Electronic Supplementary Information

Wet and Dry Processes for the Selective Transformation of Phosphonates to Phosphonic Acids Catalyzed by Brønsted Acids

Chunya Li,[a,b] Yuta Saga,[c] Shun-ya Onozawa, [a] Shu Kobayashi, [a] Kazuhiko Sato, [a] Norihisa Fukaya, [a] and Li-Biao Han*[a,b]

[a] *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan*

[b] *Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan*

[c] *New Products Development Laboratory, Maruzen Petrochemical Co., Ltd., Ichihara, Chiba 290-8503, Japan*

E-mail: libiao-han@aist.go.jp

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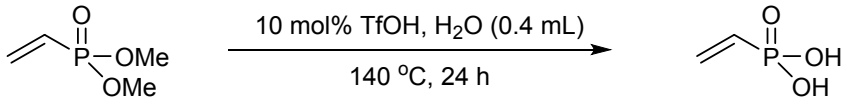
1. Typical Procedures for the Transformation of Phosphonates to Phosphonic Acids Catalyzed by Brønsted Acids

1.1. A typical procedure for TfOH-catalyzed hydrolysis of phosphonate esters in H_2O

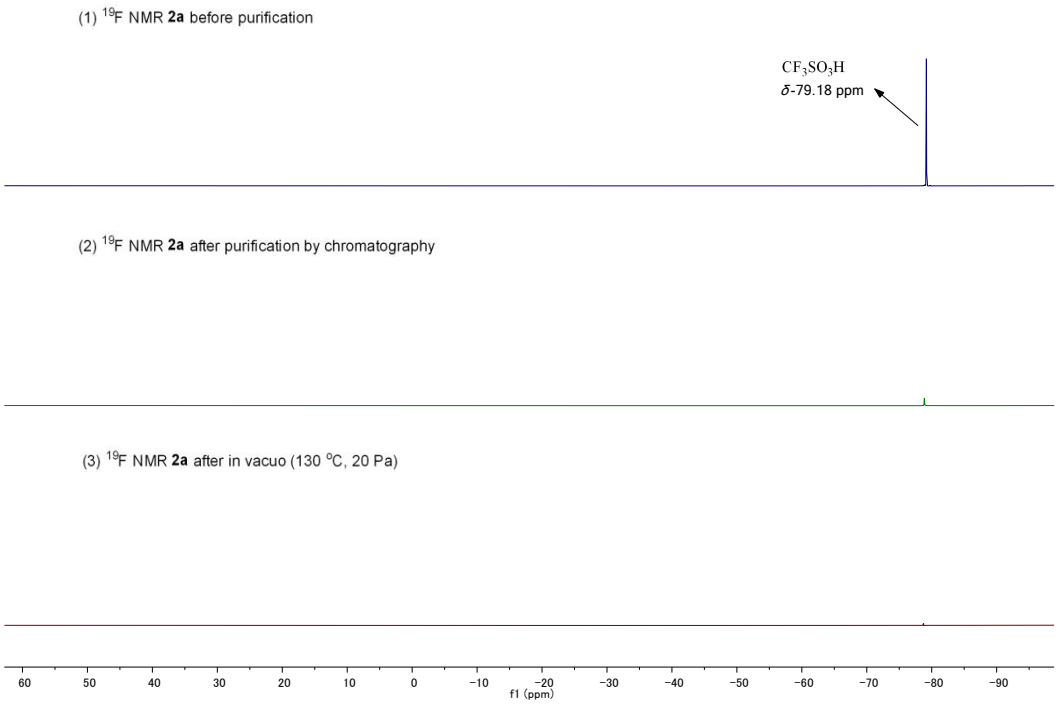


1a
5 mmol

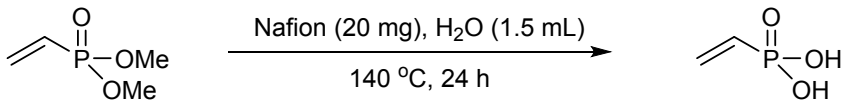
2a, 491.5 mg
91% isolated yield

To a 10 mL Schlenk tube in air was added dimethyl vinylphosphonate **1a** (0.59 mL, 5 mmol), H_2O (0.4 mL) and trifluoromethanesulfonic acid (44.2 μL, 10 mol%). The tube was heated at 140 °C using a heating aluminum block for 24 h and **1a** was consumed as confirmed by ^{31}P NMR spectroscopy. After removal of the volatile, the residues (light brown oil) were passed through a short silica column (200-300 mesh, dichloromethane/methanol = 4:1 as eluent) to obtain pure product **2a** (colorless oil) in 91% isolated yield (491.5 mg) after removing the volatiles under vacuum (ca 20 Pa) at 130 °C overnight.

^{19}F NMR (377 MHz, D_2O) (2a) before and after purification



1.2. 10 mmol-Scale hydrolysis of dimethyl vinylphosphonate with H_2O using Nafion as catalyst

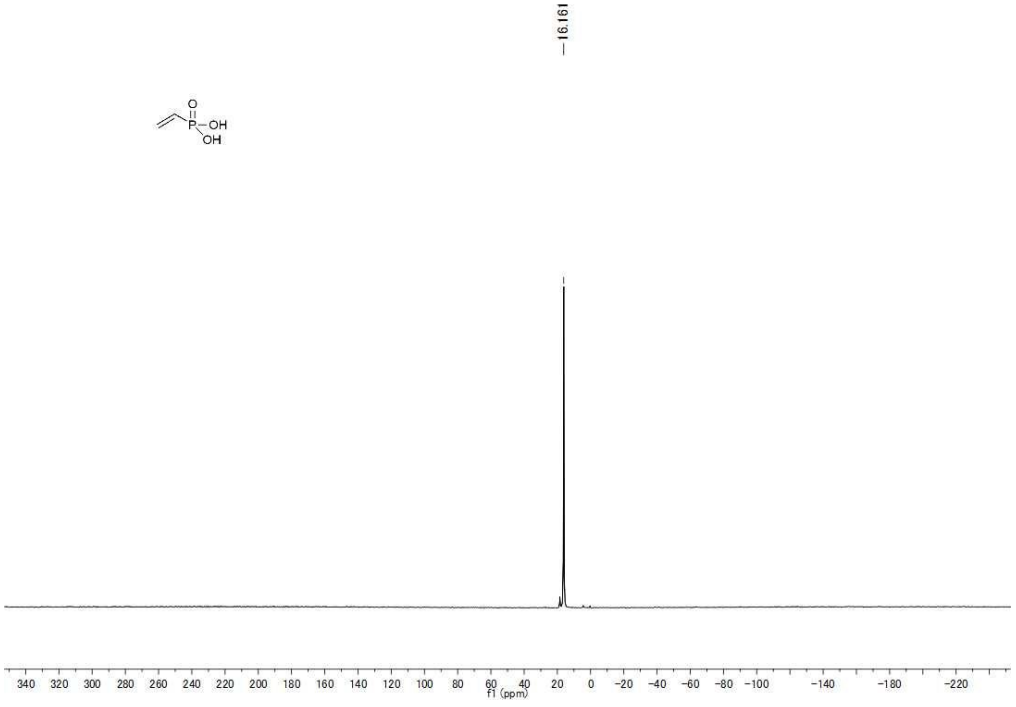


1a
10 mmol

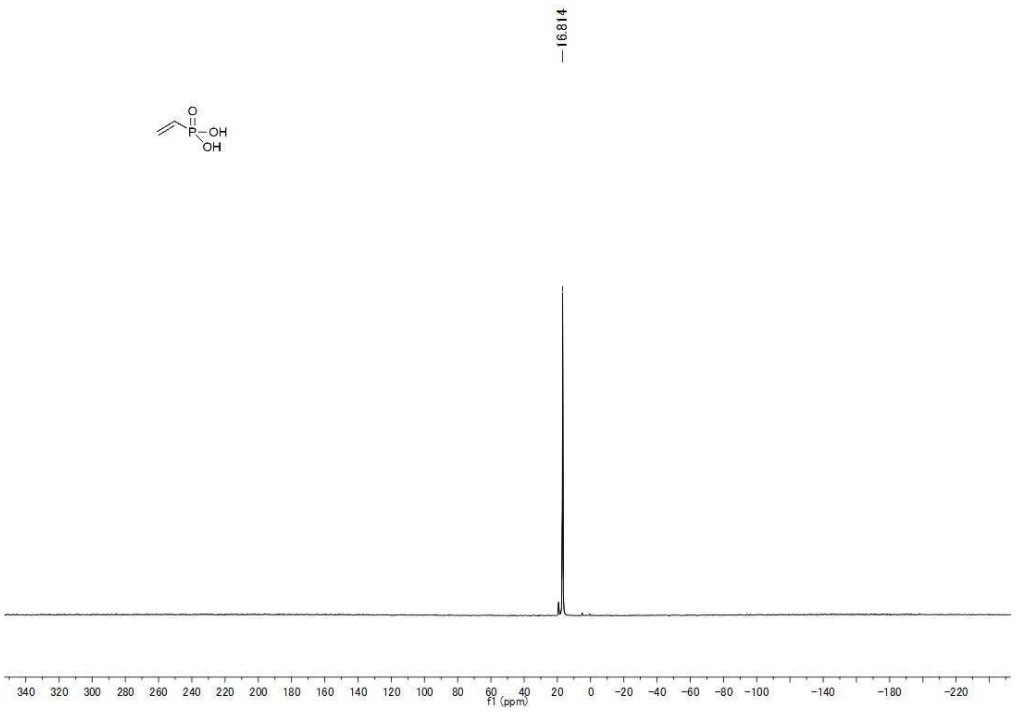
2a, 1.03 g
95% isolated yield

To a 10 mL Schlenk tube was added dimethyl vinylphosphonate **1a** (1.19 mL, 10 mmol), H_2O (1.5 mL) and Nafion (20 mg). The tube was then heated at 140 °C for 24 h. Pure **2a** was obtained after filtration removing Nafion and evaporation under vaccum removing volatiles in 95% isolated yield (1.03 g).

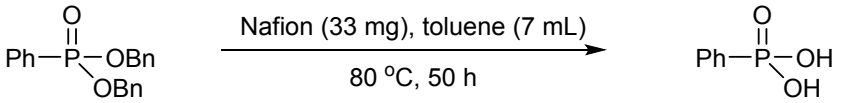
^{31}P NMR (162 MHz, H_2O) (2a) before filtration



^{31}P NMR (162 MHz, D_2O) (2a) after filtration



1.3. 10 mmol-Scale debenzylation of phosphonates in toluene using Nafion as catalyst

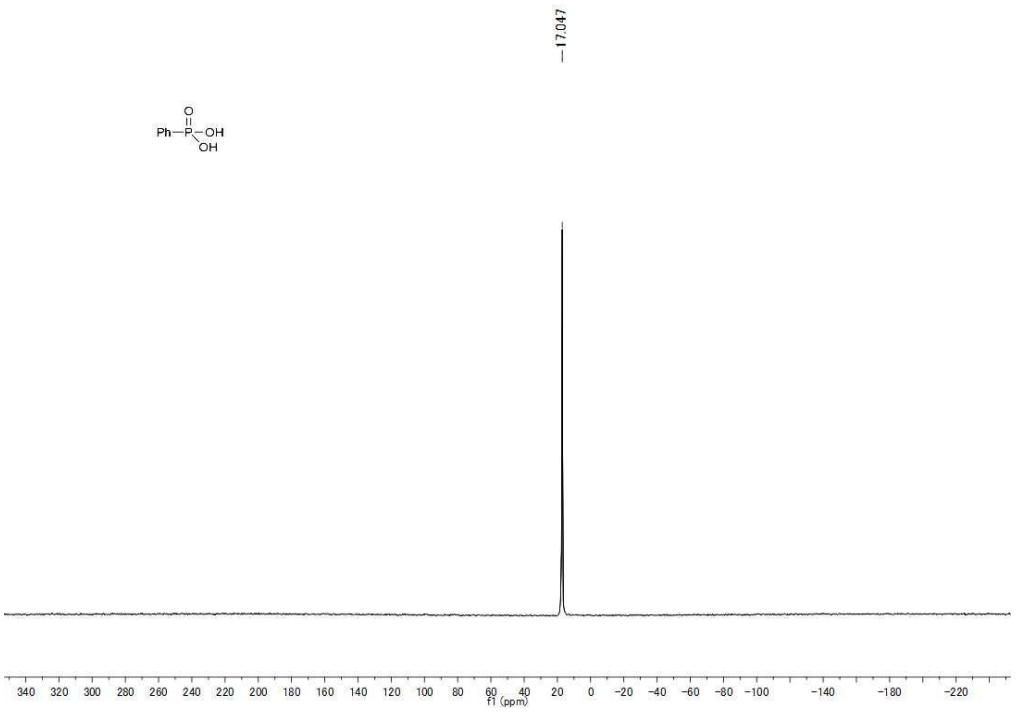


1j
10 mmol

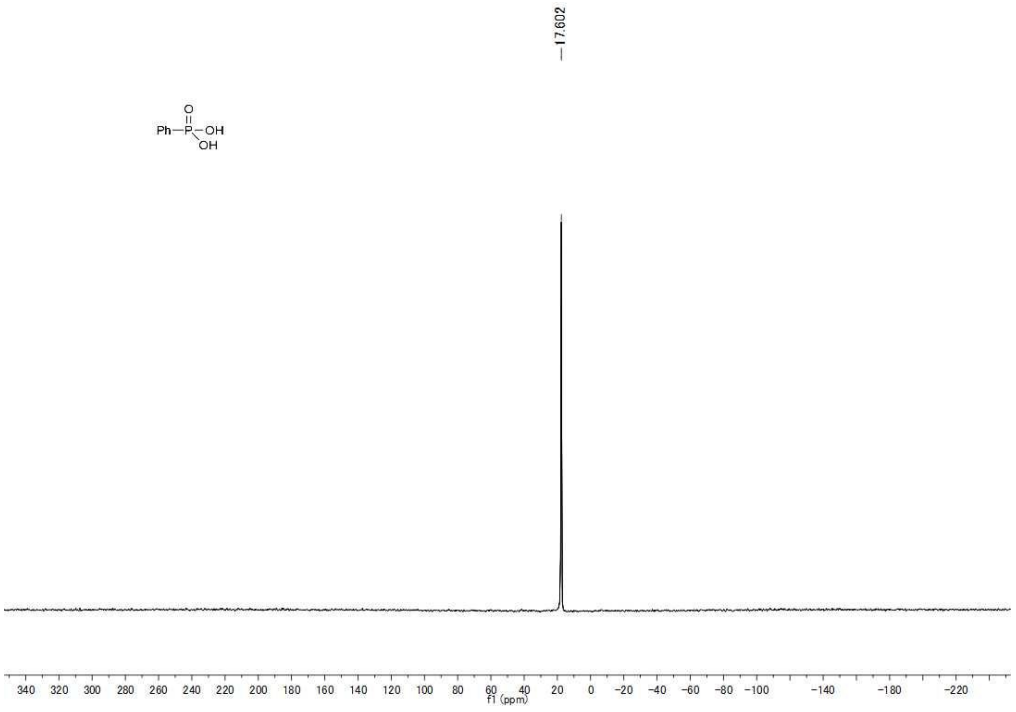
2g, 1.48 g
94% isolated yield

To a 25 mL Schlenk tube was added dibenzyl phenylphosphonate **1j** (3.4 g, 10 mmol), Nafion (33 mg) and toluene (7 mL) under Ar. The tube was then heated at 80 °C for 50 h. Water was added to dissolve the product precipitated out and then Nafion was removed by filtration. The aqua solution was collected and volatiles were pumped off under vacuum to give pure **2g** as a white solid 94% isolated yield (1.48g).

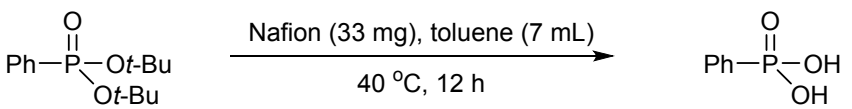
^{31}P NMR (162 MHz, MeOH) (2g) before filtration



^{31}P NMR (162 MHz, D_2O) (2g) after filtration



1.4. 10 mmol-Scale de-*tert* butylation of phosphonates in toluene catalyzed by Nafion



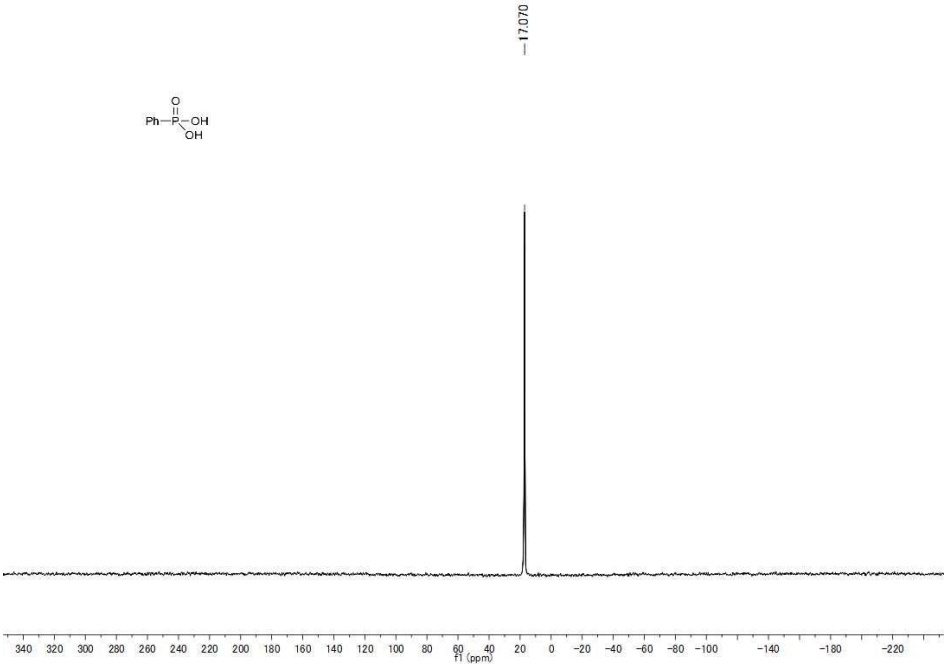
1q
10 mmol

2g, 1.53 g
97% isolated yield

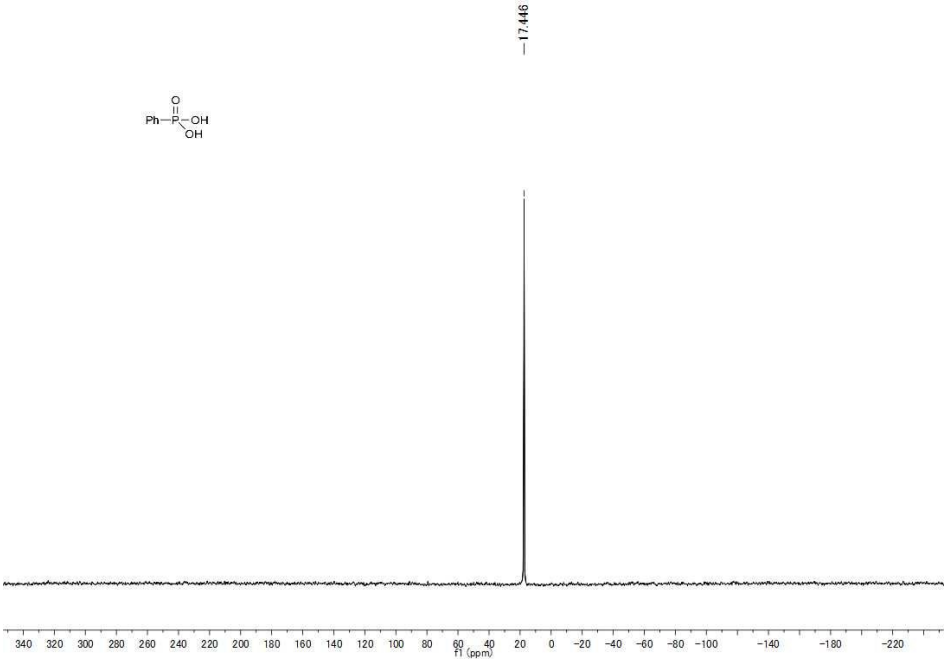
To a 25 mL Schlenk tube was added di*tert*-butyl phenylphosphonate **1q** (2.7 g, 10 mmol),

Nafion (33 mg) and toluene (7 mL) under Ar. The tube was then heated at 40 °C for 12 h. The product precipitated as a white solid. 7 mL MeOH was added to dissolve the white solid. Pure **2g** was obtained after filtration removing Nafion and pumping off the volatiles under vacuum in 97% isolated yield (white solid, 1.53 g).

^{31}P NMR (162 MHz, MeOH) (2g) before filtration

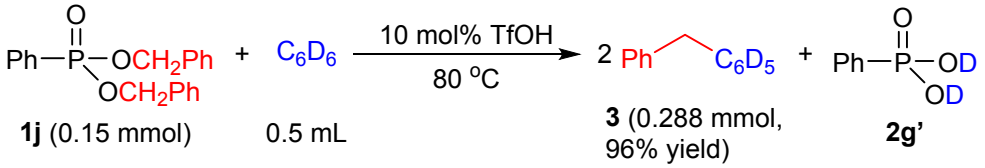


^{31}P NMR (162 MHz, D_2O) (2g) after filtration



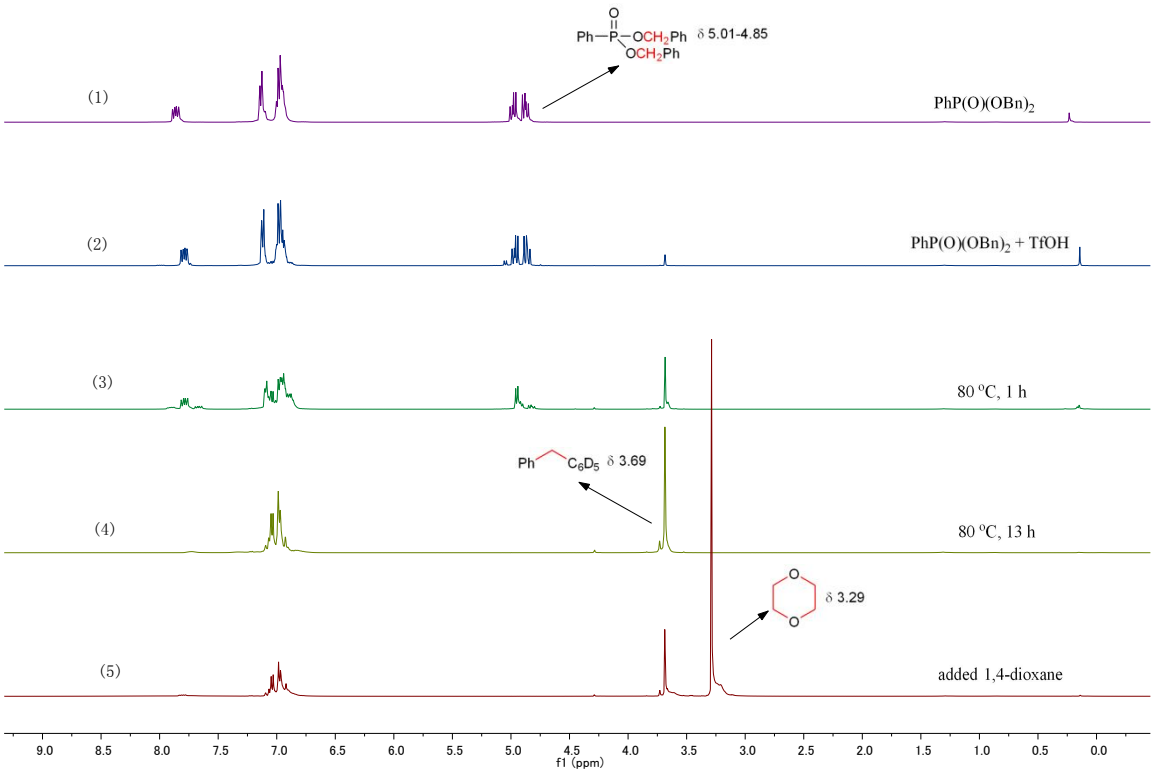
2. Control Experiments of the Mechanistic Studies

2.1. The reaction of dibenzyl phenylphosphonate (1j) in benzene-d_6 catalyzed by TfOH

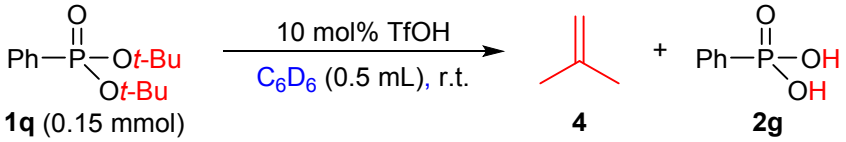


To an NMR tube was added dibenzyl phenylphosphonate **1j** (50.8 mg, 0.15 mmol) and C_6D_6 (0.5 mL), and its ^{1}H NMR was taken. Trifluoromethanesulfonic acid (1.3 μL, 10 mol%) was then added to the NMR tube. The tube was gently shaken at room temperature for ca. 0.5 h, and was subjected to ^{1}H NMR measurement again. The tube was then heated at 80 °C, and its ^{1}H NMR were taken after 1 h and 13 h, respectively. ^{1}H NMR revealed that the reaction completed after 13 h at 80 °C. 1,4-Dioxane (25.7 μL, 0.3 mmol) was added to the NMR tube as an internal standard, and ^{1}H NMR showed that diphenylmethane-d_5 was obtained in 96% yield (0.288 mmol).

Monitored by ^{1}H NMR (400 MHz, C_6D_6) spectroscopy



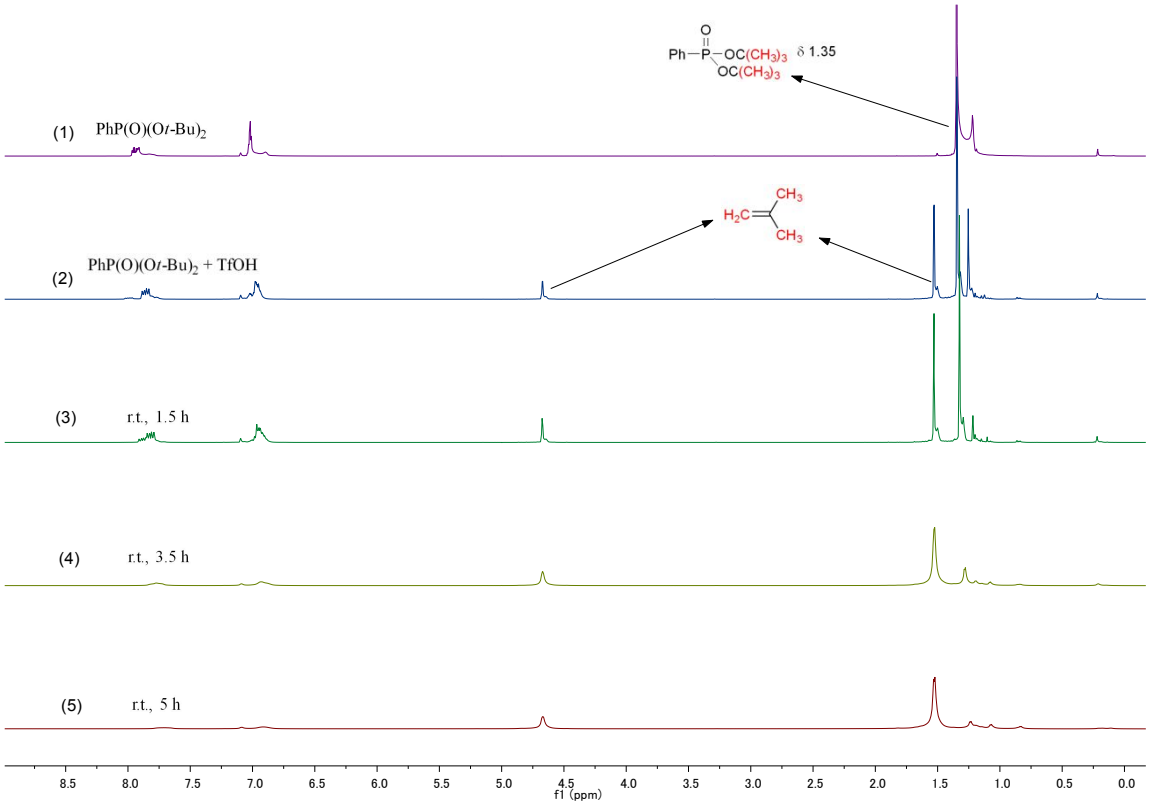
2.2. The de*tert*-butylation of di*tert*-butyl phenylphosphonate (1q) in benzene-d_6 catalyzed by TfOH



1q (0.15 mmol) **4** **2g**

To an NMR tube was added di*tert*-butyl phenylphosphonate **1q** (40.6 mg, 0.15 mmol) and C_6D_6 (0.5 mL) and subjected to ^{1}H NMR measurement. Trifluoromethanesulfonic acid (1.3 μL, 10 mol%) was then added to the NMR tube. The tube was slightly shaken at room temperature and subjected to ^{1}H NMR measurement after 0.5 h, 1.5 h, 3.5 h and 5 h, respectively. ^{1}H NMR showed that the reaction completed after 5 h and isobutene **4** was generated.

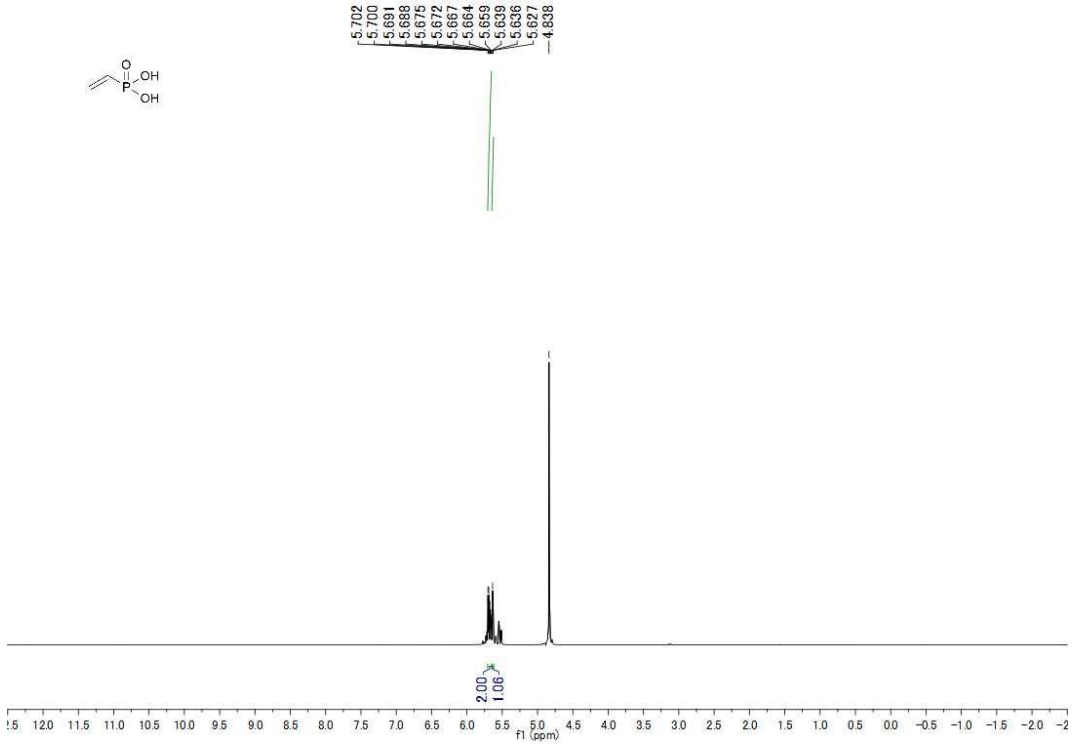
Monitored by ^{1}H NMR (400 MHz, C_6D_6) spectroscopy



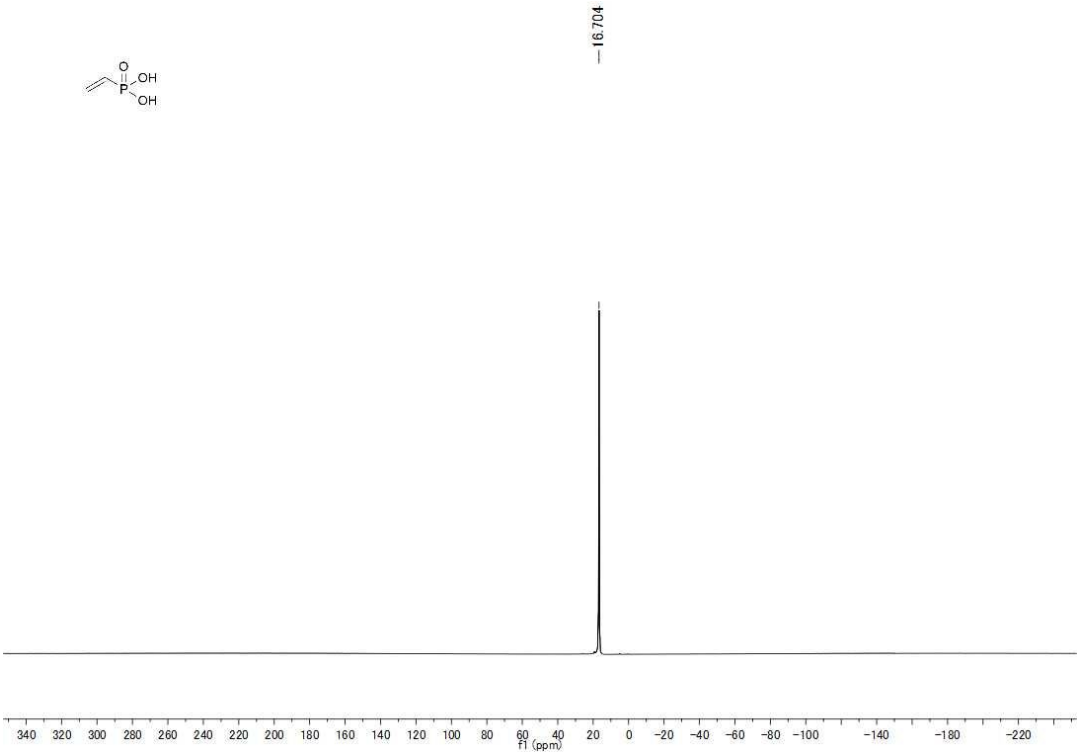
3. Copies of ^{1}H, ^{31}P and ^{13}C NMR Spectra of the Products

Vinylphosphonic acid (2a)

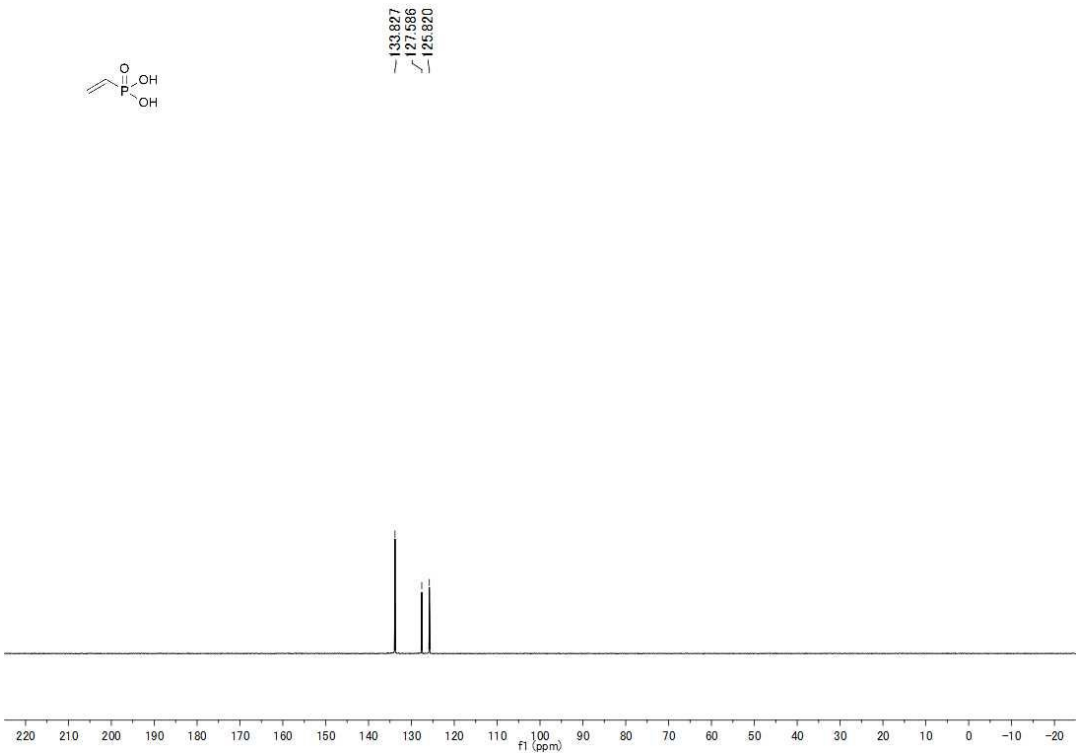
^{1}H NMR (400 MHz, D_2O)



^{31}P NMR (162 MHz, D_2O)

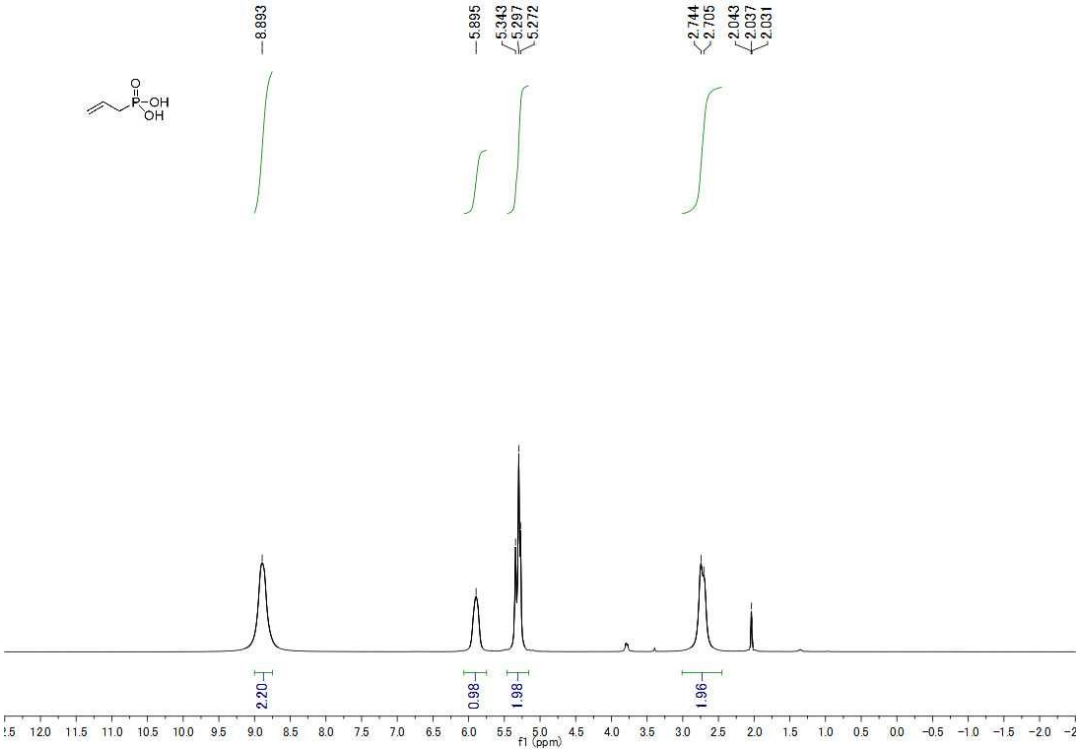


$^{13}C\{1H\}$ NMR (100 MHz, D_2O)

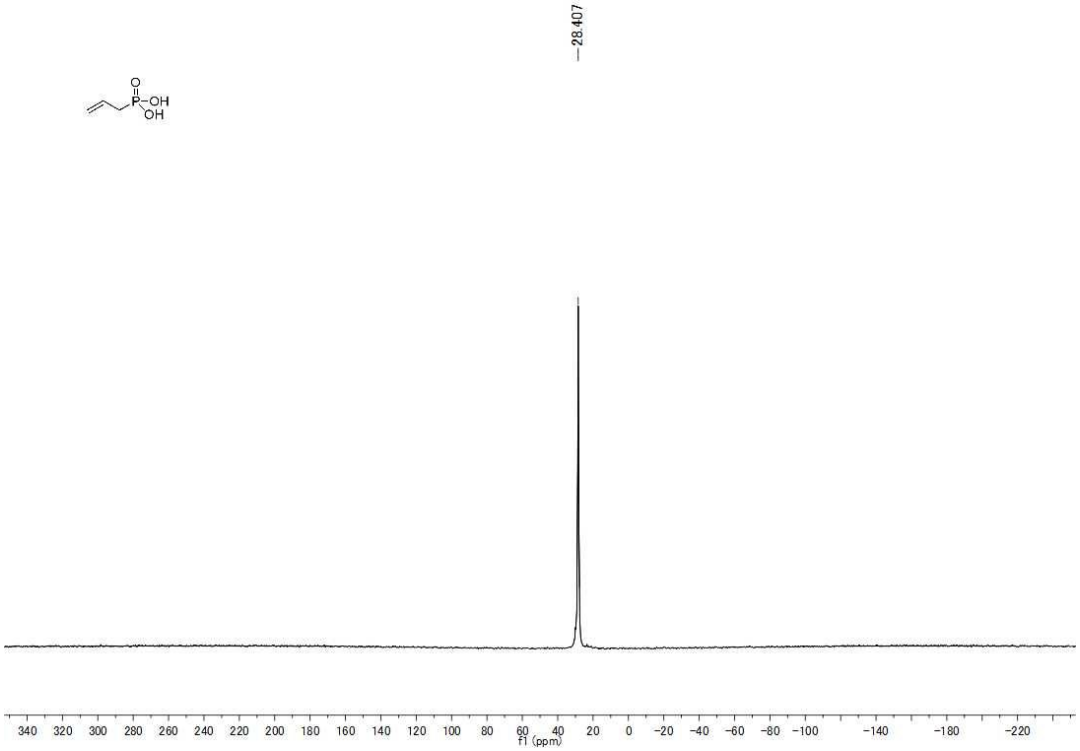


Allylphosphonic acid (2e)

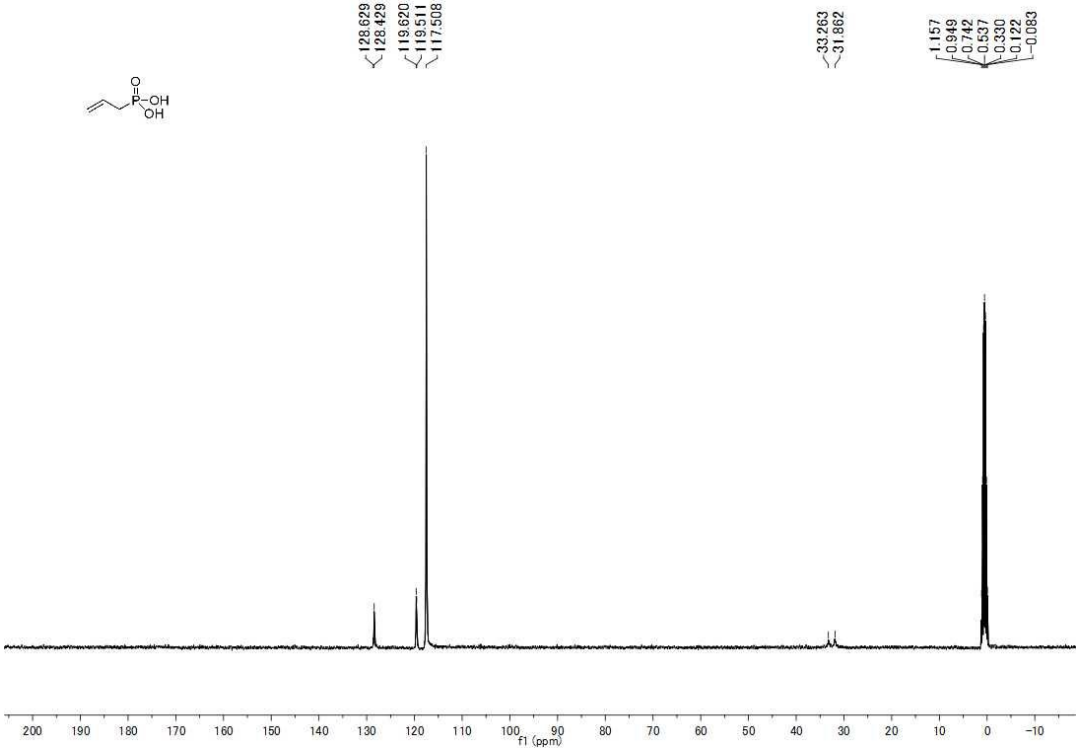
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



^{31}P NMR (162 MHz, $(CD_3)_2CO$)

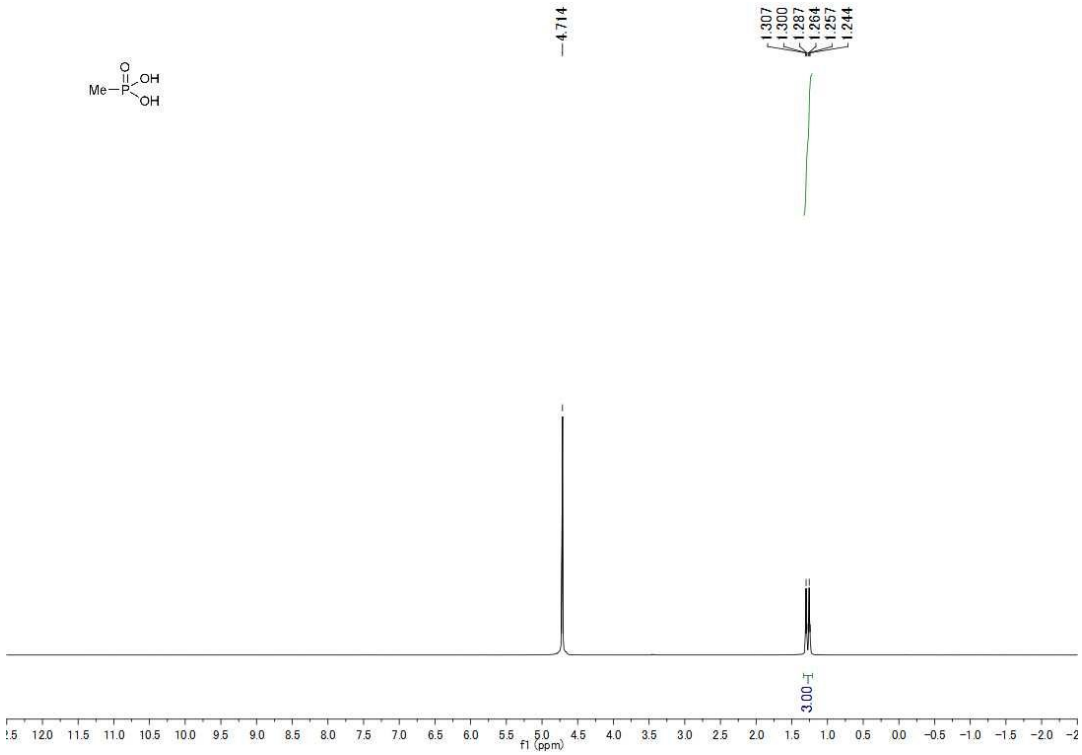


$^{13}C\{1H\}$ NMR (100 MHz, $(CD_3)_2CO$)

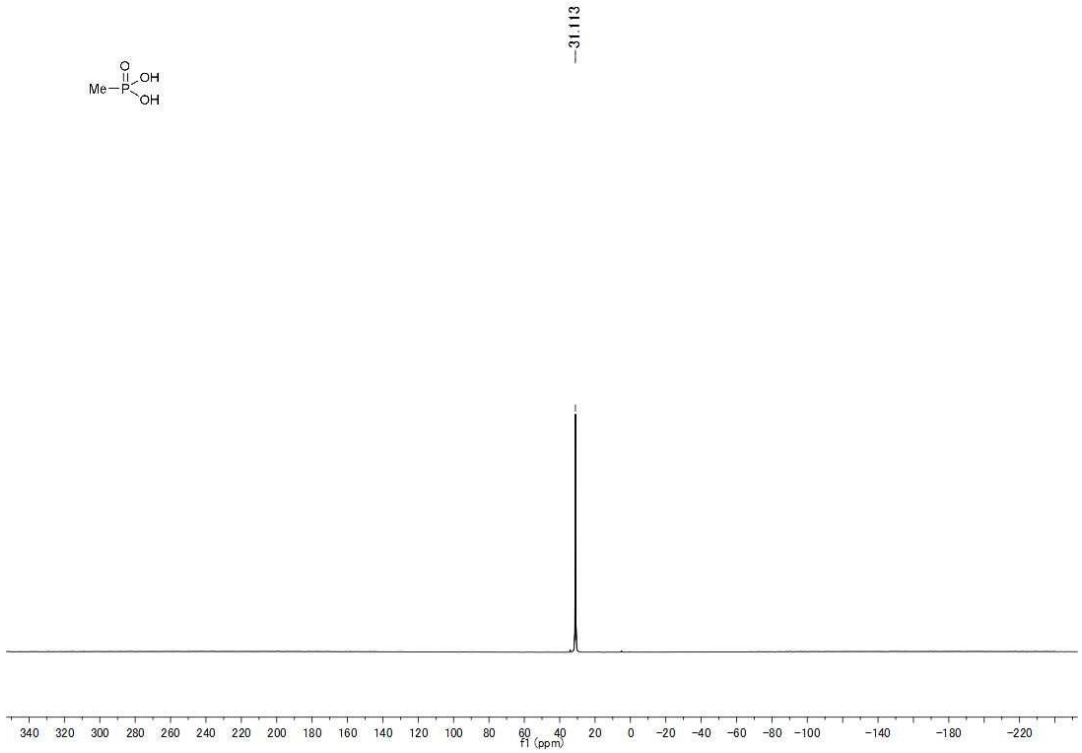


Methylphosphonic acid (2f)

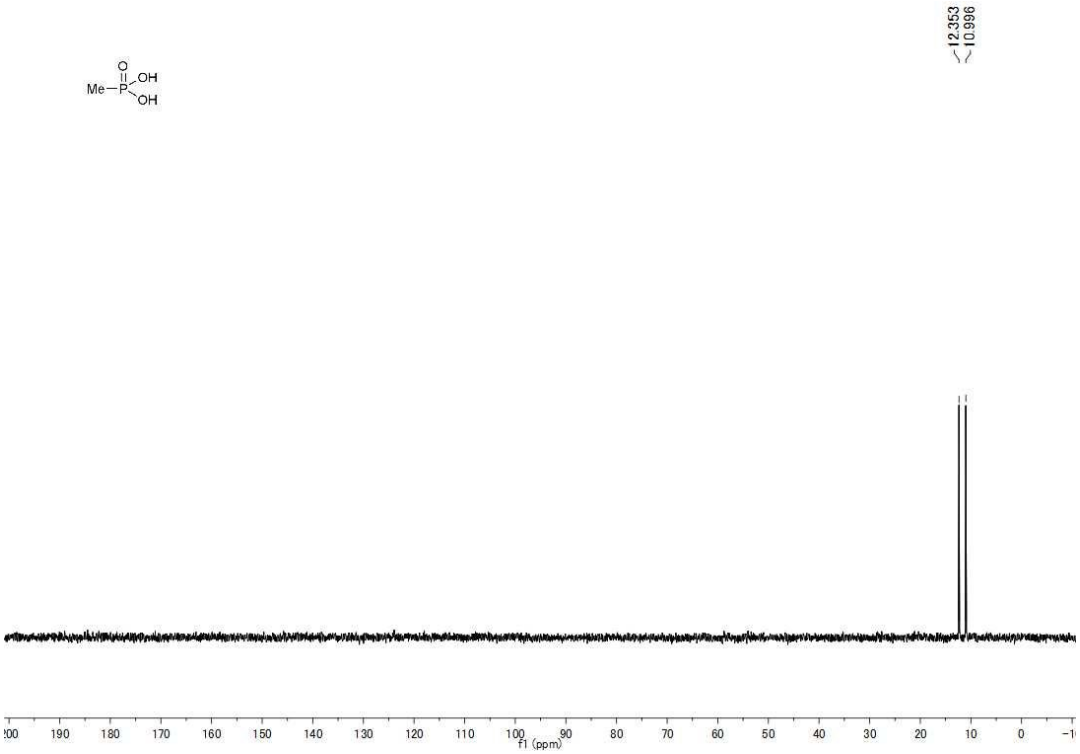
^{1}H NMR (400 MHz, D_2O)



^{31}P NMR (162 MHz, D_2O)

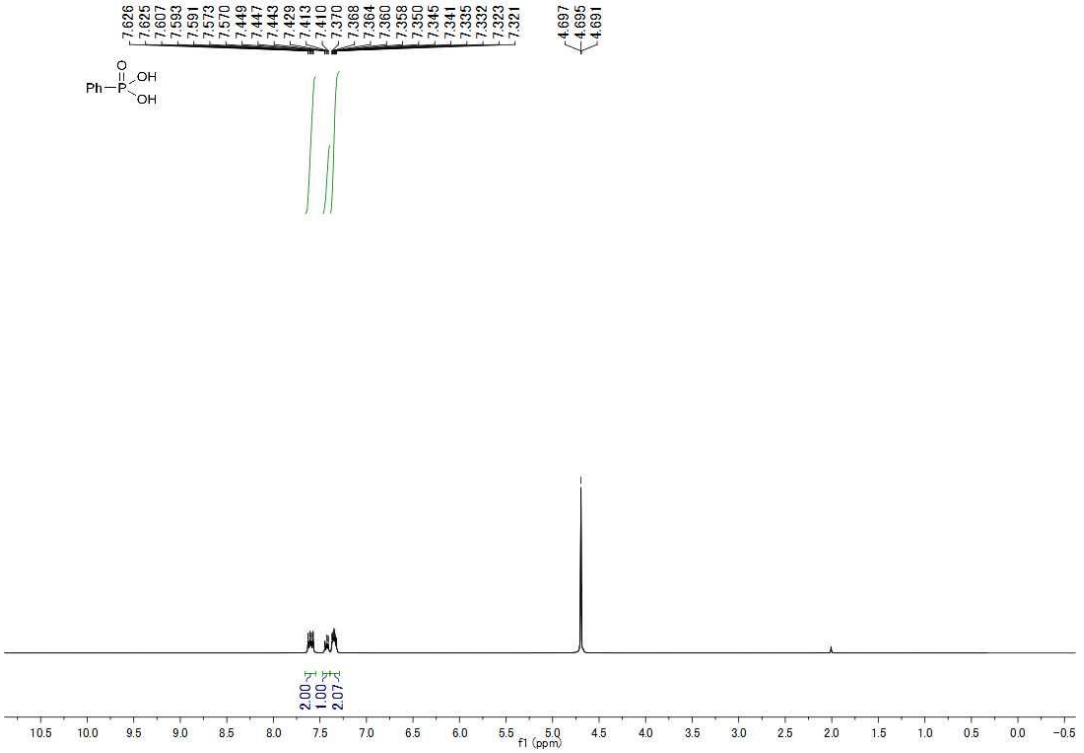


$^{13}C\{1H\}$ NMR (100 MHz, D_2O)

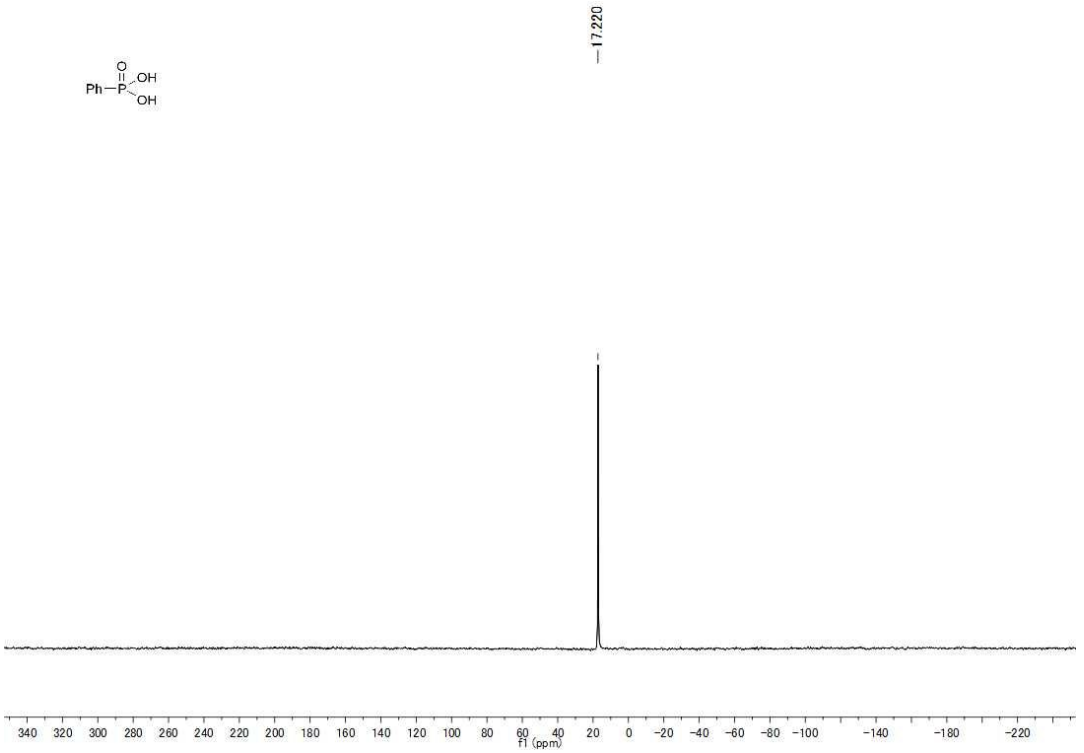


Phenylphosphonic acid (2g)

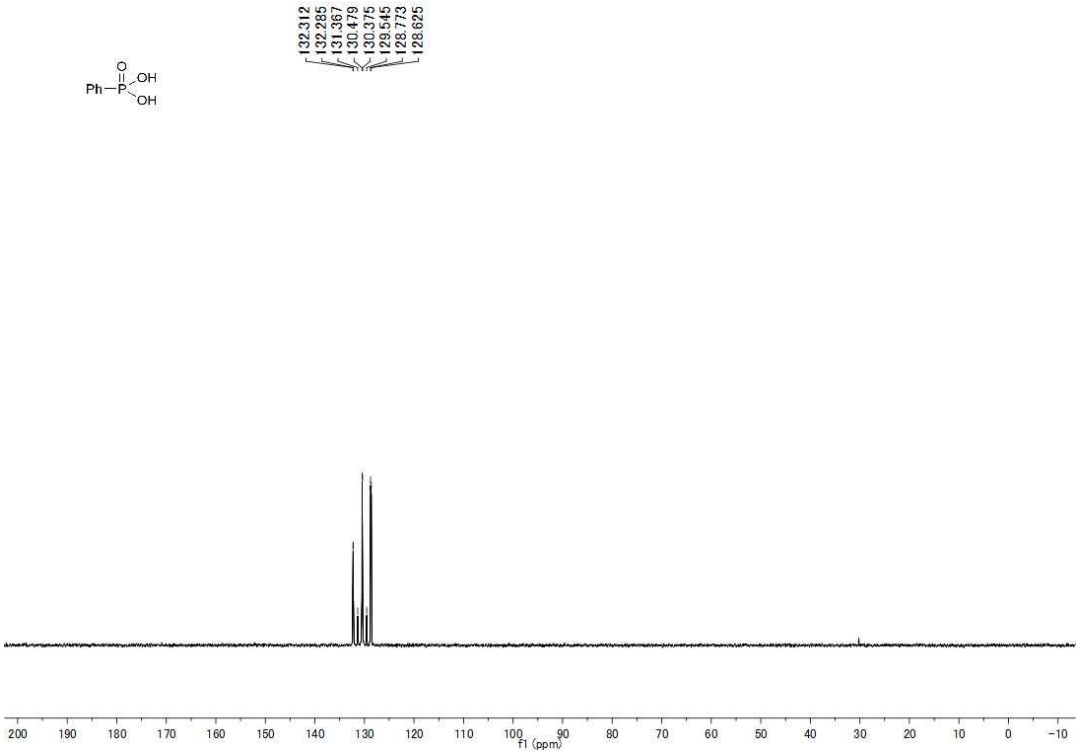
^{1}H NMR (400 MHz, D_2O)



^{31}P NMR (162 MHz, D_2O)

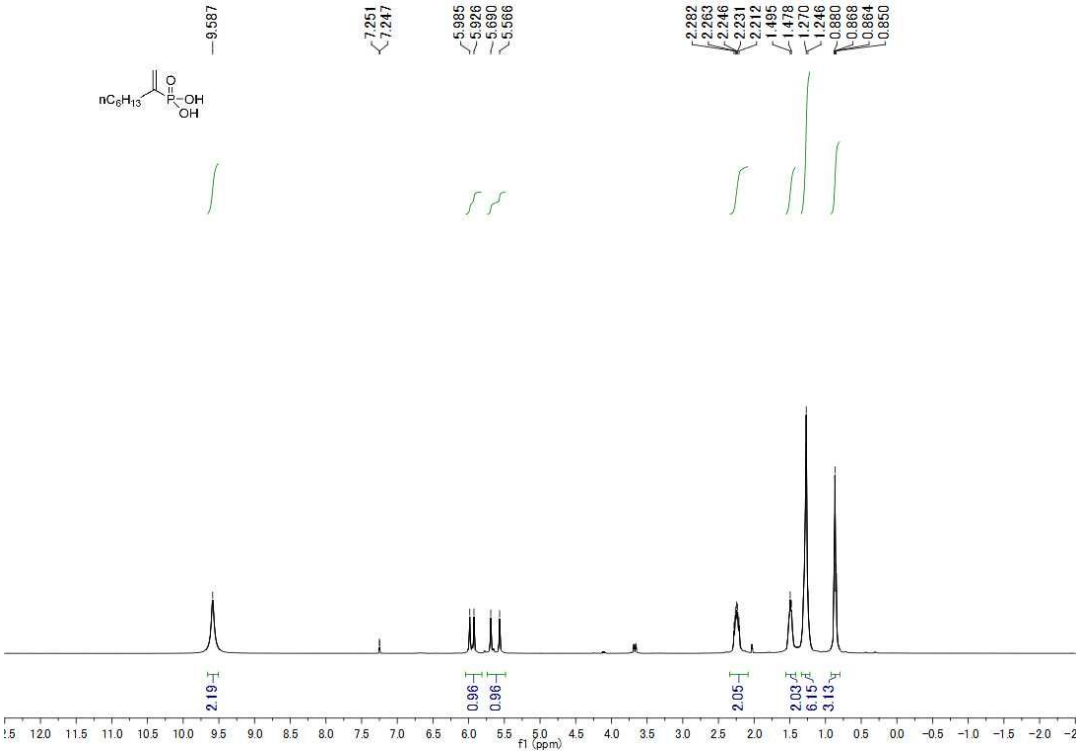


$^{13}C\{1H\}$ NMR (100 MHz, D_2O)

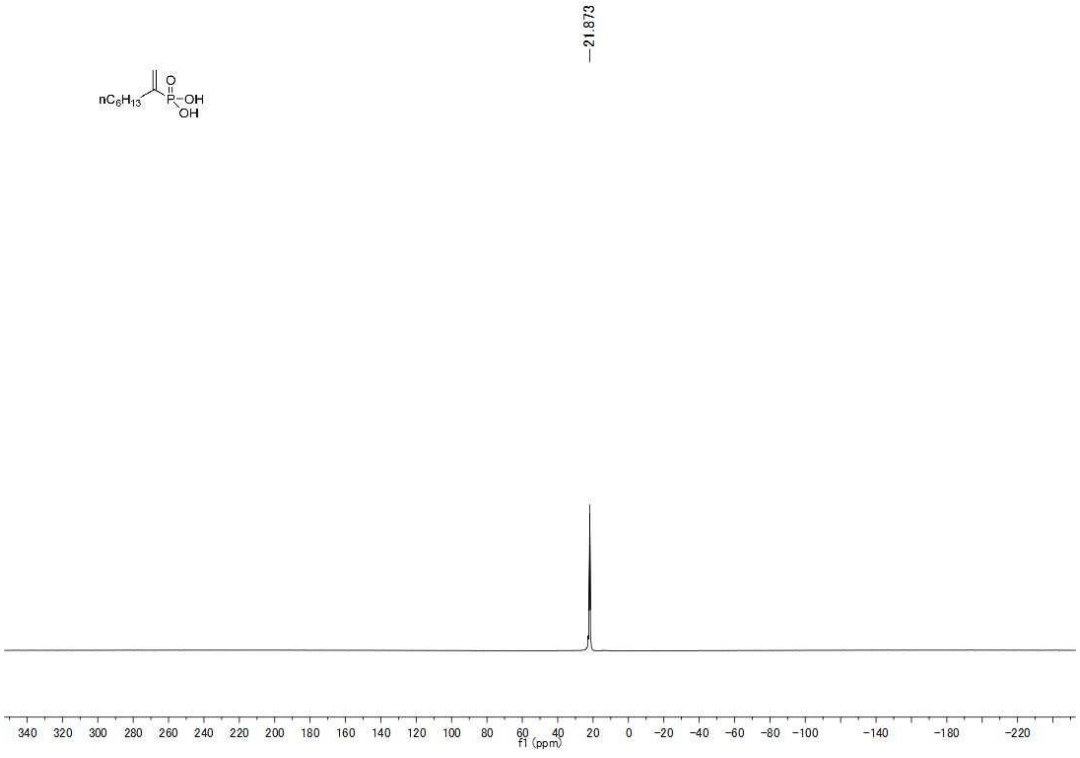


Oct-1-en-2-ylphosphonic acid (2h)

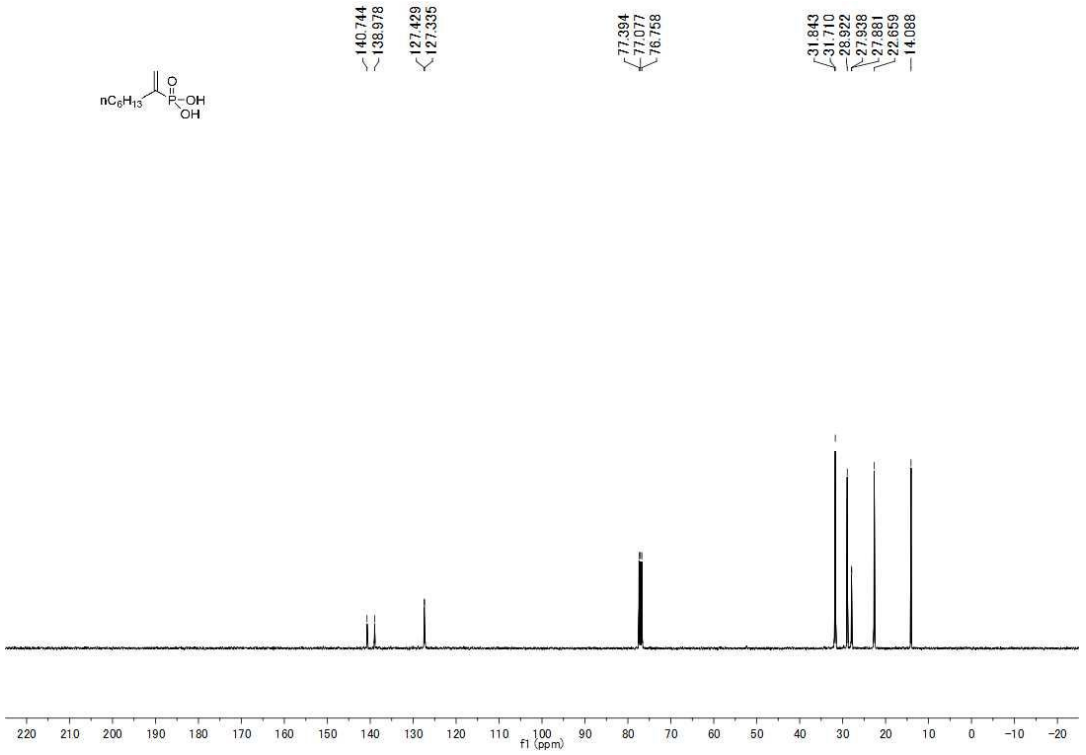
^{1}H NMR (400 MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)

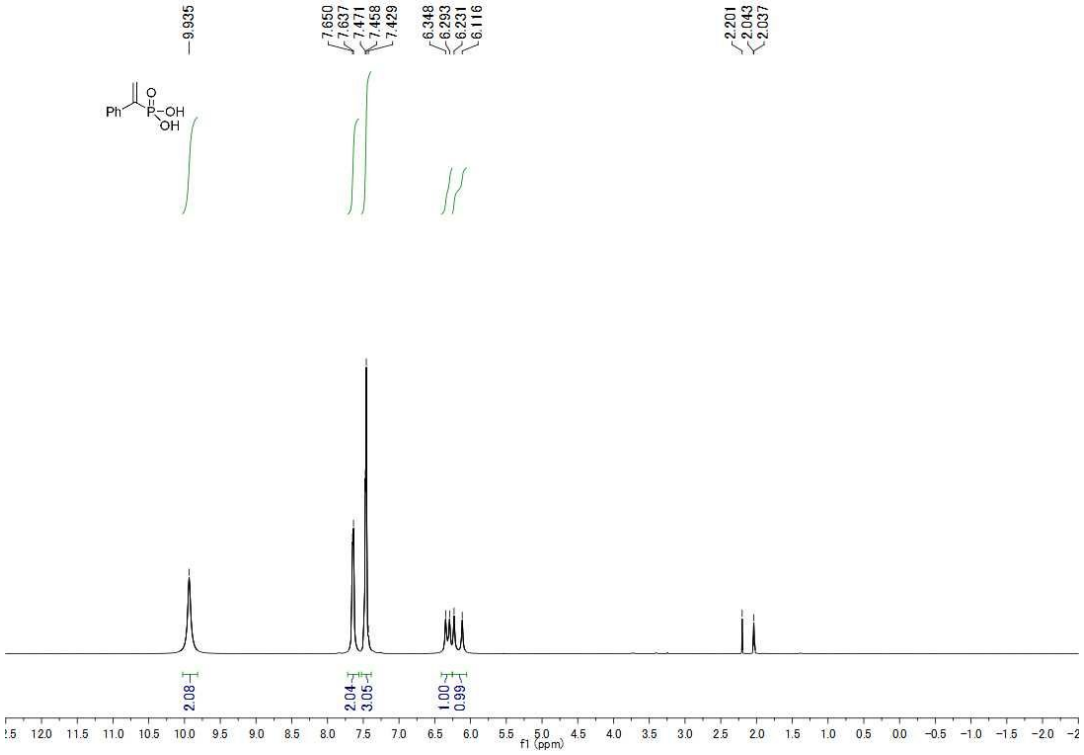


$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)

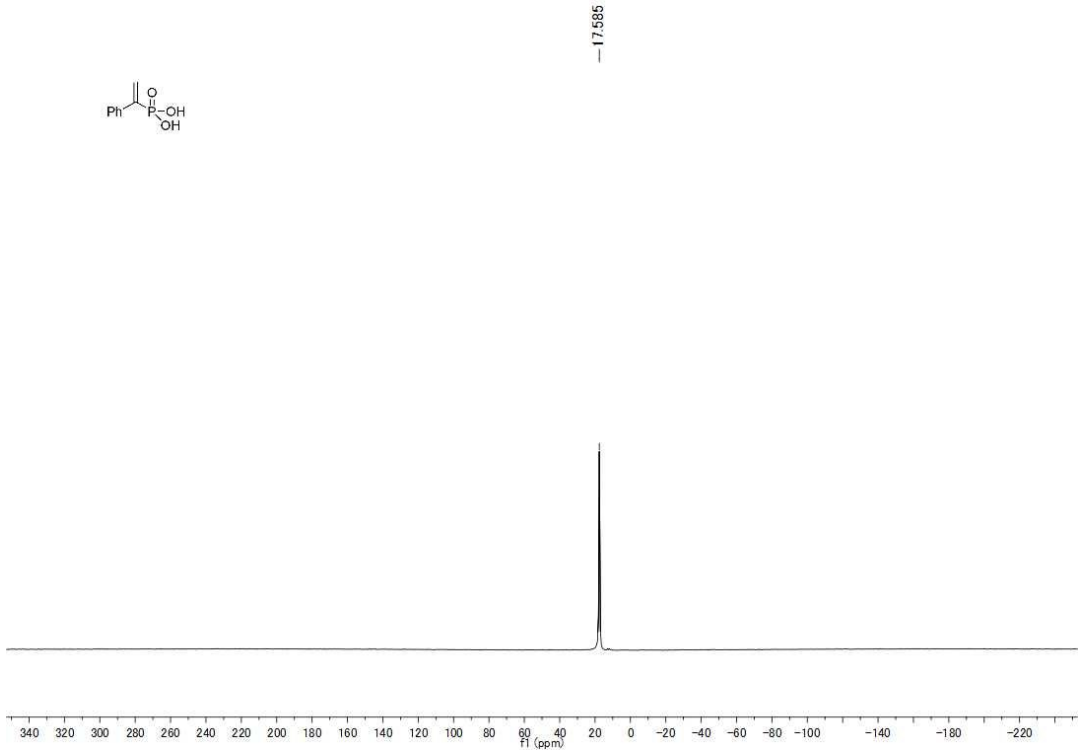


1-Phenylvinylphosphonic acid (2i)

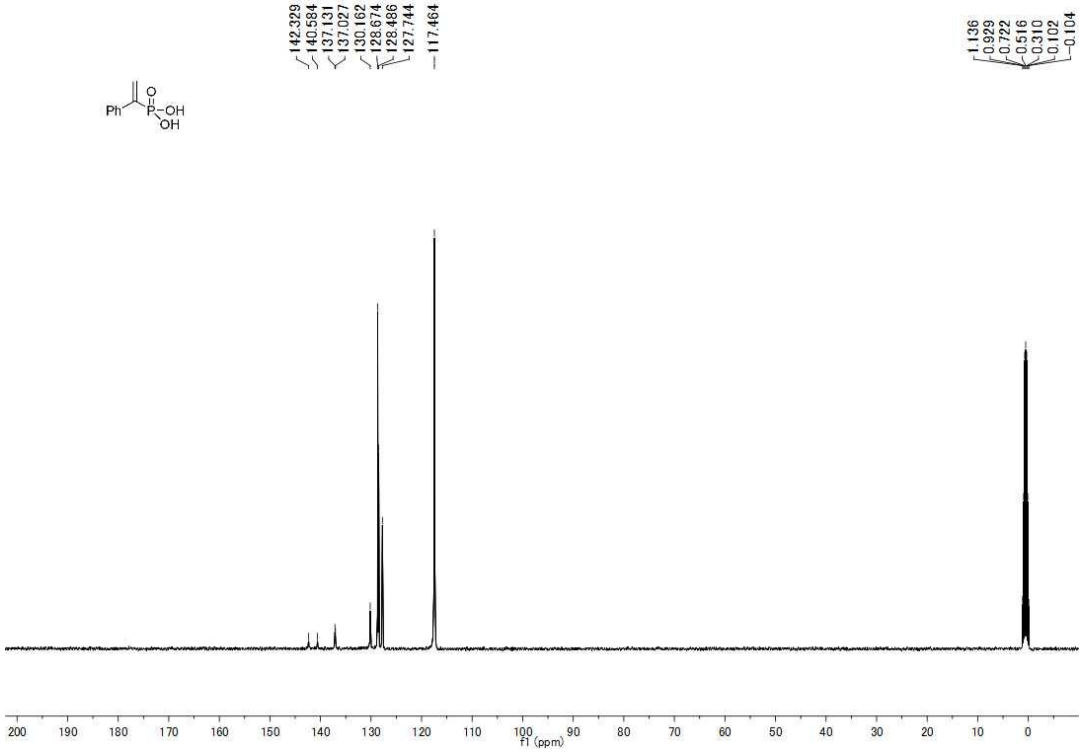
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



^{31}P NMR (162 MHz, $(CD_3)_2CO$)

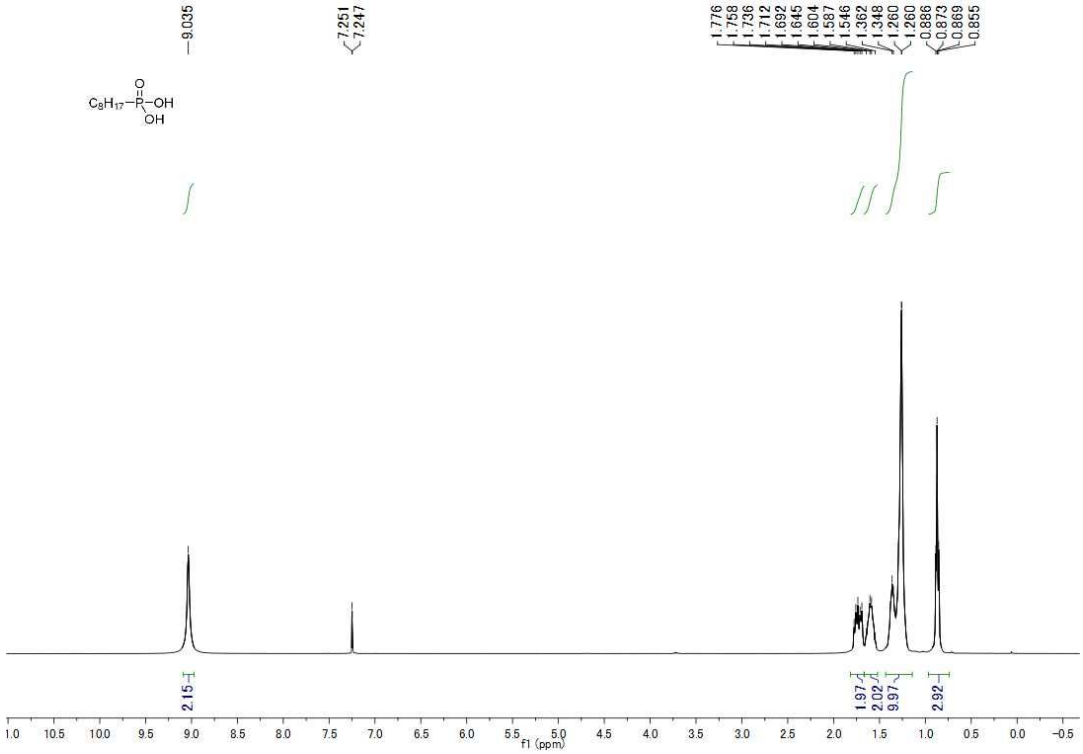


$^{13}C\{1H\}$ NMR (100 MHz, $(CD_3)_2CO$)

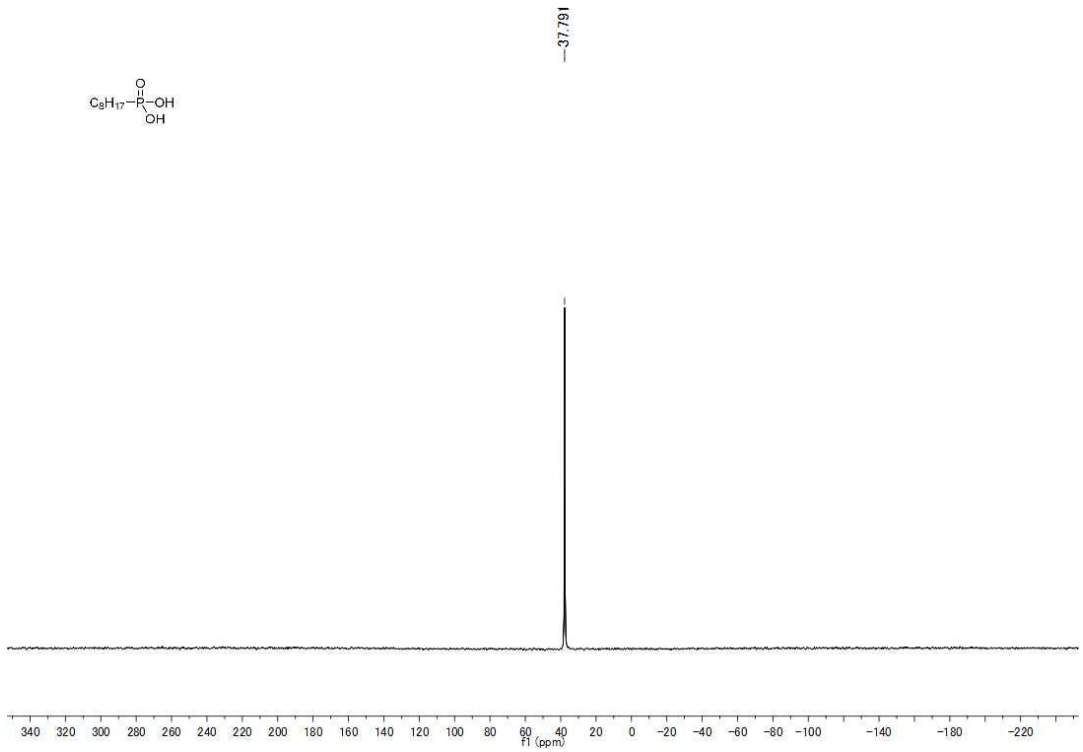


n-Octylphosphonic acid (2l)

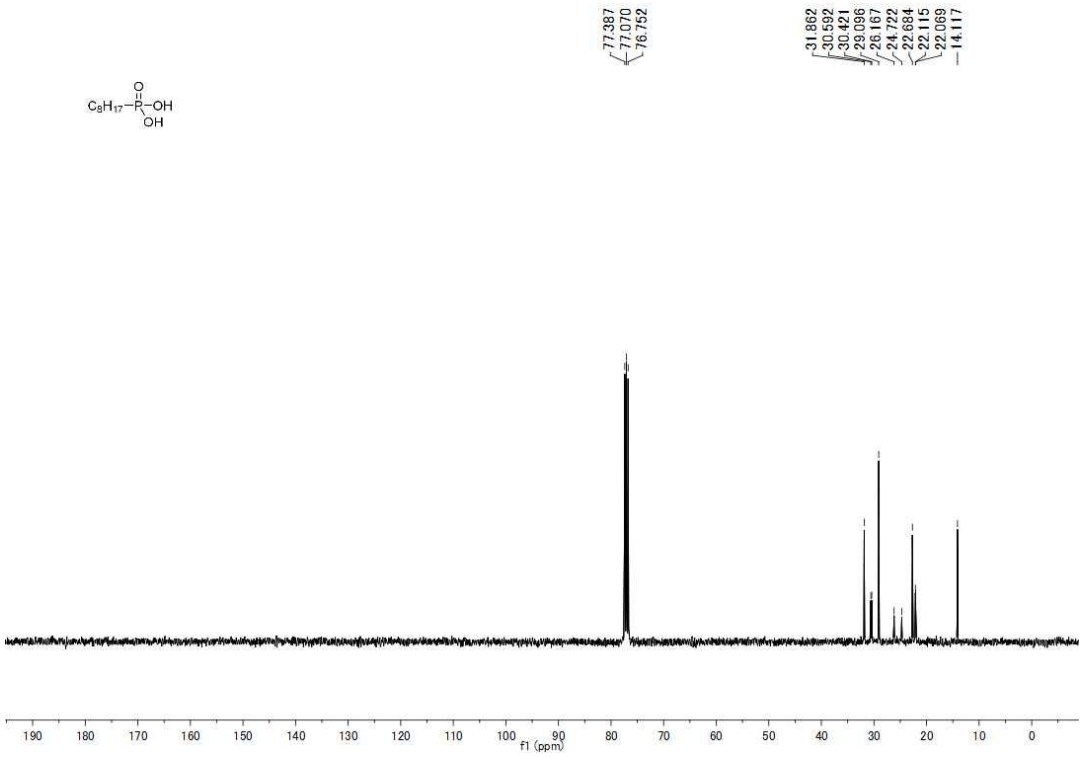
^{1}H NMR (400 MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)

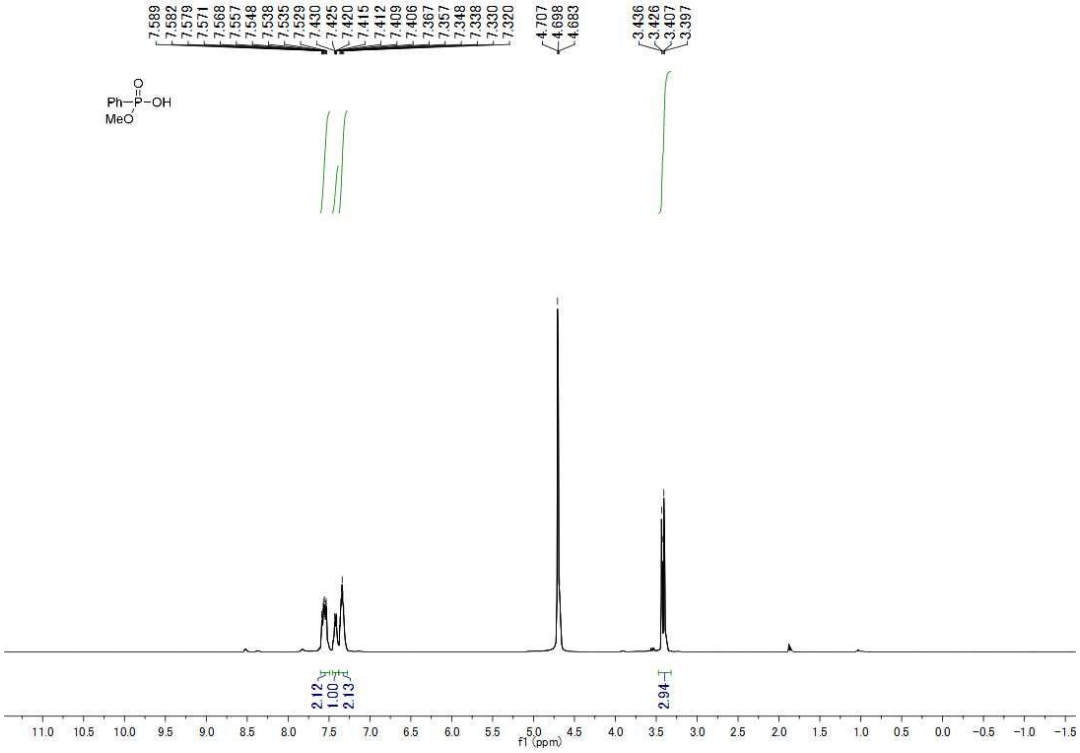


$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)

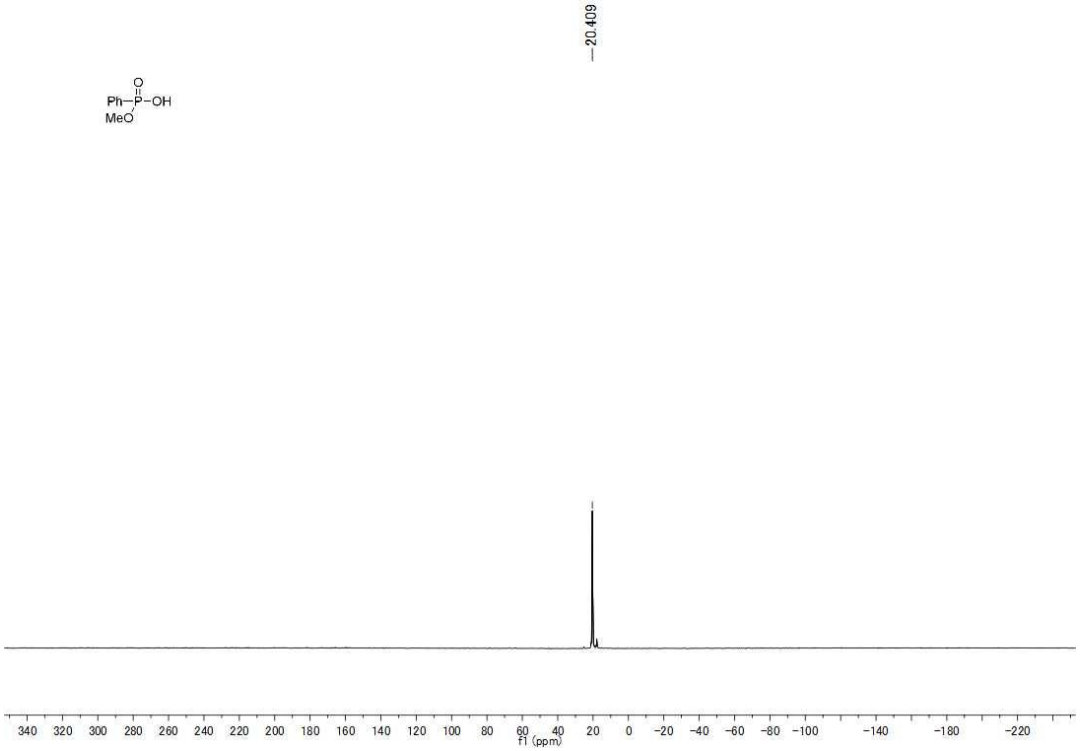


Methyl phenylphosphonic acid (2n)

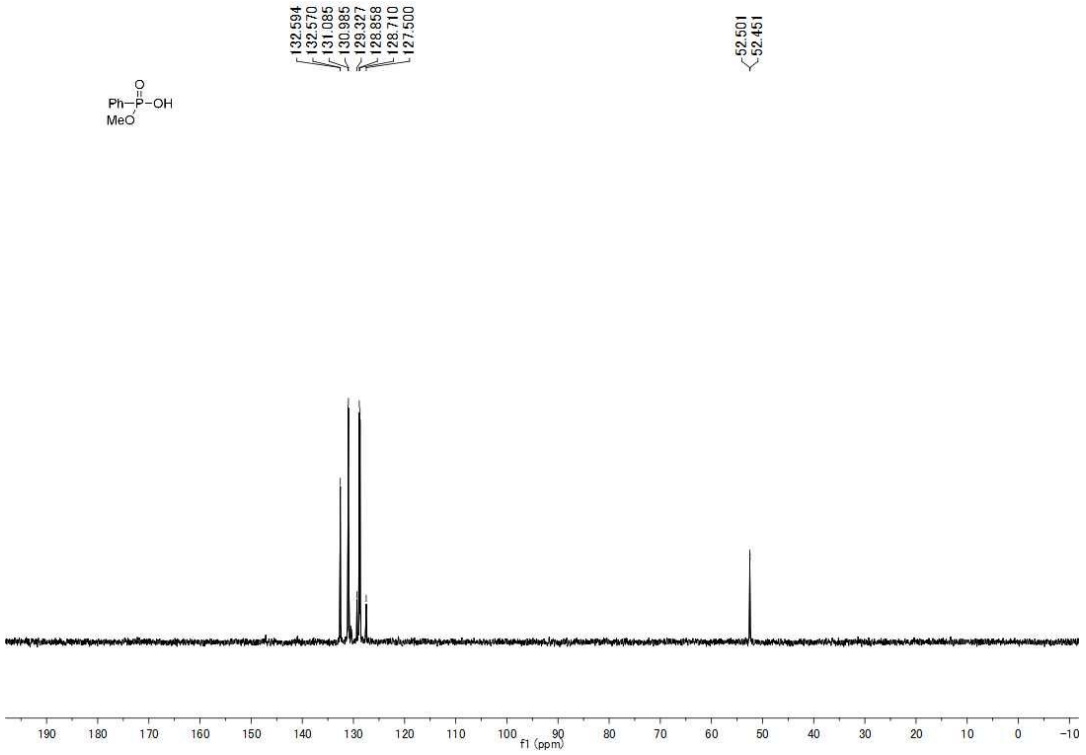
^{1}H NMR (400 MHz, D_2O)



^{31}P NMR (162 MHz, D_2O)

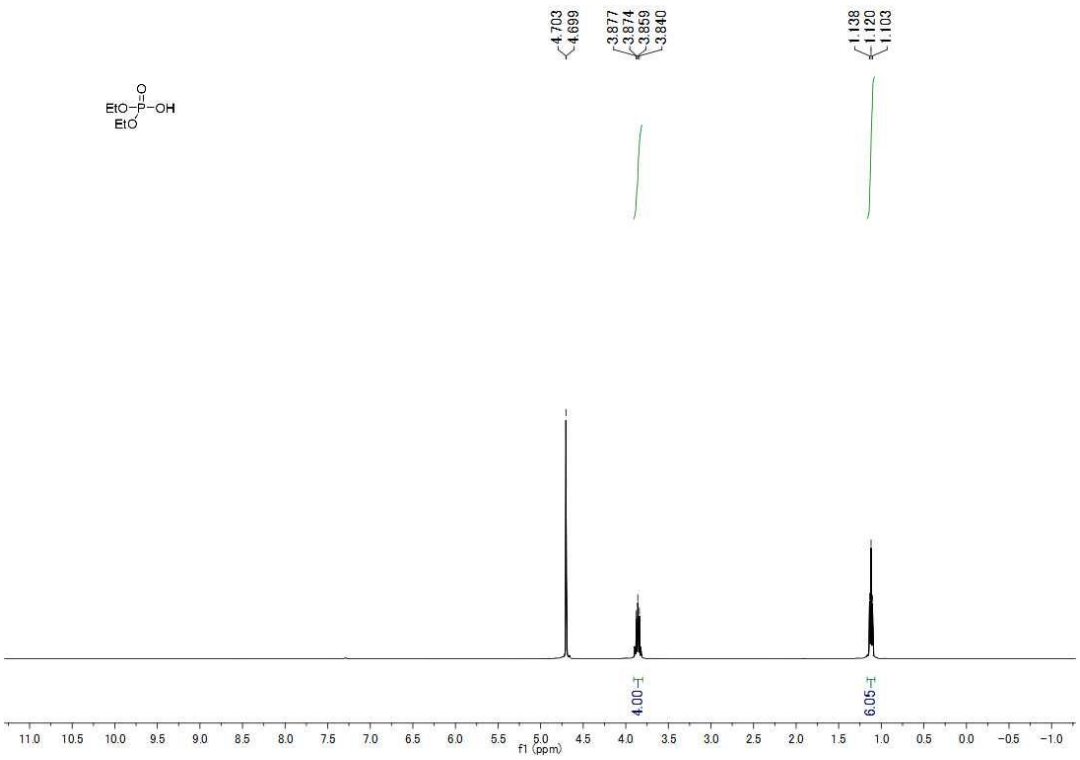


$^{13}C\{1H\}$ NMR (100 MHz, D_2O)

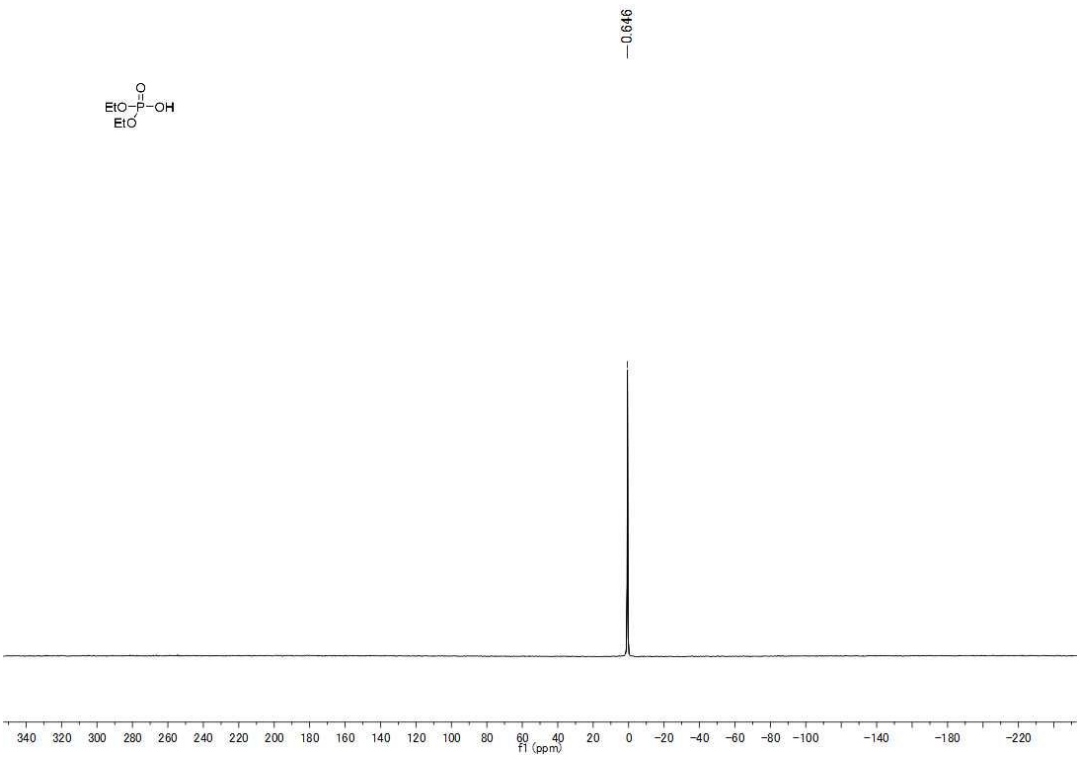


Diethyl phosphoric acid (2o)

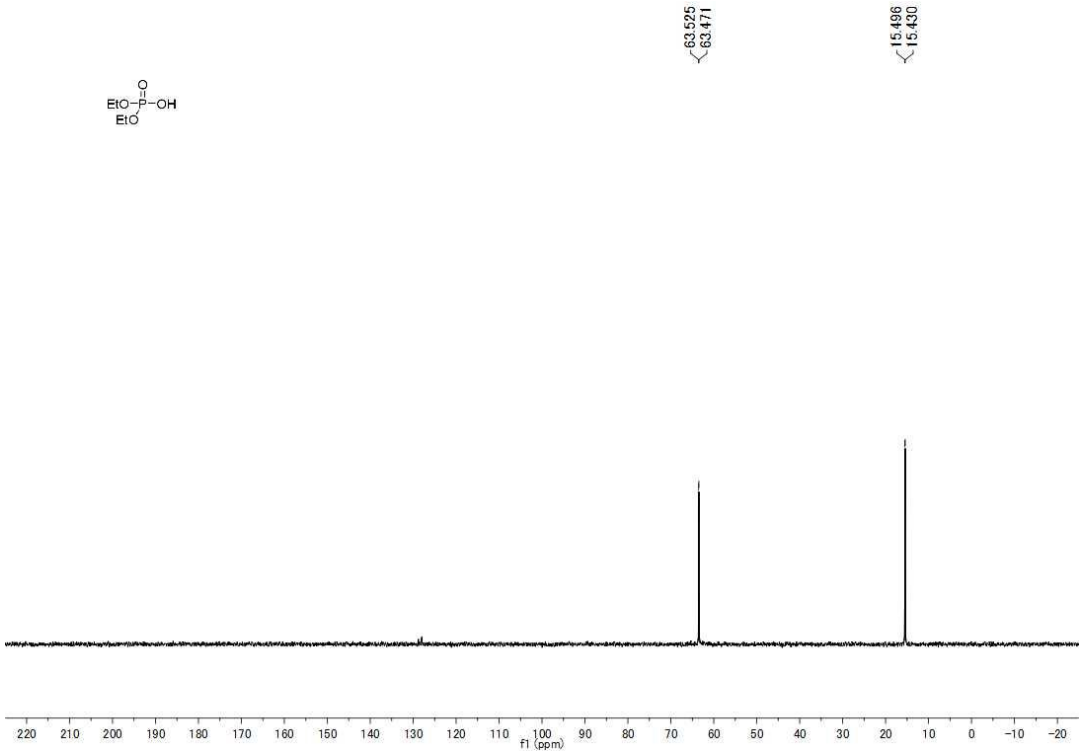
^{1}H NMR (400 MHz, D_2O)



^{31}P NMR (162 MHz, D_2O)

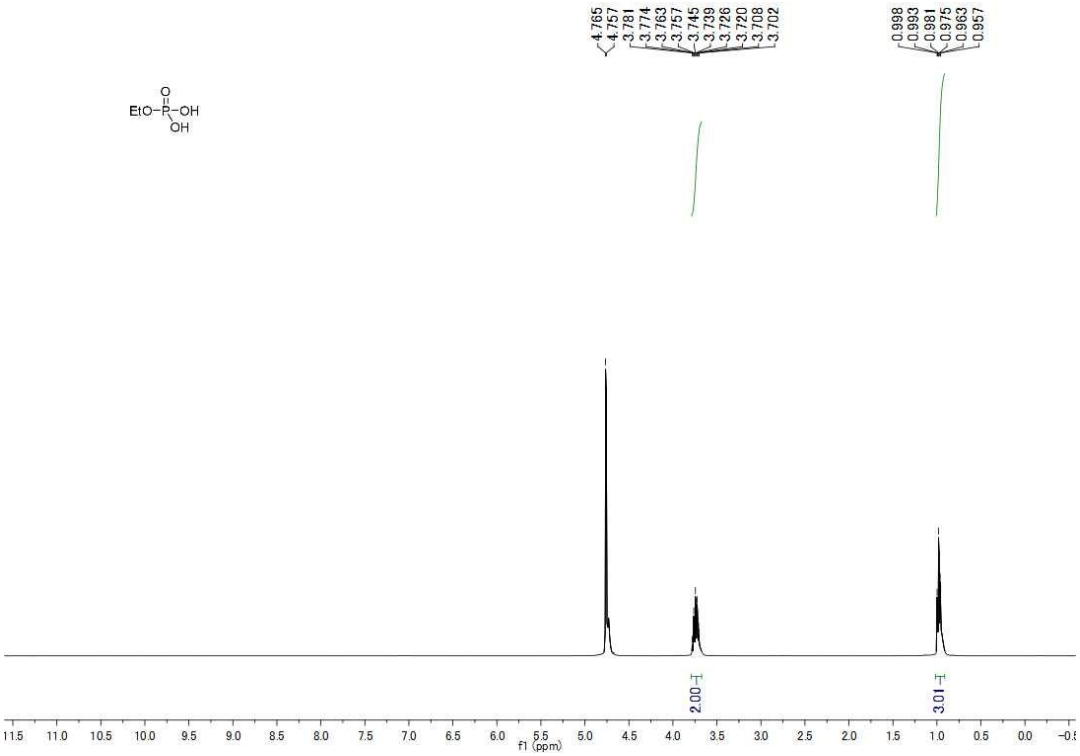


$^{13}C\{1H\}$ NMR (100 MHz, D_2O)

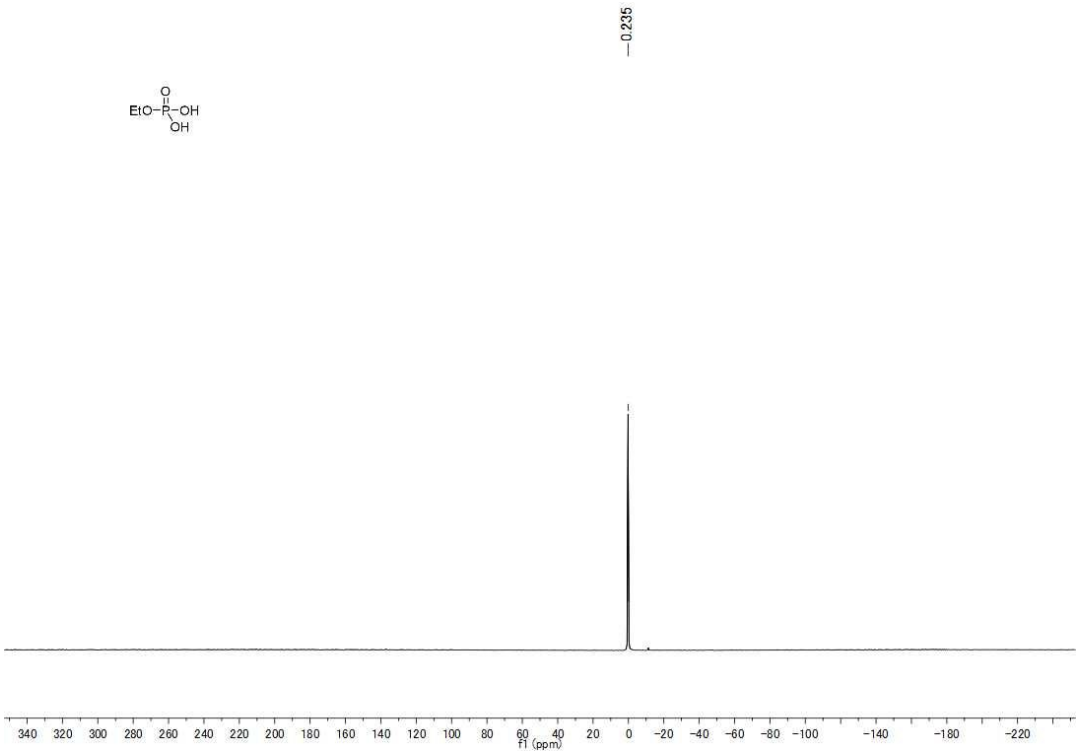


Monoethyl phosphoric acid (2p)

^{1}H NMR (400 MHz, D_2O)



^{31}P NMR (162 MHz, D_2O)



$^{13}C\{1H\}$ NMR (100 MHz, D_2O)