.09 (d, *J* = 2.0 Hz), 132.76 (d, *J* = 7.9 Hz), 132.59 (d, *J* = 2.8 Hz), 132.47 (d, *J* = 2.8 Hz), 132.37 (d, *J* = 8.0 Hz), 129.03 (d, *J* = 8.0 Hz), 128.93, 128.88, 128.67 (d, *J* = 11.3 Hz), 128.38 (d, *J* = 11.4 Hz), 128.09 (d, *J* = 10.1 Hz), 123.92, 122.80 (d, *J* = 2.6 Hz), 45.48 (d, *J* = 61.1 Hz), 43.56, 20.03. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 34.19. **HRMS (ESI)** Calcd. for $C_{28}H_{24}N_2O_6P$ $[M+H]^+$: 515.1366, found 515.1368.



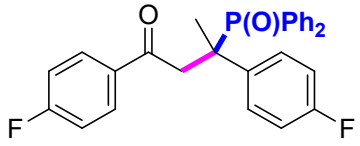
3fa

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 24.6 mg (85%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 – 7.66 (m, 4H), 7.63 – 7.43 (m, 8H), 7.42 – 7.34 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 6.99 – 6.87 (m, 2H), 4.05 (dd, *J* = 18.0, 7.8 Hz, 1H), 3.71 (dd, *J* = 17.9, 4.9 Hz, 1H), 1.86 (d, *J* = 16.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 195.04 (d, *J* = 15.7 Hz), 137.87 (d, *J* = 3.5 Hz), 135.94 (d, *J* = 2.1 Hz), 132.86 (d, *J* = 7.7 Hz), 132.61 (d, *J* = 7.9 Hz), 132.07 (d, *J* = 2.7 Hz), 132.00 (d, *J* = 2.7 Hz), 131.81, 130.77 (d, *J* = 2.7 Hz), 129.92 (d, *J* = 4.7 Hz), 129.53 (d, *J* = 29.0 Hz), 129.30, 128.60 (d, *J* = 28.0 Hz), 128.37, 128.23 (d, *J* = 11.1 Hz), 128.06 (d, *J* = 11.2 Hz), 121.09 (d, *J* = 4.1 Hz), 44.58 (d, *J* = 63.2 Hz) , 42.08, 19.71. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 34.61. **HRMS (ESI)** Calcd. for $C_{28}H_{24}Br_2O_2P$ $[M+H]^+$: 580.9875, found 580.9887.



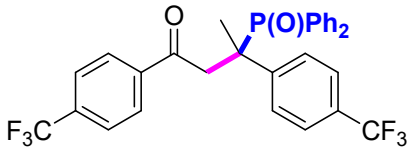
3ga

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 20.4 mg (83%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 – 7.68 (m, 4H), 7.63 – 7.53 (m, 3H), 7.53 – 7.44 (m, 3H), 7.42 – 7.34 (m, 4H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.99 (dd, *J* = 8.8, 2.2 Hz, 2H), 4.06 (dd, *J* = 17.1, 7.1 Hz, 1H), 3.71 (dd, *J* = 17.9, 5.0 Hz, 1H), 1.87 (d, *J* = 16.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.91 (d, *J* = 15.7 Hz), 139.67, 137.36 (d, *J* = 3.6 Hz), 135.58 (d, *J* = 2.2 Hz), 132.91 (d, *J* = 7.7 Hz), 132.87, 132.66 (d, *J* = 7.9 Hz), 132.09 (d, *J* = 2.7 Hz), 132.01 (d, *J* = 2.7 Hz), 129.62 (d, *J* = 30.3 Hz), 129.60 (d, *J* = 4.7 Hz), 129.24, 128.85, 128.55, 128.25 (d, *J* = 11.1 Hz), 128.09 (d, *J* = 11.2 Hz), 127.87 (d, *J* = 2.7 Hz), 44.53 (d, *J* = 63.3 Hz), 42.14, 19.79. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 34.74. **HRMS (ESI)** Calcd. for $C_{28}H_{24}Cl_2O_2P$ $[M+H]^+$: 493.0885, found 493.0882.



3ha

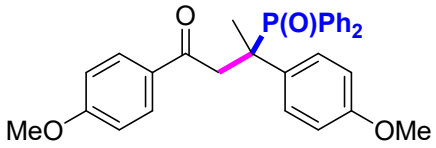
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 20.2 mg (88%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 – 7.82 (m, 2H), 7.72 (t, *J* = 9.2 Hz, 2H), 7.64 – 7.54 (m, 3H), 7.52 – 7.43 (m, 3H), 7.43 – 7.33 (m, 2H), 7.12 – 6.98 (m, 4H), 6.88 (t, *J* = 8.6 Hz, 2H), 4.09 (dd, *J* = 17.7, 7.9 Hz, 1H), 3.70 (dd, *J* = 17.7, 5.0 Hz, 1H), 1.88 (d, *J* = 16.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.67 (d, *J* = 15.8 Hz), 165.71 (d, *J* = 255.2 Hz), 134.45 (t, *J* = 3.3 Hz), 133.83 (t, *J* = 2.7 Hz), 132.96 (d, *J* = 7.6 Hz), 132.67 (d, *J* = 7.9 Hz), 132.04 (d, *J* = 2.7 Hz), 131.94 (d, *J* = 2.7 Hz), 130.50 (d, *J* = 9.4 Hz), 129.91 (d, *J* = 4.9 Hz), 129.83 (d, *J* = 4.8 Hz), 128.86 (d, *J* = 31.7 Hz), 128.23 (d, *J* = 11.0 Hz), 128.05 (d, *J* = 11.1 Hz), 115.63 (d, *J* = 21.9 Hz), 114.73 (d, *J* = 2.7 Hz), 114.52 (d, *J* = 2.7 Hz), 44.38 (d, *J* = 63.9 Hz), 42.09, 19.98. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 35.08. **HRMS (ESI)** Calcd. for $C_{28}H_{24}F_2O_2P$ $[M+H]^+$: 461.1476, found 461.1476.



3ia

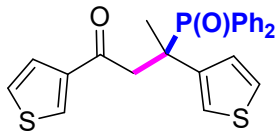
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 12.6 mg (45%) of **3aa**. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.81 – 7.66 (m, 4H), 7.60 – 7.35 (m, 10H), 7.22 (d, *J* = 7.1

Hz, 2H), 4.25 (dd, *J* = 18.2, 7.8 Hz, 1H), 3.75 (dd, *J* = 18.1, 4.9 Hz, 1H), 1.93 (d, *J* = 16.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 195.17 (d, *J* = 15.6 Hz), 143.12 (d, *J* = 2.1 Hz), 139.78, 134.56 (d, *J* = 32.7 Hz), 132.88 (d, *J* = 7.8 Hz), 132.53 (d, *J* = 8.0 Hz), 132.31 (d, *J* = 2.7 Hz), 132.20 (d, *J* = 2.7 Hz), 130.99 (d, *J* = 20.7 Hz), 129.38 (q, *J* = 8.8 Hz), 129.21 (d, *J* = 3.2 Hz), 128.89 (d, *J* = 3.3 Hz), 128.84 (d, *J* = 4.2 Hz), 128.49, 128.42 (d, *J* = 6.3 Hz), 128.19, 128.19 (d, *J* = 11.3 Hz), 125.70 (q, *J* = 3.7 Hz), 125.45 (d, *J* = 13.8 Hz), 124.75 (d, *J* = 11.9 Hz), 124.62 (q, *J* = 3.8 Hz), 124.62, 45.08 (d, *J* = 62.2 Hz), 42.88, 19.86. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 34.74. **HRMS (ESI)** Calcd. for $C_{30}H_{24}F_6O_2P$ $[M+H]^+$: 561.1413, found 561.1420.



3ja

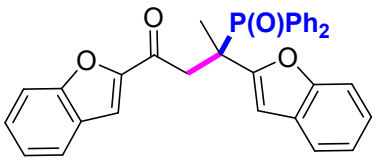
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/2) to afford 19.3 mg (80%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.67 – 7.54 (m, 4H), 7.53 – 7.32 (m, 6H), 6.91 (d, *J* = 7.3 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 3.94 (dd, *J* = 17.4, 7.9 Hz, 1H), 3.82 (s, 3H), 3.79 – 3.69 (m, 4H), 1.84 (d, *J* = 16.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.94 (d, *J* = 16.0 Hz, 1H), 163.37, 158.33 (d, *J* = 3.2 Hz, 0H), 133.08 (d, *J* = 7.6 Hz, 2H), 132.89 (d, *J* = 7.9 Hz, 1H), 131.78 (d, *J* = 2.7 Hz, 1H), 131.72 (d, *J* = 2.7 Hz, 1H), 130.77 (d, *J* = 2.9 Hz, 1H), 130.57 (d, *J* = 13.6 Hz, 0H), 130.44 (d, *J* = 6.9 Hz, 0H), 130.17, 129.52 (d, *J* = 4.9 Hz, 2H), 128.89 (d, *J* = 12.9 Hz, 1H), 128.06, 127.96, 127.85, 113.58, 113.06 (d, *J* = 2.7 Hz, 1H), 55.43, 55.13, 44.26 (d, *J* = 64.7 Hz, 1H), 41.42, 19.86. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 35.45. **HRMS (ESI)** Calcd. for $C_{30}H_{30}O_4P$ $[M+H]^+$: 485.1876, found 485.1867.



3ka

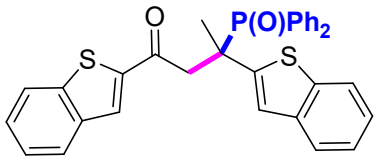
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 17.0 mg (78%) of **3aa**. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 – 7.96 (m, *J* = 2.8, 1.1 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.64 – 7.43 (m, 6H), 7.43 – 7.36 (m, *J* = 8.7, 3.0 Hz, 3H), 7.25 – 7.17 (m, 2H), 6.86 – 6.77 (m, *J* = 20.3, 11.0, 3.2 Hz, 2H), 3.80 (dd, *J* = 16.5, 7.5 Hz, 1H), 3.63 (dd, *J* = 16.5, 5.7 Hz, 1H), 1.84 (d, *J* =

16.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.02 (d, *J* = 15.8 Hz), 142.96 (d, *J* = 2.3 Hz), 140.11 (d, *J* = 3.4 Hz), 132.99 (d, *J* = 7.7 Hz), 132.67 (d, *J* = 8.0 Hz), 132.20, 131.97 (d, *J* = 2.7 Hz), 131.88 (d, *J* = 2.8 Hz), 129.92 (d, *J* = 77.9 Hz), 128.99 (d, *J* = 76.6 Hz), 128.21, 128.18, 128.10, 127.99, 126.84, 126.17, 124.70 (d, *J* = 1.6 Hz), 123.14 (d, *J* = 7.3 Hz), 43.43, 43.26 (d, *J* = 66.2 Hz), 20.22. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 35.14. **HRMS (ESI)** Calcd. for $C_{24}H_{22}O_2PS_2$ $[M+H]^+$: 437.0793, found 437.0795.



3la

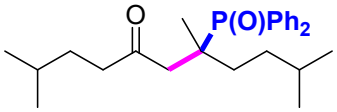
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 18.4 mg (73%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (dd, *J* = 17.7, 8.3 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.58 – 7.37 (m, 5H), 7.30 – 7.25 (m, 1H), 7.21 (d, *J* = 2.5 Hz, 1H), 6.41 (d, *J* = 3.8 Hz, 0H), 3.98 – 3.80 (m, *J* = 16.6, 6.4 Hz, 2H), 1.83 (d, *J* = 15.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 187.44 (d, *J* = 15.5 Hz), 155.52, 154.11 (d, *J* = 1.3 Hz), 152.50 (d, *J* = 2.4 Hz), 132.59 (d, *J* = 3.9 Hz), 132.51 (d, *J* = 4.7 Hz), 132.08 (d, *J* = 15.5 Hz), 132.08, 130.09, 128.35 (d, *J* = 2.9 Hz), 128.26 (d, *J* = 3.5 Hz), 128.21, 128.11 (d, *J* = 2.4 Hz), 126.91, 124.06, 123.85, 123.26, 122.91, 120.88 (d, *J* = 1.0 Hz), 113.05, 112.45, 111.00 (d, *J* = 0.6 Hz), 105.84 (d, *J* = 7.4 Hz), 43.03 (d, *J* = 65.9 Hz), 40.64, 18.27. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 33.24. **HRMS (ESI)** Calcd. for $C_{32}H_{26}O_4P$ $[M+H]^+$: 505.1563, found 505.1567.



3ma

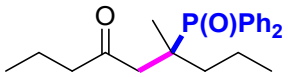
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 19.5 mg (73%) of **3aa**. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (s, 1H), 7.91 – 7.65 (m, 7H), 7.63 – 7.33 (m, 9H), 7.31 – 7.20 (m, 2H), 6.98 (d, *J* = 3.5 Hz, 1H), 4.08 (dd, *J* = 16.5, 7.2 Hz, 1H), 3.83 (dd, *J* = 16.4, 5.5 Hz, 1H), 2.01 (d, *J* = 16.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.67 (d, *J* = 15.3 Hz), 144.61 (d, *J* = 4.5 Hz), 144.23 (d, *J* = 2.9 Hz), 142.46, 139.34 (d, *J* = 3.0 Hz), 138.96, 139.27 (d, *J* = 1.6 Hz), 133.07 (d, *J* = 7.9 Hz), 132.85 (d, *J* = 8.2 Hz), 132.24 (d, *J* = 2.7 Hz),

132.16 (d, J = 2.7 Hz), 129.59 (d, J = 21.1 Hz), 129.49, 128.92 (d, J = 34.6 Hz), 128.22 (d, J = 5.7 Hz), 128.13 (d, J = 11.4 Hz), 127.45, 126.02, 124.92, 124.06 (d, J = 13.5 Hz), 123.78 (d, J = 7.0 Hz), 123.32, 122.78, 121.93, 44.59 (d, J = 65.7 Hz), 44.06, 20.82. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 35.14. **HRMS (ESI)** Calcd. for $C_{32}H_{26}O_2PS_2$ $[M+H]^+$: 537.1106, found 537.1120.



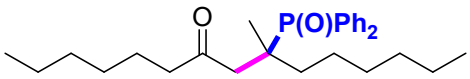
3na

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 15.0 mg (73%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08 – 7.89 (m, 4H), 7.60 – 7.41 (m, 6H), 3.06 (dd, J = 16.2, 9.3 Hz, 1H), 2.51 (dd, J = 16.2, 10.4 Hz, 1H), 2.44 – 2.25 (m, 2H), 1.83 – 1.75 (m, 2H), 1.52 – 1.22 (m, 8H), 1.17 – 0.98 (m, 1H), 0.84 (d, J = 6.6 Hz, 6H), 0.72 (dd, J = 13.9, 6.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.44 (d, J = 12.3 Hz), 132.26 (d, J = 3.6 Hz), 132.18 (d, J = 3.7 Hz), 132.01, 131.63 (d, J = 2.6 Hz), 131.53 (d, J = 2.8 Hz), 131.13, 128.40 (d, J = 1.0 Hz), 128.29 (d, J = 1.0 Hz), 43.70, 43.03 (d, J = 1.2 Hz), 40.47 (d, J = 68.0 Hz), 33.29 (d, J = 4.6 Hz), 32.80, 32.32, 28.60, 27.53, 22.44, 22.33, 22.31, 22.25, 21.31. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 36.53. **HRMS (ESI)** Calcd. for $C_{26}H_{38}O_2P$ $[M+H]^+$: 413.2604, found 413.2602.



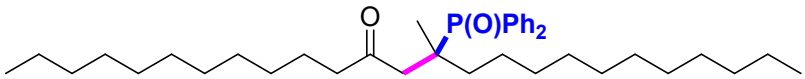
3oa

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 14.2 mg (80%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 – 7.89 (m, 4H), 7.61 – 7.42 (m, 6H), 3.03 (dd, J = 16.2, 9.3 Hz, 1H), 2.50 (dd, J = 16.2, 10.9 Hz, 1H), 2.42 – 2.24 (m, 2H), 1.87 – 1.66 (m, 2H), 1.54 – 1.35 (m, 6H), 1.35 – 1.12 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H), 0.76 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.20 (d, J = 12.2 Hz), 132.22 (d, J = 2.2 Hz), 132.14 (d, J = 2.2 Hz), 131.66 (d, J = 39.8 Hz), 131.61 (d, J = 2.7 Hz), 131.53 (d, J = 2.7 Hz), 130.77 (d, J = 40.5 Hz), 128.40, 128.29, 46.83, 43.83, 40.73 (d, J = 68.1 Hz), 37.11, 21.00, 17.93 (d, J = 5.3 Hz), 16.93, 14.62, 13.56. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 36.57. **HRMS (ESI)** Calcd. for $C_{22}H_{30}O_2P$ $[M+H]^+$: 357.1978, found 357.1960.



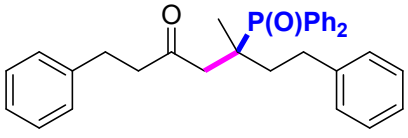
3pa

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 18.0 mg (82%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 – 7.90 (m, 4H), 7.59 – 7.37 (m, 6H), 3.05 (dd, *J* = 16.2, 9.3 Hz, 1H), 2.50 (dd, *J* = 16.2, 10.7 Hz, 1H), 2.45 – 2.24 (m, 2H), 1.85 – 1.71 (m, 2H), 1.52 – 1.02 (m, 21H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.81 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.36 (d, *J* = 12.3 Hz), 132.22, 132.14, 131.62 (d, *J* = 43.6 Hz), 131.60 (d, *J* = 2.6 Hz), 131.51 (d, *J* = 2.7 Hz), 130.73 (d, *J* = 44.2 Hz), 128.38, 128.27, 44.96, 43.74, 40.60 (d, *J* = 68.0 Hz), 34.84, 31.54, 31.40, 29.79, 28.69, 24.43 (d, *J* = 5.0 Hz), 23.47, 22.44 (d, *J* = 2.8 Hz), 21.07, 13.98, 13.97. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 36.64. **HRMS (ESI)** Calcd. for $C_{28}H_{42}O_2P$ $[M+H]^+$: 441.2917, found 441.2904.



3qa

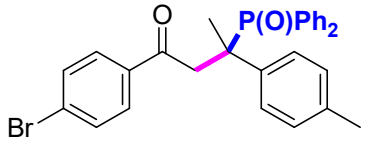
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 21.7 mg (75%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 – 7.85 (m, 4H), 7.68 – 7.34 (m, 6H), 3.04 (dd, *J* = 16.2, 9.3 Hz, 1H), 2.50 (dd, *J* = 16.2, 10.6 Hz, 1H), 2.41 – 2.23 (m, 2H), 1.86 – 1.70 (m, 2H), 1.46 – 1.34 (m, 6H), 1.30 – 1.10 (m, 33H), 0.88 (t, *J* = 6.8 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ209.36 (d, *J* = 12.3 Hz), 132.24, 132.16, 131.73 (d, *J* = 42.4 Hz), 131.59 (d, *J* = 2.7 Hz), 131.51 (d, *J* = 2.2 Hz), 130.84 (d, *J* = 43.4 Hz), 128.38, 128.27, 44.99, 43.81, 40.64 (d, *J* = 68.0 Hz), 34.90, 31.89, 31.88, 30.16, 29.58, 29.48, 29.44, 29.39, 29.31 (d, *J* = 1.4 Hz), 29.24, 29.06, 24.50 (d, *J* = 4.9 Hz), 23.55, 22.65, 21.08, 14.09. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 36.56. **HRMS (ESI)** Calcd. for $C_{38}H_{62}O_2P$ $[M+H]^+$: 581.4482, found 581.4482.



3ra

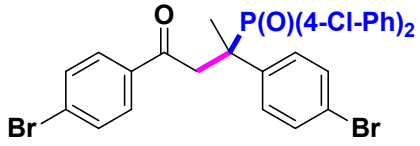
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 20.8 mg (87%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 – 7.90 (m, 4H), 7.60 – 7.43 (m, 6H), 7.30 – 7.07 (m, 8H), 6.95 (d, *J* = 7.1 Hz,

2H), 3.17 (dd, *J* = 16.6, 8.5 Hz, 1H), 2.84 – 2.67 (m, 5H), 2.61 – 2.43 (m, 2H), 2.20 – 1.96 (m, 3H), 1.43 (d, *J* = 16.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 207.92, 207.80, 142.14, 140.76, 132.22, 132.17, 132.14, 132.09, 131.82 (d, *J* = 2.7 Hz), 131.67 (d, *J* = 2.7 Hz), 131.38 (d, *J* = 44.4 Hz), 130.49 (d, *J* = 44.9 Hz), 128.56, 128.50, 128.45, 128.41, 128.39, 128.29, 128.26, 128.24, 126.05, 125.68, 46.30, 46.29, 43.76, 40.64 (d, *J* = 67.8 Hz), 37.12, 31.24 (d, *J* = 4.3 Hz), 29.55, 21.44. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 36.31. **HRMS (ESI)** Calcd. for $C_{32}H_{34}O_2P$ $[M+H]^+$: 481.2291, found 481.2285.



3sa

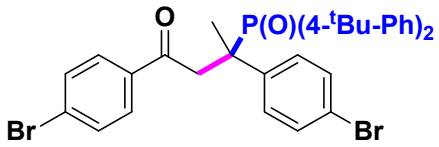
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 30.9 mg (60%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 – 7.35 (m, 15H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.91 – 6.86 (m, 2H), 3.99 (dd, *J* = 17.7, 7.9 Hz, 1H), 3.77 (dd, *J* = 17.7, 5.1 Hz, 1H), 2.32 (s, 3H), 1.86 (d, *J* = 16.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 195.49 (d, *J* = 16.1 Hz), 136.60 (d, *J* = 3.4 Hz), 136.29 (d, *J* = 2.4 Hz), 135.20 (d, *J* = 3.5 Hz), 133.05 (d, *J* = 7.6 Hz), 132.89 (d, *J* = 7.9 Hz), 131.85 (d, *J* = 2.8 Hz), 131.79 (d, *J* = 4.0 Hz), 131.77, 129.96 (d, *J* = 53.8 Hz), 129.42, 129.04 (d, *J* = 53.0 Hz), 128.53 (d, *J* = 2.8 Hz), 128.20 (d, *J* = 4.9 Hz), 127.97, 127.97 (d, *J* = 22.1 Hz), 44.51 (d, *J* = 64.0 Hz), 42.01, 21.03, 19.73. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 35.21. **HRMS (ESI)** Calcd. for $C_{29}H_{27}BrO_2P$ $[M+H]^+$: 517.0927, found 517.0922.



3ab

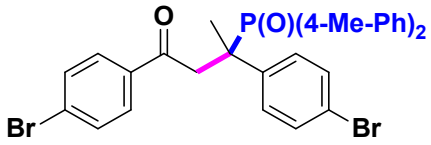
Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 26.2 mg (81%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.6 Hz, 2H), 7.64 – 7.52 (m, 4H), 7.51 – 7.43 (m, 4H), 7.42 – 7.32 (m, 4H), 6.93 (dd, *J* = 8.7, 2.2 Hz, 2H), 3.97 (dd, *J* = 17.9, 8.2 Hz, 1H), 3.68 (dd, *J* = 17.9, 5.0 Hz, 1H), 1.84 (d, *J* = 16.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.66 (d, *J* = 15.9 Hz), 139.20 (s), 139.07 (s), 137.34 (d, *J* = 3.6 Hz), 135.79 (d, *J* = 2.3 Hz), 134.18 (d, *J* = 8.4 Hz), 133.96 (d, *J* = 8.7 Hz), 131.94, 131.11 (d, *J* = 2.8 Hz), 129.88 (d, *J* = 4.8 Hz), 129.32, 128.79 (d, *J* = 11.6 Hz), 128.62, 128.60 (d, *J* = 11.8 Hz), 127.66 (d, *J*

= 35.2 Hz), 126.72 (d, *J* = 34.0 Hz), 121.55 (d, *J* = 4.3 Hz), 121.55 (d, *J* = 4.3 Hz), 44.67 (d, *J* = 64.4 Hz), 41.88, 19.71. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 34.03. **HRMS (ESI)** Calcd. for $C_{28}H_{22}Br_2Cl_2O_2P$ $[M+H]^+$: 648.9096, found 648.9094.



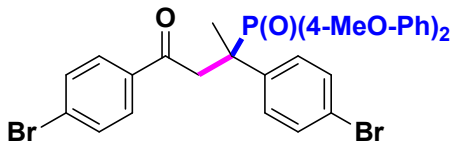
3ac

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 29.7 mg (86%) of **3aa**. White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.65 – 7.33 (m, 10H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 6.6 Hz, 2H), 4.04 (dd, *J* = 17.9, 7.4 Hz, 1H), 3.75 (d, *J* = 16.6 Hz, 1H), 1.84 (d, *J* = 16.1 Hz, 3H), 1.30 (d, *J* = 13.9 Hz, 18H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 195.34 (d, *J* = 15.8 Hz), 155.44 (d, *J* = 2.6 Hz), 138.19, 136.03 (d, *J* = 2.2 Hz), 132.78 (d, *J* = 8.1 Hz), 132.58 (d, *J* = 8.3 Hz), 131.82, 130.70 (d, *J* = 2.6 Hz), 130.07 (d, *J* = 4.7 Hz), 129.43, 128.35, 125.19 (d, *J* = 11.4 Hz), 125.05 (d, *J* = 11.5 Hz), 120.97 (d, *J* = 4.0 Hz), 44.57 (d, *J* = 63.5 Hz), 42.19, 34.95, 34.91, 31.06, 31.01. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 35.18. **HRMS (ESI)** Calcd. for $C_{36}H_{40}Br_2O_2P$ $[M+H]^+$: 693.1127, found 693.1125.



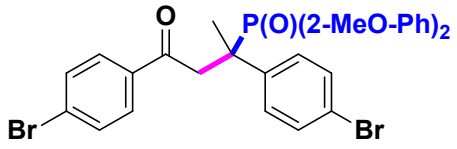
3ad

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 27.3 mg (90%) of **3aa**. White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.69 (d, *J* = 8.6 Hz, 2H), 7.62 – 7.51 (m, 4H), 7.45 (dd, *J* = 10.0, 8.2 Hz, 2H), 7.35 – 7.22 (m, 4H), 7.18 (dd, *J* = 8.0, 2.4 Hz, 2H), 6.92 (dd, *J* = 8.7, 2.2 Hz, 2H), 4.02 (dd, *J* = 18.0, 7.8 Hz, 1H), 3.70 (dd, *J* = 18.0, 4.9 Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 1.83 (d, *J* = 16.0 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 195.28 (d, *J* = 15.7 Hz), 142.55 (d, *J* = 2.8 Hz), 142.48 (d, *J* = 2.7 Hz), 138.16 (d, *J* = 3.4 Hz), 136.04 (d, *J* = 2.1 Hz), 132.91 (d, *J* = 7.9 Hz), 132.69 (d, *J* = 8.2 Hz), 131.83, 130.74 (d, *J* = 2.6 Hz), 130.04 (d, *J* = 4.6 Hz), 129.36, 128.97 (d, *J* = 11.5 Hz), 128.83 (d, *J* = 11.6 Hz), 128.35, 126.36 (d, *J* = 39.7 Hz), 125.41 (d, *J* = 38.8 Hz), 121.00 (d, *J* = 4.0 Hz), 44.56 (d, *J* = 63.5 Hz), 42.20, 21.51, 19.70. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 35.14. **HRMS (ESI)** Calcd. for $C_{30}H_{28}Br_2O_2P$ $[M+H]^+$: 609.0188, found 609.0180.



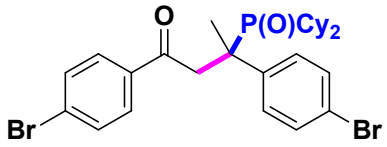
3ae

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 28.8 mg (90%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.64 – 7.52 (m, 4H), 7.47 (t, *J* = 9.2 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.02 – 6.82 (m, 6H), 3.99 (dd, *J* = 18.0, 7.7 Hz, 1H), 3.84 (d, *J* = 11.9 Hz, 6H), 3.70 (dd, *J* = 18.0, 4.9 Hz, 1H), 1.82 (d, *J* = 16.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 195.33 (d, *J* = 15.7 Hz), 162.46 (d, *J* = 2.9 Hz), 162.36 (d, *J* = 2.9 Hz), 138.26 (d, *J* = 3.4 Hz), 136.01 (d, *J* = 2.2 Hz), 134.67 (d, *J* = 8.8 Hz), 134.46 (d, *J* = 9.2 Hz), 131.83, 130.74 (d, *J* = 2.7 Hz), 130.02 (d, *J* = 4.6 Hz), 129.36, 128.35, 120.98 (d, *J* = 3.9 Hz), 120.96, 120.19 (d, *J* = 44.8 Hz), 119.43, 113.69 (d, *J* = 27.6 Hz), 113.69 (d, *J* = 3.4 Hz), 55.30 (d, *J* = 2.3 Hz), 44.68 (d, *J* = 64.4 Hz), 42.13, 19.66. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 35.14. **HRMS (ESI)** Calcd. for $C_{30}H_{28}Br_2O_4P$ $[M+H]^+$: 641.0086, found 641.0076.



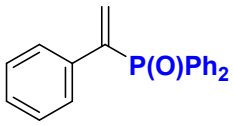
3af

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 17.0 mg (53%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 – 7.83 (m, *J* = 12.3, 7.7, 1.7 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.22 – 7.12 (m, 3H), 7.05 – 6.94 (m, 4H), 6.91 – 6.84 (m, *J* = 7.5, 1.4 Hz, 1H), 6.56 – 6.50 (m, *J* = 8.2, 5.4 Hz, 1H), 4.61 (dd, *J* = 18.1, 8.1 Hz, 1H), 4.08 (dd, *J* = 18.0, 4.7 Hz, 1H), 3.95 (s, 3H), 3.57 (s, 3H), 1.86 (d, *J* = 19.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.09 (d, *J* = 16.1 Hz), 160.79 (d, *J* = 2.8 Hz), 158.46 (d, *J* = 3.2 Hz), 141.15 (d, *J* = 2.9 Hz), 136.67 (d, *J* = 2.6 Hz), 135.48 (d, *J* = 4.9 Hz), 134.87 (d, *J* = 8.9 Hz), 133.66 (d, *J* = 2.2 Hz), 133.50 (d, *J* = 1.8 Hz), 131.67, 129.64 (d, *J* = 2.4 Hz), 129.45, 128.92 (d, *J* = 5.8 Hz), 127.92, 121.00 (d, *J* = 5.5 Hz), 120.71 (d, *J* = 11.9 Hz), 119.99 (d, *J* = 13.0 Hz), 119.88 (d, *J* = 1.7 Hz), 111.55 (d, *J* = 6.7 Hz), 109.45 (d, *J* = 6.8 Hz), 55.76, 54.15, 46.07, 45.44 (d, *J* = 67.2 Hz), 18.08. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 51.58. **HRMS (ESI)** Calcd. for $C_{30}H_{28}Br_2O_4P$ $[M+H]^+$: 641.0086, found 641.0076.



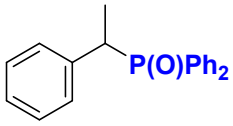
3ag

Purification was performed by column chromatography (petroleum ether/ethyl acetate = 1/1) to afford 13.0 mg (44%) of **3aa**. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.48 – 7.35 (m, 4H), 4.54 (dd, *J* = 17.5, 8.1 Hz, 1H), 3.26 (dd, *J* = 17.6, 3.2 Hz, 1H), 2.26 – 1.95 (m, 3H), 1.88 (d, *J* = 15.3 Hz, 6H), 1.78 – 1.16 (m, 15H), 1.05 – 0.76 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.17 (d, *J* = 12.7 Hz), 140.42 (d, *J* = 4.4 Hz), 136.31 (d, *J* = 1.6 Hz), 131.76, 131.21 (d, *J* = 1.9 Hz), 129.45, 129.01 (d, *J* = 4.1 Hz), 128.25, 44.37 (d, *J* = 50.6 Hz), 44.19, 37.72 (d, *J* = 58.8 Hz), 36.99 (d, *J* = 54.7 Hz), 27.67 (d, *J* = 3.1 Hz), 27.34 (d, *J* = 3.6 Hz), 27.04 (d, *J* = 1.5 Hz), 26.95 (d, *J* = 2.1 Hz), 25.86 (d, *J* = 4.5 Hz), 19.29. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 53.24. **HRMS (ESI)** Calcd. for $C_{28}H_{36}Br_2O_2P$ $[M+H]^+$: 593.0814, found 593.0836.



4

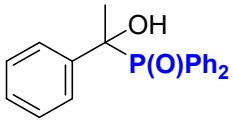
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 11.8, 7.2 Hz, 4H), 7.57 – 7.37 (m, 8H), 7.26 – 7.21 (m, 3H), 6.25 (d, *J* = 40.2 Hz, 1H), 5.75 (d, *J* = 19.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ144.20 (d, *J* = 92.5 Hz, 1H), 137.42 (d, *J* = 9.9 Hz, 1H), 131.94, 131.85, 131.82, 131.49 (d, *J* = 103.6 Hz, 18H), 128.45, 128.33, 128.12, 128.03 (d, *J* = 4.7 Hz, 4H).



5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.84 (m, *J* = 10.5, 7.8, 1.5 Hz, 2H), 7.58 – 7.43 (m, 5H), 7.41 – 7.32 (m, 1H), 7.32 – 7.23 (m, 2H), 7.14 – 7.07 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 3.63 – 3.50 (m, *J* = 7.5 Hz, 1H), 2.26 (s, 3H), 1.55 (dd, *J* = 16.1, 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.40 (d, *J* = 2.6 Hz, 0H), 134.67 (d, *J* = 5.6 Hz, 0H), 132.50 (d, *J* = 4.3 Hz, 0H), 131.56 (d, *J* = 2.5 Hz, 1H), 131.16, 131.30 (d, *J* = 8.4 Hz, 1H), 131.07, 128.94 (d, *J* = 8.9 Hz, 2H), 128.92 (d, *J* = 1.0 Hz, 1H), 128.54 (d, *J* = 11.1 Hz, 1H), 127.95 (d, *J* = 11.5 Hz, 1H), 40.36 (d, *J* = 67.6 Hz, 1H), 20.97,

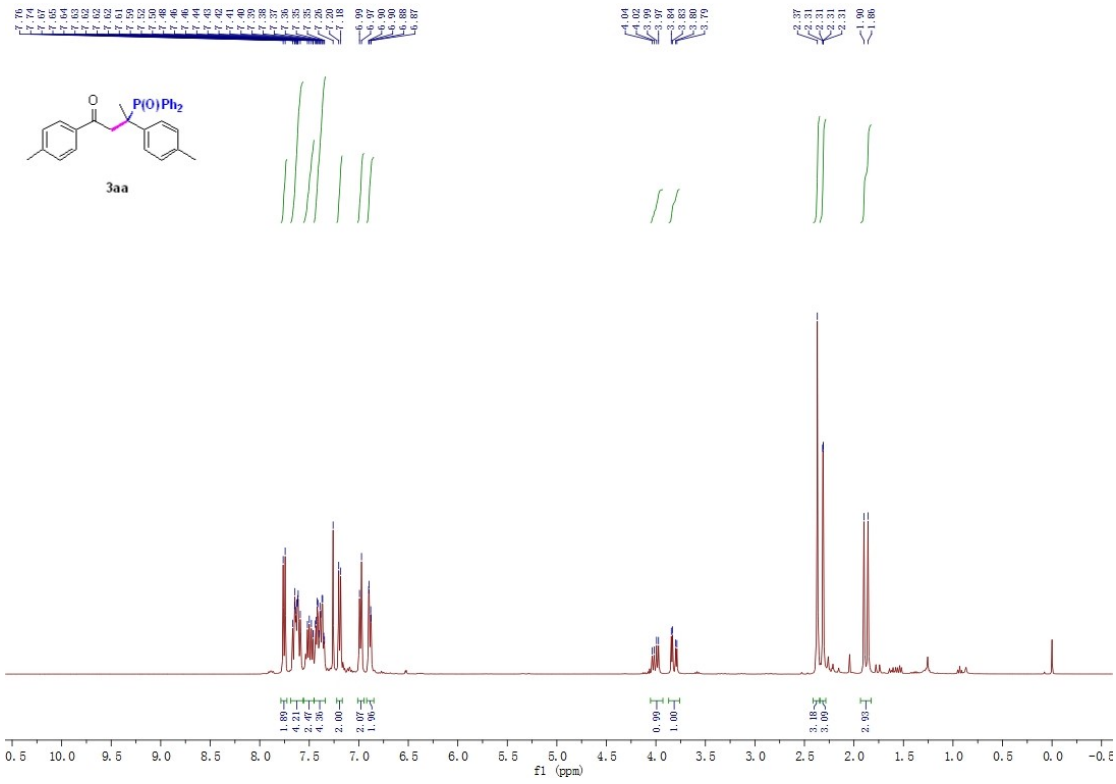
15.49 (d, *J* = 2.6 Hz, 1H).

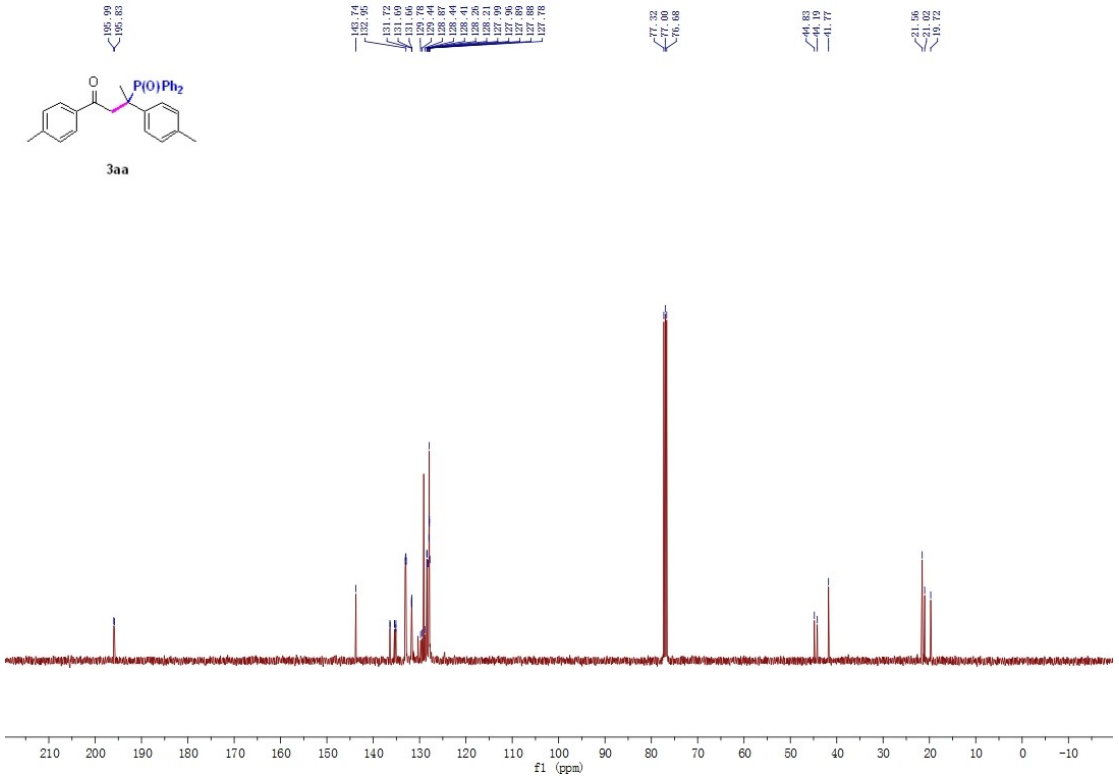


6

^{1}H NMR (400 MHz, DMSO) δ 8.08 (t, *J* = 8.4 Hz, 2H), 7.78 – 7.63 (m, 2H), 7.63 – 7.28 (m, 8H), 7.16 (dt, *J* = 23.5, 7.2 Hz, 3H), 6.43 (d, *J* = 18.9 Hz, 1H), 1.65 (d, *J* = 14.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 143.49 (d, *J* = 3.2 Hz), 133.07 (d, *J* = 7.7 Hz), 132.27 (d, *J* = 7.8 Hz), 131.97 (d, *J* = 2.6 Hz), 131.70 (d, *J* = 2.4 Hz), 128.63 (d, *J* = 10.6 Hz), 128.22 (d, *J* = 10.9 Hz), 128.22 (d, *J* = 10.9 Hz), 127.72 (d, *J* = 2.1 Hz), 127.17 (d, *J* = 2.3 Hz), 126.82 (d, *J* = 3.3 Hz), 75.67 (d, *J* = 89.6 Hz), 25.95 (d, *J* = 4.0 Hz), 25.95 (d, *J* = 4.0 Hz). **^{31}P NMR (162 MHz, DMSO)** δ 30.14.

^{1}H, ^{13}C and ^{31}P NMR Spectra of Products

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131.66
129.78
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128.44
128.41
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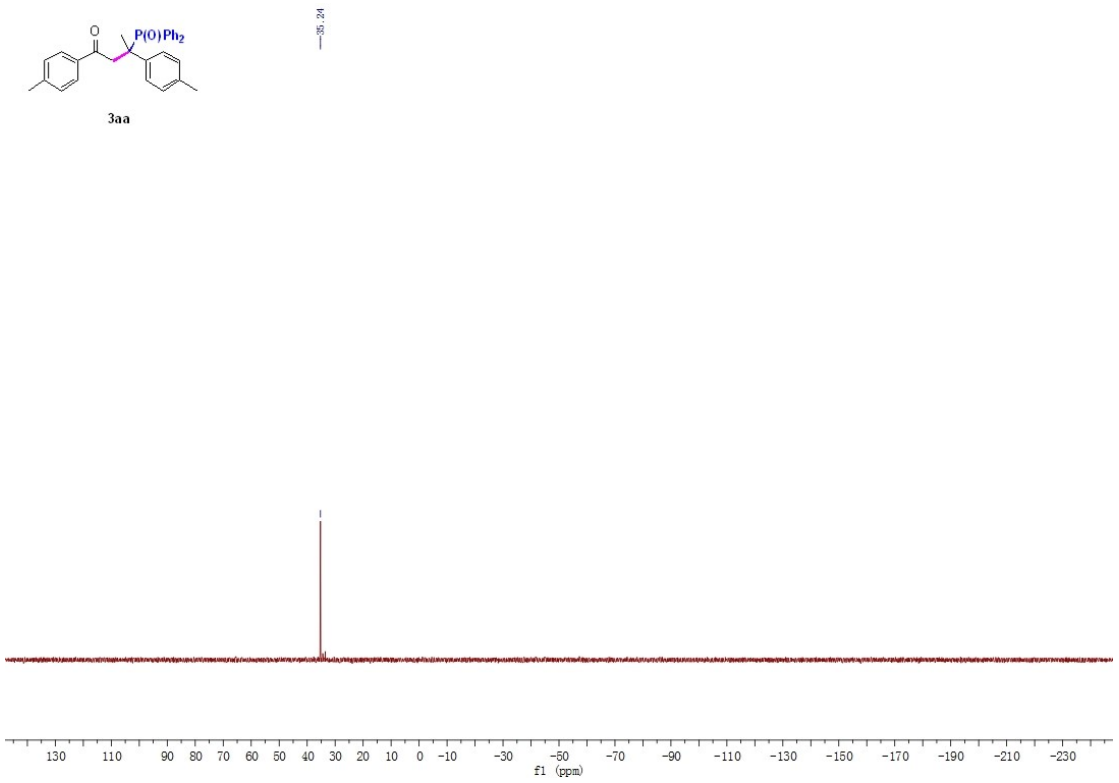
128.21
127.99
127.96
127.89
127.88
127.78
77.32
77.00
76.68
44.83
44.19
41.77
21.56
21.02
19.72
O
P(O)Ph2
3aa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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-70
-90
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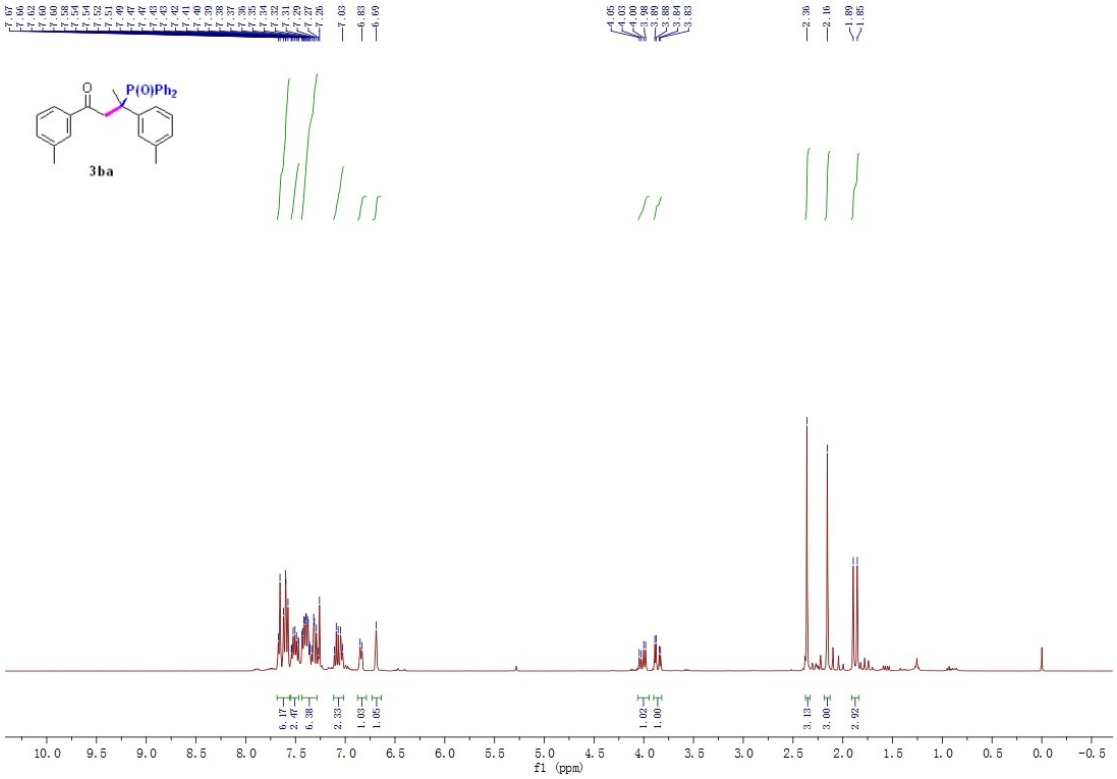
-130
-150
-170
-190
-210
-230
f1 (ppm)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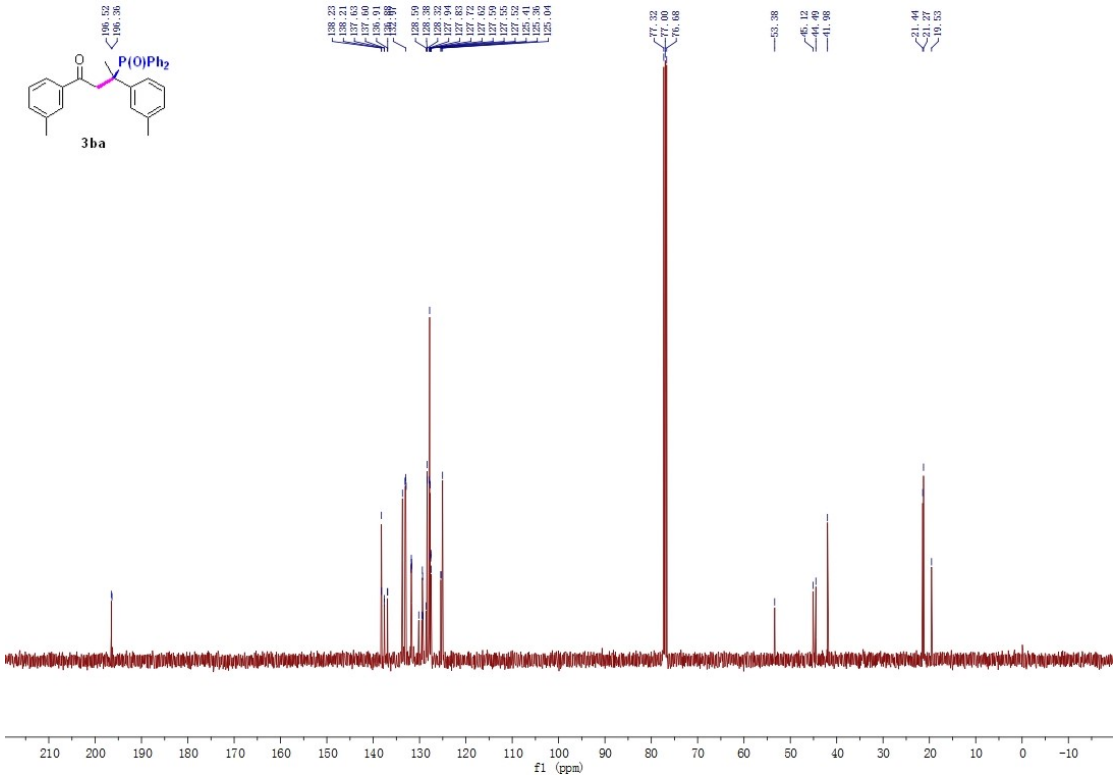
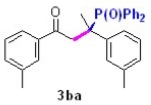
3ba
f1 (ppm)


P(O)Ph2
3ba
f1 (ppm)


P(O)Ph2

3ba

35.62
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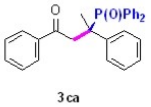
f1 (ppm)


P(O)Ph2

3ca

7.86
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7.48
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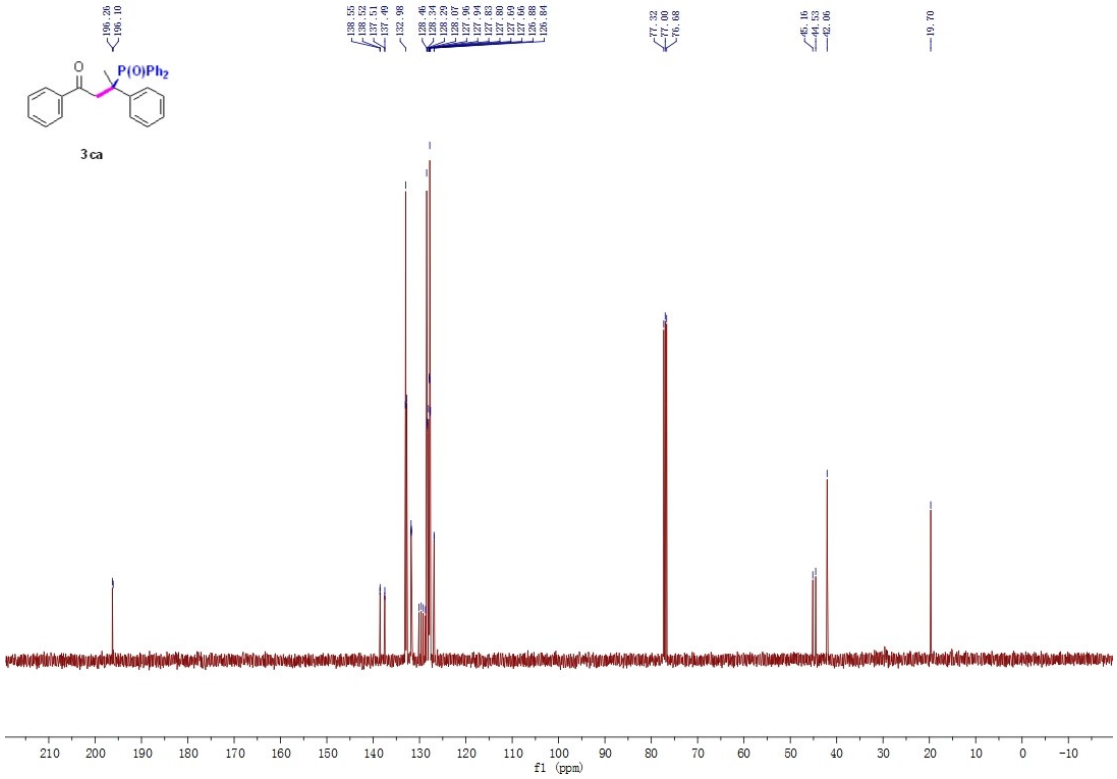
f1 (ppm)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137.49
132.98
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128.29
128.07
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127.56
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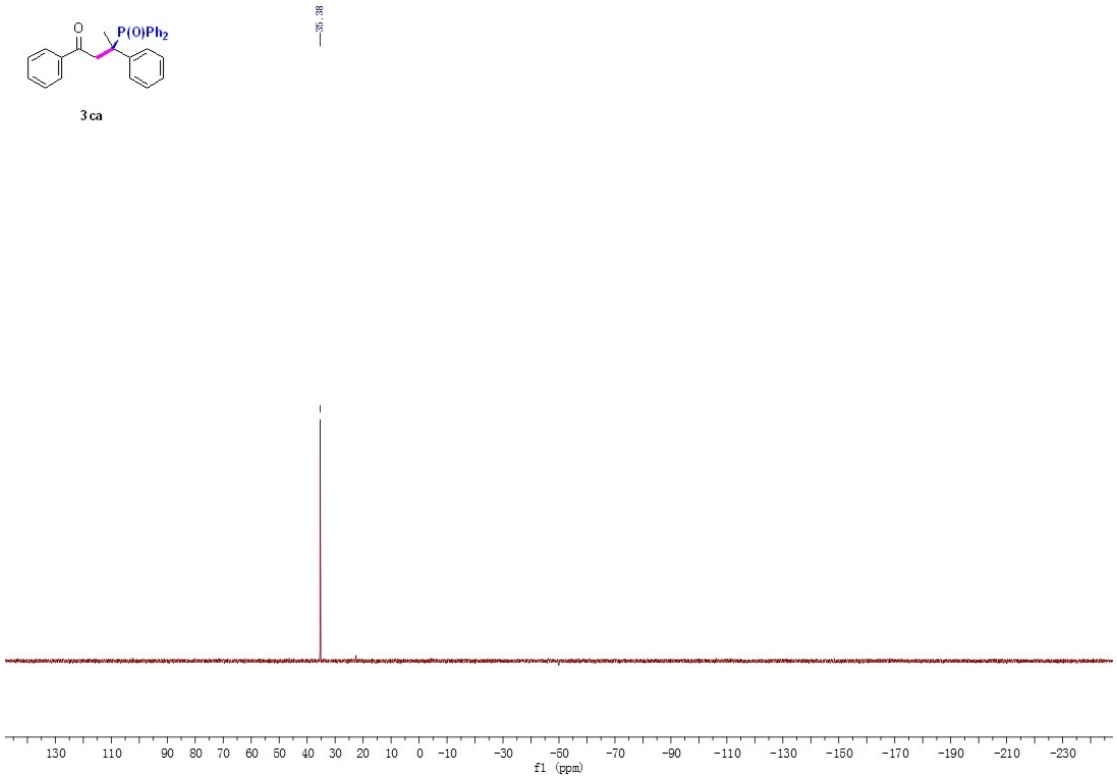
42.06
19.70
P(O)Ph2
3ca
f1 (ppm)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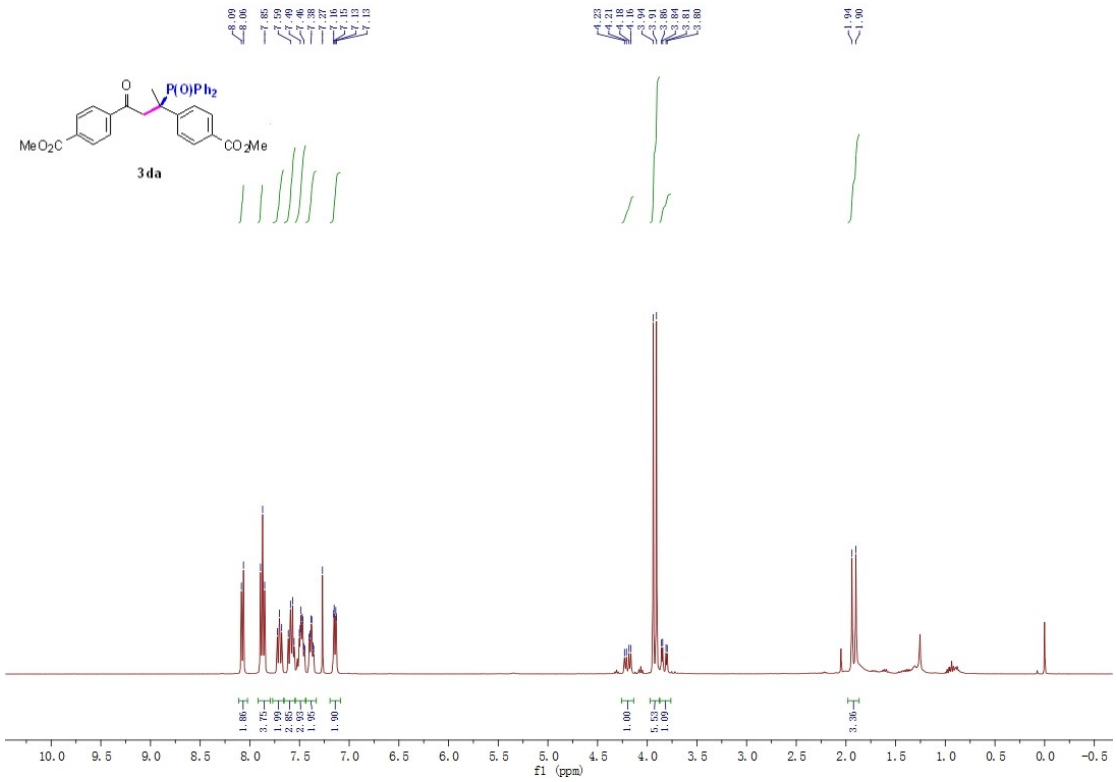
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7.49
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7.27
7.15
7.13
4.23
4.21
4.18
4.16
3.94
3.91
3.86
3.84
3.81
3.80
1.94
1.90
P(O)Ph2
MeO2C
CO2Me
3da
1.86
3.75
1.99
2.85
2.93
1.95
1.98
1.00
5.53
1.09
3.36
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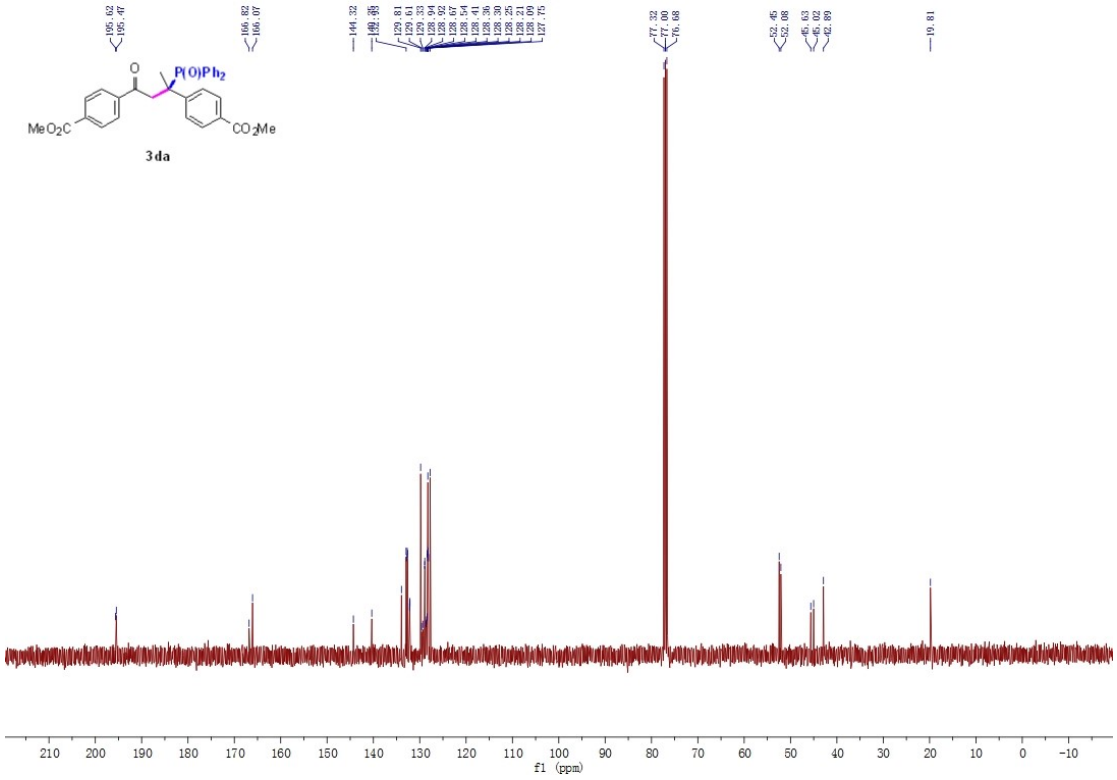
f1 (ppm)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129.61
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128.67
128.54
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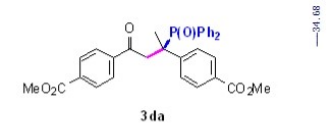
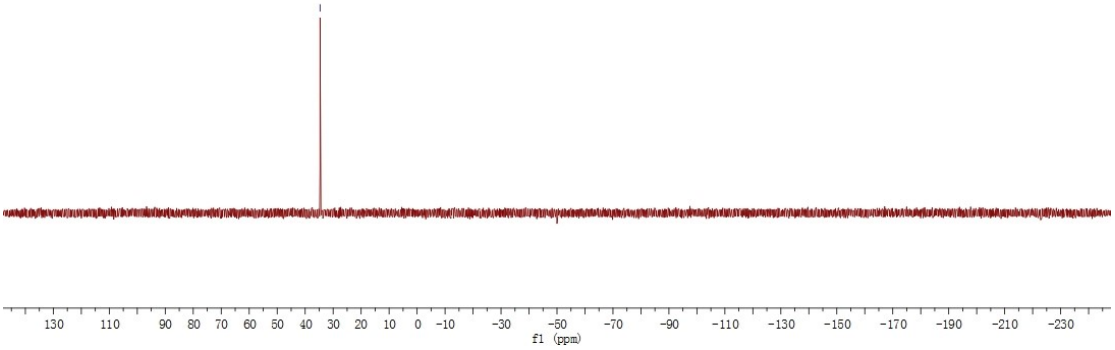
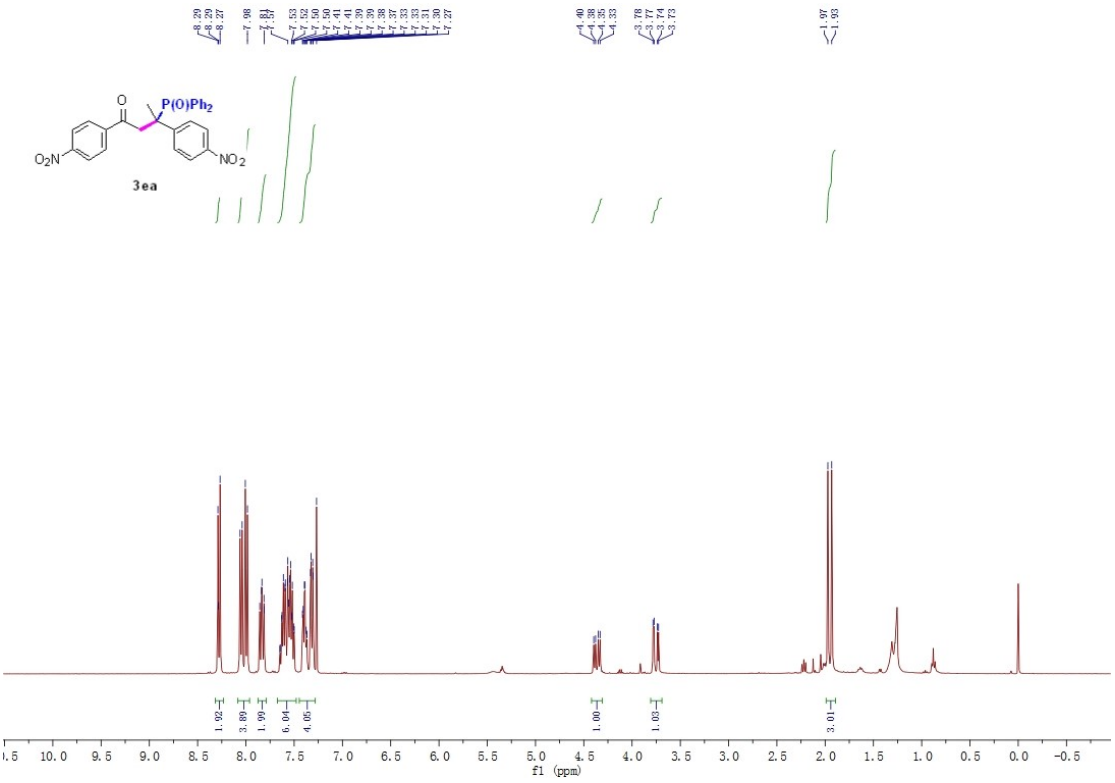
128.09
127.75
77.32
77.00
76.68
52.45
52.08
45.63
45.02
42.89
19.81
P(O)Ph2
MeO2C
CO2Me
3da
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

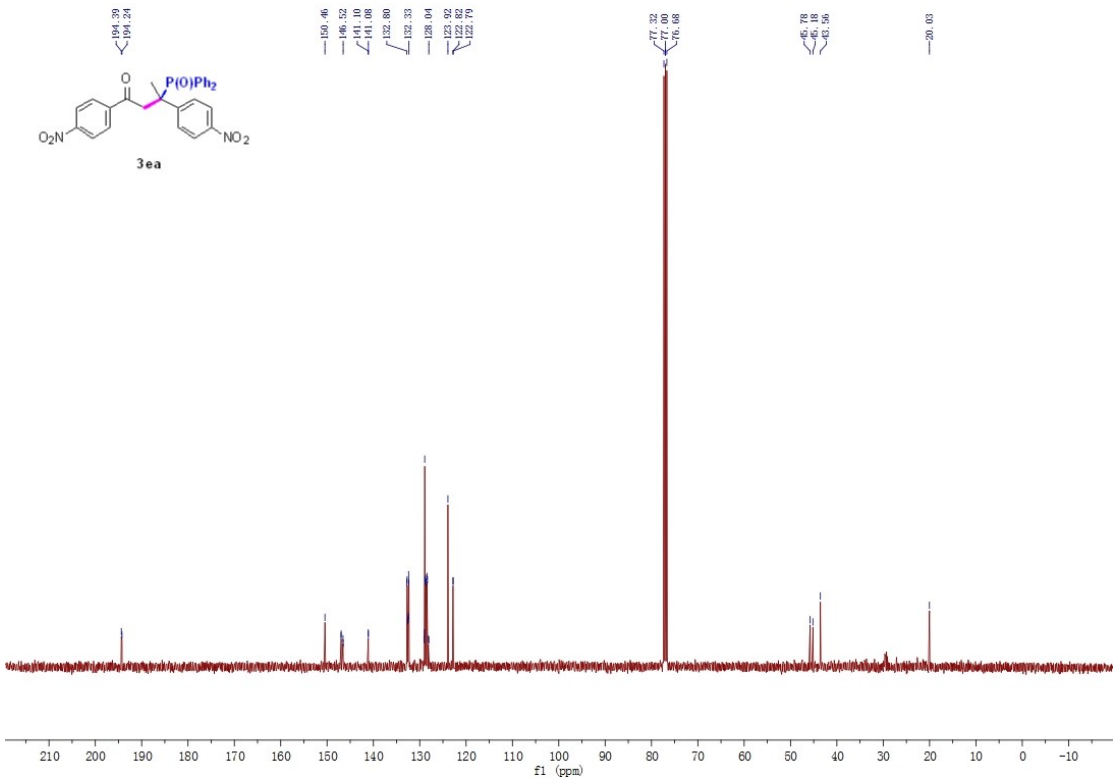

P(O)Ph2
MeO2C
CO2Me

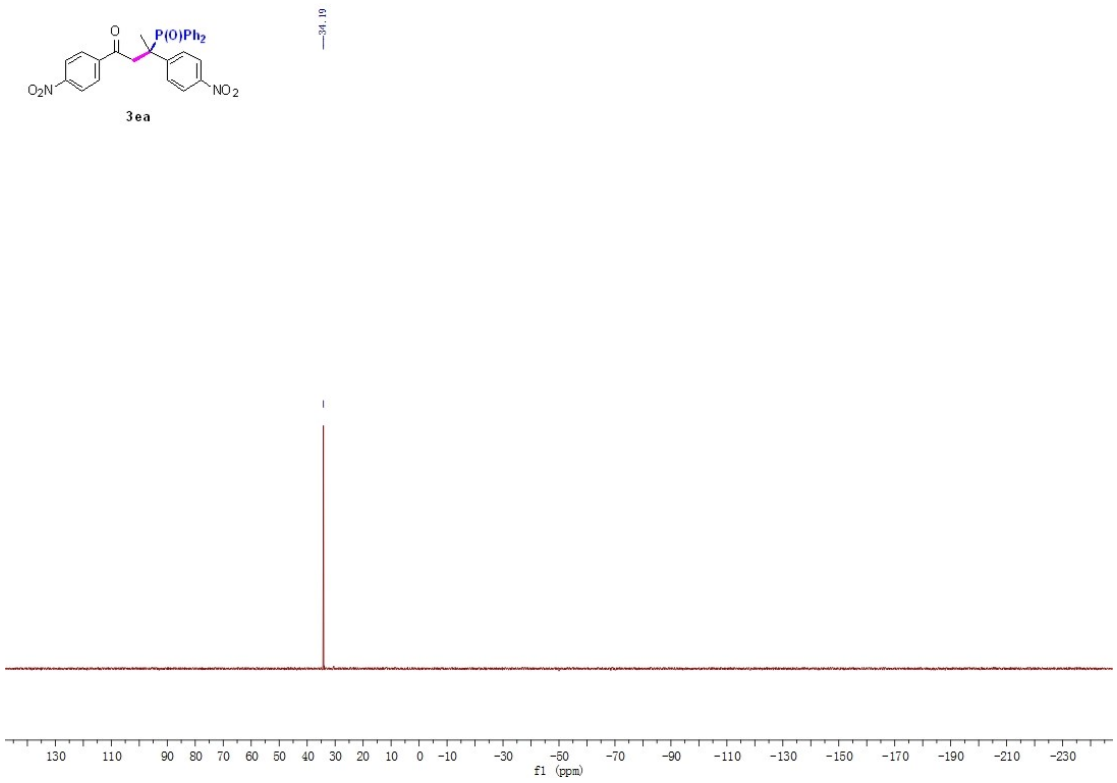
3da

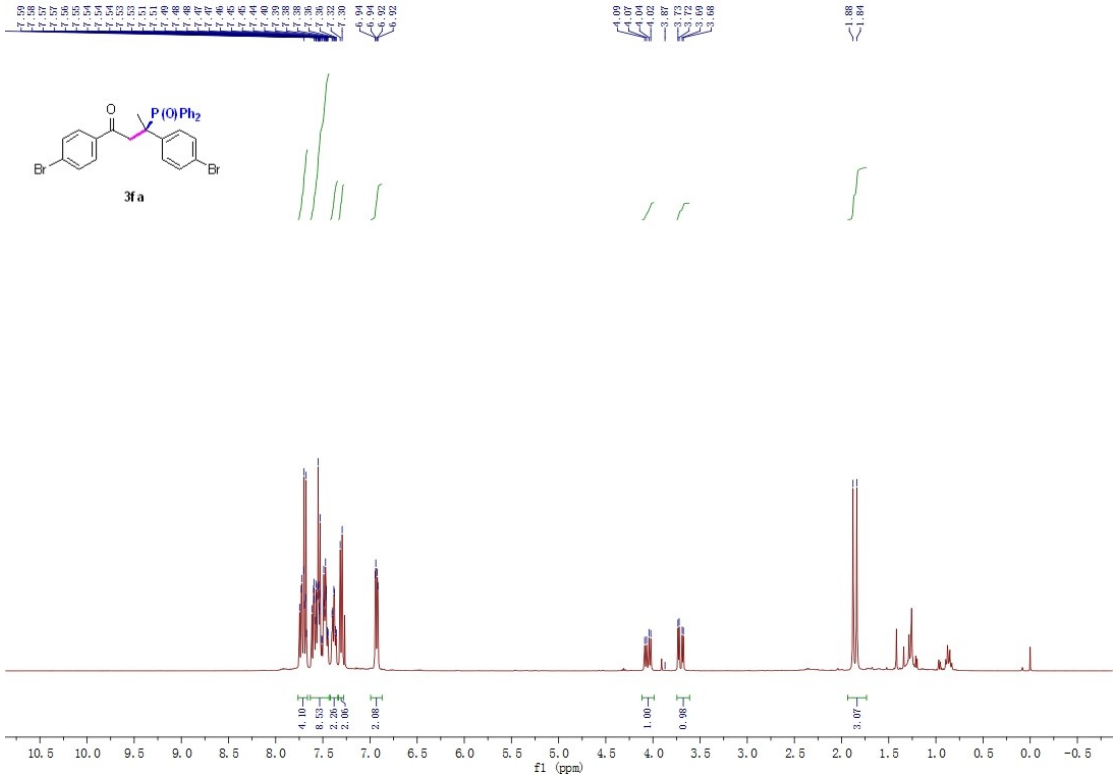

34.68
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

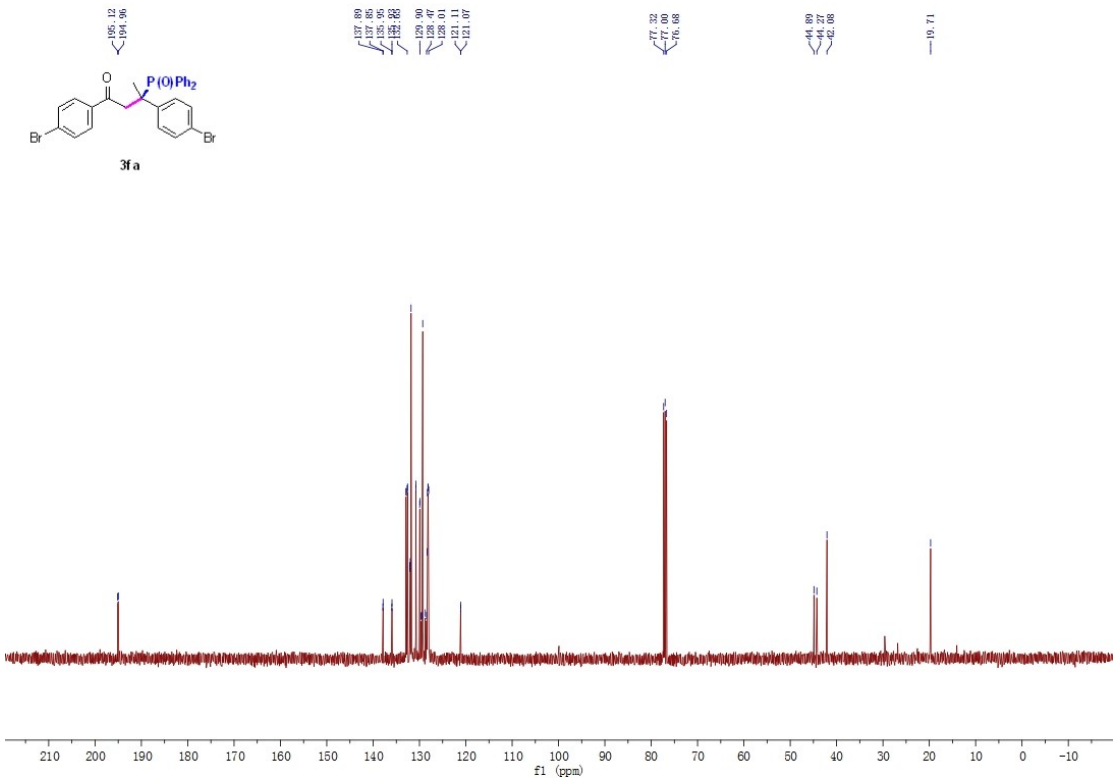

8.29
8.29
8.27
7.98
7.84
7.82
7.53
7.52
7.50
7.41
7.41
7.40
7.39
7.38
7.37
7.33
7.33
7.31
7.30
7.27
4.40
4.38
4.35
4.33
3.78
3.77
3.74
3.73
1.97
1.93
P(O)Ph2
O2N
NO2
1.92
3.89
1.99
6.04
4.05
1.00
1.03
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

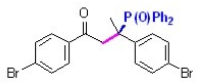
3ea


194.39
194.24
150.46
146.52
141.10
141.08
132.80
132.33
128.04
123.92
123.82
122.79
77.32
77.00
76.68
65.78
65.18
63.56
20.03
O
P(O)Ph2
O2N
NO2
3ea
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)


34.19
O
P(O)Ph2
O2N
NO2
3ea
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

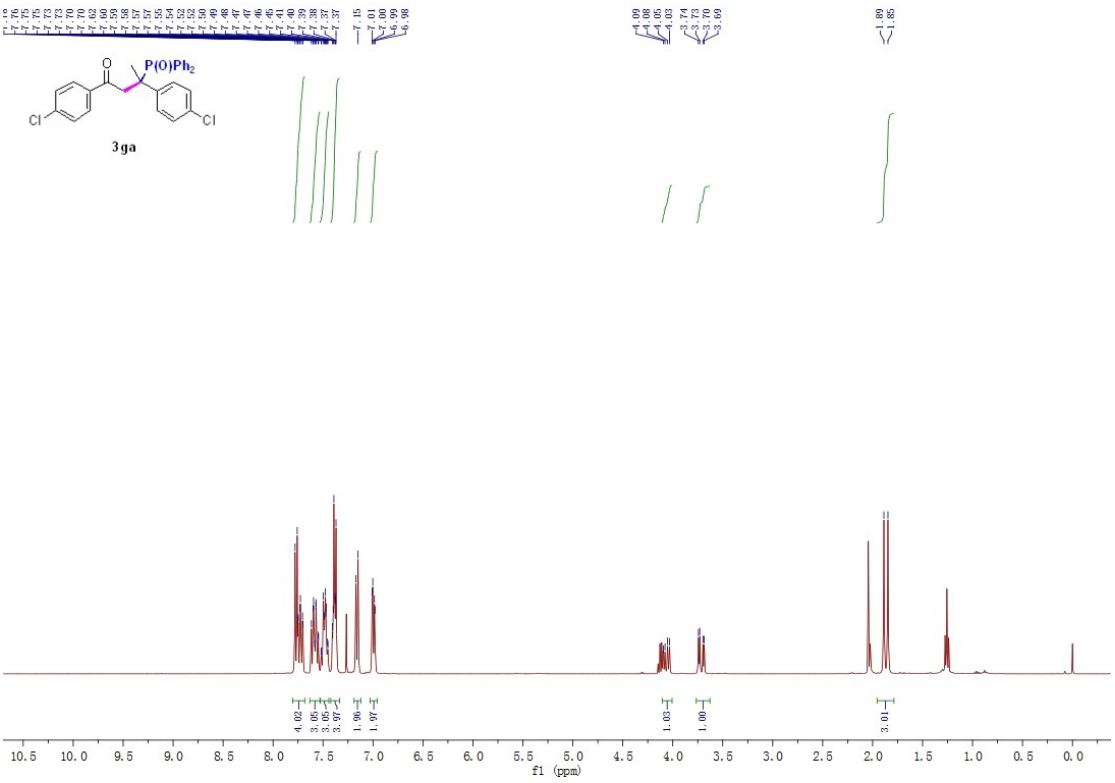

P(O)Ph2
Br
Br
3f a
f1 (ppm)


P(O)Ph2
Br
Br
3f a
f1 (ppm)

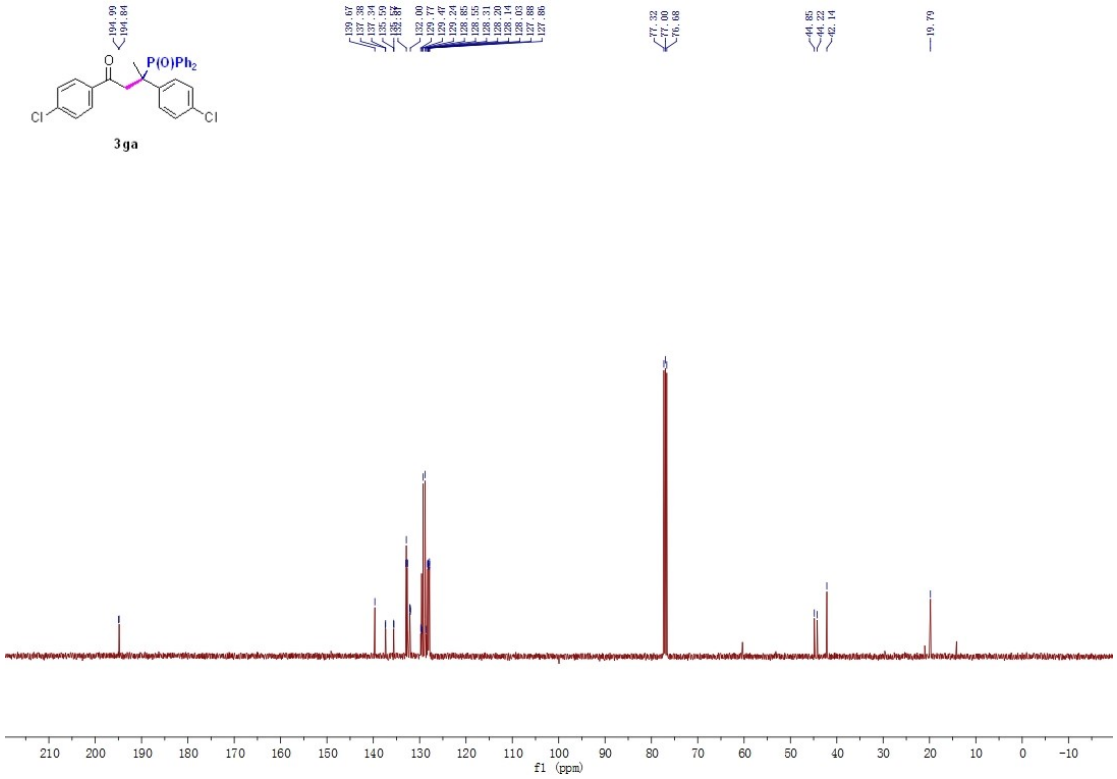

O
P(O)Ph2
Br
Br

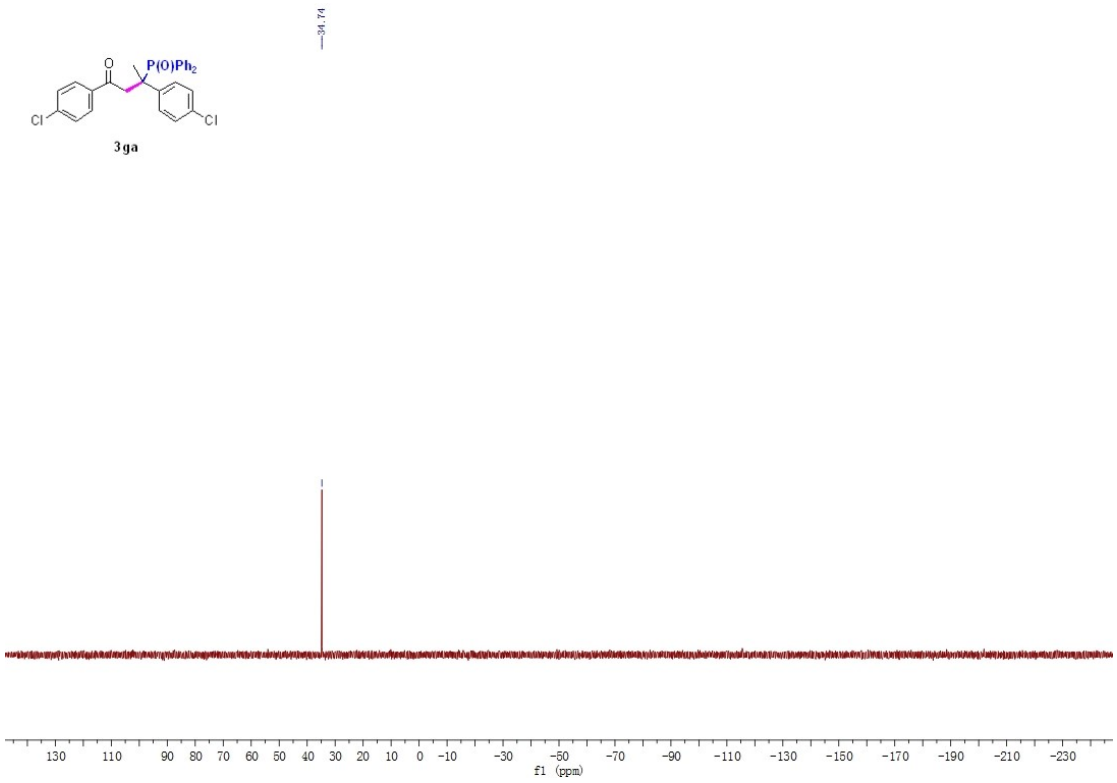
3fa

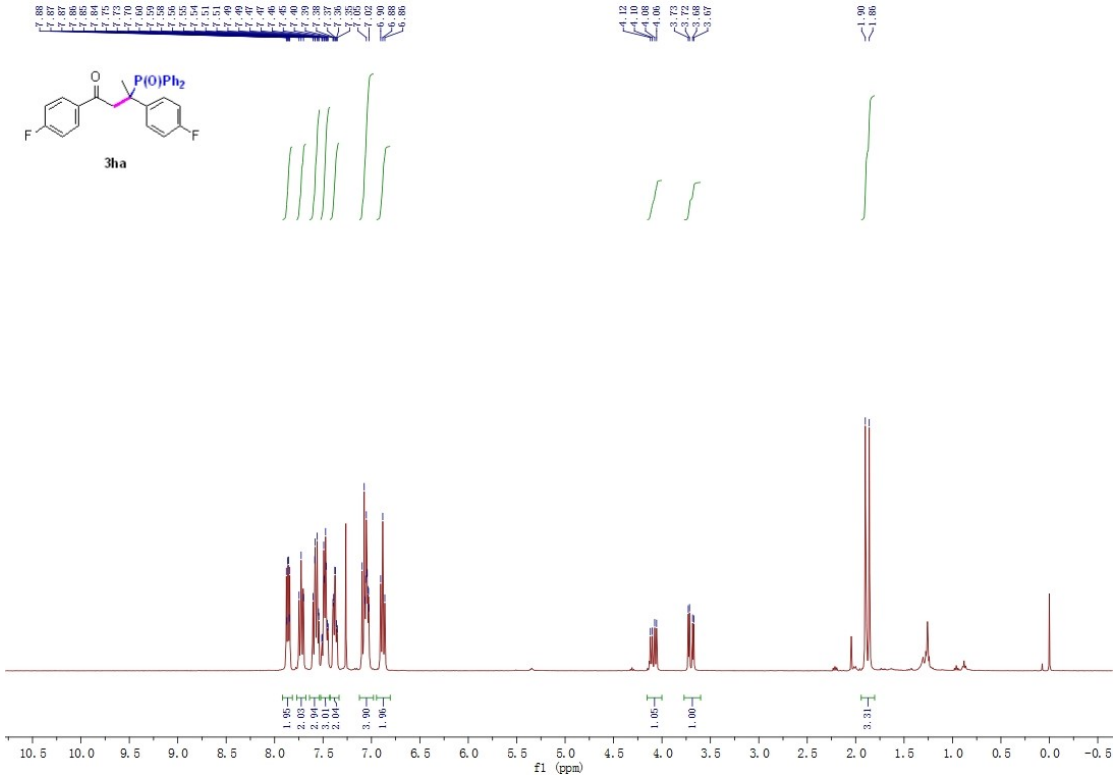
34.61
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

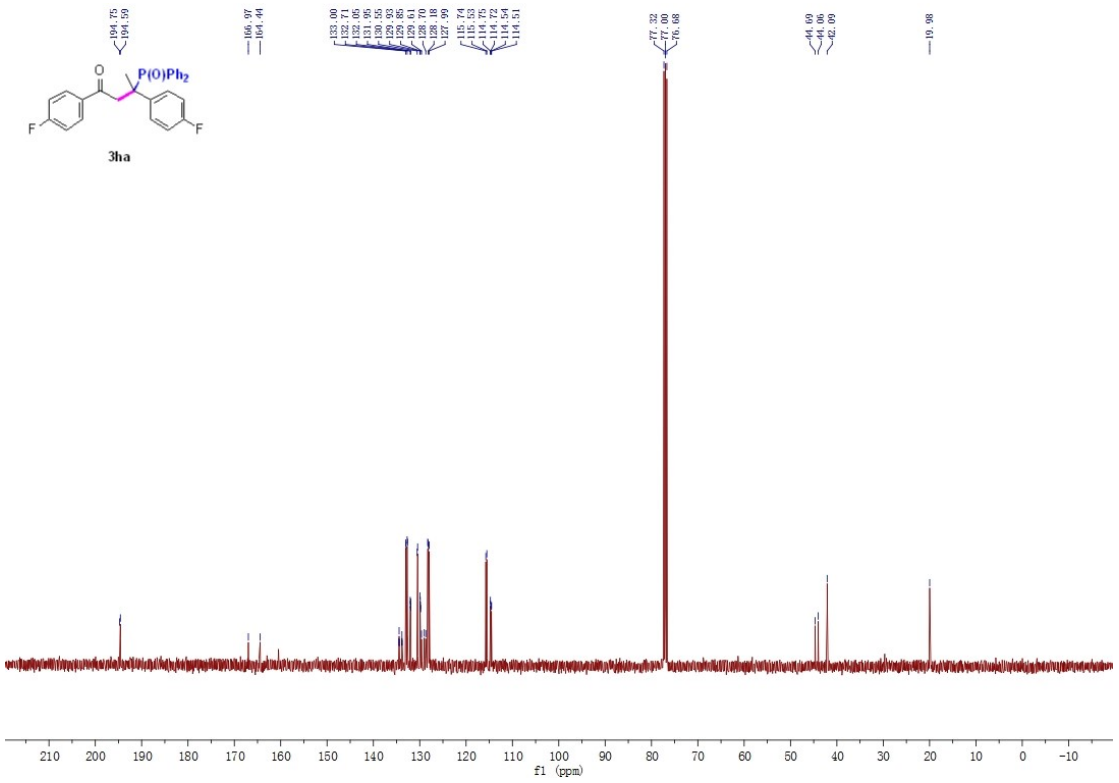

7.76 7.75 7.73 7.70 7.69 7.60 7.59 7.58 7.57 7.55 7.54 7.52 7.51 7.50 7.49 7.48 7.47 7.46 7.45 7.41 7.40 7.39 7.38 7.37
7.15 7.01 7.00 6.99 6.98
4.09 4.08 4.05 4.03 3.74 3.73 3.70 3.69
1.89 1.85
O
P(O)Ph2
Cl
Cl
4.02 3.05 3.05 3.97 1.96 1.97 1.03 1.00 3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

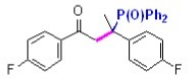
3ga


194.99
194.84
139.67
137.38
137.34
135.59
132.87
132.00
130.77
129.47
129.24
128.65
128.55
128.31
128.20
128.14
128.03
127.88
127.86
77.32
77.00
76.68
44.85
44.22
42.14
19.79
P(O)Ph2
Cl
Cl
O
3ga
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)


34.74
P(O)Ph2
Cl
Cl
O
3ga
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

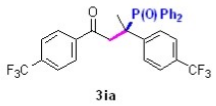

3ha


3ha


O
P(O)Ph2
F
F

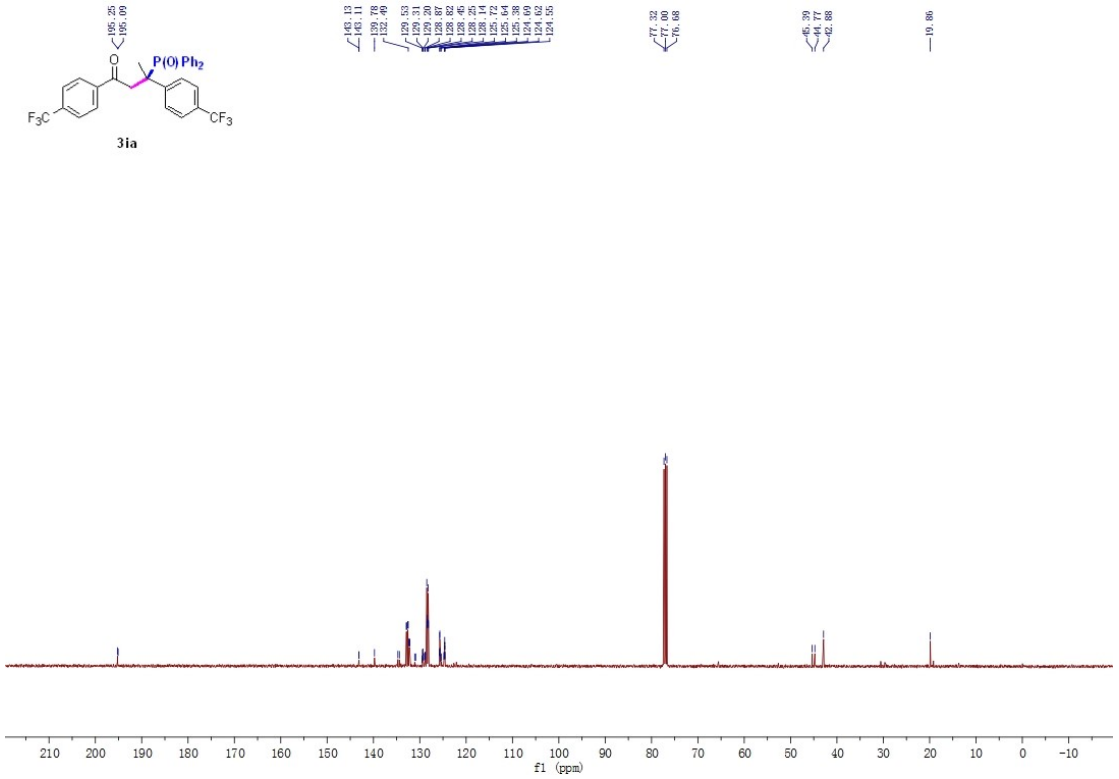
3ha

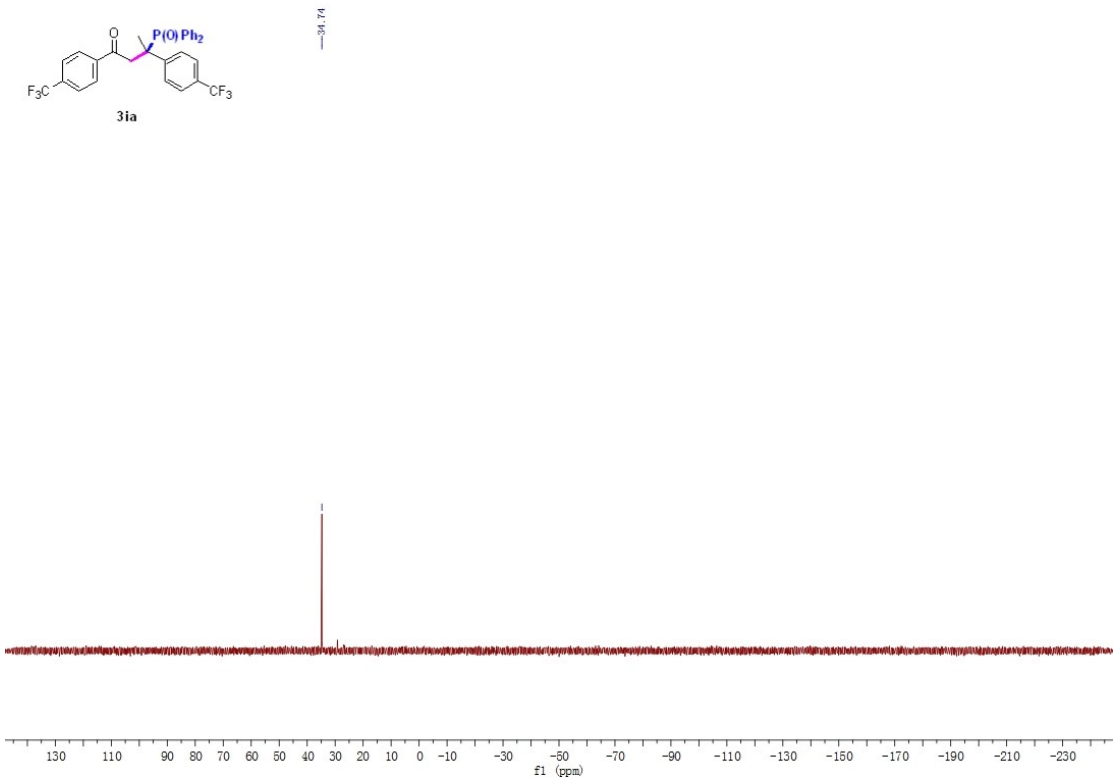
35.08
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

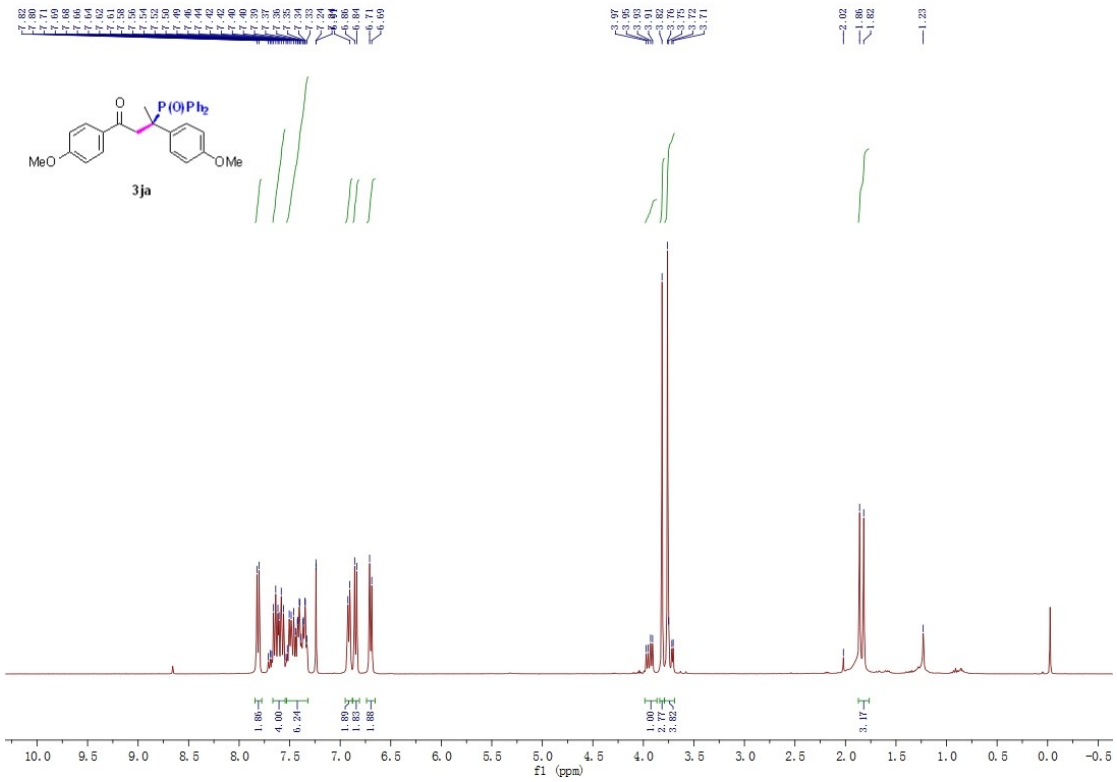

O
P(O)Ph2
F3C
CF3

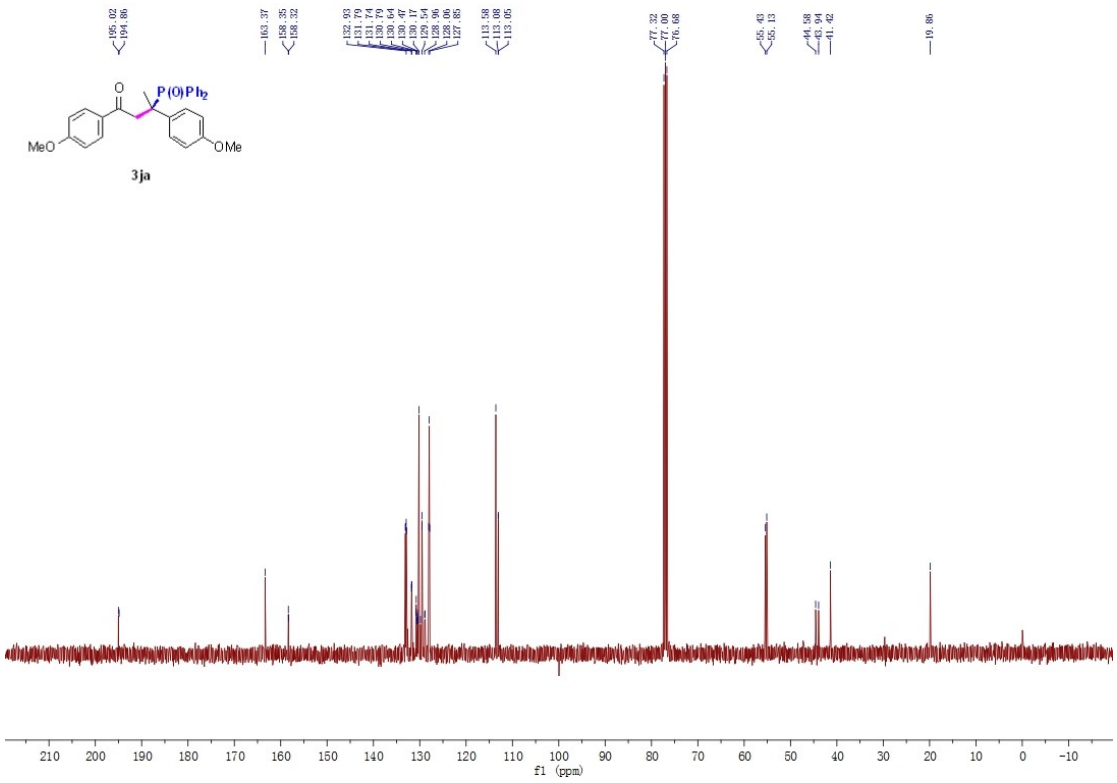
3ia

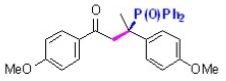
7.94
7.92
7.77
7.70
7.59
7.58
7.57
7.56
7.54
7.53
7.52
7.50
7.48
7.46
7.45
7.40
7.38
7.36
7.26
7.21
4.29
4.27
4.24
4.22
3.78
3.76
3.73
3.72
1.95
1.91
2.02
4.37
10.49
2.01
1.02
1.00
3.50
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


195.25
195.09
143.13
143.11
139.78
132.49
129.53
129.31
129.20
128.87
128.82
128.45
128.25
128.14
125.72
125.64
125.58
124.99
124.62
124.55
77.32
77.00
76.68
45.39
44.77
42.88
19.86
P(O)Ph2
F3C
CF3
3ia
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)


34.74
P(O)Ph2
F3C
CF3
3ia
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

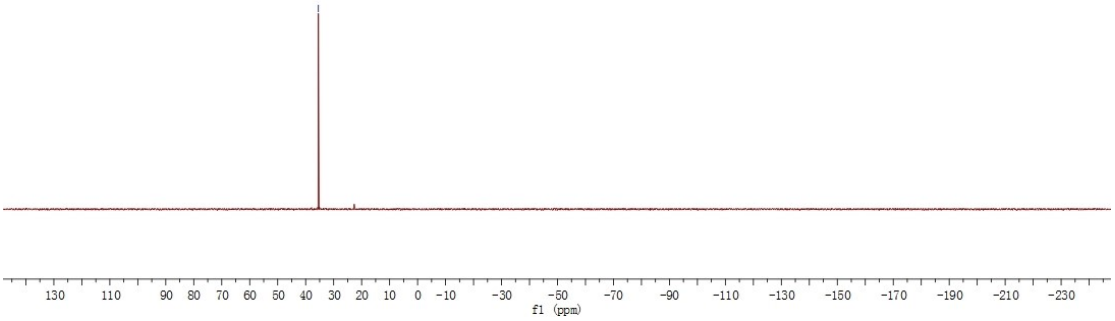

P(O)Ph2
MeO
OMe
3ja
f1 (ppm)

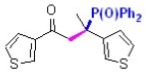

P(O)Ph2
MeO
OMe
3ja
f1 (ppm)


P(O)Ph2
MeO
OMe

3ja

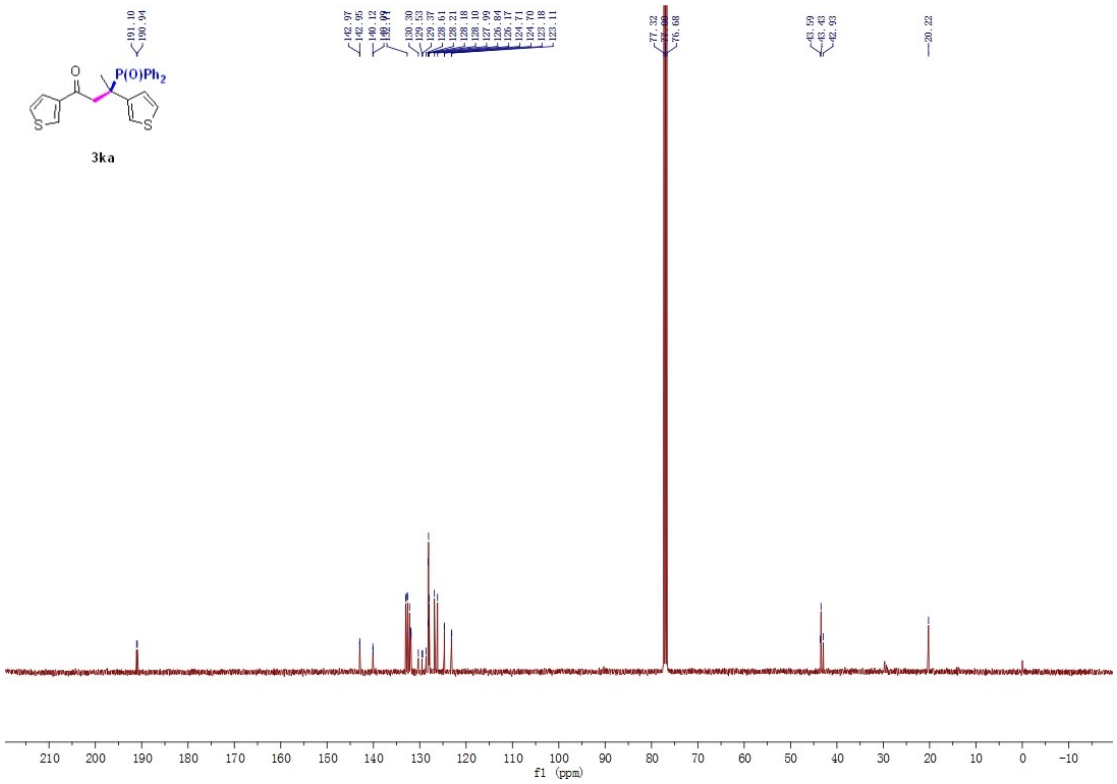
35.45

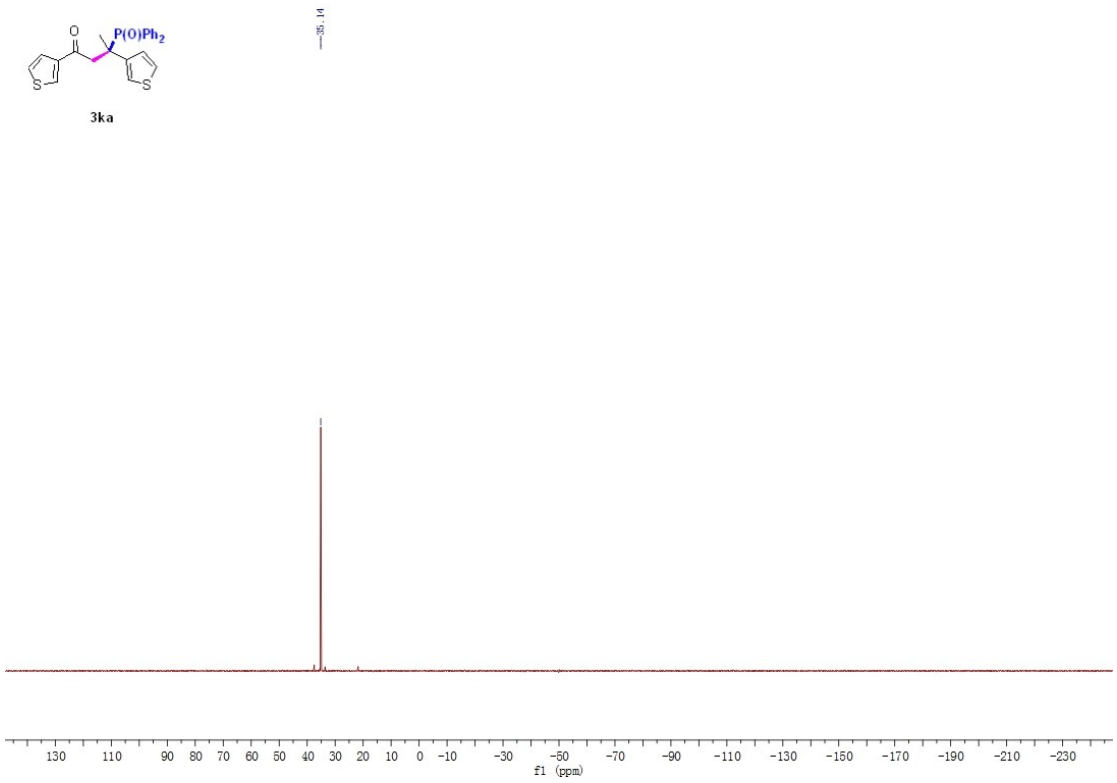

130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

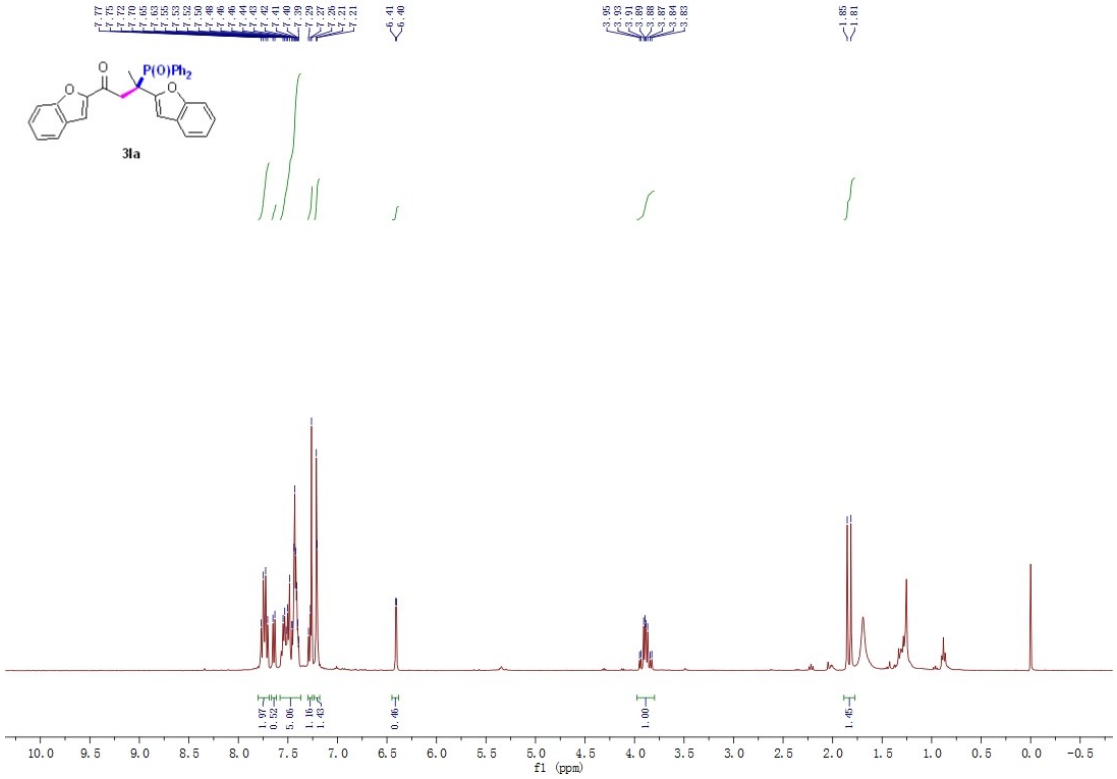

P(O)Ph2

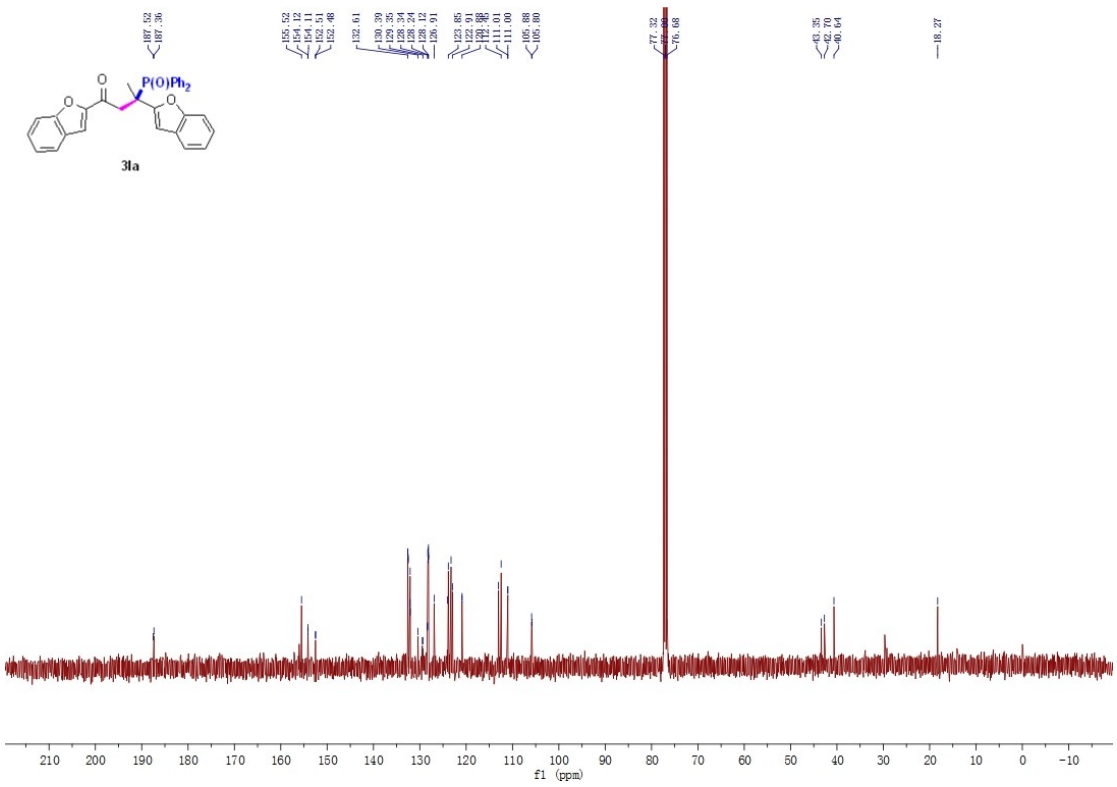
3ka

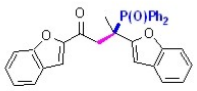
7.98
7.97
7.54
7.47
7.41
7.37
7.23
7.17
6.85
6.84
6.83
6.80
6.78
3.83
3.81
3.79
3.77
3.06
3.05
3.02
3.00
1.86
1.82
0.89
2.00
6.17
3.01
1.97
1.89
1.00
1.02
4.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


191.10
190.94
142.97
142.95
140.12
130.30
129.53
129.37
128.61
128.21
128.18
128.10
127.99
126.84
126.17
124.71
124.70
123.18
123.11
77.32
77.00
76.68
43.59
43.43
42.93
20.22
P(O)Ph2
S
S
O
3ka
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)


35.14
P(O)Ph2
S
S
O
3ka
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

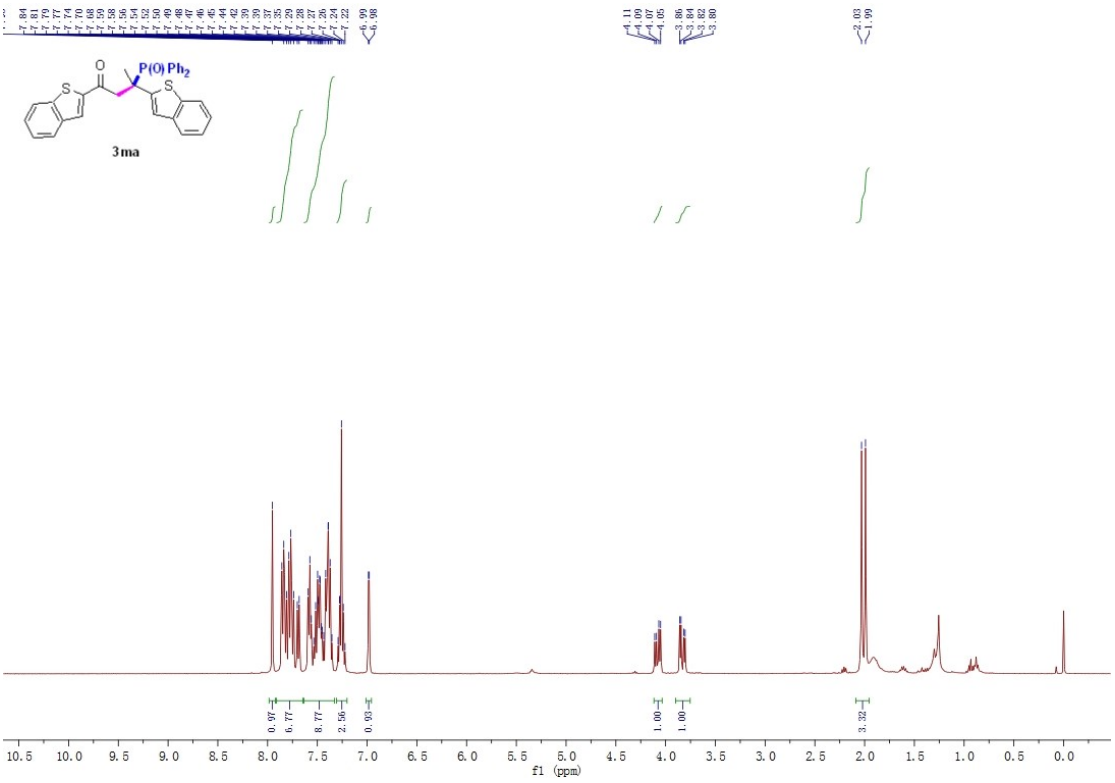

7.77
7.75
7.72
7.70
7.65
7.55
7.53
7.52
7.50
7.48
7.46
7.44
7.43
7.42
7.41
7.40
7.39
7.29
7.27
7.26
7.21
6.41
6.40
3.95
3.93
3.91
3.90
3.88
3.87
3.84
3.83
1.85
1.81
P(O)Ph2
3la
1.97
0.52
5.06
1.10
1.45
0.46
1.00
1.46
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


187.52
187.36
155.52
154.12
154.11
152.74
152.48
132.61
130.39
129.35
128.34
128.24
128.12
126.91
123.85
122.91
122.68
122.48
111.01
111.00
105.88
105.80
77.32
77.00
76.68
43.35
42.70
40.64
18.27
P(O)Ph2
3la
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)

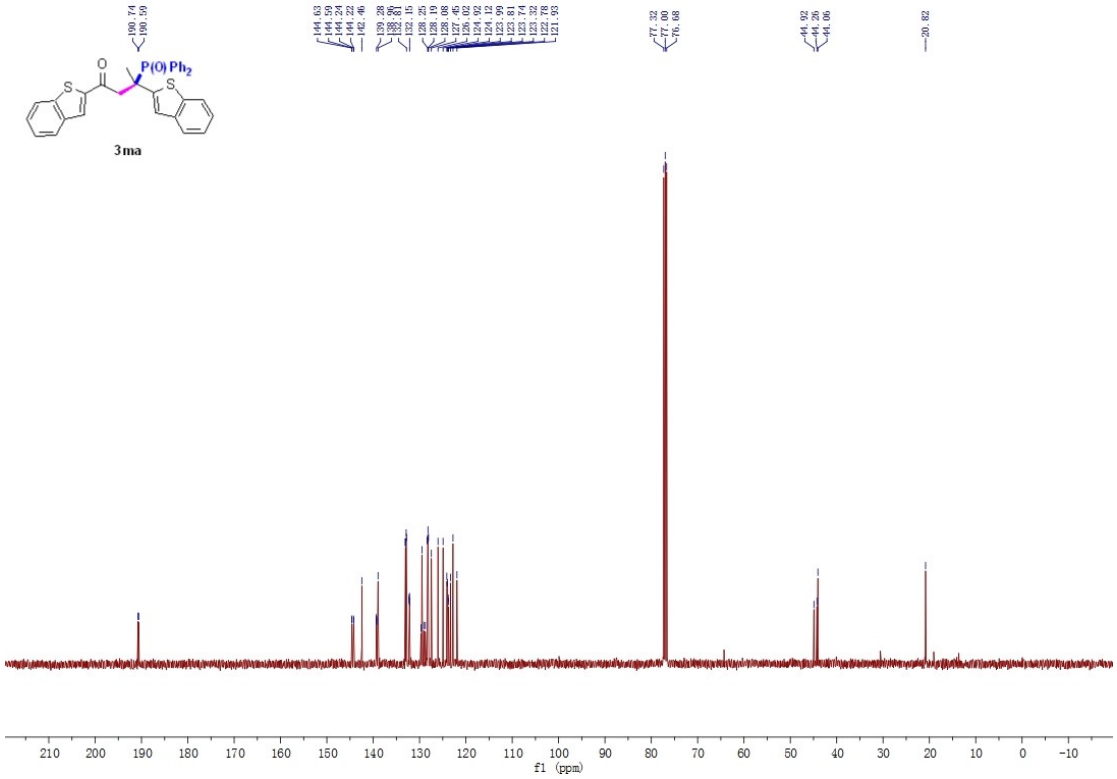

P(O)Ph2
O
O

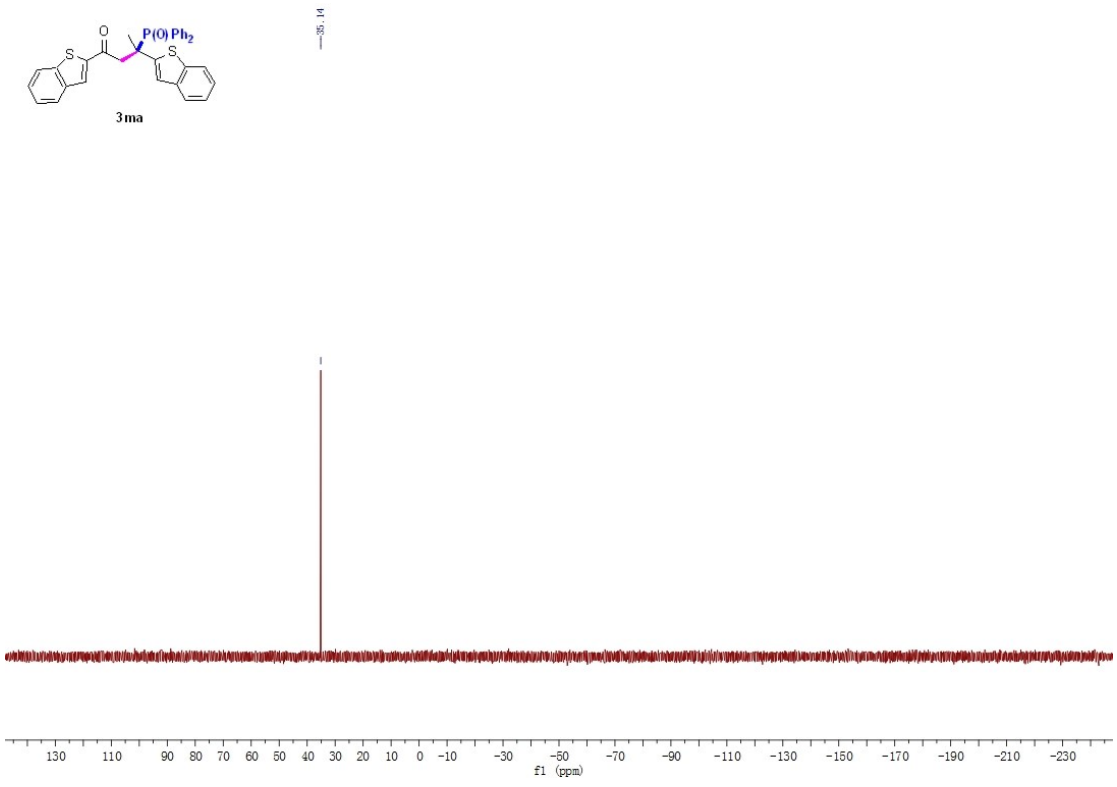
3la

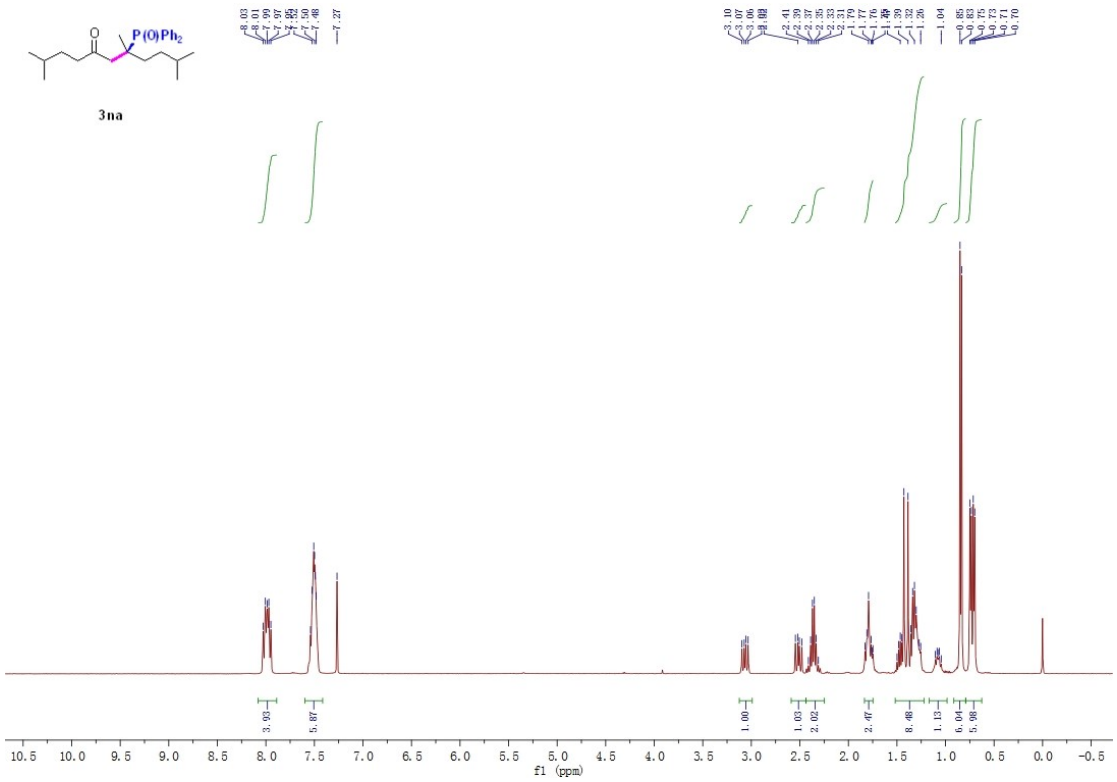
33.24
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

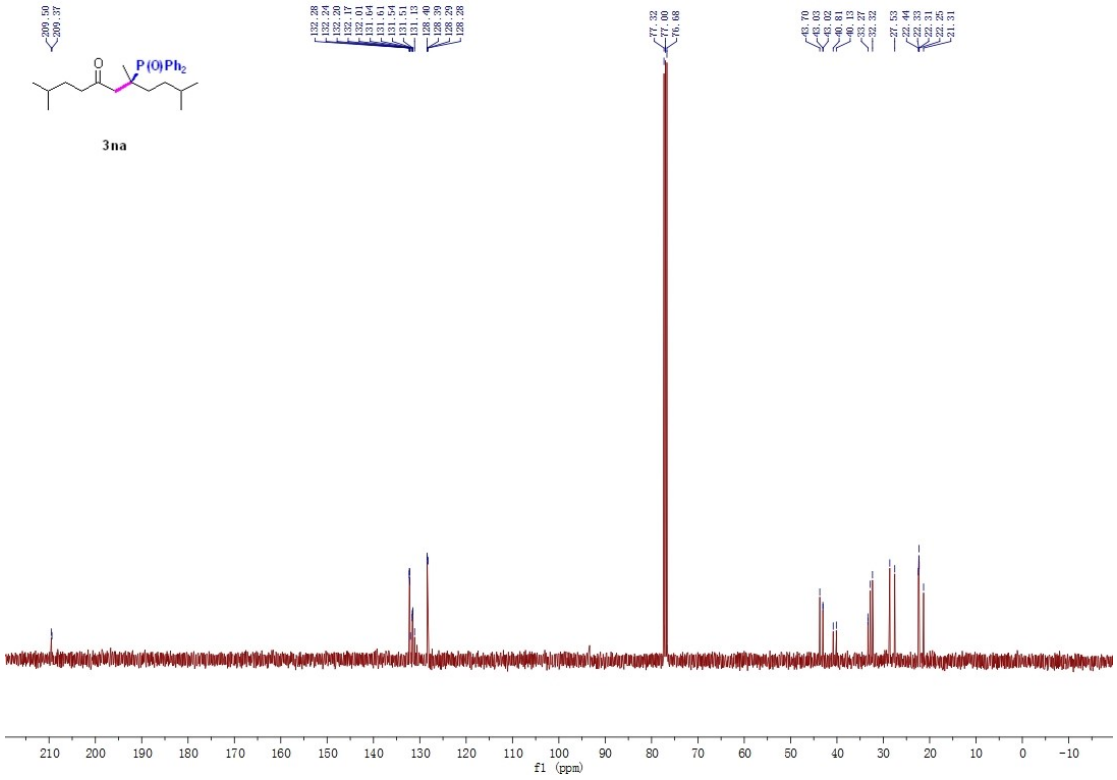

7.84
7.81
7.79
7.77
7.74
7.70
7.68
7.59
7.58
7.56
7.54
7.52
7.50
7.49
7.48
7.47
7.46
7.45
7.44
7.42
7.40
7.39
7.37
7.35
7.33
7.28
7.27
7.26
7.24
7.22
6.99
6.98
4.11
4.09
4.07
4.05
3.86
3.84
3.82
3.80
2.03
1.99
P(O)Ph2
S
S
0.97
6.77
8.77
2.56
0.93
1.00
1.00
3.32
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

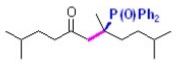
3ma


190.74
190.59
144.63
144.59
144.24
144.22
142.46
139.28
139.06
138.87
138.81
132.15
128.25
128.19
128.08
127.45
126.02
124.92
124.12
123.99
123.81
123.74
123.32
123.28
121.93
77.32
77.00
76.68
44.92
44.26
44.06
20.82
P(O)Ph2
S
S
O
3ma
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)


35.14
P(O)Ph2
S
S
O
3ma
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

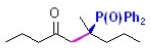

P(O)Ph2
3na
f1 (ppm)


P(O)Ph2
3na
f1 (ppm)


P(O)Ph2

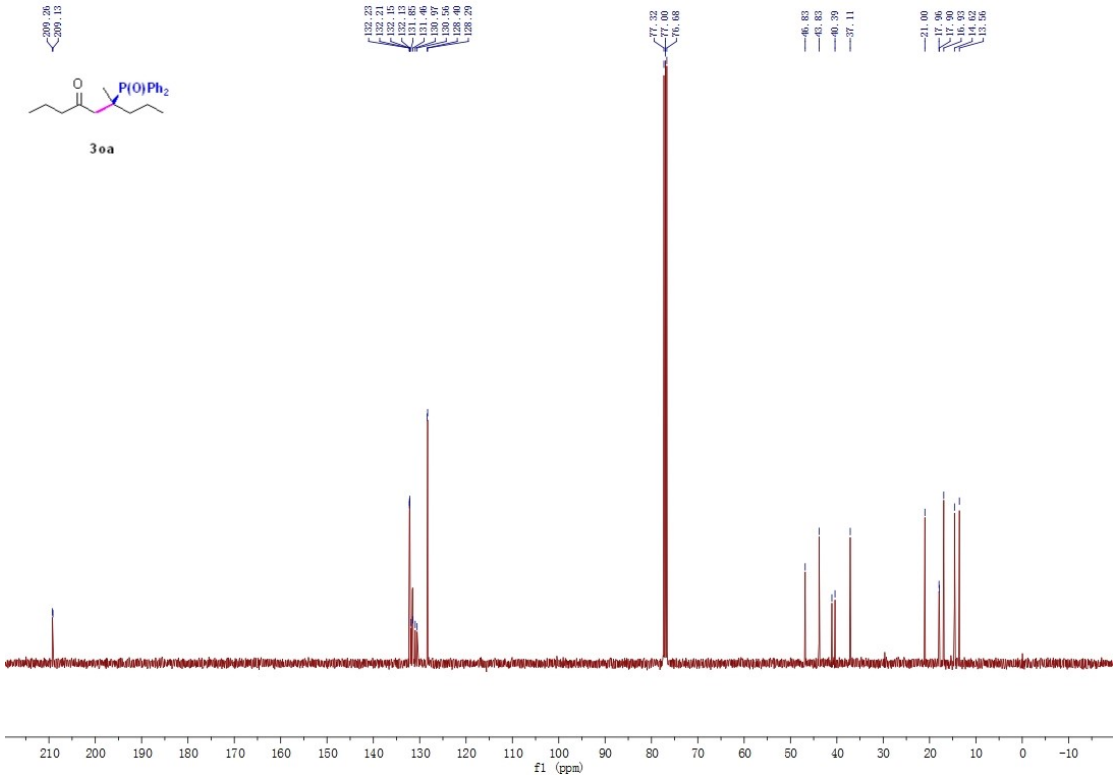
3na

36.53
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


P(O)Ph2

3oa

8.02
8.00
7.99
7.97
7.97
7.95
7.51
7.49
7.46
7.27
3.07
3.04
3.03
2.36
2.35
2.34
2.33
2.32
1.77
1.74
1.72
1.39
1.21
0.86
0.86
0.84
0.84
0.82
0.82
0.78
0.76
0.74
4.12
6.24
1.00
1.03
2.15
2.13
6.31
2.16
3.13
3.24
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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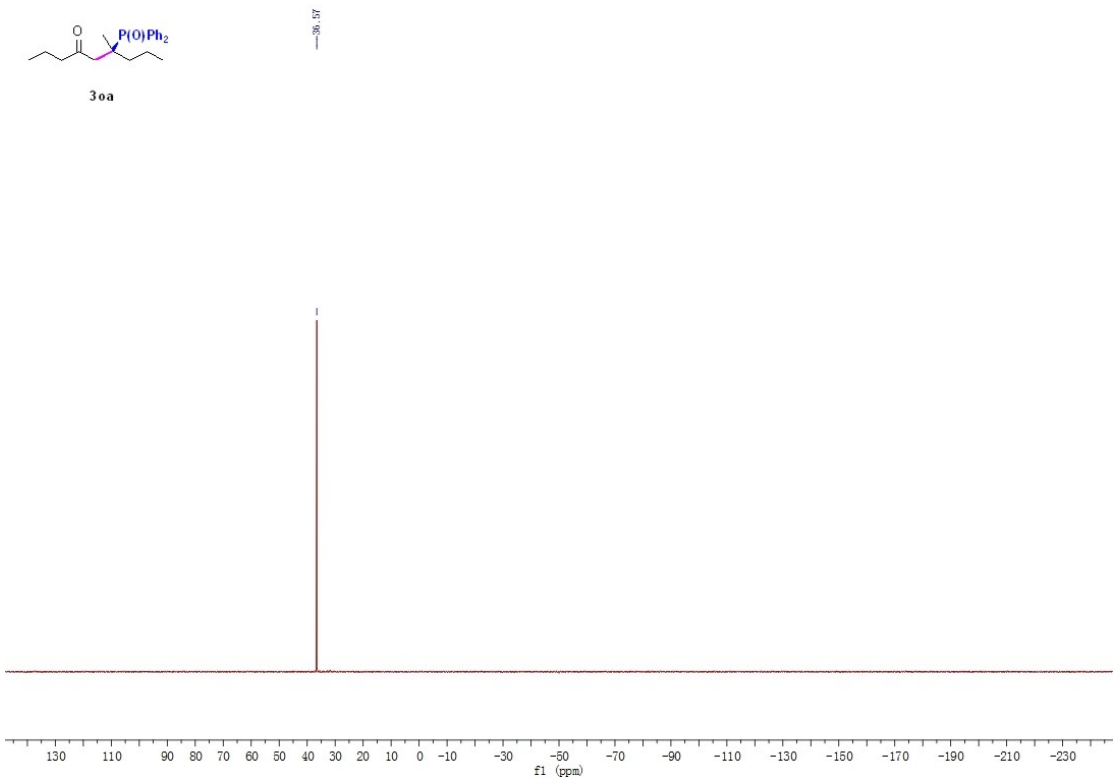
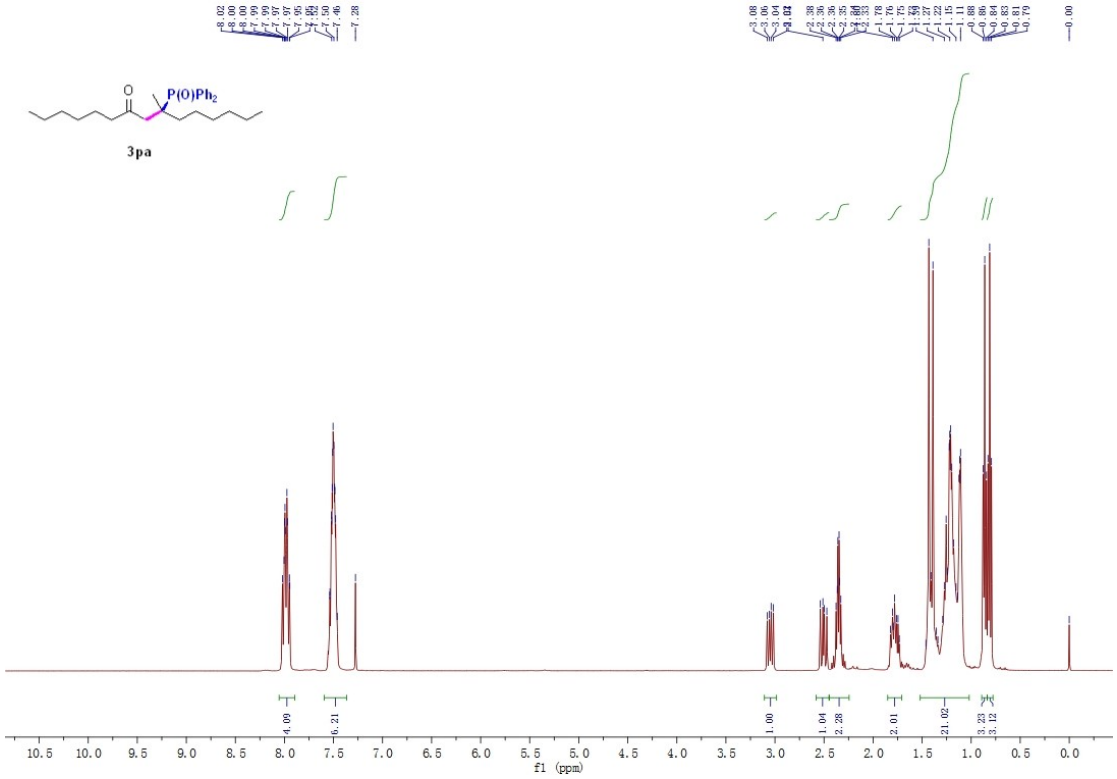
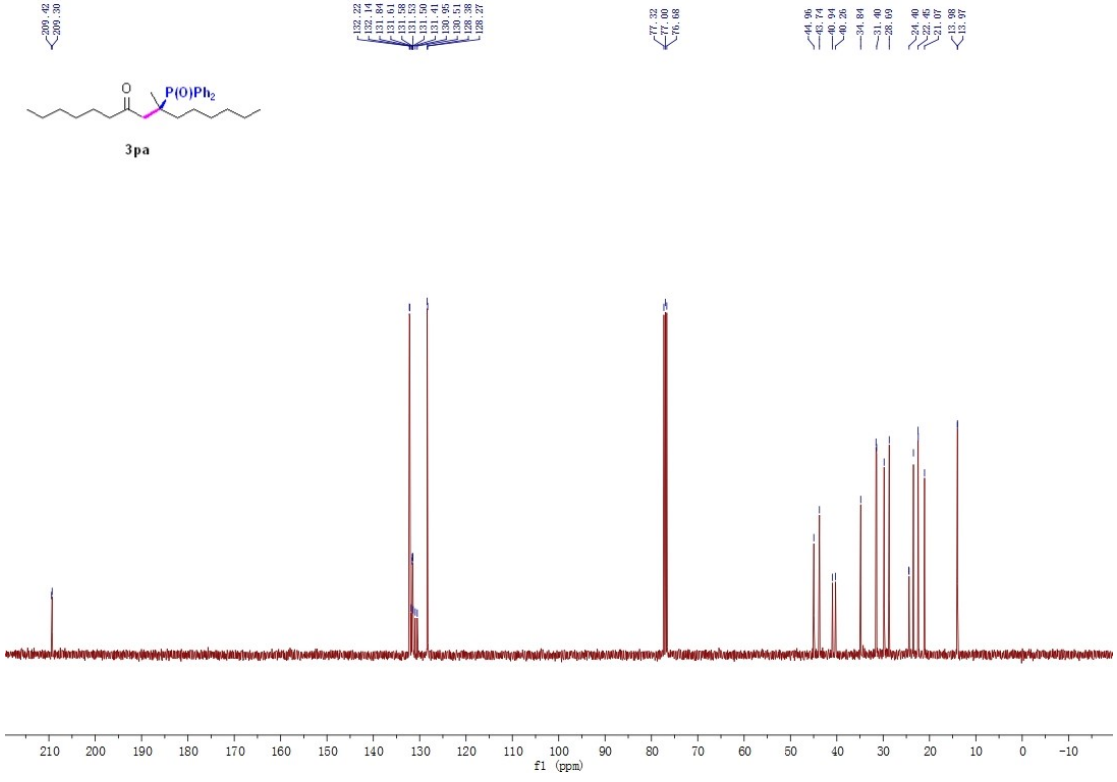
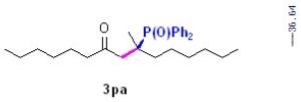
209.13
132.23
132.21
132.15
132.13
131.85
131.49
130.97
130.56
128.40
128.29
77.32
77.00
76.68
46.83
43.83
40.39
37.11
21.00
17.96
17.80
16.93
14.62
13.56
O
P(O)Ph2
3oa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

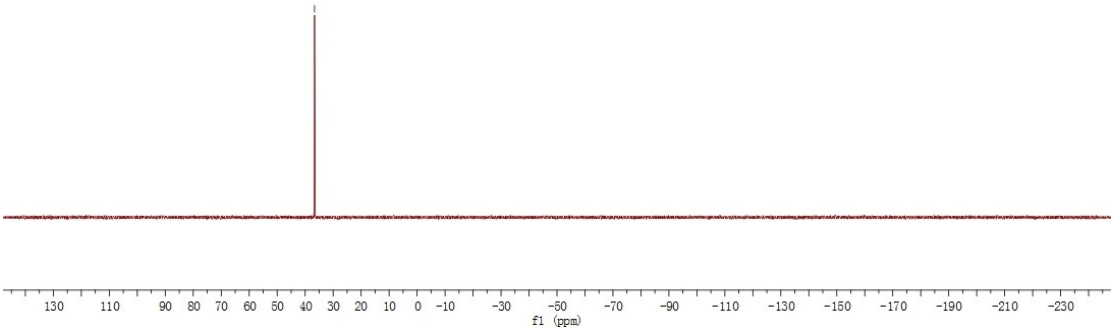

36.57
O
P(O)Ph2
3oa
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


P(O)Ph2
3pa
f1 (ppm)

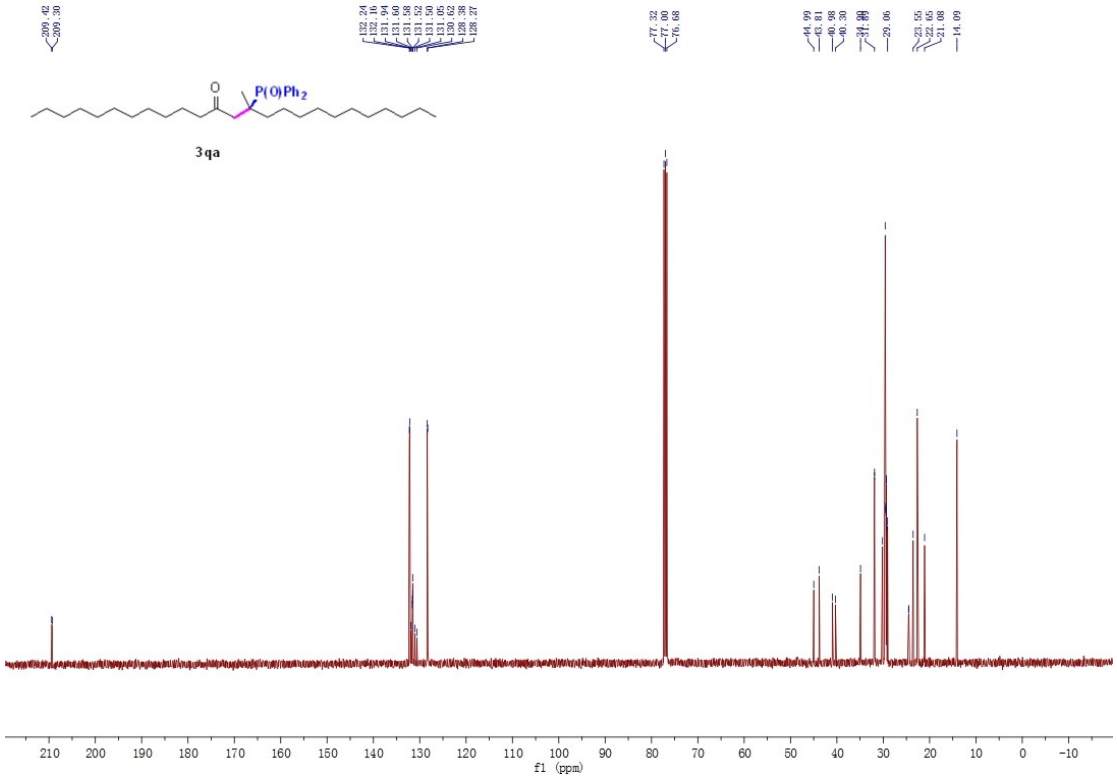

P(O)Ph2
3pa
f1 (ppm)



3pa



3qa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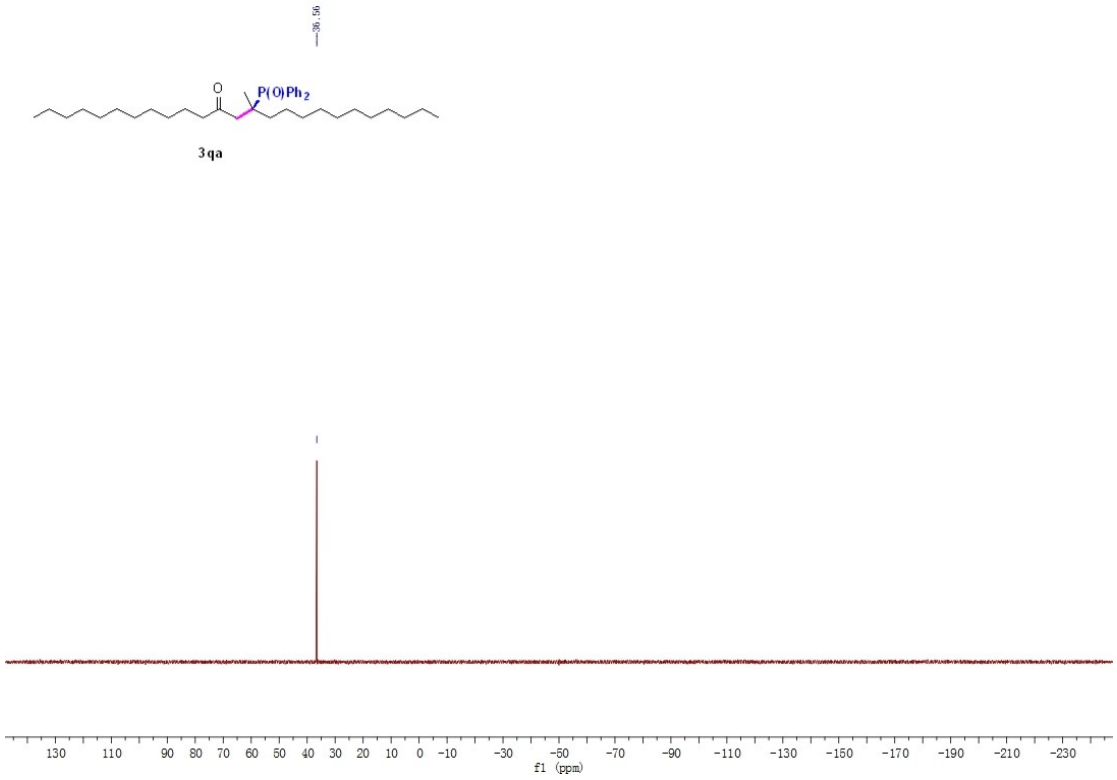
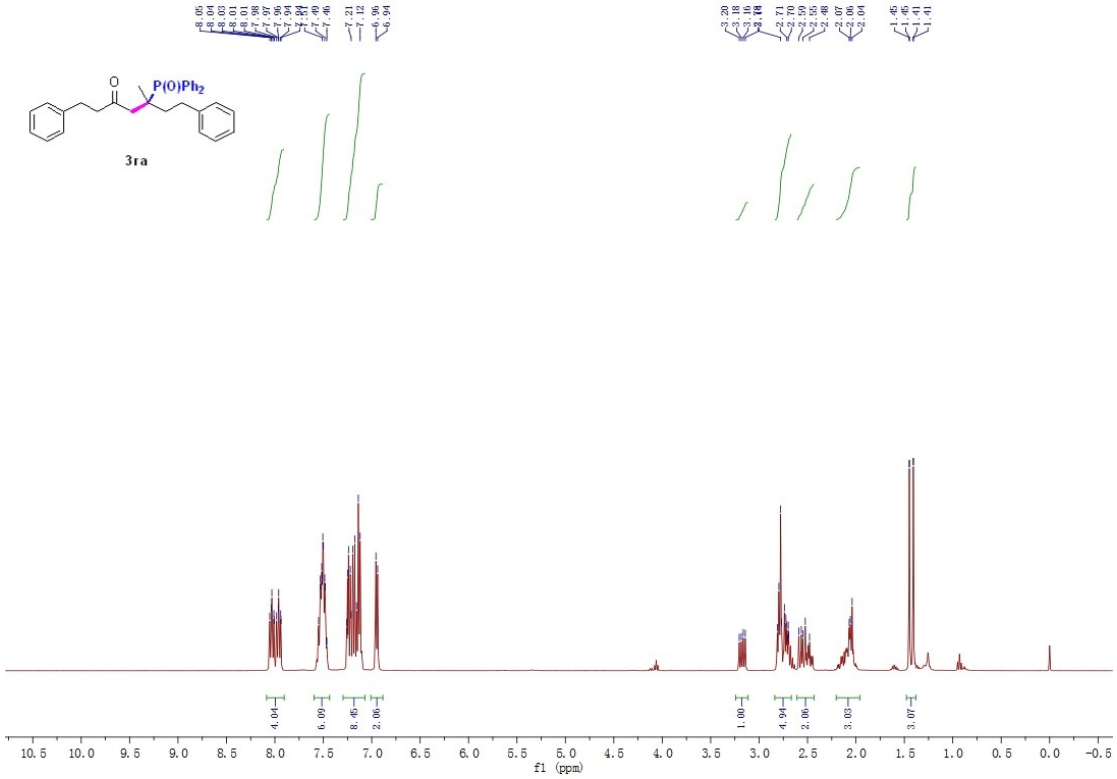
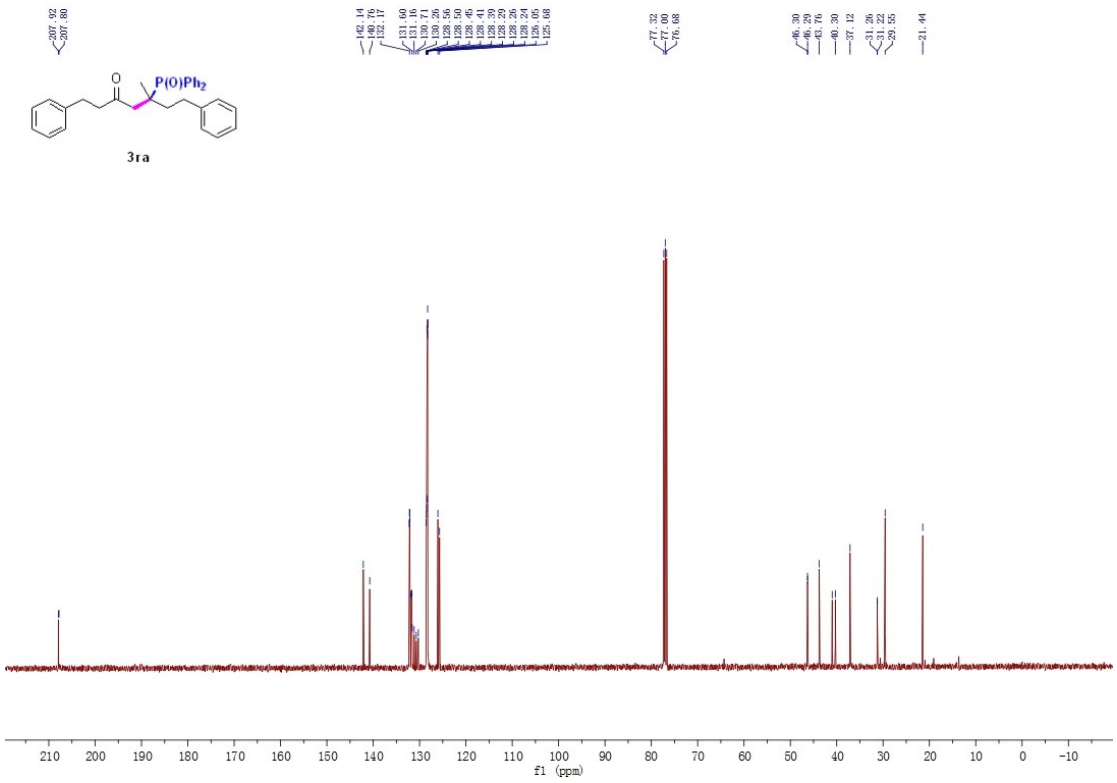
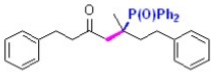
209.30
132.24
132.10
131.94
131.60
131.58
131.32
131.30
131.05
130.62
128.38
128.27
77.32
77.00
76.68
44.99
43.81
40.98
40.30
31.89
29.06
23.55
22.65
21.08
14.09
O
P(O)Ph2
3qa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


36.56
O
P(O)Ph2
3qa
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

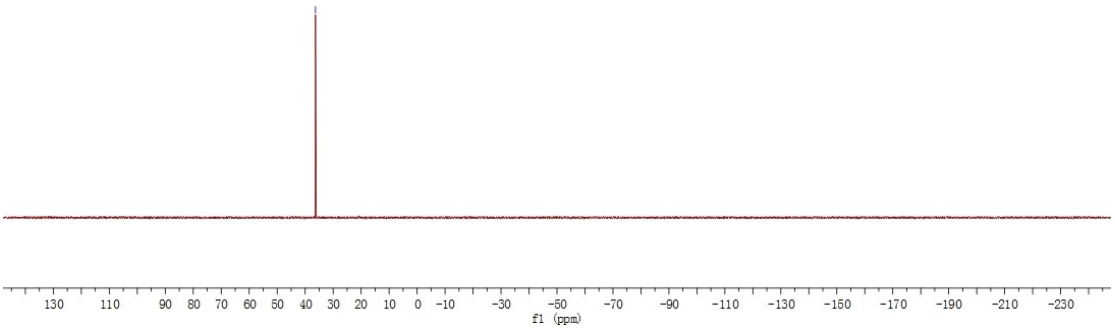

P(O)Ph2
3ra
f1 (ppm)


P(O)Ph2
3ra
f1 (ppm)

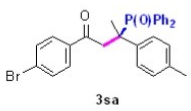

O
P(O)Ph2

3ra

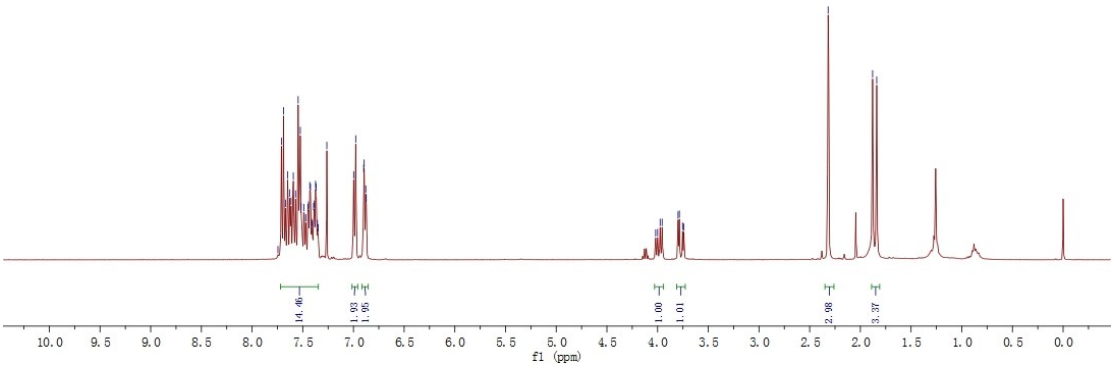
36.31

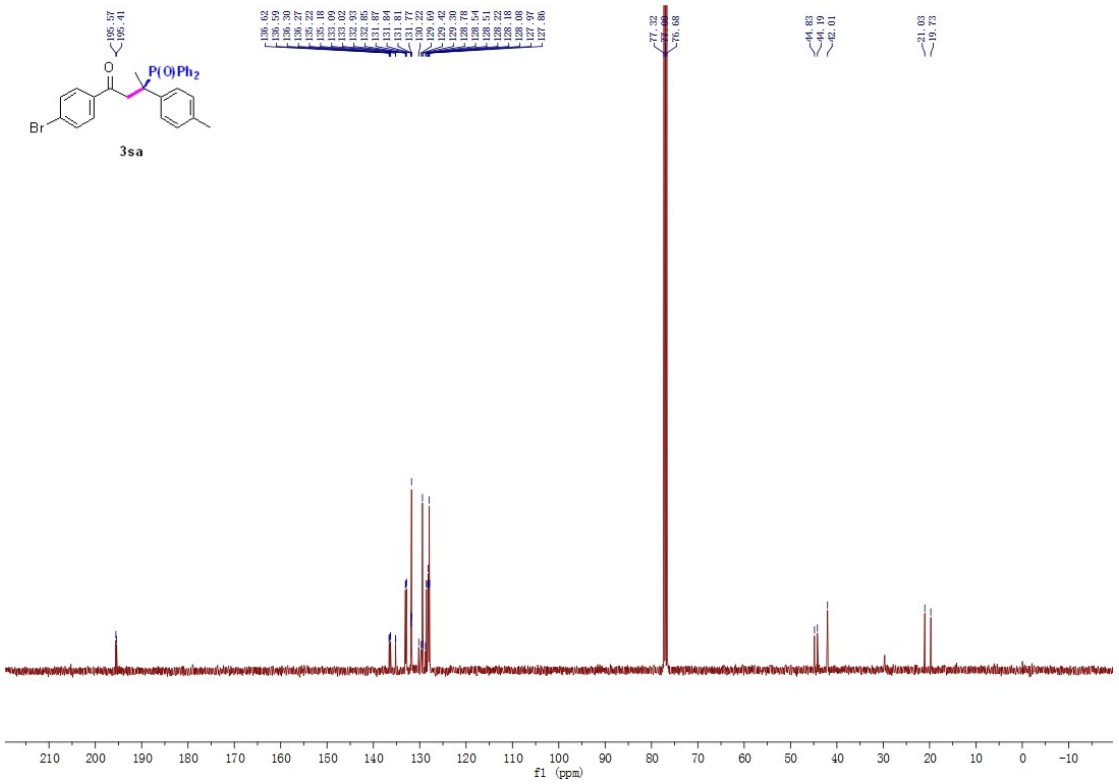

130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


7.74
7.71
7.69
7.67
7.65
7.63
7.62
7.59
7.57
7.55
7.52
7.49
7.47
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.37
7.37
7.36
7.35
7.26
7.00
6.98
6.90
6.89
6.88
6.87
4.02
4.00
3.98
3.96
3.80
3.79
3.73
3.74
2.32
1.88
1.84


O
P(O)Ph2
Br

3sa


14.46
1.93
1.95
1.00
1.01
2.98
3.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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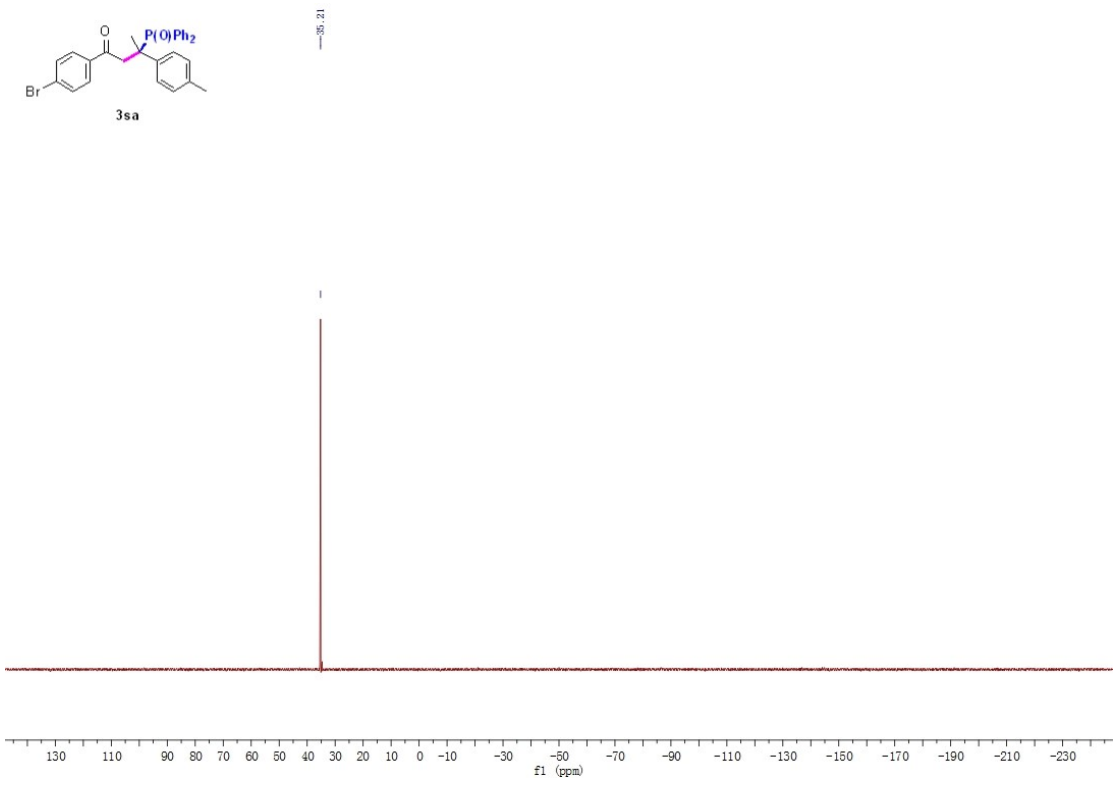
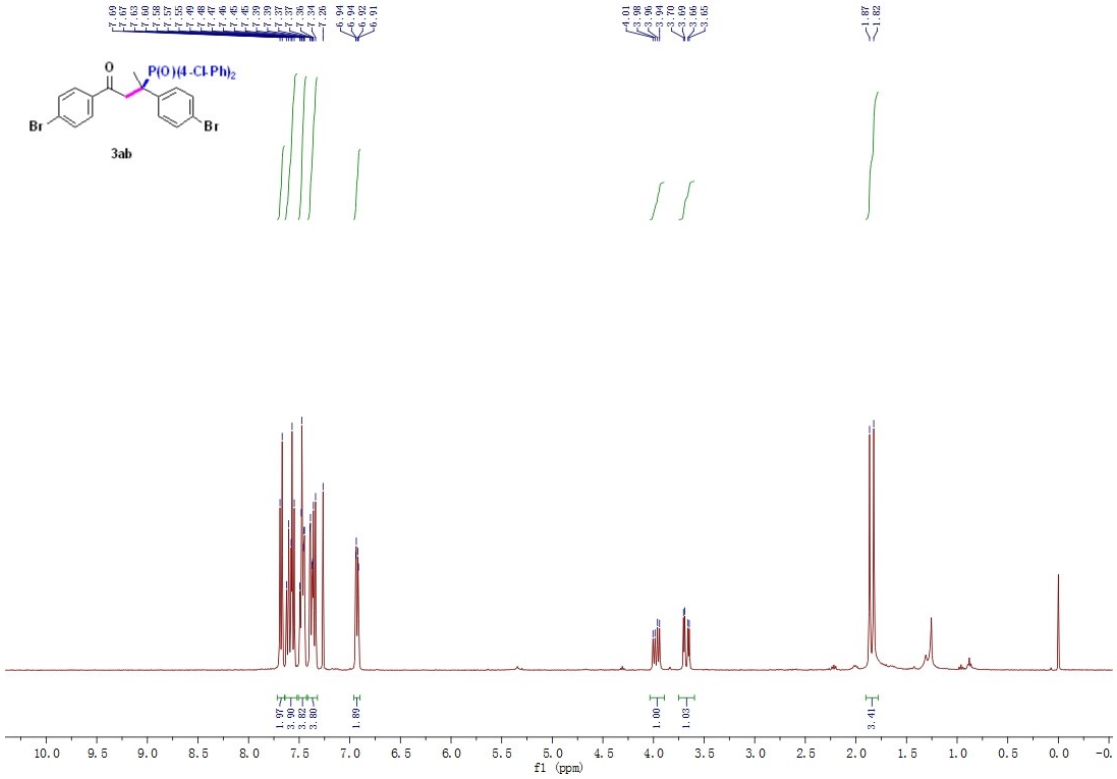
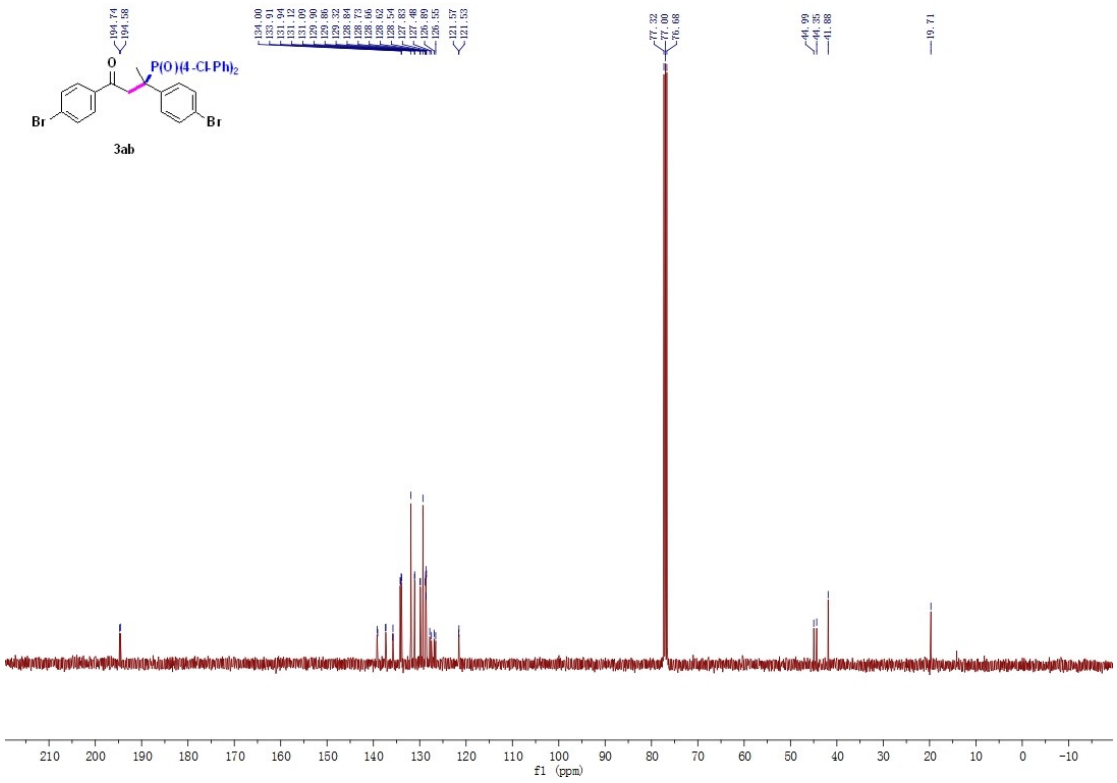
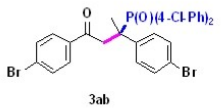
195.41
136.62
136.59
136.30
136.27
135.22
135.18
133.09
133.02
132.93
132.85
131.87
131.84
131.81
131.77
130.22
130.00
129.42
129.30
128.78
128.54
128.51
128.22
128.18
128.08
127.97
127.86
77.32
77.00
76.68
44.83
44.19
42.01
21.03
19.73
O
P(O)Ph2
Br
3sa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


35.21
O
P(O)Ph2
Br
3sa
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

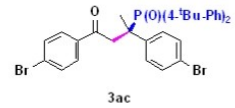

P(O)(4-Cl-Ph)2
Br
Br
3ab
f1 (ppm)


P(O)(4-Cl-Ph)2
Br
Br
3ab
f1 (ppm)


O
P(O)(4-Cl-Ph)2
Br
Br

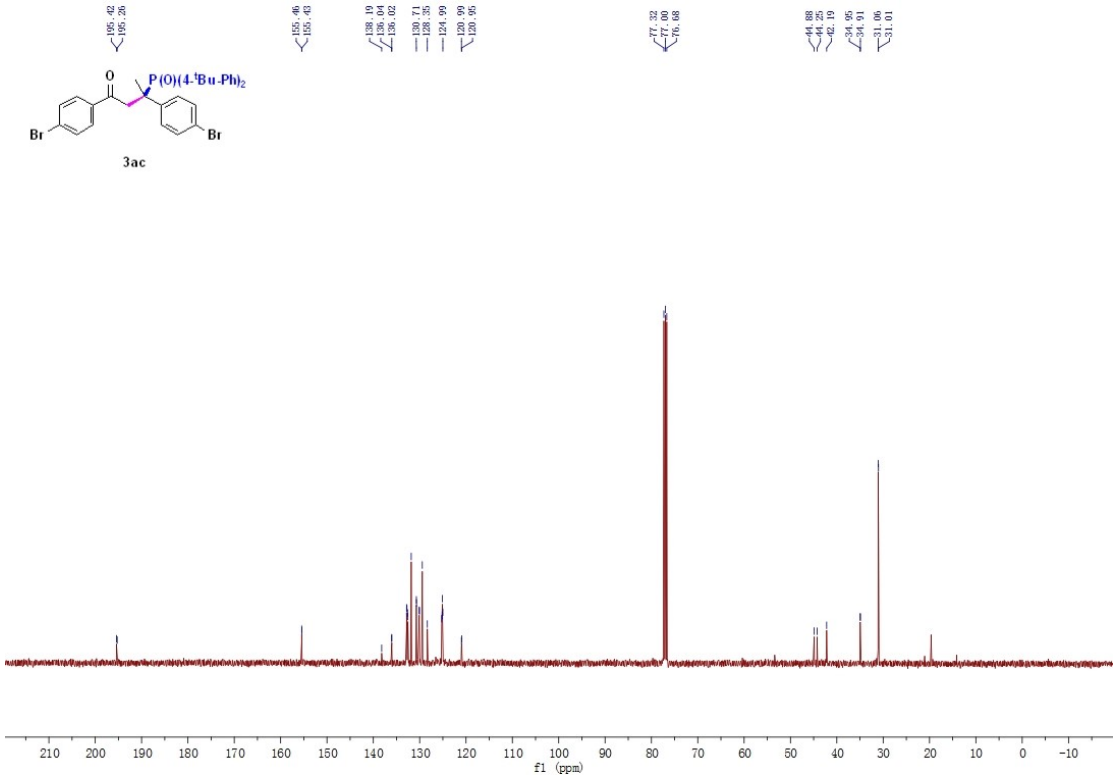
3ab

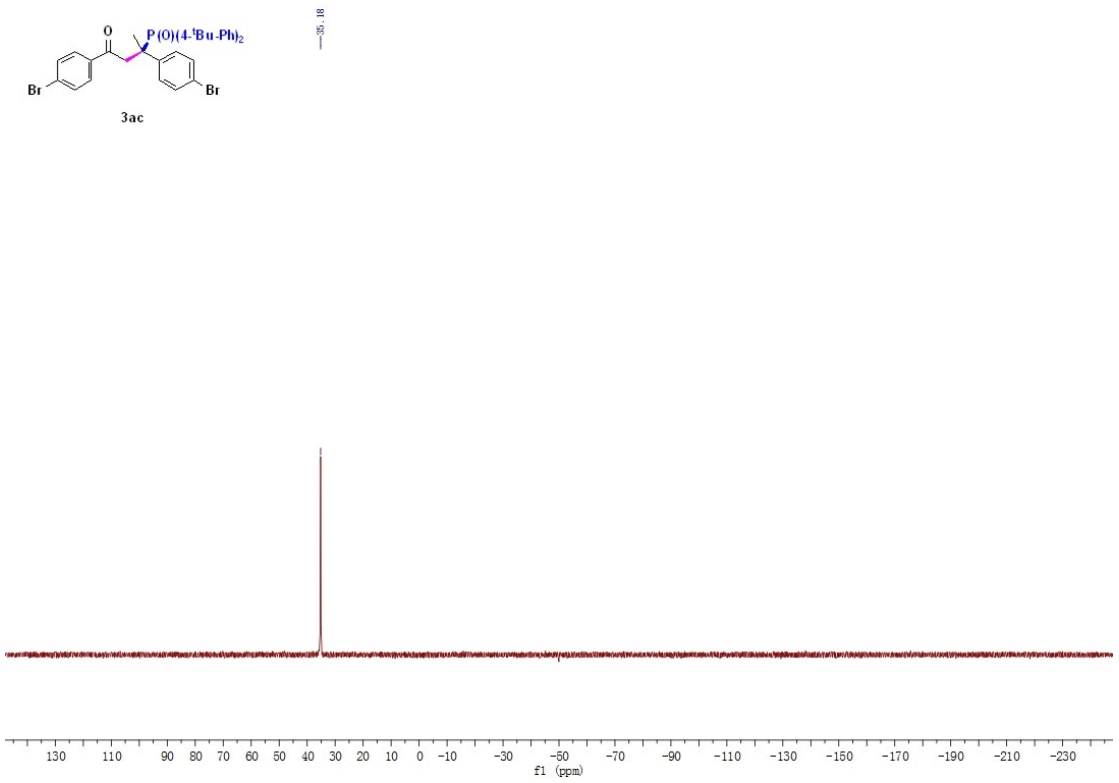
34.03
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

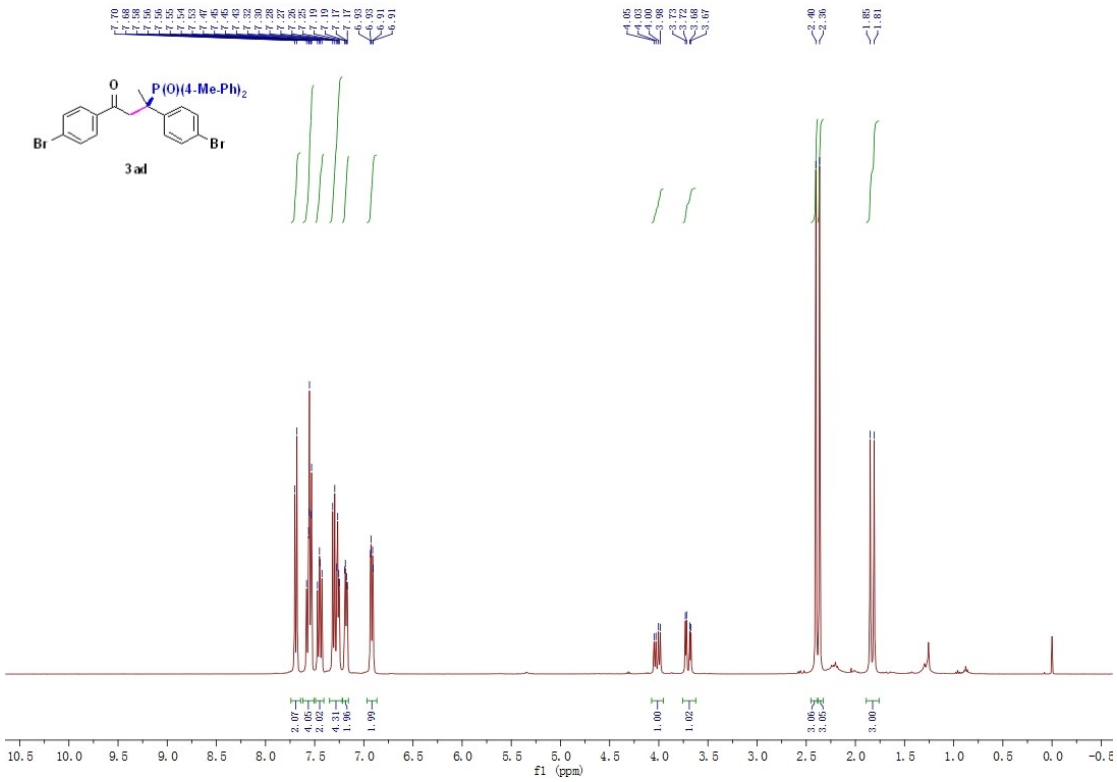

O
P(O)(4-tBu-Ph)2
Br
Br

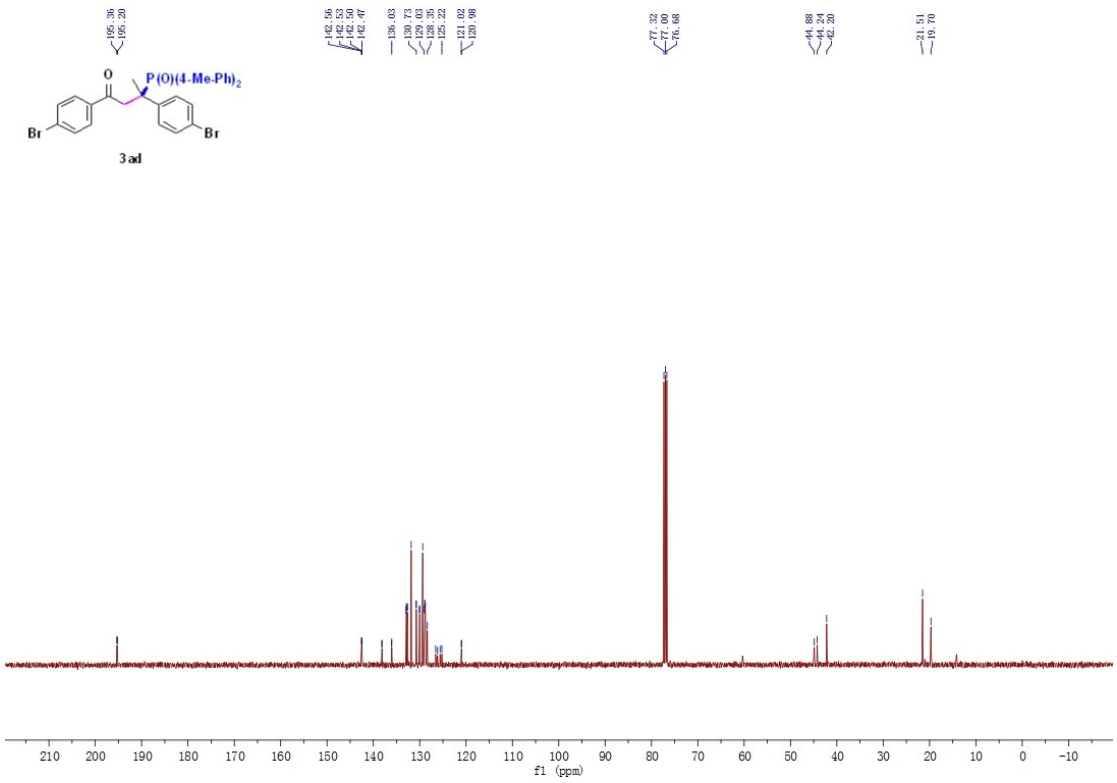
3ac

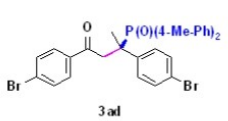
7.73
7.71
7.63
7.61
7.59
7.56
7.54
7.51
7.49
7.46
7.37
7.36
7.31
7.29
7.26
6.95
6.93
4.11
4.09
4.07
4.06
4.03
4.01
3.77
3.73
1.86
1.82
1.32
1.29
2.23
10.91
2.24
2.09
1.03
1.00
3.23
18.33
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


195.42
195.26
155.46
155.43
138.19
136.04
136.02
130.71
128.35
124.99
120.99
120.95
77.32
77.00
76.68
44.88
44.25
42.19
34.95
34.91
31.06
31.01
O
P(O)(4-tBu-Ph)2
Br
Br
3ac
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)


35.18
O
P(O)(4-tBu-Ph)2
Br
Br
3ac
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

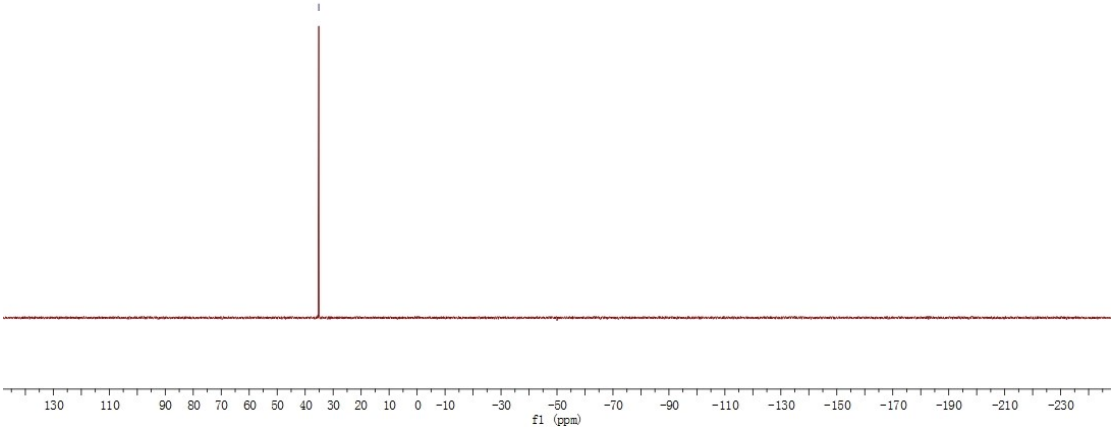

P(O)(4-Me-Ph)2
Br
Br
3ad
f1 (ppm)

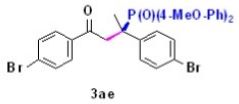

P(O)(4-Me-Ph)2
Br
Br
3ad
f1 (ppm)


O
P(O)(4-Me-Ph)2
Br
Br

3ad

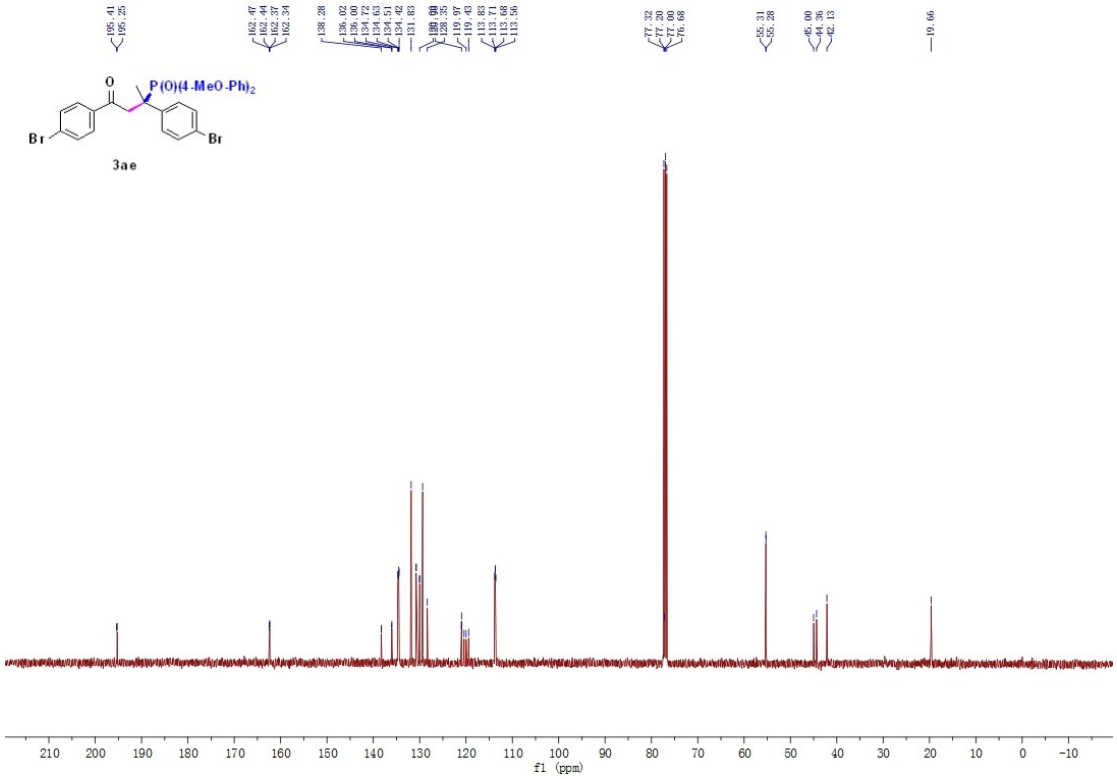
35.14


130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


O
P(O)(4-MeO-Ph)2
Br
Br

3ae

7.71
7.69
7.61
7.58
7.56
7.54
7.49
7.47
7.45
7.27
6.98
6.97
6.95
6.95
6.92
6.92
6.90
6.88
6.87
4.02
4.00
3.98
3.96
3.73
3.72
3.70
3.68
1.84
1.80
2.02
4.03
2.08
1.97
6.09
1.05
6.17
1.15
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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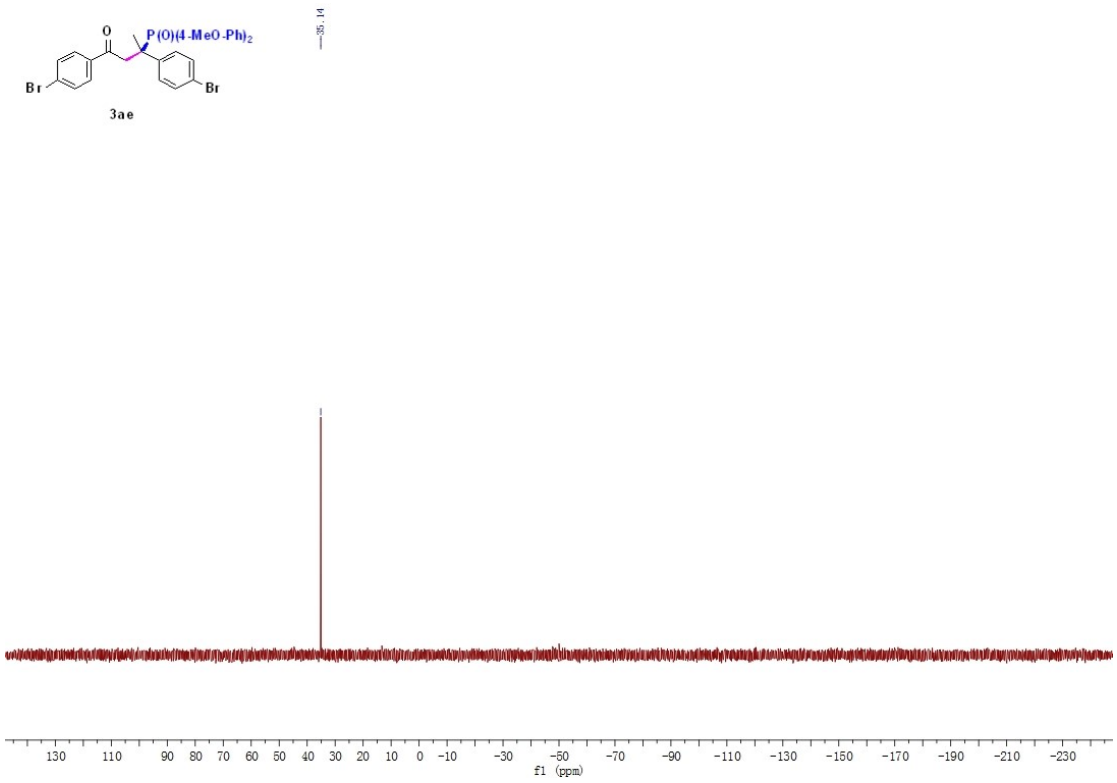
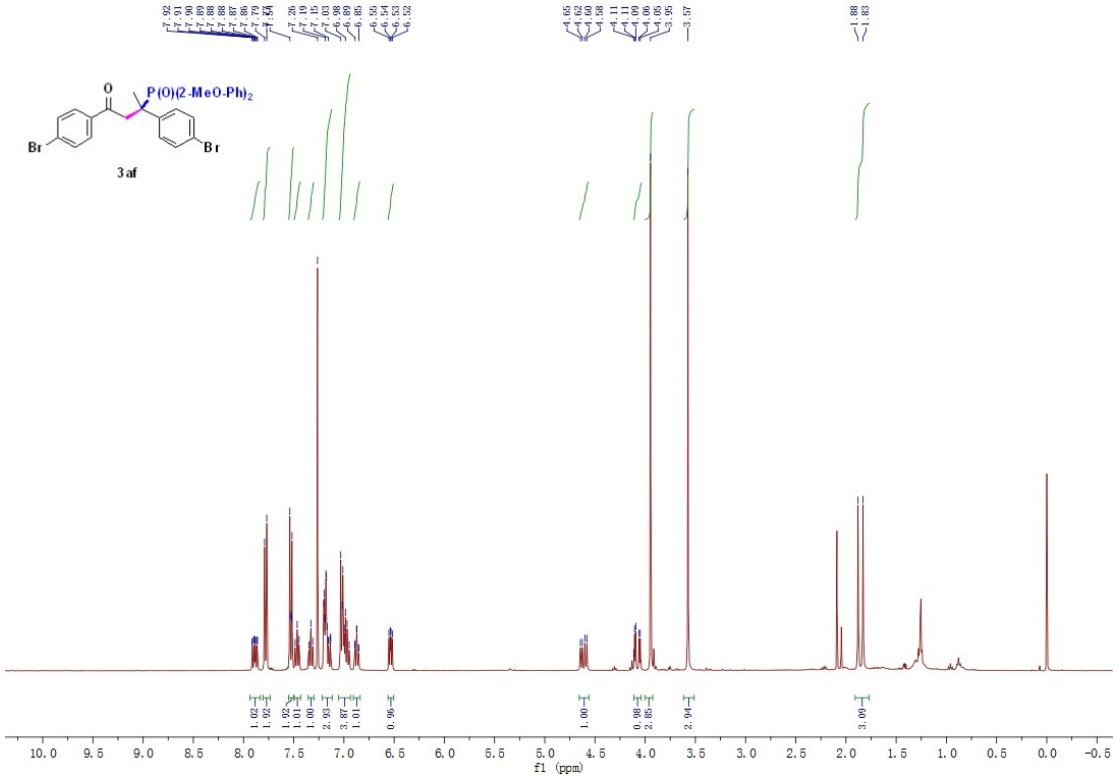
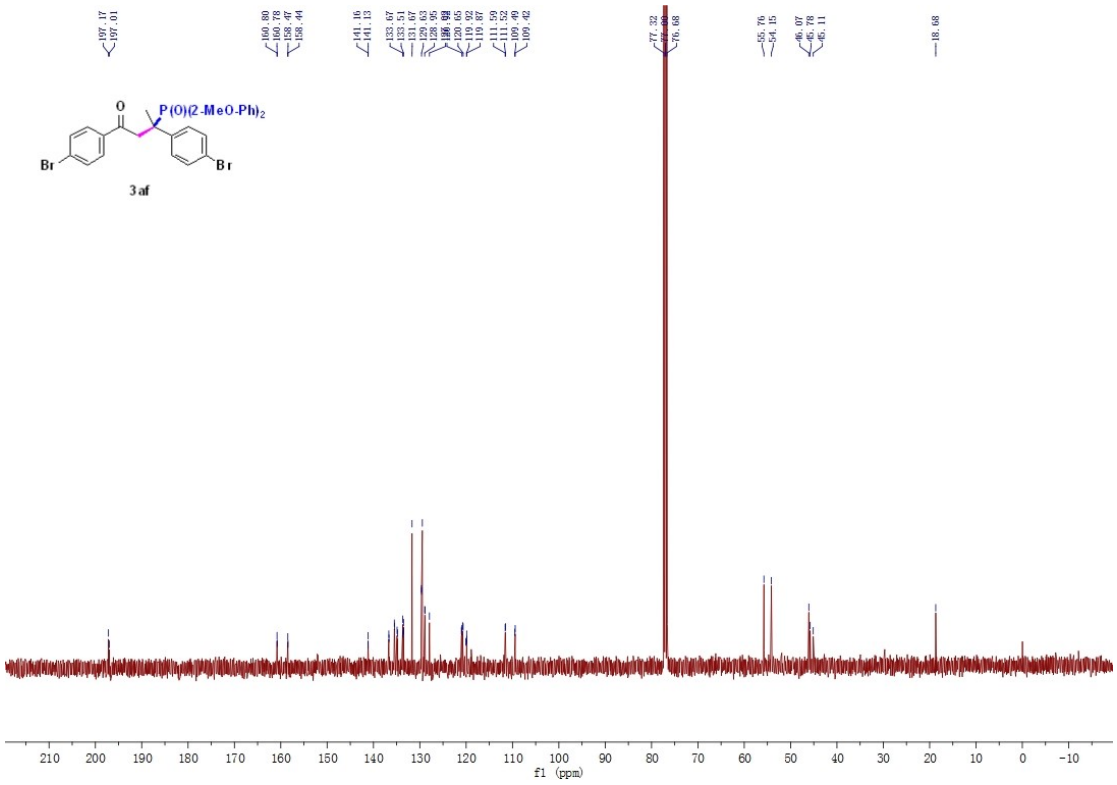
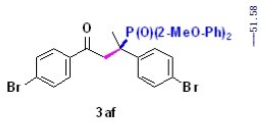
162.44
162.37
162.34
138.28
136.02
136.00
134.72
134.65
134.51
134.42
131.83
119.97
119.43
113.83
113.71
113.58
113.56
77.32
77.20
77.00
76.68
55.31
55.28
45.00
44.36
42.13
19.66
O
P(O)(4-MeO-Ph)2
Br
Br
3ae
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

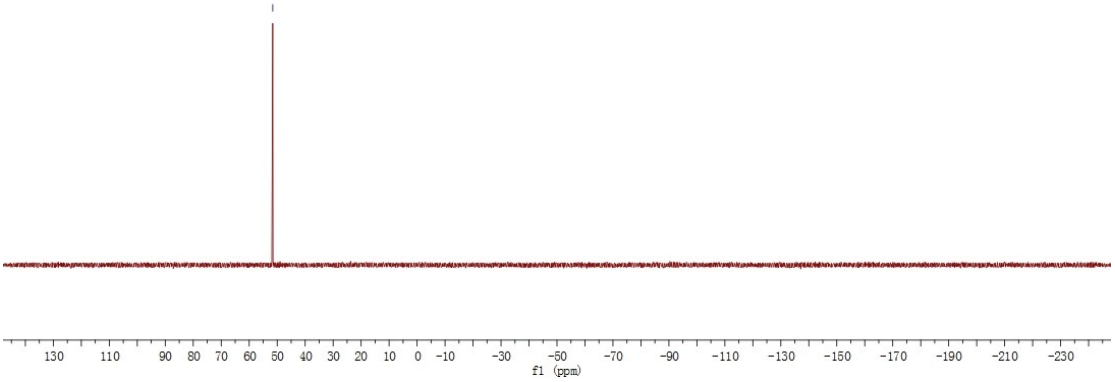

35.14
O
P(O)(4-MeO-Ph)2
Br
Br
3ae
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

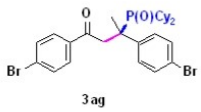

P(O)(2-MeO-Ph)2
Br
Br
3af
f1 (ppm)


P(O)(2-MeO-Ph)2
Br
Br
3af
f1 (ppm)

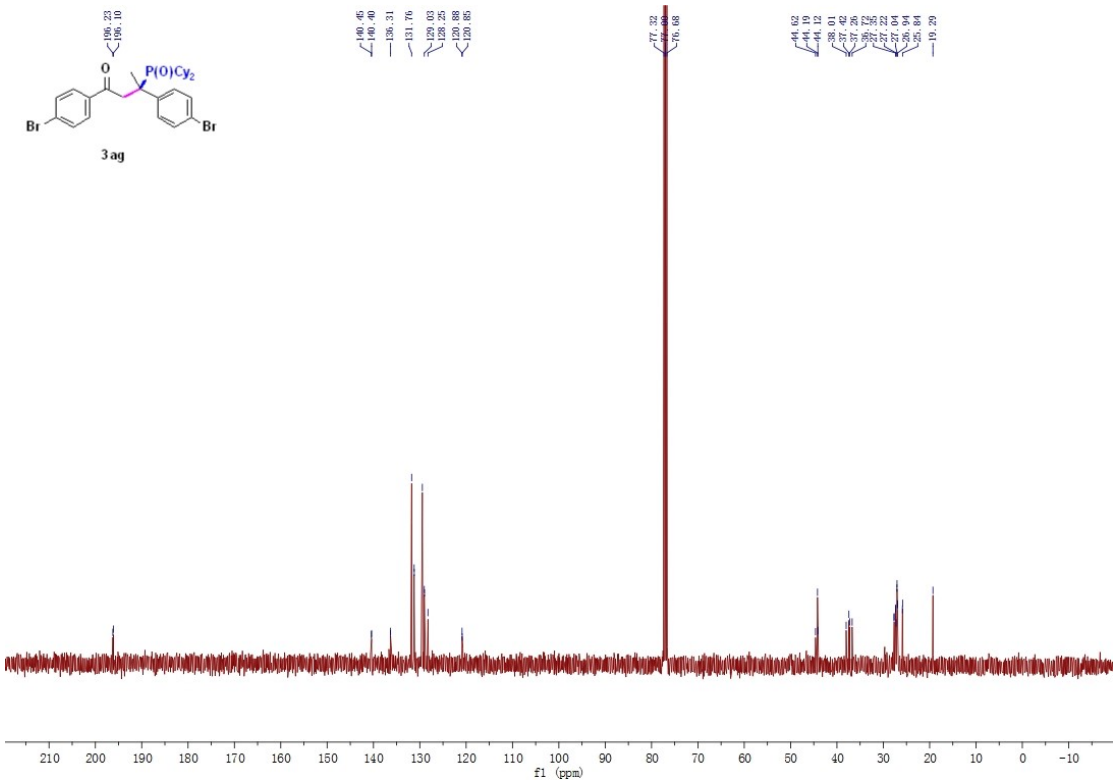


3af





3ag


196.23
196.10
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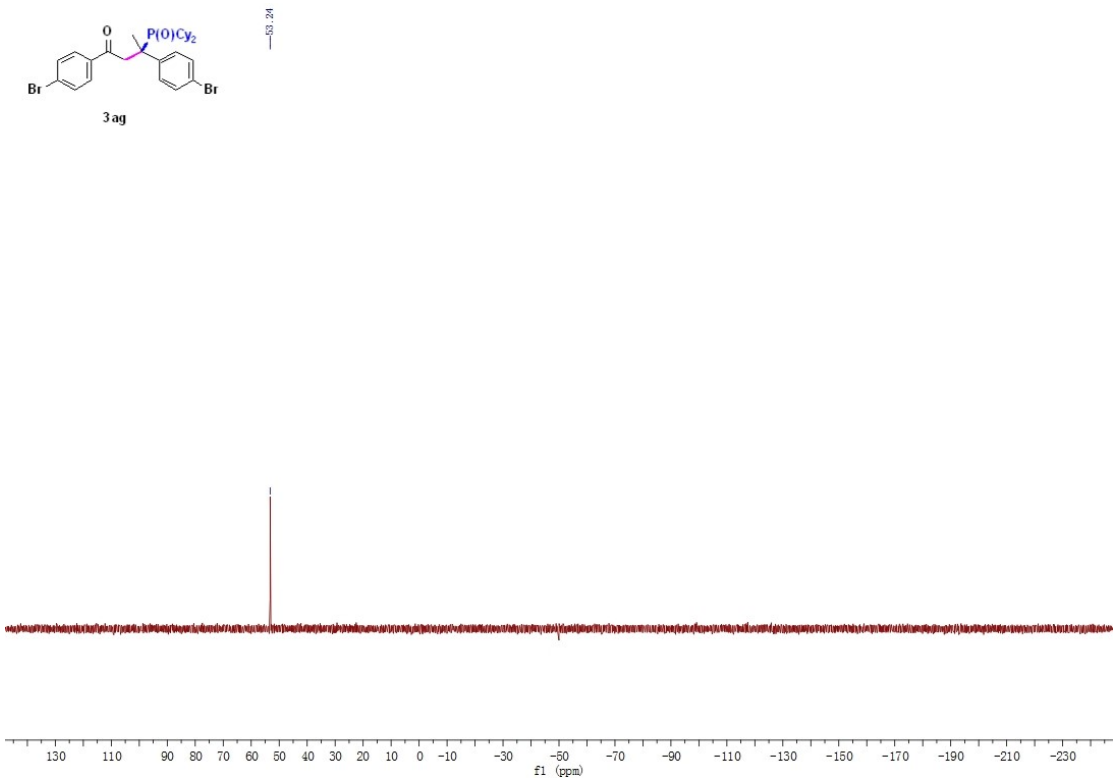
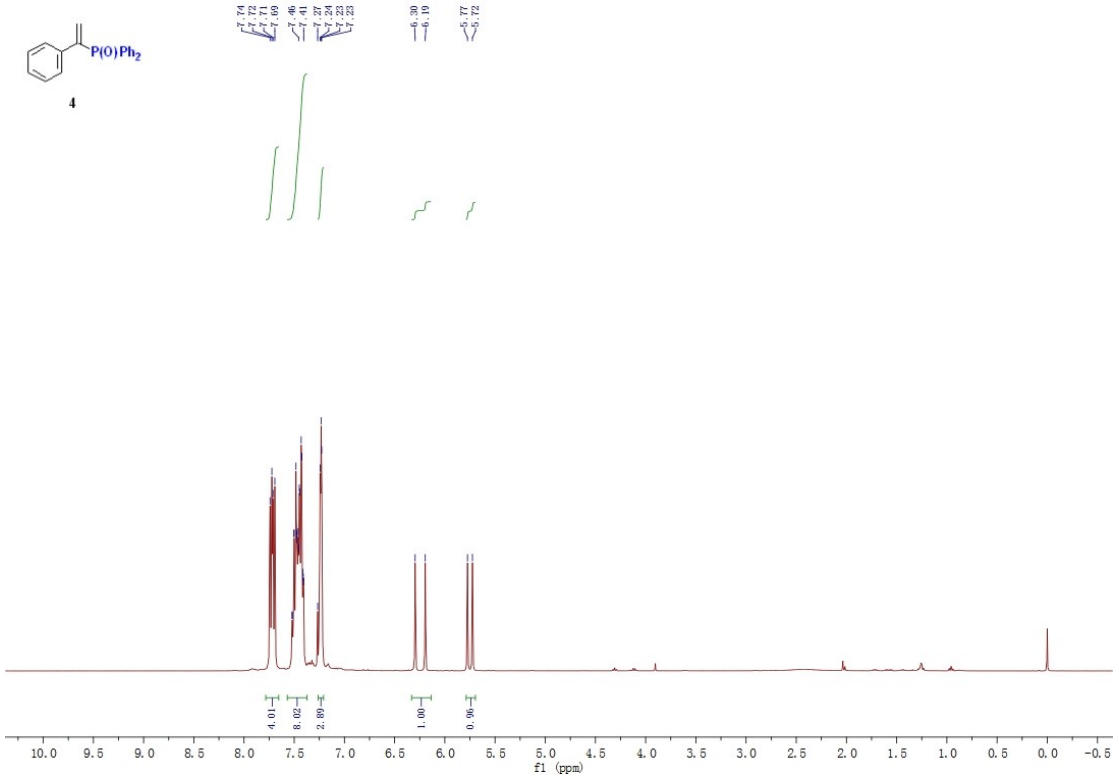
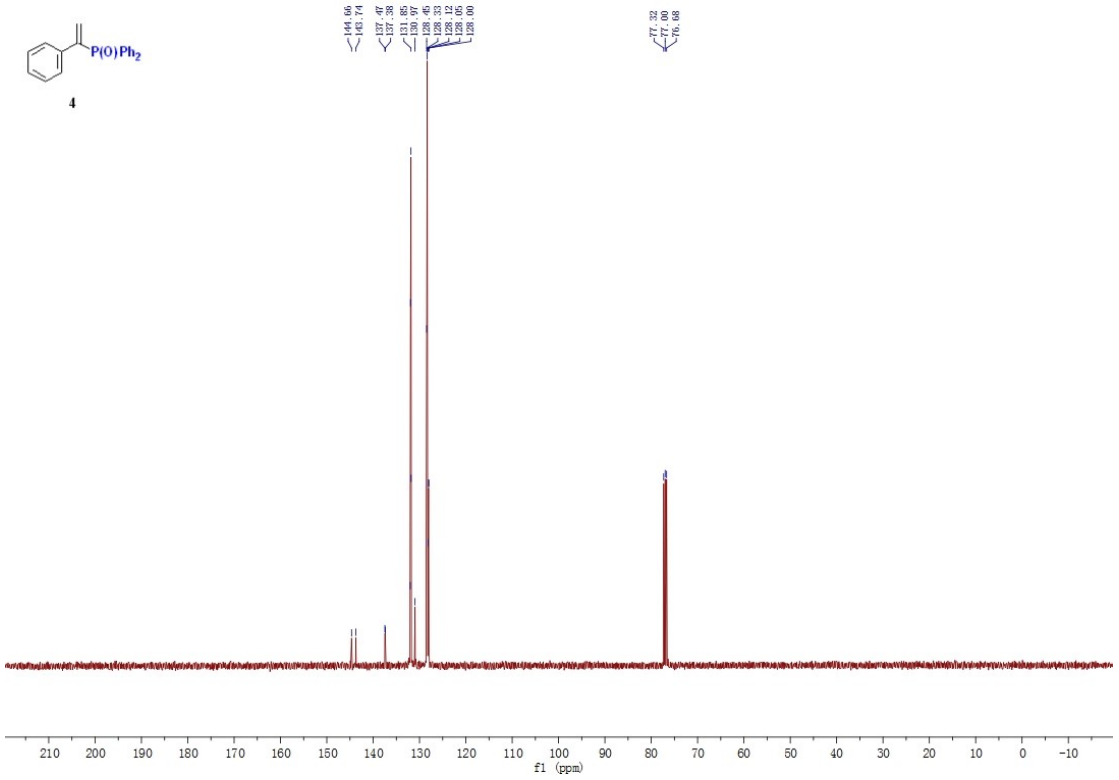
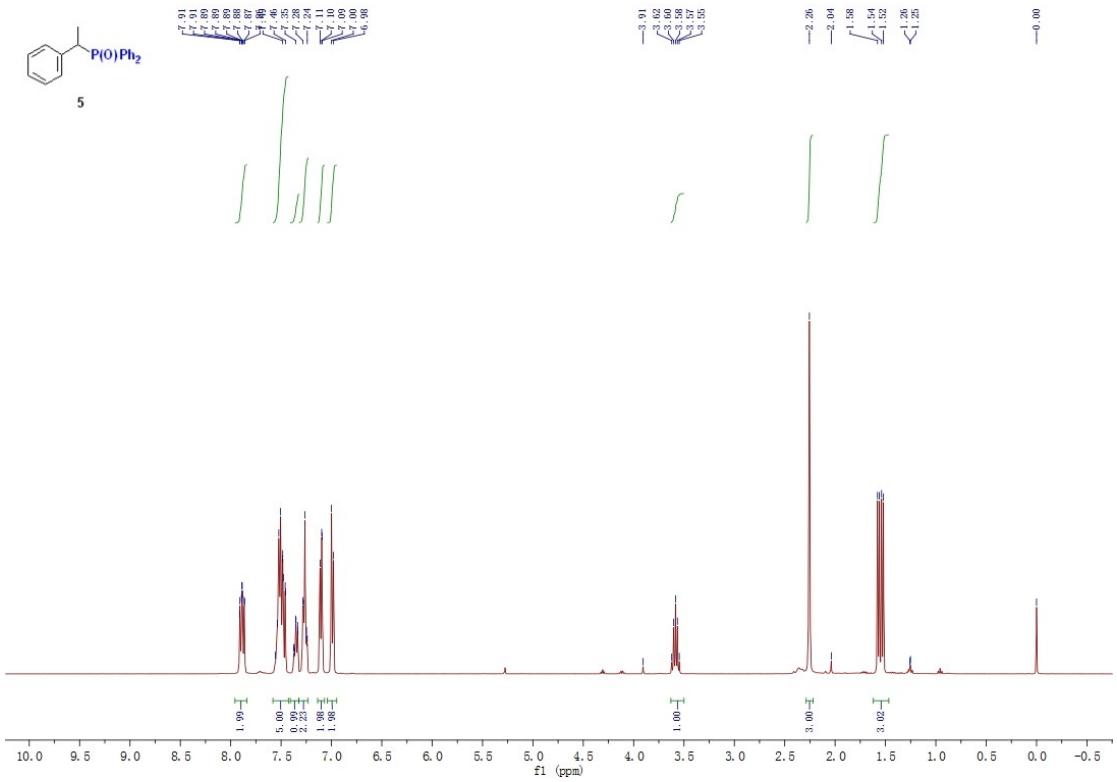
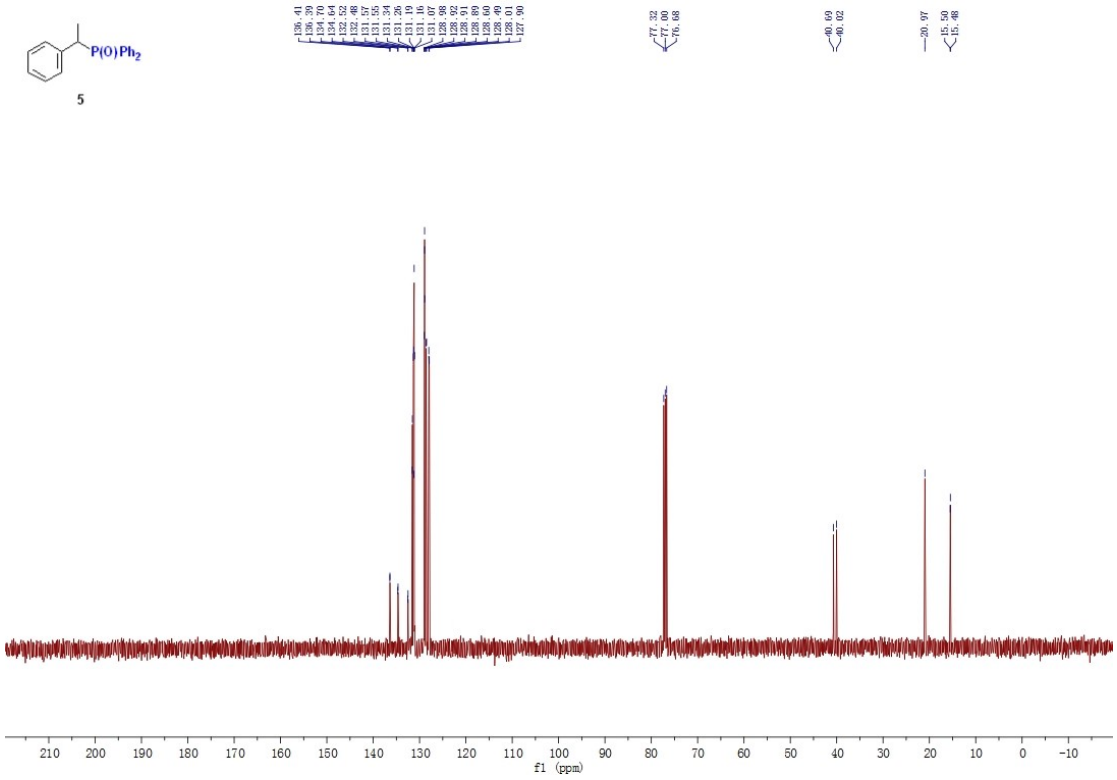
140.40
136.31
131.76
129.03
128.25
120.88
120.85
77.32
77.00
76.68
44.62
44.19
44.12
38.01
37.42
37.25
30.72
27.35
27.22
27.04
26.94
25.84
19.29
O
P(O)Cy2
Br
Br
3ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

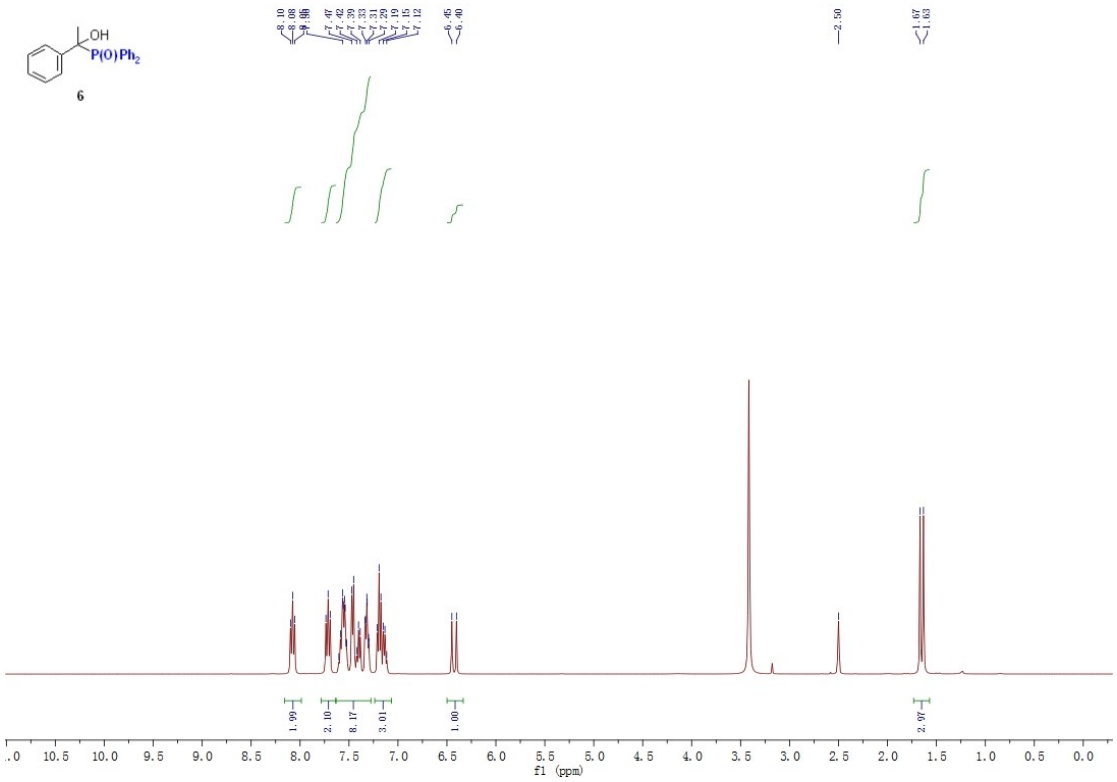

53.24
O
P(O)Cy2
Br
Br
3ag
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

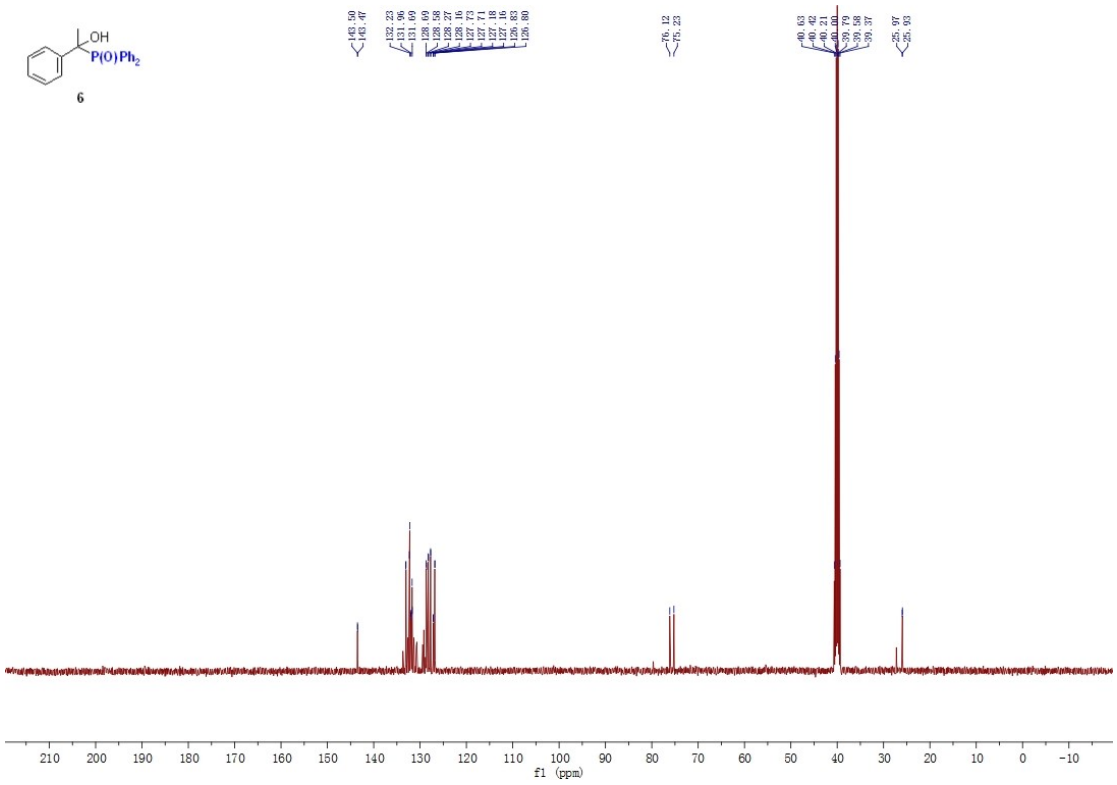

P(O)Ph2
4
7.74
7.72
7.71
7.69
7.46
7.41
7.27
7.24
7.23
7.23
6.30
6.19
5.77
5.72
4.01
8.02
2.89
1.00
0.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

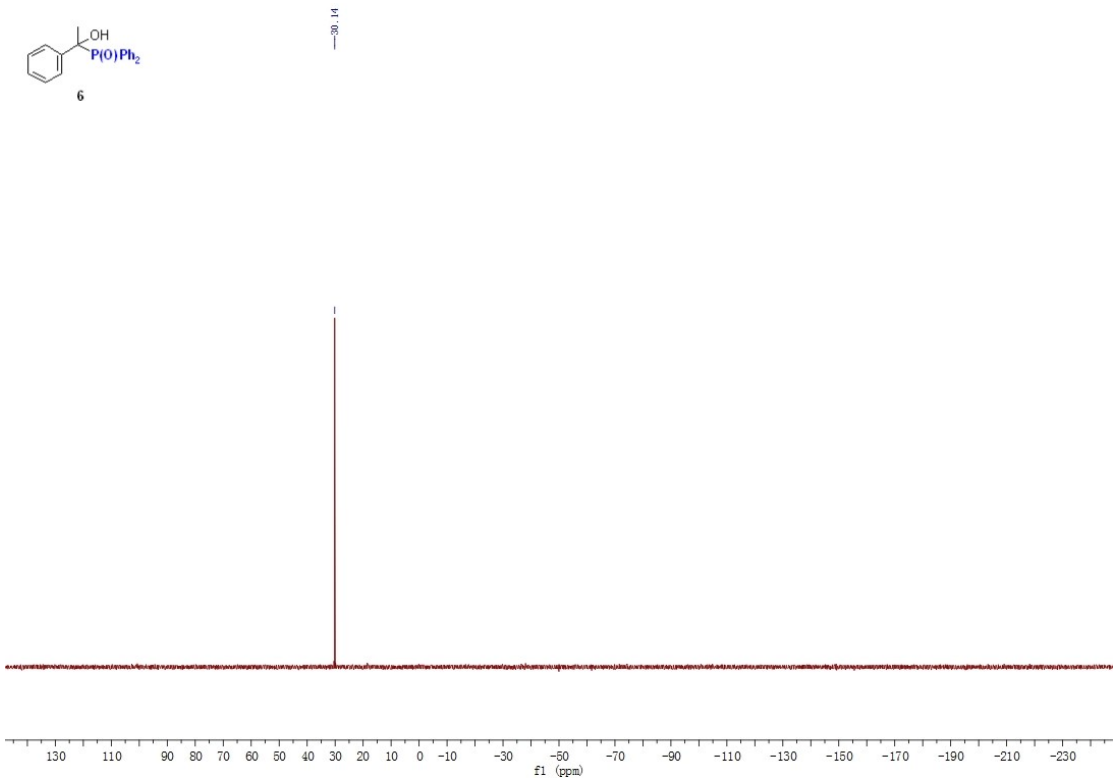

P(O)Ph2
4
144.66
143.74
137.47
137.38
131.85
130.97
128.45
128.33
128.12
128.06
128.00
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


P(O)Ph2
5
f1 (ppm)


P(O)Ph2
5
f1 (ppm)


OH
P(O)Ph2
6
8.10
8.08
7.47
7.42
7.39
7.33
7.31
7.29
7.19
7.15
7.12
6.45
6.40
2.50
1.67
1.63
1.99
2.10
8.17
3.01
1.00
2.97
f1 (ppm)


OH
P(O)Ph2
6
143.50
140.47
132.23
131.96
131.69
128.69
128.58
128.27
128.16
127.73
127.71
127.18
127.15
126.83
126.80
76.12
75.23
40.63
40.42
40.21
40.00
39.79
39.58
39.37
25.97
25.93
f1 (ppm)


OH
P(O)Ph2
6
30.14
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)