Supporting Information

Stereoselective Synthesis of (E)-α,β-Unsaturated Esters: Triethylamine-Catalyzed Allylic Rearrangement of Enol Phosphates

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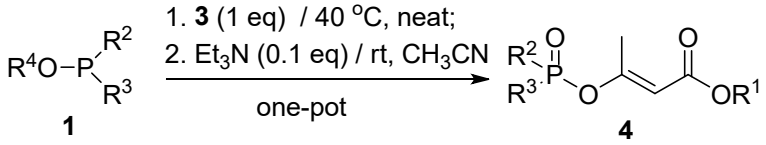
General information

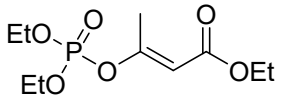
All reactions were carried out in oven-dried glassware with magnetic stirring bar. Dry solvents (THF, toluene, CH_3CN and DCM) were obtained by solvent purification system under argon. All commercially available reagents were used as received without further purification. Purification of products was carried out by flash column chromatography using silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on 0.25 mm aluminum-backed silica gel 60-F plates. Visualization was accompanied with UV light and $KMnO_4$ solution. Concentration under reduced pressure refers to the removal of volatiles using a rotary evaporator attached to a dry diaphragm pump (10-15 mm Hg) followed by pumping to a constant weight with an oil pump (< 300 mTorr). High-resolution mass spectra (HRMS) were recorded on LCMS-IT-TOF mass spectrometer using ESI (electrospray ionization) or APCI (Atmospheric Pressure Chemical Ionization). ^1H NMR spectra were recorded in $CDCl_3$ on 600 MHz and 300 MHz NMR spectrometer. The ^1H chemical shifts are referenced to residual solvent signals at δ 7.26 ($CHCl_3$) or δ 0.00 (TMS). ^1H NMR coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), app s (apparent singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), tt (triplet of triplets). ^{13}C NMR spectra were proton decoupled and recorded in $CDCl_3$ on 151 MHz and 75 MHz NMR spectrometer. The ^{13}C chemical shifts are referenced to solvent signals at δ 77.16 ($CDCl_3$). ^{31}P NMR spectra were proton decoupled and recorded in $CDCl_3$ on 243 MHz and 122 MHz NMR spectrometer.

General procedure for synthesis of EPs **4**



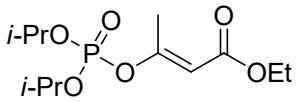
To an oven dried 10 mL test tube with a stir bar was added phosphite **1** (1.0 equiv, 1.0 mmol) and 4-chloroacetoacetate **3** (1.0 equiv, 1.0 mmol). After stirring for 2 h at 40 °C, the reaction mixture was then cooled to room temperature followed by the addition of a solution of triethylamine (10 mol%) and 3 mL of dry CH_3CN. After stirring for 12 h at room temperature, the resulting mixture was concentrated to give the crude product which was then purified by column chromatography on silica gel (PE/EA = 1:1) to afford the product of conjugated *E*-β-phosphoroxylated α,β-unsaturated ester **4**.

(*E*)-ethyl 3-((diethoxyphosphoryl)oxy)but-2-enoate (4a):



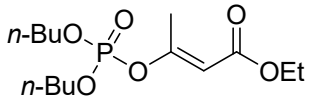
92% yield, brown oil. R_f = 0.45 (PE/EA= 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.77 (s, 1H), 4.38–3.87 (m, 6H), 2.36 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.28, 163.14 (d, *J* = 6.0 Hz), 106.06 (d, *J* = 4.5 Hz), 64.74 (d, *J* = 7.5 Hz), 60.06, 18.49, 18.46. ^{31}P NMR (243 MHz, $CDCl_3$) δ -8.14; HRMS (ESI-MS) $[M+H]^+$: found 267.0909; calculated for $C_{10}H_{20}O_6P$: 267.0919.

(*E*)-ethyl 3-((diisopropoxyphosphoryl)oxy)but-2-enoate (4b):



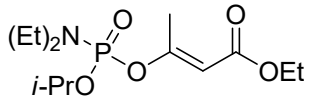
96% yield, brown oil. R_f = 0.32 (PE/EA= 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71 (s, 1H), 4.76–4.43 (m, 2H), 4.19–3.85 (m, 2H), 2.30 (s, 3H), 1.28 (s, 12H), 1.21–1.07 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.34, 163.71–162.66 (m), 105.67 (d, *J* = 5.1 Hz), 73.73 (d, *J* = 6.2 Hz), 59.91, 24.39–22.12 (m), 18.48 (d, *J* = 4.6 Hz), 14.15; ^{31}P NMR (121 MHz, $CDCl_3$) δ -9.94; HRMS (ESI-MS) $[M+H]^+$: found 295.127; calculated for $C_{12}H_{24}O_6P$: 295.1232.

(*E*)-ethyl 3-((dibutoxyphosphoryl)oxy)but-2-enoate (4c):



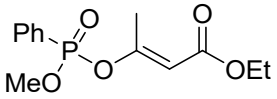
90% yield, colorless oil, R_f = 0.52 (PE/EA= 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72 (s, 1H), 4.45–3.70 (m, 6H), 2.59–1.96 (m, 3H), 1.70–1.53 (m, 4H), 1.42–1.26 (m, 4H), 1.23–1.12 (m, 3H), 0.95–0.75 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.23, 163.16 (d, *J* = 8.2 Hz), 110.93–99.91 (m), 68.36 (d, *J* = 6.3 Hz), 59.99, 32.06 (d, *J* = 6.9 Hz), 18.54, 18.42 (d, *J* = 5.2 Hz), 14.15, 13.45; ^{31}P NMR (121 MHz, $CDCl_3$) δ -7.94; HRMS (ESI-MS) $[M+H]^+$: found 323.1549; calculated for $C_{14}H_{28}O_6P$: 323.1545.

(*E*)-ethyl 3-(((diethylamino)(isopropoxy)phosphoryl)oxy)but-2-enoate (4d):



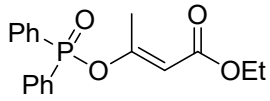
90% yield, colorless oil. R_f = 0.44 (PE/EA= 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82 (s, 1H), 4.29–3.91 (m, 2H), 3.68 (d, *J* = 11.6 Hz, 3H), 3.41 (dp, *J* = 20.2, 6.7 Hz, 2H), 2.33 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.86, 164.05 (d, *J* = 8.7 Hz), 105.01 (d, *J* = 5.3 Hz), 59.80, 52.89 (d, *J* = 5.8 Hz), 46.38 (d, *J* = 4.9 Hz), 22.37 (d, *J* = 26.2 Hz), 18.81 (d, *J* = 5.2 Hz), 14.25; ^{31}P NMR (121 MHz, $CDCl_3$) δ 3.32; HRMS (ESI-MS) $[M+H]^+$: found 308.1552; calculated for $C_{13}H_{27}NO_5P$: 308.1549.

(*E*)-ethyl 3-((methoxy(phenyl)phosphoryl)oxy)but-2-enoate (4e):



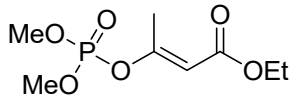
96% yield, white solid, **m.p.** = 98–108 °C, R_f = 0.36 (PE/EA= 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 13.9, 8.1 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.51–7.41 (m, 2H), 5.77 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.81 (d, *J* = 11.5 Hz, 3H), 2.33 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.26 , 163.23 (d, *J* = 8.7 Hz), 133.21 (d, *J* = 3.1 Hz), 131.86 (d, *J* = 10.3 Hz), 128.71 (d, *J* = 15.7 Hz), 126.50 (d, *J* = 191.8 Hz), 106.58 (d, *J* = 5.3 Hz), 60.04, 53.12 (d, *J* = 5.9 Hz), 18.99 (d, *J* = 4.1 Hz), 14.18; ^{31}P NMR (243 MHz, $CDCl_3$) δ 15.95; HRMS (ESI-MS) $[M+H]^+$: found 285.085; calculated for $C_{13}H_{18}O_5P$: 285.0814.

(*E*)-ethyl 3-((diphenylphosphoryl)oxy)but-2-enoate (4f):



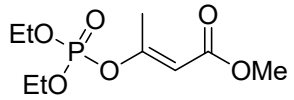
90% yield, white solid, **m.p.** = 99–104 °C, R_f = 0.34 (PE/EA= 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84–7.80 (m, 4H), 7.56–7.54 (m, 2H), 7.48–7.45 (m, 4H), 5.88 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.39 , 163.77 (d, *J* = 9.7 Hz), 132.72 (d, *J* = 2.7 Hz), 131.54 (d, *J* = 10.5 Hz), 130.62 (d, *J* = 138.3 Hz), 128.74 (d, *J* = 13.6 Hz), 106.58 (d, *J* = 5.8 Hz), 59.99, 19.41 (d, *J* = 4.3 Hz), 14.18; ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.29; HRMS (ESI-MS) $[M+H]^+$: found 331.1028; calculated for $C_{18}H_{20}O_4P$: 331.1021.

(*E*)-ethyl 3-((dimethoxyphosphoryl)oxy)but-2-enoate (4g):



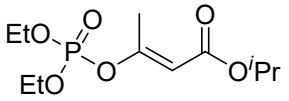
90% yield, slightly yellow oil. R_f = 0.38 (PE/EA= 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.73 (s, 1H), 4.09 (q, *J* = 6.8 Hz, 2H), 3.78 (d, *J* = 12.2 Hz, 6H), 2.34 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.07, 162.90 (d, *J* = 7.5 Hz), 109.99, 106.25 (d, *J* = 6.0 Hz), 60.09, 54.91 (d, *J* = 7.5 Hz), 18.33 (d, *J* = 4.5 Hz), 14.13; ^{31}P NMR (243 MHz, $CDCl_3$) δ -5.93; HRMS (ESI-MS) $[M+H]^+$: found 239.0609; calculated for $C_8H_{16}O_6P$: 239.0606.

(*E*)-methyl 3-((diethoxyphosphoryl)oxy)but-2-enoate (4h):



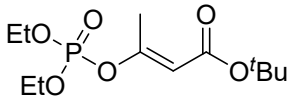
92% yield, colorless oil, R_f = 0.34 (PE/EA= 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.80 (s, 1H), 4.18 (p, *J* = 7.3 Hz, 4H), 3.68 (s, 3H), 2.38 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.74, 163.45 (d, *J* = 7.5 Hz), 105.61 (d, *J* = 6.0 Hz), 64.78 (d, *J* = 7.5 Hz), 51.27, 18.51 (d, *J* = 6.0 Hz), 16.01 (d, *J* = 6.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ -8.17; HRMS (ESI-MS) $[M+H]^+$: found 253.0768; calculated for $C_9H_{18}O_6P$: 253.0763.

(*E*)-isopropyl 3-((diethoxyphosphoryl)oxy)but-2-enoate (4i):



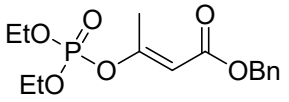
95% yield, colorless oil, Rf = 0.34 (PE/EA= 1:1). 1H NMR (300 MHz, $CDCl_3$) δ 5.67 (s, 1H), 4.92 (p, J = 6.2 Hz, 1H), 4.10 (p, J = 7.2 Hz, 4H), 2.29 (s, 3H), 1.27 (t, J = 7.1 Hz, 6H), 1.14 (d, J = 6.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.72, 162.80 (d, *J* = 8.4 Hz), 106.47 (d, *J* = 5.1 Hz), 67.30, 64.68 (d, *J* = 6.2 Hz), 21.78, 18.40 (d, *J* = 5.1 Hz), 15.96 (d, *J* = 6.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ -8.20; HRMS (ESI-MS) $[M+H]^+$: found 281.1079; calculated for $C_{11}H_{22}O_6P$: 281.1076.

(*E*)-tert-butyl 3-((diethoxyphosphoryl)oxy)but-2-enoate (4j):



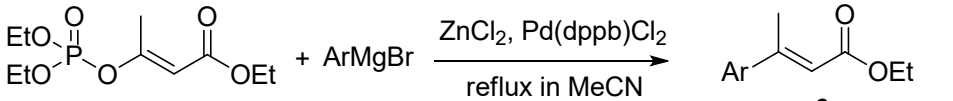
93% yield, colorless oil, Rf = 0.54 (PE/EA= 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.68 (s, 1H), 4.14 (p, *J* = 7.4 Hz, 4H), 2.31 (s, 3H), 1.41 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.56, 162.02 (d, *J* = 9.0 Hz), 107.84 (d, *J* = 4.5 Hz), 80.31, 64.63 (d, *J* = 6.0 Hz), 28.12, 18.27 (d, *J* = 4.5 Hz), 15.95; ^{31}P NMR (243 MHz, $CDCl_3$) δ -8.09; HRMS (ESI-MS) $[M+H]^+$: found 295.1235; calculated for $C_{12}H_{24}O_6P$: 295.1232.

(*E*)-benzyl 3-((diethoxyphosphoryl)oxy)but-2-enoate (4k):



94% yield, colorless oil, Rf = 0.60 (PE/EA= 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.28 (m, 5H), 5.86 (s, 1H), 5.13 (s, 2H), 4.17 (t, *J* = 7.6 Hz, 4H), 2.40 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.11, 163.78, 135.94, 128.50, 128.15, 105.69 (d, *J* = 6.0 Hz), 65.96, 64.80 (d, *J* = 6.0 Hz), 18.61 (d, *J* = 4.5 Hz), 16.02 (d, *J* = 6.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ -8.22; HRMS (ESI-MS) $[M+H]^+$: found 329.2978; calculated for $C_{15}H_{22}O_6P$: 329.2974.

General procedure for synthesis of α,β-unsaturated esters **6**

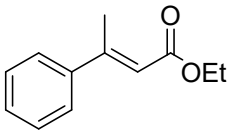


4a
93% yield; 50 mmol scale

6
100% *E*-configuration

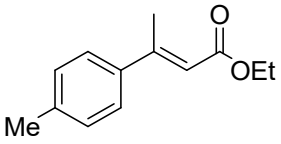
ArMgBr (1.5 mmol) was added to a stirred suspension of $ZnCl_2$ (1.5 mmol) in CH_3CN (3.0 mL) at 0–5 °C under N_2 atmosphere. The mixture was stirred at the same temperature for 0.5 h, then the β-phosphoroxylated α,β-unsaturated ester **4a** (1 mmol) in CH_3CN (5 mL) and $Pd(dppb)Cl_2$ (0.02 mmol) in CH_3CN (0.5 mL) were successively added and stirred at 60 °C for 2 h. After cooling down, aq.1 M HCl solution was added to the mixture which was extracted twice with AcOEt. The combined organic phase was washed with brine, dried (Na_2SO_4) and concentrated. The obtained crude product was then purified by SiO_2-column chromatography (hexane/AcOEt = 100:0 - 10:1) to give the desired product (*E*)-**6.**

(*E*)-ethyl 3-phenylbut-2-enoate (6a):



84% yield, colorless oil, Rf = 0.59 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (s, 2H), 7.36 (s, 3H), 6.14 (s, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 2.59 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.90, 155.56, 142.22, 129.01, 128.51, 126.32, 117.18, 59.88, 17.97, 14.39; HRMS (ESI-MS) $[M+H]^+$: found 191.0998; calculated for $C_{12}H_{15}O_2$: 191.0994.

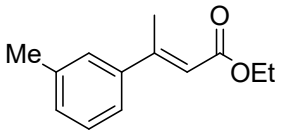
(*E*)-ethyl 3-(p-tolyl)but-2-enoate (6b):



80% yield, colorless oil, Rf = 0.42 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.14 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.58 (d, *J* = 1.2 Hz, 3H), 2.37 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.04, 155.47, 139.23,

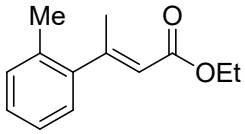
129.21, 126.24, 116.27, 59.81, 21.23, 17.83, 14.40; HRMS (ESI-MS) $[M+H]^+$: found 221.1095; calculated for $C_{13}H_{16}O_3$: 221.1099.

(*E*)-ethyl 3-(m-tolyl)but-2-enoate (6c):



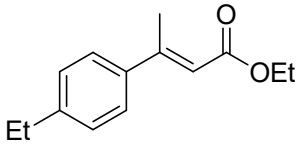
93% yield, colorless oil, Rf = 0.34 (PE/EA= 20:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–6.79 (m, 5H), 6.12 (s, 1H), 4.45–4.00 (m, 2H), 2.57 (s, 3H), 2.37 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.95, 155.80, 142.25, 138.11, 129.76, 128.40, 127.04, 123.47, 116.95, 59.84, 21.50, 18.01, 14.39; HRMS (ESI-MS) $[M+H]^+$: found 205.2645; calculated for $C_{13}H_{17}O_2$: 205.2649.

(*E*)-ethyl 3-(o-tolyl)but-2-enoate (6d):



88% yield, colorless oil, Rf = 0.72 (PE/EA= 20:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–6.85 (m, 4H), 5.76 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.45 (d, *J* = 1.3 Hz, 3H), 2.28 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.66, 158.35, 143.92, 133.87, 130.42, 127.72, 127.10, 125.77, 119.41, 59.85, 20.85, 19.77, 14.37; HRMS (ESI-MS) $[M+H]^+$: found 205.1155; calculated for $C_{13}H_{17}O_2$: 205.1150.

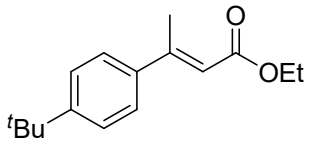
(*E*)-ethyl 3-(4-ethylphenyl)but-2-enoate (6e):



94% yield, colorless oil, Rf = 0.62 (PE/EA= 20:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.16 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.59 (d, *J* = 1.1 Hz, 3H), 1.29 (dt, *J* = 21.6, 7.4 Hz, 6H); ^{13}C NMR (75 MHz, CDCl3) δ 167.01,

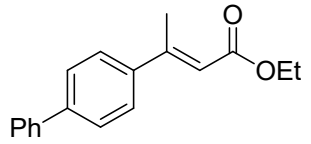
155.45, 145.45, 139.48, 128.01, 126.32, 116.33, 77.51, 77.09, 76.67, 59.78, 28.59, 17.83, 15.45, 14.39; HRMS (ESI-MS) $[M+H]^+$: found 219.1309; calculated for $C_{14}H_{19}O_2$: 219.1307.

(*E*)-ethyl 3-(4-(tert-butyl)phenyl)but-2-enoate (6f):



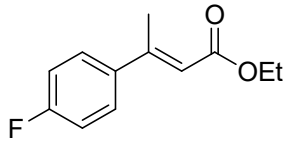
92% yield, colorless oil, Rf = 0.62 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.30 (m, 4H), 6.17 (s, 1H), 4.41–4.06 (m, 2H), 2.59 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.05, 155.34, 152.32, 139.07, 126.08, 125.45, 116.36, 59.80, 34.68, 31.37, 17.79, 14.41; HRMS (ESI-MS) $[M+H]^+$: found 247.1629; calculated for $C_{16}H_{22}O_2$: 247.1620.

(*E*)-ethyl 3-([1,1'-biphenyl]-4-yl)but-2-enoate (6g):



88% yield, colorless oil, Rf = 0.58 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73–7.30 (m, 9H), 6.24 (s, 1H), 4.26 (q, *J* = 6.9 Hz, 2H), 2.65 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.94, 154.96, 141.86, 140.95, 140.29, 128.91, 127.69, 127.19, 127.08, 126.82, 116.97, 59.93, 17.84, 14.43; HRMS (ESI-MS) $[M+H]^+$: found 267.1310; calculated for $C_{18}H_{19}O_2$: 267.1307.

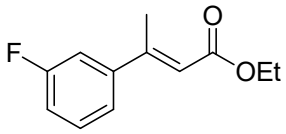
(*E*)-ethyl 3-(4-fluorophenyl)but-2-enoate (6h):



95% yield, colorless oil, Rf = 0.82 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.33 (m, 2H), 7.03 (t, *J* = 8.5 Hz, 2H), 6.07 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.54 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.71, 164.84, 161.54, 154.22, 138.15, 128.15, 117.06,

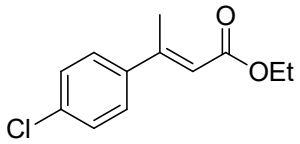
115.56, 115.28, 59.90, 17.91, 14.33; ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.69 – -118.10 (m); HRMS (ESI-MS) $[M+H]^+$: found 209.0888; calculated for $C_{12}H_{14}FO_2$: 209.0900.

(*E*)-ethyl 3-(3-fluorophenyl)but-2-enoate (6i):



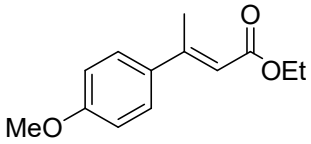
90% yield, colorless oil, Rf = 0.52 (PE/EA= 20:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.29 (m, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 10.3 Hz, 1H), 7.05 (t, *J* = 8.2 Hz, 1H), 6.14 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.56 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.59, 164.40, 161.13, 154.77–152.61 (m), 144.41 (d, *J* = 7.3 Hz), 130.01 (d, *J* = 8.3 Hz), 121.98 (d, *J* = 2.8 Hz), 118.02, 115.79 (d, *J* = 21.2 Hz), 113.35 (d, *J* = 22.4 Hz), 60.03, 17.82, 14.33; ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.70 – -112.87 (m); HRMS (ESI-MS) $[M+H]^+$: found 209.0905; calculated for $C_{12}H_{14}FO_2$: 209.0900.

(*E*)-ethyl 3-(4-chlorophenyl)but-2-enoate (6j):



96% yield, colorless oil, Rf = 0.64 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.28 (m, 4H), 6.11 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.54 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.67, 154.08, 140.52, 134.97, 128.70, 127.63, 117.49, 60.01, 17.82, 14.37; HRMS (ESI-MS) $[M+H]^+$: found 225.0600; calculated for $C_{12}H_{13}ClO_2$: 225.0604.

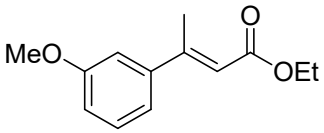
(*E*)-ethyl 3-(4-methoxyphenyl)but-2-enoate (6k):



82% yield, colorless oil, Rf = 0.58 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 0H), 6.89 (d, *J* = 8.7 Hz, 0H), 6.11 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 0H), 3.82 (s, 0H), 1.31 (t, *J* =

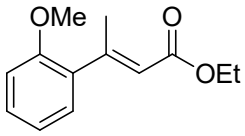
7.1 Hz, 0H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.11, 160.41, 154.92, 134.29, 127.73, 115.29, 113.81, 59.75, 55.35, 17.67, 14.40; HRMS (ESI-MS) $[M+H]^+$: found 221.1095; calculated for $C_{13}H_{16}O_3$: 221.1099.

(*E*)-ethyl 3-(3-methoxyphenyl)but-2-enoate (6l):



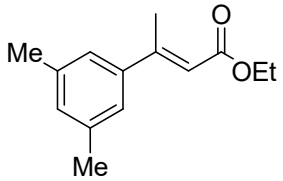
87% yield, colorless oil, Rf = 0.54 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.99 (s, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.13 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 2.56 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.85, 159.57, 155.44, 143.72, 129.51, 118.78, 117.28, 114.33, 112.05, 59.91, 55.29, 18.05, 14.38; HRMS (ESI-MS) $[M+H]^+$: found 221.1103; calculated for $C_{13}H_{17}O_3$: 221.1099.

(*E*)-ethyl 3-(2-methoxyphenyl)but-2-enoate (6m):



94% yield, colorless oil, Rf = 0.72 (PE/EA= 20:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (p, *J* = 9.3, 8.7 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.97–6.84 (m, 2H), 5.90 (s, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.81 (s, 3H), 2.50 (s, 3H), 1.51–1.12 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.80, 156.71, 156.31, 133.06, 129.50, 128.82, 120.55, 119.25, 110.96, 59.75, 55.44, 19.90, 14.39; HRMS (ESI-MS) $[M+H]^+$: found 237.1415; calculated for $C_{14}H_{21}O_3$: 237.1412.

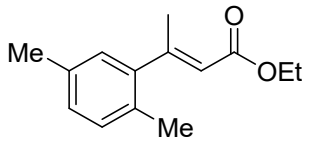
(*E*)-ethyl 3-(3,5-dimethylphenyl)but-2-enoatee (6n):



85% yield, colorless oil, Rf = 0.62 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 2H), 7.01 (s, 1H), 6.14 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 3H), 2.35 (s, 6H), 1.33 (t, *J* = 7.1 Hz,

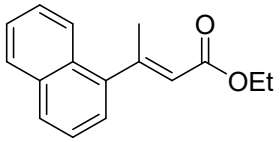
3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.99, 156.03, 142.30, 138.00, 130.67, 124.21, 116.74, 59.81, 21.36, 18.05, 14.40; HRMS (ESI-MS) $[M+H]^+$: found 219.1310; calculated for $C_{14}H_{19}O_2$: 219.1307.

(*E*)-ethyl 3-(2,5-dimethylphenyl)but-2-enoate (6o):



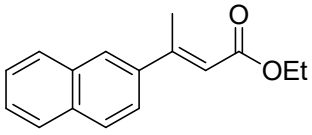
90% yield, colorless oil, Rf = 0.57 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (q, *J* = 7.8 Hz, 2H), 6.90 (s, 1H), 5.76 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 2.31 (s, 3H), 2.25 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.74, 158.56, 143.79, 135.21, 130.72, 130.34, 128.39, 127.76, 119.21, 59.83, 20.89, 19.28, 14.37; HRMS (ESI-MS) $[M+H]^+$: found 219.1304; calculated for $C_{14}H_{19}O_2$: 219.1307.

(*E*)-ethyl 3-(naphthalen-1-yl)but-2-enoate (6p):



92% yield, colorless oil, Rf = 0.49 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99–7.78 (m, 3H), 7.48 (dd, *J* = 18.1, 5.7 Hz, 3H), 7.31 (d, *J* = 6.9 Hz, 1H), 6.03 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.67 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.67, 157.18, 142.12, 133.71, 130.08, 128.51, 128.20, 126.33, 126.02, 125.38, 125.28, 124.25, 120.62, 60.00, 21.76, 14.42; HRMS (ESI-MS) $[M+H]^+$: found 241.1150; calculated for $C_{16}H_{17}O_2$: 241.1150.

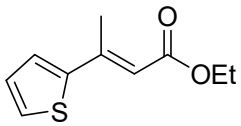
(*E*)-ethyl 3-(naphthalen-2-yl)but-2-enoate (6q):



89% yield, colorless oil, Rf = 0.69 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.92 – 7.76 (m, 3H), 7.61 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.52 (dt, *J* = 6.3, 3.2 Hz, 2H), 6.31 (s, 1H),

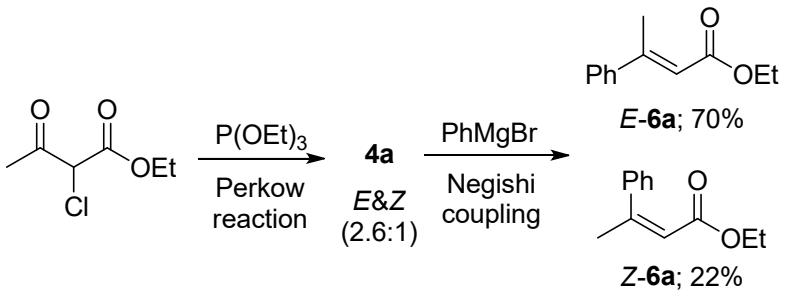
4.26 (q, J = 7.1 Hz, 2H), 2.71 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.95, 155.30, 139.33, 133.49, 133.12, 128.54, 128.17, 127.61, 126.73, 126.54, 125.98, 123.98, 117.51, 59.96, 17.95, 14.44; HRMS (ESI-MS) $[M+H]^+$: found 241.1153; calculated for $C_{16}H_{17}O_2$: 241.1150.

(*E*)-ethyl 3-(thiophen-2-yl)but-2-enoate (6r):



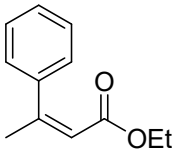
85% yield, colorless oil, Rf = 0.70 (PE/EA= 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 4.2 Hz, 2H), 7.12–6.96 (m, 1H), 6.25 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.60 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.70, 147.77, 145.55, 127.93, 127.07, 126.71, 114.26, 77.56, 77.14, 76.71, 59.86, 17.28, 14.37; HRMS (ESI-MS) $[M+H]^+$: found 197.0556; calculated for $C_{10}H_{13}O_2S$: 197.0558.

Synthesis of the (Z) and (E) isomers of **6a** using 2-chloroacetoacetate



ArMgBr (1.5 mmol) was added to a stirred suspension of $ZnCl_2$ (1.5 mmol) in CH_3CN (3.0 mL) at 0–5 °C under N_2 atmosphere, and then stirred at the same temperature for 0.5 h. The mixture of (*E)* and (*Z)*-β-phosphoroxylated α,β-unsaturated ester **4a** (1 mmol), derived according to the previous procedure, was dissolved in CH_3CN (1 mL) and Pd(dppb)Cl_2 (0.02 mmol) in CH_3CN (0.5 mL) were successively added to the mixture and stirred at 60 °C for 2 h. After cooling down, 1 M HCl solution was added to the mixture, which was extracted twice with AcOEt. The combined organic phase was washed with brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by SiO_2-column chromatography (hexane/AcOEt = 100:0 –10:1) to give the desired product **6a** (*E* and *Z*-isomers)**.**

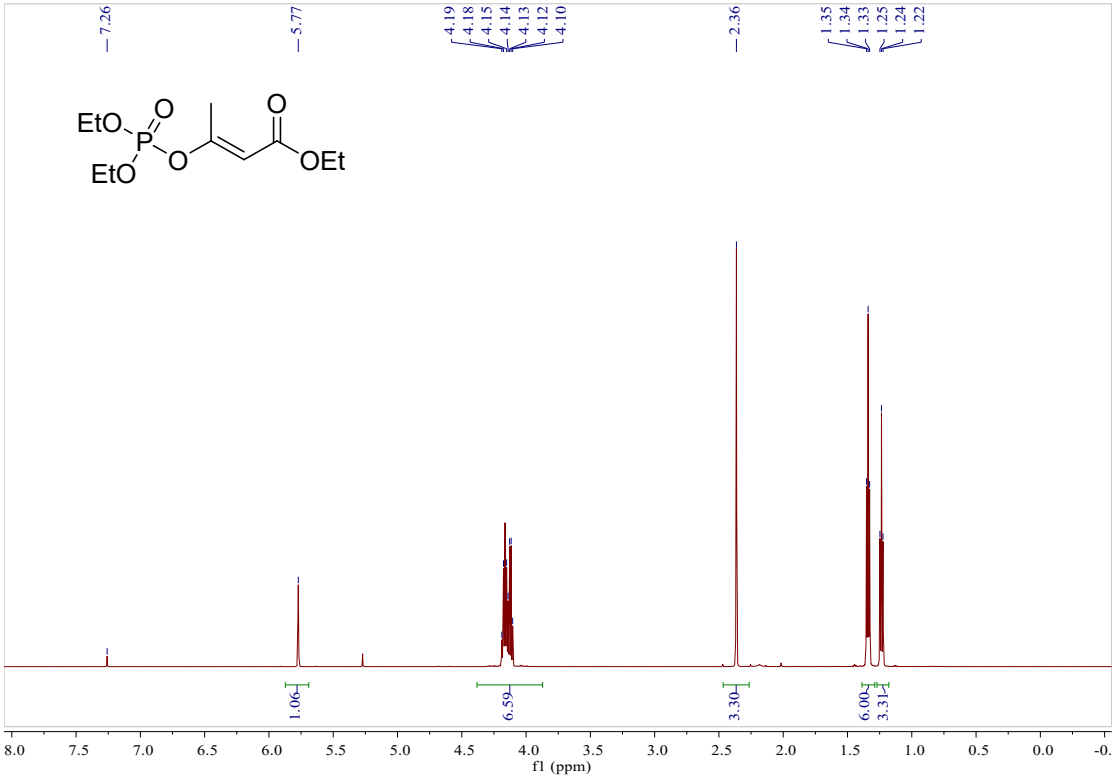
(*Z*)-ethyl 3-phenylbut-2-enoate (6a):



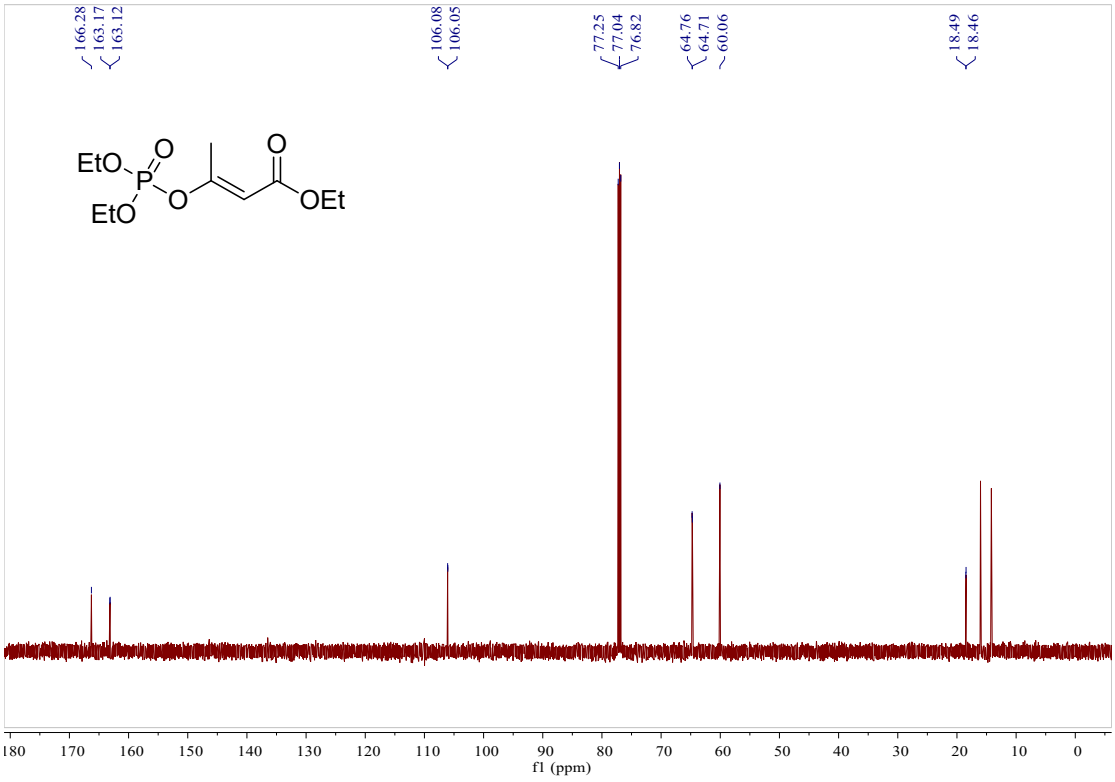
22% yield, colorless oil, Rf = 0.62 (PE/EA= 10:1). 1H NMR (300 MHz, CDCl3) δ 7.33 (t, J = 7.1 Hz, 3H), 7.20 (d, J = 7.3 Hz, 2H), 5.92 (s, 1H), 4.00 (q, J = 7.1 Hz, 2H), 2.18 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 165.94, 155.40, 140.88, 127.90, 127.74, 126.83, 117.80, 59.77, 27.19, 13.99; HRMS (ESI-MS) [M+H]+: found 191.0990; calculated for C12H15O2: 191.0994.

Spectra of products **4** & **6**

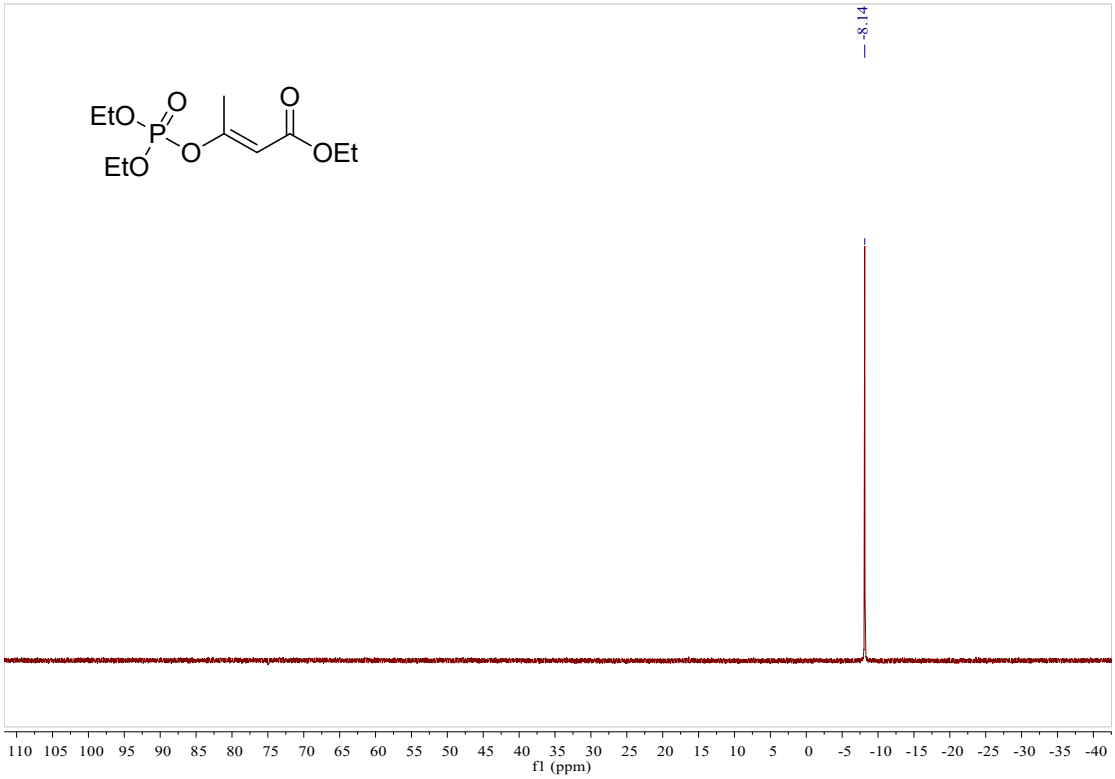
Compound 4a ^{1}H NMR



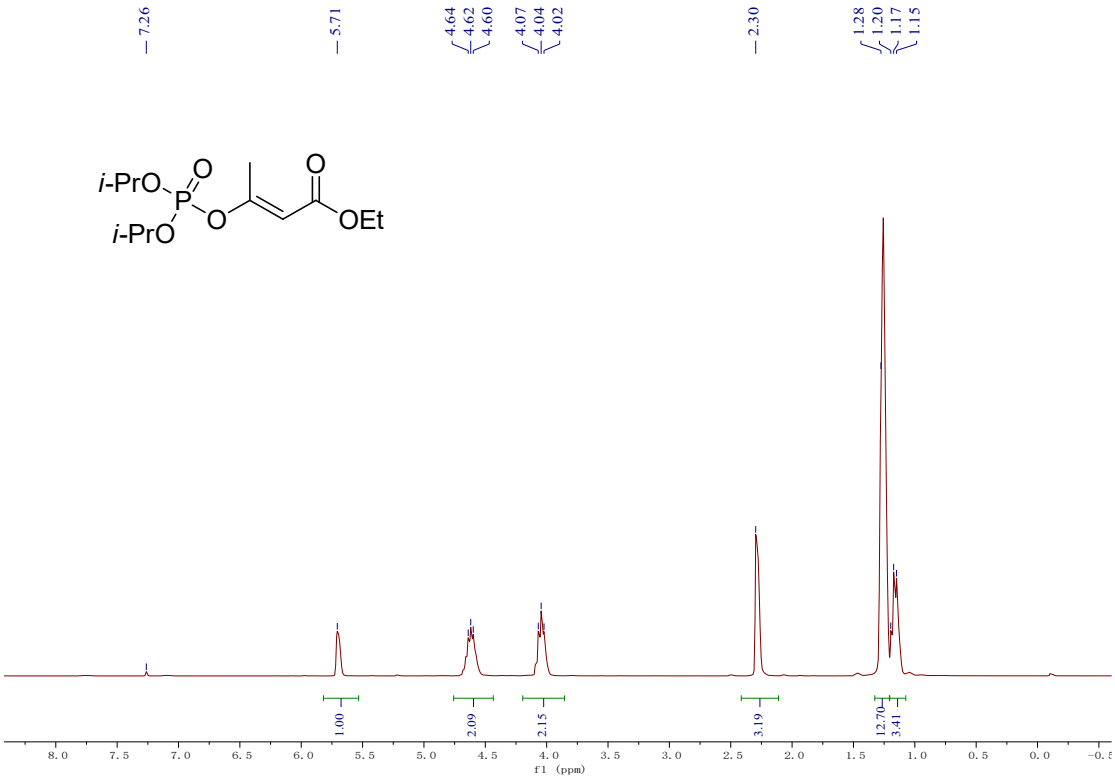
Compound 4a ^{13}C NMR



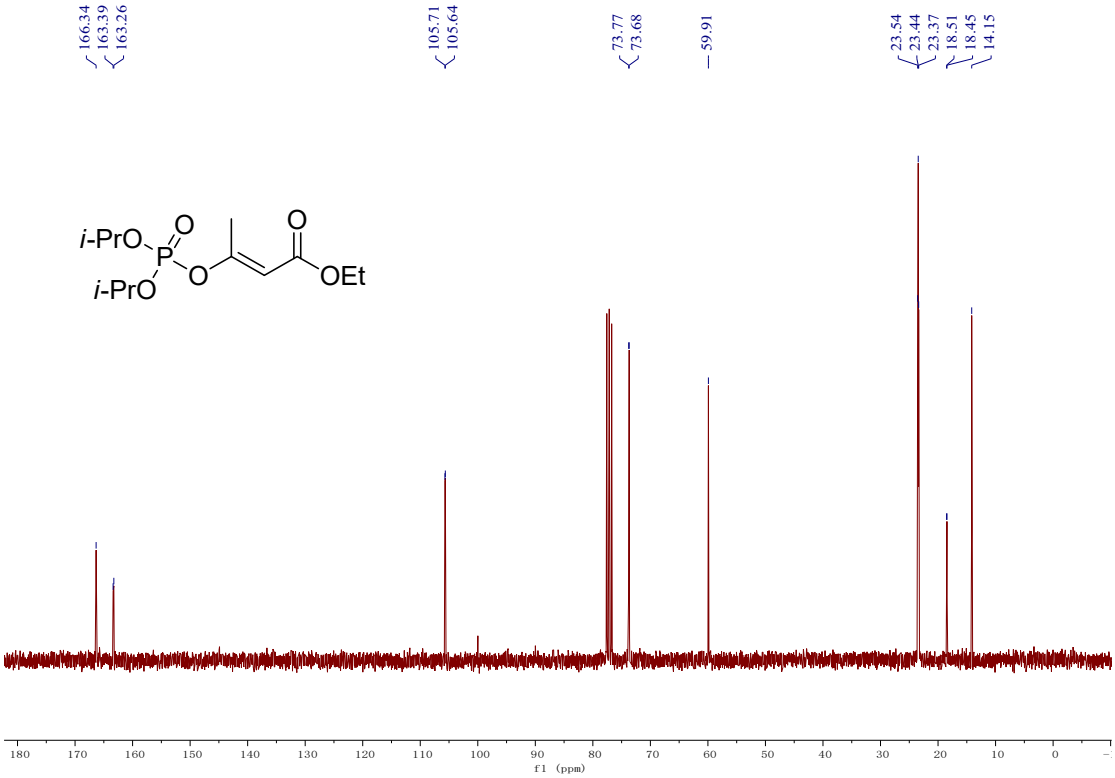
Compound 4a ^{31}P NMR



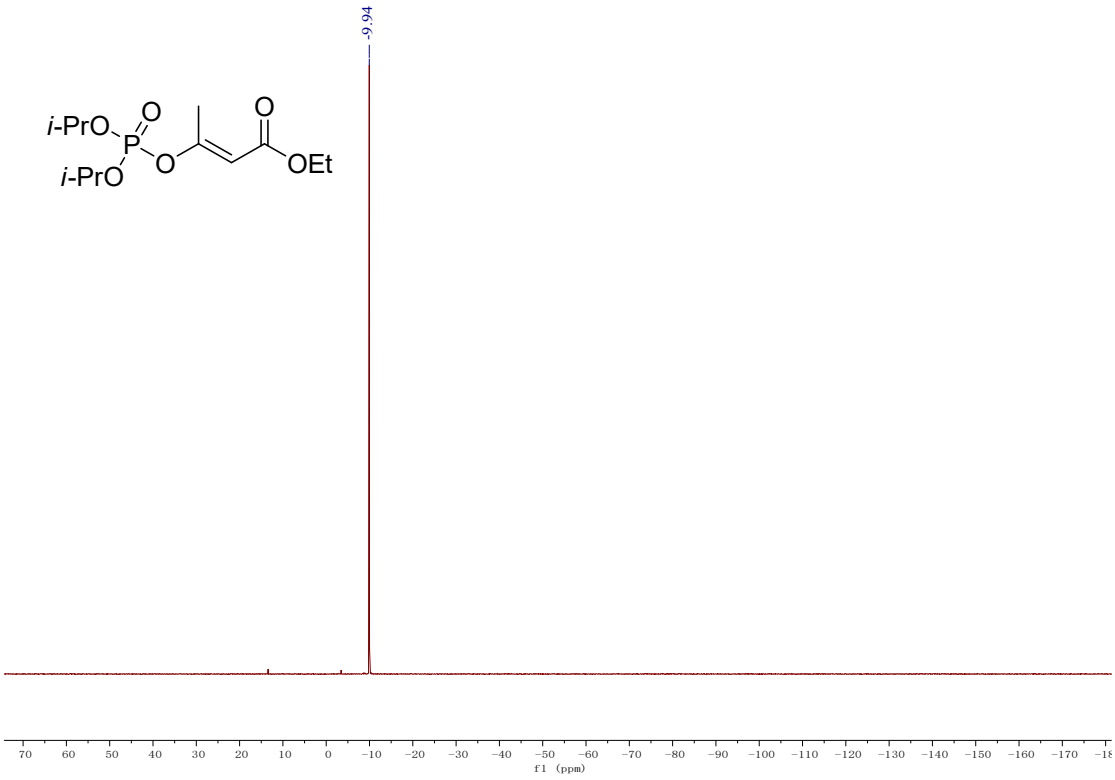
Compound 4b ^{1}H NMR



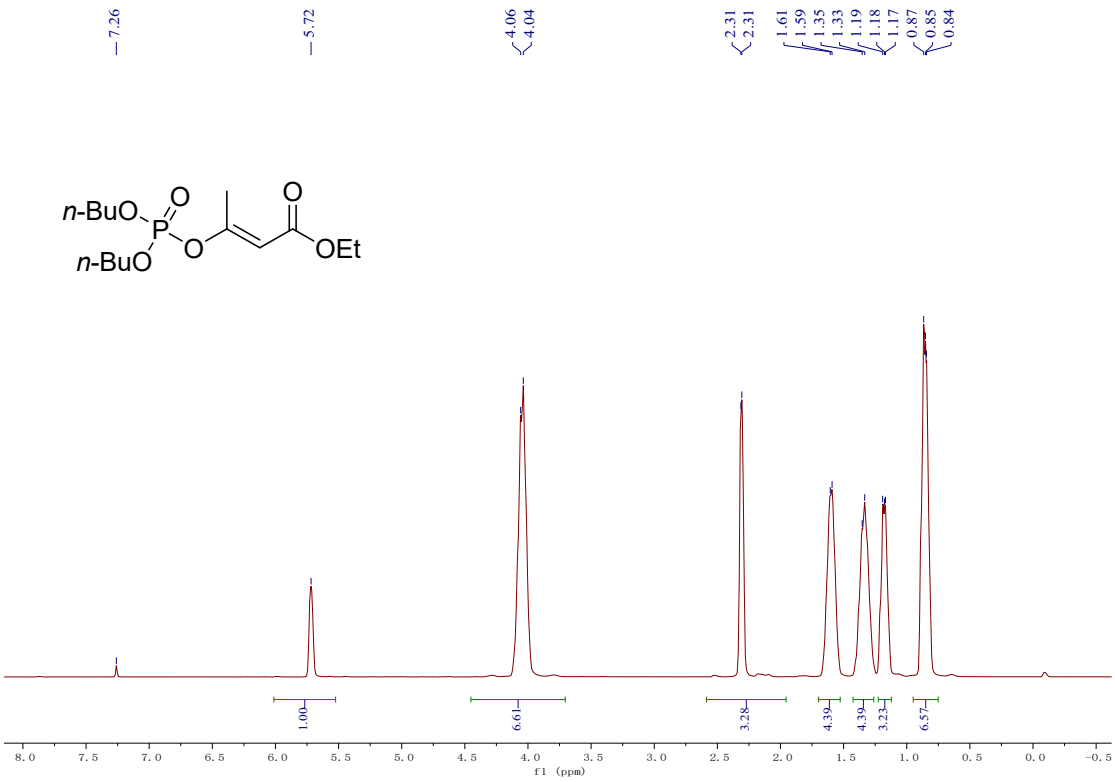
Compound 4b ^{13}C NMR



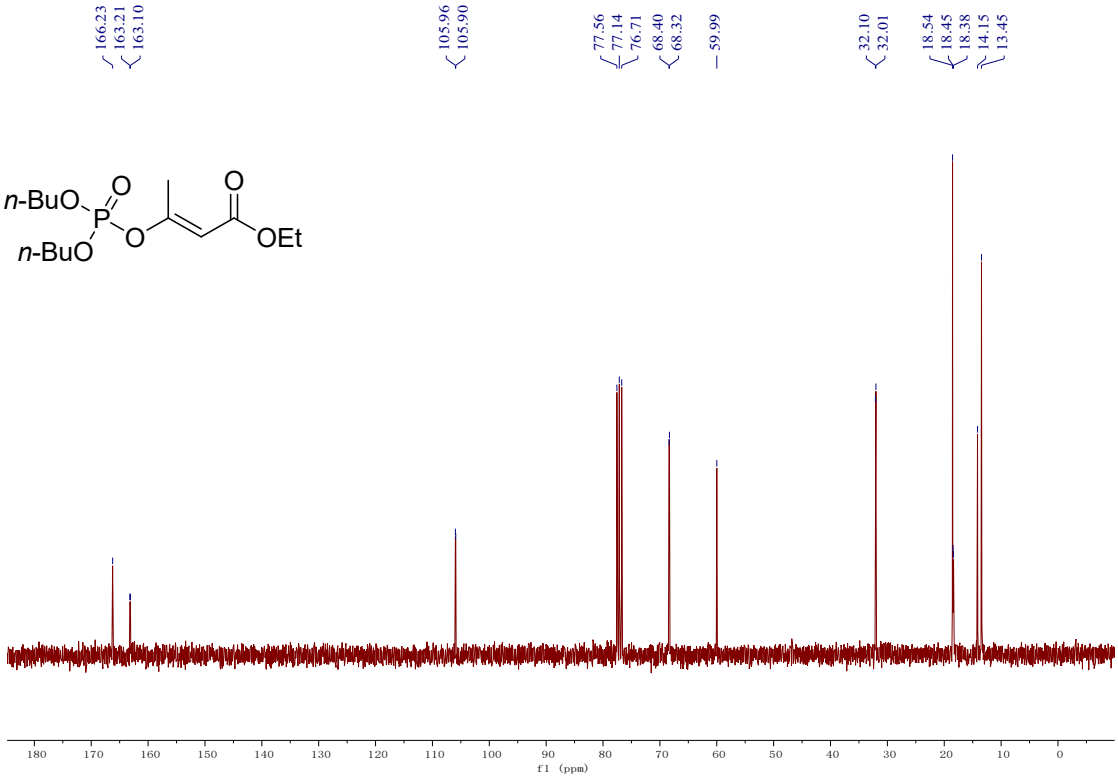
Compound 4b ^{31}P NMR



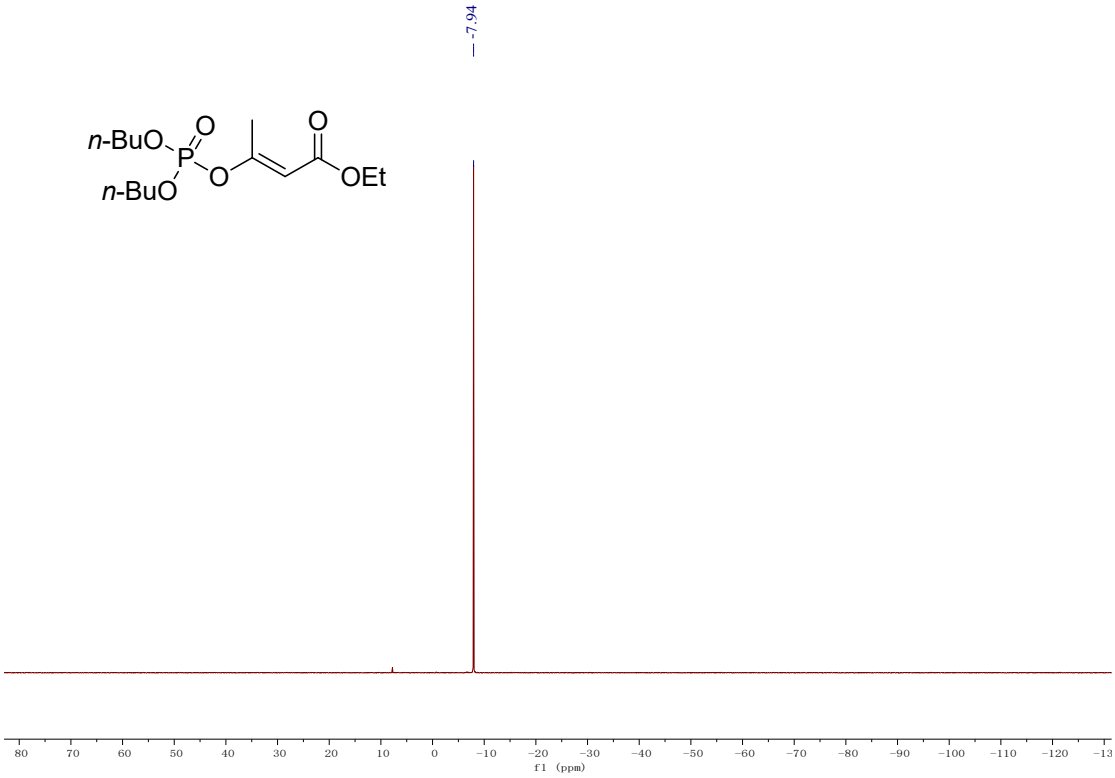
Compound 4c ^{1}H NMR



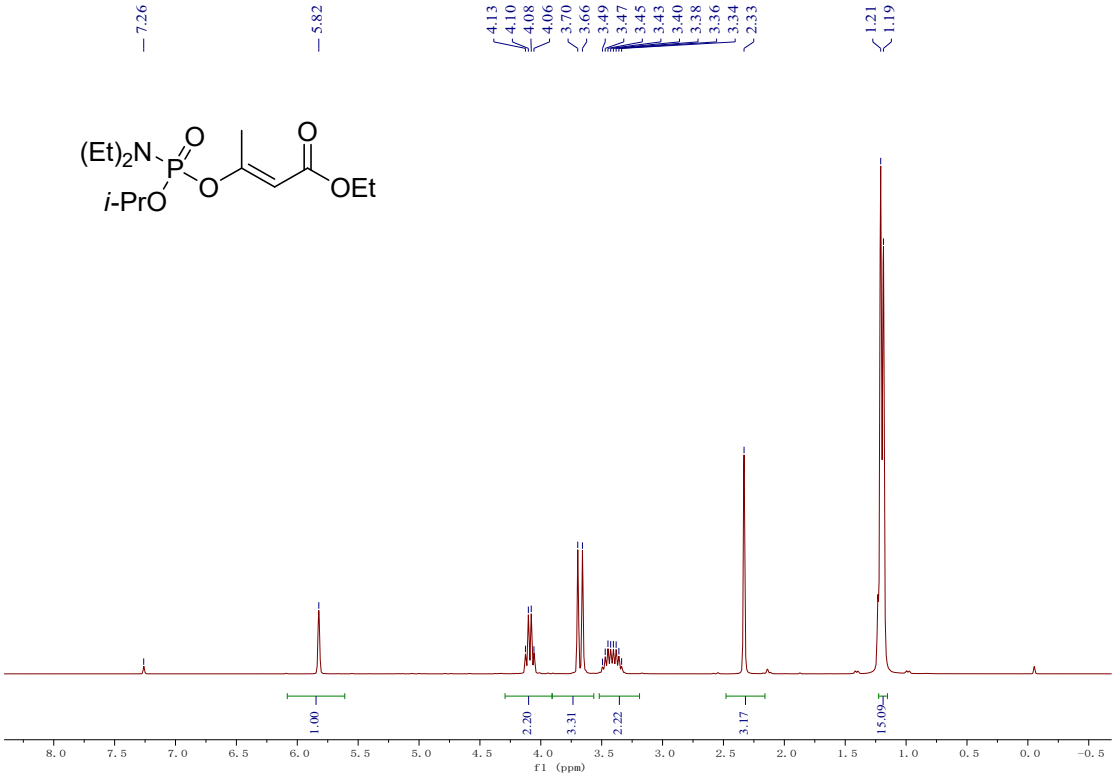
Compound 4c ^{13}C NMR



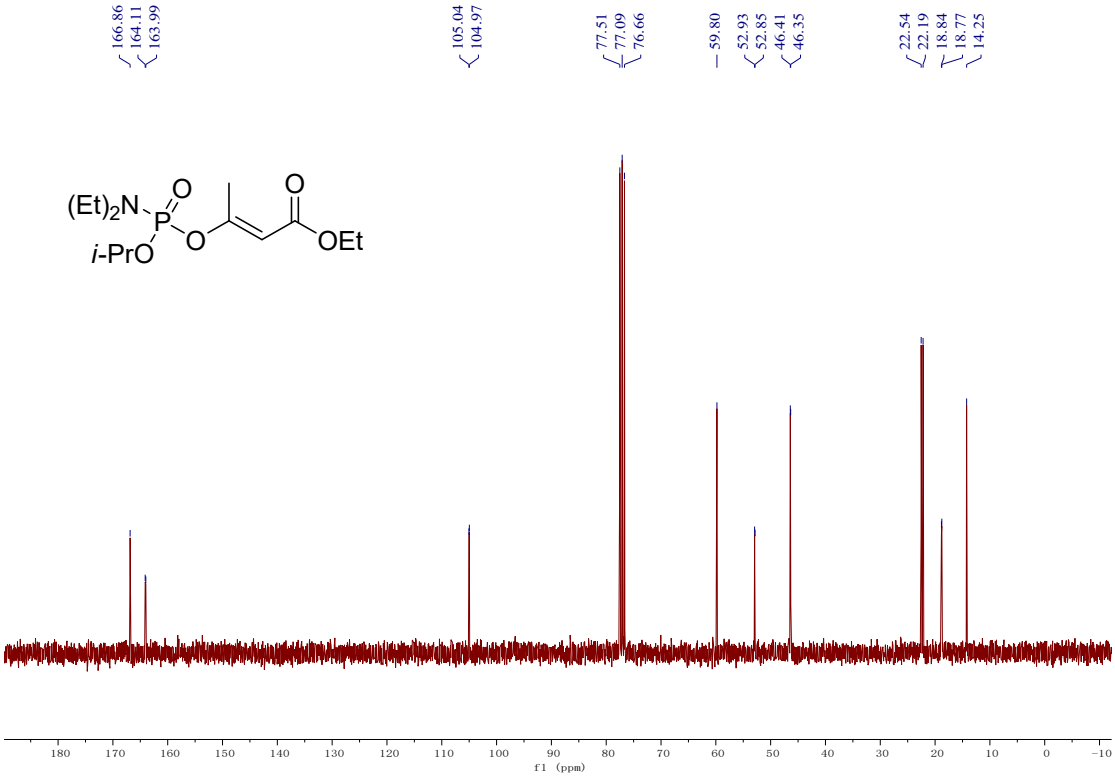
Compound 4c ^{31}P NMR



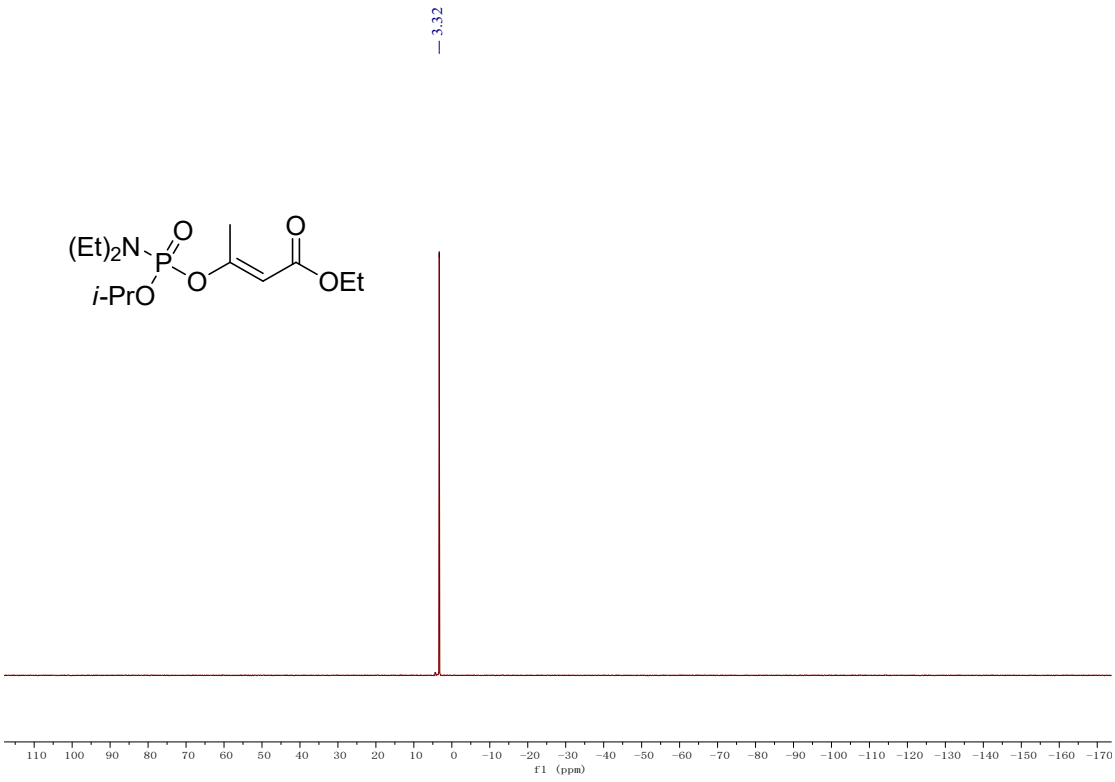
Compound 4d ^{1}H NMR



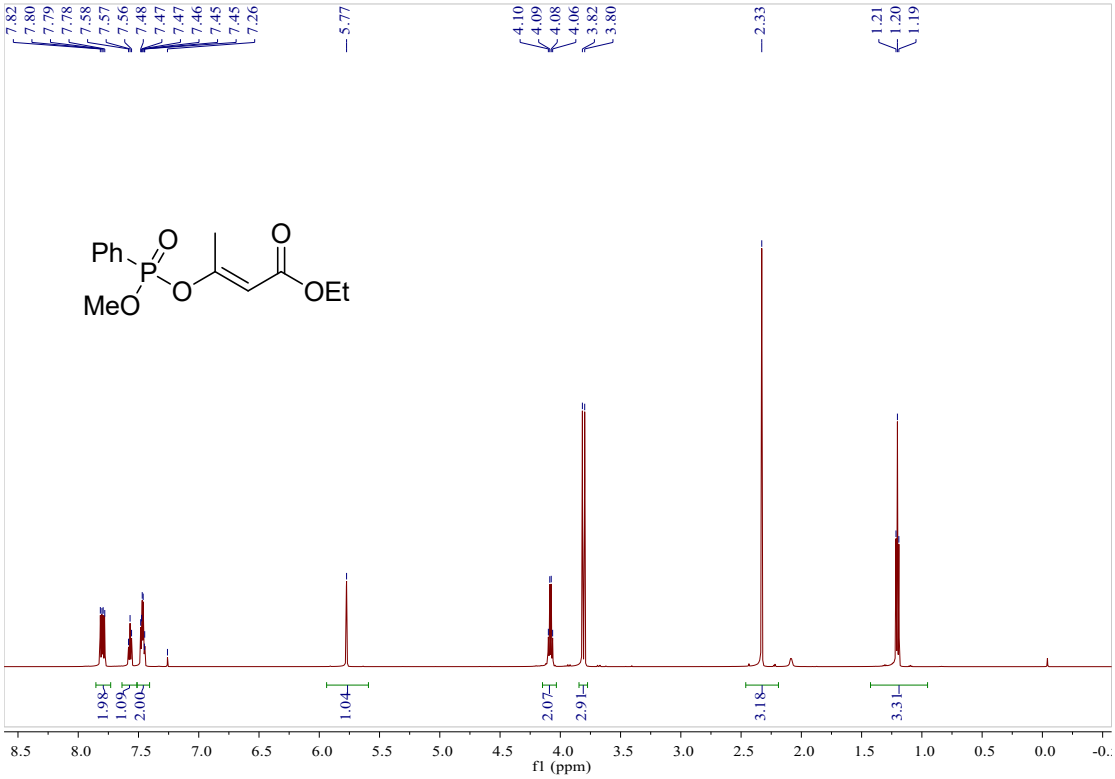
Compound 4d ^{13}C NMR



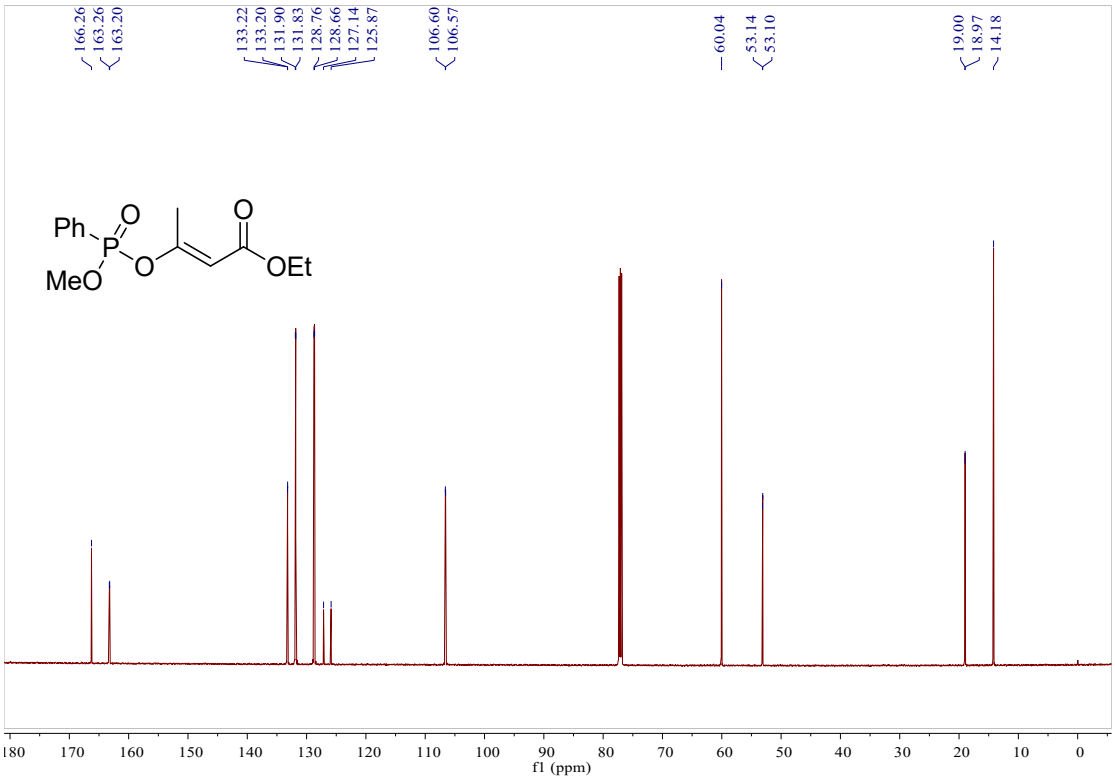
Compound 4d ^{31}P NMR



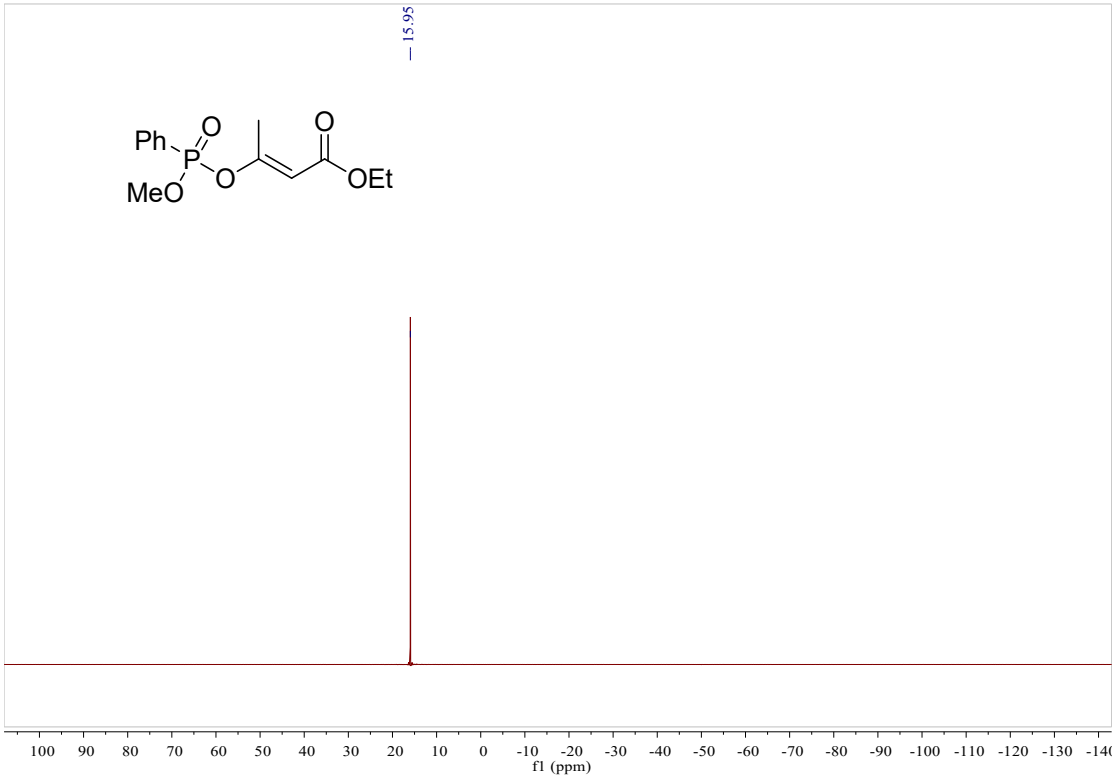
Compound 4e ^{1}H NMR



Compound 4e ^{13}C NMR



Compound 4e ^{31}P NMR



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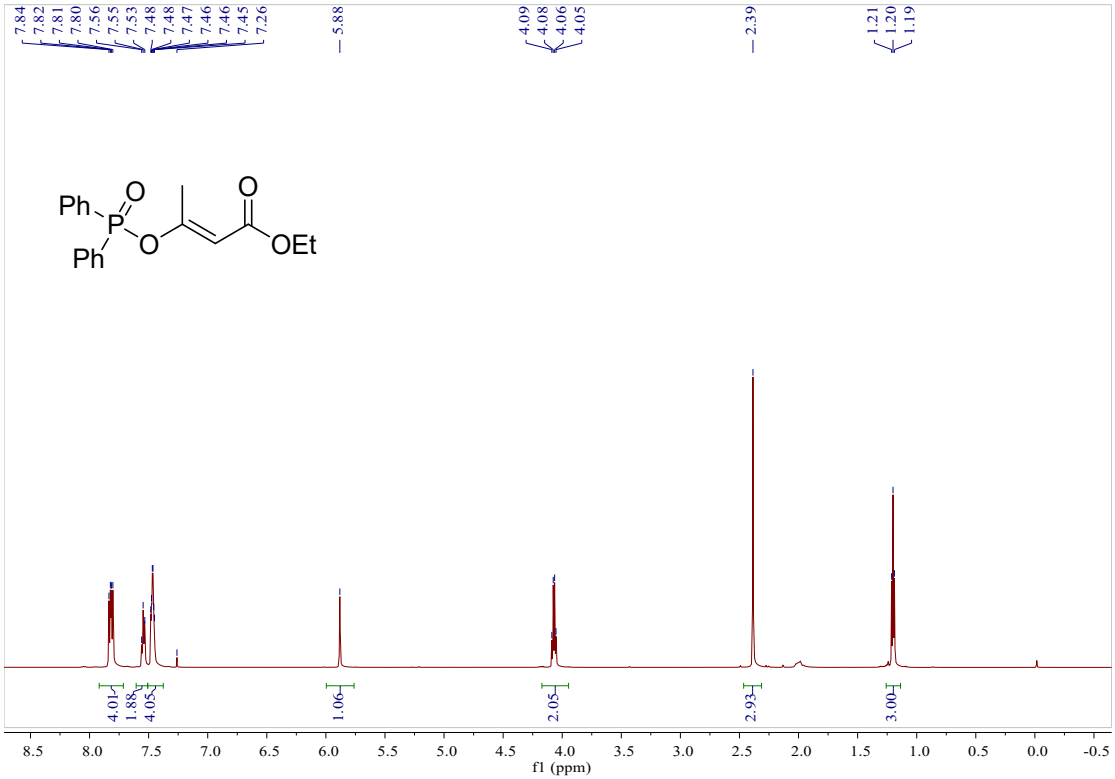

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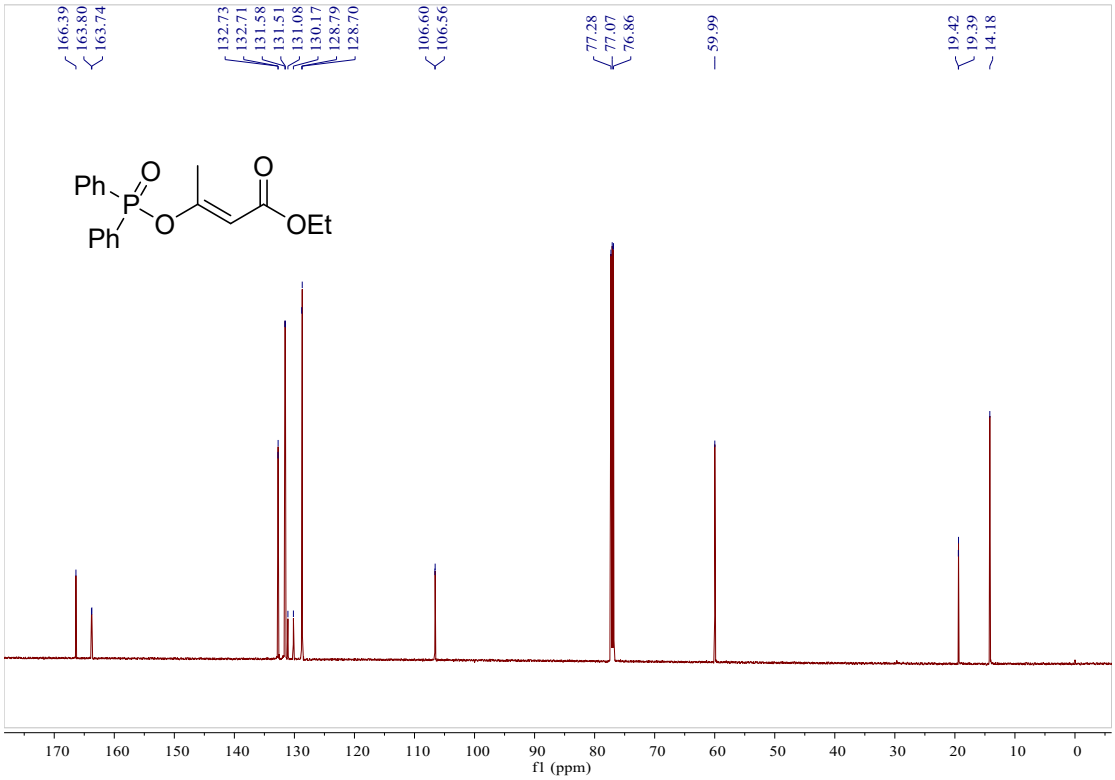

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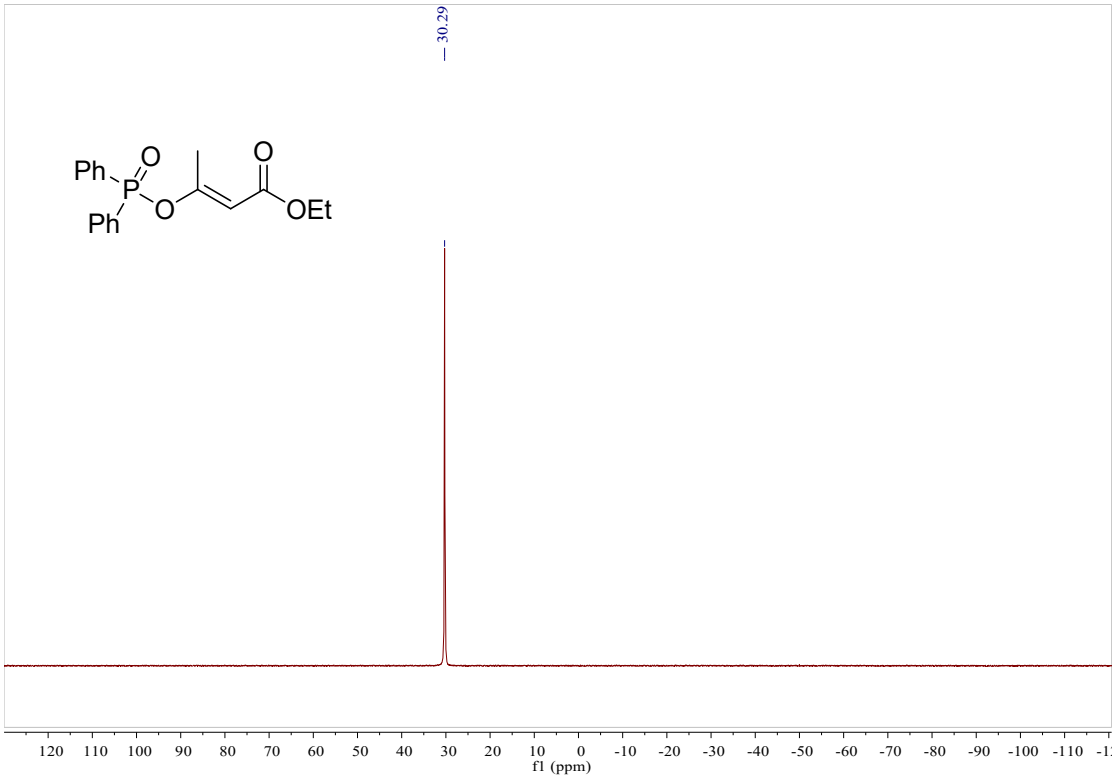

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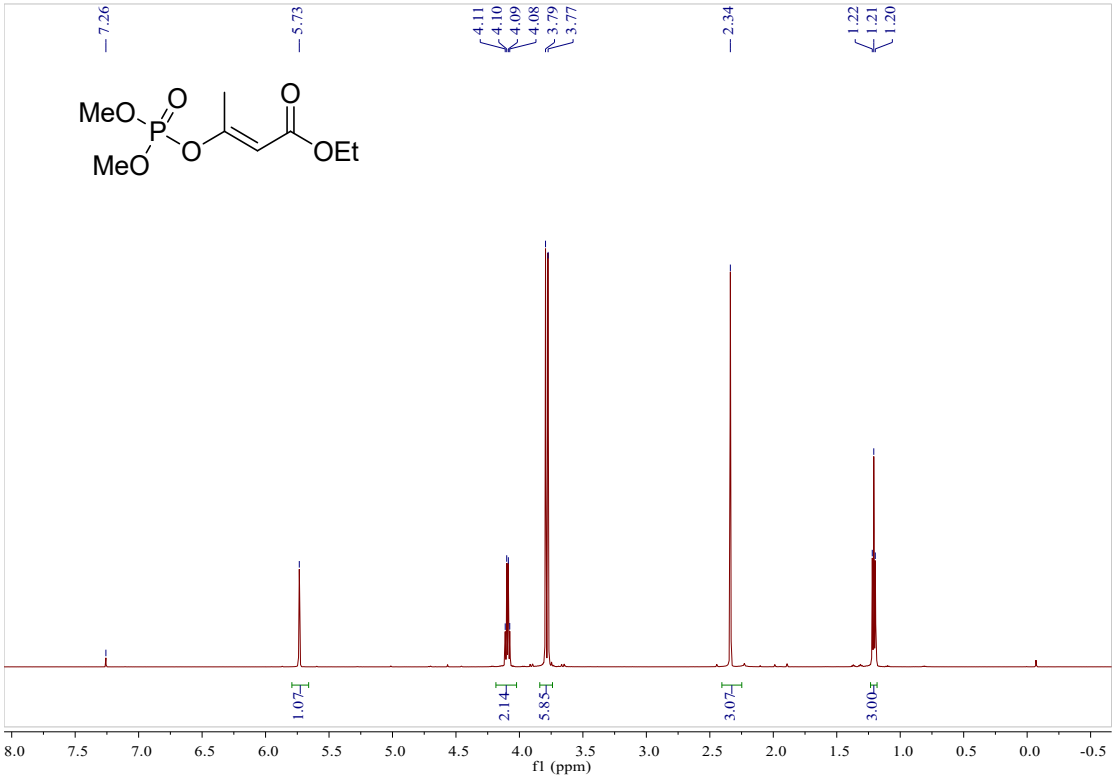

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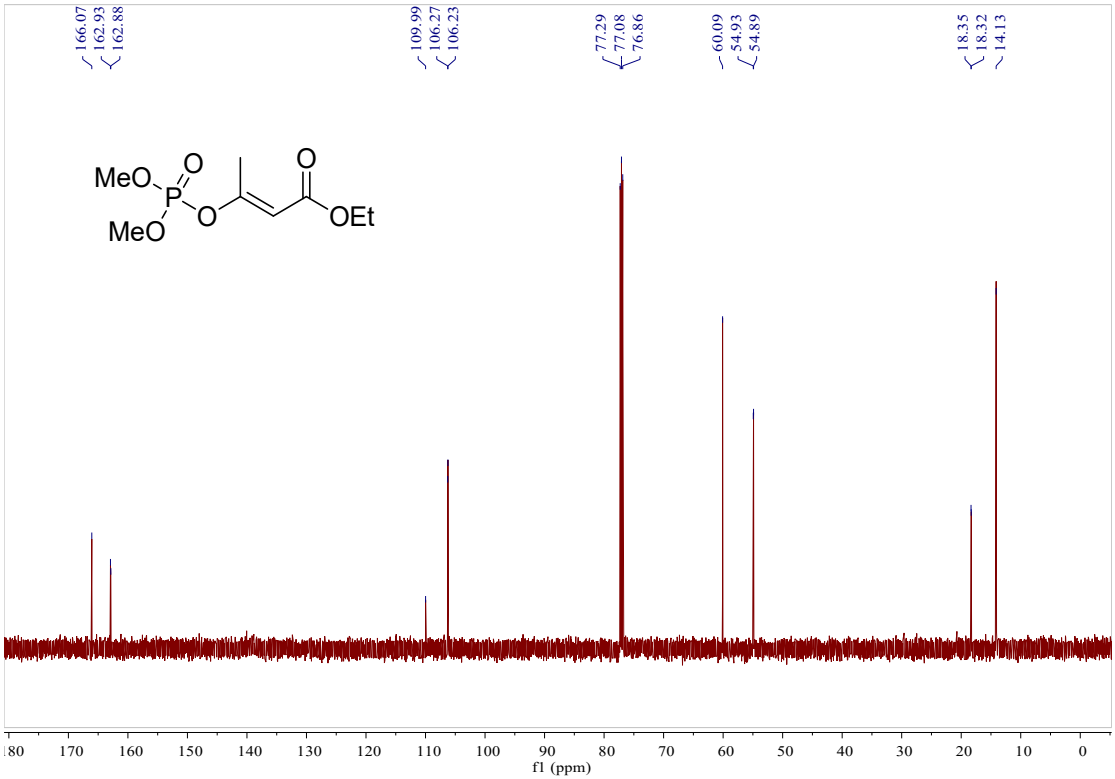

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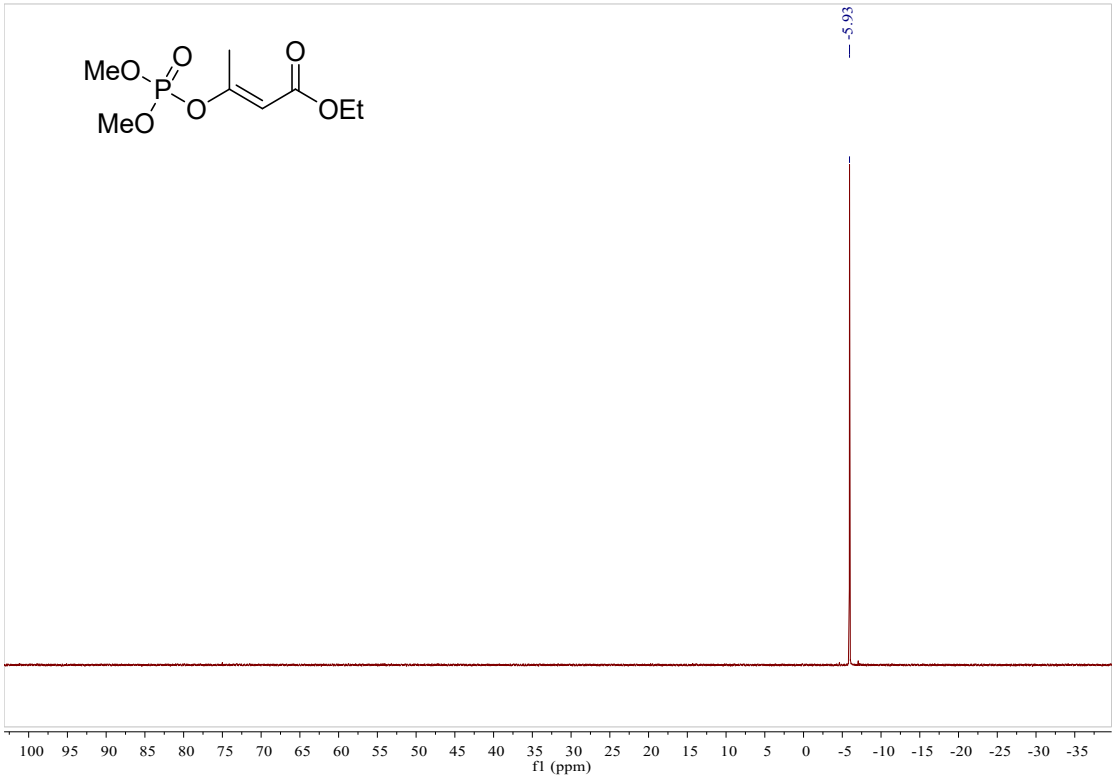

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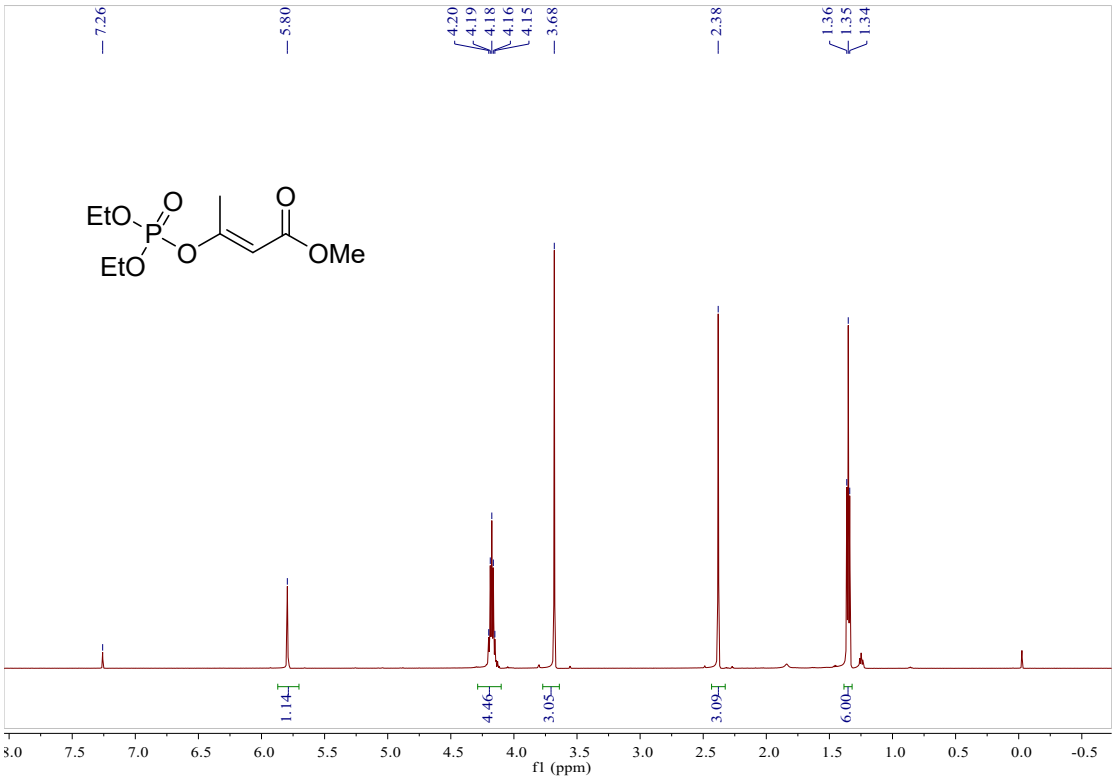

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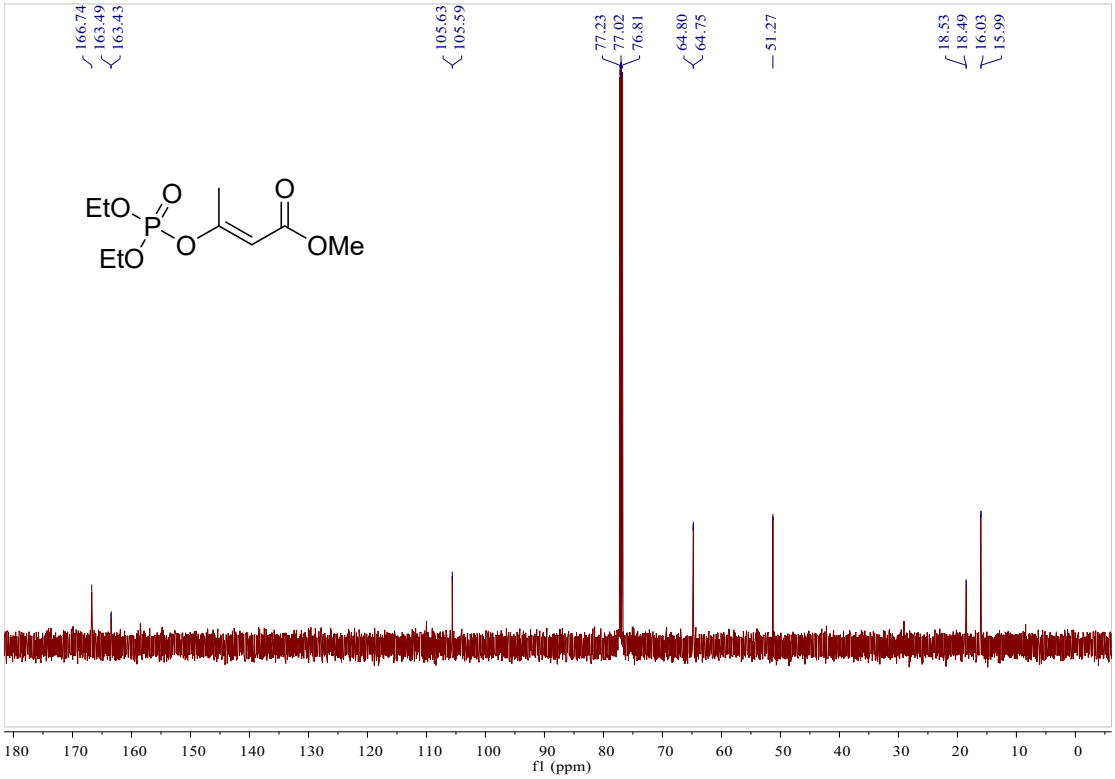

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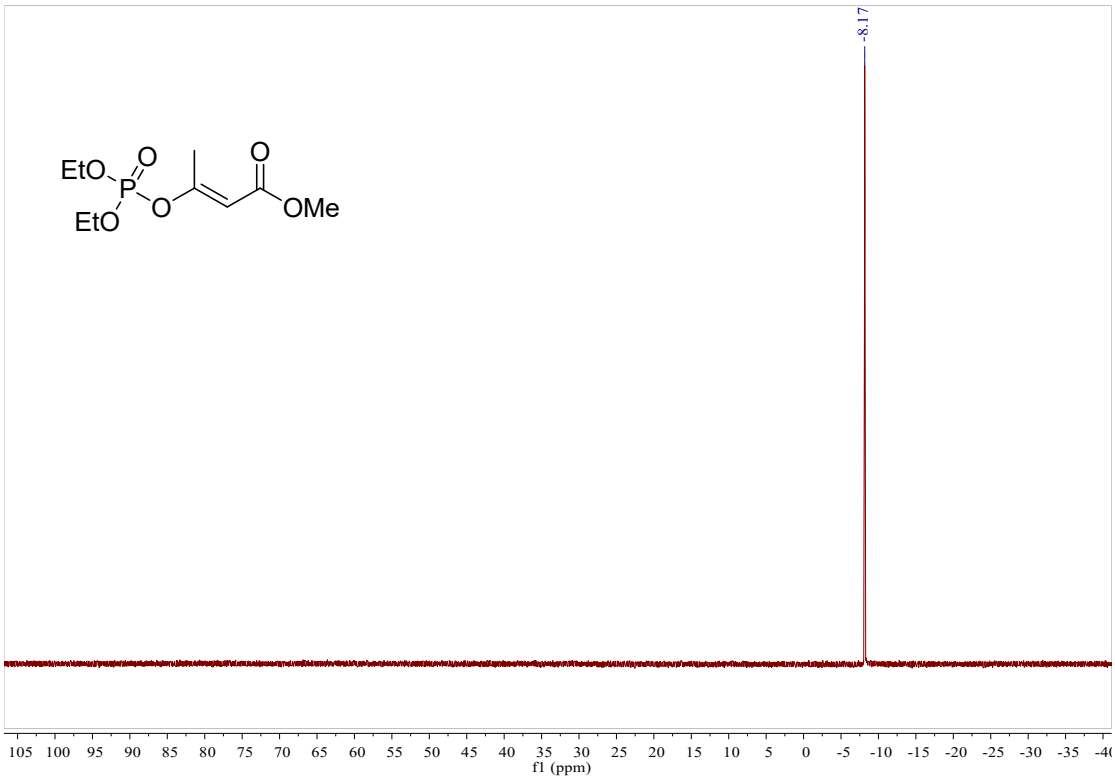

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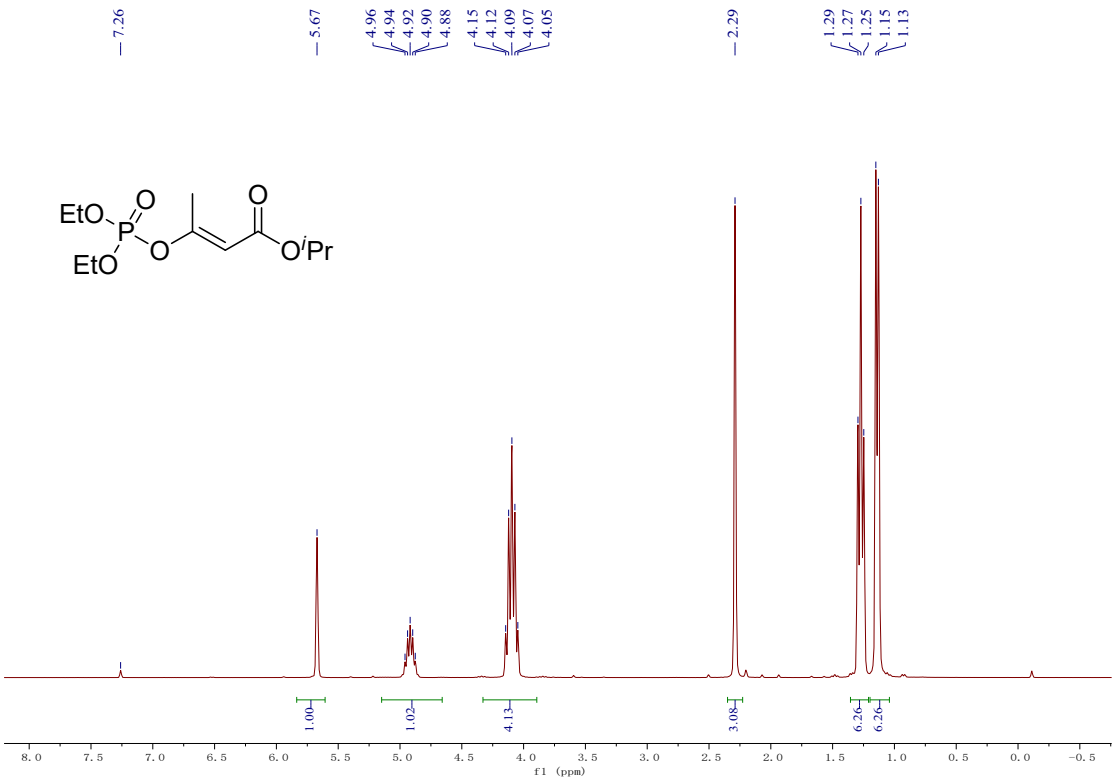

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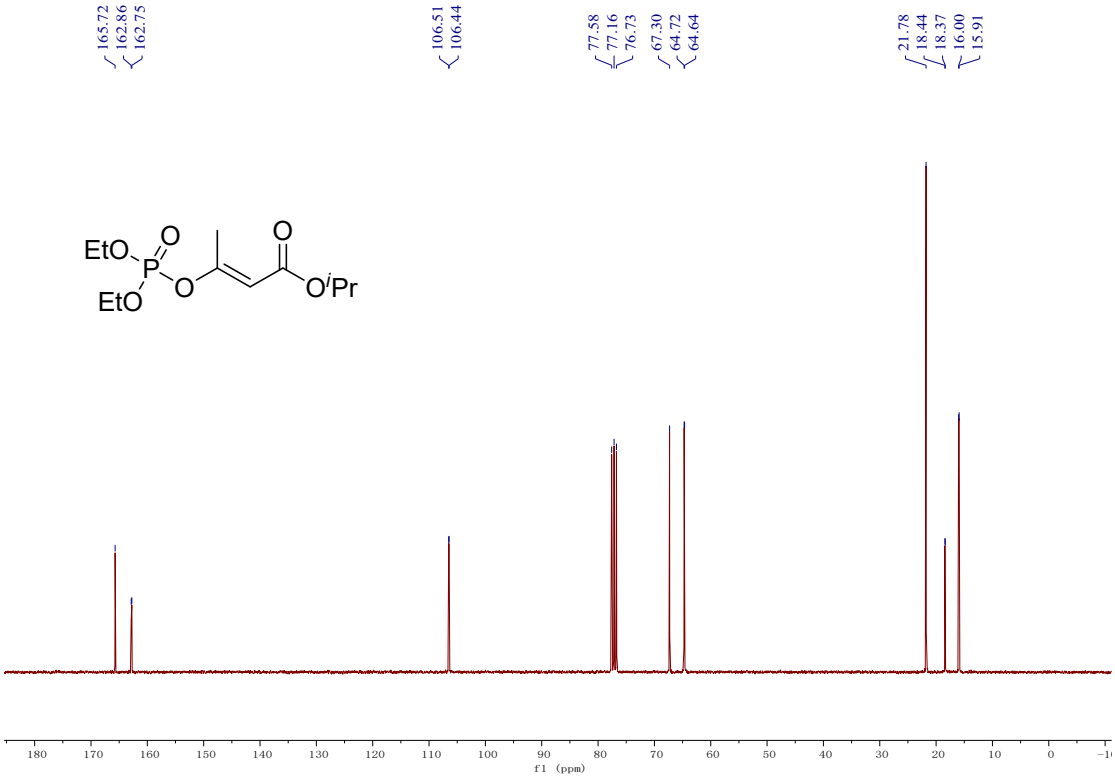

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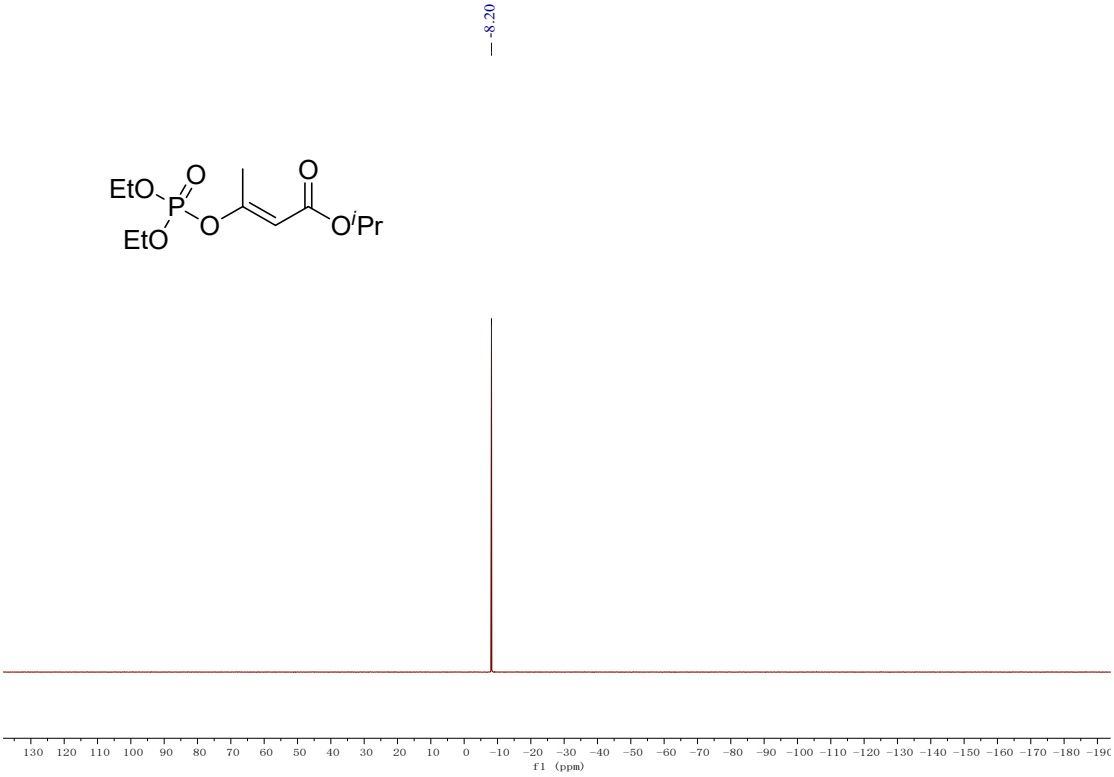

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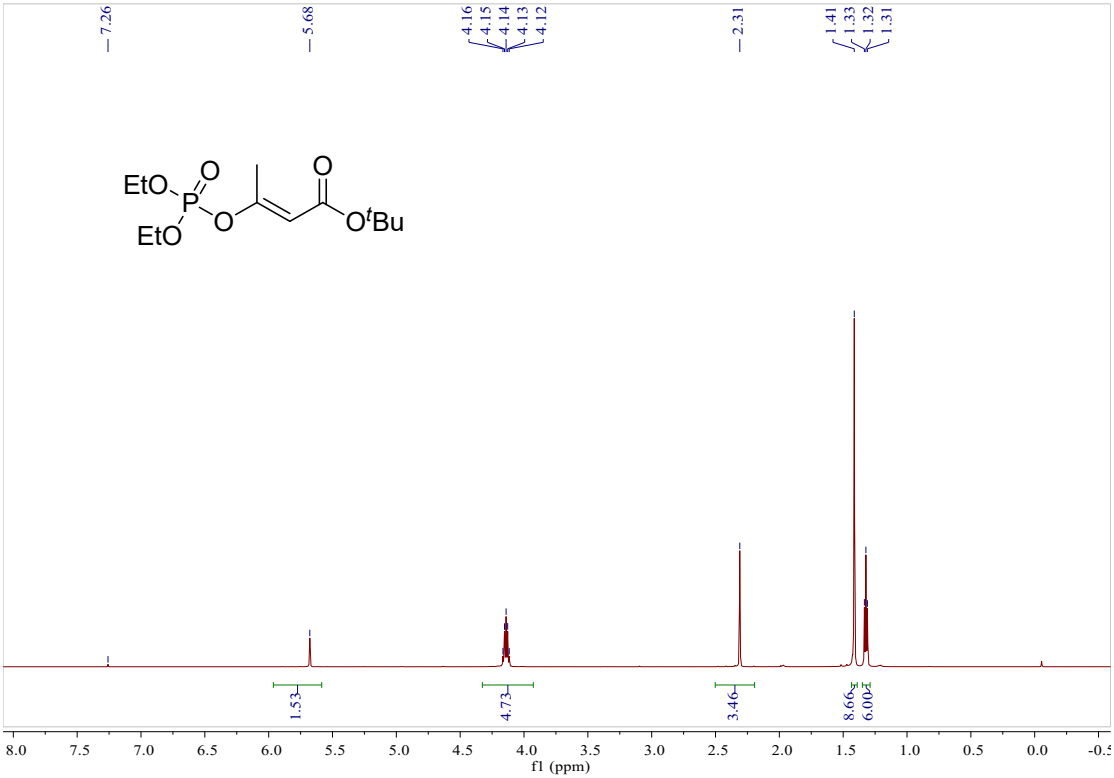

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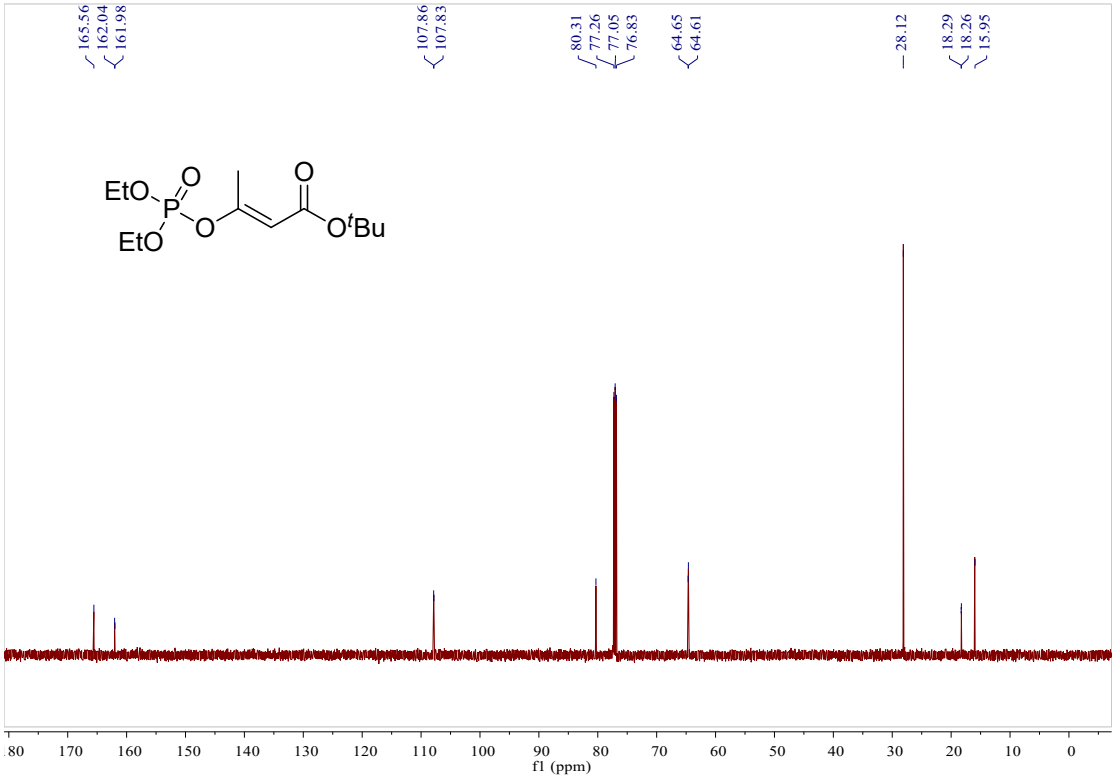

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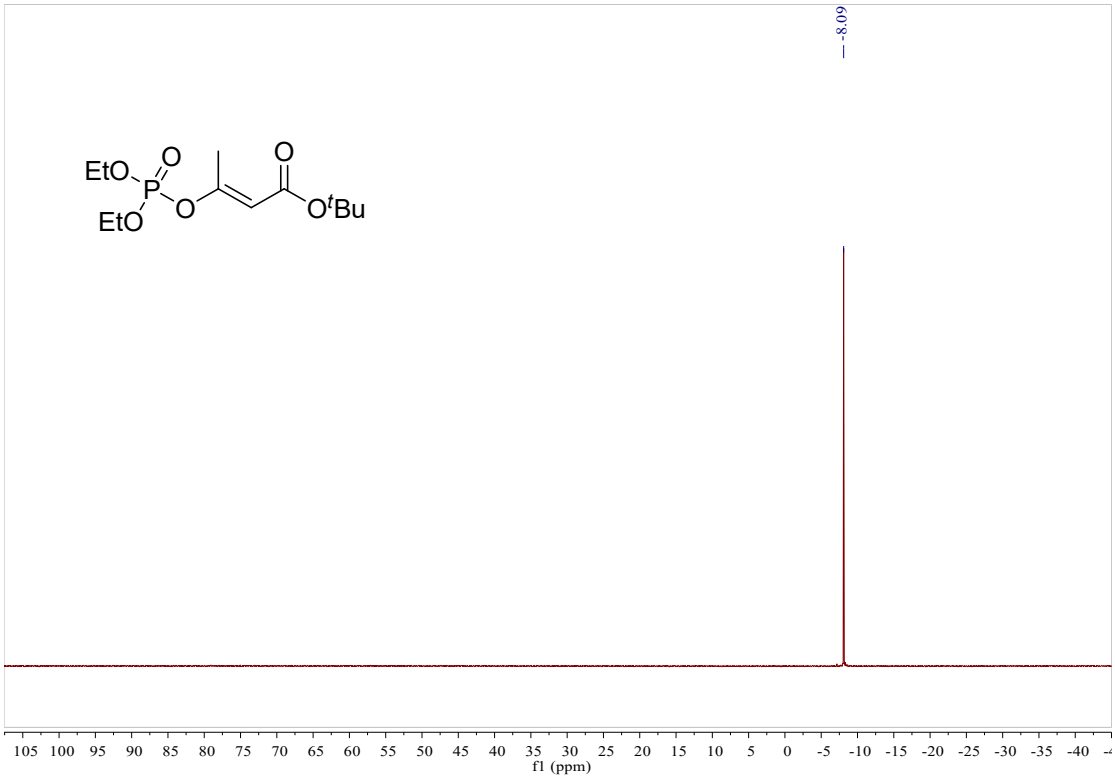

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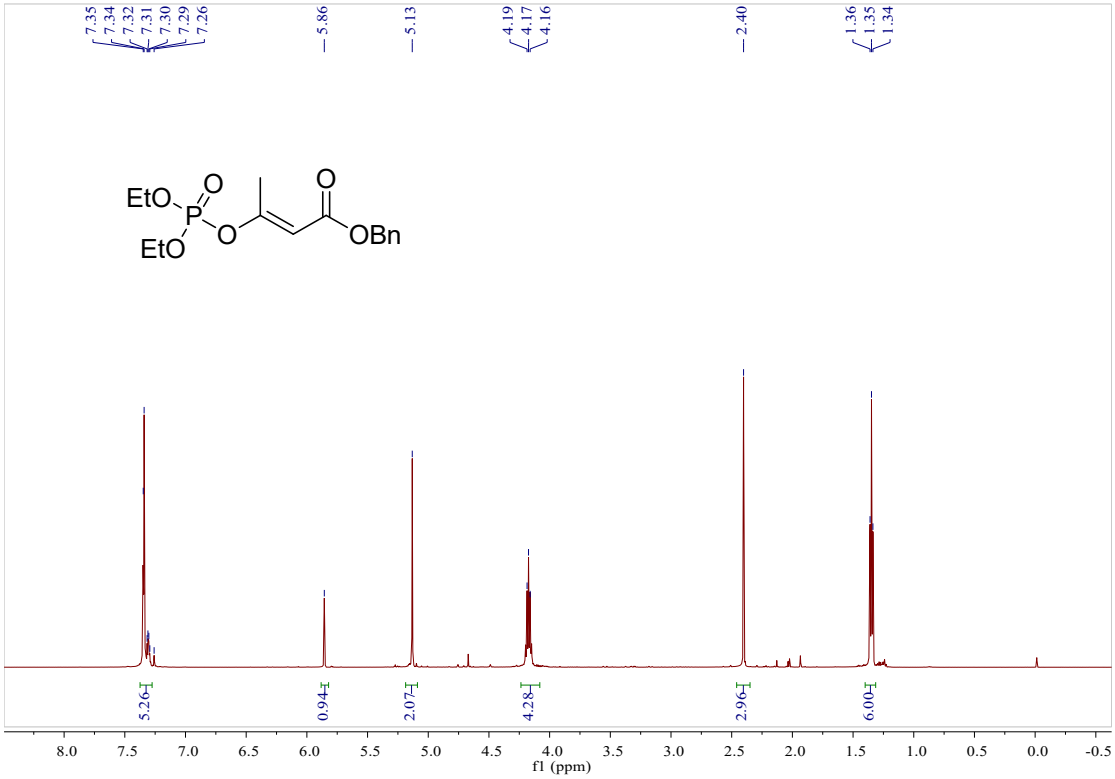

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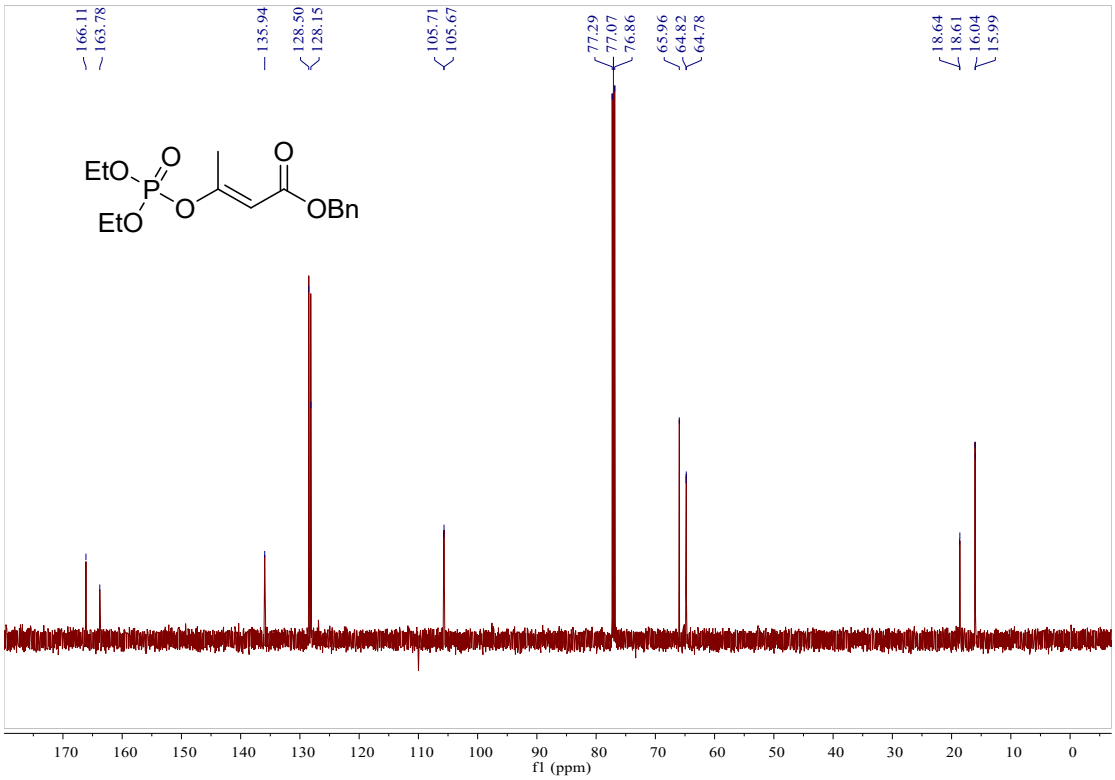

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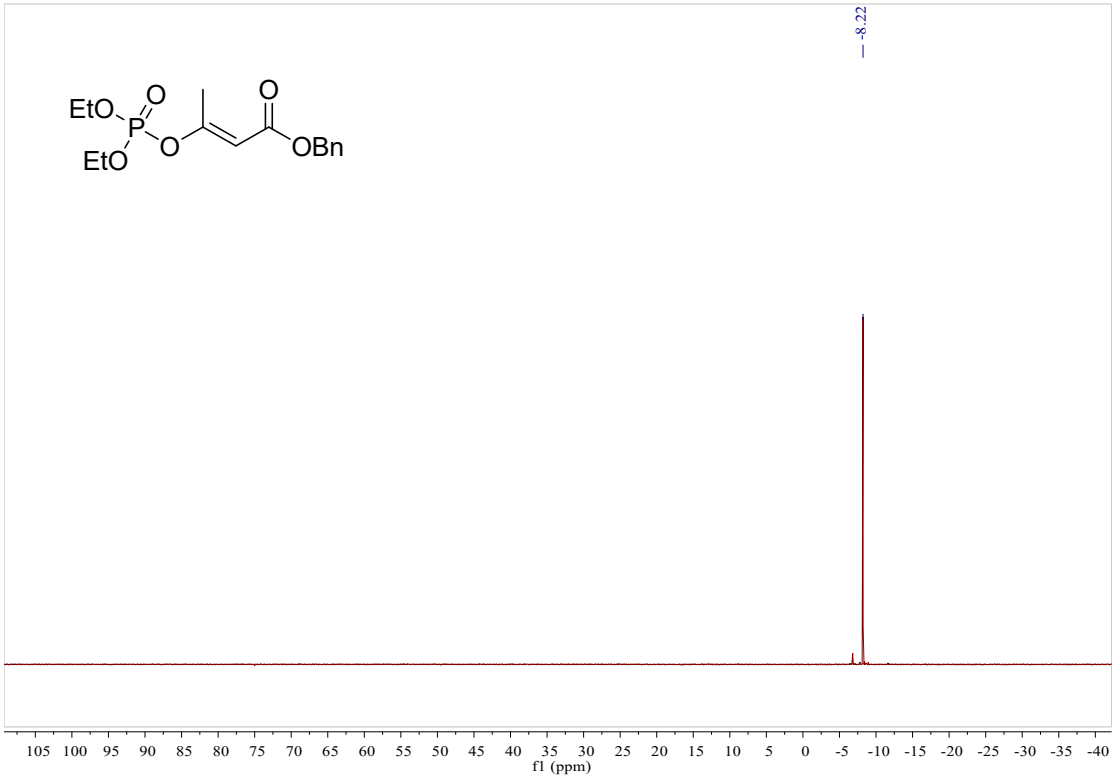
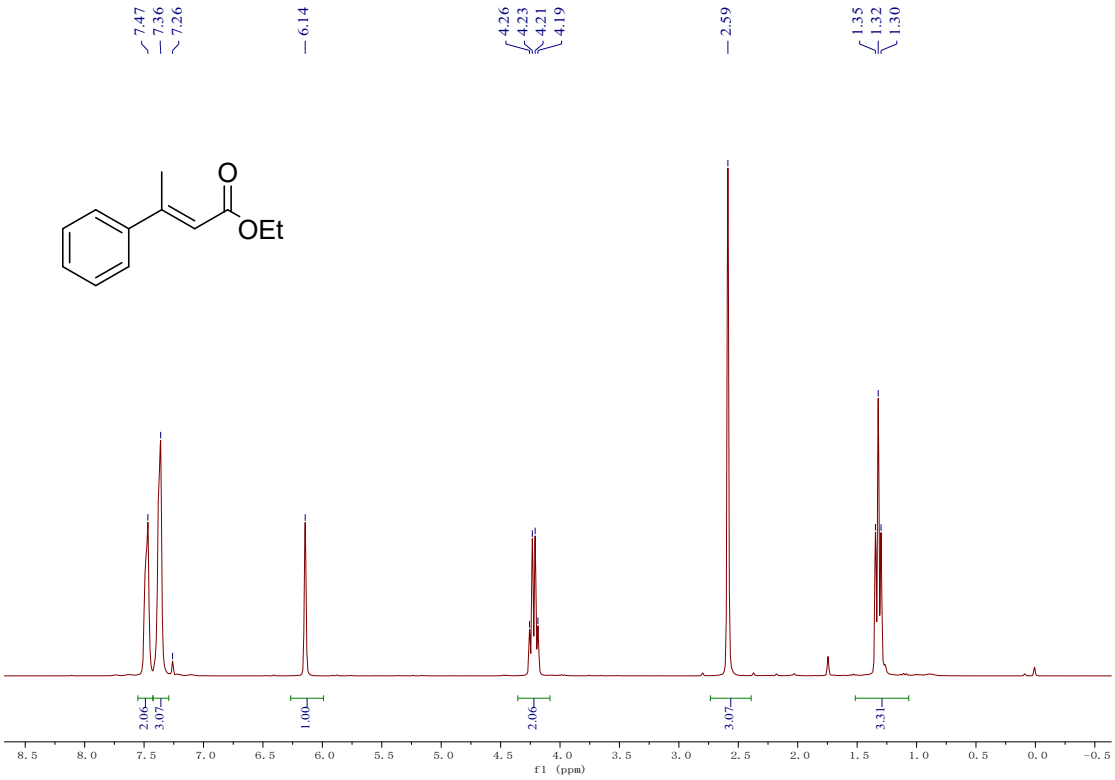
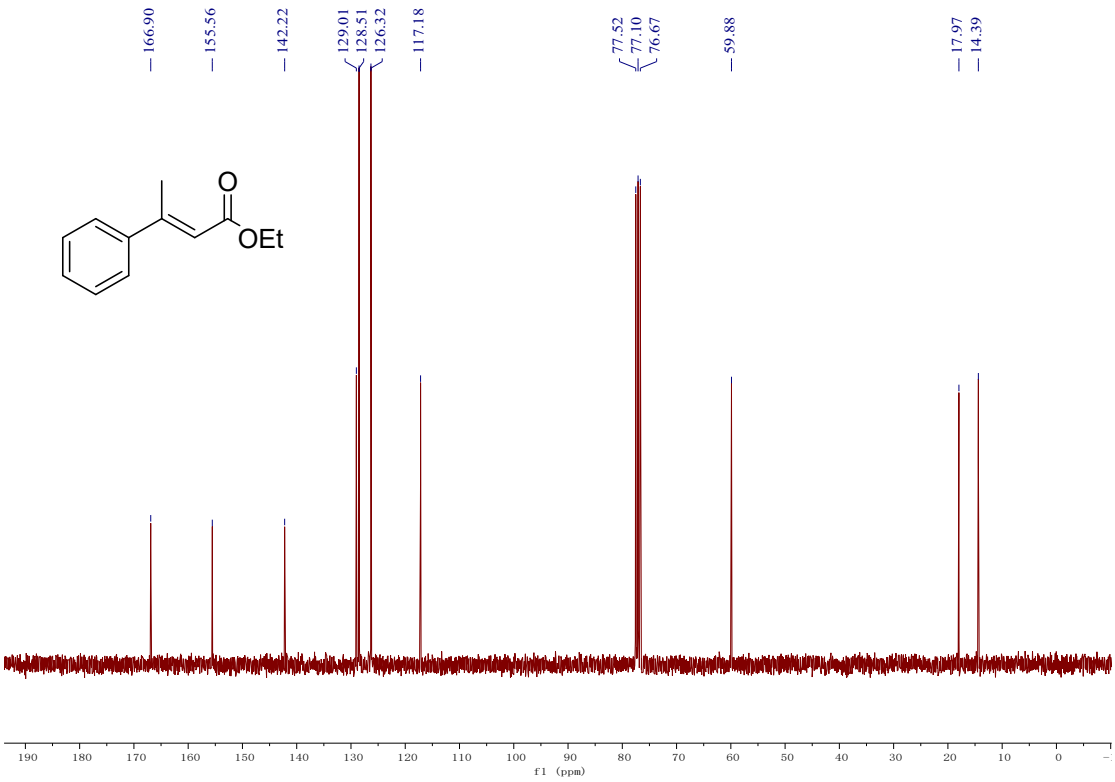


Compound *E*-6a ^{1}H NMR



Compound *E*-6a ^{13}C NMR



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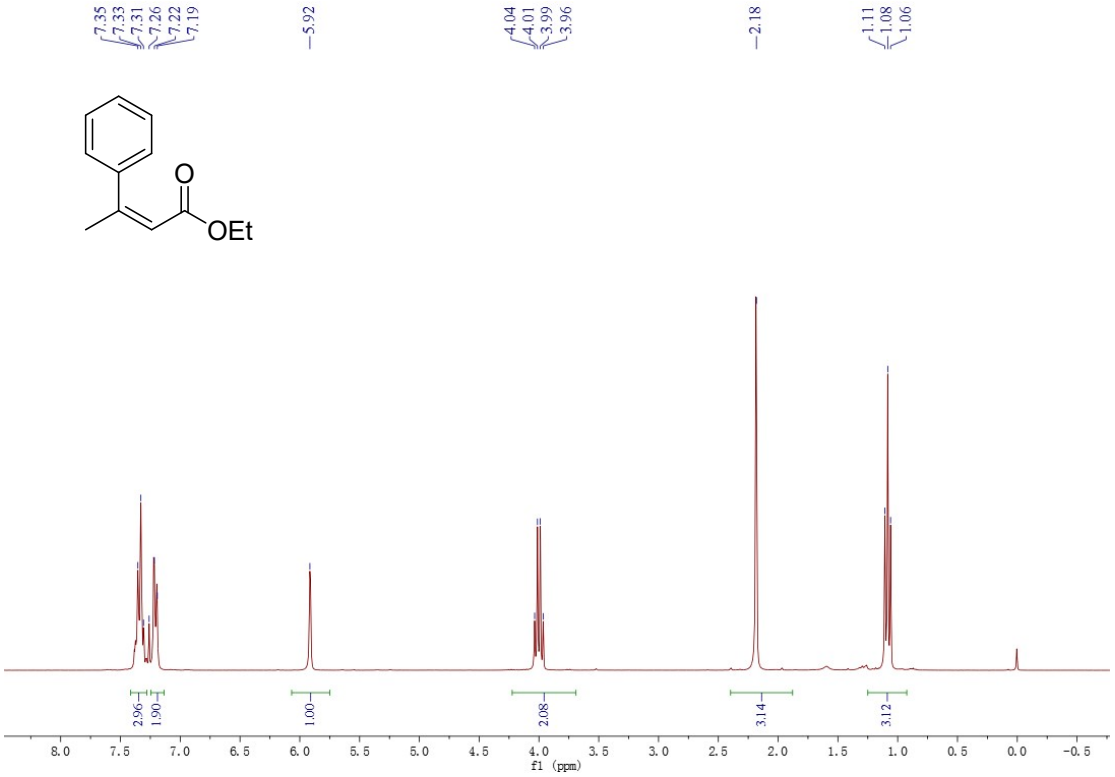
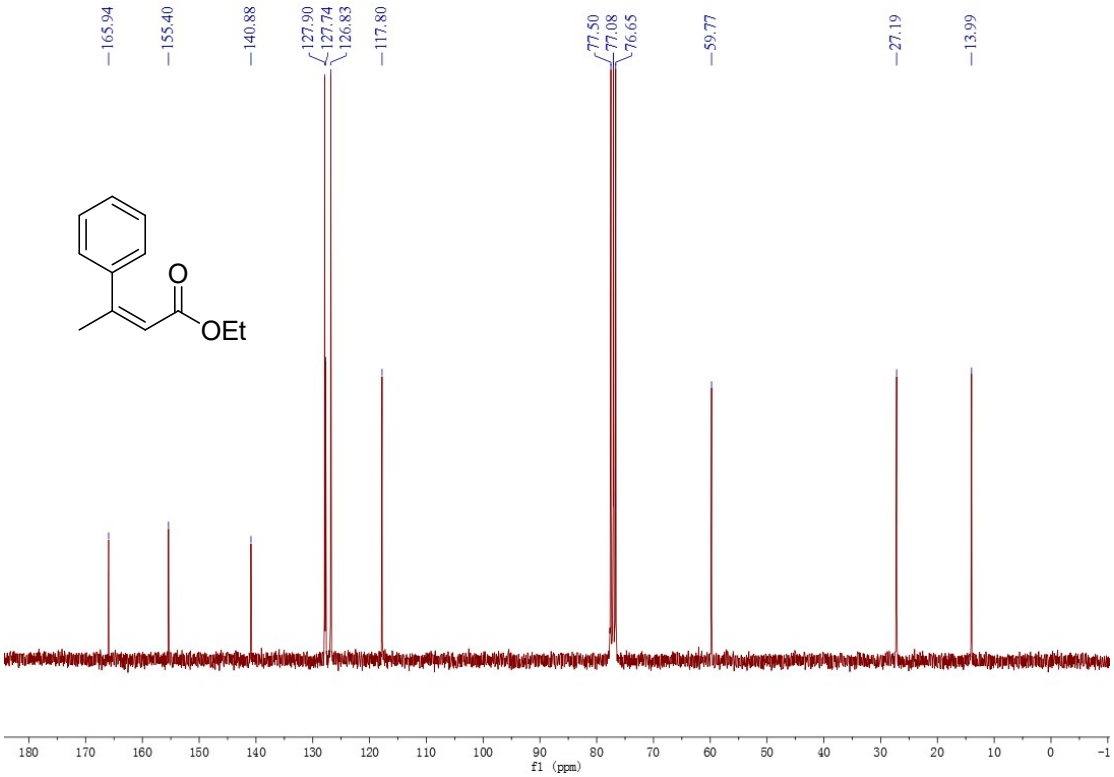
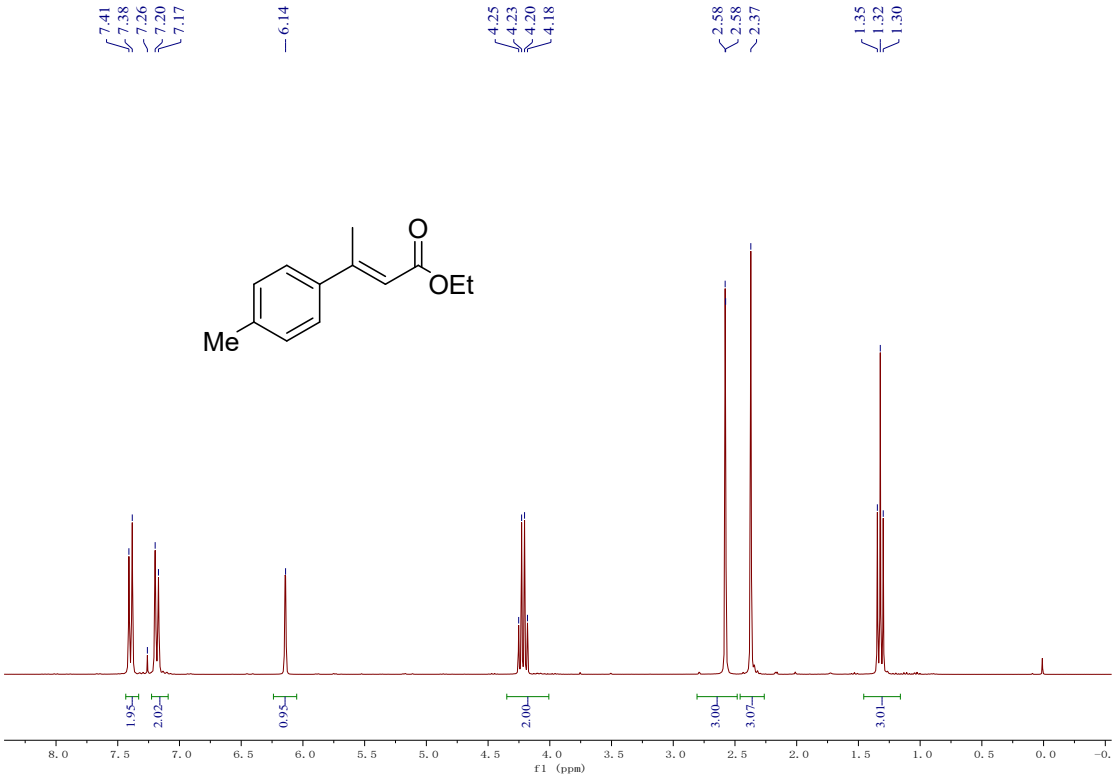


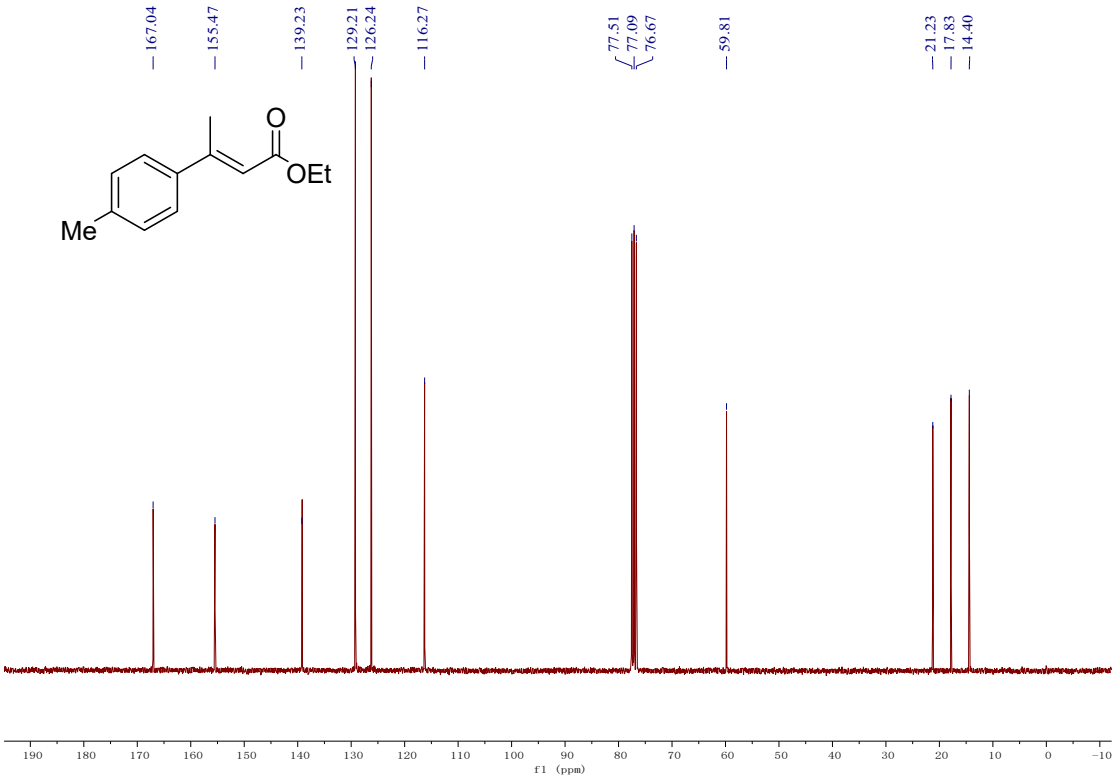
Compound *Z*-6a ^{13}C NMR



Compound 6b ^{1}H NMR



Compound 6b ^{13}C NMR



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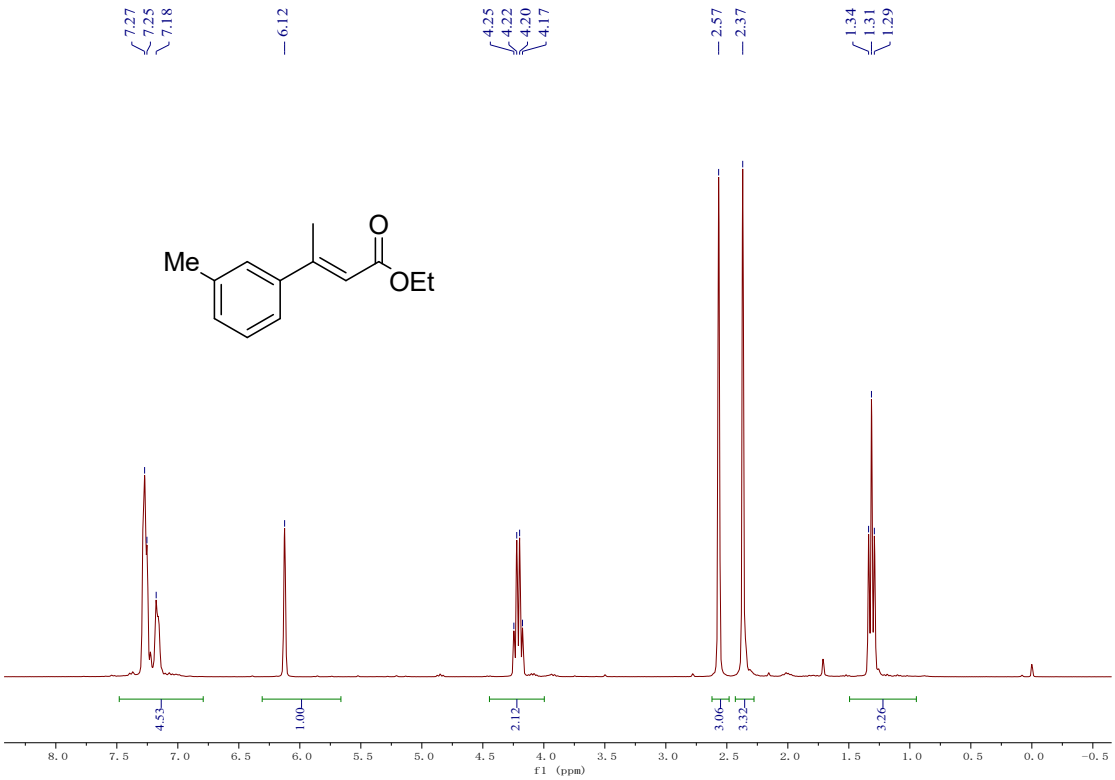

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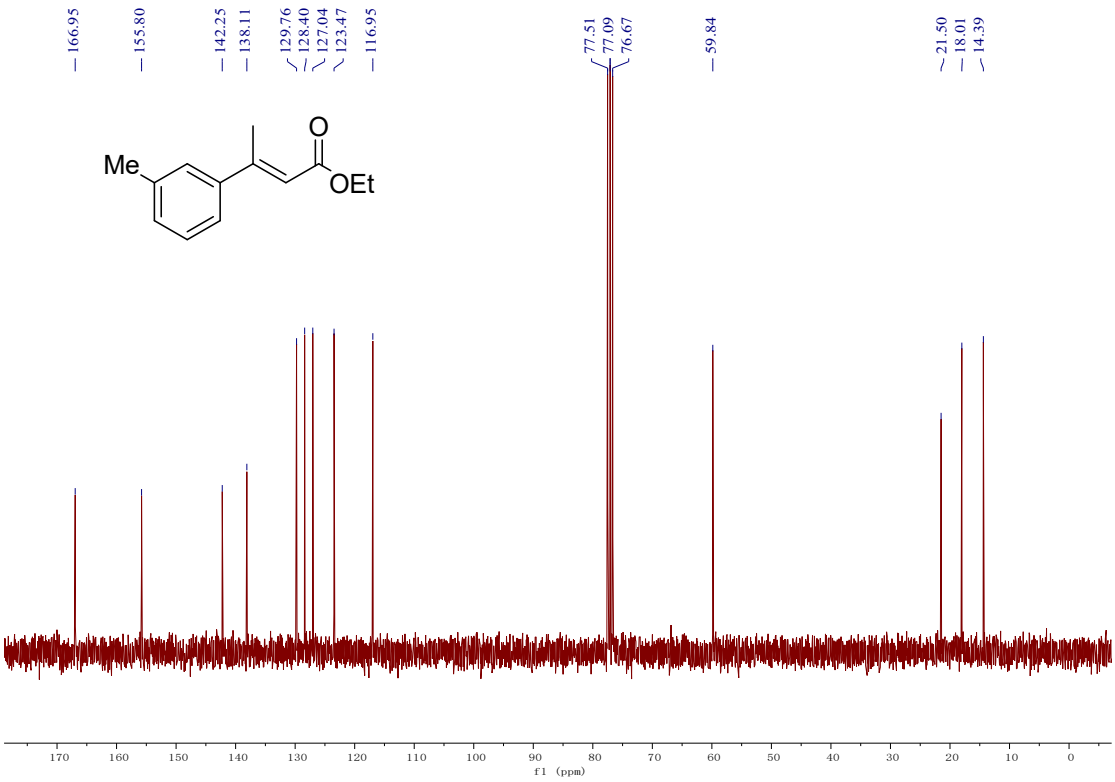

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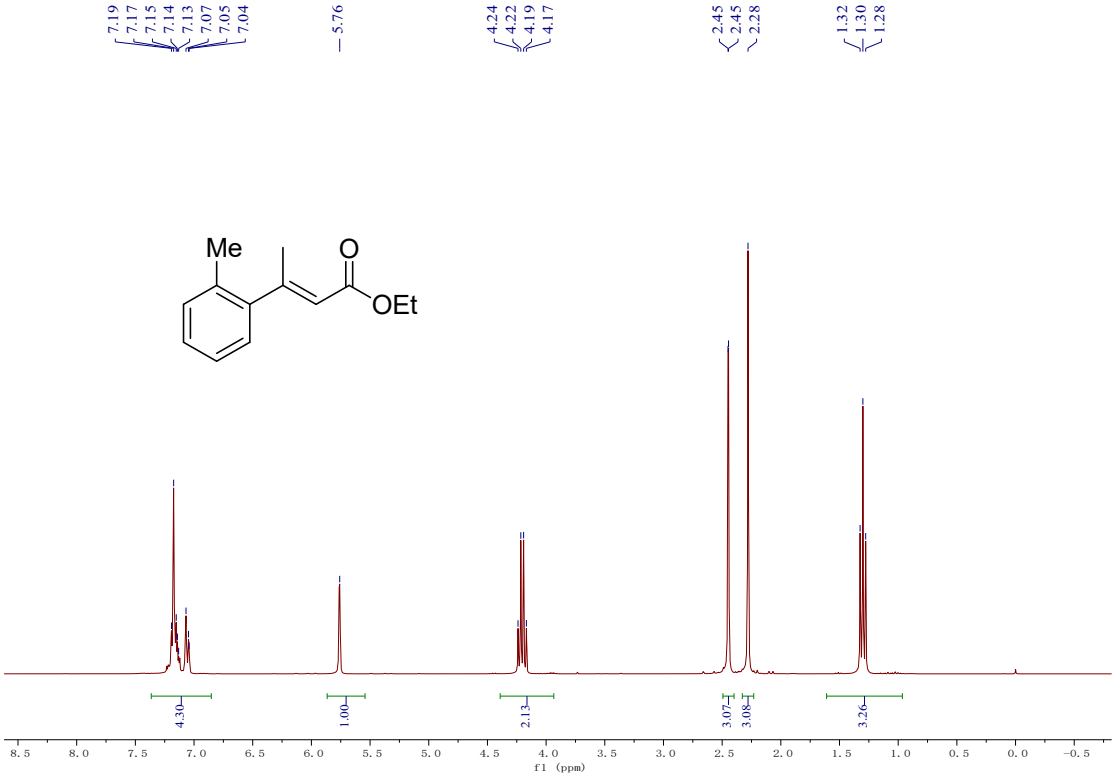

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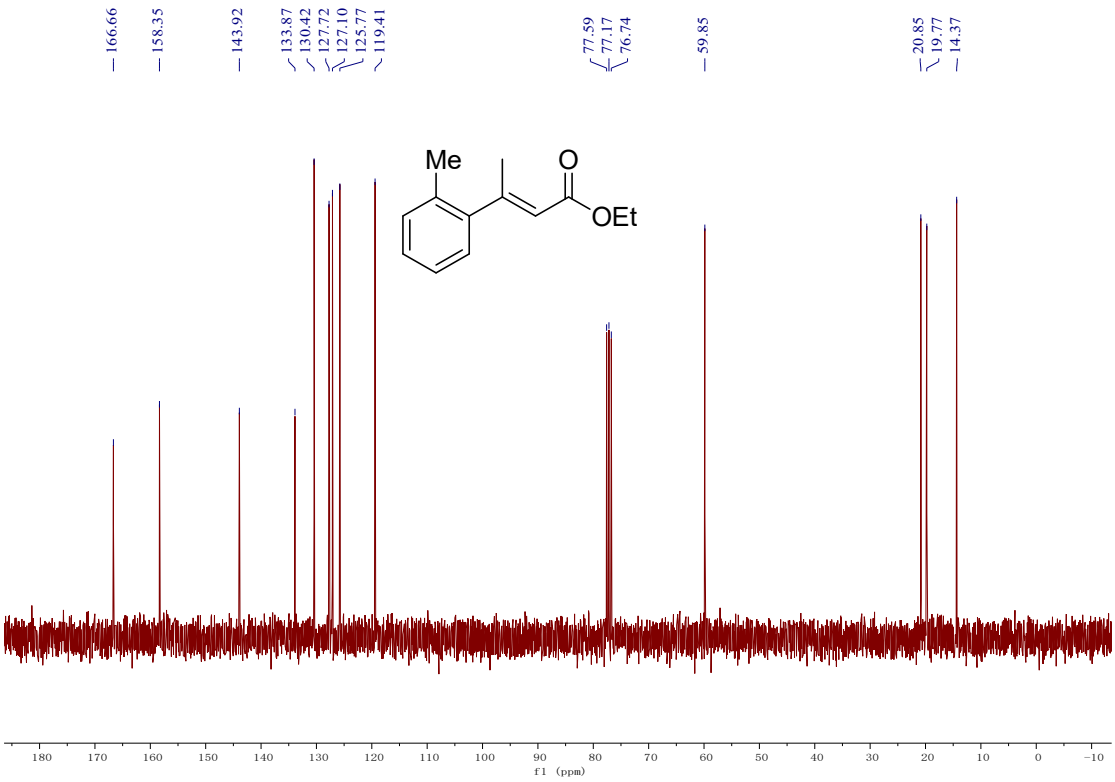

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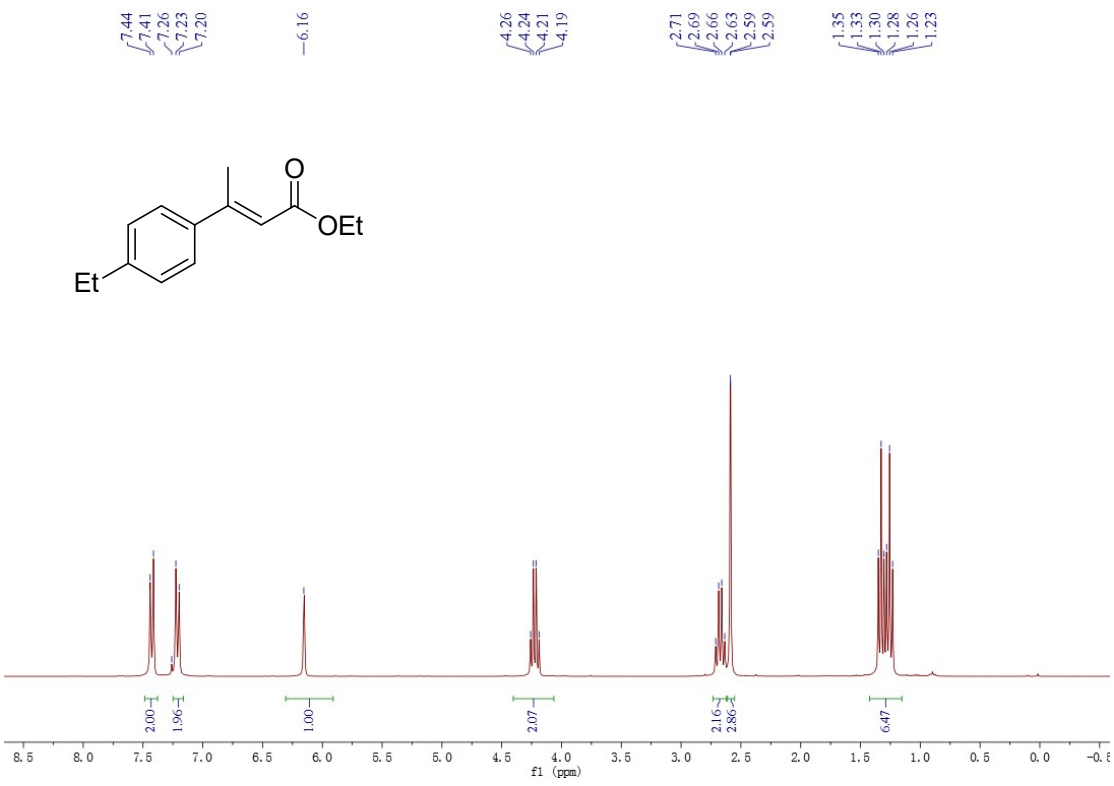

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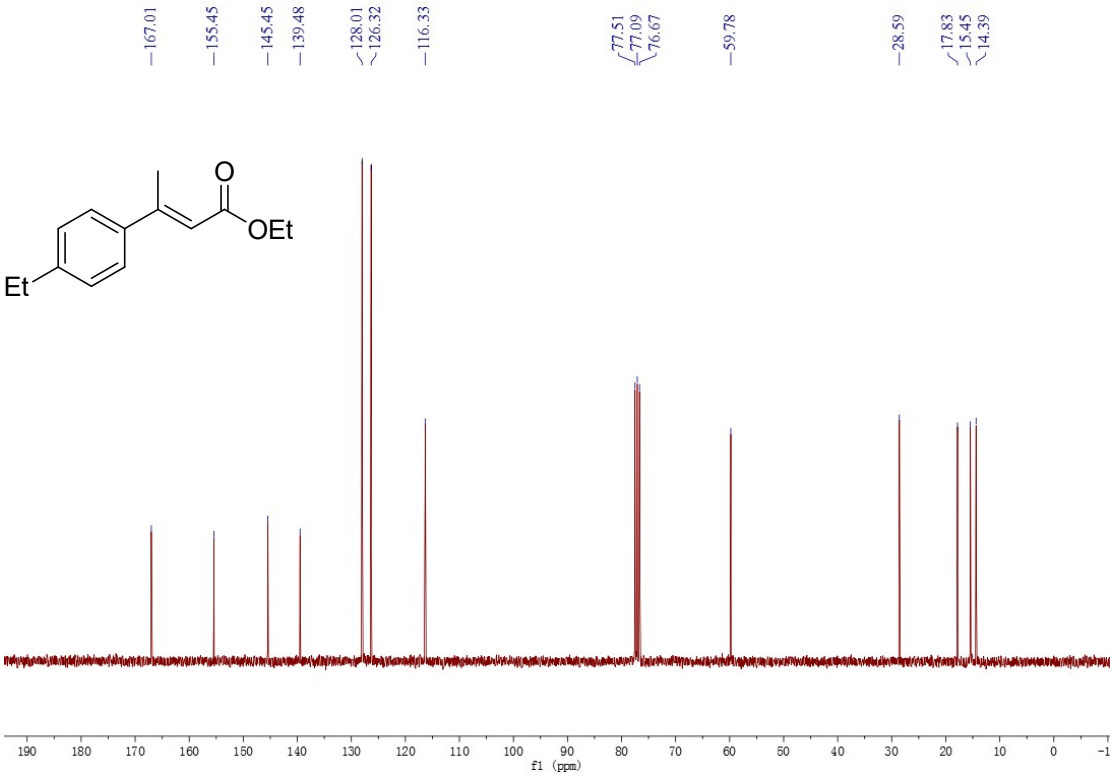

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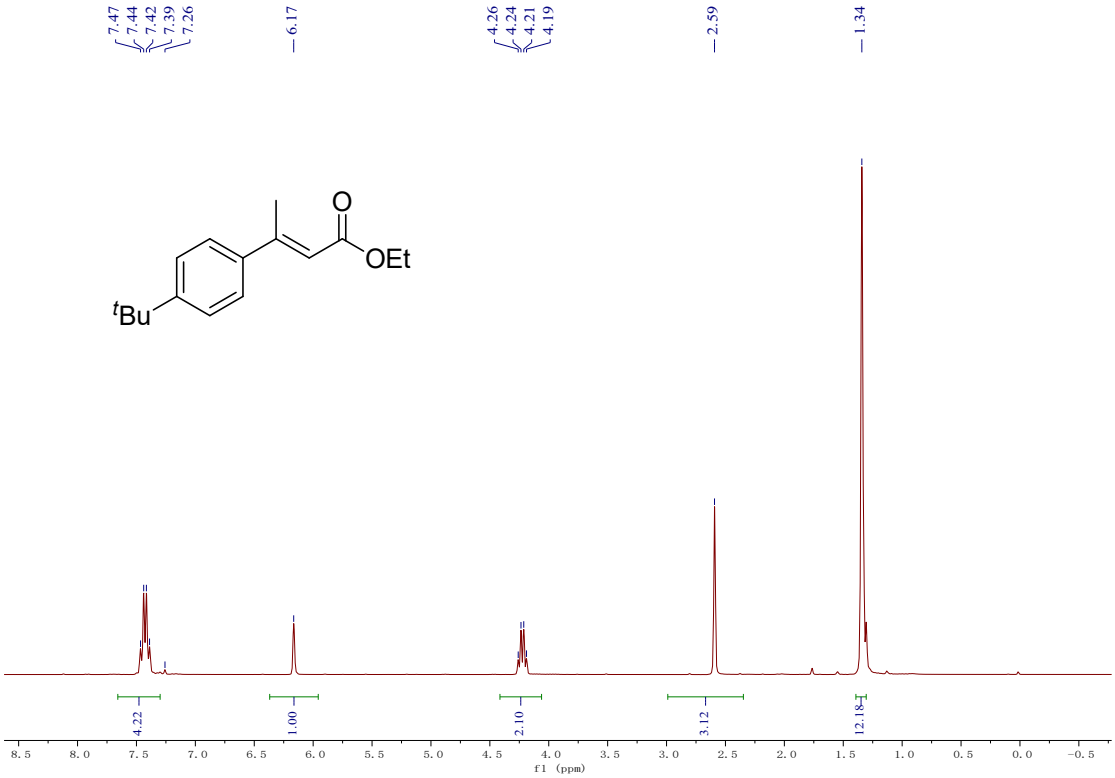

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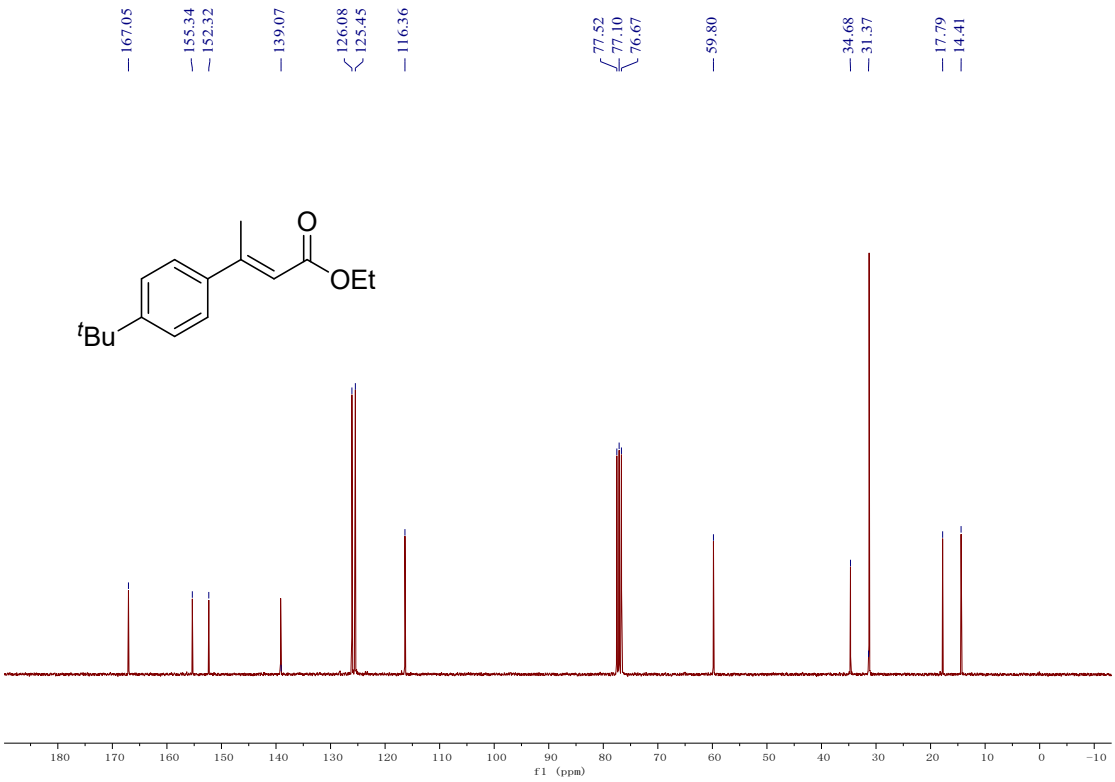

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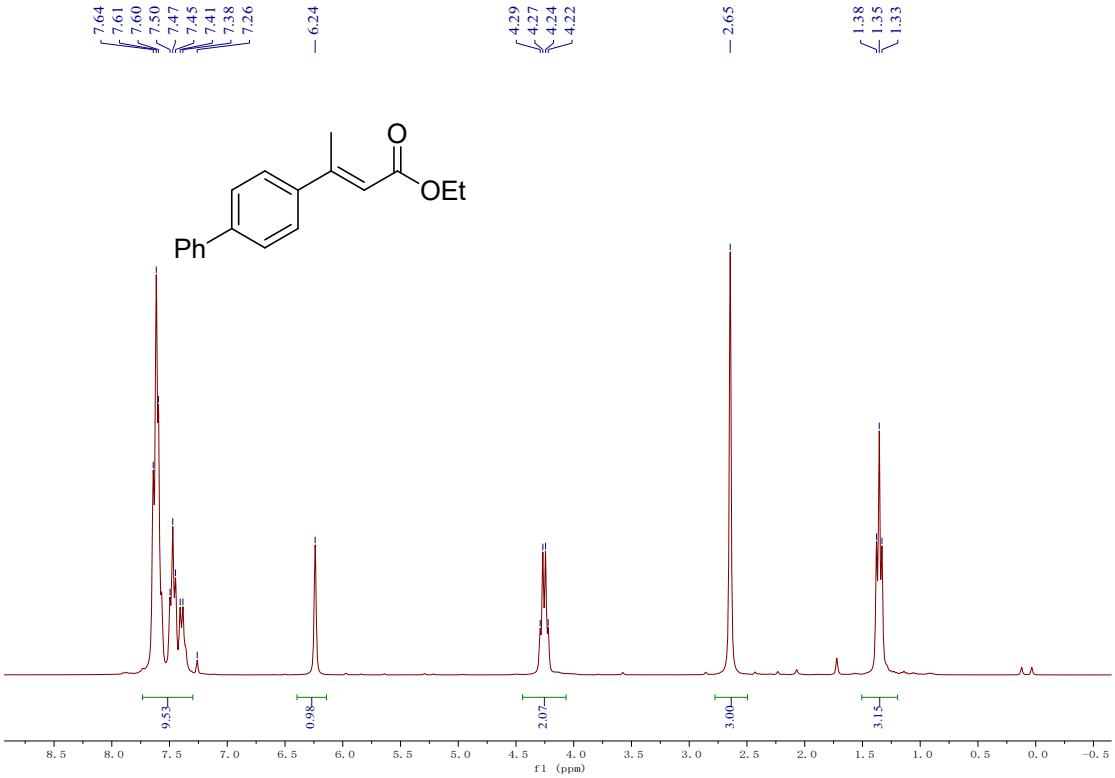

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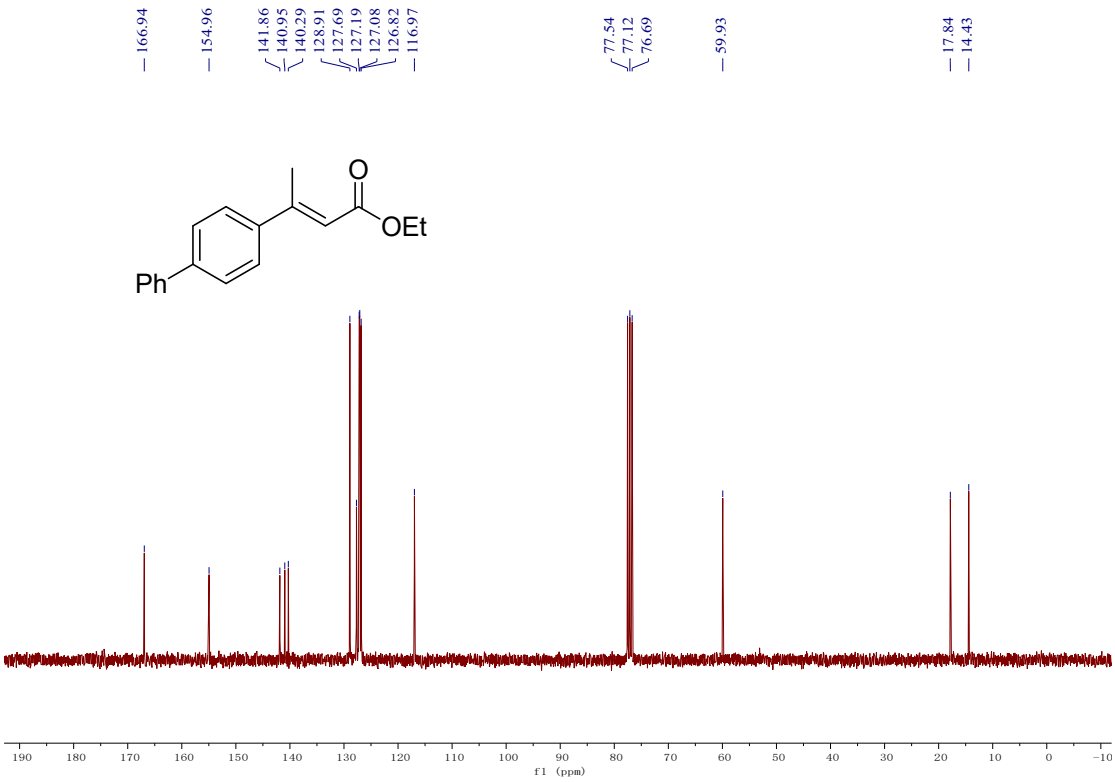

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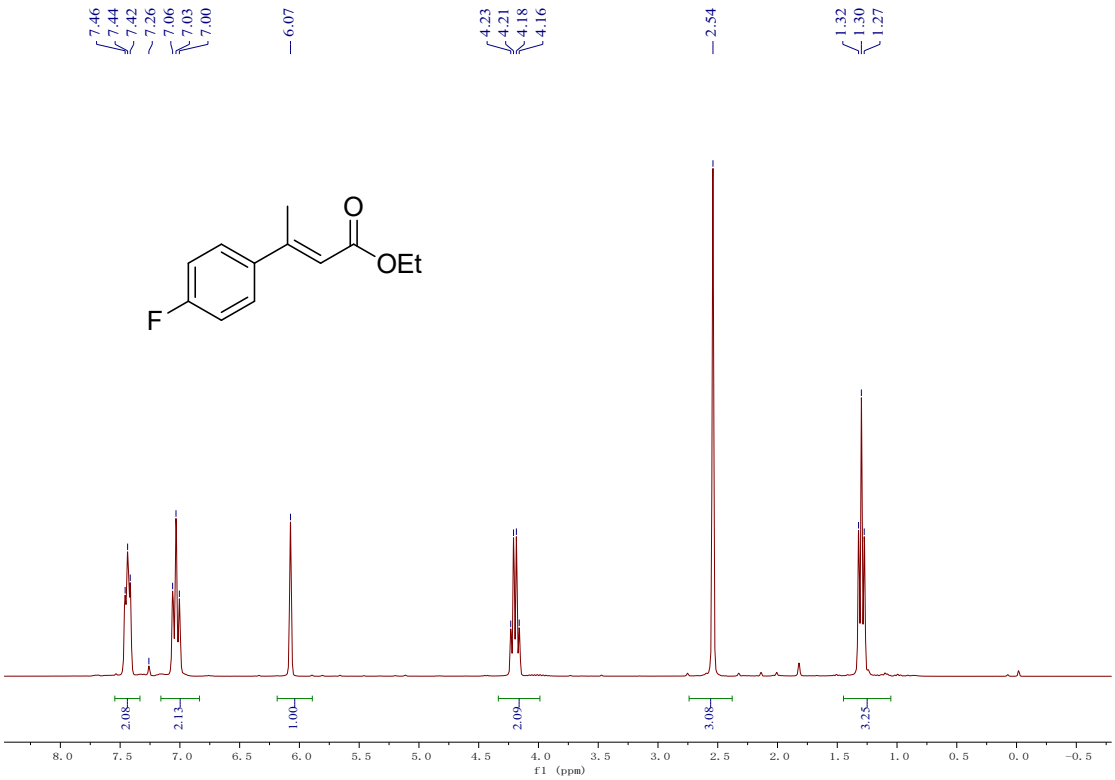

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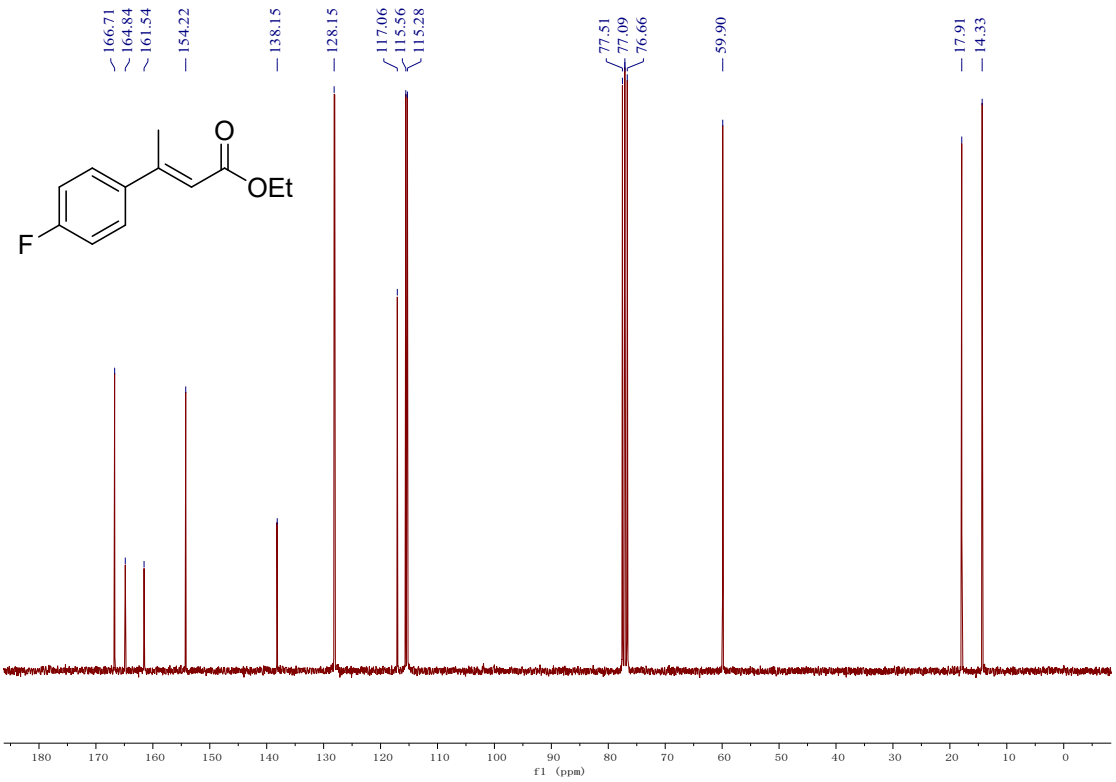
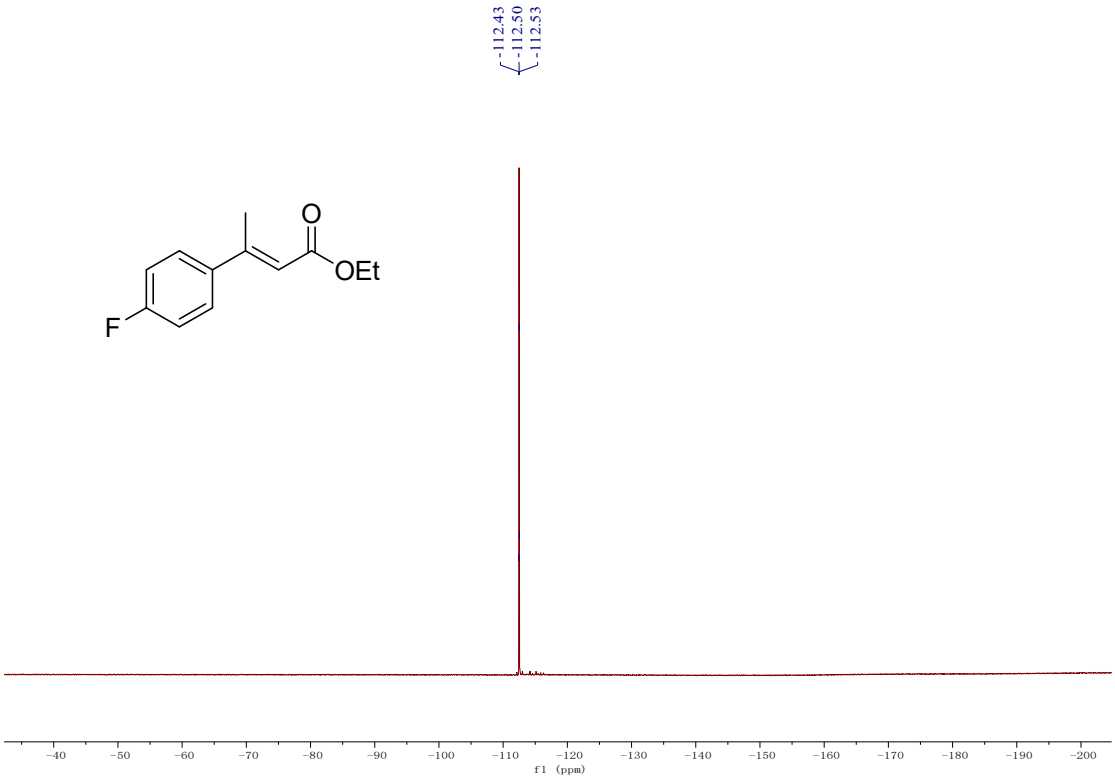
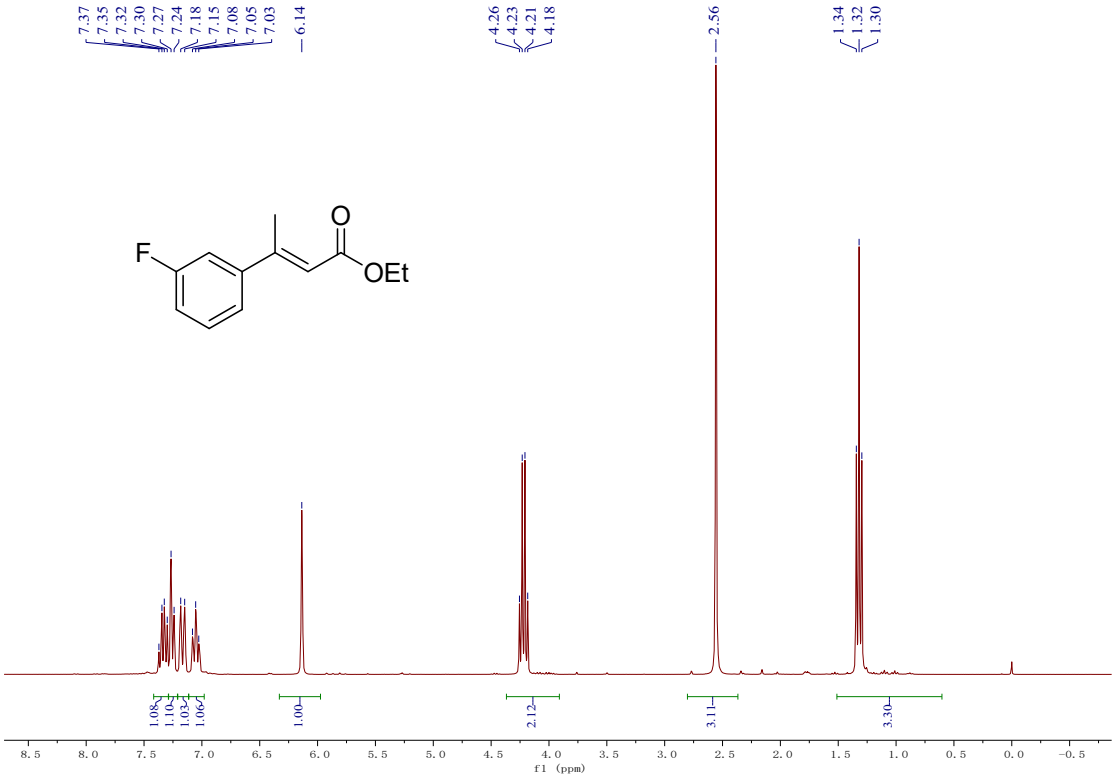


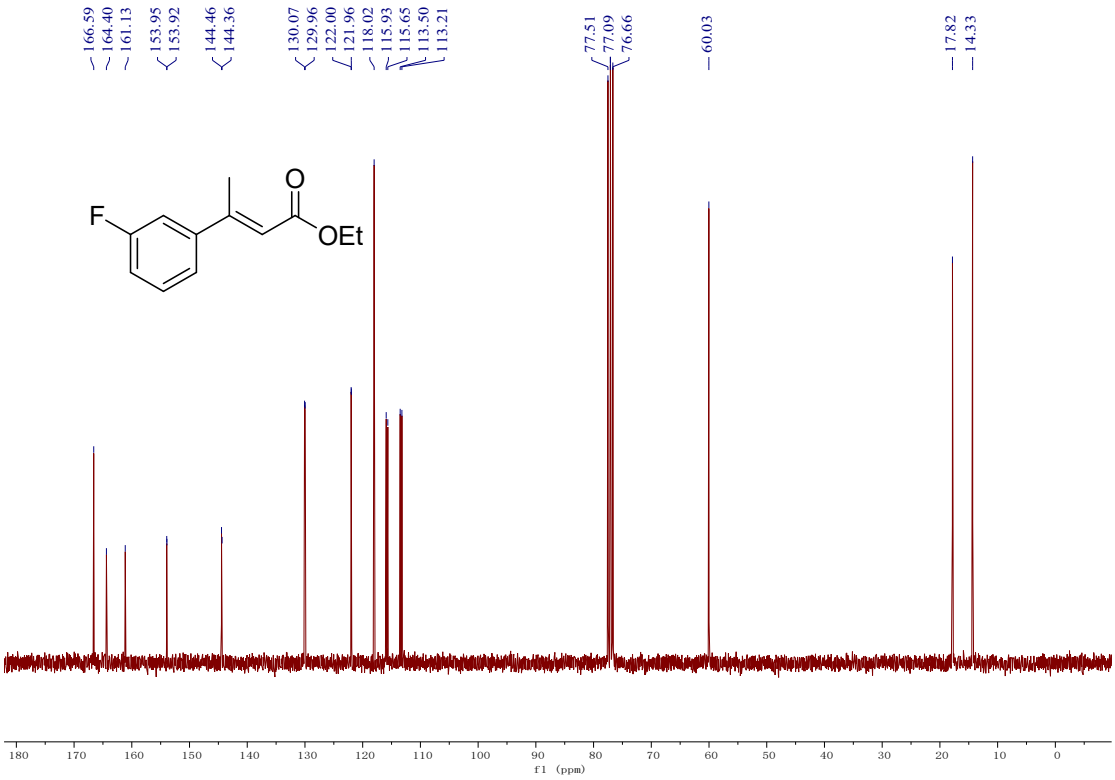
Compound 6h ^{19}F NMR



Compound 6i ^{1}H NMR



Compound 6i ^{13}C NMR



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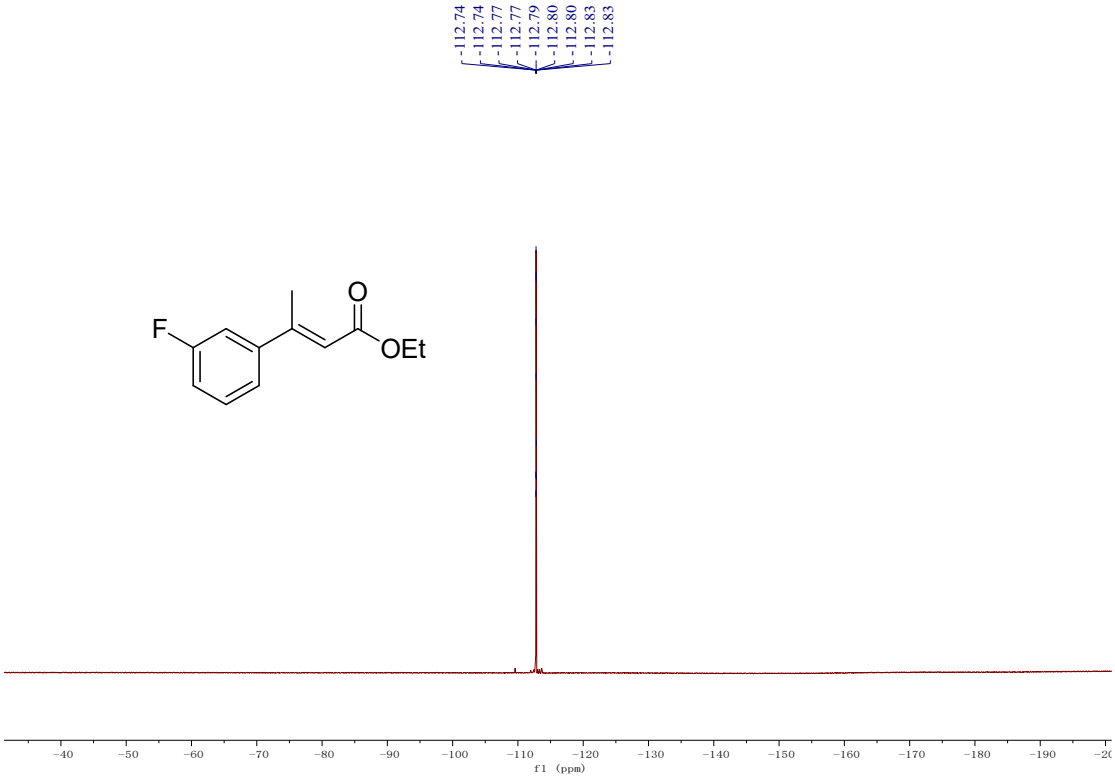

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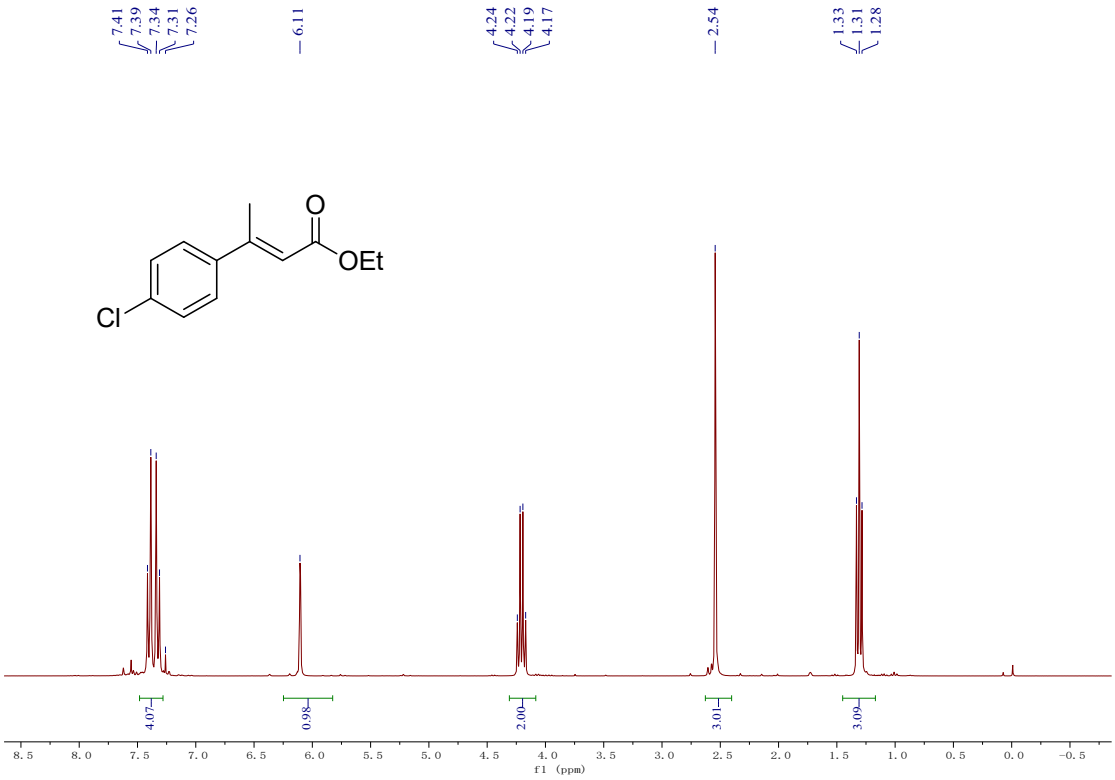

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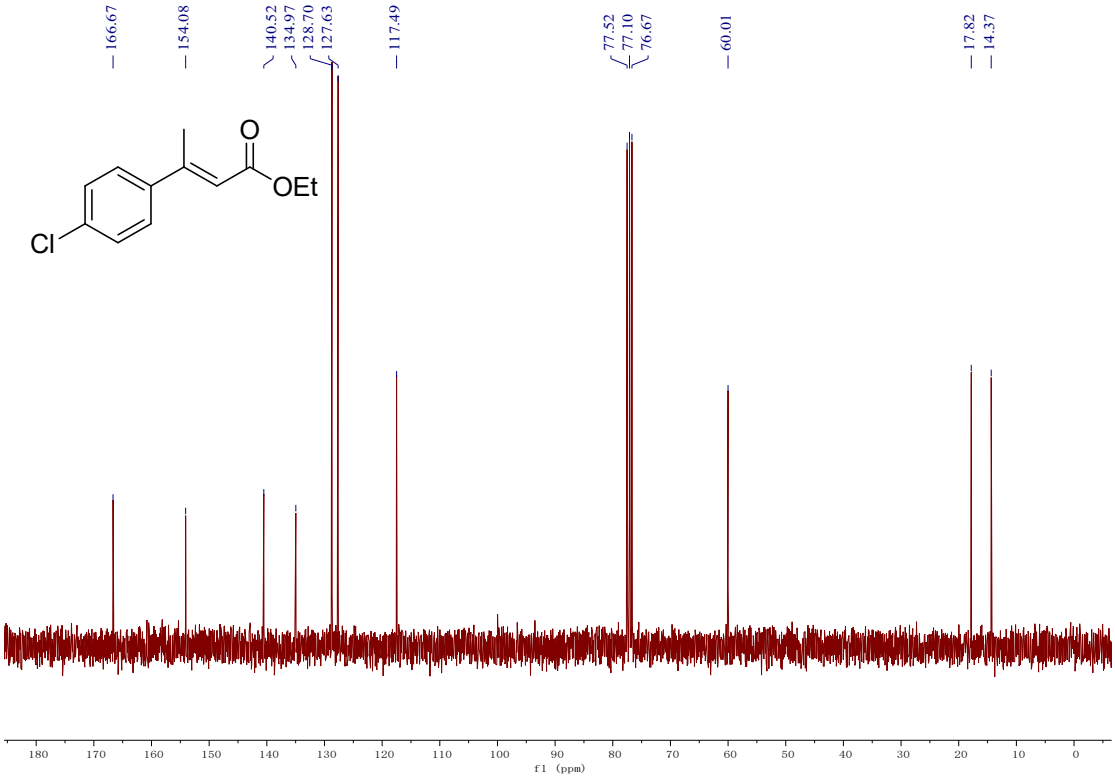
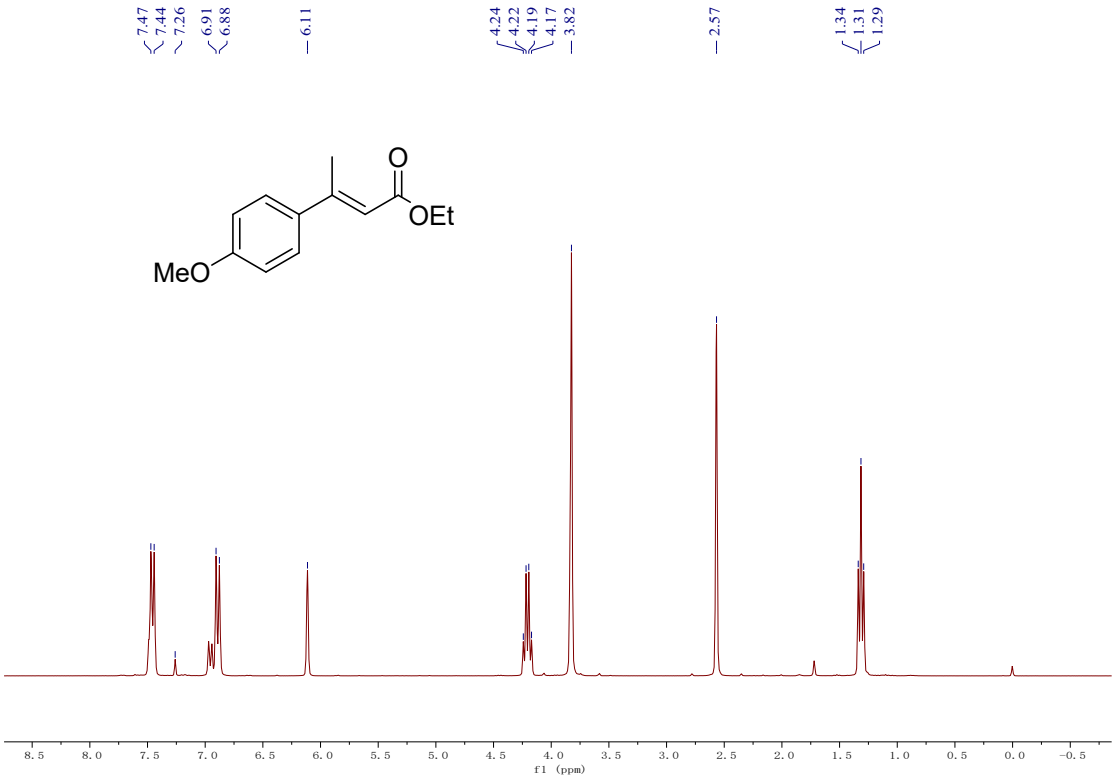


Compound 6k ^{1}H NMR



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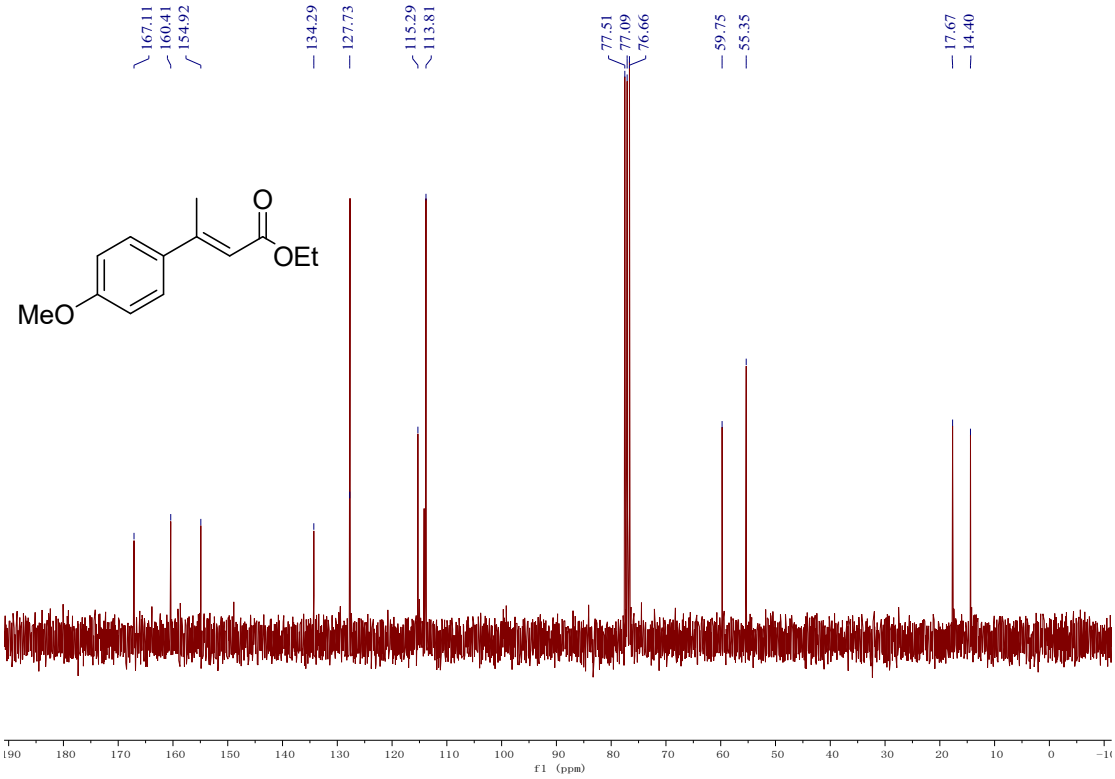
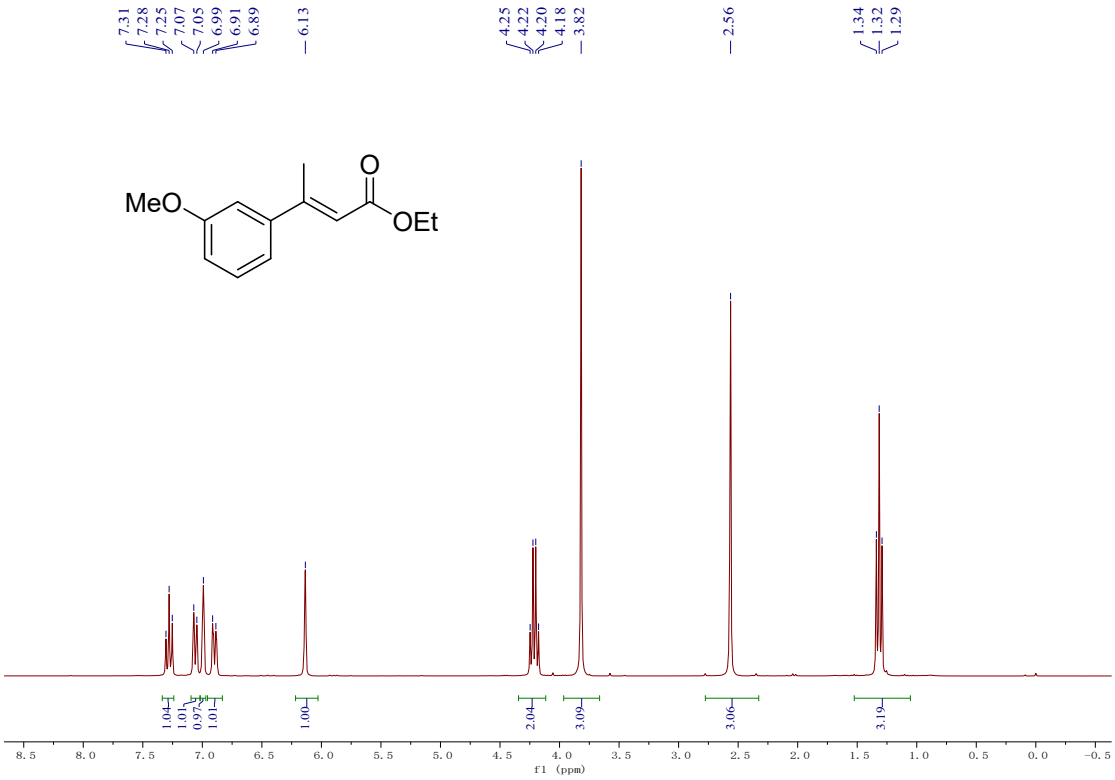


Compound 6l ^{1}H NMR



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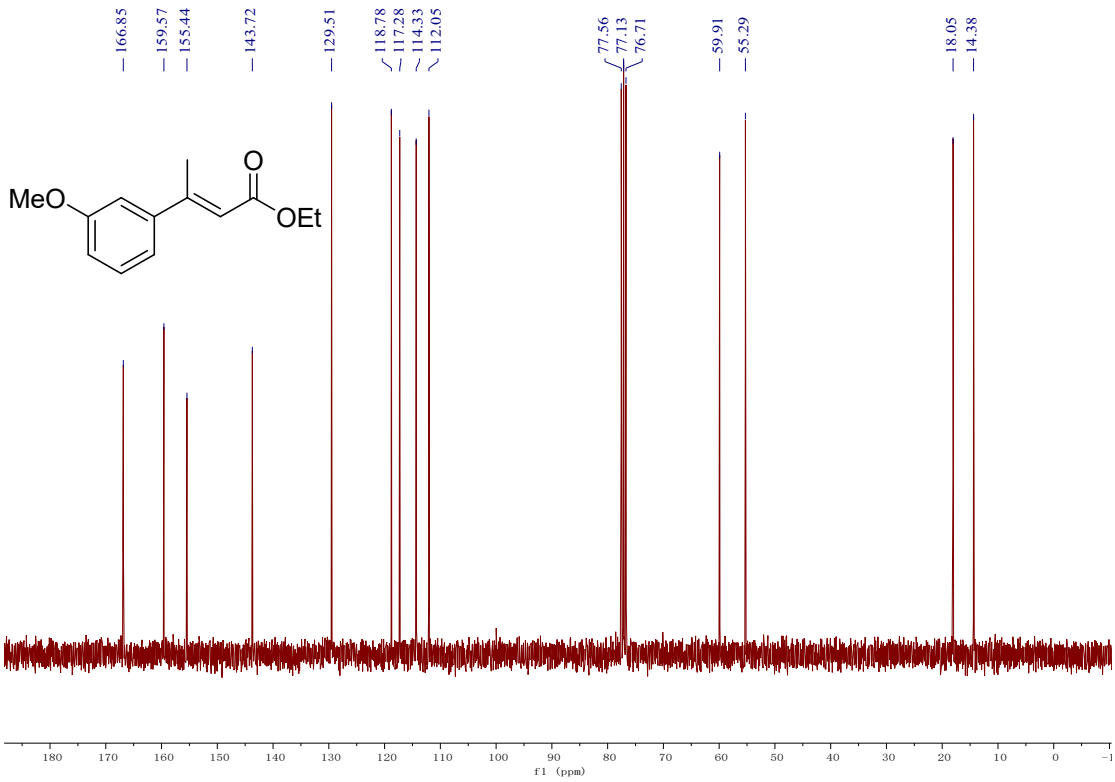
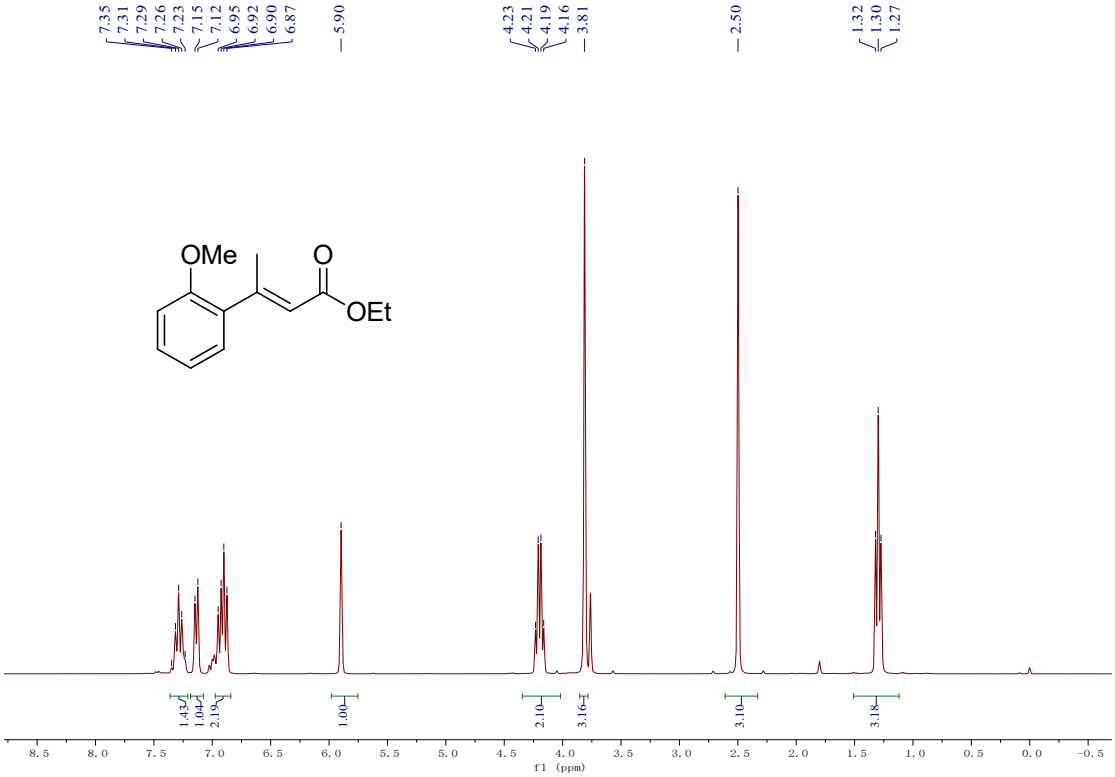


Compound 6m ^{1}H NMR



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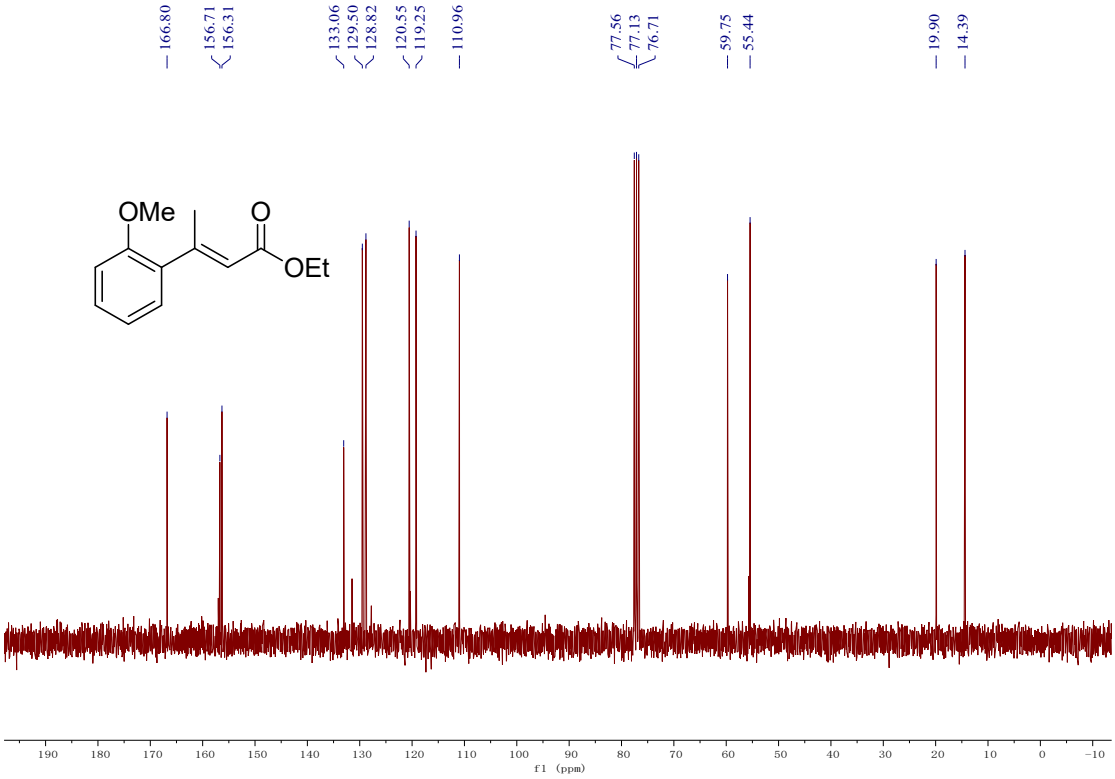
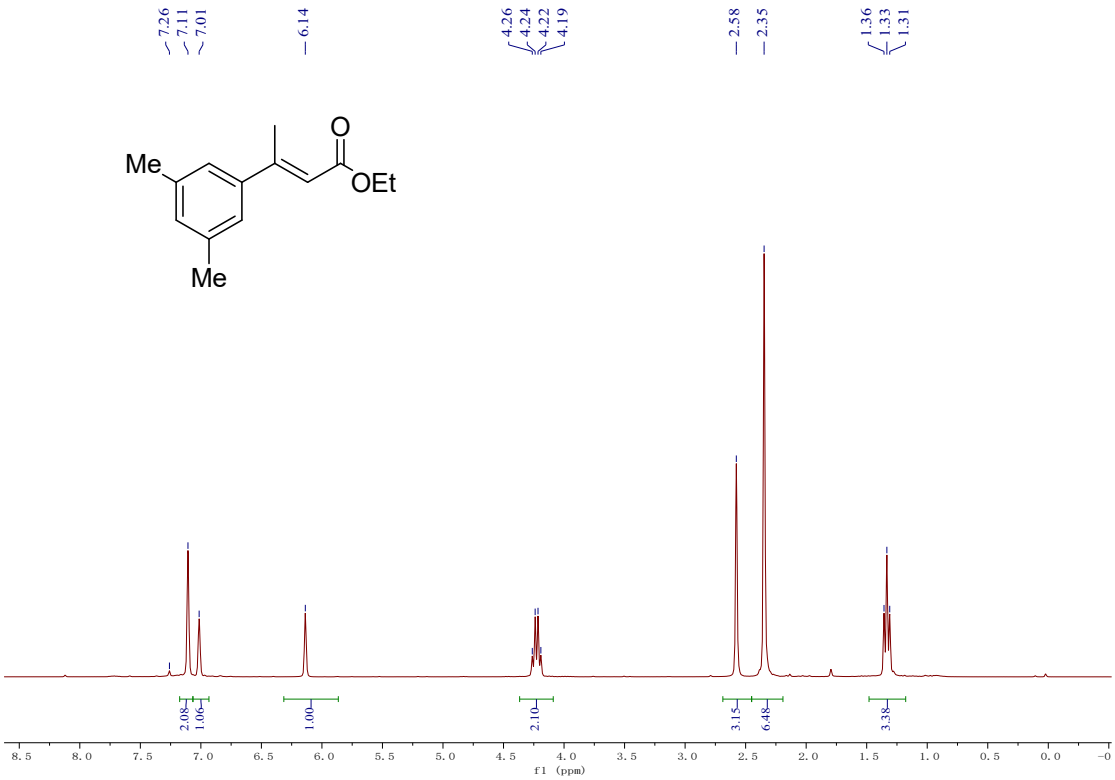
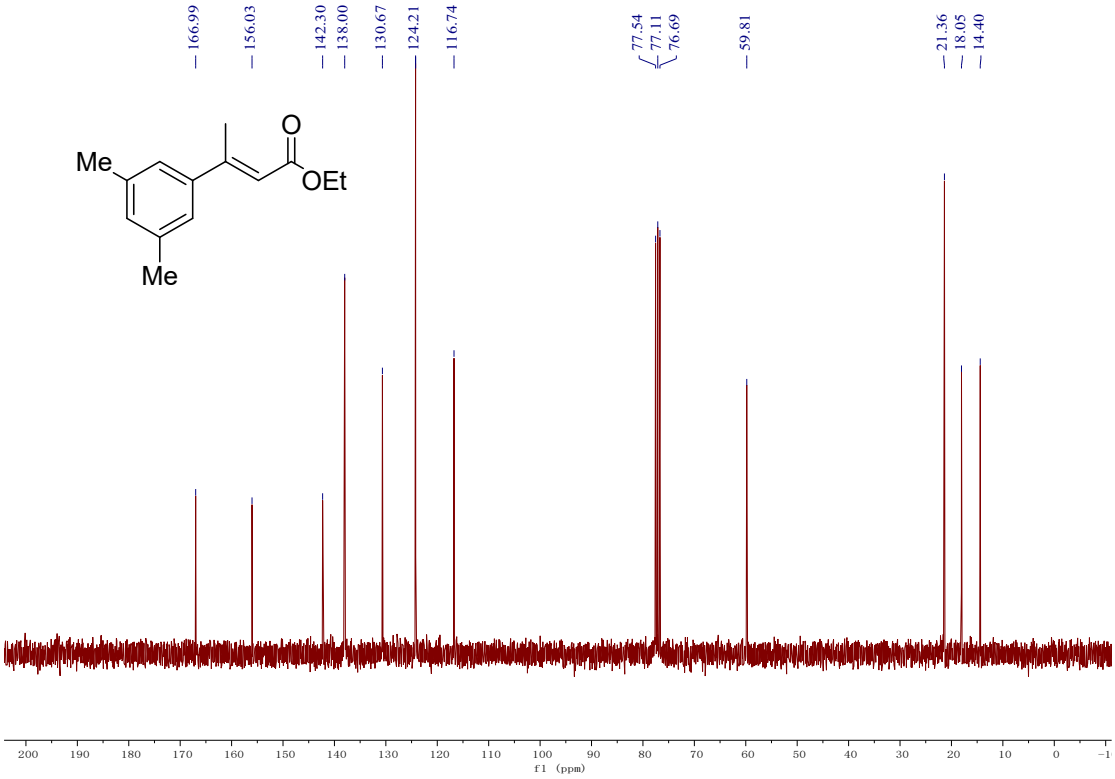


Compound 6n ^{1}H NMR



Compound 6n ^{13}C NMR



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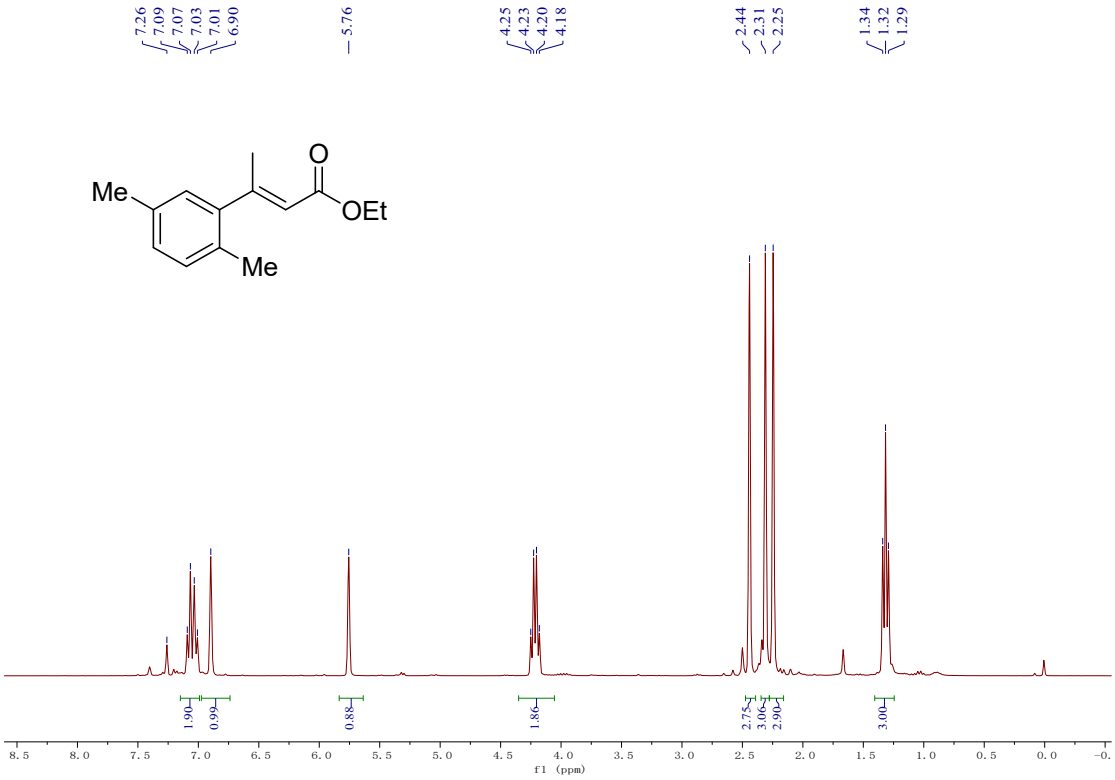

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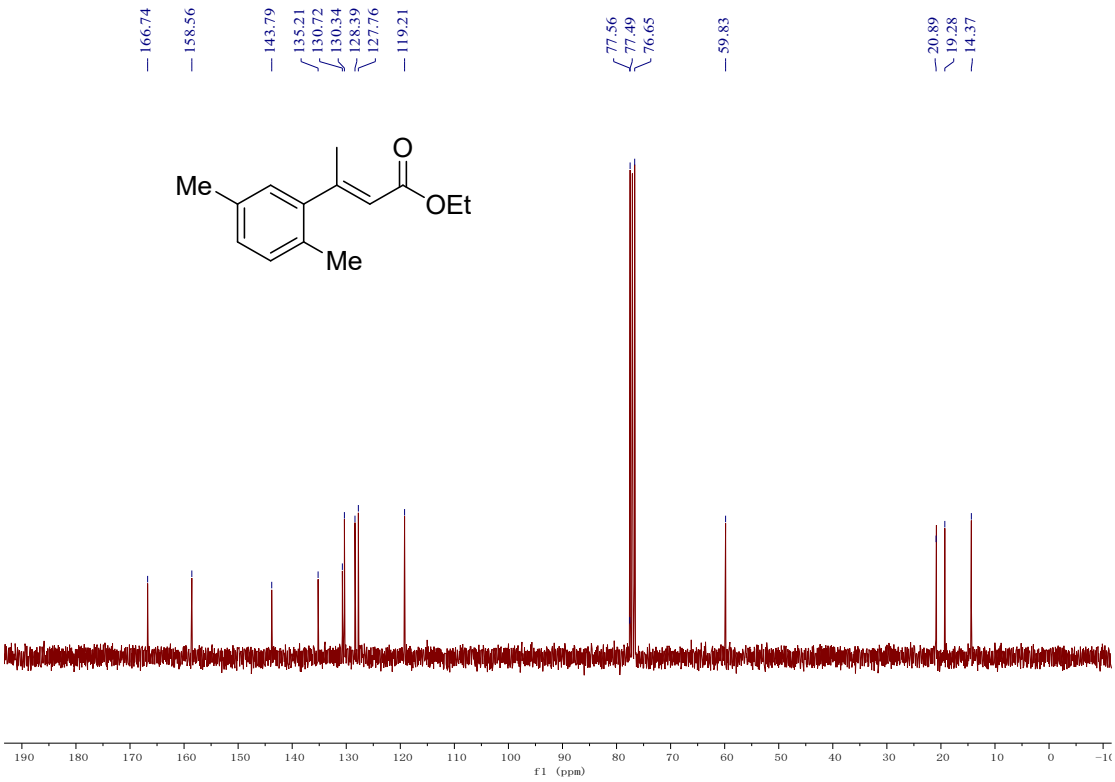

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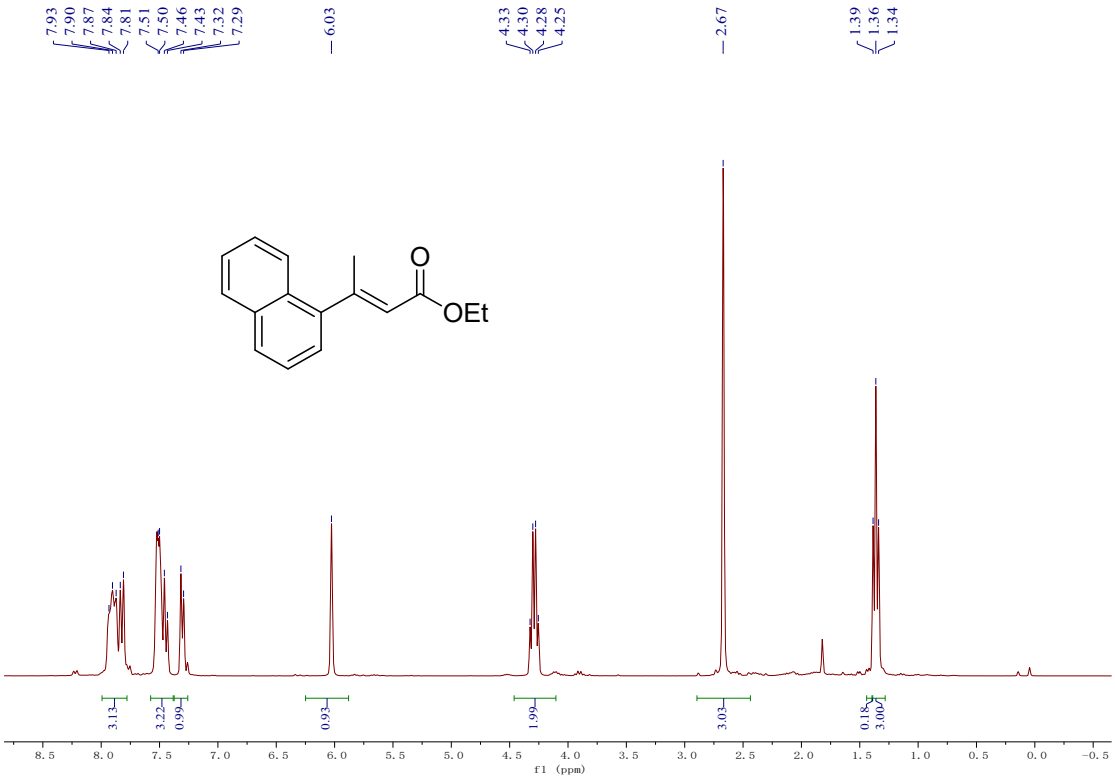
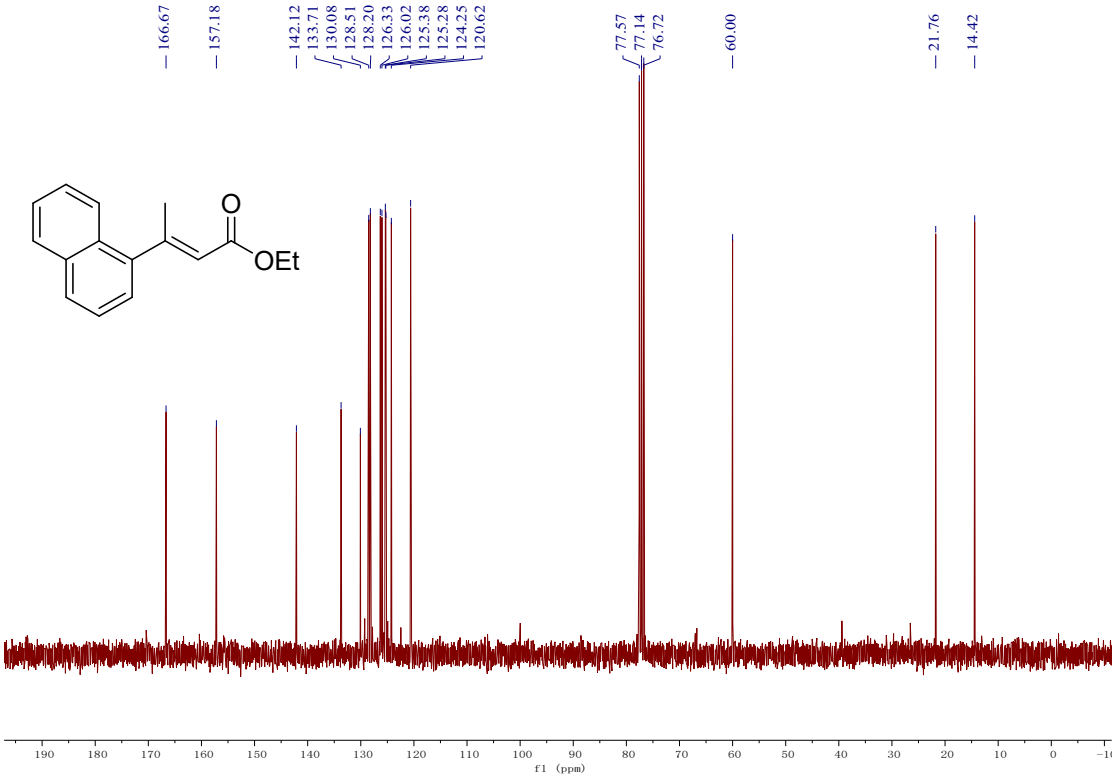
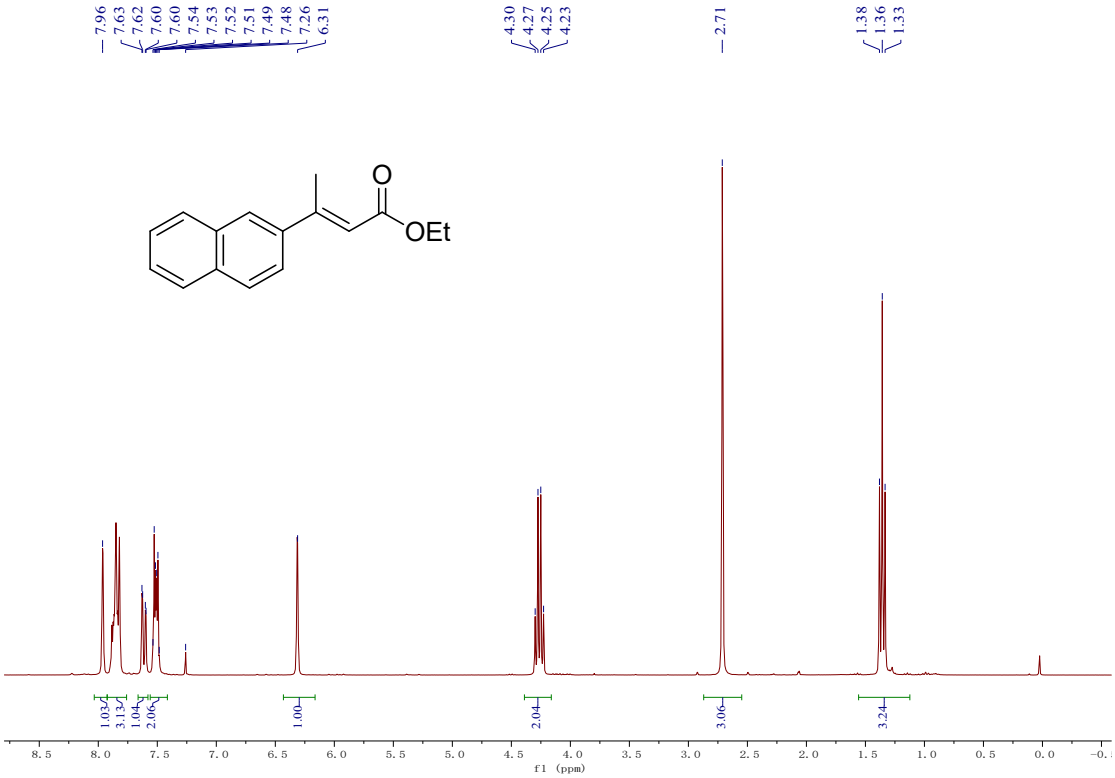


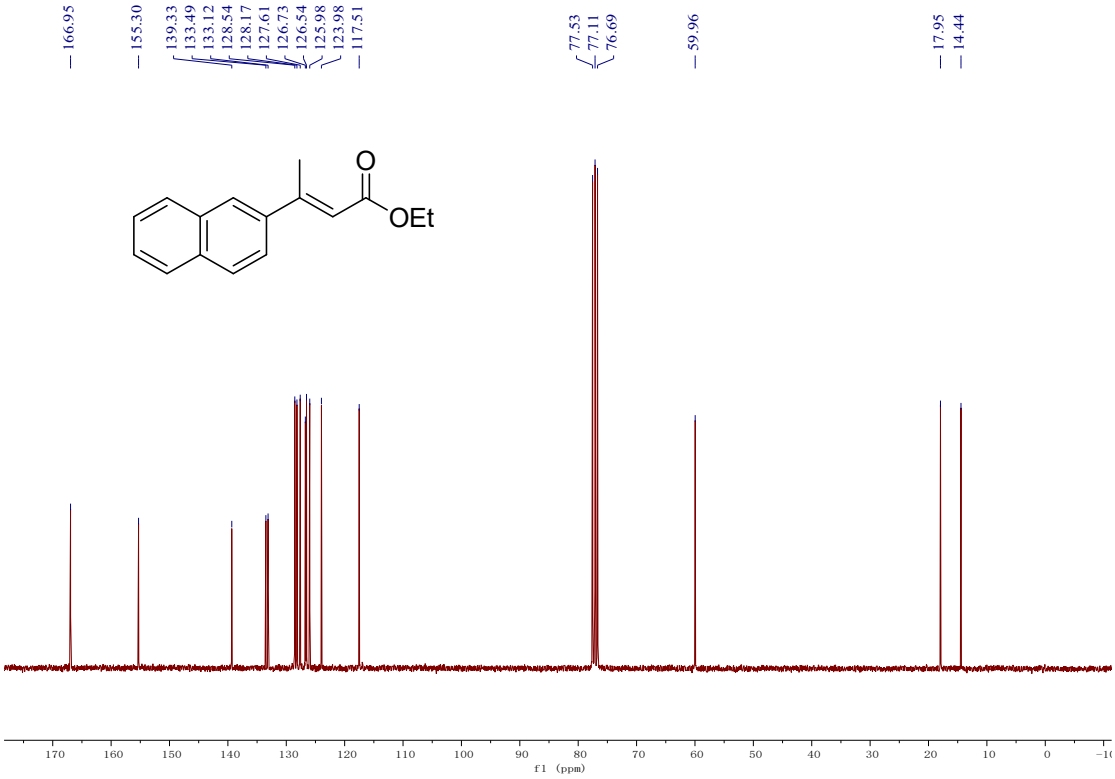
Compound 6p ^{13}C NMR



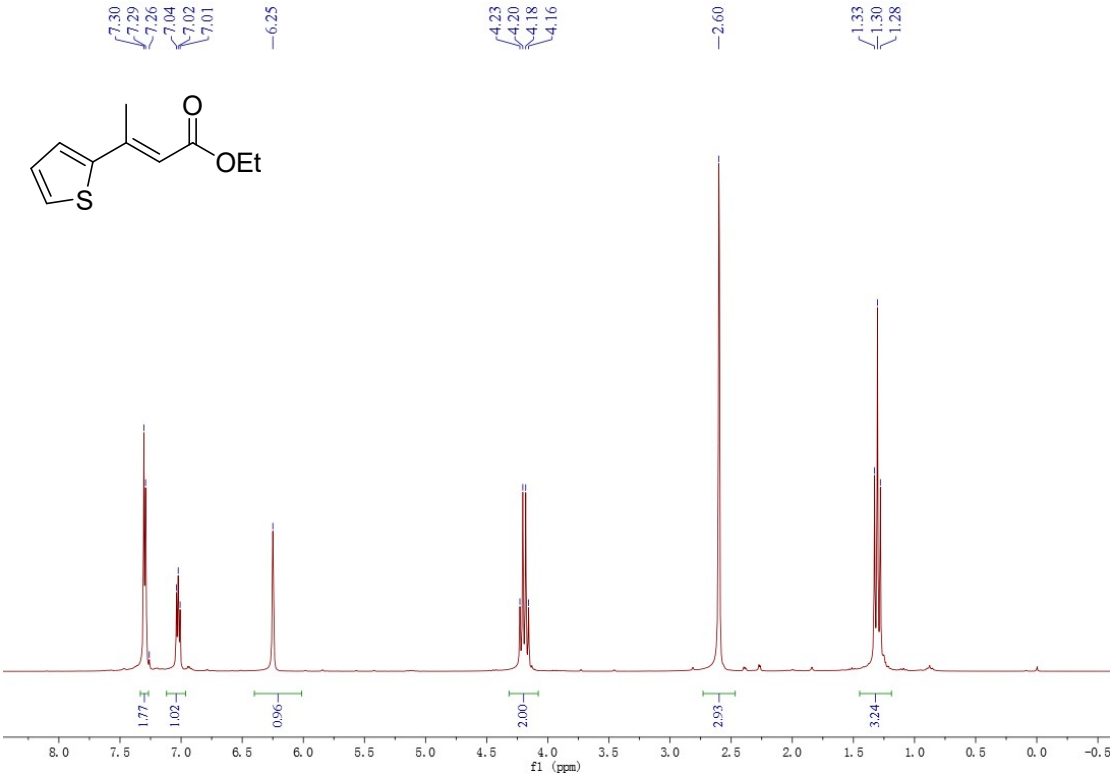
Compound 6q ^{1}H NMR



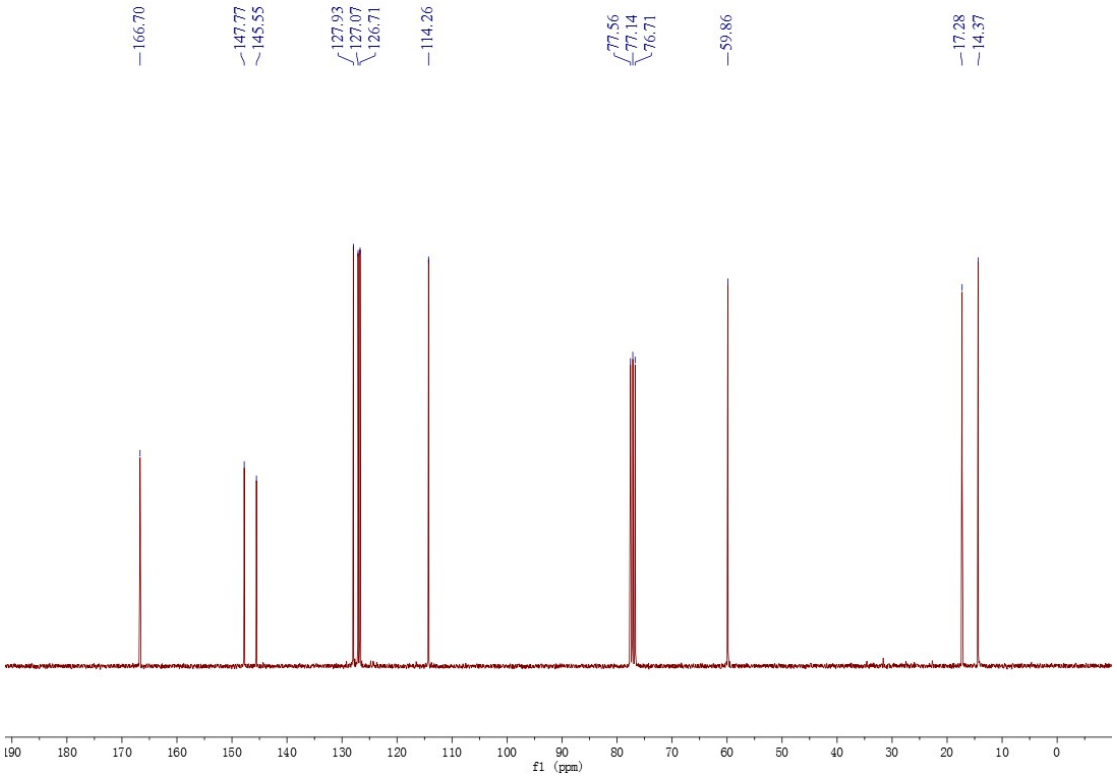
Compound 6q ^{13}C NMR



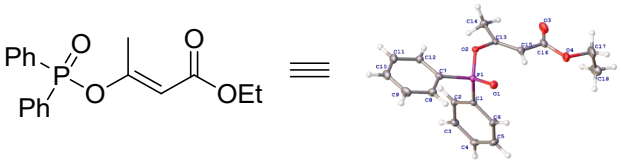
Compound 6r ^{1}H NMR



Compound 6r ^{13}C NMR



X-ray crystal structure of product **4f**



Identification code	**4f**
Empirical formula	$C_{18}H_{19}O_4P$
Formula weight	330.30
Temperature/K	169.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.1976(8)
b/Å	12.1637(13)
c/Å	12.6520(13)
α/°	107.828(9)
β/°	102.923(10)
γ/°	104.503(11)
Volume/Å^3	831.07(18)
Z	2
ρ_{calc}g/cm^3	1.320
μ/mm^{-1}	1.619
F(000)	348.0
Crystal size/mm^3	0.15 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.764 to 133.2
Index ranges	$-7 \le h \le 5$, $-14 \le k \le 14$, $-15 \le l \le 15$
Reflections collected	5688
Independent reflections	2912 [R_{int} = 0.0988, R_{sigma} = 0.0746]
Data/restraints/parameters	2912/0/210
Goodness-of-fit on F^2	1.113
Final R indexes [I>=2σ (I)]	R_1 = 0.0931, wR_2 = 0.2526
Final R indexes [all data]	R_1 = 0.1060, wR_2 = 0.2603
Largest diff. peak/hole / e Å^{-3}	0.81/-0.74