Markovnikov-Addition of *H*-Phosphonates to Terminal Alkynes under Metal- and Solvent-Free Conditions

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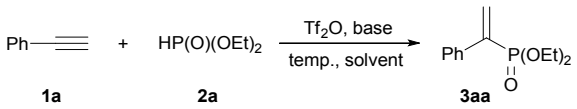
General

All reagents were used as received. The solvents were distilled prior to use under calcium hydride. All reactions were carried out under N_2 atmosphere in dry glassware using Schlenk-line techniques. Air and moisture sensitive liquids and solutions were transferred via syringe. ^{1}H NMR (400 MHz, 500 MHz), ^{13}C NMR (100 MHz, 125 MHz), ^{31}P NMR (162 MHz, 202 MHz) spectra were recorded on spectrometer at room temperature in deuterated solvents. ^{1}H and ^{13}C NMR signals are reported as δ (ppm) downfield from the signal for tetramethylsilane. ^{31}P NMR is reported relative to external 85% phosphoric acid. TLC plates were visualized by UV. Chromatographic purifications were conducted with silica gel of mesh 200−300. All products were further characterized by HRMS. Copies of their ^{1}H, ^{31}P and ^{13}C NMR spectrum were provided.

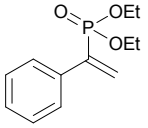
Part 1. Optimization of reaction conditions



Typical procedure (for entry 15 of Table 1)

To a Schlenk tube, **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol), Tf_2O (34 μL, 0.2 mmol) and pyridine (16 μL, 0.2 mmol) were added in sequence. The mixture was stirred at room temperature for about 10 min and then heated at 65 °C for 24 hours. After cooling, water (2 mL) was added and the mixture was extracted with ethyl acetate (10 mL), dried over anhydrous sodium sulfate. The solvent was removed in vacuo. The residue was dissolved in 0.5 mL $CDCl_3$ and was analyzed with NMR spectrum. Two peaks of vinyl hydrogen at 6.34 and 6.17 ppm were observed, which were assigned as **3aa** (99%). Other two peaks of vinyl hydrogen at 5.61 and 5.38 ppm were observed, which were assigned as **5** (1%). The conversion of **3aa** was estimated as 99%. After removing solvents in vacuo, the residue was purified from column chromatography (petroleum/ethyl acetate = 10/1 as eluent), and **3aa** was obtained as pale yellow oil (30.0 mg, 64%).

Diethyl 1-phenylethenylphosphonate (3aa)



3aa

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, 3H), 4.10 (m, 4H), 6.15 (dd, J = 46 Hz, 1 Hz, 1H), 6.33 (dd, J = 22 Hz, 1 Hz, 1H), 7.34 (m, 3H), 7.53 (d, 2H). ^{31}P NMR ($CDCl_3$, 162 MHz) δ 17.03. ^{13}C NMR ($CDCl_3$, 100 MHz) 16.2 (d, J = 6 Hz), 62.1 (d, J = 5 Hz), 127.4 (d, J = 6 Hz), 128.2, 128.3, 131.5 (d, J = 8 Hz), 136.6 (d, J = 11 Hz), 139.7 (d, J = 172 Hz). Q-TOF-ESI-HRMS-Positive $C_{12}H_{18}PO_3$ ($M + H^+$) calculated 241.0994, found 241.1003.

Entry 1 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and Tf_2O (34 μL, 0.2 mmol) was stirred at room temperature for about 24 hours. Two peaks of **3aa** were observed in 12%, and two peaks of **5** were observed in 88%. The conversion of **3aa** was estimated as 12%.

Entry 2 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and Tf_2O (34 μL, 0.2 mmol) was stirred at 40 °C for about 24 hours. Two peaks of **3aa** were observed in 46%, and two peaks of **5** were observed in 54%. The conversion of **3aa** was estimated as 46%.

Entry 3 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and Tf_2O (34 μL, 0.2 mmol) was stirred at 60 °C for about 24 hours. Two peaks of **3aa** were observed in 92%, and two peaks of **5** were observed in 8%. The conversion of **3aa** was estimated as 92%.

Entry 4 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and Tf_2O (34 μL, 0.2 mmol) was stirred at 65 °C for about 24 h. Two peaks of **3aa** were observed in 98%, and two peaks of **5** were observed in 2%. The conversion of **3aa** was estimated as 98%.

Ethyl acetate (10 mL) was added to the cooled solution and the mixture was washed with saturated sodium bicarbonate (5 mL × 2), water (5 mL × 2) and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified with column chromatography (petroleum/ethyl acetate = 10/1 as eluent). **3aa** (24.6 mg, 53%) was afforded, which gave the same NMR spectrum to the sample obtained in entry 15.

Entry 5 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and Tf_2O (34 μL, 0.2 mmol) was stirred at 80 °C for about 24 hours. Two peaks of **3aa** were observed in 98%, and two peaks of **5** were observed in 2%. The conversion of **3aa** was estimated in 98%. When the reaction was completed, the crude product was purified similarly to entry 4, **3aa** was obtained in 56% yield.

Entry 6 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and Tf_2O (17 μL, 0.1 mmol) was stirred at 65 °C for about 24 hours. The peaks of **3aa** were observed in 79%, and the peak at 1.87 ppm was assigned as an unidentified methyl of by-product (21%). By comparing 1/2 peak of **3aa** and 1/3 peak of by product, the conversion of **3aa** was estimated as 79%.

Entry 7 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and Tf_2O (27 μL, 0.16 mmol) was stirred at 65 °C for about 24 hours. The peaks of **3aa** were observed in 92%, two peaks of **5** were observed in 3%, and the peak at 1.87 ppm was unconfirmed (5%). By integrating one peak of compound **3aa** and **5**, and comparing to 1/3 peak of by-product, the conversion of **3aa** was estimated as 92%.

Entry 8 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and Tf_2O (41 μL, 0.24 mmol) was stirred at 65 °C for about 24 hours. The peaks of **3aa** were observed in 86%, two peaks of **5** were observed in 14%. The conversion of **3aa** was estimated as 86%.

Entry 9 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and TfOH

(17.6 μL, 0.2 mmol) was stirred at 65 °C for about 24 hours. Two peaks of **3aa** were not observed, and the conversion was thought as 0.

Entry 10 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and Tf_2O (34 μL, 0.2 mmol) was stirred in CH_2Cl_2 (1 mL) at 65 °C for 24 hours. Two peaks of **3aa** were observed in 3%, two peaks of **5** were observed in 82% and the peak at 2.60 ppm was assigned to **1a** (5%). By integrating one peak of compound **3aa** and **5**, and comparing to the peak of compound **1a**, the conversion of **3aa** was estimated as 3%.

Entry 11 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and Tf_2O (34 μL, 0.2 mmol) was stirred in toluene (1 mL) at 65 °C for about 24 hours. Two peaks of **3aa** were observed in 9%, two peaks of **5** were observed in 91%. The conversion of **3aa** was estimated as 9%.

Entry 12 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and Tf_2O (34 μL, 0.2 mmol) was stirred in THF (1 mL) at 65 °C for about 24 hours. Two peaks of **3aa** were not observed. The conversion of **3aa** was thought as 0.

Entry 13 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol) and Tf_2O (34 μL, 0.2 mmol) was stirred in ethyl acetate (1 mL) at 65 °C for about 24 hours. Two peaks of **3aa** were observed in 22%, two peaks of **5** were observed in 78%. The conversion of **3aa** was estimated as 22%.

Entry 14 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol), Tf_2O (34 μL, 0.2 mmol) and Na_2CO_3 (22.3 mg, 0.21 mmol) was stirred at room temperature for about 10 min and then heated to 65 °C for 24 hours. In the same way with above entry 15, two peaks of vinyl hydrogen at 6.34 and 6.17 ppm of **3aa** were not observed. The conversion of **3aa** was thought as 0.

Entry 16 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol), Tf_2O (34 μL, 0.2 mmol) and 2, 6-lutidine (23 μL, 0.2 mmol) was performed at room temperature for about 10 min and then heated to 65 °C for 24 hours. In the same way with above entry 15, two peaks of **3aa** were observed in 99%. Two peaks of **5** were observed in 1%. The conversion of **3aa** was estimated as 99%. The isolated yield of **3aa** was 54% (24.6 mg).

Entry 17 of Table 1: The mixture of **1a** (22 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol), Tf_2O (34 μL, 0.2 mmol) and DBU (30 μL, 0.2 mmol) was stirred at room temperature for about 10 min and then heated to 65 °C for 24 hours. In the same way with above entry 15, two peaks of **3aa** were

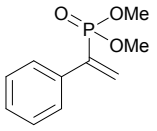
observed in 99%. Two peaks of **5** were observed in 1%. The conversion of **3aa** was estimated as 99%. The isolated yield of **3aa** was 64% (29.3 mg).

Part 2. Markovnikov-addition of *H*-Phosphonates to terminal alkynes

Typical procedure:

To a Schlenk tube, **1a** (22 μL, 0.2 mmol), **2b** (37 μL, 0.40 mmol), Tf_2O (34 μL, 0.2 mmol) and pyridine (16 μL, 0.2 mmol) were added in sequence. The mixture was stirred at room temperature for about 10 min and then heated to 65 ^oC for 24 hours. Ethyl acetate (10 mL) was added and the solution was washed with saturated sodium bicarbonate for two times. The combined organic layer was washed subsequently with water and dried over Na_2SO_4. After removing solvent in vacuo, the residue was purified with column chromatography (petroleum/ethyl acetate = 10/1 as eluent). The compound **3ab** was obtained from **1a** and **2b** as a colorless oil (17.3 mg, 43%).

Dimethyl 1-phenylethenylphosphonate (**3ab**)



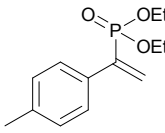
3ab

^1H NMR ($CDCl_3$, 500 MHz) δ 3.75 (d, *J* = 10 Hz, 6H), 6.20 (dd, *J* = 47 Hz, 1 Hz, 1H), 6.35 (dd, *J* = 22 Hz, 1 Hz, 1H), 7.36 (m, 3H), 7.51 (d, 2H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 20.0. ^{13}C NMR ($CDCl_3$, 125 MHz) 52.7 (d, *J* = 5 Hz), 127.4 (d, *J* = 6 Hz), 128.4, 128.5, 132.5 (d, *J* = 8 Hz), 136.4 (d, *J* = 11 Hz), 138.6 (d, *J* = 175 Hz). Q-TOF-ESI-HRMS-Positive $C_{10}H_{14}PO_3$ ($M + H^+$) calculated 213.0681, found 213.0693.

Typical procedure:

To a Schlenk tube, **1b** (25.3 μL, 0.2 mmol), **2a** (51 μL, 0.40 mmol), Tf_2O (34 μL, 0.2 mmol) and pyridine (16 μL, 0.2 mmol) were added in sequence. The mixture was stirred at room temperature for about 10 min and then heated to 65 ^oC for 24 hours. Ethyl acetate (10 mL) was added and the solution was washed with saturated sodium bicarbonate for two times. The combined organic layer was washed subsequently with water and dried over Na_2SO_4. After removing solvent in vacuo, the residue was purified with column chromatography (petroleum/ethyl acetate = 10/1 as eluent). The compound **3ba** was obtained from **1b** and **2a** as a pale yellow oil (31.4 mg, 62%).

Diethyl 1-(4-methylphenyl) ethenyl phosphonate (**3ba**)

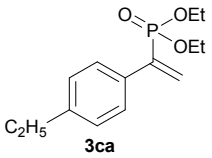


3ba

^1H NMR ($CDCl_3$, 500 MHz) δ 1.29 (t, 6H), 2.35 (s, 3H), 4.10 (m, 4H), 6.14 (dd, *J* = 45 Hz, 1 Hz, 1H), 6.29 (dd, *J* = 25 Hz, 1 Hz, 1H), 7.16 (d, 2H), 7.43 (d, 2H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 17.4. ^{13}C NMR ($CDCl_3$, 125 MHz) 16.2 (d, *J* = 6 Hz), 21.2, 62.1 (d, *J* = 5 Hz), 127.3 (d, *J* = 6 Hz), 129.1, 131.0 (d, *J* = 9 Hz), 133.7 (d, *J* = 12 Hz), 138.1, 139.4 (d, J = 173 Hz). Q-TOF-ESI-HRMS-Positive $C_{13}H_{20}PO_3$ ($M + H^+$) calculated

255.1150, found 255.1159.

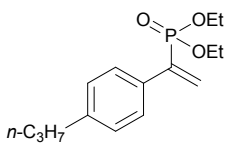
Diethyl 1-(4-ethylphenyl) ethenyl phosphonate (3ca)



3ca

The compound **3ca** was obtained from **1c** and **2a** as a pale yellow oil (22.4 mg, 42%) . ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.24 (t, 3H), 1.29 (t, 6H), 2.65 (m, 2H), 4.10 (m, 4H), 6.14 (dd, *J* = 45 Hz, 1 Hz, 1H), 6.29 (dd, *J* = 25 Hz, 1 Hz, 1H), 7.18 (d, 2H), 7.45 (d, 2H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 17.4. ^{13}C NMR ($CDCl_3$, 125 MHz) 15.3, 16.2 (d, *J* = 6 Hz), 28.5, 62.1 (d, *J* = 6 Hz), 127.3 (d, *J* = 6 Hz), 127.9, 130.9 (d, *J* = 8 Hz), 134.0 (d, *J* = 11 Hz), 139.5 (d, *J* = 173 Hz), 144.4. Q-TOF-ESI-HRMS-Positive $C_{14}H_{22}PO_3$ ($M + H^+$) calculated 269.1307, found 269.1313.

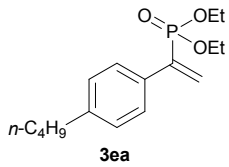
Diethyl 1-(4-propylphenyl) ethenyl phosphonate (3da)



3da

The compound **3da** was obtained from **1d** and **2a** as a pale yellow oil (14.7 mg, 26%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.94 (t, 3H), 1.28 (t, 6H), 1.64 (m, 2H), 2.59 (m, 2H), 4.11 (m, 4H), 6.15 (dd, *J* = 45 Hz, 1 Hz, 1H), 6.29 (dd, *J* = 25 Hz, 1 Hz, 1H), 7.16 (d, 2H), 7.44 (m, 2H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 17.5. ^{13}C NMR ($CDCl_3$, 125 MHz) 13.8, 16.3 (d, *J* = 6 Hz), 24.4, 37.7, 62.2 (d, *J* = 5 Hz), 127.3 (d, *J* = 6 Hz), 128.5, 131.0 (d, *J* = 8 Hz), 133.9 (d, *J* = 13 Hz), 139.5 (d, *J* = 173 Hz), 142.9. Q-TOF-ESI-HRMS-Positive $C_{15}H_{24}PO_3$ ($M + H^+$) calculated 283.1463, found 283.1472.

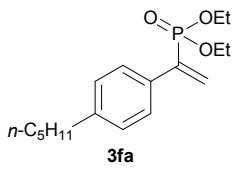
Diethyl 1-(4-butylphenyl) ethenyl phosphonate (3ea)



3ea

The compound **3ea** was obtained from **1e** and **2a** as a pale yellow oil (19.8 mg, 33%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.93 (t, 3H), 1.28 (t, 6H), 1.35 (m, 2H), 1.60 (m, 2H), 2.61 (m, 2H), 4.10 (m, 4H), 6.14 (dd, *J* = 45 Hz, 1 Hz, 1H), 6.29 (dd, *J* = 23 Hz, 1 Hz, 1H), 7.16 (d, 2H), 7.45 (m, 2H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 17.5. ^{13}C NMR ($CDCl_3$, 125 MHz) 13.9, 16.2 (d, *J* = 6 Hz), 22.3, 33.4, 35.3, 62.1 (d, *J* = 5 Hz), 127.3 (d, *J* = 5 Hz), 128.5, 130.9 (d, *J* = 8 Hz), 133.9 (d, *J* = 13 Hz), 139.5 (d, *J* = 173 Hz), 143.2. Q-TOF-ESI-HRMS-Positive $C_{16}H_{26}PO_3$ ($M + H^+$) calculated 297.1620, found 297.1628.

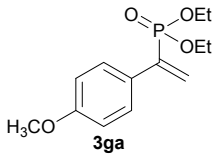
Diethyl 1-(4-amylphenyl) ethenyl phosphonate (3fa)



3fa

The compound **3fa** was obtained from **1f** and **2a** as a pale yellow oil (18.9 mg, 30%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.89 (t, 3H), 1.28 (t, 6H), 1.32 (m, 4H), 1.61 (m, 2H), 2.60 (m, 2H), 4.10 (m, 4H), 6.14 (dd, *J* = 45 Hz, 1 Hz, 1H), 6.29 (dd, *J* = 20 Hz, 1 Hz, 1H), 7.16 (d, 2H), 7.44 (d, 2H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 17.4. ^{13}C NMR ($CDCl_3$, 125 MHz) 14.0, 16.2 (d, *J* = 6 Hz), 22.5, 31.0, 31.5, 35.6, 62.1 (d, *J* = 5 Hz), 127.3 (d, *J* = 6 Hz), 128.4, 130.9 (d, *J* = 8 Hz), 133.9 (d, *J* = 11 Hz), 139.5 (d, *J* = 173 Hz), 143.2. Q-TOF-ESI-HRMS-Positive $C_{17}H_{28}PO_3$ ($M + H^+$) calculated 311.1776, found 311.1782.

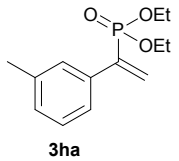
Diethyl 1-(4-methoxyphenyl) ethenyl phosphonate (3ga)



3ga

The compound **3ga** was obtained from **1g** and **2a** as a pale yellow oil (19.7 mg, 36%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.29 (t, 6H), 3.82 (s, 3H), 4.10 (m, 4H), 6.10 (dd, *J* = 45 Hz, 1 Hz, 1H), 6.24 (dd, *J* = 25 Hz, 1 Hz, 1H), 6.88 (d, 2H), 7.48 (m, 2H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 17.5. ^{13}C NMR ($CDCl_3$, 125 MHz) 16.3 (d, *J* = 6 Hz), 55.3, 62.1 (d, *J* = 6 Hz), 113.8, 128.7 (d, *J* = 6 Hz), 129.1(d, *J* = 11 Hz), 130.0 (d, *J* = 8 Hz), 139.0 (d, *J* = 173 Hz), 159.7. Q-TOF-ESI-HRMS-Positive $C_{13}H_{20}PO_4$ ($M + H^+$) calculated 271.1099, found 271.1111.

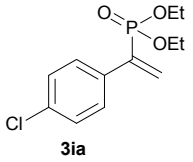
Diethyl 1-(3-methylphenyl) ethenyl phosphonate (3ha)



3ha

The compound **3ha** was obtained from **1h** and **2a** as a yellow oil (8.4 mg, 17%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.29 (t, 6H), 2.36 (s, 3H), 4.10 (m, 4H), 6.14 (dd, *J* = 45 Hz, 1 Hz, 1H), 6.31 (dd, *J* = 20 Hz, 1 Hz, 1H), 7.14 (d, 1H), 7.24 (t, 1H), 7.33 (d, 2H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 17.2. ^{13}C NMR ($CDCl_3$, 125 MHz) 16.3 (d, *J* = 6 Hz), 21.4, 62.2 (d, *J* = 6 Hz), 124.6 (d, *J* = 5 Hz), 128.1 (d, *J* = 6 Hz), 128.3, 129.0, 131.5 (d, *J* = 9 Hz), 136.7 (d, *J* = 11 Hz), 138.0, 139.9 (d, *J* = 173 Hz). Q-TOF-ESI-HRMS-Positive $C_{13}H_{20}PO_3$ ($M + H^+$) calculated 255.1150, found 255.1076.

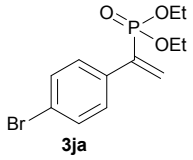
Diethyl 1-(4-chlorophenyl) ethenyl phosphonate (3ia)



3ia

The compound **3ia** was obtained from **1i** and **2a** as a pale yellow oil (29.6 mg, 56%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.29 (t, 6H), 4.11 (m, 4H), 6.15 (dd, *J* = 45 Hz, 1 Hz, 1H), 6.34 (dd, *J* = 20 Hz, 1 Hz, 1H), 7.33 (d, 2H), 7.48 (d, 2H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 16.5. ^{13}C NMR ($CDCl_3$, 125 MHz) 16.3 (d, *J* = 6 Hz), 62.3 (d, *J* = 6 Hz) , 128.6, 128.8 (d, *J* = 5 Hz), 131.9 (d, *J* = 8 Hz), 134.3, 135.1 (d, *J* = 11 Hz), 138.7 (d, *J* = 175 Hz). Q-TOF-ESI-HRMS-Positive $C_{12}H_{17}PO_3Cl$ (M + H^+) calculated 275.0604, found 275.0613.

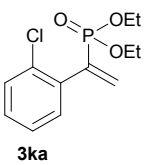
Diethyl 1-(4-bromophenyl) ethenyl phosphonate (**3ja**)



3ja

The compound **3ja** was obtained from **1j** and **2a** as a pale yellow oil (28.7 mg, 46%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.29 (t, 6H), 4.11 (m, 4H), 6.15 (dd, *J* = 45 Hz, 1 Hz, 1H), 6.34 (dd, *J* = 22 Hz, 1 Hz, 1H), 7.41 (m, 2H), 7.48 (d, 2H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 16.3. ^{13}C NMR ($CDCl_3$, 125 MHz) 16.3 (d, *J* = 6 Hz), 62.3 (d, *J* = 5 Hz), , 122.6, 129.1 (d, *J* = 6 Hz), 131.6, 131.9 (d, *J* = 8 Hz), 135.6 (d, *J* = 13 Hz), 138.9 (d, *J* = 175 Hz). Q-TOF-ESI-HRMS-Positive $C_{12}H_{17}PO_3Br$ (M + H^+) calculated 319.0099, found 319.0103.

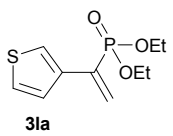
Diethyl 1-(2-chlorophenyl) ethenyl phosphonate (**3ka**)



3ka

The compound **3ka** was obtained from **1k** and **2a** with 2.0 equivalent Tf_2O and pyridine as a pale yellow oil (9.3 mg, 17%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.29 (t, 6H), 4.11 (m, 4H), 6.02 (dd, *J* = 47.5 Hz, 1 Hz, 1H), 6.55 (dd, *J* = 22.5 Hz, 1 Hz, 1H), 7.24 (m, 2H), 7.36 (m,1H), 7.42 (m,1H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 15.1. ^{13}C NMR ($CDCl_3$, 125 MHz) 16.2 (d, *J* = 6 Hz), 62.4 (d, *J* = 6 Hz), 126.3 (d, *J* = 3 Hz), 129.1 (d, *J* = 1 Hz), 129.8, 130.7 (d, *J* = 4 Hz), 132.8 (d, *J* = 6 Hz), 135.3 (d, *J* = 8 Hz), 135.6, 135.7, 137.3 (d, *J* = 180 Hz). Q-TOF-ESI-HRMS-Positive $C_{12}H_{17}PO_3Cl$ (M + H^+) calculated 275.0604, found 275.0617.

Diethyl (1-(thiophen-3-yl)vinyl)phosphonate (**3la**)

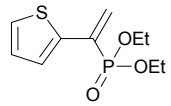


3la

The compound **3la** was obtained from **1l** and **2a** as a pale yellow oil (11.9 mg,

23%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.31 (t, 6H), 4.13 (m, 4H), 6.22 (d, *J* = 20 Hz, 1H), 6.29 (s, 1H), 7.30 (s, 2H), 7.59 (s, 1H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 17.1. ^{13}C NMR ($CDCl_3$, 125 MHz) 16.3 (d, *J* = 6 Hz), 62.2 (d, *J* = 6 Hz), 123.9 (d, *J* = 5 Hz), 125.7, 126.2 (d, *J* = 8 Hz), 129.4 (d, *J* = 8 Hz), 133.8 (d, *J* = 176 Hz), 136.6 (d, *J* = 9 Hz). Q-TOF-ESI-HRMS-Positive $C_{10}H_{16}PO_3S$ (M + H^+) calculated 247.0558, found 247.0566.

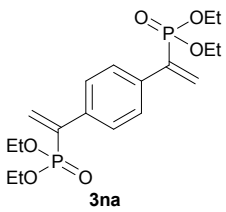
Diethyl (1-(thiophen-2-yl)vinyl)phosphonate (**3ma**)



3ma

The compound **3ma** was obtained from **1m** and **2a** as a yellow oil (4.3 mg, 9%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.32 (t, 6H), 4.14 (m, 4H), 6.18 (d, *J* = 15 Hz, 1H), 6.25 (d, *J* = 40 Hz, 1H), 7.01 (m, 1H), 7.25 (d, 1H), 7.36 (d, 1H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 15.5. ^{13}C NMR ($CDCl_3$, 125 MHz) 16.3 (d, *J* = 6 Hz), 62.4 (d, *J* = 6 Hz), 125.6, 123.9 (d, *J* = 5 Hz), 127.3 (d, *J* = 4 Hz), 127.7, 129.1 (d, *J* = 6 Hz), 132.7 (d, *J* = 175 Hz), 139.0 (d, *J* = 16 Hz). Q-TOF-ESI-HRMS-Positive $C_{10}H_{16}PSO_3$ (M + H^+) calculated 247.0558, found 247.0484.

Diethyl 1-(1,4-diethynylphenyl) ethenyl phosphonate (**3na**)

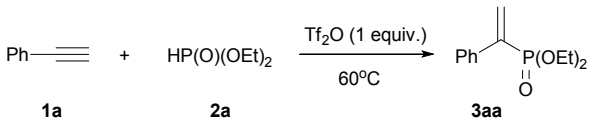


3na

The compound **3na** was obtained from **1n** (25.8 mg, 0.2 mmol), **2a** (102 μL, 0.80 mmol), Tf_2O (68 μL, 0.4 mmol), and pyridine (32 μL, 0.4 mmol) as a pale yellow oil (6.9 mg, 8%) ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.29 (t, 12H), 4.12 (m, 8H), 6.18 (d, *J* = 48 Hz, 2H), 6.34 (d, *J* = 25 Hz, 2H), 7.53 (s, 4H). ^{31}P NMR ($CDCl_3$, 202 MHz) δ 16.9. ^{13}C NMR ($CDCl_3$, 125 MHz) 16.3 (d, *J* = 6 Hz), 62.3 (d, *J* = 5 Hz), 127.5 (d, *J* = 6 Hz), 131.8 (d, *J* = 8 Hz), 136.6 (d, *J* = 11 Hz), 139.2 (d, *J* = 174 Hz). Q-TOF-ESI-HRMS-Positive $C_{18}H_{29}P_2O_6$ (M + H^+) calculated 403.1439, found 403.1440.

Part 3: Exploring the mechanism of the reaction

Table S1. In situ experimental results of **1a** and **2a**.



1a **2a** **3aa**

Entry	molar ratio of **1a/2a**/Cat	reaction conditions	conversion of **3aa** %[a]	^{1}HNMR	^{31}P NMR
1	0:2:1	rt, 10 min	0	Fig. 1 A	Fig. S1 A
2	1:2:1	rt, 10 min	0	Fig. 1 B	Fig. S1 B
3	1:2:1	60 °C, 1h	20	Fig. 1 C	Fig. S1 C
4	1:2:1	60 °C, 4h	44	Fig. 1 D	Fig. S1 D
5	1:0:1	rt, 10 min	0	Fig. 1 E	-
6	1:2:1	rt, 10 min	0	Fig. 1 F	Fig. S1 F
7	1:2:1	60 °C, 1h	54	Fig. 1 G	Fig. S1 G
8	1:2:1	60 °C, 8h	93	Fig. 1 H	Fig. S1 H

[a] The conversions were estimated based on ^{1}H NMR spectrum.

The in situ experiments were summarized in Table S1

Experiment 1

Step 1: In a Schlenk tube, **2a** (51 μL, 0.4 mmol) and Tf_2O (34 μL, 0.2 mmol) were stirred under N_2 atmosphere at room temperature for about 10 min. One drop of the solution was transferred to a NMR tube and diluted with $CDCl_3$ (ca. 0.50 mL), and analyzed with NMR measurement. The peak was observed at 12.13 ppm, which was assigned as **TfOH** (Fig. 1 A). The corresponding ^{31}P NMR spectrum could be found in Fig. S1 A.

Step 2: **1a** (22 μL, 0.2 mmol) was added to the above Schlenk tube. The mixture was stirred at room temperature for another 10 min, and analyzed similarly with NMR spectrum as above. The peaks at 5.61 and 5.38 ppm were observed, which were assigned as vinyl hydrogen of **5**. One of the peaks was calculated in 72% by integral. The peak at 2.62 ppm was assigned to **1a** (28%). The conversion of **5** was estimated as 72% (Fig. 1 B). The corresponding ^{31}P NMR spectrum could be found in Fig. S1 B.

Step 3: After addition of **1a**, the solution was further heated to 60 °C for 1 h. The sample was

analyzed as above. Two peaks of vinyl hydrogen at 6.34 and 6.17 ppm were observed, which were assigned as **3aa** (20%). Two peaks of **5** were observed in 30%. The peak of **1a** was observed in 50%. The conversion of **3aa** was estimated as 20% (Fig. 1 C). The conversion of **3aa** was estimated by integrating one peak of compound **3aa** and **5**, and comparing to the peak of compound **1a**. The corresponding ^{31}P NMR spectrum could be found in Fig. S1 C.

Step 4: After heating for 4h, two peaks of **3aa** were observed in 44%. Two peaks of **5** were not observed (0). The peak of **1a** was observed in 56%. The conversion of **3aa** was estimated by integrating one peak of compound **3aa** and comparing to the peak of compound **1a** as 44% (Fig. 1 D). The corresponding ^{31}P NMR spectrum could be found in Fig. S1 D.

Experiment 2

Step 1: In a Schlenk tube, **1a** (22 μL, 0.2 mmol) and Tf_2O (34 μL, 0.2 mmol) were stirred under N_2 atmosphere at room temperature for about 10 min. One drop of the solution was transferred to a NMR tube and diluted with $CDCl_3$ (ca. 0.50 mL), and analyzed with NMR measurement. Two peaks of vinyl hydrogen at 5.61 and 5.38 ppm were observed, which were assigned as **5** (39%). The peak at 3.07ppm, which was assigned as **1a**, was observed in 61% (Fig. 1 E). The conversion of **5** was estimated by integrating one peak of compound **5** and comparing to the peak of compound **1a**.

Step 2: **2a** (51 μL, 0.4 mmol) was added to the above Schlenk tube, and the mixture was stirred at room temperature for another 10 min. No peak of **3aa** was observed. Two peaks of **5** were observed in 62%. The peak of **1a** was observed in 38%. (Fig. 1 F). The conversion of **5** was calculated as above step 1. The corresponding ^{31}P NMR spectrum could be found in Fig. S1 F.

Step 3: The above solution was further heated to 60 ^{o}C. After 1h, two peaks of **3aa** were observed in 54%. Two peaks of **5** were observed in 39%. The peak of **1a** was observed in 7%. The conversion of **3aa** was estimated by integrating one peak of compounds **3aa** and **5**, and comparing to the peak of compound **1a** as 54% (Fig. 1 G). The corresponding ^{31}P NMR spectrum could be found in Fig. S1 G.

Step 4: After heating for 8h, two peaks of **3aa** were observed in 93%. Two peaks of **5** were observed in 7%. The peak of **1a** was disappeared. The conversion of **3aa** was estimated as 93% (Fig. 1 H). The corresponding ^{31}P NMR spectrum could be found in Fig. S1 H.

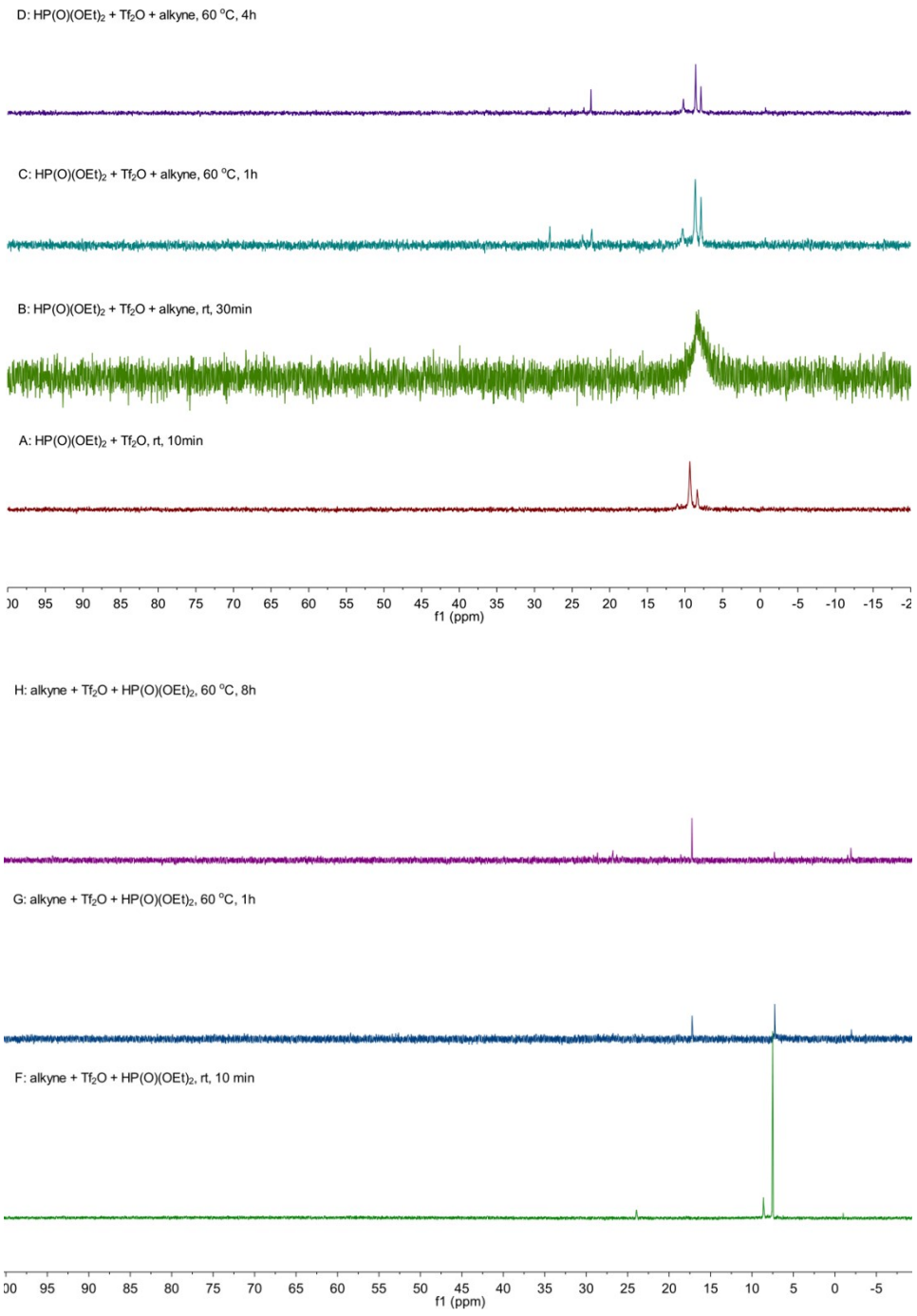
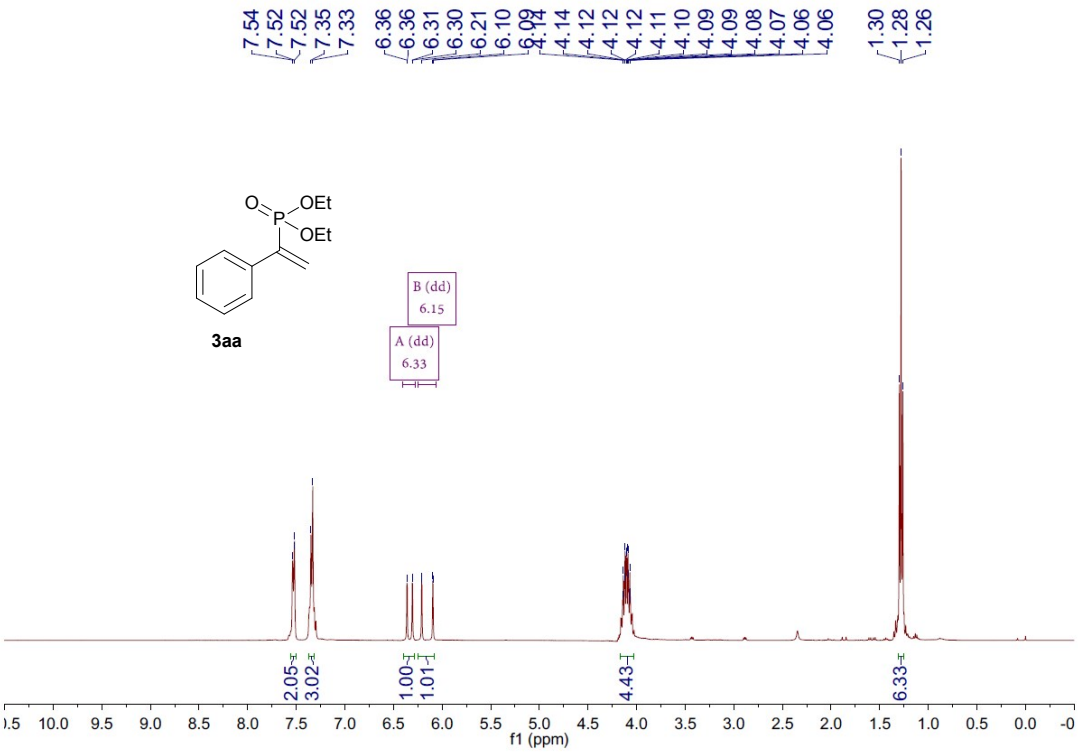


Fig. S1. The results of in situ NMR experiments of the reaction of **1a** with **2a** in the presence of triflic anhydride.

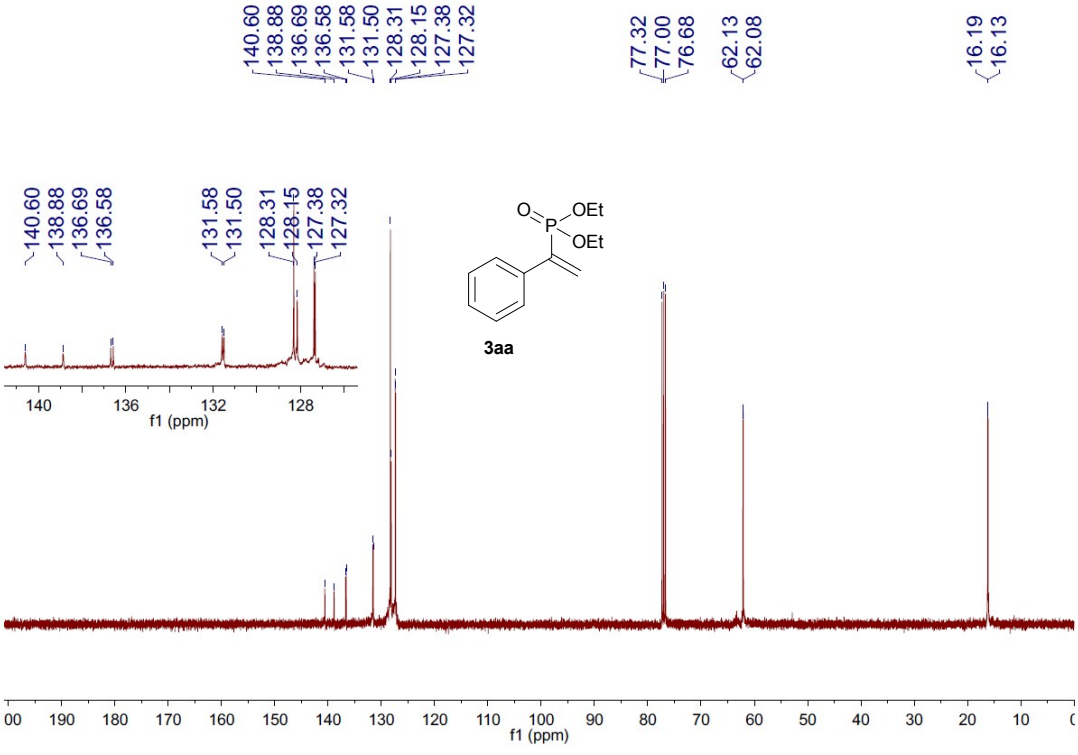
Part 4. References of known compounds.

Compounds	References
3aa, 3ab, 3ba, 3ga, 3ia, 3ja	D.-Y. Wang, X.-P. Hu, J. Deng, S.-B. Yu, Z.-C. Duan, Z. Zheng, *J. Org. Chem.* **2009**, *74*, 4408–4410.
3ha, 3ka, 3la	Y. Fang, L. Zhang, J. Li, X. Jin, M. Yuan, R. Li, R. Wu, J. Fang, *Org. Lett.* **2015**, *17*, 798–801.

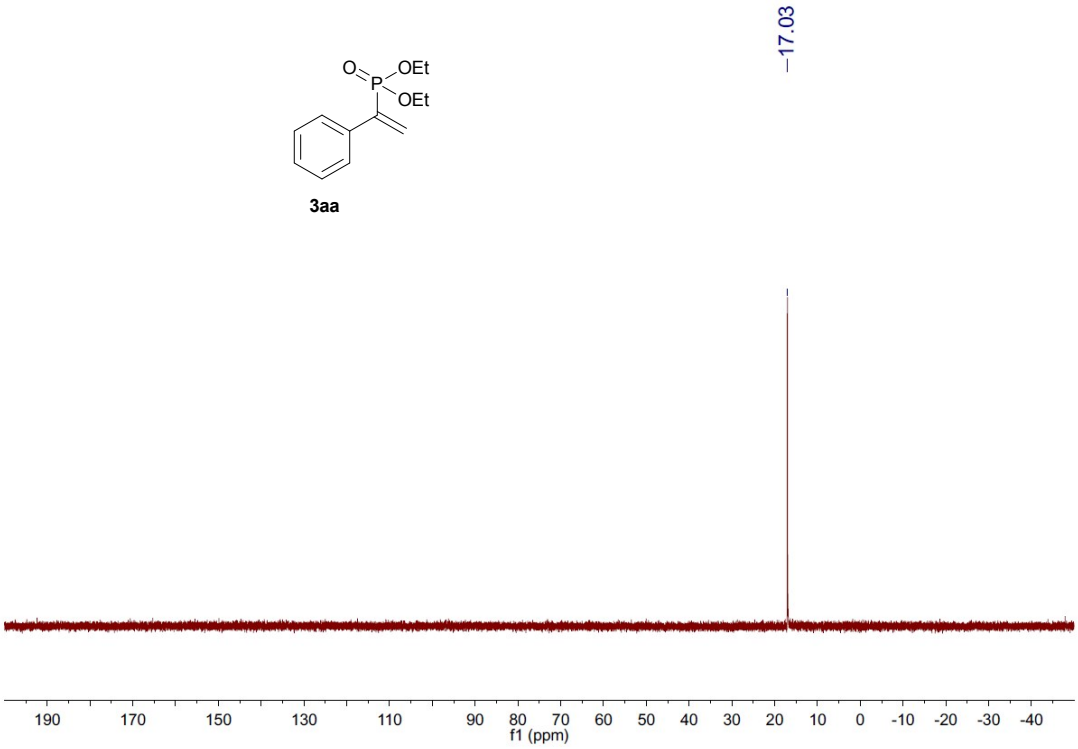
Part 5. Spectra of compounds



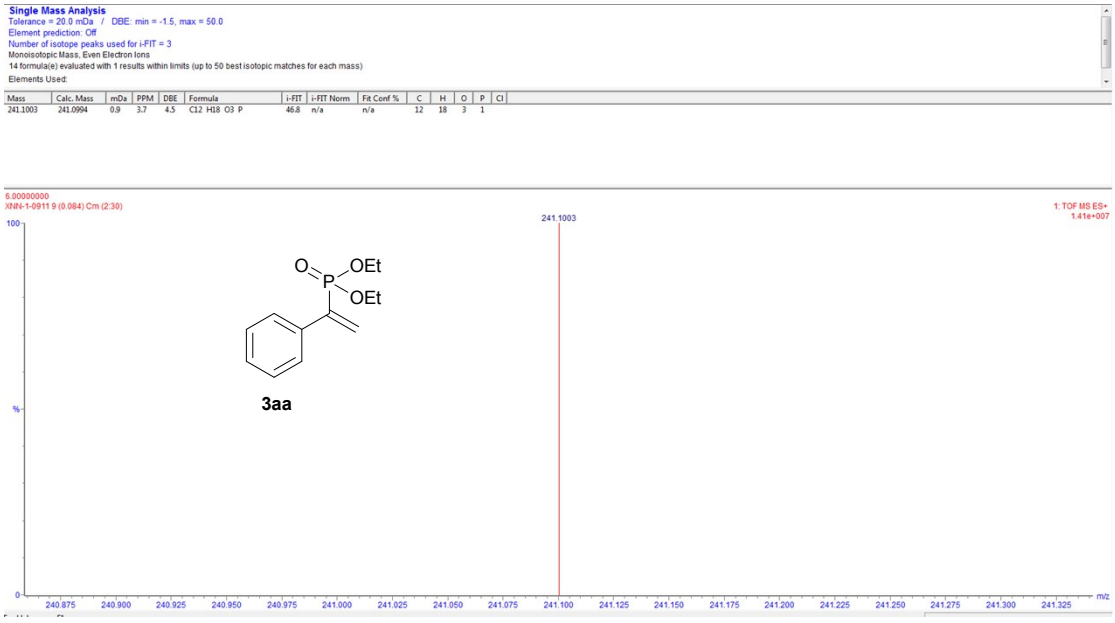
^{1}H NMR of **3aa**



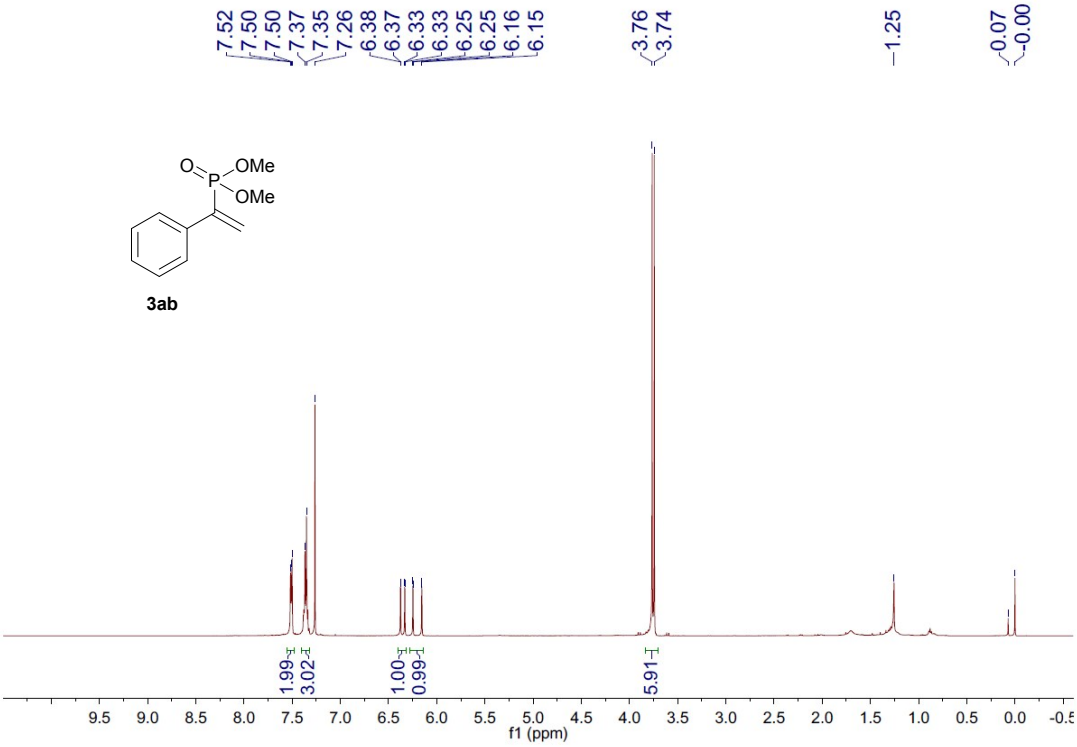
^{13}C NMR of **3aa**



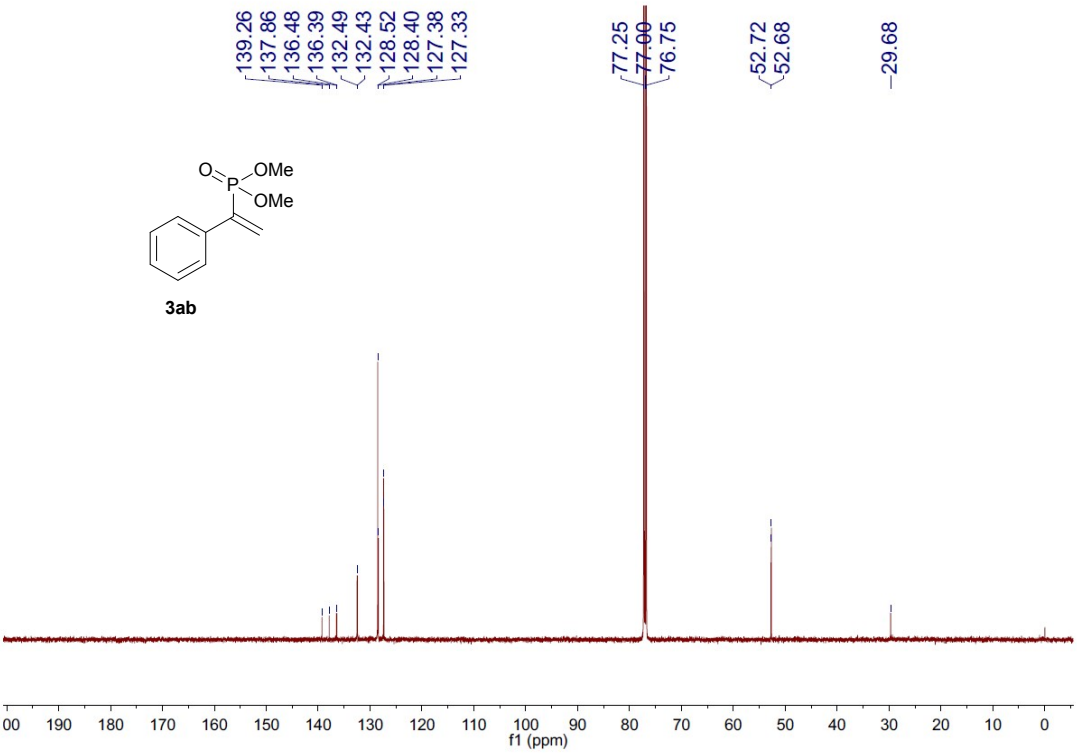
^{31}P NMR of **3aa**



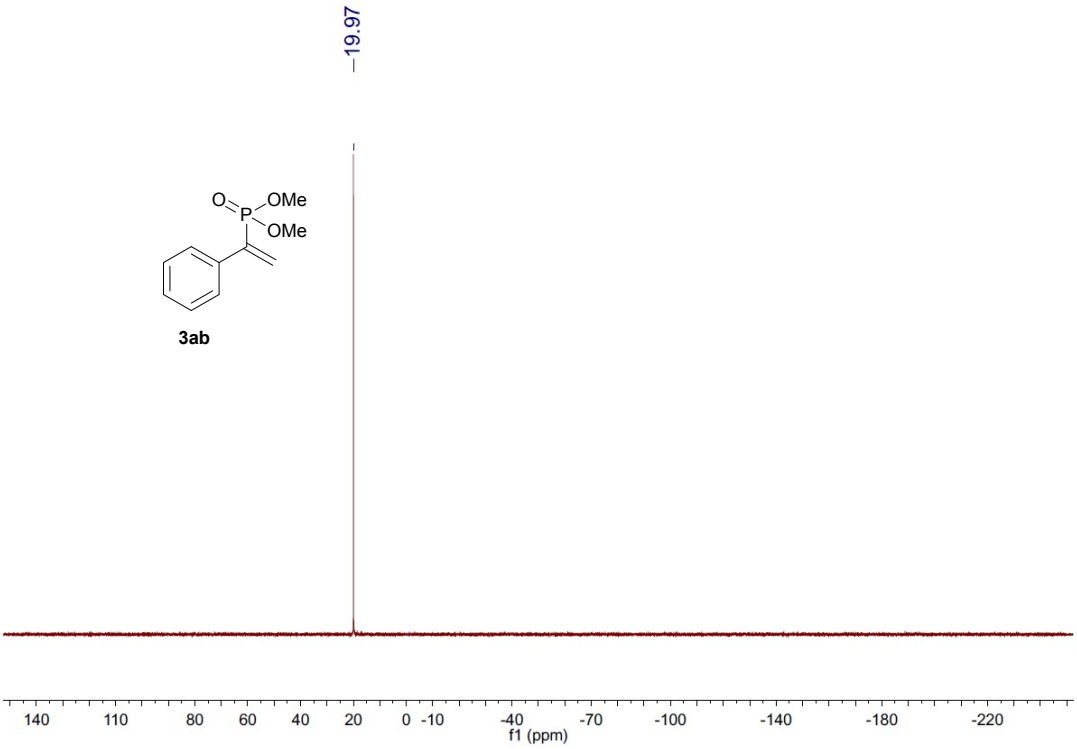
HRMS of **3aa**



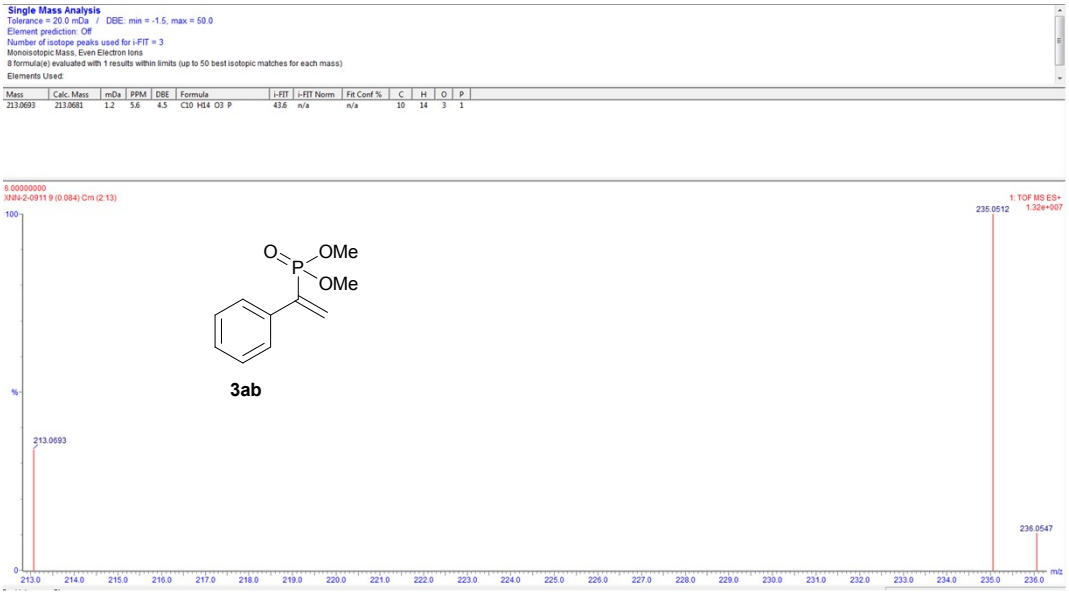
^{1}H NMR of **3ab**



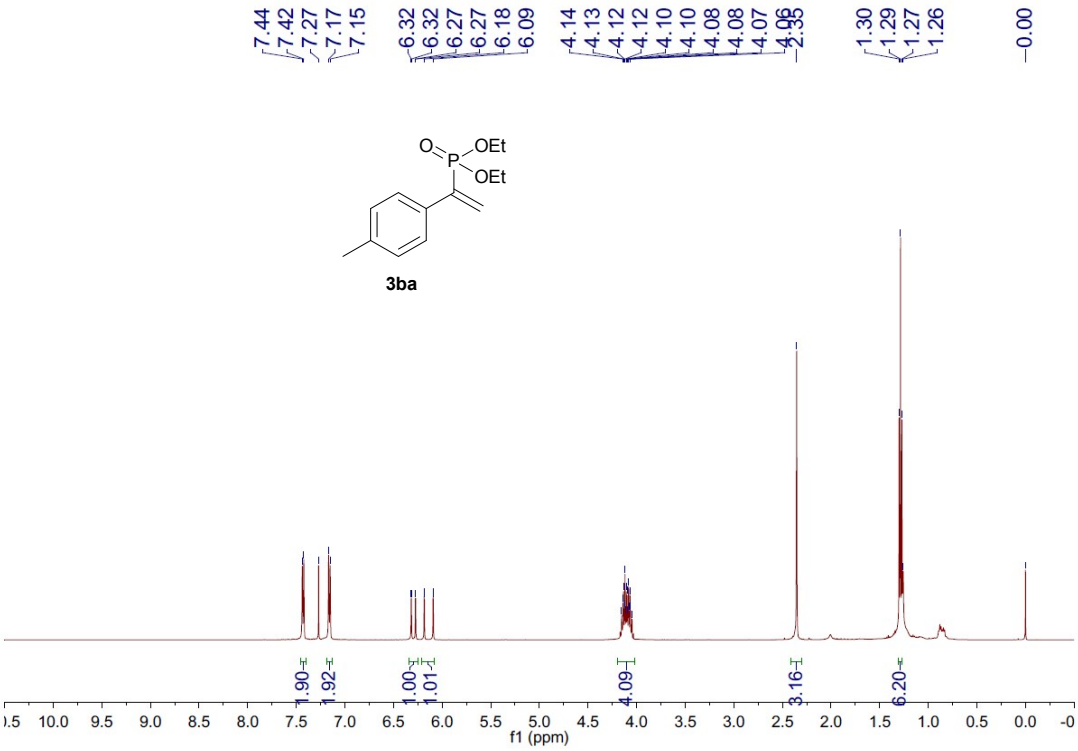
^{13}C NMR of **3ab**



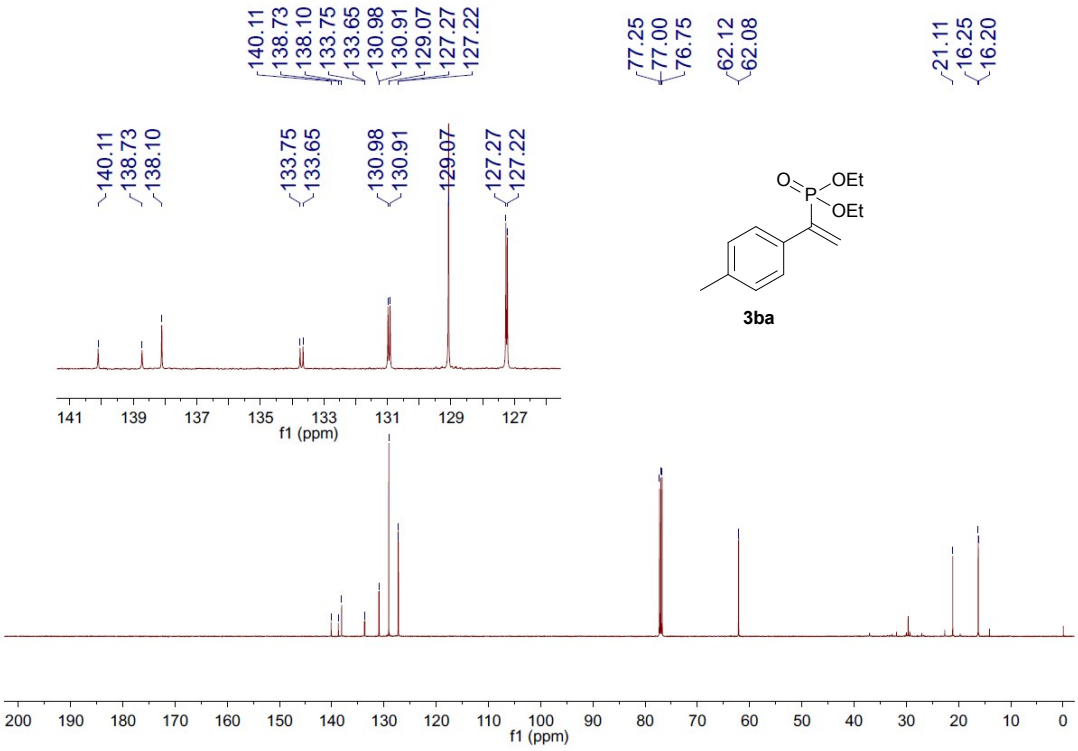
^{31}P NMR of **3ab**



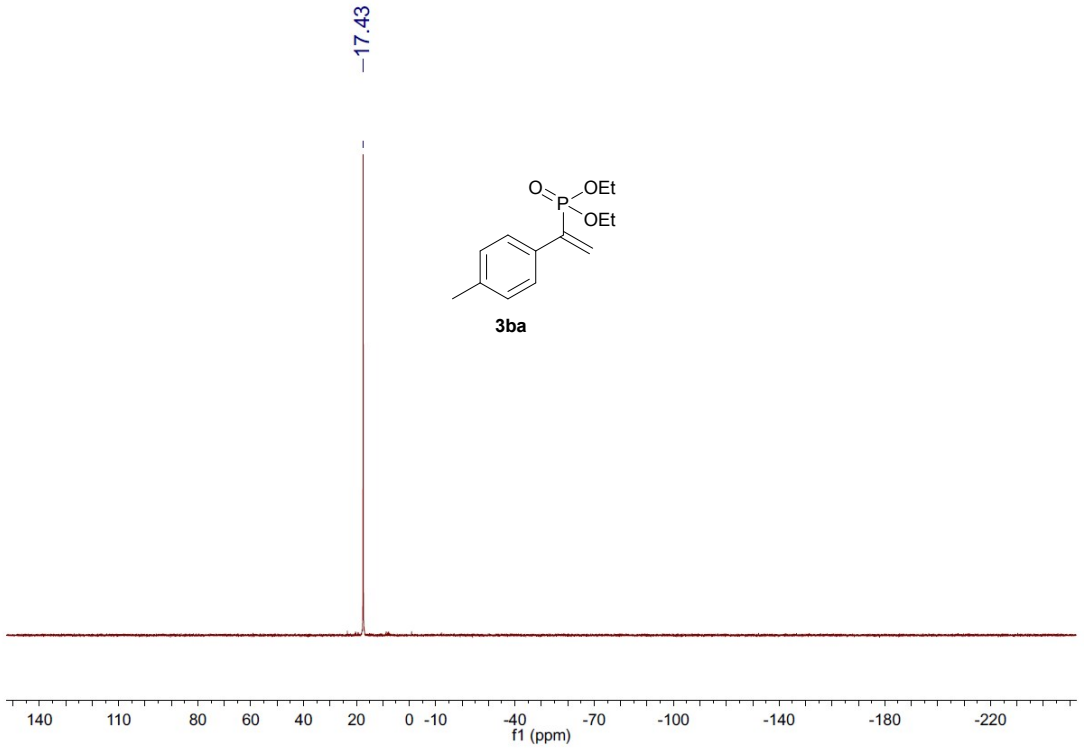
HRMS of **3ab**



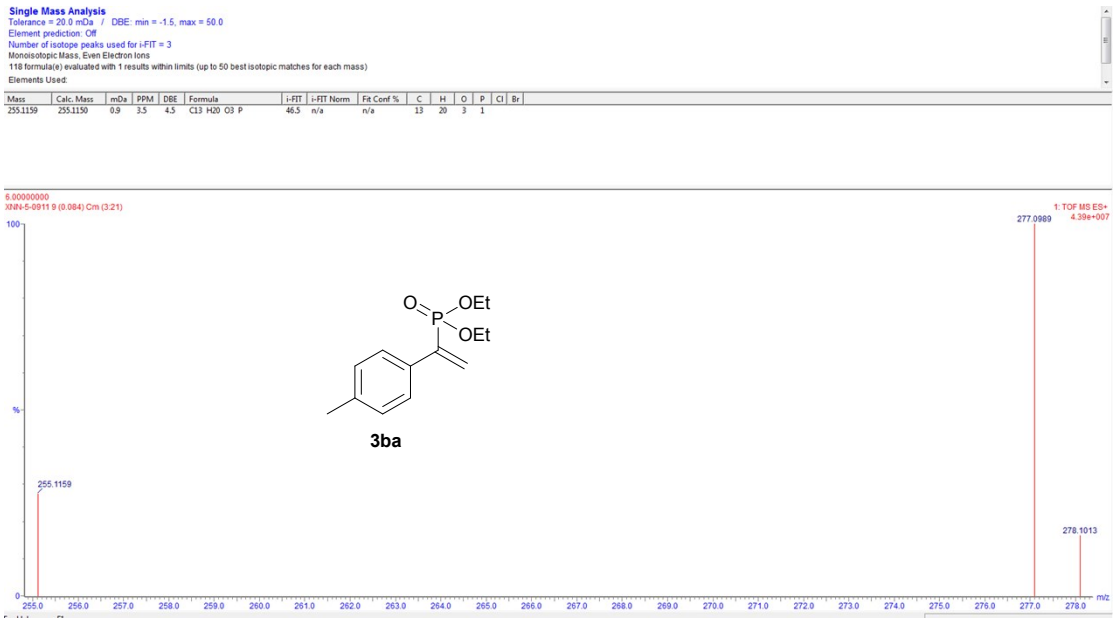
^{1}H NMR of **3ba**



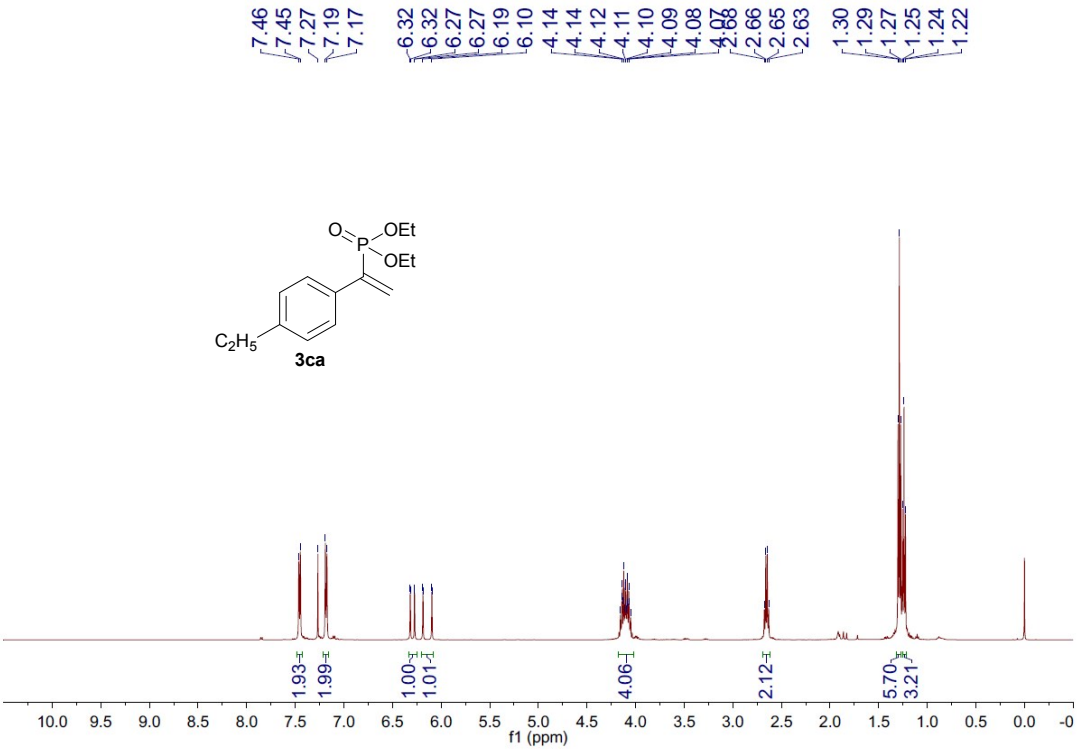
^{13}C NMR of **3ba**



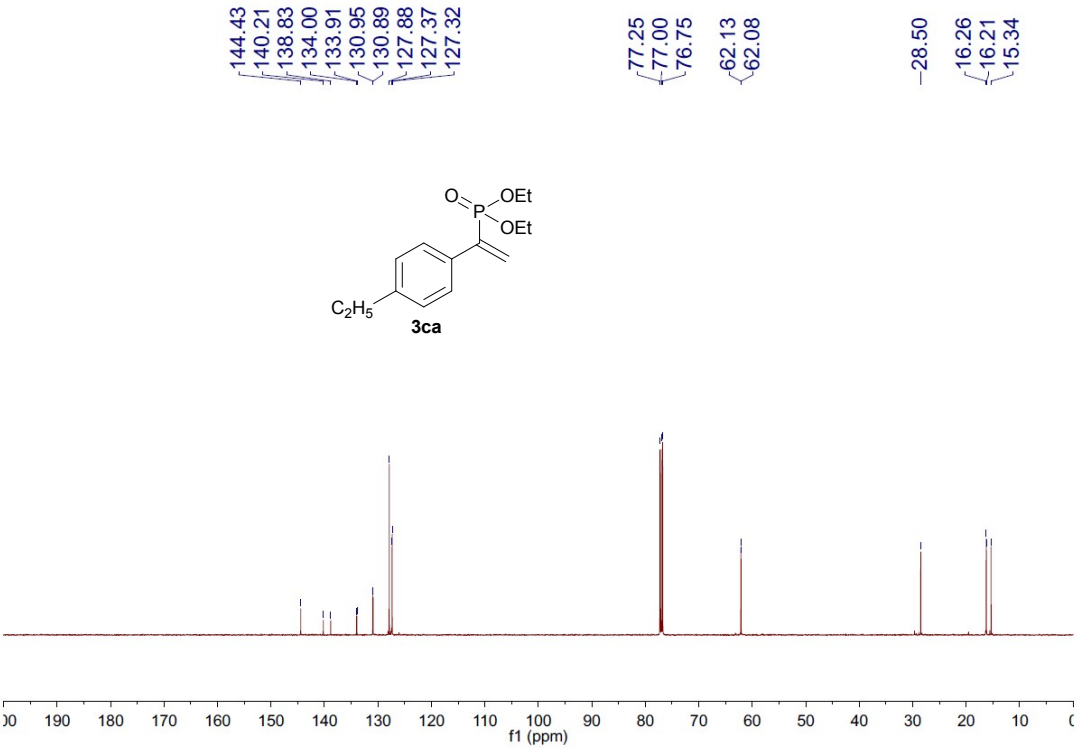
^{31}P NMR of **3ba**



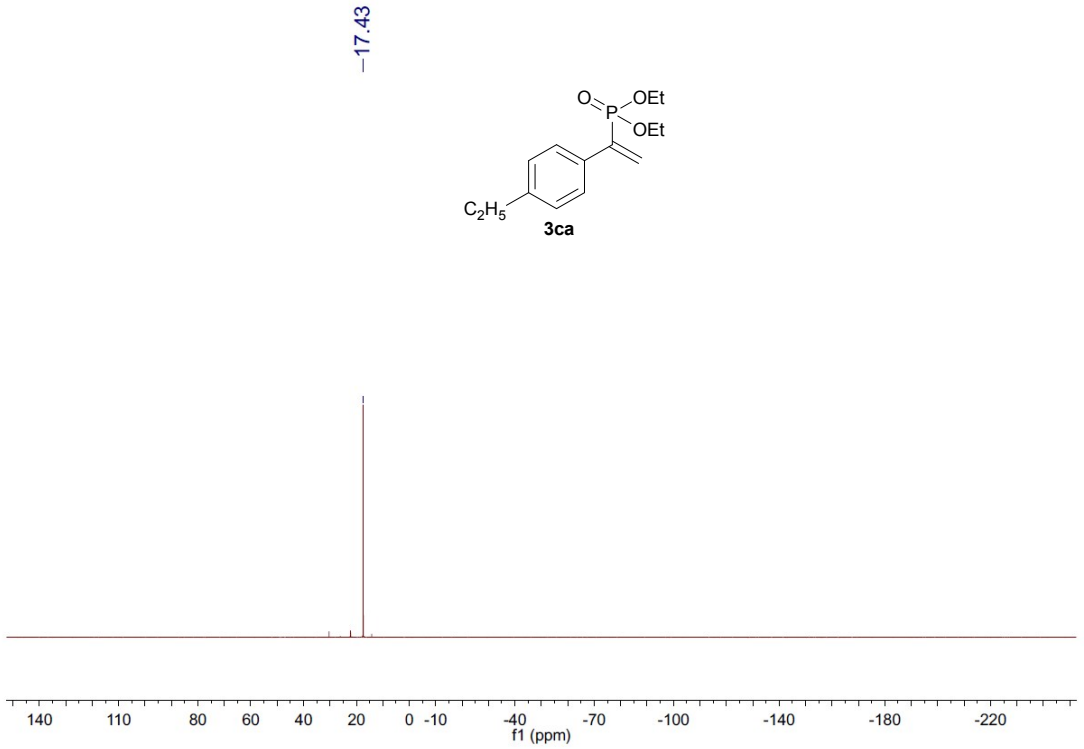
HRMS of **3ba**



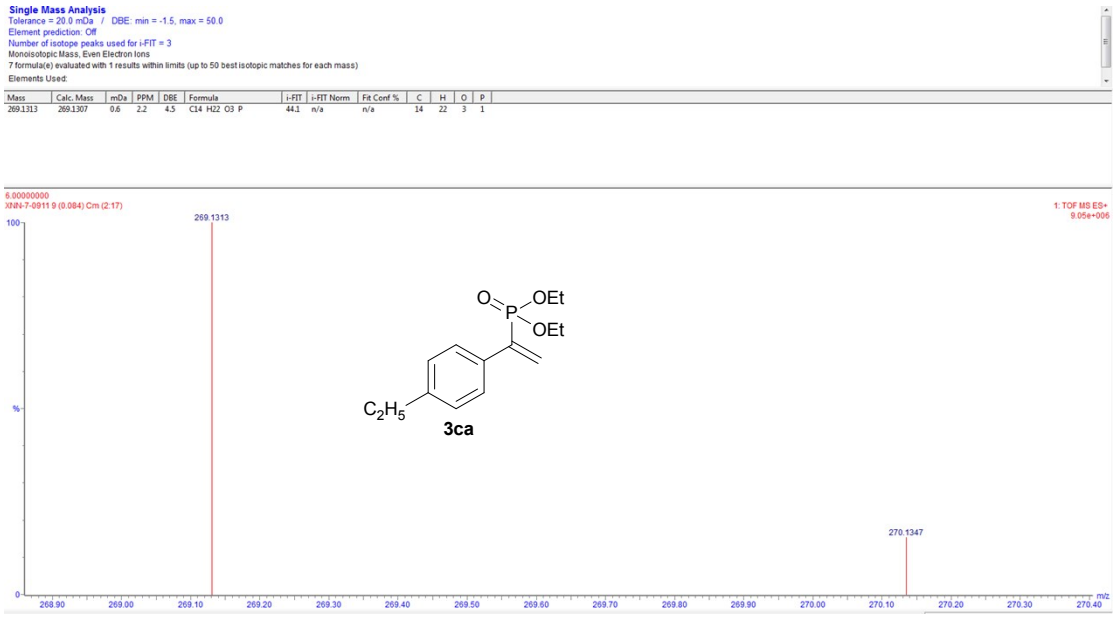
^{1}H NMR of **3ca**



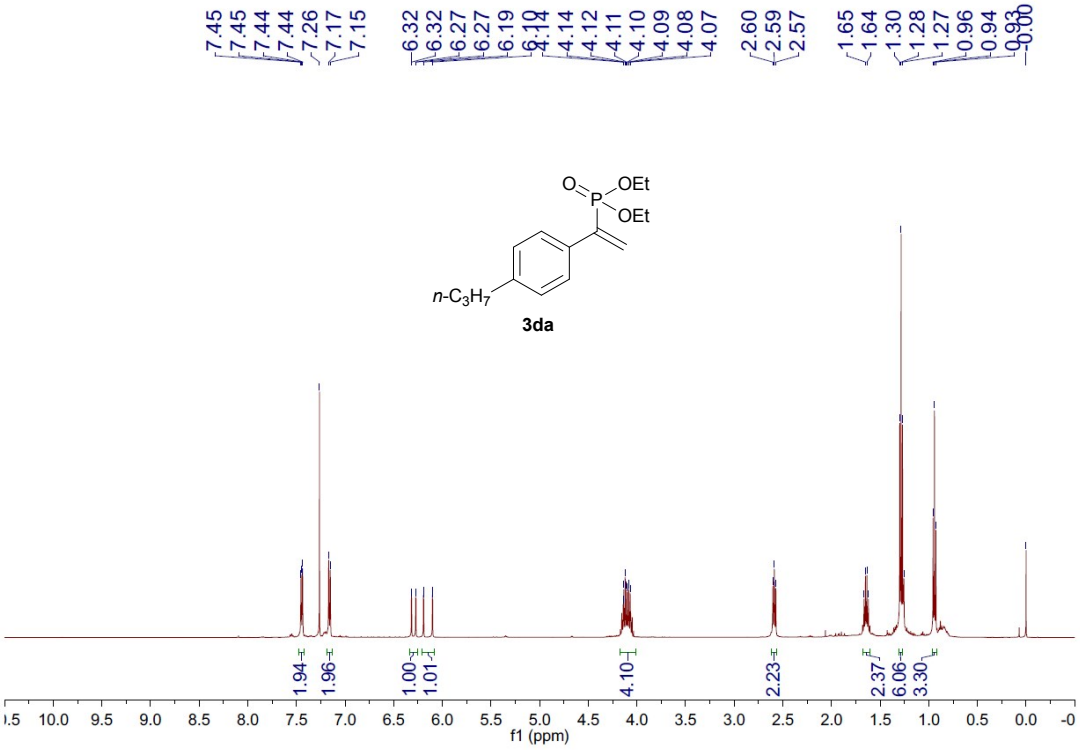
^{13}C NMR of **3ca**



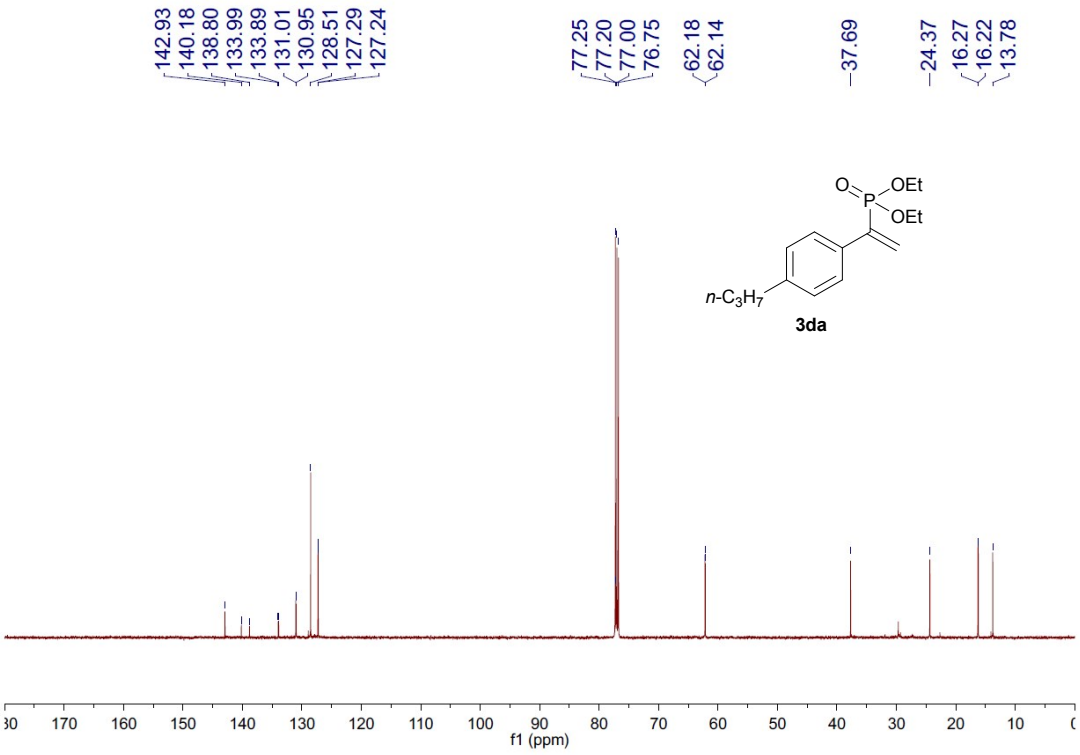
^{31}P NMR of **3ca**



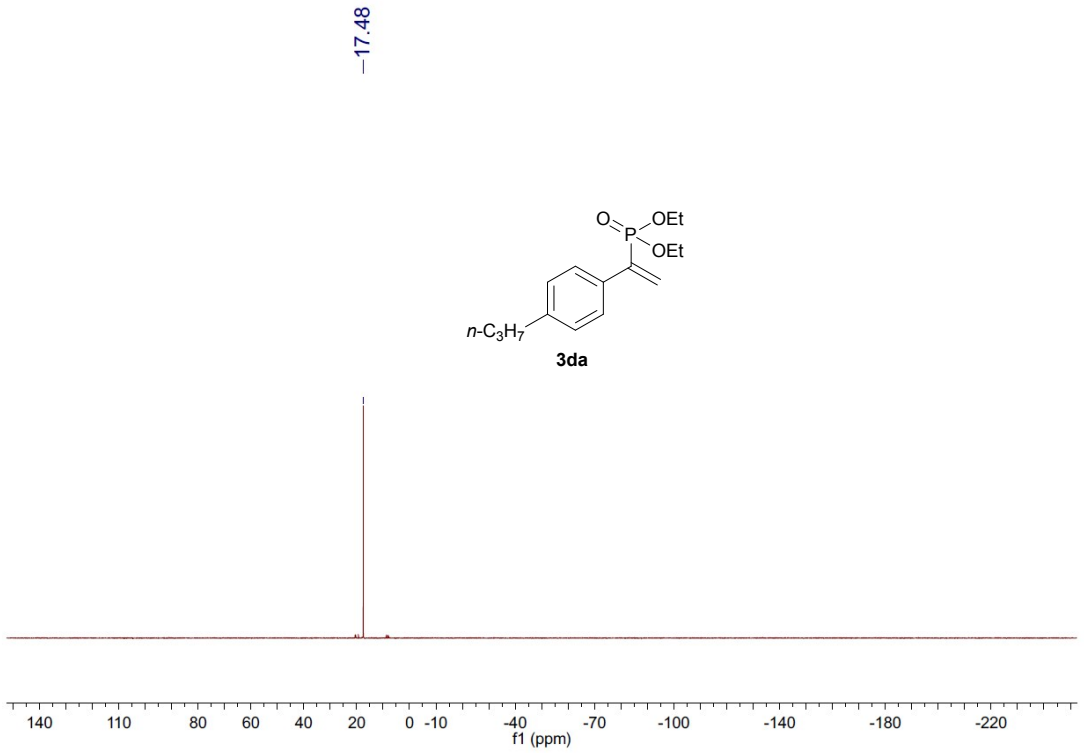
HRMS of **3ca**



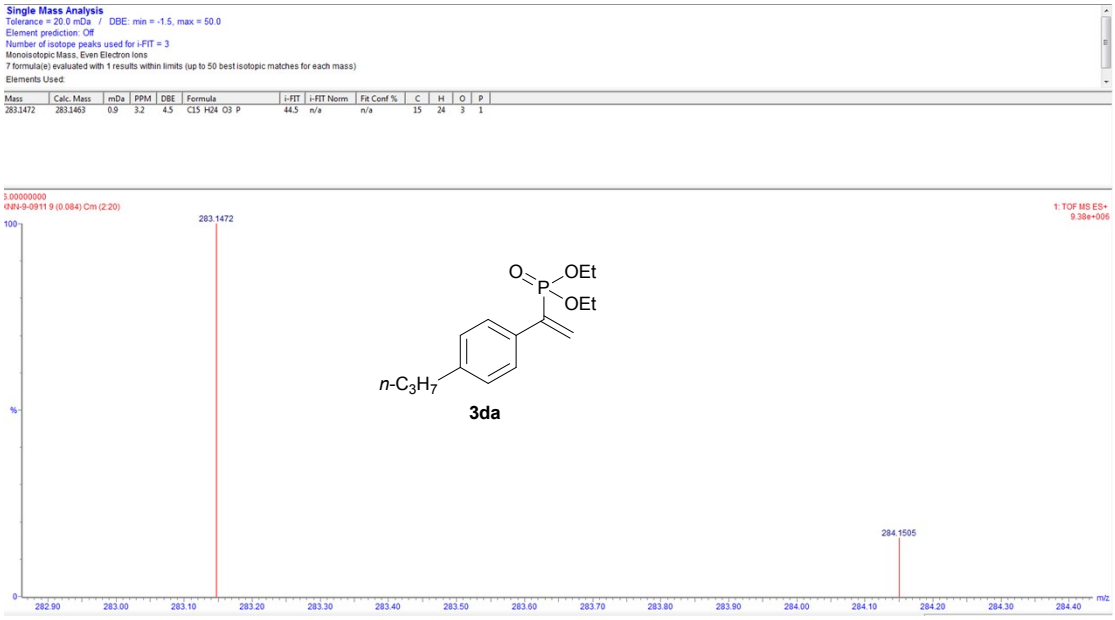
^{1}H NMR of **3da**



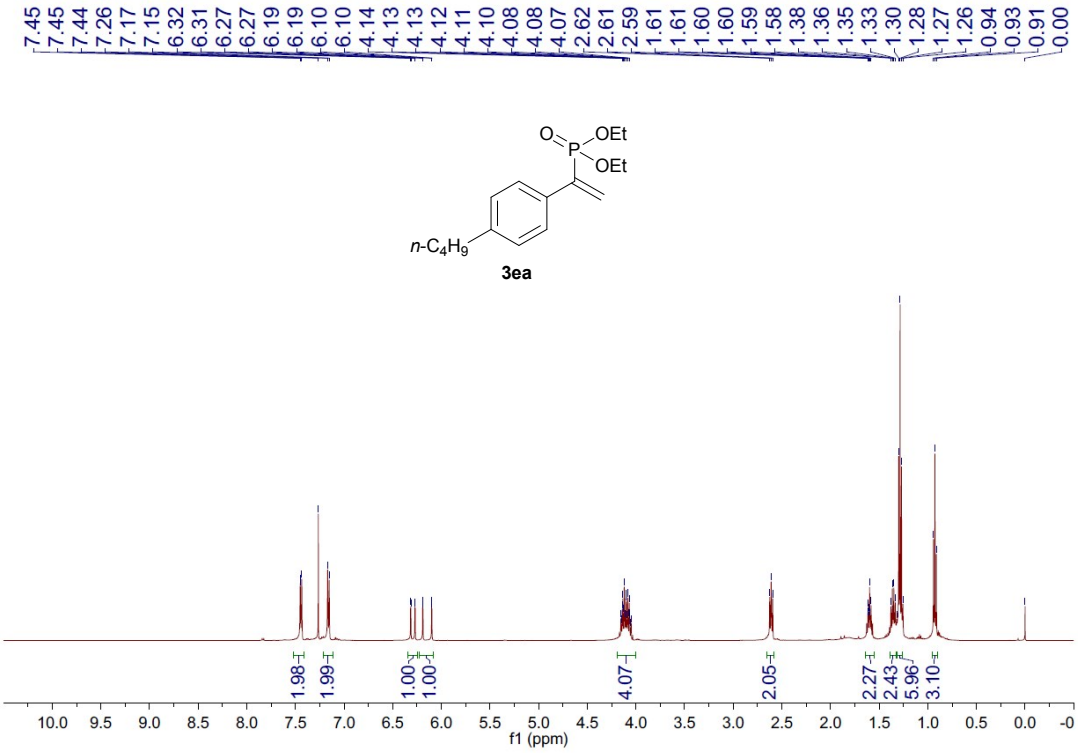
^{13}C NMR of **3da**



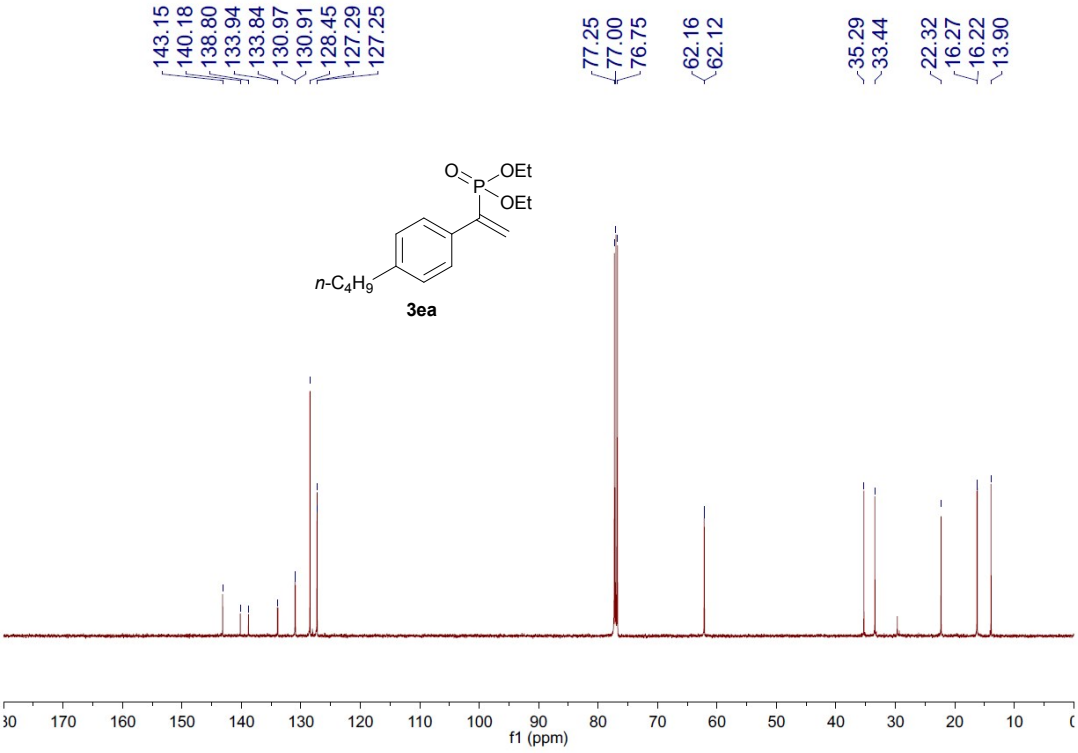
^{31}P NMR of **3da**



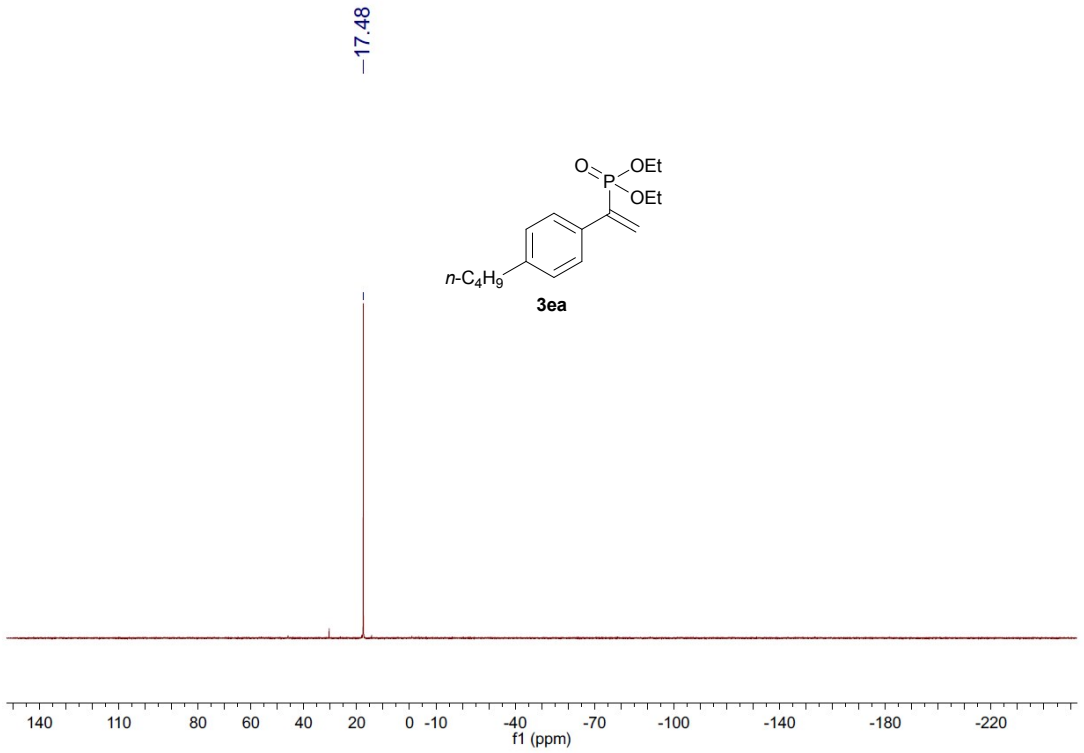
HRMS of **3da**



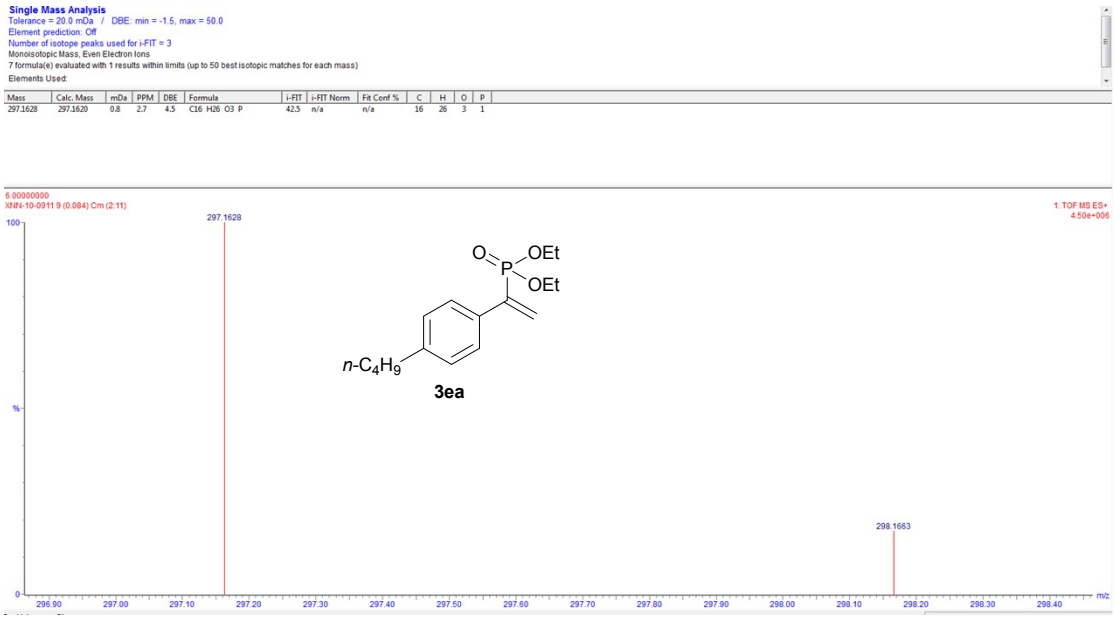
^{1}H NMR of **3ea**



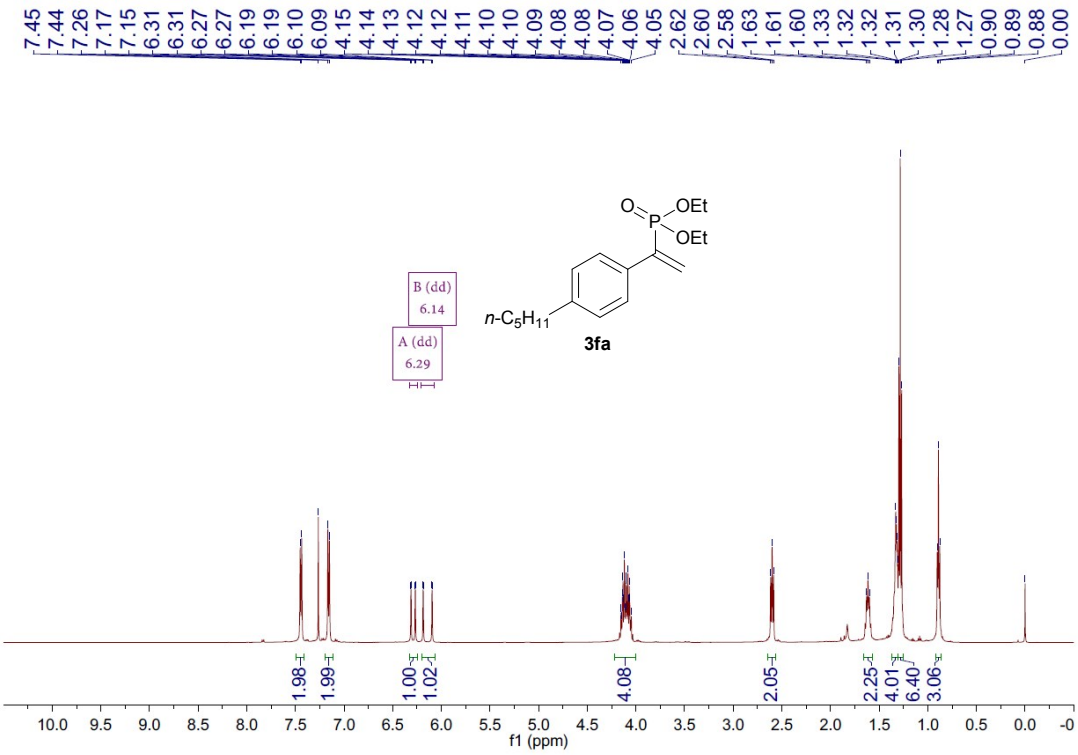
^{13}C NMR of **3ea**



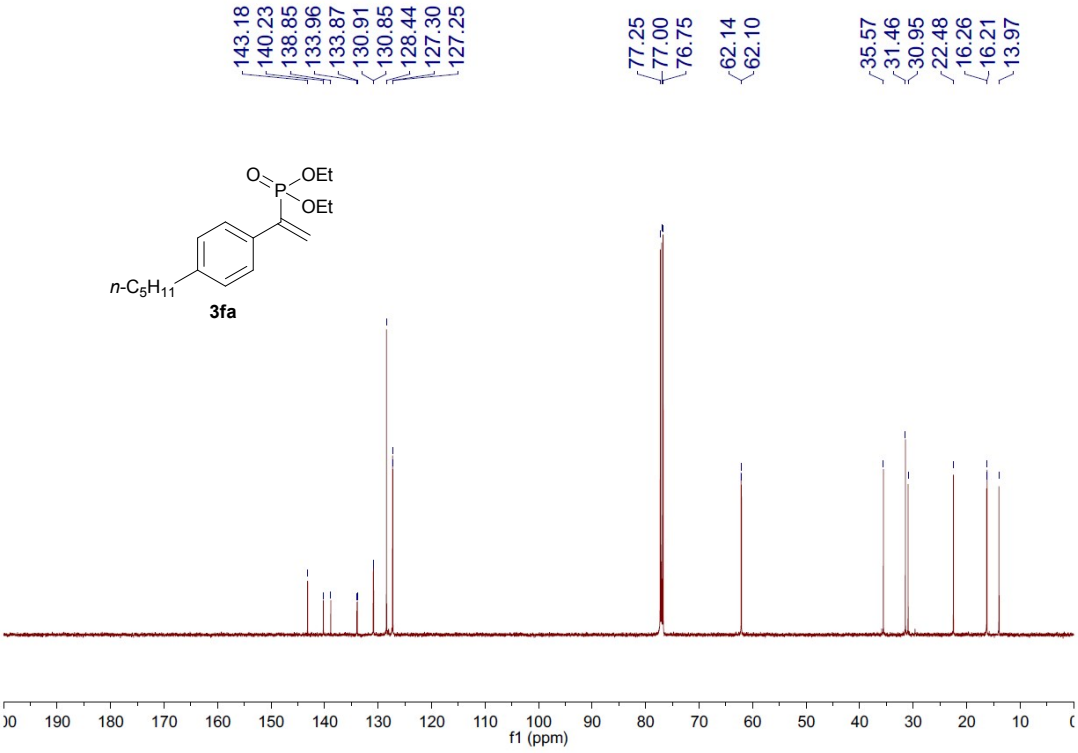
^{31}P NMR of **3ea**



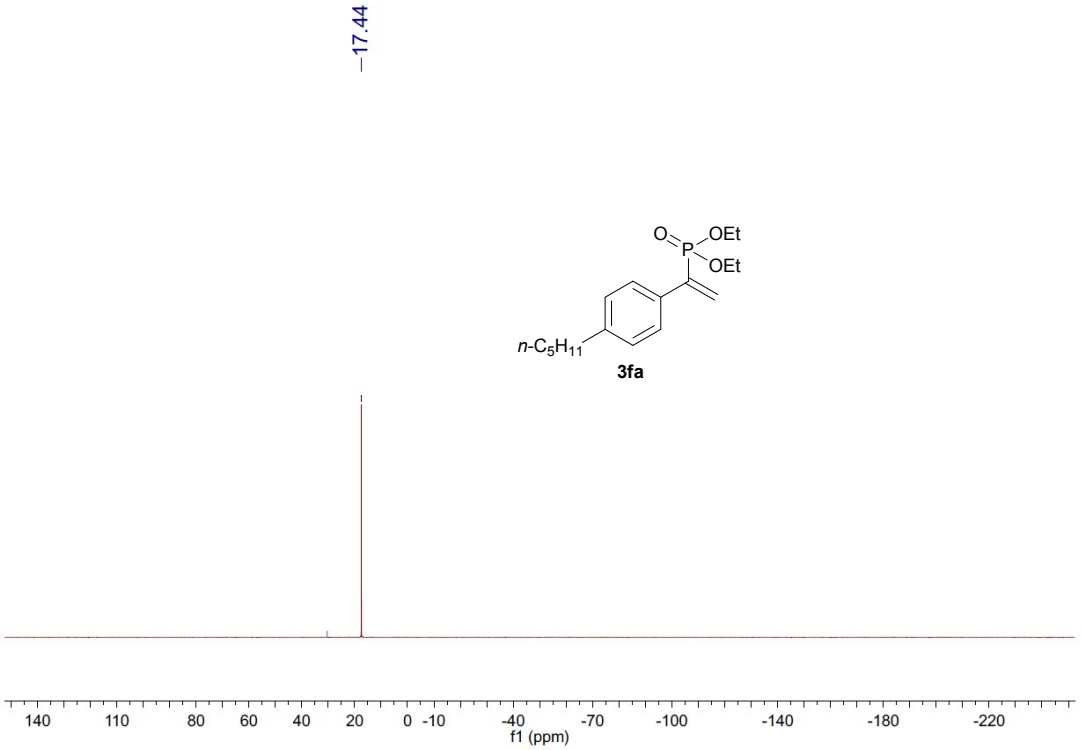
HRMS of **3ea**



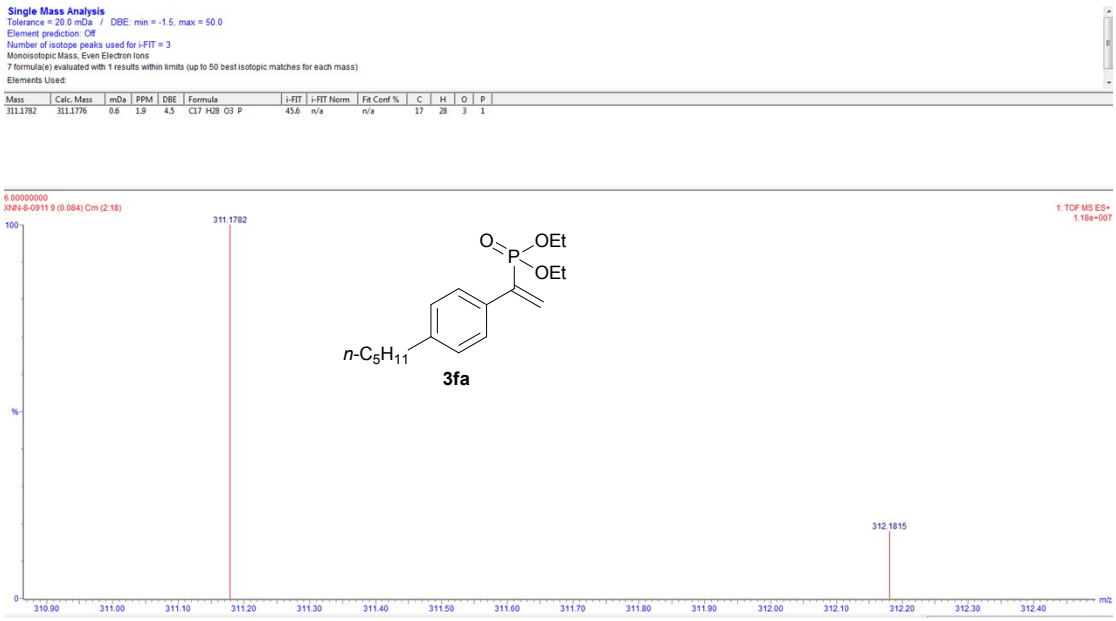
^{1}H NMR of **3fa**



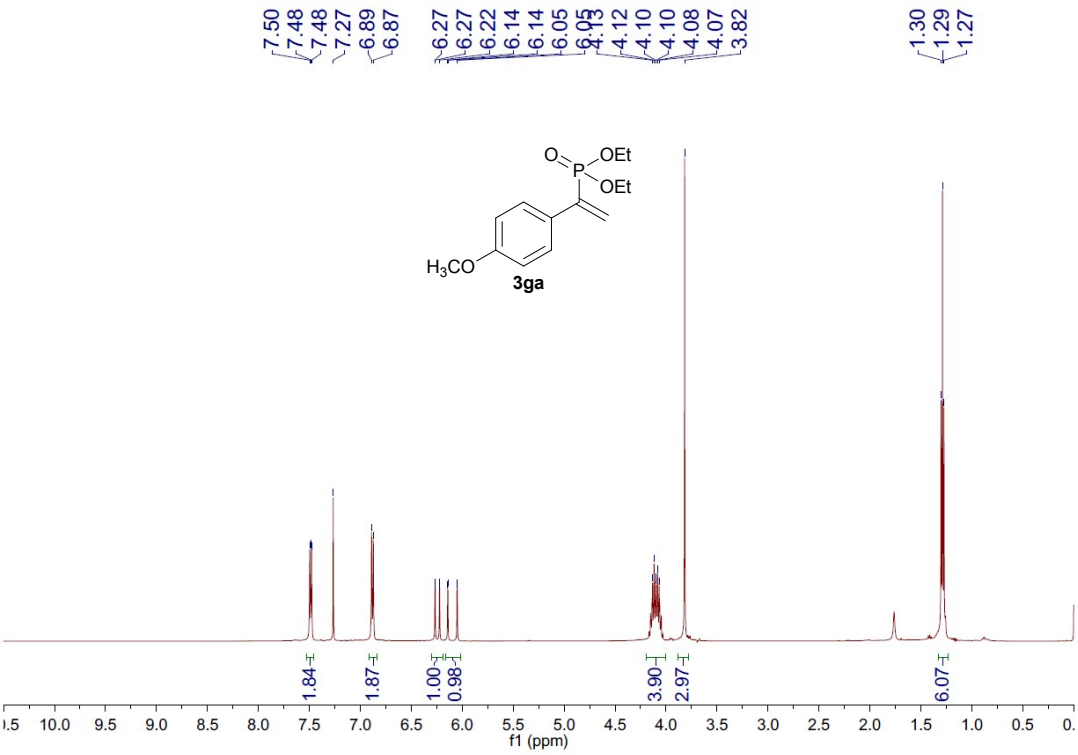
^{13}C NMR of **3fa**



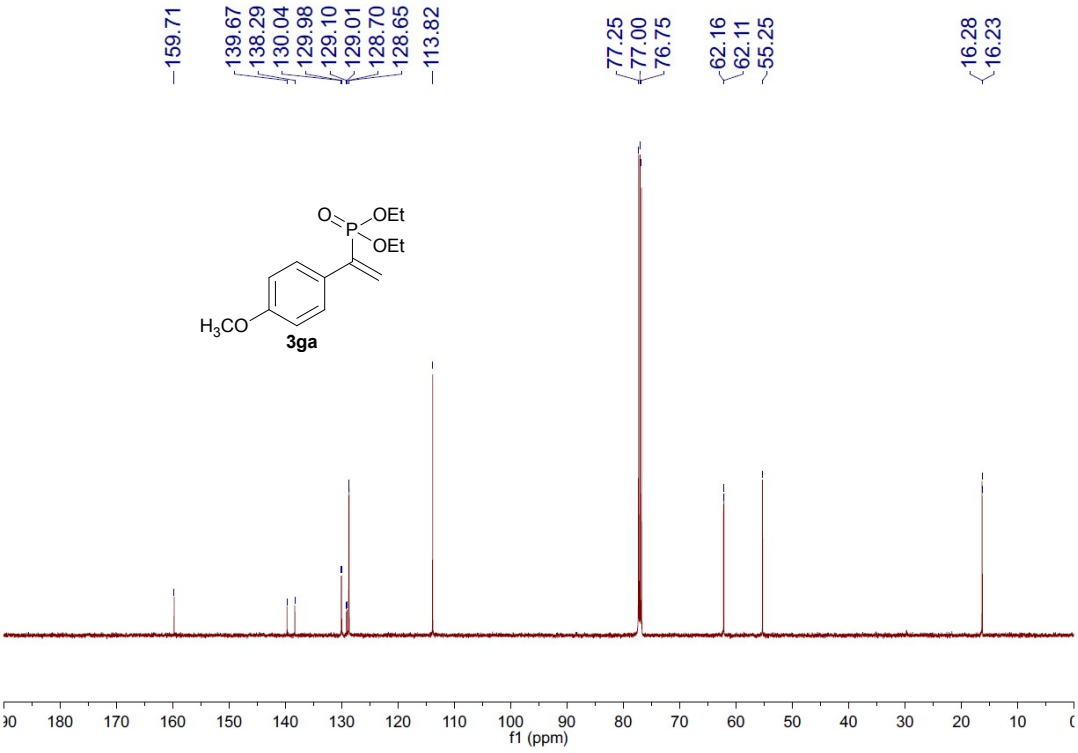
^{31}P NMR of **3fa**



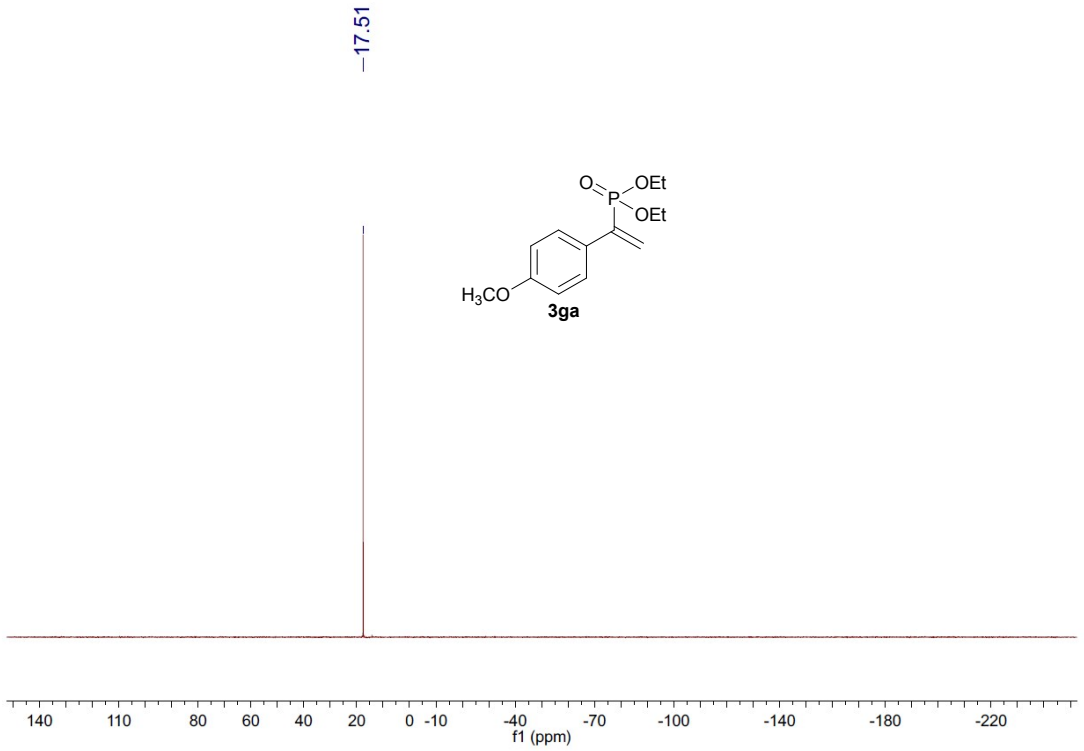
HRMS of **3fa**



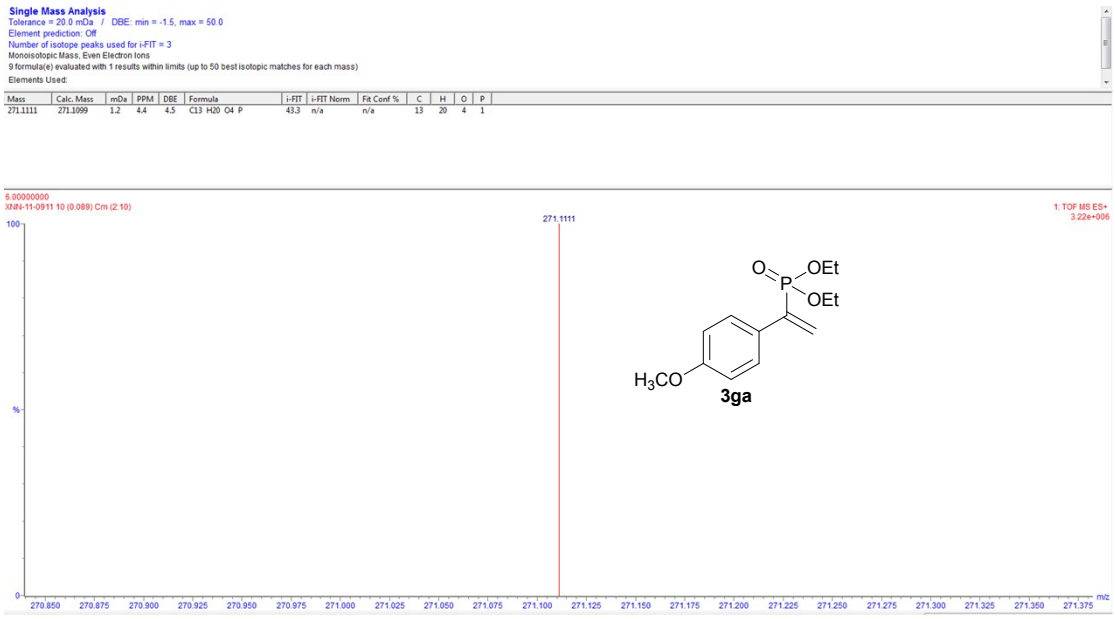
^{1}H NMR of **3ga**



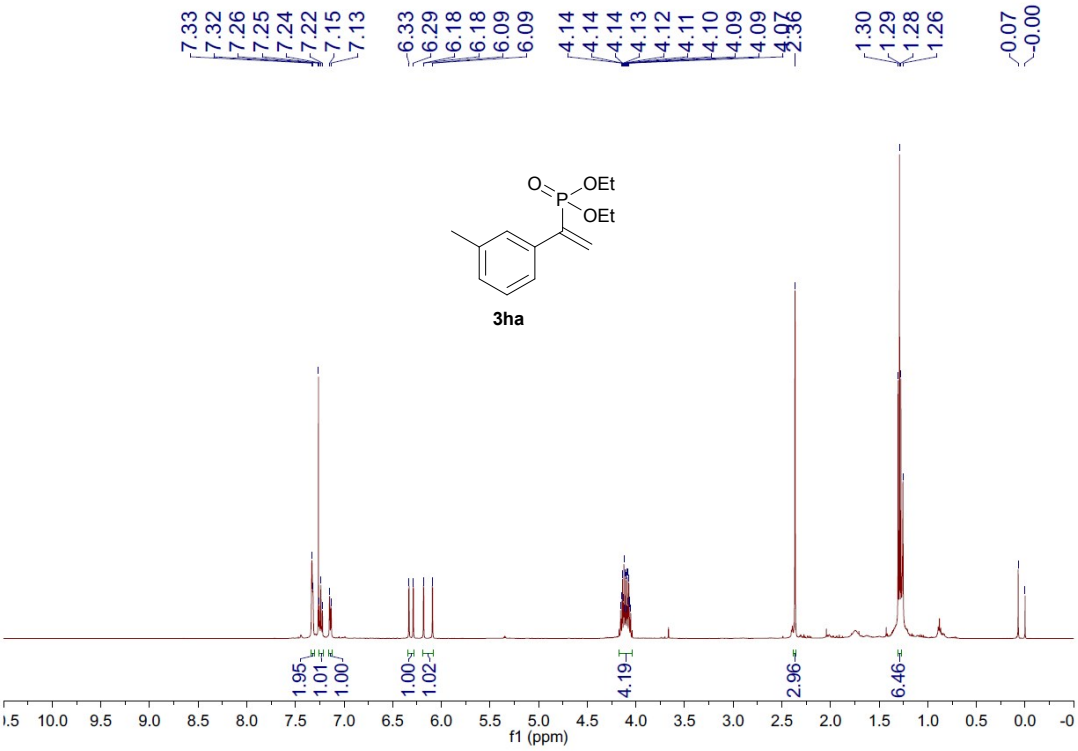
^{13}C NMR of **3ga**



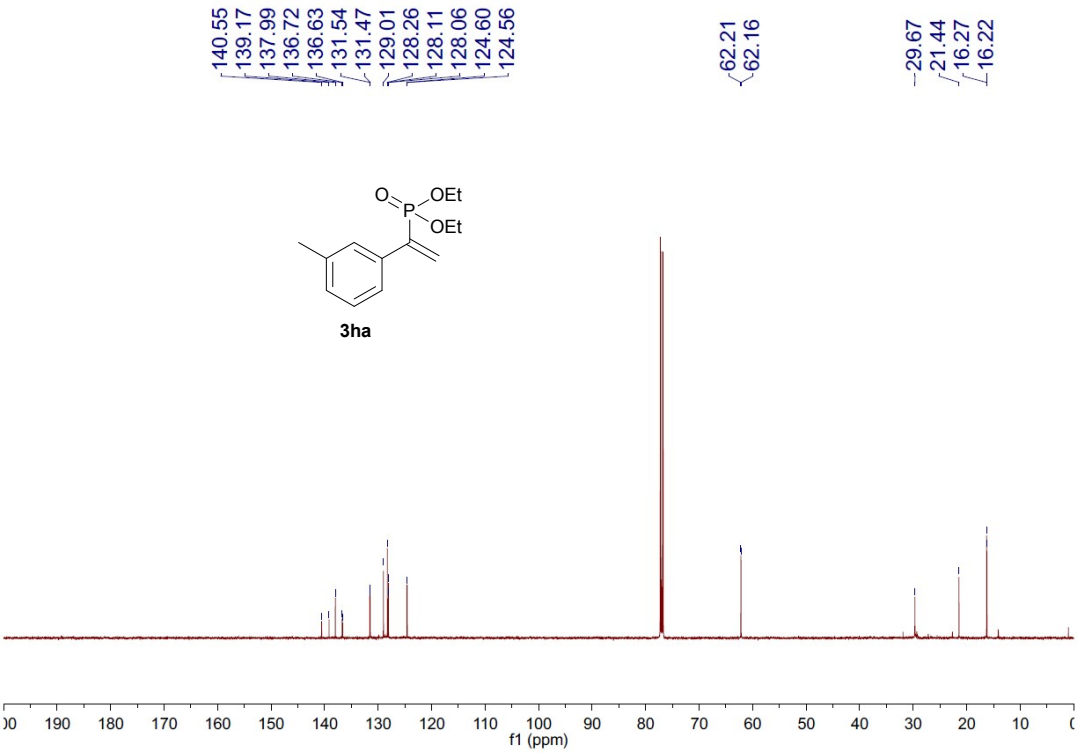
^{31}P NMR of **3ga**



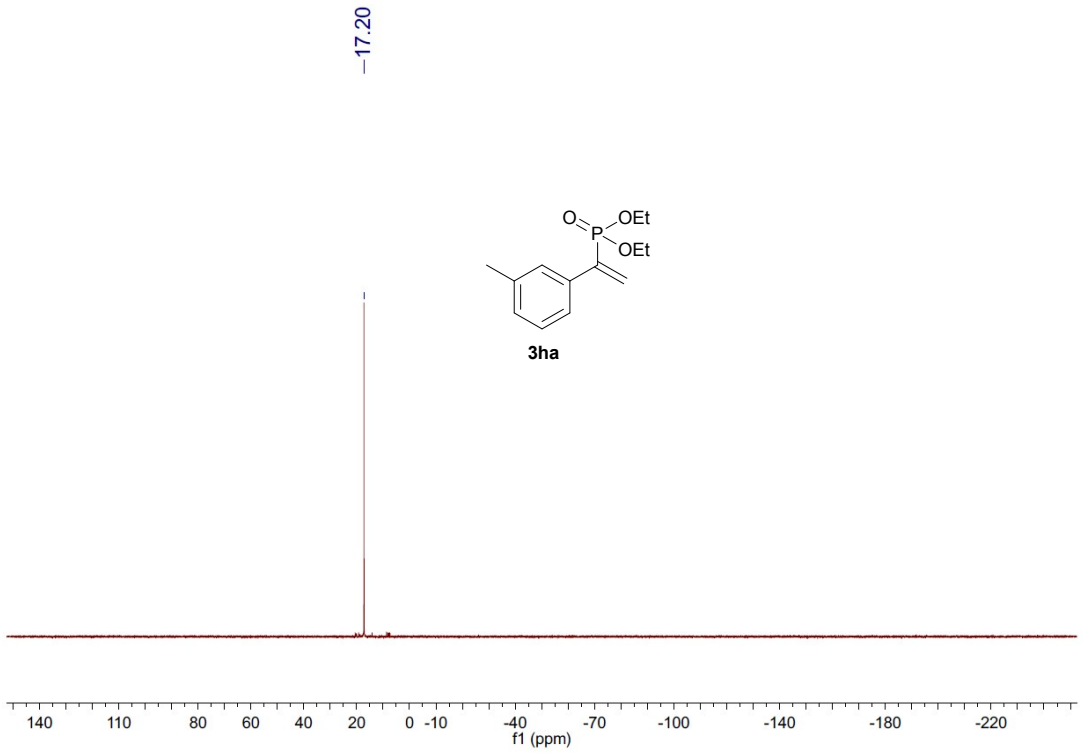
HRMS of **3ga**



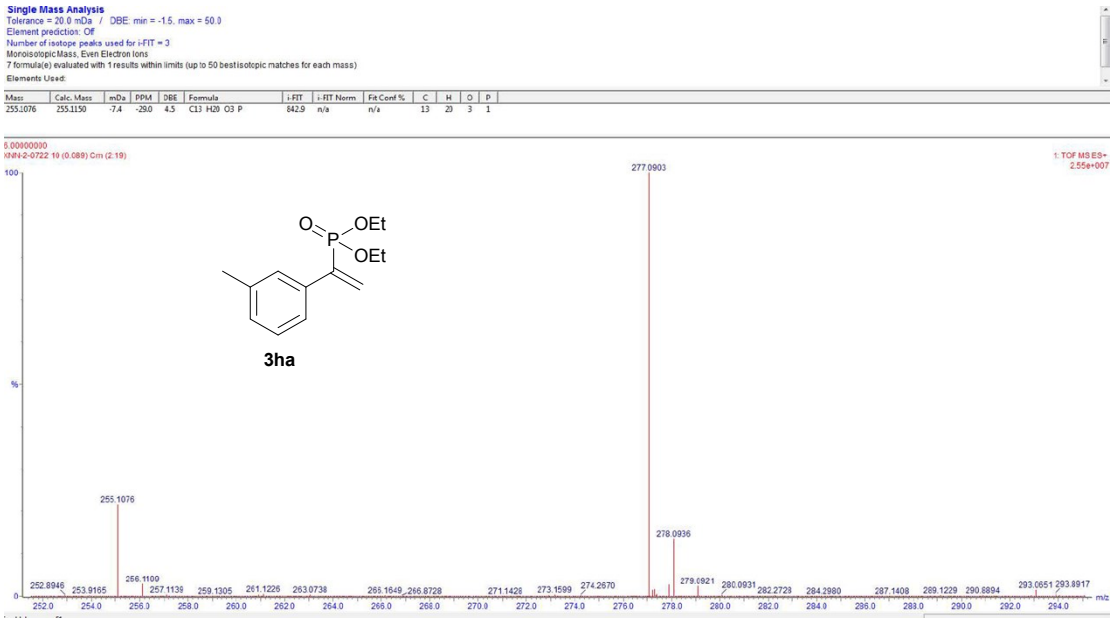
^{1}H NMR of **3ha**



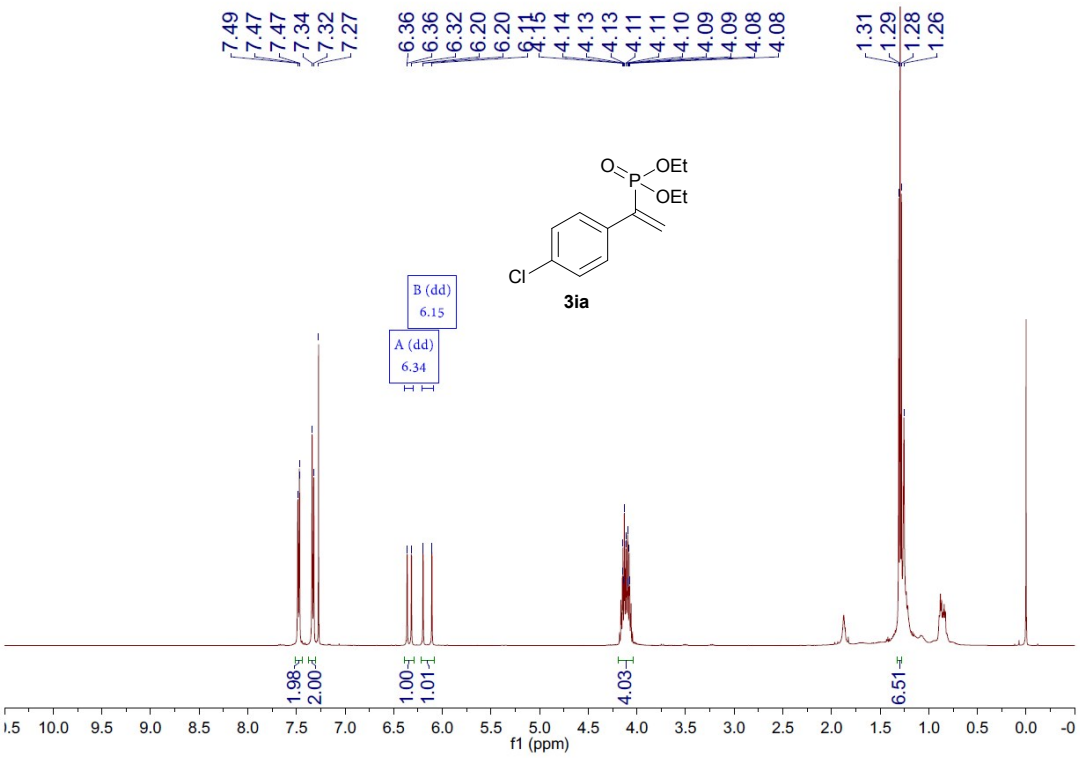
^{13}C NMR of **3ha**



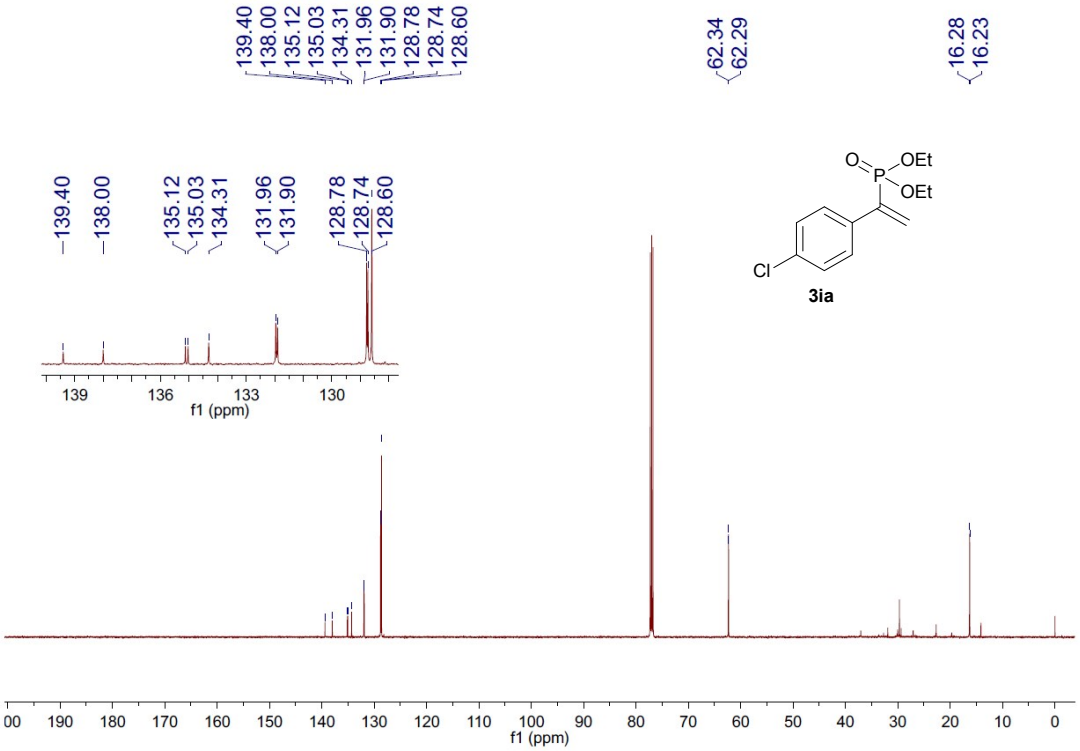
^{31}P NMR of **3ha**



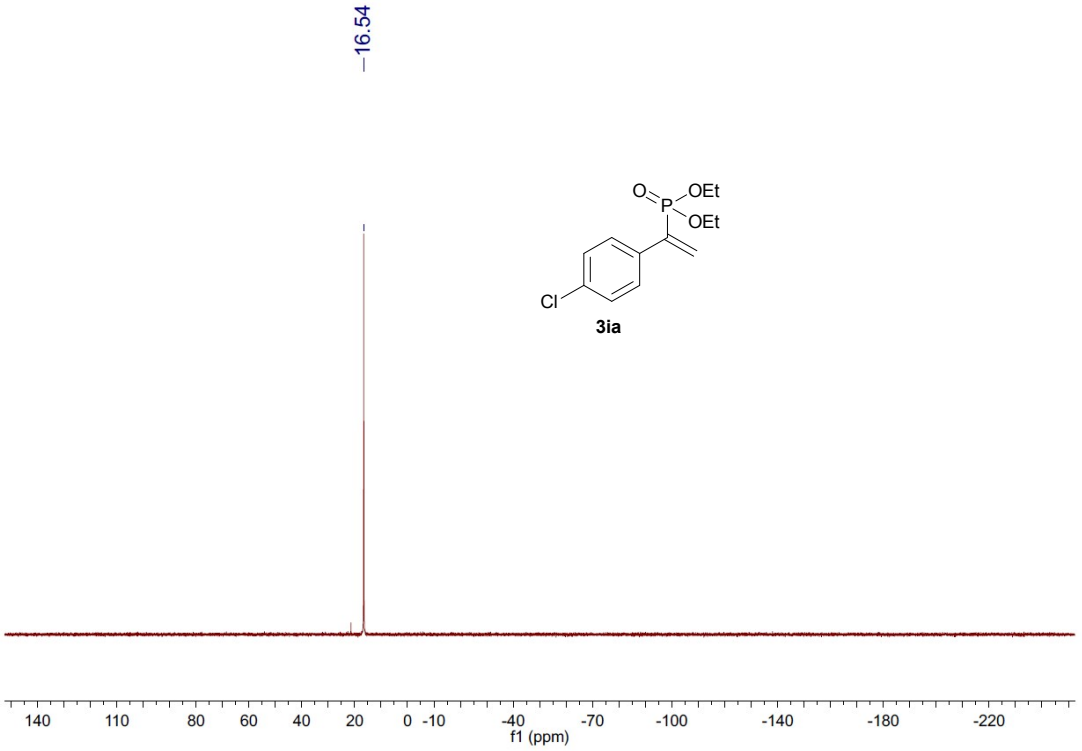
HRMS of **3ha**



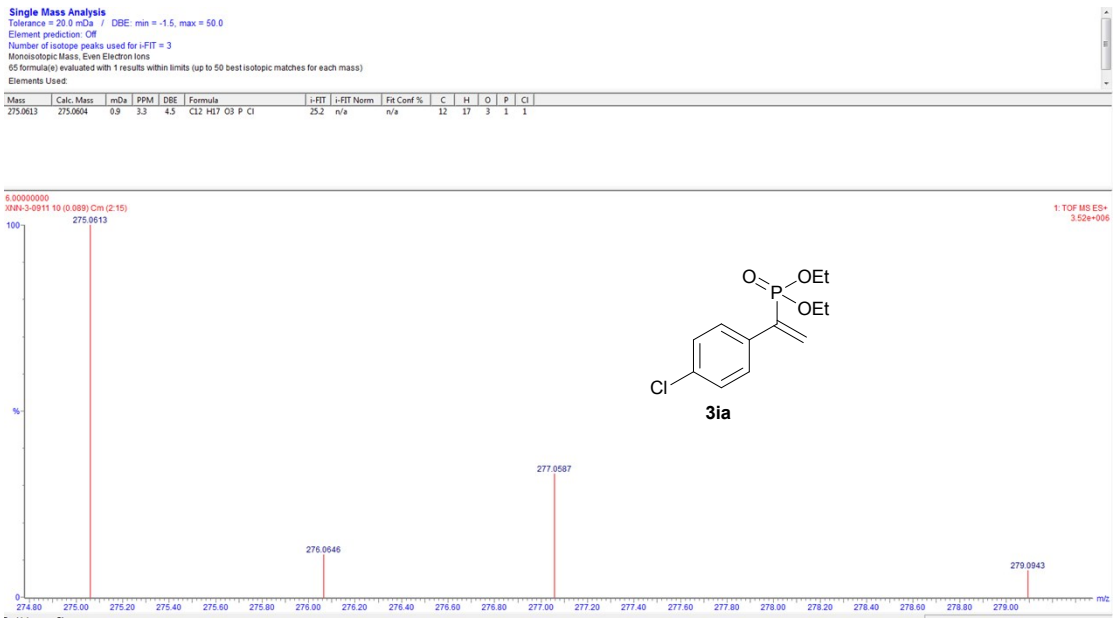
^{1}H NMR of **3ia**



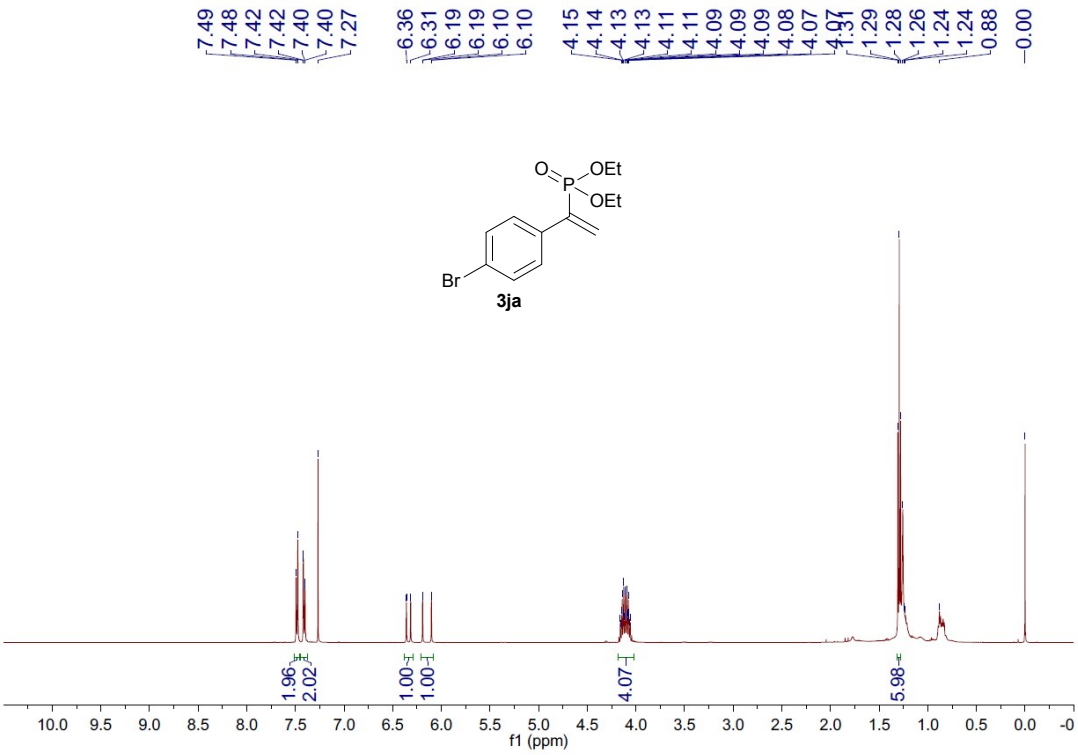
^{13}C NMR of **3ia**



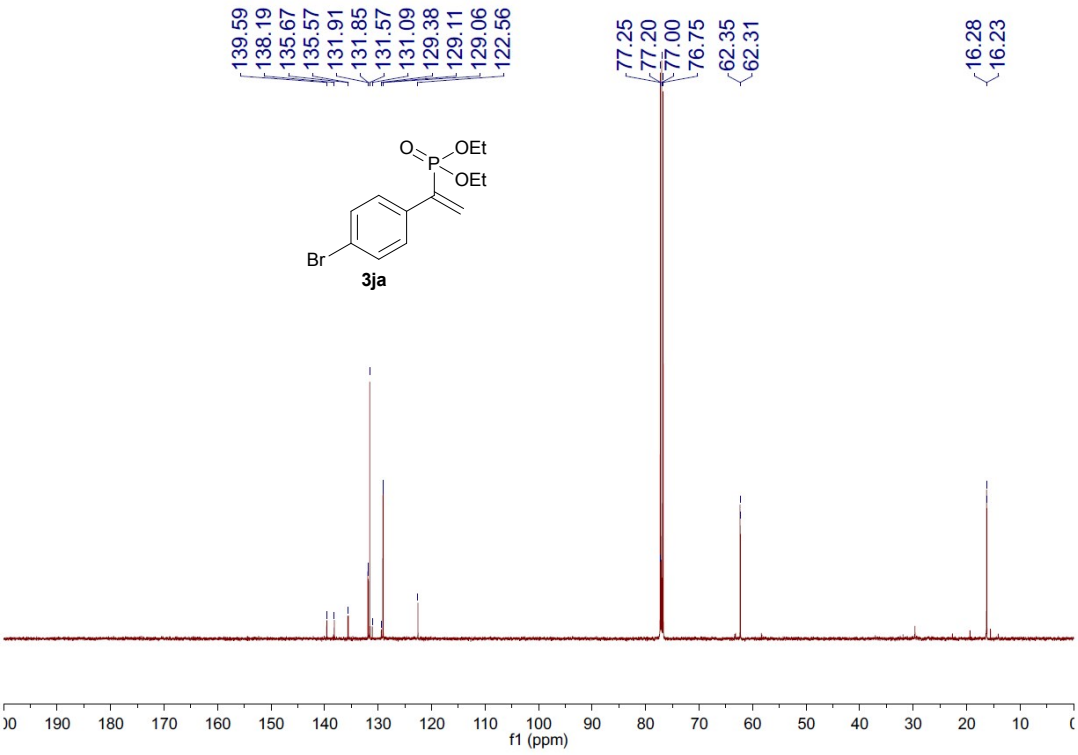
^{31}P NMR of **3ia**



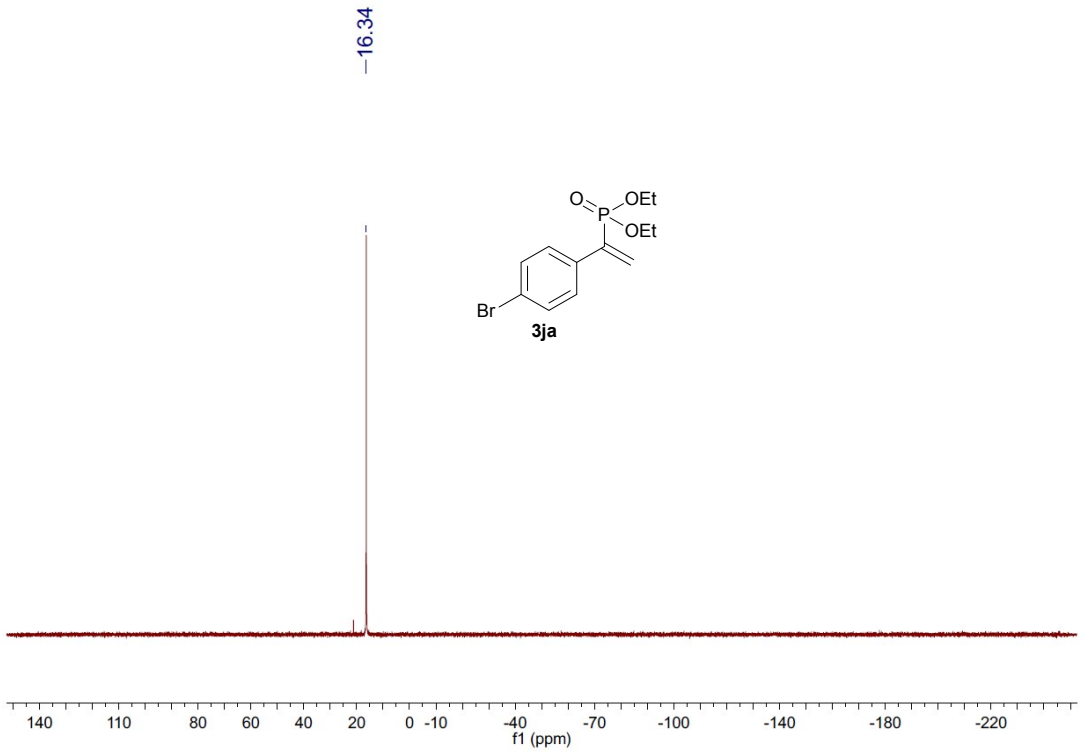
HRMS of **3ia**



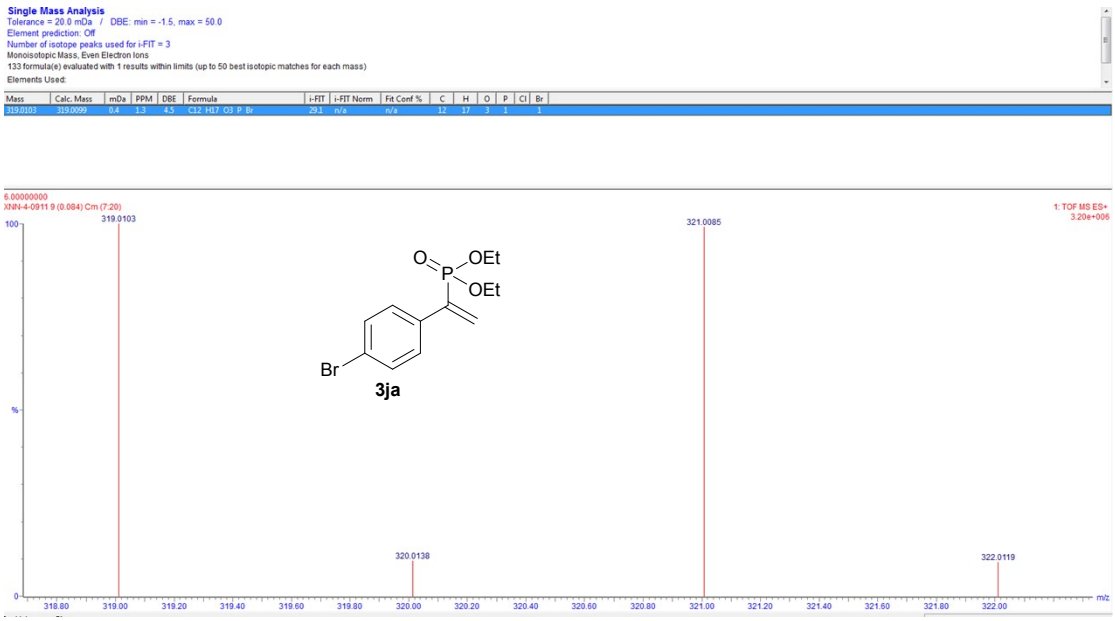
^{1}H NMR of **3ja**



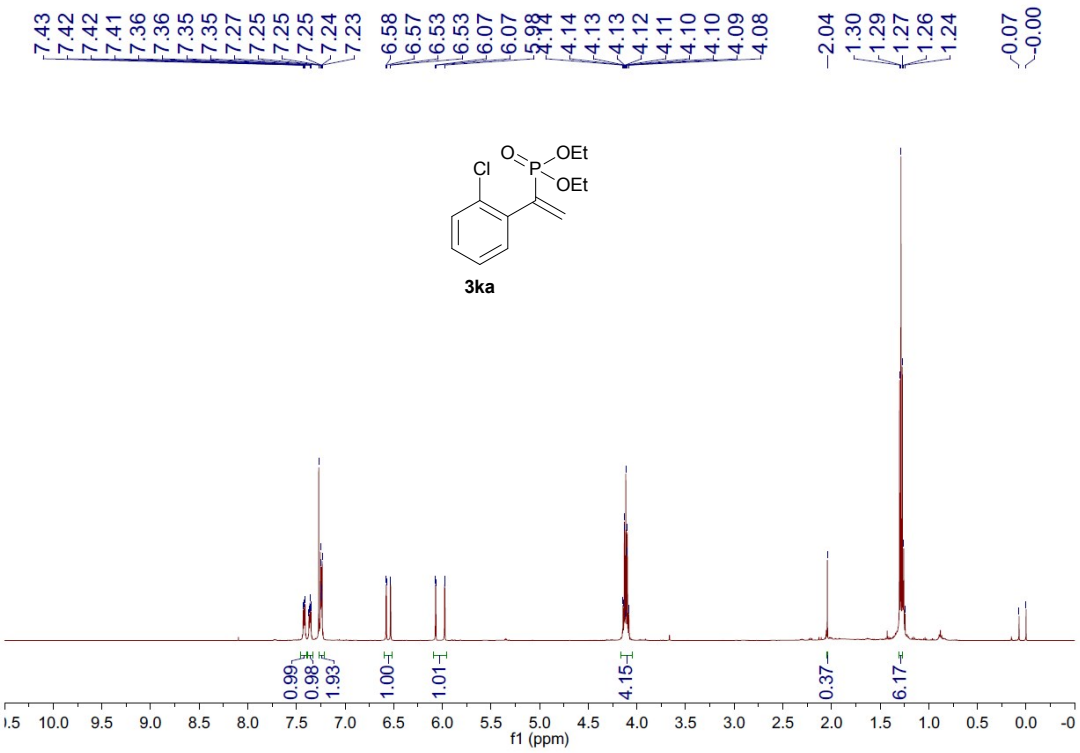
^{13}C NMR of **3ja**



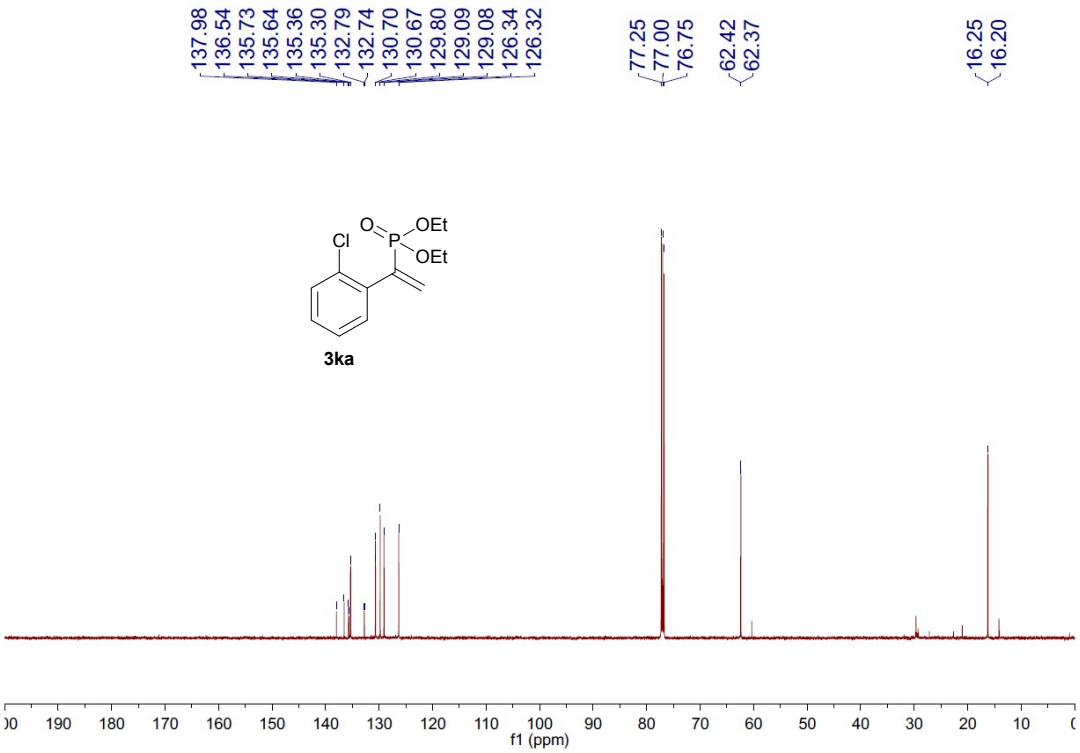
^{31}P NMR of **3ja**



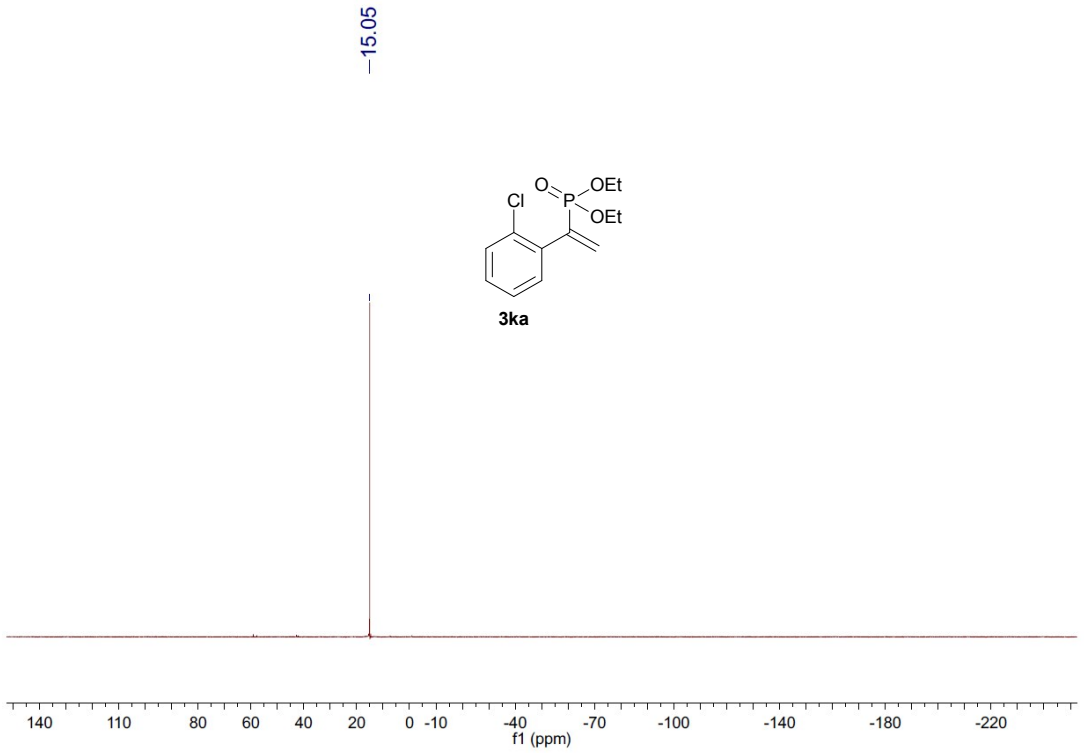
HRMS of **3ja**



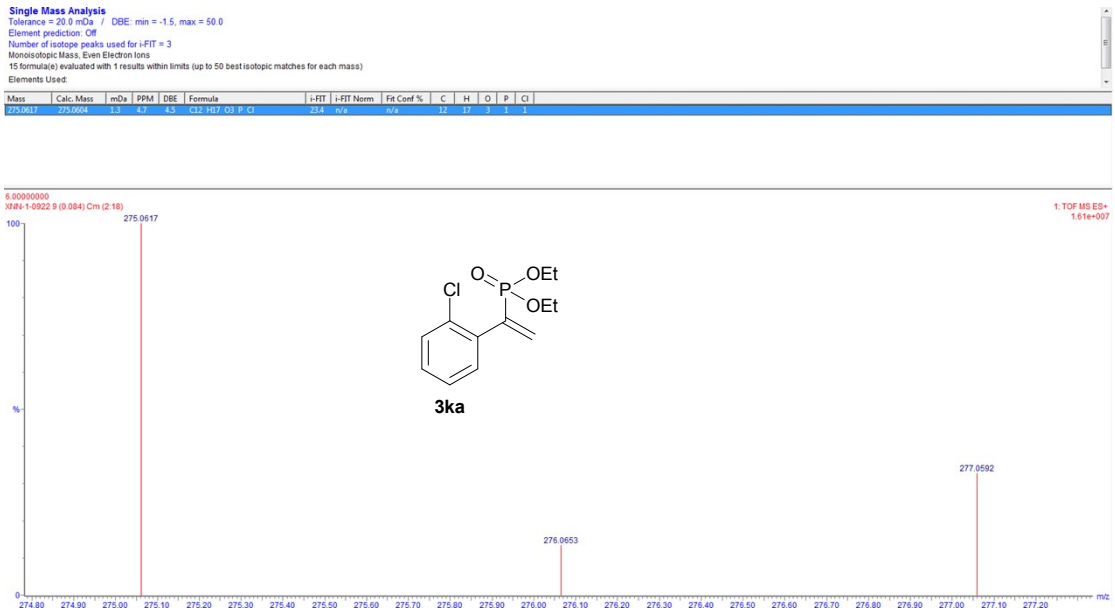
^{1}H NMR of **3ka**



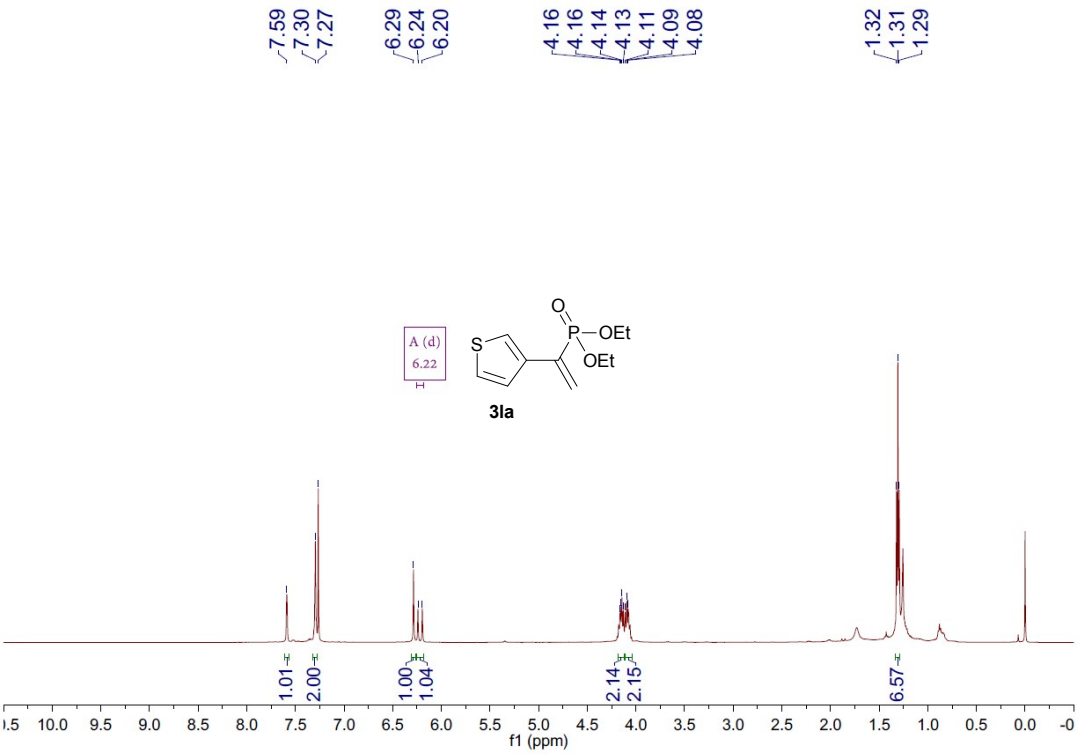
^{13}C NMR of **3ka**



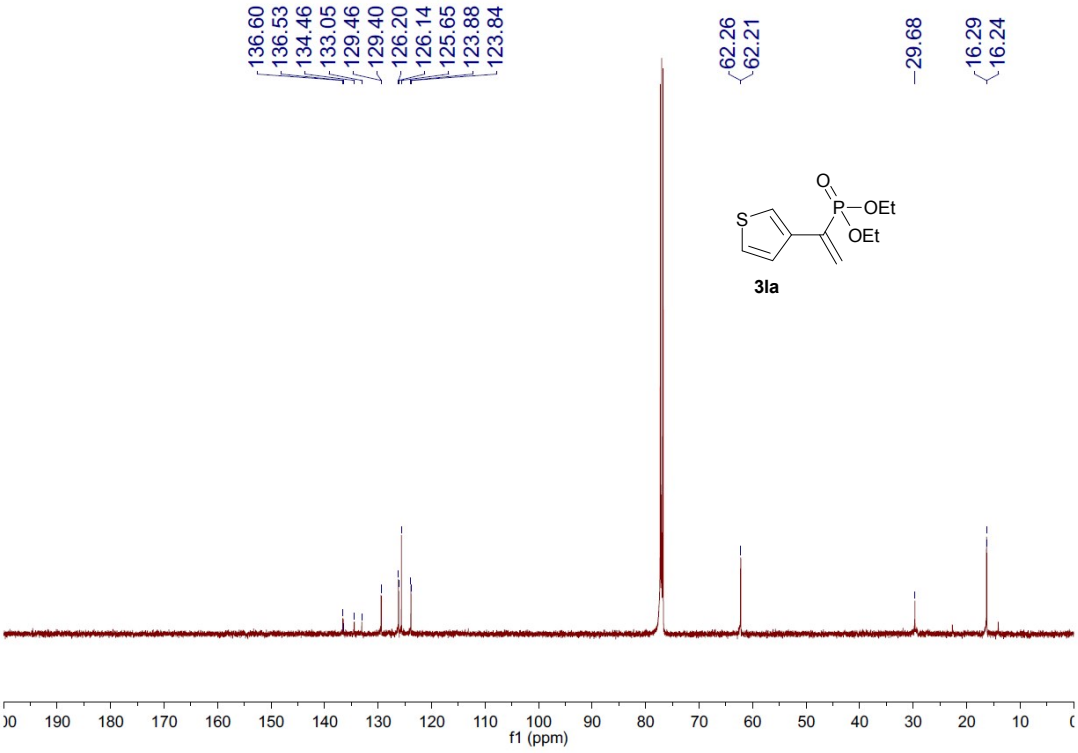
^{31}P NMR of **3ka**



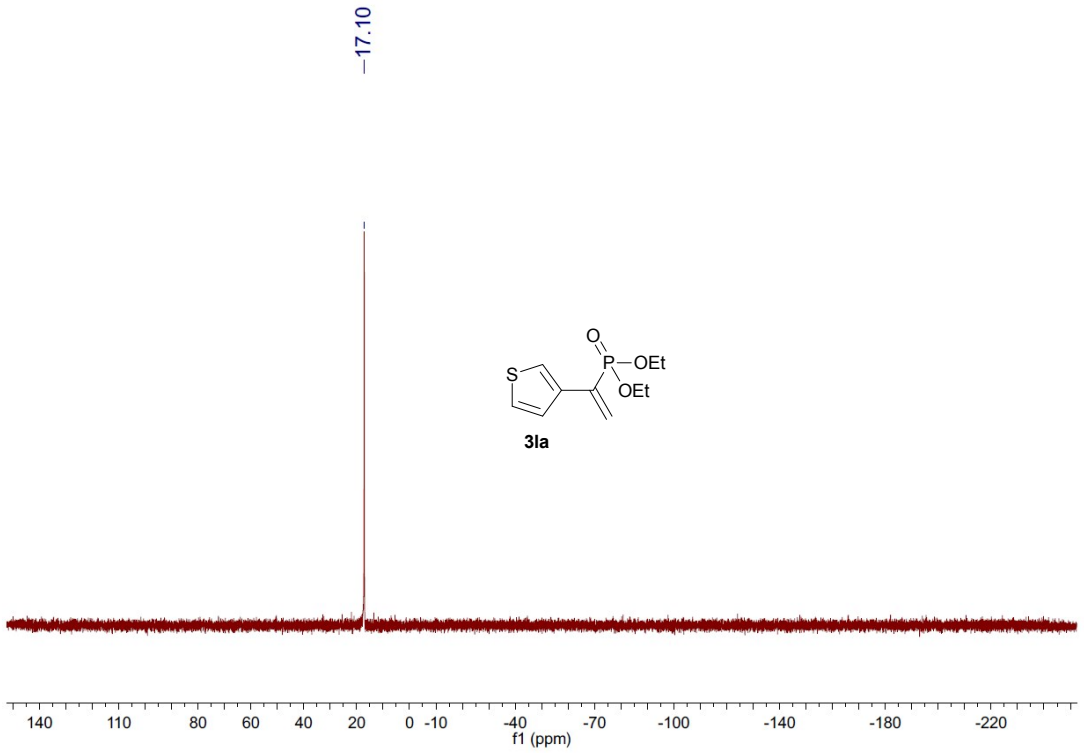
HRMS of **3ka**



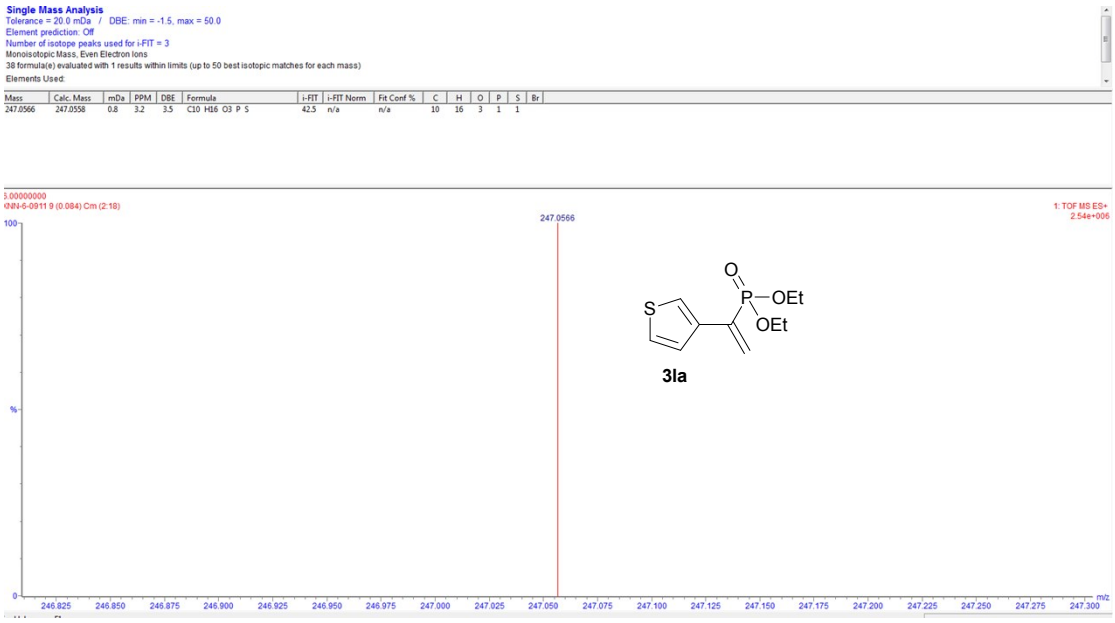
^{1}H NMR of **3la**



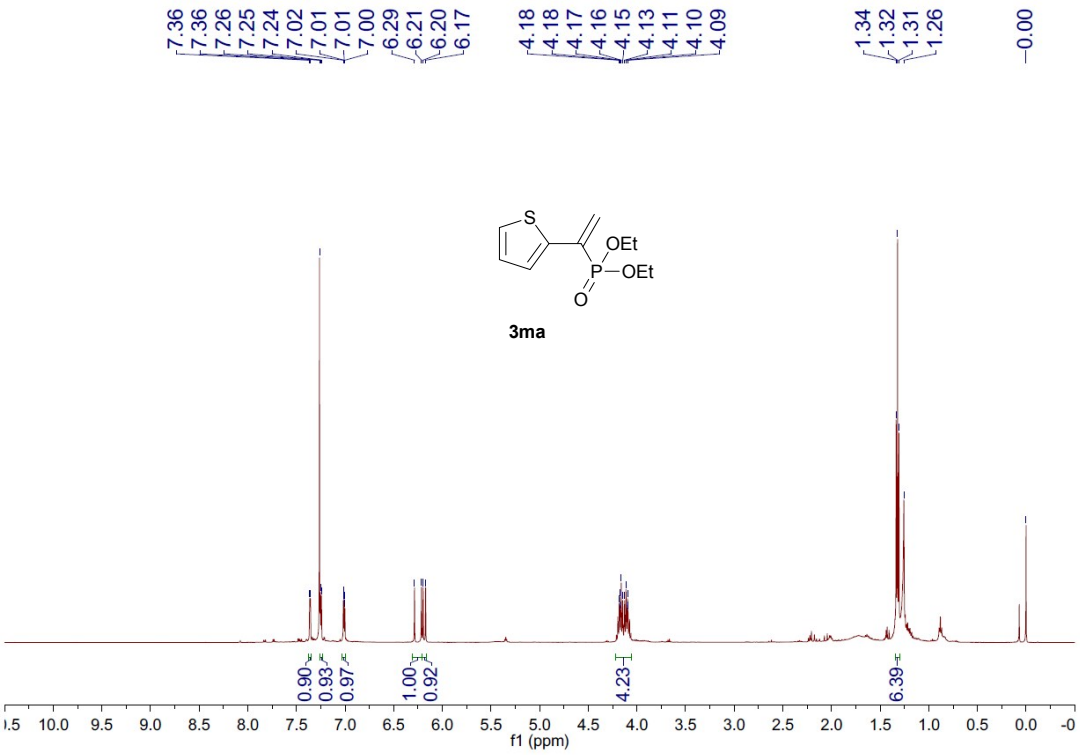
^{13}C NMR of **3la**



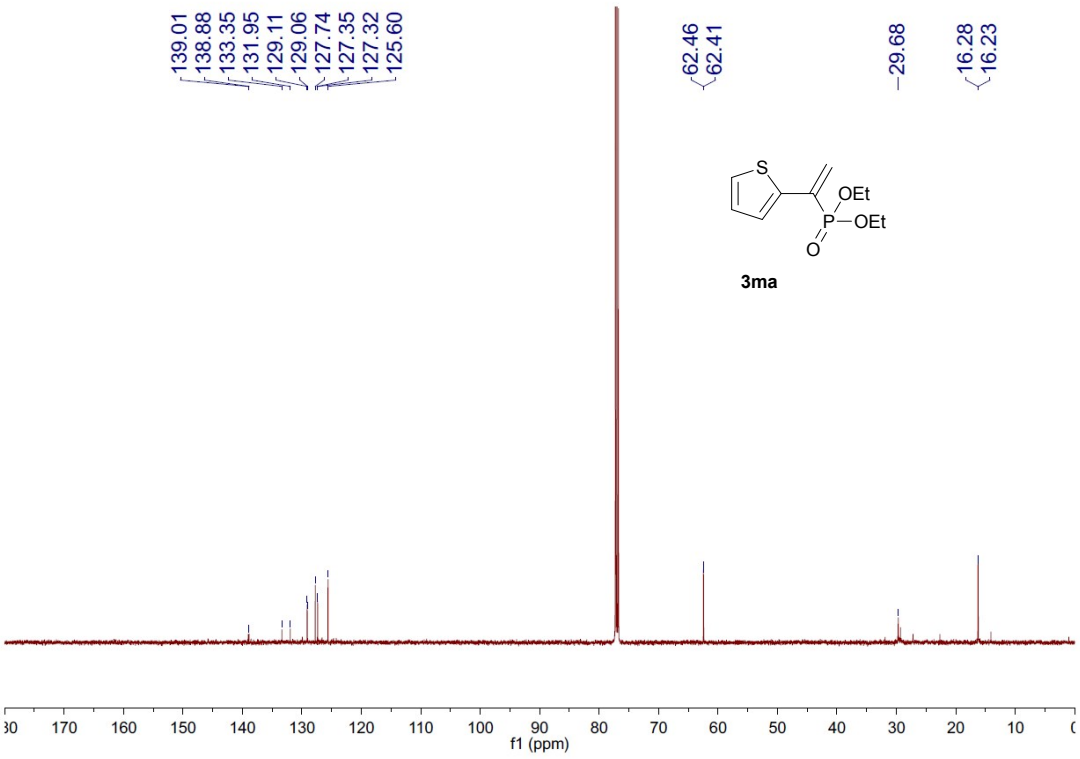
^{31}P NMR of **3la**



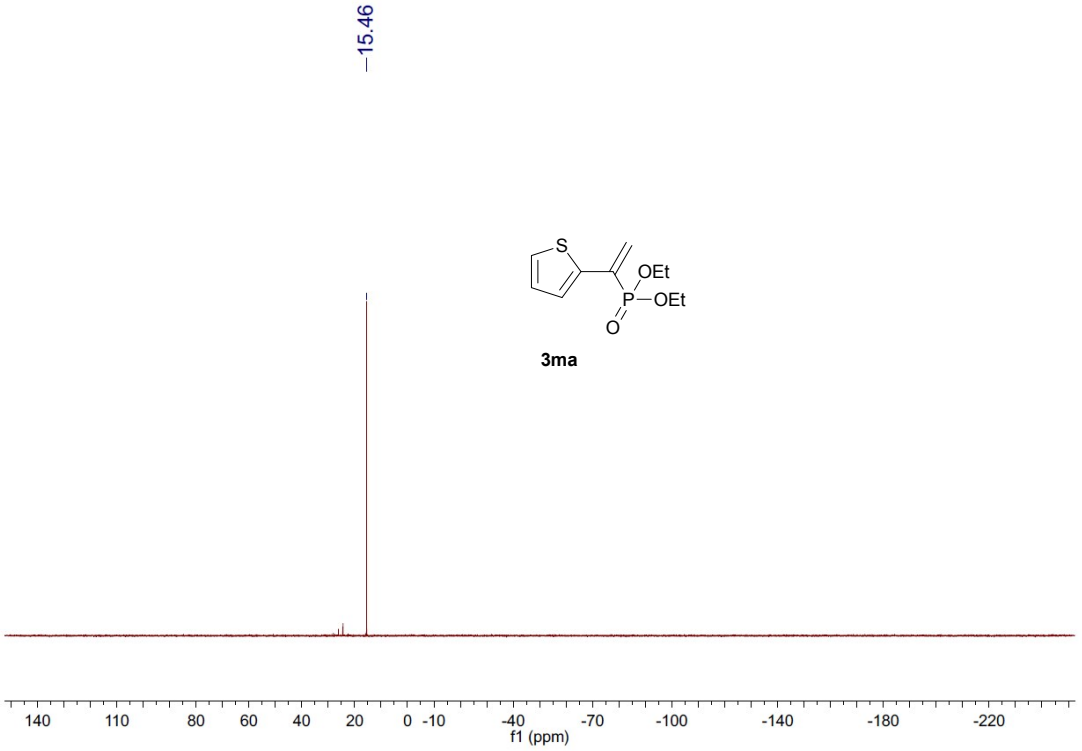
HRMS of **3la**



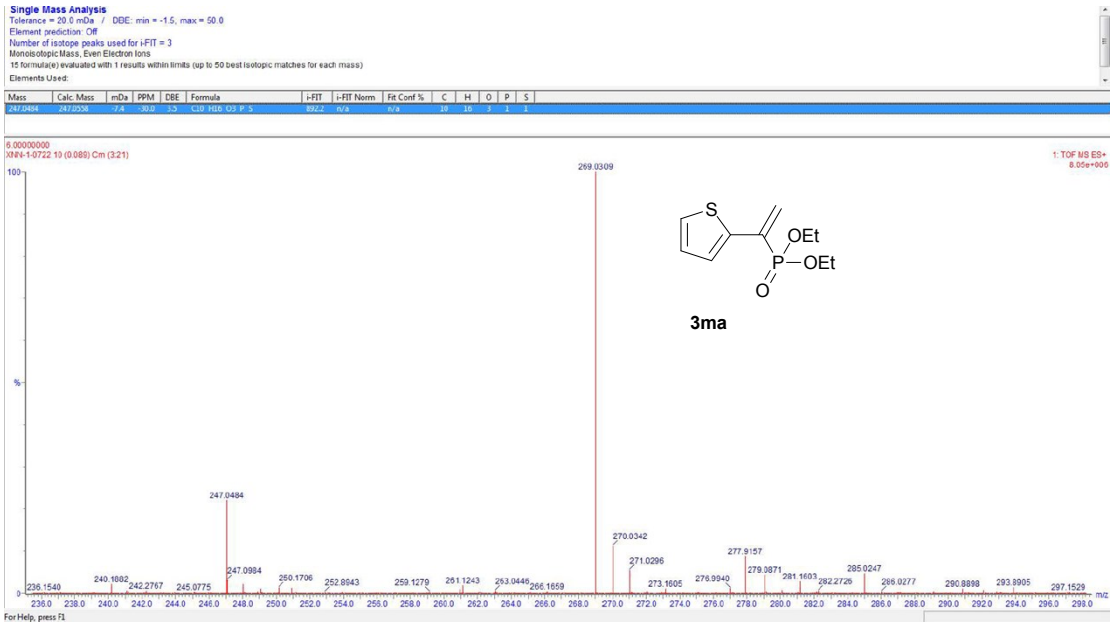
^{1}H NMR of **3ma**



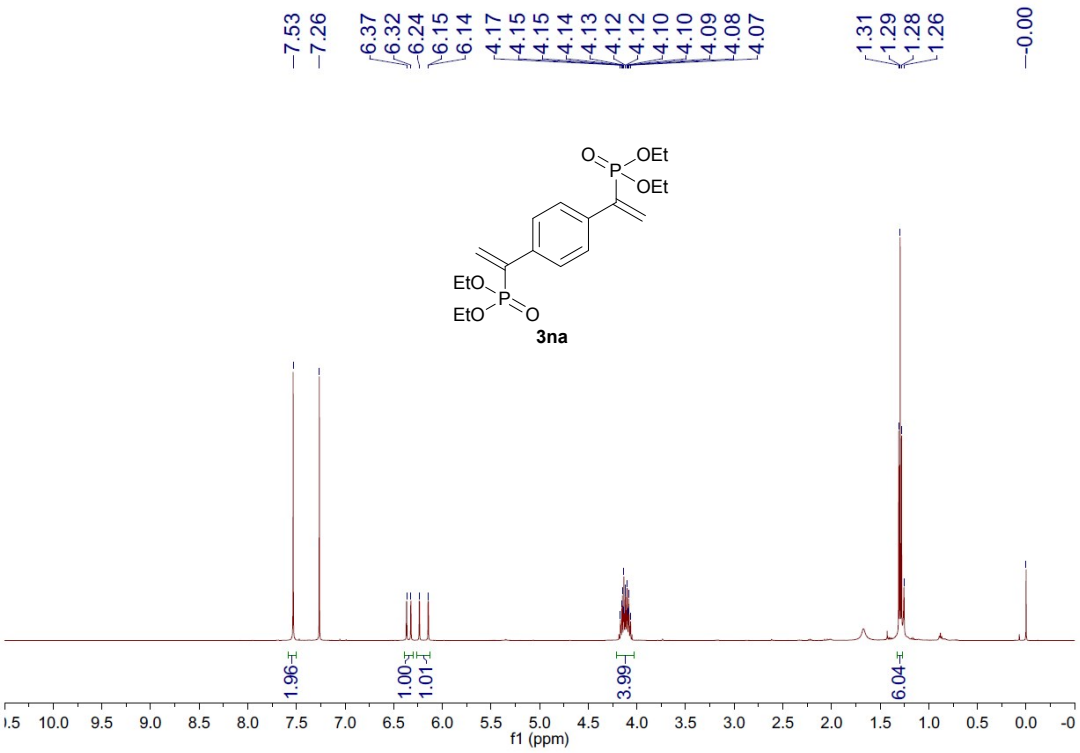
^{13}C NMR of **3ma**



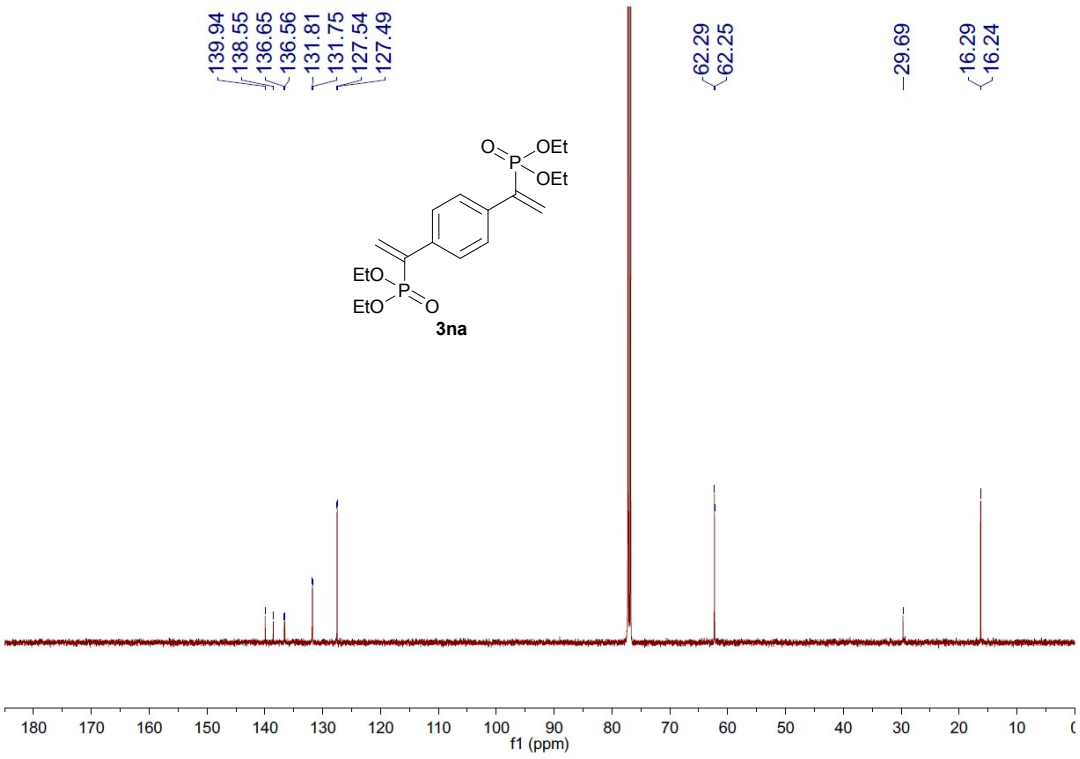
^{31}P NMR of **3ma**



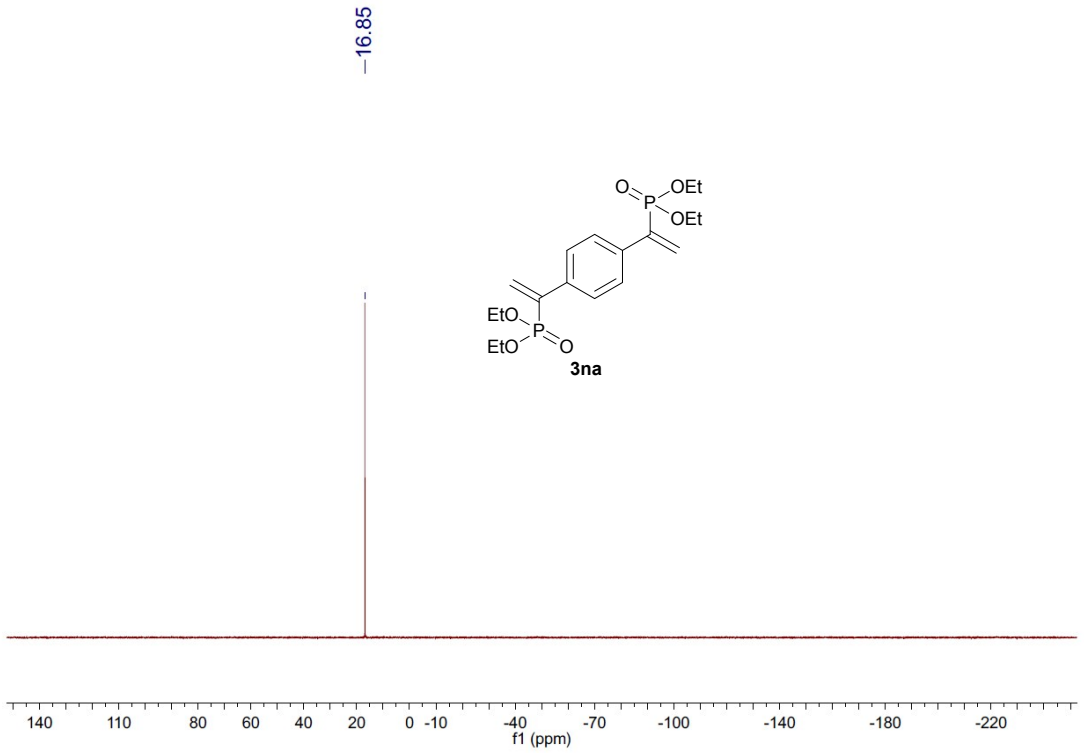
HRMS of **3ma**



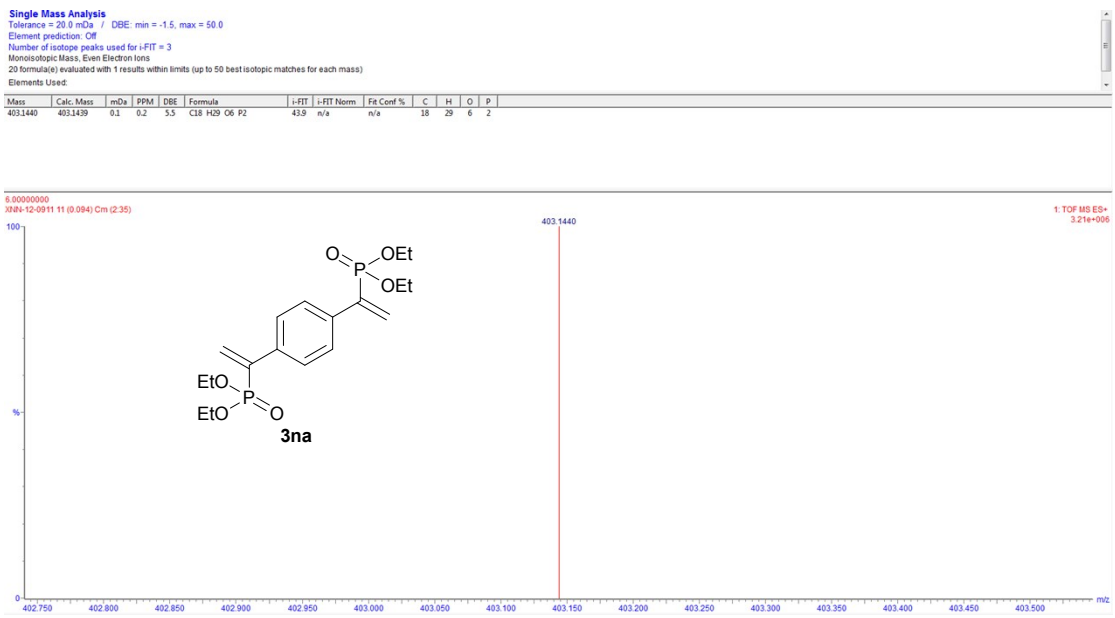
^{1}H NMR of **3na**



^{13}C NMR of **3na**



^{31}P NMR of **3na**



HRMS of **3na**