Electronic Supplementary Information

Water Determines the Products: an Unexpected Brønsted Acid-Catalyzed PO-R Cleavage of P(III) Esters Selectively Producing P(O)-H and P(O)-R Compounds

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1. Experimental Section

1.1. General Information

Unless otherwise noted, small scale reactions with water were carried out in NMR tubes under air atmosphere and solvent-free condition; reactions without water were carried out in oven-dried Schlenk tubes under N_2 atmosphere and solvent-free condition. Dry solvents were obtained according to standard procedures. Unless otherwise noted, all reagents were purchased and used as received. Trivalent phosphorus compounds were either purchased (from TCI if commercially available) or prepared from the corresponding alcohols and phosphorus (III) chloride according to the literature procedure (P.-Y. Renard, P. Vayron, E. Leclerc, A. Valleix, C. Mioskowski, *Angew. Chem. Int. Ed*. **2003**, *42*, 2389). Product **2** were mostly purified by vacuum distillation. Product **3** were purified by a preparative GPC apparatus (JAPAN ANALYTICAL INDUSTRY LC-908 with JAIGEL-1H, polystyrene-based column) using $CHCl_3$ as the eluent (smaller scale reactions). Quaternary phosphonium salt $MeP^{+}(OMe)_3 \cdot {}^{-}OTf$ (**6c**) used in the control reactions was obtained in 84% isolated yield according to the literature method (K. S. Colle, E. S. Lewis, *J. Org. Chem*. **1978**, *43*, 571). Theoretical calculation of the energy barriers of the mono- and bi-molecular transition states are obtained using GAUSSIAN 09 software with pm6 semi-empirical algorithm (M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian 09, revision B. 01; Gaussian, Inc.: Wallingford CT, 2009). ^{1}H, ^{13}C, and ^{31}P NMR spectra of the products were acquired on a JEOL JNM-ECS400 (400 MHz for ^{1}H, 100 MHz for ^{13}C, and 162 MHz for ^{31}P NMR spectroscopy). Chemical shifts for ^{1}H NMR are referred to internal Me_4Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Chemical shifts for ^{31}P NMR were relative to H_3PO_4 (85% solution in D_2O, 0 ppm).

1.2. Typical procedure for Brønsted acid-catalyzed C-O cleavage of P(III) esters in the presence of H_2O: To an NMR tube was added triisopropyl phosphite (**1a**) (0.52 mL, 2.3 mmol), 1 equiv. H_2O (41.4 uL), trifluorormethanesulfonic acid (4 uL, 2 mol%) under air atmosphere. The tube was then sealed, slightly shaken at room temperature, and subjected to ^{31}P NMR measurement in ca. 5 min. ^{31}P NMR spectra revealed that the reaction was very fast and completed (>99% NMR yield) in the 5 min. Pure **2a** was obtained by distillation in 94% isolated yield. Except solid products $HP(O)Ph_2$ (**2k**) and $HP(O)Cy_2$ (**2p**) that were obtained by

recrystalization, all other products were purified by vacuum distillation.

$HP(O)(Oi\text{-}Pr)_2$

Diisopropyl phosphite (2a). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 0.5H), 5.95 (s, 0.5H), 4.74-4.66 (m, 2H), 1.33 (d, J = 2.4 Hz, 6H), 1.32 (d, J = 2.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.8 (d, $J_{C\text{-}P}$ = 5.4 Hz), 24.0 (d, $J_{C\text{-}P}$ = 4.0 Hz), 23.8 (d, $J_{C\text{-}P}$ = 4.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 4.92. This compound was known: H. C. Fisher, L. Prost, J.-L. Montchamp, *Eur. J. Org. Chem.* **2013**, *2013*, 7973.

$HP(O)(OEt)_2$

Diethyl phosphite (2b). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 0.5H), 5.90 (s, 0.5H), 4.14-4.06 (m, 4H), 1.32 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.7, 16.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ 7.80. This compound was known: H. C. Fisher, L. Prost, J.-L. Montchamp, *Eur. J. Org. Chem.* **2013**, *2013*, 7973.

$HP(O)(OMe)_2$

Dimethyl phosphite (2c). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 0.5H), 5.85 (s, 0.5H), 3.74 (t, J = 12.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.1 (d, $J_{C\text{-}P}$ = 5.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.1. This compound was known: H. Fakhraian, A. Mirzaei, *Org. Process Res. Dev.* **2004**, *8*, 401.

$HP(O)(On\text{-}Bu)_2$

Dibutyl phosphite (2d). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 0.5H), 5.93 (s, 0.5H), 4.06 (q, J = 6.8 Hz, 4H), 1.70-1.63 (m, 4H), 1.46-1.36 (m, 4H), 0.93 (d, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.6 (d, $J_{C\text{-}P}$ = 5.8 Hz), 32.5 (d, $J_{C\text{-}P}$ = 6.2 Hz), 18.8, 13.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.41. This compound was known: H. C. Fisher, L. Prost, J.-L. Montchamp, *Eur. J. Org. Chem.* **2013**, *2013*, 7973.

$HP(O)(OCH_2CH{=}CH_2)_2$

Diallyl phosphite (2e). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 0.5H), 6.00 (s, 0.5H), 5.98-5.89 (m, 2H), 0.93 (d, J = 7.4 Hz, 2H), 0.93 (d, J = 7.4 Hz, 2H), 4.59-4.55 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.3 (d, $J_{C\text{-}P}$ = 5.9 Hz), 118.6, 66.2 (d, $J_{C\text{-}P}$ = 5.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.26. This compound was known: P. A. Lohse, R. Felber, *Tetrahedron Lett.* **1998**, *39*, 2067.

$HP(O)(OCH_2Ph)_2$

Dibenzyl phosphite (2f). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.25 (m, 10H), 6.93 (d, J = 707.6 Hz, 1H), 5.11-5.00 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.7, 135.6, 128.8, 128.1,67.4 (d, $J_{C\text{-}P}$ = 5.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.36. This compound was known: H. C. Fisher, L. Prost, J.-L. Montchamp, *Eur. J. Org. Chem.* **2013**, *2013*, 7973.

$HP(O)(OPh)_2$

Diphenyl phosphite (2i). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 0.5H), 7.37-7.33 (m, 4H), 7.25-7.19 (m, 6H), 6.39 (s, 0.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4 (d, $J_{C\text{-}P}$ = 8.1 Hz), 130.1, 125.9, 120.6 (d, $J_{C\text{-}P}$ = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 0.82. This compound was known: H. C. Fisher, L. Prost, J.-L. Montchamp, *Eur. J. Org. Chem.* **2013**, *2013*, 7973.

HP(O)(OMe)Ph

Methoxyphenylphosphine oxide (2j). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 0.5H), 7.25-7.19 (m, 2H), 6.90-76.85 (m, 3H), 5.89 (s, 0.5H), 3.78 (d, J = 11.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 129.6, 120.2, 115.5, 52.5 (d, $J_{C\text{-}P}$ = 5.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.1. This compound was known: E. Jablonkai, R. Henyecz, M. Milen, J. Kóti, G. Keglevich, *Tetrahedron* **2014**, *70*, 8280.

$HP(O)Ph_2$

Diphenylphosphine oxide (2k). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 0.5H), 7.72-7.66 (m, 4H), 7.57-7.53 (m, 2H), 7.50-7.46 (m, 4.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.6, 131.6 (d, $J_{C\text{-}P}$ = 101.3 Hz), 130.8 (d, $J_{C\text{-}P}$ = 11.3 Hz), 129.0 (d, $J_{C\text{-}P}$ = 12.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.02. This compound was known: C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, *Org. Lett.* **2005**, *7*, 4277.

$HP(O)Cy_2$

Dicyclohexylphosphine oxide (2p). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (t, J = 2.6 Hz, 0.5H), 5.75 (t, J = 2.8 Hz, 0.5H), 1.99-1.71 (m, 12H), 1.48-1.40 (m, 4H), 1.31-1.19(m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.9 (d, $J_{C\text{-}P}$ = 64.2 Hz), 26.2 (d, $J_{C\text{-}P}$ = 25.8 Hz), 26.2, 25.8, 25.0 (d, $J_{C\text{-}P}$ = 3.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 50.22. This compound was known: C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, *Org. Lett.* **2005**, *7*, 4277.

1.3. Typical procedure for Brønsted acid-catalyzed C-O cleavage of P(III) esters in the absence of H_2O: To a 10 mL Schlenk tube was added triethyl phosphite (**1b**) (0.4 mL, 2.3 mmol) and trifluorormethanesulfonic acid (4 uL, 2 mol%) under N_2. The tube was then heated at 60 ^oC for 16 h and **1b** was totally consumed. Pure **3b** was obtained by preparative GPC in 95% isolated yield.

***i*-PrP(O)(O*i*-Pr)$_2$**

Diisopropyl isopropylphosphonate (3a). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.69-4.61 (m, 2H), 1.89-1.77 (m, 1H), 1.27 (dd, J = 6.4 Hz, 2.0 Hz, 12H), 1.15 (d, J = 6.8 Hz 3H), 1.10 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.6 (d, $J_{C\text{-}P}$ = 7.0 Hz), 26.4 (d, $J_{C\text{-}P}$ = 143 Hz), 24.1 (d, $J_{C\text{-}P}$ = 3.2 Hz), 24.0 (d, $J_{C\text{-}P}$ = 4.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.01. This compound was known: J. Acharya, P. D. Shakya, D. Pardasani, M. Palit, D. K. Dubey, A. K. Gupta, *J. Chem. Res.* **2005**, *2005*, 194.

EtP(O)(OEt)$_2$

Diethyl ethylphosphonate (3b). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.15-4.01 (m, 4H), 1.72 (dq, J = 18.1, 7.6 Hz, 2H), 1.31 (t, J = 7.1 Hz, 6H), 1.15 (dt, J = 20.0 Hz, 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.5 (d, $J_{C\text{-}P}$ = 6.5 Hz), 18.8 (d, $J_{C\text{-}P}$ = 141.9 Hz), 16.5 (d, $J_{C\text{-}P}$ = 5.9 Hz), 6.6 (d, $J_{C\text{-}P}$ = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.19. This compound was known: J. Acharya, P. D. Shakya, D. Pardasani, M. Palit, D. K. Dubey, A. K. Gupta, *J. Chem. Res.* **2005**, *2005*, 194.

MeP(O)(OMe)$_2$

Dimethyl methylphosphonate (3c). Colorless oil. ^{1}H NMR (400 MHz $CDCl_3$): δ 3.67 (d, J = 11.2 Hz, 6H), 1.41 (d, J = 17.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.2 (d, $J_{C\text{-}P}$ = 6.1 Hz), 9.9 (d, $J_{C\text{-}P}$ = 143.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.81. This compound was known: P.-Y. Renard, P. Vayron, E. Leclerc, A. Valleix, C. Mioskowski, *Angew. Chem. Int. Ed*. **2003**, *42*, 2389. This compound was known:

***n*-BuP(O)(O*n*-Bu)$_2$**

Dibutyl butylphosphonate (3d). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.95-3.86 (m, 4H), 1.66-1.41 (m, 8H), 1.34-1.25 (m, 6H), 0.85-0.78 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.1 (d, $J_{C\text{-}P}$ = 6.7 Hz), 32.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 25.2 (d, $J_{C\text{-}P}$ = 146.4 Hz), 24.5, 23.7 (d, $J_{C\text{-}P}$ = 17.2 Hz), 18.8, 13.6, 13.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.12. This compound was known: T.

Wolf, T. Steinbach, F. R. Wurm, *Macromolecules* **2015**, *48*, 3853.

CH_2=CHCH_2P(O)(OCH_2CH=CH_2)$_2$

Diallyl allylphosphonate (3e). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90-5.80 (m, 2H), 5.79-5.67 (m, 1H), 5.30-5.25 (m, 2H), 5.18-5.11 (m, 4H), 4.49-4.44 (m, 4H), 2.62-2.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 127.2 (d, $J_{C\text{-}P}$ = 11.3 Hz), 120.3 (d, $J_{C\text{-}P}$ = 14.5 Hz), 117.9, 66.4 (d, $J_{C\text{-}P}$ = 6.5 Hz), 31.9 (d, $J_{C\text{-}P}$ = 138.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.45. This compound was known: X. Lu, J. Zhu, *J. Organometallic Chemistry* **1986**, *304*, 239.

PhCH_2P(O)(OCH_2Ph)$_2$

Dibenzyl benzylphosphonate (3f). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.24 (m, 15H), 4.92 (d, J = 8.4 Hz, 4H), 3.19 (d, J = 21.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4 (d, $J_{C\text{-}P}$ = 5.9 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.0 (d, $J_{C\text{-}P}$ = 6.6 Hz), 128.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.6, 128.4, 128.0, 127.1 (d, $J_{C\text{-}P}$ = 3.6 Hz), 67.7 (d, $J_{C\text{-}P}$ = 6.6 Hz), 34.2 (d, $J_{C\text{-}P}$ = 137.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.13. This compound was known: L. Gavara, C. Petit, J.-L. Montchamp, *Tetrahedron Lett.* **2012**, *53*, 5000.

MeP(O)(OMe)(OPh)

Methyl phenyl methylphosphonate (3g). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 2H), 7.15-7.08 (m, 3H), 3.73 (dd, J = 11.2 Hz, 1.2 Hz, 2H), 1.55 (dd, J = 17.6 Hz, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5 (d, $J_{C\text{-}P}$ = 8.0 Hz), 129.9, 125.1, 120.5 (d, $J_{C\text{-}P}$ = 4.1 Hz), 52.7 (d, $J_{C\text{-}P}$ = 6.6 Hz), 10.8 (d, $J_{C\text{-}P}$ = 144.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.37. This compound was known: M. Fañanás-Mastral, B. L. Feringa, *J. Am. Chem. Soc.* **2014**, *136*, 9894.

MeP(O)(OPh)$_2$

Diphenyl methylphosphonate (3h). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.29 (m, 4H), 7.20-7.14 (m, 6H), 1.78 (d, J = 17.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4 (d, $J_{C\text{-}P}$ = 8.3 Hz), 129.9, 125.3, 120.6 (d, $J_{C\text{-}P}$ = 4.5 Hz), 11.6 (d, $J_{C\text{-}P}$ = 144.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.55. This compound was known: L. Gavara, C. Petit, J.-L. Montchamp, *Tetrahedron Lett.* **2012**, *53*, 5000.

MeP(O)(OMe)Ph

Methyl methylphenylphosphinate (3j). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 2H), 7.55-7.44 (m, 3H), 3.58 (d, J = 11.2 Hz, 3H), 1.64 (d, J = 14.8 Hz, 3H). ^{13}C NMR (100

MHz, $CDCl_3$): δ 132.4 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.4 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 125.9 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.6 Hz), 51.1 (d, $J_{C\text{-}P}$ = 6.1 Hz), 15.6(d, $J_{C\text{-}P}$ = 102.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 44.43. This compound was known: P.-Y. Renard, P. Vayron, E. Leclerc, A. Valleix, C. Mioskowski, *Angew. Chem. Int. Ed*. **2003**, *42*, 2389.

$MeP(O)Ph_2$

Methyldiphenylphosphine oxide (3k). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.69 (m, 4H), 7.51-7.43 (m, 6H), 2.01 (d, J = 13.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.1 (d, $J_{C\text{-}P}$ = 100.9 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.6 (d, $J_{C\text{-}P}$ = 9.7 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.0 Hz), 16.6 (d, $J_{C\text{-}P}$ = 73.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.57. This compound was known: P.-Y. Renard, P. Vayron, E. Leclerc, A. Valleix, C. Mioskowski, *Angew. Chem. Int. Ed*. **2003**, *42*, 2389.

$EtP(O)Ph_2$

Ethydiphenylphosphine oxide (3l). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.68 (m, 4H), 7.50-7.41 (m, 6H), 2.29-2.21 (m, 2H), 1.21-1.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.1 (d, $J_{C\text{-}P}$ = 100.9 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.6 (d, $J_{C\text{-}P}$ = 9.7 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.0 Hz), 16.6 (d, $J_{C\text{-}P}$ = 73.4 Hz), 5.7 (d, $J_{C\text{-}P}$ = 5.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.73. This compound was known: P.-Y. Renard, P. Vayron, E. Leclerc, A. Valleix, C. Mioskowski, *Angew. Chem. Int. Ed*. **2003**, *42*, 2389.

$PhCH_2P(O)Ph_2$

Benzyldiphenylphosphine oxide (3n). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.65 (m, 4H), 7.49-7.38 (m, 6H), 7.16-7.08 (m, 5H), 3.63 (d, J = 14.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.4 (d, $J_{C\text{-}P}$ = 98.9 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.2 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.2 Hz), 130.2 (d, $J_{C\text{-}P}$ = 5.1 Hz), 128.6, 128.5, 128.5 (d, $J_{C\text{-}P}$ = 1.9 Hz), 126.9 (d, $J_{C\text{-}P}$ = 2.6 Hz), 38.2 (d, $J_{C\text{-}P}$ = 66.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.78. This compound was known: P.-Y. Renard, P. Vayron, E. Leclerc, A. Valleix, C. Mioskowski, *Angew. Chem. Int. Ed*. **2003**, *42*, 2389.

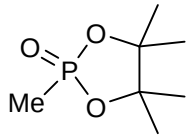
$PhCH(CH_3)P(O)Ph_2$

Diphenyl(1-phenylethyl)phosphine oxide (3o). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.87 (m, 2H), 7.50-7.40 (m, 5H), 7.32-7.14 (m, 8H), 3.61-3.56 (m, 1H), 1.55 (dq, J = 4.0 Hz, 16.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0 (d, $J_{C\text{-}P}$ = 5.3 Hz), 132.5 (d, $J_{C\text{-}P}$ = 14.4 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.3 Hz), 131.5 (d, $J_{C\text{-}P}$ = 8.5 Hz), 131.2 (d, $J_{C\text{-}P}$ = 8.6 Hz), 129.3 (d, $J_{C\text{-}P}$ = 5.2 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.1 Hz), 128.3, 128.1 (d, $J_{C\text{-}P}$ = 11.4 Hz), 127.0, 41.0 (d, $J_{C\text{-}P}$ = 66.9

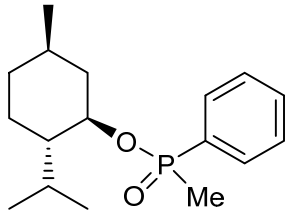
Hz), 15.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.21. This compound was known: P.-Y. Renard, P. Vayron, E. Leclerc, A. Valleix, C. Mioskowski, *Angew. Chem. Int. Ed*. **2003**, *42*, 2389.

MeP(O)Cy$_2$

Dicyclohexylmethylphosphine oxide (3p). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.10-1.95 (m, 3H), 1.83-1.62 (m, 10H), 1.41-1.19 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.9 (d, $J_{C\text{-}P}$ = 66.5 Hz), 26.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 26.4 (d, $J_{C\text{-}P}$ = 9.7 Hz), 26.0, 25.8 (d, $J_{C\text{-}P}$ = 1.5 Hz), 24.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 8.6 (d, $J_{C\text{-}P}$ = 62.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 51.32. This compound was known: E. Korzeniowska, A. E. Kozioł, E. Łastawiecka, A. Flis, M. Stankevič, *Tetrahedron* **2017**, *73*, 5153.

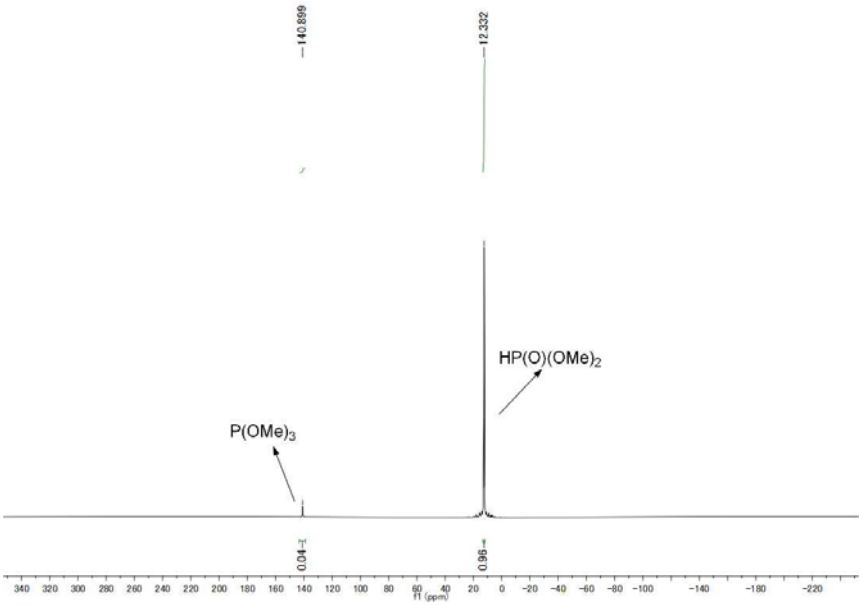


2,4,4,5,5-pentamethyl-1,3,2-dioxaphosphole 2-oxide (3q). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (d, J = 17.6 Hz, 3H), 1.38 (d, J = 52.0 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 88.2, 24.7 (d, $J_{C\text{-}P}$ = 3.4 Hz), 23.9 (d, $J_{C\text{-}P}$ = 5.2 Hz), 13.5 (d, $J_{C\text{-}P}$ = 135.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.28. This compound was known: H. Gonçalves, J. P. Majoral, *Phosphorus, Sulfur Silicon Relat. Elem.* **1978**, *4*, 343.

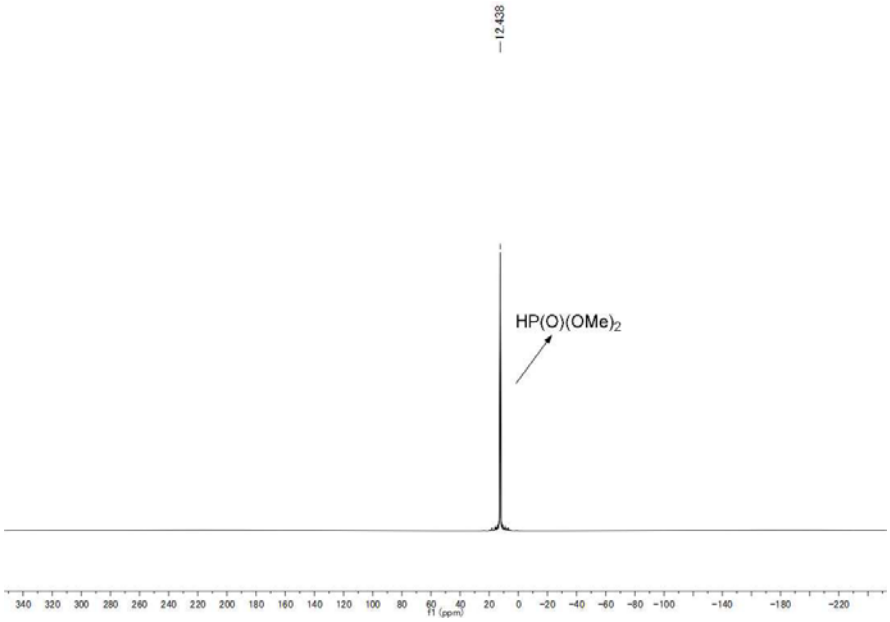


Menthyl methylphenylphosphinate (3r). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.76 (m, 4H), 7.53-7.49 (m, 2H), 7.46-7.42 (m, 4H), 4.30-3.90 (m, 2H), 2.2.-2.16 (m, 1H), 1.92-1.87 (m, 1H), 1.70-1.58 (m, 10H), 1.38-1.23 (m, 6H), 1.02-0.74 (m, 22H), 0.30 (d, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.0 (d, $J_{C\text{-}P}$ = 128.6 Hz), 132.5 (d, $J_{C\text{-}P}$ = 127.3 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.2 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.9 (d, $J_{C\text{-}P}$ = 10.2 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.6 Hz), 76.5 (d, $J_{C\text{-}P}$ = 7.2 Hz), 48.8 (d, $J_{C\text{-}P}$ = 6.4 Hz), 43.9, 43.3, 34.2, 31.6, 31.5, 25.9, 25.5, 23.1, 22.8, 22.0, 21.9, 21.2, 21.1, 17.1 (d, $J_{C\text{-}P}$ = 3.7 Hz), 16.1 (d, $J_{C\text{-}P}$ = 2.4 Hz), 15.9, 15.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.22, 40.56. This compound was known: W. Dabkowski, A. Ozarek, S. Olejniczak, M. Cypryk, J. Chojnowski, J. Michalski, *Chem. Eur. J*. **2009**, *15*, 1747.

1.4. Detailed procedure for a fast and simple way to remove $P(OMe)_3$ (1c) contaminated in $HP(O)(OMe)_2$ (2c) using TfOH as the catalyst (eq. 1 in the main text): To a NMR tube was added dimethyl phosphite **2c** (0.78 mL, 8.46 mmol) and trimethyl phosphite **1c** (50 uL, 0.42 mmol, 5 mol%) under air and subjected to ^{31}P NMR measurement. Then, TfOH (0.75 uL, 0.17 mmol, 2 mol%) and H_2O (7.6 uL, 0.42 mmol, 5 mol%) were added to the NMR tube. The tube was slightly shaken at room temperature and subjected to ^{31}P NMR measurement in ca. 5 min. ^{31}P NMR spectra revealed that the reaction completed quantitatively in the 5 min. Pure **2c** was observed in 100% ^{31}P NMR yield.

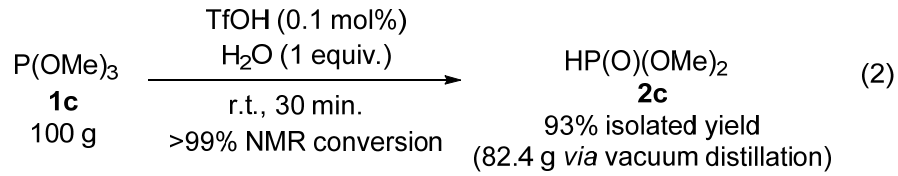


^{31}P NMR before the reaction [$HP(O)(OMe)_2$ + 5 mol% $P(MeO)_3$]



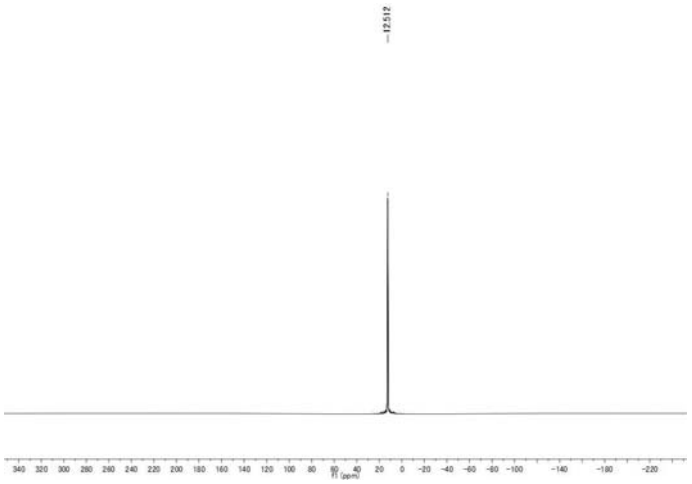
^{31}P NMR after the reaction [$HP(O)(OMe)_2$ only]

1.5. Detailed procedure for 100 gram scale reaction of TfOH-catalyzed C-O cleavage of $P(OMe)_3$ in the presence of H_2O (eq. 2 in the main text): Trimethyl phosphite **1c** (100 g, 806 mmol), TfOH (71 μL, 0.1 mol%), and H_2O (14.5 mL, 1 equiv.) was mixed by stirring in a 300 mL round-bottomed flask at 0 °C under air, slowly warmed to room temperature, and then stirred at room temperature for more 30 min. ^{31}P NMR analysis of the reaction mixture revealed that the reaction completed in the 30 min. to afford dimethyl phosphite **2c** in almost quantitative yield (>99% NMR yield). Pure **2c** was obtained by usual vacuum distillation in 93% yield (82.4 g, see the ^{31}P NMR spectra below for purity).



(2)

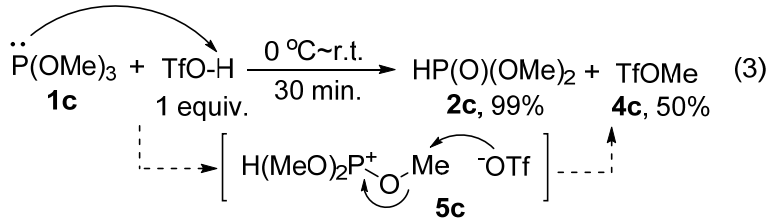
Before the reaction **After the reaction**



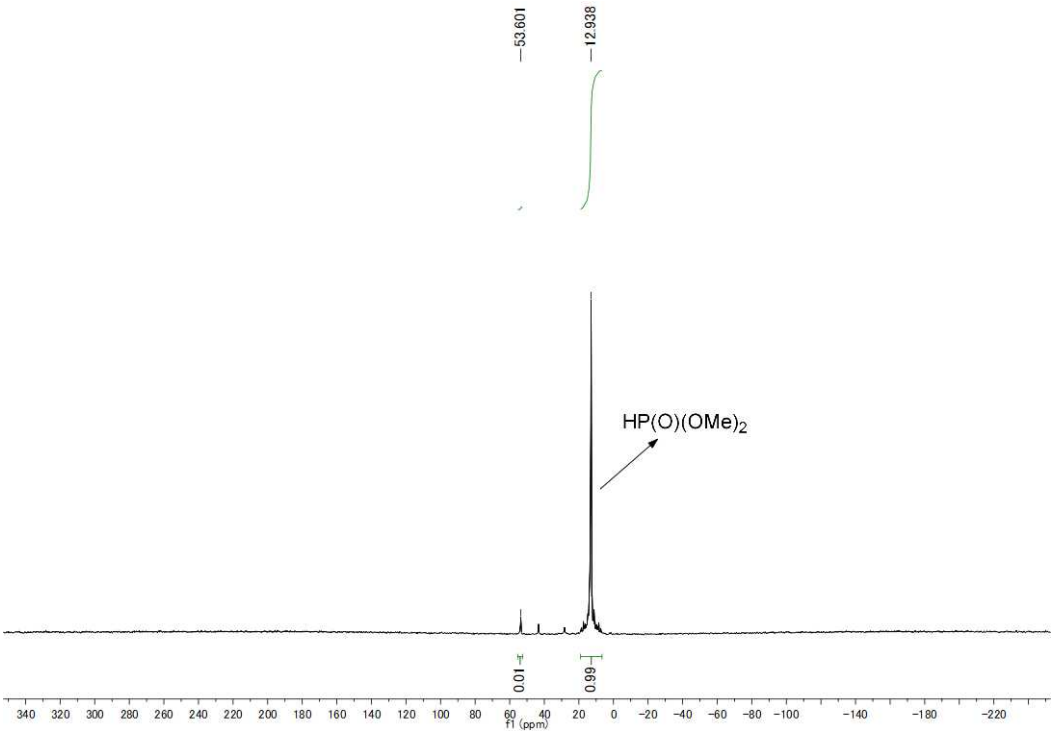
^{31}P NMR of purified $HP(O)(OMe)_2$ (2c)

2. Control Reactions of the Mechanistic Studies

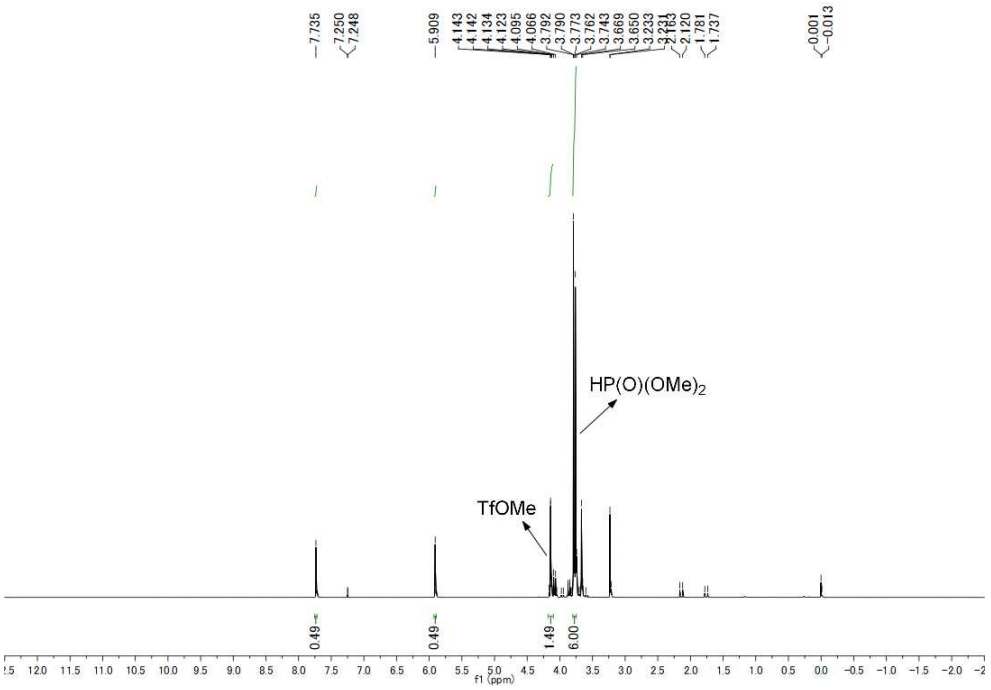
2.1. Stoichiometric reaction of $P(OMe)_3$ (1a) and TfOH (eq. 3 in the main text)



Detailed Procedure: To an NMR tube cooled at 0 °C were successively added $CDCl_3$ (0.5 mL), trifluorormethanesulfonic acid (37.5 uL, 0.424 mmol), and trimethyl phosphite (**1a**) (50 uL, 1 equiv.) dropwise under N_2. The tube was then slowly warmed to room temperature and remained for 2 h. ^{31}P NMR spectra of the reaction mixture revealed that the reaction completed to afford dimethyl phosphite **2c** in almost quantitative yield (see the ^{31}P NMR spectra below). ^{1}H NMR spectra of the reaction mixture revealed that methyl trifluorormethanesulfonate (**4c**) was generated in ca. 50% yield (see the ^{1}H NMR spectra below).



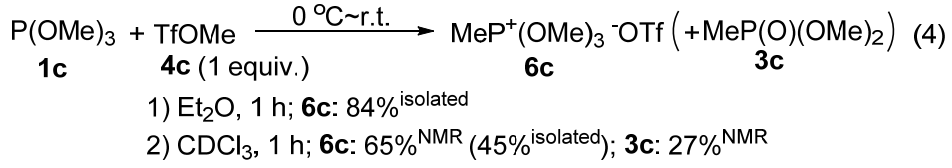
^{31}P NMR



^{1}H NMR

Results and Discussion: This reaction confirmed that stoichiometric reaction of $P(OMe)_3$ (**1a**) and TfOH can afford a quantitative yield of dimethyl phosphite **2c** (ref. 11 in the main text), which very possibly proceeded via the formation of phosphonium salt $HP^+(OMe)_3 \cdot {}^-OTf$ (**5c**) by protonation of **1c** with TfOH followed by an intramolecular S_N2 attack of TfO^- at a Me group of **5c** (ref. 11a-b in the main text).

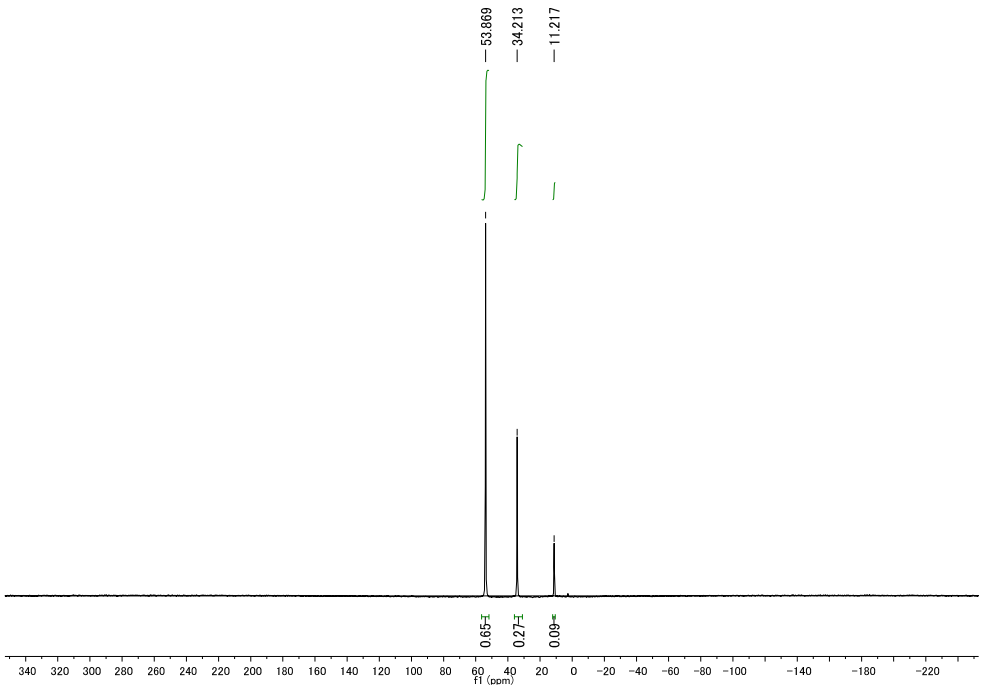
2.2. Stoichiometric reaction of $P(OMe)_3$ (1a) and TfOMe (eq. 4 in the main text)



Detailed Procedure for Entry 1 (according to the literature method: K. S. Colle, E. S. Lewis, *J. Org. Chem*. **1978**, *43*, 571): To a 10 mL Schlenk tube containing a stirring bar cooled at 0 °C were successively added Et_2O (2 mL), methyl trifluorormethanesulfonate (**4c**) (186 uL, 1.7 mmol), and trimethyl phosphite (**1a**) (0.2 mL, 1 equiv.) dropwise under N_2. The tube was then slowly warmed to room temperature and stirred for 1 h. A white solid precipitated form the reaction mixture, which was collected by filtration and washed twice with Et_2O under N_2 (in

glove box). The white solid, $MeP^{+}(OMe)_3 \cdot {}^{-}OTf$ (**6c**), was obtained in 84% isolated yield (412.3 mg) after vacuum drying.

Detailed Procedure for Entry 2: To an NMR tube cooled at 0 ^{o}C were successively added $CDCl_3$ (2 mL), methyl trifluorormethanesulfonate (**4c**) (186 uL, 1.7 mmol), and trimethyl phosphite (**1a**) (0.2 mL, 1 equiv.) dropwise under N_2. The tube was then slowly warmed to room temperature and stirred for 1 h. ^{31}P NMR spectra revealed that the reaction completed to afford **6c** in 65% NMR yield (45% isolated yield) and **3c** in 27% **NMR** yield, respectively (see the NMR spectra below).



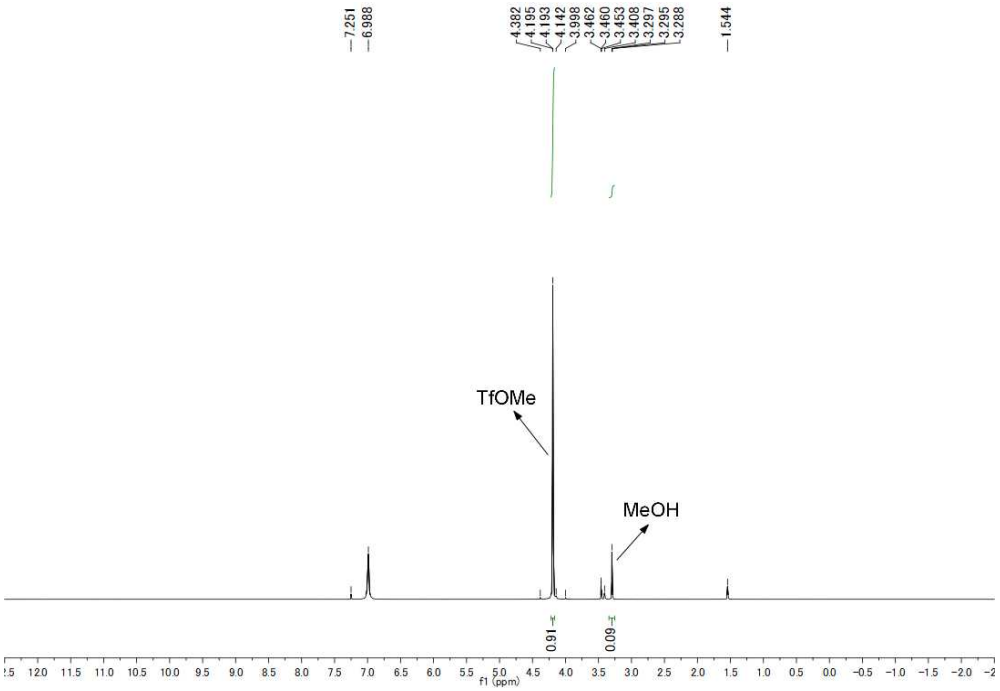
^{31}P NMR of the reaction mixture of entry 2

Results and Discussion: According to the literature method (K. S. Colle, E. S. Lewis, *J. Org. Chem*. **1978**, *43*, 571), Et_2O is not a good solvent for $MeP^{+}(OMe)_3 \cdot {}^{-}OTf$ (**6c**), so it can easily precipitated from the Et_2O mixture of **4c** and **1c** and be obtained in a good 84% isolated yield by filtration (entry 1). In contrast, $CDCl_3$ is a better solvent (see also eqs. 9 and 10, in which solvation of **6c** in $CDCl_3$ quickly leads to its conversion to **3c**). Most likely for the same reason, the generated **6c** in the $CDCl_3$ mixture of **4c** and **1c** also quickly converted to **3c**. Subsequently, only a much lower yield of **6c** was observed with observation of a considerable amount of **3c** (entry 2). This result suggests that the conversion of **6c** to **3c** may be very fast.

2.3. Hydrolysis of TfOMe (4c) (eq. 5 in the main text)

$$\underset{\textbf{4c}}{\text{TfOMe}} + \underset{1\text{ equiv.}}{H_2O} \xrightarrow[\text{r.t., overnight}]{CDCl_3} \text{TfOH} + \text{MeOH} \quad (5)$$

Detailed Procedure: To an NMR tube was added $CDCl_3$ (0.5 mL), methyl trifluorormethanesulfonate (**4c**) (46.4 uL, 0.424 mmol), and H_2O (7.7uL, 1 equiv.) under N_2. After standing at room temperature overnight, the tube was subjected to ^1H NMR measurement, revealing that **4c** was partially hydrolyzed to MeOH (see the NMR spectra below). This result confirmed the hydrolysis of TfOMe (**4c**) in the presence of water.



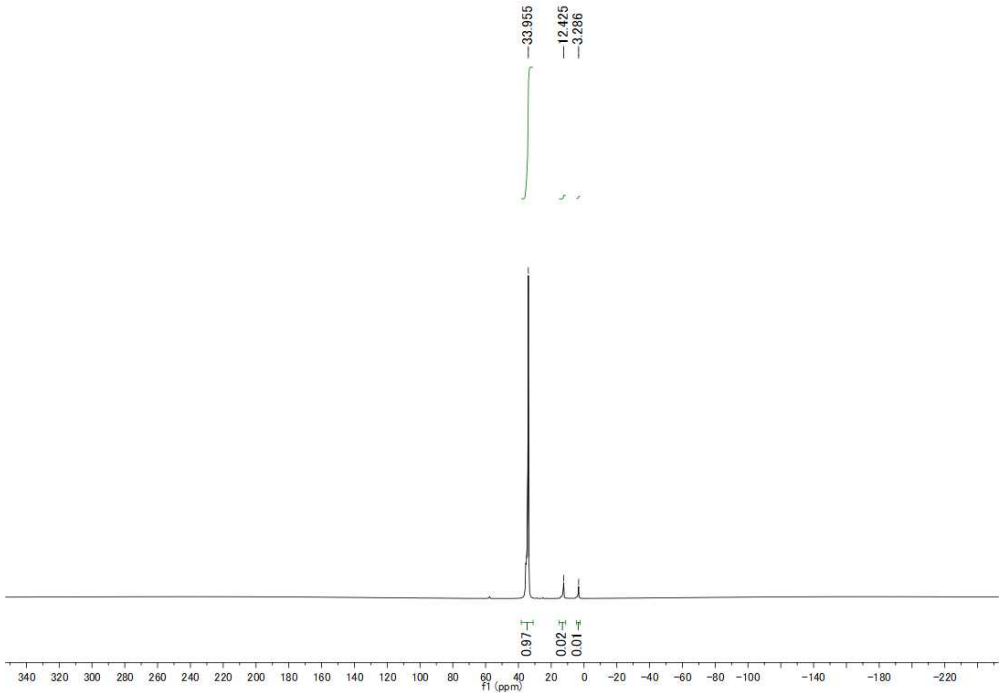
^1H NMR

2.4. TfOMe (4c) or $MeP^+(OMe)_3 \cdot {}^-OTf$ (6c) catalyzed transformation of $P(OMe)_3$ (1c) (eq. 6 in the main text)

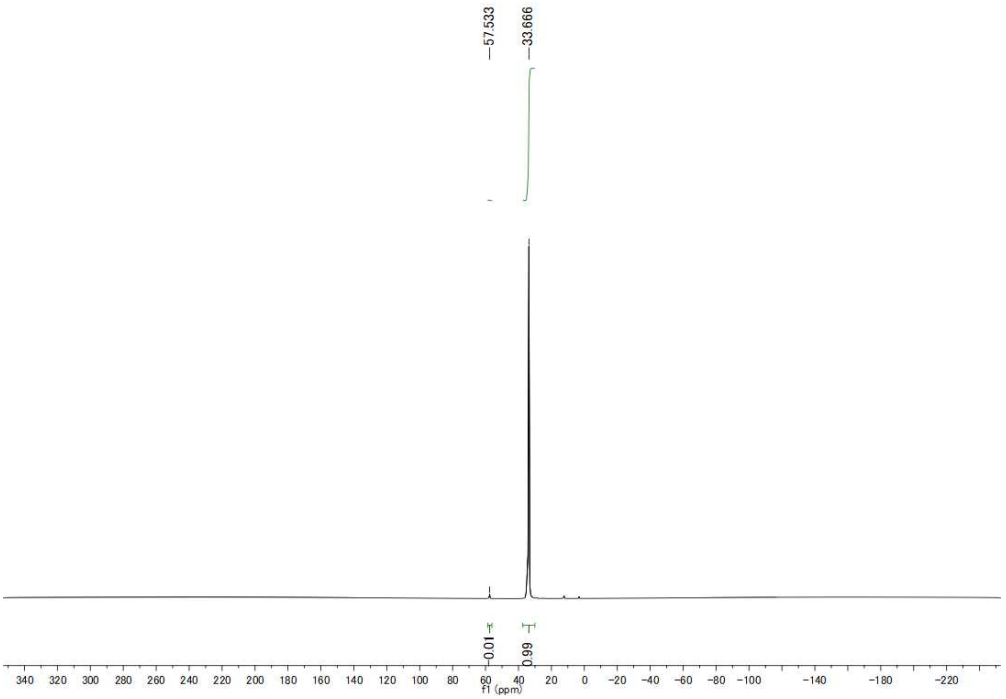
$$\underset{\textbf{1c}}{P(OMe)_3} \xrightarrow[60\ ^oC,\ 16\ h]{\textbf{4c}\text{ or }\textbf{6c}\ (2\ mol\%)} \underset{\textbf{3c},\ 97\sim99\%}{MeP(O)(OMe)_2} \quad (6)$$

Detailed Procedures: To an NMR tube was added trimethyl phosphite (**1a**) (0.4 mL, 3.4 mmol) and methyl trifluorormethanesulfonate (**4c**) (7.4 uL, 2 mol%) or phosphonium salt $MeP^+(OMe)_3 \cdot {}^-OTf$ (**6c**) (19.7 mg, 2 mol%) under N_2. The mixtures were then heated to 60 ^{o}C for 16 h. ^{31}P NMR spectra revealed that the reactions were complete. The methyl

trifluorormethanesulfonate (**4c**) catalyzed reaction afforded **3c** in 97% yield (see the NMR spectra below). The phosphonium salt $MeP^{+}(OMe)_3 \cdot {}^{-}OTf$ (**6c**) catalyzed reaction afforded **3c** in 99% yield (see the NMR spectra below).



^{31}P NMR of 4c-catalyzed reaction



^{31}P NMR of 6c-catalyzed reaction

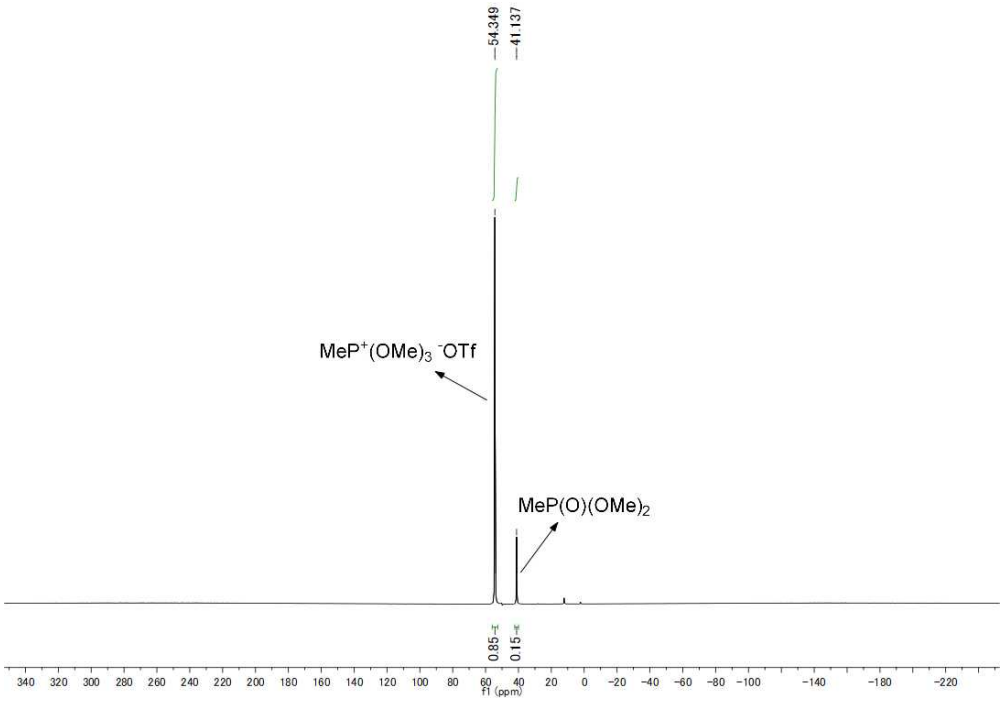
Results and Discussion: The above results indicated that **4c** and **6c** could catalyze the model reaction effectively to give almost quantitative yields of **3c**, suggesting an interesting

mechanism that may involve TfOR (**4**) and $RP^{+}(OR)_3 \cdot {}^{-}OTf$ (**6**) as the active catalysts/intermediates.

2.5. Stoichiometric reaction of $MeP(O)(OMe)_2$ (3c) and TfOMe (4c) (eq. 7 in the main text)

$$\underset{\textbf{3c}}{MeP(O)(OMe)_2} + \underset{\substack{\textbf{4c}\\ 1\ equiv.}}{TfOMe} \xrightarrow[30\ min.]{r.t.} \underset{\textbf{6c},\ 85\%}{MeP^{+}(OMe)_3\ {}^{-}OTf} \qquad (7)$$

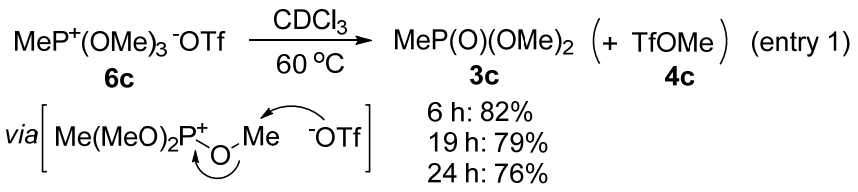
Detailed procedure: To an NMR tube was added dimethyl methylphosphonate (**3c**) (0.37 mL, 3.4 mmol) and methyl trifluorormethanesulfonate (**4c**) (0.37 mL, 1 equiv.) under N_2 at room temperature. The tube was then sealed, slightly shaken, and subjected to ^{31}P NMR measurement in ca. 30 min. ^{31}P NMR spectra revealed that **6c** was obtained in 85% yield (see the NMR spectra below).



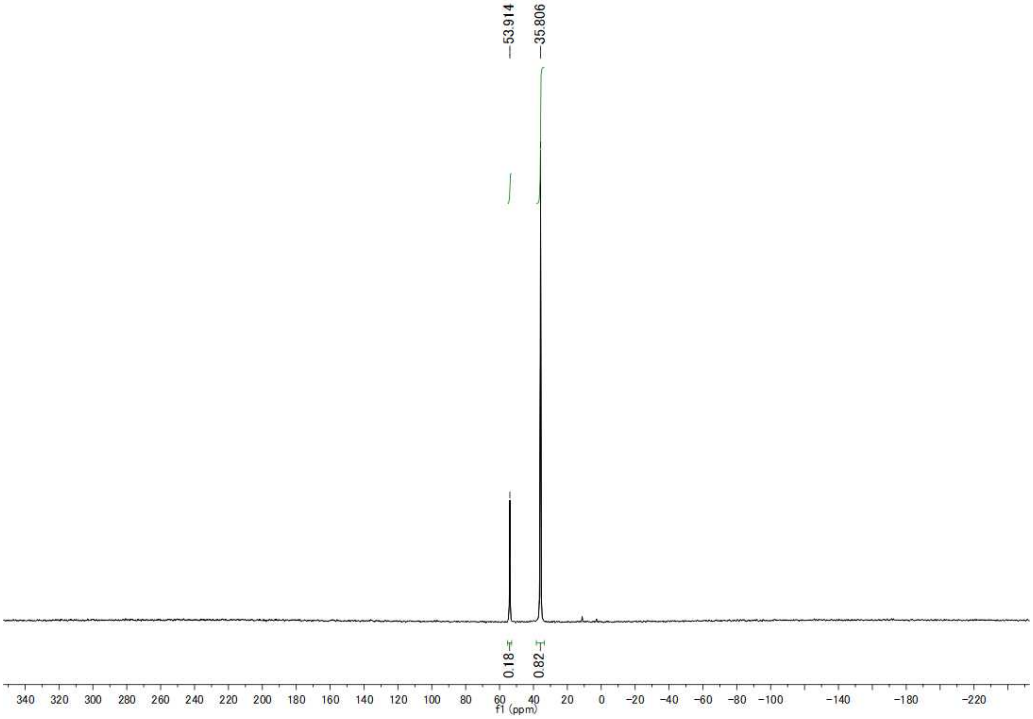
^{31}P NMR

Results and Discussion: The above result indicated that product **3c** could also react with **4c** fastly to give a high yield of **6c**. This is consistent with the equilibrium between **3**, **4** and **6** as documented from the literature (ref. 14 in the main text).

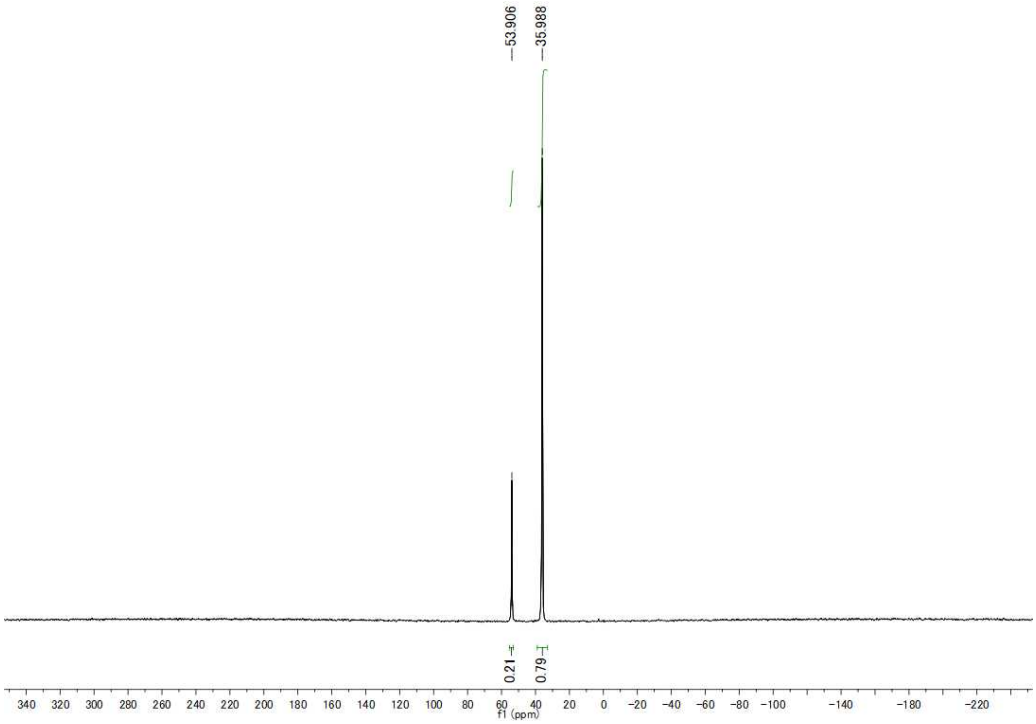
2.6. Conversion of pure $MeP^{+}(OMe)_3 \cdot {}^{-}OTf$ (6c) to product 3c (eq. 9 in the main text)



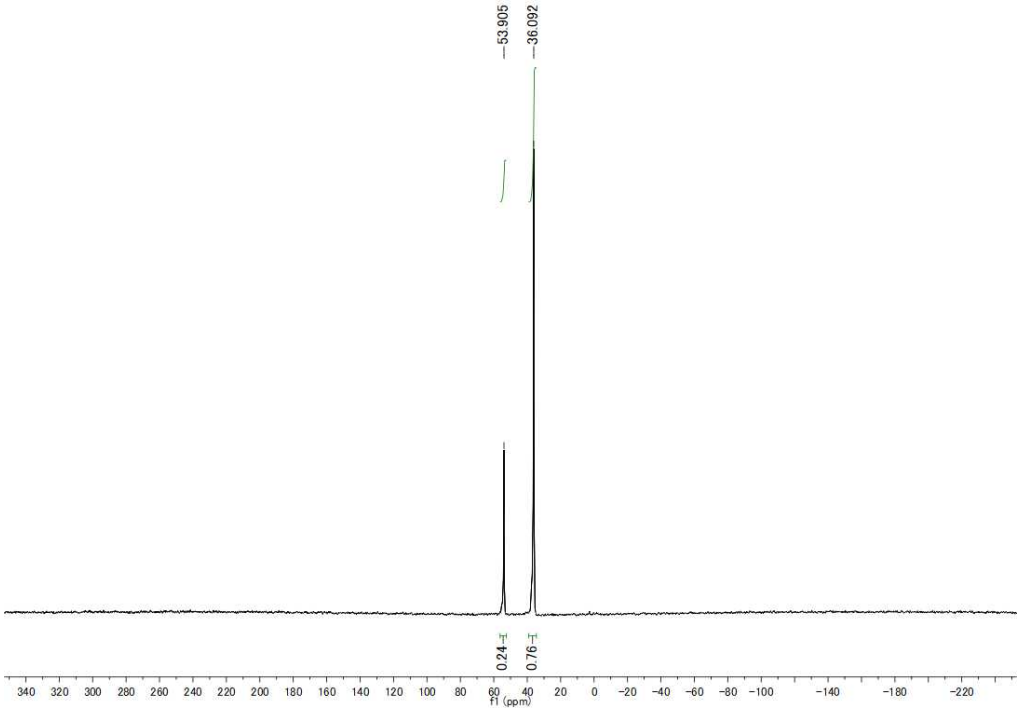
Detailed Procedure for Entry 1 at 60 °C: The phosphonium salt $MeP^{+}(OMe)_3 \cdot {}^{-}OTf$ (**6c**) (121.8 mg, 0.42 mmol) solved in $CDCl_3$ (0.5 mL) sealed in an NMR tube under N_2 was heated at 60 °C and measured by ^{31}P NMR at 6 h, 19 h, and 24 h, respectively. ^{31}P NMR spectra revealed that **3c** was formed in 82%, 79%, and 76% yields, respectively (see the NMR spectra below).



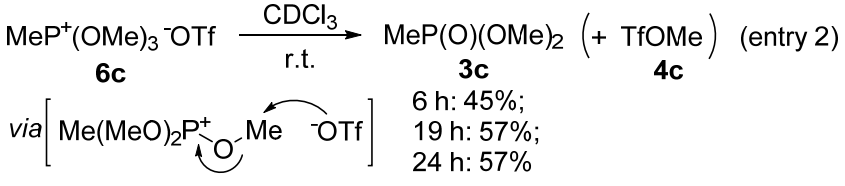
^{31}P NMR (60 °C, 6 h)



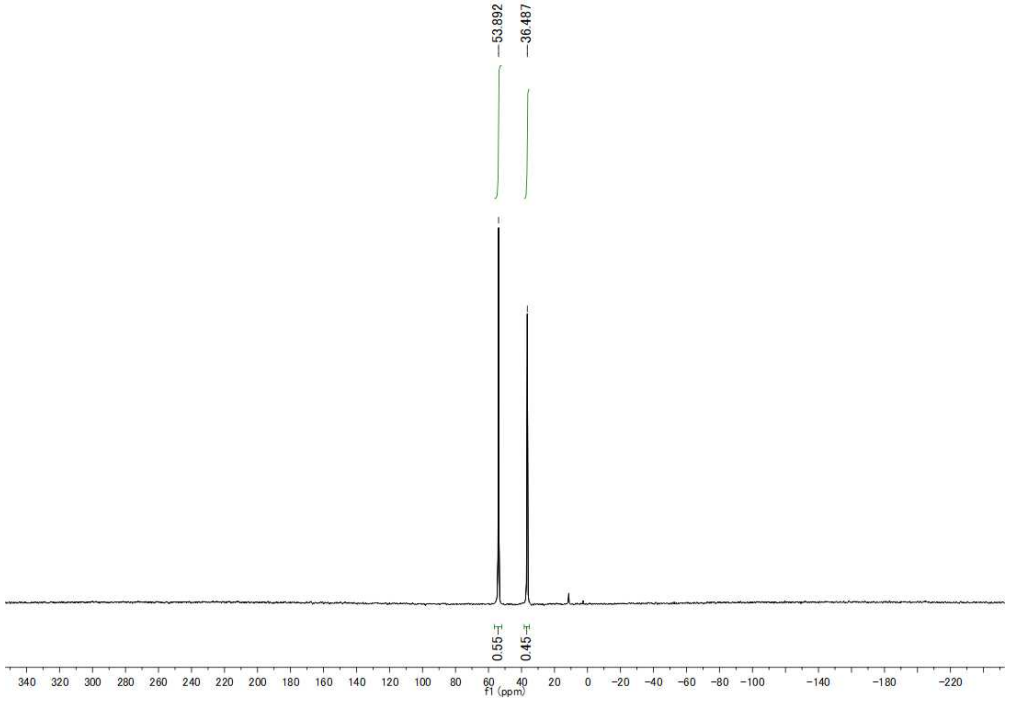
^{31}P NMR (60 ^{o}C, 19 h)



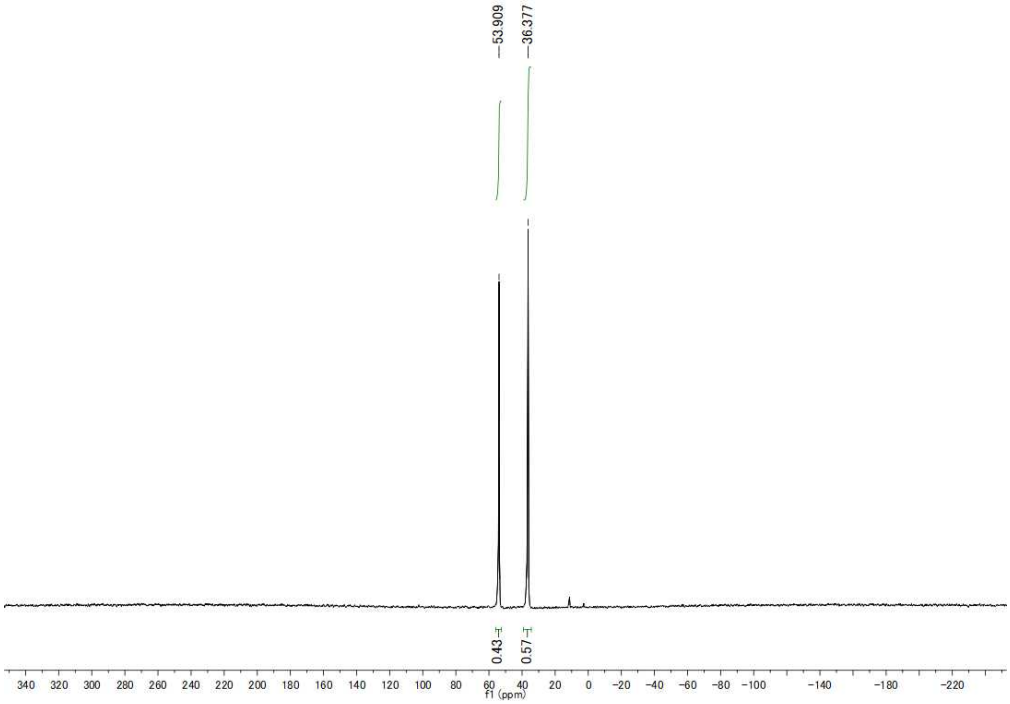
^{31}P NMR (60 ^{o}C, 24 h)



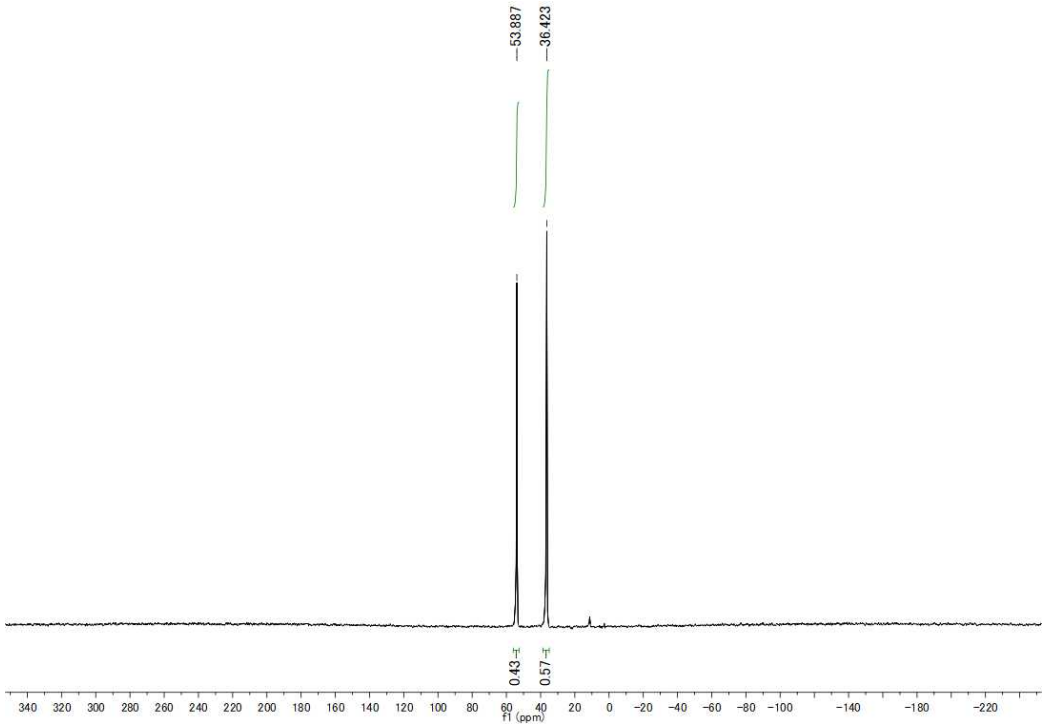
Detailed Procedure for Entry 2 at Room Temperature: The phosphonium salt $MeP^{+}(OMe)_3 \cdot {}^{-}OTf$ (**6c**) (121.8 mg, 0.42 mmol) solved in $CDCl_3$ (0.5 mL) sealed in an NMR tube under N_2 was slightly shaked at room temperature and measured by ^{31}P NMR at 6 h, 19 h, and 24 h, respectively. ^{31}P NMR spectra revealed that **3c** was formed in 45%, 57%, and 57% yields, respectively (see the NMR spectra below).



^{31}P NMR (r.t., 6 h)



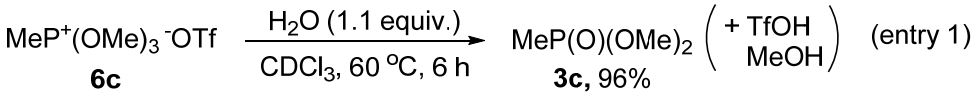
^{31}P NMR (r.t., 19 h)



^{31}P NMR (r.t., 24 h)

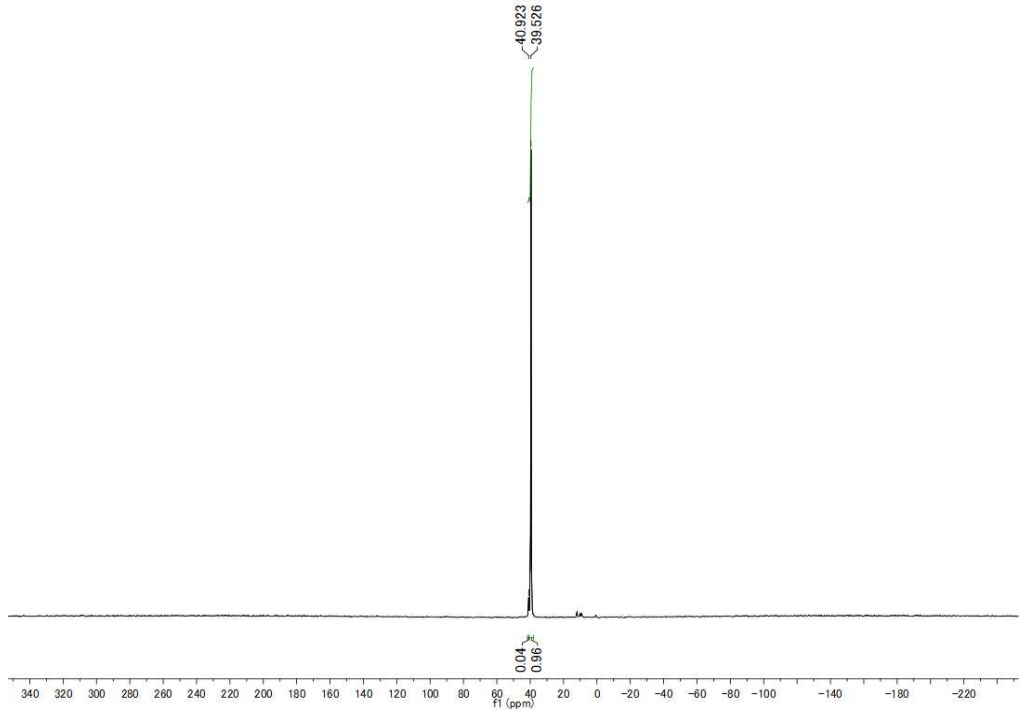
Results and Discussion: The above results indicated that conversion of **6c** to **3c** is rather fast under the standard conditions (60 ^{o}C) or even at room temperature. The close yields of **3c** at 19 and 24 h (79% and 76% yields at 60 ^{o}C; 57% and 57% yields at room temperature) also revealed that both reactions have reached the equilibrium between **3c**, **4c**, and **6c** at 60 ^{o}C or at room temperature. Since **1c** did not present in the reaction, the reaction possibly proceeded via a monomolecular mechanism (the textbook mechanism suggested by Arbuzov) involving the S_N2 attack of TfO^- at a Me group of **6c** (similar to the one shown in eq. 3)

2.7. Conversion of pure $MeP^+(OMe)_3 \cdot {}^-OTf$ (6c) to product 3c in the presence of H_2O (eq. 10 in the main text)

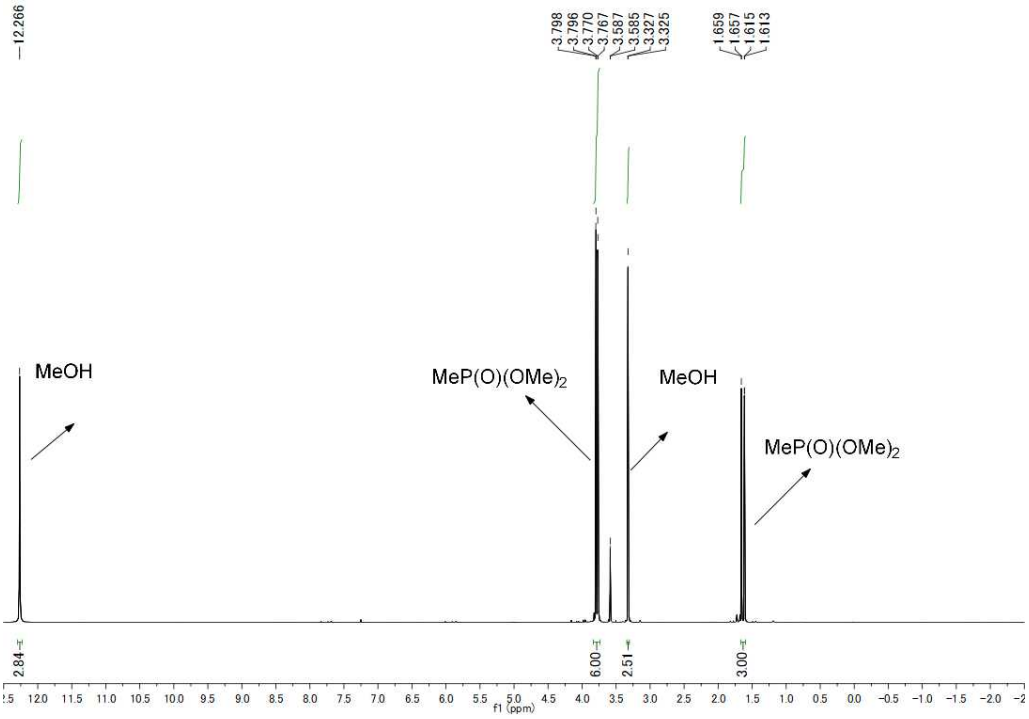


Detailed Procedure for Entry 1 at 60 ^{o}C: The mixture of phosphonium salt $MeP^+(OMe)_3 \cdot {}^-OTf$ (**6c**) (121.8 mg, 0.42 mmol) and H_2O (8.3 uL, 1.1 equiv.) in $CDCl_3$ (0.5 mL) in an NMR tube sealed under N_2 was heated at 60 ^{o}C for 6 h. ^{31}P NMR spectra of the reaction

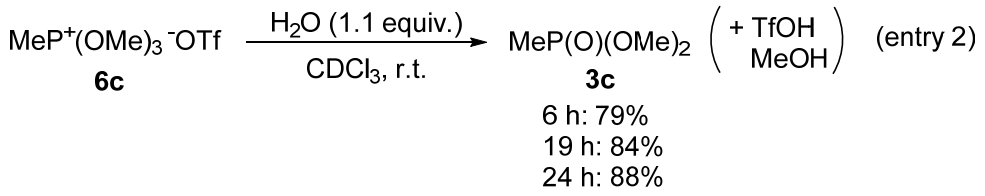
mixture revealed that the reaction completed to afford **3c** in 96% yield (see the ^{31}P NMR spectra below). ^{1}H NMR spectra revealed that MeOH (TfOH altogether) was also generated (see the ^{1}H NMR spectra below).



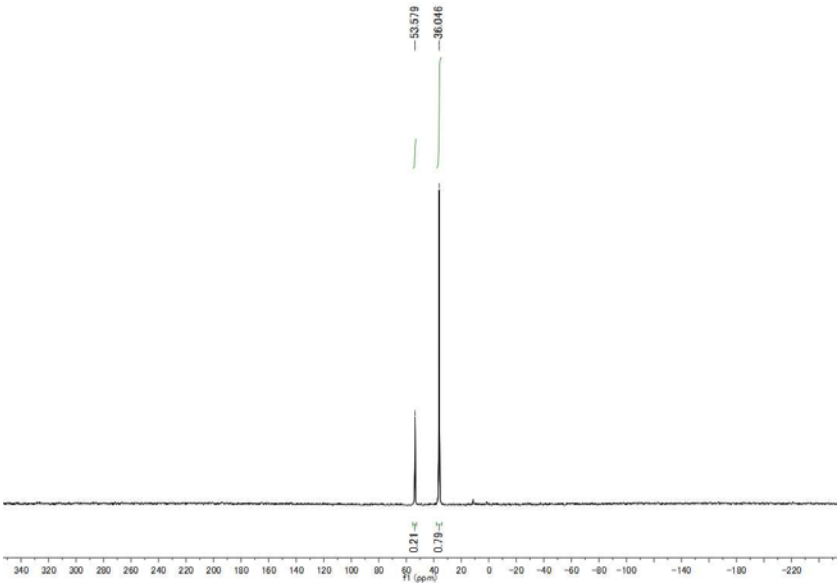
^{31}P NMR (60 ^{o}C, 6 h)



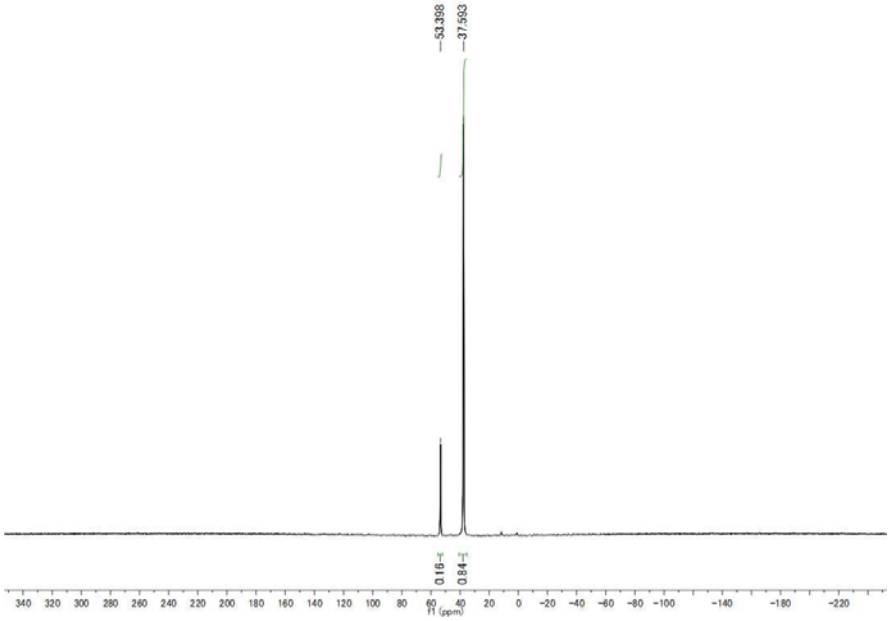
^{1}H NMR (60 ^{o}C, 6 h)



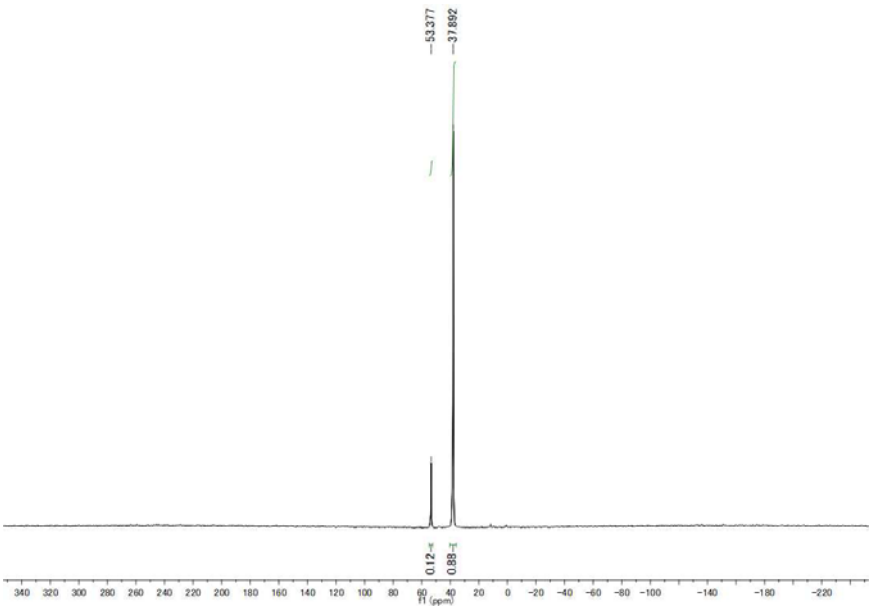
Detailed Procedure for Entry 2 at Room Temperature: The mixture of phosphonium salt $MeP^{+}(OMe)_3 \cdot {}^{-}OTf$ (**6c**) (121.8 mg, 0.42 mmol) and H_2O (8.3 uL, 1.1 equiv.) in $CDCl_3$ (0.5 mL) in an NMR tube sealed under N_2 was slightly shaked at room temperature and measured by ^{31}P NMR at 6 h, 19 h, and 24 h, respectively. ^{31}P NMR spectra revealed that **3c** was formed in 79%, 84% and 88% yield, respectively (see the NMR spectra below).



^{31}P NMR (r.t., 6 h)



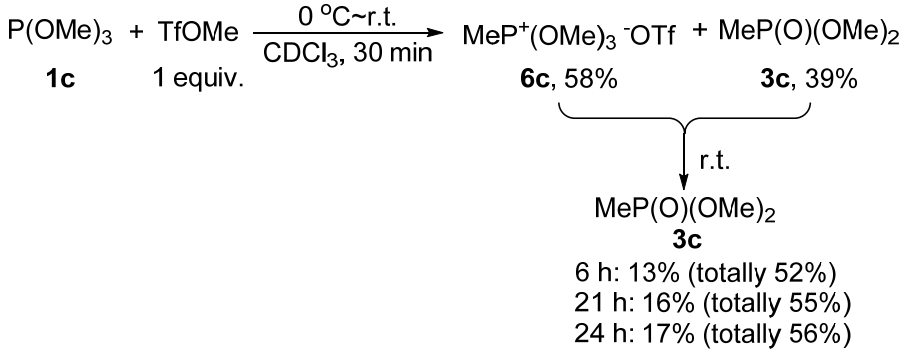
^{31}P NMR (r.t., 19 h)



^{31}P NMR (r.t., 24 h)

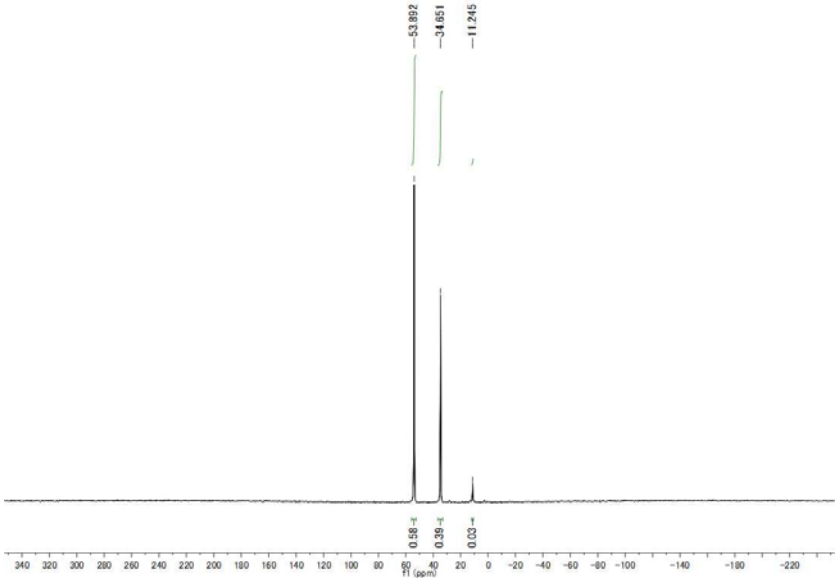
Results and Discussion: The above results indicated that, quite differently to the reactions of pure **6c** in $CDCl_3$ without water (eq. 9) that reached the equilibrium (eq. 8) and gave close yields of **3c**, in the presence of 1.1 equiv. of water, the conversion of **6c** to **3c** can be much faster and give much higher yields of **3c**. This is most likely due to the removal of **4c** by the added water through hydrolysis (eq. 5). Hence, without the presence of **4c**, the equilibrium can be broken and driven rightward to ensure more efficient and faster conversion of **6c** and higher yields of **3c**.

2.8. Conversion of not isolated $MeP^+(OMe)_3 \cdot {}^-OTf$ (6c) to product 3c (ref. 17 in the manuscript and for comparison with eq. 9)



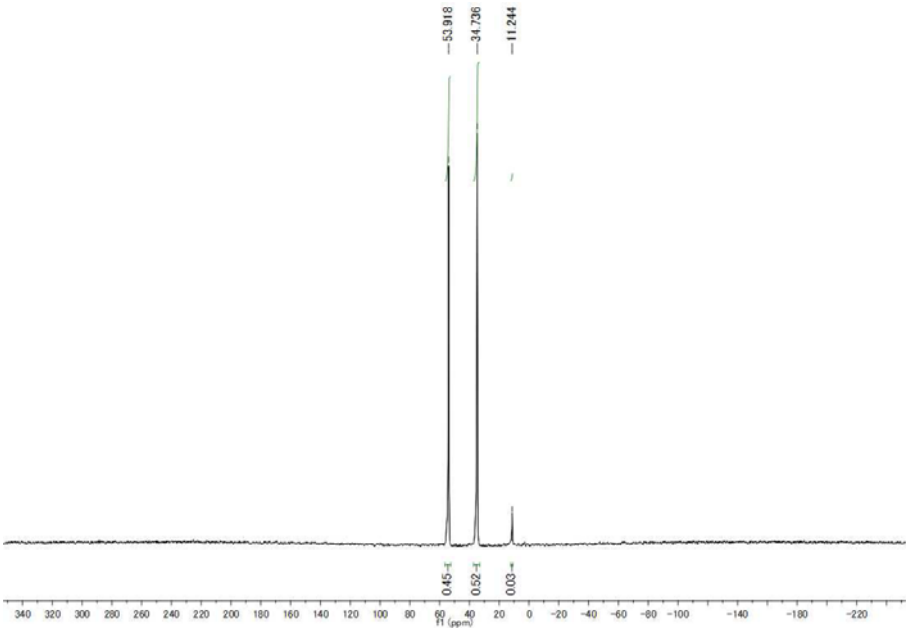
Detailed procedure for Reaction at Room Temperature: To an NMR tube cooled at 0 °C were successively added $CDCl_3$ (0.5 mL), methyl trifluorormethanesulfonate (**4c**) (46.4 uL,

0.424 mmol), and trimethyl phosphite (**1a**) (50 uL, 1 equiv.) dropwise under N_2. The tube was then slowly warmed to room temperature and stirred for 30 min. ^{31}P NMR spectra revealed that the reaction completed to afford **6c** in 58% NMR yield and **3c** in 39% NMR yield, respectively (see the NMR spectra below).

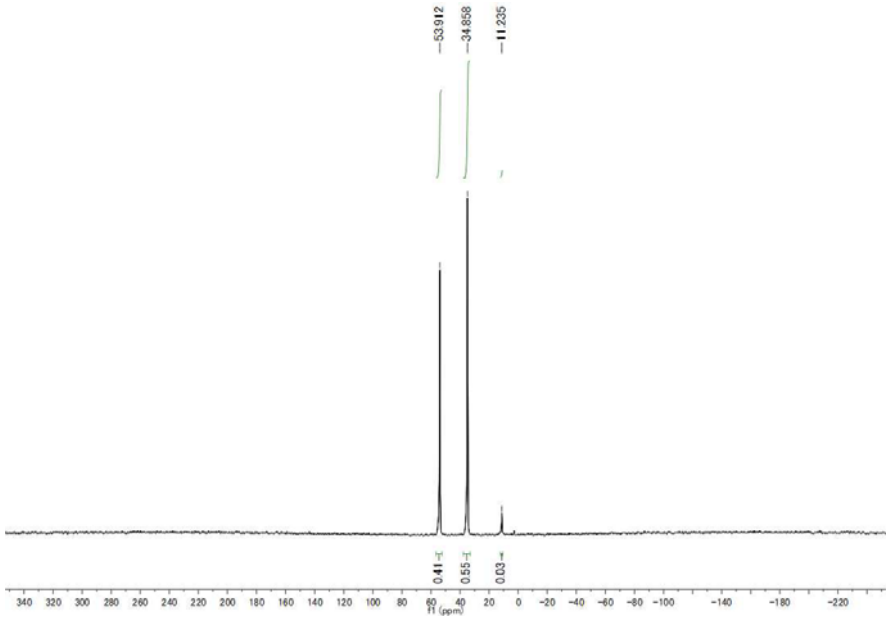


^{31}P NMR (r.t., 30 min)

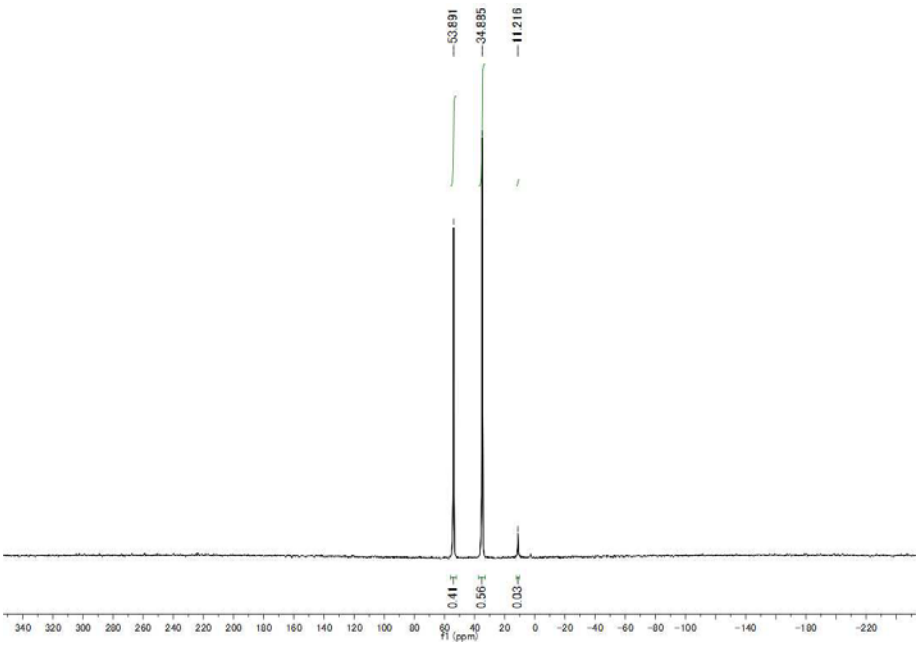
Without isolation of **6c**, the above reaction mixture (containing TfOMe **4c**) was directly shaked slightly at room temperature for 6 h, 21 h and 24h, respectively. ^{31}P NMR spectra revealed that total yields of **3c** are 52%, 55% and 56% yields, respectively (see the NMR spectra below). This means the yields of **3c** generated from **6c** are 13%, 16%, and 17%, respectively.



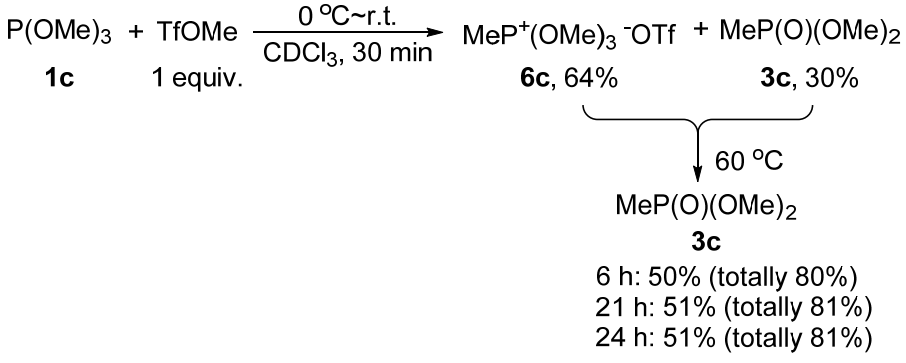
^{31}P NMR (r.t., 6 h)



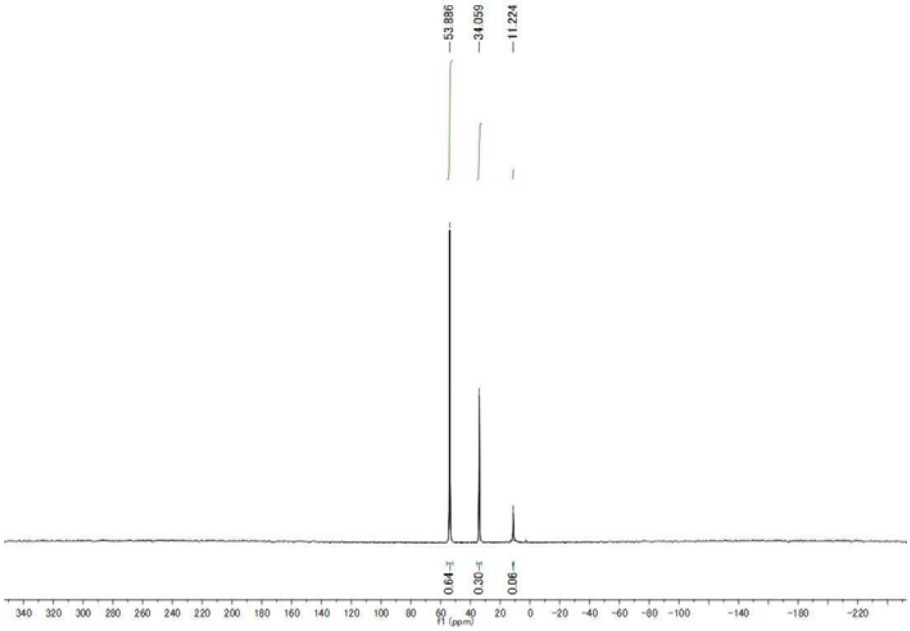
^{31}P NMR (r.t., 21 h)



^{31}P NMR (r.t., 24 h)

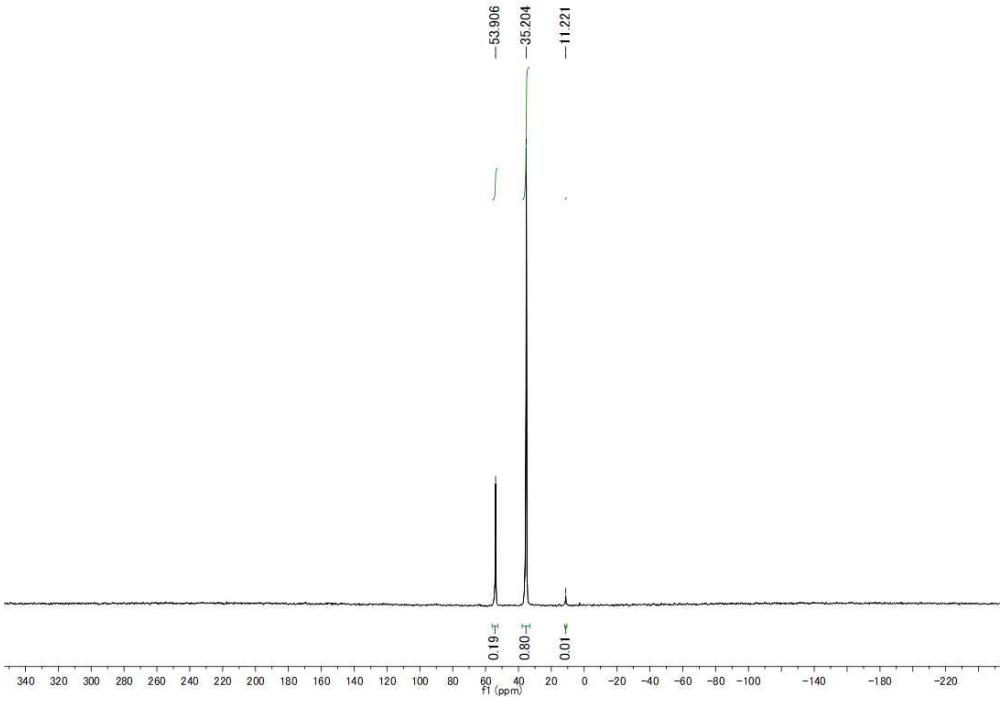


Detailed Procedure for Reaction at 60 °C: To an NMR tube cooled at 0 °C were successively added $CDCl_3$ (0.5 mL), methyl trifluorormethanesulfonate (**4c**) (46.4 uL, 0.424 mmol), and trimethyl phosphite (**1a**) (50 uL, 1 equiv.) dropwise under N_2. The tube was then slowly warmed to room temperature and stirred for 30 min. ^{31}P NMR spectra revealed that the reaction completed to afford **6c** in 64% NMR yield and **3c** in 30% NMR yield, respectively (see the NMR spectra below).

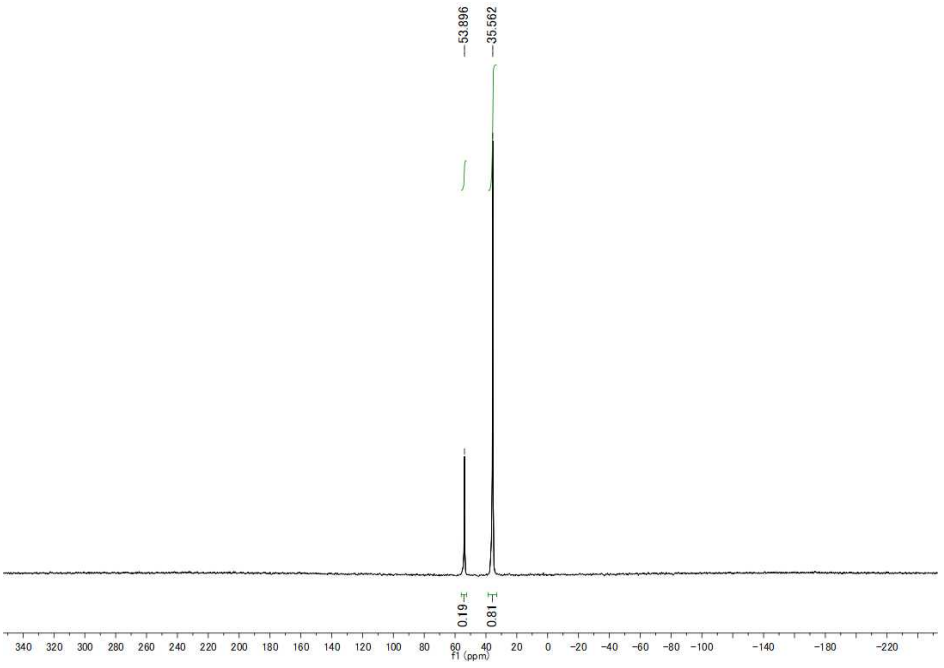


^{31}P NMR (r.t., 30 min)

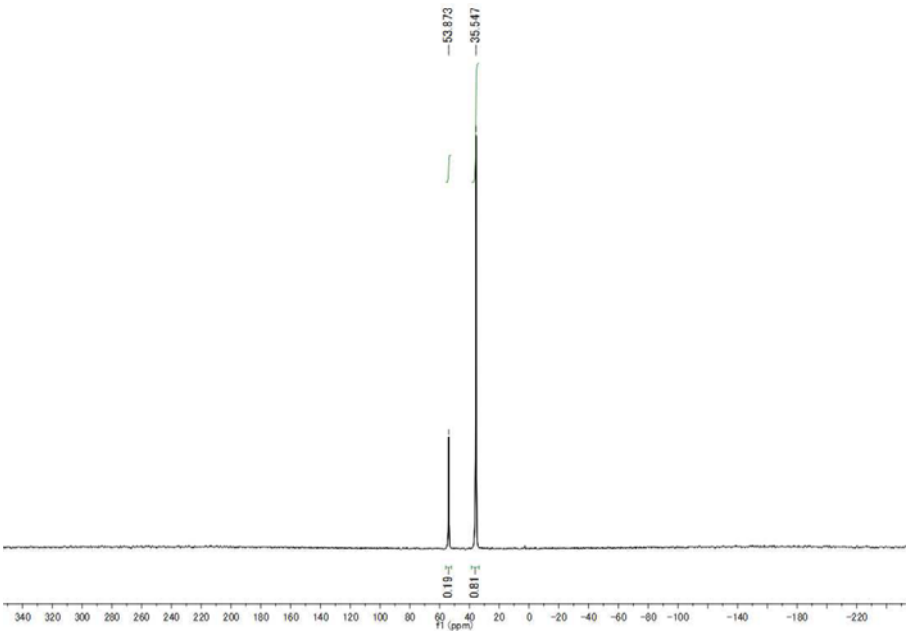
Without isolation of **6c**, the above reaction mixture (containing TfOMe **4c**) was directly heated at 60 °C for 6 h, 21 h and 24 h, respectively. ^{31}P NMR spectra revealed that total yields of **3c** are 80%, 81%, and 81%, respectively (see the NMR spectra below). This means the yields of **3c** generated from **6c** are 50%, 51%, and 51%, respectively.



^{31}P NMR (60 ^{o}C, 6 h)



^{31}P NMR (60 ^{o}C, 21 h)

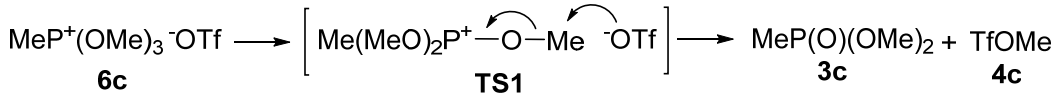


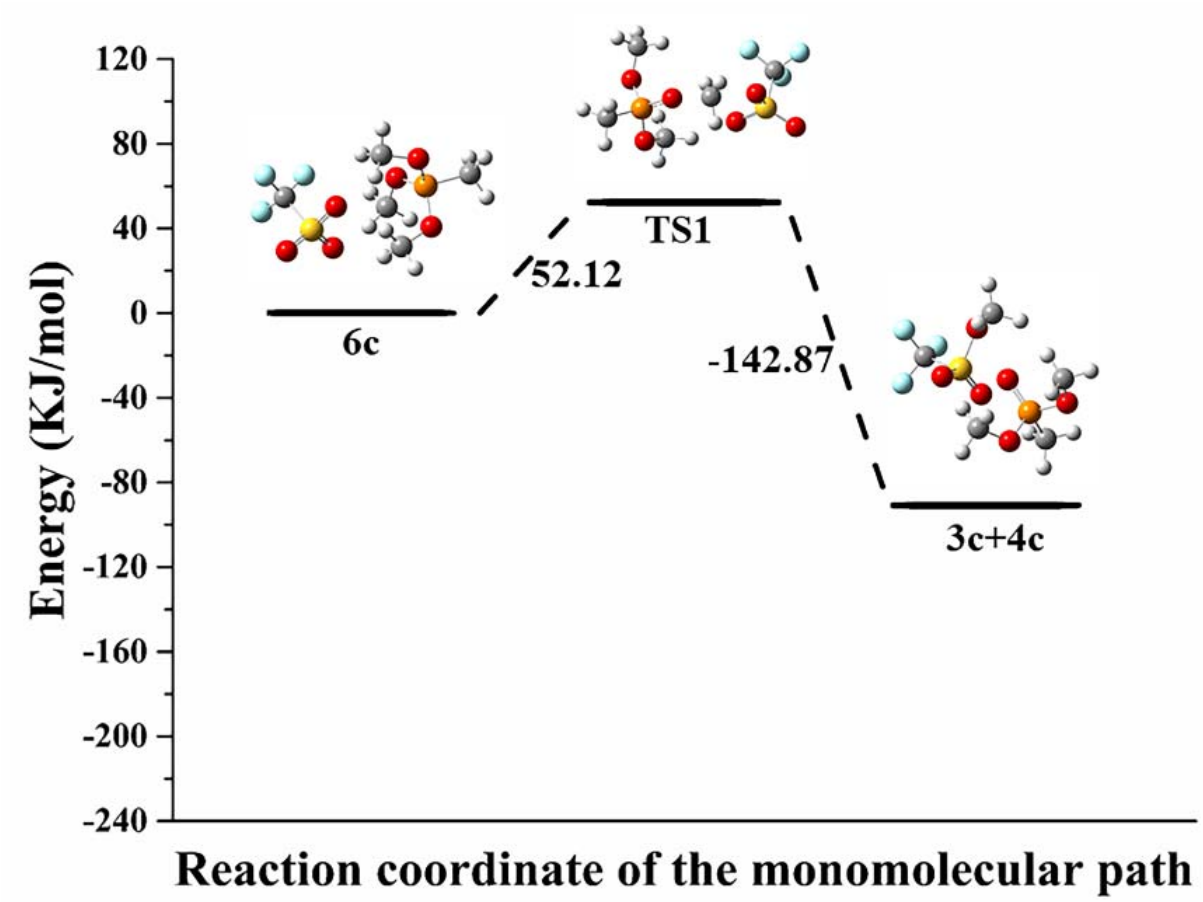
^{31}P NMR (60 ^{o}C, 24 h)

Results and Discussion: Without isolation of **6c**, considerable amounts of TfOMe (**4c**) should be remained in the reaction mixture of **1c** and **4c**. Since **4c** can hinder the conversion of **6c** to **3c** by reacting with **3c** to give **6c** according the their equilibrium (eq. 8 in the main text), in the presence of the contaminant **4c** in the reaction mixture, conversion of **6c** to **3c** can be much slower in comparison with the reactions using pure **6c** (eq. 9). Even though, the close yields of **3c** (52~56% yields at room temperature; 80~81% yields at 60 ^{o}C) also revealed that both reactions have reached the equilibrium between **3c**, **4c**, and **6c** at 60 ^{o}C or at room temperature.

3. Theoretical Calculation of the Transition States (Figure 1 in the main text)

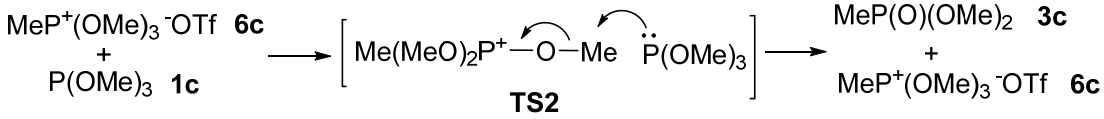
3.1. Theoretical Calculation of the monomolecular transition state

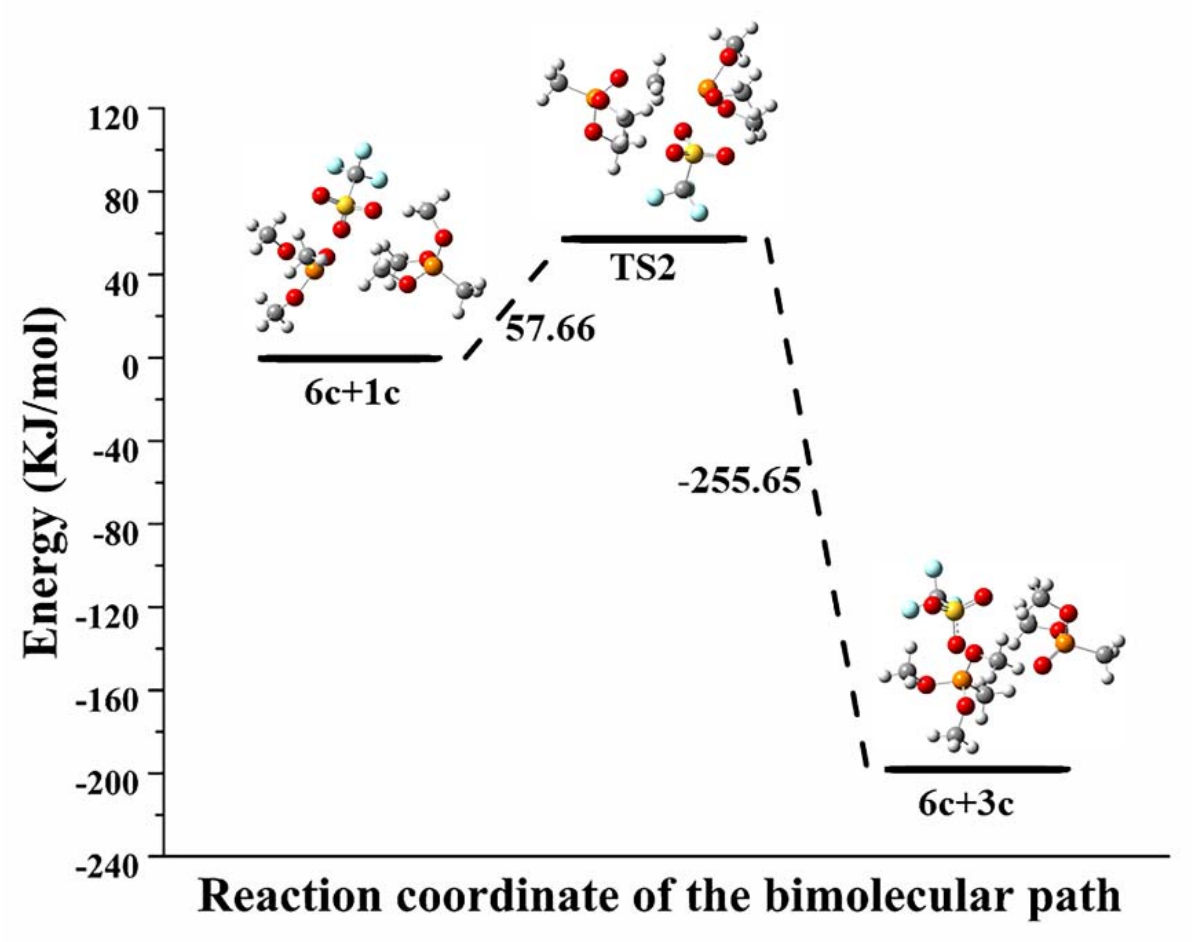




Ball-and-stick representations. Atoms: red: oxygen; blue: fluorine; white: hydrogen; light yellow: sulfur; gray: carbon; orange: phosphorus.

3.2. Theoretical Calculation of the bimolecular transition state





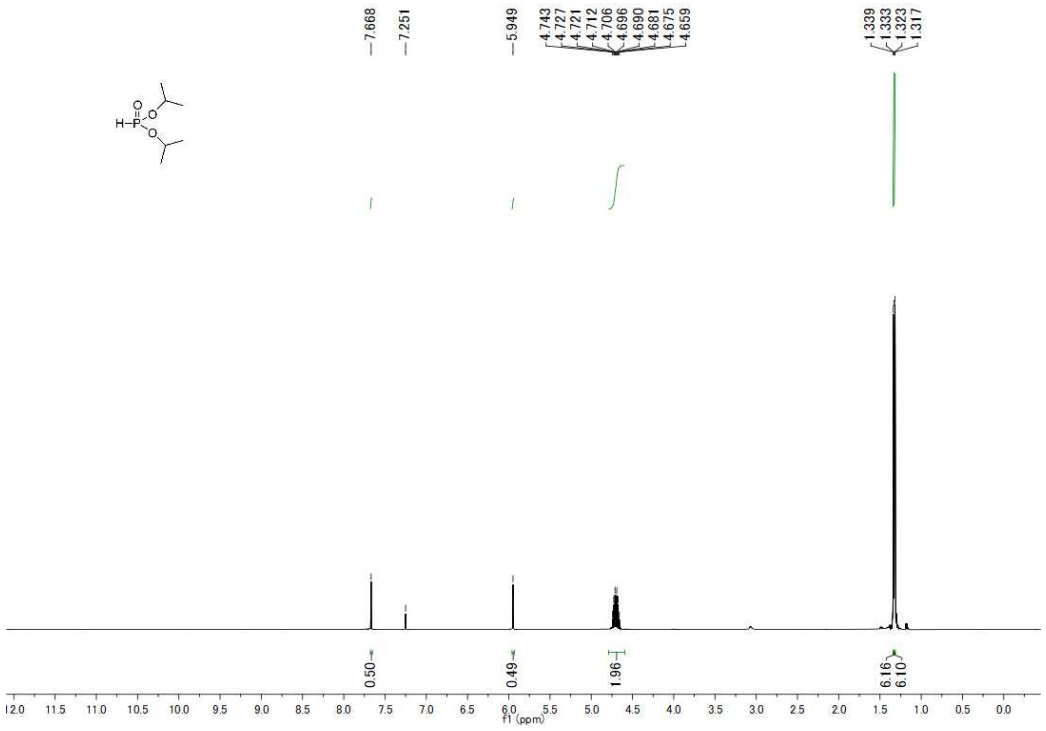
Ball-and-stick representations. Atoms: red: oxygen; blue: fluorine; white: hydrogen; light yellow: sulfur; gray: carbon; orange: phosphorus.

3.3. Results and Discussion: The lower energy barrier of the monomolecular transition state (TS1: 52.12KJ/mol) than that of the bimolecular transition state (TS2: 57.66KJ/mol) also supports that the monomolecular mechanism might be more favoured than the bimolecular mechanism.

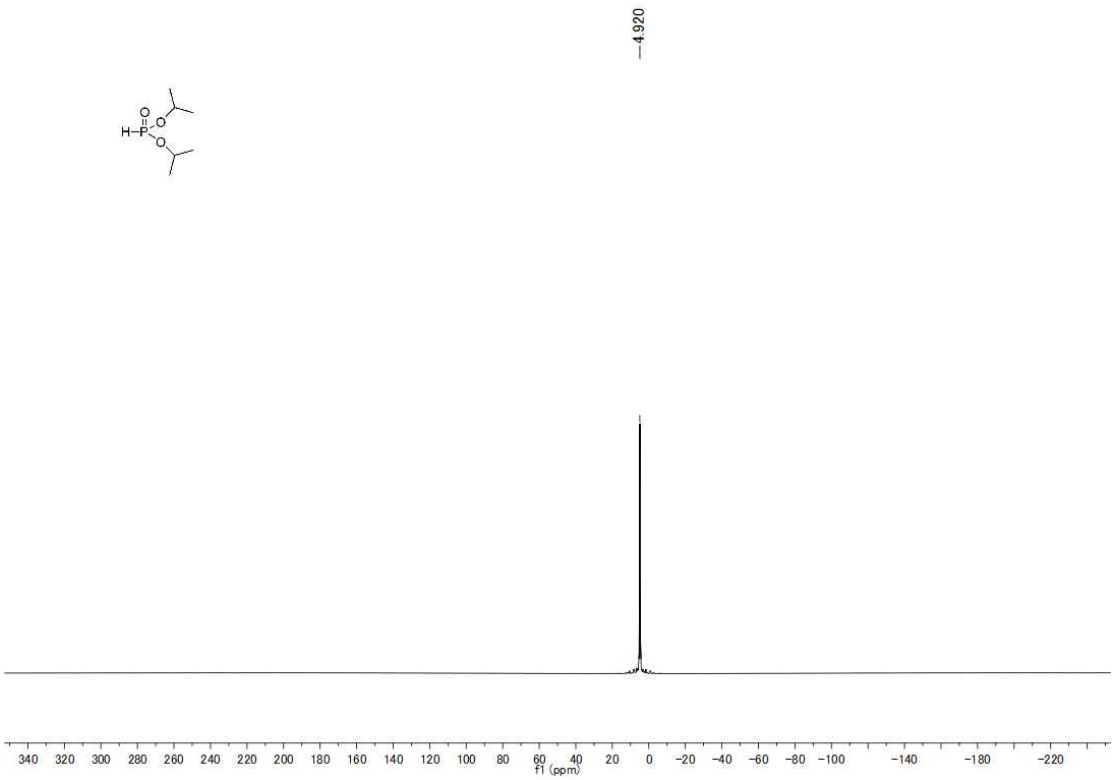
4. Copies of ^{1}H, ^{13}C, and ^{31}P NMR spectra of the products

$HP(O)(O\textit{i}\text{-}Pr)_2$ (2a)

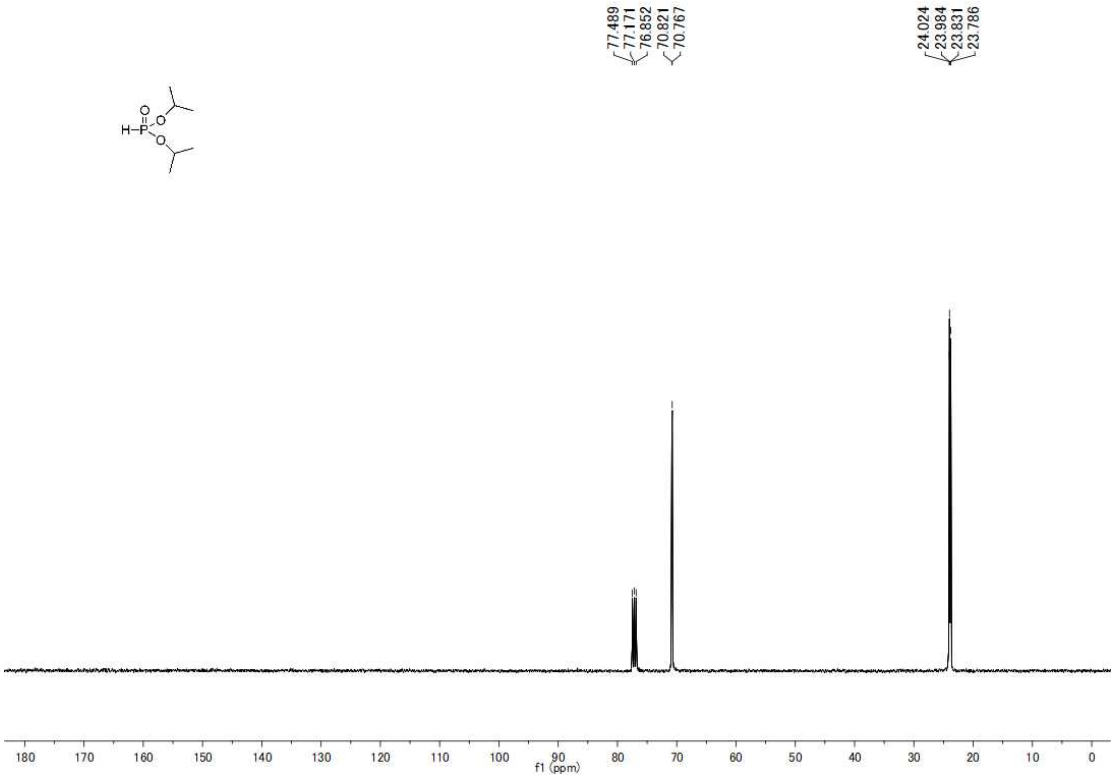
^{1}H NMR



^{31}P NMR

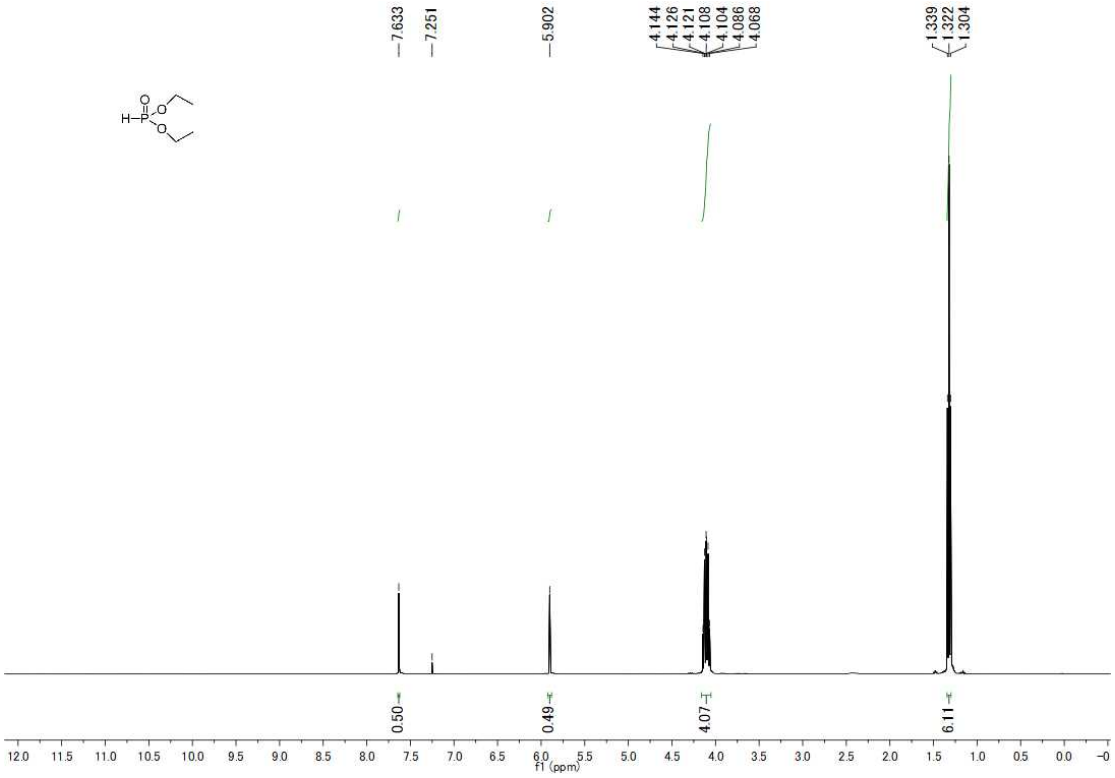


^{13}C NMR

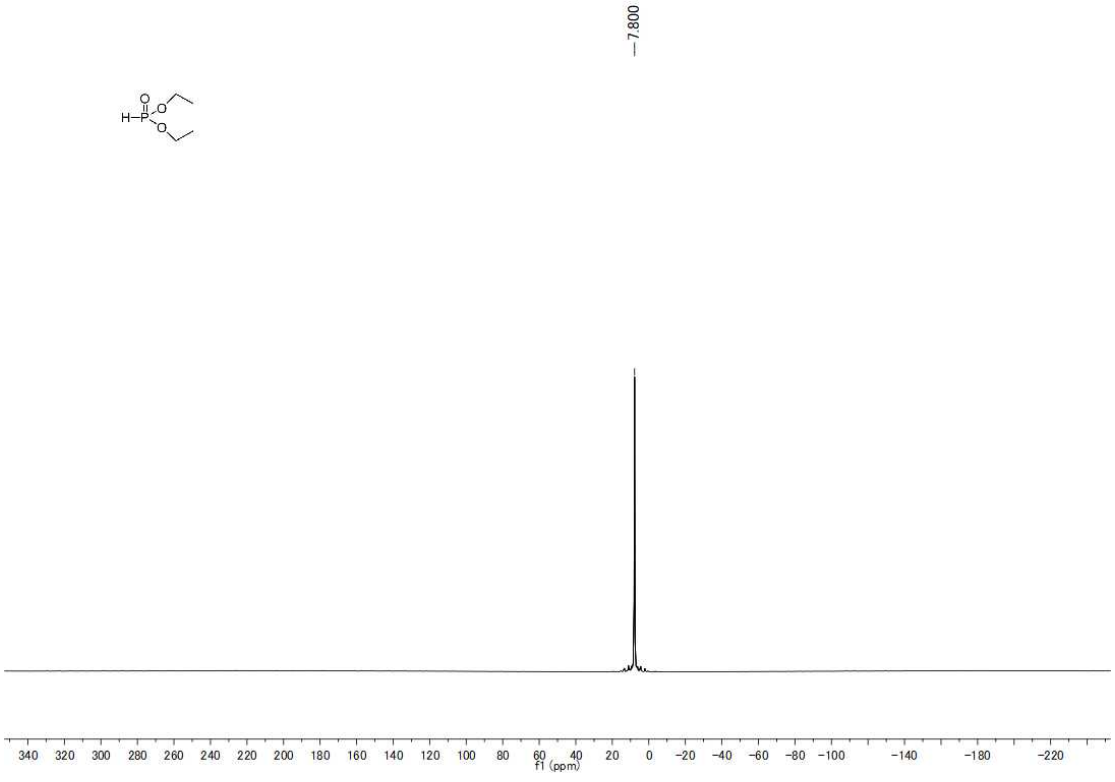

77.489
77.171
76.852
70.821
70.767
24.024
23.984
23.831
23.786
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$HP(O)(OEt)_2$ (2b)

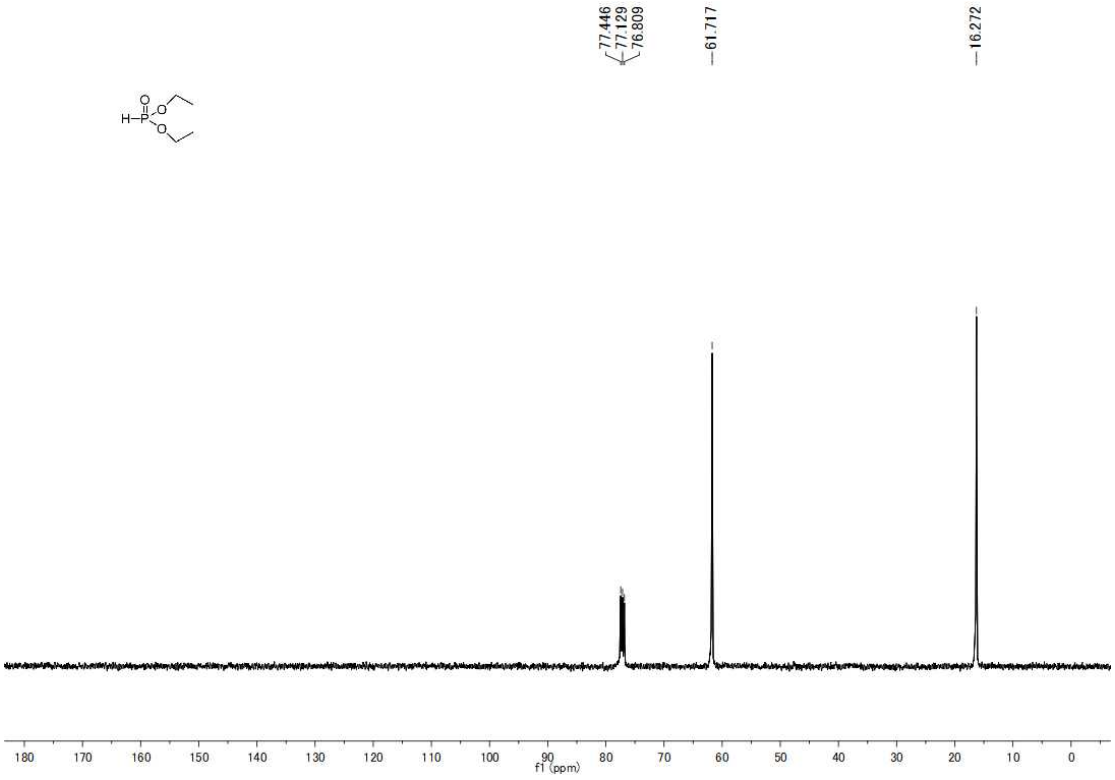
^{1}H NMR



^{31}P NMR

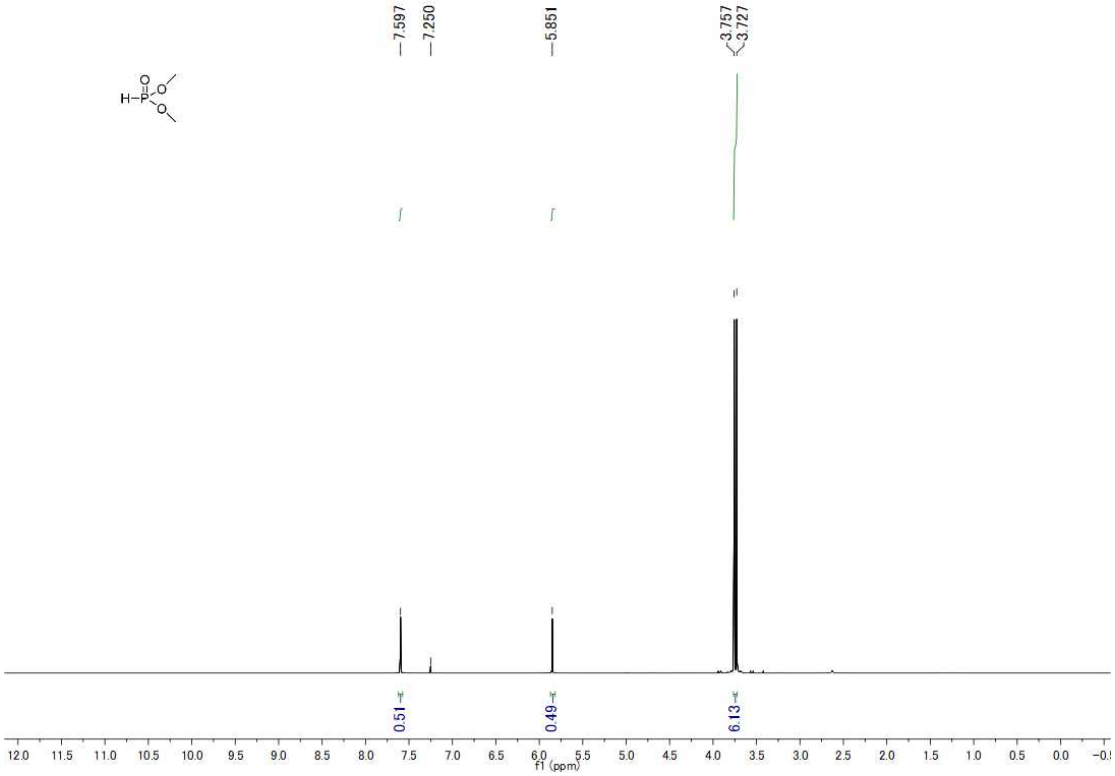


^{13}C NMR

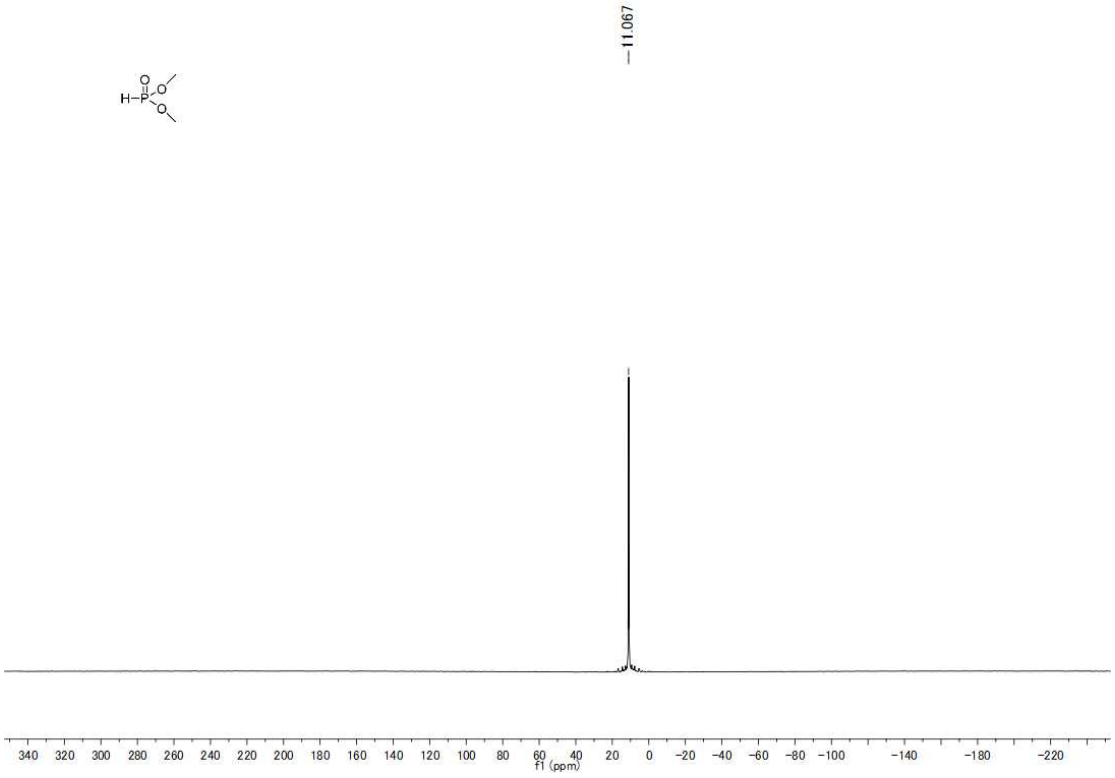


$HP(O)(OMe)_2$ (2c)

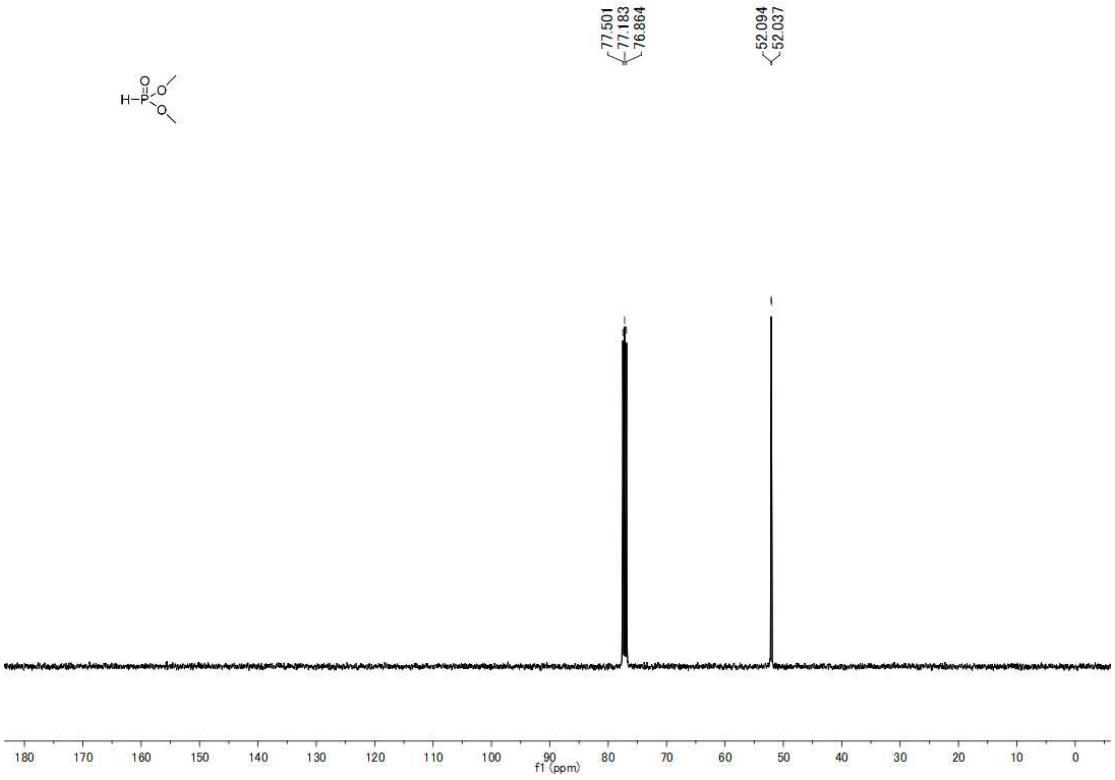
^{1}H NMR



^{31}P NMR

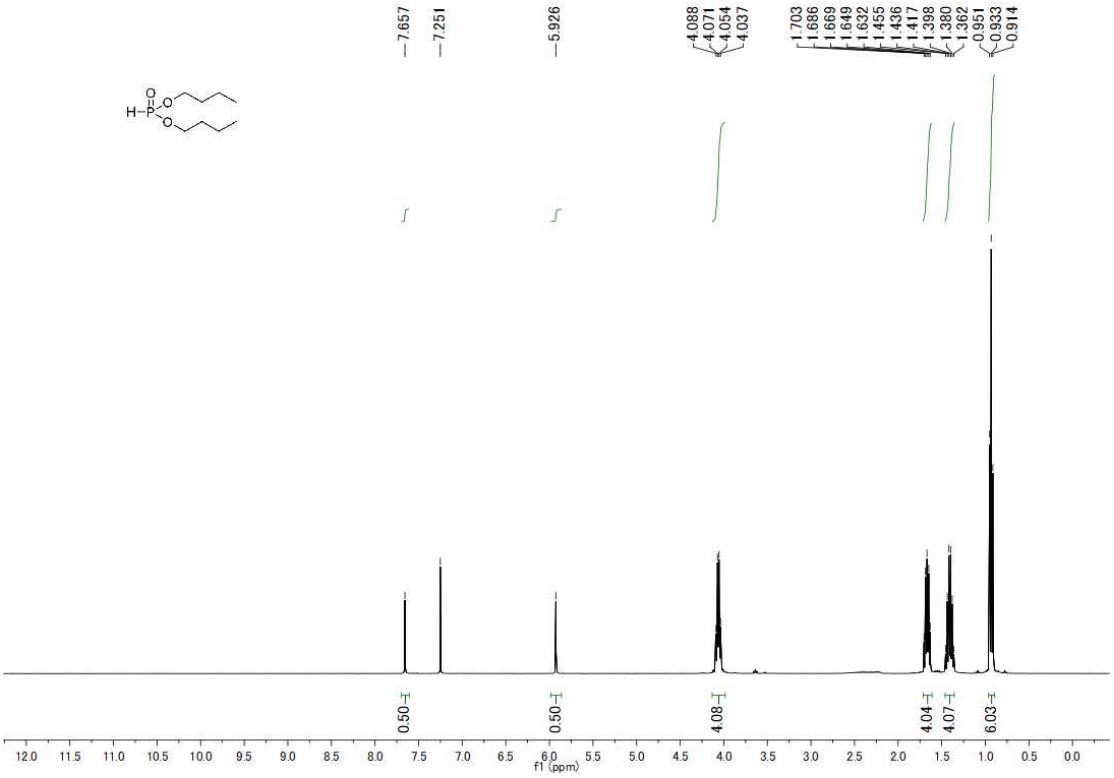


^{13}C NMR

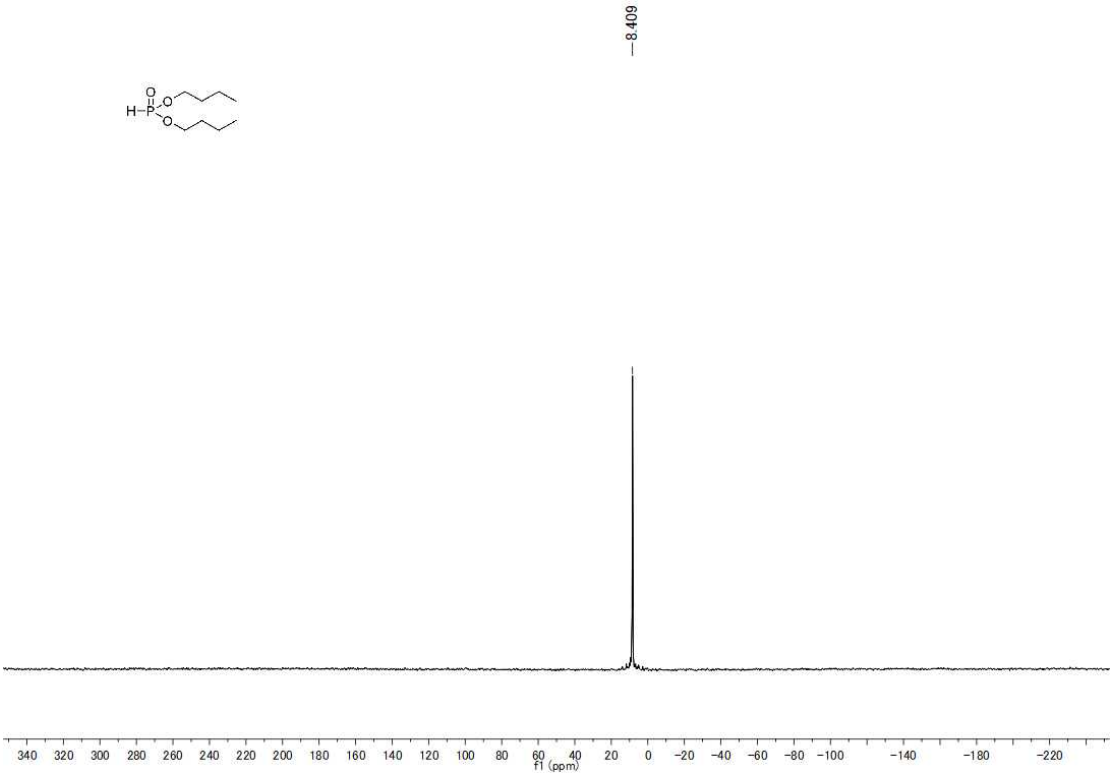

77.501
77.183
76.864
52.094
52.037
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

HP(O)(O*n*-Bu)$_2$ (2d)

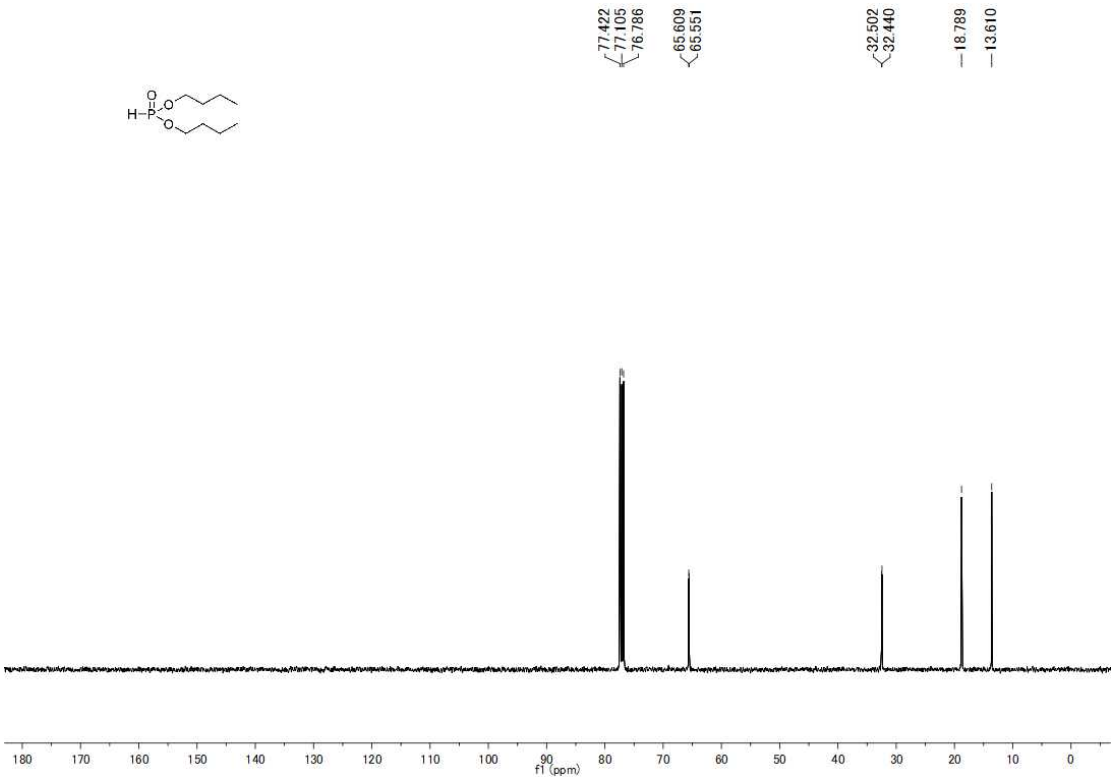
^{1}H NMR



^{31}P NMR

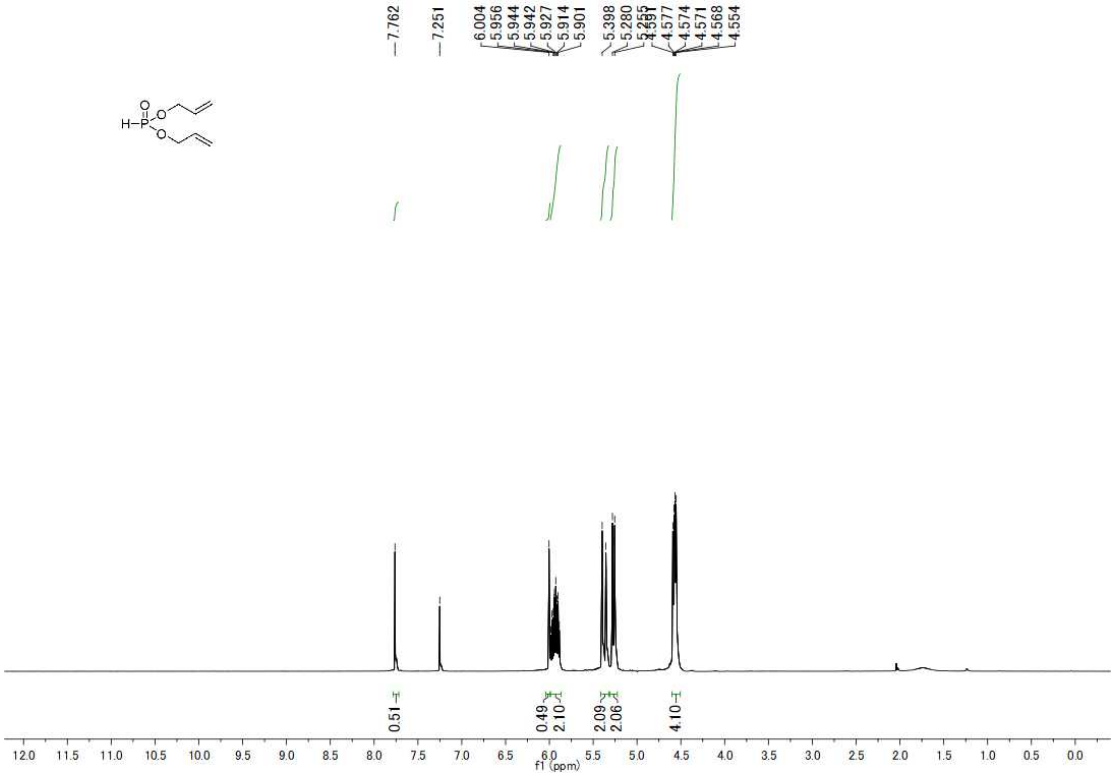


^{13}C NMR

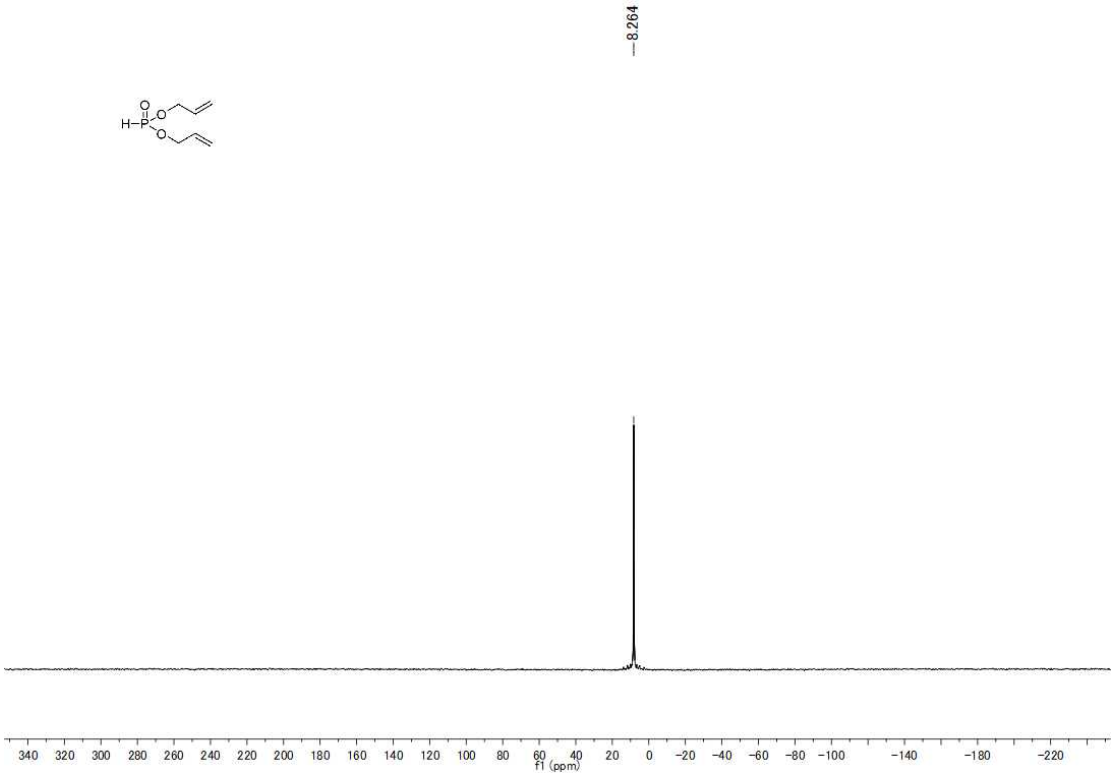

77.422
77.105
76.786
65.609
65.551
32.502
32.440
18.789
13.610
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$HP(O)(Oally)_2$ (2e)

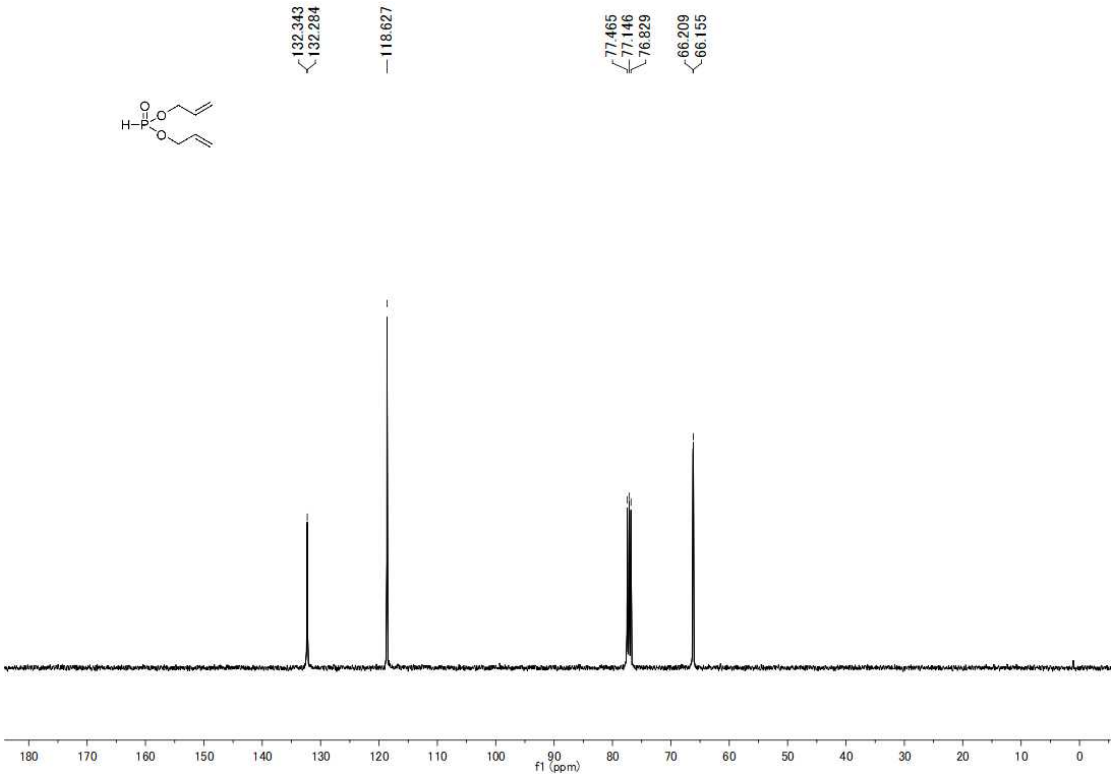
^{1}H NMR



^{31}P NMR

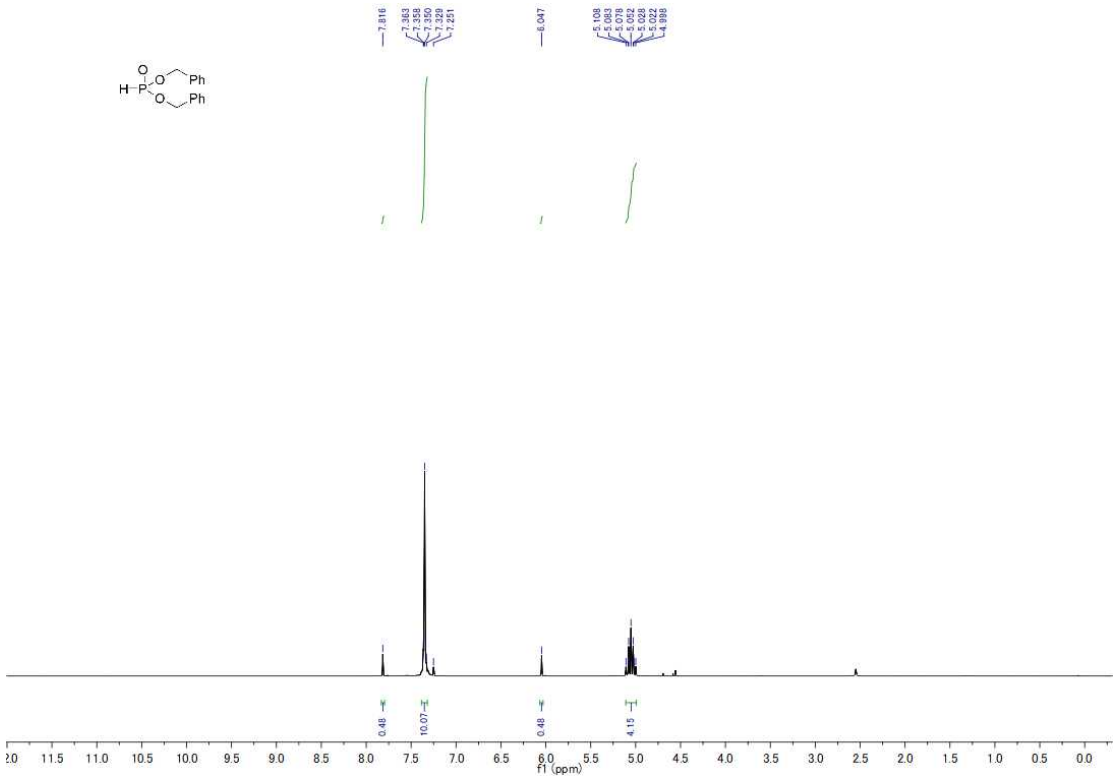


^{13}C NMR

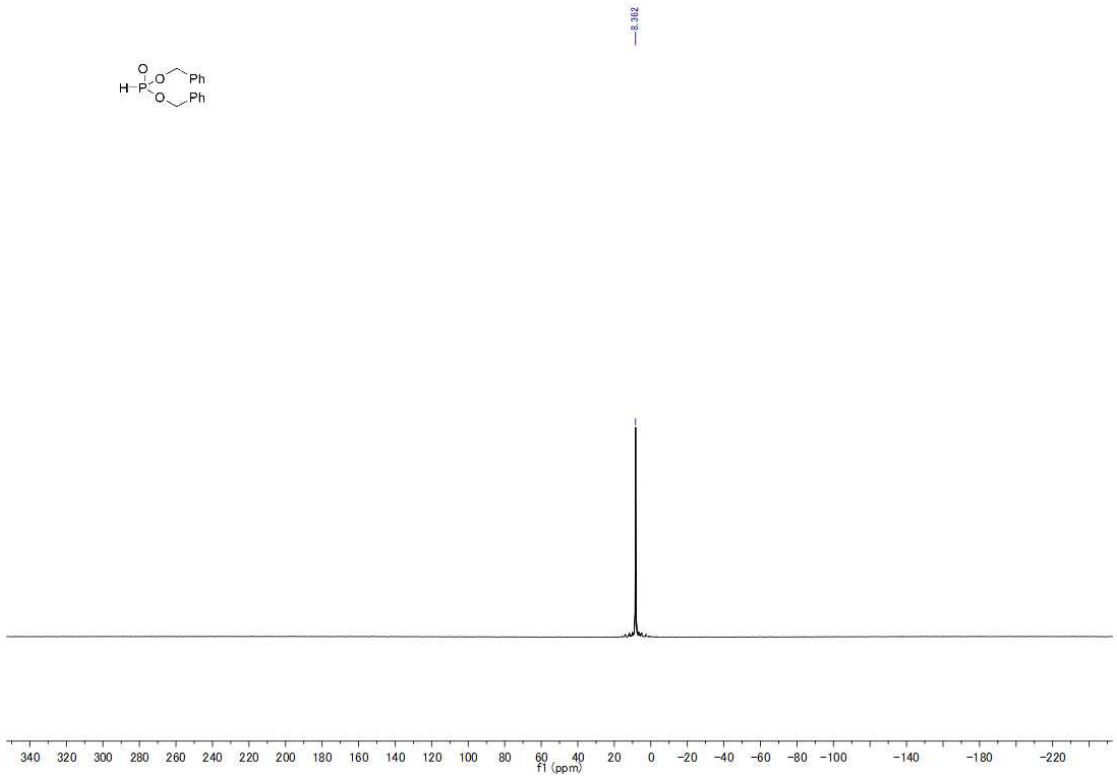

132.343
132.284
118.627
77.465
77.146
76.829
66.209
66.155
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$HP(O)(OCH_2Ph)_2$ (2f)

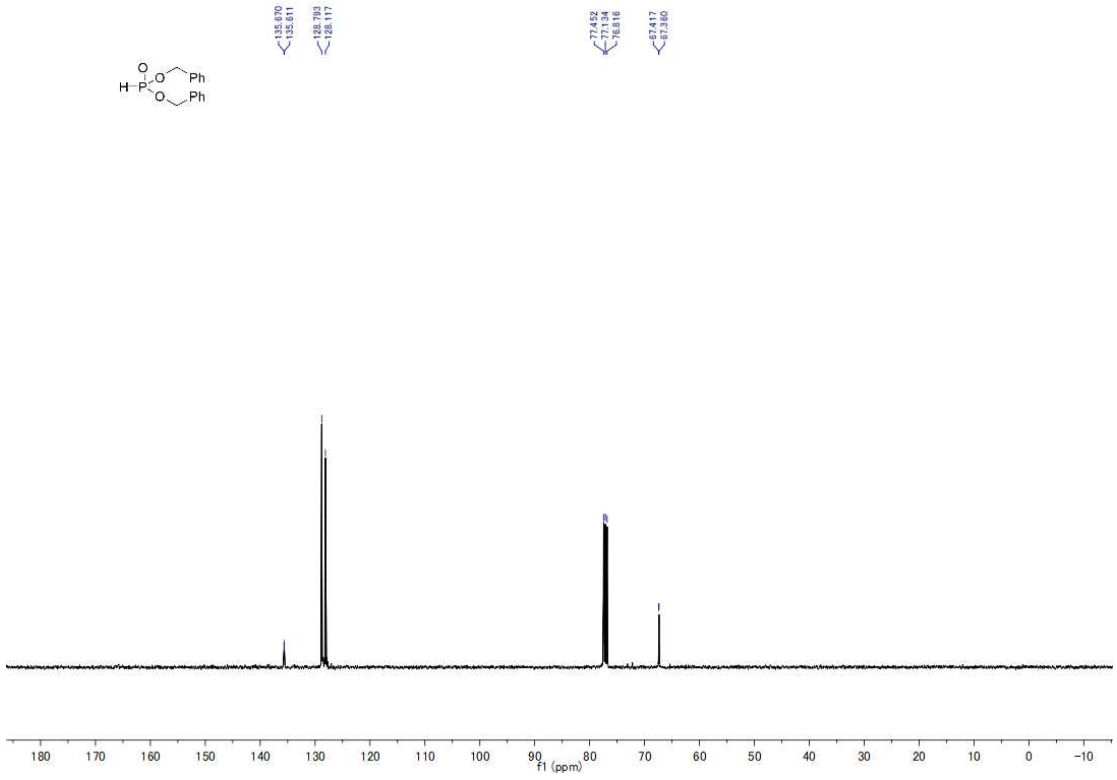
^{1}H NMR



^{31}P NMR

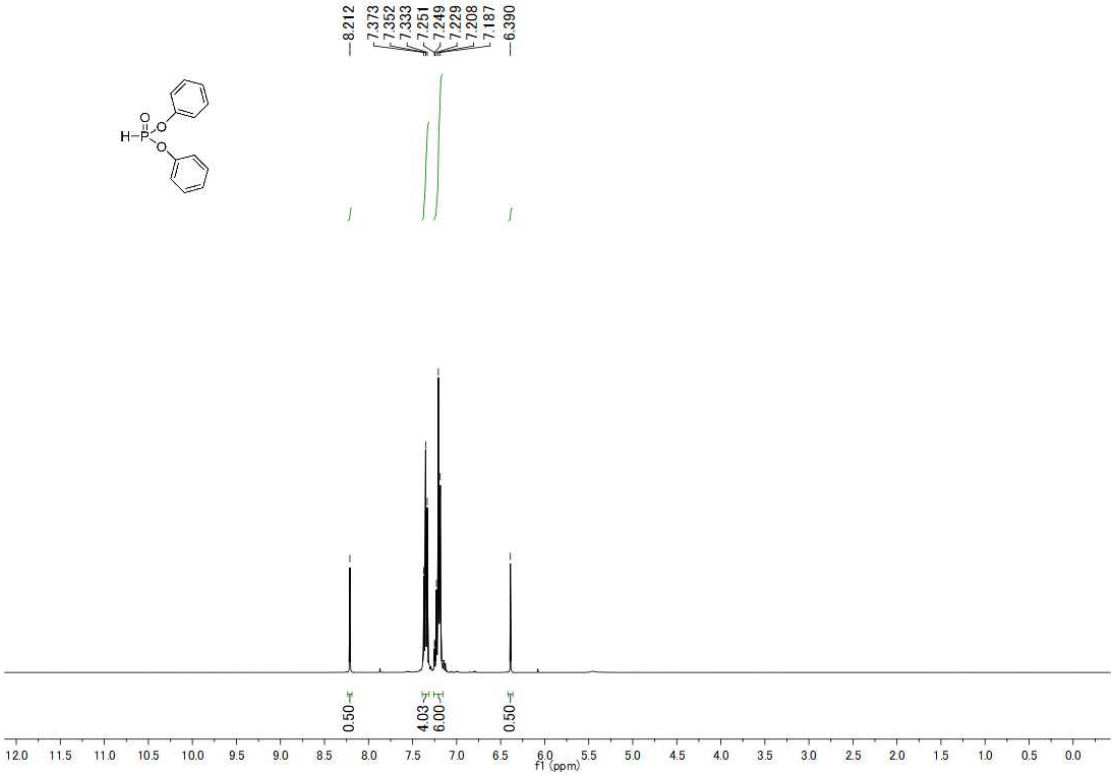


^{13}C NMR

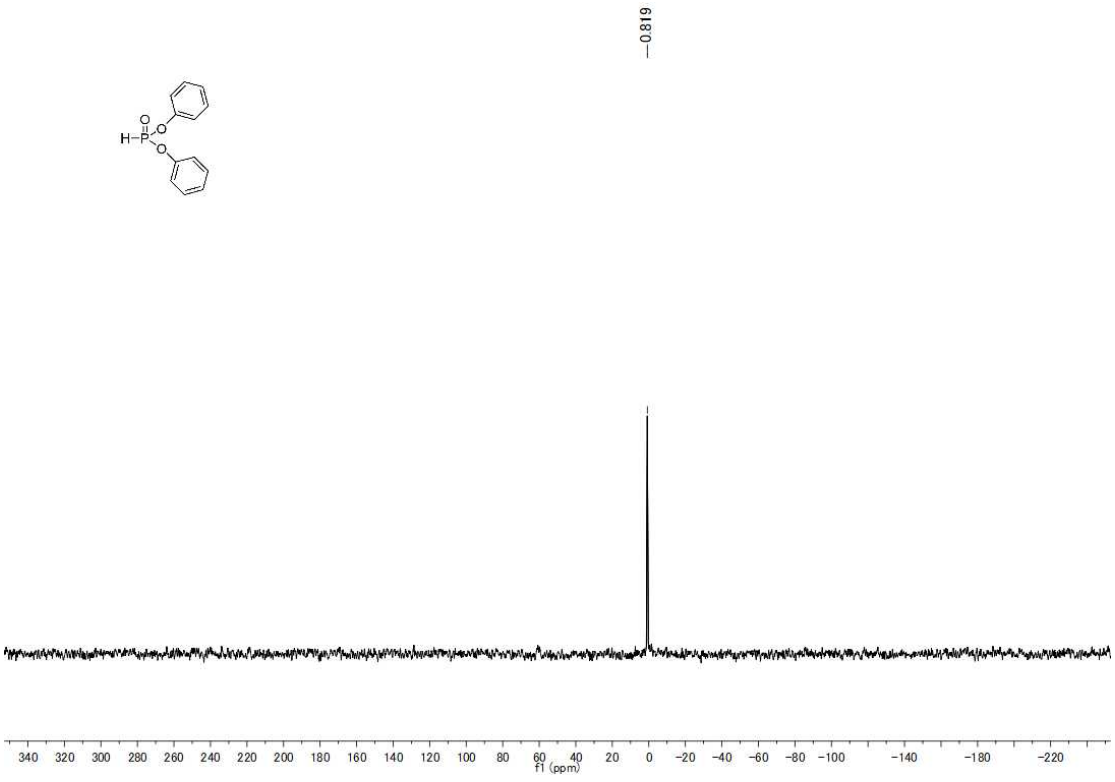

135.670
135.611
128.793
128.117
77.458
77.134
76.810
67.417
67.380
Ph
Ph
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

$HP(O)(OPh)_2$ (2i)

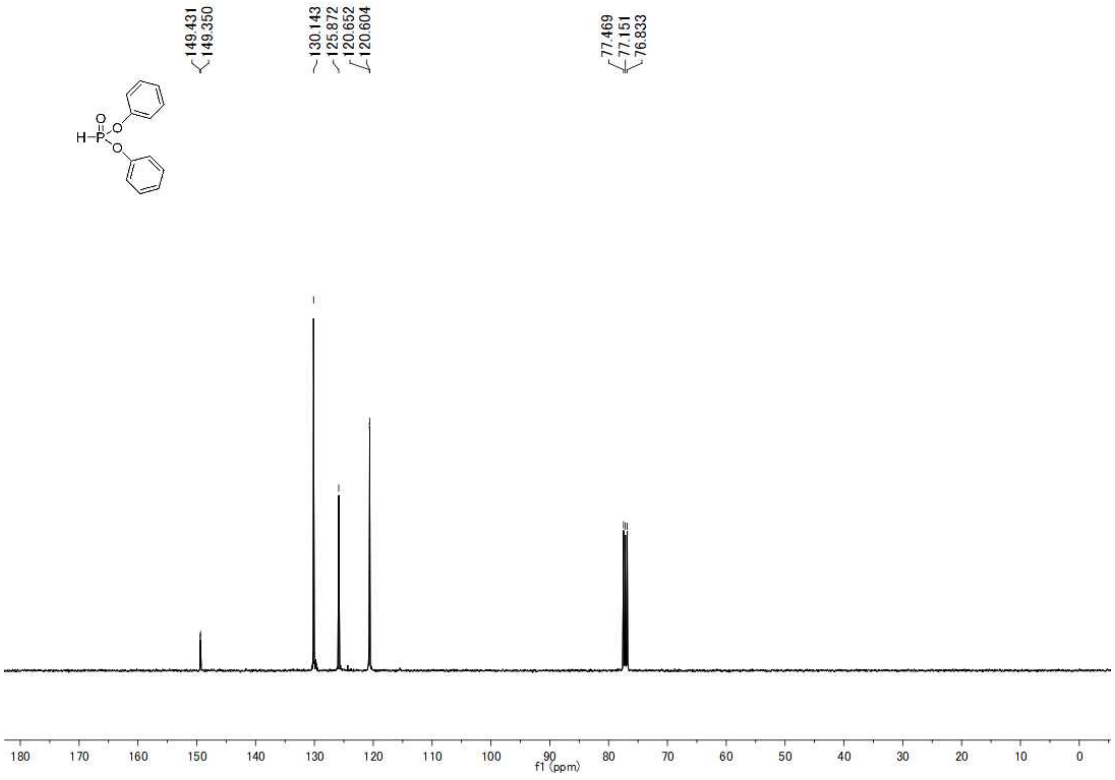
^1H NMR



^{31}P NMR

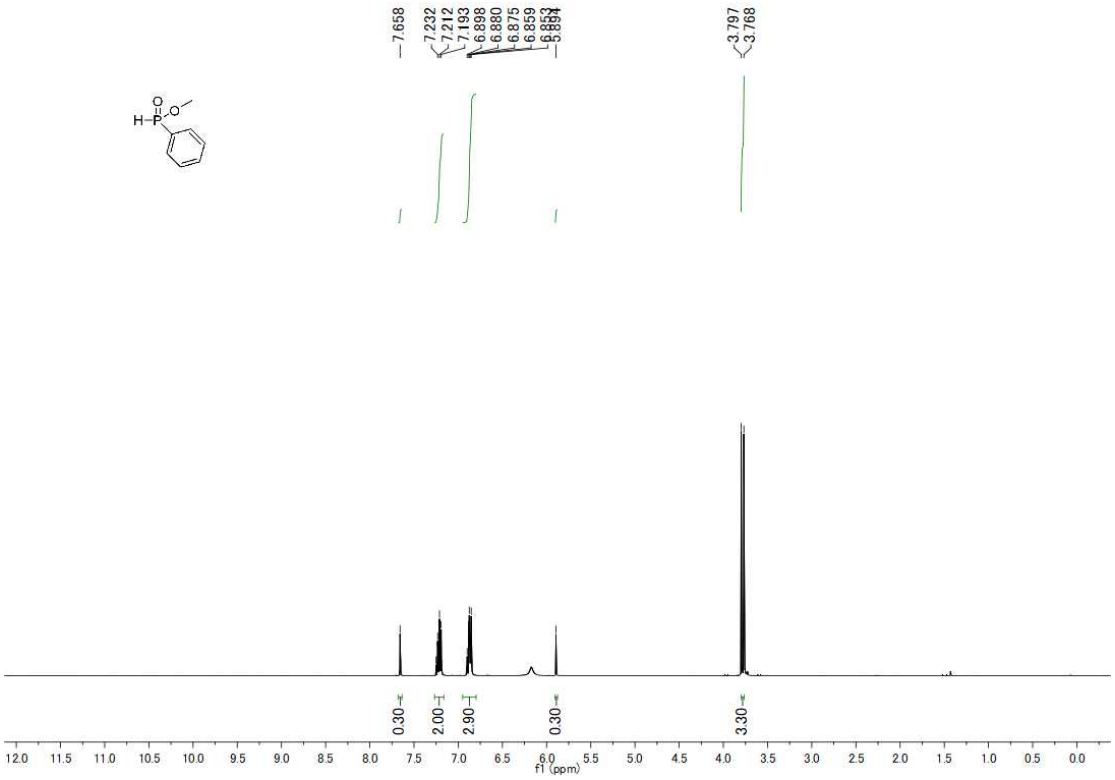


^{13}C NMR

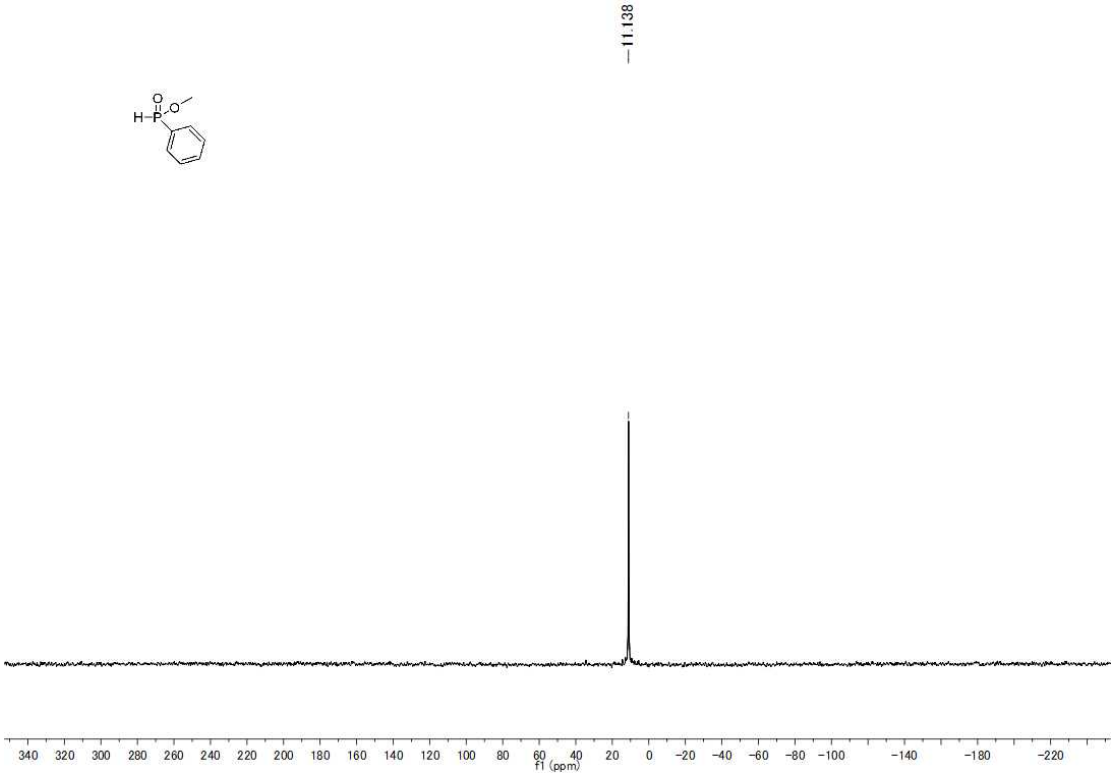

149.431
149.350
130.143
125.872
120.652
120.604
77.469
77.151
76.833
H-P
O
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

HP(O)(OMe)Ph (2j)

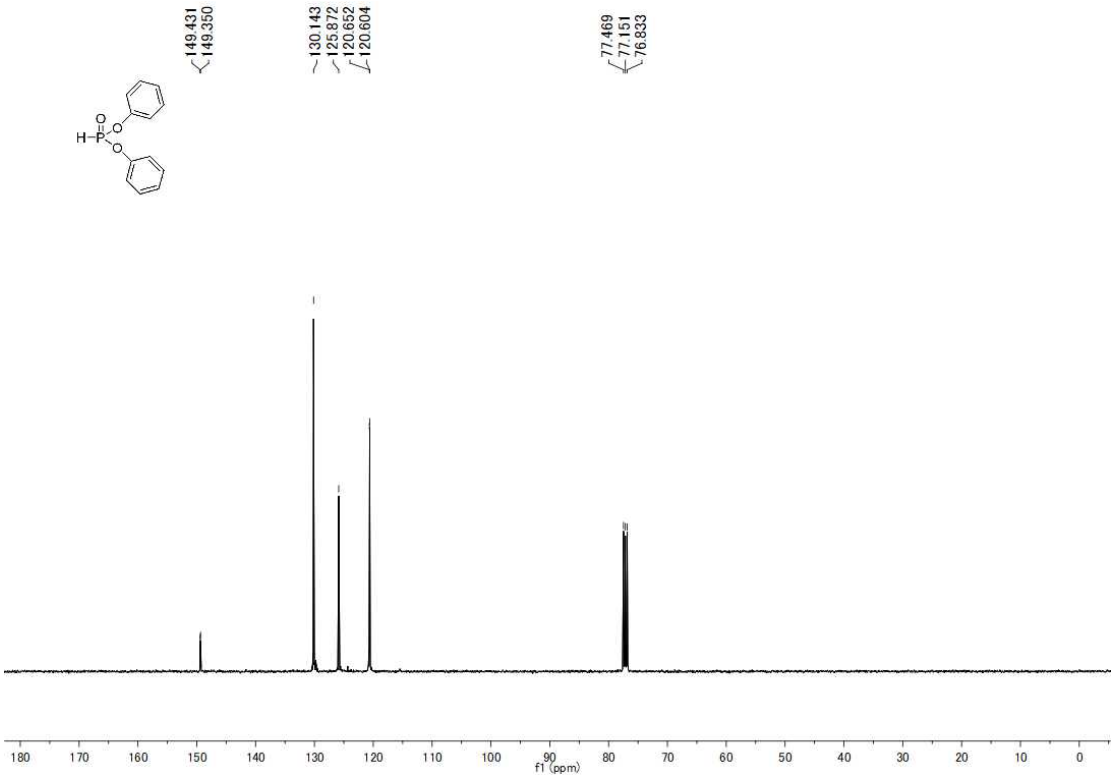
^{1}H NMR



^{31}P NMR

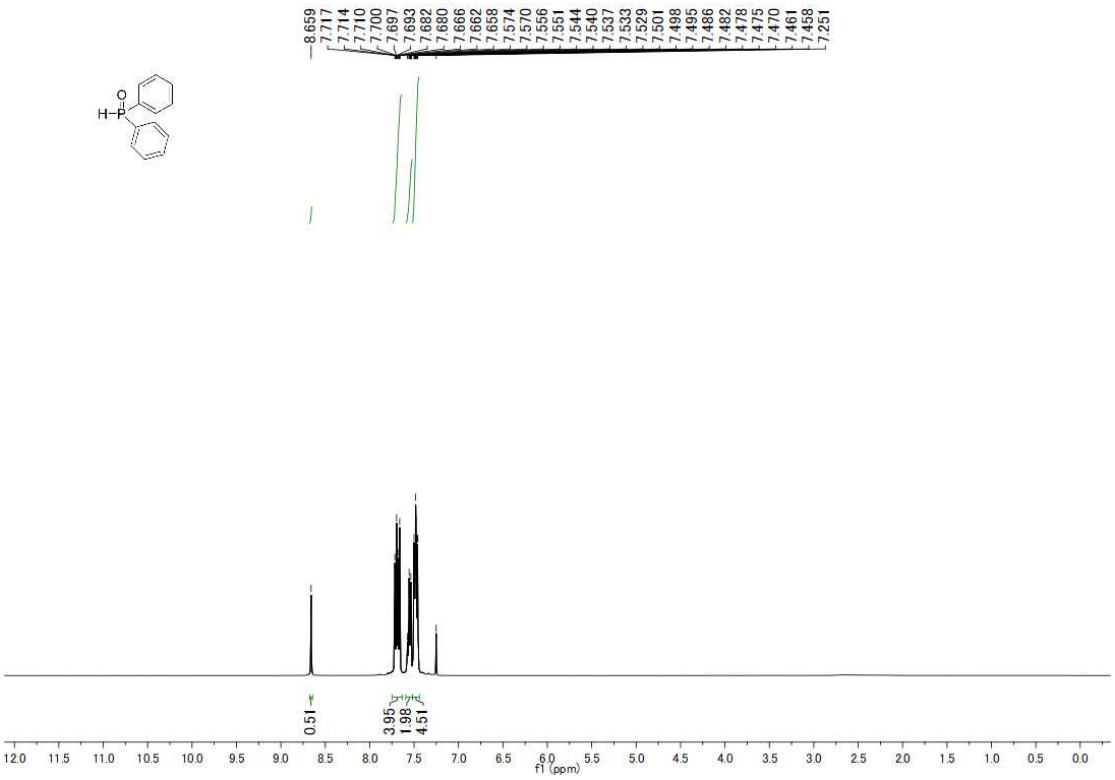


^{13}C NMR

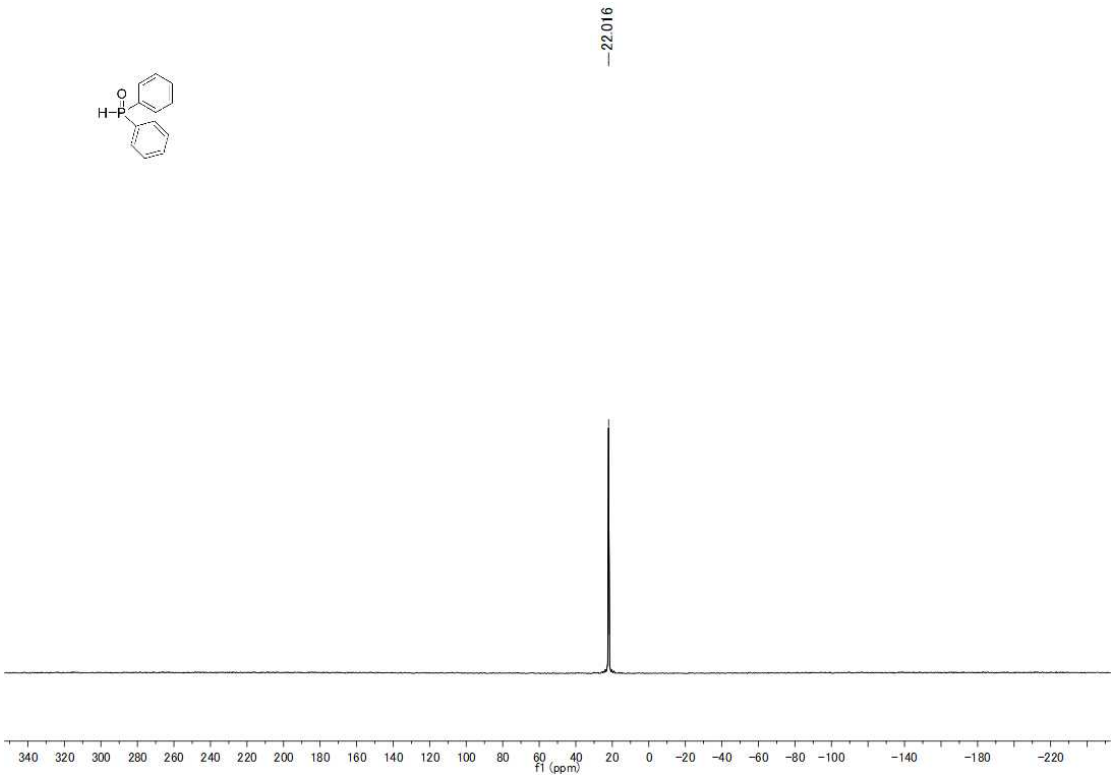

149.431
149.350
130.143
125.872
120.652
120.604
77.469
77.151
76.833
H-P
O
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$HP(O)Ph_2$ (2k)

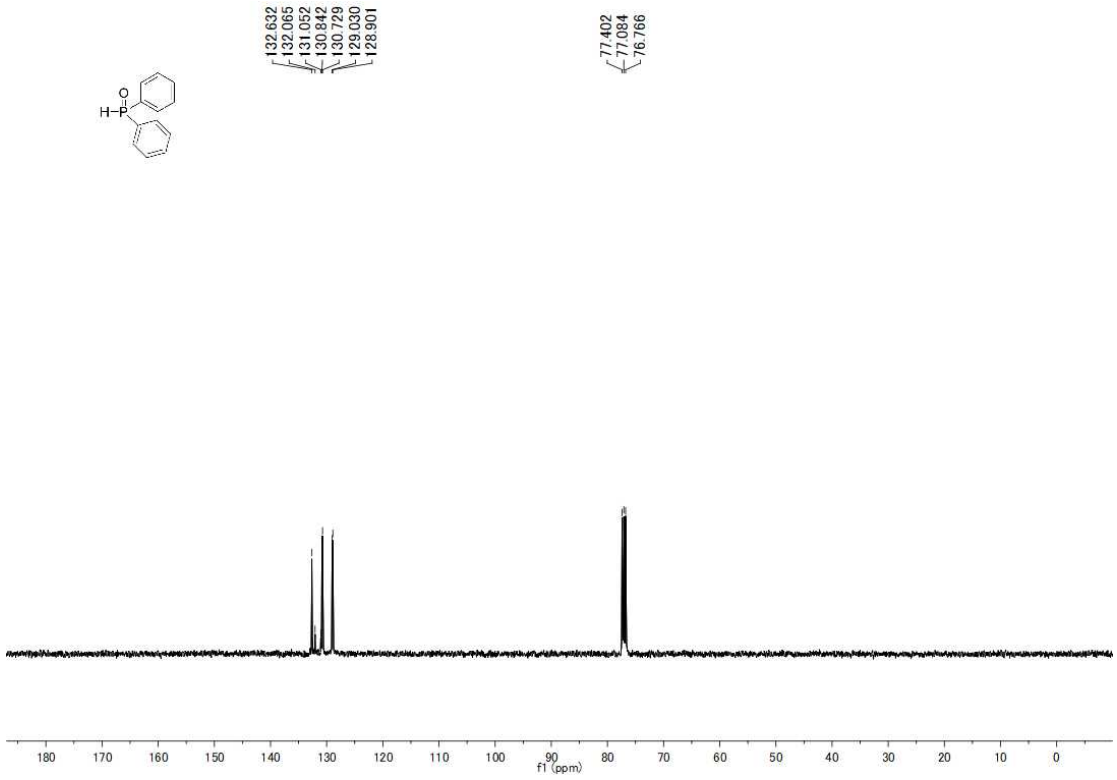
^{1}H NMR



^{1}P NMR

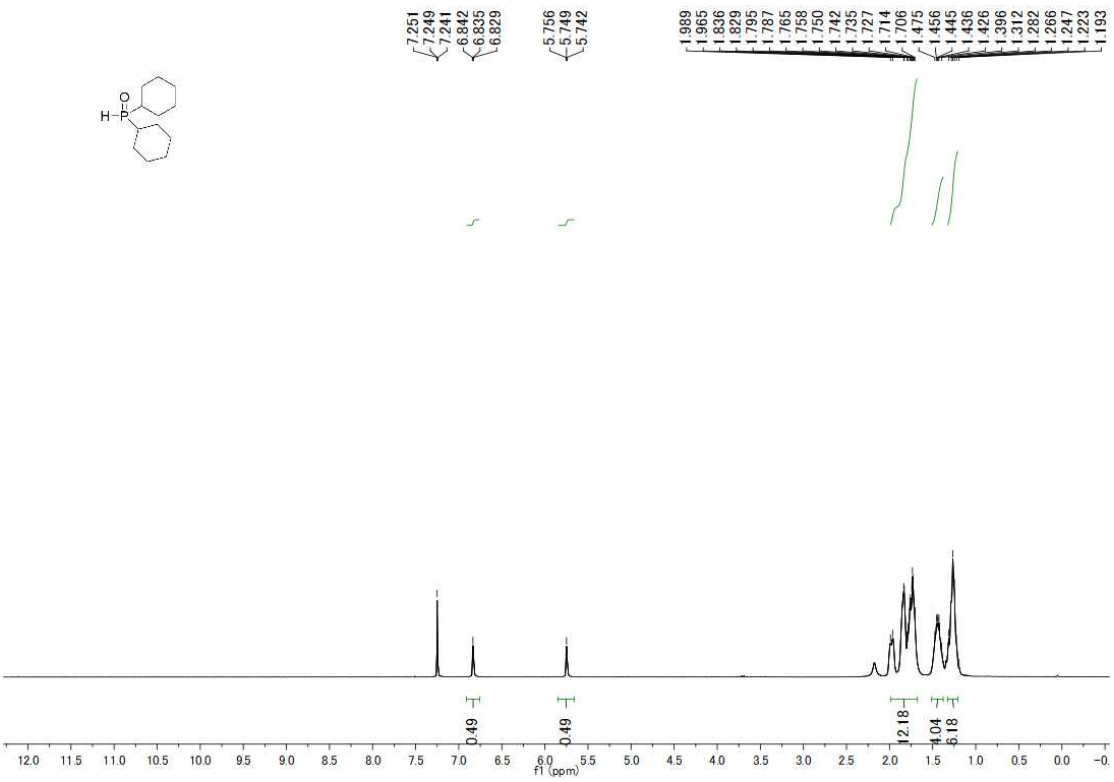


^{13}C NMR

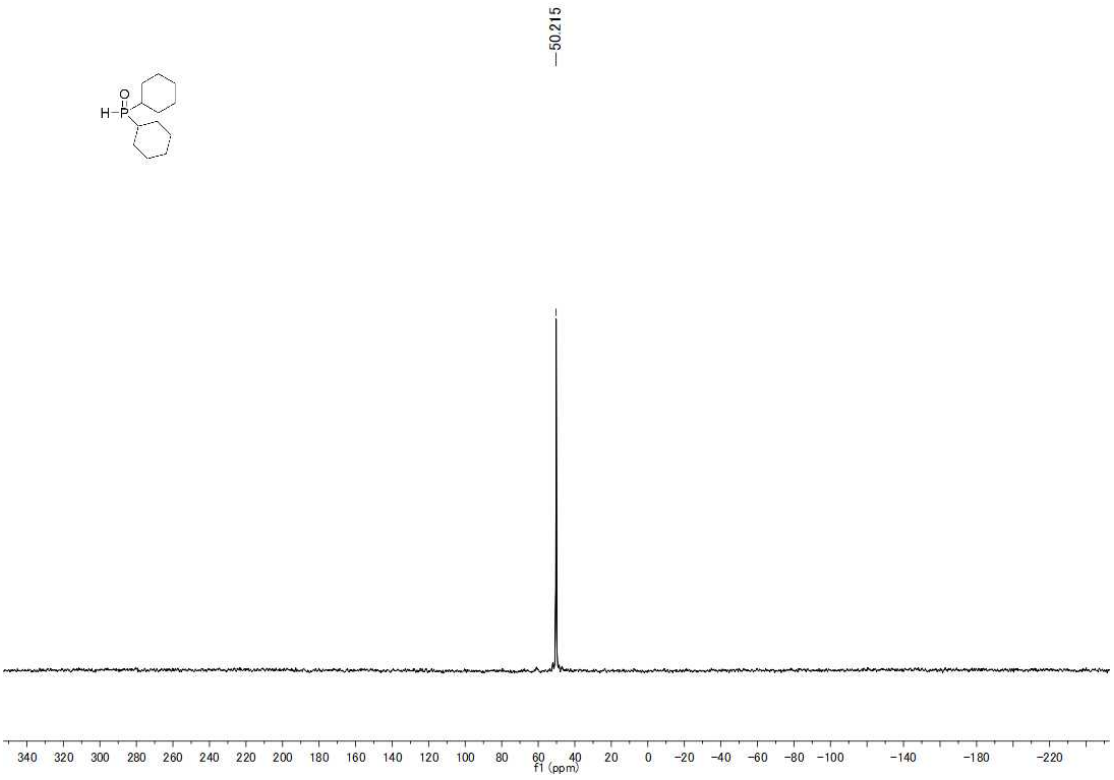

132.632
132.065
131.052
130.842
130.729
129.030
128.901
77.402
77.084
76.766
O
H–P
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$HP(O)Cy_2$ (2p)

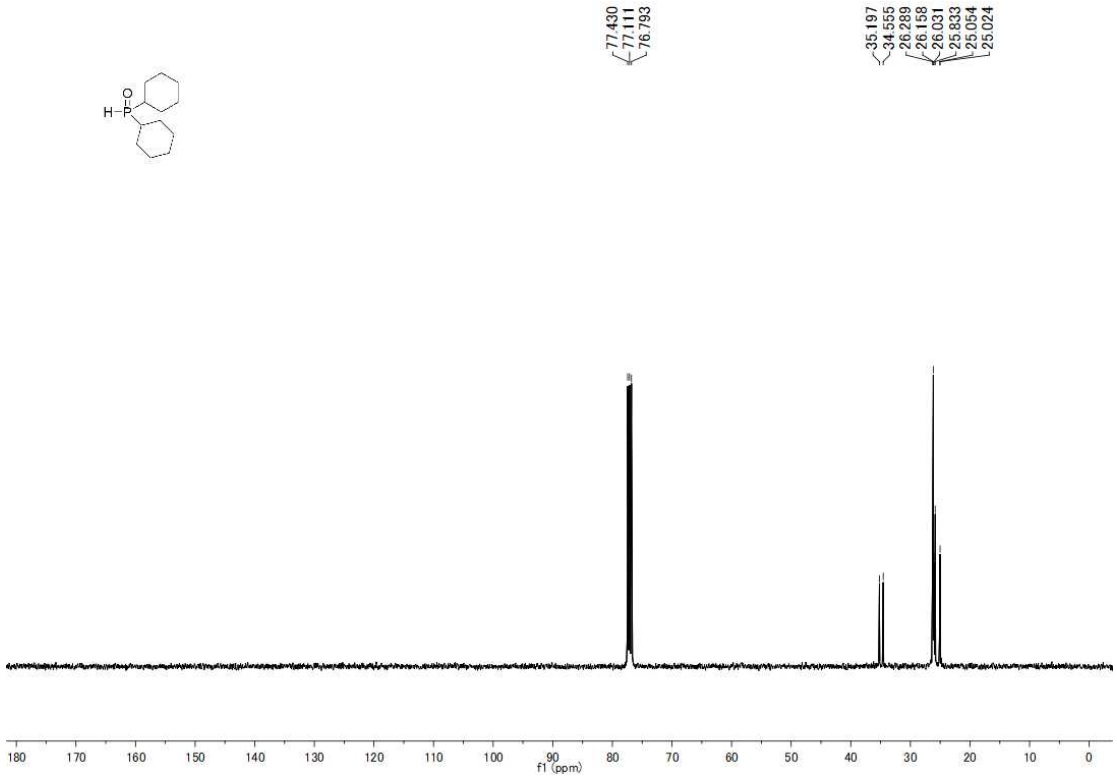
^1H NMR



^{31}P NMR

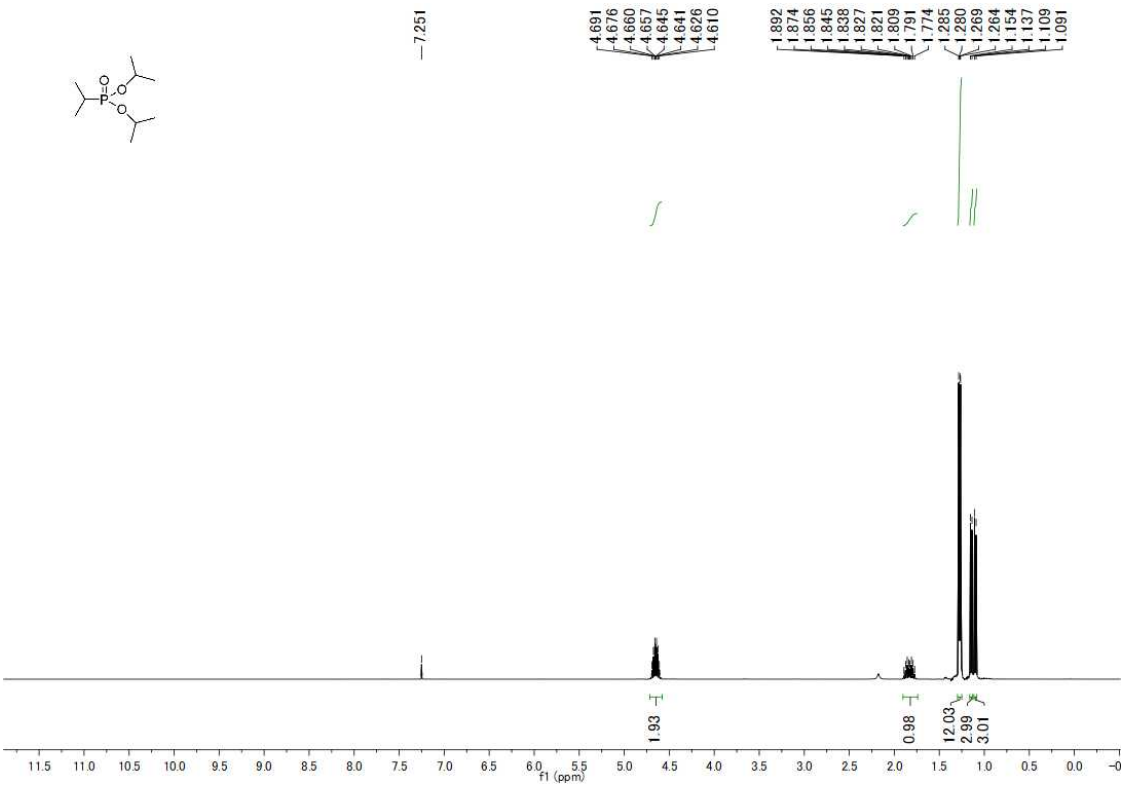


^{13}C NMR

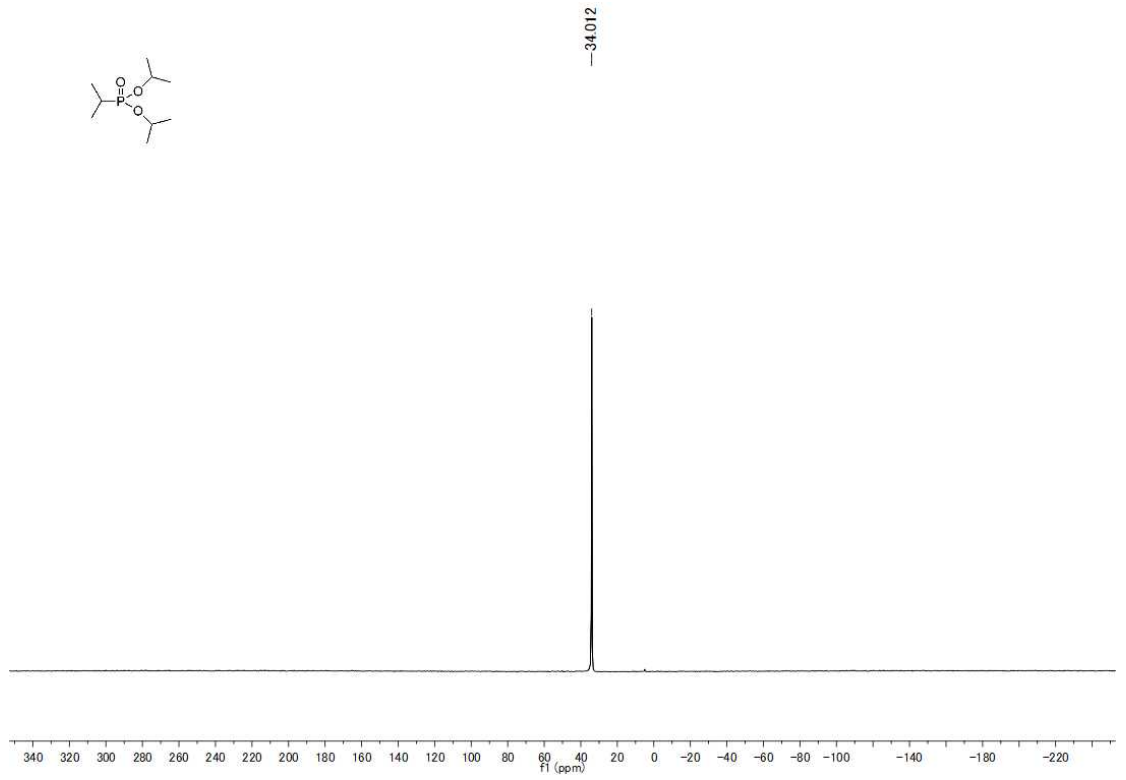

77.430
77.111
76.793
35.197
34.555
26.289
26.158
26.031
25.833
25.054
25.024
O
H–P
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

i-PrP(O)(O*i*-Pr)$_2$ (3a)

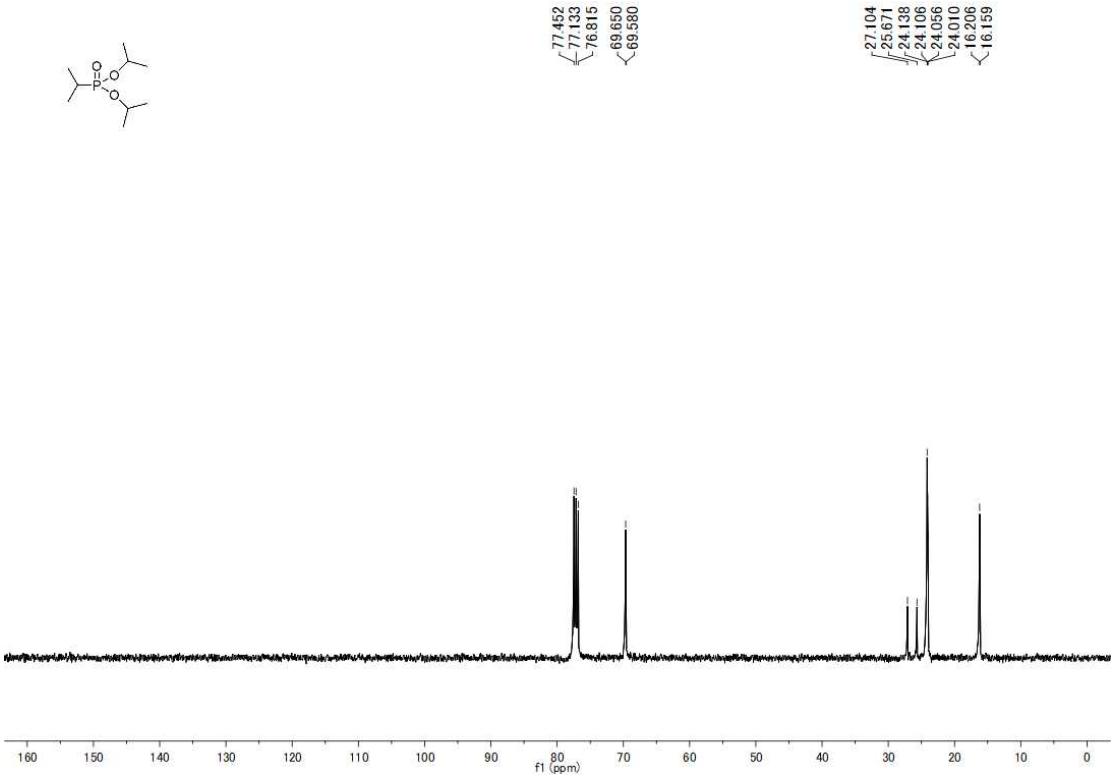
^{1}H NMR



^{31}P NMR

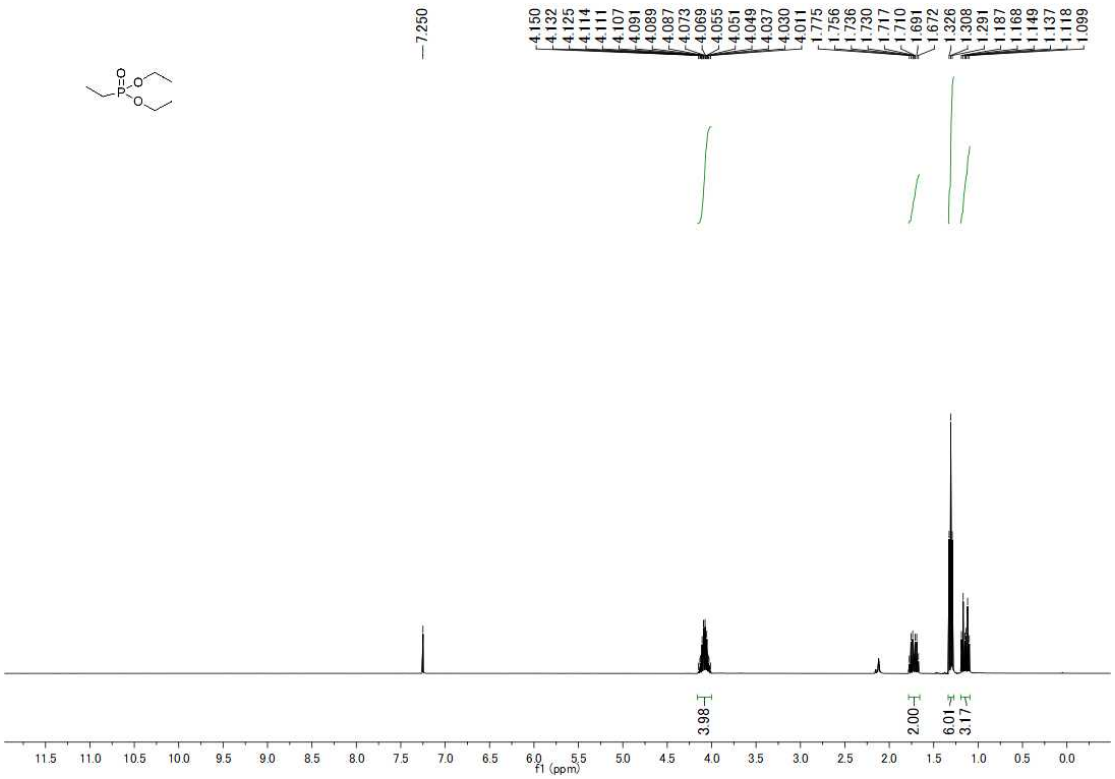


^{13}C NMR

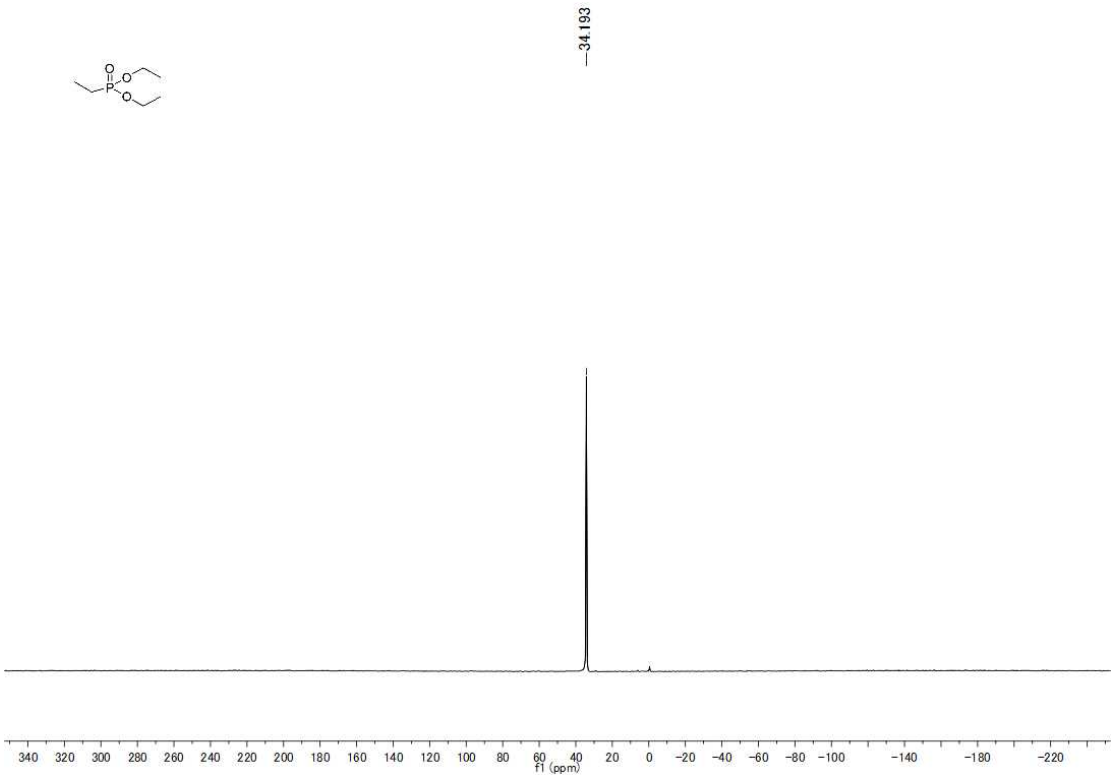

77.452
77.133
76.815
69.650
69.580
27.104
25.671
24.138
24.106
24.056
24.010
16.206
16.159
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$EtP(O)(OEt)_2$ (3b)

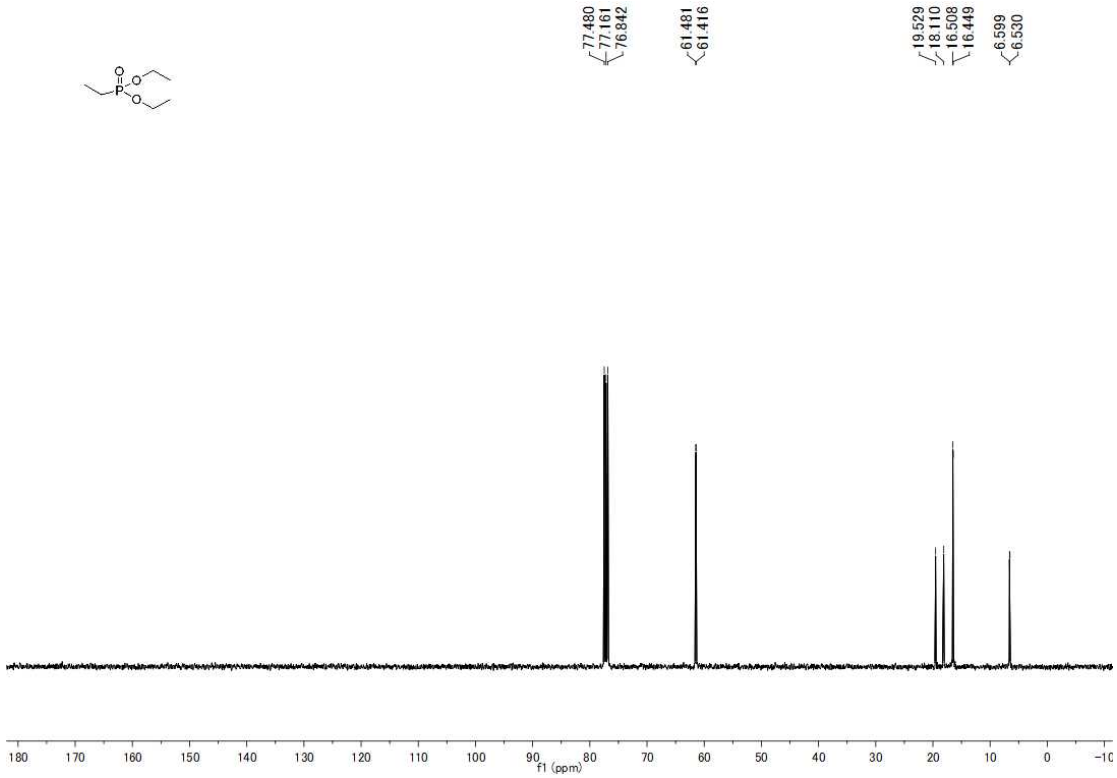
^1H NMR



^{31}P NMR

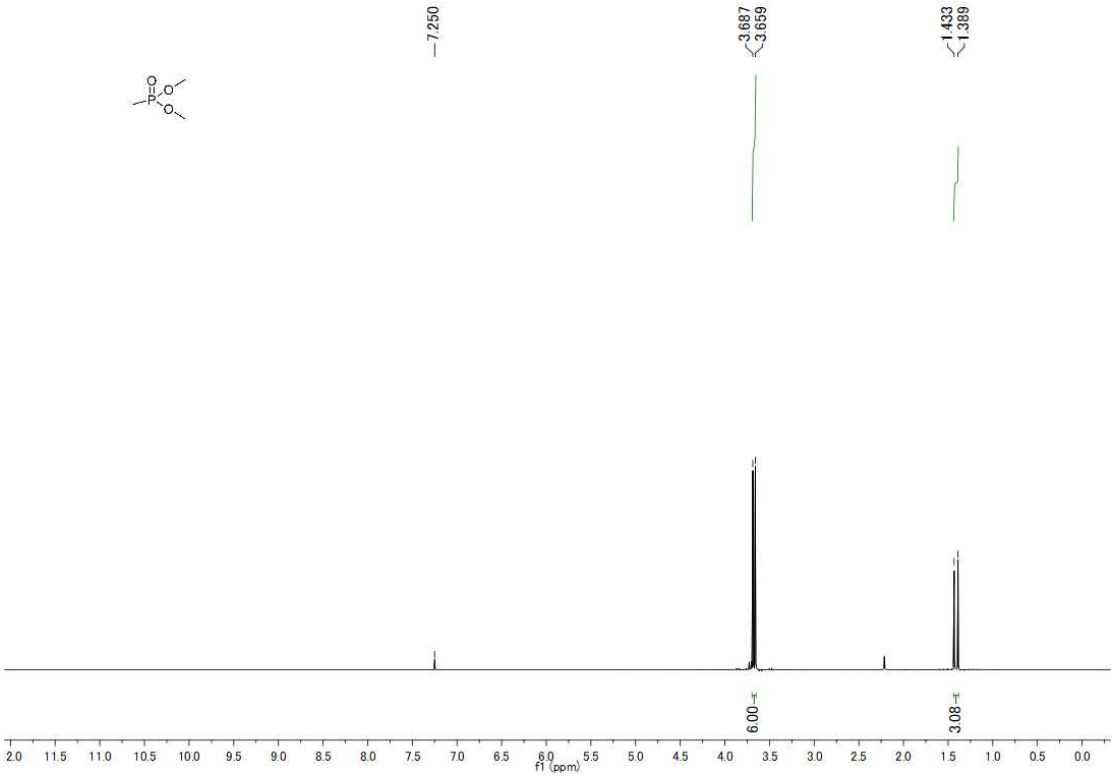


^{13}C NMR

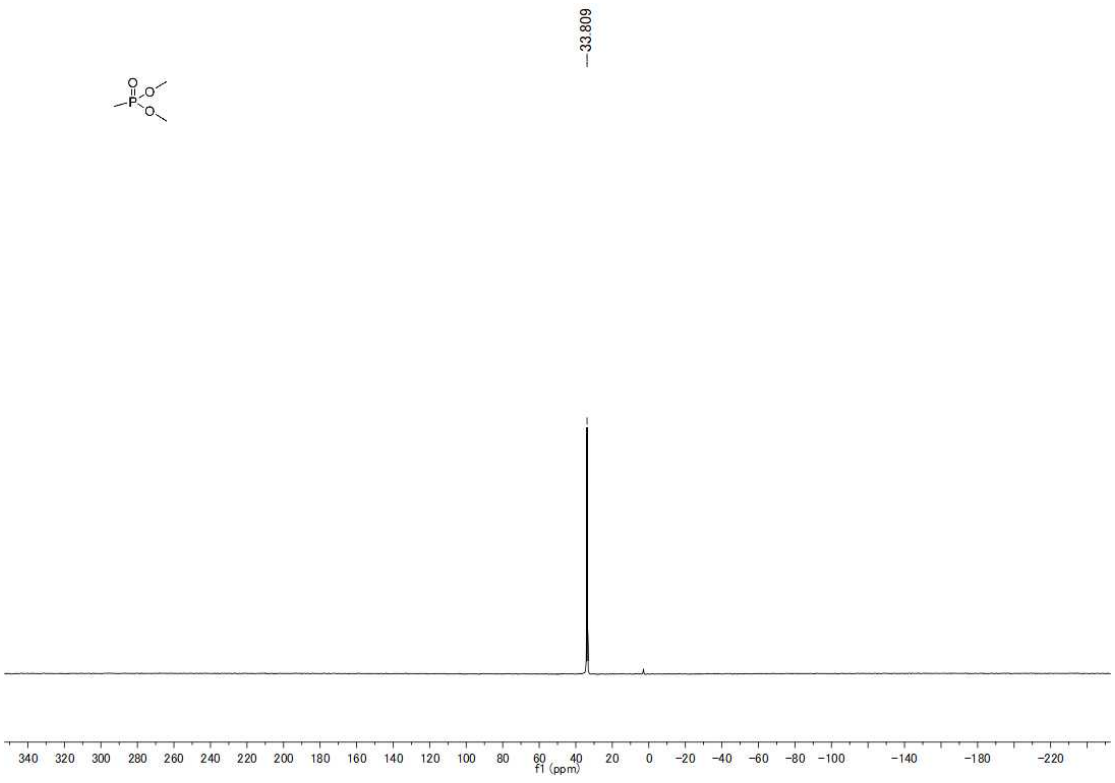

77.480
77.161
76.842
61.481
61.416
19.529
18.110
16.508
16.449
6.599
6.530
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

$MeP(O)(OMe)_2$ (3c)

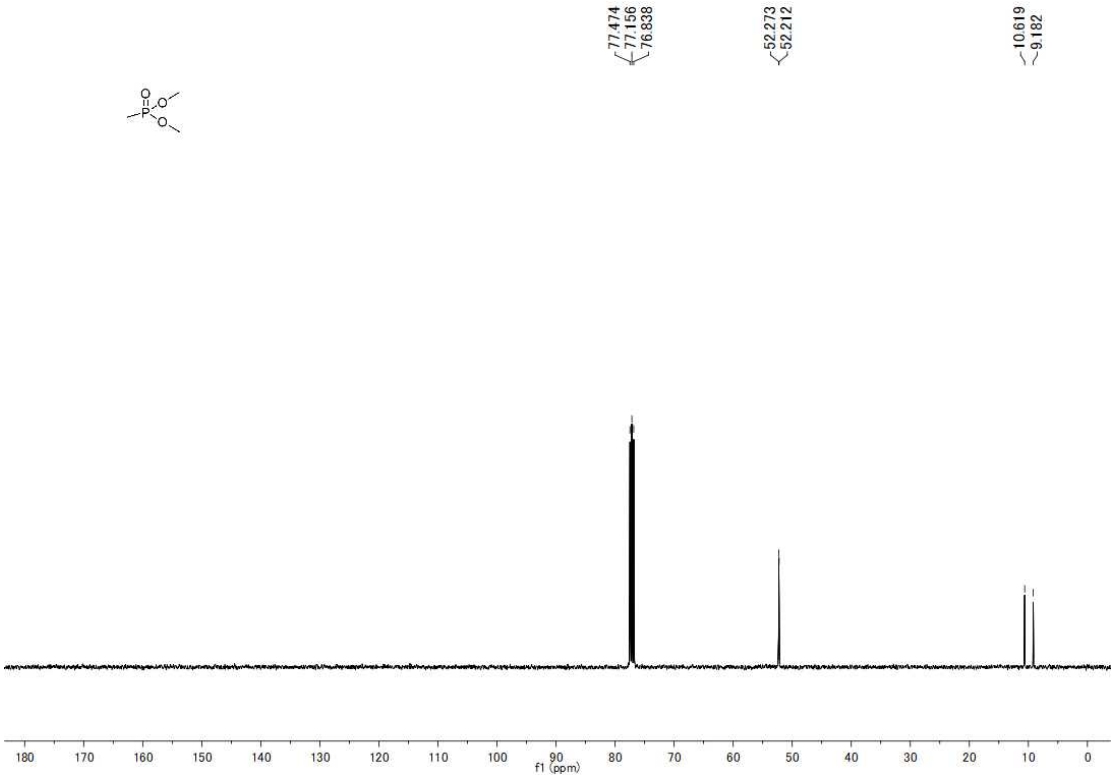
^{1}H NMR



^{31}P NMR

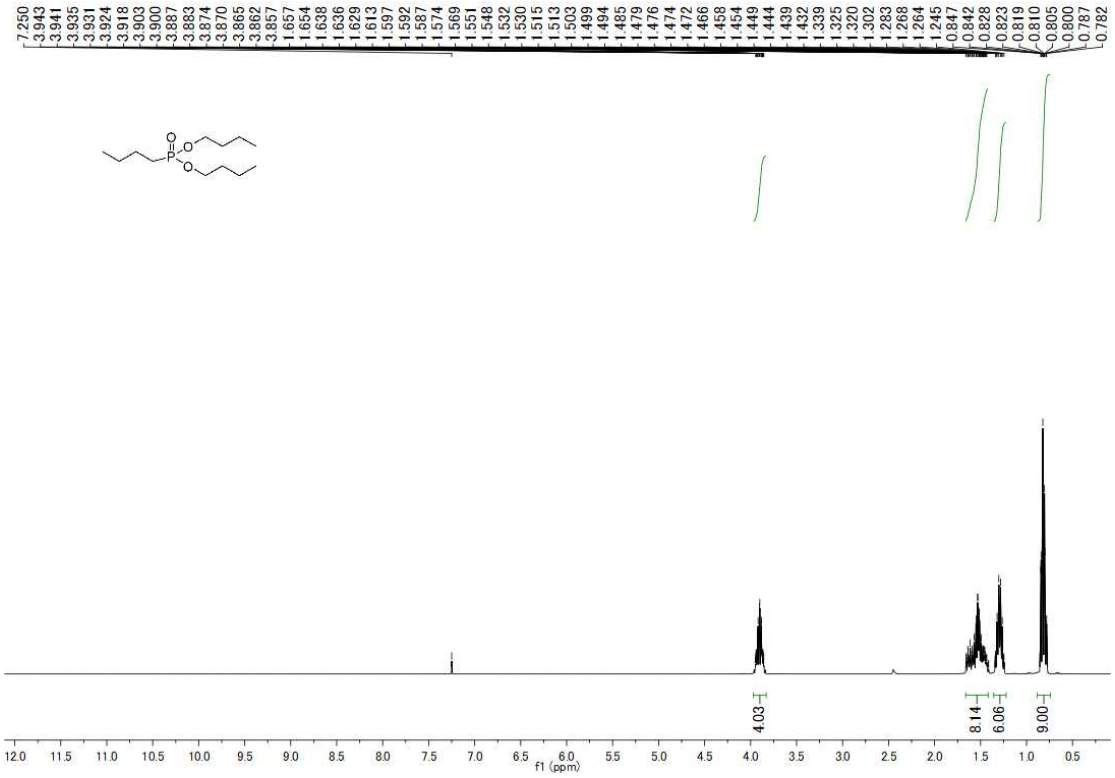


^{13}C NMR

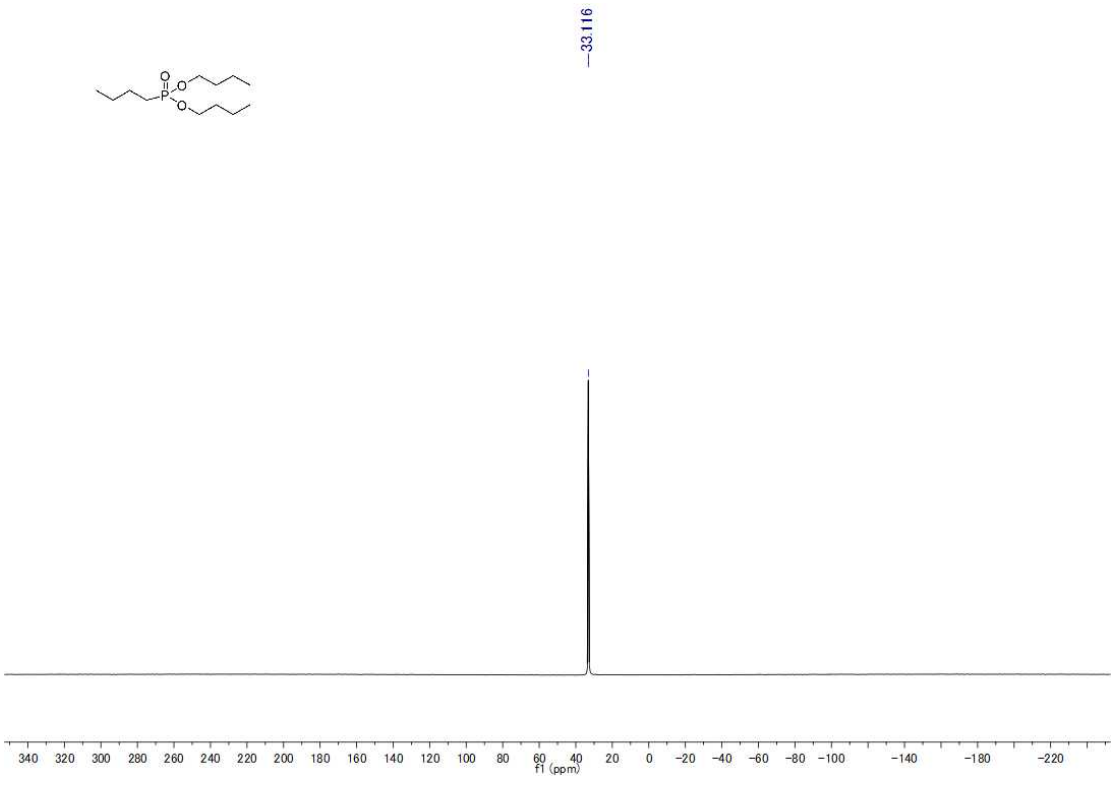

77.474
77.156
76.838
52.273
52.212
10.619
9.182
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

n-BuP(O)(O*n*-Bu)$_2$ (3d)

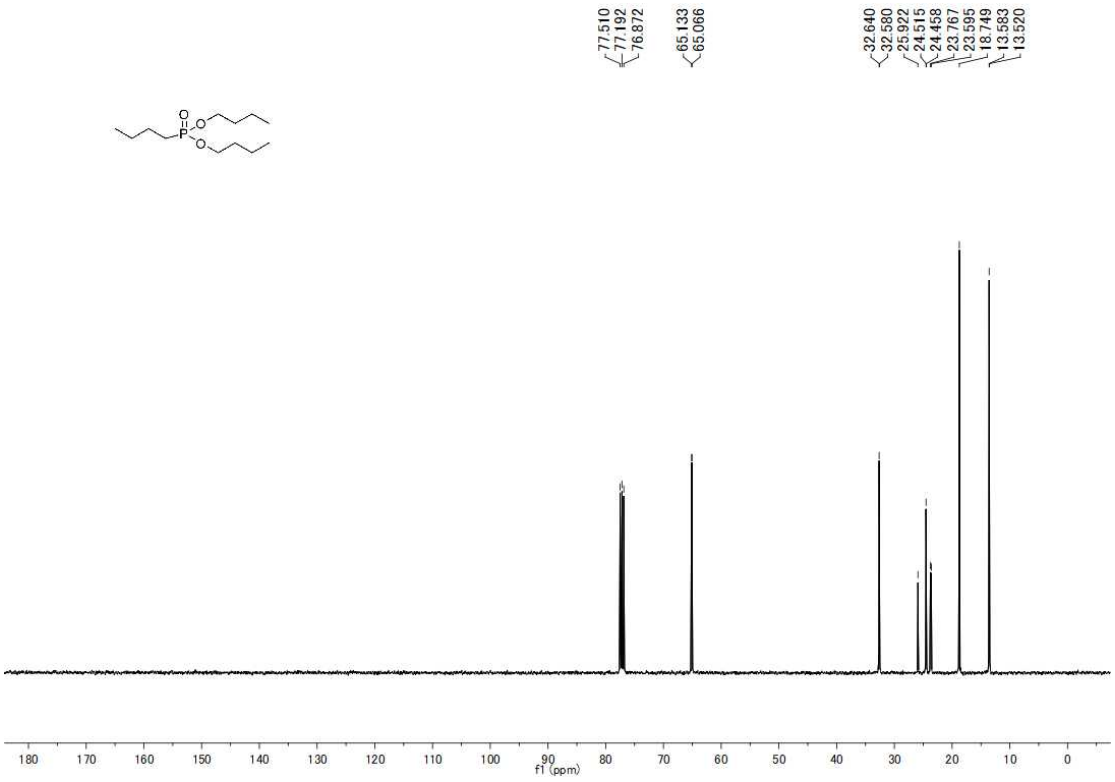
^{1}H NMR



^{31}P NMR

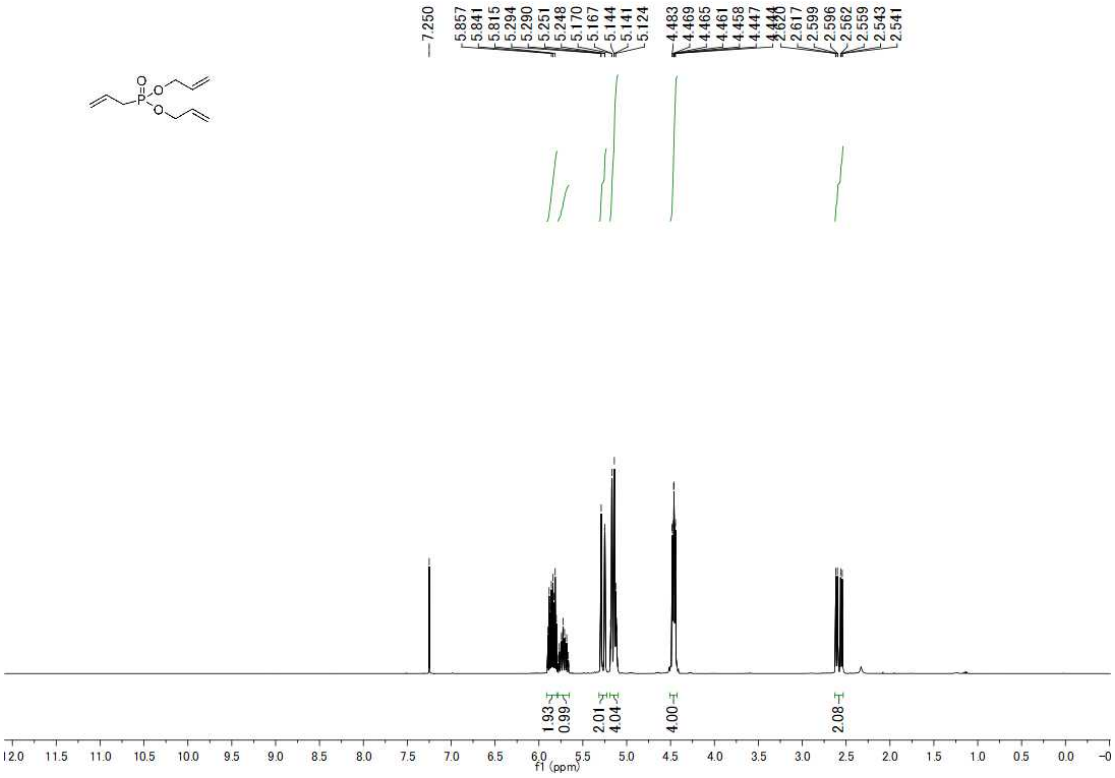


^{13}C NMR

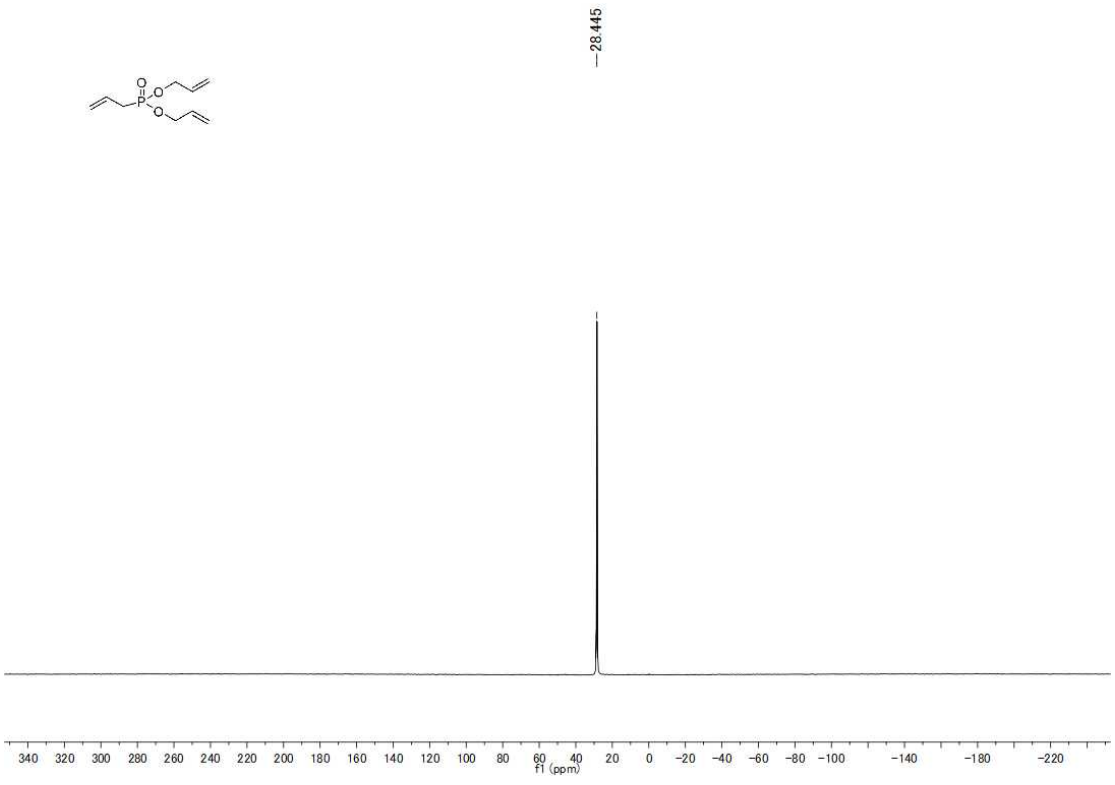

77.510
77.192
76.872
65.133
65.066
32.640
32.580
25.922
24.515
24.458
23.767
23.595
18.749
13.583
13.520
O
P
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

allyP(O)(Oally)$_2$ (3e)

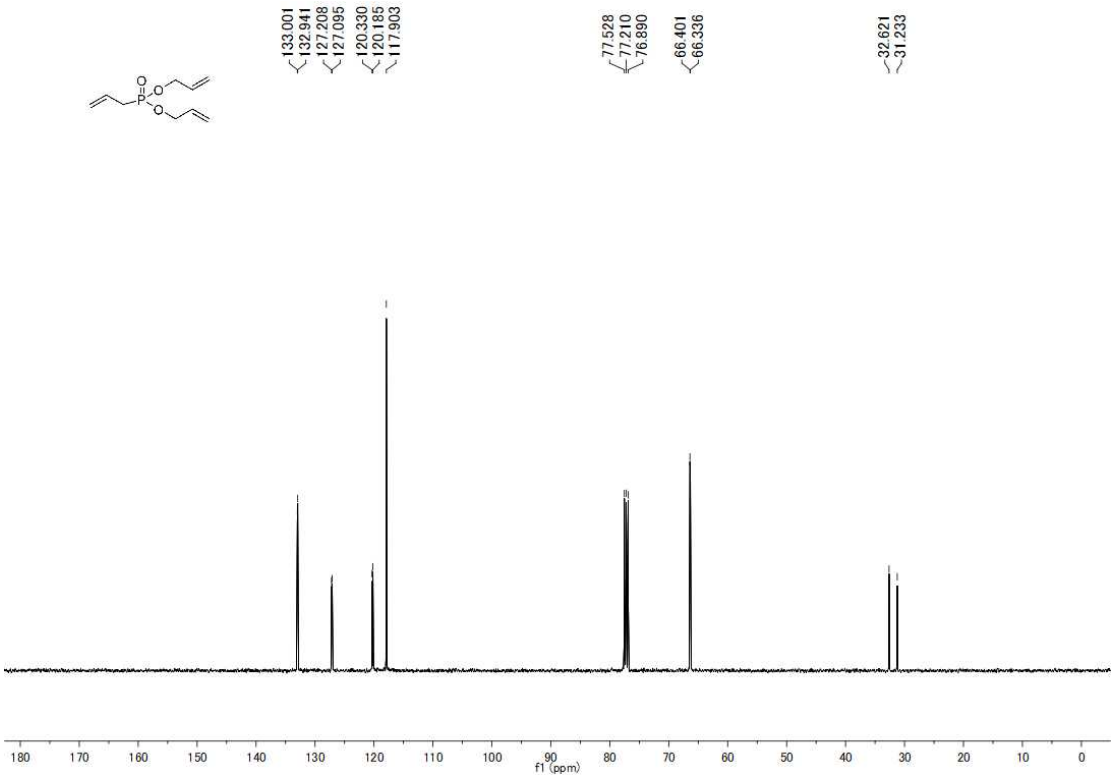
^{1}H NMR



^{31}P NMR

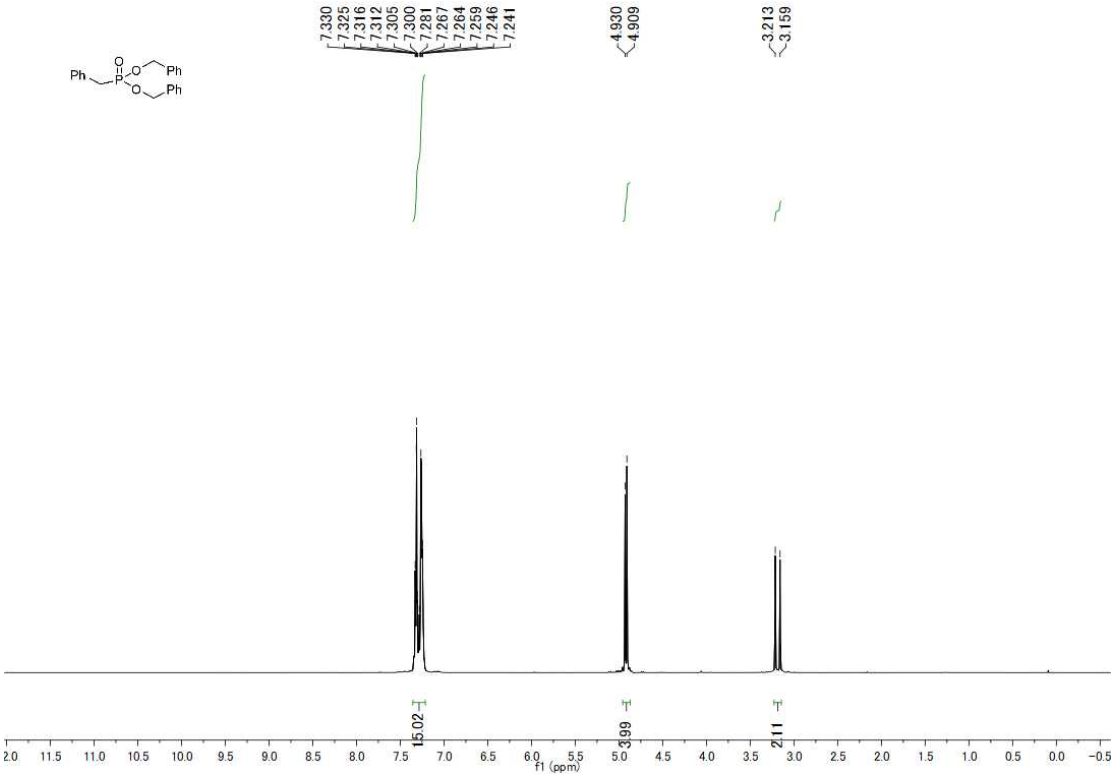


^{13}C NMR

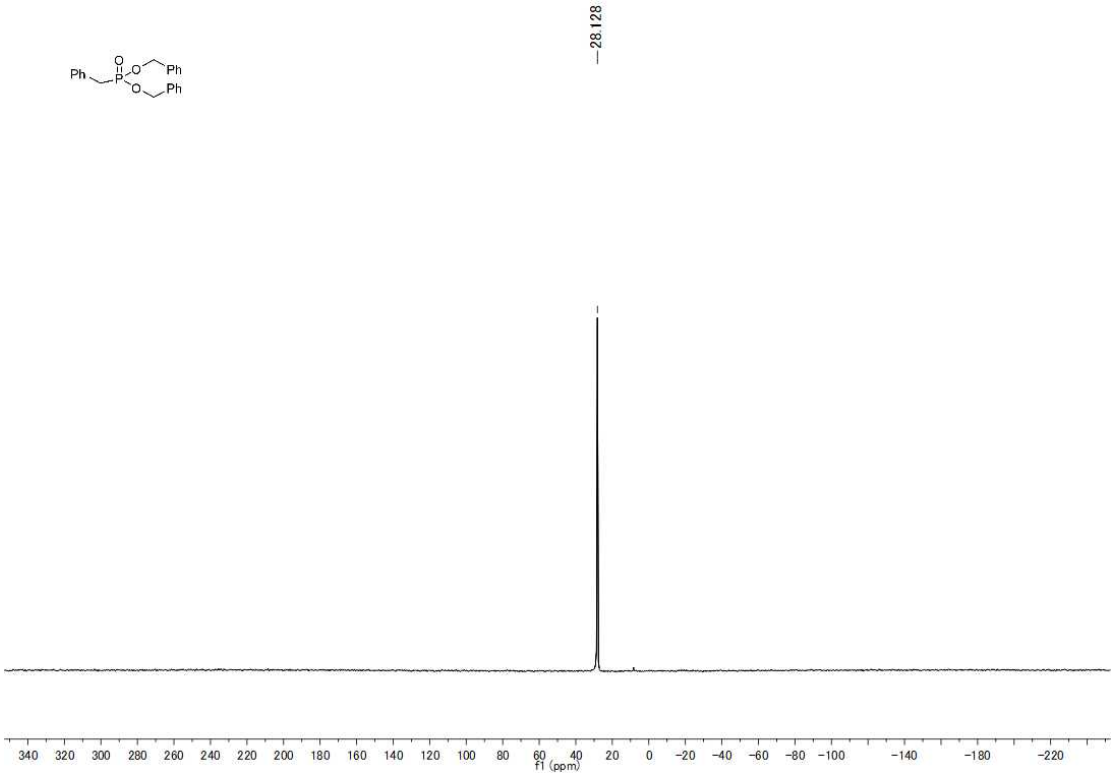

133.001
132.941
127.208
127.095
120.330
120.185
117.903
77.528
77.210
76.890
66.401
66.336
32.621
31.233
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$PhCH_2P(O)(OCH_2Ph)_2$ (3f)

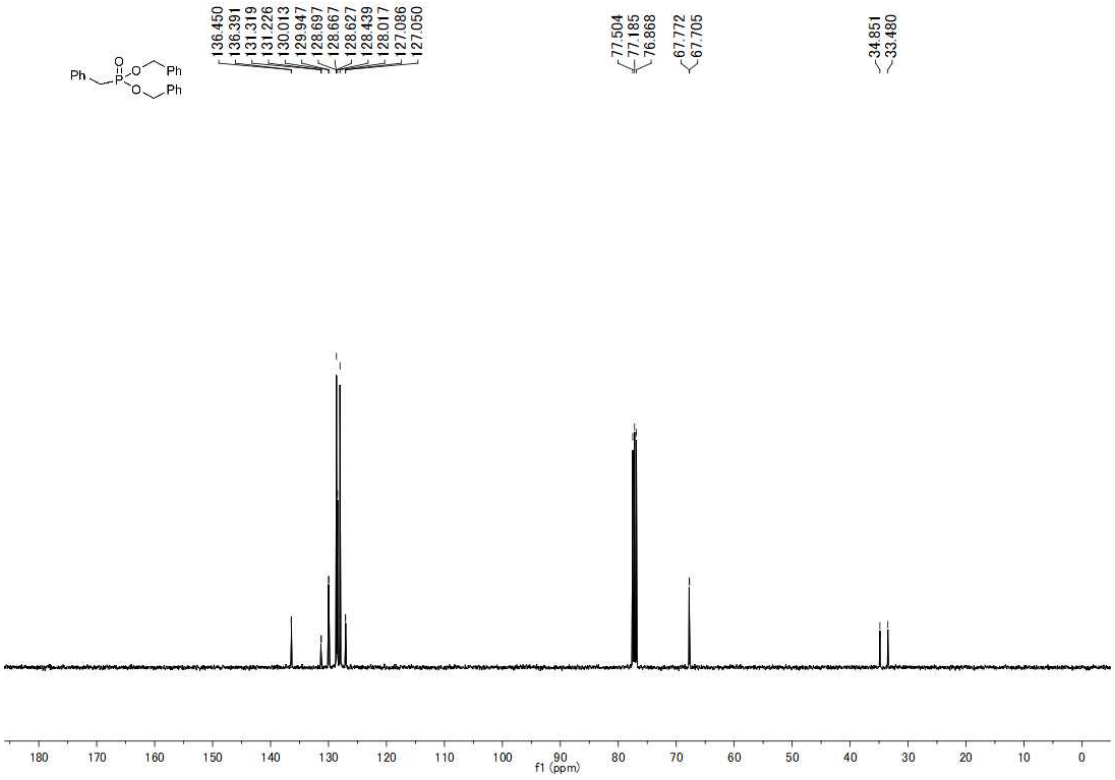
^{1}H NMR



^{31}P NMR

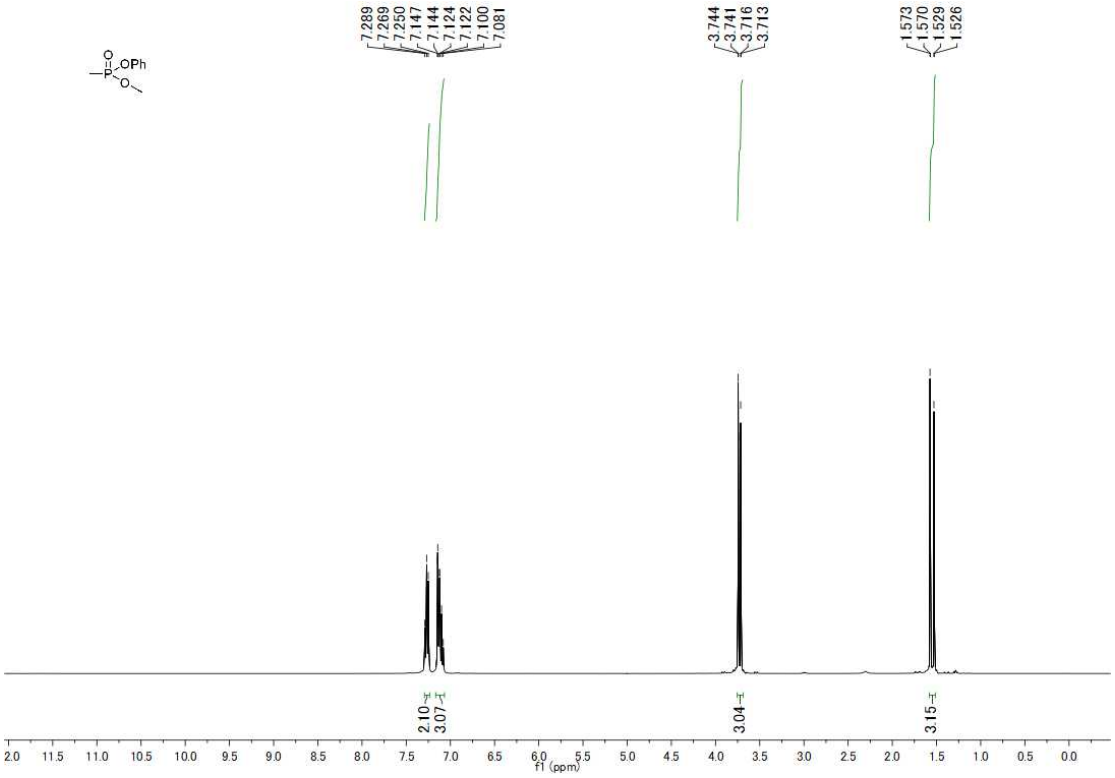


^{13}C NMR

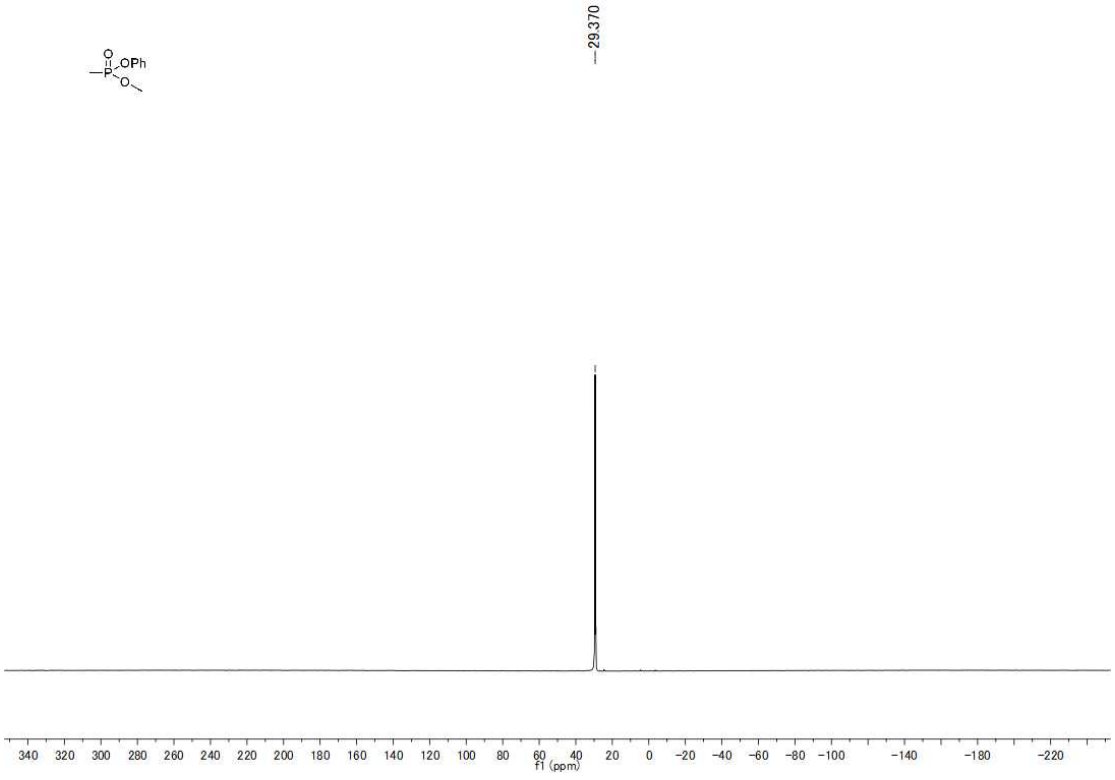

136.450
136.391
131.319
131.226
130.013
129.947
128.697
128.667
128.627
128.439
128.017
127.086
127.050
77.504
77.185
76.868
67.772
67.705
34.851
33.480
Ph
Ph
Ph
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

MeP(O)(OMe)(OPh) (3g)

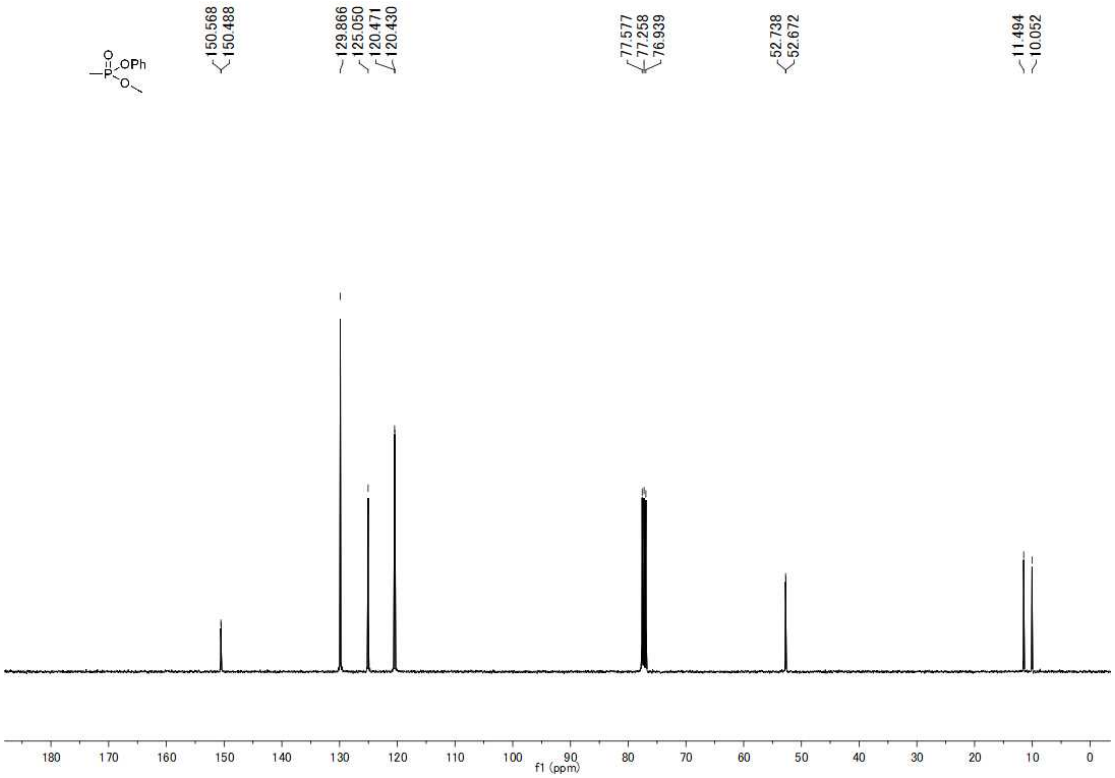
^{1}H NMR



^{31}P NMR

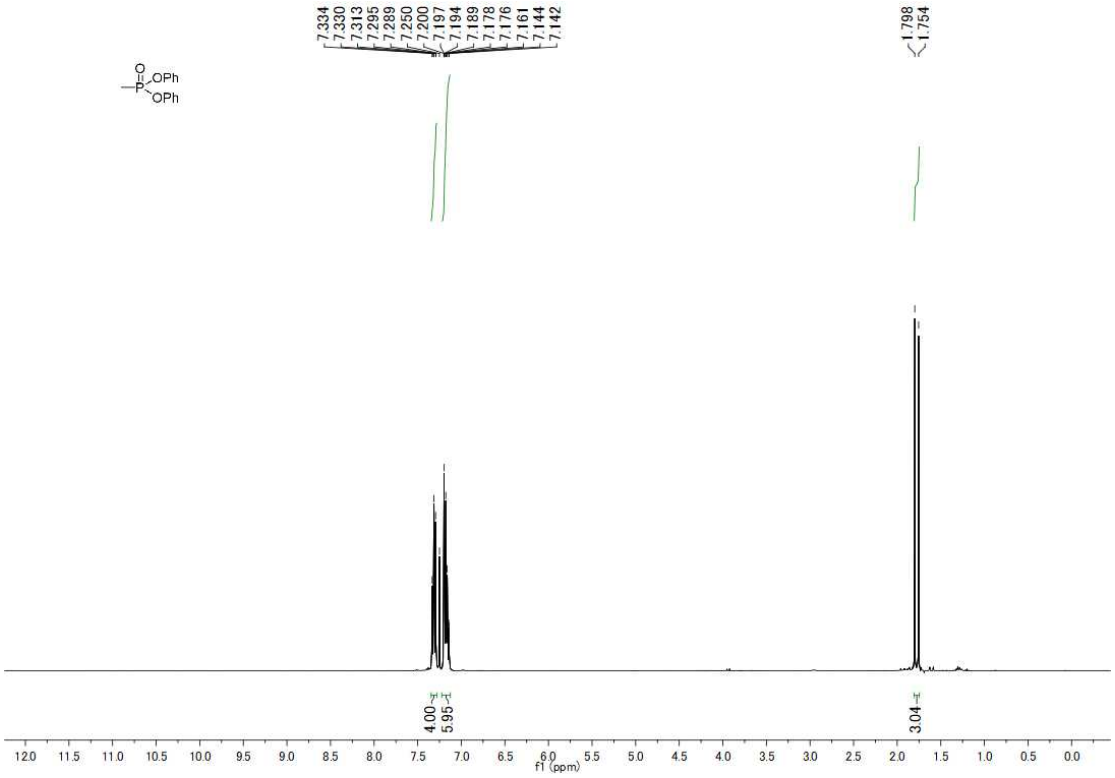


^{13}C NMR

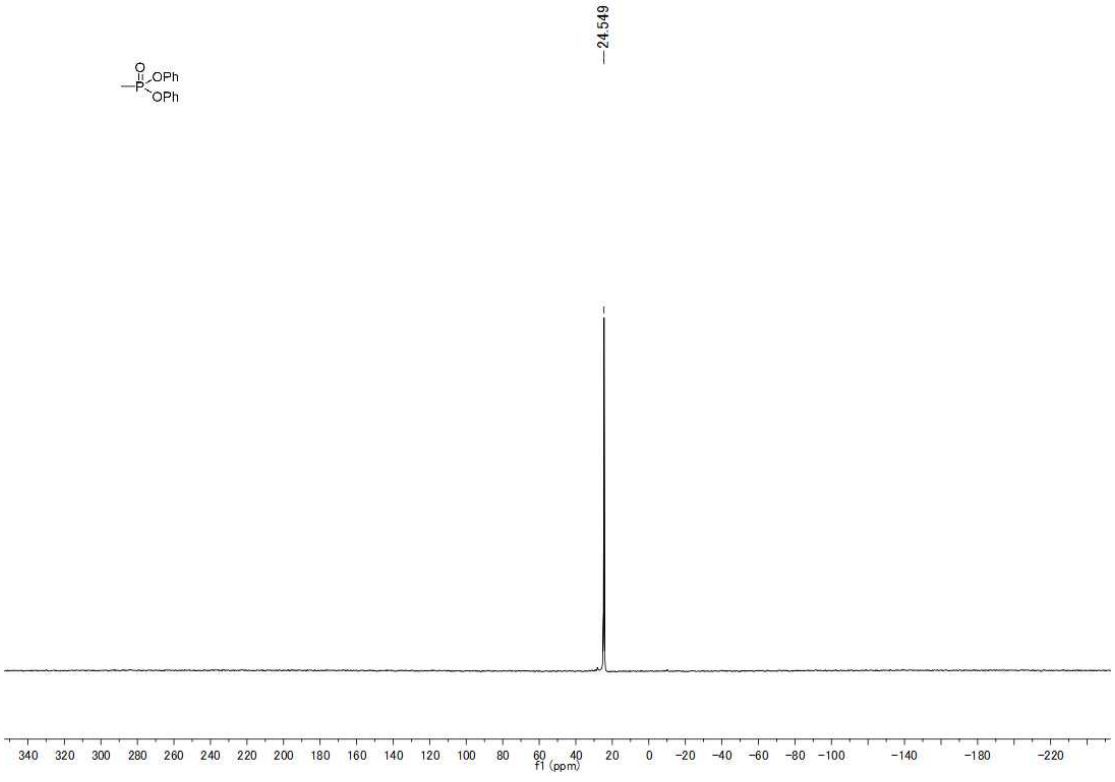

150.568
150.488
129.866
125.050
120.471
120.430
77.577
77.258
76.939
52.738
52.672
11.494
10.052
OPh
f1 (ppm)

$MeP(O)(OPh)_2$ (3h)

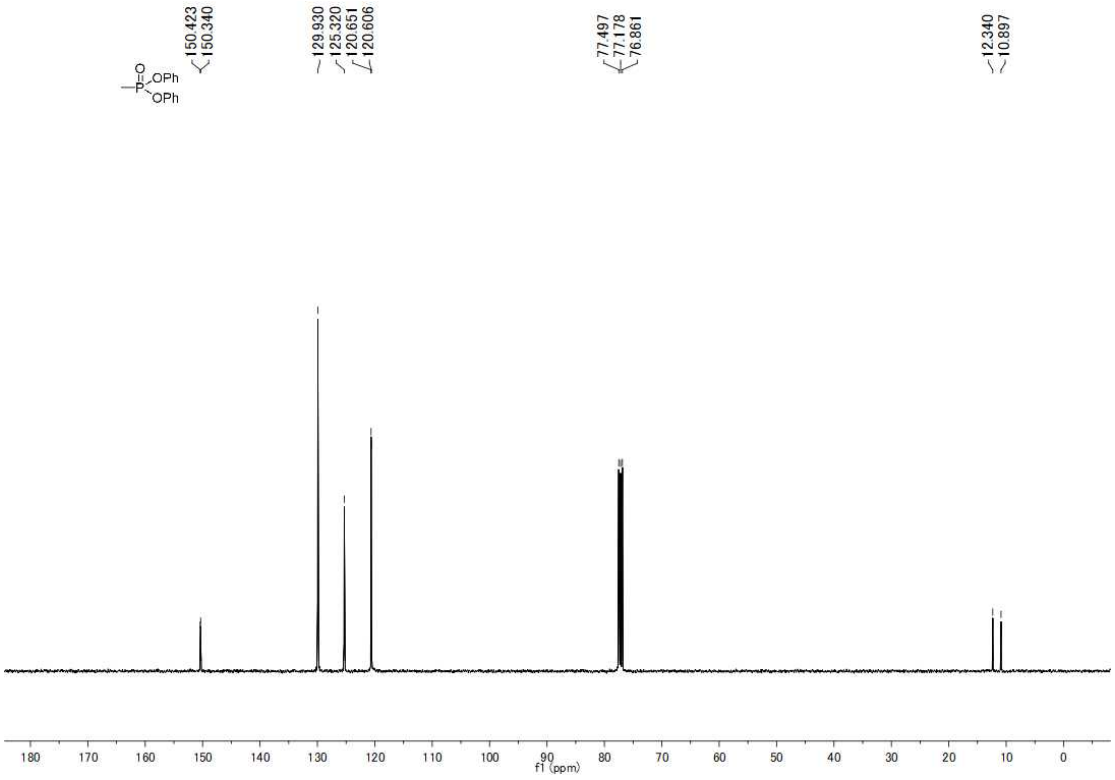
^1H NMR



^{31}P NMR

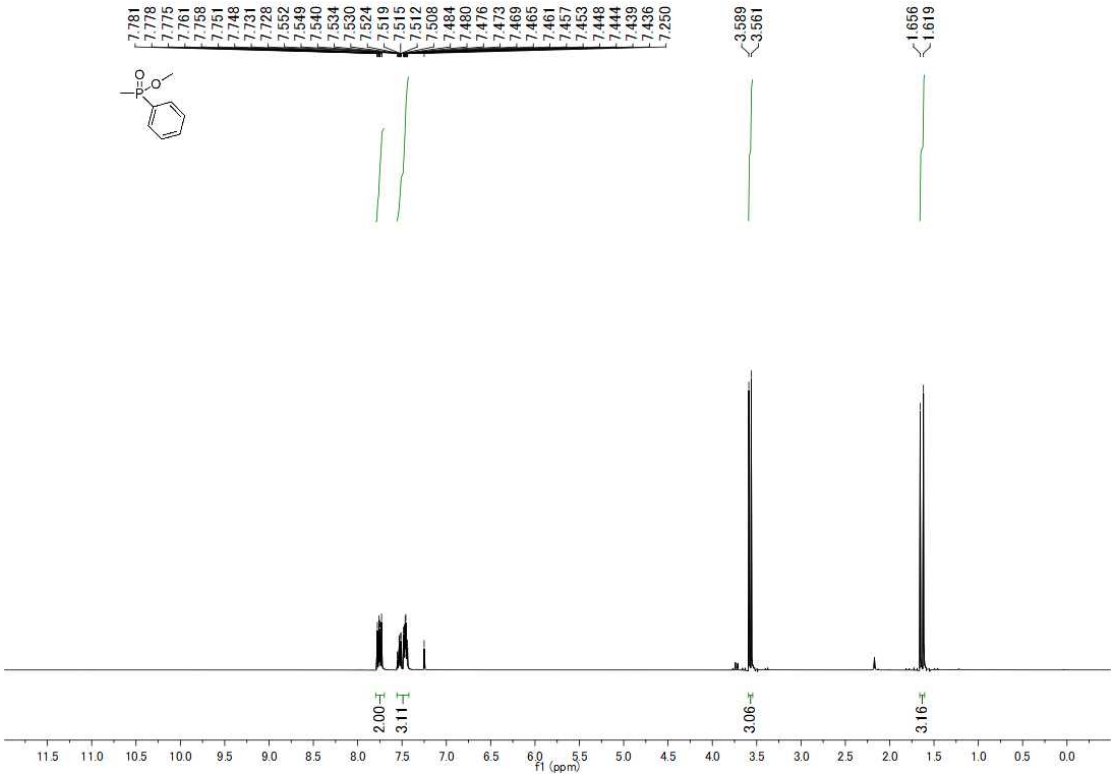


^{13}C NMR

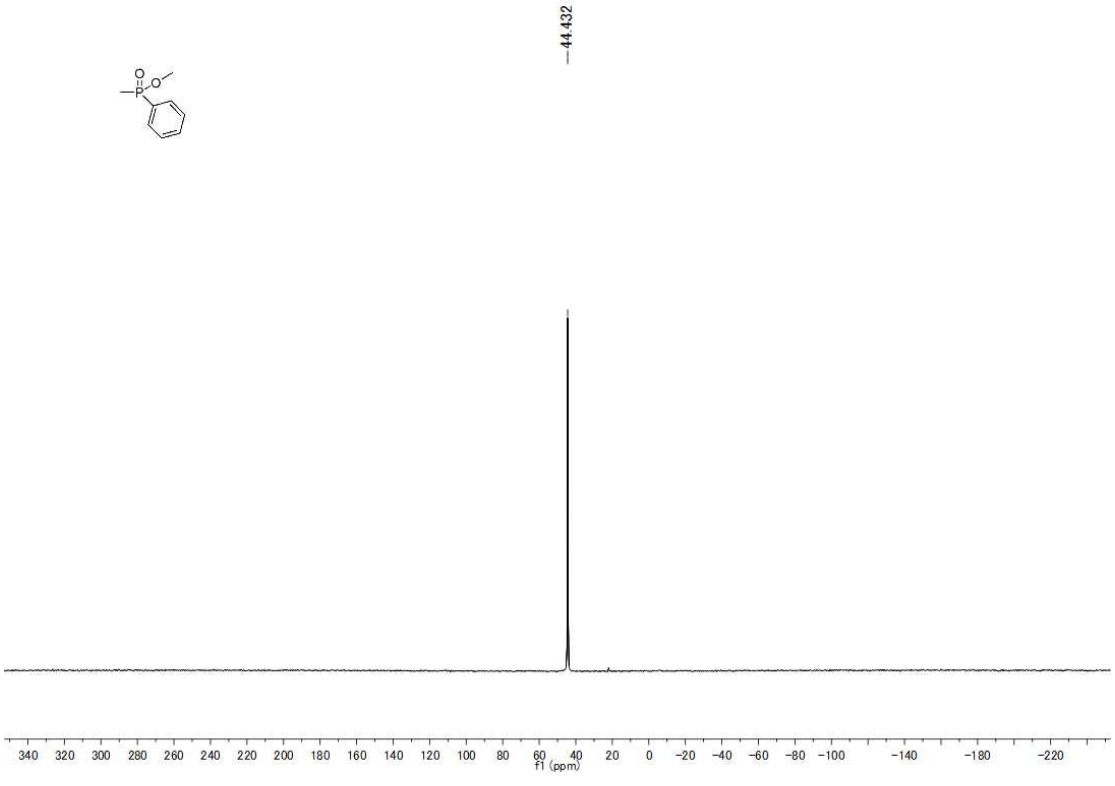

150.423
150.340
129.930
125.320
120.651
120.606
77.497
77.178
76.861
12.340
10.897
OPh
OPh
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

MeP(O)(OMe)Ph (3j)

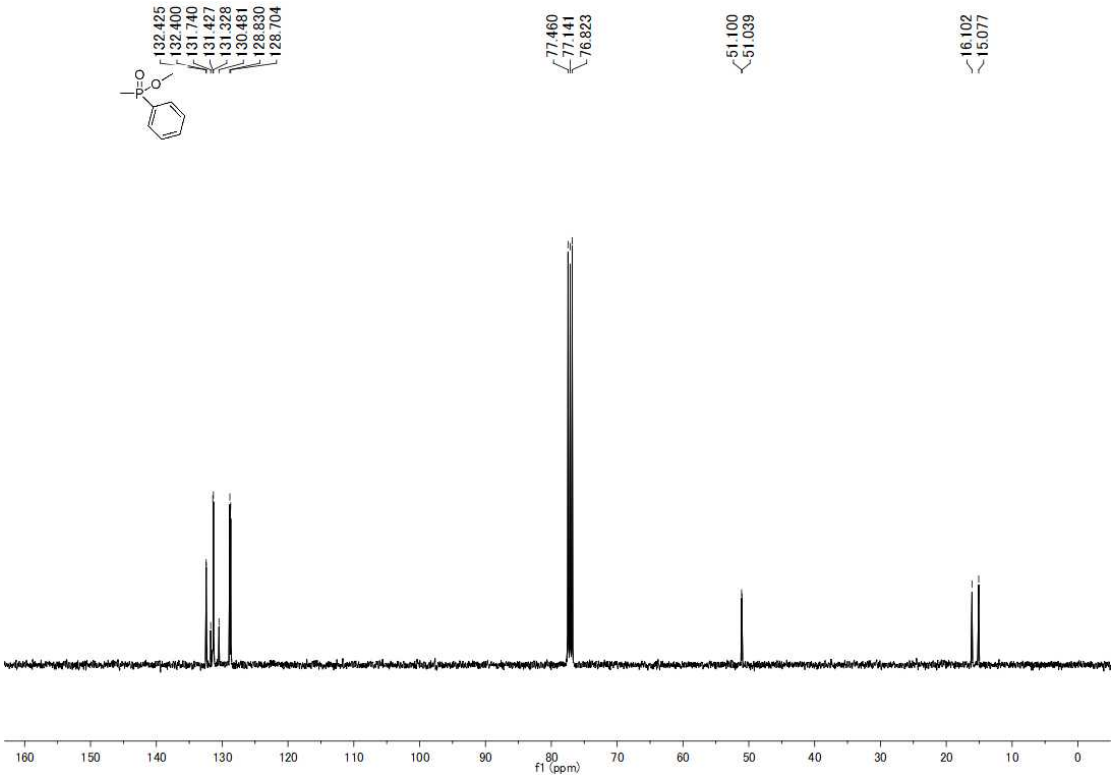
^{1}H NMR



^{31}P NMR

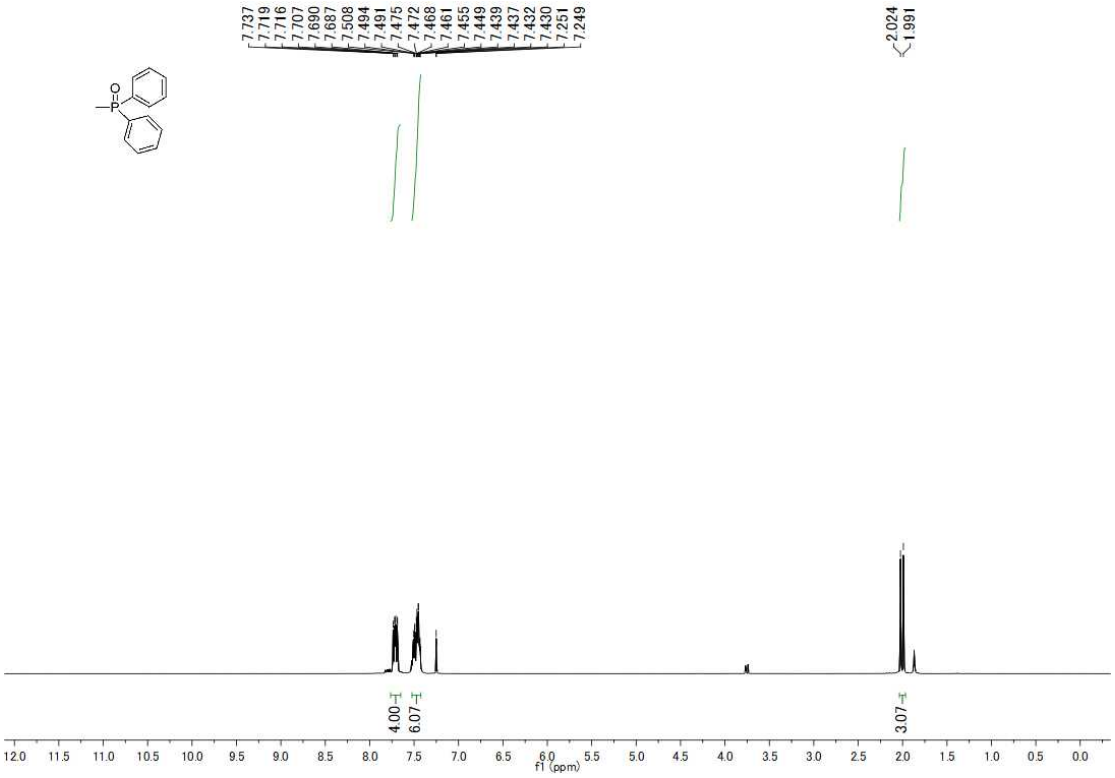


^{13}C NMR

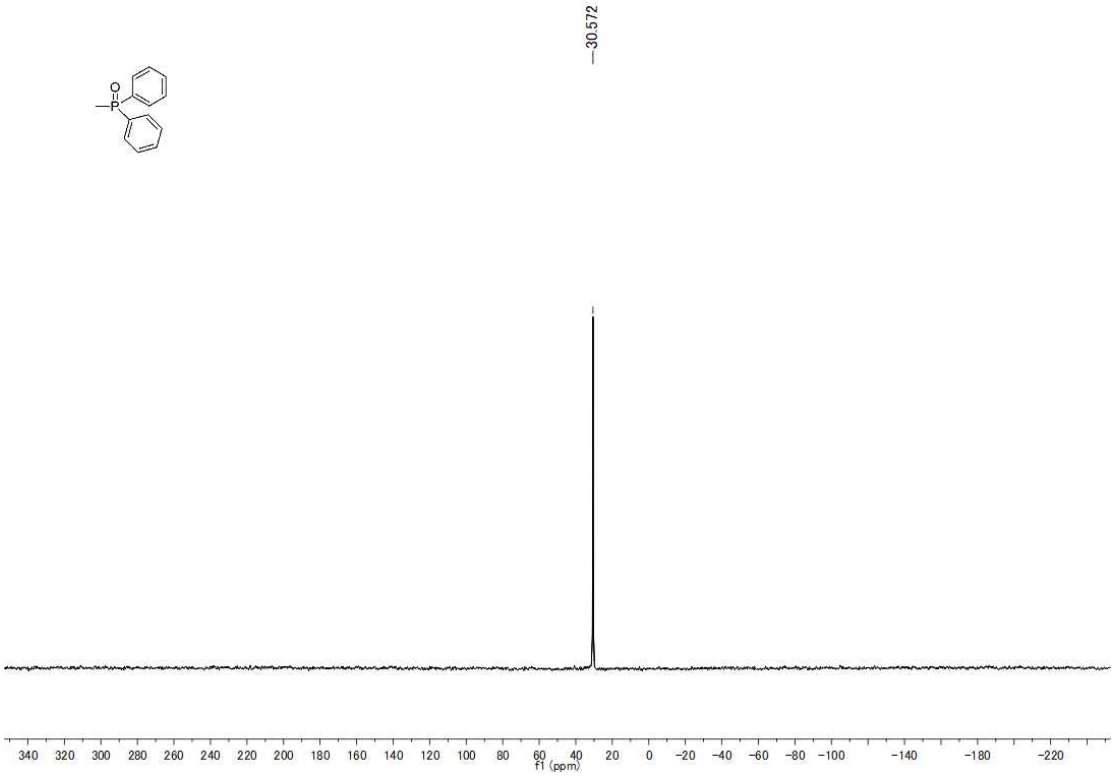

132.425
132.400
131.740
131.427
131.328
130.481
128.830
128.704
77.460
77.141
76.823
51.100
51.039
16.102
15.077
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$MeP(O)Ph_2$ (3k)

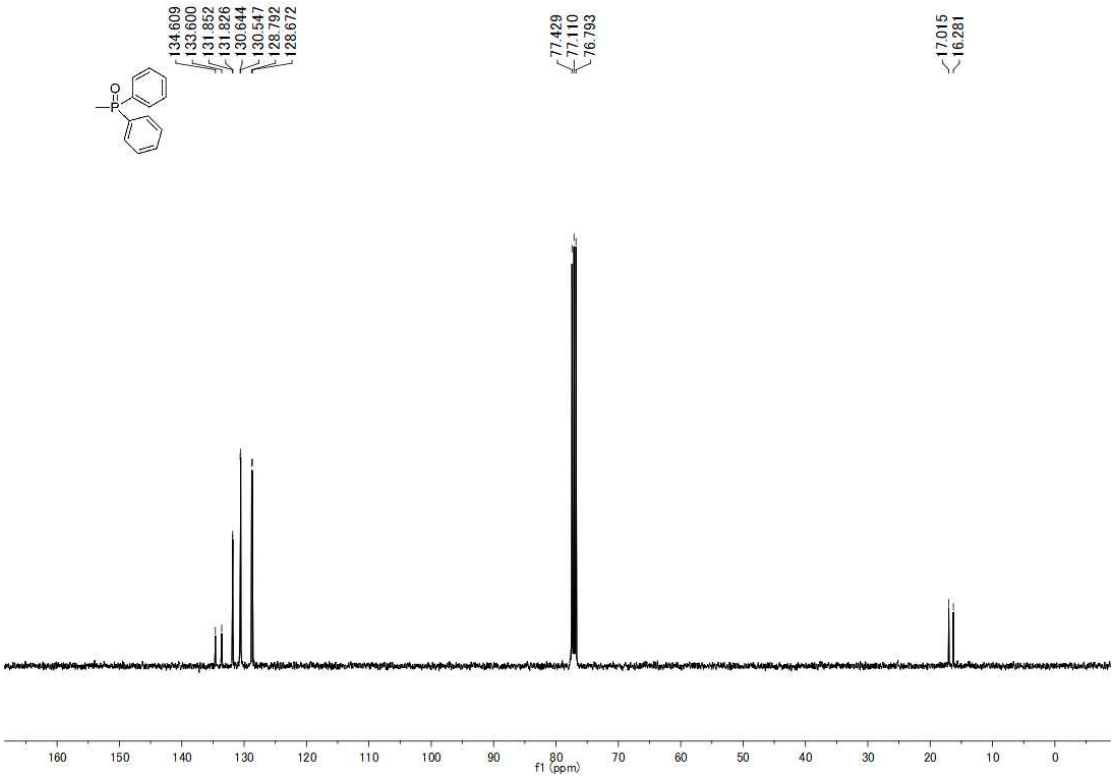
^{1}H NMR



^{31}P NMR

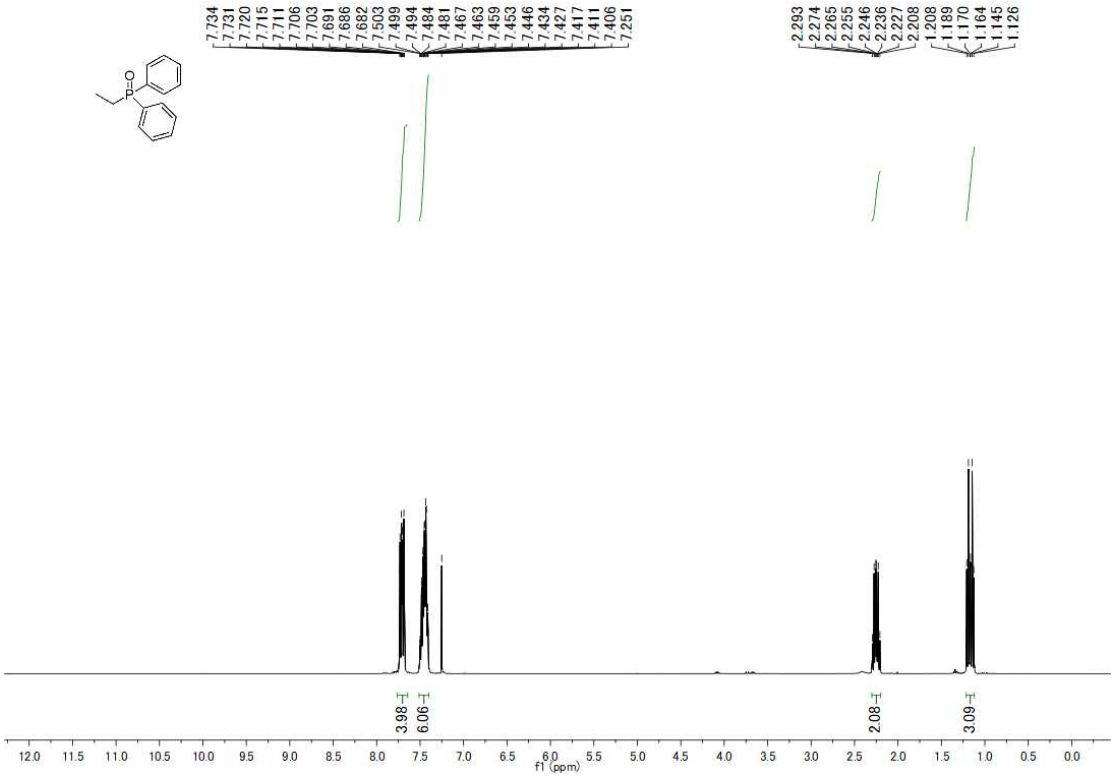


^{13}C NMR

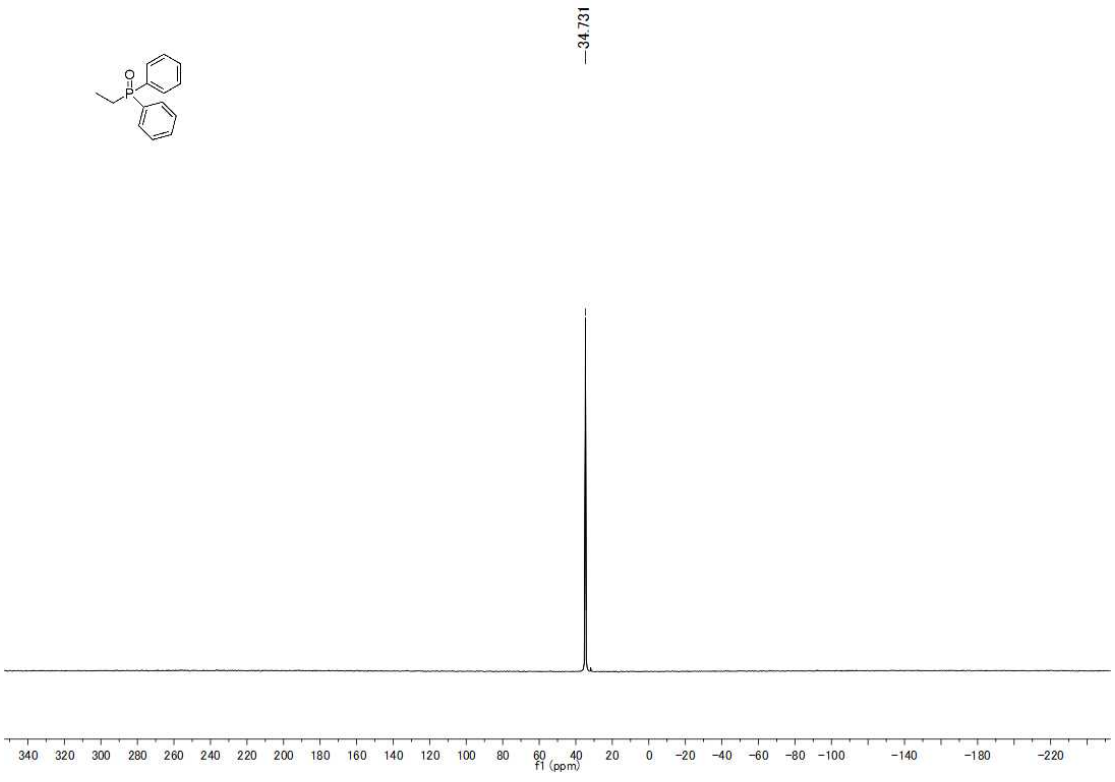

134.609
133.600
131.852
131.826
130.644
130.547
128.792
128.672
77.429
77.110
76.793
17.015
16.281
O
P
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$EtP(O)Ph_2$ (3l)

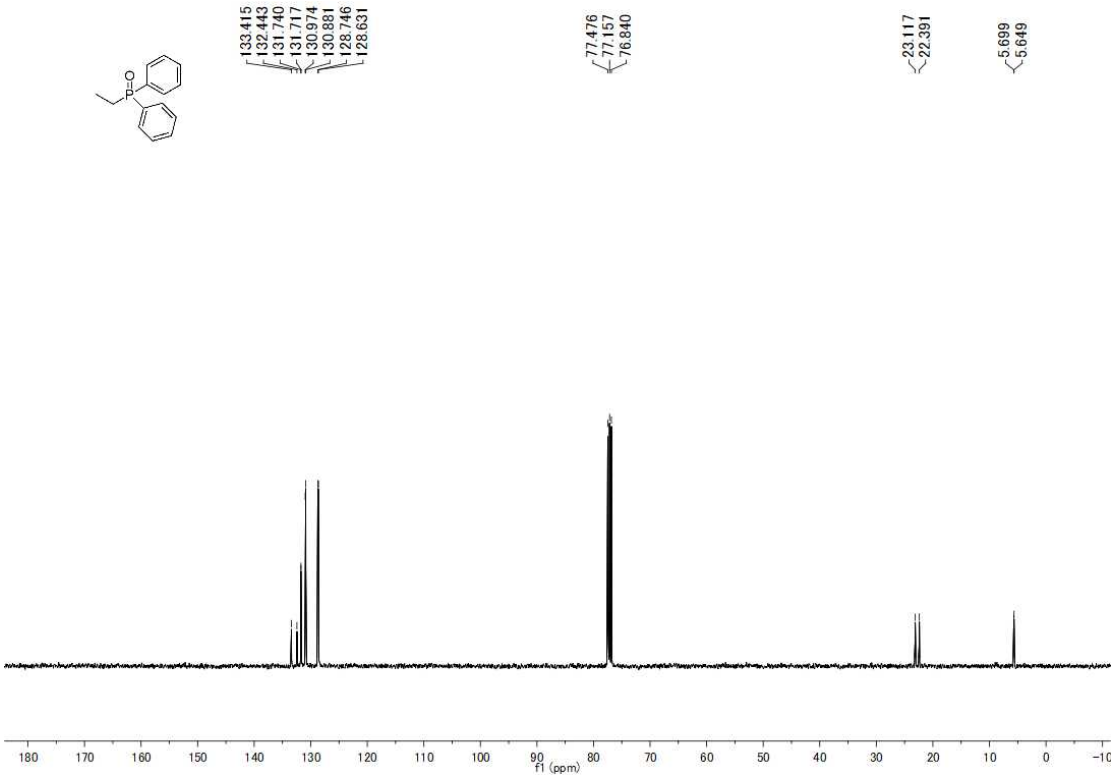
^{1}H NMR



^{31}P NMR

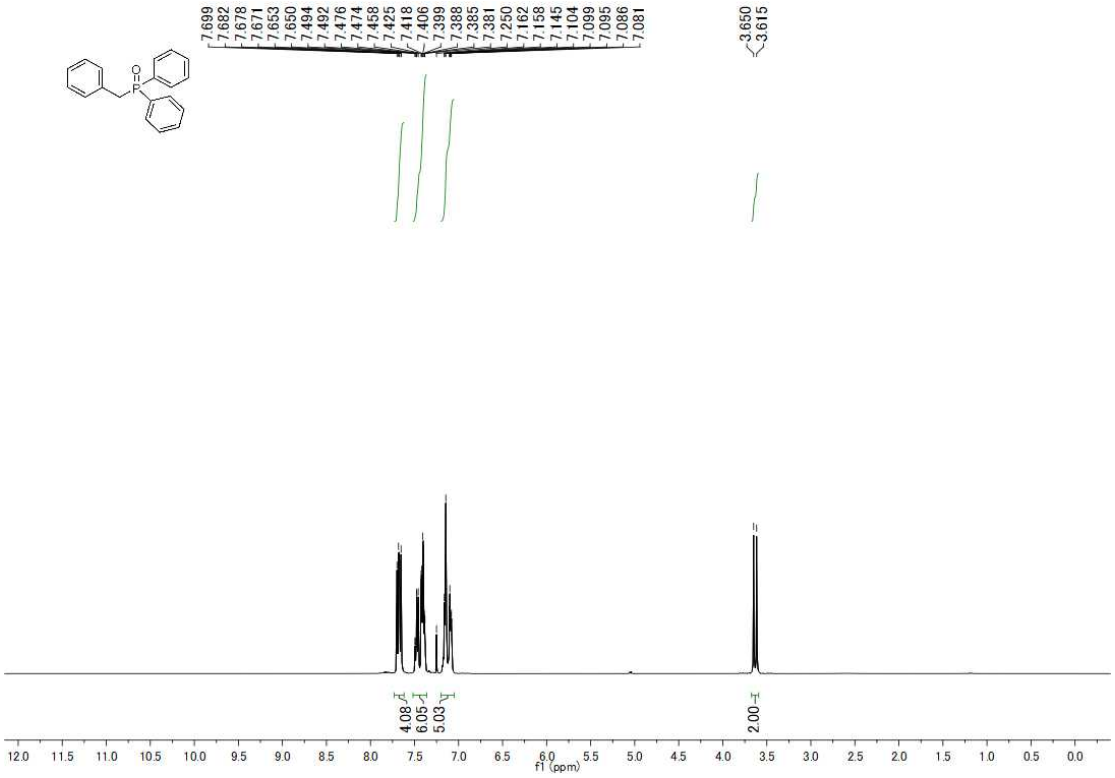


^{13}C NMR

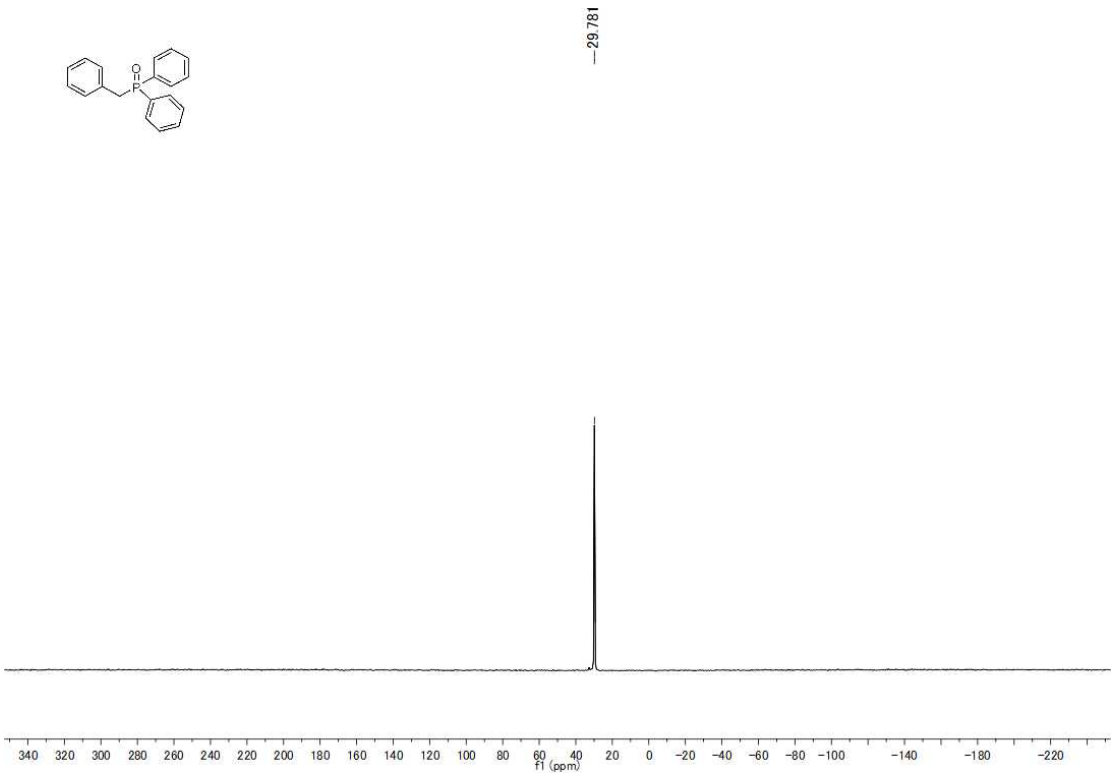

133.415
132.443
131.740
131.717
130.974
130.881
128.746
128.631
77.476
77.157
76.840
23.117
22.391
5.699
5.649
f1 (ppm)

$PhCH_2P(O)Ph_2$ (3n)

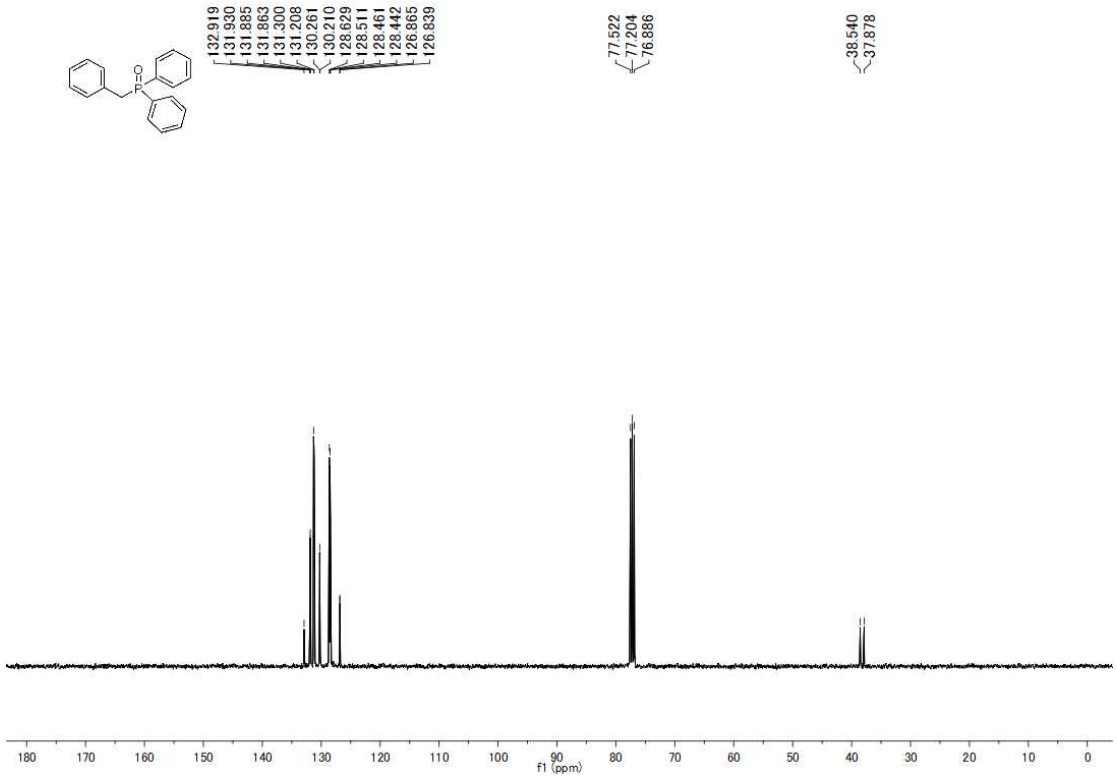
^{1}H NMR



^{31}P NMR

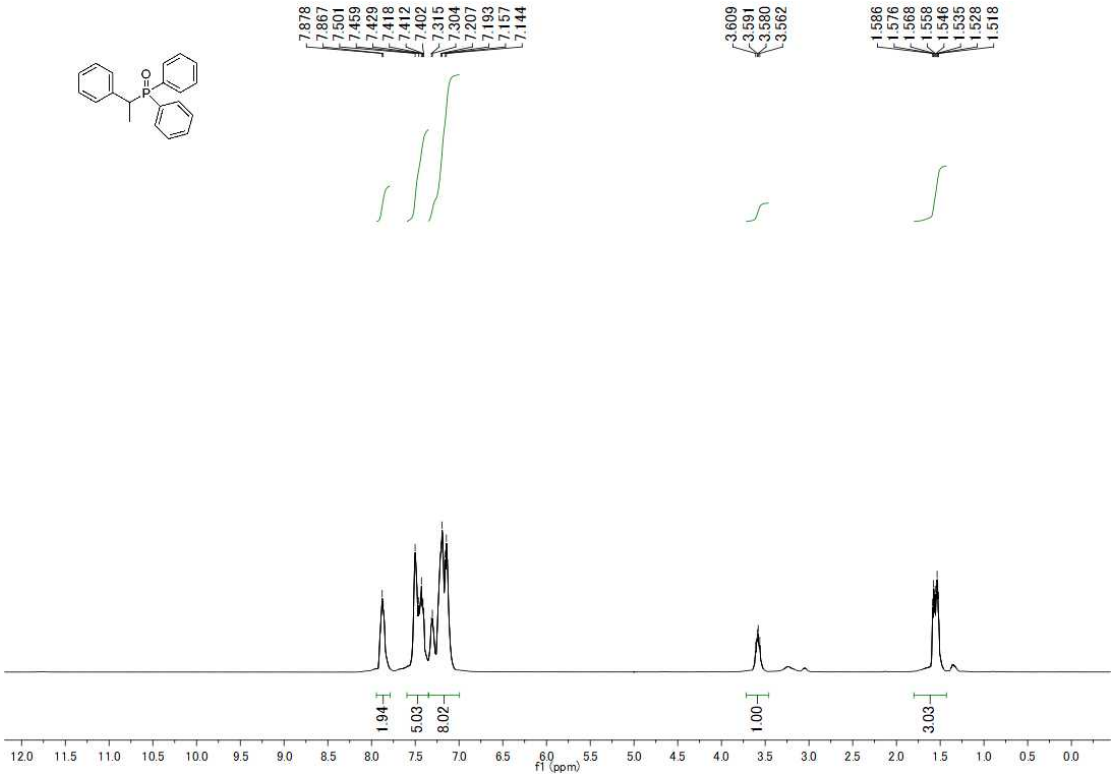


^{13}C NMR

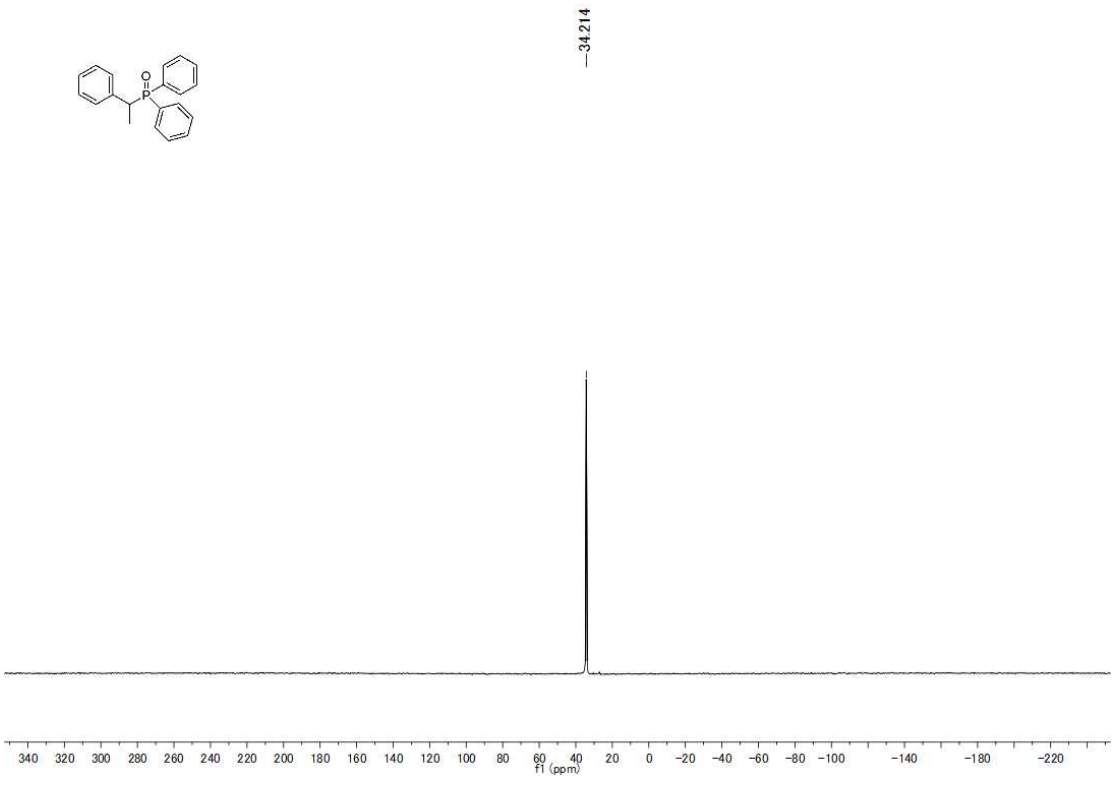

132.919
131.930
131.885
131.863
131.300
131.208
130.261
130.210
128.629
128.511
128.461
128.442
126.865
126.839
77.522
77.204
76.886
38.540
37.878
O
P
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$PhCH(CH_3)P(O)Ph_2$ (3o)

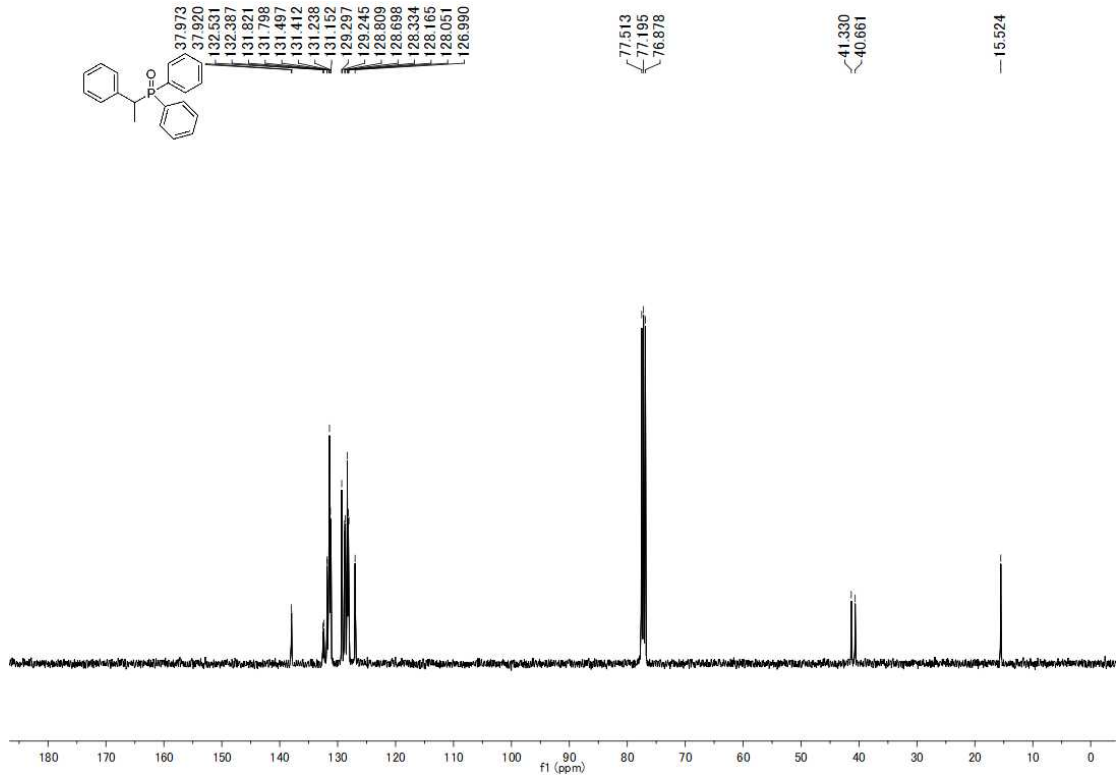
^{1}H NMR



^{31}P NMR

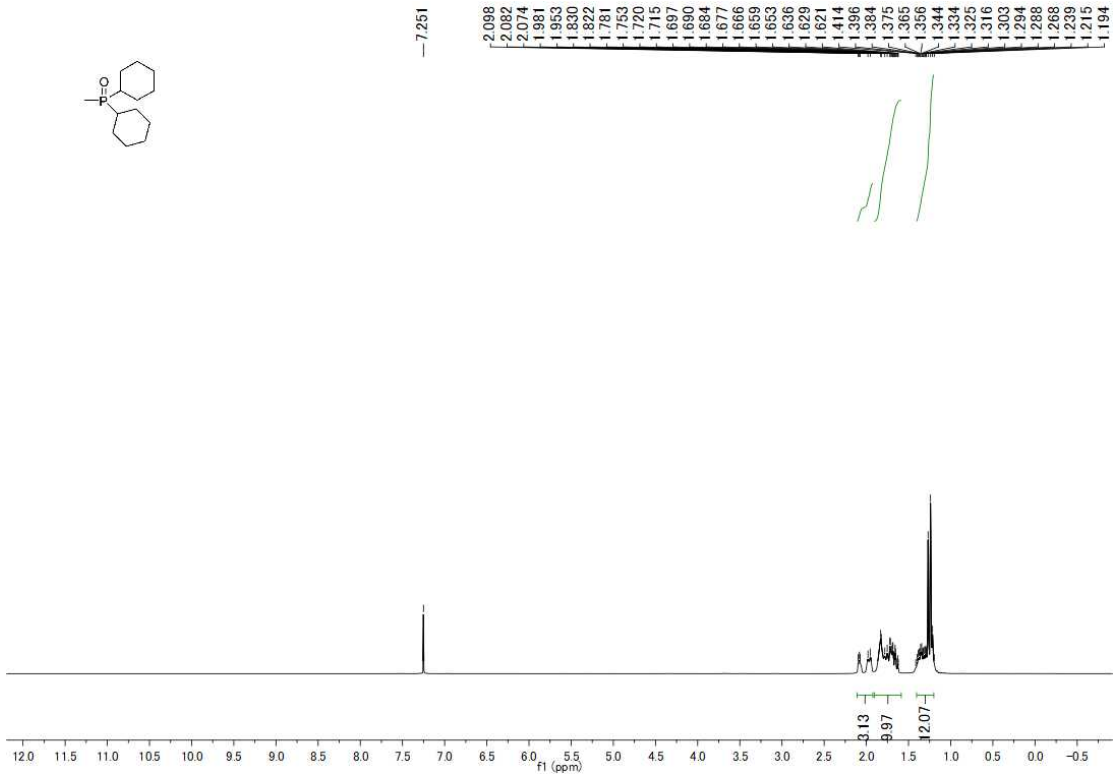


^{13}C NMR

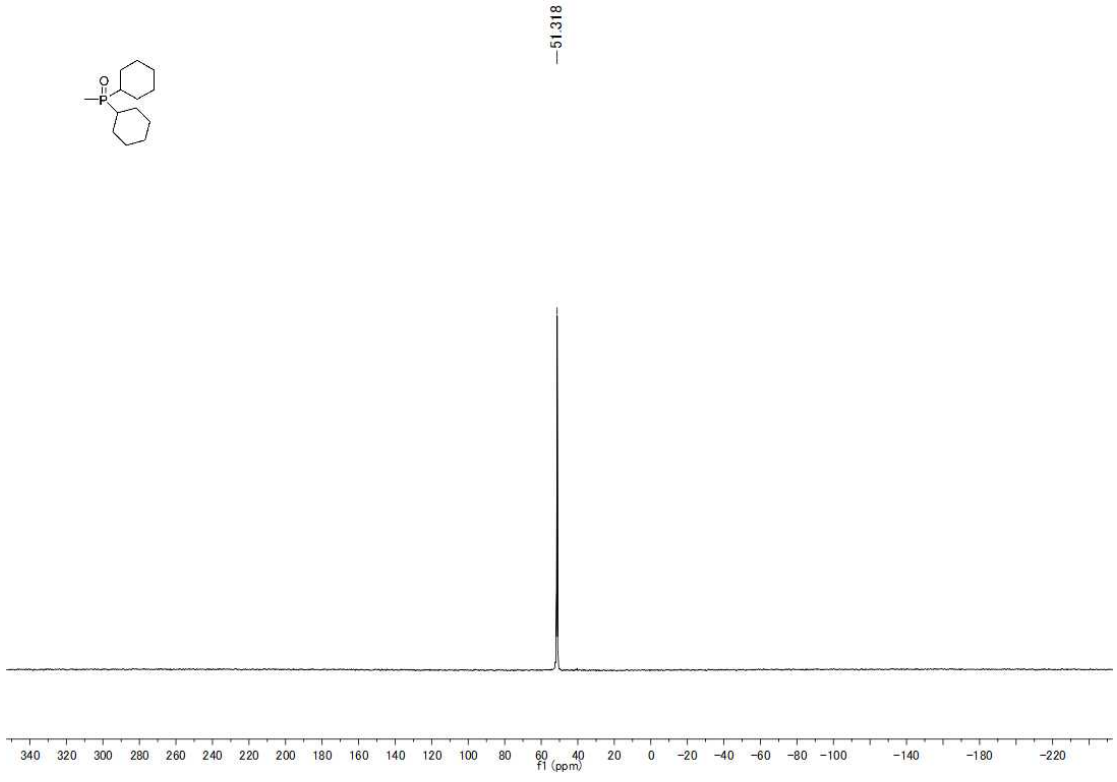

37.973
37.920
132.531
132.387
131.821
131.798
131.497
131.412
131.238
131.152
129.297
129.245
128.809
128.698
128.334
128.165
128.051
126.990
77.513
77.195
76.878
41.330
40.661
15.524
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$MeP(O)Cy_2$ (3p)

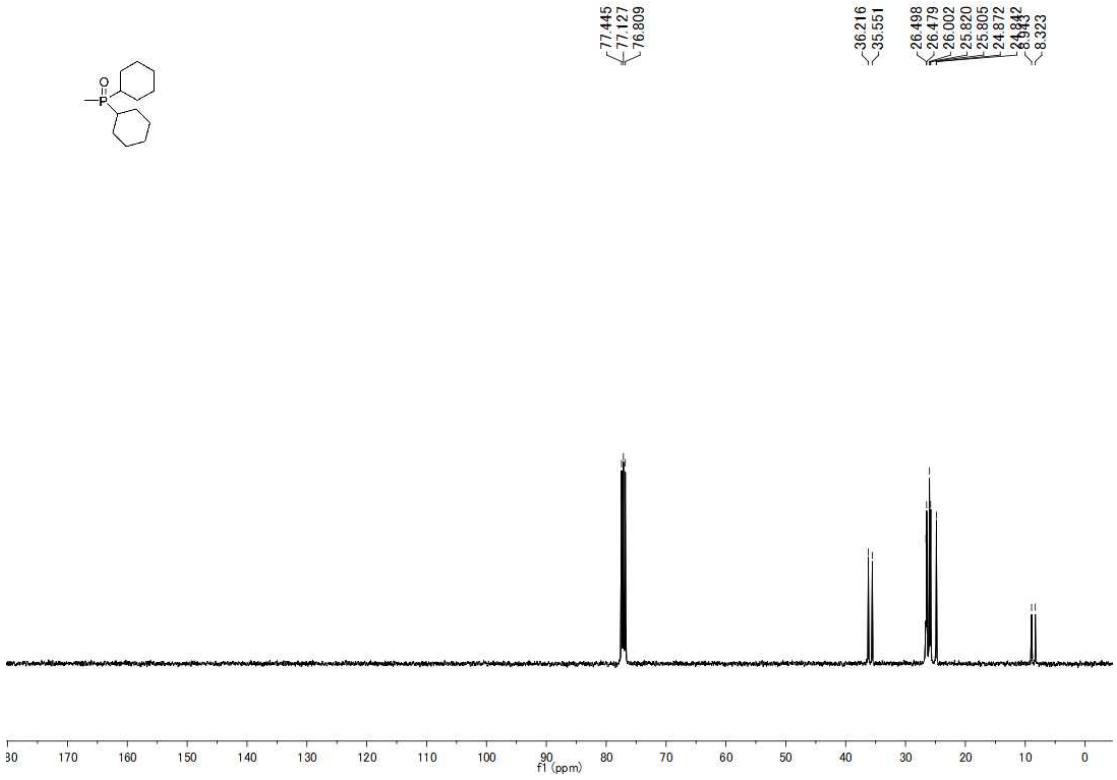
^{1}H NMR

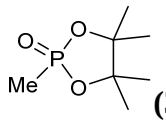


^{31}P NMR



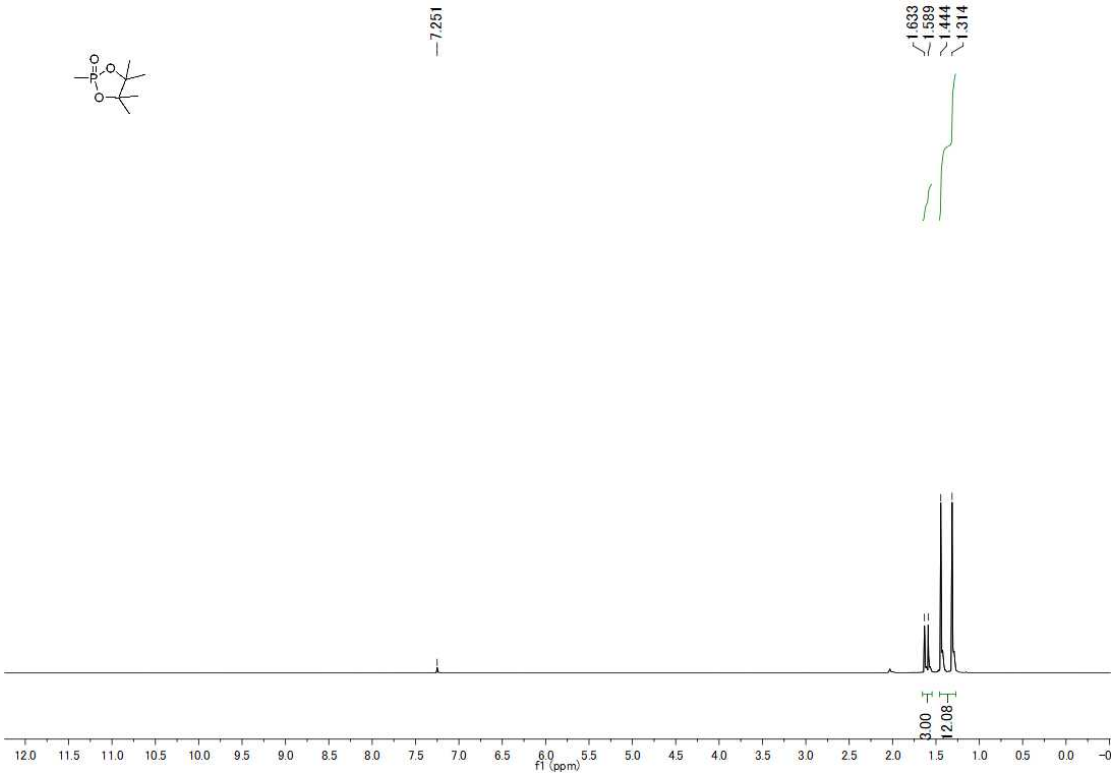
^{13}C NMR


77.445
77.127
76.809
36.216
35.551
26.498
26.479
26.002
25.820
25.805
24.872
8.323
f1 (ppm)

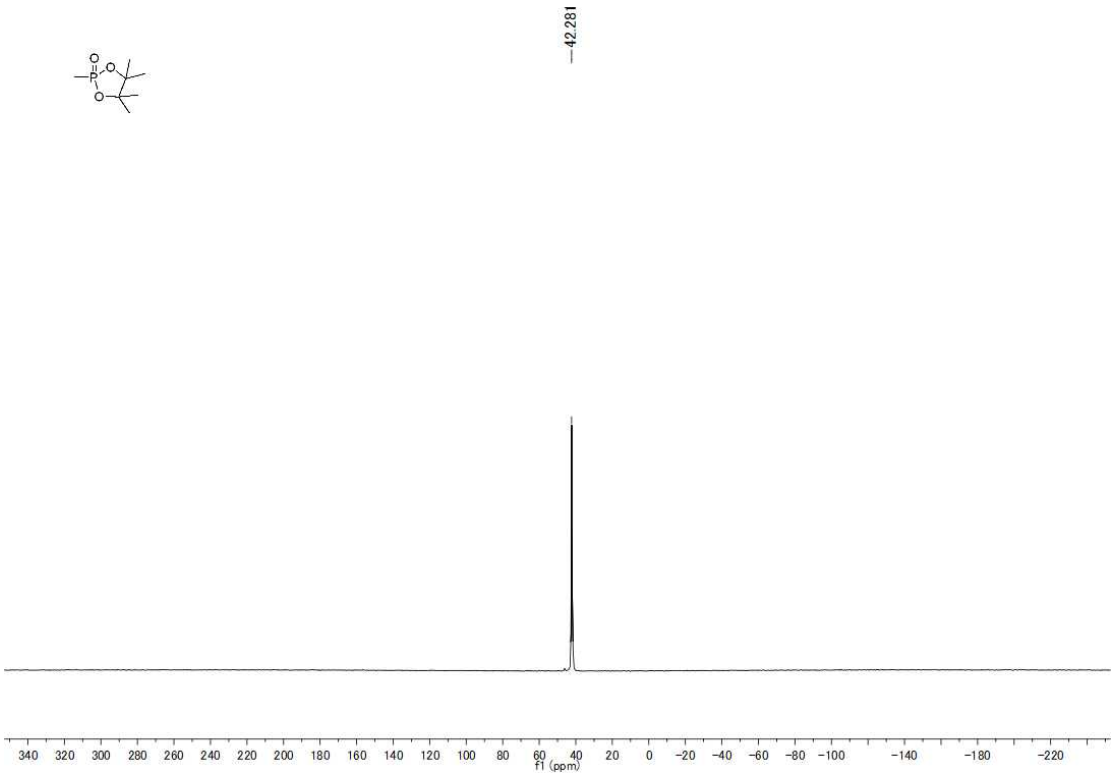


(3q)

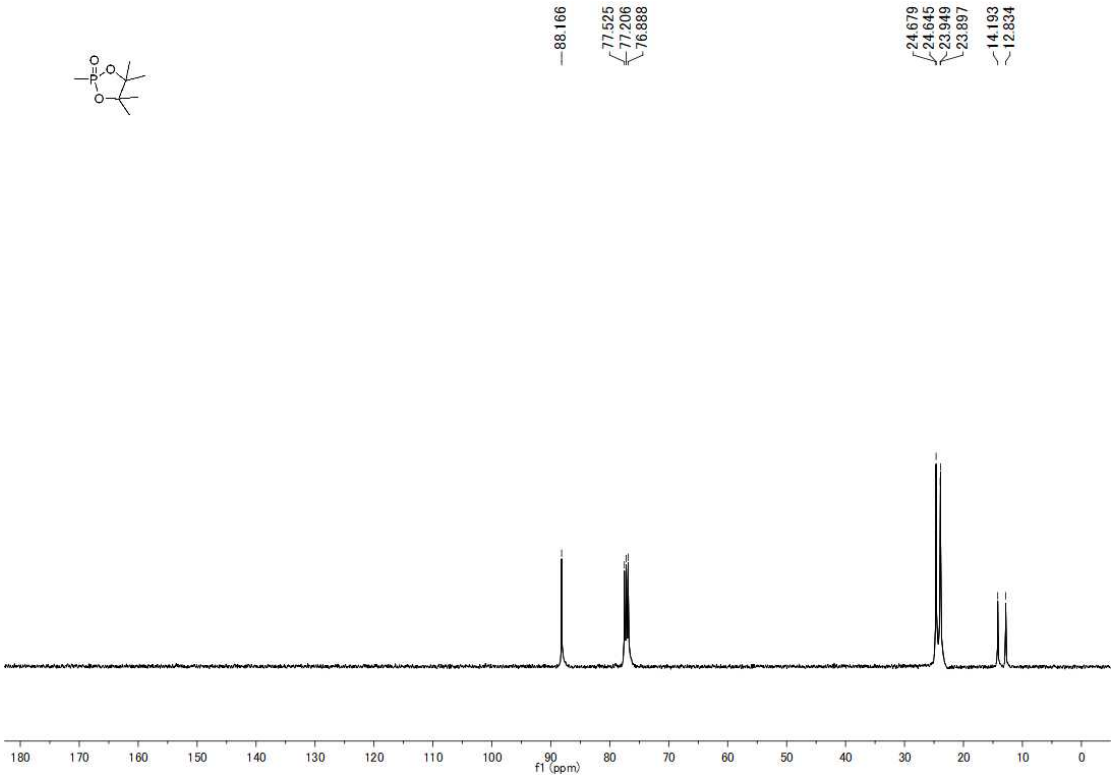
^{1}H NMR

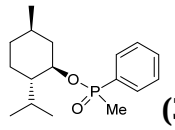


^{31}P NMR



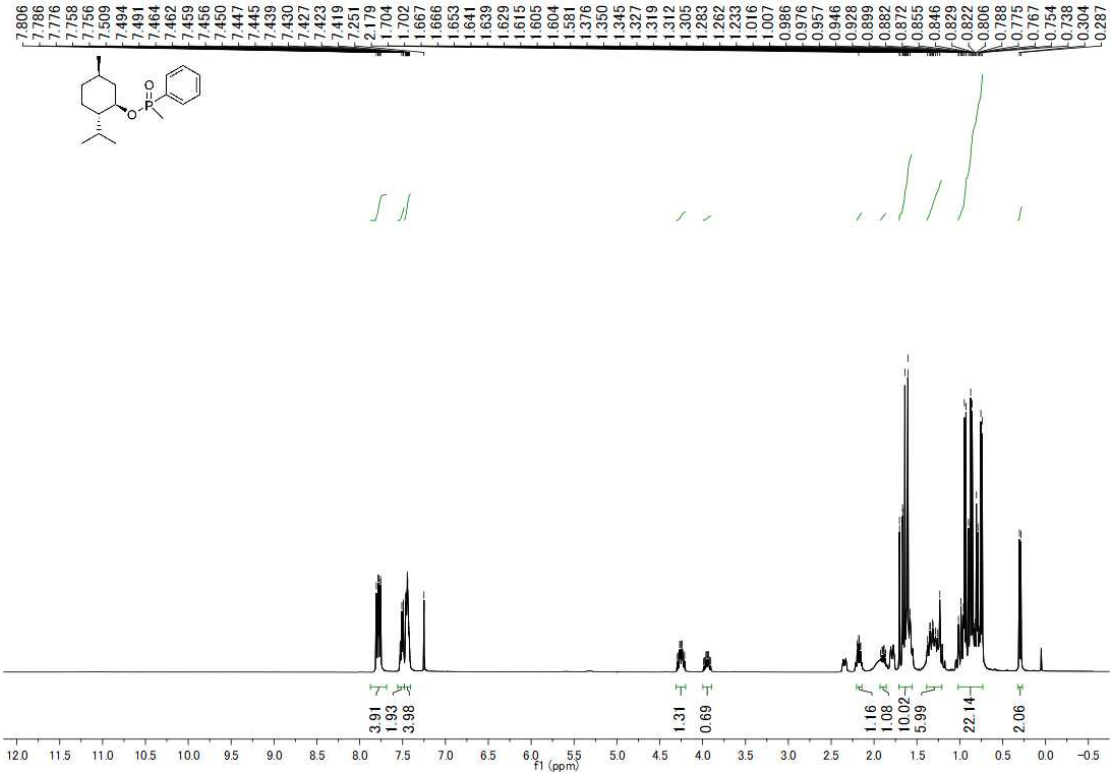
^{13}C NMR


88.166
77.525
77.206
76.888
24.679
24.645
23.949
23.897
14.193
12.834
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

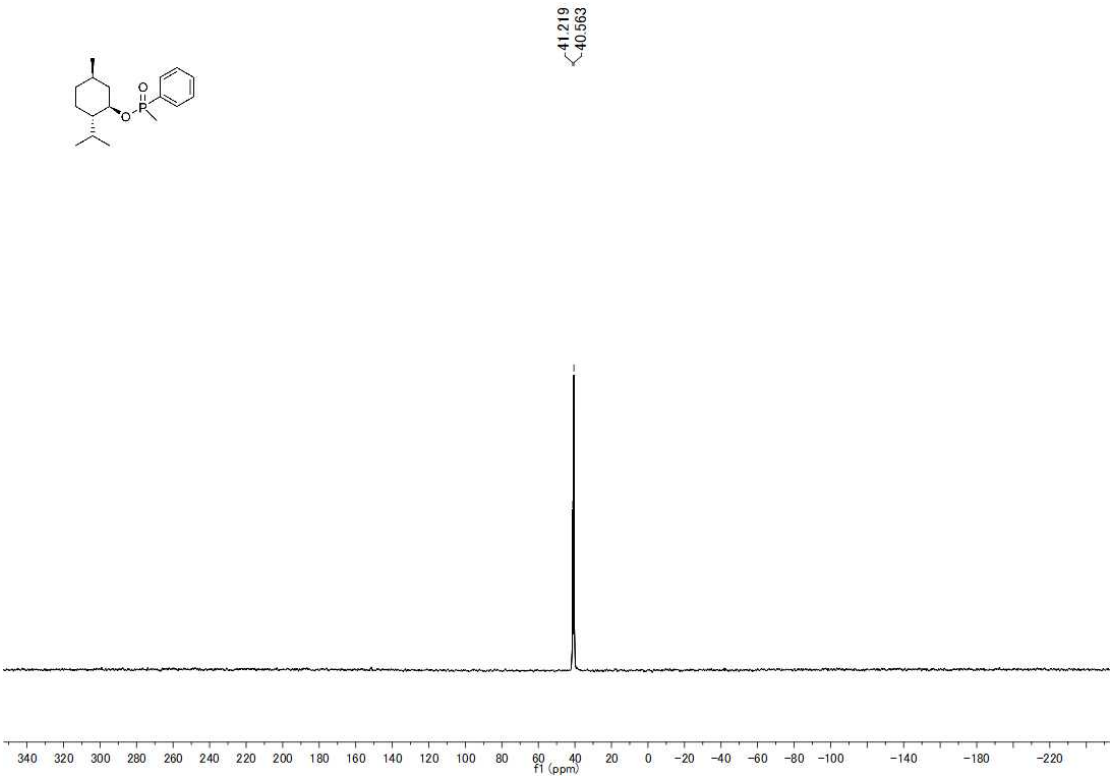


(3r)

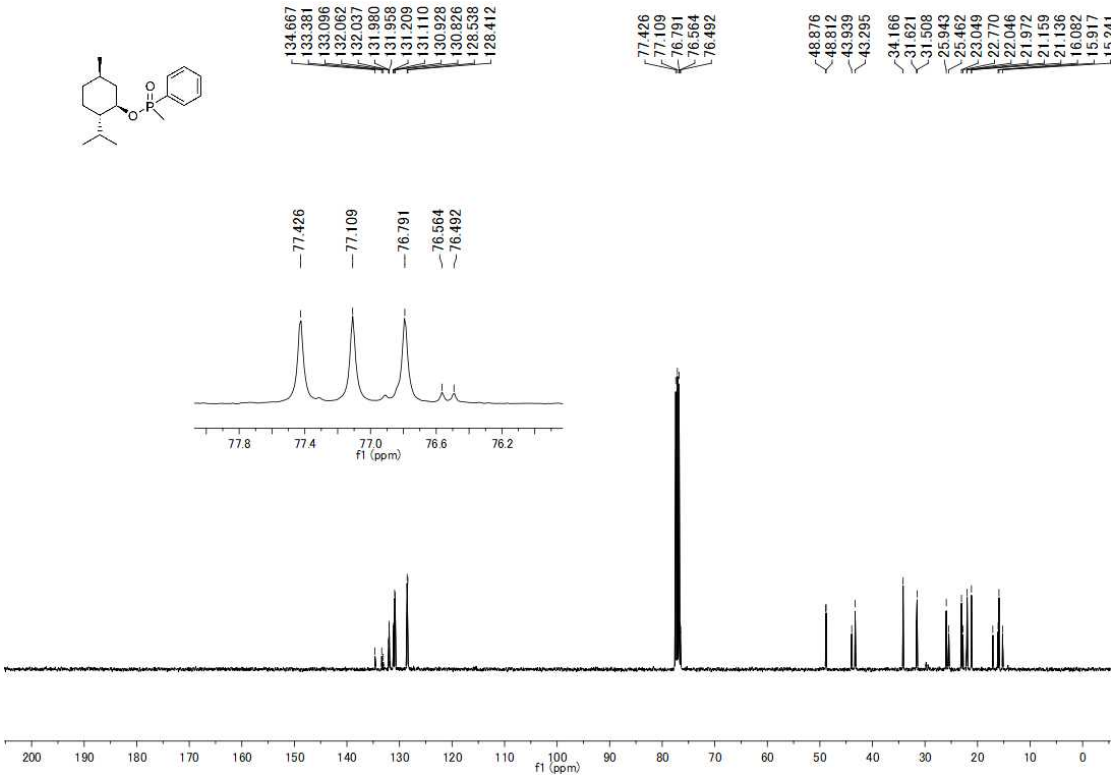
^{1}H NMR



^{31}P NMR



^{13}C NMR


134.667
133.381
133.096
132.062
132.037
131.980
131.958
131.209
131.110
130.928
130.826
128.538
128.412
77.426
77.109
76.791
76.564
76.492
48.876
48.812
43.939
43.295
34.166
31.621
31.508
25.943
25.462
23.049
22.770
22.046
21.972
21.159
21.136
16.082
15.917
77.8
77.4
77.0
76.6
76.2
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)