

Electronic Supplementary Information for Copper/Iron-Catalyzed C–P Cross-Coupling of styrenes with H-Phosphine Oxides: A Facile and Selective Synthesis of Alkenylphosphine Oxides and β -Ketophosphonates

Jian Gu,^a Chun Cai^{a*}

^a Chemical Engineering College, Nanjing University of Science & Technology, Nanjing, Jiangsu 210094, P. R. China

* Corresponding Author Fax: (+86)-25-8431-5030; phone: (+86)-25-8431-5514; e-mail: c.cai@mail.njust.edu.cn

1. General information
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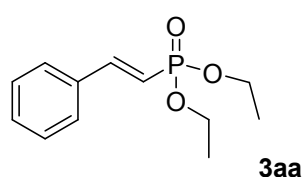
1. General Information

All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are characterized by ^1H NMR, ^{13}C NMR, and compared with previously reported data. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Thermo Scientific ISQ LT GC-MS instrument in the electron ionization (EI) mode. ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz, 125 MHz and 202 MHz in CDCl_3 , respectively, and chemical shifts are reported in ppm. High-resolution mass spectra data were obtained on Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

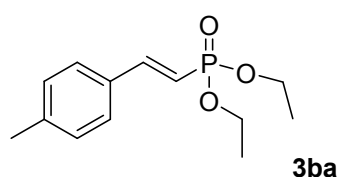
2. General Procedure

General Procedure for the Synthesis of alkenylphosphine oxides and β -Ketophosphonates from Alkenyls and H-Phosphonates: A mixture of alkenyls (0.5 mmol), H-phosphonates (2.0 mmol), CuCl (0.05 mmol), FeCl_3 (0.1 mmol), DTBP (1.0 mmol) and Et_3N (0.5 mmol) in DMSO (2.0 mL) under Ar was stirred at 110°C or 90°C for 15 h. After the completion of the reaction, the mixture was cooled to 25°C and then EtOAc and H_2O were added to it. The organic layer was separated and washed with brine, dried over Na_2SO_4 . The volatiles were removed under vacuum to afford the crude product, and analyzed by GC. The crude product was purified by column chromatography on silica gel and eluted with EtOAc /hexanes (25/75) to afford the desired pure product.

3. Characterization Data

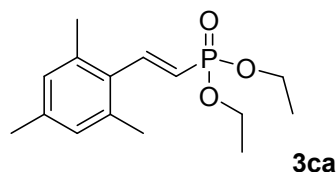


(E)-diethyl styrylphosphonate **3aa**^[1], yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.54 – 7.46 (m, 3H), 7.37 (dd, $J = 5.0, 1.7$ Hz, 3H), 6.25 (t, $J = 17.6$ Hz, 1H), 4.17 – 4.07 (m, 4H), 1.35 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 148.92 (s), 135.08 (s), 130.37 (s), 128.98 (s), 127.83 (s), 114.83 (s), 113.31 (s), 62.25 (s), 16.50 (s). MS (EI) m/z : 240 $[\text{M}^+]$.

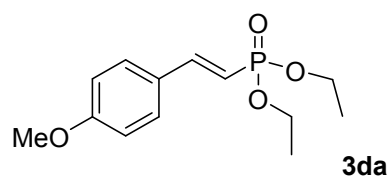


(E)-diethyl 4-methylstyrylphosphonate **3ba**^[1], yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.45 (dd, $J = 22.6, 17.5$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 7.9$ Hz, 2H), 6.17 (t, $J = 17.7$ Hz, 1H), 4.15 – 4.06 (m, 4H), 2.34 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 148.88

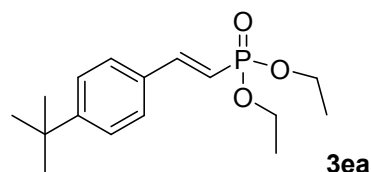
(s), 140.71 (s), 132.34 (s), 132.15 (s), 129.66 (s), 127.80 (s), 113.39 (s), 111.86 (s), 61.91 (s), 21.49 (s), 16.47 (s).



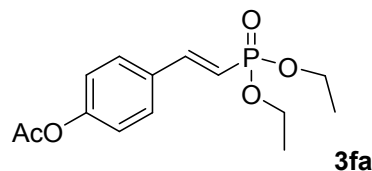
(E)-diethyl 2,4,6-trimethylstyrylphosphonate **3ca**^[1], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.65 (dd, *J* = 23.8, 17.9 Hz, 1H), 6.94 (s, 2H), 5.91 (dd, *J* = 20.6, 17.9 Hz, 1H), 4.25 – 4.17 (m, 4H), 2.34 (d, *J* = 16.4 Hz, 9H), 1.42 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 147.71 (s), 138.28 (s), 136.03 (s), 129.21 (s), 120.91 (s), 119.44 (s), 70.64 (s), 61.95 (s), 21.01 (s), 16.58 (s).



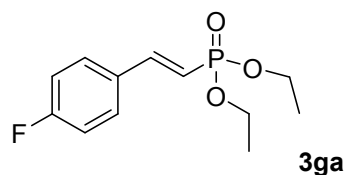
(E)-diethyl 4-methoxystyrylphosphonate **3da**^[1], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.48 (q, *J* = 15.9 Hz, 3H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.12 (t, *J* = 17.6 Hz, 1H), 4.20 – 4.11 (m, 4H), 3.86 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 161.43 (s), 148.60 (s), 129.45 (s), 127.67 (s), 114.36 (s), 111.71 (s), 110.18 (s), 61.86 (s), 55.49 (s), 16.50 (s).



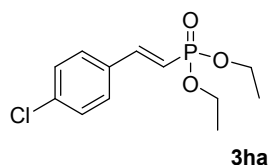
(E)-diethyl 4-tert-butylstyrylphosphonate **3ea**, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.55 – 7.47 (m, 1H), 7.47 – 7.44 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.22 (t, *J* = 17.7 Hz, 1H), 4.18 – 4.08 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H), 1.33 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 153.72 (s), 148.81 (s), 127.67 (s), 125.93 (s), 125.58 (s), 113.68 (s), 112.15 (s), 61.91 (s), 35.28 (s), 31.28 (s), 16.49 (s). ³¹P NMR (202 MHz, CDCl₃) δ 20.21 (s). HRMS (ESI) Calcd. For 319.1439, C₁₆H₂₅O₃P [M-Na]⁺, found 319.1435.



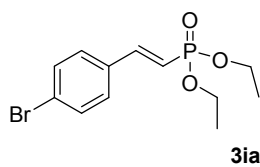
(E)-4-(2-(diethoxyphosphoryl)vinyl)phenyl acetate **3fa**, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.42 (m, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.22 (t, *J* = 17.4 Hz, 1H), 4.14 (tdt, *J* = 10.1, 6.8, 3.2 Hz, 4H), 2.32 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 169.29 (s), 152.18 (s), 147.83 (s), 128.99 (s), 122.24 (s), 114.99 (s), 113.46 (s), 62.06 (s), 21.25 (s), 16.54 (s). ³¹P NMR (202 MHz, CDCl₃) δ 19.40 (s). HRMS (ESI) Calcd. For 321.0868, C₁₄H₁₉O₅P [M-Na]⁺, found 321.0861.



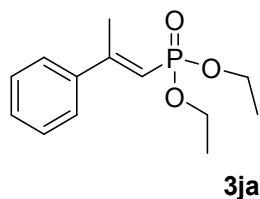
(E)-diethyl 4-fluorostyrylphosphonate **3ga**^[2], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.58 – 7.46 (m, 3H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.22 (t, *J* = 17.4 Hz, 1H), 4.23 – 4.13 (m, 4H), 1.40 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 164.99 (s), 162.99 (s), 147.84 (s), 129.74 (s), 116.19 (s), 114.64 (s), 113.11 (s), 62.00 (s), 16.51 (s).



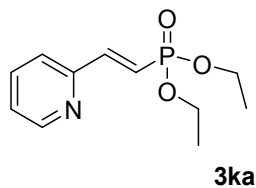
(E)-diethyl 4-chlorostyrylphosphonate **3ha**^[1], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.46 (dt, *J* = 14.3, 11.7 Hz, 3H), 7.37 (d, *J* = 8.5 Hz, 2H), 6.24 (t, *J* = 17.3 Hz, 1H), 4.20 – 4.10 (m, 4H), 1.37 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 147.37 (s), 136.29 (s), 129.25 (s), 129.02 (s), 115.63 (s), 114.10 (s), 62.10 (s), 16.51 (s).



(E)-diethyl 4-bromostyrylphosphonate **3ia**^[1], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.43 (dd, *J* = 22.5, 17.5 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.25 (t, *J* = 17.3 Hz, 1H), 4.20 – 4.05 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 147.46 (s), 132.22 (s), 129.24 (s), 124.62 (s), 115.77 (s), 114.25 (s), 62.09 (s), 16.52 (s).

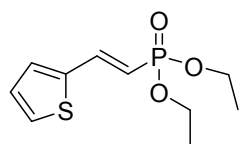


(E)-diethyl 2-phenylprop-1-enylphosphonate **3ja**^[3], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.47 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.39 – 7.34 (m, 3H), 5.91 (d, *J* = 16.6 Hz, 1H), 4.13 (p, *J* = 7.3 Hz, 4H), 2.51 (d, *J* = 3.2 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 158.30 (s), 129.26 (s), 128.59 (s), 126.08 (s), 124.87 (s), 114.34 (s), 112.83 (s), 16.48 (s).

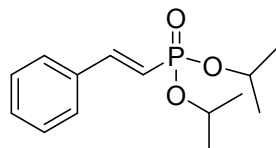


(E)-diethyl 2-(pyridin-2-yl)vinylphosphonate **3ka**, white solid. ¹H NMR (500 MHz, CDCl₃) δ 8.65 (d, *J* = 4.5 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.54 (dd, *J* = 21.8, 17.1 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 4.9 Hz, 1H), 6.95 – 6.84 (m, 1H), 4.20 – 4.12 (m, 4H), 1.37 (t, *J* = 7.1 Hz, 6H). ¹³C NMR

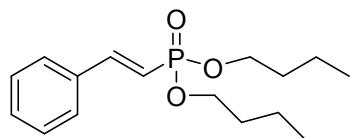
(125 MHz, CDCl₃) δ 152.96 (s), 150.16 (s), 147.44 (s), 137.05 (s), 124.46 (s), 119.60 (s), 118.10 (s), 62.14 (s), 16.49 (s). ³¹P NMR (202 MHz, CDCl₃) δ 18.88 (s). HRMS (ESI) Calcd. For 264.0765, C₁₁H₁₆NO₃P [M-Na]⁺, found 264.0762.

**3la**

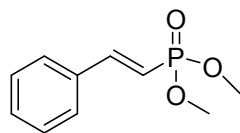
(E)-diethyl 2-(thiophen-2-yl)vinylphosphonate **3la**^[3], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.55 (dd, J = 21.9, 17.2 Hz, 1H), 7.32 (d, J = 5.0 Hz, 1H), 7.17 (d, J = 3.4 Hz, 1H), 7.00 (dd, J = 4.8, 3.8 Hz, 1H), 5.96 (t, J = 17.0 Hz, 1H), 4.12 – 4.04 (m, 4H), 1.31 (t, J = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 141.38 (s), 140.96 (d, J = 88.3 Hz), 140.40 (s), 130.37 (s), 128.31 (s), 128.12 (s), 113.26 (s), 111.72 (s), 62.00 (s), 16.49 (s).

**3ab**

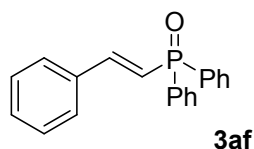
(E)-diisopropyl styrylphosphonate **3ab**^[1], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.48 (m, 3H), 7.38 (dd, J = 5.1, 2.0 Hz, 3H), 6.27 (t, J = 17.5 Hz, 1H), 4.72 (qd, J = 12.4, 6.2 Hz, 2H), 1.35 (dd, J = 24.3, 6.2 Hz, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 147.95 (s), 128.98 (t, J = 150.2 Hz), 115.78 (d, J = 191.2 Hz), 70.67 (s), 24.20 (s).

**3ac**

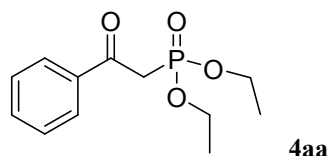
(E)-dibutyl styrylphosphonate **3ac**^[4], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.57 – 7.49 (m, 3H), 7.47 – 7.44 (m, 1H), 7.39 (dd, J = 5.0, 1.9 Hz, 2H), 6.26 (t, J = 17.6 Hz, 1H), 4.07 (hd, J = 10.1, 6.7 Hz, 4H), 1.71 – 1.66 (m, 4H), 1.48 – 1.37 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 148.84 (s), 130.33 (s), 129.31 (s), 128.98 (s), 127.83 (s), 113.29 (s), 65.75 (s), 32.67 (s), 18.89 (s), 13.73 (s).

**3ad**

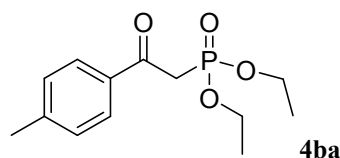
(E)-dimethyl styrylphosphonate **3ad**^[5], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.56 – 7.49 (m, 3H), 7.41 – 7.39 (m, 2H), 7.30 (d, J = 4.5 Hz, 1H), 6.23 (t, J = 17.7 Hz, 1H), 3.77 (t, J = 10.6 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 130.55 (s), 129.03 (s), 127.89 (s), 127.47 (s), 113.28 (s), 111.52 (s), 52.61 (s).



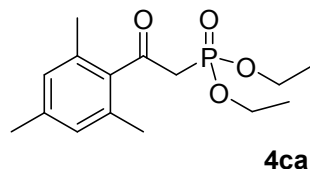
(E)-diphenyl styrylphosphonate **3af**^[1], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.85 – 7.78 (m, 4H), 7.59 (dt, *J* = 6.0, 4.7 Hz, 4H), 7.57 – 7.51 (m, 5H), 7.44 (dd, *J* = 5.1, 1.9 Hz, 3H), 6.90 (dd, *J* = 22.3, 17.4 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 147.73 (s), 132.02 (s), 131.54 (d, *J* = 9.3 Hz), 130.25 (s), 129.00 (s), 128.77 (d, *J* = 11.7 Hz), 127.92 (s), 119.78 (s), 118.95 (s).



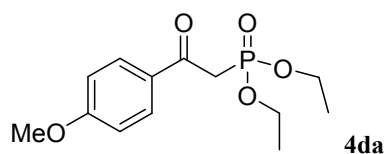
diethyl 2-oxo-2-phenylethylphosphonate **4aa**^[6], light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 4.17 – 4.10 (m, 4H), 3.63 (d, *J* = 22.7 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 192.11 (s), 133.80 (s), 128.96 (d, *J* = 55.1 Hz), 62.84 (s), 39.12 (s), 38.09 (s), 16.38 (s). MS (EI) *m/z*: 256 [M⁺].



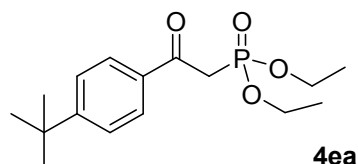
diethyl 2-oxo-2-p-tolyethylphosphonate **4ba**^[6], light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 4.10 – 4.03 (m, 4H), 3.53 (d, *J* = 22.7 Hz, 2H), 2.35 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 191.63 (s), 144.80 (s), 134.21 (s), 129.38 (d, *J* = 11.6 Hz), 62.73 (s), 39.02 (s), 37.99 (s), 21.64 (s), 16.37 (s).



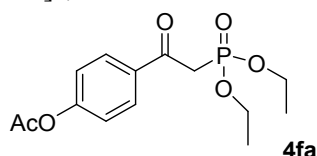
diethyl 2-mesityl-2-oxoethylphosphonate **4ca**, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 6.85 (s, 2H), 4.19 – 4.09 (m, 4H), 3.44 (d, *J* = 21.7 Hz, 2H), 2.28 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 200.88 (s), 139.21 (s), 138.59 (s), 133.62 (s), 130.32 (s), 128.97 (s), 62.55 (s), 44.27 (s), 43.23 (s), 22.27 (s), 20.95 (d, *J* = 61.2 Hz), 19.71 (s), 16.36 (s). ³¹P NMR (202 MHz, CDCl₃) δ 19.84 (s). HRMS (ESI) Calcd. For 321.1232, C₁₅H₂₃O₄P [M-Na]⁺, found 321.1229.



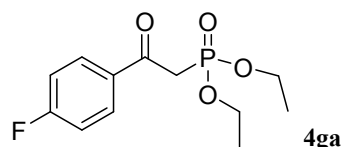
diethyl 2-(4-methoxyphenyl)-2-oxoethylphosphonate **4da**^[6], light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 7.0 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 4.07 (p, *J* = 7.1 Hz, 4H), 3.81 (s, 3H), 3.51 (d, *J* = 22.7 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 190.21 (s), 164.18 (s), 131.54 (s), 129.82 – 129.66 (m), 113.67 (s), 62.80 (s), 55.56 (s), 16.31 (s).



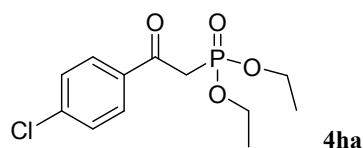
diethyl 2-(4-tert-butylphenyl)-2-oxoethylphosphonate **4ea**^[6], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 4.18 – 4.11 (m, 4H), 3.62 (d, *J* = 22.7 Hz, 2H), 1.35 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 191.62 (s), 134.23 (s), 129.17 (s), 125.69 (s), 62.72 (s), 39.02 (s), 37.99 (s), 32.35 (s), 31.35 (d, *J* = 49.7 Hz), 16.34 (s). ³¹P NMR (202 MHz, CDCl₃) δ 20.38 (s). HRMS (ESI) Calcd. For 335.1388, C₁₆H₂₅O₄P [M-Na]⁺, found 335.1385.



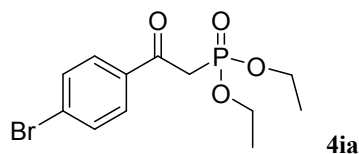
4-(2-(diethoxyphosphoryl)acetyl)phenyl acetate **4fa**, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.05 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 4.17 – 4.10 (m, 4H), 3.60 (d, *J* = 22.7 Hz, 2H), 2.32 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 190.82 (s), 168.83 (s), 154.95 (s), 134.20 (s), 130.89 (s), 121.93 (s), 62.92 (s), 39.21 (s), 38.18 (s), 21.27 (s), 16.38 (s). ³¹P NMR (202 MHz, CDCl₃) δ 19.59 (s). HRMS (ESI) Calcd. For 337.0817, C₁₄H₁₉O₆P [M-Na]⁺, found 337.0813.



diethyl 2-(4-fluorophenyl)-2-oxoethylphosphonate **4ga**^[6], brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.99 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 4.11 – 4.03 (m, 4H), 3.53 (d, *J* = 22.8 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 190.46 (s), 133.09 (s), 132.01 (d, *J* = 9.0 Hz), 115.99 (s), 115.81 (s), 62.89 (s), 39.28 (s), 38.25 (s), 16.41 (s).

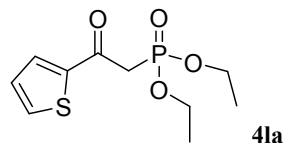


diethyl 2-(4-chlorophenyl)-2-oxoethylphosphonate **4ha**^[6], yellow green oil. ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 4.12 – 4.02 (m, 4H), 3.53 (d, *J* = 22.8 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 190.84 (s), 140.32 (s), 134.75 (s), 128.84 (s), 62.79 (s), 39.18 (s), 38.17 (s), 16.31 (s).

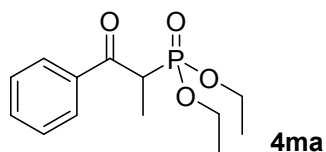


Diethyl 2-(4-bromophenyl)-2-oxoethylphosphonate **4ia**^[6], yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 4.10 – 4.04 (m, 4H), 3.53 (d, *J* = 22.8 Hz,

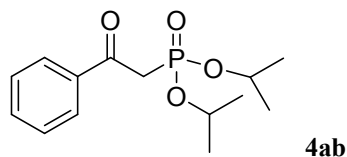
2H), 1.22 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 191.12 (s), 135.35 (s), 132.08 (s), 130.72 (s), 129.24 (s), 62.90 (s), 38.76 (d, $J = 129.5$ Hz), 16.40 (s).



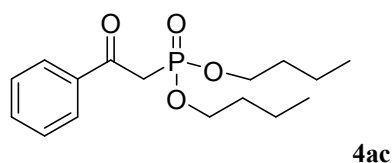
diethyl 2-oxo-2-(thiophen-2-yl)ethylphosphonate **4la**^[6], yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.81 (d, $J = 3.8$ Hz, 1H), 7.68 (d, $J = 4.9$ Hz, 1H), 7.17 – 7.12 (m, 1H), 4.16 – 4.11 (m, 4H), 3.54 (d, $J = 22.5$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 184.36 (s), 144.05 (s), 135.24 (s), 134.32 (s), 128.47 (s), 62.95 (s), 40.01 (s), 38.97 (s), 16.38 (s).



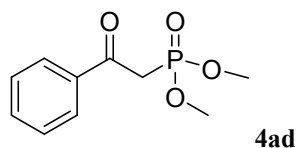
diethyl (1-oxo-1-phenylpropan-2-yl)phosphonate **4ma**, yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 8.05 – 7.98 (m, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 2H), 4.21 (q, $J = 7.0$ Hz, 1H), 4.16 – 4.04 (m, 4H), 1.54 (dd, $J = 18.0, 7.0$ Hz, 3H), 1.25 (dt, $J = 42.3, 7.1$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 135.89 (s), 132.38 (s), 127.89 (s), 127.54 (s), 61.80 (s), 39.84 (s), 15.53 (s), 11.29 (s).



diisopropyl 2-oxo-2-phenylethylphosphonate **4ab**^[6], light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 8.03 (d, $J = 8.1$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 2H), 4.73 (dq, $J = 12.9, 6.3$ Hz, 2H), 3.60 (d, $J = 22.9$ Hz, 2H), 1.28 (dd, $J = 6.0, 3.9$ Hz, 12H). ^{13}C NMR (125 MHz, CDCl_3) δ 192.23 (s), 136.80 (s), 133.63 (s), 129.28 (s), 128.94 (d, $J = 80.1$ Hz), 71.60 (s), 40.36 (s), 39.32 (s), 24.08 (s).



dibutyl 2-oxo-2-phenylethylphosphonate **4ac**^[6], yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, $J = 7.7$ Hz, 2H), 7.59 (t, $J = 7.3$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 2H), 4.13 – 4.02 (m, 4H), 3.64 (d, $J = 22.8$ Hz, 2H), 1.67 – 1.55 (m, 4H), 1.33 (dq, $J = 14.8, 7.4$ Hz, 4H), 0.89 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 192.08 (s), 140.00 (s), 133.74 (s), 129.70 – 129.32 (m), 128.95 (d, $J = 59.4$ Hz), 66.45 (s), 39.32 (s), 37.98 (s), 32.48 (s), 18.74 (s), 13.67 (s).

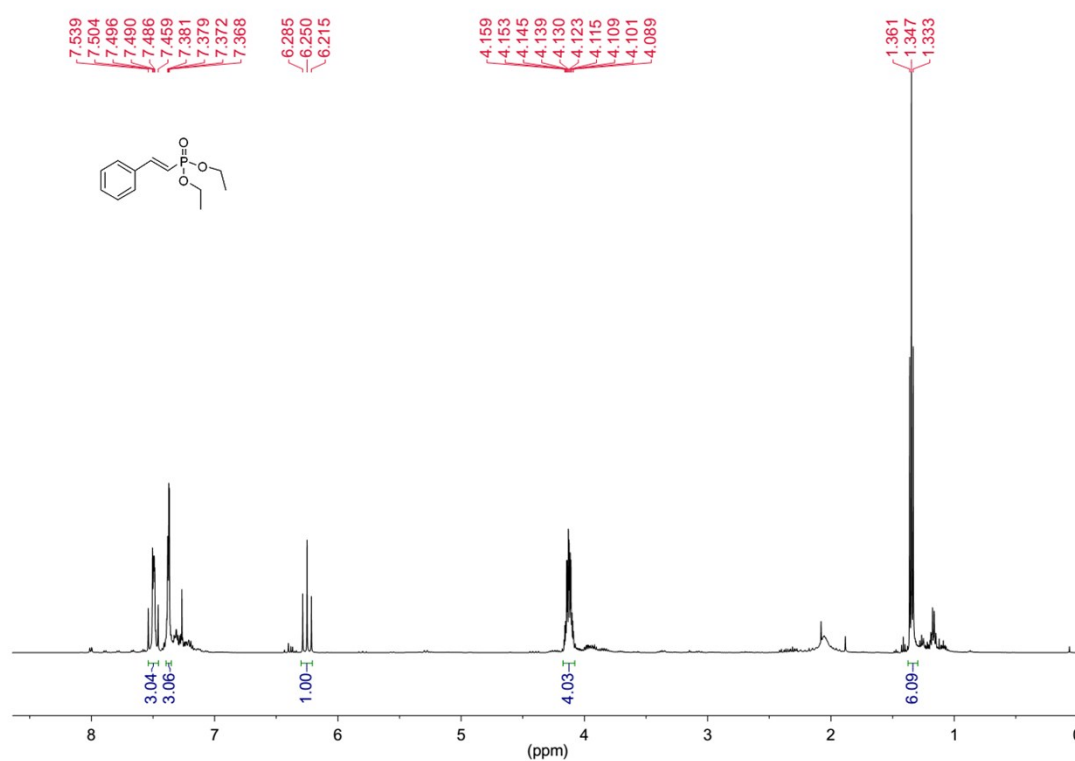


dimethyl 2-oxo-2-phenylethylphosphonate **4ad**^[6], colorless and transparent oil. ^1H NMR (500 MHz, CDCl_3) δ 8.00 (d, $J = 8.0$ Hz, 2H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.7$ Hz, 2H), 3.78 (d,

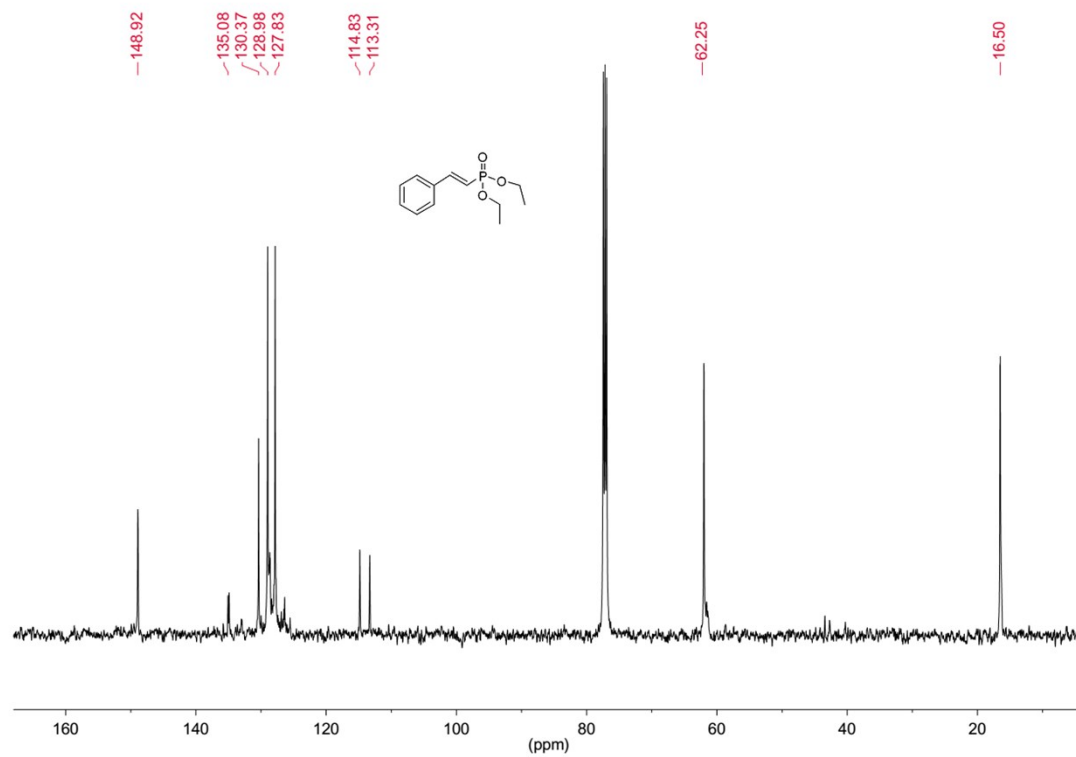
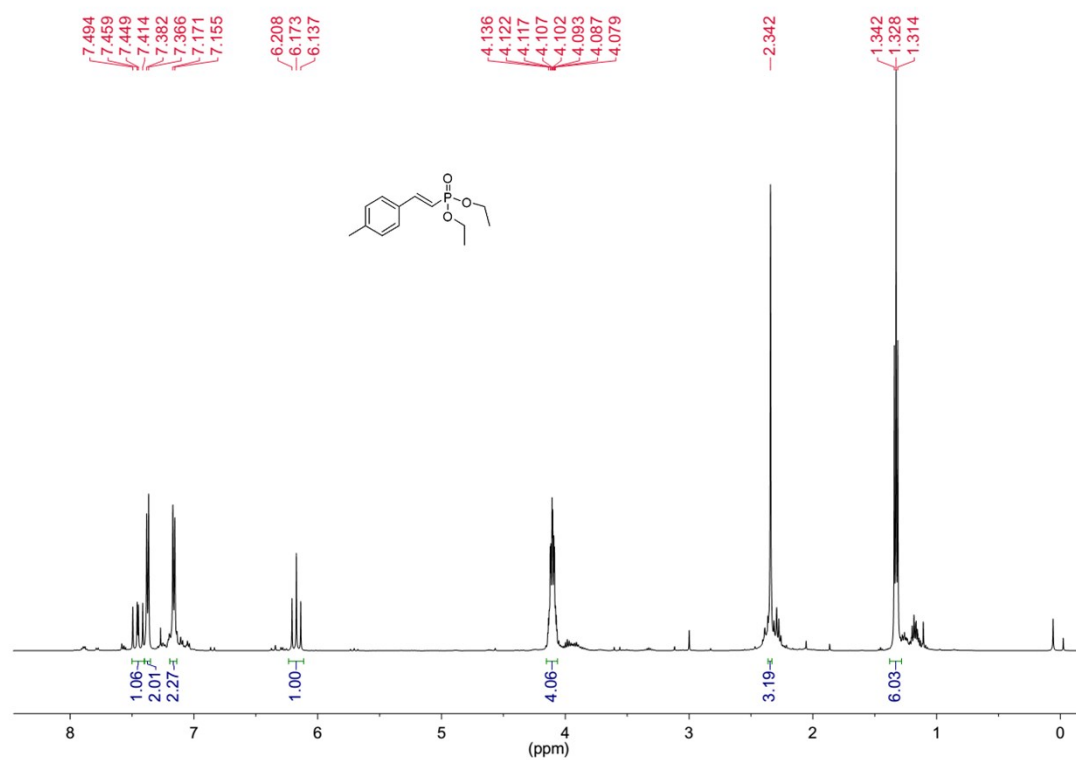
$J = 11.2$ Hz, 6H), 3.64 (d, $J = 22.6$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 191.90 (s), 136.54 (s), 133.94 (s), 128.98 (d, $J = 33.7$ Hz), 53.29 (s), 38.14 (s), 37.09 (s).

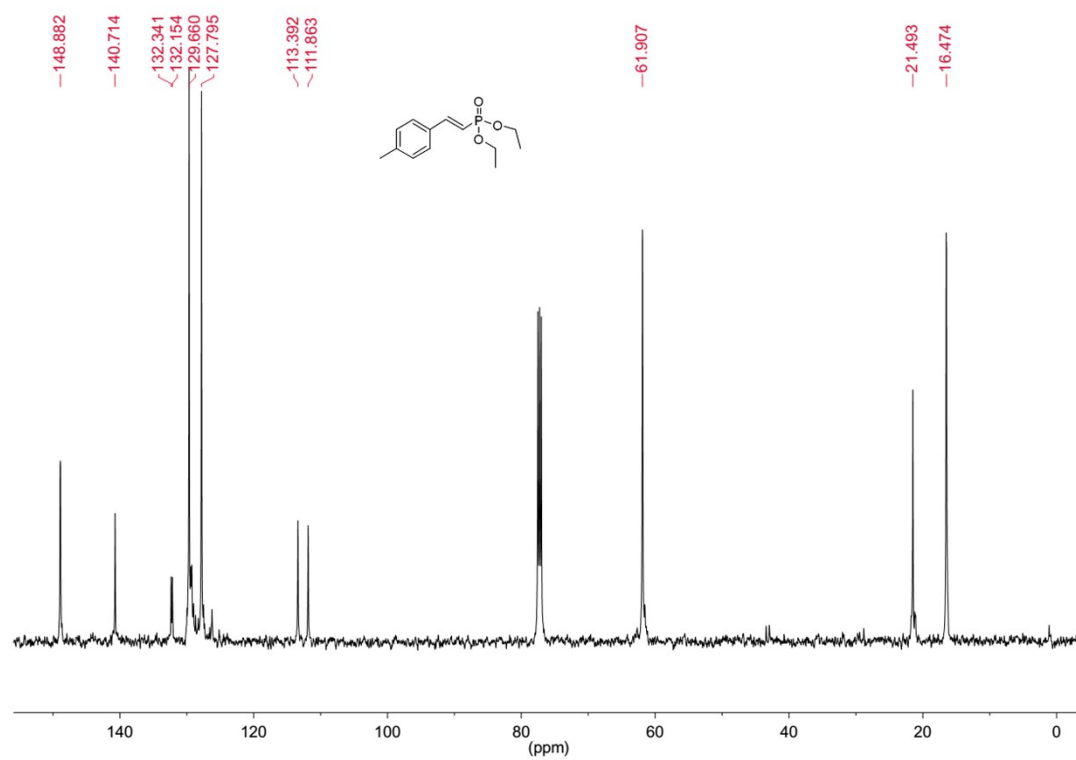
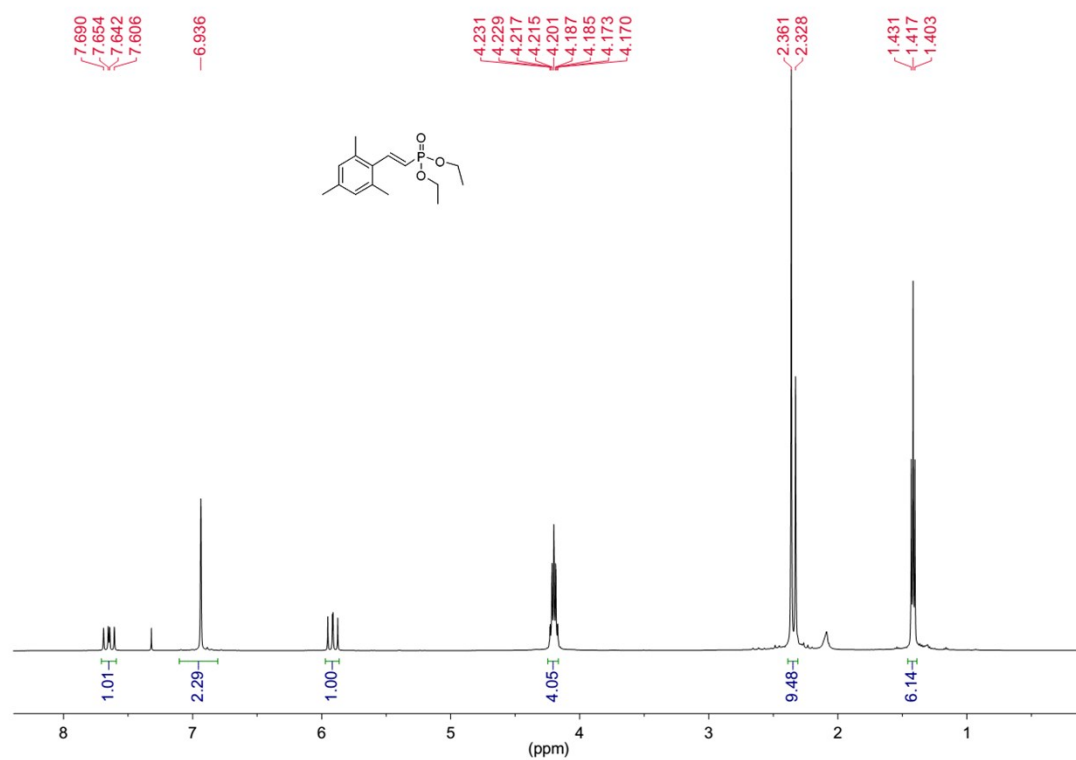
- [1] Q. Gui, L. Hu, X. Chen, J. Liu, Z. Tan, *Chem. Commun.*, **2015**, 51, 13922—13924.
 [2] G. W. Kabalka, S. K. Guchhait, *Org. Lett.*, **2003**, 5, 729-731.
 [3] J. Xue, S. Zhou, Y. Liu, X. Pan, J. Zou, O. T. Asekun, *Org. Biomol. Chem.*, **2015**, 13, 4896–4902.
 [4] G. Evano, K. Tadiparthi, F. Couty, *Chem. Comm.*, **2011**, 47, 179-181
 [5] H. Lebel, M. Davi, *Adv. Synth. Catal.* **2008**, 350, 2352 – 2358
 [6] N.Yi, R.Wang, H. Zou, W. He . *J. Org. Chem.* **2015**, 80, 5023-5029.

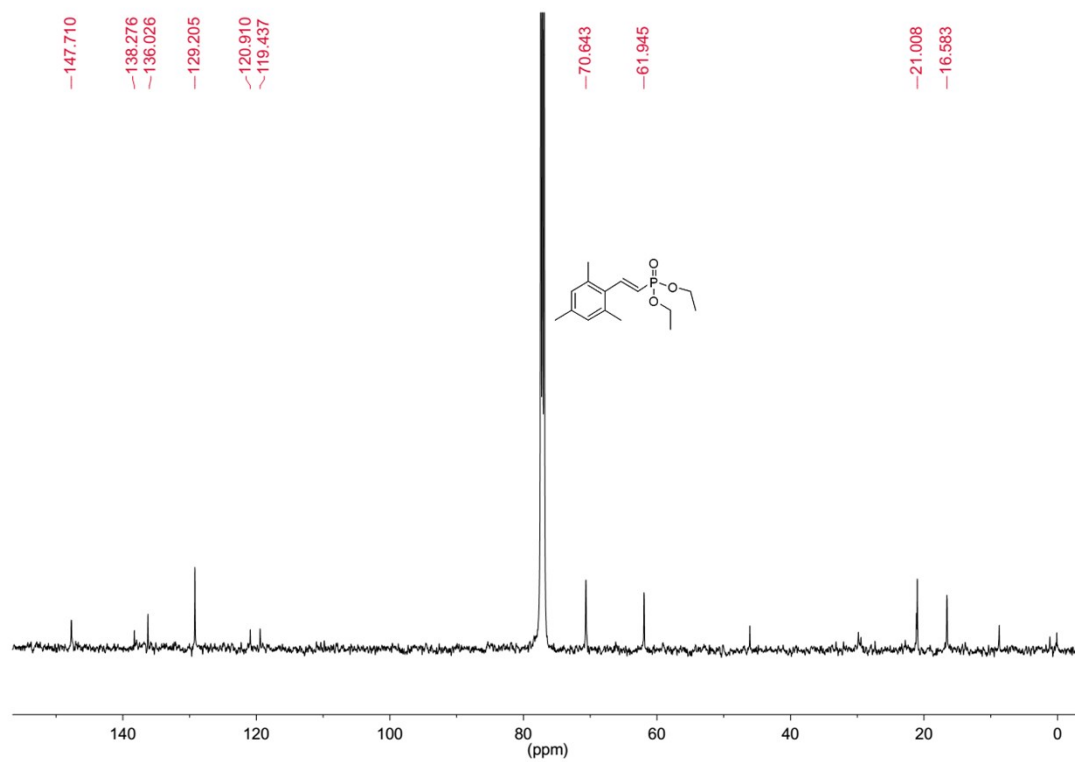
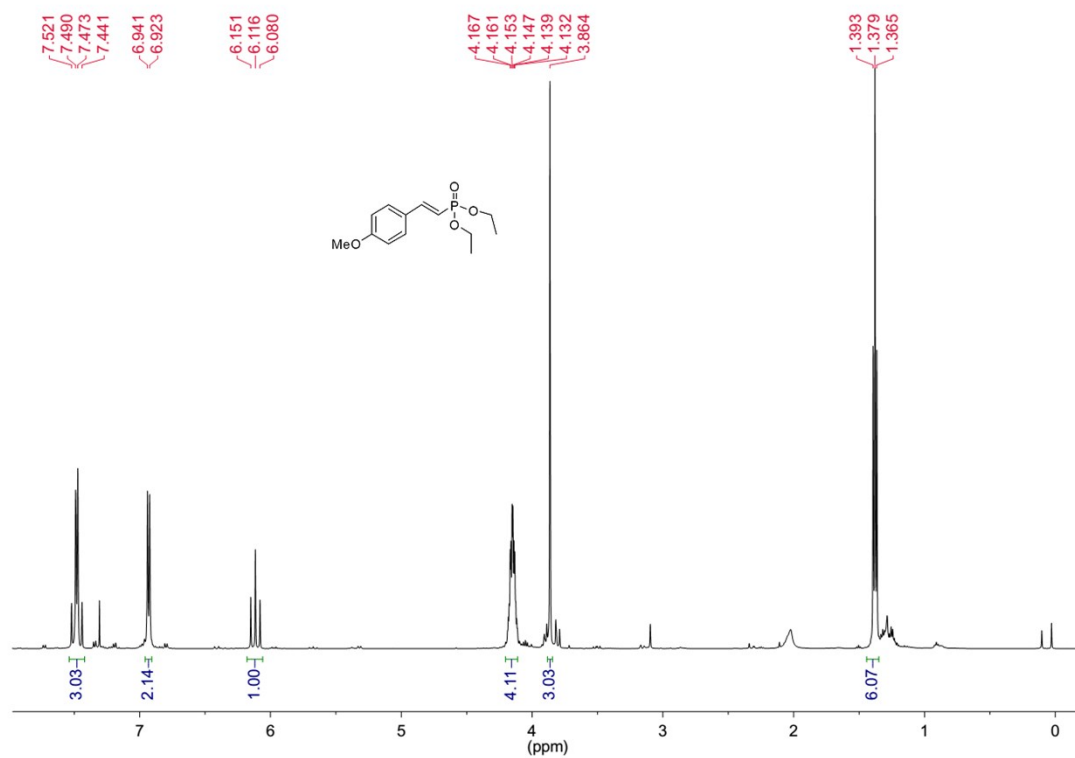
4. NMR Spectra of All Products

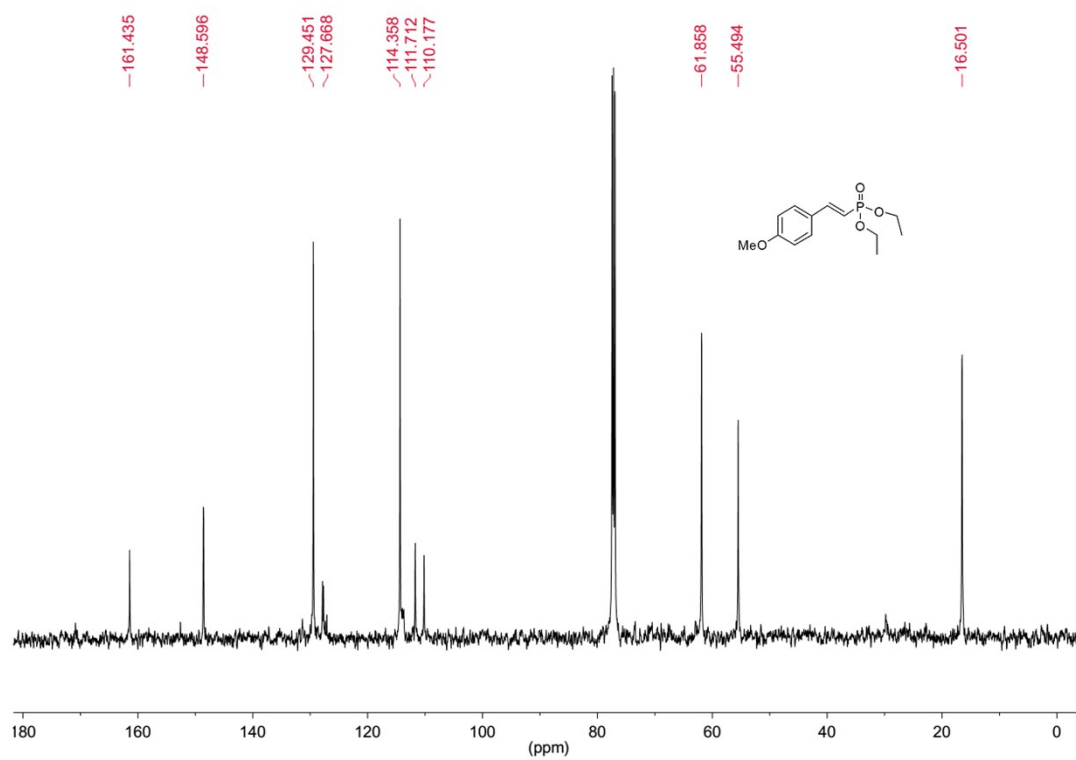
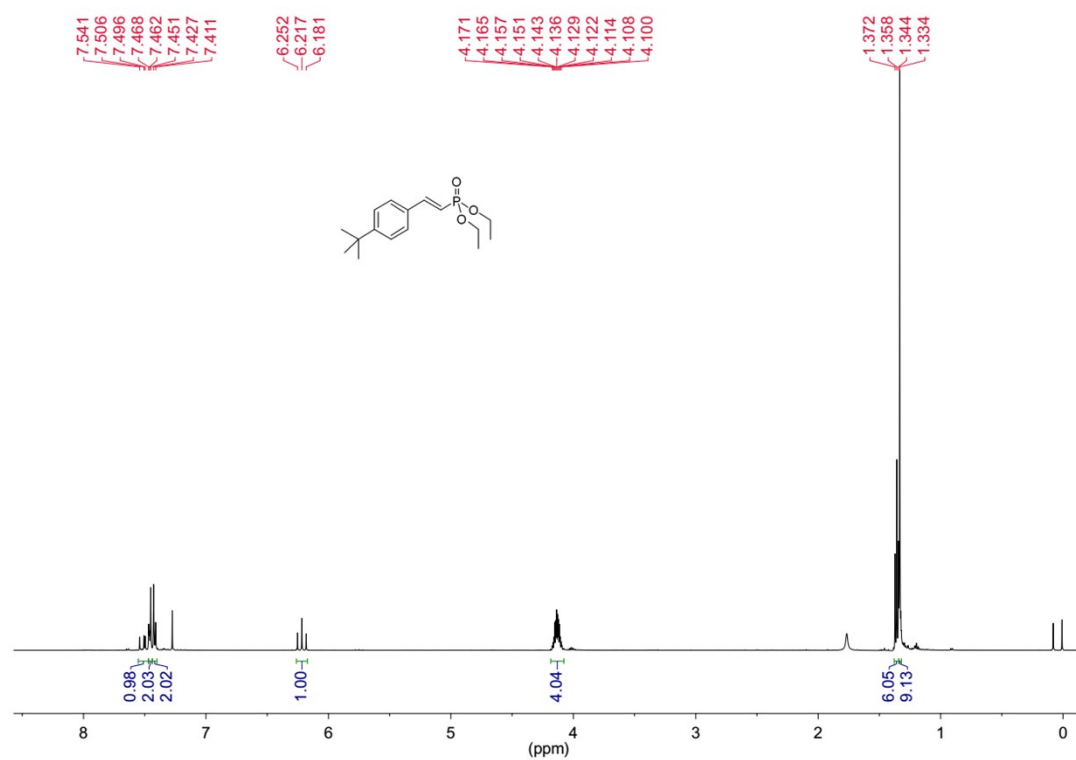


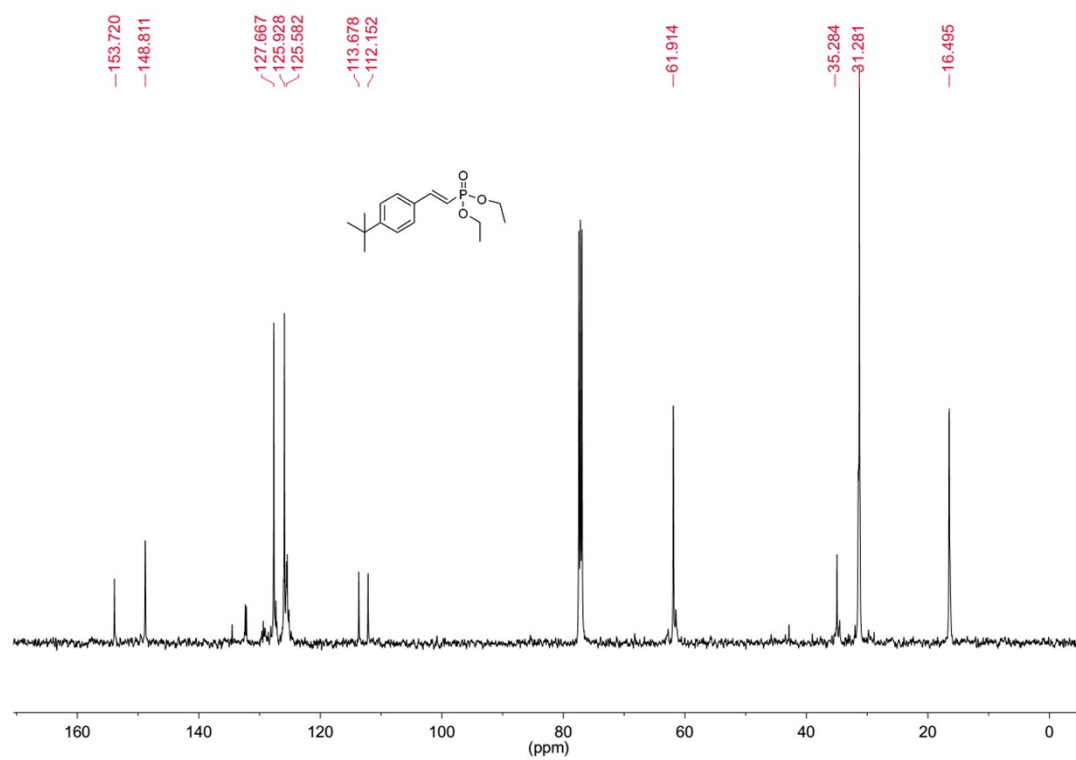
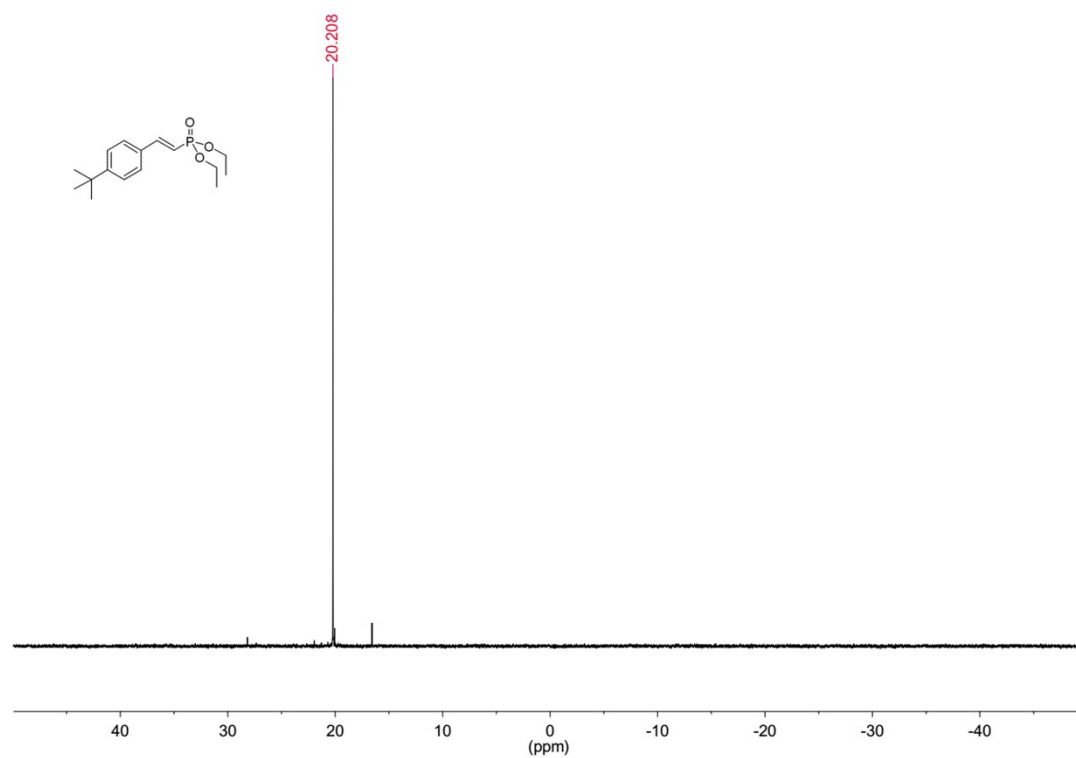
^1H NMR **3aa**

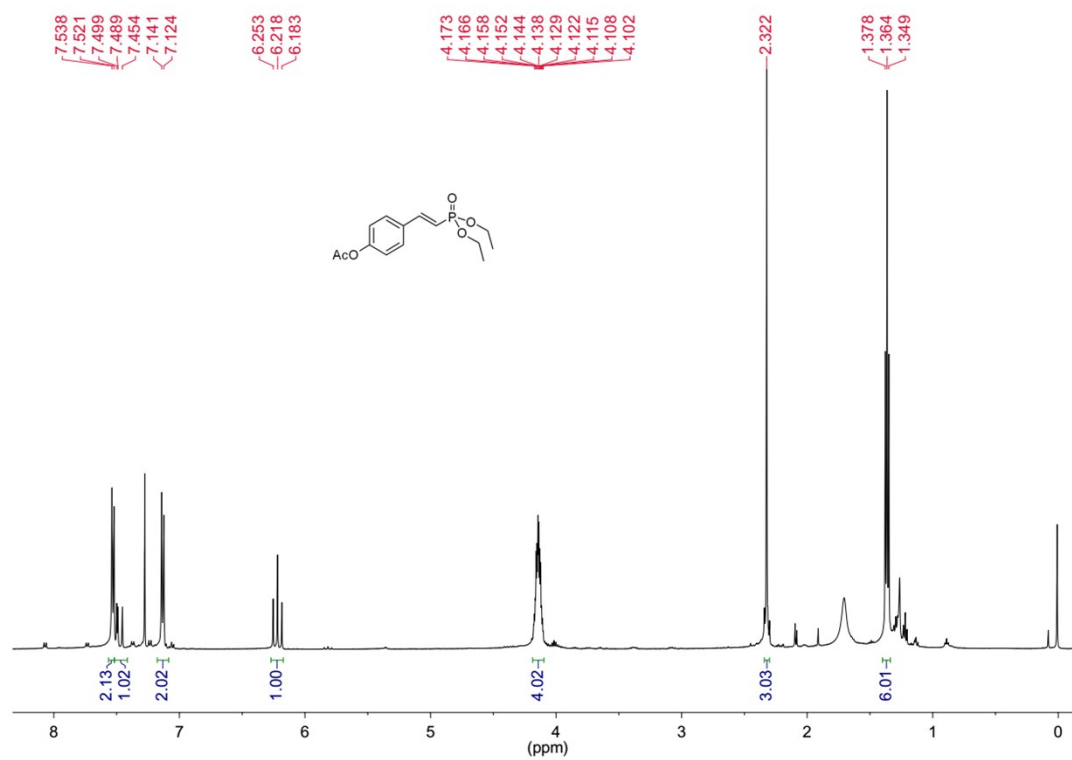
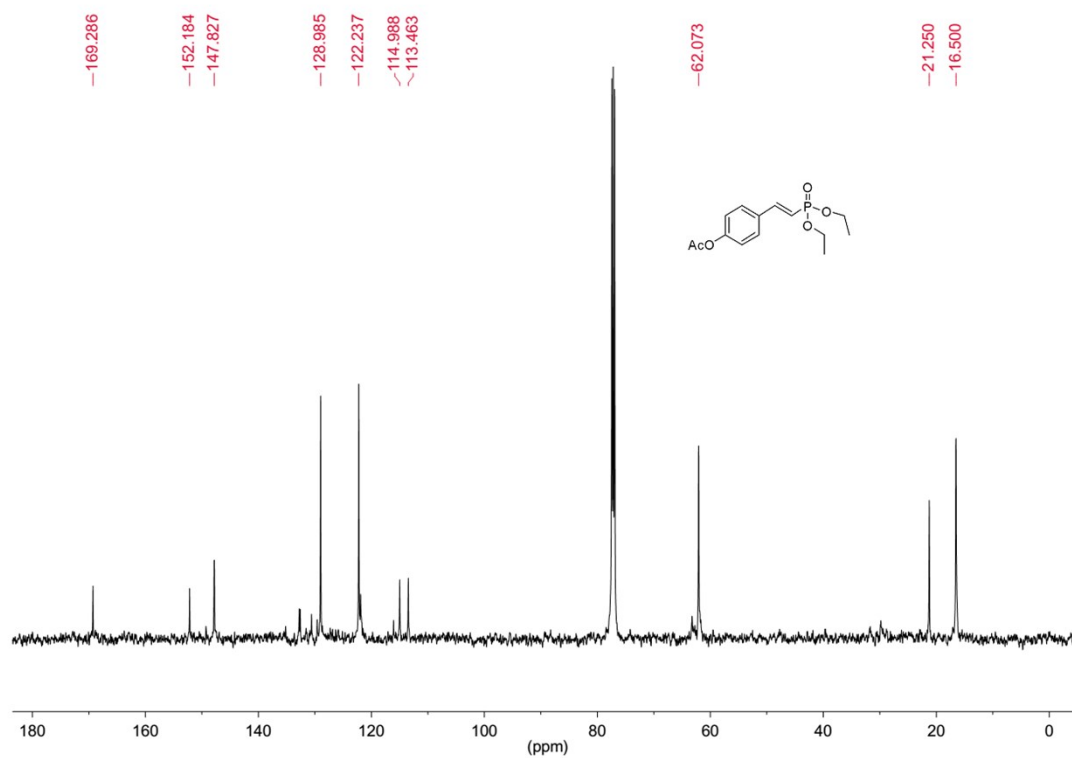
¹³C NMR **3aa**¹H NMR **3ba**

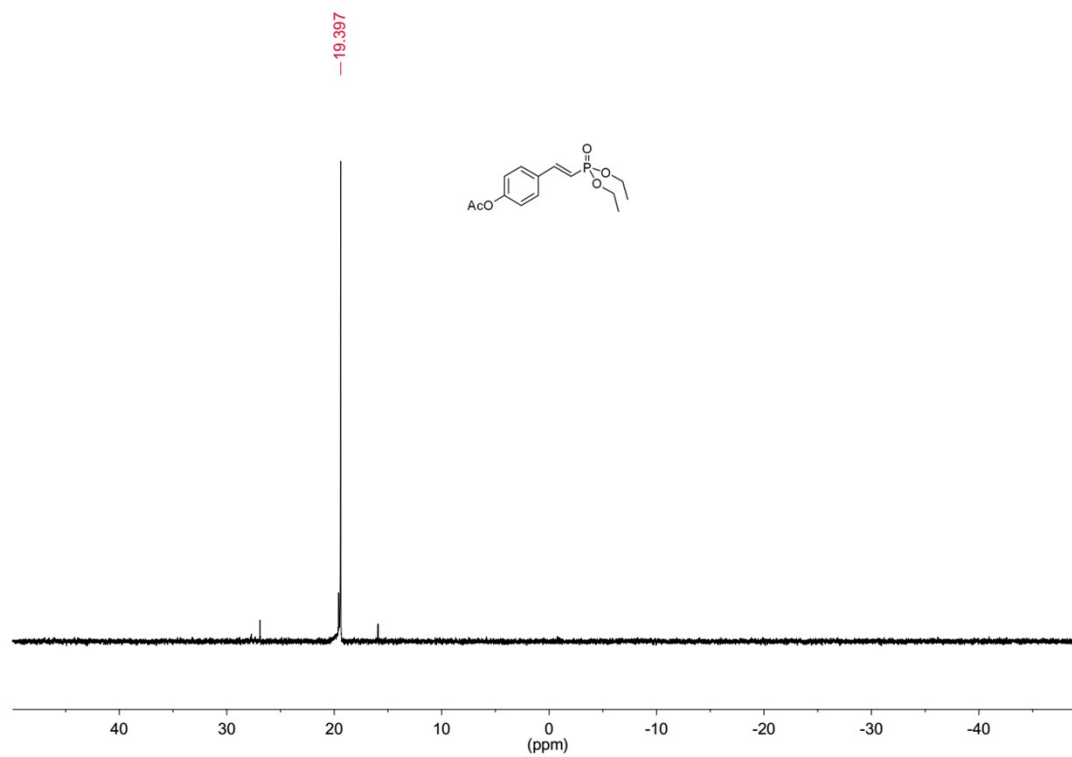
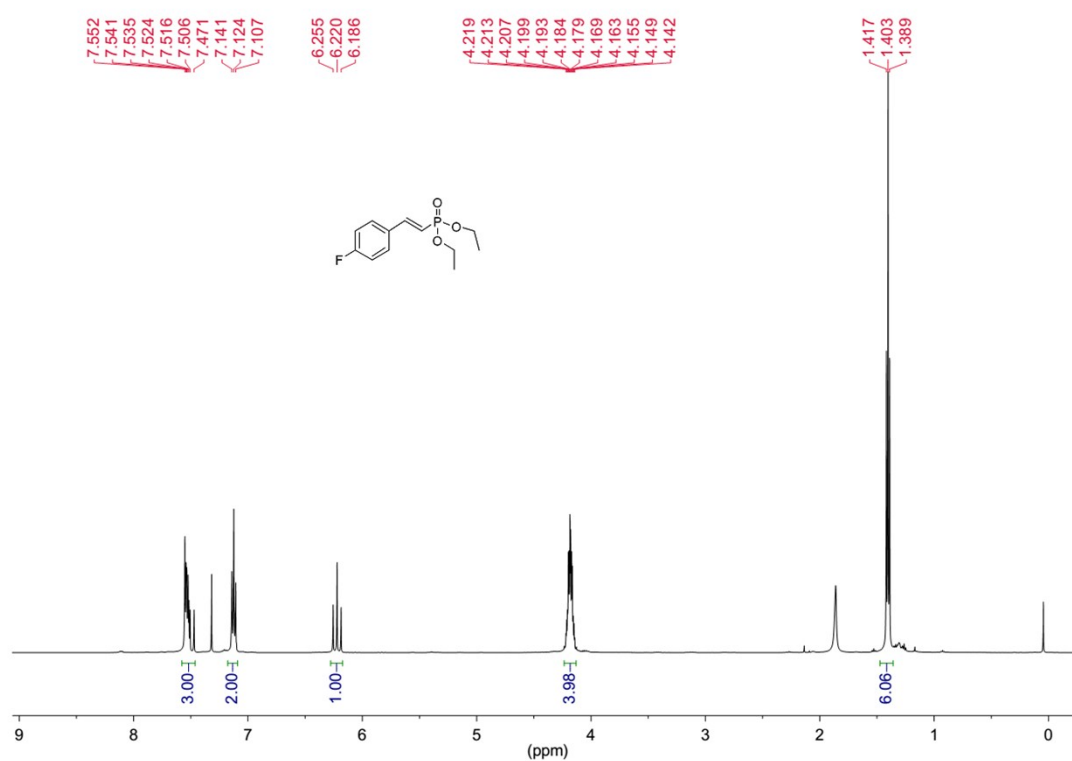
¹³C NMR **3ba**¹H NMR **3ca**

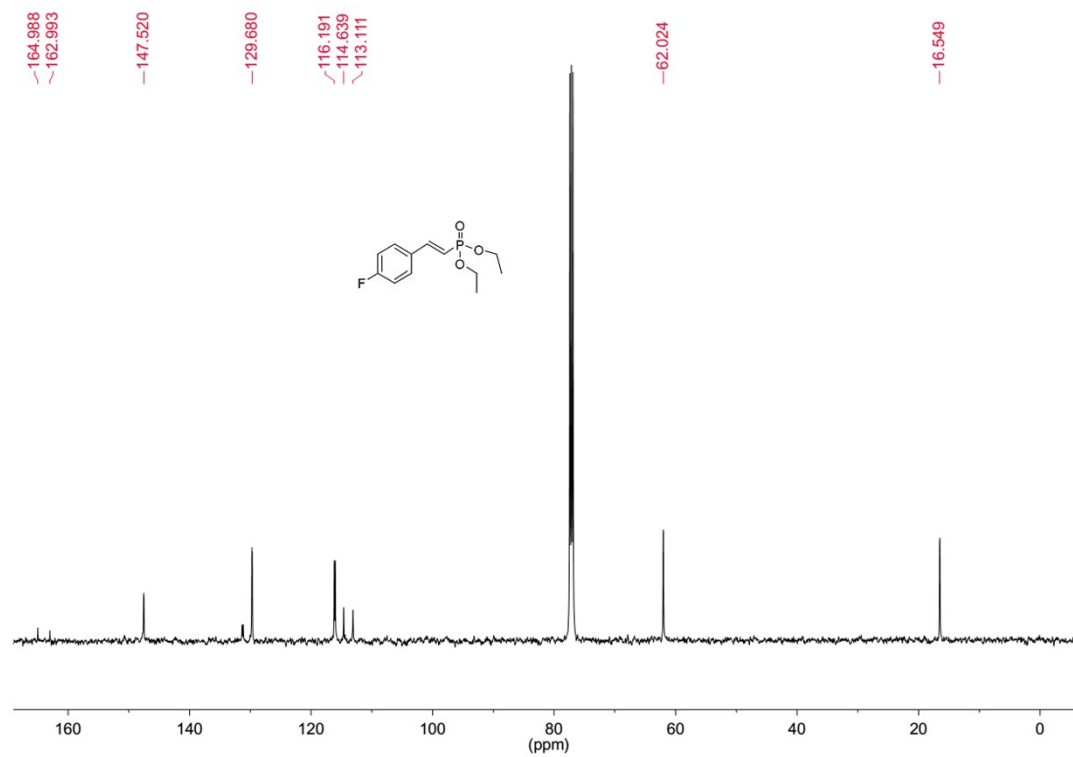
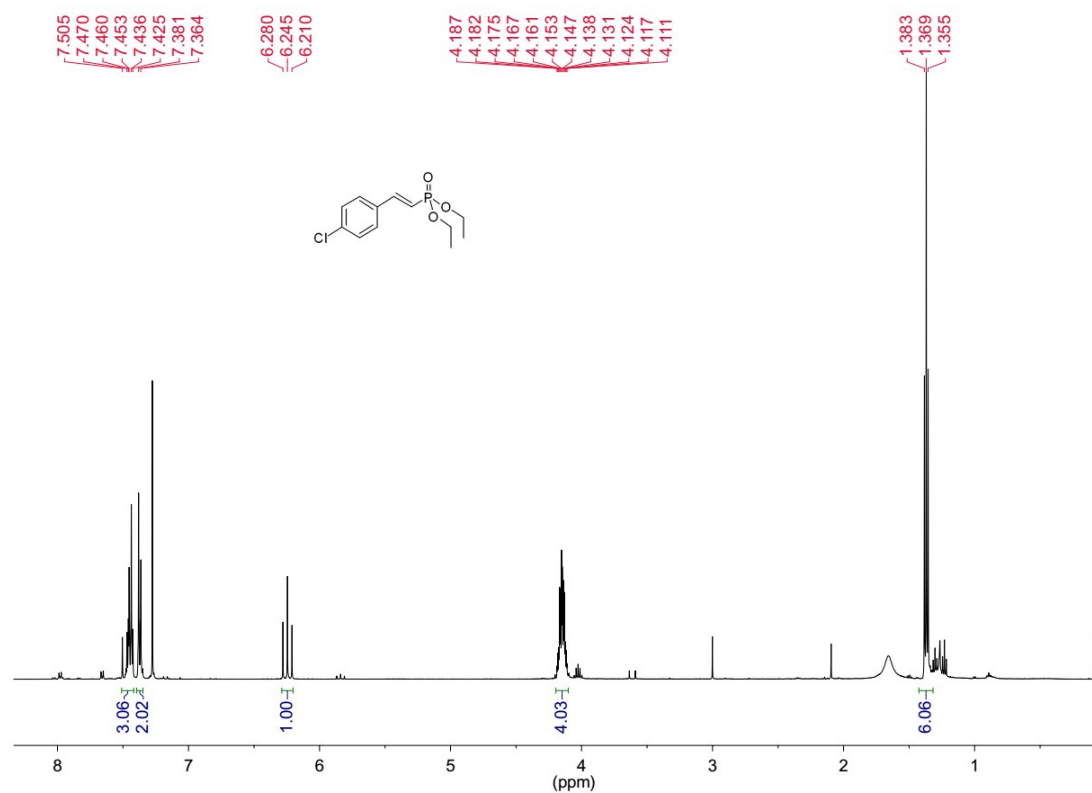
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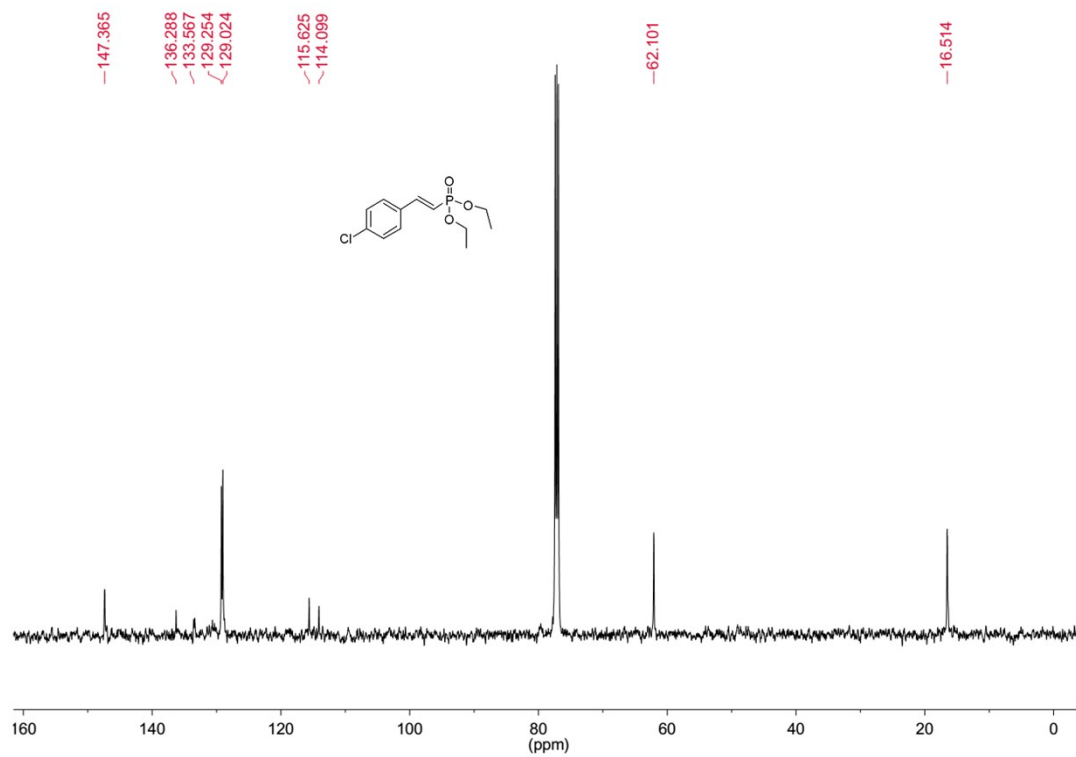
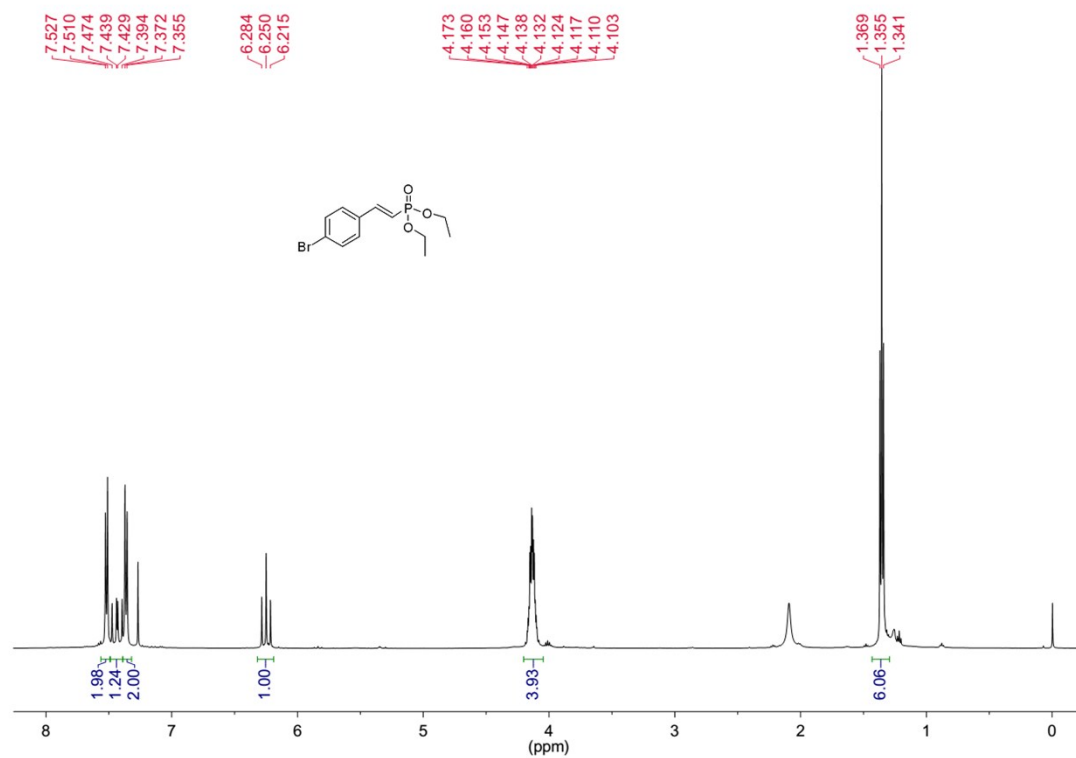
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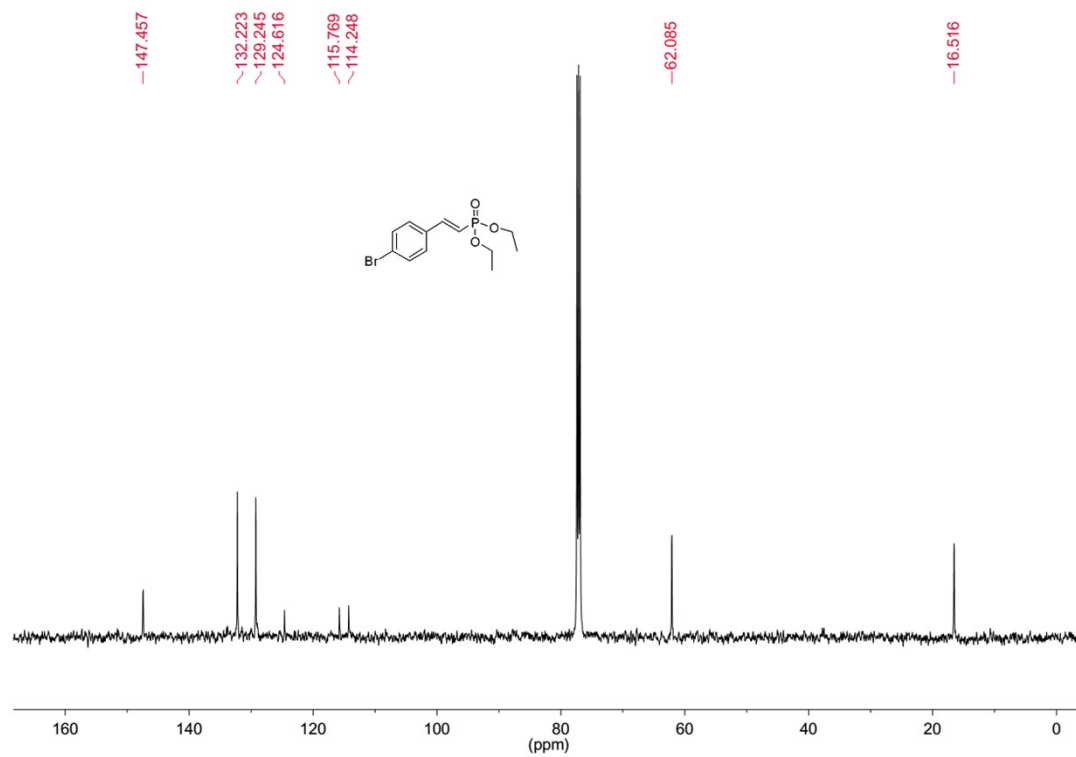
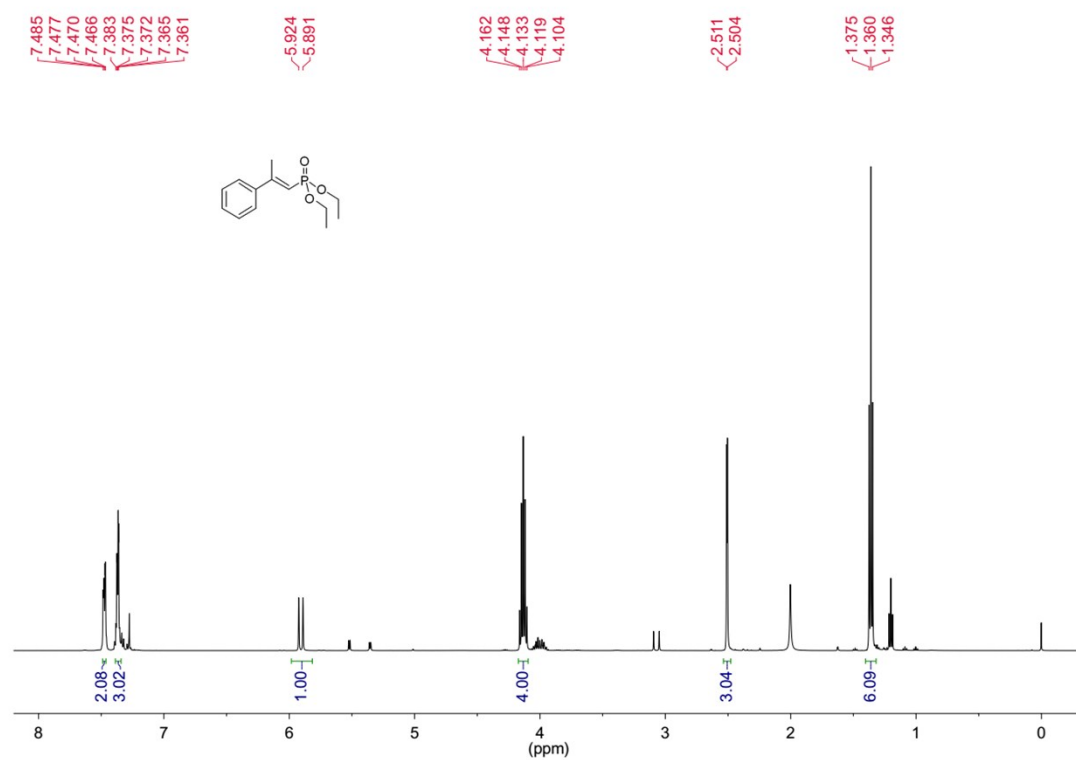
¹³C NMR 3ea³¹P NMR 3ea

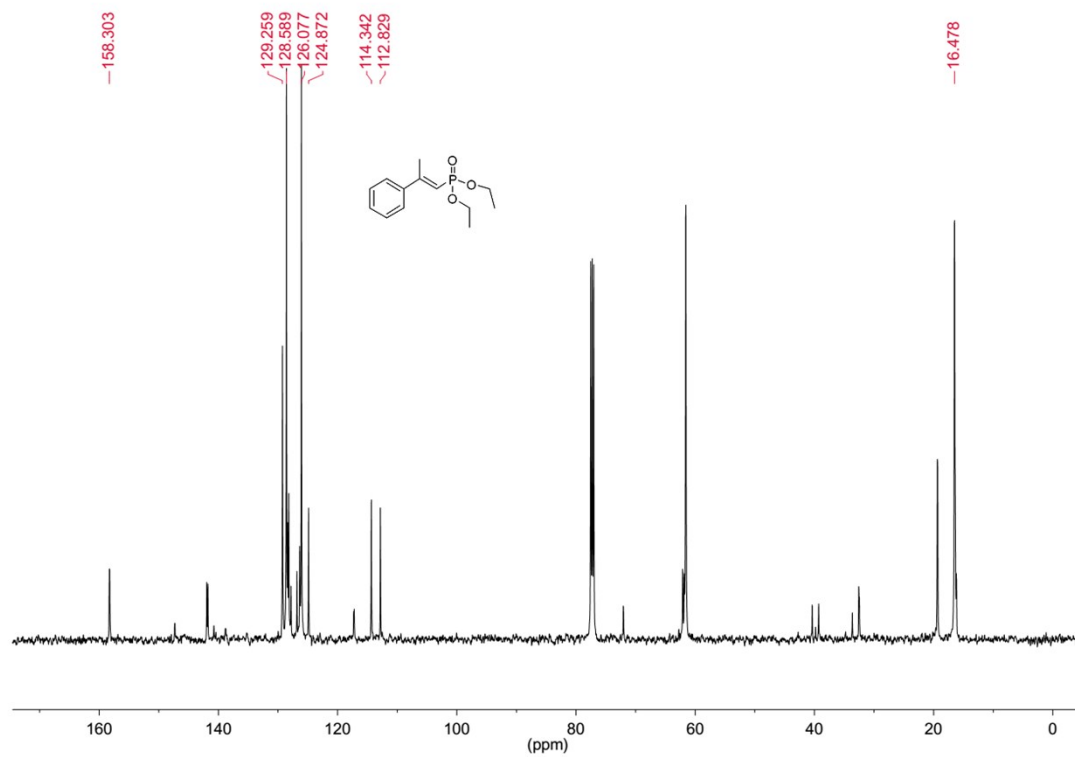
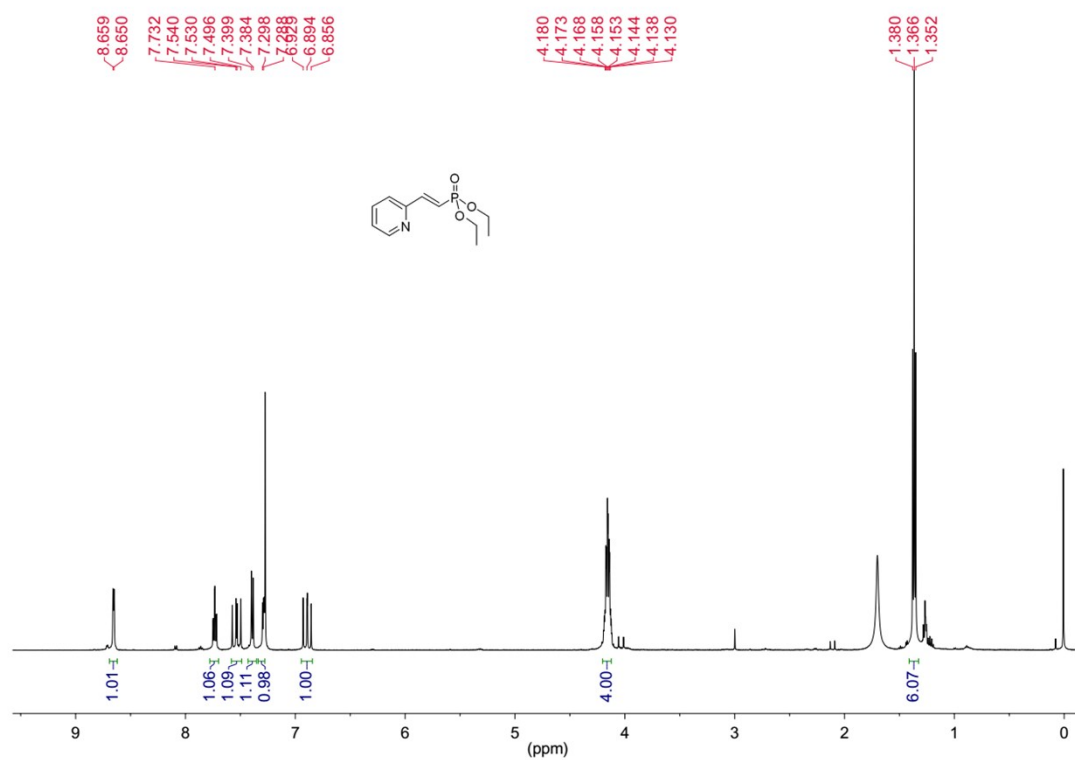
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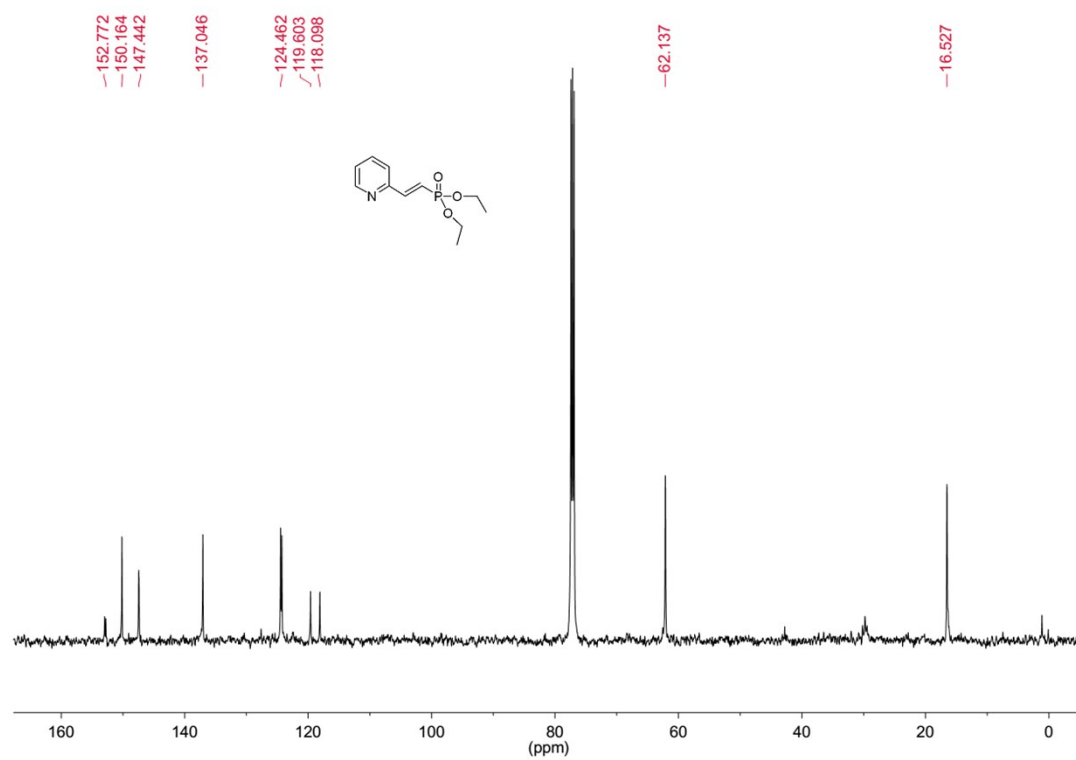
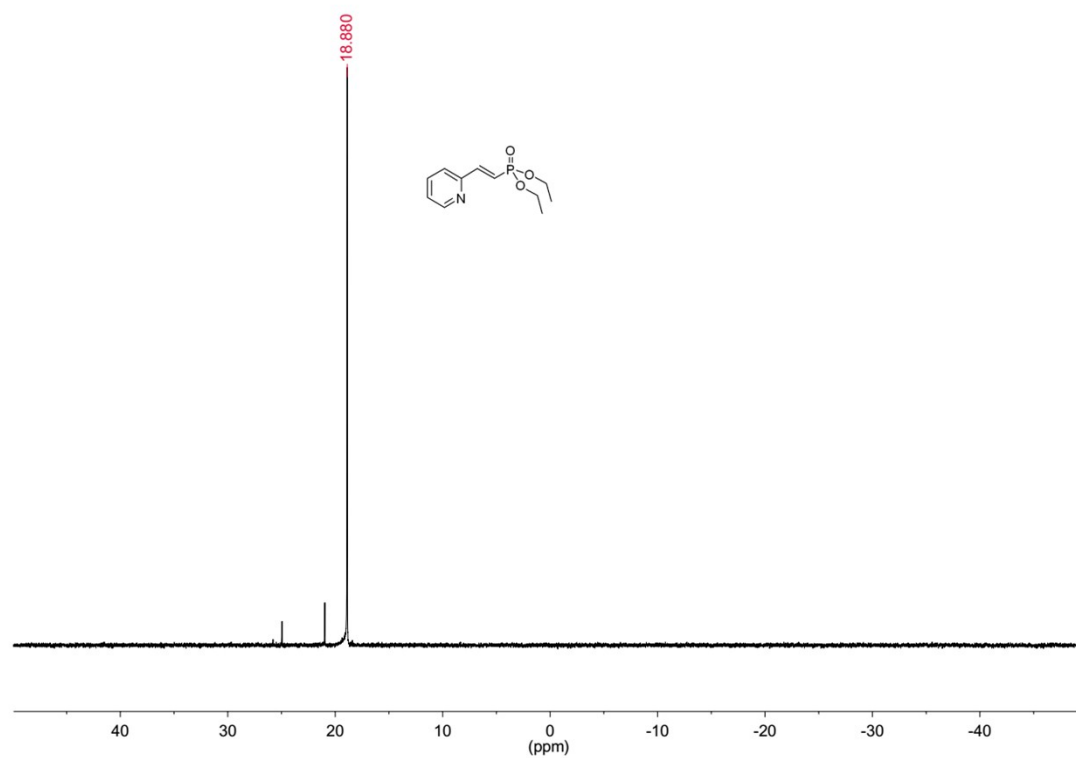
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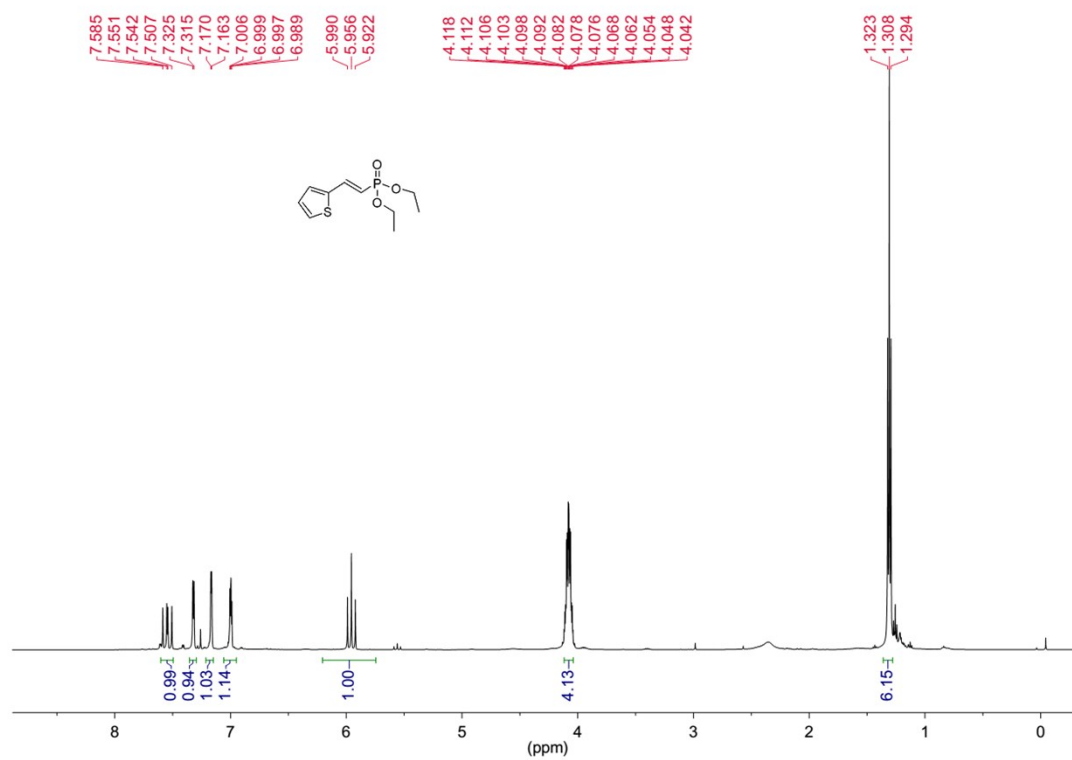
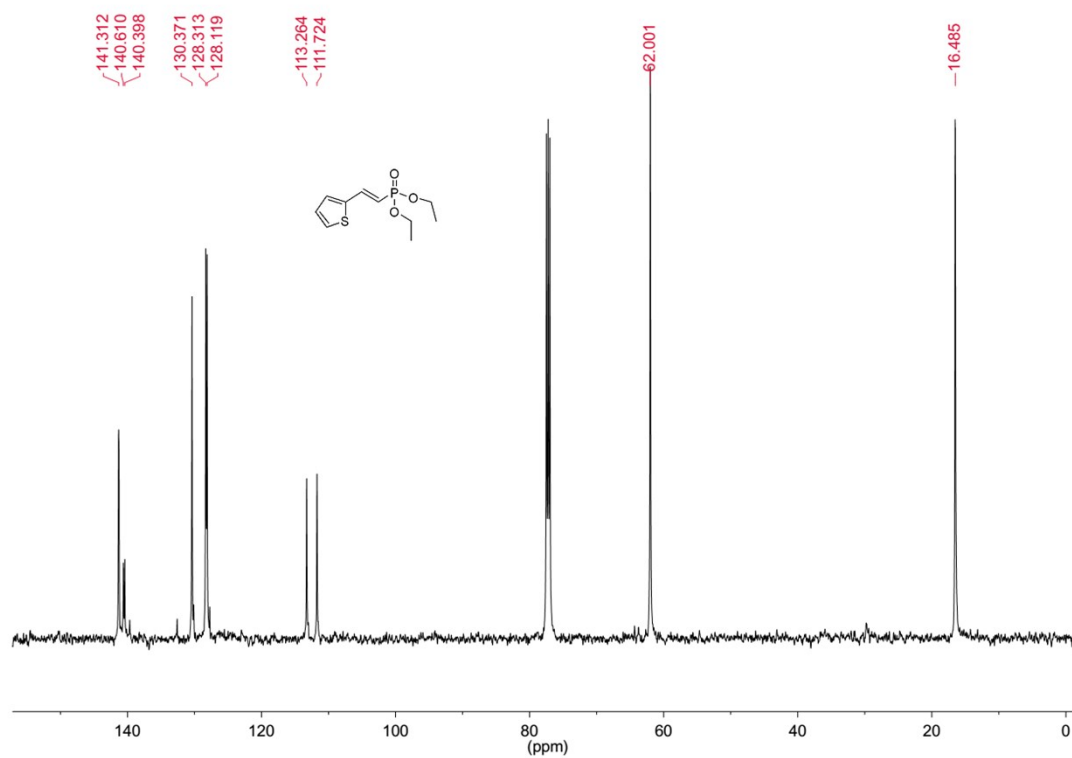
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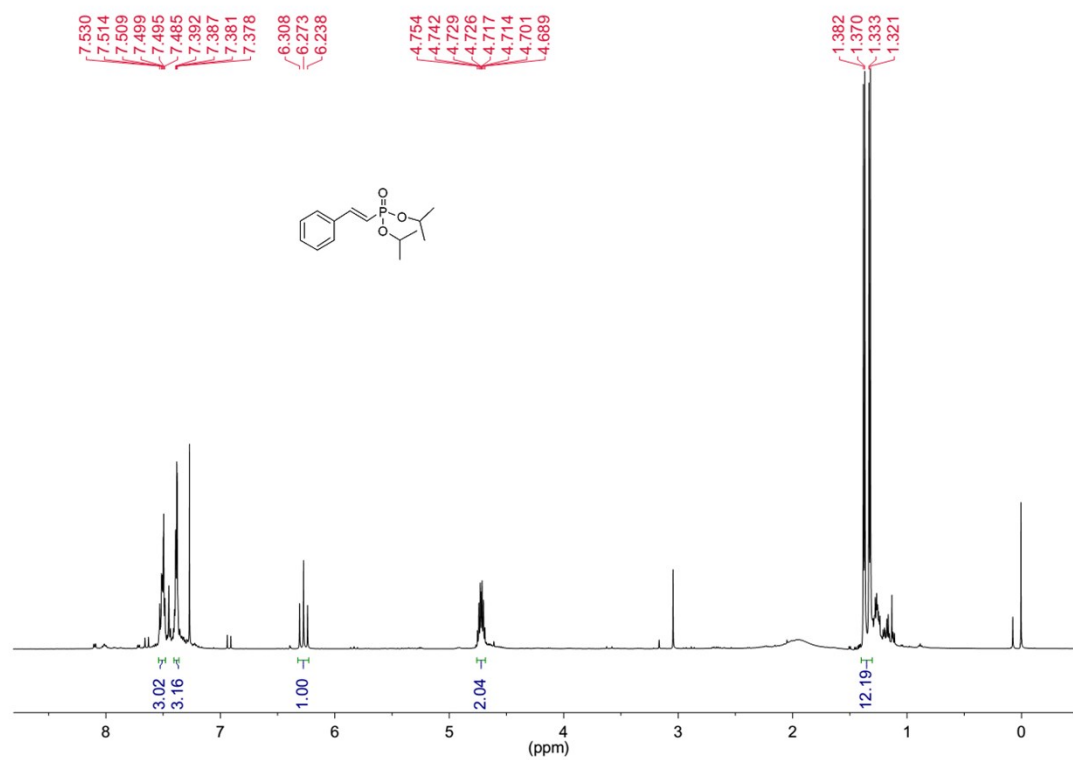
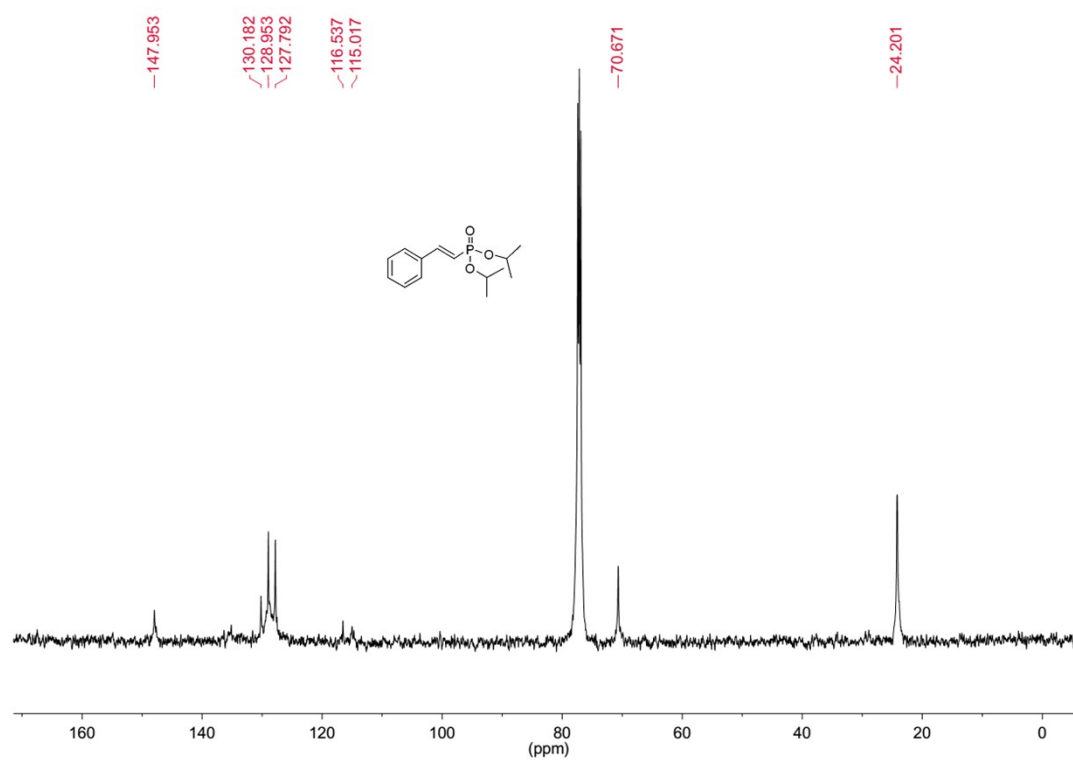
¹³C NMR 3ha¹H NMR 3ia

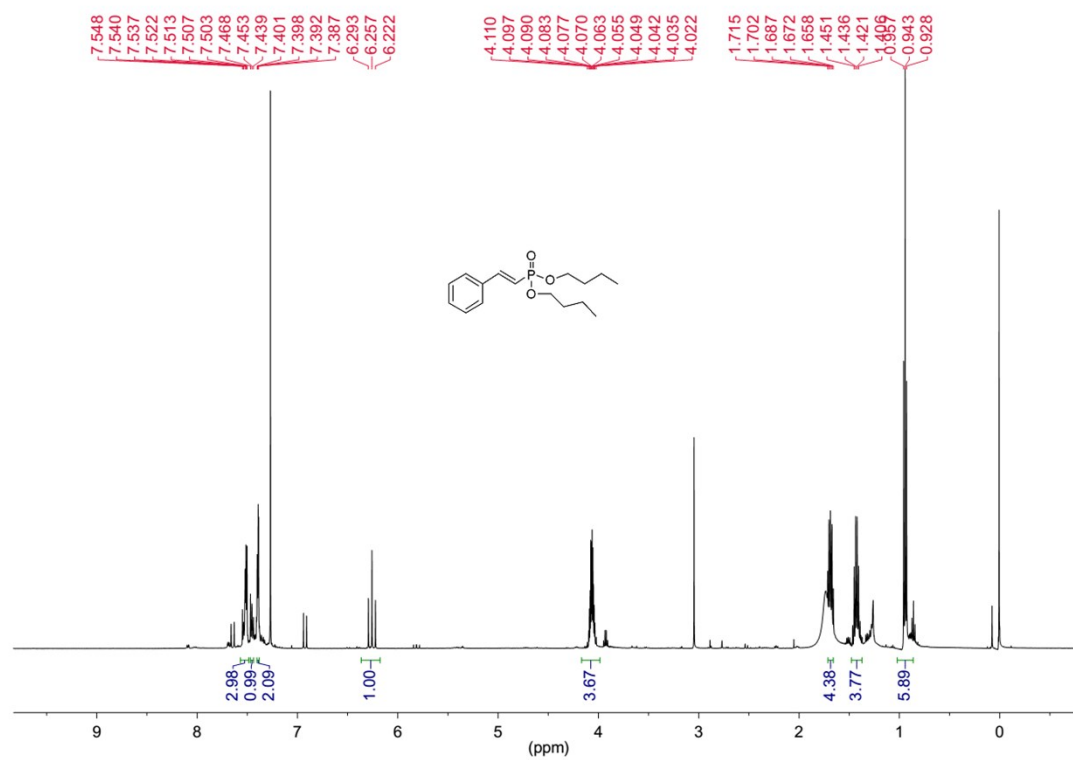
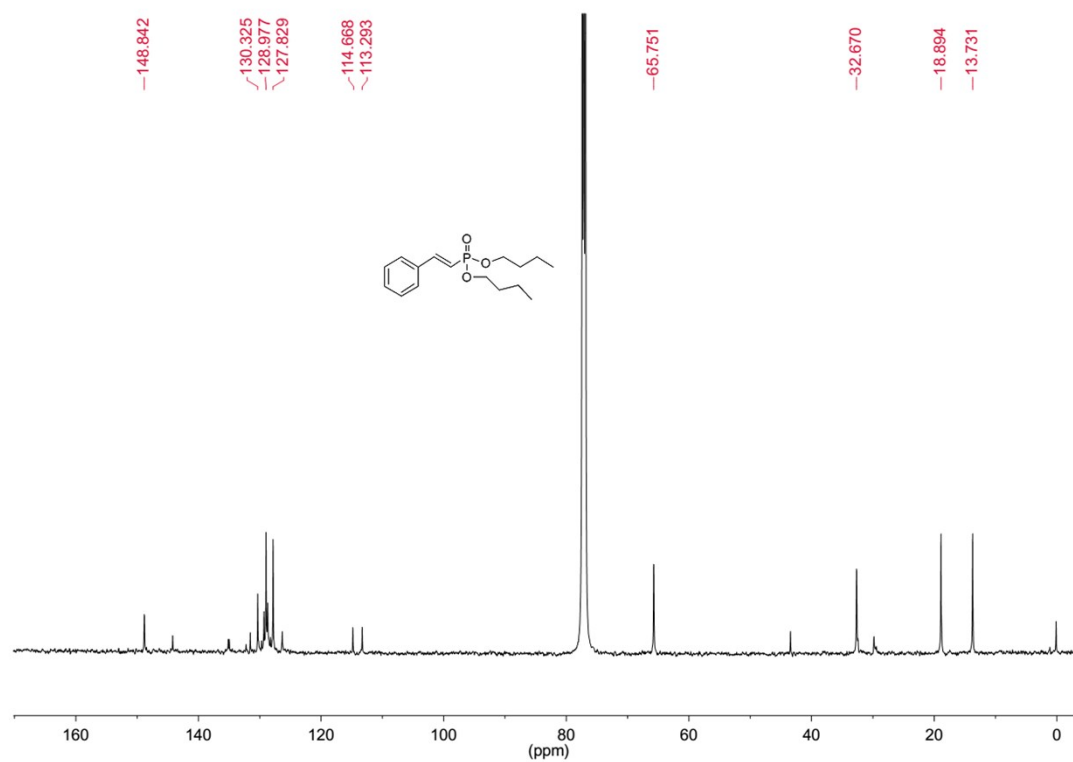
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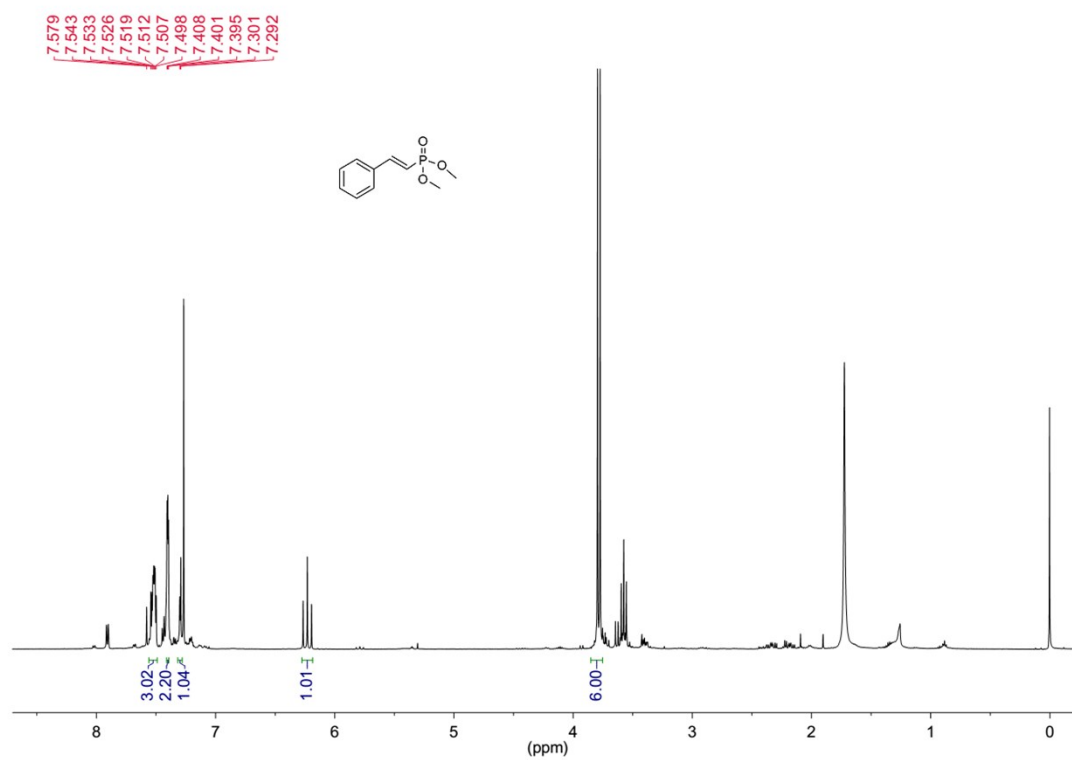
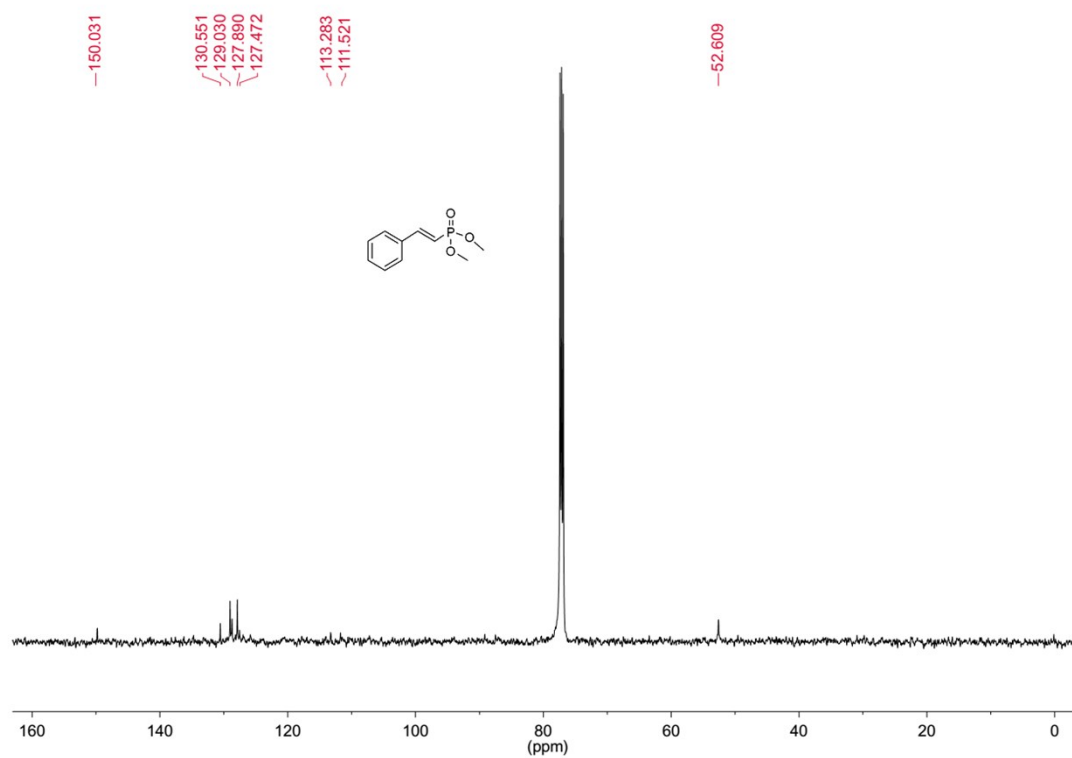
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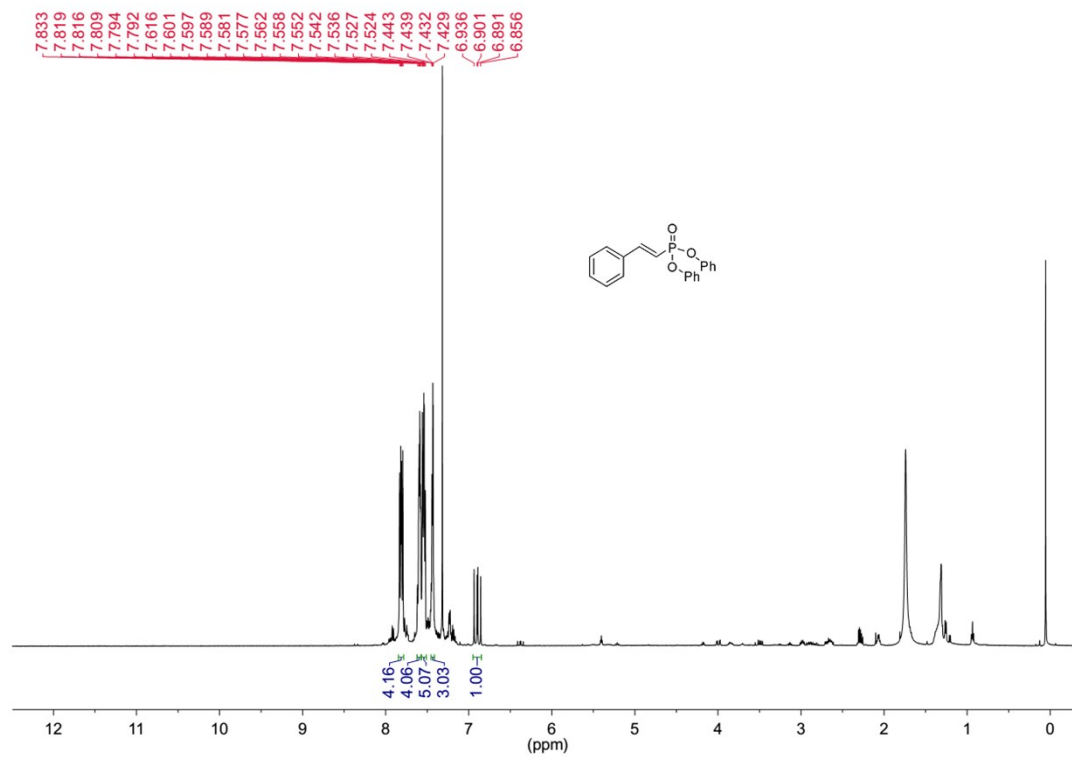
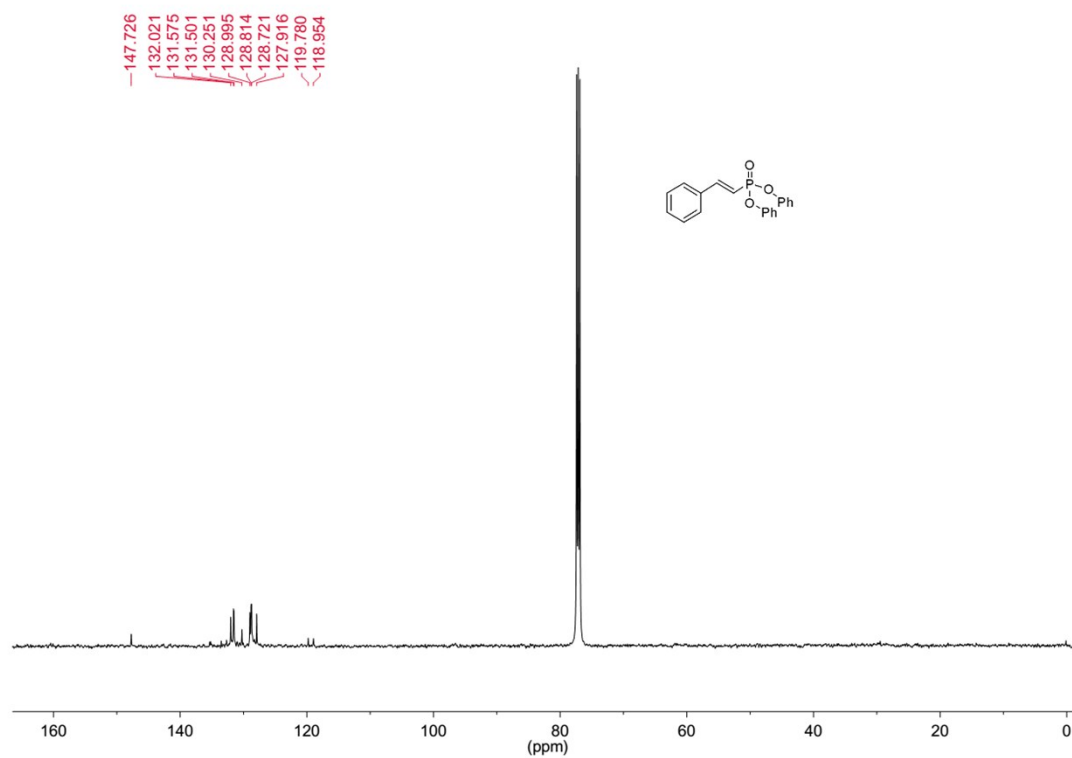
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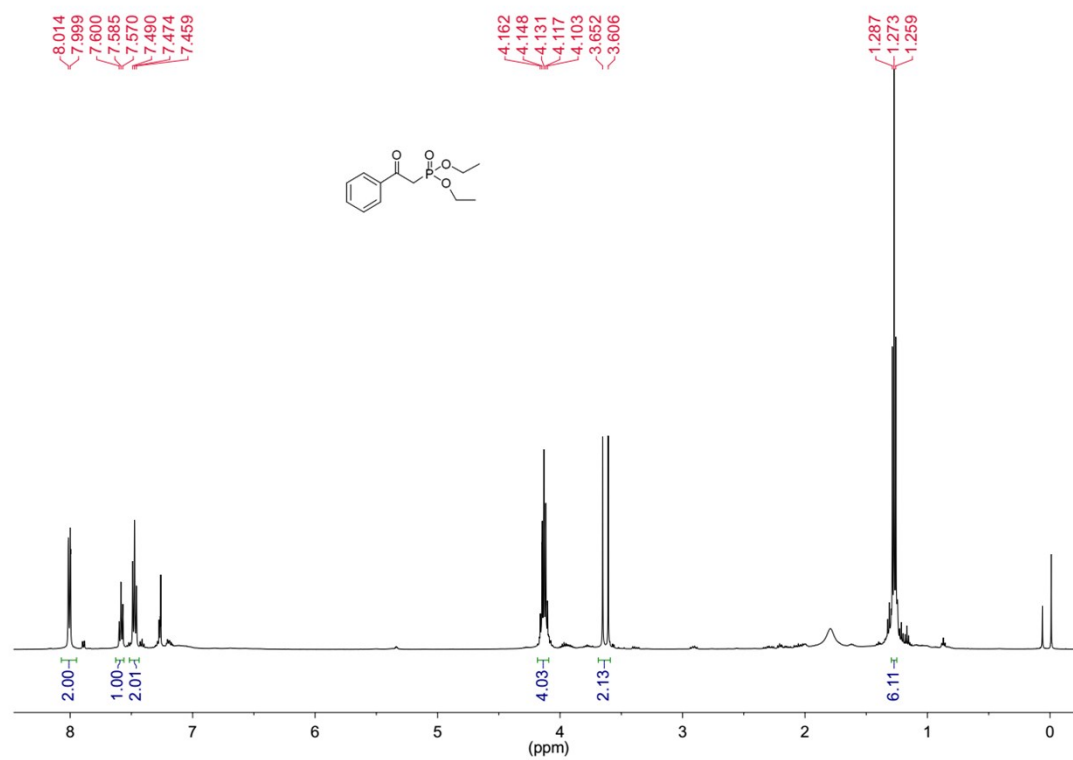
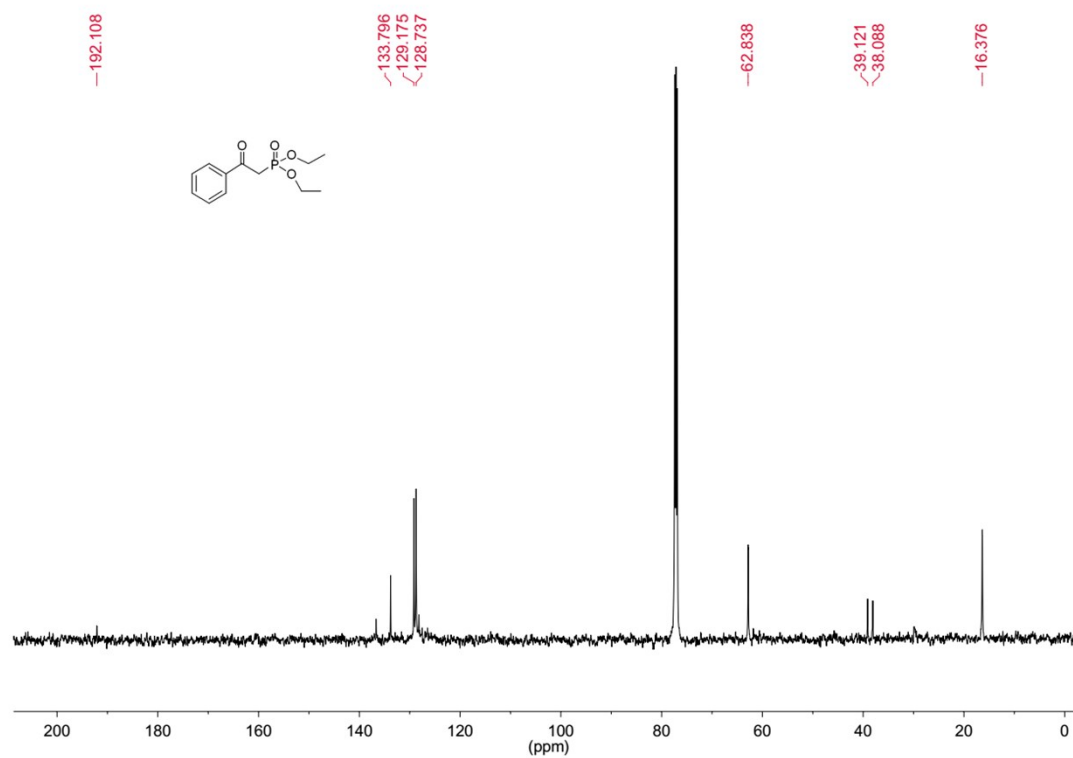
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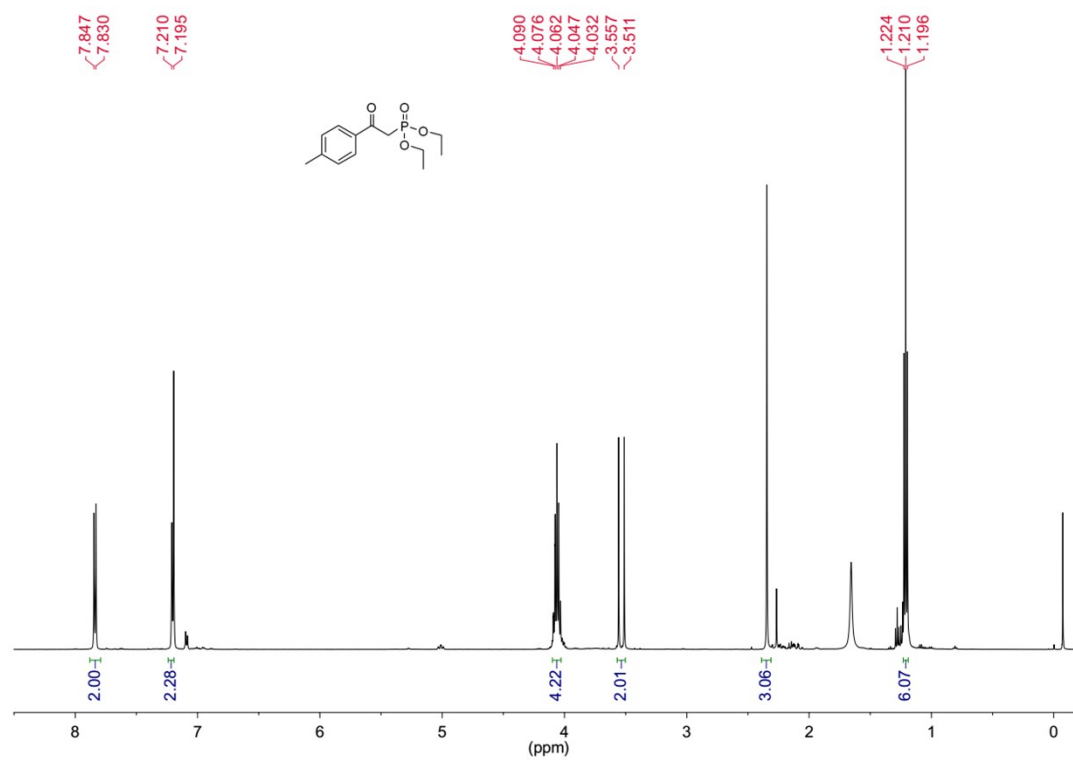
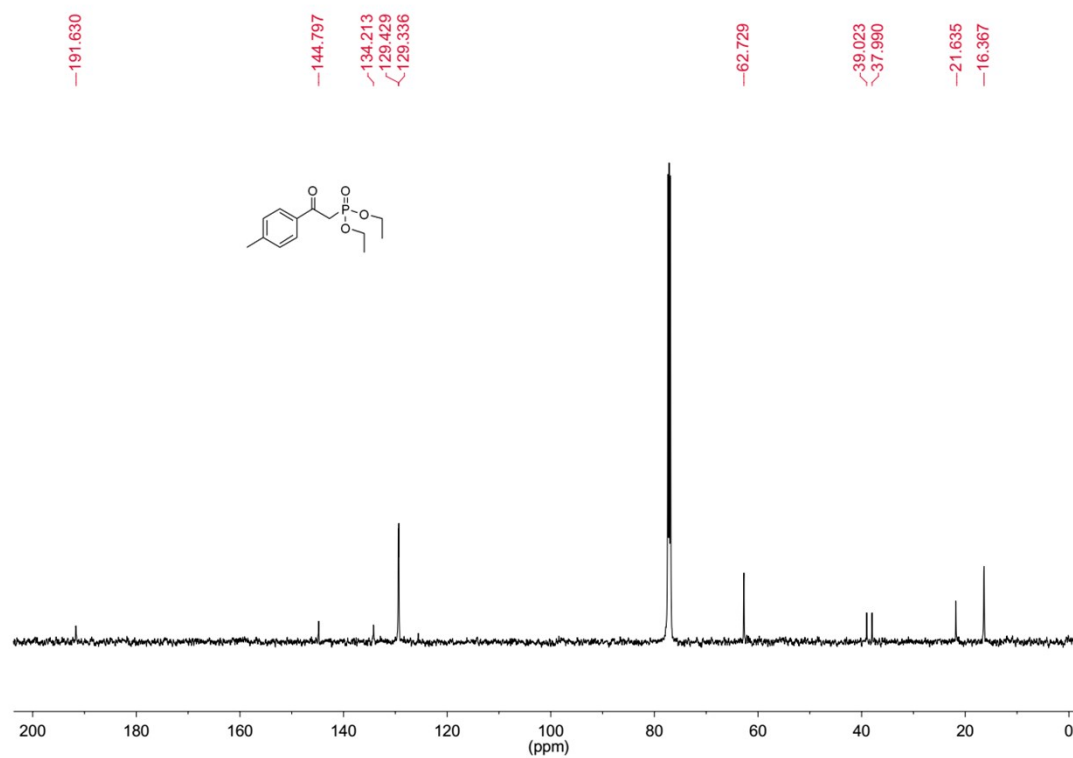
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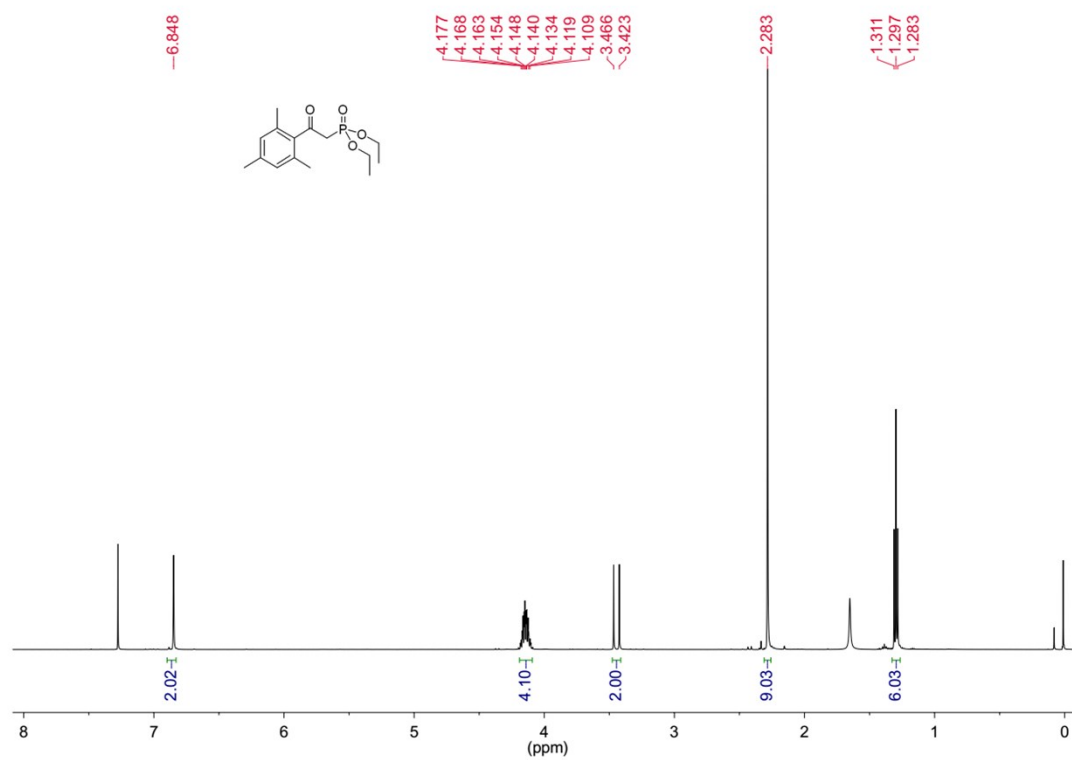
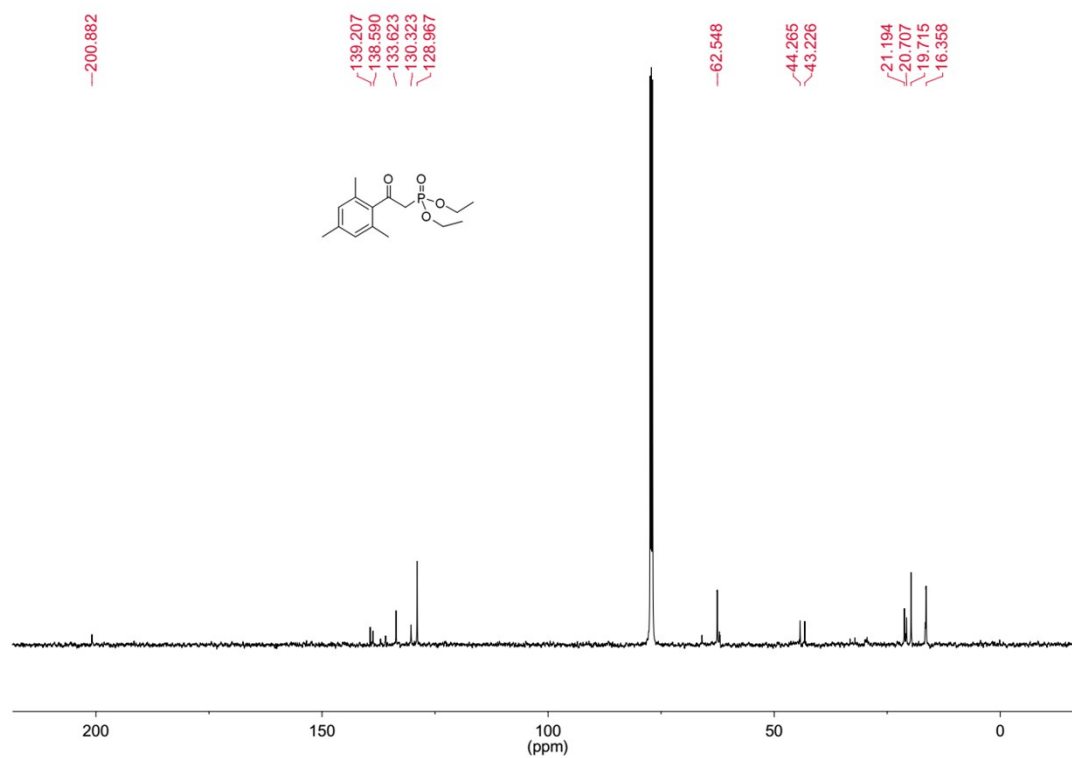
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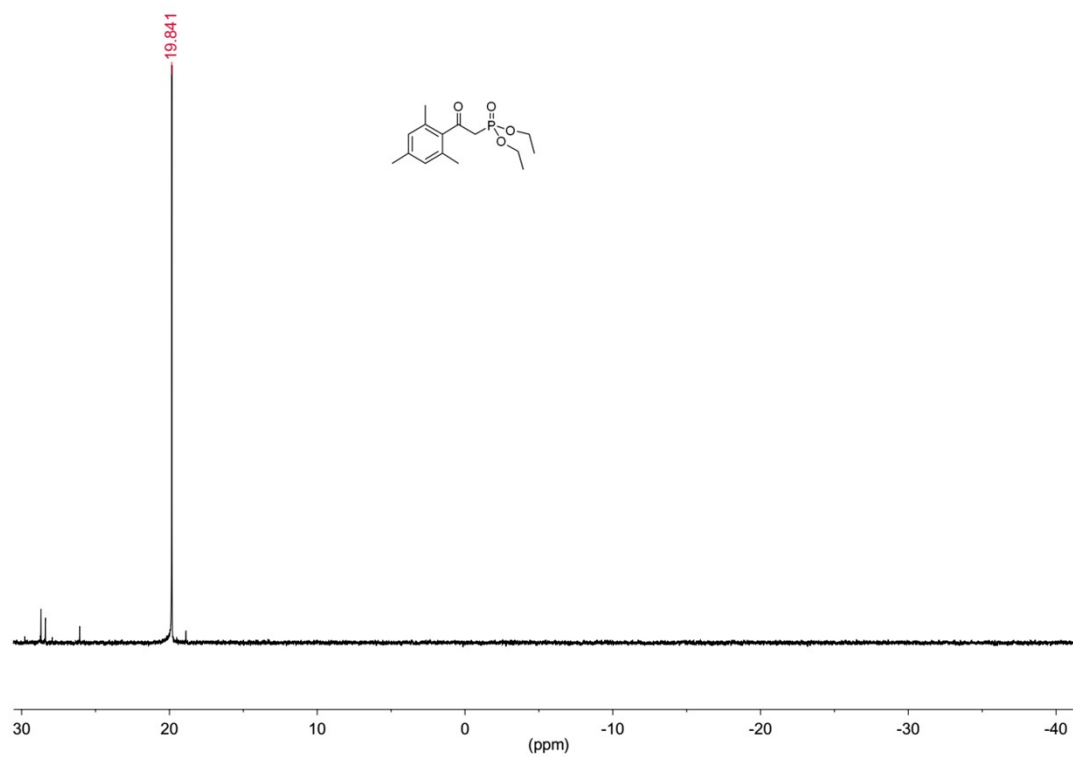
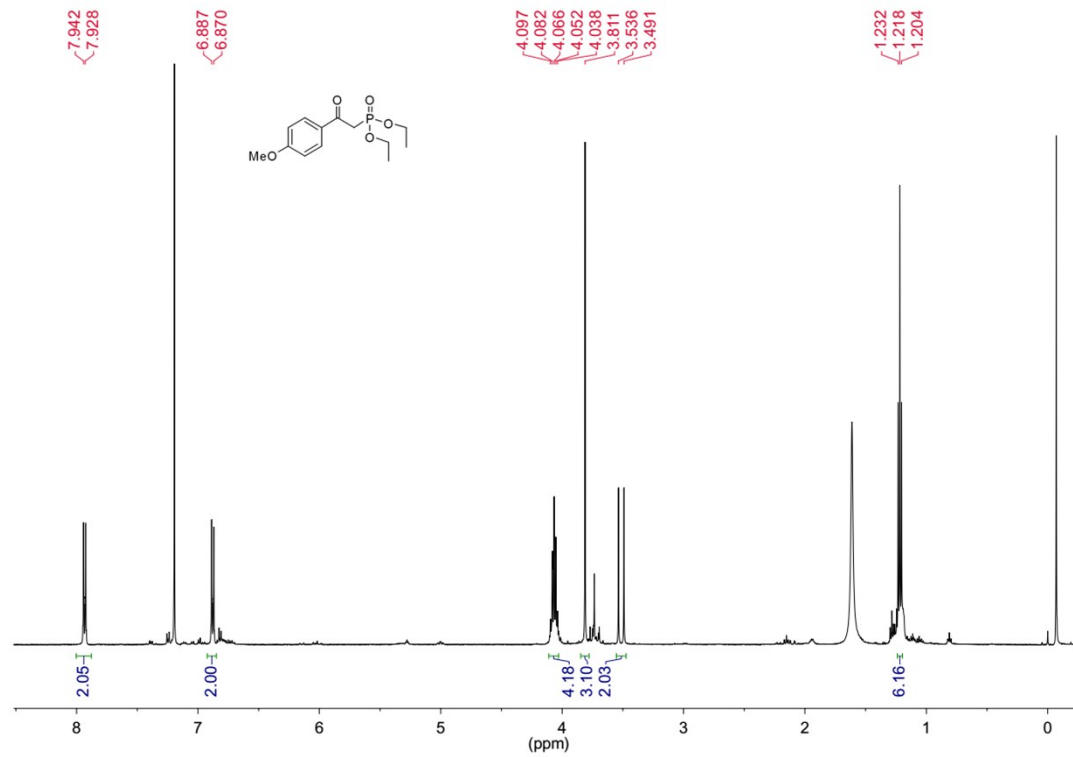
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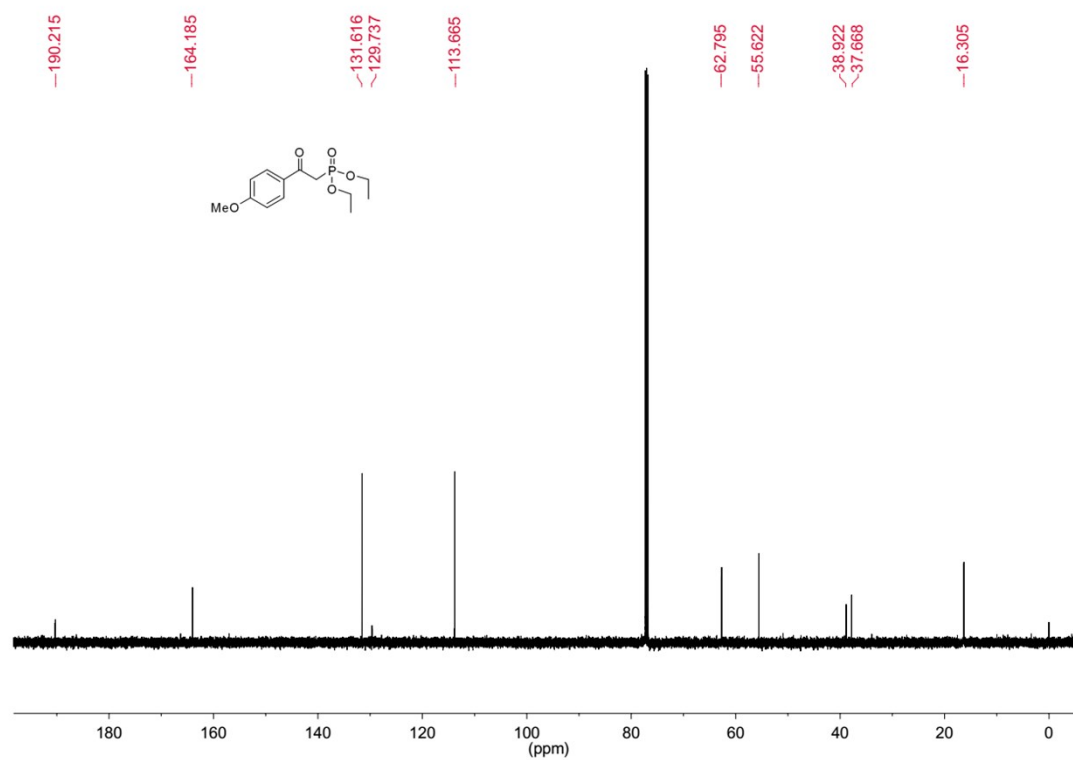
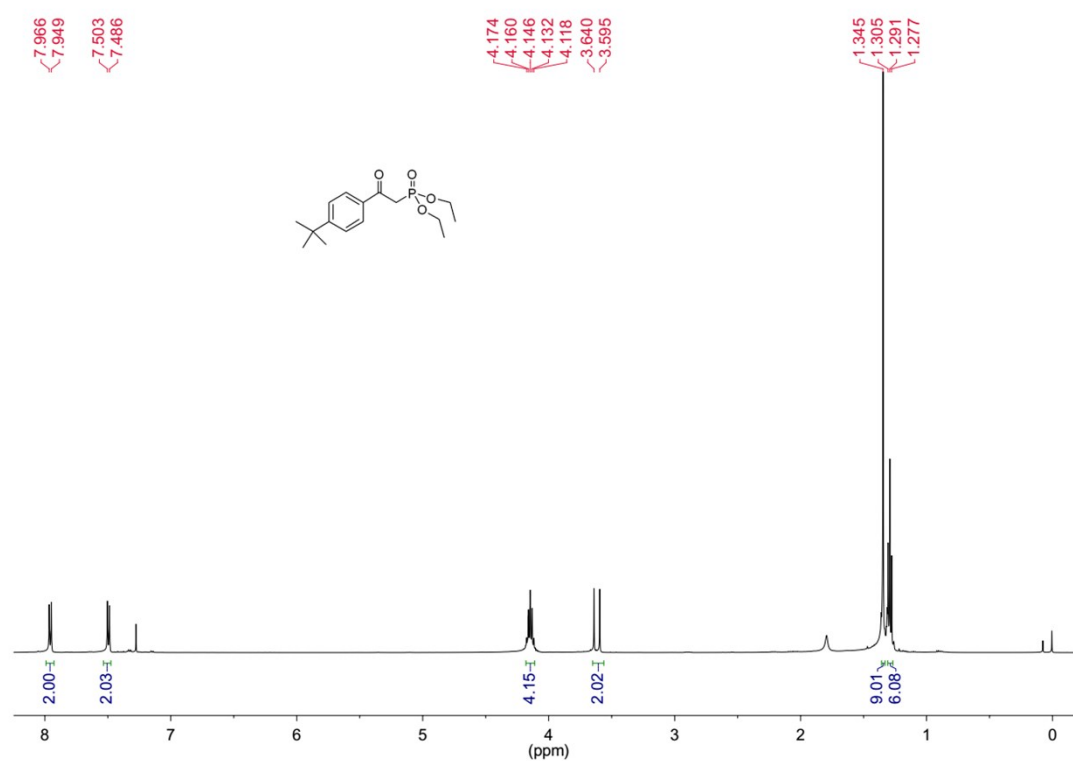
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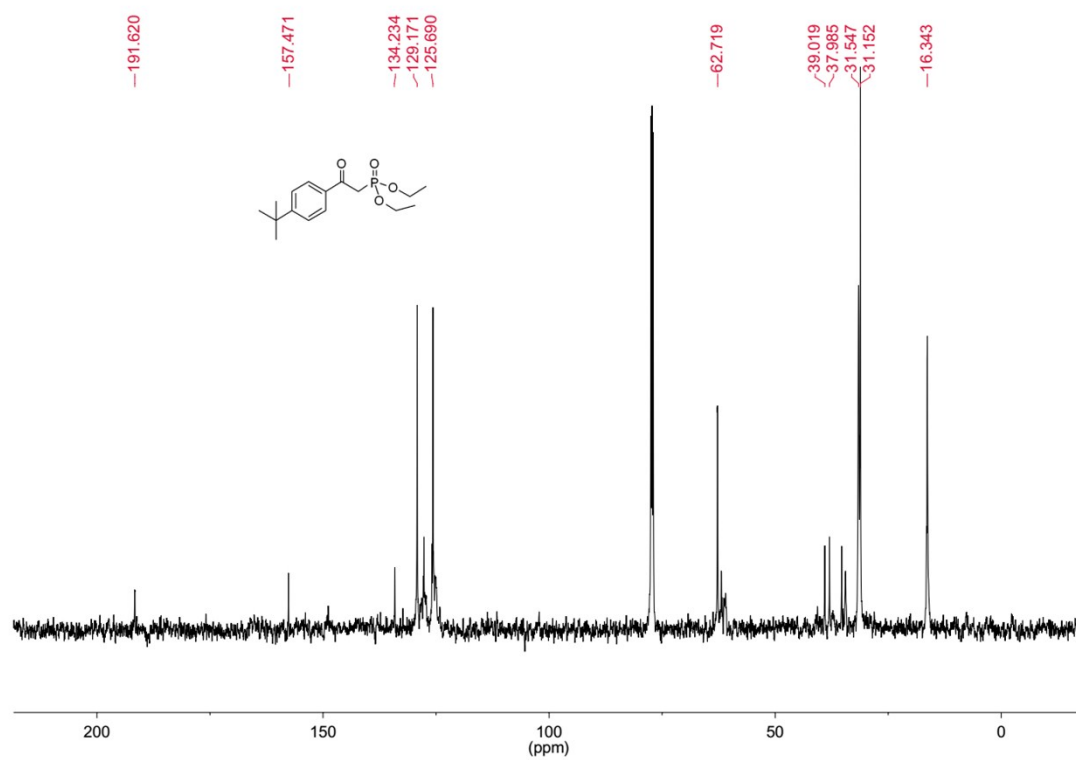
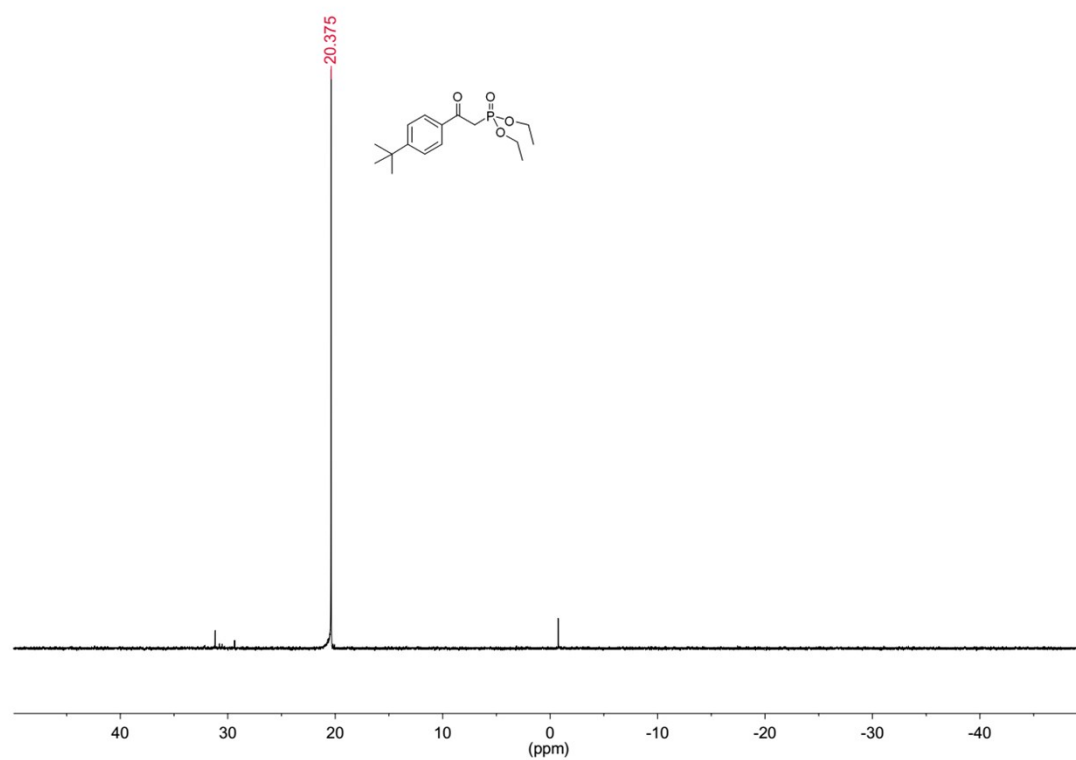
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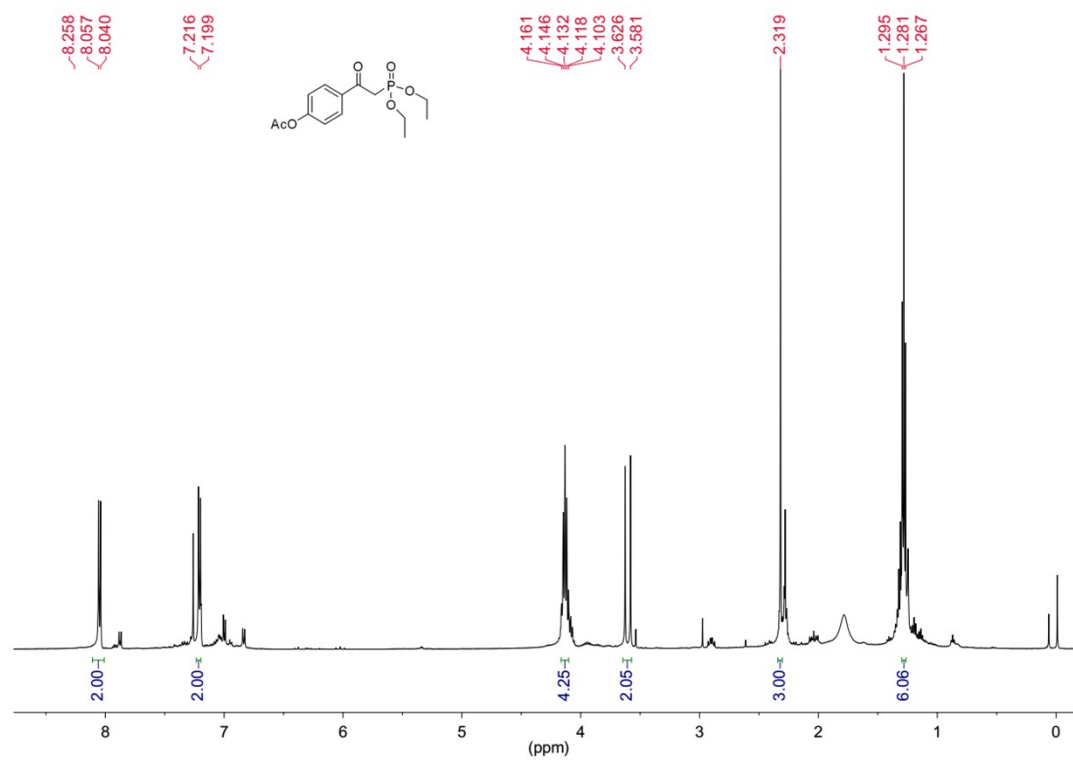
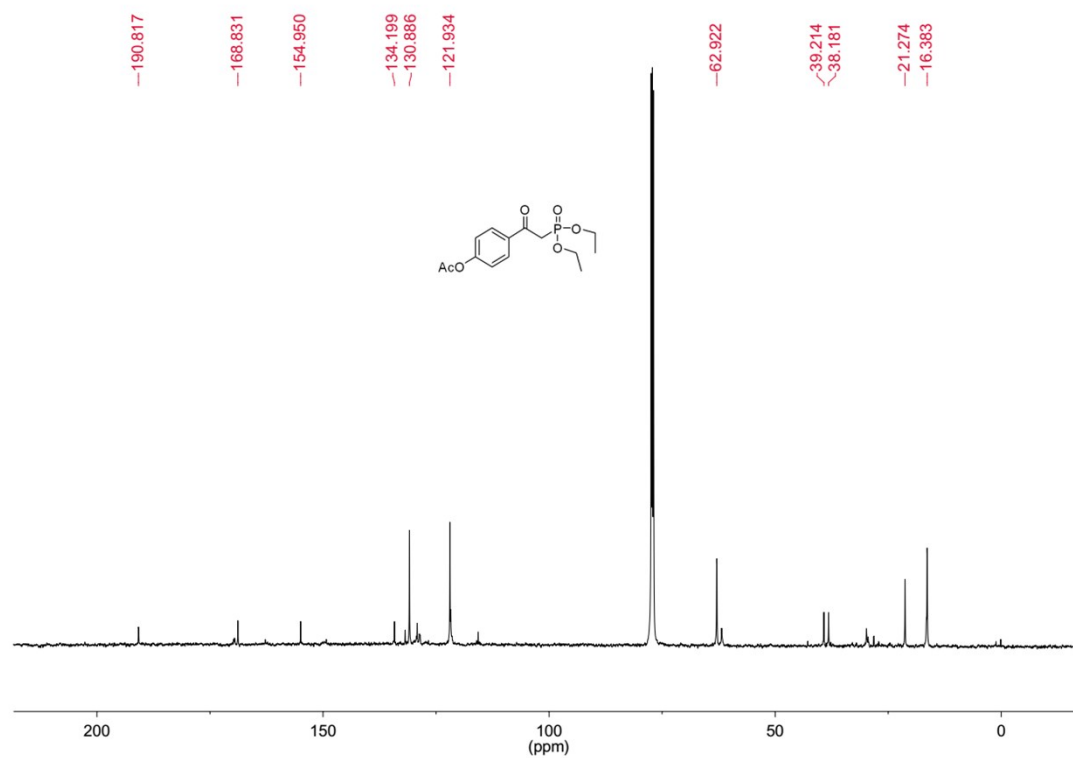
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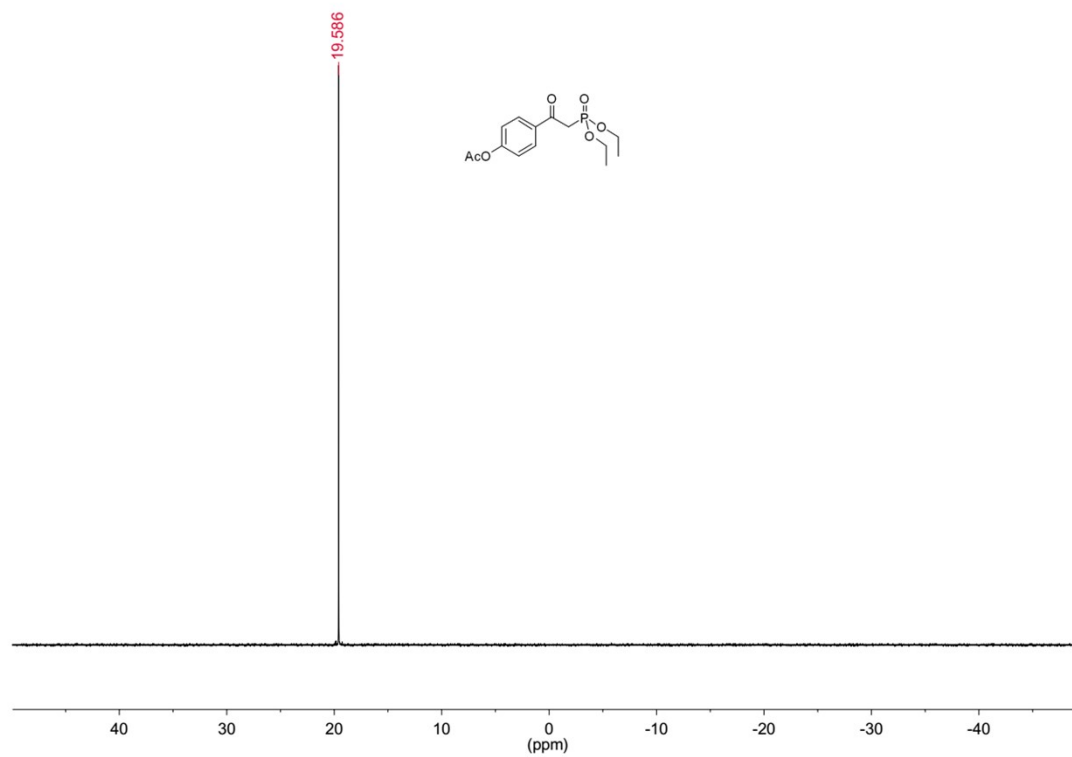
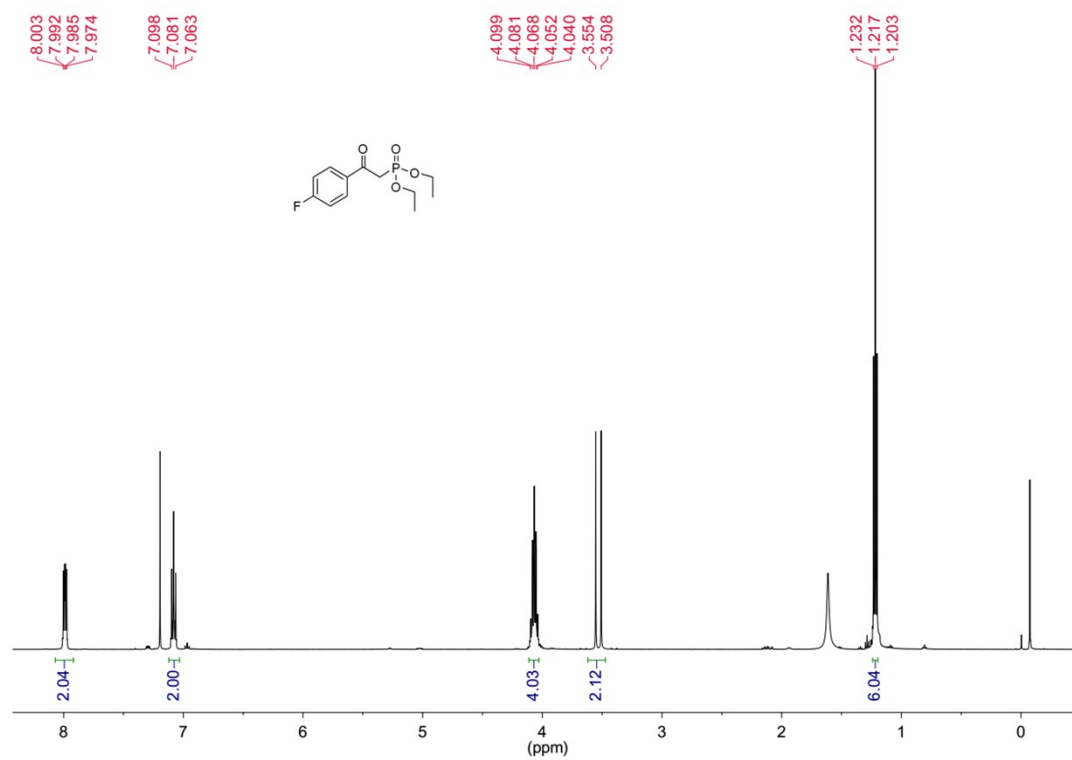
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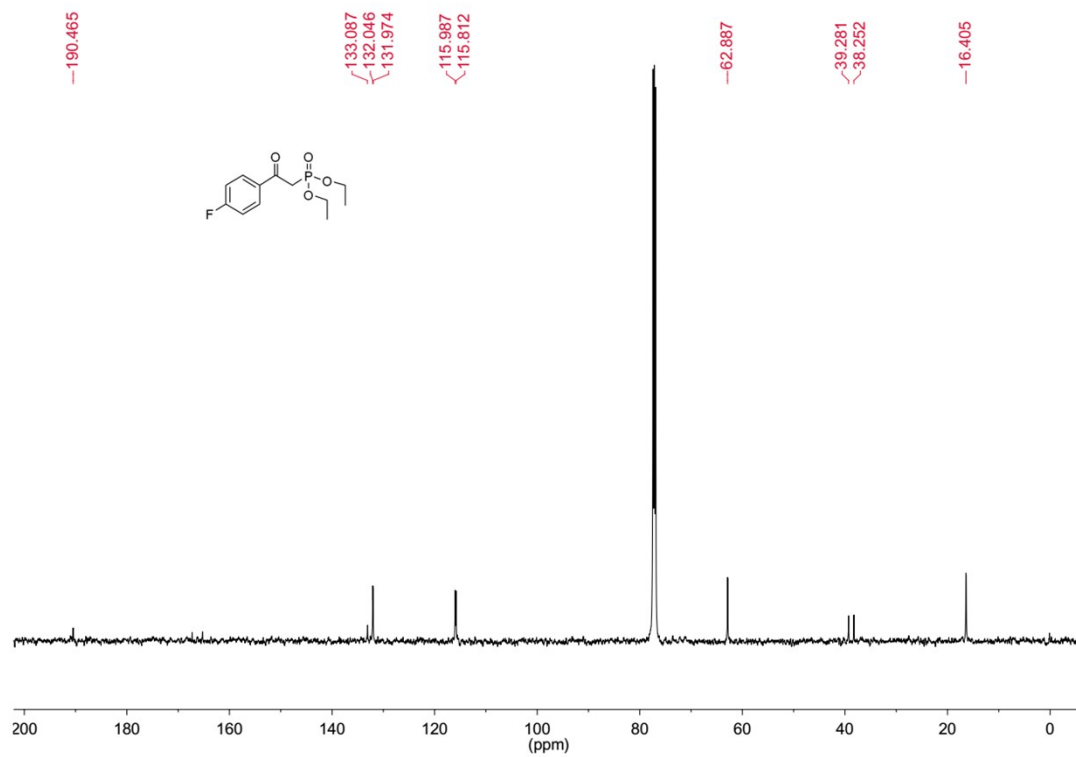
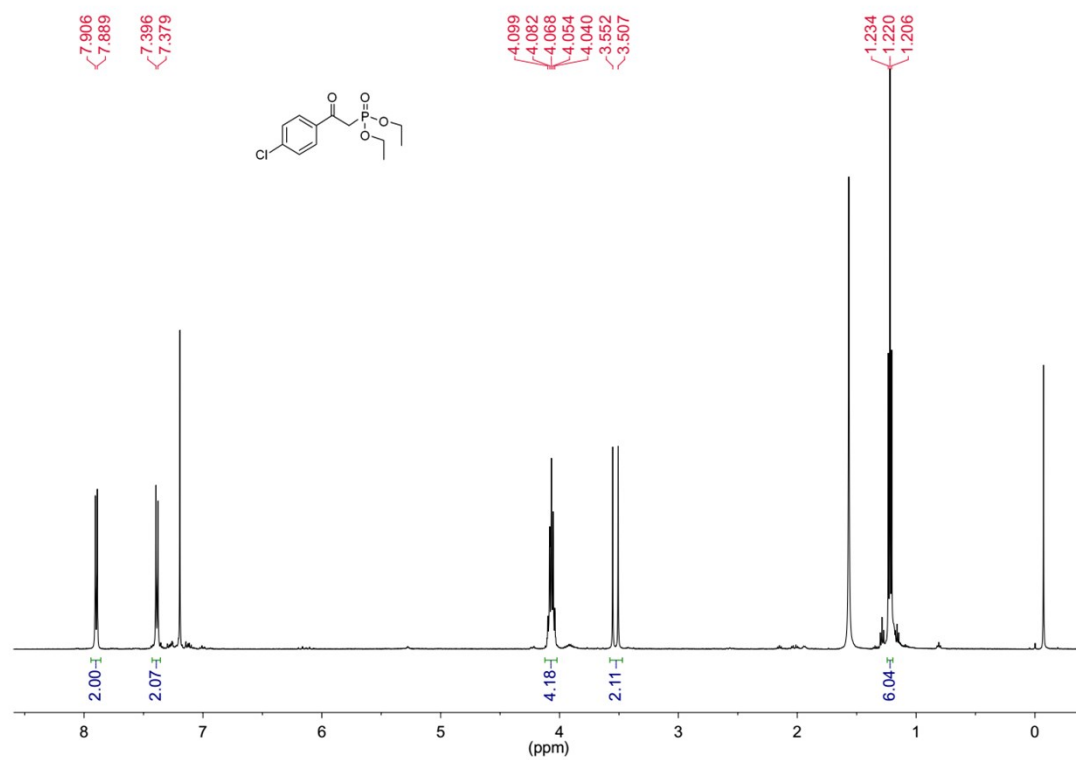
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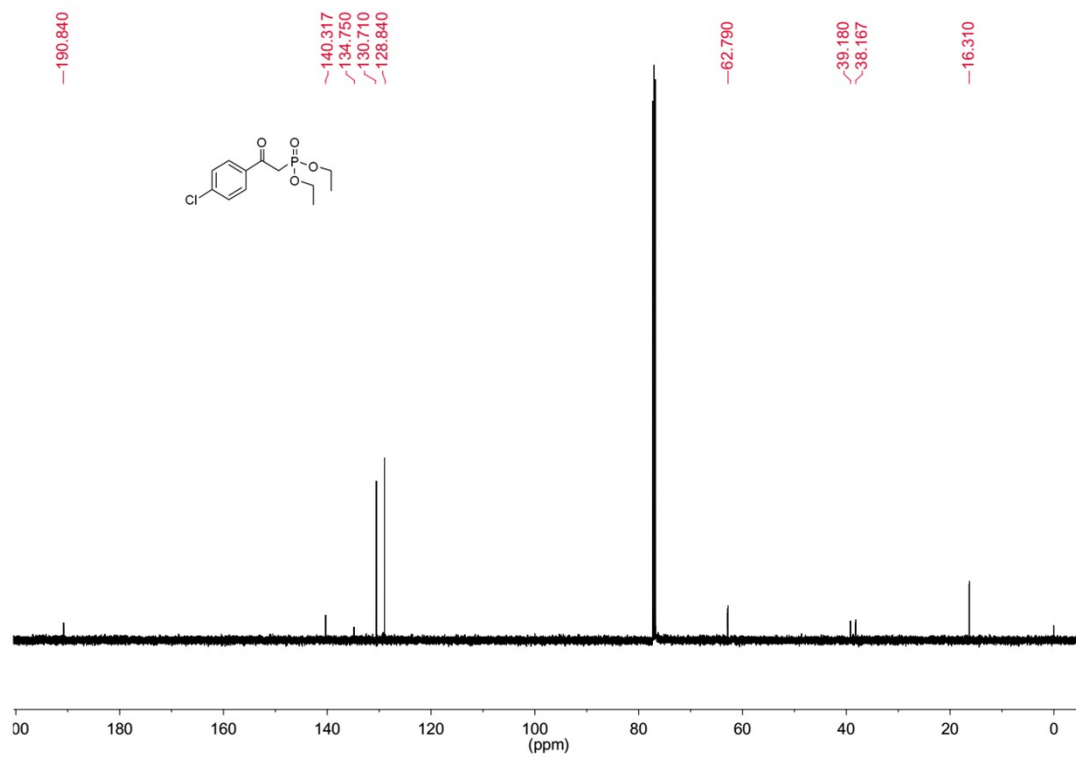
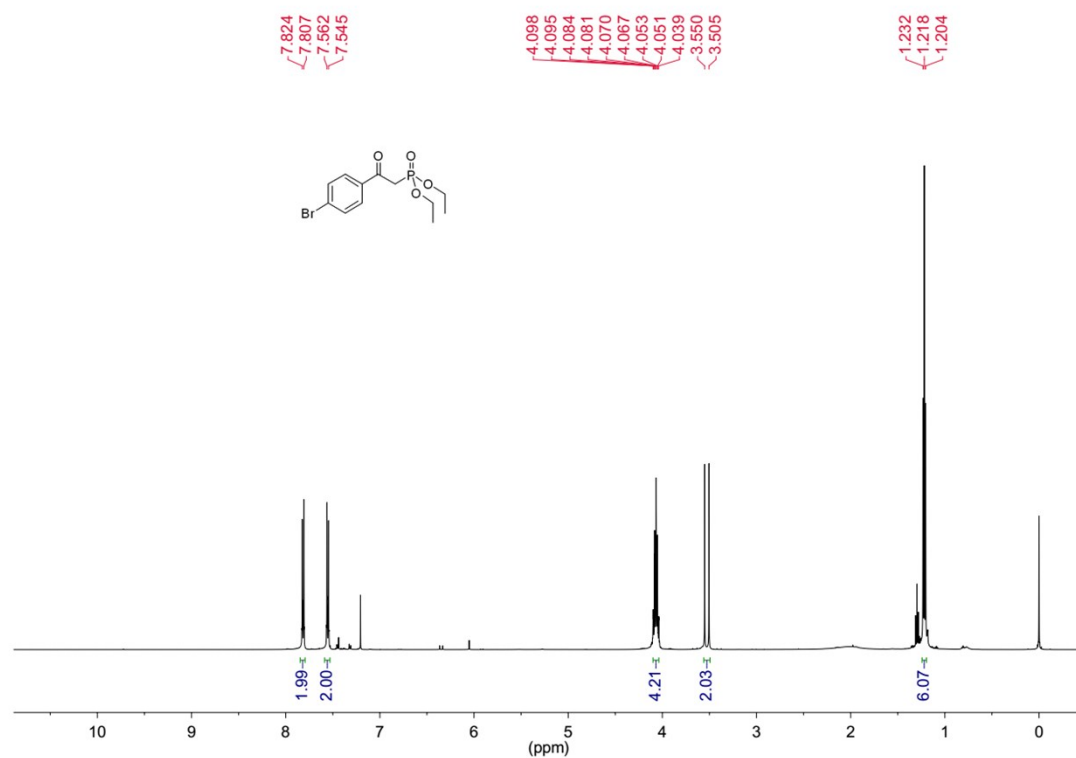
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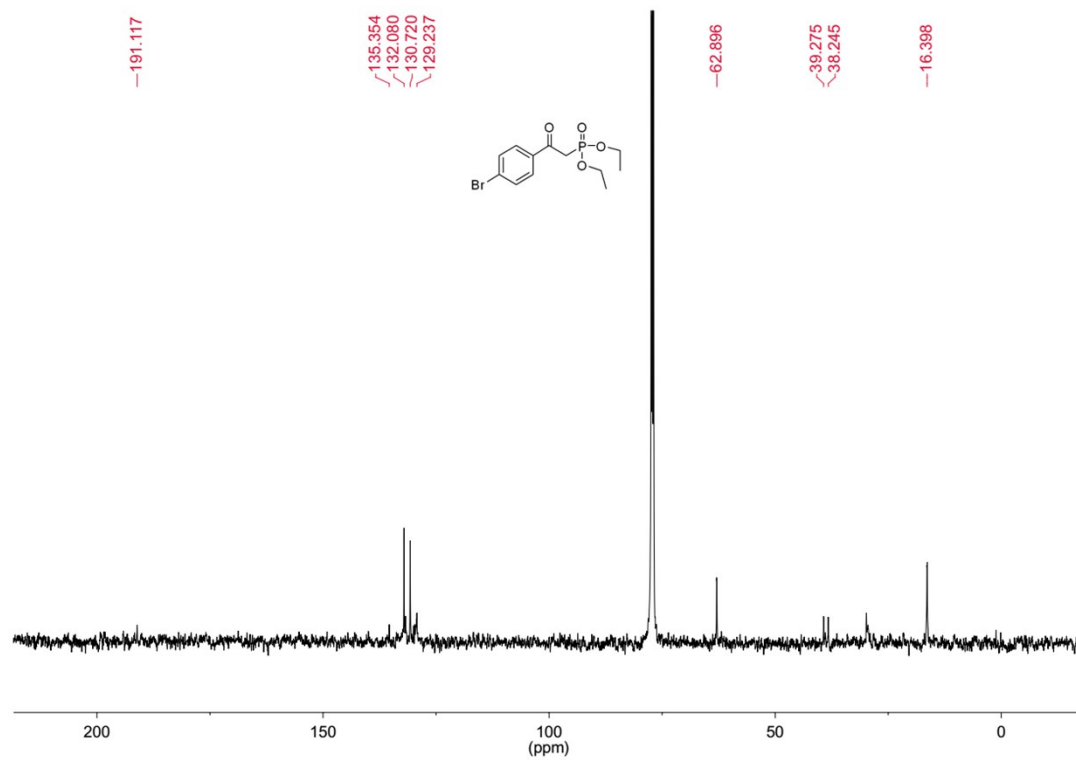
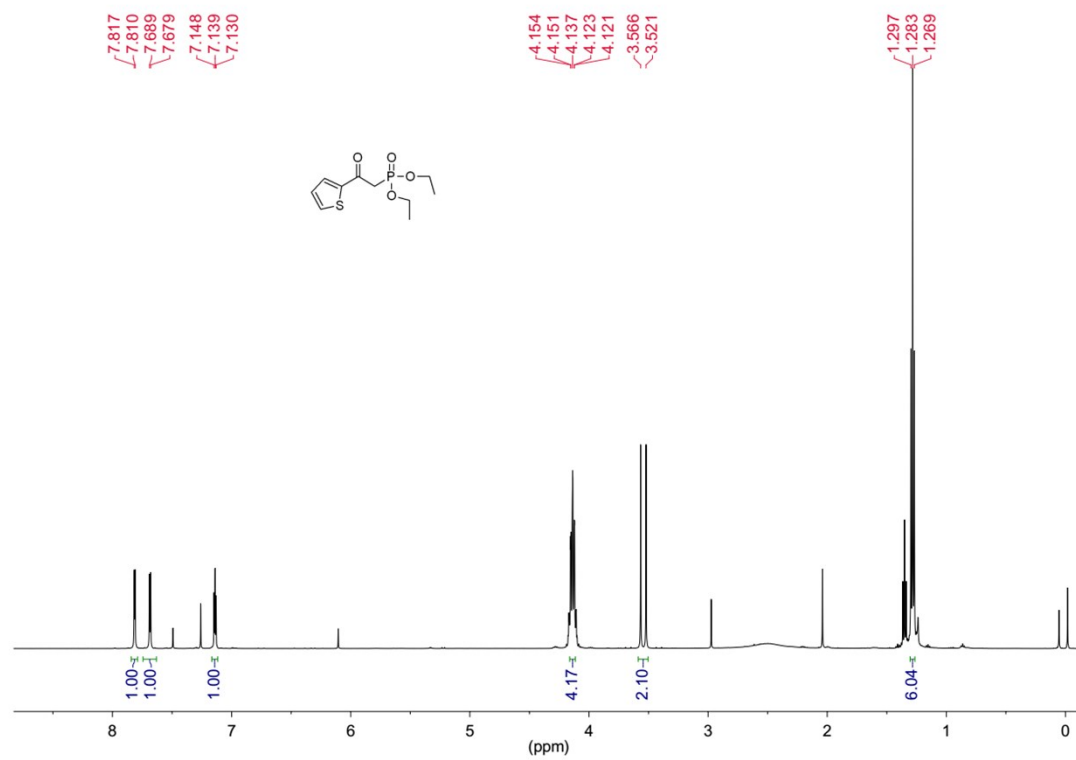
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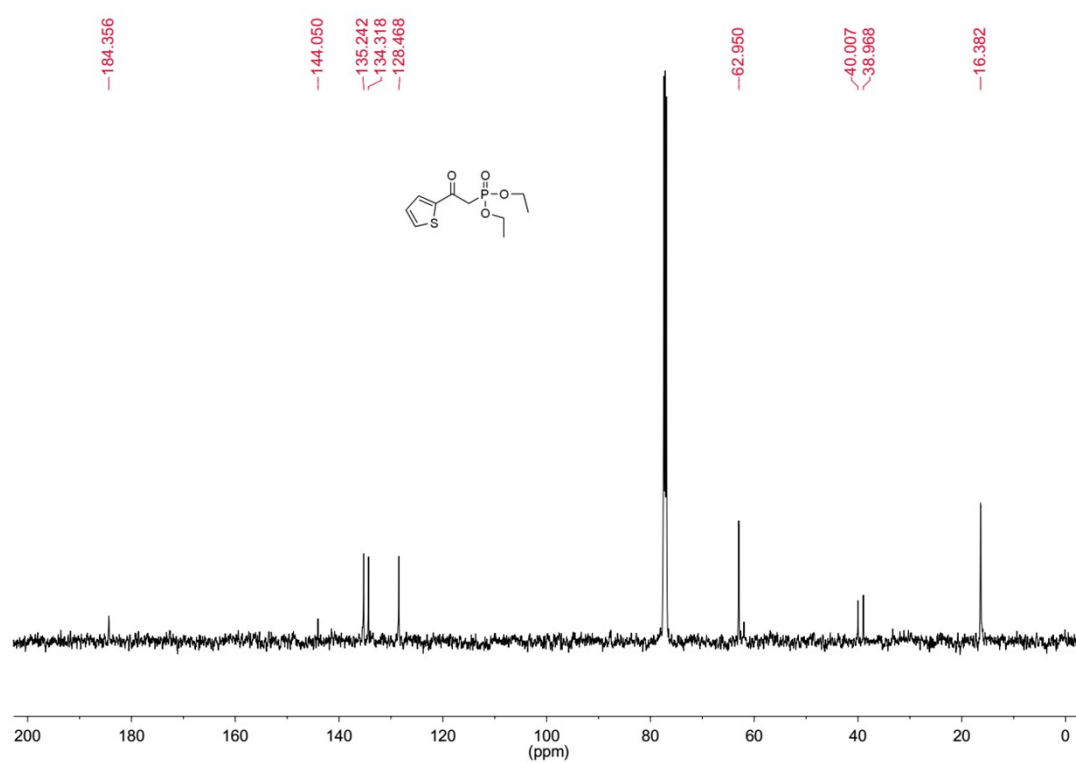
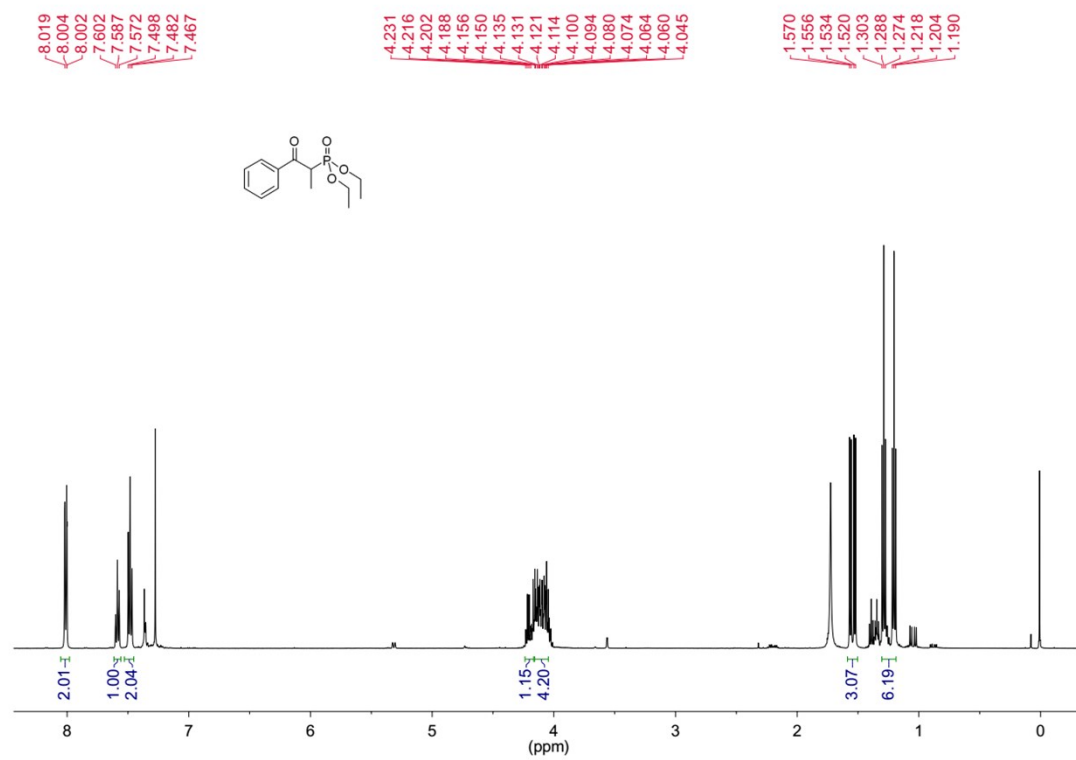
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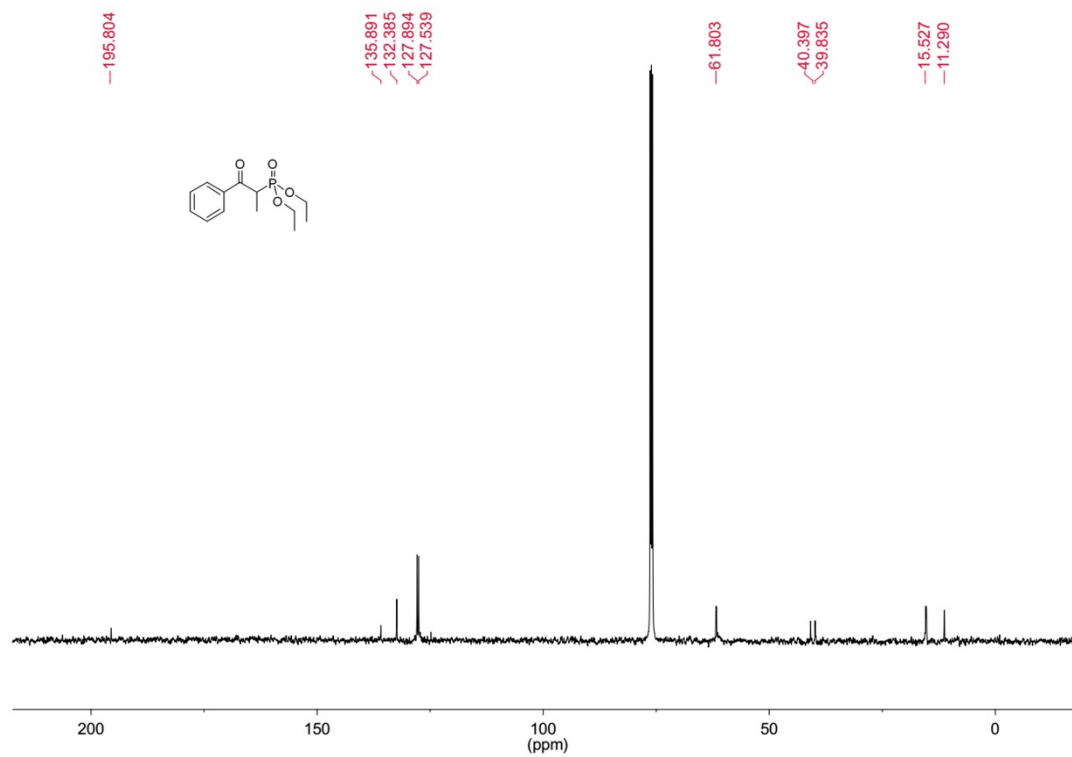
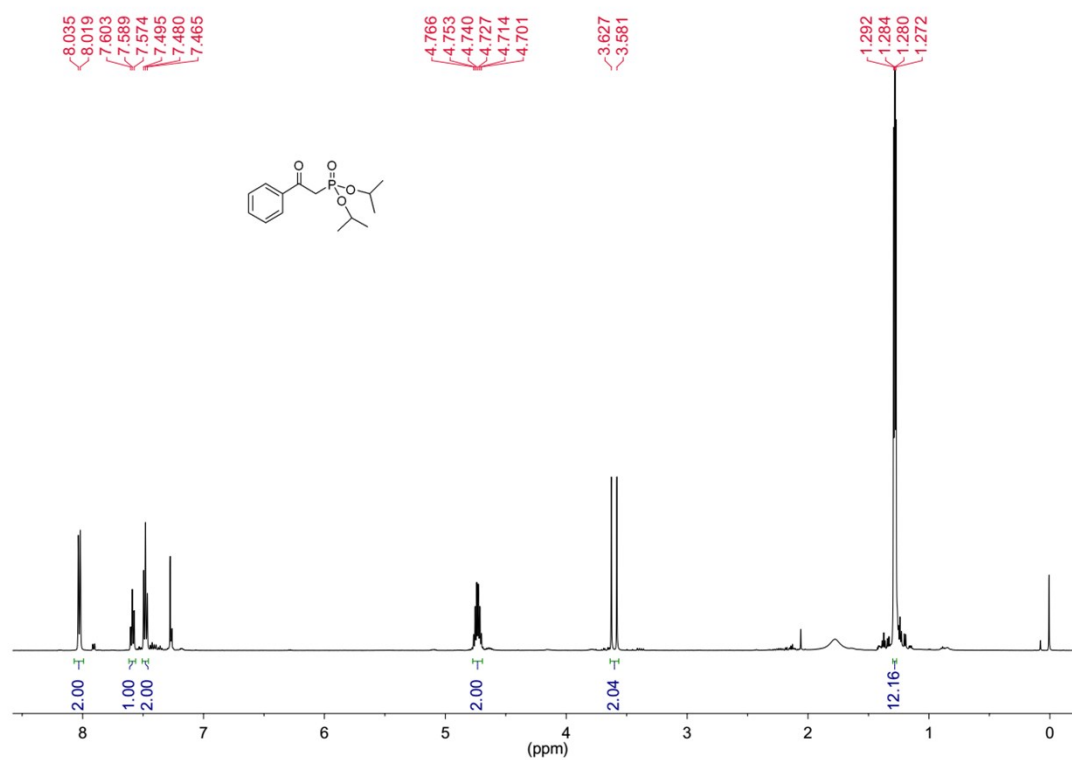
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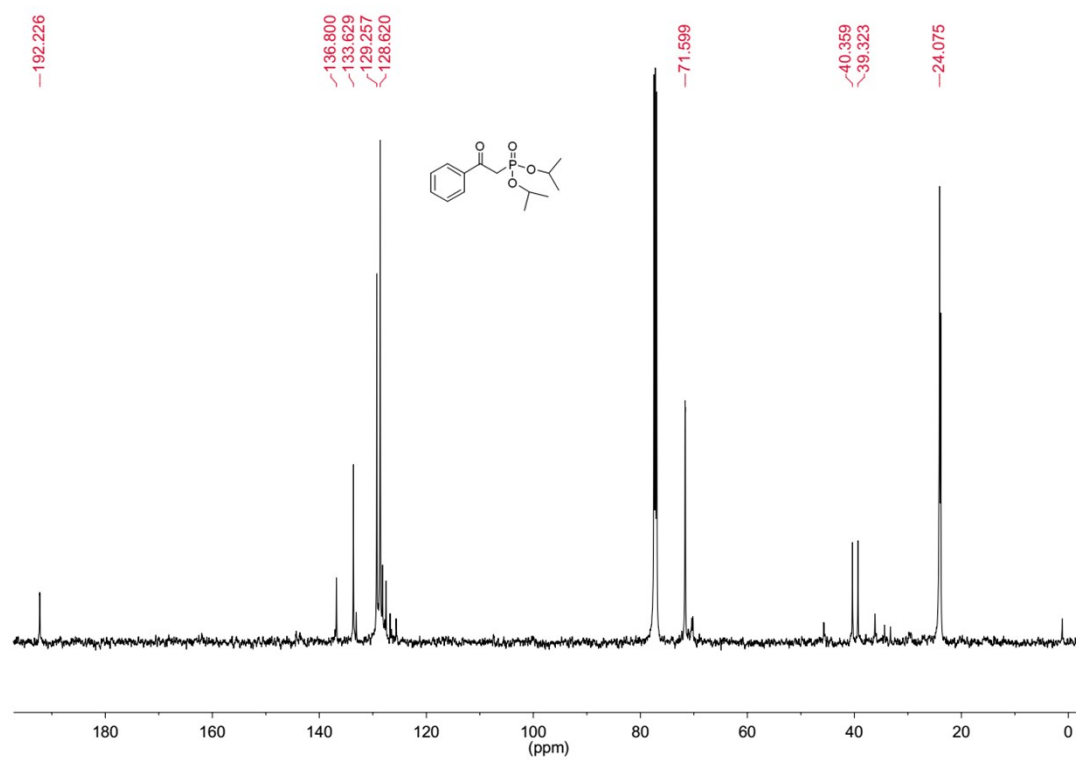
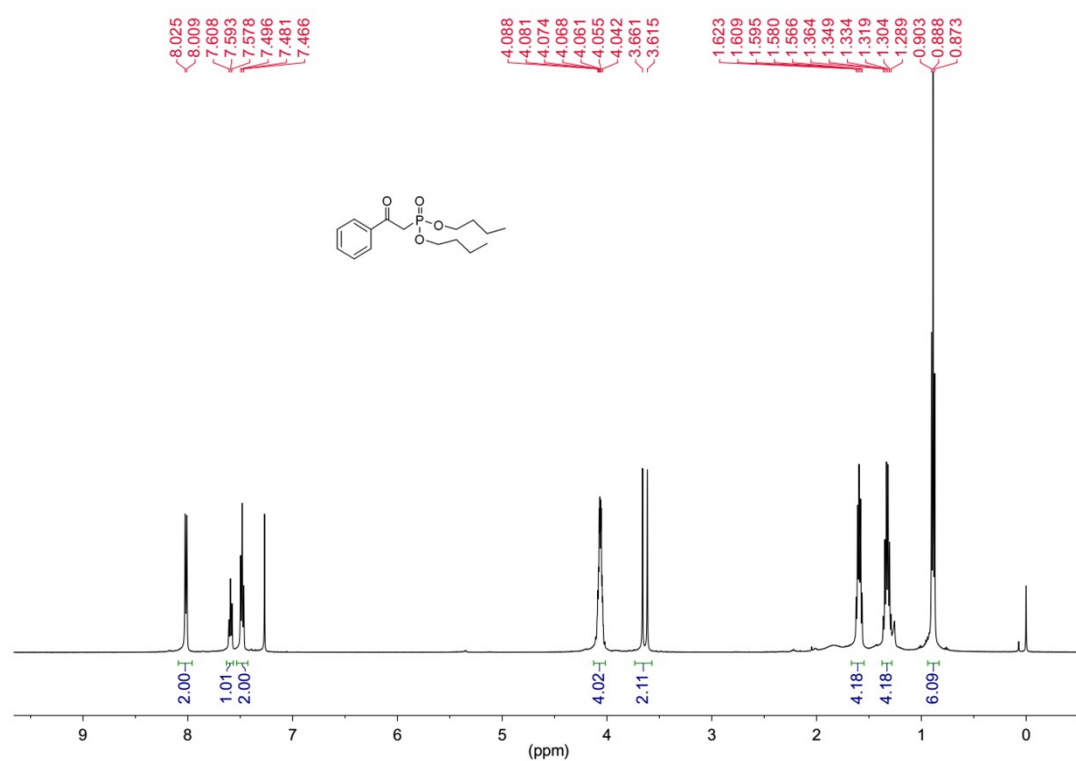
¹³C NMR 4ga¹H NMR 4ha

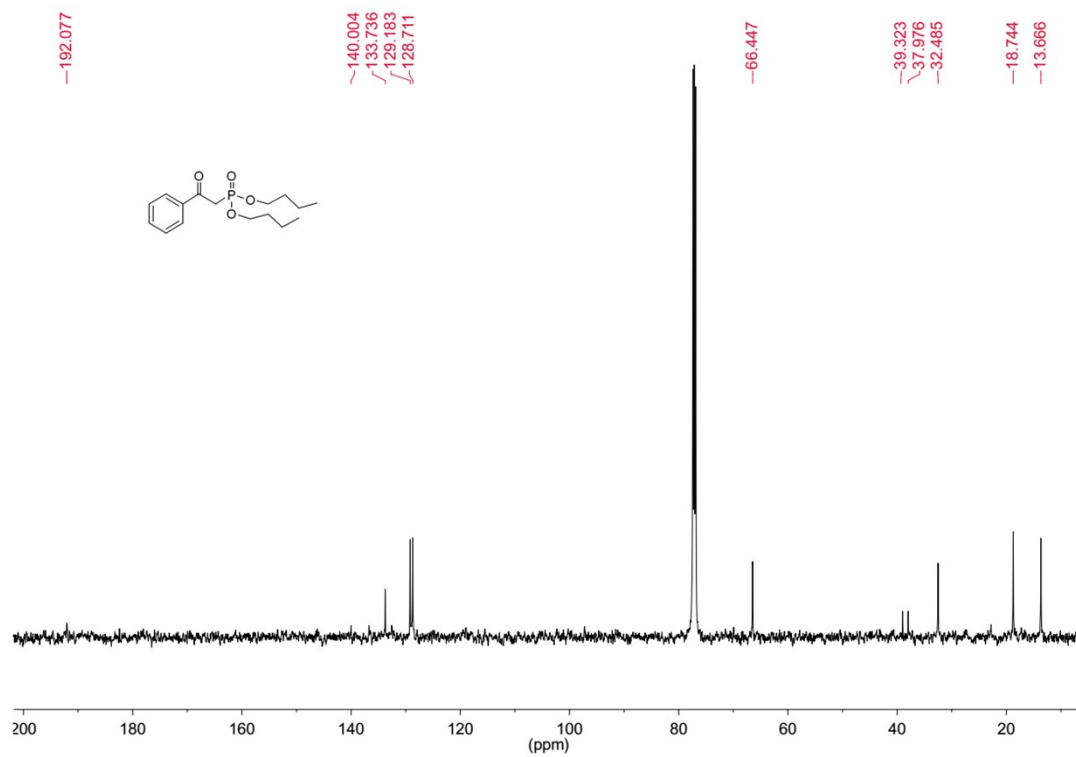
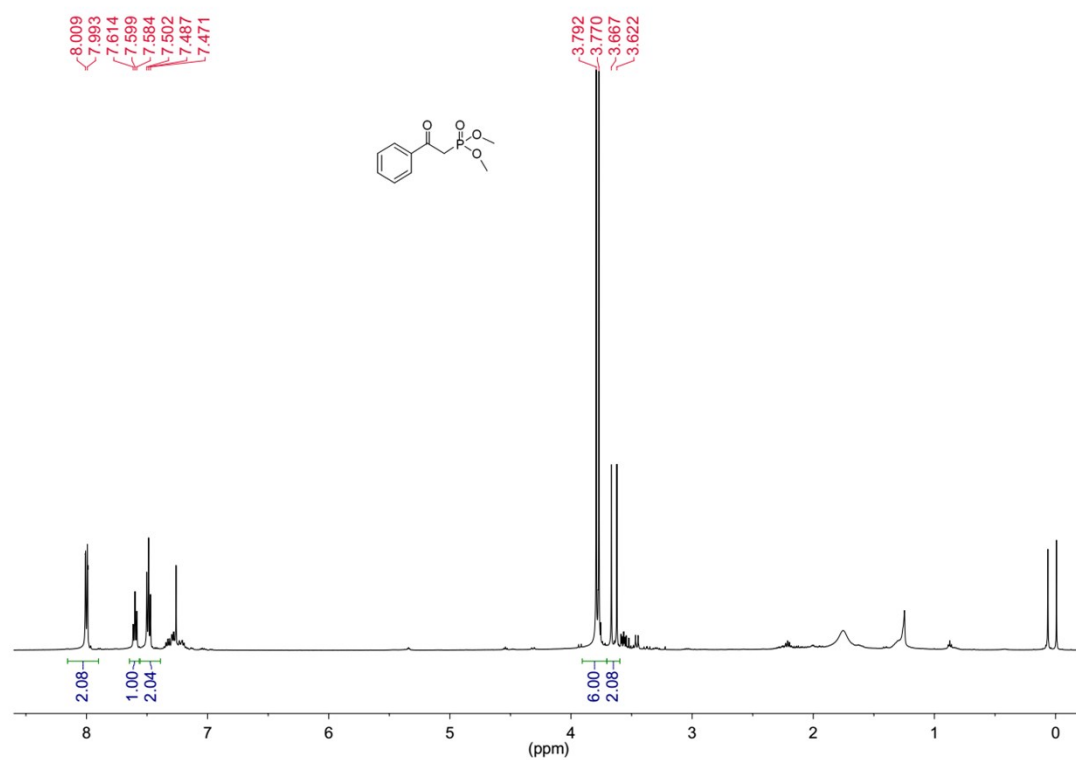
¹³C NMR 4ha¹H NMR 4ia

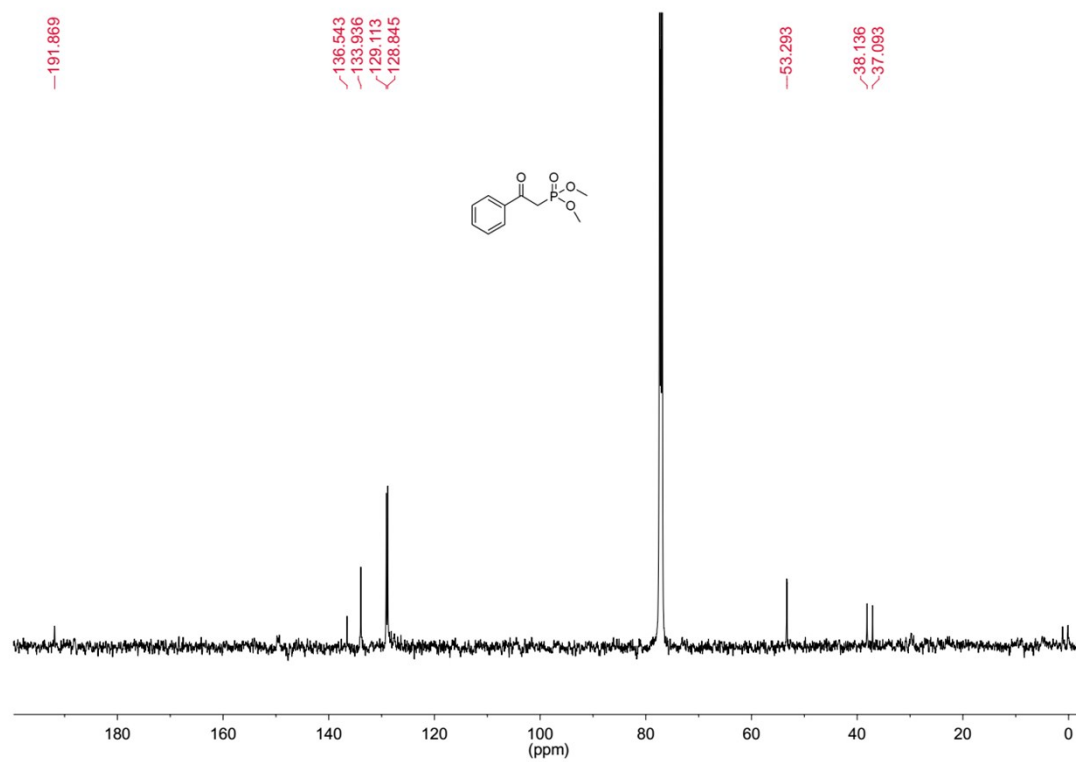
¹³C NMR **4ia**¹H NMR **4ia**

¹³C NMR 4la¹H NMR 4ma

¹³C NMR 4ma¹H NMR 4ab

¹³C NMR 4ab¹H NMR 4ac

¹³C NMR **4ac**¹H NMR **4ad**

¹³C NMR 4ad