

Supporting Information

Cu₂O/TiO₂ nanoparticles as visible light photocatalyst concerning C(sp²)-P bond formation

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General Information

All chemicals were either made ready in our laboratories or were purchased from Fluka, Aldrich, Acros, and Merck and all solvents were obtained from commercial sources and purified using standard methods. Products were purified by thin-layer chromatography. Progress of the reactions was followed by TLC using silica gel polygrams SIL G/UV 254 plates. Optical characteristics of catalyst were determined by UV/vis spectrophotometer (Shimadzu UV-2450 spectrophotometer). IR spectra were run on a Shimadzu FT-IR 8300 spectrophotometer and Perkin Elmer spectrum RXI. ^1H -NMR and spectra were recorded in CDCl_3 using a Bruker Avance DPX instrument (operating at 250 MHz for ^1H), ^{13}C NMR (100 MHz, CDCl_3) and ^{31}P NMR (162 MHz, CDCl_3). Catalysts were characterized by power X-ray diffraction (XRD) on a Bruker D8-advance X-ray diffractometer with Cu Ka ($\lambda=1.54178 \text{ \AA}$) incident radiation. The distribution morphology of the product was analyzed by scanning electron microscope (JEOL, JSM-7610F Fe-SEM) and transmission electron microscopy (JEM-2100F, TEM at 200 kV). Metal contents were determined by ICP analyzer (Varian, Vista-pro). The specific surface areas (SSABET; (m^2/g)) of the nanopowders were determined with the nitrogen adsorption measurement applying the BET method at 77 K (BELsorp-mini II). The lamps for irradiation were compact fluorescent lamp (CFL) 15 W white, blue LED 12 W, green LED 12 W and red LED 12 W.

Preparation of TiO_2 nanoparticles

TiO_2 nanostructure was synthesized by the following method. 3.2 mL (0.011 mol) of PEG-300 was added in 600 mL of distilled water under vigorous stirring. Afterward, 0.7 g (0.002 mol) of tetrabutyl titanate digested with ethanol (2-3 mL, Merck) was added drop by drop into the solution. So a white precipitate was produced during the mixing. Then, 5 mL of 5 M NaOH and 15 mL of 5 M hydrazine were added dropwise into the above mixture under

strong stirring, and the resulting mixture was hold onto 12-14°C for 15 min. A white precipitate was then formed. It was filtered and then washed with distilled water to neutral and further 3 times washed with acetone. The sample was then kept at 200°C for 3 h in oven then in 40°C for 24 h in vacuum oven.¹

Preparation of Cu₂O nanoparticles

13.2 g (0.066 mol) of cupric acetate monohydrate was dissolved in 600 mL of distilled water, followed by the addition of 3.2 mL (0.011 mol) of PEG-300 under vigorous stirring. Afterward, 5mL of 5 M NaOH and 15 mL of 5 M hydrazine were added drop by drop sequentially into the above slurry under vigorous stirring, and the resulting mixture was kept standing at 12–14°C for 15 min. An orange precipitate was formed. It was filtered, washed with distilled water to neutral and further 3 times washed with acetone. The sample was then kept at 200°C for 3 h in oven then in 40°C for 24 h in vacuum oven.¹

General procedure for the synthesis of arylhydrazines

Freshly distilled aniline (4 g) was added to a solution of 11 mL concentrate hydrochloric acid in 26 mL water. Sequentially, sodium nitrite solution (3.2 g in 12 mL H₂O) was added to above solution for diazotized. Then, the solution was kept in ice bath. Afterward, 12 g (0.2 mol) NaCl was added with shaking, and the solution cooled in an ice bath. Then, 24 g (0.12 mol) stannous chloride in 11 mL concentrate hydrochloric acid was added to the obtained solution, and after standing for 2h, the salt of arylhydrazine was filtered off and washed with a little saturated NaCl solution. Afterward, it was transferred to a flask and extracted several times with diethyl ether and caustic sodium carbonate solution. Consecutively, the ethereal solution was dried with potassium hydroxide, and concentrated by evaporation.²

Characterization data for compounds

Diethyl phenylphosphonate (3a). Oil³; FT-IR (neat, cm⁻¹): 751, 799, 970, 1031, 1257 (P=O), 2984. ¹H NMR (250 MHz, CDCl₃, ppm): δ = 1.25 (t, J = 7.50 Hz, 6H, 2CH₃), 3.97-4.12 (m, 4H, 2CH₂), 7.34-7.52 (m, 3H, ArH), 7.70-7.78 (m, 2H, ArH). ¹³C NMR (100.6 MHz, CDCl₃, ppm): δ = 132.2 (d, J = 3.0 Hz), 131.5 (d, J = 10.0 Hz), 128.3 (d, J = 15.0 Hz), 128.1 (d, J = 187.0 Hz), 61.9 (d, J = 6.0 Hz), 16.1 (d, J = 6.0 Hz). ³¹P NMR (162 MHz, CDCl₃, ppm): δ = 18.5.

Dimethyl phenylphosphonate (3b). Oil⁴; IR (neat, cm⁻¹): 3459, 2955, 1440, 1242 (P=O), 1050, 753, 696. ¹H NMR (250 MHz, CDCl₃, ppm): δ = 3.69 (d, J = 10.00 Hz, 6H, 2CH₃), 7.34-7.53 (m, 3H, ArH), 7.69-7.77 (m, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 132.6 (d, J = 3.0 Hz), 131.9 (d, J = 11.0 Hz), 128.5 (d, J = 15.0 Hz), 126.9 (d, J = 188.0 Hz), 52.7 (d, J = 5.0 Hz). ³¹P NMR (162 MHz, CDCl₃, ppm): δ = 21.8.

Diethyl (4-nitrophenyl)phosphonate (3c). Yellowish oil⁴; FT-IR (neat, cm⁻¹): 768, 973, 1018, 1049, 1252 (P=O), 1352, 1526, 2985, 3475. ¹H NMR (250 MHz, CDCl₃, ppm): δ = 1.26 (t, J = 15.00 Hz, 6H, 2CH₃), 4.00-4.18 (m, 4H, 2CH₂), 7.89-7.98 (m, 2H, ArH), 8.19-8.24 (m, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 149.6 (d, J = 3.0 Hz), 135.4 (d, J = 186.0 Hz), 132.5 (d, J = 10.0 Hz), 122.8 (d, J = 15.0 Hz), 62.2 (d, J = 6.0 Hz), 15.7 (d, J = 6.0 Hz). ³¹P NMR (162 MHz, CDCl₃, ppm): δ = 14.3.

Dimethyl (4-nitrophenyl)phosphonate (3d). Yellow oil⁵; FT-IR (neat, cm⁻¹): 831, 1025, 1059, 1256 (P=O), 1529, 2961, 3577. ¹H NMR (250 MHz, CDCl₃, ppm): δ = 3.74 (d, J = 10.00 Hz, 6H, 2CH₃), 7.88-7.97 (m, 2H, ArH), 8.21-8.25 (m, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 150.1 (d, J = 3.0 Hz), 134.1 (d, J = 186.0 Hz), 132.9 (d, J = 10.0 Hz), 123.1 (d, J = 15.0 Hz), 52.8 (d, J = 5.0 Hz). ³¹P NMR (162 MHz, CDCl₃, ppm): δ = 17.2.

Diethyl (2-methoxyphenyl)phosphonate (3e). Oil⁶; FT-IR (neat, cm⁻¹): 567, 692, 788, 965, 1026, 1253 (P=O), 1594, 2983, 3463.7. ¹H NMR (250 MHz, CDCl₃, ppm): δ = 2.05 (t, J = 12.50 Hz, 6H, 2CH₃), 4.57 (s, 3H, OMe), 4.75-4.93 (m, 4H, 2CH₂), 7.78-7.85 (m, 1H, ArH), 8.01-8.14 (m, 3H, ArH). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 159.4 (d, J = 19.0 Hz), 129.7 (d, J = 18.0 Hz), 129.5 (d, J = 185.0 Hz), 123.9 (d, J = 10.0 Hz), 118.7 (d, J = 3.0 Hz), 116.3 (d, J = 12.0 Hz), 62.1 (d, J = 5.0 Hz), 55.43, 16.3 (d, J = 7.0 Hz). ³¹P NMR (162 MHz, CDCl₃, ppm): δ = 18.6.

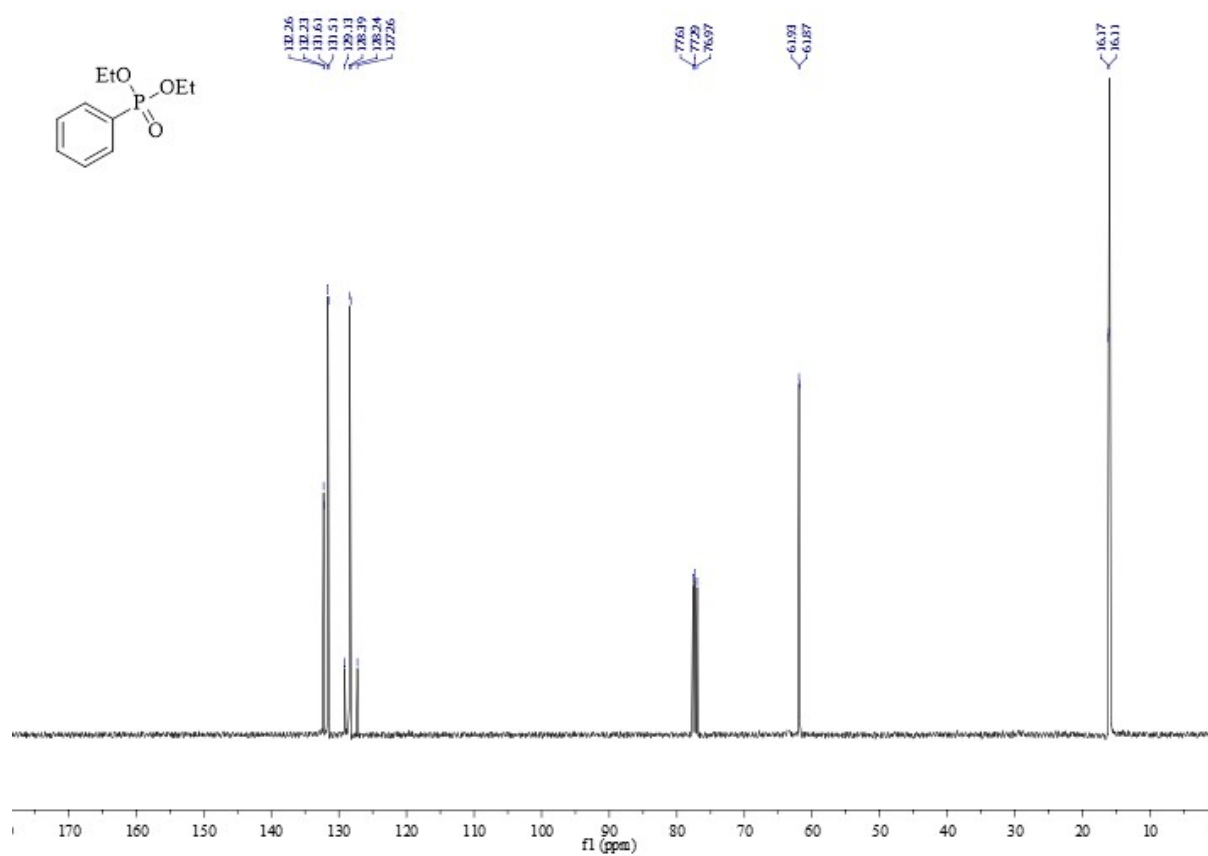
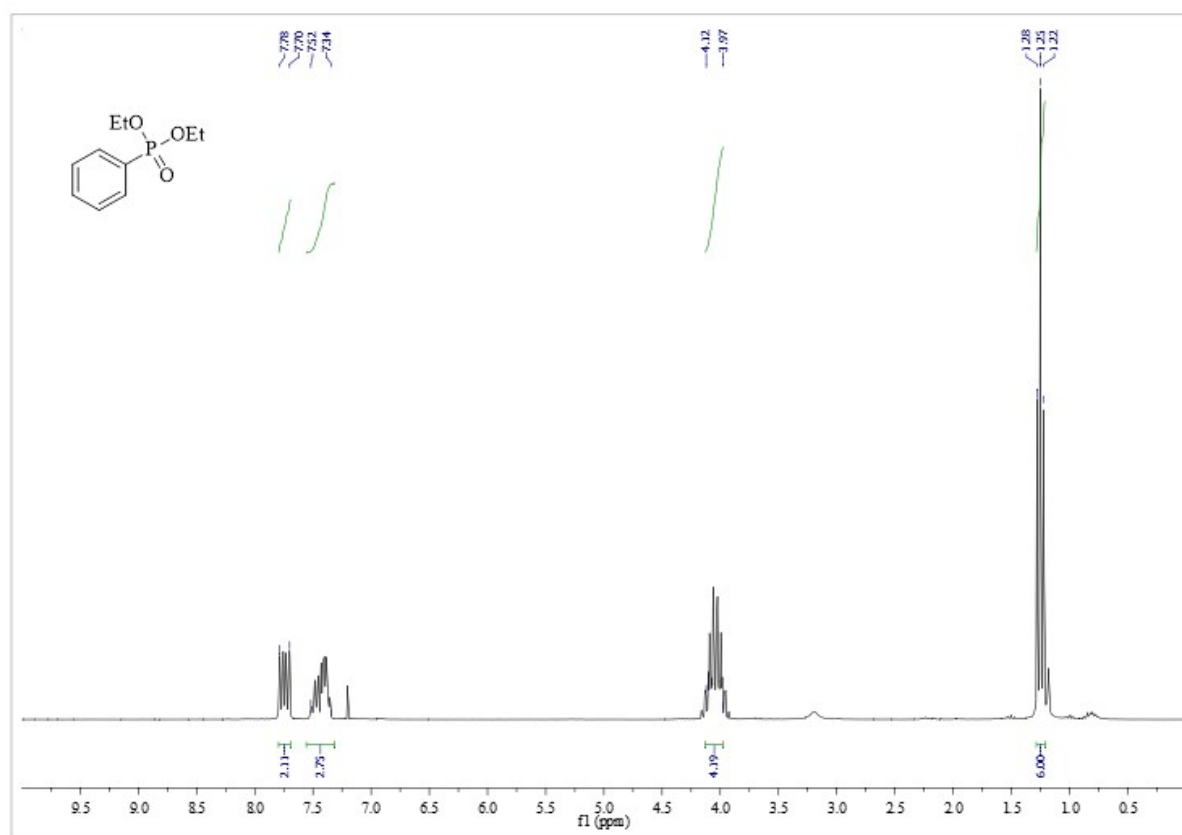
Dimethyl (2-methoxyphenyl)phosphonate (3f). Oil⁷; FT-IR (neat, cm⁻¹): 567, 788, 966, 1029, 1288 (P=O), 1485, 1594, 2983, 3459. ¹H NMR (250 MHz, CDCl₃, ppm): δ = 3.69 (d, J = 12.50 Hz, 6H, 2CH₃), 3.78 (s, 3H, OMe), 6.96-7.11 (m, 1H, ArH), 7.22-7.37 (m, 3H, ArH). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 159.4 (d, J = 19.0 Hz), 129.7 (d, J = 18.0 Hz), 129.6 (d, J = 187.0 Hz), 124.0 (d, J = 8.0 Hz), 118.8 (d, J = 2.0 Hz), 116.3 (d, J = 11.0 Hz), 62.2 (d, J = 5.0 Hz), 55.4. ³¹P NMR (162 MHz, CDCl₃, ppm): δ = 18.9.

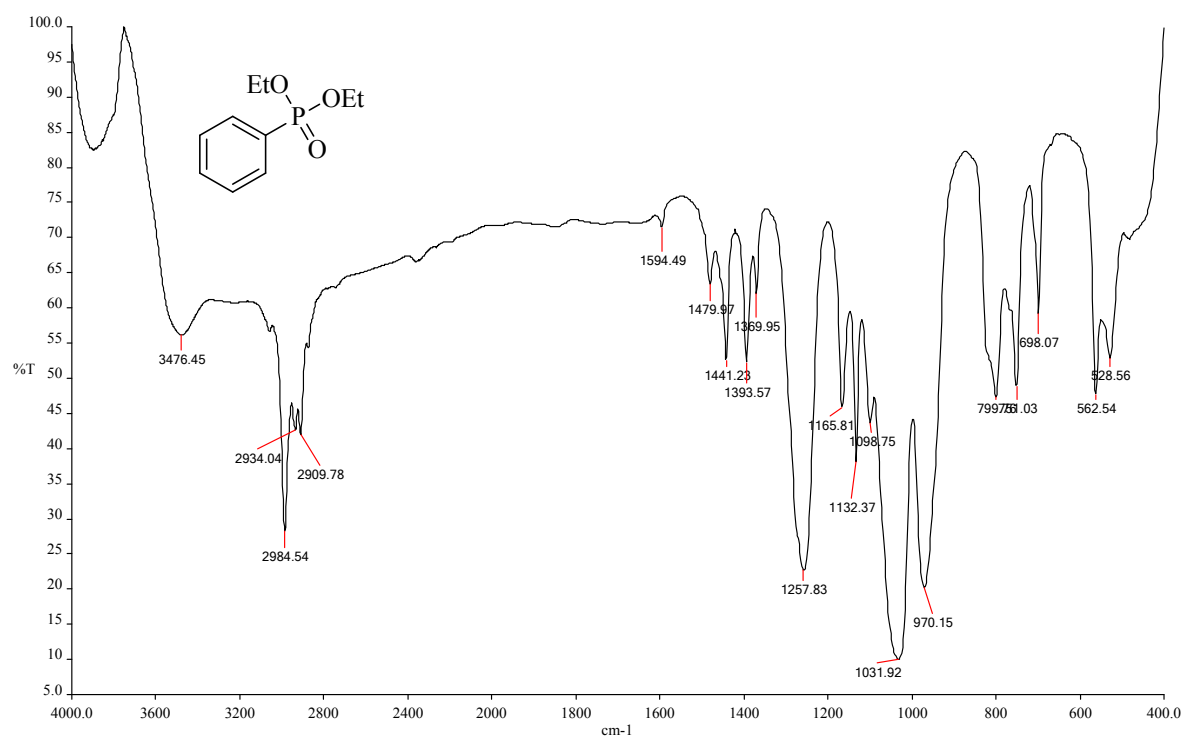
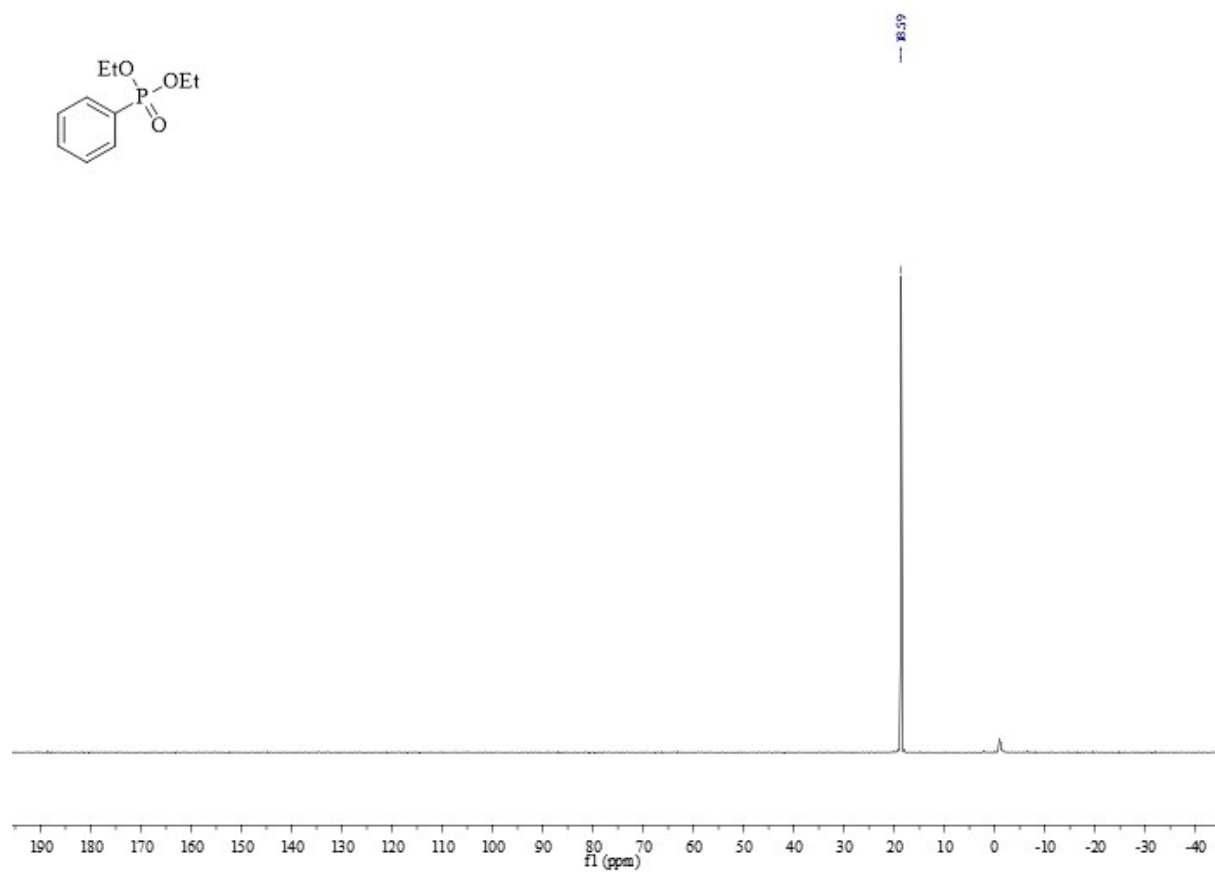
Diethyl (4-chlorophenyl)phosphonate (3g). Colorless oil^{8,9}; FT-IR (neat, cm⁻¹): 743, 1073, 1124, 1275, 1461, 1729, 2927, 2958. ¹H NMR (250 MHz, CDCl₃, ppm): δ = 1.34 (t, J = 7.5 Hz, 6H, 2CH₃), 4.12-4.20 (m, 4H, 2CH₂), 7.42-7.50 (m, 2H, ArH), 7.58-7.67 (m, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 138.8 (d, J = 4.0 Hz), 132.9 (d, J = 10.8 Hz), 128.7 (d, J = 15.6 Hz), 126.9 (d, J = 190 Hz), 62.1 (d, J = 5.5 Hz), 16.1 (d, J = 6.4 Hz).

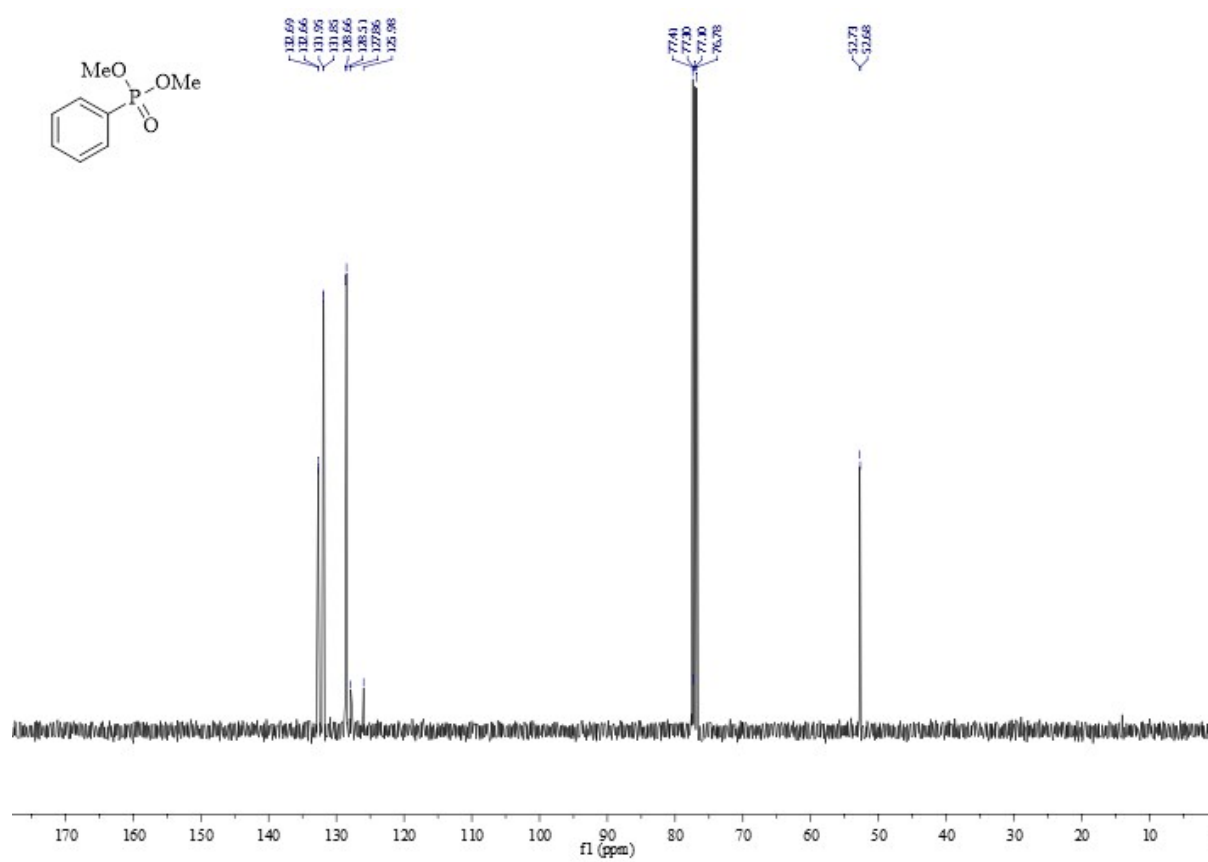
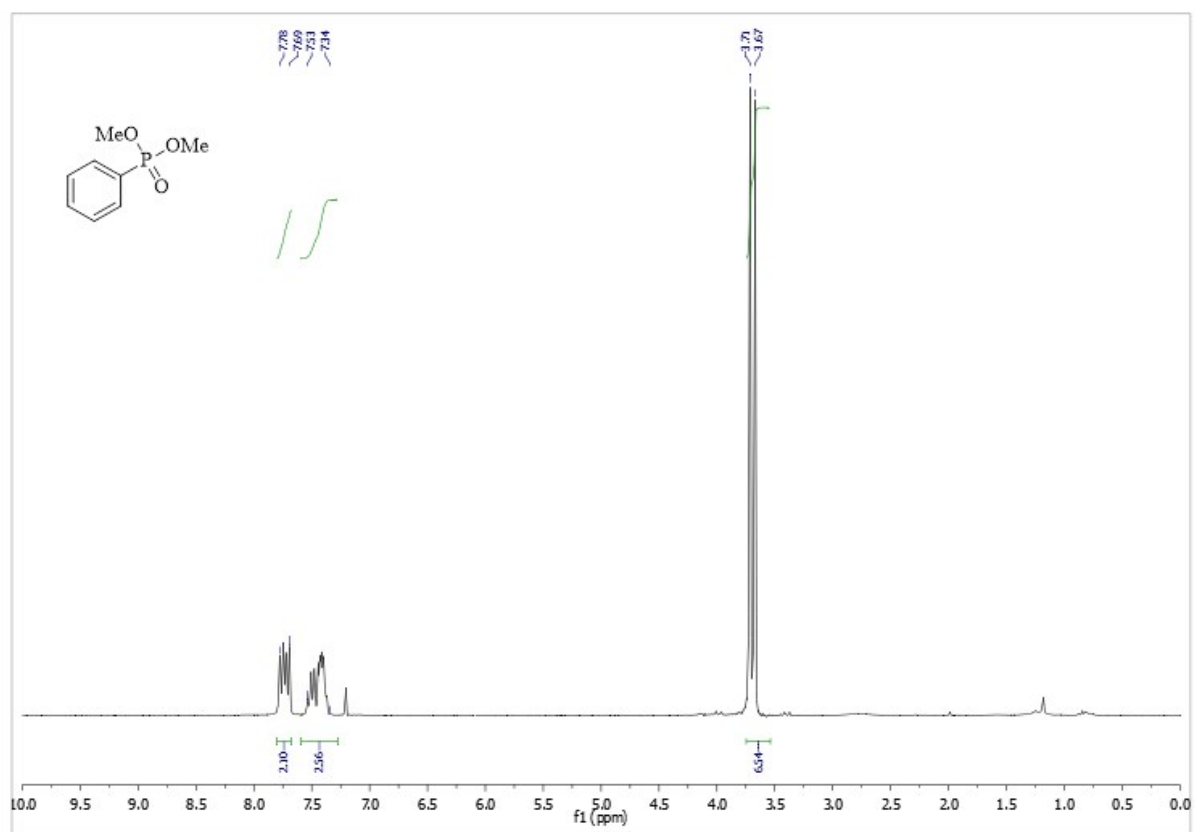
Dimethyl(4-Chlorophenyl)phosphonate (3h). Colorless oil⁵; FT-IR (neat, cm⁻¹): 743, 1072, 1123, 12.74, 14.63, 1730, 2930, 2959. ¹H NMR (250 MHz, CDCl₃, ppm): δ = 4.15 (d, J = 10.0 Hz, 6H), 7.42-7.50 (m, 2H, ArH), 7.60-7.68 (m, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 139.6 (d, J = 6.8 Hz), 133.6 (d, J = 14.4 Hz), 129.0 (d, J = 3.8 Hz), 126.1 (d, J = 193.6 Hz), 53.2 (d, J = 5.4 Hz).

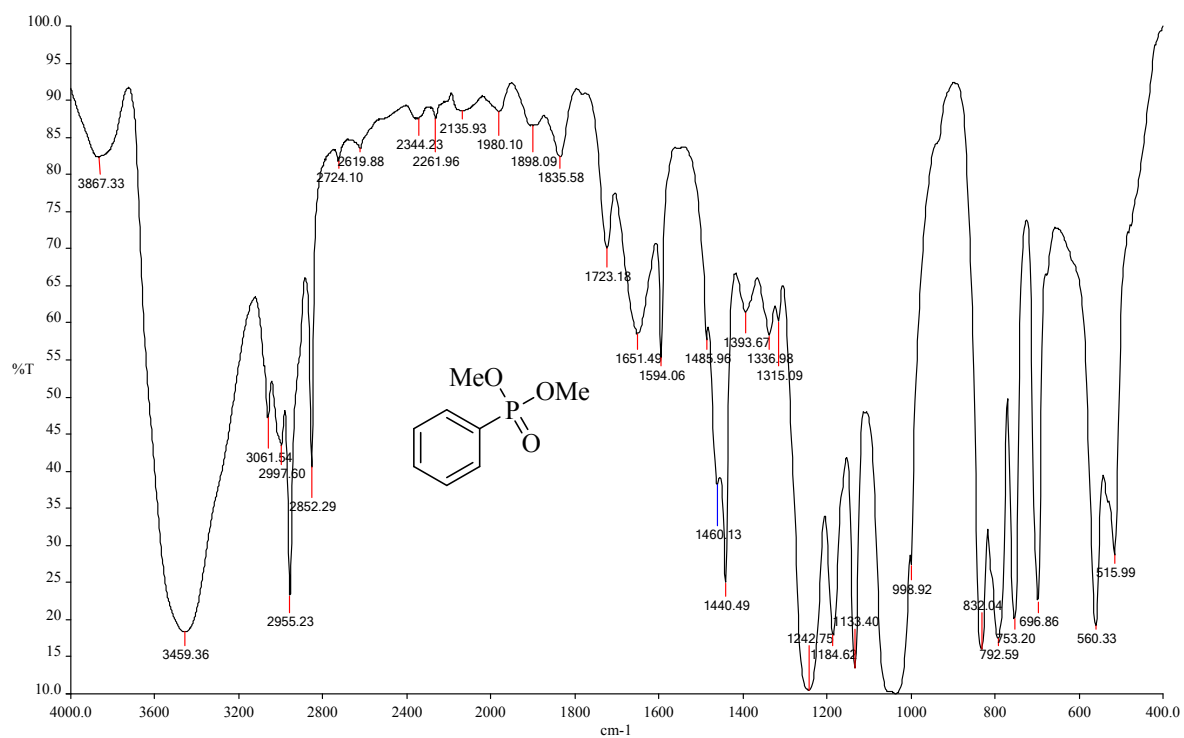
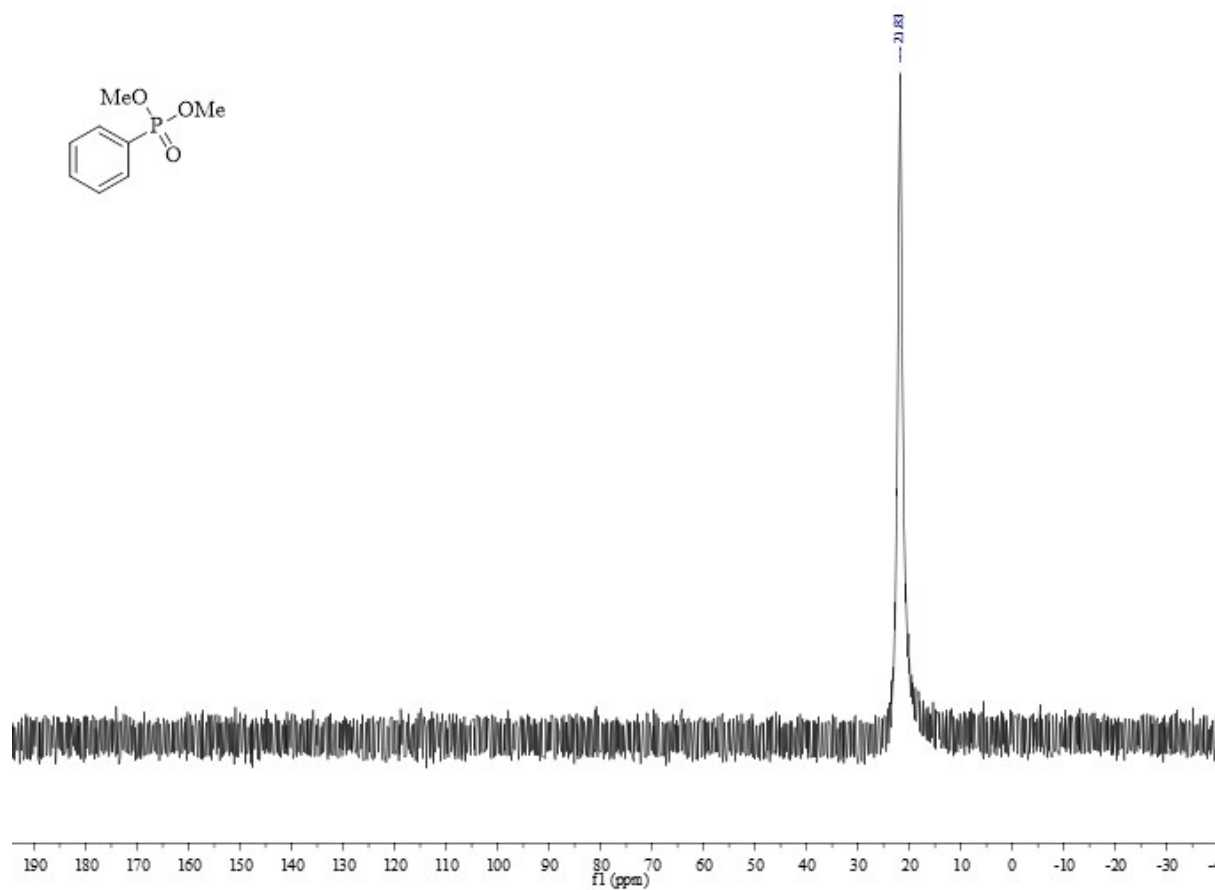
Diethyl (3-nitrophenyl)phosphonate (3i). Yellow oil¹⁰; FT-IR (neat, cm⁻¹): 743, 831, 1007, 1284, 1343, 1530, 1608, 1744, 2854, 2925, 3086. ¹H NMR (250 MHz, CDCl₃, ppm): δ = 1.18 (t, J = 7.5 Hz, 6H, 2CH₃), 3.99-4.08 (m, 4H, 2CH₂), 7.12-7.17 (m, 2H, ArH), 8.36-8.41 (m, 1H, ArH), 8.69-8.70 (m, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 148.0 (d, J = 18.3 Hz), 137.4 (d, J = 9.9 Hz), 131.3 (d, J = 190.9 Hz), 129.7 (d, J = 15.7 Hz), 126.8 (d, J = 3.1 Hz), 126.5 (d, J = 11.5 Hz), 62.8 (d, J = 5.9 Hz), 16.3 (d, J = 6.1 Hz).

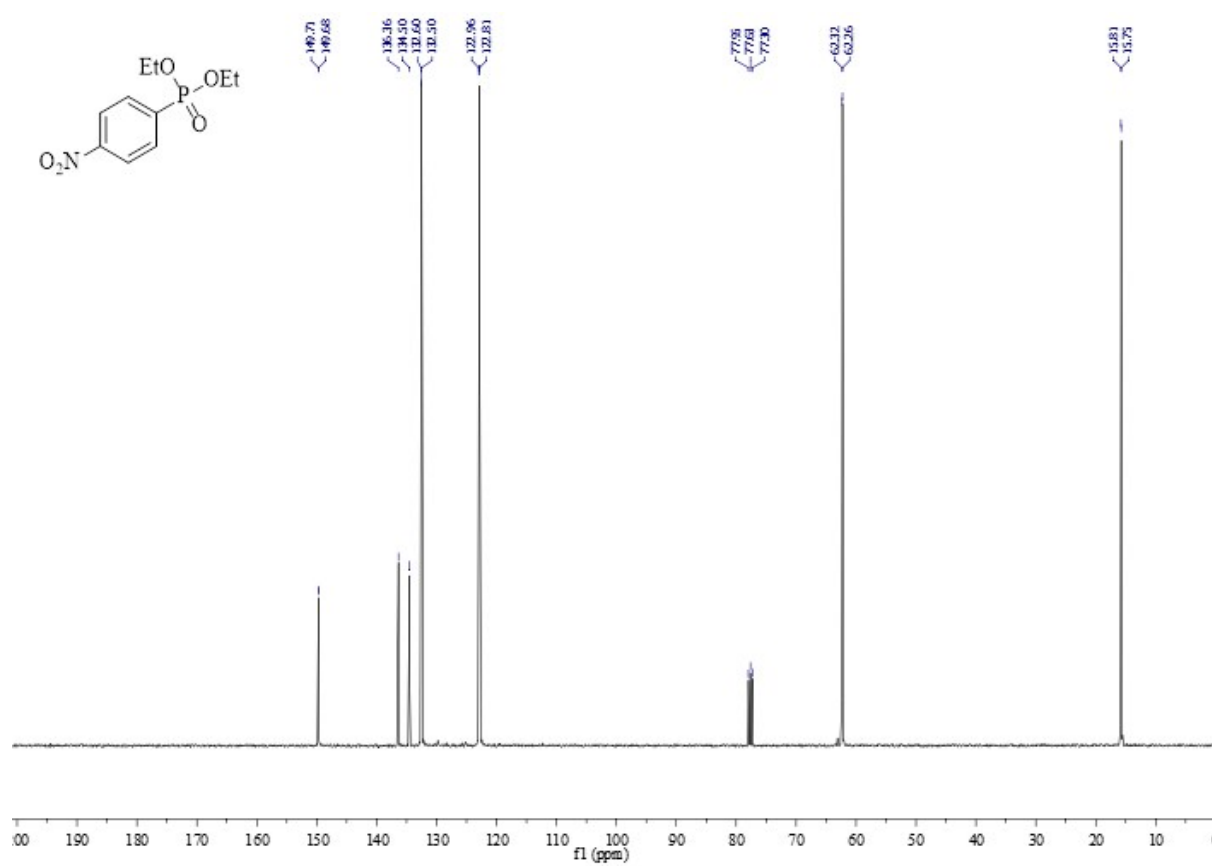
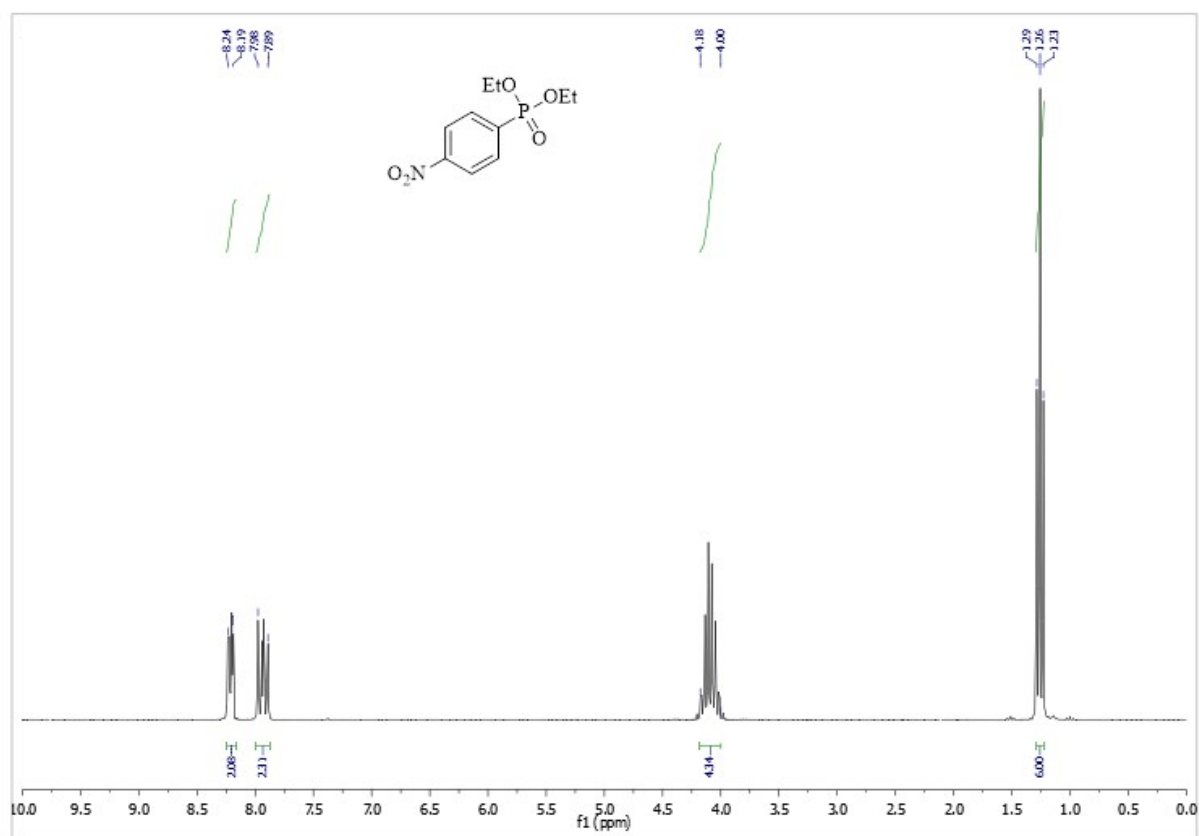
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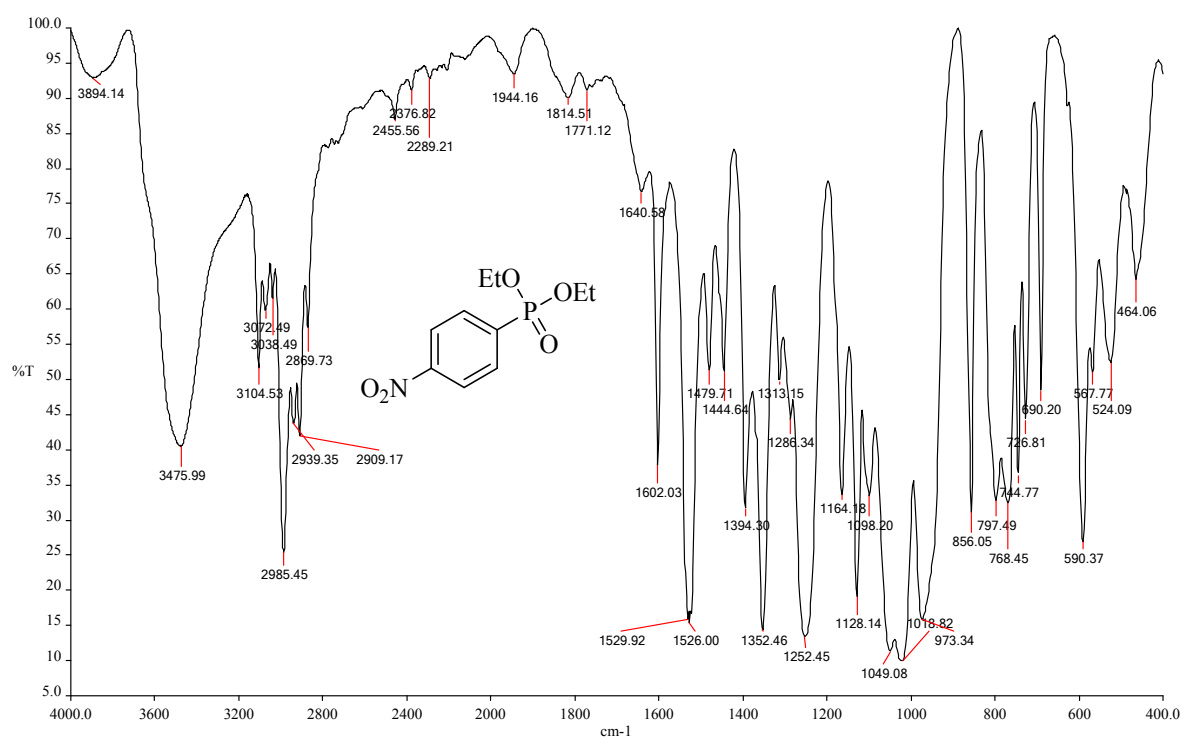
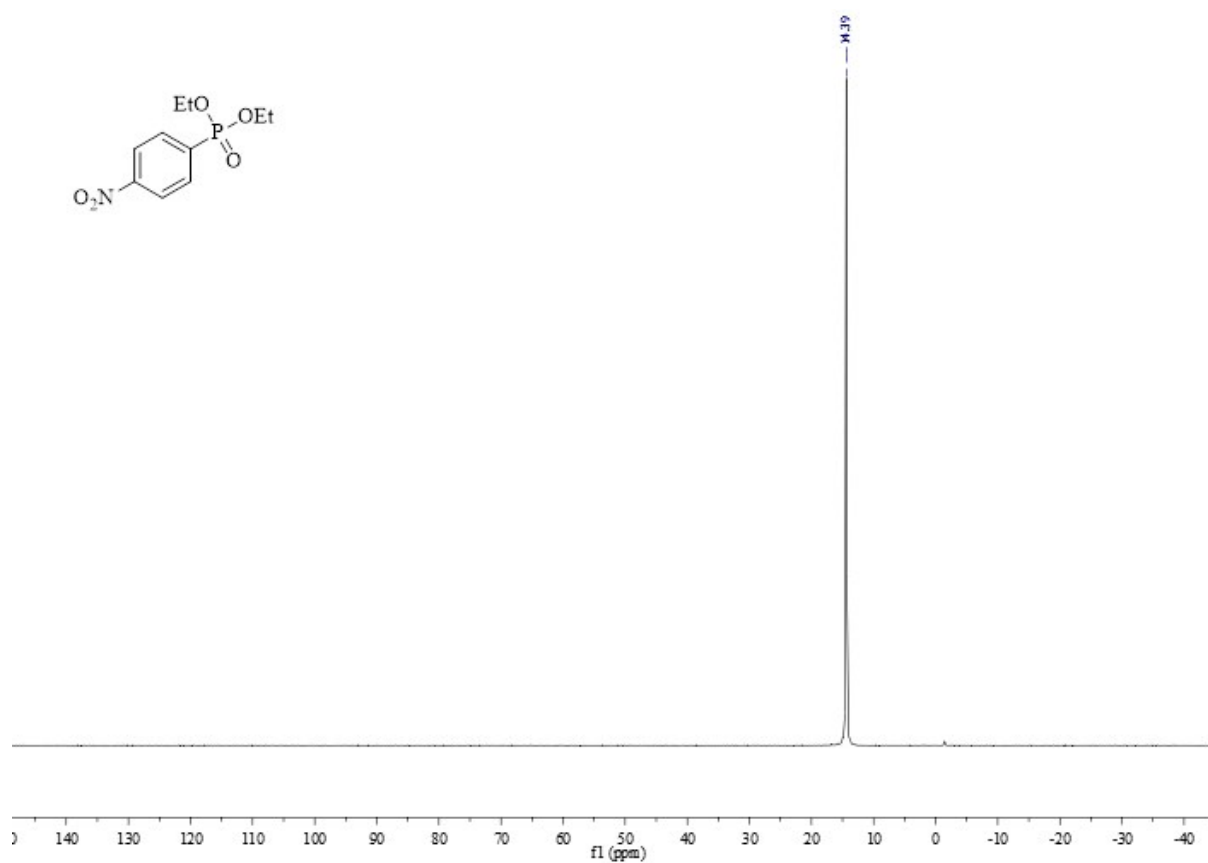


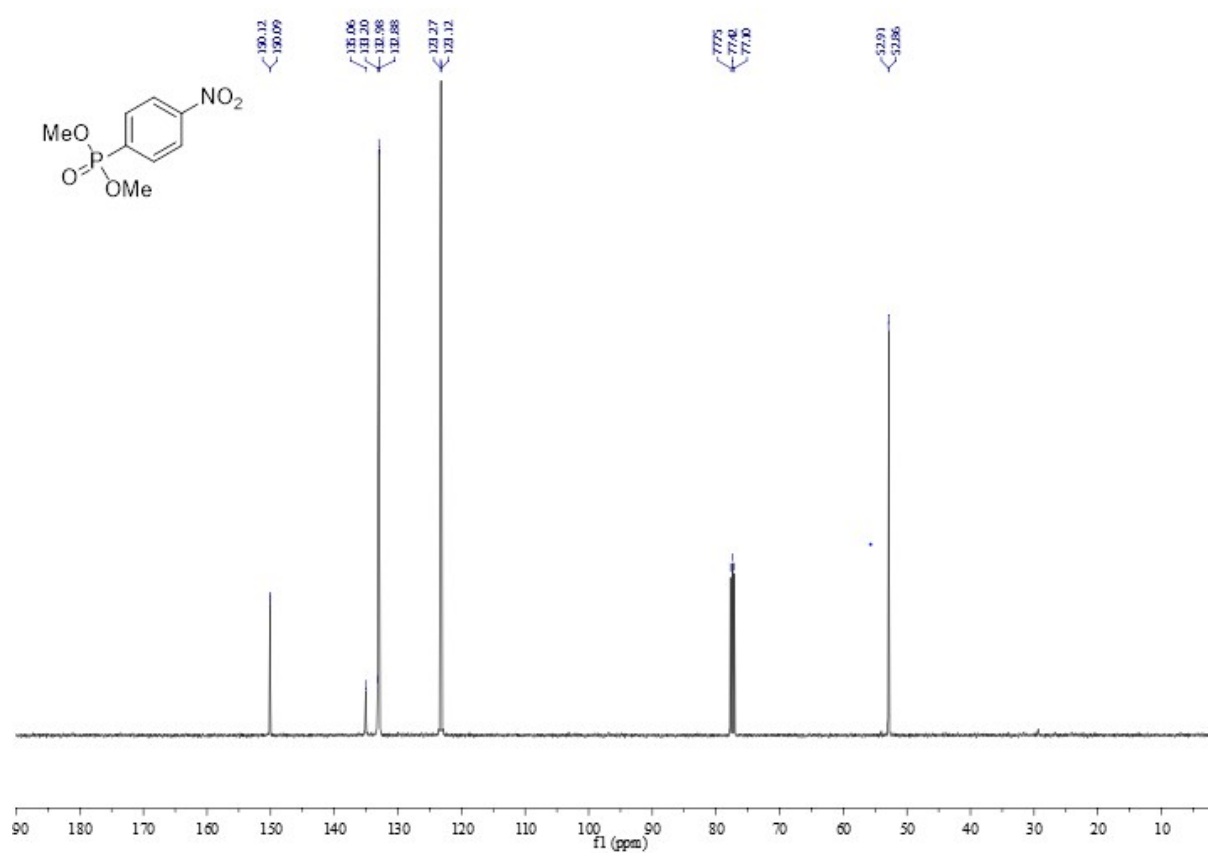
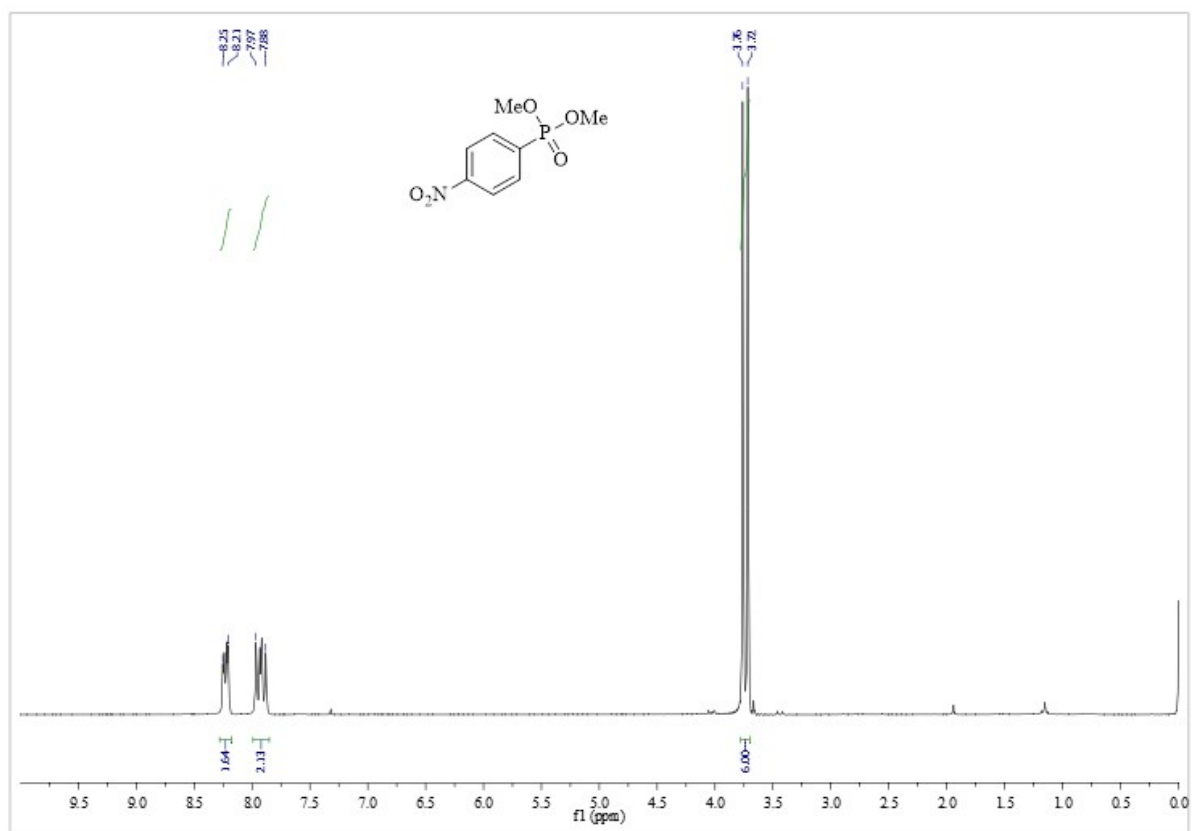


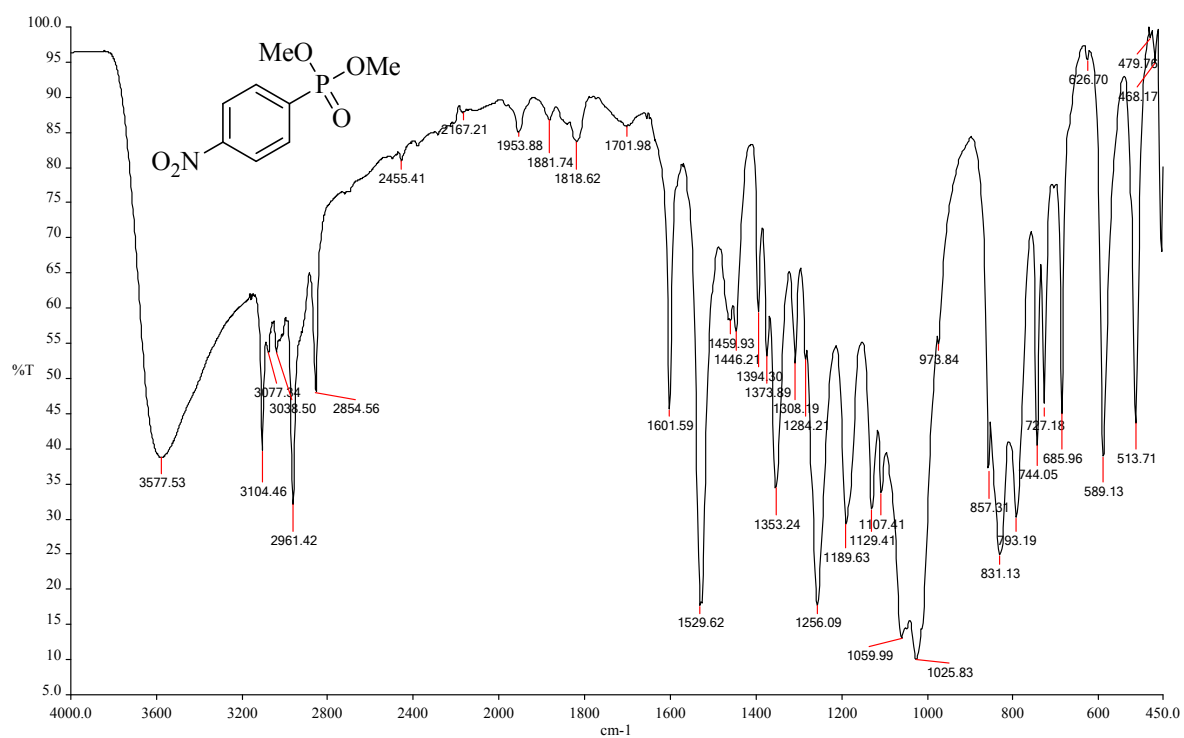
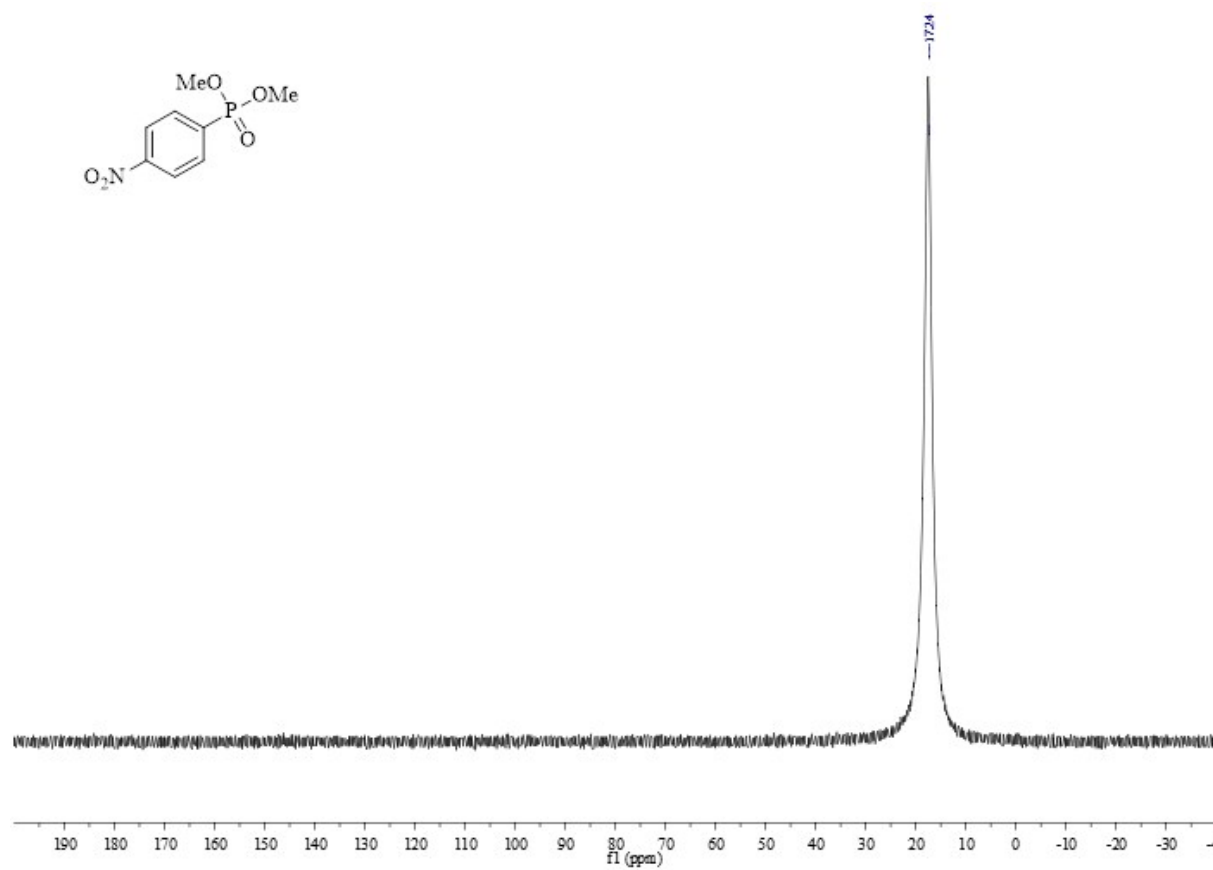


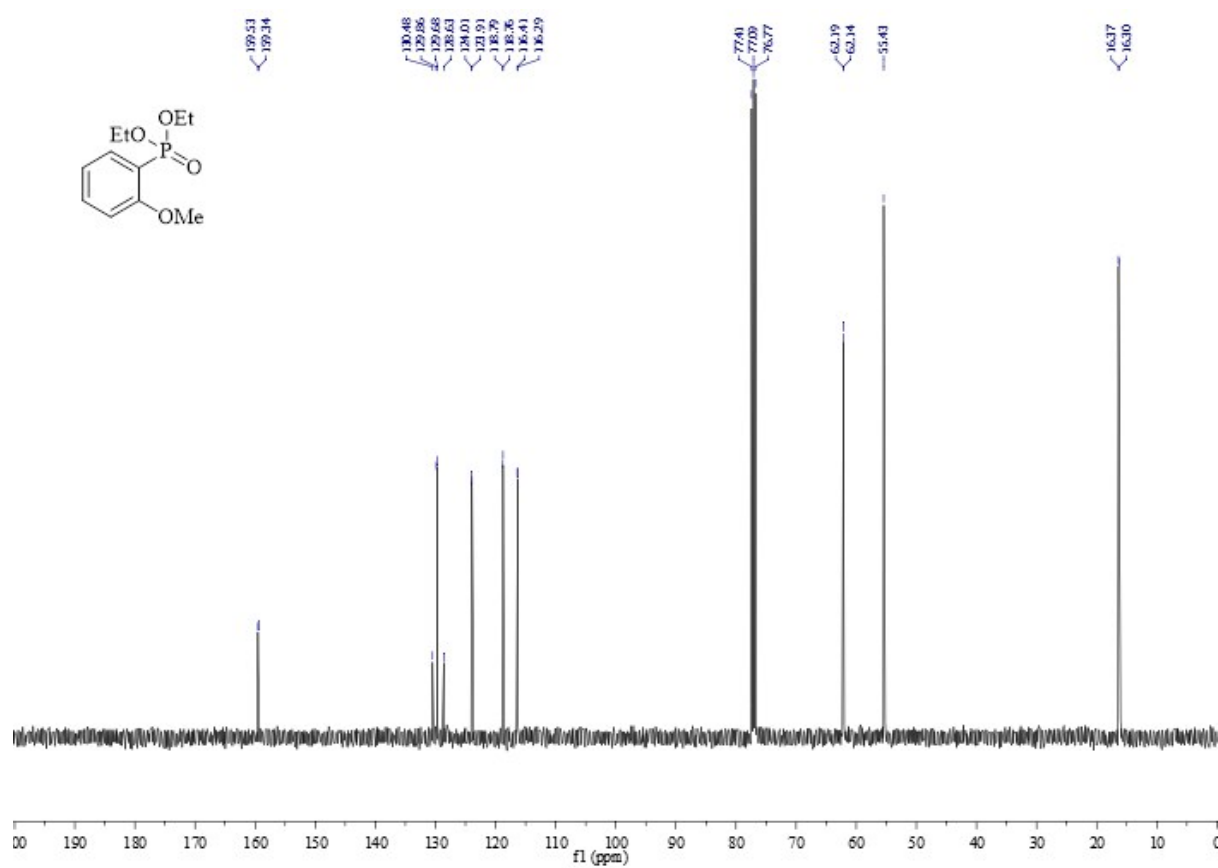
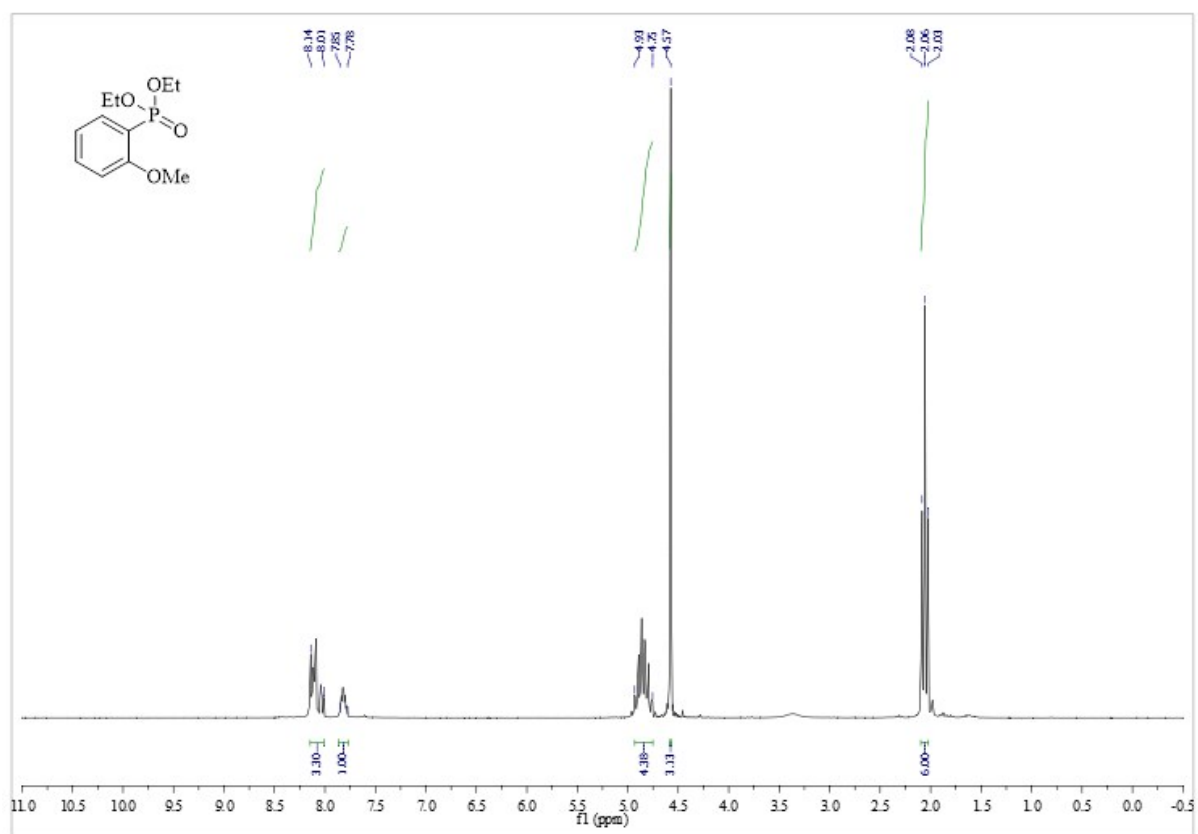


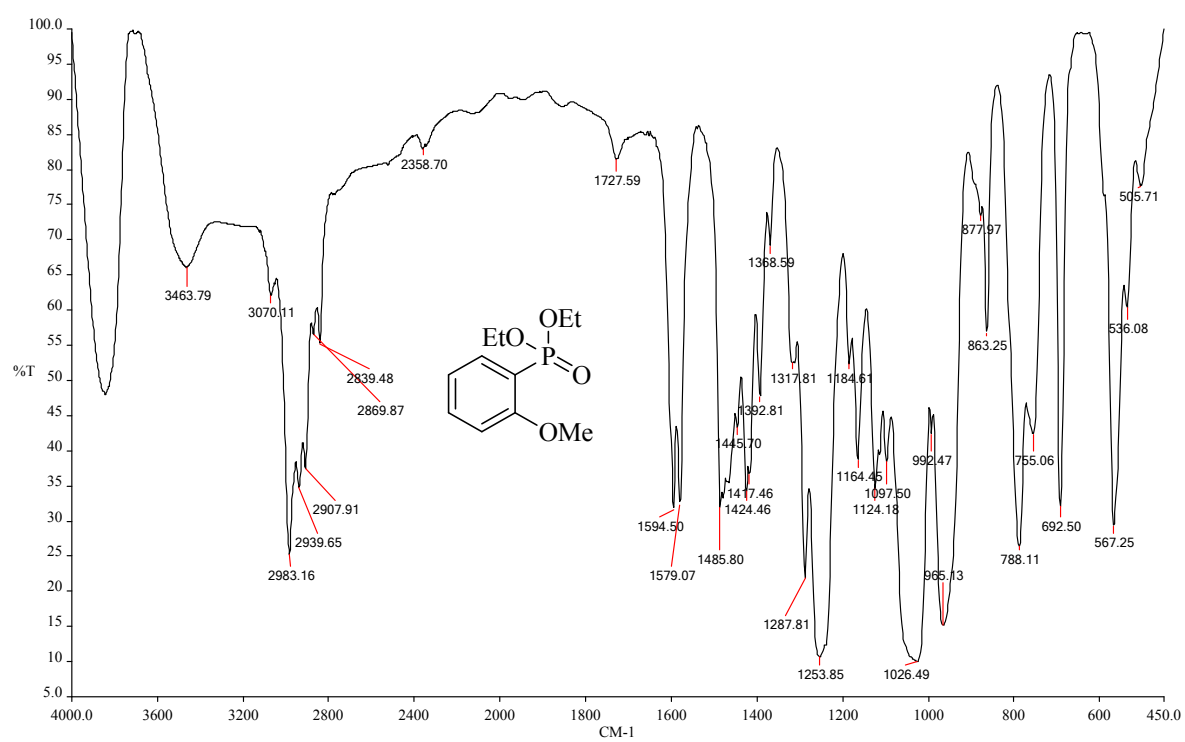
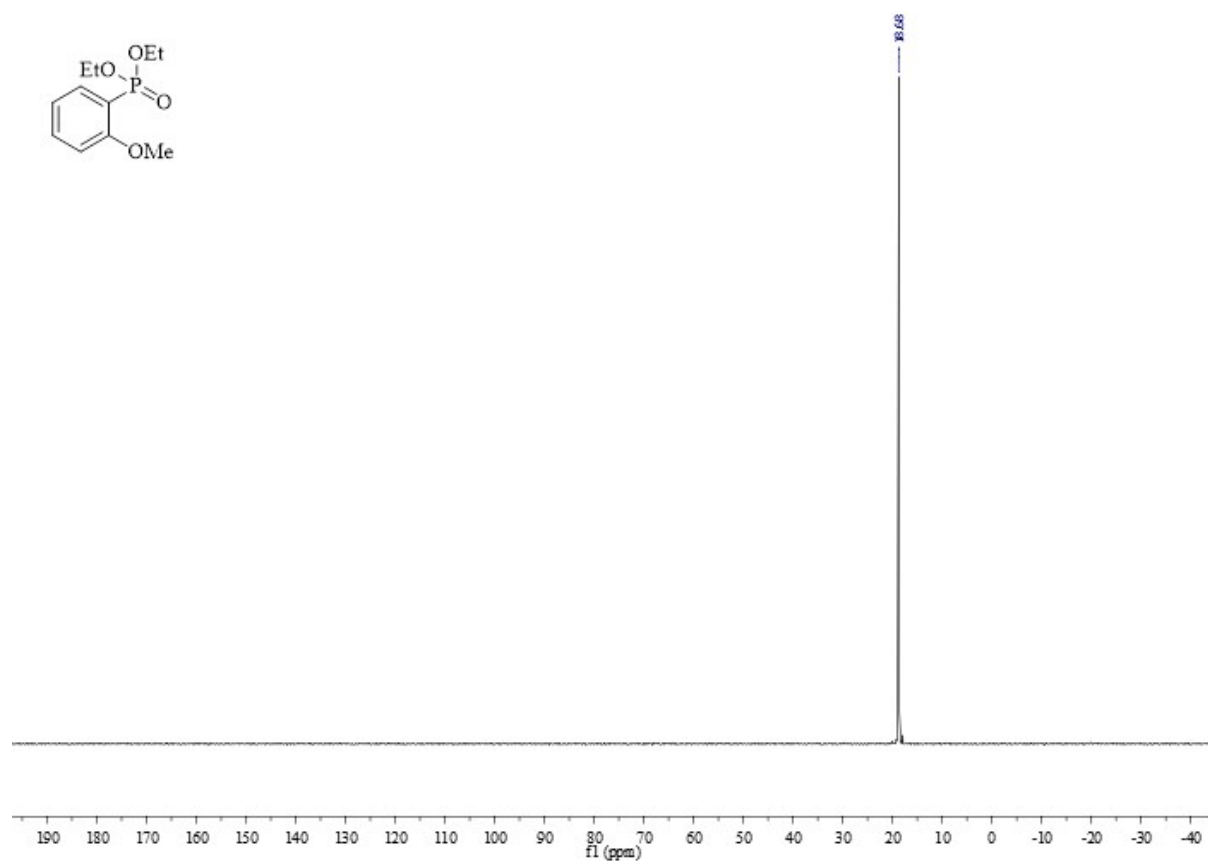


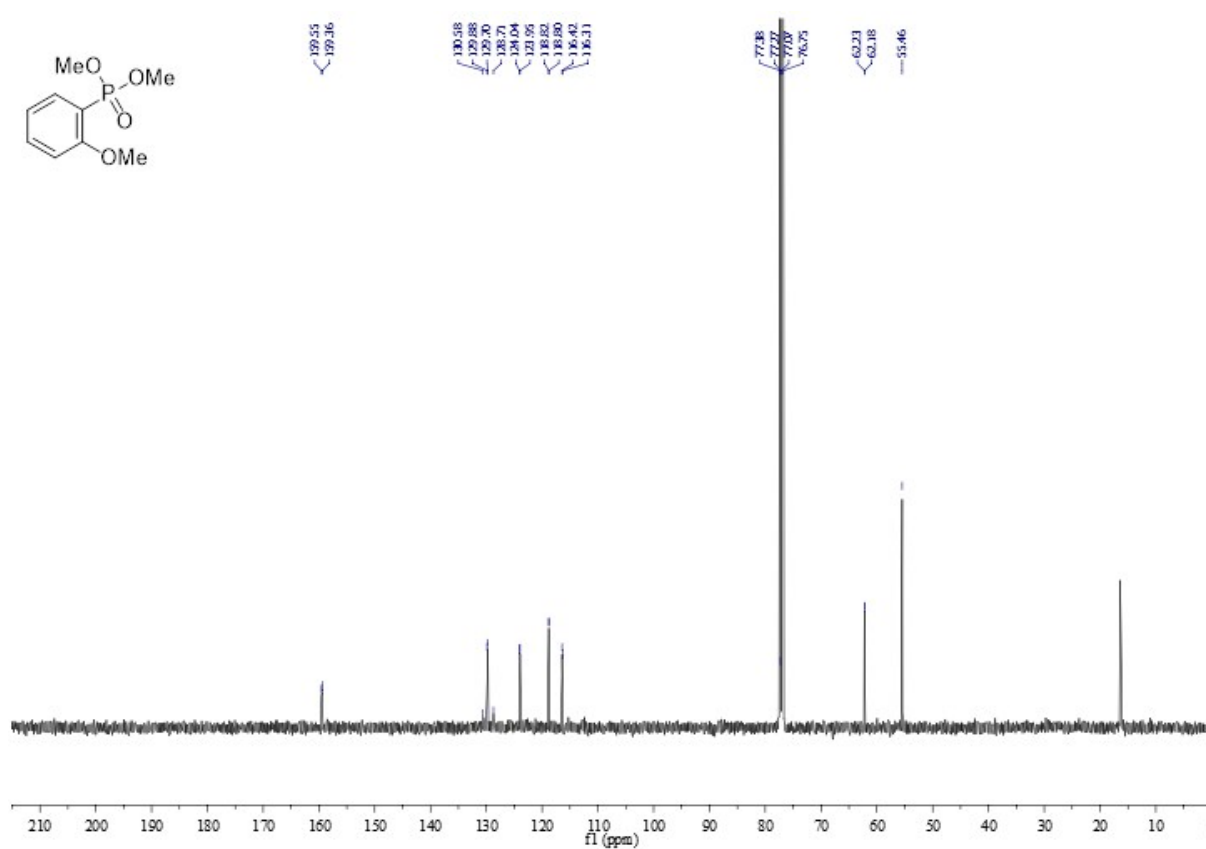
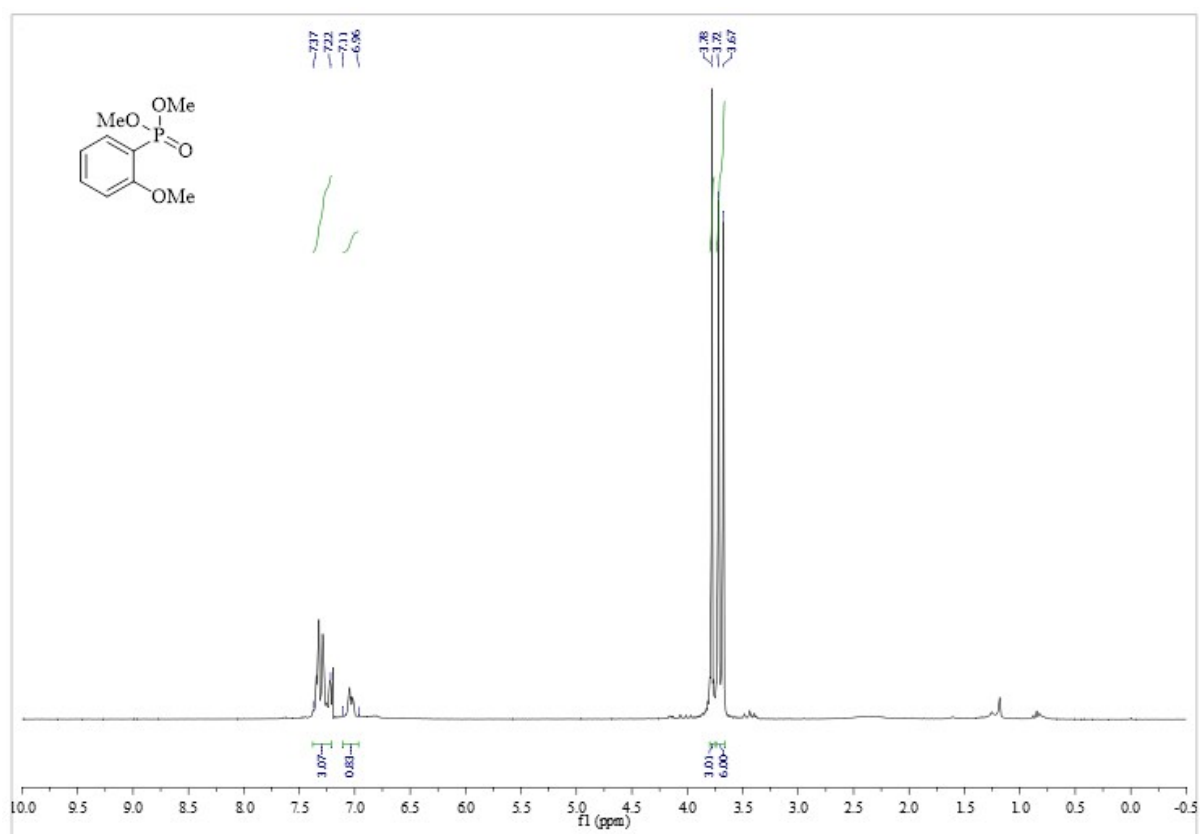


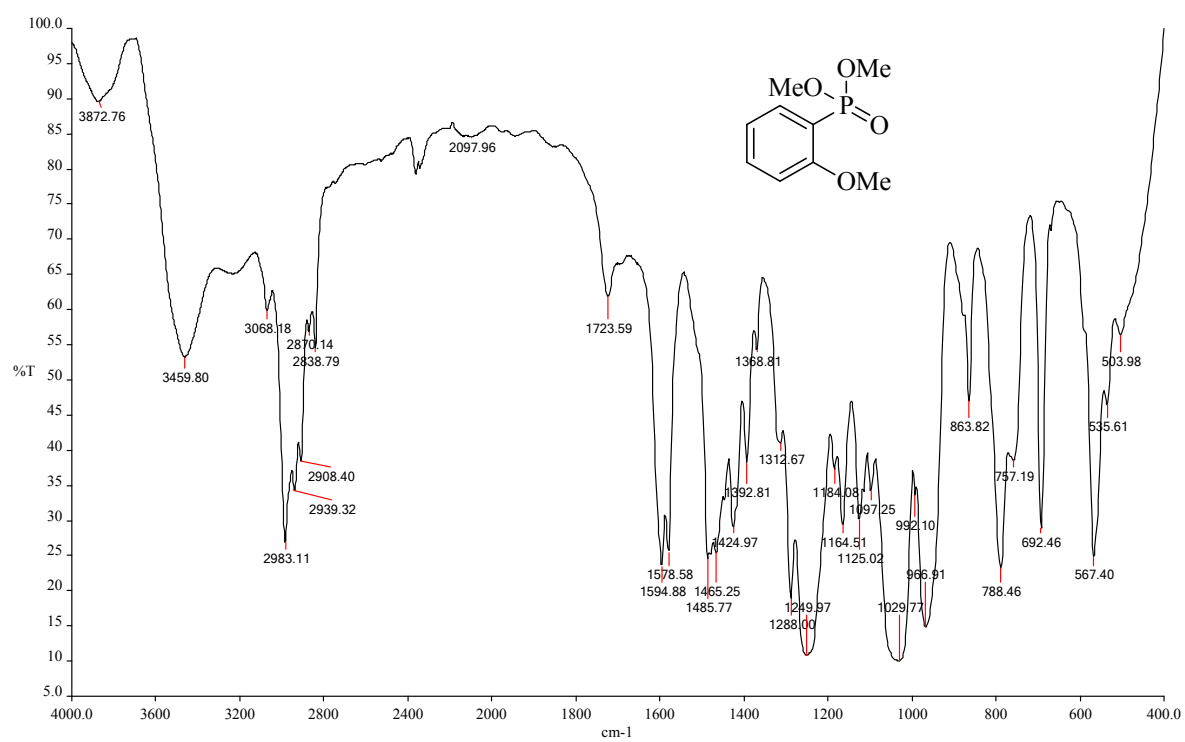
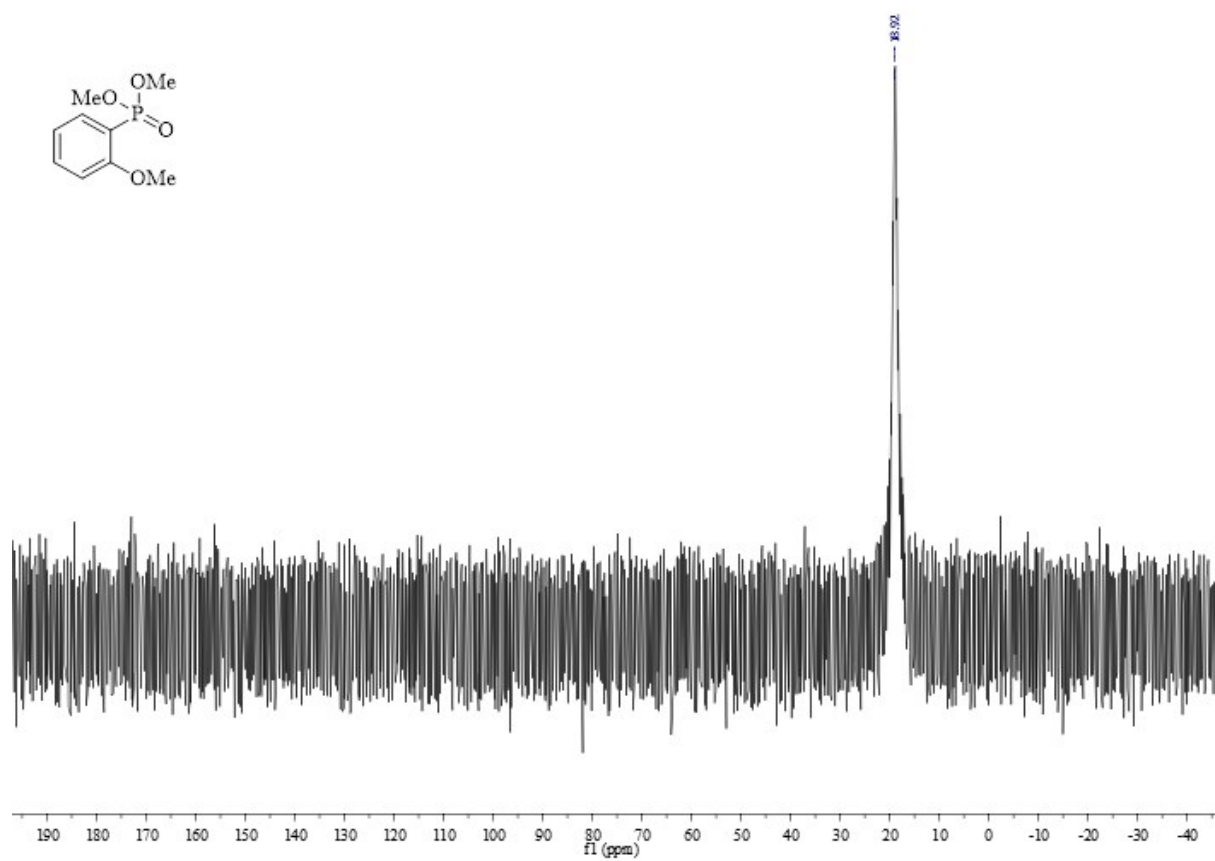


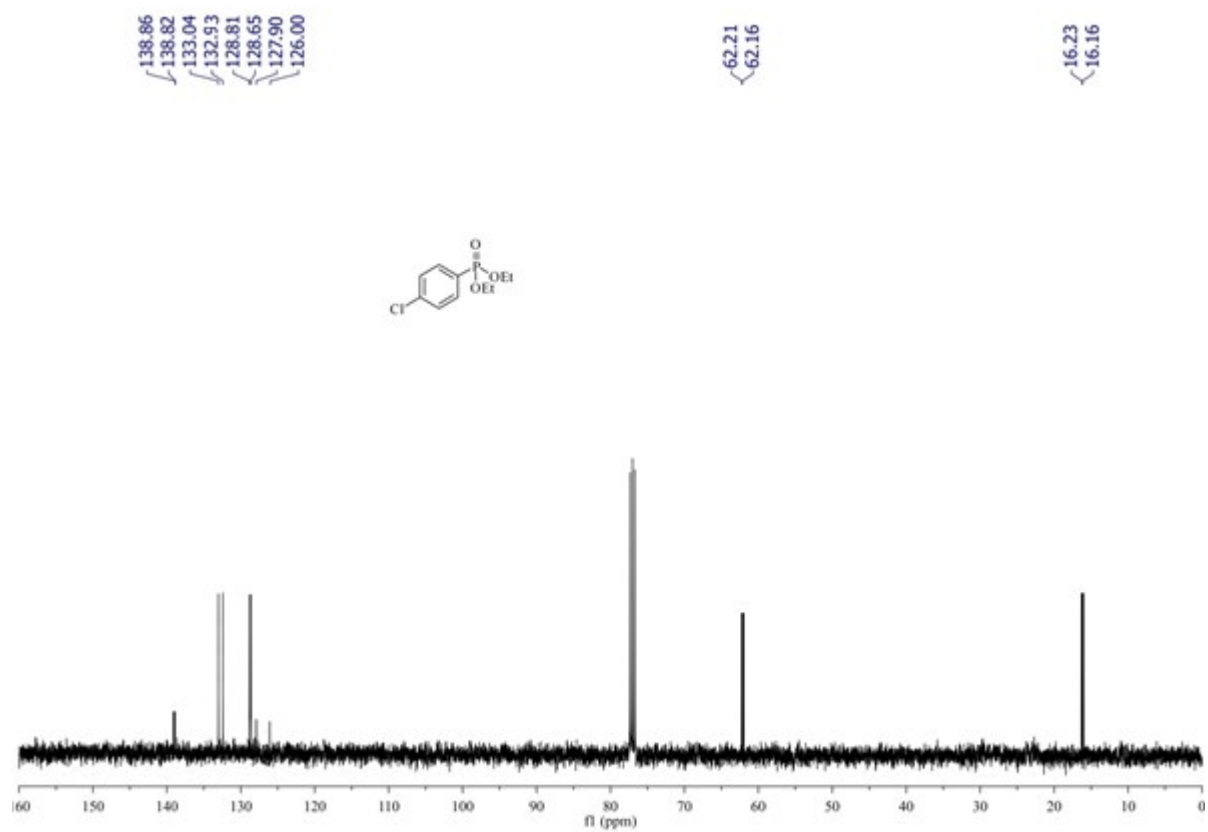
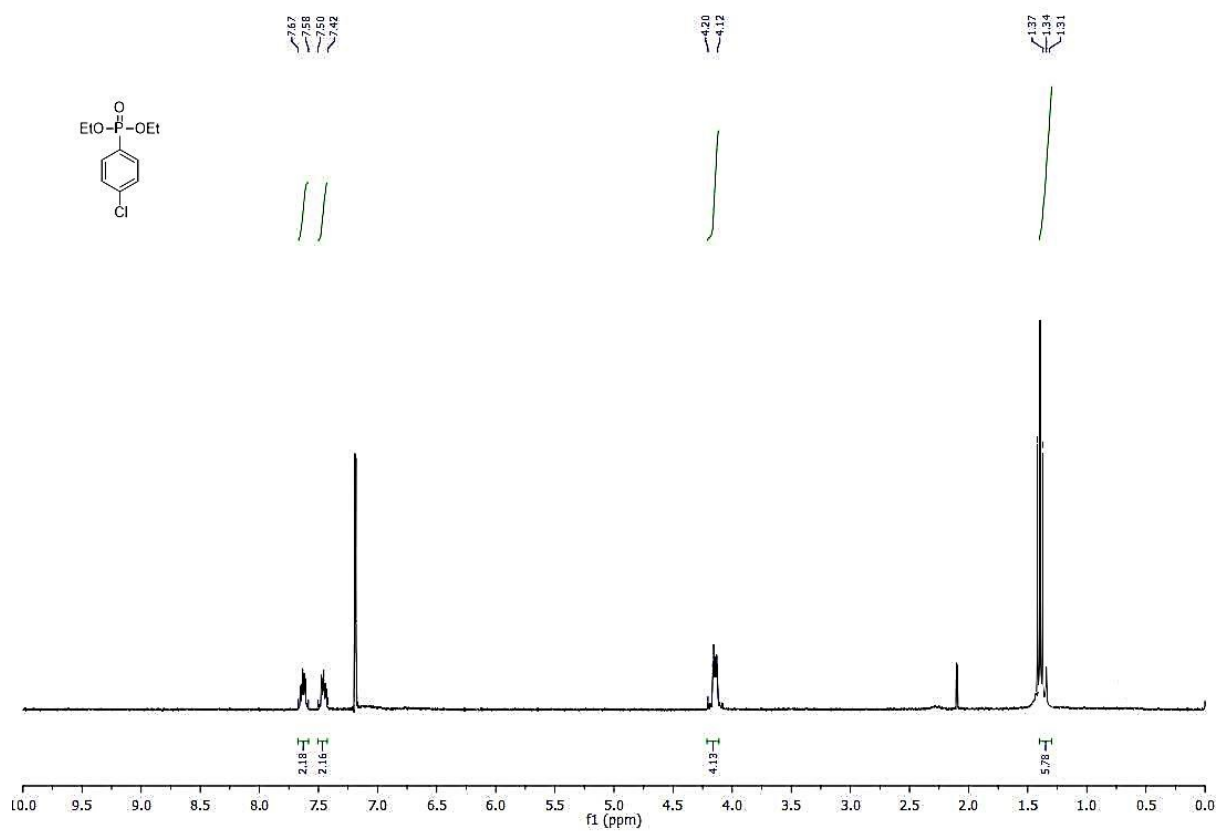


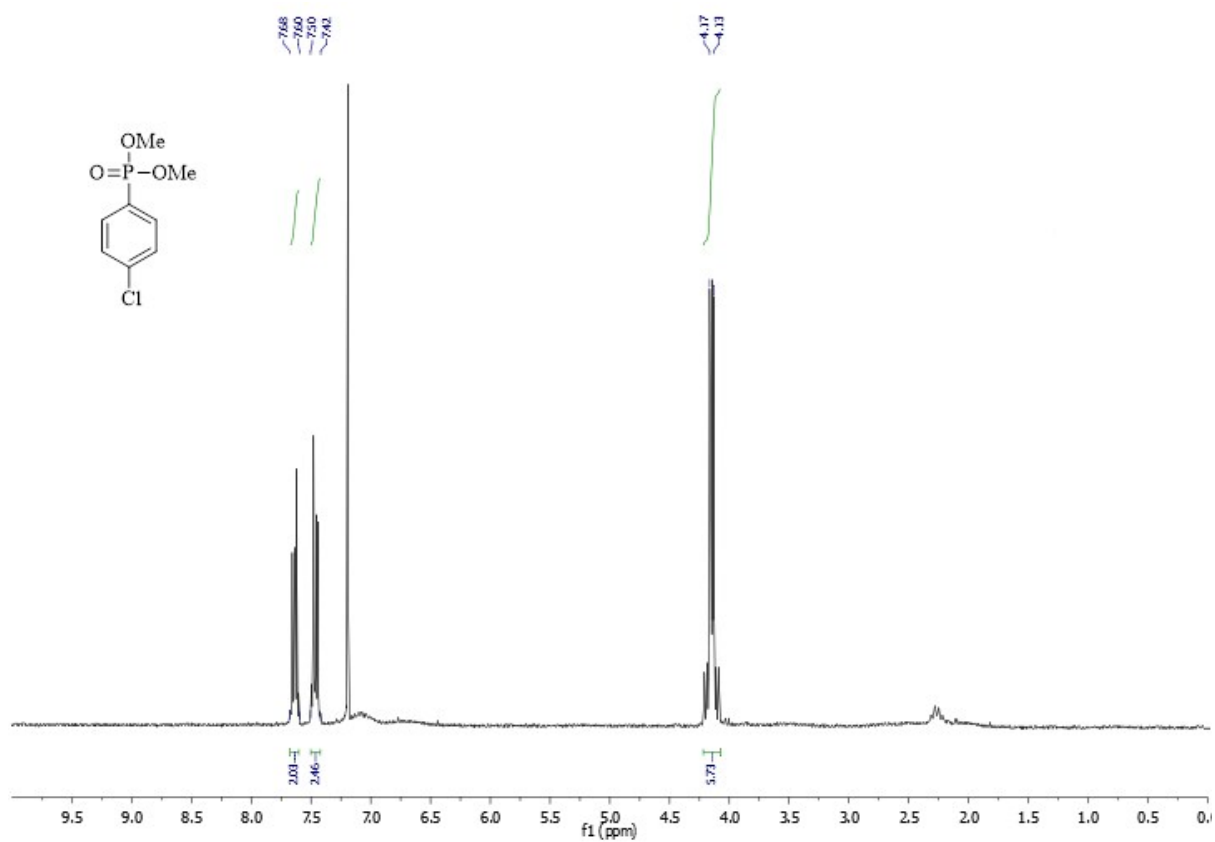
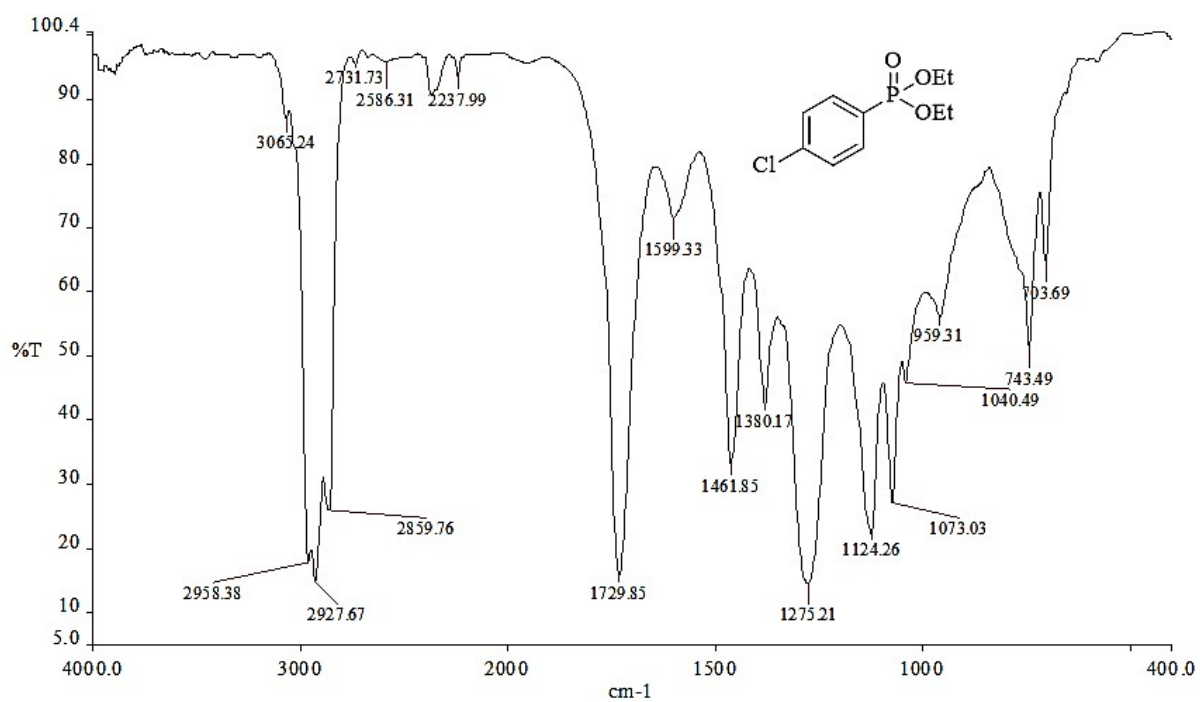


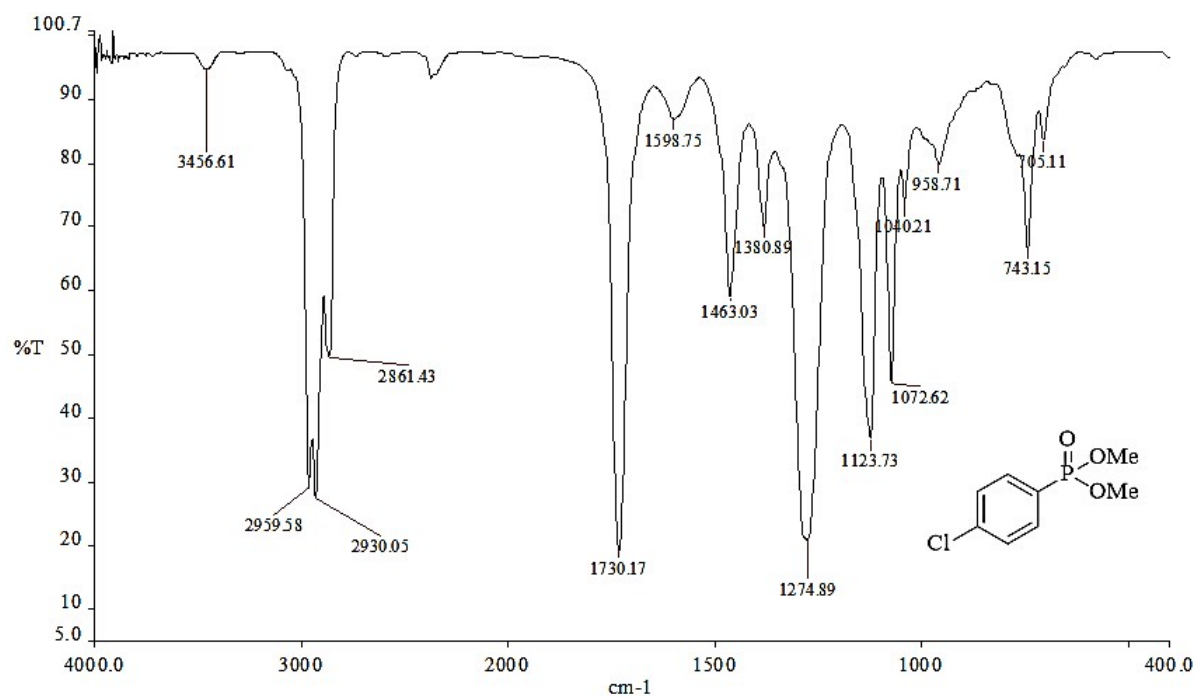
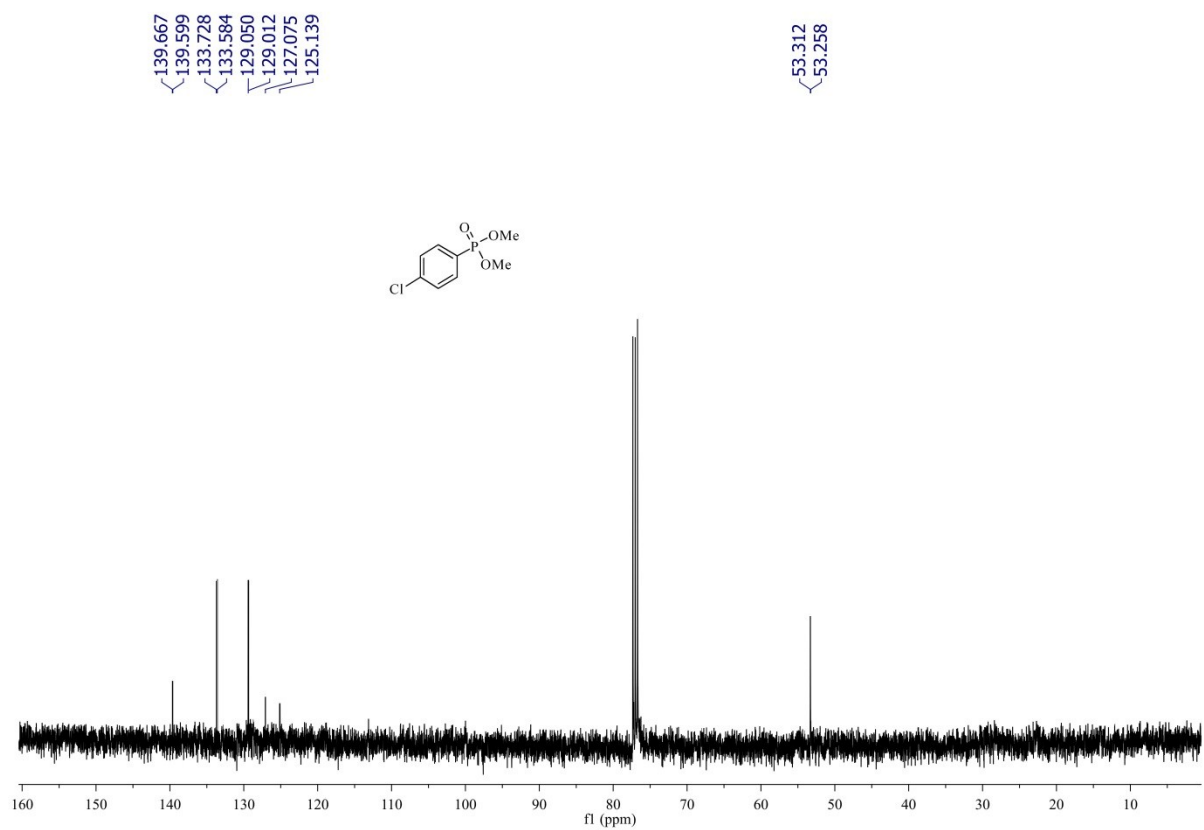


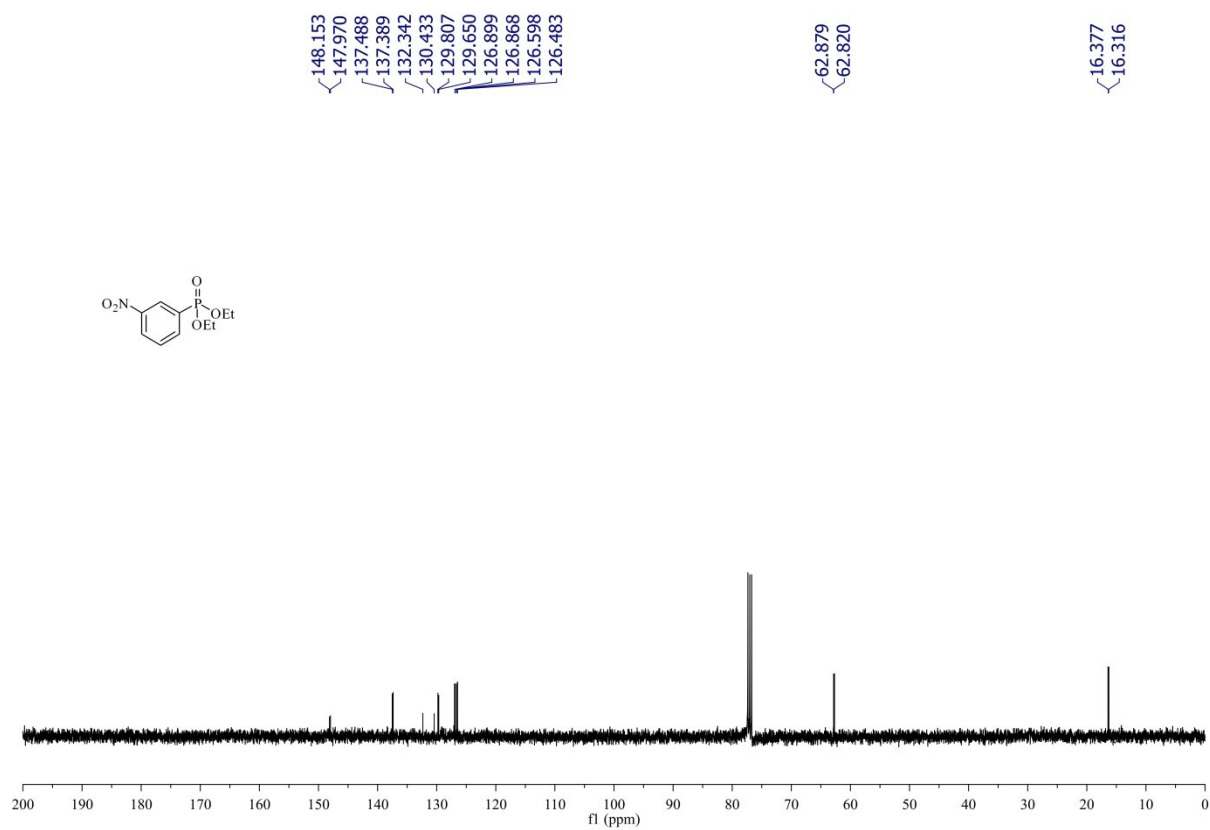
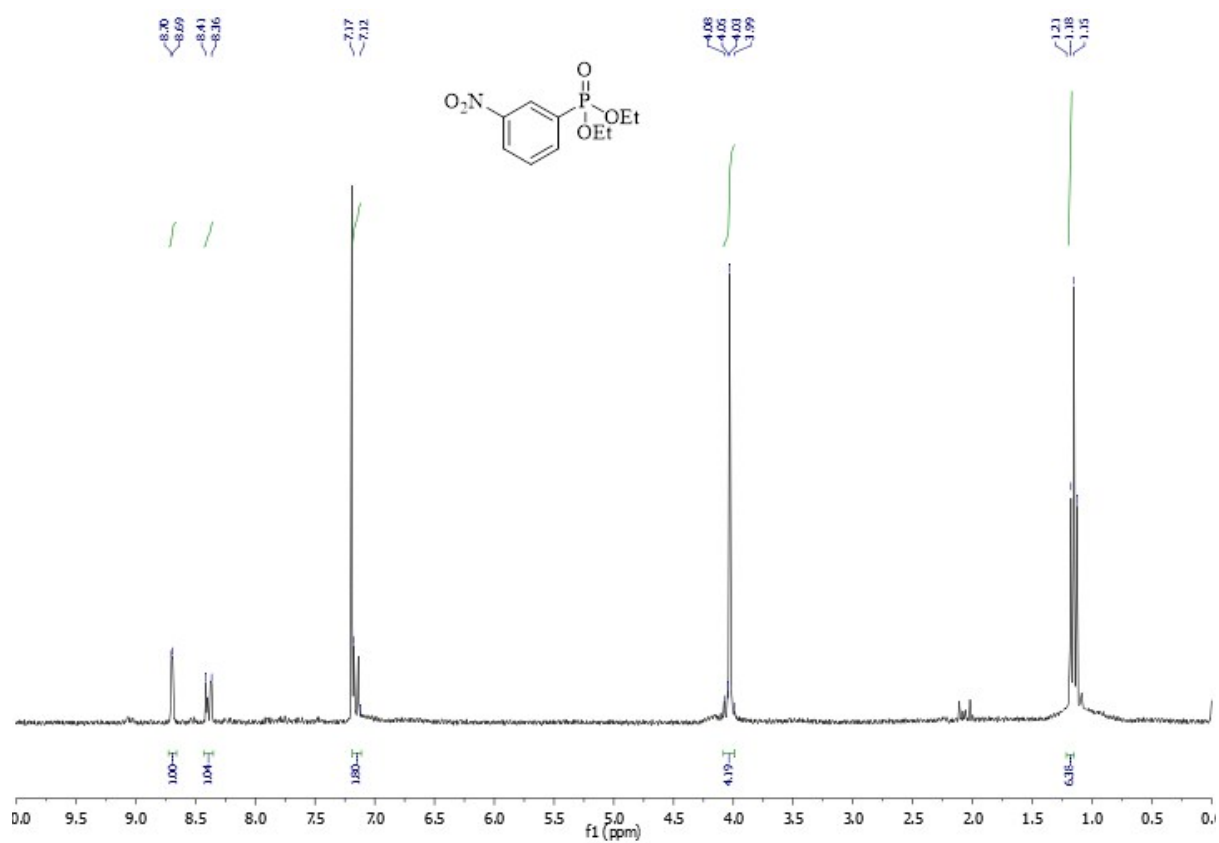


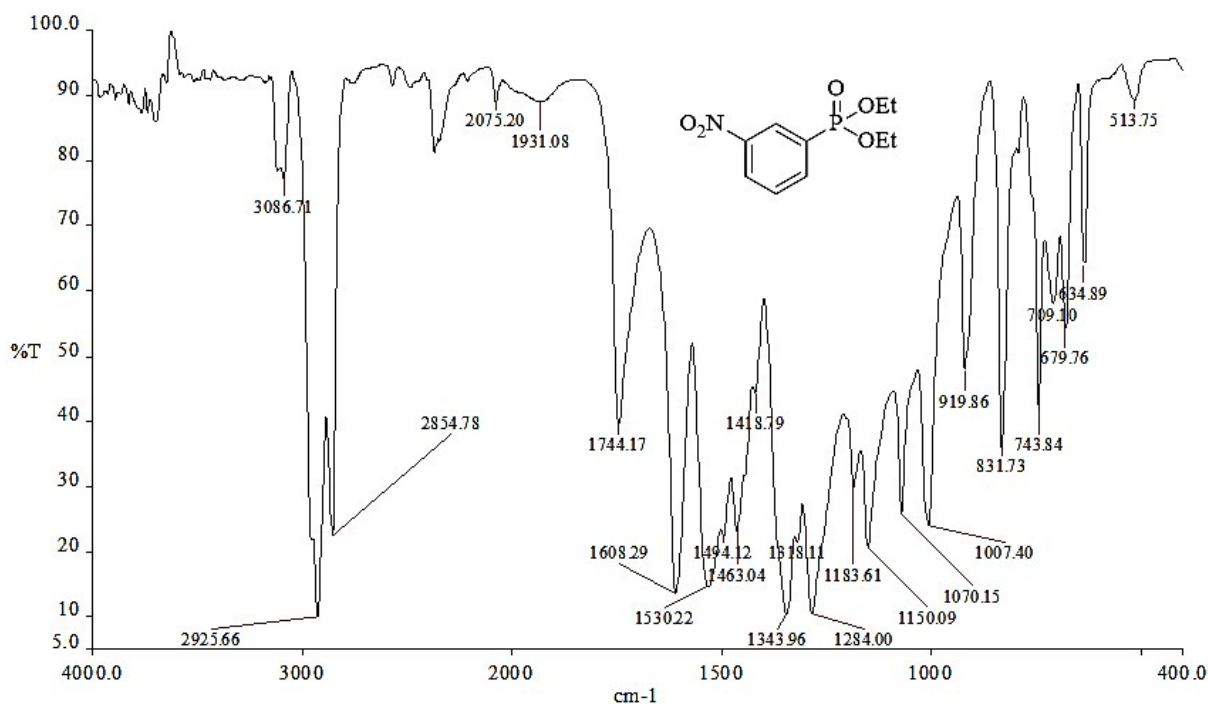












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