Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Dioxygen-induced oxidative activation of P-H bond: radical oxyphosphorylation of alkenes and alkynes toward β-oxy phosphonates

Pan Peng, Qingquan Lu, Long Peng, Chao Liu, Guangyu Wang and Aiwen Lei*

aiwenlei@whu.edu.cn

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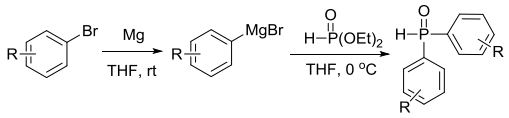
General information

All reactions were run under air atmosphere with a dry air balloon fitted on a Schlenk tube. All the solvents were purified according to the solvents handbook. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel. EPR spectra were recorded on a Bruker A-200 spectrometer. HPLC yields were recorded with a DIONEX P680 HPLC Pump. IR spectra were recorded on a Mettler Toledo React IR TM 15 spectrometer using a diamond comb. ESI-MS spectra were recorded on a SHIMADZU LCMS-2020. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. The known compounds were characterized by ^{1}H NMR, ^{13}C NMR. ^{1}H and ^{13}C NMR data were recorded with ADVANCE III 400 MHz with tetramethylsilane as an internal standard. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument. All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), and $CDCl_3$ (77.16 ppm for ^{13}C), respectively.

Experimental section

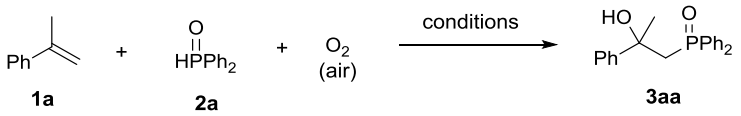
1) General procedure for preparation of phosphine oxides[1]



Diethylphosphite (1.29 mL, 10.0 mmol) was added dropwise at 0 °C to a solution of phenylmagnesium bromide in tetrahydrofuran which was prepared from aryl bromides (32.6 mmol) and magnesium (0.95 g, 39.6 mmol). The mixture was aged for 15 minutes at 0 °C, then stirred at ambient temperature for two hours. After that it was cooled again to 0 °C, and 75 mL NH_4Cl aqueous was then added slowly. The mixture was extracted with diethyl ether and the organic phase was washed with $NaHCO_3$ aqueous and brine, then it was dried over Na_2SO_4. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 1/1 as eluent to give the product.

2) Optimization of α-methylstyrene with diphenylphosphine oxide

Table S1. Optimization of α-methylstyrene with diphenylphosphine oxide[a]

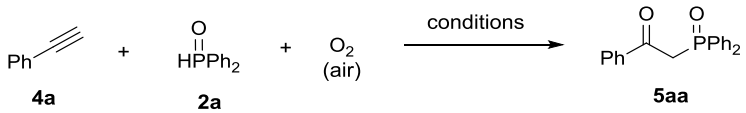


Entry	Temp.	Solvent	Yield[b]
1[c]	45	THF	34
2	45	THF	87(94)
3	r.t.	THF	32
4	45	DMF	80
5	45	Toluene	44
6	45	CH_3CN	54
7	45	DMSO	87
8	45	DCE	43
9[d]	45	THF	18
10[e]	45	THF	0

[a] Unless otherwise specified, all reactions were carried out using **1a** (0.2 mmol), **2a** (0.6 mmol) in THF (2.0 mL) at 45 °C for 2 h under 1 atm of air (ballon). [b] Yield was determined by ^1H NMR analysis using CH_2Br_2 as internal standard, isolated yield in parentheses. [c] **2a** (0.4 mmol) was used. [d] Under O_2. [e] Under N_2.

3) Optimization of phenylacetylene with diphenylphosphine oxide

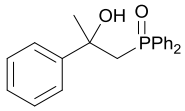
Table S2. Optimization of phenylacetylene with diphenylphosphine oxide[a]



Entrya	Temp. / °C	Solvent	Yield[b]
1	45	THF	24
2	60	NMP	30
3[c]	60	NMP	39
4[c][d]	60	NMP	71(71)

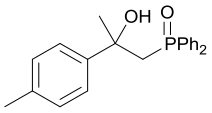
[a] Unless otherwise specified, all reactions were carried out using **4a** (0.2 mmol), **2a** (0.6 mmol) in solvent (2.0 mL) at for 2 h under air. [b] Yield was determined by HPLC analysis using naphthalene as internal standard, isolated yield in parentheses. [c] O_2/N_2 = 1:1 was used. [d] phenylboronic acid (0.2 mmol) was added.

4) Procedure and analytical data of compounds 3aa-5ae

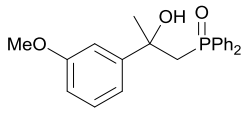


(2-hydroxy-2-phenylpropyl)diphenylphosphine oxide (3aa):[2] Typical procedure: To a Schlenk tube equipped with a stir bar was added diphenylphosphine oxides **2a** (121.3 mg, 0.6 mmol), and a

balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. Then, α-methylstyrene **1a** (23.6 mg, 0.2 mmol), THF (2.0 mL) were injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir at 45 ºC for 2 h. Thereafter, the reaction organic layer was concentrated under reduced pressure. The residue was separated on a silica gel column with petroleum ether (60-90 ºC), ethyl acetate (2:1) as eluent to afford the desired product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.72 (m, 2H), 7.56-7.46 (m, 3H), 7.36-7.31 (m, 5H), 7.24-7.19 (m, 2H), 7.09-7.00 (m, 3H), 6.06 (s, 1H), 2.92 (d, J = 9.4 Hz, 2H), 1.60 (d, J = 1.5 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7 (d, $J_{C\text{-}P}$ = 5.9 Hz), 134.0 (d, $J_{C\text{-}P}$ = 98.8 Hz), 132.4 (d, $J_{C\text{-}P}$ = 100.4 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.4 (d, $J_{C\text{-}P}$ = 1.3 Hz), 130.3 (d, $J_{C\text{-}P}$ = 1.8 Hz) 128.9 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.3 (d, $J_{C\text{-}P}$ = 12.1 Hz), 127.9, 126.7, 124.9, 74.3 (d, $J_{C\text{-}P}$ = 5.4 Hz), 42.3 (d, $J_{C\text{-}P}$ = 69.2 Hz), 32.9 (d, $J_{C\text{-}P}$ = 9.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.88.

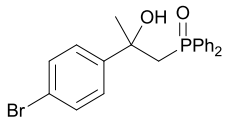


(2-hydroxy-2-(p-tolyl)propyl)diphenylphosphine oxide (3ab): The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.71 (m, 2H), 7.54-7.46 (m, 3H), 7.35-7.29 (m, 3H), 7.23-7.17 (m, 4H), 6.84 (d, J = 8.0 Hz, 2H), 5.98 (s, 1H), 2.90 (m, 2H), 2.20 (s, 3H), 1.59 (d, J = 1.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8 (d, $J_{C\text{-}P}$ = 5.9 Hz), 136.1, 134.0 (d, $J_{C\text{-}P}$ = 98.7 Hz), 132.4 (d, $J_{C\text{-}P}$ = 100.4 Hz),132.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.5 (d, $J_{C\text{-}P}$ = 6.1 Hz), 130.4 (d, $J_{C\text{-}P}$ = 5.7 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.7 Hz), 128.5, 128.2 (d, $J_{C\text{-}P}$ = 12.1 Hz), 124.8, 74.2 (d, $J_{C\text{-}P}$ = 5.4 Hz), 42.7 (d, $J_{C\text{-}P}$ = 69.3 Hz), 32.8 (d, $J_{C\text{-}P}$ = 9.8 Hz), 20.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.86. HRMS (ESI+) calculated for $C_{22}H_{24}O_2P$ (M+H): 351.1508; found: 351.1501.

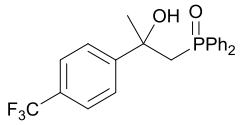


(2-hydroxy-2-(3-methoxyphenyl)propyl)diphenylphosphine oxide (3ac): The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.71 (m, 2H), 7.54-7.49 (m, 3H), 7.39-7.32 (m, 3H), 7.26-7.22 (m, 2H), 7.00-6.97 (m, 1H), 6.90-6.87 (m, 2H), 6.56-6.54 (m, 1H), 6.07 (s, 1H), 3.71 (s, 3H), 2.90 (d, J = 8.9 Hz, 2H), 1.59 (d, J = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 148.6 (d, $J_{C\text{-}P}$= 5.8 Hz), 134.0 (d, $J_{C\text{-}P}$ = 98.7 Hz), 132.42 (d, $J_{C\text{-}P}$= 100.9 Hz), 132.1 (d, $J_{C\text{-}P}$= 2.6 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.4, 130.3, 129.0, 128.9 (d, $J_{C\text{-}P}$ = 11.8), 128.3 (d, $J_{C\text{-}P}$ = 12.1 Hz), 117.4, 112.3,

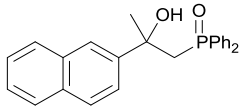
110.7, 74.3 (d, J_{C-P} = 5.4 Hz), 55.2, 42.3 (d, J_{C-P} = 69.1 Hz), 32.9 (d, J_{C-P} = 9.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.84. HRMS (ESI+) calculated for $C_{22}H_{24}O_3P$ (M+H): 367.1458; found: 367.1458.



(2-(4-bromophenyl)-2-hydroxypropyl)diphenylphosphine oxide (3ad): The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.69 (m, 2H), 7.56-7.46 (m, 3H), 7.42-7.38 (m, 1H), 7.31-7.22 (m, 4H), 7.12 (q, *J* = 8.6 Hz, 4H), 6.12 (s, 1H), 2.89 (ddd, *J* = 22.5, 14.9, 9.4 Hz, 2H), 1.57 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6 (d, J_{C-P} = 4.9 Hz), 133.8 (d, J_{C-P} = 99.3 Hz), 132.2 (d, J_{C-P} = 2.5 Hz), 131.3 (d, J_{C-P} = 2.6 Hz), 130.8, 130.4 (t, J_{C-P} = 9.5 Hz), 129.0 (d, J_{C-P} = 11.8 Hz), 128.4 (d, J_{C-P} = 12.1 Hz), 127.0, 120.8, 74.1 (d, J_{C-P} = 5.5 Hz), 42.4 (d, J_{C-P} = 69.4 Hz), 33.1 (d, J_{C-P} = 10.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.81. HRMS (ESI+) calculated for $C_{21}H_{21}BrO_2P$ (M+H): 415.0457; found: 415.0450.

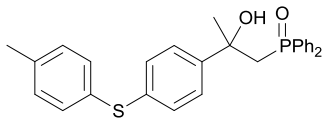


(2-hydroxy-2-(4-(trifluoromethyl)phenyl)propyl)diphenylphosphine oxide (3ae): The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.70 (m, 2H), 7.57-7.47 (m, 3H), 7.38 (m, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.28-7.23 (m, 4H), 7.20-7.16 (m, 2H), 6.28 (s, 1H), 2.94 (ddd, *J* = 22.1, 14.9, 9.4 Hz, 2H), 1.61 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3 (d, J_{C-P} = 5.1 Hz), 133.6 (d, J_{C-P} = 99.6 Hz), 132.3 (d, J_{C-P} = 2.7 Hz), 132.0, 131.52 (d, J_{C-P} = 2.8 Hz), 131.49 (d, J_{C-P} = 99.9 Hz), 130.5, 130.4, 130.3, 129.2 (d, J_{C-P} = 11.8 Hz), 128.8 (q, J_{C-F} = 32.3 Hz), 128.4 (d, J_{C-P} = 12.1 Hz), 125.6, 124.8 (q, J_{C-F} = 3.8 Hz), 124.2 (q, J_{C-F} = 272.8 Hz), 74.3 (d, J_{C-P} = 5.5 Hz), 42.0 (d, J_{C-P} = 69.5 Hz), 33.3 (d, J_{C-P} = 11.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.84. HRMS (ESI+) calculated for $C_{22}H_{21}F_3O_2P$ (M+H): 405.1226; found: 405.1216.

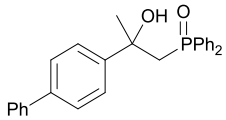


(2-hydroxy-2-(naphthalen-2-yl)propyl)diphenylphosphine oxide (3af): The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.77-7.70 (m, 3H), 7.66-7.63 (m, 1H), 7.55-7.38 (m, 6H), 7.28-7.19 (m, 3H), 7.06 (t, *J* = 7.0 Hz, 1H), 6.94-6.89 (m, 2H), 6.25 (s, 1H), 3.05

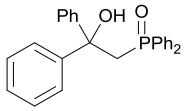
– 2.94 (m, 2H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9 (d, J_{C-P} = 5.4 Hz), 134.0 (d, J_{C-P} = 98.2 Hz), 133.0, 132.3, 132.1 (d, J_{C-P} = 2.8 Hz), 131.8 (d, J_{C-P} = 100.8 Hz), 130.9 (d, J_{C-P} = 2.8 Hz), 130.4 (d, J_{C-P} = 9.7 Hz), 130.3 (d, J_{C-P} = 10.1 Hz), 129.0 (d, J_{C-P} = 11.8 Hz), 128.4, 127.9 (d, J_{C-P} = 12.1 Hz), 127.6, 127.3, 125.9, 125.7, 123.9, 123.4, 74.5 (d, J_{C-P} = 5.2 Hz), 42.4 (d, J_{C-P} = 69.4 Hz), 32.9 (d, J_{C-P} = 10.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.88. HRMS (ESI+) calculated for $C_{25}H_{24}O_2P$ (M+H): 387.1508; found: 387.1500.



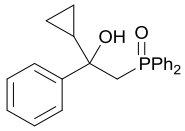
(2-hydroxy-2-(4-(p-tolylthio)phenyl)propyl)diphenylphosphine oxide (3ag): The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.69 (m, 2H), 7.55-7.45 (m, 3H), 7.40-7.30 (m, 3H), 7.25-7.18 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.07 (s, 1H), 2.95-2.84 (m, 2H), 2.35 (s, 3H), 1.57 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2 (d, J_{C-P} = 5.5 Hz), 137.7, 135.0, 133.9 (d, J_{C-P} = 99.1 Hz), 132.2, 132.1 (d, J_{C-P} = 100.3 Hz), 132.2 (d, J_{C-P} = 2.7 Hz), 131.3 (d, J_{C-P} = 2.8 Hz), 131.3, 130.4 (d, J_{C-P} = 7.3 Hz), 130.4 (d, J_{C-P} = 7.0 Hz), 130.1, 129.2, 128.9 (d, J_{C-P} = 11.8 Hz), 128.4 (d, J_{C-P} = 12.1 Hz), 125.8, 74.2 (d, J_{C-P} = 5.4 Hz), 42.3 (d, J_{C-P} = 69.3 Hz), 33.0 (d, J_{C-P} = 10.1 Hz), 21.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.88. HRMS (ESI+) calculated for $C_{28}H_{28}O_2PS$ (M+H): 459.1542; found: 459.1531.



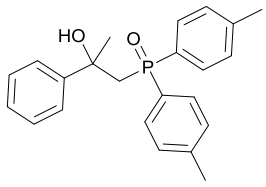
(2-([1,1'-biphenyl]-4-yl)-2-hydroxypropyl)diphenylphosphine oxide (3ah): The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, DMSO) δ 7.78-7.74 (m, 2H), 7.60-7.43 (m, 11H), 7.38-7.30 (m, 6H), 5.78 (s, 1H), 3.18-3.02 (m, 2H), 1.60 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 147.1 (d, J_{C-P} = 6.2 Hz), 140.3, 138.2, 134.9 (d, J_{C-P} = 97.0 Hz), 134.4 (d, J_{C-P} = 98.3 Hz), 131.4 (d, J_{C-P} = 2.5 Hz), 130.8 (d, J_{C-P} = 2.2 Hz), 130.2, 130.1, 130.0, 128.8, 128.6 (d, J_{C-P} = 11.4 Hz), 128.10 (d, J_{C-P} = 11.7 Hz), 127.2, 126.6, 125.9, 125.5, 73.3 (d, J_{C-P} = 4.8 Hz), 42.0 (d, J_{C-P} = 68.3 Hz), 31.8 (d, J_{C-P} = 6.7 Hz). ^{31}P NMR (162 MHz, DMSO) δ 29.45. HRMS (ESI+) calculated for $C_{27}H_{26}O_2P$ (M+H): 413.1665; found: 413.1655.



(2-hydroxy-2,2-diphenylethyl)diphenylphosphine oxide (3ai):[3] The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 11.7, 7.9 Hz, 4H), 7.42 (t, *J* = 6.9 Hz, 2H), 7.37-7.30 (m, 8H), 7.10-7.02 (m, 6H), 6.83 (s, 1H), 3.39 (d, *J* = 9.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1 (d, *J* = 7.3 Hz), 133.0 (d, *J* = 100.3 Hz), 131.7 (d, *J* = 2.7 Hz), 130.5 (d, *J* = 9.7 Hz), 128.6 (d, *J* = 12.0 Hz), 128.0, 127.0, 126.0, 77.8 (d, *J* = 4.9 Hz), 40.9 (d, *J* = 69.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.30.

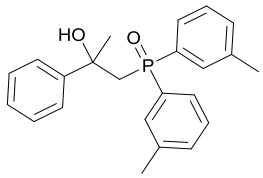


(2-cyclopropyl-2-hydroxy-2-phenylethyl)diphenylphosphine oxide (3aj): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.79 (m, 2H), 7.56-7.48 (m, 3H), 7.41-7.33 (m, 5H), 7.26-7.22 (m, 2H), 7.12-7.04 (m, 3H), 5.83 (s, 1H), 3.05 – 2.93 (m, 2H), 1.14 (tt, *J* = 8.3, 5.3 Hz, 1H), 0.73 (td, *J* = 9.7, 5.2 Hz, 1H), 0.38 (td, *J* = 9.7, 5.5 Hz, 1H), 0.22 – 0.15 (m, 1H), 0.13 – 0.06 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7 (d, $J_{C\text{-}P}$ = 6.8 Hz), 133.8 (d, $J_{C\text{-}P}$ = 98.9 Hz), 133.1 (d, $J_{C\text{-}P}$ = 99.8 Hz), 132,0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.6 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.3 (d, $J_{C\text{-}P}$ = 9.8 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.8, 126.6, 125.2, 74.1 (d, $J_{C\text{-}P}$ = 5.1 Hz), 41.7 (d, $J_{C\text{-}P}$ = 68.4 Hz), 23.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 3.2, 1.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.00. HRMS (ESI+) calculated for $C_{25}H_{24}O_2P$ (M+H): 363.1508; found: 363.1502.

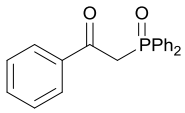


(2-hydroxy-2-phenylpropyl)di-p-tolylphosphine oxide (3ba): The synthesis procedure is the same as for **3aa.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 10.8, 7.8 Hz, 2H), 7.32 (dd, *J* = 15.4, 7.8 Hz, 4H), 7.23 (dd, *J* = 11.6, 8.1 Hz, 2H), 7.12-7.02 (m, 5H), 6.09 (s, 1H), 2.86 (d, *J* = 9.5 Hz, 2H), 2.40 (s, 3H), 2.30 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2 (d, $J_{C\text{-}P}$ = 6.5 Hz), 142.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 141.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 130.7 (d, $J_{C\text{-}P}$ = 101.2 Hz), 130.4 (d, $J_{C\text{-}P}$ = 5.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 5.9 Hz), 129.5(3) (d, $J_{C\text{-}P}$ = 12.2 Hz), 129.4(7) (d, $J_{C\text{-}P}$ = 102.4 Hz), 129.0 (d, $J_{C\text{-}P}$ = 12.5 Hz), 127.8, 126.4, 124.7,

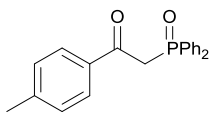
74.2 (d, $J_{C\text{-}P}$ = 5.4 Hz), 42.3 (d, $J_{C\text{-}P}$ = 69.1 Hz), 32.6 (d, $J_{C\text{-}P}$ = 8.9 Hz), 21.6, 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.30. HRMS (ESI+) calculated for $C_{23}H_{26}O_2P$ (M+H): 365.1665; found: 365.1660.



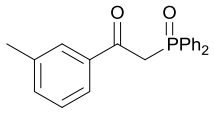
(2-hydroxy-2-phenylpropyl)di-m-tolylphosphine oxide (3ca): The synthesis procedure is the same as for **3aa.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 12.0 Hz, 1H), 7.52-7.47 (m, 1H), 7.38-7.32 (m, 4H), 7.13-6.99 (m, 7H), 6.12 (s, 1H), 2.95-2.85 (m, 2H), 2.38 (s, 3H), 2.21 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8 (d, *J* = 5.8 Hz), 138.8 (d, *J* = 11.6 Hz), 138.0 (d, *J* = 11.9 Hz), 133.8 (d, *J* = 98.4 Hz), 132.8 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 99.6 Hz), 132.0 (d, *J* = 2.9 Hz), 131.1 (d, *J* = 9.1 Hz), 130.8 (d, *J* = 9.1 Hz), 128.7 (d, *J* = 12.5 Hz), 128.1 (d, *J* = 13.0 Hz), 127.7, 127.3 (d, *J* = 9.8 Hz), 127.1 (d, *J* = 10.5 Hz), 126.5, 124.8, 74.2 (d, *J* = 5.4 Hz), 42.3 (d, *J* = 68.9 Hz), 32.9 (d, *J* = 9.8 Hz), 21.6, 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.15. HRMS (ESI+) calculated for $C_{23}H_{26}O_2P$ (M+H): 365.1665; found: 365.1663.



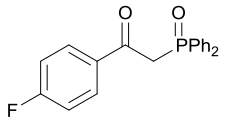
2-(diphenylphosphoryl)-1-phenylethan-1-one (5aa):[4] Typical procedure: To an Schlenk tube equipped with a stir bar were added di(phenyl) phosphine oxides **2a** (121.3 mg, 0.6 mmol), and a balloon filled with air and nitrogen (1:1) was connected to the Schlenk tube through the side arm and purged one time. Then, phenylacetylene **4** (20.4 mg, 0.2 mmol), NMP (2.0 mL) was injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir at 60 °C for 2 h. Thereafter, the reaction organic layers were concentrated under reduced pressure. The residue was separated on a silica gel column with petroleum ether (60-90 °C), ethyl acetate (1:1) as eluent to afford the desired product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.4 Hz, 2H), 7.83-7.79 (m, 4H), 7.56-7.40 (m, 9H), 4.15 (d, *J* = 15.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9 (d, $J_{C\text{-}P}$ = 5.3 Hz), 137.7, 133.7, 132.3 (d, *J* = 2.6 Hz), 132.0 (d, $J_{C\text{-}P}$ = 103.1 Hz), 131.2 (d, *J* = 9.7 Hz), 129.4, 128.7 (d, *J* = 12.3 Hz), 128.6, 43.4 (d, *J* = 57.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.01.



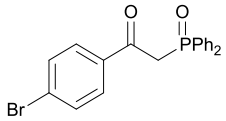
2-(diphenylphosphoryl)-1-(p-tolyl)ethan-1-one (5ab):[4] The synthesis procedure is the same as for **5aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.83 – 7.78 (m, 4H), 7.54 – 7.43 (m, 6H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.12 (d, *J* = 15.3 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.35 (d, *J* = 5.6 Hz), 144.6, 134.5, 132.2 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 103.3 Hz), 131.1 (d, *J* = 9.8 Hz), 129.4, 129.3, 128.6 (d, *J* = 12.3 Hz), 43.23 (d, *J* = 58.2 Hz), 21.73. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.04.



2-(diphenylphosphoryl)-1-(m-tolyl)ethan-1-one (5ac):[4] The synthesis procedure is the same as for **5aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.78 (m, 5H), 7.73 (s, 1H), 7.52-7.44 (m, 7H), 7.35-7.30 (m, 2H), 4.14 (d, *J* = 15.4 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.1 (d, *J* = 5.6 Hz), 138.4, 137.0, 134.5, 132.2 (d, *J* = 2.9 Hz), 132.0 (d, $J_{C\text{-}P}$ = 103.4 Hz), 131.2 (d, *J* = 9.8 Hz), 129.6, 128.7 (d, *J* = 12.3 Hz), 128.5, 126.7, 43.3 (d, *J* = 58.5 Hz), 21.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.24.



2-(diphenylphosphoryl)-1-(4-fluorophenyl)ethan-1-one (5ad):[4] The synthesis procedure is the same as for **5aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.80 (dd, *J* = 11.9, 7.4 Hz, 4H), 7.54-7.46 (m, 6H), 7.07 (t, *J* = 8.5 Hz, 2H), 4.11 (d, *J* = 15.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2 (d, $J_{C\text{-}P}$ = 5.6 Hz), 166.1 (d, $J_{C\text{-}F}$ = 256.0 Hz), 133.4 (d, $J_{C\text{-}F}$ = 2.8 Hz) 132.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.2 (d, $J_{C\text{-}F}$ = 9.6 Hz), 131.7 (d, $J_{C\text{-}P}$ = 103.5 Hz), 131.1 (d, $J_{C\text{-}F}$ = 9.8 Hz), 128.7 (d, $J_{C\text{-}F}$ = 12.4 Hz), 115.7 (d, $J_{C\text{-}F}$ = 22.0 Hz), 43.5 (d, $J_{C\text{-}P}$ = 57.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.88.



1-(4-bromophenyl)-2-(diphenylphosphoryl)ethan-1-one (5ae):[4] The synthesis procedure is the same as for 5aa. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.79 (dd, *J* = 12.1, 7.8 Hz, 4H), 7.54 (dd, *J* = 10.8, 8.0 Hz, 4H), 7.49-7.45 (m, 4H), 4.10 (d, *J* = 15.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9 (d, $J_{C\text{-}P}$ = 5.6 Hz), 135.7, 132.4 (d, *J* = 2.8 Hz), 132.2, 131.9, 131.1 (d, *J* = 9.7 Hz), 130.9, 129.2, 128.8 (d, *J* = 12.4 Hz), 43.6 (d, *J* = 56.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.82.

5) General procedure for the electron paramagnetic resonance (EPR) experiment

Typical procedure: To an Schlenk tube equipped with a stir bar was added diphenylphosphine oxides **2a** (0.6 mmol), and a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. Then, THF (2.0 mL) was injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir at 45 °C for 10 min, followed by the addition of 10 ul DMPO and stir at room temperature for 5 min. Then, this reaction was taken out by capillary and was analyzed by EPR at room temperature. This result was shown in Figure 1.

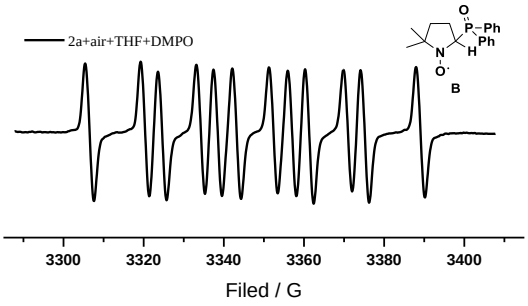
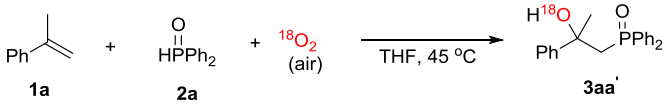


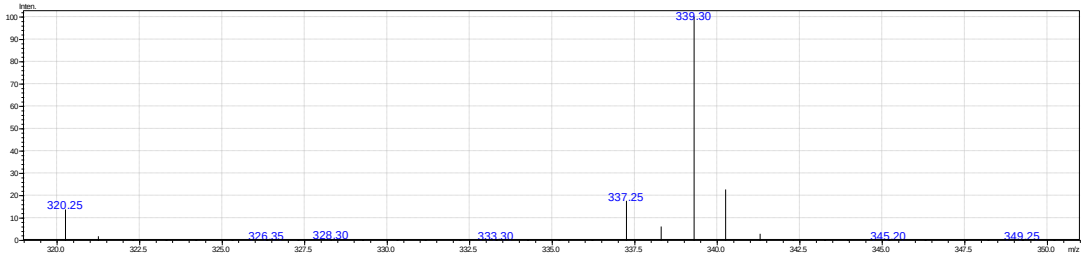
Figure 1. The electron paramagnetic resonance (EPR) spectra (X band, 9.4 GHz, room temperature)

6) Labeling experiments



^{18}O-**3aa**':^{16}O-**3aa**=85:15 80%

Typical procedure for $^{18}O_2$ labeling experiments: To an Schlenk tube equipped with a stir bar were added diphenylphosphine oxides **2a** (0.6 mmol), and dry THF (2.0 ml) was quickly added under N_2. The reaction mixture was degassed the air by the method of freeze-pump-thaw cycle for 4 times. Then $^{18}O_2/N_2$ (1:4) was purged one time, α-methylstyrene **1a** (0.2 mmol) was further injected into the reaction tube with magnetic stirring. The reaction mixture was vigorous stirred at 45 °C for 2 h. Thereafter, the reaction mixture was analyzed by LC-MS and the yield was isolated. The ESI-MS spectral of the reaction



7) *In-situ* NMR spectra

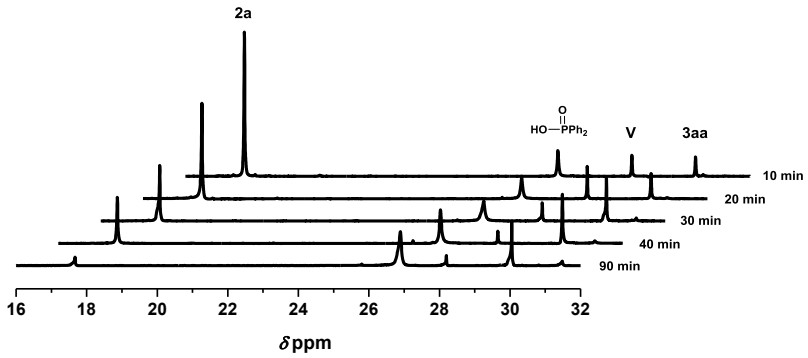
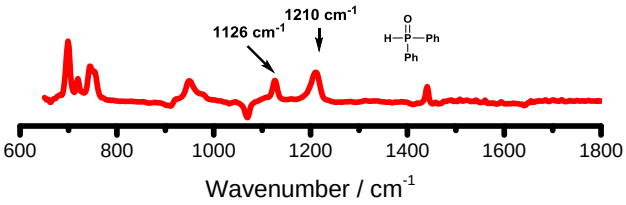


Figure 2. Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol) in THF (2.0 mL) at 45 ºC for different time under air.

8) General procedure for the reaction of 1a with 2a detected by *oprendo* IR

Typical procedure: a three-necked reaction vessel was equipped with a stir bar, the operando IR probe was inserted through an adapter into the middle neck, other two necks were capped by septa for injections and a dry air balloon. Then diphenylphosphine oxides **2a** (242.6 mg, 1.2 mmol) were added. After evacuation under vacuum and flushing with air through the dry air balloon for three times, THF (4.0 mL) was added to the vessel via a springe and the reaction was monitored by operando IR at 45 ºC. Afterwards, **1a** (47.2 mg, 0.4 mmol) was added under air and the reaction mixture was allowed to stir vigorously at 45 ºC for 2 h.



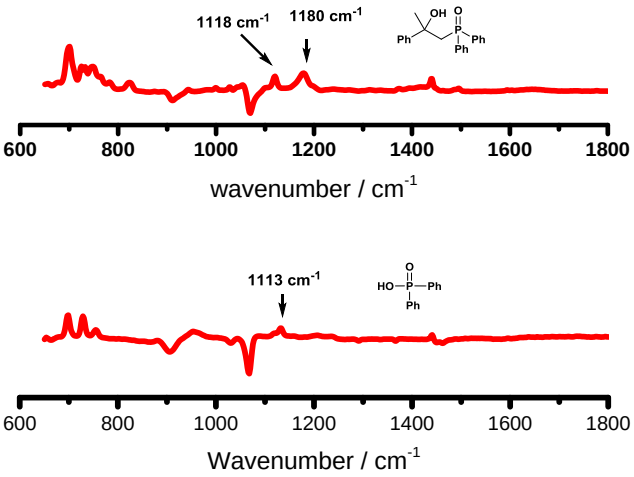


Figure 3. The Characteristic IR band of the different species (in THF).

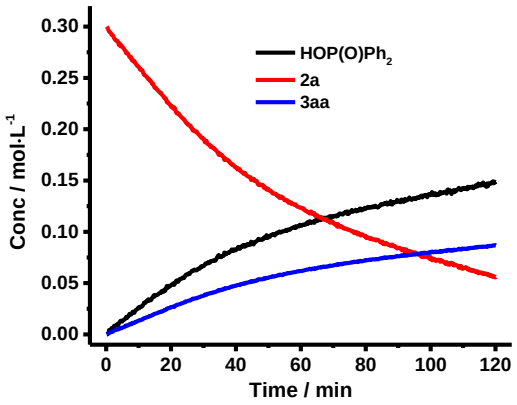
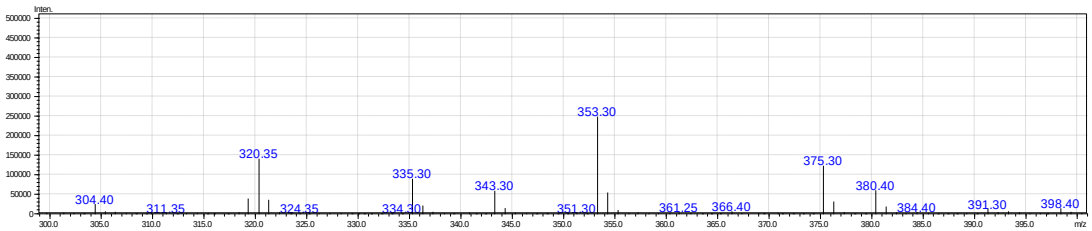
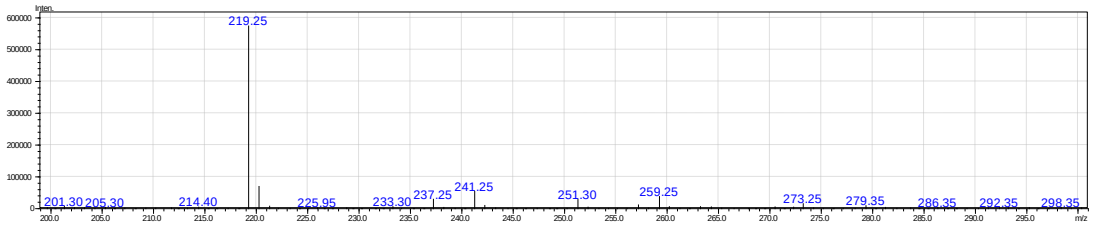


Figure 4. The kinetic profile of the reaction of **1a** (0.4 mmol), **2a** (1.2 mmol) in THF (4.0 mL) at 45 ºC under air.

9) General procedure for the reaction of 1a with 2a detected by LC-MS

A mixture of α-methylstyrene **1a** (0.2 mmol) with diphenylphosphine oxide **2a** (0.6 mmol) in THF (2 mL) was stirred under air at 45 ºC for 1 h. After completion of the reaction, a sample of this mixture was analyzed by LC-MS directly. The intermediate **IV** and $HOP(O)Ph_2$ were detected ($[M+H]^+$ = 353.30 and $[M+H]^+$ = 219.25).





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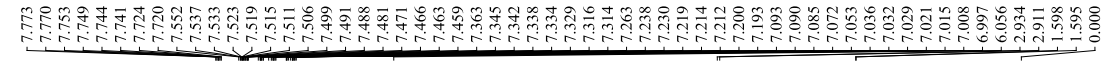
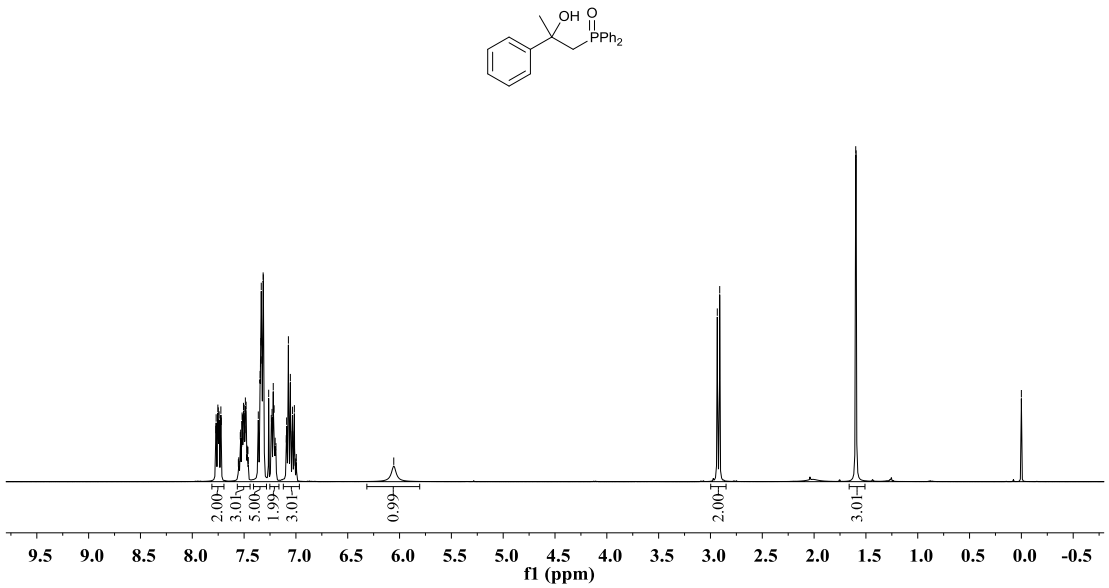
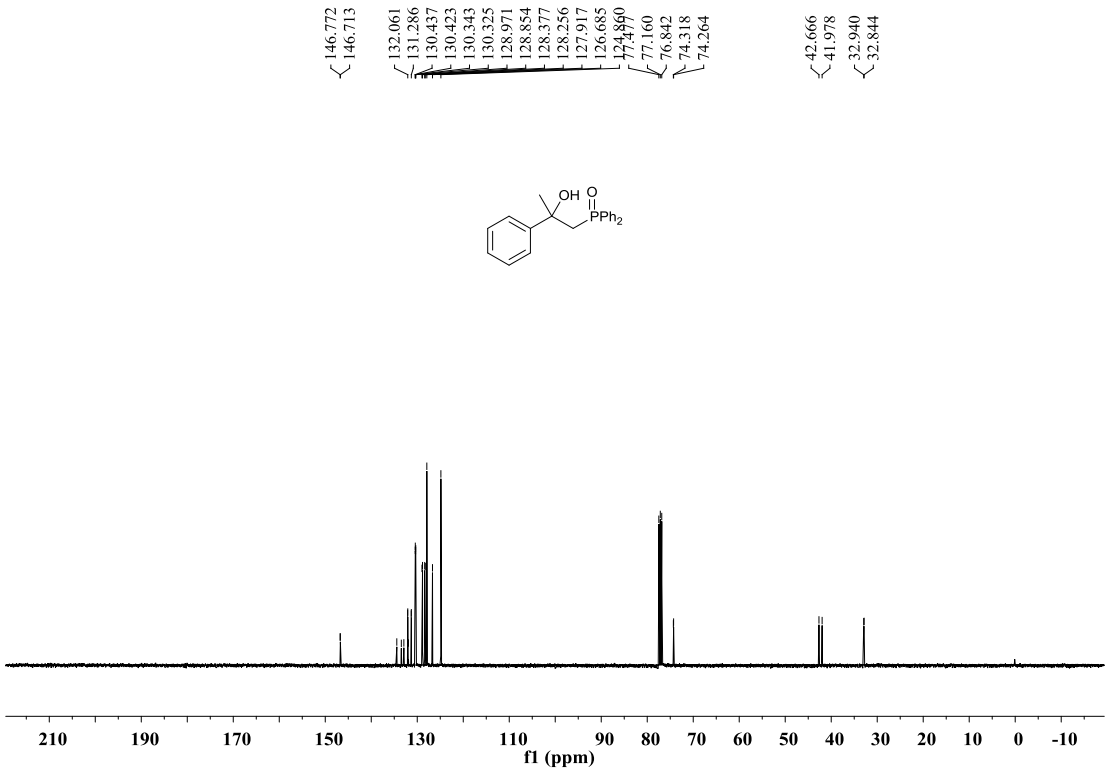
2. G. Bartoli, L. Sambri, E. Marcantoni and M. Petrini, *Tetrahedron Lett.*, 1994, **35**, 8453-8456.
3. S.-F. Zhou, D.-P. Li, K. Liu, J.-P. Zou and O. T. Asekun, *J. Org. Chem.*, 2015, **80**, 1214-1220.
4. P. Zhang, L. Zhang, Y. Gao, J. Xu, H. Fang, G. Tang and Y. Zhao, *Chem. Commun.*, 2015, **51**, 7839-7842.

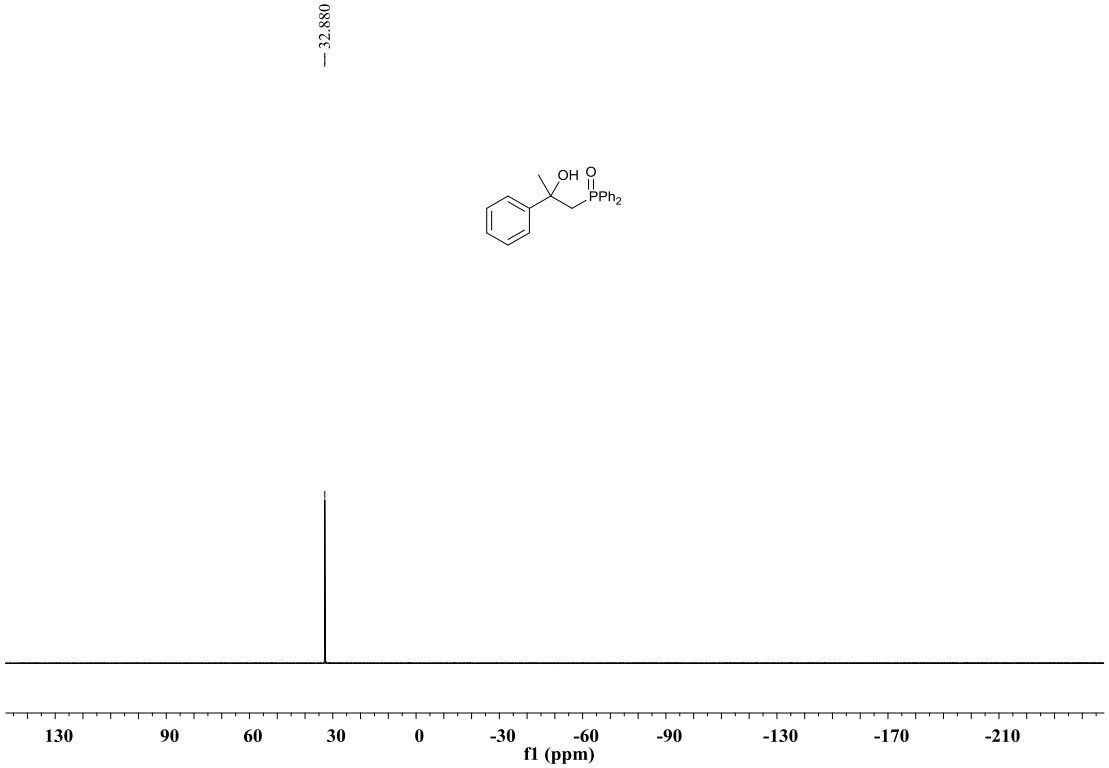
NMR spectra of products

3aa





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O
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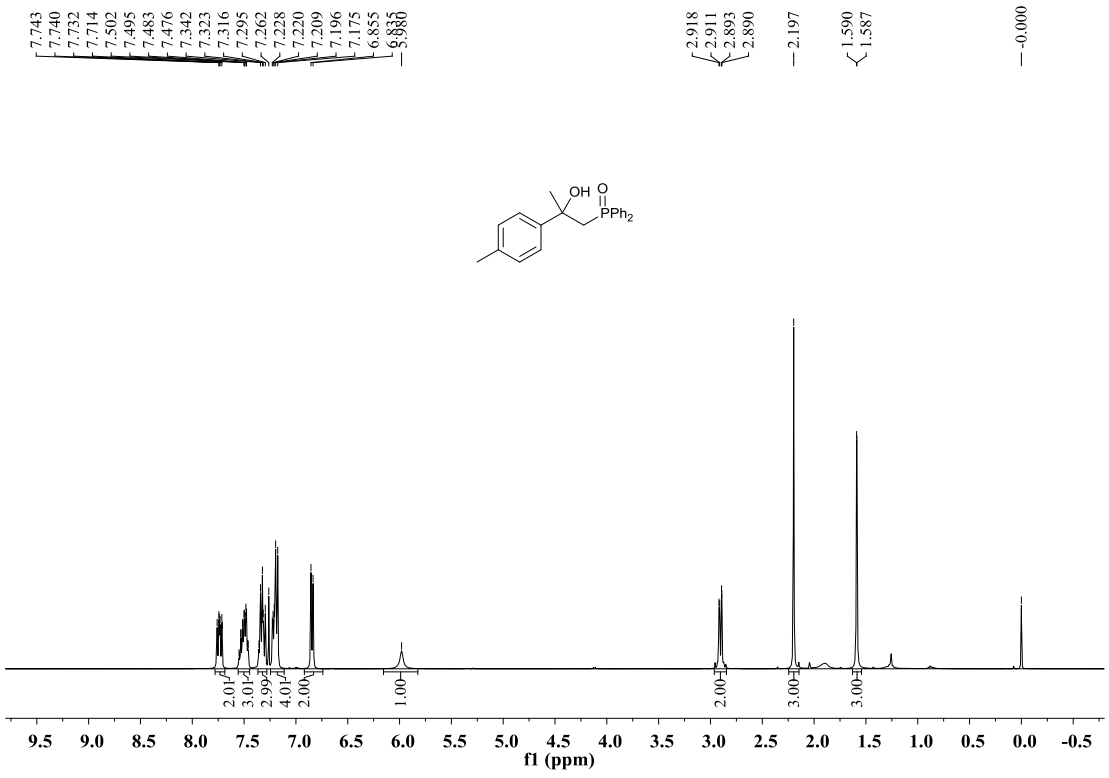
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

3ab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7.502
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7.175
6.855
6.835
6.980
2.918
2.911
2.893
2.890
2.197
1.590
1.587
0.000
OH
O
PPh2
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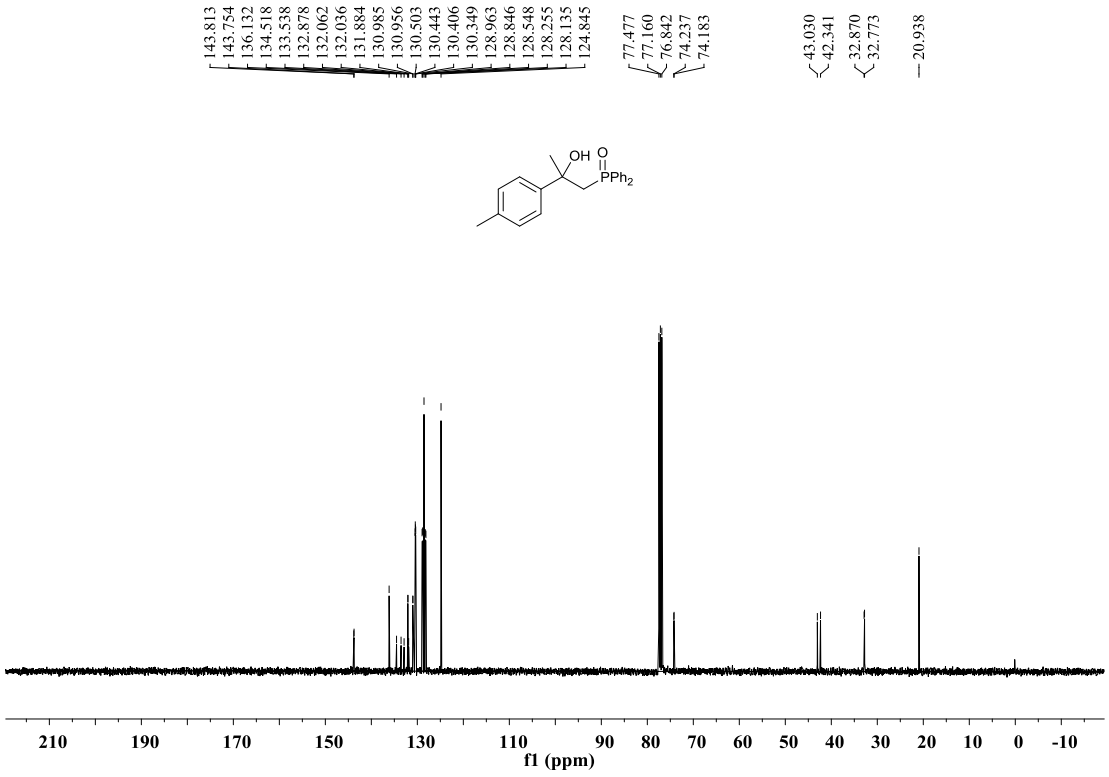
3.01
2.99
4.01
2.00
1.00
2.00
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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20.938
OH
O
PPh2
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170
150
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110
90
80
70
60
50
40
30
20
10
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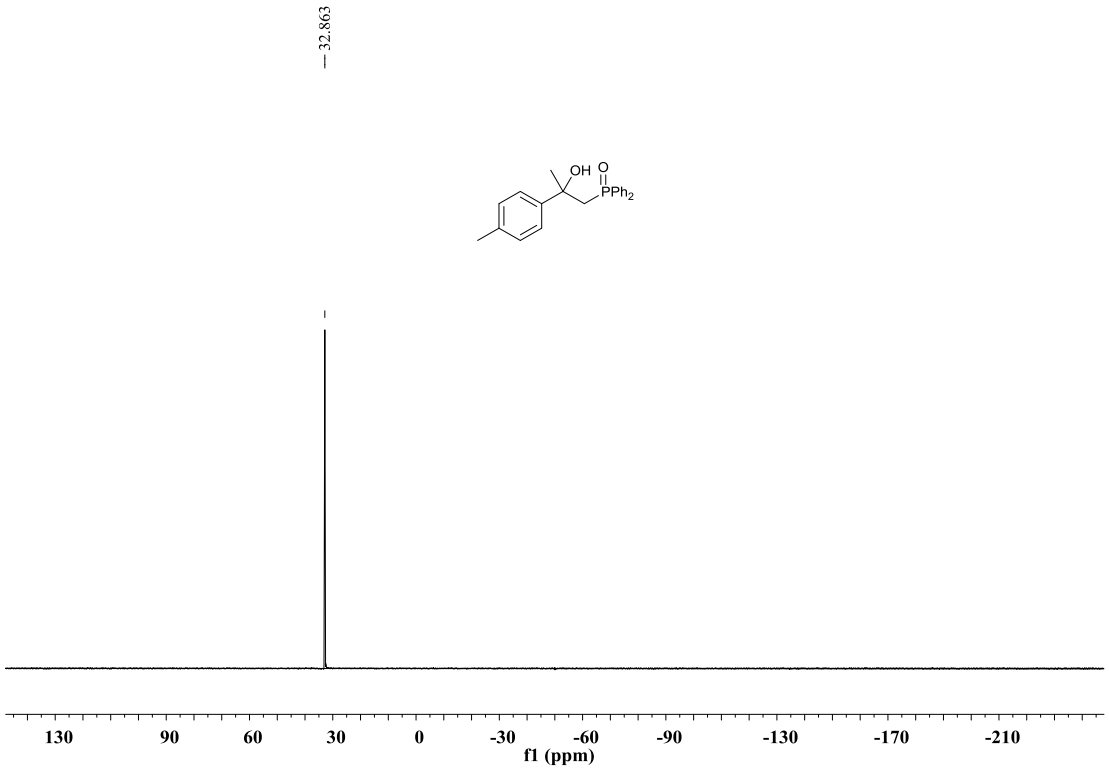
f1 (ppm)


32.863
OH
O
PPh2
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90
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30
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-30
-60
-90
-130
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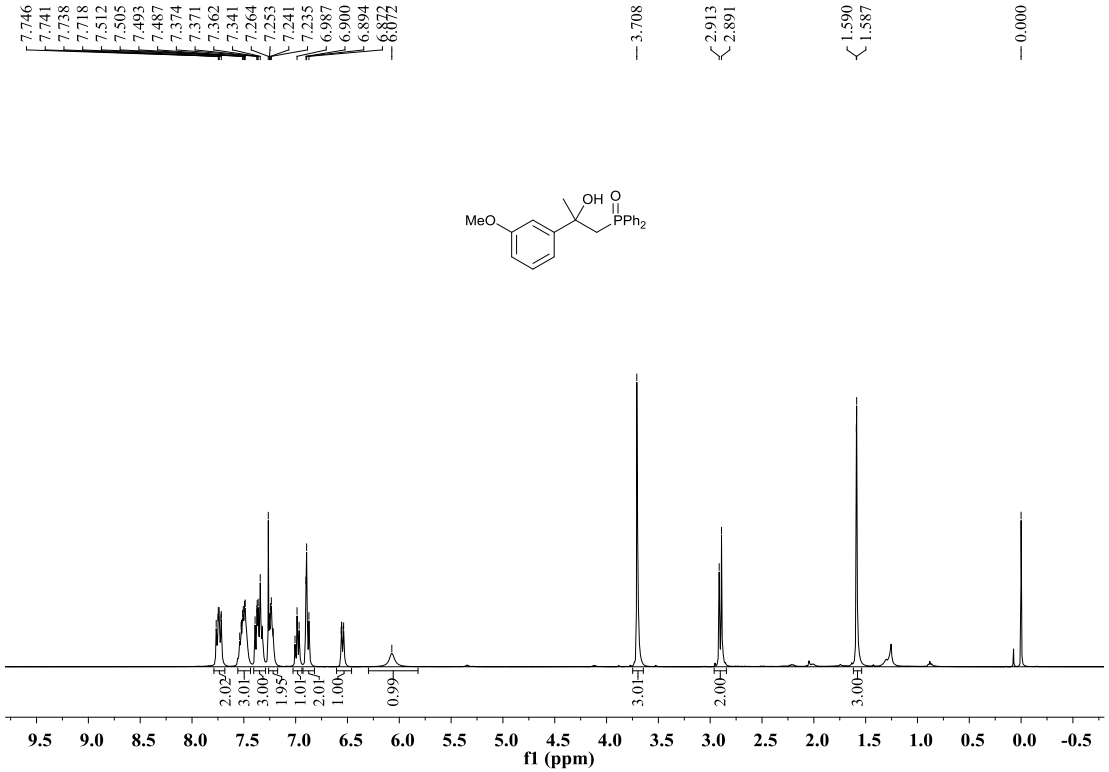
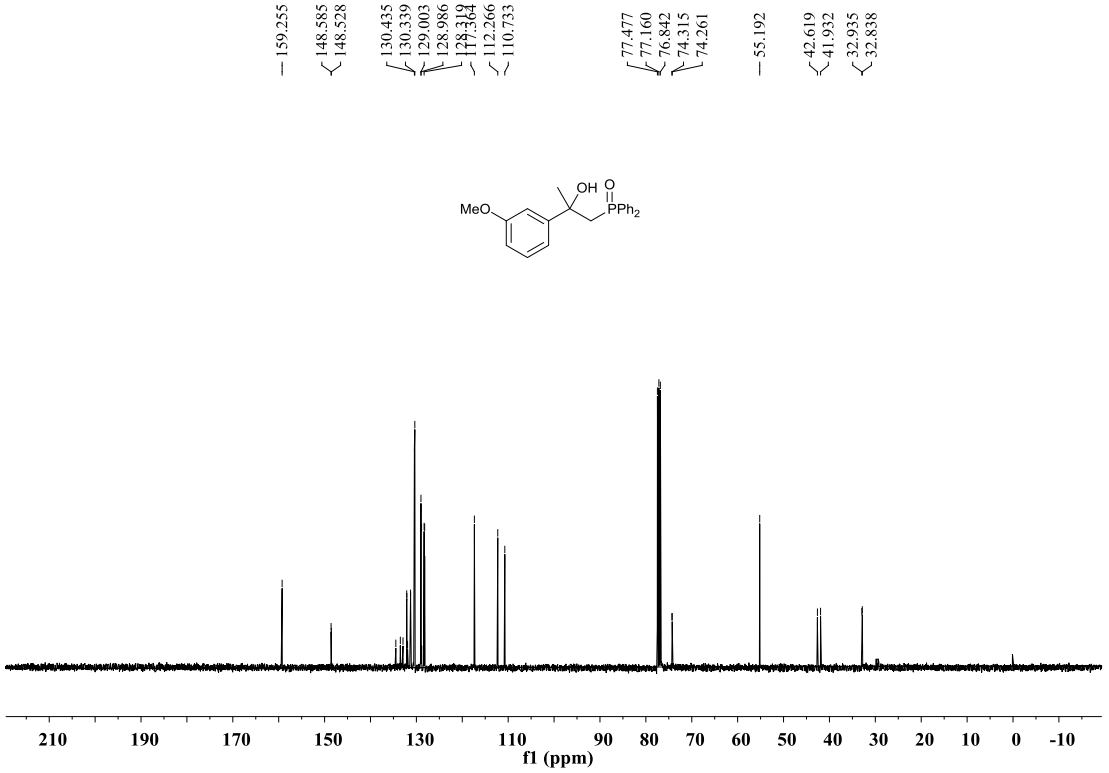
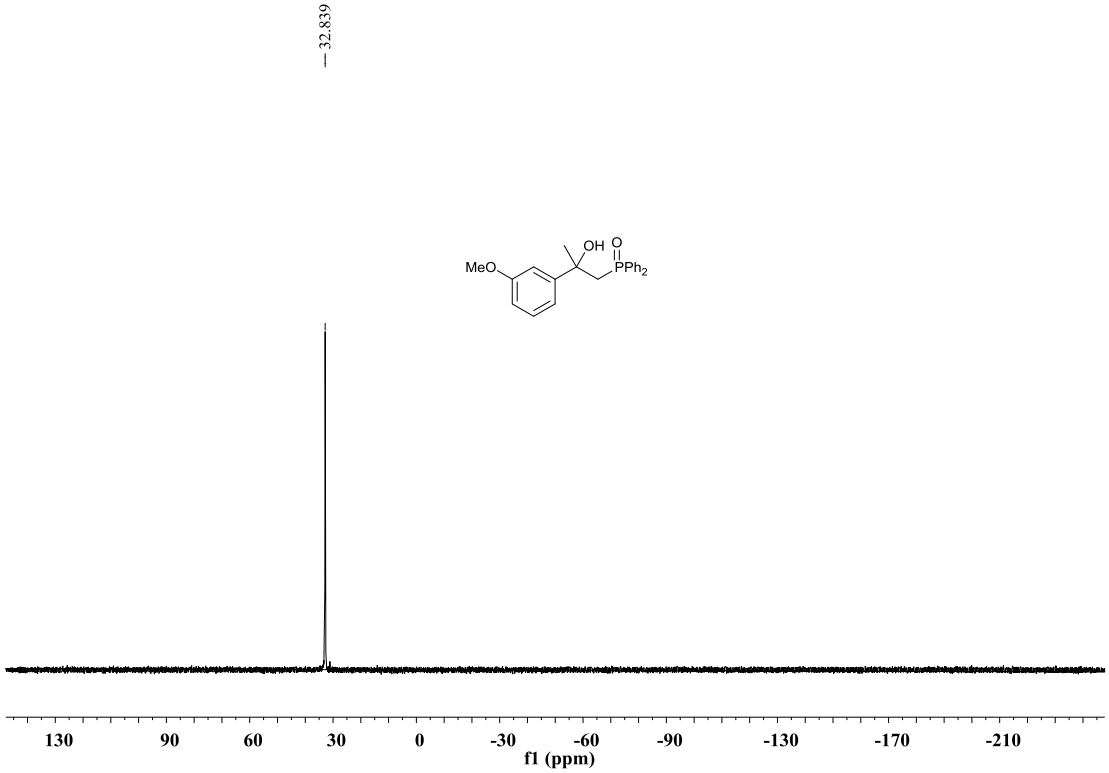
-210
f1 (ppm)

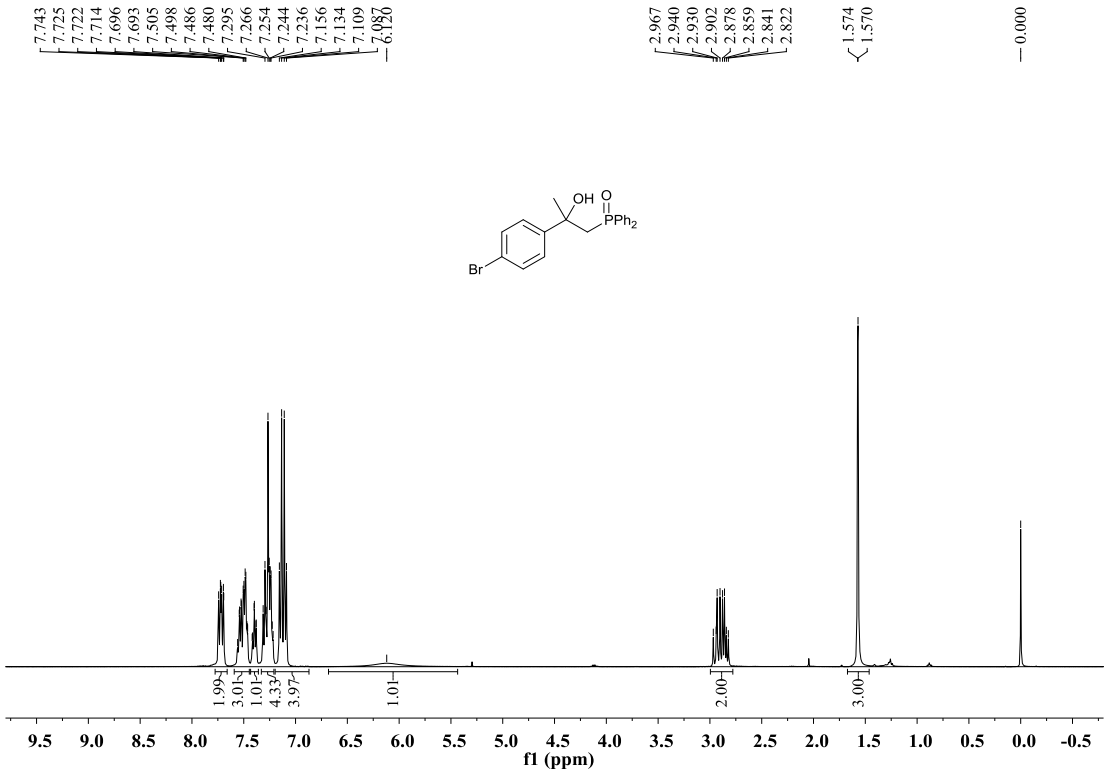
3ac

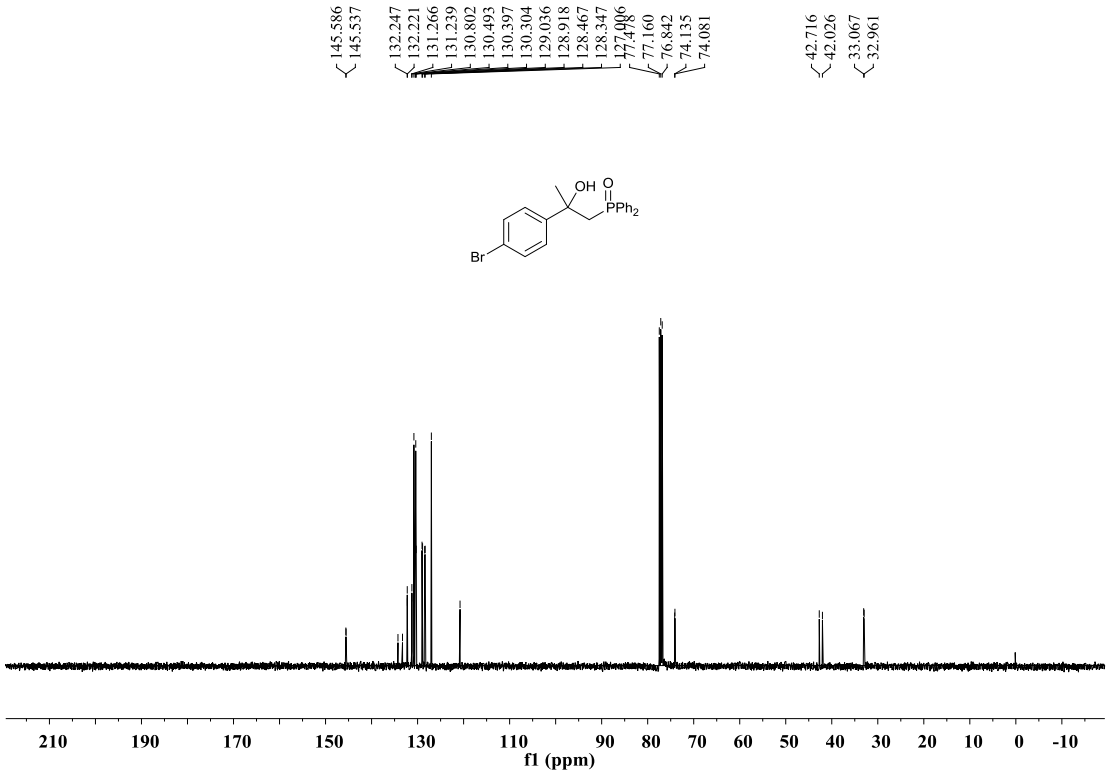

7.746
7.741
7.738
7.718
7.512
7.505
7.493
7.487
7.374
7.371
7.362
7.341
7.264
7.253
7.241
7.235
6.987
6.900
6.894
6.872
3.708
2.913
2.891
1.590
1.587
0.000
MeO
OH
O
PPh2
2.02
3.01
3.00
1.95
1.01
2.01
1.00
0.99
3.01
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

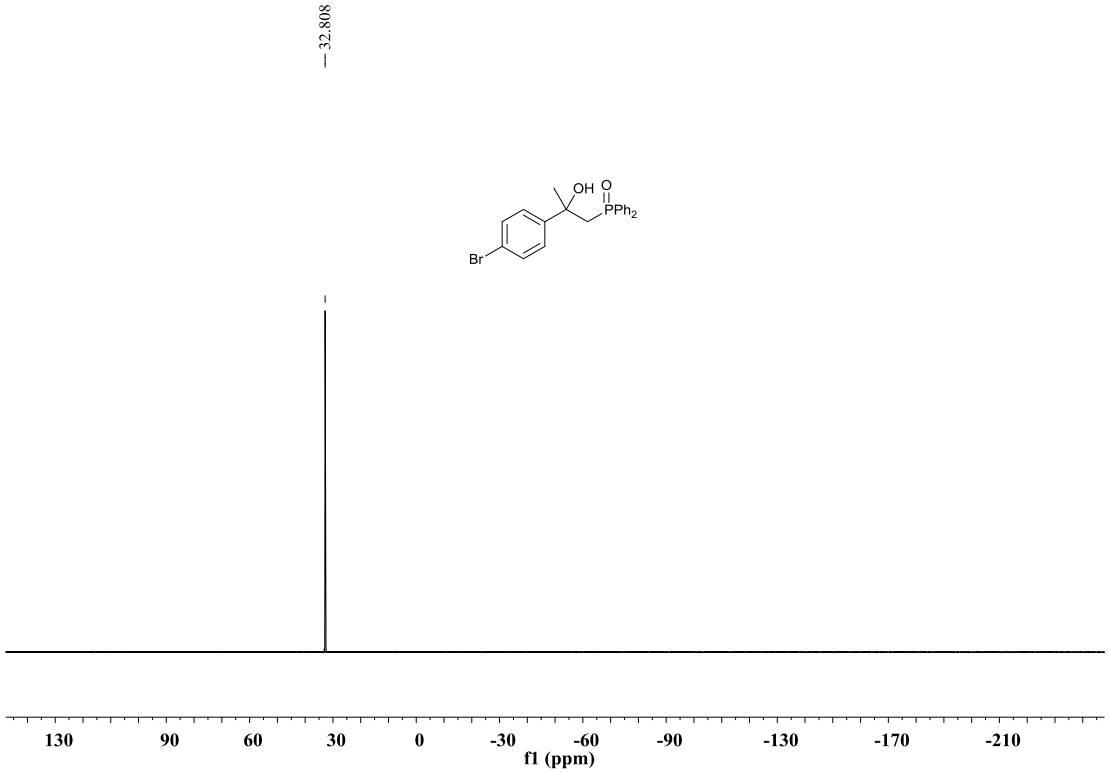

159.255
148.585
148.528
130.435
130.339
129.003
128.986
128.319
117.364
112.266
110.733
77.477
77.160
76.842
74.315
74.261
55.192
42.619
41.932
32.935
32.838
MeO
OH
O
PPh2
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


32.839
MeO
OH
O
PPh2
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

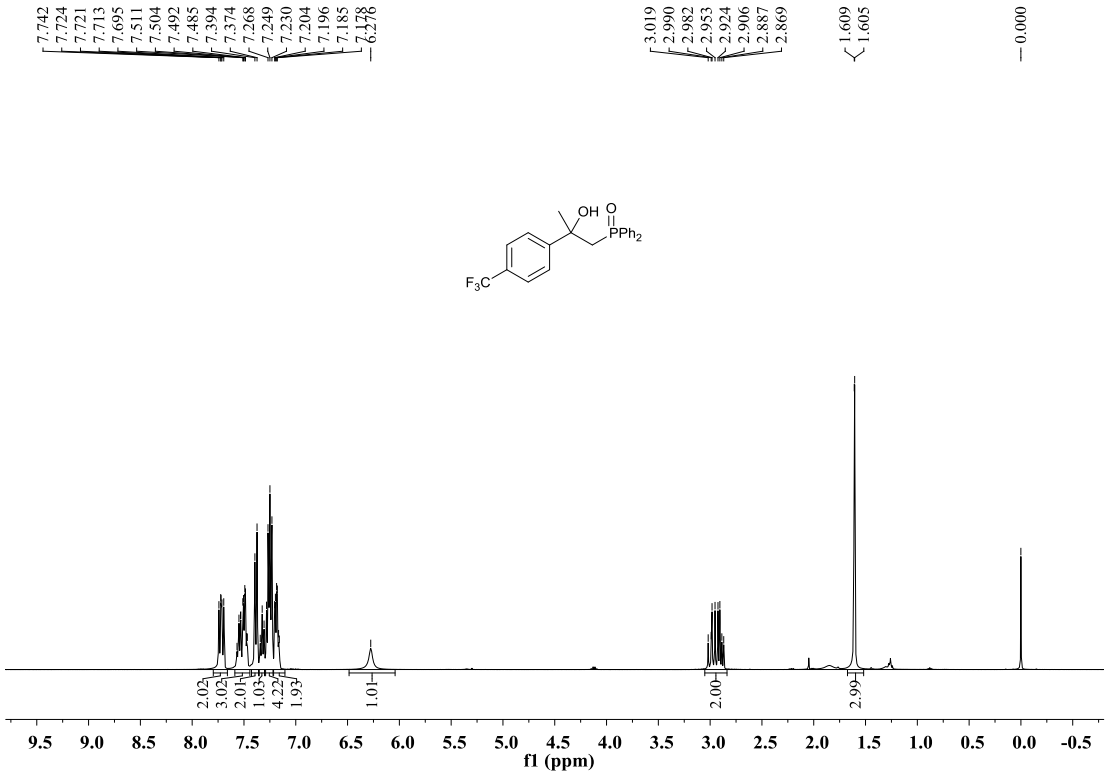
3ad

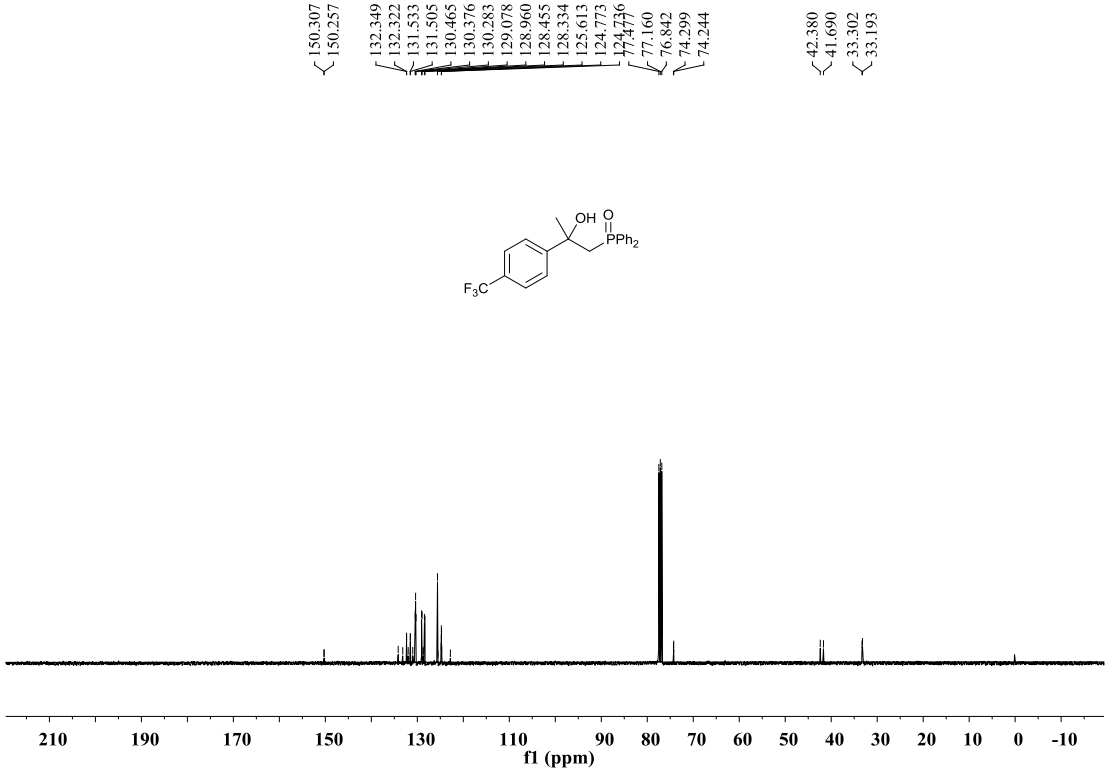

7.743
7.725
7.722
7.714
7.696
7.693
7.505
7.498
7.486
7.480
7.295
7.266
7.254
7.244
7.236
7.156
7.134
7.109
7.087
6.120
2.967
2.940
2.930
2.902
2.878
2.859
2.841
2.822
1.574
1.570
0.000
OH
O
PPh2
Br
1.99
3.01
1.01
4.33
3.97
1.01
2.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

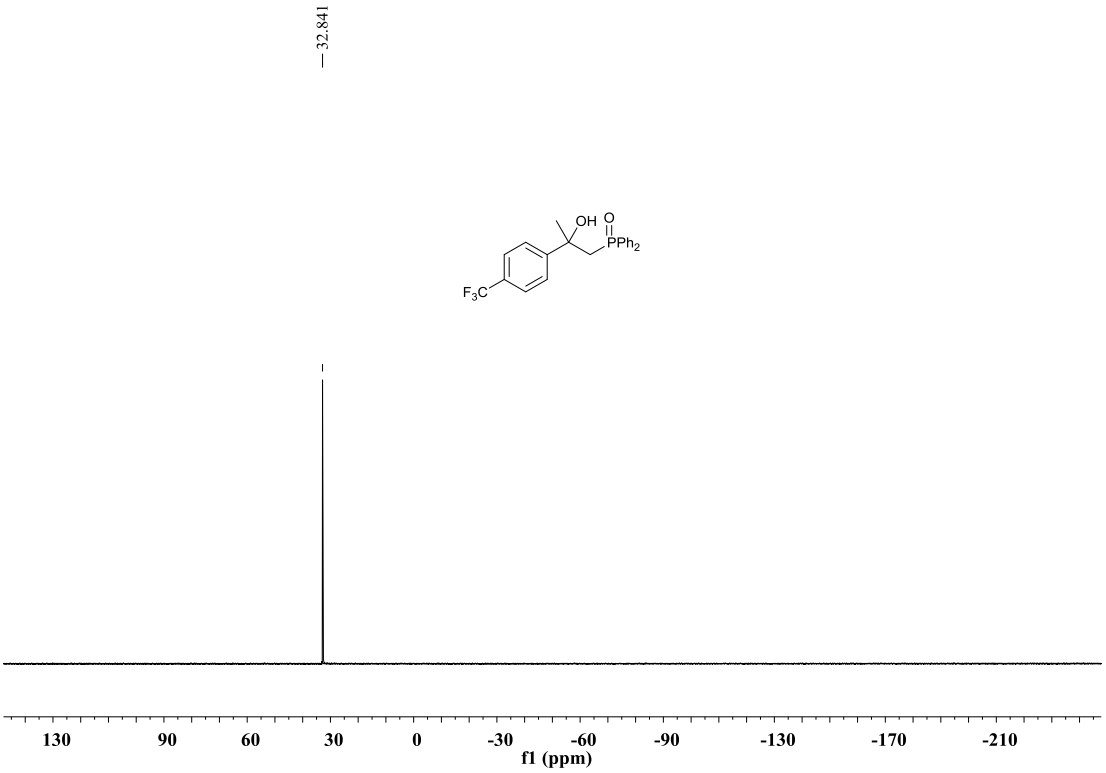

145.586
145.537
132.247
132.221
131.266
131.239
130.802
130.493
130.397
130.304
129.036
128.918
128.467
128.347
127.006
77.478
77.160
76.842
74.135
74.081
42.716
42.026
33.067
32.961
OH
O
PPh2
Br
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


32.808
OH
O
PPh2
Br
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

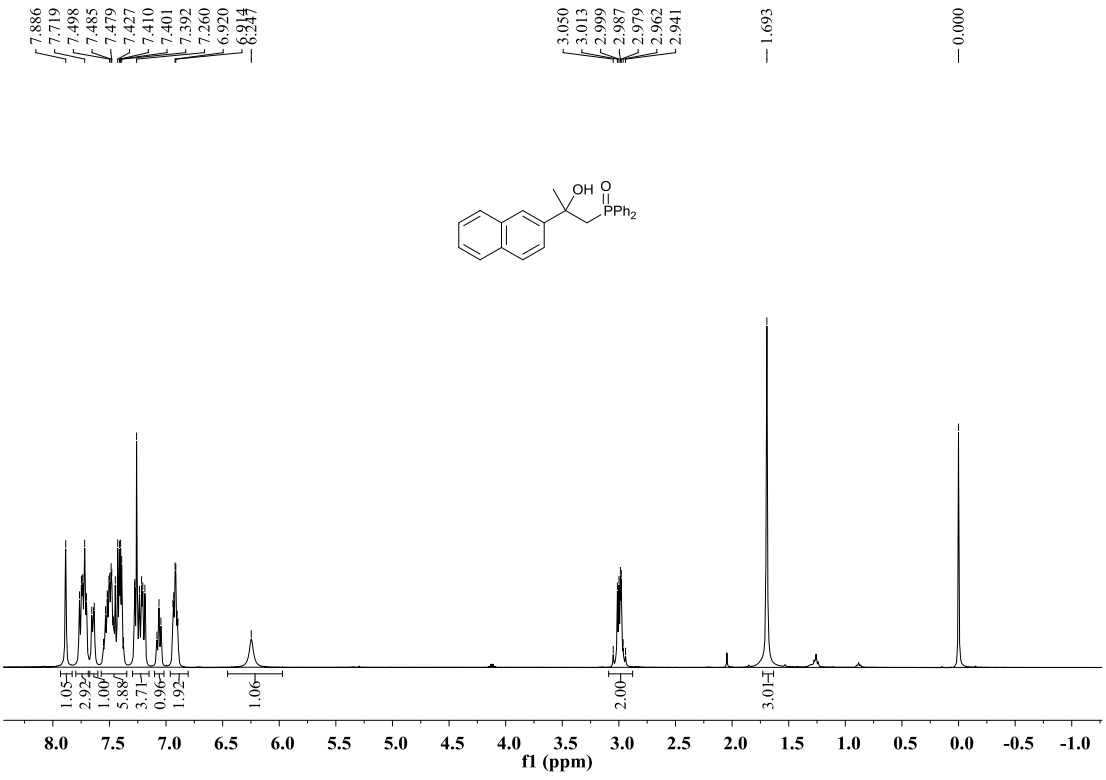
3ae

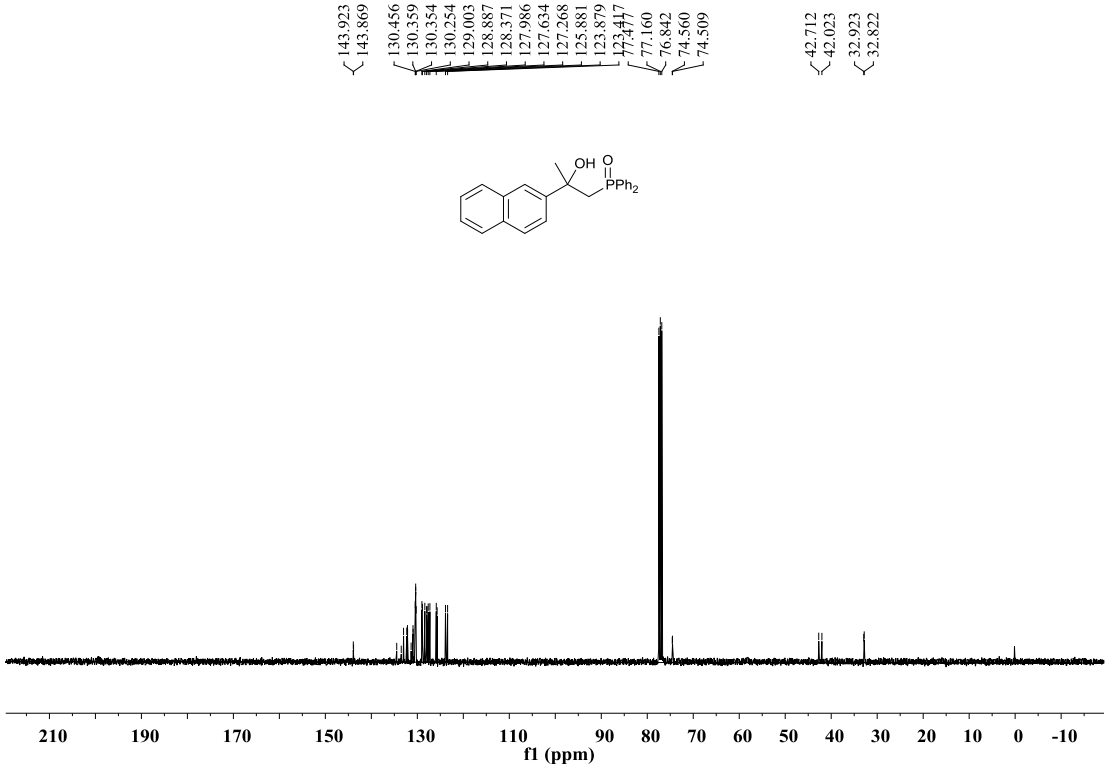

7.742
7.724
7.721
7.713
7.695
7.511
7.504
7.492
7.485
7.394
7.374
7.268
7.249
7.230
7.204
7.196
7.185
7.178
6.278
3.019
2.990
2.982
2.953
2.924
2.906
2.887
2.869
1.609
1.605
0.000
OH
O
PPh2
F3C
2.02
3.02
2.01
1.03
4.22
1.93
1.01
2.00
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

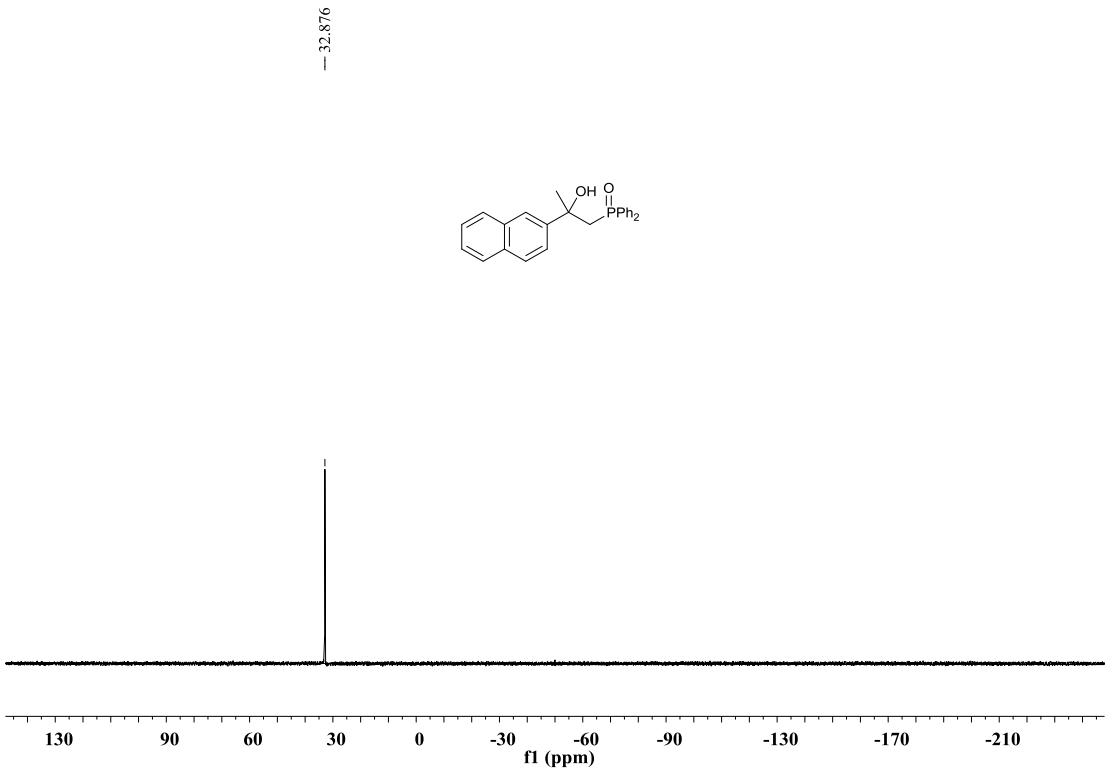

150.307
150.257
132.349
132.322
131.533
131.505
130.465
130.376
130.283
129.078
128.960
128.455
128.334
125.613
124.773
77.477
77.160
76.842
74.299
74.244
42.380
41.690
33.302
33.193
OH
O
PPh2
F3C
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


32.841
OH
O
PPh2
F3C
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

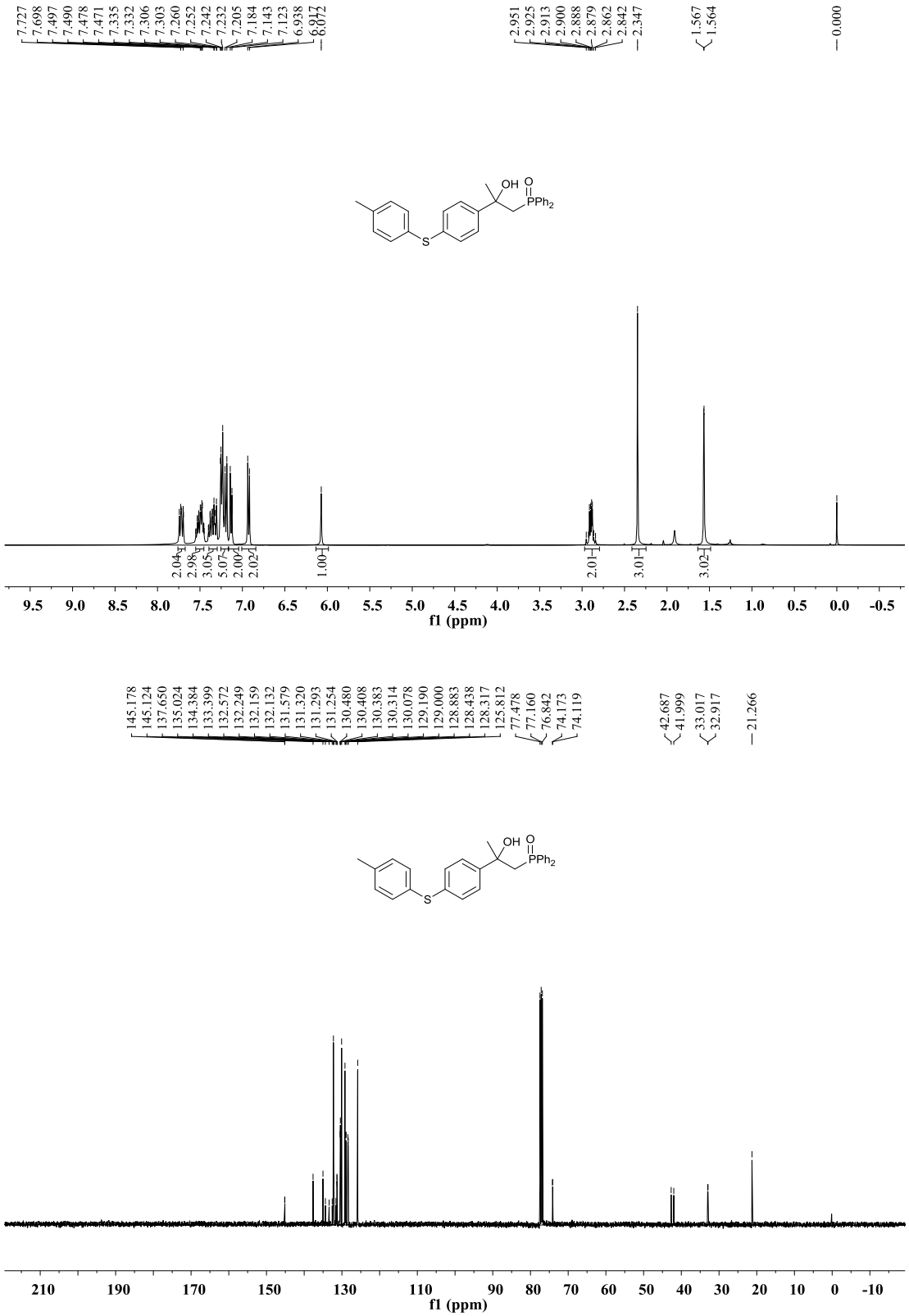
3af

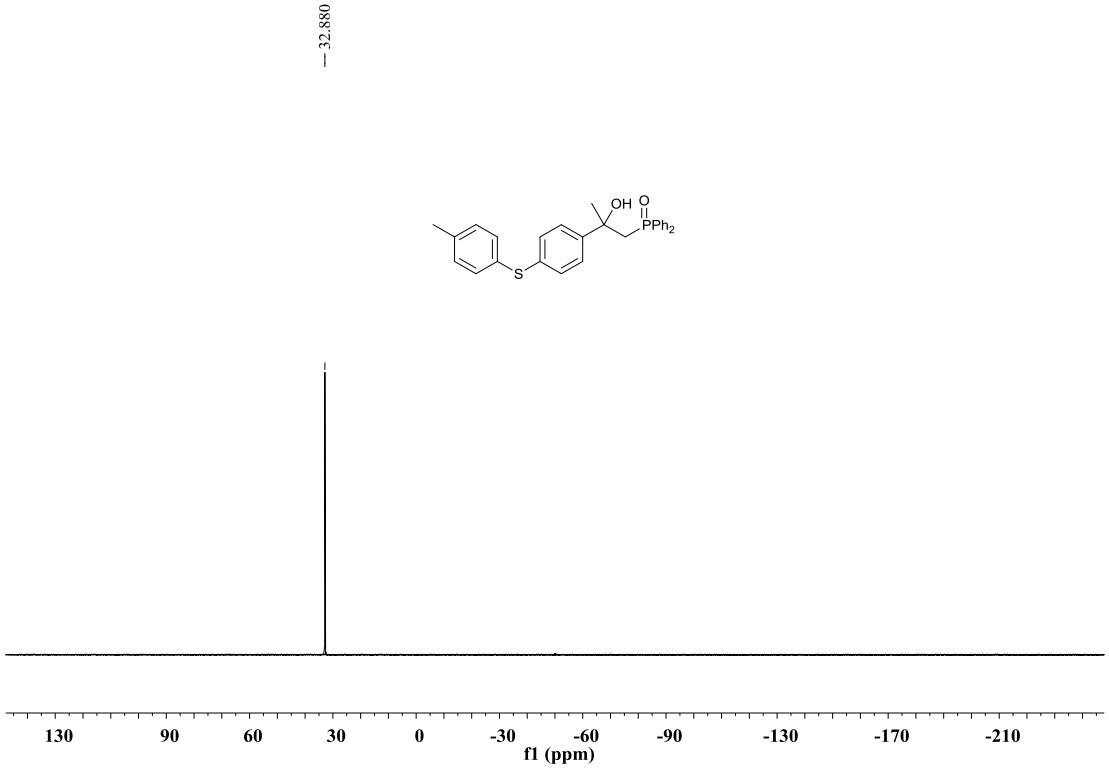

7.886
7.719
7.498
7.485
7.479
7.427
7.410
7.401
7.392
7.260
6.920
6.914
6.247
3.050
3.013
2.999
2.987
2.979
2.962
2.941
1.693
0.000
OH
O
PPh2
1.05
2.92
1.00
5.88
3.71
0.96
1.92
1.06
2.00
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


143.923
143.869
130.456
130.359
130.354
130.254
129.003
128.887
128.371
127.986
127.634
127.268
125.881
123.879
123.447
123.417
77.477
77.160
76.842
74.560
74.509
42.712
42.023
32.923
32.822
OH
O
PPh2
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

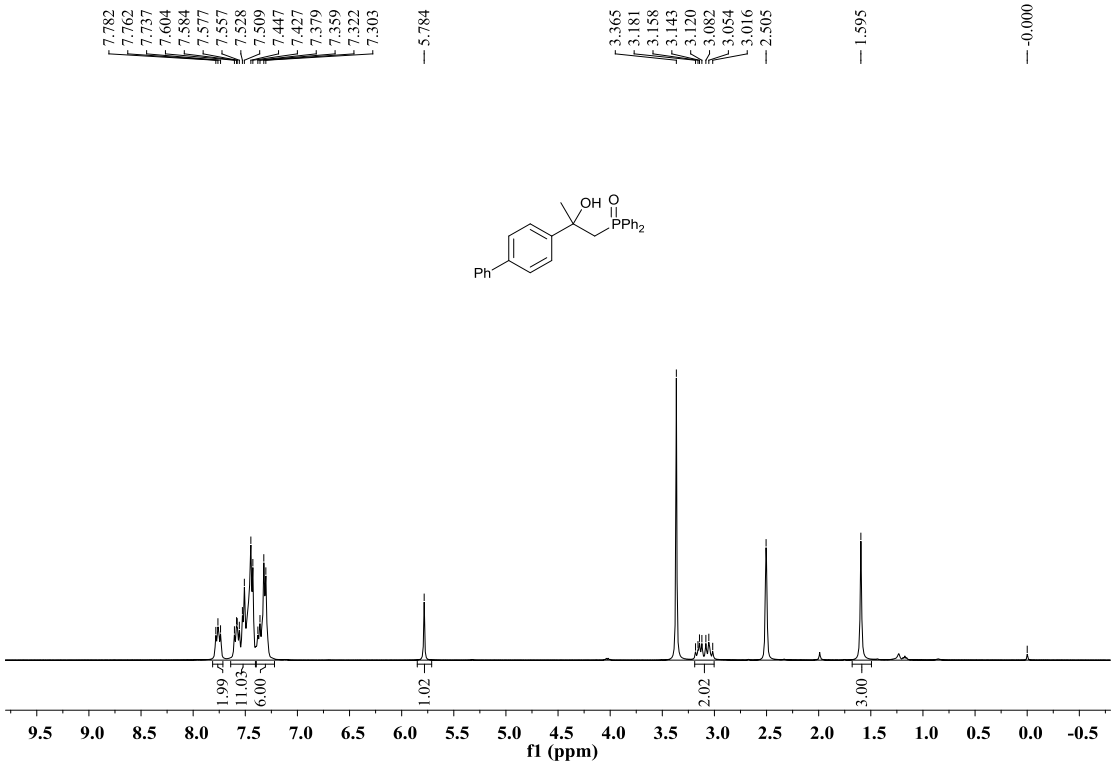

32.876
OH
O
PPh2
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

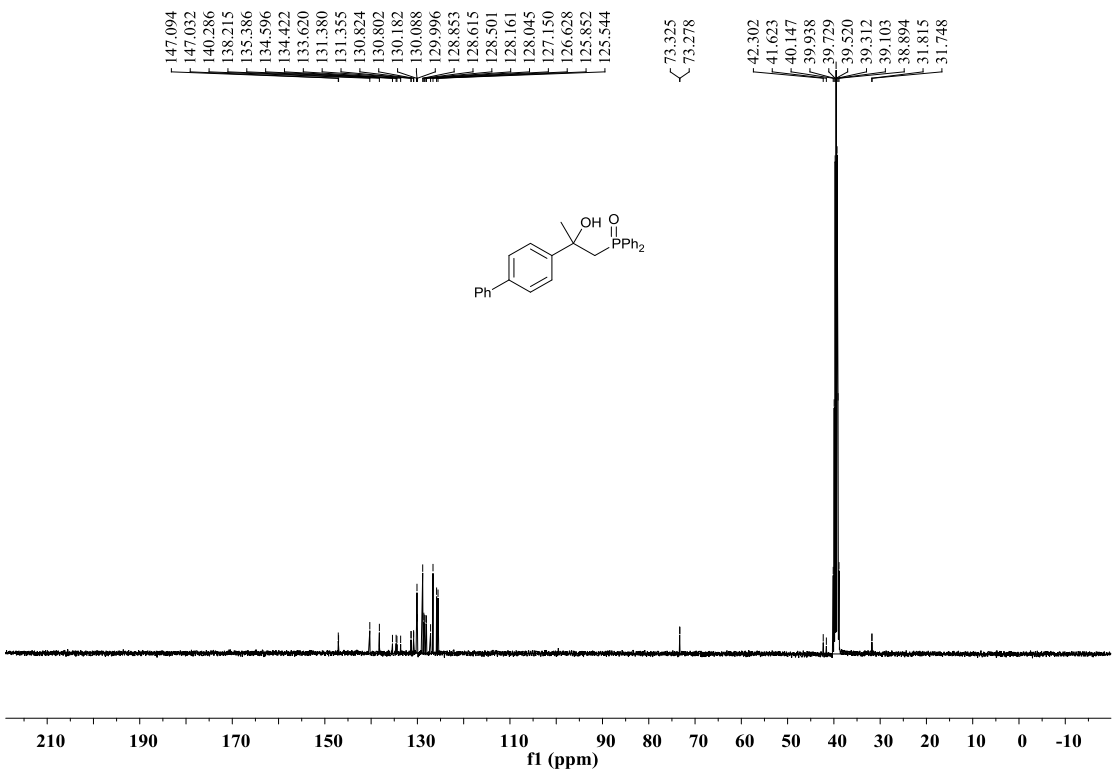
3ag

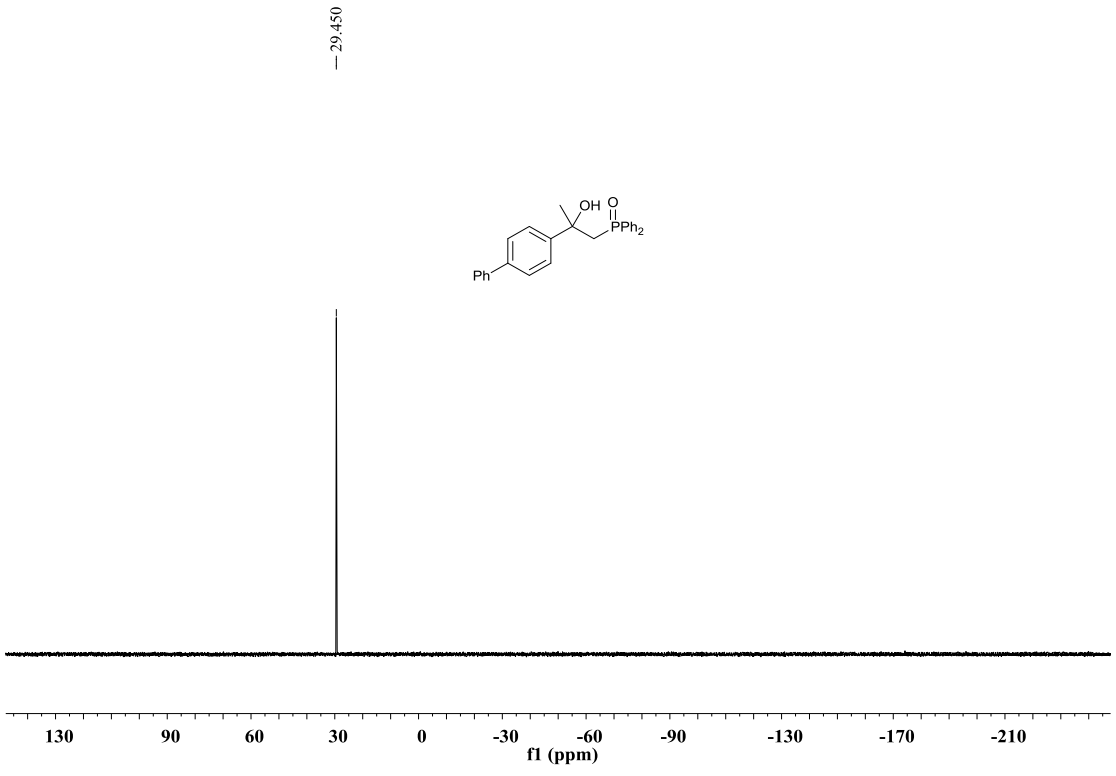

7.727
7.698
7.497
7.490
7.478
7.471
7.335
7.332
7.306
7.303
7.260
7.252
7.242
7.232
7.205
7.184
7.143
7.123
6.938
6.072
2.951
2.925
2.913
2.900
2.888
2.879
2.862
2.842
2.347
1.567
1.564
0.000
OH
O
PPh2
S
2.04
2.98
3.05
5.07
2.00
2.02
1.00
2.01
3.01
3.02
f1 (ppm)
145.178
145.124
137.650
135.024
134.384
133.399
132.572
132.249
132.159
132.132
131.579
131.320
131.293
131.254
130.480
130.408
130.383
130.314
130.078
129.190
129.000
128.883
128.438
128.317
125.812
77.478
77.160
76.842
74.173
74.119
42.687
41.999
33.017
32.917
21.266
f1 (ppm)


32.880
OH
O
PPh2
S
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

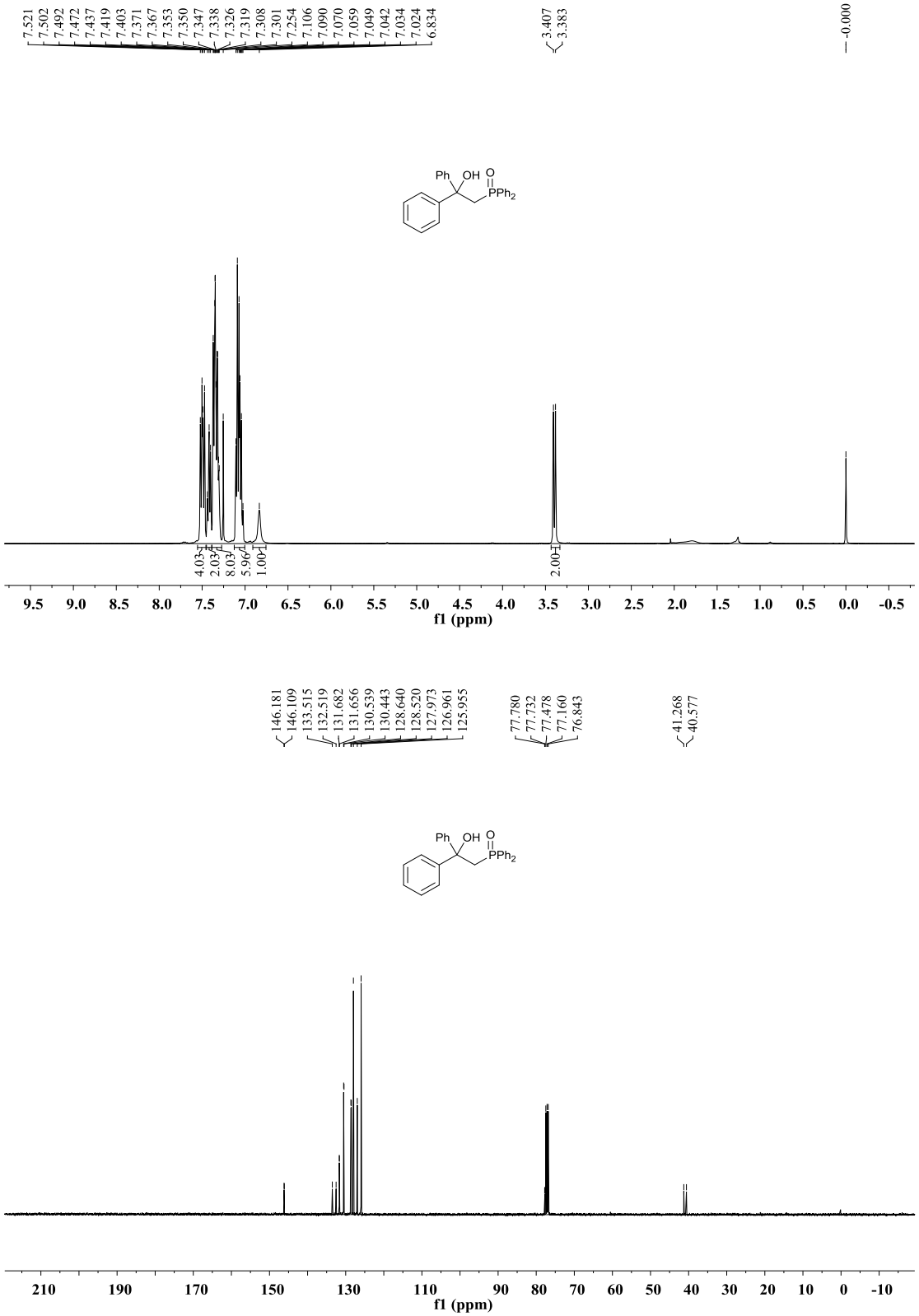
3ah

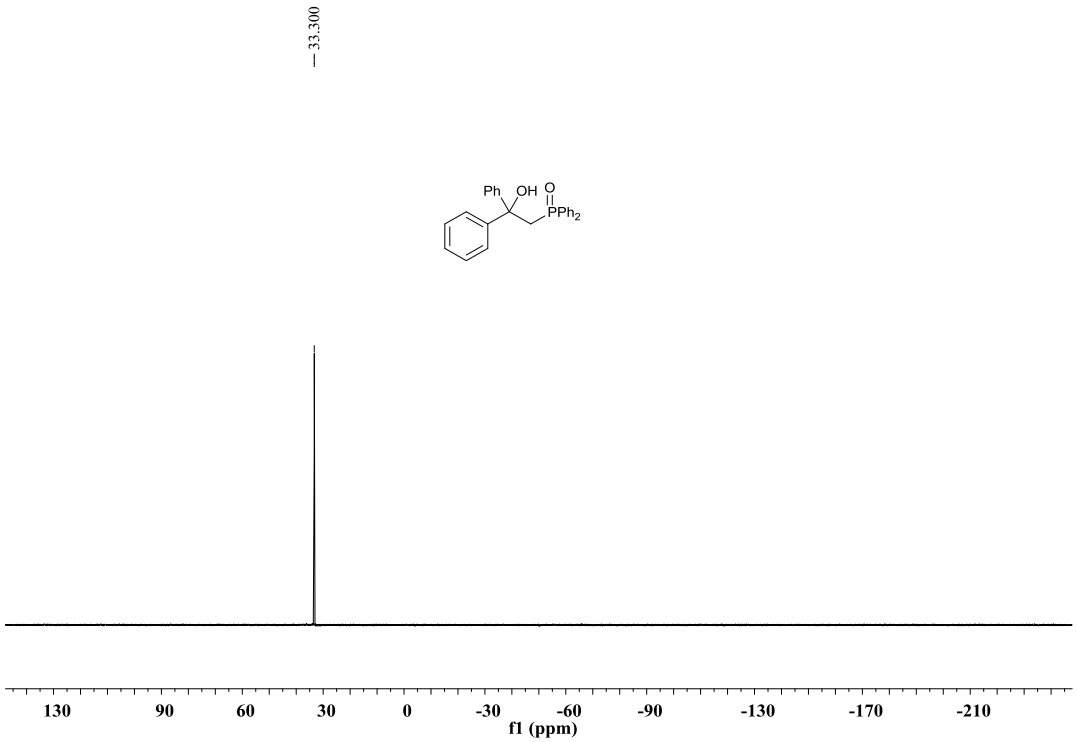

7.782
7.762
7.737
7.604
7.584
7.577
7.557
7.528
7.509
7.447
7.427
7.379
7.359
7.322
7.303
5.784
3.365
3.181
3.158
3.143
3.120
3.082
3.054
3.016
2.505
1.595
-0.000
OH
O
PPh2
Ph
1.99
11.03
6.00
1.02
2.02
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


147.094
147.032
140.286
138.215
135.386
134.596
134.422
133.620
131.380
131.355
130.824
130.802
130.182
130.088
129.996
128.853
128.615
128.501
128.161
128.045
127.150
126.628
125.852
125.544
73.325
73.278
42.302
41.623
40.147
39.938
39.729
39.520
39.312
39.103
38.894
31.815
31.748
OH
O
PPh2
Ph
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

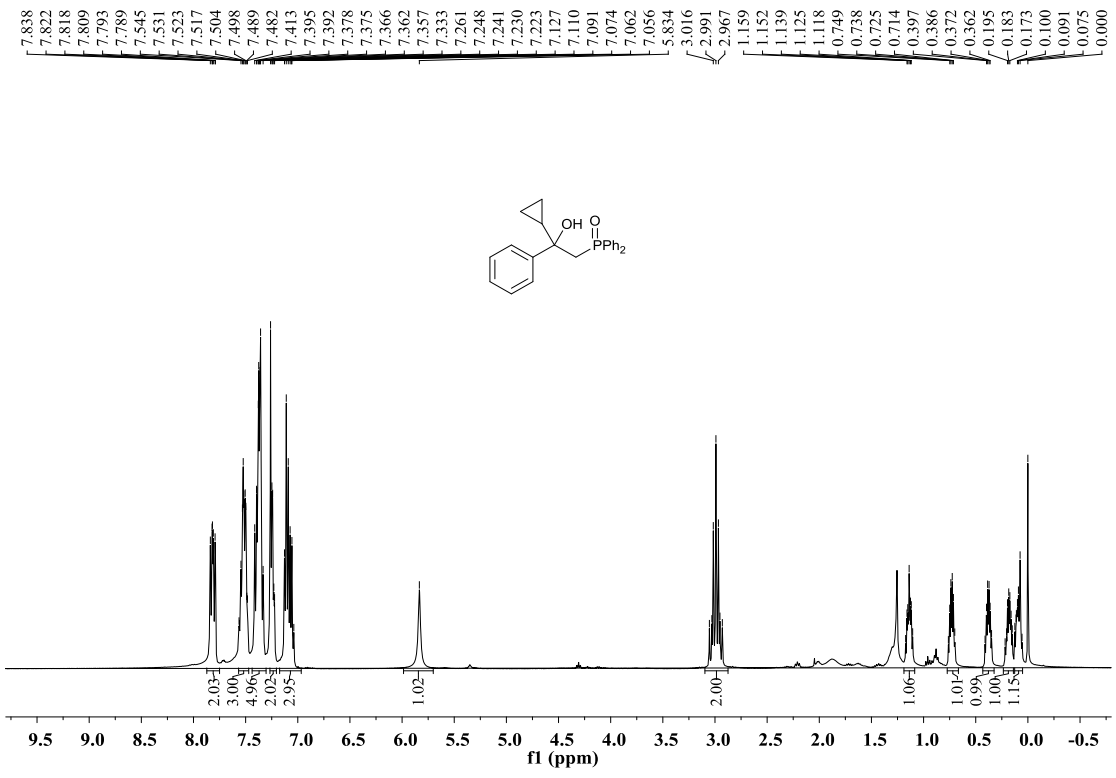

29.450
OH
O
PPh2
Ph
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

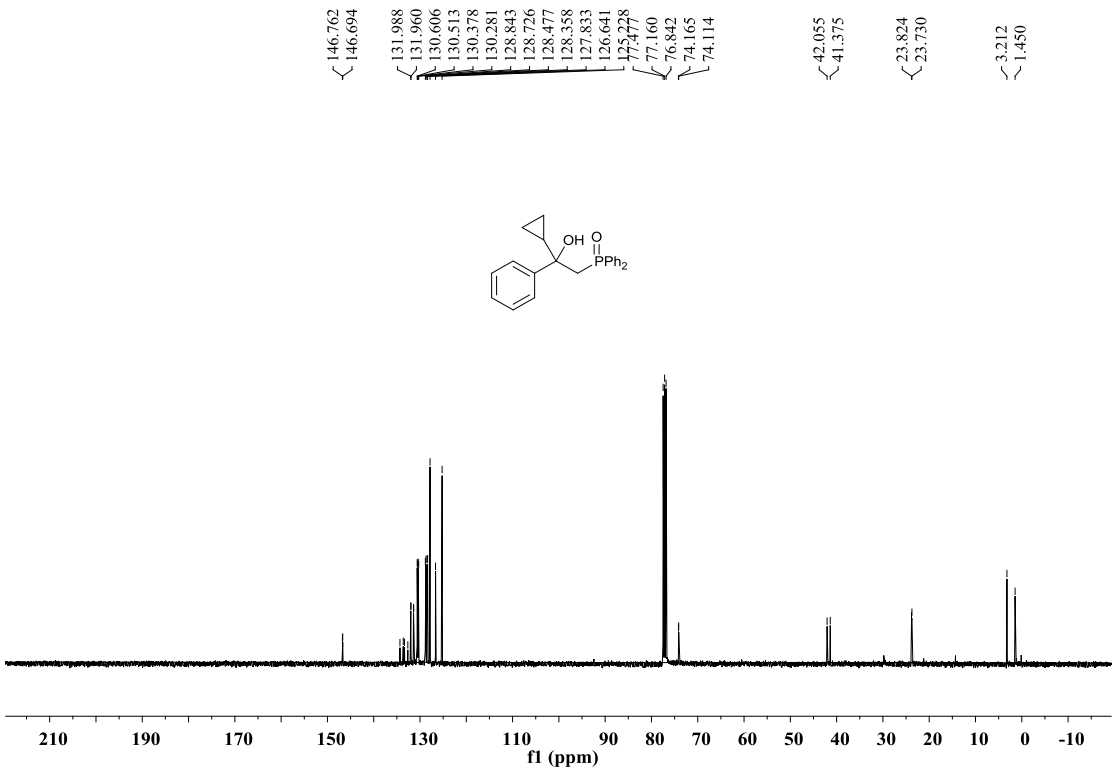
3ai

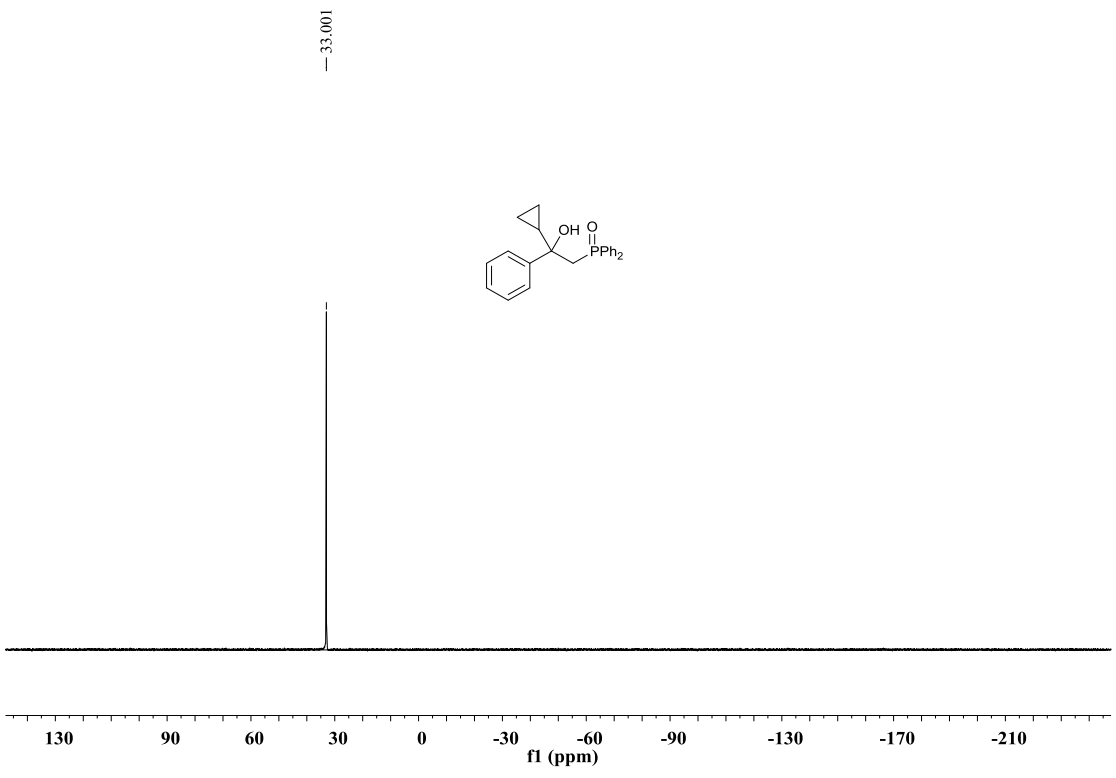

7.521
7.502
7.492
7.472
7.437
7.419
7.403
7.371
7.367
7.353
7.350
7.347
7.338
7.326
7.319
7.308
7.301
7.254
7.106
7.090
7.070
7.059
7.049
7.042
7.034
7.024
6.834
3.407
3.383
-0.000
Ph
OH
O
PPh2
4.03
2.03
8.03
5.96
1.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
146.181
146.109
133.515
132.519
131.682
131.656
130.539
130.443
128.640
128.520
127.973
126.961
125.955
77.780
77.732
77.478
77.160
76.843
41.268
40.577
Ph
OH
O
PPh2
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


33.300
Ph
OH
O
PPh2
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

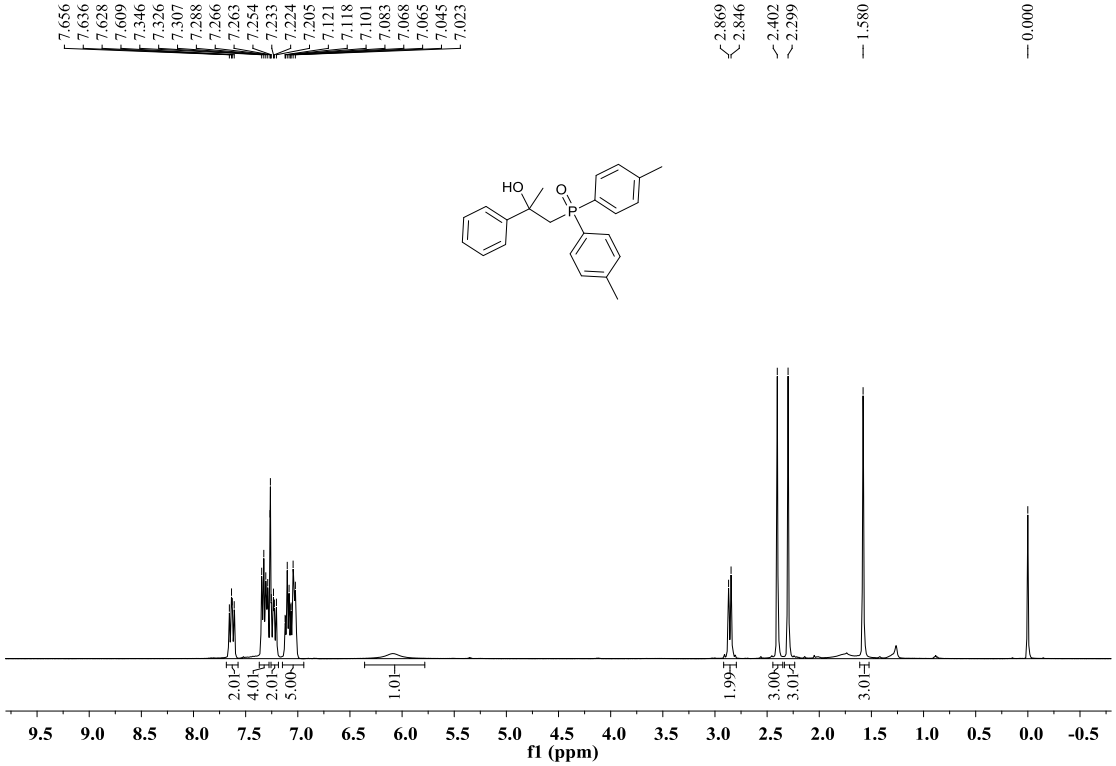
3aj

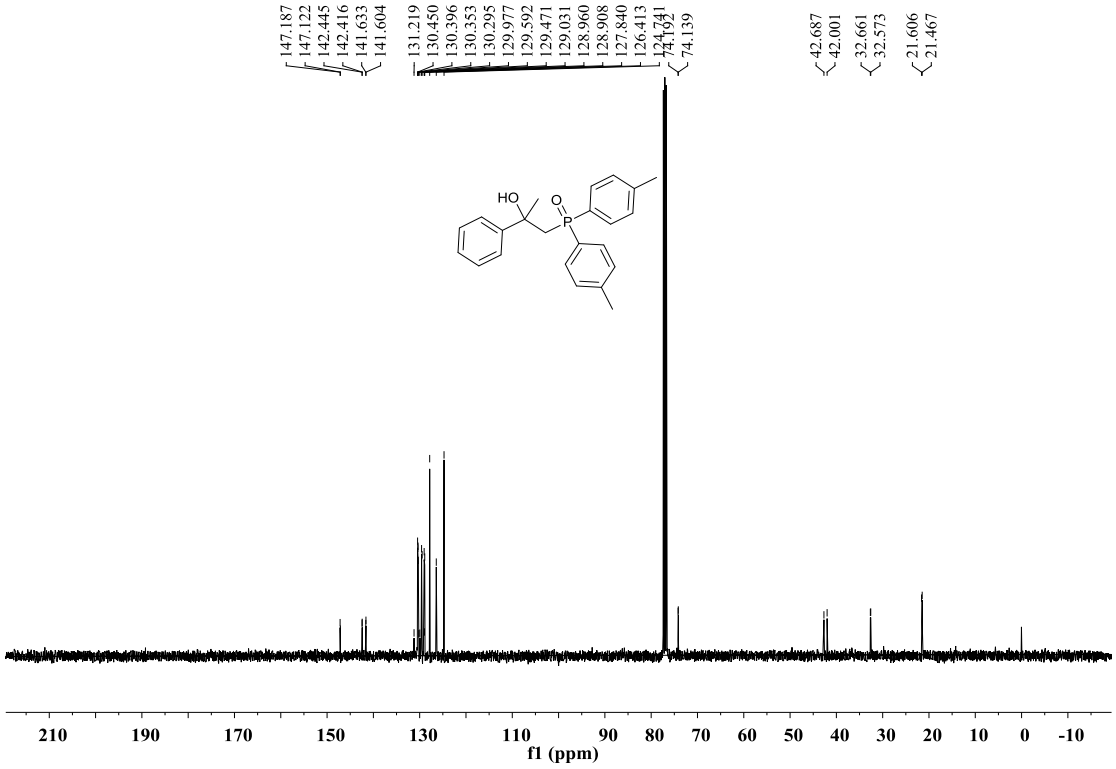

7.838
7.822
7.818
7.809
7.793
7.789
7.545
7.531
7.523
7.517
7.504
7.498
7.489
7.482
7.413
7.395
7.392
7.378
7.375
7.366
7.362
7.357
7.333
7.261
7.248
7.241
7.230
7.223
7.127
7.110
7.091
7.074
7.062
7.056
5.834
3.016
2.991
2.967
1.159
1.152
1.139
1.125
1.118
0.749
0.738
0.725
0.714
0.397
0.386
0.372
0.362
0.195
0.183
0.173
0.100
0.091
0.075
0.000
OH
O
PPh2
2.03
3.00
4.96
2.02
2.95
1.02
2.00
1.06
1.01
0.99
1.00
1.15
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)

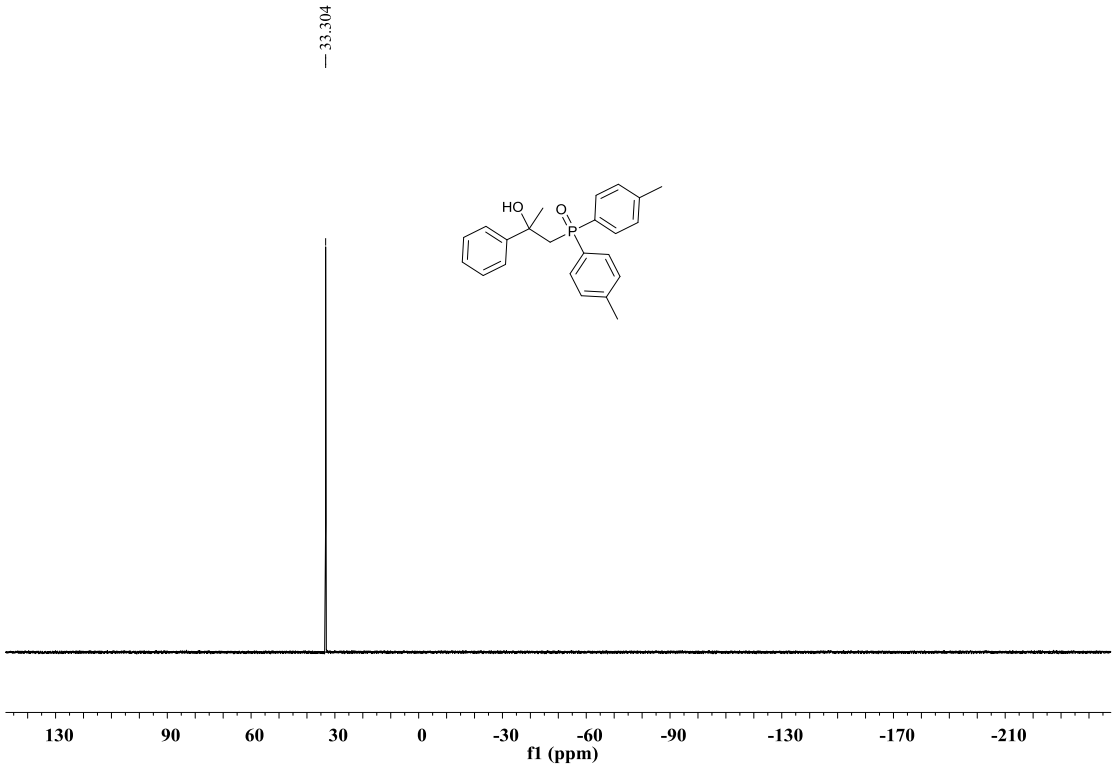

146.762
146.694
131.988
131.960
130.606
130.513
130.378
130.281
128.843
128.726
128.477
128.358
127.833
126.641
125.228
77.477
77.160
76.842
74.165
74.114
42.055
41.375
23.824
23.730
3.212
1.450
OH
O
PPh2
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


33.001
OH
O
PPh2
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

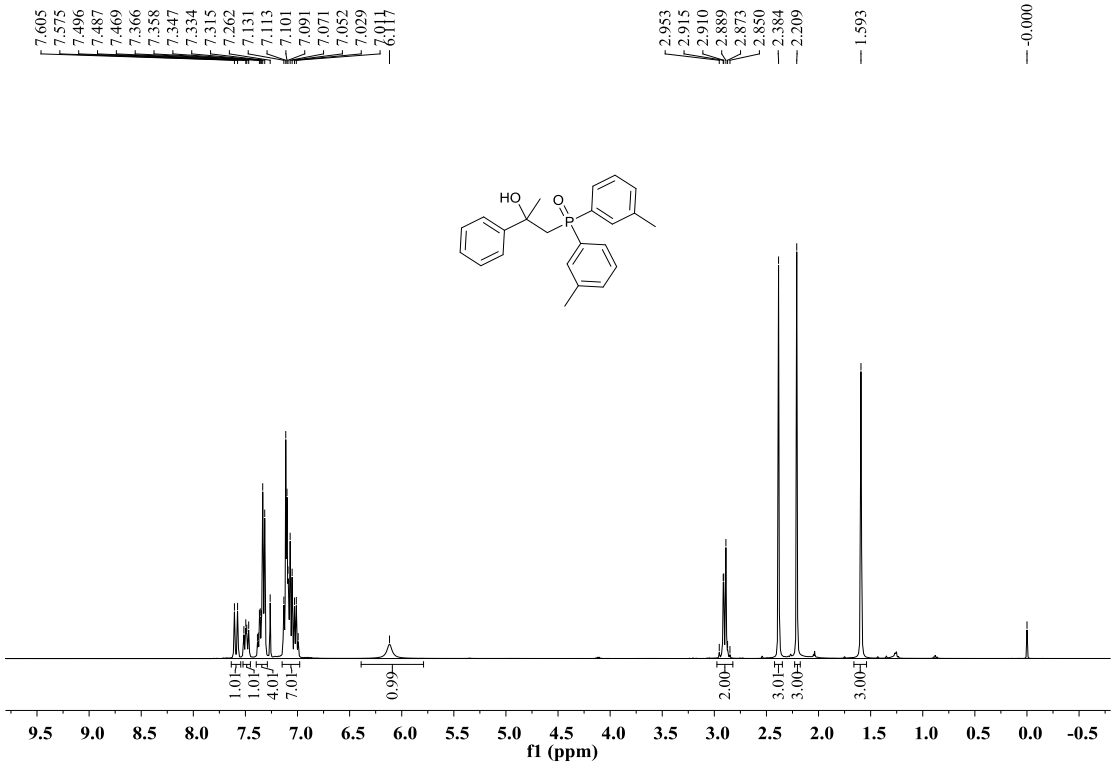
3ba

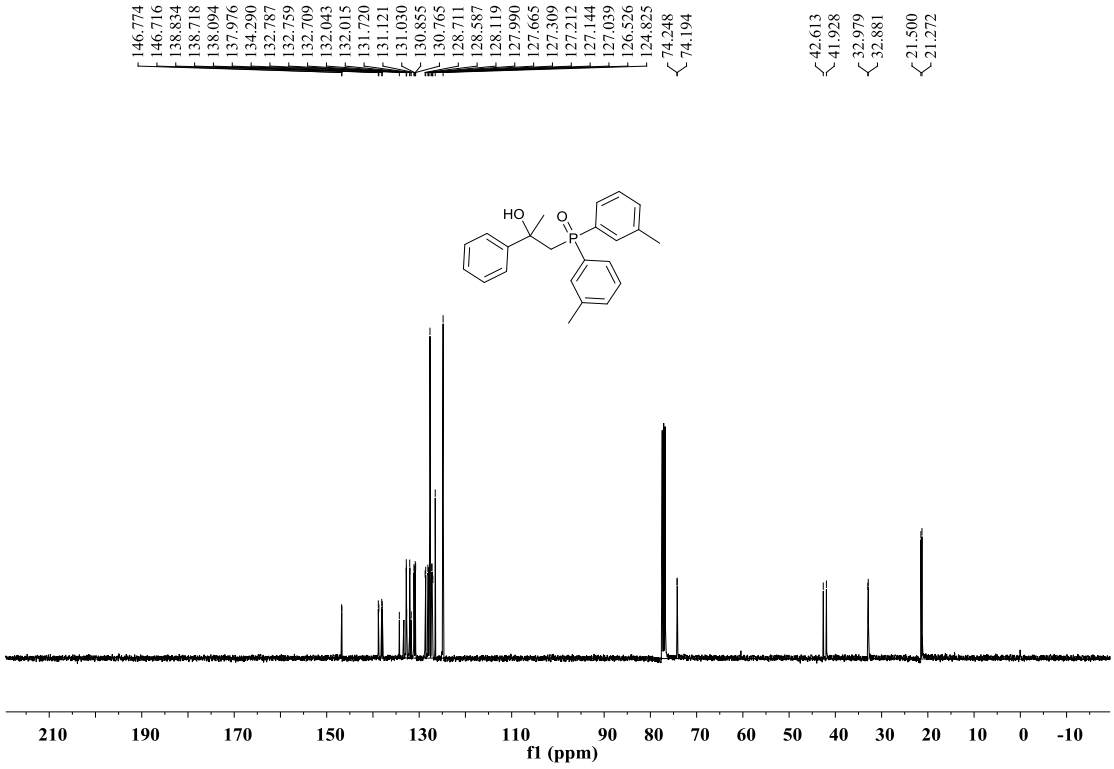

7.656
7.636
7.628
7.609
7.346
7.326
7.307
7.288
7.266
7.263
7.254
7.233
7.224
7.205
7.121
7.118
7.101
7.083
7.068
7.065
7.045
7.023
2.869
2.846
2.402
2.299
1.580
0.000
HO
O
P
2.01
4.01
2.01
5.00
1.01
1.99
3.00
3.01
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

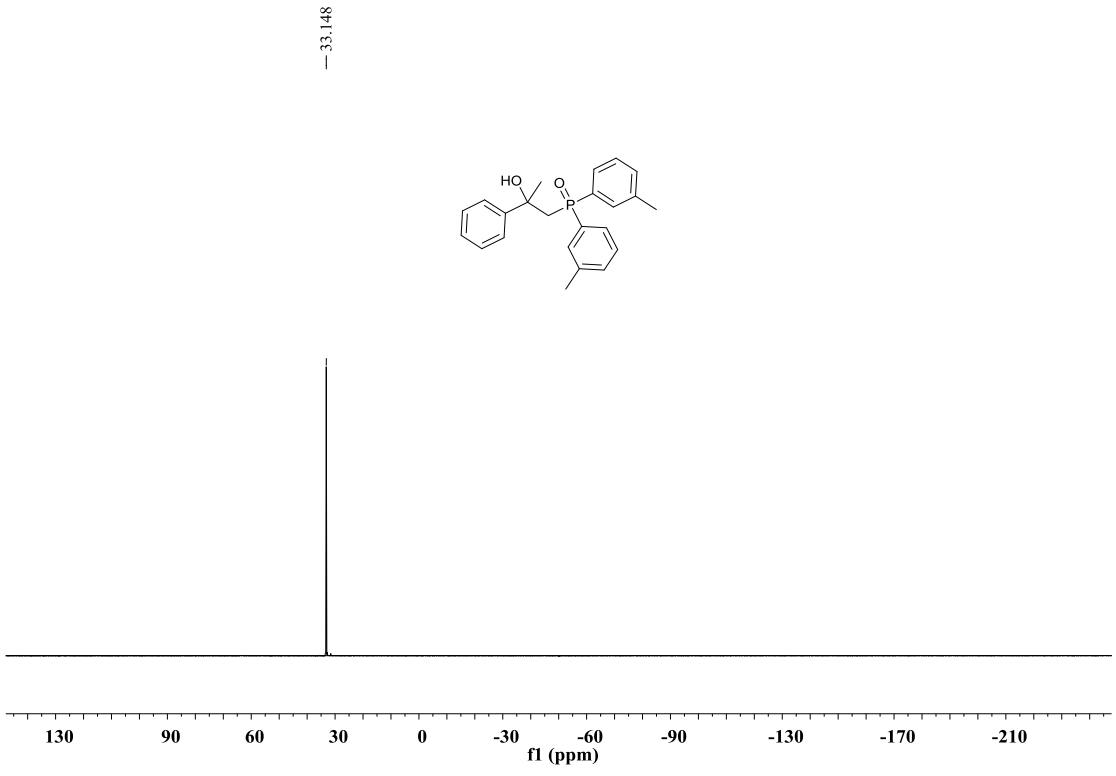

147.187
147.122
142.445
142.416
141.633
141.604
131.219
130.450
130.396
130.353
130.295
129.977
129.592
129.471
129.031
128.960
128.908
127.840
126.413
124.741
124.692
74.139
42.687
42.001
32.661
32.573
21.606
21.467
HO
O
P
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


33.304
HO
O
P
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

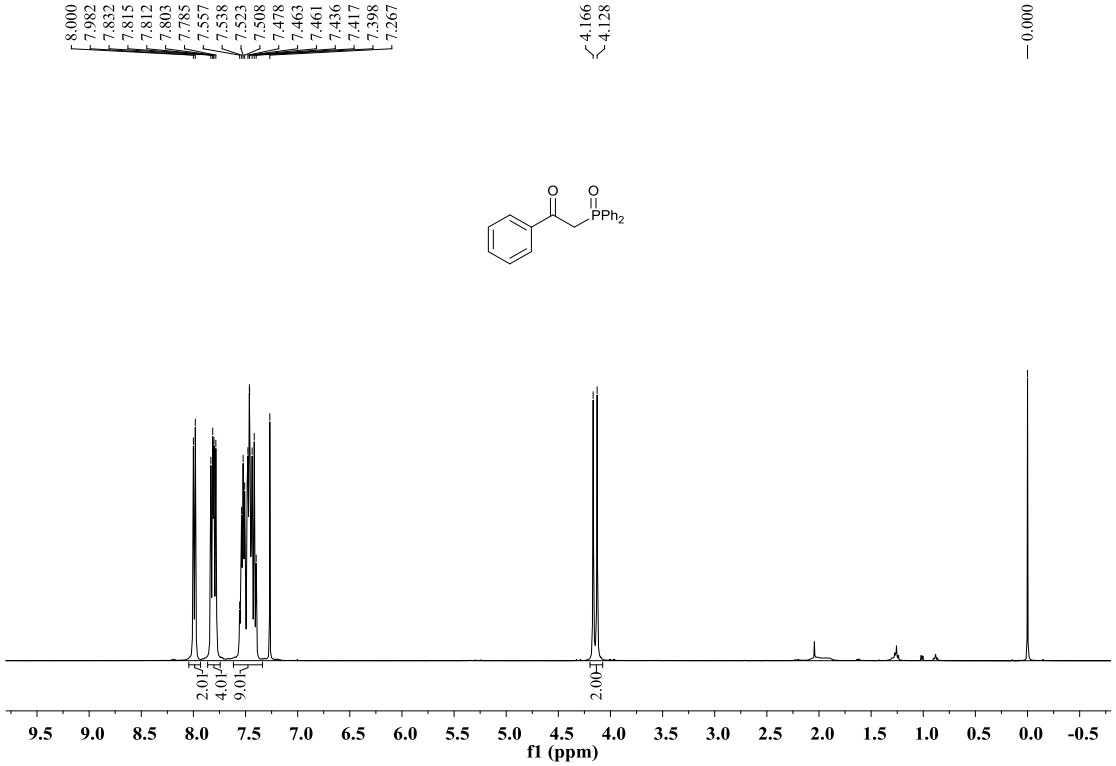
3ca

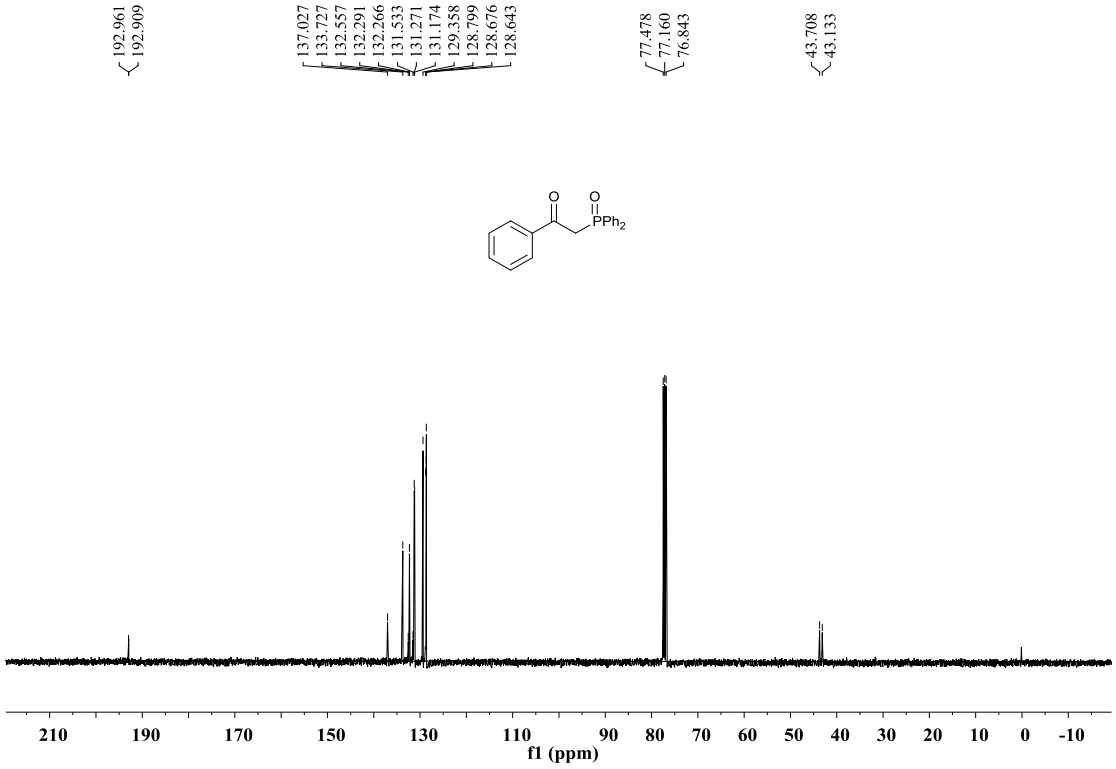

7.605
7.575
7.496
7.487
7.469
7.366
7.358
7.347
7.334
7.315
7.262
7.131
7.113
7.101
7.091
7.071
7.052
7.029
7.014
6.117
2.953
2.915
2.910
2.889
2.873
2.850
2.384
2.209
1.593
-0.000
HO
O
P
1.01
1.01
4.01
7.01
0.99
2.00
3.01
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

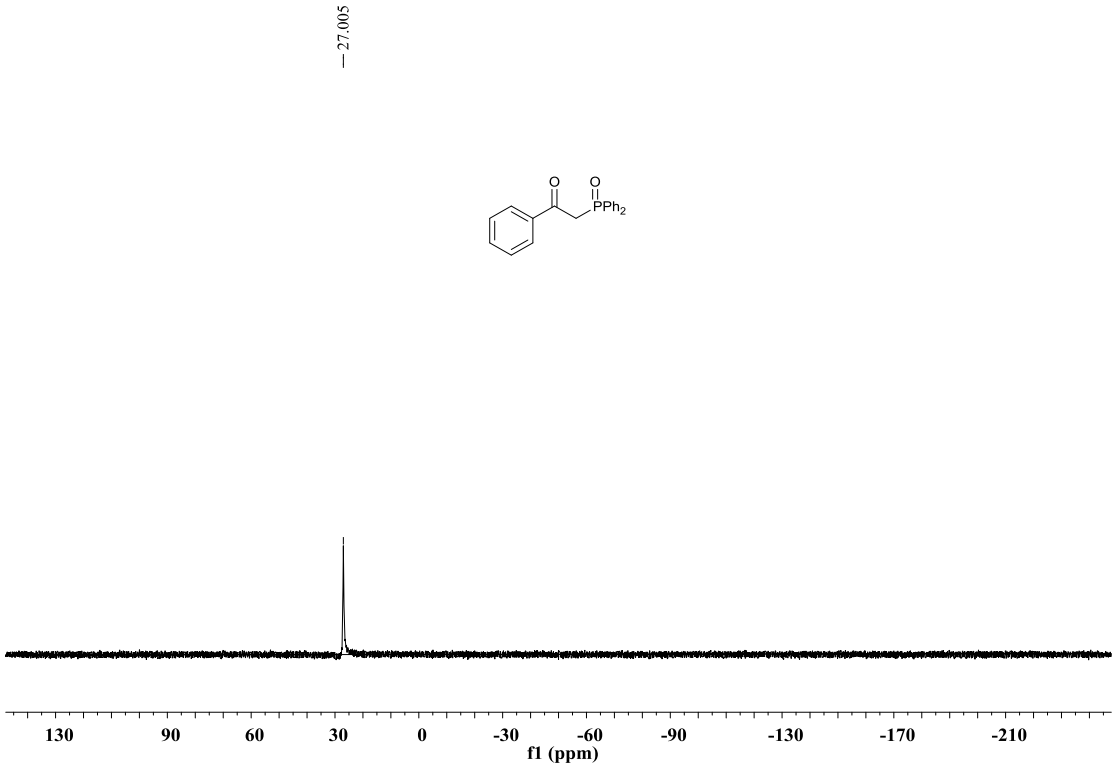

146.774
146.716
138.834
138.718
138.094
137.976
134.290
132.787
132.759
132.709
132.043
132.015
131.720
131.121
131.030
130.855
130.765
128.711
128.587
128.119
127.990
127.665
127.309
127.212
127.144
127.039
126.526
124.825
74.248
74.194
42.613
41.928
32.979
32.881
21.500
21.272
HO
O
P
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


33.148
HO
O
P
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

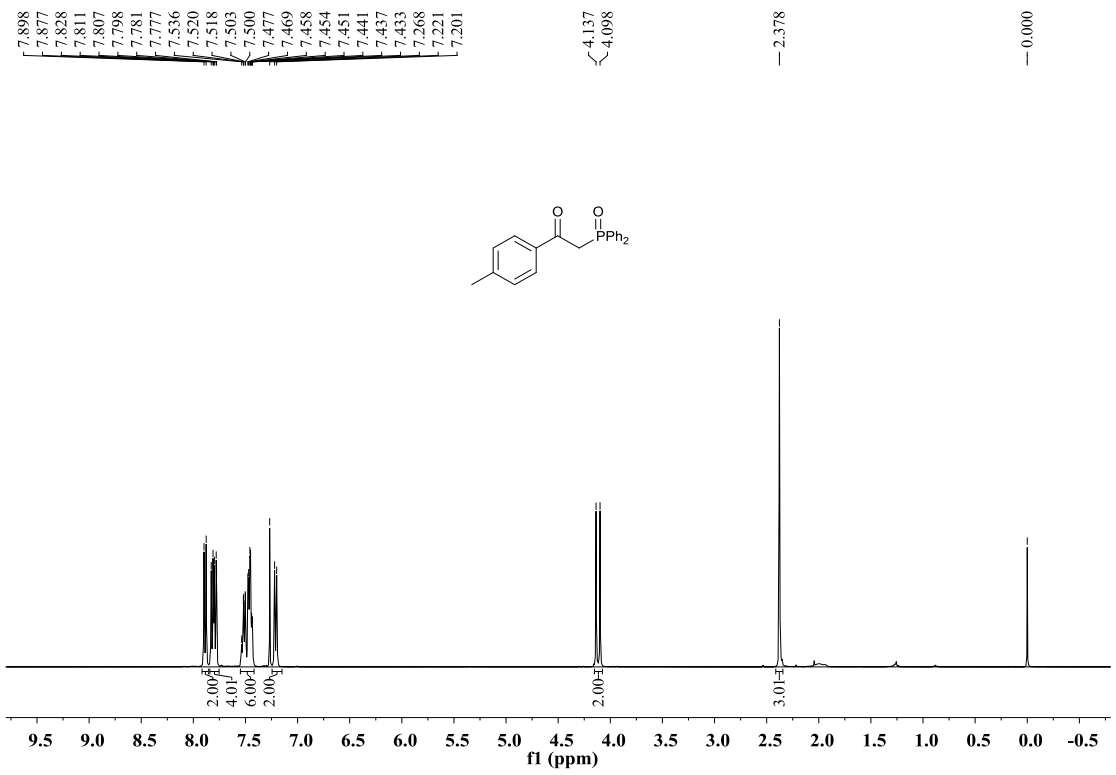
5aa

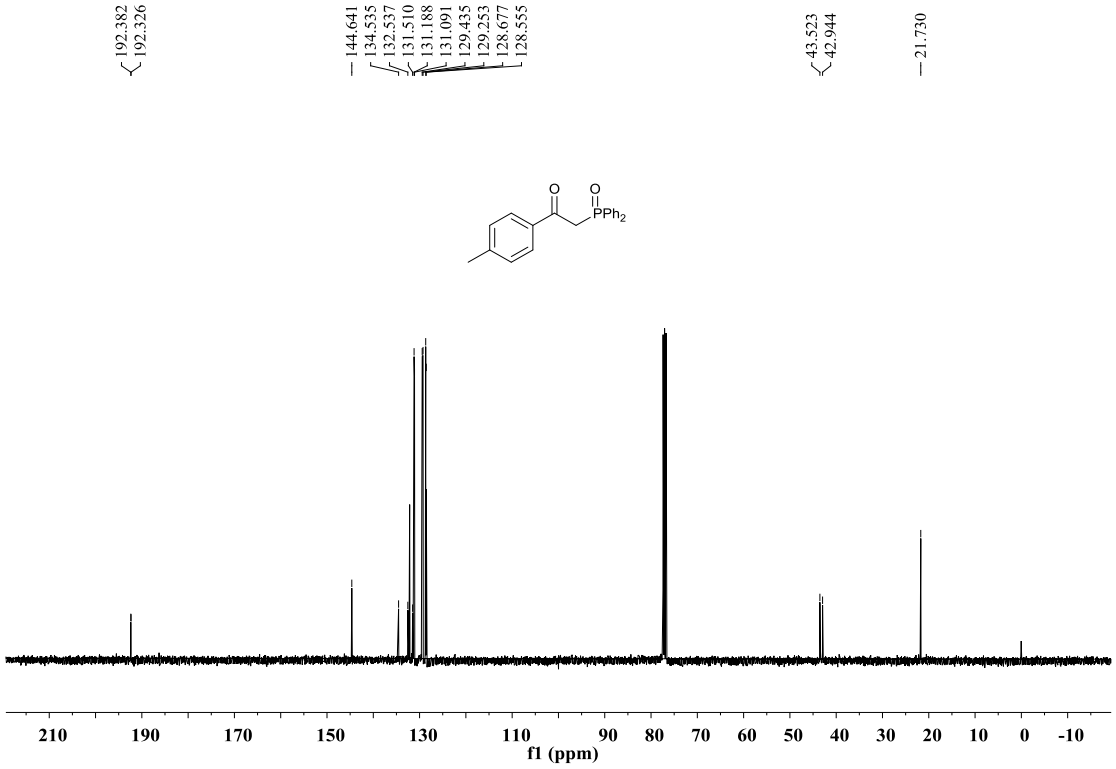

8.000
7.982
7.832
7.815
7.812
7.803
7.785
7.557
7.538
7.523
7.508
7.478
7.463
7.461
7.436
7.417
7.398
7.267
4.166
4.128
0.000
O
O
PPh2
2.01
4.01
9.01
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

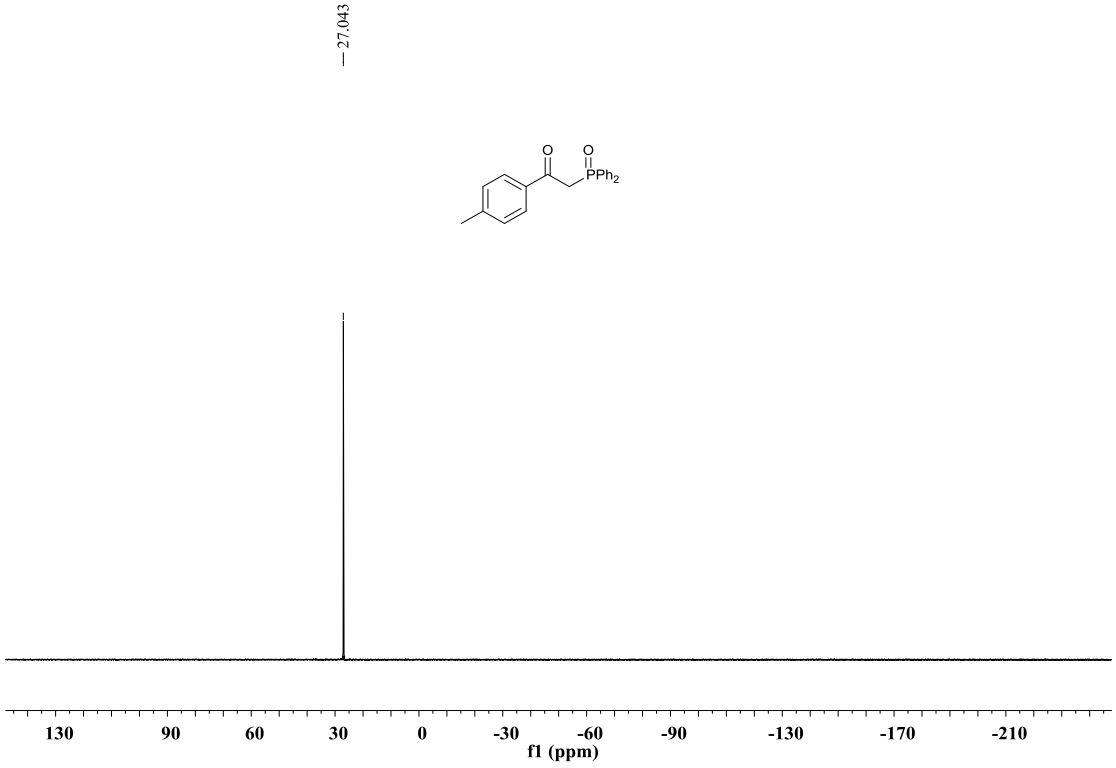

192.961
192.909
137.027
133.727
132.557
132.291
132.266
131.533
131.271
131.174
129.358
128.799
128.676
128.643
77.478
77.160
76.843
43.708
43.133
O
O
PPh2
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


27.005
O
O
PPh2
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

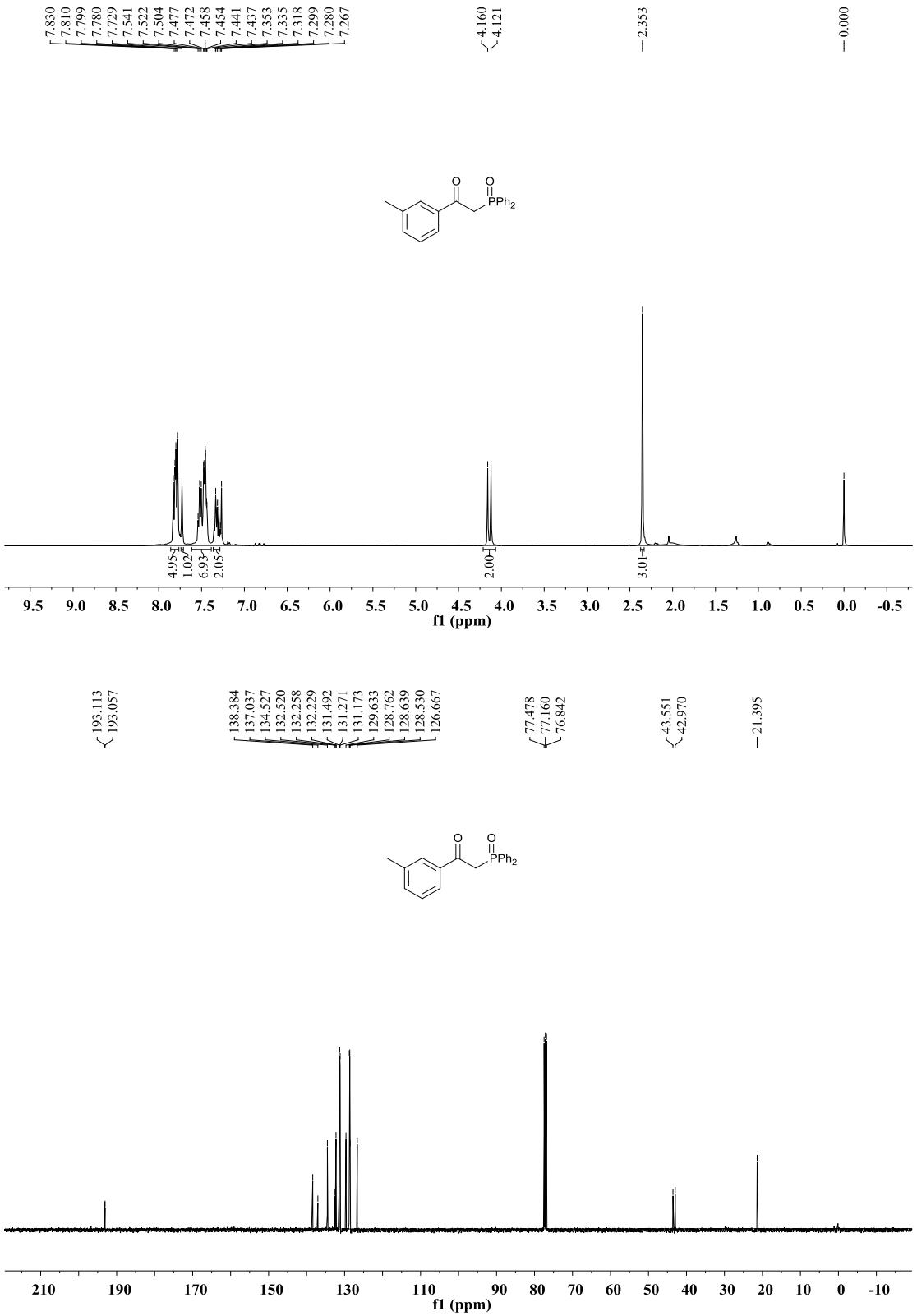
5ab

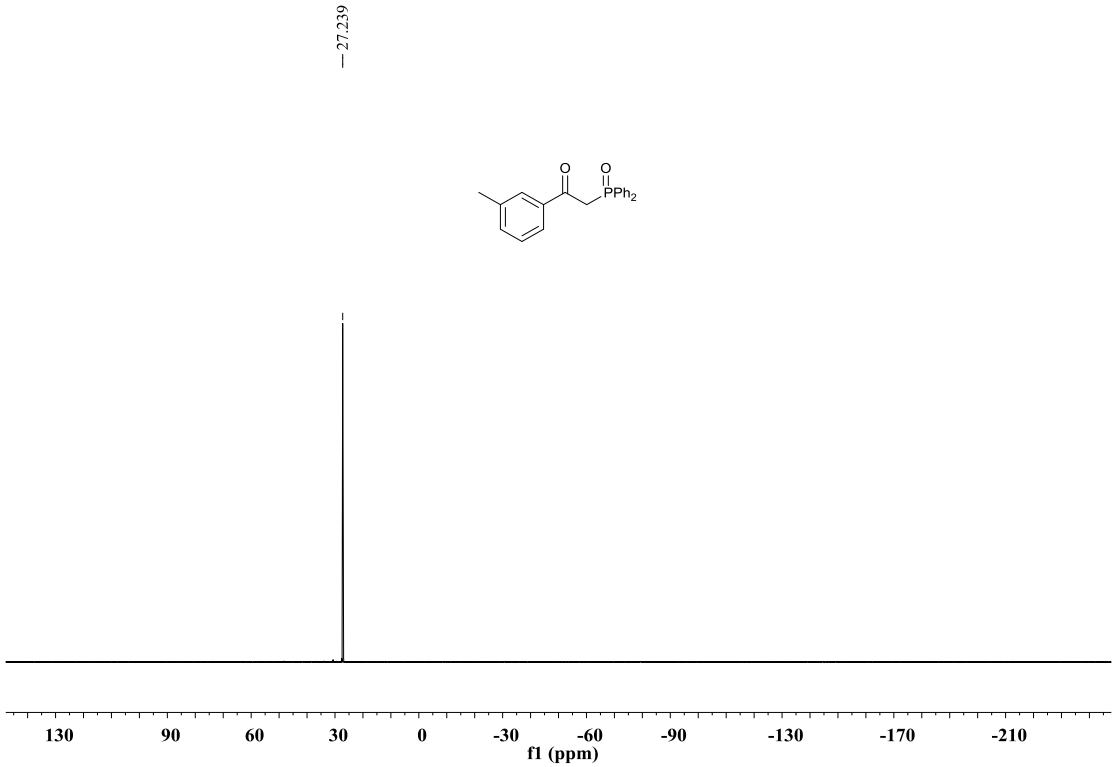

7.898
7.877
7.828
7.811
7.807
7.798
7.781
7.777
7.536
7.520
7.518
7.503
7.500
7.477
7.469
7.458
7.454
7.451
7.441
7.437
7.433
7.268
7.221
7.201
4.137
4.098
2.378
0.000
O
O
PPh2
2.00
4.01
6.00
2.00
2.00
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


192.382
192.326
144.641
134.535
132.537
131.510
131.188
131.091
129.435
129.253
128.677
128.555
43.523
42.944
21.730
O
O
PPh2
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

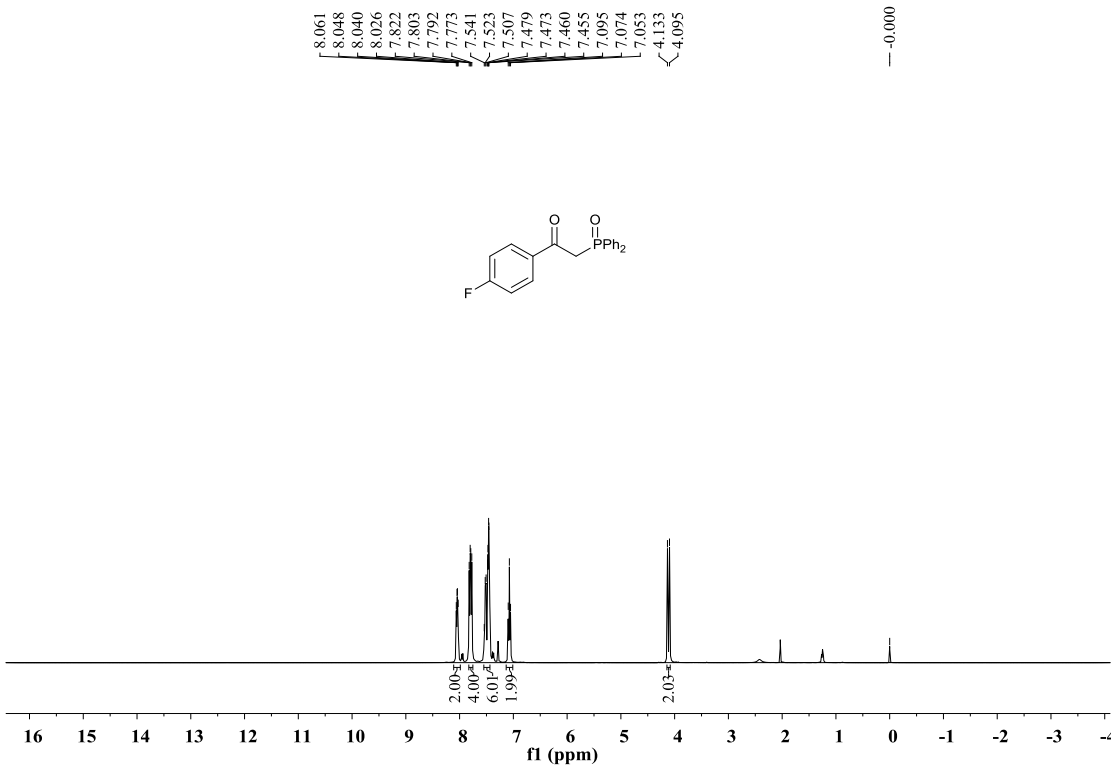

27.043
O
O
PPh2
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

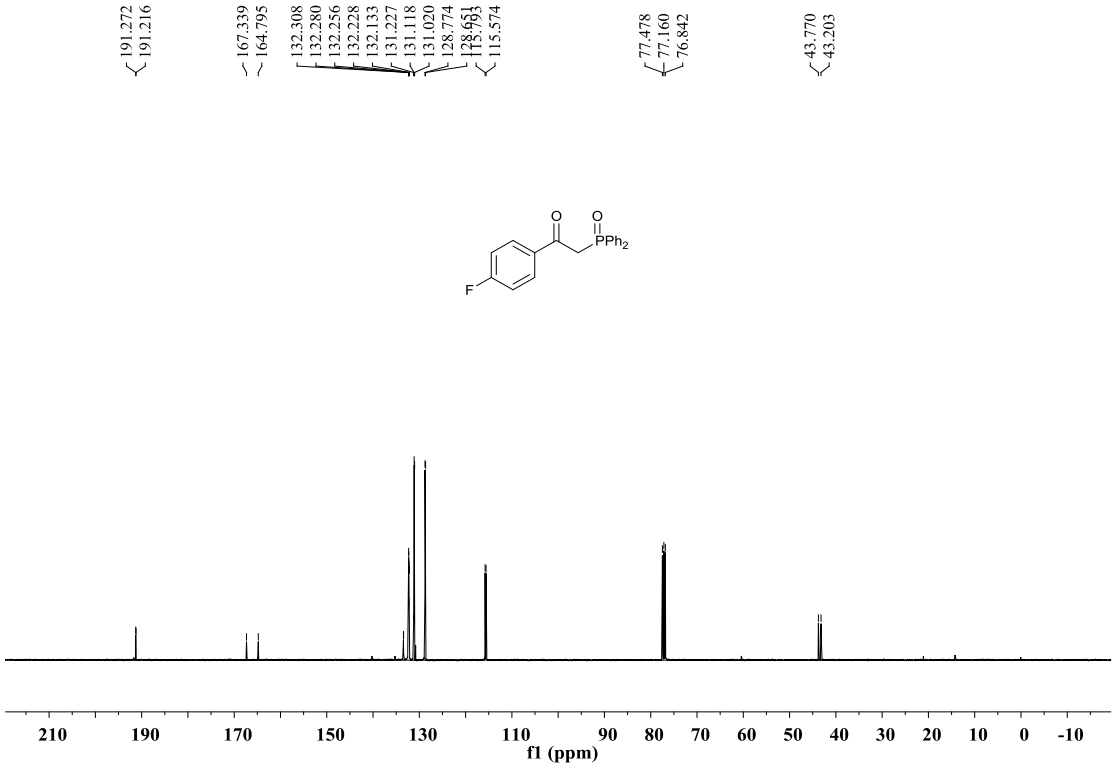
5ac

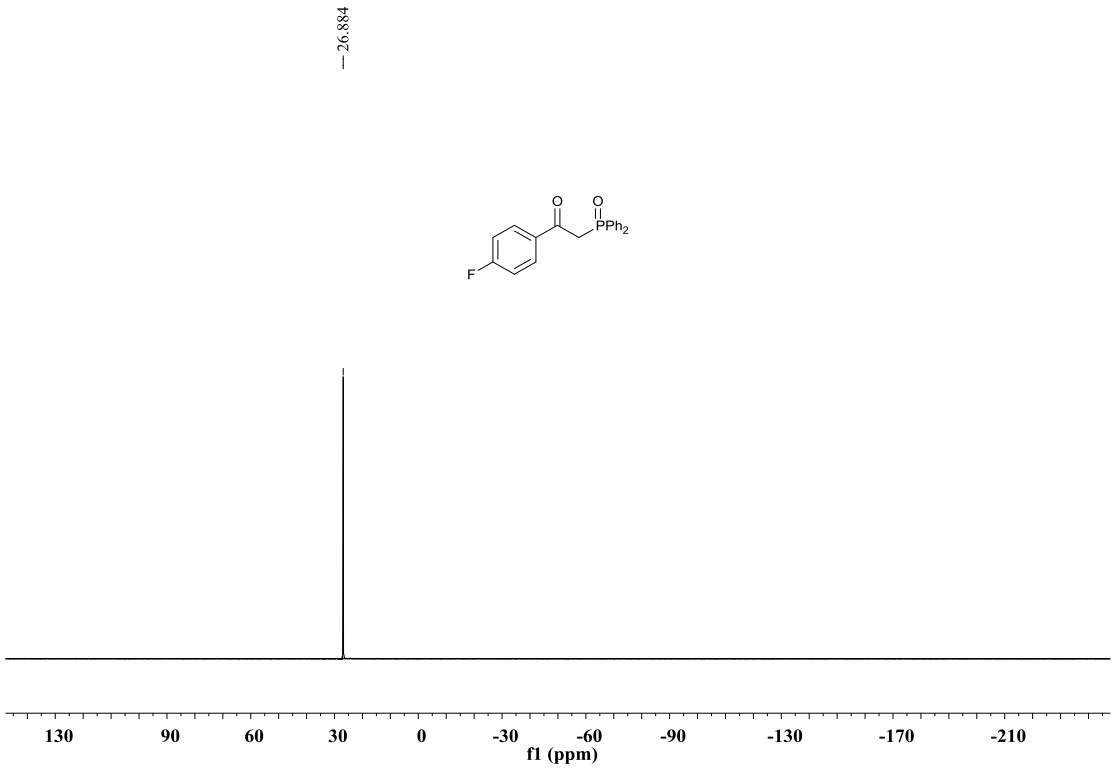

7.830
7.810
7.799
7.780
7.729
7.541
7.522
7.504
7.477
7.472
7.458
7.454
7.441
7.437
7.353
7.335
7.318
7.299
7.280
7.267
4.160
4.121
2.353
0.000
O
O
PPh2
4.95
1.02
6.93
2.05
2.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
193.113
193.057
138.384
137.037
134.527
132.520
132.258
132.229
131.492
131.271
131.173
129.633
128.762
128.639
128.530
126.667
77.478
77.160
76.842
43.551
42.970
21.395
O
O
PPh2
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


27.239
O
O
PPh2
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

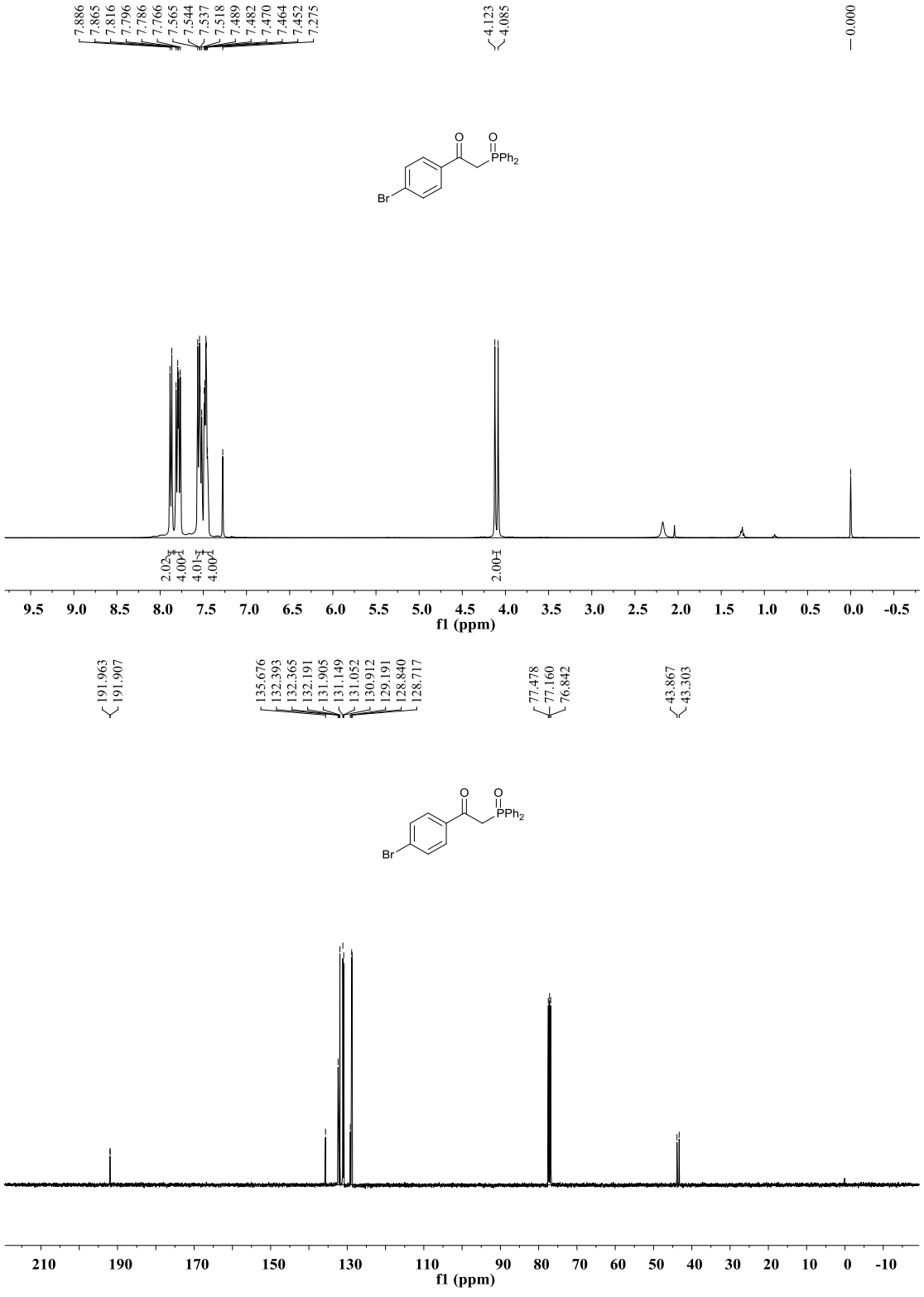
5ad

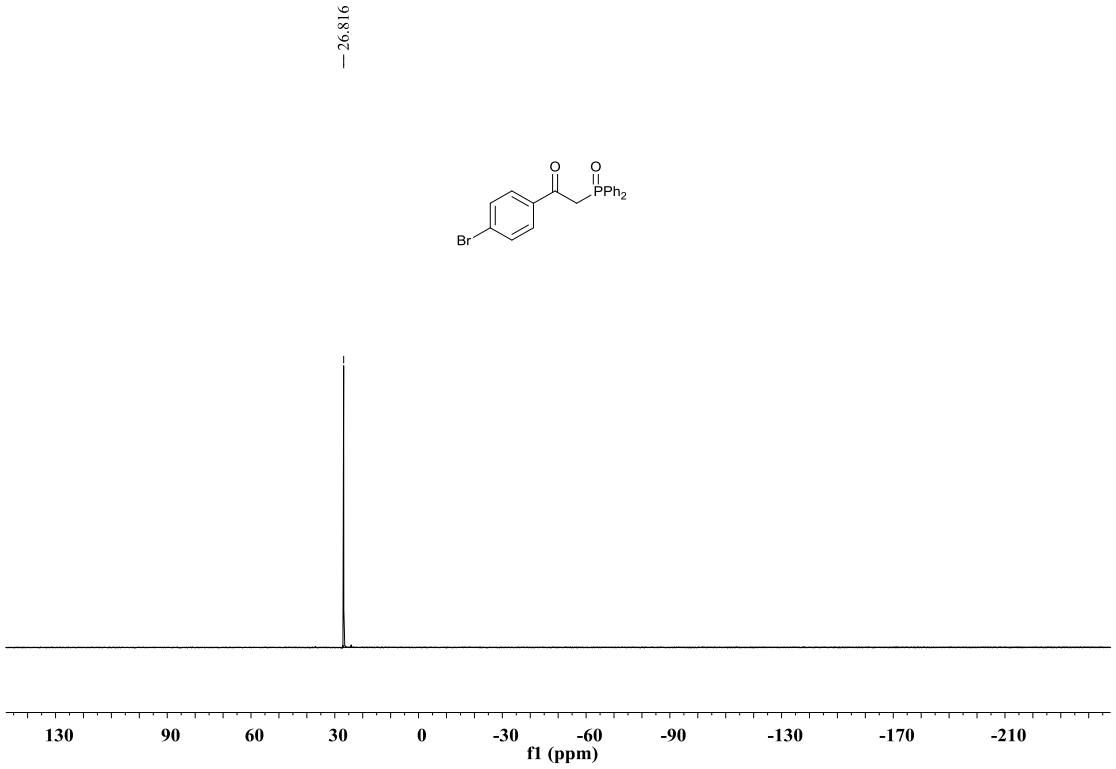

8.061
8.048
8.040
8.026
7.822
7.803
7.792
7.773
7.541
7.523
7.507
7.479
7.473
7.460
7.455
7.095
7.074
7.053
4.133
4.095
-0.000
O
O
PPh2
F
2.00
4.00
6.01
1.99
2.03
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


191.272
191.216
167.339
164.795
132.308
132.280
132.256
132.228
132.133
131.227
131.118
131.020
128.774
128.681
128.593
115.793
115.574
77.478
77.160
76.842
43.770
43.203
O
O
PPh2
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


26.884
O
O
PPh2
F
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

5ae


7.886
7.865
7.816
7.796
7.786
7.766
7.565
7.544
7.537
7.518
7.489
7.482
7.470
7.464
7.452
7.275
4.123
4.085
0.000
O
O
PPh2
Br
2.02
4.00
4.01
4.00
2.00
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)
191.963
191.907
135.676
132.393
132.365
132.191
131.905
131.149
131.052
130.912
129.191
128.840
128.717
77.478
77.160
76.842
43.867
43.303
O
O
PPh2
Br
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


26.816
O
O
PPh2
Br
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)