Supporting Information

Phosphine-mediated partial reduction of alkynes to form both (*E*)- and (*Z*)-alkenes

Brett M. Pierce, Brittany F. Simpson, Kane H. Ferguson, and Rachel E. Whittaker*

Department of Chemistry, Murray State University, Murray, KY, 42071

Email: rwhittaker1@murraystate.edu

Contents

1. General Experimental Methods

Air and moisture-sensitive reactions were carried out in flame-dried glassware under nitrogen. All other reactions were setup in 8 mL oven-dried glass vials under an ambient atmosphere. Unless otherwise indicated, reagents and materials were obtained from commercial suppliers and used without further purification. Analytical TLC was performed with 0.25 mm silica gel F plates with a 254 nm indicator. Purification of products was achieved by column chromatography on Sorbtech silica gel (40-60 μm), with the indicated solvents.

NMR spectra were measured on a Joel 400 Hz (ECS-400) nuclear magnetic resonance spectrometer. For $CDCl_3$ solutions the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $CDCl_3$ δ ^1H (7.26 ppm) and $CDCl_3$ δ ^{13}C (77.0 ppm). Coupling constants are reported in Hertz (Hz). Characterization data for ^1H-NMR spectra are reported as followed: chemical shift (ppm, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, m = multiplet), and integration. Infrared spectra were recorded on a Perkin Elmer FTIR Spectrum II spectrometer, and are reported in wavenumber (cm^{-1}) and relative intensity (br = broad, vw = very weak, w = weak, s = strong, vs = very strong, sh = shoulder).

Abbreviations:

PPh_3 = triphenylphosphine

THF = tetrahydrofuran

DCM = dichloromethane

EtOAc = ethyl acetate

n-BuLi = *n*-Butyllithium

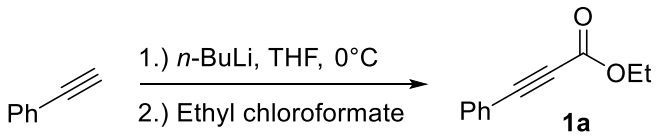
TEA = triethylamine

DMF = dimethylformamide

Et_2O = diethyl ether

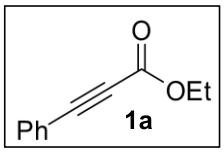
2. Experimental Procedures and Characterization Data

General Procedure 1: Preparation of Ynoate Substrates (1a and 1f):

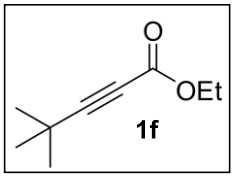


Procedure adapted from the literature.[1] To a flame-dried Schlenk flask, a solution of the corresponding terminal alkyne (1.0 equiv.) and dry THF (0.25 M) was cooled to 0°C under nitrogen. *n*-BuLi (1.1 equiv.) was added dropwise, and the reaction solution was stirred for 1 hr at this temperature. Ethyl chloroformate (1.5 equiv.) was added dropwise, and the reaction was allowed to warm to rt. The reaction solution was quenched with DI water after 3 hr, extracted with EtOAc, and dried over $MgSO_4$ to afford the crude product. The solvent was removed under reduced pressure, and the crude product was purified via column chromatography on silica gel with hexanes/EtOAc and concentrated to afford the ynoate compound.

Ynoate substrates **1a** and **1f** are known compounds from the literature.[2,3]

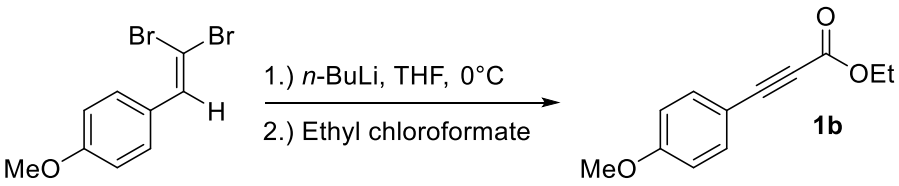


Ethyl 3-phenylpropiolate (1a)[2]: Product isolated as a yellow oil (624.2 mg, 3.58 mmol, 73%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.58-7.56 (m, 2H), 7.45-7.41 (m, 1H), 7.37-7.33 (m, 2H), 4.31-4.26 (q, *J* = 8 Hz, 2H), 1.36-1.32 (t, *J* = 8 Hz, 3H). IR (cm^{-1}): 2235.0 (sh), 2209.5, 1703.6 (vs), 1490.2 (w), 1444.6 (w), 1390.2 (vw), 1366.7, 1282.5 (vs), 1187.9 (vs), 1171.5 (sh), 1114.4 (sh), 1019.6.



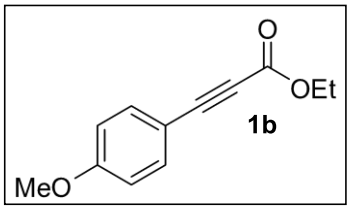
Ethyl 4,4-dimethylpent-2-ynoate (1f)[3]: Product isolated as a colorless oil (119.7 mg, 0.776 mmol, 74%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 4.24-4.18 (q, *J* = 8 Hz, 2H), 1.32-1.28 (t, *J* = 8 Hz, 3H), 1.28 (s, 9H). IR (cm^{-1}): 2973.1, 2930.1 (sh), 2871.4, 2222.1, 1709.6 (vs), 1459.9 (w), 1365.8, 1272.1 (s), 1220.2 (vs), 1095.1 (vw), 1034.5 (s).

General Procedure 2: Preparation of Ynoate Substrates (1b-1e):

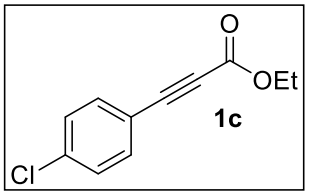


Procedure adapted from the literature.[4] To a flame-dried Schlenk flask, a solution of the corresponding 2,2-dibromoethenyl compound (1.0 equiv.) and dry THF (0.25 M) was cooled to 0°C under nitrogen. *n*-BuLi (2.0 equiv.) was added dropwise, and the reaction solution was stirred for 1 hr at this temperature. Ethyl chloroformate (1.5 equiv.) was added dropwise, and the reaction was allowed to warm to rt. The reaction solution was quenched with DI water after 1 hr, extracted with EtOAc, washed with brine, and dried over $MgSO_4$ to afford the crude product. The solvents were removed under reduced pressure, and the crude product was purified via column chromatography on silica gel with hexanes/EtOAc and concentrated to afford the ynoate compound.

Ynoate substrates **1b-1e** are compounds known to literature.[4-6]

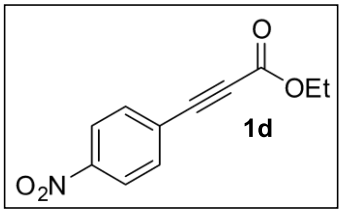


Ethyl 3-(4-methoxyphenyl)-prop-2-ynoate (1b)[4]: Product isolated as a yellow-white solid (116.2 mg, 0.569 mmol, 68%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.55-7.53 (d, *J* = 8 Hz, 2H), 6.89-6.87 (d, *J* = 8 Hz, 2H), 4.31-4.26 (q, *J* = 8 Hz, 2H), 3.83 (s, 3H), 1.37-1.33 (t, *J* = 8 Hz, 3H). IR (cm^{-1}): 2986.5 (vw), 2934.3 (sh), 2203.1, 1700.3 (s), 1603.0, 1598.0, 1497.2 (w), 1444.8 (sh), 1370.2 (w), 1284.0 (s), 1250.2 (s), 1191.5 (s), 1158.2 (vs), 1022.0 (s).

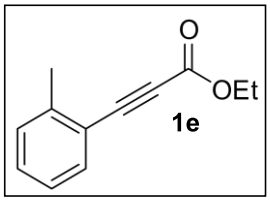


Ethyl 3-(4-chlorophenyl)-prop-2-ynoate (1c)[4]: Product isolated as a red solid (520.0 mg, 2.887 mmol, 88%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.53-7.51 (d, *J* = 8 Hz, 2H), 7.37-7.35 (d, *J* = 8 Hz, 2H), 4.33-4.27

(q, *J* = 8 Hz, 2H), 1.37-1.34 (t, *J* = 8 Hz, 3H). IR (cm^{-1}): 2243.7 (sh), 2210.4, 1698.8 (s), 1592.8 (w), 1481.7, 1286.2 (vs), 1187.6 (vs), 1085.6, 1011.9.

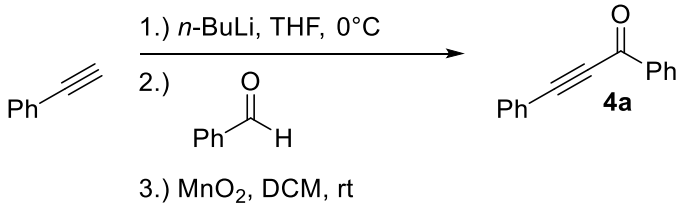


(4-nitrophenyl)-Propynoic acid ethyl ester (1d)[5]: Product isolated as an orange solid (20.8 mg, 0.0949 mmol, 19%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.26-8.24 (d, *J* = 8 Hz, 2H), 7.76-7.74 (d, *J* = 8 Hz, 2H), 4.36-4.30 (q, *J* = 8 Hz, 2H), 1.39-1.36 (t, *J* = 8 Hz, 3H). IR (cm^{-1}): 2965.7 (sh), 2924.5, 2236.2 (w), 1701.1 (vs), 1600.3 (w), 1516.2 (vs), 1345.8 (s), 1290.1 (s), 1192.3 (vs), 1110.2 (sh), 1019.9.



***O*-Tolyl-propynoic acid ethyl ester (1e)[6]:** Product isolated as an amber oil (235.0 mg, 1.249 mmol, 83%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.55-7.53 (d, *J* = 8 Hz, 1H), 7.35-7.31 (t, *J* = 8 Hz, 1H), 7.27-7.23 (t, *J* = 8 Hz, 1H), 7.16-7.20 (t, *J* = 8 Hz, 1H), 4.33-4.28 (q, *J* = 8 Hz, 2H), 2.49 (s, 3H), 1.38-1.34 (t, *J* = 8 Hz, 3H). IR (cm^{-1}): 2982.8 (vw), 2938.0 (sh), 2209.3 (sh), 2206.0, 1704.8 (vs), 1785.8 (w), 1366.7, 1294.0 (sh), 1185.7 (vs), 1023.4.

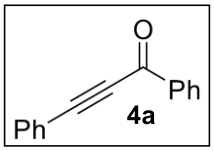
General Procedure 3: Preparation of Ynone Substrates (4a-4e):



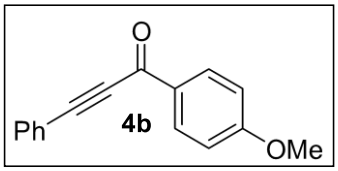
Procedure adapted from the literature.[7] To a flame-dried Schlenk flask, a solution of phenylacetylene (1.0 equiv.) and dry THF (0.25 M) was cooled to 0°C under nitrogen. *n*-BuLi (1.1 equiv.) was added dropwise, and the reaction solution was stirred for 1 hr at this temperature. The corresponding aldehyde (1.5 equiv.) was added dropwise, and the reaction was allowed to warm to rt. The

reaction solution was quenched with DI water after 4 hr, extracted with EtOAc, and dried over $MgSO_4$. The solvents were removed under reduced pressure to give the crude alcohol product to which DCM (0.25 M) and MnO_2 (10 equiv) were added and the solution was stirred at rt and in the dark for two hr. The reaction solution was filtered over celite, solvents were removed, and the crude product was purified via column chromatography on silica gel with hexanes/EtOAc and concentrated to afford the ynone compound.

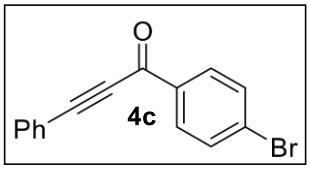
The ynone substrates **4a-4e** are compounds known to literature.[8-11]



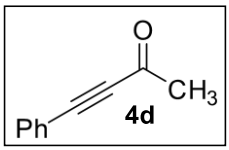
1,3-Diphenylprop-2-yn-1-one (4a)[8]: Product isolated as a white solid (220.2 mg, 1.068 mmol, 86%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.25-8.22 (m, 2H), 7.71-7.69 (m, 2H), 7.66-7.62 (t, *J* = 8 Hz, 1H), 7.55-7.52 (m, 2H), 7.51-7.48 (t, *J* = 8 Hz, 1H), 7.45-7.41 (t, *J* = 8 Hz, 2H). IR (cm^{-1}): 2195.6 (s), 1630.4 (vs), 1600.3, 1488.0, 1450.7, 1313.6, 1286.9 (s), 1206.5 (s), 1168.9, 1010.4 (s).



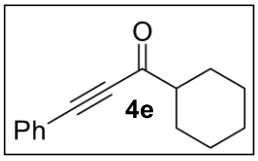
1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (4b)[9]: Product isolated as a yellow-white solid (519.3 mg, 2.198 mmol, 88%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.22-8.18 (m, 2H), 7.69-7.67 (m, 2H), 7.50-7.46 (m, 1H), 7.44-7.40 (m, 2H), 7.01-6.98 (m, 2H), 3.91 (s, 3H). IR (cm^{-1}): 2194.9 (s), 1626.8 (s), 1594.9 (vs), 1569.8 (sh), 1510.5, 1420.7 (w), 1256.6 (s), 1155.2, 1027.9, 1009.2 (sh).



1-(4-bromophenyl)-3-phenylprop-2-yne-1-one (4c)[10]: Product isolated as a white solid (125.8 mg, 0.441 mmol, 88%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.10-8.07 (m, 2H), 7.70-7.65 (m, 4H), 7.53-7.49 (m, 1H), 7.46-7.42 (t, *J* = 8 Hz, 2H). IR (cm^{-1}): 2197.7 (vs), 1652.1, 1585.6 (w), 1394.5 (vw), 1298.5, 1206.7, 1169.7, 1067.7 (w).

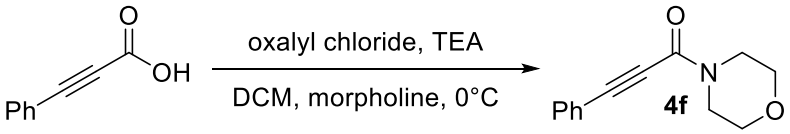


4-Phenyl-3-butyn-2-one (4d)[8]**:** Product isolated as a clear, yellow oil (608.4 mg, 4.22 mmol, 86%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.58-7.57 (d, *J* = 4 Hz, 2H), 7.47-7.43 (m, 1H), 7.40-7.36 (m, 2H), 2.45 (s, 3H). IR (cm^{-1}): 2200.0 (s), 1668.4 (vs), 1489.4 (w), 1447.0 (w), 1424.5 (w), 1357.7, 1278.2, 1154.6 (s), 1020.5 (vw).



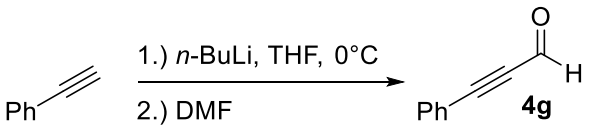
1-Cyclohexyl-3-phenylprop-2-yn-1-one (4e)[11]**:** Product isolated as a colorless oil (571.0 mg, 2.690 mmol, 94%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.47-7.43 (m, 1H), 7.40-7.36 (m, 2H), 2.09-2.03 (m, 2H), 1.84-1.79 (m, 2H), 1.55-1.45 (m, 2H), 1.39-1.32 (m, 2H), 1.30-1.21 (m, 2H). IR (cm^{-1}): 2929.0, 2854.1 (sh), 2197.7 (s), 1661.2 (vs), 1491.8 (w), 1446.4, 1262.5, 1142.0 (w), 1091.1 (sh), 1070.2.

Preparation of 1-Morpholino-3-phenylprop-2-yn-1-one (4f)[12]**:**



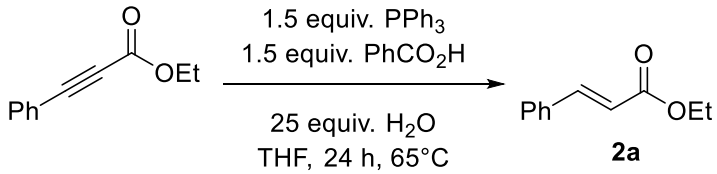
Procedure adapted from the literature.[12] To a flame-dried Schlenk flask with a solution of 3-phenylpropiolic acid (1.0 equiv.) and DCM (0.27 M), TEA (2.0 equiv.) and oxalyl chloride (1.3 equiv.) was added dropwise at 0°C under nitrogen. Morpholine (1.1 equiv.) was added, and the reaction proceeded at rt for 5 hr. The reaction solution was extracted with EtOAc, washed with brine and dried over Na_2SO_4 to afford the crude product. The solvents were removed under reduced pressure, and the crude product was purified via column chromatography on silica gel with hexanes/EtOAc and concentrated to afford **4f** (247.1 mg, 1.148 mmol, 84%) as a yellow solid. ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.56-7.54 (d, *J* = 8 Hz, 2H), 7.45-7.42 (m, 1H), 7.39-7.35 (t, *J* = 8 Hz, 2H), 3.90 (s, 2H), 3.78-3.72 (m, 6H). IR (cm^{-1}): 2920.8 (sh), 2864.7 (w), 2217.5, 1617.4 (vs), 1495.5, 1428.3 (s), 1278.8, 1213.1, 1110.0 (s), 1042.9.

Preparation of 3-Phenylpropiolaldehyde (4g)[13]:



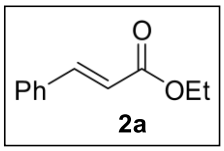
Procedure adapted from the literature.[13] To a flame-dried Schlenk flask, a solution of phenylacetylene (1.0 equiv.) and dry THF (0.25 M) was cooled to 0°C under nitrogen. *n*-BuLi (1.1 equiv.) was added dropwise, and the reaction solution was stirred for 1 hr. DMF (2 equiv.) was added followed by a temperature elevation to rt, and the solution stirred for 1 hr. The reaction solution was quenched with DI water, extracted with EtOAc, and dried over $MgSO_4$. The solvents were removed under reduced pressure, and the crude product was purified via column chromatography on silica gel with hexanes/EtOAc and concentrated to afford **4g** (94.4 mg, 0.7253 mmol, 36%) as a yellow oil. ^{1}H-NMR (400MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.62-7.60 (m, 2H), 7.52-7.48 (m, 1H), 7.43-7.39 (m, 2H). IR (cm^{-1}): 2953.6 (sh), 2924.0 (vs), 2853.9 (s), 1730.6 (w), 1461.8, 756.9 (w), 693.5 (w).

Synthesis of (*E*)-Alkene Products (2a-2e, 5a-5g):



To an oven-dried 8 mL reaction vial was added PPh_3 (1.5 equiv.), benzoic acid (1.5 equiv.), the corresponding substrate (1.0 equiv, 0.10 mmol), DI water (25 equiv.), and dry THF (0.1 M). The solution was heated to 65°C and stirred for 24 hr. The solvents were removed under reduced pressure, toluene was added, and the solution dried over $MgSO_4$. The toluene was removed under reduced pressure, and cold Et_2O was added and filtered over silica. Et_2O was removed under reduced pressure, and the crude residue was purified via column chromatography on silica gel with hexanes/Et_2O (100:1 to 20:1) to afford the alkene product.

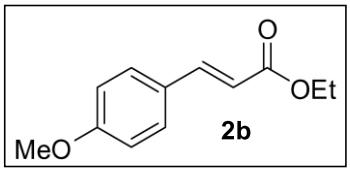
All (*E*)-alkene products **2a-2e** and **5a-5g** are compounds known to literature.[14-26]



The E/Z selectivity was 86:14 from ^{1}H-NMR spectroscopic analysis of the crude residue.

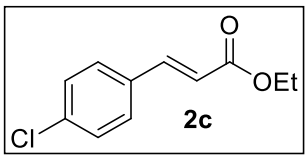
***Trans*-Ethyl cinnamate (2a)[14]:** Product isolated as a colorless oil (14.2 mg, 0.0806 mmol, 81%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.71-7.67 (d, *J* = 16 Hz, 1H), 7.54-7.52 (m, 2H), 7.39-7.38 (m, 3H), 6.46-6.42 (d, *J* = 16 Hz, 1H), 4.30-4.24 (q, *J* = 8 Hz, 2H), 1.36-1.33 (t, *J* = 8 Hz, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 167.2, 144.7, 134.6, 130.4, 129.0, 128.2, 118.4, 60.7, 14.5. IR (cm^{-1}): 2925.0, 2861.0 (sh), 1712.4 (vs), 1638.3, 1450.1 (w), 1368.4 (w), 1309.7, 1268.2 (w), 1201.4 (sh), 1171.4 (vs), 1039.2, 980.0.

***Cis*-Ethyl cinnamate (3a):** Product isolated as a colorless oil (1.8 mg, 0.0102 mmol, 10%). Total yield (16.0 mg, 0.0908 mmol, 91%).



The E/Z selectivity was 92:8 from ^{1}H-NMR spectroscopic analysis of the crude residue.

Ethyl (E)-3-(4-methoxyphenyl) acrylate (2b)[15]: Product isolated as a white solid (16.7 mg, 0.0810 mmol, 84%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.66-7.62 (d, *J* = 16 Hz, 1H), 7.49-7.47 (d, *J* = 8 Hz, 2H), 6.91-6.89 (d, *J* = 8 Hz, 2H), 6.33-6.29 (d, *J* = 16 Hz, 1H), 4.28-4.23 (q, *J* = 8 Hz, 2H), 3.84 (s, 3H), 1.35-1.31 (t, *J* = 8 Hz, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 167.5, 161.5, 144.4, 129.8, 127.3, 115.9, 114.4, 60.5, 55.5, 14.5. IR (cm^{-1}): 1706.8, 1633.7 (w), 1604.0, 1512.2, 1304.3 (sh), 1288.5 (w), 1252.1 (s), 1167.4 (vs), 1031.6. MP: 45.2-46.6°C.

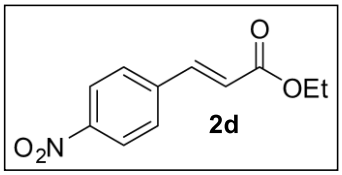


The E/Z selectivity was 75:25 from ^{1}H-NMR spectroscopic analysis of the crude residue.

Ethyl (E)-3-(4-chlorophenyl) acrylate (2c)[16]: Product isolated as a colorless oil (15.7 mg, 0.0745 mmol, 68%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.65-7.61 (d, *J* = 16 Hz, 1H), 7.46-7.43 (m, 2H), 7.37-7.34 (m, 2H), 6.42-6.38 (d, *J* = 16 Hz, 1H), 4.29-4.24 (q, *J* = 8 Hz, 2H), 1.35-1.31 (t, *J* = 8 Hz, 3H). ^{13}C-NMR

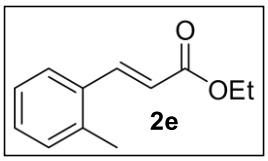
(400MHz, $CDCl_3$) δ 166.8, 143.2, 136.2, 133.0, 129.3, 129.2, 118.9, 60.7, 14.4. IR (cm^{-1}): 1710.4 (s), 1638.2, 1491.1, 1309.1 (s), 1268.5, 1201.1 (sh), 1168.1 (vs), 1088.2, 1035.6, 980.4.

Ethyl (Z)-3-(4-chlorophenyl) acrylate (3c): Product isolated as a colorless oil (3.4 mg, 0.0161 mmol, 15%). Total yield (19.1 mg, 0.0907 mmol, 83%).



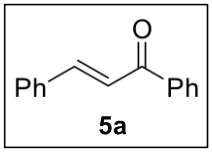
The E/Z selectivity was 76:24 from ^{1}H-NMR spectroscopic analysis of the crude residue (The (*Z*)-isomer was not isolated). Total yield (17.4 mg, 0.0787 mmol, 90%).

Ethyl (E)-3-(4-nitrophenyl) acrylate (2d)[17]: Product isolated as a tan solid. ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.26-8.24 (d, *J* = 8 Hz, 2H), 7.73-7.66 (m, 3H), 6.58-6.54 (d, *J* = 16 Hz, 1H), 4.32-4.27 (q, *J* = 8 Hz, 2H), 1.37-1.33 (t, *J* = 8 Hz, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 166.1, 148.5, 141.7, 140.7, 128.7, 124.3, 122.7, 61.1, 14.4. IR (cm^{-1}): 1710.2 (vs), 1645.2 (w), 1596.7 (w), 1518.0, 1343.9 (vs), 1310.4 (sh), 1192.4, 1117.3 (w), 1031.8 (w), 978.7 (w). MP: 130.6-133.3°C.



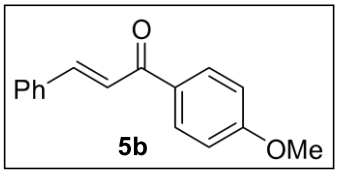
The E/Z selectivity was 42:58 from ^{1}H-NMR spectroscopic analysis of the crude residue (The (*Z*)-isomer was not isolated). Total yield (18.0 mg, 0.0946 mmol, 68%).

Ethyl (E)-3-(*o*-tolyl) acrylate (2e)[18]: Product isolated as a yellow oil. ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.00-7.96 (d, *J* = 16 Hz, 1H), 7.56-7.54 (d, *J* = 8 Hz, 1H), 7.30-7.28 (d, *J* = 8 Hz, 1H), 7.23-7.19 (t, *J* = 8 Hz, 2H), 6.38-6.34 (d, *J* = 16 Hz, 1H), 4.30-4.22 (q, *J* = 8 Hz, 2H), 2.44 (s, 3H), 1.36-1.33 (t, *J* = 8 Hz, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 168.6, 142.4, 130.9, 130.1, 126.5, 126.4, 119.4, 60.7, 19.9, 14.5. IR (cm^{-1}): 2924.3 (vs), 2859.6, 1717.3 (s), 1639.0 (w), 1467.2 (w), 1318.0, 1269.4, 1179.8 (s), 1041.7 (w), 985.7 (vw).



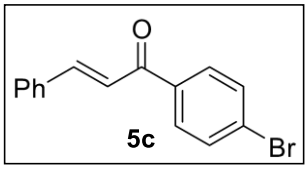
The E/Z selectivity of the reaction was >99:1 from ^{1}H-NMR spectroscopic analysis of the crude residue.

(E)-Chalcone (5a)[19]**:** Product isolated as a white solid (17.1 mg, 0.0821 mmol, 90%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.71-7.67 (d, *J* = 16 Hz, 1H), 7.54-7.52 (m, 2H), 7.39-7.38 (m, 3H), 6.46-6.42 (d, *J* = 16 Hz, 1H), 4.30-4.24 (q, *J* = 8 Hz, 2H), 1.36-1.33 (t, *J* = 8 Hz, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 167.2, 144.7, 134.6, 130.4, 129.0, 128.2, 118.4, 60.7, 14.5. IR (cm^{-1}): 2925.0, 2861.0 (sh), 1712.4 (vs), 1638.3, 1450.1 (w), 1368.4 (w), 1309.7, 1268.2 (w), 1201.4 (sh), 1171.4 (vs), 1039.2, 980.0. MP: 51.6-54.4°C.



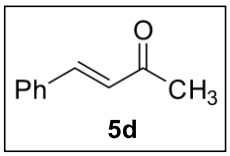
The E/Z selectivity of the reaction was >99:1 from ^{1}H-NMR spectroscopic analysis of the crude residue.

(E)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (5b)[20]**:** Product isolated as a white solid (15.6 mg, 0.0655 mmol, 68%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.06-8.04 (d, *J* = 8 Hz, 2H), 7.83-7.79 (d, *J* = 16 Hz, 1H), 7.65-7.64 (m, 2H), 7.57-7.53 (d, *J* = 16 Hz, 1H), 7.43-7.41 (m, 3H), 7.00-6.98 (d, *J* = 8 Hz, 2H), 3.90 (s, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 188.9, 163.6, 144.1, 135.2, 131.2, 131.0, 130.5, 129.1, 128.5, 122.0, 114.0, 55.7. IR (cm^{-1}): 2917.0 (w), 1656.4, 1597.6 (vs), 1570.8 (sh), 1255.6, 1220.6, 1181.0 (s), 1013.9, 971.7 (s). MP: 98.9-100.6°C



The E/Z selectivity of the reaction was >99:1 from ^{1}H-NMR spectroscopic analysis of the crude residue.

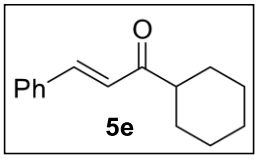
(E)-1-(4-bromophenyl)-3-phenylprop-2-en-1-one (5c)[21]**:** Product isolated as a white solid (27.3 mg, 0.0951 mmol, 83%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.90-7.88 (d, *J* = 8 Hz, 2H), 7.84-7.80 (d, *J* = 16 Hz, 1H), 7.66-7.64 (m, 4H), 7.50-7.46 (d, *J* = 16 Hz, 1H), 7.44-7.42 (m, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 189.6, 145.6, 137.1, 134.8, 132.1, 130.9, 130.2, 129.2, 128.7, 128.1, 121.6. IR (cm^{-1}): 2924.8, 1659.1 (vs), 1603.4 (vs), 1583.1 (sh), 1450.7 (w), 1336.1, 1217.8, 1069.4, 1008.5, 982.2. MP: 97.2-98.9°C



5d

The E/Z selectivity of the reaction was >99:1 from ^{1}H-NMR spectroscopic analysis of the crude residue.

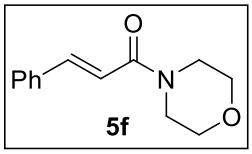
(E)-4-phenylbut-3-en-one (5d)[22]**:** Product isolated as a yellow oil (9.8 mg, 0.0670 mmol, 71%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.56-7.50 (m, 3H), 7.41-7.40 (m, 3H), 6.74-6.70 (d, *J* = 16 Hz, 1H), 2.39 (s, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 198.6, 143.6, 130.7, 129.1, 128.4, 127.3, 27.7. IR (cm^{-1}): 2855.0 (vw), 2810.0 (sh), 1690.2 (sh), 1668.1 (vs), 1601.0, 1450.5 (w), 1358.8 (w), 1256.8 (s), 1204.5 (w), 1178.4 (w).



5e

The E/Z selectivity was 98:2 from ^{1}H-NMR spectroscopic analysis of the crude residue.

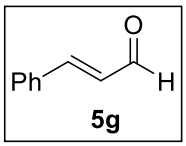
(E)-1-cyclohexyl-3-phenylprop-2-en-1-one (5e)[23]**:** Product isolated as a white solid (18.1 mg, 0.845 mmol, 91%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.61-7.55 (m, 3H), 7.40-7.38 (m, 3H), 6.84-6.80 (d, *J* = 16 Hz, 1H), 2.70-2.63 (m, 1H), 1.92-1.88 (m, 2H), 1.86-1.81 (m, 2H), 1.73-1.69 (m, 1H), 1.48-1.23 (m, 5H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 203.4, 142.4, 134.9, 130.4, 129.0, 128.4, 124.9, 49.6, 28.9, 26.1, 25.9. IR (cm^{-1}): 2928.7 (s), 1680.4 (s), 1604.8 (s), 1446.6, 1338.4, 1319.7, 1200.0, 1065.8. MP: 54.8-56.2°C.



5f

The E/Z selectivity was 95:5 from ^{1}H-NMR spectroscopic analysis of the crude residue.

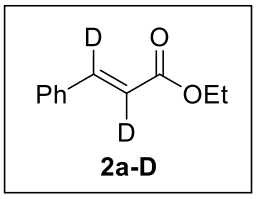
(E)-1-morpholino-3-phenylprop-2-en-1-one (5f)[24]**:** Product isolated as a white solid (10.0 mg, 0.0460 mmol, 53%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.72-7.68 (d, *J* = 16 Hz, 1H), 7.54-7.51 (m, 2H), 7.38-7.36 (m, 3H), 6.86-6.82 (d, *J* = 16 Hz, 1H), 3.73 (s, 8H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 165.7, 143.4, 135.2, 129.9, 128.9, 127.9, 116.6, 67.0. IR (cm^{-1}): 2923.8, 2853.8, 1649.1 (vs), 1603.7, 1459.2 (sh), 1431.4, 1228.3, 1115.2, 1044.0 (w), 977.9 (w). MP: 60.1-63.5°C.



5g

The E/Z selectivity was >99:1 from ^{1}H-NMR spectroscopic analysis of the crude residue.

***trans*-Cinnamaldehyde (5g)**[25]**:** Product isolated as a yellow oil (9.6 mg, 0.0726 mmol, 87%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 9.73-9.71 (d, *J* = 8 Hz, 1H), 7.59-7.57 (m, 2H), 7.51-7.47 (d, *J* = 16 Hz, 1H), 7.47-7.44 (m, 3H), 6.76-6.70 (dd, *J* = 8 Hz, 16Hz, 1H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 193.9, 152.9, 134.1, 131.4, 129.2, 128.7, 128.6. IR (cm^{-1}): 2924.8 (w), 2853.3 (w), 1676.7 (vs), 1625.8, 1450.4 (vw), 1254.3 (vw), 1123.5, 973.0.



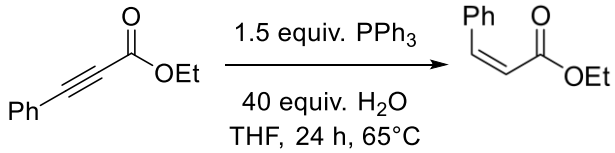
2a-D

The E/Z selectivity was 97:3 from ^{1}H-NMR spectroscopic analysis of the crude residue. The reaction was run using D_2O instead of H_2O.

(E)-2-Propenoic-*2,3-d*$_2$ acid, 3-phenyl-ethyl ester (2a-D): Product isolated as a colorless oil (24.2 mg, 0.1358 mmol, 66%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H), 7.39-7.38 (m, 3H), 4.30-4.24 (q, *J* = 8 Hz, 2H), 1.36-1.32 (7, *J* = 8 Hz, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 167.1, 144.3 (t), 134.5, 130.4, 129.0, 128.2, 118.0 (t), 60.6, 14.5. IR (cm^{-1}): 2921.3 (w), 1706.8 (vs), 1608.0, 1447.9 (w), 1366.1 (w), 1266.4 (s), 1200.4 (vs), 1084.2 (vw), 1049.2.

(Z)-2-Propenoic-*2,3-d*$_2$ acid, 3-phenyl-ethyl ester (3a-D): Product isolated as a colorless oil (0.6 mg, 0.0034 mmol, 2%). Total yield (24.8mg, 0.1391 mmol, 68%).

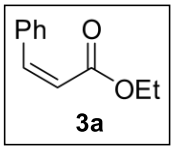
Synthesis of (*Z*)-Alkene Products (3a-3e):



To an oven-dried 8 mL reaction vial was added PPh_3 (1.5 equiv.), the corresponding substrate (1.0 equiv, 0.10 mmol), DI water (40 equiv.), and dry THF (0.1 M). The solution was heated to 65°C and stirred for 24 hr. The solvents were removed under reduced pressure, toluene was added, and the solution

dried over $MgSO_4$. The toluene was removed under reduced pressure, and cold Et_2O was added and filtered over silica. Et_2O was removed under reduced pressure, and the crude residue was purified via column chromatography on silica gel with hexanes/Et_2O (100:1 to 10:1) to afford the alkene product.

All *cis*-alkene products **3a-3e** are compounds known to literature.[26-29]

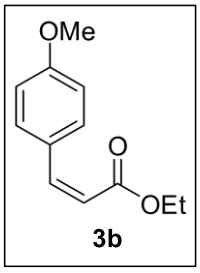


3a

The E/Z selectivity was 15:85 from ^{1}H-NMR spectroscopic analysis of the crude residue.

***Cis*-Ethyl cinnamate (3a)[26]:** Product isolated as a colorless oil (10.1 mg, 0.0573 mmol, 56%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.37-7.32 (m, 3H), 6.97-6.94 (d, *J* = 12 Hz, 1H), 5.97-5.94 (d, *J* = 12 Hz, 1H), 4.20-4.15 (q, *J* = 8 Hz, 2H), 1.26-1.23 (t, *J* = 8 Hz, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 166.3, 143.1, 135.0, 129.8, 129.1, 128.1, 120.0, 60.4, 14.2. IR (cm^{-1}): 2924.1, 2853.7 (sh), 1720.1 (s), 1629.5, 1452.2 (w), 1262.3 (w), 1161.6 (vs), 1028.5, 830.3 (w).

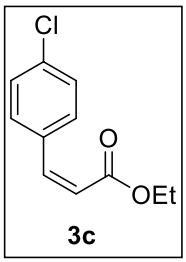
***Trans*-Ethyl cinnamate (2a):** Product isolated as a colorless oil (2.1 mg, 0.0119 mmol, 12%). Total yield (12.2 mg, 0.0692 mmol, 68%).



3b

The E/Z selectivity was 22:78 from ^{1}H-NMR spectroscopic analysis of the crude residue.

Ethyl (Z)-3-(4-methoxyphenyl) acrylate (3b)[26]: The (*Z*)-isomer was inseparable from the remaining starting material through column chromatography. ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.70-7.68 (d, *J* = 8 Hz, 2H), 6.87-6.83 (m, 3H), 5.84-5.81 (d, *J* = 12 Hz, 1H), 4.22-4.16 (q, *J* = 8 Hz, 2H), 3.83 (s, 3H), 1.30-1.26 (t, *J* = 8 Hz, 3H).

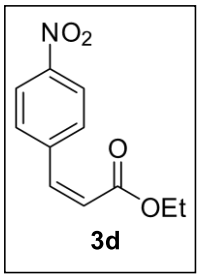


3c

The E/Z selectivity was 12:88 from ^{1}H-NMR spectroscopic analysis of the crude residue.

Ethyl (Z)-3-(4-chlorophenyl) acrylate (3c)[27]: Product isolated as a colorless oil (21.6 mg, 0.1026 mmol, 68%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.56-7.54 (d, *J* = 8 Hz, 2H), 7.33-7.31 (d, *J* = 8 Hz, 2H), 6.90-6.87 (d, *J* = 12 Hz, 1H), 5.97-5.94 (d, *J* = 12 Hz, 1H), 4.20-4.15 (q, *J* = 8Hz, 2H), 1.28-1.24 (t, *J* = 8 Hz, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 166.0, 142.0, 135.0, 133.3, 131.3, 128.3, 120.5, 60.5, 14.2. IR (cm^{-1}): 1718.0 (s), 1630.8, 1591.5 (vw), 1491.2, 1442.1 (vw), 1397.9 (w), 1175.2 (vs), 1092.8, 1029.4, 1016.1, 849.1.

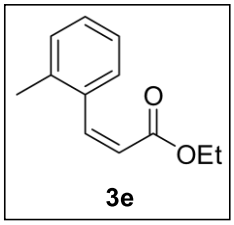
Ethyl (E)-3-(4-chlorophenyl) acrylate (2c): Product isolated as a colorless oil (3.6 mg, 0.0171 mmol, 10%). Total yield (25.2 mg, 0.1196 mmol, 80%).



3d

The E/Z selectivity was 28:72 from ^{1}H-NMR spectroscopic analysis of the crude residue (The (*E*)-isomer was not isolated). Total yield (9.8 mg, 0.0443 mmol, 87%).

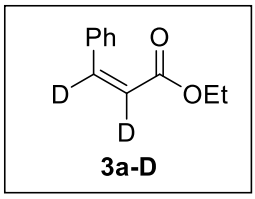
Ethyl (Z)-3-(4-nitrophenyl) acrylate (S33)[28]: Product isolated as yellow solid. ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.22-8.20 (d, *J* = 8 Hz, 2H), 7.68-7.66 (d, *J* = 8 Hz, 2H), 7.03-6.99 (d, *J* = 12 Hz, 1H), 6.14-6.11 (d, *J* = 12 Hz, 1H), 4.20-4.15 (q, *J* = 8 Hz, 2H), 1.26-1.22 (t, *J* = 8 Hz, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 165.4, 147.6, 141.6, 140.7, 130.3, 123.4, 123.3, 60.8, 14.1. IR (cm^{-1}): 2930.3, 1718.1 (vs), 1596.9, 1521.1 (vs), 1466.7 (vw), 1345.2 (s), 1299.4 (w), 1218.1 (s), 1058.3 (w), 857.3 (w). MP: 85.6-87.9°C.



3e

The E/Z selectivity was 2:98 from ^{1}H-NMR spectroscopic analysis of the crude residue.

Ethyl (Z)-3-(*o*-tolyl) acrylate (3e)[29]**:** Product isolated as a tan oil (15.4 mg, 0.0809 mmol, 69%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.22-7.15 (m, 4H), 7.14-7.11 (d, *J* = 12 Hz, 1H), 6.04-6.01 (d, *J* = 12 Hz, 1H), 4.11-4.06 (q, *J* = 8 Hz, 2H), 1.11-1.08 (t, *J* = 8 Hz, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 159.2, 143.1, 129.7, 128.9, 128.5, 125.3, 121.2, 60.3, 20.0, 14.1. IR (cm^{-1}): 2962.0 (sh), 2924.0 (vs), 2851.6, 1735.5, 1465.1, 1381.3 (w), 1267.0 (w), 1175.6, 1118.5 (w), 1023.3 (w), 977.6.



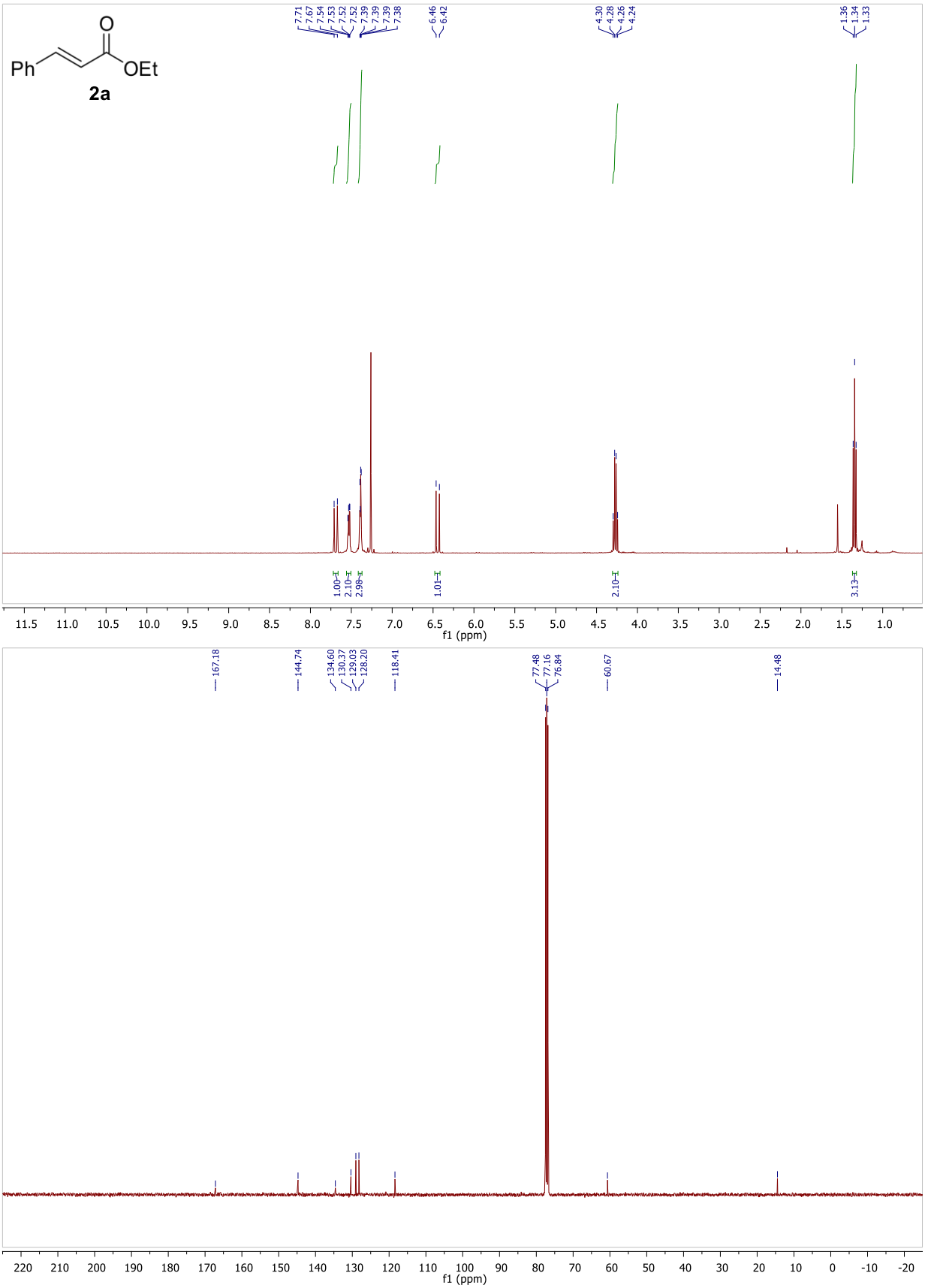
3a-D

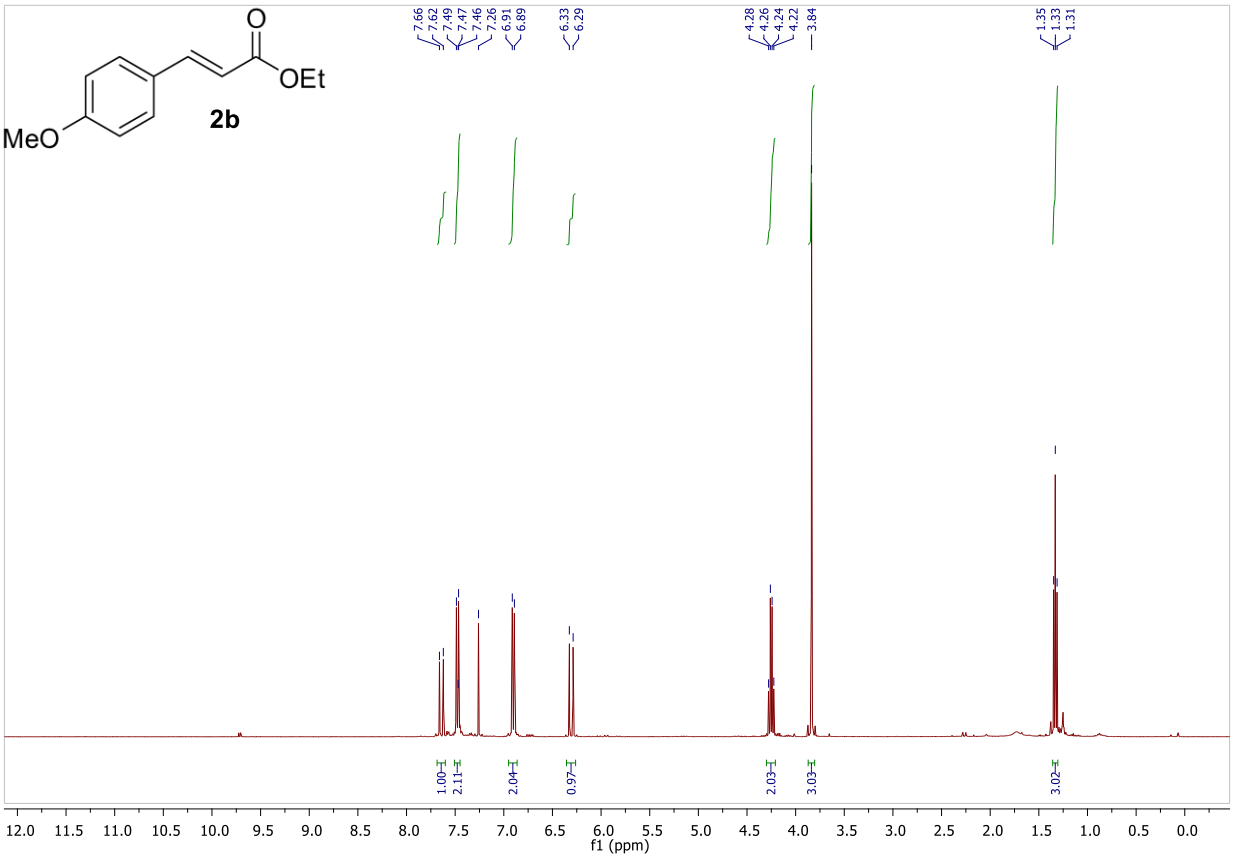
The E/Z selectivity was 17:83 from ^{1}H-NMR spectroscopic analysis of the crude residue. The reaction was run using D_2O instead of H_2O.

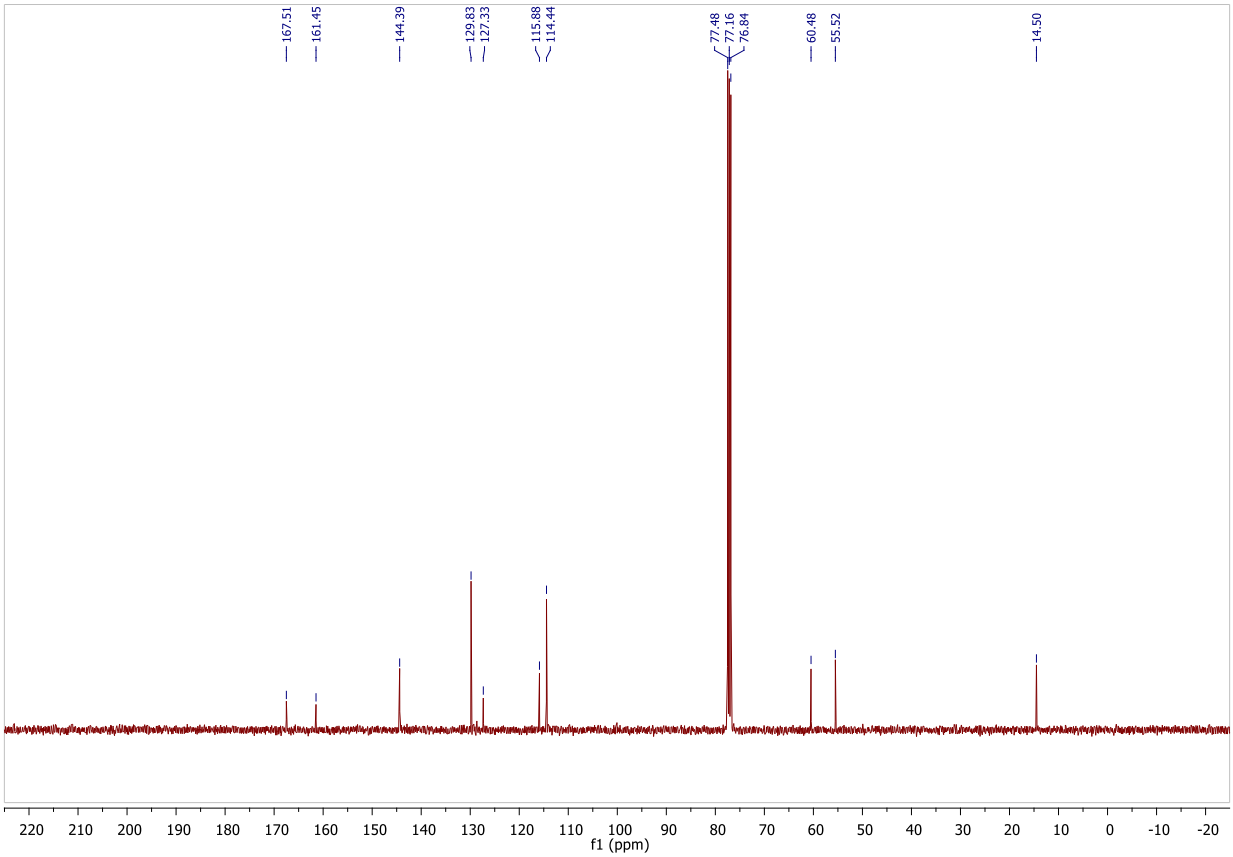
(Z)-2-Propenoic-*2,3-d*$_2$ acid, 3-phenyl-ethyl ester (3a-D): Product isolated as a clear oil (25.2 mg, 0.1414 mmol, 74%). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.61-7.59 (m, 2H), 7.38-7.32 (m, 3H), 4.21-4.15 (q, *J* = 8 Hz, 2H), 1.27-1.23 (t, *J* = 8 Hz, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 166.4, 142.8 (t), 134.5, 129.9, 129.1, 128.1, 119.5 (t), 60.4, 14.2. IR (cm^{-1}): 2923.4 2853.3 (sh), 1738.0 (vs), 1606.0 (w), 1461.3 (s), 1377.5, 1267.7 (s), 1171.8, 1057.5.

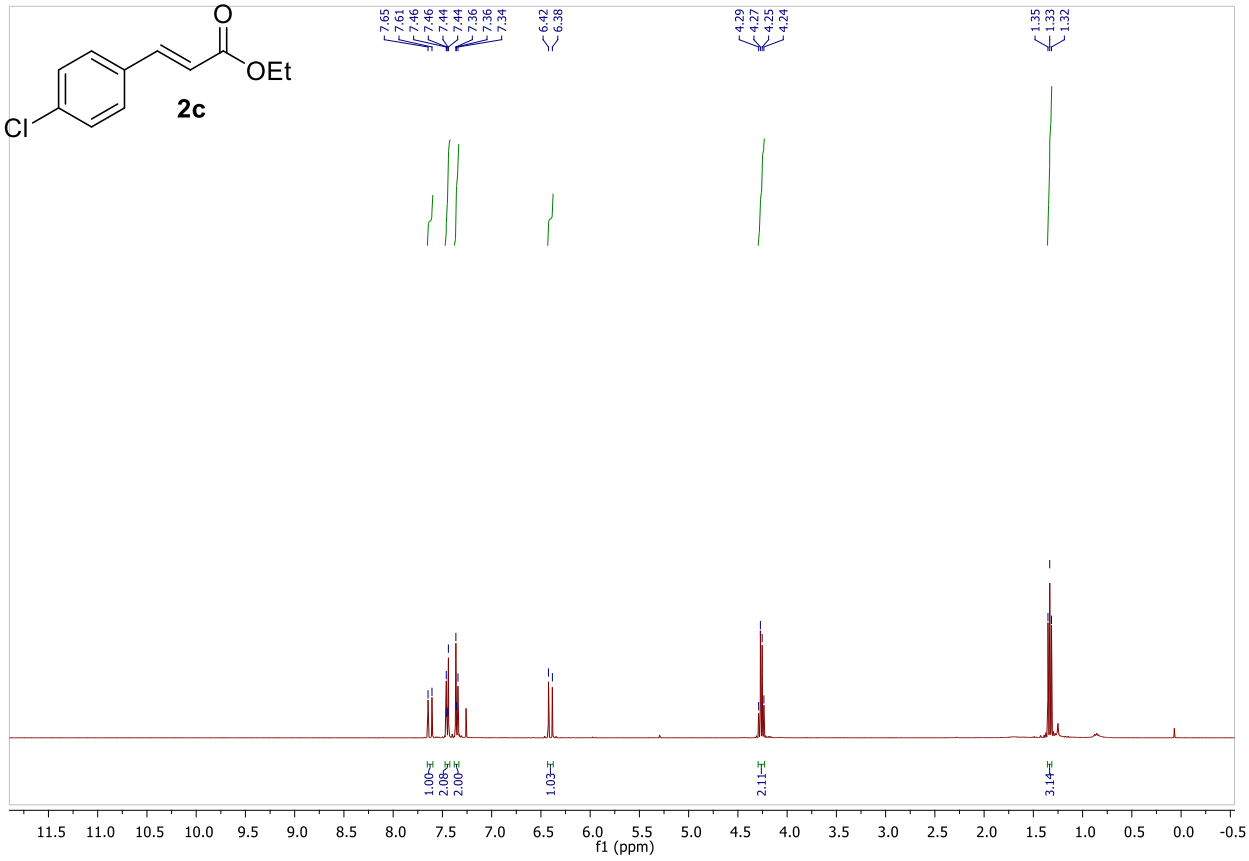
(E)-2-Propenoic-*2,3-d*$_2$ acid, 3-phenyl-ethyl ester (2a-D): Product isolated as a colorless oil (5.3 mg, 0.0297 mmol, 16%). Total yield (30.5 mg, 0.1711 mmol, 90%).

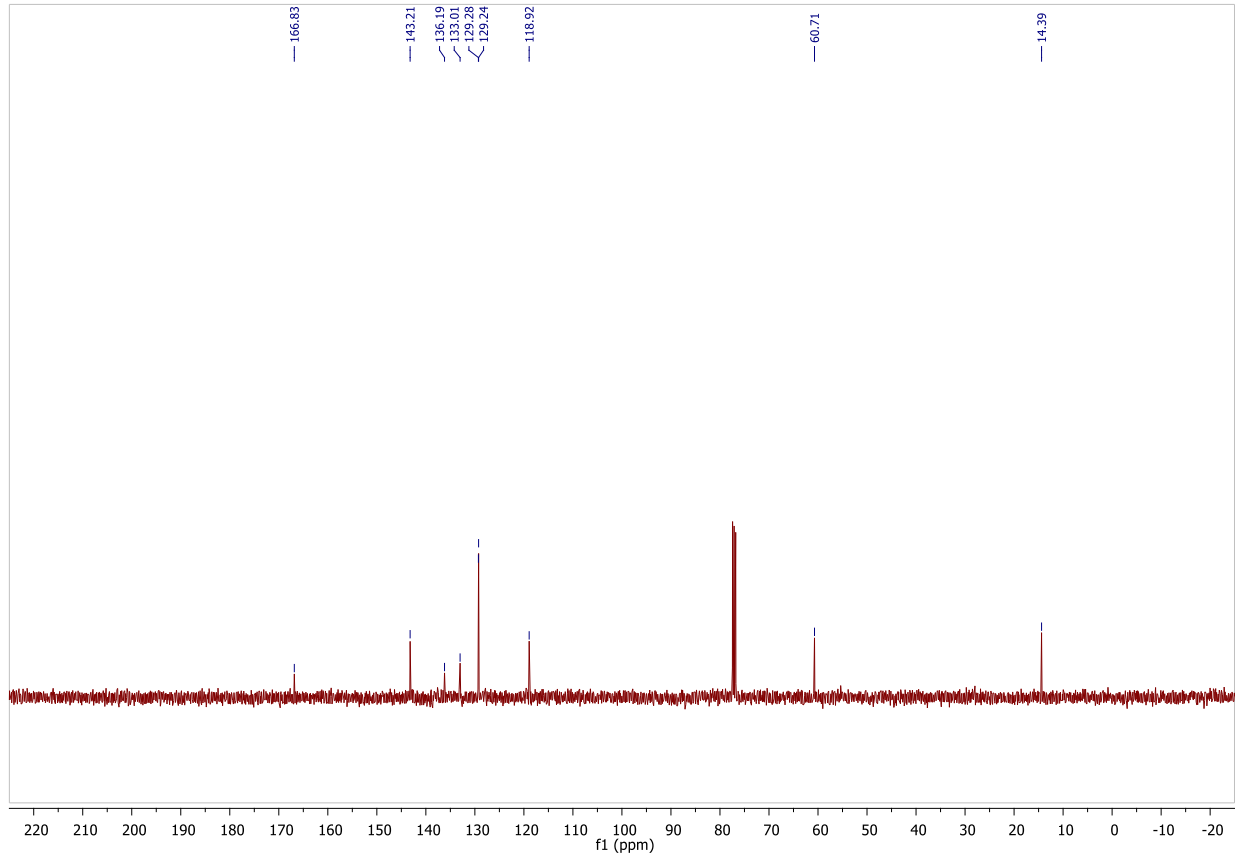
3. ^{1}H-NMR and ^{13}C-NMR Spectra for Alkene Products


Ph
O
OEt
2a
7.71
7.67
7.54
7.53
7.52
7.52
7.39
7.39
7.39
7.38
6.46
6.42
4.30
4.28
4.26
4.24
1.36
1.34
1.33
1.00
2.10
2.98
1.01
2.10
3.13
f1 (ppm)
167.18
144.74
134.60
130.37
129.03
128.20
118.41
77.48
77.16
76.84
60.67
14.48
f1 (ppm)


O
OEt
MeO
2b
7.66
7.62
7.49
7.47
7.46
7.26
6.91
6.89
6.33
6.29
4.28
4.26
4.24
4.22
3.84
1.35
1.33
1.31
1.00
2.11
2.04
0.97
2.03
3.03
3.02
f1 (ppm)


167.51
161.45
144.39
129.83
127.33
115.88
114.44
77.48
77.16
76.84
60.48
55.52
14.50
f1 (ppm)


O
OEt
Cl
2c
7.65
7.61
7.46
7.46
7.44
7.44
7.36
7.36
7.34
6.42
6.38
4.29
4.27
4.25
4.24
1.35
1.33
1.32
1.00
2.08
2.00
1.03
2.11
3.14
f1 (ppm)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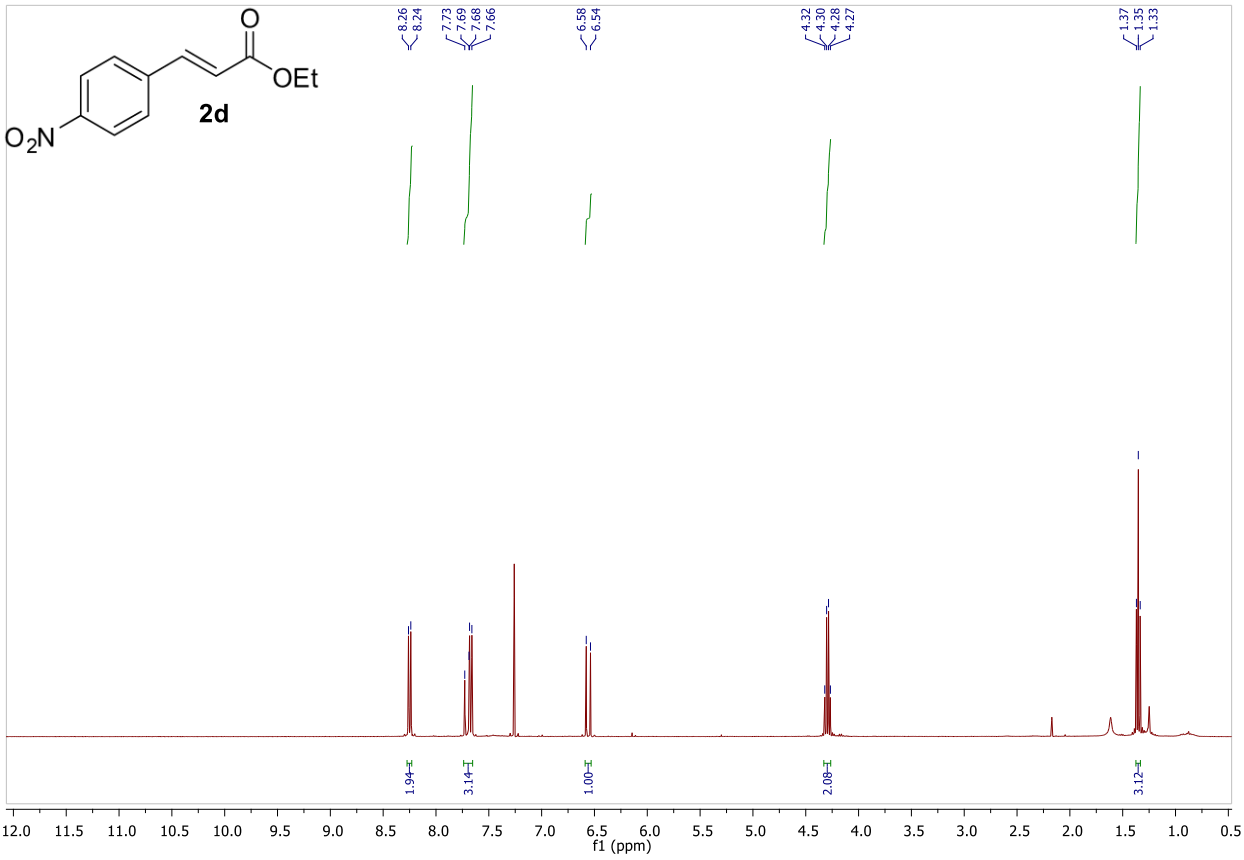
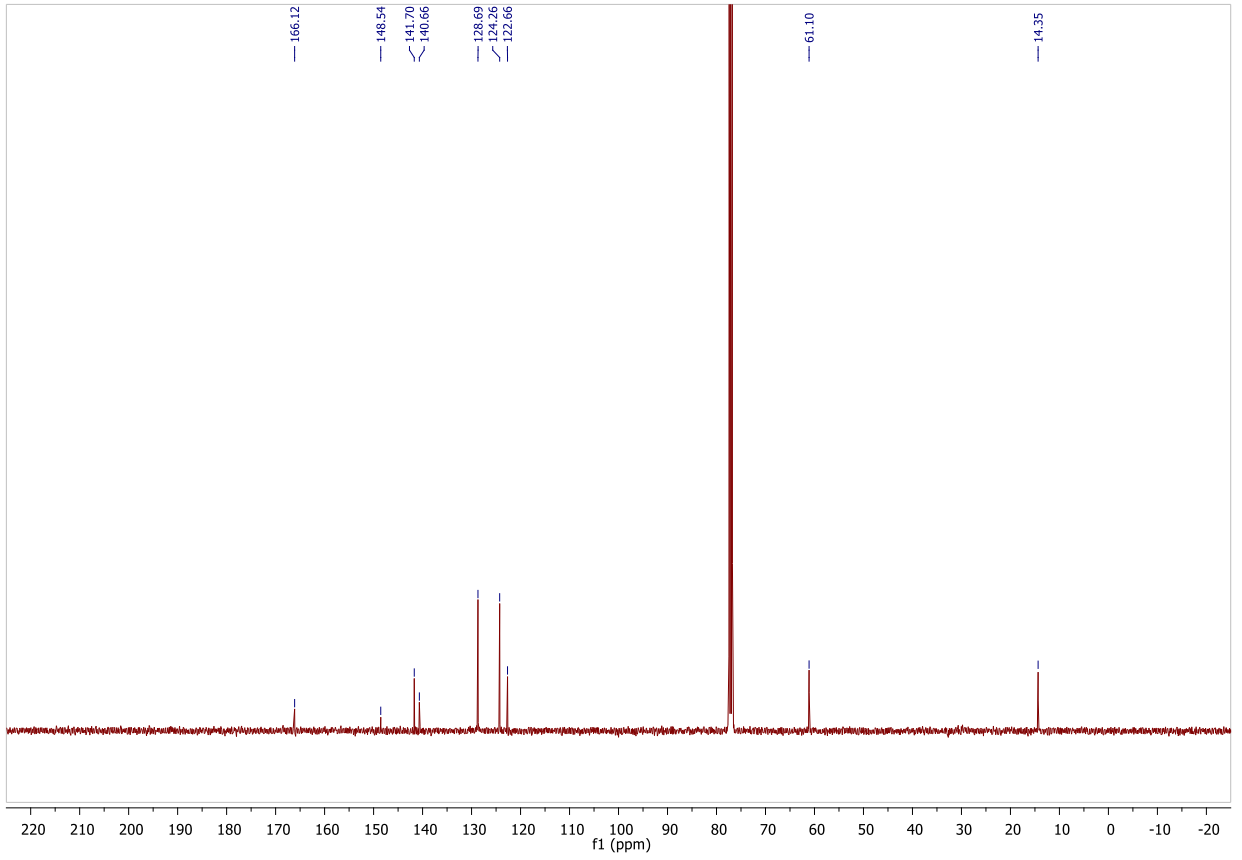
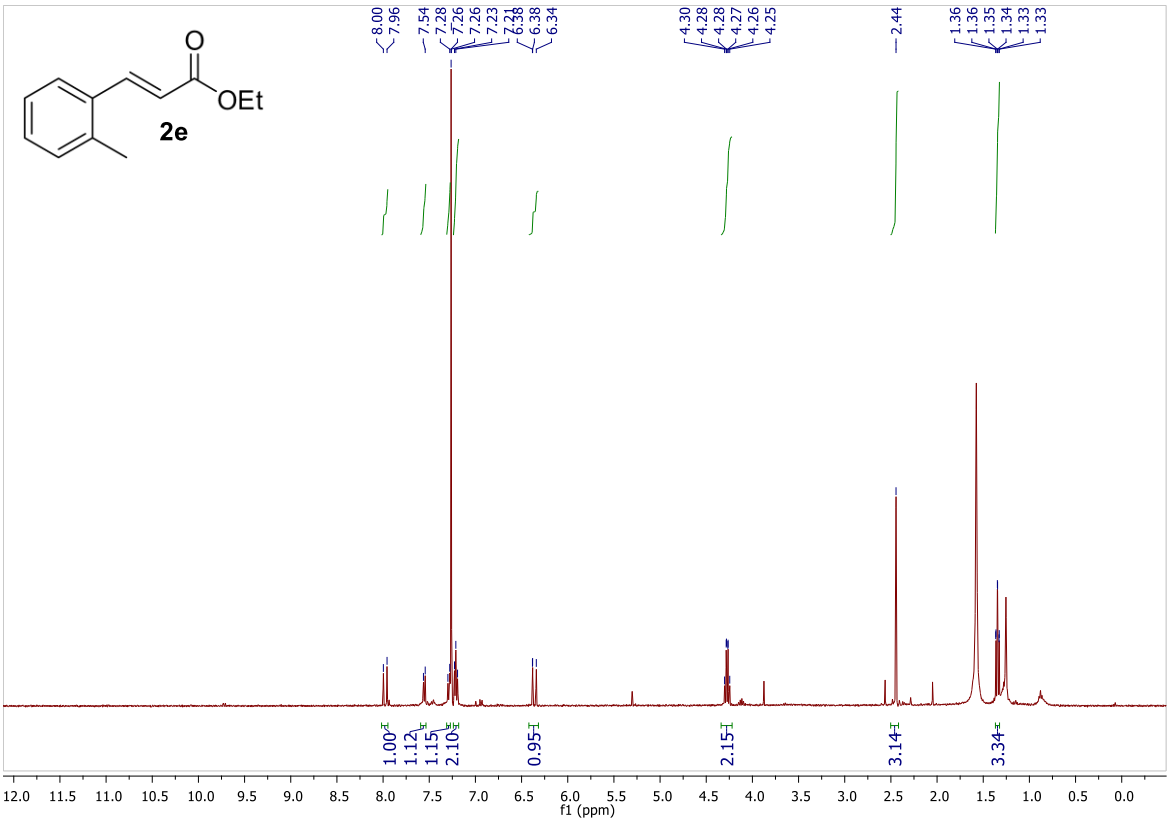
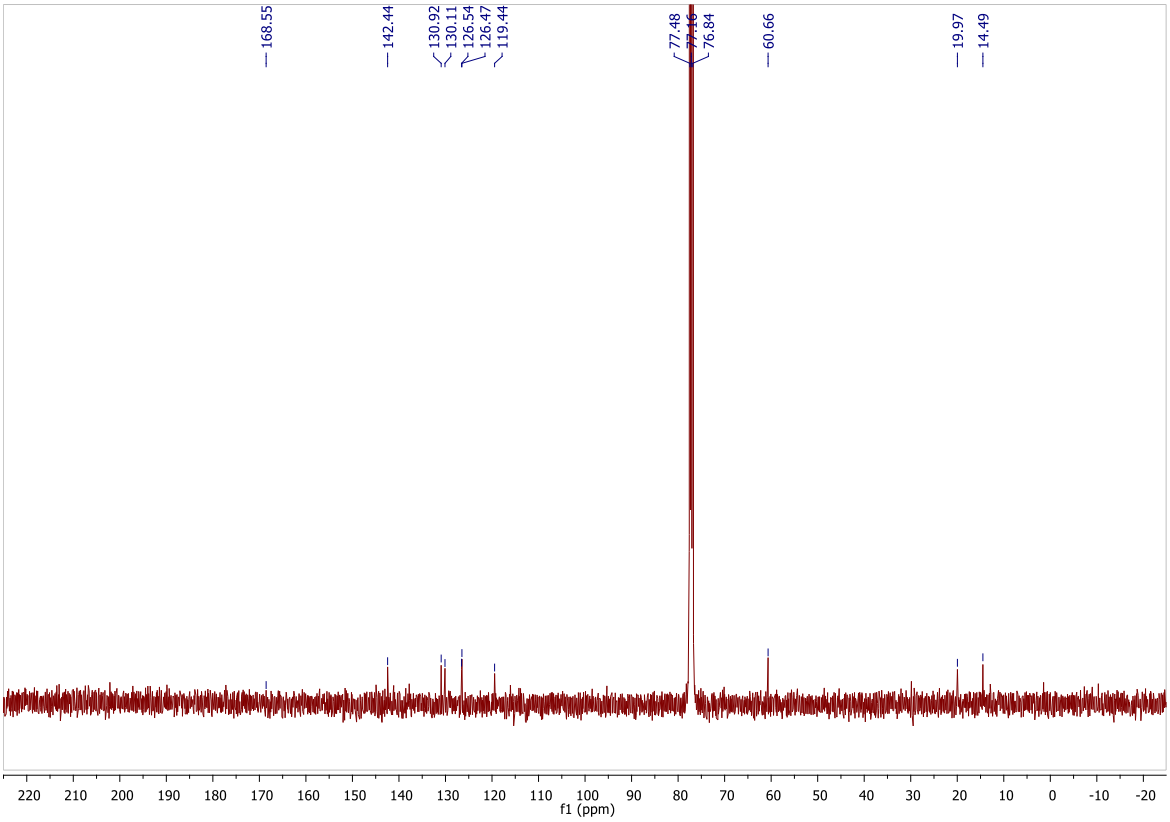
143.21
136.19
133.01
129.28
129.24
118.92
60.71
14.39
f1 (ppm)


O
OEt
O2N
2d
8.26
8.24
7.73
7.69
7.68
7.66
6.58
6.54
4.32
4.30
4.28
4.27
1.37
1.35
1.33
1.94
3.14
1.00
2.08
3.12
f1 (ppm)


166.12
148.54
141.70
140.66
128.69
124.26
122.66
61.10
14.35
f1 (ppm)


O
OEt
2e
8.00
7.96
7.54
7.28
7.26
7.26
7.23
7.21
6.38
6.34
4.30
4.28
4.28
4.27
4.26
4.25
2.44
1.36
1.36
1.35
1.34
1.33
1.33
1.00
1.12
1.15
2.10
0.95
2.15
3.14
3.34
f1 (ppm)


168.55
142.44
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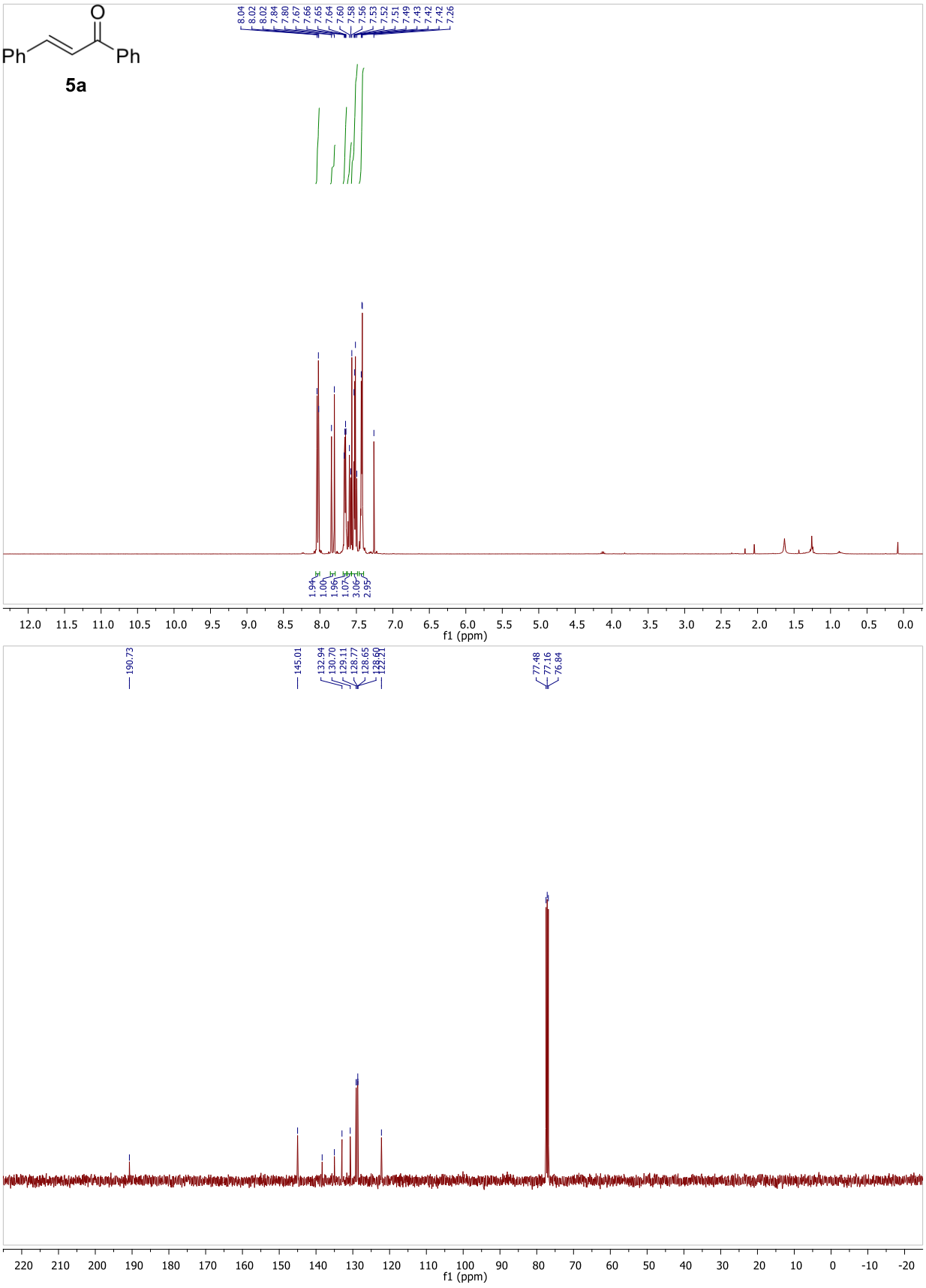
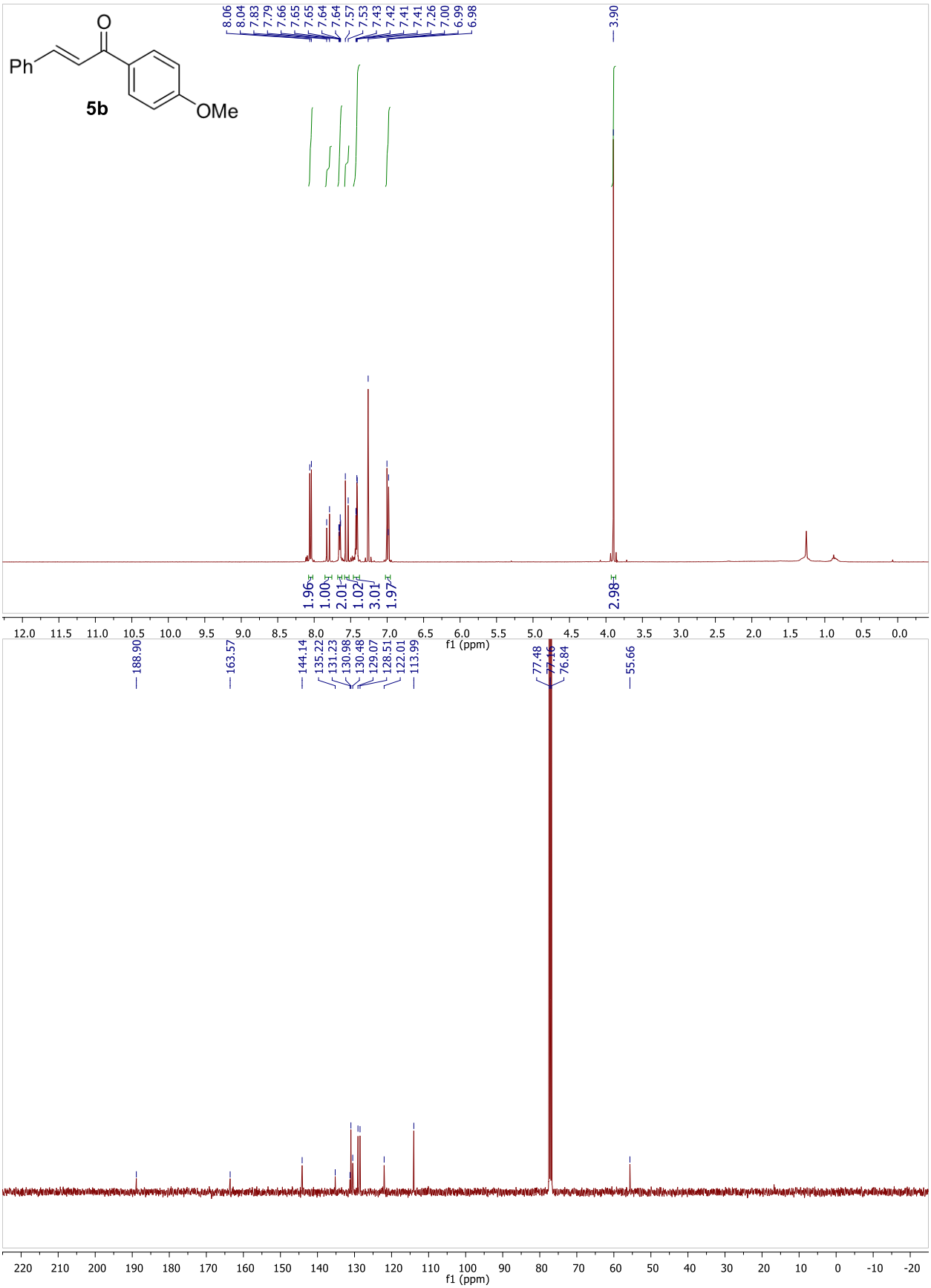
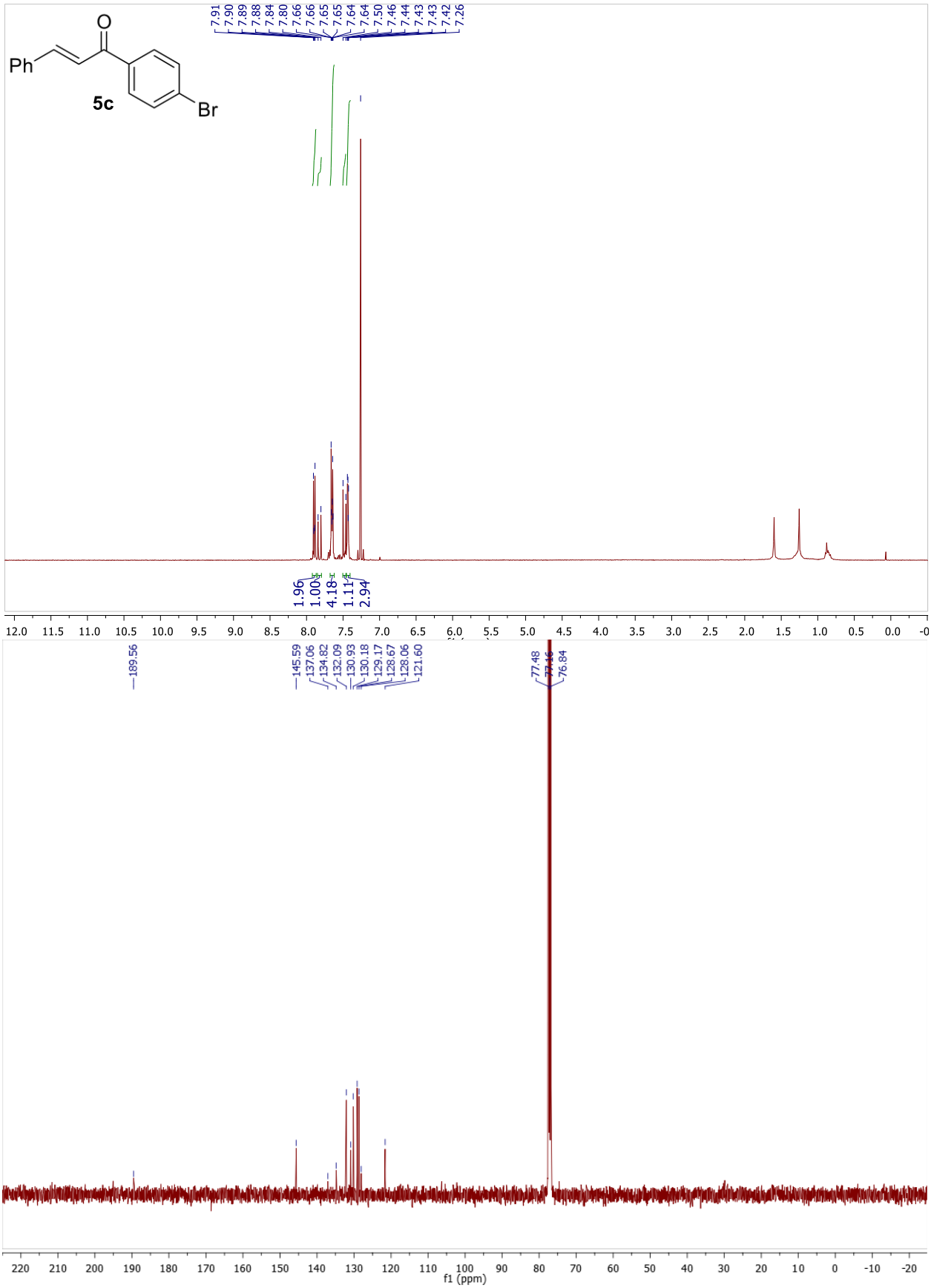
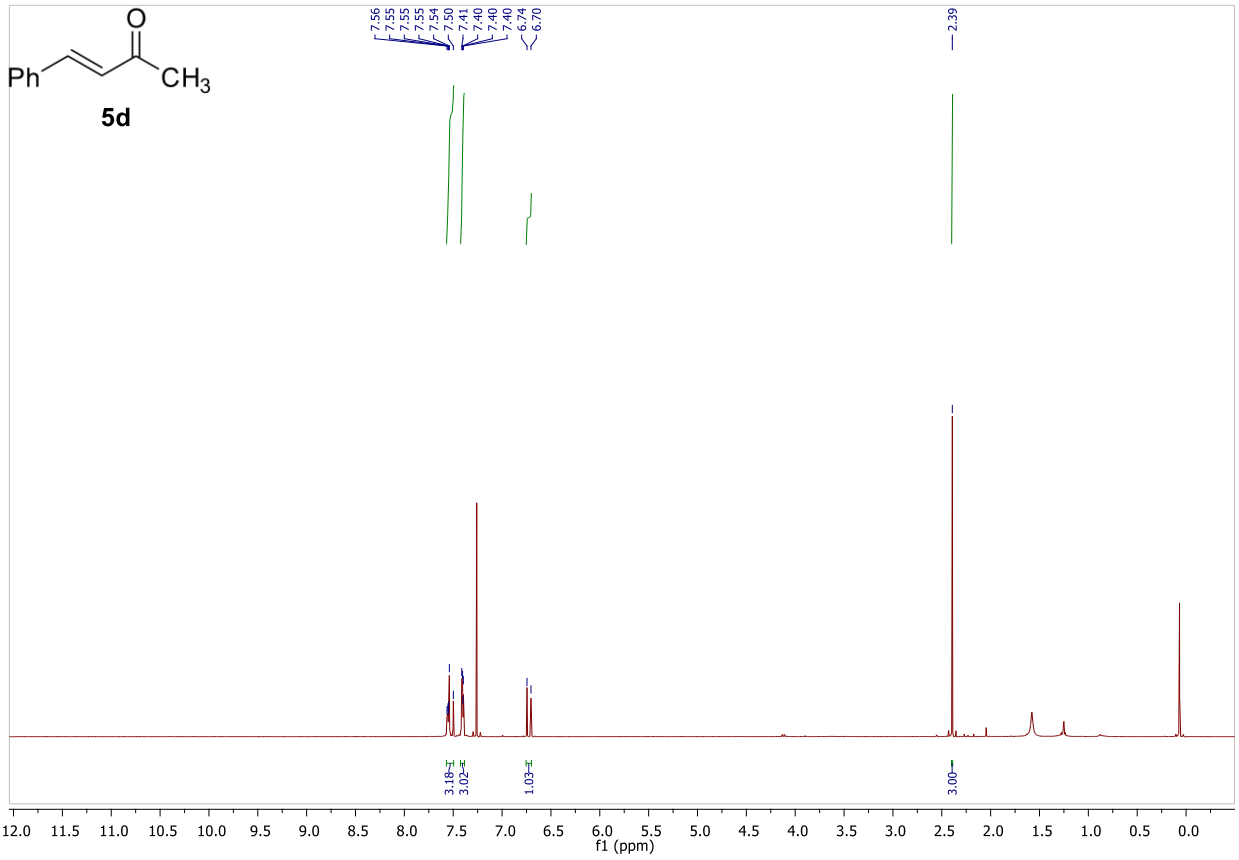
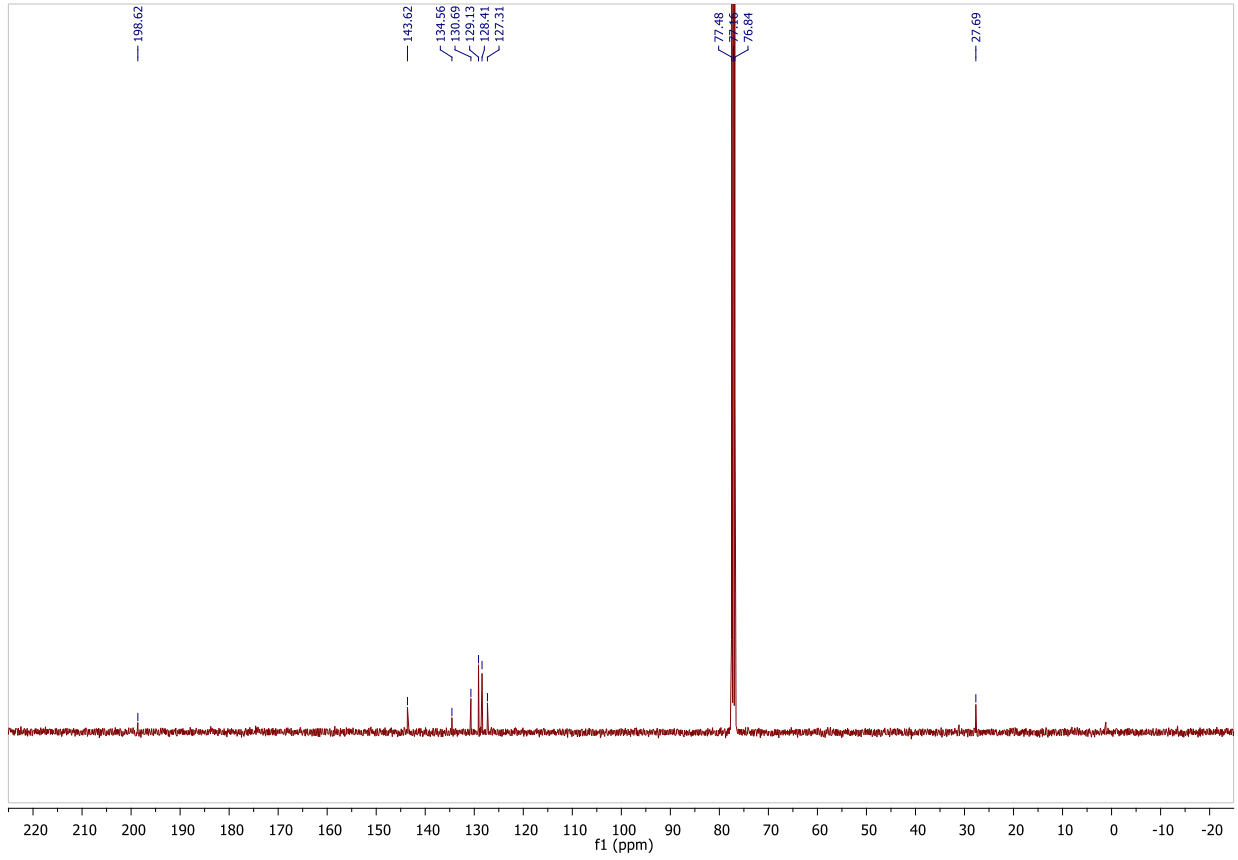
130.11
126.54
126.47
119.44
77.48
77.16
76.84
60.66
19.97
14.49
f1 (ppm)


Ph
Ph
O
5a
8.04
8.02
8.02
7.84
7.80
7.67
7.66
7.65
7.64
7.60
7.58
7.56
7.53
7.52
7.51
7.49
7.43
7.42
7.42
7.26
1.94
1.00
1.96
1.07
3.06
2.99
f1 (ppm)
190.73
145.01
132.94
130.70
129.11
128.77
128.65
77.48
77.16
76.84
f1 (ppm)


O
Ph
OMe
5b
8.06
8.04
7.83
7.79
7.66
7.65
7.65
7.64
7.64
7.57
7.53
7.43
7.42
7.41
7.41
7.26
7.00
6.99
6.98
3.90
1.96
1.00
2.01
1.02
3.01
1.97
2.98
f1 (ppm)
188.90
163.57
144.14
135.22
131.23
130.98
130.48
129.07
128.51
122.01
113.99
77.48
77.16
76.84
55.66
f1 (ppm)


Ph
O
Br
5c
7.91
7.90
7.89
7.88
7.84
7.80
7.66
7.66
7.65
7.65
7.64
7.64
7.50
7.46
7.44
7.43
7.43
7.42
7.26
1.96
1.00
4.18
1.11
2.94
189.56
145.59
137.06
134.82
132.09
130.93
130.18
129.17
128.67
128.06
121.60
77.48
77.16
76.84
f1 (ppm)


O
Ph
CH3
5d
7.56
7.55
7.55
7.55
7.54
7.50
7.41
7.40
7.40
7.40
6.74
6.70
2.39
3.18
3.02
1.03
3.00
f1 (ppm)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143.62
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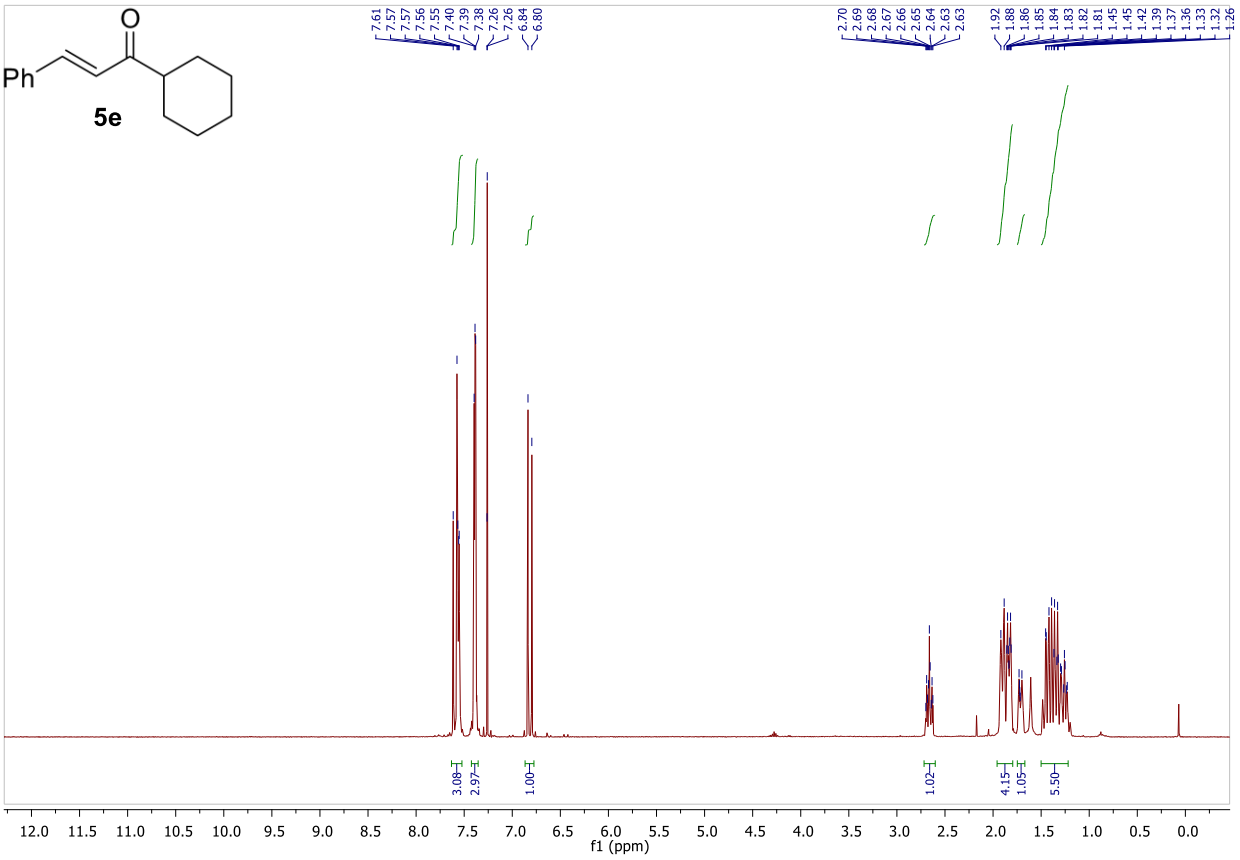
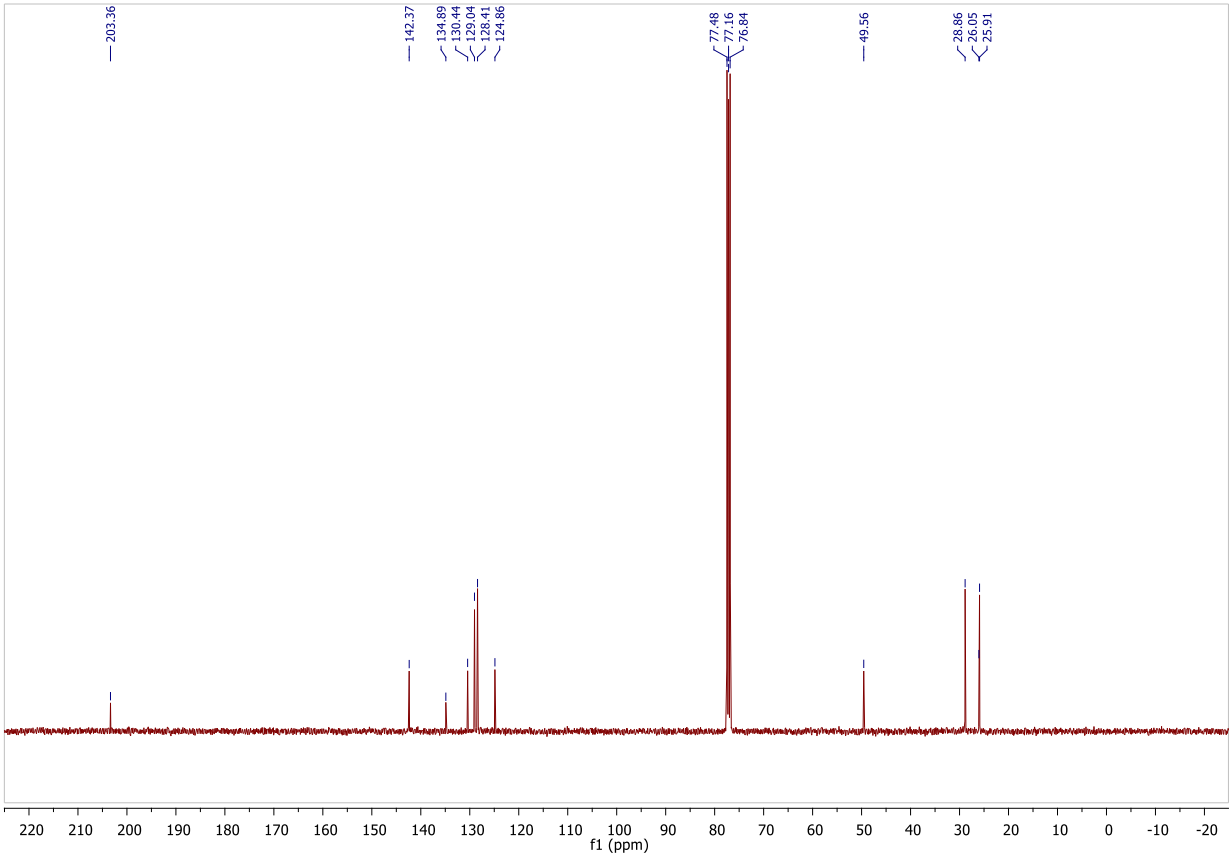
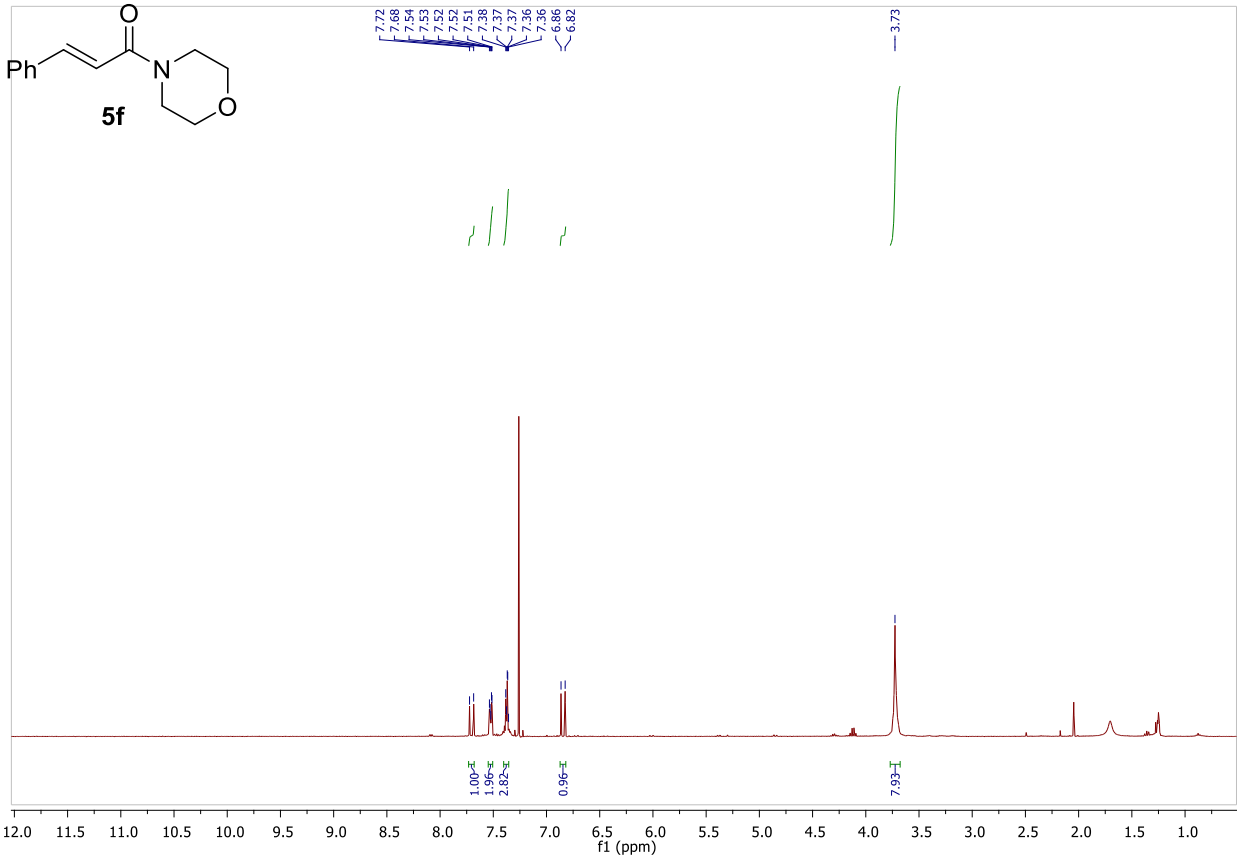
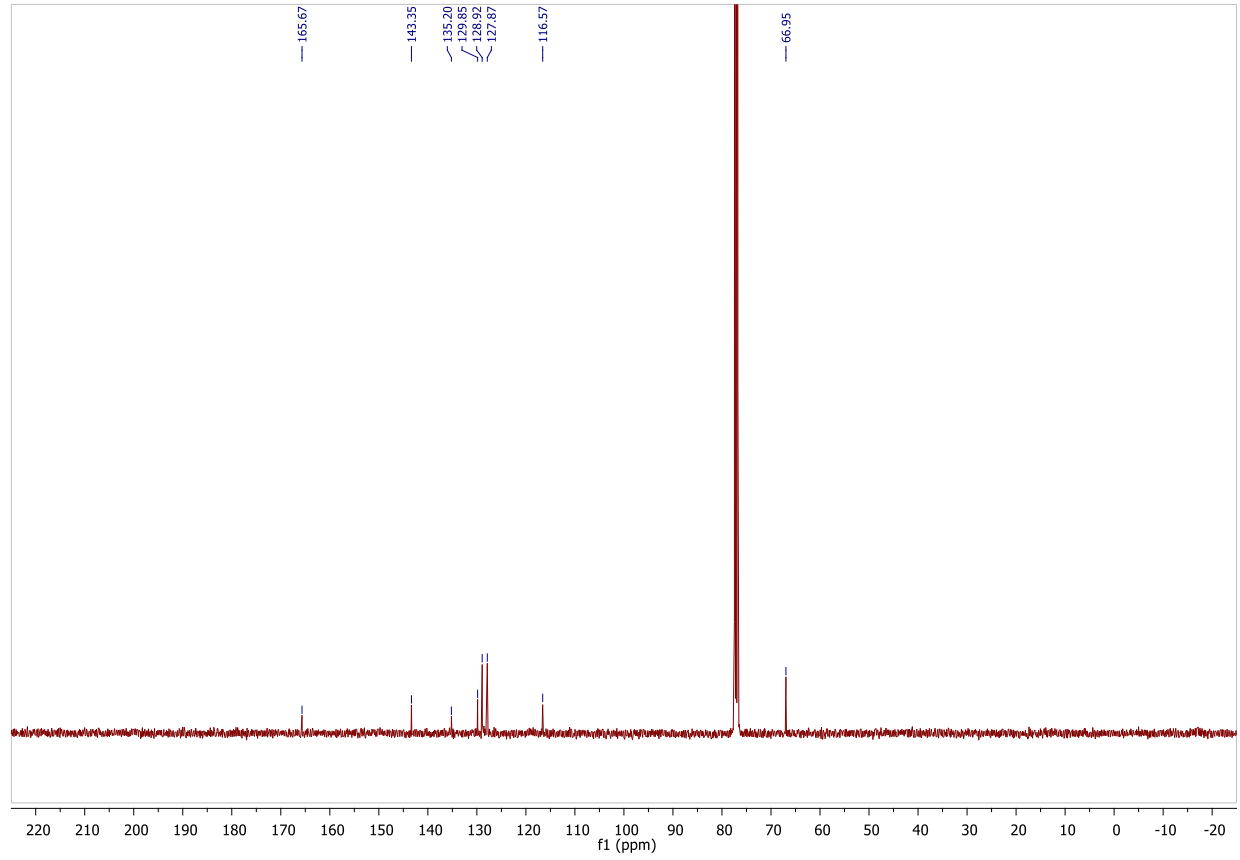
130.69
129.13
128.41
127.31
77.48
77.16
76.84
27.69
f1 (ppm)


Ph
O
5e
7.61
7.57
7.57
7.56
7.55
7.40
7.39
7.38
7.26
7.26
6.84
6.80
2.70
2.69
2.68
2.67
2.66
2.65
2.64
2.63
2.63
1.92
1.88
1.86
1.85
1.84
1.83
1.82
1.81
1.45
1.45
1.42
1.39
1.37
1.36
1.33
1.32
1.26
3.08
2.97
1.00
1.02
4.15
1.05
5.50
f1 (ppm)


203.36
142.37
134.89
130.44
129.04
128.41
124.86
77.48
77.16
76.84
49.56
28.86
26.05
25.91
f1 (ppm)


Ph
O
N
O
5f
7.72
7.68
7.54
7.53
7.52
7.52
7.51
7.38
7.37
7.37
7.36
6.86
6.82
3.73
1.00
1.96
2.82
0.96
7.93
f1 (ppm)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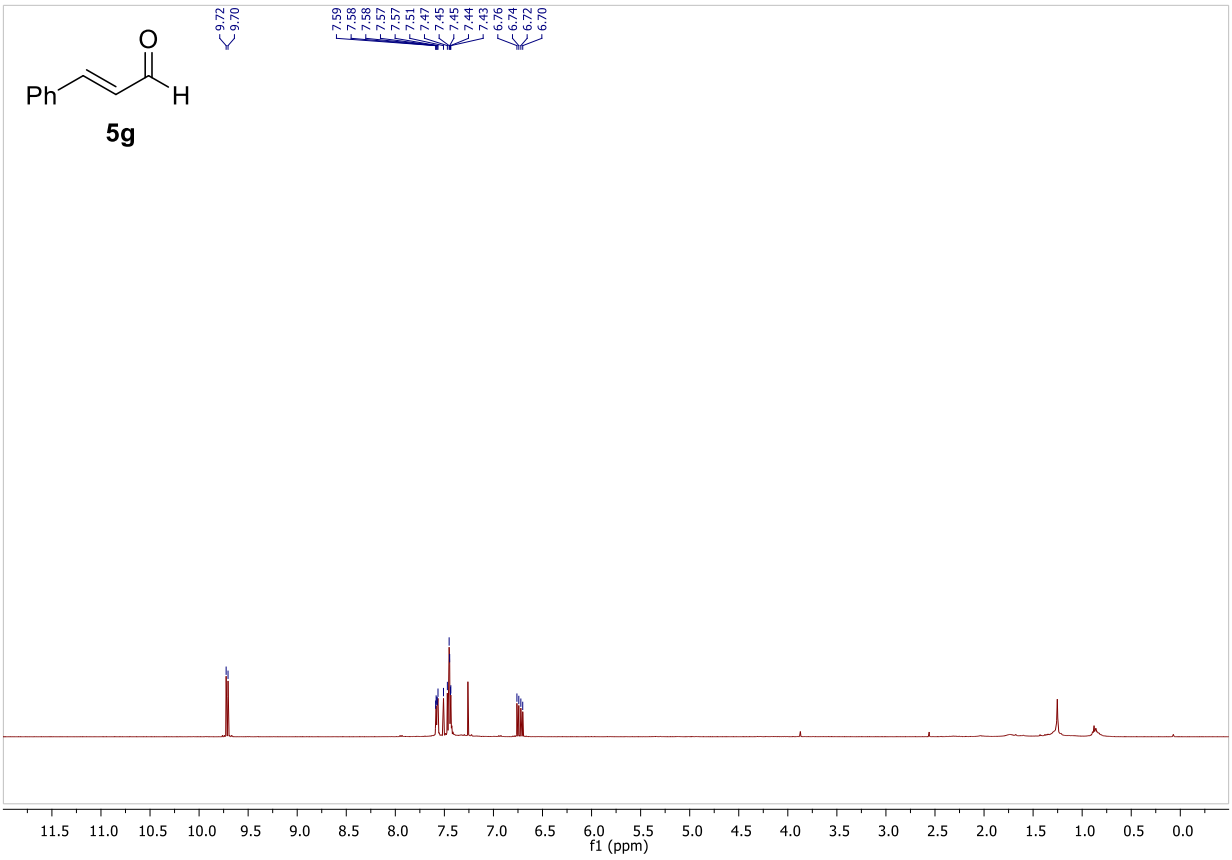
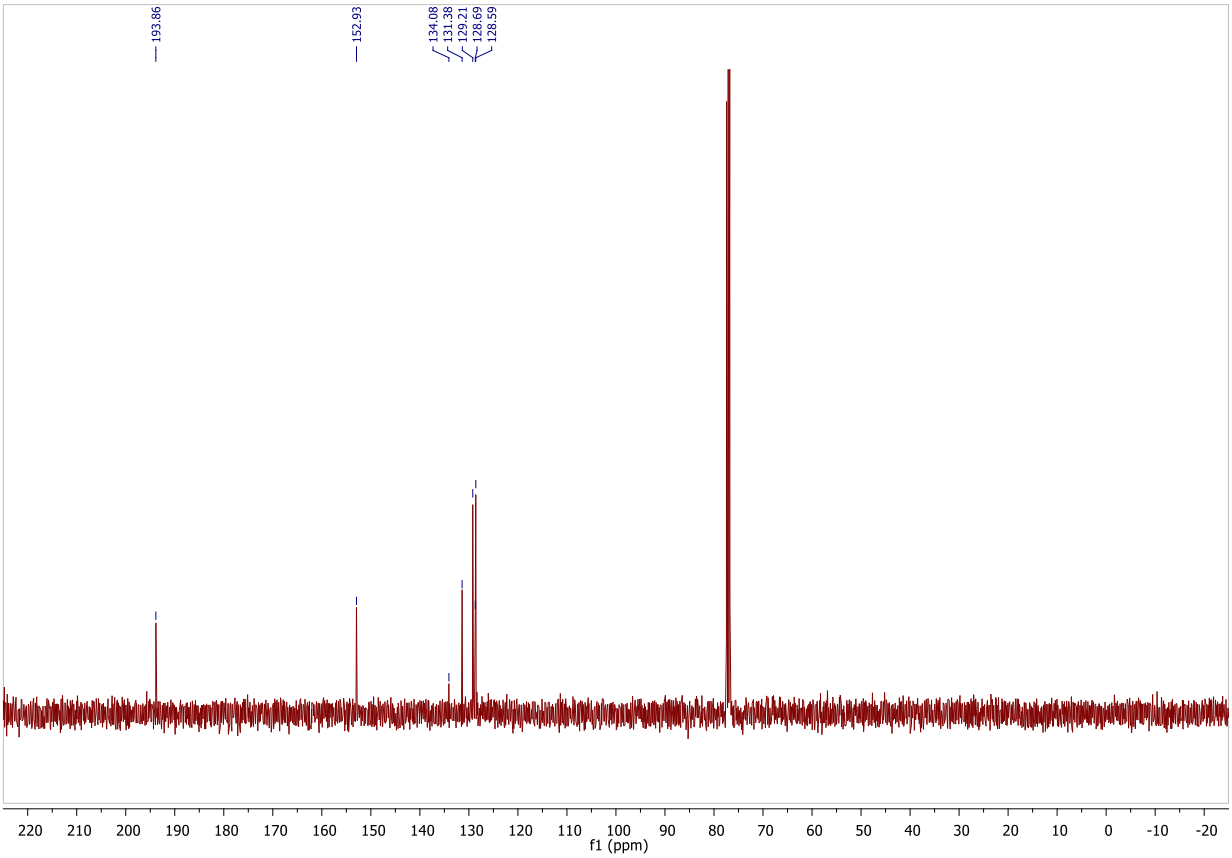
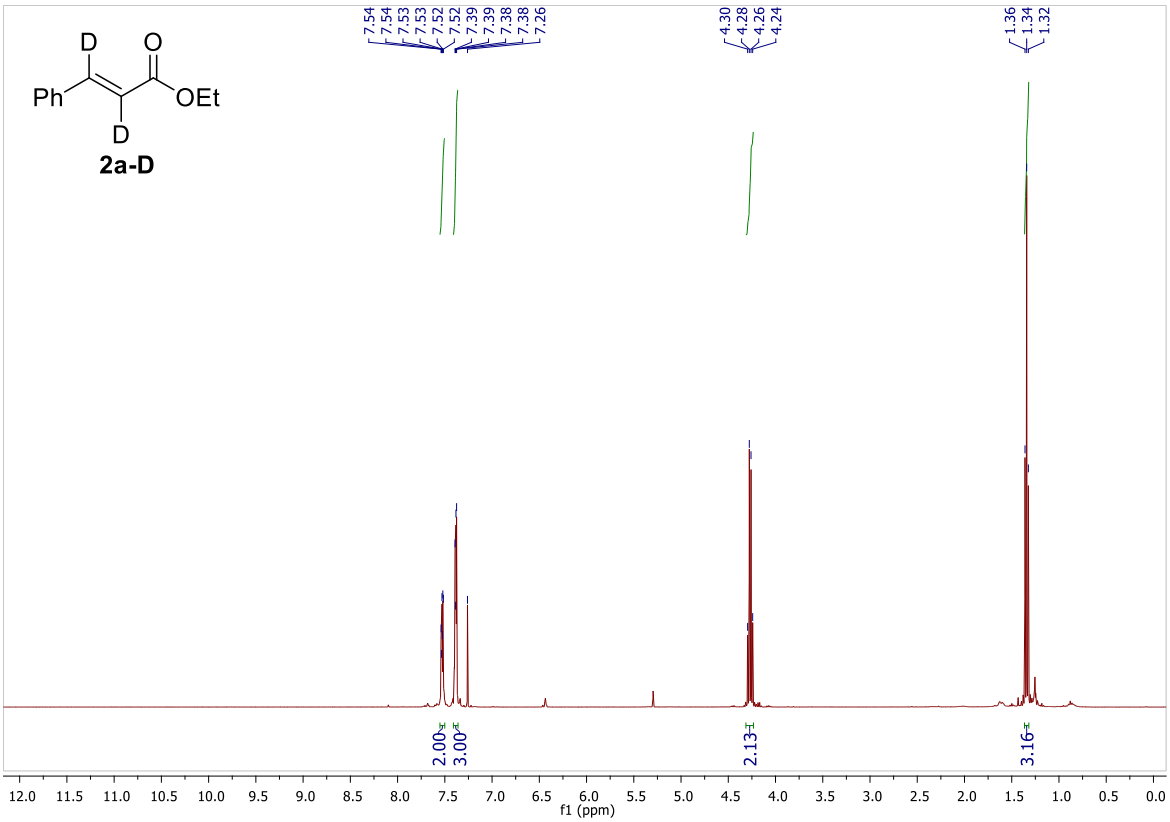
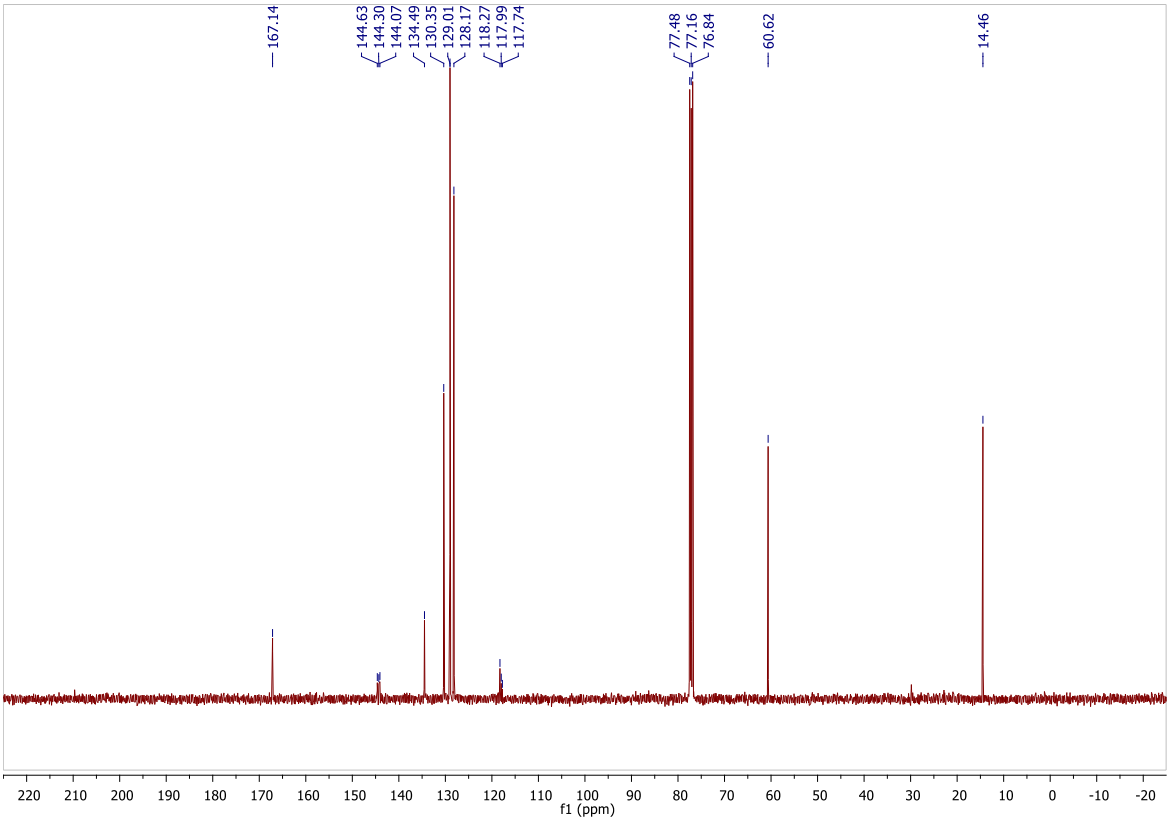
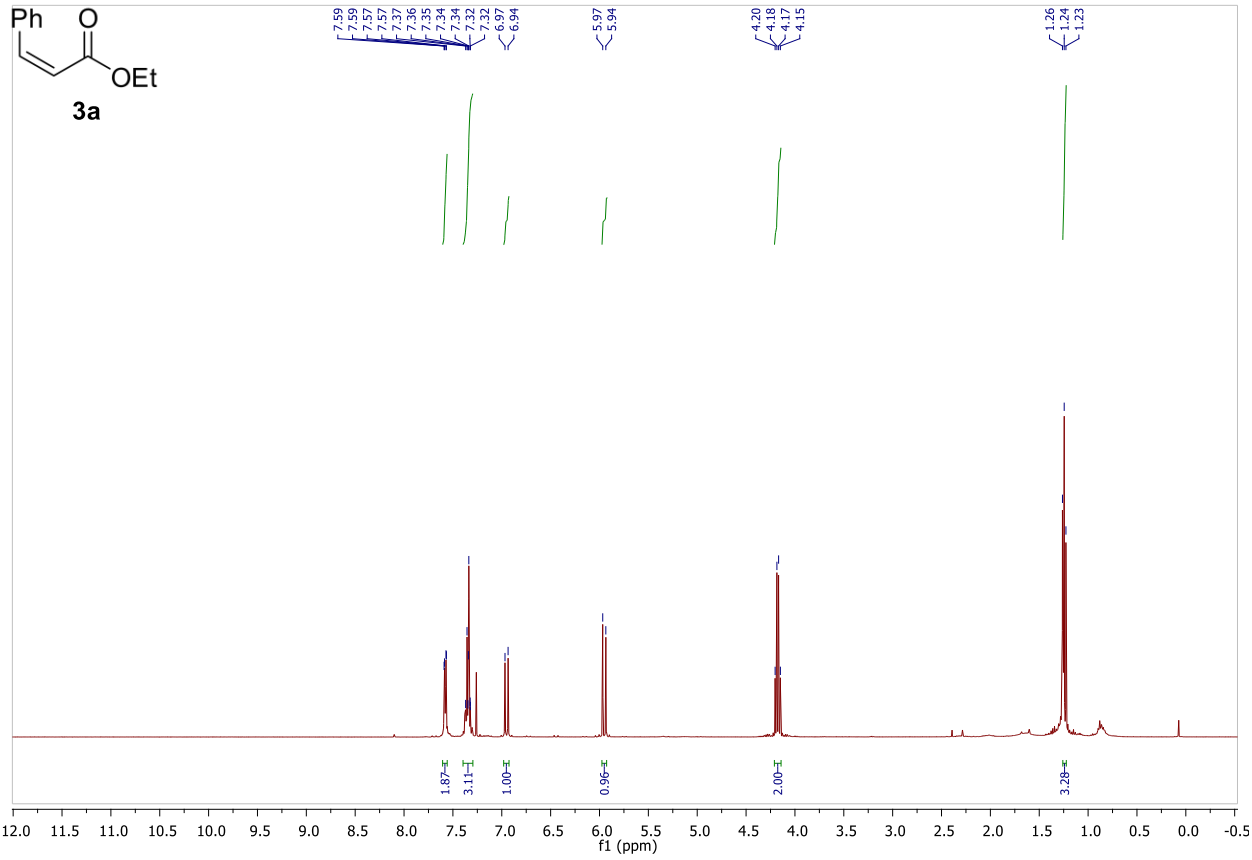
129.85
128.92
127.87
116.57
66.95
f1 (ppm)

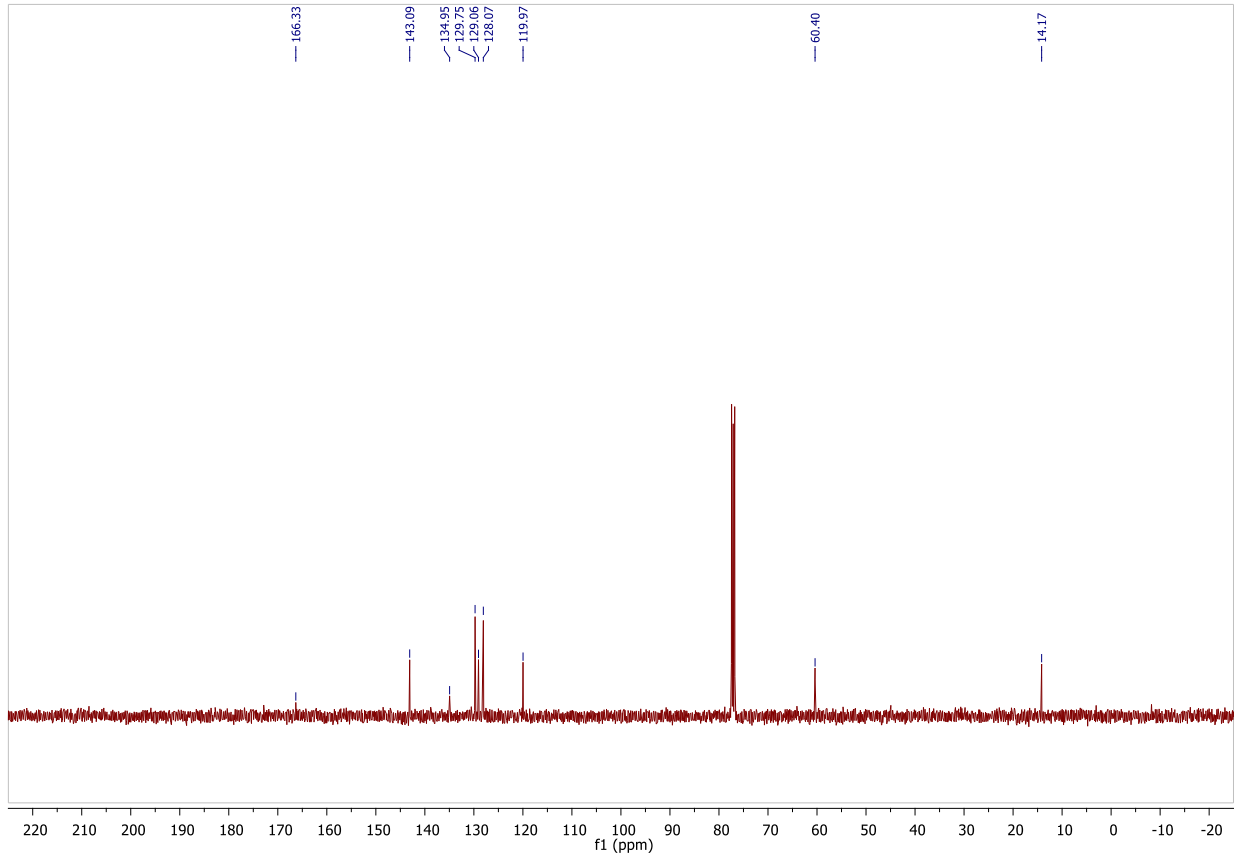

O
Ph
H
5g
9.72
9.70
7.59
7.58
7.58
7.57
7.57
7.51
7.47
7.45
7.45
7.44
7.43
6.76
6.74
6.72
6.70
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


193.86
152.93
134.08
131.38
129.21
128.69
128.59
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


D
O
Ph
OEt
D
2a-D
7.54
7.54
7.53
7.53
7.52
7.52
7.39
7.39
7.38
7.38
7.26
4.30
4.28
4.26
4.24
1.36
1.34
1.32
2.00
3.00
2.13
3.16
f1 (ppm)


167.14
144.63
144.30
144.07
134.49
130.35
129.01
128.17
118.27
117.99
117.74
77.48
77.16
76.84
60.62
14.46
f1 (ppm)


Ph
O
OEt
3a
7.59
7.59
7.57
7.57
7.37
7.36
7.35
7.34
7.34
7.32
7.32
6.97
6.94
5.97
5.94
4.20
4.18
4.17
4.15
1.26
1.24
1.23
1.87
3.11
1.00
0.96
2.00
3.28
f1 (ppm)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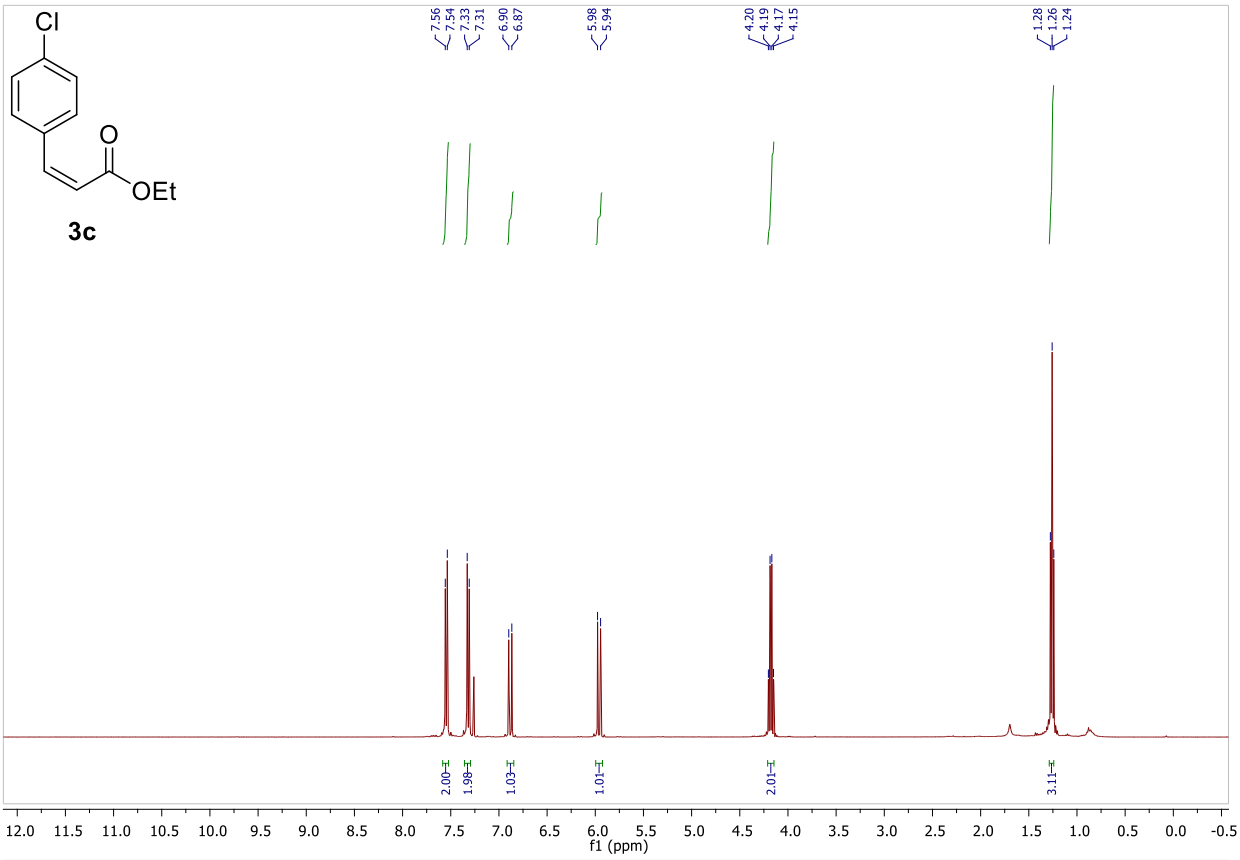
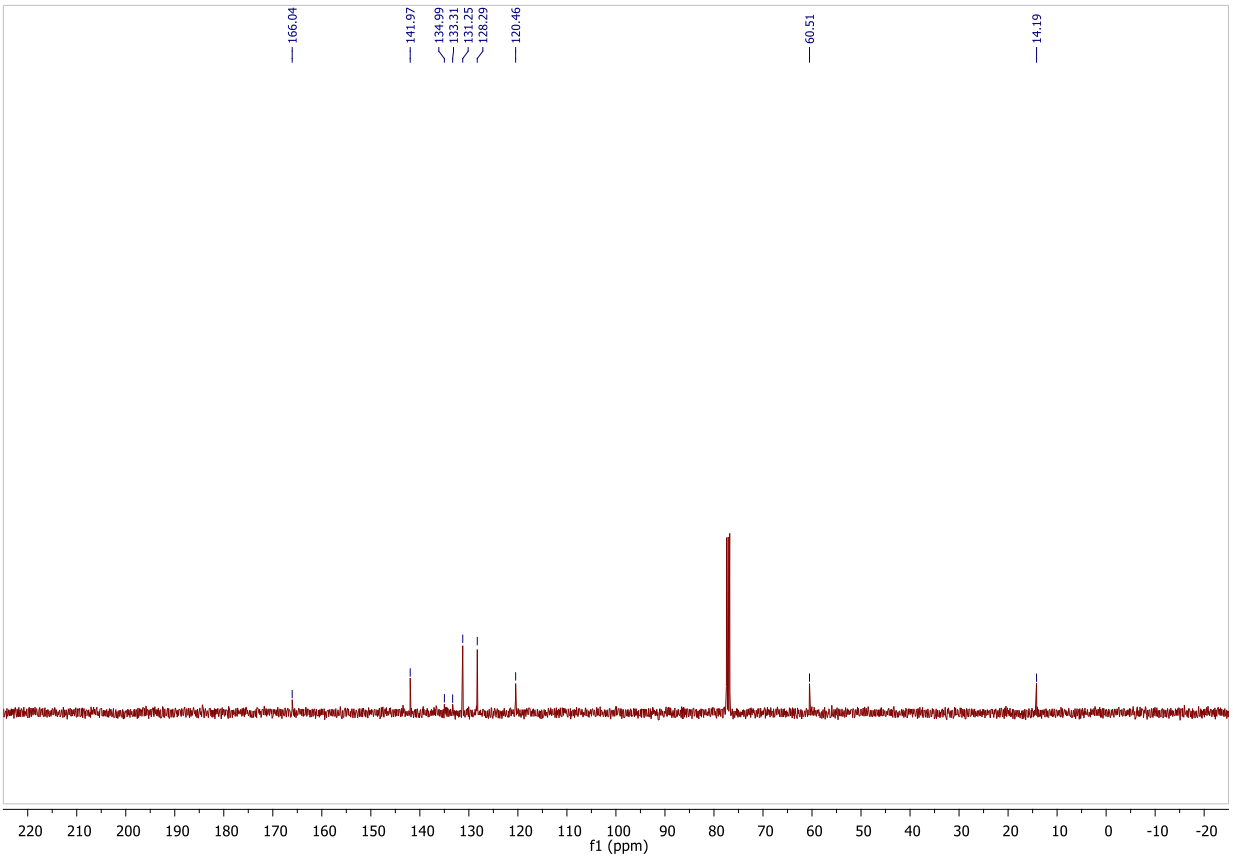
129.75
129.06
128.07
119.97
60.40
14.17
f1 (ppm)


Cl
O
OEt
3c
7.56
7.54
7.33
7.31
6.90
6.87
5.98
5.94
4.20
4.19
4.17
4.15
1.28
1.26
1.24
2.00
1.98
1.03
1.01
2.01
3.11
f1 (ppm)


166.04
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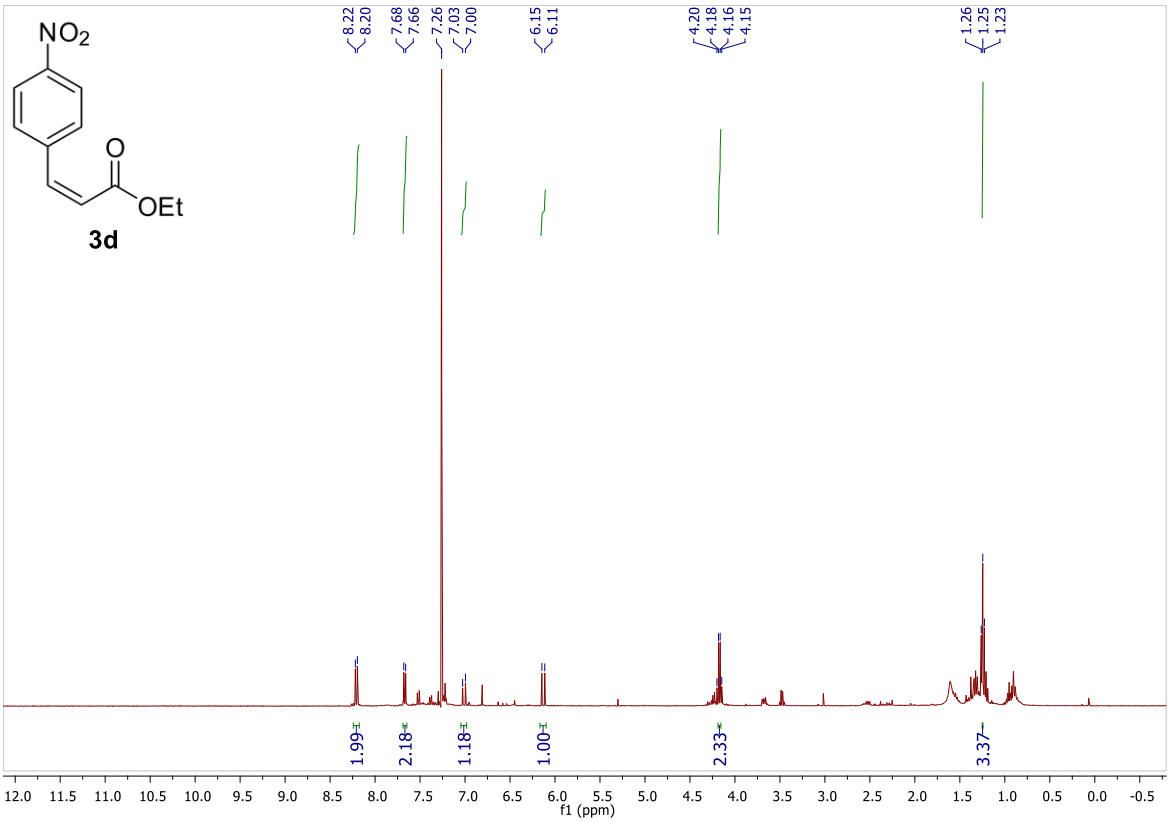
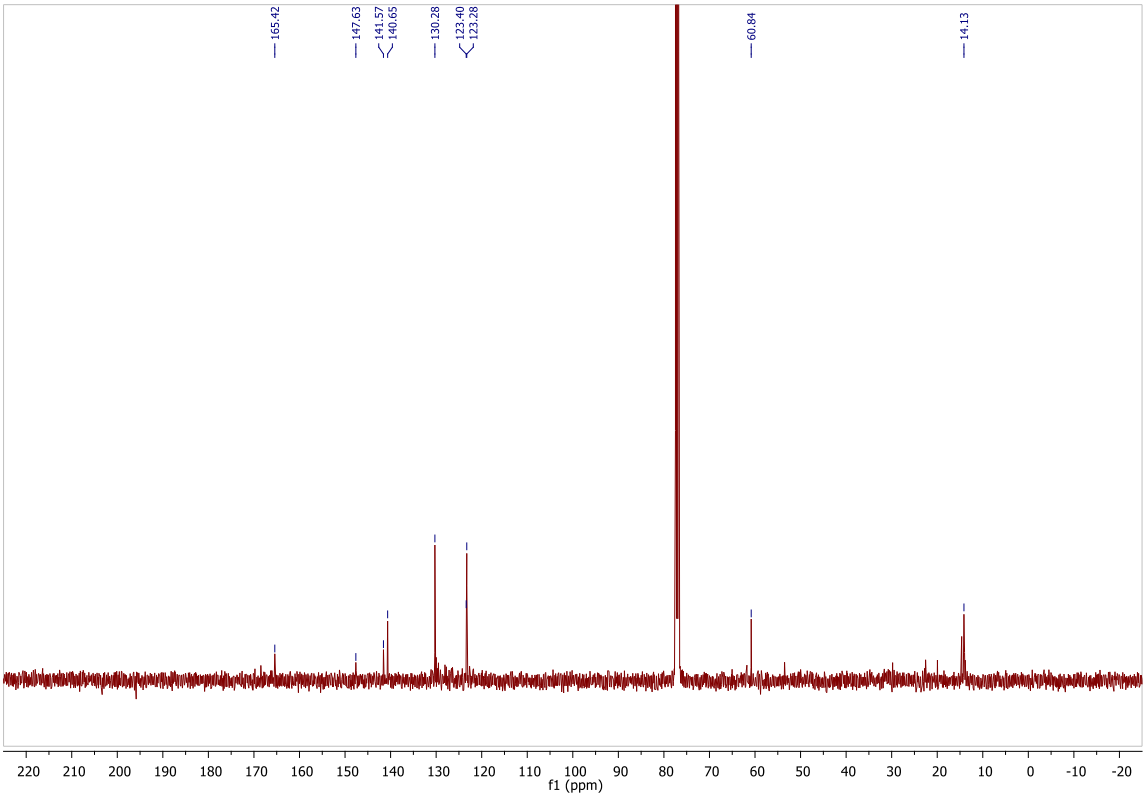
134.99
133.31
131.25
128.29
120.46
60.51
14.19
f1 (ppm)


NO2
O
OEt
3d
8.22
8.20
7.68
7.66
7.26
7.03
7.00
6.15
6.11
4.20
4.18
4.16
4.15
1.26
1.25
1.23
1.99
2.18
1.18
1.00
2.33
3.37
f1 (ppm)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147.63
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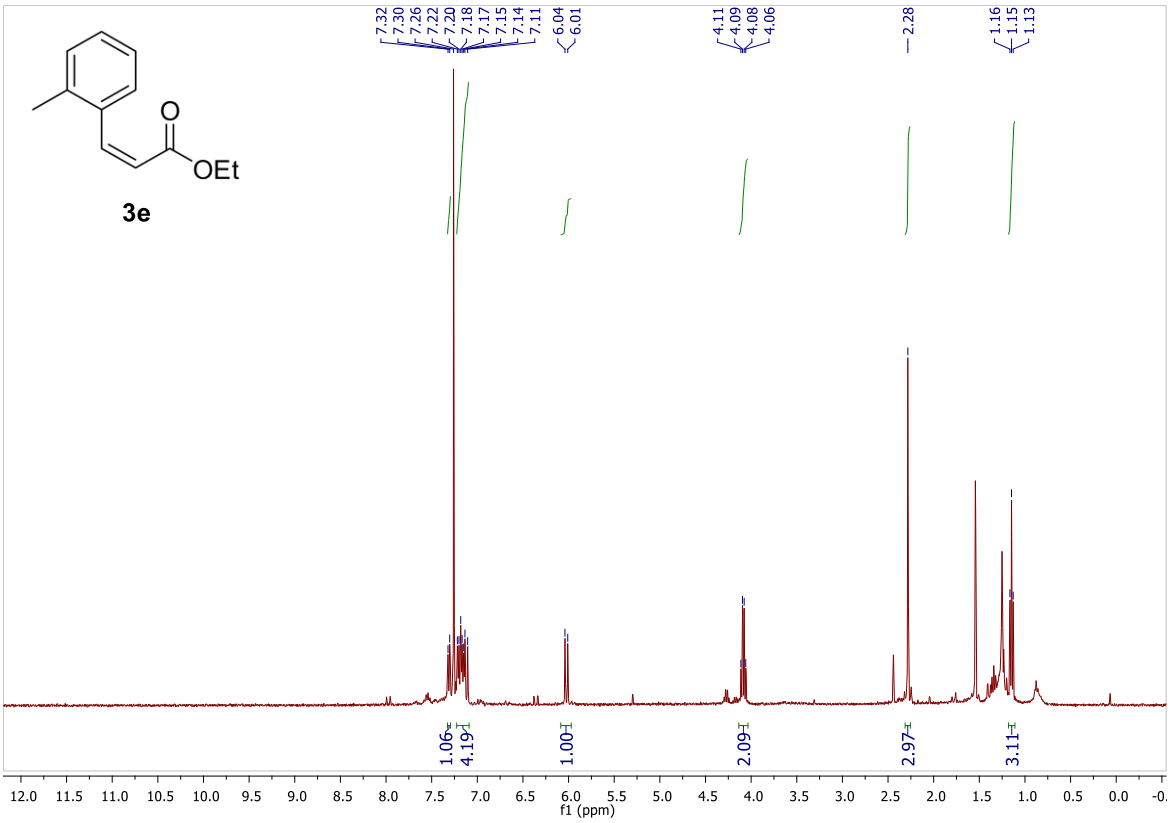
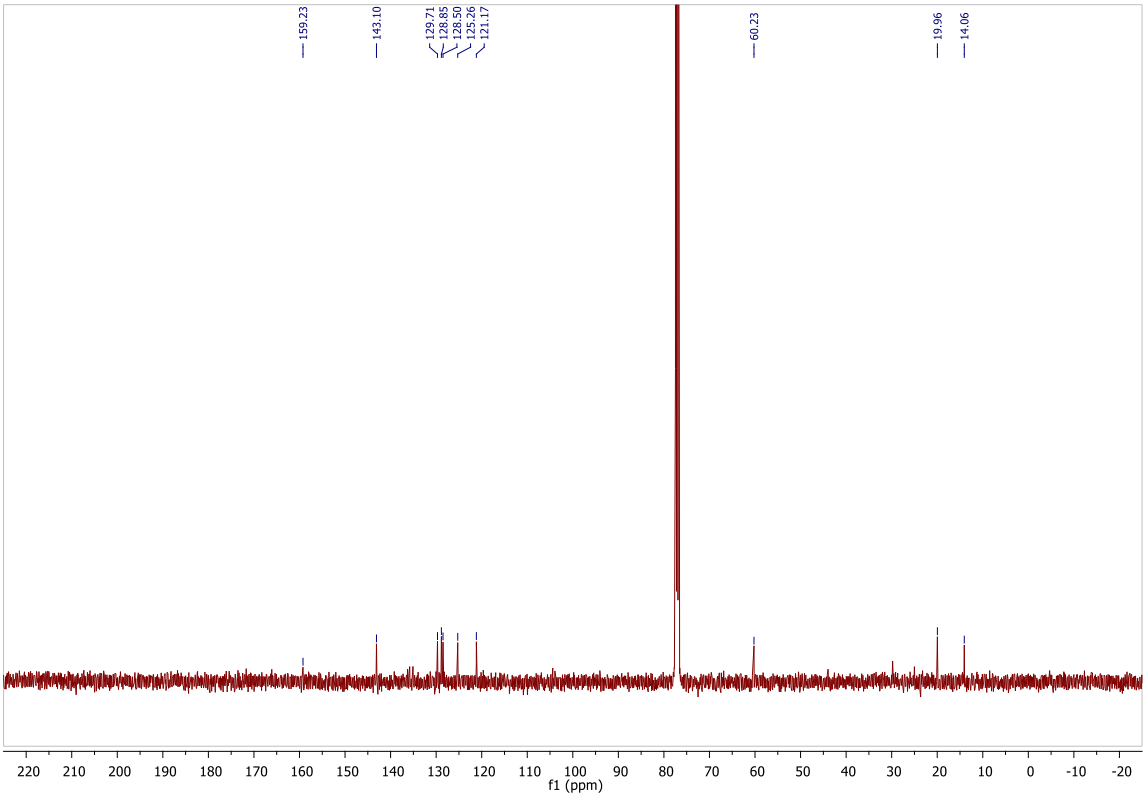
140.65
130.28
123.40
123.28
60.84
14.13
f1 (ppm)


7.32
7.30
7.26
7.22
7.20
7.18
7.17
7.15
7.14
7.11
6.04
6.01
4.11
4.09
4.08
4.06
2.28
1.16
1.15
1.13
O
OEt
3e
1.06
4.19
1.00
2.09
2.97
3.11
f1 (ppm)


159.23
143.10
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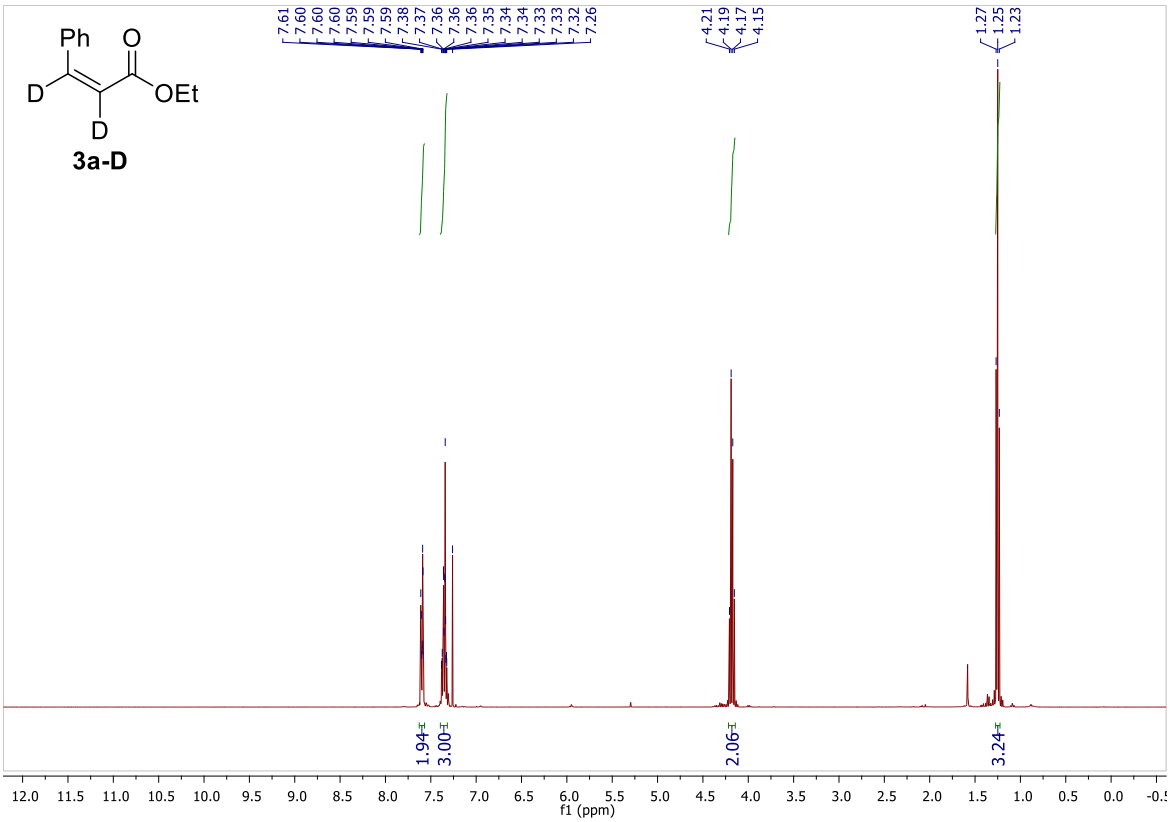
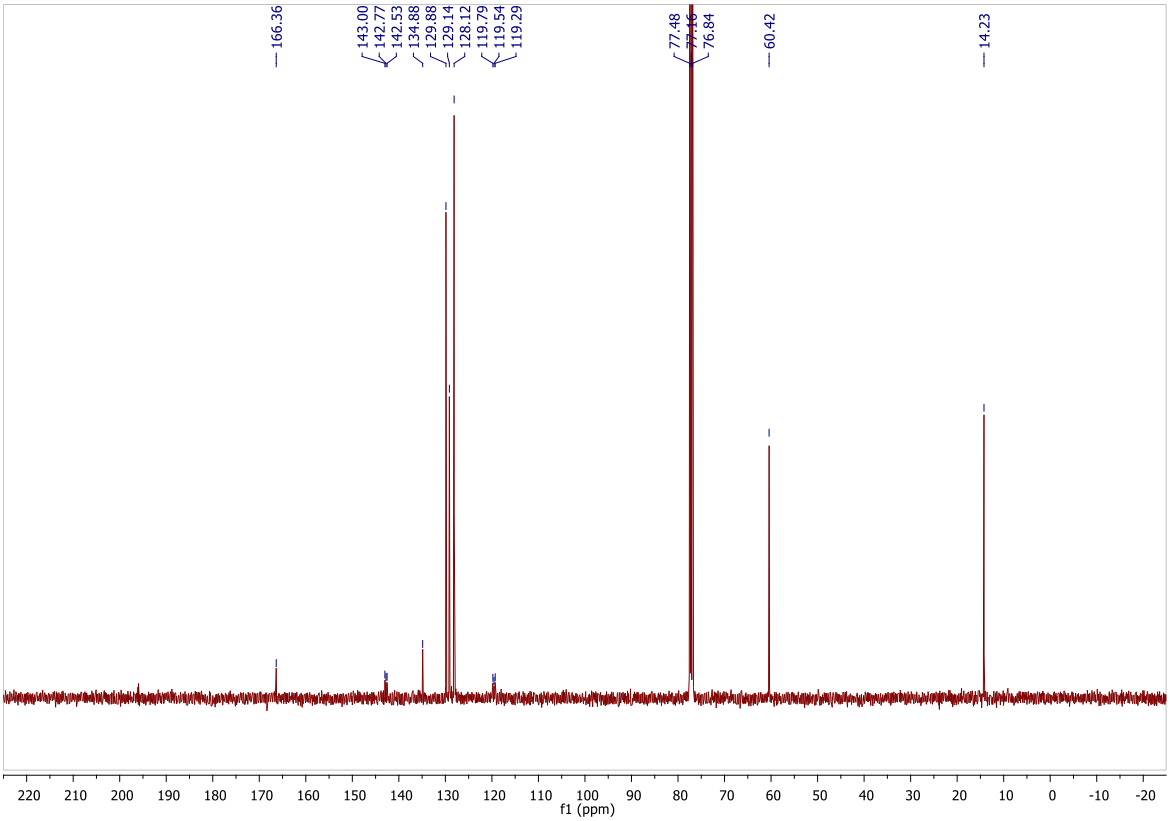
128.85
128.50
125.26
121.17
60.23
19.96
14.06
f1 (ppm)


Ph
O
D
OEt
D
3a-D
7.61
7.60
7.60
7.60
7.59
7.59
7.59
7.38
7.37
7.36
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.26
4.21
4.19
4.17
4.15
1.27
1.25
1.23
1.94
3.00
2.06
3.24
f1 (ppm)


166.36
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142.53
134.88
129.88
129.14
128.12
119.79
119.54
119.29
77.48
77.16
76.84
60.42
14.23
f1 (ppm)

4. References

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