Electronic Supplementary Material (ESI) for ChemComm.

Cu-Catalyzed Coupling of Vinylidene Cyclopropanes with Allyl and Allenyl Boronates

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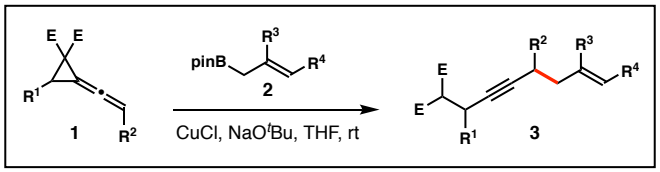
Supporting Information: Experimental Procedures, Tabulated Spectroscopic Data, ^{1}H and ^{13}C Spectra of New Compounds

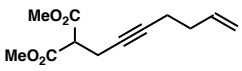
General Experimental Details. All reaction solvents were purified before use. Tetrahydrofuran, diethyl ether and toluene were purified by passing through a solvent column composed of activated A-1 alumina. Unless indicated otherwise, all reactions were conducted under an atmosphere of argon using flame-dried or oven-dried (120 ˚C) glassware. The term "concentrated under reduced pressure" refers to the removal of solvents and other volatile materials using a rotary evaporator with the water bath temperature below 30 ˚C, followed by the removal of residual solvents at high vacuum (< 0.2 mbar).

Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired on commercial instruments (500 and 600 MHz) at Auburn University NMR facility. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were acquired at 126 and 151 MHz. The proton signal for the residual non-deuterated solvent (δ 7.26 for chloroform and δ 2.05 for acetone) was used as an internal reference for ^{1}H NMR spectra. For ^{13}C NMR spectra, chemical shifts are reported relative to the resonance of chloroform (δ 77.36) and acetone (δ 29.84). Coupling constants are reported in Hz. High-resolution mass spectra were recorded on a commercial high-resolution mass spectrometer via the Micro Mass/Analytical Facility operated by the College of Chemistry and Biochemistry, Auburn University.

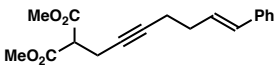
Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with Hanessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid) or $KMnO_4$. Column chromatography was generally performed using Kieselgel 60 (230-400 mesh) silica gel, typically using a 50-100:1 weight ratio of silica gel to crude product.



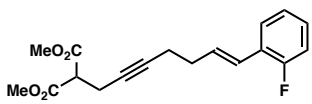
General procedure for the syntheses of compounds 3: In an Ar-filled glove box, to a reaction vial containing a Teflon-coated magnetic stirring bar were added CuCl (0.01 mmol, 10 mol %), NaO^{t}Bu (0.12 mmol, 1.2 equiv) and THF (0.5 mL). The mixture was stirred for 15 min at ambient temperature. Allylboronate **2** (0.11 mmol, 1.1 equiv) was then added and the mixture was stirred for 5 min. Vinylidene cyclopropane **1** (0.1 mmol, 1.0 equiv) was added and the mixture was stirred for 3 – 6 h at ambient temperature. Upon complete consumption of vinylidene cyclopropane **1**, the reaction mixture was filtered through a pad of silica gel and the solution was concentrated under reduced pressure. Purification of the crude product was performed by column chromatography (gradient elution with hexane and ethyl acetate) to give product **3**.



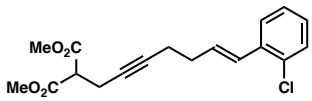
Dimethyl 2-(hept-6-en-2-yn-1-yl)malonate (3a) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 85% yield (19 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 – 5.86 (m, 1H), 4.99 – 5.06 (m, 2H), 3.76 (s, 6H), 3.56 (t, J = 7.8 Hz, 1H), 2.75 (d, J = 7.7 Hz, 2H), 2.20 (*app.* s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 137.3, 115.8, 82.3, 76.3, 53.1, 51.9, 33.3, 19.3, 18.8. HRMS (ESI$^+$): m/z for $C_{16}H_{25}O_4$ $[M+H]^+$ calcd. 281.1753, found 281.1752. HRMS (ESI$^+$): m/z for $C_{12}H_{16}O_4Na$ $[M+Na]^+$ calcd. 247.0946, found 247.0947.



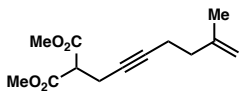
Dimethyl (*E*)-2-(7-phenylhept-6-en-2-yn-1-yl)malonate (3b) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 73% yield (22 mg, E:Z > 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 7.8 Hz, 2H), 7.30 (dd, J = 7.5, 7.5 Hz, 2H), 7.20 (dd, J = 7.1, 7.1 Hz, 1H), 6.42 (d, J = 15.8 Hz, 1H), 6.24 (dt, J = 15.8, 6.7 Hz, 1H), 3.73 (s, 6H), 3.57 (t, J = 7.5 Hz, 1H), 2.77 (d, J = 7.3 Hz, 2H), 2.36 (dt, J = 7.1, 6.7 Hz, 2H), 2.29 (t, J = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 137.9, 131.2, 129.1, 128.8, 127.4, 126.4, 82.2, 76.5, 53.1, 51.9, 32.7, 19.35, 19.30. HRMS (ESI$^+$): m/z for $C_{18}H_{21}O_4$ $[M+H]^+$ calcd. 301.1440, found 301.1430.



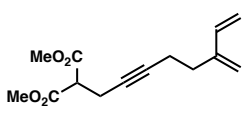
Dimethyl (*E*)-2-(7-(2-fluorophenyl)hept-6-en-2-yn-1-yl)malonate (3c) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 85% yield (27 mg, *E*:*Z* > 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.16 – 7.18 (m, Hz, 1H), 7.08 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.01 (dd, *J* = 9.8, 9.2 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.31 (dt, *J* = 16.0, 6.8 Hz, 1H), 3.74 (s, 6H), 3.57 (t, *J* = 7.6 Hz, 1H), 2.77 (d, *J* = 7.6 Hz, 2H), 2.39 (dt, *J* = 7.0, 6.7 Hz, 2H), 2.30 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 160.3 (d, *J* = 986.6 Hz), 131.8 (d, *J* = 17.9 Hz), 128.6 (d, *J* = 33.4 Hz), 127.5 (d, *J* = 15.8 Hz), 125.6 (d, *J* = 48.4 Hz), 124.4 (d, *J* = 14.2 Hz), 123.6 (d, *J* = 14.7 Hz), 115.9 (d, *J* = 87.9 Hz), 82.0, 76.7, 53.0, 51.9, 33.0, 19.3, 19.2. HRMS (ESI$^+$): m/z for $C_{18}H_{20}FO_4$ $[M+H]^+$ calcd. 319.1346, found 319.1331.



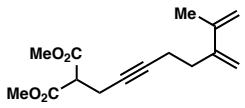
Dimethyl (*E*)-2-(7-(2-chlorophenyl)hept-6-en-2-yn-1-yl)malonate (3d) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 81% yield (27 mg, *E*:*Z* > 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.21 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.14 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.80 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.73 (s, 6H), 3.58 (t, *J* = 7.8 Hz, 1H), 2.77 (d, *J* = 7.6 Hz, 2H), 2.41 (dt, *J* = 7.0, 6.8 Hz, 2H), 2.31 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 135.9, 133.0, 132.1, 129.9, 128.5, 127.5, 127.12, 127.10, 82.0, 76.7, 53.0, 51.9, 32.8, 19.29, 19.25. HRMS (ESI$^+$): m/z for $C_{18}H_{20}ClO_4$ $[M+H]^+$ calcd. 335.1050, found 335.1051.



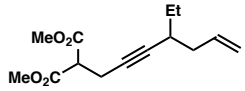
Dimethyl 2-(6-methylhept-6-en-2-yn-1-yl)malonate (3e) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 84% yield (20 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.74 (s, 1H), 4.69 (s, 1H), 3.76 (s, 6H), 3.55 (t, *J* = 7.7 Hz, 1H), 2.75 (d, *J* = 7.7 Hz, 2H), 2.25 (t, *J* = 7.3 Hz, 2H), 2.16 (t, *J* = 7.3 Hz, 2H), 1.71 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 144.5, 111.0, 82.5, 76.2, 53.0, 51.9, 37.2, 22.6, 19.3, 17.7. HRMS (ESI$^+$): m/z for $C_{13}H_{19}O_4$ $[M+H]^+$ calcd. 239.1283, found 239.1289.



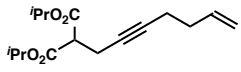
Dimethyl 2-(6-methyleneoct-7-en-2-yn-1-yl)malonate (3f) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 72% yield (18 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.20 (d, *J* = 17.7 Hz, 1H), 5.02 – 5.07 (m, 3H), 3.76 (s, 6H), 3.56 (t, *J* = 7.7 Hz, 1H), 2.75 (d, *J* = 7.7 Hz, 2H), 2.38 (t, *J* = 7.4 Hz, 2H), 2.31 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 144.9, 138.8, 116.7, 113.6, 82.5, 76.4, 53.1, 51.9, 31.1, 19.3, 18.1. HRMS (ESI^+): m/z for $C_{14}H_{18}O_4Na$ $[M+Na]^+$ calcd. 273.1103, found 273.1101.



Dimethyl 2-(7-methyl-6-methyleneoct-7-en-2-yn-1-yl)malonate (3g) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 83% yield (22 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12 (s, 1H), 5.04 (s, 1H), 4.98 (s, 2H), 3.76 (s, 6H), 3.56 (t, *J* = 7.7 Hz, 1H), 2.75 (d, *J* = 7.5 Hz, 2H), 2.44 (t, *J* = 7.5 Hz, 2H), 2.29 (t, *J* = 7.1 Hz, 2H), 1.90 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 146.4, 142.5, 113.2, 112.9, 82.6, 76.3, 53.1, 51.9, 33.4, 21.4, 19.3, 18.8. HRMS (ESI^+): m/z for $C_{15}H_{20}O_4Na$ $[M+Na]^+$ calcd. 287.1259, found 287.1261.

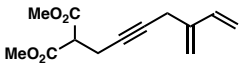


Dimethyl 2-(4-ethylhept-6-en-2-yn-1-yl)malonate (3h) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 83% yield (21 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.79 – 5.85 (m, 1H), 5.04 (d, *J* = 17.8 Hz, 1H), 5.01 (d, *J* = 10.0 Hz, 1H), 3.75 (s, 6H), 3.58 (t, *J* = 7.9 Hz, 1H), 2.77 (dd, *J* = 7.8, 1.9 Hz, 2H), 2.23 – 2.26 (m, 1H), 2.11 – 2.18 (m, 2H), 1.42 – 1.49 (m, 1H), 1.30 – 1.38 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 136.5, 116.6, 85.6, 77.3, 53.1, 51.9, 39.4, 33.4, 27.8, 19.3, 11.9. HRMS (ESI^+): m/z for $C_{14}H_{21}O_4$ $[M+H]^+$ calcd. 253.1440, found 253.1448.

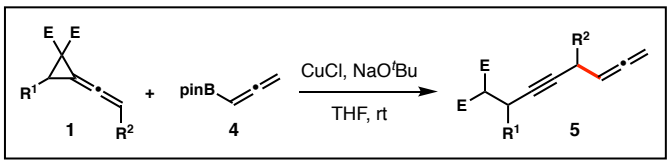


Diisopropyl 2-(hept-6-en-2-yn-1-yl)malonate (3i) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 86% yield (24 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.79 – 5.86 (m, 1H), 5.02 – 5.09 (m, 3H), 4.99 (d, *J* = 10.3 Hz, 1H), 3.44 (t, *J* = 7.8 Hz, 1H), 2.71 (d, *J* = 7.7 Hz, 2H), 2.19 (*app.* s, 4H), 1.25 (d, *J* = 5.9 Hz, 6H), 1.24 (d, *J* = 5.8

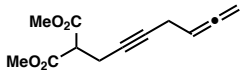
Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1, 137.4, 115.8, 81.9, 76.5, 69.5, 52.4, 33.3, 22.0, 21.9, 18.9, 18.8. HRMS (ESI^+): m/z for $C_{16}H_{25}O_4$ $[M+H]^+$ calcd. 281.1753, found 281.1752.



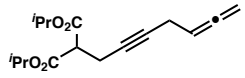
Dimethyl 2-(5-methylenehept-6-en-2-yn-1-yl)malonate (12) Prepared according to the general procedure. The crude mixture was purified (hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 89% yield (21 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.42 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.35 (s, 1H), 5.18 (d, *J* = 17.6 Hz, 1H), 5.13 (s, 1H), 5.08 (d, *J* = 10.9 Hz, 1H), 3.76 (s, 6H), 3.60 (t, *J* = 7.7 Hz, 1H), 3.05 (s, 2H), 2.81 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 141.3, 138.0, 117.5, 113.9, 79.4, 78.9, 53.1, 51.7, 22.0, 19.3. HRMS (ESI^+): m/z for $C_{13}H_{16}O_4Na$ $[M+Na]^+$ calcd. 259.0946, found 259.0948.



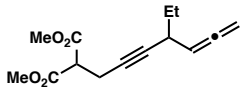
General procedure for the synthesis of compound 5: In an Ar-filled glove box, to a reaction vial containing a Teflon-coated magnetic stirring bar were added CuCl (0.01 mmol, 10 mol %), NaO^{t}Bu (0.12 mmol, 1.2 equiv) and THF (0.5 mL). The mixture was stirred for 15 min at ambient temperature. Allenyl boronate **4** (0.11 mmol, 1.1 equiv) was then added and the mixture was stirred for 5 min. Vinylidene cyclopropane **1** (0.1 mmol, 1.0 equiv) was added and the mixture was stirred for 3 – 6 h at ambient temperature. Upon complete consumption of vinylidene cyclopropane **1**, the reaction mixture was filtered through a pad of silica gel and the solution was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate) to give product **5**.



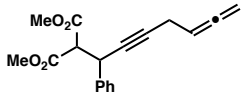
Dimethyl 2-(hepta-5,6-dien-2-yn-1-yl)malonate (5a) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 76% yield (17 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.05 – 5.10 (m, 1H), 4.76 – 4.78 (m, 2H), 3.76 (s, 6H), 3.57 (t, *J* = 7.7 Hz, 1H), 2.86 – 2.87 (m, 2H), 2.78 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.8, 168.9, 87.1, 80.0, 77.2, 76.9, 53.1, 51.8, 19.2, 19.1. HRMS (ESI^+): m/z for $C_{12}H_{15}O_4$ $[M+H]^+$ calcd. 223.0964, found 223.0970.



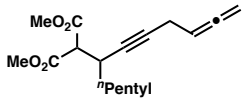
Diisopropyl 2-(hepta-5,6-dien-2-yn-1-yl)malonate (5b) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 90% yield (25 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.03 – 5.09 (m, 3H), 4.75 – 4.77 (m, 2H), 3.45 (t, *J* = 7.8 Hz, 1H), 2.85 – 2.87 (m, 2H), 2.73 – 2.74 (m, 2H), 1.25 (d, *J* = 5.9 Hz, 6H), 1.24 (d, *J* = 5.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.7, 168.1, 87.1, 79.6, 77.4, 76.9, 69.5, 52.2, 22.0, 21.9, 19.1, 19.0. HRMS (ESI$^+$): m/z for $C_{16}H_{22}O_4Na$ $[M+Na]^+$ calcd. 301.1416, found 301.1421.



Dimethyl 2-(4-ethylhepta-5,6-dien-2-yn-1-yl)malonate (5c) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 80% yield (20 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.05 – 5.08 (m, 1H), 4.78 (d, *J* = 2.0 Hz, 1H), 4.77 (d, *J* = 2.0 Hz, 1H), 3.76 (s, 6H), 3.58 (t, *J* = 7.8 Hz, 1H), 2.90 – 2.94 (m, 1H), 2.79 (dd, *J* = 7.8, 1.7 Hz, 2H), 1.46 – 1.59 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.9, 168.9, 92.3, 83.8, 77.8, 77.1, 53.1, 51.8, 33.1, 28.9, 19.3, 11.7. HRMS (ESI$^+$): m/z for $C_{14}H_{19}O_4$ $[M+H]^+$ calcd. 251.1283, found 251.1277.

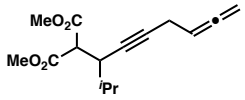


Dimethyl 2-(1-phenylhepta-5,6-dien-2-yn-1-yl)malonate (5d) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 74% yield (22 mg). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.42 (d, *J* = 7.7 Hz, 2H), 7.32 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.26 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.12 – 5.17 (m, 1H), 4.79 – 4.81 (m, 2H), 4.33 (d, *J* = 10.4 Hz, 1H), 3.78 (d, *J* = 10.4 Hz, 1H), 3.74 (s, 3H), 3.48 (s, 3H), 2.91 – 2.93 (m, 2H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 209.4, 168.0, 167.6, 139.6, 129.3, 129.2, 128.4, 87.4, 82.2, 81.0, 76.9, 60.1, 52.9, 52.7, 38.6, 19.0. HRMS (ESI$^+$): m/z for $C_{18}H_{18}O_4Na$ $[M+Na]^+$ calcd. 321.1103, found 321.1117.

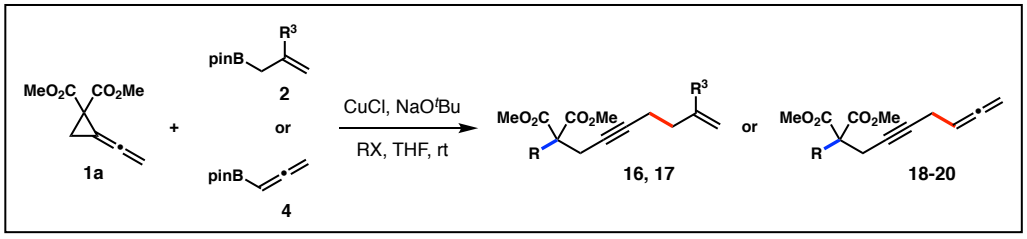


Dimethyl 2-(dodeca-10,11-dien-7-yn-6-yl)malonate (5e) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 86% yield (25 mg). ^{1}H NMR (500 MHz, Acetone-d_6) δ 5.10 – 5.15 (m, 1H), 4.78 – 4.80 (m, 2H), 3.70 (s, 6H), 3.45 (d, *J* = 9.5 Hz, 1H), 3.04 – 3.07 (m, 1H), 2.87 – 2.89 (m, 2H), 1.55 – 1.61 (m, 1H), 1.48 –

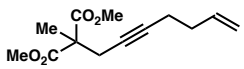
1.52 (m, 1H), 1.38 – 1.45 (m, 2H), 1.25 – 1.31 (m, 4H), 0.89 (t, J = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 209.3, 168.6, 168.5, 87.7, 81.4, 81.1, 76.8, 57.4, 52.7, 52.6, 33.4, 32.7, 32.1, 27.5, 23.2, 19.0, 14.3. HRMS (ESI$^+$): m/z for $C_{17}H_{25}O_4$ $[M+H]^+$ calcd. 293.1753, found 293.1751.



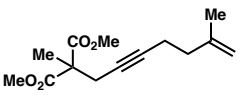
Dimethyl 2-(2-methylnona-7,8-dien-4-yn-3-yl)malonate (5f) Prepared according to the general procedure. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give the title compound as colorless oil in 83% yield (22 mg). ^{1}H NMR (500 MHz, Acetone-d_6) δ 5.11 – 5.16 (m, 1H), 4.79 – 4.81 (m, 2H), 3.70 (s, 6H), 3.50 (d, J = 10.8 Hz, 1H), 3.08 (dd, J = 10.8, 1.4 Hz, 1H), 2.90 – 2.91 (m, 2H), 1.71 – 1.77 (m, 1H), 1.01 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 209.4, 168.6, 168.5, 87.7, 82.4, 78.8, 76.9, 55.8, 52.9, 52.7, 39.5, 29.5, 22.1, 19.0, 17.0. HRMS (ESI$^+$): m/z for $C_{15}H_{21}O_4$ $[M+H]^+$ calcd. 265.1440, found 265.1446.



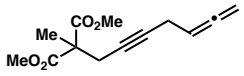
General procedure for the three-component reactions: In an Ar-filled glove box, to a reaction vial containing a Teflon-coated magnetic stirring bar were added CuCl (0.01 mmol, 10 mol %), NaO^{t}Bu (0.12 mmol, 1.2 equiv) and THF (0.5 mL), the resulting mixture was stirred for 15 min at ambient temperature. Allylboronate **2** or allenylboronate **4** (0.11 mmol, 1.1 equiv) was added and the mixture was stirred for 5 min. Then vinylidene cyclopropane **1a** (0.1 mmol, 1.0 equiv) and the trapping agent RX (0.2 mmol, 2.0 equiv) were added sequentially. The mixture was stirred for 3 – 6 h at ambient temperature. Upon complete consumption of vinylidene cyclopropane **1a**, the reaction mixture was filtered through a pad of silica gel and the solution was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate) to give product as colorless oil.



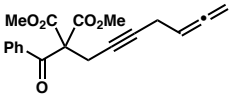
Dimethyl 2-(hept-6-en-2-yn-1-yl)-2-methylmalonate (16) Prepared according to the general procedure from **1a** and **2a** with iodomethane as the trapping agent. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give compound **16** as colorless oil in 84% yield (20 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 – 5.86 (m, 1H), 5.05 (d, *J* =17.1 Hz, 1H), 5.01 (d, *J* =10.1 Hz, 1H), 3.73 (s, 6H), 2.75 (s, 2H), 2.21 (*app.* s, 4H), 1.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 137.3, 115.9, 83.1, 75.5, 53.9, 53.1, 33.4, 26.6, 20.3, 18.9. HRMS (ESI$^+$): m/z for $C_{13}H_{19}O_4$ $[M+H]^+$ calcd. 239.1283, found 239.1277.



Dimethyl 2-methyl-2-(6-methylhept-6-en-2-yn-1-yl)malonate (17) Prepared according to the general procedure from **1a** and **2e** with iodomethane as the trapping agent. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give compound **17** as colorless oil in 71% yield (18 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.74 (s, 1H), 4.70 (s, 1H), 3.73 (s, 6H), 2.75 (s, 2H), 2.26 (t, *J* = 7.2 Hz, 2H), 2.16 (t, *J* = 7.3 Hz, 2H), 1.71 (s, 3H), 1.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 144.5, 111.1, 83.3, 75.3, 53.9, 53.0, 37.3, 26.6, 22.6, 20.2, 17.7. HRMS (ESI$^+$): m/z for $C_{14}H_{21}O_4$ $[M+H]^+$ calcd. 253.1440, found 253.1443.

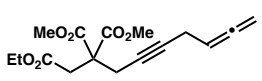


Dimethyl 2-(hepta-5,6-dien-2-yn-1-yl)-2-methylmalonate (18) Prepared according to the general procedure from **1a** and **4** with iodomethane as the trapping agent. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 20:1 to 15:1) to give compound **18** as colorless oil in 85% yield (20 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.08 – 5.13 (m, 1H), 4.78 – 4.81 (m, 2H), 3.76 (s, 6H), 2.89 – 2.91 (m, 2H), 2.80 (s, 2H), 1.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.9, 171.9, 87.2, 80.8, 77.0, 76.3, 53.8, 53.1, 26.6, 20.3, 19.1. HRMS (ESI$^+$): m/z for $C_{13}H_{16}O_4Na$ $[M+Na]^+$ calcd. 259.0946, found 259.0942.

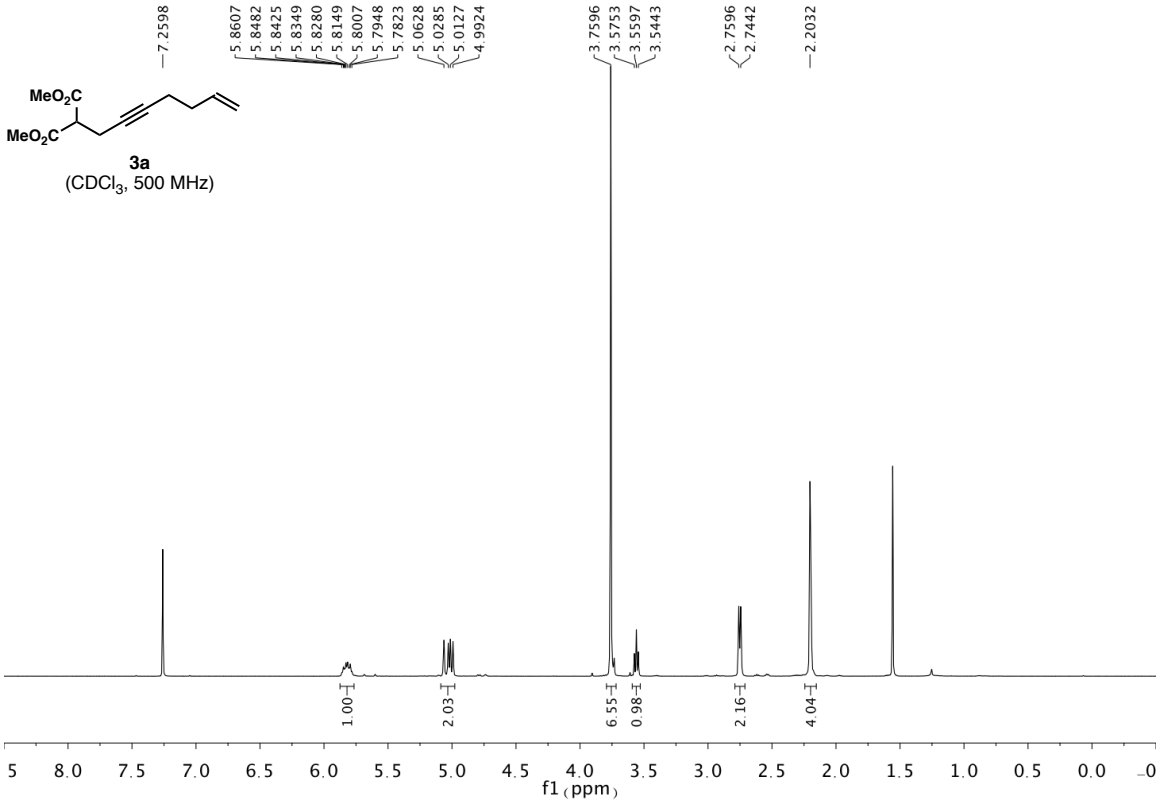


Dimethyl 2-benzoyl-2-(hepta-5,6-dien-2-yn-1-yl)malonate (19) Prepared according to the general procedure from **1a** and **4** with benzoyl fluoride as the trapping agent. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 15:1 to 10:1) to give compound **19** as colorless oil in 67% yield (22 mg). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.86 (d, *J* = 7.9 Hz, 2H), 7.63 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.51 (dd, *J* = 7.6, 7.6 Hz, 2H), 5.00 – 5.05 (m, 1H), 4.73 – 4.75 (m, 2H), 3.74 (s, 6H), 3.11 (s, 2H), 2.78 –

2.82 (m, 2H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 209.3, 191.8, 168.1, 136.6, 134.0, 129.7, 129.4, 87.4, 81.1, 76.7, 76.6, 69.4, 53.4, 25.3, 19.1. HRMS (ESI$^+$): m/z for $C_{19}H_{18}O_5Na$ $[M+Na]^+$ calcd. 349.1052, found 349.1055.



Ethyl 2,2-dimethyl nona-7,8-dien-4-yne-1,2,2-tricarboxylate (20) Prepared according to the general procedure from **1a** and **4** with ethyl bromoacetate as the trapping agent. The crude mixture was purified by column chromatography (gradient elution, hexane:ethyl acetate = 15:1 to 10:1) to give compound **20** as colorless oil in 75% yield (23 mg). ^{1}H NMR (500 MHz, Acetone-d_6) δ 5.10 – 5.15 (m, 1H), 4.79 – 4.82 (m, 2H), 4.10 (q, J = 7.1 Hz, 2H), 3.70 (s, 6H), 3.12 (s, 2H), 2.94 (s, 2H), 2.87 – 2.89 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 209.4, 170.7, 169.9, 87.5, 81.6, 77.0, 76.5, 61.2, 55.8, 53.3, 37.5, 24.4, 18.9, 14.4. HRMS (ESI$^+$): m/z for $C_{16}H_{21}O_6$ $[M+H]^+$ calcd. 309.1338, found 309.1335.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5.8425
5.8349
5.8280
5.8149
5.8007
5.7948
5.7823
5.0628
5.0285
5.0127
4.9924
3.7596
3.5753
3.5597
3.5443
2.7596
2.7442
2.2032
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MeO2C
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(CDCl3, 500 MHz)
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0.98
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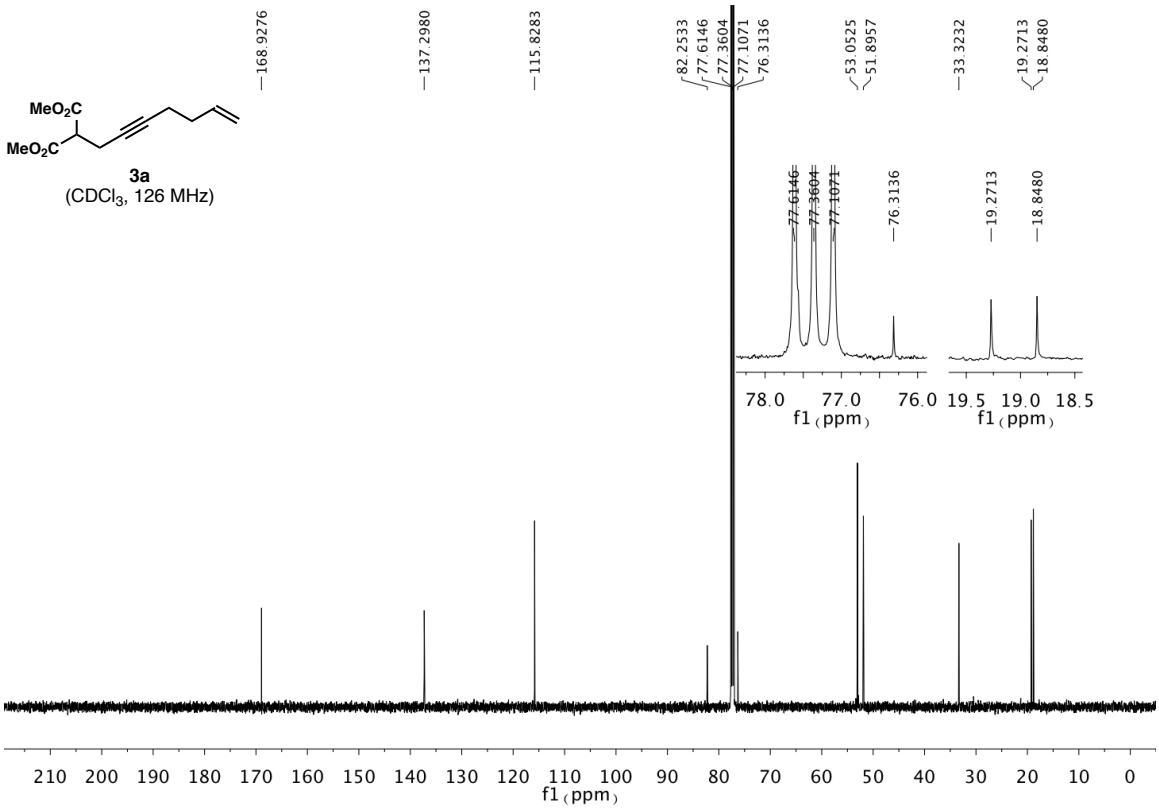
4.04
f1 (ppm)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53.0525
51.8957
33.3232
19.2713
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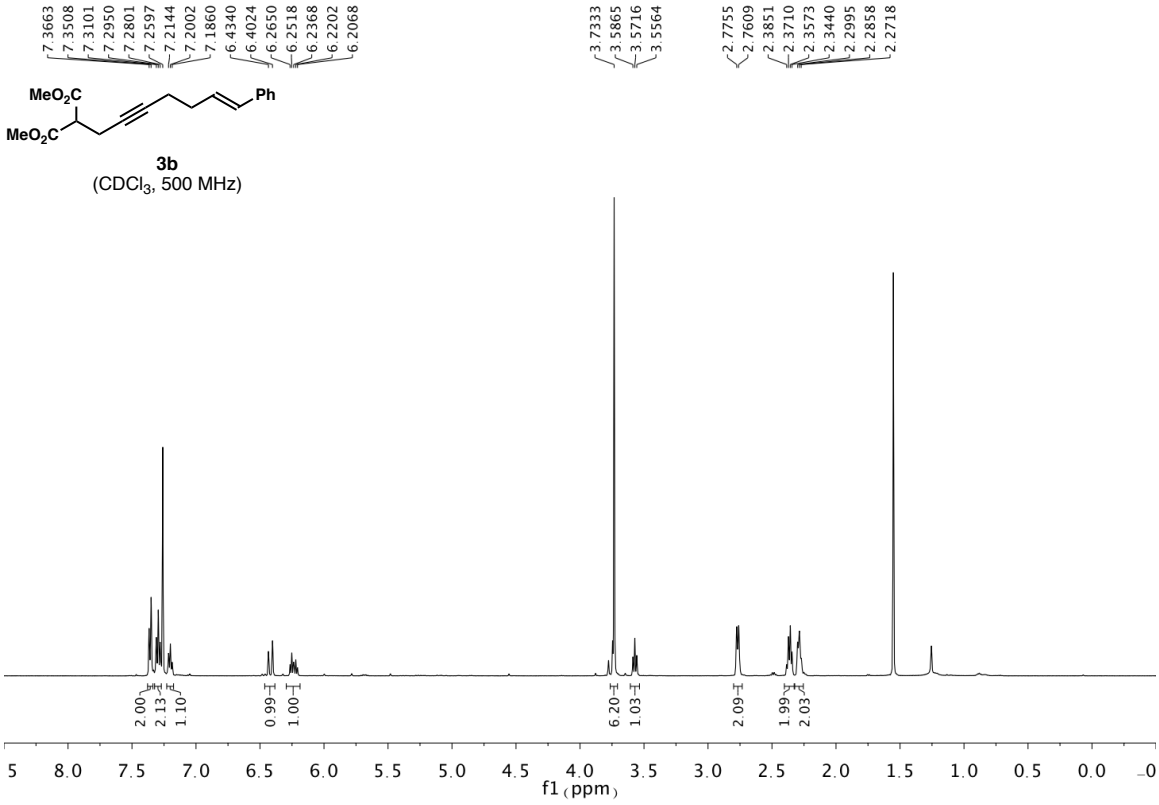
MeO2C
MeO2C
3a
(CDCl3, 126 MHz)
f1 (ppm)
f1 (ppm)
f1 (ppm)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7.2801
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6.4024
6.2650
6.2518
6.2368
6.2202
6.2068
3.7333
3.5865
3.5716
3.5564
2.7755
2.7609
2.3851
2.3710
2.3573
2.3440
2.2995
2.2858
2.2718
MeO2C
MeO2C
Ph
3b
(CDCl3, 500 MHz)
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1.10
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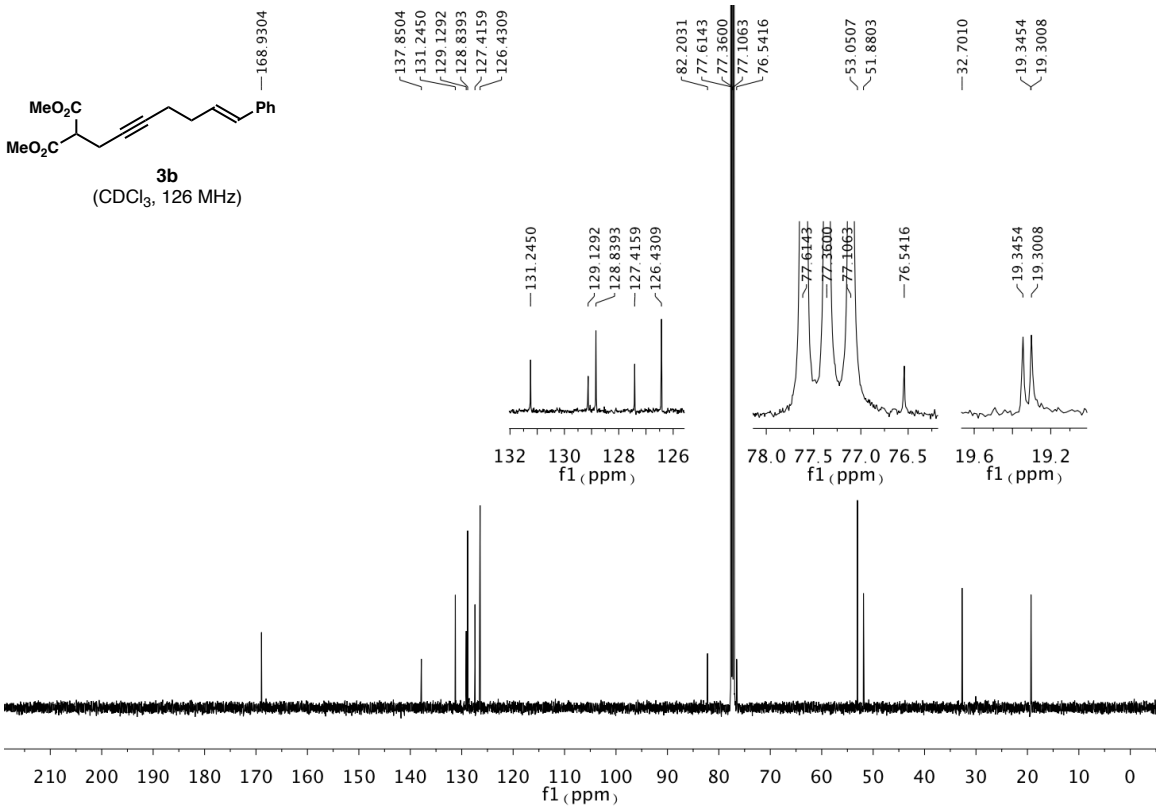
1.00
6.20
1.03
2.09
1.99
2.03
f1 (ppm)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76.5416
53.0507
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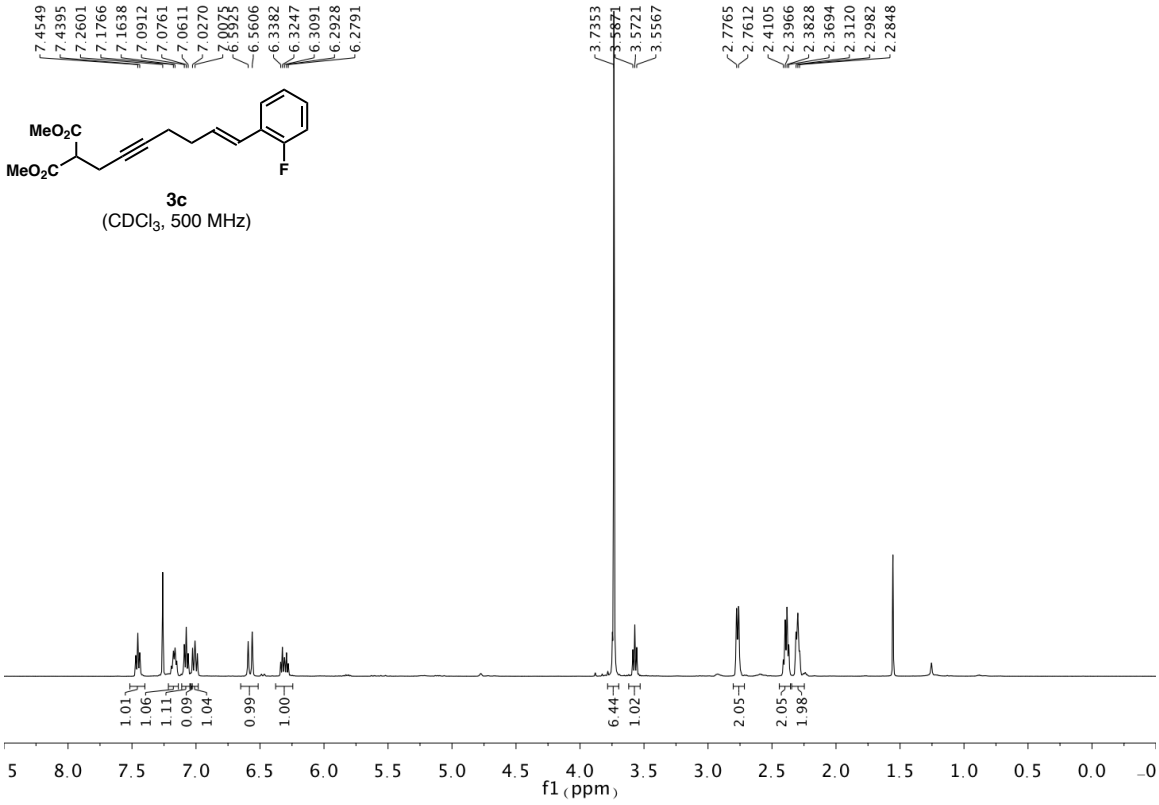
19.3454
19.3008
MeO2C
MeO2C
Ph
3b
(CDCl3, 126 MHz)
f1 (ppm)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6.3247
6.3091
6.2928
6.2791
3.7353
3.5871
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3.5567
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2.4105
2.3966
2.3828
2.3694
2.3120
2.2982
2.2848
MeO2C
MeO2C
F
3c
(CDCl3, 500 MHz)
1.01
1.06
1.11
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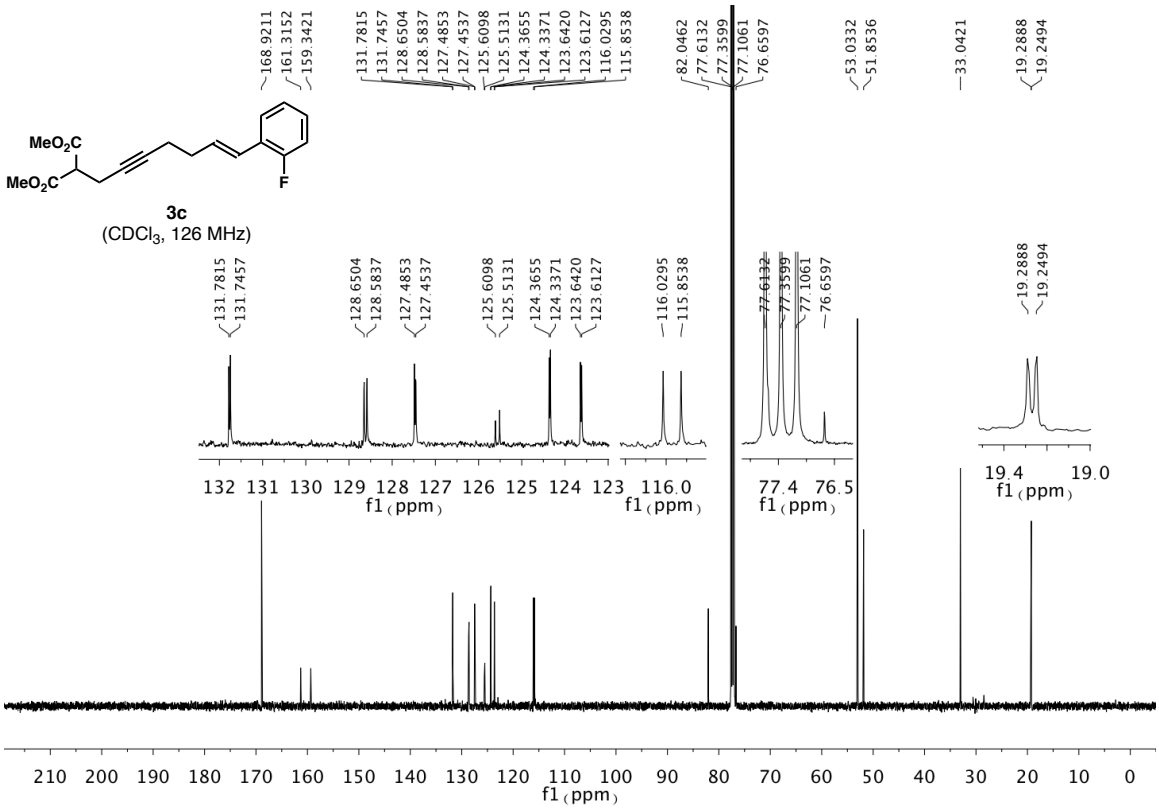
1.04
0.99
1.00
6.44
1.02
2.05
2.05
1.98
f1 (ppm)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123.6420
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77.6132
77.3599
77.1061
76.6597
53.0332
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MeO2C
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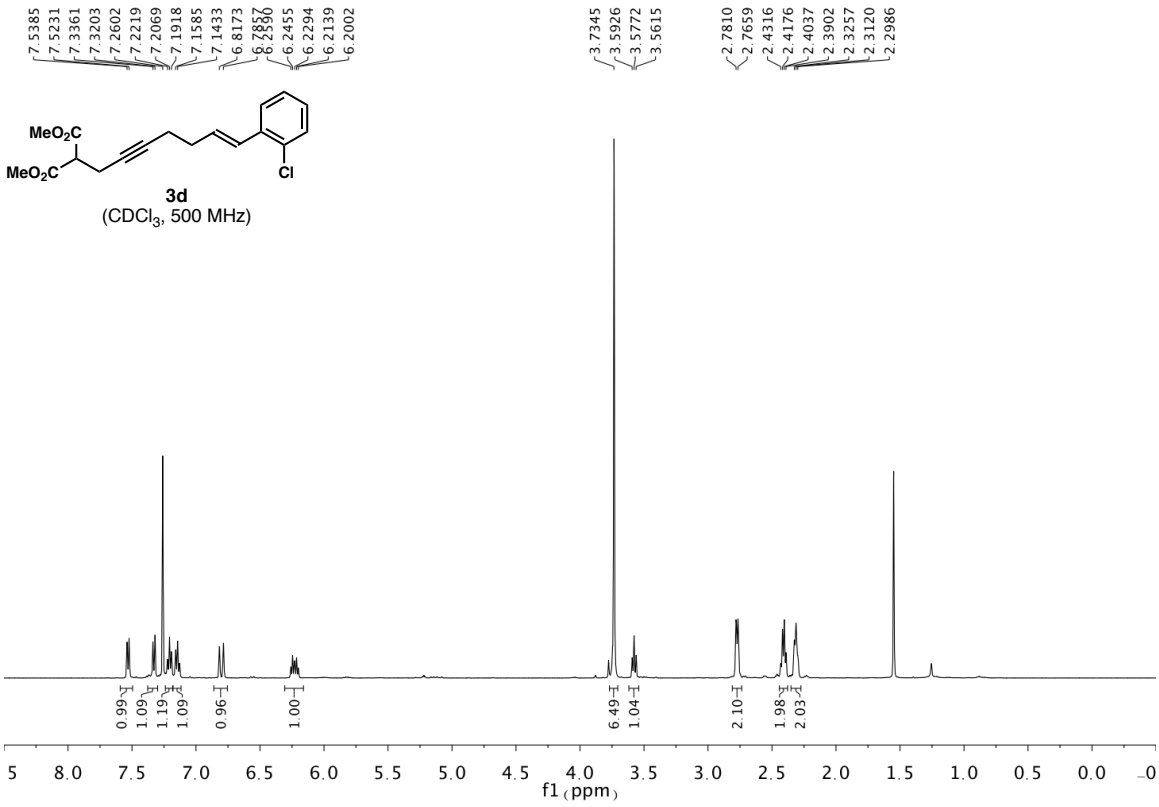
f1 (ppm)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6.2002
3.7345
3.5926
3.5772
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2.7810
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2.4176
2.4037
2.3902
2.3257
2.3120
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MeO2C
MeO2C
Cl
3d
(CDCl3, 500 MHz)
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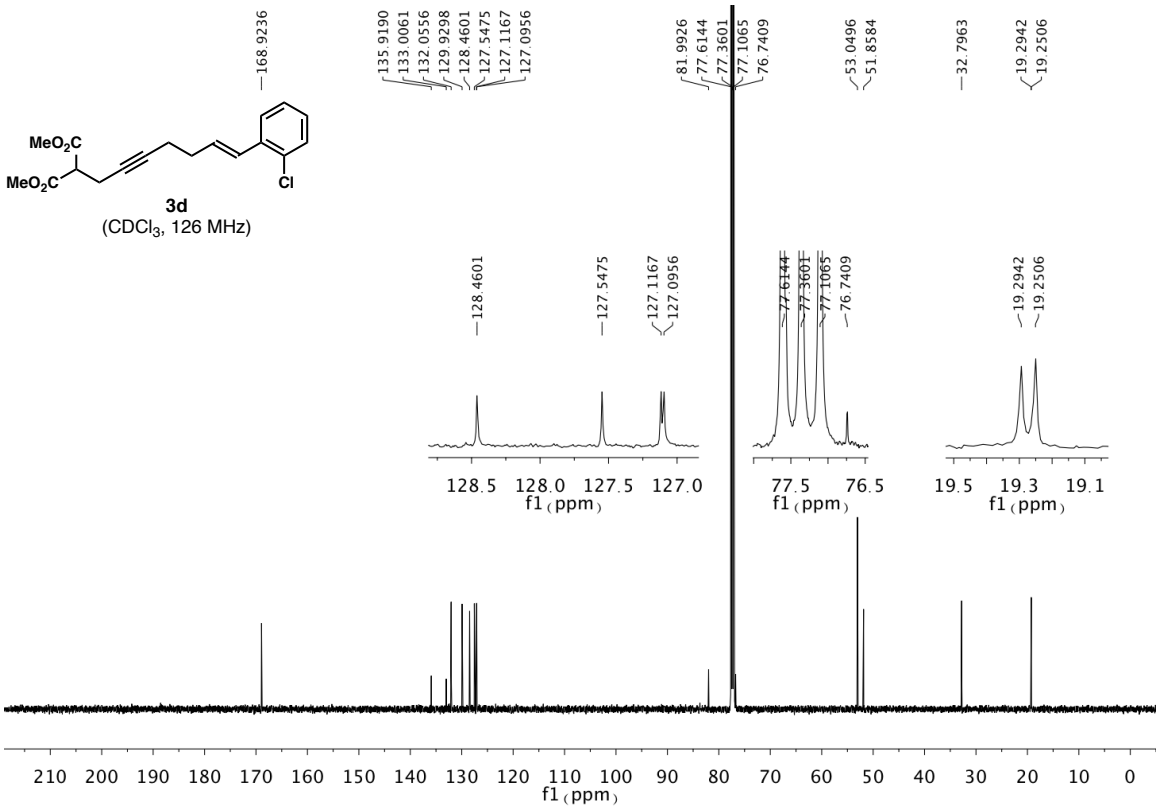
2.03
f1 (ppm)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77.3601
77.1065
76.7409
53.0496
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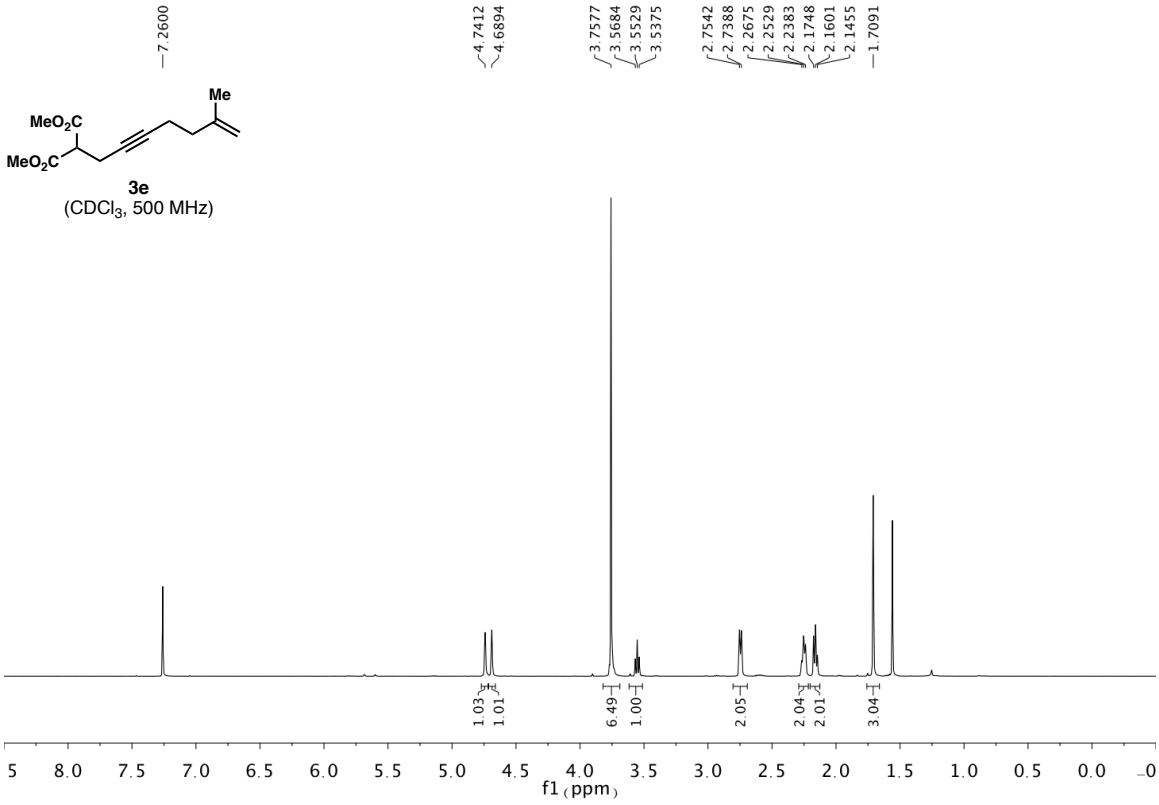
19.2942
19.2506
MeO2C
MeO2C
Cl
3d
(CDCl3, 126 MHz)
f1 (ppm)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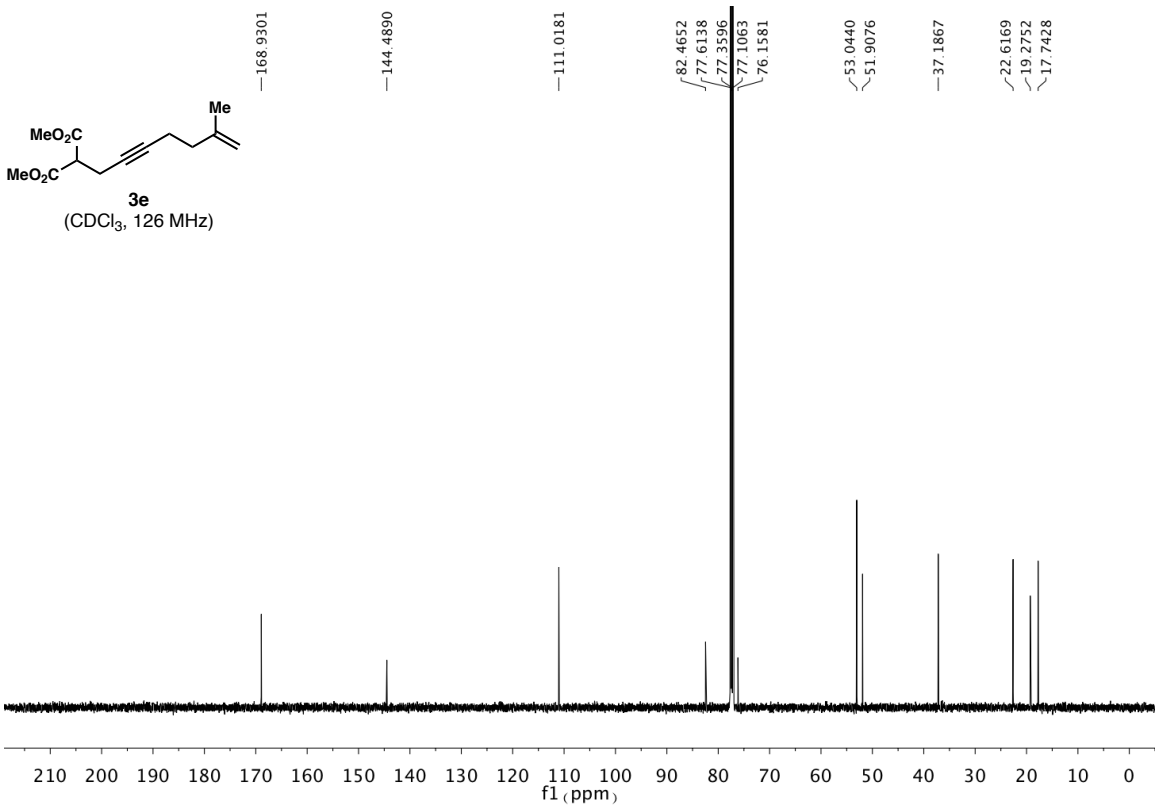
2.7388
2.2675
2.2529
2.2383
2.1748
2.1601
2.1455
1.7091
Me
MeO2C
MeO2C
3e
(CDCl3, 500 MHz)
1.03
1.01
6.49
1.00
2.05
2.04
2.01
3.04
f1 (ppm)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19.2752
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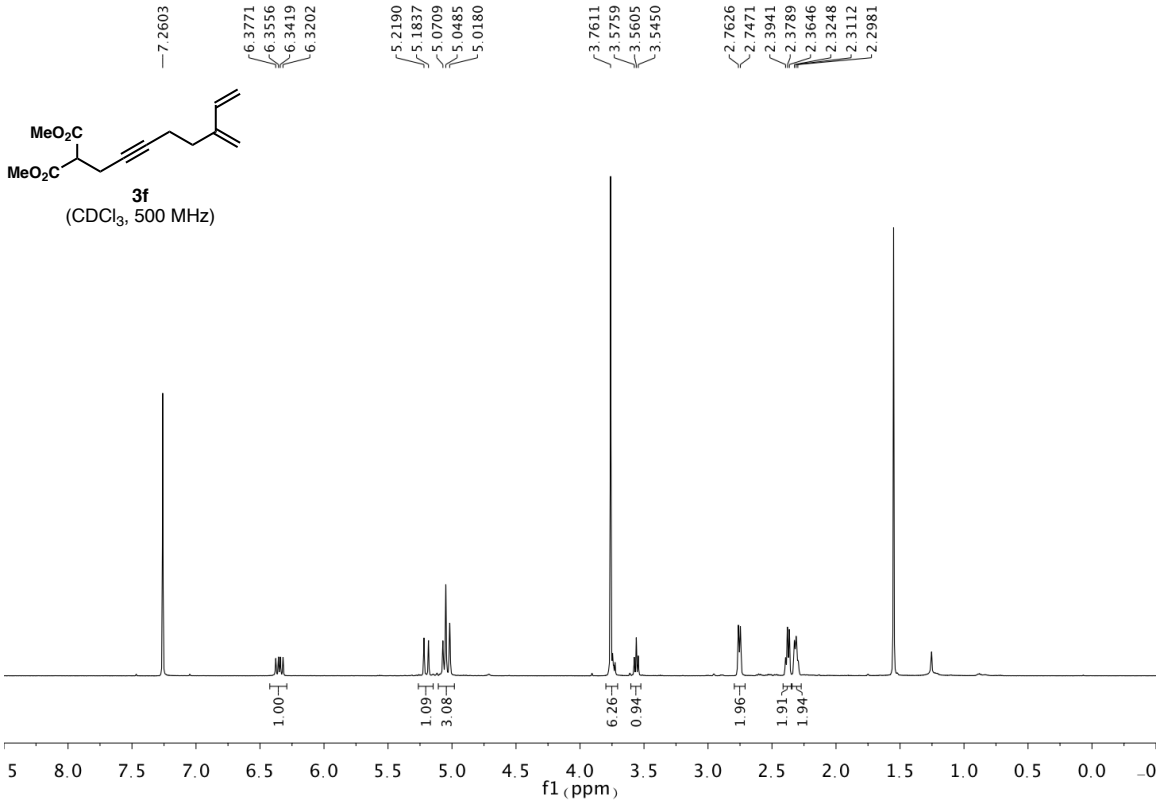
Me
MeO2C
MeO2C
3e
(CDCl3, 126 MHz)
f1 (ppm)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2.3112
2.2981
MeO2C
MeO2C
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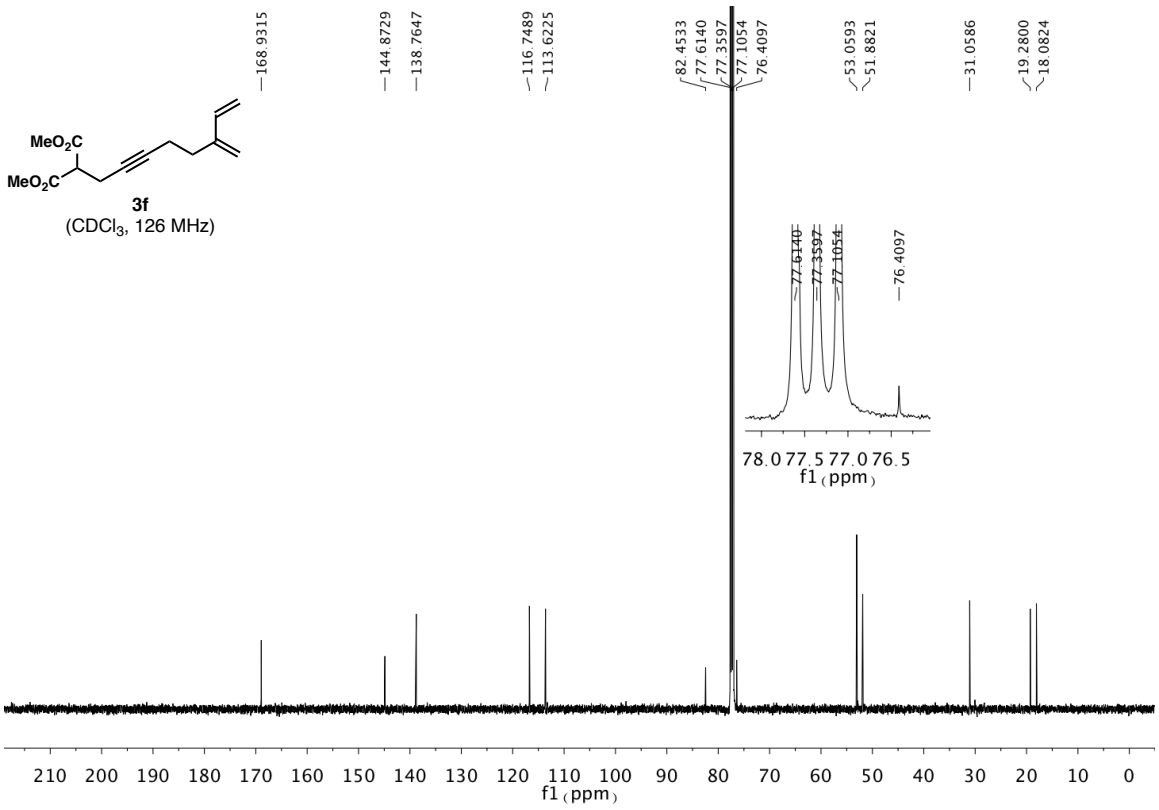
f1 (ppm)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53.0593
51.8821
31.0586
19.2800
18.0824
MeO2C
MeO2C
3f
(CDCl3, 126 MHz)
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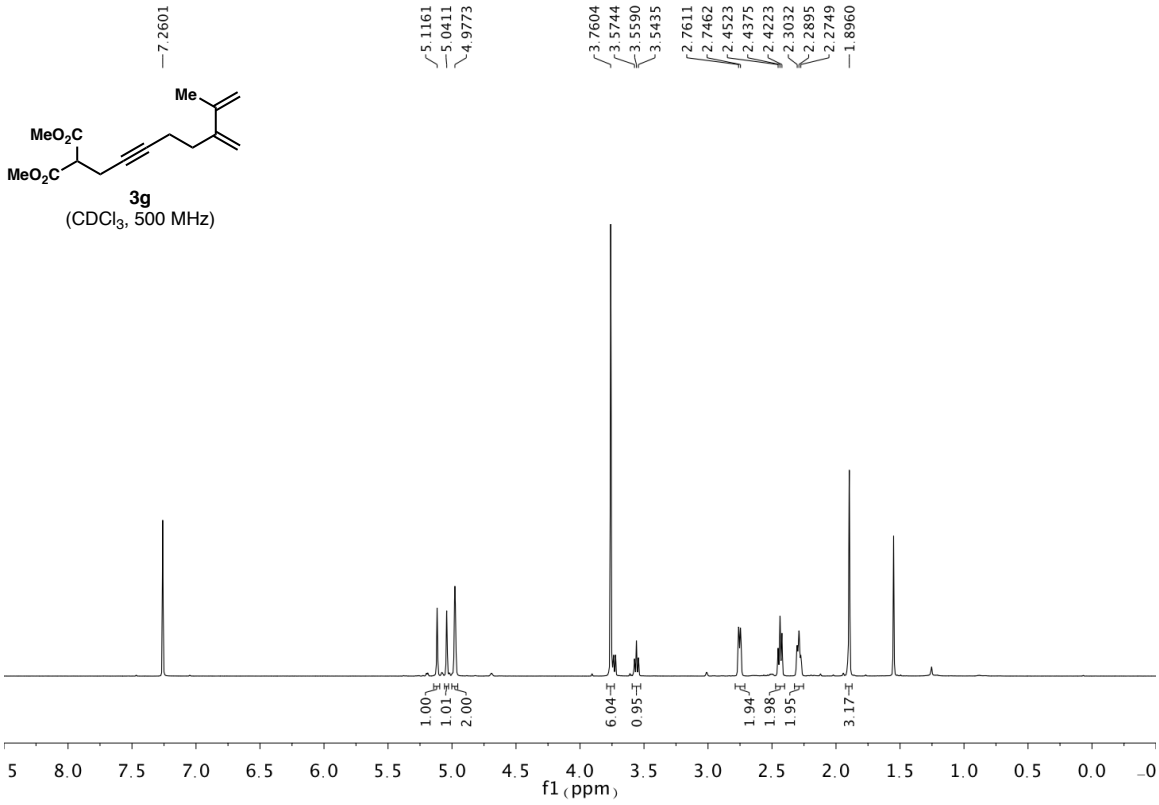
f1 (ppm)
f1 (ppm)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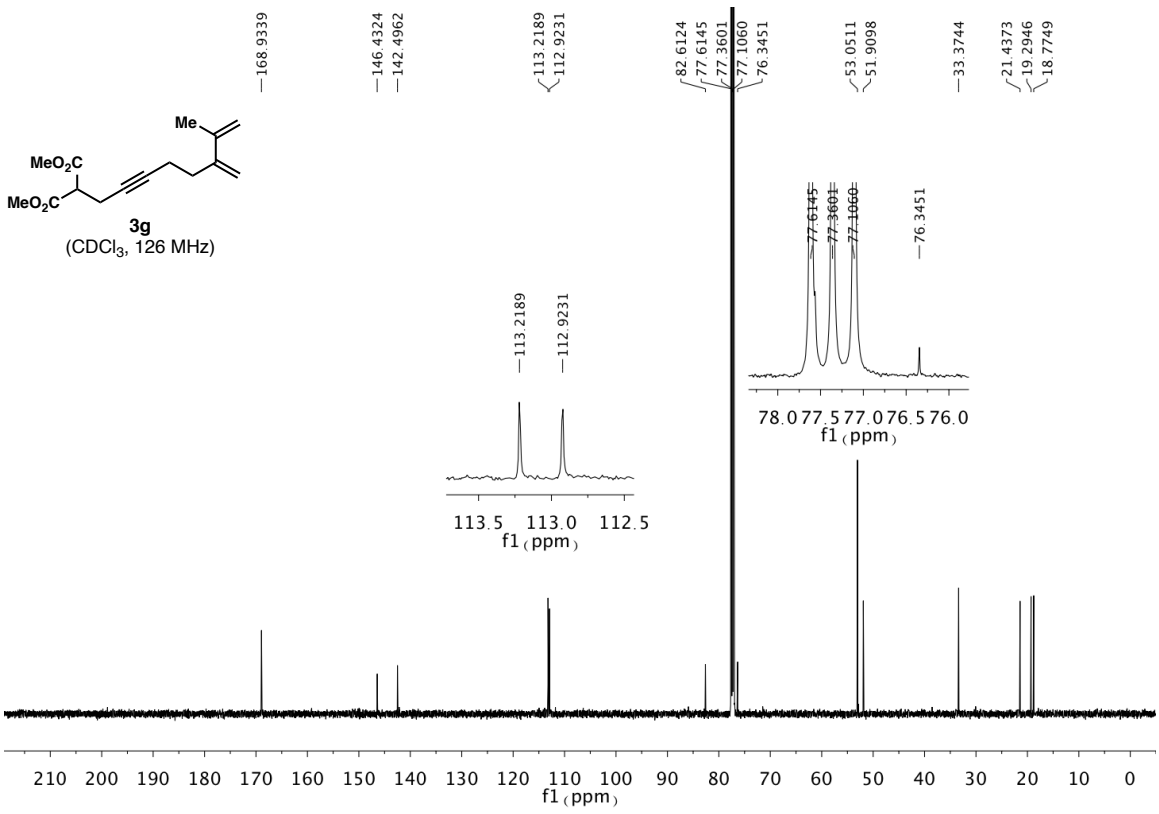
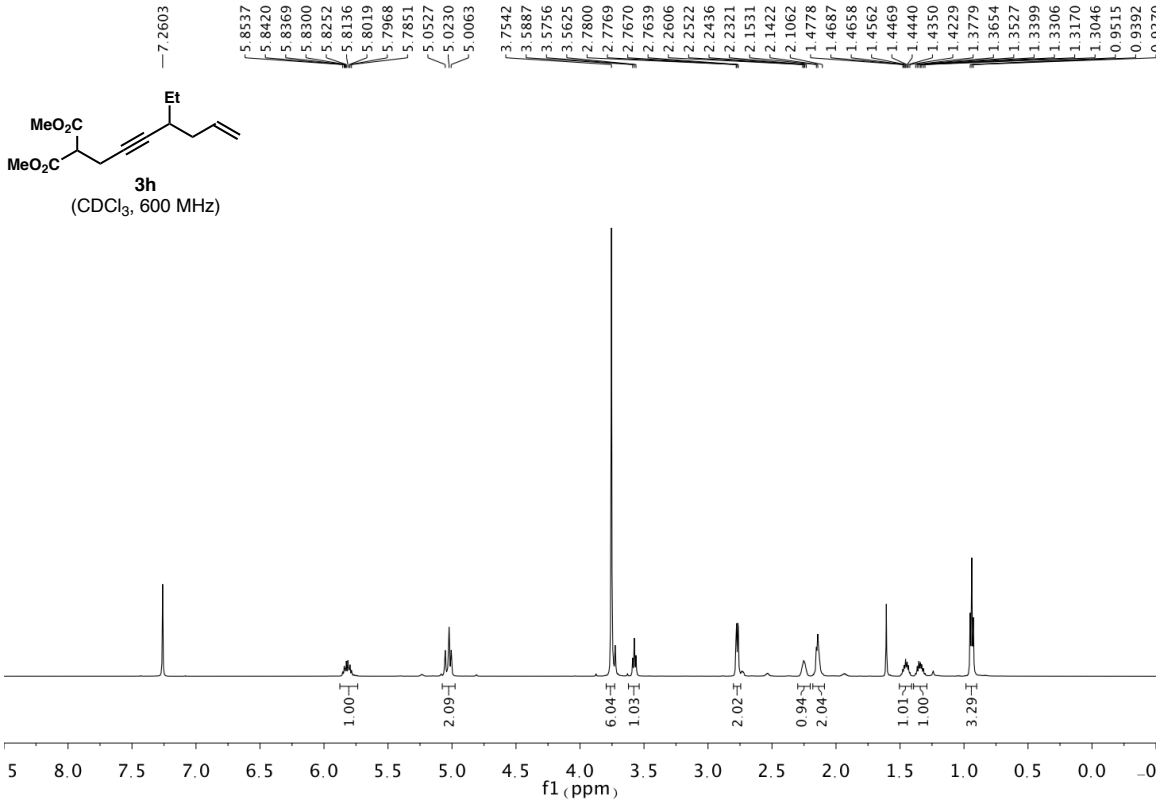
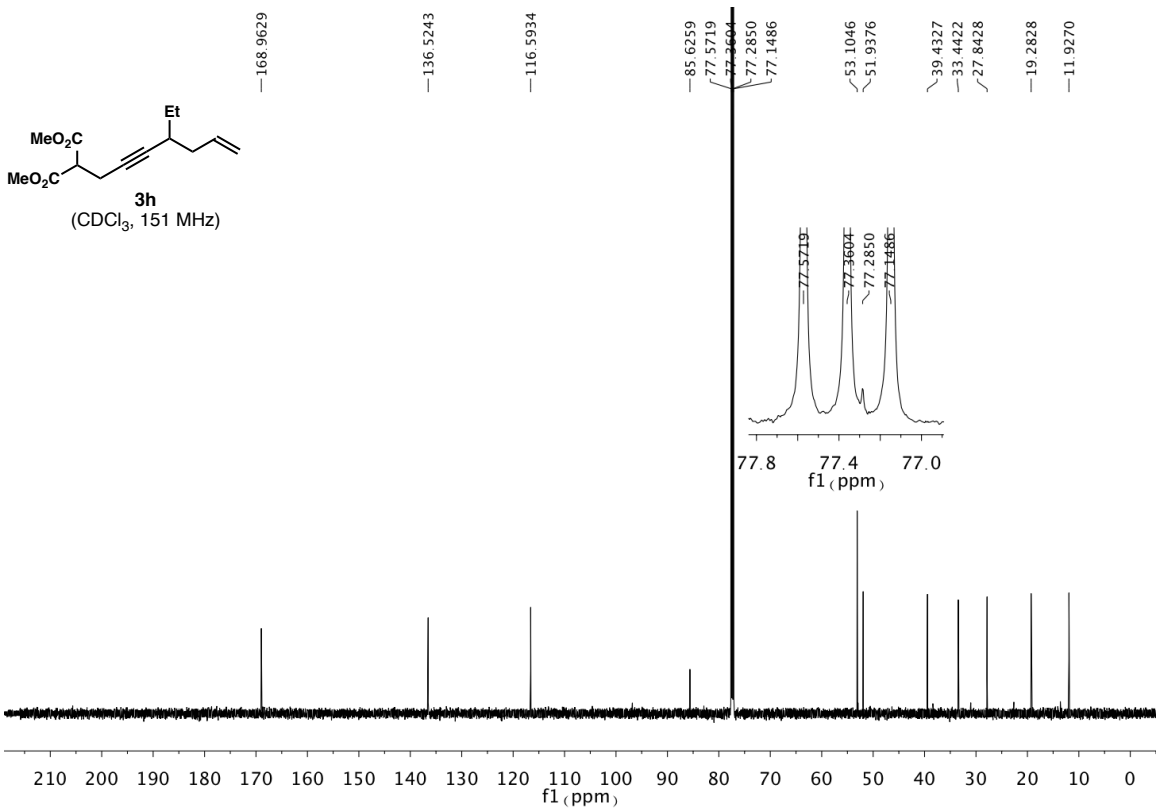
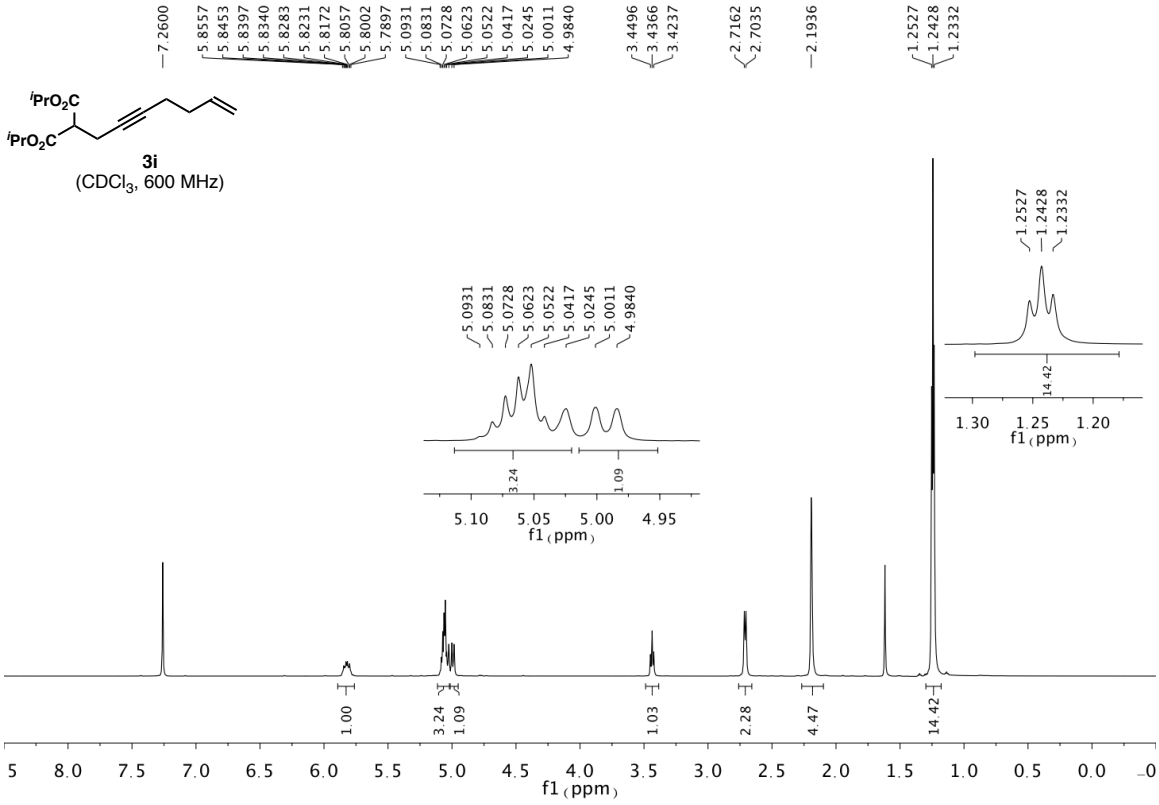
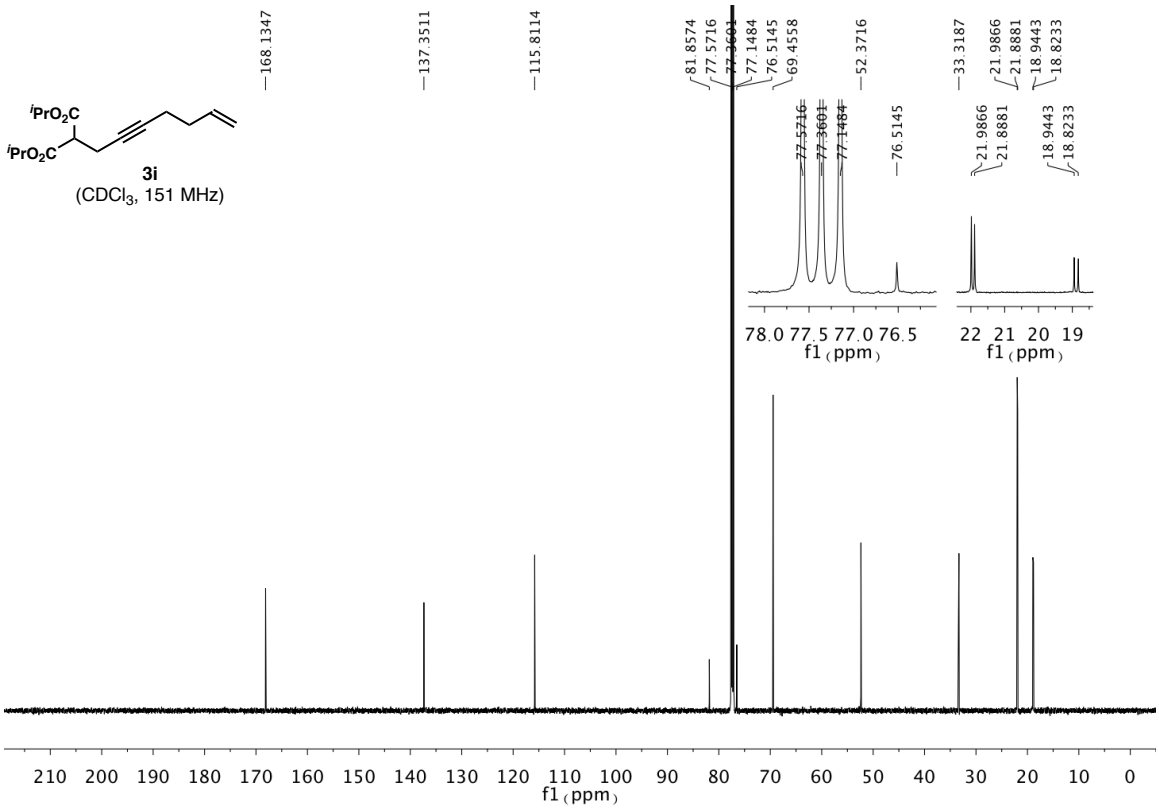
2.4375
2.4223
2.3032
2.2895
2.2749
1.8960
Me
MeO2C
MeO2C
3g
(CDCl3, 500 MHz)
1.00
1.01
2.00
6.04
0.95
1.94
1.98
1.95
3.17
f1 (ppm)

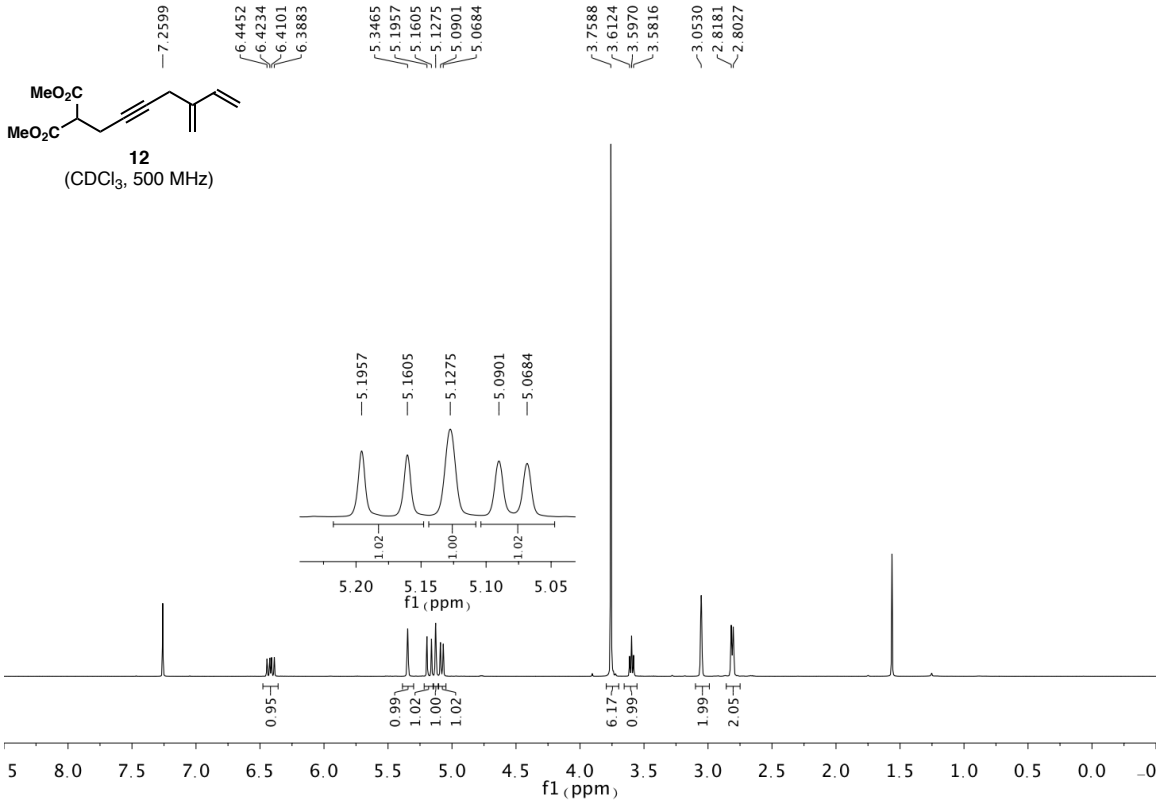

168.9339
146.4324
142.4962
113.2189
112.9231
82.6124
77.6145
77.3601
77.1060
76.3451
53.0511
51.9098
33.3744
21.4373
19.2946
18.7749
Me
MeO2C
MeO2C
3g
(CDCl3, 126 MHz)
113.5 113.0 112.5
f1 (ppm)
78.0 77.5 77.0 76.5 76.0
f1 (ppm)
f1 (ppm)

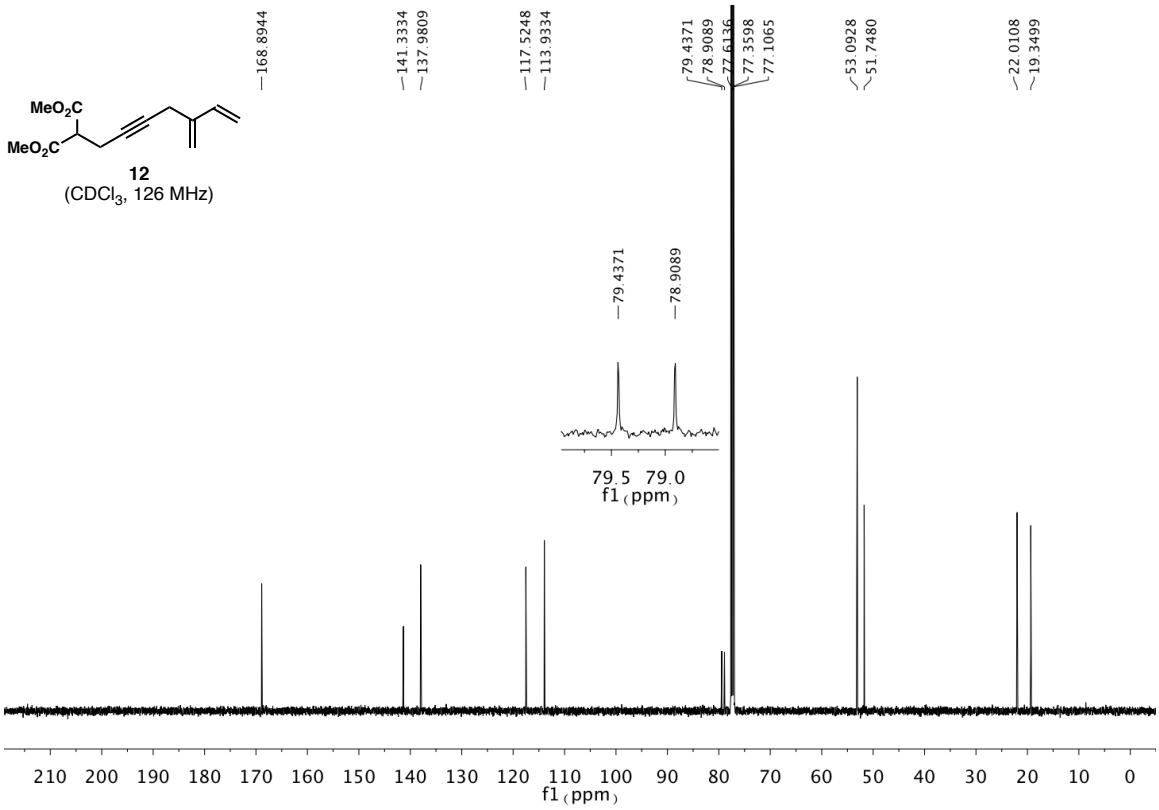

7.2603
5.8537
5.8420
5.8369
5.8300
5.8252
5.8136
5.8019
5.7968
5.7851
5.0527
5.0230
5.0063
3.7542
3.5887
3.5756
3.5625
2.7800
2.7769
2.7670
2.7639
2.2606
2.2522
2.2436
2.2321
2.1531
2.1422
2.1062
1.4778
1.4687
1.4658
1.4562
1.4469
1.4440
1.4350
1.4229
1.3779
1.3654
1.3527
1.3399
1.3306
1.3170
1.3046
0.9515
0.9392
Et
MeO2C
MeO2C
3h
(CDCl3, 600 MHz)
1.00
2.09
6.04
1.03
2.02
0.94
2.04
1.01
1.00
3.29
f1 (ppm)

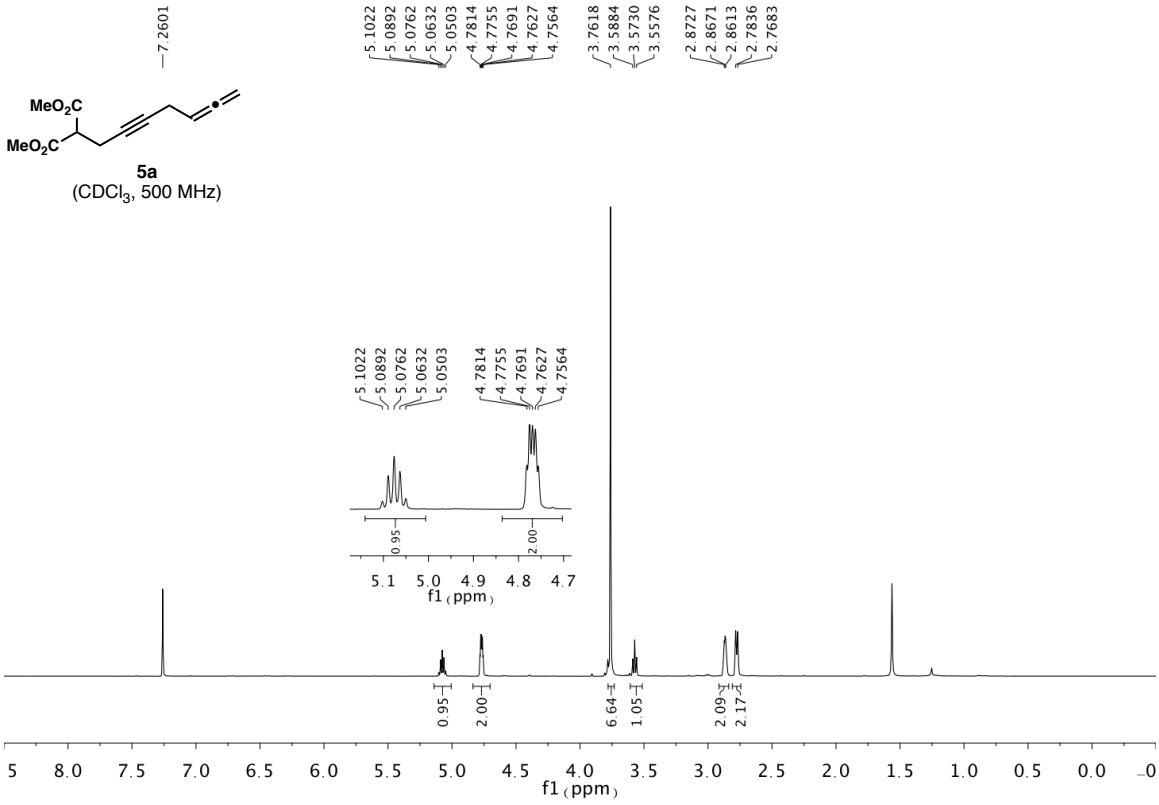

168.9629
136.5243
116.5934
85.6259
77.5719
77.3604
77.2850
77.1486
53.1046
51.9376
39.4327
33.4422
27.8428
19.2828
11.9270
Et
MeO2C
MeO2C
3h
(CDCl3, 151 MHz)
77.8
77.4
77.0
f1 (ppm)
f1 (ppm)

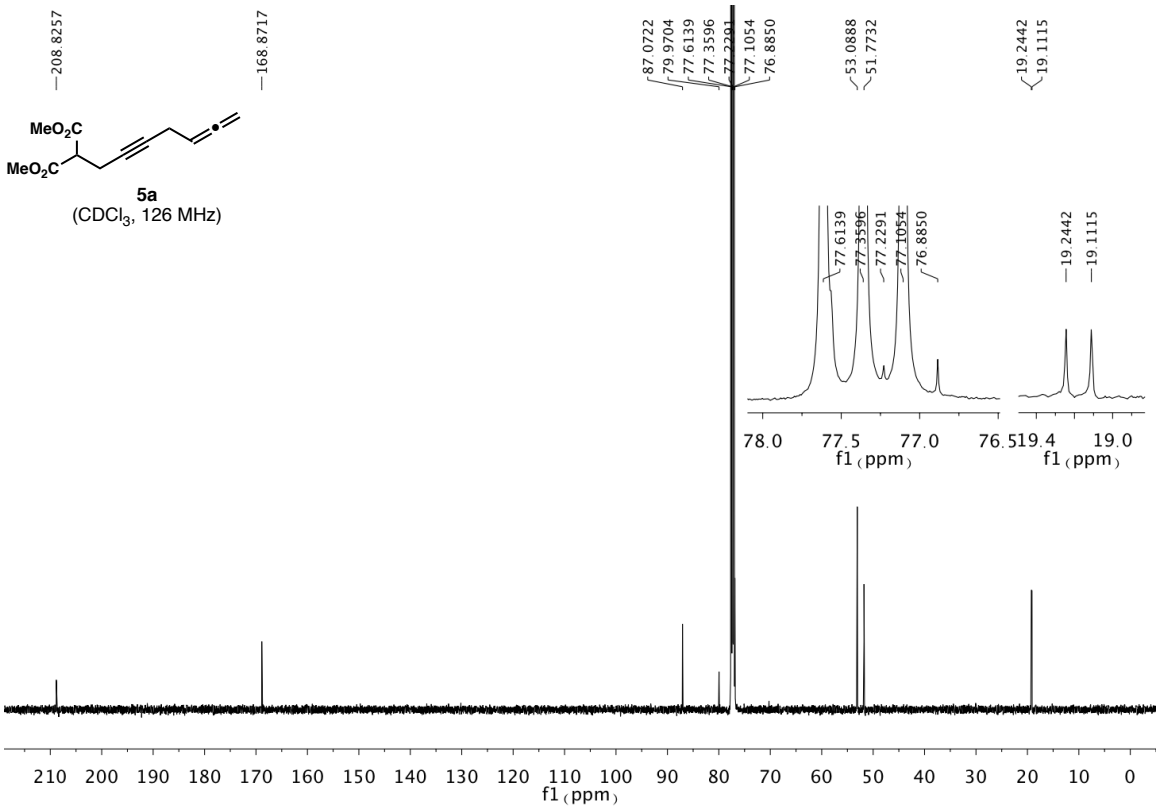

7.2600
5.8557
5.8453
5.8397
5.8340
5.8283
5.8231
5.8172
5.8057
5.8002
5.7897
5.0931
5.0831
5.0728
5.0623
5.0522
5.0417
5.0245
5.0011
4.9840
3.4496
3.4366
3.4237
2.7162
2.7035
2.1936
1.2527
1.2428
1.2332
iPrO2C
iPrO2C
3i
(CDCl3, 600 MHz)
1.00
3.24
1.09
1.03
2.28
4.47
14.42
f1 (ppm)

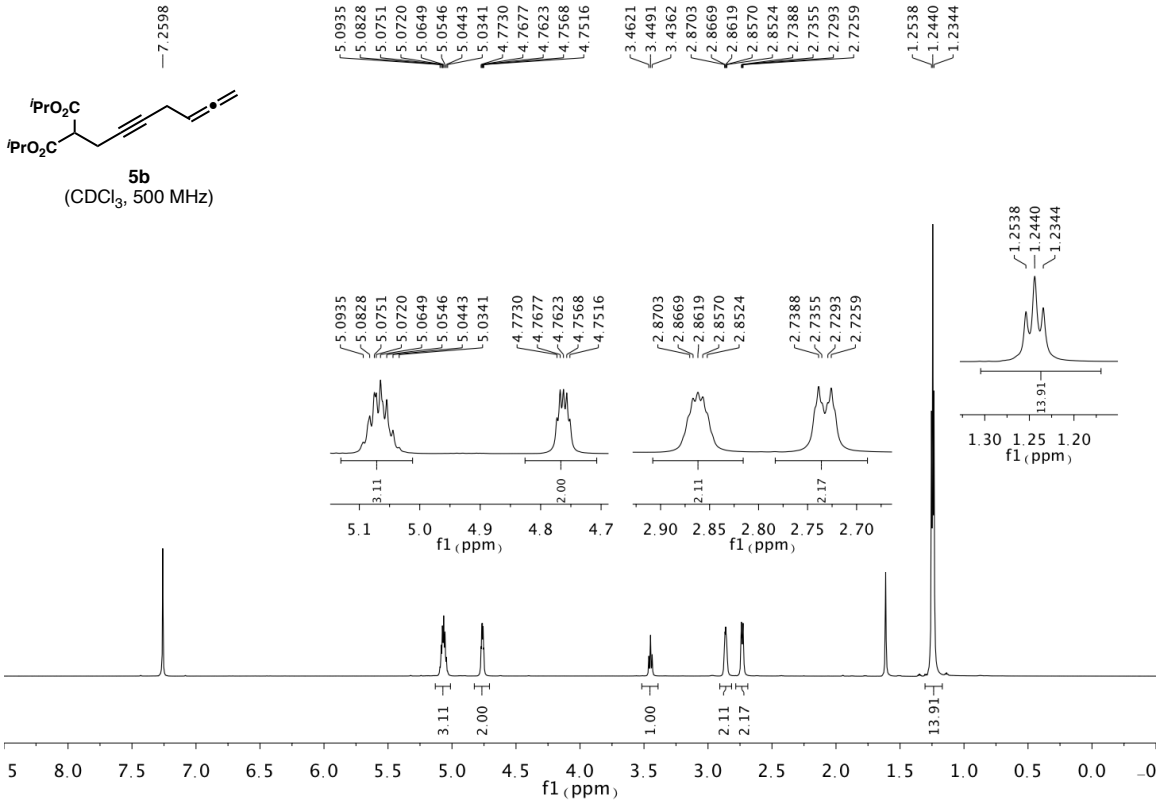

168.1347
137.3511
115.8114
81.8574
77.5716
77.3601
77.1484
76.5145
69.4558
52.3716
33.3187
21.9866
21.8881
18.9443
18.8233
iPrO2C
iPrO2C
3i
(CDCl3, 151 MHz)
f1 (ppm)

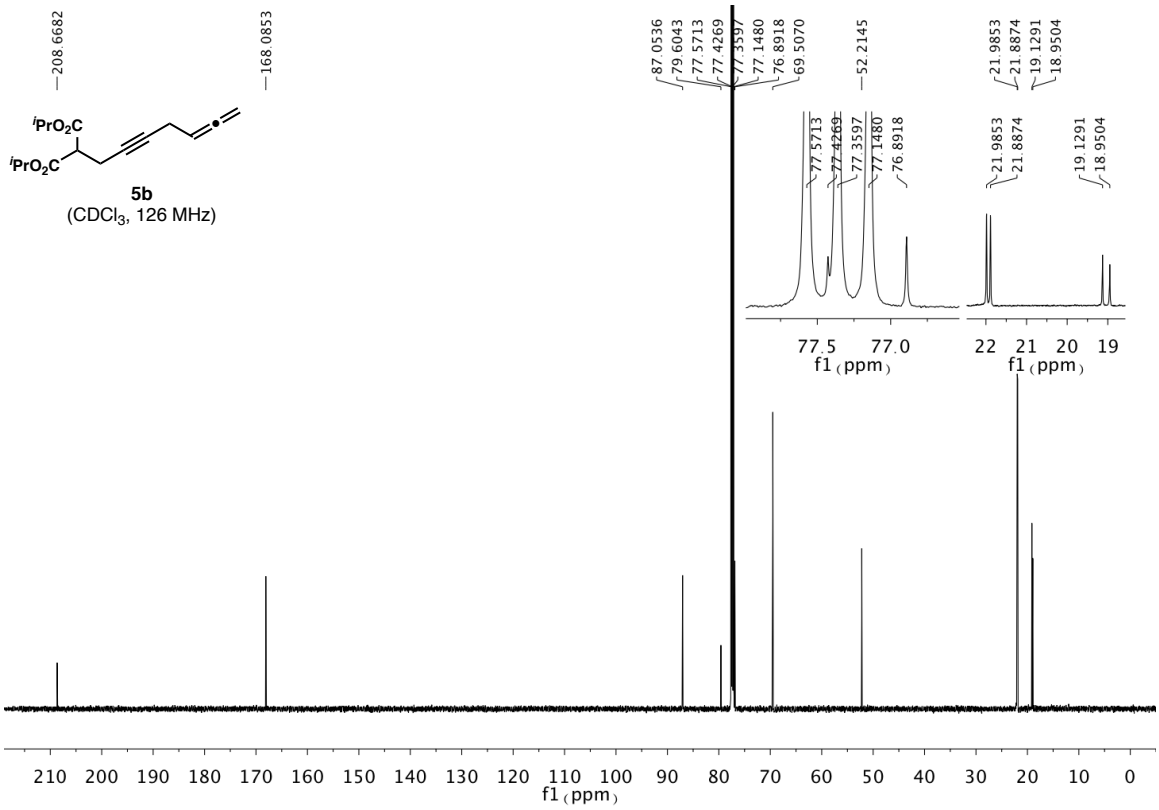

MeO2C
MeO2C
12
(CDCl3, 500 MHz)
7.2599
6.4452
6.4234
6.4101
6.3383
5.3465
5.1957
5.1605
5.1275
5.0901
5.0684
3.7588
3.6124
3.5970
3.5816
3.0530
2.8181
2.8027
0.95
0.99
1.02
1.00
1.02
6.17
0.99
1.99
2.05
f1 (ppm)

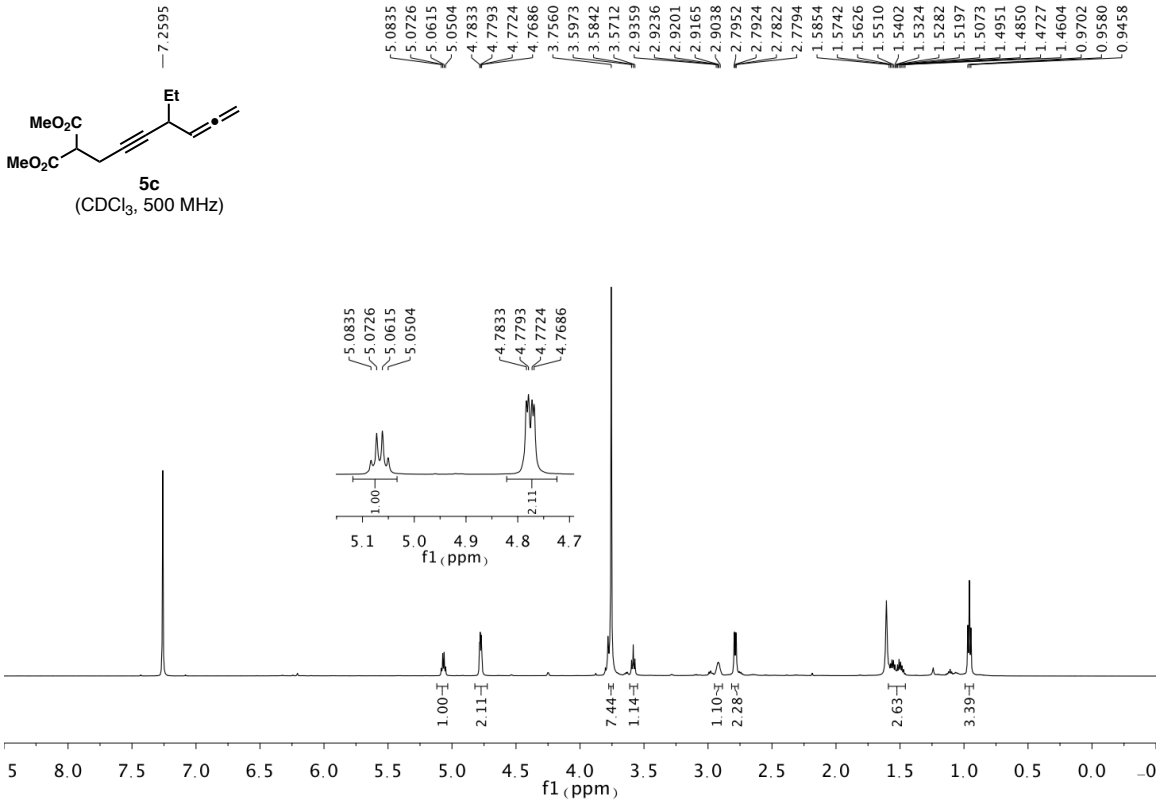

MeO2C
MeO2C
12
(CDCl3, 126 MHz)
168.8944
141.3334
137.9809
117.5248
113.9334
79.4371
78.9089
77.6136
77.3598
77.1065
53.0928
51.7480
22.0108
19.3499
f1 (ppm)

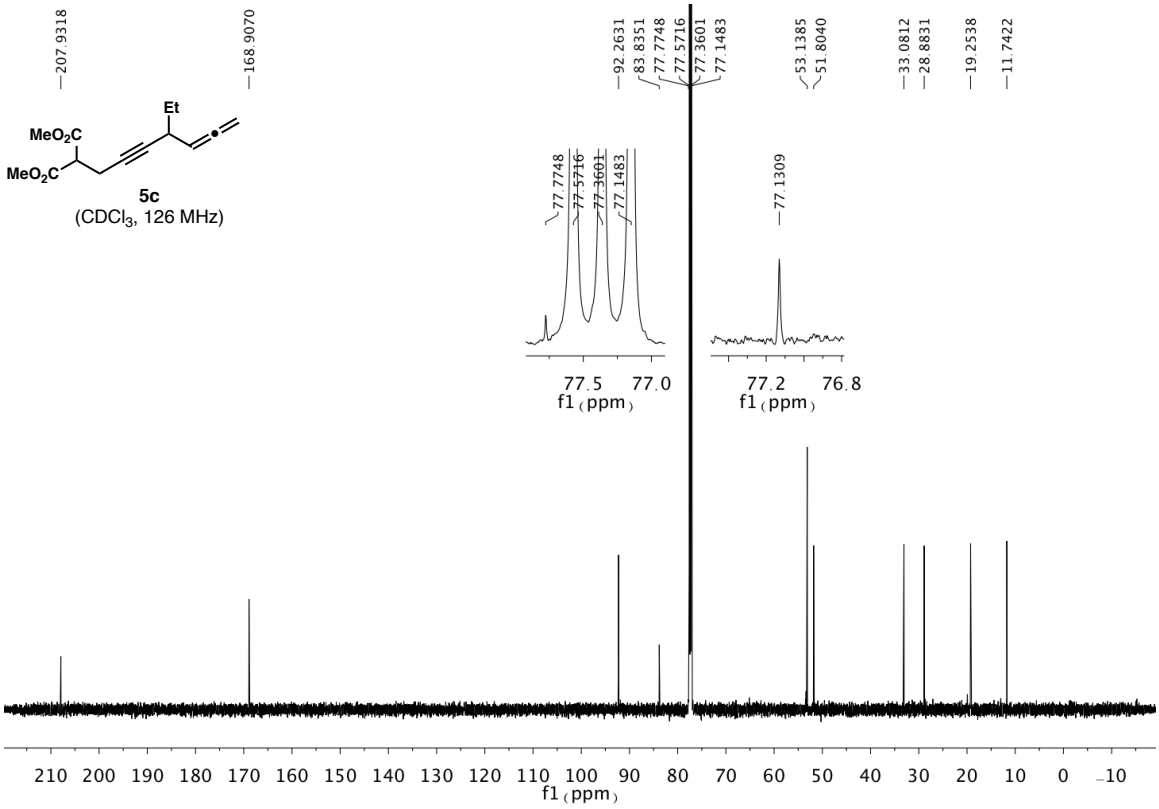

7.2601
5.1022
5.0892
5.0762
5.0632
5.0503
4.7814
4.7755
4.7691
4.7627
4.7564
3.7618
3.5884
3.5730
3.5576
2.8727
2.8671
2.8613
2.7836
2.7683
MeO2C
MeO2C
5a
(CDCl3, 500 MHz)
0.95
2.00
6.64
1.05
2.09
2.17
f1 (ppm)

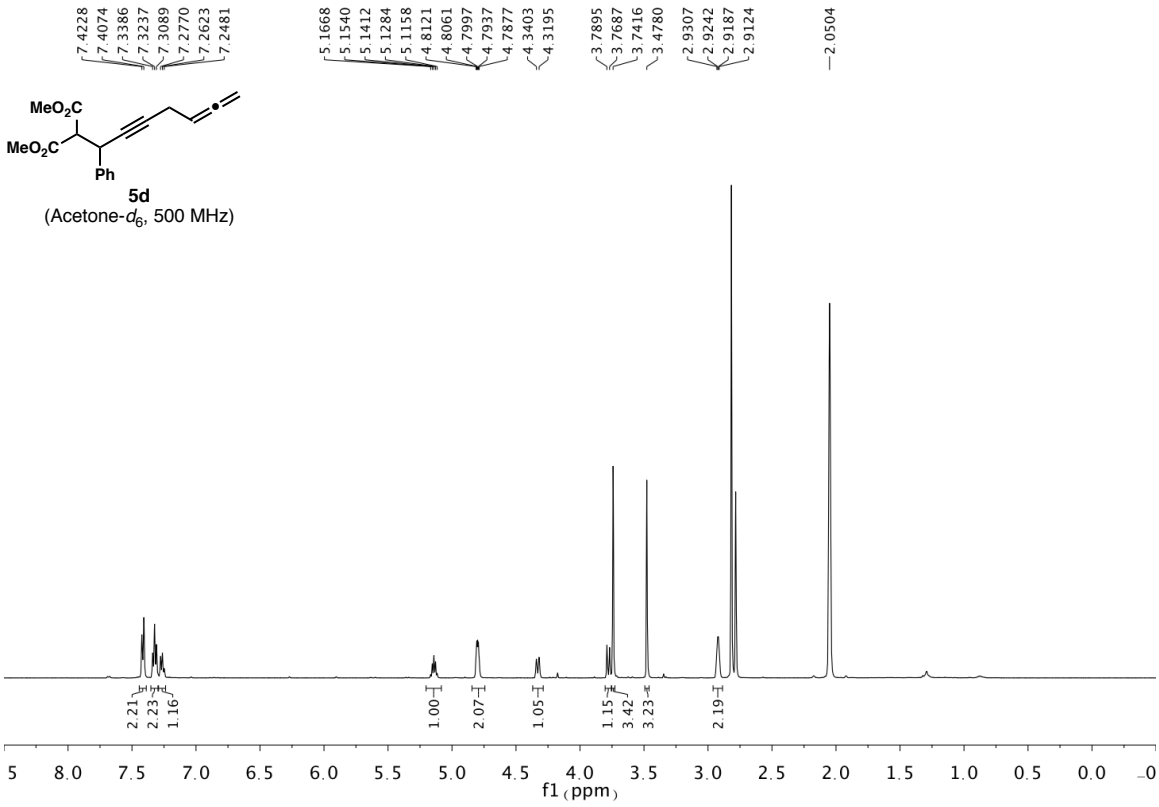

208.8257
168.8717
87.0722
79.9704
77.6139
77.3596
77.2291
77.1054
76.8850
53.0888
51.7732
19.2442
19.1115
MeO2C
MeO2C
5a
(CDCl3, 126 MHz)
f1 (ppm)

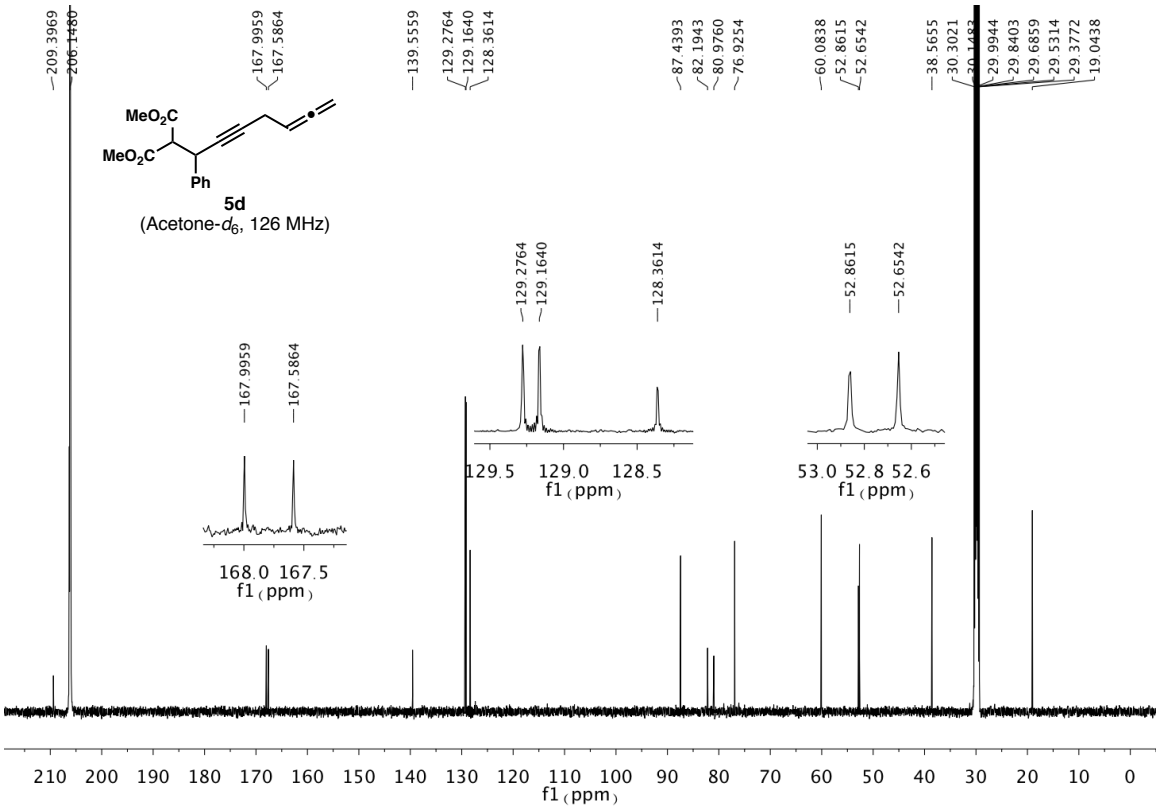

7.2598
5.0935
5.0828
5.0751
5.0720
5.0649
5.0546
5.0443
5.0341
4.7730
4.7677
4.7623
4.7568
4.7516
3.4621
3.4491
3.4362
2.8703
2.8669
2.8619
2.8570
2.8524
2.7388
2.7355
2.7293
2.7259
1.2538
1.2440
1.2344
iPrO2C
iPrO2C
5b
(CDCl3, 500 MHz)
3.11
2.00
1.00
2.11
2.17
13.91
f1 (ppm)

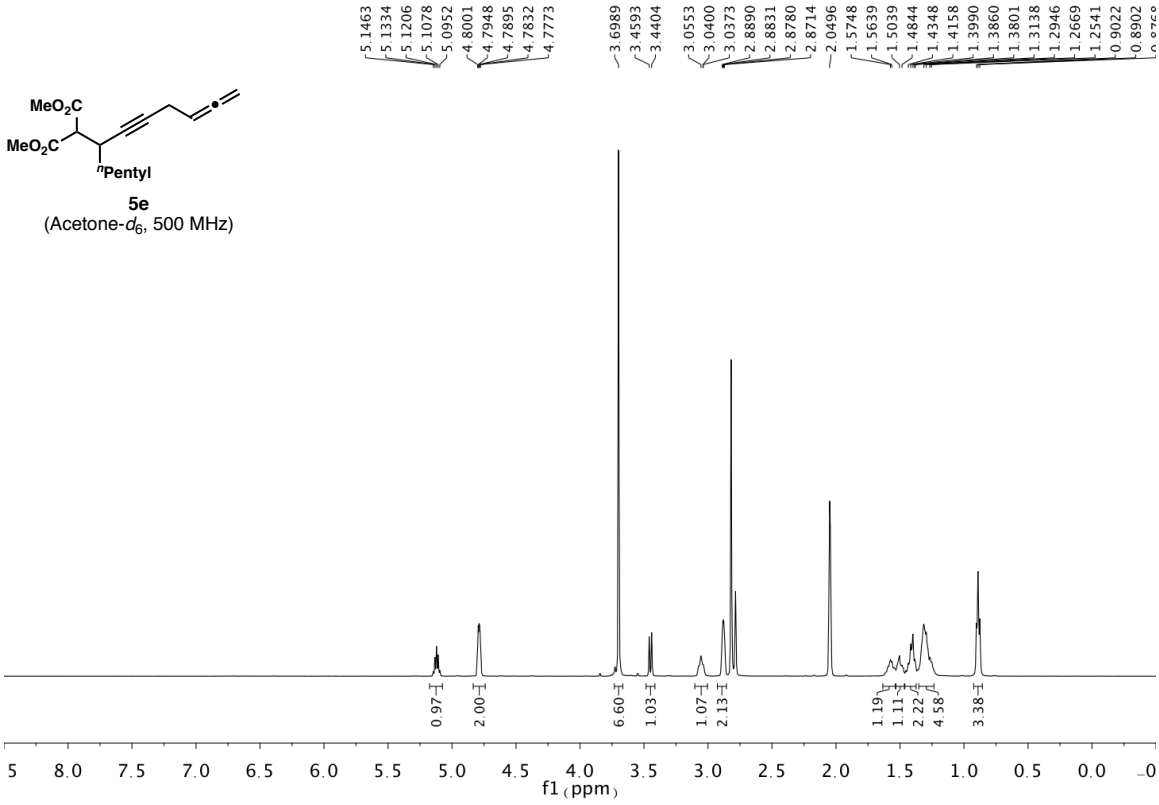

208.6682
168.0853
87.0536
79.6043
77.5713
77.4269
77.3597
77.1480
76.8918
69.5070
52.2145
21.9853
21.8874
19.1291
18.9504
iPrO2C
iPrO2C
5b
(CDCl3, 126 MHz)
f1 (ppm)

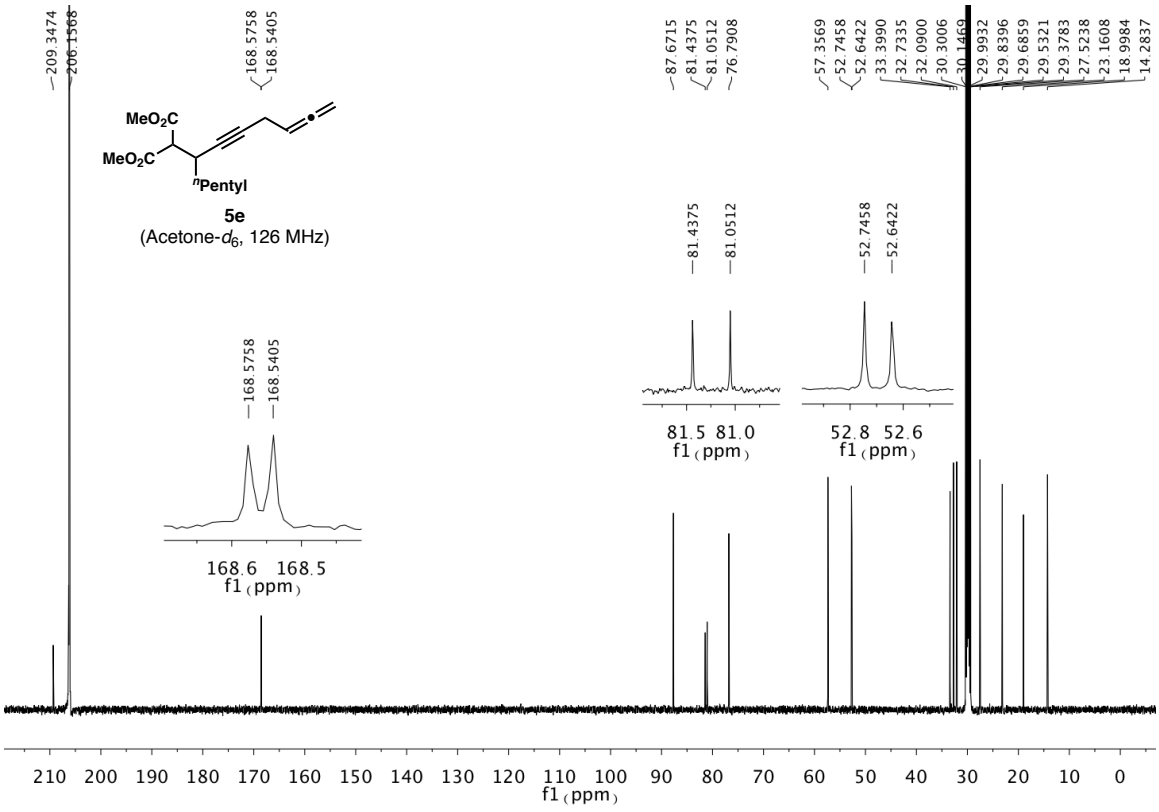

5c
(CDCl3, 500 MHz)
f1 (ppm)

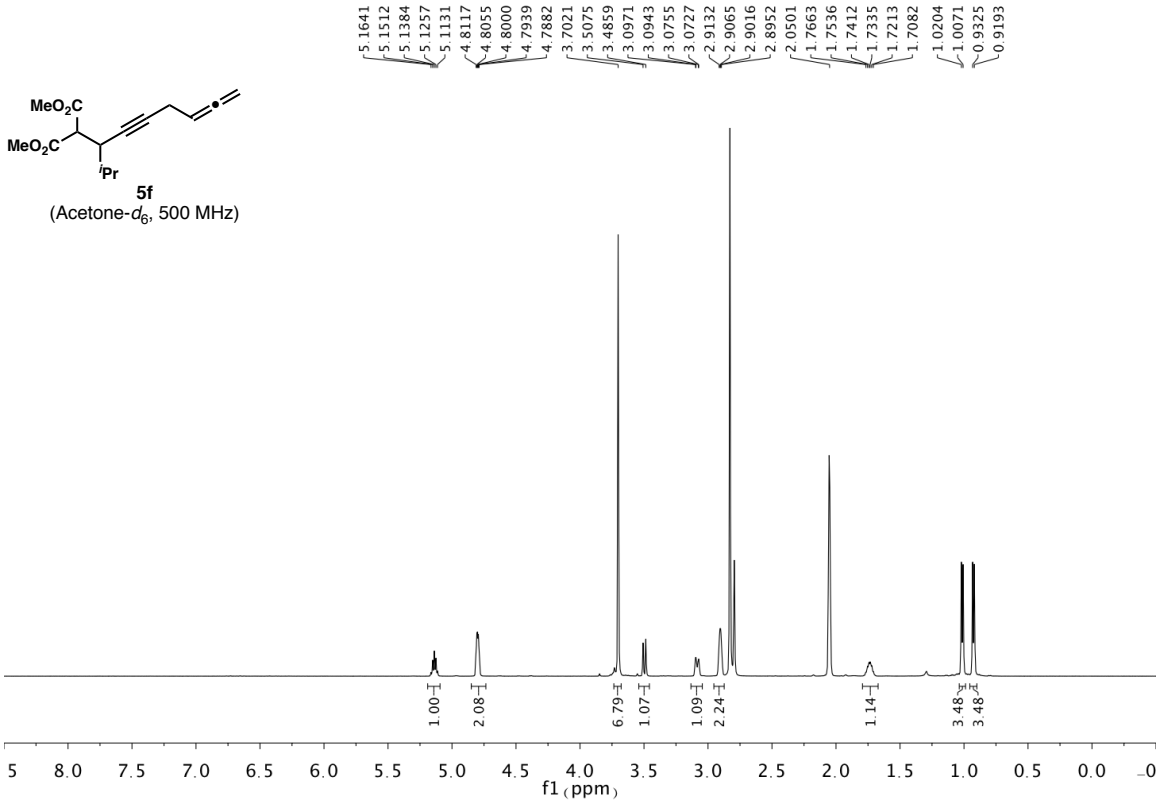

5c
(CDCl3, 126 MHz)
f1 (ppm)

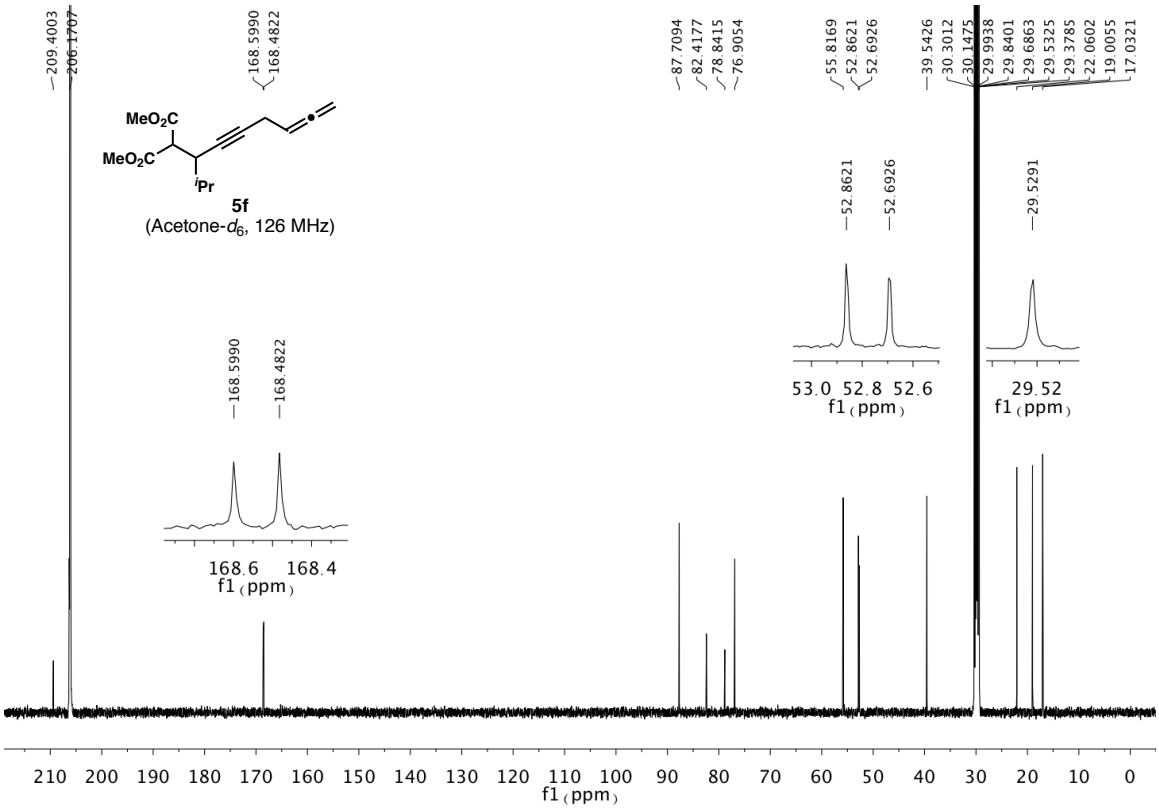

7.4228
7.4074
7.3386
7.3237
7.3089
7.2770
7.2623
7.2481
5.1668
5.1540
5.1412
5.1284
5.1158
4.8121
4.8061
4.7997
4.7937
4.7877
4.3403
4.3195
3.7895
3.7687
3.7416
3.4780
2.9307
2.9242
2.9187
2.9124
2.0504
MeO2C
MeO2C
Ph
5d
(Acetone-d6, 500 MHz)
2.21
2.23
1.16
1.00
2.07
1.05
1.15
3.42
3.23
2.19
f1 (ppm)

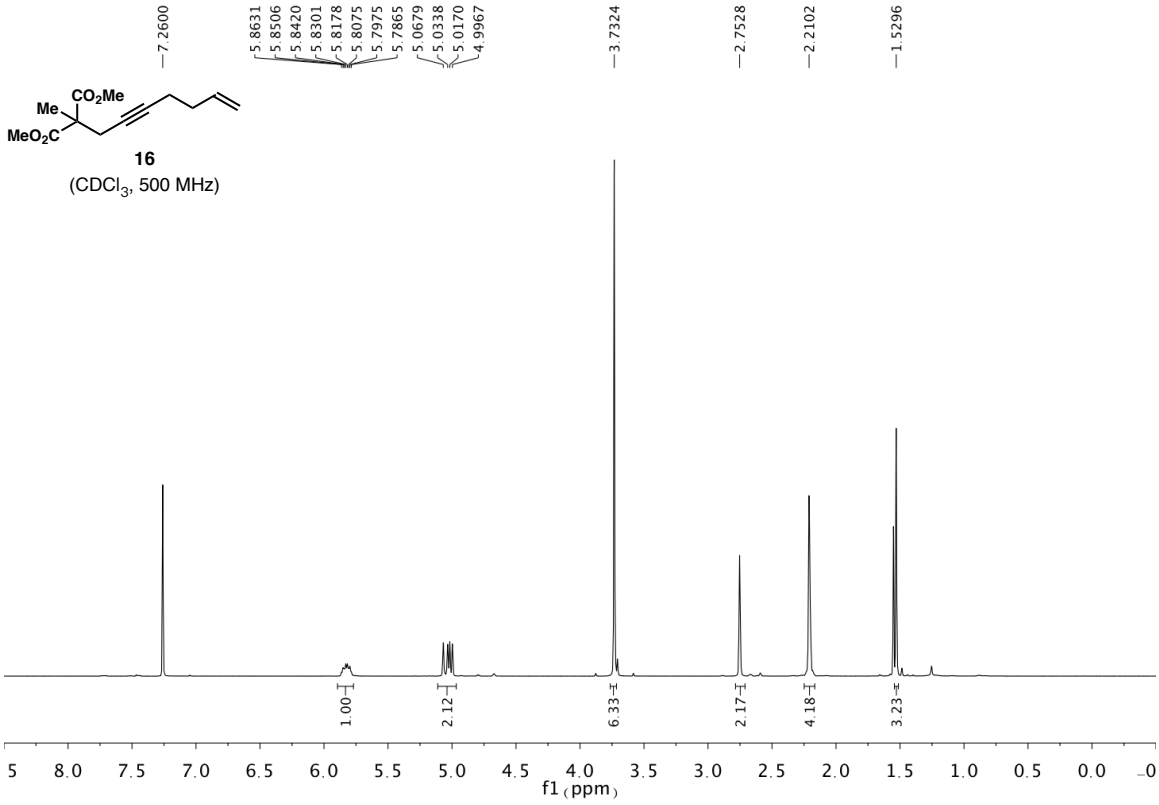

209.3969
206.1480
167.9959
167.5864
139.5559
129.2764
129.1640
128.3614
87.4393
82.1943
80.9760
76.9254
60.0838
52.8615
52.6542
38.5655
30.3021
29.9944
29.8403
29.6859
29.5314
29.3772
19.0438
MeO2C
MeO2C
Ph
5d
(Acetone-d6, 126 MHz)
168.0 167.5
f1 (ppm)
129.5 129.0 128.5
f1 (ppm)
53.0 52.8 52.6
f1 (ppm)
f1 (ppm)

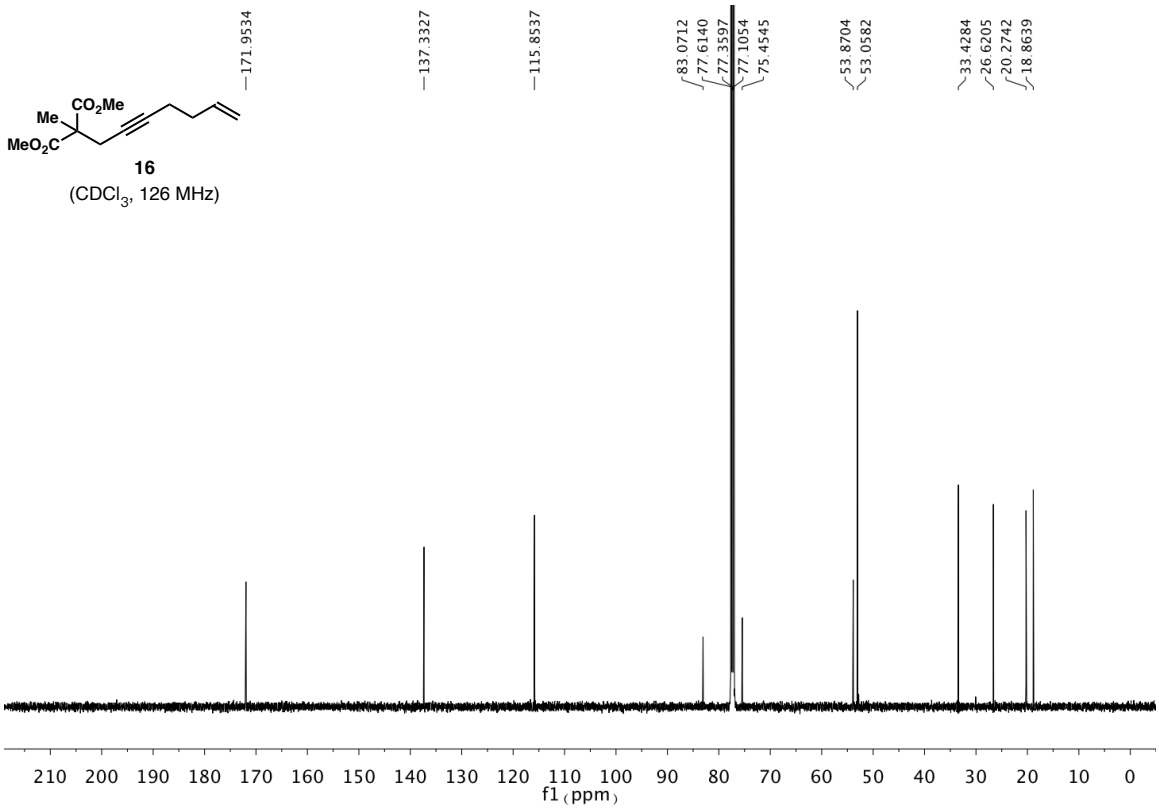

MeO2C
MeO2C
nPentyl
5e
(Acetone-d6, 500 MHz)
f1 (ppm)

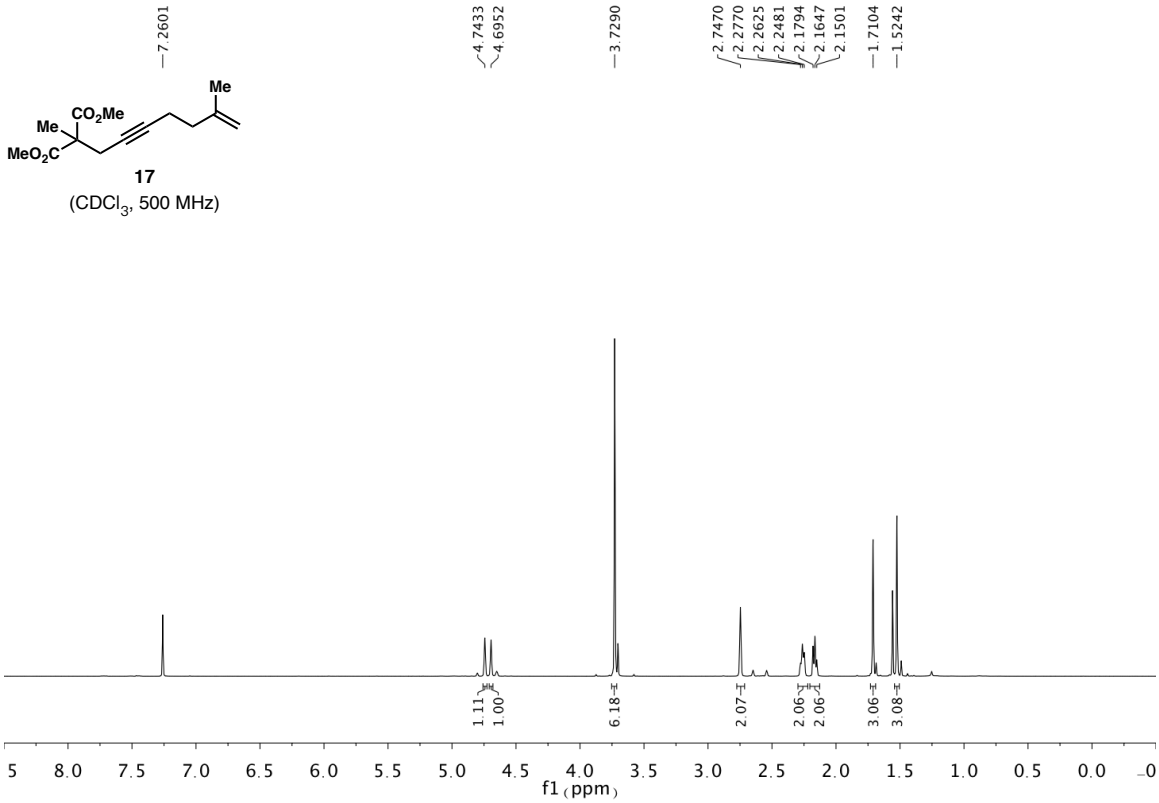

MeO2C
MeO2C
nPentyl
5e
(Acetone-d6, 126 MHz)
f1 (ppm)


MeO2C
MeO2C
iPr
5f
(Acetone-d6, 500 MHz)
f1 (ppm)


MeO2C
MeO2C
iPr
5f
(Acetone-d6, 126 MHz)
f1 (ppm)

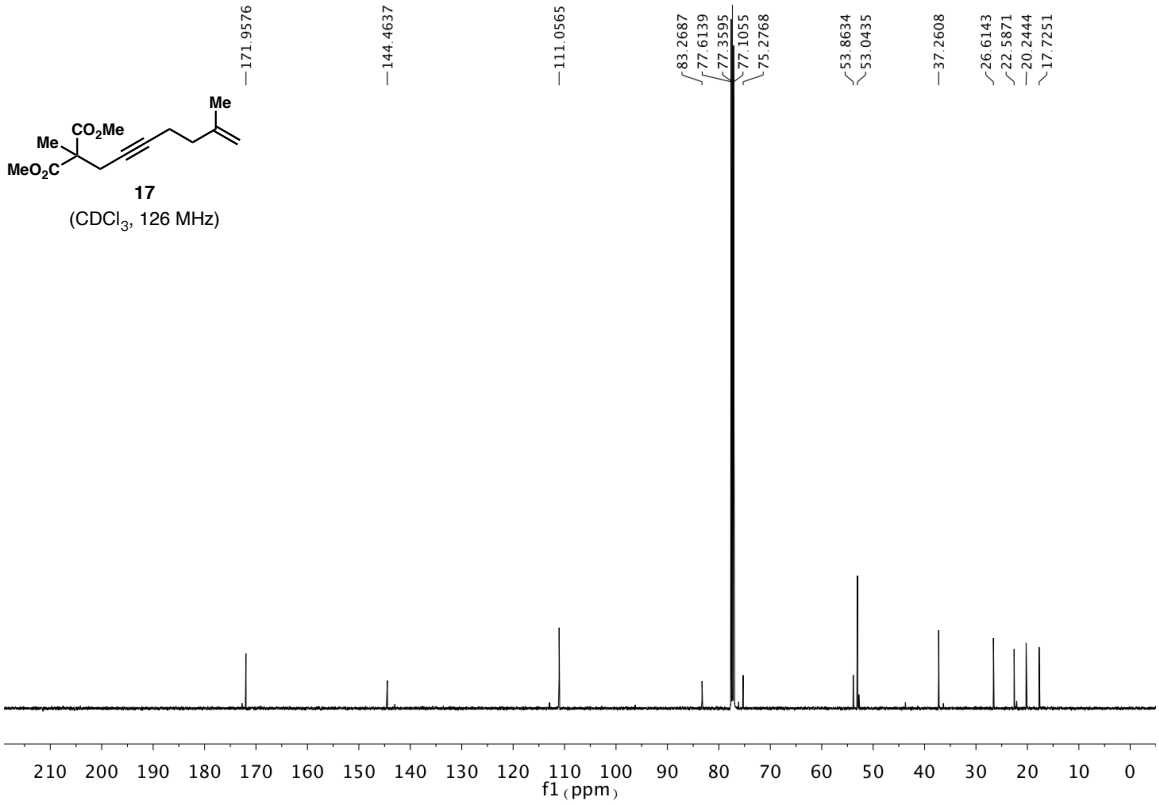

7.2600
5.8631
5.8506
5.8420
5.8301
5.8178
5.8075
5.7975
5.7865
5.0679
5.0338
5.0170
4.9967
3.7324
2.7528
2.2102
1.5296
CO2Me
Me
MeO2C
16
(CDCl3, 500 MHz)
1.00
2.12
6.33
2.17
4.18
3.23
f1 (ppm)


171.9534
137.3327
115.8537
83.0712
77.6140
77.3597
77.1054
75.4545
53.8704
53.0582
33.4284
26.6205
20.2742
18.8639
CO2Me
Me
MeO2C
16
(CDCl3, 126 MHz)
f1 (ppm)



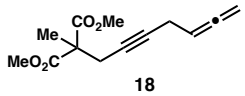
17

($CDCl_3$, 500 MHz)



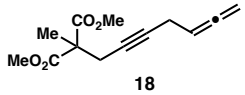
17

($CDCl_3$, 126 MHz)



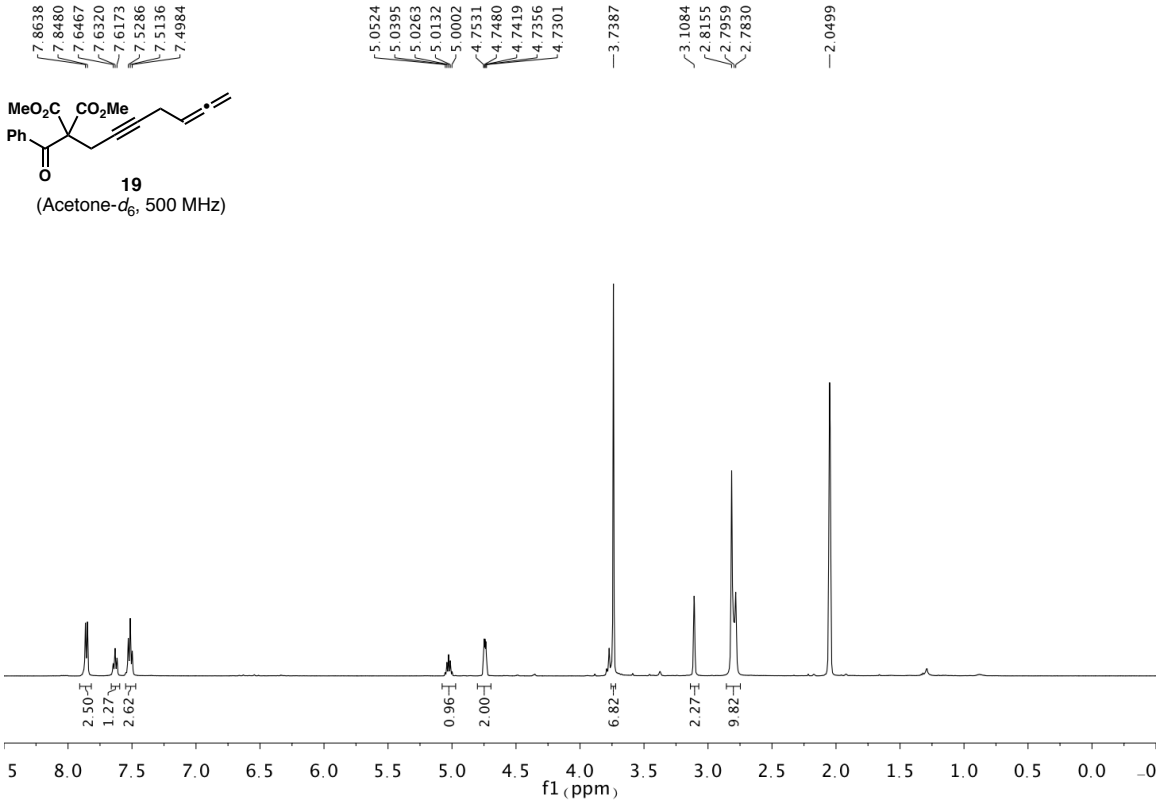
18

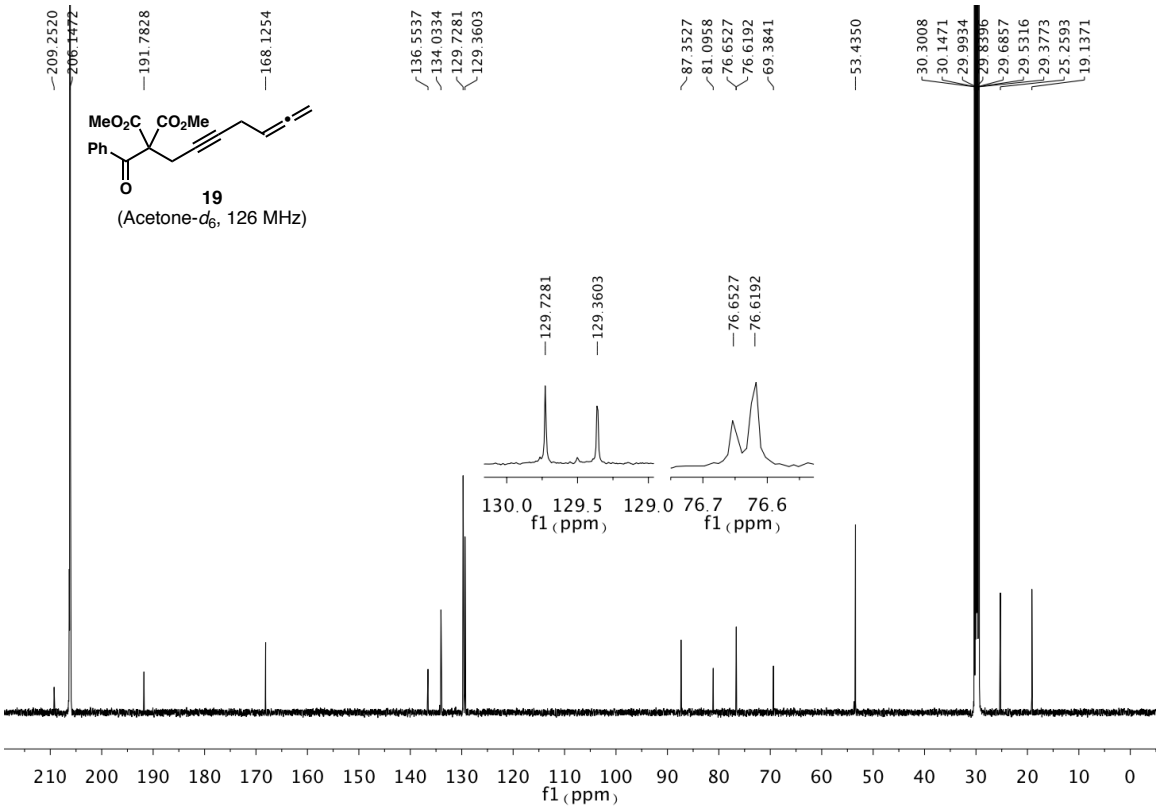
($CDCl_3$, 500 MHz)

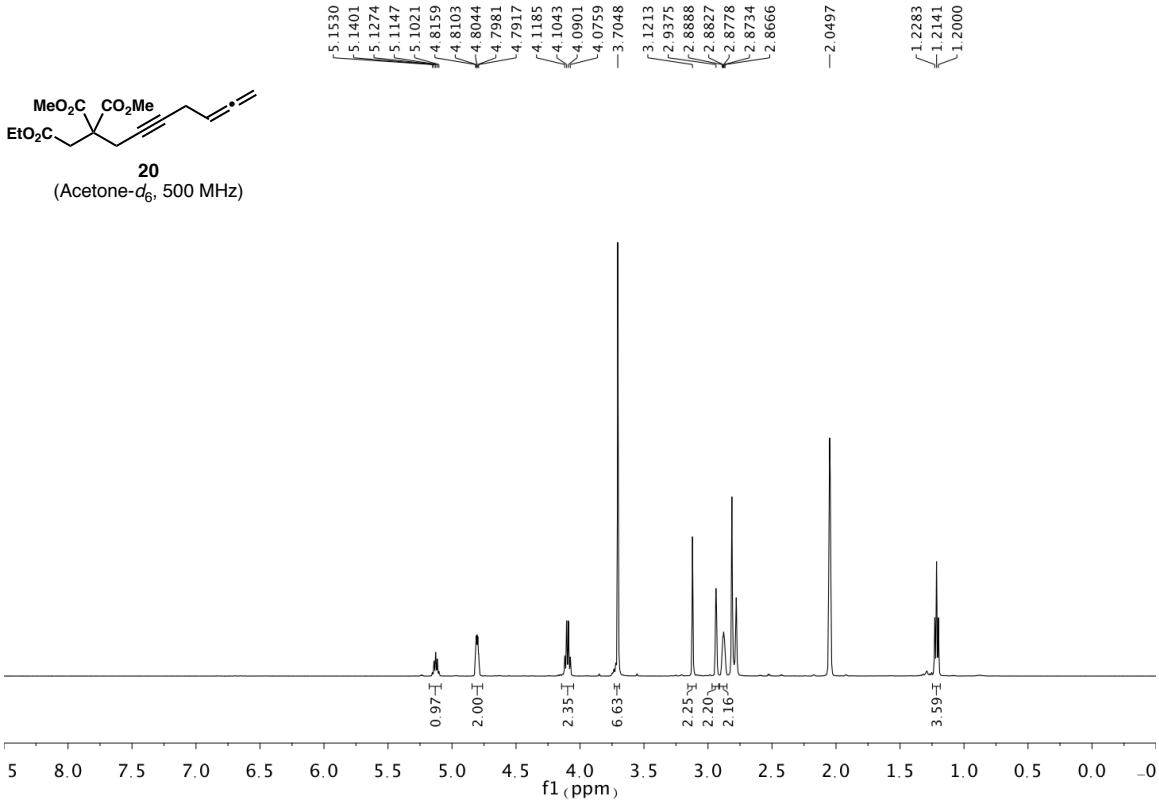


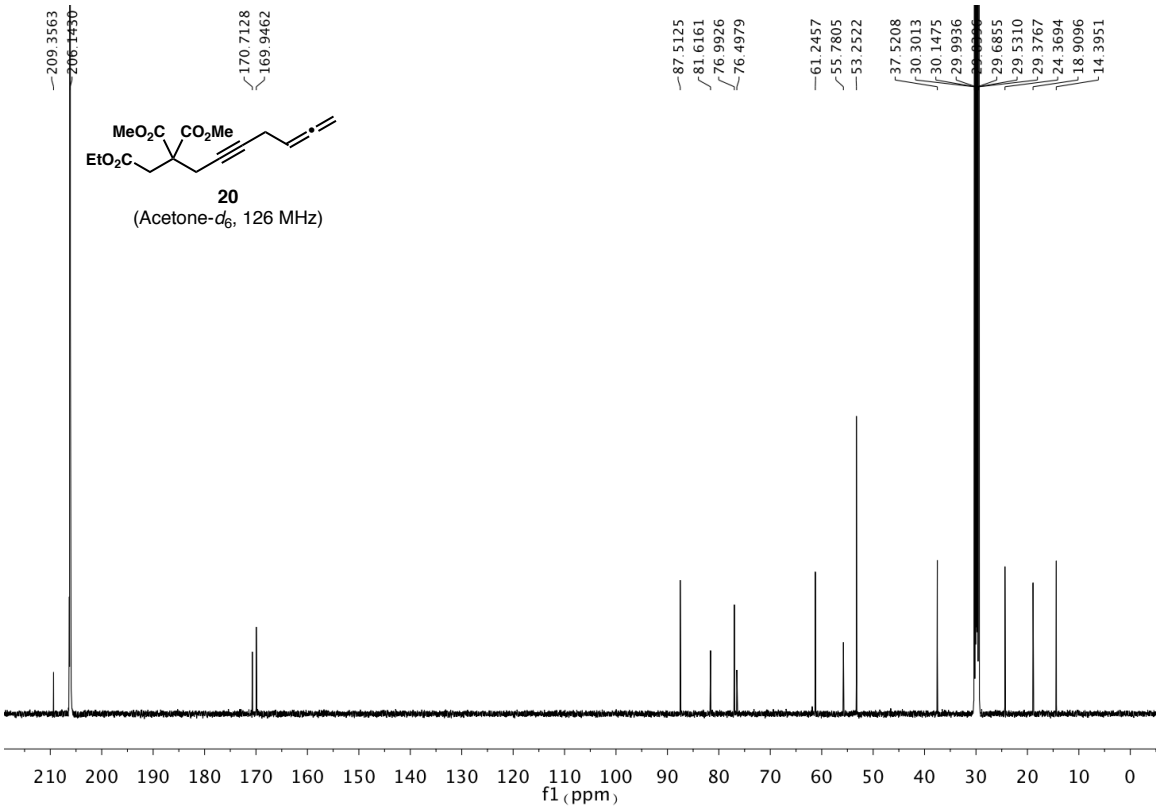
18

($CDCl_3$, 126 MHz)


7.8638
7.8480
7.6467
7.6320
7.6173
7.5286
7.5136
7.4984
5.0524
5.0395
5.0263
5.0132
5.0002
4.7531
4.7480
4.7419
4.7356
4.7301
3.7387
3.1084
2.8155
2.7959
2.7830
2.0499
MeO2C
CO2Me
Ph
O
19
(Acetone-d6, 500 MHz)
2.50
1.27
2.62
0.96
2.00
6.82
2.27
9.82
f1 (ppm)


209.2520
206.1472
191.7828
168.1254
136.5537
134.0334
129.7281
129.3603
87.3527
81.0958
76.6527
76.6192
69.3841
53.4350
30.3008
30.1471
29.9934
29.8596
29.6857
29.5316
29.3773
25.2593
19.1371
MeO2C
CO2Me
Ph
O
19
(Acetone-d6, 126 MHz)
129.7281
129.3603
76.6527
76.6192
130.0
129.5
129.0
76.7
76.6
f1 (ppm)


MeO2C CO2Me
EtO2C
20
(Acetone-d6, 500 MHz)
f1 (ppm)


MeO2C CO2Me
EtO2C
20
(Acetone-d6, 126 MHz)
f1 (ppm)