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# Methyltrioxorhenium-Catalyzed Highly Selective Dihydroxylation of 1,2-Allenylic Diphenyl Phosphine Oxides

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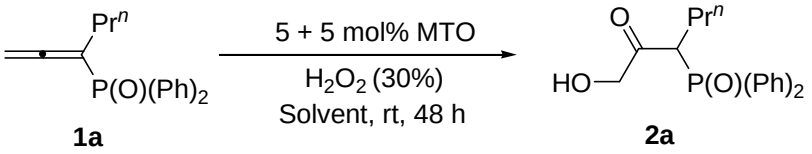
## Electronic Supplementary Information

**Optimization of the reaction conditions**

To explore the reactivity of MTO-catalyzed dihydroxylation of allenes, 1,2-allenylic diphenyl phosphine oxide **1a** was chosen as model substrate for reaction condition optimization (Table S1). Firstly, 10 mol% of MTO was used. After full consumption of **1a**, β-carbonyl-γ-hydroxyl diphenyl phosphine oxide **2a** was formed in 54% isolated yield (entry 1, Table S1). After several attempts, it was found that the reaction yield can be significantly improved if 10 mol % of MTO is added separately in two portions to the system. When 5 mol% of MTO is added into the reaction mixture at the beginning, and an additional 5 mol% of MTO are added after 24 hours, the isolated yield of **2a** can reach up to 83% (entry 2, Table S1).Then we tried to reduce the amount of the catalyst. However, when 1 + 1 mol% MTO was applied, **2a** was not formed (entry 3, Table S1). These observations might be due to the decomposition of MTO in this reaction system. Thus, 5 + 5 mol % of MTO was added separately in the further studies. The solvent effect was also examined. It was found that the reactions only proceed in biphasic systems, as in the cases of $CH_2Cl_2$ and toluene (entries 2 and 4, Table S1), forming solvent/$H_2O_2$ systems. Reactions in other solvents did not proceed at all (entries 5-8, Table S1). Despite the solutions turned yellow after adding $H_2O_2$ (indicating the formation of the well documented orange-yellow active peroxo species),[1] the color turned white after a few hours of the reaction, indicating catalyst decomposition to colorless perrhenate. Moreover, carrying out the reaction under reflux conditions also leads to the decomposition of MTO (entry 9,Table S1), as a similar color change is observed. Finally, different amounts of $H_2O_2$ were applied to the reaction system. However, no better results were observed with either decreased or increased amounts of $H_2O_2$ (entries10-12, Table S1). Thus, condition A (5 + 5 mol% of MTO, 2 equiv. of$H_2O_2$ (30%), $CH_2Cl_2$, rt) was applied.

**Table S1. Optimization of the reaction conditions.**[a]

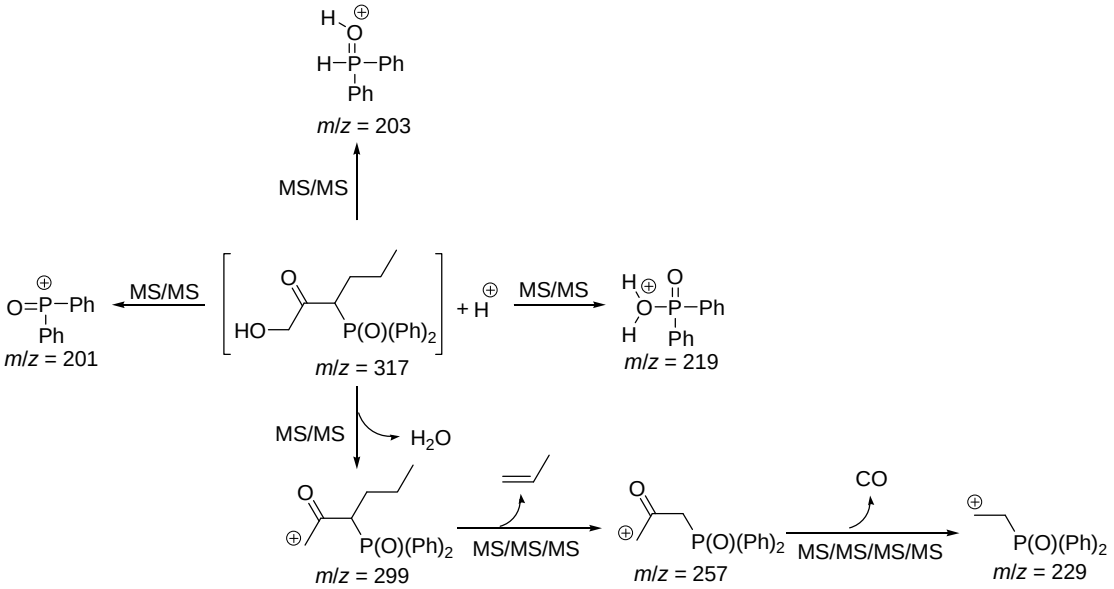



**1a** **2a**

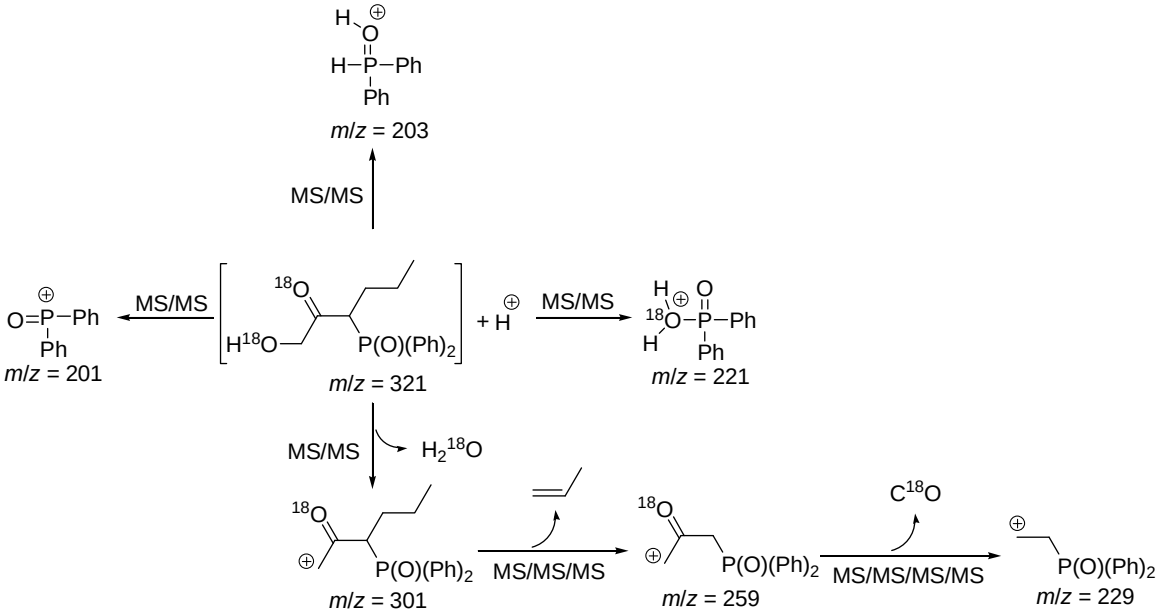
| Entry | Solvent | $H_2O_2$ (equiv.) | Isolated yield of **2a** (%) |
|---|---|---|---|
| 1[b] | $CH_2Cl_2$ | 2 | 54[c] |
| 2 | $CH_2Cl_2$ | 2 | 83 |
| 3[d] | $CH_2Cl_2$ | 2 | 0 (95)[e] |
| 4 | toluene | 2 | 45 (27)[e] |
| 5 | $CH_3CN$ | 2 | 0 (90)[e] |
| 6 | THF | 2 | 0 (93)[e] |
| 7 | EtOH | 2 | 0 (93)[e] |
| 8 | acetone | 2 | 0 (86)[e] |
| 9[f] | $CH_2Cl_2$ | 2 | 0 (75)[e] |
| 10 | $CH_2Cl_2$ | 1 | 68 |
| 11 | $CH_2Cl_2$ | 3 | 76 |
| 12 | $CH_2Cl_2$ | 8 | 67 |

[a] The reaction was carried out using **1a** (0.25 mmol), MTO (0.0125 + 0.0125 mmol), and $H_2O_2$ (30%) in solvent (850 μL) at rt. [b] MTO (0.025 mmol) was added to the reaction mixture at the beginning. [c] Unidentified by-products were formed. [d] MTO (0.0025 + 0.0025 mmol) was applied. [e] Recovered yield of **1a**. [f] The reaction was carried out under reflux conditions.

## Schemes




**Scheme S1** The fragmentation way from the $[M+H]^+$ ion of **2a** at *m*/*z* = 317.




**Scheme S2** The fragmentation way from the $[M+H]^+$ ion of **2a*** at *m*/z = 321.

## Experimental Section

### General experimental methods:

$^{1}H$ (400 MHz), $^{13}C$ (100 MHz) and $^{31}P$ (162 MHz) NMR spectra of samples in $CDCl_3$ were recorded on an AVANCE III 400 spectrometer. IR spectra were recorded on a Avatar 360 FT-IR spectrometer. HRMS (ESI) determinations were carried out on a Bruker Daltonics micr OTOF II spectrometer. Melting points were determined on a WRS-2 apparatus. The enantiomeric excesses (*ee*) were determined by HPLC (Infinity. LC 1220) analysis with chiral column (Chiralcel AD-H, *n*-Hexane : *i*-PrOH = 9 : 1, 0.6 mL/min, 230 nm). Specific rotations were determined on a P-1020 apparatus. Compounds**1a**[2], **1b**[2], **1c**[2], **1d**[3], **1e**[2], (*R*)-**1e**[2], (*S*)-**1e**[2], **1g**[2], and **1h**[3]were prepared according to literature procedures.

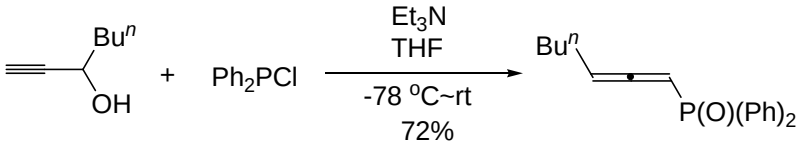
The ESI-MS experiments for the mechanistic study were performed in positive ion mode on a Thermo Finnigan LCQ-Classic mass spectrometer. The basic ESI conditions were: convectron vacuum, 1.31 torr, ion vacuum, $1.93\times10^{-5}$ torr; sheath gas flow rate, 69.1; aux/sweep gas flow rate, 7; ISpray voltage, 4.25 KV; capillary voltage, 44.00 V; capillary temperature, 200 °C; Tube lens, 20 V. In tandem mass spectrometry experiments, the precursor ions of interest were isolated with an isolation width of *m/z* = 1.4 and then collided with helium gas. The normalized collision energy was 25% to 35%. The spectra are collected from 55 to 600 *m/z* at an acquisition rate of 1-2 s per scan. **2a** (10 mg) was dissolved in acetonitrile (200 mL). The samples were injected at a flow rate of $0.55mL\cdot min^{-1}$ of 80 % acetonitrile + 0.1% HCOOH for the MS detection under the basic conditions. In tandem mass spectrometry experiments, the precursor ion of the interest was isolated by the selection ion mode, then the isolated ion was collided by helium gas to give the ESI-$MS^2$, $MS^3$ and $MS^4$ spectra.

The high resolution mass spectrometrys were studied by LC-ESI-MS on a Thermo Finnigan LTQ FT-ICR and were eluted by a Dionex Ultimate 3000. The chromatographic eluent was 1:10 (110 μL / min) introduced into the ion source. The basic ESI conditions were: convectron vacuum, 1.06 torr, ion vacuum, $0.63\times10^{-5}$ torr; sheath gas flow rate, 60; aux/sweep gas flow rate, 10; ISpray voltage, 4.00 KV;

capillary voltage, 48.00 V; capillary temperature, 275 °C; Tube lens, 60 V. In tandem mass spectrometry experiments, the precursor ions of interest were isolated with an isolation width of *m/z* 1.0 and then collided with helium gas. The normalized collision energy was 25% to 35%. The spectra are collected from 55 to 600 *m/z* at an acquisition rate of 1-2 s per scan. **2a** (10 mg) was dissolved in acetonitrile (200 mL).The samples were injected at a flow rate of 1.1 mL·min$^{-1}$ of 80 % acetonitrile + 0.1% HCOOH for the MS detection under the basic conditions. In tandem mass spectrometry experiments, the precursor ion of the interest was isolated by the selection ion mode, then the isolated ion was collided by helium gas to give the ESI-$MS^2$ spectra.

**Typical Procedure I**

**Synthesis of (hepta-1,2-dien-1-yl)diphenylphosphine oxide (1f)**



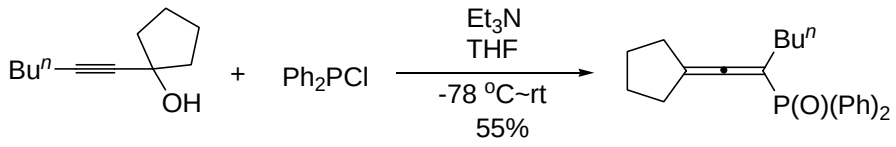

**1f**

A solution of hept-1-yn-3-ol (650 μL, 5.0 mmol) and $Et_3N$ (1.1 mL, 7.9 mmol) in anhydrous THF (15 mL) was added $Ph_2PCl$ (1.4 mL, 7.7 mmol) dropwise at -78 °C. After the addition, the cooling bath was removed, and the reaction mixture was allowed to warm up to room temperature naturally. After complete conversion of the corresponding propargylic alcohol as monitored by TLC (eluent: petroleum ether/ethyl acetate = 1/1), the mixture was filtered off. Evaporation of the solvent and flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1→3/1→2/1) afforded **1f** as a liquid (1.076 g, 72%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79-7.71 (m, 4 H), 7.51-7.39 (m, 6 H), 5.83-5.78 (m, 1 H), 5.29-5.19 (m, 1 H), 1.95-1.84 (m, 2 H), 1.18-1.12 (m, 4 H), 0.80 (t, $J$ = 6.8 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 211.1, 132.3 (d, $J_{PC}$ = 106.1 Hz), 132.2 (d, $J_{PC}$ = 106.1 Hz), 131.33 (d, $J_{PC}$ = 1.4 Hz), 131.30 (d, $J_{PC}$ = 1.4 Hz), 131.0, 130.9, 127.9 (d, $J_{PC}$ = 1.4 Hz), 127.8 (d, $J_{PC}$ = 1.4 Hz), 92.4 (d, $J_{PC}$ = 13.4 Hz), 84.8 (d, $J_{PC}$ = 105.4 Hz), 30.4 (d, $J_{PC}$ = 3.5 Hz), 26.4 (d, $J_{PC}$ = 5.0 Hz), 21.5, 13.3; $^{31}$P NMR (162 MHz, $CDCl_3$) δ 31.0; IR (neat) 1950,

1592, 1485, 1468, 1439 $cm^{-1}$; HRMS (ESI) calcd for $C_{19}H_{22}OP$ ($M + H^+$) 297.1403, found 297.1407.

**The following compound was synthesized according to Typical Procedure I**.

**(1) (1-Cyclopentylidenehex-1-en-2-yl)diphenylphosphine oxide (1i)**

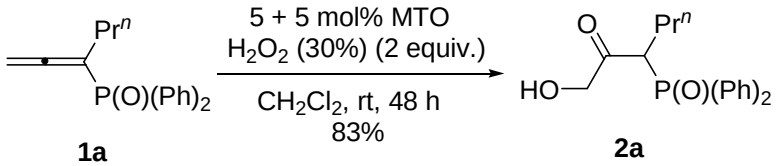



**1i**

The reaction of 1-(hex-1-yn-1-yl)cyclopentanol (831 mg, 5.0 mmol), $Et_3N$ (1.1 mL, 7.9 mmol), and $Ph_2PCl$ (1.7 mL, 9.5 mmol) in anhydrous THF (15 mL) afforded **1i** as a liquid (0.964, 55%); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.74-7.66 (m, 4 H), 7.50-7.39 (m, 6 H), 2.35-2.18 (m, 4 H), 1.95-1.84 (m, 2 H), 1.53-1.44 (m, 4 H), 1.35-1.26 (m, 4 H), 0.85 (t, $J$ = 7.2 Hz, 3 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 203.2 (d, $J_{PC}$ = 7.1 Hz), 132.6 (d, $J_{PC}$ = 102.6 Hz), 131.5 (d, $J_{PC}$ = 9.1 Hz), 131.3 (d, $J_{PC}$ = 2.8 Hz), 128.0 (d, $J_{PC}$ = 12.0 Hz), 106.7 (d, $J_{PC}$ = 15.5 Hz), 98.6 (d, $J_{PC}$ = 102.6 Hz), 30.6 (d, $J_{PC}$ = 5.6 Hz), 30.5 (d, $J_{PC}$ = 5.6 Hz), 27.2 (d, $J_{PC}$ = 7.8 Hz), 26.7, 25.6, 22.1, 21.1, 13.8; $^{31}P$ NMR (162 MHz, $CDCl_3$) δ 30.0; IR (neat) 1945, 1464, 1433, 1378 $cm^{-1}$; HRMS (ESI) calcd for $C_{23}H_{28}OP$ ($M + H^+$) 351.1872, found 351.1878.

**Typical Procedure II for the reaction under Condition A.**

**Synthesis of 3-(diphenylphosphoryl)-1-hydroxyhexan-2-one (2a)**



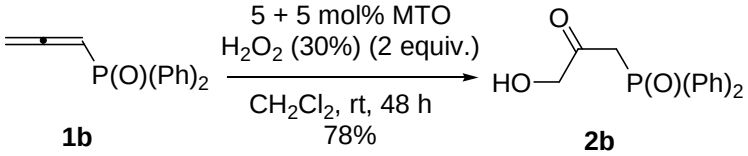

**1a** **2a**

A solution of **1a** (70 mg, 0.25 mmol), MTO (3 mg, 0.0125 mmol) and $H_2O_2$ (30%) (50 μL, 0.5 mmol) in $CH_2Cl_2$ (850 μL) was stirred at rt for 24 hours. Then MTO (3 mg, 0.0125 mmol) was added into the reaction mixture again. The resulted mixture was stirred at rt for another 24 hours. When the reaction was completed, as monitored by TLC (eluent: ethyl acetate), the solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1→2/1→1/1→ethyl acetate) toafforded **2a** as a solid (65 mg, 83%); mp 122-123 °C

(ethyl acetate / petroleum ether); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.82-7.68 (m, 4 H), 7.62-7.47 (m, 6 H), 4.57 (brs, 1 H), 4.30-4.10 (m, 3 H), 2.17-2.04 (m, 1 H), 1.57-1.45 (m, 1 H), 1.35-1.12 (m, 2 H), 0.82 (t, $J$ = 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 207.9 (d, $J_{PC}$ = 2.8 Hz), 132.61 (d, $J_{PC}$ = 2.8 Hz), 132.58 (d, $J_{PC}$ = 2.8 Hz), 131.6 (d, $J_{PC}$ = 9.2 Hz), 131.1 (d, $J_{PC}$ = 9.1 Hz), 130.5 (d, $J_{PC}$ = 100.5 Hz), 128.92 (d, $J_{PC}$ = 99.8 Hz), 128.89 (d, $J_{PC}$ = 12.0 Hz), 128.6 (d, $J_{PC}$ = 11.9 Hz), 69.9, 52.4 (d, $J_{PC}$ = 54.9 Hz), 28.0 (d, $J_{PC}$ = 2.1 Hz), 22.0 (d, $J_{PC}$ = 12.6 Hz), 13.6; $^{31}$P NMR (162 MHz, $CDCl_3$) δ 32.8; IR (neat) 3281, 1717, 1595, 1485, 1461, 1436 cm$^{-1}$, HRMS (ESI) calcd for $C_{18}H_{22}O_3P$ ($M + H^+$) 317.1301, found 317.1308.

**The following compound was prepared according to Typical Procedure II**.

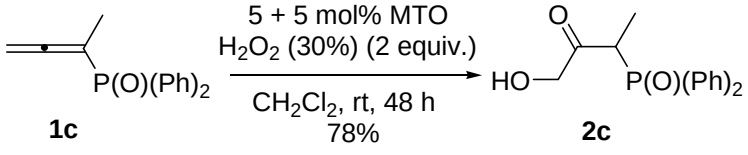
**(1) 1-(Diphenylphosphoryl)-3-hydroxypropan-2-one (2b)**




**1b** **2b**

The reaction of **1b** (60 mg, 0.25 mmol), MTO (3 + 3 mg, 0.0125 + 0.0125 mmol) and $H_2O_2$ (30%) (50 μL, 0.5 mmol) in $CH_2Cl_2$ (850 μL) afforded **2b** as a solid (54 mg, 78%); mp 94-95 $^{o}$C (ethyl acetate / petroleum ether); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.78-7.71 (m, 4 H), 7.62-7.49 (m, 6 H), 4.85 (t, $J$ = 6.8 Hz, 1 H), 4.23 (d, $J$ = 6.8 Hz, 2 H), 3.83 (d, $J$ = 14.8 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 205.1 (d, $J_{PC}$ = 5.6 Hz), 132.7 (d, $J_{PC}$ = 3.5 Hz), 130.79 (d, $J_{PC}$ = 9.8 Hz),130.78 (d, $J_{PC}$ = 104.0 Hz), 128.9 (d, $J_{PC}$ = 11.9 Hz), 69.7, 44.0 (d, $J_{PC}$ = 54.8 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) δ 29.5; IR (neat) 3378, 1703, 1601, 1583, 1493, 1443 cm$^{-1}$; HRMS (ESI) calcd for $C_{15}H_{16}O_3P$ ($M + H^+$) 275.0832, found 275.0847.

**(2) 3-(Diphenylphosphoryl)-1-hydroxybutan-2-one (2c)**

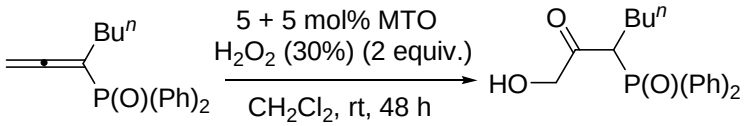



**1c** **2c**

The reaction of **1c** (64 mg, 0.25 mmol), MTO (3 + 3 mg, 0.0125 + 0.0125 mmol) and $H_2O_2$ (30%) (50 μL, 0.5 mmol) in $CH_2Cl_2$ (850 μL) afforded **2c** as a solid (57 mg, 78%); mp 99-100 $^{o}$C (ethyl acetate / petroleum ether); $^{1}$H NMR (400 MHz, $CDCl_3$) δ

7.82-7.67 (m, 4 H), 7.62-7.47 (m, 6 H), 4.33-4.17 (m, 3 H), 1.32 (dd, $J$ = 16.4, 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 208.4 (d, $J_{PC}$ = 1.4 Hz), 132.72 (d, $J_{PC}$ = 2.1 Hz), 132.70 (d, $J_{PC}$ = 2.1 Hz), 131.8 (d, $J_{PC}$ = 9.1 Hz), 131.3 (d, $J_{PC}$ = 9.8 Hz), 131.2 (d, $J_{PC}$ = 106.1 Hz), 129.1 (d, $J_{PC}$ = 105.4 Hz), 128.9 (d, $J_{PC}$ = 11.9 Hz), 128.7 (d, $J_{PC}$ = 11.9 Hz), 69.3, 46.1 (d, $J_{PC}$ = 55.5 Hz), 10.8 (d, $J_{PC}$ = 2.8 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) δ 34.8; IR (neat) 3297, 1706, 1588, 1480, 1465, 1435 cm$^{-1}$; HRMS (ESI) calcd for $C_{16}H_{18}O_3P$ (M + H$^+$) 289.0988, found 289.0989.

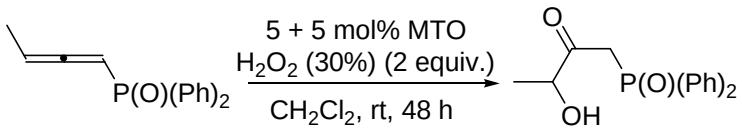
**(3) 3-(Diphenylphosphoryl)-1-hydroxyheptan-2-one (2d)**




**1d** **2d**

The reaction of **1d** (74 mg, 0.25 mmol), MTO (3 + 3 mg, 0.0125 + 0.0125 mmol) and $H_2O_2$ (30%) (50 μL, 0.5 mmol) in $CH_2Cl_2$ (850 μL) afforded **2d** as a solid (64 mg, 77%); mp 129-130 $^o$C (ethyl acetate / petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81-7.68 (m, 4 H), 7.62-7.49 (m, 6 H), 4.30-4.05 (m, 3 H), 2.14-2.08 (m, 1 H), 1.62-1.47 (m, 1 H), 1.26-1.12 (m, 4 H), 0.78 (t, $J$ = 6.8 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 207.9 (d, $J_{PC}$ = 2.1 Hz), 132.64 (d, $J_{PC}$ = 2.8 Hz), 132.61 (d, $J_{PC}$ = 2.8 Hz), 131.6 (d, $J_{PC}$ = 9.1 Hz), 131.1 (d, $J_{PC}$ = 9.8 Hz), 130.5 (d, $J_{PC}$ = 100.5 Hz), 129.0 (d, $J_{PC}$ = 99.8 Hz), 128.9 (d, $J_{PC}$ = 12.6 Hz), 128.7 (d, $J_{PC}$ = 11.9 Hz), 69.9, 52.7 (d, $J_{PC}$ = 54.2 Hz), 31.0 (d, $J_{PC}$ = 12.0 Hz), 25.8, 22.1, 13.6; $^{31}$P NMR (162 MHz, $CDCl_3$) δ 32.2; IR (neat) 3293, 1711, 1595, 1488, 1467, 1440 cm$^{-1}$; HRMS (ESI) calcd for $C_{19}H_{24}O_3P$ (M + H$^+$) 331.1458, found 331.1469.

**(4) 1-(Diphenylphosphoryl)-3-hydroxybutan-2-one (2e)**

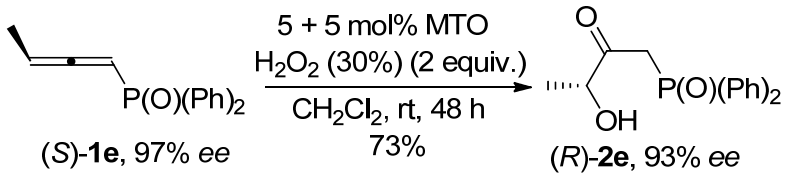



**1e** **2e**

The reaction of **1e** (64 mg, 0.25 mmol), MTO (3 + 3 mg, 0.0125 + 0.0125 mmol) and $H_2O_2$ (30%) (50 μL, 0.5 mmol) in $CH_2Cl_2$ (850 μL) afforded **2e** as a solid (54 mg, 74%); mp 107-108 $^o$C (ethyl acetate / petroleum ether); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79-7.69 (m, 4 H), 7.61-7.48 (m, 6 H), 5.68 (brs, 1 H), 4.22-4.15 (m, 1 H), 4.05 (dd,

*J* = 16.0, 12.4 Hz, 1 H), 3.73 (dd, *J* = 13.2, 12.0 Hz, 1 H), 1.33 (d, *J* = 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 208.2 (d, $J_{PC}$ = 5.6 Hz), 132.71 (d, $J_{PC}$ = 1.4 Hz), 132.69 (d, $J_{PC}$ = 1.4 Hz), 131.3 (d, $J_{PC}$ = 102.6 Hz), 131.0 (d, $J_{PC}$ = 9.9 Hz), 130.8 (d, $J_{PC}$ = 9.8 Hz), 130.7 (d, $J_{PC}$ = 104.0 Hz), 129.0 (d, $J_{PC}$ = 2.8 Hz), 128.9 (d, $J_{PC}$ = 2.9 Hz), 74.2, 43.3 (d, $J_{PC}$ = 54.8 Hz), 19.1; $^{31}$P NMR (162 MHz, $CDCl_3$) δ 30.8; IR (neat) 3294, 1711, 1585, 1480, 1438 cm$^{-1}$; HRMS (ESI) calcd for $C_{16}H_{18}O_3P$ ($M + H^+$) 289.0988, found 289.0988.

**(5) (*R*)-1-(diphenylphosphoryl)-3-hydroxybutan-2-one ((*R*)-2e)**




(*S*)-**1e**, 97% *ee* (*R*)-**2e**, 93% *ee*

The reaction of (*S*)-**1e** (64 mg, 0.25 mmol), MTO (3 + 3 mg, 0.0125 + 0.0125 mmol) and $H_2O_2$ (30%) (50 μL, 0.5 mmol) in $CH_2Cl_2$ (850 μL) afforded (*R*)-**2e** as a solid (53 mg, 73%), and 94% *ee* as determined by HPLC analysis (Chiralcel AD-H, *n*-Hexane : *i*-PrOH = 9 : 1, 0.6 mL/min, 230 nm, T = 30 $^o$C), $t_r$ = 37.5 (major), 52.3 (minor); $[\alpha]^{20}_D$ = 22.4 (c = 1.00, $CH_2Cl_2$). The $^1$H NMR data are the same as those for the racemic compound available in the Supporting Information. Crystal data for (*R*)-**2e**: $C_{16}H_{17}O_3P$, MW = 288.26, Monoclinic, space group P 21, Mo Kα, final R indices [I>2sigma(I)], R1 = 0.0747, wR2 = 0.2087, a = 5.8589(19) Å, b = 17.826(5) Å, c = 14.463(5) Å, α = 90 $^o$, β = 93.258(5) $^o$, γ = 90 $^o$, V = 1508.1(8) Å$^3$, T = 223 (2) K, *Z* = 4, reflections collected / unique: 9387 / 5122 [R(int) = 0.0427], parameters 365, absolute structure parameter 0.07(7). Supplementary crystallographic data have beendeposited at the Cambridge Crystallographic Data Center. CCDC: 1040646.

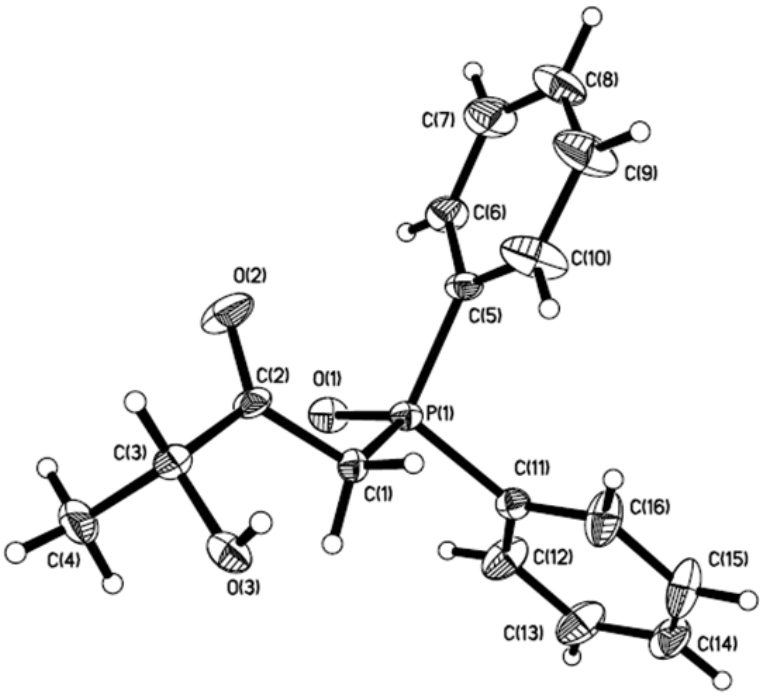
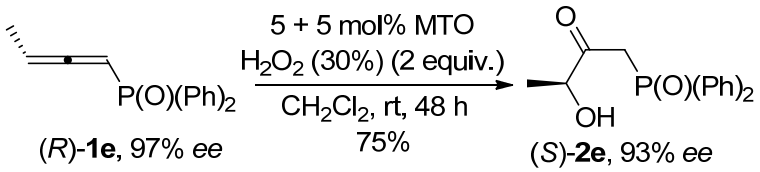



**Figure S1. ORTEP representation of (*R*)-2e.**

**(6) (*S*)-1-(diphenylphosphoryl)-3-hydroxybutan-2-one ((*S*)-2e)**




The reaction of (*R*)-**1e** (64 mg, 0.25 mmol), MTO (3 + 3 mg, 0.0125 + 0.0125 mmol) and $H_2O_2$ (30%) (50 μL, 0.5 mmol) in $CH_2Cl_2$ (850 μL) afforded (*S*)-**2e** as a solid (55 mg, 75%), and 94% *ee* as determined by HPLC analysis (Chiralcel AD-H, *n*-Hexane : *i*-PrOH = 9 : 1, 0.6 mL/min, 230 nm, T = 30 $^{o}$C), $t_r$ = 36.8 (minor), 50.5 (major); $[\alpha]^{20}_{D}$ = -23.7 (c = 1.00, $CH_2Cl_2$). The $^1$H NMR data are the same as those for the racemic compound available in the Supporting Information. Crystal data for (*S*)-**2e**: $C_{16}H_{17}O_3P$, MW = 288.26, Monoclinic, space group P21, Mo Kα, final R indices [I > 2sigma(I)], R1 = 0.0962, wR2 = 0.2391, a = 5.826(4) Å, b = 17.749(10) Å, c = 14.404(9) Å, α = 90 $^{o}$, β = 93.154(9) $^{o}$, γ = 90 $^{o}$, V = 1487.1(15) Å$^3$, T = 213(2) K, Z = 4, reflections collected / unique: 10019 / 5774 [R(int) = 0.0721], parameters 368, absolute structure parameter - 0.07(12). Supplementary crystallographic data have beendeposited at the Cambridge Crystallographic Data Center. CCDC: 1040645.

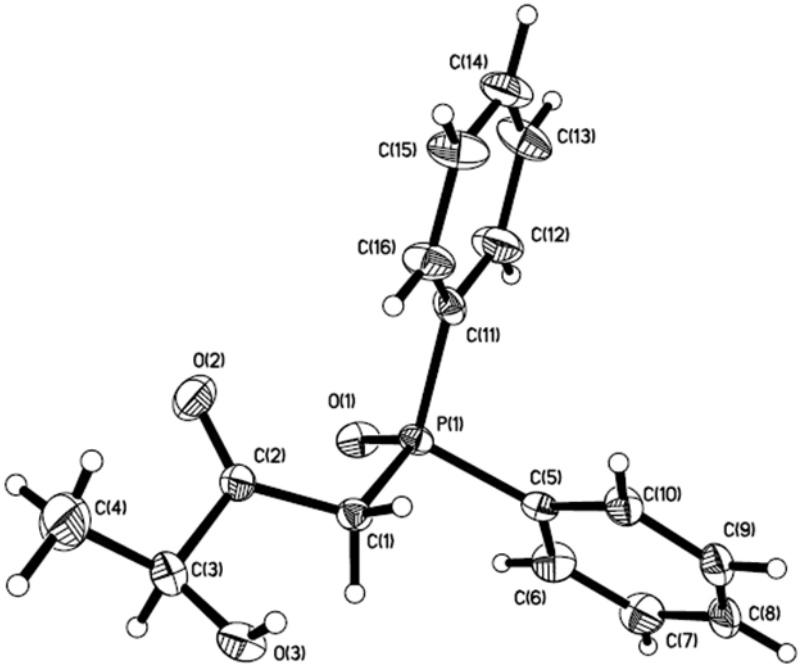
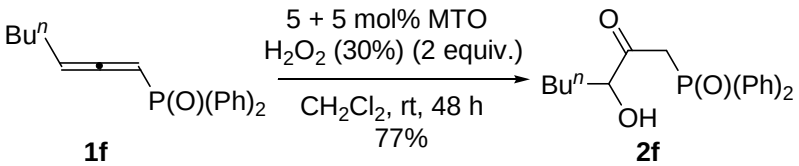



**Figure S2. ORTEP representation of (*S*)-2e.**

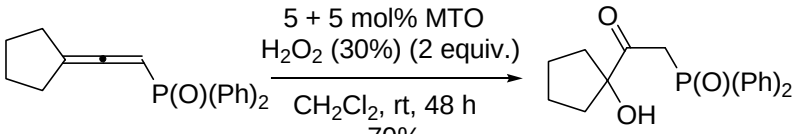
**(7) 1-(Diphenylphosphoryl)-3-hydroxyheptan-2-one (2f)**




**1f** **2f**

The reaction of **1f** (74 mg, 0.25 mmol), MTO (3 + 3 mg, 0.0125 + 0.0125 mmol) and $H_2O_2$ (30%) (50 μL, 0.5 mmol) in $CH_2Cl_2$ (850 μL) afforded **2f** as a solid (64 mg, 77%); mp 92-93 $^oC$ (ethyl acetate / petroleum ether); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.79-7.69 (m, 4 H), 7.61-7.48 (m, 6 H), 5.54 (brs, 1 H), 4.10-4.02 (m, 2 H), 3.68 (dd, $J$ = 13.2, 12.0 Hz, 1 H), 1.76-1.55 (m, 2 H), 1.45-1.24 (m, 4 H), 0.87 (t, $J$ = 7.6 Hz, 3 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 208.1 (d, $J_{PC}$ = 6.3 Hz), 132.61 (d, $J_{PC}$ = 1.4 Hz), 132.60 (d, $J_{PC}$ = 1.4 Hz), 131.3 (d, $J_{PC}$ = 106.1 Hz), 131.0 (d, $J_{PC}$ = 9.8 Hz), 130.73 (d, $J_{PC}$ = 9.8 Hz), 130.66 (d, $J_{PC}$ = 104.0 Hz), 128.9 (d, $J_{PC}$ = 3.5 Hz), 128.8 (d, $J_{PC}$ = 3.6 Hz), 78.0, 43.6, (d, $J_{PC}$ = 54.1 Hz), 33.1, 27.3, 22.4, 13.9; $^{31}P$ NMR (162 MHz, $CDCl_3$) δ 31.0; IR (neat) 3281, 1708, 1588, 1483, 1459, 1435 $cm^{-1}$; HRMS (ESI) calcd for $C_{19}H_{24}O_3P$ ($M + H^+$) 331.1458, found 331.1458.

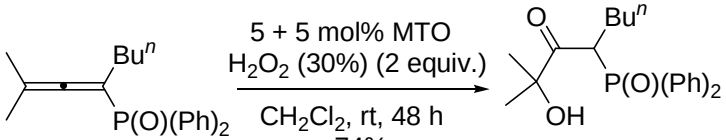
**(8)2-(Diphenylphosphoryl)-1-(1-hydroxycyclopentyl)ethanone (2g)**




**1g** **2g**

The reaction of **1g** (74 mg, 0.25 mmol), MTO (3 + 3 mg, 0.0125 + 0.0125 mmol) and $H_2O_2$ (30%) (50 μL, 0.5 mmol) in $CH_2Cl_2$ (850 μL) afforded **2g** as a solid (58 mg, 70%); mp 129-130 $^oC$ (ethyl acetate / petroleum ether); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.77-7.70 (m, 4 H), 7.62-7.47 (m, 6 H), 5.71 (s, 1 H), 3.98 (d, $J$ = 14.8 Hz, 2 H), 1.92-1.78 (m, 6 H), 1.73-1.65 (m, 2 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 210.9 (d, $J_{PC}$ = 6.4 Hz), 132.5 (d, $J_{PC}$ = 2.8 Hz), 131.1 (d, $J_{PC}$ = 103.3 Hz), 130.8 (d, $J_{PC}$ = 10.6 Hz), 128.8 (d, $J_{PC}$ = 12.7 Hz), 88.3, 44.1 (d, $J_{PC}$ = 54.1 Hz), 39.9, 24.9; $^{31}P$ NMR (162 MHz, $CDCl_3$) δ 31.4; IR (neat) 3304, 1722, 1590, 1480, 1438, $cm^{-1}$; HRMS (ESI) calcd for $C_{19}H_{22}O_3P$ ($M + H^+$) 329.1301, found 329.1309.

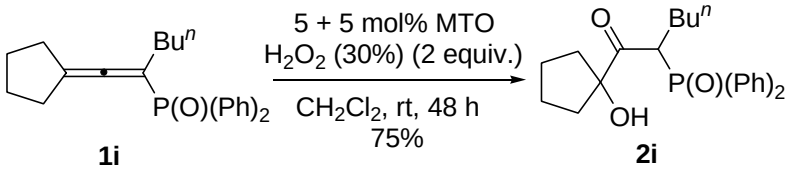
**(9) 4-(Diphenylphosphoryl)-2-hydroxy-2-methyloctan-3-one (2h)**




**1h** **2h**

The reaction of **1h** (81 mg, 0.25 mmol), MTO (3 + 3 mg, 0.0125 + 0.0125 mmol) and $H_2O_2$ (30%) (50 μL, 0.5 mmol) in $CH_2Cl_2$ (850 μL) afforded **2h** as a solid (67 mg, 74%); mp 99-100 $^oC$ (ethyl acetate / petroleum ether); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.81-7.73 (m, 2 H), 7.65-7.42 (m, 8 H), 6.03 (s, 1 H), 4.95-4.85 (m, 1 H), 1.94-1.83 (m, 1 H), 1.48-1.35 (m, 4 H), 1.25-1.05 (m, 7 H), 0.79 (t, $J$ = 6.8 Hz, 3 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 212.4 (d, $J_{PC}$ = 5.0 Hz), 132.7 (d, $J_{PC}$ = 2.8 Hz), 132.6 (d, $J_{PC}$ = 2.1 Hz), 132.5 (d, $J_{PC}$ = 9.8 Hz), 131.2 (d, $J_{PC}$ = 9.1 Hz), 130.8 (d, $J_{PC}$ = 100.5 Hz), 129.0 (d, $J_{PC}$ = 12.6 Hz), 128.4 (d, $J_{PC}$ = 12.0 Hz), 127.9 (d, $J_{PC}$ = 100.5 Hz), 77.6, 49.0 (d, $J_{PC}$ = 54.1 Hz), 31.0 (d, $J_{PC}$ = 13.4 Hz), 26.5, 26.1 (d, $J_{PC}$ = 14.0 Hz), 22.2, 13.6; $^{31}P$ NMR (162 MHz, $CDCl_3$) δ 32.3; IR (neat) 3318, 1708, 1593, 1559, 1462, 1435 $cm^{-1}$; HRMS (ESI) calcd for $C_{21}H_{28}O_3P$ ($M + H^+$) 359.1771, found 359.1779.

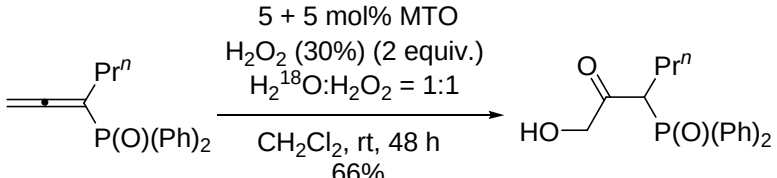
**(10) 2-(Diphenylphosphoryl)-1-(1-hydroxycyclopentyl)hexan-1-one (2i)**




**1i** **2i**

The reaction of **1i** (88 mg, 0.25 mmol), MTO (3 + 3 mg, 0.0125 + 0.0125 mmol) and $H_2O_2$ (30%) (50 μL, 0.5 mmol) in $CH_2Cl_2$ (850 μL) afforded **2i** as a solid (72 mg, 75%); mp 137-138 $^oC$ (ethyl acetate / petroleum ether); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.81-7.73 (m, 2 H), 7.67-7.45 (m, 8 H), 5.88 (s, 1 H), 4.91-4.80 (m, 1 H), 2.19-2.12 (m, 1 H), 2.01-1.65 (m, 8 H), 1.43-1.34 (m, 1 H), 1.22-1.05 (m, 4 H), 0.78 (t, $J$ = 7.2 Hz, 3 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 213.0 (d, $J_{PC}$ = 4.9 Hz), 132.66 (d, $J_{PC}$ = 2.9 Hz), 132.60 (d, $J_{PC}$ = 2.8 Hz), 132.4 (d, $J_{PC}$ = 9.2 Hz), 131.3 (d, $J_{PC}$ = 9.8 Hz), 131.0 (d, $J_{PC}$ = 99.8 Hz), 128.9 (d, $J_{PC}$ = 11.9 Hz), 128.4 (d, $J_{PC}$ = 11.9 Hz), 128.1 (d, $J_{PC}$ = 100.5 Hz), 88.6, 50.6 (d, $J_{PC}$ = 53.5 Hz), 39.7 (d, $J_{PC}$ = 7.1 Hz), 31.1 (d, $J_{PC}$ = 13.3 Hz), 26.3 (d, $J_{PC}$ = 1.4 Hz), 25.0 (d, $J_{PC}$ = 11.3 Hz), 22.1, 13.7; $^{31}P$ NMR (162 MHz, $CDCl_3$) δ 37.8; IR (neat) 3281, 1717, 1595, 1485, 1461, 1435 $cm^{-1}$; HRMS (ESI) calcd for $C_{23}H_{30}O_3P$ ($M + H^+$) 385.1927, found 385.1933.

**Synthesis of $^{18}$O-labeled 3-(diphenylphosphoryl)-1-hydroxyhexan-2-one (2a*)**




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

A solution of **1a** (72 mg, 0.26 mmol), MTO (3 mg, 0.0125 mmol), $H_2{}^{18}O$ (50 μL) and $H_2O_2$ (30%) (50 μL, 0.5 mmol) in $CH_2Cl_2$ (850 μL) was stirred at rt for 24 hours. Then MTO (3 mg, 0.0125 mmol) was added into the reaction mixture again. The resulted mixture was stirred at rt for another 24 hours. When the reaction was completed, as monitored by TLC (eluent: petroleum ether/ethyl acetate = 1/1), the solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1→2/1→1/1) to afforded **2a***as a solid (52 mg, 66%).

## ESI-MS Spectra

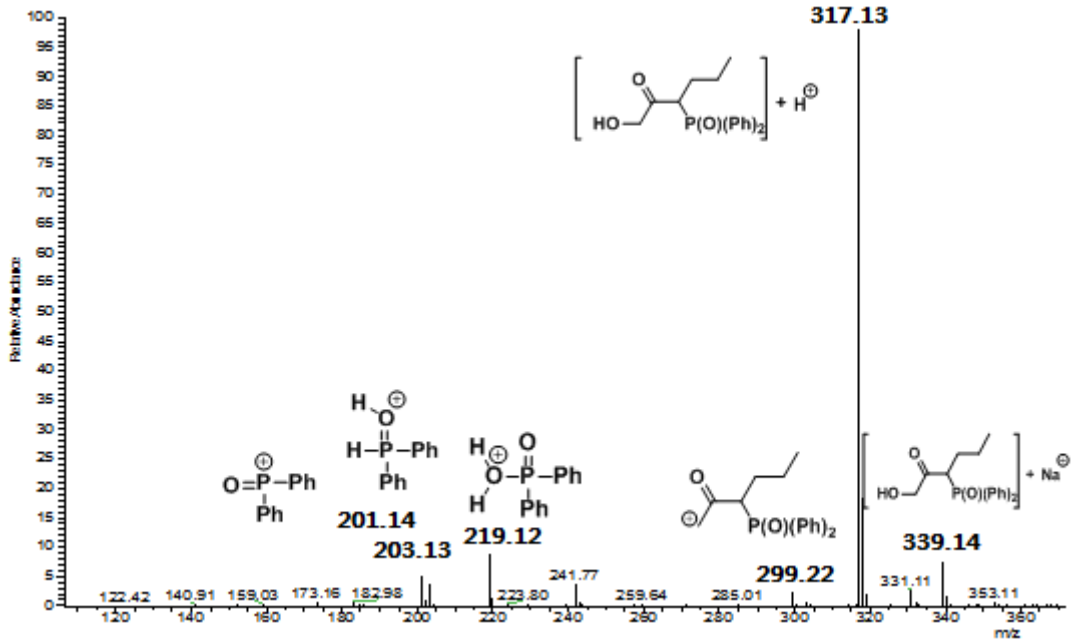



**Fig. S3**. ESI-MS spectrum for **2a**

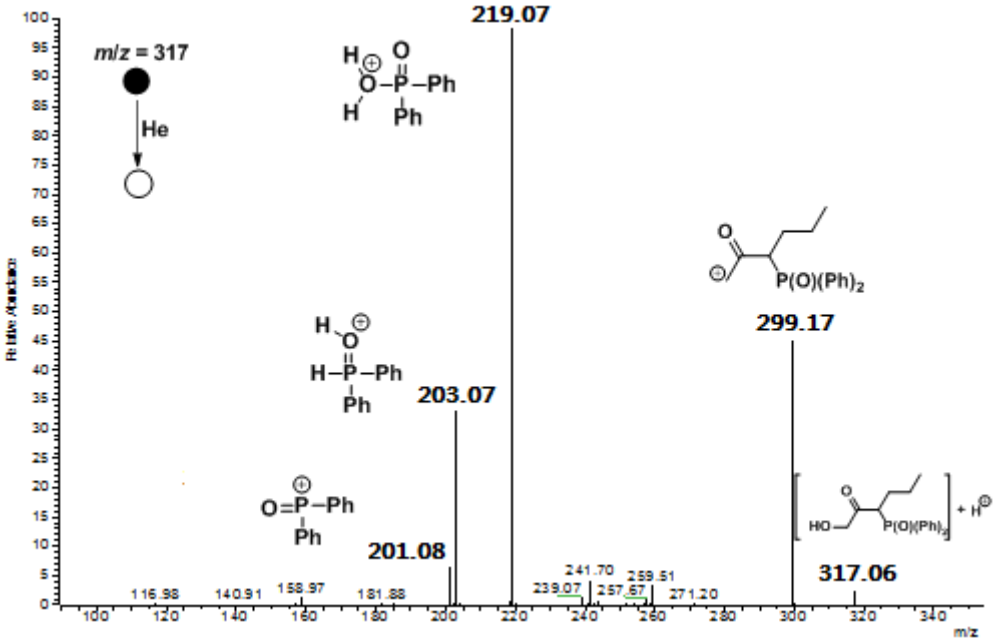



**Fig. S4.** ESI-MS$^2$ spectrum for the precursor ion at *m/z* = 317

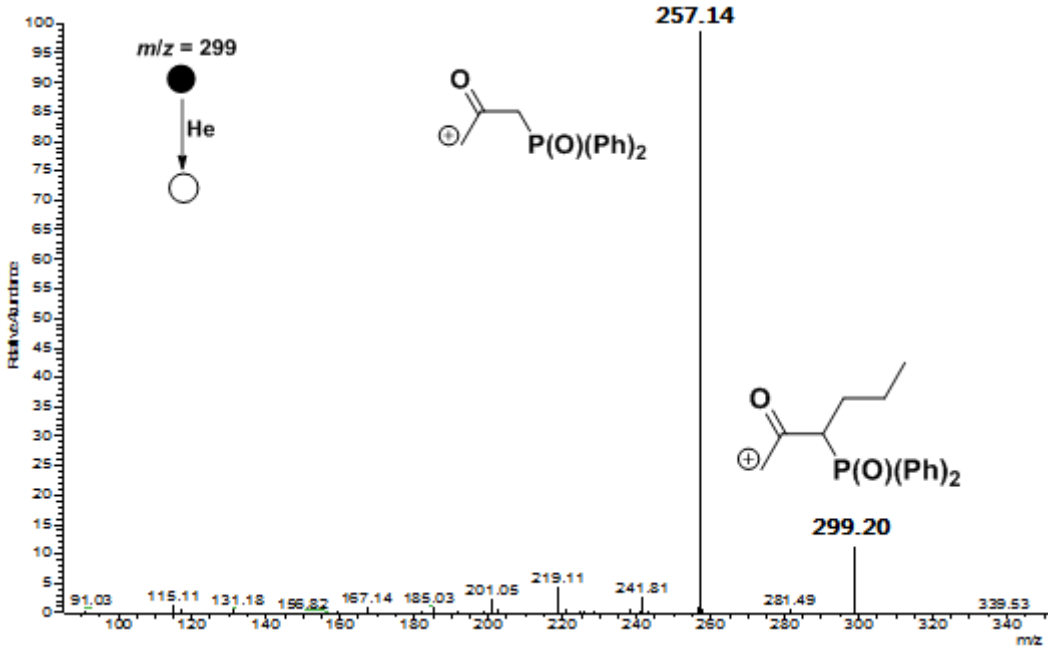



**Fig. S5.** ESI-MS$^3$ spectrum for the precursor ion at *m/z* = 299

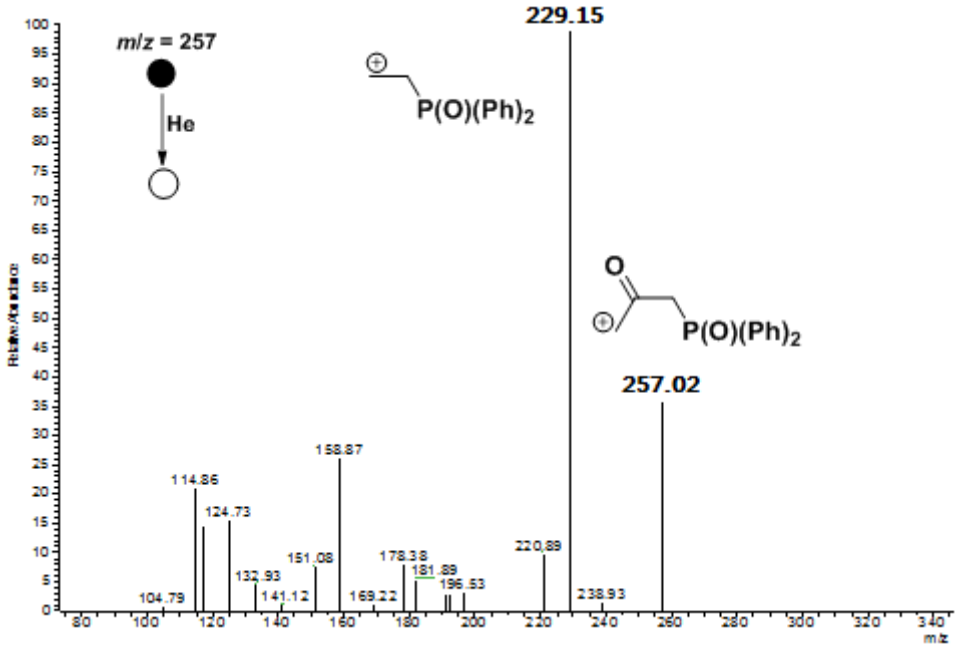



**Fig. S6.** ESI-MS$^4$ spectrum for the precursor ion at *m/z* = 257

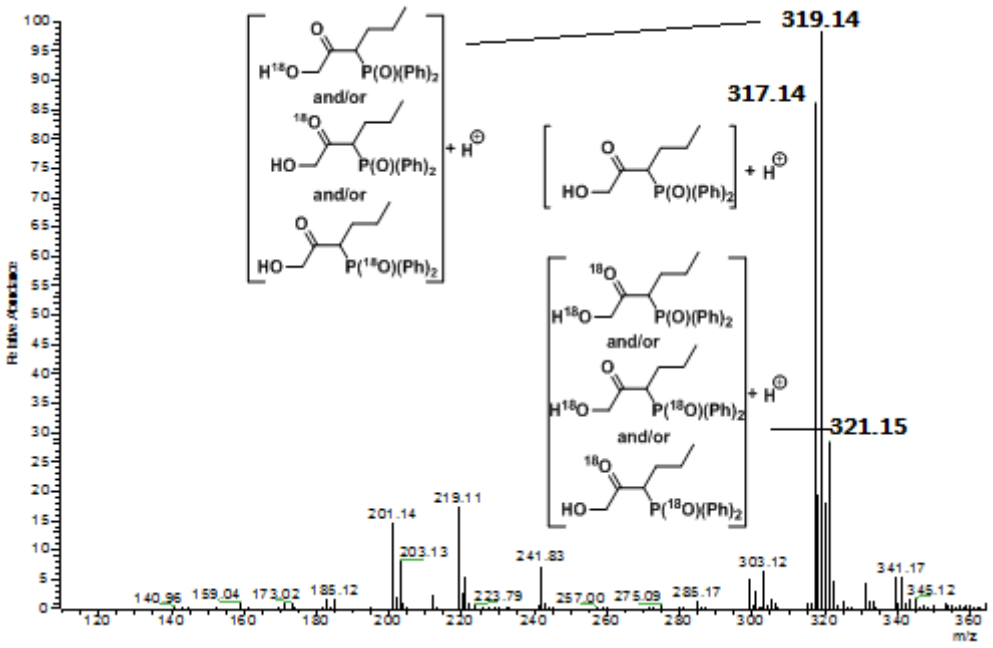



**Fig. S7.** ESI-MS spectrum for **2a***

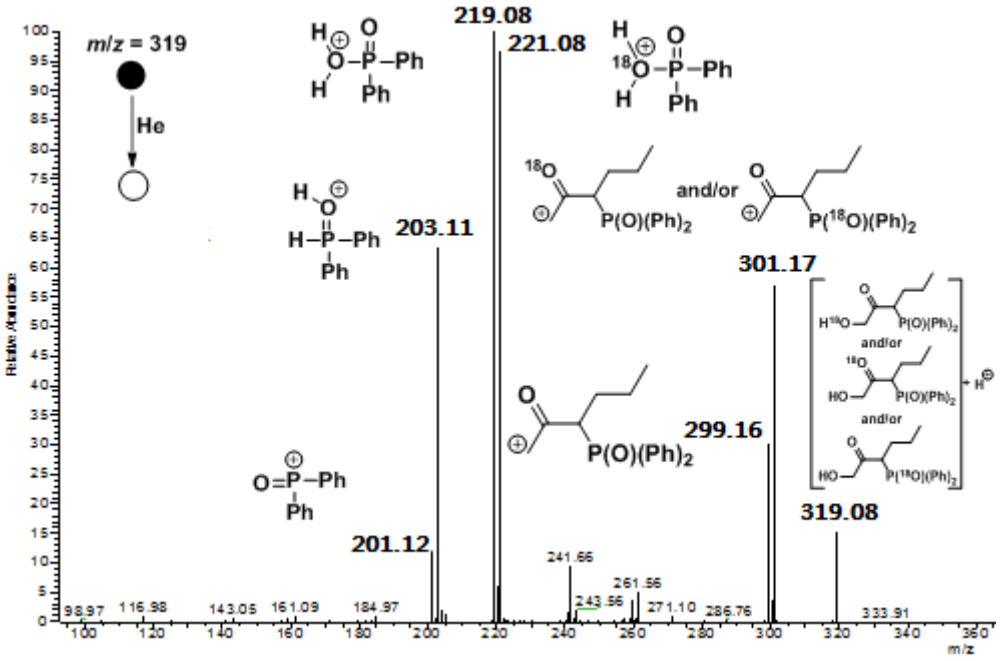



**Fig. S8.** ESI-MS$^2$ spectrum for the precursor ion at *m/z* = 319

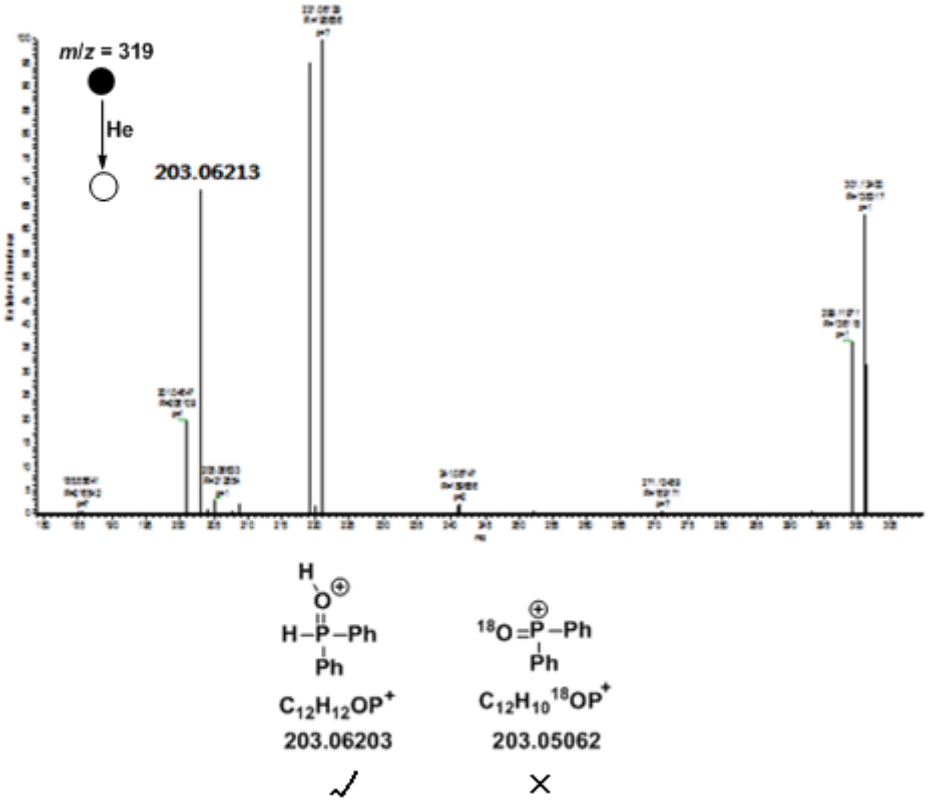



**Fig. S9.** High resolutionESI-MS$^2$ spectrum for the precursor ion at *m/z* = 319

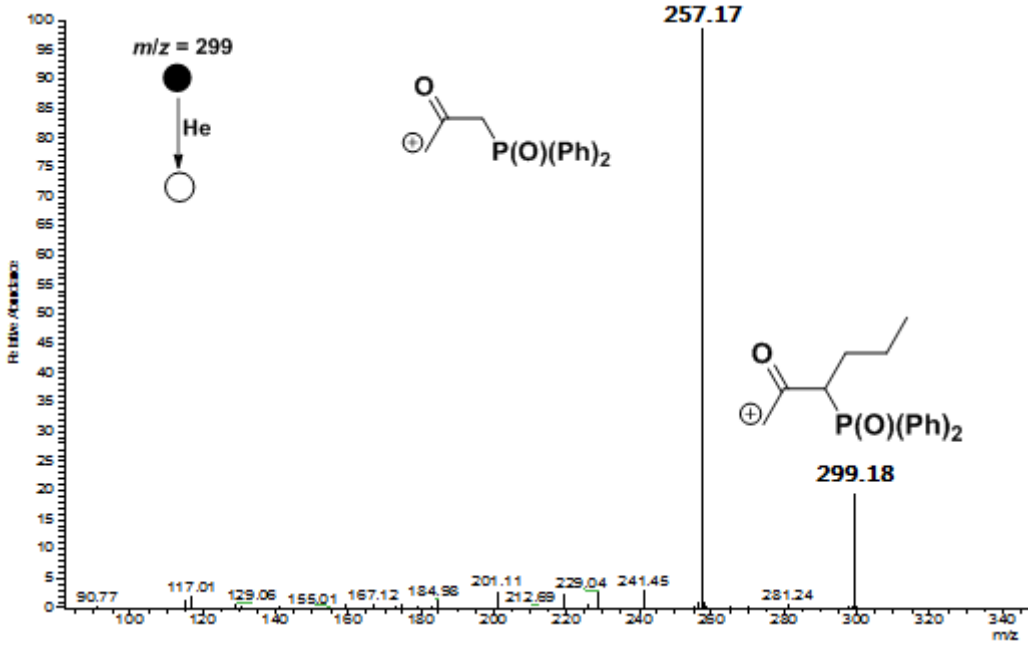



**Fig. S10.** ESI-MS$^3$ spectrum for the precursor ion at *m/z* = 299

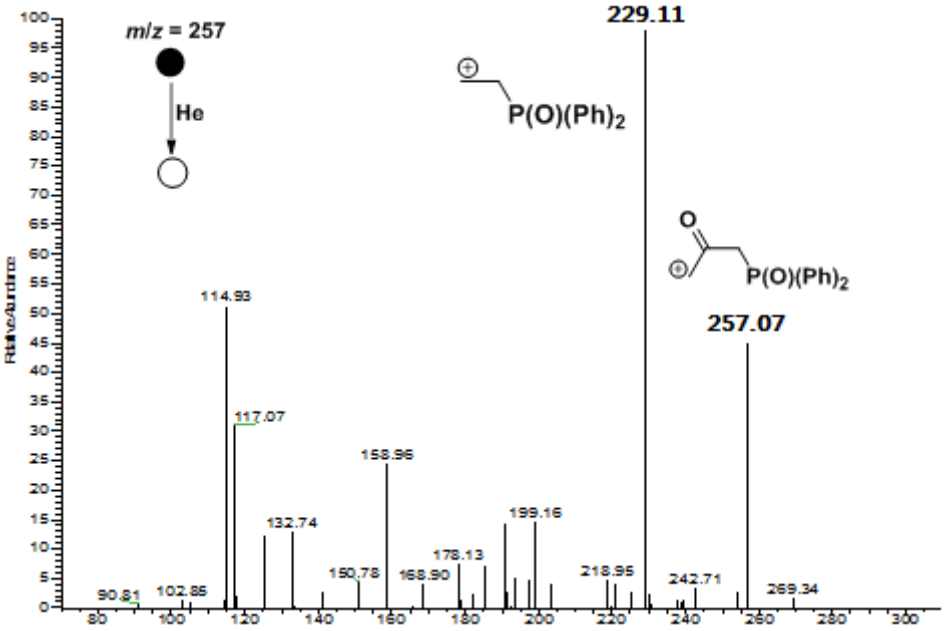



**Fig. S11.** ESI-MS$^4$ spectrum for the precursor ion at *m/z* = 257

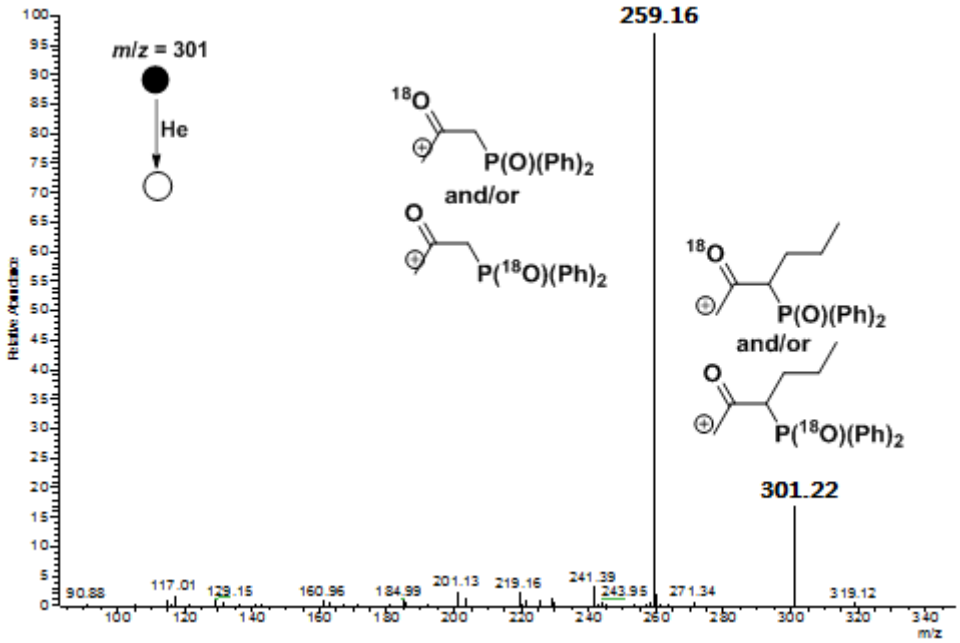



**Fig. S12.** ESI-MS$^3$ spectrum for the precursor ion at *m/z* = 301

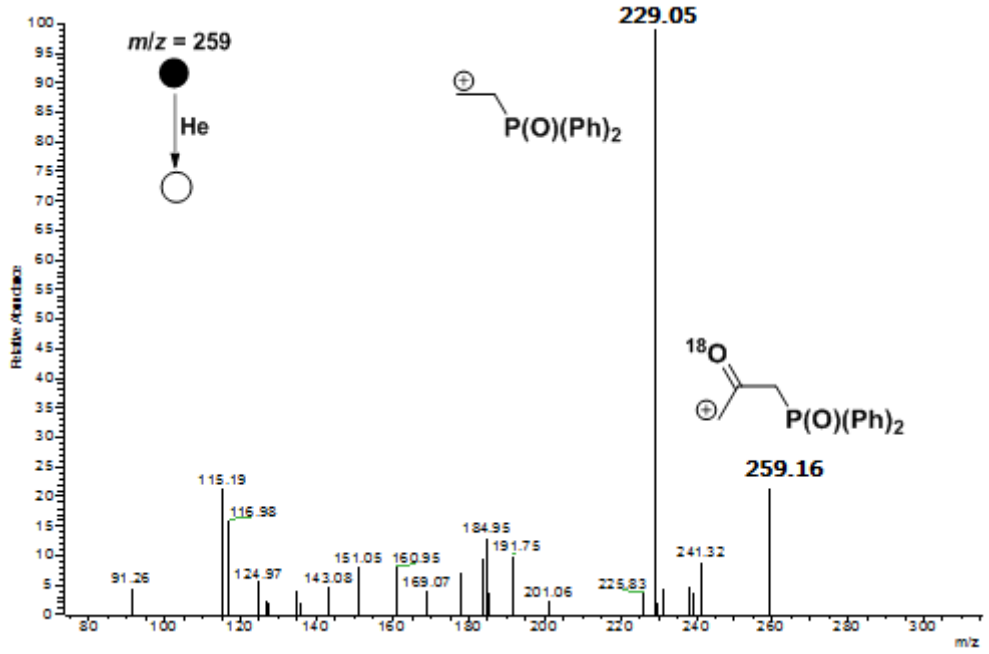



**Fig. S13.** ESI-MS$^4$ spectrum for the precursor ion at *m/z* = 259

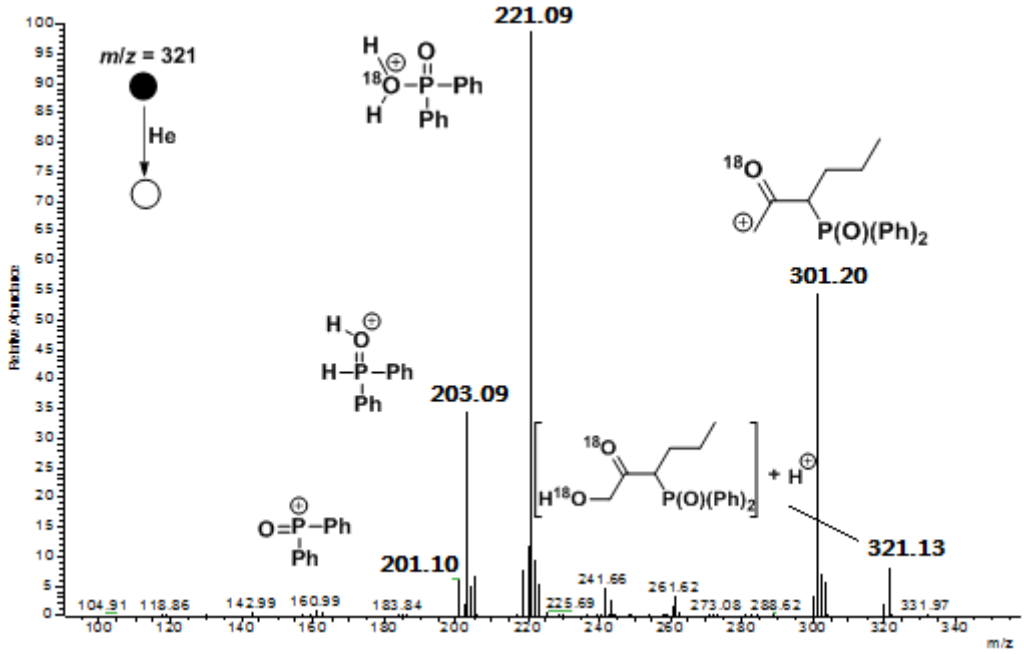



**Fig. S14.** ESI-MS$^2$ spectrum for the precursor ion at *m/z* = 321

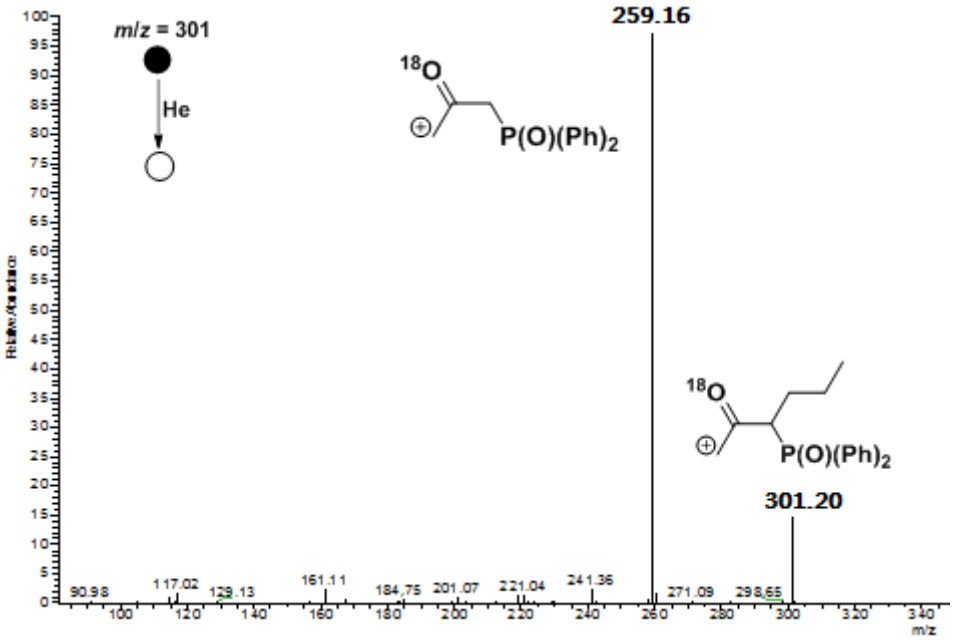



**Fig. S15.** ESI-MS$^3$ spectrum for the precursor ion at *m/z* = 301

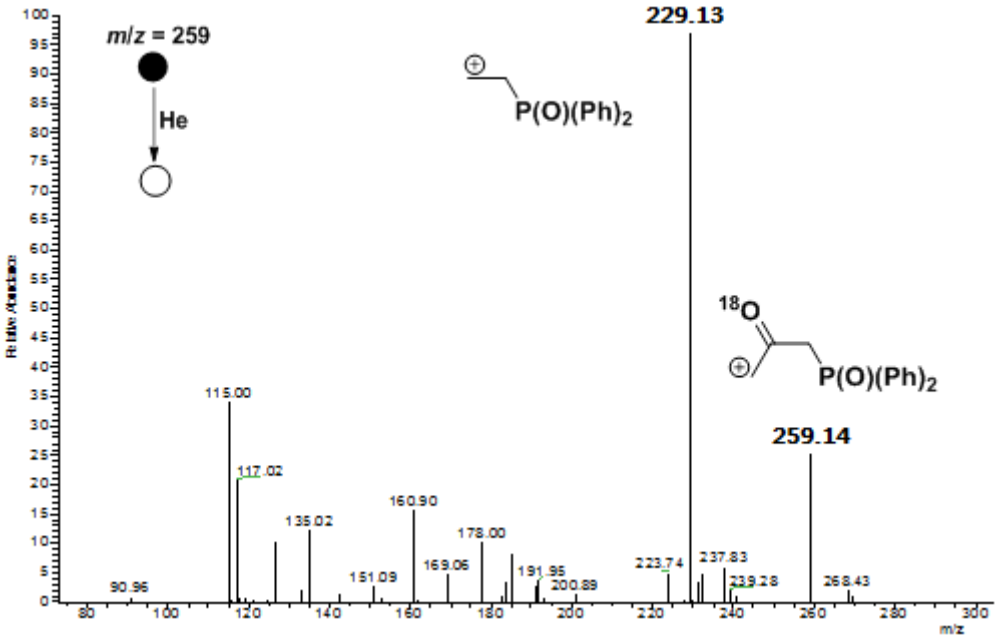



**Fig. S16.** ESI-MS$^4$ spectrum for the precursor ion at *m/z* = 259

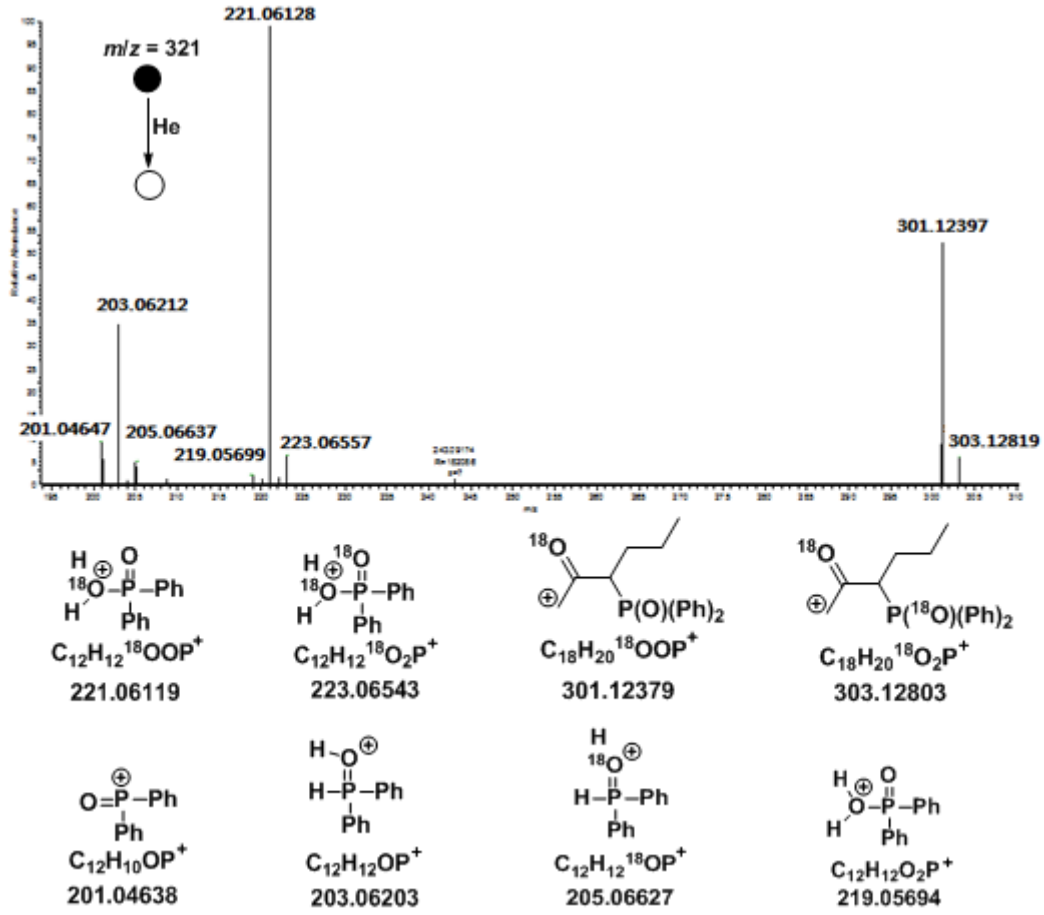
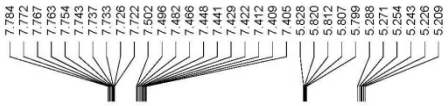
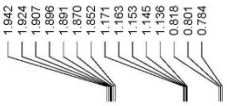
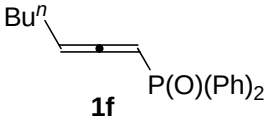



**Fig. S17.** High resolution ESI-MS$^2$ spectrum for the precursor ion at *m/z* = 321

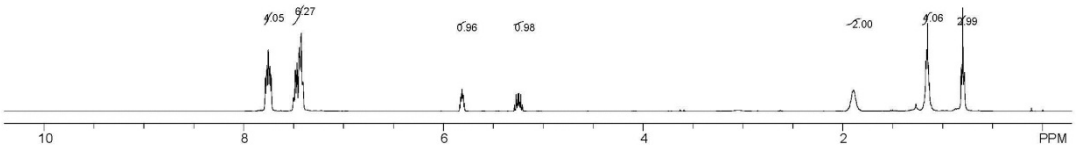
## NMR Spectra

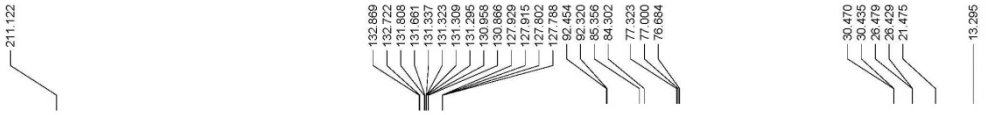


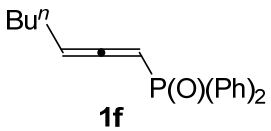



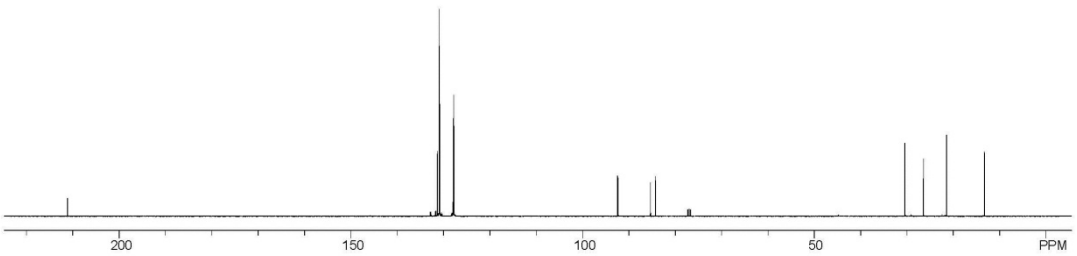

**1f**

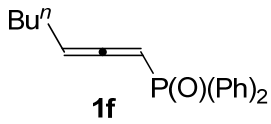



**1f**

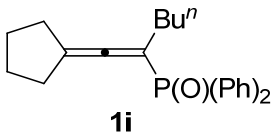



Bu$^n$
P(O)(Ph)$_2$

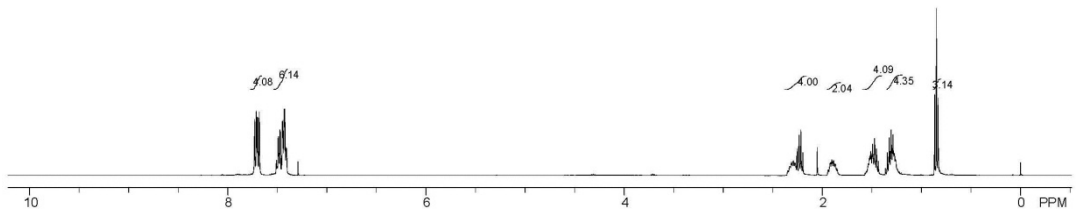
**1f**


31.017
400
300
200
100
0
-100
-200
-300
PPM


7.732
7.729
7.726
7.717
7.712
7.709
7.703
7.700
7.697
7.688
7.683
7.679
7.493
7.488
7.478
7.474
7.471
7.467
7.450
7.443
7.436
7.432
7.428
7.425
7.415
7.411
7.407
7.404
7.292
2.348
2.329
2.312
2.292
2.276
2.256
2.235
2.217
2.197
2.051
1.940
1.920
1.903
1.887
1.870
1.851
1.524
1.513
1.510
1.492
1.486
1.472
1.453
1.344
1.324
1.306
1.287
1.276
1.271
0.867
0.849
0.831
-0.000


Bu$^n$
P(O)(Ph)$_2$

**1i**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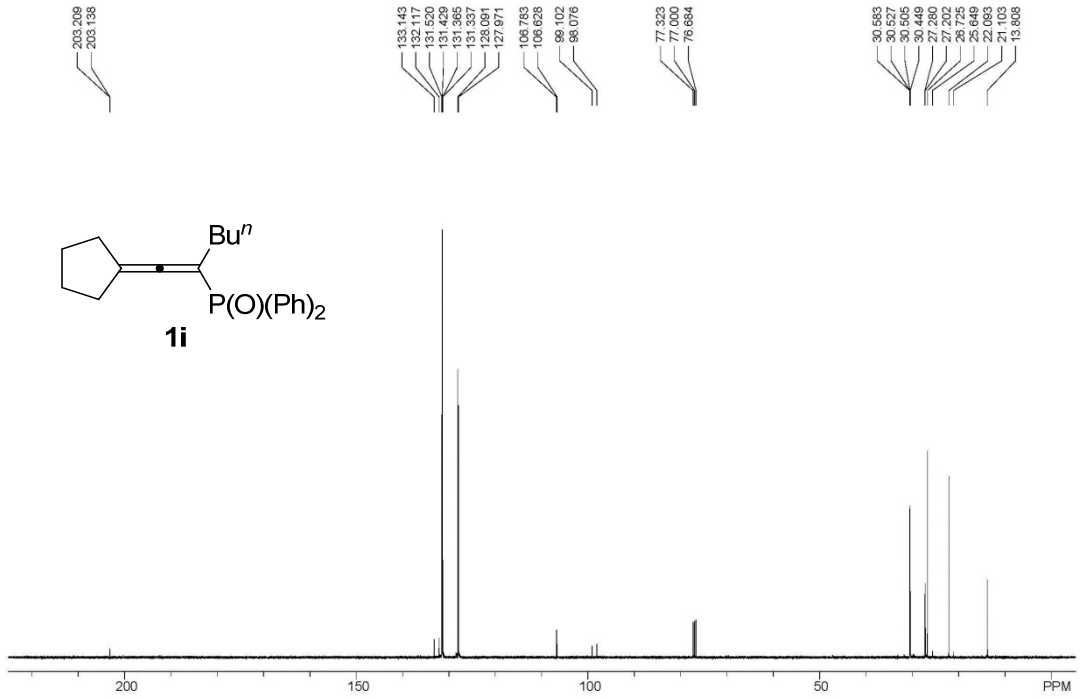
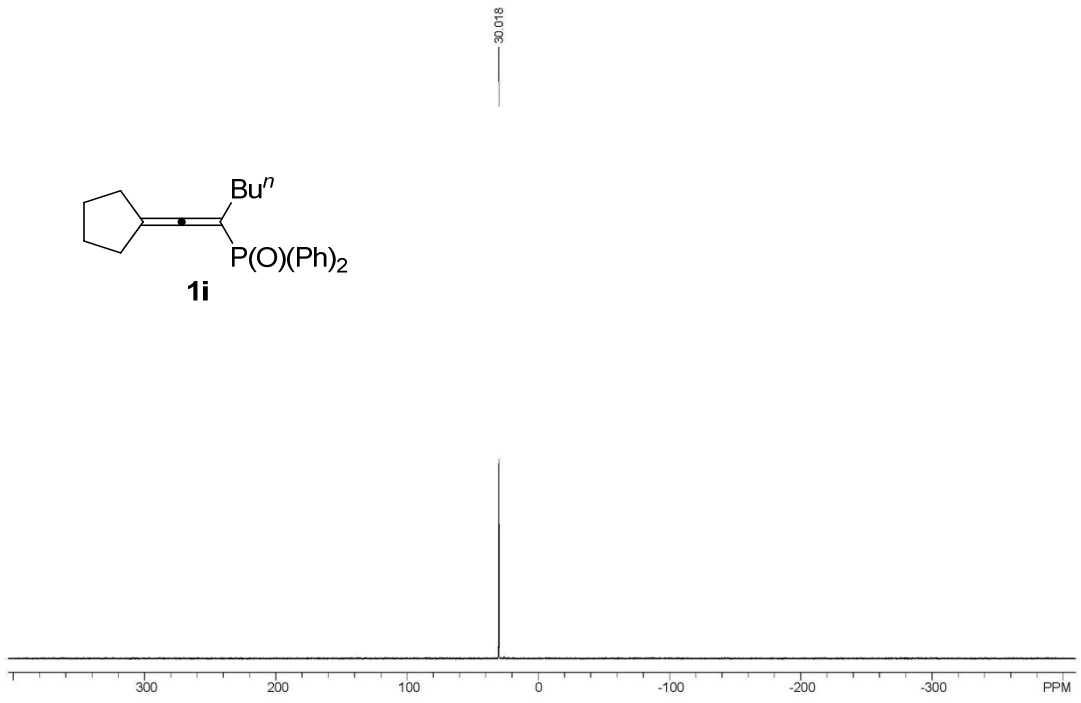
6.14
4.00
2.04
4.09
4.35
3.14
10
8
6
4
2
0
PPM


203.209
203.138
133.143
132.117
131.520
131.429
131.365
131.337
128.091
127.971
106.783
106.628
89.102
88.076
77.323
77.000
76.684
30.583
30.527
30.505
30.449
27.280
27.202
26.725
25.649
22.093
21.103
13.808
Bu$^n$
P(O)(Ph)$_2$
1i
200
150
100
50
PPM


30.018
Bu$^n$
P(O)(Ph)$_2$
1i
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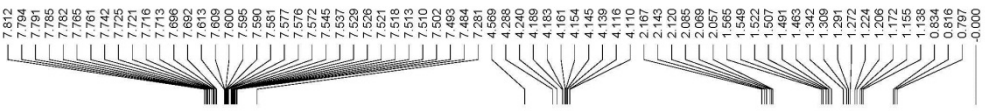
200
100
0
-100
-200
-300
PPM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7.713
7.696
7.692
7.613
7.609
7.600
7.595
7.590
7.581
7.577
7.576
7.572
7.545
7.537
7.529
7.526
7.521
7.518
7.513
7.510
7.502
7.493
7.484
7.281
4.569
4.288
4.240
4.189
4.183
4.161
4.154
4.145
4.139
4.116
4.110
2.167
2.143
2.120
2.085
2.069
2.057
1.565
1.549
1.522
1.507
1.491
1.463
1.342
1.309
1.291
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1.155
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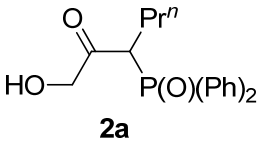
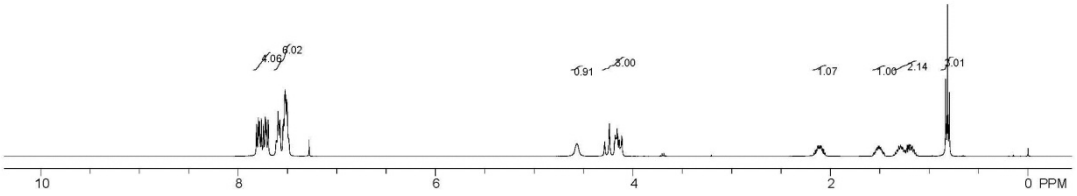
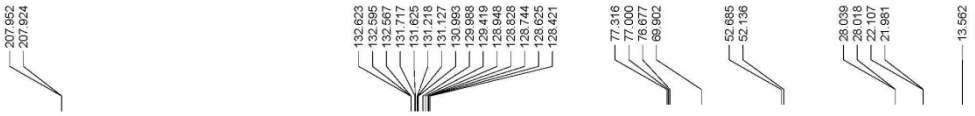
0.797
0.000


O
Pr$^n$
HO
P(O)(Ph)$_2$

**2a**


4.06
0.02
0.91
8.00
1.07
1.00
2.14
3.01
10
8
6
4
2
0 PPM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207.924
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132.595
132.567
131.717
131.625
131.218
131.127
130.993
129.988
129.419
128.948
128.828
128.744
128.625
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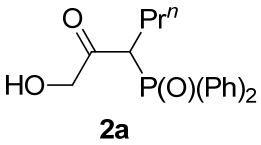
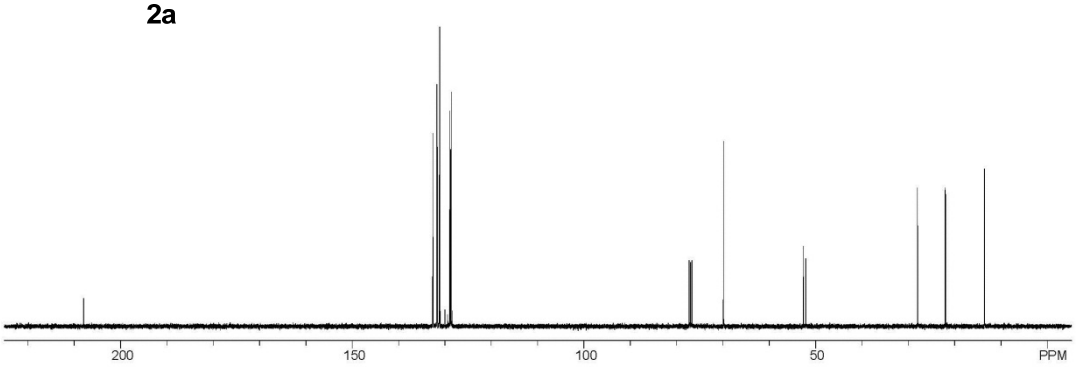
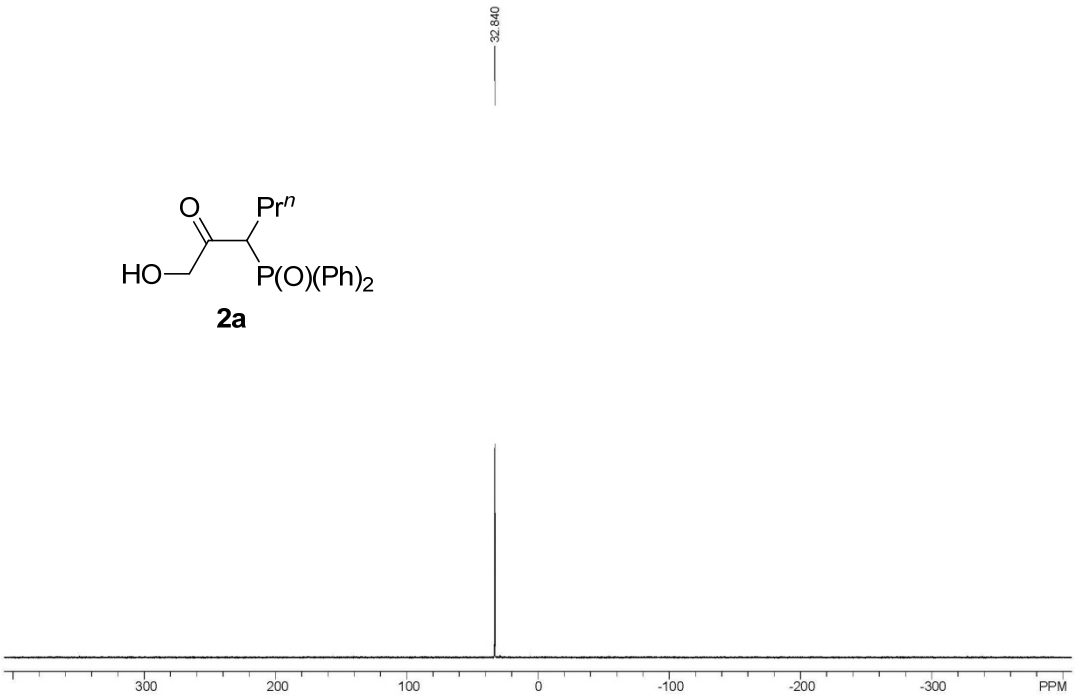
52.136
28.039
28.018
22.107
21.981
13.562

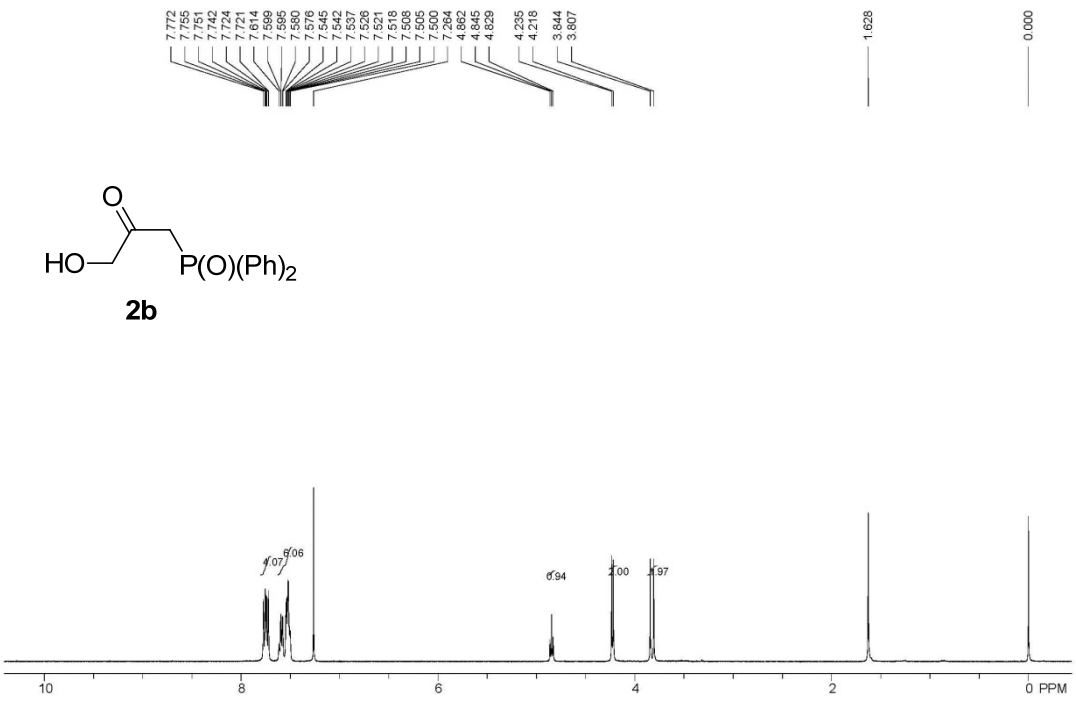

O
Pr$^n$
HO
P(O)(Ph)$_2$

**2a**


200
150
100
50
PPM


32.840
O
Pr$^n$
HO
P(O)(Ph)$_2$
300
200
100
0
-100
-200
-300
PPM

**2a**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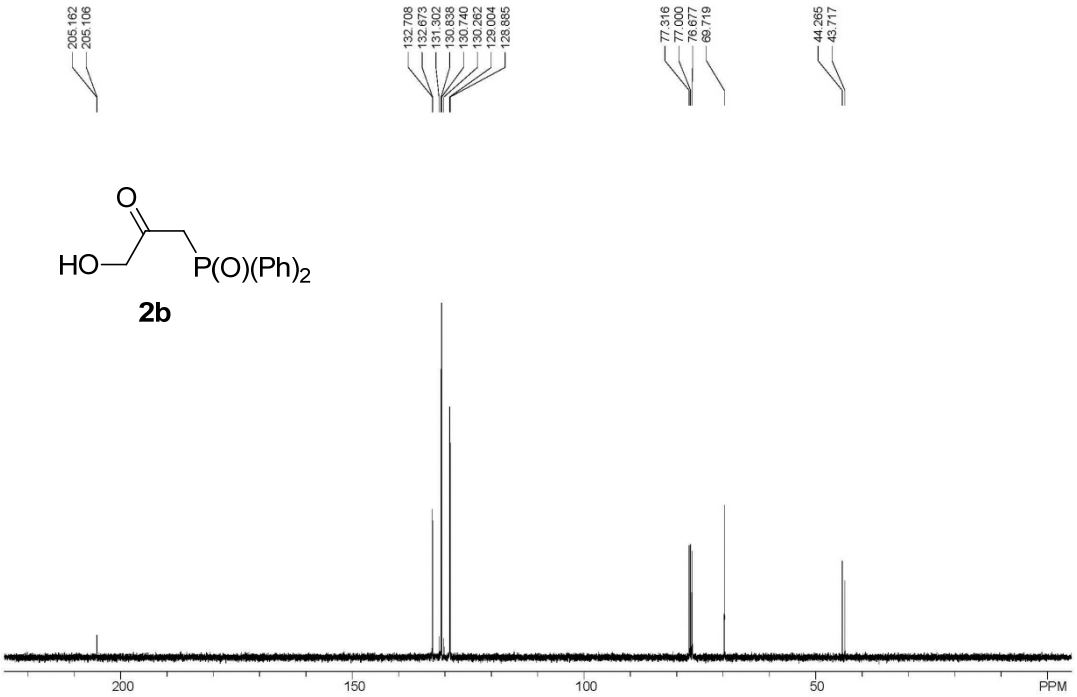
7.755
7.751
7.742
7.724
7.721
7.614
7.599
7.595
7.580
7.576
7.545
7.542
7.537
7.526
7.521
7.518
7.508
7.505
7.500
7.264
4.862
4.845
4.829
4.235
4.218
3.844
3.807
1.628
0.000
O
HO
P(O)(Ph)$_2$
1.07
0.06
0.94
2.00
1.97
10
8
6
4
2
0 PPM

**2b**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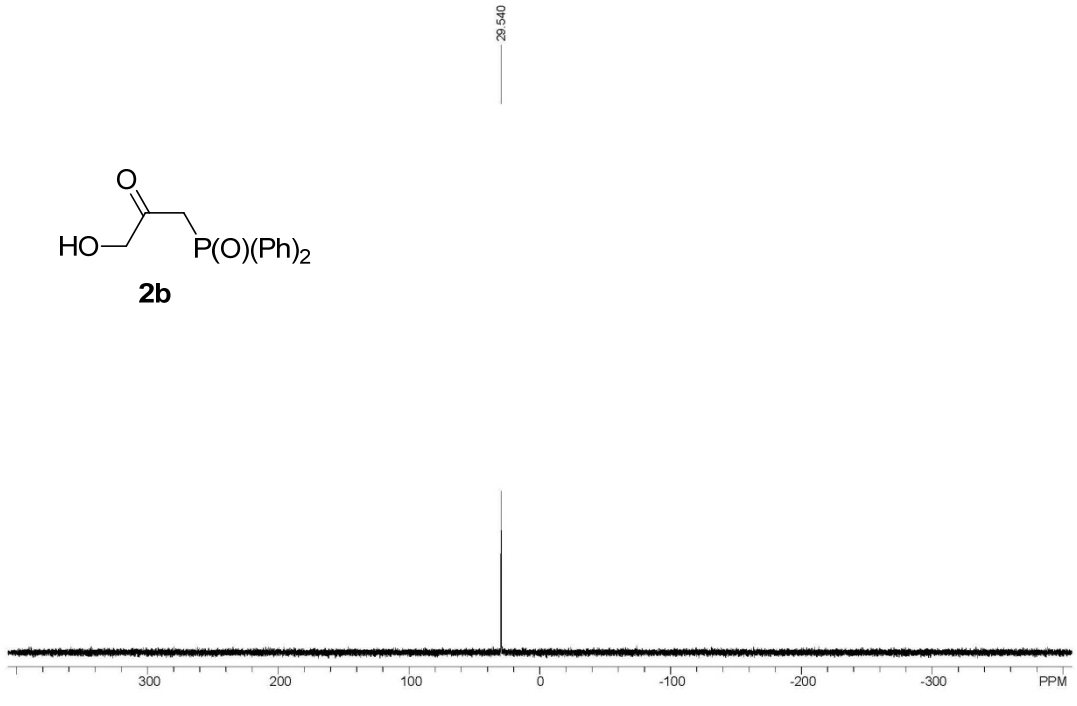
205.106
132.708
132.673
131.302
130.838
130.740
130.262
129.004
128.885
77.316
77.000
76.677
69.719
44.265
43.717
O
HO
P(O)(Ph)2
200
150
100
50
PPM

**2b**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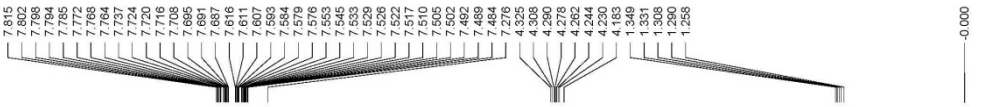
O
HO
P(O)(Ph)2
300
200
100
0
-100
-200
-300
PPM

**2b**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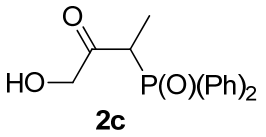
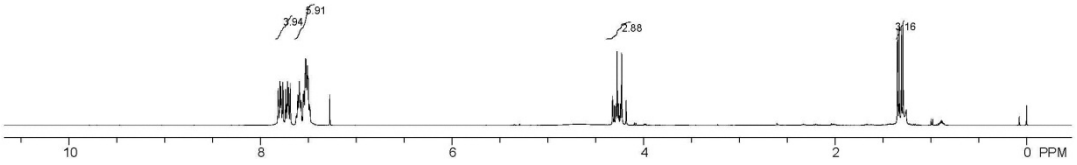
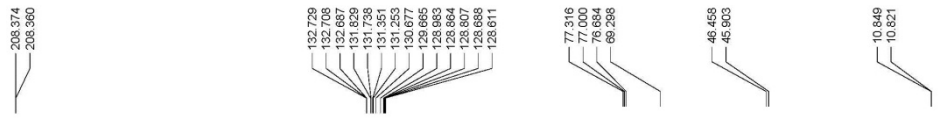
7.802
7.798
7.794
7.785
7.772
7.768
7.764
7.737
7.724
7.720
7.716
7.708
7.695
7.691
7.687
7.616
7.611
7.607
7.593
7.584
7.579
7.576
7.553
7.545
7.533
7.529
7.526
7.522
7.517
7.510
7.505
7.502
7.492
7.489
7.484
7.276
4.325
4.308
4.290
4.278
4.262
4.244
4.200
4.183
1.349
1.331
1.308
1.290
1.258
-0.000


O
HO
P(O)(Ph)2

**2c**


3.94
5.91
2.88
3.16
10
8
6
4
2
0 PPM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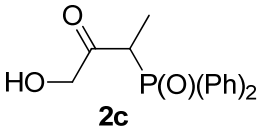
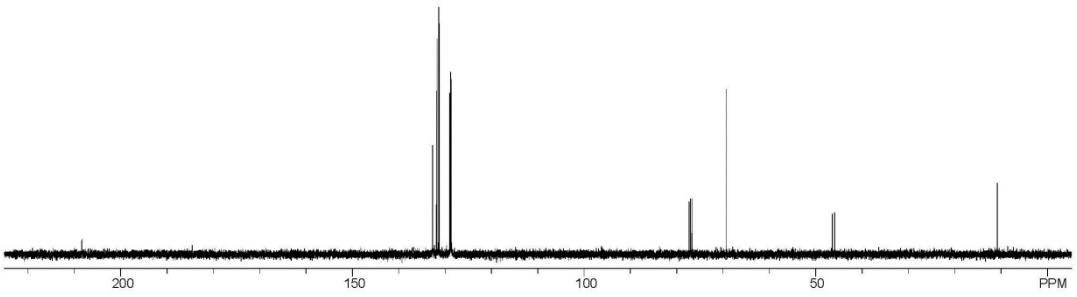
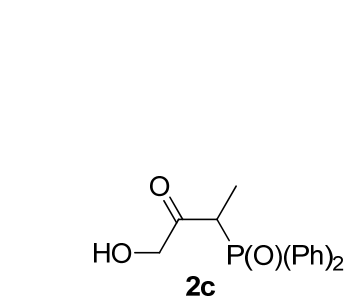
208.360
132.729
132.708
132.687
131.829
131.738
131.351
131.253
130.677
129.665
128.983
128.864
128.807
128.688
128.611
77.316
77.000
76.684
69.298
46.458
45.903
10.849
10.821

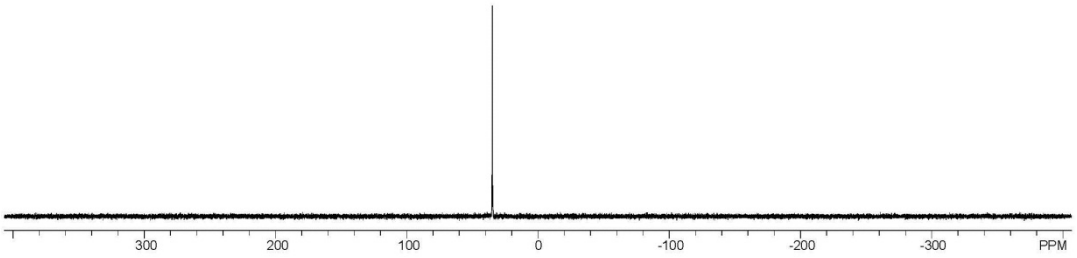

O
HO
P(O)(Ph)2

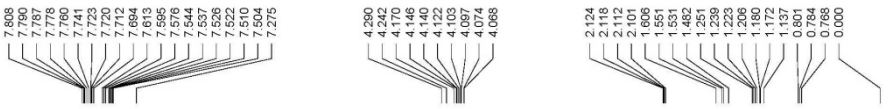
**2c**


200
150
100
50
PPM


34.776
O
HO
P(O)(Ph)2

**2c**


300
200
100
0
-100
-200
-300
PPM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7.720
7.712
7.694
7.613
7.585
7.576
7.544
7.537
7.526
7.522
7.510
7.504
7.275
4.290
4.242
4.170
4.146
4.140
4.122
4.103
4.097
4.074
4.068
2.124
2.118
2.112
2.101
1.606
1.551
1.531
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1.180
1.172
1.137
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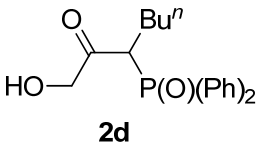
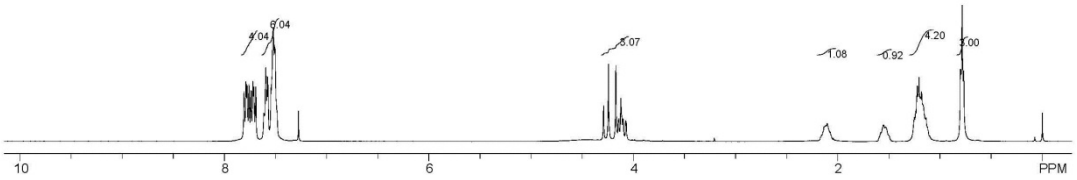
0.000


O
Bu$^n$
HO
P(O)(Ph)2

**2d**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1.08
0.92
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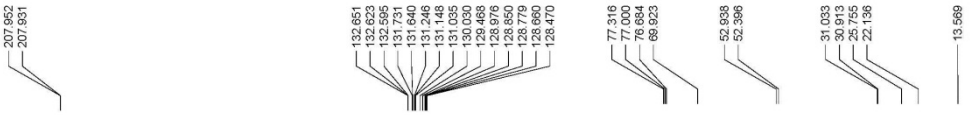
3.00
10
8
6
4
2
PPM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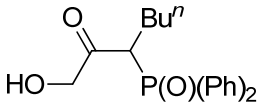
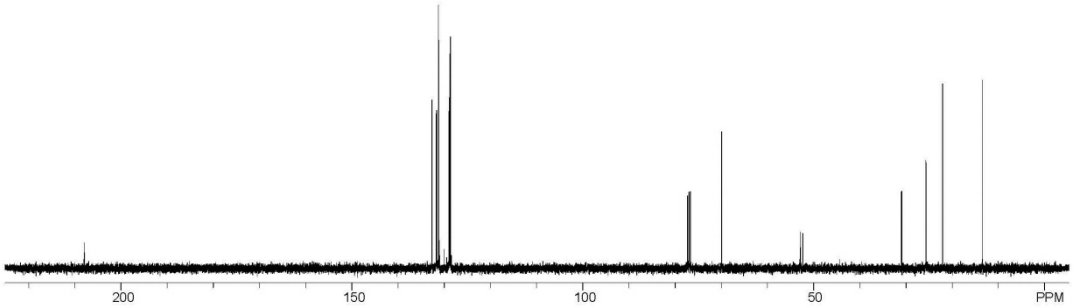
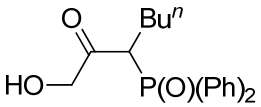

O
Bu$^n$
HO
P(O)(Ph)$_2$

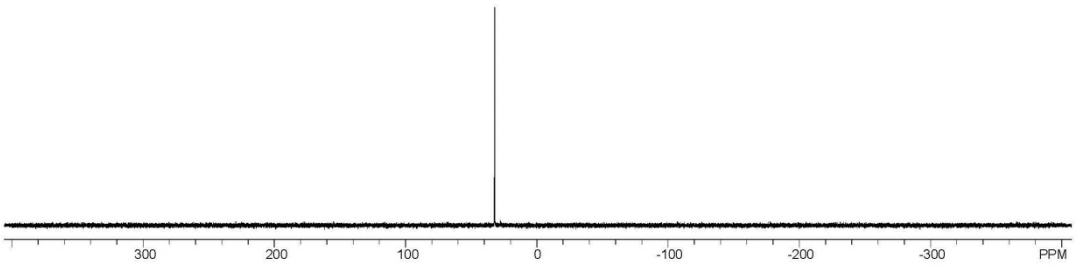
**2d**


200
150
100
50
PPM


32.163


O
Bu$^n$
HO
P(O)(Ph)$_2$

**2d**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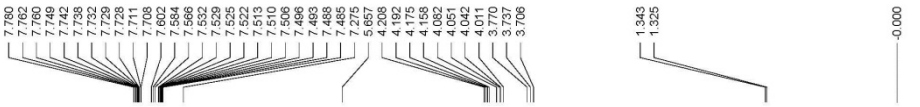
200
100
0
-100
-200
-300
PPM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7.532
7.529
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7.513
7.510
7.506
7.496
7.493
7.488
7.485
7.275
5.657
4.208
4.192
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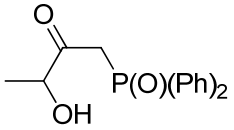
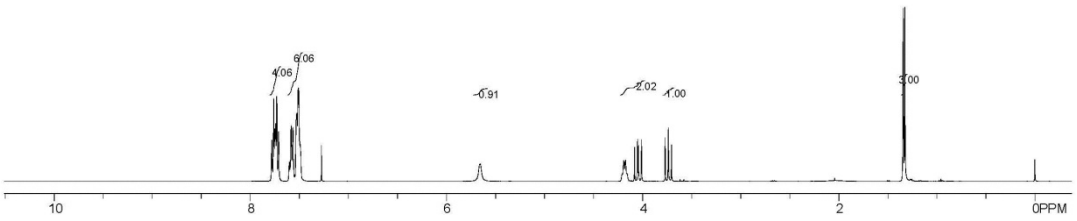
1.325
0.000


O
P(O)(Ph)2
OH

**2e**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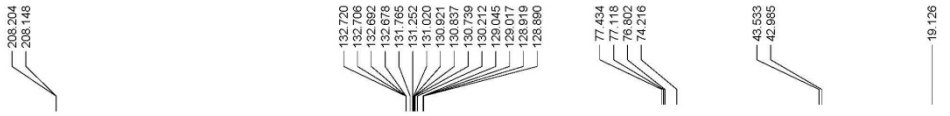
6.06
0.91
2.02
1.00
3.00
10
8
6
4
2
0PPM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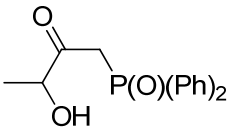
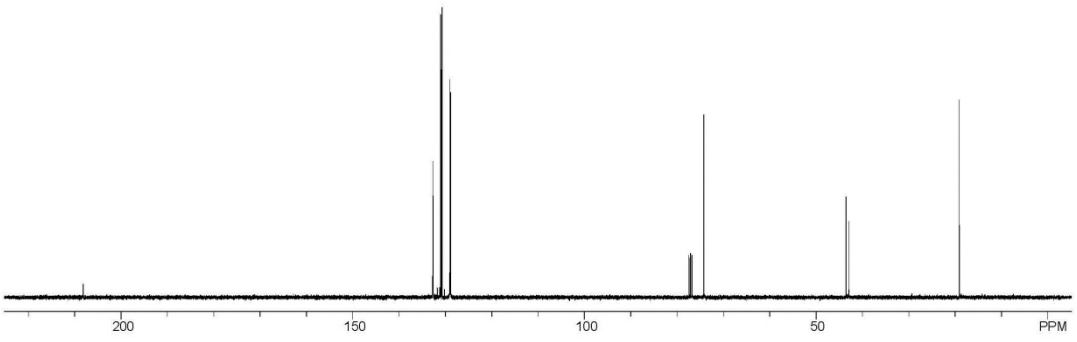
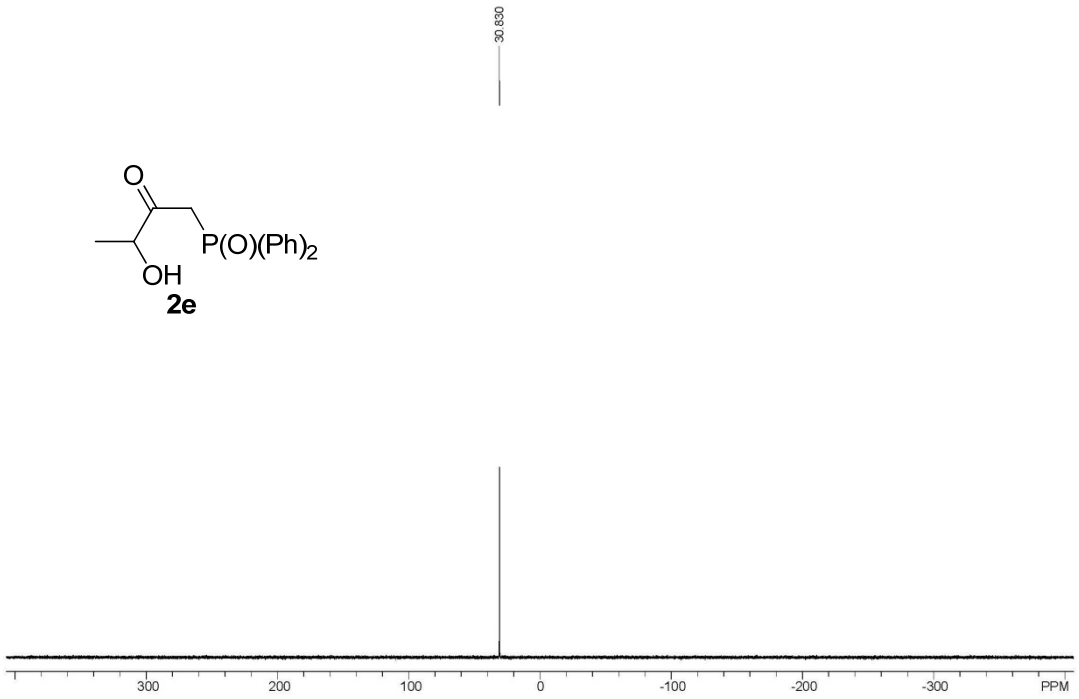
208.148
132.720
132.706
132.692
132.678
131.765
131.252
131.020
130.921
130.837
130.739
130.212
129.045
129.017
128.919
128.890
77.434
77.118
76.802
74.216
43.533
42.985
19.126

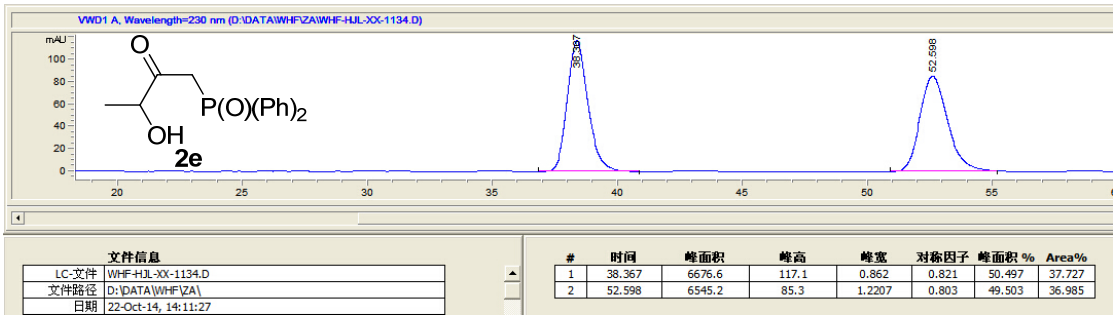

O
P(O)(Ph)2
OH

**2e**


200
150
100
50
PPM




**2e** HPLC analysis report

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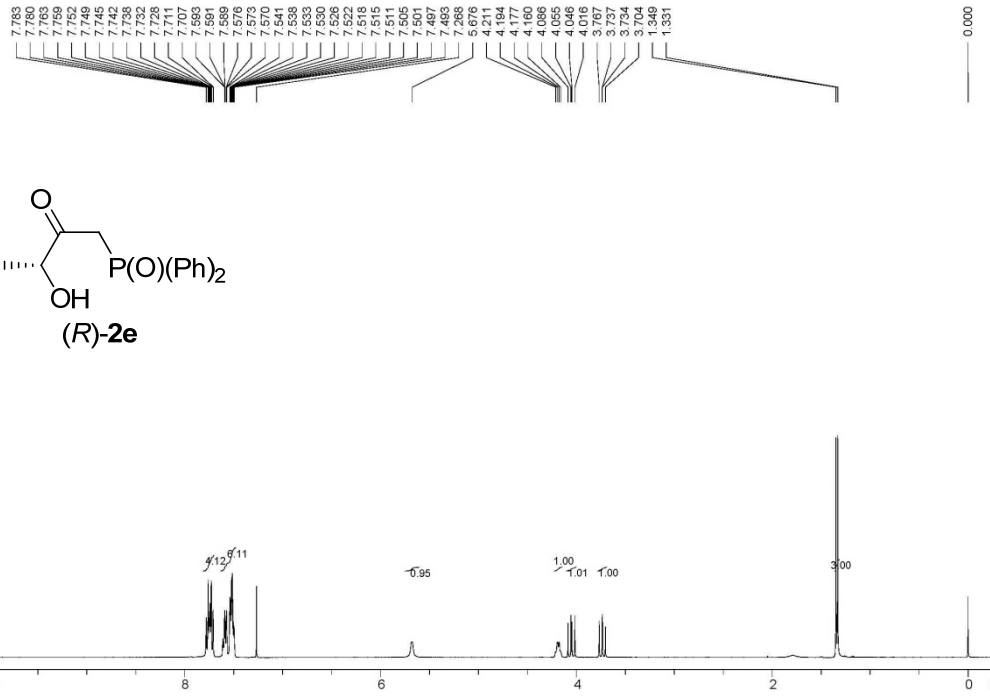
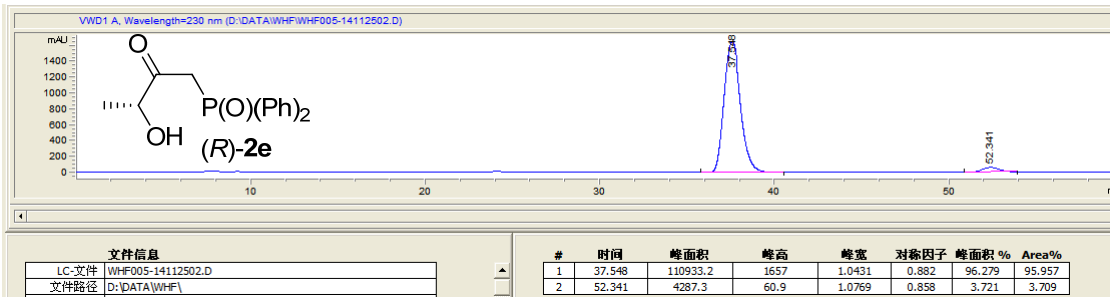
|---|---|
| LC-文件 | WHF-HJL-XX-1134.D |
| 文件路径 | D:\DATA\WHF\ZA\ |
| 日期 | 22-Oct-14, 14:11:27 |

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % | Area% |
|---|---|---|---|---|---|---|---|
| 1 | 38.367 | 6676.6 | 117.1 | 0.862 | 0.821 | 50.497 | 37.727 |
| 2 | 52.598 | 6545.2 | 85.3 | 1.2207 | 0.803 | 49.503 | 36.985 |

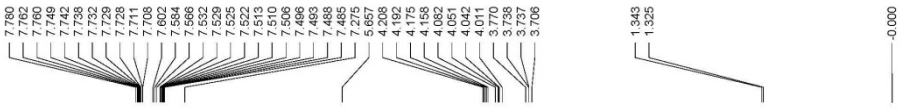


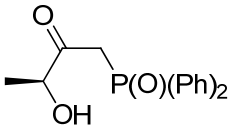

(*R*)-**2e** HPLC analysis report



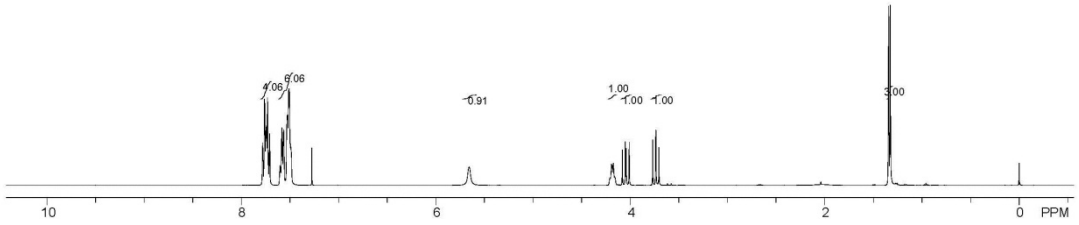

| 文件信息 | |
|---|---|
| LC-文件 | WHF005-14112502.D |
| 文件路径 | D:\DATA\WHF\ |

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % | Area% |
|---|---|---|---|---|---|---|---|
| 1 | 37.548 | 110933.2 | 1657 | 1.0431 | 0.882 | 96.279 | 95.957 |
| 2 | 52.341 | 4287.3 | 60.9 | 1.0769 | 0.858 | 3.721 | 3.709 |

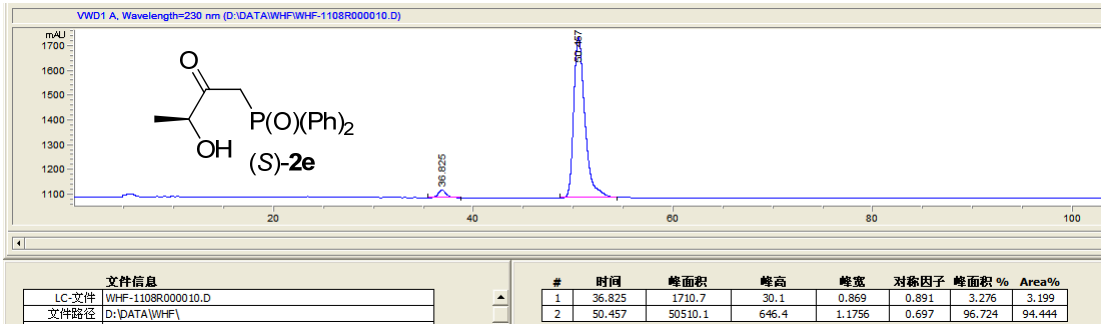



(*S*)-**2e**

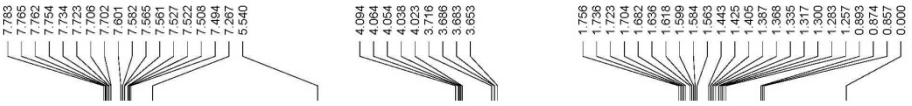


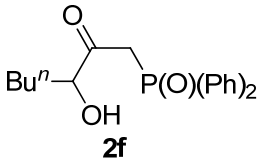

(*S*)-**2e** HPLC analysis report



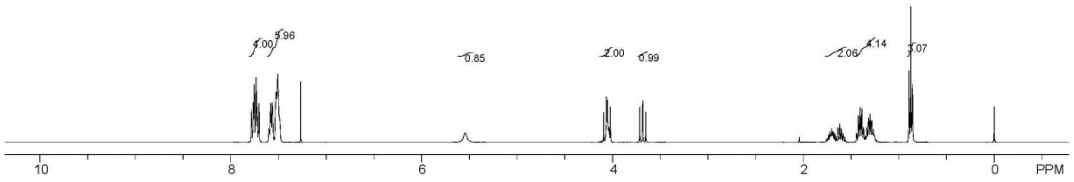

| 文件信息 | |
|---|---|
| LC-文件 | WHF-1108R000010.D |
| 文件路径 | D:\DATA\WHF\ |

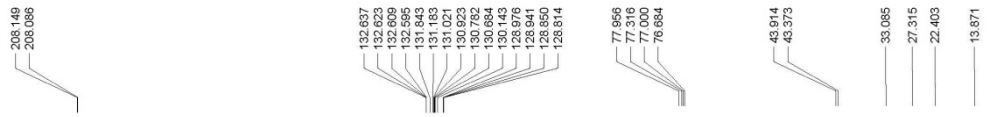
| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % | Area% |
|---|---|---|---|---|---|---|---|
| 1 | 36.825 | 1710.7 | 30.1 | 0.869 | 0.891 | 3.276 | 3.199 |
| 2 | 50.457 | 50510.1 | 646.4 | 1.1756 | 0.697 | 96.724 | 94.444 |

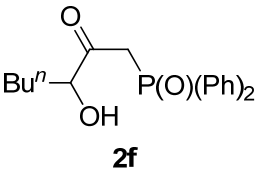

7.783
7.765
7.762
7.754
7.734
7.723
7.706
7.702
7.601
7.582
7.565
7.561
7.527
7.522
7.508
7.494
7.267
5.540
4.094
4.084
4.064
4.044
4.038
4.023
3.716
3.686
3.683
3.653
1.756
1.736
1.723
1.704
1.682
1.636
1.618
1.598
1.584
1.563
1.443
1.425
1.405
1.387
1.368
1.335
1.317
1.300
1.283
1.257
0.893
0.874
0.857
0.000


O
Bu$^n$
P(O)(Ph)$_2$
OH

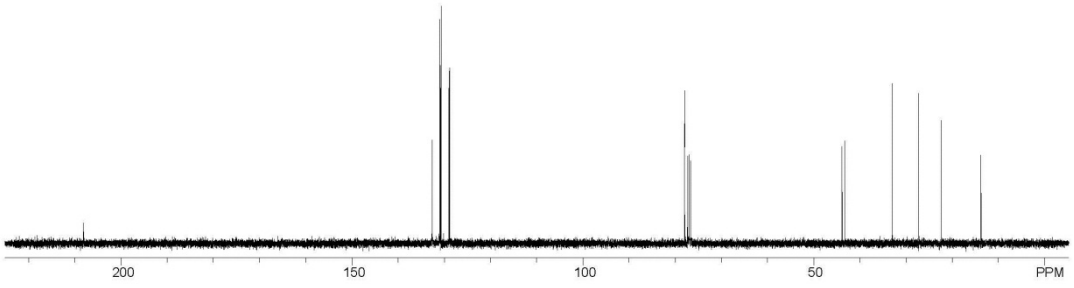
**2f**

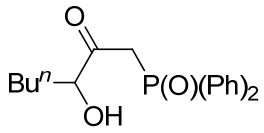

1.00
5.96
0.85
1.00
0.99
2.06
4.14
3.07
10
8
6
4
2
0
PPM


208.149
208.086
132.637
132.623
132.609
132.595
131.643
131.183
131.021
130.923
130.782
130.684
130.143
128.976
128.841
128.850
128.814
77.956
77.316
77.000
76.684
43.914
43.373
33.085
27.315
22.403
13.871


O
Bu$^n$
P(O)(Ph)$_2$
OH

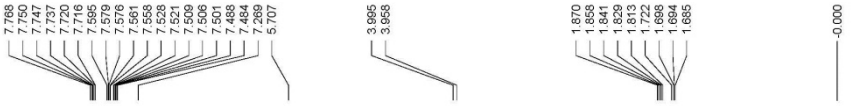
**2f**

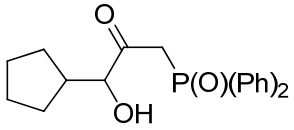

200
150
100
50
PPM


O
Bu$^n$
P(O)(Ph)$_2$
OH

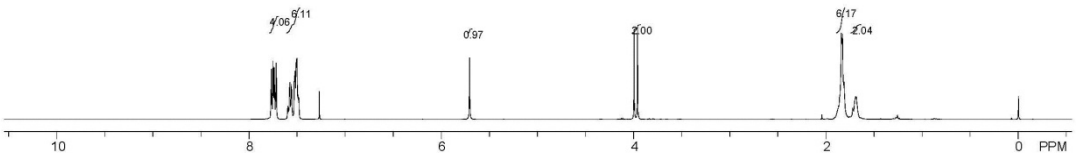
**2f**

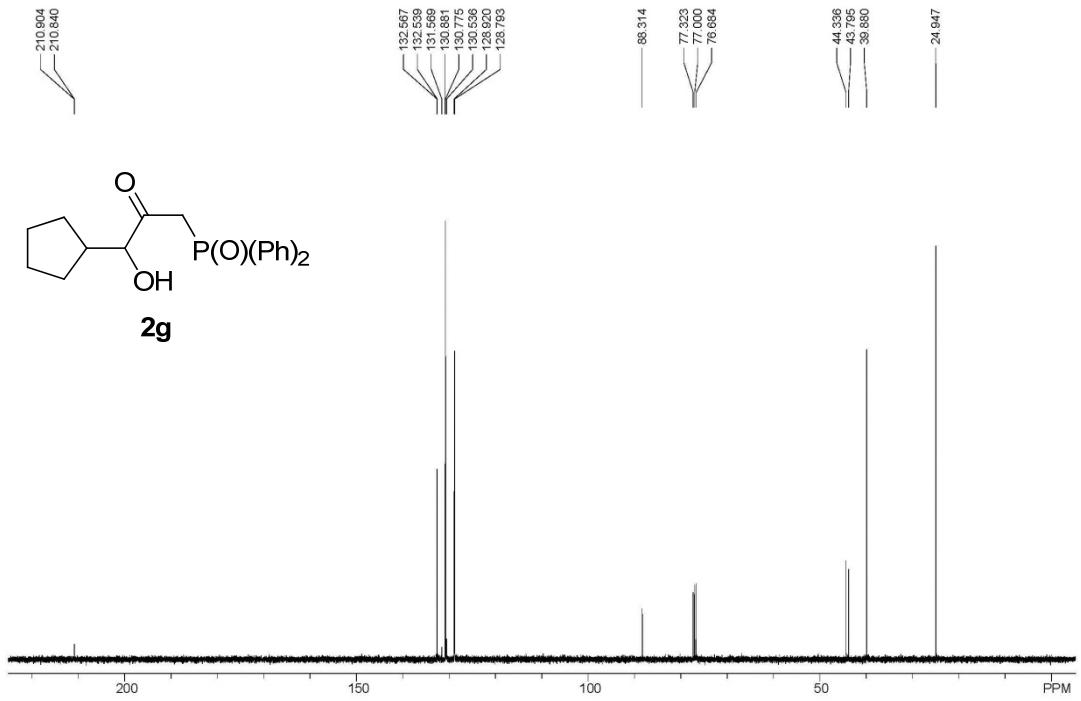

31.006
300
200
100
0
-100
-200
-300
PPM


7.768
7.750
7.747
7.737
7.720
7.716
7.595
7.578
7.576
7.561
7.558
7.528
7.521
7.509
7.506
7.501
7.488
7.484
7.269
5.707
3.995
3.968
1.870
1.858
1.841
1.829
1.813
1.722
1.698
1.694
1.685
0.000

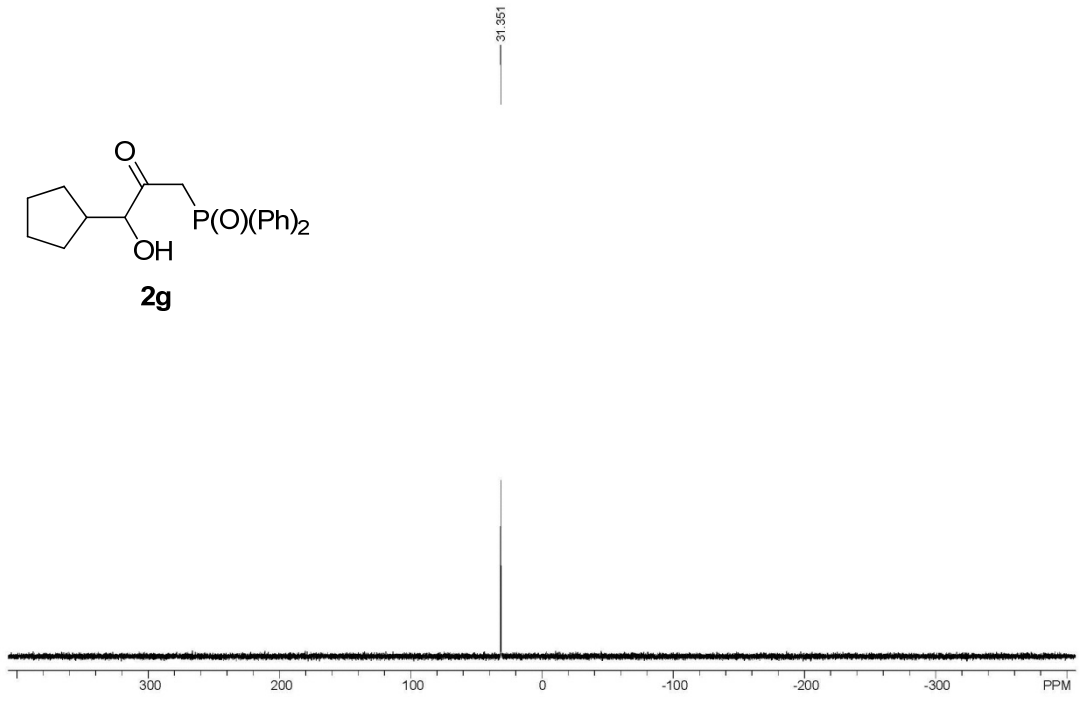

O
P(O)(Ph)$_2$
OH

**2g**

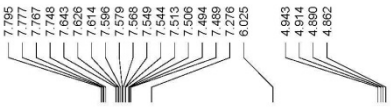

4.06
6.11
0.97
2.00
6.17
2.04
10
8
6
4
2
0
PPM

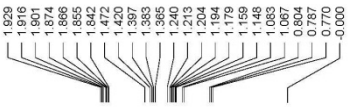

210.904
210.840
132.567
132.539
131.589
131.571
130.771
130.575
129.596
129.020
128.793
88.314
77.323
77.000
76.684
44.336
43.795
39.880
24.947
O
P(O)(Ph)2
OH
200
150
100
50
PPM

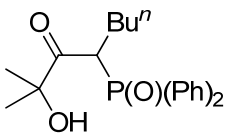
**2g**


31.351
O
P(O)(Ph)2
OH
300
200
100
0
-100
-200
-300
PPM

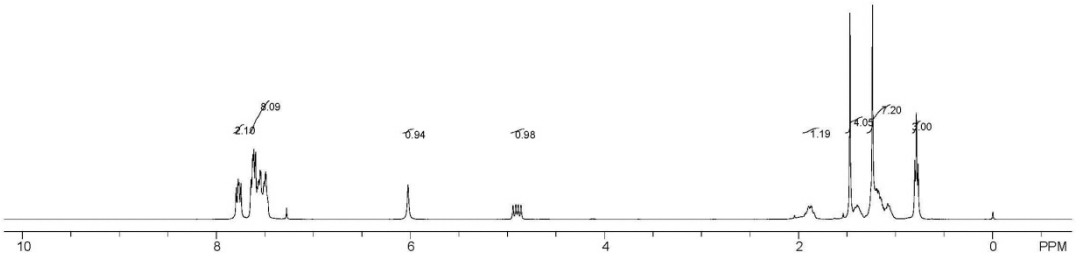
**2g**

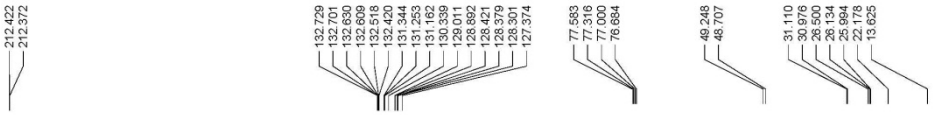

7.795
7.777
7.767
7.748
7.643
7.626
7.614
7.596
7.579
7.568
7.549
7.544
7.513
7.506
7.494
7.489
7.276
6.025
4.943
4.914
4.890
4.862


1.929
1.916
1.901
1.874
1.866
1.855
1.842
1.472
1.420
1.397
1.383
1.365
1.240
1.213
1.204
1.194
1.179
1.159
1.148
1.083
1.067
0.804
0.787
0.770
-0.000


O
Bu$^n$
P(O)(Ph)$_2$
OH

**2h**


2.09
2.16
0.94
0.98
1.19
4.05
7.20
3.00
10
8
6
4
2
0
PPM


212.422
212.372
132.729
132.701
132.630
132.609
132.518
132.420
131.344
131.253
131.162
130.339
129.011
128.892
128.421
128.379
128.301
127.374
77.583
77.316
77.000
76.684
49.248
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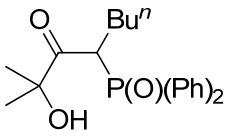
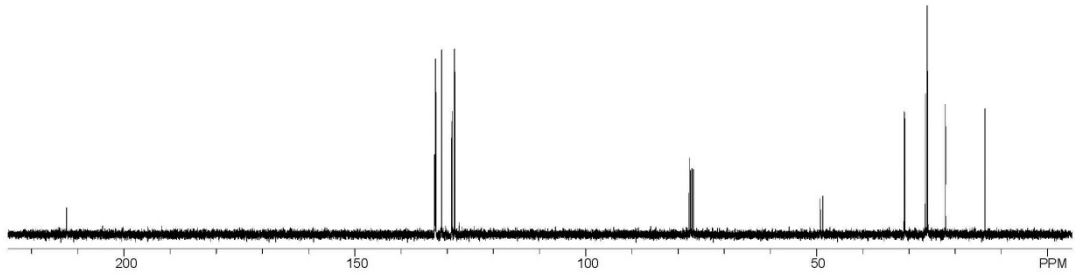
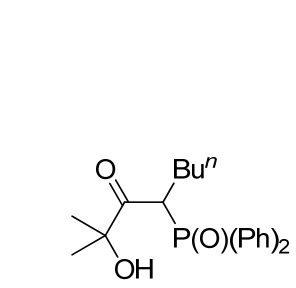
30.976
26.500
26.134
25.994
22.178
13.825


O
Bu$^n$
P(O)(Ph)$_2$
OH

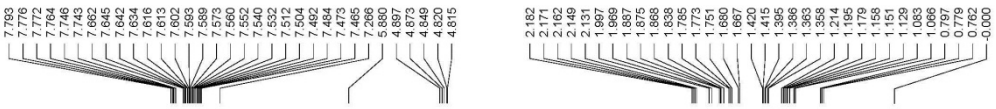
**2h**

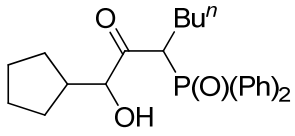

200
150
100
50
PPM


O
Bu$^n$
P(O)(Ph)$_2$
OH

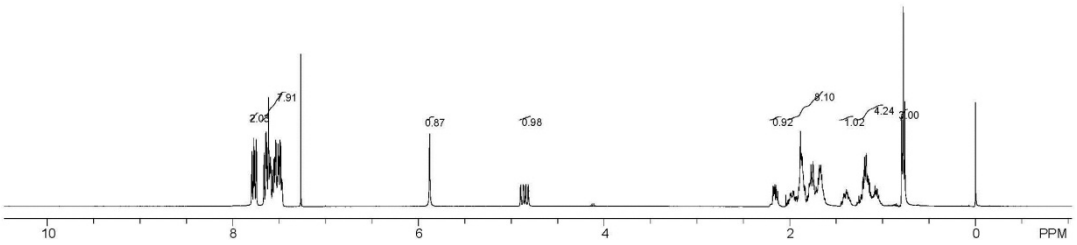
**2h**

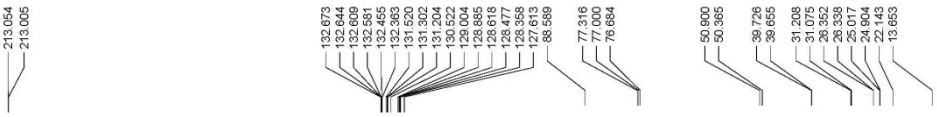

32.306
300
200
100
0
-100
-200
-300
PPM

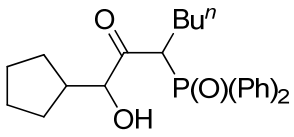

7.793
7.776
7.772
7.764
7.746
7.743
7.662
7.645
7.642
7.634
7.616
7.613
7.602
7.593
7.589
7.573
7.560
7.552
7.540
7.532
7.512
7.504
7.492
7.484
7.473
7.465
7.266
5.880
4.897
4.873
4.849
4.820
4.815
2.162
2.171
2.162
2.149
2.131
1.997
1.989
1.887
1.875
1.868
1.838
1.795
1.773
1.751
1.680
1.667
1.420
1.415
1.395
1.386
1.363
1.358
1.214
1.195
1.179
1.158
1.151
1.129
1.083
1.066
0.797
0.779
0.762
0.000


O
Bu$^n$
P(O)(Ph)$_2$
OH

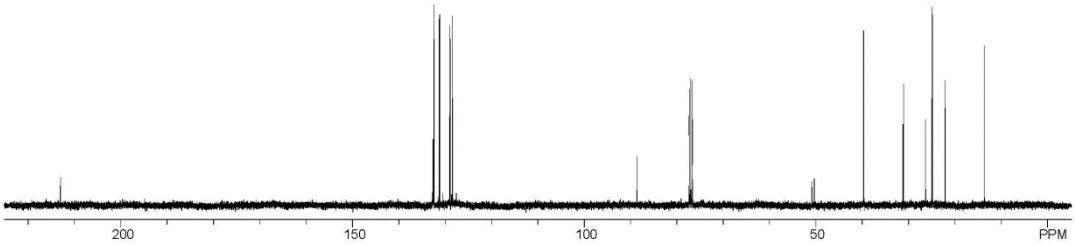
**2i**


2.05
7.91
0.87
0.98
0.92
8.10
1.02
4.24
3.00
10
8
6
4
2
0
PPM

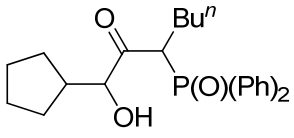

213.054
213.005
132.673
132.644
132.609
132.581
132.455
132.363
131.520
131.302
131.204
130.522
129.004
128.885
128.618
128.477
128.358
127.613
88.589
77.316
77.000
76.684
50.900
50.365
39.726
39.665
31.208
31.075
28.352
28.338
25.017
24.904
22.443
13.653


O
Bu$^n$
P(O)(Ph)$_2$
OH

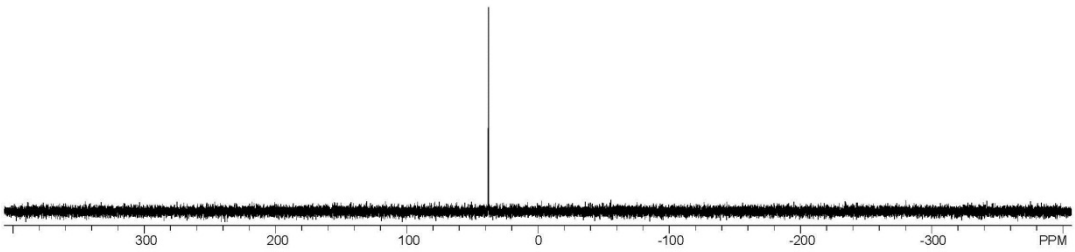
**2i**


200
150
100
50
PPM


37.778


O
Bu$^n$
P(O)(Ph)$_2$
OH

**2i**


300
200
100
0
-100
-200
-300
PPM

## References

1 Romão, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.***1997**, *97*, 3197.

2 Guo, H.; Qian, R.; Guo, Y.; Ma, S. *J. Org. Chem*. **2008**, *73*, 7934.

3 He, G.; Guo, H,; Qian, R.; Guo, Y.; Fu, C.; Ma, S. *Tetrahedron*. **2009**, *65*, 4877.